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Division of Chemistry and Chemical Engineering, California Institute of Technology, 1200 East California Boulevard, MC 164-30, Pasadena, California 91125

stoltz@caltech.edu

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Experimental Procedures

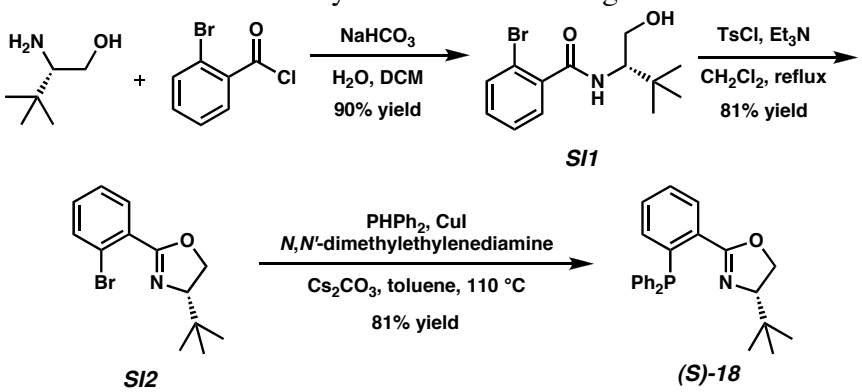
Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon. Tetrabutylammonium difluorotriphenylsilicate (TBAT) was purchased from Sigma-Aldrich and azeotropically dried five times from acetonitrile prior to use. Bis(di(3,5-dimethoxybenzylidene)acetone)palladium(0) ($Pd(dmdba)_2$), alkyl halides, triethylsilyl chloride, diallyl carbonate, Select-fluor®, pimelic acid, and all other ketone starting materials were purchased from Sigma-Aldrich and used as received, unless otherwise noted. 3-Methylcyclohex-2-en-1-one, cyclohex-2-en-1-one, and NaH (60% dispersion in mineral oil) were purchased from Acros and used as received. Dimethallyl carbonate was purchased from Alfa Aesar and used as received. Trimethylsilyl chloride (TMSCl) and triethylamine were purchased from Sigma-Aldrich and distilled from sodium hydride immediately prior to use. Sodium iodide was dried by heating at 90 °C (2 torr) for 12 h. Molecular sieves were purchased from Aldrich as activated 5 μm powder and stored in a 120 °C drying oven until immediately prior to use unless otherwise noted. (*R,R*)-Trost Ligand, (*R*)-BINAP, (*R,R*)-Me-DUPHOS, (*R,R*)-DIOP, (*R*)-MOP, (*R*)-QUINAP, (*R*)-*i*-Pr-PHOX, (1*S*,2*R*)-*cis*-1-amino-indan-2-ol, and tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$) were purchased from Strem and stored in a glovebox until immediately before use. (*R*)-Ph-PHOX and (*S*)-Bn-PHOX were prepared by the method of Helmchen.[1] (*S*)-*tert*-Leucine was purchased from Aldrich or Degussa and used as received. Other chiral amino acids were purchased from Chem-Impex International, Inc. and reduced to the corresponding amino alcohols according to literature precedent,[2] unless otherwise noted. Methallyl chloroformate was prepared by the method of Kirby.[3] Allyl cyanoformate was prepared by known methods.[4] Ruthenium olefin metathesis catalysts were generously donated by Materia and stored under argon in a dessicator jar at –20 °C until just prior to use.

Reaction temperatures were controlled by an IKAmag temperature modulator. Thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, $KMnO_4$ or CAM staining. ICN Silica gel (particle size 0.032-0.063 mm) was used for flash chromatography. Analytical chiral HPLC was performed with an Agilent 1100 Series HPLC utilizing chiralcel AD, OD-H, or OJ columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd., with visualization at 254 nm. Analytical chiral GC was performed with an Agilent 6850 GC utilizing a Chiraldex G-TA (30.0 m x 0.25 mm) column (1.0 mL/min He carrier gas flow). Analytical achiral GC was performed with an Agilent 6850 GC utilizing an Agilent DB-WAX (30.0 m x 0.25 mm) column (1.0 mL/min He carrier gas flow). Optical rotations were measured with a Jasco P-1010 polarimeter at 589 nm. ^1H and ^{13}C NMR spectra were recorded on a Varian Mercury 300 (at 300 MHz and 75 MHz, respectively) or a Varian Inova 500 (at 500 MHz and 125 MHz, respectively) and are reported relative to Me_4Si (δ 0.0). Data for ^1H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, sept. = septet, m = multiplet, comp. m = complex multiplet, app. = apparent, br s = broad singlet. Data for ^{13}C NMR spectra are reported in terms of chemical shift relative to Me_4Si (δ 0.0). ^{19}F NMR spectra were recorded on a Varian Mercury 300 spectrometer at 282 MHz, and are reported relative to the external standard F_3CCO_2H (δ –76.53 ppm) or $CFCl_3$ (δ 0.0 ppm). ^{31}P NMR spectra were recorded on a Varian Mercury 300 spectrometer at 121 MHz, and are reported relative to the external standard H_3PO_4 (δ 0.0 ppm). Temperature controlled ^1H NMR kinetic experiments were performed on a Varian Inova 500 MHz. IR spectra were recorded on a Perkin Elmer Paragon 1000 spectrometer and are reported in frequency of absorption (cm^{-1}). High-resolution mass spectra were obtained from the Caltech Mass Spectral Facility. Crystallographic data have been deposited at the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, and copies can be obtained on request, free of charge, by quoting the publication citation and the deposition number.

Synthesis of PHOX ligands[5,6]

General Procedure 1: Synthesis of PHOX Ligands

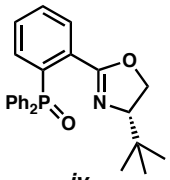


Amide SI1: To a solution of (*S*)-*t*-leucinol[2,6] (3.57 g, 30.5 mmol, 1.0 equiv) in CH_2Cl_2 (100 mL) was added a solution of Na_2CO_3 (9.70 g, 91.5 mmol, 3.0 equiv) in water (75.0 mL). To the vigorously stirred biphasic mixture was added 2-bromobenzoyl chloride (4.58 mL, 35.1 mmol, 1.15 equiv) in a dropwise manner. After 12 h ambient temperature, the layers were separated, and aqueous layer extracted with CH_2Cl_2 (2 x 50 mL). The combined organics were treated with KOH (15 mL of a 1 M methanolic solution) for 15 min, neutralized with 3 M HCl, and water (50 mL) was added. The layers were separated, and the aqueous layer extracted with CH_2Cl_2 (2 x 50 mL). The combined organics were dried (Na_2SO_4), evaporated, and the residue chromatographed (25→35% Acetone in Hexanes on SiO_2) to give amide **SI1** (8.19 g, 89.5% yield): mp 50-51 °C from acetone/hexanes; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 7.8, 0.9 Hz, 1H), 7.54 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.34 (app. dt, *J* = 7.4, 1.1 Hz, 1H), 7.26 (app. dt, *J* = 7.7, 1.8 Hz, 1H), 6.24 (bd, *J* = 8.1 Hz, 1H), 4.05 (m, 1H), 3.93 (dd, *J* = 11.4, 3.6 Hz, 1H), 3.66 (dd, *J* = 11.4, 7.5 Hz, 1H), 2.68 (br s, 1H), 1.03 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.7, 137.9, 133.3, 131.2, 129.7, 127.6, 119.0, 62.9, 60.2, 33.8, 27.1; IR (Neat Film NaCl) 3245, 3070, 2963, 1640, 1557 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{13}H_{19}NO_2Br$ [M + H]$^+$: 300.0599, found 300.0590; $[\alpha]_D^{29}$ +20.19 (*c* 2.38, methanol).

Phenyloxazoline SI2:[1] A solution of amide **SI1** (8.10 g, 27.0 mmol, 1.0 equiv), tosyl chloride (6.69 g, 35.1 mmol, 1.3 equiv), triethylamine (18.7 mL, 135.0 mmol, 5.0 equiv) in CH_2Cl_2 (200 mL) in a rb flask equipped with a reflux condenser was heated at 55 °C for 22 h. At which time, water (28 mL) was added and heating continued at 75 °C for 2 h. The reaction mixture was cooled, the layers separated, and the aqueous layer extracted with CH_2Cl_2 (2 x 25 mL). The combined organics were dried (Na_2SO_4), evaporated, and the residue chromatographed (5% EtOAc in Hexanes on SiO_2) to give phenyloxazoline **SI2** (6.19 g, 81.2% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64 (app. dt, *J* = 8.7, 1.7 Hz, 2H), 7.33 (app. dt, *J* = 7.7, 1.5 Hz, 1H), 7.26 (m, 1H), 4.38 (dd, *J* = 10.5, 8.9 Hz, 1H), 4.25 (app. t, *J* = 8.3 Hz, 1H), 4.10 (dd, *J* = 10.2, 8.1 Hz, 1H), 1.00 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 133.6, 131.4, 131.2, 130.2, 127.0, 121.8, 76.6, 69.0, 34.0, 25.9; IR (Neat Film NaCl) 2956, 1661, 1478, 1354, 1099, 1022, 963 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{13}H_{17}NOBr$ [M + H]$^+$: 282.0493, found 282.0488; $[\alpha]_D^{29}$ –48.32 (*c* 3.77, hexane).

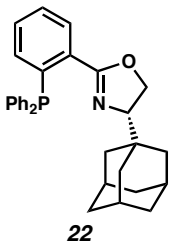
(*S*)-*t*-Bu-PHOX (19): A mixture of CuI (338.3 mg, 1.77 mmol, 0.125 equiv), diphenylphosphine (4.64 mL, 26.7 mmol, 1.88 equiv), *N*,*N*'-dimethylethylenediamine (1.32 mL, 12.4 mmol, 0.875 equiv) in toluene (60 mL) was stirred for 20 min at ambient temperature. At which point, phenyloxazoline **SI2** (4.00 g, 14.2 mmol, 1.0 equiv), cesium carbonate (17.4 g, 53.3 mmol, 3.75 equiv), and toluene (60 mL) were added, the flask sealed and heated to 110 °C with stirring. The reaction mixture became deep red after ~15 min of heating. After 6 h, the reaction mixture was allowed to cool to ambient temperature, filtered, and washed with CH_2Cl_2 (2 x 50 mL). Evaporation of the solvent and chromatography (3→7% Et_2O in Hexanes on SiO_2) afforded the known[1] (*S*)-*t*-Bu-PHOX (4.48 g, 81.4% yield).

Characterization Data for New PHOX Ligands:



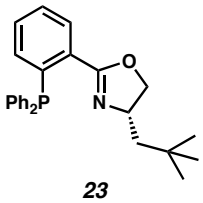
iv

(*S*)-*t*-Bu-PHOX oxide (iv): To a solution of (*S*)-*t*-Bu-PHOX (150 mg, 0.387 mmol, 1.00 equiv) in THF (2.5 mL) was added a 5% aqueous H_2O_2 solution (1.94 mL). After 15 min the reaction mixture was diluted with EtOAc (5 mL) and brine (5 mL), washed with 10% aqueous Na_2CO_3 (5 mL) and brine (5 mL), dried ($MgSO_4$), and purified by flash chromatography on silica gel (5% MeOH in CH_2Cl_2) to give (*S*)-*t*-Bu-PHOX oxide **20** (149.3 mg, 96% yield) as a white foam: R_f 0.47 (10% MeOH in CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (ddd, *J* = 7.5, 3.9, 1.2 Hz, 1H), 7.81-7.33 (comp. m, 7H), 7.52-7.31 (comp. m, 7H), 3.84 (dd, *J* = 8.1, 8.1 Hz, 1H), 3.57 (dd, *J* = 9.9, 9.9 Hz, 1H), 3.41 (dd, *J* = 9.9, 8.4 Hz, 1H), 0.77 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 135.0 (d, *J* = 10.1 Hz), 133.7 (d, *J* = 107.1 Hz), 133.3 (d, *J* = 107.1 Hz), 132.6, 132.4-131.0 (7 lines), 130.8 (d, *J* = 8.6 Hz), 130.3 (d, *J* = 11.7 Hz), 138.2 (app. dd, *J* = 12.3, 1.4 Hz), 75.9, 68.8, 33.6, 25.8; ^{31}P NMR (121 MHz, $CDCl_3$) δ 30.3; IR (Neat Film NaCl) 3057, 2957, 2903, 2868, 2217, 1664, 1589, 1565, 1477, 1438, 1356, 1337, 1307, 1248, 1201, 1119, 1108, 1067, 1028, 963, 930, 905 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{25}H_{27}O_2NP$ $[M]^+$: 404.1779, found 404.1799; $[\alpha]_D^{27.6}$ –69.3 (*c* 1.96, CH_2Cl_2).



22

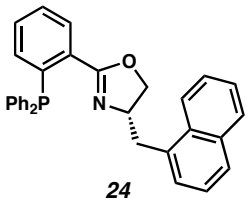
(*S*)-(Adamant-1-yl)-PHOX (22, Table 4, Entry 5): Prepared by general procedure 1 from 2-(1-adamantyl)-glycine[7] in 71% yield as a white solid; mp 163-164 ºC; R_f = 0.59 (5:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (m, 1H), 7.40-7.20 (m, 12H), 6.85 (m, 1H), 4.11 (t, *J* = 9.0 Hz, 1H), 4.03 (t, *J* = 9.0 Hz, 1H), 3.73 (t, *J* = 9.0 Hz, 1H), 1.85 (m, 3H), 1.68-1.46 (m, 6H), 1.44-1.34 (m, 3H), 1.24-1.14 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4 (d, J_{CP} = 3 Hz), 138.8-138.3 (6 lines), 134.4 (d, J_{CP} = 21 Hz), 134.1, 133.4 (d, J_{CP} = 20 Hz), 132.0 (d, J_{CP} = 20 Hz), 130.3, 129.7 (d, J_{CP} = 3 Hz), 128.5-128.0 (7 lines), 76.8, 66.8, 38.2, 37.0, 35.3, 28.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ –5.67; IR (Neat Film NaCl) 3053, 2902, 2848, 1651, 1586, 1477, 1434, 1346, 1248, 1089, 1044, 1026, 963, 744, 696 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{31}H_{33}NOP$ $[M + H]^+$: 466.2300, found 466.2309; $[\alpha]_D^{27}$ –31.8 (*c* 0.48, $CHCl_3$).



23

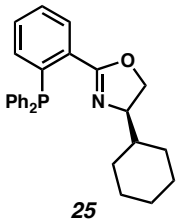
(*S*)-Neopentyl-PHOX (23, Table 4, Entry 6; Table 15, Entry 2): Prepared by general procedure 1 from D-neopentyl-glycine in 73% yield as a white solid; mp 83-86 ºC; R_f = 0.52 (5:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 7.8, 3.6, 1.5 Hz, 1H), 7.38-7.23 (m, 12H), 6.84 (ddd, *J* = 7.8, 4.5, 1.5 Hz, 1H), 4.25 (dd, *J* = 9.3, 8.1 Hz, 1H), 4.03 (m, 1H), 3.58 (t, *J* = 8.1 Hz, 1H), 1.52 (dd, *J* = 14.1, 4.5 Hz, 1H), 0.93 (dd, *J* = 14.1, 8.1 Hz, 1H), 0.84 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0 (d, J_{CP} = 3 Hz), 138.7 (d, J_{CP} = 25 Hz), 137.9 (d, J_{CP} = 12 Hz), 137.8 (d, J_{CP} = 10 Hz), 134.3 (d, J_{CP} = 21 Hz), 133.9 (d, J_{CP} = 21 Hz), 133.5 (d, J_{CP} = 2 Hz), 131.8 (d, J_{CP} = 18 Hz), 130.3, 129.8 (d, J_{CP} = 3 Hz), 128.6-

128.3 (6 lines), 127.9, 73.9, 64.0, 49.7, 30.0, 29.8; ^{31}P NMR (121 MHz, $CDCl_3$) δ –3.95; IR (Neat Film NaCl) 3054, 2955, 1652, 1586, 1476, 1434, 1355, 1248, 1089, 1035, 968, 742, 697 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{26}H_{29}NOP$ $[M + H]^+$: 402.1987, found 402.2002; $[\alpha]_D^{26}$ –6.9 (*c* 1.03, $CHCl_3$).



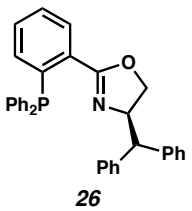
24

(*S*)-(Naphth-1-ylmethyl)-PHOX (24, Table 4, Entry 7; Table 15, Entry 4): Prepared by general procedure 1 (*S*)-3-(1-napthyl)-alanine in 54% yield as a white amorphous solid; R_f = 0.29 (25% Et_2O in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (m, 1H), 7.91 (m, 1H), 7.85 (m, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.56-7.45 (m, 2H), 7.42-7.28 (m, 13H), 7.16 (m, 1H), 6.87 (m, 1H), 4.55 (m, 1H), 3.97 (t, *J* = 8.4 Hz, 1H), 3.86 (dd, *J* = 8.4, 7.2 Hz, 1H), 3.44 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.39 (dd, *J* = 14.4, 10.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.1 (d, J_{CP} = 3 Hz), 138.9 (d, J_{CP} = 25 Hz), 137.84 (d, J_{CP} = 10 Hz), 137.79 (d, J_{CP} = 12 Hz), 134.5 (d, J_{CP} = 21 Hz), 134.0, 133.82 (d, J_{CP} = 21 Hz), 133.80, 133.5 (d, J_{CP} = 3 Hz), 131.9, 131.3 (d, J_{CP} = 17 Hz), 130.6, 130.0 (d, J_{CP} = 3 Hz), 128.8-128.4 (6 lines), 127.9, 127.2, 126.6, 126.0, 125.6, 125.4, 123.8, 71.7, 66.7, 38.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ –3.59; IR (Neat Film NaCl) 3052, 2962, 1651, 1585, 1511, 1476, 1434, 1354, 1216, 1089, 1037, 963, 745, 697 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{32}H_{27}NOP$ $[M + H]^+$: 472.1830, found 472.1835; $[\alpha]_D^{24}$ +29.7 (*c* 0.50, $CHCl_3$).



25

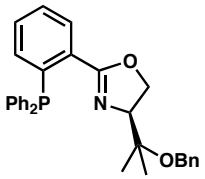
(*S*)-Cyclohexyl-PHOX (25, Table 4, Entry 8): Prepared by general procedure 1 from (*R*)-cyclohexyl-glycine[8] in 68% yield as a white solid; mp 122-124 ºC; R_f = 0.57 (20% EtOAc in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (ddd, *J* = 7.7, 4.1, 1.7 Hz, 1H), 7.27 (m, 13H), 6.82 (ddd, *J* = 7.7, 4.1, 1.1 Hz, 1H), 4.12 (ddd, *J* = 14.6, 9.1, 1.4 Hz, 1H), 3.85 (t, *J* = 8.3 Hz, 1H), 3.81 (t, *J* = 8.5 Hz, 1H), 1.60 (m, 4H), 1.28 (d, *J* = 13.5 Hz, 1H), 1.05 (m, 4H), 0.80 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7 (d, J_{CP} = 3 Hz), 139.0-138.0 (6 lines), 134.5 (d, J_{CP} = 21 Hz), 133.8, 133.7 (d, J_{CP} = 20 Hz), 131.8 (d, J_{CP} = 19 Hz), 130.4, 129.8 (d, J_{CP} = 3 Hz), 128.6-128.0 (7 lines), 71.2, 70.1, 42.7, 29.4, 29.0, 26.4, 26.1, 26.0; ^{31}P NMR (121 MHz, $CDCl_3$) δ –4.21; IR (Neat Film NaCl) 3053, 2923, 2852, 1651, 1478, 1434, 1356, 1089, 1044, 964, 908 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{27}H_{28}NOP$ $[M^+]$: 413.1909, found 413.1923; $[\alpha]_D^{25}$ +47.9 (*c* 0.175, $CHCl_3$).



26

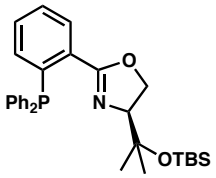
(*R*)-Benzhydryl-PHOX (26, Table 4, Entry 9): Prepared by general procedure 1 from (*R*)-3,3-diphenyl-alanine in 89% yield as a white amorphous solid; R_f = 0.45 (5:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (m, 1H), 7.38-7.13 (m, 22H), 6.88 (m, 1H), 4.92 (q, *J* = 9.0 Hz, 1H), 4.13 (dd, *J* = 9.3, 9.0 Hz, 1H), 3.79 (t, *J* = 9.0 Hz, 1H), 3.72 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.2, 142.2, 142.1, 138.8 (d, J_{CP} = 25 Hz), 138.0-137.7 (3 lines), 134.1 (d, J_{CP} = 21 Hz), 133.9 (d, J_{CP} = 21 Hz), 133.7 (d, J_{CP} = 2 Hz), 131.7 (d, J_{CP} = 19 Hz), 130.5, 130.0 (d, J_{CP} = 3 Hz), 128.7-128.2 (9 lines),

128.0, 126.5, 126.2, 71.1, 70.1, 56.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ –5.22; FTIR (Neat Film NaCl) 3056, 3026, 2895, 1649, 1598, 1584, 1494, 1477, 1451, 1434, 1356, 1091, 1029, 909, 741 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{34}H_{29}NOP$ [M + H]$^+$: 498.1987, found 498.1963; $[\alpha]_D^{24}$ +10.4 (*c* 1.00, $CHCl_3$).



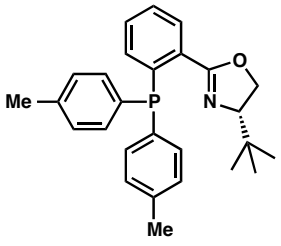
27

(*S*)-(2-(Benzyloxy)propan-2-yl)-PHOX (27, Table 4, Entry 10): The aryl bromide was prepared from L-serine using the analogous procedure reported by Helmchen.[1] Coupling was achieved by general procedure 1 in 75% yield as a colorless viscous oil; R_f = 0.45 (5:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (ddd, *J* = 7.5, 3.6, 1.2 Hz, 1H), 7.41-7.19 (m, 17H), 6.88 (ddd, *J* = 7.5, 4.2, 0.9 Hz, 1H), 4.43-4.23 (m, 4H), 4.15 (dd, *J* = 9.6, 7.8 Hz, 1H), 1.21 (s, 3H), 0.88 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.8 (d, J_{CP} = 3 Hz), 139.5, 139.1-138.3 (5 lines), 134.4 (d, J_{CP} = 21 Hz), 134.2, 133.5 (d, J_{CP} = 20 Hz), 131.6 (d, J_{CP} = 19 Hz), 130.5, 129.9 (d, J_{CP} = 3 Hz), 128.6-128.1 (6 lines), 127.14, 127.12, 76.9, 74.9, 68.5, 63.9, 23.9, 19.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ –5.51; IR (Neat Film NaCl) 3067, 2973, 2905, 1649, 1586, 1478, 1434, 1352, 1248, 1155, 1091, 1065, 1027, 964, 743, 697 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{31}H_{31}NO_2P$ [M + H]$^+$: 480.2092, found 480.2078; $[\alpha]_D^{26}$ –2.0 (*c* 1.03, $CHCl_3$).



28

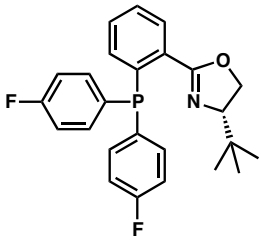
(*S*)-(2-(*tert*-Butyldimethylsilyloxy)propan-2-yl)-PHOX (28, Table 4, Entry 11): The aryl bromide was prepared from L-serine using the analogous procedure reported by Helmchen.[1] Coupling was achieved by general procedure 1 in 84% yield as a white solid; mp 104-106 ºC; R_f = 0.62 (5:1 HexanesEtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (ddd, *J* = 7.5, 3.6, 1.2 Hz, 1H), 7.40-7.20 (m, 12H), 6.88 (ddd, *J* = 7.5, 3.9, 0.9 Hz, 1H), 4.32 (dd, *J* = 7.5, 6.6 Hz, 1H), 4.09 (dd, *J* = 10.2, 7.5 Hz, 1H), 4.02 (dd, *J* = 10.2, 6.6 Hz, 1H), 1.15 (s, 3H), 0.86 (s, 3H), 0.78 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.6, 139.0-138.3 (6 lines), 134.3 (d, J_{CP} = 21 Hz), 134.2, 133.5 (d, J_{CP} = 20 Hz), 131.9 (d, J_{CP} = 19 Hz), 130.4, 129.8 (d, J_{CP} = 3 Hz), 128.5-128.0 (5 lines), 76.8, 74.9, 68.7, 28.7, 25.7, 23.9, 17.9, –2.2, –2.3; ^{31}P NMR (121 MHz, $CDCl_3$) δ –5.99; IR (Neat Film NaCl) 3054, 2955, 2929, 2856, 1652, 1586, 1472, 1434, 1353, 1251, 1162, 1091, 1058, 835, 774, 743, 696 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{30}H_{39}NO_2PSi$ [M + H]$^+$: 504.2488, found 504.2469; $[\alpha]_D^{26}$ +19.8 (*c* 1.16, $CHCl_3$).



31

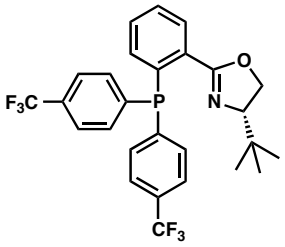
(*S*)-4-*tert*-Butyl-2-(2-(di-*p*-tolylphosphino)phenyl)-4,5-dihydrooxazole (31, Table 5, Entry 1): Prepared by general procedure 1 using (*p*-Tol)$_2$PH in 73% yield as a colorless viscous oil; R_f = 0.39 (10% EtOAc in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (ddd, *J* = 7.5, 3.6, 1.5 Hz, 1H), 7.33 (m, 1H), 7.26 (m, 1H), 7.23-7.05 (m, 8H), 6.89 (ddd, *J* = 7.5, 4.2, 1.5 Hz, 1H), 4.06 (dd, *J* = 10.2, 8.4 Hz,

1H), 3.98 (t, J = 8.3 Hz, 1H), 3.85 (dd, J = 10.2, 7.8 Hz, 1H), 2.33 (s, 3H), 2.32 (s, 3H), 0.75 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0 (d, J_{CP} = 3 Hz), 139.3 (d, J_{CP} = 25 Hz), 138.4, 138.1, 135.0-134.7 (4 lines), 134.3 (d, J_{CP} = 21 Hz), 133.9, 133.6 (d, J_{CP} = 20 Hz), 131.9 (d, J_{CP} = 20 Hz), 130.2, 129.9 (d, J_{CP} = 3 Hz), 129.2 (d, J_{CP} = 7 Hz), 129.0 (d, J_{CP} = 7 Hz), 127.8, 76.5, 68.3, 33.6, 25.7, 21.3, 21.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ –6.98; IR (Neat Film NaCl) 2953, 1653, 1496, 1476, 1394, 1353, 1306, 1248, 1185, 1134, 1089, 1024, 967, 805, 743 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{27}H_{30}NOP$ [M$^+$]: 415.2065, found 415.2065; $[\alpha]_D^{25}$ –58.8 (*c* 2.23, $CHCl_3$).



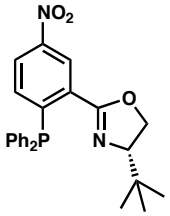
32

(*S*)-2-(2-(bis(4-fluorophenyl)phosphino)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole (32, Table 5, Entries 3 and 11): Prepared by Helmchen's Grignard method[1] in 14% yield as a colorless oil; R_f = 0.50 (5% Et_2O in hexanes developed twice); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (ddd, J = 7.0, 3.0, 1.0 Hz, 1H), 7.39 (ddd, J = 8.0, 8.0, 1.5 Hz, 1H), 7.31 (ddd, J = 7.5, 7.5, 1.0 Hz, 1H), 7.26-7.14 (comp. m, 4H), 7.01 (app. dt, J = 13.0, 8.5 Hz, 4H), 6.83 (ddd, J = 7.5, 4.0, 1.0 Hz, 1H), 4.12 (dd, J = 10.0, 8.5 Hz, 1H), 4.03 (dd, J = 8.0, 8.0 Hz, 1H), 3.90 (dd, J = 10.0, 8.0 Hz, 1H), 0.74 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.3 (d, $J_{C\text{-}F}$ = 247.5 Hz), 163.1 (d, $J_{C\text{-}F}$ = 246.5 Hz), 162.3, 138.6 (d, $J_{C\text{-}P}$ = 25.3 Hz), 136.1 (dd, $J_{C\text{-}P}$ = 22.5 Hz, $J_{C\text{-}F}$ = 8.1 Hz), 135.3 (dd, $J_{C\text{-}P}$ = 21.9 Hz, $J_{C\text{-}F}$ = 8.1 Hz), 134.1 (dd, $J_{C\text{-}P}$ = 12.5, $J_{C\text{-}F}$ = 4.1 Hz), 134.0 (dd, $J_{C\text{-}P}$ = 10.4 Hz, $J_{C\text{-}F}$ = 4.0 Hz), 133.9, 131.7 (d, $J_{C\text{-}P}$ = 20.0 Hz), 130.5, 130.0 (d, $J_{C\text{-}P}$ = 2.9 Hz), 128.3, 115.6 (dd, $J_{C\text{-}F}$ = 18.6 Hz, $J_{C\text{-}P}$ = 7.6 Hz), 115.5 (dd, $J_{C\text{-}F}$ = 18.6 Hz, $J_{C\text{-}P}$ = 7.6 Hz) 76.8, 68.3, 33.6, 25.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ –8.2 (app. t, J = 3.8 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –113.6, –114.1; IR (Neat Film NaCl) 2955, 2904, 2868, 1653, 1587, 1494, 1392, 1354, 1336, 1225, 1159, 1091, 1039, 1025, 966, 827, 744 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{25}H_{25}ONPF_2$ [M + H]$^+$: 424.1642, found 424.1622; $[\alpha]_D^{26.4}$ –17.7 (*c* 0.53, CH_2Cl_2).



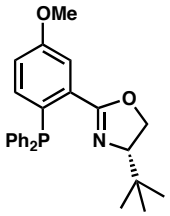
33

(*S*)-2-(2-(Bis(4-(trifluoromethyl)phenyl)phosphino)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole (33, Table 5, Entries 4 and 12): Prepared by general procedure 1 using (p-$CF_3Ph)_2PH$ in 75% yield as a white amorphous powder; R_f = 0.44 (10% EtOAc in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (ddd, J = 7.5, 3.9, 1.2 Hz, 1H), 7.62-7.50 (m, 4H), 7.44 (m, 1H), 7.40-7.28 (m, 5H), 6.82 (ddd, J = 7.5, 3.9, 0.9 Hz, 1H), 4.20 (dd, J = 10.2, 8.4 Hz, 1H), 4.06 (t, J = 8.4 Hz, 1H), 3.93 (dd, J = 10.2, 8.4 Hz, 1H), 0.69 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8 (d, J_{CP} = 3 Hz), 143.4-143.2 (m), 136.7 (d, J_{CP} = 24 Hz), 134.4 (d, J_{CP} = 21 Hz), 134.2, 133.7 (d, J_{CP} = 20 Hz), 132.0 (d, J_{CP} = 20 Hz), 130.74, 130.65 (q, J_{CF} = 32 Hz), 130.5 (q, J_{CF} = 32 Hz), 129.9 (d, J_{CP} = 3 Hz), 128.9, 125.3-124.9 (m), 124.1 (q, J_{CF} = 271 Hz,), 77.0, 68.4, 33.6, 25.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ –7.29; ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.23, –63.28; IR (Neat Film NaCl) 2958, 1653, 1606, 1480, 1396, 1324, 1166, 1128, 1106, 1061, 1017, 831, 700 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{27}H_{24}NOPF_6$ [M$^+$]: 523.1500, found 523.1494; $[\alpha]_D^{25}$ –21.1 (*c* 2.26, $CHCl_3$).



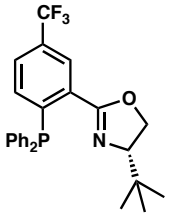
34

(*S*)-4-*tert*-Butyl-2-(2-(diphenylphosphino)-5-nitrophenyl)-4,5-dihydrooxazole (34, Table 5, Entries 5 and 13): Prepared by a modification of Andreas' method[9] in 8% yield as a red oil; R_f = 0.57 (25% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 3.0, 3.0 Hz, 1H), 8.07 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.40-7.29 (comp. m, 6H), 7.29-7.18 (comp. m, 4H), 7.04 (dd, *J* = 8.5, 3.0 Hz, 1H), 4.15 (dd, *J* = 10.0, 8.5 Hz, 1H), 4.04 (dd, *J* = 9.0, 8.0 Hz, 1H), 3.90 (dd, *J* = 9.5, 8.0 Hz, 1H), 0.72 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.7 (d, *J* = 3.8 Hz), 148.6 (d, *J* = 33.0 Hz), 147.4, 137.2 (d, *J* = 12.0 Hz), 136.9 (d, *J* = 8.5 Hz), 135.1 (d, *J* = 1.4 Hz), 134.3 (d, *J* = 21.5 Hz), 133.6 (d, *J* = 20.5 Hz), 132.7 (d, *J* = 18.6 Hz), 129.2-128.6 (6 lines), 124.4 (d, *J* = 1.9 Hz), 124.1, 77.2, 68.6, 33.6, 25.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ –3.4; IR (Neat Film NaCl) 3071, 2956, 2904, 2868, 1656, 1522, 1478, 1434, 1346, 1118, 1086, 1026, 970, 913, 742, 696 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{25}H_{26}O_3N_2P$ $[M + H]^+$: 433.1681, found 433.1702; $[\alpha]_D^{26.4}$ –16.2 (*c* 0.87, $CHCl_3$).



35

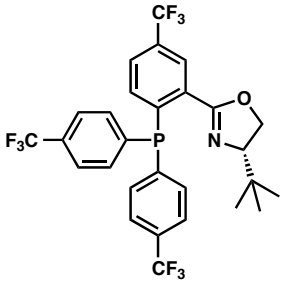
(*S*)-4-*tert*-Butyl-2-(2-(diphenylphosphino)-5-methoxyphenyl)-4,5-dihydrooxazole (35, Table 5, Entry 8): Prepared by general procedure 1 using 2-bromo-5-methoxybenzoyl chloride[10] in 72% yield as a white amorphous powder; R_f = 0.61 (25% EtOAc in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48 (t, *J* = 2.9 Hz, 1H), 7.34-7.18 (m, 10H), 6.84 (ddd, *J* = 8.7, 2.4, 0.6 Hz, 1H), 6.78 (ddd, *J* = 8.7, 3.3, 0.6 Hz, 1H), 4.13 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.03 (t, *J* = 8.1 Hz, 1H), 3.92 (dd, *J* = 10.2, 8.1 Hz, 1H), 3.82 (s, 3H), 0.73 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.5 (d, J_{CP} = 3 Hz), 159.4, 139.0 (d, J_{CP} = 13 Hz), 138.7 (d, J_{CP} = 10 Hz), 135.8, 134.1 (d, J_{CP} = 20 Hz), 133.41 (d, J_{CP} = 33 Hz), 133.36 (d, J_{CP} = 20 Hz), 129.3 (d, J_{CP} = 22 Hz), 128.3-128.0 (6 lines), 116.5, 114.9 (d, J_{CP} = 4 Hz), 76.7, 68.3, 55.3, 33.6, 25.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ –10.1; IR (Neat Film NaCl) 3069, 2956, 2903, 1654, 1594, 1561, 1479, 1434, 1354, 1336, 1297, 1224, 1181, 1093, 1050, 1022, 973, 744, 697 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{26}H_{28}NO_2P$ $[M^+]$: 417.1858, found 417.1844; $[\alpha]_D^{25}$ –48.8 (*c* 2.11, $CHCl_3$).



36

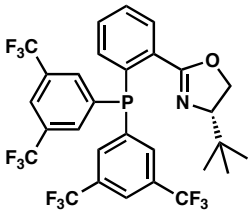
(*S*)-4-*tert*-Butyl-2-(2-(diphenylphosphino)-5-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (36, Table 5, Entry 10): Prepared by general procedure 1 from 2-bromo-5-trifluoromethylbenzoyl chloride[11] in 77% yield as a white powder; mp 98-100 ºC; R_f = 0.45 (10% EtOAc in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 (m, 1H), 7.51 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.38-7.18 (m, 10H), 6.99 (dd, *J* = 8.1, 3.3 Hz, 1H), 4.12 (dd, *J* = 10.2, 8.4 Hz, 1H), 4.03 (t, *J* = 8.4 Hz, 1H), 3.90 (dd, *J* = 10.2, 8.4 Hz, 1H), 0.72 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.4 (d, J_{CP} = 3 Hz), 144.2 (d, J_{CP} = 30 Hz), 137.7 (d, J_{CP} = 12 Hz), 137.3 (d, J_{CP} = 9 Hz), 134.6, 134.3 (d, J_{CP} = 21 Hz), 133.6 (d, J_{CP} = 20 Hz), 132.2 (d, J_{CP} = 19

Hz), 130.1 (q, J_{CF} = 33 Hz), 128.9-128.4 (6 lines), 126.6-126.3 (m), 123.7 (q, J_{CF} = 271 Hz), 77.0 (d, J_{CP} = 1 Hz), 68.4, 33.6, 25.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ –6.55 (J_{PF} = 2 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.36; IR (Neat Film NaCl) 3071, 2957, 1655, 1478, 1434, 1407, 1357, 1343, 1326, 1302, 1262, 1244, 1174, 1131, 1080, 969, 744, 696 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{26}H_{25}NOPF_3$ [M$^+$]: 455.1626, found 455.1646; $[\alpha]_D^{25}$ –36.3 (*c* 2.39, $CHCl_3$).



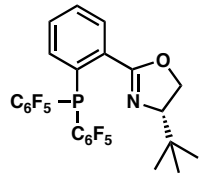
37

(*S*)-2-(2-(Bis(4-(trifluoromethyl)phenyl)phosphino)-5-(trifluoromethyl)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole (37, Table 5, Entry 14): Prepared by general procedure 1 using (*p*-$CF_3Ph)_2PH$ in 74% yield as a white amorphous powder; R_f = 0.63 (10% EtOAc in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (m, 1H), 7.64-7.54 (m, 5H), 7.39-7.27 (m, 4H), 6.95 (dd, *J* = 7.8, 3.0 Hz, 1H), 4.25 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.09 (t, *J* = 8.7 Hz, 1H), 3.95 (dd, *J* = 10.2, 8.7 Hz, 1H), 0.69 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7 (d, J_{CP} = 4 Hz), 142.6-141.7 (6 lines), 134.7-133.6 (5 lines), 132.4 (d, J_{CP} = 20 Hz), 131.1 (q, J_{CF} = 32 Hz), 130.9 (q, J_{CF} = 32 Hz), 127.0 (q, J_{CF} = 3 Hz), 126.7-126.4 (6 lines), 125.6-125.1 (8 lines), 123.9 (q, J_{CF} = 271 Hz), 123.5 (q, J_{CF} = 271 Hz), 77.3 (d, J_{CP} = 1 Hz), 68.6, 33.5, 25.6; ^{31}P NMR (121 MHz, $CDCl_3$) δ –6.57; ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.33, –63.39, –63.53; IR (Neat Film NaCl) 2960, 1657, 1606, 1479, 1397, 1324, 1169, 1129, 1107, 1082, 1061, 1017, 832, 700 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{28}H_{24}F_9NOP$ [M + H]$^+$: 592.1452, found 592.1480; $[\alpha]_D^{24}$ –16.0 (*c* 2.56, $CHCl_3$).



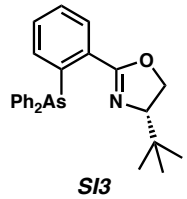
38

(*S*)-2-(2-(Bis(3,5-bis(trifluoromethyl)phenyl)phosphino)phenyl)-4-*tert*-butyl-4,5-dihydrooxazole (38, Table 5, Entry 6): Prepared by Helmchen's Grignard method[1] in 6% yield as a colorless oil; R_f = 0.29 (5% Et_2O in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.04 (ddd, *J* = 7.5, 4.0, 1.5 Hz, 1H), 7.86 (app. d, *J* = 11.0 Hz, 2H), 7.64 (app. dd, *J* = 21.0, 6.0 Hz, 4H), 7.53 (ddd, *J* = 7.0, 7.0, 1.0, 1H), 7.42 (ddd, *J* = 7.5, 7.5 1.0 Hz, 1H), 6.77 (ddd, *J* = 7.5, 3.5, 1.0 Hz, 1H), 4.28 (dd, *J* = 10.0, 8.5 Hz, 1H), 4.12 (dd, *J* = 9.0, 9.0 Hz, 1H), 3.91 (dd, *J* = 10.5, 9.0 Hz, 1H), 0.68 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4 (d, *J* = 3.4 Hz), 141.9 (d, *J* = 13.9 Hz), 141.8 (d, *J* = 11.9 Hz), 134.8 (d, *J* = 23.9 Hz), 134.0, 133.7 (d, *J* = 19.1 Hz), 133.2 (d, *J* = 21.5 Hz), 131.8 (app. dq, *J* = 31.5, 4.8 Hz), 131.3, 130.0 (d, *J* = 2.9 Hz), 129.8, 123.1 (q, *J* = 271.8 Hz), 122.7 (app. d of septets, *J* = 25.3, 3.3 Hz), 77.1, 68.7, 33.4, 25.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ –6.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.9 (2 peaks); HRMS (FAB) *m/z* calc'd for $C_{29}H_{23}ONPF_{12}$ [M + H]$^+$: 660.1325, found 660.1328; $[\alpha]_D^{26.2}$ –5.0 (*c* 0.35, $CHCl_3$).



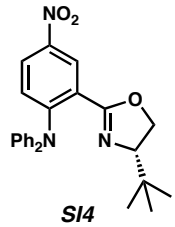
39

(*S*)-4-*tert*-Butyl-2-(2-(diperfluorophenylphosphino)phenyl)-4,5-dihydrooxazole (39, Table 5, Entry 7): Prepared by Helmchen's Grignard method[1] in 13% yield as a colorless oil; R_f = 0.39 (2.5% Et_2O in hexanes developed twice); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.00 (ddd, *J* = 7.4, 4.8, 1.3 Hz, 1H), 7.51 (app. tt, *J* = 7.5, 1.3 Hz, 1H), 7.41 (app. tt, *J* = 7.7, 1.3 Hz, 1H), 7.16 (dd, *J* = 7.7, 3.5 Hz, 1H), 4.35 (dd, *J* = 10.1, 8.8 Hz, 1H), 4.18 (dd, *J* = 8.8, 8.8 Hz, 1H), 3.93 (dd, *J* = 10.1, 8.8 Hz, 1H), 0.75 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3 (d, *J* = 5.0 Hz), 132.5, 130.9, 129.7 (2 peaks), 129.6, 77.3, 69.1, 33.6, 25.7; ^{31}P NMR (121 MHz, $CDCl_3$) δ –54.7 (app. quintet, *J* = 38.1 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –130.6 (app. t, *J* = 27.5 Hz), –131.1 (app. t, *J* = 27.5 Hz), –151.9 (app. t, *J* = 18.6 Hz), –152.4 (app. t, *J* = 21.2 Hz), –161.8 (app. t, *J* = 18.0 Hz), –162.0 (app. t, *J* = 15.0 Hz); IR (Neat Film NaCl) 2962, 2908, 2872, 1654, 1516, 1476, 1382, 1360, 1287, 1139, 1087, 1052, 978, 908, 834, 740 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{25}H_{17}ONPF_{10}$ $[M + H]^+$: 568.0888, found 568.0868; $[\alpha]_D^{26.2}$ –6.3 (*c* 0.56, CH_2Cl_2).



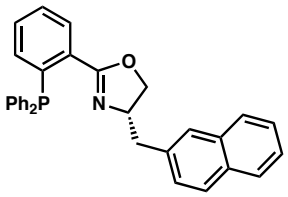
SI3

(*S*)-4-*tert*-Butyl-2-(2-(diphenylarsino)phenyl)-4,5-dihydrooxazole (SI3, Table 6, Entry 2): Prepared by Helmchen's S_NAr method[1] in 40% yield using lithium diphenylarsine generated by lithium reduction of triphenylarsine as a colorless oil; R_f = 0.42 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.37 (ddd, *J* = 7.5, 7.5, 1.0 Hz, 1H), 7.34-7.23 (comp. m, 10H), 7.01 (dd, *J* = 8.0, 1.0, 1H), 4.15 (dd, *J* = 9.5, 8.0 Hz, 1H), 4.04 (dd, *J* = 8.5, 8.5 Hz, 1H), 3.88 (dd, *J* = 10.5, 9.0 Hz, 1H), 0.75 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 141.9 (2 peaks), 141.5, 134.6, 134.0, 133.7, 131.8, 130.6, 129.5, 128.4 (2 peaks), 128.0, 127.9, 76.7, 68.3, 33.6, 25.7; IR (Neat Film NaCl) 3066, 3052, 2955, 2903, 2867, 1652, 1480, 1433, 1354, 1336, 1306, 1253, 1132, 1088, 1024, 967, 903, 736, 696 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{25}H_{27}ONAs$ $[M + H]^+$: 432.1309, found 432.1290; $[\alpha]_D^{25.6}$ –33.8 (*c* 1.47, $CHCl_3$).



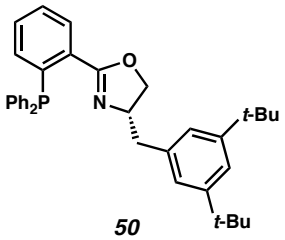
SI4

(*S*)-4-*tert*-Butyl-2-(2-(diphenylamino)-5-nitrophenyl)-4,5-dihydrooxazole (SI4, Table 6, Entry 3): Prepared by a modification of Zhu's method[12] in 18% yield as a red oil; R_f = 0.45 (10% Et_2O in hexanes developed thrice); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 3.0 Hz, 1H), 8.13 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.28 (app. t, *J* = 7.5 Hz, 4H), 7.09 (app. t, *J* = 7.5, 2H), 7.09 (d, *J* = 9.0 Hz, 1H), 7.03 (app. d, *J* = 7.5 Hz, 4H), 3.77 (dd, *J* = 8.5, 8.5 Hz, 1H), 3.59 (dd, *J* = 10.0, 8.5 Hz, 1H), 3.24 (dd, *J* = 10.0, 8.0 Hz, 1H), 0.80 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 151.8, 146.6, 141.8, 129.4, 128.6, 126.6, 126.5, 124.6, 124.3, 123.3, 75.0, 68.7, 33.6, 25.9; IR (Neat Film NaCl) 2958, 2904, 2868, 1647, 1588, 1574, 1518, 1490, 1333, 1299, 1278, 1116, 968, 912, 860, 751, 695 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{25}H_{26}O_3N_3$ $[M + H]^+$: 416.1974, found 416.1969; $[\alpha]_D^{25.6}$ +203.9 (*c* 0.55, $CHCl_3$).



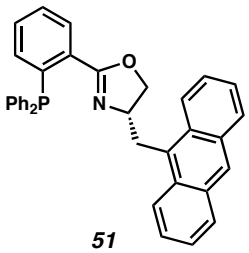
49

(*S*)-(Napth-2-ylmethyl)-PHOX (49, Table 15, Entry 5): Prepared by general procedure 1 from 3-(2-napthyl)-alanine in 71% yield as a white amorphous solid; R_f = 0.24 (25% Et_2O in Hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (m, 1H), 7.82-7.72 (m, 3H), 7.53 (br s, 1H), 7.49-7.27 (m, 14H), 7.23 (m, 1H), 6.88 (m, 1H), 4.46 (m, 1H), 4.05 (dd, *J* = 9.0, 8.7 Hz, 1H), 3.83 (dd, *J* = 9.0, 7.5 Hz, 1H), 3.08 (dd, *J* = 14.1, 5.1 Hz, 1H), 2.30 (dd, *J* = 14.1, 9.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.0 (d, J_{CP} = 3 Hz), 138.9 (d, J_{CP} = 25 Hz), 137.0-137.7 (3 lines), 135.6, 134.4 (d, J_{CP} = 21 Hz), 133.8 (d, J_{CP} = 21 Hz), 133.5 (d, J_{CP} = 2 Hz), 133.4, 132.1, 131.4 (d, J_{CP} = 18 Hz), 130.5, 129.9 (d, J_{CP} = 3 Hz), 128.7-127.4 (12 lines), 125.9, 125.4, 71.4, 67.7, 41.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ –4.05; FTIR (Neat Film NaCl) 3052, 1651, 1508, 1476, 1434, 1354, 1217, 1090, 1027, 964, 817, 743, 697 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{32}H_{27}NOP$ $[M + H]^+$: 472.1830, found 472.1845; $[\alpha]_D^{25}$ +42.7 (*c* 0.50, $CHCl_3$).



50

(*R*)-(3,5-Di-*tert*-butylbenzyl)-PHOX (50, Table 15, Entry 6): Prepared by general procedure 1 from (*R*)-3-(3,5-di-*tert*-butylphenyl)-alaninol[13] in 55% yield as a colorless viscous oil; R_f = 0.52 (5:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (m, 1H), 7.40-7.28 (m, 13H), 6.92 (d, *J* = 1.8 Hz, 2H), 6.86 (m, 1H), 4.33 (m, 1H), 4.00 (t, *J* = 8.7 Hz, 1H), 3.78 (dd, *J* = 8.7, 7.5 Hz, 1H), 2.95 (dd, *J* = 13.8, 4.2 Hz, 1H), 2.01 (dd, *J* = 13.8, 10.2 Hz, 1H), 1.30 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.9 (d, J_{CP} = 3 Hz), 150.8, 138.9 (d, J_{CP} = 25 Hz), 137.9 (d, J_{CP} = 12 Hz), 137.8 (d, J_{CP} = 10 Hz), 137.2, 134.4 (d, J_{CP} = 21 Hz), 134.0 (d, J_{CP} = 21 Hz), 133.4 (d, J_{CP} = 3 Hz), 131.5 (d, J_{CP} = 17 Hz), 130.5, 130.0 (d, J_{CP} = 3 Hz), 128.8-128.4 (6 lines), 127.9, 123.3, 120.3, 71.6, 68.1, 41.6, 34.7, 31.5; ^{31}P NMR (121 MHz, $CDCl_3$) δ –3.60; IR (Neat Film NaCl) 2963, 1649, 1598, 1477, 1434, 1361, 1248, 1090, 1027, 965, 742, 696 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{36}H_{41}NOP$ $[M + H]^+$: 534.2926, found 534.2905; $[\alpha]_D^{25}$ –49.3 (*c* 0.36, $CHCl_3$).



51

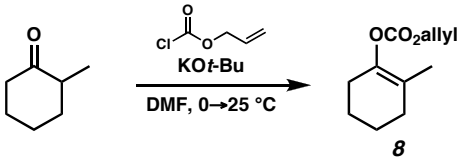
(*S*)-(Anthracen-9-ylmethyl)-PHOX (51, Table 15, Entry 7): Prepared by general procedure 1 from 3-(9-anthracenyl)-alanol[13] in 42% yield as a yellow powder; mp 165-169 ºC; R_f = 0.38 (5:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.34 (s, 1H), 8.16 (m, 2H), 7.99 (m, 2H), 7.94 (m, 1H), 7.55-7.29 (comp. m, 16H), 6.88 (m, 1H), 4.63 (m, 1H), 3.92 (dd, *J* = 9.0, 6.3 Hz, 1H), 3.77 (dd, *J* = 14.7, 4.5 Hz, 1H), 3.68 (t, *J* = 9.0 Hz, 1H), 3.17 (dd, *J* = 14.7, 10.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3 (d, J_{CP} = 3 Hz), 138.9 (d, J_{CP} = 25 Hz), 138.1 (d, J_{CP} = 10 Hz), 137.8 (d, J_{CP} = 13 Hz), 134.6 (d, J_{CP} = 21 Hz), 133.8 (d, J_{CP} = 21 Hz), 133.5 (d, J_{CP} = 3 Hz), 131.5, 130.7, 130.2, 130.0, 129.2, 128.9-128.5 (6

lines), 128.0, 126.5, 125.8, 124.9, 124.5, 71.2, 67.8, 32.1; ^{31}P NMR (121 MHz, $CDCl_3$) δ –3.57; IR (Neat Film NaCl) 3051, 2961, 1648, 1476, 1434, 1353, 1092, 1032, 956, 742, 696 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{36}H_{29}NOP$ [M$^+$]: 521.1909, found 521.1905; $[\alpha]_D^{26}$ –5.1 (*c* 0.20, $CHCl_3$).

Synthesis of Allyl Enol Carbonates

General Procedures for the Synthesis of Allyl Enol Carbonates.

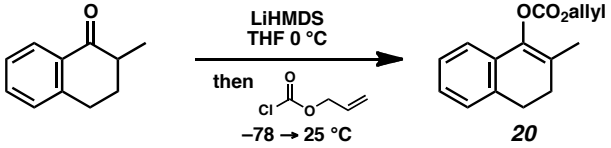
General Procedure 2:



8

Allyl 2-methylcyclohex-1-enyl carbonate (8, Table 7, Entries 1–3):[14] To a solution of potassium *t*-butoxide (5.88 g, 52.5 mmol, 1.05 equiv) in DMF (100 mL) was added 2-methylcyclohexanone (6.13 mL, 50 mmol, 1.0 equiv). After 12 h, the reaction mixture was cooled in an ice bath and allyl chloroformate (6.4 mL, 60 mmol, 1.2 equiv) was added in a dropwise fashion. After an additional 30 min in the ice bath and 15 min at 25 °C, the reaction mixture was quenched into water (250 mL), extracted with 2:1 CH_2Cl_2:hexanes (4 x 125 mL), dried ($MgSO_4$), and evaporated. Chromatography (2.5→4% Et_2O in Hexanes on SiO_2) afforded the allyl enol carbonate **8** (4.49 g, 46% yield) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 (ddt, *J* = 17.4, 10.5, 5.6 Hz, 1H), 5.36 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.2, 1.2 Hz, 1H), 4.63 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.13 (m, 2H), 2.02 (m, 2H), 1.70 (m, 2H), 1.59 (m, 2H), 1.55 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 142.2, 131.5, 120.8, 118.8, 68.5, 30.0, 26.6, 23.1, 22.3, 15.7; IR (Neat Film NaCl) 3936, 1755, 1275, 1239, 1037 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{16}O_3$ [M]$^+$: 196.1100, found 196.1092.

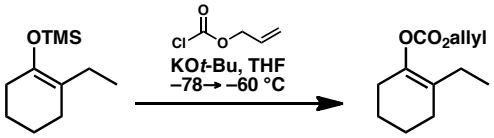
General Procedure 3:



20

Allyl 2-methyl-3,4-dihydronaphthalen-1-yl carbonate (20, Table 7, Entry 12):[15] To a cooled (0 °C) solution of LiHMDS (17.16 mmol, 1.1 equiv) in THF (37 mL) was added 2-methyl-1-tetralone (2.37 mL, 15.6 mmol, 1.0 equiv) in a dropwise manner over 15 min. After an additional 1.5 h at 0 °C, the enolate solution was added dropwise over 15 min to a –78 °C solution of allyl chloroformate (2.0 mL, 18.7 mmol, 1.2 equiv) in THF (80 mL). The reaction mixture was allowed to warm to 25 °C in a Dewar vessel over 8 h. At which time, the reaction was quenched into CH_2Cl_2 (100 mL) and half-saturated aq NH_4Cl (100 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (2 x 50 mL). The organic fractions were washed with brine (100 mL), and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure, and chromatography (2→5% Et_2O in Hexanes on SiO_2) afforded the allyl enol carbonate **20** (3.34 g, 88% yield) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20-7.08 (m, 4H), 6.01 (ddt, *J* = 17.7, 10.4, 5.6 Hz 1H), 5.41 (dq, *J* = 17.3, 1.5 Hz, 1H), 5.32 (dd, *J* = 10.2, 1.0 Hz, 1H), 4.72 (dt, *J* = 6.3, 1.4 Hz, 2H), 2.87 (t, *J* = 8.0 Hz, 2H), 2.40 (t, *J* = 8.0 Hz, 2H), 1.83 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 140.6, 135.2, 131.3, 130.8, 127.3, 127.0, 126.4, 124.4, 119.9, 119.1, 68.9, 28.8, 27.4, 16.5; IR (Neat Film NaCl) 2935, 2833, 1760, 1239 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{16}O_3$ [M]$^+$: 244.1100, found 244.1098.

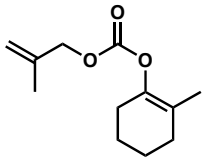
General Procedure 4:



SI22 ***SI5***

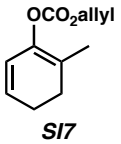
Allyl 2-ethylcyclohex-1-enyl carbonate (SI5, Table 7, Entry 7):[16] To a solution of (2-ethylcyclohex-1-enyloxy)trimethylsilane (**SI22**, vide infra) (1.50 g, 7.56 mmol, 1.0 equiv) in THF (14 mL) cooled to –78 °C was added a solution of potassium *t*-butoxide (0.933 g, 8.32 mmol, 1.1 equiv) in THF (8 mL) in a dropwise fashion over 2 min. The reaction mixture was maintained at –60 °C for 2.5 h, at which time allyl chloroformate (847 μL, 7.93 mmol, 1.05 equiv) in THF (3 mL) was added. After 1 h at –50 °C, the reaction mixture was poured into a mixture of CH_2Cl_2 (20 mL) and half-saturated aqueous NH_4Cl (20 mL). The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 x 10 mL). The organic fractions were washed with water (50 mL), brine (50 mL), and dried (Na_2SO_4). Evaporation of the solvents under reduced pressure followed by chromatography on (2% Et_2O in Hexanes on SiO_2) and heating (room temperature to 105 °C) at 2 torr in a kugelrohr distillation apparatus afforded allyl enol carbonate **SI5** (0.944 g, 59% yield) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, J = 17.4, 10.5, 5.6 Hz, 1H), 5.37 (dq, J = 17.2, 1.5 Hz, 1H), 5.27 (dq, J = 10.5, 1.2 Hz, 1H), 4.64 (dt, J = 5.7, 1.5 Hz, 2H), 2.16 (m, 2H), 2.05 (m, 2H), 1.99 (q, J = 7.8, 2H), 1.70 (m, 2H), 1.61 (m, 2H), 0.4 (t, J = 7.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 141.7, 131.5, 126.3, 118.8, 68.5, 27.2, 26.6, 23.0, 22.9, 22.3, 11.9; IR (Neat Film NaCl) 2936, 1754, 1239 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O_3$ [M]$^+$: 210.1256, found 210.1255.

Characterization Data for Allyl Enol Carbonates:



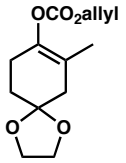
SI6

2-Methylallyl 2-methylcyclohex-1-enyl carbonate (SI6, Table 7, Entry 4): Prepared by general procedure 4 from 2-methylcyclohexanone and methallyl chloroformate[3] in 16% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.03 (s, 1H), 4.96 (s, 1H), 4.57 (s, 2H), 2.16 (m, 2H), 2.034 (br s, 2H), 1.79 (s, 3H), 1.77-1.58 (m, 4H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 142.2, 139.4, 120.9, 113.4, 71.1, 30.1, 26.6, 23.1, 22.3, 19.3, 15.8; IR (Neat Film NaCl) 2926, 1755, 1236 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O_3$ [M]$^+$: 210.1256, found 210.1259.



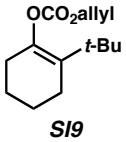
SI7

Allyl 2-methylcyclohexa-1,5-dienyl carbonate (SI7, Table 7, Entry 5): Prepared by general procedure 3 from 6-methyl-cyclohex-2-en-1-one[17] in 45% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (ddt, J = 17.1, 10.5, 5.7 Hz, 1H), 5.75 (m, 2H), 5.39 (dq, J = 17.1, 1.5 Hz, 1H), 5.29 (d, J = 10.5, 1.2 Hz, 1H), 4.67 (app. dt, J = 5.7, 1.5 Hz, 2H), 2.42 (br s, 4H), 1.69 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 140.4, 131.3, 126.1, 122.7, 120.0, 119.1, 68.8, 28.2, 22.4, 15.7; IR (Neat Film NaCl) 2933, 1760, 1260 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{14}O_3$ [M]$^+$: 194.0943, found 194.0938.



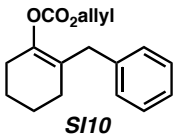
SI8

Allyl 7-methyl-1,4-dioxaspiro[4.5]dec-7-en-8-yl carbonate (SI8, Table 7, Entry 6): Prepared by general procedure 4 from 2-methyl-1,4-cyclohexanedione monoethylene ketal[18] in 31% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.41 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.65 (app. dt, *J* = 5.7, 1.5 Hz, 2H), 3.97 (m, 4H), 2.37 (m, 2H), 2.30 (br s, 2H), 1.87 (app. t, *J* = 6.6 Hz, 2H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9, 141.3, 131.4, 119.0, 118.5, 107.3, 68.6, 64.5, 39.9, 31.3, 25.3, 15.8; IR (Neat Film NaCl) 2919, 1756, 1250 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{19}O_5$ $[M + H]^+$: 255.1232, found 255.1227.



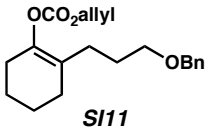
SI9

Allyl 2-*tert*-butylcyclohex-1-enyl carbonate (SI9, Table 7, Entry 8): Prepared by general procedure 4 from 2-*tert*-butylcyclohexanone in 18% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 5.27 (d, *J* = 10.5 Hz, 1H), 5.65 (app. dt, *J* = 5.7, 1.2 Hz, 2H), 2.19 (m, 2H), 2.10 (m, 2H), 1.63 (m, 4H), 1.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 142.1, 131.6, 130.7, 118.9, 68.4, 34.8, 29.4, 28.1, 26.4, 23.1, 22.7; IR (Neat Film NaCl) 2926, 1754, 1241 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{22}O_3$ $[M]^+$: 238.1569, found 238.1566.



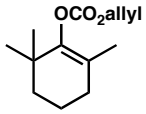
SI10

Allyl 2-benzylcyclohex-1-enyl carbonate (SI10, Table 7, Entry 9): Prepared by general procedure 2 from 2-benzylcyclohexanone in 52% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30-7.16 (m, 5H), 5.95 (ddt, *J* = 17.3, 10.4, 5.7 Hz, 1H), 5.38 (dq, *J* = 17.3, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.2,1.2 Hz, 1H), 4.66 (app. dt, *J* = 5.7, 1.2 Hz, 2H), 3.35 (s, 2H), 2.27 (app. t, *J* = 6.3 Hz, 2H), 1.95 (m, 2H), 1.73 (m, 2H), 1.58 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 143.1, 139.3, 131.4, 128.8, 128.3, 126.0, 123.9, 119.0, 68.6, 36.0, 27.5, 26.7, 23.0, 22.2; IR (Neat Film NaCl) 2937, 1754, 1702, 1648, 1600, 1239 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{20}O_3$ $[M]^+$: 272.1413, found 272.1416.



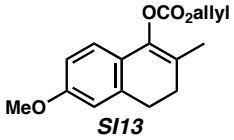
SI11

Allyl 2-(3-(benzyloxy)propyl)cyclohex-1-enyl carbonate (SI11, Table 7, Entry 10): Prepared by general procedure 2 from 2-(3-(benzyloxy)propyl)cyclohexanone[19] in 48% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34-7.26 (comp. m, 5H), 5.92 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.35 (app. dq, *J* = 17.1, 1.5 Hz, 1H), 5.25 (app. dq, *J* = 10.5, 1.1 Hz, 1H), 4.60 (app. dt, *J* = 5.7, 0.9 Hz, 2H), 4.49 (s, 2H), 3.44 (t, *J* = 6.6 Hz, 2H), 2.11 (comp. m, 6H), 1.64 (comp. m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.2, 142.6, 138.7, 131.5, 128.3, 127.6, 127.4, 124.3, 118.8, 72.7, 70.0, 68.5, 27.7, 27.3, 26.6, 26.5, 23.0, 22.3; IR (Neat Film NaCl) 2924, 1754, 1240 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{20}H_{27}O_4$ $[M + H]^+$: 331.1909, found 331.1907.



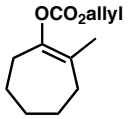
SI12

Allyl 2,6,6-trimethylcyclohex-1-enyl carbonate (SI12, Table 7, Entry 11): Prepared by general procedure 3 from 2,2,6-trimethylcyclohexanone in 59% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (m, 1H), 5.38 (d, *J* = 17.4 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 6.9 Hz, 2H), 2.05 (t, *J* = 5.4 Hz, 2H), 1.56 (m, 4H), 1.49 (s, 3H), 1.04 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.3, 147.9, 131.6, 120.7, 118.8, 68.5, 39.2, 34.9, 31.1, 26.7, 19.1, 16.5; IR (Neat Film NaCl) 2935, 1759, 1238 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{20}O_3$ [M]$^+$: 224.1413, found 224.1418.



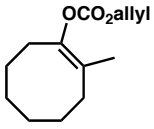
SI13

Allyl 6-methoxy-2-methyl-3,4-dihydronaphthalen-1-yl carbonate (SI13, Table 7, Entry 13): Prepared by general procedure 3 from 2-methyl-6-methoxy-1-tetralone[20] in 88% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (m, 1H), 6.70 (m, 2H), 5.98 (ddt, *J* = 17.1, 10.4, 5.7 Hz 1H), 5.42 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.32 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.71 (dt, *J* = 5.7, 1.2 Hz, 2H), 3.78 (s, 3H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.38 (t, *J* = 8.1 Hz, 2H), 1.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 153.1, 140.4, 137.2, 131.3, 123.9, 121.4, 121.1, 119.1, 113.7, 110.9, 68.9, 55.2, 28.8, 27.8, 16.3; IR (Neat Film NaCl) 2933, 1758, 1237 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{18}O_4$ [M]$^+$: 274.1205, found 274.1213.



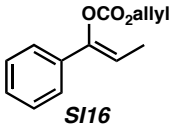
SI14

Allyl 2-methylcyclohept-1-enyl carbonate (SI14, Table 7, Entry 14): Prepared by general procedure 4 from 2-methylcycloheptanone in 36% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.1, 10.5, 5.7 Hz 1H), 5.37 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.65 (app. dt, *J* = 6.0, 1.5 Hz, 2H), 2.33 (m, 2H), 2.10 (m, 2H), 1.70-1.54 (m, 6H), 1.63 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 146.2, 131.5, 125.5, 118.8, 68.5, 32.8, 32.5, 31.0, 25.7, 25.3, 18.3; IR (Neat Film NaCl) 2925, 1753, 1255, 1226 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O_3$ [M]$^+$: 210.1256, found 210.1253.



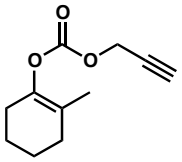
SI15

Allyl 2-methylcyclooct-1-enyl carbonate (SI15, Table 7, Entry 15): Prepared by general procedure 4 from 2-methylcyclooctanone in 28% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (m, 1H), 5.39 (d, *J* = 16.5 Hz, 1H), 5.29 (d, *J* = 10.5 Hz, 1H), 4.66 (d, *J* = 5.4 Hz, 2H), 2.34 (app. t, *J* = 5.7 Hz, 2H), 2.15 (app. t, *J* = 5.4 Hz, 2H), 1.59 (s, 3H), 1.64-1.48 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.4, 143.7, 131.5, 123.0, 118.8, 68.5, 31.4, 29.7, 28.7, 28.4, 26.6, 25.6, 15.5; IR (Neat Film NaCl) 2927, 1754, 1227 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{20}O_3$ [M]$^+$: 224.1413, found 224.1419.



SI16

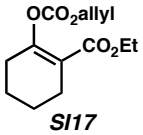
(*Z*)-Allyl 1-phenylprop-1-enyl carbonate (SI16, Table 14, Entries 1–2): Prepared by general procedure 3 from propiophenone in 69% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46-7.43 (m, 2H), 7.37-7.26 (m, 3H), 6.04-5.85 (m, 2H), 5.44-5.28 (m, 2H), 4.71 (dt, *J* = 5.7, 1.5 Hz, 2H), 1.80 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.6, 150.7, 147.2, 134.6, 131.1, 128.4, 128.1, 119.0, 68.9, 11.2; IR (Neat Film NaCl) 3061, 2920, 1760, 1673, 1496, 1446, 1366, 1227, 1186, 966, 765, 693 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{14}O_3$ [M]$^+$: 218.0943, found 218.0938.



47

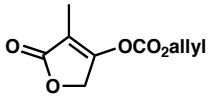
2-Methylcyclohex-1-enyl prop-2-ynyl carbonate (47, Table 15): A 50 mL flask equipped with a septum was flame-dried under vacuum and cooled under dry nitrogen. To this was added methyllithium in Et_2O (1.6 M, 7.5 mL, 12.0 mmol, 1.10 equiv) followed by dry Et_2O (10 mL). To this solution was added a solution of trimethyl(2-methylcyclohex-1-enyloxy)silane (vide infra) (2.003 g, 10.9 mmol, 1.00 equiv) in Et_2O (5 mL) at 0 ºC and the resulting colorless solution was stirred for 1.5 h at ambient temperature to afford a solution of lithium enolate in Et_2O.

To a solution of propargyl chloroformate (1.18 mL, 12.0 mmol, 1.10 eq.) in Et_2O (10 mL) was added the above lithium enolate solution at 0 ºC. The resulting mixture was stirred and warmed to 10 ºC over 1 h. The resulting mixture was poured into saturated aq NH_4Cl and extracted with Et_2O twice. The combined organic layers were washed with water, brine, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a crude oil. The crude residue was purified by SiO_2 chromatography (2 → 10% Et_2O in hexanes) to give propargyl enol carbonate **47** (733 mg, 35% yield) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.75 (d, *J* = 2.4 Hz, 2H), 2.53 (t, *J* = 2.4 Hz, 1H), 2.20-2.11 (m, 2H), 2.07-2.00 (m, 2H), 1.76-1.66 (m, 2H), 1.66-1.56 (m, 2H), 1.57 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 142.3, 121.1, 76.9, 75.7, 55.4, 30.0, 26.5, 23.1, 22.3, 15.8; IR (Neat Film NaCl) 3295, 2937, 2862, 2130, 1756, 1709, 1439, 1376, 1275, 1250, 1220, 1045 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{14}O_3$ [M]$^+$: 194.0943, found 194.0939.



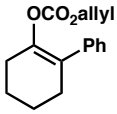
SI17

Ethyl 2-(allyloxycarbonyloxy)cyclohex-1-enecarboxylate (SI17, Table 16, Entry 1): Prepared by general procedure 2 from ethyl 2-oxocyclohexanecarboxylate in 78% yield as a light yellow oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.39 (ddt, *J* = 17.1, 1.5, 1.5 Hz, 1H), 5.28 (ddt, *J* = 10.5, 1.5, 1.2 Hz, 1H), 4.67 (ddd, *J* = 5.7, 1.2, 1.2 Hz, 2H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.44-2.34 (m, 2H), 2.32-2.24 (m, 2H), 1.80-1.58 (comp. m, 4H), 1.24 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 154.8, 152.2, 131.2, 119.2, 118.3, 69.0, 60.5, 28.6, 25.1, 21.9, 21.5, 14.0; IR (Neat Film NaCl) 3087, 1983, 2942, 2866, 1760, 1715, 1666, 1449, 1368, 1233, 1189, 1081, 1056, 1035, 994, 946, 767 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{18}O_5$ [M]$^+$: 254.1154, found 254.1153.



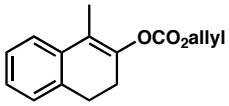
SI18

Allyl 4-methyl-5-oxo-2,5-dihydrofuran-3-yl carbonate (SI18, Table 16, Entry 2): Prepared by a modification of general procedure 2 from 3-methyltetronic acid using Et_3N as the base and THF as solvent in 79% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (ddt, *J* = 17.1, 10.2, 6.0 Hz, 1H), 4.93 (ddt, *J* = 17.1, 2.7, 1.2 Hz, 1H), 5.37 (ddt, *J* = 10.2, 2.1, 0.9 Hz, 1H), 5.07 (q, *J* = 1.8 Hz, 2H), 4.74 (ddd, *J* = 6.0, 1.2, 0.9 Hz, 2H), 1.81 (t, *J* = 1.8 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 163.4, 150.2, 130.0, 120.8, 109.4, 70.3, 67.5, 6.9; IR (Neat Film NaCl) 3089, 2958, 2931, 1774, 1702, 1446, 1392, 1360, 1330, 1240, 1132, 1079, 1025, 945, 889, 775, 754 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_9H_{11}O_5$ $[M + H]^+$: 199.0606, found 199.0600.



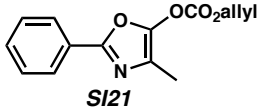
SI19

Allyl 2-phenylcyclohex-1-enyl carbonate (SI19, Table 16, Entry 3): Prepared by general procedure 2 from 2-phenylcyclohexanone in 43% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.18 (comp. m, 5H), 5.80 (ddt, *J* = 17.4, 10.5, 5.4 Hz, 1H), 5.20 (ddt, *J* = 17.4, 1.8, 1.2 Hz, 1H), 5.18 (ddt, *J* = 10.5, 1.5, 1.2 Hz, 1H), 5.02 (ddd, *J* = 5.7, 1.5, 1.5 Hz, 2H), 2.46-2.38 (m, 2H), 2.37-2.30 (m, 2H), 1.90-1.72 (comp. m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.8, 143.4, 138.8, 131.3, 128.1, 127.6, 126.8, 125.9, 118.4, 68.4, 30.1, 27.1, 22.8, 22.5; IR (Neat Film NaCl) 3081, 3057, 3024, 2938, 2862, 1753, 1687, 1601, 1492, 1444, 1367, 1238, 1178, 1091, 1036, 941, 784, 760, 700 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{18}O_3$ $[M]^+$: 258.1256, found 258.1256.



SI20

Allyl 1-methyl-3,4-dihydronaphthalen-2-yl carbonate (SI20, Table 16, Entry 4): Prepared by general procedure 2 from 2-tetralone in 59% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.11 (comp. m, 4H), 6.00 (ddt, *J* = 17.1, 10.2, 6.0 Hz, 1H), 5.43 (ddt, *J* = 17.1, 1.8, 1.2 Hz, 1H), 5.33 (ddt, *J* = 10.2, 1.5, 1.2 Hz, 1H), 4.72 (ddd, *J* = 6.0, 1.5, 1.2 Hz, 2H), 2.97 (t, *J* = 7.8 Hz, 2H), 2.55 (tq, *J* = 8.1, 1.5 Hz, 2H), 2.00 (t, *J* = 1.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.7, 145.9, 135.0, 134.1, 131.2, 127.1, 126.6, 126.5, 123.4, 119.7, 119.2, 68.9, 28.7, 26.0, 10.9; IR (Neat Film NaCl) 3021, 2993, 2944, 2891, 2836, 1757, 1674, 1488, 1451, 1365, 1304, 1279, 1246, 1217, 1181, 1157, 1031, 1018, 986, 943, 782, 760 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{16}O_3$ $[M]^+$: 244.1100, found 244.1095.

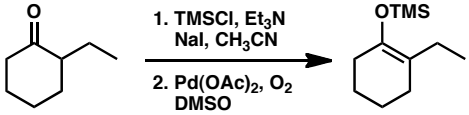


SI21

Allyl 4-methyl-2-phenyloxazol-5-yl carbonate (SI21, Table 16, Entry 5): Prepared by a modification of Leplawy's procedure[21] in 96% yield as a colorless oil that solidifies on standing; mp 37.5–39 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97-7.90 (m, 2H), 7.45-7.38 (comp. m, 3H), 5.99 (ddt, *J* = 17.4, 10.5, 5.7 Hz, 1H), 5.45 (ddt, *J* = 17.4, 1.5, 1.2 Hz, 1H), 5.36 (ddt, *J* = 10.5, 1.2, 1.2 Hz, 1H), 4.78 (ddd, *J* = 6.0, 1.2, 1.2 Hz, 2H), 2.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.3, 155.0, 151.6, 146.2, 130.5 (2C), 128.9, 127.3, 126.1, 120.6, 70.7, 10.5; IR (Neat Film NaCl) 3066, 2930, 1786, 1669, 1554, 1490, 1450, 1367, 1213, 1082, 1069, 1026, 992, 939, 774, 711, 692 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{13}O_4N$ $[M]^+$: 259.0845, found 259.0855.

Synthesis of Silyl Enol Ethers from Cycloalkanones

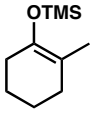
General Procedure 5:



SI22

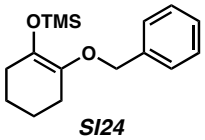
(2-Ethylcyclohex-1-enyloxy)trimethylsilane (SI22, Table 8, Entry 2):[22] To a solution of NaI (15.0 g, 100 mmol, 1.25 equiv) in CH_3CN (125 mL) were added 2-ethylcyclohexanone (10.1 g, 80 mmol, 1.0 equiv), Et_3N (14.0 mL, 100 mmol, 1.25 equiv), and finally TMSCl (11.6 mL, 91.2 mmol, 1.14 equiv) in a dropwise fashion. After 1 h, pentane (75 mL) was added, the biphasic mixture was stirred for 2 min, and the pentane decanted. After additional pentane extractions (5 x 75 mL), the combined pentane fractions were washed with water (2 x 50 mL) and brine (1 x 50 mL), and then dried (Na_2SO_4). Evaporation under reduced pressure gave the crude silyl enol ether (12.0 g) as an 80:20 mixture (NMR) of isomers favoring the tetrasubstituted silyl enol ether. An oxygen balloon was affixed to a flask containing a solution of the crude silyl enol ether (6.0 g) and $Pd(OAc)_2$ (338.9 mg, 1.51 mmol) in DMSO (250 mL). The reaction mixture darkened and became heterogeneous. After 48 h, ^{1}H NMR analysis of an aliquot indicated less than 2% of the undesired isomer, and the reaction mixture was poured into a separatory funnel containing pentane (300 mL), water (300 mL), and ice (200 g). The layers were separated and the aqueous layer extracted with pentane (3 x 200 mL). The pentane fractions were washed with water (2 x 100 mL) and brine (100 mL), and then dried (Na_2SO_4). Evaporation and chromatography (2% Et_2O in Hexanes on SiO_2) afforded the pure silyl enol ether **SI22** (3.21 g, 41% yield) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.08-1.90 (comp. m, 6H), 1.62 (m, 2H), 1.54 (m, 2H), 0.92 (t, J = 7.8 Hz, 3H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 117.4, 30.4, 27.0, 23.7, 23.1, 22.9, 12.2, 0.7; IR (Neat Film NaCl) 2961, 2933, 1680, 1252, 922, 843 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{22}OSi$ [M]$^+$: 198.1440, found 198.1436.

Characterization Data for Cycloalkanone Silyl Enol Ethers:



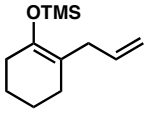
SI23

Trimethyl(2-methylcyclohex-1-enyloxy)silane (SI23, Table 8, Entries 1 and 4): Prepared by general procedure 5 from 2-methylcyclohexanone. The initial 10:1 mixture favoring the tetrasubstituted isomer was purified by fractional distillation with a spinning band column[23] to give silyl enol ether **SI23** (84% yield) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00 (m, 2H), 1.94 (m, 2H), 1.64 (m, 2H), 1.58-1.49 (comp. m, 5H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.9, 111.8, 30.3, 30.1, 23.8, 23.0, 16.3, 0.7; IR (Neat Film NaCl) 2930, 1688, 1252, 1185, 843 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{20}OSi$ [M]$^+$: 184.1284, found 184.1275.



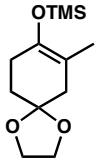
SI24

(2-(Benzyloxy)cyclohex-1-enyloxy)trimethylsilane (SI24, Table 8, Entry 3): Prepared by general procedure 5 from 2-(benzyloxy)cyclohexanone[24] in 11% yield as a colorless oil; ^{1}H NMR (300 MHz, C_6D_6) δ 7.40 (d, J = 7.2 Hz, 2H), 7.19 (dd, J = 7.2, 7.2 Hz, 2H), 7.09 (t, J = 7.5 Hz, 1H), 4.77 (s, 2H), 2.12-1.98 (comp. m, 4H), 1.39 (app. quintet, J = 3.3 Hz, 4H), 0.25 (s, 9H); ^{13}C NMR (75 MHz, C_6D_6) δ 139.9, 136.9, 135.5, 128.8, 128.2, 128.0, 71.3, 30.8, 27.1, 23.9, 23.7, 1.2; IR (Neat Film NaCl) 3065, 3032, 2934, 2860, 2841, 1694, 1497, 1454, 1343, 1250, 1245, 1195, 1122, 1017, 930, 860, 844, 750, 698 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{24}O_2Si$ [M]$^+$: 276.1546, found 276.1545.



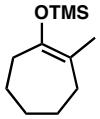
SI25

(2-Allylcyclohex-1-enyloxy)trimethylsilane (SI25, Table 8, Entry 5): Prepared by general procedure 5 from 2-allylcyclohexanone in 59% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.72 (ddt, *J* = 16.8, 9.9, 6.9 Hz, 1H), 4.99 (ddt, *J* = 16.5, 2.1, 1.8 Hz, 1H), 4.95 (ddt, *J* = 9.6, 2.1, 1.5 Hz, 1H), 2.77 (app. d, *J* = 6.6 Hz, 2H), 2.14-1.88 (comp. m, 4H), 1.75-1.42 (comp. m, 4H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 144.7, 136.9, 114.6, 113.5, 34.8, 30.4, 27.5, 23.7, 23.0, 0.7; IR (Neat Film NaCl) 3077, 2931, 2838, 1682, 1638, 1448, 1433, 1355, 1252, 1204, 1168, 948, 905, 888, 844, 753 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{22}OSi$ [M]$^+$: 210.1440, found 210.1449.



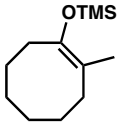
SI26

Trimethyl(7-methyl-1,4-dioxaspiro[4.5]dec-7-en-8-yloxy)silane (SI26, Table 8, Entry 6): Prepared by general procedure 5 from 2-methyl-1,4-cyclohexanedione monoethylene ketal[18] in 51% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.96 (br s, 4H), 2.21 (comp. m, 4H), 1.79 (app. t, *J* = 6.9 Hz, 2H), 1.54 (s, 3H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.2, 108.9, 108.0, 64.4, 39.9, 31.7, 28.7, 16.2, 0.7; IR (Neat Film NaCl) 2956, 1691, 1252 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{22}O_3Si$ [M]$^+$: 242.1338, found 242.1334.



SI27

Trimethyl(2-methylcyclohept-1-enyloxy)silane (SI27, Table 8, Entry 7): Prepared by general procedure 5 from 2-methylcycloheptanone in 39% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23 (app. t, *J* = 5.4 Hz, 2H), 2.01 (app. t, *J* = 5.1 Hz, 2H), 1.66 (m, 2H), 1.59 (s, 3H), 1.56-1.45 (comp. m, 4H), 0.16 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.9, 116.9, 35.1, 32.7, 31.6, 26.5, 25.5, 18.7, 0.6; IR (Neat Film NaCl) 2921, 1678, 1251, 1171, 892, 842 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{22}OSi$ [M]$^+$: 198.1440, found 198.1439.

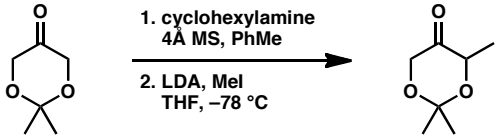


SI28

Trimethyl(2-methylcyclooct-1-enyloxy)silane (SI28, Table 8, Entry 8): Prepared by general procedure 5 (pyridine substituted for Et_3N) from 2-methylcyclooctanone in 29% yield as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (m, 2H), 2.05 (m, 2H), 1.61-1.44 (comp. m, 8H), 1.57 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.1, 113.5, 31.7, 28.9, 28.8, 26.7, 26.3, 15.8, 0.8; IR (Neat Film NaCl) 2924, 1678, 1251 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{24}OSi$ [M]$^+$: 212.1597, found 212.1590.

Synthesis of Silyl Enol Ethers from Dioxanones.

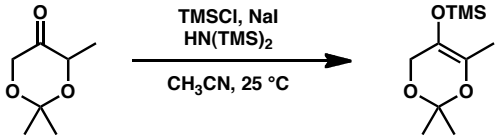
General Procedure 6: Dioxanone Alkylation



SI29

2,2,4-Trimethyl-1,3-dioxan-5-one (SI29):[25] To a solution of 2,2-dimethyl-1,3-dioxan-5-one (5.0 g, 38.4 mmol, 1.0 equiv)[26] in toluene (125 mL, 0.3 M) were added 4Å molecular sieves (5.0 g) and cyclohexylamine (8.50 mL, 74.3 mmol, 1.94 equiv) at room temperature (ca. 25 °C). The mixture was stirred for 14 h, then the molecular sieves were removed by filtration. The filtrate was concentrated under reduced pressure to give crude imine (7.95 g). Lithium diisopropylamide (LDA) was prepared in a separate flask by dropwise addition of *n*-BuLi (2.50 M in hexanes, 15.4 mL, 38.5 mmol, 1.0 equiv) via syringe to a solution of diisopropylamine (5.40 mL, 38.5 mmol, 1.0 equiv) in THF (60 mL, 0.64 M) at –78 °C. The mixture was stirred at 0 °C for 10 min and then cooled to –78 °C. A solution of the imine (7.95 g) in THF (40.0 mL) was added dropwise via syringe to the resulting LDA solution at –78 °C. The reaction mixture was warmed to –35 °C, and stirred for 2 h, after which point it was re-cooled to –78 °C, and MeI (2.39 mL, 38.4 mmol, 1.0 equiv) was added. The reaction was warmed to room temperature (ca. 25 °C) over 3 h. Saturated aq NH_4Cl (60 mL) was added to the reaction mixture and the mixture was stirred at room temperature overnight. The phases were separated and the aq phase was extracted with Et_2O (3 x 50 mL). The combined organic layers were washed with brine (1 x 30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated under reduced pressure and the residue was purified by flash chromatography (20% Et_2O in pentane on silica gel) to give **SI29** (3.93 g, 71% yield) as a pale orange oil. R_f 0.72 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.37 (dq, J = 6.9, 1.5 Hz, 1H), 4.28 (dd, J = 17.1, 1.5 Hz, 1H), 4.01 (d, J = 17.1 Hz, 1 H), 1.47 (s, 3H), 1.43 (s, 3H), 1.31 (d, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2, 101.0, 71.1, 66.6, 24.1, 23.9, 14.3; IR (Neat Film NaCl) 2994, 2944, 1745, 1376, 1227, 1101 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_7H_{12}O_3$ $[M]^+$: 144.0786, found 144.0786.

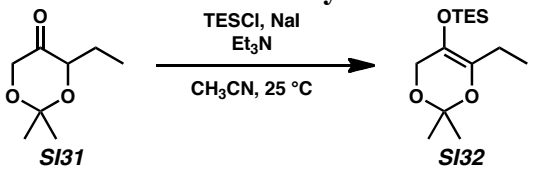
General Procedure 7: Synthesis of Dioxanone TMS-enol ethers



SI29 ***SI30***

2,2,4-Trimethyl-5-trimethylsilyloxy-1,3-diox-4-ene (SI30, Table 10, Entry 2): To a solution of **SI29** (1.0 g, 6.94 mmol, 1.0 equiv), hexamethyldisilazane (1.75 mL, 13.4 mmol, 1.9 equiv), and sodium iodide (1.17 g, 7.81 mmol, 1.1 equiv) in acetonitrile (10.0 mL, 0.7 M) was added TMSCl (1.0 mL, 7.82 mmol, 1.1 equiv) at room temperature (ca. 25 °C). After the mixture was stirred at room temperature for 16 h, pentane (20 mL) was added to the mixture. The mixture was stirred at room temperature for 2 min, and then the pentane was decanted. After additional pentane extractions (5 x 10 mL), the combined pentane layers were washed with water (3 x 30 mL) and brine (30 mL), then dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (2% Et_2O in pentane on Florisil®) to give **SI30** (0.481 g, 32% yield) as a colorless oil. R_f 0.25 (10% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.04 (q, J = 1.8 Hz, 2H), 1.76 (t, J = 1.8 Hz, 3H), 1.45 (s, 6H), 0.20 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.9, 125.5, 98.3, 61.1, 24.2, 14.2, 0.8; IR (Neat Film NaCl) 2995, 2958, 2939, 1384, 1370, 1276, 1254, 1224, 1151, 1120, 1072, 893, 846 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_7H_{11}O_3$ $[M - C_3H_9Si]^+$: 143.0708, found 143.0718.

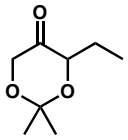
General Procedure 8: Synthesis of Dioxanone TES-enol ethers



SI31 ***SI32***

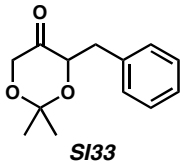
4-Ethyl-2,2-dimethyl-5-triethylsilyloxy-1,3-diox-4-ene (SI32, Table 10, Entry 5): To a solution of 4-ethyl-2,2-dimethyl-1,3-dioxane-5-one (**SI31**, 0.50 g, 3.16 mmol, 1.0 equiv), Et_3N (0.71 mL, 5.09 mmol, 1.6 equiv), and NaI (0.62 g, 4.14 mmol, 1.3 equiv) in acetonitrile (5.0 mL, 0.63 M) was added TESCl (0.69 mL, 4.11 mmol, 1.3 equiv) at room temperature (ca. 25 °C). After the mixture was stirred for 20 h, pentane (10 mL) was added. The mixture was stirred at room temperature for 2 min, and then the pentane was decanted. After additional pentane extractions (5 x 10 mL), the combined pentane layers were washed with water (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (1% Et_2O in petroleum ether on silica gel) to give triethylsilyl enol ether **SI32** (0.659 g, 77% yield) and 4-ethyl-2,2-dimethyl-5-triethylsilyloxy-1,3-diox-5-ene (70.6 mg, 8% yield).[27] Data for desired isomer: Colorless oil; R_f 0.53 (5% Et_2O in toluene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.04 (t, J = 1.2 Hz, 2H), 2.19 (qt, J = 7.5, 1.2 Hz, 2H), 1.43 (s, 6H), 1.02–0.96 (m, 12H), 0.65 (q, J =7.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 124.8, 98.0, 61.1, 24.3, 20.7, 11.1, 6.9, 5.5; IR (Neat Film NaCl) 2958, 2878, 1383, 1369, 1276, 1221, 1198, 1147, 1121, 1079, 1012, 857, 745, 730 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{13}O_3Si$ [M – C_6H_{15}]$^+$: 185.0634, found 185.0639.

Characterization Data for Alkylated Dioxanones:



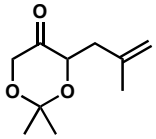
SI31

4-Ethyl-2,2-dimethyl-1,3-dioxan-5-one (SI31):[28] 72% yield. Colorless oil; R_f 0.58 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.27 (dd, J = 17.0, 1.5 Hz, 1H), 4.17–4.13 (m, 1H), 3.98 (d, J = 17.0 Hz, 1H), 1.97–1.83 (m, 1H), 1.66–1.51 (m, 1H), 1.46 (s, 3H), 1.44 (s, 3H), 0.98 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 100.9, 76.0, 66.9, 24.2, 23.7, 22.0, 9.7; IR (Neat Film NaCl) 2986, 2940, 2881, 1749, 1376, 1225, 1165, 1115, 1077, 1011, 867 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{14}O_3$ [M]$^+$: 158.0943, found 158.0939.



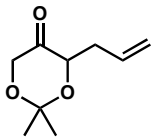
SI33

4-Benzyl-2,2-dimethyl-1,3-dioxan-5-one (SI33):[28] 73% yield. Yellow oil; R_f 0.54 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.16 (m, 5H), 4.46 (ddd, J = 9.3, 3.3, 1.8 Hz, 1H), 4.26 (dd, J = 17.1, 1.8 Hz, 1H), 4.01 (d, J = 17.1 Hz, 1H), 3.24 (dd, J = 15.0, 3.3 Hz, 1H), 2.79 (dd, J = 15.0, 9.3 Hz, 1H), 1.43 (s, 3H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.1, 137.9, 129.4, 128.4, 126.6, 101.2, 75.8, 66.8, 34.6, 24.1, 23.7; IR (Neat Film NaCl) 3030, 2988, 2938, 2884, 1747, 1498, 1454, 1375, 1252, 1223, 1173, 1101, 1062, 748, 700 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{16}O_3$ [M]$^+$: 220.1100, found 220.1092.



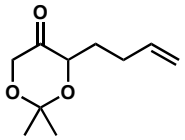
SI34

2,2-Dimethyl-4-(2-methylallyl)-1,3-dioxan-5-one (SI34): 66% yield. Pale orange oil; R_f 0.56 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.83 (s, 1H), 4.81 (s, 1H), 4.42 (ddd, *J* = 9.6, 3.0, 1.2 Hz, 1H), 4.29 (dd, *J* = 17.1, 1.8 Hz, 1H), 4.01 (d, *J* = 17.1 Hz, 1H), 2.69 (app. dd, *J* = 15.6, 3.0 Hz, 1H), 2.20 (dd, *J* = 15.8, 9.6 Hz, 1H), 1.77 (s, 3H), 1.48 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.5, 141.6, 112.5, 101.1, 73.8, 66.7, 36.2, 24.1, 23.8, 23.0; IR (Neat Film NaCl) 3079, 2988, 2940, 1748, 1650, 1426, 1374, 1223, 1175, 1106, 1076, 1048, 1016, 899, 833 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{10}H_{16}O_3$ $[M]^+$: 184.1100, found 184.1101.



SI35

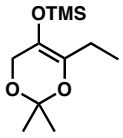
4-Allyl-2,2-dimethyl-1,3-dioxan-5-one (SI35):[28a,29] 65% yield. Colorless oil; R_f 0.43 (10% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92–5.78 (m, 1H), 5.20–5.08 (m, 2H), 4.33–4.24 (m, 2H), 4.01 (d, *J* = 16.8 Hz, 1H), 2.69–2.60 (m, 1H), 2.38–2.27 (m, 1H), 1.47 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.2, 133.6, 117.7, 101.1, 74.6, 66.8, 32.9, 24.1, 23.8; IR (Neat Film NaCl) 2989, 1749, 1376, 1254, 1224, 1177, 1162, 1103 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_9H_{14}O_3$ $[M]^+$: 170.0943, found 170.0951.



SI36

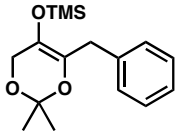
4-(But-3-enyl)-2,2-dimethyl-1,3-dioxan-5-one (SI36):[30] 53% yield. Colorless oil; R_f 0.38 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85–5.72 (m, 1H), 5.09–4.98 (m, 2H), 4.29–4.21 (m, 2H), 3.98 (d, *J* = 16.8 Hz, 1H), 2.30–2.08 (m, 2H), 2.03-1.92 (m, 1H), 1.70–1.58 (m, 1H), 1.45 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 137.7, 115.8, 101.0, 73.8, 66.8, 29.3, 27.6, 24.1, 23.9; IR (Neat Film NaCl) 2988, 2938, 2884, 1748, 1642, 1434, 1376, 1251, 1225, 1175, 1103, 1071, 916, 864 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{10}H_{16}O_3$ $[M]^+$: 184.1100, found 184.1131.

Characterization Data for Dioxanone Silyl Enol Ethers:



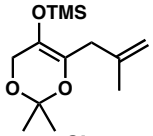
SI37

2,2-Dimethyl-4-ethyl-5-trimethylsilyloxy-1,3-diox-4-ene (SI37): 35% yield. Colorless oil; R_f 0.52 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.03 (app. t, *J* = 1.2 Hz, 2H), 2.16 (q, *J* = 7.4 Hz, 2H), 1.43 (s, 6H), 1.00 (t, *J* = 7.4 Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.5, 124.7, 98.1, 61.1, 24.2, 20.8, 11.1, 0.7; IR (Neat Film NaCl) 2964, 1384, 1369, 1276, 1254, 1223, 1199, 1148, 1122, 1079, 1035, 894, 867, 844, 752 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{13}O_3$ $[M - C_3H_9Si]^+$: 157.0865, found 157.0749.



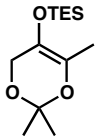
SI38

2,2-Dimethyl-4-benzyl-5-trimethylsilyloxy-1,3-diox-4-ene (SI38): 16% yield. Colorless oil; R_f 0.44 (10% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32–7.12 (m, 5H), 4.09 (t, J = 1.2 Hz, 2H), 3.47 (app. s, 2H), 1.35 (s, 6H), 0.17 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.9, 136.9, 128.9, 128.3, 126.4, 126.2, 98.4, 61.1, 34.0, 24.1, 0.9; IR (Neat Film NaCl) 3029, 2994, 2957, 2837, 1748, 1603, 1495, 1454, 1382, 1370, 1276, 1253, 1230, 1199, 1144, 1093, 888, 845 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{24}O_3Si$ [M]$^+$: 292.1495, found 292.1482.



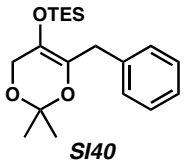
SI39

2,2-dimethyl-4-(2-methylallyl)-5-trimethylsilyloxy-1,3-diox-4-ene (SI39): 32% yield. Colorless oil; R_f 0.46 (50% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.779 (s, 1H), 4.775 (s, 1H), 4.07 (t, J = 1.1 Hz, 2H), 2.86 (s, 2H), 1.73 (s, 3H), 1.44 (s, 6H), 0.18 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 136.0, 126.6, 111.7, 98.3, 61.1, 36.2, 24.2, 22.7, 0.8; IR (Neat Film NaCl) 3077, 2994, 2902, 2838, 1749, 1653, 1454, 1382, 1370, 1276, 1253, 1229, 1198, 1146, 1096, 891, 846 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{24}O_3Si$ [M]$^+$: 256.1495, found 256.1500.



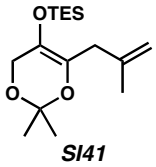
42

4-Methyl-2,2-dimethyl-5-triethylsilyloxy-1,3-diox-4-ene (42, Table 9, Table 10, Entries 1, 3, and 4): 77% yield. Colorless oil; R_f 0.50 (10% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.04 (q, J = 1.9 Hz, 2H), 1.77 (t, J = 1.9 Hz, 3H), 1.43 (s, 6H), 0.98 (t, J = 8.1 Hz, 9H), 0.65 (q, J = 8.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.4, 125.6, 98.2, 61.2, 24.3, 14.0, 6.9, 5.5; IR (Neat Film NaCl) 2995, 2956, 2915, 2878, 1459, 1383, 1369, 1276, 1221, 1198, 1150, 1120, 1071, 1002, 873, 850, 729 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{26}O_3Si$ [M]$^+$: 258.1651, found 258.1642.



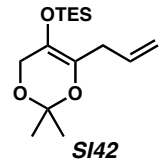
SI40

4-Benzyl-2,2-dimethyl-5-triethylsilyloxy-1,3-diox-4-ene (SI40, Table 10, Entry 6): 78% yield. Colorless oil; R_f 0.41 (10% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.12 (m, 5H), 4.10 (t, J = 1.2 Hz, 2H), 3.49 (s, 2H), 1.33 (s, 6H), 0.98 (t, J = 8.1 Hz, 9H), 0.66 (q, J = 8.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.0, 136.5, 128.9, 128.3, 126.5, 126.1, 98.3, 61.2, 33.8, 24.1, 6.9, 5.7; IR (Neat Film NaCl) 2956, 2877, 1454, 1382, 1370, 1276, 1226, 1198, 1145, 1093, 1016, 867, 746, 729, 731, 696 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{19}H_{30}O_3Si$ [M]$^+$: 334.1964, found 334.1978.



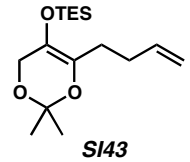
SI41

2,2-Dimethyl-6-(2-methylallyl)-4*H*-1,3-dioxin-5-yloxy)triethylsilane (SI41, Table 10, Entry 7): 46% yield. Colorless oil; R_f 0.19 (10% Et_2O in hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 4.78 (s, 2H), 4.08 (t, J = 1.1 Hz, 2H), 2.89 (s, 2H), 1.74 (s, 3H), 1.43 (s, 6H), 0.98 (t, J = 8.1 Hz, 9H), 0.65 (q, J = 8.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.5, 135.6, 126.7, 111.7, 98.3, 61.1, 36.0, 24.3, 22.7, 6.9, 5.6; IR (Neat Film NaCl) 2956, 2913, 2878, 1382, 1369, 1276, 1225, 1198, 1146, 1095, 1010, 851, 730 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{26}O_3Si$ $[M - H_2]^+$ 297.1886, found 297.1851.



SI42

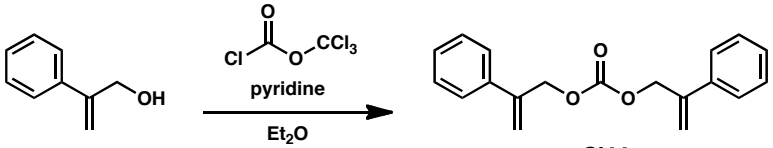
4-Allyl-2,2-dimethyl-5-triethylsilyloxy-1,3-diox-4-ene (SI42, Table 10, Entry 8): 69% yield. Colorless oil; R_f 0.58 (10% EtOAc in hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 5.87–5.73 (m, 1H), 5.15–5.01 (m, 2H), 4.06 (t, J = 1.2 Hz, 2H), 2.96–2.91 (m, 2H), 1.44 (s, 6H), 0.99 (t, J = 8.1 Hz, 9H), 0.66 (q, J = 8.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.8, 134.4, 126.0, 116.2, 98.3, 61.1, 32.1, 24.3, 6.9, 5.6; IR (Neat Film NaCl) 2995, 2957, 2913, 2879, 1639, 1458, 1414, 1382, 1370, 1278, 1241, 1196, 1147, 1084, 1016, 970, 909, 871, 851, 746, 731 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{15}H_{28}O_3Si$ $[M]^+$: 284.1808, found 284.1836.



SI43

(6-(But-3-enyl)-2,2-dimethyl-4*H*-1,3-dioxin-5-yloxy)triethylsilane (SI43, Table 10, Entry 9): 66% yield. Colorless oil; R_f 0.58 (10% Et_2O in hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 5.90–5.77 (m, 1H), 5.07-5.0 (m, 1H), 5.0–4.93 (m, 1H), 4.05 (s, 2H), 2.30–2.13 (m, 4H), 1.43 (s, 6H), 0.98 (t, J = 7.8 Hz, 9H), 0.65 (q, J = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.5, 137.2, 125.7, 114.8, 98.2, 61.1, 30.9, 27.0, 24.3, 6.9, 5.6; IR (Neat Film NaCl) 2995, 2957, 2914, 2878, 2838, 1383, 1369, 1277, 1223, 1198, 1147, 1085, 1006, 857, 745, 730 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{30}O_3Si$ $[M]^+$: 298.1964, found 298.1967.

Synthesis of Bis(2-phenylallyl) carbonate (SI44, Table 10, Entry 4):



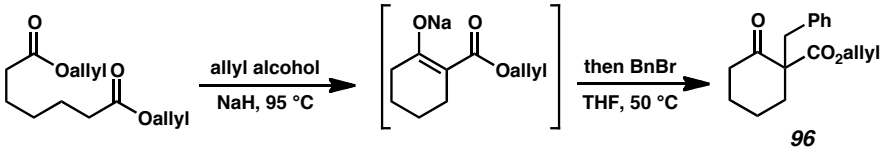
SI44

To a 0 °C solution of 2-phenylallyl alcohol[31] (2.0 g, 14.9 mmol, 1.0 equiv) and pyridine (1.2 mL, 14.9 mmol, 1.0 equiv) in Et_2O (11 mL, 1.35 M) was added diphosgene (0.45 mL, 3.73 mmol, 0.25 equiv) dropwise via syringe over 20 min. The mixture was stirred at room temperature (ca. 25 °C) for 20 h. The white solid was removed by filtration, and the filter cake was washed with Et_2O. The filtrate was washed with aqueous $CuSO_4$ (5 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (10% EtOAc in hexanes on silica gel) to give carbonate **SI44** (1.26 g, 57% yield) as a colorless oil. R_f 0.61 (10% EtOAc in hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.44–7.23 (m, 10H), 5.55 (s, 2H), 5.38 (s, 2H), 5.04 (s, 4H); ^{13}C NMR (75 MHz,

$CDCl_3$) δ 155.1, 142.2, 138.0, 128.7, 128.4, 126.2, 115.9, 69.4; IR (Neat Film NaCl) 3058, 1747, 1496, 1448, 1395, 1254, 970, 912, 778, 706 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{19}H_{18}O_3$ $[M]^+$: 294.1256, found 294.1250.

Synthesis of Allyl β-Ketoesters.

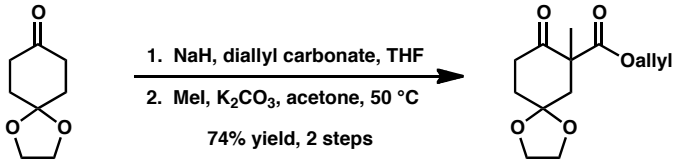
General Procedure 9: Dieckmann Cyclization Method[32,33]



96

Allyl 1-benzyl-2-oxocyclohexanecarboxylate (96, Table 12, entry 6; Figure 2). To a suspension of NaH (166.4 mg, 4.16 mmol, 1.0 equiv) in toluene (2 mL) was added allyl alcohol (79.2 μL, 1.17 mmol, 0.28 equiv). Once gas evolution ceased, pimelic acid diallyl ester (1.00 g, 4.16 mmol, 1.0 equiv) was added slowly and the resulting mixture heated to 95 °C for 1 h. Additional toluene (~2 mL) was added during this time to maintain a fluid reaction mixture. The reaction mixture was cooled to room temperature and the solvent removed by rotary evaporation *in vacuo*. The resulting solid salt was placed under dry N_2 and dissolved in THF (9 mL). Benzyl bromide (643.2 μL, 5.4 mmol, 1.3 equiv) was then added dropwise. The resulting mixture was warmed to 50 °C for 2.5 h, cooled to ambient temperature, and quenched with saturated aq NH_4Cl (5 mL) followed by H_2O (5 mL). The phases were separated and the aqueous phase was extracted with EtOAc (3 x 5 mL). The combined organic extracts were washed with brine (1 x 10 mL), then dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (5 x 18 cm SiO_2, 10% Et_2O in pentane) to afford the quaternary compound **96** as a colorless oil (781.4 mg, 70% yield). R_f = 0.30 (10% Et_2O in pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.33-7.23 (comp. m, 3H), 7.20-7.13 (comp. m, 2H), 5.86 (dddd, *J* = 17.2, 10.3, 5.9, 5.9 Hz, 1H), 5.29 (m, 2H), 4.57 (m, 2H), 3.38 (d, 1H, *J* = 13.8 Hz), 2.94 (d, *J* = 13.8 Hz, 1H), 2.60-2.39 (comp. m, 3H), 2.14-1.97 (m, 1H), 1.83-1.60 (comp. m, 3H), 1.59-1.45 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.8, 170.5, 136.3, 131.2, 130.2, 127.9, 126.5, 119.0, 65.6, 62.1, 41.1, 40.3, 35.7, 27.4, 22.3; IR (Neat Film NaCl) 3029, 2942, 1713, 1452, 1179, 1085 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{20}O_3$ $[M]^+$: 272.1412, found 272.1425.

General Procedure 10: Diallyl Carbonate Method



SI45

Allyl 7-methyl-8-oxo-1,4-dioxaspiro[4.5]decane-7-carboxylate (SI45, Table 13, entries 1 and 2):

Part A, Acylation:

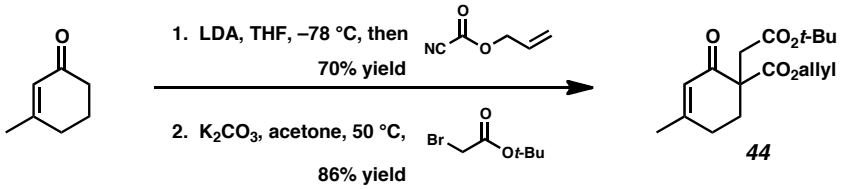
To a cooled (0 °C) suspension of NaH (9.22 g, 240.1 mmol, 2.5 equiv) in THF (125 mL) was added a solution of 1,4-cyclohexanedione monoethylene ketal (15.0 g, 96 mmol, 1.0 equiv) in THF (30 mL) dropwise over 15 min. The reaction mixture was warmed to room temperature and diallyl carbonate (20.65 mL, 144.0 mmol, 1.5 equiv) was added and the reaction mixture stirred for 16 h. The reaction was quenched with saturated aq NH_4Cl and 1 N aq HCl until a pH of 4 was reached. The phases were separated and the aq phase was extracted with EtOAc (7 x 150 mL). The combined organic extracts were dried (Na_2SO_4), filtered, concentrated, redissolved in CH_2Cl_2, dried ($MgSO_4$), filtered, and concentrated.

Part B, Alkylation:

The resulting oil was added to a suspension of anhydrous K_2CO_3 (26.5 g, 192.0 mmol, 2.0 equiv) in acetone (128 mL). To the reaction mixture was added iodomethane (12.0 mL, 192.0 mmol, 2.0 equiv) and the reaction mixture was then heated to 50 °C for 14 h. The mixture was then cooled, filtered, and

the solids washed with acetone. The filtrate was concentrated and the resulting oil purified by flash chromatography (SiO_2, 5 → 40% Et_2O in hexanes) to afford the desired quaternary quaternary β-ketoester **SI45** as a colorless oil (18.0 g, 74% yield). R_f = 0.28 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (dddd, *J* = 17.4, 10.5, 5.7, 5.7 Hz, 1H), 5.26 (m, 2H), 4.60 (m, 2H), 3.97 (comp. m, 4H), 3.02 (dt, *J* = 14.8, 10.2 Hz, 1H), 2.68 (dt, *J* = 14.0, 2.0 Hz, 1H), 2.49 (dt, *J* = 14.8, 4.4 Hz, 1H), 2.00 (comp. m, 2H), 1.72 (d, *J* = 14.1 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.0, 172.9, 131.6, 118.5, 106.5, 65.9, 64.8, 64.3, 54.6, 43.6, 37.4, 35.2, 21.7; IR (Neat Film NaCl) 2939, 2891, 1733, 1717, 1304, 1141 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{18}O_5$ [M]$^+$: 254.1154, found 254.1153.

General Procedure 11: Mander's Reagent Method[4]

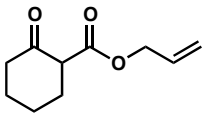


44

Allyl 1-(2-*tert*-butoxy-2-oxoethyl)-4-methyl-2-oxocyclohex-3-enecarboxylate (44): To a cooled (–78 °C) solution of LDA (18.70 mmol, 1.05 equiv) in THF (90 mL) was added 3-methylcyclohex-2-enone (2.02 mL, 17.81 mmol, 1.0 equiv) in a dropwise fashion. The resulting solution was stirred at –78 °C for 30 min and then allyl cyanoformate[4] (2.00 g, 18.17 mmol, 1.02 equiv) was added dropwise. The dry ice bath was removed and the reaction mixture slowly warmed to room temperature and stirred for 8 h. The reaction mixture was quenched with saturated aq NH_4Cl (15 mL) followed by H_2O (15 mL). The phases were separated and the aq phase was extracted with EtOAc (3 x 15 mL). The combined organic extracts were washed with brine (1 x 30 mL), dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (5 x 24 cm SiO_2, 50% EtOAc in hexanes) to afford the intermediate β-ketoester as a yellow oil (2.4152 g, 70% yield).

A portion of this β-ketoester (500.0 mg, 2.57 mmol, 1.0 equiv) was added to a suspension of anhydrous K_2CO_3 (711.8 mg, 5.15 mmol, 2.0 equiv) in acetone (2.5 mL). To the reaction mixture was added *t*-butyl bromoacetate (760.5 μL, 5.15 mmol, 2.0 equiv). The reaction mixture was then warmed to 50 °C and stirred for 48 h. The reaction mixture was then cooled, filtered, and the solids washed with acetone. The filtrate was concentrated and purified by flash chromatography (3 x 20 cm SiO_2, 10→30% EtOAc in hexanes) to afford the desired quaternary β-ketoester **44** as a colorless oil (684.7 mg, 86% yield; 60% overall yield for 2 steps). R_f = 0.28 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (s, 1H), 5.87 (dddd, *J* = 17.3, 10.5, 5.4, 5.4 Hz, 1H), 5.23 (m, 2H), 4.61 (m, 2H), 2.83 (d, *J* = 16.4 Hz, 1H), 2.73 (d, *J* = 16.4 Hz, 1H), 2.58–2.36 (comp. m, 2H), 2.31–2.16 (comp. m, 2H), 1.94 (s, 3H), 1.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.2, 169.8, 161.9, 131.7, 125.6, 118.2, 81.1, 65.8, 54.2, 39.8, 30.5, 28.7, 28.0, 24.2; IR (Neat Film NaCl) 2979, 1733, 1677, 1368, 1153 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{24}O_5$ [M]$^+$: 308.1624, found 308.1609.

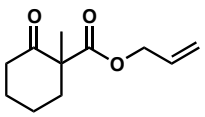
Characterization Data for β-Ketoesters:



SI46

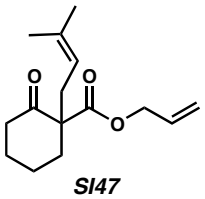
Allyl 2-oxocyclohexanecarboxylate (SI46): Prepared by general procedure 9. The reaction was quenched with 10% HCl. The product was isolated by bulb-to-bulb distillation once at 150-155 °C (bath temp, 2 torr), then at 136 °C (bath temp, 2 torr). 75% yield. R_f = 0.53 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$, mixture of keto and enol tautomers) δ 12.14 (s, 0.7H), 5.99 (dddd, *J* = 5.7, 5.7, 10.8, 17.1 Hz, 0.7H), 5.96 (dddd, *J* = 5.7, 5.7, 10.2, 17.1 Hz, 0.3H), 5.38 (dddd, *J* = 1.5, 1.5, 1.5, 17.1 Hz, 0.3H), 5.37 (dddd, *J* = 1.5, 1.5, 1.5, 17.1 Hz, 0.7H), 5.24 (dddd, *J* = 1.5, 1.5, 1.5, 10.5 Hz, 1H), 4.72-4.55 (m, 2H), 3.41 (ddd, *J* = 1.5, 6.6, 9.6 Hz, 0.3H), 2.52 (dddd, *J* = 1.5, 5.4, 5.4, 14.1 Hz, 0.3H), 2.37

(m, 0.3H), 2.26 (m, 2.7H), 2.22-2.10 (m, 0.6H), 2.04-1.78 (m, 0.9H), 1.75-1.55 (m, 3.3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.9, 172.4, 172.2, 169.6, 132.3, 131.8, 118.4, 117.7, 97.5, 65.6, 64.6, 57.2, 41.5, 29.9, 29.1, 27.0, 23.3, 22.3, 22.3, 21.9; IR (Neat Film NaCl) 3086, 2941, 1746, 1716, 1659, 1617, 1299, 1259, 1217, 1176, 831 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{14}O_3$ [M]$^+$: 182.0943, found 182.0941.



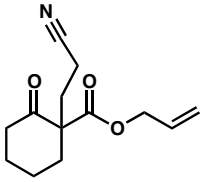
10

Allyl 1-methyl-2-oxocyclohexanecarboxylate (10, Table 11; Table 12, entries 1 and 2): Prepared by general procedure 9. 62% yield. R_f = 0.38 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (dddd, *J* = 17.1, 10.2, 5.9, 5.9 Hz, 1H), 5.24 (m, 2H), 4.59 (d, *J* = 5.7 Hz, 2H), 2.58-2.34 (comp. m, 3H), 2.08-1.88 (m, 1H), 1.80-1.54 (comp. m, 3H), 1.52-1.37 (m, 1H), 1.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9, 172.6, 131.4, 118.7, 65.6, 57.1, 40.5, 38.1, 27.4, 22.5, 21.1; IR (Neat Film NaCl) 3086, 2939, 2867, 1715, 1452, 1259, 1211, 1159, 1084, 976 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{16}O_3$ [M]$^+$: 196.1099, found 196.1096.



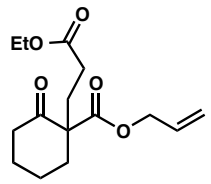
SI47

Allyl 1-(3-methylbut-2-enyl)-2-oxocyclohexanecarboxylate (SI47, Table 12, entry 3): Prepared by general procedure 10 part B from ketoester **SI46** and prenyl bromide. Flash chromatography (SiO_2, 2→12% Et_2O in pentane). 20% yield. R_f = 0.24 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (dddd, *J* = 17.1, 10.4, 5.8, 5.8 Hz, 1H), 5.31 (d, *J* = 17.1 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 5.06 (t, *J* = 7.7 Hz, 1H), 4.59 (d, *J* = 5.7 Hz, 2H), 2.65-2.27 (comp. m, 5H), 2.07-1.93 (m, 1H), 1.79-1.69 (m, 1H), 1.68 (s, 3H), 1.66-1.59 (m, 1H), 1.58 (s, 3H), 1.54-1.39 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.7, 171.4, 134.8, 131.6, 118.8, 118.5, 65.7, 61.3, 41.2, 35.5, 33.2, 27.5, 26.0, 22.5, 17.8; IR (Neat Film NaCl) 2938, 2863, 1714, 1451, 1438, 1210, 1178, 989 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{22}O_3$ [M]$^+$: 250.1569, found 250.1574.



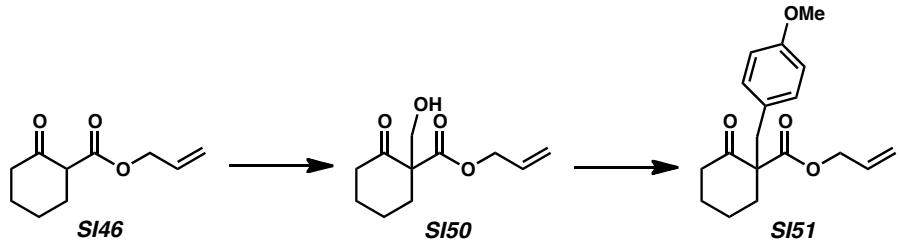
SI48

Allyl 1-(cyanomethyl)-2-oxocyclohexanecarboxylate (SI48, Table 12, entry 4): Prepared by general procedure 10 part B from ketoester **SI46** and acrylonitrile. Flash chromatography (SiO_2, 10% Et_2O in pentane). 55% yield. R_f = 0.27 (CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (dddd, *J* = 17.6, 10.2, 6.0, 6.0 Hz, 1H), 5.41-5.25 (m, 2H), 4.68 (d, *J* = 6.0 Hz, 2H), 2.64-2.38 (comp. m, 4H), 2.37-2.13 (comp. m, 2H), 2.13-1.86 (comp. m, 2H), 1.85-1.40 (comp. m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.0, 170.6, 130.9, 120.0, 119.3, 66.4, 59.7, 40.9, 36.7, 30.8, 27.4, 22.4, 13.0; IR (Neat Film NaCl) 2945, 2868, 2248, 1713, 1450, 1192, 1136, 941 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{17}NO_3$ [M]$^+$: 235.1208, found 235.1218.



SI49

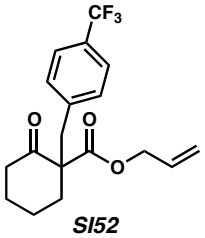
Allyl 1-(3-ethoxy-3-oxopropyl)-2-oxocyclohexanecarboxylate (SI49, Table 12, entry 5): Prepared by general procedure 10 part B from ketoester **SI46** and ethyl acrylate. Flash chromatography (SiO_2, 10% Et_2O in pentane). 81% yield. $R_f = 0.37$ (30% Et_2O in pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 5.89 (dddd, J = 17.3, 10.3, 5.9, 5.9 Hz, 1H), 5.33 (dd, J = 17.3, 1.1 Hz, 1H), 5.26 (dd, J = 10.4, 1.3 Hz, 1H), 4.63 (app. t, J = 14.9 Hz, 2H), 4.11 (q, J = 7.2 Hz, 2H), 2.51-2.31 (comp. m, 4H), 2.31-2.11 (comp. m, 2H), 2.08-1.85 (comp. m, 2H), 1.84-1.57 (comp. m, 3H), 1.55-1.40 (m, 1H), 1.24 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.4, 173.0, 171.4, 131.3, 119.3, 65.9, 60.4, 60.1, 41.0, 36.2, 29.6, 29.5, 27.5, 22.5, 14.2; IR (Neat Film NaCl) 2943, 2868, 1734, 1715, 1456, 1181 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{22}O_5$ $[M]^+$: 282.1467, found 282.1474.



SI46 ***SI50*** ***SI51***

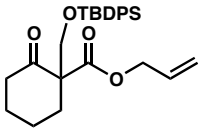
Allyl 1-(4-methoxybenzyl)-2-oxocyclohexanecarboxylate (SI51, Table 12, entry 7): To a cooled (0 °C) solution of ketoester **SI46** (4.00 g, 22.0 mmol, 1.0 equiv) in THF (40 ml) was added 35% aqueous formaldehyde (11.3 mL) and $KHCO_3$ (5.93 g, 65.9 mmol, 3.0 equiv). After 30 min at 0 °C the reaction mixture was allowed to warm to ambient temperature. After an additional 90 min, the reaction was quenched with water (100 mL) and CH_2Cl_2 (100mL). After the layers were separated, the aqueous layer was extracted with CH_2Cl_2 (4 x 50 mL), the combined organics dried (Na_2SO_4) and evaporated. The oil obtained was treated with THF (40 mL) and 3 M aq HCl (4 drops) for 60 min, concentrated, and purified by flash chromatography (SiO_2, 10→45% EtOAc in hexanes) to give **SI50** (3.75 g, 81% yield).

To a cooled (0 °C) suspension of 60% NaH (251 mg, 6.28 mmol, 1.1 equiv) in DMF (20 mL) was added **SI50** (1.20g, 5.71 mmol, 1.0 equiv) in a dropwise manner over 2 min. Once gas evolution had ceased (10 min), Bu_4NI (527 mg, 1.43 mmol. 0.25 equiv) and PMB-Cl (930 µL, 6.85 mmol, 1.2 equiv) were added, and the reaction mixture slowly allowed to warm to ambient temperature. After 12 h, the reaction mixture was quenched with water (50 mL) and 2:1 CH_2Cl_2:hexanes (50 mL), the aqueous layer extracted with 2:1 CH_2Cl_2:hexanes (3 x 50 mL), dried (Na_2SO_4), evaporated, and purified by flash chromatography (SiO_2, 10→20% Et_2O in hexanes) to give the desired compound **SI51** (485 mg, 28% yield). $R_f = 0.30$ (30% Et_2O in pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 7.03 (d, J = 8.7 Hz, 2H), 6.77 (d, J = 8.7 Hz, 2H), 5.89-5.76 (m, 1H) 5.31-5.21 (m, 2H), 4.59-4.47 (m, 2H), 3.76 (s, 3H), 3.25 (d, J = 14.1 Hz, 1H), 2.84 (d, J = 14.1 Hz, 1H), 2.51-2.35 (m, 3H), 2.04-1.96 (m, 1H), 1.76-1.54 (m, 3H), 1.50-1.40 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2, 170.8, 158.4, 131.4, 131.3, 128.4, 119.1, 113.4, 65.8, 62.3, 55.1, 41.3, 39.5, 35.8, 27.5, 22.5; IR (Neat Film NaCl) 2943, 1713, 1612, 1513, 1247, 1179 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{18}H_{22}O_4$ $[M]^+$: 302.1518, found 302.1514.



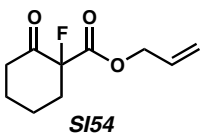
SI52

Allyl 2-oxo-1-(4-(trifluoromethyl)benzyl)cyclohexanecarboxylate (SI52, Table 12, entry 8): Prepared by general procedure 9 with 4-(trifluoromethyl)benzyl bromide. Flash chromatography (SiO_2, 2→12% Et_2O in pentane). 56% yield. mp 40-41 ºC; R_f = 0.63 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, C_6D_6) δ 7.29 (d, J = 8.1 Hz, 2H), 7.02 (d, J = 8.1 Hz, 2H), 5.45 (dddd, J = 17.3, 10.4, 6.0, 6.0 Hz, 1H), 4.91 (m, 2H), 4.18 (m, 2H), 3.34 (d, J = 13.7 Hz, 1H), 2.78 (d, J = 13.7 Hz, 1H), 2.37-2.15 (comp. m, 3H), 1.57-1.38 (comp. m, 2H), 1.32-1.11 (comp. m, 2H), 1.09-0.94 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.7, 170.4, 140.8 (q, J_{CF} = 1.2 Hz), 131.0, 130.7, 129.0 (q, J_{CF} = 32.3 Hz), 124.9 (q, J_{CF} = 3.9 Hz), 124.2 (q, J_{CF} = 271.7 Hz), 119.4, 65.9, 62.2, 41.2, 40.2, 36.2, 27.5, 22.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.0; IR (Neat Film NaCl) 2945, 1715, 1326, 1164, 1123, 1068 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{18}H_{19}F_3O_3$ [M]$^+$: 340.1286, found 340.1277.



SI53

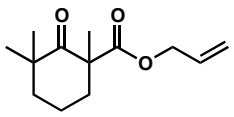
Allyl 1-((*tert*-butyldiphenylsilyloxy)methyl)-2-oxocyclohexanecarboxylate (SI53, Table 12, entry 9): To a solution of **SI50** (vide supra) (1.20 g, 5.71 mmol. 1.0 equiv), imidazole (583 mg, 8.57 mmol, 1.5 equiv), and DMAP (1.04 g, 8.57 mmol, 1.5 equiv) in DMF (20 mL) was added TBDPS-Cl (1.75 mL, 6.85 mmol, 1.2 equiv). After 24 h at ambient temperature, the reaction mixture was poured into water (75 mL) and 2:1 CH_2Cl_2:hexanes (150 mL), extracted with 2:1 CH_2Cl_2:hexanes (4 x 30 mL), dried (Na_2SO_4), and evaporated. Flash chromatography (SiO_2, 2.5→12% EtOAc in hexanes) gave the desired compound (1.85 g, 72% yield). mp 59-60 °C; R_f = 0.24 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72-7.68 (m, 4H), 7.48-7.37 (m, 6H), 6.00-5.86 (m, 1H), 5.38-5.31 (m, 1H), 5.28-5.23 (m, 1H), 4.74-4.59 (m, 2H), 4.24 (d, J = 9.9 Hz, 1H), 3.82 (d, J = 9.9 Hz, 1H), 2.78 (dq, J = 13.4, 3.3 Hz, 1H), 2.53-2.38 (m, 2H), 2.10-1.99 (m, 1H), 1.88-1.54 (m, 4H) 1.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.4, 169.8, 135.6, 135.5, 133.1, 132.9, 131.5, 129.6, 127.6 (2C), 118.8, 66.4, 65.8, 62.9, 41.2, 33.6, 27.3, 26.6, 22.1, 19.2; IR (Neat Film NaCl) 3072, 2933, 2858, 1715, 1428, 1200, 1112, 703 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{27}H_{33}O_4Si$ [M – H]$^+$: 449.2148, found 449.2165.



SI54

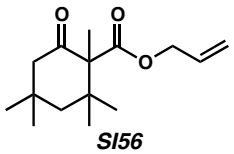
Allyl 1-fluoro-2-oxocyclohexanecarboxylate (SI54, Table 12, entry 10): To a solution of ketoester **SI46** (946.4 mg, 5.19 mmol, 1 equiv) in 50 mL CH_3CN, was added $TiCl_4$ (50 μL, 0.456 mmol, 0.09 equiv). Select-fluor® (2.2224 g, 6.27 mmol, 1.2 equiv) was added after 10 min and the mixture stirred at room temperature for 2 h and 40 min, over which time the orange color disappeared. The mixture was partitioned between H_2O (200 mL) and Et_2O (50 mL). The aqueous layer was separated and washed with Et_2O (30 mL). The combined organic layers were dried ($MgSO_4$), concentrated to about 30 mL, passed through a pad of silica that was washed with Et_2O (5 x 10 mL), and evaporated *in vacuo*. The residue was then bulb-to-bulb distilled at 180–190 °C (bath temp, 2 torr) to afford the title compound as a colorless oil (947.6 mg, 91% yield). R_f = 0.19 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93 (dddd, J = 5.7, 5.7, 10.5, 17.1 Hz, 1H), 5.37 (dddd, J = 1.5, 1.5, 1.5, 17.4 Hz, 1H), 5.29 (dddd, J = 1.5, 1.5, 1.5, 10.5 Hz, 1H), 4.73 (bd, J = 5.7 Hz, 2H), 2.80-2.67 (m, 1H), 2.66-2.38 (m, 2H), 2.24-2.10

(m, 1H), 1.98-1.80 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5 (d, $J_{C\text{-}F}$ = 19.8 Hz), 166.4 (d, $J_{C\text{-}F}$ = 24.8 Hz), 130.8, 119.2, 96.2 (d, $J_{C\text{-}F}$ = 196.9 Hz), 66.5, 39.4, 35.8 (d, $J_{C\text{-}F}$ = 21.8 Hz), 26.4, 20.7 (d, $J_{C\text{-}F}$ = 6.0 Hz); IR (Neat Film NaCl) 3087, 2952, 1759, 1735, 1650, 1452, 1281, 1223, 1150, 1097, 990 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{13}O_3F$ [M]$^+$: 200.0849, found 200.0858.



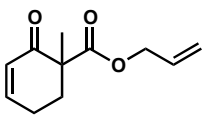
SI55

Allyl 1,3,3-trimethyl-2-oxocyclohexanecarboxylate (SI55, Table 13, entry 3): To a cooled (–78 °C) solution of LDA (13.5 mmol, 1.12 equiv) in THF (30 mL) was added 2,2,6-trimethylcyclohexanone (1.6938 g, 12.08 mmol, 1.0 equiv) dropwise. The resulting solution was warmed to 0 °C for 1 h, cooled to –78 °C and HMPA (2.2 mL, 12.6 mmol, 1.04 equiv) was added. After 5 min, allyl cyanoformate[4] (1.5014g, 13.5 mmol, 1.12 equiv) was added dropwise. The reaction was warmed to room temperature and allowed to stir overnight. The reaction was then quenched with 50% saturated aq NH_4Cl (40 mL). The aqueous layer was separated and washed with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (SiO_2, 3% Et_2O in hexanes) to afford the β-ketoester as a colorless oil (585.6 mg, 22%), along with the known enol carbonate[34] (R_f = 0.53, 10:1 Hexane:EtOAc) as a colorless oil (1.3117 g, 48%). R_f = 0.50 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (dddd, *J* = 5.7, 5.7, 10.2, 16.8 Hz, 1H), 5.30 (dddd, *J* = 1.2, 1.2, 1.2, 17.1 Hz, 1H), 5.22 (dddd, *J* = 0.9, 0.9, 0.9, 10.2 Hz, 1H), 4.62 (dddd, *J* = 1.2, 1.2, 5.7, 13.2 Hz, 1H), 4.51 (dddd, *J* = 1.2, 1.2, 5.7, 13.2 Hz, 1H), 2.54 (dddd, *J* = 2.4, 3.9, 3.9, 13.8 Hz, 1H), 1.98 (ddddd, *J* = 3, 4.2, 12, 14.1, 15.6 Hz, 1H), 1.77-1.68 (m, 1H), 1.66-1.52 (m, 2H), 1.42 (ddd, *J* = 4.2, 12.3, 13.8, 1H), 1.32 (s, 3H), 1.09 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.4, 172.4, 131.5, 118.8, 65.7, 55.1, 46.1, 40.6, 36.8, 26.8, 25.5, 23.6, 18.5; IR (Neat Film NaCl) 3089, 2938, 1736, 1707, 1649, 1456, 1377, 1243, 1209, 1174, 1150, 972 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{20}O_3$ [M]$^+$: 224.1413, found 224.1413.



SI56

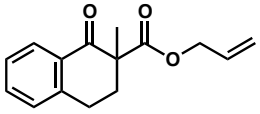
Allyl 1,2,2,4,4-pentamethyl-6-oxocyclohexanecarboxylate (SI56, Table 13, entry 4): Prepared by a modification of general procedure 10. Part A: Reaction of 3,3,5,5-tetramethylcyclohexanone in benzene (1 M) at 80 °C for 40 h using NaH (2 equiv) and diallylcarbonate (3 equiv) gave an ~1:1 mixture of mono- and bis-acylated material after flash chromatography (SiO_2, 1 → 8% Et_2O in hexanes). Part B: Reaction in acetone (0.42 M) at 75 °C in a sealed flask for 24 h using Cs_2CO_3 (3 equiv) and MeI (4 equiv). Flash chromatography (SiO_2, 1→4% Et_2O in hexanes) gave the desired compound. 25% overall yield. R_f = 0.60 (25% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (dddd, *J* = 17.4, 10.5, 6.0, 6.0 Hz, 1H), 5.29 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 10.5 Hz, 1H), 4.55 (d, *J* = 6.0 Hz, 2H), 2.78 (d, *J* = 13.5 Hz, 1H), 2.23-2.12 (comp. m, 2H), 1.33 (d, *J* = 14.4 Hz, 1H), 1.26 (s, 3H), 1.11 (s, 3H), 1.04 (s, 3H), 1.01 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.9, 171.5, 131.5, 118.8, 65.5, 62.6, 51.7, 49.4, 40.9, 34.8, 34.5, 29.6, 27.7, 26.9, 14.7; IR (Neat Film NaCl) 3087, 2959, 1715, 1456, 1371, 1216, 1101, 979 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{24}O_3$ [M]$^+$: 252.1725, found 252.1719.



SI57

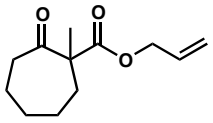
Allyl 1-methyl-2-oxocyclohex-3-enecarboxylate (SI57, Table 13, entry 5): Prepared by general procedure 10 from cyclohex-2-en-1-one. Flash chromatography (SiO_2, CH_2Cl_2). 23% yield. R_f = 0.38

(30% Et_2O in pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 6.92 (m, 1H), 6.06 (dt, *J* = 10.1, 2.1 Hz, 1H), 5.86 (dddd, *J* = 17.3, 10.4, 5.6, 5.6 Hz, 1H), 5.24 (m, 2H), 4.61 (m, 2H), 2.57-2.41 (m, 2H), 2.41-2.27 (m, 1H), 1.97-1.82 (m, 1H), 1.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.8, 172.3, 149.4, 131.6, 128.9, 118.3, 65.7, 53.4, 33.3, 23.6, 20.3; IR (Neat Film NaCl) 2936, 1733, 1678, 1249, 1192, 1110 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{14}O_3$ $[M]^+$: 194.0943, found 194.0941.



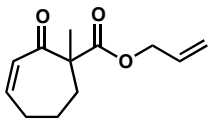
SI58

Allyl 2-methyl-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (SI58, Table 13, entry 6): Prepared by general procedure 10 from 1-tetralone. Flash chromatography (SiO_2, 10% Et_2O in pentane). 60% yield. R_f = 0.61 (30% Et_2O in pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.8 Hz, 1H), 7.47 (app. t, *J* = 7.5 Hz, 1H), 7.31 (app. t, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 5.79 (dddd, *J* = 17.1, 10.7, 5.4, 5.4 Hz, 1H), 5.19-5.09 (m, 2H), 4.58 (m, 2H), 3.12-2.87 (m, 2H), 2.68-2.57 (m, 1H), 2.13-2.01 (m, 1H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.9, 172.5, 143.1, 133.4, 131.7, 131.5, 128.7, 128.0, 126.8, 118.0, 65.6, 53.9, 33.9, 26.0, 20.6; IR (Neat Film NaCl) 3071, 2982, 2938, 1736, 1690, 1602, 1456, 1377, 1308, 1228, 1189, 1112, 979, 743 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{16}O_3$ $[M]^+$: 244.1099, found 244.1094.



SI59

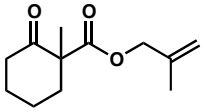
Allyl 1-methyl-2-oxocycloheptanecarboxylate (SI59, Table 13, entry 7): Prepared by general procedure 10 from cycloheptanone. Flash chromatography (SiO_2, 25→100% CH_2Cl_2 in pentane). 30% yield. R_f = 0.60 (30% Et_2O in pentane); ^1H NMR (300 MHz, $CDCl_3$) δ 5.88 (dddd, *J* = 17.3, 10.4, 5.6, 5.6 Hz, 1H), 5.26 (m, 2H), 4.61 (m, 2H), 2.81-2.67 (m, 1H), 2.57-2.45 (m, 1H), 2.25-2.11 (m, 1H), 1.91-1.70 (comp. m, 3H), 1.69-1.49 (comp. m, 4H), 1.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 131.6, 118.5, 65.6, 58.8, 42.0, 35.4, 30.1, 25.8, 24.7, 21.5; IR (Neat Film NaCl) 2936, 1740, 1710, 1229, 1151, 1105 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O_3$ $[M]^+$: 210.1256, found 210.1249.



SI60

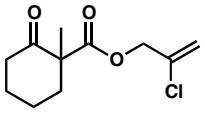
Allyl 1-methyl-2-oxocyclohept-3-enecarboxylate (SI60, Table 13, entry 8): To a cooled (–78 °C) solution of LHMDS (1.0 M soln in THF, 10 mL, 10 mmol, 1.5 equiv) in THF (20 mL) was added cyclohept-2-enone (759 μL, 6.73 mmol, 1.0 equiv). After 30 min, allyl cyanoformate[4] (813 mg, 7.32 mmol, 1.1 equiv) was added. The reaction was allowed to stir at –78 °C for 30 min and was then quenched with 50% saturated aq NH_4Cl (40 mL) and allowed to thaw. The aqueous layer was separated and extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting oil was dissolved in 10 mL CH_3CN, then Cs_2CO_3 (3.3271 g, 10.21 mmol, 1.5 equiv) and MeI (2.1 mL, 33.73 mmol, 5.0 equiv) were added. The mixture was then heated to 80 °C for 4 h and then cooled to ambient temperature. The mixture was diluted with ~10 mL EtOAc and filtered through a 3 x 3 cm plug of silica gel which was then washed with 3 x 25 mL EtOAc. Evaportation *in vacuo* gave an oil that was purified by flash chromatography (3 x 24 cm, 15:1 Hexanes:EtOAc) to afford the title compound as a colorless oil (735.2 mg, 52%). R_f = 0.20 (10:1 Hexane:EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 6.38 (ddd, *J* = 4.8, 4.8, 12.6 Hz, 1H), 6.03 (ddd, *J* = 2.4, 2.4, 12.9 Hz, 1H), 5.86 (dddd, *J* = 5.4, 5.4, 10.8, 17.1 Hz, 1H), 5.29 (dddd, *J* = 1.5, 1.5,

1.5, 17.4 Hz, 1H), 5.21 (dddd, J = 1.2, 1.2, 1.2, 10.5 Hz, 1H), 4.65-4.59 (m, 1H), 4.59-4.52 (m, 1H), 2.44-2.30 (m, 3H), 2.10 (m, 1H), 1.82-1.65 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.6, 173.3, 143.2, 131.6, 130.9, 118.2, 65.6, 59.9, 34.2, 31.5, 23.3, 23.1; IR (Neat Film NaCl) 3080, 3018, 2937, 1737, 1686, 1454, 1377, 1232, 1171, 1113, 978, 931, 820 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{16}O_3$ [M]$^+$: 208.1100, found 208.1109.



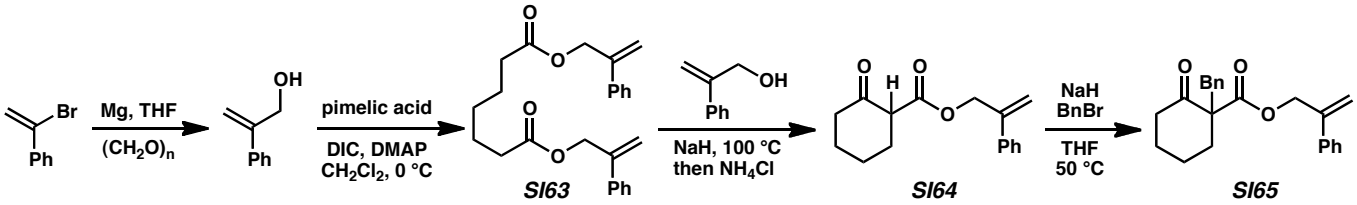
SI61

2-Methylallyl 1-methyl-2-oxocyclohexanecarboxylate (SI61, Table 13, entry 9): Prepared by general procedure 10 from cyclohexanone with dimethyallyl carbonate in part A. Flash chromatography (SiO_2, 10% Et_2O in pentane). 46% yield. R_f = 0.24 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.94 (m, 2H), 4.54 (s, 2H), 2.58-2.42 (comp. m, 3H), 2.08-1.93 (m, 1H), 1.80-1.57 (comp. m, 6H), 1.55-1.40 (m, 1H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.1, 172.8, 139.4, 113.5, 68.4, 57.2, 40.6, 38.2, 27.5, 22.6, 21.3, 19.5; IR (Neat Film NaCl) 2940, 2867, 1715, 1452, 1260, 1211, 1160, 1086, 907 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O_3$ [M]$^+$: 210.1256, found 210.1256.



SI62

2-Chloroallyl 1-methyl-2-oxocyclohexanecarboxylate (SI62, Table 13, entry 10): Prepared by general procedure 10 from cyclohexanone with 1.25 equiv of 2-chloroallyl carbonate[35,36] in part A. Flash chromatography (SiO_2, 10% Et_2O in pentane). 62% yield. R_f = 0.20 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.45 (m, 2H), 4.71 (m, 2H), 2.62-2.41 (comp. m, 3H), 2.10-1.93 (m, 1H), 1.81-1.62 (comp. m, 3H), 1.57-1.41 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.8, 172.3, 135.4, 115.8, 66.5, 57.2, 40.6, 38.2, 27.4, 22.5, 21.2; IR (Neat Film NaCl) 2942, 2868, 1716, 1640, 1453, 1248, 1221, 1153, 1084, 903 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{15}O_3Cl$ [M]$^+$: 230.0710, found 230.0711.



2-Phenylallyl alcohol.[37] A 250 mL two-neck round-bottomed flask equipped with an addition funnel, a condenser, a stir bar, and two septa was charged with Mg turnings (1.71 g, 70.3 mmol), cutting several turnings during addition. The system was then flame dried under vacuum. After refilling with Ar, anhydrous THF (50 mL) and bromoethane (300 μL, 4.02 mmol) were added via syringe. The flask was opened and iodine (110.9 mg, 0.437 mmol) was added under positive Ar pressure. The flask was then sealed and flushed with Ar. After stirring at 23 °C for 15 min, the reaction turned a greenish color. α-Bromostyrene (8.4 mL, 64.7 mmol) in anhydrous THF (15 mL) was then added dropwise over 1 h via the addition funnel, during which time a significant exotherm was observed. The reaction was then placed in an oil bath and heated at reflux for 41 min. After cooling to 23 °C, the flask was opened, and paraformaldehyde (3.00 g, 99.9 mmol) was added. The flask was then sealed and flushed with Ar. After stirring at 23 °C for 1.5 h, saturated NH_4Cl (aq) (40 mL) and H_2O (40 mL) were added to quench the reaction and dissolve all solids. The mixture was extracted with Et_2O (3 x 40 mL), and the combined organic layers were washed with H_2O (2 x 50 mL) and brine (50 mL). After drying over $MgSO_4$, solvent was removed under reduced pressure. The crude product was then distilled under high vacuum

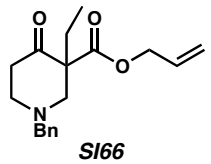
to provide 2-phenylallyl alcohol (6.542 g, 75%) as a colorless liquid containing minor unidentified impurities by ^{1}H NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.43 (m, 2H), 7.39-7.33 (m, 2H), 7.31-7.28 (m, 1H), 5.48 (dt, *J* = 0.9, 0.7 Hz, 1H), 5.36 (dt, *J* = 1.3, 1.2 Hz, 1H), 4.56 (ddd, *J* = 6.1, 1.3, 0.7 Hz, 2H), 1.58-1.52 (m, 1H).

Bis(ester) SI63. A flame-dried 250 mL round-bottomed flask equipped with a stir bar and a septum was charged with 2-phenylallyl alcohol (98.6% pure by mass (contained 1.4% CH_2Cl_2 by mass), 5.42 g, 39.8 mmol), pimelic acid (3.35 g, 20.9 mmol), and DMAP (1.95 g, 16.0 mmol). The flask was evacuated under high vacuum and refilled with Ar. Anhydrous CH_2Cl_2 (80 mL) was added via syringe, and the reaction was cooled to 0 °C in an ice bath. *N,N'*-Diisopropylcarbodiimide (6.4 mL, 41.3 mmol) was added in one portion via syringe, and the reaction was stirred for 5 min at 0 °C. The ice bath was removed, and the reaction was allowed to warm to 23 °C as it was stirred for 10.75 h. A white precipitate formed during this time. The reaction was filtered through filter paper and then diluted with CH_2Cl_2 (200 mL). The solution was washed with 0.1 M HCl (aq) (200 mL), saturated $NaHCO_3$ (aq) (100 mL), and brine (100 mL). After drying over $MgSO_4$, solvent was removed under reduced pressure. Flash chromatography over silica gel (10 x 5 cm silica, 20% Et_2O/pentane eluent) then provided bis(ester) **SI63** (6.251 g, 80%) as a colorless oil containing <1% Et_2O by mass. R_f 0.28 (20% Et_2O/pentane); ^{1}H NMR (300 MHz, acetone-d_6) δ 7.53-7.44 (m, 4H), 7.43-7.27 (m, 6H), 5.60-5.55 (m, 2H), 5.37 (dt, *J* = 1.2, 1.1 Hz, 2H), 5.02-4.98 (m 4H), 2.28 (t, *J* = 7.4 Hz, 4H), 1.59-1.47 (m, 4H), 1.32-1.18 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 142.6, 138.0, 128.4, 128.0, 126.0, 115.2, 65.5, 34.0, 28.4, 24.5; IR (neat film, NaCl) ν 3084, 3057, 3031, 2938, 2864, 1736, 1633, 1601, 1575, 1496, 1462, 1445, 1417, 1383, 1320, 1309, 1227, 1167, 1083, 1027, 1014, 987, 911, 779, 708 cm^{-1}; HRMS (EI+) *m/z* calc'd. for $C_{25}H_{28}O_4$ $[M]^+$: 392.1988, found 392.1998.

β-ketoester SI64. A flame-dried 100 mL round-bottomed flask equipped with a stir bar and a septum was charged with NaH (60% dispersion in mineral oil, 679 mg, 17.0 mmol) and evacuated under high vacuum. After refilling with Ar, anhydrous toluene (50 mL) was added via syringe. 2-Phenylallyl alcohol (182 mg, 1.36 mmol) in anhydrous toluene (1 mL) was added via syringe, washing the original flask with anhydrous toluene (1 mL). Bis(ester) **SI63** (6.079 g, 15.5 mmol) in anhydrous toluene (4 mL) was added via syringe, washing the original flask with anhydrous toluene (4 mL). The reaction was then placed in an oil bath and stirred at 100 °C for 15.7 h. After cooling to 23 °C, saturated NH_4Cl (aq) (50 mL) and 1 M HCl (aq) (25 mL) were added to quench the reaction. The mixture was extracted with Et_2O (2 x 50 mL), and the combined organic layers were washed with 50% H_2O/50% brine (150 mL) and brine (150 mL). After drying over $MgSO_4$, solvent was removed under reduced pressure. Flash chromatography over silica gel (10 x 5 cm silica, 10% Et_2O/pentane eluent) then provided β-ketoester **SI64** (3.172 g, 78%) as a colorless oil containing 2.2% pentane by mass. A 2.7:1 ratio of enol:ketone tautomer was observed by ^{1}H NMR spectroscopy. R_f 0.19-0.60 (10% Et_2O/pentane, appears as a streak on TLC plate); ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.1 (s, 0.73 H), 7.48-7.40 (m, 2H), 7.40-7.28 (m, 3H), 5.58-5.55 (m, 1H), 5.41-5.36 (m, 1H), 5.15-5.00 (m 2H), 3.43-3.35 (m, 0.27H), 2.52-1.52 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.0, 172.6, 172.2, 169.7, 142.5, 142.2, 138.1, 137.8, 128.47, 128.45, 128.06, 128.03, 126.02, 125.95, 115.7, 114.7, 97.6, 66.3, 65.2, 57.2, 41.4, 29.9, 29.1, 27.0, 23.2, 22.31, 22.28, 21.8; IR (neat film, NaCl) ν 3084, 3057, 2938, 2859, 1744, 1715, 1655, 1614, 1576, 1496, 1446, 1421, 1396, 1357, 1334, 1294, 1258, 1216, 1175, 1108, 1080, 1059, 1028, 973, 909, 830, 815, 778, 708 cm^{-1}; HRMS (EI+) *m/z* calc'd. for $C_{16}H_{18}O_3$ $[M]^+$: 258.1256, found 258.1250.

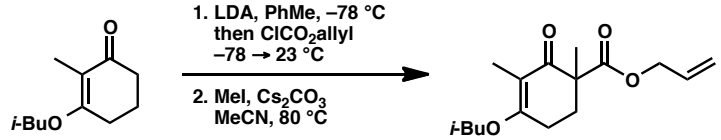
β-ketoester SI65 (Table 13, entry 11). A flame-dried 1 dram screw-cap vial equipped with a stir bar and a septum-bearing cap was charged with NaH (60% dispersion in mineral oil, 31.7 mg, 0.793 mmol) and evacuated under high vacuum. After refilling with Ar, anhydrous THF (0.4 mL) was added via syringe. β-Ketoester **SI64** (200 mg, 0.774 mmol) in anhydrous THF (0.5 mL) was added dropwise via syringe, washing the original flask with anhydrous THF (0.5 mL). Benzyl bromide (120 μL, 1.01 mmol) was then added in one portion via syringe. The vial cap was wrapped in Teflon tape, and the Ar inlet was removed. The reaction was then placed in an oil bath and stirred at 55 °C for 5.25 h. After cooling to 23 °C, saturated NH_4Cl (aq) (0.5 mL) and H_2O (0.5 mL) were added to quench the reaction.

The organic layer was separated, and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with 50% H_2O/50% brine (15 mL), and brine (15 mL), then dried over $MgSO_4$. Solvent was removed under reduced pressure. Flash chromatography over silica gel (7 x 2 cm silica, 20% Et_2O/pentane eluent) then provided β-ketoester **SI65** (199 mg, 73%) as a thick yellow syrup containing <1% Et_2O by mass. R_f 0.45 (20% Et_2O/pentane); ^{1}H NMR (300 MHz, CD_3OD) δ 7.42-7.24 (m, 5H), 7.26-7.11 (m, 3H), 7.08-7.01 (m, 2H), 5.53 (d, *J* = 1.1 Hz, 1H), 5.32 (ddd, *J* = 1.1 Hz, 1H), 5.05 (dd, *J* = 12.8, 1.1 Hz, 1H), 4.90 (dd, *J* = 12.9, 0.9 Hz, 1H), 3.18 (d, *J* = 13.6 Hz, 1H), 2.78 (d, *J* = 13.6 Hz, 1H), 2.34-1.98 (m, 3H), 1.91-1.73 (m, 1H), 1.68-1.34 (m, 4H); ^{13}C NMR (75 MHz, CD_3OD) δ 208.5, 172.0, 144.3, 139.3, 137.8, 131.4, 129.6, 129.2, 129.0, 127.7, 127.3, 117.0, 67.6, 63.4, 42.0, 41.4, 36.8, 28.6, 23.3; IR (neat film, NaCl) ν 3086, 3060, 3029, 2941, 2866, 1714, 1634, 1603, 1575, 1496, 1453, 1442, 1309, 1264, 1248, 1216, 1175, 1133, 1086, 1053, 1030, 1003, 987, 963, 913, 804, 779, 743, 702 cm^{-1}; HRMS (EI+) *m/z* calcd. for $C_{23}H_{24}O_3$ [M]$^+$: 348.1726, found 348.1712.



SI66

Allyl 1-benzyl-3-ethyl-4-oxopiperidine-3-carboxylate (SI66, Table 13, entry 12): Prepared by general procedure 10 from 1-benzylpiperidin-4-one (part A) and iodoethane (part B). Flash chromatography (SiO_2, 2.5→20% EtOAc in hexanes). 55% yield. R_f = 0.50 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33-7.25 (m, 5H), 5.90 (dddd, *J* = 17.4, 10.7, 5.7, 5.7 Hz, 1H), 5.33 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.24 (dq, *J* = 10.4, 1.5 Hz, 1H), 4.70 (ddt, *J* = 13.0, 6.0, 1.4 Hz, 1H), 4.62 (ddt, *J* = 13.0, 6.0, 1.4 Hz, 1H), 3.62 (d, *J* = 13.2 Hz, 1H), 3.56 (d, *J* = 13.2 Hz, 1H), 3.42 (dd, *J* = 11.4, 2.7 Hz, 1H), 3.04-2.80 (m, 2H), 2.45-2.35 (m, 2H), 2.25 (d, *J* = 11.7 Hz, 1H), 1.94-1.82 (m, 1H), 1.65-1.53 (m, 1H), 0.87 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.9, 171.3, 137.9, 131.7, 128.8, 128.2, 127.3, 118.7, 65.6, 61.8, 61.5, 61.0, 53.5, 40.6, 25.2, 9.1; IR (Neat Film NaCl) 2966, 2939, 1719, 1224, 1139, 699 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{18}H_{23}O_3$ [M]$^+$: 301.1678, found 301.1691.



SI67 (55% yield) ***SI68***

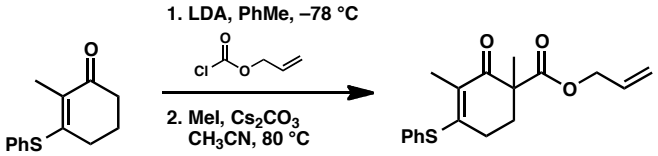
Vinylogous ester SI68 (Table 13, entry 13):

The following procedure is adapted from a report by Trost and coworkers.[38]

To a –78 °C solution of *i*-Pr_2NH (425 μL, 3.03 mmol, 1.9 equiv) in PhMe (10 mL) was added dropwise *n*-BuLi (2.55 M in hexanes, 1.16 mL, 2.96 mmol, 1.85 equiv). The reaction vessel was placed in an ice/water bath and allowed to stir for 10 min, and then cooled to –78 °C. A solution of vinylogous ester **SI67**[39] (291 mg, 1.60 mmol, 1.0 equiv) in PhMe (1.4 mL) was added dropwise via cannula to the reaction vessel, and the resulting solution was allowed to stir for 30 min. Allyl chloroformate (173 μL, 1.63 mmol, 1.02 equiv) was added dropwise, and the reaction vessel was allowed to warm to 23 °C over 1 h. After stirring for 4 h, the reaction was slowly quenched with aq $KHSO_4$ (1 N, 4 mL) and the resulting biphasic mixture was allowed to stir for 10 min. The phases were separated, and the aq phase was extracted with Et_2O (2 x 10 mL). The combined organic extracts were washed with brine (10 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The isolated crude yellow oil was used in the next step without further purification.

The resulting crude yellow oil was dissolved in MeCN (5.9 mL, 0.27 M), and Cs_2CO_3 (603 mg, 1.85 mmol, 1.16 equiv), and MeI (276 μL, 4.44 mmol, 2.8 equiv) were added. The flask was affixed a water-cooled condenser and resulting suspension was warmed to reflux in an 80 °C oil bath with vigorous stirring. After 10 h, the reaction was cooled to room temperature, diluted with EtOAc (25 mL). The

organics were dried with $MgSO_4$, filtered, and the solvent was evaporated *in vacuo*. Purification by flash chromatography (15:1 → 9:1 → 4:1 hexanes-EtOAc) afforded β-ketoester (±)-**SI68** as pale yellow oil (246 mg, 55% yield over two steps). R_f = 0.27 (2:1 hexanes-EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.82 (dddd, *J* = 17.2, 10.7, 5.4, 5.4 Hz, 1H), 5.22 (dddd, *J* = 17.2, 1.6, 1.6, 1.6 Hz, 1H), 5.15 (dddd, *J* = 10.5, 1.2, 1.2, 1.2 Hz, 1H), 4.56 (dddd, *J* = 13.5, 5.4, 1.5, 1.5 Hz, 2H), 3.72 (ddd, *J* = 9.2, 6.6, 3.2 Hz, 2H), 2.69-2.62 (m, 1H), 2.53-2.44 (comp m, 2H), 1.95 (app septuplet, *J* = 6.6 Hz, 1H), 1.85-1.80 (m, 1H), 1.70 (dd, *J* = 1.5, 1.5 Hz, 3H), 1.36 (s, 3H), 0.95 (dd, *J* = 6.7, 0.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 195.8, 172.6, 170.3, 131.9, 117.8, 113.8, 73.9, 65.5, 51.6, 31.2, 28.8, 23.0, 20.8, 19.1, 19.0, 8.0; IR (Neat Film NaCl) 2961, 2935, 2875, 1733, 1649, 1618, 1460, 1382, 1354, 1237, 1176, 1103, 983 cm^{-1}; HRMS (FAB+) *m/z*: calc'd for $C_{16}H_{25}O_4$ [M + H]$^+$: 281.1753, found 281.1740.



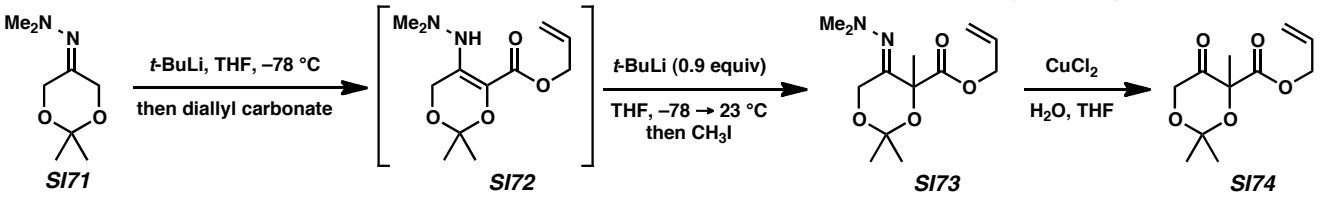
SI69 (78% yield, two steps) ***SI70***

Vinylogous thioester SI70 (Table 13, entry 14):

The following procedure is adapted from a report by Trost and coworkers.[38]

To a –78 °C solution of diisopropylamine (2.63 mL, 18.78 mmol, 2.00 equiv) in toluene (70 mL) was added dropwise *n*-BuLi (2.53 M in hexanes, 7.24 mL, 2.00 equiv). The reaction vessel was warmed to 0 °C, allowed to stir for 10 min, and cooled to –78 °C. A solution of thioester **SI69**[38] (2.00 g, 9.16 mmol, 1.00 equiv) in toluene (15 mL) was added dropwise via cannula to the reaction vessel, and the resulting solution was allowed to stir for 30 min. Allyl chloroformate (1.02 mL, 9.62 mmol, 1.05 equiv) was added dropwise, and the reaction vessel was allowed to warm to 23 °C over 1 h. Stirring was continued for 4 h, then aq $KHSO_4$ (1 N, 70 ml) was added, and the resulting solution was allowed to stir for 10 min. The phases were separated, and the aq phase was extracted with Et_2O (3 x 30 mL). The combined organic extracts were washed with brine (1 x 30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The isolated crude yellow oil was used in the next step without further purification.

To a solution of the crude yellow oil (3.32 g) in CH_3CN (40 mL) was added cesium carbonate (4.48 g, 13.74 mmol, 1.50 equiv), and iodomethane (1.71 mL, 27.48 mmol, 3.00 equiv). The resulting suspension was refluxed at 80 °C for 5 h, and then MeI (1.00 mL, 16.06 mmol, 1.75 equiv) was added. The reaction was refluxed at 80 °C for 2 h, cooled to room temperature, filtered through Celite (EtOAc eluent), dried over Na_2SO_4, filtered, and the solvent was evaporated in vacuo. Purification by flash chromatography (18% EtOAc in hexanes) afforded β-ketoester (±)-**SI70** (2.26 g, 78% yield over two steps) as white solid. R_f = 0.35 (30% EtOAc in hexanes); mp 34 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.35 (comp m, 5H), 5.87 (app ddt, *J* = 10.5, 17.1, 5.4 Hz, 1H), 5.27 (app ddt, *J* = 17.1, 1.7, 1.8 Hz, 1H), 5.22 (app ddt, *J* = 9.9, 1.7, 1.2 Hz, 1H), 4.65 (dddd, *J* = 1.5, 1.8, 5.7, 13.5 Hz, 1H), 4.55 (dddd, *J* = 1.5, 1.8, 5.7, 13.5 Hz, 1H), 2.41-2.32 (m, 1H), 2.30-2.21 (m, 1H), 2.16-2.06 (1H), 2.00 (t, *J* = 1.8 Hz, 3H), 1.78 (ddd, *J* = 4.5, 8.1, 13.2 Hz, 1H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.0, 172.6, 156.7, 135.6, 131.9, 129.7, 129.5, 128.9, 118.1, 65.7, 52.3, 33.1, 27.4, 20.7, 12.9; IR (Neat Film NaCl) 2936, 1733, 1656, 1580, 1314, 1254, 1238, 1174, 985, 752, 693 cm^{-1}; HRMS (FAB+) *m/z*: calc'd for $C_{18}H_{20}O_3S$ [M + H]$^+$: 317.1211, found 317.1211.



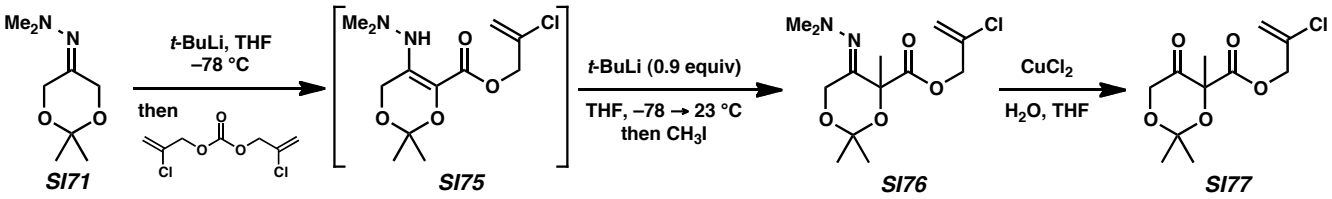
SI71 ***SI72*** ***SI73*** ***SI74***

Allyl 5-(2,2-dimethylhydrazono)-2,2,4-trimethyl-1,3-dioxane-4-carboxylate (SI73): A flask was charged with a solution of hydrazone **SI71**[40] (7.440 g, 43.2 mmol, 1 equiv) in THF (172 mL, 0.25 M) under N_2 at –78 °C. The solution was treated dropwise with *t*-BuLi (1.7 M in pentane, 28 mL, 47.6 mmol, 1.1 equiv) over 40 min, and then allowed to stir for 6 min. The deep yellow mixture was treated dropwise with diallyl carbonate (5.3 mL, 36.9 mmol, 0.85 equiv) over 7 min. After stirring for an additional 46 min, the yellow solution was treated dropwise with *t*-BuLi (1.7 M in pentane, 22 mL, 37.4 mmol, 0.87 equiv) over 22 min, and then allowed to stir for 6 min. The yellow solution was treated dropwise with diallyl carbonate (4 mL, 27.9 mmol, 0.65 equiv) over 4 min. The mixture was allowed to gradually warm to room temperature (ca. 24 °C) over several hours. Seventeen hours after diallyl carbonate addition, the reaction was quenched by addition of phosphate buffer[41] (ca. 120 mL) until the aq layer reached a pH of 8, and was then extracted with Et_2O (to 600 mL over several extractions). Each extract was sequentially washed with 1 N aq HCl (28 mL, to a pH of 3), phosphate buffer (ca. 20 mL, to a pH of 7), and brine (ca. 20 mL). Extracts were dried over $MgSO_4$, filtered, and concentrated under reduced pressure to a yellow oil. The oil was purified through silica gel chromatography (ca. 600 mL of SiO_2 on a column with 5 cm diameter; eluent 1:5 Et_2O:hexanes). Mixed fractions were further purified by silica gel chromatography (eluent 1:7 Et_2O:hexanes) to give β-hydrazone ester **SI72** as a yellow semi-solid (7.56 g, 68.3% yield).

A flask was charged with a solution of β-hydrazone ester **SI72** (7.56 g, 29.5 mmol, 1 equiv) in THF (118 mL, 0.25 M), and cooled to –78 °C under N_2. The yellow solution was treated dropwise with *t*-BuLi (1.7 M in pentane, 15.6 mL, 26.5 mmol, 0.9 equiv). The reaction was allowed to gradually warm to room temperature (ca. 24 °C) over 9 h, after which point it was recooled to –78 °C. The solution was then treated dropwise with CH_3I (9.2 mL, 147 mmol, 5.0 equiv) over 12 min, before gradually warming to room temperature (ca. 24 °C). After 5 h of stirring at this temperature, the reaction was quenched with phosphate buffer (ca. 40 mL) and saturated aq NH_4Cl (ca. 30 mL). The mixture was extracted with Et_2O (to 400 mL). Extracts were further washed with brine (ca. 25 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow oil. The oil was purified by silica gel chromatography (ca. 600 mL of SiO_2 on a column with 5 cm diameter; eluent 1:5 Et_2O:hexanes). Mixed fractions were further purified by silica gel chromatography (eluent 1:7 Et_2O:hexanes) to give **SI73** as a yellow semi-solid (6.18 g, 77.5% yield). R_f 0.57 (50% Et_2O in hexanes; visualized with anisaldehyde); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.33 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.22 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.72 (d, *J* = 17.0 Hz, 1H), 4.62 (dtt, *J* = 8.5, 5.7, 1.4 Hz, 2H), 4.44 (d, *J* = 17.0 Hz, 1H), 2.47 (s, 6H), 1.52 (s, 3H), 1.47 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.2, 163.2, 131.8, 118.8, 101.3, 76.9, 66.1, 61.3, 47.2, 28.3, 25.1, 21.8; IR (NaCl) 2990, 2955, 2862, 2824, 2980, 1757, 1731, 1444, 1383, 1372, 1270, 1230, 1210, 1178, 1135, 1114, 1103, 1062, 996, 931, 848, 798; HRMS (EI+) *m/z* calc'd for $C_{13}H_{22}O_4N_2$ $[M]^+$: 270.1580, found 270.1577.

Allyl 2,2,4-trimethyl-5-oxo-1,3-dioxane-4-carboxylate (SI74, Table 13, entry 15): A flask was charged with hydrazone **SI73** (28.0 mg, 0.103 mmol, 1 equiv) in THF (1 mL, 0.1 M) at room temperature (ca. 24 °C). The yellow solution was treated with a 1 M solution of $CuCl_2$ in H_2O (0.12 mL, 0.12 mmol, 1.2 equiv). After 7 h, the yellow solution was treated with NH_4OH (5 drops). The resultant blue solution was extracted with Et_2O (3 x 8 mL), washed with brine (ca. 1 mL), dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give ketone **SI74** (23.6 mg, 95% yield) as a crude yellow oil. The yellow oil could be further purified through SiO_2 chromatography with Et_2O in hexanes to furnish ketone **SI74** as a colorless oil. R_f 0.63 (50% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (ddd, *J* = 16.3, 11.0, 5.8, 1H), 5.32 (dd, *J* = 17.2, 1.5, 1H), 5.24 (dd, *J* = 10.4, 1.2 Hz, 1H), 4.68 (ddd, *J* = 7.3, 5.6, 3.6 Hz, 1H), 4.64–4.59 (m, 1H), 4.31 (d, *J* = 18.3 Hz, 1H), 4.26 (d, *J* = 18.4 Hz, 1H),

1.54 (s, 3H), 1.45 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.6, 170.3, 131.3, 119.4, 102.5, 80.2, 66.7, 66.4, 27.7, 24.6, 19.9; IR (NaCl) 2994, 2943, 1748, 1728, 1445, 1423, 1386, 1375, 1276, 1232, 1210, 1178, 1136, 1117, 1094, 1070, 996, 932, 838; HRMS (EI+) *m/z* calc'd for $C_{11}H_{16}O_5$ [M + H]$^+$: 229.1071, found 229.1071.



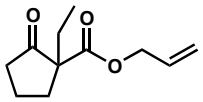
SI71 *SI75* *SI76* *SI77*

For a representative procedure, see the conversion of hydrazone **SI71**[40] to ketone **SI74**.

2-Chloroallyl 5-(2,2-dimethylhydrazinyl)-2,2-dimethyl-4*H*-1,3-dioxine-6-carboxylate (SI75): 49.5% yield. Yellow solid. R_f 0.57 (50% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (s, 1H), 5.44 (dd, *J* = 3.2, 1.5 Hz, 1H), 5.36 (dt, *J* = 2.0, 1.0 Hz, 1H), 4.75–4.72 (m, 2H), 4.49 (s, 2H), 2.46 (s, 6H), 1.46 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 113.7, 65.0, 59.2, 49.0, 24.2; IR (NaCl) 2992, 2951, 2856, 2777, 1679, 1619, 1441, 1372, 1324, 1264, 1233, 1201, 1137, 1074, 1012, 958, 883, 812, 767; HRMS-MM: ESI–APCI *m/z* calc'd for $C_{12}H_{19}ClN_2O_4$ [M + H]$^+$: 290.1033, found 290.1030.

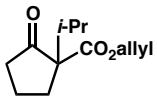
(*E*)-2-Chloroallyl 5-(2,2-dimethylhydrazono)-2,2,4-trimethyl-1,3-dioxane-4-carboxylate (SI76): 73% yield. Yellow oil. R_f 0.65 (50% Et_2O in hexanes; stains yellow in anisaldehyde); ^{1}H NMR (300 MHz, C_6D_6) δ 5.08 (dd, *J* = 2.8, 1.2 Hz, 1H), 5.03 (d, *J* = 1.7 Hz, 1H), 4.77 (d, *J* = 16.9 Hz, 1H), 4.60 (d, *J* = 16.9 Hz, 1H), 4.52 (ddd, *J* = 13.6, 1.2, 0.6 Hz, 1H), 4.33 (ddd, *J* = 13.6, 1.1, 0.5 Hz, 1H), 2.35 (s, 6H), 1.82 (s, 3H), 1.61 (d, *J* = 0.6 Hz, 3H), 1.22 (d, *J* = 0.6 Hz, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 172.9, 163.5, 136.4, 115.8, 101.7, 77.5, 67.0, 61.9, 47.4, 28.8, 25.4, 22.3; IR (NaCl) 2991, 2956, 2962, 2942, 2824, 2780, 1761, 1739, 1639, 1468, 1444, 1383, 1373, 1267, 1230, 1209, 1134, 1100, 1062, 997, 930, 901, 845, 644, 530; HRMS (EI+) *m/z* calc'd for $C_{13}H_{21}ClN_2O_4$ [M + H]$^+$: 305.1263, found 305.1268.

2-Chloroallyl 2,2,4-trimethyl-5-oxo-1,3-dioxane-4-carboxylate (SI77, Table 13, entry 16): 94% yield. Yellow oil. R_f 0.67 (50% Et_2O in hexanes; stains blue in anisaldehyde); ^{1}H NMR (300 MHz, C_6D_6) δ 5.00 (d, *J* = 1.1 Hz, 2H), 4.41 (d, *J* = 13.5 Hz, 1H), 4.21 (d, *J* = 13.6 Hz, 1H), 4.14 (d, *J* = 18.3 Hz, 1H), 3.91 (dd, *J* = 18.3, 2.8 Hz, 1H), 1.55 (s, 6H), 1.04 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6) δ 202.8, 170.1, 135.8, 116.0, 102.8, 80.6, 66.9, 28.1, 24.5, 20.3; IR (NaCl) 2996, 2944, 1749, 1640, 1445, 1423, 1386, 1376, 1274, 1232, 1209, 1177, 1136, 1113, 1094, 1071, 998, 907, 838; HRMS (EI+) *m/z* calc'd for $C_{11}H_{15}ClO_5$ [M]$^+$: 262.0608, found 262.0599.



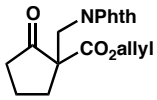
SI78

Allyl 1-ethyl-2-oxocyclopentanecarboxylate (SI78, Table 17, entry 1): Prepared by general procedure 10 part B from allyl 2-cyclopentanonecarboxylate[42] and using ethyl iodide as the electrophile. Flash chromatography (3 x 25 cm SiO_2, 10% Et_2O in hexanes) afforded the title compound as a colorless oil (1.5335 g, 85% yield). R_f = 0.27 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dddd, *J* = 5.7, 5.7, 10.5, 17.4 Hz, 1H), 5.30 (dddd, *J* = 1.6, 1.6, 1.6, 17.1 Hz, 1H), 5.23 (dddd, *J* = 1.4, 1.4, 1.4, 10.5 Hz, 1H), 4.60 (dddd, *J* = 1.4, 1.4, 1.4, 5.7 Hz, 2H), 2.57-2.36 (m, 2H), 2.31-2.19 (m, 1H), 2.08-1.86 (m, 4H), 1.64 (dddd, *J* = 7.5, 7.5, 7.5, 21 Hz, 1H), 0.89 (dd, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.6, 170.6, 131.5, 118.1, 65.5, 60.7, 37.9, 32.0, 26.6, 19.4, 9.0; IR (Neat Film NaCl) 3085, 2971, 1752, 1726, 1225, 1142 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{16}O_3$ [M]$^+$: 196.1100, found 196.1099.



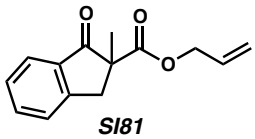
SI79

Allyl 1-isopropyl-2-oxocyclopentanecarboxylate (SI79, Table 17, entry 2): Prepared by general procedure 10 part B from allyl 2-cyclopentanonecarboxylate[42] and using 2-iodopropane as the electrophile. Flash chromatography (3 x 25 cm SiO_2, 10%→30% Et_2O in hexane) afforded the title compound as a colorless oil (1.5521 g, 82% yield). R_f = 0.32 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (dddd, *J* = 5.7, 5.7, 10.5, 17.1 Hz, 1H), 5.30 (dddd, *J* = 1.6, 1.6, 1.6, 17.4 Hz, 1H), 5.22 (dddd, *J* = 1.4, 1.4, 1.4, 10.5 Hz, 1H), 4.59 (dddd, *J* = 1.4, 1.4, 1.4, 5.7 Hz, 2H), 2.59 (qq, *J* = 6.9, 6.9 Hz, 1H), 2.51-2.34 (m, 2H), 2.19-2.06 (m, 1H), 1.99-1.83 (m, 3H), 0.87 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.4, 169.8, 131.5, 118.3, 65.6, 65.3, 38.9, 31.9, 27.2, 19.5, 18.3, 17.6; IR (Neat Film NaCl) 3085, 2967, 1752, 1723, 1228, 1130 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O_3$ [M]$^+$: 210.1256, found 210.1255.



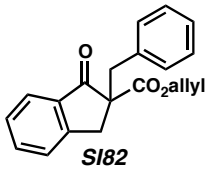
SI80

Allyl 1-((1,3-dioxoisoindolin-2-yl)methyl)-2-oxocyclopentanecarboxylate (SI80, Table 17, entry 3): Prepared by general procedure 10 part B from allyl 2-cyclopentanonecarboxylate[42] and using (*N*-chloromethyl)phthalimide as the electrophile. Purified by flash chromatography (SiO_2, 20→30% EtOAc in hexanes). 54% yield. mp 56-57 °C; R_f = 0.27 (30% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.73 (dd, *J* = 5.6, 3.2 Hz, 2H), 5.92 (dddd, *J* = 17.0, 10.6, 5.9, 5.9 Hz, 1H), 5.32 (app. ddd, *J* = 17.0, 2.9, 1.6 Hz, 1H), 5.23 (app. ddd, *J* = 10.6, 2.7, 1.3 Hz, 1H), 4.65 (app. ddt, *J* = 5.9, 4.5, 1.3 Hz, 2H), 4.34 (d, *J* = 14.4 Hz, 1H), 3.99 (d, *J* = 14.4 Hz, 1H), 2.59-2.47 (m, 1H), 2.46-2.25 (comp. m, 2H), 2.11-1.84 (comp. m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.0, 169.0, 168.3, 134.3, 131.9, 131.6, 123.7, 118.8, 66.8, 60.5, 41.0, 37.7, 32.1, 19.5; IR (Neat Film NaCl) 2953, 1774, 1752, 1718, 1467, 1457, 1428, 1395, 1359, 1256, 1231, 1170, 991, 722 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{18}H_{17}O_5N$ [M]$^+$: 327.1107, found 327.1106.



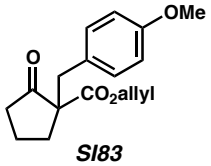
SI81

Allyl 2-methyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (SI81, Table 17, entry 4): Prepared by general procedure 10 from 1-indanone and using methyl iodide as the electrophile. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 30% yield. R_f = 0.55 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.7 Hz, 1H), 7.63 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.41 (dd, *J* = 7.6, 7.3 Hz, 1H), 5.83 (dddd, *J* = 17.2, 10.6, 5.6, 5.6 Hz, 1H), 5.21 (dddd, *J* = 17.2, 2.7, 1.6, 1.1 Hz, 1H), 5.16 (dddd, *J* = 10.5, 2.4, 1.3, 1.3 Hz, 1H), 4.58 (ddd, *J* = 5.6, 2.7, 1.1 Hz, 1H), 4.58 (ddd, *J* = 5.6, 2.7, 1.1 Hz, 1H), 3.73 (d, *J* = 17.1 Hz, 1H), 3.01 (d, *J* = 17.1 Hz, 1H), 1.54 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.5, 171.8, 152.7, 135.5, 134.9, 131.7, 128.0, 126.6, 125.2, 118.3, 66.0, 56.2, 40.2, 21.2; IR (Neat Film NaCl) 3080, 2982, 2935, 1745, 1715, 1608, 1495, 1282, 1184, 967, 747 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{14}O_3$ [M]$^+$: 230.0943, found 230.0936.



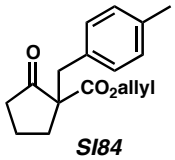
SI82

Allyl 2-benzyl-1-oxo-2,3-dihydro-1*H*-indene-2-carboxylate (SI82, Table 17, entry 5): Prepared by general procedure 10 from 1-indanone and using benzyl bromide as the electrophile. Purified by flash chromatography (SiO_2, 20% Et_2O in pentane). 78% yield. mp 49-50 °C; R_f = 0.18 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 1H), 7.53 (dd, *J* = 8.0, 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.33 (dd, *J* = 7.7, 7.7 Hz, 1H), 7.23-7.06 (comp. m, 5H), 5.84 (dddd, *J* = 17.3, 10.4, 5.6, 5.3 Hz, 1H), 5.22 (app. ddd, *J* = 17.3,, 2.9, 1.6 Hz, 1H), 5.18 (dddd, *J* = 10.4, 2.4, 1.3, 1.1 Hz, 1H), 4.65-4.57 (m, 2H), 3.63 (d, *J* = 17.6 Hz, 1H), 3.50 (d, *J* = 13.8 Hz, 1H), 3.31 (d, *J* = 14.1 Hz, 1H), 3.18 (d, *J* = 17.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.2, 170.6, 153.3, 136.4, 135.5, 135.3, 131.6, 130.2, 128.4, 127.8, 127.0, 126.4, 124.8, 118.5, 66.3, 61.9, 39.8, 35.5; IR (Neat Film NaCl) 3031, 2929, 1744, 1711, 1606, 1589, 1496, 1464, 1454, 1432, 1277, 1244, 1210, 1178, 1051, 1028, 930, 752, 703 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{20}H_{18}O_3$ [M]$^+$: 306.1256, found 306.1259.



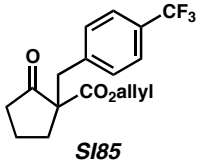
SI83

Allyl 1-(4-methoxybenzyl)-2-oxocyclopentanecarboxylate (SI83, Table 17, entry 6): Prepared by general procedure 10 part B from allyl 2-cyclopentanonecarboxylate[42] and using 4-methoxybenzyl chloride as the electrophile. Flash chromatography (3 x 25 cm SiO_2, 10:1 hexanes:EtOAc) afforded the title compound as a colorless oil (2.5584 g, 95% yield). R_f = 0.17 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.87 (dddd, *J* = 5.7, 5.7, 10.8, 17.1 Hz, 1H), 5.31 (dddd, *J* = 1.5, 1.5, 1.5, 17.1 Hz, 1H), 5.24 (dddd, *J* = 1.2, 1.2, 1.2, 10.5 Hz, 1H), 4.61 (dddd, *J* = 1.4, 1.4, 1.4, 5.7 Hz, 2H), 3.77 (s, 3H), 3.15 (d, *J* = 13.8 Hz, 1H), 3.09 (d, *J* = 13.8 Hz, 1H), 2.45-2.31 (m, 2H), 2.08-1.81 (m, 3H), 1.67-1.53 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 170.5, 158.3, 131.5, 131.0, 128.2, 118.3, 113.6, 65.8, 61.4, 55.0, 38.3, 38.0, 31.5, 19.3; IR (Neat Film NaCl) 2958, 1751, 1726, 1611, 1513, 1249 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{20}O_4$ [M]$^+$: 288.1362, found 288.1369.



SI84

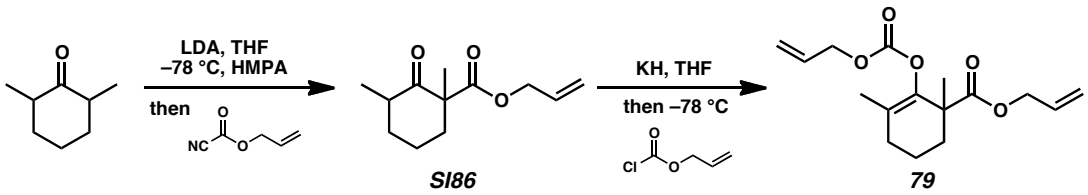
Allyl 1-(4-methylbenzyl)-2-oxocyclopentanecarboxylate (SI84, Table 17, entry 7): Prepared by general procedure 10 part B from allyl 2-cyclopentanonecarboxylate[42] and using 4-methylbenzyl bromide as the electrophile. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 89% yield. R_f = 0.20 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 5.89 (dddd, *J* = 17.3, 10.5, 5.5, 5.5 Hz, 1H), 5.31 (app. ddd, *J* = 17.3, 3.0, 1.7 Hz, 1H), 5.24 (app. ddd, *J* = 10.5, 2.4, 1.1 Hz, 1H), 4.61 (app. ddd, *J* = 6.9, 2.8, 1.4 Hz, 1H), 4.61 (app. ddd, *J* = 6.9, 2.8, 1.4 Hz, 1H), 3.17 (d, *J* = 13.8 Hz, 1H), 3.10 (d, *J* = 13.8 Hz, 1H), 2.52-2.32 (m, 2H), 2.30 (s, 3H), 2.12-1.81 (comp. m, 3H), 1.68-1.52 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.1, 170.9, 136.6, 133.5, 131.7, 130.2, 129.2, 118.7, 66.1, 61.6, 38.7, 38.6, 31.8, 21.2, 19.6; IR (Neat Film NaCl) 2963, 2925, 1752, 1724, 1652, 1515, 1456, 1404, 1264, 1220, 1184, 1158, 1141, 1116, 992, 924, 813 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{20}O_3$ [M]$^+$: 272.1412, found 272.1412.



SI85

Allyl 2-oxo-1-(4-(trifluoromethyl)benzyl)cyclopentanecarboxylate (SI85, Table 17, entry 8): Prepared by general procedure 10 part B from allyl 2-cyclopentanonecarboxylate[42] and using 4-(trifluoromethyl)benzyl bromide as the electrophile. Purified by flash chromatography (SiO_2, 10:1 hexanes:EtOAc) to afford the title compound as a colorless oil (1.9312 g, 65% yield). R_f = 0.24 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 5.87 (dddd, *J* = 6.0, 6.0, 10.5, 17.4 Hz, 1H), 5.30 (dddd, *J* = 1.7, 1.7, 1.7, 17.4 Hz, 1H), 5.25 (dddd, *J* = 1.1, 1.1, 1.1, 10.5 Hz, 1H), 4.61 (bd, *J* = 6 Hz, 2H), 3.29 (d, *J* = 13.5 Hz, 1H), 3.15 (d, *J* = 13.5 Hz, 1H), 2.50-2.33 (m, 2H), 2.13-1.86 (m, 3H), 1.73-1.62 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.1, 170.3, 140.7, 131.3, 130.6, 142.0, 133.1, 130.6, 129.2 (q, $J_{C\text{-}F}$ = 32.2 Hz), 125.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.1 (q, $J_{C\text{-}F}$ = 271.5 Hz), 118.8, 66.2, 61.3, 38.6, 38.1, 31,8, 19.4; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.54; IR (Neat Film NaCl) 3080, 2966, 1754, 1728, 1619, 1326, 1164, 1116, 1068 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{17}O_3F_3$ [M]$^+$: 326.1130, found 326.1129.

Synthesis of Double-Alkylation Substrates

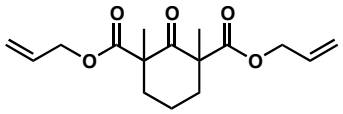


SI86 ***79***

Allyl 1,3-dimethyl-2-oxocyclohexanecarboxylate (SI86): To a cooled (–78 °C) solution of LDA (8.0 mmol, 1.09 equiv) in THF (24 mL) was added 2,6-dimethylcyclohexanone (1 mL, 7.33 mmol, 1.0 equiv) dropwise. The resulting solution was warmed to 0 °C for 1 h, cooled to –78 °C and HMPA (1.3 mL, 7.47 mmol, 1.02 equiv) was added. After 15 min, allyl cyanoformate[4] (845.3 mg, 7.61 mmol, 1.04 equiv) was added dropwise. The reaction was warmed to ambient temperature for 30 min and then quenched with 50% saturated aq NH_4Cl. The aq layer was separated and extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4), filtered, and concentrated *in vacuo*. The resulting oil was purified by flash chromatography (3 x 20 cm, SiO_2, 4% Et_2O in hexanes, then 8% Et_2O in hexanes) to afford β-ketoester **SI86** as a colorless oil (629.1 mg, 41%), along with the corresponding enol carbonate as a colorless oil (187.1 mg, 12%); R_f = 0.43 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (dddd, *J* = 6.0, 6.0, 10.5, 17.4 Hz, 1H), 5.28 (dddd, *J* = 1.5, 1.5, 1.5, 17.1 Hz, 1H), 5.22 (dddd, *J* = 1.2, 1.2, 1.2, 10.5 Hz, 1H), 4.63 (dddd, *J* = 1.2, 1.2, 5.4, 13.2 Hz, 1H), 4.56 (dddd, *J* = 1.5, 1.5, 5.7, 13.2 Hz, 1H), 2.61-2.46 (m, 2H), 2.01 (dddd, *J* = 3.2, 3.2, 6.3, 16.2 Hz, 1H), 1.85-1.63 (m, 2H), 1.45-1.31 (m, 2H), 1.28 (s, 3H), 1.03 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.1, 172.9, 131.5, 118.7, 65.6, 57.1, 44.3, 38.9, 36.7, 22.8, 21.5, 14.7; IR (Neat Film NaCl) 3087, 2936, 1743, 1715, 1649, 1452, 1377, 1253, 1214, 1161, 976 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O_3$ [M]$^+$: 210.1256, found 210.1249.

Allyl 2-(allyloxycarbonyloxy)-1,3-dimethylcyclohex-2-enecarboxylate (79, Scheme 11a): To a suspension of KH (155.9 mg, 3.89 mmol, 1.2 equiv, from a ~30% dispersion in mineral oil, oil removed by washing with hexane) in 10 mL THF was added **SI86** (680.9 mg, 3.24 mmol, 1 equiv) dropwise. The mixture was stirred at room temperature for 2.5 h, at which time it was cooled to –78 °C. Allyl chloroformate (420 μL, 3.95 mmol, 1.2 equiv) was added and the mixture stirred 30 min at –78 °C, then 30 min at room temperature. The reaction was quenched with 50% saturated aq NH_4Cl (10 mL). Et_2O (5 mL) was added and the organic layer separated. The aqueous layer was extracted with Et_2O (3 x 10 mL). The combined organic layers were dried (Na_2SO_4) and evaporated *in vacuo*. Silica gel chromatography (2 x 16 cm, 20:1 hexanes:EtOAc) afforded the title compound **79** as a colorless oil (883

mg, 93% yield). R_f = 0.29 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.94 (dddd, *J* = 5.7, 5.7, 10.2, 17.1 Hz, 1H), 5.90 (dddd, *J* = 5.7, 5.7, 10.5, 17.1 Hz, 1H), 5.37 (dddd, *J* = 1.2, 1.2, 1.2, 17.1 Hz, 1H), 5.31 (dddd, *J* = 1.2, 1.2, 1.2, 17.1 Hz, 1H), 5.27 (dddd, *J* = 1.2, 1.2, 1.2, 10.2 Hz, 1H), 5.20 (dddd, *J* = 1.5, 1.5, 1.5, 10.5 Hz, 1H), 4.66-4.58 (m. 3H), 4.55 (dddd, *J* = 1.2, 1.2, 5.4, 13.5 Hz, 1H), 2.25-2.10 (m, 3H), 1.80-1.52 (m, 3H), 1.58 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 152.9, 142.0, 132.2, 131.5, 124.7, 118.9, 117.7, 68.7, 65.5, 46.7, 35.8, 30.6, 22.4, 19.2, 17.0; IR (Neat Film NaCl) 3087, 2942, 1760, 1732, 1649, 1452, 1366, 1235, 1168, 992 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{22}O_5$ [M]$^+$: 294.1467, found 294.1464.



81

Bis(ester) 81 (Scheme 11b): Prepared by general procedure 10 using (±)-**10**. Purified by flash chromatography on SiO_2 using 2% EtOAc in hexanes as eluent. The relative stereochemistries of the diastereomers have not been established.

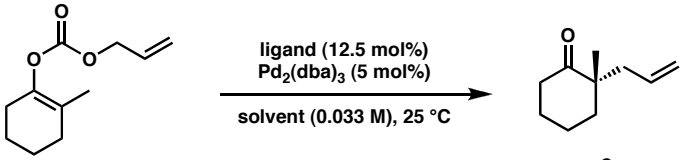
First diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.88 (dddd, *J* = 5.7, 5.7, 10.4, 17.0 Hz, 2H), 5.30 (dddd, *J* = 1.4, 1.4, 3.1, 17.0 Hz, 2H), 5.23 (dddd, *J* = 1.4, 1.4, 2.7, 10.4 Hz, 2H), 4.65 (dddd, *J* = 1.4, 1.4, 5.6, 13.4 Hz, 2H), 4.44 (dddd, *J* = 1.4, 1.4, 5.6, 13.4 Hz, 2H), 2.55-2.50 (m, 2H), 2.23 (dtt, *J* = 4.1, 12.3, 14.5 Hz, 1H), 1.67 (dtt, *J* = 4.4, 4.4, 14.5 Hz, 1H), 1.54–1.47 (m, 2H), 1.39 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.9, 171.7, 131.9, 118.4, 66.1, 57.1, 37.3, 23.6, 19.6; IR (Neat Film NaCl) 3086, 2937, 1726, 1710, 1648, 1456, 1378, 1240, 1183, 1149, 975 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{22}O_5$ [M + H]$^+$: 295.1540, found 295.1538.

Second diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90 (dddd, *J* = 6.1, 6.1, 10.4, 17.1 Hz, 2H), 5.32 (dddd, *J* = 1.6, 1.6, 1.6, 17.1 Hz, 2H), 5.24 (dddd, *J* = 1.3, 1.3, 1.3, 10.4 Hz, 2H), 4.63-4.60 (comp. m, 4H), 2.44 (ddd, *J* = 6.0, 6.0, 13.0 Hz, 2H), 1.82 (dtt, *J* = 6.8, 6.8, 0.5 Hz, 2H), 1.85–1.80 (m, 2 H), 1.73–1.67 (m, 2H), 1.36 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 172.4, 131.7, 118.9, 66.1, 56.9, 35.3, 22.3, 17.9; IR (Neat Film NaCl) 2984, 2940, 2877, 1734, 1709, 1647, 1458, 1378, 1234, 1150, 1119, 9780 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{22}O_5$ [M + H]$^+$: 295.1540, found 295.1535.

Enantioselective Allylic Alkylation Methods

General Procedures for Asymmetric Tsuji Allylation.

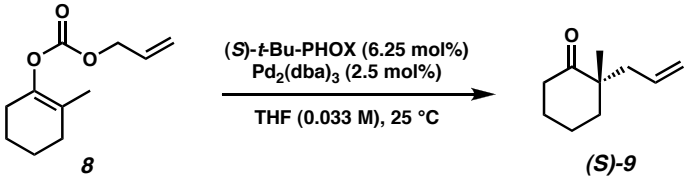
General Procedure 12: 0.1 mmol Optimization Reactions of Allyl Enol Carbonates



8 ***9***

A 1 dram vial equipped with a magnetic stir bar was flame dried under vacuum. After cooling under dry argon, $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol, 0.05 equiv) and ligand (0.0125 mmol, 0.125 equiv) were added. After the vial was flushed with argon, solvent (3.0 mL) was added, and the contents were stirred at 25 °C for 30 min, at which time tridecane (12.25 μL) and allyl enol carbonate **8** (19.6 mg, 0.1 mmol, 1.0 equiv) were added by syringe. When the reaction was complete by TLC, the reaction mixture was diluted with hexanes (5 mL), filtered through a small plug of silica gel and analyzed by GC. GC yield determined on DB-WAX column (70 °C initial temp, 5 °C/min ramp to 180 °C), tridecane ret. time = 7.000 min, ketone **9** ret. time = 12.309 min.

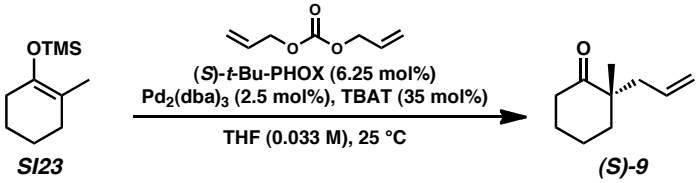
General Procedure 13: 1.0 mmol Preparative Reactions of Allyl Enol Carbonates



8 *(S)-9*

A 50 mL round-bottom flask equipped with a magnetic stir bar was flame dried under vacuum. After cooling under dry argon, $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 0.025 equiv) and (*S*)-*t*-Bu-PHOX (24.2 mg, 0.0625 mmol, 0.0625 equiv) were added. After the flask was flushed with argon, THF (30 mL) was added, and the contents were stirred at 25 °C for 30 min, at which time allyl enol carbonate **8** (196.2 mg, 1.0 mmol, 1.0 equiv) was added by syringe in one portion. When the reaction was complete by TLC (2 h), the reaction mixture was evaporated under reduced pressure and the residue chromatographed (2→3% Et_2O in pentane on SiO_2) to afford (*S*)-2-allyl-2-methylcyclohexanone ((*S*)-**9**) (129.6 mg, 85.1% yield, 87% ee) as a colorless oil; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.75–5.61 (m, 1H), 5.05 (s, 1H), 5.01 (m, 1H), 2.40–2.31 (comp. m, 3H), 2.21 (dd, *J* = 13.8, 7.5 Hz, 1H), 1.78 (comp. m, 5H), 1.56 (m, 1H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.4, 133.7, 117.9, 48.4, 41.9, 38.8, 38.5, 27.4, 22.6, 21.0; IR (Neat Film NaCl) 2934, 2865, 1707, 1451, 912 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{16}O$ $[M]^+$: 152.1201, found 152.1204; $[\alpha]_D^{21}$ –49.64 (*c* 2.38, hexane, 98% ee).

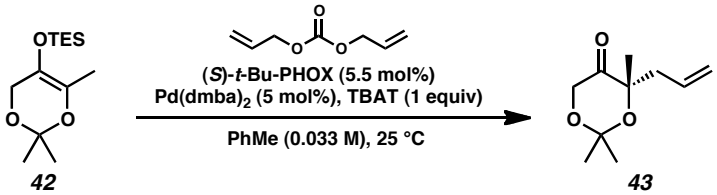
General Procedure 14: 1.0 mmol Preparative Reactions of Cycloalkanone Silyl Enol Ethers



SI23 *(S)-9*

A 50 mL round-bottom flask equipped with a magnetic stir bar was flame dried under vacuum. After cooling under dry argon, $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 0.025 equiv), (*S*)-*t*-Bu-PHOX (24.2 mg, 0.0625 mmol, 0.0625 equiv), and TBAT (189 mg, 0.35 mmol, 0.35 equiv) were added. After the flask was flushed with argon, THF (30 mL) was added, and the contents were stirred at 25 °C for 30 min, at which time diallyl carbonate (150.6 μL, 1.05 mmol, 1.05 equiv) and **SI23** (184.35 mg, 1.0 mmol, 1.0 equiv) were added sequentially by syringe in single portions. When the reaction was complete by TLC (2 h), the reaction mixture was evaporated under reduced pressure and the residue chromatographed (2→3% Et_2O in pentane on SiO_2) to afford ketone (*S*)-**9** (144.3 mg, 94.8% yield, 87% ee).

General Procedure 15: 0.5 mmol Preparative Reactions of Dioxanone TES Enol Ethers

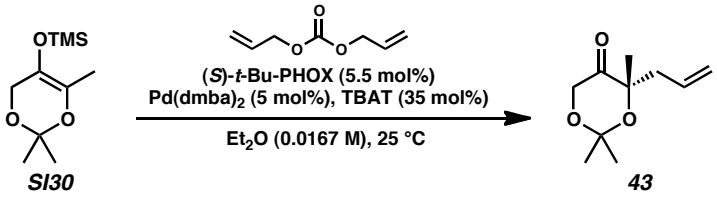


42 *43*

A 100 mL round-bottom flask equipped with a magnetic stir bar was flame dried under vacuum and back-filled with argon. After cooling, $Pd(dmdba)_2$ (20.3 mg, 0.025 mmol, 0.05 equiv), (*S*)-*t*-Bu-PHOX (10.6 mg, 0.027 mmol, 0.055 equiv), and TBAT (270 mg, 0.50 mmol, 1.0 equiv) were added to the flask. The system was evacuated under vacuum and back-filled with argon (3 x). Toluene (15 mL, 0.033 M) was added by syringe and the mixture was stirred at room temperature (ca. 25 °C) for 30 min. Diallyl carbonate (75.2 μL, 0.52 mmol, 1.05 equiv) and silyl ether **42** (108 mg, 0.50 mmol, 1.0 equiv) were added. When the reaction was complete by TLC (ca. 9 h), the reaction mixture was loaded onto a silica gel column and eluted with 2% Et_2O in petroleum ether to give tetrasubstituted **43** (78.8 mg, 86% yield, 87% ee). Colorless oil; R_f 0.22 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90–5.76 (m, 1H), 5.13–5.04 (m, 2H), 4.21 (s, 2H), 2.57–2.50 (m, 1H), 2.45–2.37 (m, 1H), 1.49 (s, 3H), 1.48 (s,

3H), 1.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.9, 132.6, 119.0, 100.1, 82.2, 67.1, 43.6, 26.9, 26.7, 24.4; IR (Neat Film NaCl) 3079, 2989, 2942, 1742, 1641, 1429, 1382, 1373, 1229, 1203, 1180, 1161, 1143, 1080, 1007, 919 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{10}H_{18}O_3$ [M]$^+$: 184.1100, found 184.1096; $[\alpha]_D^{23.0}$ –68.6 (*c* 0.510, CH_2Cl_2, 90% ee); $[\alpha]_D^{27.5}$ –60.3° (*c* 0.845, CH_2Cl_2, 87% ee).

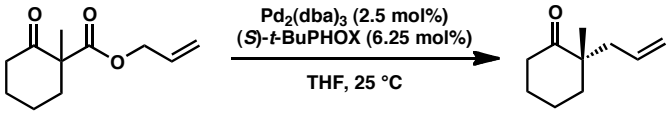
General Procedure 16: 0.5 mmol Preparative Reactions of Dioxanone TMS Enol Ethers



SI30 *43*

A 100 mL round-bottom flask was flame dried under vacuum and back-filled with argon. After cooling, Pd(dmdba)$_2$ (20.3 mg, 0.025 mmol, 0.05 equiv), (*S*)-*t*-Bu-PHOX (10.6 mg, 0.027 mmol, 0.055 equiv), and TBAT (94.3 mg, 0.18 mmol, 0.35 equiv) were added to the flask. The system was evacuated under vacuum and back-filled with argon (x 3). Diethyl ether (30 mL) was added by syringe, and the mixture was stirred at room temperature (ca. 28 °C) for 30 min. Diallyl carbonate (75.2 μL, 0.52 mmol, 1.05 equiv) and silyl ether **SI30** (108 mg, 0.50 mmol, 1.0 equiv) were added. When the reaction was complete by TLC (ca. 5 h), the reaction mixture was filtered through silica gel, and eluted with Et_2O. The filtrate was evaporated under reduced pressure (~60 mmHg), and the residue was purified by flash chromatography (2% Et_2O in petroleum ether on silica gel) to give tetrasubstituted **43** (76.2 mg, 83% yield, 90% ee).

General Procedure 17: 1.0 mmol Preparative Reactions of Allyl β-Ketoesters (Table 12; Table 13, entries 1 and 2)



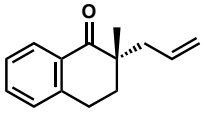
(±)-10 *(S)-9*

A 100 mL rb flask was equipped with a magnetic stir bar and flame dried under vacuum. After cooling under dry nitrogen, $Pd_2(dba)_3$ (22.9 mg, 0.025 mmol, 0.025 equiv) and (*S*)-*t*-Bu-PHOX (**19**, 24.2 mg, 0.0625 mmol, 0.0625 equiv) were added. The flask containing the solids was evacuated for 15 min and then refilled with dry nitrogen. Dry THF (30 mL) was then added and the resulting solution stirred at 25 ºC for 30 min. At this point, allyl 1-methyl-2-oxocyclohexanecarboxylate ((±)-**10**) was added via syringe in one portion. When the reaction was complete by TLC (7.5 h), the reaction mixture was evaporated under reduced pressure and the residue purified by column chromatography (SiO_2, 1.5 → 2.5% Et_2O in pentane) to afford ketone (*S*)-**9** (129.6 mg, 85% yield, 88% ee).

A procedure for alkylation with dioxanone β-ketoester is found below.

In all cases, the products produced by any of the three methods (general procedures 12–17) using (*S*)-*t*-Bu-PHOX ((*S*)-**19)** as ligand provided the same major product enantiomer. Absolute configuration is noted for product compounds where the configuration has been established (crystallographically or by comparison with literature data, see below). All other configurations shown are inferred by analogy.

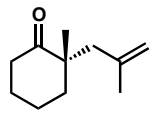
Characterization Data for Ketones Prepared by Enantioselective Alkylation:



(S)-3

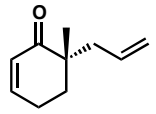
(*S*)-2-Allyl-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (3, Table 7, Entry 12; Table 13, Entry 6): Reaction time: from allyl enol carbonate, 2 h, 10 °C; from β-ketoester, 10 h, performed in Et_2O. ^{1}H

NMR (300 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.45 (dt, *J* = 7.7, 1.5 Hz, 1H), 7.29 (app. t, *J* = 7.2 Hz, 1H), 7.21 (app. d, *J* = 7.5 Hz, 1H), 5.85–5.71 (m, 1H), 5.10 (s, 1H), 5.05 (s, 1H), 2.97 (t, *J* = 6.3 Hz, 2H), 2.46 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.27 (ddt, *J* = 14.0, 7.5, 1.2 Hz, 1H), 2.07 (ddd, *J* = 13.4, 7.2, 6.0 Hz 1H), 1.89 (ddd, *J* = 14.0, 6.9, 5.7 1H), 1.18 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 202.0, 143.2, 133.9, 133.0, 131.5, 128.6, 127.9, 126.5, 118.1, 44.5, 41.0, 33.2, 25.3, 21.8; IR (Neat Film NaCl) 3073, 2930, 1682, 1455, 1220, 916, 742 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{16}O$ $[M]^+$: 200.1201, found 200.1194; $[\alpha]_D^{27}$ –18.59 (*c* 2.08, hexane, 88% ee).



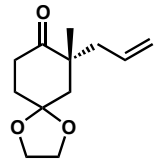
SI87

2-Methyl-2-(2-methylallyl)cyclohexanone (SI87, Table 7, Entry 4; Table 8, Entry 4; Table 13, Entry 9): Reaction time: from allyl enol carbonate, 8 h, performed with 5 mol% $Pd_2(dba)_3$, 12.5 mol% (*S*)-**19**; from silyl enol ether, 4 h, performed with dimethallyl carbonate; from β-ketoester, 6.5 h performed with 5 mol% $Pd_2(dba)_3$, 12.5 mol% (*S*)-**19**, in Et_2O at 35 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.81 (s, 1H), 4.64 (s, 1H), 2.52 (m, 1H), 2.48 (d, *J* = 13.5 Hz, 1H), 2.36 (app. dt, *J* = 14.7, 6.0 Hz, 1H), 2.25 (d, *J* = 13.8 Hz, 1H), 1.94-1.53 (comp. m, 6H), 1.65 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.8, 142.2, 114.7, 48.7, 45.4, 40.0, 38.9, 27.6, 24.3, 23.3, 21.1; IR (neat) 2927, 1707 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{18}O$ $[M]^+$: 166.1358, found 166.1358; $[\alpha]_D^{27}$ –26.42 (*c* 1.85, hexane, 90% ee).



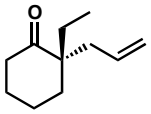
(S)-iii

(*S*)-6-Allyl-6-methylcyclohex-2-enone (iii, Table 7, Entry 5; Table 13, Entry 5): Reaction time: from allyl enol carbonate, 1 h; from β-ketoester, 4 h, performed with 4 mol% $Pd_2(dba)_3$, 10 mol% (*S*)-**19**, in Et_2O. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.87 (app. dt, *J* = 10.2, 4.2 Hz, 1H), 5.91 (app. dt, *J* = 10.2, 2.1 Hz, 1H), 5.72 (m, 1H), 5.07 (m, 1H), 5.02 (d, *J* = 9.3 Hz, 1H), 2.35 (m, 3H), 2.16 (dd, *J* = 13.8, 7.5, Hz, 1H), 1.91 (dt, *J* = 13.8, 6.0 Hz, 1H), 1.74 (dt, *J* = 13.8, 6.0 Hz, 1H), 1.07 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.7, 148.8, 134.0, 128.4, 118.0, 44.4, 40.9, 32.9, 23.1, 21.6; IR (Neat Film NaCl) 2927, 1673 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{14}O$ $[M]^+$: 150.1045, found 150.1039; $[\alpha]_D^{26}$ +14.62 (*c* 1.56, hexane, 89% ee).



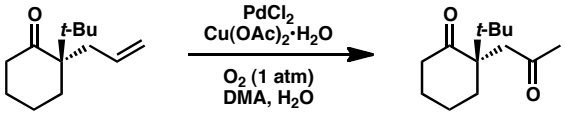
70

7-Allyl-7-methyl-1,4-dioxaspiro[4.5]decan-8-one (70, Table 7, Entry 6; Table 8, Entry 6; Table 13, Entries 1–2; Scheme 10c): Reaction time: from allyl enol carbonate, 1 h; from silyl enol ether, 2 h; from β-ketoester, 1.5 h (1 mmol scale), 24 h (25 mmol scale) with 1.5 mol% $Pd_2(dba)_3$, 3.75 mol% (*S*)-**19**, in Et_2O. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (ddt, *J* = 17.1, 10.5, 7.2 Hz, 1H), 5.07 (br s, 1H), 5.02 (app. d, *J* = 9.3 Hz, 1H), 3.99 (app. d, *J* = 1.5 Hz, 4H), 2.57 (app. t, *J* = 6.3 Hz, 1H), 2.42 (m, 2H), 2.00 (d, *J* = 13.8 Hz, 1H), 1.98 (app. t, *J* = 7.2 Hz, 1H), 1.75 (d, *J* = 14.1 Hz, 1H), 1.12 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.9, 133.7, 118.4, 107.6, 64.4, 64.3, 47.5, 44.3, 42.7, 35.7, 34.5, 23.9; IR (Neat Film NaCl) 2964, 1710, 1116 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O_3$ $[M]^+$: 210.1256, found 210.1255; $[\alpha]_D^{29}$ –7.99 (*c* 2.41, hexane, 86% ee).



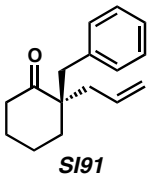
SI88

(*S*)-2-allyl-2-ethylcyclohexanone (SI88, Table 7, Entry 7; Table 8, Entry 2): Reaction time: from allyl enol carbonate, 2 h; from silyl enol ether, 3 h. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (m, 1H), 5.02 (m, 2H), 2.47-2.18 (m, 4H), 1.90-1.60 (m, 7H), 1.46 (ddd, *J* = 21.6, 15.0, 7.2 Hz, 1H), 0.75 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.0, 134.2, 117.6, 51.6, 39.2, 38.5, 36.0, 27.2, 27.1, 20.7, 7.8; IR (Neat Film NaCl) 2937, 1703 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{18}O$ [M]$^{+}$: 166.1358, found 166.1362; $[\alpha]_D^{28}$ +28.58 (*c* 1.51, hexane, 92% ee).



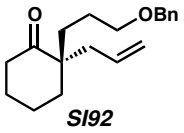
SI89 ***SI90***

2-*tert*-Butyl-2-(2-oxopropyl)cyclohexanone (SI90, Table 7, Entry 8): Allylation reaction time: from allyl enol carbonate, 10 h. Isolated yield determined by Wacker oxidation (vide infra) of ketone **SI89** and isolation of **SI90**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.29 (d, *J* = 18.0 Hz, 1H), 2.58 (app. dt, *J* = 16.2, 4.8 Hz, 1H), 2.34 (d, *J* = 17.7 Hz, 1H), 2.23 (dd, *J* = 11.1, 6.0 Hz, 1H), 2.18-2.00 (m, 2H), 2.07 (s, 3H), 1.92-1.60 (comp. m, 4H), 0.94 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 207.6, 53.0, 51.3, 43.2, 36.6, 31.6, 30.5, 27.7, 24.0, 23.9; IR (Neat Film NaCl) 2955, 1716, 1692, 1372, 1171 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{22}O_2$ [M]$^{+}$: 210.1620, found 210.1615; $[\alpha]_D^{28}$ +132.01 (*c* 1.38, hexane, 81% ee).



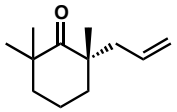
SI91

2-Allyl-2-benzylcyclohexanone (SI91, Table 7, Entry 9; Table 12, Entry 6; Figure 2): Reaction time: from allyl enol carbonate, 2 h; from β-ketoester, 0.5 h. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (comp. m, 3H), 7.12 (comp. m, 2H), 5.74 (ddt, *J* = 17.2, 10.1, 7.2 Hz, 1H), 5.12-5.03 (m, 2H), 2.91 (s, 2H), 2.46 (m, 2H), 2.28 (d, *J* = 7.2 Hz, 2H), 1.86-1.65 (comp. m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.1, 137.5, 133.7, 130.6, 127.9, 126.3, 118.2, 52.5, 40.8, 39.6, 39.2, 35.5, 26.8, 20.8; IR (Neat Film NaCl) 2937, 1704, 1638, 1602 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{20}O$ [M]$^{+}$: 228.1514, found 228.1514; $[\alpha]_D^{28}$ –12.34 (*c* 2.07, hexane, 85% ee).



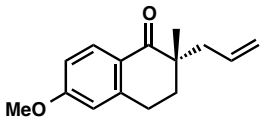
SI92

2-Allyl-2-(3-(benzyloxy)propyl)cyclohexanone (SI92, Table 7, Entry 10): Reaction time: from allyl enol carbonate, 2 h. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.26 (comp. m, 5H), 5.68 (m, 1H), 5.06 (s, 1H), 5.01 (m, 1H), 4.84 (s, 2H), 3.44 (app. t, *J* = 6.3 Hz, 2H), 2.32 (comp. m, 4H), 1.88-1.24 (comp. m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.8, 138.5, 133.9, 128.3, 127.5, 127.5, 117.8, 72.8, 70.5, 51.2, 39.2, 39.0, 36.4, 31.2, 27.1, 23.8, 20.7; IR (Neat Film NaCl) 2926, 1703, 1102 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{19}H_{27}O_2$ [M + H]$^{+}$: 287.2011, found 287.2001; $[\alpha]_D^{27}$ +24.19 (*c* 2.73, hexane, 88% ee).



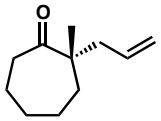
(S)-64

(*S*)-2-Allyl-2,6,6-trimethylcyclohexanone (64, Table 7, Entry 11; Table 13, Entry 3; Scheme 10a): Reaction time: from allyl enol carbonate, 1 h; from β-ketoester, 9 h, performed at 30 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63 (m, 1H), 5.01 (m, 2H), 2.33 (dd, *J* = 13.8, 6.9 Hz, 1H), 2.18 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.82-1.53 (comp. m, 6H), 1.11 (s, 3H), 1.09 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 219.8, 134.6, 117.9, 47.6, 44.4, 43.9, 39.7, 36.8, 27.8, 27.2, 25.5, 17.7; IR (Neat Film NaCl) 2933, 1697, 1463 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{20}O$ $[M]^+$: 180.1514, found 180.1521; $[\alpha]_D^{27}$ –35.69 (*c* 2.15, hexane, 92% ee).



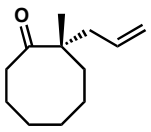
SI93

2-Allyl-6-methoxy-2-methyl-3,4-dihydronaphthalen-1(2*H*)-one (SI93, Table 7, Entry 13): Reaction time: from allyl enol carbonate, 8 h, 10 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.7 Hz, 1H), 6.82 (dd, *J* = 8.7, 2.4 Hz, 1H), 6.66 (d, *J* = 2.4 Hz, 1H), 5.78 (m, 1H), 5.09 (s, 1H), 5.04 (m, 1H), 3.84 (s, 3H), 3.93 (app. t, *J* = 6 Hz, 2H), 2.45 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.25 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.05 (m, 1H), 1.87 (m, 1H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 200.9, 163.3, 145.7, 134.1, 130.4, 125.1, 118.0, 113.2, 112.2, 55.4, 44.3, 41.3, 33.4, 25.7, 22.0; IR (Neat Film NaCl) 2931, 1672, 1601, 1256 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{18}O_2$ $[M]^+$: 230.1307, found 230.1313; $[\alpha]_D^{26}$ –13.71 (*c* 1.5, hexane, 89% ee).



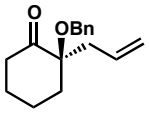
SI94

2-Allyl-2-methylcycloheptanone (SI94, Table 7, Entry 14; Table 8, Entry 7; Table 13, Entry 7): Reaction time: from allyl enol carbonate, 6 h; from silyl enol ether, 2 h; from β-ketoester, 9.5 h. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (ddt, *J* = 16.8, 10.2, 7.5, 1H), 5.02 (m, 2H), 2.59 (app. dt, *J* = 11.1, 2.7 Hz, 1H), 2.42 (app. t, *J* = 9.0 Hz, 1H), 2.24 (dd, *J* = 13.8, 7.5 Hz, 1H), 2.16 (dd, *J* = 13.8, 7.8 Hz, 1H), 1.78-1.30 (comp. m, 8H), 1.03 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.4, 133.8, 117.9, 50.8, 43.6, 40.6, 36.6, 30.6, 26.4, 24.4, 22.3; IR (Neat Film NaCl) 2930, 1702, 1458 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{18}O$ $[M]^+$: 166.1358, found 166.1360; $[\alpha]_D^{28}$ –34.70 (*c* 1.52, hexane, 87% ee).



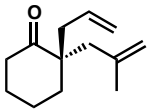
SI95

2-Allyl-2-methylcyclooctanone (SI95, Table 7, Entry 15; Table 8, Entry 8): Reaction time: from allyl enol carbonate, 2 h; from silyl enol ether, 3 h. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (m, 1H), 5.04 (app. d, *J* = 1.2 Hz, 1H), 5.00 (app. d, *J* = 8.1 Hz, 1H), 2.59 (m, 1H), 2.29 (m, 2H), 2.12 (dd, *J* = 14.1, 7.7 Hz, 1H), 2.01 (m, 1H), 1.83-1.70 (comp. m, 3H), 1.61-1.32 (comp. m, 5H), 1.18 (m, 1H), 1.01 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 220.3, 133.9, 117.8, 50.1, 42.0, 36.8, 33.5, 30.4, 25.9, 24.8, 24.3, 19.8; IR (Neat Film NaCl) 2929, 1699 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{20}O$ $[M]^+$: 180.1514, found 180.1508; $[\alpha]_D^{26}$ –21.22 (*c* 1.56, hexane, 79% ee).



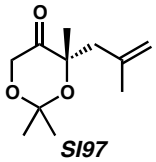
SI96

2-Allyl-2-(benzyloxy)cyclohexanone (SI96, Table 8, Entry 3): Reaction time: from silyl enol ether, 3 h. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.25 (comp. m, 5H), 5.83 (dddd, *J* = 16.5, 10.8, 6.9, 6.9 Hz, 1H), 5.15 (app. ddd, *J* = 16.5, 3.0, 1.5 Hz, 1H), 5.13 (app. d, *J* = 10.8 Hz, 1H), 4.54 (d, *J* = 11.1 Hz, 1H), 4.16 (d, *J* = 11.1 Hz, 1H), 2.85-2.68 (m, 2H), 2.42-2.24 (comp. m, 3H), 2.13-1.95 (comp. m, 2H), 1.76-1.44 (comp. m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.5, 138.2, 132.8, 128.4, 127.5, 127.3, 118.3, 82.1, 65.3, 39.5, 37.8, 36.0, 27.9, 20.6; IR (Neat Film NaCl) 3068, 3032, 2942, 2864, 1715, 1640, 1498, 1454, 1433, 1384, 1311, 1254, 1157, 1121, 1085, 1060, 1028, 997, 970, 915, 735, 696 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{20}O_2$ [M]$^+$: 244.1463, found 244.1455; $[\alpha]_D^{28.3}$ +47.3 (*c* 2.38, hexanes, 59% ee).



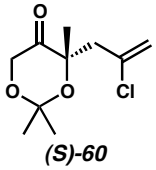
57

2-Allyl-2-(2-methylallyl)cyclohexanone (57, Table 8, Entry 5; Scheme 9b; Scheme 9c): Reaction time: from silyl enol ether, 5 h, performed with dimethallyl carbonate. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.69 (dddd, *J* = 16.5, 10.8, 7.5, 7.2 Hz, 1H), 5.00 (dddd, *J* = 16.5, 2.1, 1.2, 1.2 Hz, 1H), 5.01 (dddd, *J* = 10.2, 2.1, 1.5, 1.5 Hz, 1H), 4.82 (app. ddd, *J* = 2.7, 1.2, 1.2 Hz, 1H), 4.66 (app. ddd, *J* = 3.0, 0.9, 0.9 Hz, 1H), 2.56-2.28 (comp. m, 6H), 1.91-1.66 (comp. m, 6H), 1.64 (app. ddd, *J* = 0.9, 0.9, 0.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 142.1, 134.1, 118.0, 115.0, 51.5, 43.0, 39.9, 39.5, 36.5, 27.1, 24.3, 20.9; IR (Neat Film NaCl) 3075, 2938, 2865, 1704, 1640, 1453, 1376, 1312, 1206, 1124, 1062, 997, 913, 894 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{20}O$ [M]$^+$: 192.1514, found 192.1514; $[\alpha]_D^{29.3}$ +3.9 (*c* 3.52, hexanes, 91% ee).



SI97

2,2,4-Trimethyl-4-(2-methylallyl)-1,3-dioxan-5-one (SI97, Table 10, Entry 2): From TES enol ether: 73% yield, 82% ee; from TMS enol ether: 59% yield, 89% ee. Colorless oil; R_f 0.46 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.88 (s, 1H), 4.72 (s, 1H), 4.27 (d, *J* = 17.9 Hz, 1H), 4.19 (d, *J* = 17.9 Hz, 1H), 2.50 (d, *J* = 13.7 Hz, 1H), 2.39 (d, *J* = 13.7 Hz, 1H), 1.81 (s, 3H), 1.51 (s, 3H), 1.48 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.1, 141.5, 115.4, 100.0, 83.0, 67.3, 46.8, 27.0, 26.6, 25.0, 24.6; IR (Neat Film NaCl) 2987, 2943, 2919, 1742, 1645, 1440, 1382, 1373, 1230, 1200, 1159, 1106, 1010, 896 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{11}H_{18}O_3$ [M]$^+$: 198.1256, found 198.1263; $[\alpha]_D^{26.5}$ – 87.7 (*c* 0.735, CH_2Cl_2, 89% ee).



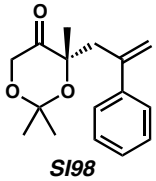
(S)-60

(*S*)-4-(2-Chloroallyl)-2,2,4-trimethyl-1,3-dioxan-5-one (60, Table 10, Entry 3; Table 13, Entry 16; Scheme 9d): From TES enol ether: 59% yield, 92% ee; from TMS enol ether: 28% yield, 91% ee.

A procedure for synthesis from the β-ketoester is found below.

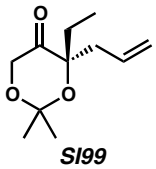
Colorless oil; R_f 0.50 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.30 (d, *J* = 1.2 Hz, 1H), 5.22 (d, *J* = 0.6 Hz, 1H), 4.37 (d, *J* = 17.7 Hz, 1H), 4.21 (d, *J* = 17.9 Hz, 1H), 2.91 (d, *J* = 14.4 Hz, 1H),

2.73 (d, J = 14.4 Hz, 1H), 1.55 (s, 3H), 1.51 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 137.1, 117.0, 100.5, 81.3, 67.1, 48.1, 27.4, 26.2, 25.1; IR (Neat Film NaCl) 2991, 2941, 2897, 1744, 1633, 1425, 1383, 1374, 1229, 1203, 1182, 1158, 1106, 1060, 1011, 891 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{20}O_3$ [M – CH_3]$^+$: 203.0475, found 203.0484; [α]$_D^{20.7}$ –89.7 (*c* 1.030, $CHCl_3$, 93% ee).



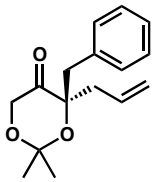
SI98

2,2,4-Trimethyl-4-(2-phenylallyl)-1,3-dioxan-5-one (SI98, Table 10, Entry 4): From TES enol ether: 73% yield, 94% ee. Colorless oil; R_f 0.23 (5% Et_2O in toluene); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40–7.19 (m, 5H), 5.33 (d, J = 1.5 Hz, 1H), 5.13 (s, 1H), 4.08 (d, J = 17.7 Hz, 1H), 3.95 (d, J = 17.7 Hz, 1H), 2.98 (s, 2H), 1.39 (s, 3H), 1.38 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.8, 144.5, 142.3, 128.1, 127.4, 127.0, 117.9, 99.9, 82.7, 67.3, 44.9, 26.5, 25.5; IR (Neat Film NaCl) 2988, 2940, 1742, 1626, 1495, 1444, 1382, 1372, 1229, 1198, 1158, 1117, 1010, 905, 778, 699 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{20}O_3$ [M]$^+$: 260.1412, found 260.1417; [α]$_D^{23.1}$ –45.9 (*c* 0.940, CH_2Cl_2, 94% ee).



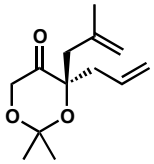
SI99

4-Allyl-4-ethyl-2,2-dimethyl-1,3-dioxan-5-one (SI99, Table 10, Entry 5): From TES enol ether: 79% yield, 93% ee; from TMS enol ether: 79% yield, 93% ee. Colorless oil; R_f 0.48 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89–5.70 (m, 1H), 5.14–5.02 (m, 2H), 4.17 (s, 2H), 2.60–2.39 (m, 2H), 1.91–1.64 (m, 2H), 1.49 (s, 3H), 1.48 (s, 3H), 0.88 (t, J = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.8, 132.6, 118.9, 100.0, 85.2, 67.5, 41.4, 29.9, 27.0, 26.7, 7.7; IR (Neat Film NaCl) 3079, 2984, 2941, 2884, 1737, 1428, 1382, 1372, 1231, 1200, 1172, 1150, 1086, 1009, 918 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{11}H_{18}O_3$ [M]$^+$: 198.1256, found 198.1258; [α]$_D^{24.4}$ –0.20 (*c* 0.575, CH_2Cl_2, 93% ee).



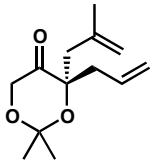
SI100

4-Allyl-4-benzyl-2,2-dimethyl-1,3-dioxan-5-one (SI100, Table 10, Entry 6): From TES enol ether: 85% yield, 86% ee; from TMS enol ether: 84% yield, 85% ee. Colorless oil; R_f 0.44 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29–7.18 (m, 5H), 5.97–5.83 (m, 1H), 5.17–5.10 (m, 2H), 4.05 (d, J = 18.0 Hz, 1H), 3.87 (d, J = 18.0 Hz, 1H), 3.08 (d, J = 13.5 Hz, 1H), 2.93 (d, J = 13.5 Hz, 1H), 2.63-2.45 (m, 2H), 1.50 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 136.2, 132.4, 131.3, 128.0, 126.8, 119.3, 99.9, 85.5, 67.7, 43.2, 43.1, 27.7, 25.6; IR (Neat Film NaCl) 3077, 3031, 2990, 2939, 1736, 1496, 1454, 1426, 1382, 1372, 1231, 1196, 1102, 1052, 918 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{16}H_{20}O_3$ [M]$^+$: 260.1412, found 260.1417; [α]$_D^{23.3}$ +21.4 (*c* 0.825, CH_2Cl_2, 86% ee); [α]$_D^{24.2}$ +22.2 (*c* 1.055, CH_2Cl_2, 85% ee).



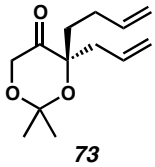
(+)-SI101

(+)-4-Allyl-2,2-dimethyl-4-(2-methylallyl)-1,3-dioxan-5-one ((+)-SI101, Table 10, Entry 7): From TES enol ether: 88% yield, 85% ee; from TMS enol ether: 86% yield, 85% ee. Colorless oil; R_f 0.55 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (dddd, J = 17.2, 10.2, 7.1, 7.1 Hz, 1H), 5.16–5.05 (m, 2H), 4.89 (ddd, J = 3.6, 1.5, 1.5 Hz, 1H), 4.74 (dd, J = 2.4, 0.9 Hz, 1H), 4.23 (d, J = 17.9 Hz, 1H), 4.15 (d, J = 17.9 Hz, 1H), 2.56-2.52 (m, 1H), 2.48–2.46 (dd, J = 4.8, 0.9 Hz, 2H), 1.81 (t, J = 1.2 Hz, 3H), 1.51 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.2, 141.4, 132.6, 119.1, 115.7, 99.9, 85.5, 67.9, 44.8, 42.5, 27.3, 26.3, 24.9; IR (Neat Film NaCl) 3078, 2986, 2944, 2919, 1740, 1642, 1427, 1383, 1372, 1231, 1197, 1159, 1001, 901 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{20}O_3$ $[M]^+$: 224.1412, found 224.1410; $[\alpha]_D^{23.3}$ +20.5 (*c* 0.515, CH_2Cl_2, 85% ee).



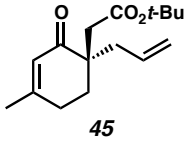
(–)-SI101

(–)-4-Allyl-2,2-dimethyl-4-(2-methylallyl)-1,3-dioxan-5-one ((–)-SI101, Table 10, Entry 8): From TES enol ether: 93% yield, 88% ee. Colorless oil; R_f 0.55 (20% Et_2O in hexanes); $[\alpha]_D^{26.6}$ –21.9 (*c* 0.620, CH_2Cl_2, 88% ee).



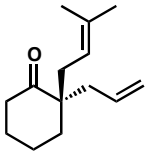
73

4-Allyl-4-(but-3-enyl)-2,2-dimethyl-1,3-dioxan-5-one (73, Table 10, Entry 9; Scheme 10d): From TES enol ether: 83% yield, 92% ee. Colorless oil; R_f 0.33 (10% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86–5.70 (m, 2H), 5.11–4.92 (m, 4H), 4.19 (d, J = 18.0 Hz, 2H), 4.15 (d, J = 18.0 Hz, 2H), 2.60–2.45 (m, 2H), 2.27–1.95 (m, 2H), 1.93–1.69 (m, 2H), 1.51 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.5, 138.2, 132.4, 119.1, 115.0, 100.1, 84.5, 67.4, 41.9, 36.1, 27.7, 27.3, 26.5; IR (Neat Film NaCl) 3079, 2987, 2941, 1738 1642, 1427, 1382 1372, 1232, 1209, 1168, 1148, 1098, 998, 915 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{20}O_3$ $[M]^+$: 224.1412, found 224.1416; $[\alpha]_D^{20.2}$ +7.04 (*c* 1.030, CH_2Cl_2, 92% ee).



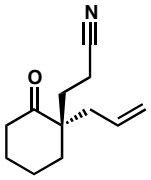
45

***tert*-Butyl 2-(1-allyl-4-methyl-2-oxocyclohex-3-enyl)ethanoate (45, Scheme 7):** Reaction time: from β-ketoester, 9 h, performed in Et_2O at 30 ºC. Flash chromatography (SiO_2, 3% Et_2O in pentane). 73% yield. R_f = 0.45 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84 (s, 1H), 5.70 (dddd, J = 16.8, 10.2, 7.3, 7.3 Hz, 1H), 5.12–5.11 (m, 2H), 2.71 (d, J = 15.6 Hz, 1H), 2.48–2.13 (comp. m, 6H), 1.93 (s, 3H), 1.91–1.81 (m, 1H), 1.40 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.0, 170.8, 160.3, 133.3, 125.4, 118.7, 80.5, 45.4, 40.5, 39.0, 29.8, 28.1, 27.8, 24.1; IR (Neat Film NaCl) 2978, 1728, 1670, 1367, 1213, 1152 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{25}O_3$ $[M + H]^+$: 265.1804, found 265.1803; $[\alpha]_D^{25.4}$ –39.22 (*c* 1.05, CH_2Cl_2, 86% ee).



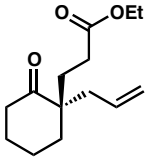
SI102

2-Allyl-2-(3-methylbut-2-enyl)cyclohexanone (SI102, Table 12, entry 3): Reaction time: from β-ketoester, 6 h, performed in Et_2O at 30 ºC. Flash chromatography (SiO_2, 1.5 → 2.5% Et_2O in pentane). 97% yield. R_f = 0.38 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.67 (dddd, J = 16.5, 10.6, 7.2, 7.2 Hz, 1H), 5.07-4.93 (comp. m, 3H), 2.44-2.24 (comp. m, 5H), 2.16 (dd, J = 14.6, 7.2 Hz, 1H), 1.89-1.64 (comp. m, 9H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.7, 134.2, 134.1, 119.0, 117.7, 52.1, 39.4, 39.3, 35.9, 33.3, 27.1, 26.0, 20.9, 18.0; IR (Neat Film NaCl) 3075, 2934, 2863, 1706, 1446, 1124, 914 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{14}H_{23}O$ [M + H]$^+$: 207.1749, found 207.1744; $[\alpha]_D^{26.0}$ +1.95 (*c* 1.29, CH_2Cl_2, 91% ee).



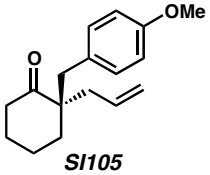
SI103

3-(1-Allyl-2-oxocyclohexyl)propanenitrile (SI103, Table 12, entry 4): Reaction time: from β-ketoester, 6.5 h, performed in Et_2O. Flash chromatography (SiO_2, 25% Et_2O in pentane). 97% yield. R_f = 0.32 (CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.60 (dddd, J = 16.7, 10.4, 7.4, 7.4 Hz, 1H), 5.17-5.07 (m, 2H), 2.53-2.16 (comp. m, 6H), 2.03-1.62 (comp. m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.2, 131.9, 120.0, 119.3, 50.8, 39.0, 38.9, 35.4, 30.6, 26.9, 20.5, 12.1; IR (Neat Film NaCl) 3081, 2939, 2863, 2246, 1702, 1453, 1126, 921 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{17}NO$ [M]$^+$: 191.1310, found 191.1307; $[\alpha]_D^{25.6}$ –27.00 (*c* 1.56, CH_2Cl_2, 88% ee).



SI104

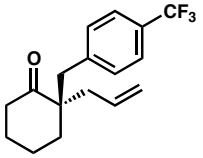
Ethyl 3-(1-allyl-2-oxocyclohexyl)propanoate (SI104, Table 12, entry 5): Reaction time: from β-ketoester, 6 h, performed in Et_2O. Flash chromatography (SiO_2, 5 → 14% Et_2O in pentane). 96% yield. R_f = 0.44 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.66 (dddd, J = 16.2, 10.9, 7.7, 7.2 Hz, 1H), 5.11-5.07 (m, 1H), 5.07-5.02 (m, 1H), 4.11 (app. q, J = 7.1 Hz, 2H), 2.48-2.18 (comp. m, 5H), 2.16-1.94 (comp. m, 2H), 1.90-1.65 (comp. m, 7H), 1.24 (app. t, J = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.2, 173.5, 133.3, 118.3, 60.4, 50.8, 39.1, 39.0, 36.2, 29.7, 28.8, 27.0, 20.7, 14.2; IR (Neat Film NaCl) 3076, 2937, 2866, 1735, 1704, 1454, 1377, 1309, 1181, 917 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{22}O_3$ [M]$^+$: 238.1569, found 238.1574; $[\alpha]_D^{25.8}$ +9.60 (*c* 1.13, CH_2Cl_2, 90% ee).



SI105

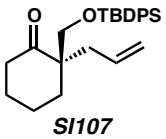
2-Allyl-2-(4-methoxybenzyl)cyclohexanone (SI105, Table 12, entry 7): Reaction time: from β-ketoester, 10 h. Flash chromatography (SiO_2, 3% Et_2O in pentane). 80% yield. R_f = 0.54 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (d, J = 9.0 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 5.72 (dddd, J

= 17.1, 9.8, 7.0, 7.0 Hz, 1H), 5.12-4.98 (m, 2H), 3.78 (s, 3H), 2.84 (s, 2H), 2.53-2.34 (m, 2H), 2.33-2.17 (m, 2H), 1.91-1.70 (comp. m, 4H), 1.70-1.61 (comp. m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.3, 158.1, 133.9, 131.5, 129.5, 118.1, 113.4, 55.2, 52.6, 40.1, 39.6, 39.3, 35.4, 26.8, 20.8; IR (Neat Film NaCl) 3076, 2935, 2863, 2361, 1702, 1611, 1513, 1456, 1249, 1179, 1036, 834 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{22}O_2$ [M]$^+$: 258.1620, found 258.1627; $[\alpha]_D^{25.9}$ +3.60 (*c* 1.05, CH_2Cl_2, 86% ee).



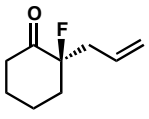
SI106

2-Allyl-2-(4-(trifluoromethyl)benzyl)cyclohexanone (SI106, Table 12, entry 8): Reaction time: from β-ketoester, 0.5 h. Flash chromatography (SiO_2, 8 → 14% Et_2O in pentane). 99% yield. R_f = 0.85 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.71 (dddd, *J* = 17.0, 10.1, 7.4, 6.9 Hz, 1H), 5.17-5.04 (m, 2H), 3.01 (d, *J* = 13.8 Hz, 1H), 2.88 (d, *J* = 13.8 Hz, 1H), 2.50-2.31 (comp. m, 3H), 2.29-2.17 (m, 1H), 1.97-1.82 (m, 1H), 1.82-1.69 (comp. m, 3H), 1.70-1.59 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.3, 142.0 (q, J_{CF} = 1.2 Hz), 133.0, 130.9, 128.4 (q, J_{CF} = 32.3 Hz), 124.7 (q, J_{CF} = 3.9 Hz), 124.2 (q, J_{CF} = 271.7 Hz), 118.5, 52.5, 40.4, 39.3, 39.3, 35.5, 26.6, 20.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.9; IR (Neat Film NaCl) 3076, 2940, 2867, 1705, 1618, 1418, 1326, 1164, 1123, 1068, 852 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{19}F_3O$ [M]$^+$: 296.1388, found 296.1402; $[\alpha]_D^{26.6}$ –16.31 (*c* 1.17, CH_2Cl_2, 82% ee).



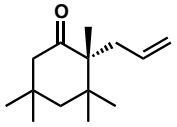
SI107

2-Allyl-2-((*tert*-butyldiphenylsilyloxy)methyl)cyclohexanone (SI107, Table 12, entry 9): Reaction time: from β-ketoester, 5 h. Flash chromatography (SiO_2, 1 → 2.5% EtOAc in hexanes). 92% yield. R_f = 0.32 (5% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68-7.64 (m, 4H), 7.46-7.36 (m, 6H), 5.69-5.55 (m, 1H), 5.38-5.31 (m, 1H), 5.08-4.99 (m, 2H), 3.84 (d, *J* = 10.2 Hz, 1H), 3.66 (d, *J* = 10.2 Hz, 1H), 2.48 (d, *J* = 7.5 Hz, 2H), 2.40-2.20 (m, 2H), 1.90-1.60 (m, 6H), 1.06 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.4, 135.7, 133.8, 133.3 (2C), 129.7, 129.6, 127.6 (2C), 117.9, 66.4, 53.8, 39.7, 37.3, 34.0, 26.9 (2C), 21.0, 19.3; IR (Neat Film NaCl) 3072, 2933, 2858, 1708, 1428, 1113, 703 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{26}H_{35}O_2Si$ [M + H]$^+$: 407.2406, found 407.2398; $[\alpha]_D^{25}$ –3.96 (*c* 5.00, $CHCl_3$, 81% ee).



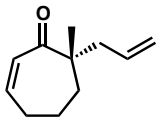
SI108

2-Allyl-2-fluorocyclohexanone (SI108, Table 12, entry 10): Reaction time: from β-ketoester, 3.5 h, performed in Et_2O at 30 ºC. Flash chromatography (SiO_2, 2% Et_2O in pentane). 80% yield. R_f = 0.36 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88-5.71 (m, 1H), 5.20-5.10 (m, 2H), 2.76-2.31 (m, 4H), 2.16-2.02 (m, 1H), 1.99-1.78 (m, 4H), 1.75-1.60 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 207.2 (d, J_{C-F} = 20.0 Hz), 130.7 (d, J_{C-F} = 3.8 Hz), 119.2, 97.7 (d, J_{C-F} = 184.3 Hz), 39.4, 38.7 (d, J_{C-F} = 22.7 Hz), 37.3 (d, J_{C-F} = 22.2 Hz), 27.2, 21.4 (d, J_{C-F} = 6.6 Hz); ^{19}F NMR (282 MHz, $CDCl_3$) δ –158.15; IR (Neat Film NaCl) 3080, 2946, 1729, 1642, 1453, 1433, 1126, 923 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_9H_{13}OF$ [M]$^+$: 156.0950, found 156.0946; $[\alpha]_D^{24.4}$ –74.65 (*c* 1.05, CH_2Cl_2, 91% ee).



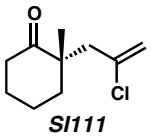
SI109

2-Allyl-2,3,3,5,5-pentamethylcyclohexanone (SI109, Table 13, entry 4): Reaction time: from β-ketoester, 5 h. Flash chromatography (SiO_2, 1 → 4% Et_2O in hexanes). 90% yield. R_f = 0.48 (10% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.63-5.46 (m, 1H), 5.10-4.94 (m, 2H), 2.61 (d, *J* = 13.5 Hz, 1H), 2.34 (d, *J* = 12.9 Hz, 1H), 2.11 (d, *J* = 12.9 Hz, 1H), 2.02 (d, *J* = 13.8 Hz, 1H), 1.83 (d, *J* = 14.6 Hz, 1H), 1.40 (d, *J* = 14.5 Hz, 1H), 1.02 (s, 3H), 0.99 (s, 3H), 0.95 (s, 3H), 0.92 (s, 3H), 0.90 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 215.5, 134.2, 117.9, 53.8, 51.0, 49.5, 40.5, 39.1, 35.7, 33.7, 29.8, 26.9, 26.3, 15.4; IR (Neat Film NaCl) 3077, 2957, 1708, 1639, 1460, 1392, 1370, 913 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{24}O$ [M]$^+$: 208.1827, found 208.1837; $[\alpha]_D^{22.5}$ –4.14 (*c* 2.705, hexane, 85% ee).



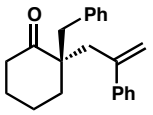
SI110

7-Allyl-7-methylcyclohept-2-enone (SI110, Table 13, entry 8): A 100 mL rb flask equipped with a magnetic stir bar was flame dried under vacuum and cycled into a N_2-filled glovebox. $Pd(dmdba)_2$ (78.3 mg, 0.096 mmol, 3 mol%) and (*S*)-*t*-Bu-PHOX (46.2 mg, 0.119 mmol, 3.76 mol%) were added, followed by THF (40 mL). The contents were stirred at 25 °C for 30 min, at which time allyl 1-methyl-2-oxocyclohept-3-enecarboxylate (660.1 mg, 3.17 mmol, 1.0 equiv) was added with a total of 10 mL of THF. The reaction was stirred for 3 h at which time TLC indicated complete reaction. The reaction mixture was cycled out of the glovebox, concentrated *in vacuo*, and the residue subjected to flash chromatography (2 x 16 cm, 25:1 Hex:EtOAc) to afford the title compound as a colorless oil (510 mg, 98% yield). R_f = 0.34 (10:1 Hexane:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.26 (ddd, *J* = 4.2, 4.2, 12.6 Hz, 1H), 5.91 (ddd, *J* = 2.1, 2.1, 12.6 Hz, 1H), 5.71 (dddd, *J* = 7.5, 7.5, 10.5, 17.1 Hz, 1H), 5.07-5.04 (m, 1H), 5.01 (dddd, *J* = 0.9, 0.9, 2.1, 9.9 Hz, 1H), 2.40-2.32 (m, 2H), 2.30 (m, 1H), 2.21 (dddd, *J* = 0.9, 0.9, 7.2, 13.5 Hz, 1H), 1.88-1.53 (m, 4H), 1.13 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.2, 141.8, 133.9, 130.3, 117.9, 52.3, 44.4, 35.1, 33.2, 24.1, 22.0; IR (Neat Film NaCl) 3075, 3013, 2929, 1662, 1455, 1419, 1396, 1375, 1199, 995, 915 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{16}O$ [M]$^+$: 164.1201, found 164.1201; $[\alpha]_D^{24.6}$ –63.58 (*c* 1.015, $CHCl_3$, 90% ee).



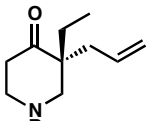
SI111

2-(2-Chloroallyl)-2-methylcyclohexanone (SI111, Table 13, entry 10): Reaction time: from β-ketoester, 2.5 h, performed in Et_2O at 35 ºC with 4 mol% $Pd_2(dba)_3$ (45.8 mg, 0.040 mmol), and 10 mol% (*S*)-*t*-BuPHOX (48.4 mg, 0.10 mmol). Flash chromatography (SiO_2, 1 → 2.5% Et_2O in pentane). 87% yield. R_f = 0.63 (30% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.27 (app. d, *J* = 1.2 Hz, 1H), 5.15-5.09 (m, 1H), 2.80 (d, *J* = 14.4 Hz, 1H), 2.61 (d, *J* = 14.4 Hz, 1H), 2.56-2.37 (m, 2H), 1.94-1.61 (comp. m, 6H), 1.17 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.4, 138.7, 116.3, 48.4, 46.5, 39.2, 38.8, 27.4, 22.7, 21.1; IR (Neat Film NaCl) 2936, 2868, 1708, 1630, 1456, 1126, 887 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{16}ClO$ [M + H]$^+$: 187.0890, found 187.0884; $[\alpha]_D^{26.6}$ –5.40 (*c* 3.21, CH_2Cl_2, 91% ee).



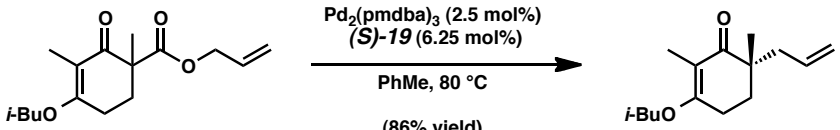
SI112

2-Benzyl-2-(2-phenylallyl)cyclohexanone (SI112, Table 13, entry 11): Reaction time: from β-ketoester, 12.25 h, performed at 30 ºC with 2.5 mol% $Pd(dmdba)_2$ (20.4 mg, 0.025 mmol), and 2.5 mol% (*S*)-*t*-BuPHOX (9.6 mg, 0.025 mmol). Flash chromatography (SiO_2, 15% Et_2O in petroleum ether). 96% yield. R_f = 0.44 (15% Et_2O in petroleum ether); ^{1}H NMR (300 MHz, CD_3OD) δ 7.36-7.10 (m, 8H), 7.07-7.00 (m, 2H), 5.25 (d, *J* = 1.9 Hz, 1H), 5.11-5.08 (m, 1H), 3.04 (d, *J* = 13.8 Hz, 1H), 2.90-2.85 (m, 2H), 2.63 (d, *J* = 13.6 Hz, 1H), 2.42-2.17 (m, 2H), 1.82-1.46 (m, 6H); ^{13}C NMR (75 MHz, CD_3OD) δ 216.6, 147.6, 144.6, 139.3, 131.9, 129.3, 128.9, 128.4, 127.9, 127.3, 118.0, 54.8, 42.9, 42.4, 40.8, 36.2, 27.2, 21.8; IR (neat film, NaCl) ν 3082, 3058, 3027, 2938, 2864, 1702, 1624, 1601, 1574, 1494, 1453, 1444, 1315, 1198, 1126, 1080, 1075, 1055, 1030, 968, 905, 778, 754, 744, 702 cm^{-1}; HRMS (EI+) *m/z* calc'd. for $C_{22}H_{24}O$ $[M]^+$: 304.1827, found 304.1841; $[\alpha]_D^{24}$ –13.67 (*c* 1.005, $CHCl_3$, 94% ee).



SI113

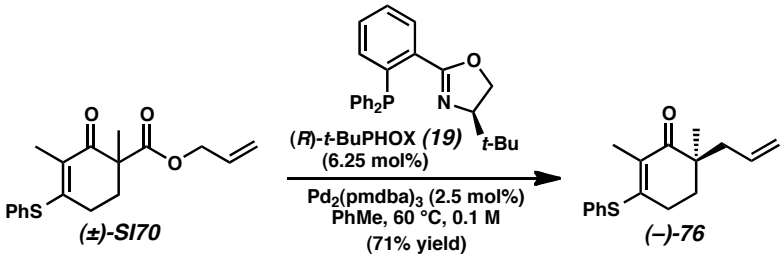
3-Allyl-1-benzyl-3-ethylpiperidin-4-one (SI113, Table 13, entry 12): Reaction time: from β-ketoester, 2.5 h. Flash chromatography (SiO_2, 5→7% Et_2O in pentane). 91% yield. R_f = 0.29 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39-7.23 (comp. m, 5H), 5.62 (dddd, *J* = 12.3, 9.6, 7.2, 7.2 Hz, 1H), 5.03 (m, 1H), 4.99 (m, 1H), 3.56 (s, 2H), 2.83-2.69 (m, 1H), 2.65-2.33 (comp. m, 6H), 2.33-2.20 (m, 1H) 1.95 (dq, *J* = 15.3, 7.5 Hz, 1H), 1.51 (dq, *J* = 15.0, 7.5 Hz, 1H), 0.75 (dd, *J* = 7.5, 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 212.6, 138.6, 133.8, 128.7, 128.3, 127.2, 117.8, 62.2, 61.8, 53.4, 52.2, 39.3, 37.3, 26.7, 7.8; IR (Neat Film NaCl) 3065, 3028, 2965, 2801, 1709, 1454, 1352, 1200, 915, 699 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{23}NO$ $[M]^+$: 257.1780, found 257.1772; $[\alpha]_D^{26.6}$ +31.21 (*c* 1.51, CH_2Cl_2, 92% ee).



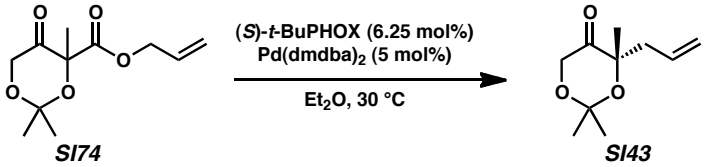
(±)-SI68 ***(+)-SI114***

Ketone (+)-SI114 from β-ketoester (±)-SI68 (Table 13, entry 13): A 2-dram vial containing a stir bar was charged with $Pd_2(pmdba)_3$ (10.6 mg, 0.00968 mmol, 0.025 equiv) and (*S*)-**19** (9.4 mg, 0.0242 mmol, 0.0625 equiv). This was connected to a 1-dram vial containing a stirbar and β-ketoester (±)-**SI68** (108.6 mg, 0.387 mmol, 1.0 equiv) via a cannula, and PhMe (3.9 mL, 0.1 M) was added to the vial containing the Pd/L and immediately immersed in liquid N_2. The vials were rigorously degassed by three freeze-pump-thaw cycles and warmed to 23 °C. After complexation for 30 min (purple → orange color change), the catalyst solution was transferred to the substrate via cannula and immersed in an 80 °C oil bath. The reaction immediately turned yellow in color. After 23 h the reaction was cooled to ambient temperature, diluted with Et_2O (4 mL), and filtered through a small SiO_2 plug. The filtrate was concentrated and purified by flash chromatography as above to afford ketone (+)-**SI114** as a colorless oil (78.5 mg, 0.332 mmol, 86% yield, 75% ee). R_f = 0.49 (4:1 hexanes-EtOAc); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.73 (dddd, *J* = 16.6, 10.6, 7.4, 7.4 Hz, 1H), 5.06-5.04 (m, 1H), 5.04-5.01 (m, 1H), 3.74 (dd, *J* = 9.7, 6.7 Hz, 2H), 2.59-2.47 (comp m, 2H), 2.33 (dd, *J* = 13.7, 7.2 Hz, 1H), 2.16 (dddd, *J* = 13.7, 7.6, 1.0, 1.0 Hz, 1H), 1.98 (app septuplet, *J* = 6.6 Hz, 1H), 1.90 (ddd, *J* = 13.3, 7.2, 5.7 Hz, 1H), 1.72-1.67 (m, 1H), 1.70 (dd, *J* = 1.6, 1.6 Hz, 3H), 1.06 (s, 3H), 0.99 (d, *J* = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.7, 169.5, 134.8, 117.8, 113.3, 73.8, 42.5, 41.9, 31.5, 29.0, 22.5, 22.4, 19.2, 8.0; IR (Neat

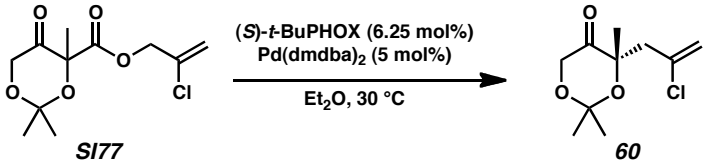
Film NaCl) 3076, 2962, 2931, 1622, 1463, 1381, 1355, 1229, 1113, 1002, 915 cm^{-1}; HRMS (EI+) *m/z*: calc'd for $C_{15}H_{24}O_2$ $[M]^+$: 236.1776, found 236.1771; $[\alpha]_D^{21.2}$ +13.2 (*c* 0.20, CH_2Cl_2, 88% ee).



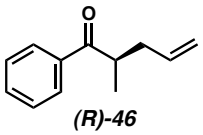
Ketone (–)-76 from β-ketoester (±)-SI70 (Table 13, entry 14): A solution of $Pd_2(pmdba)_3$ (0.1306 g, 0.1185 mmol, 0.025 equiv) and (*R*)-*t*-BuPHOX (**19**) (0.1148 g, 0.2964 mmol, 0.0625 equiv) in toluene (30 mL) was prepared in a glovebox under N_2 atmosphere, and allowed to stir at 23 °C for 30 min. A solution of β-ketoester (±)-**SI70** (1.50 g, 4.741 mmol, 1.00 equiv) in toluene (10 mL) was transferred to the reaction vessel dropwise via glass pipette, washing with toluene (7.5 mL) for quantitative transfer. The reaction vessel was sealed with a rubber septum, removed from the glove box, heated in a 60 °C oil bath, and the solution was allowed to stir for 24 h. The reaction vessel was cooled to room temperature, and the solvent was evaporated in vacuo. The resulting residue was purified by flash chromatography (5% EtOAc in hexanes) to afford allyl ketone (–)-**76** (0.92 g, 71% yield, 91.6% ee as determined by chiral HPLC using a Chiralpak AD column with 4% EtOH in hexanes as the eluent) as a colorless oil. R_f = 0.45 (30% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52-7.48 (m, 2H), 7.43-7.35 (comp m, 3H), 5.68 (app ddt, *J* = 10.8, 16.8, 7.5 Hz, 1H), 5.03 (dddd, *J* = 9.9, 2.4, 0.9, 0.6 Hz, 1H), 5.01 (dddd, *J* = 17.4, 2.4, 1.5, 1.2 Hz, 1H), 2.32 (app ddt, *J* = 13.8, 7.2, 1.2 Hz), 2.19-2.10 (comp m, 3H), 1.96 (t, *J* = 1.8 Hz, 3H), 1.86-1.75 (m, 1H), 1.66-1.56 (m, 1H), 1.04 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.5, 155.6, 135.6, 134.4 130.3, 129.6, 129.5, 128.8, 118.2, 43.1, 41.7, 33.1, 26.9, 22.3, 12.9; IR (Neat Film NaCl) 3074, 2964, 2929, 1652, 1582, 1440, 1339, 1287, 1228 cm^{-1}; HRMS (FAB+) *m/z*: calc'd for $C_{17}H_{20}OS$ $[M + H]^+$: 273.1313, found 273.1317; $[\alpha]_D^{25.4}$ –57.4 (*c* 1.00, CH_2Cl_2).



4-Allyl-2,2,4-trimethyl-1,3-dioxan-5-one (SI43, Table 13, Entry 15): A mixture of (*S*)-*t*-BuPHOX (**19**, 18.5 mg, 0.048 mmol, 0.0625 equiv) and bis(3,5,3',5'-dimethoxy-dibenzylideneacetone) palladium(0) (31 mg, 0.038 mmol, 0.05 equiv) was evacuated and backfilled with Ar. The mixture was solvated with freshly distilled Et_2O (23 mL, 0.033 M) and warmed for 30 min at 30 °C. The red/brown mixture was treated with β-ketoester **SI74** (0.150 g, 0.76 mmol, 1 equiv) in Et_2O (0.2 mL x 2). After 15 h, the reaction was concentrated under reduced pressure (>150 torr). The pale yellow residue was purified by silica gel chromatography (approx. 30 mL SiO_2 using 1:3 CH_2Cl_2:pentane then 1:1 CH_2Cl_2:pentane eluent) to give enantioenriched **SI43** as a colorless oil (96 mg, 68% yield, 83% ee). Characterization data is found above.



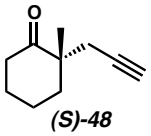
4-(2-Chloroallyl-2,2,4-trimethyl-1,3-dioxan-5-one (60, Table 13, Entry 16): Prepared using an analogous procedure to that for the preparation of **SI77**. 97% yield, 91% ee. Characterization data is found above.



(R)-46

(*R*)-2-Methyl-1-phenylpent-4-en-1-one (46, Table 14):[43] Purified by preparative TLC. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 5.77 (m, 1H), 5.00 (m, 2H), 3.52 (app. sextet, *J* = 6.9 Hz, 1H), 2.54 (m, 1H), 2.19 (m, 1H), 1.21 (d, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.6, 136.4, 135.9, 133.0, 128.5, 116.7, 40.5, 37.7, 17.1; IR (Neat Film NaCl) 3078, 2976, 2933, 1682, 1642, 1448, 1209, 976, 917, 704 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{14}O$ [M]$^+$: 174.1045, found 174.1048; $[\alpha]_D^{27.0}$ –38.1 (*c* 1.73, hexanes, 70% ee).

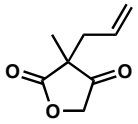
Procedure for Asymmetric Propargylation:



(S)-48

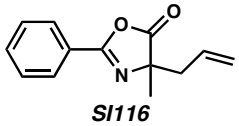
(*S*)-2-Methyl-2-(prop-2-ynyl)cyclohexanone (48, Table 15): A 50 mL two-neck rb flask containing a stirbar was equipped with a three-way stopcock, flame dried under vacuum, and cooled under dry nitrogen. To this was added $Pd_2(dba)_3$ (11.4 mg, 0.0125 mmol, 0.05 equiv) and (*S*)-*t*-Bu-PHOX (12.5 mg, 0.0313 equiv). The flask was evacuated and backfilled with dry nitrogen twice. THF (15 mL) was then added and the mixture was stirred for 30 min at 25 ºC. To the resulting yellow solution was added propargyl enol carbonate **47** (97.1 mg, 0.50 mmol) and then this mixture was stirred at 70 ºC. After the reaction was complete (~1 h), the resulting mixture was concentrated *in vacuo*. Flash chromatography gave propargyl ketone **48** (64.3 mg, 86% yield) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.55-2.29 (comp. m, 4H), 1.99 (t, *J* = 2.7 Hz, 1H), 1.98-1.65 (comp. m, 6H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.9, 81.1, 70.7, 47.8, 38.5, 37.8, 27.6, 27.3, 22.3, 21.1; IR (Neat Film NaCl) 3292, 2936, 2865, 2117, 1709, 1451, 1425, 1377, 1314, 1128, 1075 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{14}O$ [M]$^+$: 150.1045, found 150.1044; $[\alpha]_D^{25}$ +0.74 (*c* 1.50, $CHCl_3$, 31% ee).

Characterization Data for Alkylation Products of Stabilized Nucleophiles:



SI115

3-Allyl-3-methylfuran-2,4(3*H*,5*H*)-dione (SI115, Table 16, Entry 2): Purified by flash chromatography (SiO_2, 2→12% EtOAc in hexanes). 87% yield, 2% ee. R_f = 0.20 (10% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.62 (dddd, *J* = 17.7, 9.6, 7.5, 7.2 Hz, 1H), 5.13 (app. ddd, *J* = 9.6, 1.8, 0.9 Hz, 1H), 5.12 (app. ddd, *J* = 17.1, 1.5, 0.9 Hz, 1H), 4.59 (d, *J* = 17.1 Hz, 1H), 4.44 (d, *J* = 17.4 Hz, 1H), 2.53-2.37 (m, 2H), 1.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.9, 176.6, 130.1, 121.1, 72.5, 45.6, 40.2, 19.0; IR (Neat Film NaCl) 3543, 3083, 2983, 2939, 2877, 1803, 1758, 1642, 1454, 1436, 1378, 1341, 1231, 1122, 1065, 1043, 998, 912, 664 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_8H_{10}O_3$ [M]$^+$: 154.0630, found 154.0626.

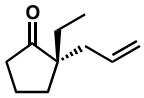


SI116

4-Allyl-4-methyl-2-phenyloxazol-5(4*H*)-one (SI116, Table 16, Entry 5): Purified by flash chromatography (SiO_2, 4→7% Et_2O in hexanes). 89% yield, 2% ee. R_f = 0.39 (25% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (ddd, *J* = 7.2, 1.5, 1.2 Hz, 2H), 7.57 (tt, *J* = 7.8, 1.2 Hz, 1H), 7.48

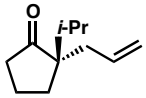
(ddd, *J* = 7.8, 6.9, 1.5 Hz, 2H), 5.67 (dddd, *J* = 17.1, 9.9, 7.5, 6.9 Hz, 1H), 5.18 (dddd, *J* = 17.1, 1.5, 1.5, 1.5 Hz, 1H), 5.11 (dddd, *J* = 10.2, 1.5, 0.9, 0.9 Hz, 1H), 2.64 (dddd, *J* = 13.8, 6.9, 0.9, 0.9 Hz, 1H), 2.57 (dddd, *J* = 13.8, 7.5, 1.2, 1.2 Hz, 1H), 1.53 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.2, 159.8, 132.7, 130.8, 128.7, 127.9, 125.9, 120.4, 69.7, 42.3, 23.2; IR (Neat Film NaCl) 3078, 2982, 2934, 1819, 1655, 1581, 1493, 1451, 1321, 1293, 1177, 1094, 1071, 1005, 930, 889, 780, 700 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{13}H_{13}O_2N$ [M]$^+$: 215.0946, found 215.0938.

Characterization Data for 5-Membered Ring Ketone Alkylation Products



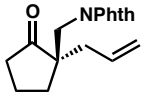
SI117

2-Allyl-2-ethylcyclopentanone (SI117, Table 17, entry 1): Reaction time: from β-ketoester, 3 h. Flash chromatography (2 x 12 cm SiO_2, 3 → 4% Et_2O in pentane). Colorless oil (125.9 mg, 82% yield). R_f = 0.44 (10:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.68 (dddd, *J* = 7.2, 7.2, 9.3, 12.3 Hz, 1H), 5.09-5.00 (m, 2H), 2.24-2.14 (m, 4H), 1.90-1.80 (m, 4H), 1.46 (q, *J* = 7.2 Hz, 1H), 1.46 (q, *J* = 7.2 Hz, 1H), 0.83 (dd, *J* = 7.2, 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.4, 169.8, 131.5, 118.3, 65.6, 38.9, 31.9, 27.2, 19.5, 18.3, 17.6; IR (Neat Film NaCl) 3077, 2965, 1735, 1640, 1460, 1406, 1162, 915 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{16}O$ [M]$^+$: 152.1201, found 152.1195; $[\alpha]_D^{25.2}$ –18.55 (*c* 1.050, CH_2Cl_2, 86% ee).



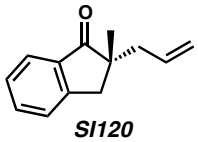
SI118

2-Allyl-2-isopropylcyclopentanone (SI118, Table 17, entry 2): Reaction time: from β-ketoester, 3 h. Flash chromatography (2 x 13 cm SiO_2, 3% Et_2O in pentane). Colorless oil (130.4 mg, 77% yield). R_f = 0.44 (10:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.70 (dddd, *J* = 7.5, 7.5, 9.3, 13.2 Hz, 1H), 5.07-5.00 (m, 2H), 2.30-2.07 (m, 4H), 2.01-1.69 (m, 5H), 0.87 (d, *J* = 7.2 Hz, 3H), 0.80 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 223.6, 134.2, 117.8, 55.1, 39.7, 39.6, 31.8, 29.0, 18.9, 18.2, 17.1; IR (Neat Film NaCl) 3077, 2963, 1734, 1640, 1471, 1406, 1388, 1370, 1190, 914 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{18}O$ [M]$^+$: 166.1358, found 166.1359; $[\alpha]_D^{24.9}$ +43.05 (*c* 1.085, CH_2Cl_2, 84% ee).



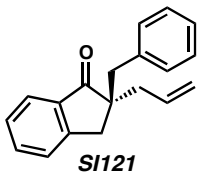
SI119

2-((1-Allyl-2-oxocyclopentyl)methyl)isoindoline-1,3-dione (SI119, Table 17, entry 3): Reaction time: from β-ketoester, 2 h. Flash chromatography (SiO_2, 10 → 15% EtOAc in hexanes). 67% yield, 48% ee. R_f = 0.34 (30% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 5.9, 3.2 Hz, 2H), 7.72 (dd, *J* = 5.9, 3.2 Hz, 2H), 5.73 (dddd, *J* = 16.8, 9.8, 7.7, 6.4 Hz, 1H), 5.18-5.06 (m, 2H), 3.80 (d, *J* = 14.1 Hz, 1H), 3.74 (d, *J* = 14.1 Hz, 1H), 2.56-2.41 (m, 1H), 2.38-2.10 (comp. m, 3H), 2.10-1.86 (comp. m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 220.1, 168.8, 134.2, 133.3, 132.0, 123.6, 119.4, 53.0, 41.8, 38.7, 38.3, 31.9, 18.9; IR (Neat Film NaCl) 2966, 1773, 1734, 1713, 1429, 1395, 1354, 715, 666 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{17}H_{17}O_3N$ [M]$^+$: 283.1208, found 283.1209; $[\alpha]_D^{26.5}$ –14.1 (*c* 1.49, CH_2Cl_2, 48% ee).



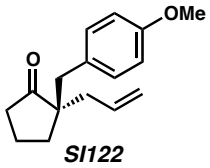
SI120

2-Allyl-2-methyl-2,3-dihydro-1*H*-inden-1-one (SI120, Table 17, entry 4): Reaction time: from β-ketoester, 1 h, performed on 0.1 mmol scale. Purified by flash chromatography (SiO_2, 10% Et_2O in pentane). 82% yield, 80% ee. R_f = 0.37 (10% Et_2O in pentane); $[\alpha]_D^{26.4}$ –38.5 (*c* 0.47, CH_2Cl_2, 80% ee). Spectral data matched that reported in the literature.[44]



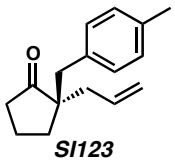
SI121

2-Allyl-2-benzyl-2,3-dihydro-1*H*-inden-1-one (SI121, Table 17, entry 5): Reaction time: from β-ketoester, 1 h. Purified by flash chromatography (SiO_2, 2 → 4% Et_2O in pentane). 93% yield, 71% ee. R_f = 0.37 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.63 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 7.49 (comp. m, 2H), 7.36-7.20 (comp. m, 5H), 5.74 (dddd, *J* = 16.7, 10.1, 8.0, 6.6 Hz, 1H), 5.21 (app. d, *J* = 16.8 Hz, 1H), 5.12 (app. d, *J* = 10.1 Hz, 1H), 3.26 (d, *J* = 17.3 Hz, 1H), 3.25 (d, *J* = 13.3 Hz, 1H), 3.10 (d, *J* = 17.3 Hz, 1H), 2.96 (d, *J* = 13.6 Hz, 1H), 2.70 (dd, *J* = 13.6, 6.4 Hz, 1H), 2.46 (dd, *J* = 13.6, 8.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.3, 153.0, 137.3, 136.8, 134.8, 133.4, 130.2, 128.0, 127.2, 126.4, 126.3, 123.8, 118.7, 53.7, 42.7, 42.5, 35.3; IR (Neat Film NaCl) 3076, 3029, 2917, 1708, 1608, 1496, 1465, 1436, 1296, 1210, 1030, 995, 922, 756, 703 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{19}H_{18}O$ $[M]^+$: 262.1358, found 262.1365; $[\alpha]_D^{26.1}$ +28.4 (*c* 1.42, CH_2Cl_2, 71% ee).



SI122

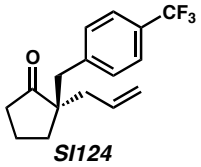
2-Allyl-2-(4-methoxybenzyl)cyclopentanone (SI122, Table 17, entry 6): Reaction time: from β-ketoester, 2 h. Flash chromatography (2 x 14 cm SiO_2, 3% Et_2O in pentane). Colorless oil (207.6 mg, 84% yield). R_f = 0.32 (10:1 Hexanes:EtOAc); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.01 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.71 (dddd, *J* = 7.5, 7.5, 10.2, 14.7 Hz, 1H), 5.14-5.01 (m, 2H), 3.78 (s, 3H), 2.86 (d, *J* = 13.8 Hz, 1H), 2.53 (d, *J* = 13.8 Hz, 1H), 2.26 (dd, *J* = 7.2, 13.5 Hz, 1H), 2.20-2.09 (m, 2H), 1.99 (dd, *J* = 6.6, 8.7 Hz, 1H), 1.95-1.66 (m, 2H), 1.86 (app. dd, *J* = 7.5, 7.5 Hz, 1H), 1.55-1.41 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 223.0, 158.2, 133.7, 131.1, 129.6, 118.5, 113.5, 55.1, 53.2, 40.8, 40.8, 38.9, 30.9, 18.6; IR (Neat Film NaCl) 3075, 2958, 1733, 1611, 1512, 1248, 1178, 1036 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{20}O_2$ $[M]^+$: 244.1463, found 156244.1465; $[\alpha]_D^{25.1}$ +7.34 (*c* 1.065, CH_2Cl_2, 73% ee).



SI123

2-Allyl-2-(4-methylbenzyl)cyclopentanone (SI123, Table 17, entry 7): Reaction time: from β-ketoester, 2 h. Flash chromatography (SiO_2, 5% Et_2O in pentane). 84% yield, 73% ee. R_f = 0.39 (10% Et_2O in pentane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, *J* = 7.7 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.72 (dddd, *J* = 17.0, 10.4, 8.0, 6.9 Hz, 1H), 5.10 (app. ddd, *J* = 10.1, 2.1, 1.1 Hz, 1H), 5.06 (app. ddd, *J* = 16.7, 2.1, 1.3 Hz, 1H), 2.87 (d, *J* = 13.3 Hz, 1H), 2.55 (d, *J* = 13.3 Hz, 1H), 2.31 (s, 3H), 2.29-2.22 (m, 1H), 2.21-2.07 (comp. m, 2H), 2.05-1.82 (comp. m, 3H), 1.82-1.65 (m, 1H), 1.56-1.41 (m, 1H); ^{13}C

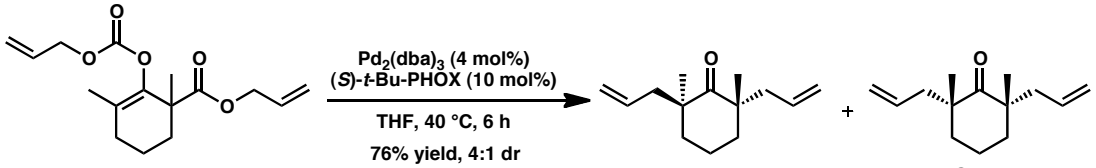
NMR (75 MHz, $CDCl_3$) δ 223.2, 136.1, 134.7, 133.9, 130.3, 129.0, 118.8, 53.4, 41.4, 41.0, 39.1, 31.1, 21.2, 18.8; IR (Neat Film NaCl) 3080, 2961, 2915, 1737, 1515, 1441, 1157, 921, 810, 666 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{20}O$ $[M]^+$: 228.1514, found 228.1505; $[\alpha]_D^{26.2}$ +9.1 (*c* 2.68, CH_2Cl_2, 73% ee).



SI124

2-Allyl-2-(4-(trifluoromethyl)benzyl)cyclopentanone (SI124, Table 17, entry 8): Reaction time: from β-ketoester, 2 h. Flash chromatography (2 x 14 cm SiO_2, 2 → 3% Et_2O in pentane). Colorless oil (239.3 mg, 83% yield). R_f = 0.39 (10:1 Hexane:EtOAc); ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.73 (dddd, *J* = 7.5, 7.5, 10.2, 17.4 Hz, 1H), 5.17-5.05 (m, 2H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.66 (d, *J* = 13.2 Hz, 1H), 2.26 (dd, *J* = 7.2, 13.5 Hz, 1H), 2.24-2.19 (m, 1H), 2.16 (dd, *J* = 7.2, 13.5 Hz, 1H), 2.01-1.70 (m, 3H), 1.59-1.43 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 222.1, 142.0, 133.1, 130.6, 128.7 (q, $J_{C\text{-}F}$ = 32.2 Hz), 125.1 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.2 (q, $J_{C\text{-}F}$ = 269.2 Hz), 119.0, 53.1, 41.0, 40.7, 38.6, 31.0, 18.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ –63.29; IR (Neat Film NaCl) 3078, 2964, 1736, 1618, 1326, 1163, 1123, 1068 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{16}H_{17}OF_3$ $[M]^+$: 282.1232, found 282.1237; $[\alpha]_D^{24.8}$ +5.65 (*c* 1.085, CH_2Cl_2, 60% ee).

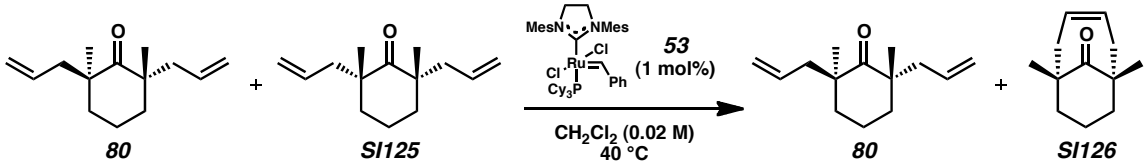
Procedures for Double-Alkylation Reactions



79 ***80*** ***SI125***

2,6-Diallyl-2,6-dimethylcyclohexanone (80, Scheme 11a). A 50 mL rb flask equipped with a magnetic stir bar was flame dried under vacuum. After cooling under nitrogen, $Pd_2(dba)_3$ (31.4 mg, 0.0343 mmol, 0.034 equiv) and (*S*)-*t*-Bu-PHOX (**2**) (31.3 mg, 0.0808 mmol, 0.080 equiv) were added. After the flask was evacuated and filled with nitrogen three times, THF (32 mL) was added and the contents were stirred at 25 °C for 30 min, at which time allyl 2-(allyloxycarbonyloxy)-1,3-dimethylcyclohex-2-enecarboxylate (**79**) (298 mg, 1.012 mmol, 1.0 equiv) was added by syringe in one portion. The reaction was stirred at 40 °C for 6 h at which time TLC indicated complete reaction. The reaction mixture was allowed to cool and then concentrated to ~1 mL under reduced pressure and the residue chromatographed (100 mL pentane, then 1 → 2% Et_2O in pentane on 2 x 14 cm SiO_2) to afford the title compound as a colorless, volatile oil (157.9 mg, 76% yield). GC analysis indicated the isolated compound was an 80:20 mixture (R_f = 0.51, 10:1 Hexane:EtOAc) of C_2-symmetric:*meso* diastereomers (**80**:**SI125**).

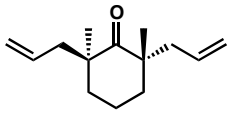
Compound **80** was also synthesized from either diastereomer of bis(β-ketoester) **81** (vide supra) following general procedure 17 with $Pd_2(dmdba)_3$ as the palladium source. In these reactions a 4.3:1 mixture of **80** to **SI125** was observed and (–)-**80** was formed with 94% ee.



80 ***SI125*** ***80*** ***SI126***

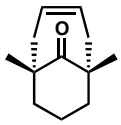
In order to obtain an analytical sample of the C_2-symmetric product (**80**), the following reaction was performed on the mixture of diastereomers: A solution of the diastereomeric ketones (50.4 mg, 0.244 mmol, 1.0 equiv) in 15 mL CH_2Cl_2 was degassed by bubbling Ar through the solution for 15 min. The second generation Grubbs catalyst (**53**)[45] (2 mg, 0.00236 mmol, 0.0097 equiv) was added and the

mixture heated to 40 °C. After 90 min, GC analysis indicated none of the minor diastereomer was present. The reaction mixture was allowed to cool and then concentrated to ~1-2 mL under reduced pressure and the residue chromatographed (75 mL pentane, then 2 → 5% Et_2O in pentane on 1.5 x 24 cm SiO_2) to afford the C_2-symmetric **80** (31 mg, 62%), the RCM product **SI126** (8.3 mg), and 5.8 mg of a mixture of the two compounds.



80

C_2-symmetric ketone **80**: R_f = 0.17 (2% Et_2O in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.65 (m, 2H), 5.10-4.95 (m, 4H), 2.33 (dd, *J* = 6.9, 13.8 Hz, 2H), 2.18 (dd, *J* = 7.8, 13.8 Hz, 2H), 1.87-1.68 (m, 4H), 1.59-1.48 (m, 2H), 1.06 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 218.6, 134.4, 118.0, 47.6, 43.9, 36.4, 25.0, 17.3; IR (Neat Film NaCl) 3076, 2930, 1694, 1639, 1461, 1374, 992, 914 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{14}H_{22}O$ [M]$^+$: 206.1671, found 206.1675; $[\alpha]_D^{23.6}$ –54.04 (*c* 0.95, hexane, 92% ee).



SI126

meso-Ketone **SI126:** R_f = 0.13 (2% Et_2O in hexane); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.83-5.72 (m, 2H), 2.53-2.35 (m, 3H), 2.03-1.85 (m, 4H), 1.75-1.62 (m. 2H), 1.48-1.37 (m, 1H), 1.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 217.9, 129.4, 48.5, 41.7, 39.0, 27.2, 20.0; IR (Neat Film NaCl) 2965, 1735, 1699, 1458, 1378, 1239 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{12}H_{18}O$ [M]$^+$: 178.1358, found 178.1360.

For details of the preparation of bis(β-ketoester) **82** (Scheme 11), conversion to diketone **83**, and synthesis of cyanthiwigin F (**84**), see ref 46.

Table SI1. Methods Utilized for the Determination of Enantiomeric Excess.

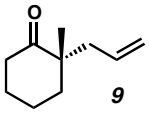
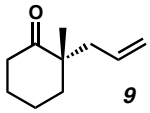
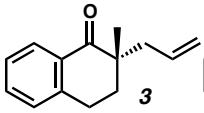
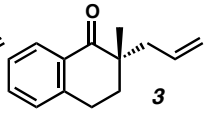
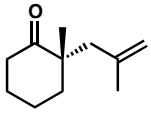
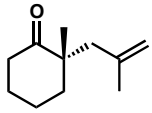
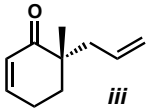
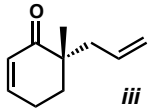
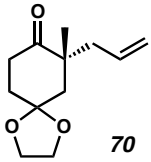
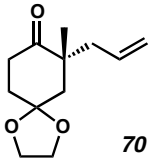
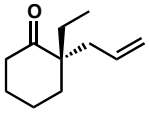
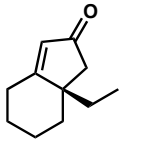
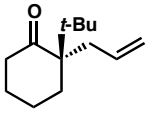
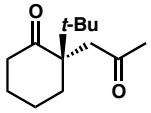
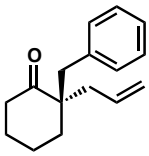
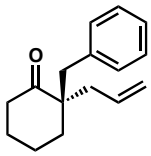
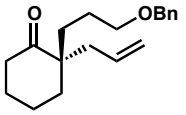
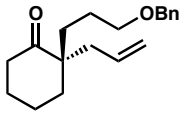
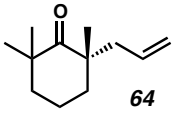
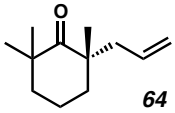
entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
1	 *9*	 *9*	GC, G-TA 100 °C isotherm	11.13	12.74	88
2	 *3*	 *3*	HPLC Chiracel OD-H 0.1% IPA in heptane isocratic, 0.7 mL/min	19.97	21.48	92
3			GC, G-TA 100 °C isotherm	15.76	17.65	92
4	 *iii*	 *iii*	GC, G-TA 100 °C isotherm	15.31	18.04	90
5	 *70*	 *70*	GC, G-TA 120 °C isotherm	26.90	28.64	86
6			GC, G-TA 100 °C isotherm	14.52	13.35	92
7			GC, G-TA 110 °C isotherm	63.65	62.01	82
8			HPLC Chiracel OJ 2% EtOH in hexane isocratic, 1.0 mL/min	19.81	13.82	85
9			HPLC Chiralpak AD 0.75% IPA in hexane isocratic, 1.0 mL/min	11.95	13.80	88
10	 *64*	 *64*	GC, G-TA 80 °C isotherm	25.48	27.90	92

Table SI1. (continued)

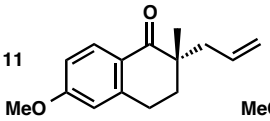
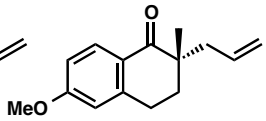
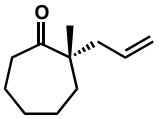
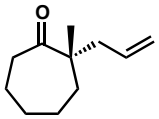
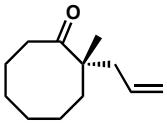
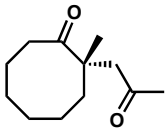
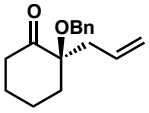
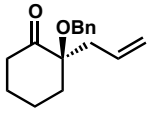
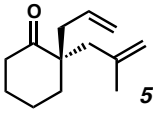
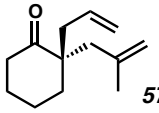
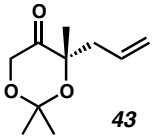
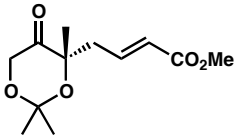
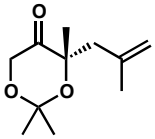
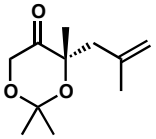
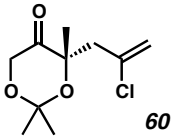
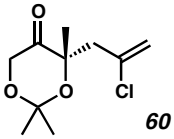
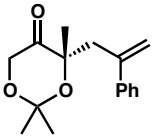
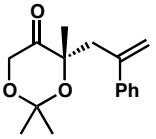
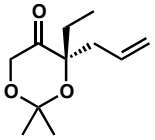
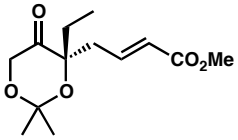
entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
11			HPLC Chiracel OJ 1% EtOH in hexane isocratic 1.0 mL/min	11.38	10.16	91
12			GC, G-TA 110 °C isotherm	9.88	10.68	87
13			GC, G-TA 110 °C isotherm	63.25	61.94	79
14			HPLC Chiracel OB-H 0.2% EtOH in hexane isocratic, 1.0 mL/min	13.56	16.96	59
15	 *57*	 *57*	GC, G-TA 95 °C isotherm	49.77	47.98	91
16	 *43*		HPLC Chiracel OD-H 5% EtOH in hexane isocratic, 1.0 mL/min	7.283	9.200	90
17			GC, G-TA 100 °C isotherm	71.824	67.568	89
18	 *60*	 *60*	GC, G-TA 100 °C isotherm	23.425	21.998	92
19			HPLC Chiracel OD-H 1% IPA in hexane isocratic, 1.0 mL/min	7.256	6.818	94
20			HPLC Chiracel OD-H 5% EtOH in hexane isocratic, 1.0 mL/min	6.332	7.197	93

Table SI1. (continued)

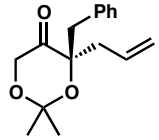
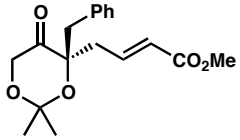
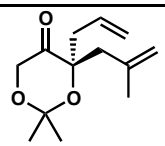
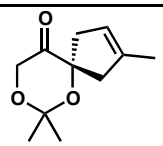
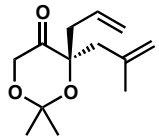
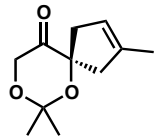
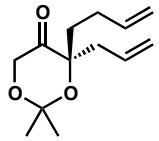
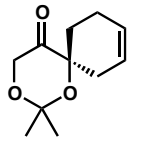
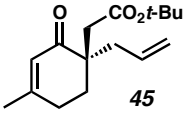
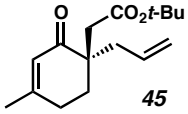
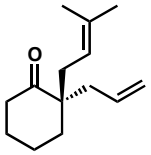
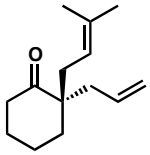
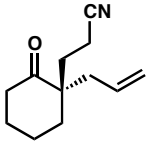
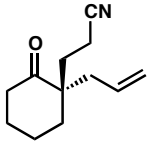
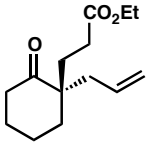
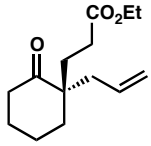
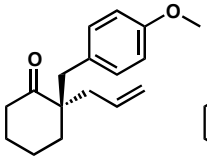
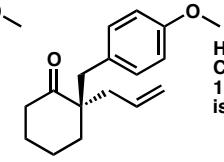
entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
21			HPLC Chiracel OD-H 5% EtOH in hexane isocratic, 1.0 mL/min	9.846	12.111	85
22			GC, G-TA 80 °C isotherm	69.974	62.451	85
23			GC, G-TA 80 °C isotherm	62.170	71.087	88
24			HPLC Chiralpak AD 100% hexane isocratic, 1.0 mL/min detected at 220 nm	11.462	10.307	92
25	 *45*	 *45*	GC, G-TA 130 °C isotherm	59.36	61.19	86
26			GC, G-TA 100 °C isotherm	55.511	52.56	91
27			GC, G-TA 150 °C isotherm	18.75	21.06	88
28			GC, G-TA 120 °C isotherm	90.98	94.22	90
29			HPLC Chiralpak AD 1 % EtOH in hexane isocratic, 1.0 mL/min	12.87	15.36	86

Table SI1. (continued)

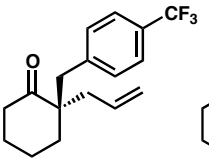
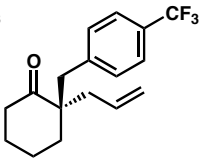
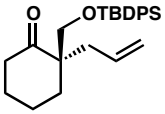
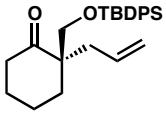
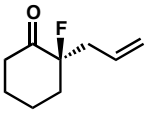
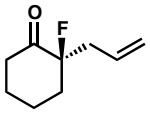
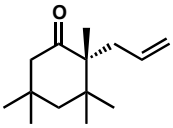
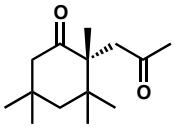
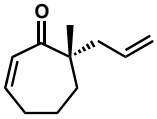
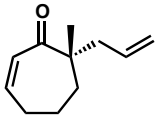
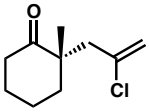
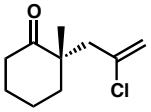
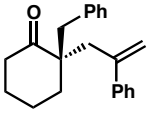
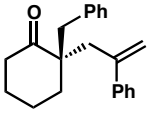
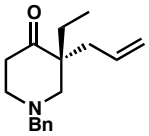
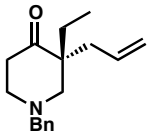
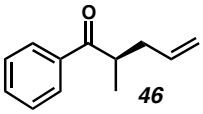
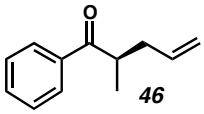
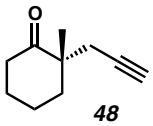
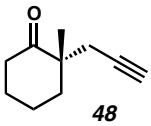
entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
30			GC, G-TA 120 °C isotherm for 120 mins, then ramp 3 °C/min	127.74	126.43	82
31			HPLC Chiracel OD-H 100% hexane isocratic, 1.0 mL/min	16.75	23.91	81
32			GC, G-TA 110 °C isotherm	6.27	8.02	91
33			GC, G-TA 120 °C isotherm	49.12	50.57	85
34			GC, G-TA 125 °C isotherm	10.08	10.61	90
35			GC, G-TA 100 °C isotherm	44.91	50.06	91
36			HPLC Chiralpak AD 2.5% EtOH in hexane isocratic, 1.0 mL/min	6.0	6.5	94
37			HPLC Chiracel OJ 1 % EtOH in hexane isocratic, 1.0 mL/min	7.95	8.82	92
38			HPLC Chiracel OD-H 0.1% IPA in heptane isocratic, 0.7 mL/min	21.63	25.04	70
39			GC, B-DM 90 °C isotherm	21.8	23.0	31

Table SI1. (continued)

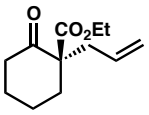
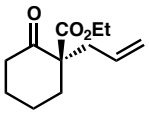
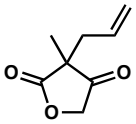
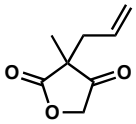
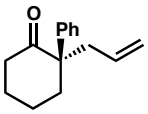
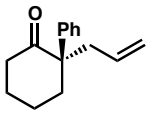
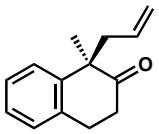
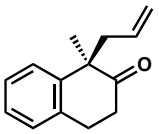
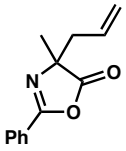
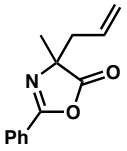
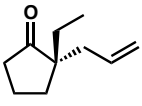
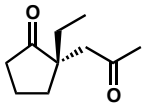
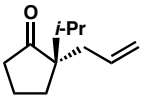
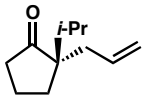
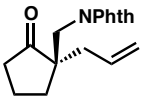
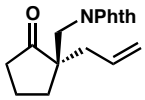
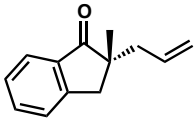
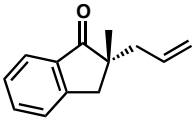
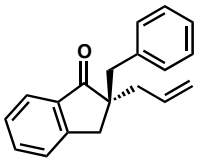
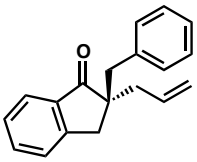
entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
40			GC, G-TA 120 °C isotherm	15.55	16.66	24
41			GC, G-TA 100 °C isotherm	19.67	21.64	2
42			HPLC Chiracel OJ 0.1% IPA in hexane isocratic, 1.0 mL/min	7.76	8.59	11
43			HPLC Chiracel OJ 3% IPA in hexane isocratic, 1.0 mL/min	9.03	7.38	0
44			HPLC Chiracel OD-H 2% IPA in hexane isocratic, 1.0 mL/min	6.61	5.40	2
45			GC, G-TA 110 °C isotherm	45.22	38.91	86
46			GC, G-TA 80 °C isotherm	43.95	49.93	84
47			HPLC Chiracel OD-H 4% IPA in hexane isocratic, 1.0 mL/min	24.13	18.26	48
48			HPLC Chiracel OD-H 0.1% IPA in hexane isocratic, 0.7 mL/min	21.78	23.74	80
49			HPLC Chiracel OJ 1% EtOH in hexane isocratic, 1.0 mL/min	28.93	22.38	71

Table SI1. (continued)

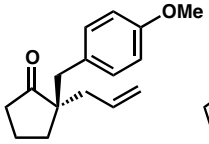
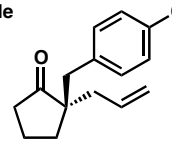
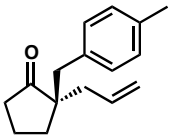
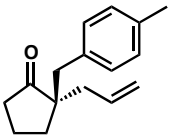
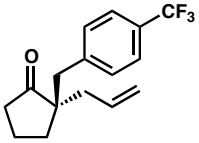
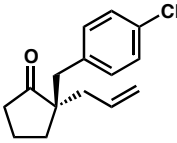
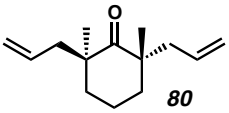
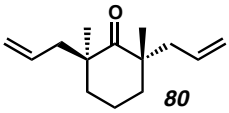
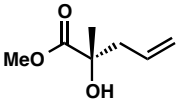
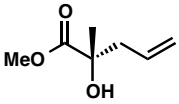
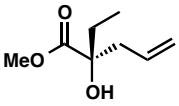
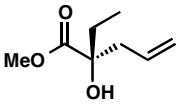
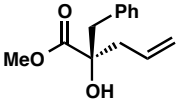
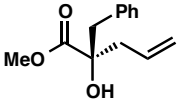
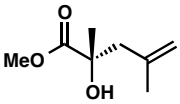
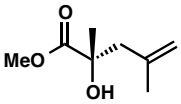
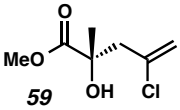
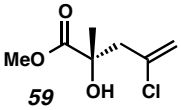
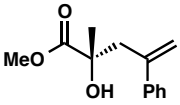
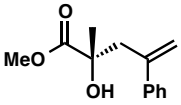
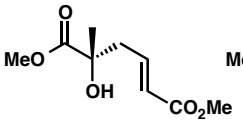
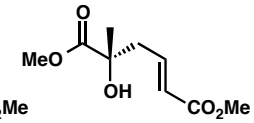
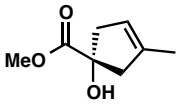
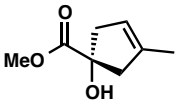
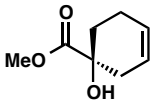
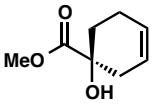
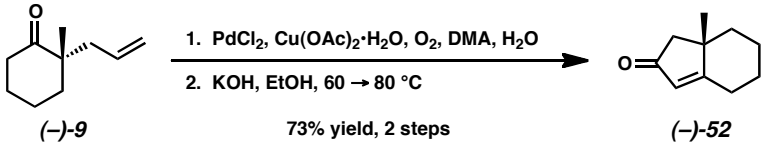
entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
50			HPLC Chiralpak AD 1% IPA in hexane isocratic, 1.0 mL/min	10.07	11.84	73
51			HPLC Chiracel OJ 0.3% EtOH in hexane isocratic, 1.0 mL/min	14.88	12.80	73
52			HPLC Chiralpak AD 1% EtOH in hexane isocratic, 1.0 mL/min	6.42	7.47	60
53			GC, G-TA 75 °C isotherm	118.51	127.37	92
54			GC, G-TA 100 °C isotherm	5.184	4.959	90
55			GC, G-TA 100 °C isotherm	6.314	6.128	93
56			GC, G-TA 110 °C isotherm	57.801	63.226	86
57			GC, G-TA 100 °C isotherm	6.321	6.064	89
58			GC, G-TA 100 °C isotherm	14.338	13.530	91
59			HPLC Chiralpak AD 3% EtOH in hexane isocratic, 1.0 mL/min	10.652	9.773	94

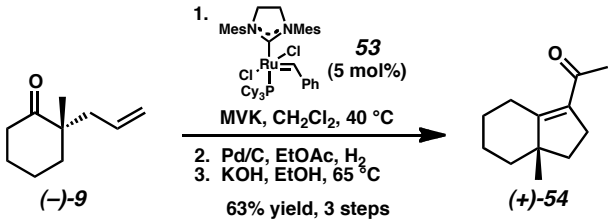
Table SI1. (continued)

entry	product	compound assayed	assay conditions	retention time of major isomer (min)	retention time of minor isomer (min)	% ee
60			GC, G-TA 100 °C isotherm	84.186	92.457	92
61			GC, G-TA 110 °C isotherm	8.300	10.900	86
62			GC, G-TA 85 °C isotherm	59.568	58.072	92

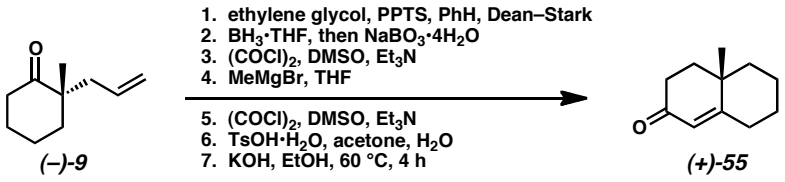
Preparation and Characterization of α-Quaternary Ketone Derivatives



(–)-7a-Methyl-5,6,7,7a-tetrahydro-1*H*-inden-2(4*H*)-one (52, Scheme 9a):[47] To a solution of ketone **9** (98% ee, 304.4 mg, 2.0 mmol, 2.0 equiv) in dimethylacetamide (2.8 mL) and water (0.4 mL) was added $PdCl_2$ (53.1 mg, 1.2 mmol, 0.15 equiv), $Cu(OAc)_2 \bullet H_2O$ (217.9 mg, 1.20 mmol, 0.60 equiv). An oxygen balloon was attached. After 24 h of vigorous stirring at 25 °C the reaction mixture was chromatographed (5→25 % EtOAc in Hexanes on SiO_2). To a solution of the resulting diketone in EtOH (30 mL) was added KOH (3.4 mL of a 50 mg/mL ethanolic solution), and the reaction mixture was heated at 60 °C for 6 h. The temperature was increased to 80 °C and additional KOH (200 mg) was added. After 4 h the reaction was cooled and concentrated. The resulting residue was partitioned between EtOAc (30 mL) and water (20 mL) and acidified to pH 2 with 3 M aq HCl. The layers were separated, and the aqueous layer extracted with EtOAc (3 x 20 mL). The combined organics were washed with brine (30 mL), dried (Na_2SO_4), and concentrated. Chromatography (10→30% Et_2O in pentane on SiO_2) afforded enone **52** (219.1 mg, 72.9% overall yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.74 (s, 1H), 2.62 (br d, *J* = 12.0 Hz, 1H), 2.35 (dt, *J* = 13.5, 5.4 Hz, 1H), 2.27 (dd, *J* = 18.3, 0.9 Hz, 1H), 2.17 (d, *J* = 18.6 Hz, 1H), 2.26-1.88 (m, 2H), 1.64 (m, 2H), 1.36 (m, 2H), 1.22 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.2, 188.6, 126.0, 52.1, 43.1, 40.6, 27.9, 27.8, 24.0, 21.8; IR (Neat Film NaCl) 2934, 1713, 1622, 1221 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{14}O$ [M]$^+$: 150.1045, found 150.1041; $[\alpha]_D^{27}$ –44.86 (*c* 3.55, hexane, 98 % ee).



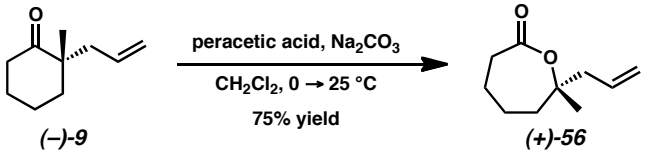
(+)-1-(7a-Methyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-3-yl)ethanone (54, Scheme 9a):[48,49] To a solution of ketone **9** (98% ee, 152.2 mg, 1.0 mmol, 1.0 equiv) and methyl vinyl ketone (208.1 μL, 2.5 mmol, 2.5 equiv) in CH_2Cl_2 (5 mL) was added Grubbs' 2nd generation catalyst (**53**)[50] (42.4 mg, 0.05 mmol, 0.05 equiv). The reaction mixture was heated at 40 °C for 18 h, cooled to 25 °C, and concentrated. Chromatography (20% EtOAc in hexanes on SiO_2) gave the enone (152.1 mg 78.3% yield), which was dissolved in EtOAc (12 mL) and treated with 10% Pd/C (30 mg) under an atmosphere of hydrogen gas for 12 h. The system was purged with argon, filtered through a small pad of silica gel, and concentrated. To a solution of the crude diketone in EtOH (12 mL) was added KOH (2.0 mL of a 50 mg/mL ethanolic solution). The reaction mixture was heated to 65 °C for 8 h, cooled to 25 °C, concentrated, and the residue partitioned between EtOAc (10 mL) and 1 M aq HCl (10 mL) The layers were separated, the aqueous layer extracted with Et_2O (3 x 25 mL), and the combined organics were washed with saturated $NaHCO_3$ (25 mL), then brine (25 mL), dried ($MgSO_4$), and concentrated. Flash chromatography (10→15 % Et_2O in hexanes on SiO_2) gave enone **54** (112.4 mg, 81% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.32 (d, *J* = 14.7 Hz, 1H), 2.59 (m, 2H), 2.23 (s, 3H), 2.01 (app. t, *J* = 13.5 Hz, 1H), 1.82 (m, 3H), 1.59 (m, 3H), 1.43-1.23 (m, 2H), 1.08 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.2, 162.2, 131.9, 48.6, 41.5, 39.0, 30.9, 30.5, 27.1, 25.2, 22.9, 22.0; IR (Neat Film NaCl) 2931, 1678, 1654, 1614, 1357 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{18}O$ [M]$^+$: 178.1358, found 178.1355; $[\alpha]_D^{27}$ +82.9 (*c* 3.26, hexane, 98% ee).



(+)-4a-Methyl-4,4a,5,6,7,8-hexahydronaphthalen-2(3*H*)-one (55, Scheme 9a):[51] A solution of ketone **9** (98% ee, 1.23 g, 8.11 mmol, 1.0 equiv), ethylene glycol (1.8 mL), pyridinium *p*-toluenesulfonate (PPTS, 0.6 g), and benzene (45 mL) was refluxed for 22 h in a Dean-Stark apparatus. The reaction mixture was cooled, poured into saturated aq $NaHCO_3$ (50 mL), the aq layer extracted with 1:1 hexanes:Et_2O (2 x 20 mL). The combined organics were washed with brine (2 x 15 mL), dried ($MgSO_4$), concentrated, and chromatographed to give the ketal (1.59 g). The ketal in THF (15 mL) was added dropwise to a cooled (–25 °C) solution of BH_3•THF (20.3 mmol, 2.5 equiv) in THF (100 mL), and after 4 h was allowed to warm to 25 °C overnight. The reaction mixture was then cooled to –10 °C and water (25 mL) was slowly added, followed by $NaBO_3$•$4H_2O$ (4.99 g, 32.4 mmol, 4.0 equiv), and the reaction mixture was allowed to warm to 25 °C. After 48 h, the reaction mixture was partitioned between water (100 mL) and EtOAc (100 mL), the layers separated, the aq layer extracted with EtOAc (5 x 75 mL), and the organic fractions were dried (Na_2SO_4). Evaporation of the solvents under reduced pressure, and chromatography (20→40% EtOAc in hexanes on SiO_2) gave the primary alcohol (1.50 g, 87% yield).

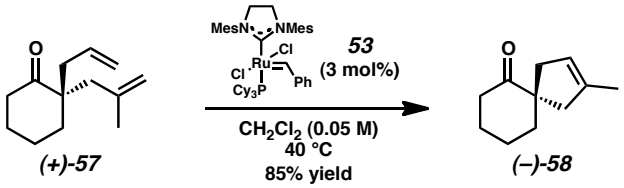
To a cooled (–78 °C) solution of DMSO (479.0 μL, 6.72 mmol, 1.6 equiv) in CH_2Cl_2 (45 mL) was added oxalyl chloride (475.2 μL, 5.45mmol, 1.3 equiv). After 45 min, the primary alcohol (900 mg, 4.19 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) was added in a dropwise manner. After an additional 30 min, Et_3N (2.32 mL, 16.8 mmol, 4.0 equiv) was added, the reaction mixture warmed to 25 °C, and quenched with half-saturated aq $NaHCO_3$. The aq layer was extracted with CH_2Cl_2 (3 x 30 mL), the combined organics dried ($MgSO_4$), and solvents evaporated. This crude aldehyde in THF (45 mL) was cooled to –10 °C, treated with methyl magnesium bromide (3 M soln in Et_2O, 8.40 mmol, 2.0 equiv), quenched with water (20 mL) and saturated aq NH_4Cl (20 mL), extracted CH_2Cl_2 (4 x 20 mL), dried ($MgSO_4$), and solvents evaporated. The resulting crude secondary alcohol was resubmitted to the Swern oxidation conditions described above to give a crude methyl ketone. A solution of the methyl ketone in acetone (45 mL) and water (0.7 mL) was treated with TsOH•H_2O (60 mg), and heated at 50 °C for 4 h. The reaction mixture was then concentrated and chromatographed (7.5→20% EtOAc in hexanes on SiO_2) to give the diketone (515.8 mg, 68% yield for 4 steps).

To a solution of KOH (300 mg 5.36 mmol, 1.91 equiv) in EtOH (40 mL) was added the diketone (510.0 mg, 2.80 mmol, 1.0 equiv) dissolved in EtOH (15 mL), and the reaction mixture heated at 60 °C for 4 h. The reaction was quenched with acetic acid (306 μL, 5.36 mmol, 1.91 equiv), concentrated and chromatographed (5→20% Et_2O in hexanes on SiO_2) to give enone **55** (334.2 mg, 73% yield, 42% overall yield for 7 steps): ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.71 (s, 1H), 2.56-2.22 (m, 4H), 1.92-1.64 (m, 6H), 1.44-1.30 (m, 2H), 1.23 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.6, 170.5, 124.1, 41.5, 38.0, 35.9, 34.0, 32.7, 27.1, 22.0, 21.7; IR (Neat Film NaCl) 2930, 1678 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{16}O$ $[M]^+$: 164.1201, found 164.1196; $[\alpha]_D^{28}$ +216.2 (*c* 1.05, EtOH, 98% ee).

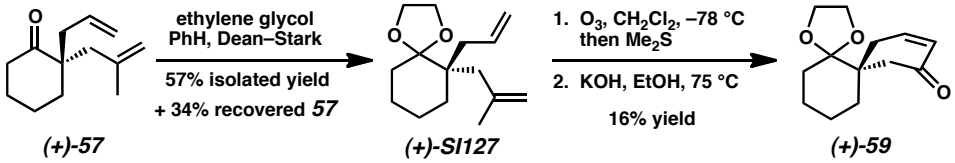


(+)-7-Allyl-7-methyloxepan-2-one (56, Scheme 9a):[52] To a cooled (0 °C) solution of ketone **9** (98% ee, 152.2 mg, 1.0 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL) was added Na_2CO_3 (593.6 mg, 5.6 mmol, 5.6 equiv) and peracetic acid (800 μL of a 32% solution in acetic acid). The reaction mixture was maintained at 0 °C for 9 h, then allowed to warm to 25 °C for an additional 12 h, diluted with saturated

aq $NaHCO_3$, and the organic layer dried (Na_2SO_4). Chromatography (5→20% EtOAc in hexanes on SiO_2) afforded lactone **56** (125.6 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (m, 1H), 5.15 (m, 1H), 5.11 (app. d, *J* = 8.4 Hz, 1H), 2.78-2.61 (m, 2H), 2.51 (dd, *J* = 13.8, 7.2 Hz, 1H), 2.42 (dd, *J* = 14.1, 7.5 Hz, 1H), 1.86-1.62 (m, 6H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 132.8, 119.0, 82.7, 46.7, 38.4, 37.3, 24.8, 23.8, 23.3; IR (Neat Film NaCl) 2936, 1717, 1172 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{10}H_{16}O_2$ [M]$^+$: 168.1150, found 168.1154; $[\alpha]_D^{27}$ +20.58 (*c* 3.46, hexane, 98% ee).



(–)-2-methylspiro[4.5]dec-2-en-6-one (58, Scheme 9b): To a sparged (Ar, 5 min) solution of ketone **57** (91% ee, 526 mg, 2.73 mmol, 1.00 equiv) in CH_2Cl_2 (56 mL) was added the 2nd generation Grubbs catalyst (**53**)[50] (69.6 mg, 0.082 mmol, 0.03 equiv) and the reaction was heated at 40 °C for 10 h. The reaction mixture was cooled to ambient temperature, concentrated, and the residue purified by flash chromatography (1→2% Et_2O in hexanes on SiO_2) to give spiro[4.5]ketone **58** (381 mg, 85% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.14 (m, 1H), 2.86-2.71 (m, 2H), 2.44-2.35 (m, 2H), 2.17 (dddd, *J* = 16.2, 5.4, 4.2, 2.1 Hz, 1H), 2.02 (ddd, *J* = 16.5, 3.0, 1.2 Hz, 1H), 1.88-1.68 (comp. m, 6H), 1.67-1.64 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.3, 137.5, 121.1, 56.3, 45.7, 41.9, 40.3, 39.4, 27.2, 22.2, 16.4; IR (Neat Film NaCl) 3042, 2930, 2860, 1710, 1666, 1438, 1338, 1312, 1207, 1129, 1056, 1019, 899, 853, 838, 807 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{16}O$ [M]$^+$: 164.1201, found 164.1201; $[\alpha]_D^{27.1}$ –21.7 (*c* 2.65, CH_2Cl_2, 91% ee).



(+)-6-Allyl-6-(2-methylallyl)-1,4-dioxaspiro[4.5]decane (SI127, Scheme 9c): A solution of ketone **57** (91% ee, 1.27 g, 6.60 mmol, 1.0 equiv), ethylene glycol (1.8 mL), pyridinium *p*-toluenesulfonate (PPTS, 0.600 g), and benzene (80 mL) was refluxed for 15 h in a Dean-Stark apparatus. The reaction mixture was cooled, poured into saturated aq $NaHCO_3$ (20 mL), and diluted with H_2O (30 mL) and CH_2Cl_2 (30 mL). The aqueous layer extracted with CH_2Cl_2 (3 x 30 mL). The combined organics were dried (Na_2SO_4), concentrated, and purified by flash chromatography (1→2% Et_2O in hexanes on SiO_2) to give ketal **SI127** (889 mg, 57% yield) plus recovered **57** (433.3 mg, 34% recovery). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.02 (dddd, *J* = 16.2, 11.1, 7.2, 7.2 Hz, 1H), 4.95 (app. ddd, *J* = 15.9, 1.8, 1.8 Hz, 1H), 4.95 (app. ddd, *J* = 11.1, 1.2, 1.2 Hz, 1H), 4.85 (app. ddd, *J* = 4.2, 2.4, 1.5 Hz, 1H), 4.78-4.71 (m, 1H), 3.98-3.84 (comp. m, 4H), 2.43-2.17 (comp. m, 4H), 1.82 (s, 3H), 1.67-1.40 (comp. m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7, 136.9, 114.9, 114.8, 112.9, 64.4, 64.1, 45.0, 39.4, 38.1, 33.1, 30.5, 25.6, 23.4, 20.7; IR (Neat Film NaCl) 3073, 2936, 2882, 1638, 1452, 11374, 1275, 1215, 1173, 1089, 1060, 1026, 957, 892 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{15}H_{24}O_2$ [M]$^+$: 236.1776, found 236.1779; $[\alpha]_D^{26.7}$ +5.0 (*c* 2.71, CH_2Cl_2, 91% ee).

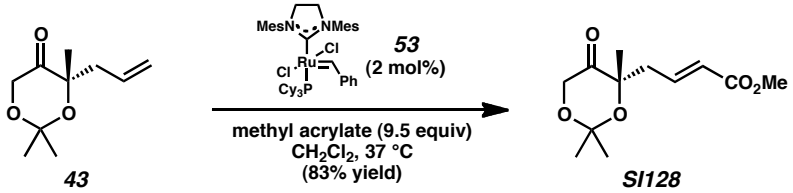
(+)-Spiro[5.5]ketone 59 (Scheme 9c): Through a cooled (–78 °C) solution of ketal **SI127** (441 mg, 1.86 mmol, 1.00 equiv) in CH_2Cl_2 (40 mL) was bubbled a stream of ozone until the reaction mixture turned blue. The reaction mixture was quenched with dimethyl sulfide (0.50 mL), allowed to warm to ambient temperature, and concentrated to an oil. This residue was dissolved in EtOH (35 mL), treated with an ethanolic KOH solution (3.0 mL of 50 mg/mL), and heated to 75 °C for 3 h. The reaction mixture was cooled to ambient temperature, neutralized with acetic acid, concentrated, and purified by flash chromatography (5→25% EtOAc in hexanes on SiO_2) to give spiro[5.5]ketone **59** (65.7 mg, 16% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.84 (ddd, *J* = 10.2, 5.7, 2.7 Hz, 1H), 5.98 (app. dd, *J* = 9.9, 3.0

Hz, 1H), 4.02-3.87 (comp. m, 4H), 2.66 (ddd, *J* = 19.2, 2.7, 2.7 Hz, 1H), 2.64 (d, *J* = 16.2 Hz, 1H), 2.46 (d, *J* = 15.9 Hz, 1H), 2.33 (ddd, 19.2, 6.0, 1.5 Hz, 1H) 1.68-1.50 (comp. m, 6H), 1.48-1.34 (comp. m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 199.9, 148.1, 128.5, 111.1, 65.0 (2C), 44.7, 43.3, 31.5, 31.1, 30.1, 23.1, 20.4; IR (Neat Film NaCl) 2935, 2865, 1677, 1448, 1389, 1346, 1253, 1179, 1142, 1101, 1063, 1022, 961, 909, 885, 736 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{13}H_{17}O_3$ [(M + H) – H_2]$^+$: 221.1178, found 221.1185; $[\alpha]_D^{28.1}$ +27.9 (*c* 1.13, CH_2Cl_2, 91% ee).

Preparation of Derivative Compounds from Dioxanones

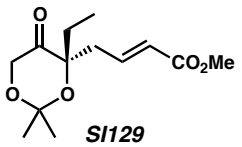
Synthesis of of α,β-Unsaturated Esters by Cross Metathesis.

Representative Procedure for the Synthesis of α,β-Unsaturated Esters:



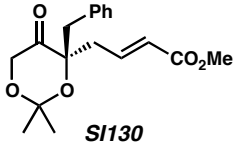
43 *SI128*

(*E*)-Methyl-4-(2,2,4-trimethyl-5-oxo-1,3-dioxan-4-yl)but-2-enoate (SI128): To a solution of terminal olefin **43** (30.0 mg, 0.163 mmol, 1 equiv) and methyl acrylate (0.14 mL, 1.55 mmol, 9.5 equiv) in CH_2Cl_2 (1.6 mL, 0.1 M) was added Grubbs' second generation catalyst **53** (2.8 mg, 0.0033 mmol, 0.02 equiv) at room temperature (ca. 25°C). The mixture was stirred at 37 °C for 40 h. Ethyl vinyl ether (0.5 mL) was added, and the mixture was stirred at 37 °C for 10 min. The mixture was filtered through silica gel with Et_2O/petroleum ether (1:2) as eluent. After the filtrate was evaporated under reduced pressure (~60 mmHg), the residue was purified by flash column chromatography (10% Et_2O in petroleum ether on silica gel) to give the α,β-unsaturated ester (32.8 mg, 83% yield). Colorless oil; R_f 0.23 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (dt, *J* = 15.6, 7.8 Hz, 1H), 5.87 (dt, *J* = 15.6, 1.3 Hz, 1H), 4.23 (s, 2H), 3.73 (s, 3H), 2.71–2.63 (m, 1H), 2.54–2.47 (m, 1H), 1.50 (s, 3H), 1.45 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.1, 166.7, 143.1, 124.7, 100.5, 81.5, 66.8, 51.7, 41.3, 27.5, 26.2, 24.5; IR (Neat Film NaCl) 2992, 2951, 1727, 1659, 1437, 1374, 1338, 1274, 1231, 1197, 1180, 1155, 1117, 1008, 990 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{12}H_{19}O_5$ [M + H]$^+$: 243.1232, found 243.1224; $[\alpha]_D^{24.8}$ –49.7 (*c* 0.715, CH_2Cl_2, 90% ee).



SI129

(*E*)-Methyl 4-(4-ethyl-2,2-dimethyl-5-oxo-1,3-dioxan-4-yl)but-2-enoate (SI129): 89% yield. Colorless oil; R_f 0.19 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.92 (dt, *J* = 15.6, 7.6 Hz, 1H), 5.88 (dt, *J* = 15.6, 1.5 Hz, 1H), 4.21 (s, 2H), 3.74 (s, 3H), 2.71–2.53 (m, 2H), 1.92–1.78 (m, 2H), 1.51 (s, 3H), 1.49 (s, 3H), 0.90 (t, *J* = 7.4 H, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.0, 166.7, 143.3, 124.6, 100.2, 84.6, 67.3, 51.7, 39.2, 30.4, 27.3, 26.4, 7.8; IR (Neat Film NaCl) 2985, 1726, 1658, 1435, 1383, 1373, 1271, 1232, 1196, 1177, 1084, 1033, 1013 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{21}O_5$ [M + H]$^+$: 257.1389, found 257.1385; $[\alpha]_D^{24.9}$ –3.14 (*c* 0.655, CH_2Cl_2, 94% ee).

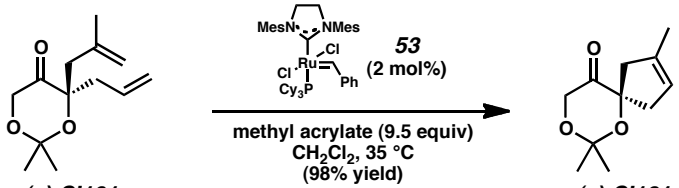


SI130

(*E*)-Methyl 4-(4-benzyl-2,2-dimethyl-5-oxo-1,3-dioxan-4-yl)but-2-enoate (SI130): 75% yield. Colorless oil; R_f 0.19 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.13 (m, 5H), 7.00 (ddd, *J* = 15.6, 8.1, 7.2 Hz, 1H), 5.89 (dt, *J* = 15.9, 1.5 Hz, 1H), 4.06 (d, *J* = 18.0 Hz, 1H), 3.86 (d, *J* = 18.0 Hz, 1H), 3.74 (s, 3H), 3.06 (d, *J* = 13.5 Hz, 1H), 2.94 (d, *J* = 13.5 Hz, 1H), 2.72 (ddd, *J*= 14.4, 6.9,

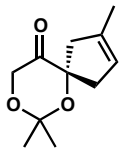
1.2 Hz, 1H), 2.58 (ddd, J = 14.4, 8.1, 1.2 Hz, 1H), 1.48 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 209.3, 166.7, 142.9, 135.5, 131.1, 128.1, 127.1, 124.9, 100.3, 84.8, 67.5, 51.8, 43.8, 40.8, 27.0, 26.3; IR (Neat Film NaCl) 2992, 2950, 1725, 1658, 1435, 1385, 1374, 1271, 1234, 1198, 1171, 1114, 1098, 1054, 988, 702 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{18}H_{22}O_5$ [M]$^+$: 318.1467, found 318.1469; $[\alpha]_D^{27.1}$ +14.9 (*c* 0.550, CH_2Cl_2, 85% ee).

Synthesis of Spiro Compounds by Ring-Closing Metathesis.
Representative Procedure for the Synthesis of Spiro Compounds:



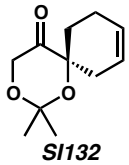
(+)-SI101 *(+)-SI131*

(+)-2,7,7-Trimethyl-6,8-dioxaspiro[4.5]dec-2-en-10-one ((+)-SI131): To a solution of diene (60 mg, 0.268 mmol, 1.0 equiv) in CH_2Cl_2 (10 mL) was added Grubbs' second generation catalyst **53** (4.6 mg, 0.0054 mmol, 0.02 equiv) at room temperature. After the mixture was stirred at 35 °C for 40 h, it was concentrated under reduced pressure. The residue was purified by flash chromatography (2% Et_2O in petroleum ether on silica gel) to give the spirocyclopentene (51.4 mg, 98% yield) as a colorless oil. R_f 0.37 (20% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.22–5.20 (m, 1H), 4.31 (s, 2H), 2.91–2.52 (m, 4H), 1.73–1.71 (m, 3H), 1.49 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 210.1, 137.1, 120.8, 100.2, 88.3, 66.8, 48.5, 45.0, 27.0, 26.8, 16.5; IR (Neat Film NaCl) 2991, 2941, 1740, 1426, 1382, 1372, 1231, 1199, 1152, 1098, 1058, 988, 846 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{11}H_{16}O_3$ [M]$^+$: 196.1100, found 196.1095; $[\alpha]_D^{23.1}$ +19.2 (*c* 0.725, CH_2Cl_2, 85% ee).



(–)-SI131

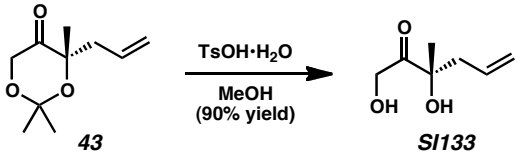
(–)-2,7,7-Trimethyl-6,8-dioxaspiro[4.5]dec-2-en-10-one ((–)-SI131): 87% yield. Colorless oil; R_f 0.37 (20% Et_2O in hexanes); $[\alpha]_D^{24.0}$ –20.4 (*c* 0.885, CH_2Cl_2, 88% ee).



SI132

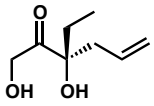
2,2-dimethyl-1,3-dioxaspiro[5.5]undec-8-en-5-one (SI132): 90% yield. Colorless oil; R_f 0.24 (10% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.80–5.70 (m, 1H), 5.67–5.58 (m, 1H), 4.27 (s, 2H), 2.60–2.47 (m, 1H), 2.38–2.18 (m, 2H), 2.17–1.81 (m, 3H), 1.51 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.1, 126.4, 122.8, 100.5, 79.9, 66.6, 33.5, 29.9, 27.7, 26.3, 21.8; IR (Neat Film NaCl) 3030, 2991, 2938, 2911, 1739, 1429, 1382, 1372, 1259, 1230, 1200, 1155, 1099, 1062, 999, 886, 836, 778, 651 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{11}H_{16}O_3$ [M]$^+$: 196.1100, found 196.1139; $[\alpha]_D^{20.2}$ –20.9 (*c* 1.045, CH_2Cl_2, 92% ee).

Acetonide Cleavage: Representative Procedure for the Synthesis of Diols



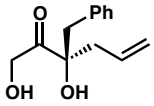
43 ***SI133***

1,3-Dihydroxy-3-methylhex-5-en-2-one (SI133): To a solution of acetonide **43** (80.5 mg, 0.44 mmol, 1.0 equiv) in MeOH (4.4 mL, 0.1 M) was added *p*-toluenesulfonic acid monohydrate (8.3 mg, 0.044 mmol, 0.1 equiv) at room temperature (ca. 25 °C). After the mixture was stirred for 3.5 h, Et_3N (0.2 mL) was added. The mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (30% EtOAc in hexanes on silica gel) to give the diol (57.4 mg, 90% yield) as a colorless oil. R_f 0.21 (33% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.79–5.65 (m, 1H), 5.23–5.14 (m, 2H), 4.55 (dd, *J* = 20.0, 5.1 Hz, 1H), 4.46 (dd, *J* = 20.0, 5.1 Hz, 1H), 2.92 (t, *J* = 5.1 Hz, 1H), 2.74 (s, 1H), 2.57–2.50 (m, 1H), 2.42–2.35 (m, 1H), 1.39 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.1, 131.5, 120.8, 78.2, 65.3, 44.5, 25.6; IR (Neat Film NaCl) 3413, 2980, 1721, 1641, 1414, 1370, 1169, 1019, 923 cm^{-1}; HRMS (ES+) *m/z* calc'd for $C_7H_{13}O_3$ $[M + H]^+$: 145.0865, found 145.0850; $[\alpha]_D^{23.5}$ –14.2 (*c* 0.810, CH_2Cl_2, 90% ee).



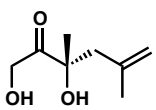
SI134

1,3-Dihydroxy-3-ethylhex-5-en-2-one (SI134): 97% yield. Colorless oil; R_f 0.32 (33% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.76–5.62 (m, 1H), 5.20–5.12 (m, 2H), 4.47 (dd, *J* = 19.8, 4.8 Hz, 1H), 4.40 (dd, *J* = 19.8, 4.8 Hz, 1H), 2.94 (t, *J* = 4.8 Hz, 1H), 2.84 (s, 1H), 2.53–2.38 (m, 2H), 1.86–1.64 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.1, 131.6, 120.5, 81.1, 66.2, 43.6, 32.2, 7.7; IR (Neat Film NaCl) 3436, 2976, 1717, 1641, 1414, 1272, 1158, 1111, 1042, 922 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{14}O_3$ $[M]^+$: 158.0943, found 158.0948; $[\alpha]_D^{24.0}$ –0.37 (*c* 0.715, CH_2Cl_2, 93% ee).



SI135

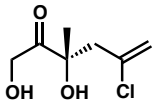
1,3-Dihydroxy-3-benzylhex-5-en-2-one (SI135): 91% yield. Colorless oil; R_f 0.50 (33% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.24 (m, 3H), 7.13 (dd, *J* = 7.4, 1.9 Hz, 2H), 5.81–5.67 (m, 1H), 5.23–5.14 (m, 2H), 4.41 (dd, *J* = 20.1, 4.8 Hz, 1H), 4.07 (dd, *J* = 20.1, 4.8 Hz, 1H), 3.14 (d, *J* = 13.8 Hz, 1H), 2.92–2.86 (m, 2H), 2.65 (dd, *J* = 13.8, 7.4 Hz, 1H), 2.51 (s, 1H), 2.45–2.38 (dd, *J* = 14.1, 7.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 134.8, 131.5, 130.3, 128.9, 127.6, 120.8, 81.4, 67.2, 45.2, 43.7; IR (Neat Film NaCl) 3436, 3079, 3030, 2917, 1717, 1640, 1496, 1454, 1429, 1412, 1259, 1098, 1043, 978, 924, 759, 703 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{16}O_3$ $[M]^+$: 220.1100, found 220.1069; $[\alpha]_D^{23.3}$ +16.1 (*c* 0.690 CH_2Cl_2, 86% ee).



SI136

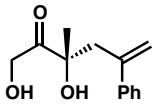
1,3-Dihydroxy-3,5-dimethylhex-5-en-2-one (SI136): 97% yield. Colorless oil; R_f 0.36 (33% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.98–4.97 (m, 1H), 4.79 (d, *J* = 0.9 Hz, 1H), 4.59 (dd, *J* = 20.0, 4.8 Hz, 1H), 4.46 (dd, *J* = 20.0, 4.8 Hz, 1H), 2.96 (t, *J* = 4.8 Hz, 1H), 2.74 (s, 1H), 2.62 (d, *J* = 14.0 Hz, 1H), 2.35 (d, *J* = 14.0 Hz, 1H), 1.70 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.8, 140.8, 116.6, 78.1, 65.5, 47.9, 26.6, 24.2; IR (Neat Film NaCl) 3429, 3078, 2976, 2917, 1720, 1644,

1452, 1373, 1229, 1135, 1101, 1024, 898 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{14}O_3$ $[M]^+$: 158.0943, found 158.0943; $[\alpha]_D^{23.3}$ –24.2 (*c* 0.420 CH_2Cl_2, 89% ee).



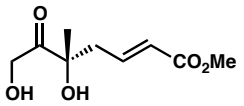
61

(*S*)-5-Chloro-1,3-dihydroxy-3-methylhex-5-en-2-one (61, Scheme 9d): 97% yield. Colorless oil; R_f 0.30 (33% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.38 (d, *J* = 0.9 Hz, 1H), 5.28 (d, *J* = 0.9 Hz, 1H), 4.65 (dd, *J* = 19.8, 5.1 Hz, 1H), 4.54 (dd, *J* = 19.8, 4.8 Hz, 1H), 2.96-2.91 (m, 3H), 2.74 (d, *J* = 14.7 Hz, 1H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.5, 136.0, 118.4, 78.0, 65.6, 49.2, 26.3; IR (Neat Film NaCl) 3422, 2981, 2922, 1722, 1633, 1452, 1416, 1371, 1267, 1167, 1087, 1021, 981, 895 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_7H_9ClO_2$ $[M\text{-}H_2O]^+$: 160.0291, found 160.0298; $[\alpha]_D^{21.2}$ –16.7 (*c* 1.000, CH_2Cl_2, 91% ee).



SI137

1,3-Dihydroxy-3-methyl-phenylhex-5-en-2-one (SI137): 92% yield. Colorless oil; R_f 0.27 (33% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35–7.26 (m, 5H), 5.41 (d, *J* = 1.2 Hz, 1H), 5.17 (d, *J* = 0.9 Hz, 1H), 4.41 (dd, *J* = 20.3, 5.0 Hz, 1H), 4.18 (dd, *J* = 20.3, 5.0 Hz, 1H), 3.12 (d, *J* = 14.0 Hz, 1H), 2.86 (d, *J* = 14.0 Hz, 1H), 2.66 (t, *J* = 5.0 Hz, 1H), 2.46 (s, 1H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 214.5, 143.7, 140.8, 128.9, 128.4, 126.8, 118.8, 78.7, 65.7, 45.6, 26.4; IR (Neat Film NaCl) 3431, 2977, 2931, 1719, 1625, 1494, 1445, 1406, 1369, 1142, 1021, 908, 780, 700 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{16}O_3$ $[M]^+$: 220.1100, found 220.1116; $[\alpha]_D^{20.6}$ –9.82 (*c* 0.355, CH_2Cl_2, 94% ee).

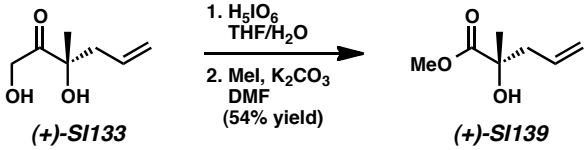


SI138

(*E*)-Methyl 5,7-dihydroxy-5-methyl-6-oxohept-2-enoate (SI138): 80% yield. Colorless oil; R_f 0.58 (50% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.85 (m, 1H), 5.94–5.88 (m, 1H), 4.52 (d, *J* = 5.1 Hz, 2H), 3.73 (s, 3H), 2.99–2.90 (m, 2H), 2.69-2.50 (m, 2H), 1.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 213.5, 166.6, 142.1, 125.5, 78.2, 65.1, 51.9, 42.4, 25.7; IR (Neat Film NaCl) 3436, 2954, 1721, 1658, 1439, 1339, 1280, 1204, 1021 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_9H_{15}O_5$ $[M + H]^+$: 203.0919, found 203.0918; $[\alpha]_D^{18.5}$ –8.35 (*c* 0.695, CH_2Cl_2, 92% ee).

Synthesis of Hydroxyesters by Oxidation and Methylation.

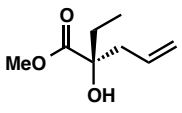
Representative Procedure for the Synthesis of α-Hydroxy Esters:



(+)-SI133 ***(+)-SI139***

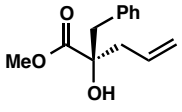
Hydroxy-2-methyl-4-pentanoate (SI139):[53] To a solution of diol (53.4 mg, 0.37 mmol, 1 equiv) in THF and water (THF/H_2O, 2:1, 11.1 mL, 0.033 M) was added H_5IO_6 (127 mg, 0.50 mmol, 1.5 equiv) at room temperature (ca. 25 °C). After the mixture was stirred at room temperature for 24 h, the mixture was extracted with Et_2O (3 x 30 mL). The organic layer was washed with water (3 mL) and brine (3 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was dissolved in DMF (3.7 mL, 0.1 M) and then K_2CO_3 (27.6 mg, 0.44 mmol, 1.2 equiv) and MeI (27.6 μL, 0.44 mmol, 1.2 equiv) were added successively. After stirring for 1 h at room temperature, water (5 mL) was

added, and the reaction was extracted with Et_2O (3 x 30 mL). The combined organic layers were washed with water (3 mL) and brine (3 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure (~80 mmHg). The residue was purified by flash chromatography (10% Et_2O in petroleum ether on silica gel) to give the methyl ester (28.9 mg, 54% yield, 90% ee). Colorless oil; R_f 0.48 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84–5.70 (m, 1H), 5.15 (s, 1H), 5.12–5.07 (m, 1H), 3.77 (s, 3H), 3.10 (s, 1H), 2.35–2.54 (m, 2H), 1.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 132.6, 119.3, 74.7, 52.9, 44.9, 25.7; IR (Neat Film NaCl) 3504, 2982, 2955, 1736, 1642, 1455, 1437, 1372, 1271, 1227, 1170, 1143, 1069, 1000, 980, 920 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_7H_{13}O_3$ $[M + H]^+$: 145.0865, found 145.0867; $[\alpha]_D^{22.7}$ +25.6 (*c* 0.365, CH_2Cl_2, 90% ee).



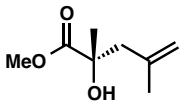
SI140

Hydroxy-2-ethyl-4-pentanoate (SI140): 60% yield. Colorless oil; R_f 0.59 (33% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.84–5.70 (m, 1H), 5.13–5.06 (m, 2H), 3.77 (s, 3H), 3.16 (s, 1H), 2.51–2.37 (m, 2H), 1.85–1.63 (m, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 132.7, 119.0, 78.2, 52.8, 43.8, 32.0, 8.1; IR (Neat Film NaCl) 3524, 2956, 1735, 1641, 1446, 1246, 1225, 1163, 1028, 999, 974, 919 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{15}O_3$ $[M + H]^+$: 159.1021, found 159.1026; $[\alpha]_D^{20.4}$ +24.3 (*c* 0.350, CH_2Cl_2, 93% ee).



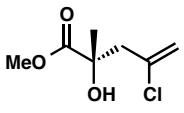
SI141

Hydroxy-2-benzyl-4-pentanoate (SI141): 85% yield. Colorless oil; R_f 0.52 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31–7.11 (m, 5H), 5.88–5.74 (m, 1H), 5.16–5.11 (m 2H), 3.72 (s, 3H), 3.07 (d, *J* = 13.5 Hz, 1H), 3.07 (s, 1H), 2.95 (d, *J* = 13.5 Hz, 1H), 2.65–2.46 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 175.7, 135.9, 132.5, 130.3, 128.4, 127.2, 119.2, 78.4, 52.7, 45.3, 43.8; IR (Neat Film NaCl) 3522, 3030, 2954, 1736, 1640, 1495, 1455, 1442, 1272, 1229, 1142, 1093, 920, 701 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{16}O_3$ $[M]^+$: 220.1100, found 220.1105; $[\alpha]_D^{23.4}$ +41.8 (*c* 0.890, CH_2Cl_2, 86% ee).



SI142

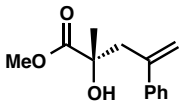
Methyl 2-hydroxy-2,4-dimethyl-pent-4-enoic acid methyl ester (SI142):[54] 84% yield. Colorless oil; R_f 0.38 (20% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.89–4.88 (m, 1H), 4.75 (s, 1H), 3.77 (s, 3H), 3.12 (s, 1H), 2.53 (d, *J* = 13.8 Hz, 1H), 2.37 (d, *J* = 13.8 Hz, 1H), 1.74 (s, 3H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.4, 141.4, 115.2, 74.9, 52.8, 48.2, 26.6, 24.0; IR (Neat Film NaCl) 3514, 2954, 1736, 1644, 1452, 1375, 1266, 1212, 1156, 1114, 896 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{14}O_3$ $[M]^+$: 158.0943, found 158.0946; $[\alpha]_D^{22.0}$ +11.4 (*c* 0.220, CH_2Cl_2, 89% ee).



62

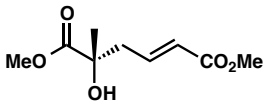
(*S*)-Methyl 4-chloro-2-hydroxy-2-methylpent-4-enoate (62, Scheme 9d):[55] 76% yield. Colorless oil; R_f 0.48 (33% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.33 (d, *J* = 0.9 Hz, 1H), 5.26 (d, *J* = 0.9 Hz, 1H), 3.80 (s, 3H), 3.32 (s, 1H), 2.86 (d, *J* = 14.3 Hz, 1H), 2.72 (d, *J* = 14.3 Hz, 1H), 1.47 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 136.6, 117.2, 73.6, 53.1, 49.6, 26.4; IR (Neat Film NaCl)

3507, 2987, 2955, 1738, 1633, 1454, 1436, 1278, 1230, 1167, 887 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_7H_{11}ClO_3$ $[M]^+$: 178.0397, found 178.0399; $[\alpha]_D^{19.0}$ +0.79 (*c* 1.190, CH_2Cl_2, 91% ee).



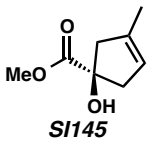
SI143

Methyl 2-hydroxy-2-methyl-4-phenyl-4-pentanoate (SI143):[54,56] 77% yield. Colorless oil; R_f 0.52 (33% EtOAc in hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 7.36–7.24 (m, 5H), 5.34 (d, *J* = 1.5 Hz, 1H), 5.17 (s, 1H), 3.18 (s, 3H), 3.07 (d, *J* = 13.5 Hz, 2H), 2.80 (d, *J* = 13.5 Hz, 1H), 1.45 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.4, 144.1, 141.4, 128.3, 127.7, 126.9, 118.1, 74.3, 52.3, 46.4, 26.1; IR (Neat Film NaCl) 3514, 2981, 2952, 1736, 1626, 1494, 1447, 1269, 1214, 1129, 980, 906, 778, 709 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_{13}H_{16}O_3$ $[M]^+$: 220.1100, found 220.1108; $[\alpha]_D^{19.9}$ –4.09 (*c* 0.610, CH_2Cl_2, 94% ee).



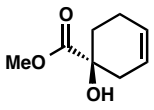
SI144

Hydroxy-5-methyl-hex-2-endioic acid dimethyl ester (SI144):[57] 51% yield. Colorless oil; R_f 0.44 (50% EtOAc in hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 6.89 (dt, *J* = 15.6, 7.7 Hz, 1H), 5.89 (dt, *J* = 15.6, 1.5 Hz, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.19 (s, 1H), 2.67–2.52 (m, 2H), 1.44 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 166.6, 142.9, 124.9, 74.3, 53.3, 51.7, 42.8, 26.2; IR (Neat Film NaCl) 3485, 2955, 1725, 1659, 1438, 1336, 1271, 1198, 1179, 1123, 1059, 1038, 983 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_9H_{15}O_5$ $[M + H]^+$: 203.0919, found 203.0911; $[\alpha]_D^{20.2}$ –1.06 (*c* 0.220, CH_2Cl_2, 92% ee).



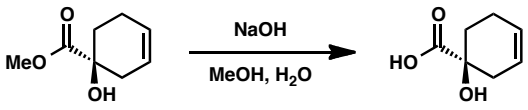
SI145

Methyl 1-hydroxy-3-methylcyclopent-3-enecarboxylate (SI145): 48% yield. Colorless oil; R_f 0.52 (33% EtOAc in hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 5.30–5.25 (m, 1H), 3.81 (s, 3H), 3.24 (s, 1H), 2.94–2.89 (m, 2H), 2.54–2.46 (m, 1H), 2.42 (d, *J* = 16.8 Hz, 1H), 1.76 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 137.4, 121.1, 80.8, 53.1, 50.9, 47.5, 16.5; IR (Neat Film NaCl) 3469, 2916, 1735, 1437, 1285, 1211, 1090, 1018, 960, 901 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{12}O_3$ $[M]^+$: 156.0786, found 156.0786; $[\alpha]_D^{21.1}$ +2.51 (*c* 0.360, CH_2Cl_2, 86% ee).



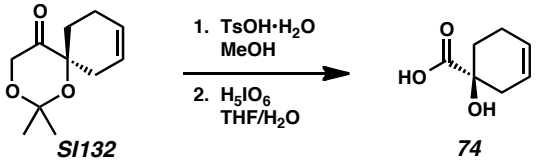
SI146

Hydroxy-cyclohex-3-ene carboxylic acid methyl ester (SI146):[58] 61% yield. Colorless oil; R_f 0.56 (33% EtOAc in hexanes); ^1H NMR (300 MHz, $CDCl_3$) δ 5.86–5.74 (m, 1H), 5.70–5.58 (m, 1H), 3.80 (s, 1H), 2.98 (s, 1H), 2.65–2.54 (m, 1H), 2.40–2.24 (m, 1H), 2.17–2.05 (m, 2H), 2.00–1.89 (m, 1H), 1.84–1.71 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 177.5, 126.6, 123.0, 72.5, 53.0, 35.2, 30.9, 21.6; IR (Neat Film NaCl) 3471, 3029, 2954, 2915, 1732, 1437, 1278, 1258, 1223, 1096, 1058, 887 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{12}O_3$ $[M]^+$: 156.0786, found 156.0794; $[\alpha]_D^{20.9}$ +32.7 (*c* 0.660, CH_2Cl_2, 92% ee).



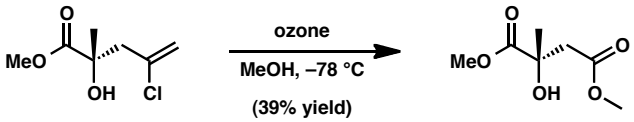
SI146 ***74***

Hydroxy-cyclohex-3-ene carboxylic acid (**74, Scheme 10d**).[58] To a solution of methyl ester **SI146** (48.0 mg, 0.307 mmol, 1 equiv) in MeOH (3.0 mL, 0.1 M) was added 1 N NaOH (aq) (0.37 mL, 0.37 mmol, 1.2 equiv) at room temperature (ca. 25 °C). After stirring for 18 h, the mixture was concentrated under reduced pressure. To the residue was added 1 N HCl (aq) (1.0 mL) and the mixture was extracted with Et_2O (3 x 20 mL). The combined organic layers were washed with brine (5.0 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give carboxylic acid **74** (41.5 mg, 95% yield, 92% ee) as a white solid: mp 79–81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88–5.79 (m, 1H), 5.72–5.61 (m, 1H), 2.79–2.62 (m, 1H), 2.37–2.11 (m, 4H), 1.95–1.80 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.5, 126.6, 122.6, 72.6, 34.9, 30.6, 21.4; IR (Neat Film NaCl) 3432, 3032, 2929, 2624, 1736, 1443, 1370, 1356, 1318, 1253, 1216, 1092, 1064, 982, 939, 886, 773, 746, 650, 736 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{12}O_3$ [M]$^+$: 143.0708, found 143.0708; $[\alpha]_D^{20.7}$ +31.7 (*c* 0.310, CH_2Cl_2, 92% ee).



SI132 ***74***

Hydroxy-cyclohex-3-ene carboxylic acid (74, Scheme 10d):[58] To a solution of acetonide **SI132** (40 mg, 0.20 mmol, 1.0 equiv) in MeOH (4 mL, 0.05 M) was added *p*-toluenesulfonic acid monohydrate (3.9 mg, 0.02 mmol, 0.1 equiv) at room temperature (24 °C). After the mixture was stirred for 3 h, Et_3N (0.1 mL) was added. The mixture was concentrated under reduced pressure to give a yellow oil. The oil was diluted with EtOAc (10 mL), filtered through SiO_2 (1 mL), and concentrated under reduced pressure to furnish a white solid (35 mg). The solid was dissolved in THF (0.4 mL) and water (0.2 mL), and the colorless solution was cooled to 0 °C (ice water bath) and then H_5IO_6 (46 mg, 0.20 mmol, 1 equiv) was added to the solution. The mixture was allowed to warm to room temperature (26 °C) over 10 min, and then stirred for 2 h. The reaction was diluted with water (0.5 mL), and extracted with EtOAc (4 x 15 mL). The combined extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting white solid was purified by column chromatography over silica gel (ca. 9 mL) with 2:1 Hexanes/EtOAc eluent to give carboxylic acid **74** (16.3 mg, 56% yield, 92% ee) as a white solid.



62 ***63***

(*S*)-Dimethyl citramalate (63, Scheme 9d):[59] Ozone was bubbled through a colorless solution of alkene **62** (25 mg, 0.14 mmol, 1 equiv) in MeOH (0.52 mL, 0.27 M) at –78 °C until the solution turned blue (50 min). The blue solution was flushed with nitrogen gas until it turned colorless, at which point it was treated with sodium sulfite (79 mg, 4.5 equiv). The mixture was allowed to warm to room temperature overnight (ca. 25 °C), at which point it was diluted with Et_2O (to 30 mL), filtered, and concentrated under vacuum to yield dimethyl citramalate (**63**) as a colorless oil (9.7 mg, 39% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H), 3.80 (s, 3H), 2.97 (d, *J* = 16.5 Hz, 1H), 2.67 (d, *J* = 16.5 Hz, 1H), 1.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.2, 171.7, 72.8, 53.2, 52.2, 44.2, 26.5; IR (Neat Film NaCl) 3500, 2988, 2957, 2851, 1740, 1439, 1356, 1292, 1207, 1120, 1012, 983 cm^{-1}; HRMS (EI+) *m/z* calc'd for $C_8H_{12}O_3$ [M]$^+$: 170.0763, found 170.0750; $[\alpha]_D^{23.6}$ +13.4 (*c* 0.485, $CHCl_3$). Comparison of optical rotation to literature data established the *S* absolute configuration.[59]

For conversion of ketone (–)-**64** to the natural product (+)-dichroanone (**66**), see ref 60.

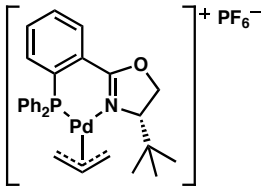
For preparation of ketone (–)-**67** and conversion to the natural products laurencenone B (**68**) and (+)-elatol (**69**), see ref 61.

For conversion of ketone (–)-**70** to the ABC tricycle (**71**) toward the natural product zoanthenol (**72**), see ref 62.

For the conversion of carboxylic acid **74** to quinic acid (**75**), see ref 58.

For conversion of vinylogous thioester **76** to the carissone (**77**) and cassiol (**78**), see refs 63 and 64.

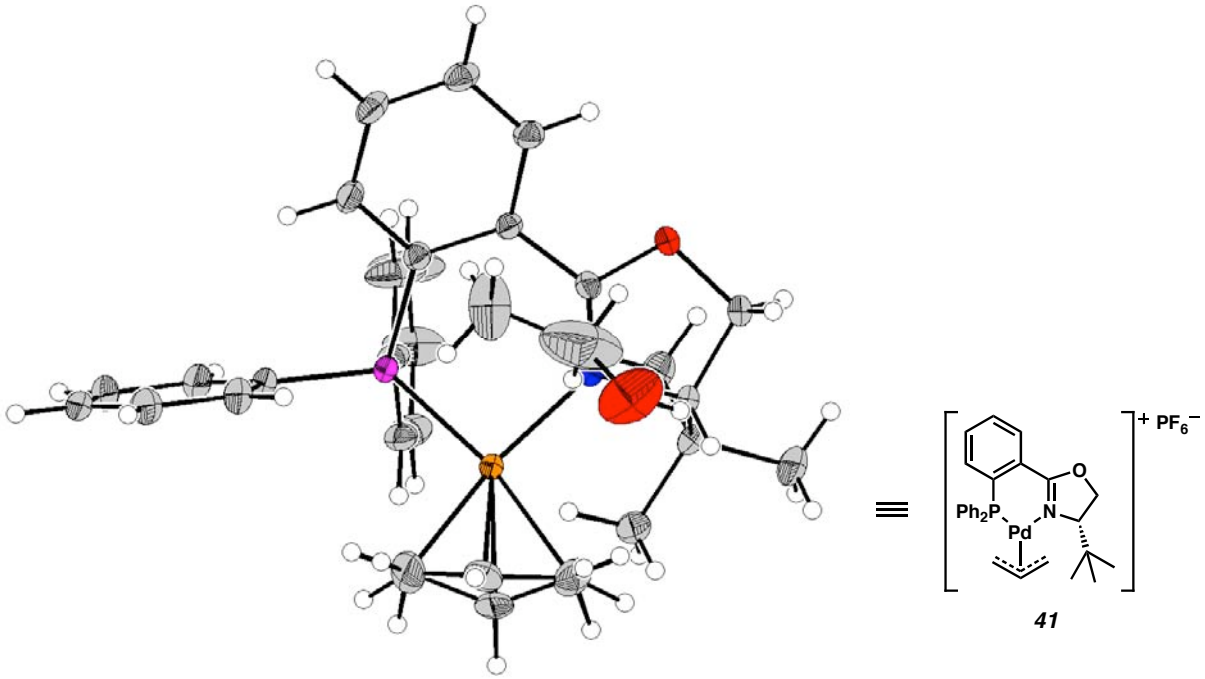
For details of the preparation of bis(β-ketoester) **82** (Scheme 11), conversion to diketone **83**, and synthesis of cyanthiwigin F (**84**), see ref 46.



41

[Pd(allyl)PHOX]•PF_6 salt 41 (Scheme 5). Prepared using Zehnder's method[65] with (*S*)-*t*-Bu-PHOX as a mixture of *endo*- and *exo*-isomers (ca. 60:40 ratio) in quantitative yield as a light yellow powder. mp (EtOH) 152-154 °C (decomp.); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.30 (app. ddd, *J* = 7.7, 4.1, 1.1 Hz, 0.6H), 8.24 (app. ddd, *J* = 7.7, 4.4, 1.1 Hz, 0.4H), 7.74-7.42 (comp. m, 8H), 7.39-7.11 (comp. m, 4H), 7.04-6.87 (comp m, 1H), 5.96-5.82 (m, 0.4H), 5.82-5.67 (m, 0.6H), 4.96-4.86 (comp. m, 1H), 4.68 (app. q, *J* = 9.9 Hz, 1H), 4.49 (app. dt, *J* = 11.3, 3.9 Hz, 1H), 4.19 (app. dt, *J* = 10.2, 4.4 Hz, 1H), 4.03 (app. dd, *J* = 14.3, 9.4 Hz, 0.6H), 3.63-3.48 (comp. m, 1H), 3.32 (app. d, *J* = 6.6 Hz, 0.4H), 3.16 (app. d, *J* = 12.7 Hz, 0.4H), 2.77 (app. d, *J* = 12.1 Hz, 0.6H), 0.64 (s, 3.5H), 0.56 (s, 5.5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.9-164.8 (3 peaks), 134.9, 134.8, 134.0-133.3 (7 peaks), 132.9-132.6 (4 peaks), 132.2-132.1 (3 peaks), 131.8 (app. d, *J* = 2.3 Hz), 130.2-128.8 (13 peaks), 128.5-127.8 (5 peaks), 127.3, 122.4 (app. d, *J* = 6.0 Hz), 122.4, 83.3-79.4 (6 peaks), 69.8, 69.7, 58.6, 54.1, 54.0, 34.3, 25.2; ^{31}P NMR (121 MHz, $CDCl_3$) δ 22.7 (d, *J* = 118.1 Hz), –143.8 (sept., $J_{P\text{-}F}$ = 711.0 Hz); IR (Neat Film from $CDCl_3$, NaCl) 3062, 2964, 2872, 2271, 1971, 1899, 1826, 1621, 1584, 1568, 1482, 1437, 1372, 1315, 1249, 1211, 1145, 1121, 1100, 1060, 1028, 958, 913, 836, 778, 732, 697, 678 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{28}H_{31}ONPPd$ [M]$^+$: 534.1178, found 534.1182; $[\alpha]_D^{27.1}$ +256.6 (*c* 3.72, CH_2Cl_2).

Figure SI1. Representation of [Pd(II)(allyl)PHOX]•PF_6 salt **41**.



41

Figure SI2. Representation of the unit cell of [Pd(II)(allyl)PHOX]•PF_6 salt **41**.

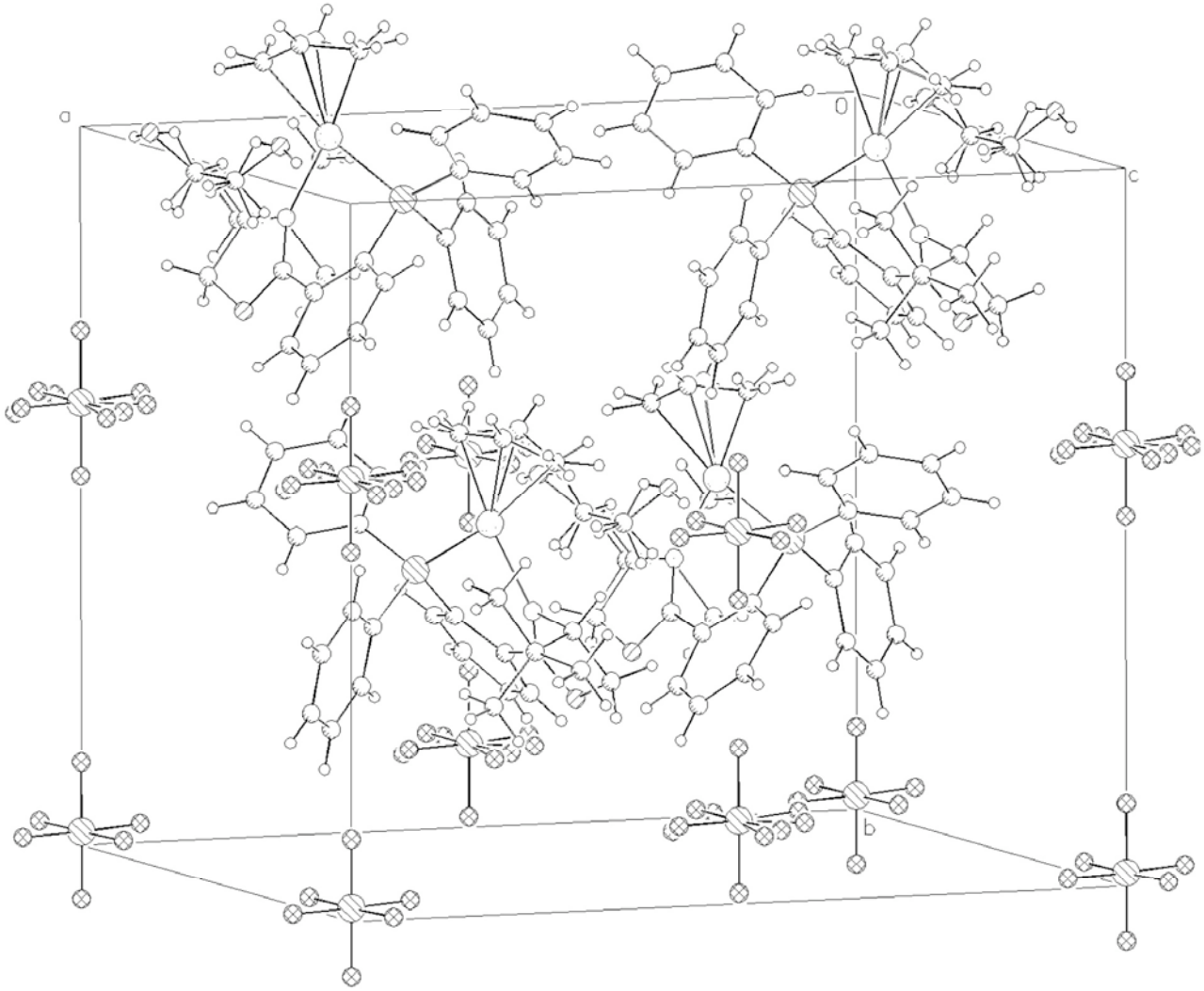


Table SI2. Crystal data and structure refinement for [Pd(II)(allyl)PHOX]•PF_6 (CCDC 245187).

Empirical formula	$[C_{28}H_{31}NOPPd]^+ PF_6^- \bullet \frac{1}{2}C_2H_5OH$
Formula weight	702.91
Crystallization Solvent	Ethanol
Crystal Habit	Fragment
Crystal size	0.35 x 0.34 x 0.23 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 15322 reflections used		
in lattice determination	2.31 to 41.00°	
Unit cell dimensions	a = 17.5183(6) Å	
	b = 15.7792(5) Å	β= 107.0990(10)°
	c = 11.3736(4) Å	
Volume	3004.98(18) $Å^3$	
Z	4	
Crystal system	Monoclinic	
Space group	C2	
Density (calculated)	1.554 Mg/m^3	
F(000)	1428	
θ range for data collection	1.77 to 42.31°	
Completeness to θ = 42.31°	85.0 %	
Index ranges	$-32 \le h \le 32, -28 \le k \le 29, -20 \le l \le 15$	
Data collection scan type	ω scans at 3 ϕ settings of 2θ=-28° and 2 at 2θ=-59°	
Reflections collected	28501	
Independent reflections	15572 [R_{int}= 0.0351]	
Absorption coefficient	0.787 mm^{-1}	
Absorption correction	SADABS	
Max. and min. transmission	0.8397 and 0.7702	

Table SI2 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	15572 / 1 / 408
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.343
Final R indices [I>2σ(I), 13582 reflections]	R1 = 0.0373, *w*R2 = 0.0725
R indices (all data)	R1 = 0.0459, *w*R2 = 0.0748
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.004
Average shift/error	0.000
Absolute structure parameter	-0.019(13)
Largest diff. peak and hole	1.422 and -0.710 e.Å^{-3}

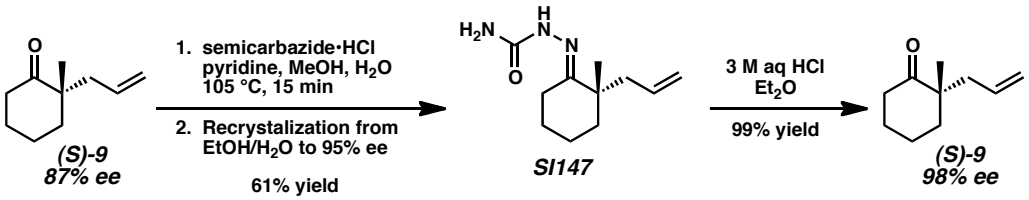
Special Refinement Details

The propyl ligand, C26-C27-C28, is disordered in two alternate orientations, differing by "up-down" positions for C27. Additional disorder is observed in one PF_6 counterion and an included solvent molecule, modeled as ethanol hydrogen bonded to a fluorine of one counterion.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

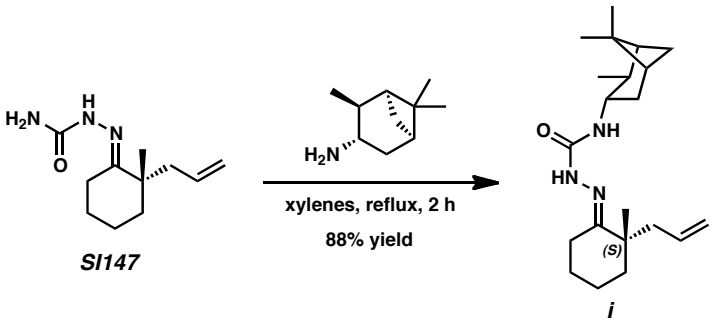
All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Preparation and Characterization of Semicarbazone Derivatives

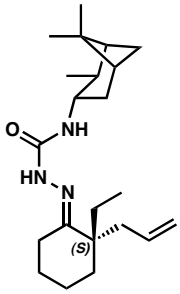


Semicarbazone SI147:[66] To a solution of ketone (*S*)-**9** (661.4 mg, 4.34 mmol, 1.0 equiv) of 88% ee in pyridine (1.22 mL), water (3.0 mL), and MeOH (8.0 mL) was added semicarbazide•HCl (848.1 mg, 7.60 mmol, 1.75 equiv). The reaction mixture was heated at 105 °C for 15 min, cooled, diluted with water (10 mL), filtered, and dried to give semicarbazone **SI147** (763 mg, 84% yield). The semicarbazone **SI147** (3.10 g, 14.8 mmol, 87% ee) was suspended in EtOH/water (35/65 v/v 355 mL) and warmed to 90 °C. When all the material had dissolved, heating was discontinued, and the flask allowed to cool in the heating bath. After 8 h, crystals were filtered and dried giving the enantioenriched semicarbazone (1.894 g, 61% yield, 95% ee). Recrystalization of this material in EtOH/water (30/70 v/v 175 mL) by the same procedure gave semicarbazone **SI147** (1.692 g, 89% yield, 98% ee) as white crystals; mp 188–189 °C (EtOH/water); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 (br s, 1H), 5.73 (m, 1H), 5.05 (s, 1H), 5.00 (app. d, J = 3.3 Hz, 1H), 2.40-2.11 (comp. m, 4H), 1.71-1.44 (comp. m, 6H), 1.10 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1, 156.8, 134.6, 117.2, 42.9, 41.5, 38.6, 25.9, 24.5, 22.5, 21.0; IR (Neat Film NaCl) 3465, 3195, 1693, 1567, 1478 cm^{-1}; HRMS (CI, CH_4) *m/z* calc'd for $C_{11}H_{20}N_3O$ [M + H]$^+$: 210.1606, found 210.1599; $[\alpha]_D^{28}$ –50.35 (*c* 2.60, MeOH).

To a biphasic mixture of Et_2O (30 mL) and 3 M aq HCl (3.0 mL) was added the enriched semicarbazone **SI147** (1.00 g, 4.77 mmol, 1.0 equiv). The reaction mixture was stirred vigorously for 2 h and then quenched with saturated aq $NaHCO_3$ (40 mL). The layers were separated, and aqueous layer extracted with Et_2O (4 x 30 mL). The combined organics were washed with brine (30 mL), dried ($MgSO_4$), and concentrated to give ketone **9** (718.2 mg, 98.9% yield).



(isopinocampheylamine)-Semicarbazone i: To a solution of the semicarbazone **SI147** (100 mg, 0.43 mmol, 1.0 equiv) in xylenes (1.0 mL) was added (1*S*,2*S*,3*S*,5*R*)-(+)-isopinocampheylamine (76.2 μL, 0.45 mmol, 1.05 equiv). The reaction mixture was refluxed for 2 h, cooled, and concentrated. Chromatography (10→50% EtOAc in Hexanes on SiO_2) afforded the (isopinocampheylamine)-semicarbazone **i** (130.5 mg, 87.8% yield). mp 131-133 °C from acetone; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (br s, 1H), 6.08 (bd, J = 8.7 Hz, 1H), 5.77 (m, 1H), 5.06 (s, 1H), 5.01 (s, 1H), 4.18 (m, 1H), 2.63 (app. tdd, J = 9.9, 3.6, 2.4 Hz, 1H), 2.45-2.13 (comp. m, 4H), 1.96 (m, 1H), 1.82 (m, 2H), 1.74-1.41 (comp. m, 8H), 1.23 (s, 3H), 1.15 (d, J = 7.2 Hz, 3H), 1.11 (s, 3H), 1.10 (s, 3H), 0.89 (d, J = 9.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.5, 155.5, 134.9, 117.0, 48.0, 47.8, 46.8, 43.0, 41.6, 41.5, 38.5, 38.3, 37.8, 35.3, 28.0, 25.9, 24.5, 23.4, 22.4, 21.0, 20.8; IR (Neat Film NaCl) 3400, 3189, 3074, 2929, 1672, 1526 cm^{-1}; HRMS (FAB) *m/z* calc'd for $C_{21}H_{36}N_3O$ [M + H]$^+$: 346.2858, found 346.2874; $[\alpha]_D^{27}$ –18.9 (*c* 0.53, hexane). The semicarbazone was recrystallized from EtOH/H_2O to provide suitable crystals for X-ray analysis (vide infra).

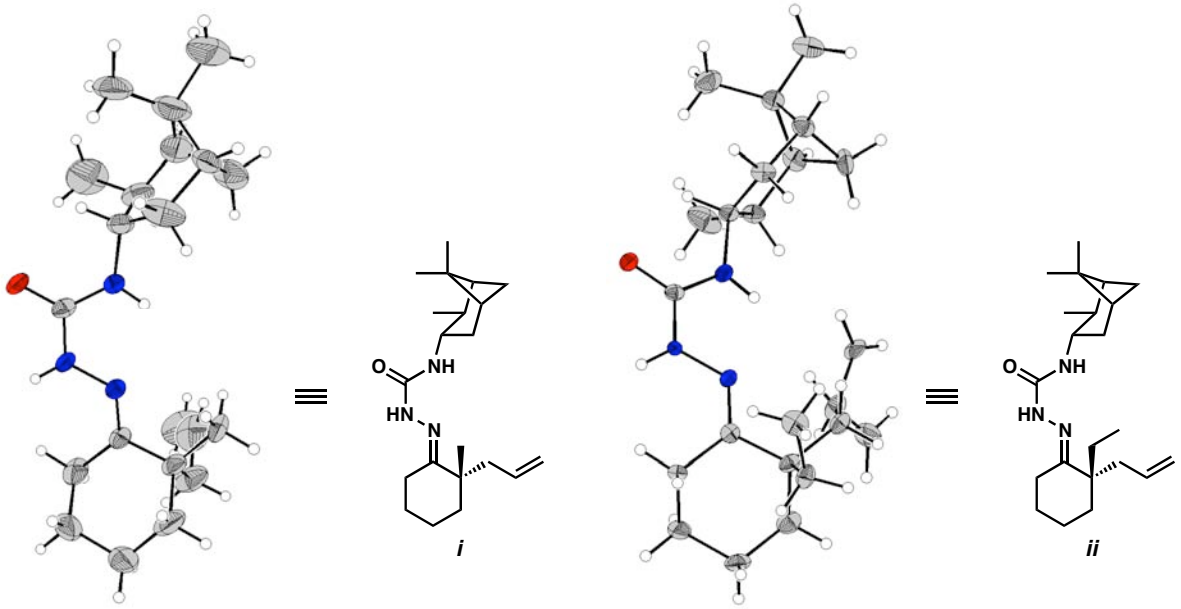


ii

(isopinocampheylamine)-Semicarbazone ii: Prepared in an analogous manner to **i**. mp 145–146 °C from acetone; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, *J* = 21.3 Hz, 1H), 6.07 (d, *J* = 4.4 Hz, 1H), 5.86-5.72 (m, 1H), 5.08-5.04 (m, 1H), 5.00 (s, 1H), 4.23-4.12 (m, 1H), 2.68-2.55 (m, 1H), 2.46-2.34 (m, 2H), 2.30 (d, *J* = 7.5 Hz, 2H), 2.12-2.00 (m, 1H), 1.98-1.90 (m, 1H), 1.88-1.40 (comp. m, 11H), 1.22 (s, 3H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.05 (s, 3H), 0.88 (d, *J* = 9.6 Hz, 1H), 0.77 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.8, 154.4, 135.3, 116.7, 48.0, 47.9, 46.8, 44.2, 41.7, 39.9, 38.3, 37.9, 35.6, 35.3, 28.1, 28.0, 25.6, 23.4, 22.6, 20.8, 20.7, 7.8; IR (Neat Film NaCl) 3402, 3194, 3074, 2930, 1672, 1526 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{22}H_{37}N_3O$ $[M]^+$: 359.2937, found 359.2940; $[\alpha]_D^{29}$ –4.43 (*c* 0.38, hexane). The semicarbazone was recrystallized from acetone to provide suitable crystals for X-ray analysis (vide infra).

X-Ray Structures of Semicarbazones i and ii.

Figure SI3. Representations of Semicarbazones **i** and **ii**.



i ***ii***

Table SI3. Crystal data and structure refinement for semicarbazone **i** (CCDC 246585).

Empirical formula	$C_{21}H_{35}N_3O$
Formula weight	345.52
Crystallization Solvent	Ethanol/water
Crystal Habit	Fragment
Crystal size	0.41 x 0.37 x 0.24 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000	
Wavelength	0.71073 Å MoKα	
Data Collection Temperature	100(2) K	
θ range for 7110 reflections used		
in lattice determination	2.31 to 24.12°	
Unit cell dimensions	a = 23.1170(16) Å	
	b = 13.6467(9) Å	β= 90.396(2)°
	c = 13.2060(9) Å	
Volume	4166.0(5) $Å^3$	
Z	8	
Crystal system	Monoclinic	
Space group	C2	
Density (calculated)	1.102 Mg/m^3	
F(000)	1520	
θ range for data collection	1.73 to 33.55°	
Completeness to θ = 33.55°	81.9 %	
Index ranges	$-29 \le h \le 34, -20 \le k \le 20, -18 \le l \le 17$	
Data collection scan type	ω scans at 4 ϕ settings	
Reflections collected	30377	
Independent reflections	12571 [R_{int}= 0.0616]	
Absorption coefficient	0.068 mm^{-1}	
Absorption correction	None	
Max. and min. transmission	0.9838 and 0.9726	

Table SI3 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	12571 / 64 / 486
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	1.972
Final R indices [I>2σ(I), 5761 reflections]	R1 = 0.0873, *w*R2 = 0.1490
R indices (all data)	R1 = 0.1657, *w*R2 = 0.1573
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.002
Average shift/error	0.000
Absolute structure parameter	0.4(16)
Largest diff. peak and hole	0.630 and -0.361 e.Å^{-3}

Special Refinement Details

The data are weak and the structure is disordered, in the allyl of molecule B. These two factors combine to produce a final structure that falls short of the desired quality. Nevertheless, the quality is sufficient to determine the relative stereochemistry around C1 and, given the known stereochemistry of another chiral center, the absolute conformation can be deduced. Care should be taken when including these results in a publication. The allylic fragments were restrained to have similar geometry and the anisotropic displacement factors of the B molecule allyl fragment (only) were restrained to tend towards isotropic behavior.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Table SI4. Crystal data and structure refinement for semicarbazone **ii** (CCDC 248956).

Empirical formula	$C_{22}H_{37}N_3O$
Formula weight	359.55
Crystallization Solvent	Acetone
Crystal Habit	Fragment
Crystal size	0.39 x 0.37 x 0.24 mm^3
Crystal color	Colorless

Data Collection

Type of diffractometer	Bruker SMART 1000
Wavelength	0.71073 Å MoKα
Data Collection Temperature	100(2) K
θ range for 13615 reflections used	
in lattice determination	2.25 to 21.58°
Unit cell dimensions	a = 13.4105(11) Å
	b = 13.4433(11) Å
	c = 24.353(2) Å
Volume	4390.4(6) $Å^3$
Z	8
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Density (calculated)	1.088 Mg/m^3
F(000)	1584
θ range for data collection	1.67 to 28.34°
Completeness to θ = 28.34°	94.5 %
Index ranges	$-17 \le h \le 17, -17 \le k \le 17, -32 \le l \le 30$
Data collection scan type	ω scans at 5 ϕ settings
Reflections collected	63444
Independent reflections	10086 [R_{int}= 0.0909]
Absorption coefficient	0.067 mm^{-1}
Absorption correction	None
Max. and min. transmission	0.9841 and 0.9744

Table SI4 (cont.)

Structure solution and Refinement

Structure solution program	SHELXS-97 (Sheldrick, 1990)
Primary solution method	Direct methods
Secondary solution method	Difference Fourier map
Hydrogen placement	Geometric positions
Structure refinement program	SHELXL-97 (Sheldrick, 1997)
Refinement method	Full matrix least-squares on F^2
Data / restraints / parameters	10086 / 447 / 570
Treatment of hydrogen atoms	Riding
Goodness-of-fit on F^2	2.208
Final R indices [I>2σ(I), 6214 reflections]	R1 = 0.0842, *w*R2 = 0.1195
R indices (all data)	R1 = 0.1330, *w*R2 = 0.1224
Type of weighting scheme used	Sigma
Weighting scheme used	$w=1/\sigma^2(Fo^2)$
Max shift/error	0.000
Average shift/error	0.000
Absolute structure parameter	0.6(17)
Largest diff. peak and hole	0.271 and -0.287 e.Å^{-3}

Special Refinement Details

The diffraction intensities fall off sharply past 2θ=40°, presumably because the structure is disordered. The asymmetric unit contains two molecules (hydrogen bonded to each other and of the same configuration) disordered in different ways. Molecule A is disordered about the terminal carbon (C11) of the allyl ligand (see figures 1 and 2). Both orientations were modeled, including riding hydrogen atoms, with the only restraint being a total occupancy of 1.0 for C11A and C11C. Molecule B is disordered in the camphene moiety, C13B-C22B. The disorder manifests as a rotation of the camphene around the N3B-C13B bond (see figures 3 and 4). Both orientations were restrained to have geometry similar to the corresponding part of the A molecule, using the SAME command. Additional restraints were imposed in this portion of molecule B as follows; 1) SIMU – to restrained bonded atoms to have similar displacement parameters and 2) ISOR – to restrain the anisotropic displacement parameters, U_{ij}, to approximate isotropic behavior without placing restraint on the refined value of the isotropic U.

Refinement of F^2 against ALL reflections. The weighted R-factor (*w*R) and goodness of fit (S) are based on F^2, conventional R-factors (R) are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating R-factors(gt) etc. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R-factors based on ALL data will be even larger.

All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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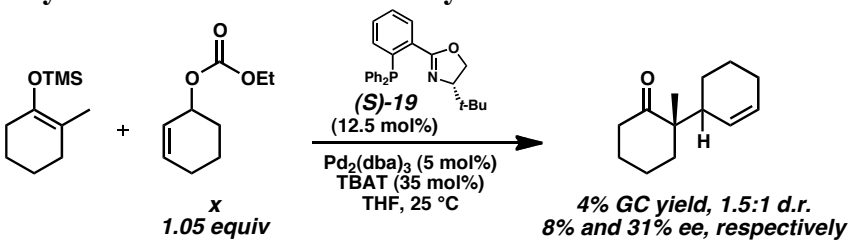
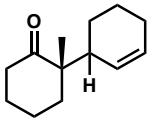
Mechanistic Experiments

Allylation with a Substituted Allyl Carbonate

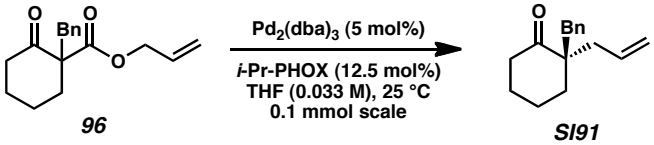


In a flame dried 1 dram vial, $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol), (*S*)-*t*-BuPHOX (4.7 mg, 0.0625 mmol), and TBAT (18.9 mg, 0.035 mmol) were combined. The vial was evacuated for 10 min prior to addition of THF (3 mL). The mixture was allowed to stir at 25 °C for 30 min prior to addition of tridecane (10 μL, 0.4 mmol), silyl enol ether (18.4 mg, 0.1 mmol), and carbonate **x**[*] (17.9 mg, 0.105 mmol) via syringe. GC yield was determined by a GC assay with tridecane as the internal standard. (Isothermal at 80 °C for 5 min, then ramp from 80 °C to 115 °C at 10 °C/min, then isothermal at 115°C for 75 min. Silyl enol ether: 5.759 min, tridecane: 7.329 min, minor product diastereomer: 72.223 min, major product diastereomer: 73.434 min). Enantiomeric excess was determined by an Agilent 6850 GC utilizing a G-TA column (30 mm x 0.25 cm) with 1.0 mL/min carrier gas flow. The method utilized for enantiomeric excess determination was isothermal at 110°C for 60 min (major product diastereomer: 47.504 min and 53.594 min (major enantiomer), minor product diastereomer: 48.282 min (major enantiomer) and 55.842 min). Isolation of products as a mixture of diastereomers was accomplished by flash chromatography (1 cm x 20 cm SiO_2, 2% ether in pentane).



2-(Cyclohex-2-enyl)-2-methylcyclohexanone: ^{1}H NMR (300 MHz) δ 5.74 (comp. m, 1H), 5.49 (dddd, 0.7H, *J* = 11.0, 1.9, 1.9, 1.9 Hz), 5.20 (dddd, 0.3H, *J* = 10.1, 2.1, 2.1, 2.1 Hz), 2.84-2.29 (comp. m, 3H), 2.01-1.22 (comp. m, 12H), 0.90 (s, 2.1 H), 0.89 (s, 0.9 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 216.7, 216.1, 129.6, 129.5, 128.0, 127.3, 52.0, 51.7, 39.5, 39.0, 38.6, 37.0, 36.0, 28.0, 27.7, 25.4, 24.0, 23.1, 23.0, 22.9, 21.1, 21.0, 19.4, 18.6; IR (Neat Film, NaCl) 3023, 2934, 2862, 1705, 1452, 1313, 1121 cm^{-1}; HRMS *m/z* calc'd for $C_{13}H_{24}O$ [M_+]: 192.1514, found 192.1519.

General Procedures for Nonlinear Experiments:



THF stock solutions with the desired enantiomeric excess of *i*-Pr-PHOX were freshly prepared prior to each experiment. The enantiomeric excess of the *i*-Pr-PHOX delivered was confirmed by subsequent chiral HPLC with a Chiracel OJ column using 1% ethanol in hexanes (1.0 mL/min) as an eluent on the remaining stock solution ((*S*)-*i*-Pr-PHOX: 13.16 min and (*R*)-*i*-Pr-PHOX: 7.60 min).

A 1-dram vial equipped with a stirbar was flame dried twice under vacuum. After cooling under nitrogen, $Pd_2(dba)_3$ (4.6 mg, 0.005 mmol) was added. The vial was evacuated for 5 min. THF (3 mL total) was added and then *i*-Pr-PHOX (4.8 mg, 0.0125 mmol) in THF was added via syringe. Contents

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(*) Genêt, J.-P.; Jugé, S.; Achi, S.; Mallart, S.; Ruiz-Montès, J.; Levif, G. *Tetrahedron* **1988**, *44*, 5263–5275.

were allowed to stir for 30 min at 25 °C prior to addition of benzyl β-ketoester **96** (27.2 mg, 0.1 mmol) via syringe. The reaction progress was monitored by TLC. Upon completion, the reaction was concentrated and purified via column chromatography (1 x 11.5 cm SiO_2, 20% Et_2O in pentane). Subsequently, the enantiomeric excess of product was determined by chiral HPLC with a Chiracel OJ column using 1% ethanol in hexanes (1.0 mL/min) as an eluent (**SI91**: 15.942 min and 24.345 min).

Comparison of the enantiomeric excess of the product versus the enantiomeric excess of the *i*-Pr-PHOX revealed a linear relationship (Figure SI4). The absence of a nonlinear effect suggests that the active catalyst in our Tsuji allylation system involves one molecule of *i*-Pr-PHOX, thus one palladium metal center. Furthermore, the absence of a nonlinear effect suggests that the rate determining step does not involve a bimetallic system, such as a palladium-enolate and a palladium π-allyl complex.

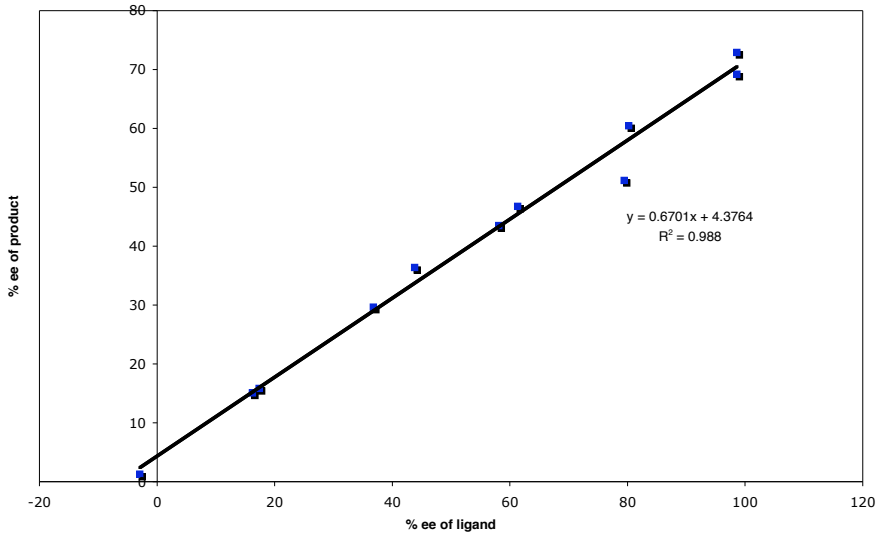
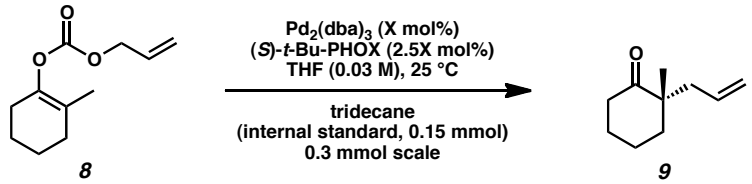


Figure SI4. Plot of Enantiomeric Excess of **SI91** versus Enantiomeric Excess of *i*-Pr-PHOX.

General Procedures for Kinetic Experiments

Determination of [Pd(PHOX)] Order



Asymmetric Tsuji allylation of enol carbonate **8** was carried out in an identical manner to general procedure 4, but at different concentrations of the in situ generated [Pd(PHOX)] complex. Reaction progress was monitored by an achiral GC equipped with a DB-WAX column with tridecane as the internal standard. GC yield was determined by using an acquisition method that ramped the temperature from 70 to 175 °C at a rate of 5 °C/min (tridecane: 6.915 min, cycloalkanone **9**: 12.185 min, and enol carbonate **8**: 17.697 min).

Rate constants (k_{obs}) were determined at 25 °C by GC analysis. The dependence of reaction rate on the concentration of the in situ generated [Pd(PHOX)] was measured at a constant concentration of **8** (0.03 M) and a constant concentration of tridecane (0.015M). Figure SI5 shows that the reaction is first-order in [Pd(PHOX)] complex.

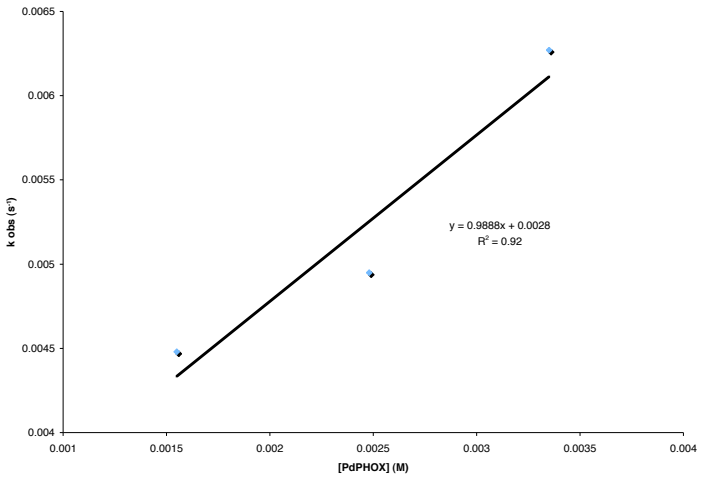
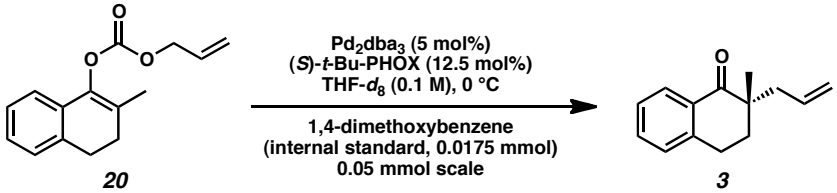


Figure SI5. Plot of k_{obs} vs. concentration of [Pd(PHOX)].

Determination of Substrate Order for Allyl Enol Carbonates



Solid $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol) and (*S*)-*t*-Bu-PHOX (2.4 mg, 0.00625 mmol) were placed in a NMR tube equipped with a screw cap and a Teflon septum. The NMR tube was then placed under vacuum and backfilled with argon (3 x 1 min). THF-d_8 (0.2 mL, dried over sodium benzophenone ketyl) was added to the NMR tube via syringe under a positive pressure of argon. The mixture was heated at 40 °C for 30 min. The mixture was then cooled to –78 °C using a CO_2/acetone bath. A THF-d_8 solution (0.3 mL, 0.1 M in substrate total) of allyl enol carbonate **20** (12.2 mg, 0.05 mmol) and 1,4-dimethoxybenzene (2.4 mg, 0.0175 mmol) were added to the reaction mixture under argon. Before recording the ^{1}H NMR spectrum, the sample was allowed to warm for 5–10 s and mixed. Reaction progress was monitored by ^{1}H NMR spectroscopy at 0 ºC, where integral areas of the allylic protons of **20** (δ 4.677 ppm, dt, J = 5.5, 1.0 Hz, 2H) relative to the phenyl protons of the dimethoxybenzene internal standard (δ 6.795 ppm, s, 4H) were obtained at 5 min intervals. The experiment was concluded upon complete conversion of **20**, which was determined by the disappearance of the allylic protons of **20**.

Analysis of consumption of **20** over time is consistent with a zero-order dependence in allyl enol carbonate (Figure SI6).

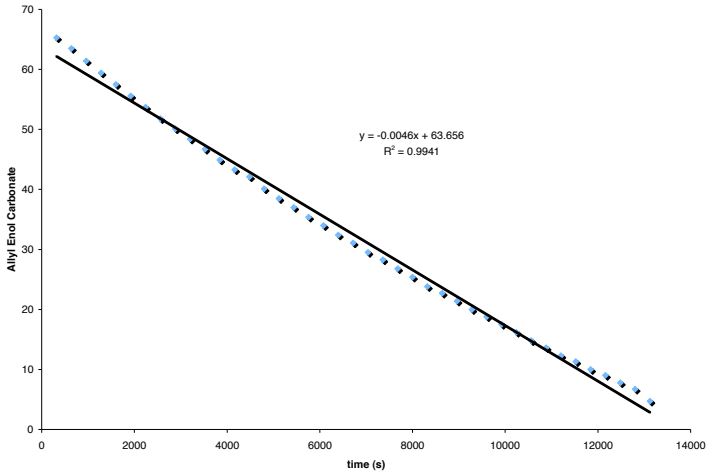
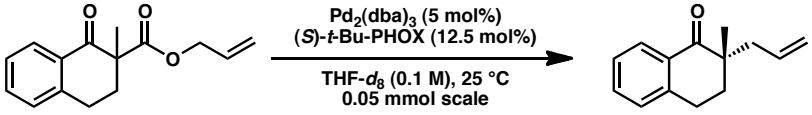


Figure SI6. Plot of Consumption of Allyl Enol Carbonate **20** versus Time as Observed by ^{1}H NMR Spectroscopy.

Determination of Substrate Order for β-Ketoesters



SI58 ***3***

Solid $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol) and (*S*)-*t*-Bu-PHOX (2.4 mg, 0.00625 mmol) were placed in a NMR tube equipped with a screw cap and a Teflon septum. The NMR tube was then placed under vacuum and backfilled with argon (3 x 2 min). THF-d_8 (0.2 mL, dried over sodium benzophenone ketyl) was added to the NMR tube via syringe under a positive pressure of argon. The mixture was heated at 40 °C for 30 min. A THF-d_8 solution (0.3 mL, 0.1 M in substrate total) of allyl β-ketoester **SI58** (12.2 mg, 0.05 mmol) was added to the reaction mixture under argon. Reaction progress was monitored by ^{1}H NMR spectroscopy at 25 ºC, where integral areas of the allylic protons of **SI58** (δ 4.494–4.574 ppm, m, 2H) relative to the OCH_2 protons of the THF (δ 3.58 ppm, s, 4H) were obtained at 8 min intervals. The experiment was concluded upon complete conversion of **SI58**, which was determined by the disappearance of the allylic protons of **SI58**.

Analysis of consumption of **SI58** over time is consistent with a zero-order dependence in allyl β-ketoester (Figure SI7).

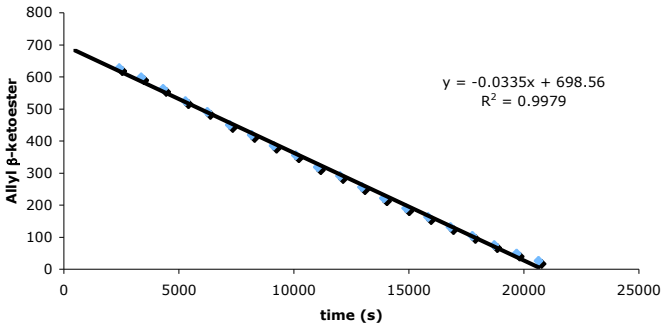
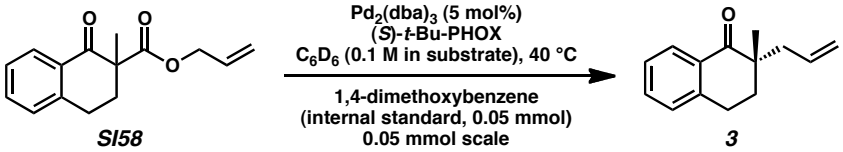


Figure SI7. Plot of Consumption of Allyl β-Ketoester **SI58** versus Time as Observed by ^{1}H NMR Spectroscopy.

Determination of the Order in (*S*)-*t*-Bu-PHOX



SI58 ***3***

Asymmetric Tsuji allylation of allyl β-ketoester **SI58** was carried out in C_6D_6 in a similar procedure to the one mentioned above. Reaction progress was monitored by ^{1}H NMR spectroscopy at 40 ºC, where integral areas of the allylic protons of **SI58** (δ 4.240–4.380 ppm, m, 2H) relative to the CH_3 protons of the internal standard 1,4-dimethoxybenezene (δ 3.338 ppm, s, 6H) were obtained at 4 min intervals.

Rate constants (k_{obs}) were determined at 40 °C by ^{1}H NMR spectroscopy. The dependence of reaction rate on the concentration of the (*S*)-*t*-Bu-PHOX was measured at constant concentrations of SI58 (0.1 M), $Pd_2(dba)_3$ (0.005 M), and 1,4-dimethoxybenzene (0.01 M). Figure SI8 shows that the reaction is zero-order in (*S*)-*t*-Bu-PHOX.

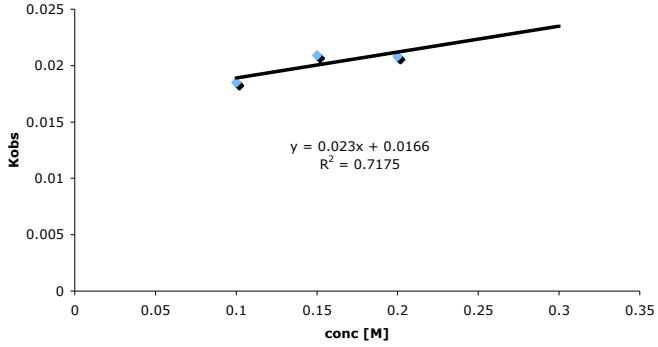
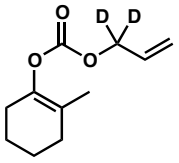


Figure SI8. Plot of k_{obs} vs. concentration of (*S*)-*t*-Bu-PHOX.

Based on these preliminary kinetic experiments, we believe that our asymmetric Tsuji allylation is zero-order in substrate (for allyl enol carbonate and allyl β-ketoester substrates), zero-order in PHOX ligand, and first-order in in situ palladium(PHOX) complex.

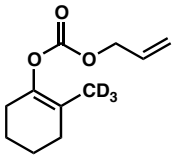
Deuterium Labeling Experiments

Characterization Data for Deuterated Allyl Enol Carbonates



97

Dideuterio allyl enol carbonate 97 (Scheme 14): Prepared by general procedure 2 with dideuterioallyl chroroformate, which was synthesized from 1,1-dideuterioallyl alcohol[†] and 20% phosgene in toluene. Flash chromatography (SiO_2, 1 → 2.5% Et_2O in hexanes) gave dideuterio allyl enol carbonate **97** (6% yield) as a colorless oil; R_f = 0.82 (25% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.95 (dd, *J* = 17.0, 10.4 Hz, 1H), 5.38 (d, *J* = 17.1 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 2.21-2.09 (comp. m, 2H), 2.08-1.98 (comp. m, 2H), 1.77-1.66 (comp. m, 2H), 1.65-1.53 (comp. m, 2H), 1.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 142.2, 131.4, 120.9, 119.0, 30.3, 26.6, 23.1, 22.3, 21.7, 15.8; IR (Neat Film NaCl) 2935, 2862, 1753, 1710, 1280, 1262, 1078 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{14}D_2O_3$ $[M]^+$: 198.1225, found 198.1217.

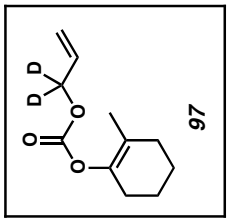


98

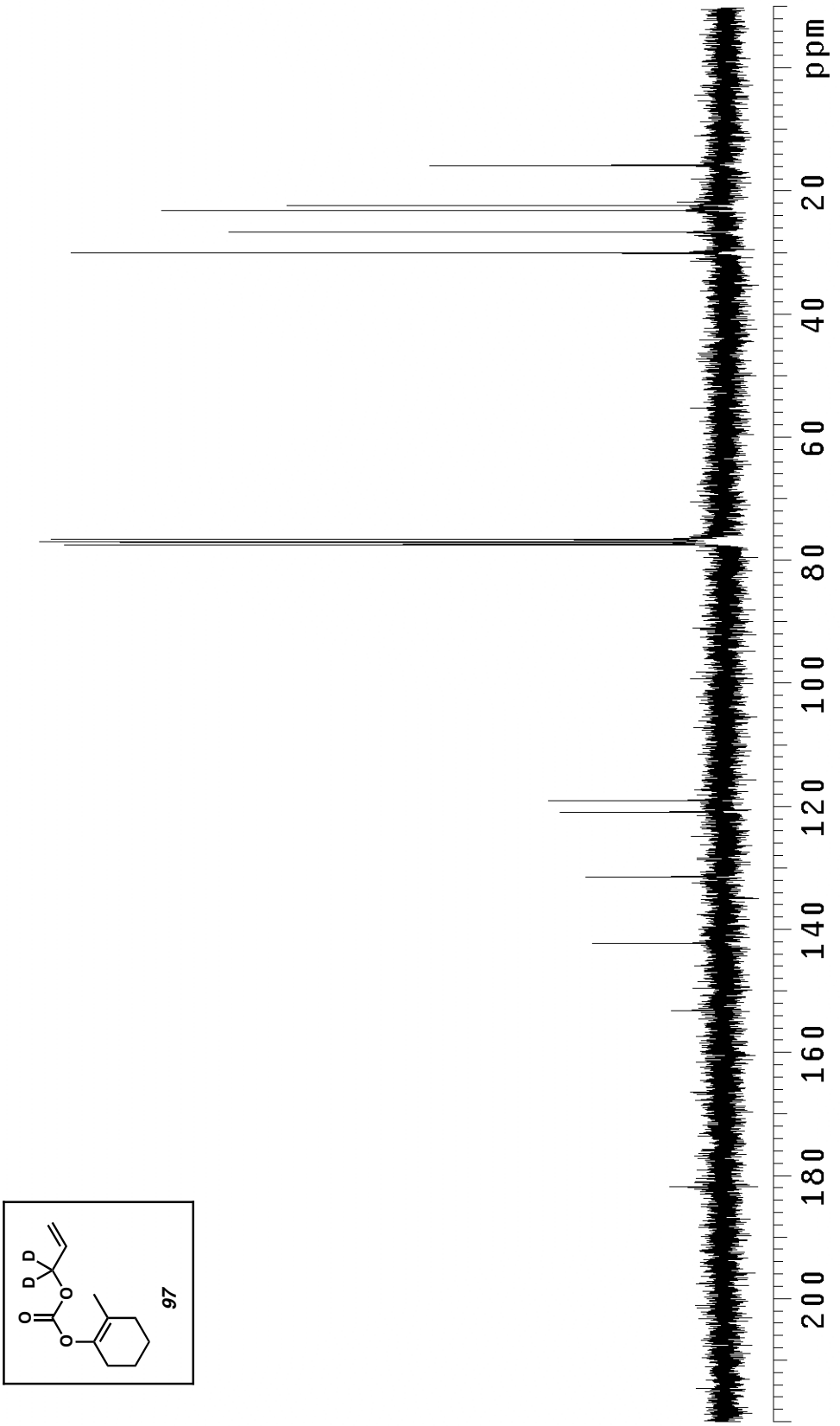
Trideuterio allyl enol carbonate 98 (Scheme 14): Prepared by general procedure 2 with 2-trideuteriomethylcyclohexanone.[‡] Flash chromatography (SiO_2, 2 → 2.5% Et_2O in hexanes) gave trideuterio allyl enol carbonate **98** (22% yield) as a colorless oil; R_f = 0.82 (25% Et_2O in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.96 (ddt, *J* = 17.1, 10.8, 6.0 Hz, 1H), 5.38 (d, *J* = 17.3 Hz, 1H), 5.28 (d, *J* = 10.5 Hz, 1H), 4.65 (d, *J* = 5.7 Hz, 2H), 2.21-2.09 (comp. m, 2H), 2.08-1.98 (comp. m, 2H), 1.77-1.66 (comp. m, 2H), 1.66-1.53 (comp. m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.1, 142.2, 131.5, 120.8, 118.8, 68.5, 30.0, 26.6, 23.1, 22.3; IR (Neat Film NaCl) 2936, 1755, 1705, 1367, 1276, 1247, 1216, 1034, 786 cm^{-1}; HRMS (EI) *m/z* calc'd for $C_{11}H_{13}D_3O_3$ $[M]^+$: 199.1288, found 199.1280.

(†) Dua, S.; Taylor, M. S.; Buntine, M. A.; Bowie, J. H. *J. Chem. Soc. Perkin Trans. 2* **1997**, 1991–1997.

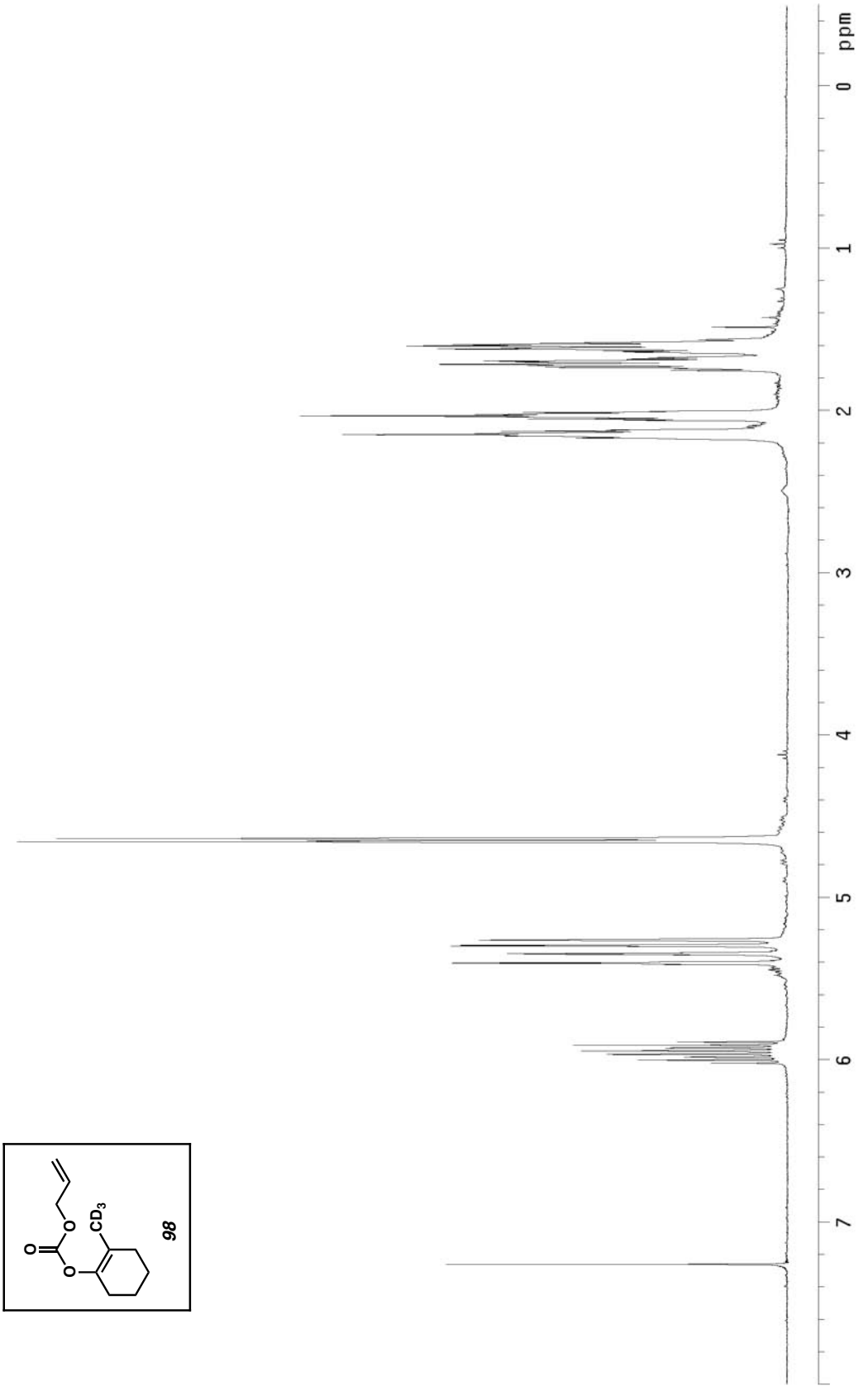
(‡) House, H. O.; Roelofs, W. L.; Trost, B. M. *J. Org. Chem.* **1966**, *31*, 646–655.



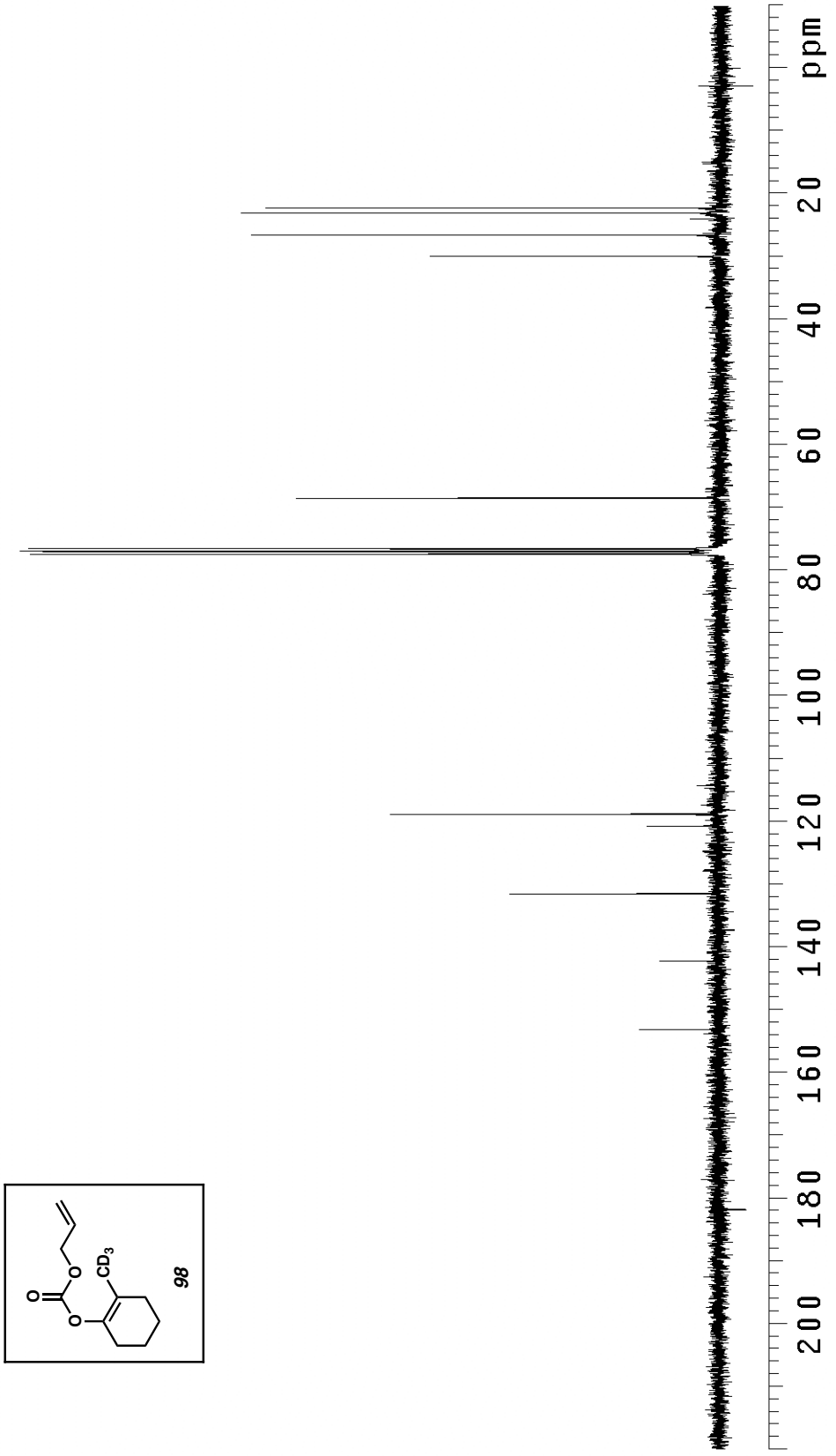
^{1}H NMR of compound **97** (300 MHz, $CDCl_3$)



^{13}C NMR of compound **97** (75 MHz, $CDCl_3$)

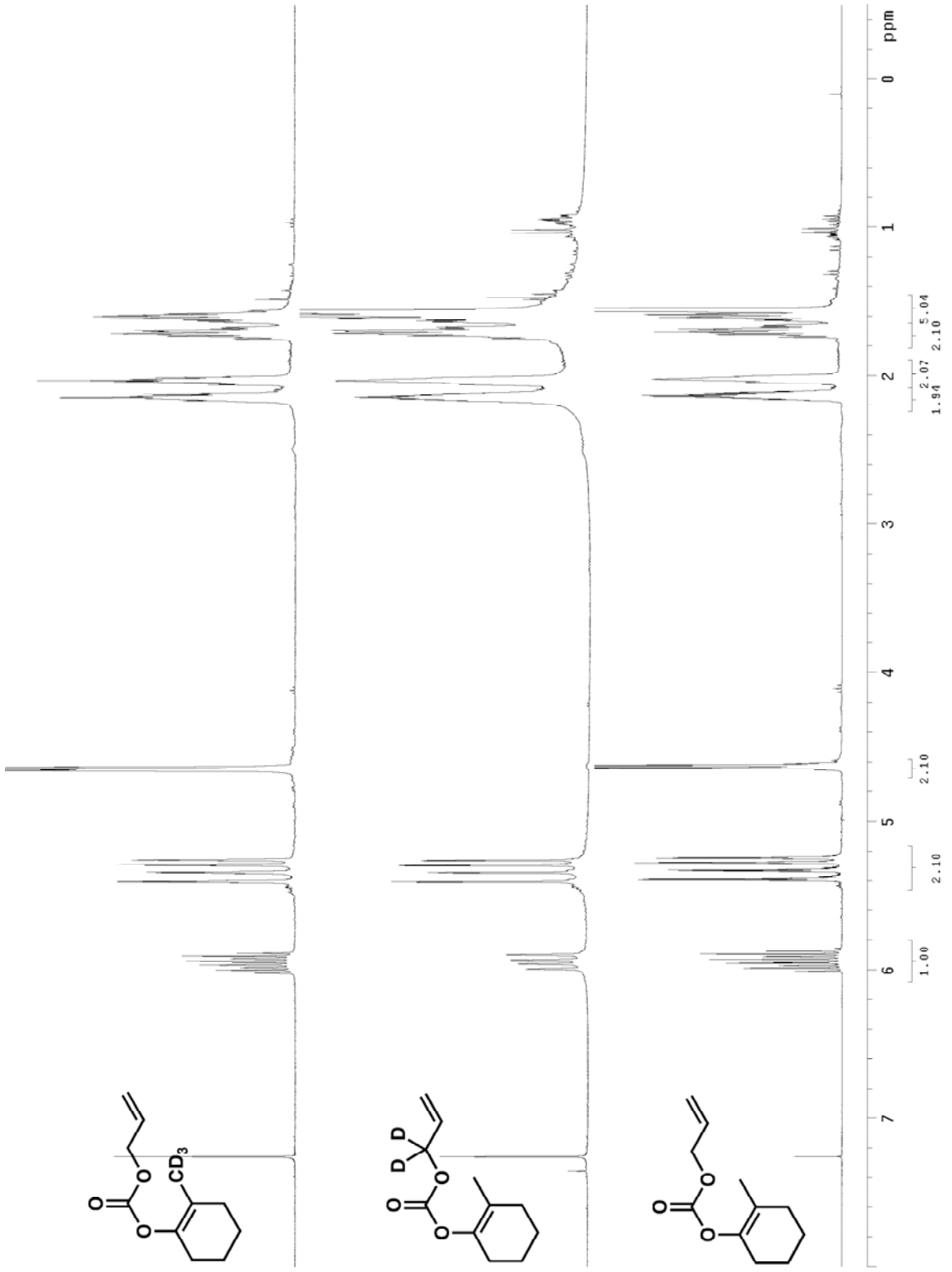


^{1}H NMR of compound **98** (300 MHz, $CDCl_3$)

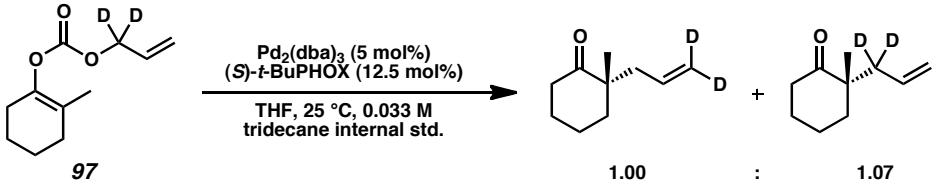


^{13}C NMR of compound **98** (75 MHz, $CDCl_3$)

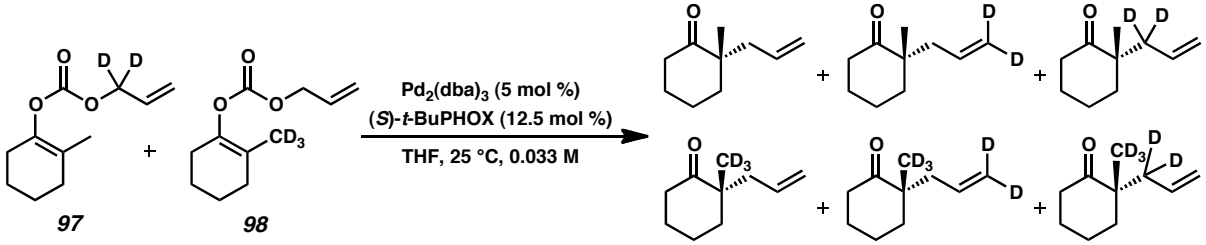
Comparison ^{1}H NMR spectra:



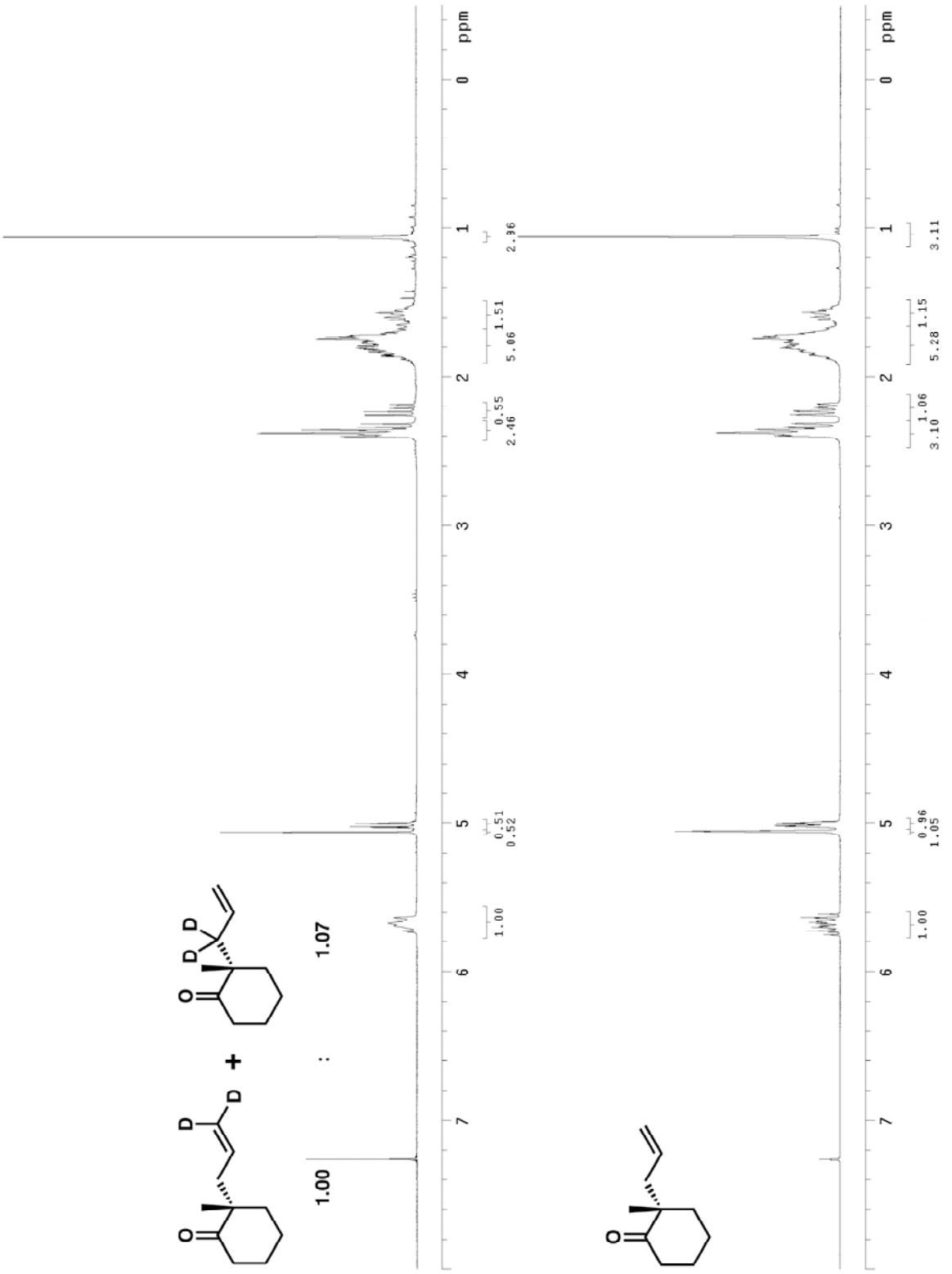
Asymmetric Tsuji Allylation of Deuterated Substrates

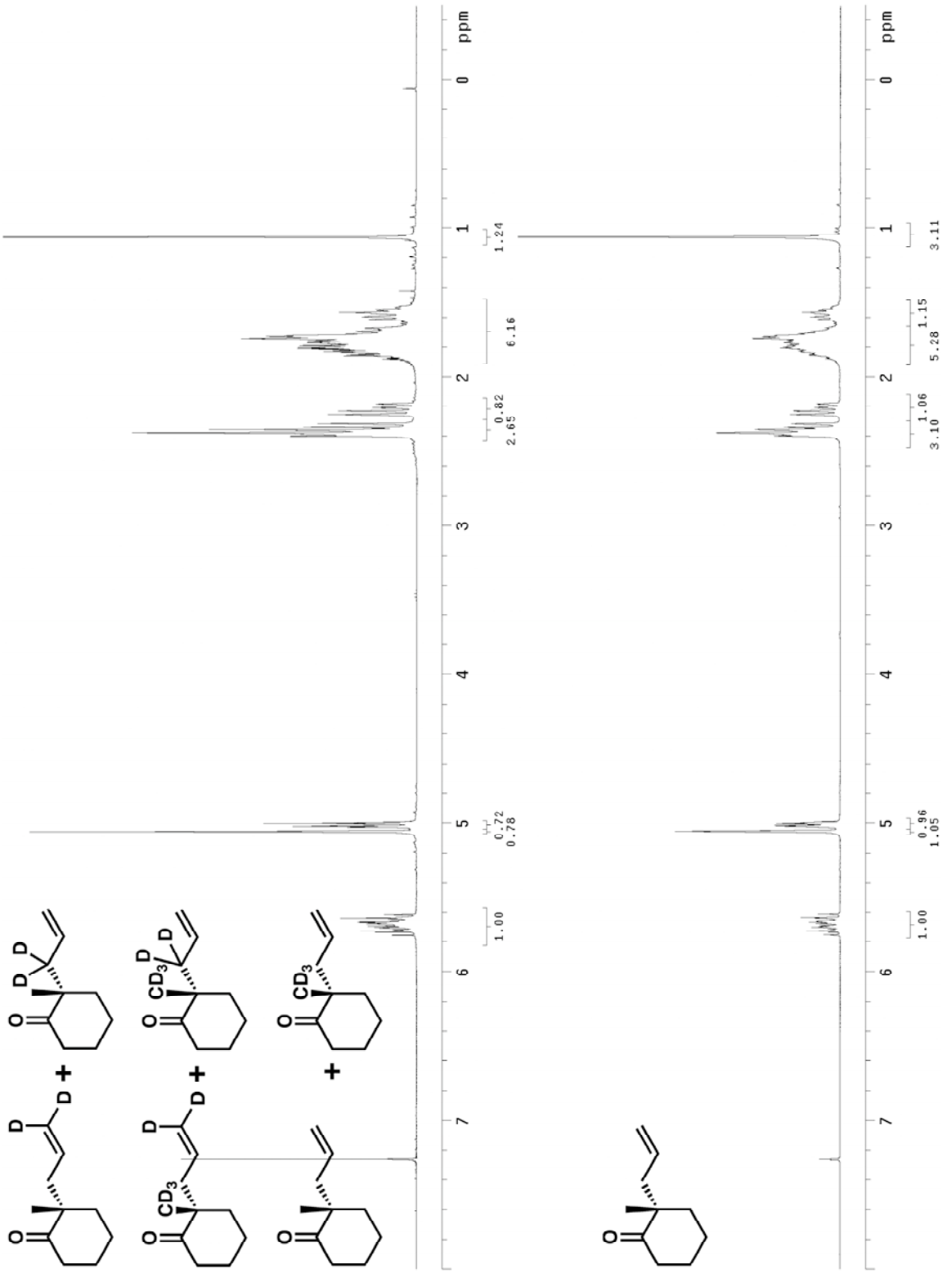


Dideuterio allyl enol carbonate **97** (39.7 mg, 0.2 mmol, 1.0 equiv) was exposed under our standard allylation conditions (general procedure 4). After 2 h, the reaction was complete by TLC. GC analysis showed an 88.1% yield and an 87% ee for the mixture of products. Flash chromatography (SiO_2, 1 → 2.5% Et_2O in pentane) afforded material for NMR analysis, which allowed the ratio of products to be quantified (vide infra).



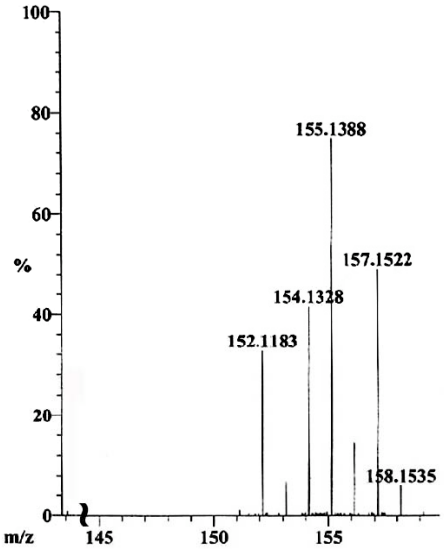
Dideuterio allyl enol carbonate **97** (19.9 mg, 0.1 mmol, 1.0 equiv) and trideuterio allyl enol carbonate **98** (19.8 mg, 0.1 mmol, 1.0 equiv) were simultaneously exposed to our standard conditions (general procedure 4). After 2 h, the reaction was complete by TLC. GC analysis showed an 88.4% yield and an 87% ee for the mixture of products. Flash chromatography (SiO_2, 1 → 2.5% Et_2O in pentane) afforded material for MS and NMR analysis, which allowed the ratio of products to be quantified (vide infra).

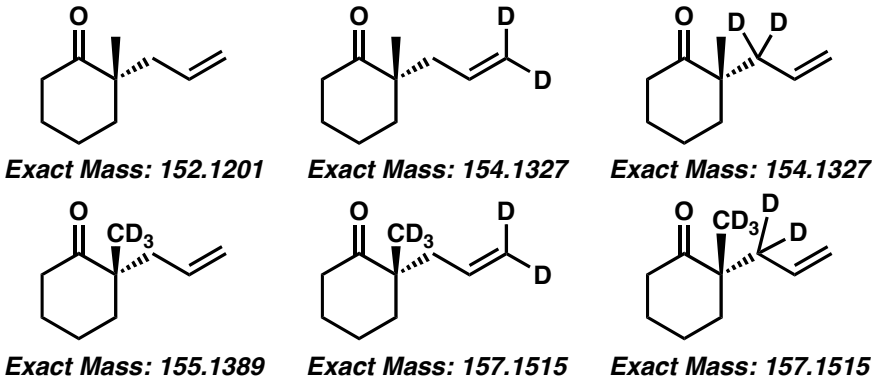

D
D
O
+
1.00
:
1.07
D
D
O
O
ppm
0
1
2
3
4
5
6
7
1.00
0.51
0.52
0.55
2.46
1.51
5.06
2.96
1.00
0.96
1.05
1.06
3.10
1.15
5.28
3.11


ppm
1.00
0.72
0.78
0.82
2.65
6.16
1.24
1.00
0.96
1.05
1.06
3.10
1.15
5.28
3.11

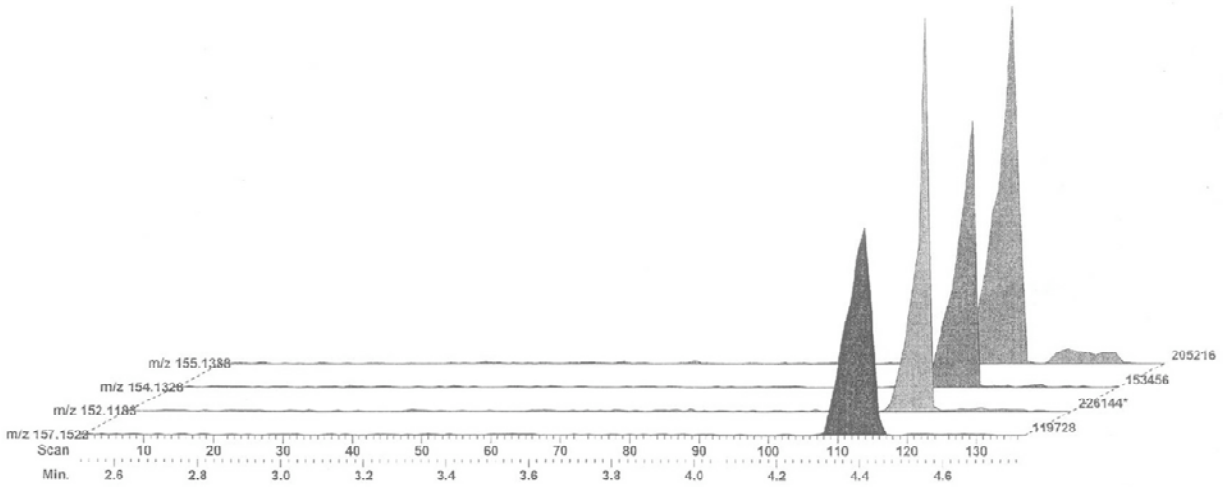
Mass Spectral Analysis of Crossover Experiments

A Representative MS Scan





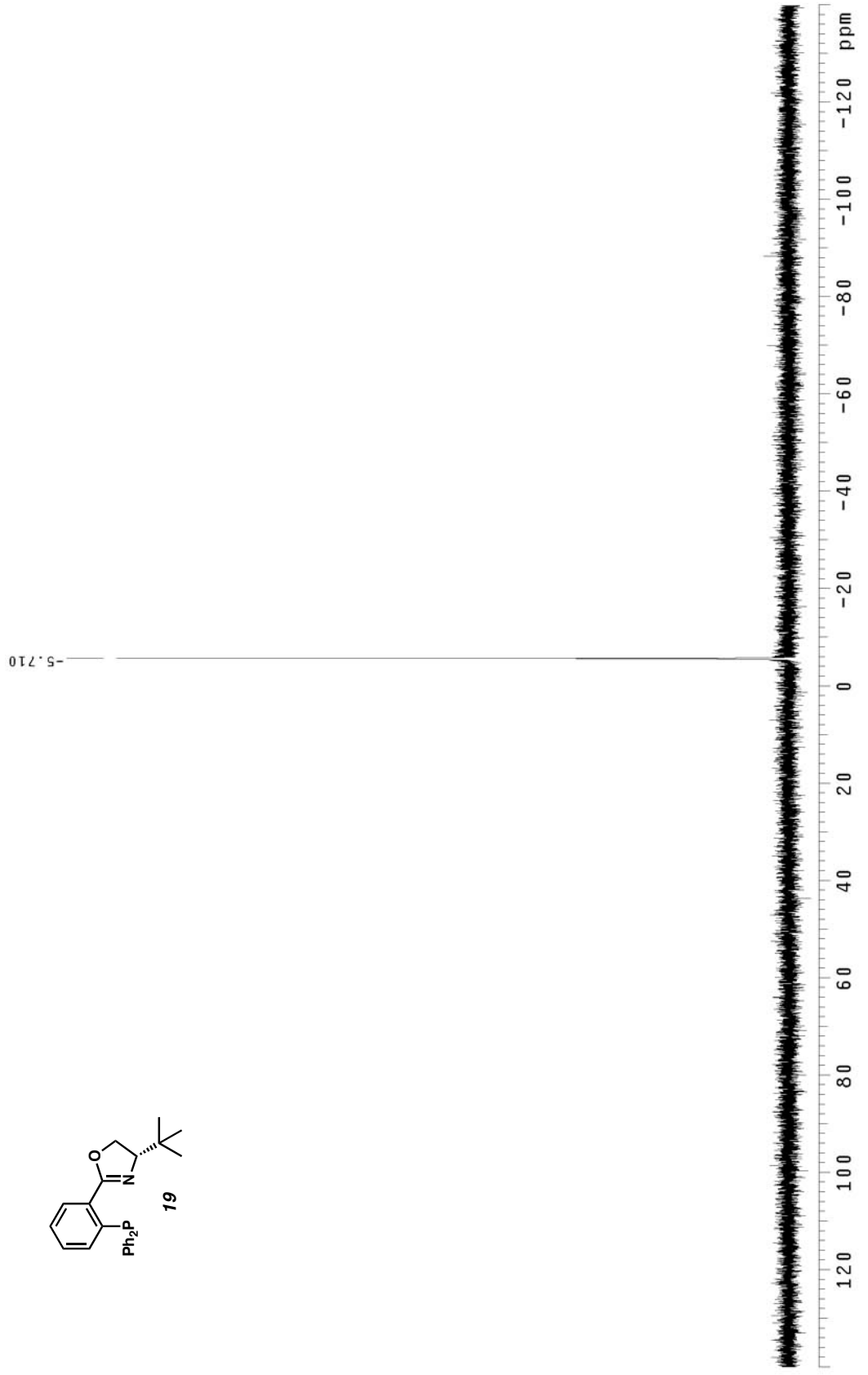
Relative Abundance of Four Product Masses



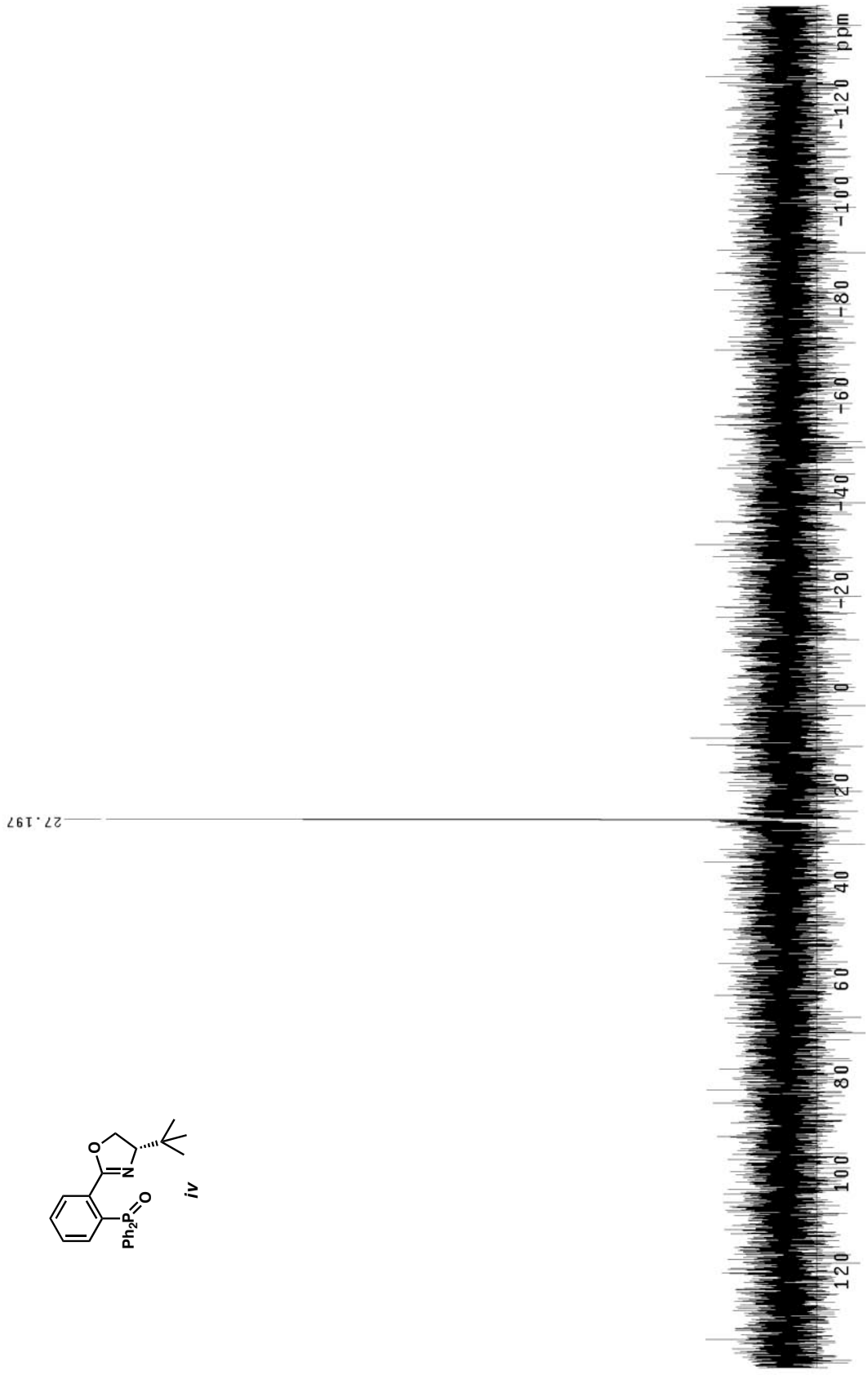
Mass	Scans	Integral	% Abundance
152.1183	110-118	459336	21.23 %
154.1328	110-118	478480	22.12 %
155.1388	108-118	720536	33.31 %
157.1522	107-118	504864	23.34 %
	Total	2163216	100 %

Although the total ion counts are not rigorously quantitative, they clearly suggest that all four masses are present in nearly equal proportions. This was the case whether the reaction was run in THF, dioxane, or benzene.

^{31}P NMR Studies:

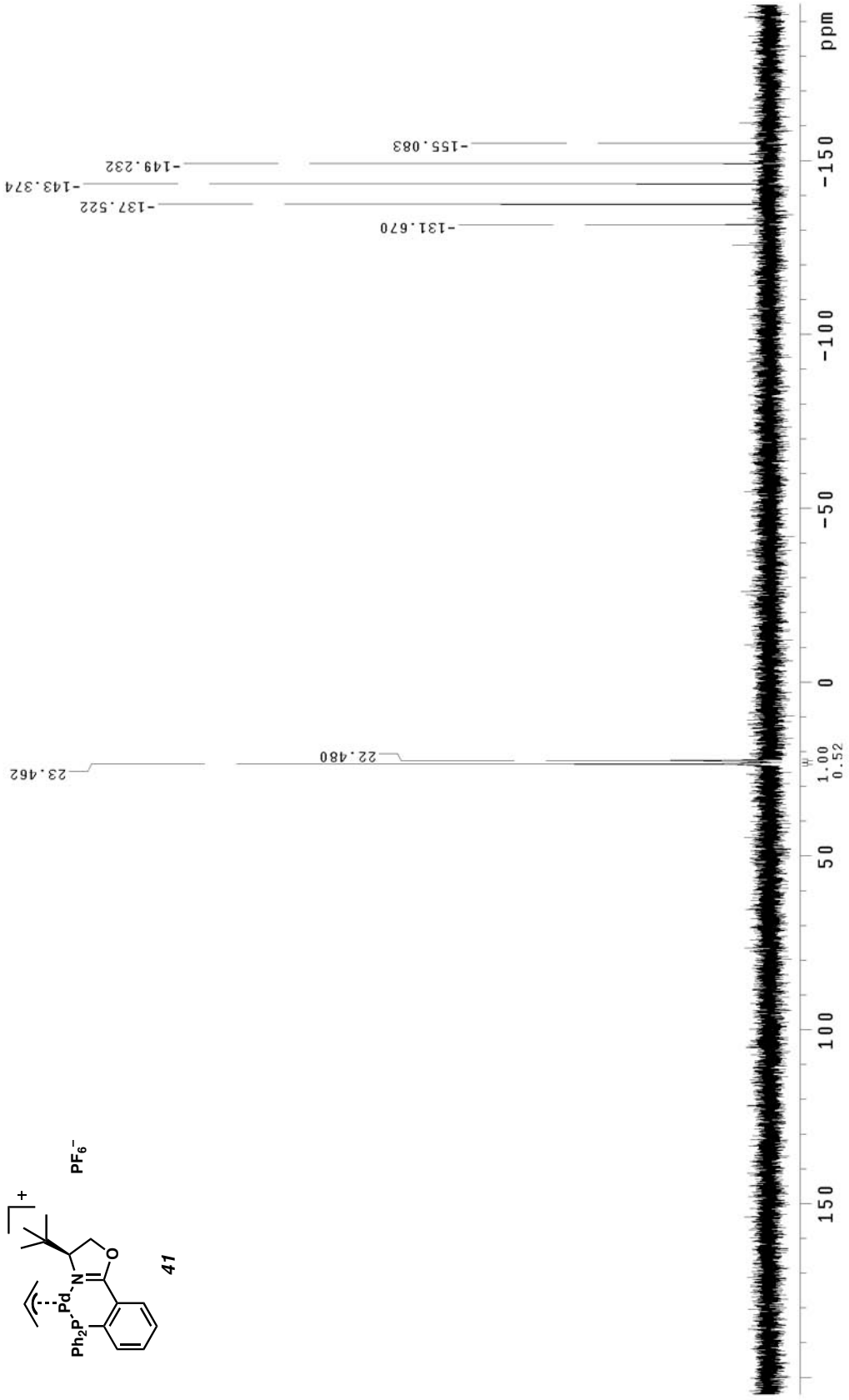


^{31}P NMR of (*S*)-*t*-Bu-PHOX (**19**) in THF



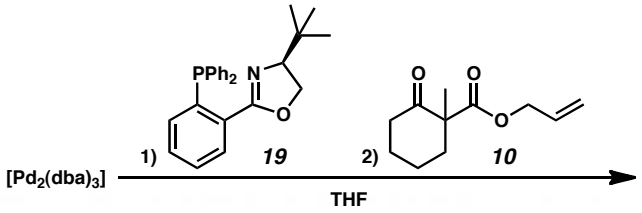
iv

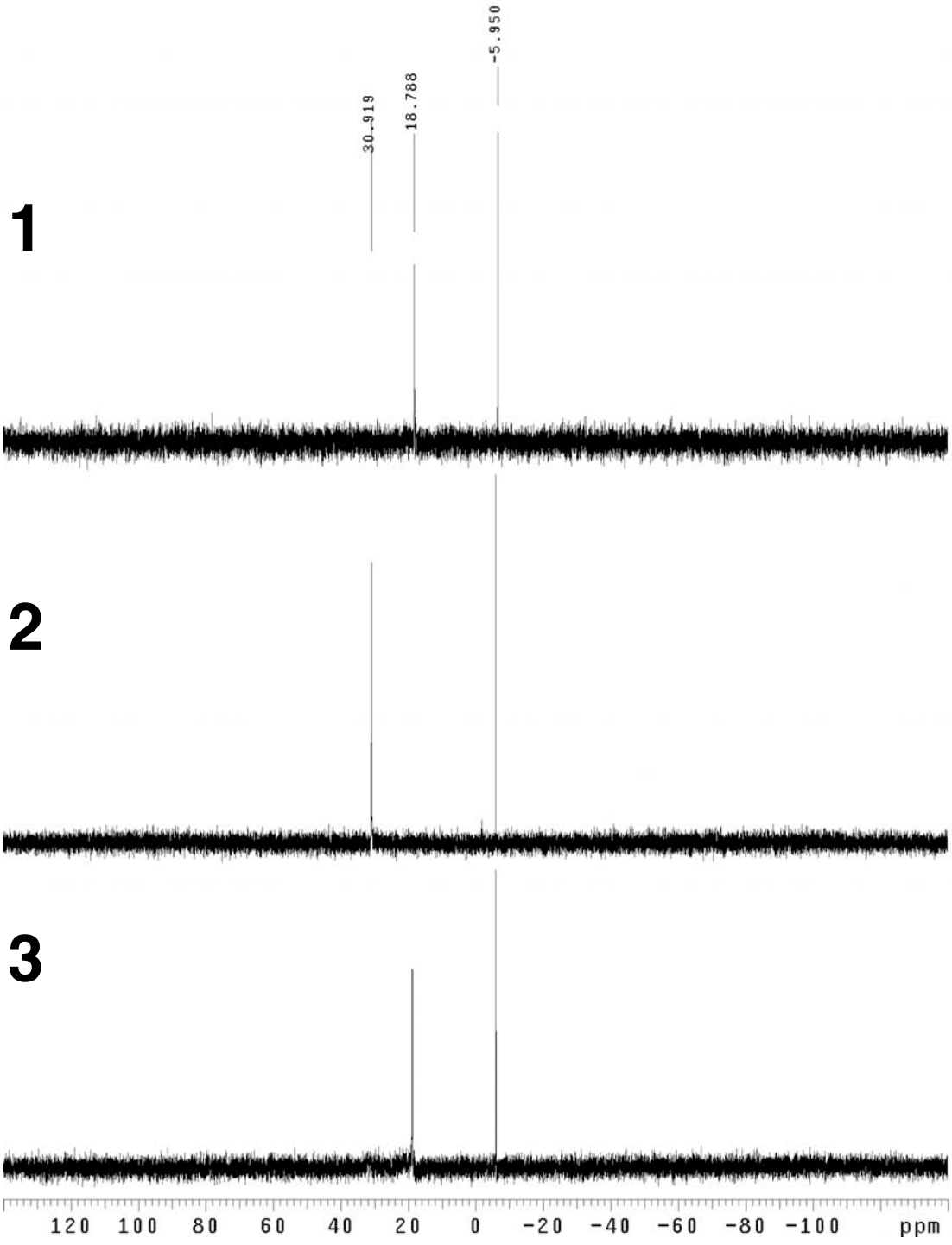
^{31}P NMR of (*S*)-*t*-Bu-PHOX oxide (**iv**) in THF



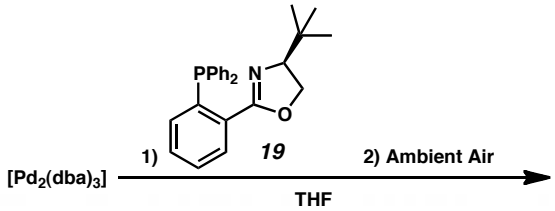
^{31}P NMR of complex **41** in THF

^{31}P NMR study of catalyst resting state. In a nitrogen atmosphere glove box $Pd_2(dba)_3$ (3.0 mg, 3.3 μmol, 1 equiv, dark red-purple powder) was weighed out in a 1 dram vial. Solid (*S*)-*t*-Bu-PHOX ligand (**19**, 3.3 mg, 8.5 μmol, 2.6 equiv, white crystalline solid) was weighed out in a second 1 dram vial. THF (1 mL) that had been dried on an alumina column and then stored over 4Å molecular sieves in the glove box was filtered through a pipette filter constructed with a 2.4 mm GF/A Whatman glass microfibre filter directly into the vial containing the (*S*)-*t*-Bu-PHOX ligand. The solution was mixed manually by pipette until all the material had dissolved forming a clear colorless solution. The solution was then moved by pipette and added to the vial containing $Pd_2(dba)_3$. This solution was mixed manually by pipette for 1 min during which time a dark red-purple solution formed that then lightened to a dark but richly orange color. This solution was then filtered through a pipette filter constructed with a 2.4 mm GF/A Whatman glass microfibre filter directly into an NMR tube separating a bright, richly orange filtrate from a black amorphous precipitate presumed to be colloidal Pd(0) particles. The NMR tube was then sealed with an appropriately sized septum and removed from the glove box. NMR spectrum #1 was taken at this time. Neat 1-methyl-2-oxo-cyclohexanecarboxylic acid allyl ester (**10**) (12.3 mg, 62.8 μmol, 19.1 equiv) was weighed out in, and added to the NMR tube via a 25 μL Hamilton syringe in a single portion. The NMR tube was shaken vigorously for 30 s, and the solution quickly changed color from a rich orange to a lighter yellow-green. NMR spectrum #2 was taken at this time. The NMR tube was then placed in an oil bath regulated at 24 °C and warmed for 3 h, which was 20 min longer than it took for the solution's color to change to a rich orange from a lighter yellow-green. NMR spectrum #3 was taken at this time.

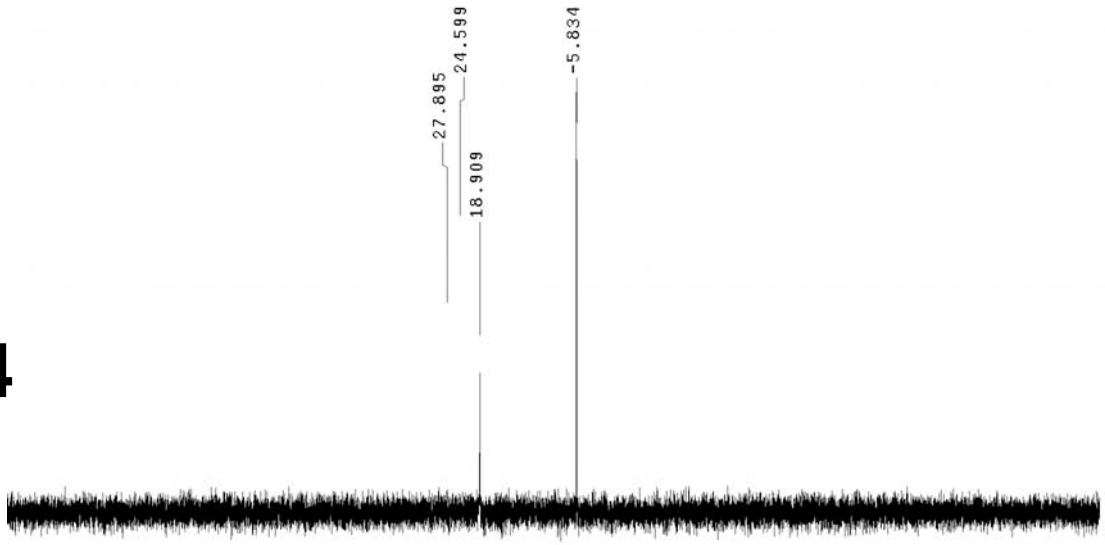

PPh2
N
O
1)
19
2)
O
O
O
10
[Pd2(dba)3]
THF


-5.950
18.788
30.919
1
2
3
120
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

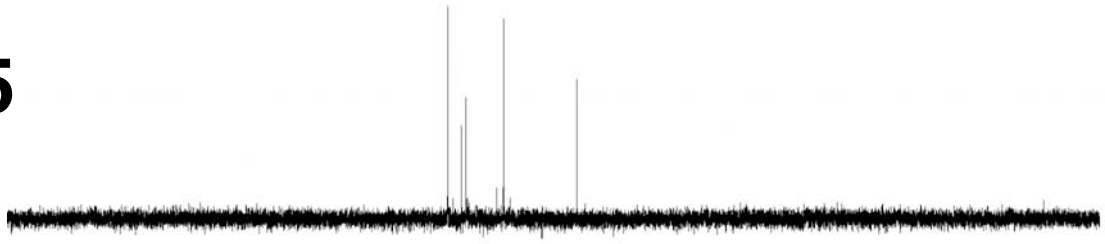
^{31}P NMR study of catalyst decomposition in ambient air. In a nitrogen atmosphere glove box, $Pd_2(dba)_3$ (3.0 mg, 3.3 μmol, 1 equiv, dark red-purple powder) was weighed out in a 1 dram vial. Solid (*S*)-*t*-Bu-PHOX ligand (**19**, 3.3 mg, 8.5 μmols, 2.6 equiv, white crystalline solid) was weighed out in a second 1 dram vial. THF (1 mL) that had been dried on an alumina column and then stored over 4Å molecular sieves in the glove box was filtered through a pipette filter constructed with a 2.4 mm GF/A Whatman glass microfibre filter directly into the vial containing the (*S*)-*t*-Bu-PHOX ligand (**19**). The solution was mixed manually by pipette until all the material had dissolved forming a clear colorless solution. The solution was then moved by pipette and added to the vial containing $Pd_2(dba)_3$. This solution was mixed manually by pipette for 1 min during which time a dark red-purple solution formed that then lightened to a dark but richly orange solution. This solution was then filtered through a pipette filter constructed with a 2.4 mm GF/A Whatman glass microfibre filter directly into an NMR tube separating a bright, richly, orange filtrate from a black amorphous precipitate presumed to be colloidal Pd(0) particles. The NMR tube was then sealed with a standard appropriately sized plastic cap and removed from the glove box. NMR spectrum #4 was taken at this time. The NMR tube was then uncapped on the bench, and quickly flushed with a jet of air to purge the inert atmosphere above the solution in the tube. After 7 h, the solution in the tube had faded from a rich orange to lighter yellow color. NMR spectrum #5 was taken at this time. The tube was left to stand for another 36 h at which point clear crystalline masses had formed. NMR spectrum #6 was taken at this time.


PPh2
N
O
19
1)
2) Ambient Air
[Pd2(dba)3]
THF

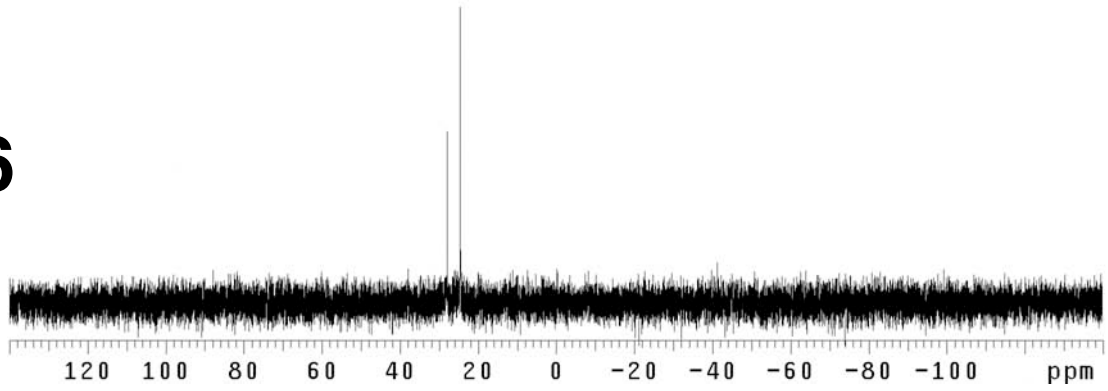
4


27.895
24.599
18.909
-5.834

5



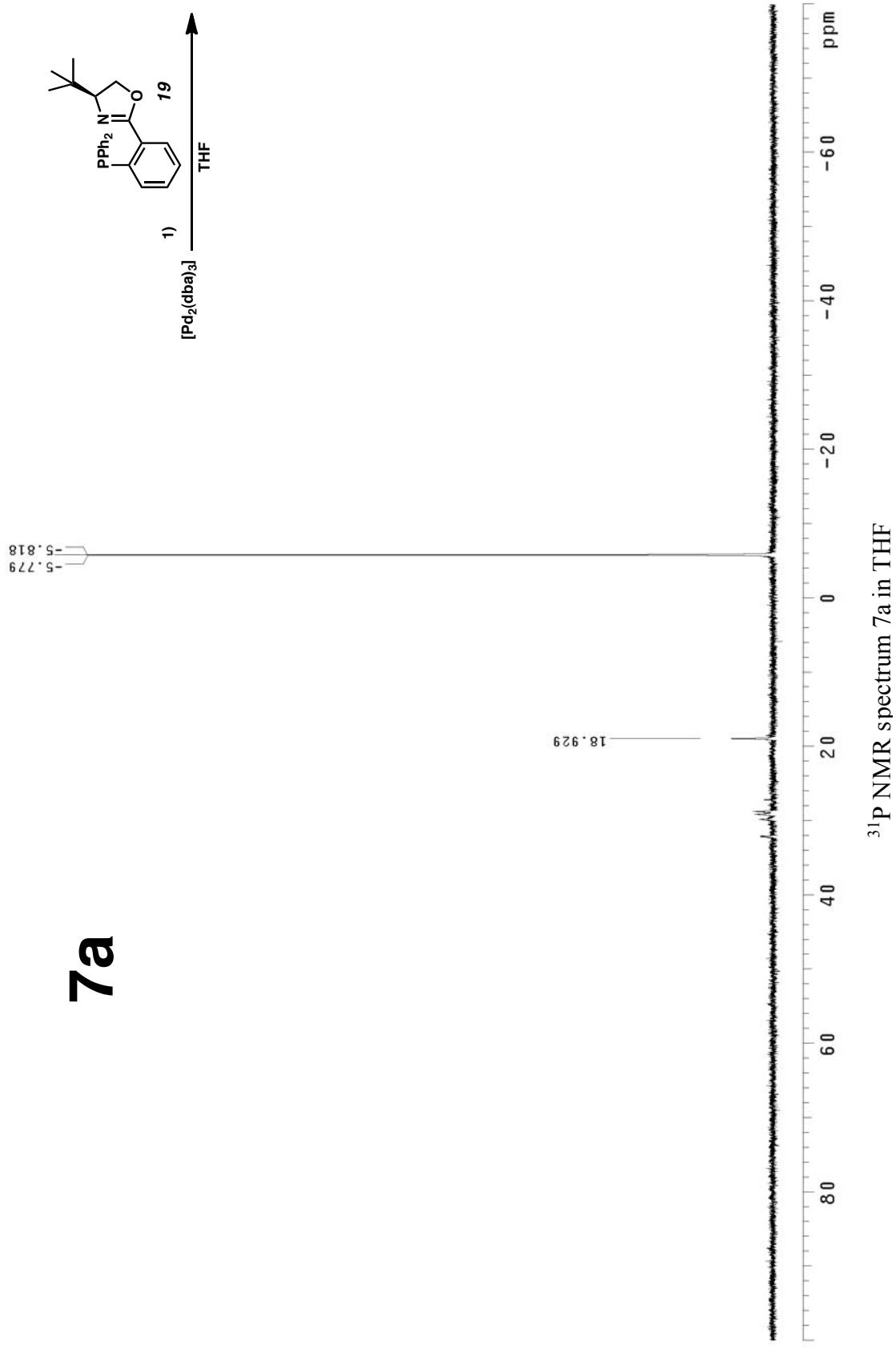
6


120
100
80
60
40
20
0
-20
-40
-60
-80
-100
ppm

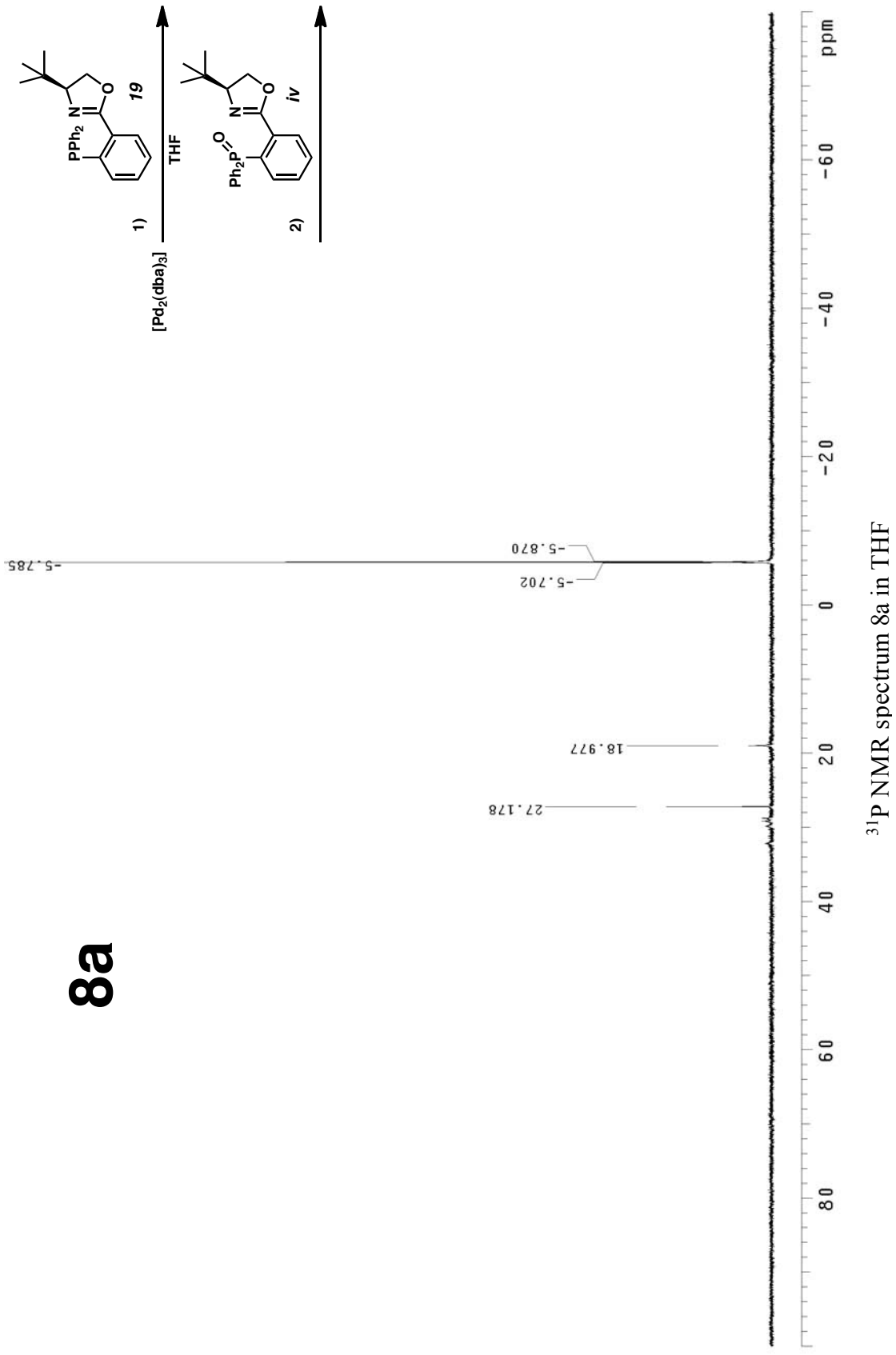
^{31}P NMR study of the Pd-catalyzed conversion of (*S*)-*t*-Bu-PHOX to (*S*)-*t*-Bu-PHOX oxide with ambient air as the oxident. In a nitrogen glove box, (*S*)-*t*-Bu-PHOX ligand (**19**, 18.7 mg, 48.3 μmol, 1 equiv, white crystalline powder) followed by $Pd_2(dba)_3$ (4.8 mg, 5.2 μmol, 0.108 equiv, 10.8 mol%, dark red-purple powder) were weighed out neat directly into a 1 dram vial. THF (1 mL) that had been dried on an alumina column and then stored over 4Å molecular sieves in the glove box was filtered through a pipette filter constructed with a 2.4 mm GF/A Whatman glass microfibre filter directly into the vial. The solution was mixed manually by pipette for 5 min and then left to mix by diffusion for another 20 min, during which time an initially dark red-purple solution formed that then lightened to a rich orange color. The solution was then filtered through a pipette filter constructed with a 2.4 mm GF/A Whatman glass microfibre filter directly into an NMR tube separating a bright, richly orange filtrate from a black amorphous precipitate presumed to be colloidal Pd(0) particles. The NMR tube was then sealed with an appropriately sized septum and removed from the glove box. NMR spectrum #7a was taken at this time. (*S*)-*t*-Bu-PHOX oxide (**iv**, 1.97 mg, 4.9 μmol, 0.101 equiv, 10 mol%, white powder) was weighed out in a 0.5 dram vial. The vial was then sealed with a septum and sparged with argon for 10 s. Anhydrous THF (0.2 mL) was added to the 0.5 dram vial by syringe. The vial was swirled manually until all of its contents dissolved forming a clear solution. The solution in the 0.5 dram vial was then moved by syringe and added as a single portion to the NMR tube. NMR spectrum #8a was taken at this time. The NMR tube was then opened up on the bench and briefly flushed with a jet of ambient air to expel the layer of inert atmosphere above the solution in the tube.

A second NMR tube was flame dried and backfilled with argon. (*S*)-*t*-Bu-PHOX ligand (**19**, 5.0 mg, 12.9 μmol, white crystalline powder) was weighed out and added to the second NMR tube. Anhydrous THF (1 mL) was added to the second NMR tube via a syringe, dissolving the contents of the tube and forming a clear solution. The second NMR tube was then opened on the bench and briefly flushed with a jet of ambient air to expel the layer of inert atmosphere above the solution in the tube.

Both NMR tubes were then left opened in an oil bath heated to 25 °C. After 2 h the NMR spectra #9a and #9b were taken of the NMR tube containing the mixture of Pd and ligand, and the NMR tube containing only the ligand, respectively. At 10 h NMR spectra #10a and #10b were taken. At 53 hours NMR spectra #11a and #11b were taken. At 160 hours NMR spectra #12a and #12b were taken.

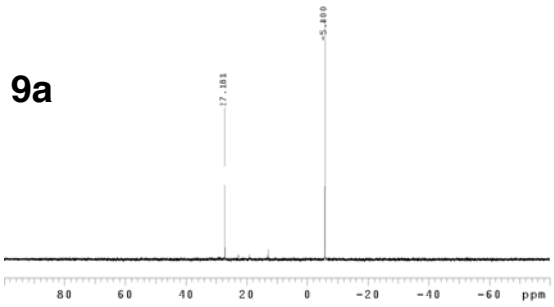


^{31}P NMR spectrum 7a in THF

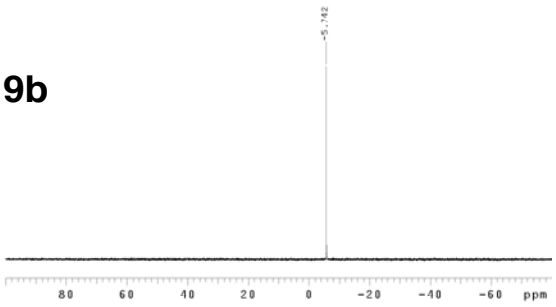


^{31}P NMR spectrum 8a in THF

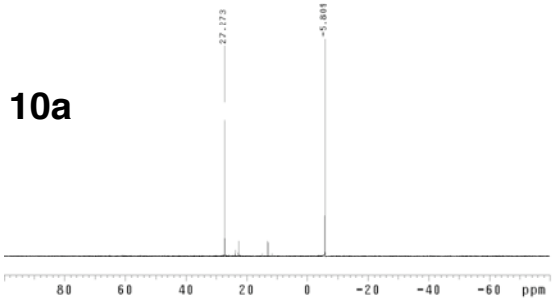
9a



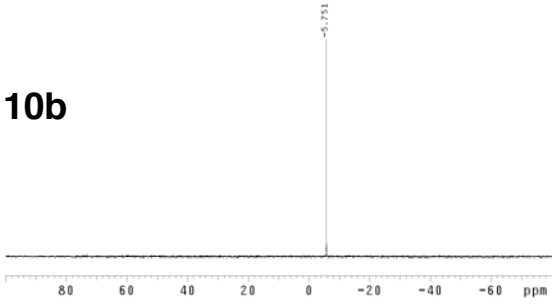
9b



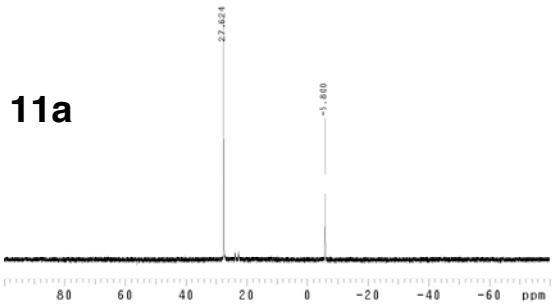
10a



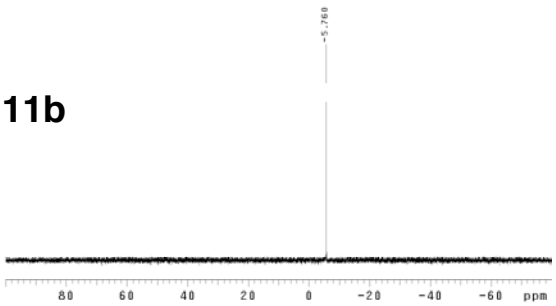
10b



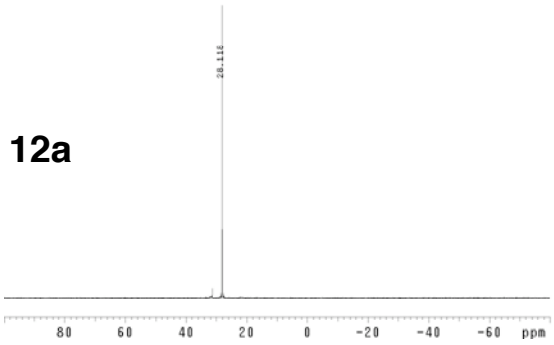
11a



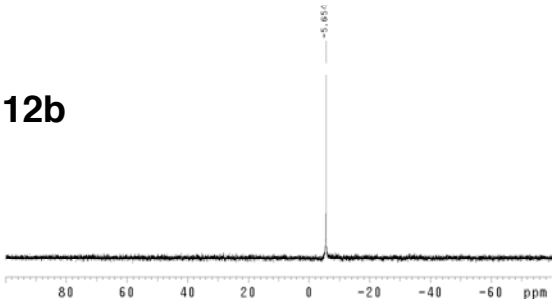
11b



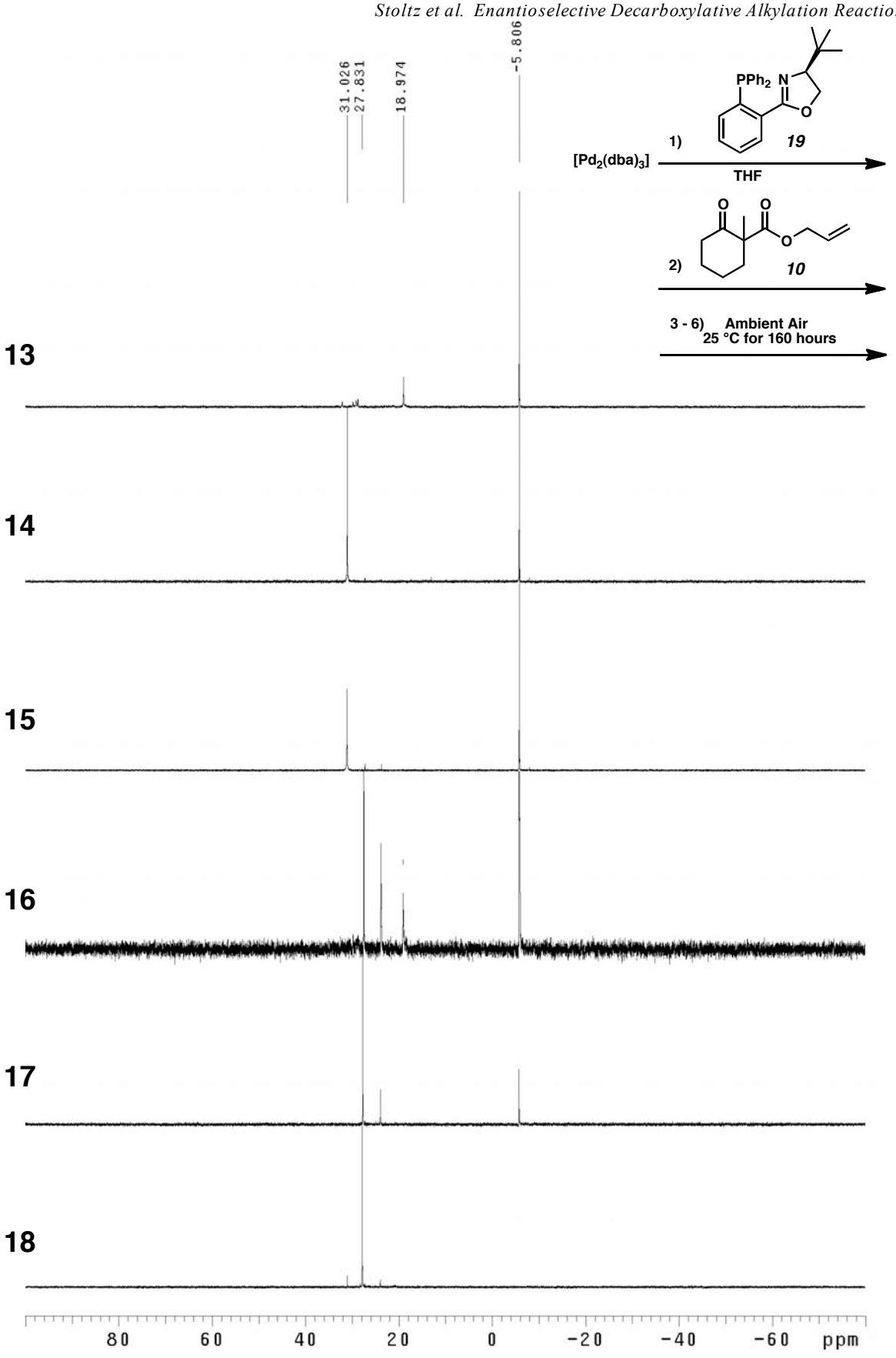
12a



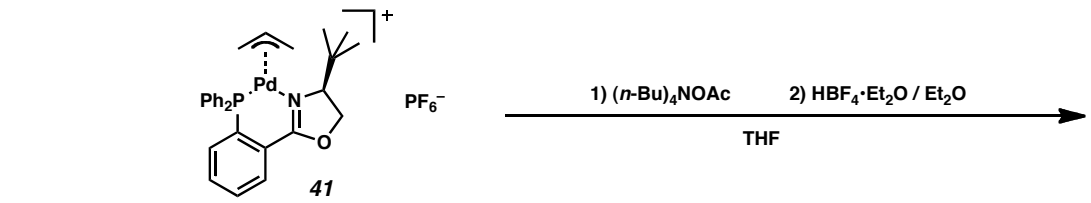
12b

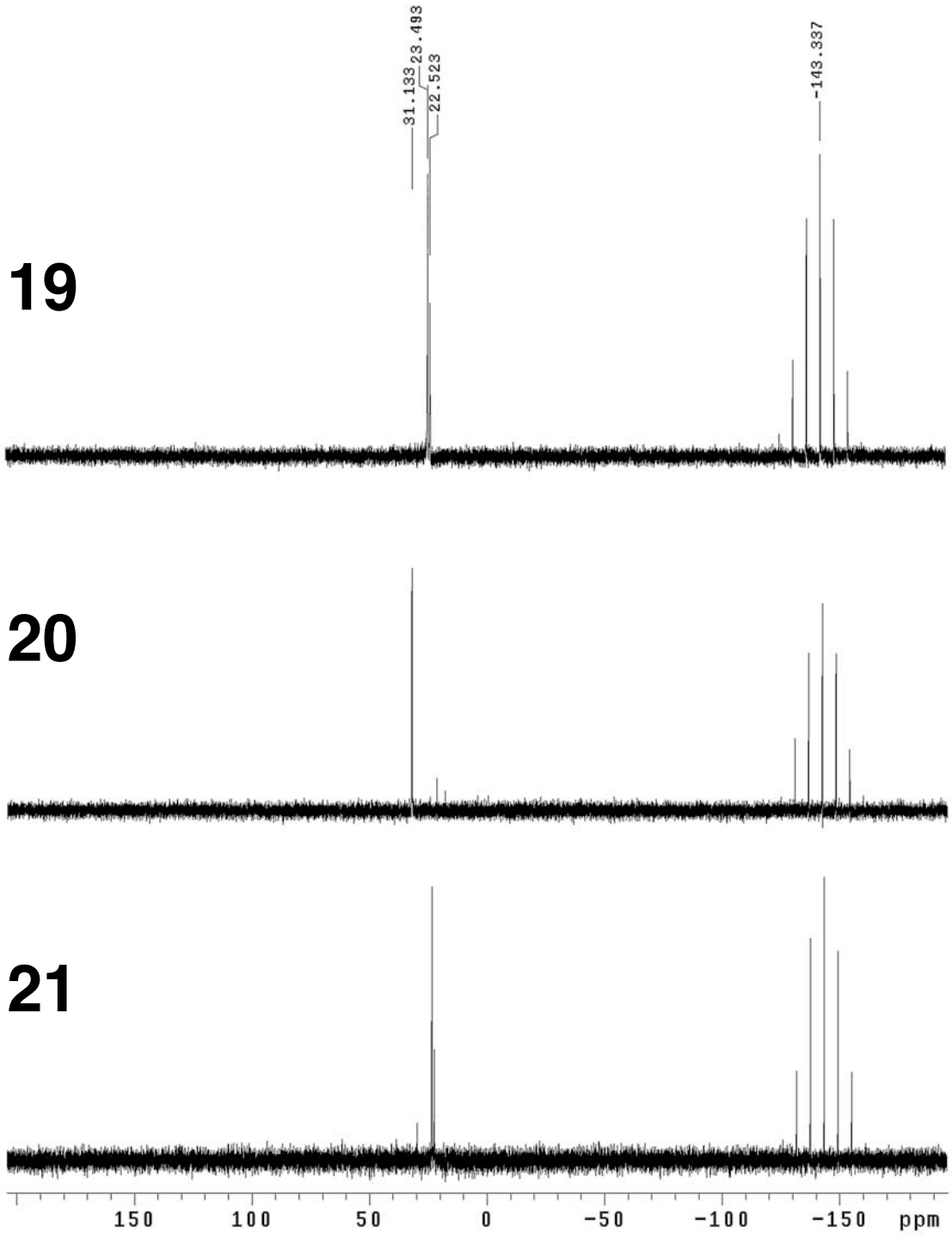


^{31}P NMR studies of catalyst decomposition in air from the catalyst's resting state. In a nitrogen glove box $Pd_2(dba)_3$ (8.4 mg, 9.17 μmol, 0.04 equiv, 4.3 mol%, dark red-purple powder) followed by (*S*)-*t*-Bu-PHOX (**19**, 22.0 mg, 56.8 μmol, 26.8 mol%, white crystalline powder) were weighed out neat into a single 1 dram vial. THF (1 mL) that had been dried on an alumina column and then stored over 4Å molecular sieves in the glove box, was filtered through a pipette filter constructed with a 2.4 mm GF/A Whatman glass microfibre filter directly into the 1 dram vial. The solution was mixed manually by pipette for 5 min and then left to mix by diffusion for another 10 min, during which time an initially dark red-purple solution formed that then lightened to a rich orange color. The solution was then filtered through a pipette filter constructed with a 2.4 mm GF/A Whatman glass microfibre filter directly into an NMR tube separating a bright, richly orange filtrate from a black amorphous precipitate presumed to be colloidal Pd(0) particles. The NMR tube was sealed with an appropriately sized septum and removed from the glove box. NMR spectrum #13 was taken at this time. Neat 1-methyl-2-oxo-cyclohexanecarboxylic acid allyl ester (**10**) (41.5 mg, 211.5 μmol, 1 equiv) was weighed out and added in a single portion via a 100 μL Hamilton syringe. The NMR tube was inverted once, and immediately changed color from a rich orange to a lighter yellow-green. NMR spectrum #14 was taken at this time. The NMR tube was then uncapped on the bench, and quickly flushed with a jet of air to expel the inert atmosphere above the solution in the tube. The NMR tube was left open and then placed in an oil bath regulated to 25 °C. After 2 h, NMR spectrum #15 was taken. After 16 h NMR spectrum #16 was taken. After 48 h NMR spectrum #17 was taken. After 160 h NMR spectrum #18 was taken. The solution had turned a light yellow by this juncture.

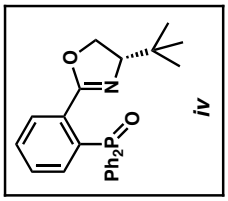

31.026
27.831
18.974
-5.806
PPh2
N
O
19
1)
[Pd2(dba)3]
THF
O
O
O
10
2)
3 - 6) Ambient Air
25 °C for 160 hours
13
14
15
16
17
18
80
60
40
20
0
-20
-40
-60
ppm

^{31}P NMR study of acetate then acid addition to the palladium π-allyl cation. [Pd(II)(allyl)PHOX]•PF_6 salt (**41**) (12.8 mg, 18.8 μmol, 1 equiv, white powder) was weighed out in a 1 dram vial. Anhydrous THF (0.5 mL) was added to the 1 dram vial via syringe. The vial was sealed, and the solution was mixed manually by swirling until all the solids had dissolved leaving a faintly colored solution. The solution was then transferred via pipette into an NMR tube. NMR spectrum #19 was then collected, showing the endo and exo isomers (23.5 ppm and 22.5 ppm, unknown correspondence) of the [Pd(II)(allyl)PHOX] cation, and the septuplet of the PF_6^- anion. Tetra-*n*-butylammonium acetate (8.8 mg, 30.6 μmol, 1.6 equiv, hygroscopic white nuggets) was weighed into a separate 1 dram vial. Anhydrous THF (0.3 mL) was added to the new vial via syringe. The vial was sealed, and the solution was mixed manually by swirling until all the solids had dissolved, forming a clear colorless solution. The solution was transferred via pipette in a single portion to the NMR tube. Upon addition, the solution instantly became yellow as the two solutions mixed. The NMR tube was sealed and mixed via a single complete inversion turning the entire solution yellow. A ^{31}P NMR spectrum was collected at this time (not depicted) that showed a broad fluxional resonance at 29.9 ppm presumed to be an averaged state of an equilibrium. An additional 7.4 mg of tetra-*n*-butylammonium acetate (25.7 μmol, 1.37 equiv, 3.07 equiv total, hygroscopic white nuggets) was weighed out in a third 1 dram vial. Anhydrous THF (0.2 mL) was added to the third vial via syringe. The vial was sealed, and the solution was mixed manually by swirling until all the solids had dissolved, forming a clear colorless solution. This solution was transferred via pipette in a single portion to the NMR tube. The NMR tube was sealed and mixed via a single complete inversion causing a very subtle color shift in the solutions appearance. NMR spectrum #20 was collected at this time. of tetrafluoroboric acid diethyl ether adduct (54% weight in diethyl ether, 19.6 mg, 65.4 μmol, 3.47 equiv, light orange viscous solution) was weighed in a 100 μL Hamilton syringe under a blanket of argon, and then added to the NMR tube in a single portion. The NMR tube was sealed and mixed via a single complete inversion, causing the color to rapidly fade from bright yellow to faint beige. NMR spectrum #21 was collected at this time.


Ph2P
Pd
N
O
+
PF6−
41
1) (n-Bu)4NOAc
2) HBF4·Et2O / Et2O
THF

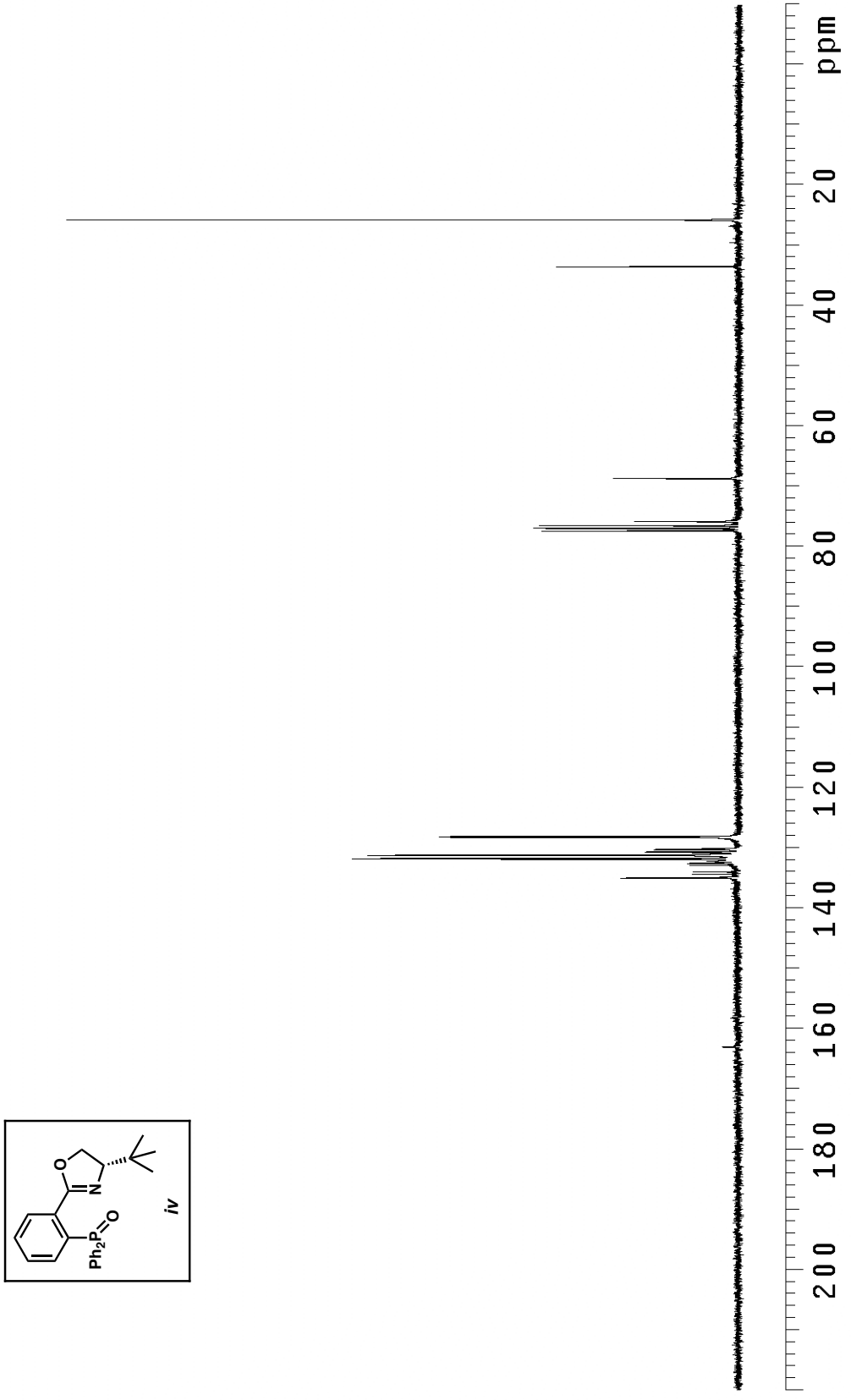

19
20
21
31.133
23.493
22.523
-143.337
150
100
50
0
-50
-100
-150
ppm

NMR Spectra:

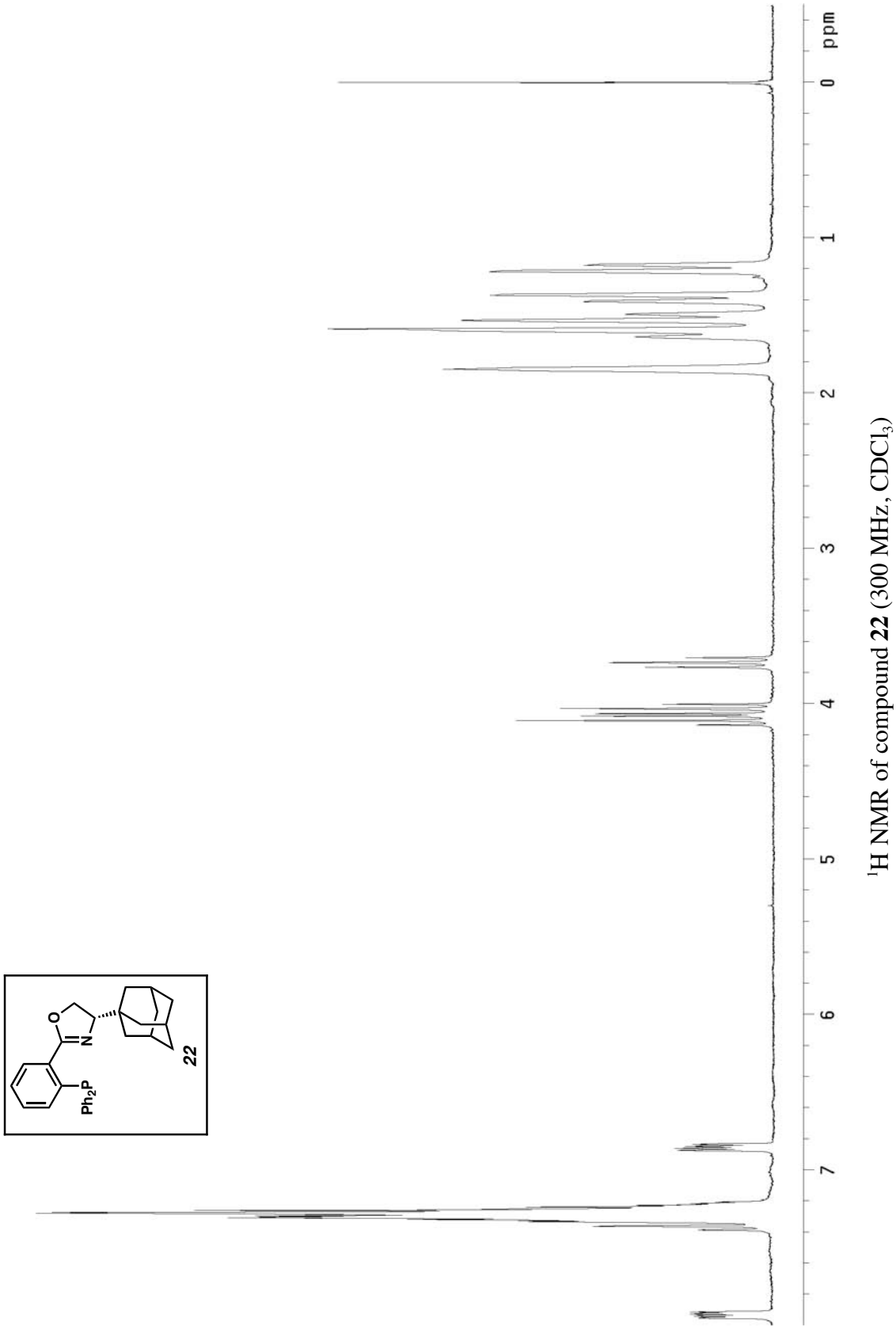


iv

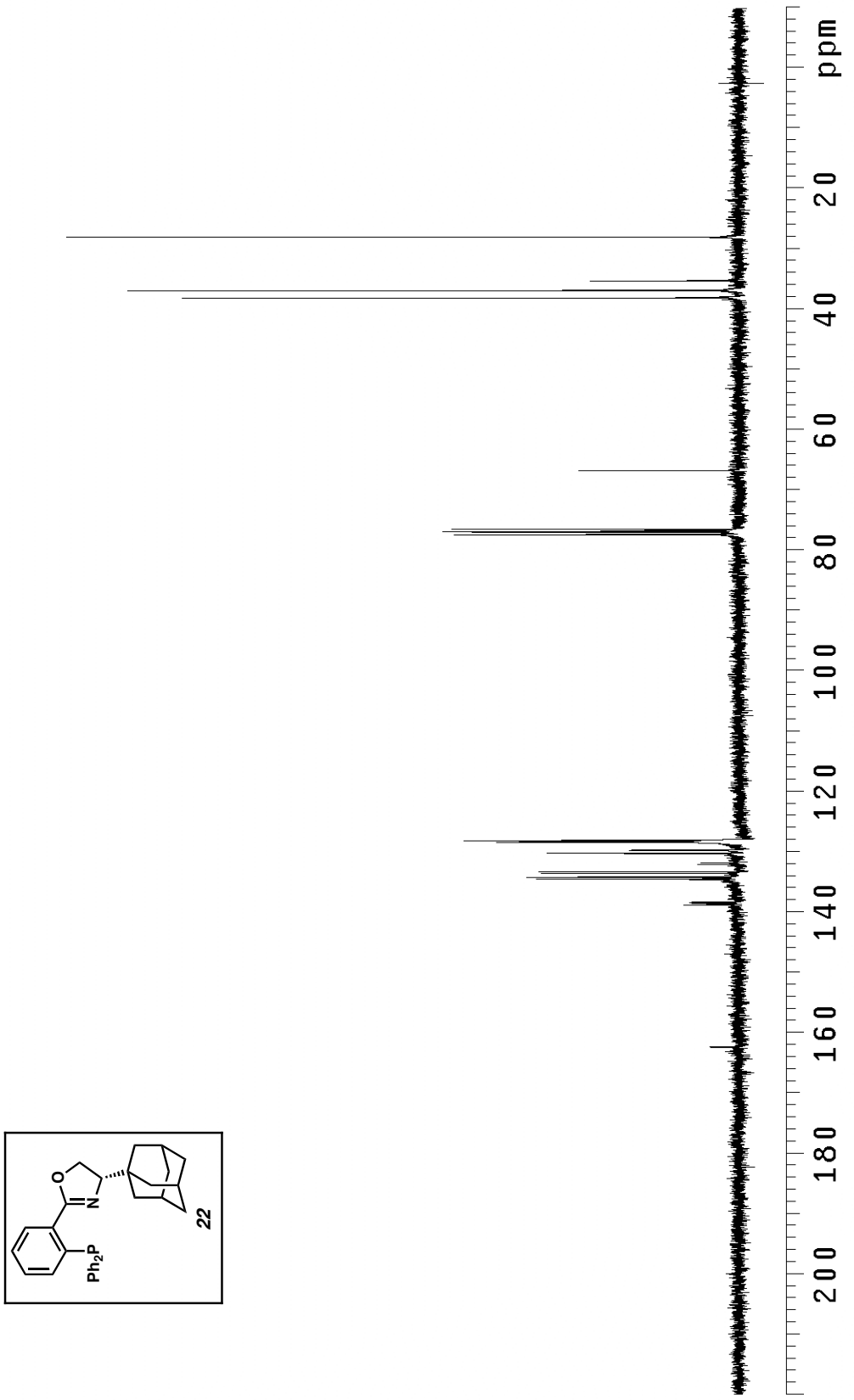
^{1}H NMR of compound **iv** (300 MHz, $CDCl_3$)



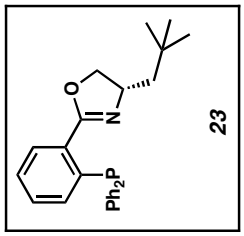
^{13}C NMR of compound **iv** (75 MHz, $CDCl_3$)



^{1}H NMR of compound **22** (300 MHz, $CDCl_3$)

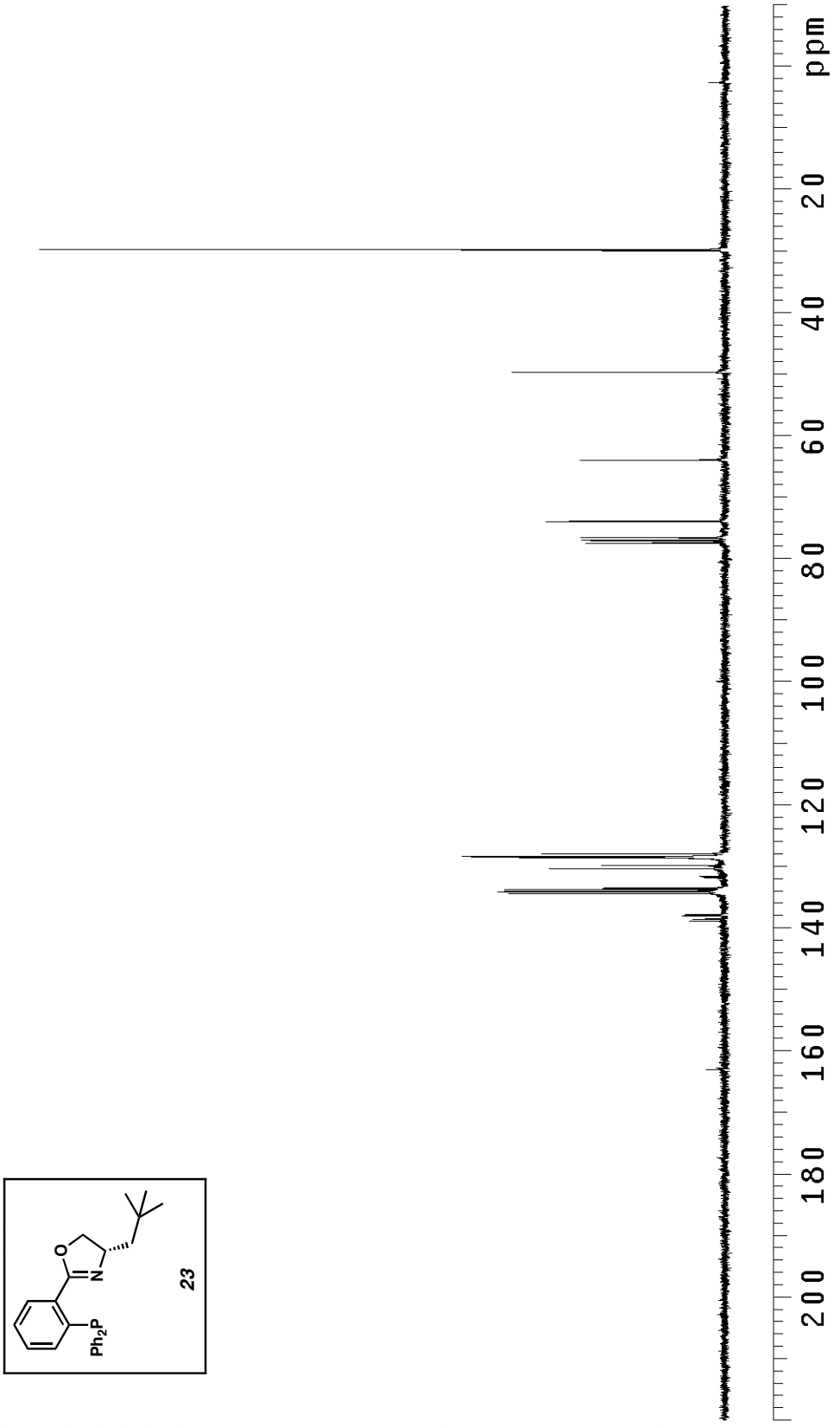


^{13}C NMR of compound **22** (75 MHz, $CDCl_3$)

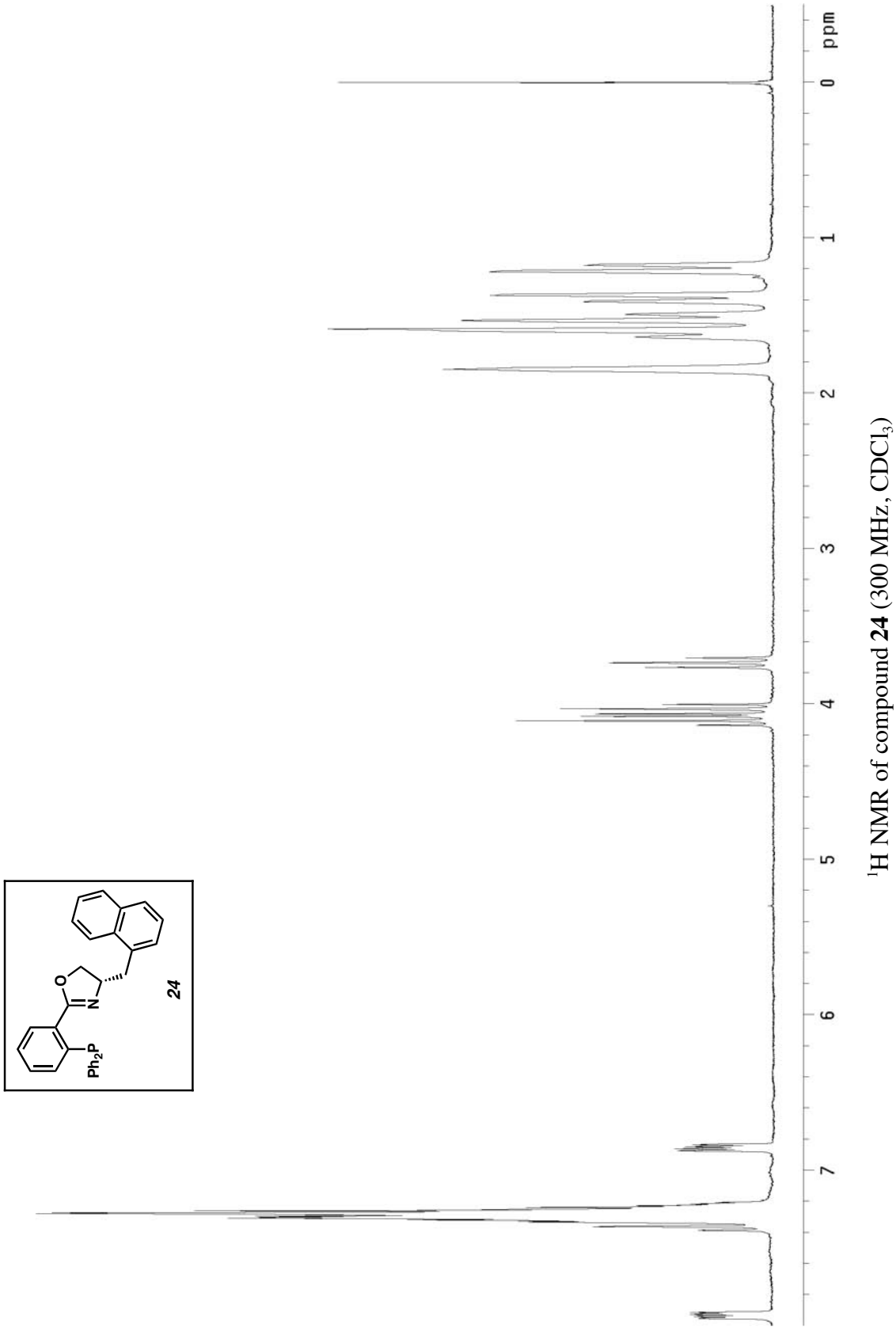


23

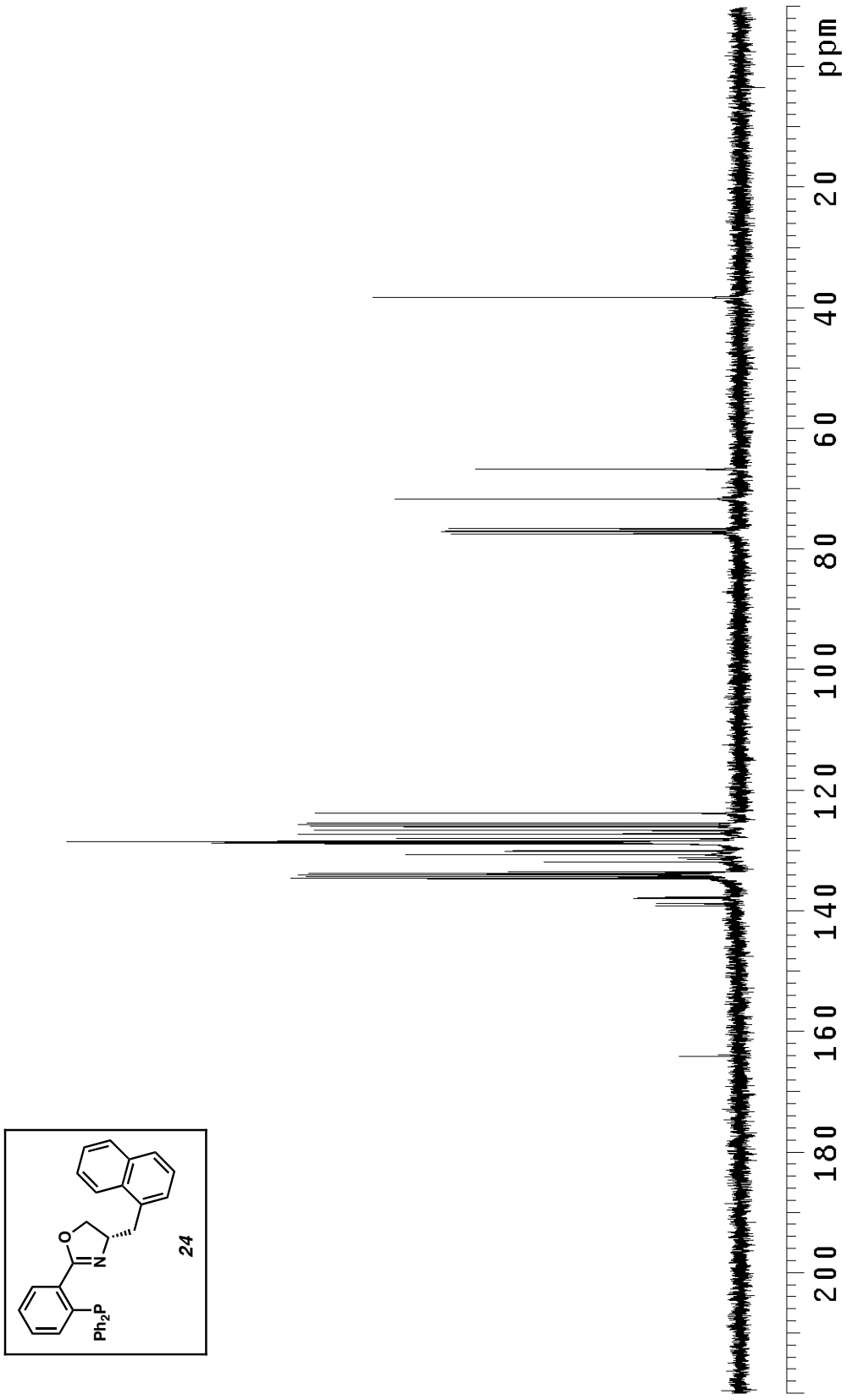
^{1}H NMR of compound **23** (300 MHz, $CDCl_3$)



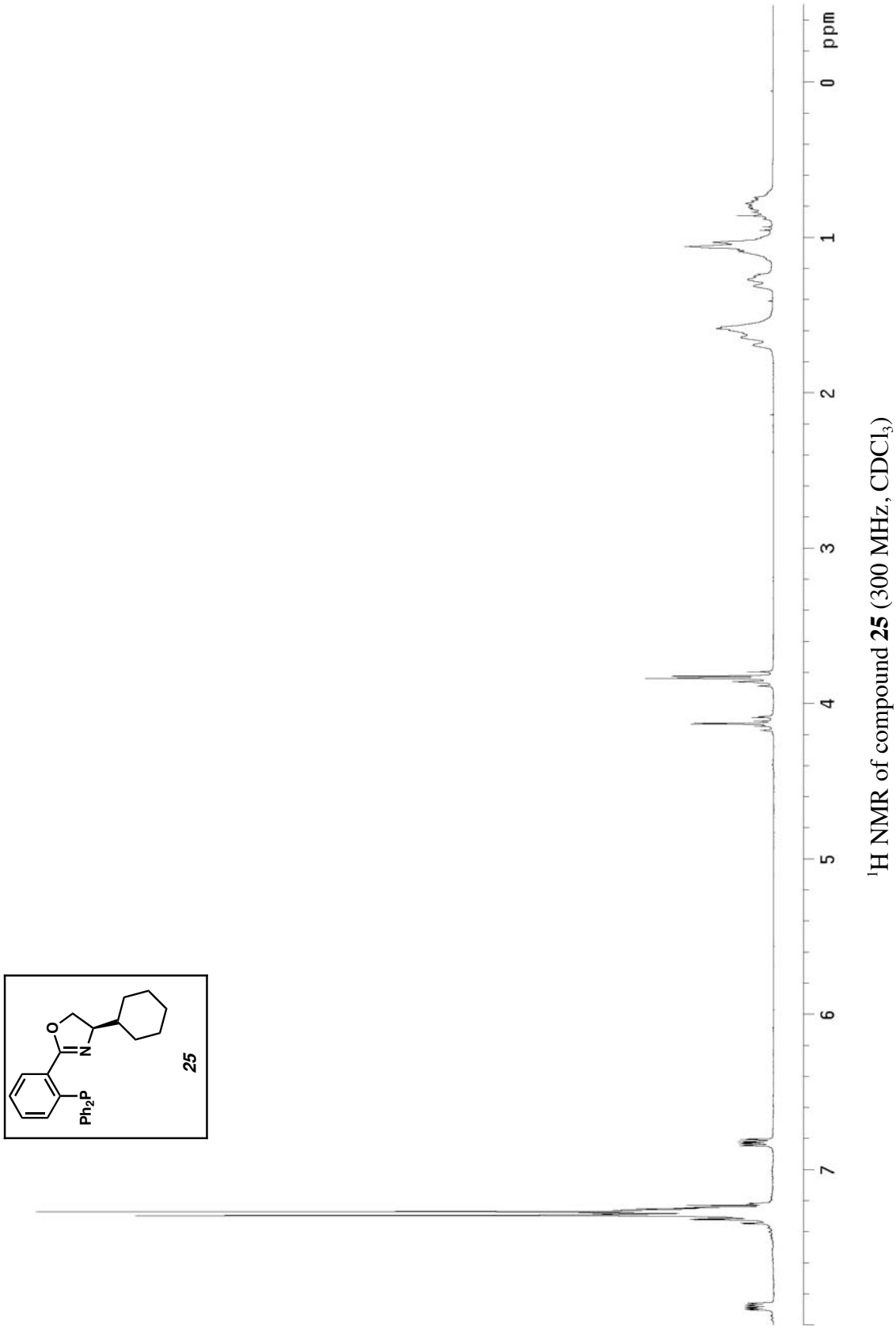
^{13}C NMR of compound **23** (75 MHz, $CDCl_3$)



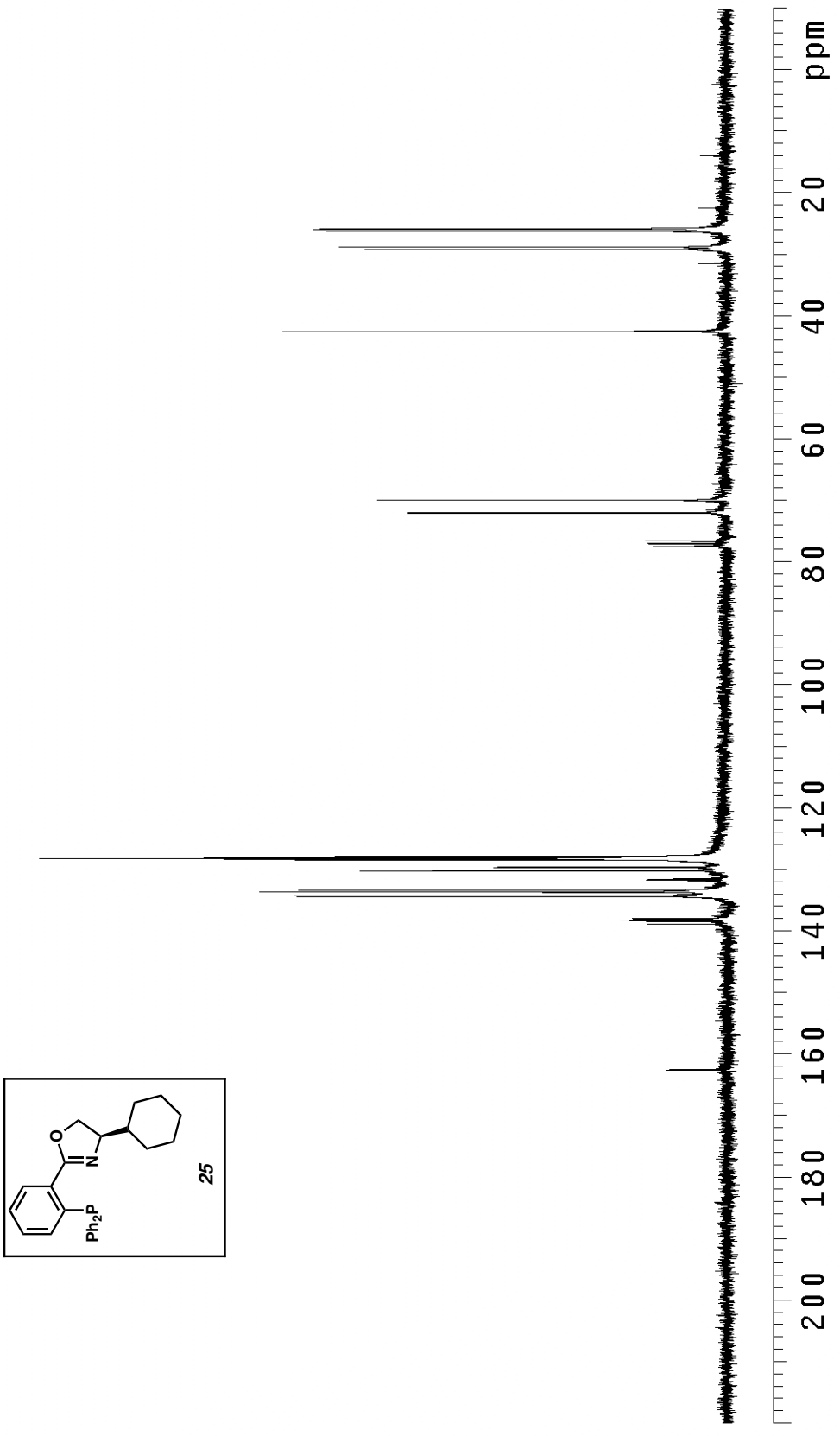
^{1}H NMR of compound **24** (300 MHz, $CDCl_3$)



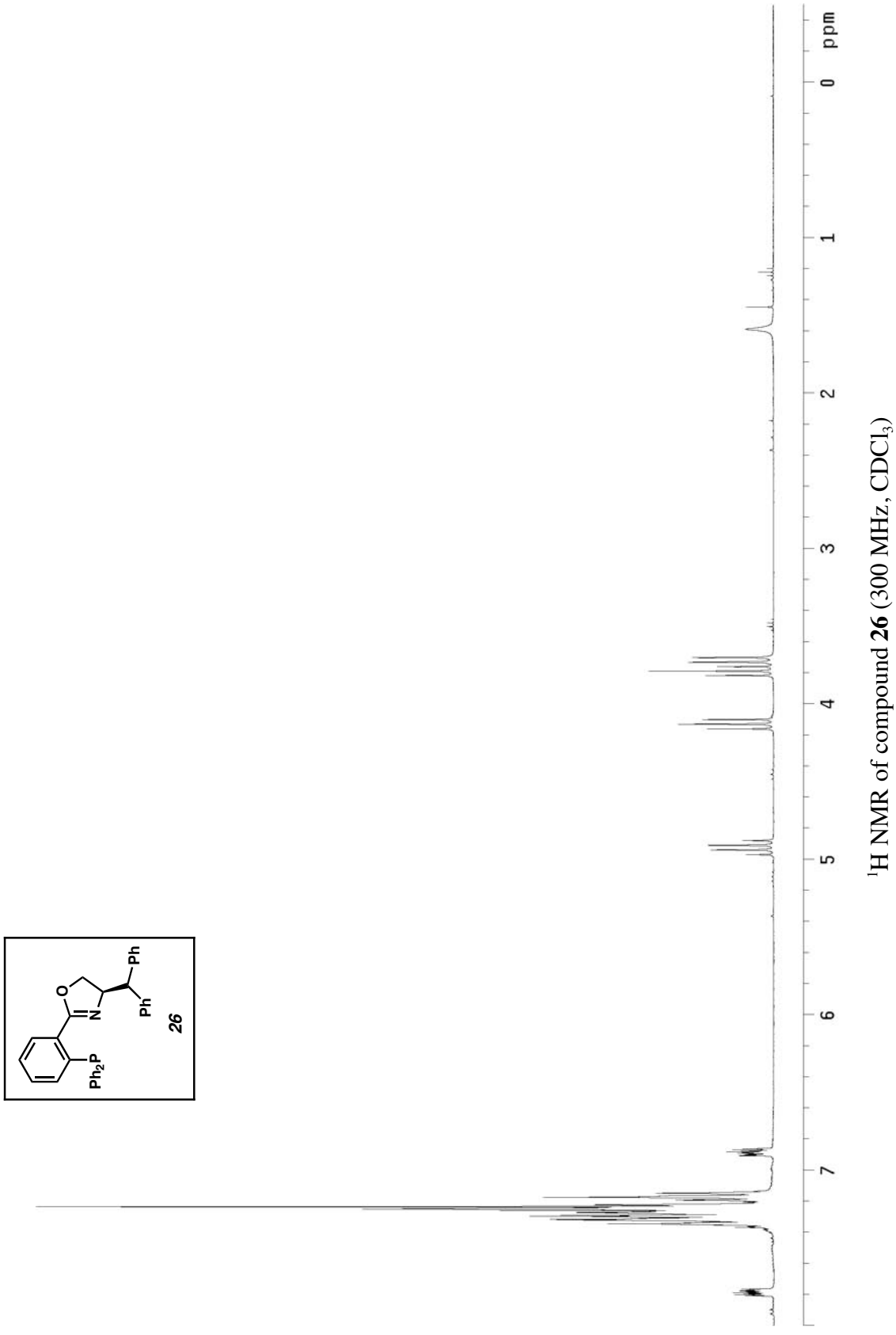
^{13}C NMR of compound **24** (75 MHz, $CDCl_3$)



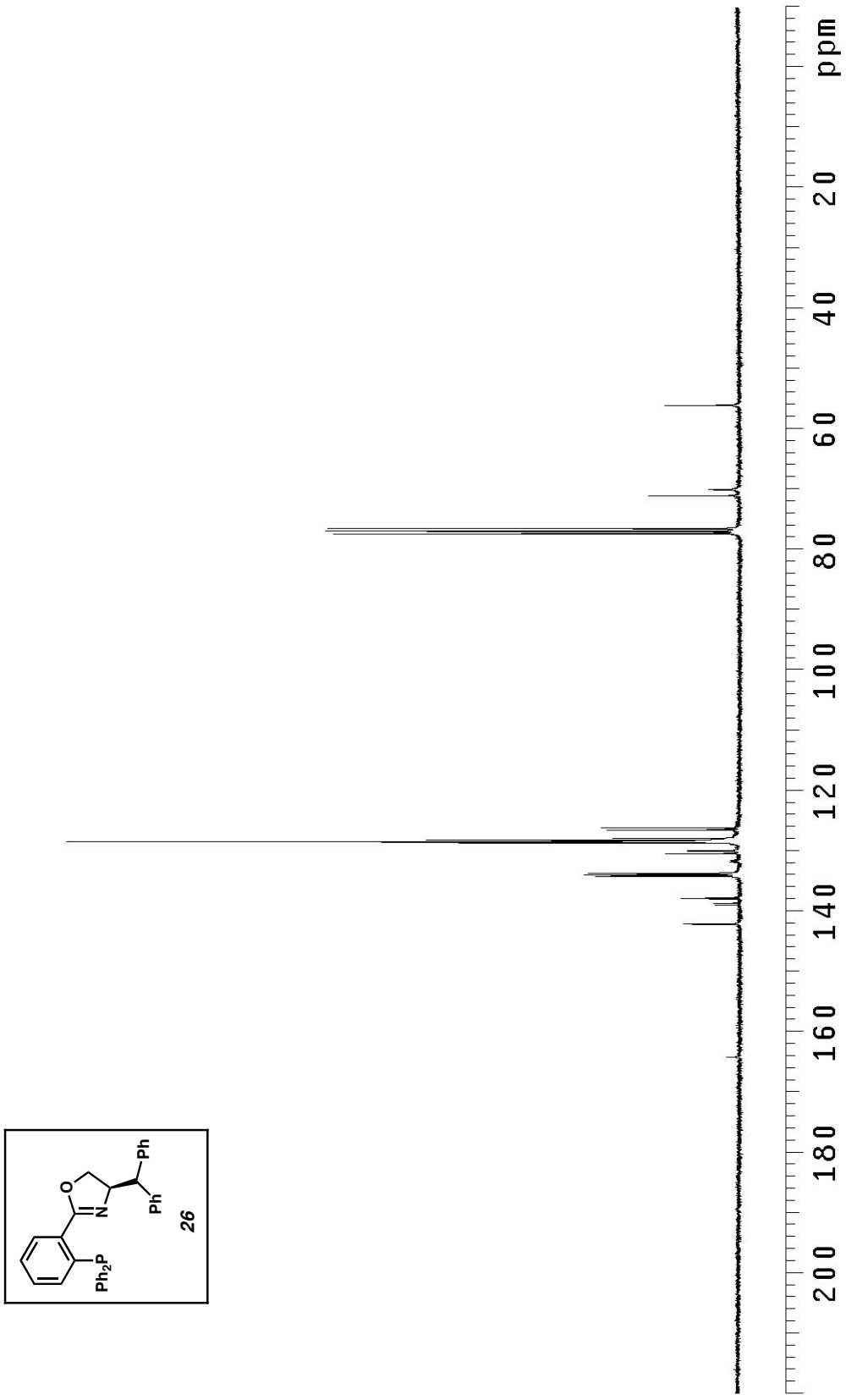
^{1}H NMR of compound **25** (300 MHz, $CDCl_3$)



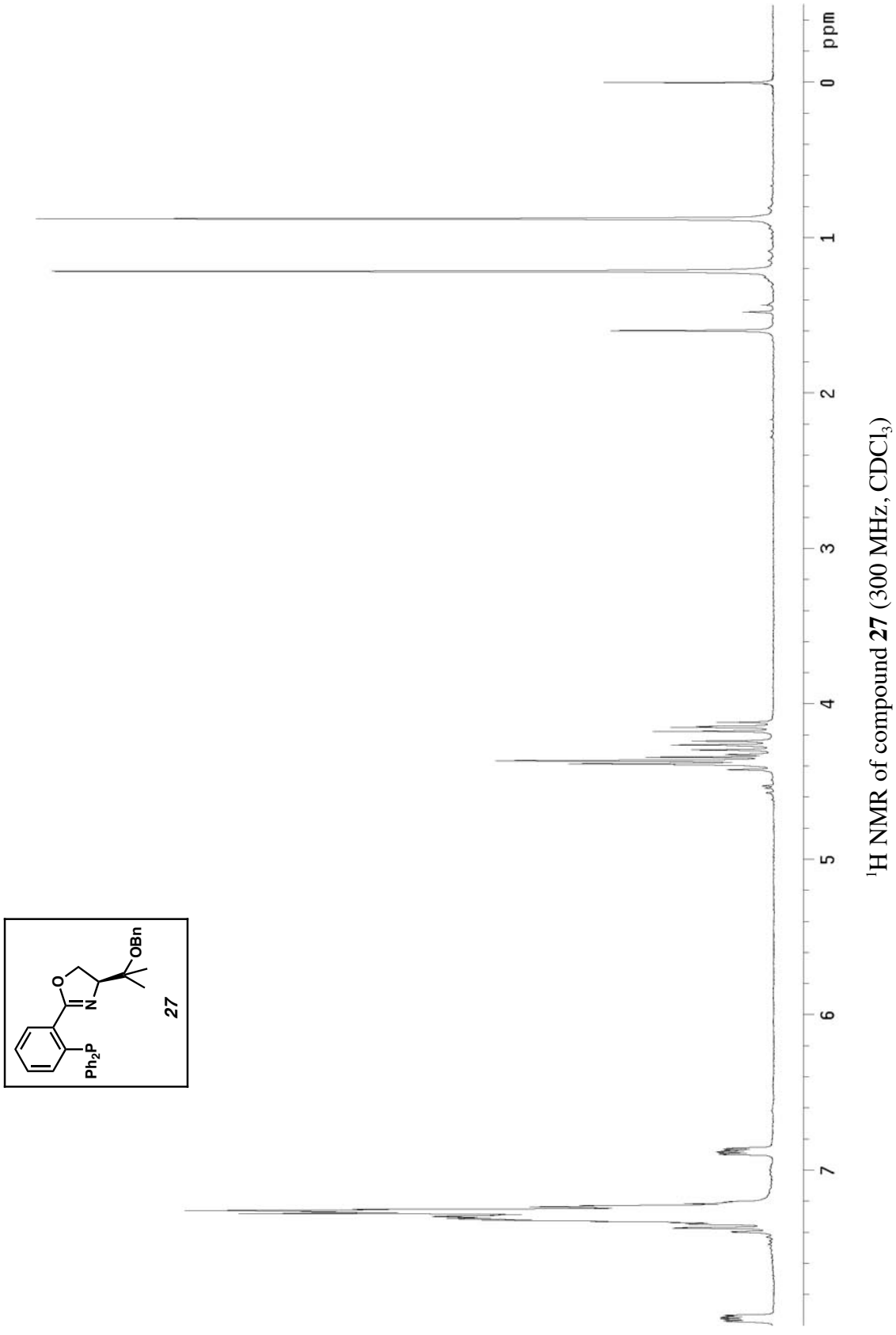
^{13}C NMR of compound **25** (75 MHz, $CDCl_3$)



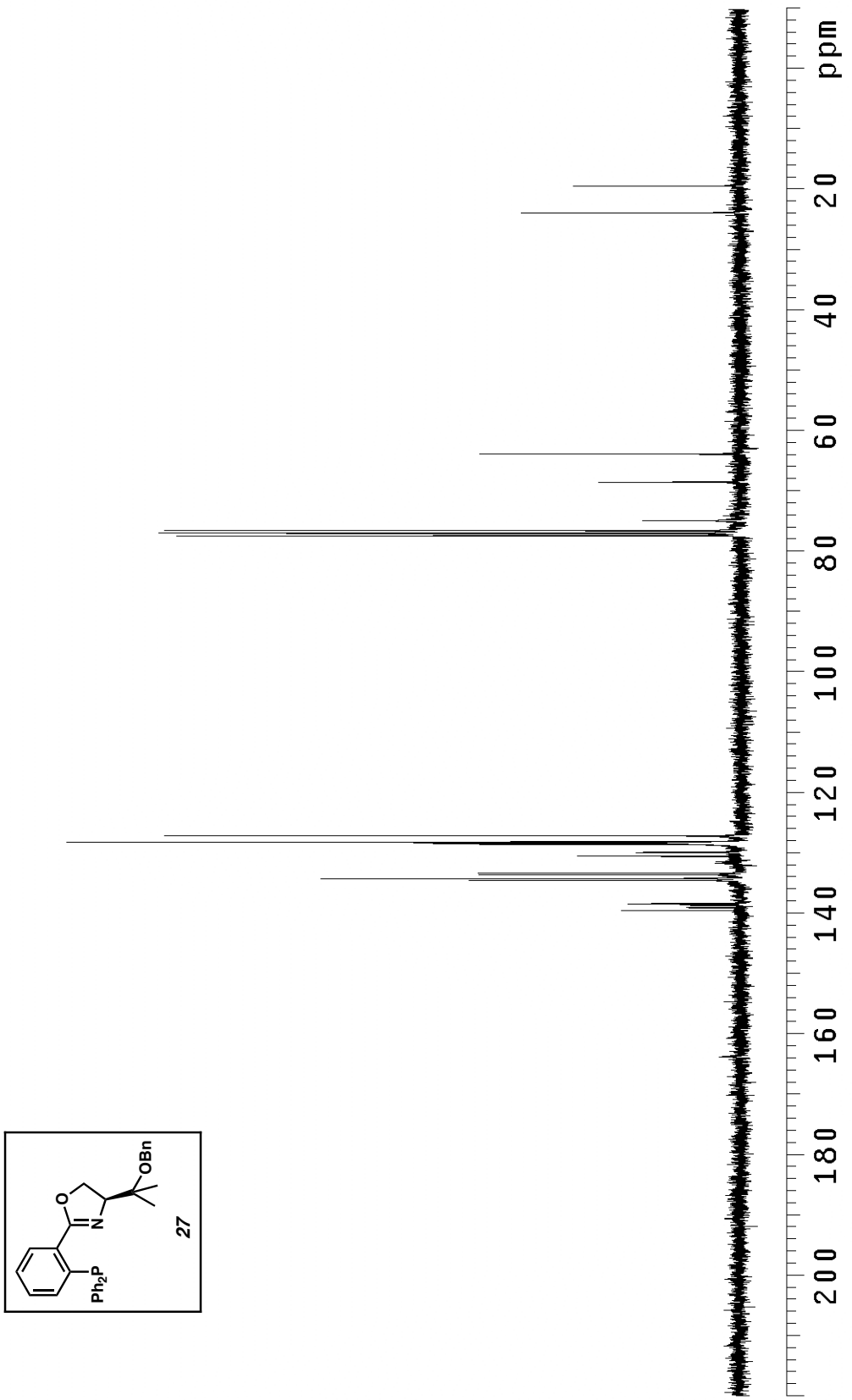
^{1}H NMR of compound **26** (300 MHz, $CDCl_3$)



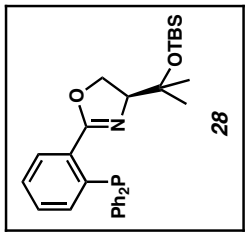
^{13}C NMR of compound **26** (75 MHz, $CDCl_3$)



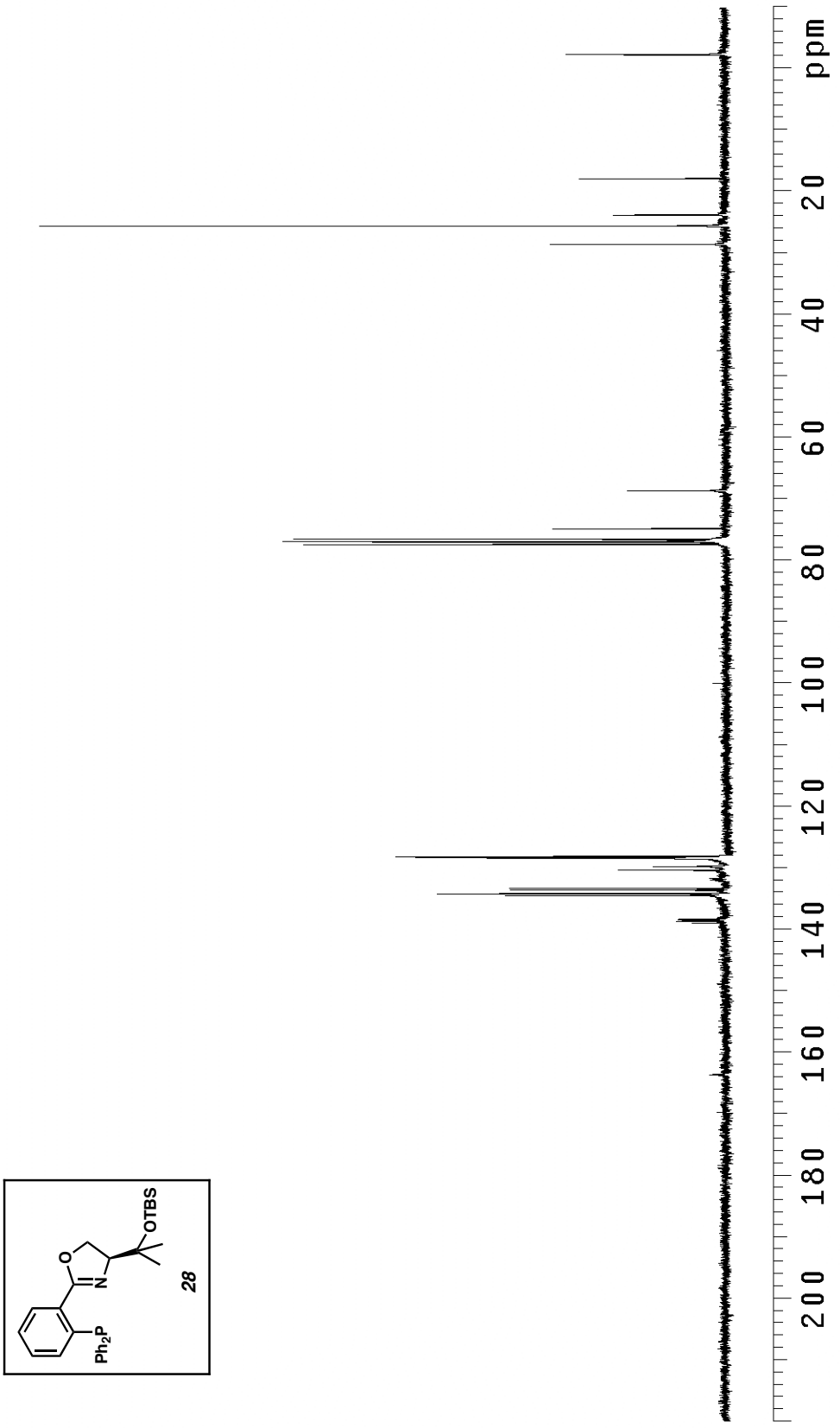
^{1}H NMR of compound **27** (300 MHz, $CDCl_3$)



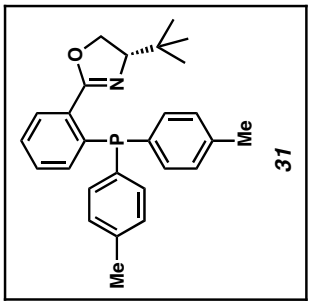
^{13}C NMR of compound **27** (75 MHz, $CDCl_3$)



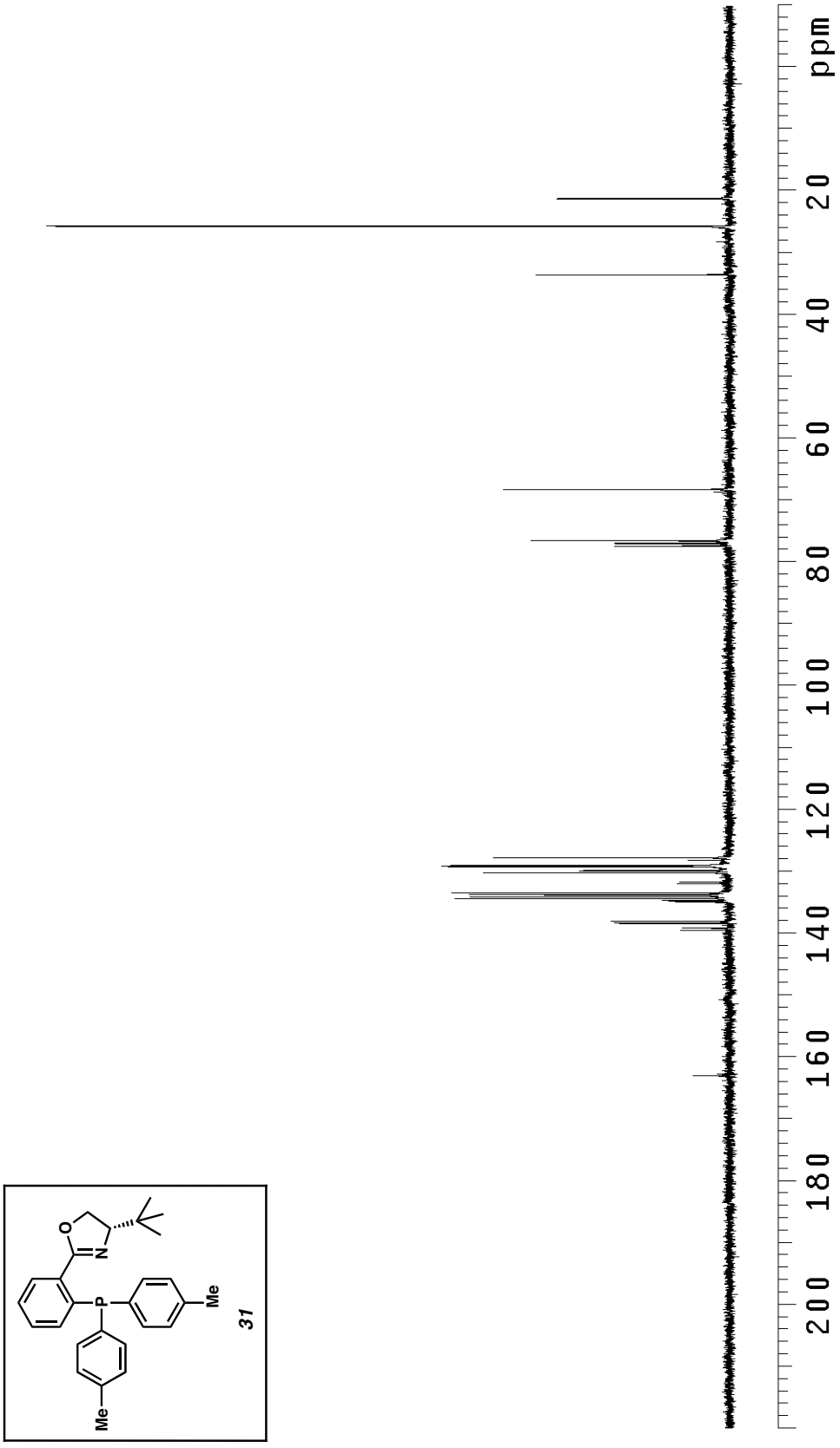
^{1}H NMR of compound **28** (300 MHz, $CDCl_3$)



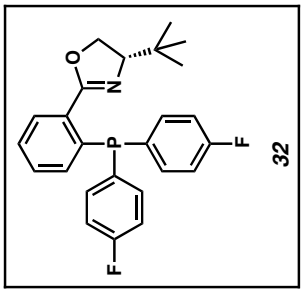
^{13}C NMR of compound **28** (75 MHz, $CDCl_3$)



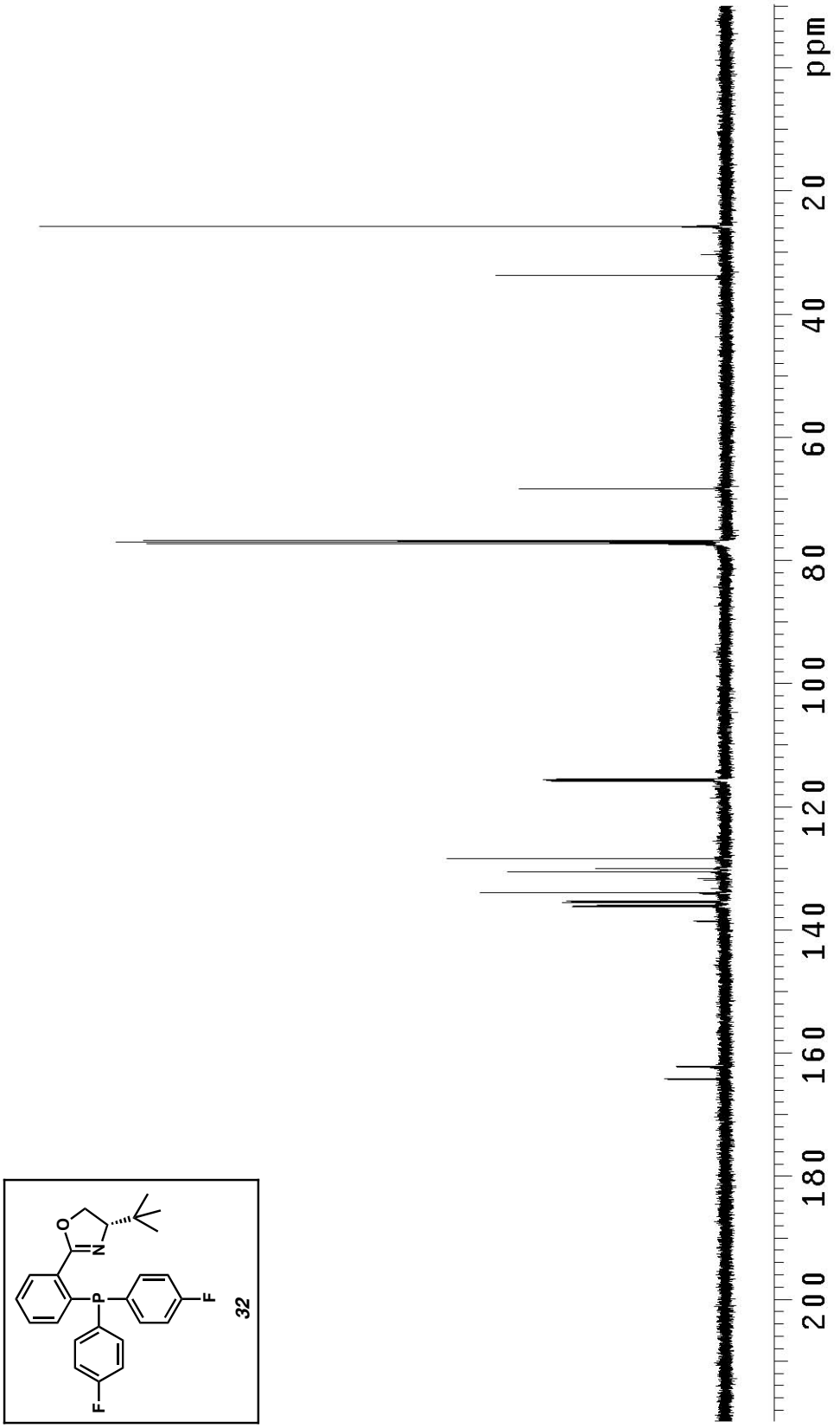
^{1}H NMR of compound **31** (300 MHz, $CDCl_3$)



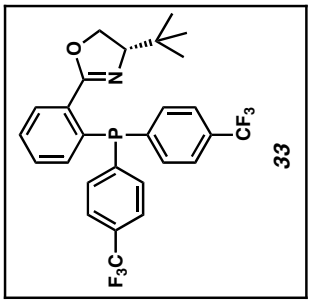
^{13}C NMR of compound **31** (75 MHz, $CDCl_3$)



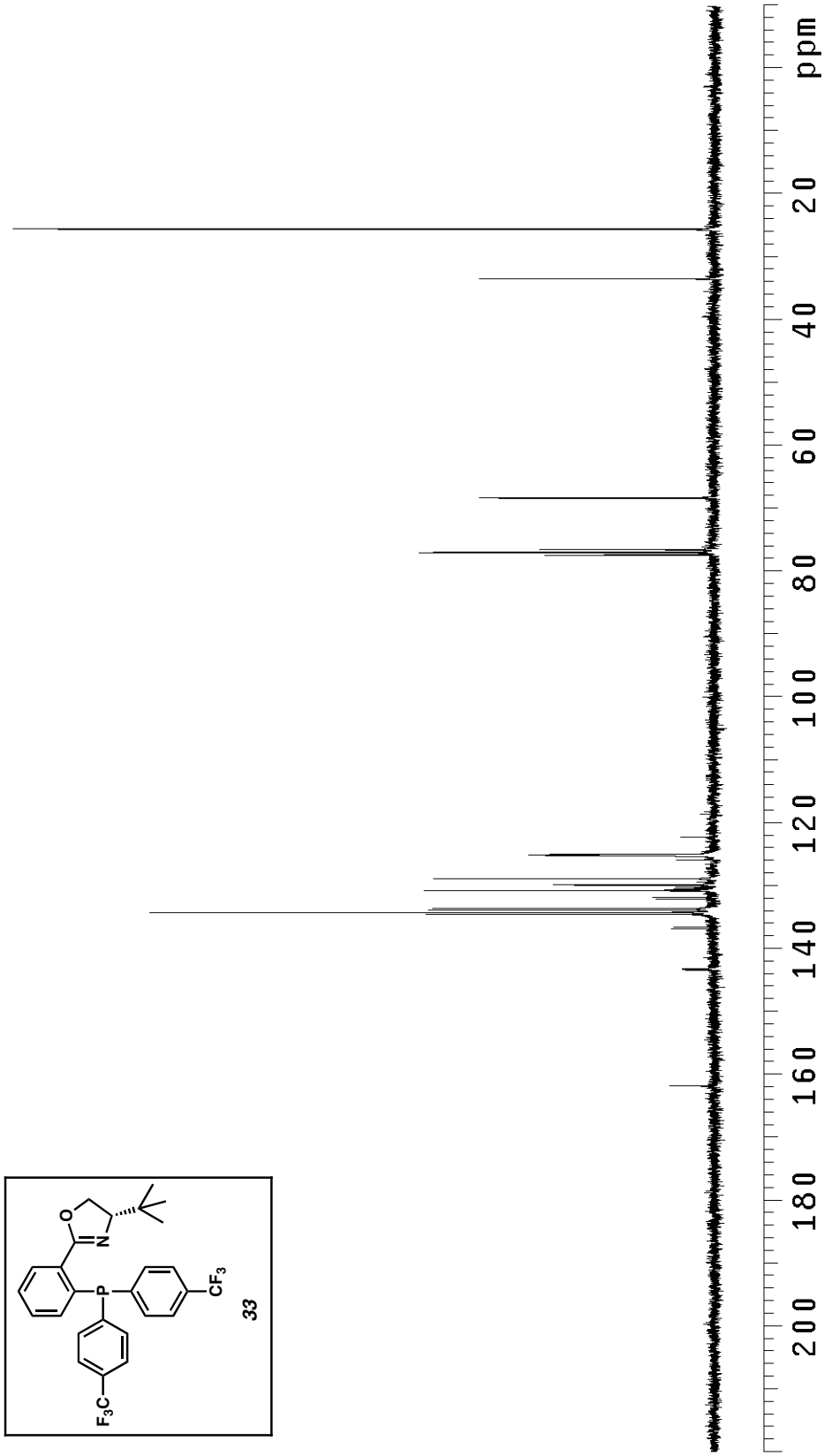
^{1}H NMR of compound **32** (500 MHz, $CDCl_3$)



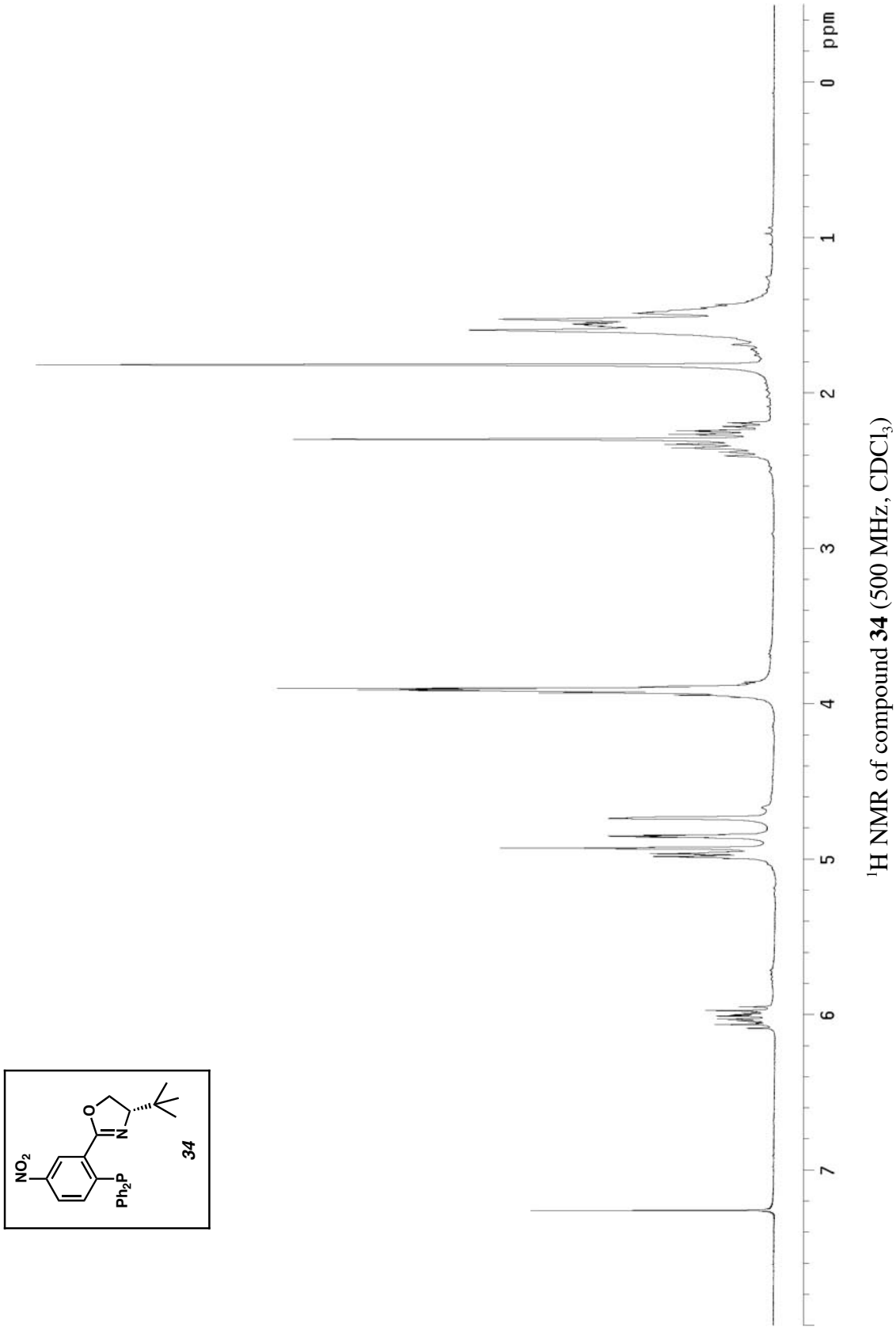
^{13}C NMR of compound **32** (125 MHz, $CDCl_3$)



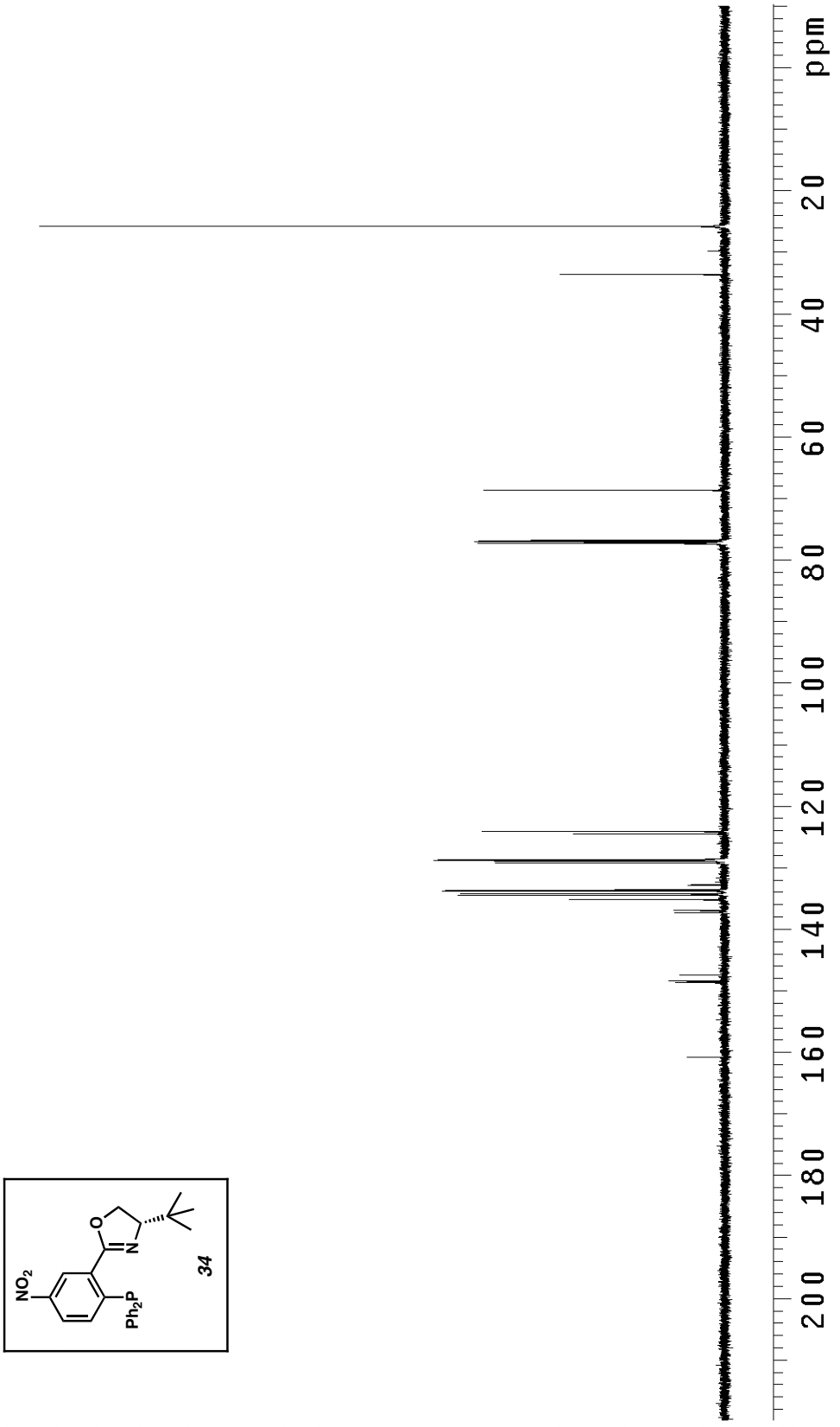
^{1}H NMR of compound **33** (300 MHz, $CDCl_3$)



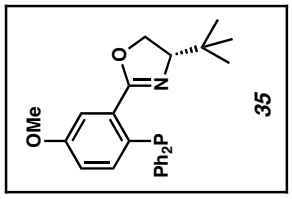
^{13}C NMR of compound **33** (75 MHz, $CDCl_3$)



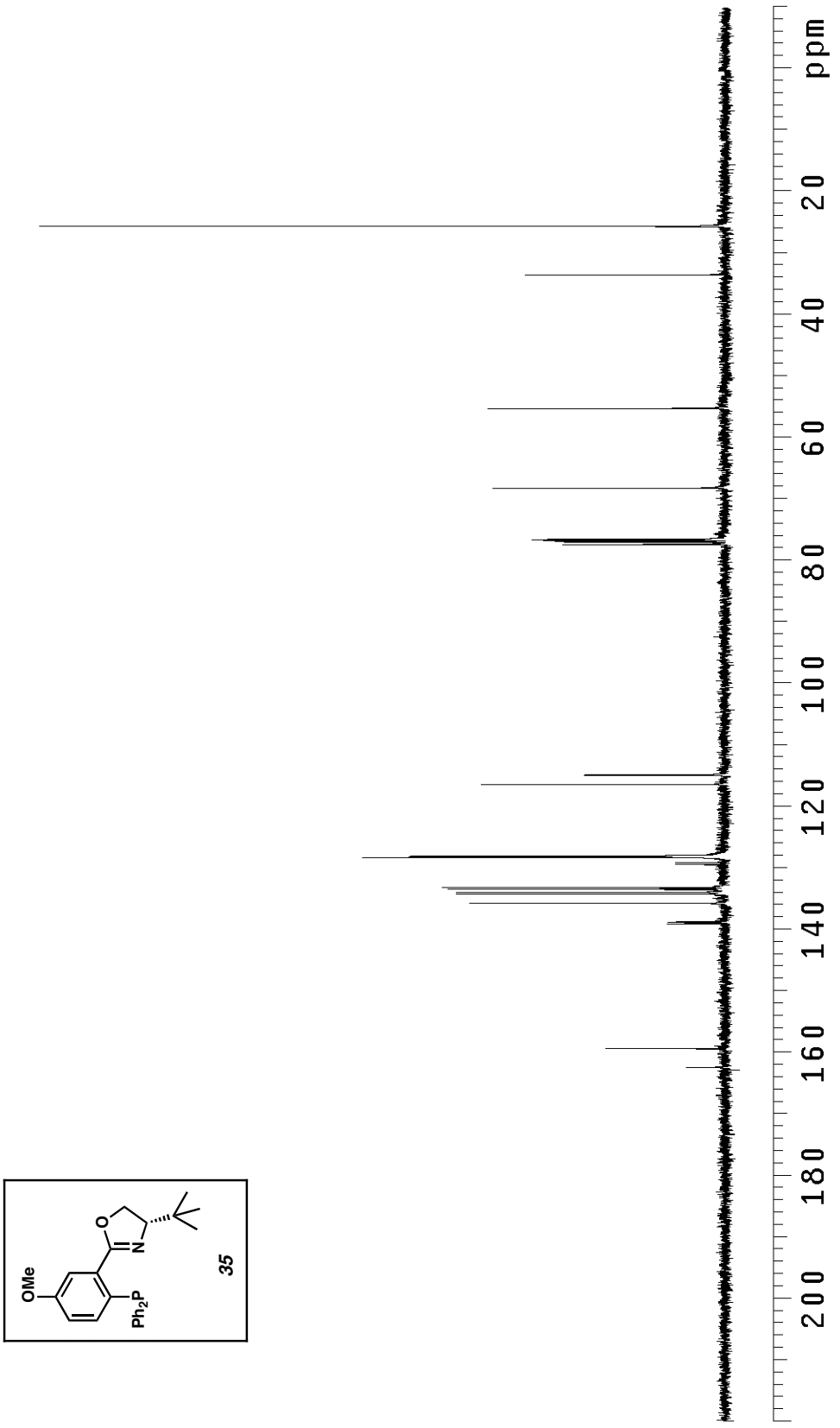
^{1}H NMR of compound **34** (500 MHz, $CDCl_3$)



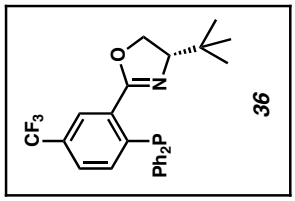
^{13}C NMR of compound **34** (75 MHz, $CDCl_3$)



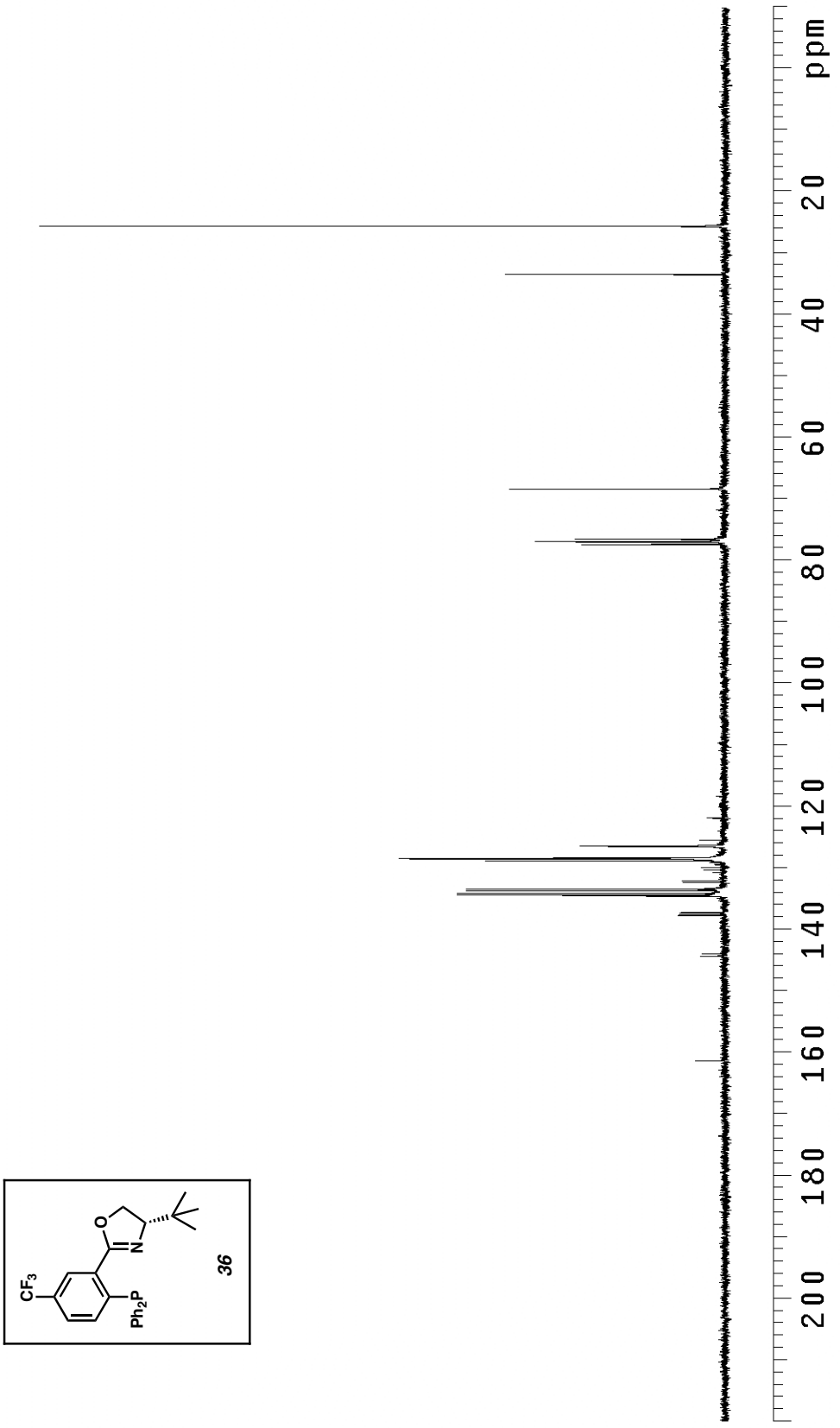
^{1}H NMR of compound **35** (300 MHz, $CDCl_3$)



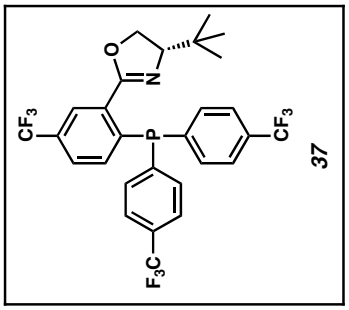
^{13}C NMR of compound **35** (75 MHz, $CDCl_3$)



^{1}H NMR of compound **36** (300 MHz, $CDCl_3$)

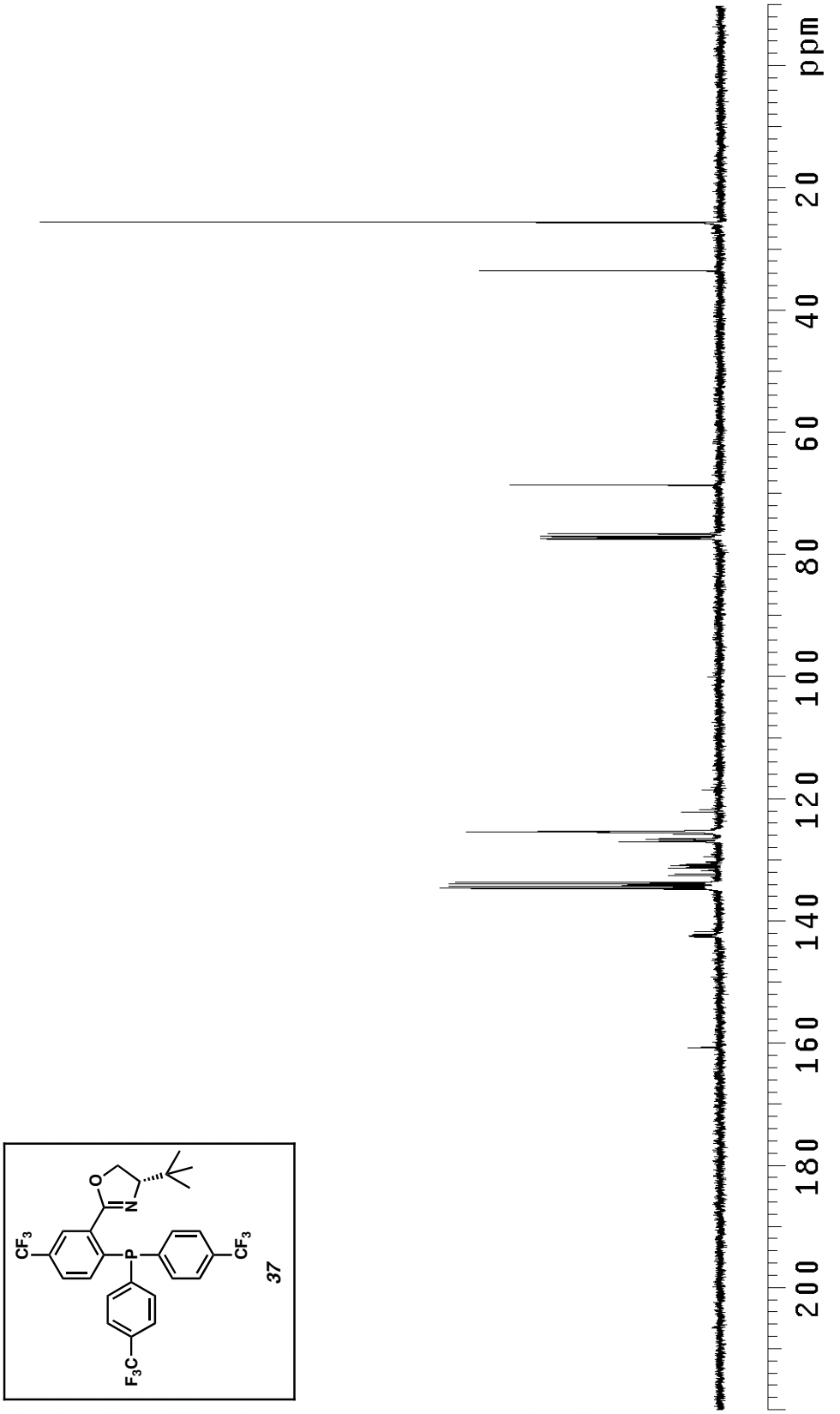


^{13}C NMR of compound **36** (75 MHz, $CDCl_3$)

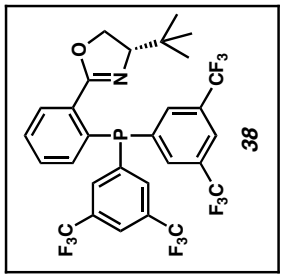


37

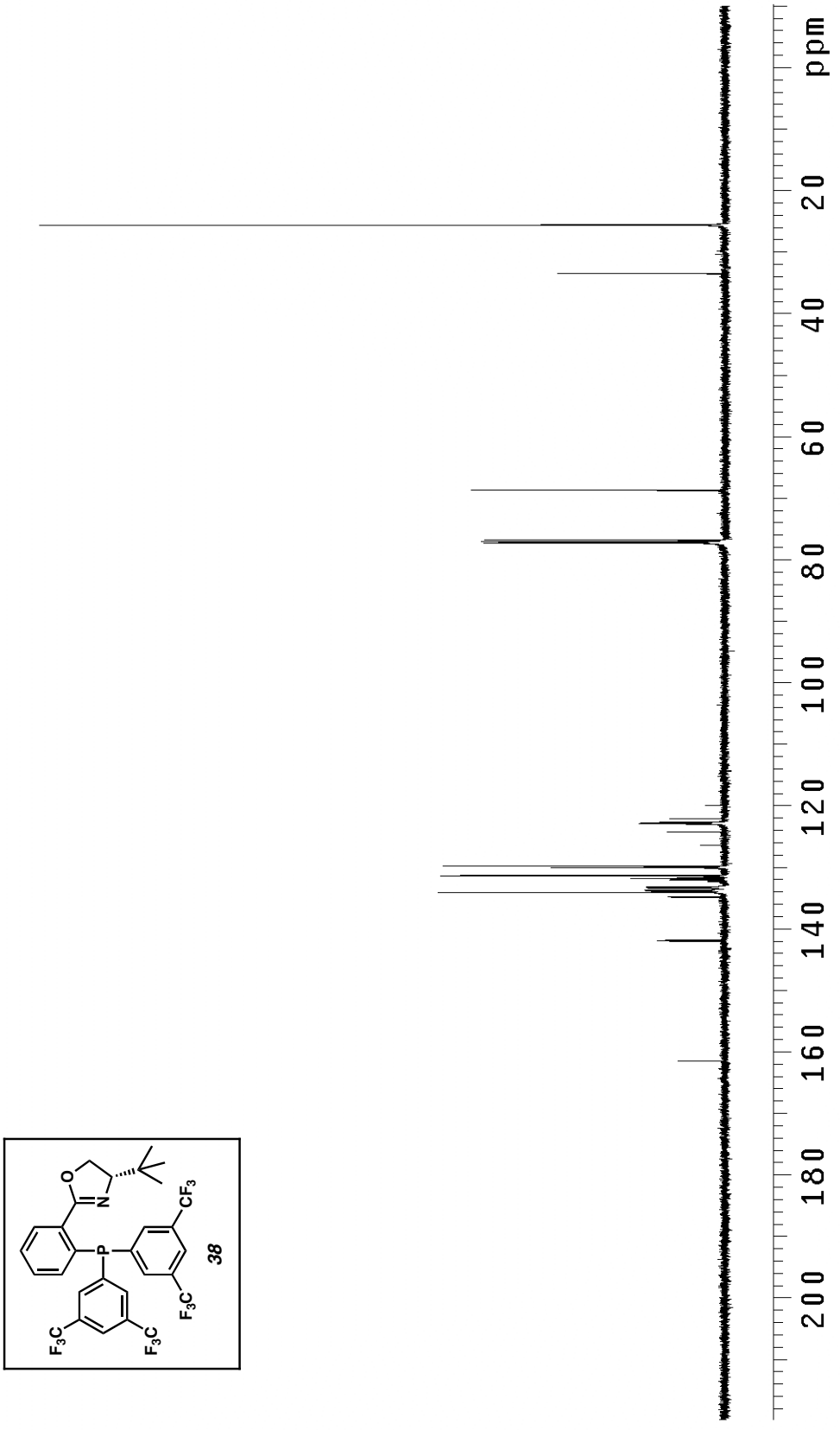
^{1}H NMR of compound **37** (300 MHz, $CDCl_3$)



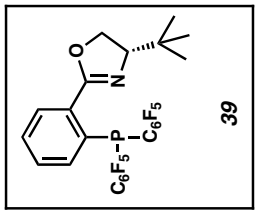
^{13}C NMR of compound **37** (125 MHz, $CDCl_3$)



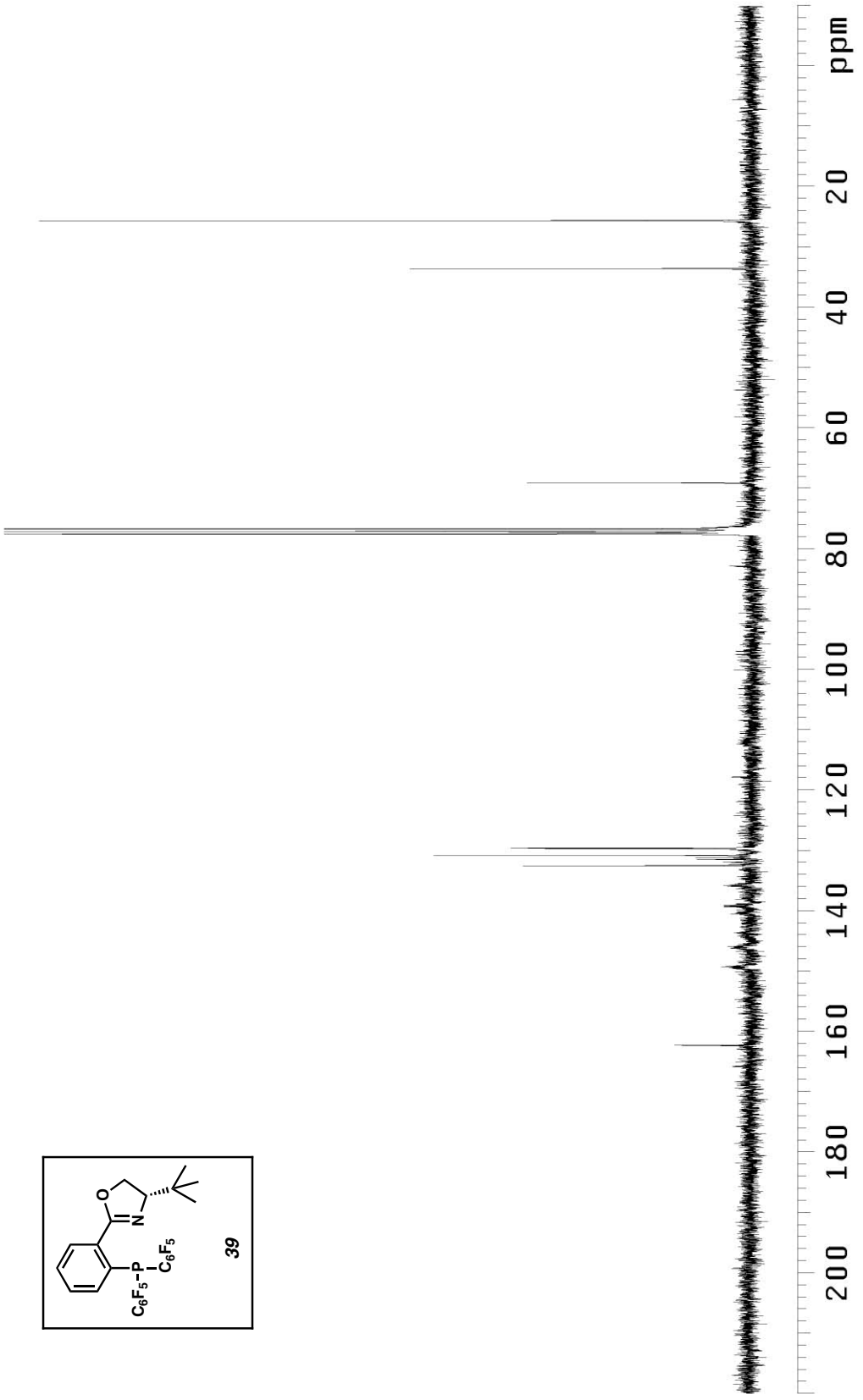
^{1}H NMR of compound **38** (500 MHz, $CDCl_3$)



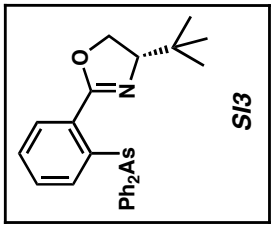
^{13}C NMR of compound **38** (125 MHz, $CDCl_3$)



^{1}H NMR of compound **39** (300 MHz, $CDCl_3$)

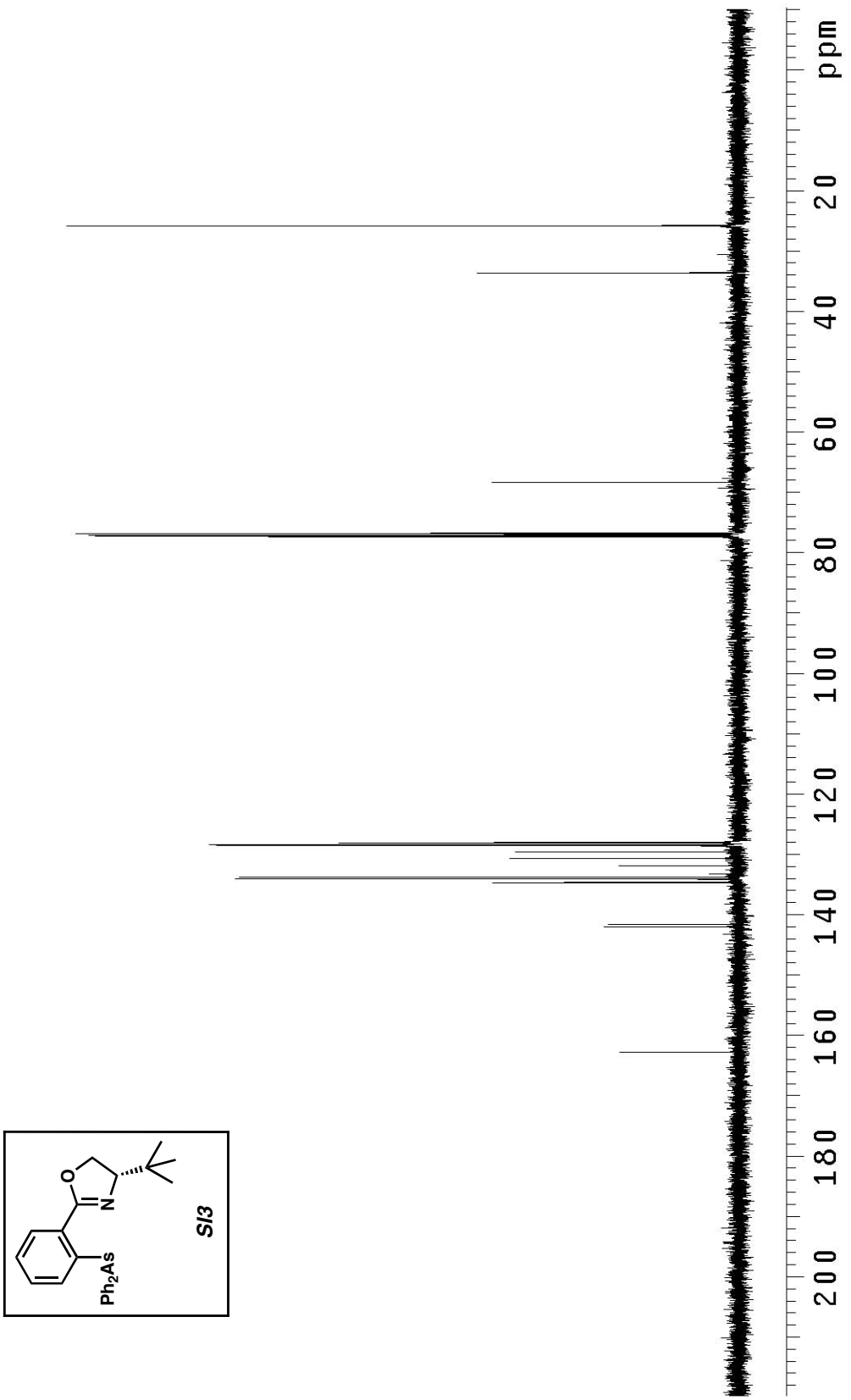


^{13}C NMR of compound **39** (75 MHz, $CDCl_3$)

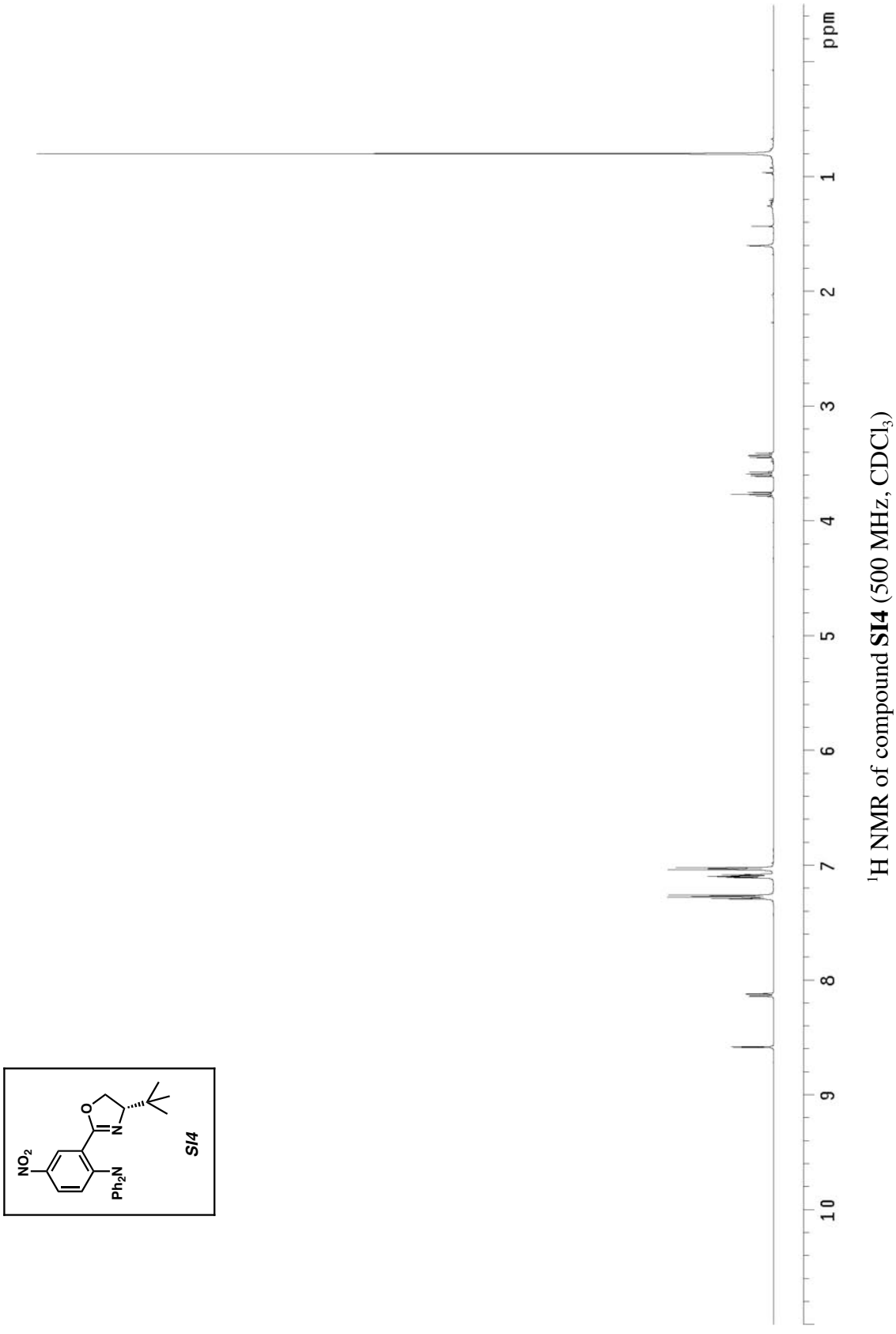


SI3

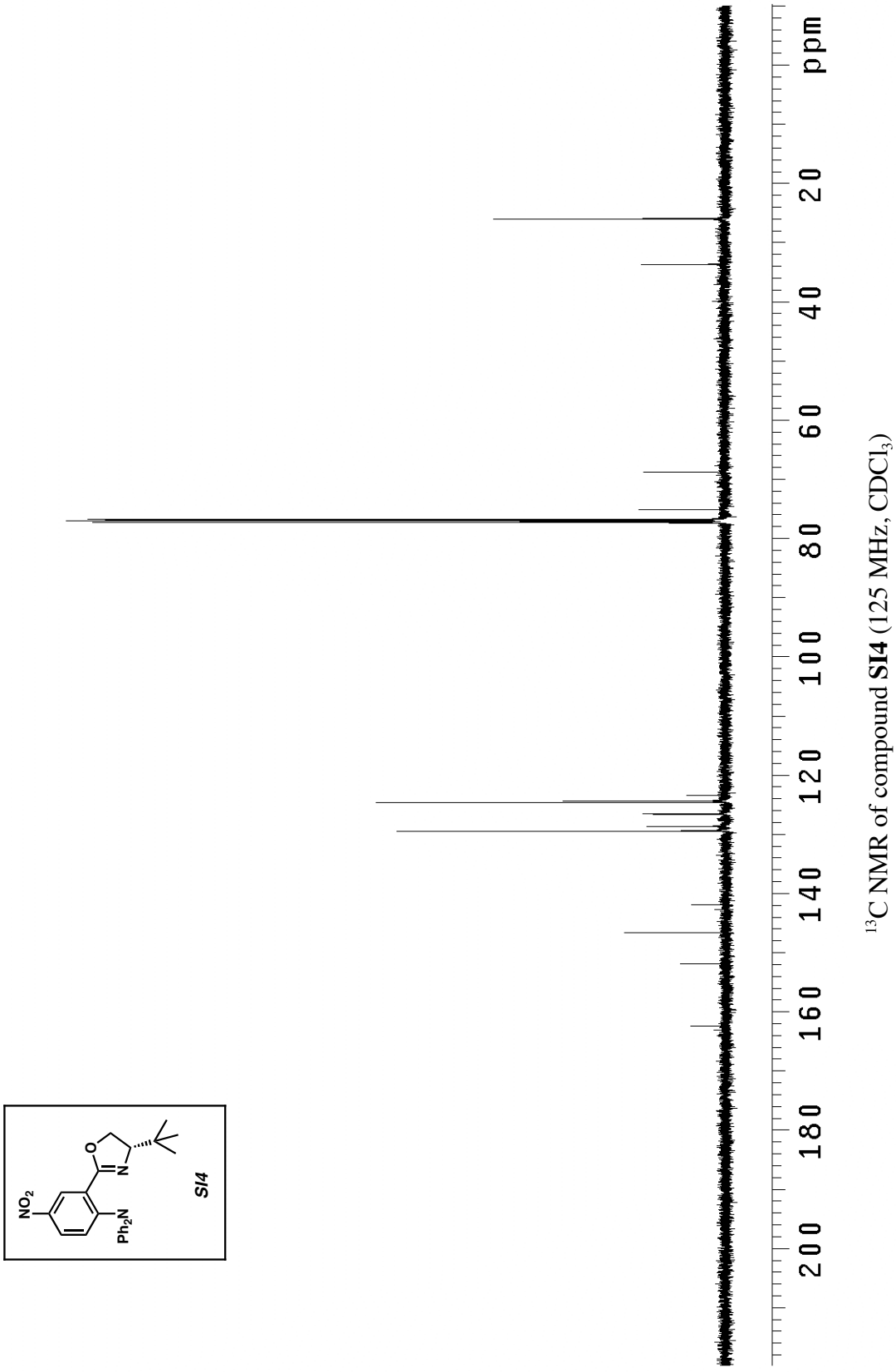
^{1}H NMR of compound **SI3** (500 MHz, $CDCl_3$)



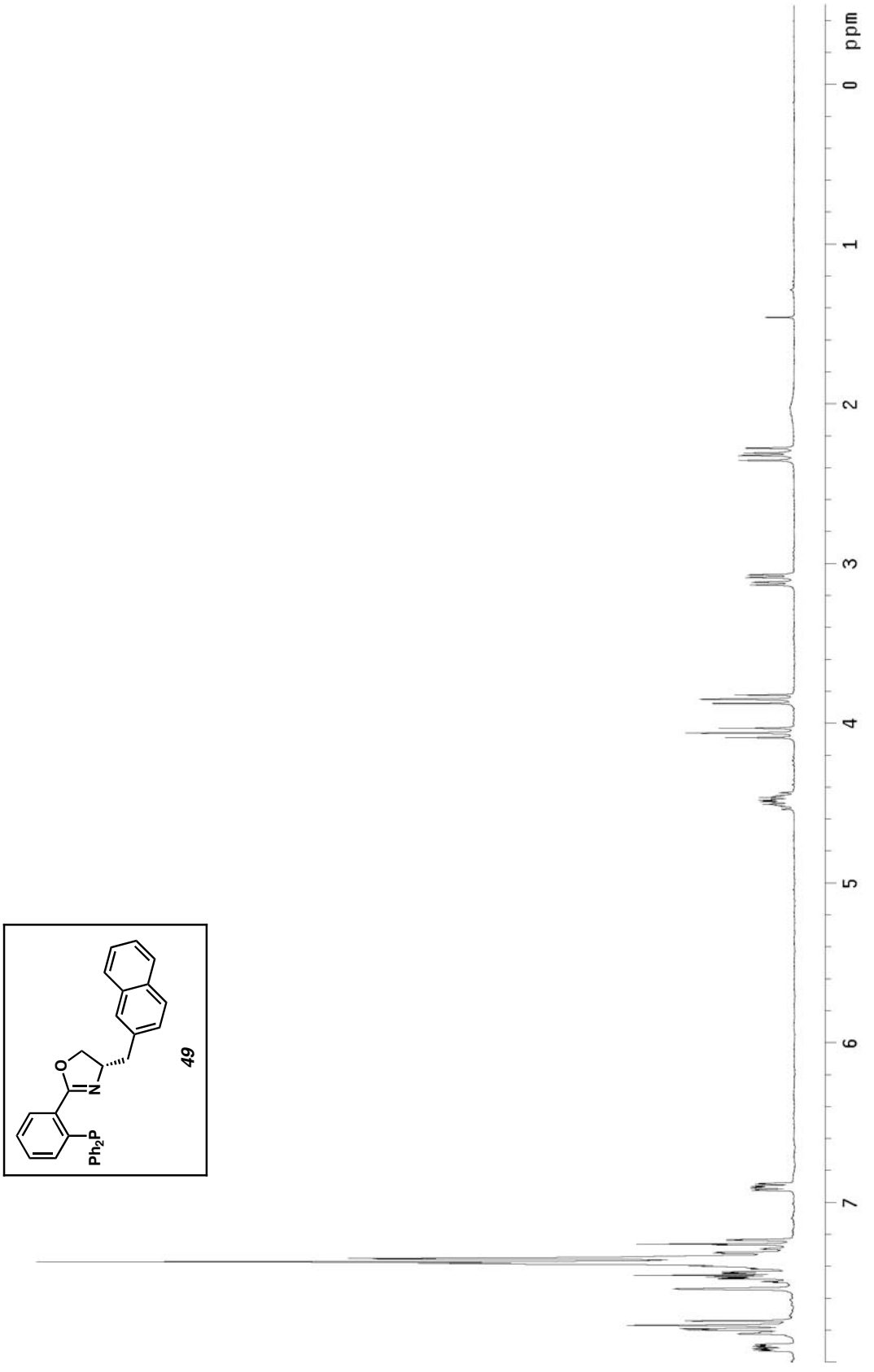
^{13}C NMR of compound **SI3** (125 MHz, $CDCl_3$)



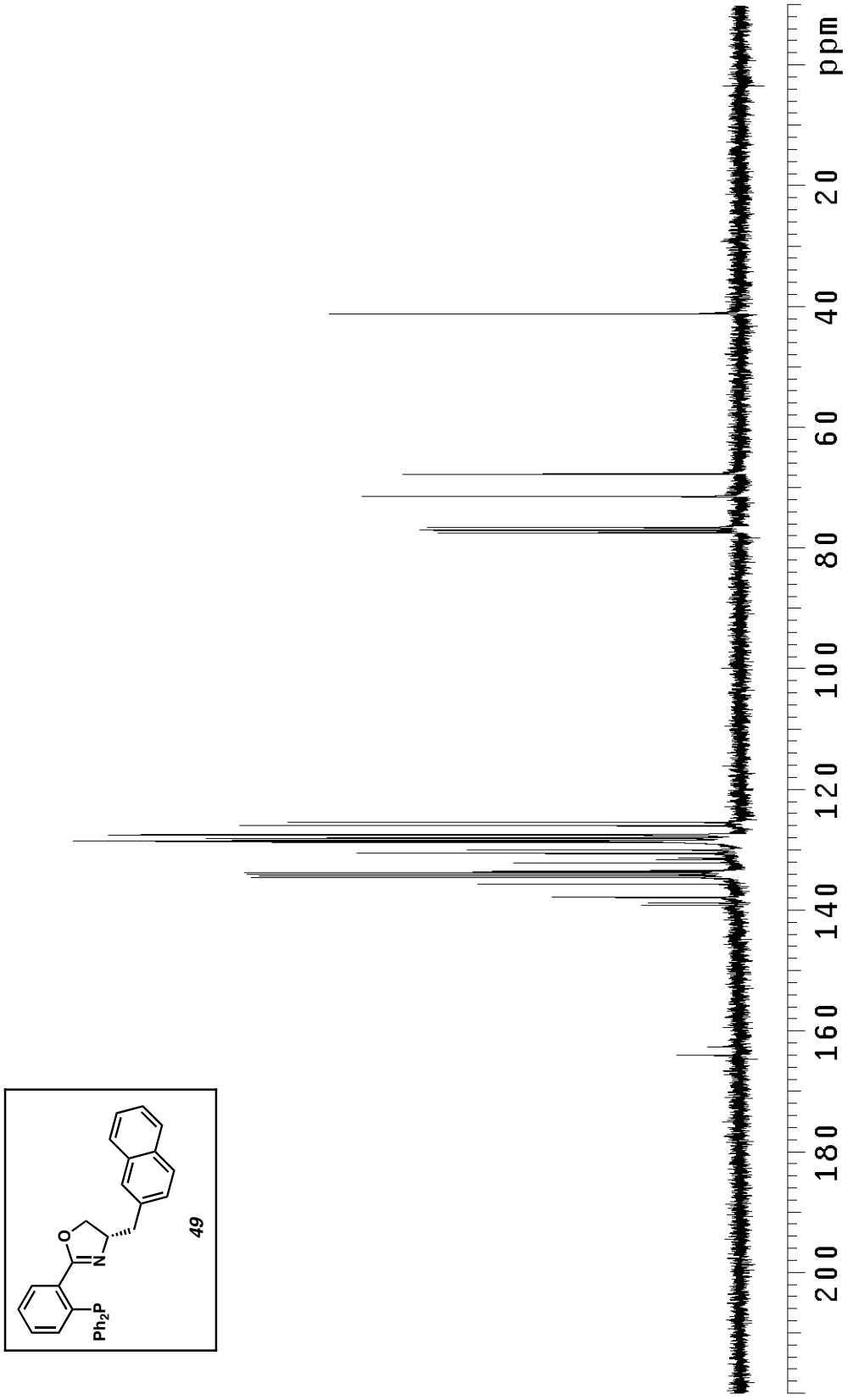
^{1}H NMR of compound **SI4** (500 MHz, $CDCl_3$)



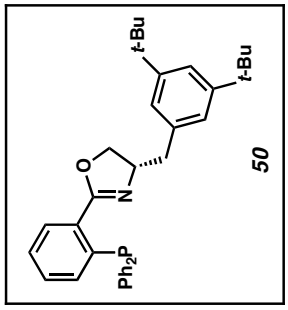
^{13}C NMR of compound **SI4** (125 MHz, $CDCl_3$)



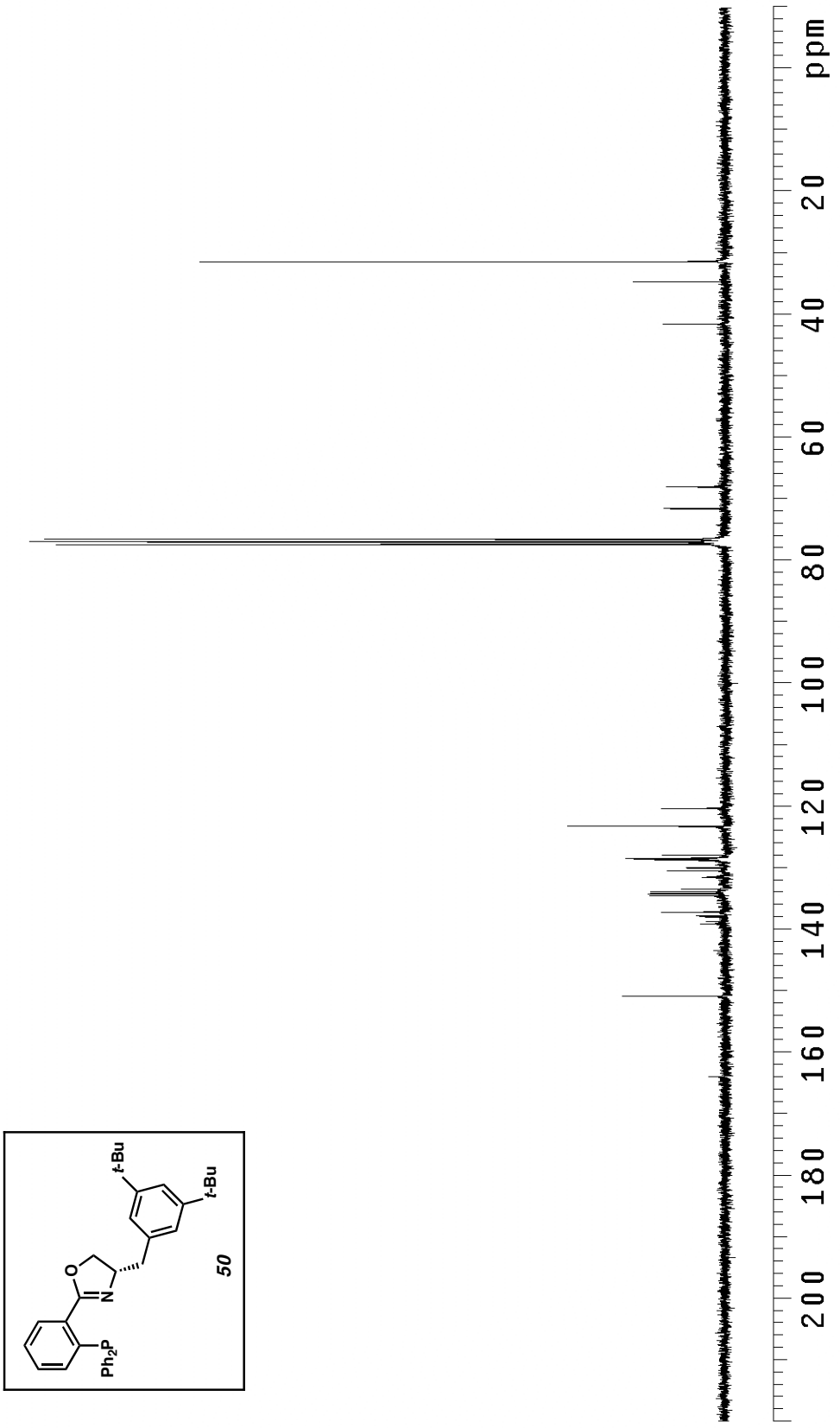
^{1}H NMR of compound **49** (300 MHz, $CDCl_3$)



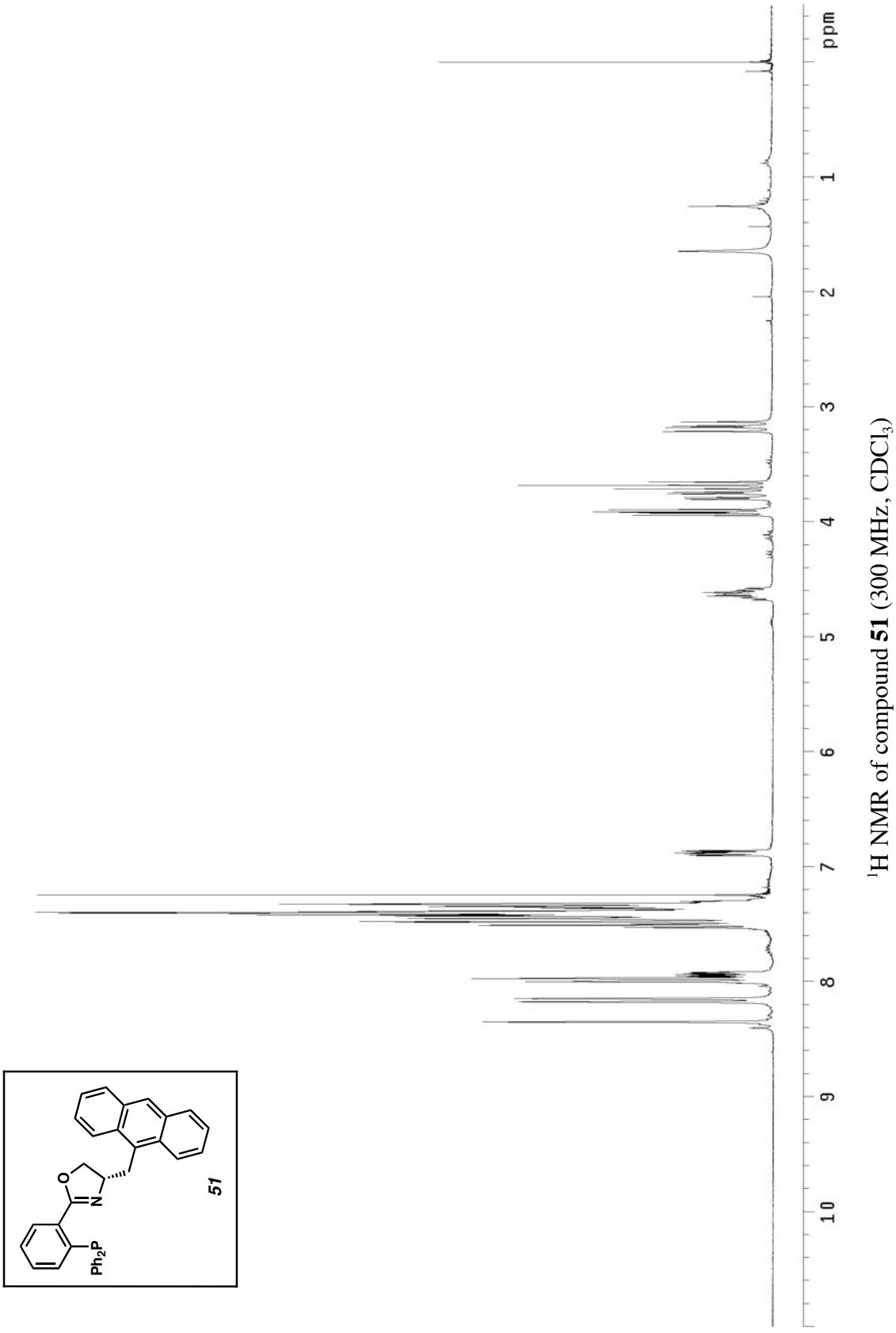
^{13}C NMR of compound **49** (75 MHz, $CDCl_3$)



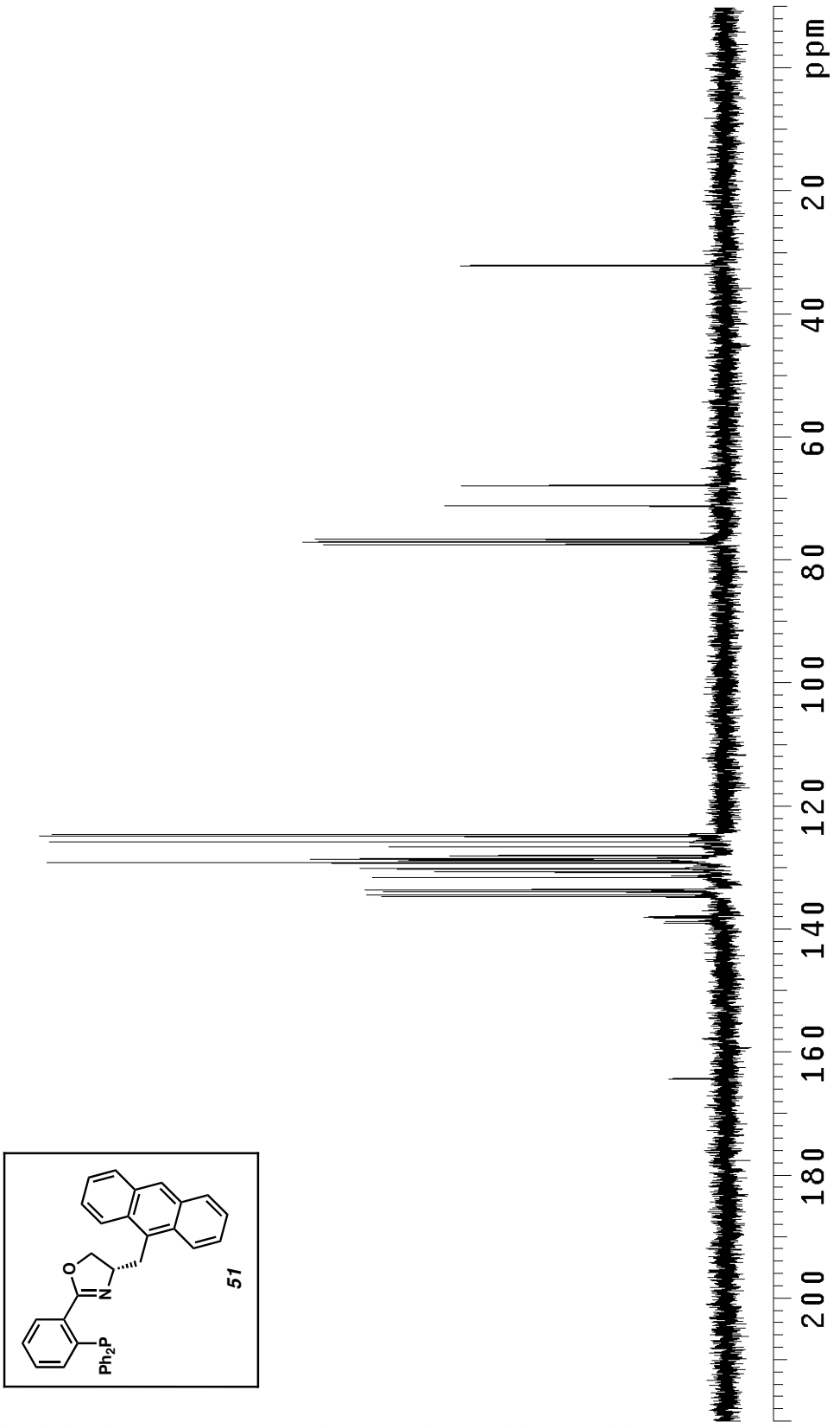
^{1}H NMR of compound **50** (300 MHz, $CDCl_3$)



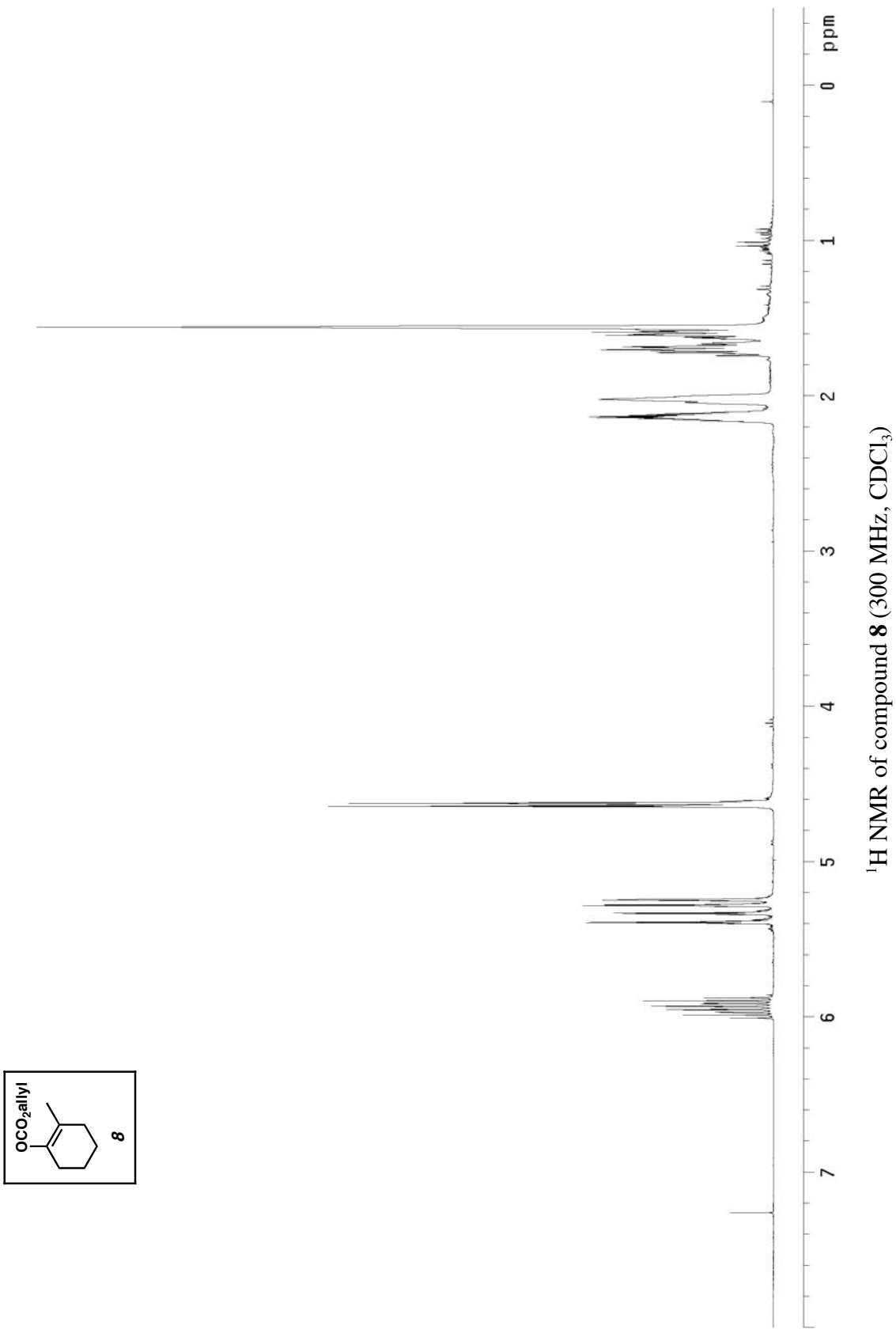
^{13}C NMR of compound **50** (75 MHz, $CDCl_3$)



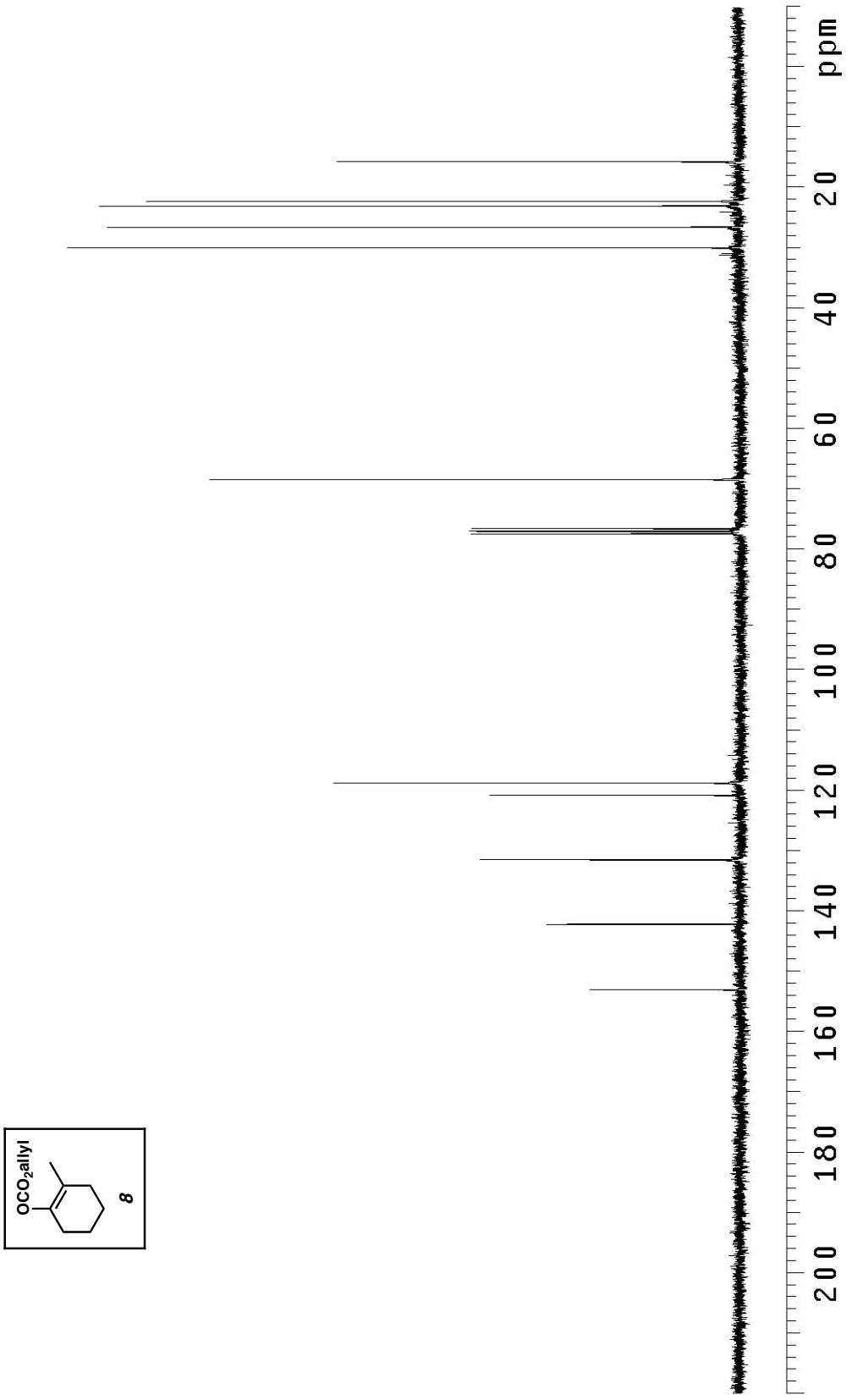
^{1}H NMR of compound **51** (300 MHz, $CDCl_3$)



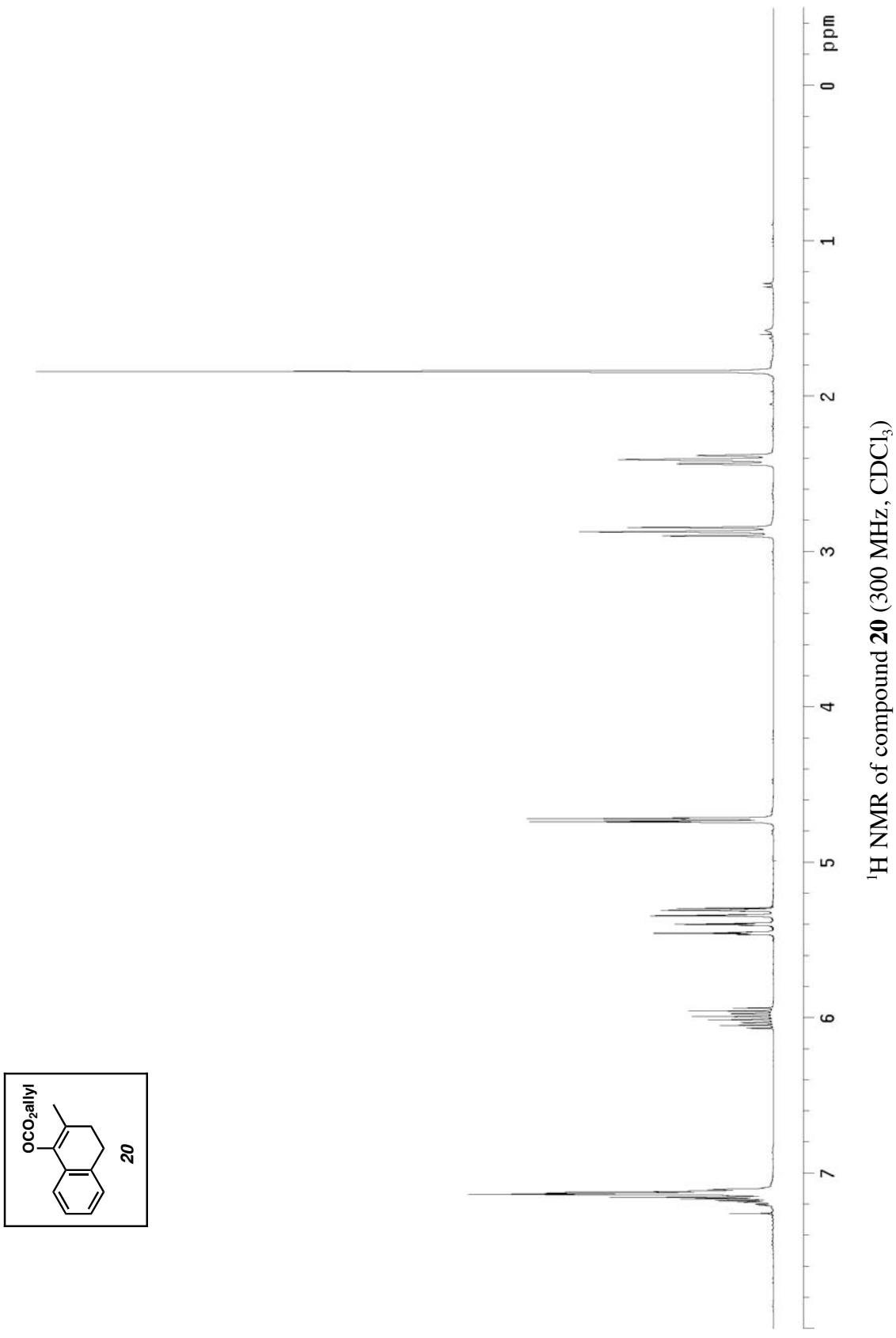
^{13}C NMR of compound **51** (75 MHz, $CDCl_3$)



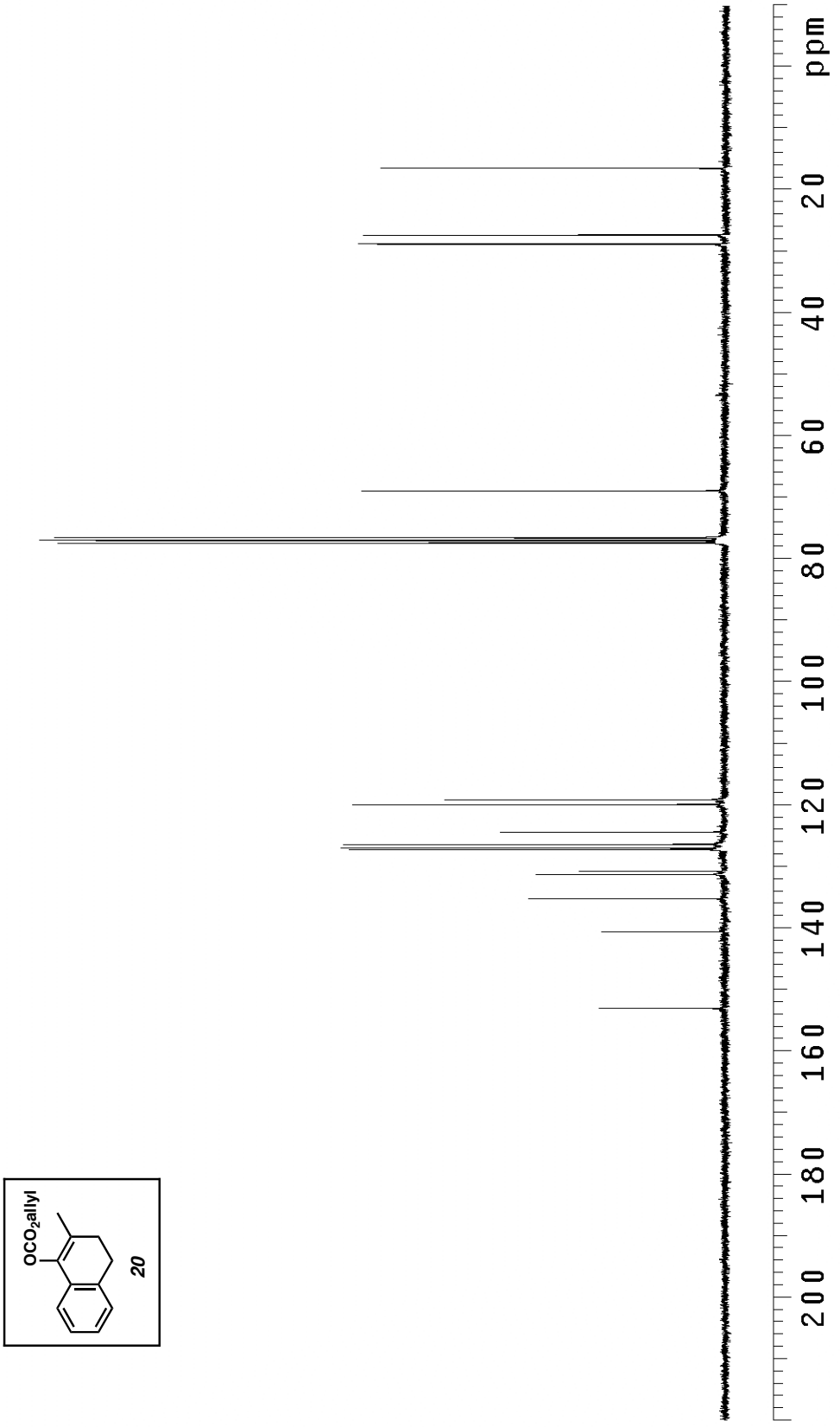
^{1}H NMR of compound **8** (300 MHz, $CDCl_3$)



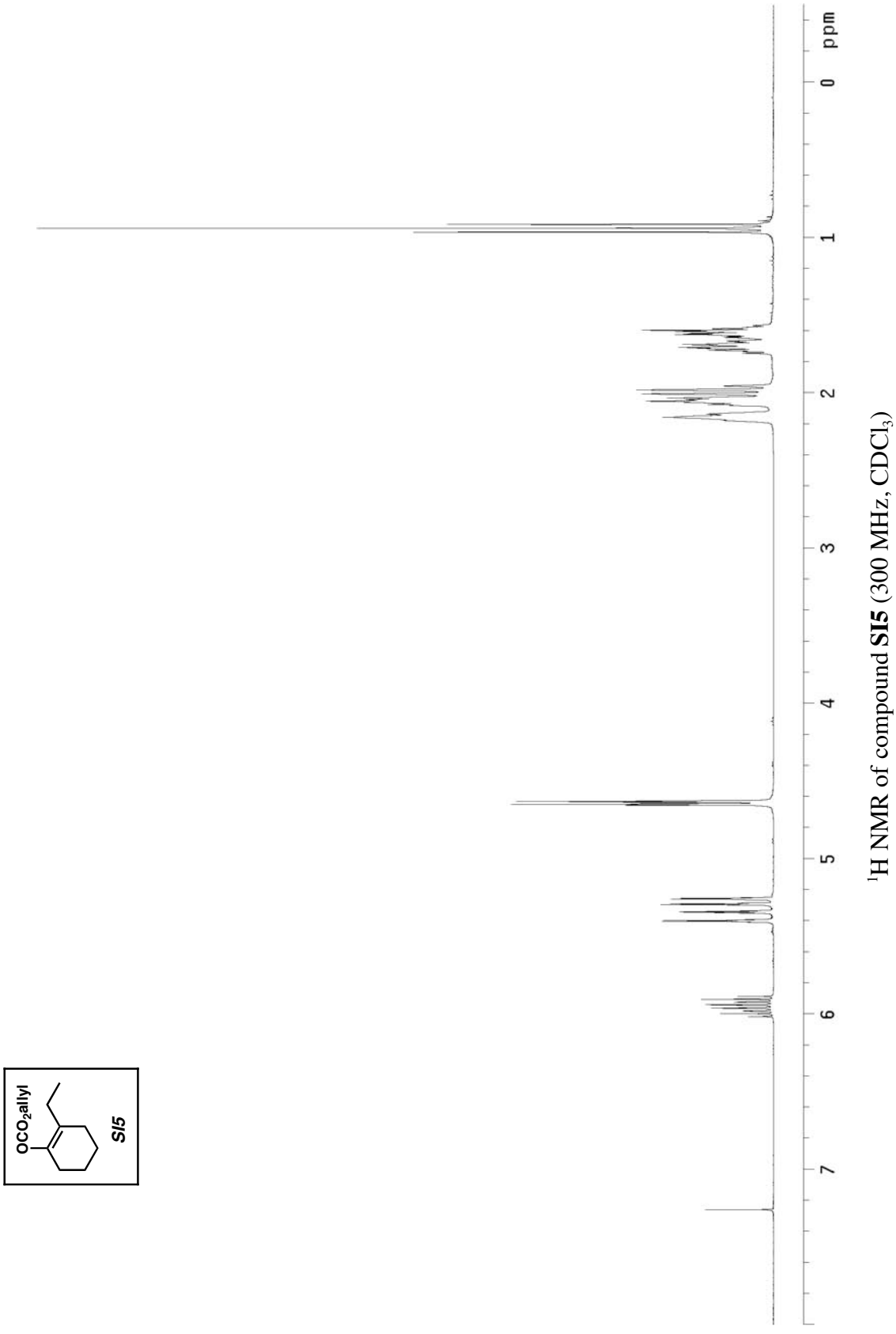
^{13}C NMR of compound **8** (75 MHz, $CDCl_3$)



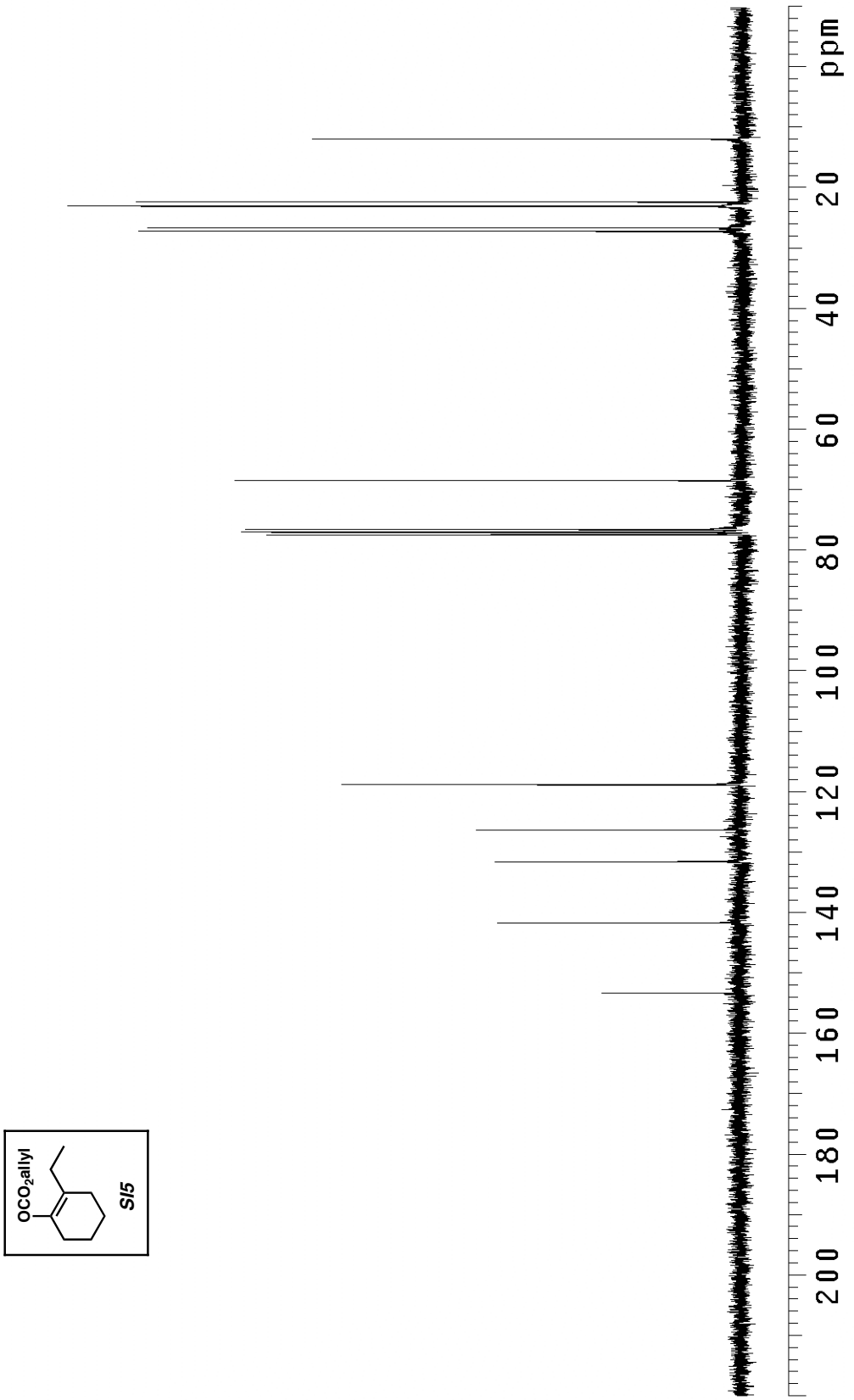
^{1}H NMR of compound **20** (300 MHz, $CDCl_3$)



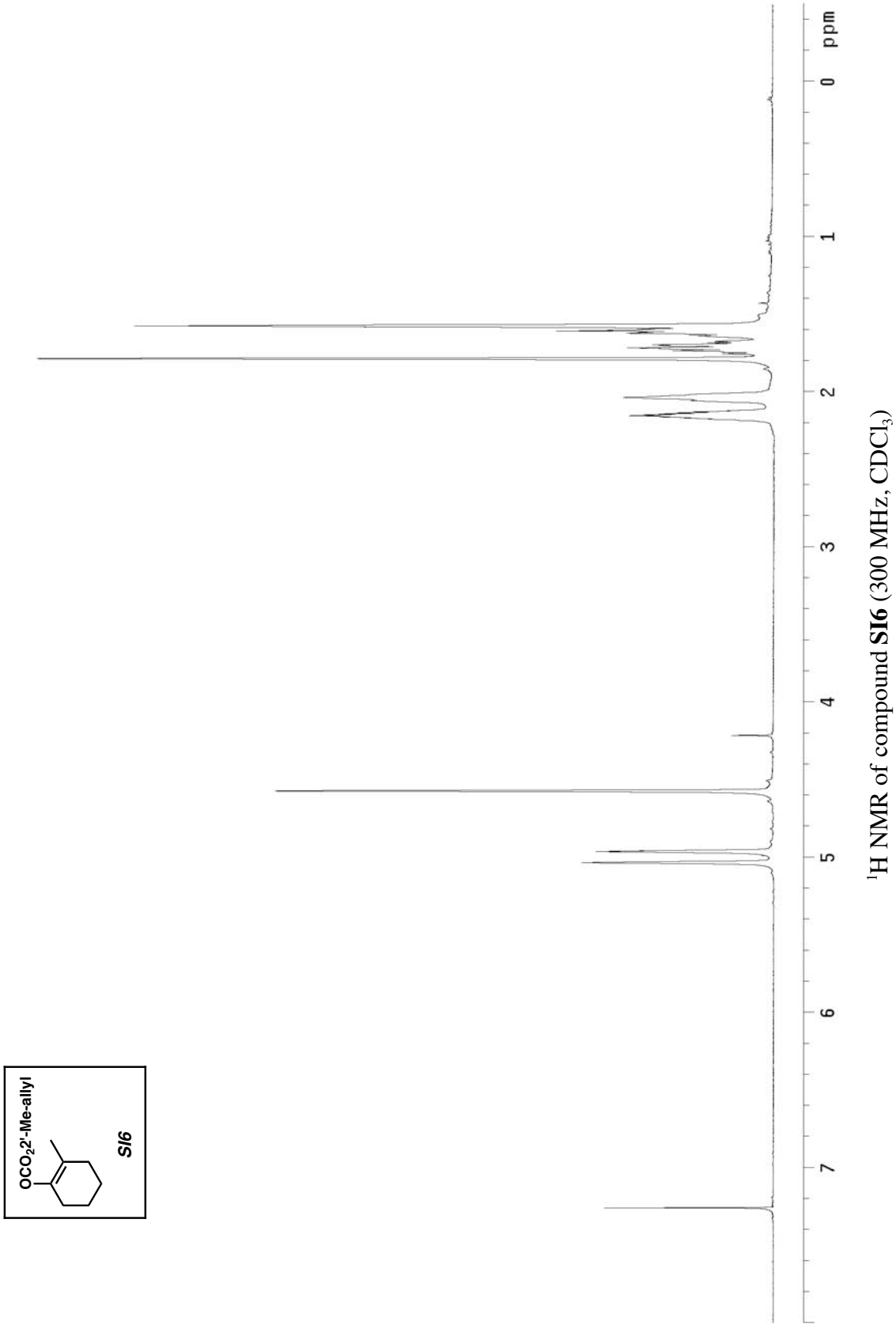
^{13}C NMR of compound **20** (75 MHz, $CDCl_3$)



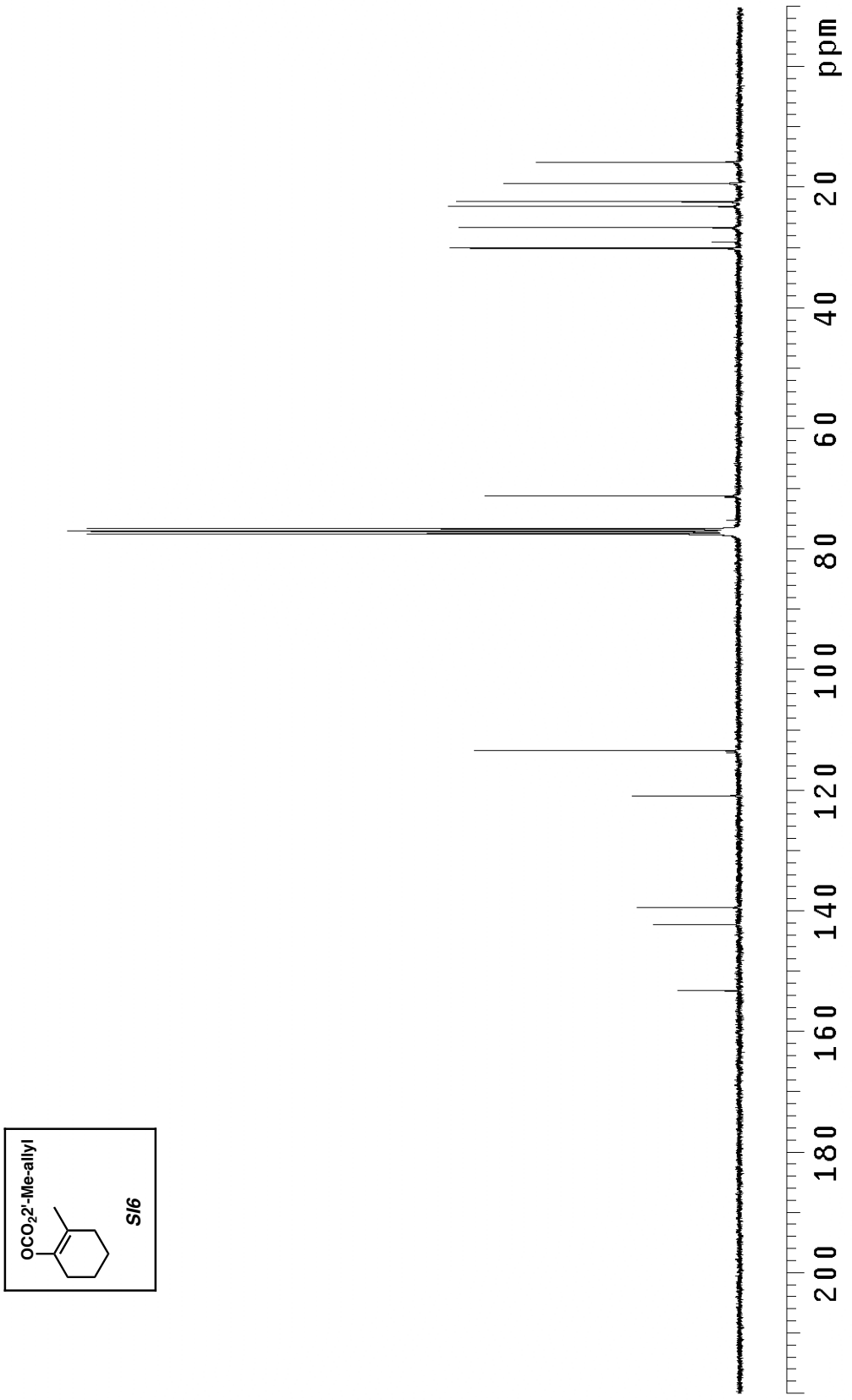
^{1}H NMR of compound **SI5** (300 MHz, $CDCl_3$)



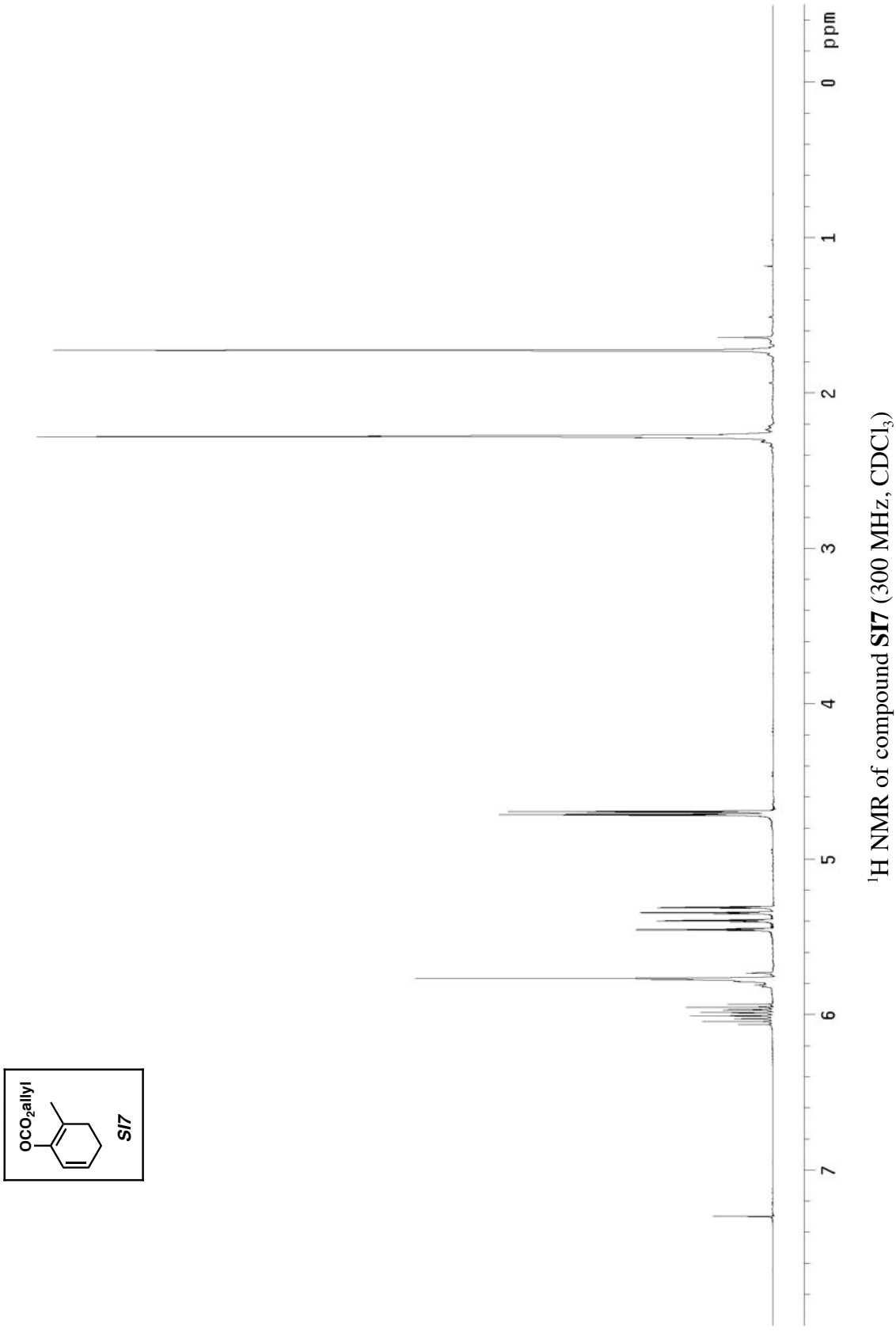
^{13}C NMR of compound **SI5** (75 MHz, $CDCl_3$)



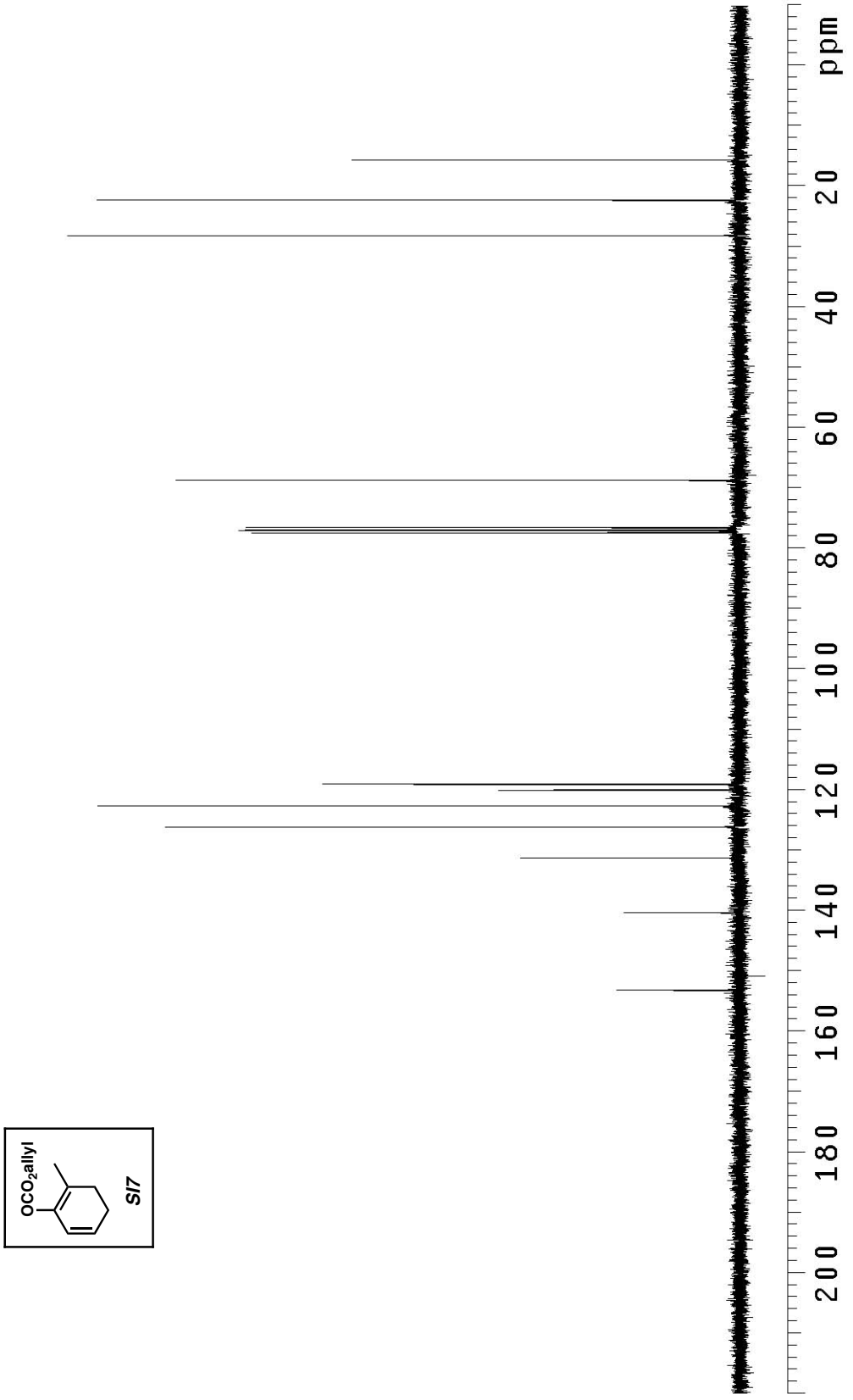
^{1}H NMR of compound **SI6** (300 MHz, $CDCl_3$)



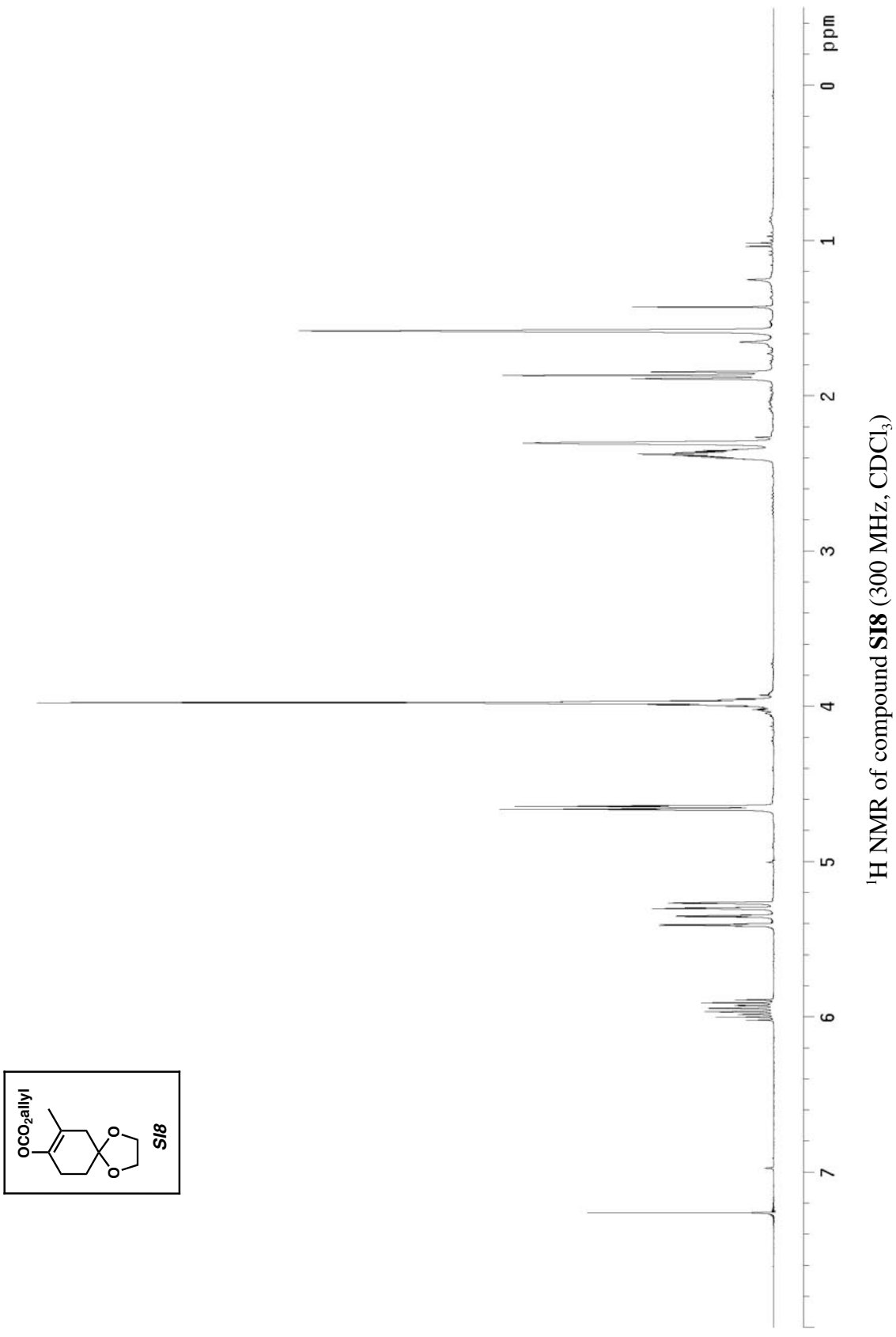
^{13}C NMR of compound **SI6** (75 MHz, $CDCl_3$)



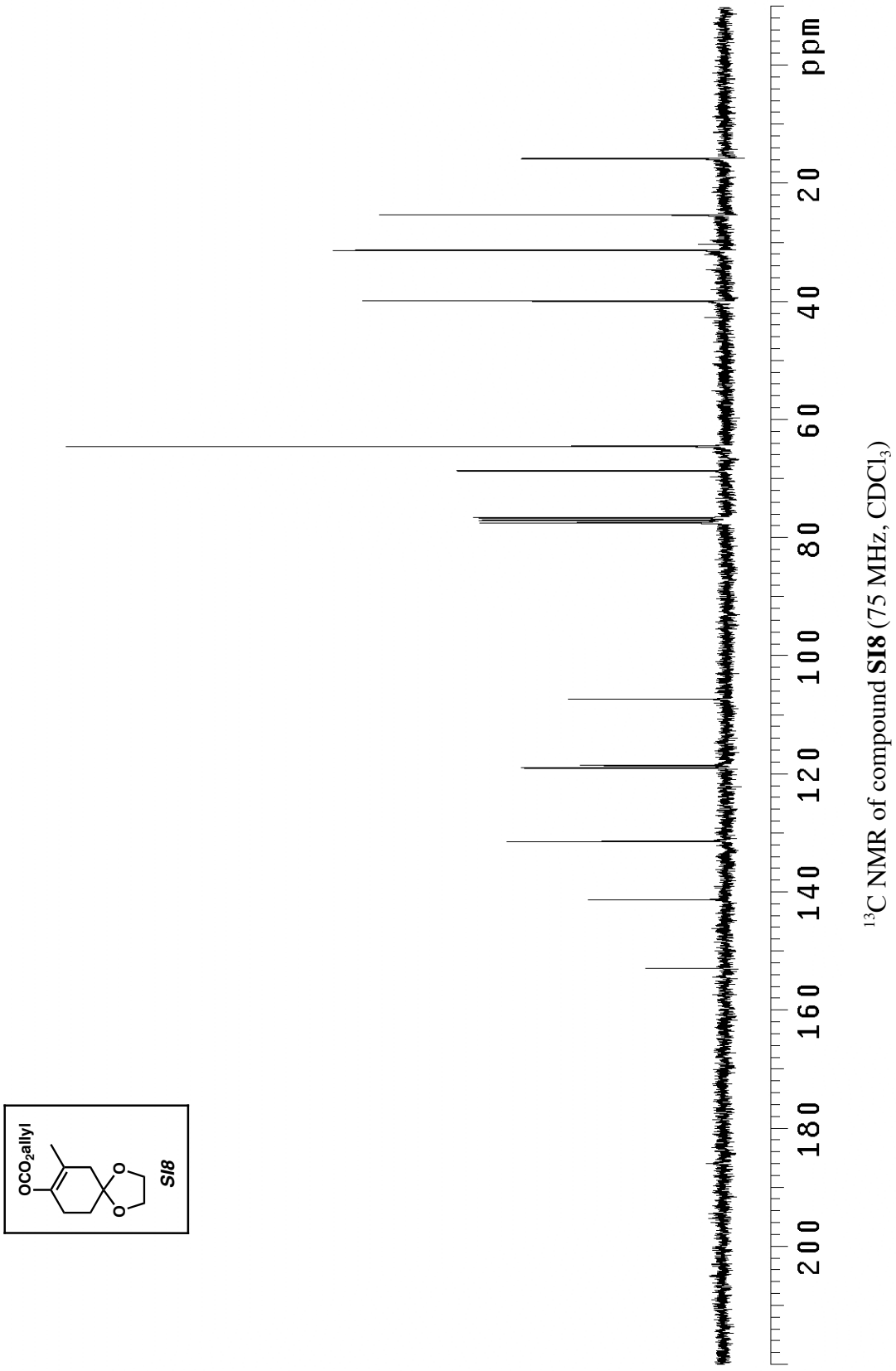
^{1}H NMR of compound **SI7** (300 MHz, $CDCl_3$)



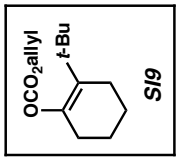
^{13}C NMR of compound **SI7** (75 MHz, $CDCl_3$)



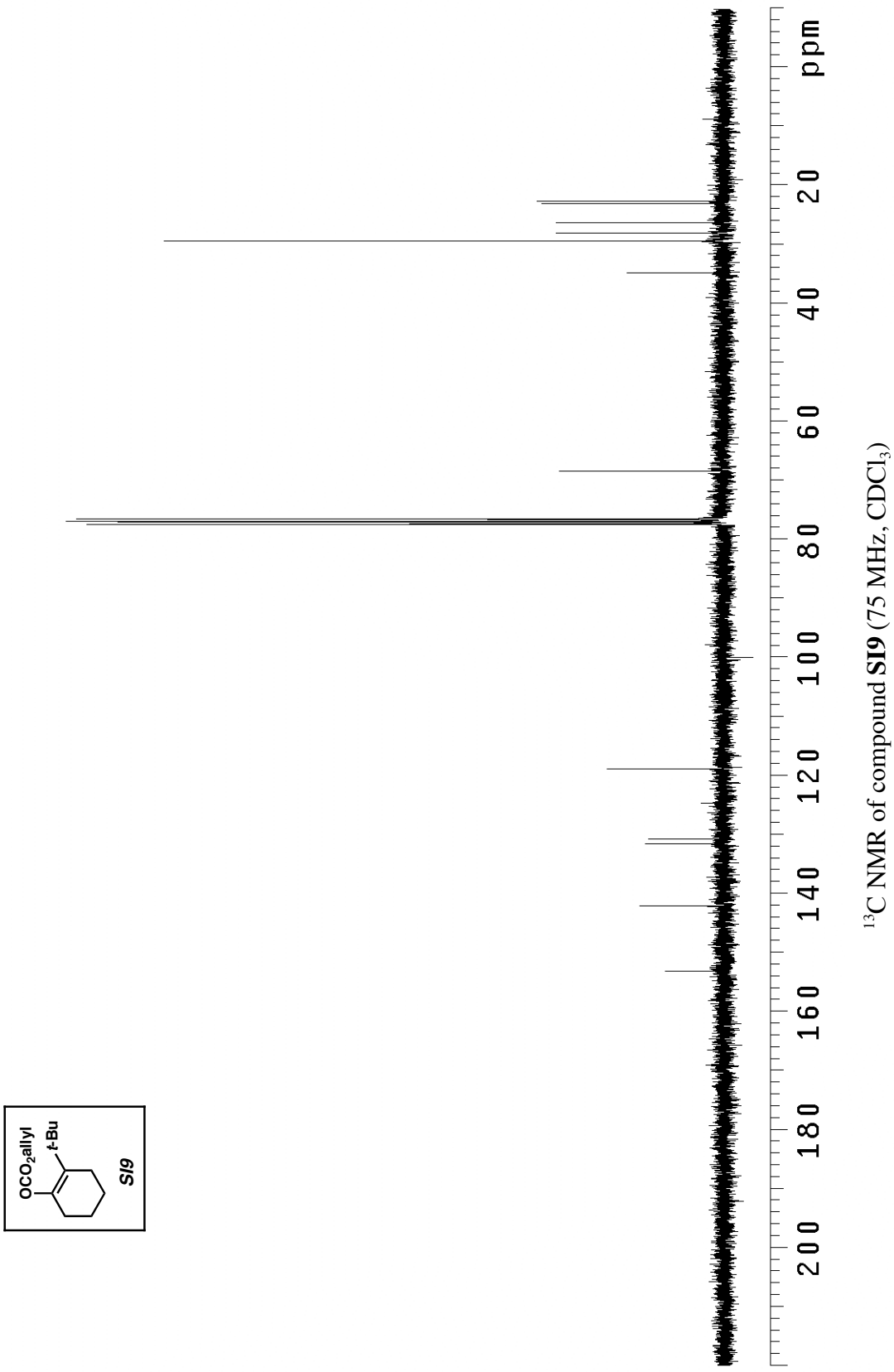
^{1}H NMR of compound **SI8** (300 MHz, $CDCl_3$)



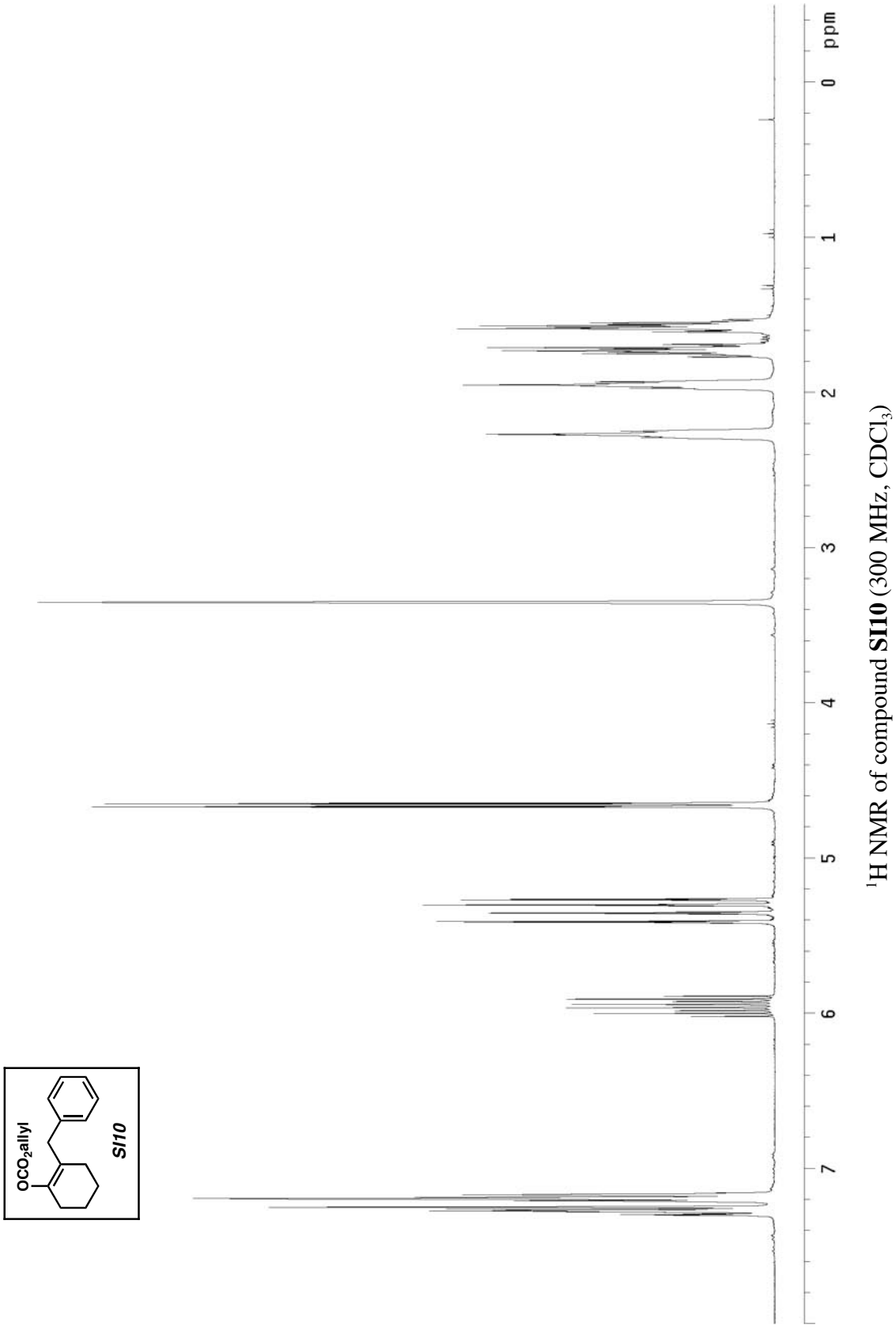
^{13}C NMR of compound **SI8** (75 MHz, $CDCl_3$)



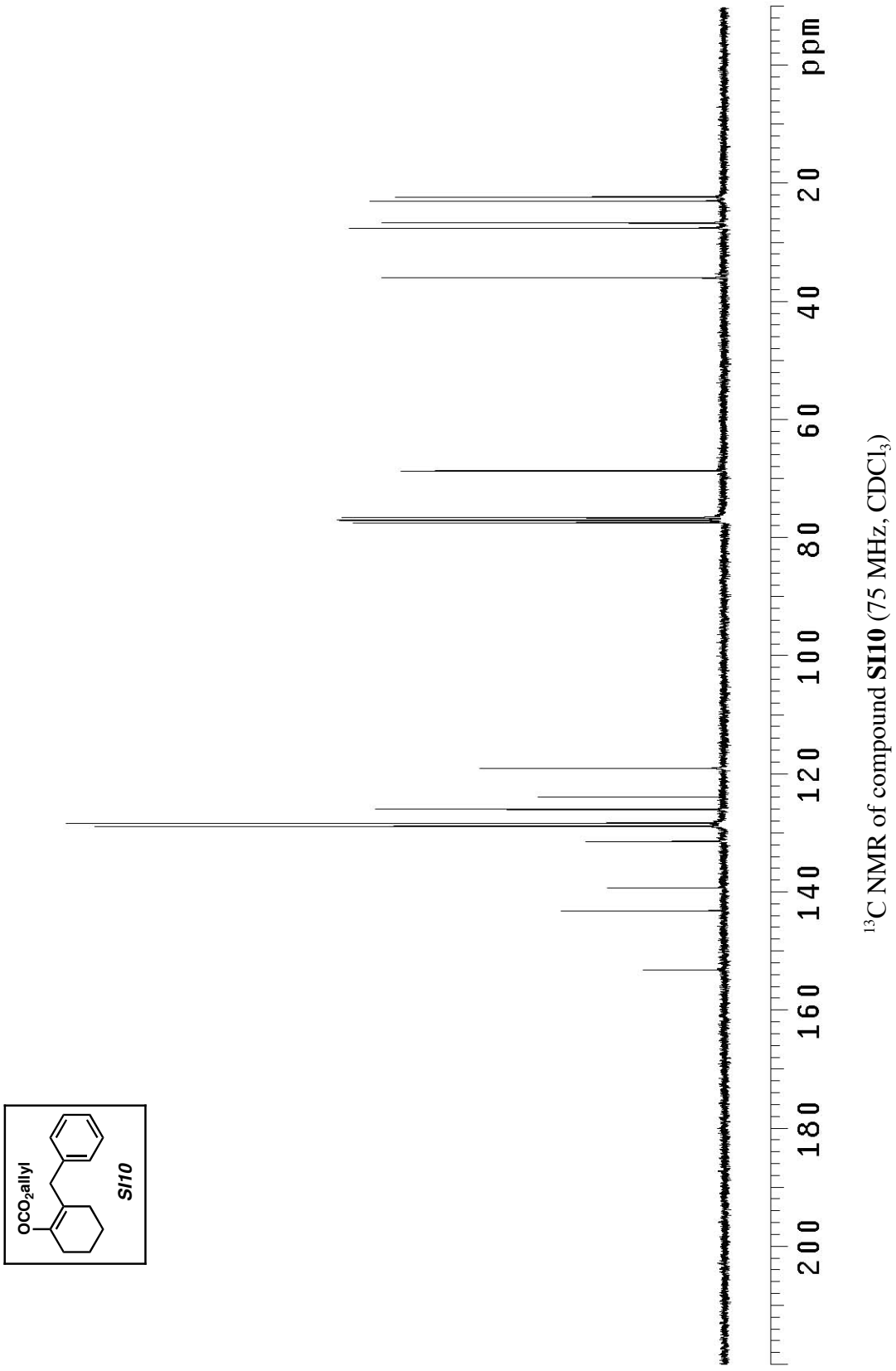
^{1}H NMR of compound **SI9** (300 MHz, $CDCl_3$)



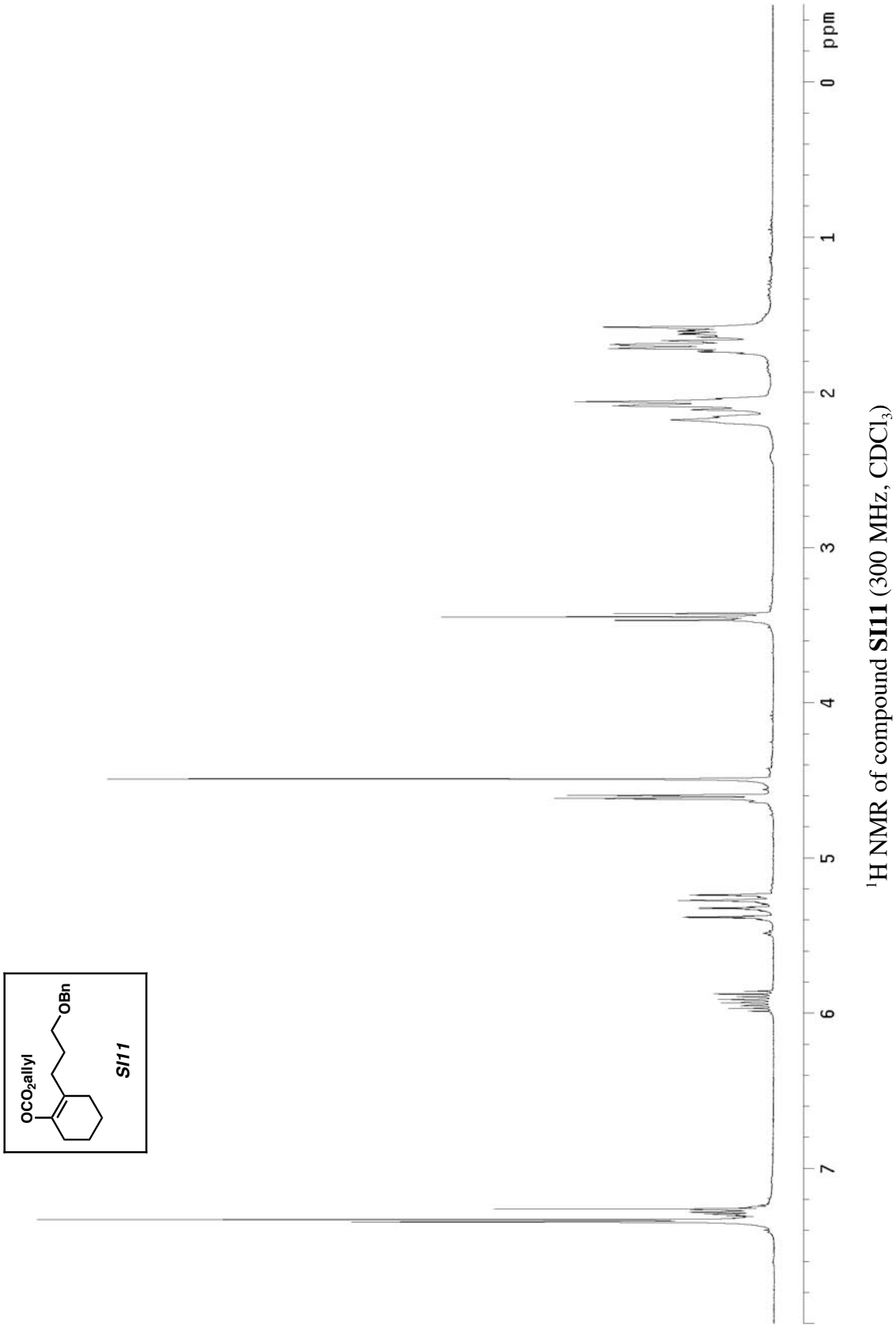
^{13}C NMR of compound **SI9** (75 MHz, $CDCl_3$)



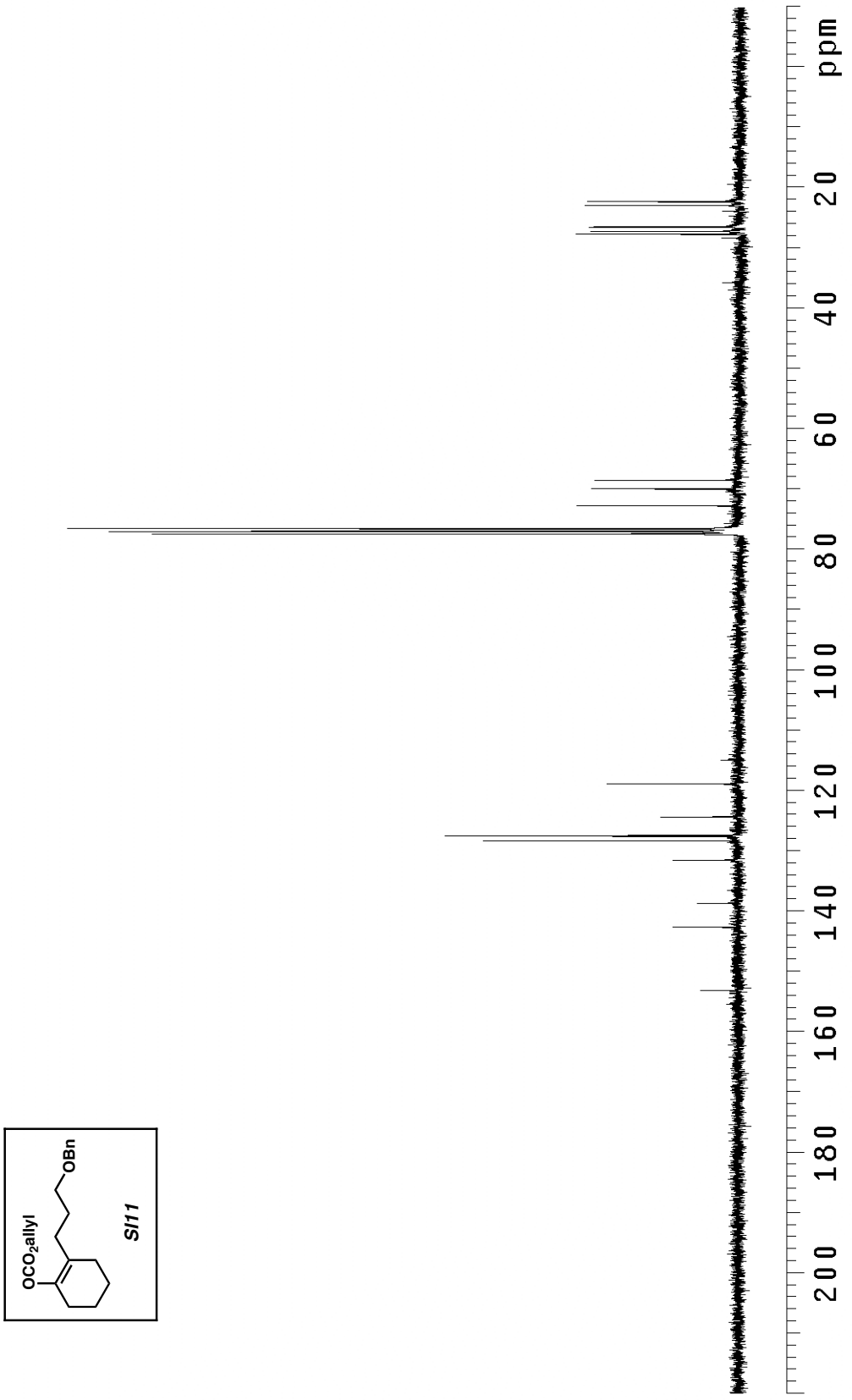
^{1}H NMR of compound **SI10** (300 MHz, $CDCl_3$)



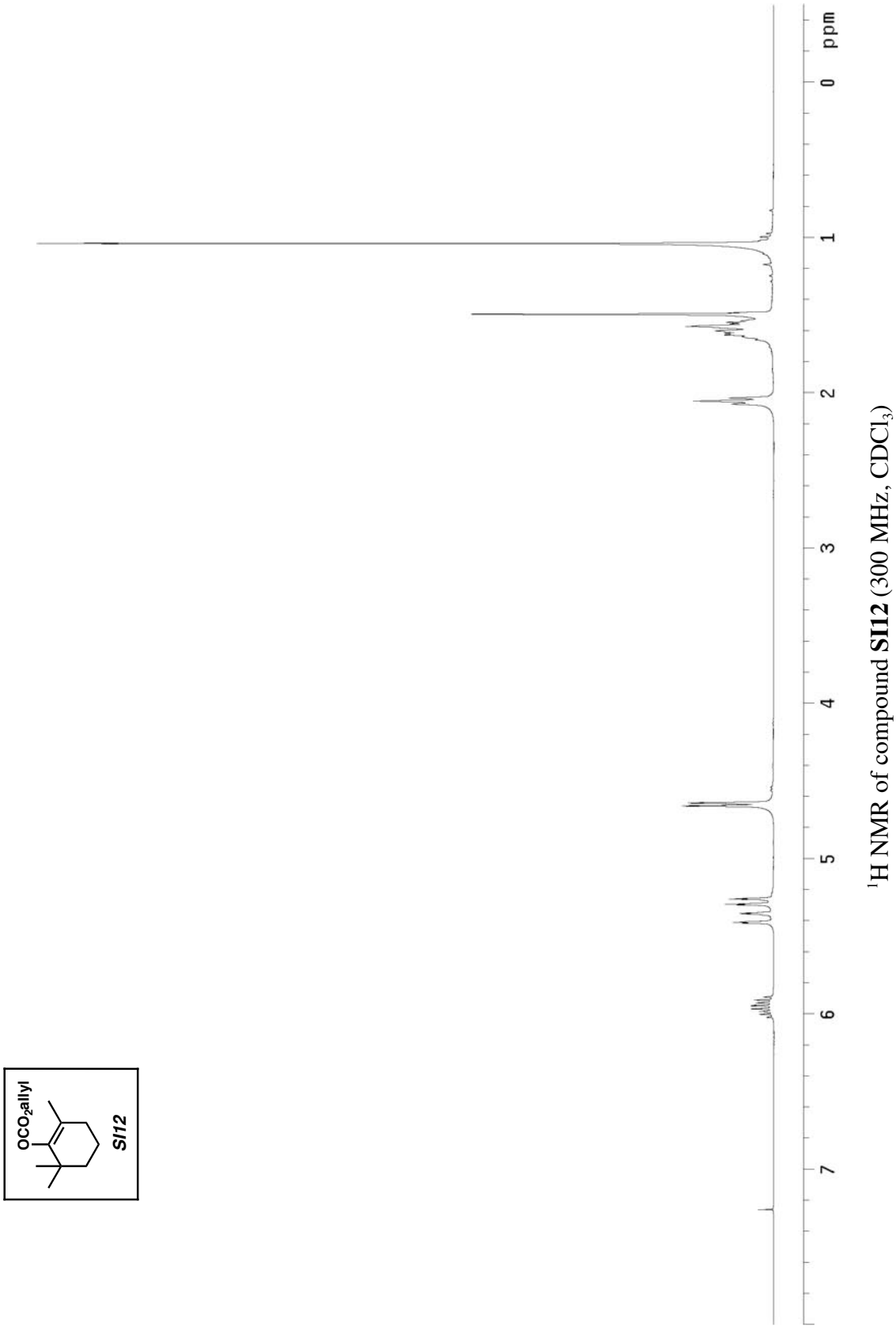
^{13}C NMR of compound **SI10** (75 MHz, $CDCl_3$)



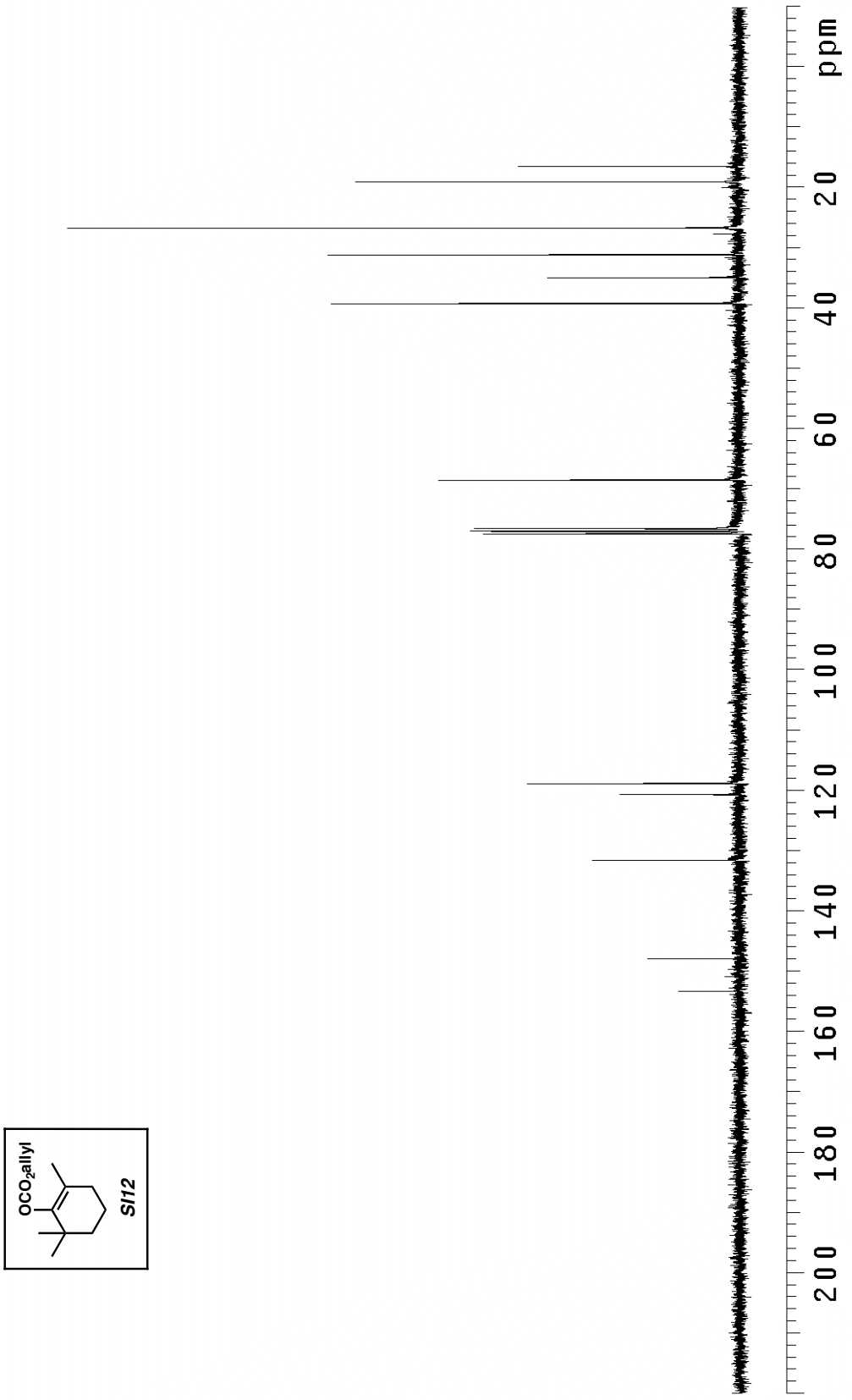
^{1}H NMR of compound **SI11** (300 MHz, $CDCl_3$)



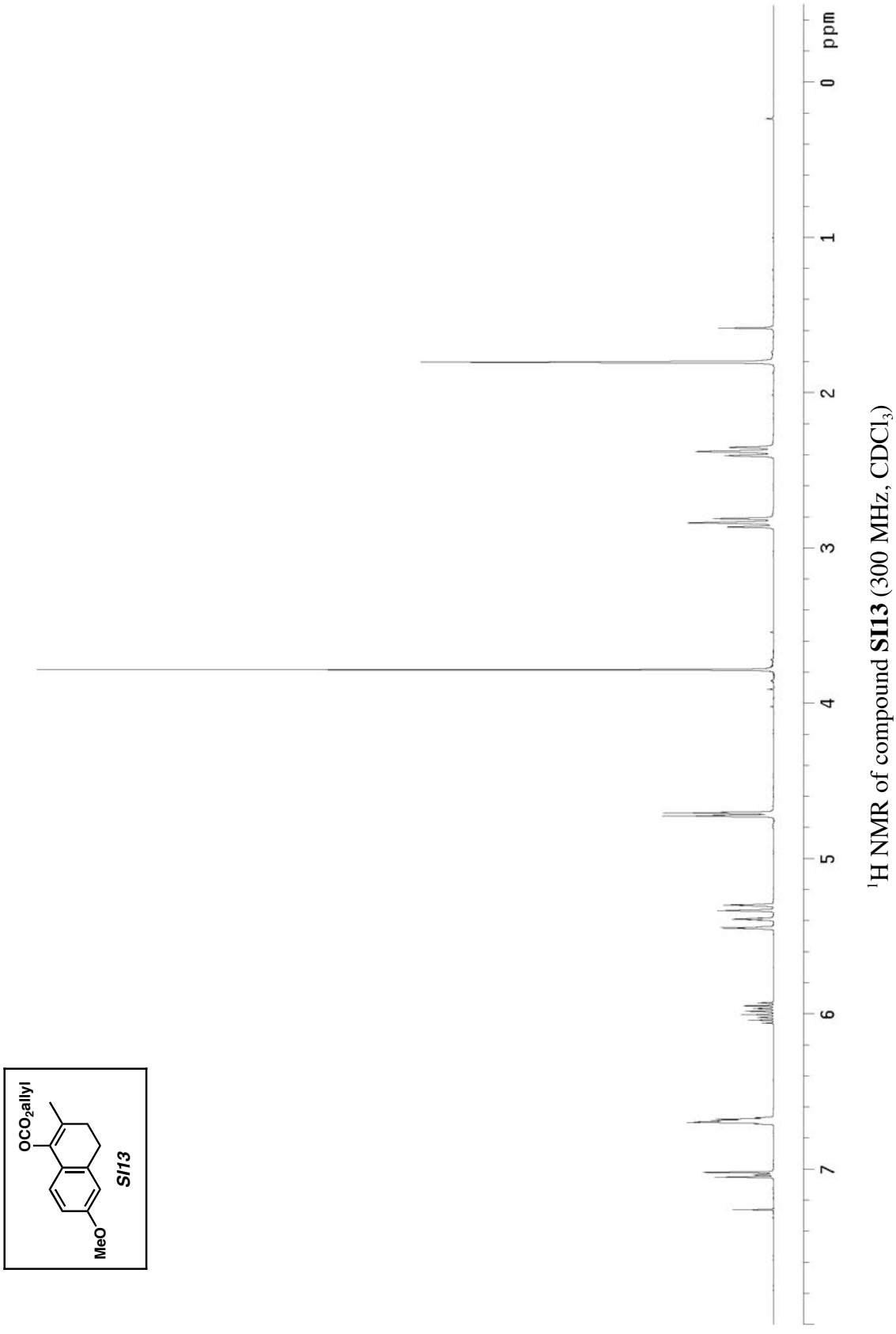
^{13}C NMR of compound **SI11** (75 MHz, $CDCl_3$)



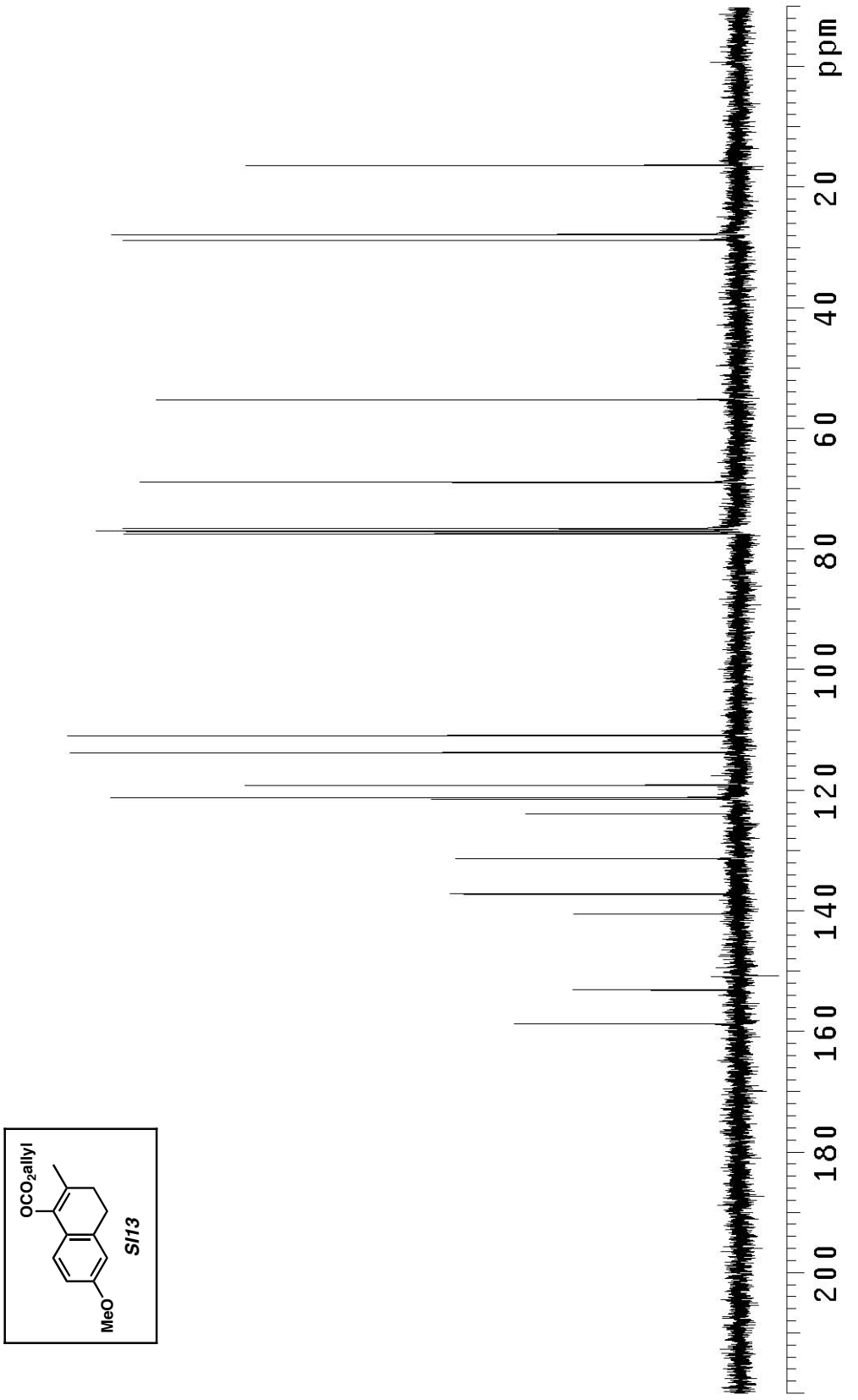
^{1}H NMR of compound **SI12** (300 MHz, $CDCl_3$)



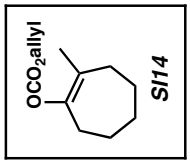
^{13}C NMR of compound **SI12** (75 MHz, $CDCl_3$)



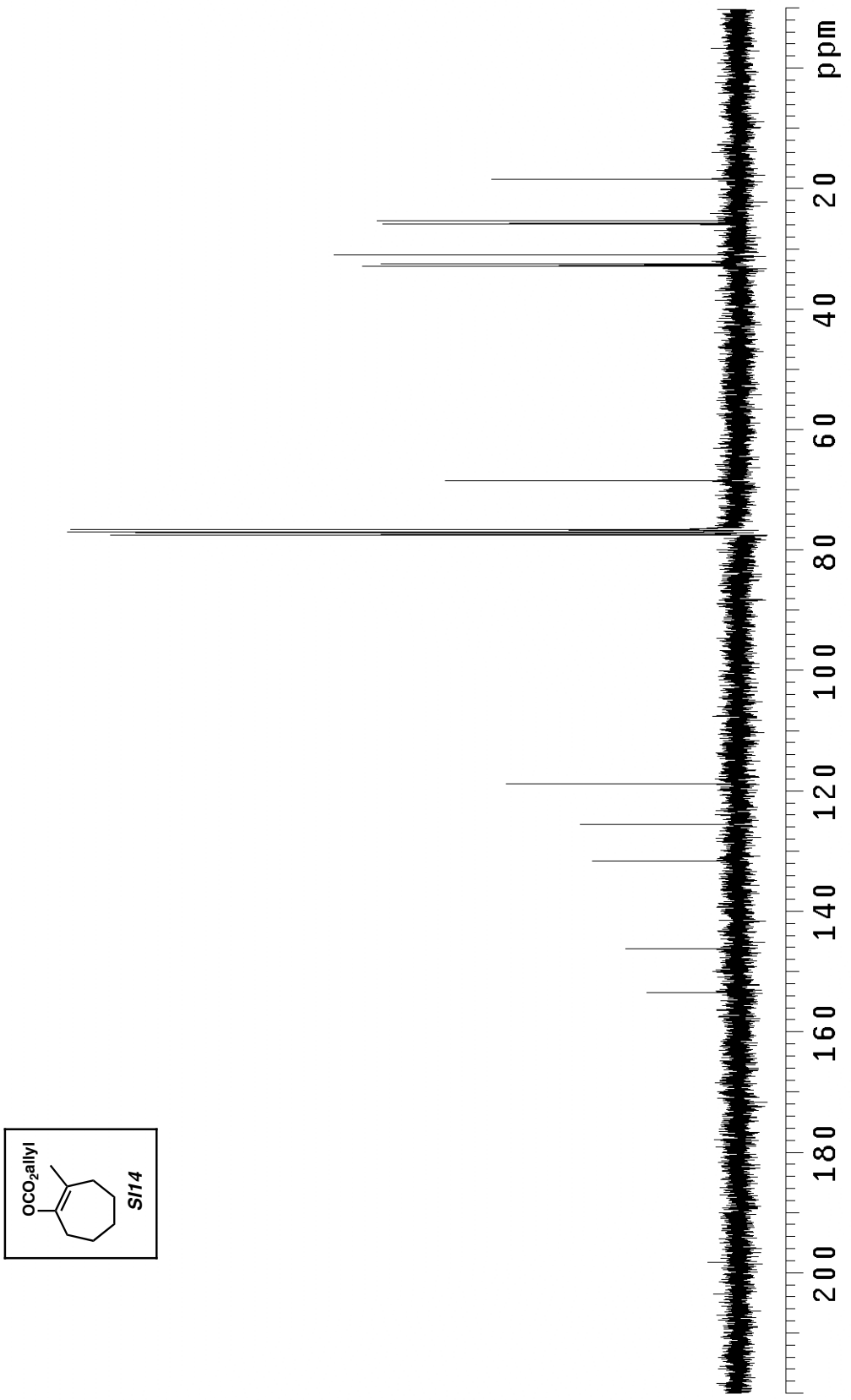
^{1}H NMR of compound **SI13** (300 MHz, $CDCl_3$)



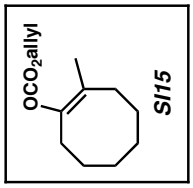
^{13}C NMR of compound **SI13** (75 MHz, $CDCl_3$)



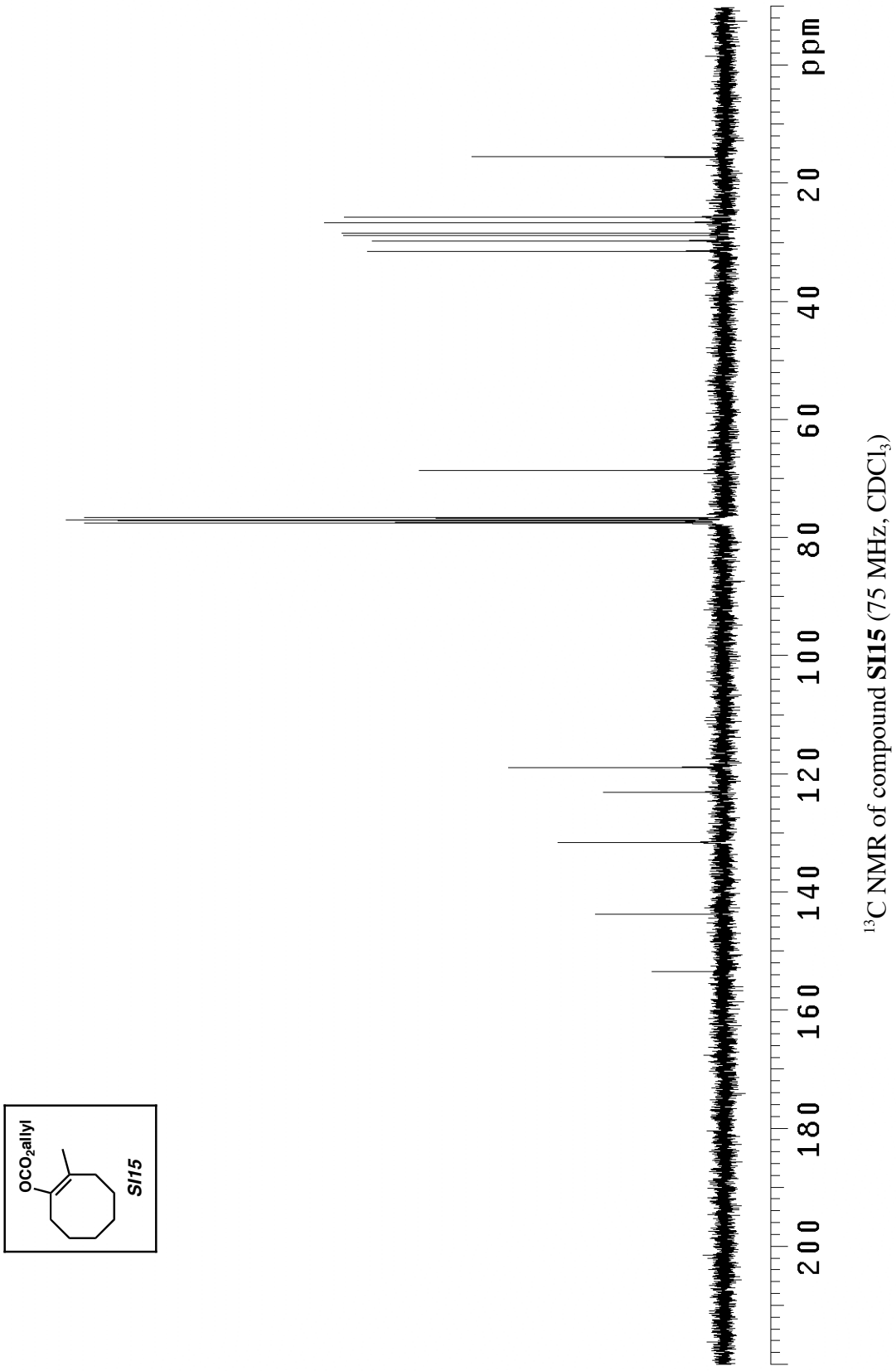
^{1}H NMR of compound **SI14** (300 MHz, $CDCl_3$)



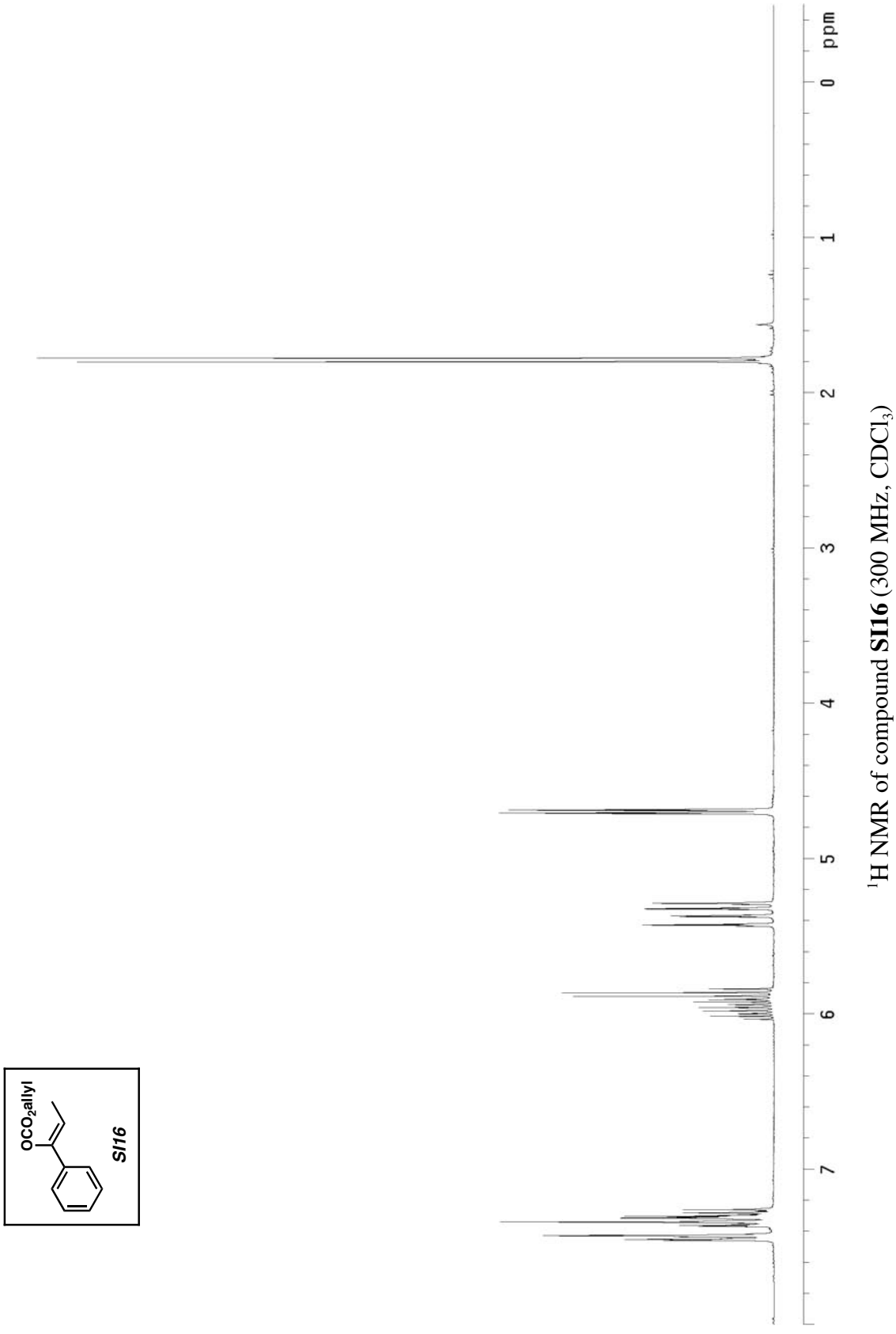
^{13}C NMR of compound **SI14** (75 MHz, $CDCl_3$)



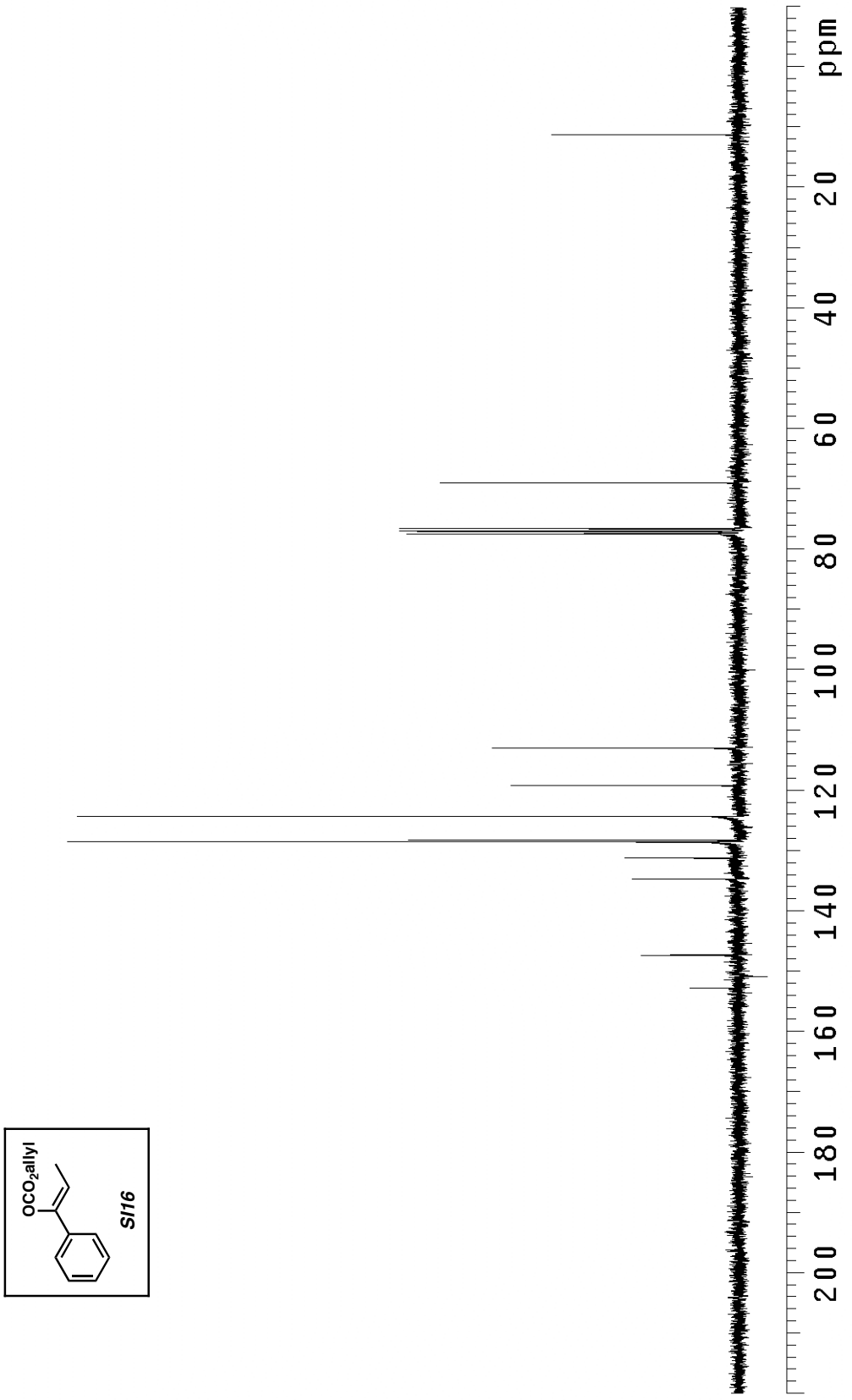
^{1}H NMR of compound **SI15** (300 MHz, $CDCl_3$)



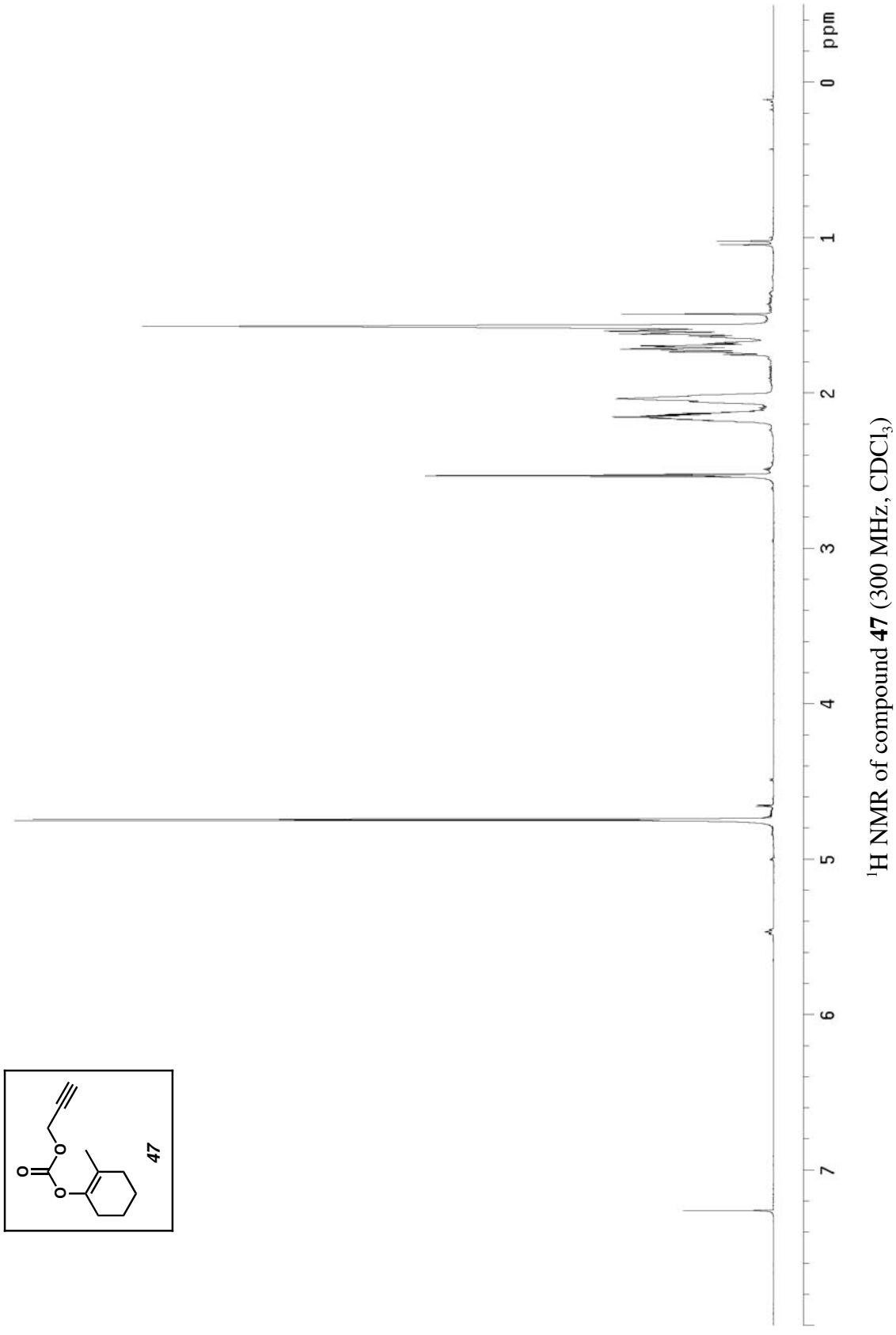
^{13}C NMR of compound **SI15** (75 MHz, $CDCl_3$)



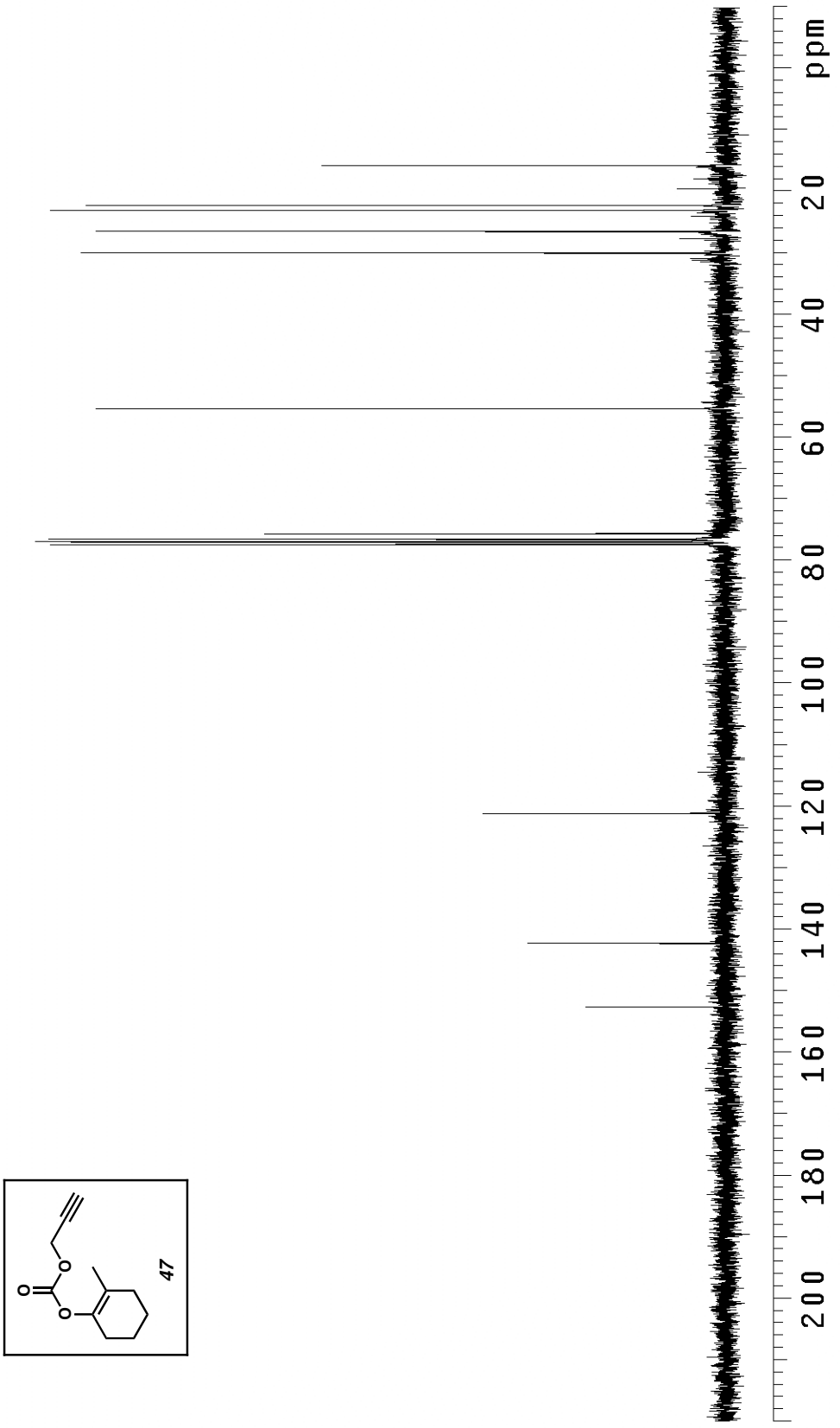
^{1}H NMR of compound **SI16** (300 MHz, $CDCl_3$)



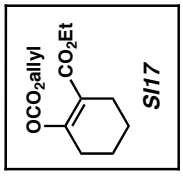
^{13}C NMR of compound **SI16** (75 MHz, $CDCl_3$)



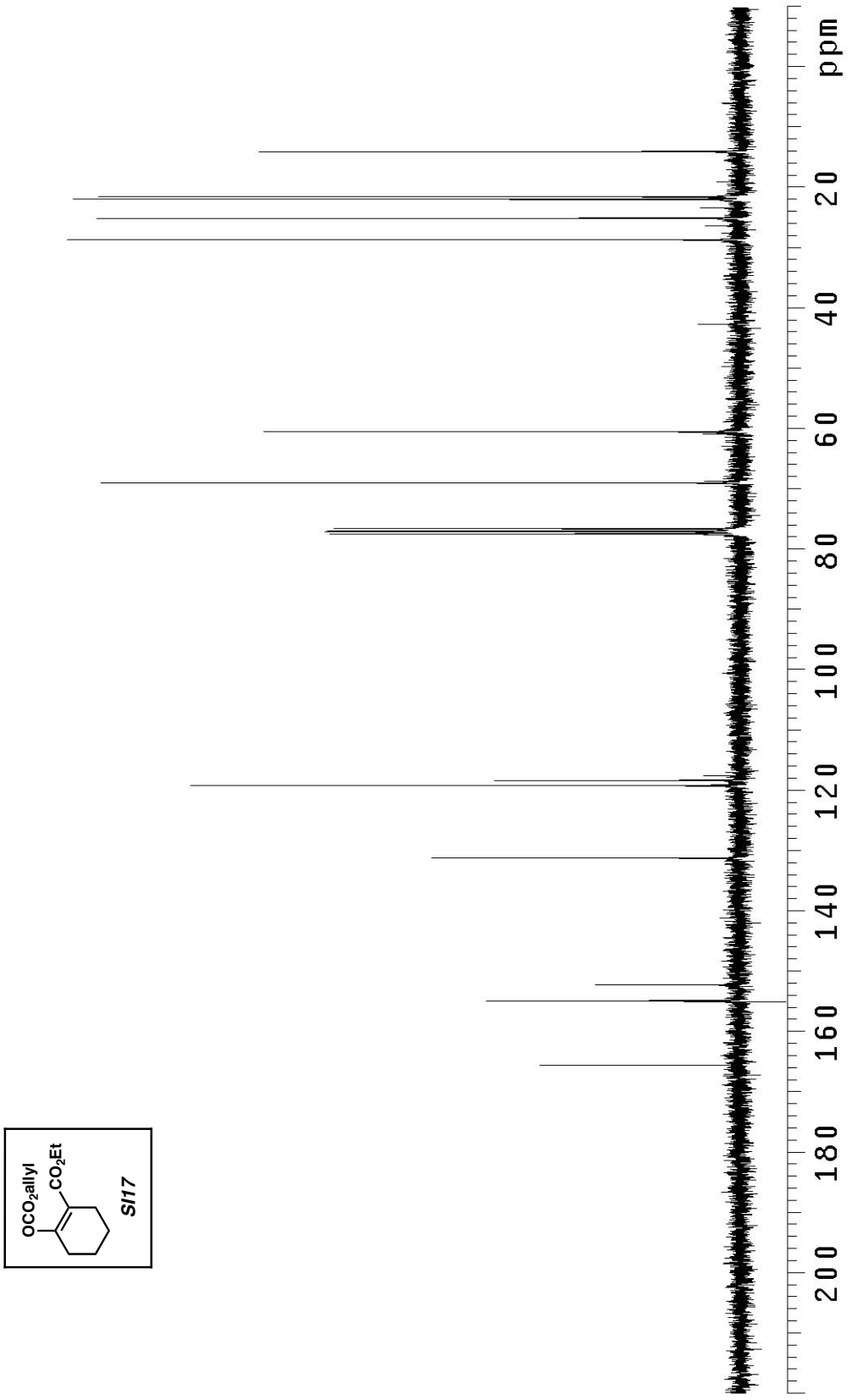
^{1}H NMR of compound **47** (300 MHz, $CDCl_3$)



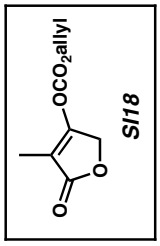
^{13}C NMR of compound **47** (75 MHz, $CDCl_3$)



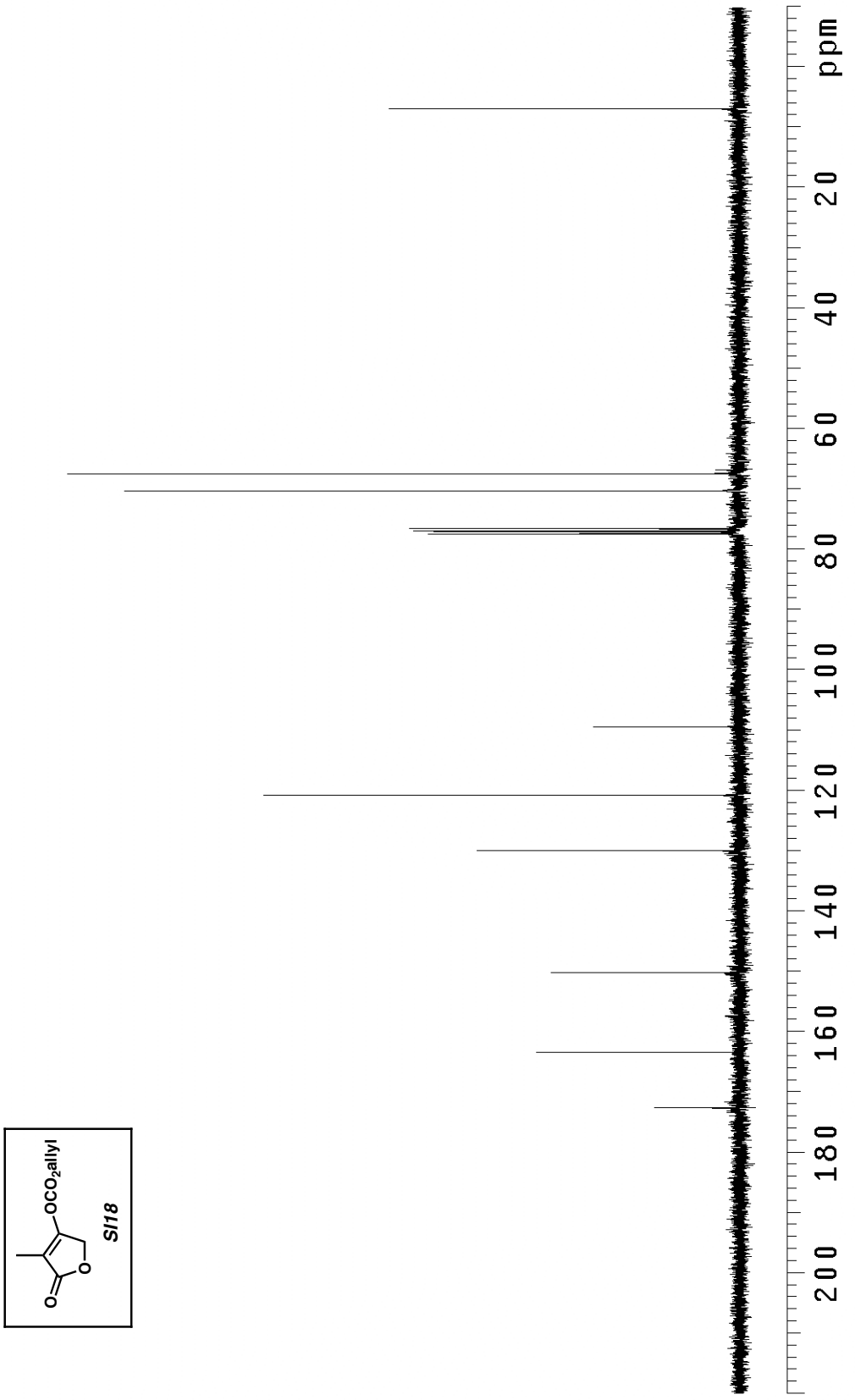
^{1}H NMR of compound **SI17** (300 MHz, $CDCl_3$)



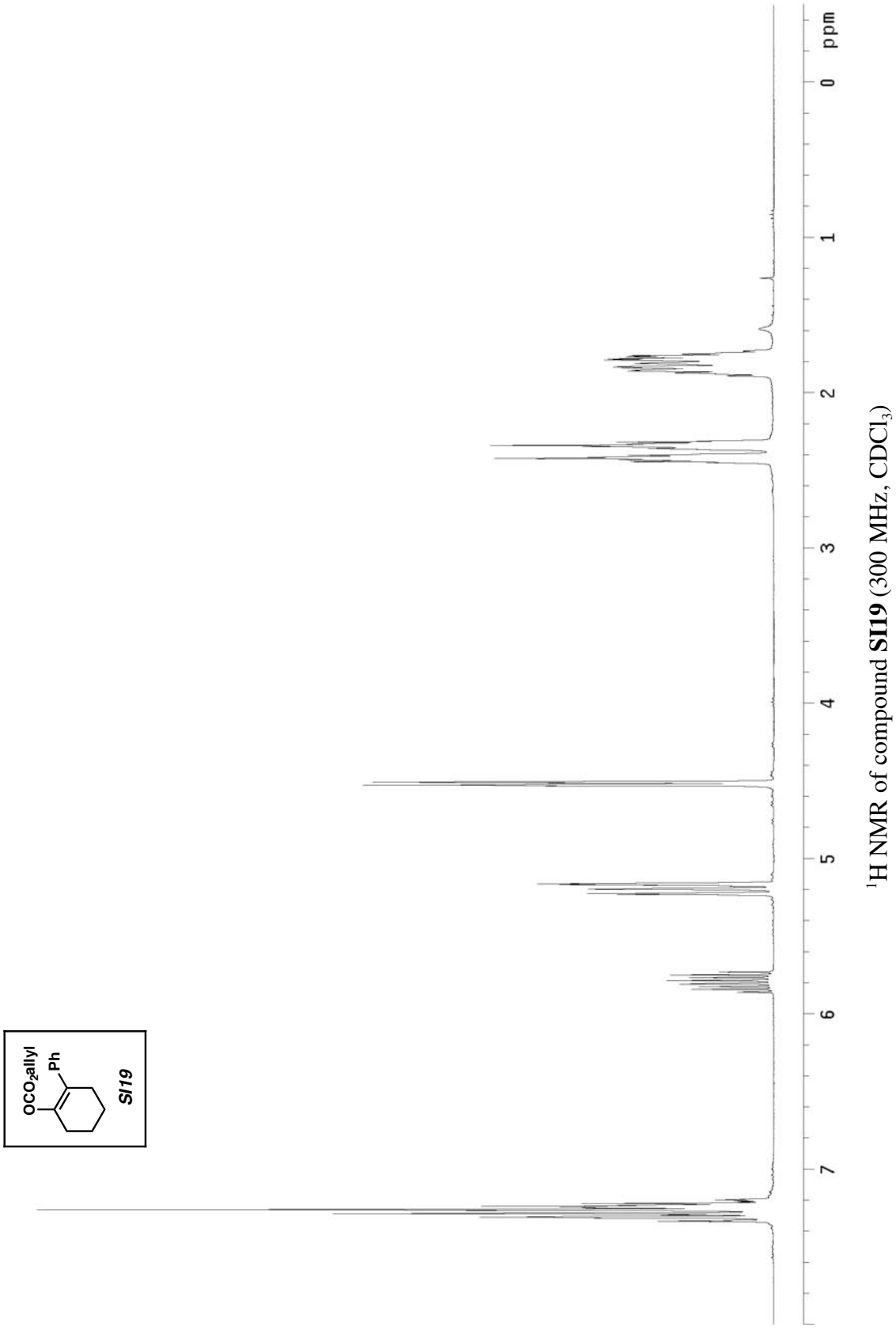
^{13}C NMR of compound **SI17** (75 MHz, $CDCl_3$)



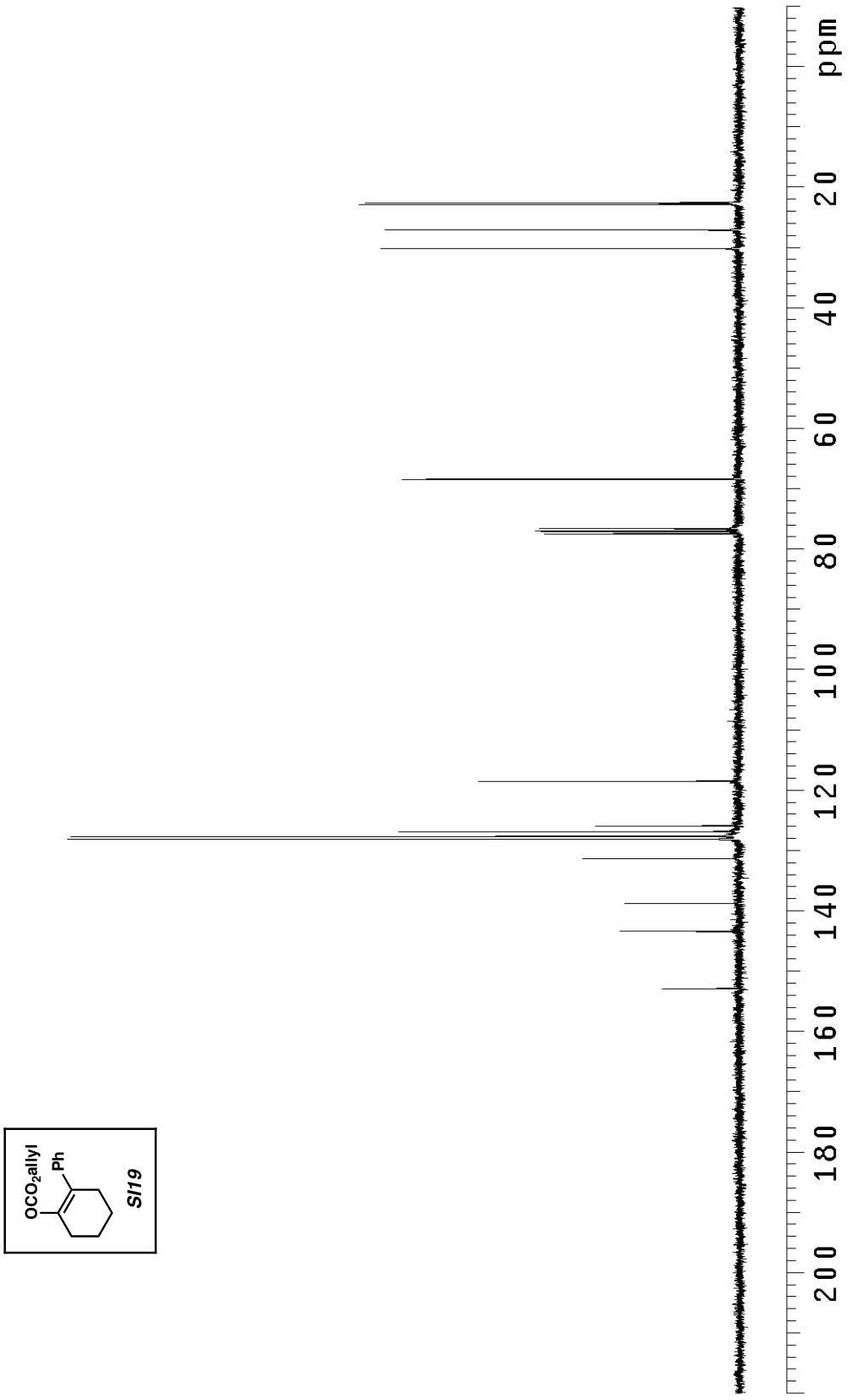
^{1}H NMR of compound **SI18** (300 MHz, $CDCl_3$)



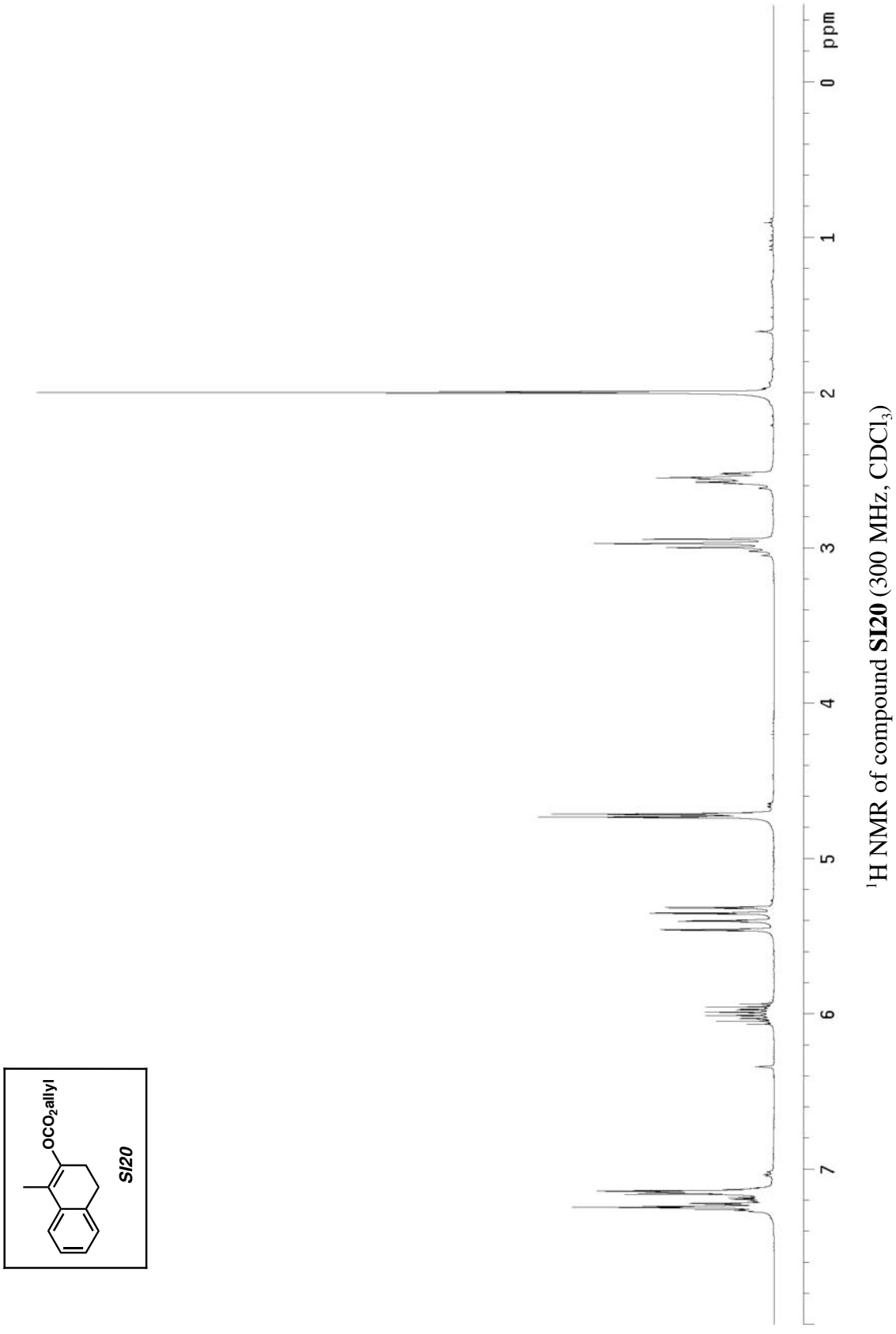
^{13}C NMR of compound **SI18** (75 MHz, $CDCl_3$)



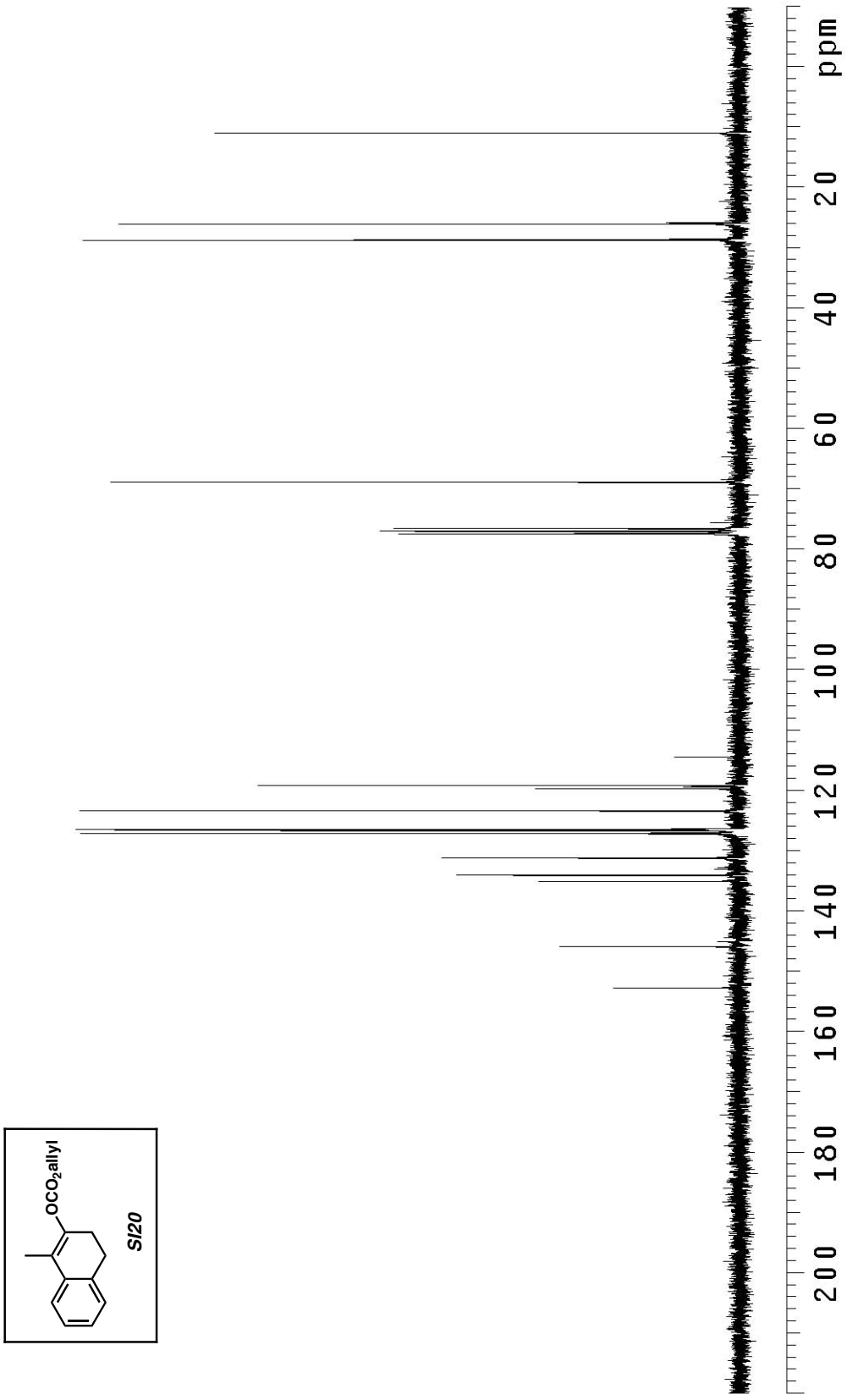
^{1}H NMR of compound **SI19** (300 MHz, $CDCl_3$)



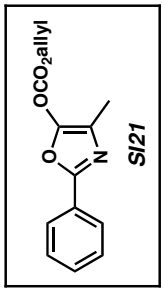
^{13}C NMR of compound **SI19** (75 MHz, $CDCl_3$)



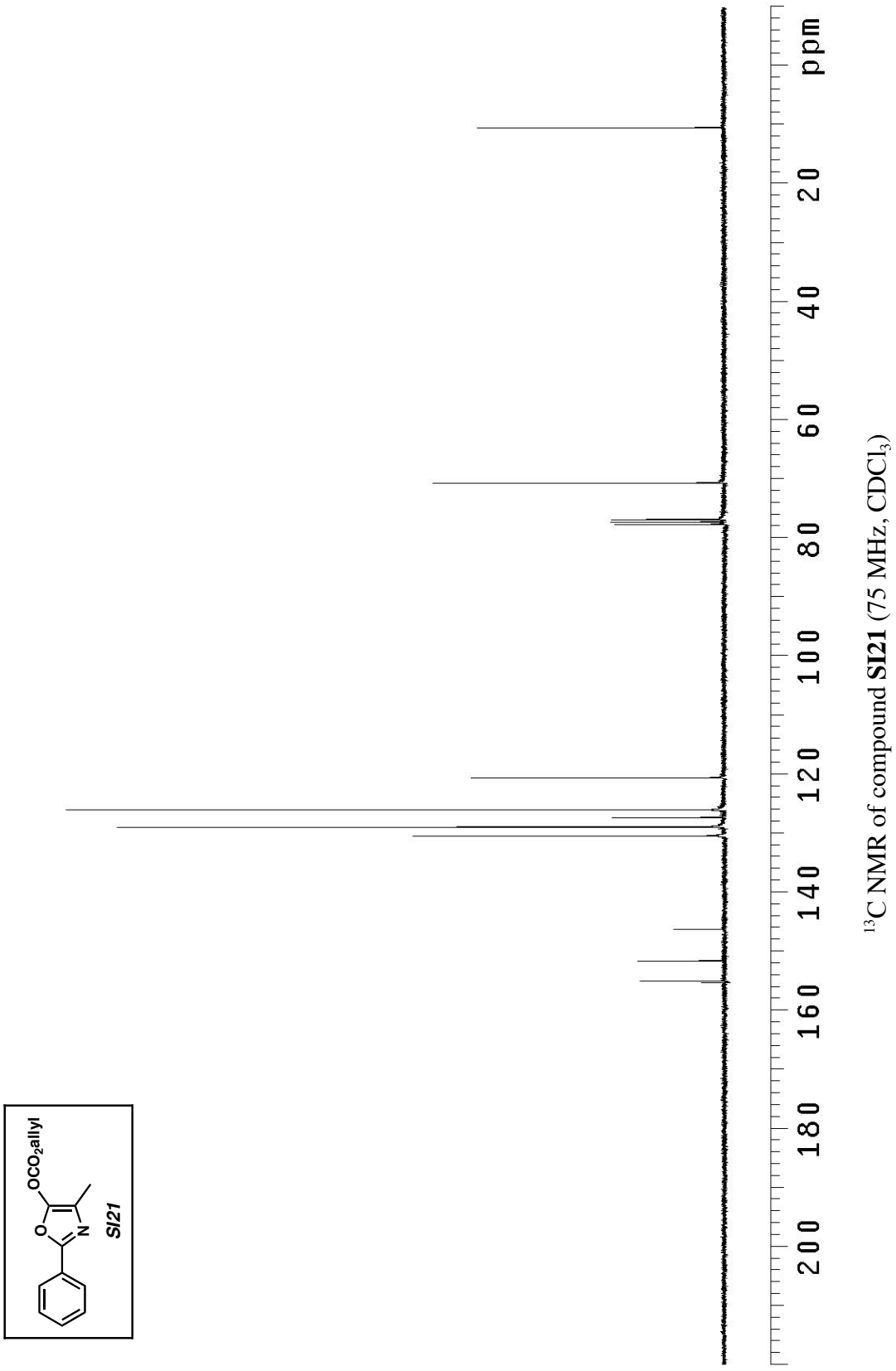
^{1}H NMR of compound **SI20** (300 MHz, $CDCl_3$)



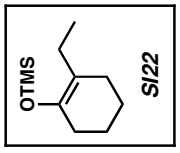
^{13}C NMR of compound **SI20** (75 MHz, $CDCl_3$)



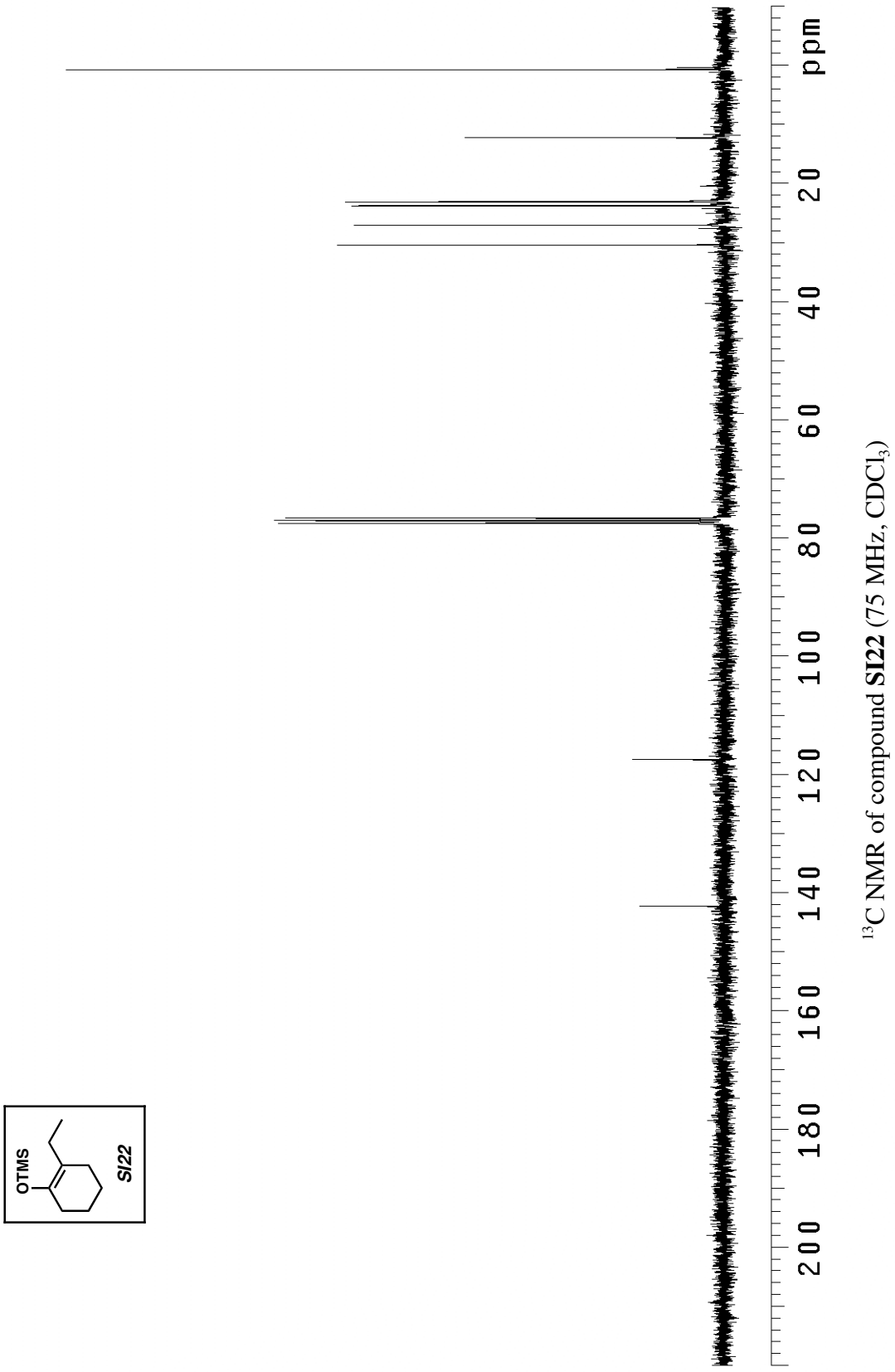
^{1}H NMR of compound **SI21** (300 MHz, $CDCl_3$)



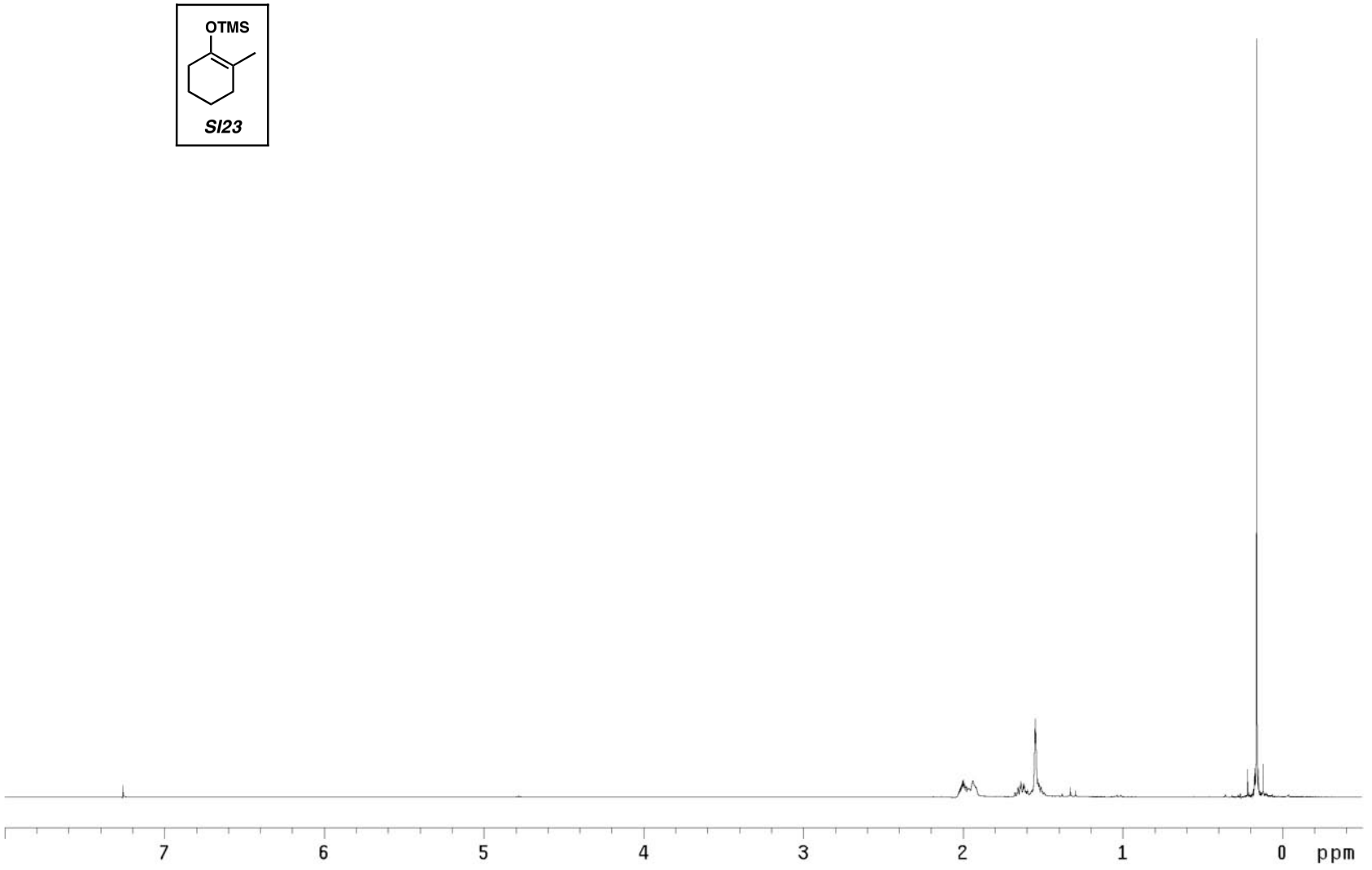
^{13}C NMR of compound **SI21** (75 MHz, $CDCl_3$)



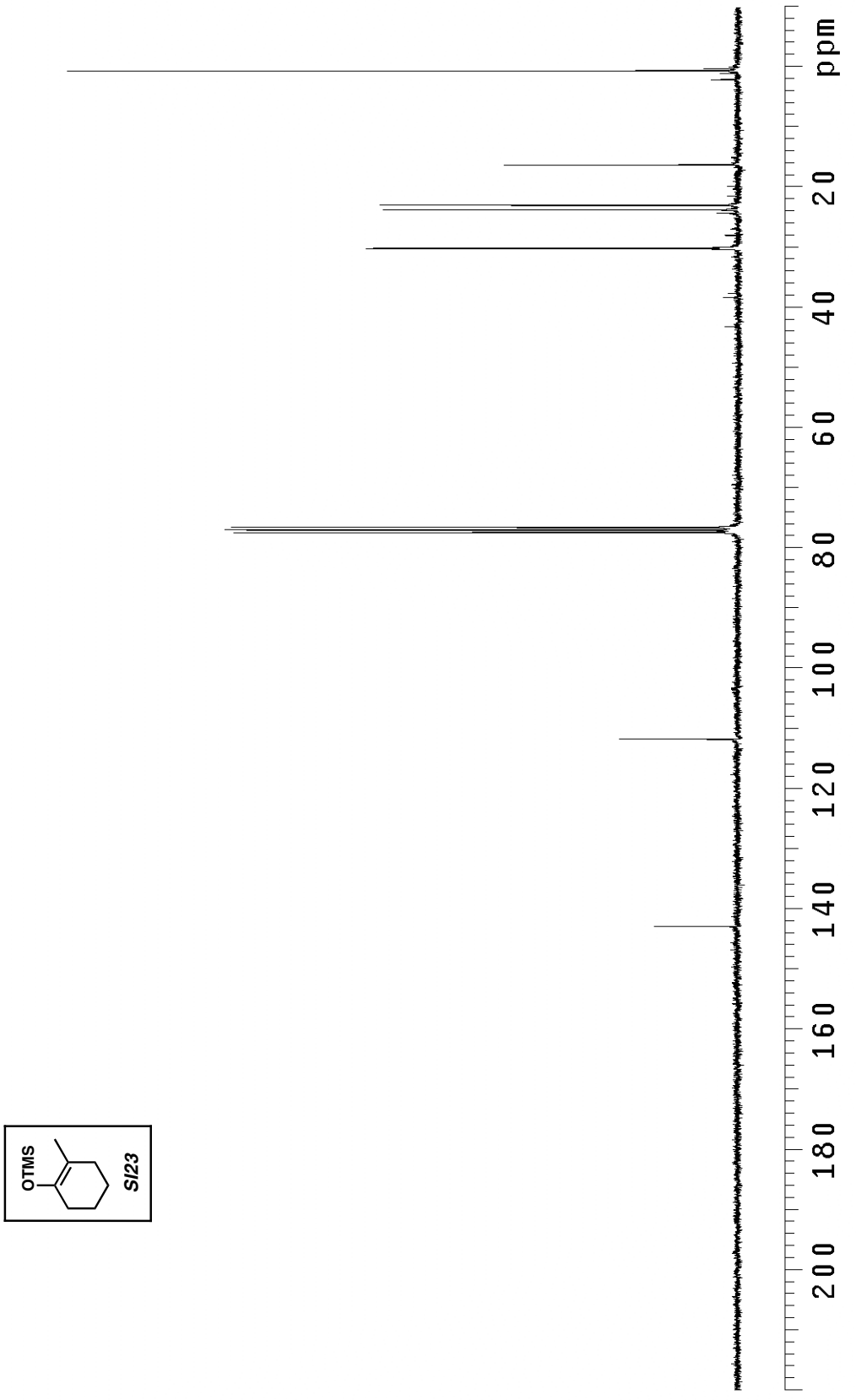
^{1}H NMR of compound **SI22** (300 MHz, $CDCl_3$)



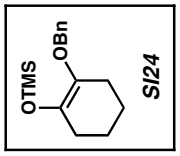
^{13}C NMR of compound **SI22** (75 MHz, $CDCl_3$)



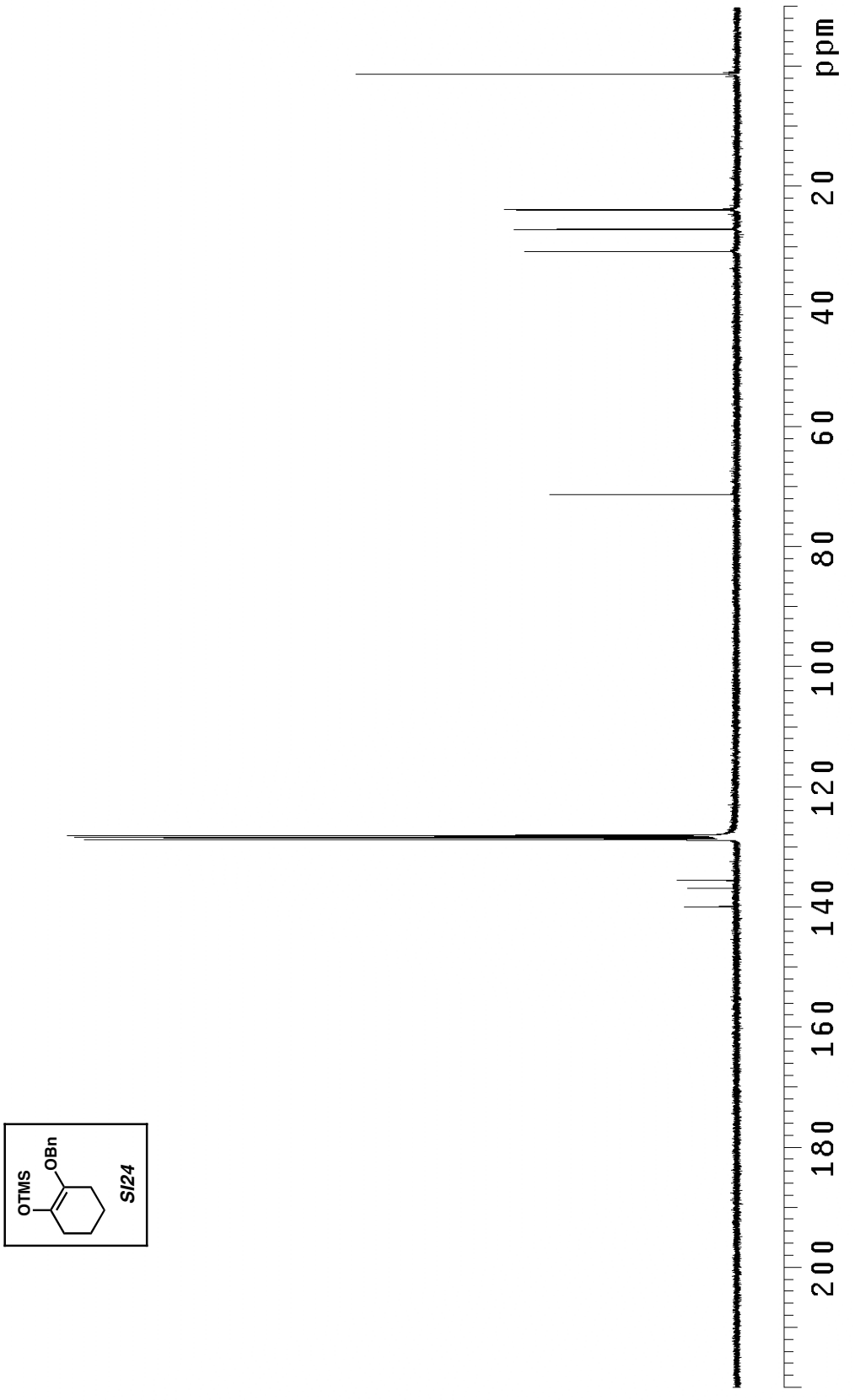
^{1}H NMR of compound **SI23** (300 MHz, $CDCl_3$)



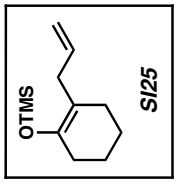
^{13}C NMR of compound **SI23** (75 MHz, $CDCl_3$)



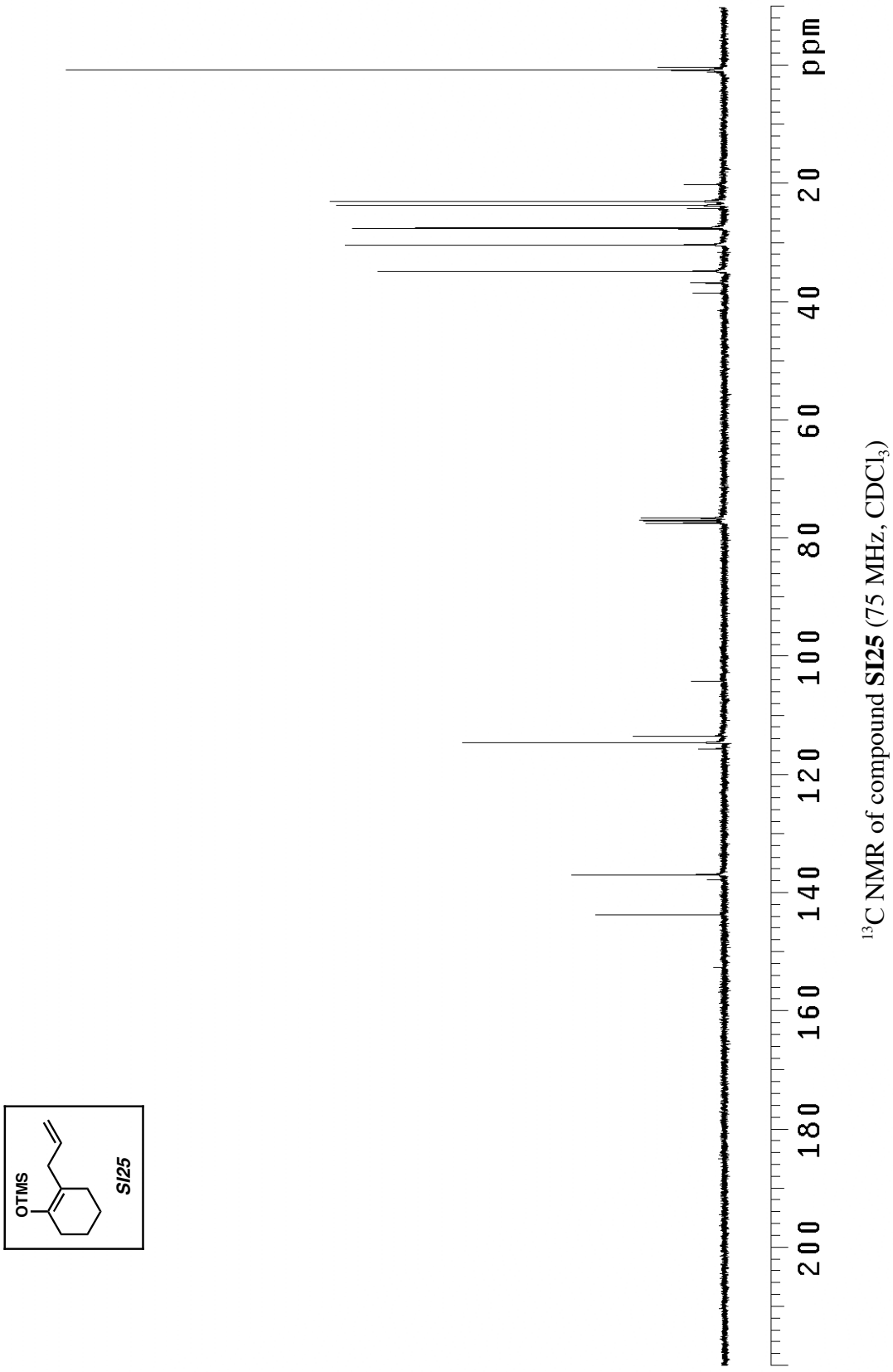
^{1}H NMR of compound **SI24** (300 MHz, C_6D_6)



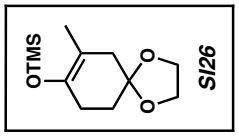
^{13}C NMR of compound **SI24** (75 MHz, C_6D_6)



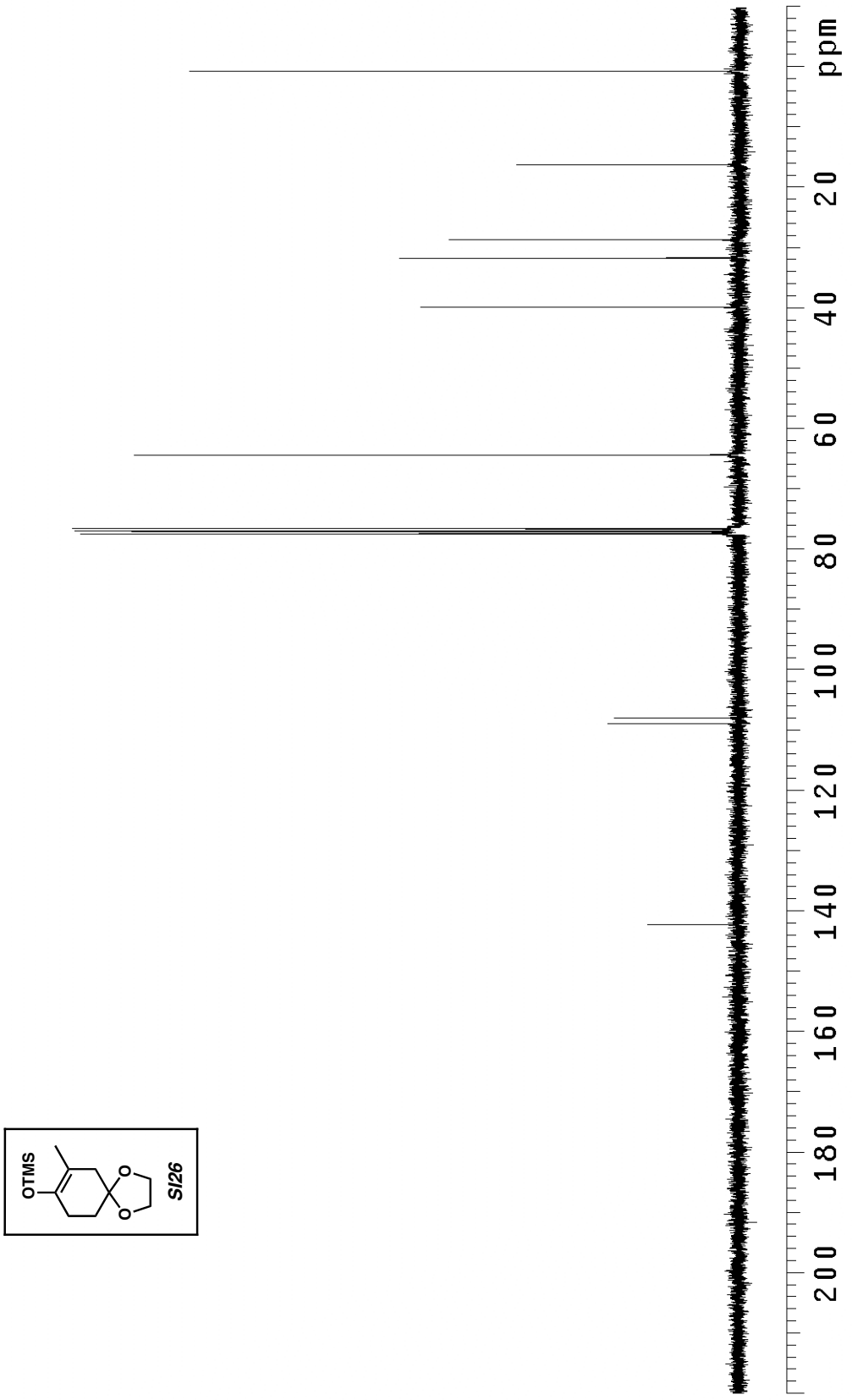
^{1}H NMR of compound **SI25** (300 MHz, $CDCl_3$)



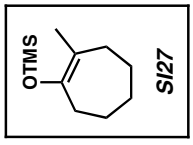
^{13}C NMR of compound **SI25** (75 MHz, $CDCl_3$)



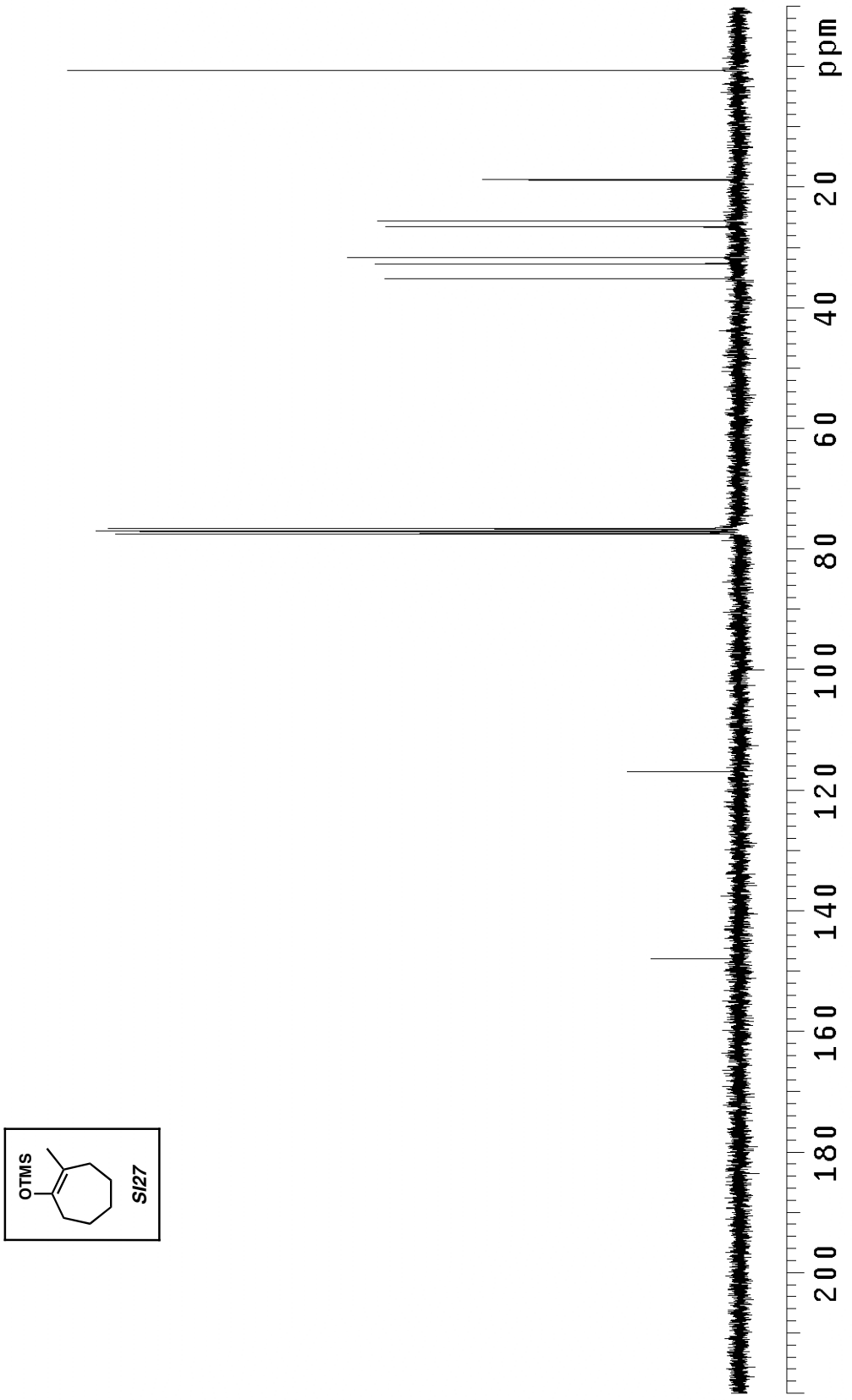
^{1}H NMR of compound **SI26** (300 MHz, $CDCl_3$)



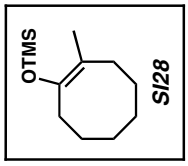
^{13}C NMR of compound **SI26** (75 MHz, $CDCl_3$)



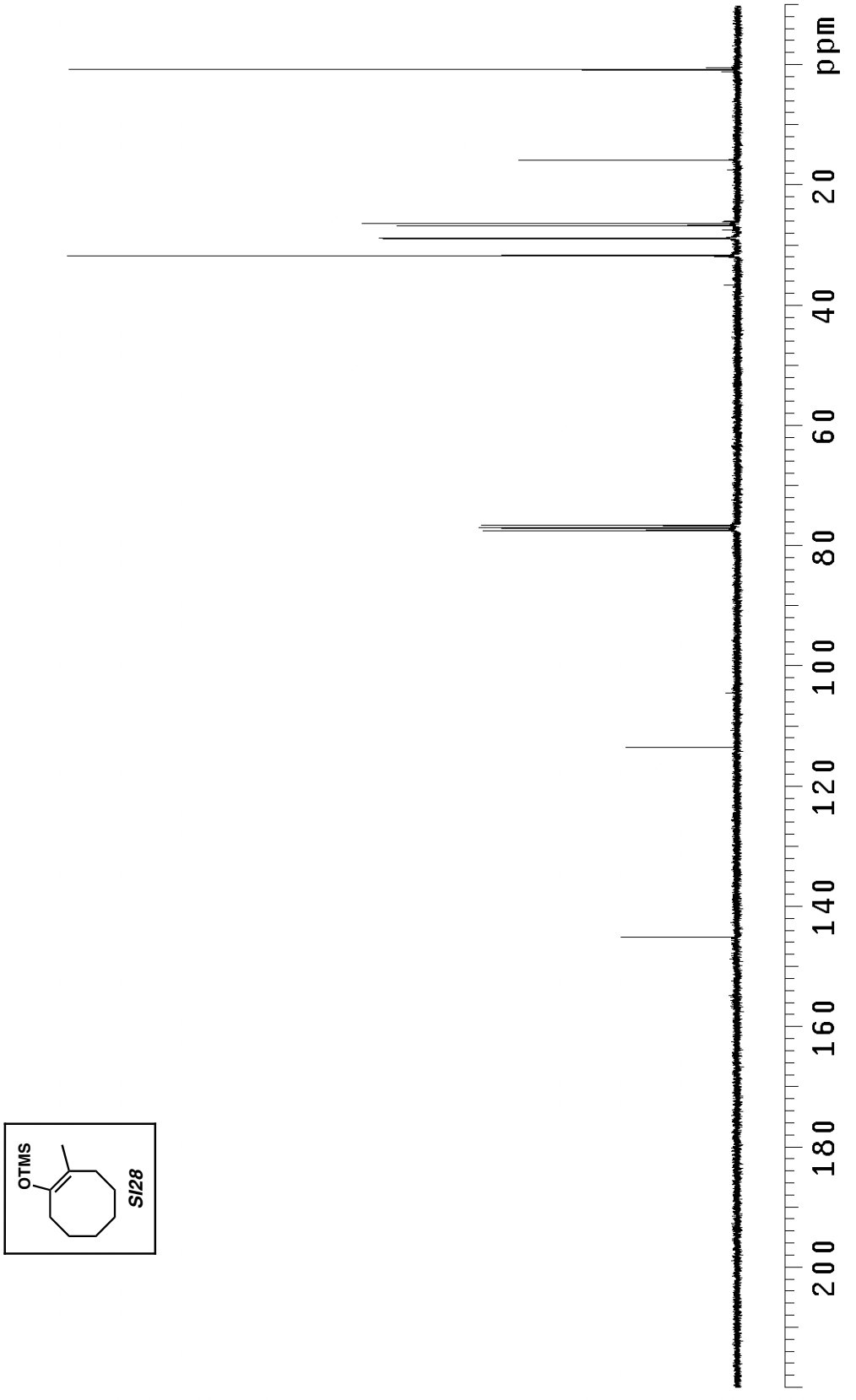
^{1}H NMR of compound **SI27** (300 MHz, $CDCl_3$)



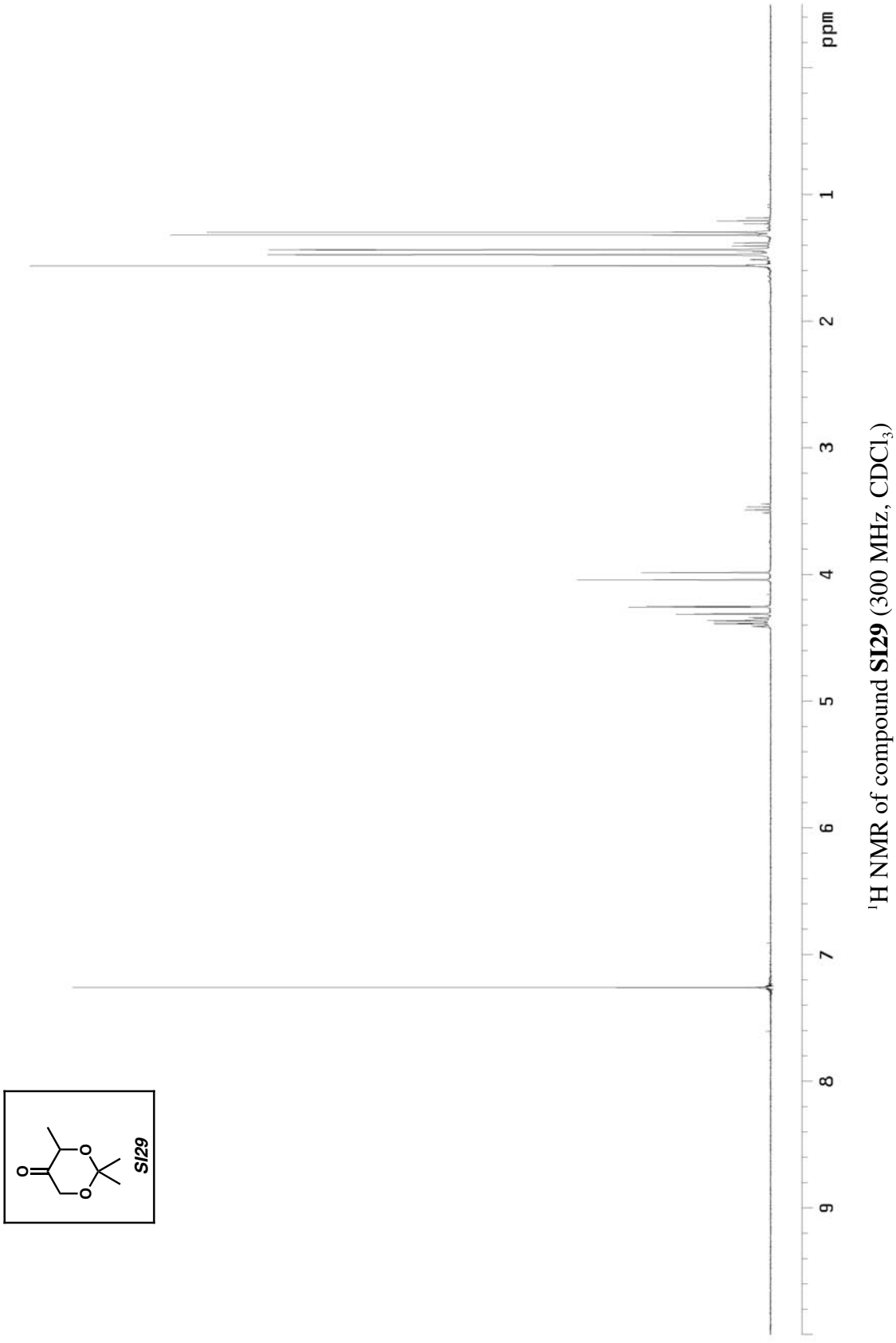
^{13}C NMR of compound **SI27** (75 MHz, $CDCl_3$)



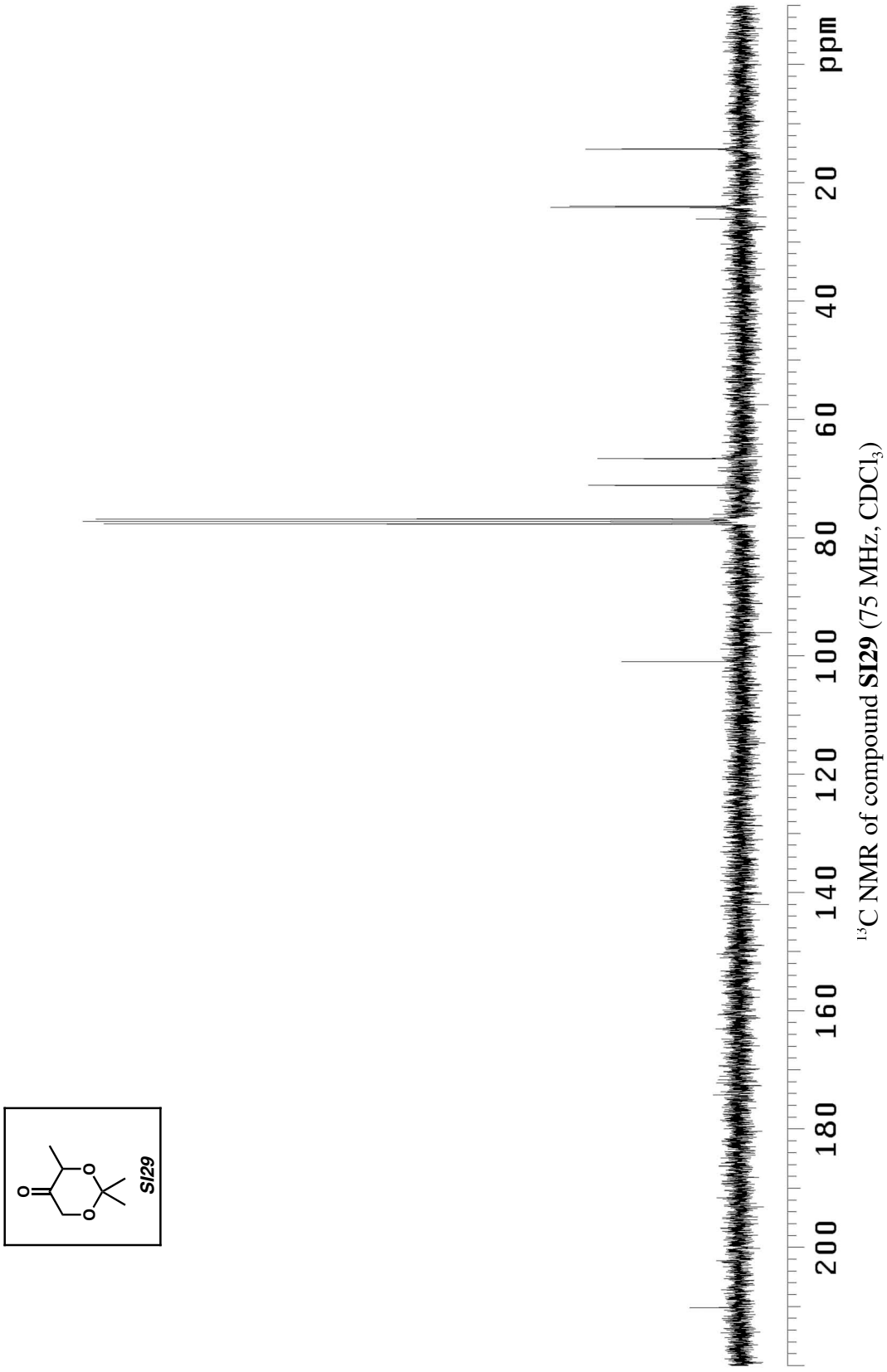
^{1}H NMR of compound **SI28** (300 MHz, $CDCl_3$)



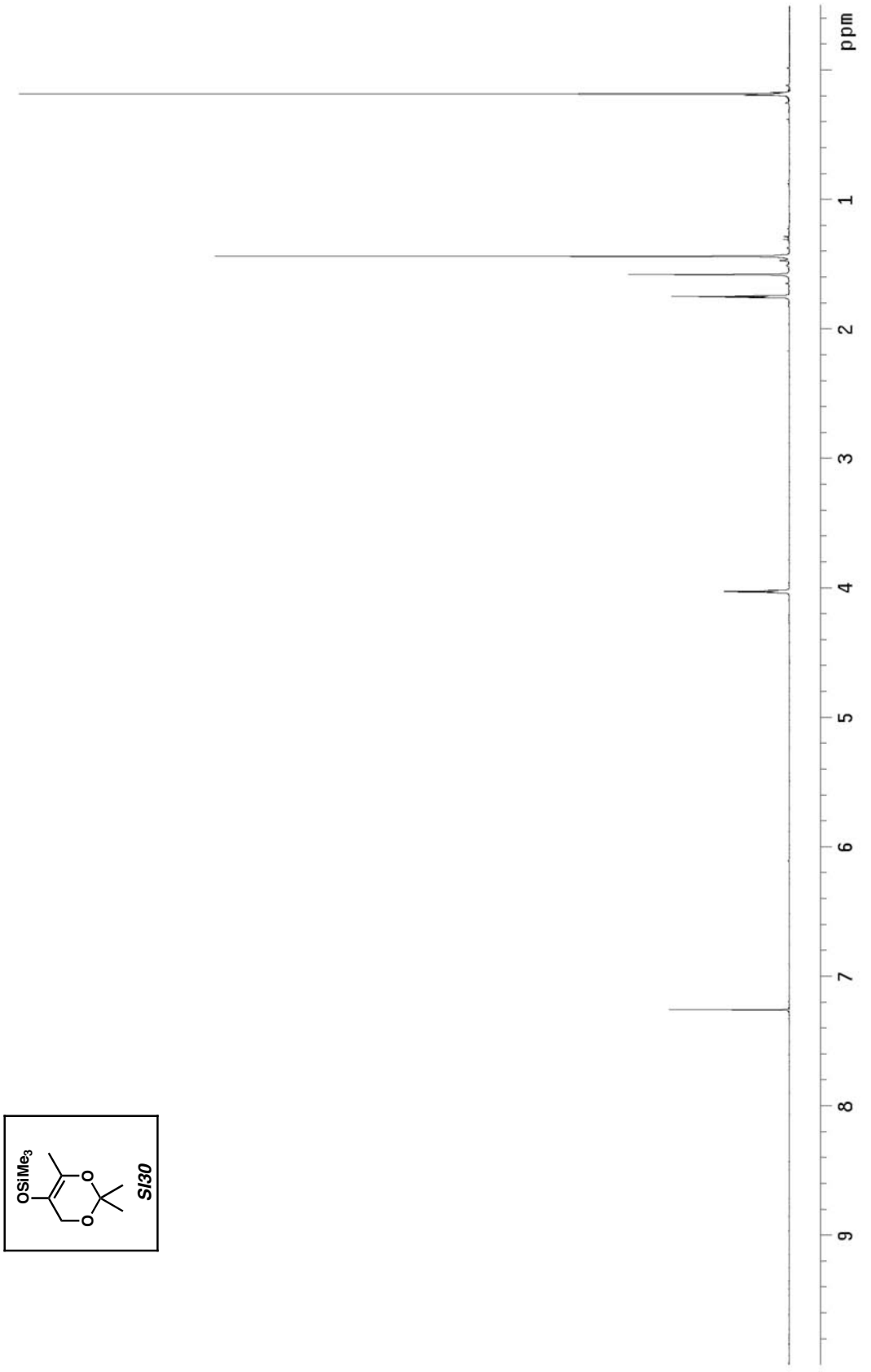
^{13}C NMR of compound **SI28** (75 MHz, $CDCl_3$)



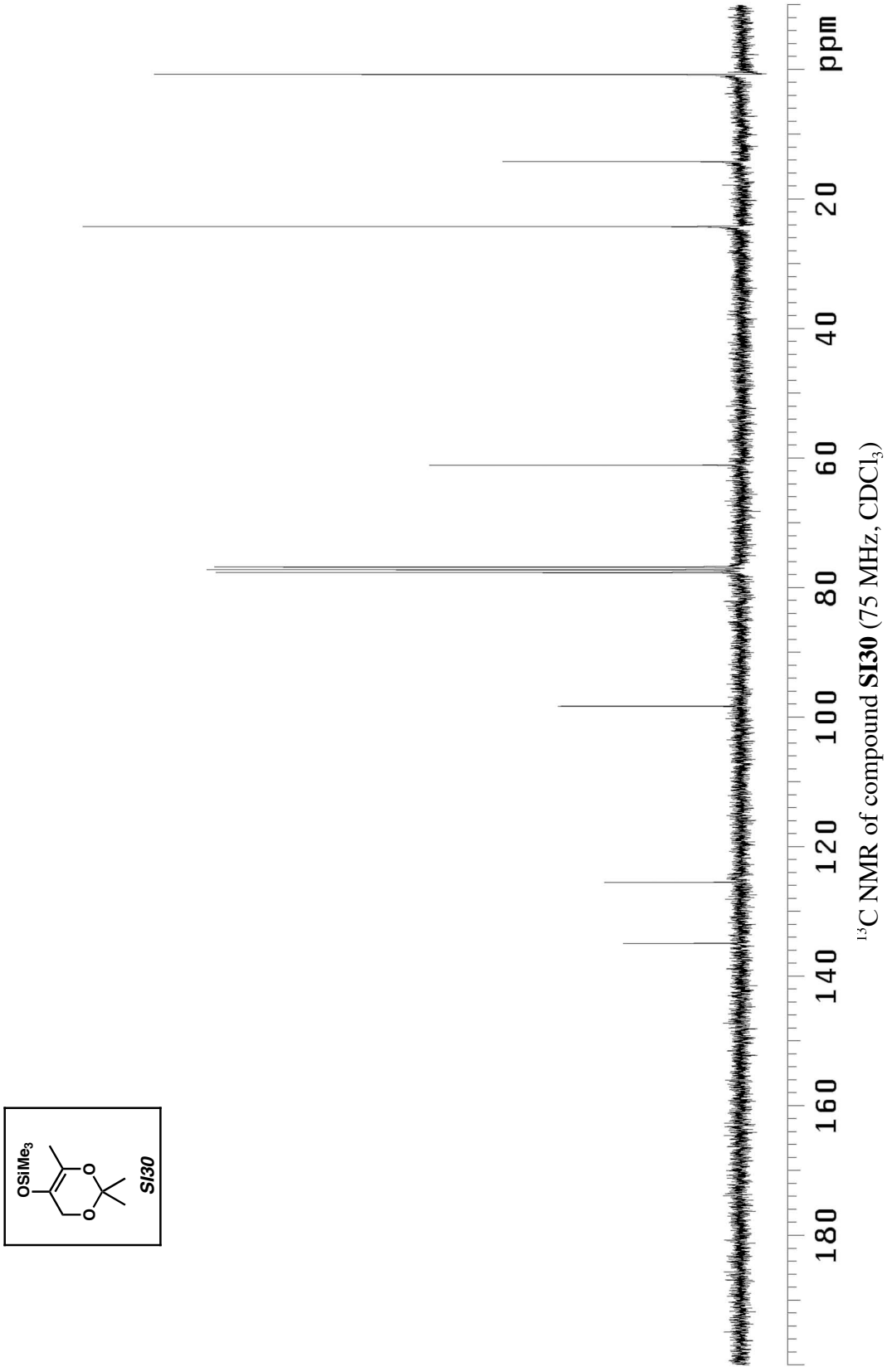
^{1}H NMR of compound **SI29** (300 MHz, $CDCl_3$)



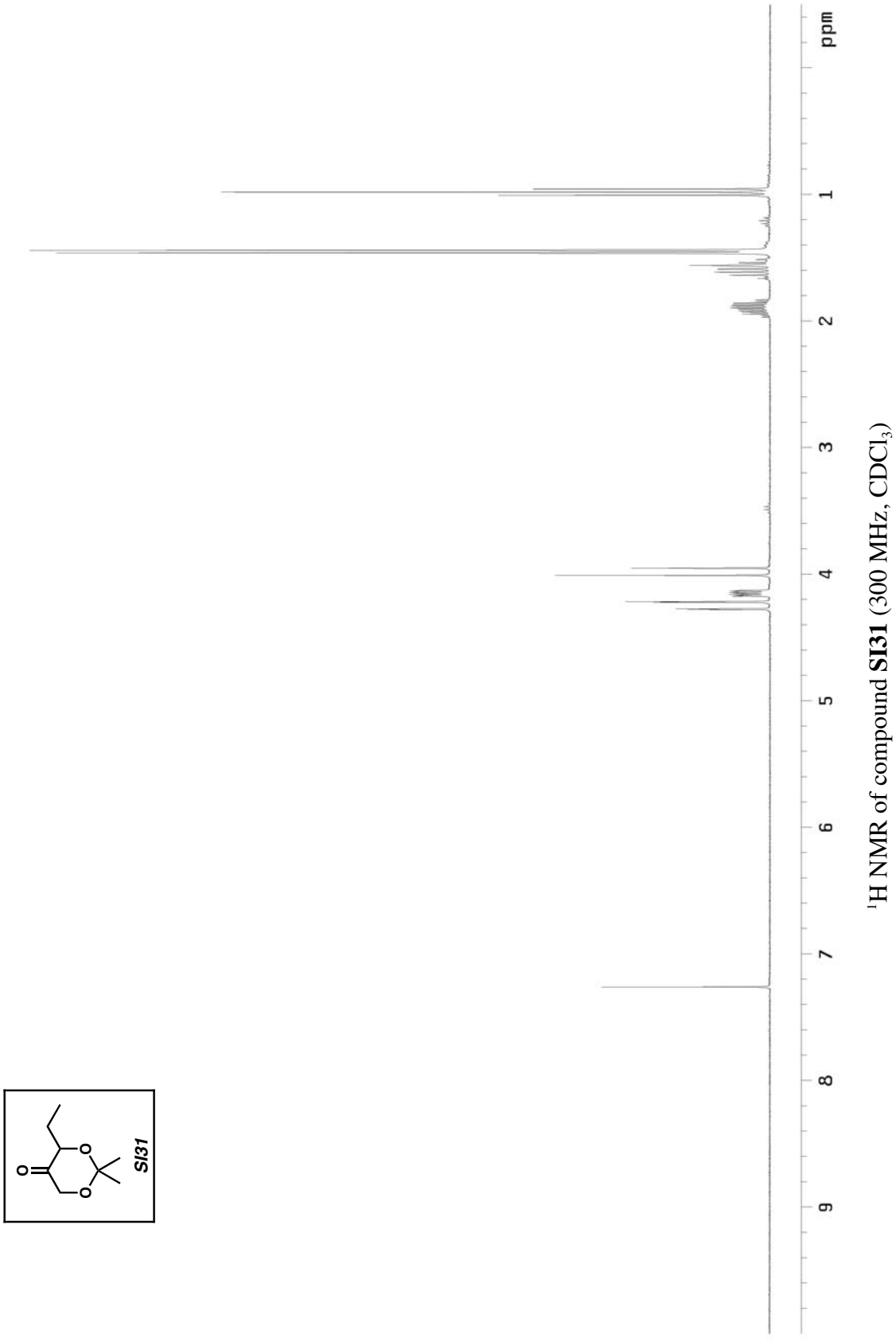
^{13}C NMR of compound **SI29** (75 MHz, $CDCl_3$)



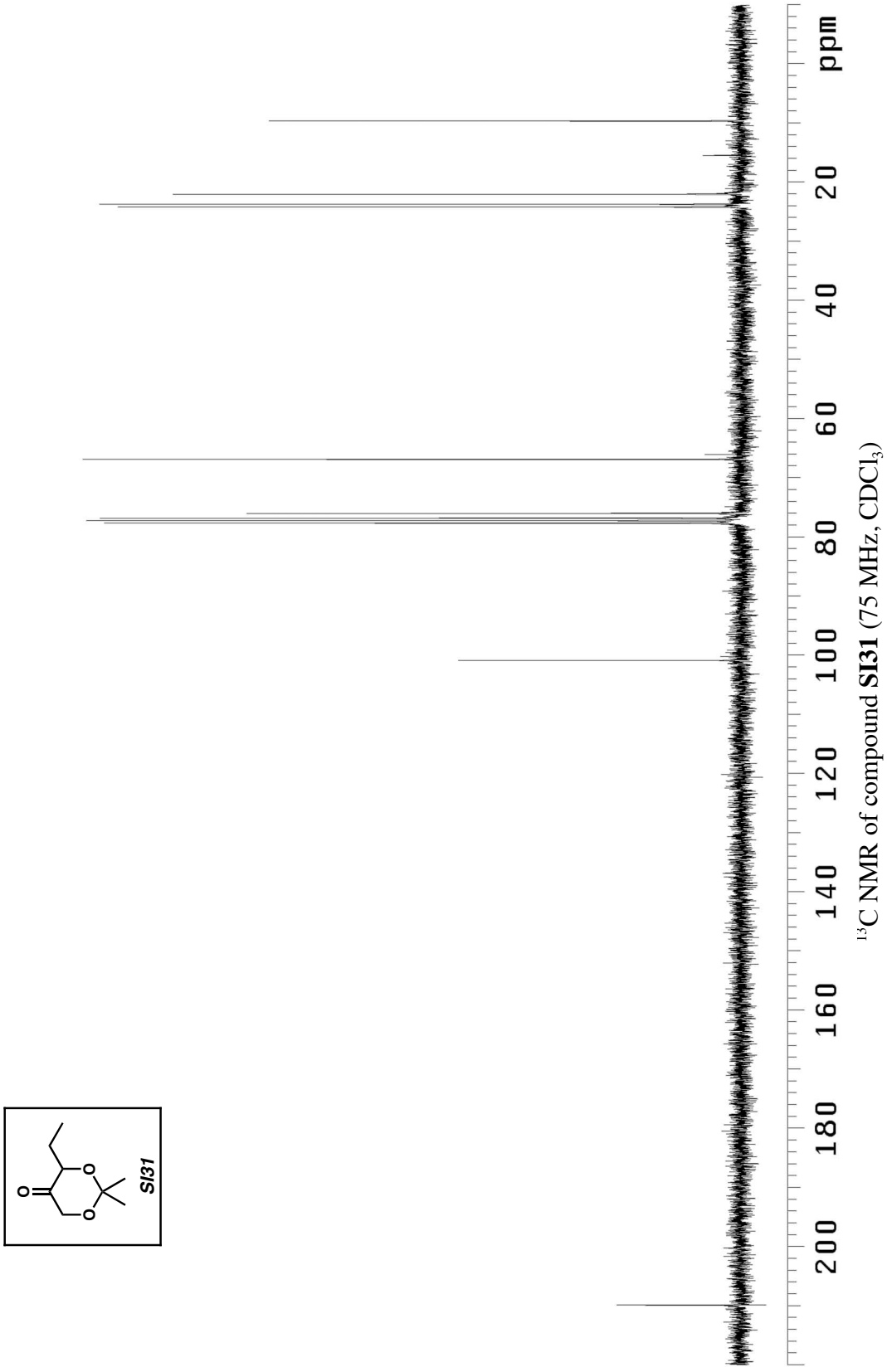
^{1}H NMR of compound **SI30** (300 MHz, $CDCl_3$)



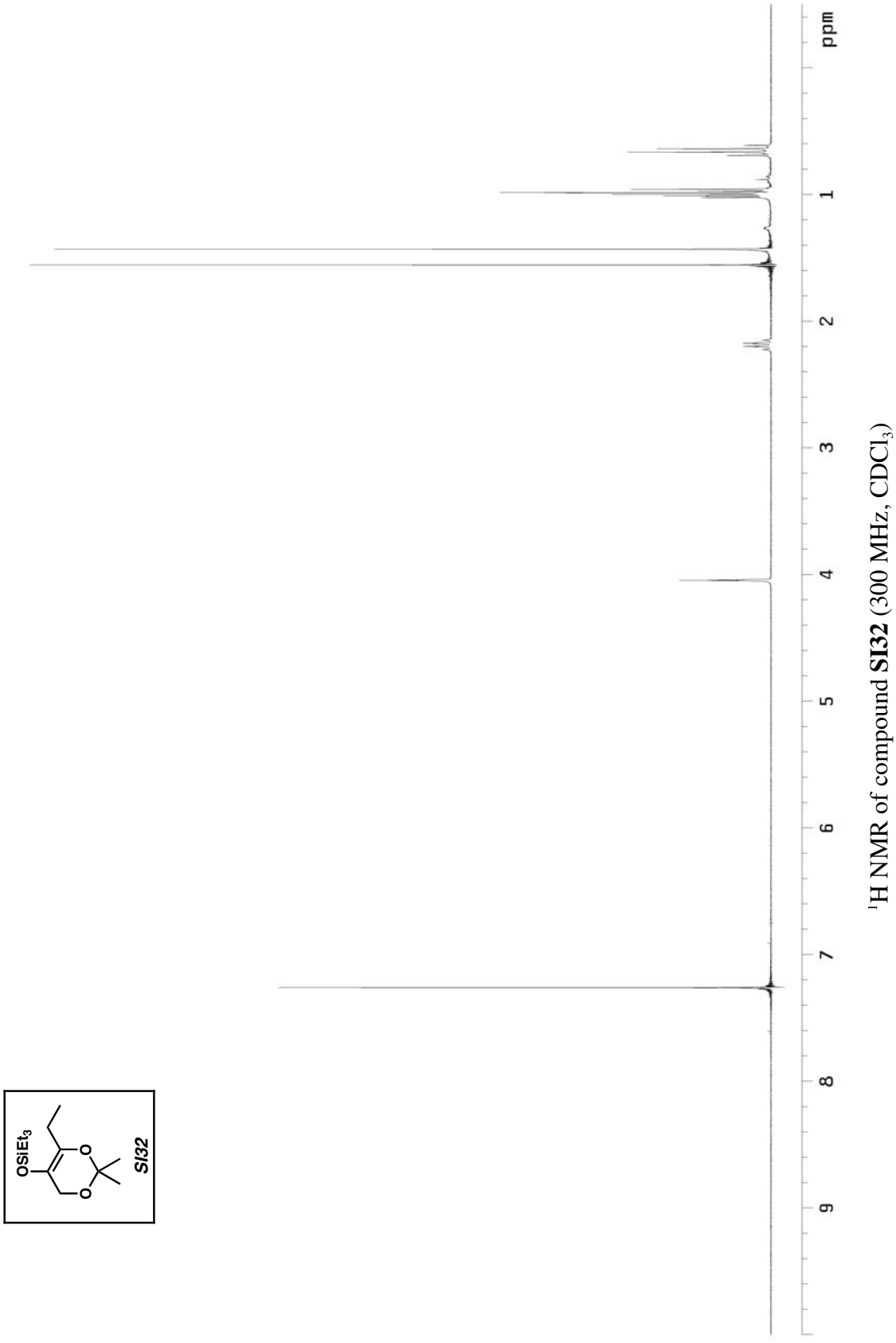
^{13}C NMR of compound **SI30** (75 MHz, $CDCl_3$)



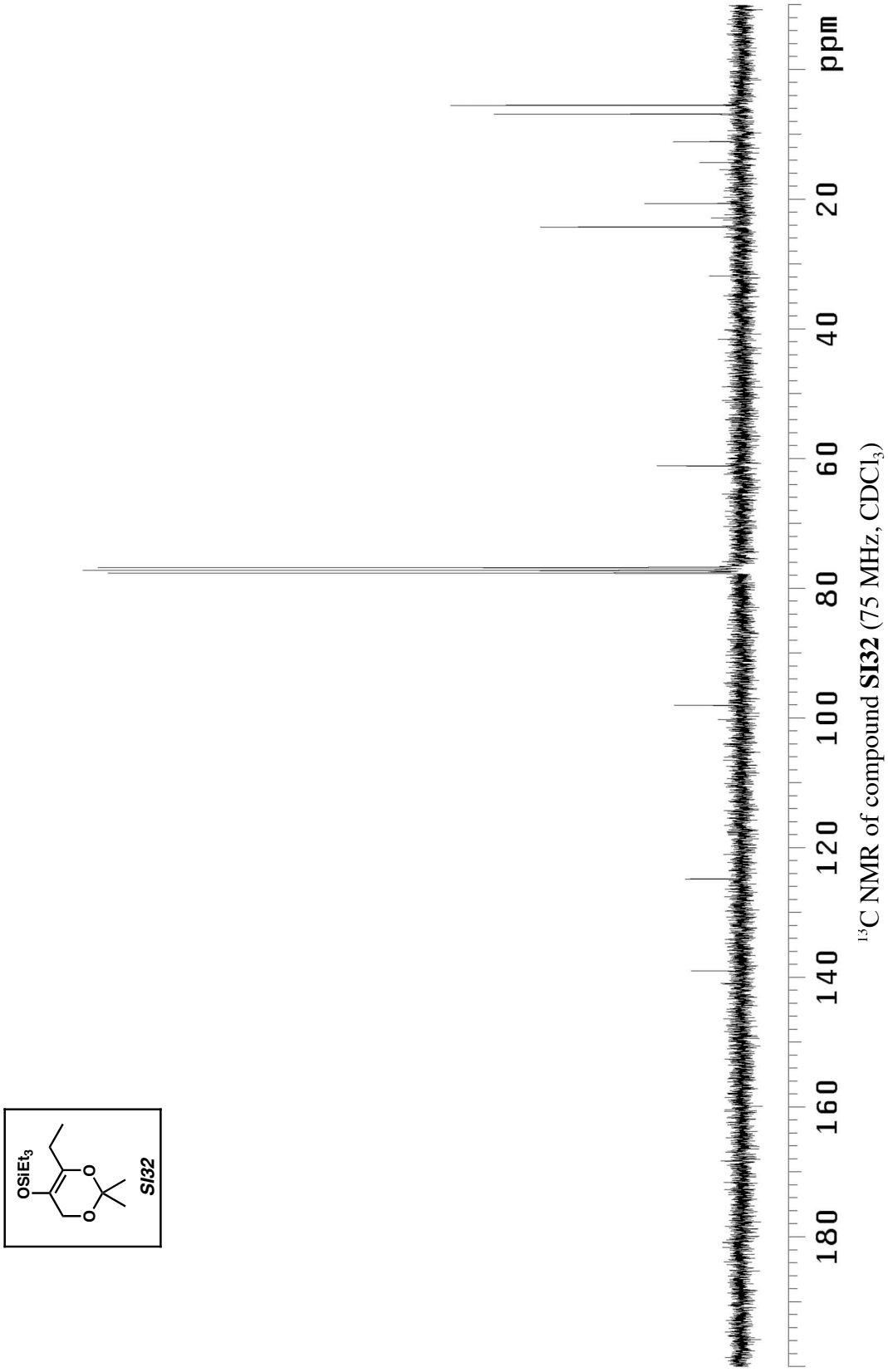
^{1}H NMR of compound **SI31** (300 MHz, $CDCl_3$)



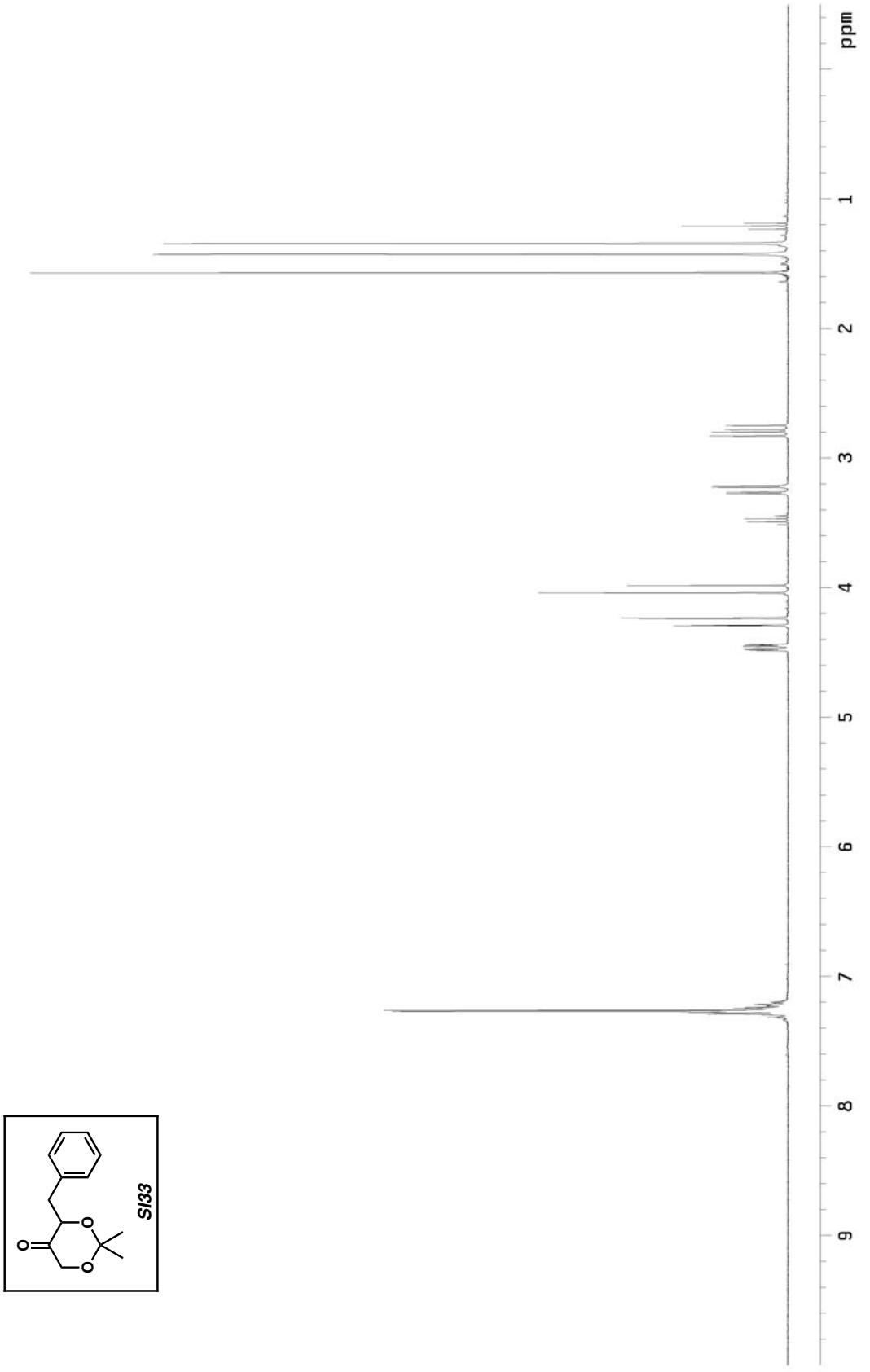
^{13}C NMR of compound **SI31** (75 MHz, $CDCl_3$)



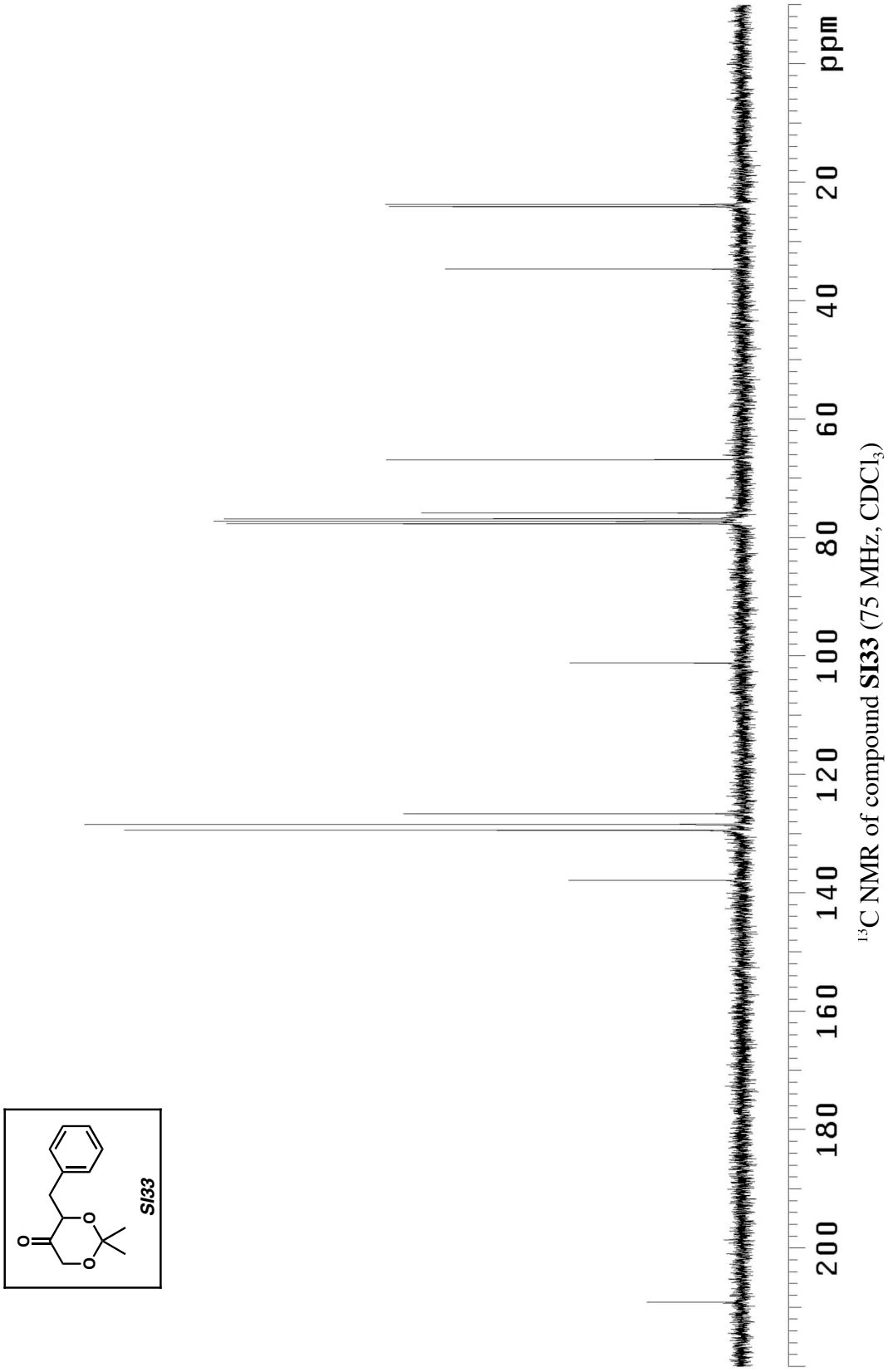
^{1}H NMR of compound **SI32** (300 MHz, $CDCl_3$)



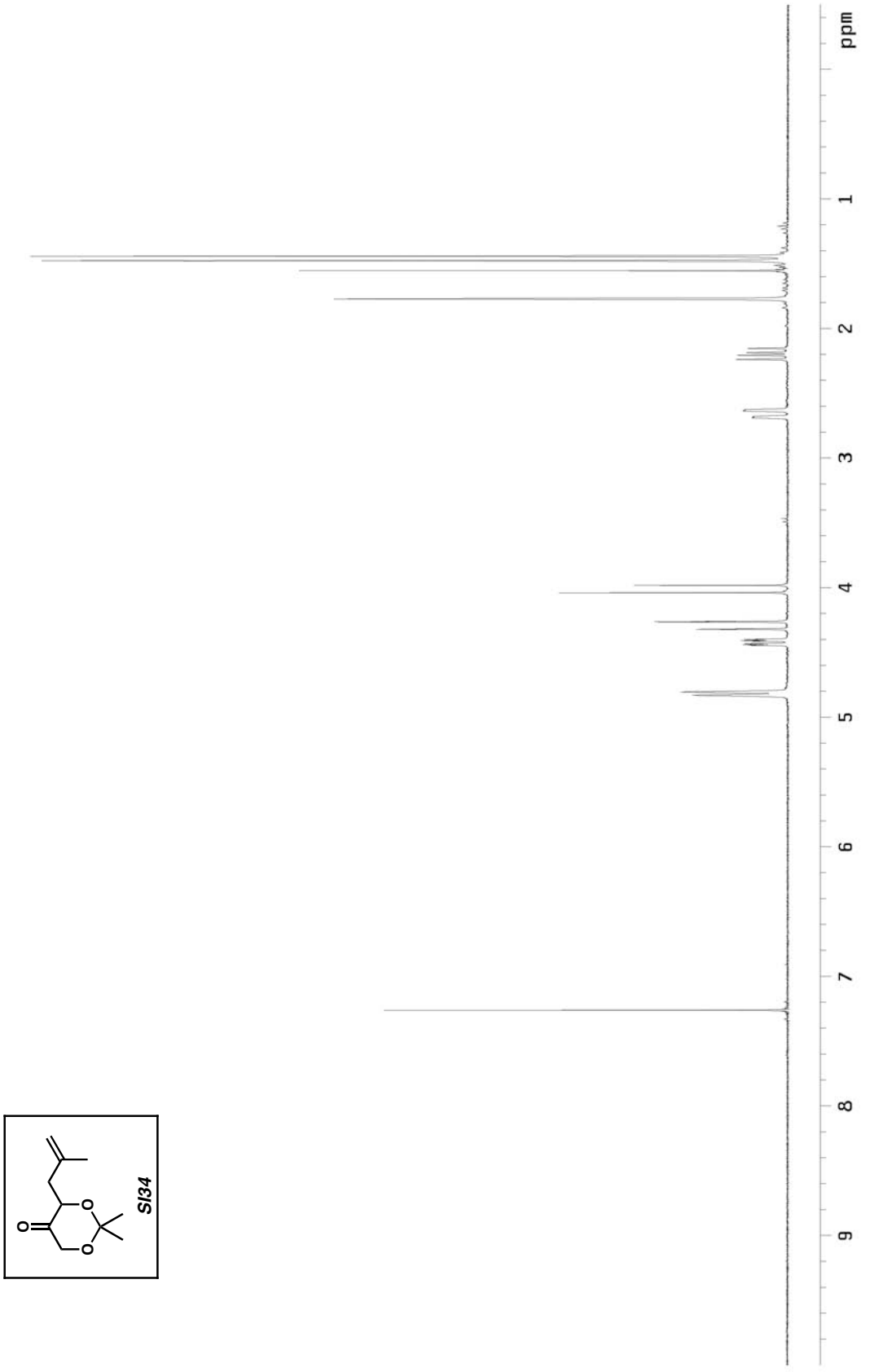
^{13}C NMR of compound **SI32** (75 MHz, $CDCl_3$)



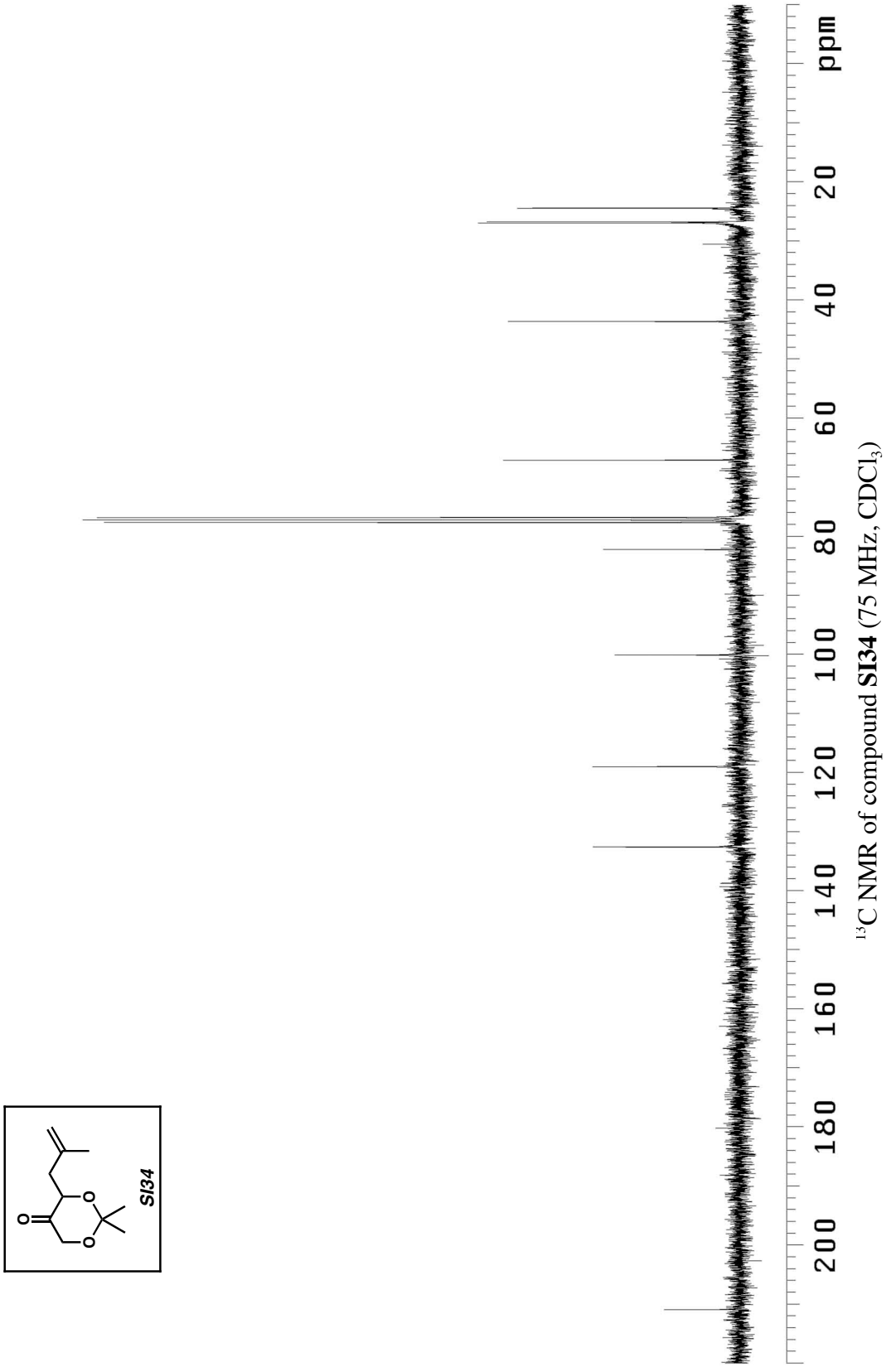
^{1}H NMR of compound **SI33** (300 MHz, $CDCl_3$)



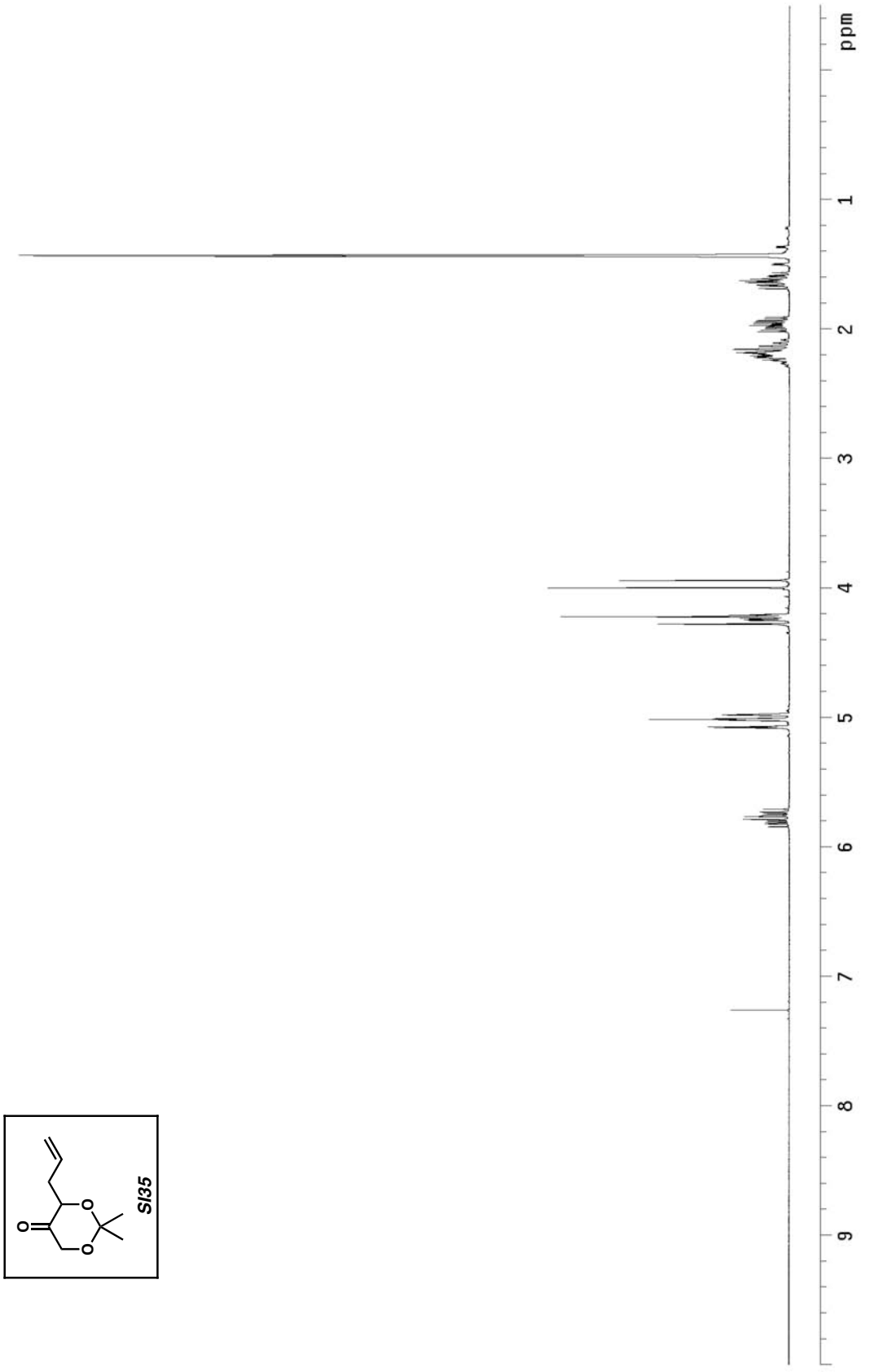
^{13}C NMR of compound **SI33** (75 MHz, $CDCl_3$)



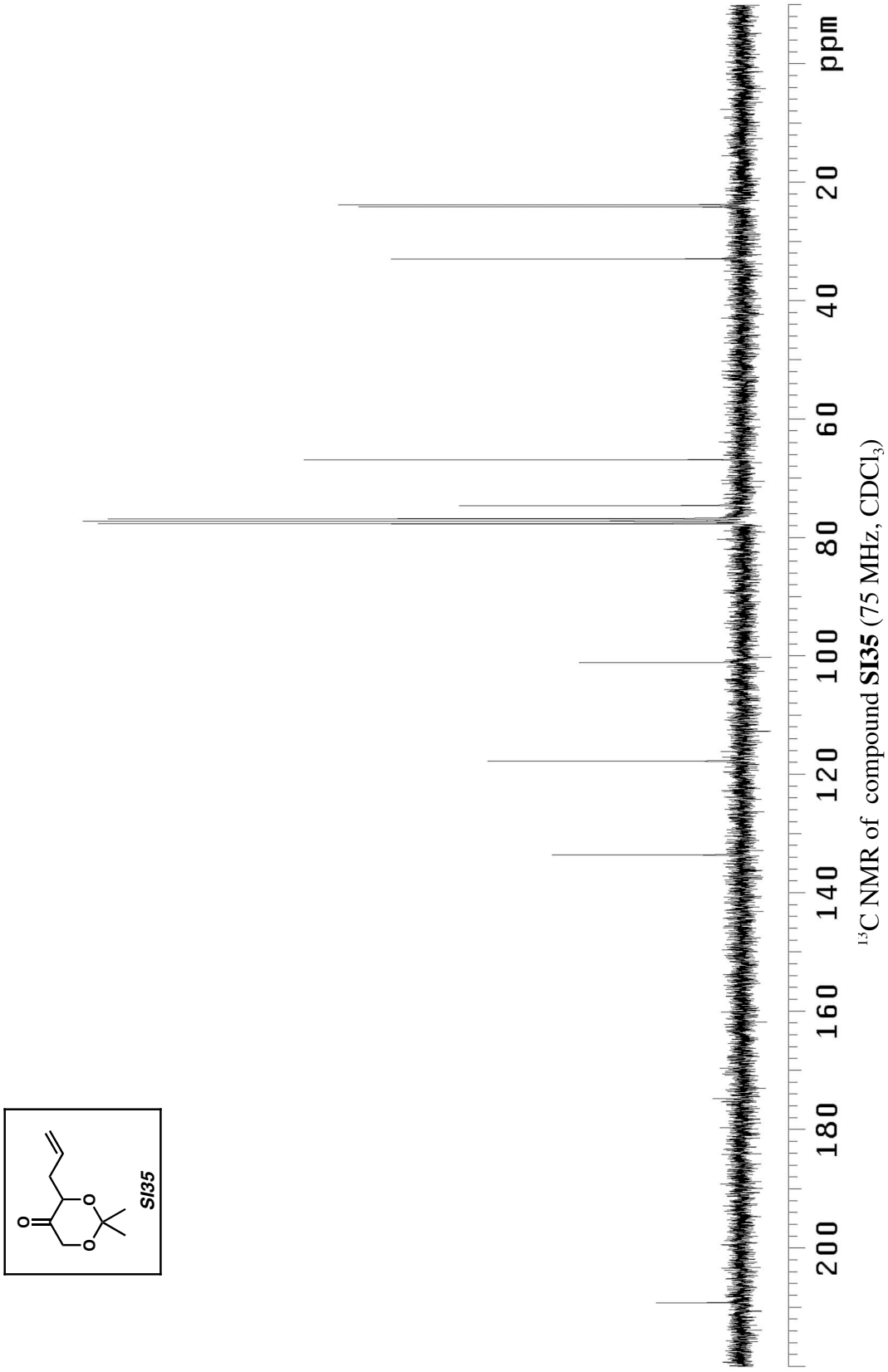
^{1}H NMR of compound **SI34** (300 MHz, $CDCl_3$)



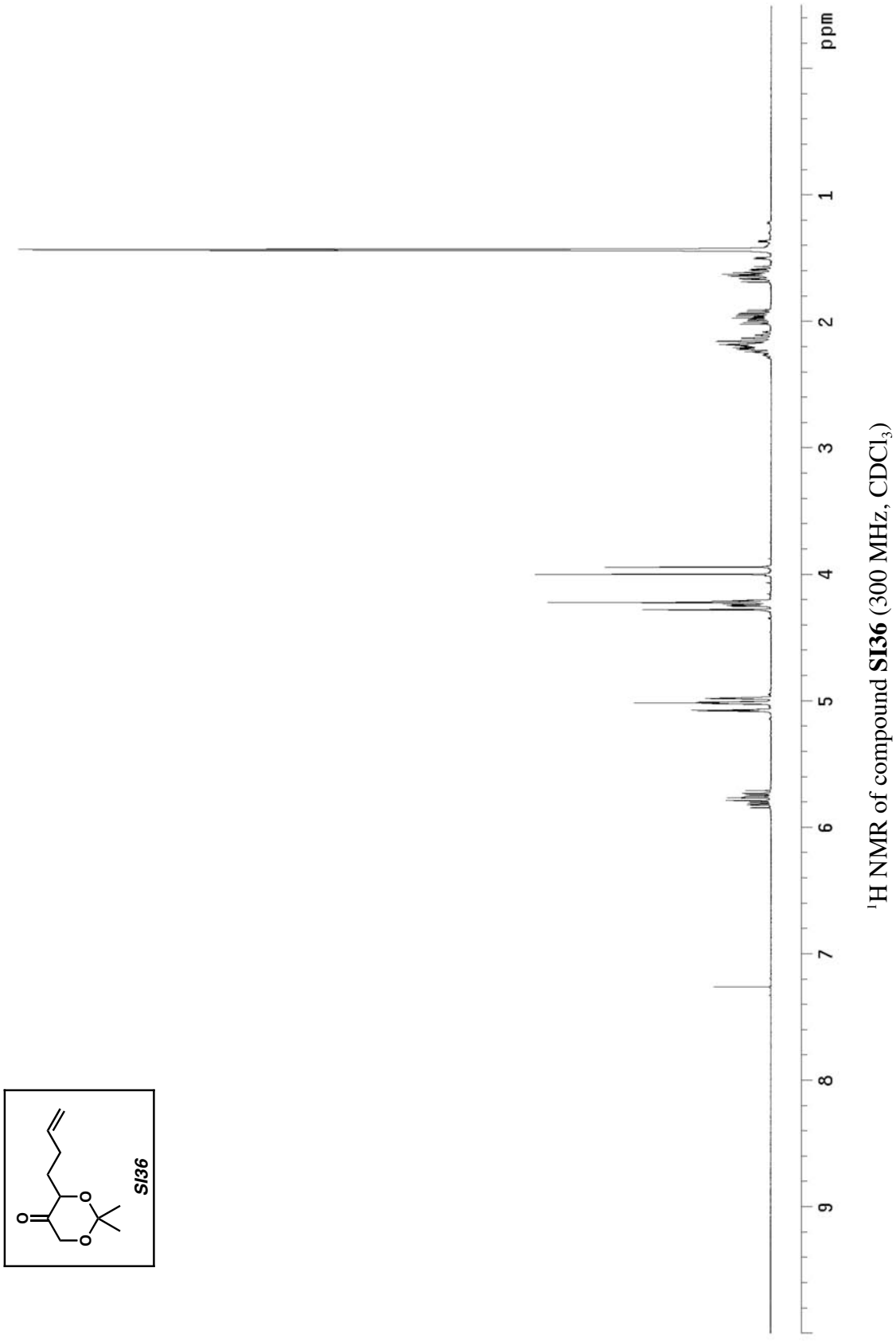
^{13}C NMR of compound **SI34** (75 MHz, $CDCl_3$)



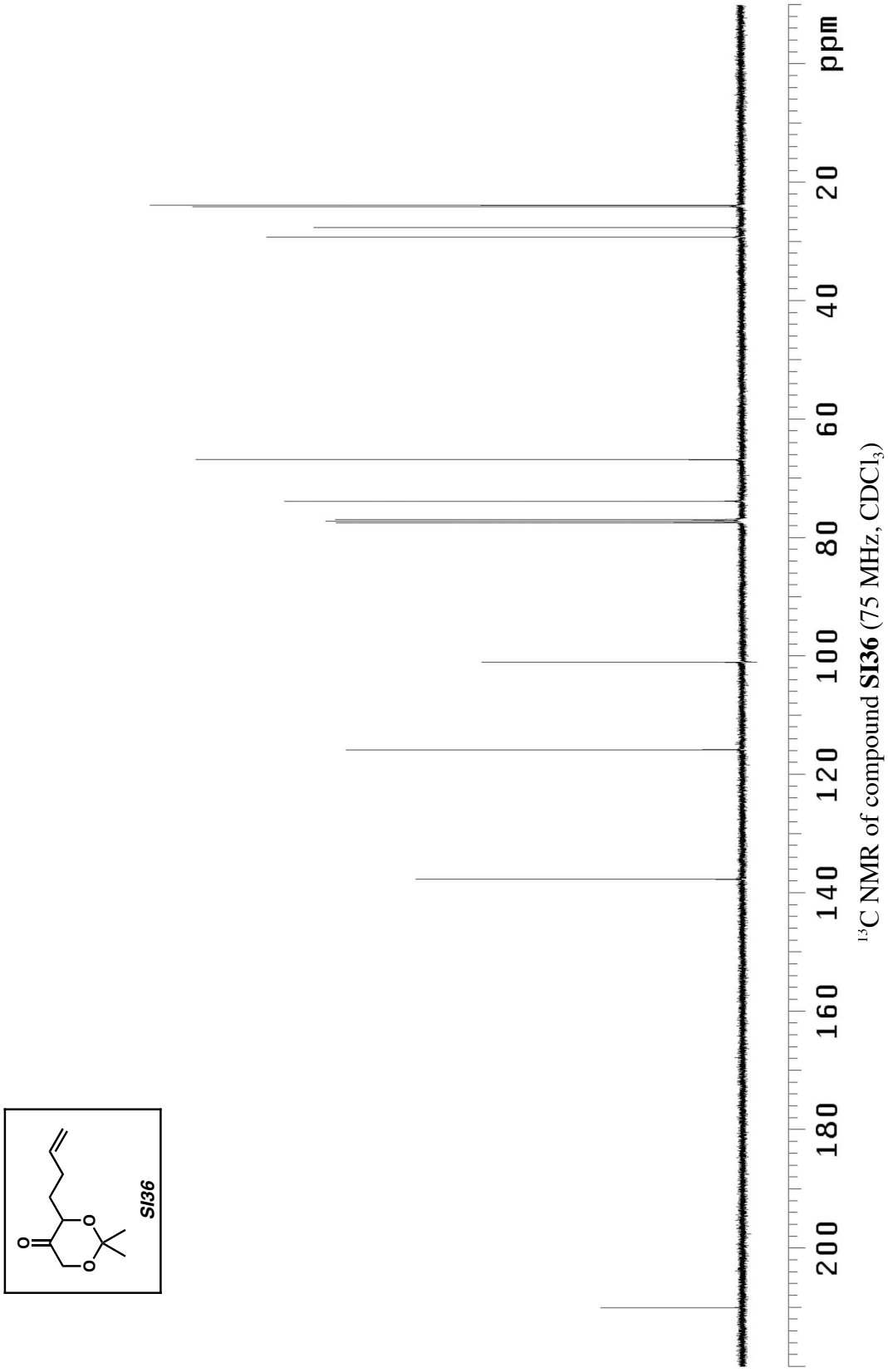
^{1}H NMR of compound **SI35** (300 MHz, $CDCl_3$)



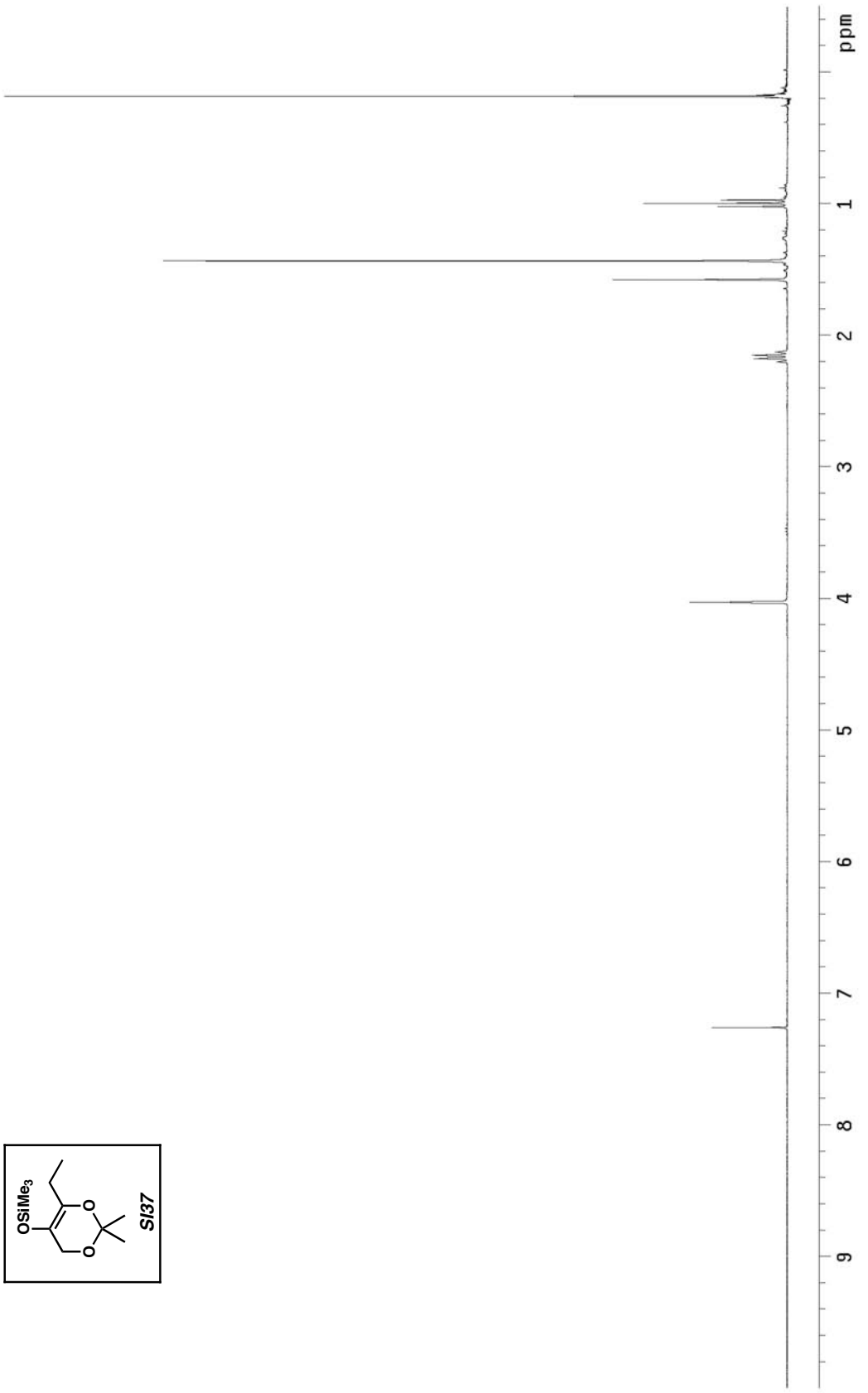
^{13}C NMR of compound **SI35** (75 MHz, $CDCl_3$)



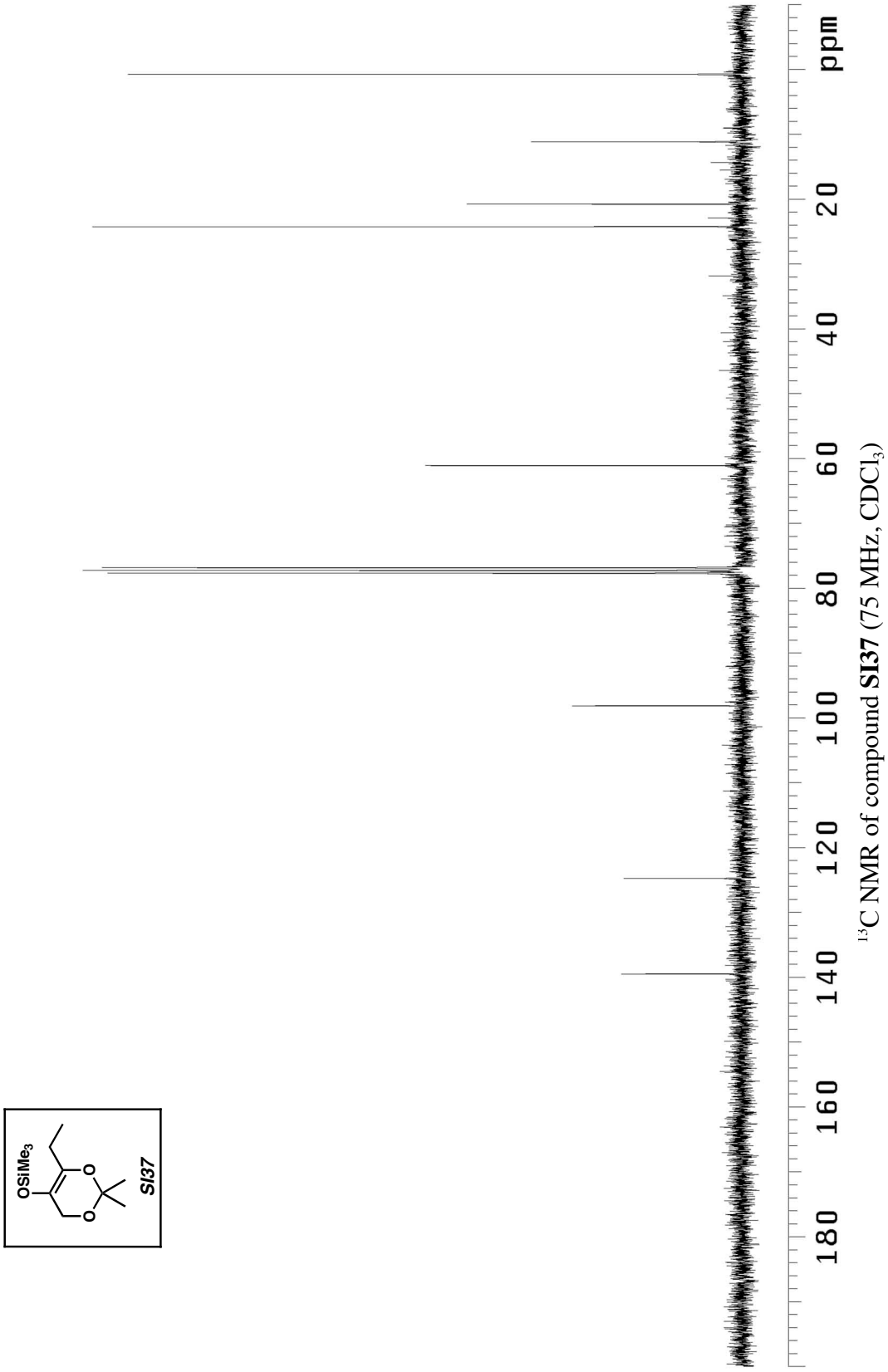
^{1}H NMR of compound **SI36** (300 MHz, $CDCl_3$)



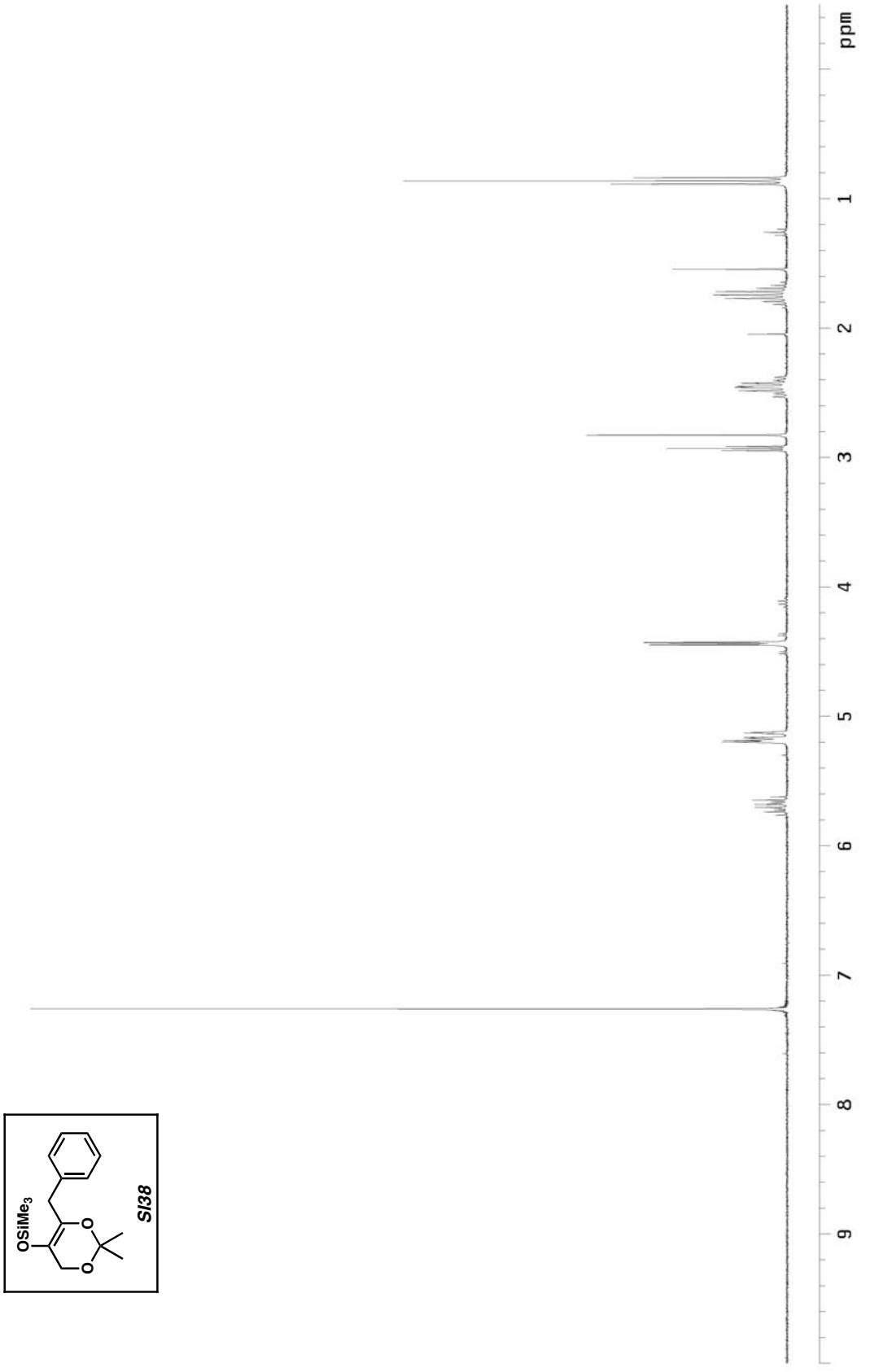
^{13}C NMR of compound **SI36** (75 MHz, $CDCl_3$)



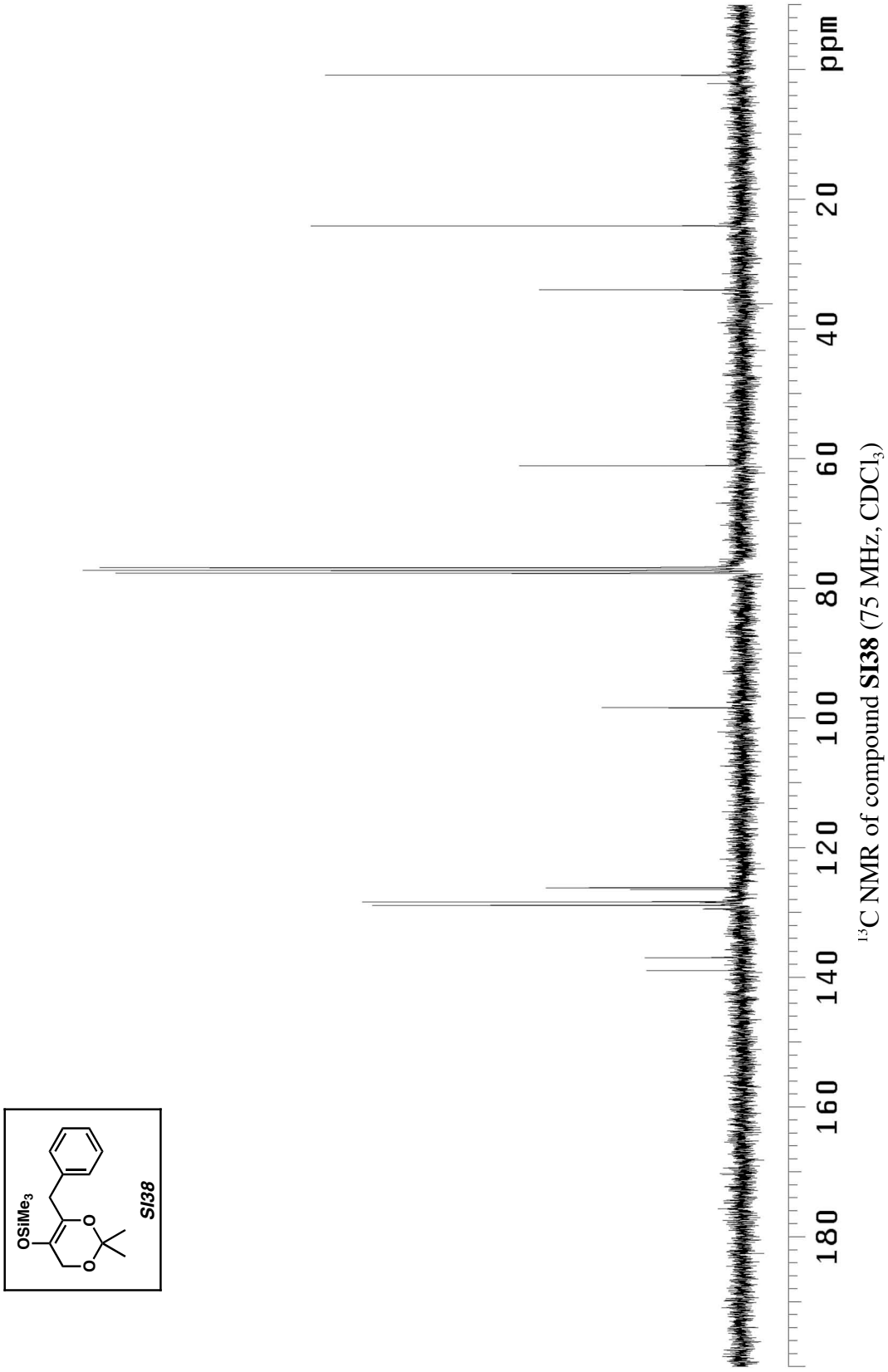
^{1}H NMR of compound **SI37** (300 MHz, $CDCl_3$)



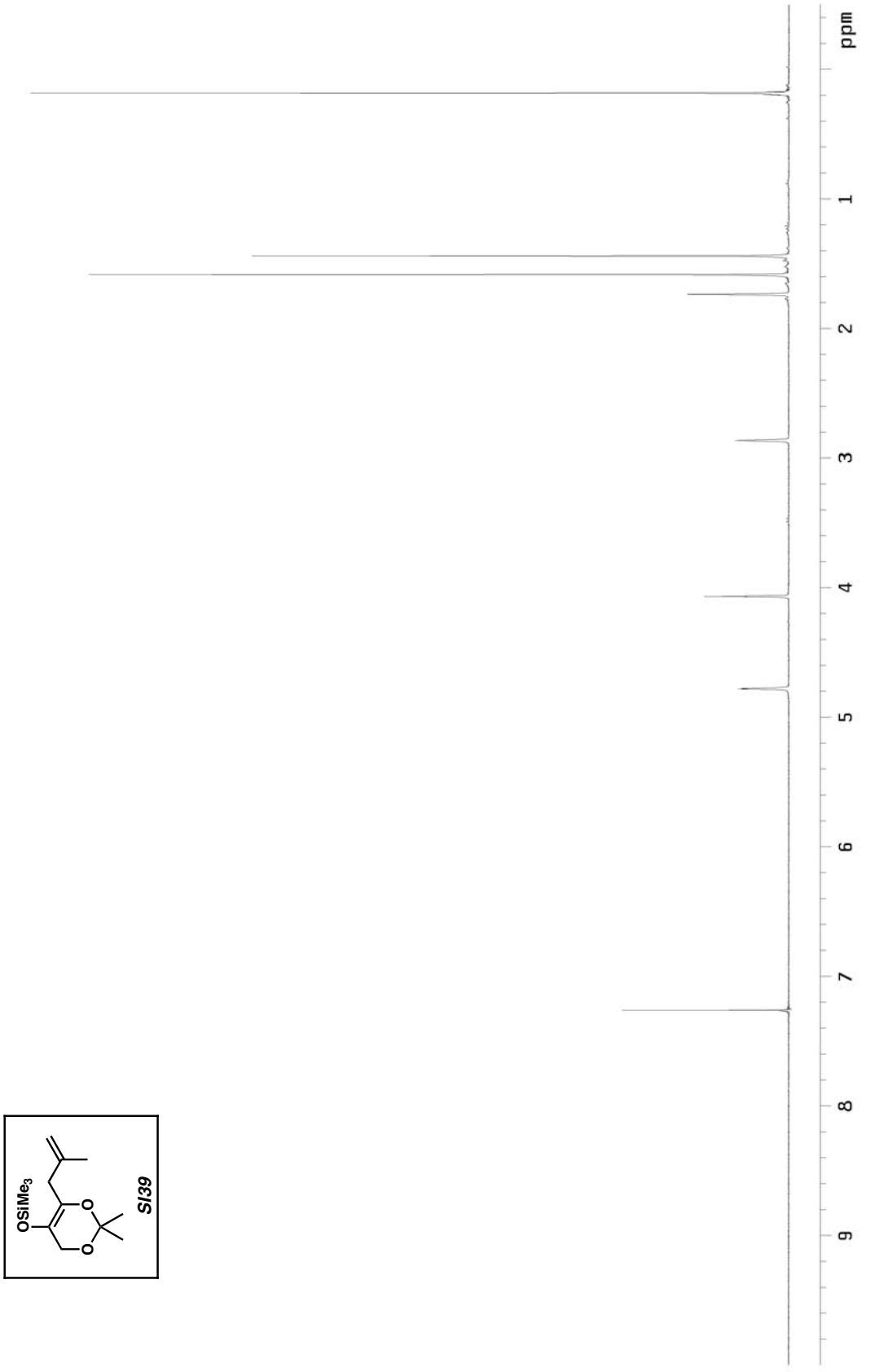
^{13}C NMR of compound **SI37** (75 MHz, $CDCl_3$)



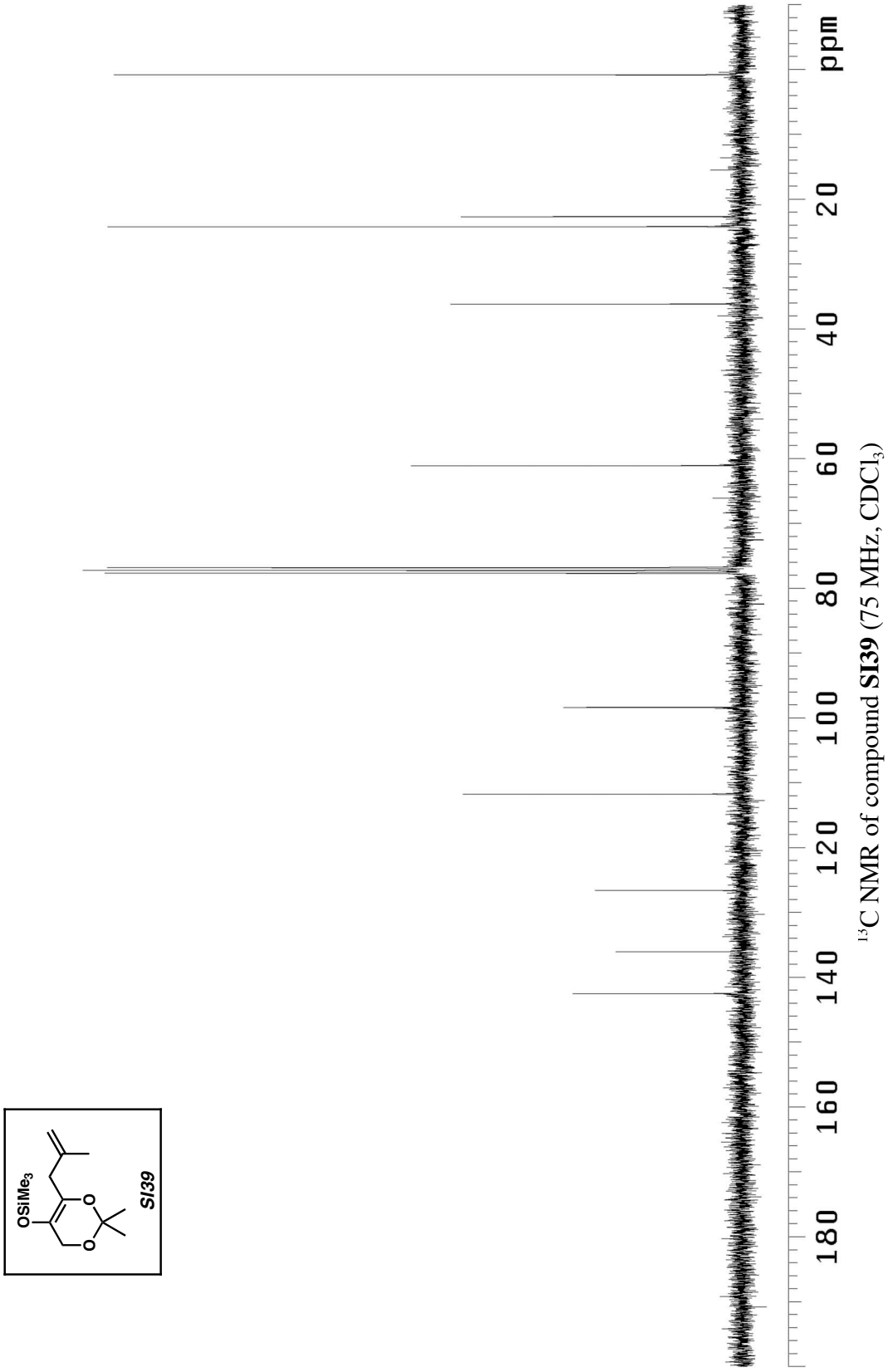
^{1}H NMR of compound **SI38** (300 MHz, $CDCl_3$)



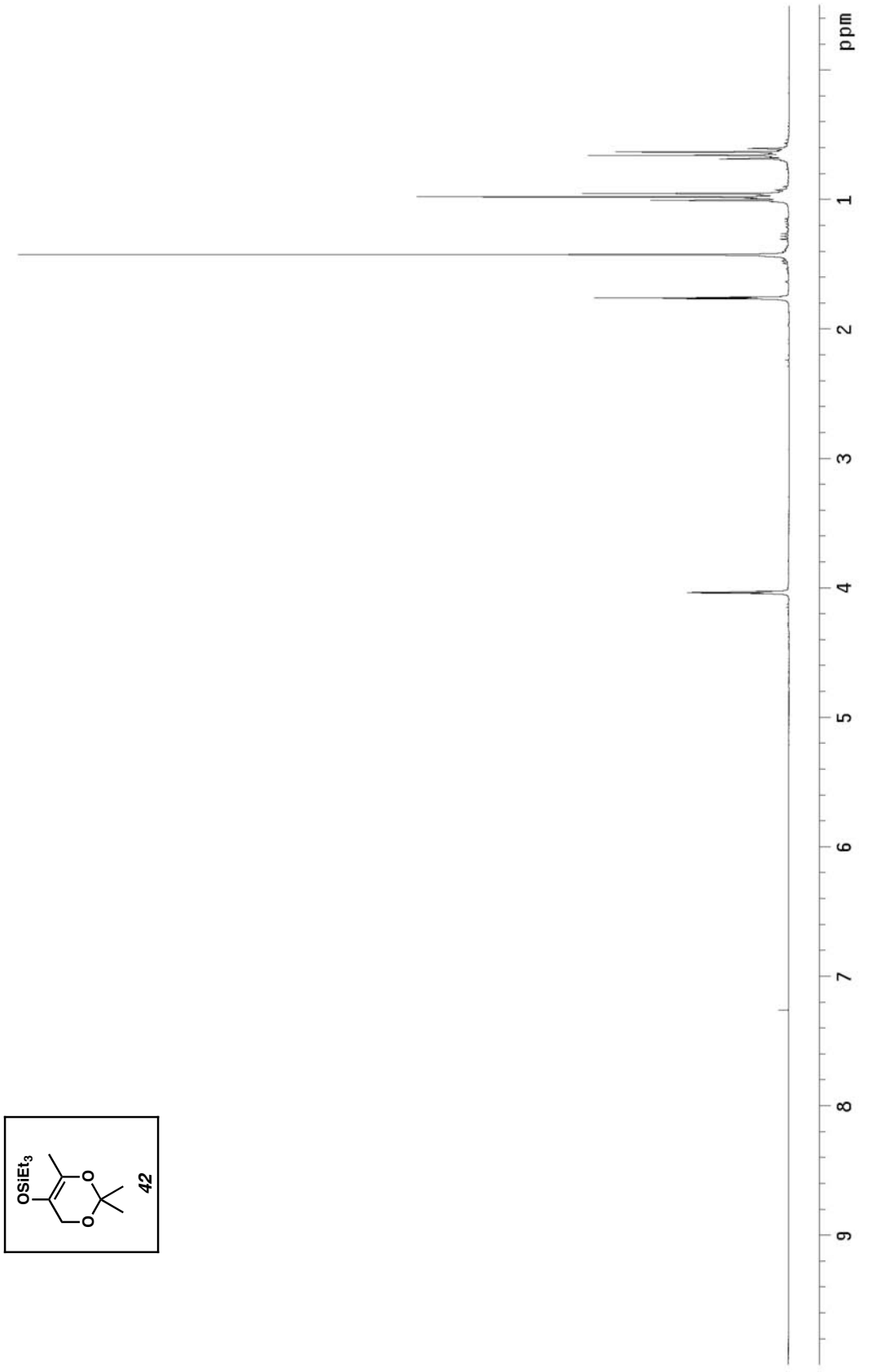
^{13}C NMR of compound **SI38** (75 MHz, $CDCl_3$)



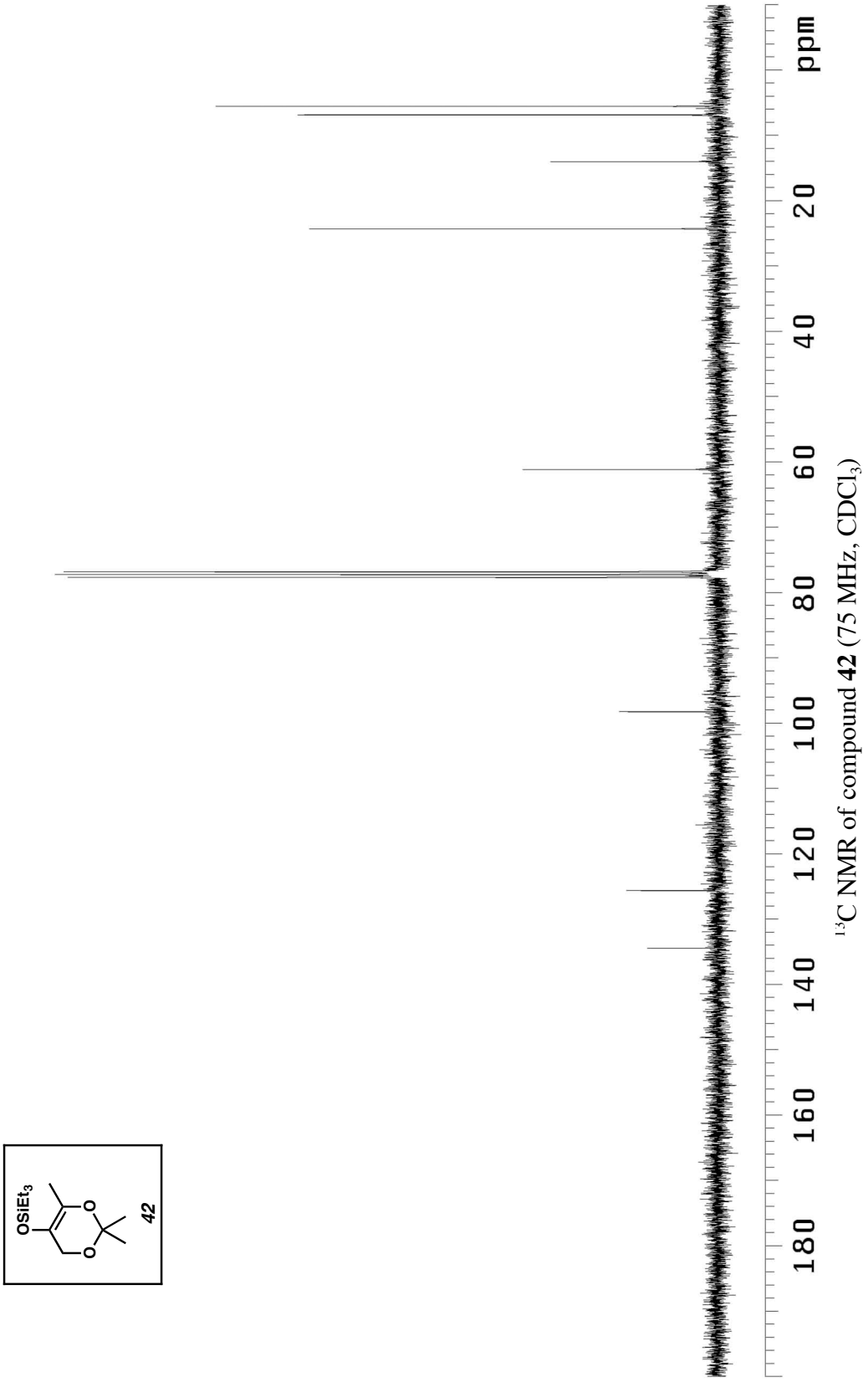
^{1}H NMR of compound **SI39** (300 MHz, $CDCl_3$)



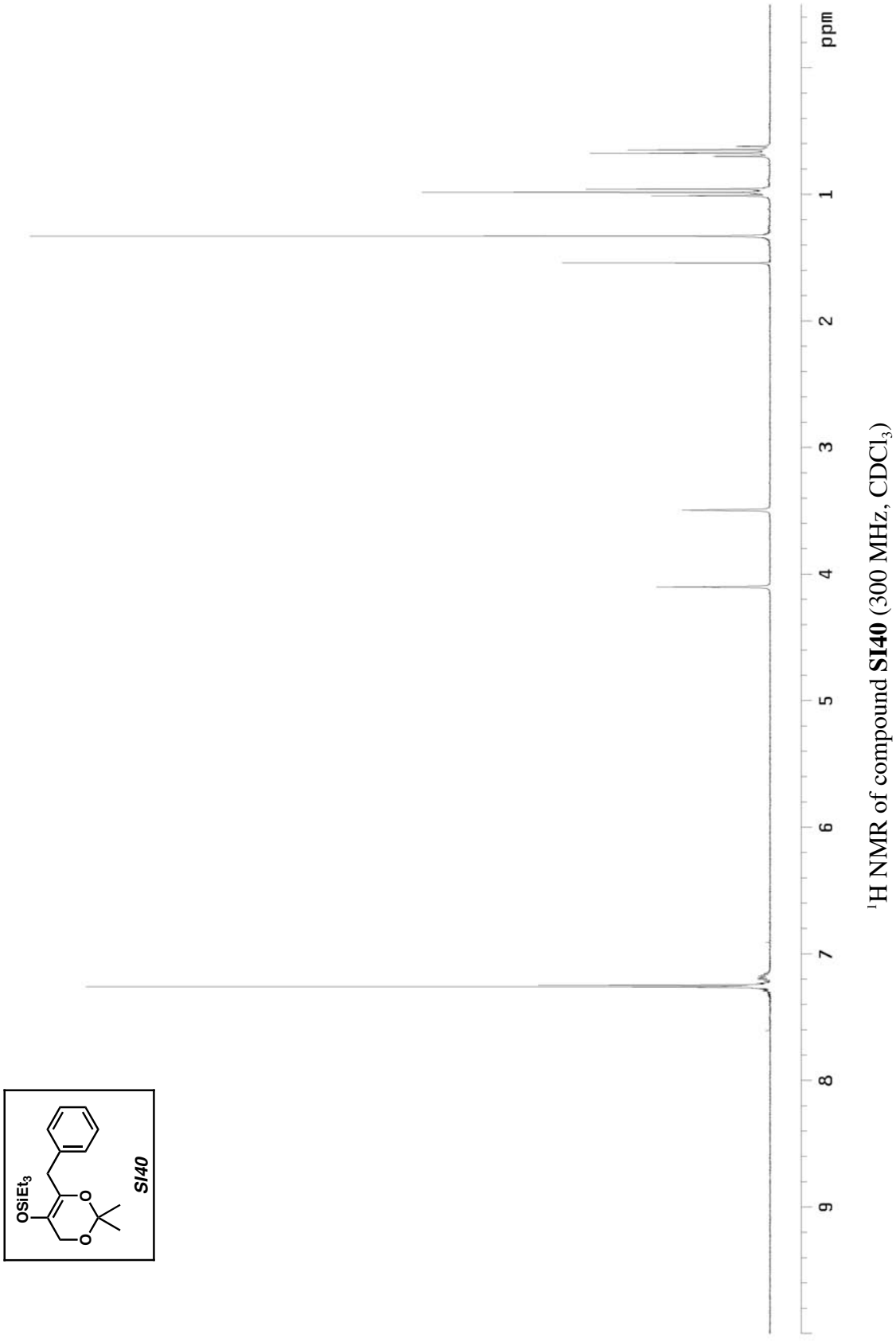
^{13}C NMR of compound **SI39** (75 MHz, $CDCl_3$)



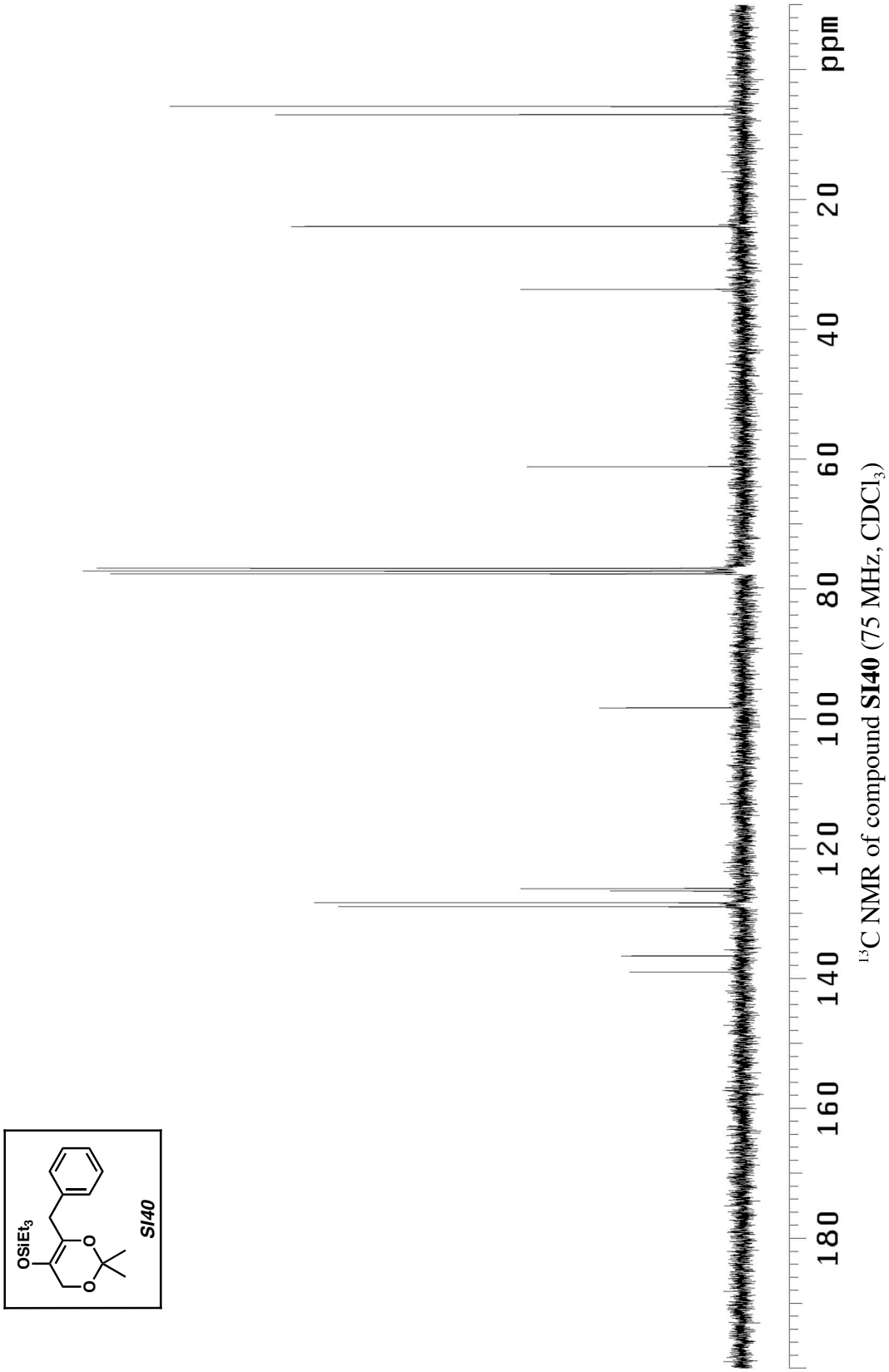
^{1}H NMR of compound **42** (300 MHz, $CDCl_3$)



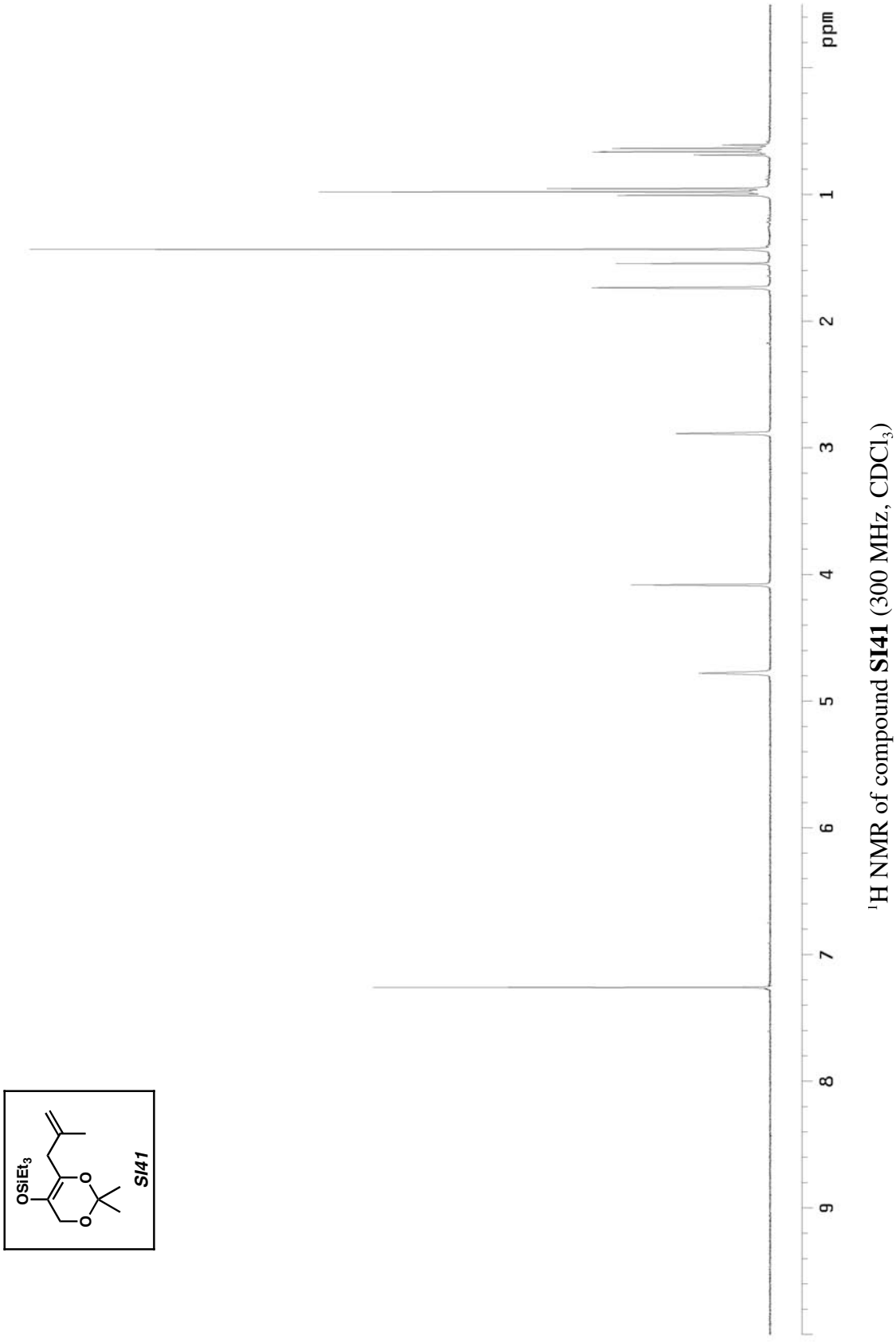
^{13}C NMR of compound **42** (75 MHz, $CDCl_3$)



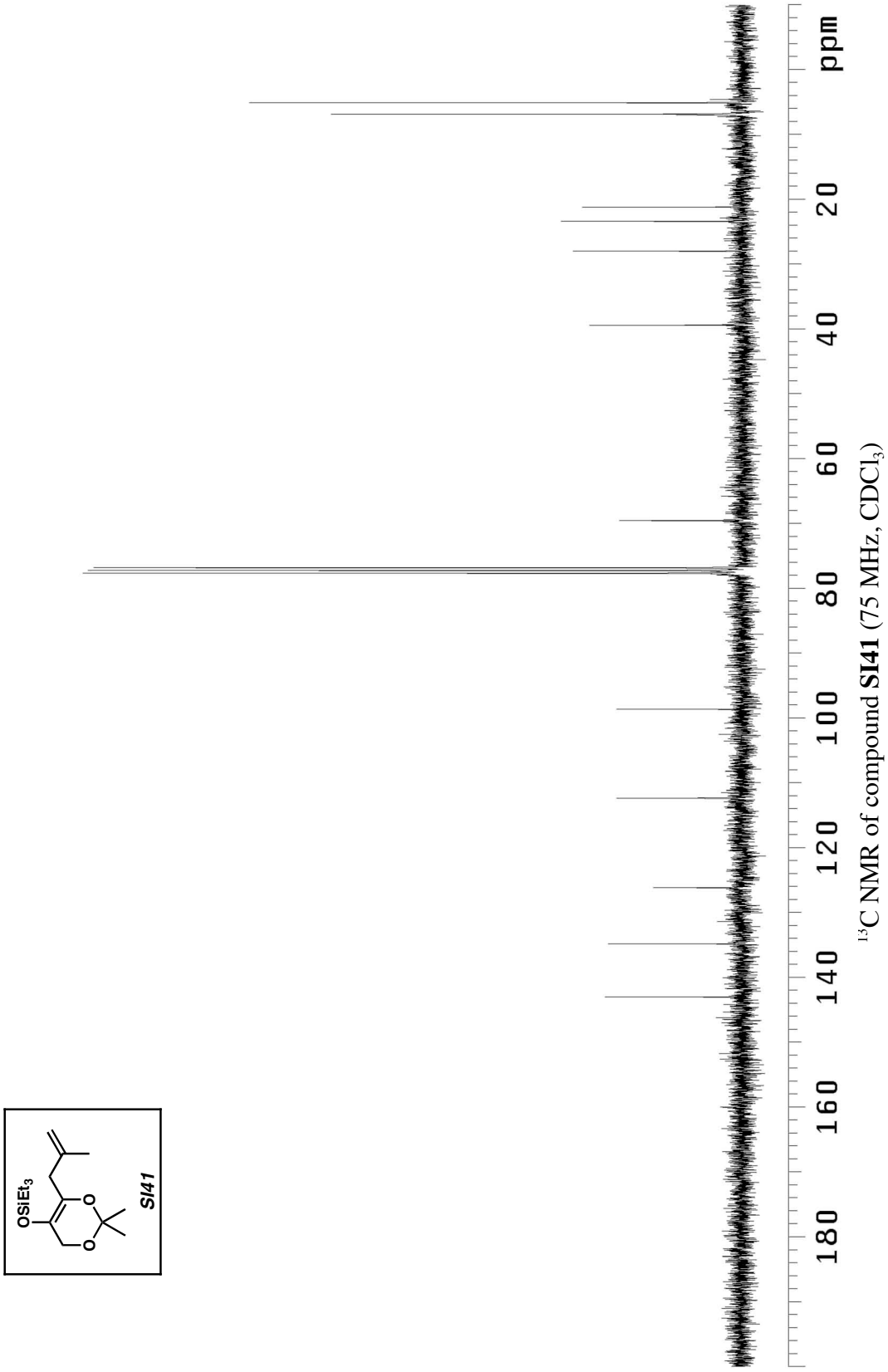
^{1}H NMR of compound **SI40** (300 MHz, $CDCl_3$)



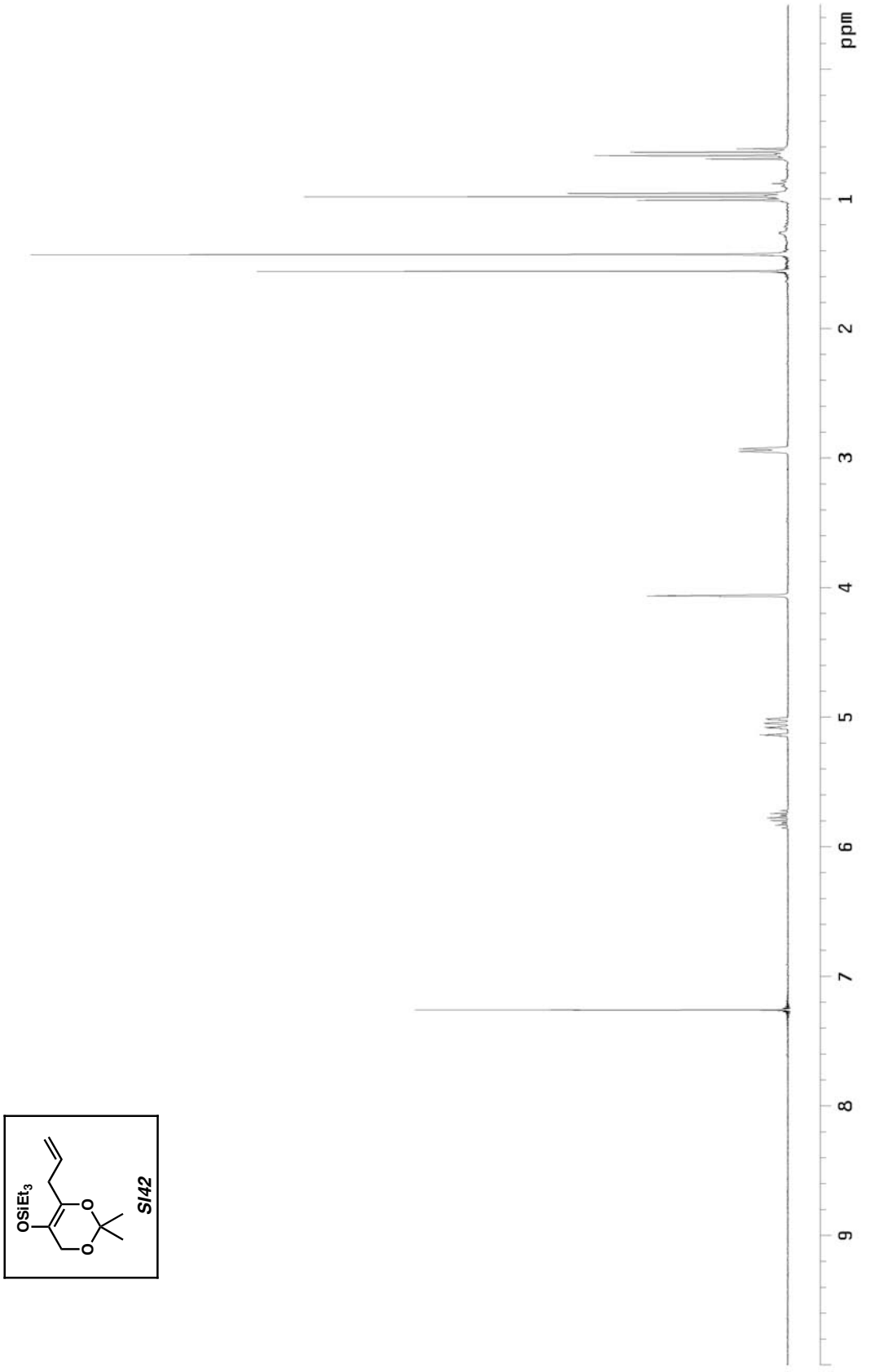
^{13}C NMR of compound **SI40** (75 MHz, $CDCl_3$)



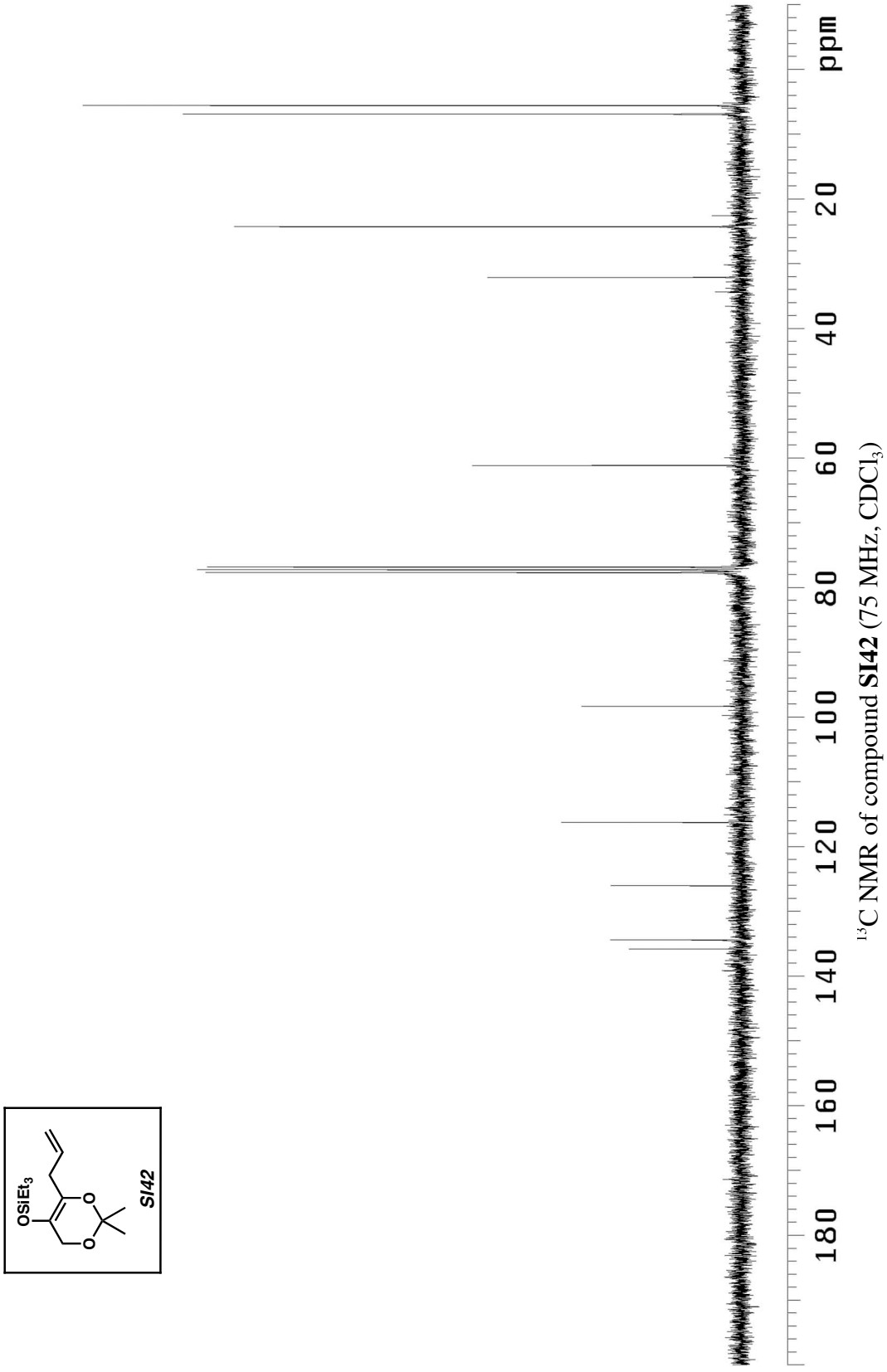
^{1}H NMR of compound **SI41** (300 MHz, $CDCl_3$)



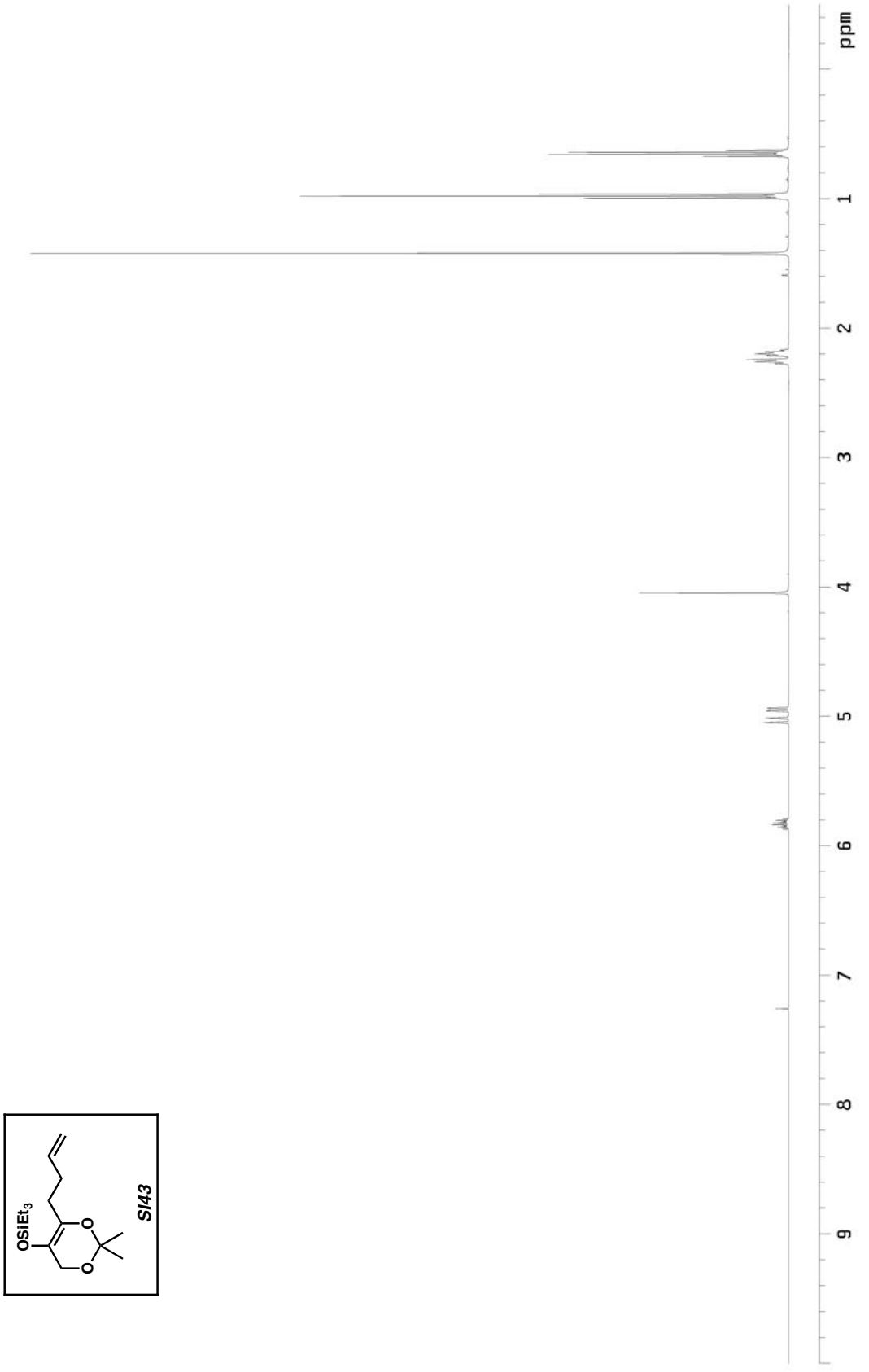
^{13}C NMR of compound **SI41** (75 MHz, $CDCl_3$)



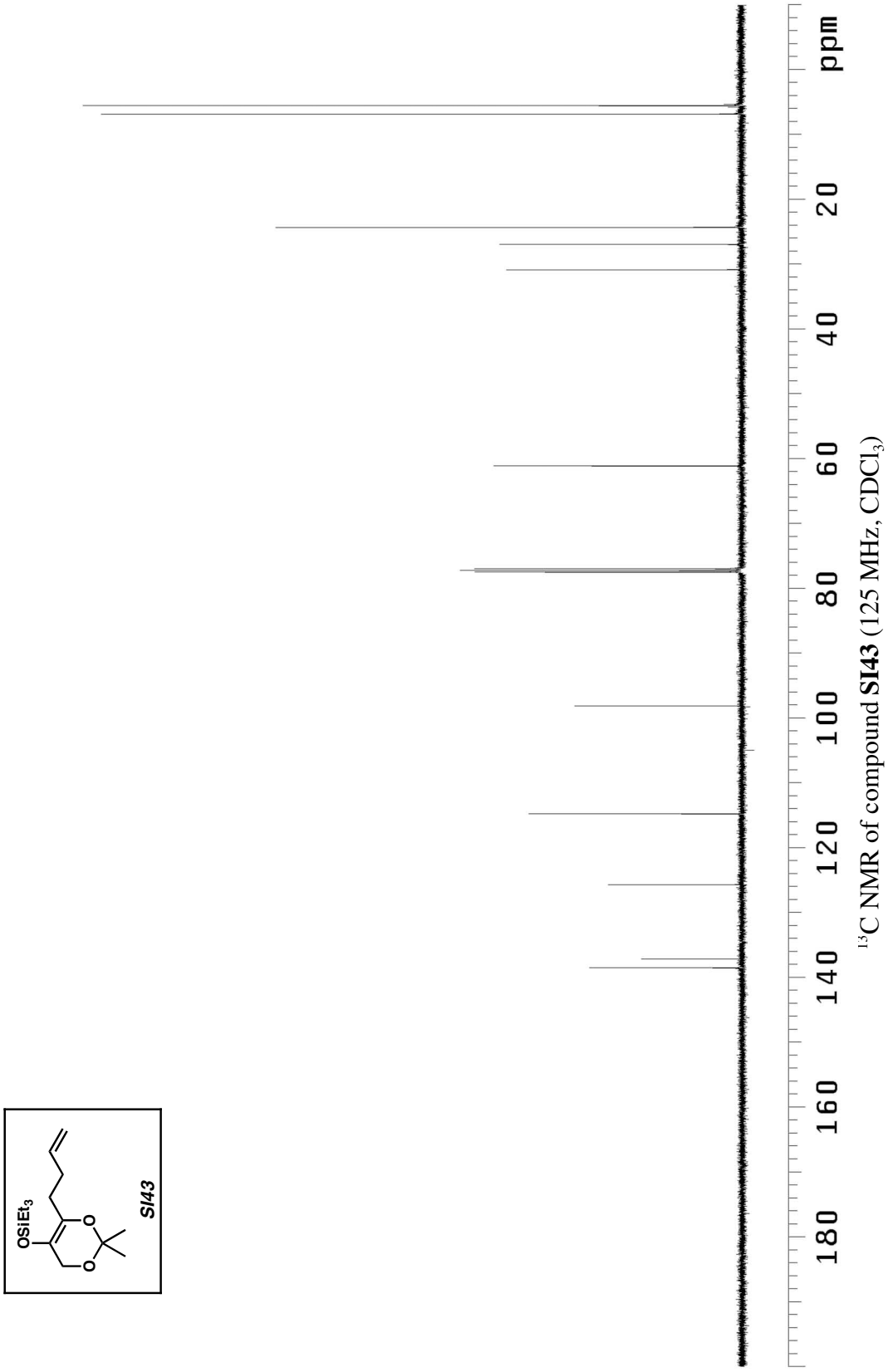
^{1}H NMR of compound **SI42** (300 MHz, $CDCl_3$)



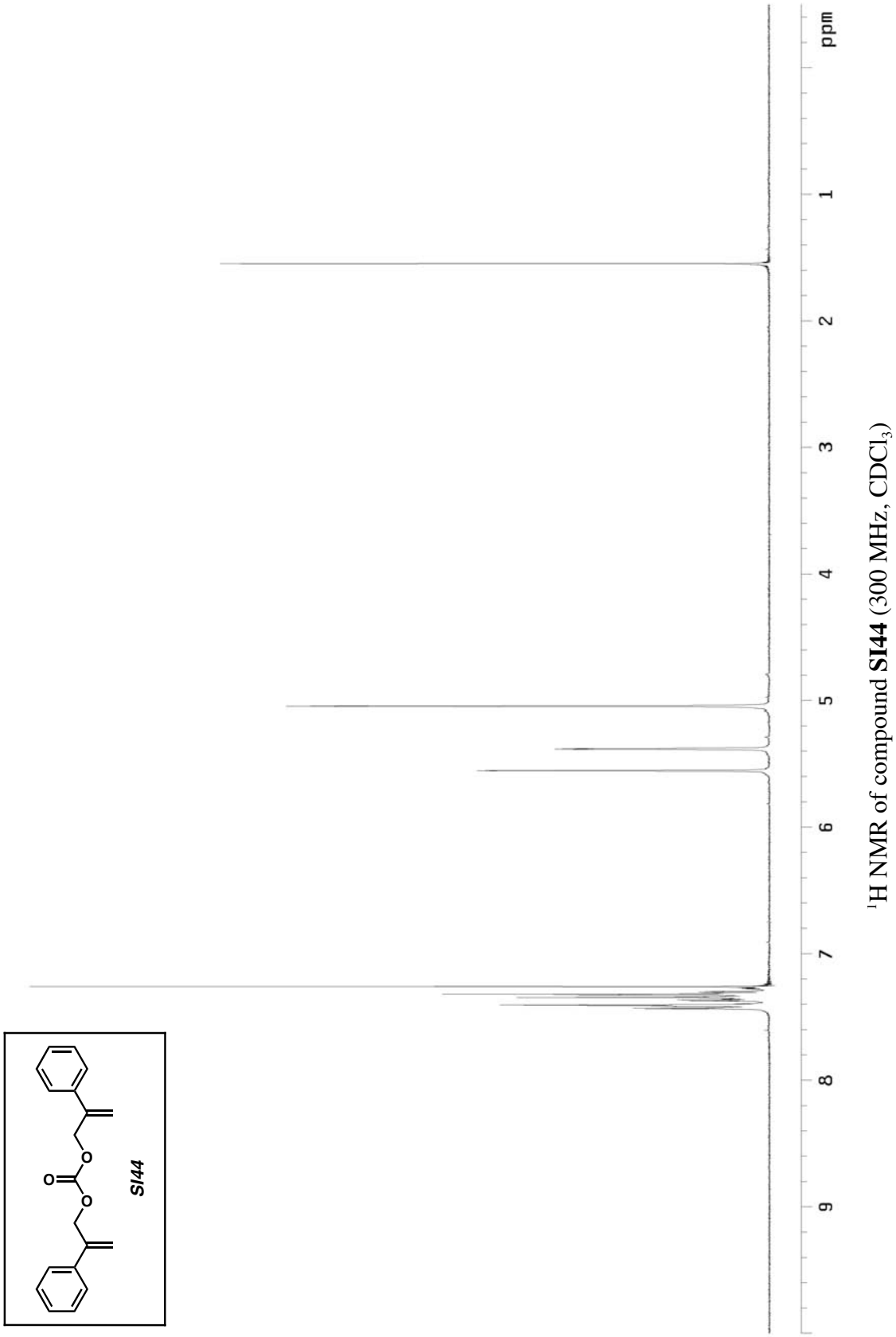
^{13}C NMR of compound **SI42** (75 MHz, $CDCl_3$)



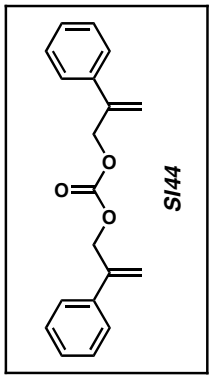
^{1}H NMR of compound **SI43** (500 MHz, $CDCl_3$)



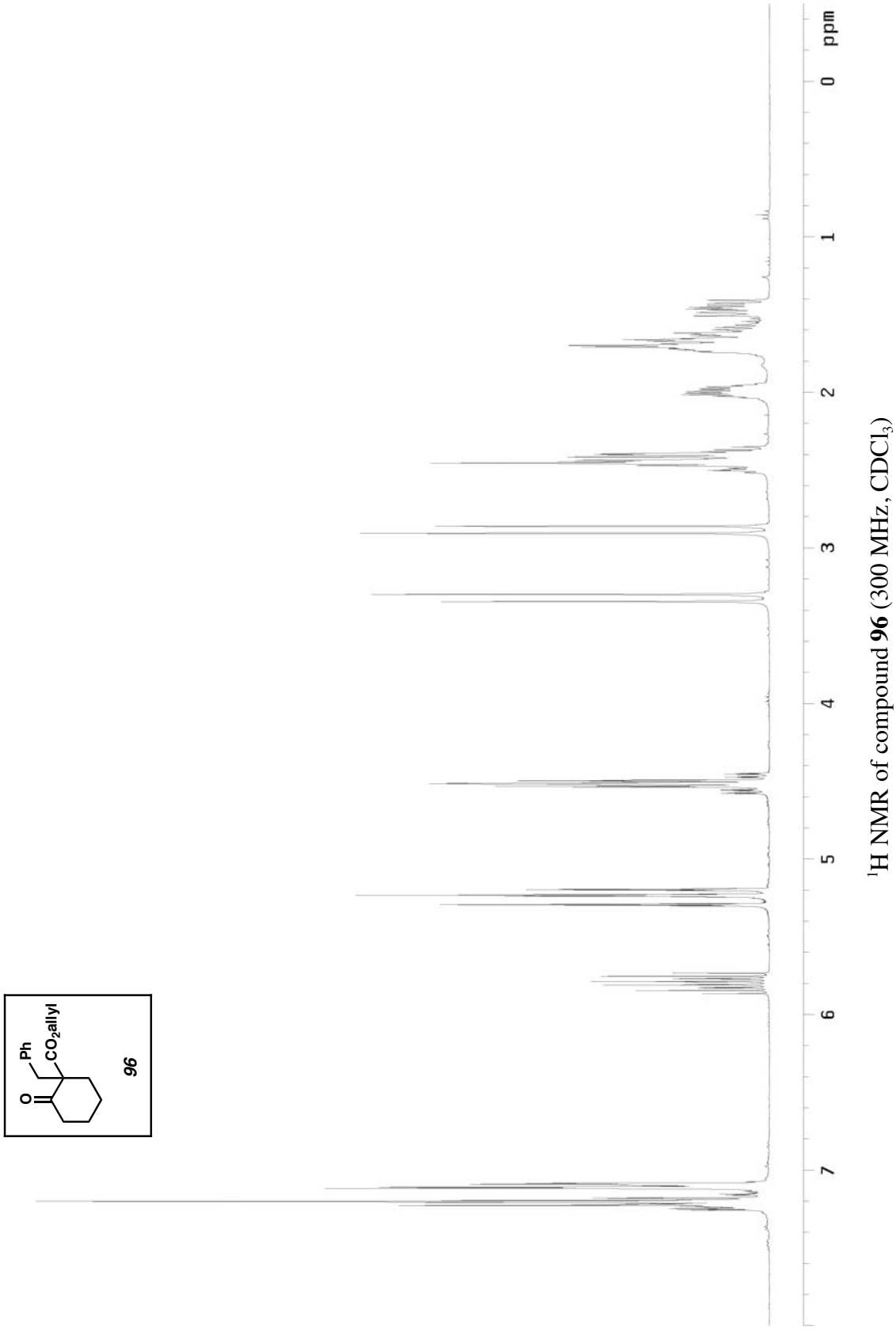
^{13}C NMR of compound **SI43** (125 MHz, $CDCl_3$)



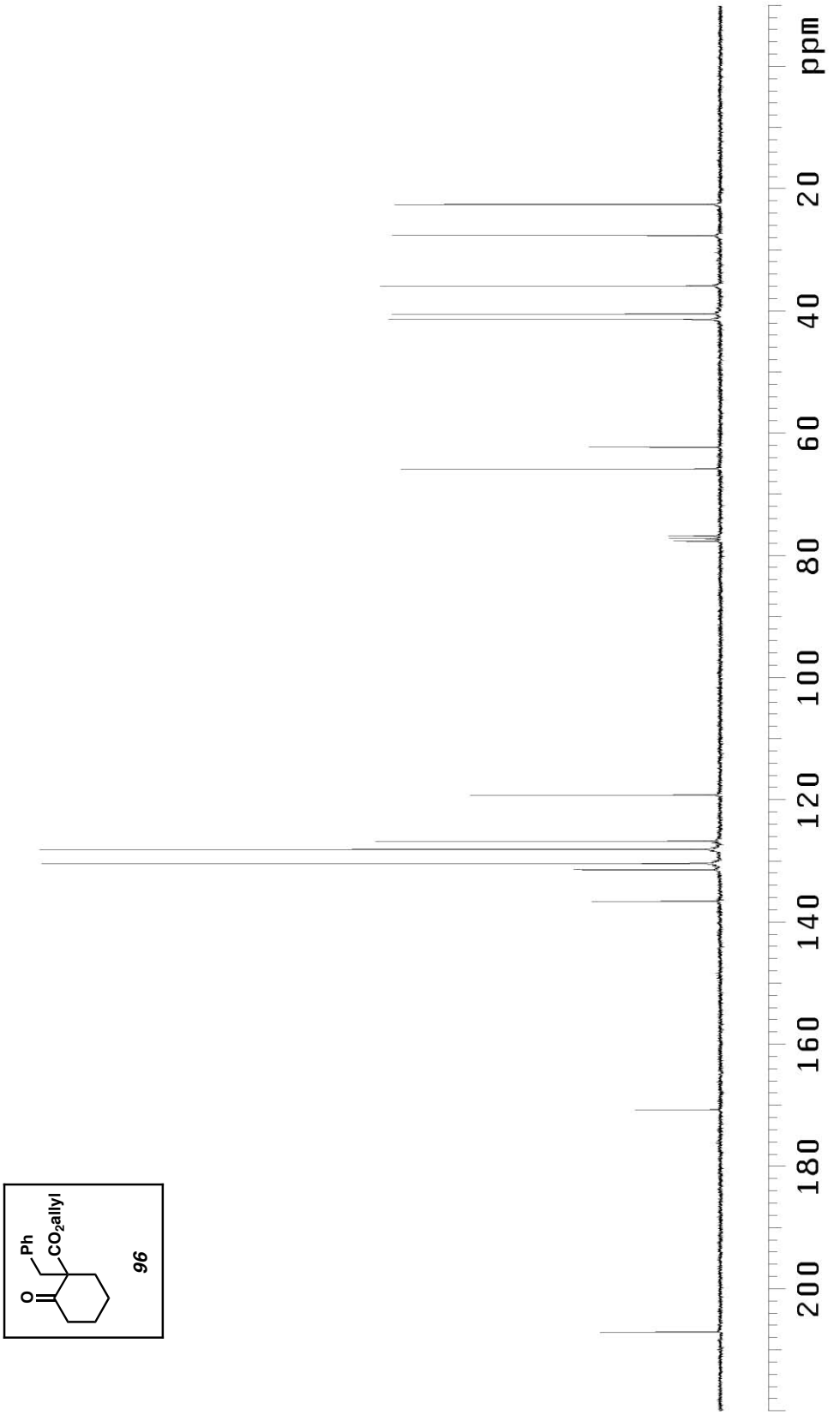
^{1}H NMR of compound **SI44** (300 MHz, $CDCl_3$)



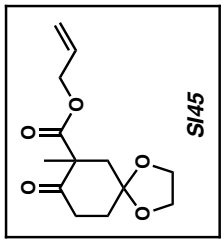
^{13}C NMR of compound **SI44** (75 MHz, $CDCl_3$)



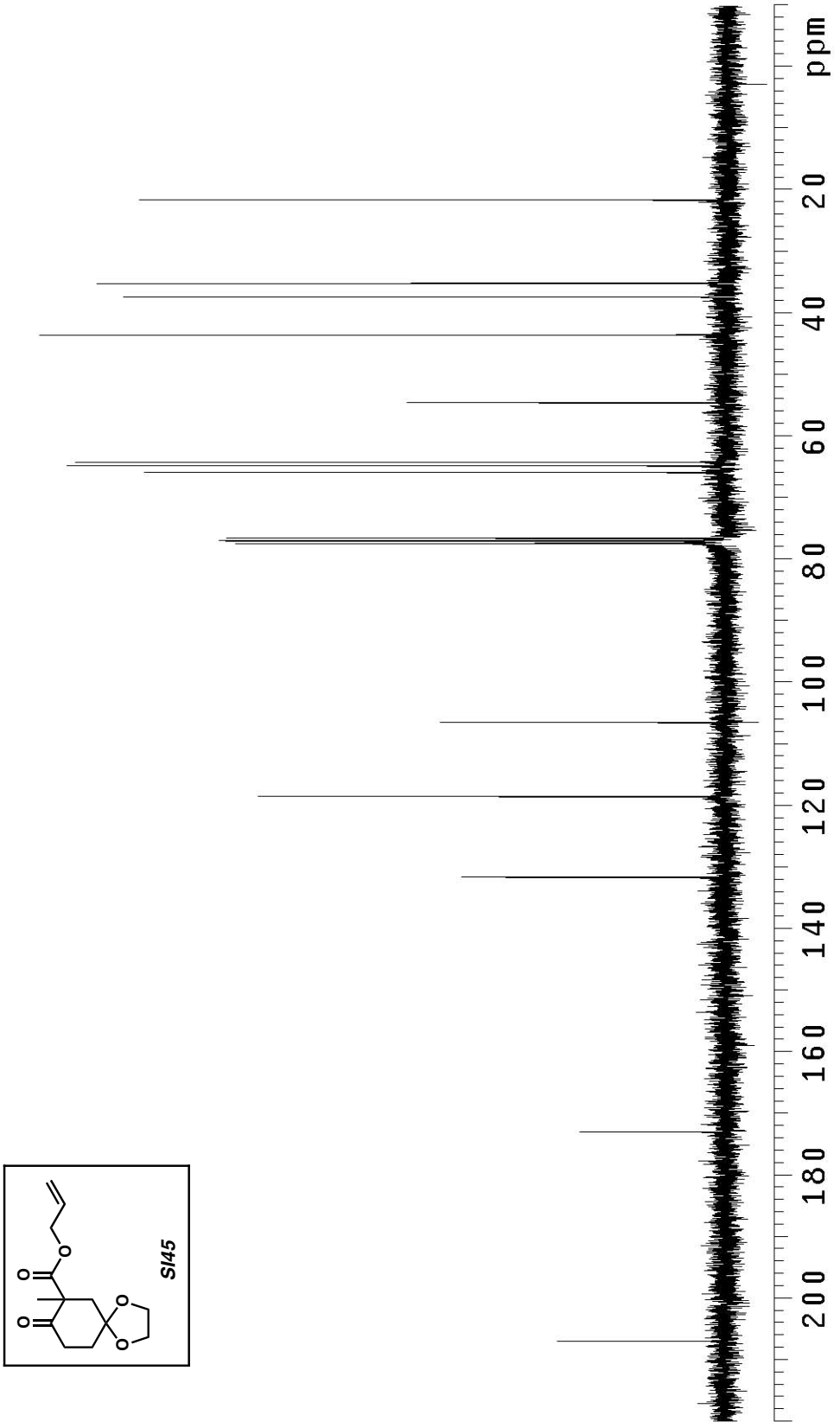
^{1}H NMR of compound **96** (300 MHz, $CDCl_3$)



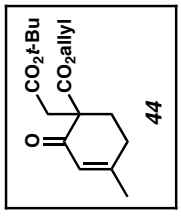
^{13}C NMR of compound **96** (75 MHz, $CDCl_3$)



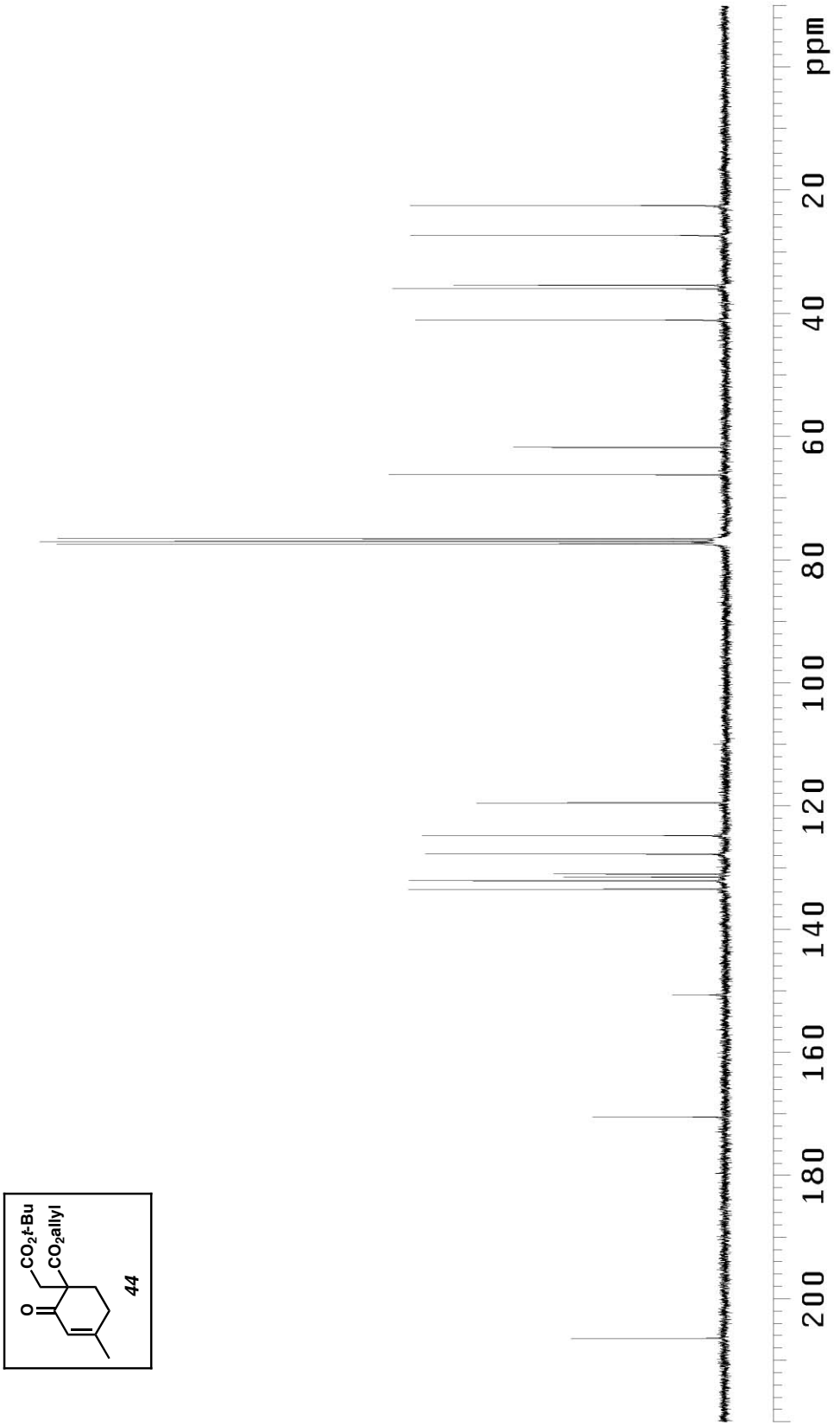
^{1}H NMR of compound **SI45** (300 MHz, $CDCl_3$)



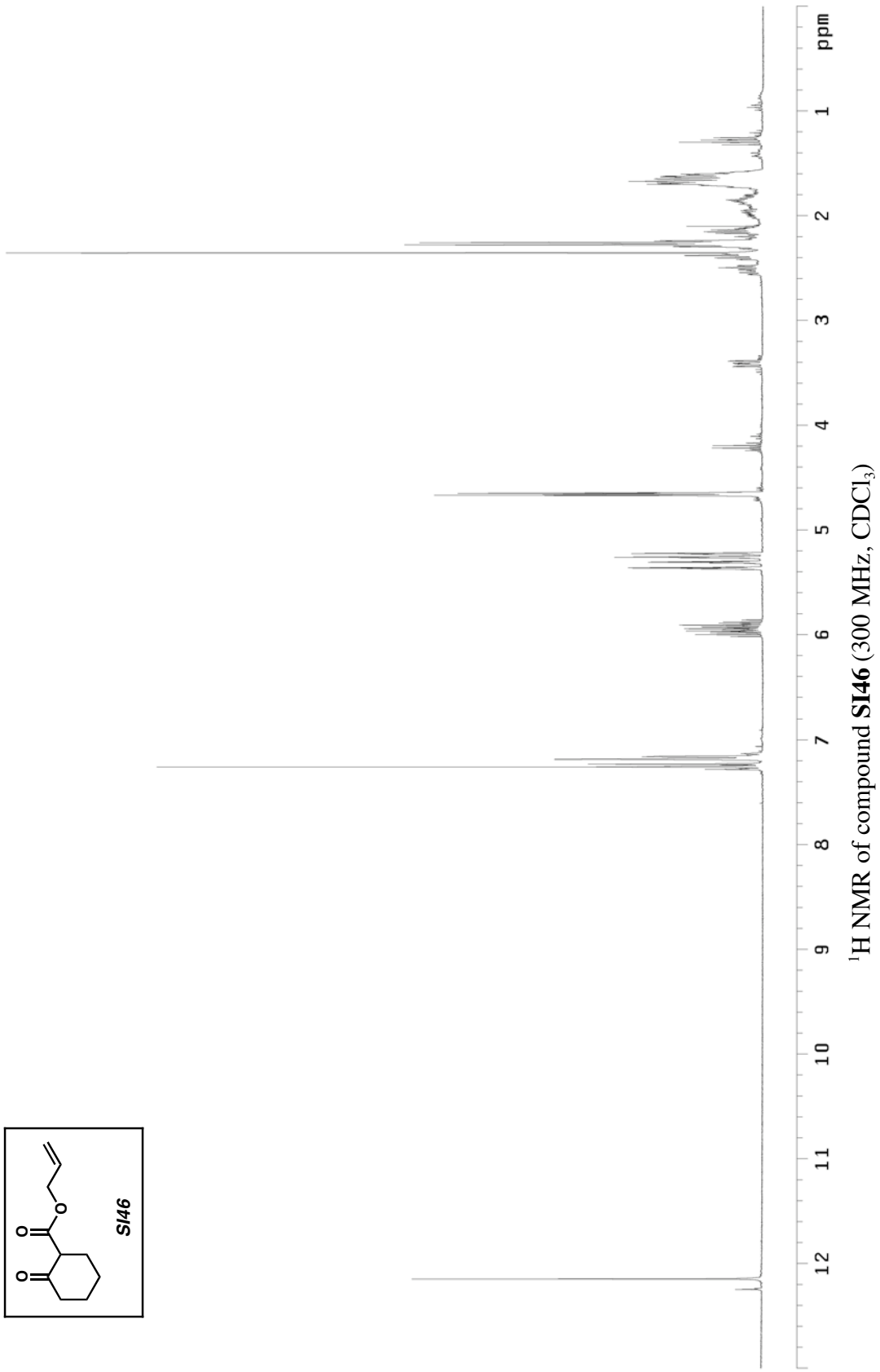
^{13}C NMR of compound **SI45** (75 MHz, $CDCl_3$)



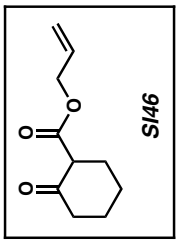
^{1}H NMR of compound **44** (300 MHz, $CDCl_3$)

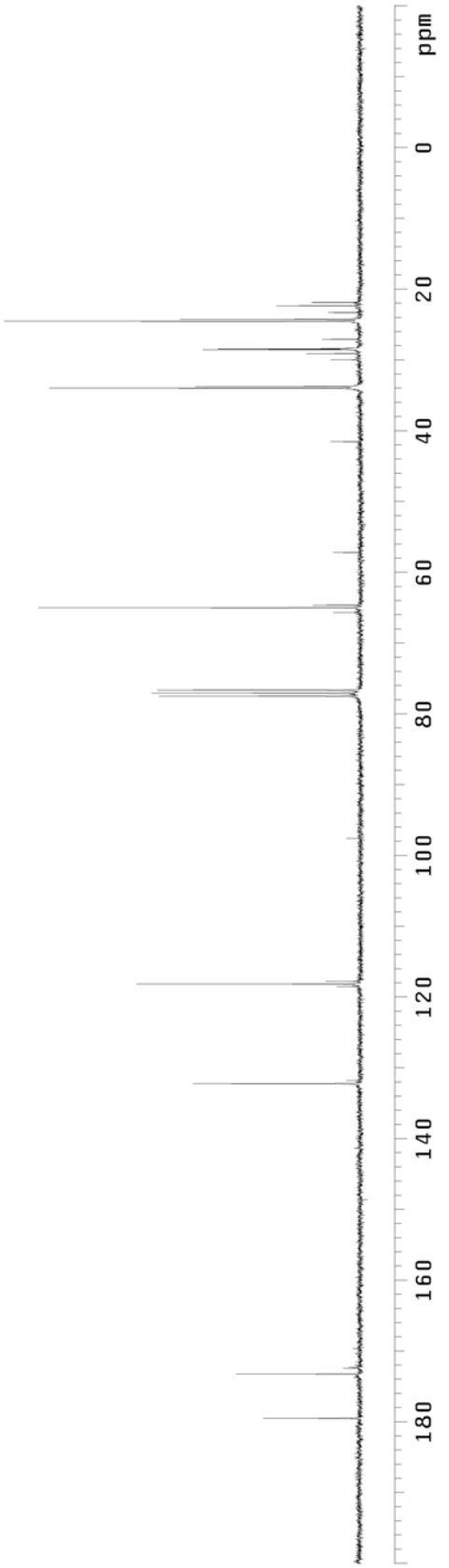


^{13}C NMR of compound **44** (75 MHz, $CDCl_3$)

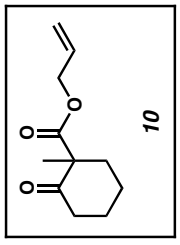


^{1}H NMR of compound **SI46** (300 MHz, $CDCl_3$)

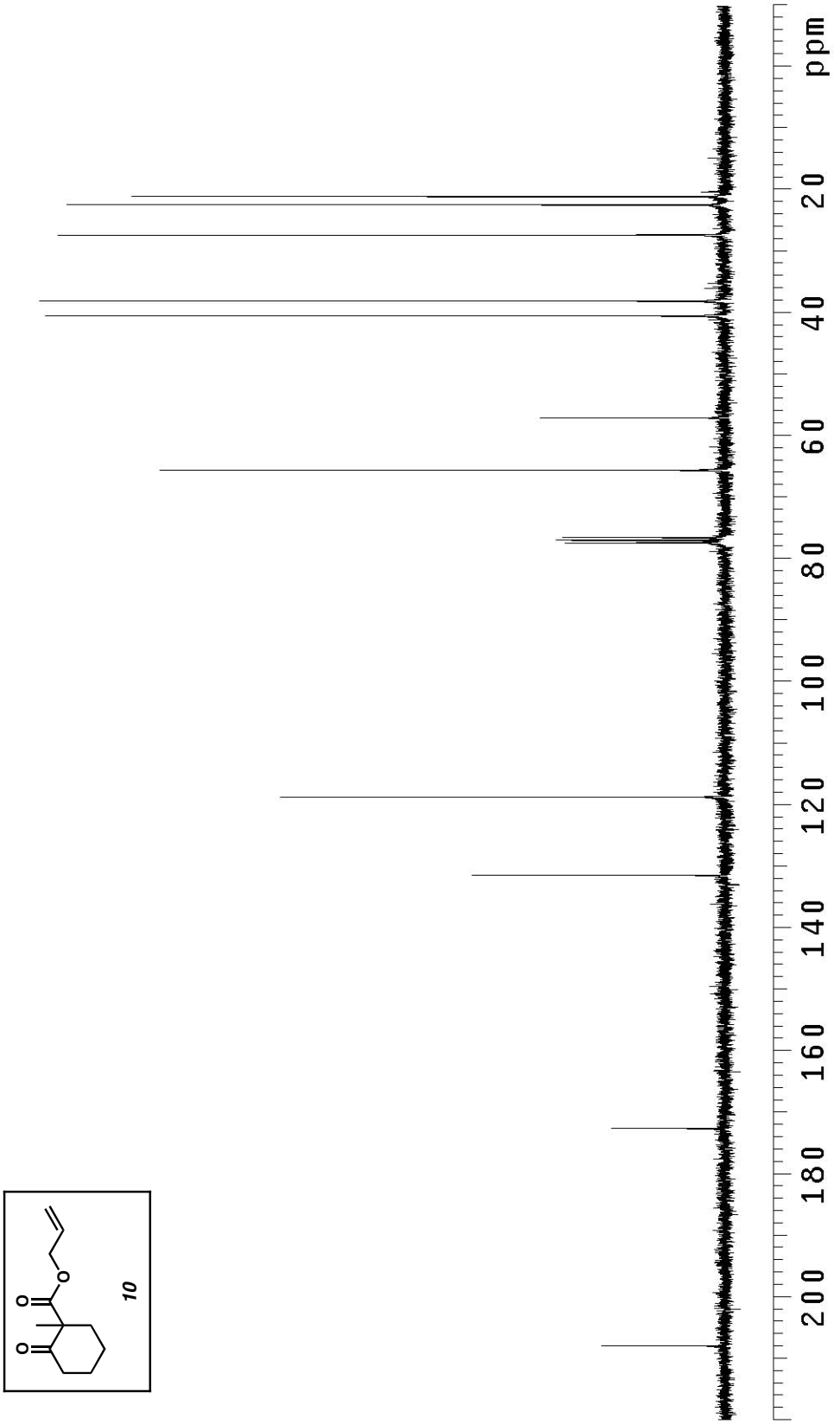




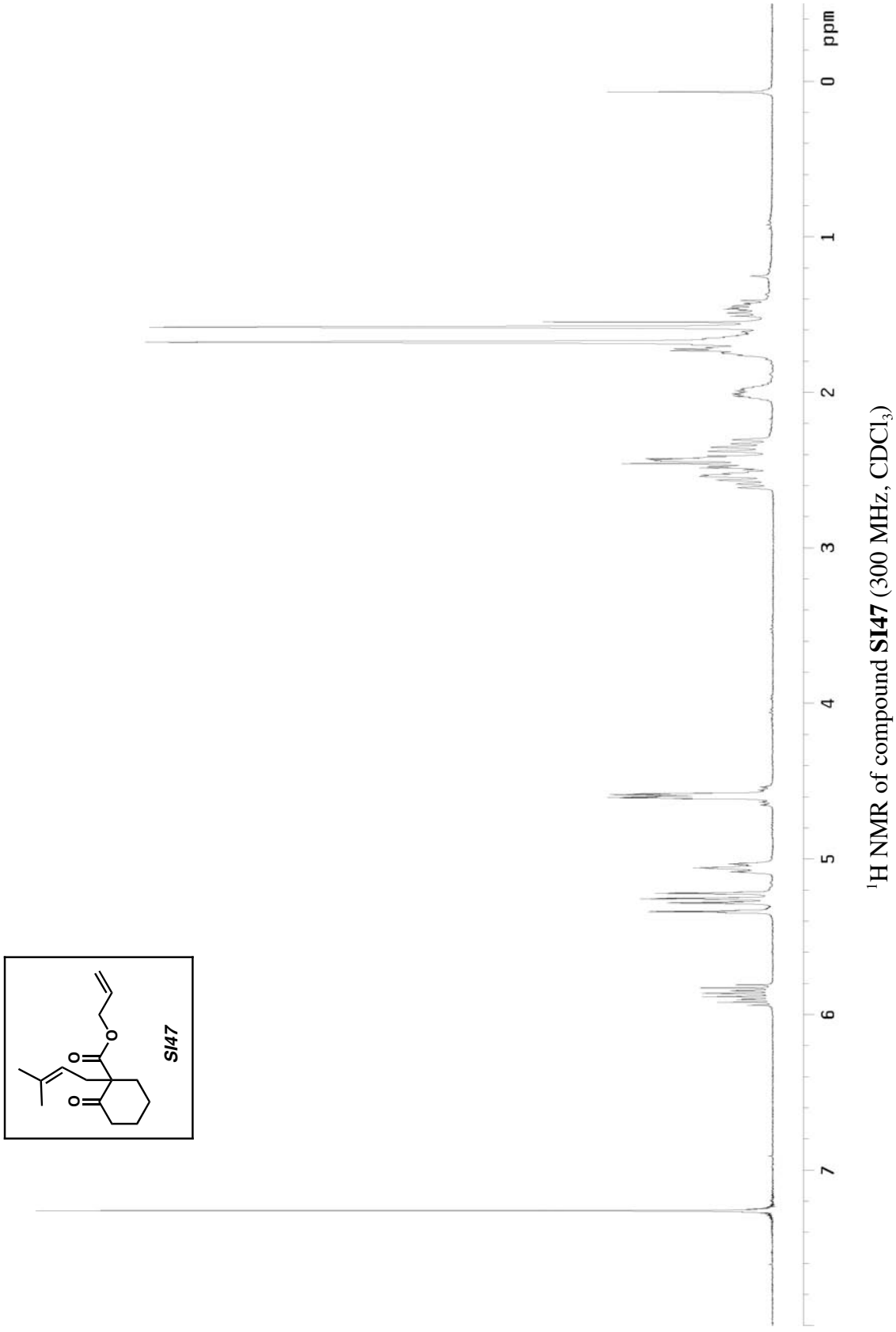
^{13}C NMR of compound **SI46** (75 MHz, $CDCl_3$)



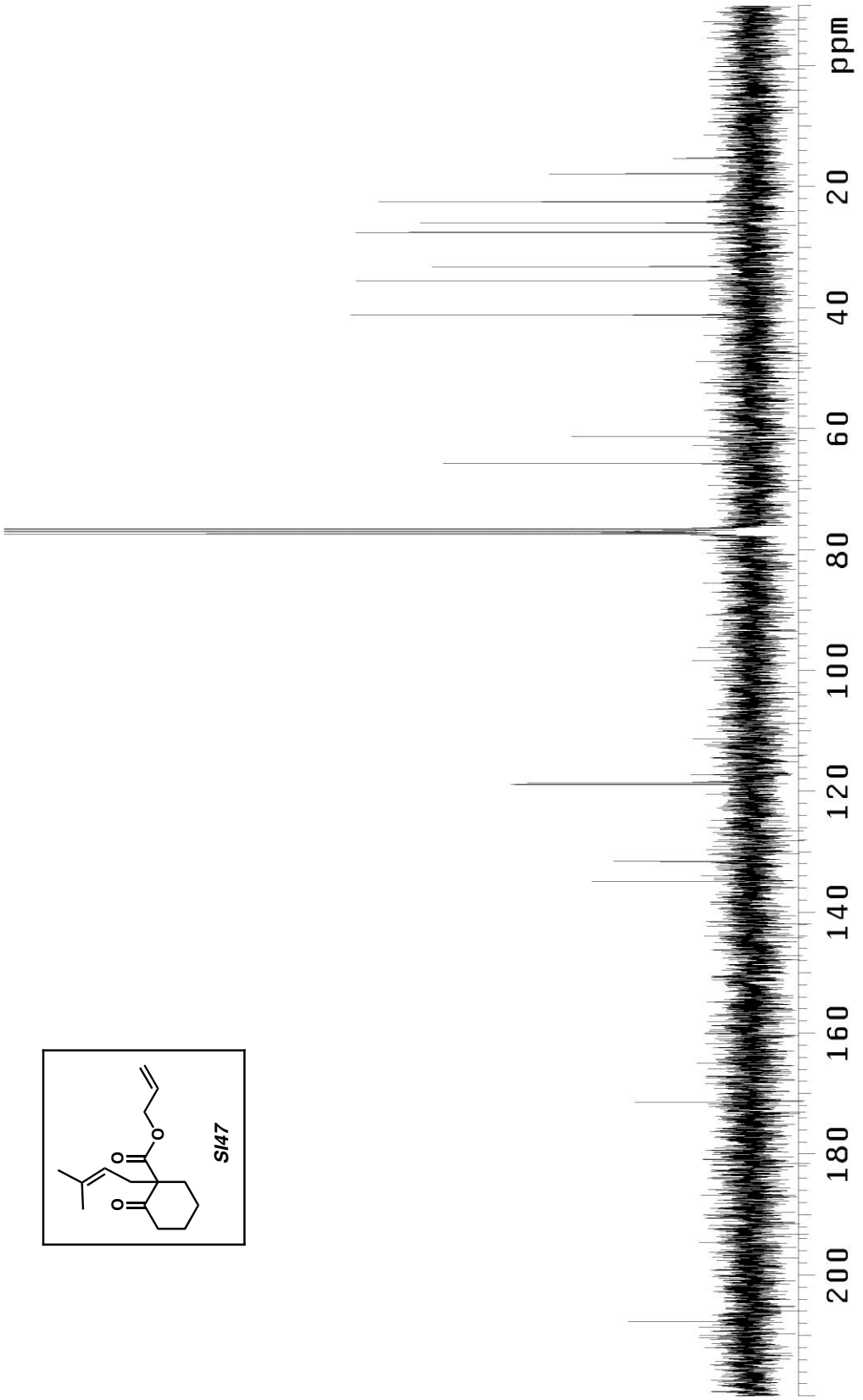
^{1}H NMR of compound **10** (300 MHz, $CDCl_3$)



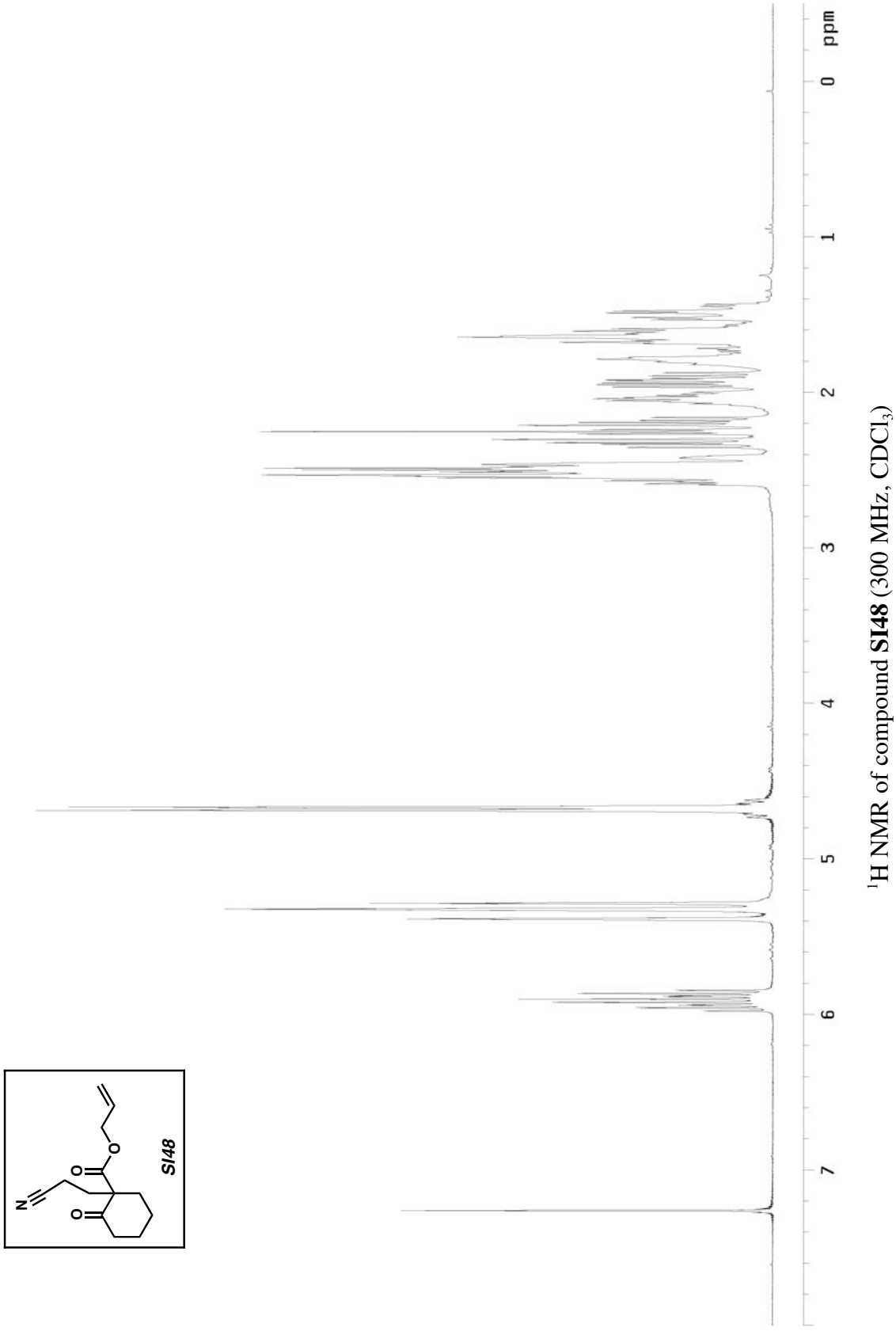
^{13}C NMR of compound **10** (75 MHz, $CDCl_3$)



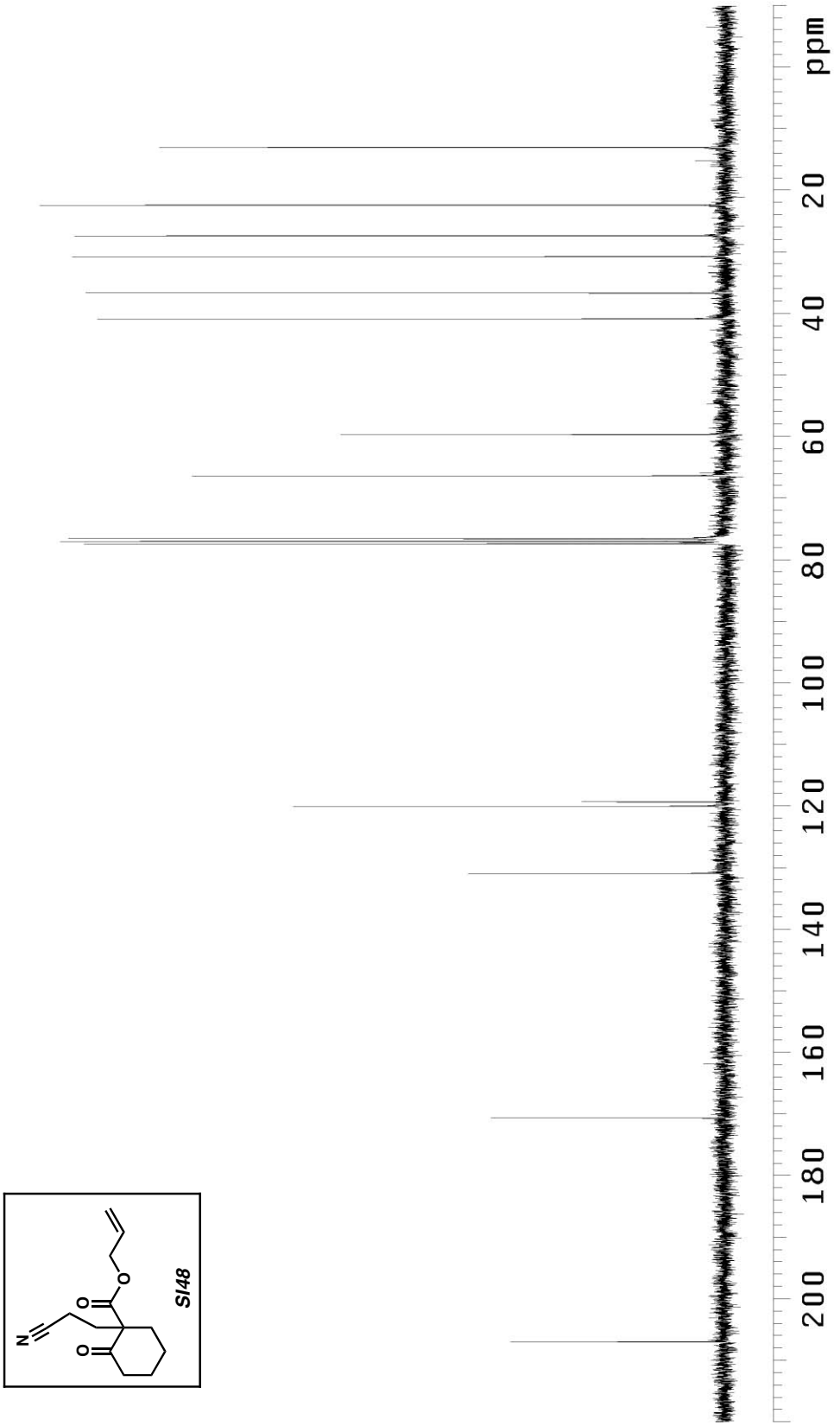
^{1}H NMR of compound **SI47** (300 MHz, $CDCl_3$)



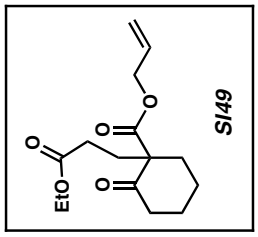
^{13}C NMR of compound **SI47** (75 MHz, $CDCl_3$)



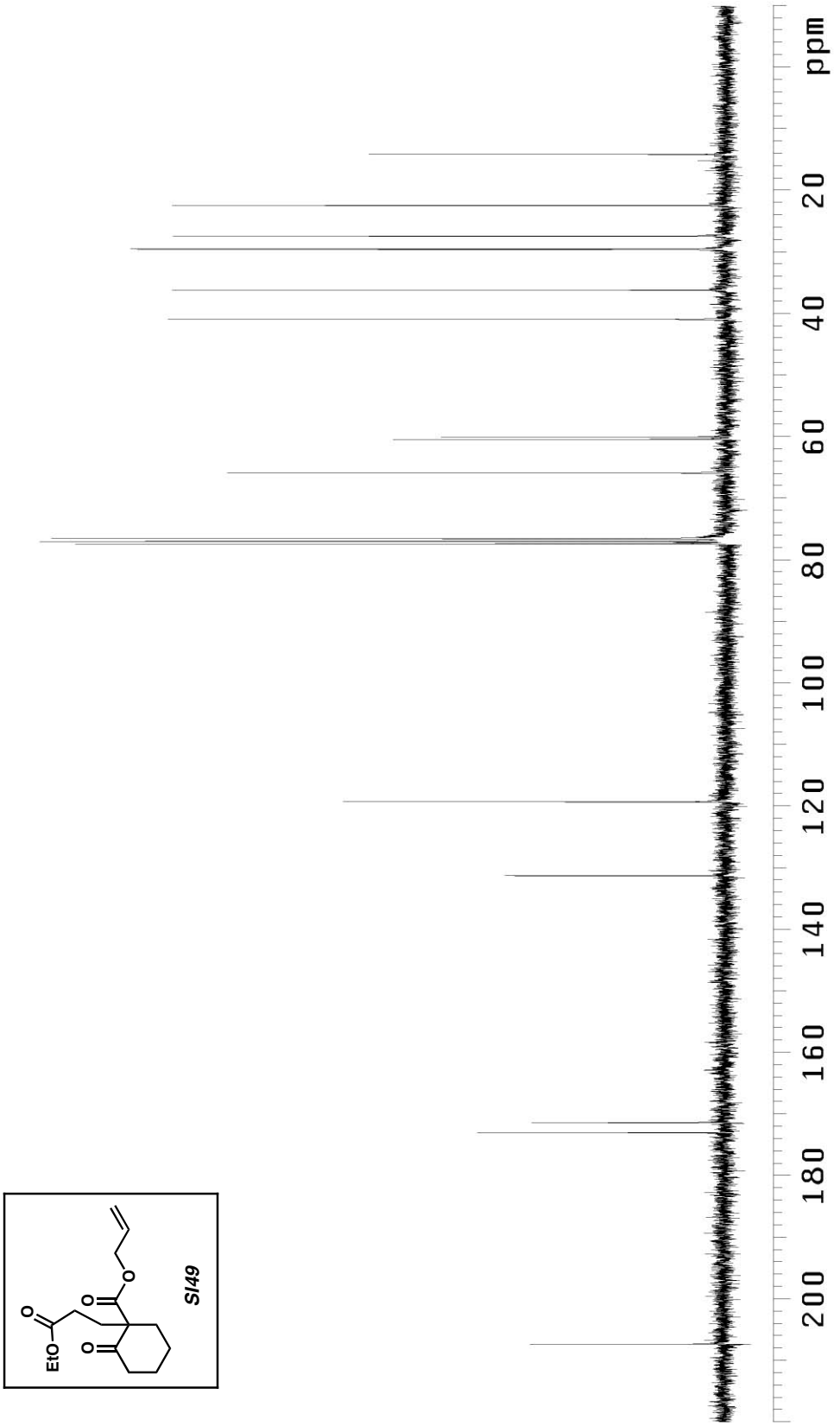
^{1}H NMR of compound **SI48** (300 MHz, $CDCl_3$)



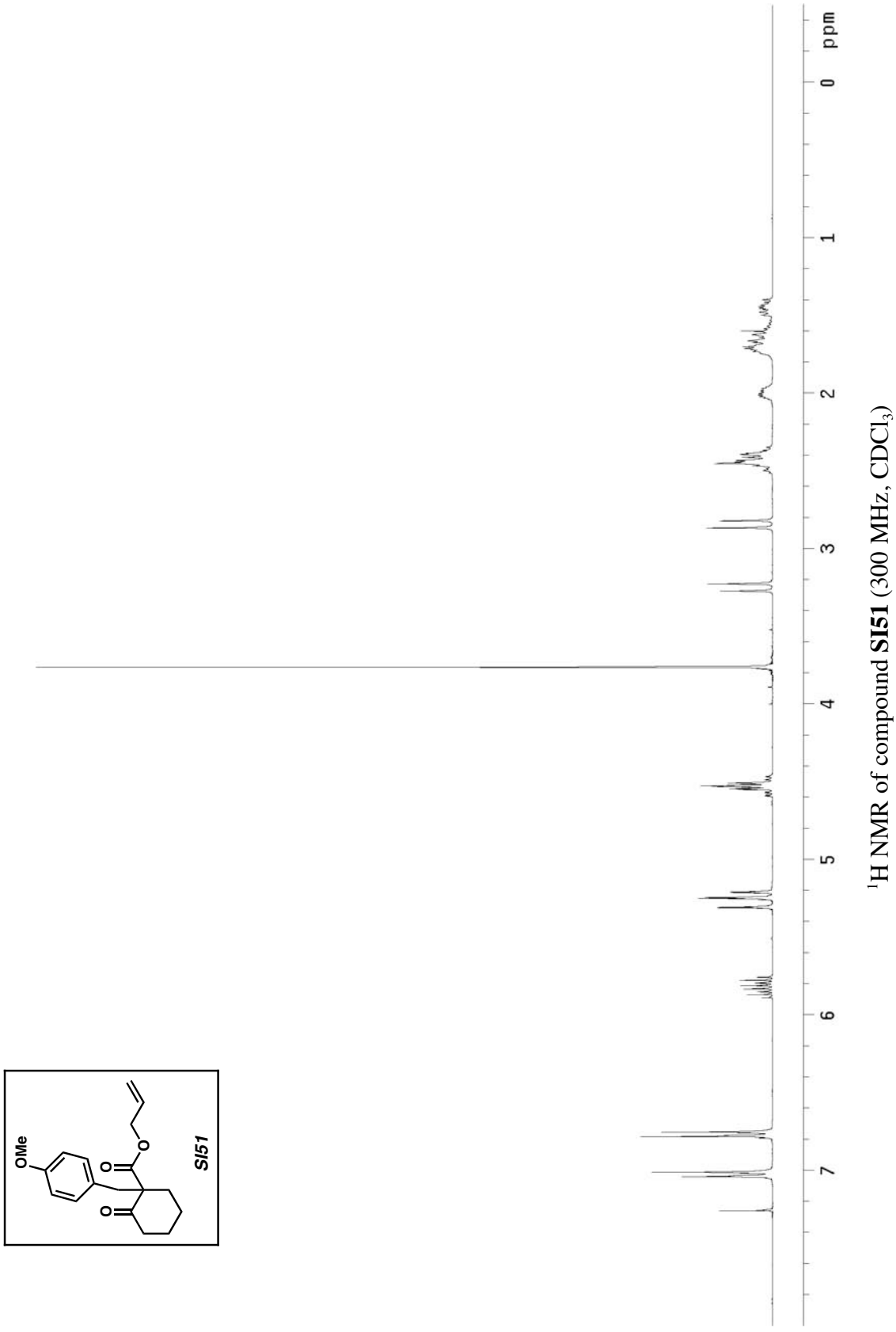
^{13}C NMR of compound **SI48** (75 MHz, $CDCl_3$)



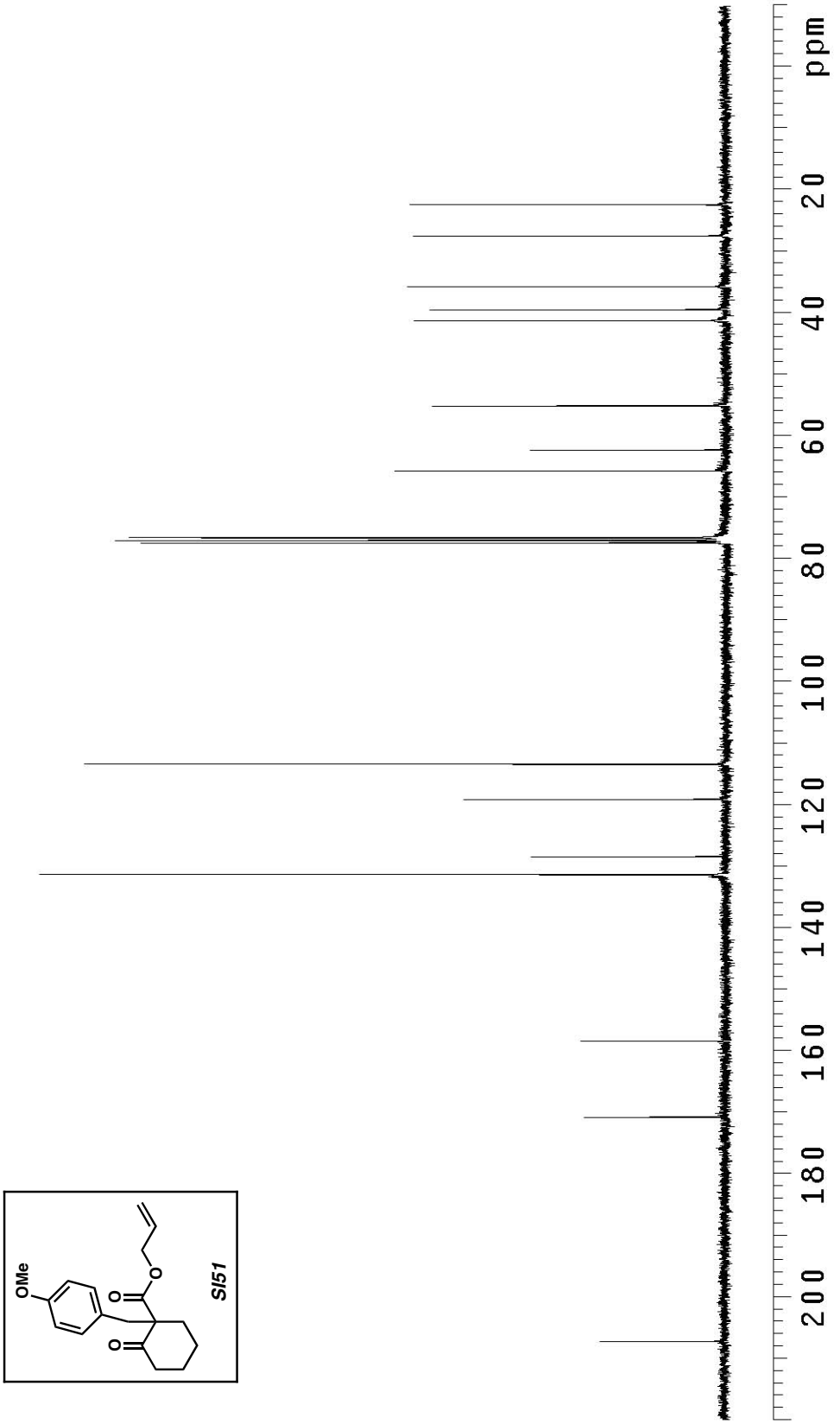
^{1}H NMR of compound **SI49** (300 MHz, $CDCl_3$)



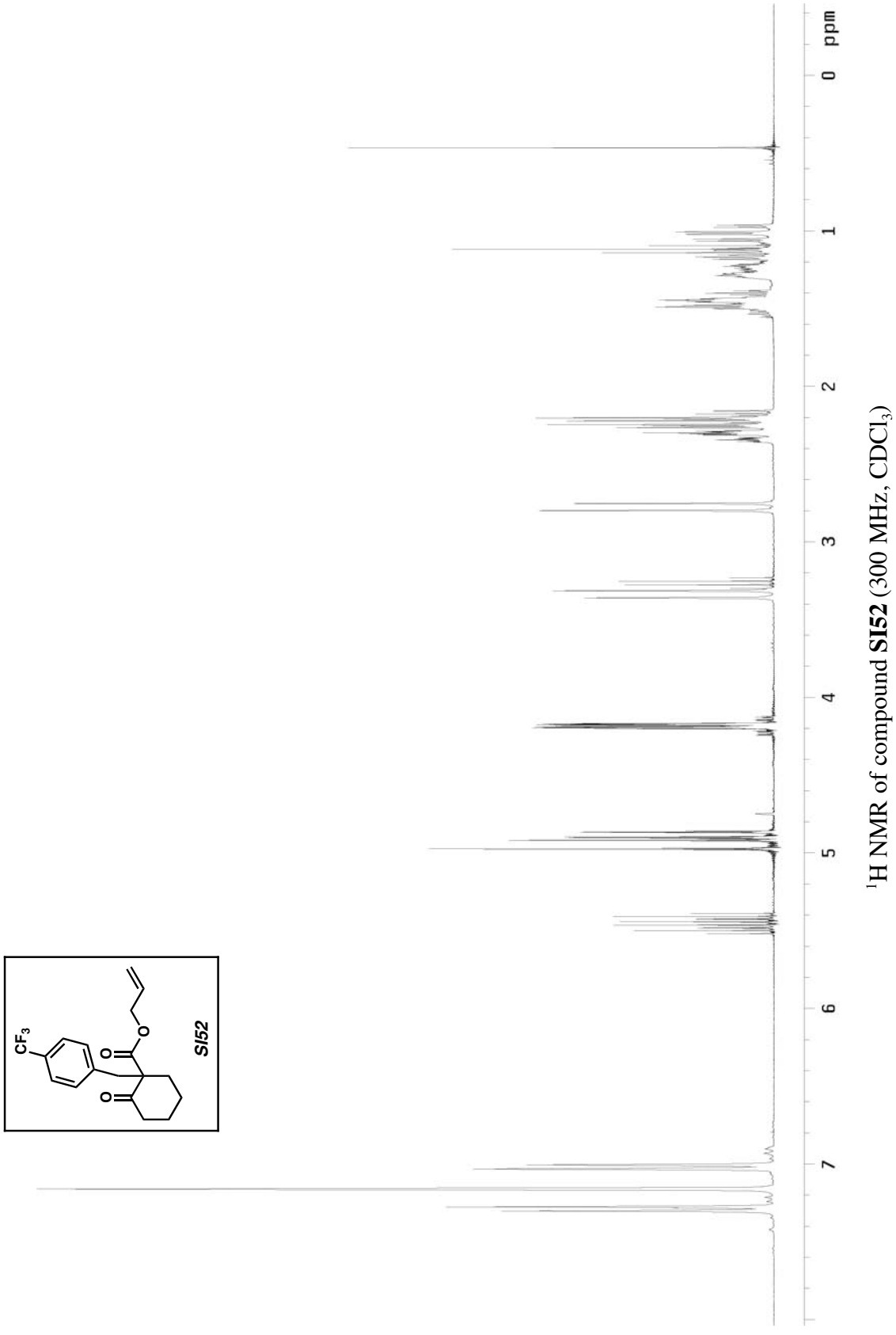
^{13}C NMR of compound **SI49** (75 MHz, $CDCl_3$)



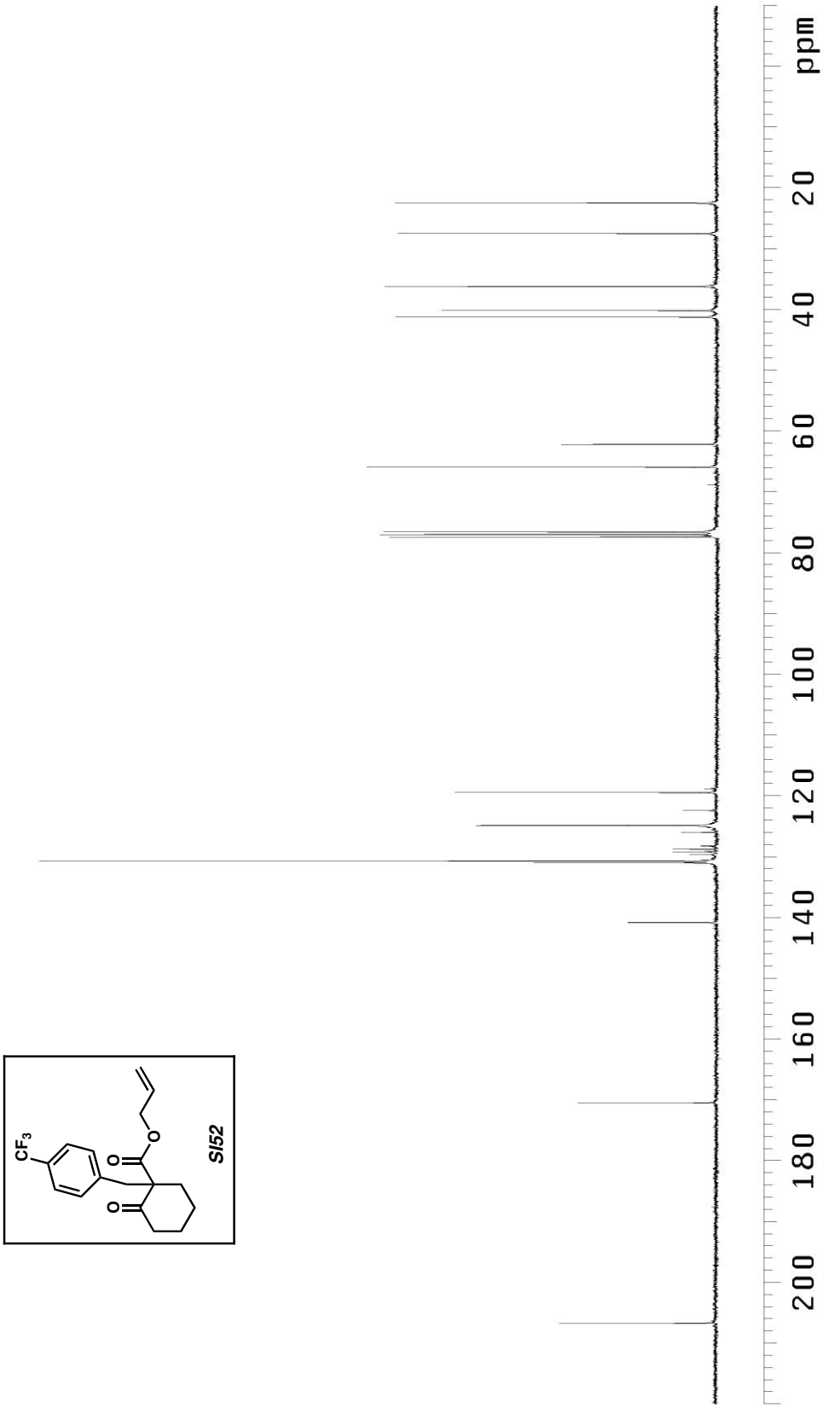
^{1}H NMR of compound **SI51** (300 MHz, $CDCl_3$)



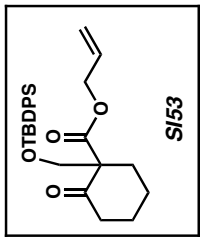
^{13}C NMR of compound **SI51** (75 MHz, $CDCl_3$)



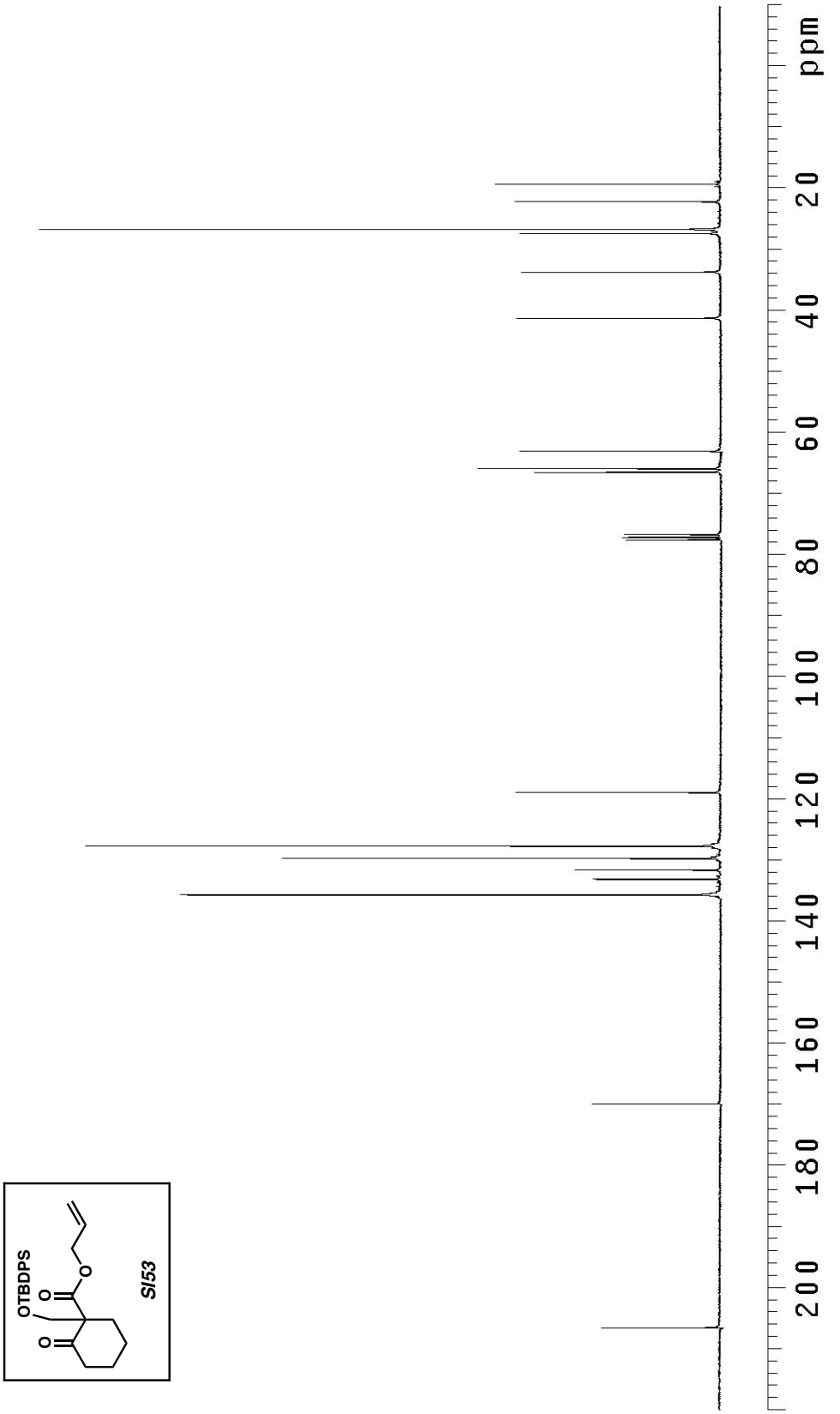
^{1}H NMR of compound **SI52** (300 MHz, $CDCl_3$)



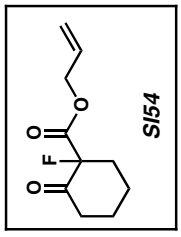
^{13}C NMR of compound **SI52** (75 MHz, $CDCl_3$)



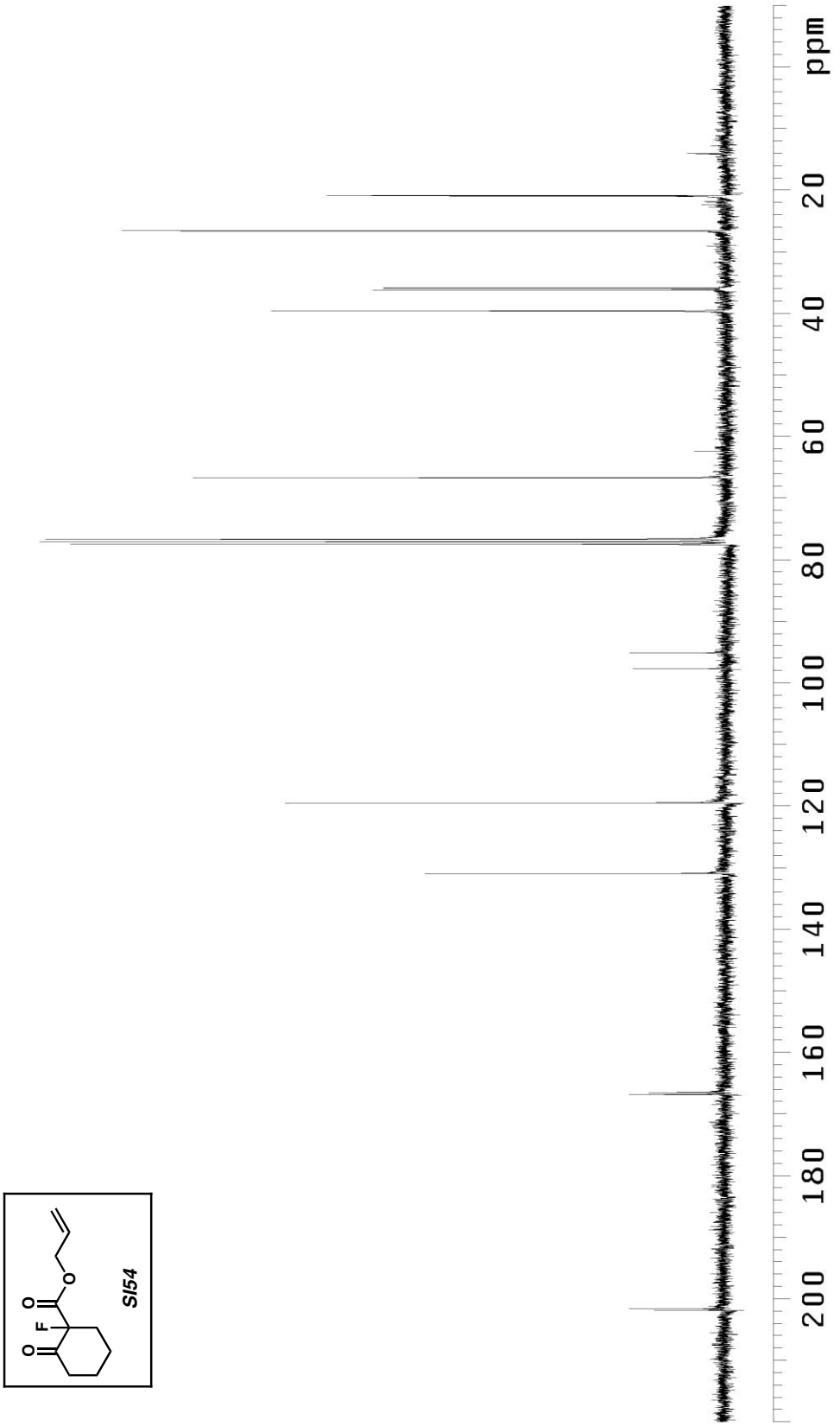
^{1}H NMR of compound **SI53** (300 MHz, $CDCl_3$)



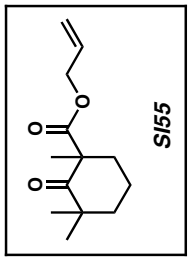
^{13}C NMR of compound **SI53** (75 MHz, $CDCl_3$)



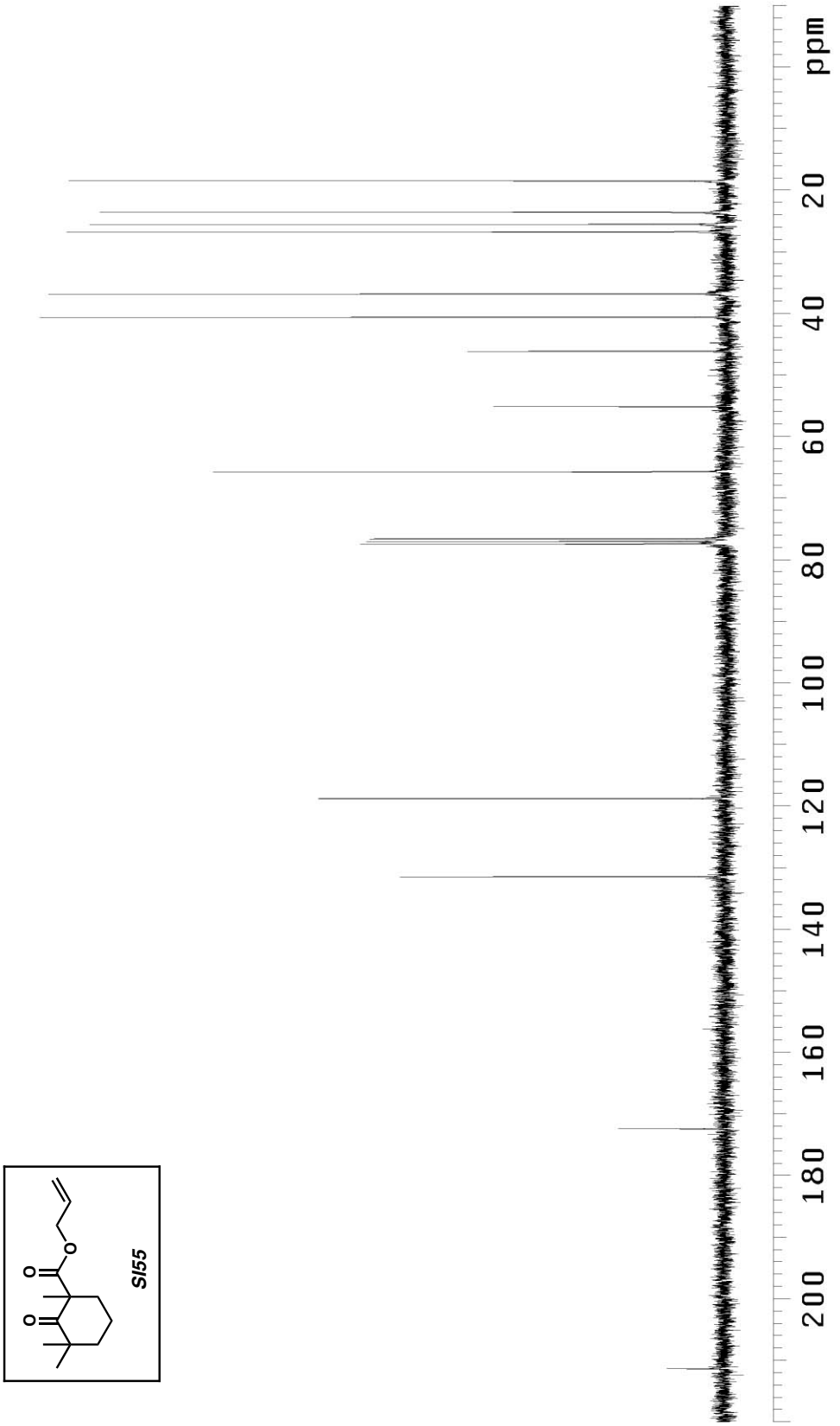
^{1}H NMR of compound **SI54** (300 MHz, $CDCl_3$)



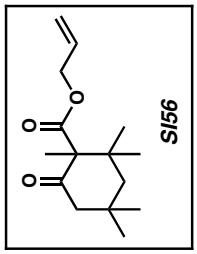
^{13}C NMR of compound **SI54** (75 MHz, $CDCl_3$)



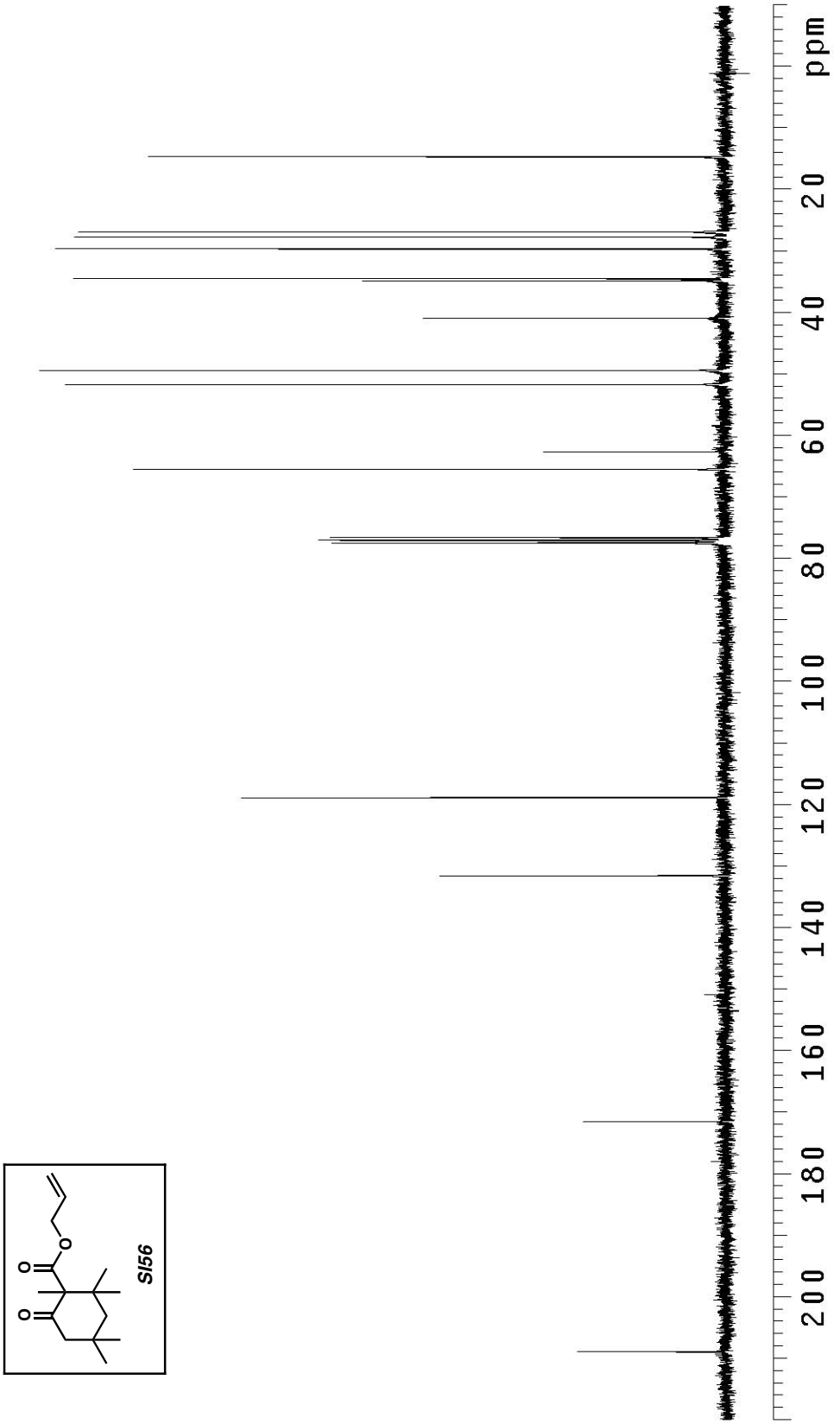
^{1}H NMR of compound **SI55** (300 MHz, $CDCl_3$)



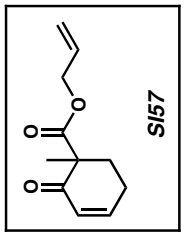
^{13}C NMR of compound **SI55** (75 MHz, $CDCl_3$)



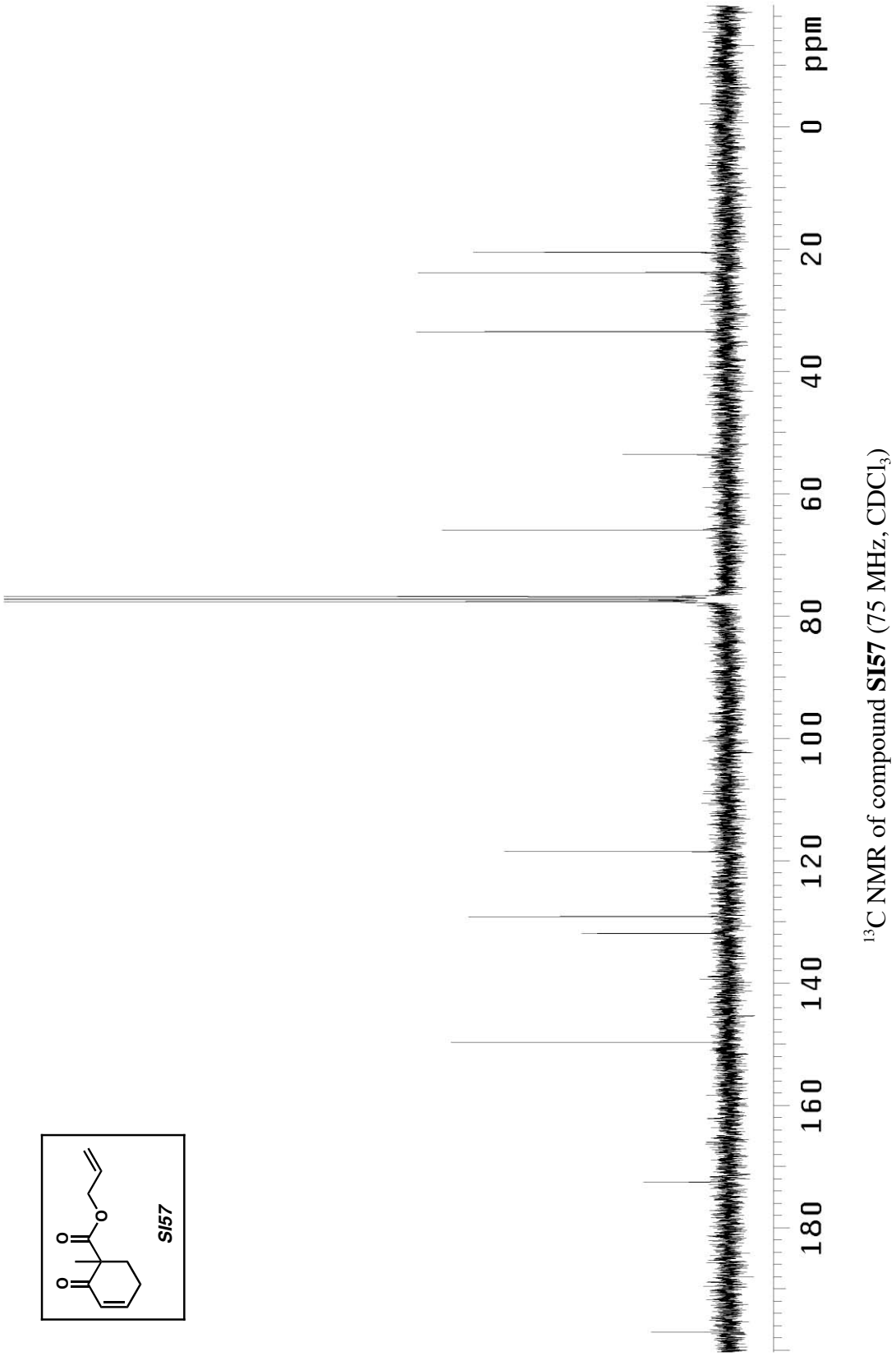
^{1}H NMR of compound **SI56** (300 MHz, $CDCl_3$)



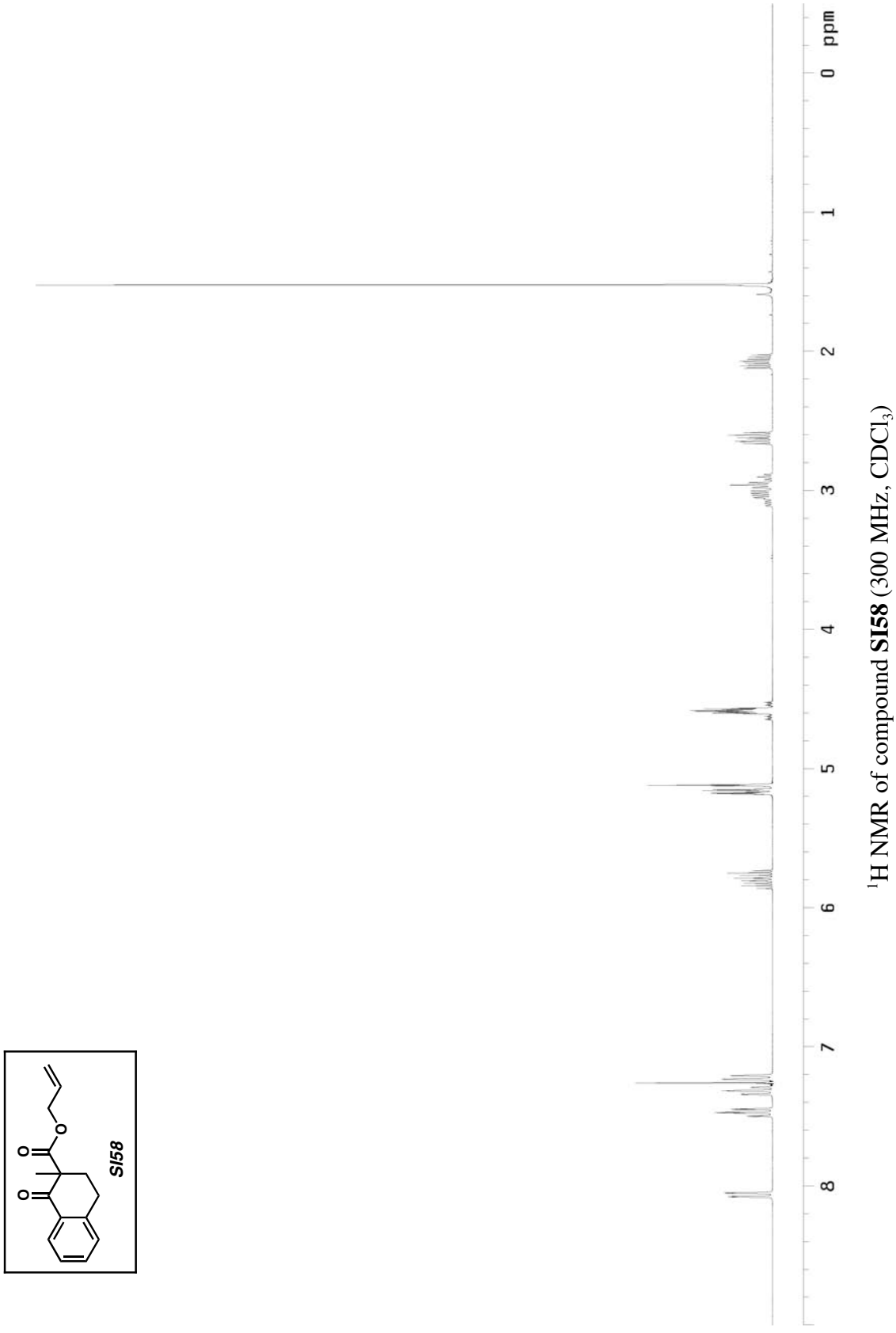
^{13}C NMR of compound **SI56** (75 MHz, $CDCl_3$)



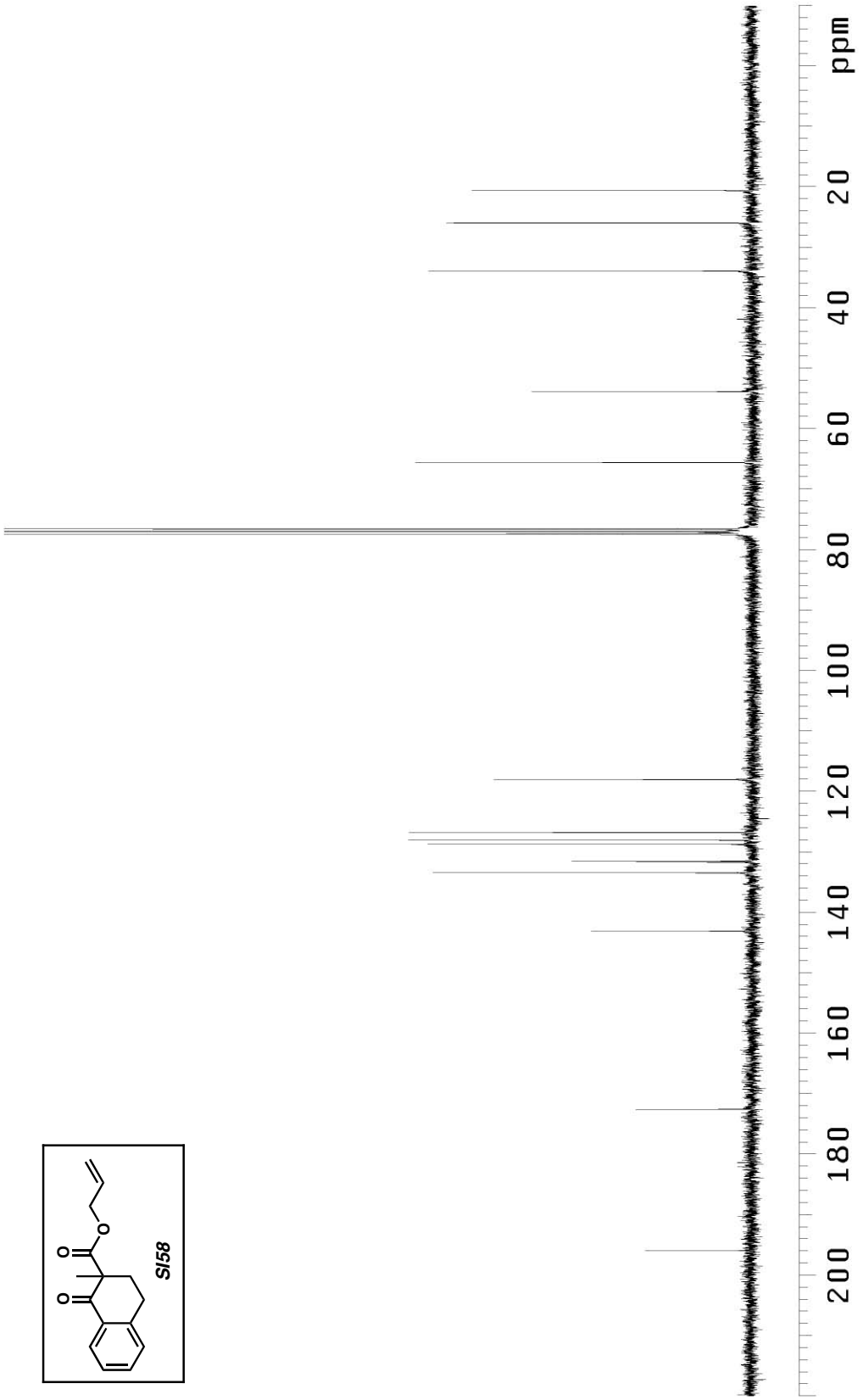
^{1}H NMR of compound **SI57** (300 MHz, $CDCl_3$)



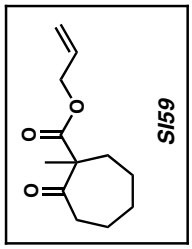
^{13}C NMR of compound **SI57** (75 MHz, $CDCl_3$)



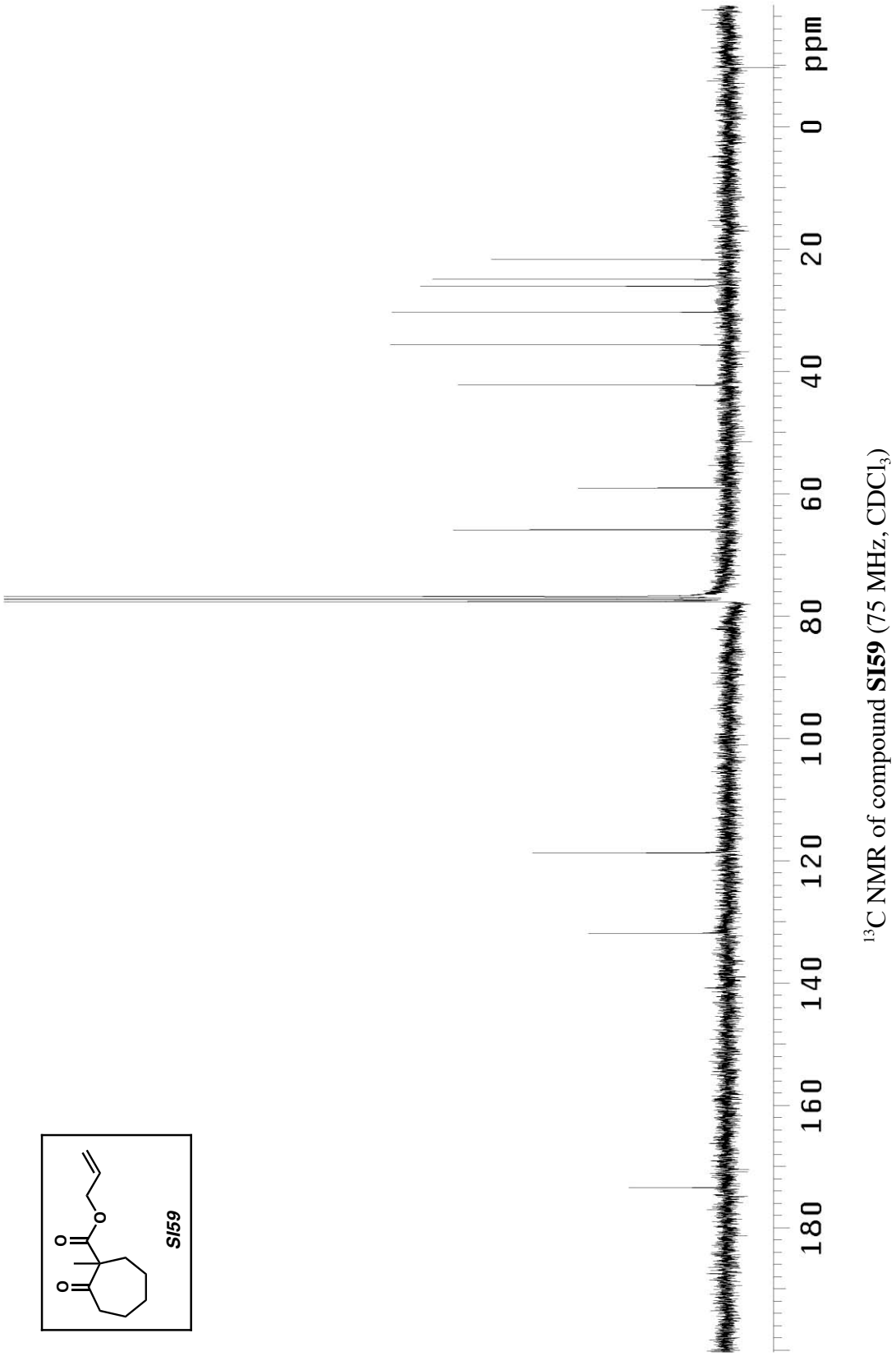
^{1}H NMR of compound **SI58** (300 MHz, $CDCl_3$)



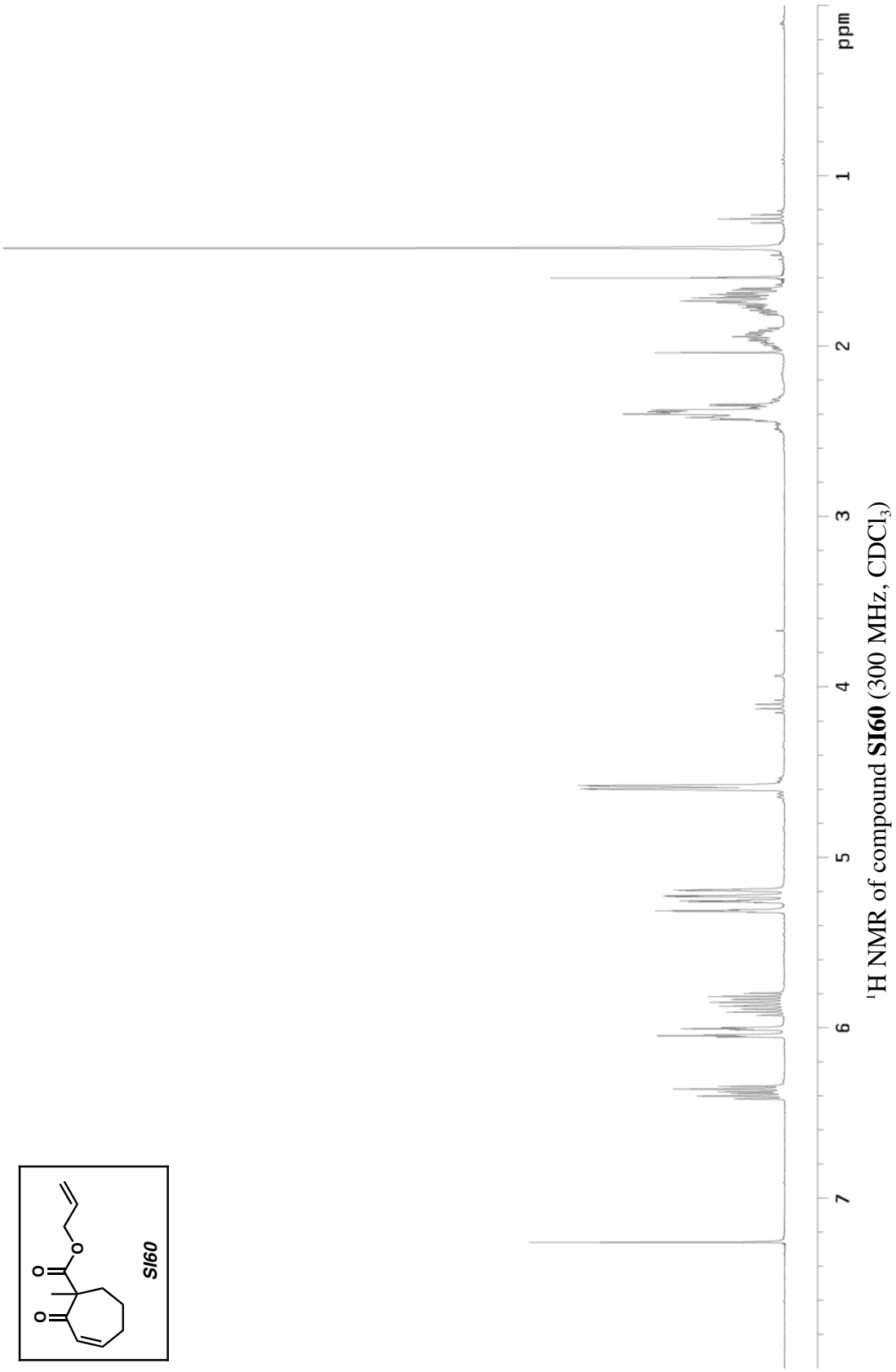
^{13}C NMR of compound **SI58** (75 MHz, $CDCl_3$)



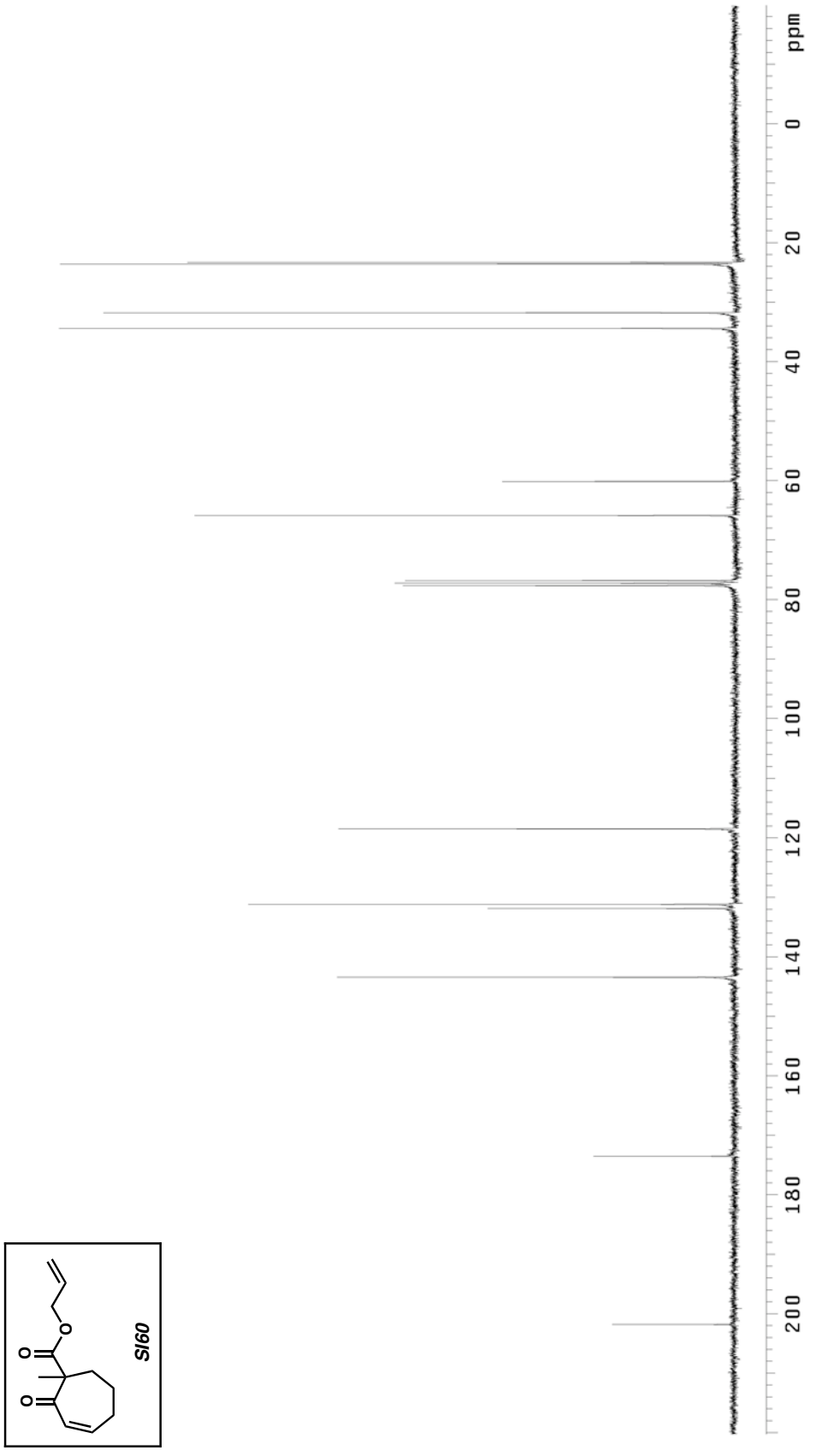
^{1}H NMR of compound **SI59** (300 MHz, $CDCl_3$)



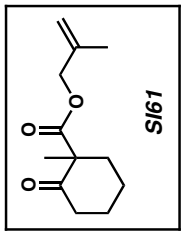
^{13}C NMR of compound **SI59** (75 MHz, $CDCl_3$)



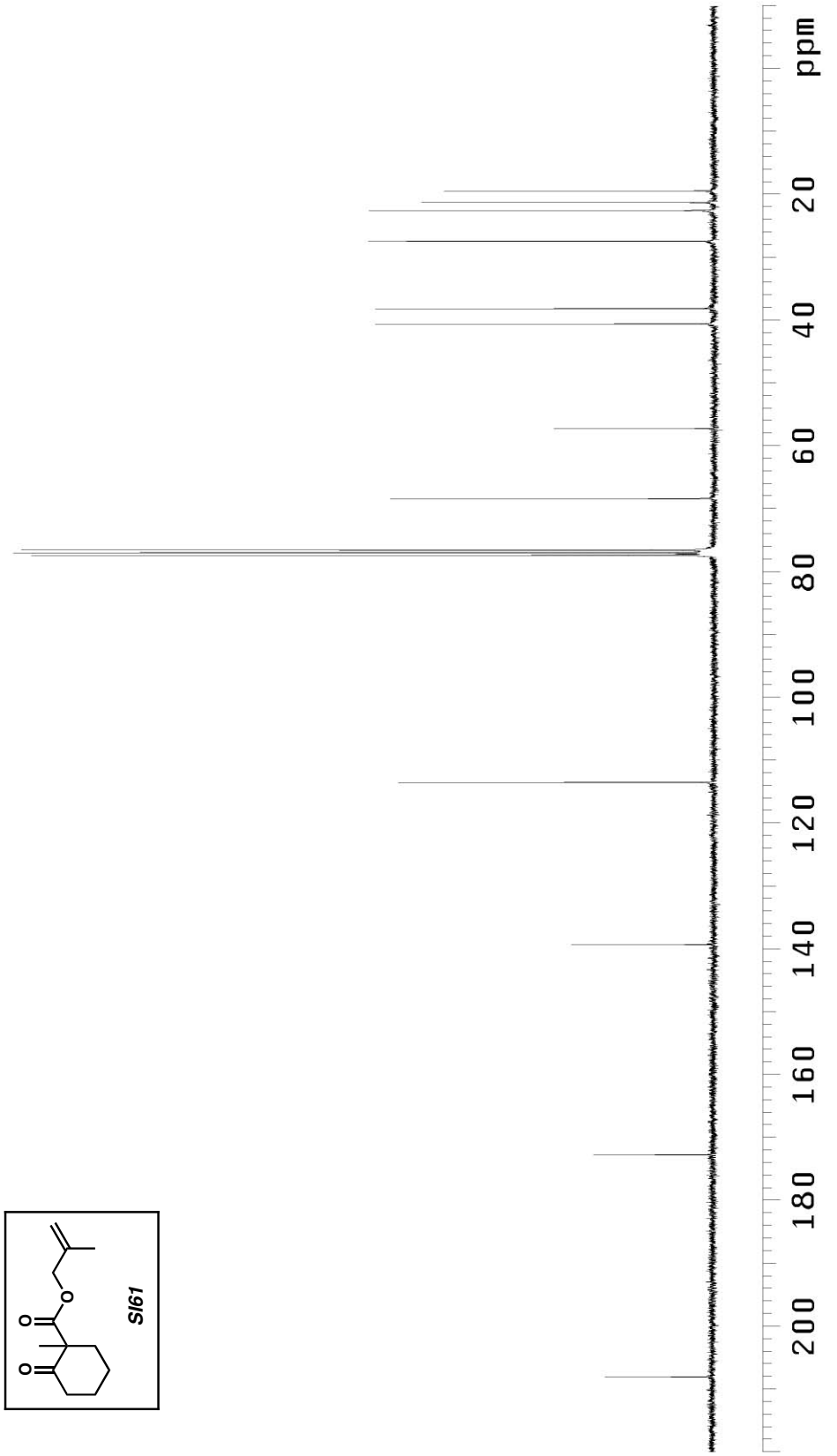
^{1}H NMR of compound **SI60** (300 MHz, $CDCl_3$)



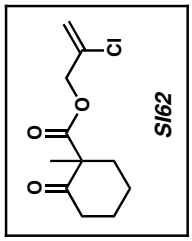
^{13}C NMR of compound **SI60** (75 MHz, $CDCl_3$)



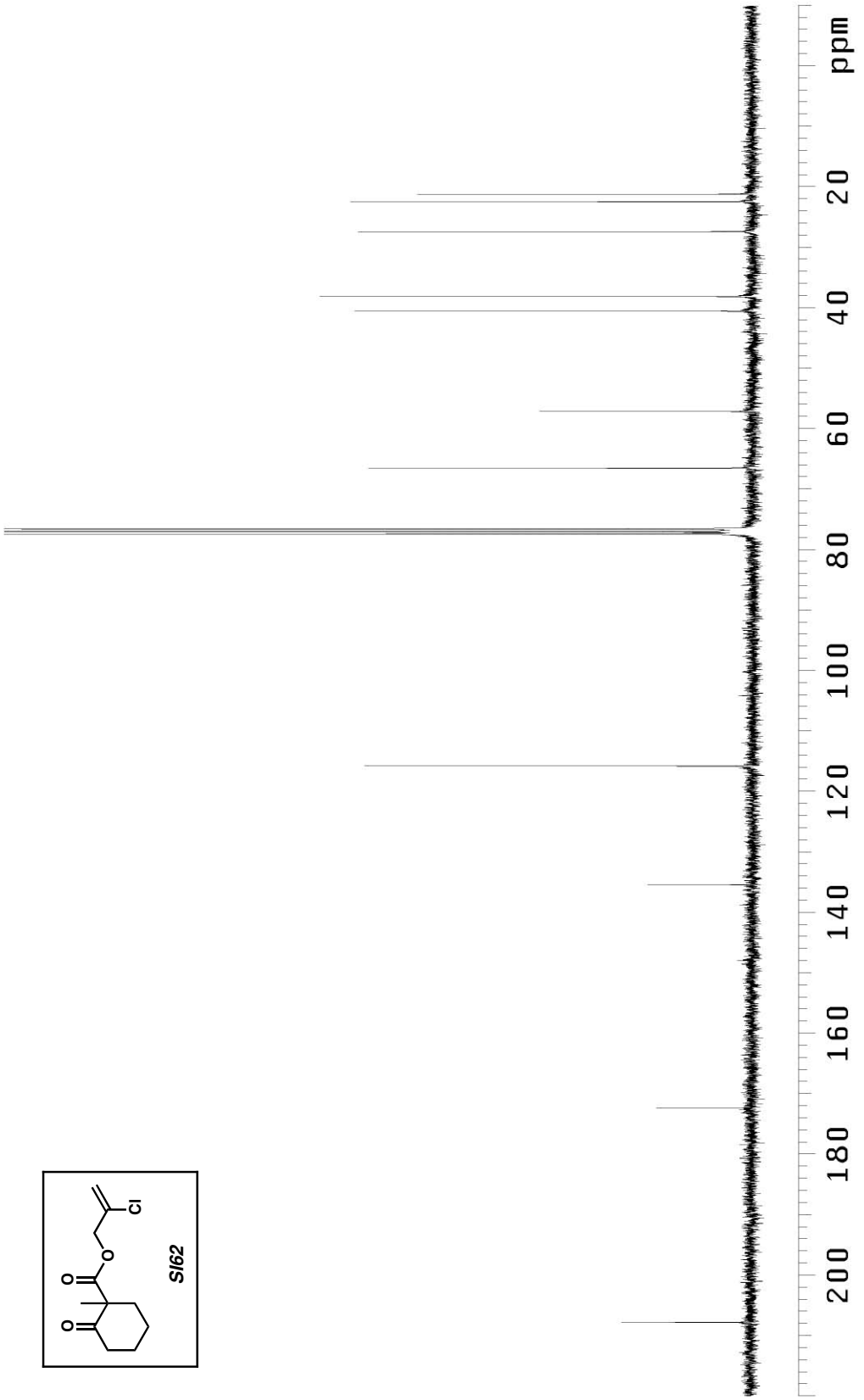
^{1}H NMR of compound **SI61** (300 MHz, $CDCl_3$)



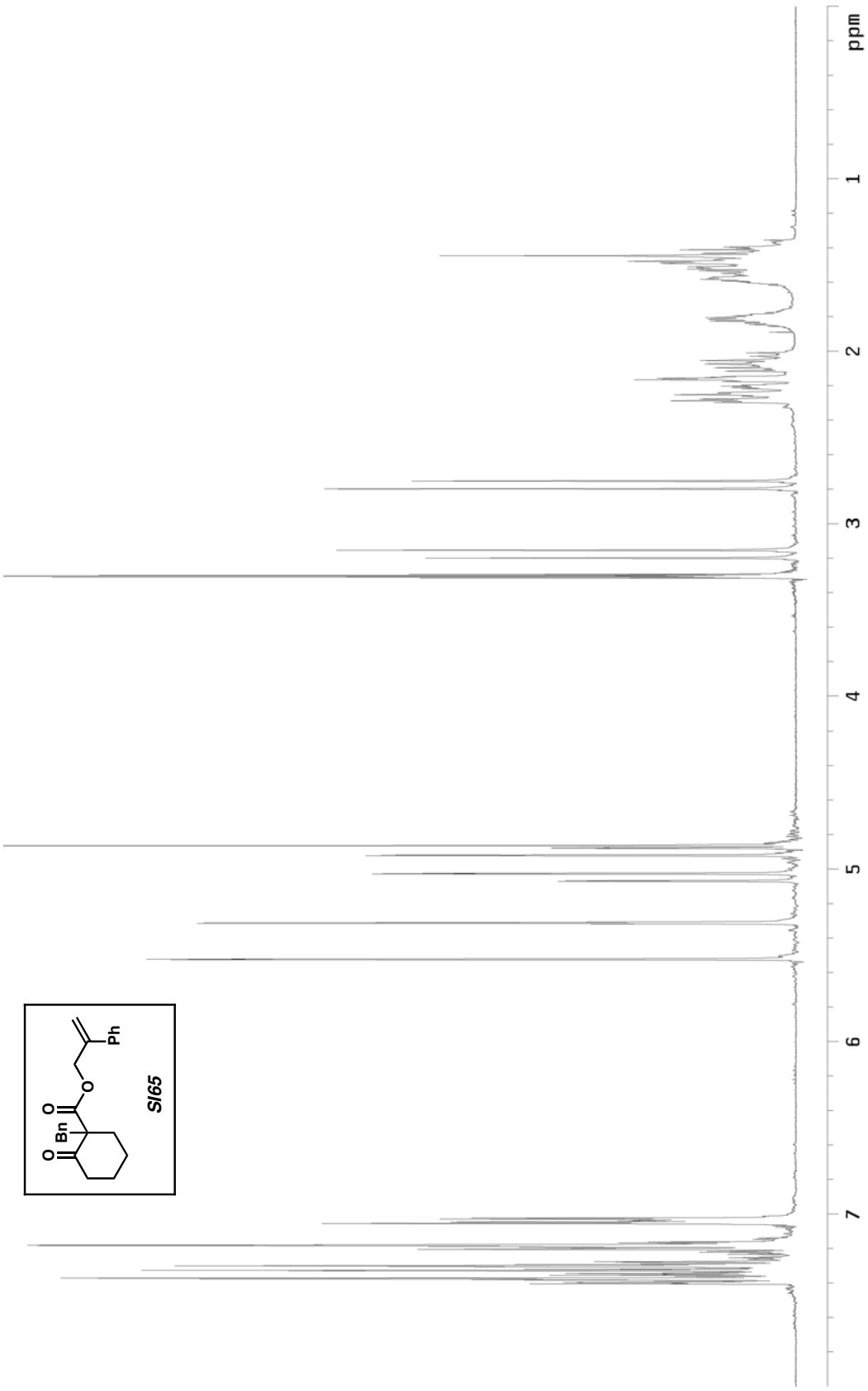
^{13}C NMR of compound **SI61** (75 MHz, $CDCl_3$)



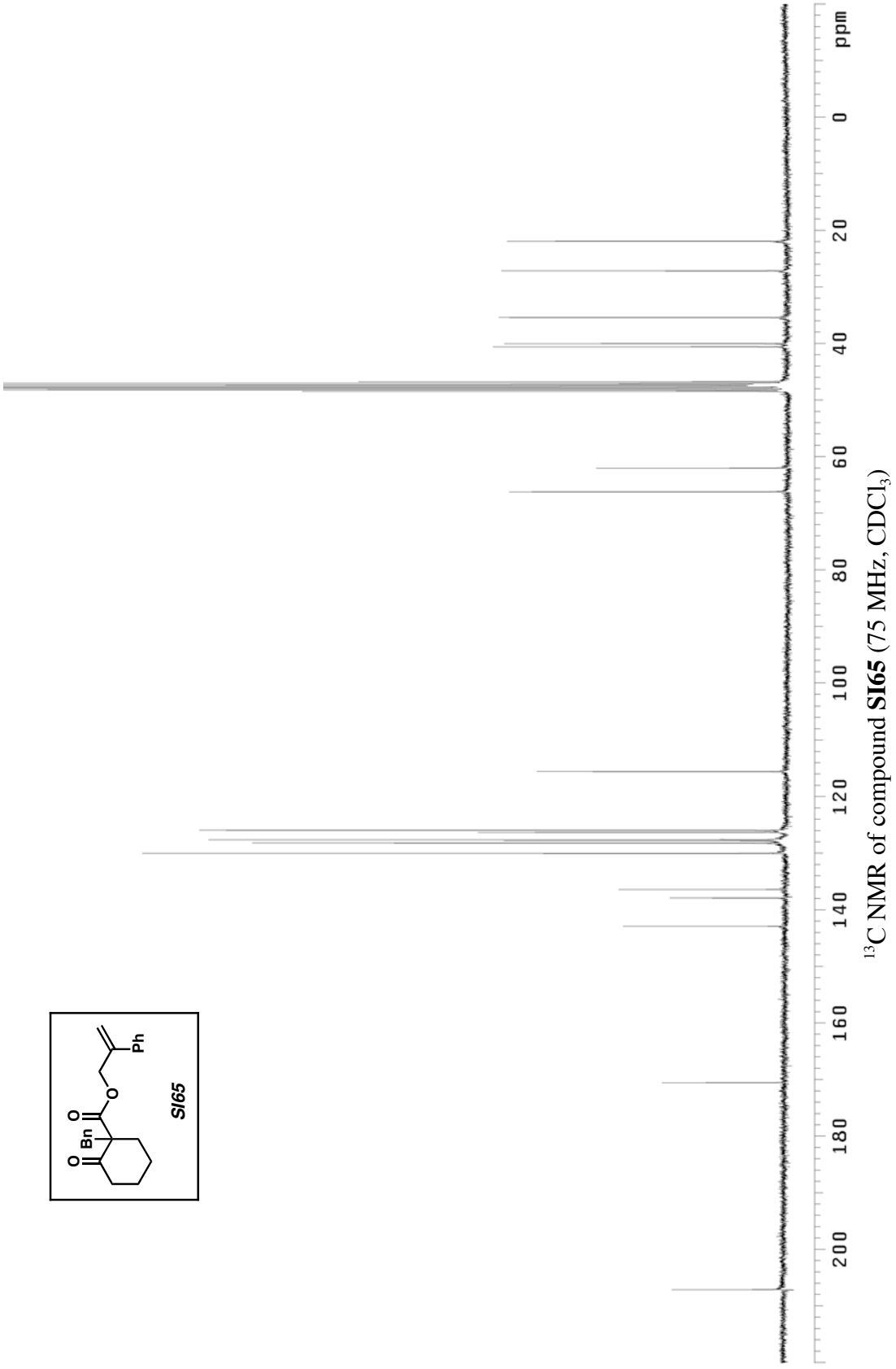
^{1}H NMR of compound **SI62** (300 MHz, $CDCl_3$)



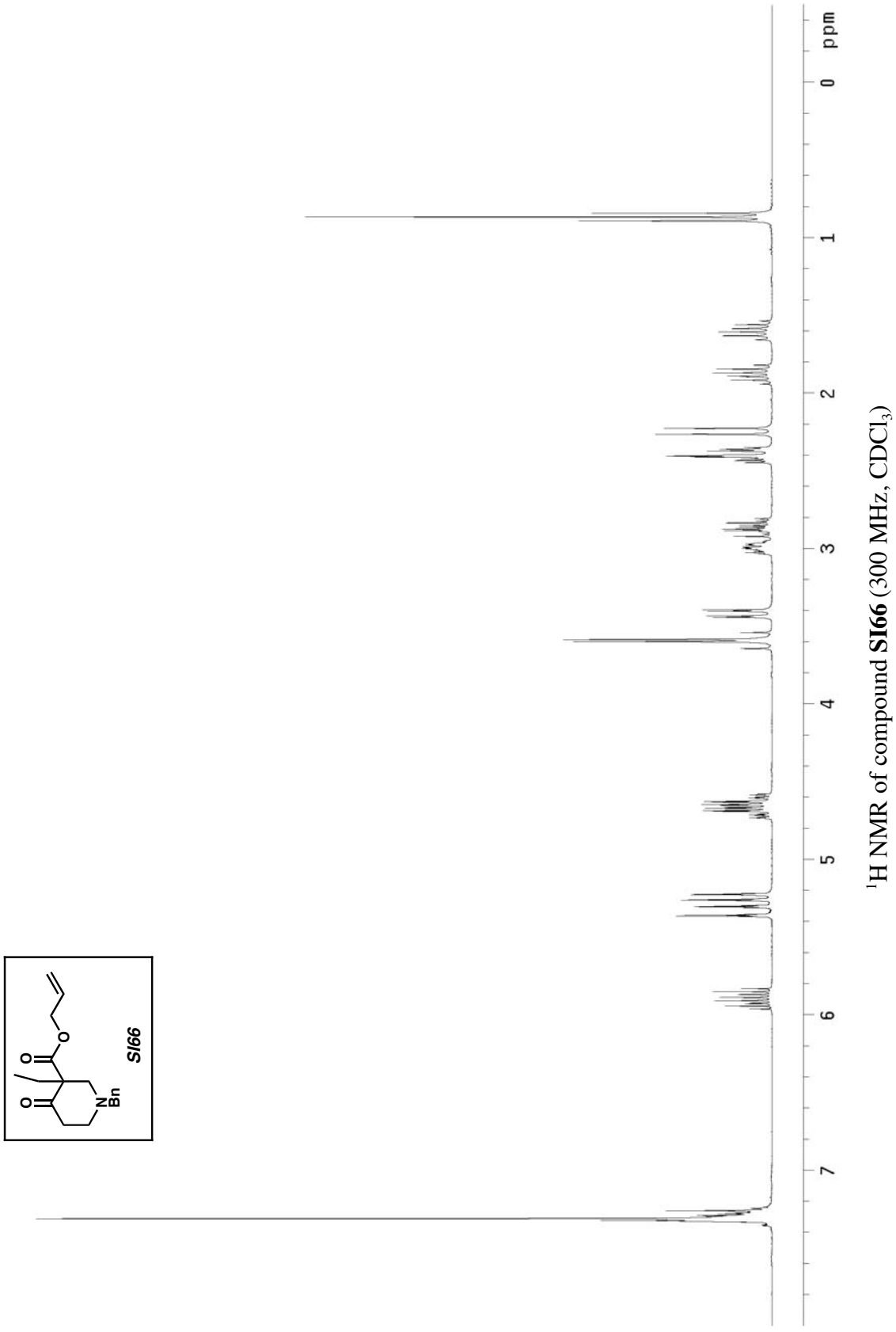
^{13}C NMR of compound **SI62** (75 MHz, $CDCl_3$)



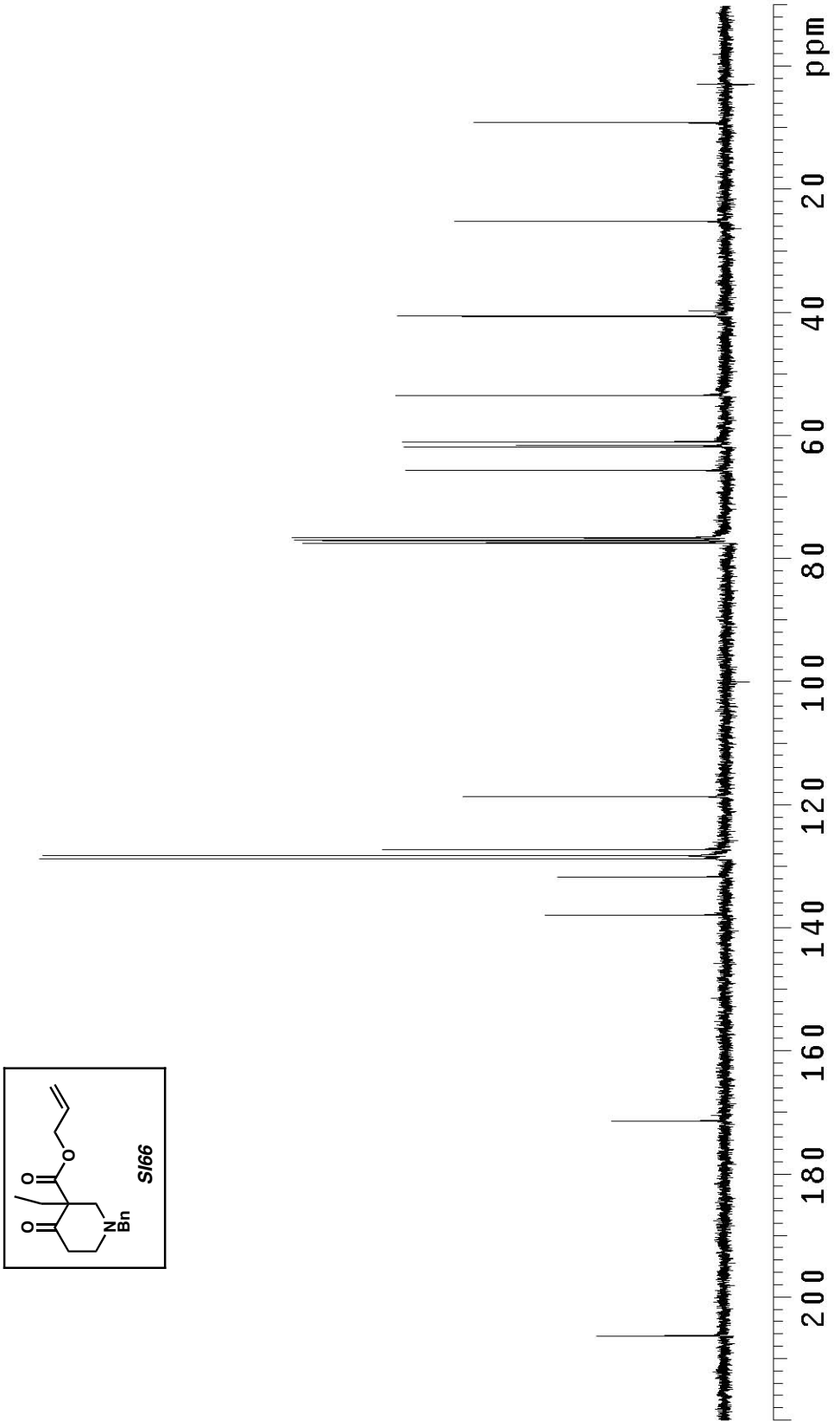
^{1}H NMR of compound **SI65** (300 MHz, $CDCl_3$)



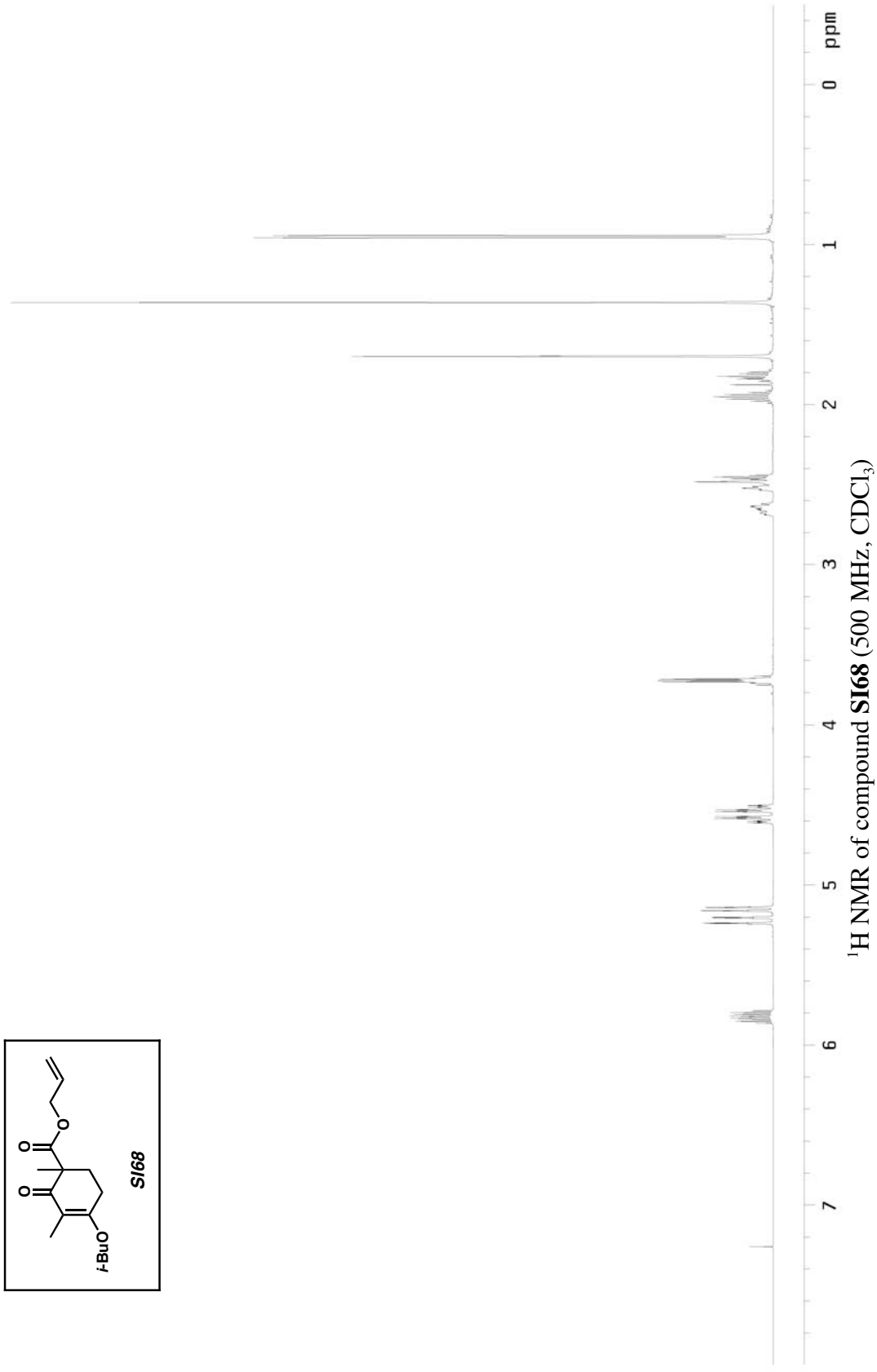
^{13}C NMR of compound **SI65** (75 MHz, $CDCl_3$)



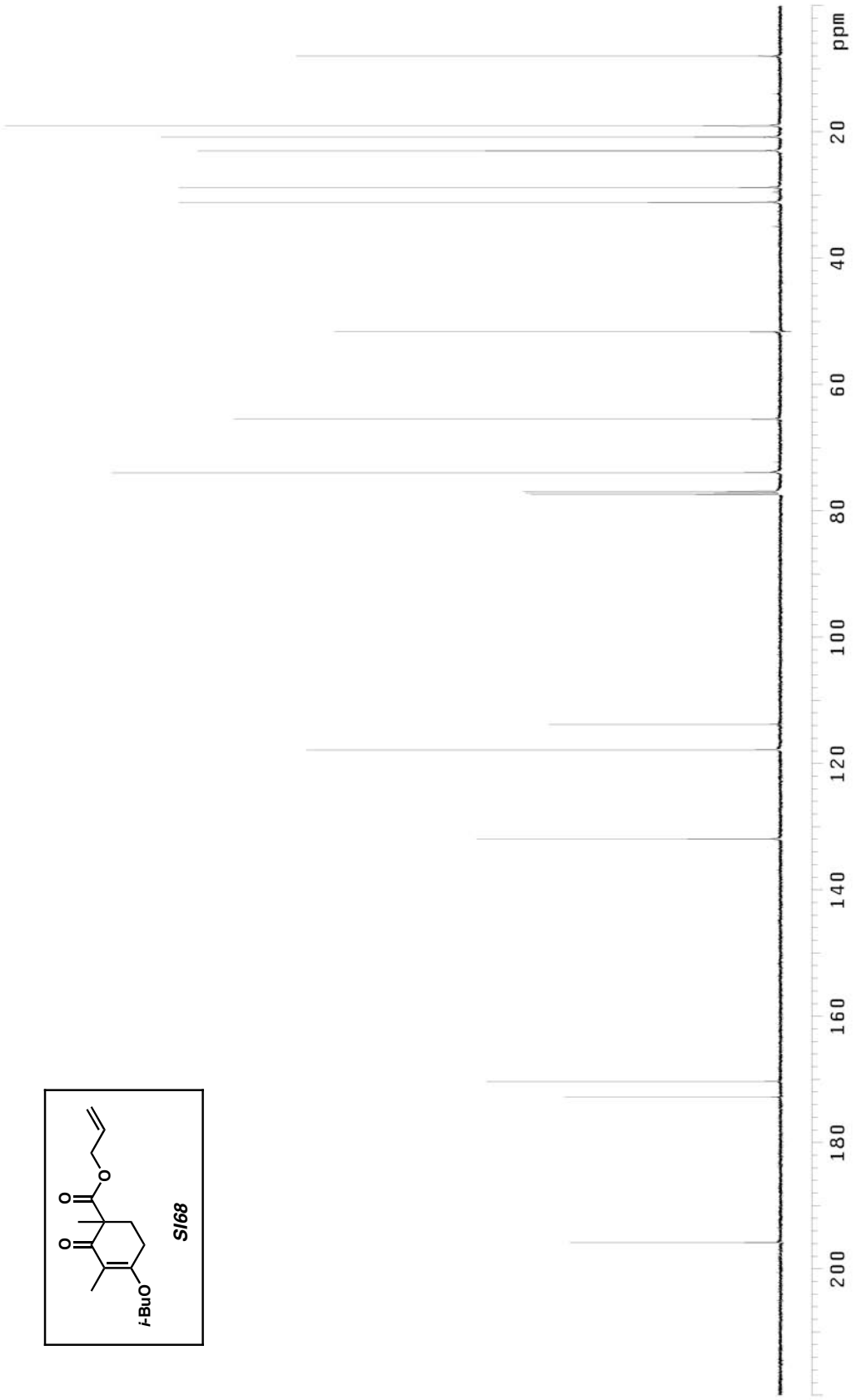
^{1}H NMR of compound **SI66** (300 MHz, $CDCl_3$)



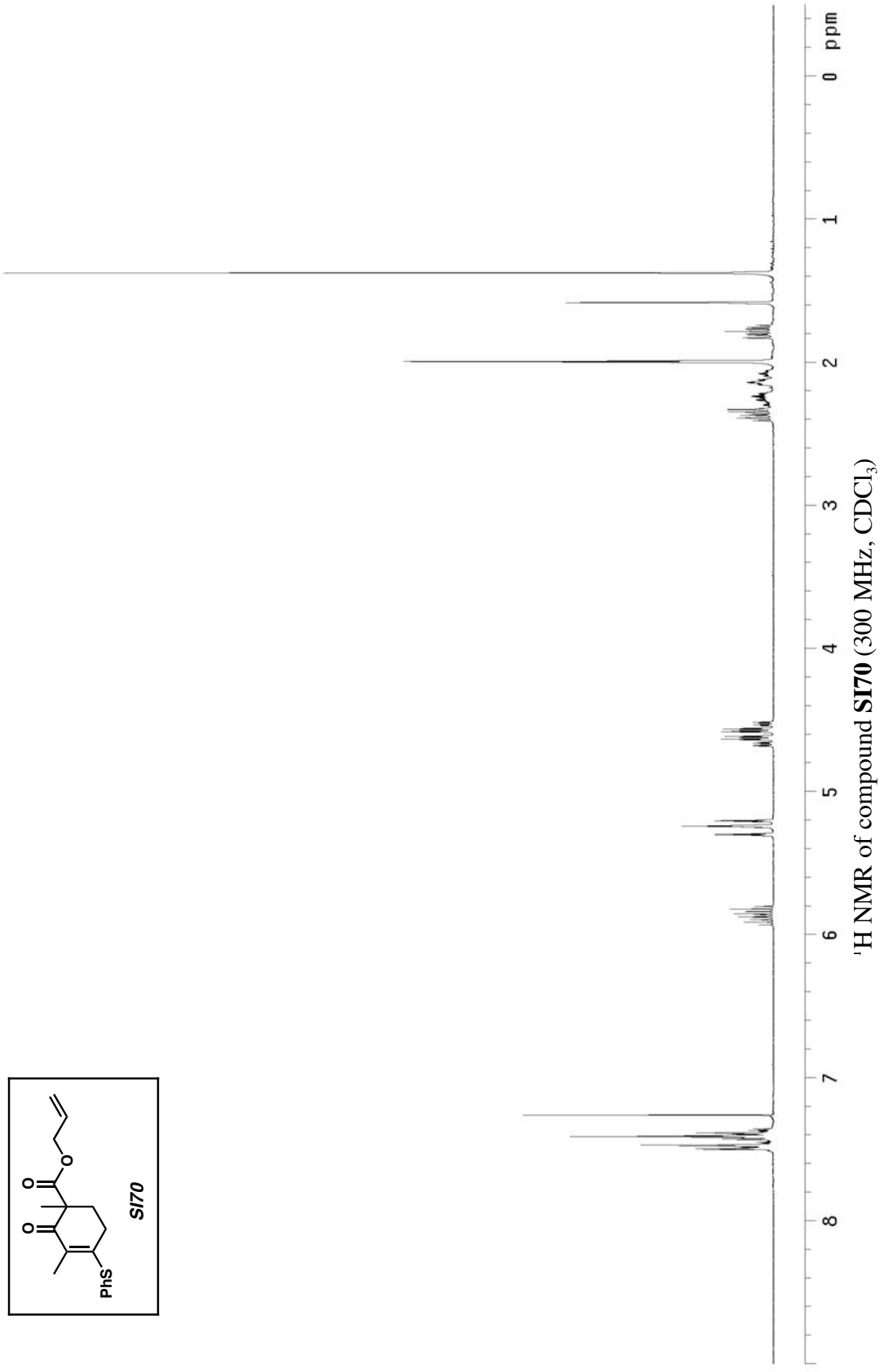
^{13}C NMR of compound **SI66** (75 MHz, $CDCl_3$)



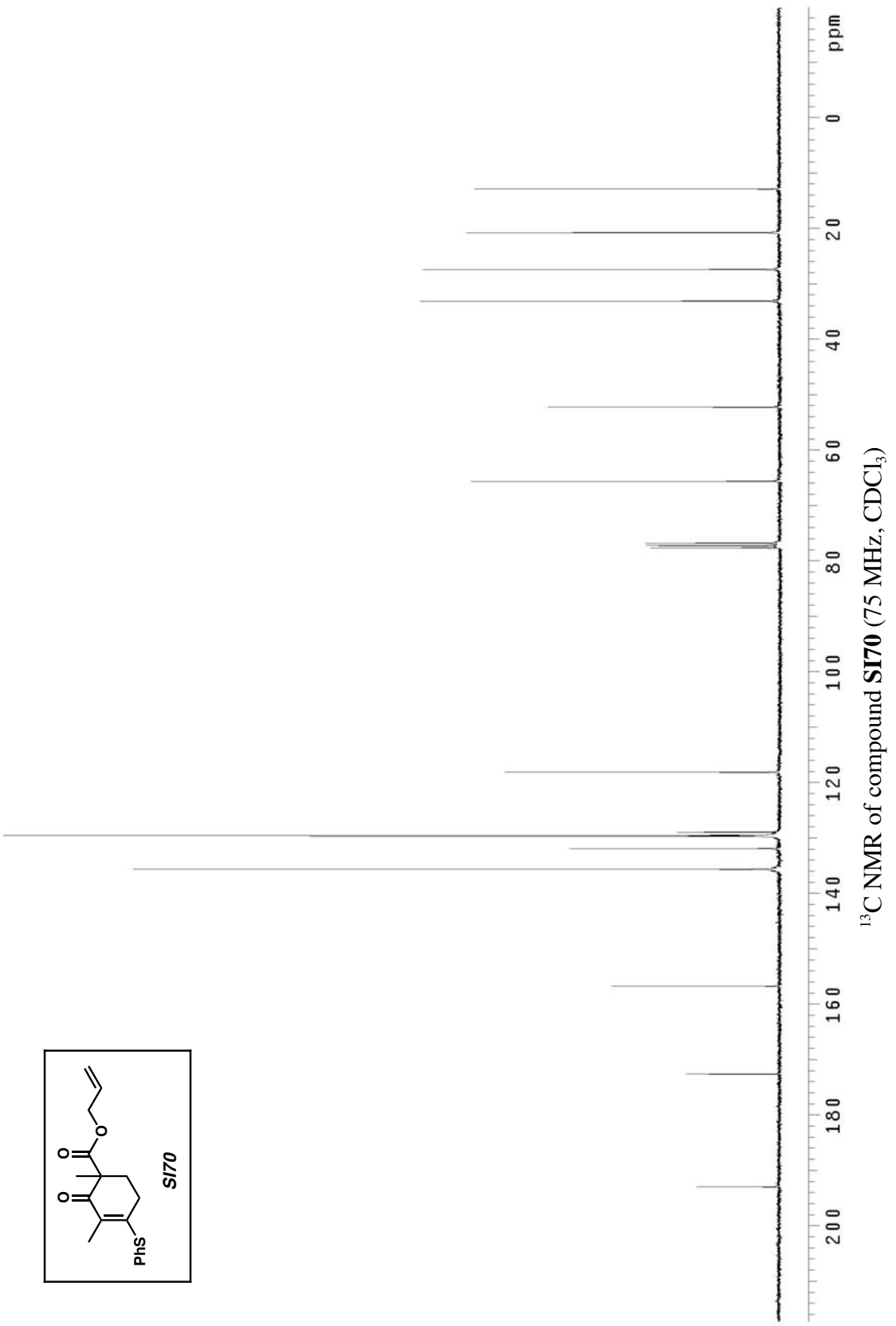
^{1}H NMR of compound **SI68** (500 MHz, $CDCl_3$)



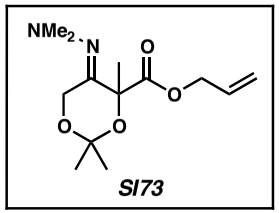
^{13}C NMR of compound **SI68** (126 MHz, $CDCl_3$)



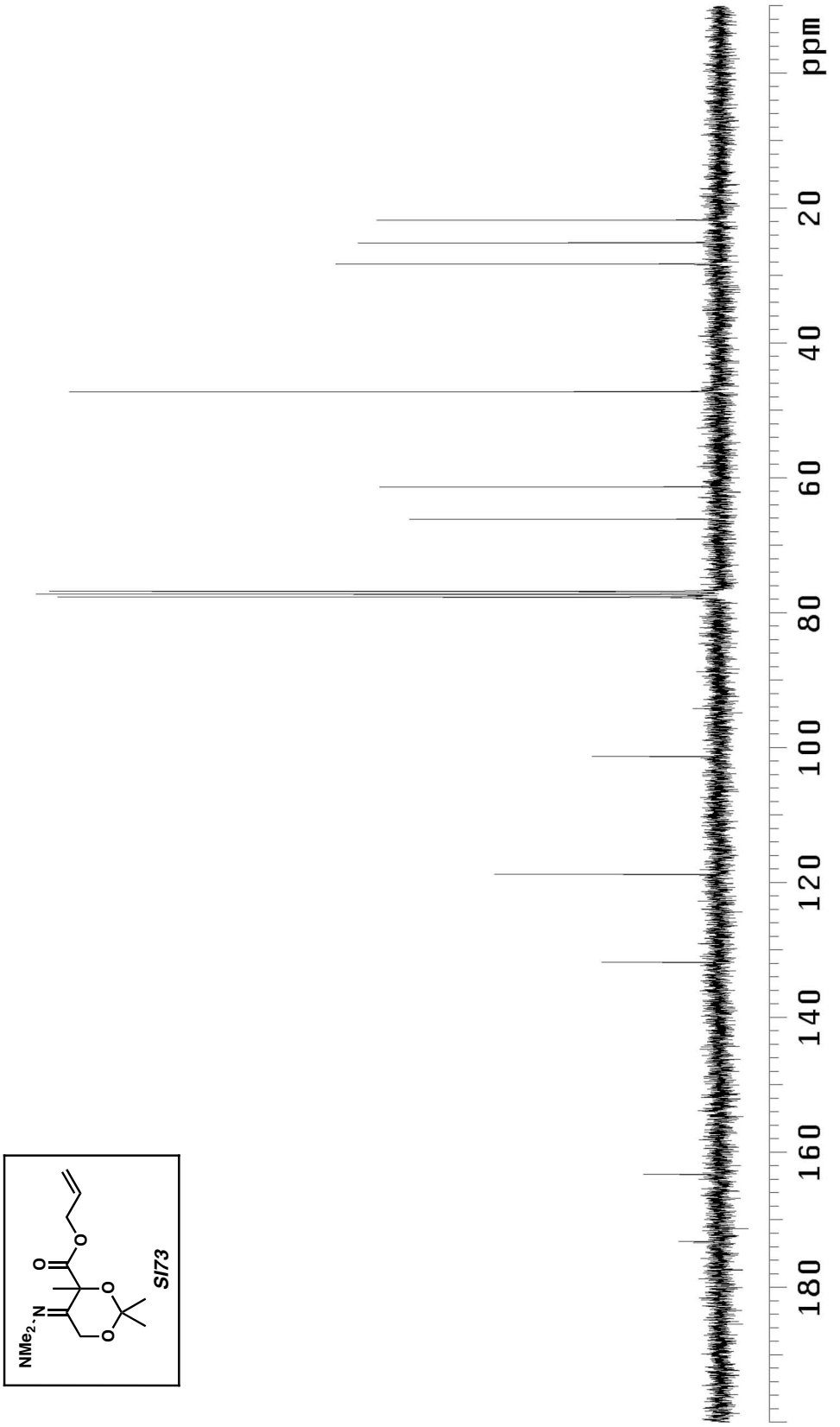
^{1}H NMR of compound **SI70** (300 MHz, $CDCl_3$)



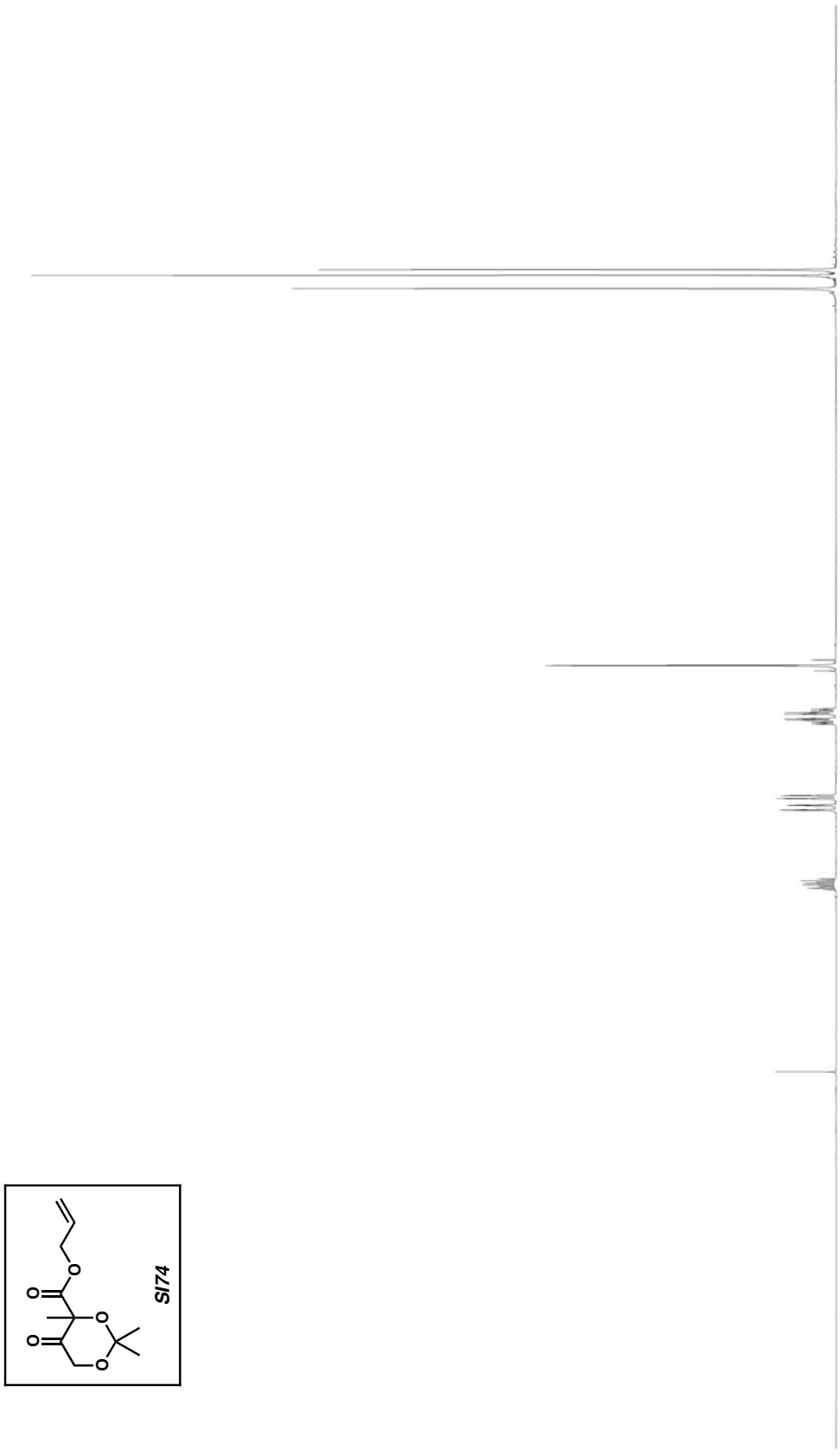
^{13}C NMR of compound **SI70** (75 MHz, $CDCl_3$)



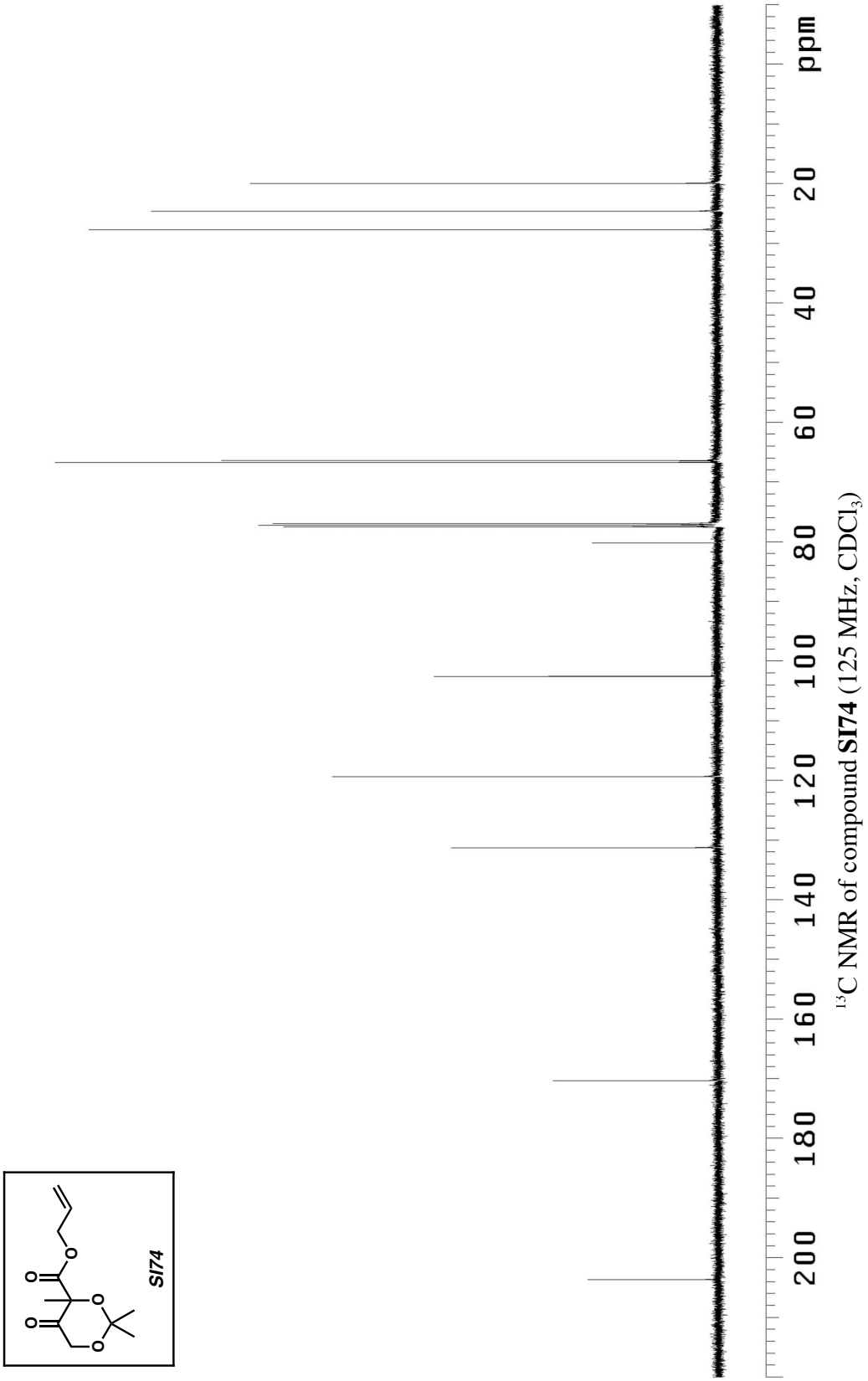
^{1}H NMR of compound **SI73** (300 MHz, $CDCl_3$)



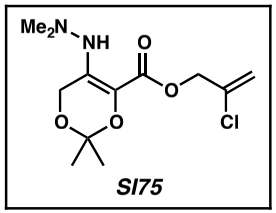
^{13}C NMR of compound **SI73** (75 MHz, $CDCl_3$)



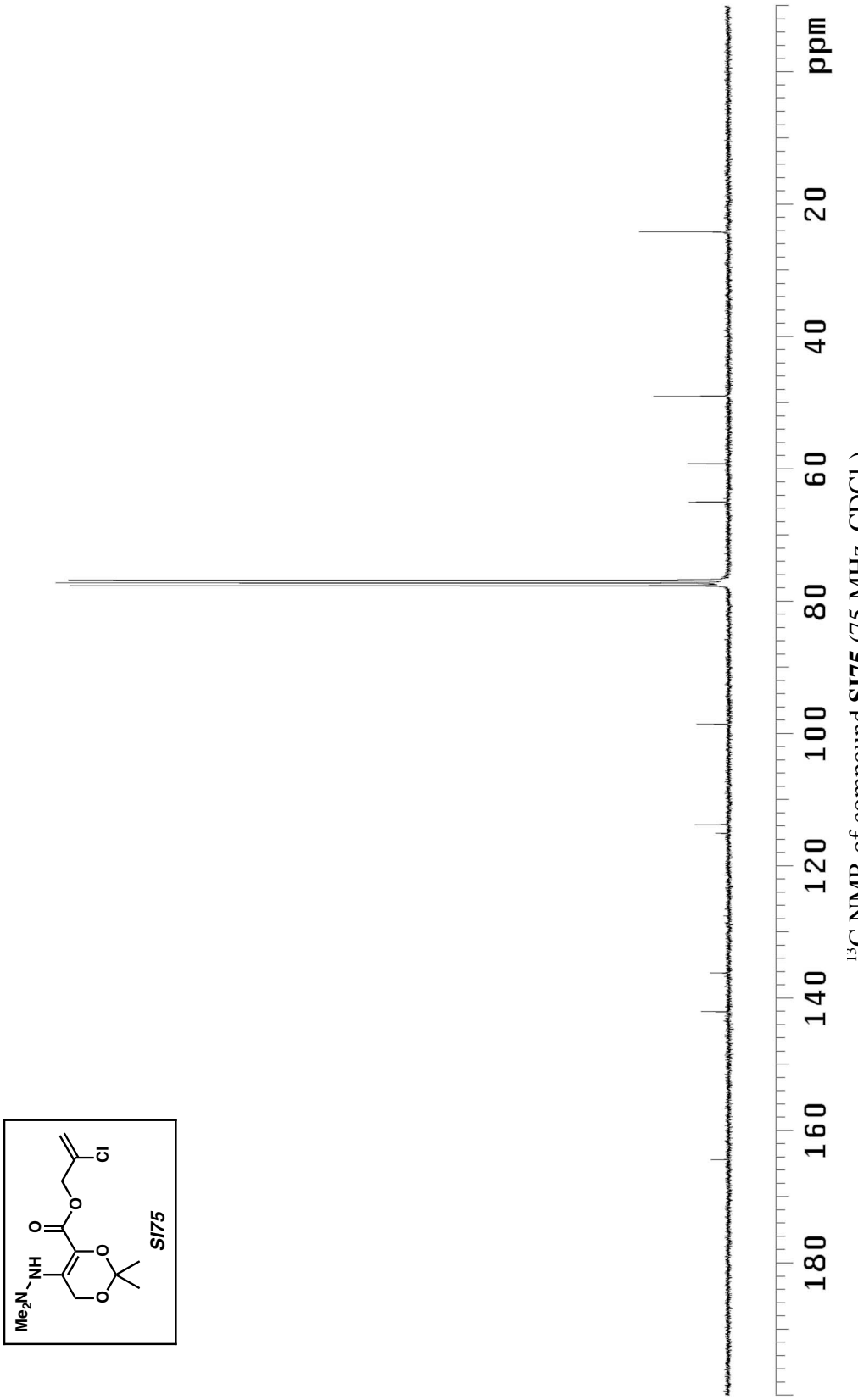
^{1}H NMR of compound **SI74** (500 MHz, $CDCl_3$)



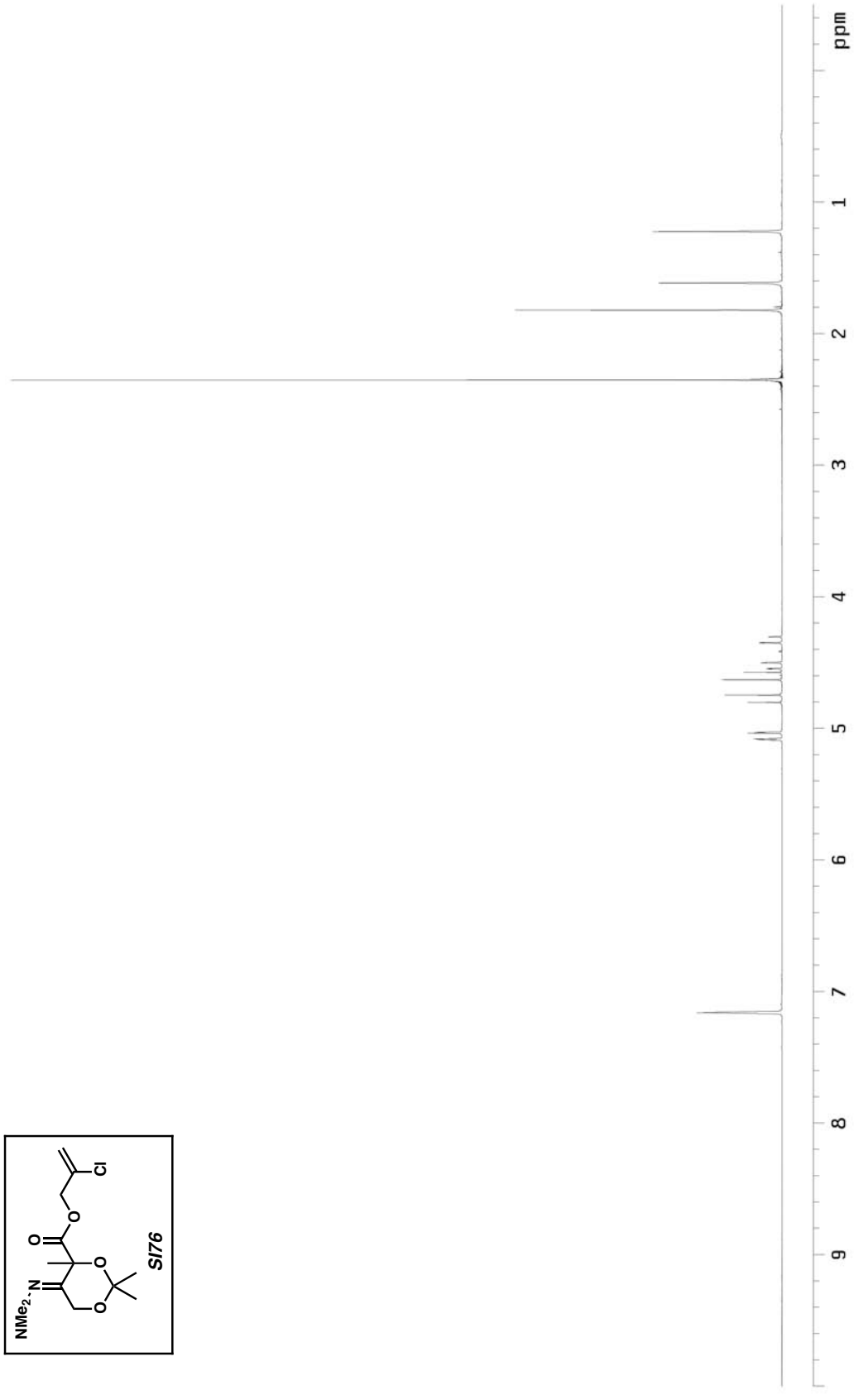
^{13}C NMR of compound **SI74** (125 MHz, $CDCl_3$)



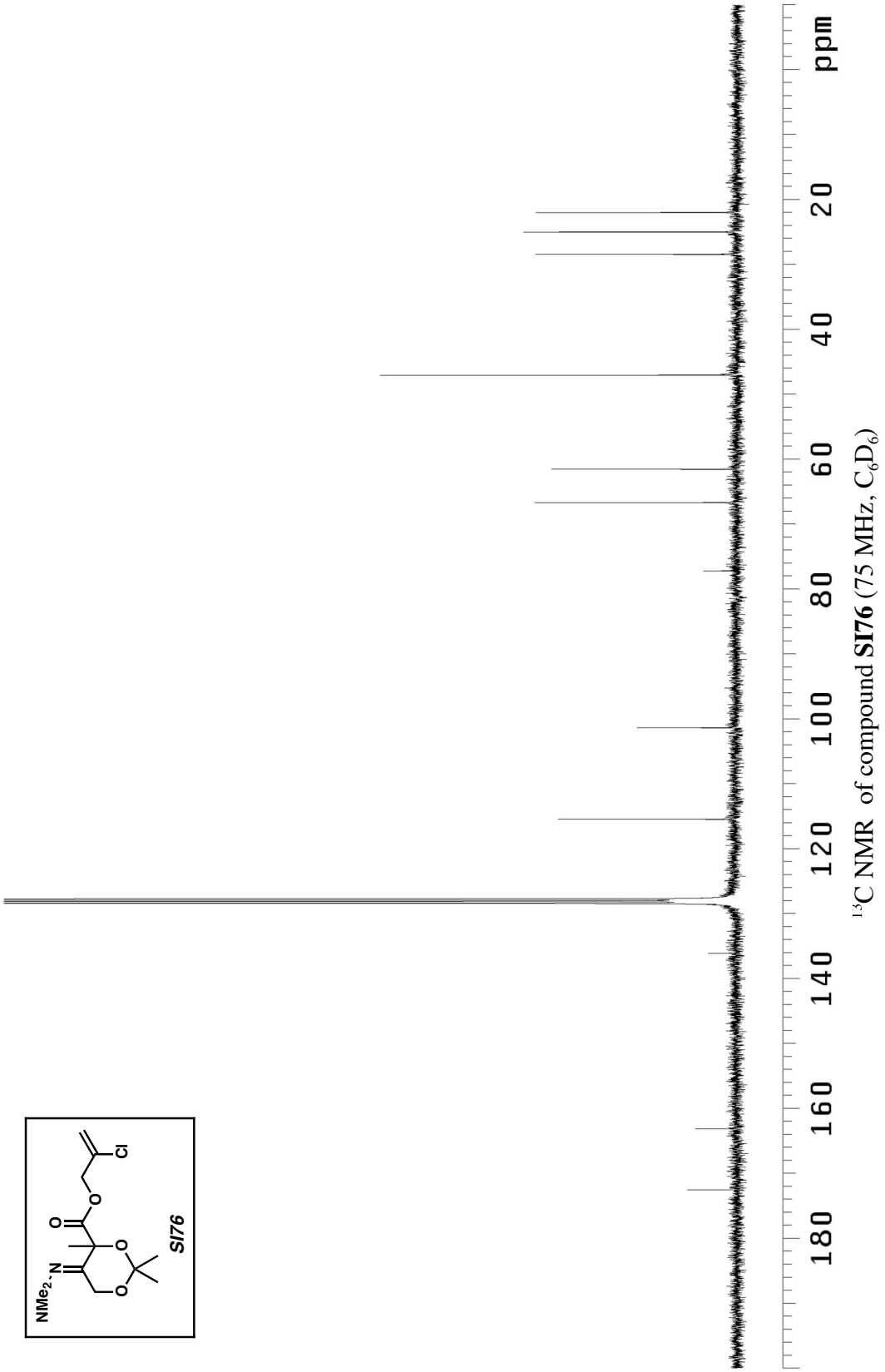
^{1}H NMR of compound **SI75** (300 MHz, $CDCl_3$)



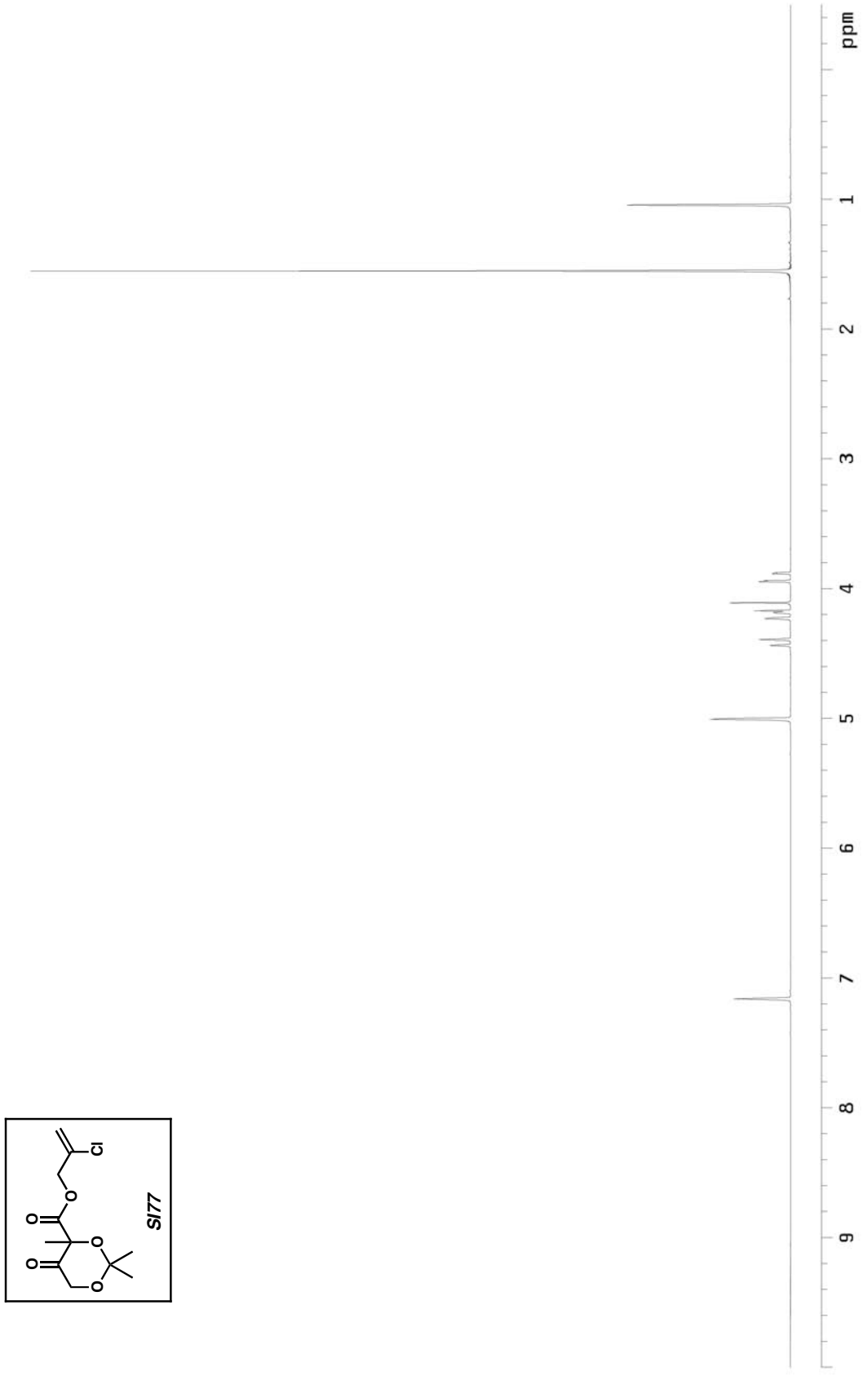
^{13}C NMR of compound **SI75** (75 MHz, $CDCl_3$)



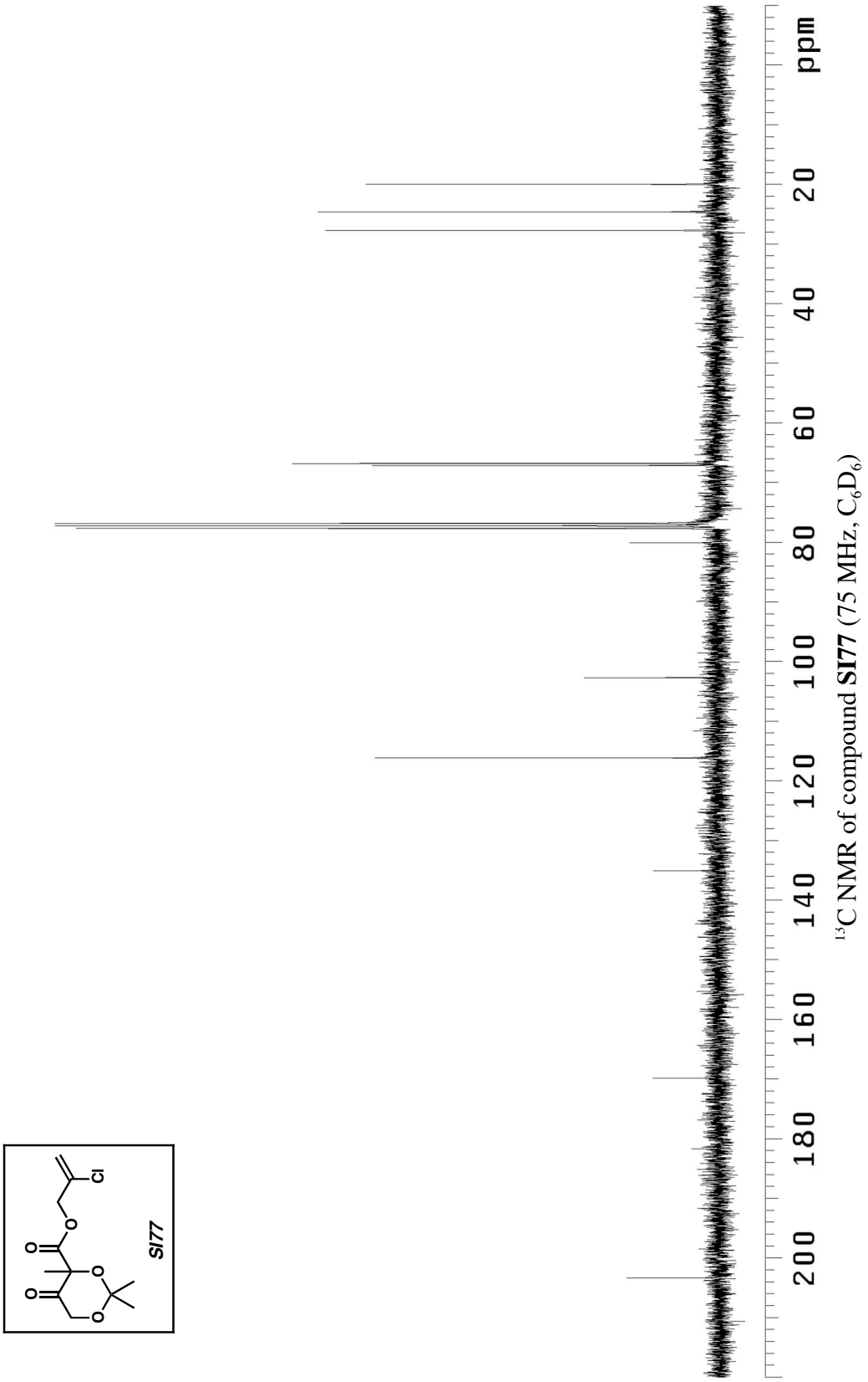
^{1}H NMR of compound **SI76** (300 MHz, C_6D_6)



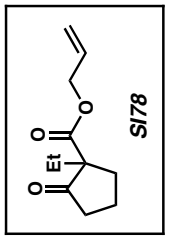
^{13}C NMR of compound **SI76** (75 MHz, C_6D_6)



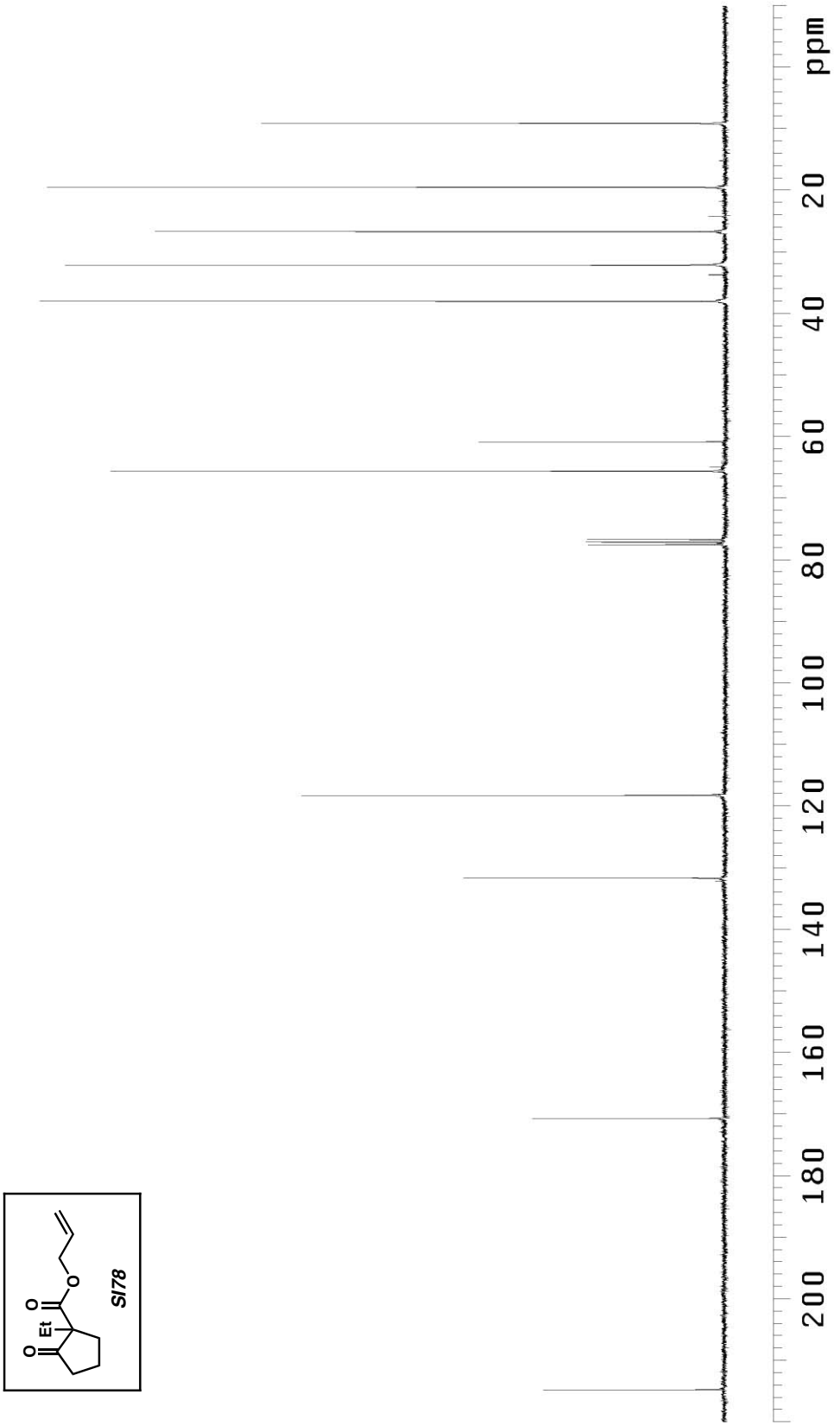
^{1}H NMR of compound **SI77** (300 MHz, C_6D_6)



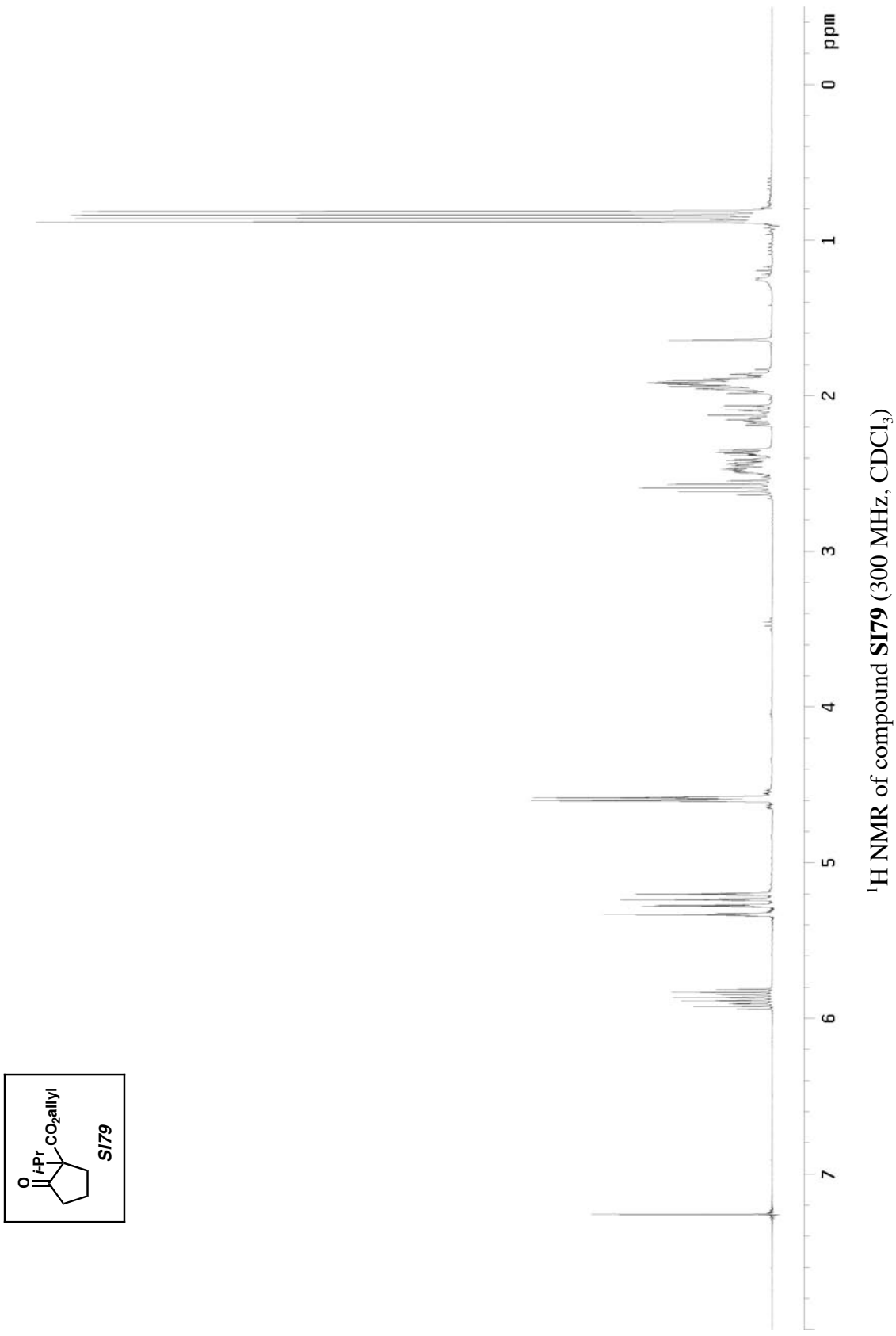
^{13}C NMR of compound **SI77** (75 MHz, C_6D_6)



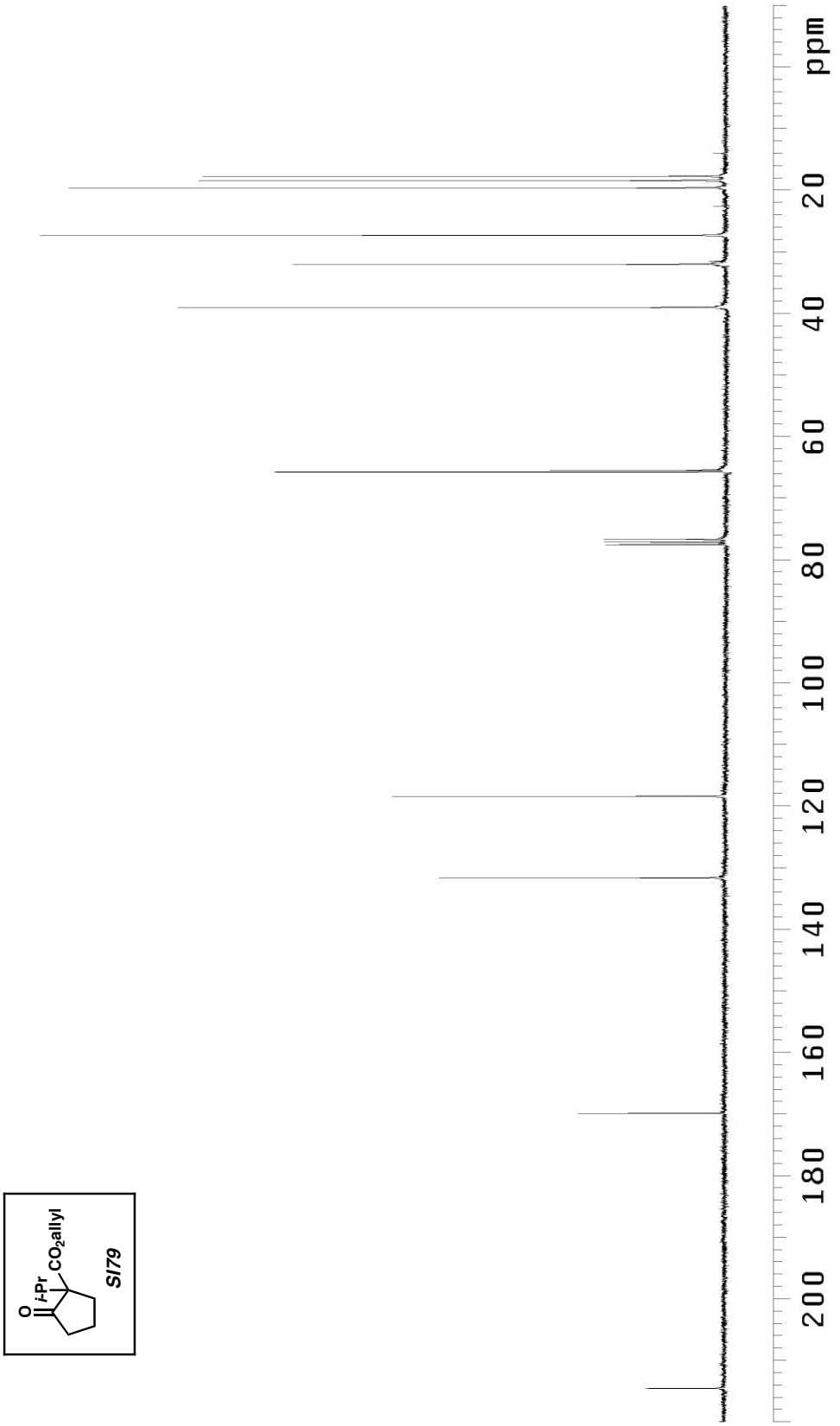
^{1}H NMR of compound **SI78** (300 MHz, $CDCl_3$)



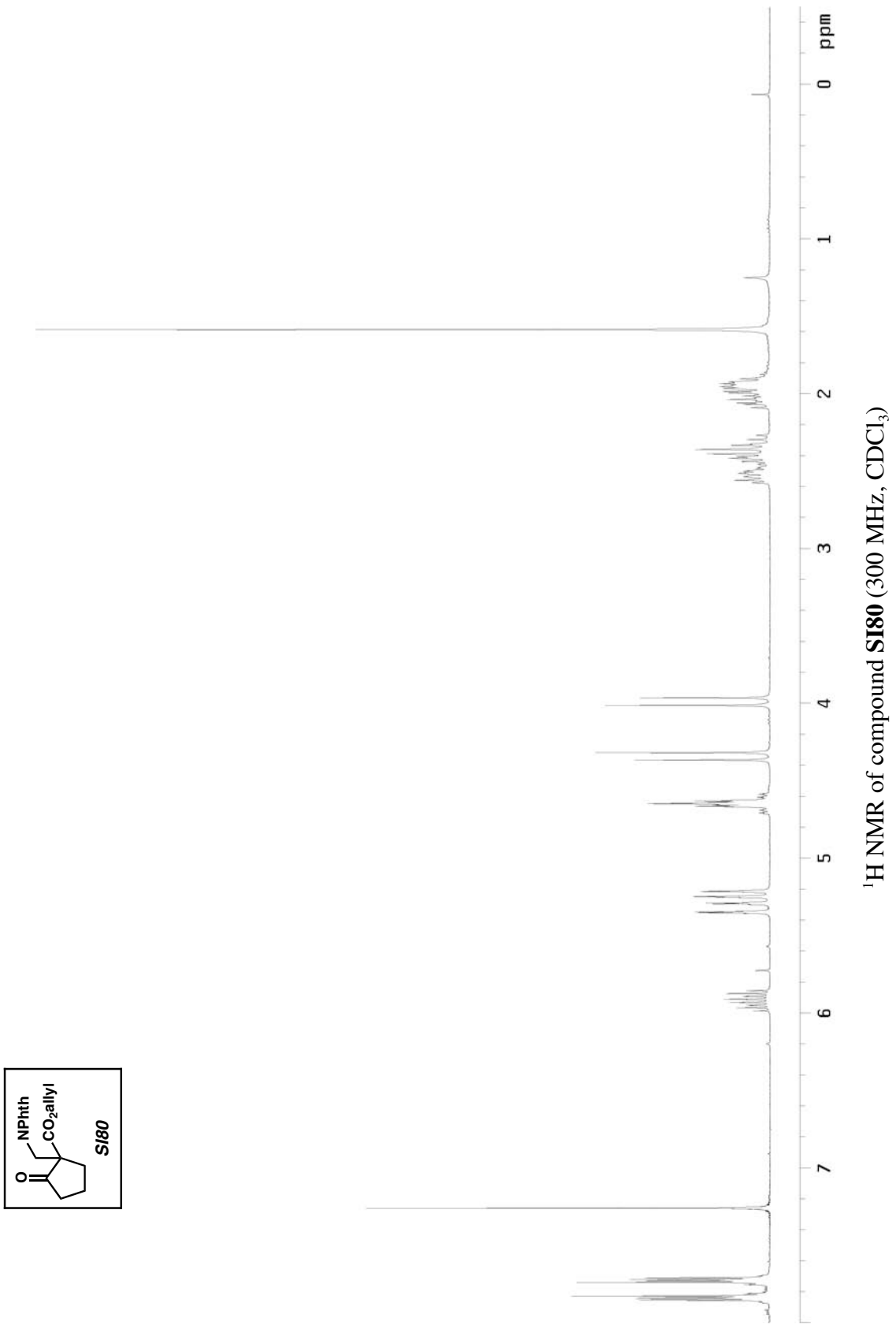
^{13}C NMR of compound **SI78** (75 MHz, $CDCl_3$)



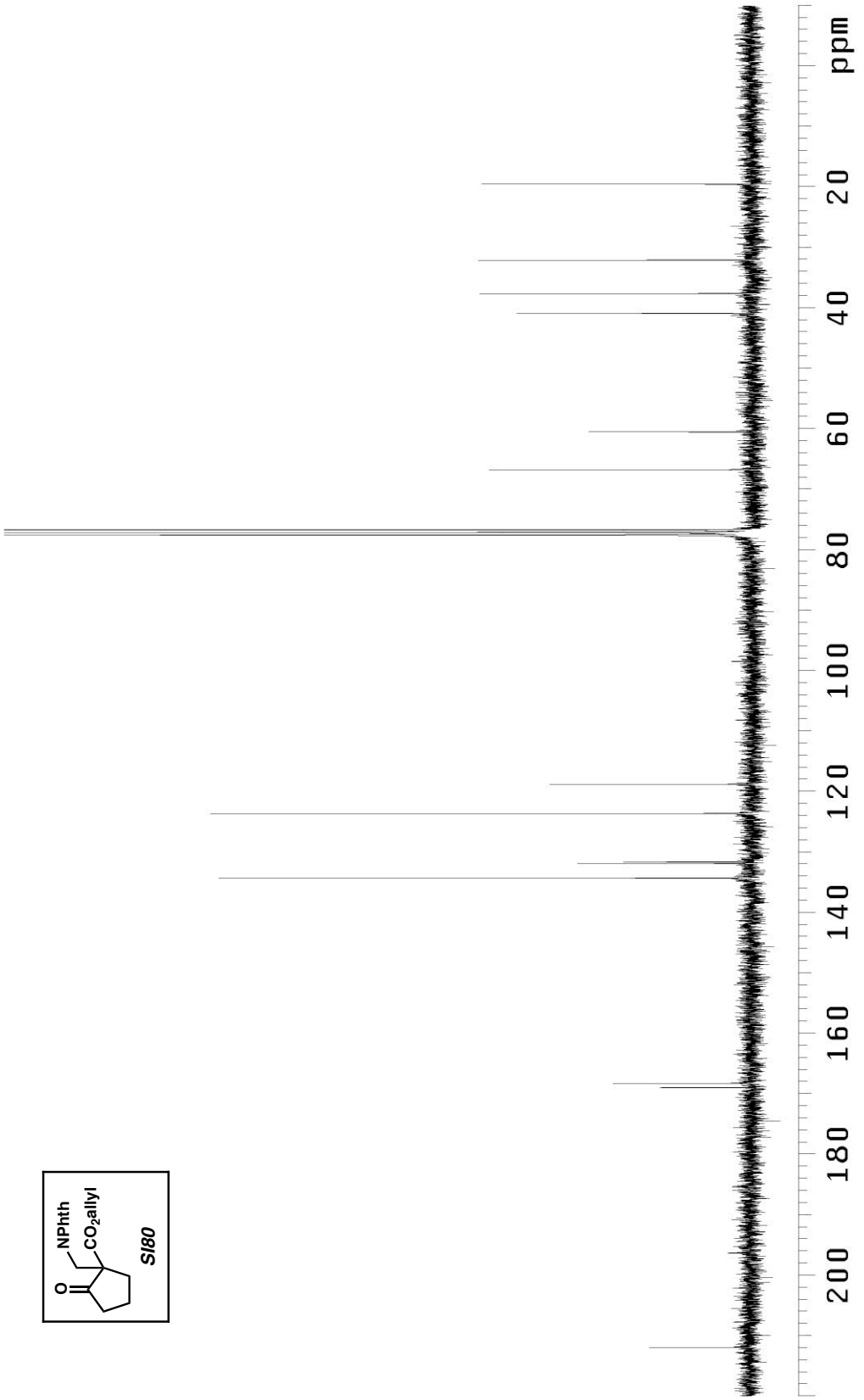
^{1}H NMR of compound **SI79** (300 MHz, $CDCl_3$)



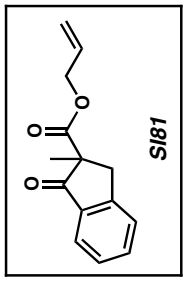
^{13}C NMR of compound **SI79** (75 MHz, $CDCl_3$)



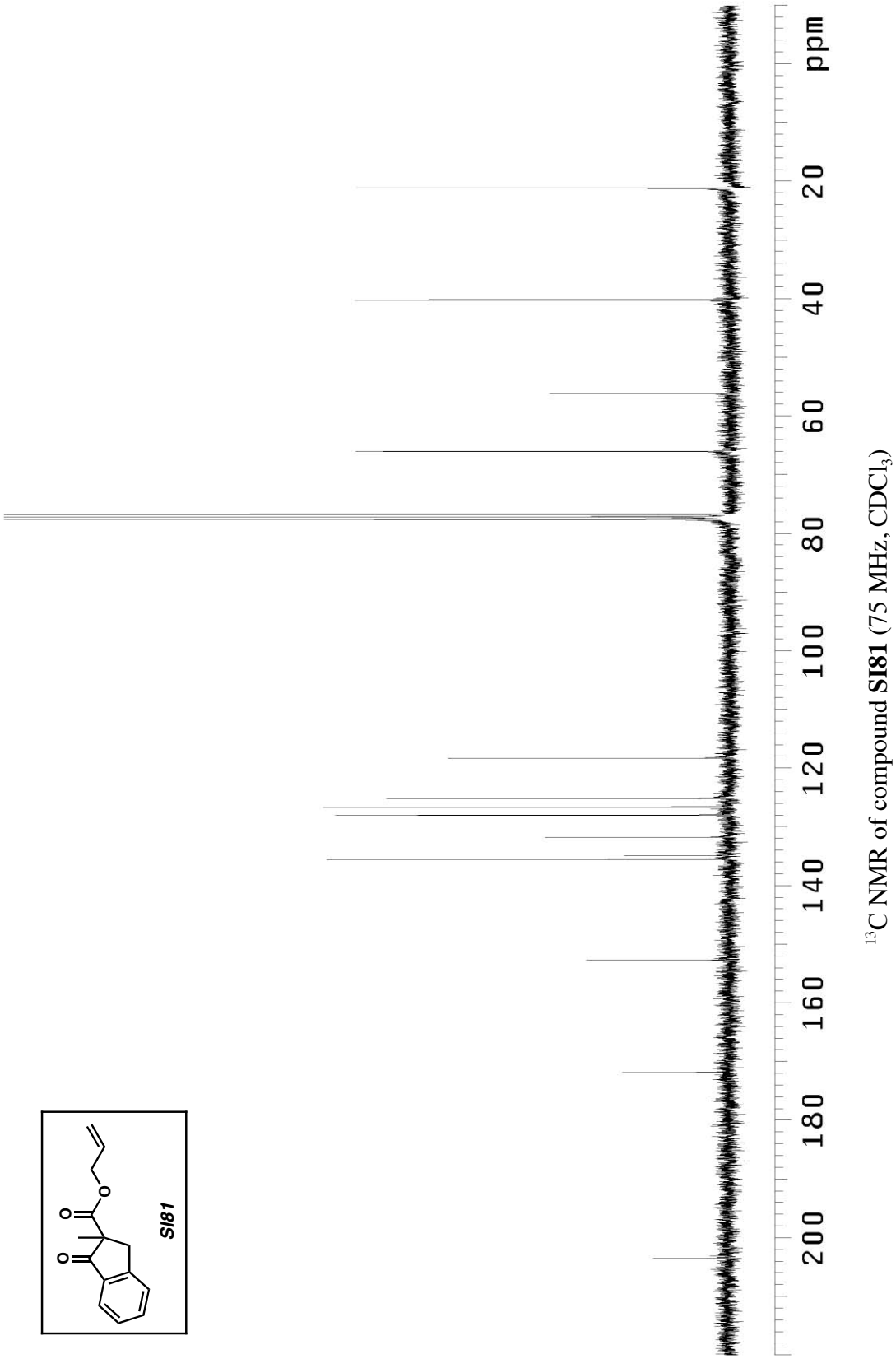
^{1}H NMR of compound **SI80** (300 MHz, $CDCl_3$)



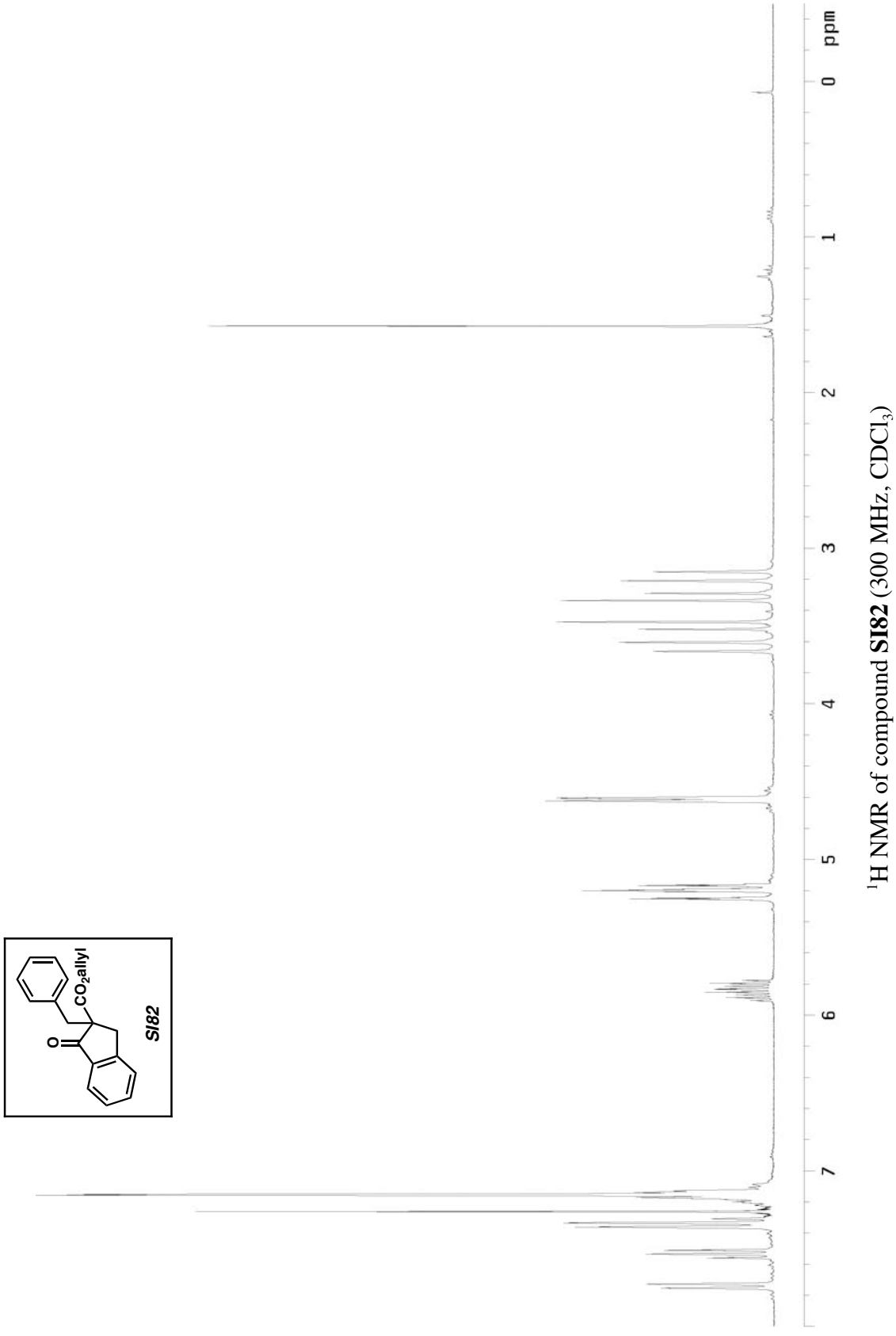
^{13}C NMR of compound **SI80** (75 MHz, $CDCl_3$)



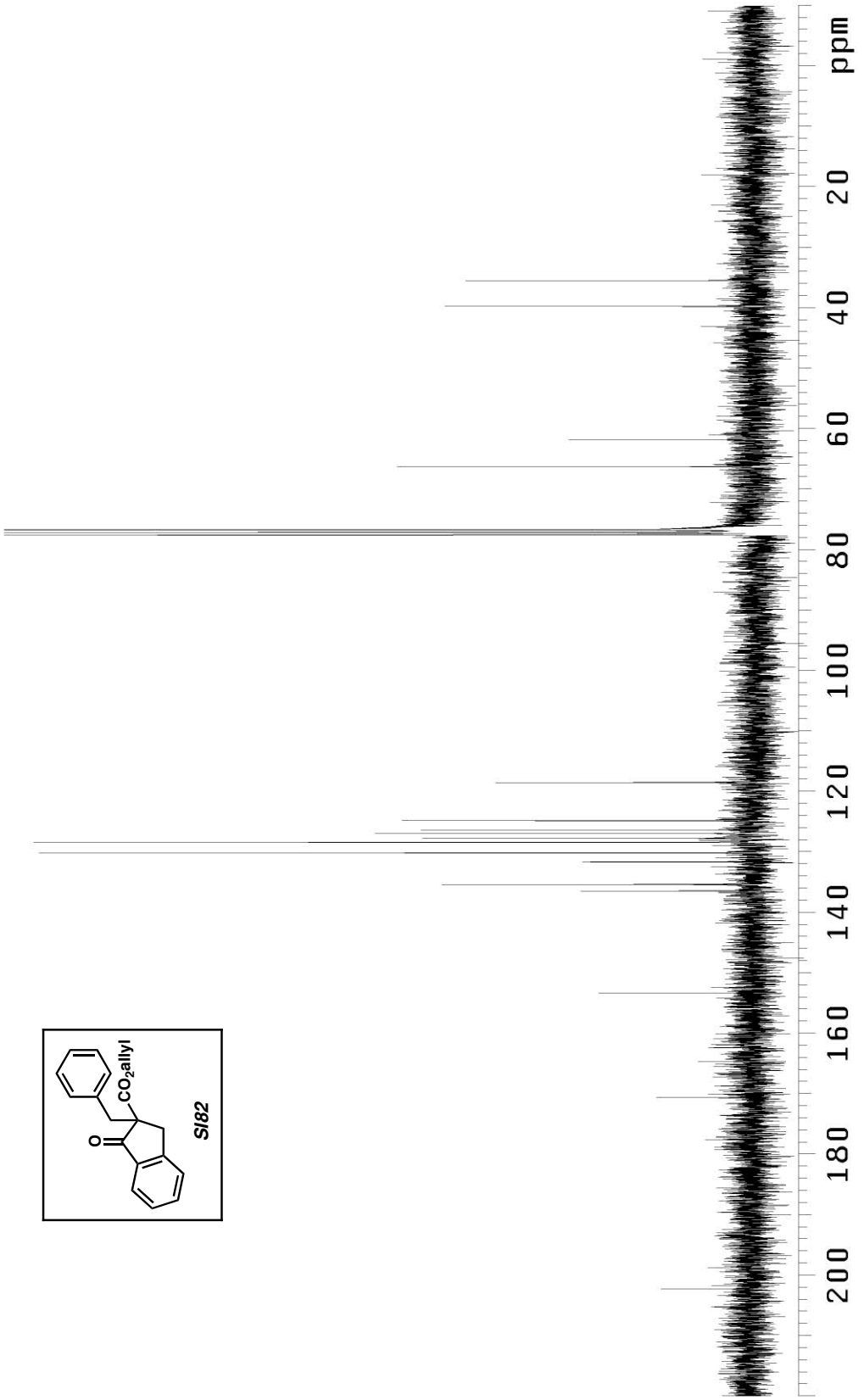
^{1}H NMR of compound **SI81** (300 MHz, $CDCl_3$)



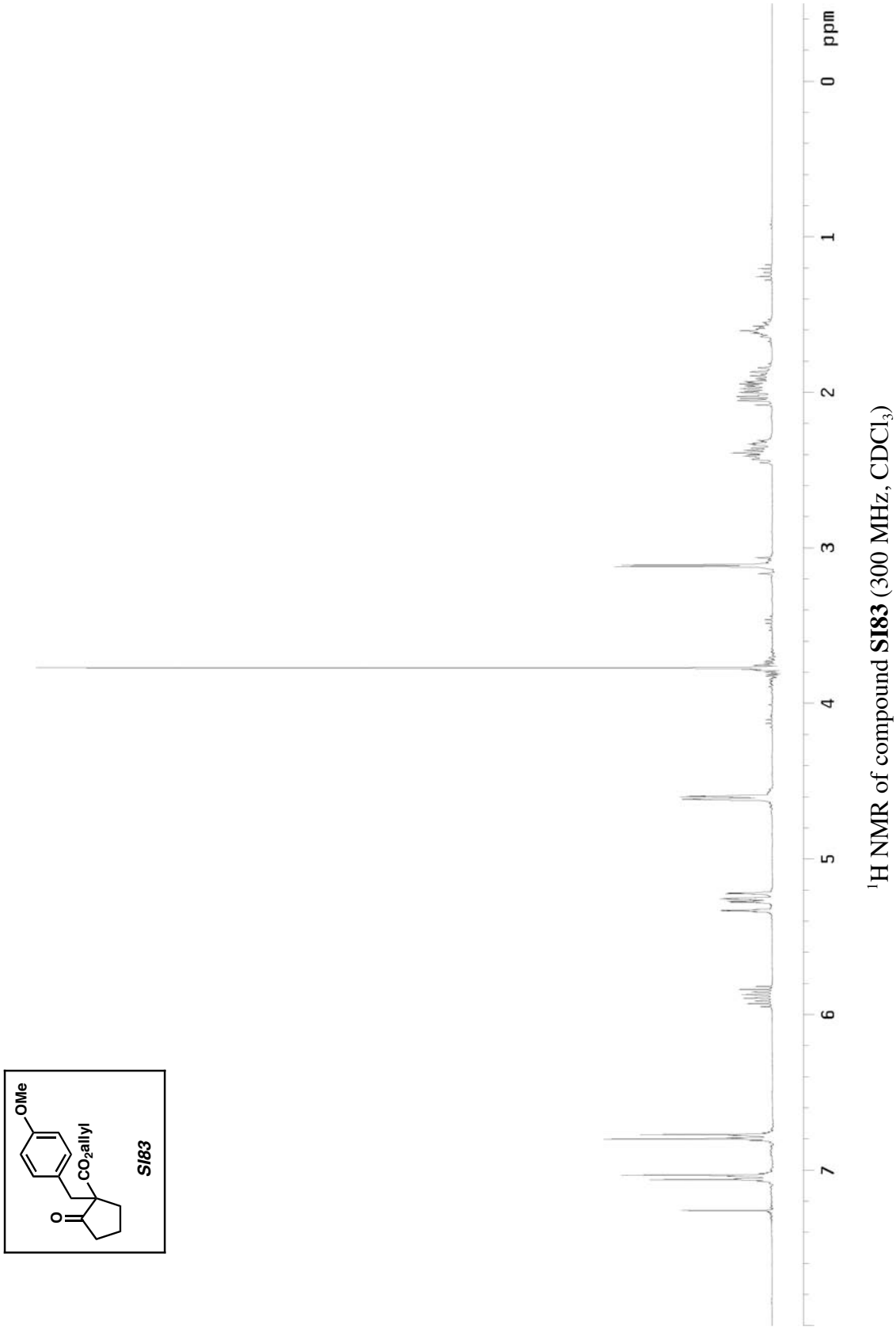
^{13}C NMR of compound **SI81** (75 MHz, $CDCl_3$)



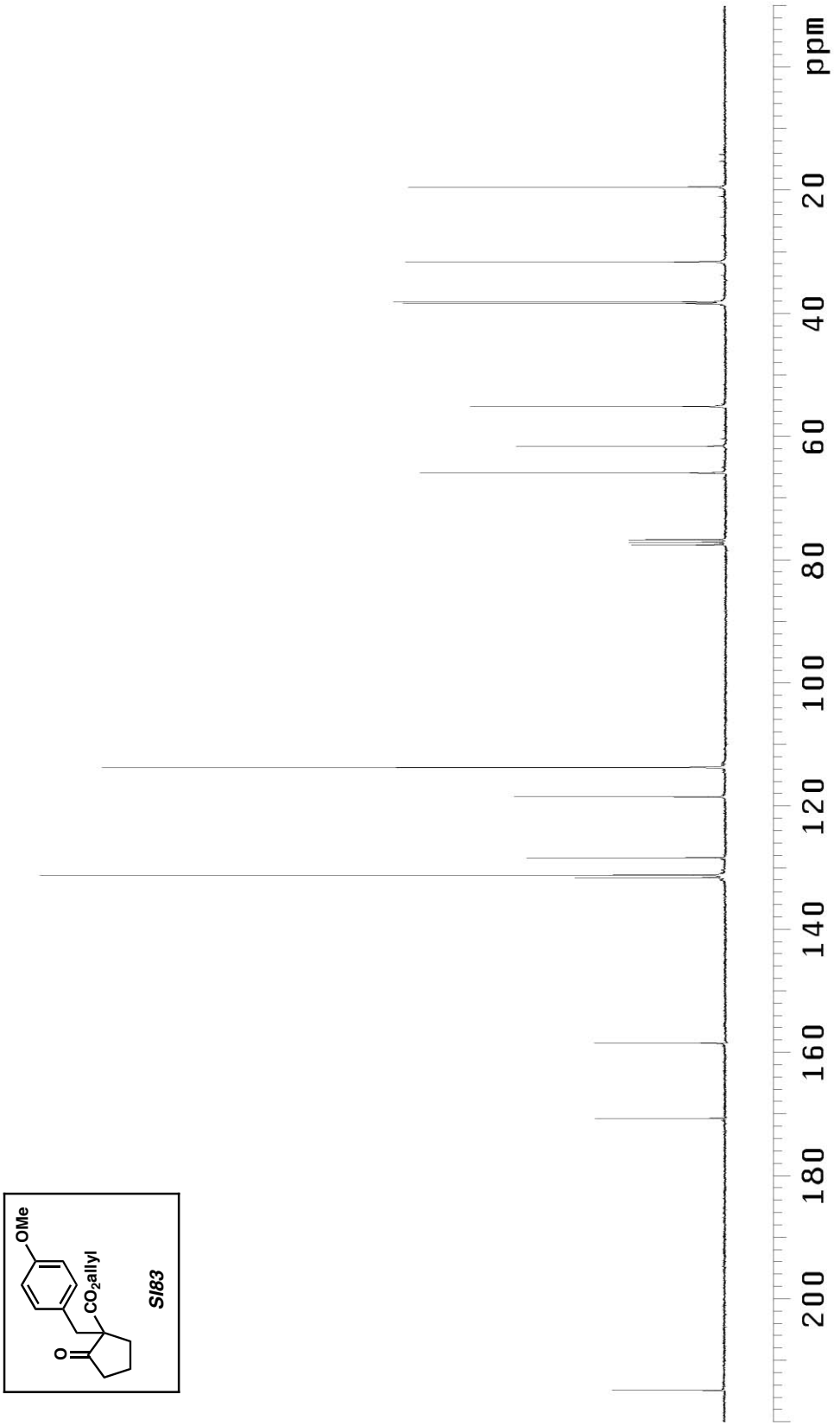
^{1}H NMR of compound **SI82** (300 MHz, $CDCl_3$)



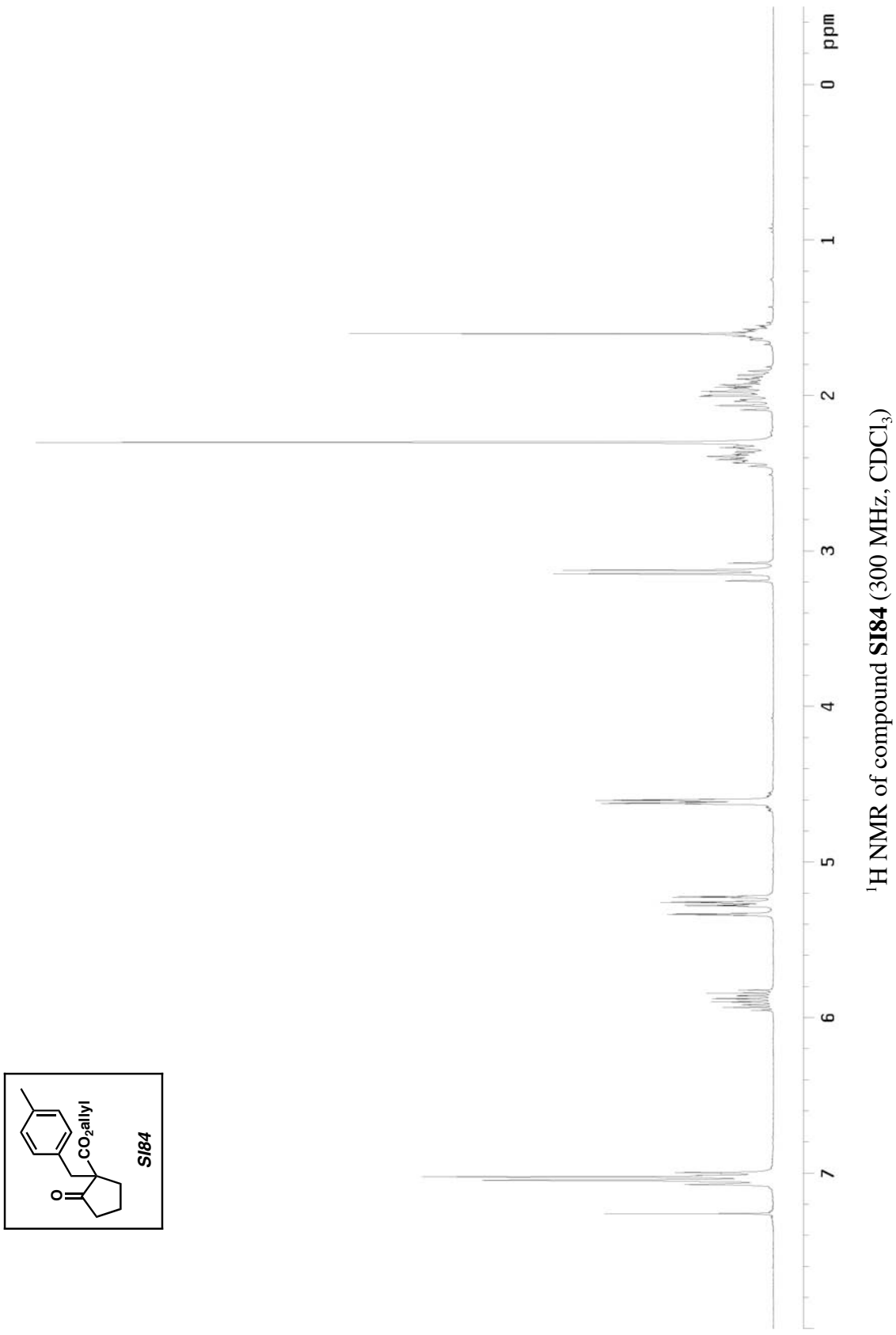
^{13}C NMR of compound **SI82** (75 MHz, $CDCl_3$)



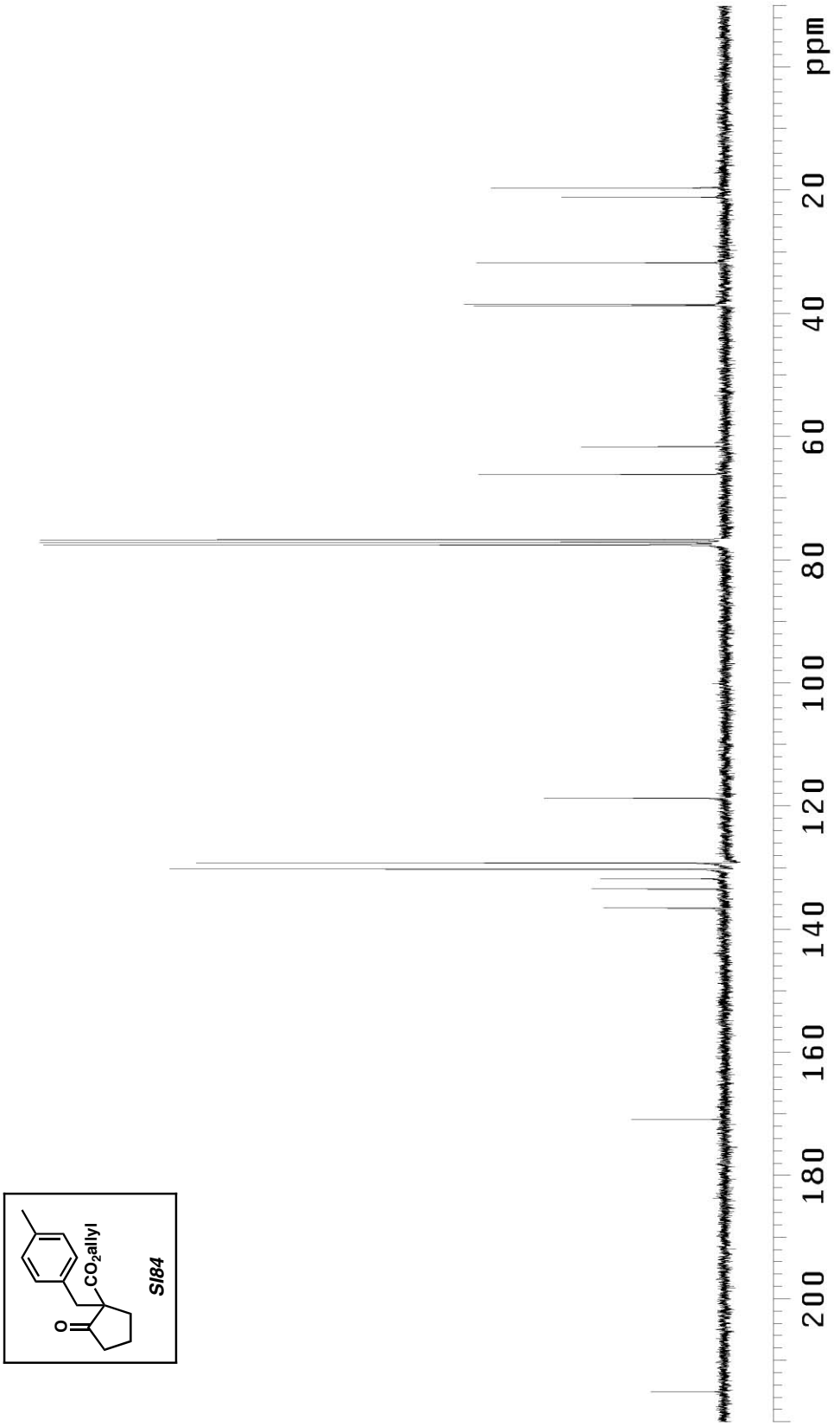
^{1}H NMR of compound **SI83** (300 MHz, $CDCl_3$)



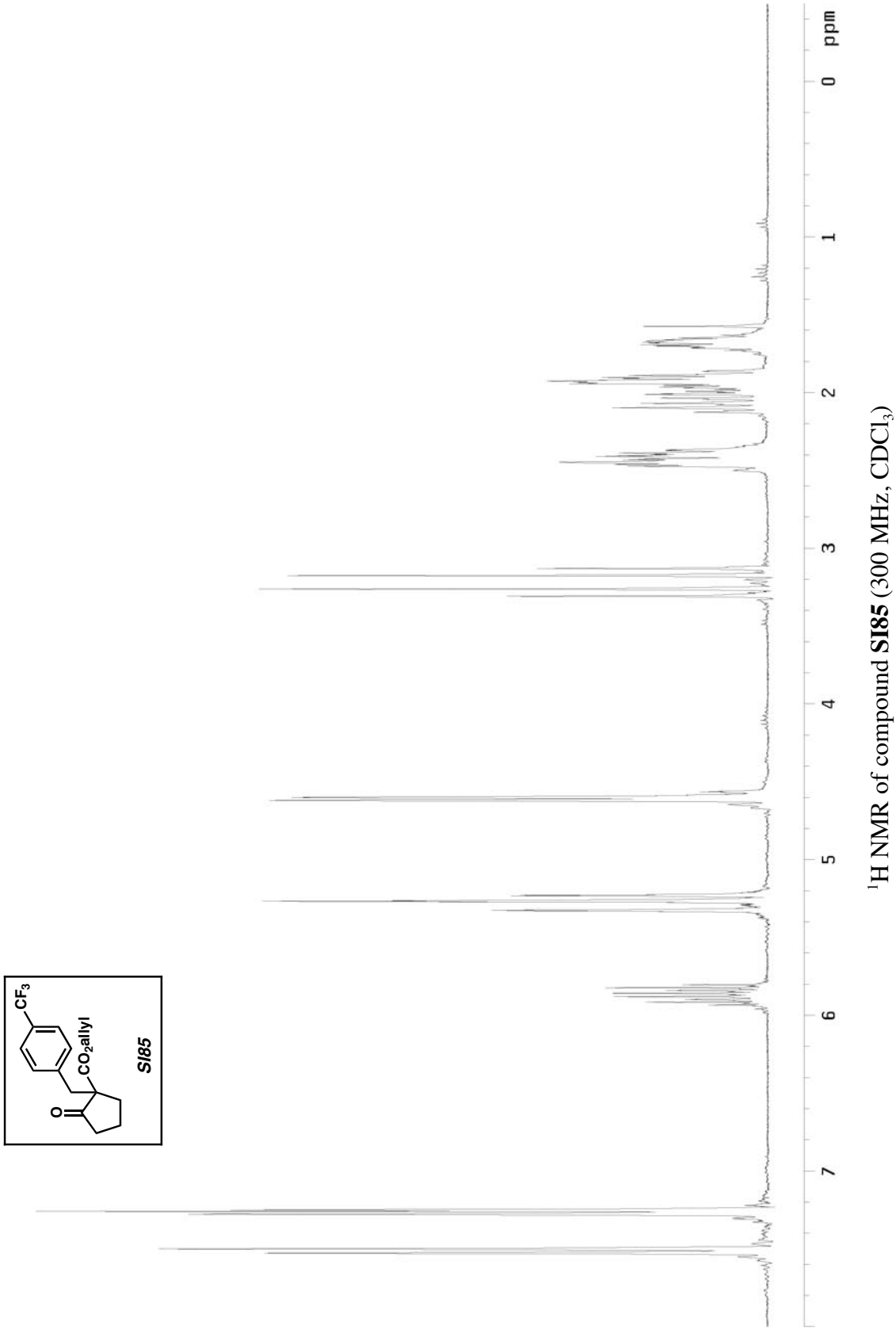
^{13}C NMR of compound **SI83** (75 MHz, $CDCl_3$)



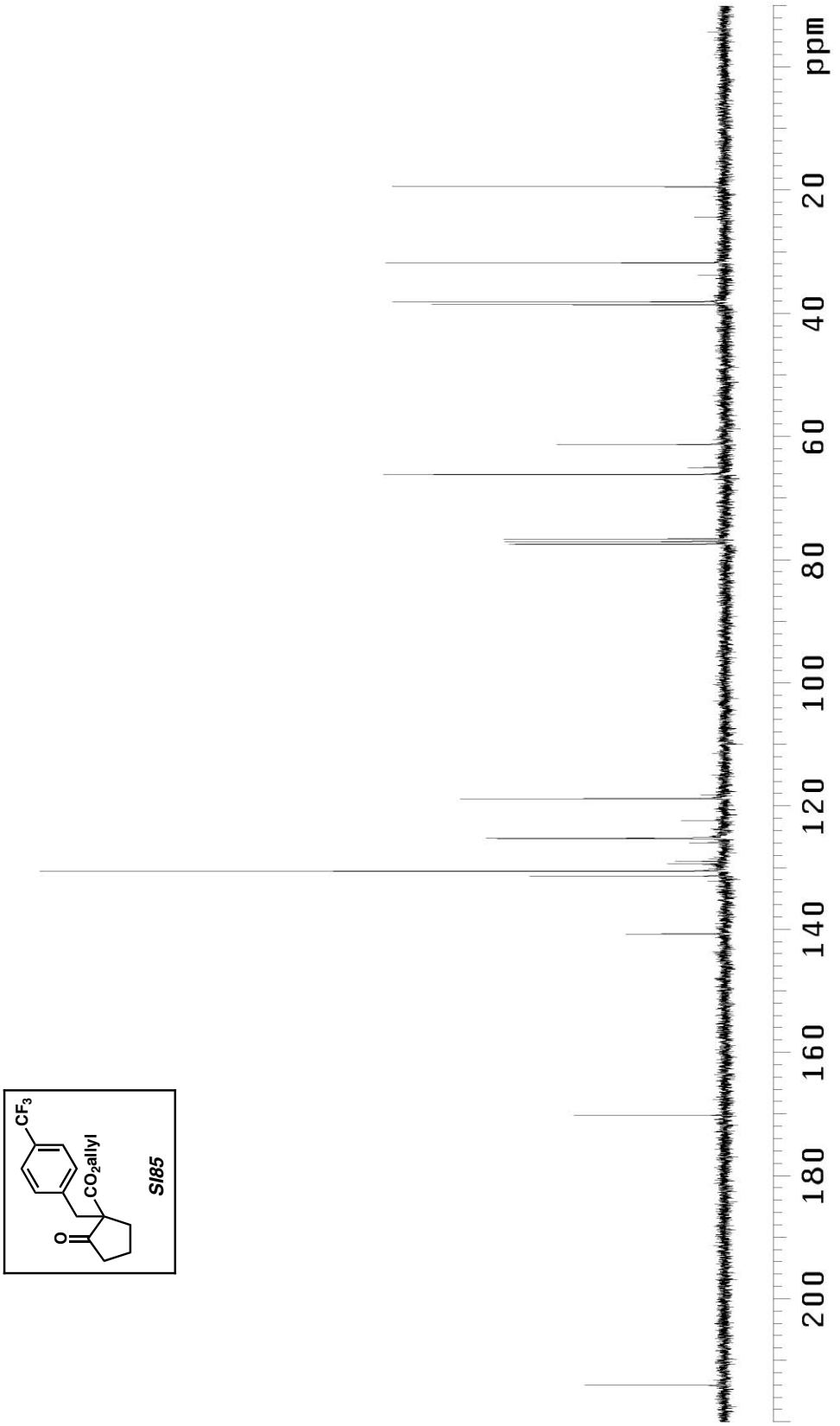
^{1}H NMR of compound **SI84** (300 MHz, $CDCl_3$)



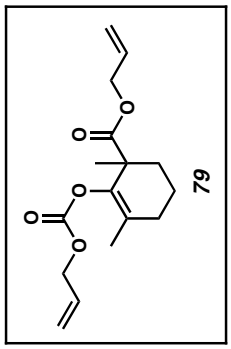
^{13}C NMR of compound **SI84** (75 MHz, $CDCl_3$)



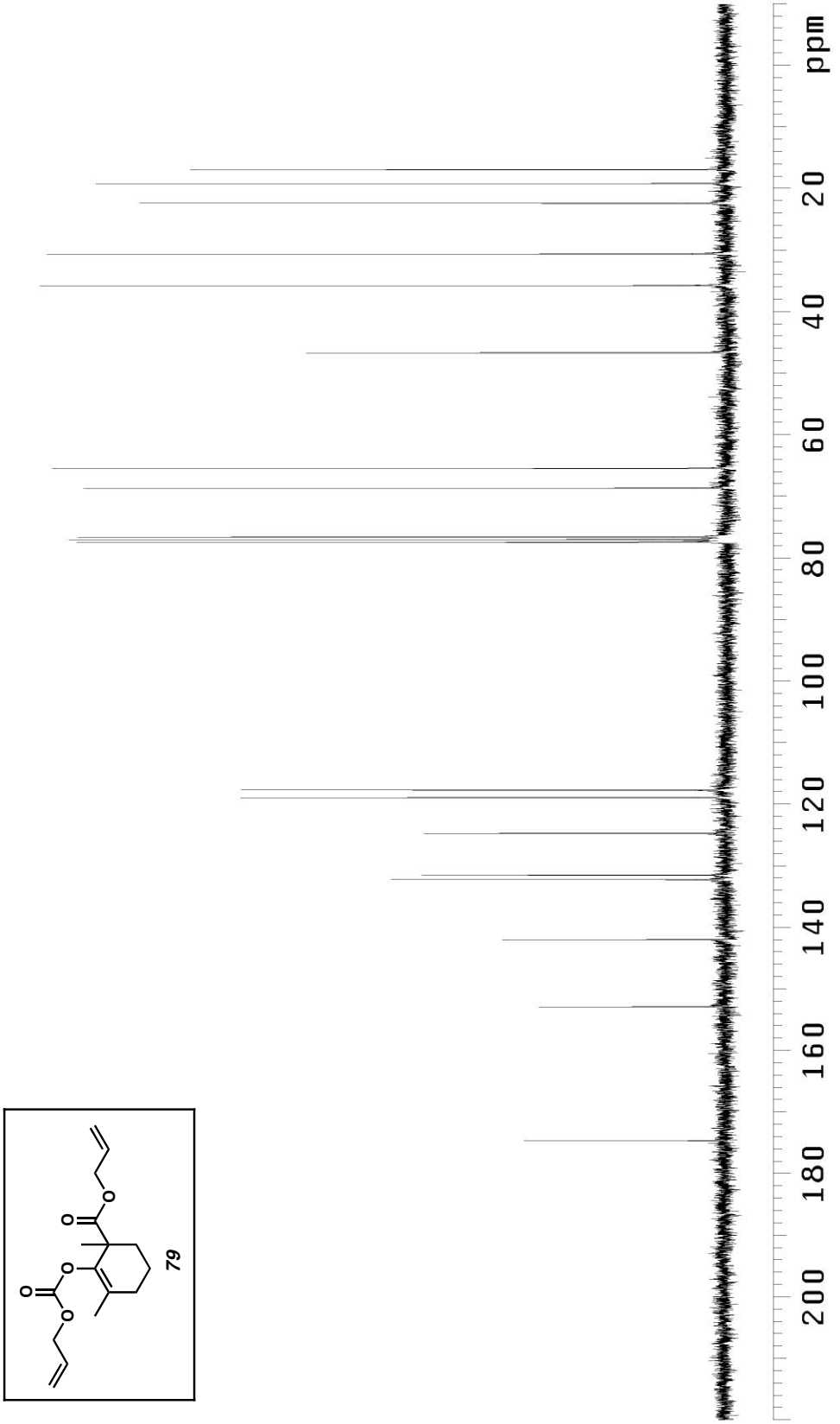
^{1}H NMR of compound **SI85** (300 MHz, $CDCl_3$)



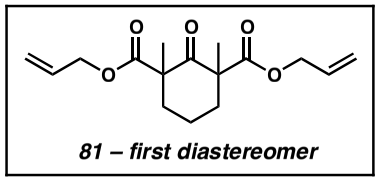
^{13}C NMR of compound **SI85** (75 MHz, $CDCl_3$)



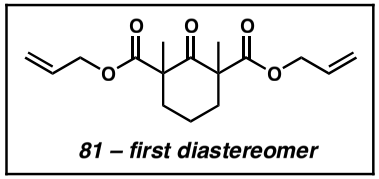
^{1}H NMR of compound **79** (300 MHz, $CDCl_3$)



^{13}C NMR of compound **79** (75 MHz, $CDCl_3$)

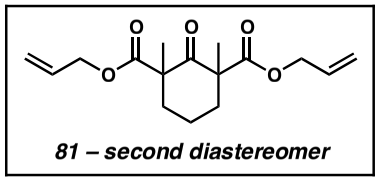


^{1}H NMR of first diastereomer of compound **81** (500 MHz, $CDCl_3$)

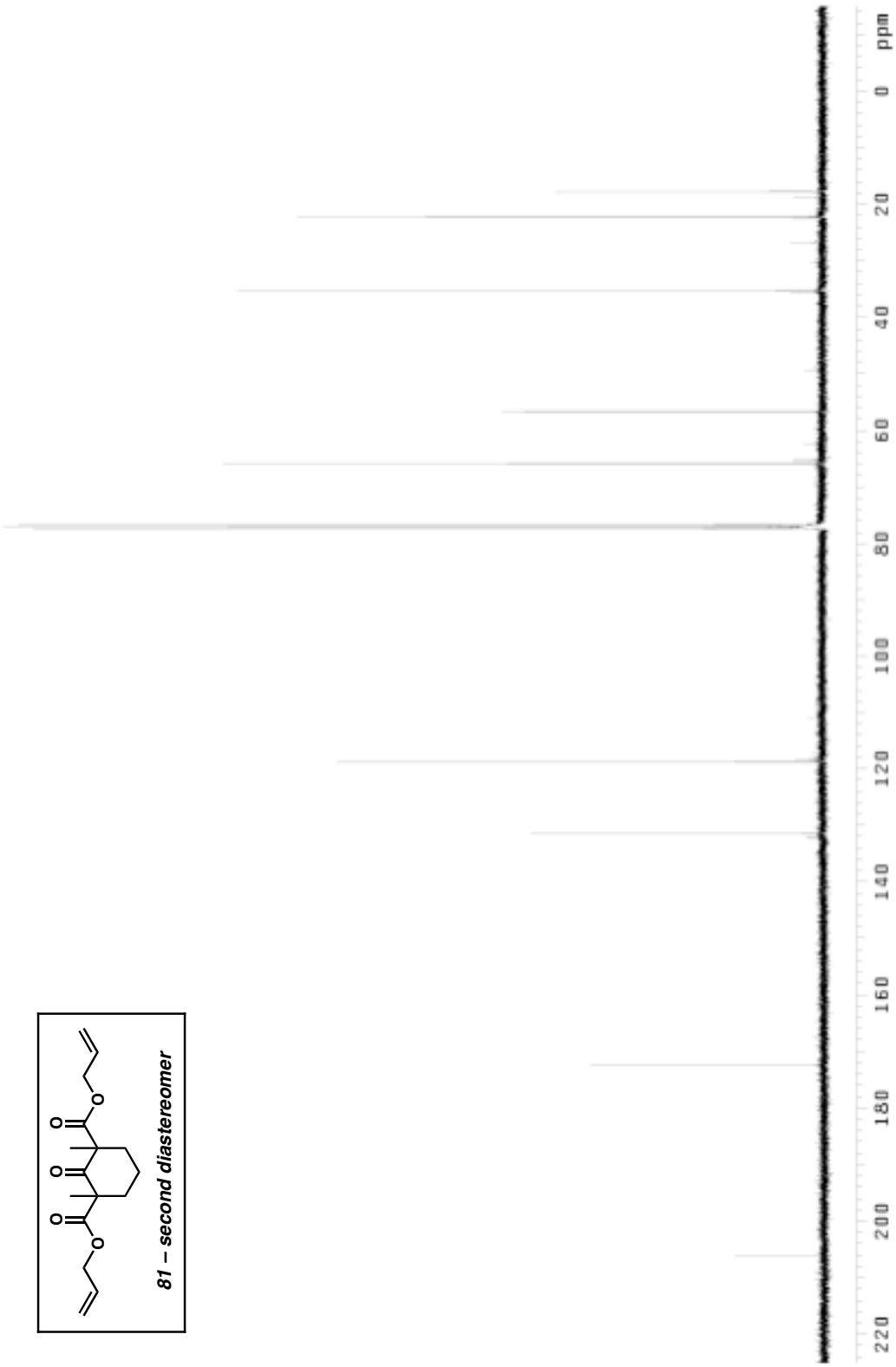


81 – first diastereomer

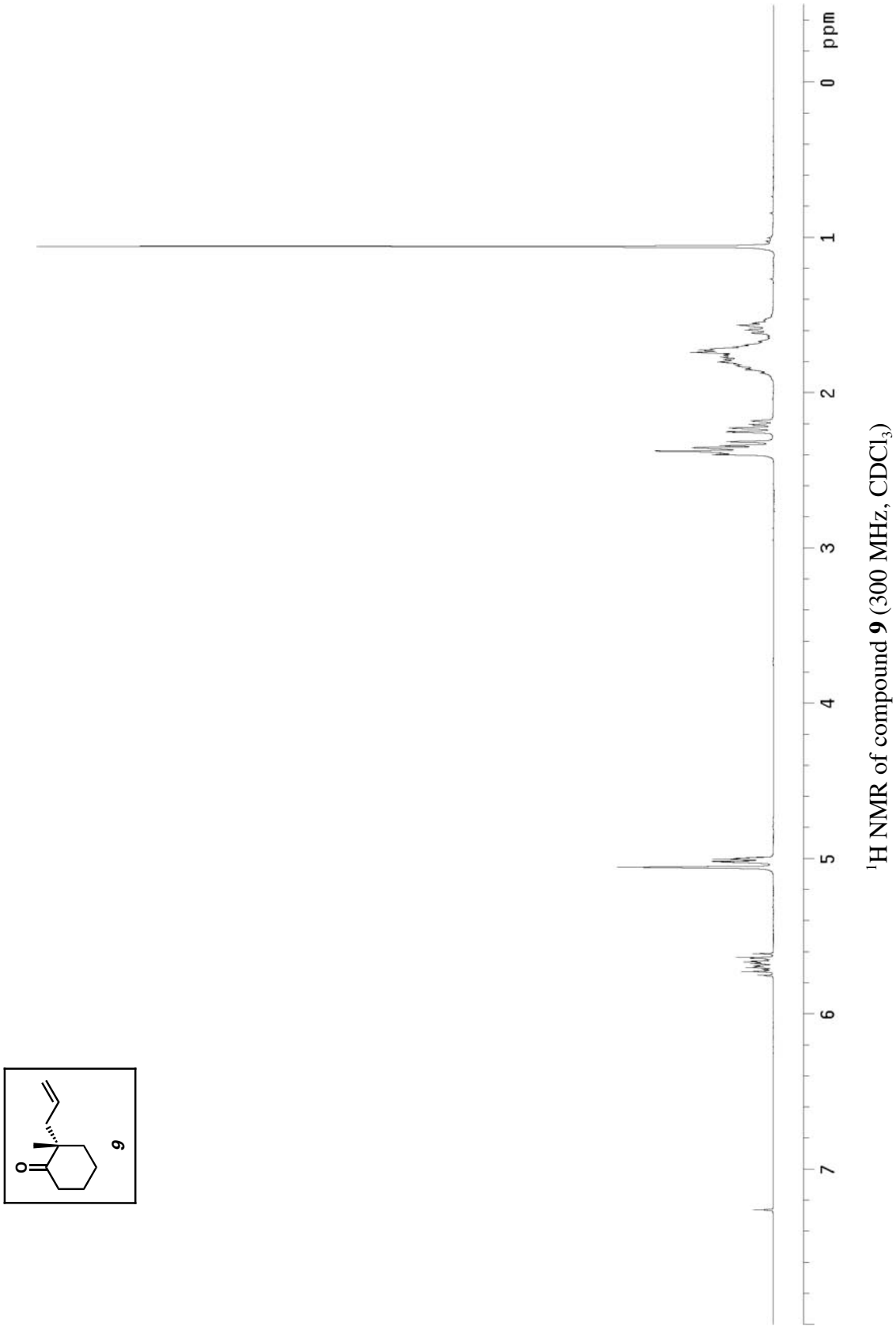
^{13}C NMR of first diastereomer of compound **81** (125 MHz, $CDCl_3$)



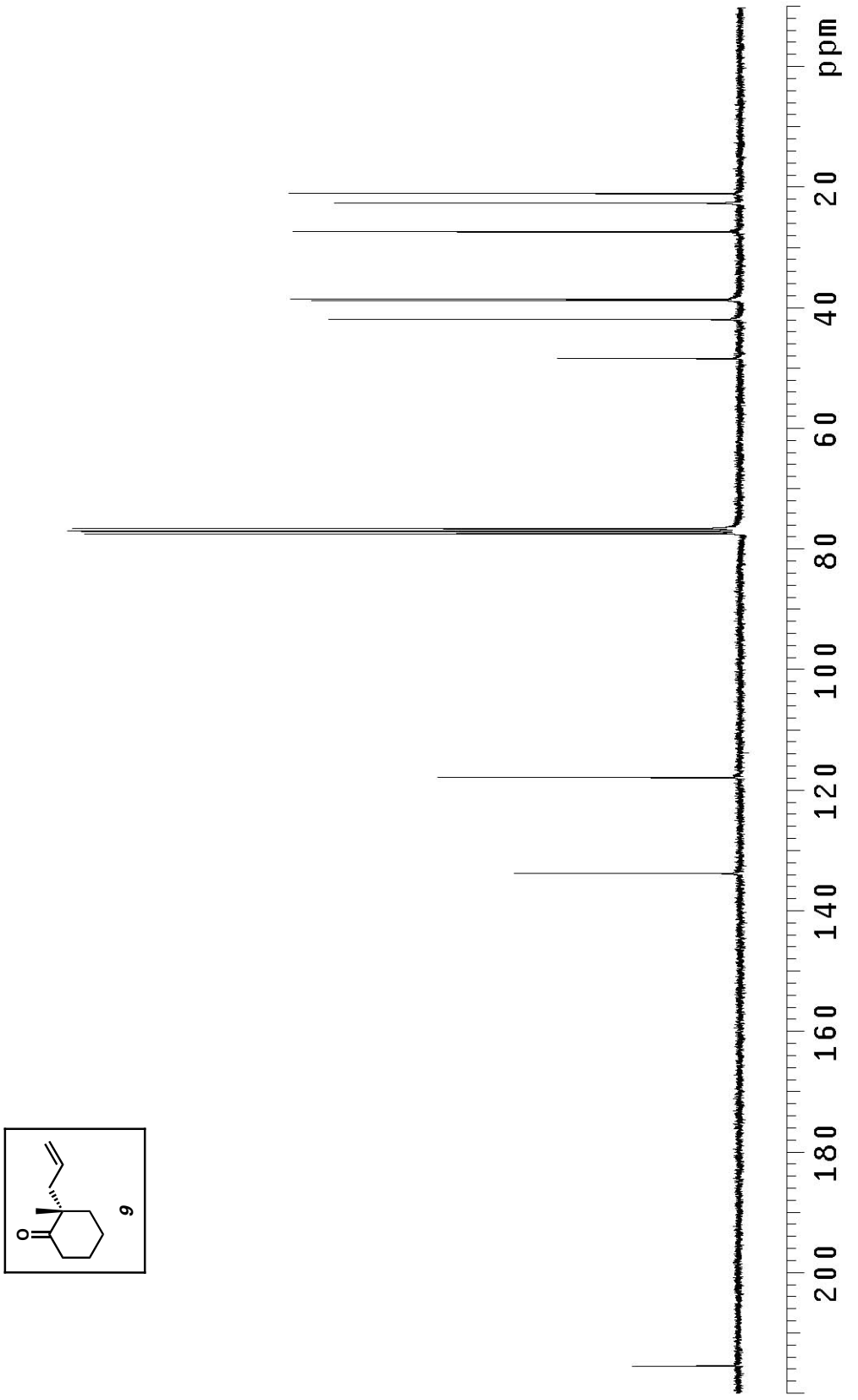
^{1}H NMR of second diastereomer of compound **81** (500 MHz, $CDCl_3$)



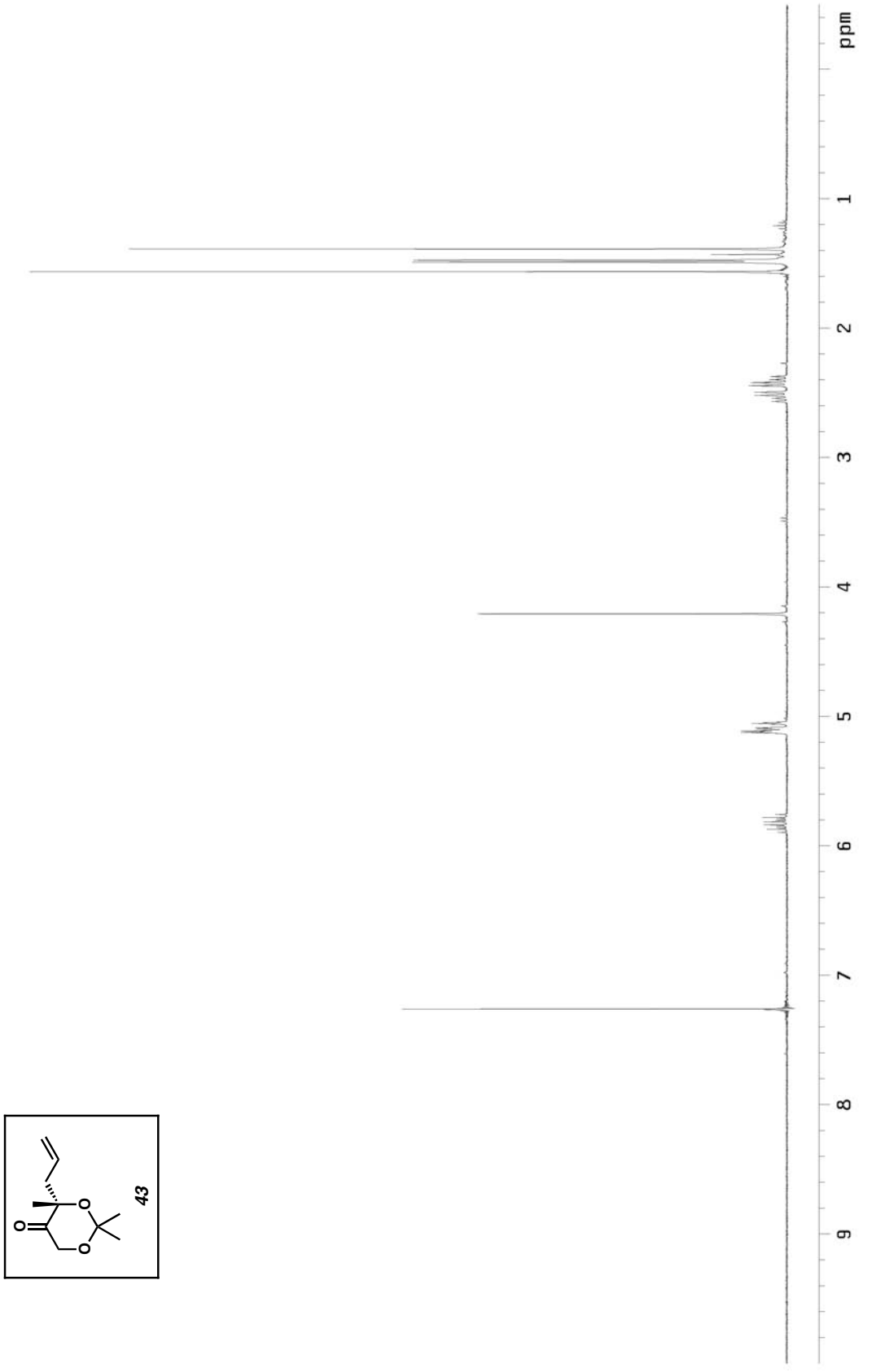
^{13}C NMR of second diastereomer of compound **81** (125 MHz,



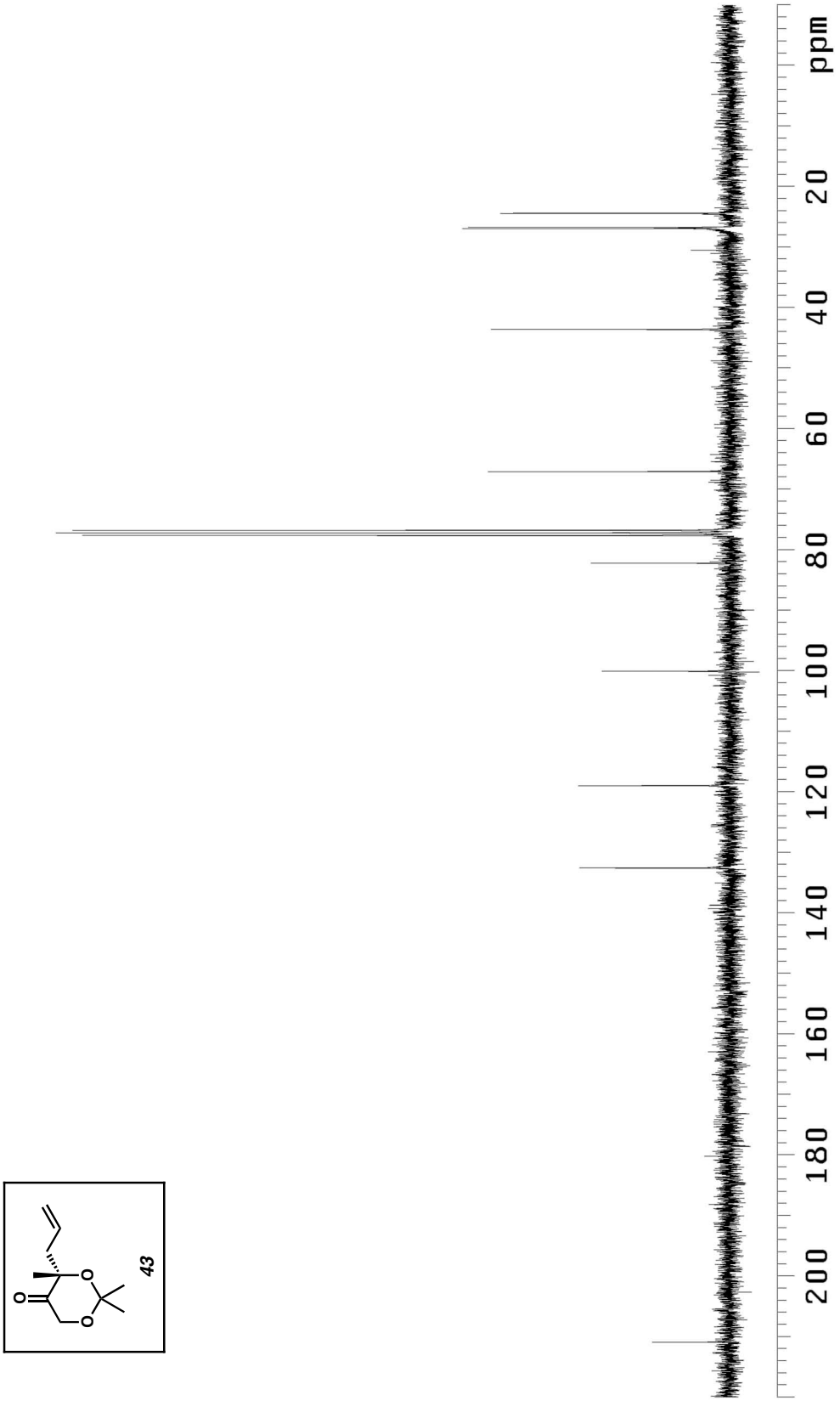
^{1}H NMR of compound **9** (300 MHz, $CDCl_3$)



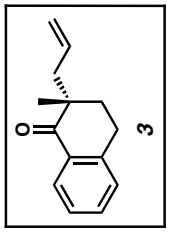
^{13}C NMR of compound **9** (75 MHz, $CDCl_3$)



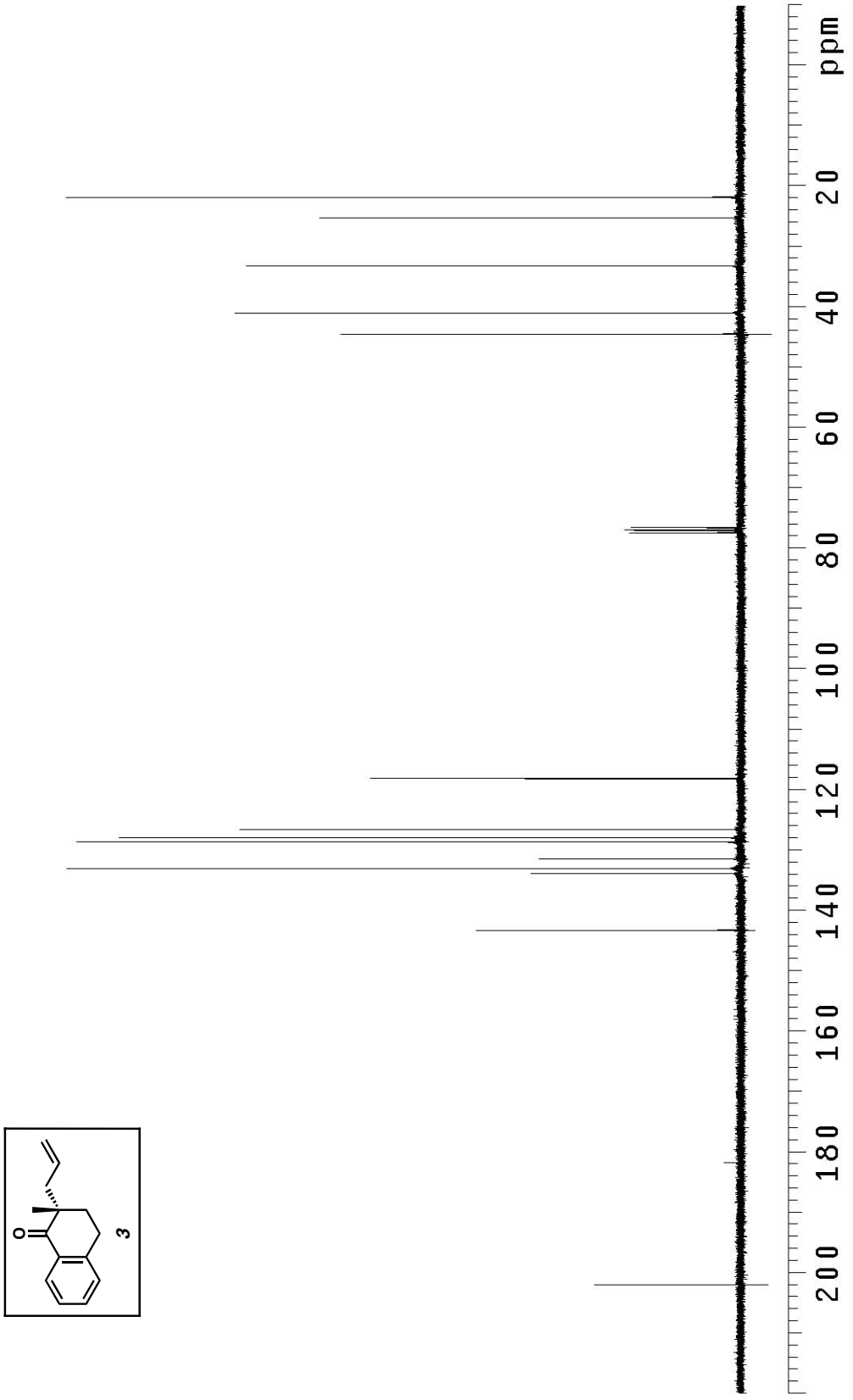
^{1}H NMR of compound **43** (300 MHz, $CDCl_3$)



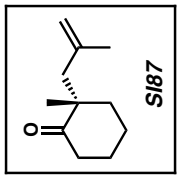
^{13}C NMR of compound **43** (75 MHz, $CDCl_3$)



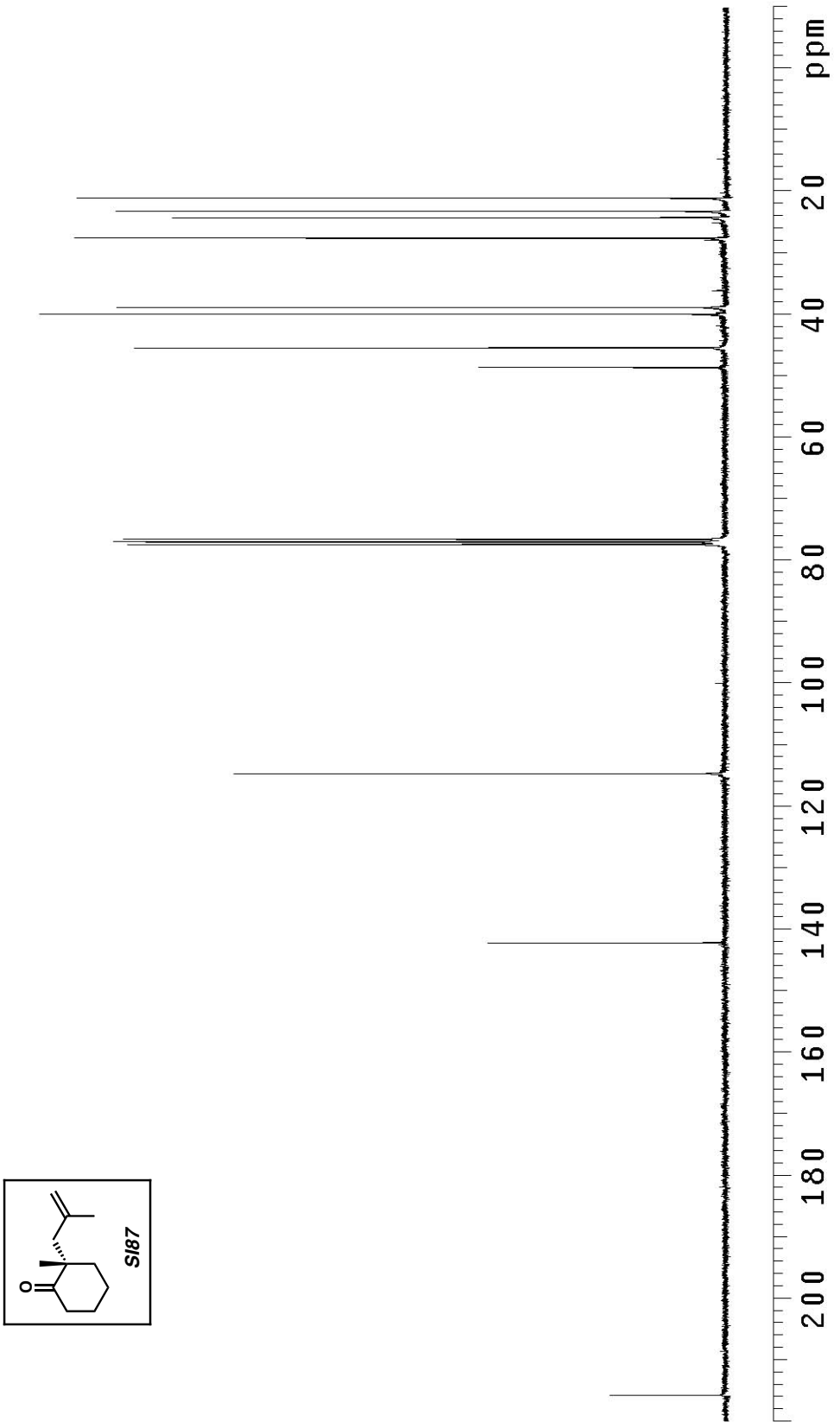
^{1}H NMR of compound **3** (300 MHz, $CDCl_3$)



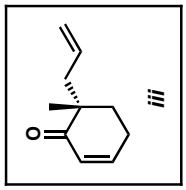
^{13}C NMR of compound **3** (75 MHz, $CDCl_3$)



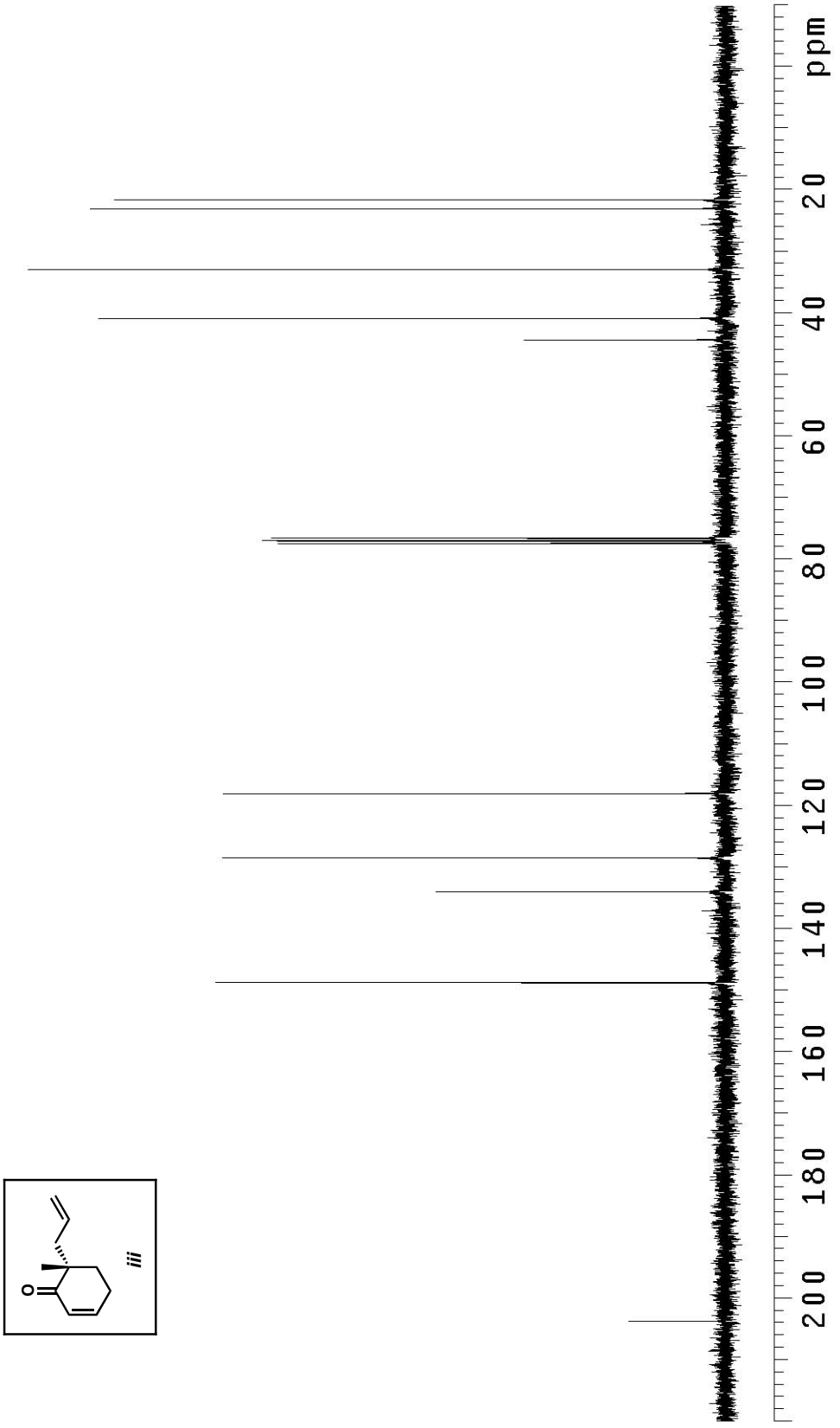
^{1}H NMR of compound **SI87** (300 MHz, $CDCl_3$)



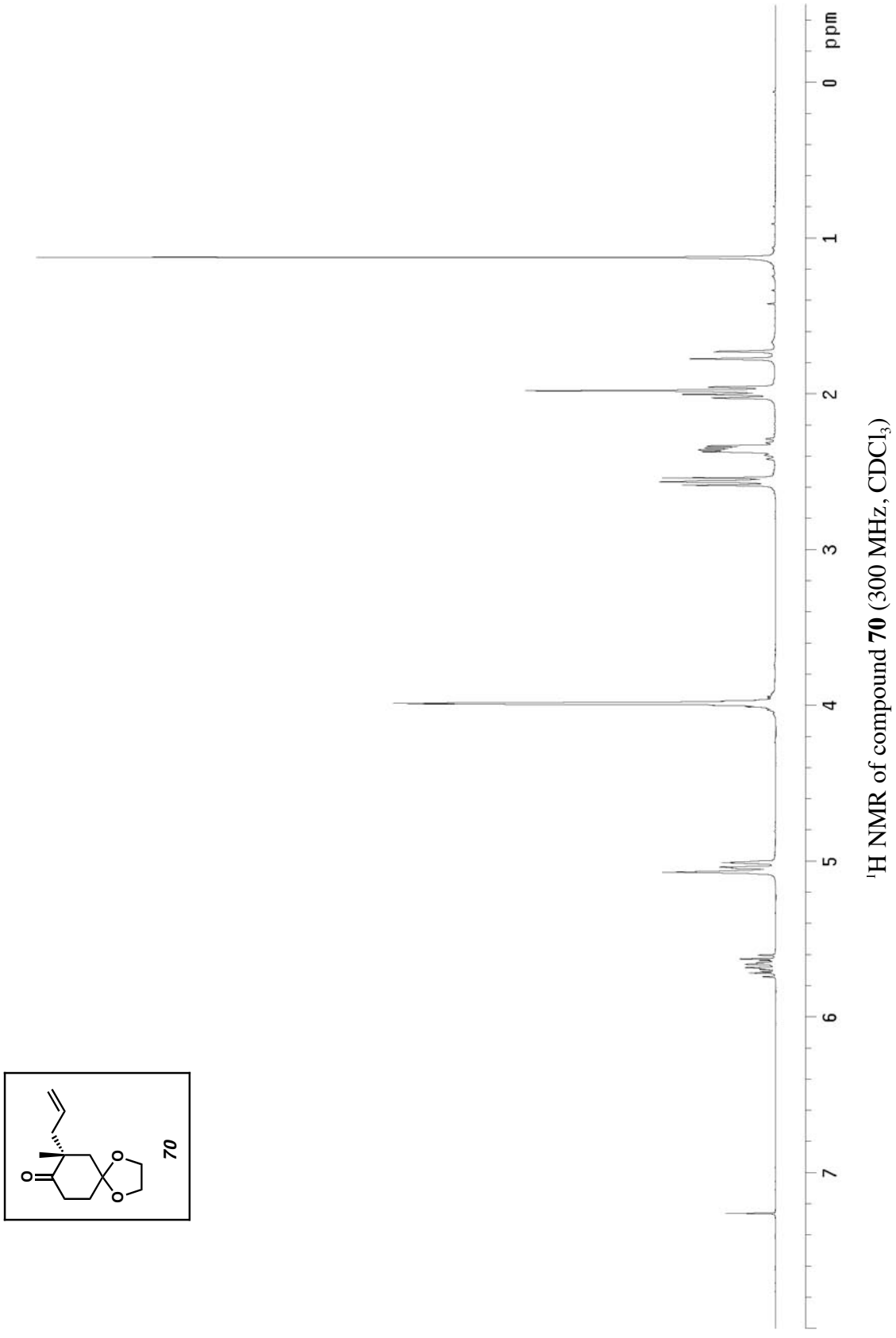
^{13}C NMR of compound **SI87** (75 MHz, $CDCl_3$)



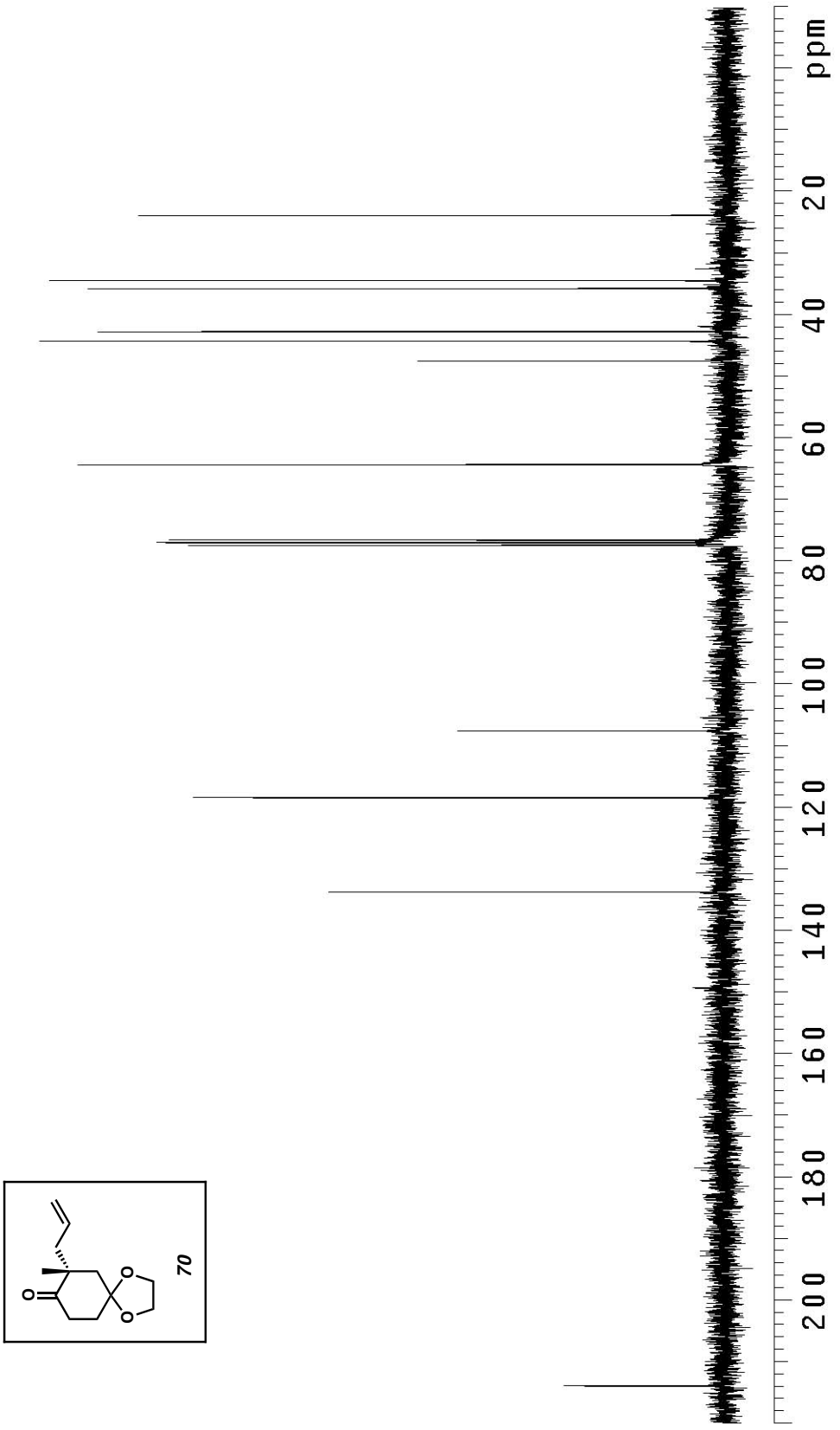
^{1}H NMR of compound **iii** (300 MHz, $CDCl_3$)



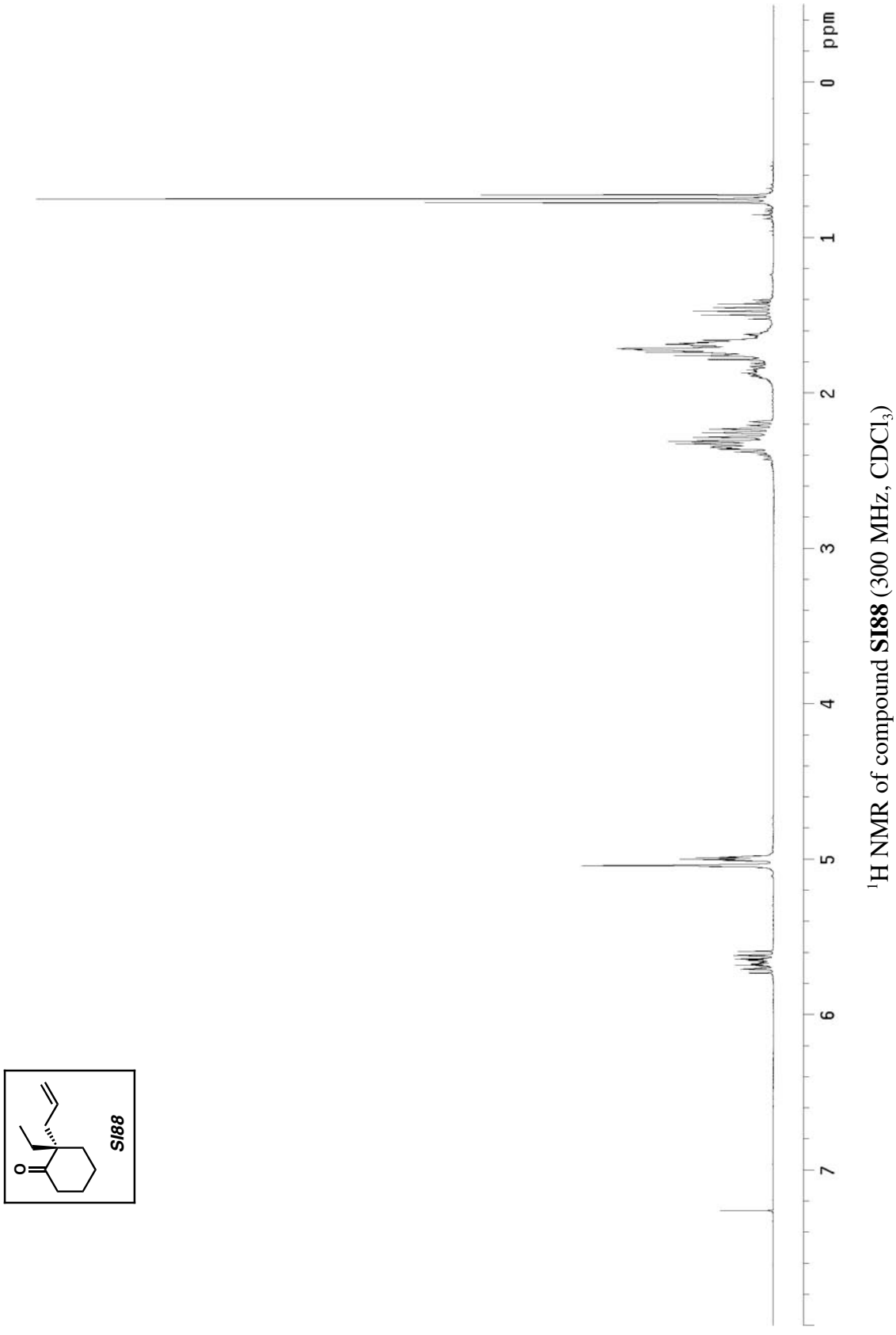
^{13}C NMR of compound **iii** (75 MHz, $CDCl_3$)



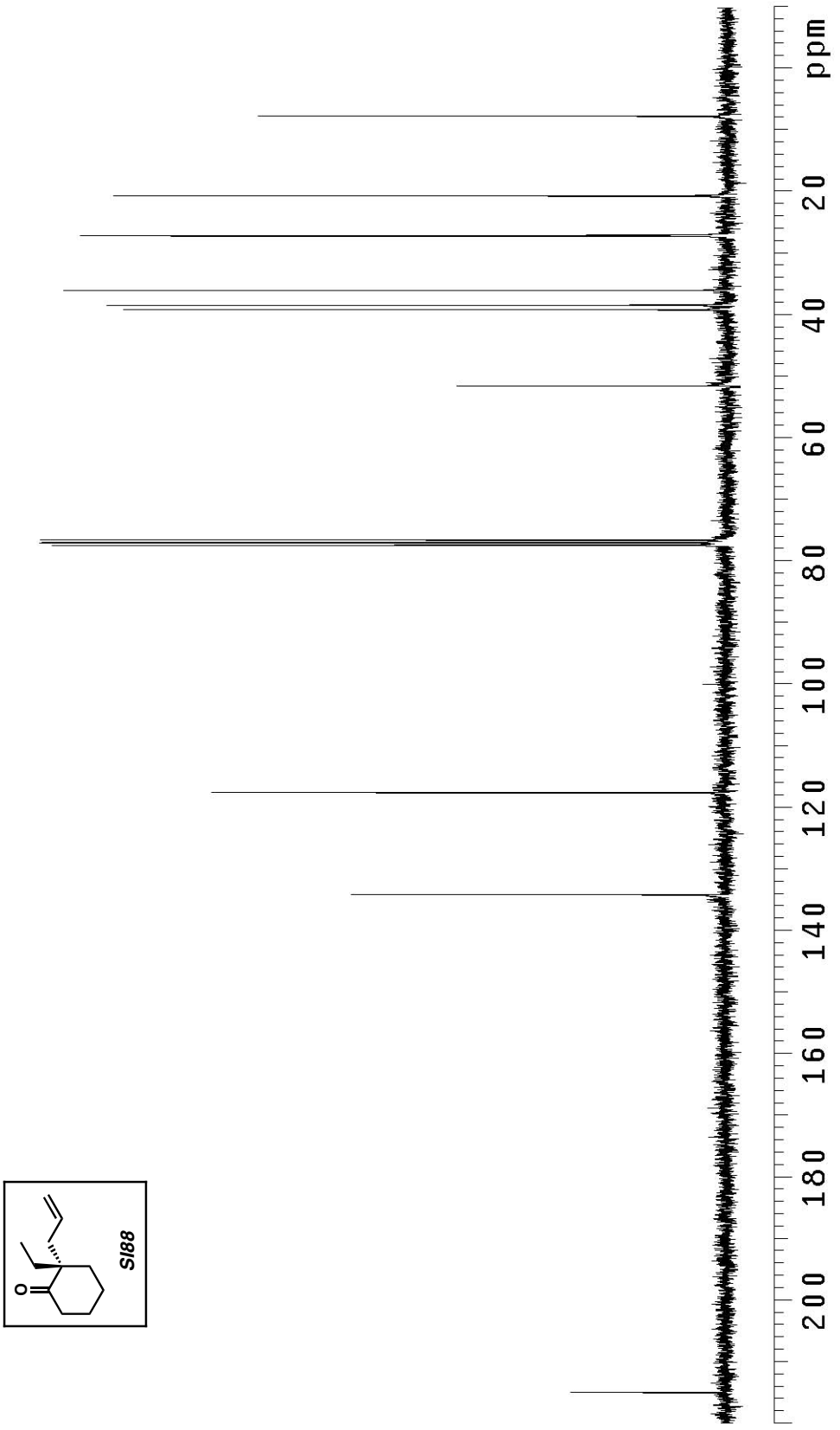
^{1}H NMR of compound **70** (300 MHz, $CDCl_3$)



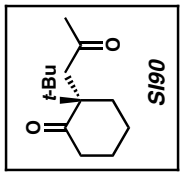
^{13}C NMR of compound **70** (75 MHz, $CDCl_3$)



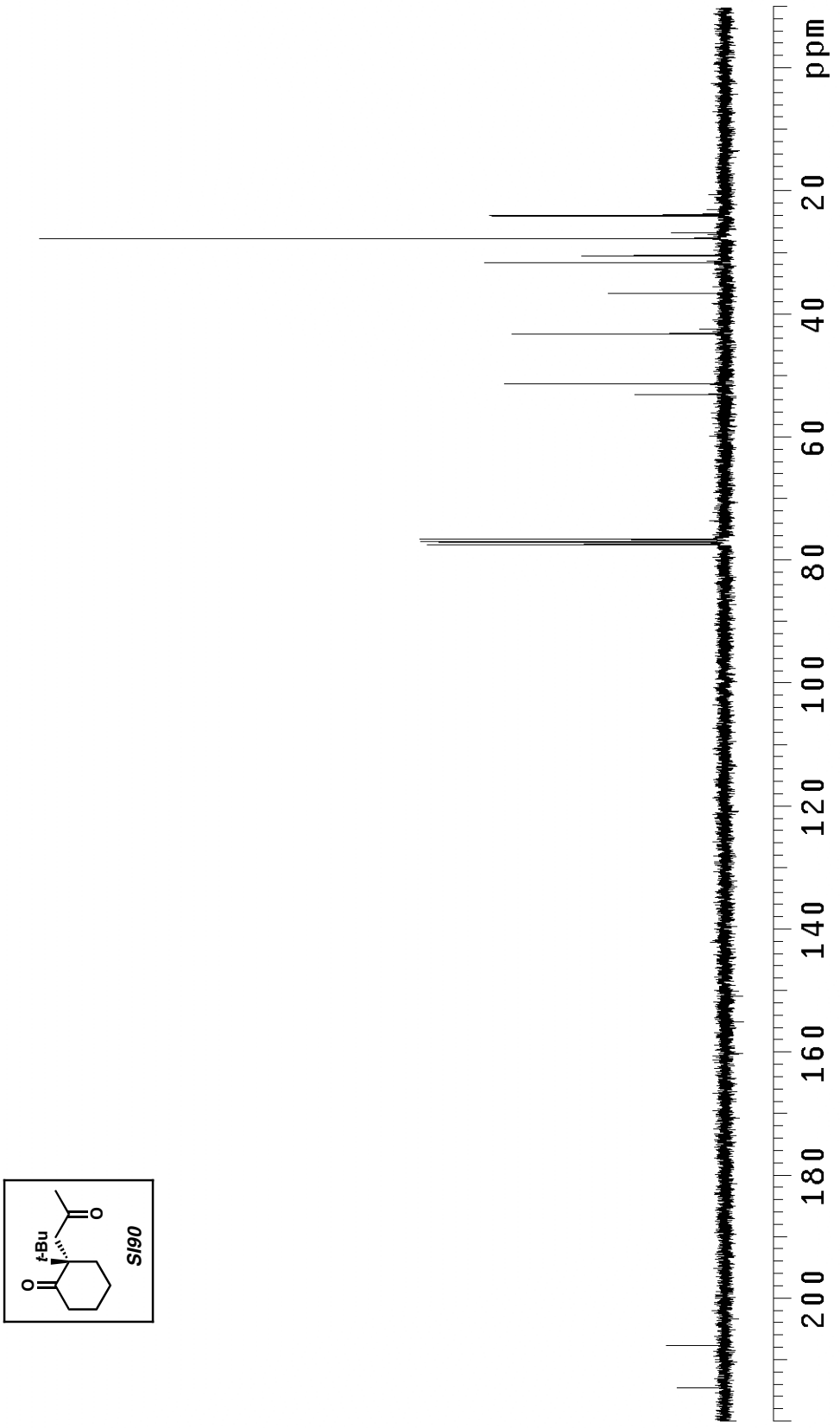
^{1}H NMR of compound **SI88** (300 MHz, $CDCl_3$)



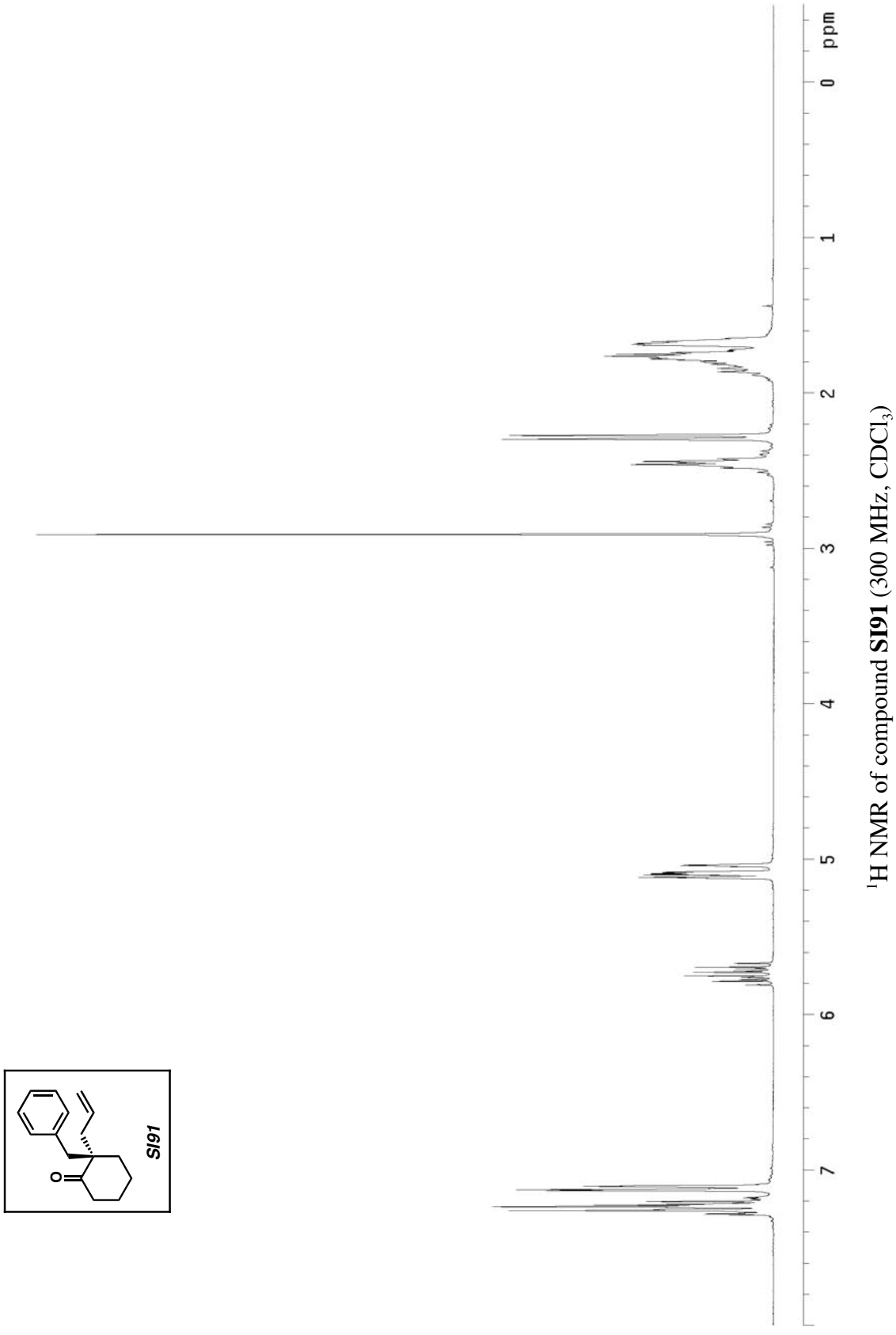
^{13}C NMR of compound **SI88** (75 MHz, $CDCl_3$)



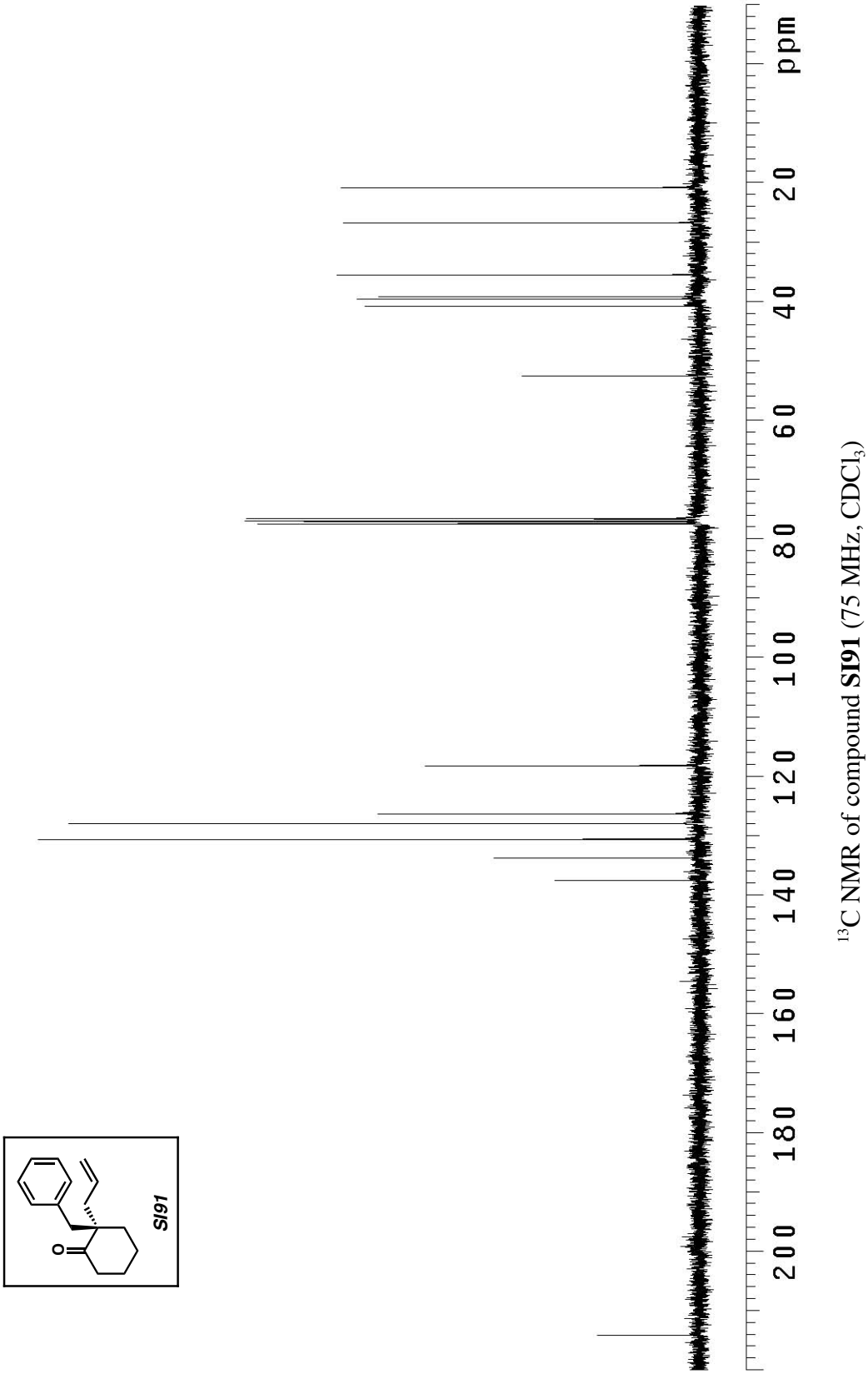
^{1}H NMR of compound **SI90** (300 MHz, $CDCl_3$)



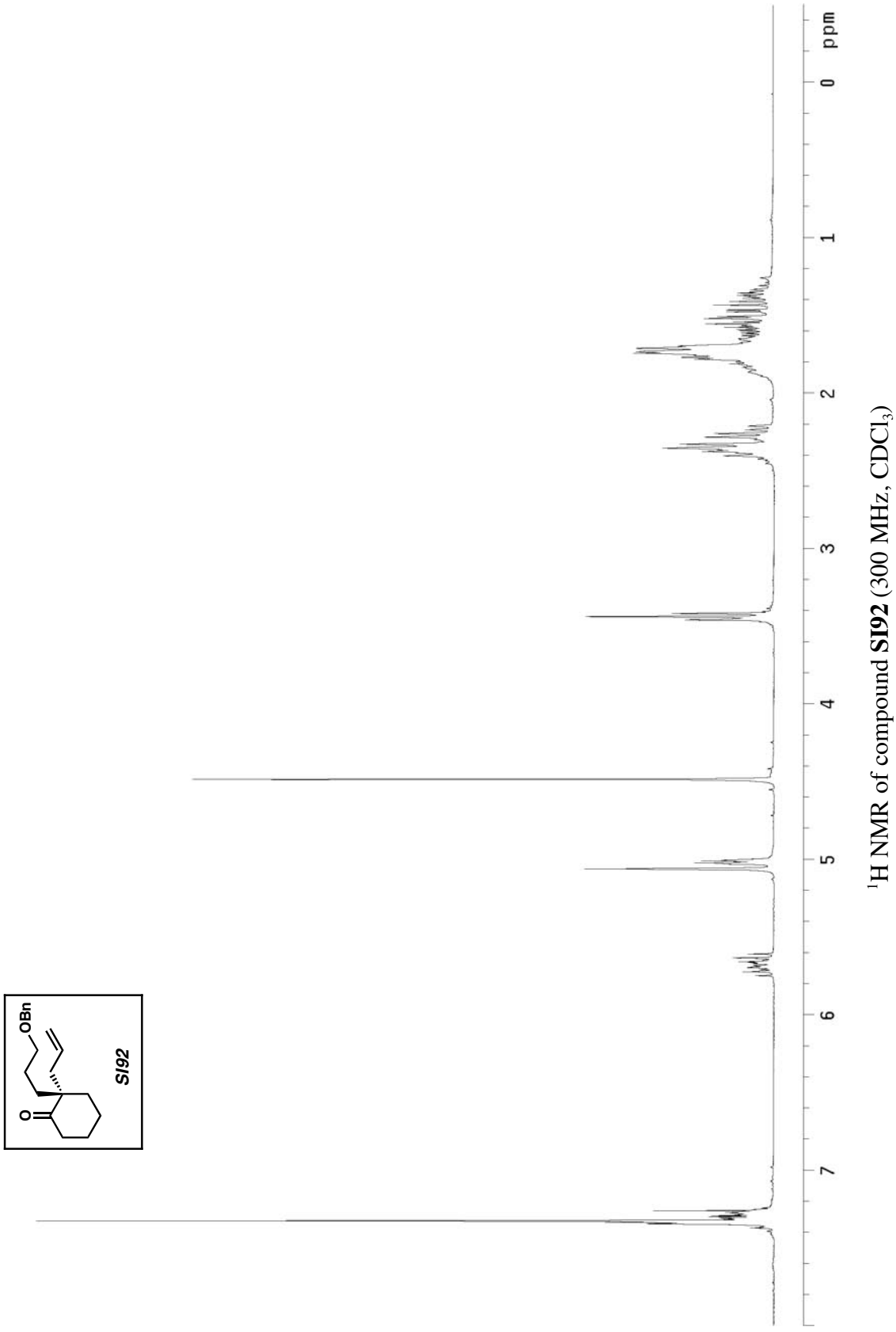
^{13}C NMR of compound **SI90** (75 MHz, $CDCl_3$)



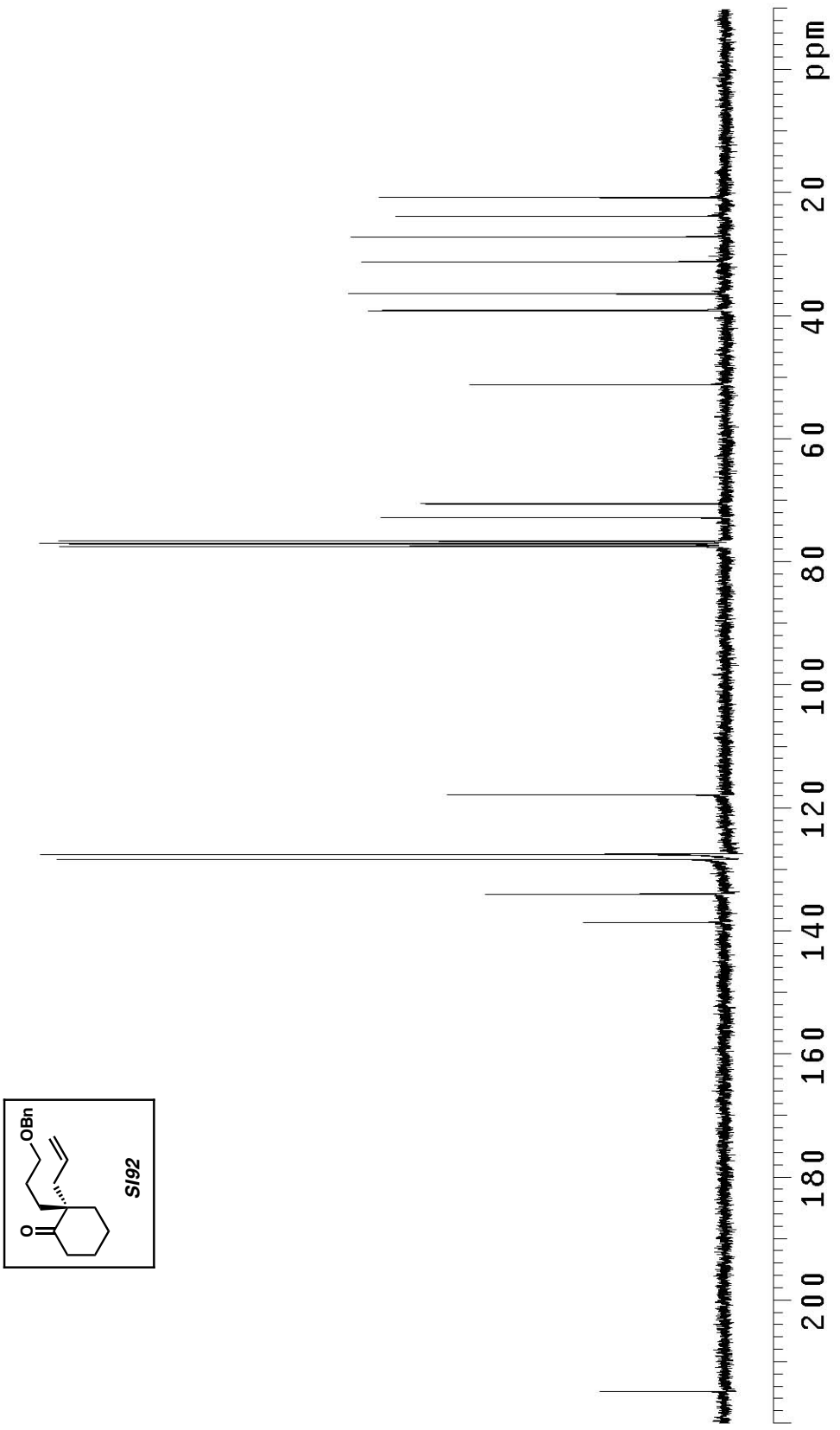
^{1}H NMR of compound **SI91** (300 MHz, $CDCl_3$)



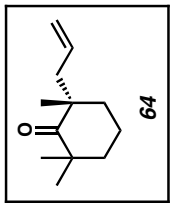
^{13}C NMR of compound **SI91** (75 MHz, $CDCl_3$)



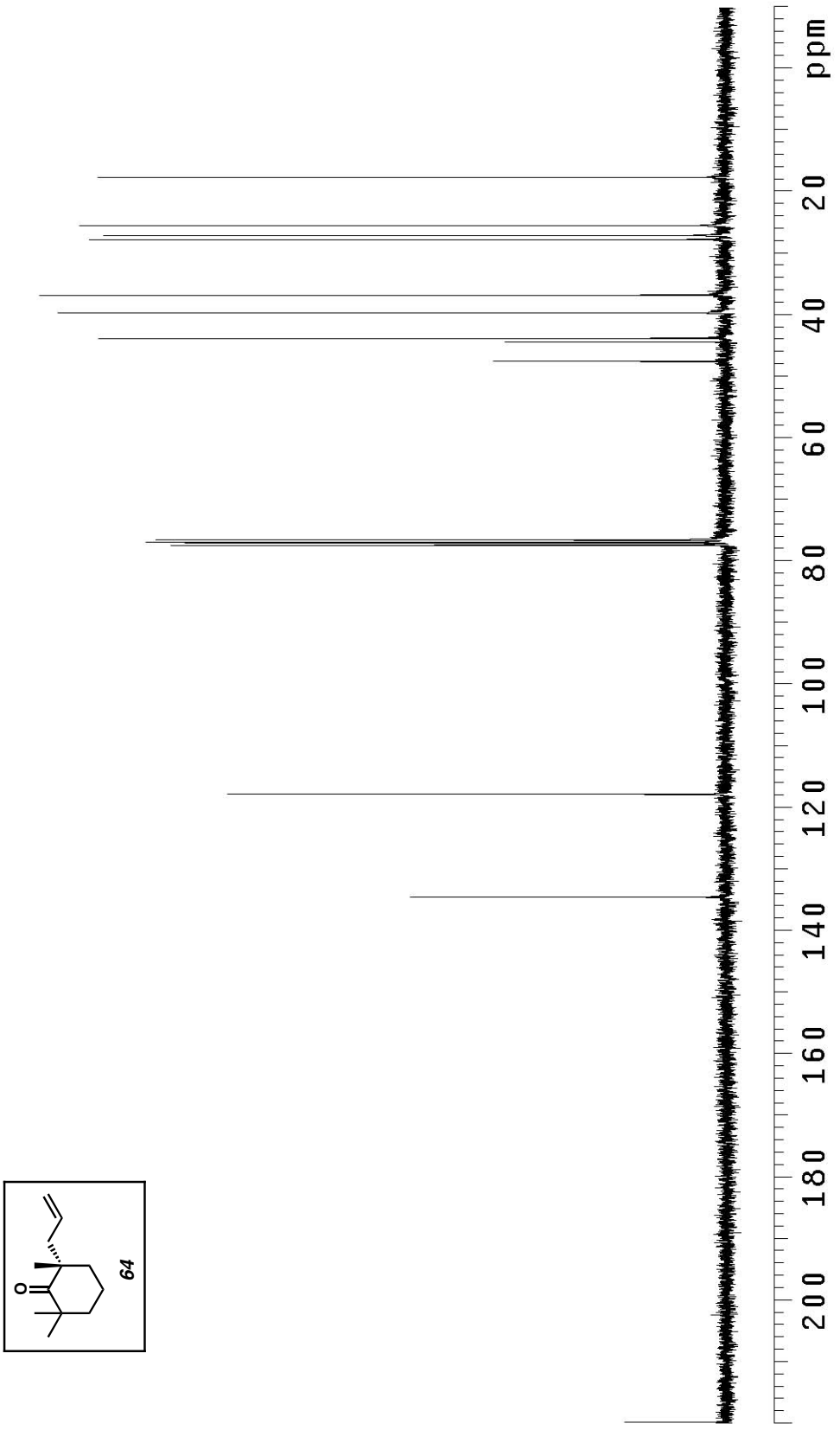
^{1}H NMR of compound **SI92** (300 MHz, $CDCl_3$)



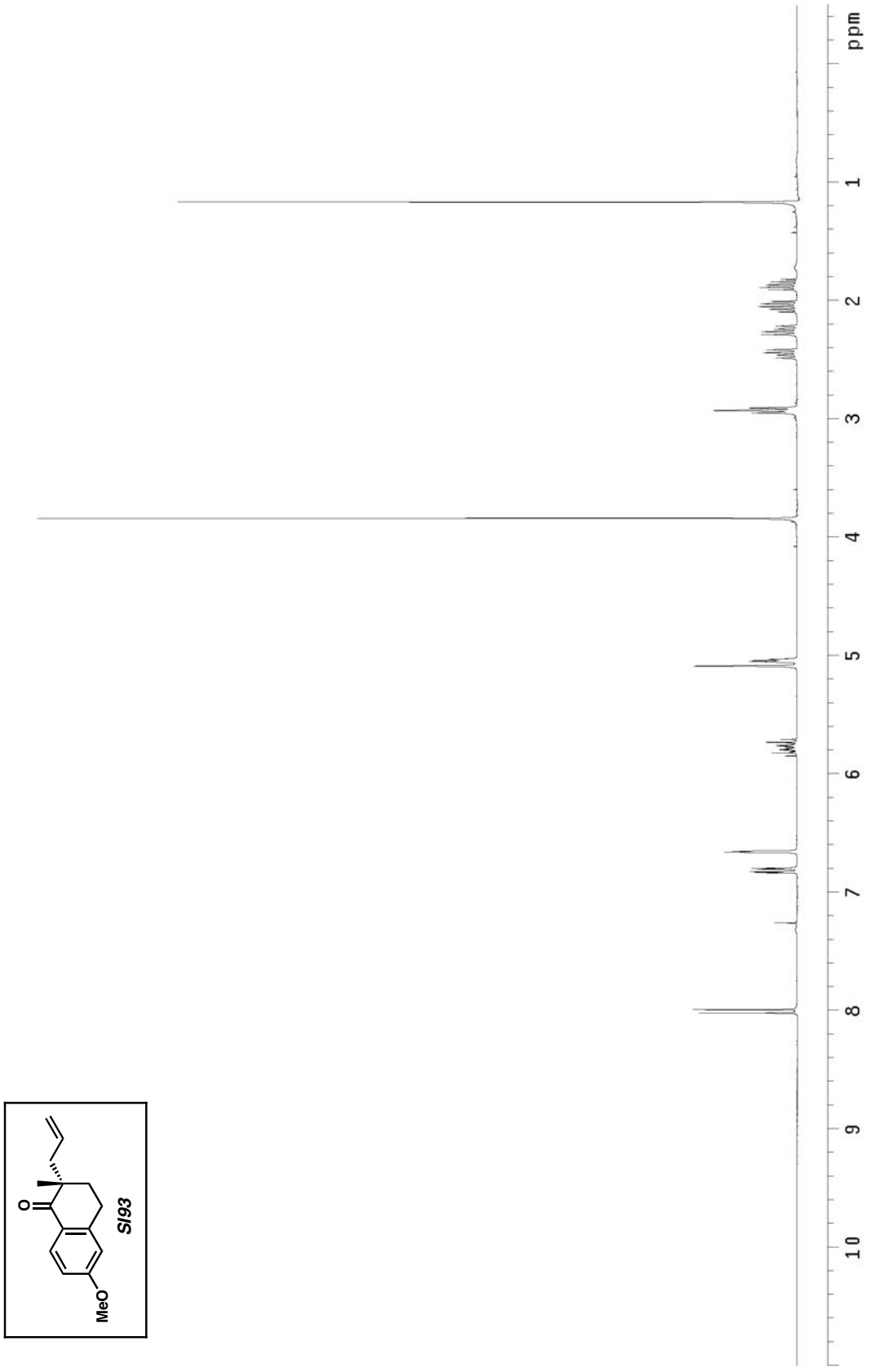
^{13}C NMR of compound **SI92** (75 MHz, $CDCl_3$)



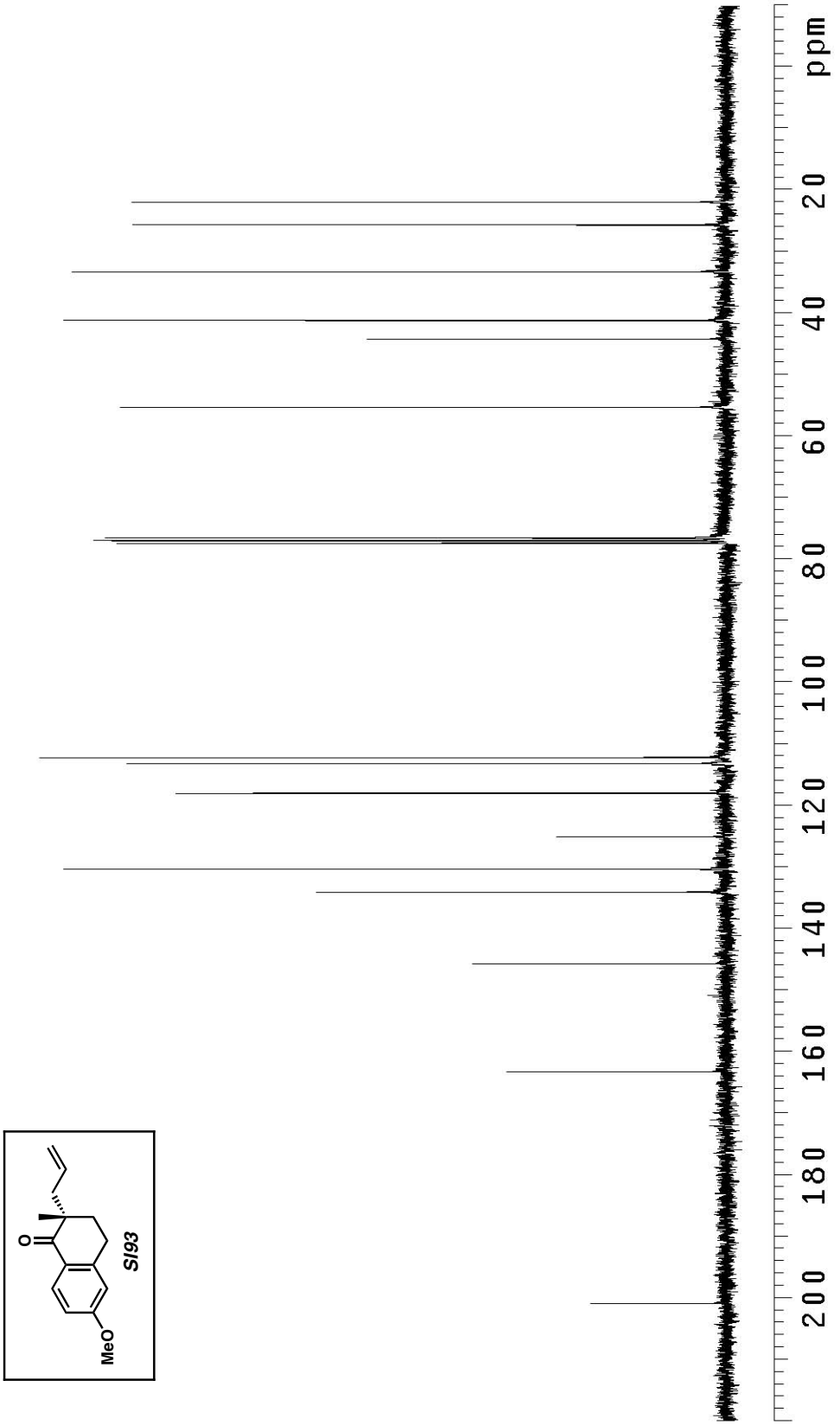
^{1}H NMR of compound **64** (300 MHz, $CDCl_3$)



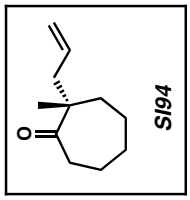
^{13}C NMR of compound **64** (75 MHz, $CDCl_3$)



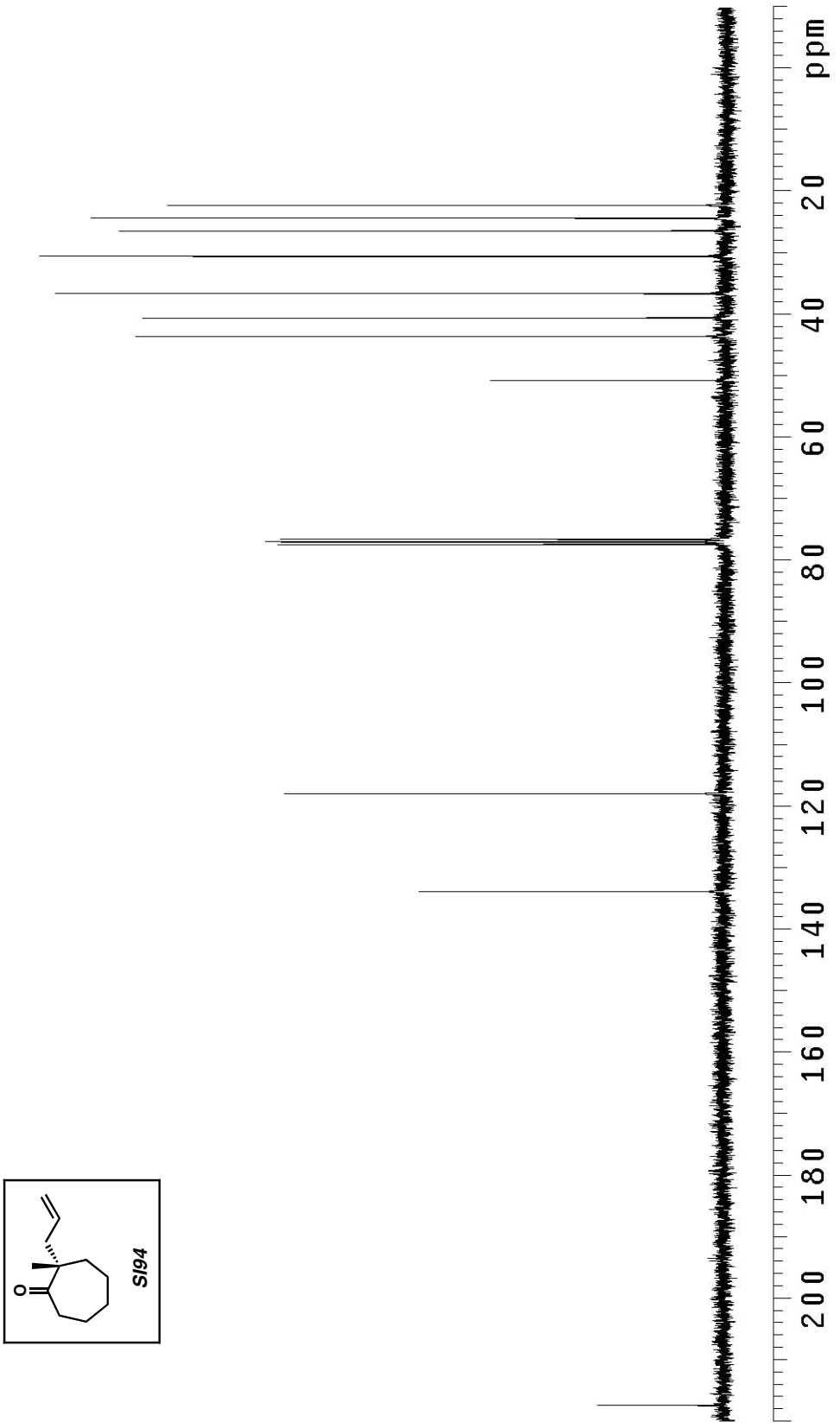
^{1}H NMR of compound **SI93** (300 MHz, $CDCl_3$)



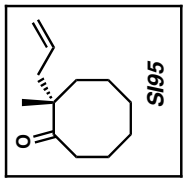
^{13}C NMR of compound **SI93** (75 MHz, $CDCl_3$)



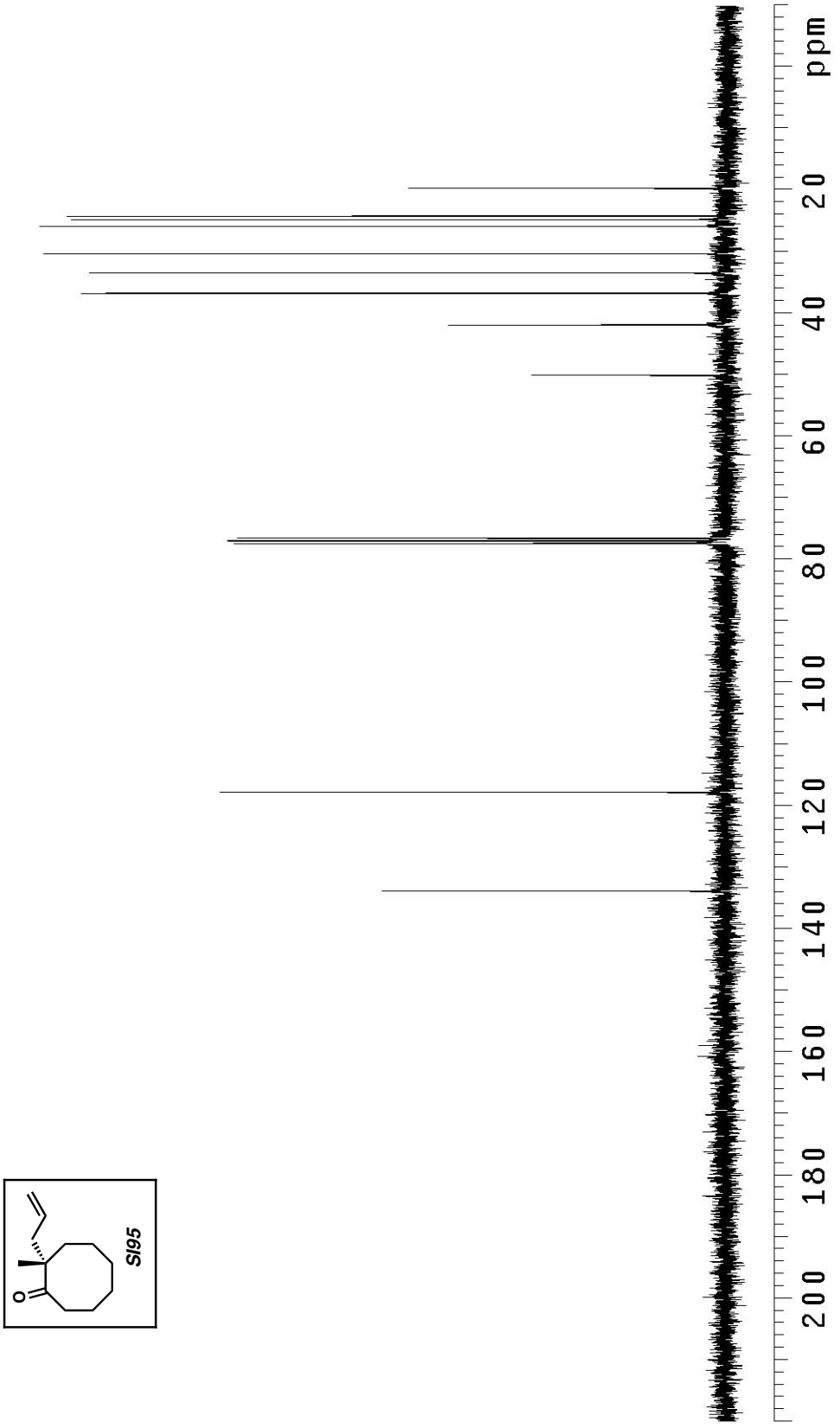
^{1}H NMR of compound **SI94** (300 MHz, $CDCl_3$)



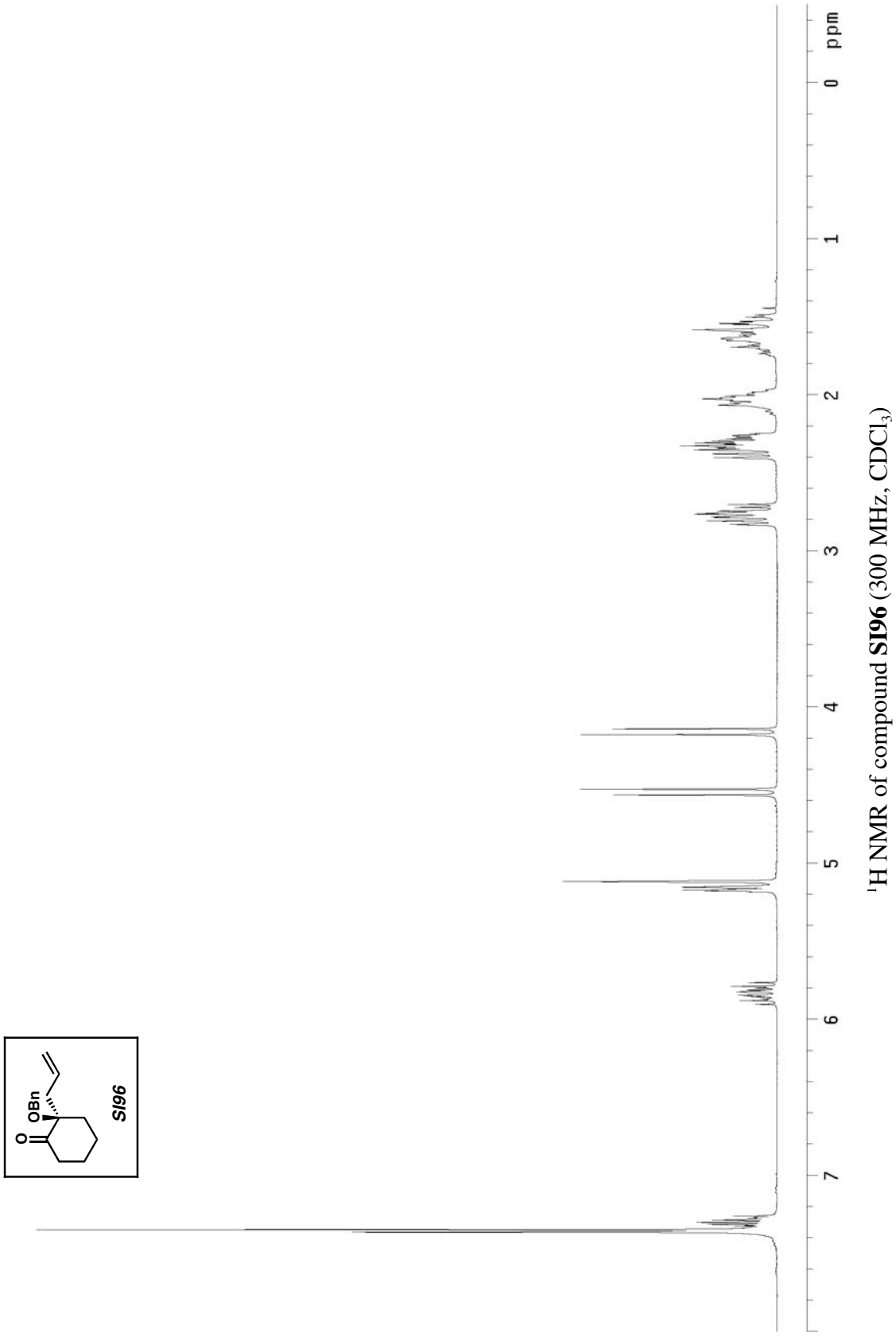
^{13}C NMR of compound **SI94** (75 MHz, $CDCl_3$)



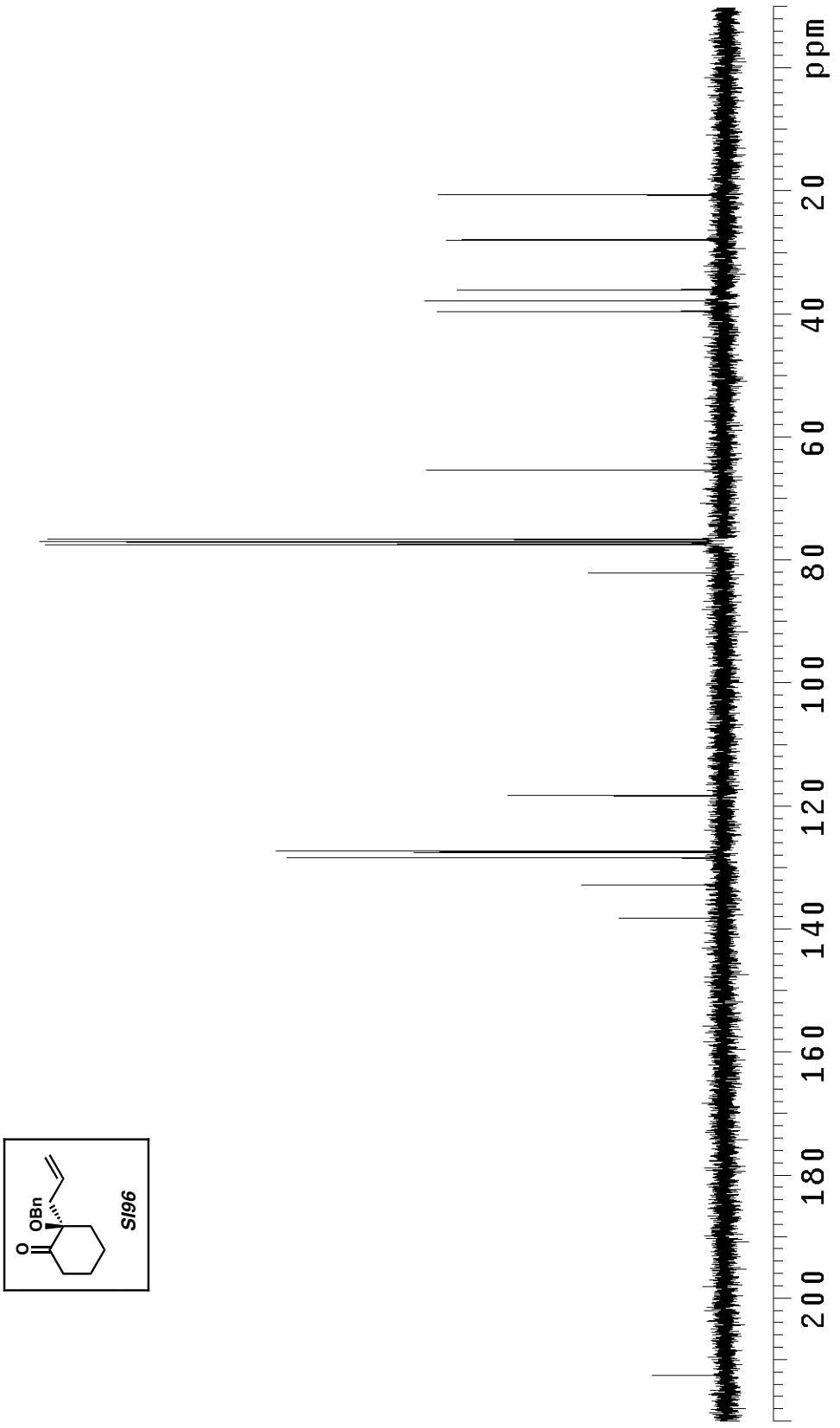
^{1}H NMR of compound **SI95** (300 MHz, $CDCl_3$)



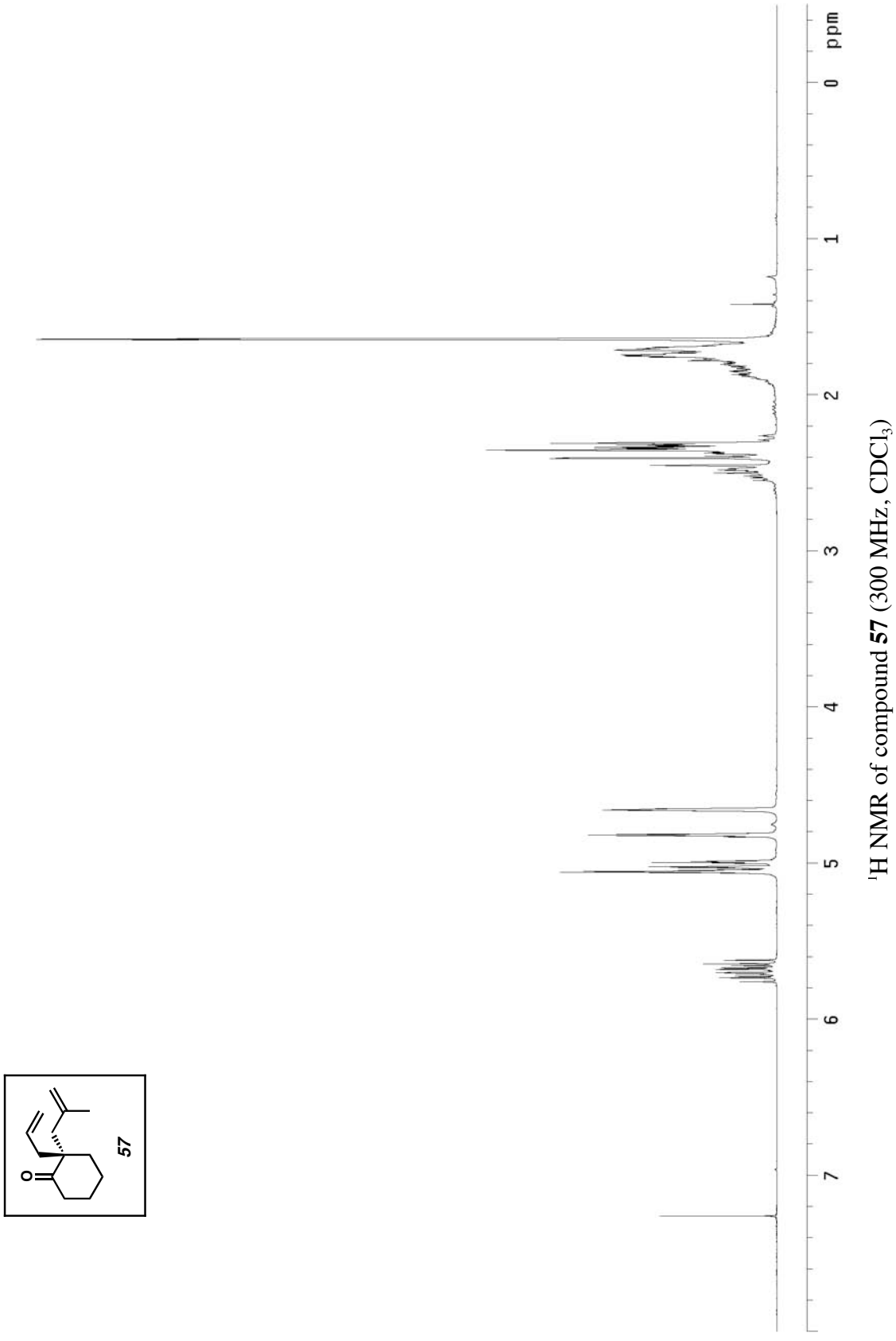
^{13}C NMR of compound **SI95** (75 MHz, $CDCl_3$)



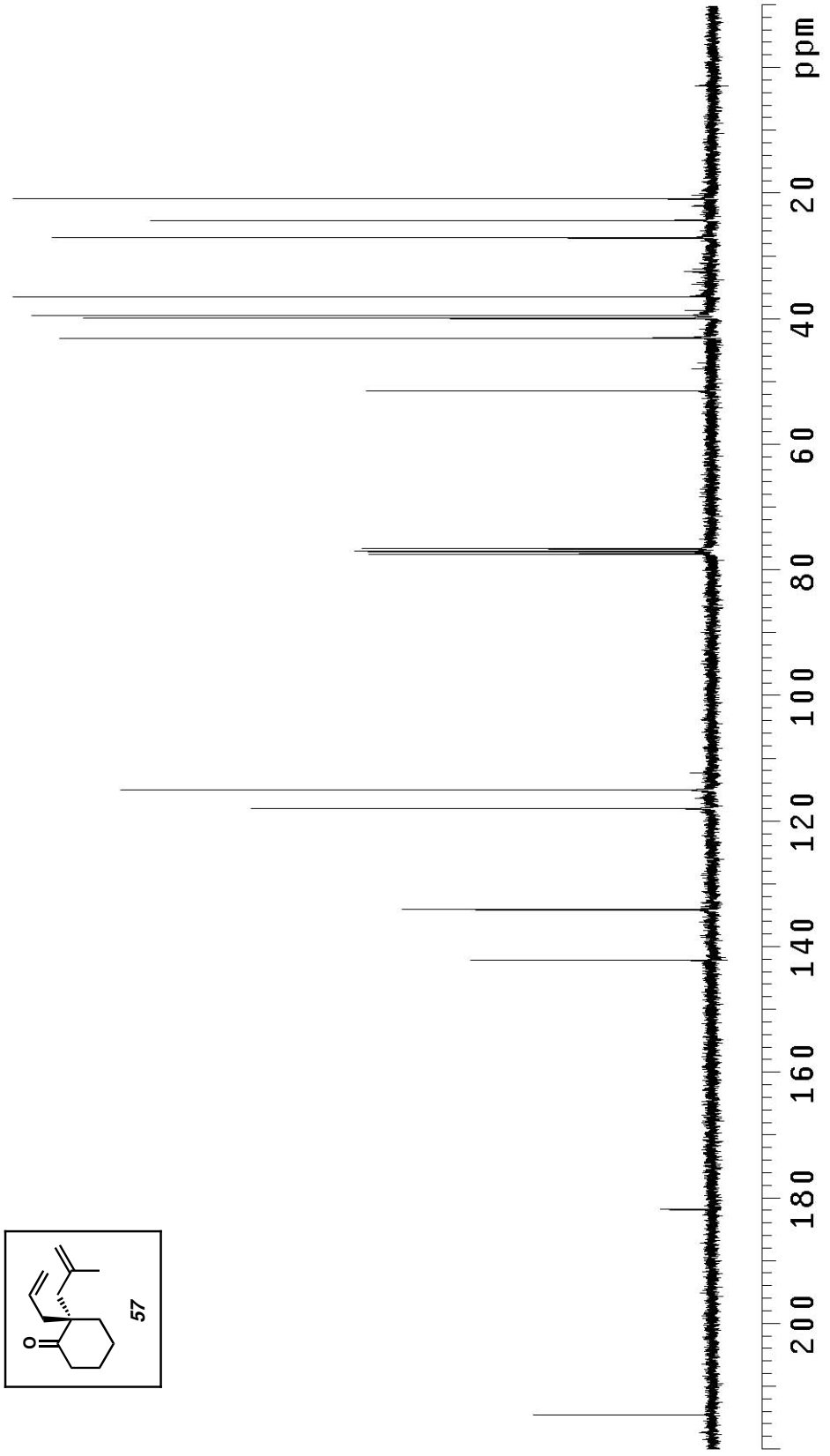
^{1}H NMR of compound **SI96** (300 MHz, $CDCl_3$)



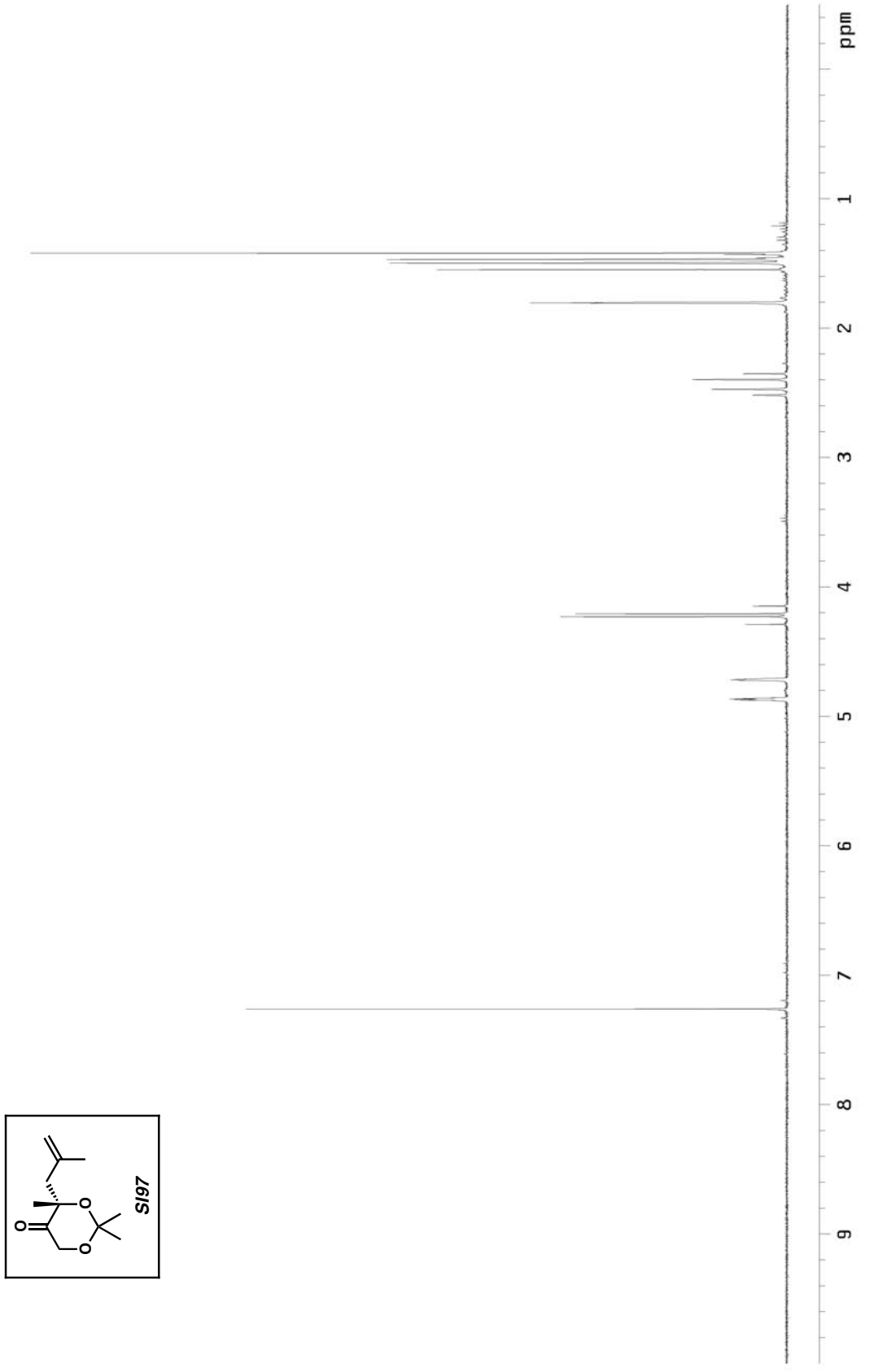
^{13}C NMR of compound **SI96** (75 MHz, $CDCl_3$)



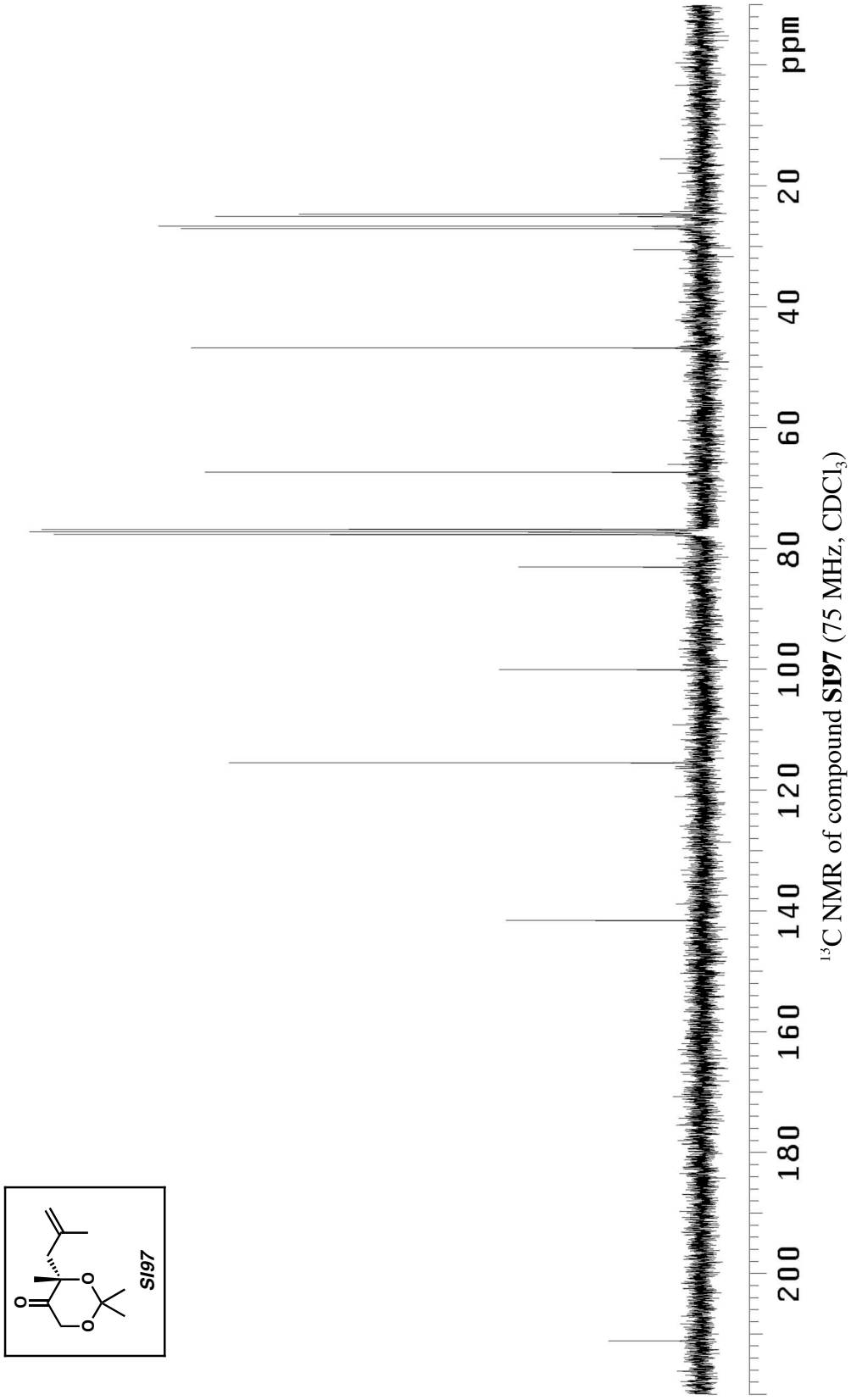
^{1}H NMR of compound ***57*** (300 MHz, $CDCl_3$)



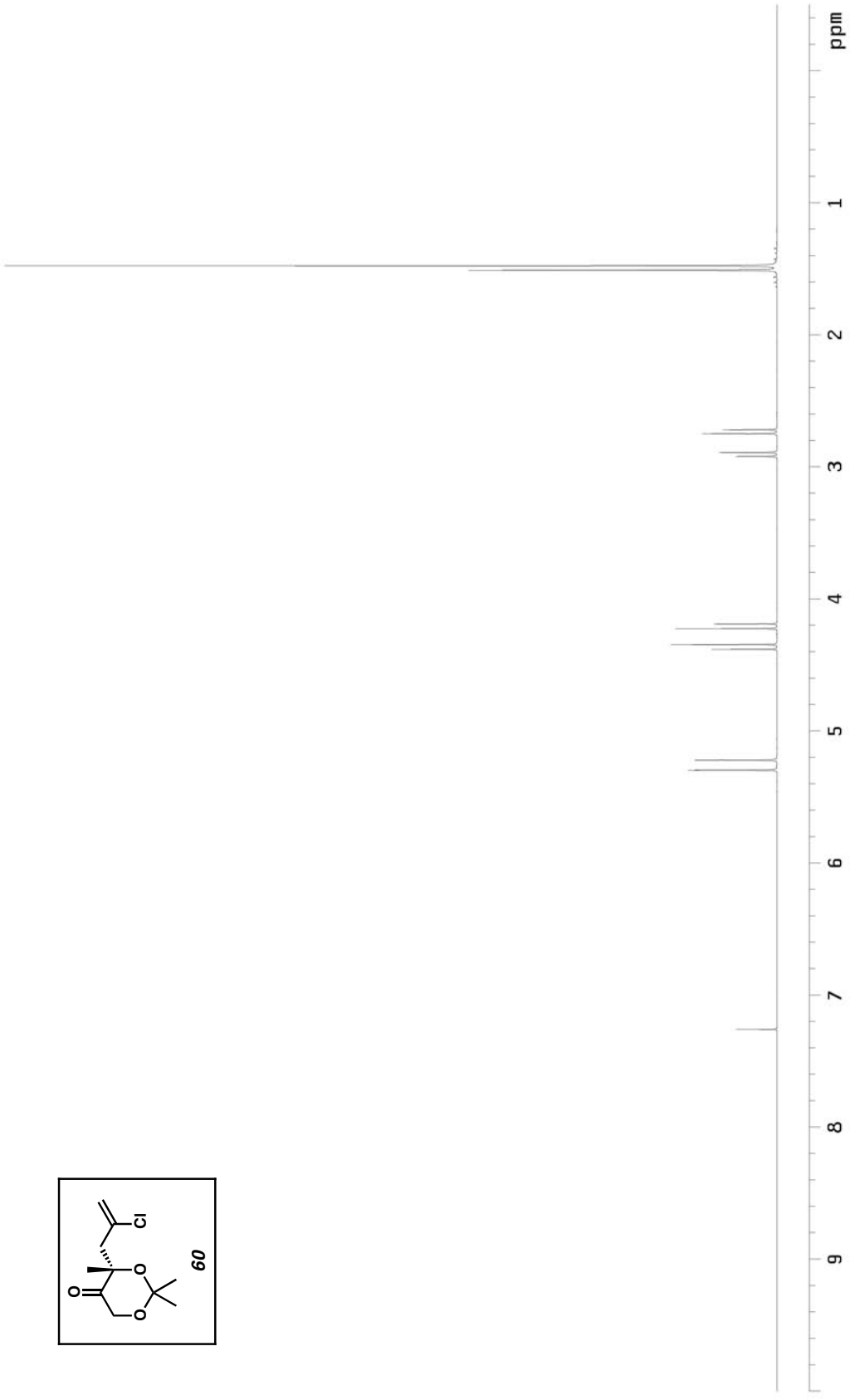
^{13}C NMR of compound **57** (75 MHz, $CDCl_3$)



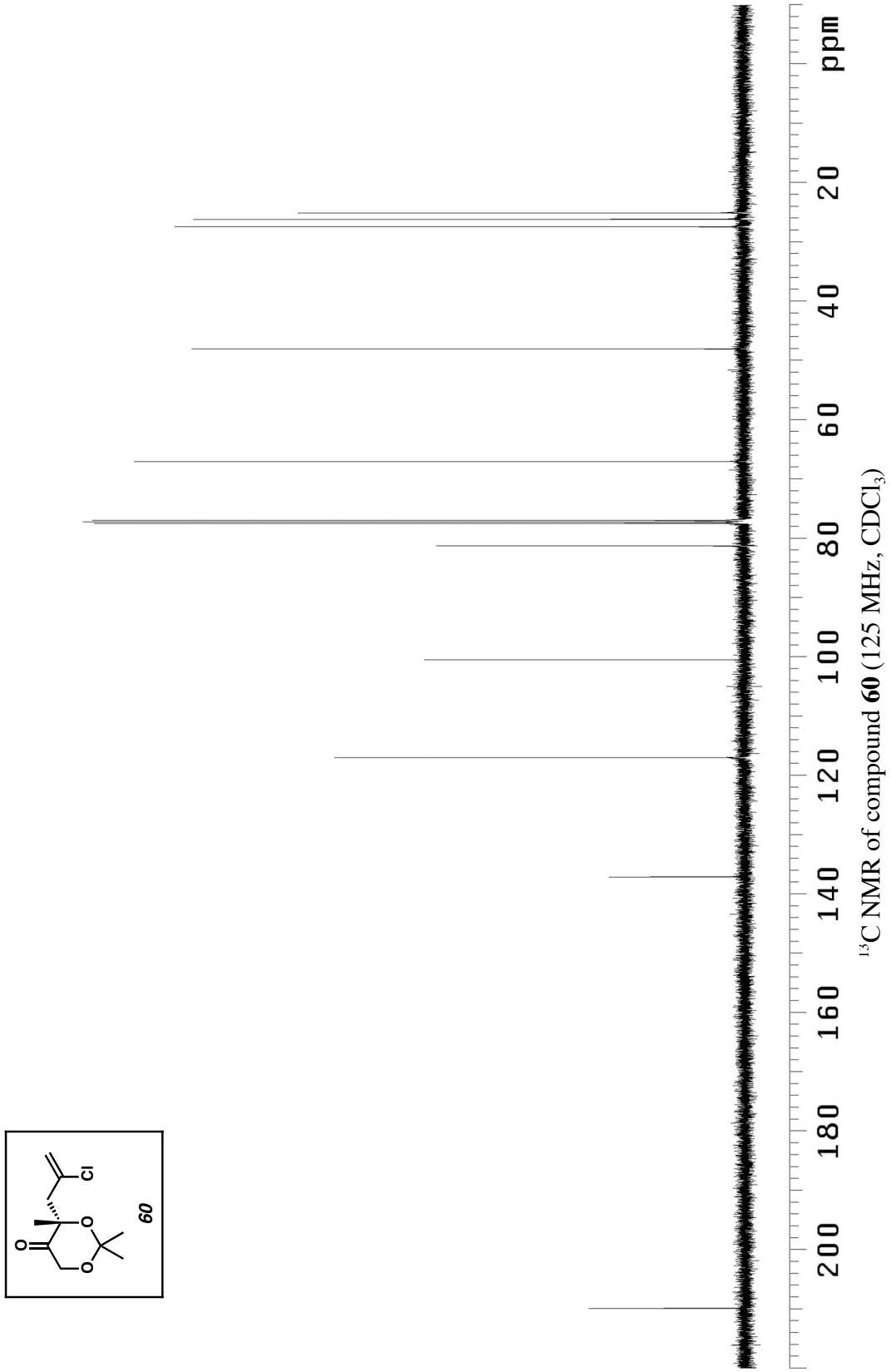
^{1}H NMR of compound **SI97** (300 MHz, $CDCl_3$)



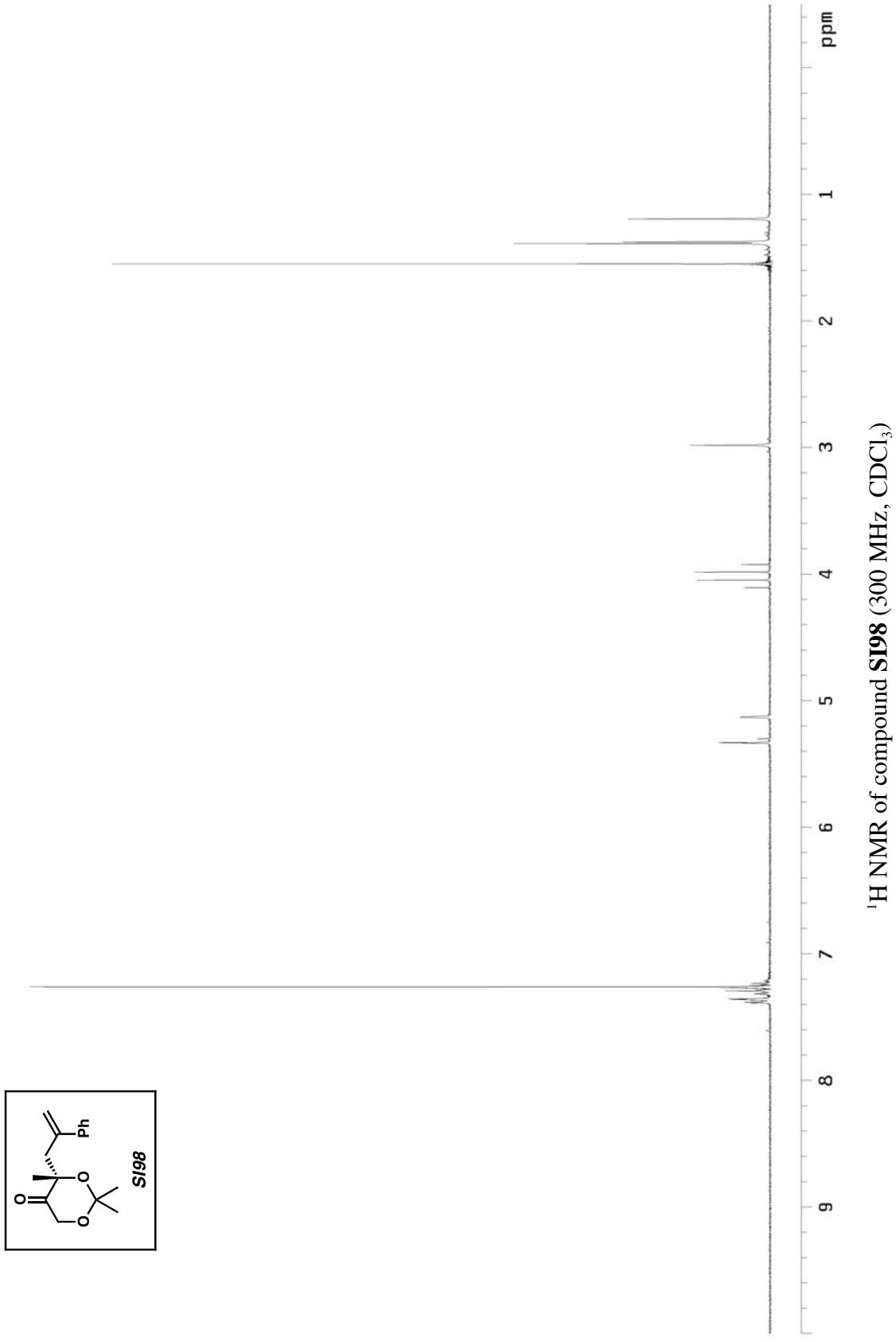
^{13}C NMR of compound **SI97** (75 MHz, $CDCl_3$)



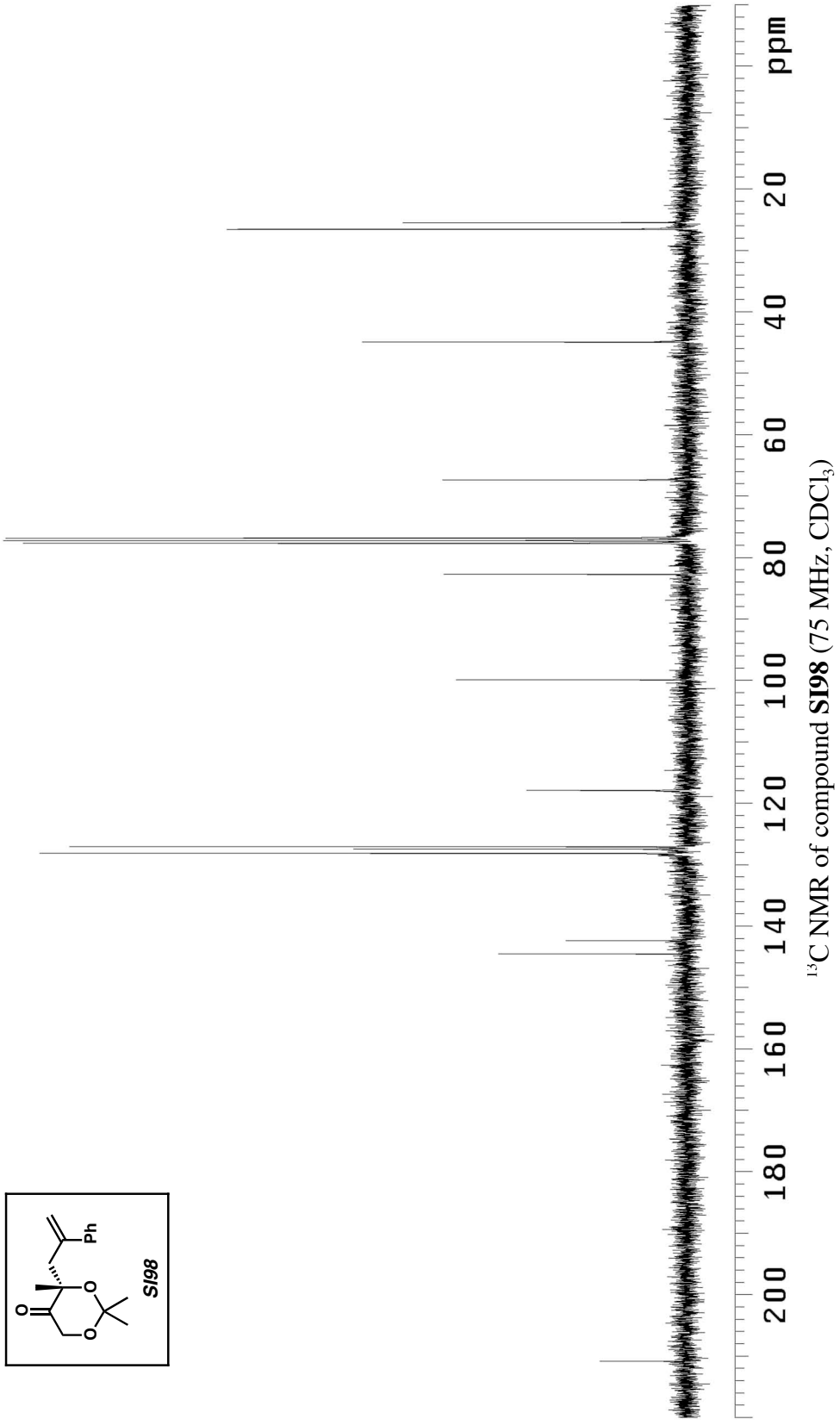
^{1}H NMR of compound **60** (500 MHz, $CDCl_3$)



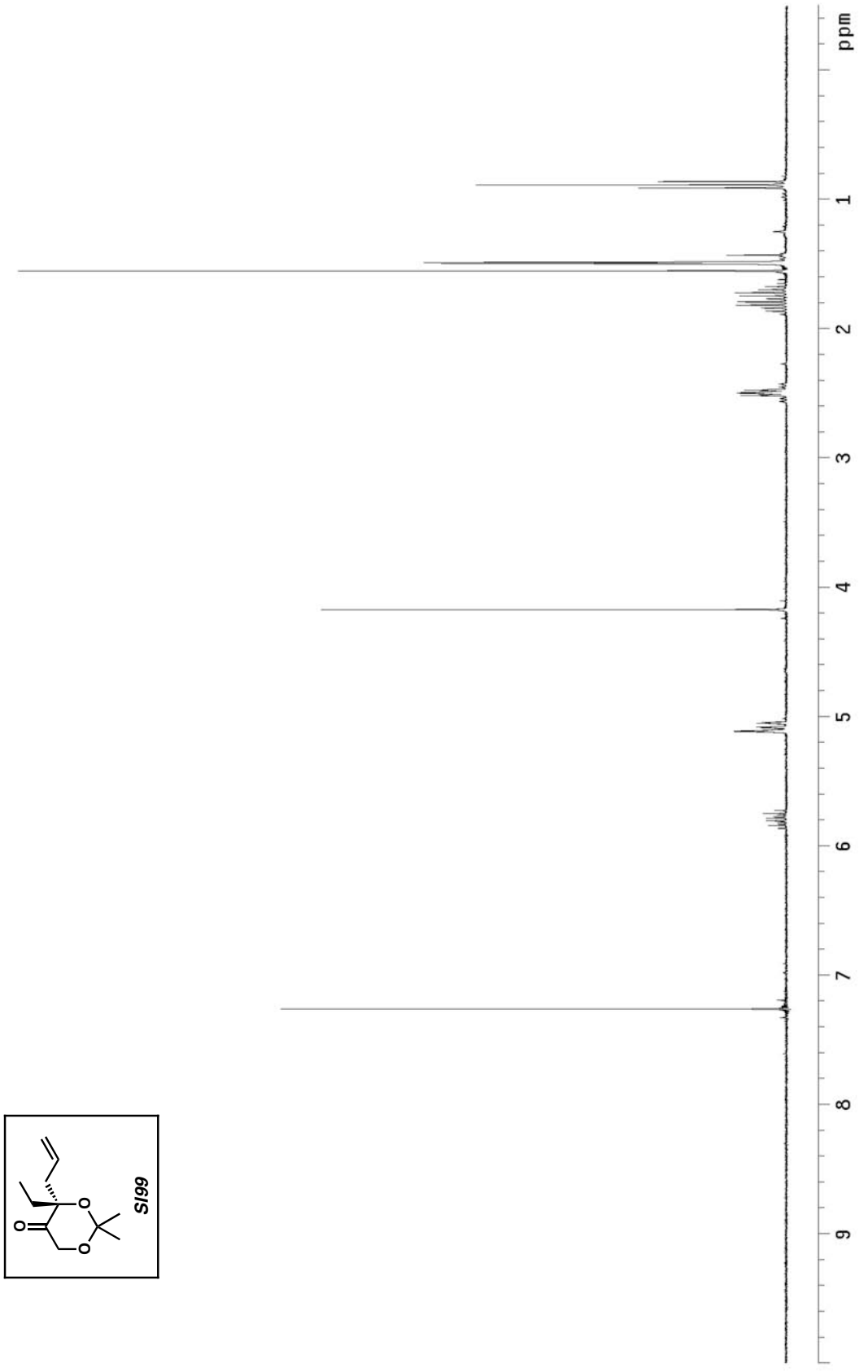
^{13}C NMR of compound **60** (125 MHz, $CDCl_3$)



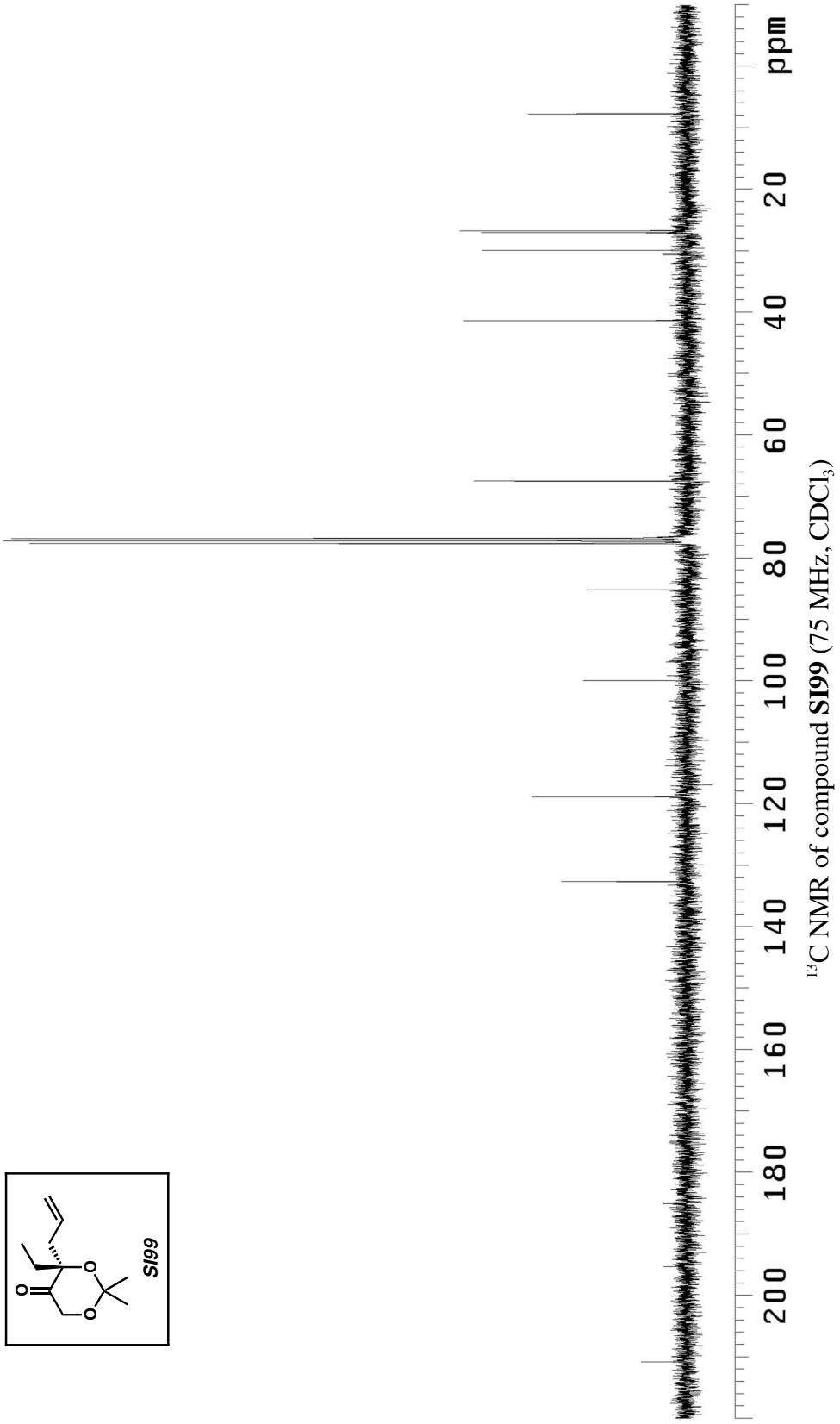
^{1}H NMR of compound **SI98** (300 MHz, $CDCl_3$)



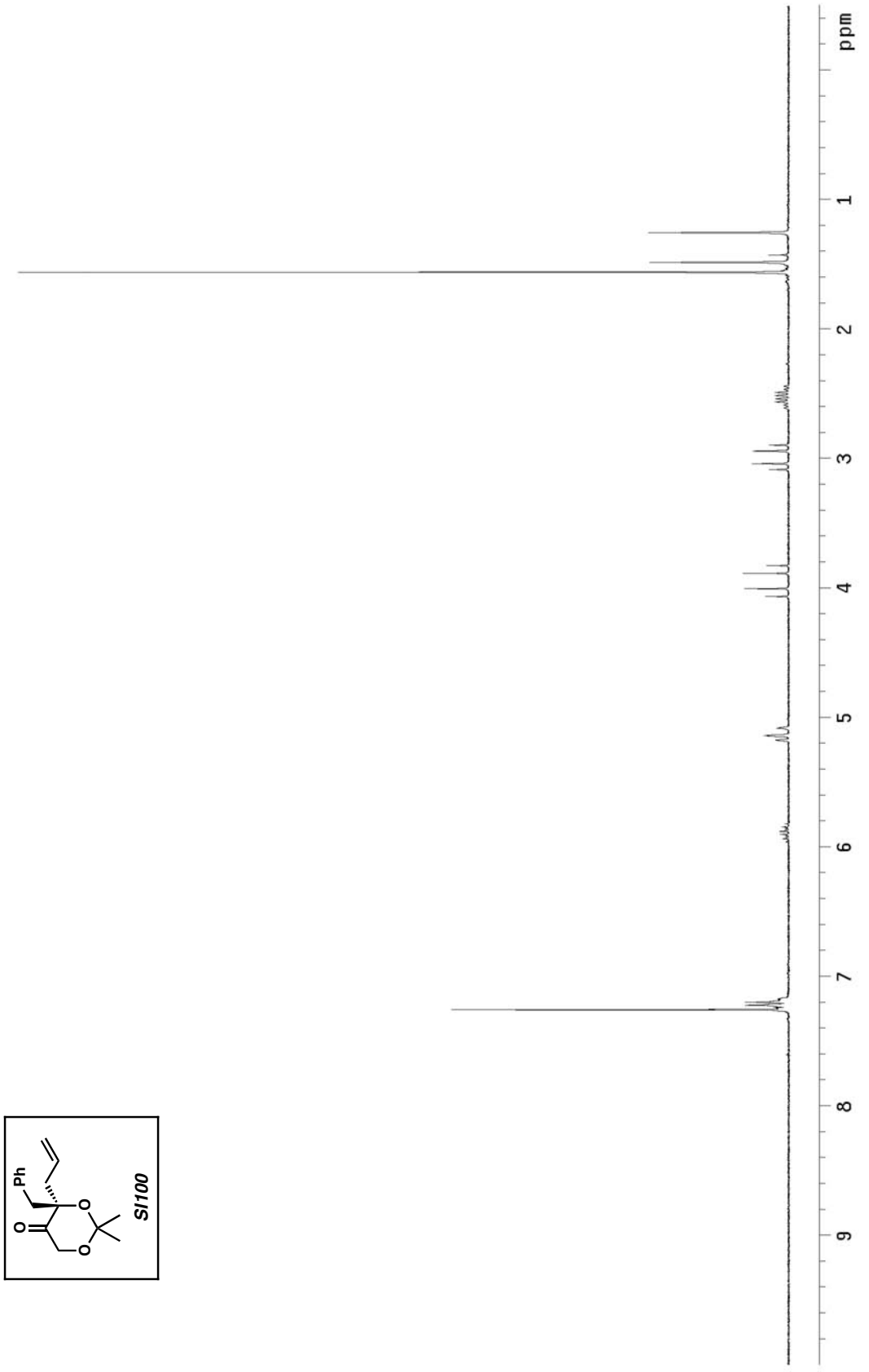
^{13}C NMR of compound **SI98** (75 MHz, $CDCl_3$)



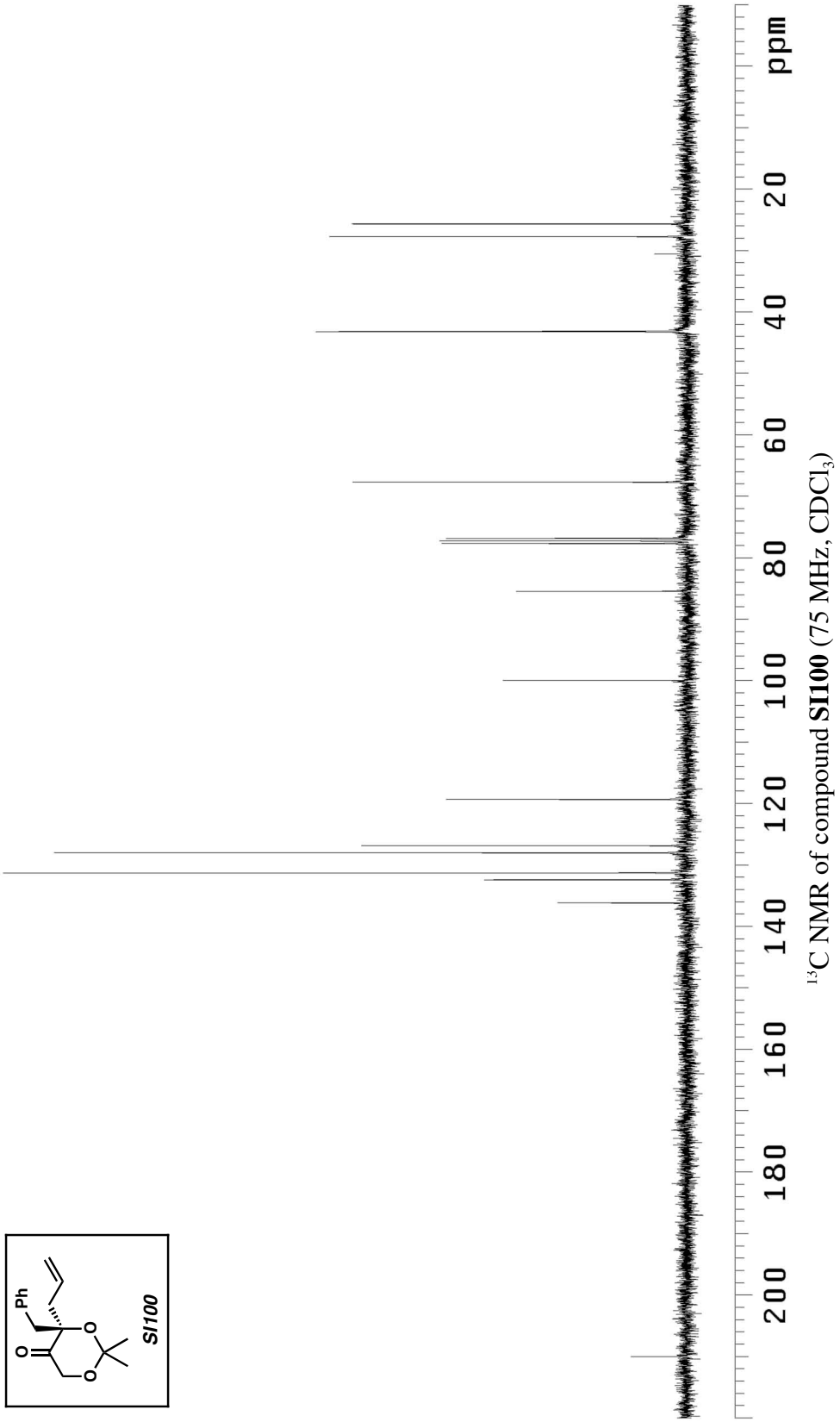
^{1}H NMR of compound **SI99** (300 MHz, $CDCl_3$)



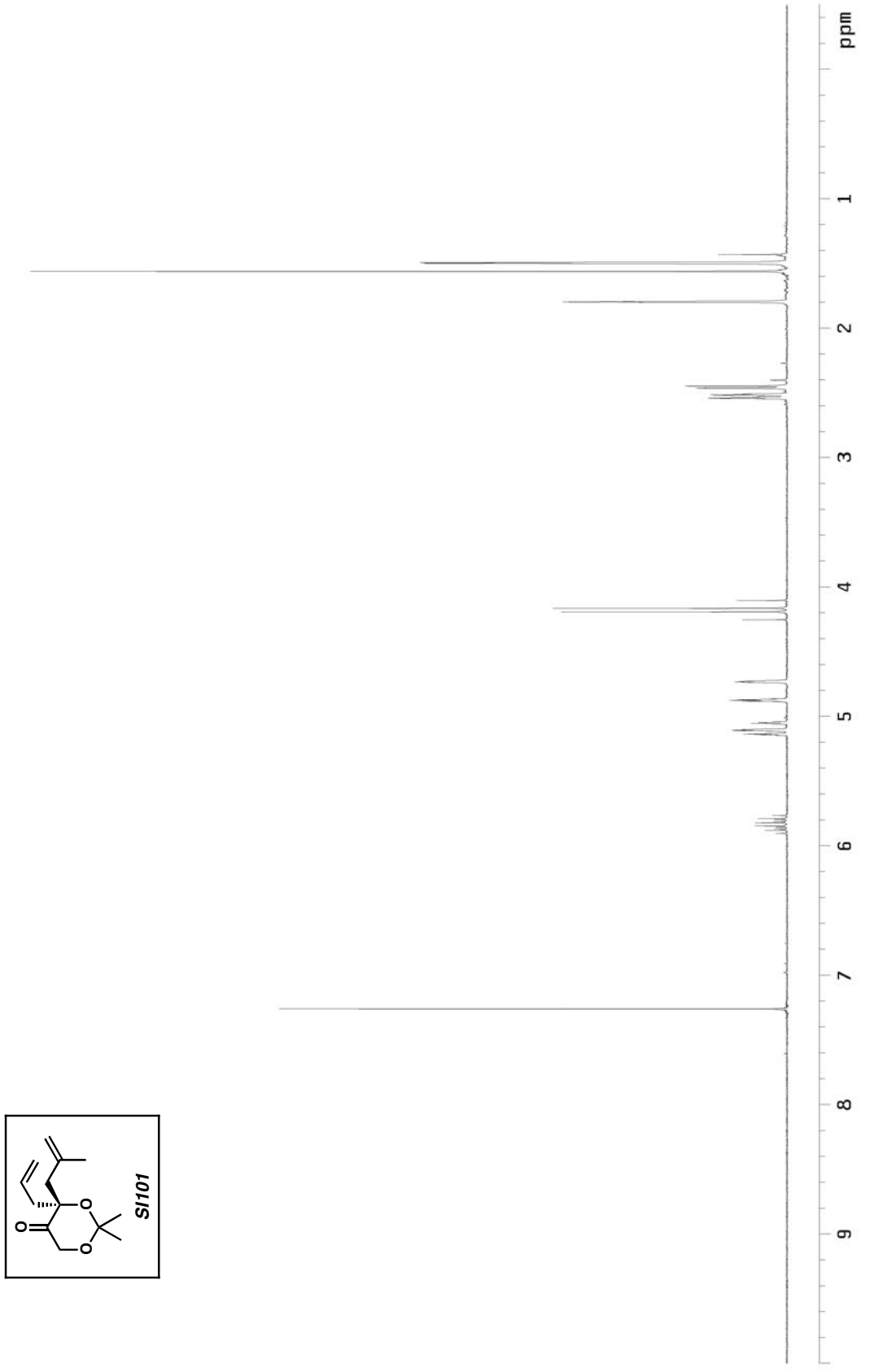
^{13}C NMR of compound **SI99** (75 MHz, $CDCl_3$)



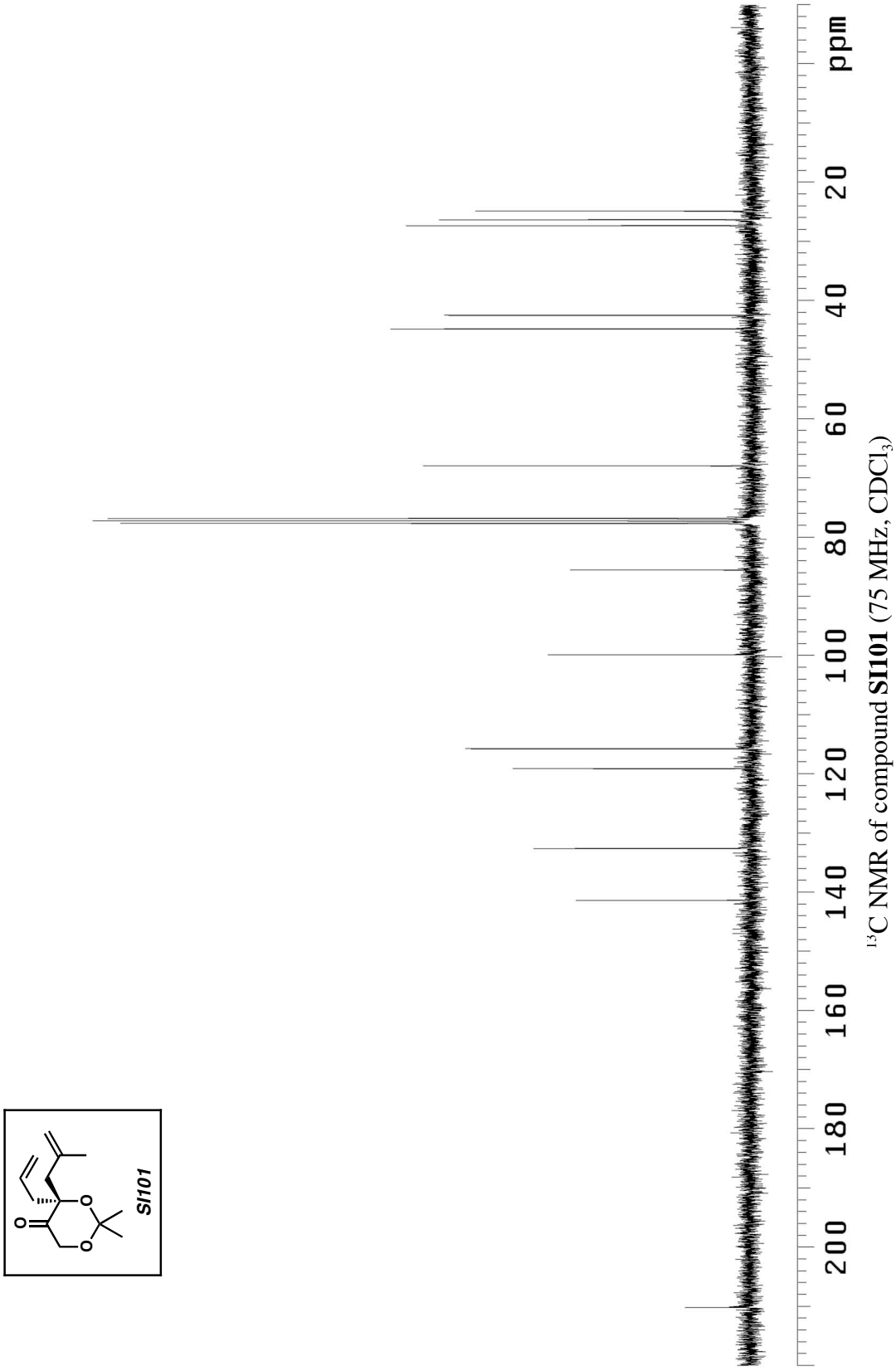
^{1}H NMR of compound **SI100** (300 MHz, $CDCl_3$)



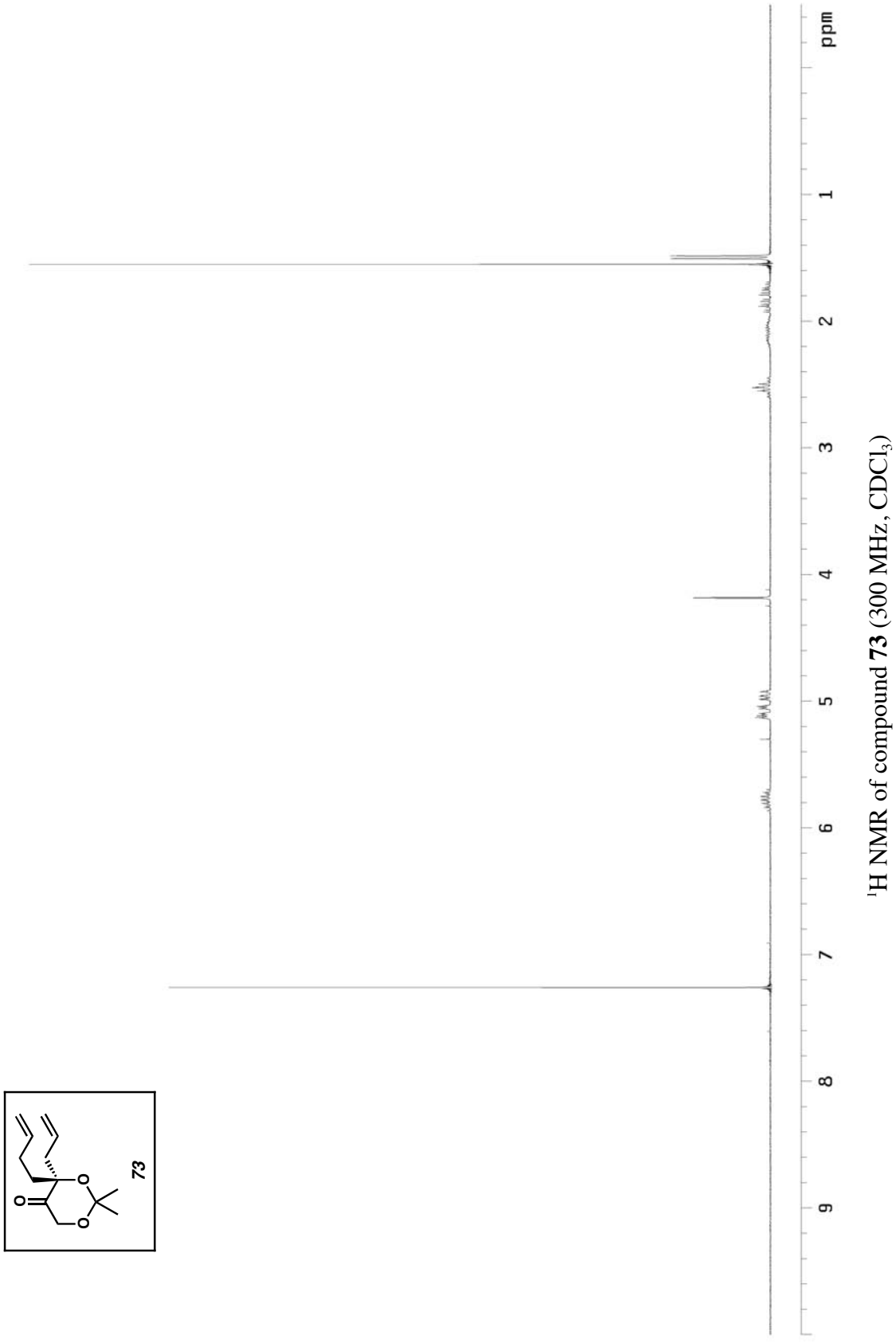
^{13}C NMR of compound **SI100** (75 MHz, $CDCl_3$)



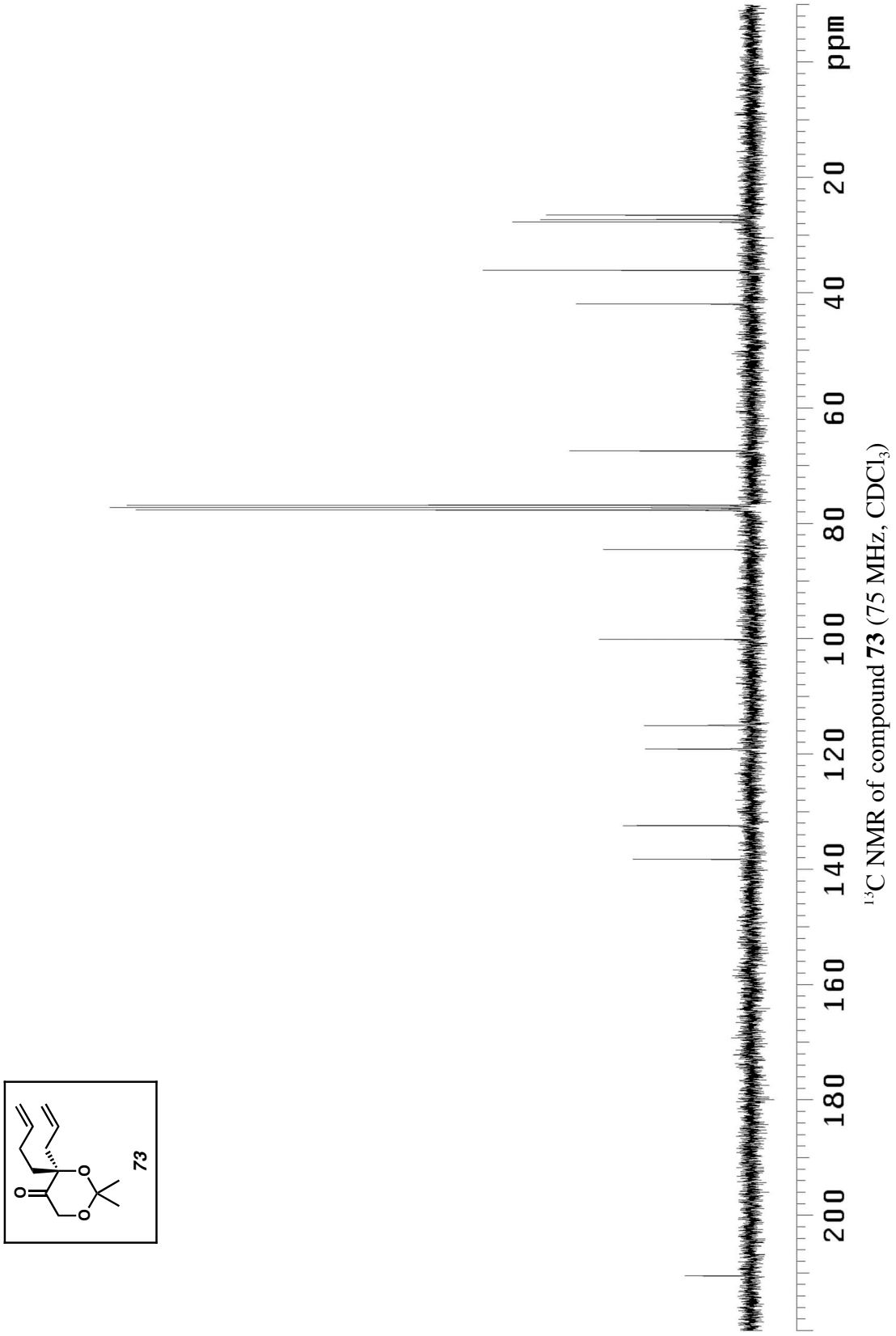
^{1}H NMR of compound **SI101** (300 MHz, $CDCl_3$)



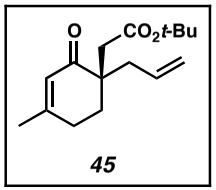
^{13}C NMR of compound **SI101** (75 MHz, $CDCl_3$)



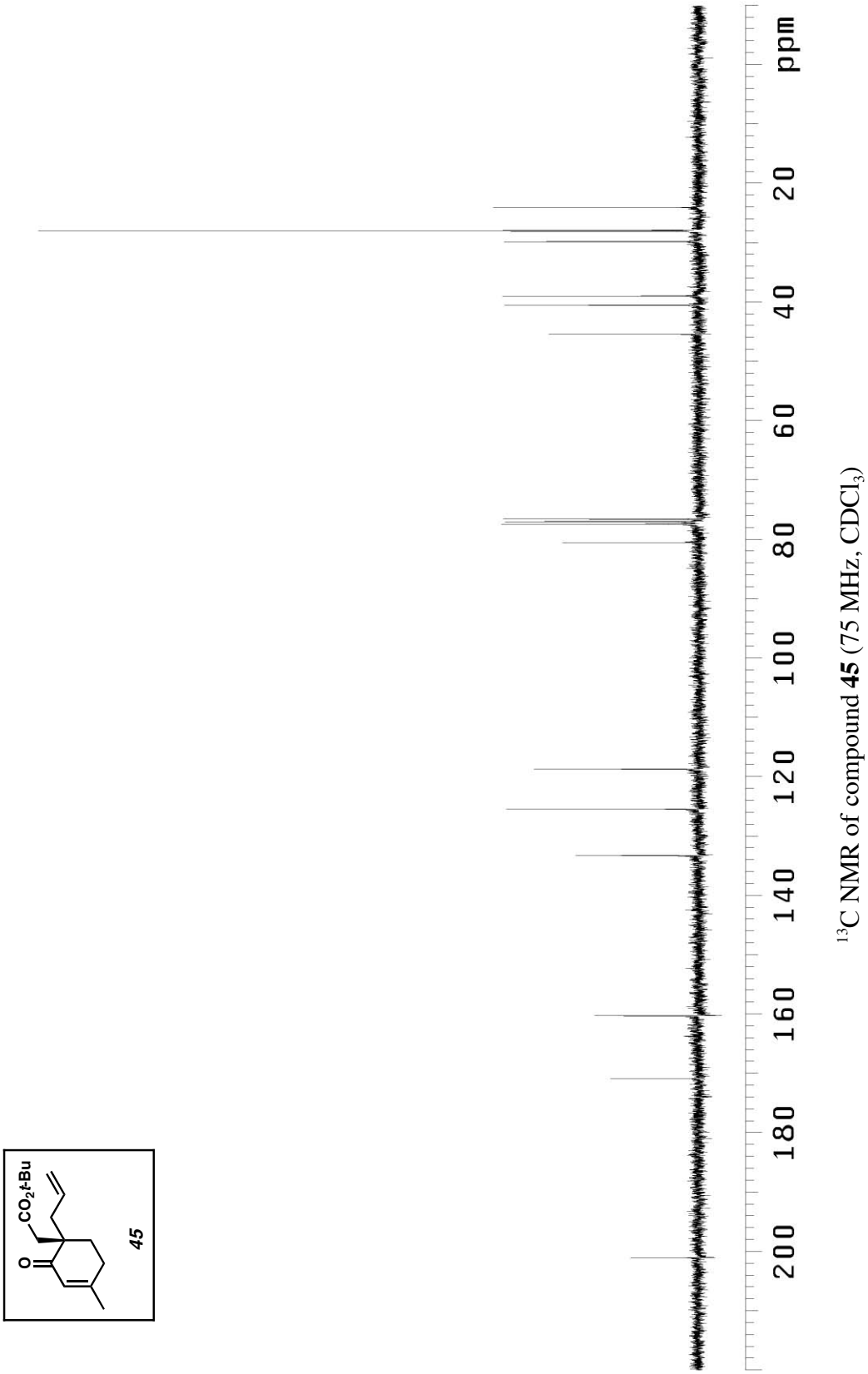
^{1}H NMR of compound **73** (300 MHz, $CDCl_3$)



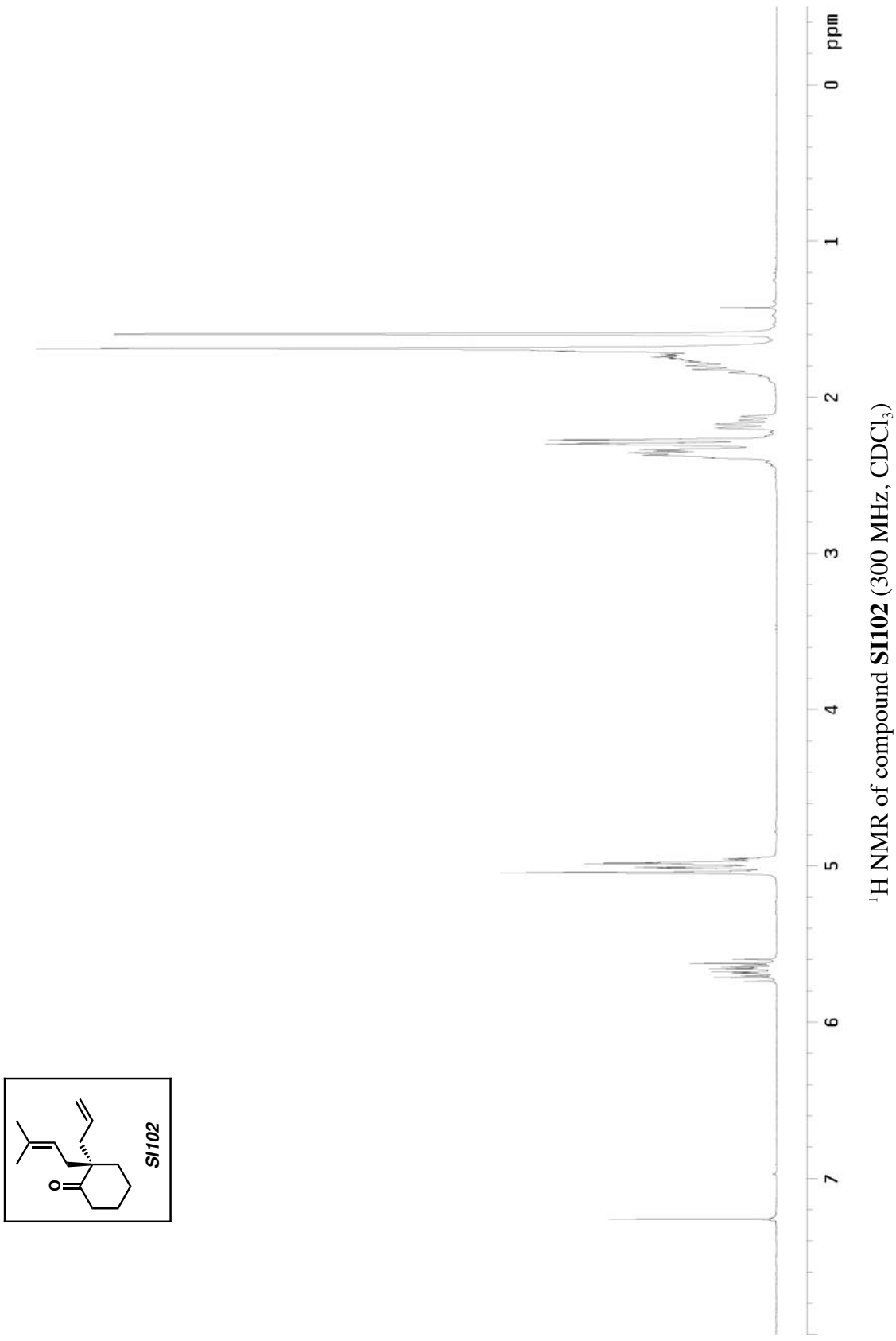
^{13}C NMR of compound **73** (75 MHz, $CDCl_3$)



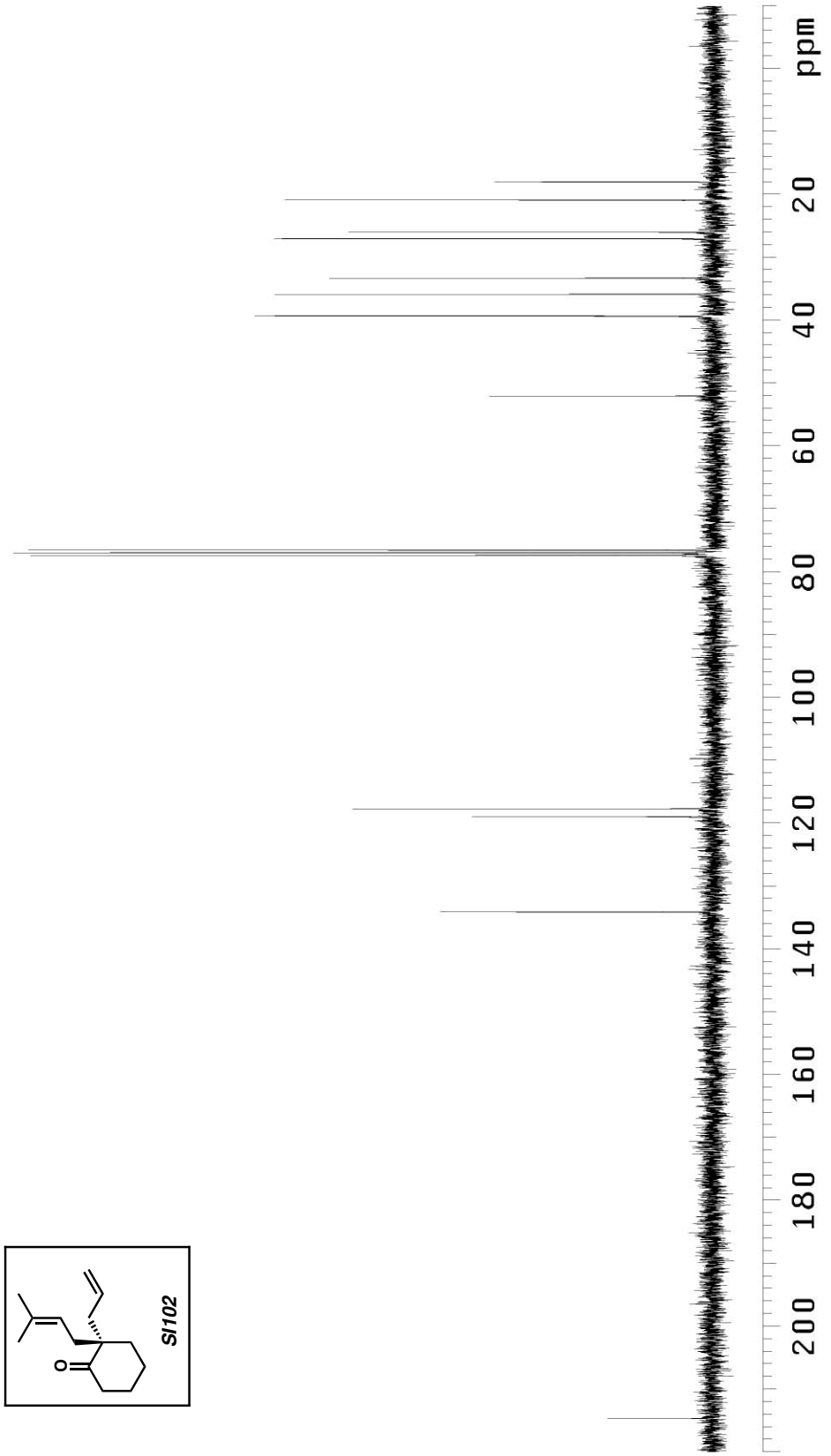
^{1}H NMR of compound **45** (300 MHz, $CDCl_3$)



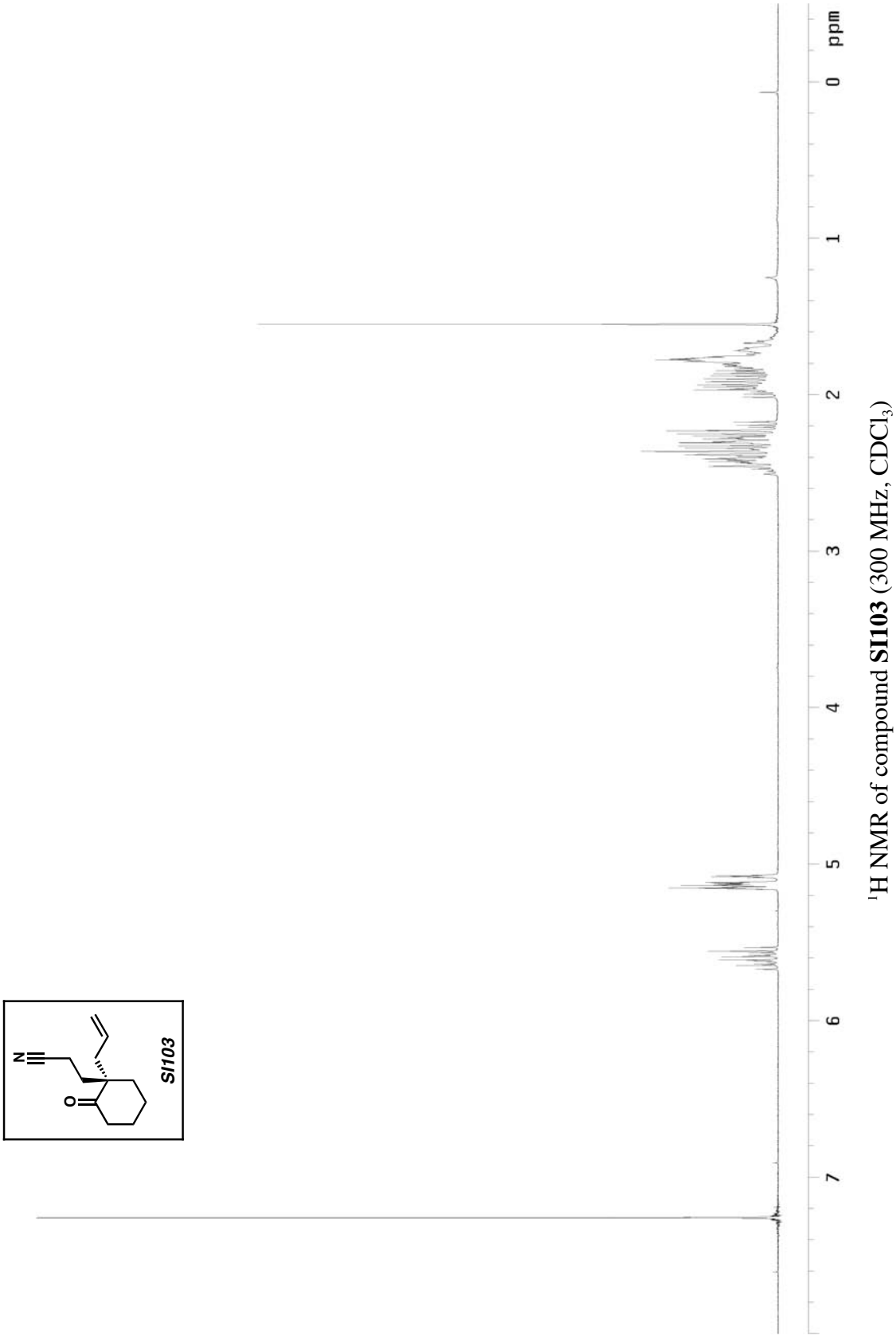
^{13}C NMR of compound **45** (75 MHz, $CDCl_3$)



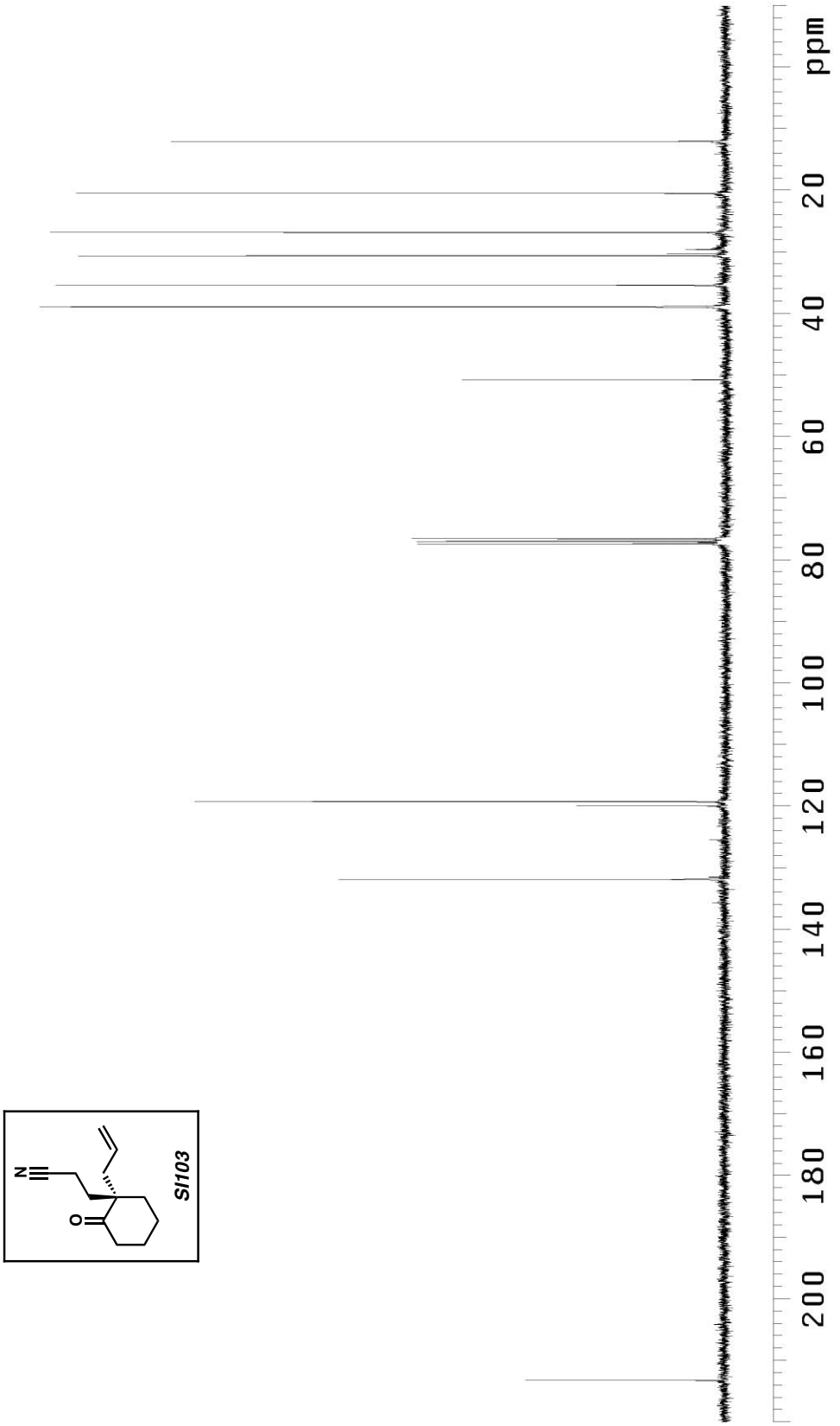
^{1}H NMR of compound **SI102** (300 MHz, $CDCl_3$)



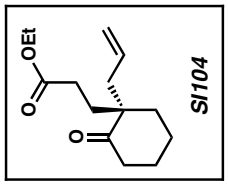
^{13}C NMR of compound **SI102** (75 MHz, $CDCl_3$)



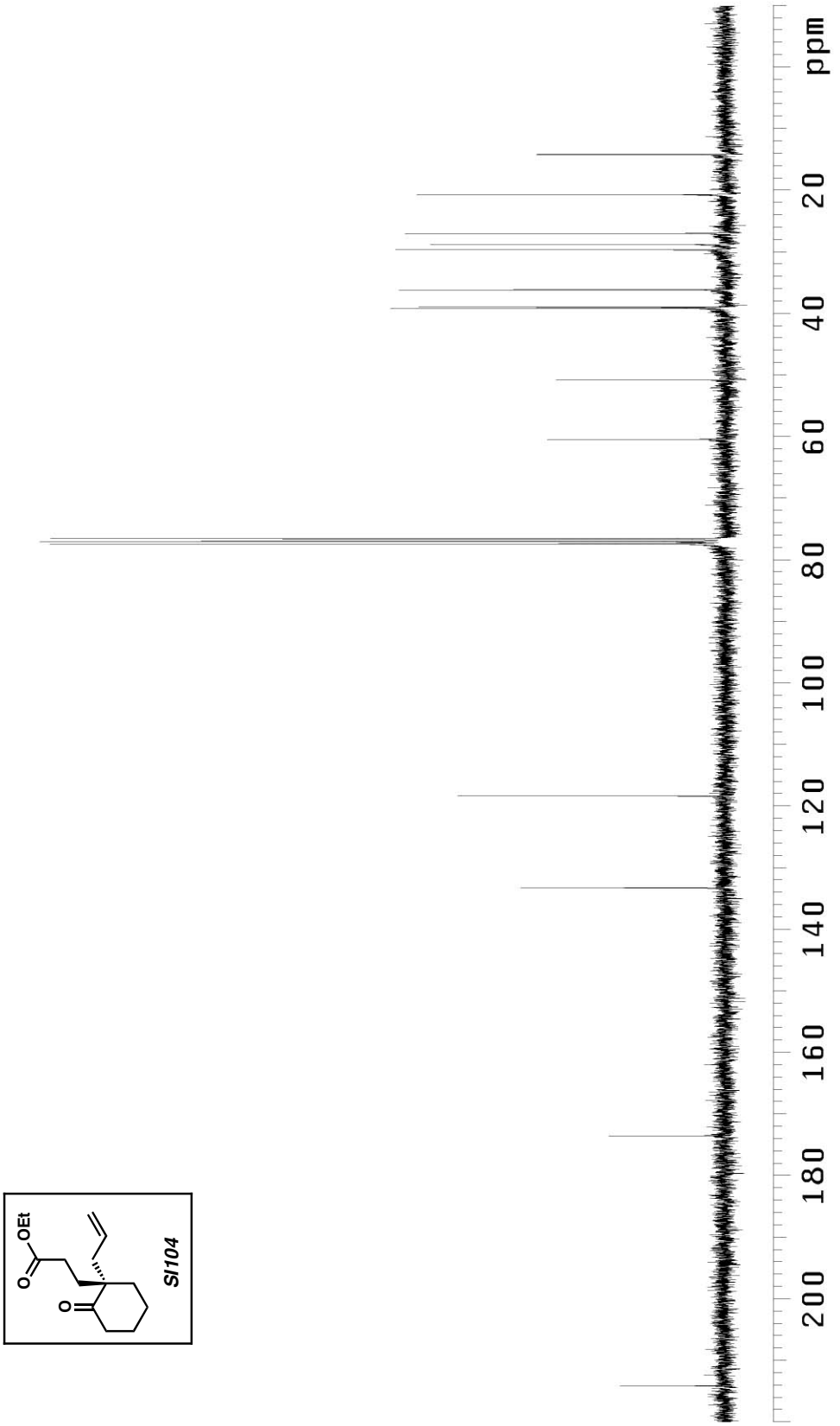
^{1}H NMR of compound **SI103** (300 MHz, $CDCl_3$)



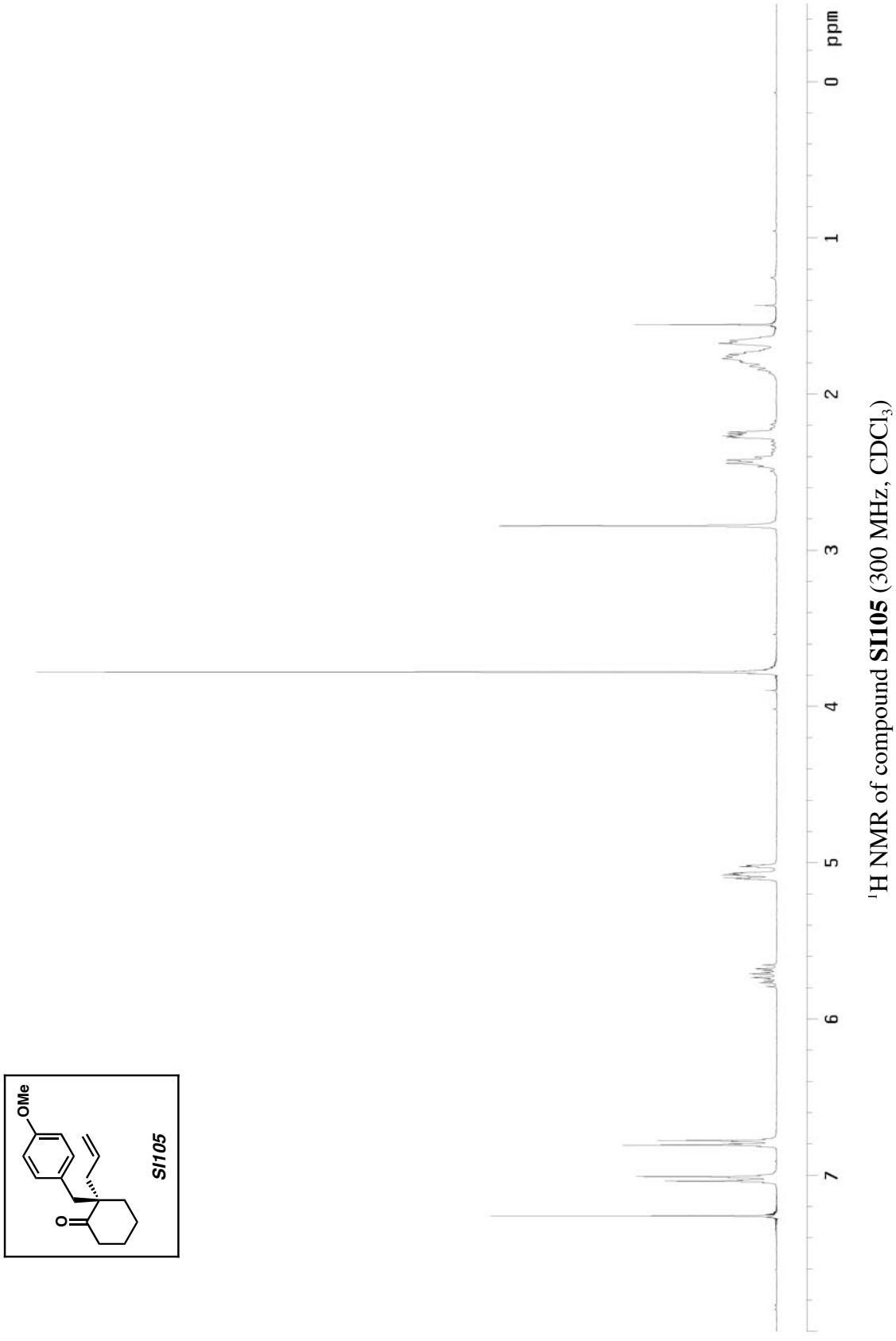
^{13}C NMR of compound **SI103** (75 MHz, $CDCl_3$)



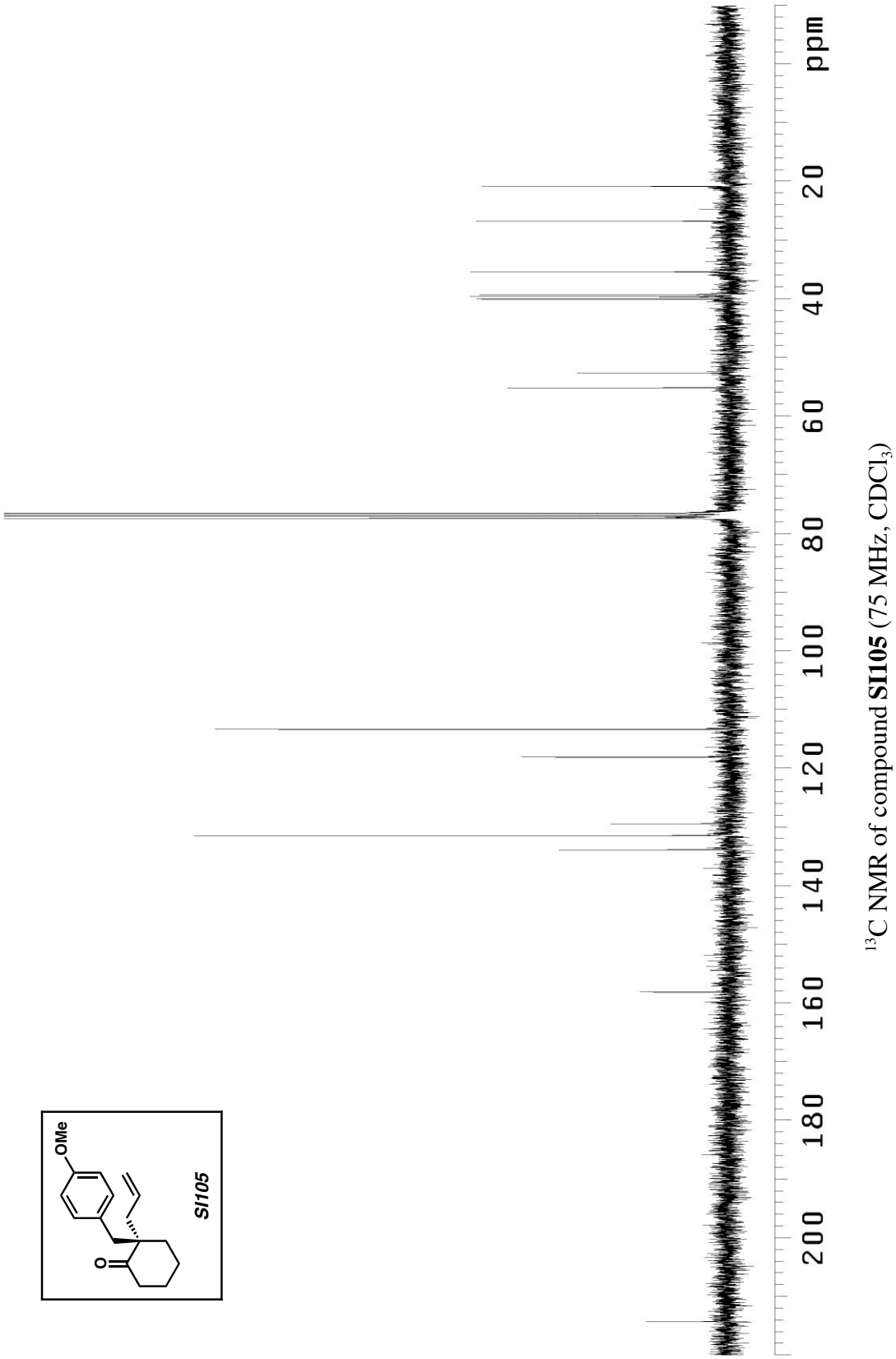
^{1}H NMR of compound **SI104** (300 MHz, $CDCl_3$)



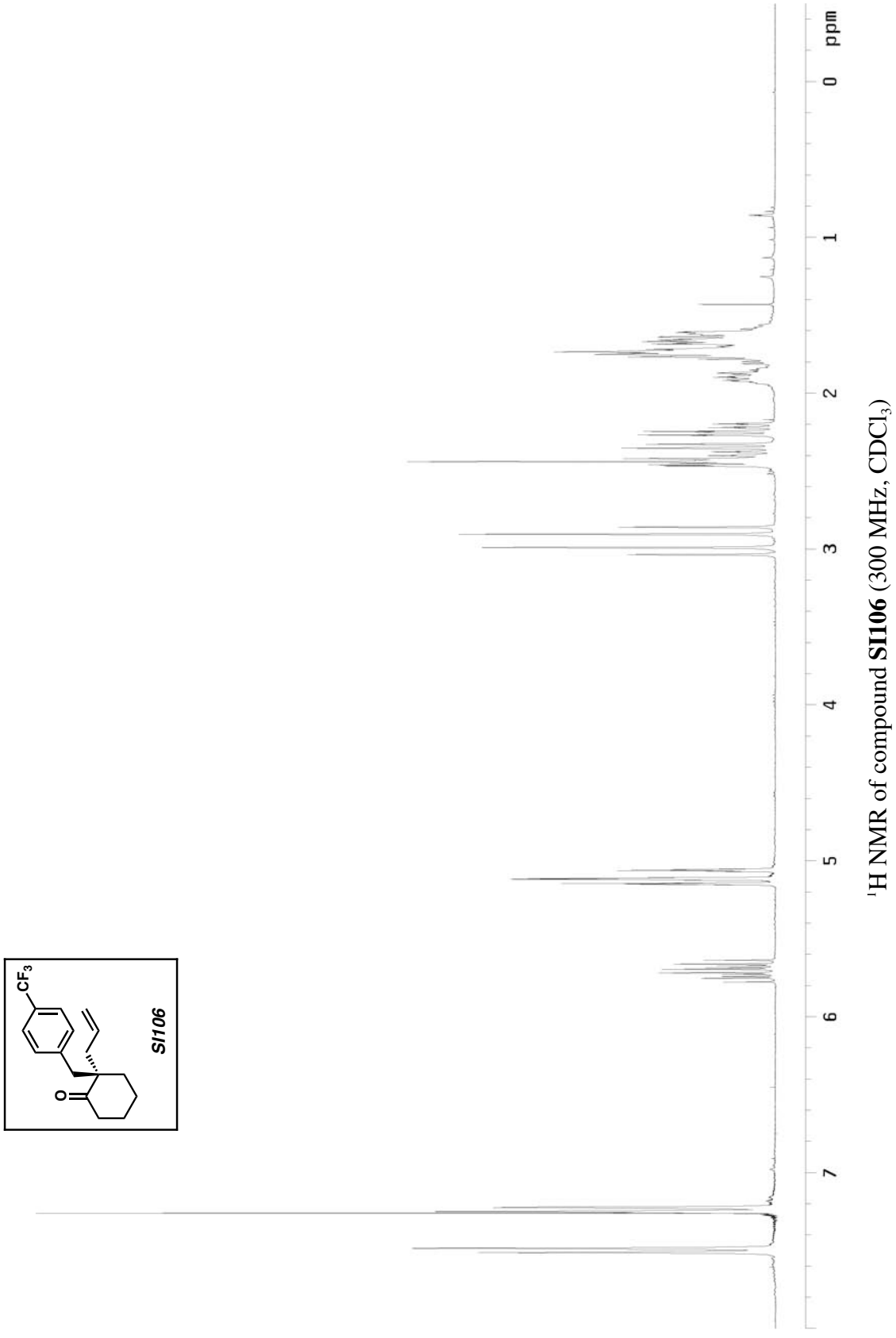
^{13}C NMR of compound **SI104** (75 MHz, $CDCl_3$)



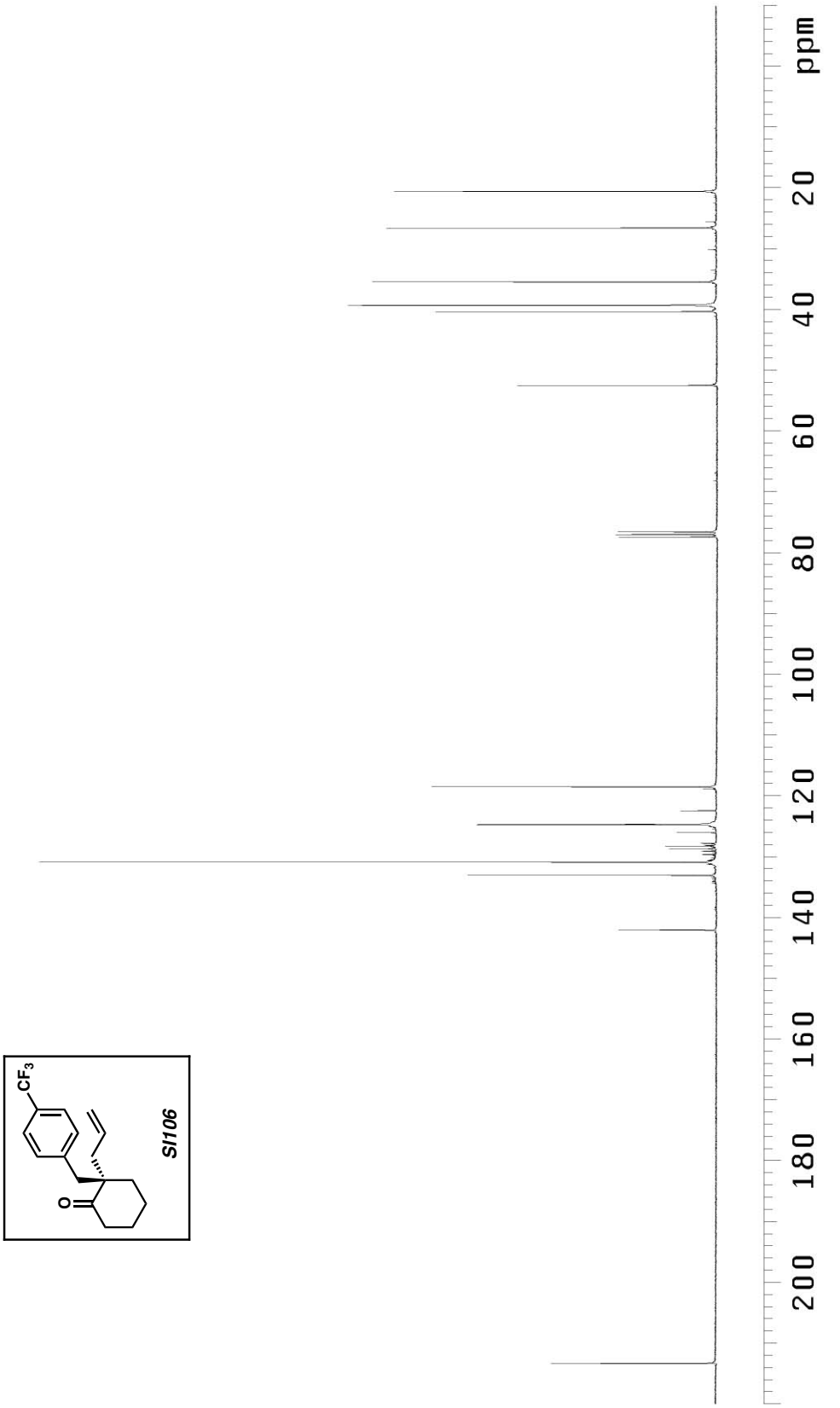
^{1}H NMR of compound **SI105** (300 MHz, $CDCl_3$)



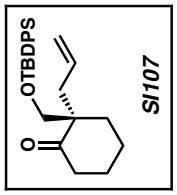
^{13}C NMR of compound **SI105** (75 MHz, $CDCl_3$)



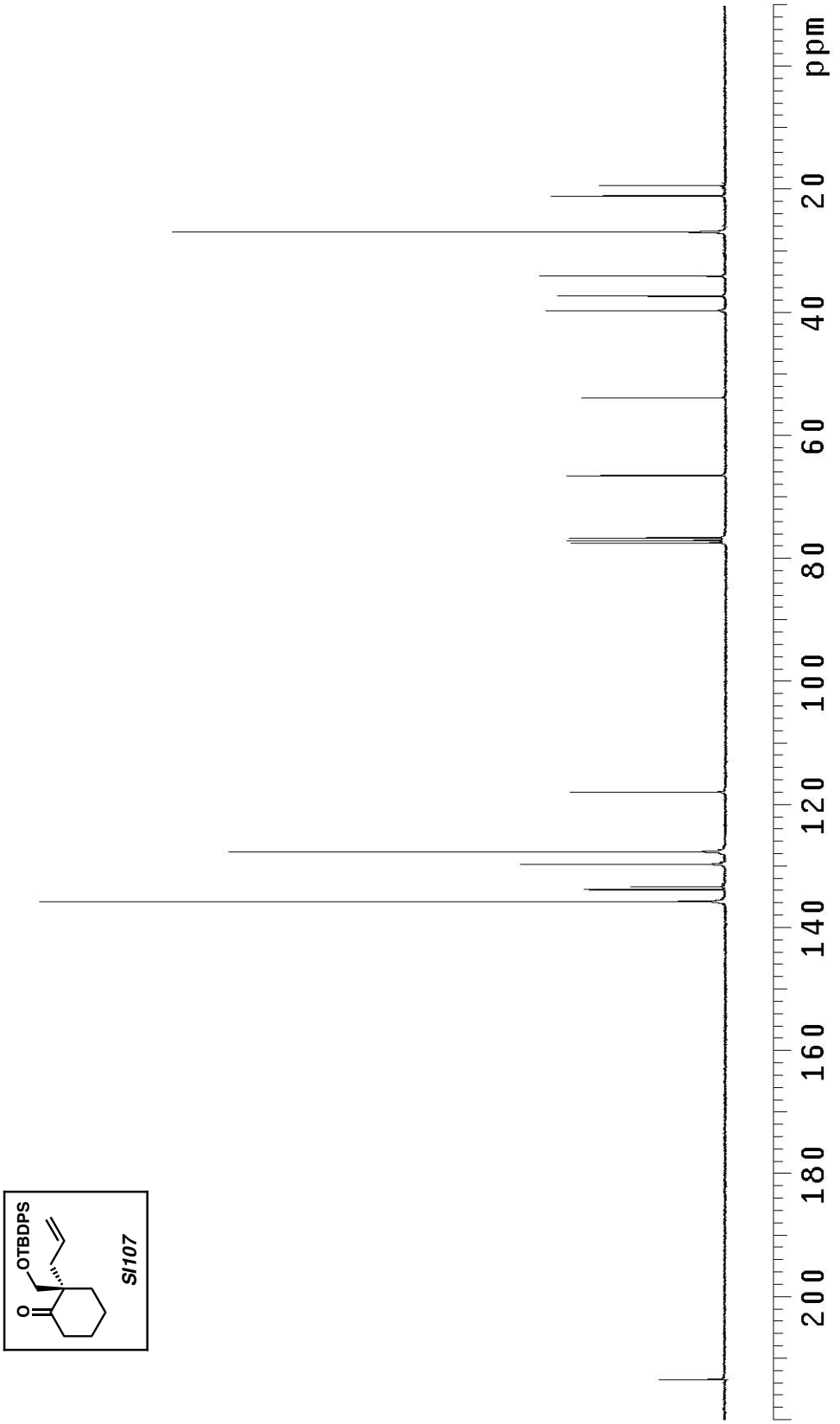
^{1}H NMR of compound **SI106** (300 MHz, $CDCl_3$)



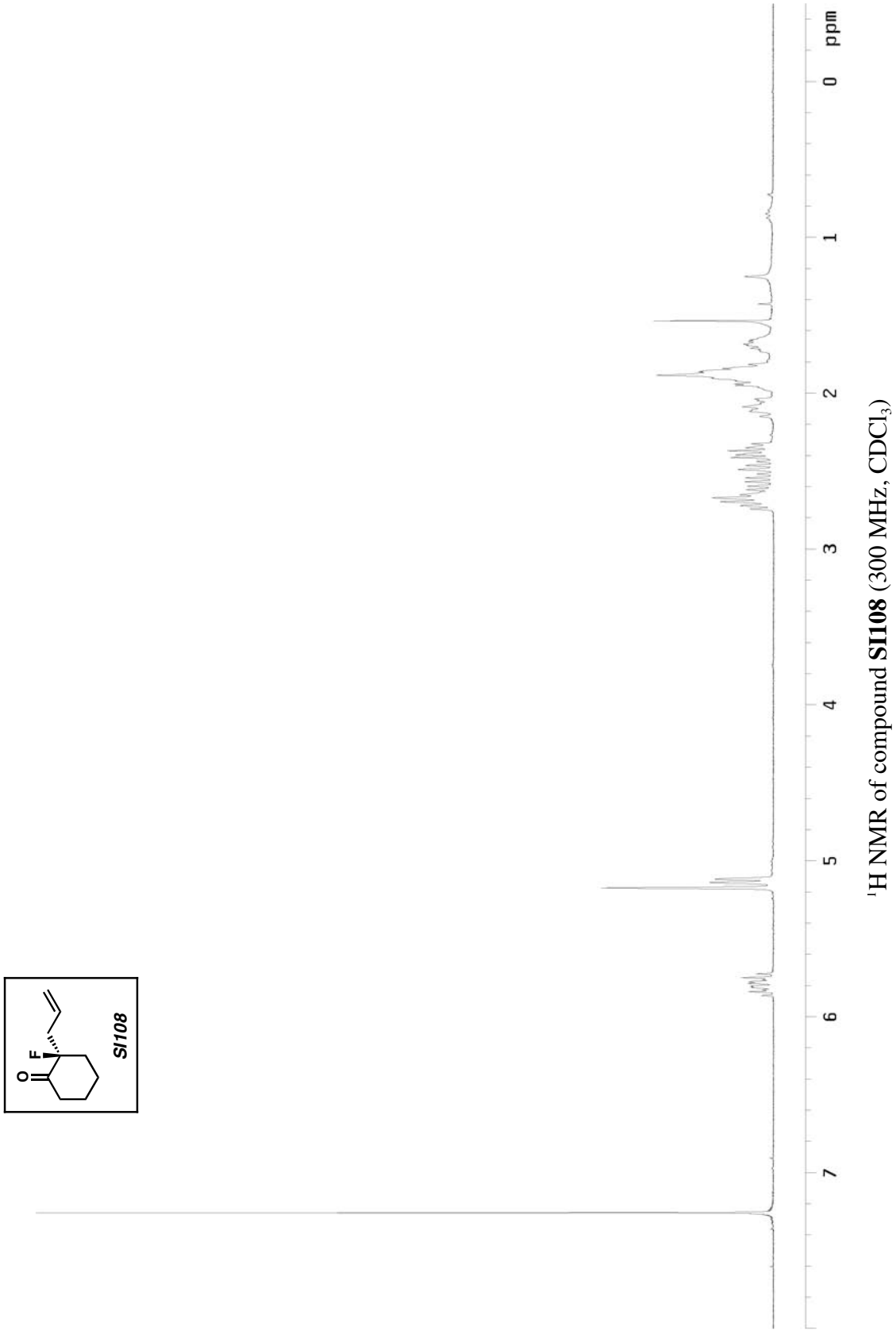
^{13}C NMR of compound **SI106** (75 MHz, $CDCl_3$)



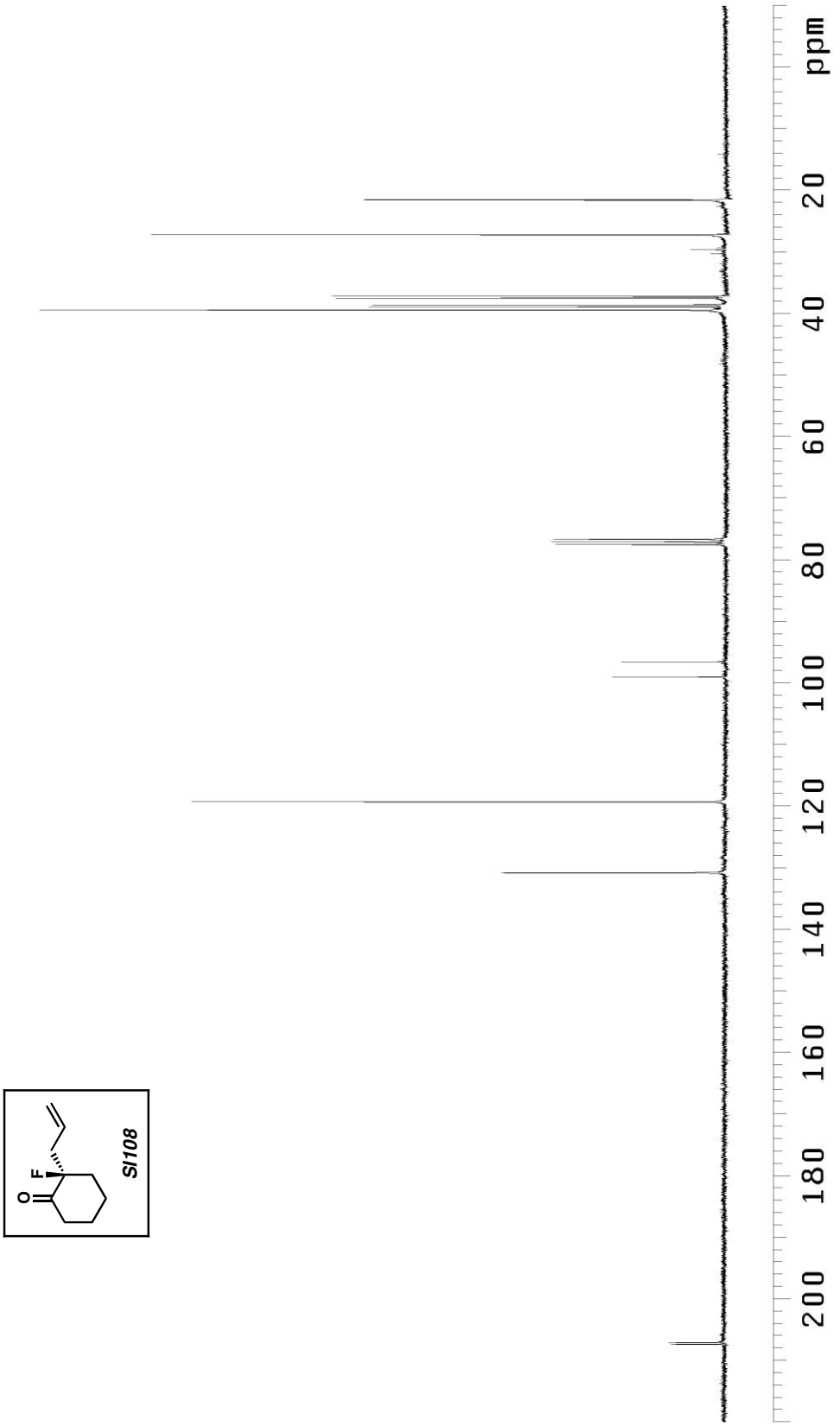
^{1}H NMR of compound **SI107** (300 MHz, $CDCl_3$)



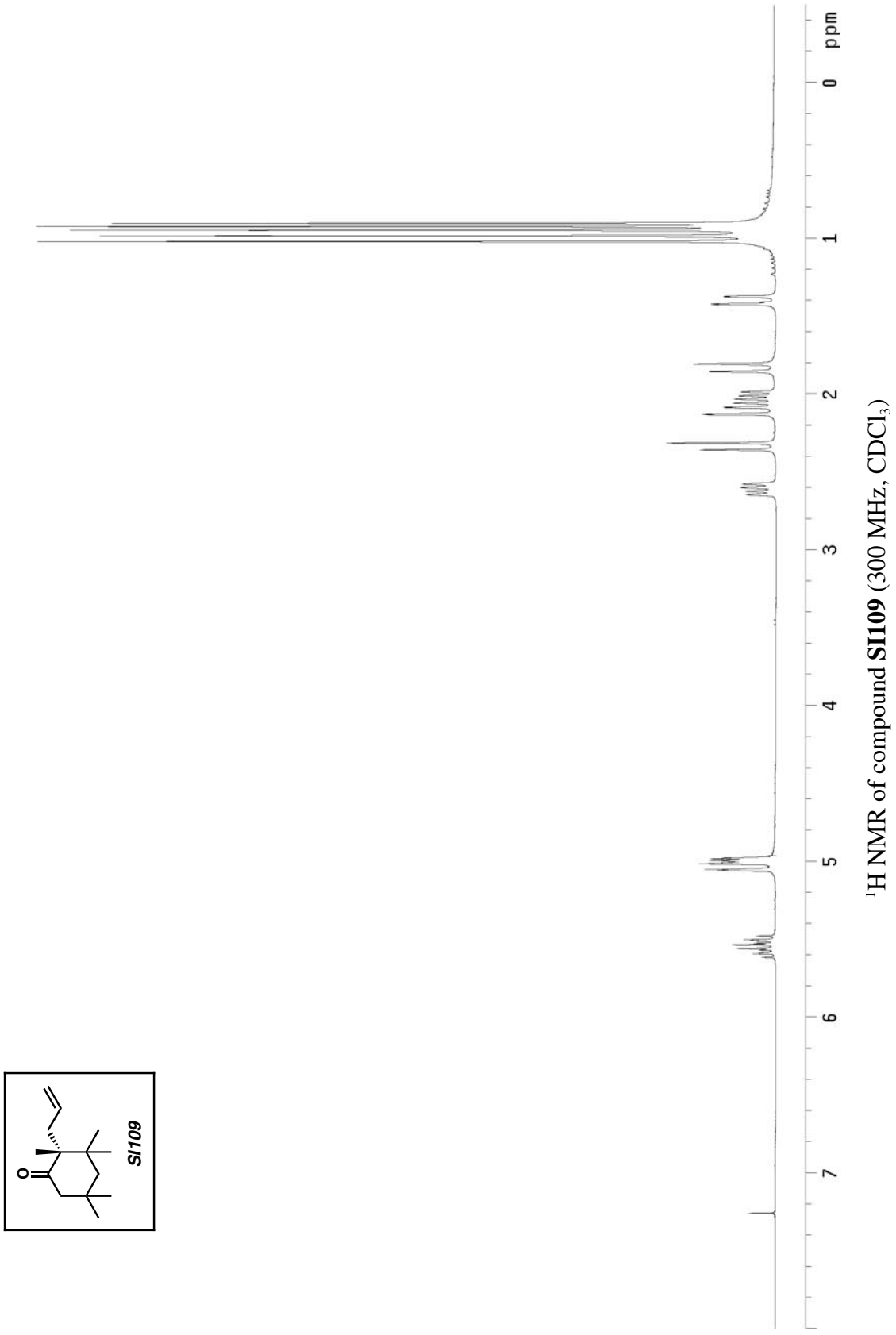
^{13}C NMR of compound **SI107** (75 MHz, $CDCl_3$)



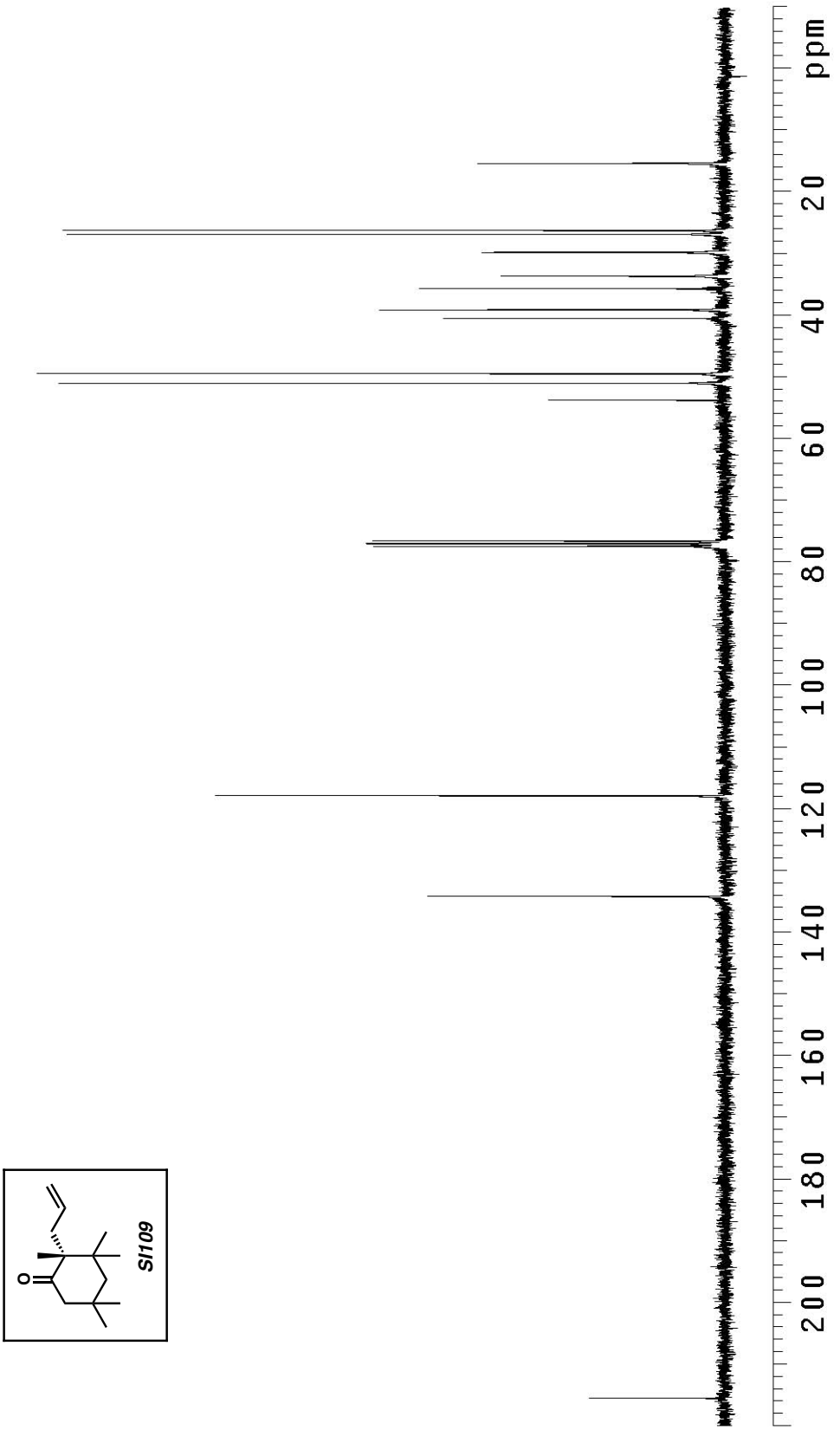
^{1}H NMR of compound **SI108** (300 MHz, $CDCl_3$)



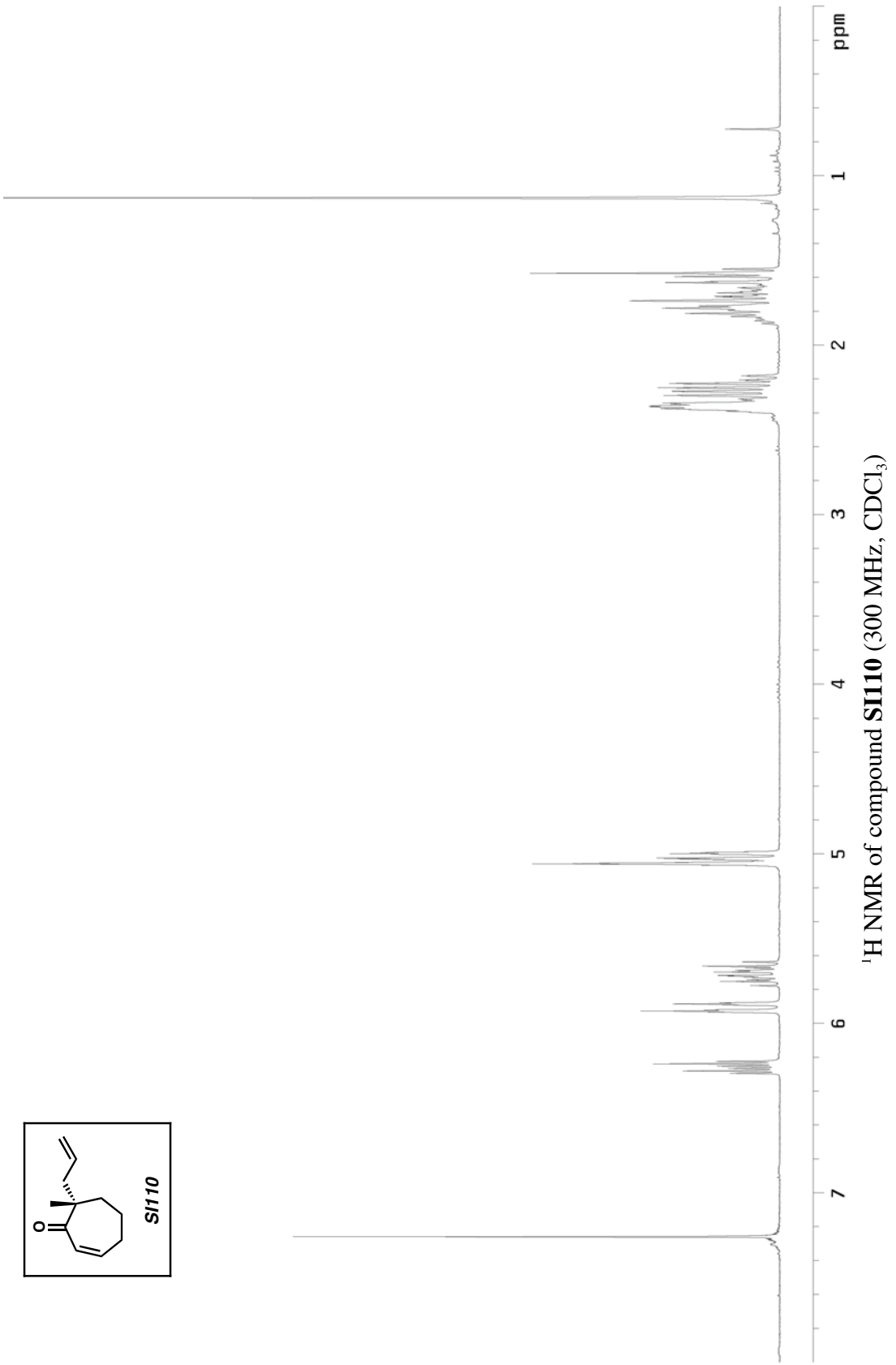
^{13}C NMR of compound **SI108** (75 MHz, $CDCl_3$)



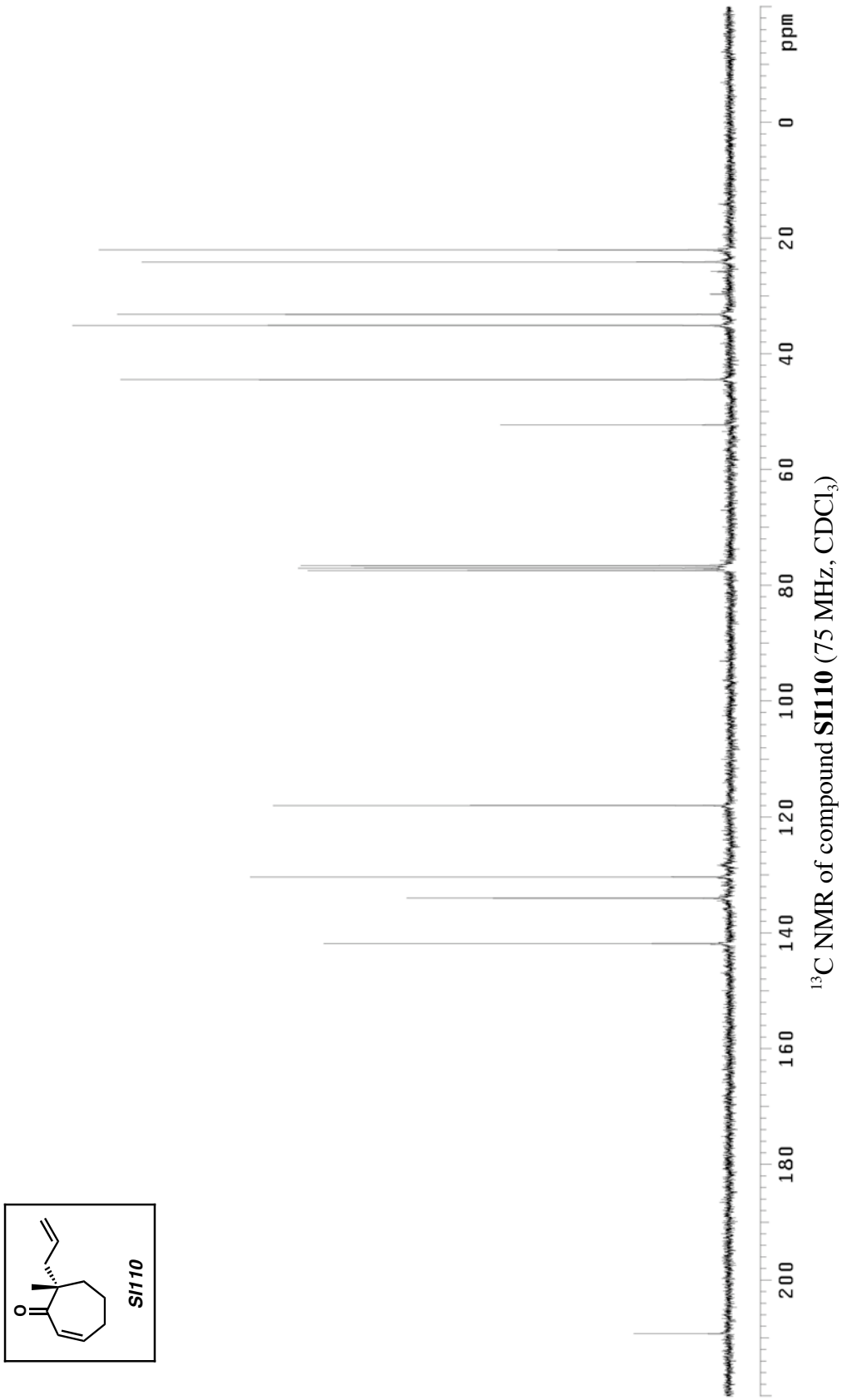
^{1}H NMR of compound **SI109** (300 MHz, $CDCl_3$)



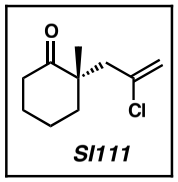
^{13}C NMR of compound **SI109** (75 MHz, $CDCl_3$)



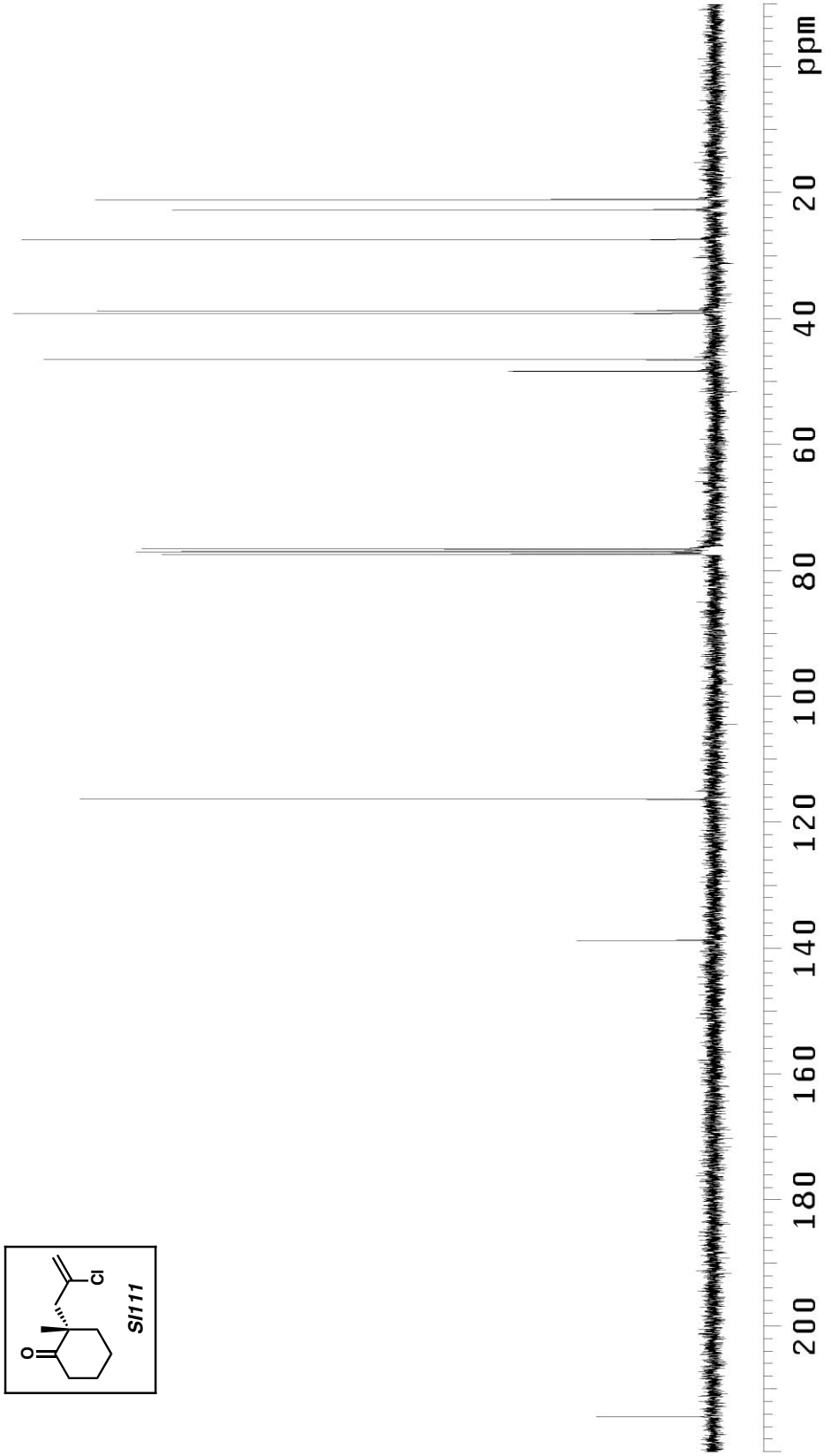
^{1}H NMR of compound **SI110** (300 MHz, $CDCl_3$)



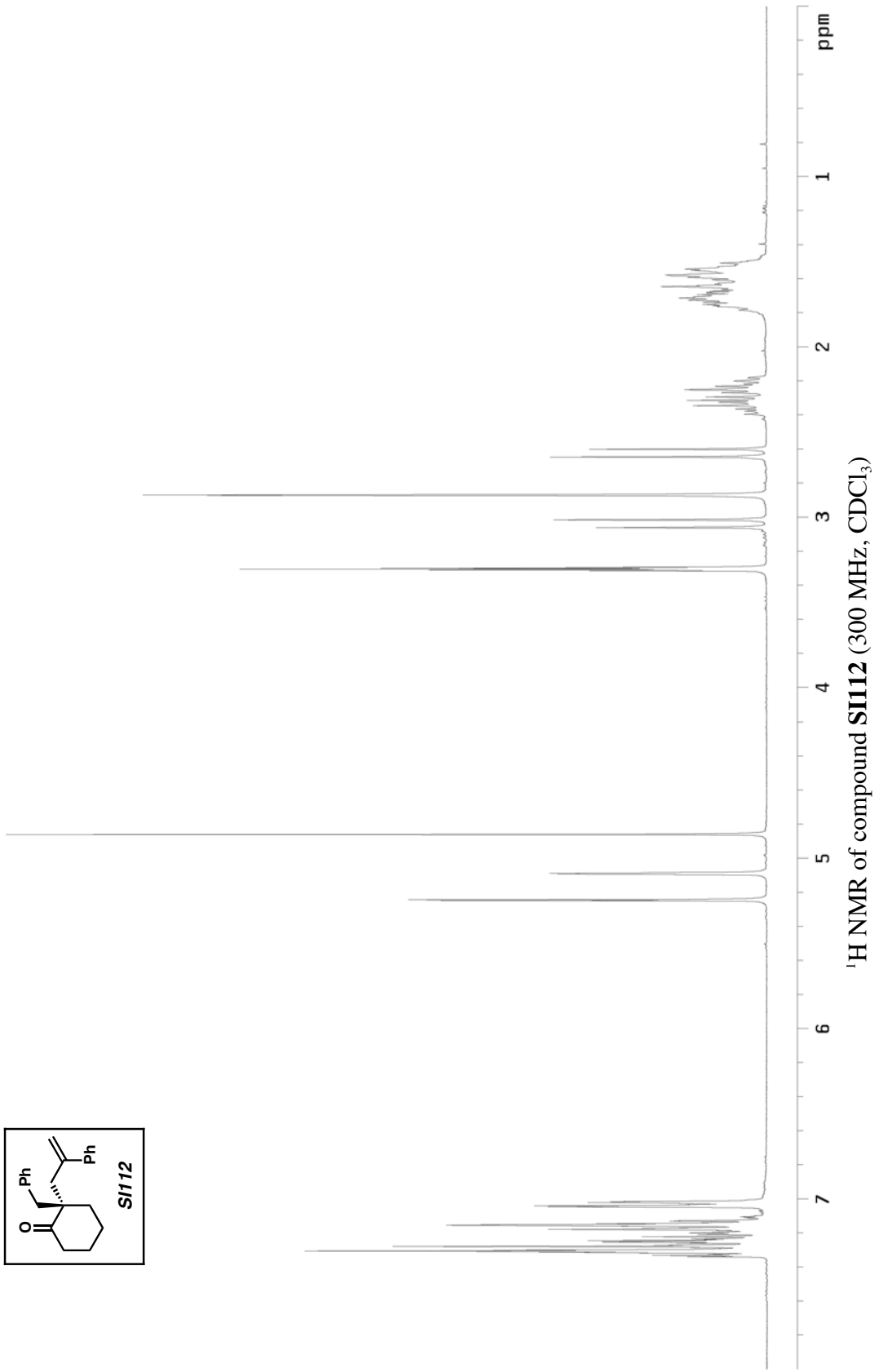
^{13}C NMR of compound **SI110** (75 MHz, $CDCl_3$)



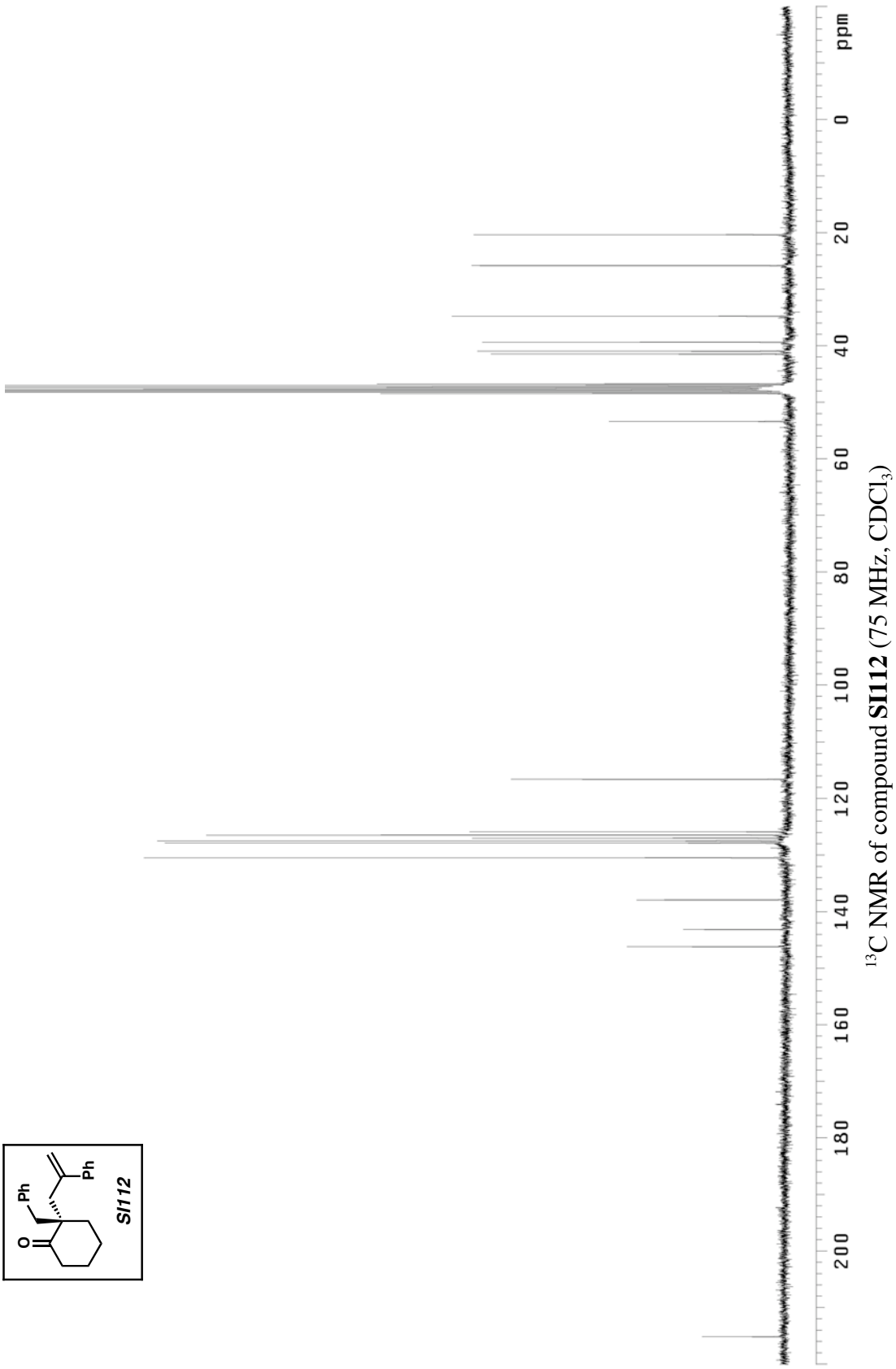
^{1}H NMR of compound **SI111** (300 MHz, $CDCl_3$)



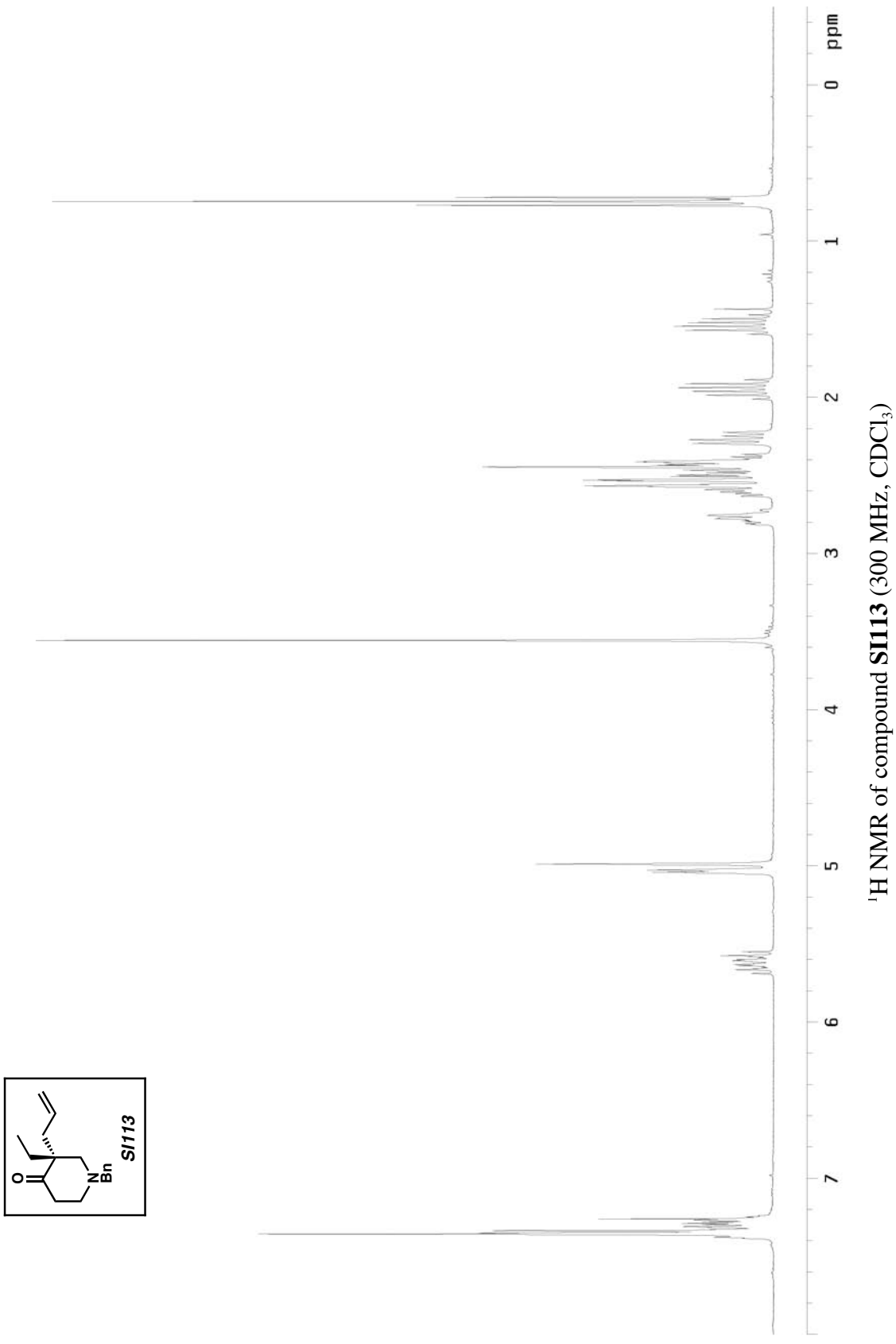
^{13}C NMR of compound **SI111** (75 MHz, $CDCl_3$)



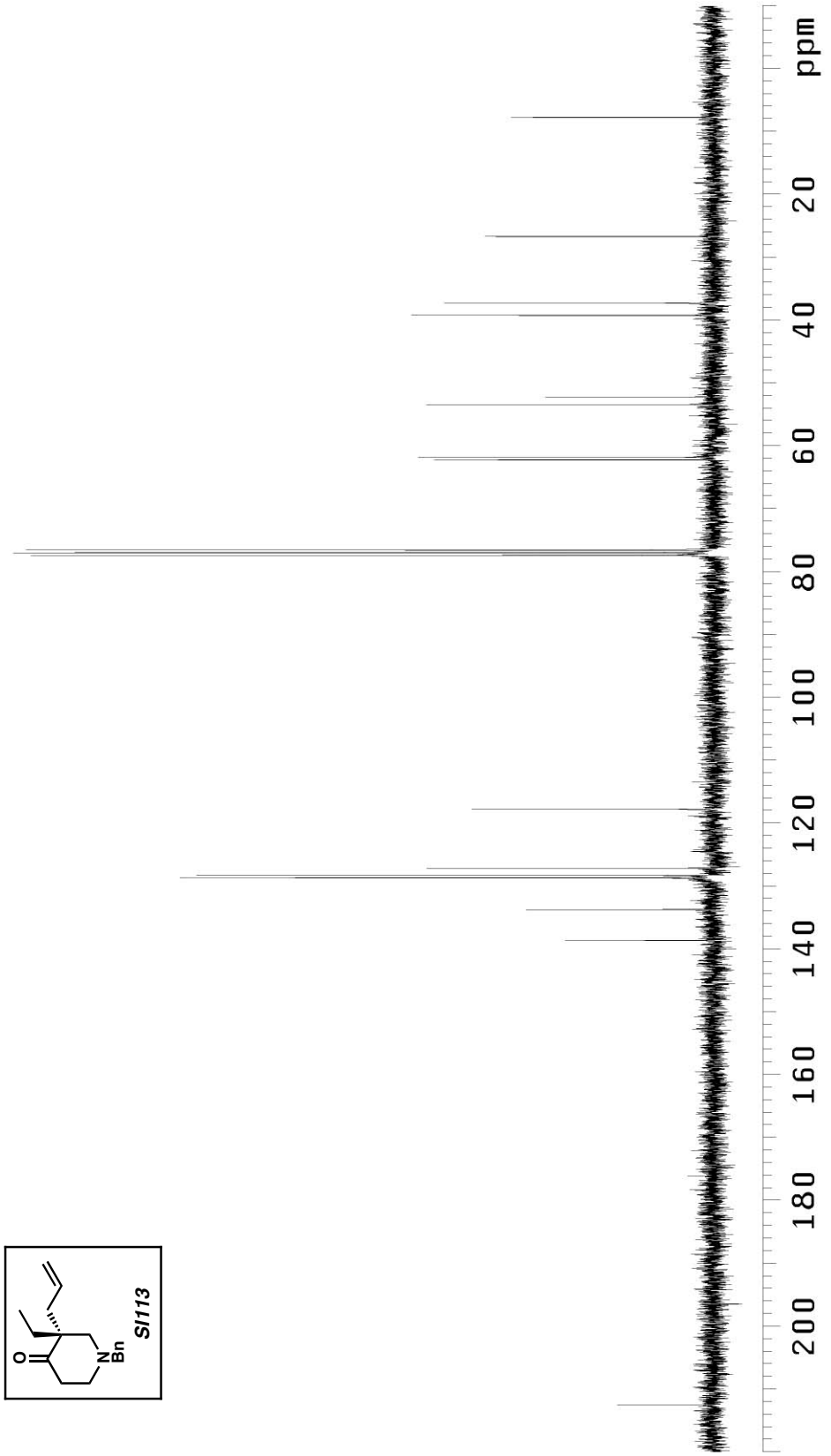
^{1}H NMR of compound **SI112** (300 MHz, $CDCl_3$)



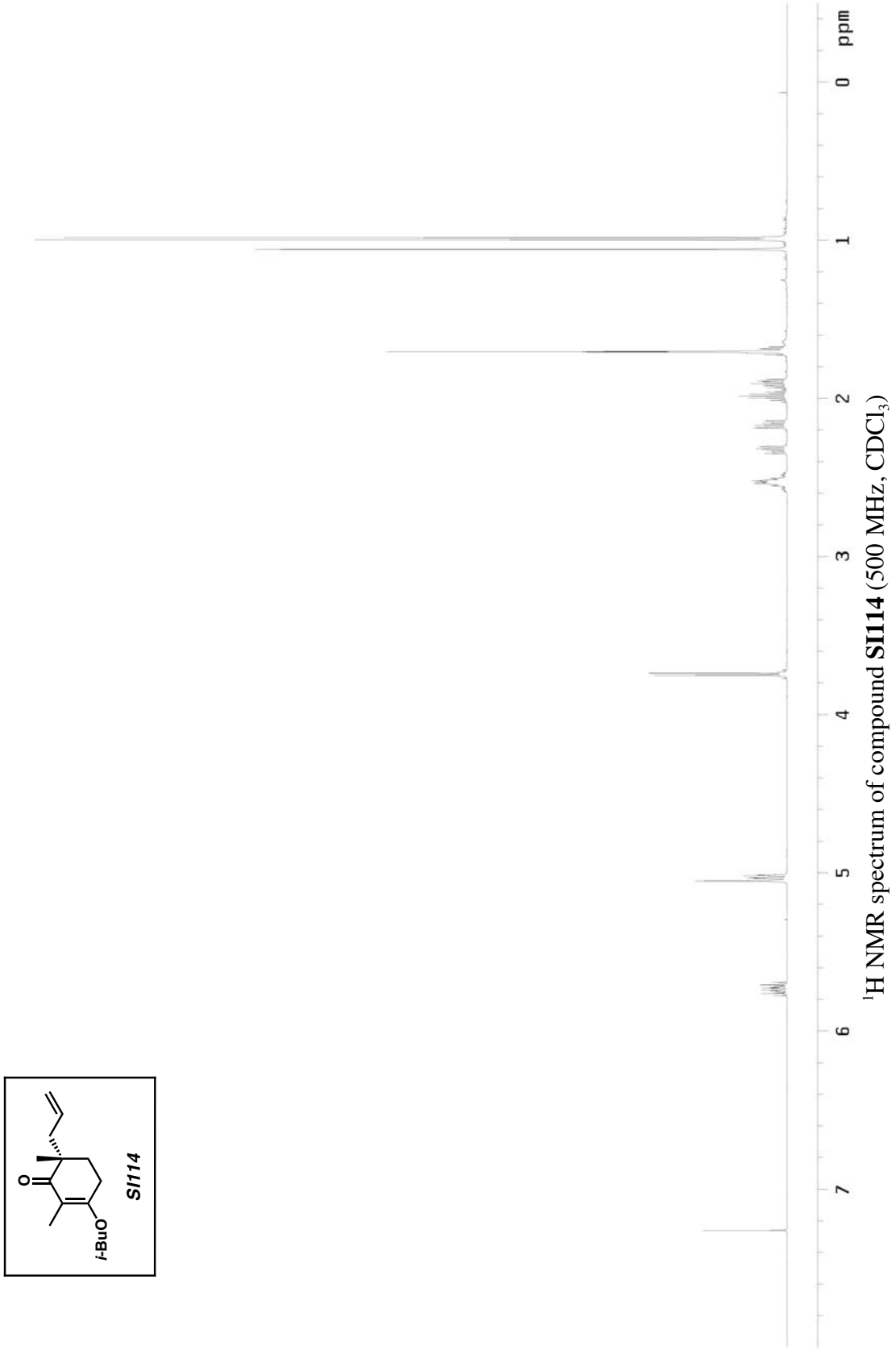
^{13}C NMR of compound **SI112** (75 MHz, $CDCl_3$)



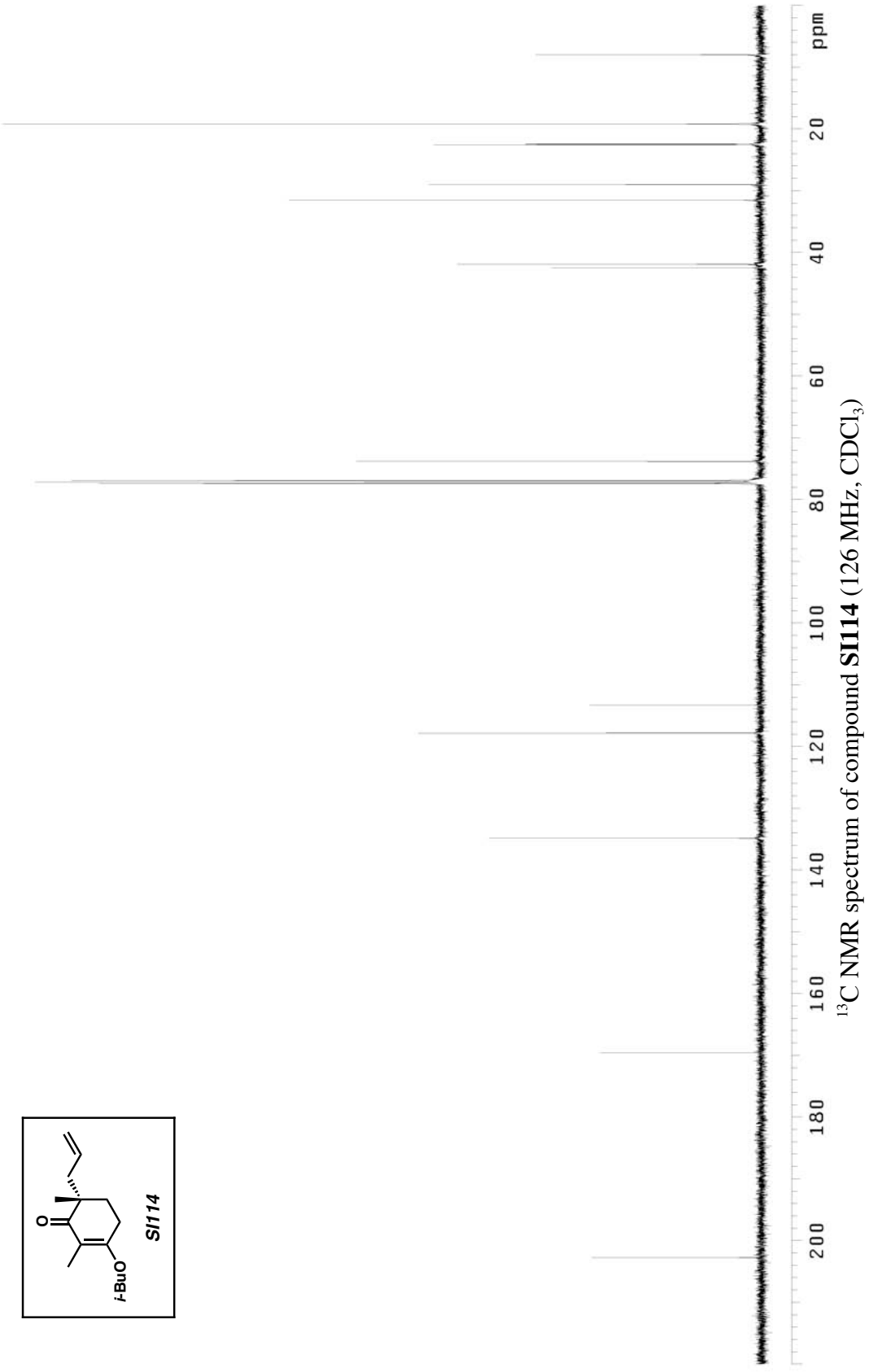
^{1}H NMR of compound **SI113** (300 MHz, $CDCl_3$)



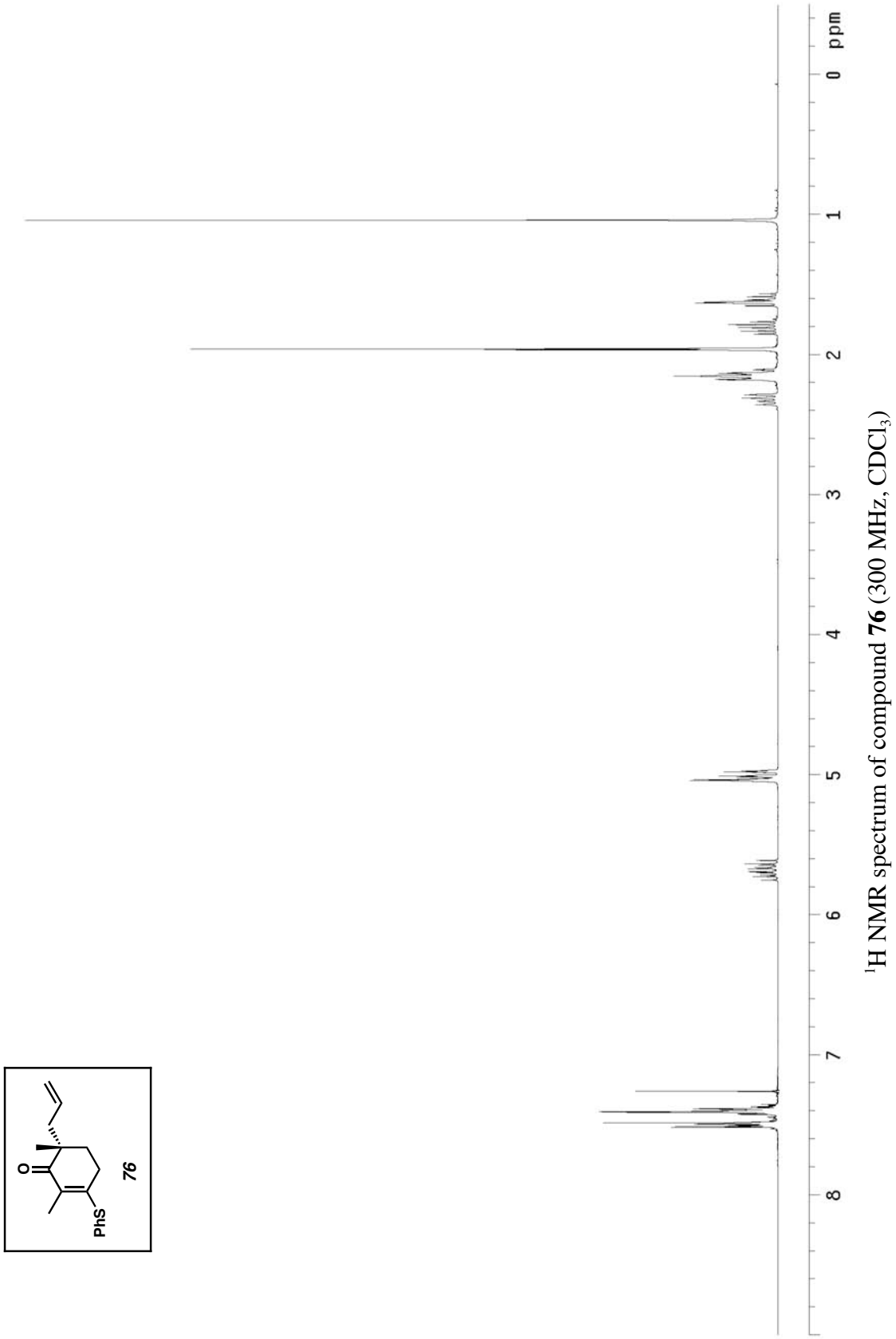
^{13}C NMR of compound **SI113** (75 MHz, $CDCl_3$)



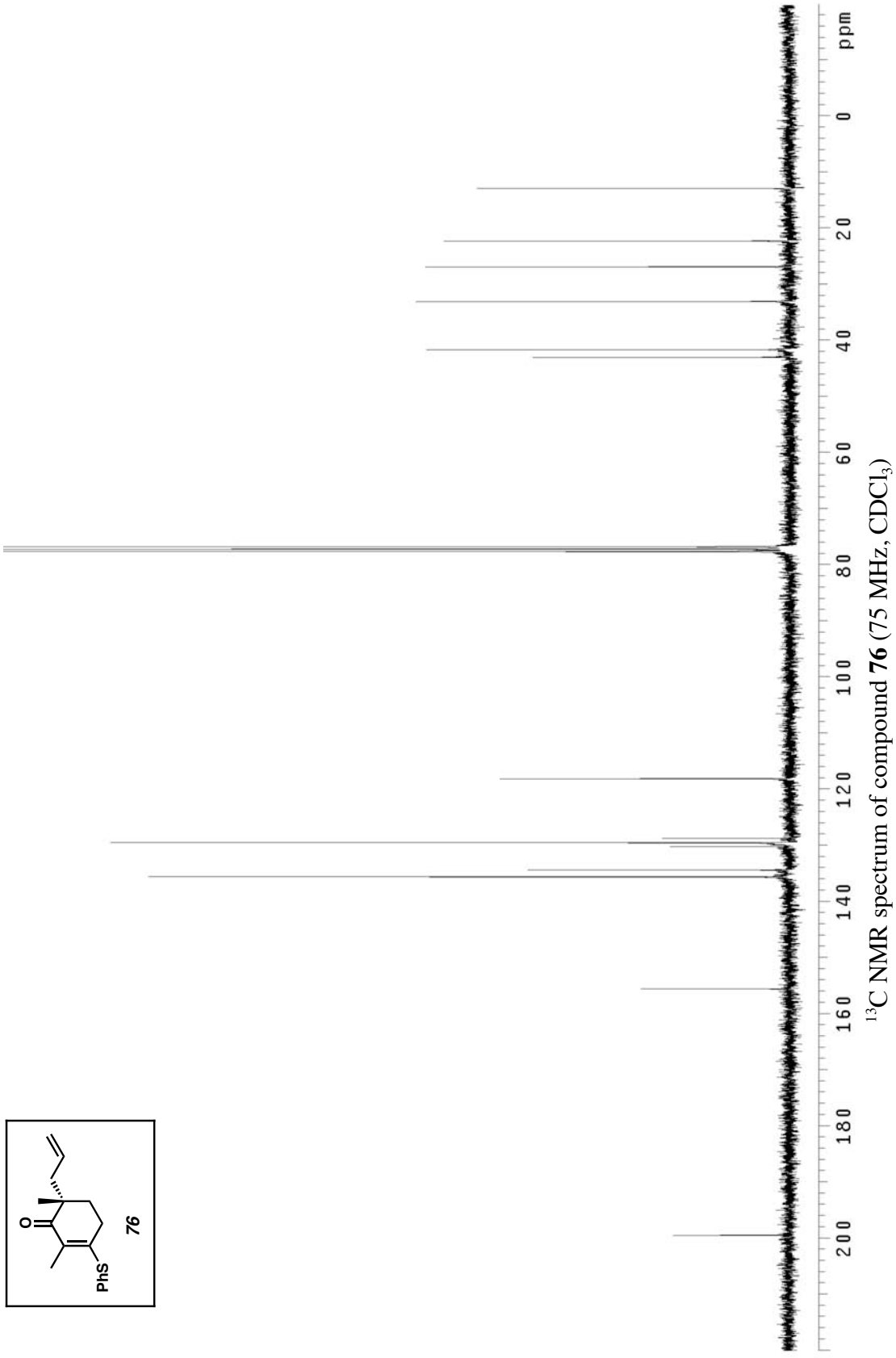
^{1}H NMR spectrum of compound **SI114** (500 MHz, $CDCl_3$)



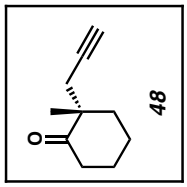
^{13}C NMR spectrum of compound **SI114** (126 MHz, $CDCl_3$)



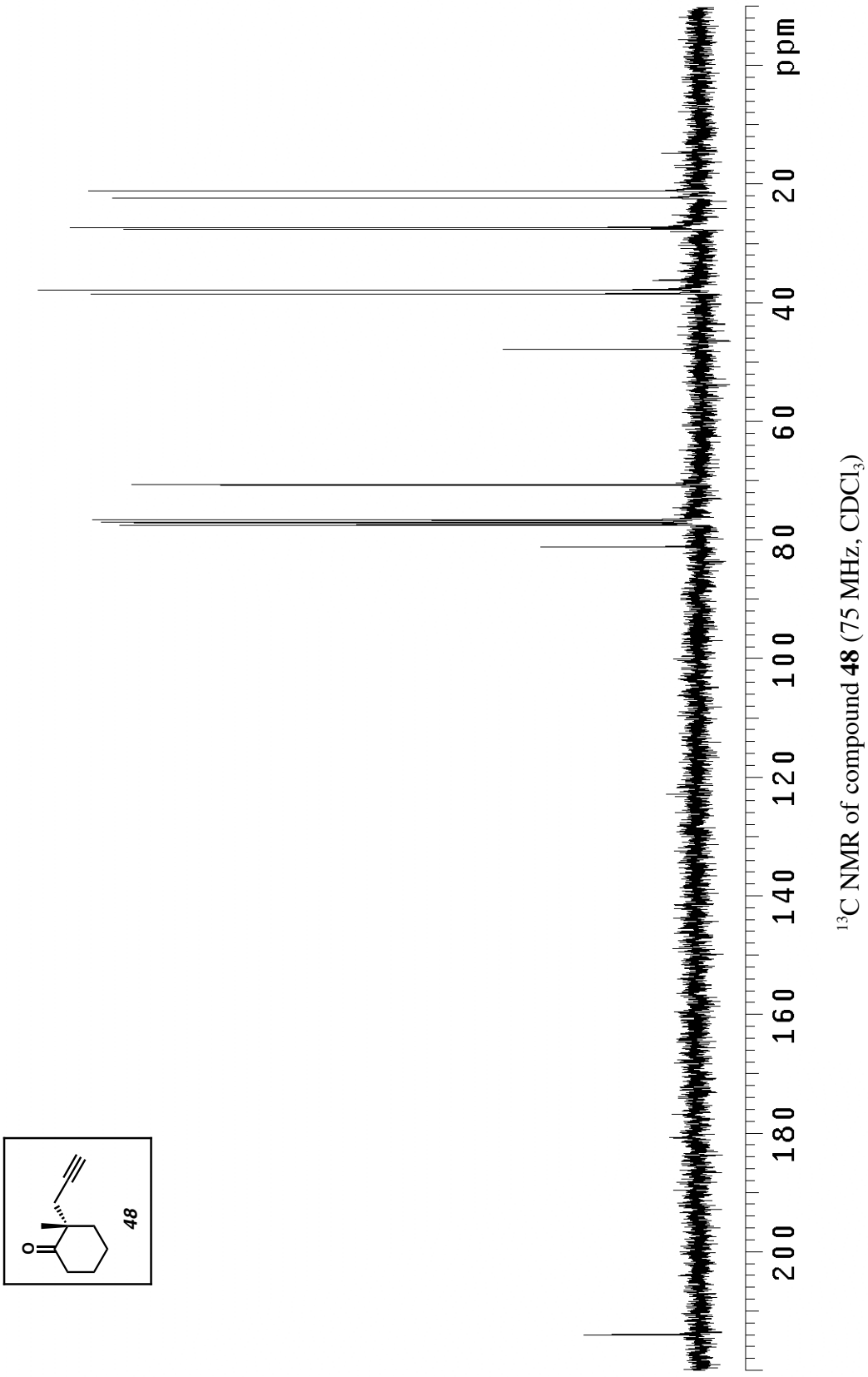
^{1}H NMR spectrum of compound **76** (300 MHz, $CDCl_3$)



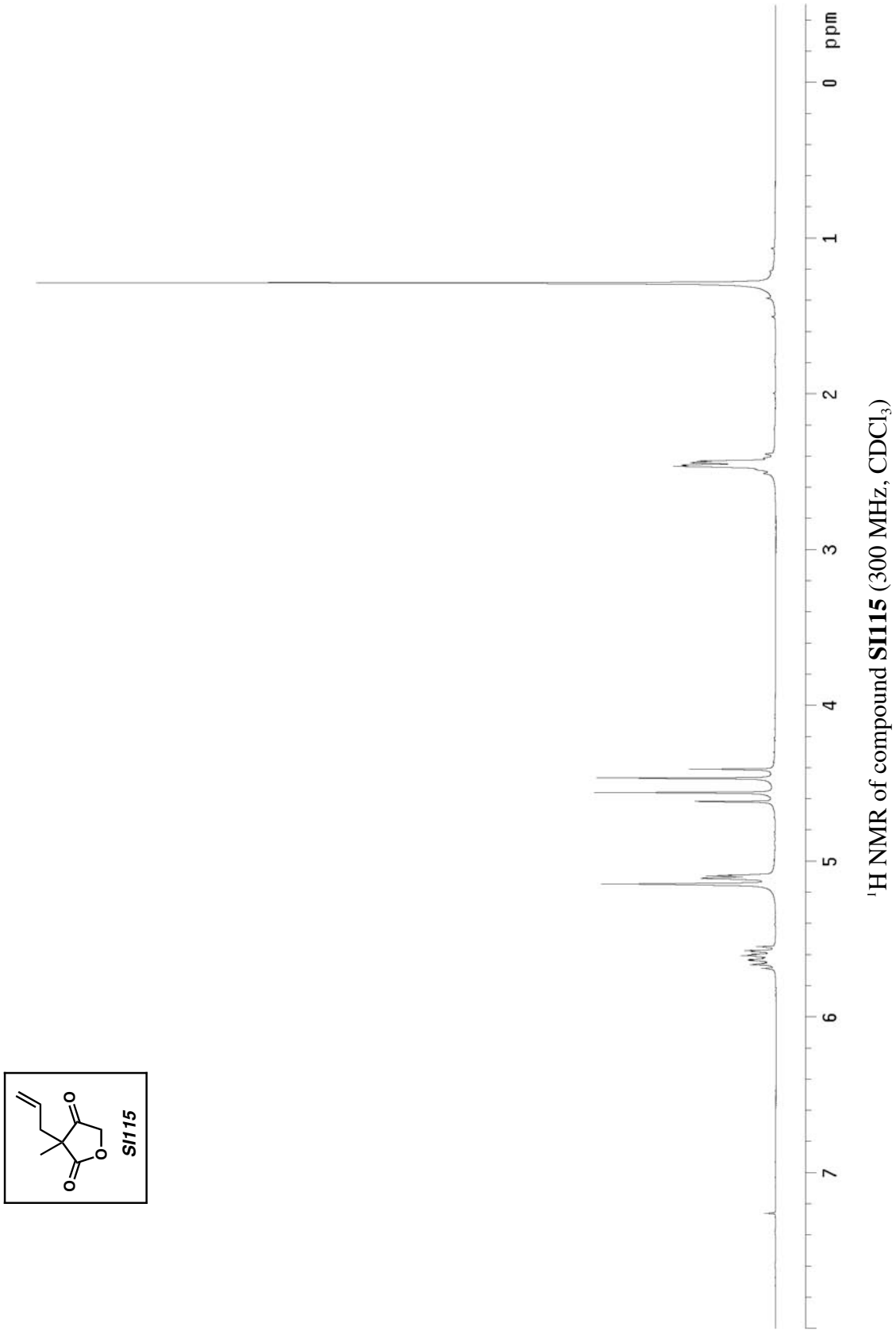
^{13}C NMR spectrum of compound **76** (75 MHz, $CDCl_3$)



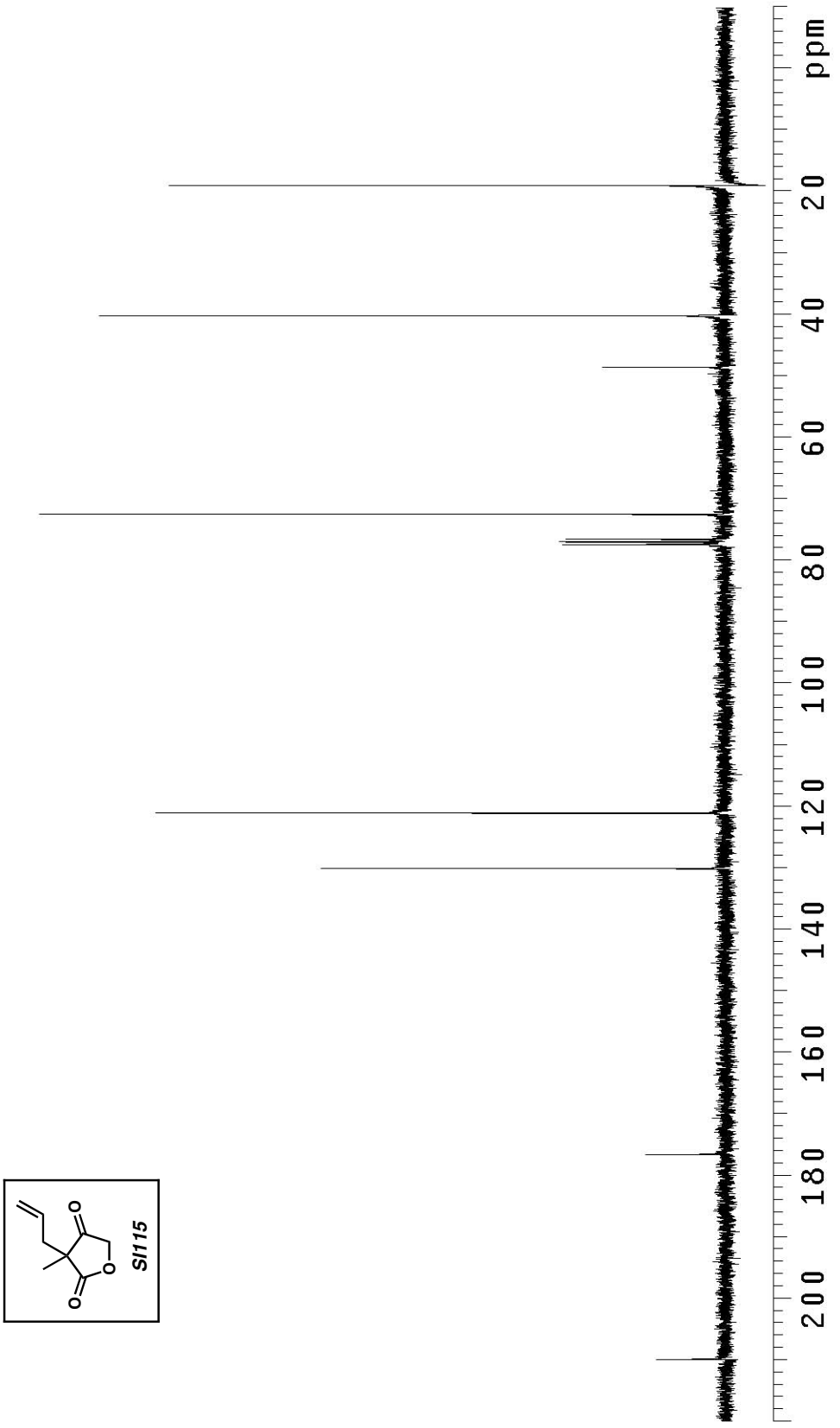
^{1}H NMR of compound **48** (300 MHz, $CDCl_3$)



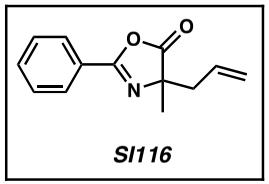
^{13}C NMR of compound **48** (75 MHz, $CDCl_3$)



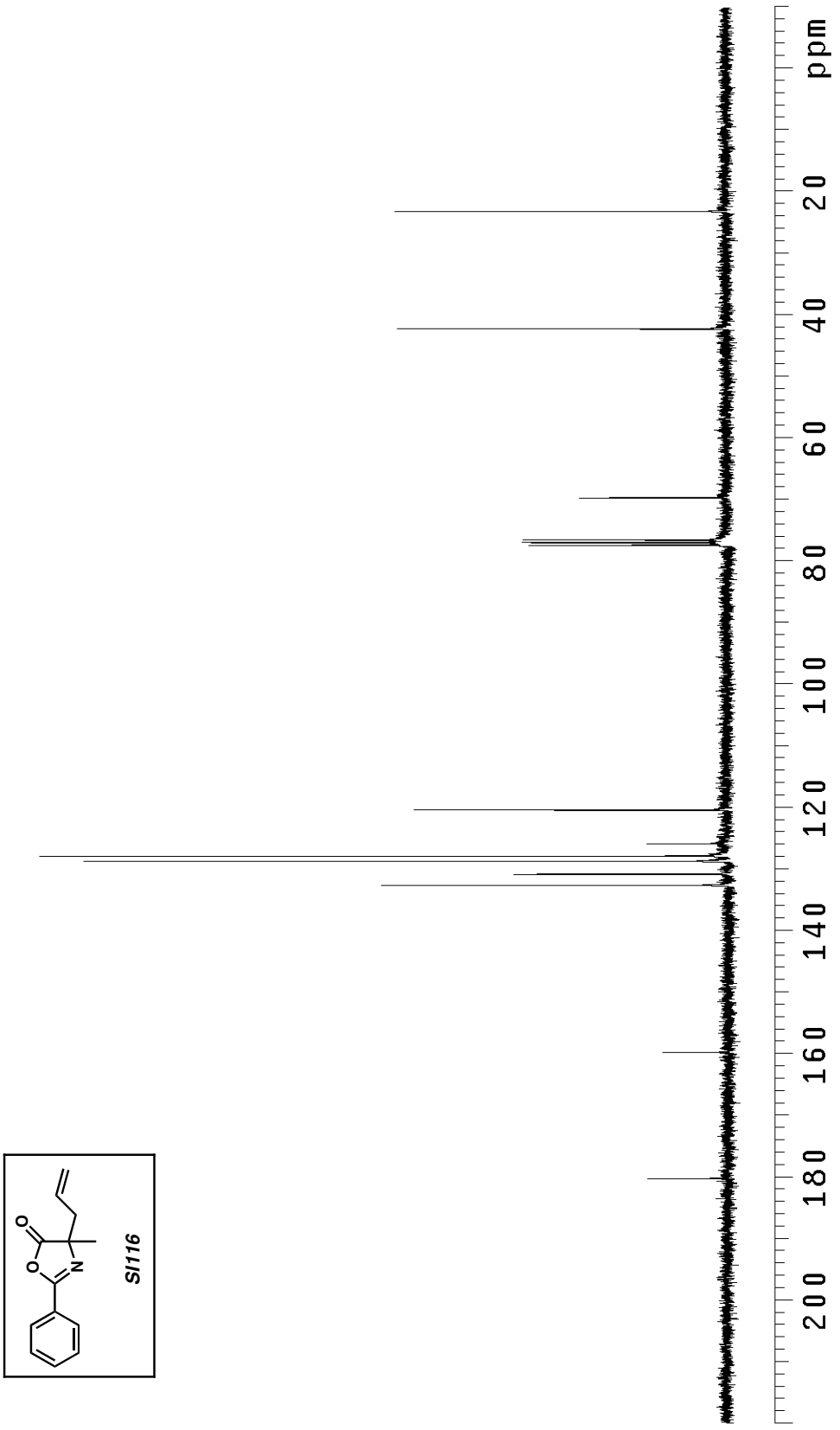
^{1}H NMR of compound **SI115** (300 MHz, $CDCl_3$)



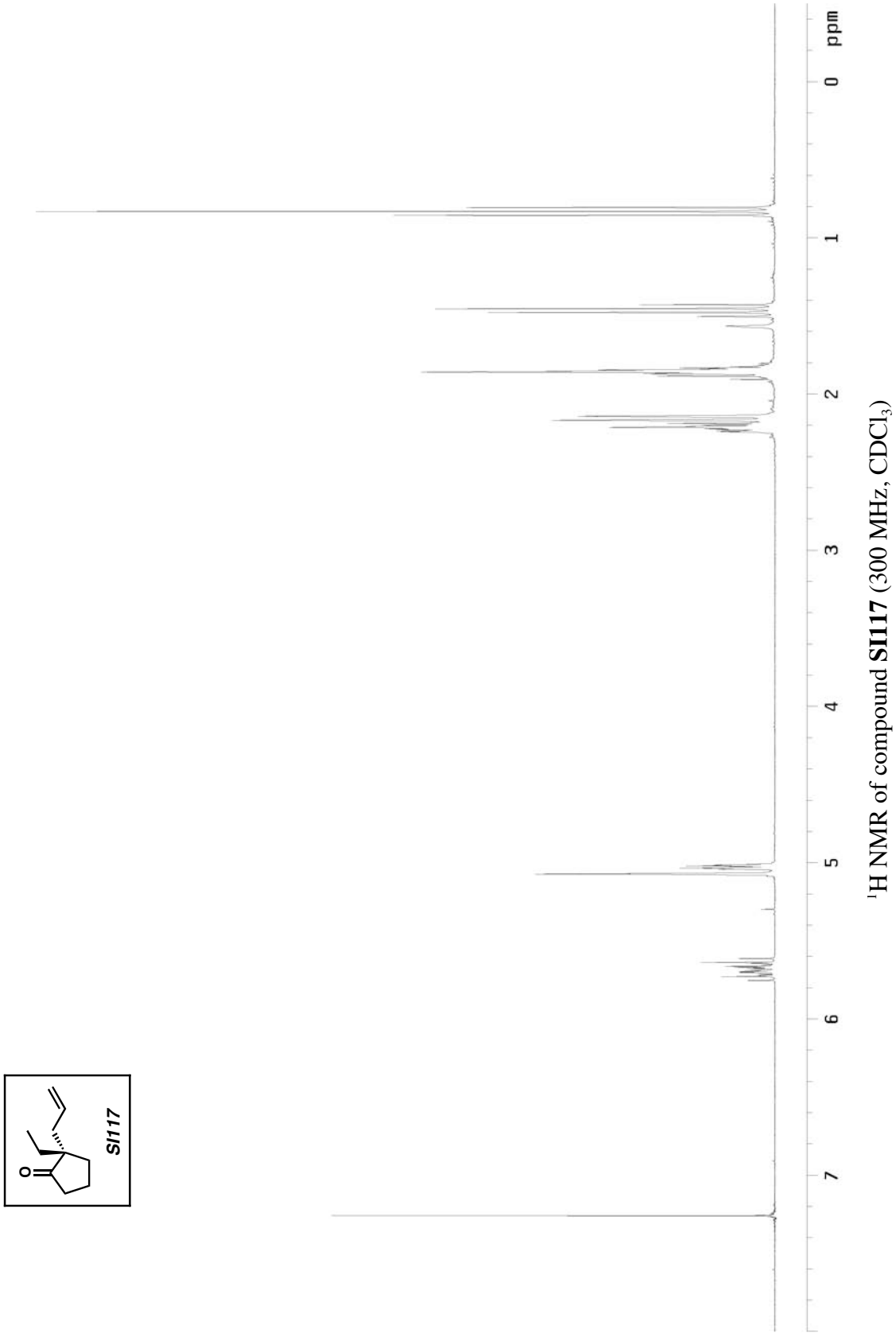
^{13}C NMR of compound **SI115** (75 MHz, $CDCl_3$)



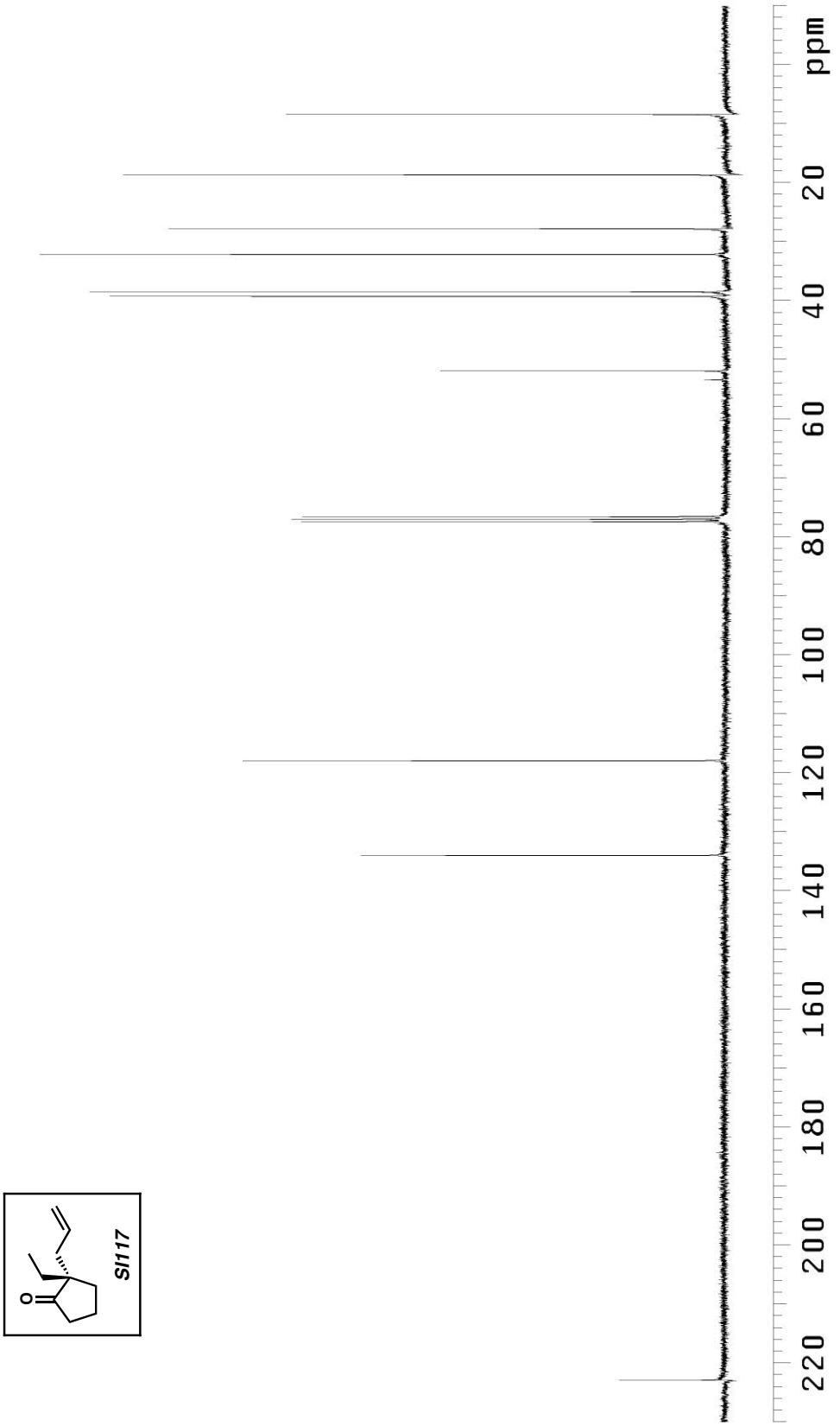
^{1}H NMR of compound **SI116** (300 MHz, $CDCl_3$)



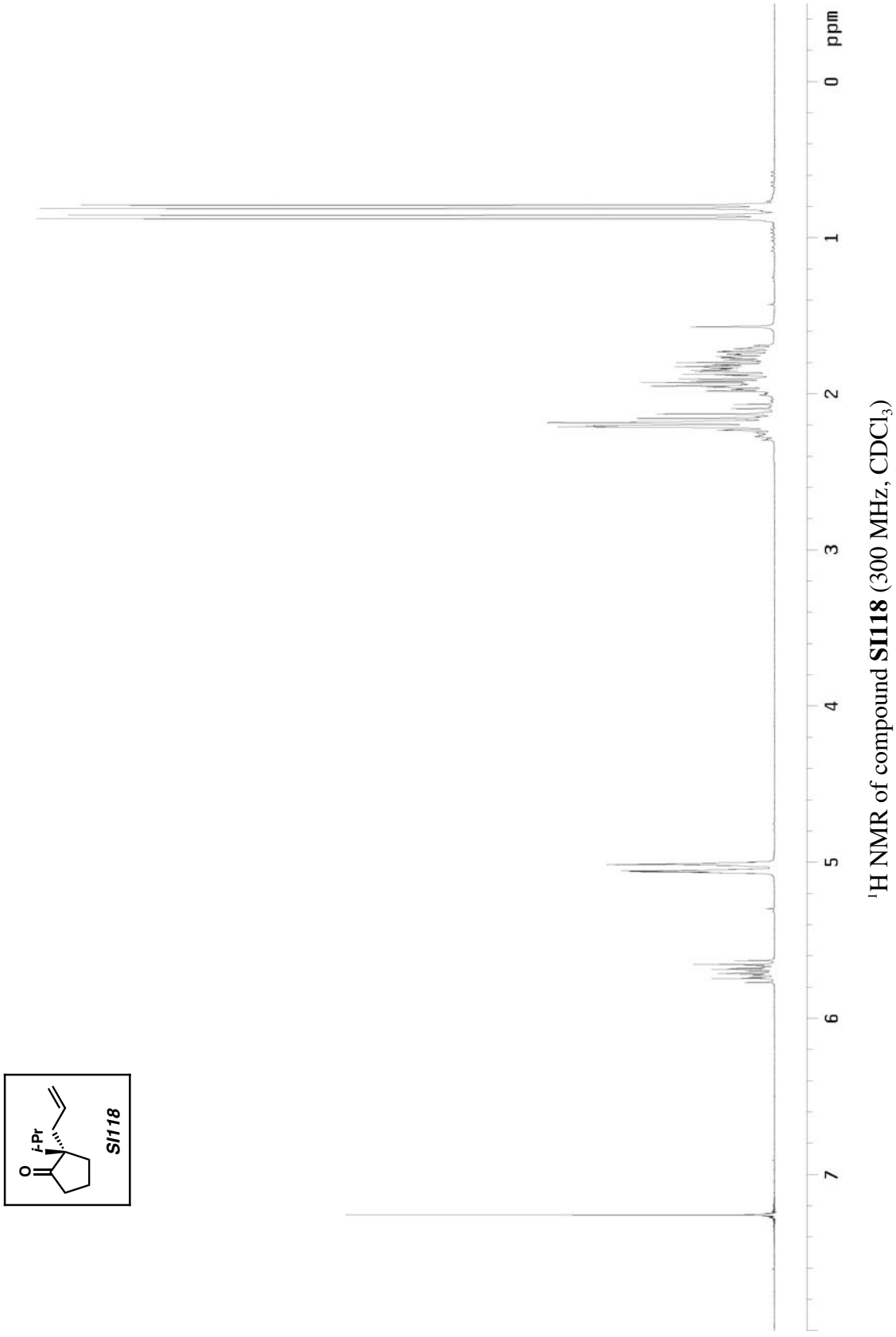
^{13}C NMR of compound **SI116** (75 MHz, $CDCl_3$)



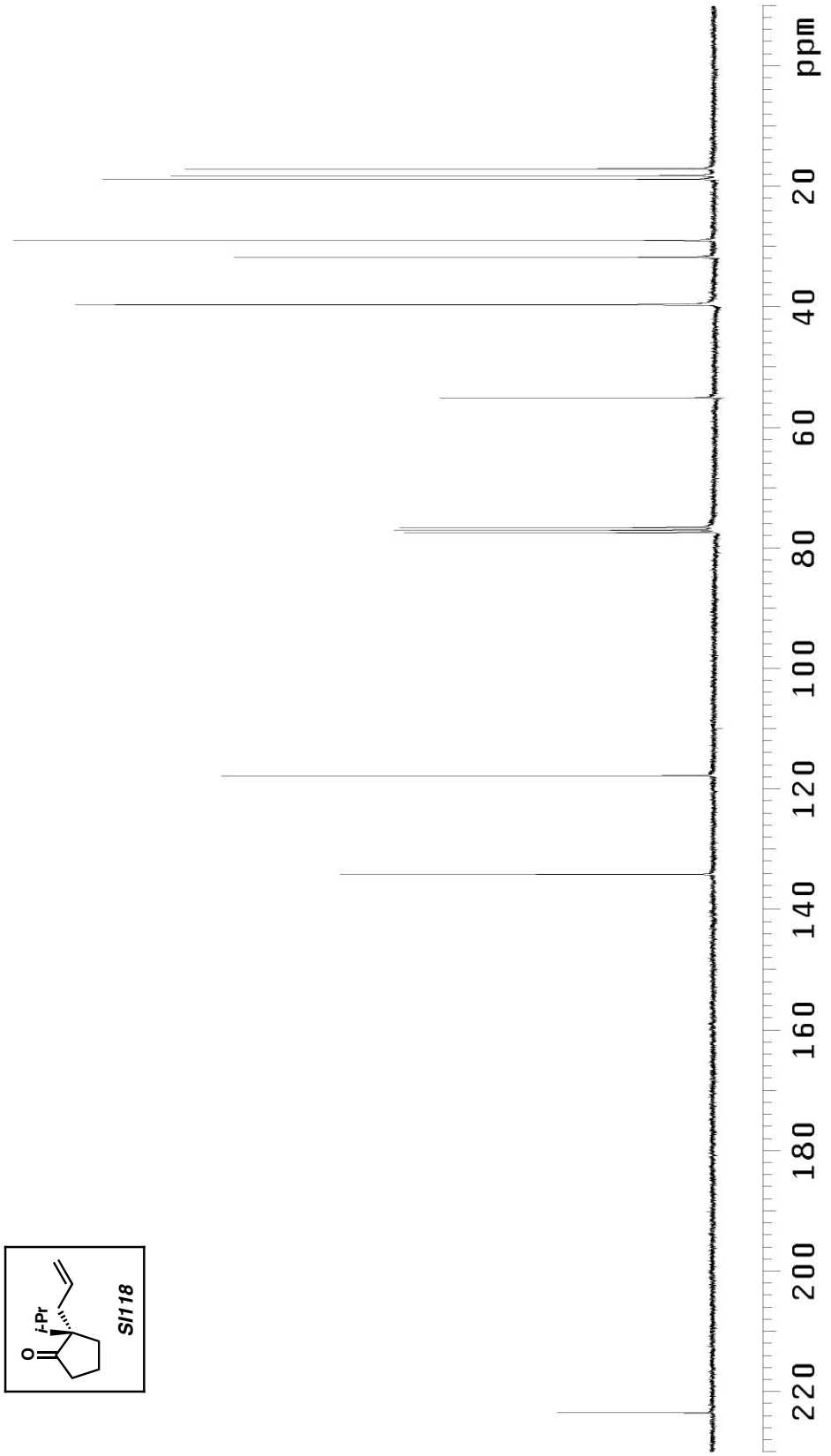
^{1}H NMR of compound **SI117** (300 MHz, $CDCl_3$)



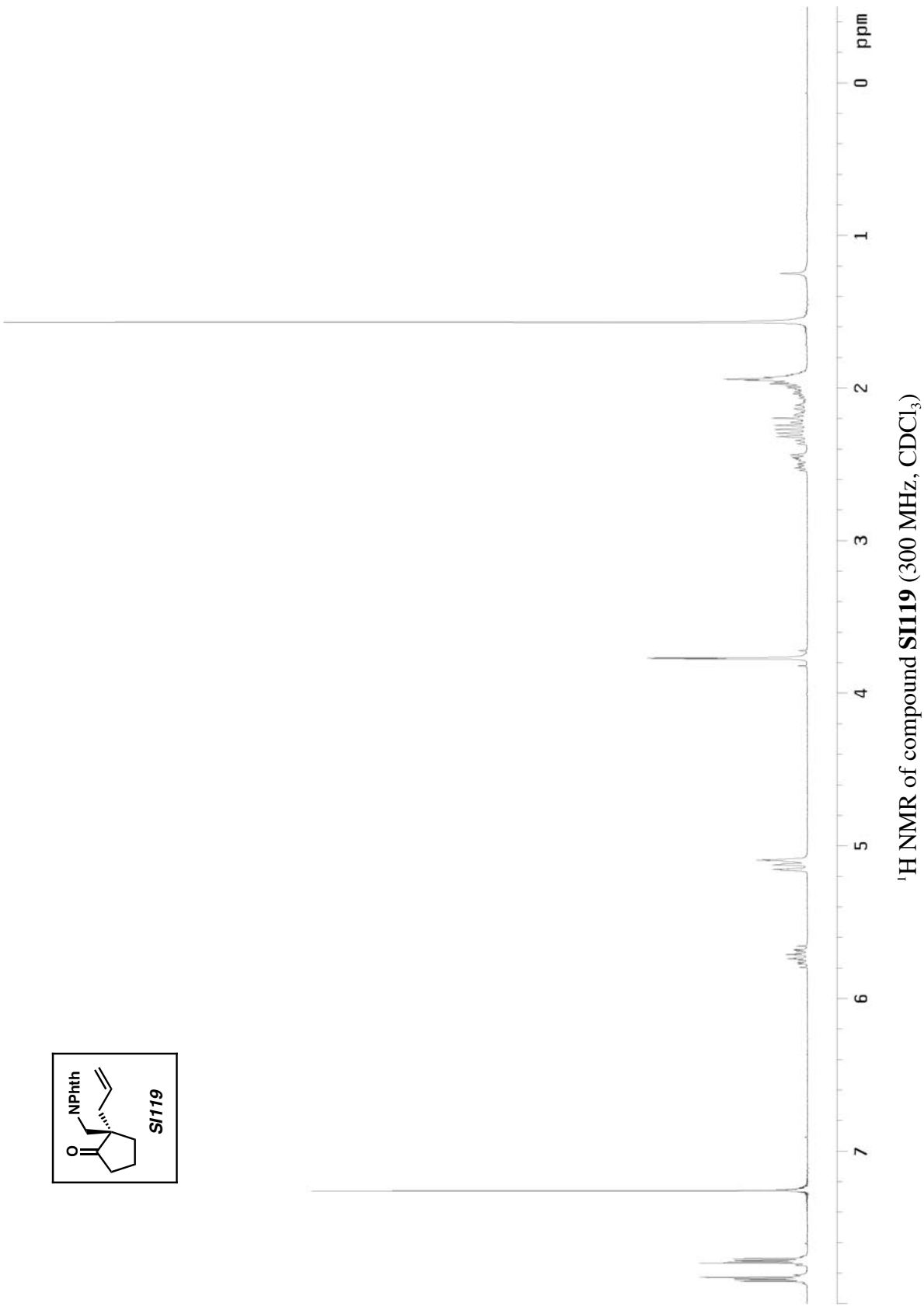
^{13}C NMR of compound **SI117** (75 MHz, $CDCl_3$)



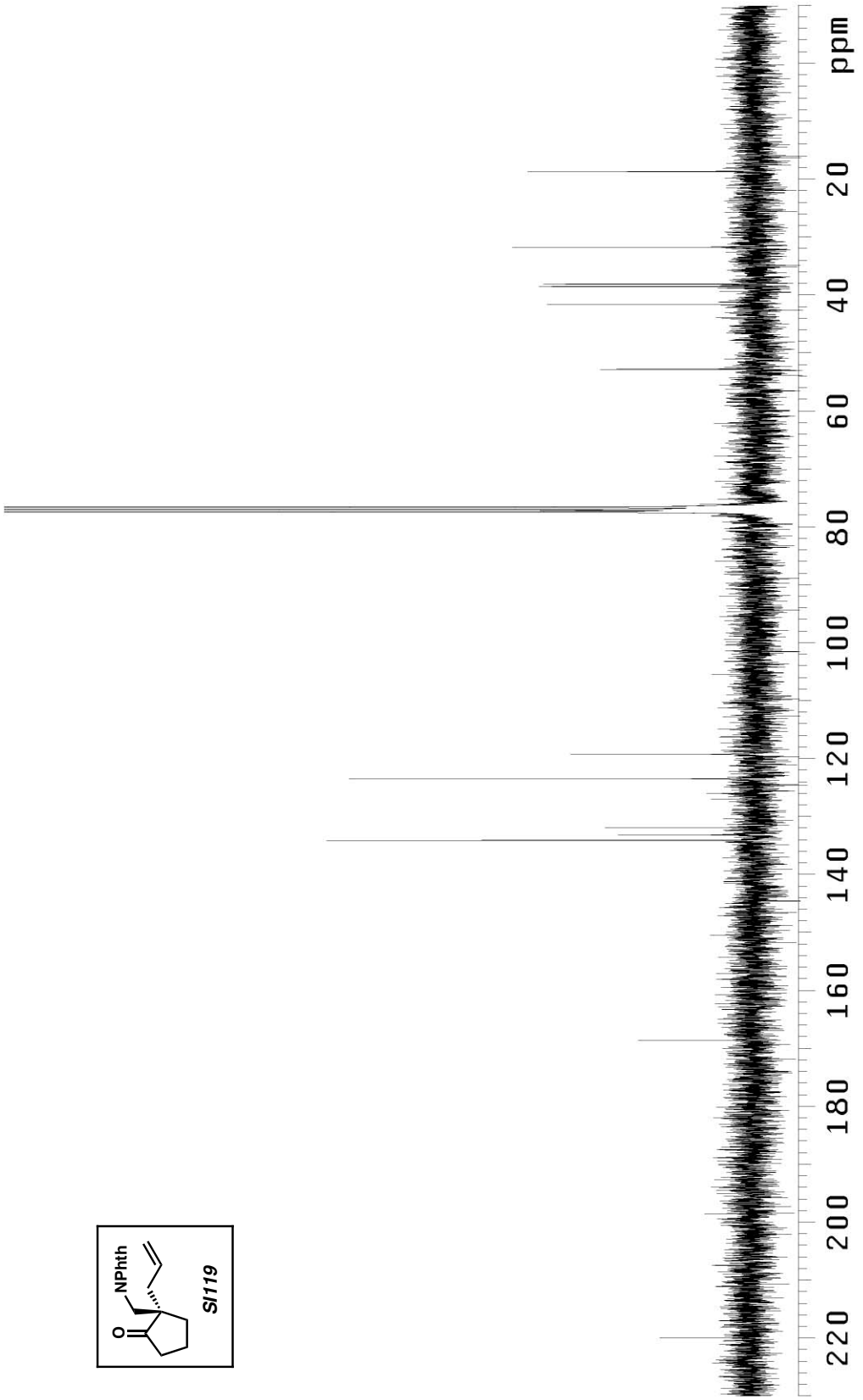
^{1}H NMR of compound **SI118** (300 MHz, $CDCl_3$)



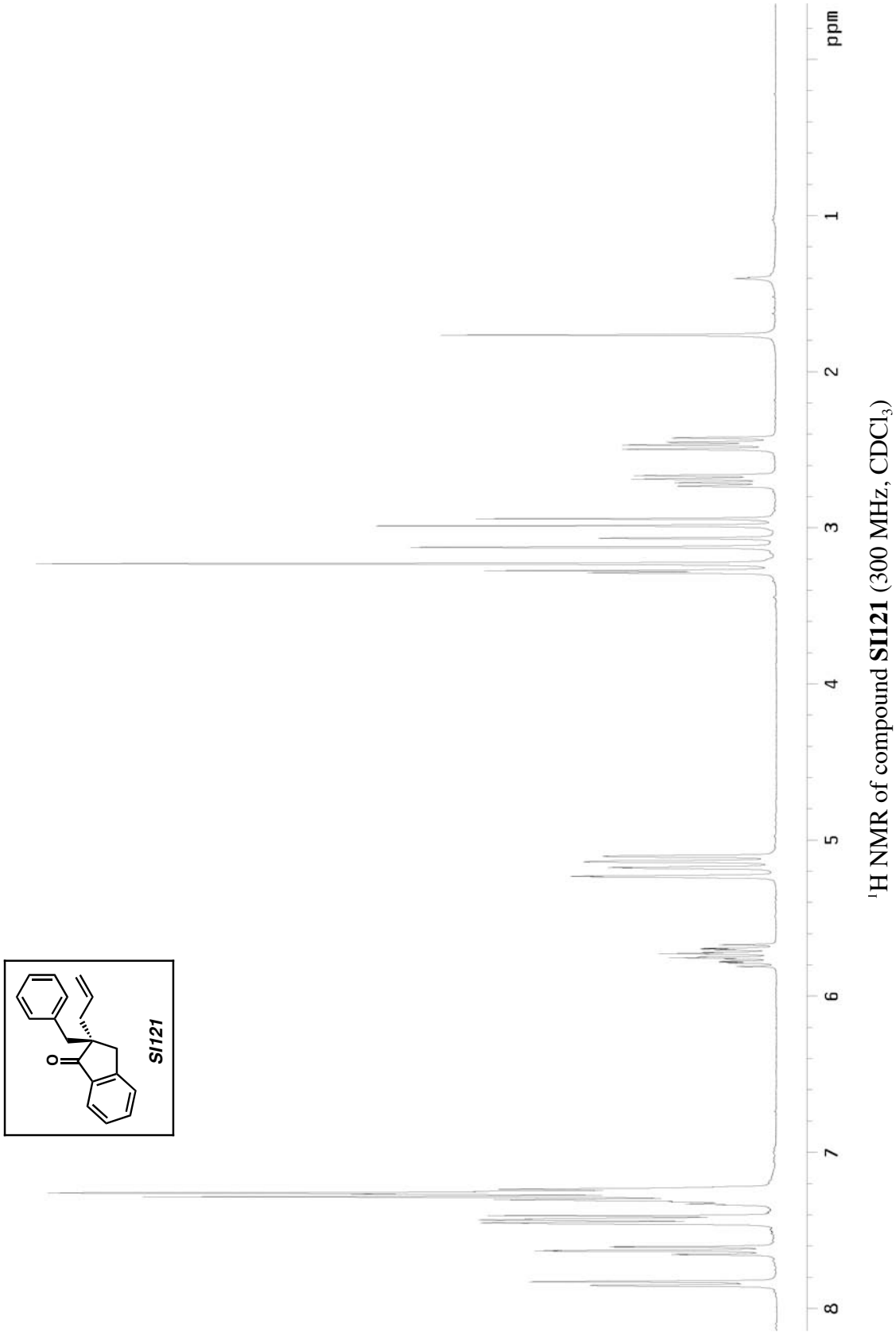
^{13}C NMR of compound **SI118** (75 MHz, $CDCl_3$)



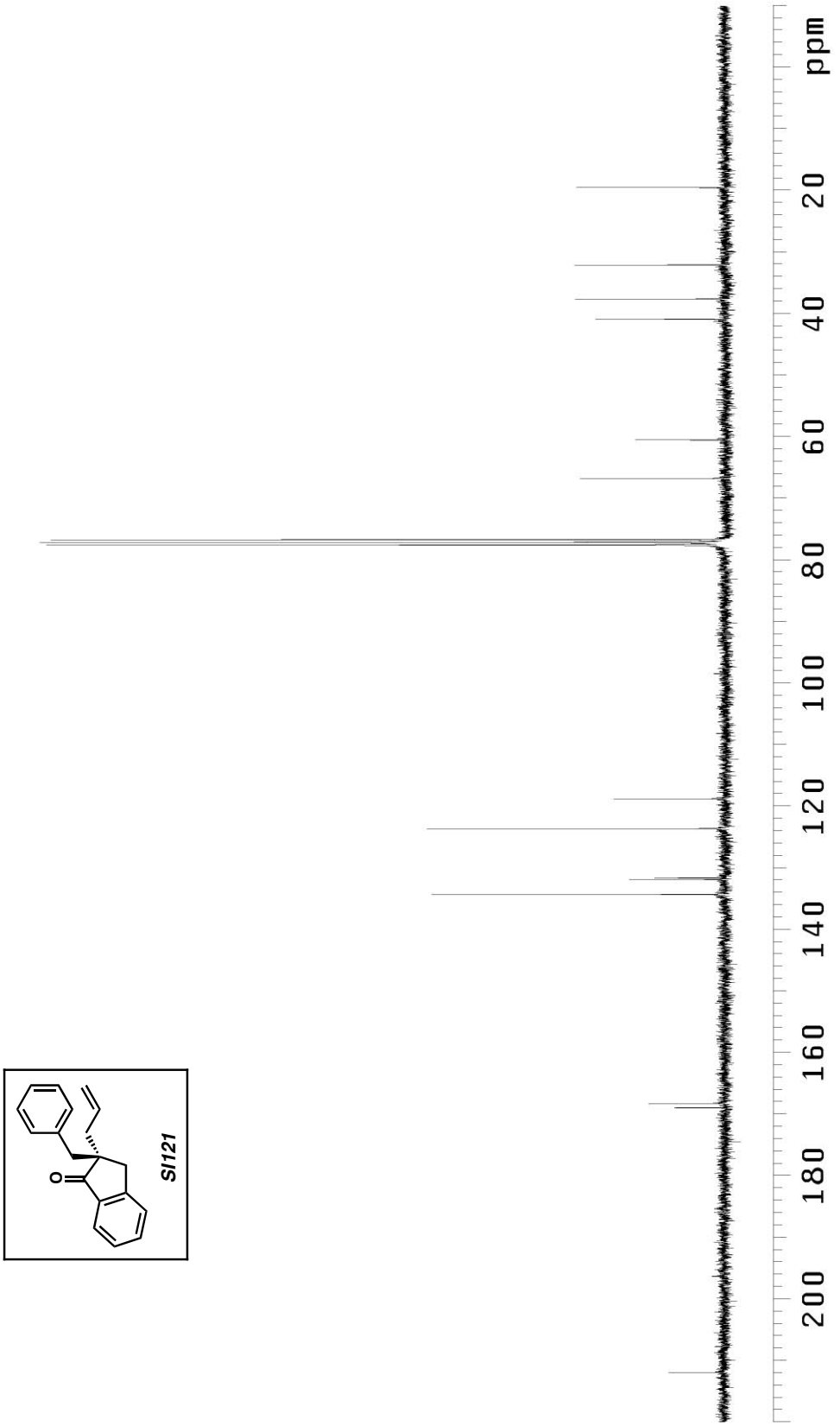
^{1}H NMR of compound **SI119** (300 MHz, $CDCl_3$)



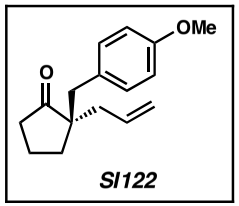
^{13}C NMR of compound **SI119** (75 MHz, $CDCl_3$)



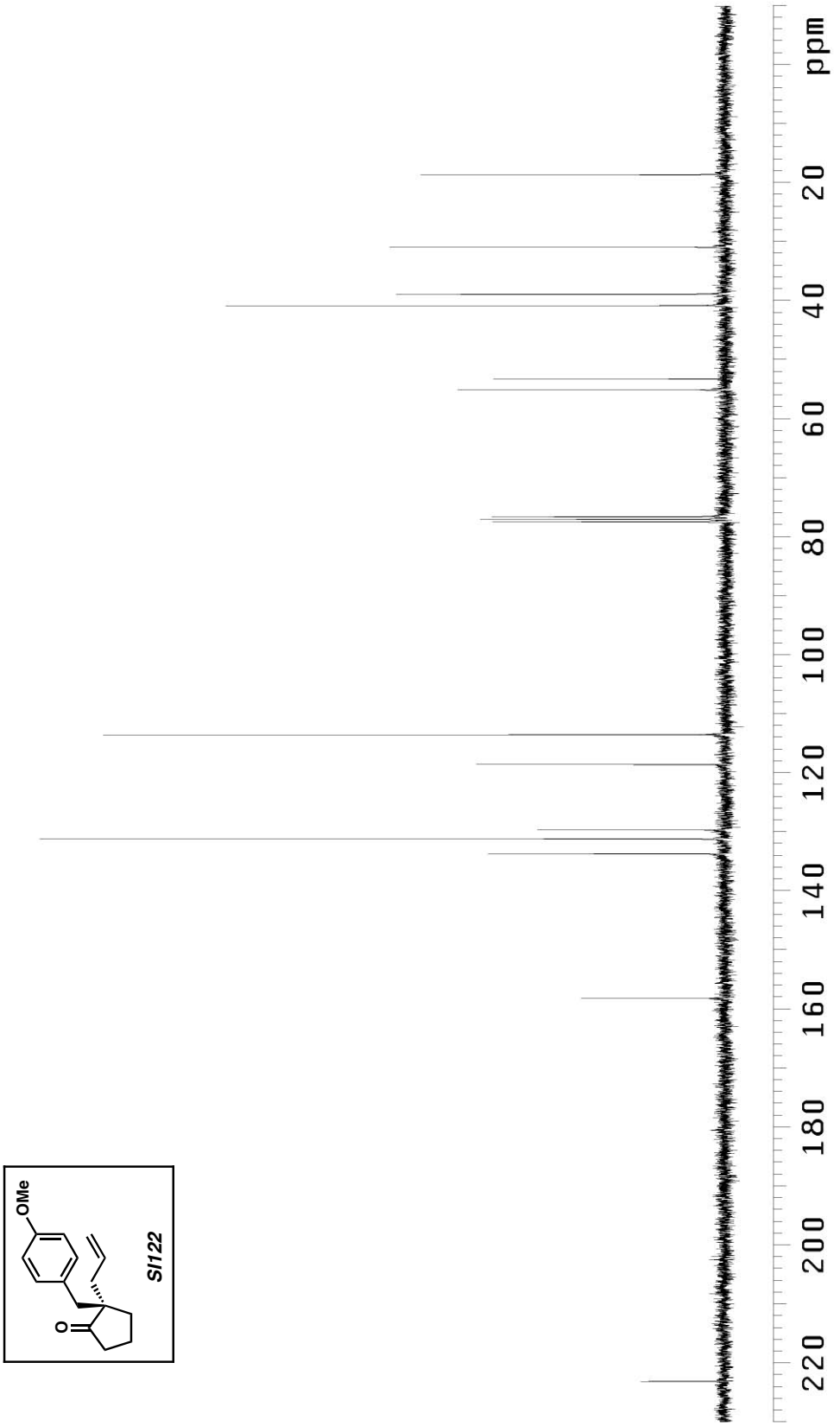
^{1}H NMR of compound **SI121** (300 MHz, $CDCl_3$)



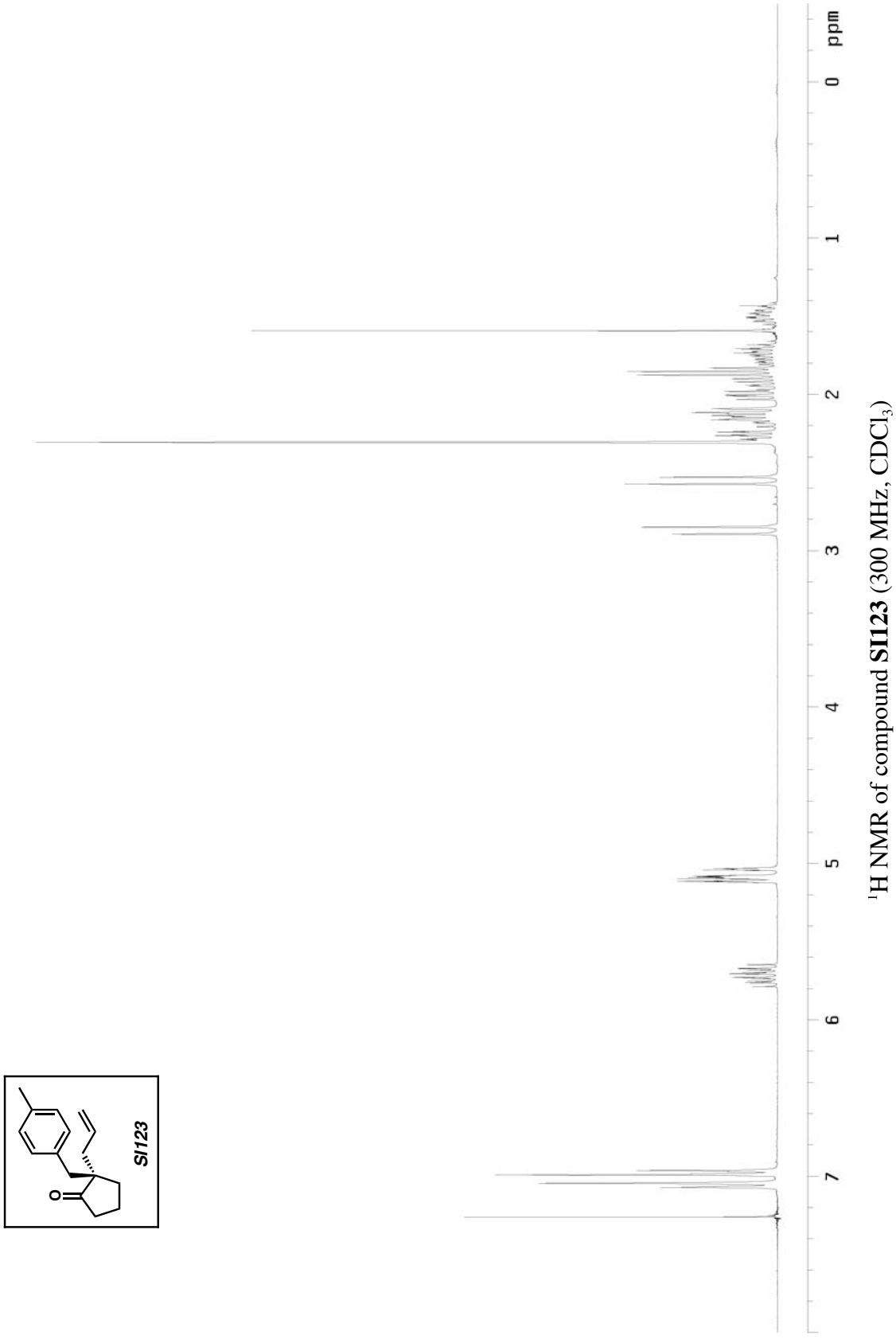
^{13}C NMR of compound **SI121** (75 MHz, $CDCl_3$)



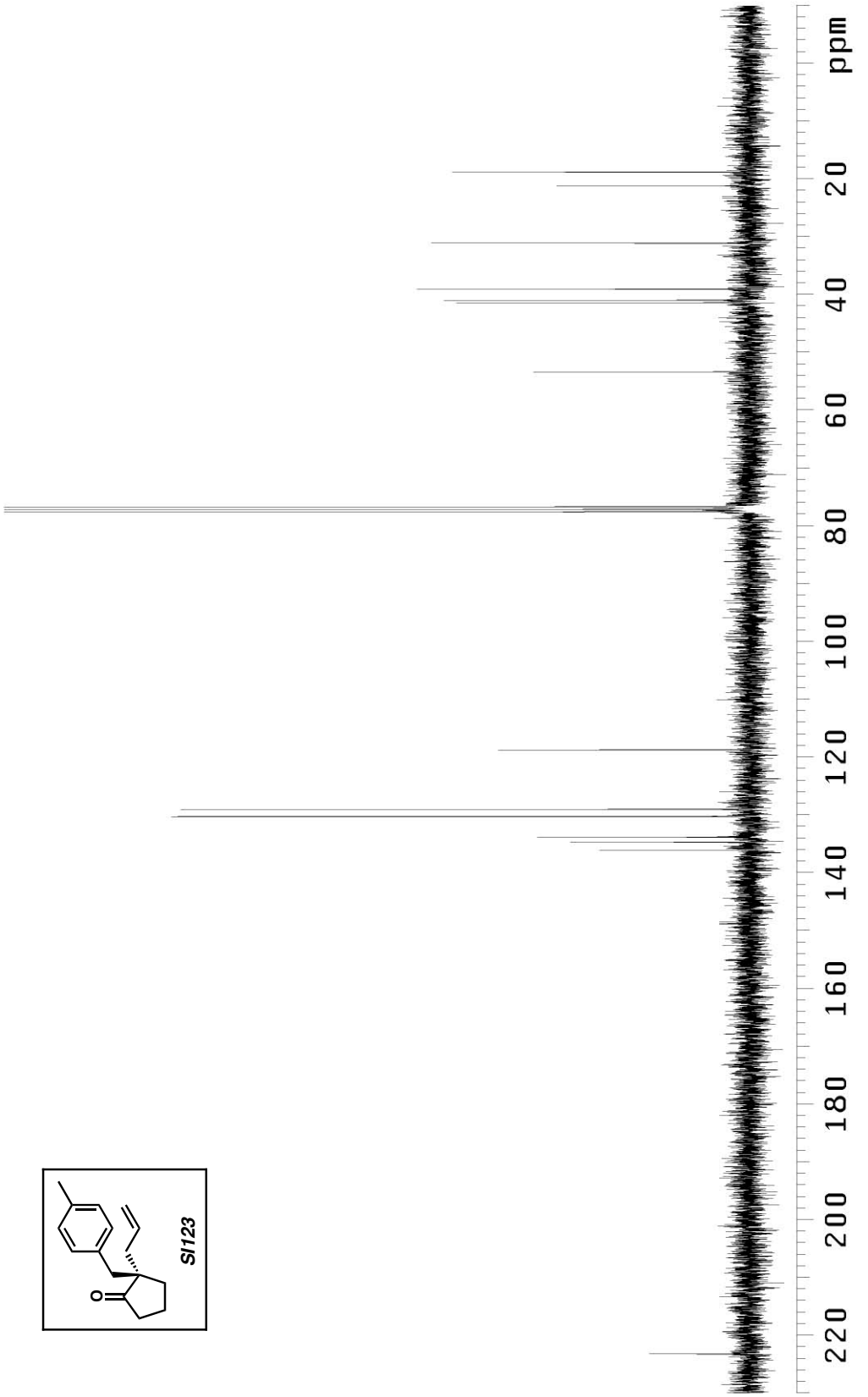
^{1}H NMR of compound **SI122** (300 MHz, $CDCl_3$)



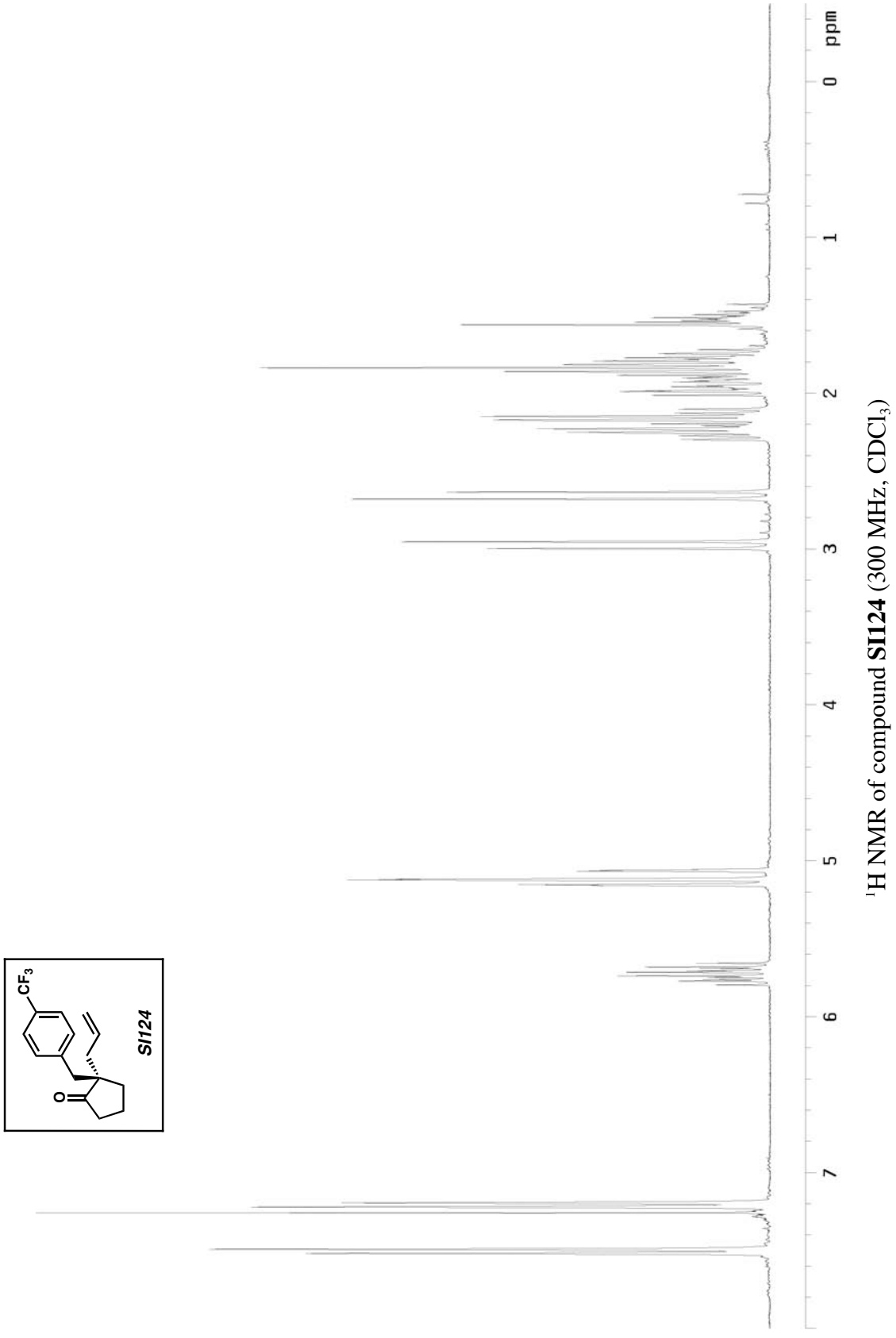
^{13}C NMR of compound **SI122** (75 MHz, $CDCl_3$)



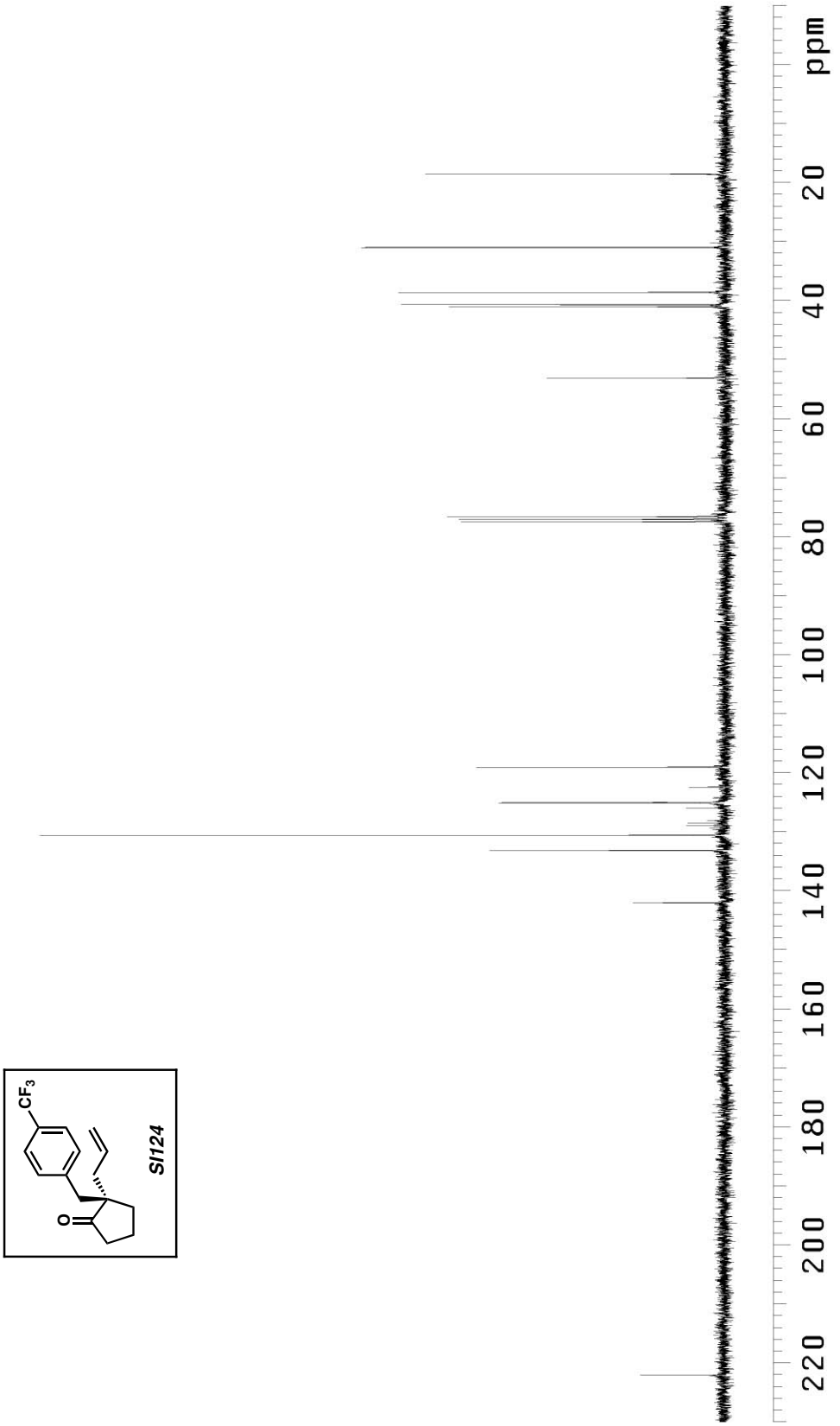
^{1}H NMR of compound **SI123** (300 MHz, $CDCl_3$)



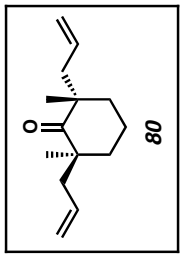
^{13}C NMR of compound **SI123** (75 MHz, $CDCl_3$)



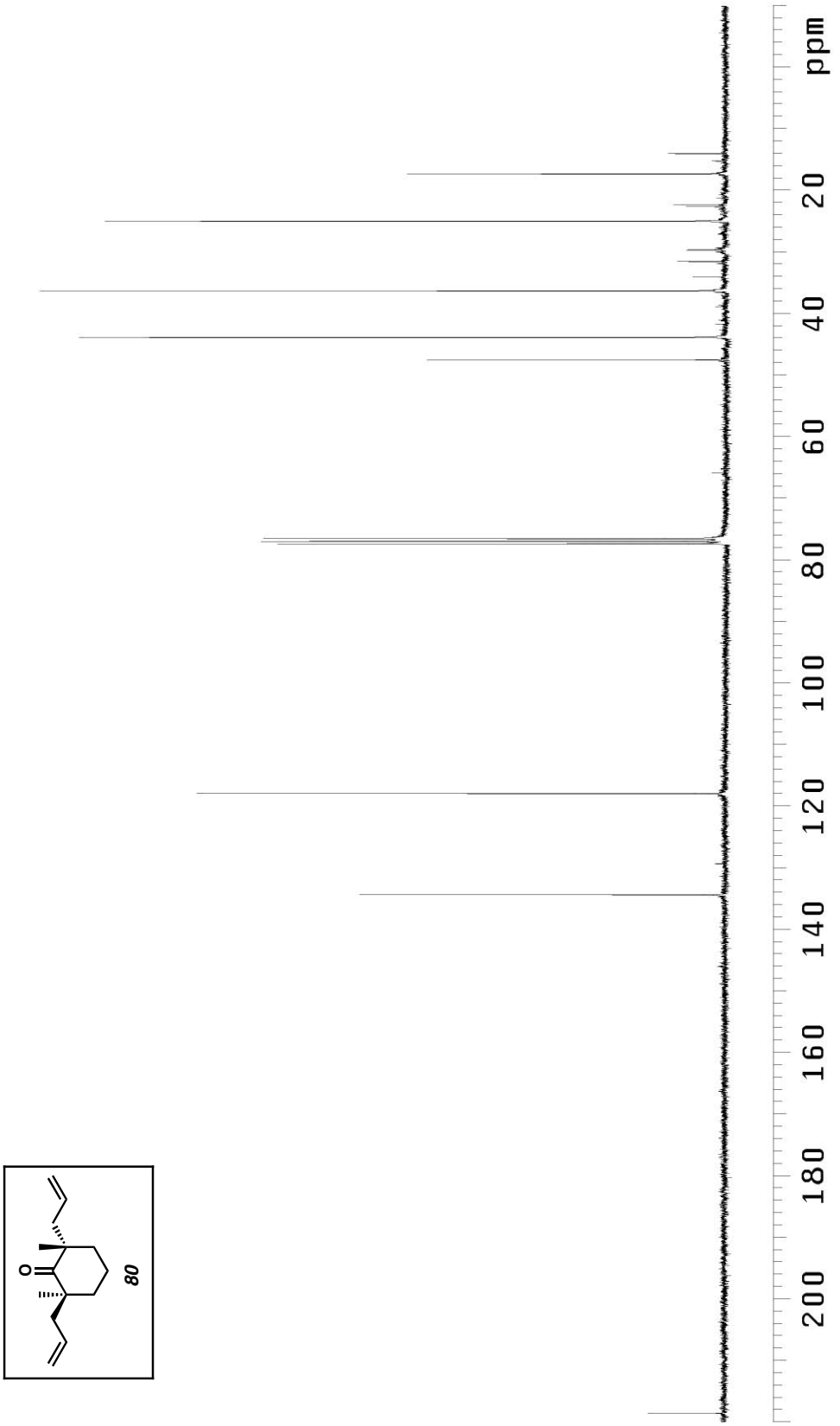
^{1}H NMR of compound **SI124** (300 MHz, $CDCl_3$)



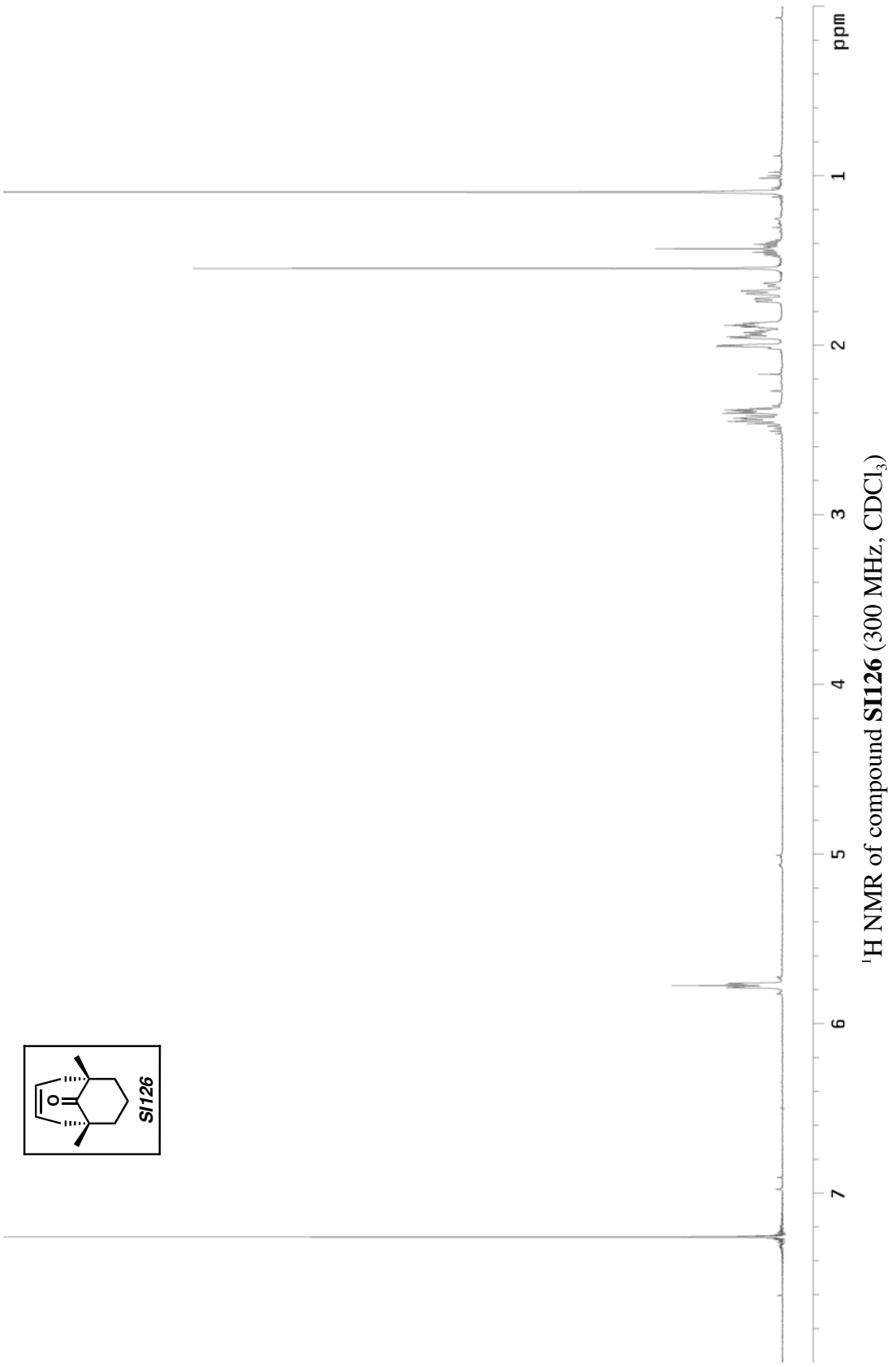
^{13}C NMR of compound **SI124** (75 MHz, $CDCl_3$)



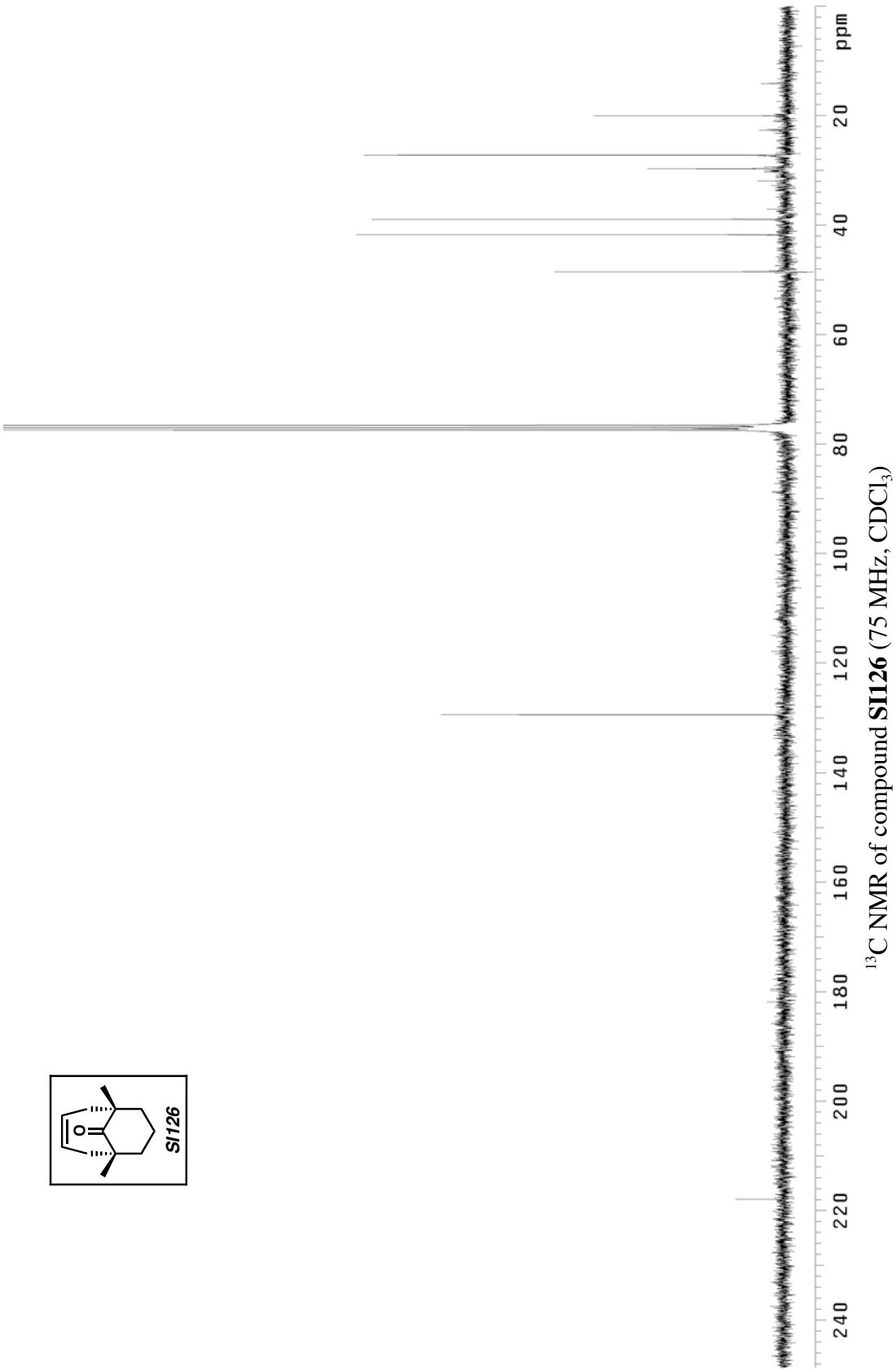
^{1}H NMR of compound **80** (300 MHz, $CDCl_3$)



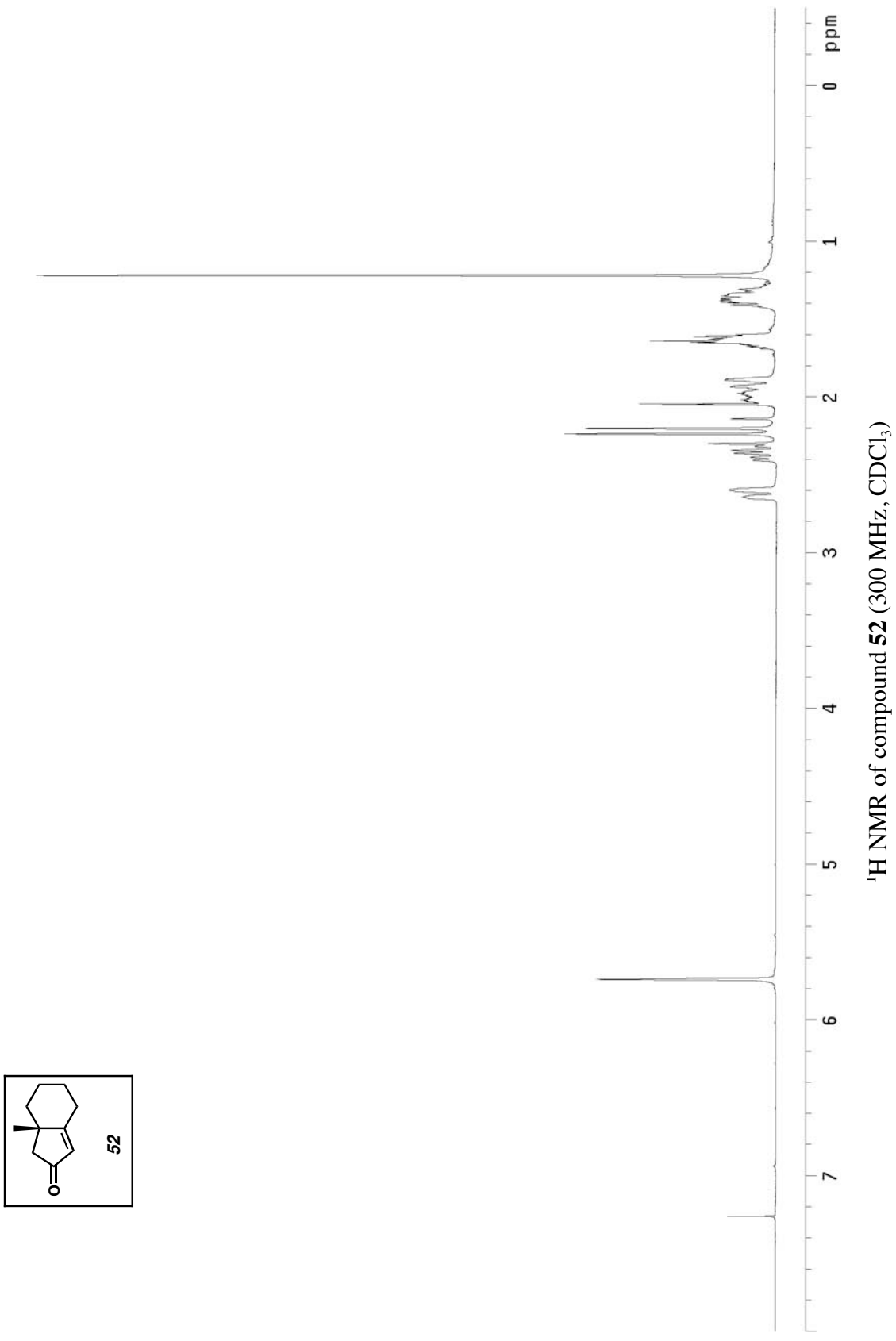
^{13}C NMR of compound **80** (75 MHz, $CDCl_3$)



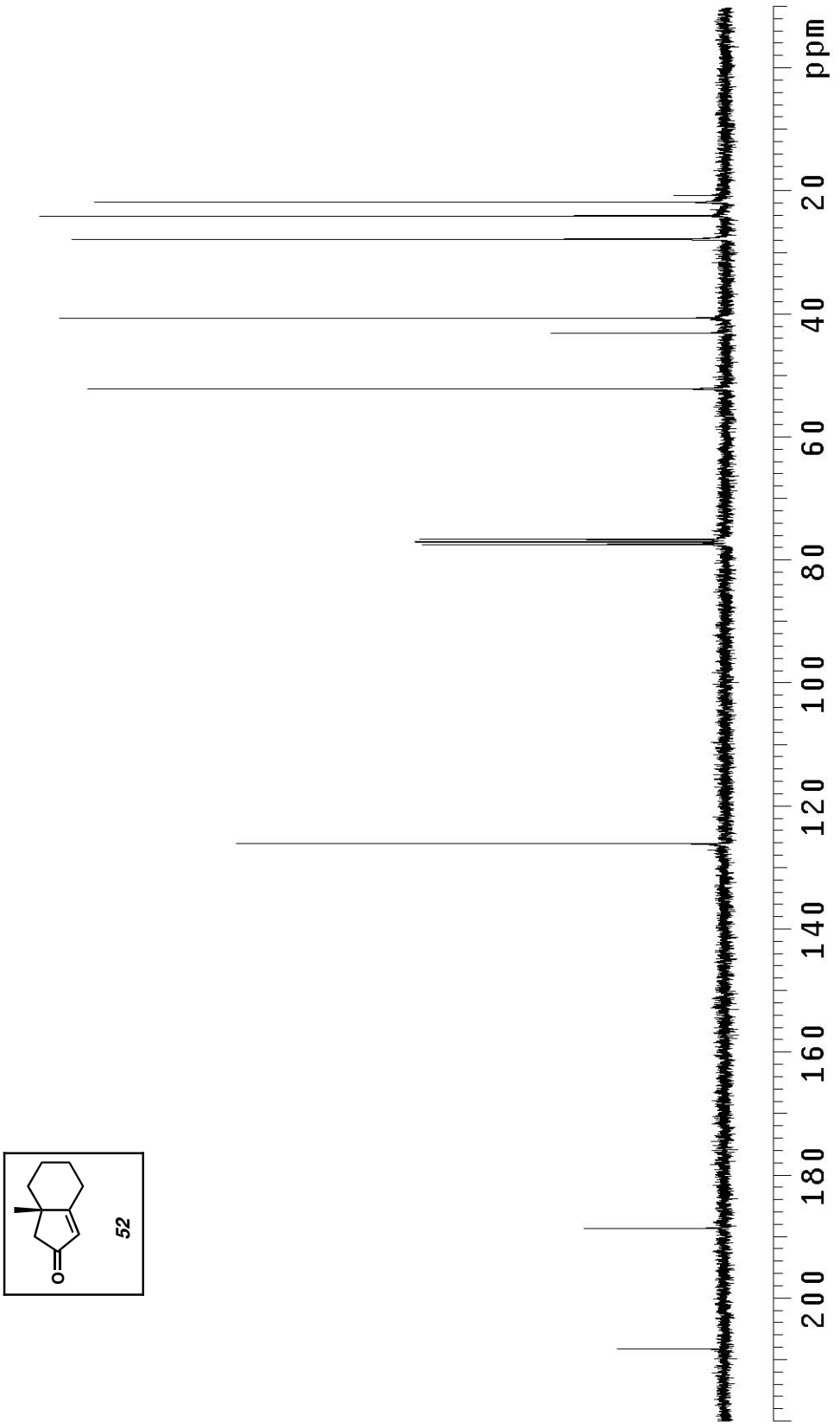
^{1}H NMR of compound **SI126** (300 MHz, $CDCl_3$)



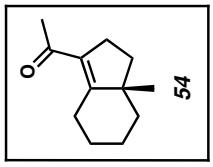
^{13}C NMR of compound **SI126** (75 MHz, $CDCl_3$)



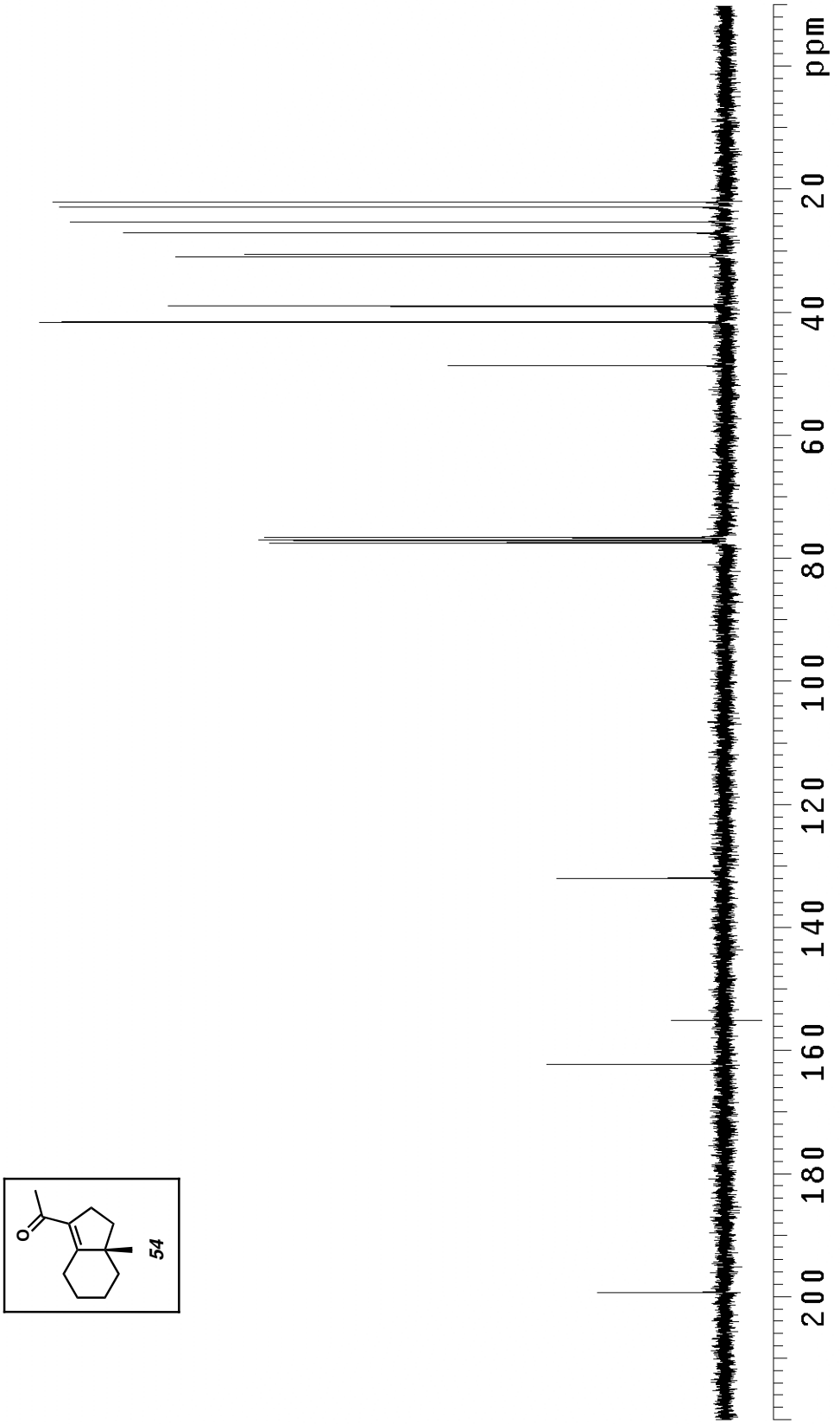
^{1}H NMR of compound **52** (300 MHz, $CDCl_3$)



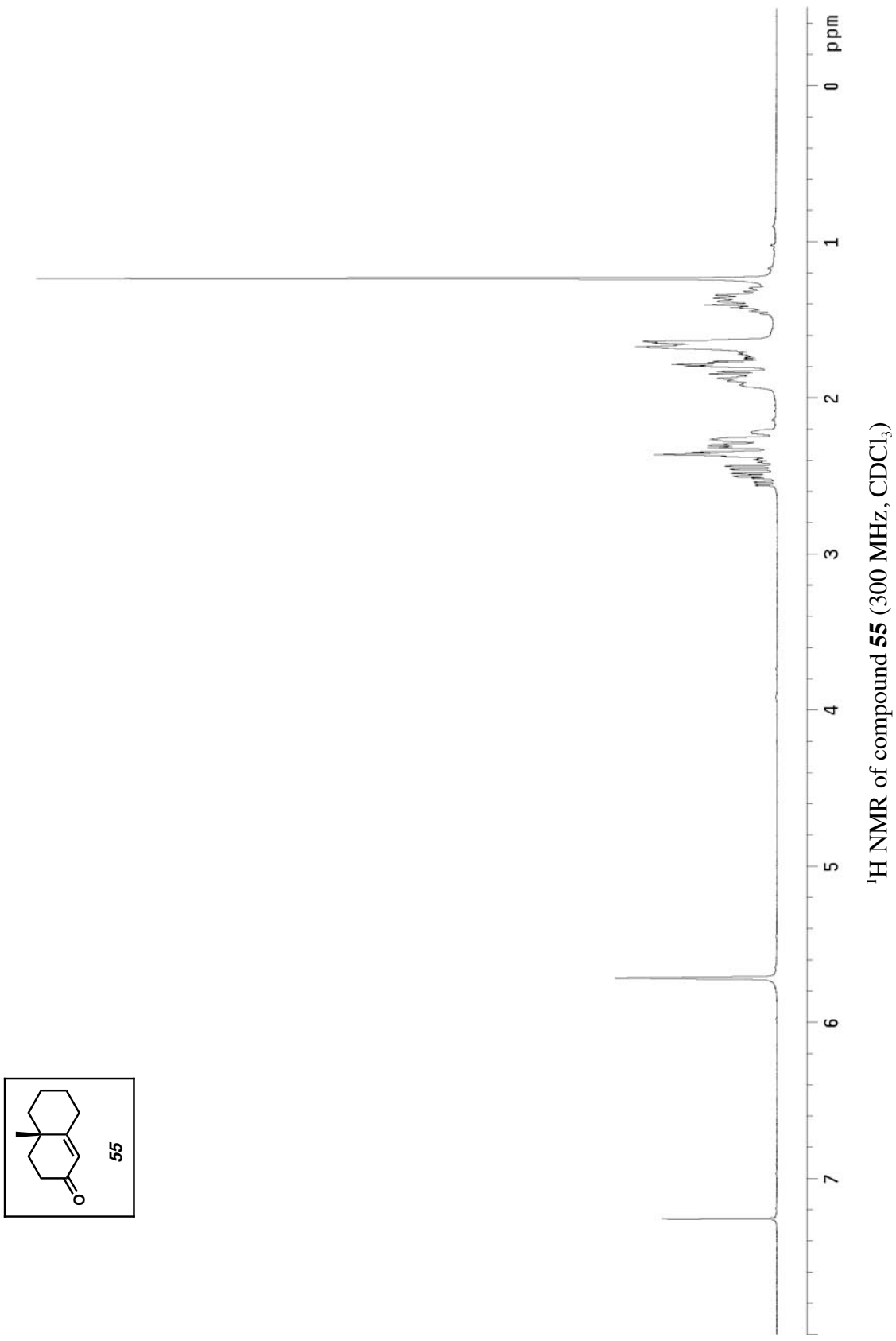
^{13}C NMR of compound **52** (75 MHz, $CDCl_3$)



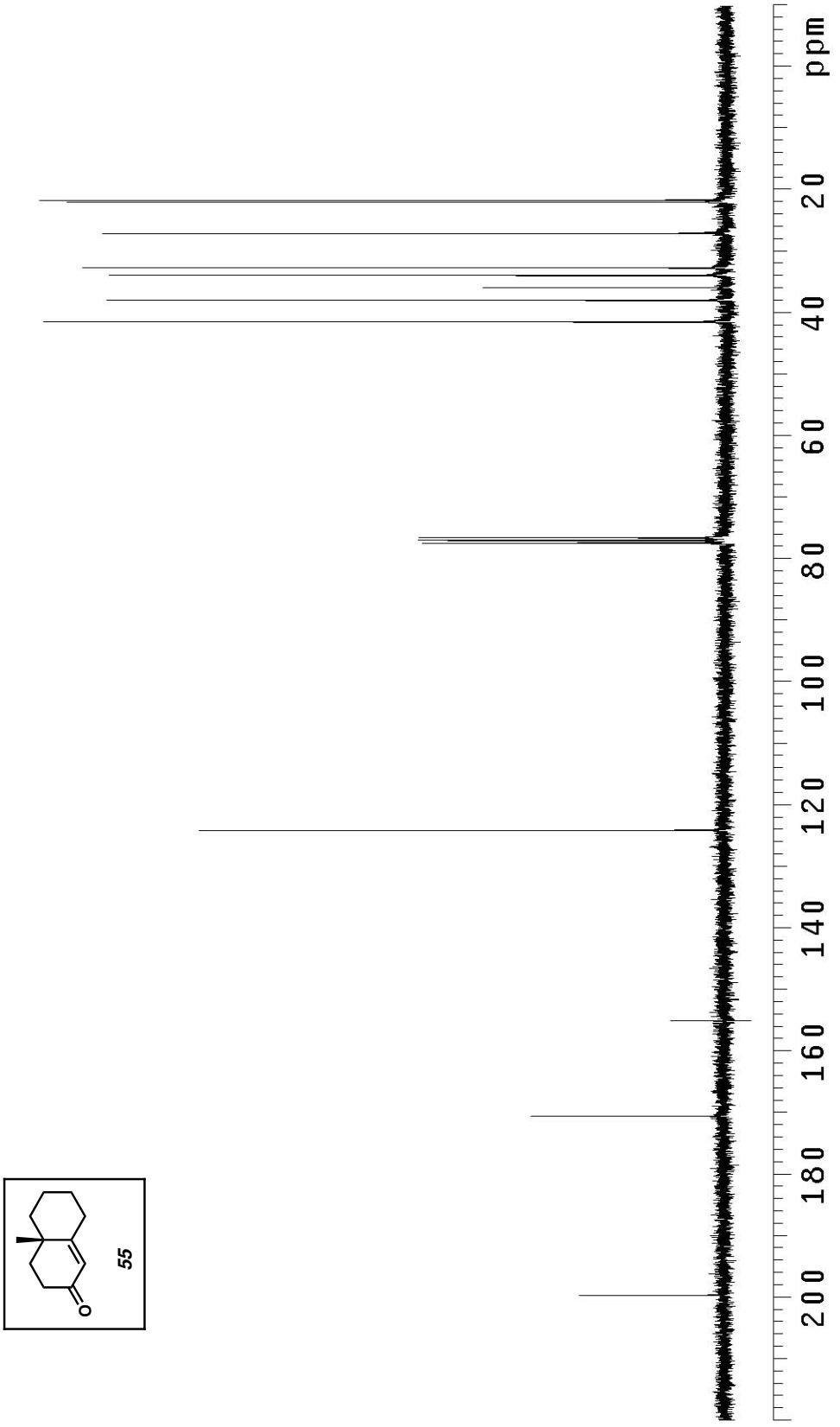
^{1}H NMR of compound **54** (300 MHz, $CDCl_3$)



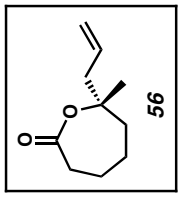
^{13}C NMR of compound **54** (75 MHz, $CDCl_3$)



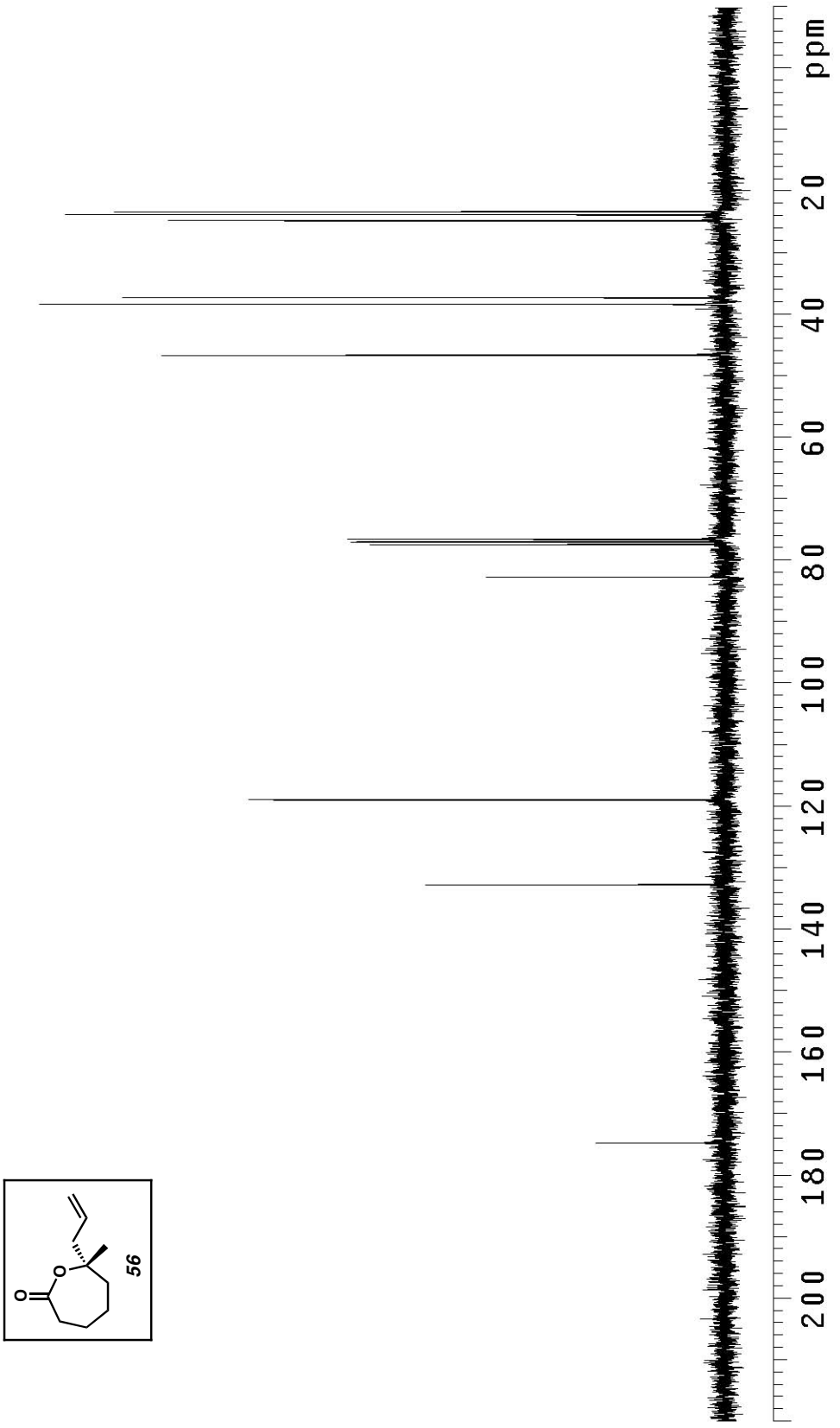
^{1}H NMR of compound **55** (300 MHz, $CDCl_3$)



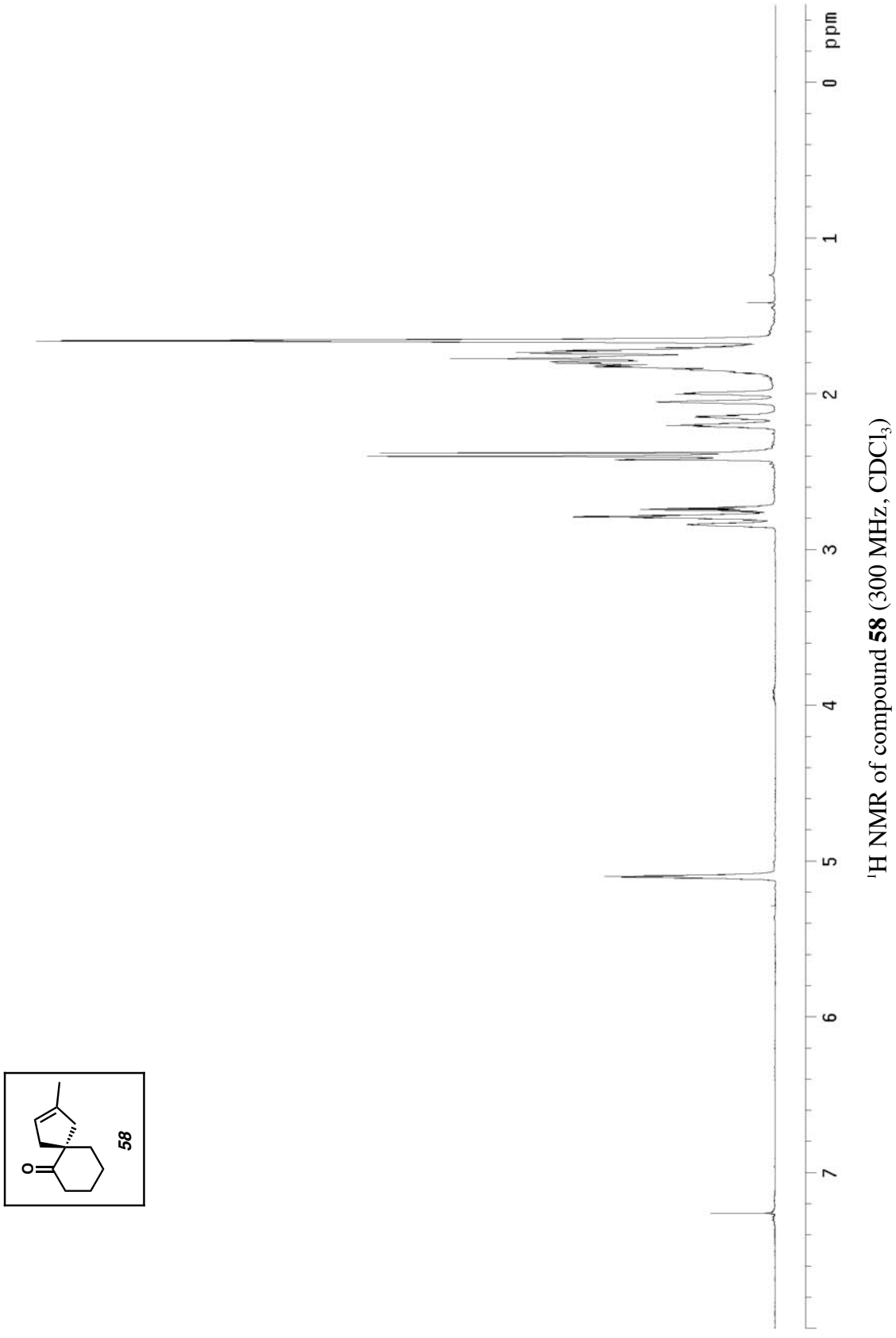
^{13}C NMR of compound **55** (75 MHz, $CDCl_3$)



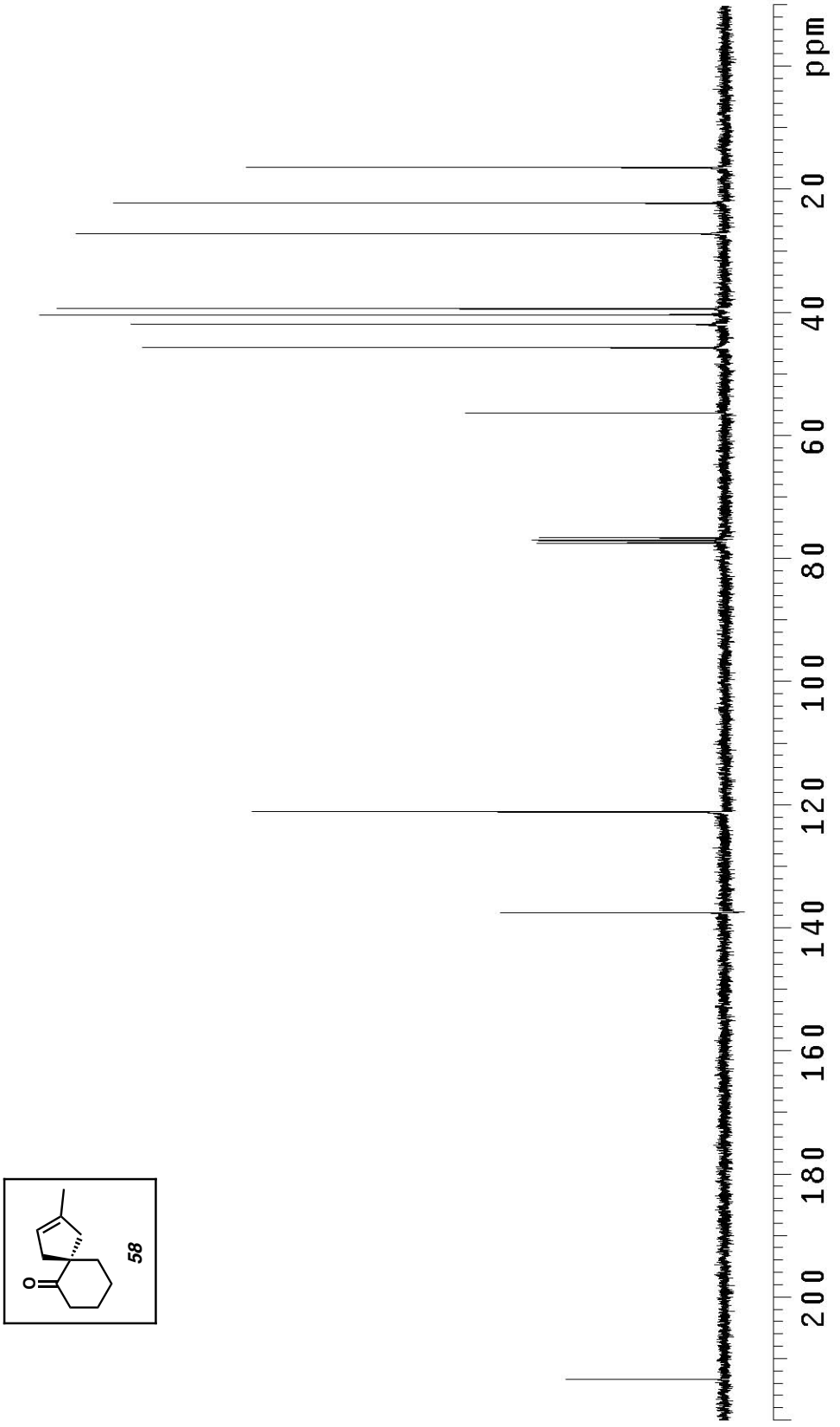
^{1}H NMR of compound **56** (300 MHz, $CDCl_3$)



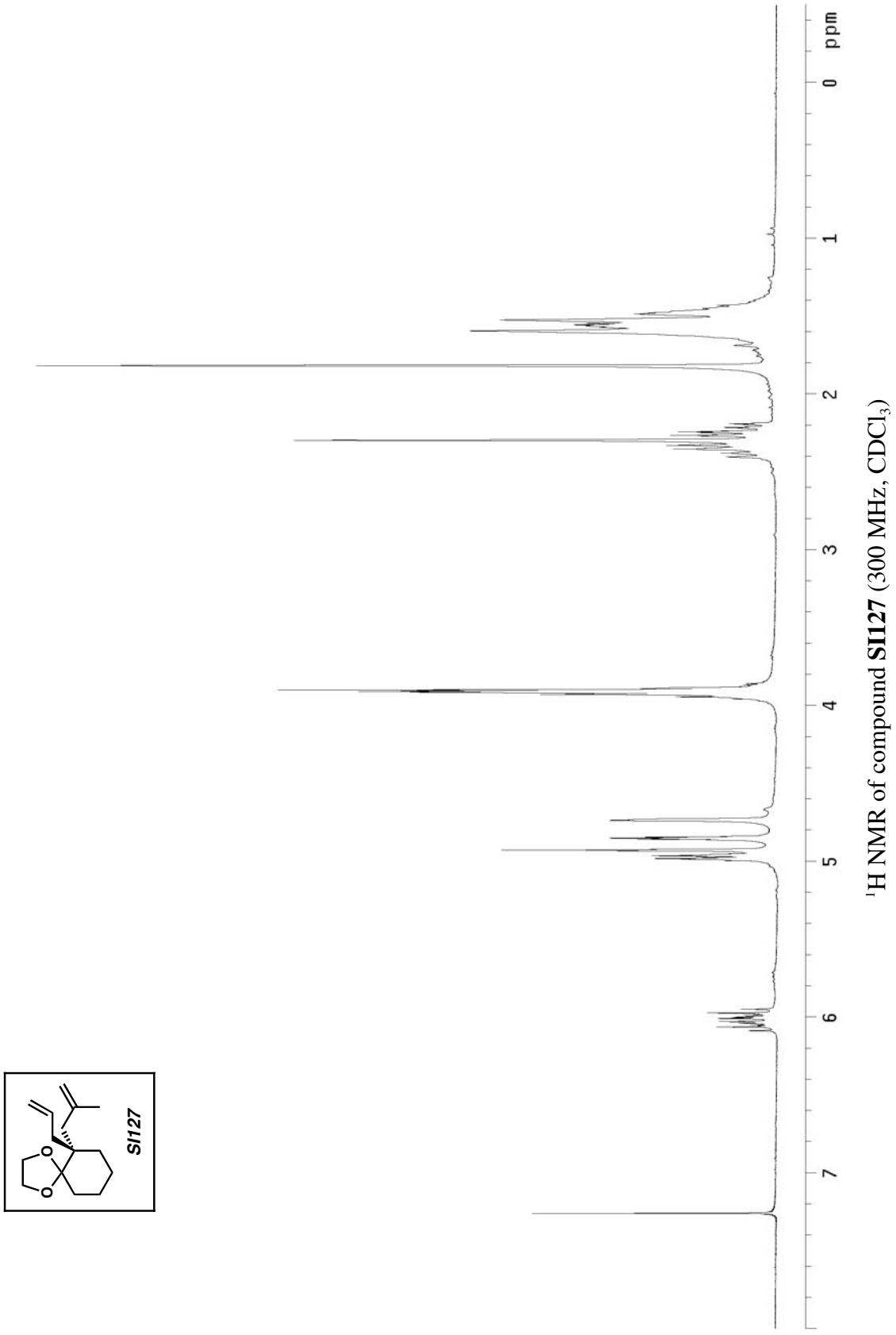
^{13}C NMR of compound **56** (75 MHz, $CDCl_3$)



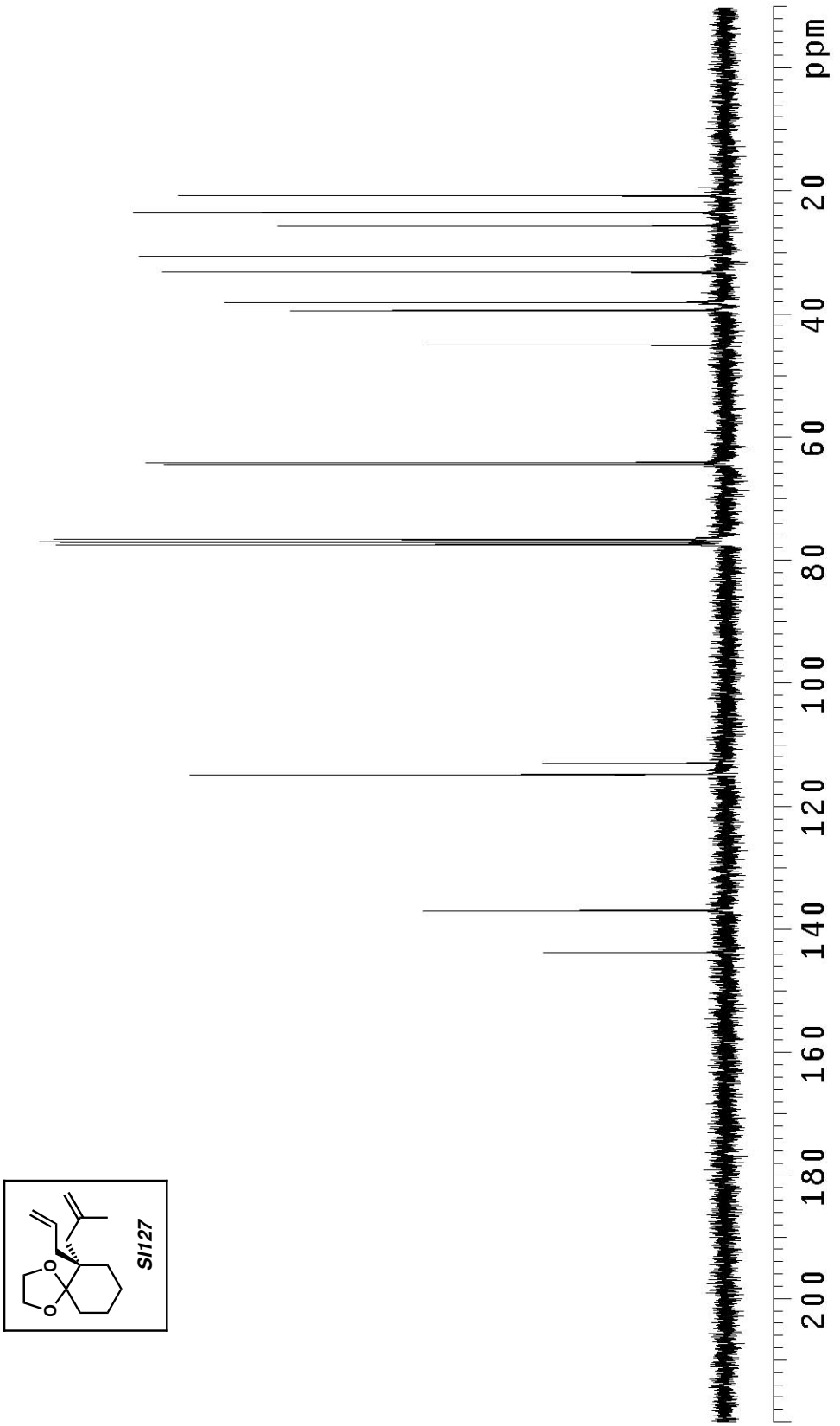
^{1}H NMR of compound **58** (300 MHz, $CDCl_3$)



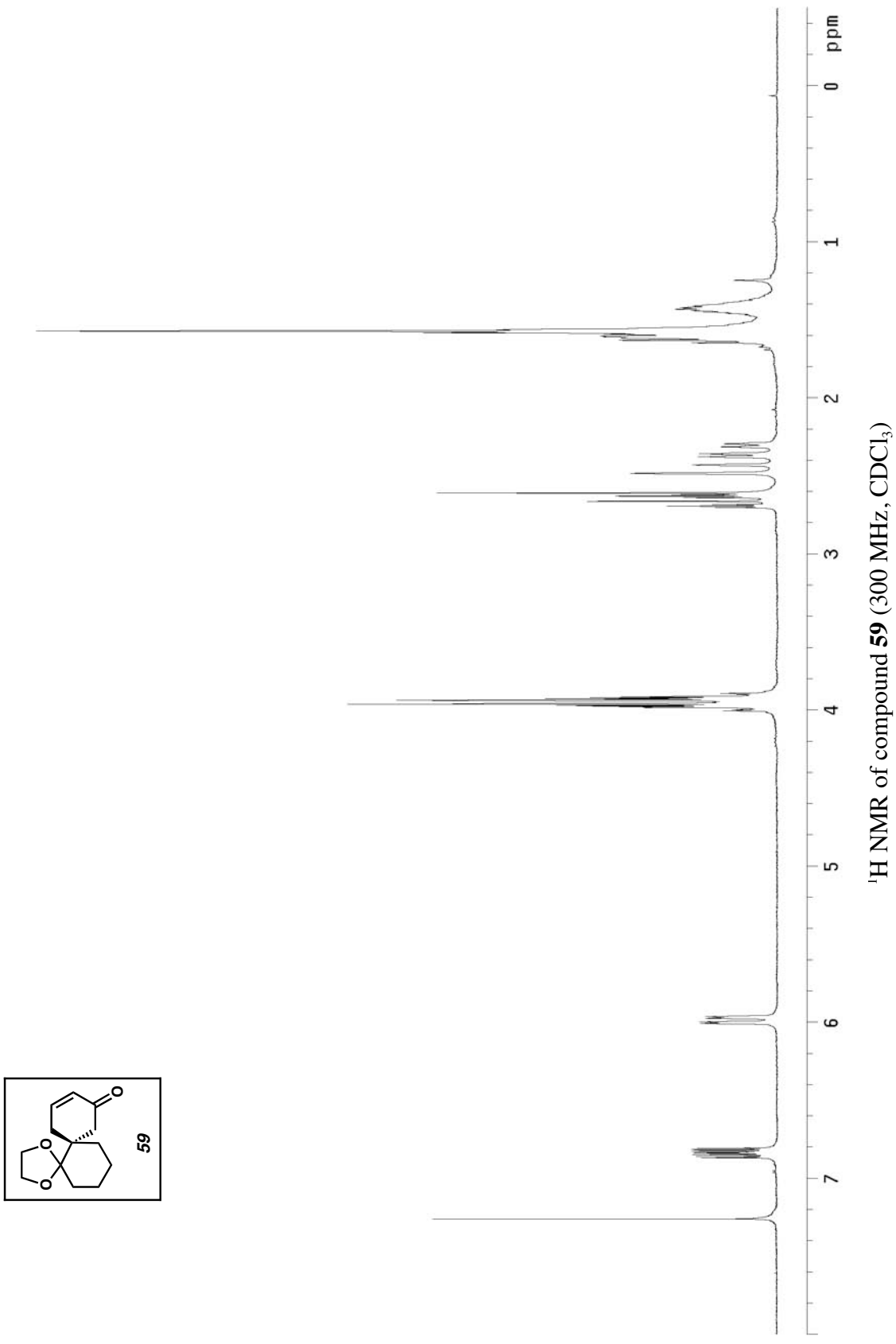
^{13}C NMR of compound **58** (75 MHz, $CDCl_3$)



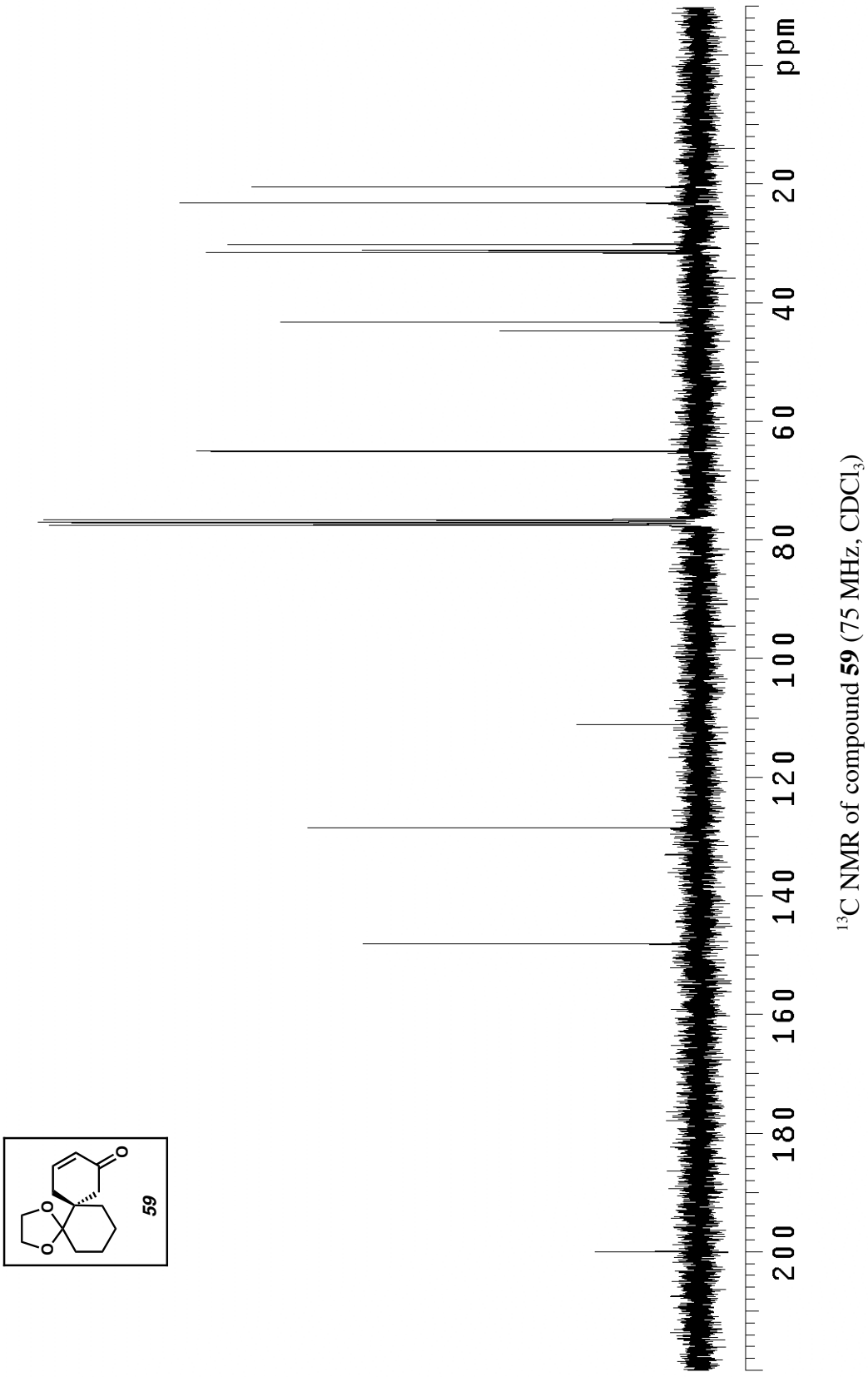
^{1}H NMR of compound **SI127** (300 MHz, $CDCl_3$)



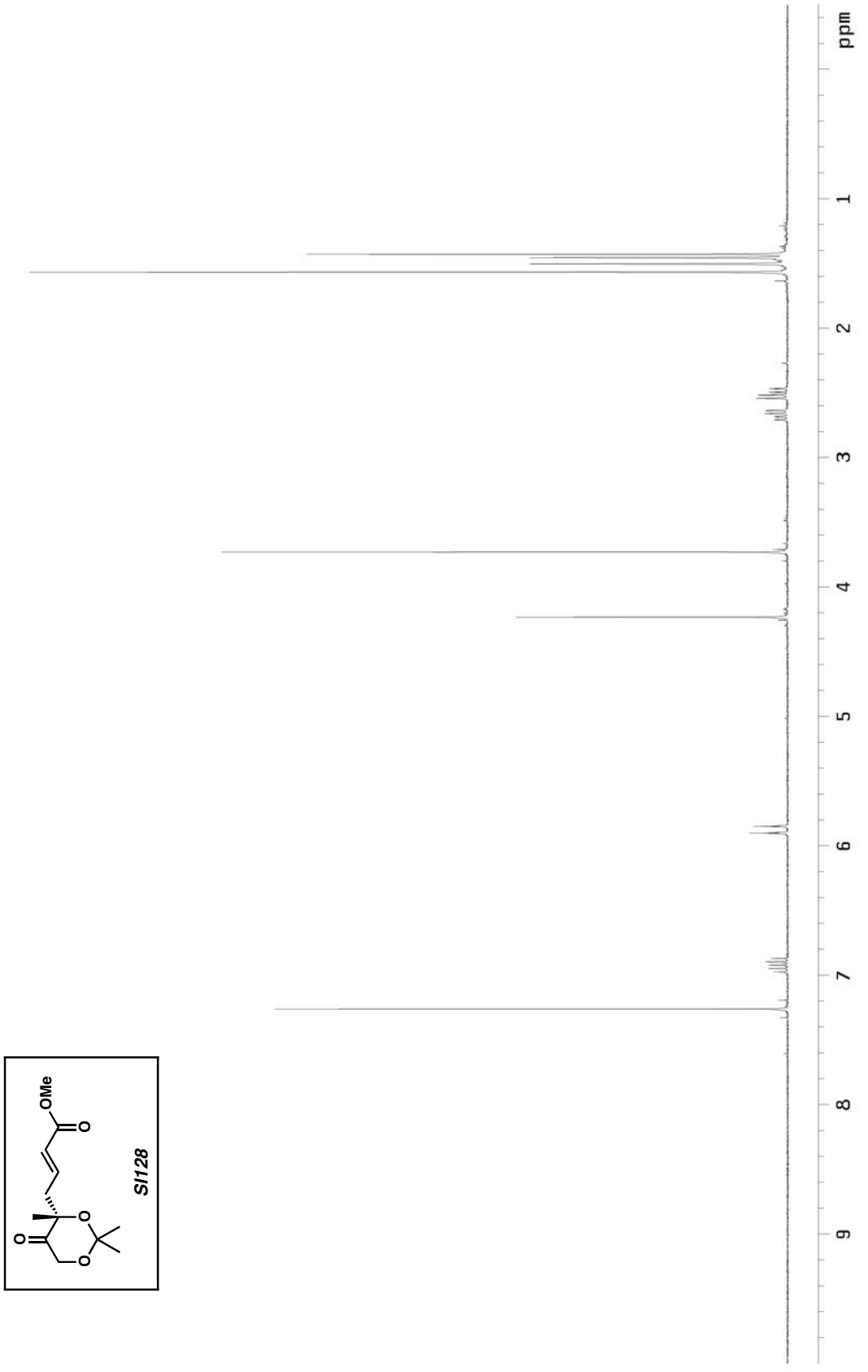
^{13}C NMR of compound **SI127** (75 MHz, $CDCl_3$)



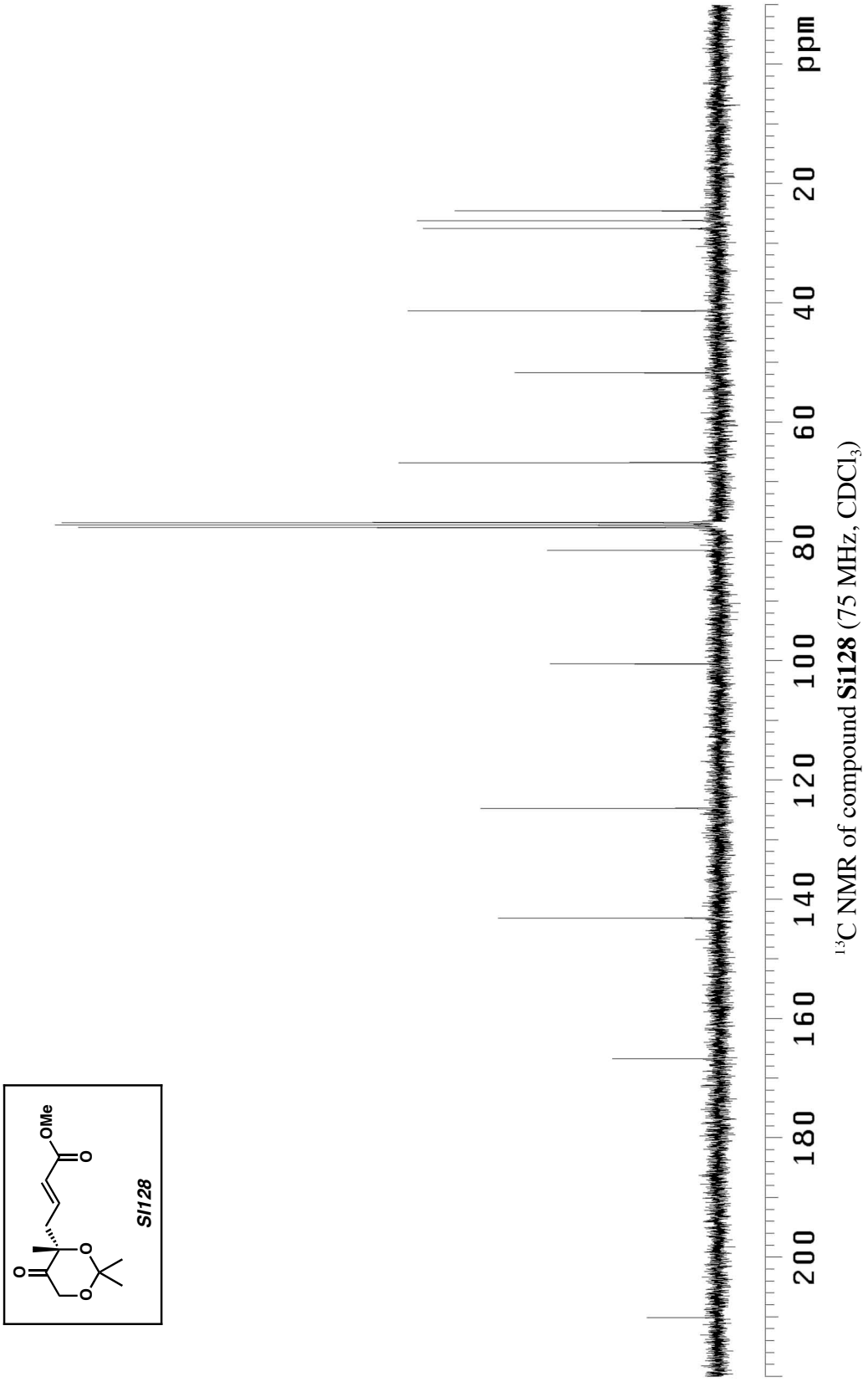
^{1}H NMR of compound **59** (300 MHz, $CDCl_3$)



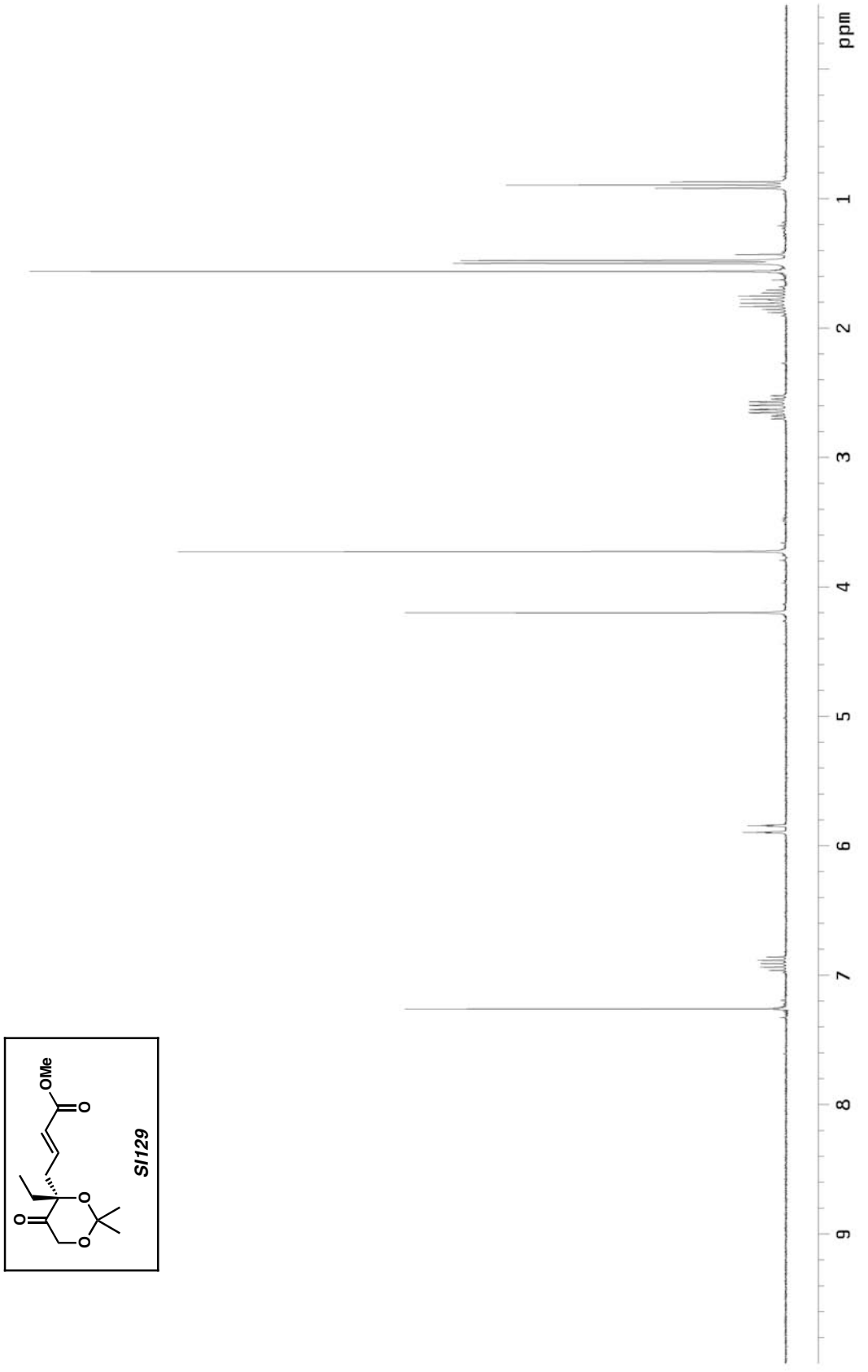
^{13}C NMR of compound **59** (75 MHz, $CDCl_3$)



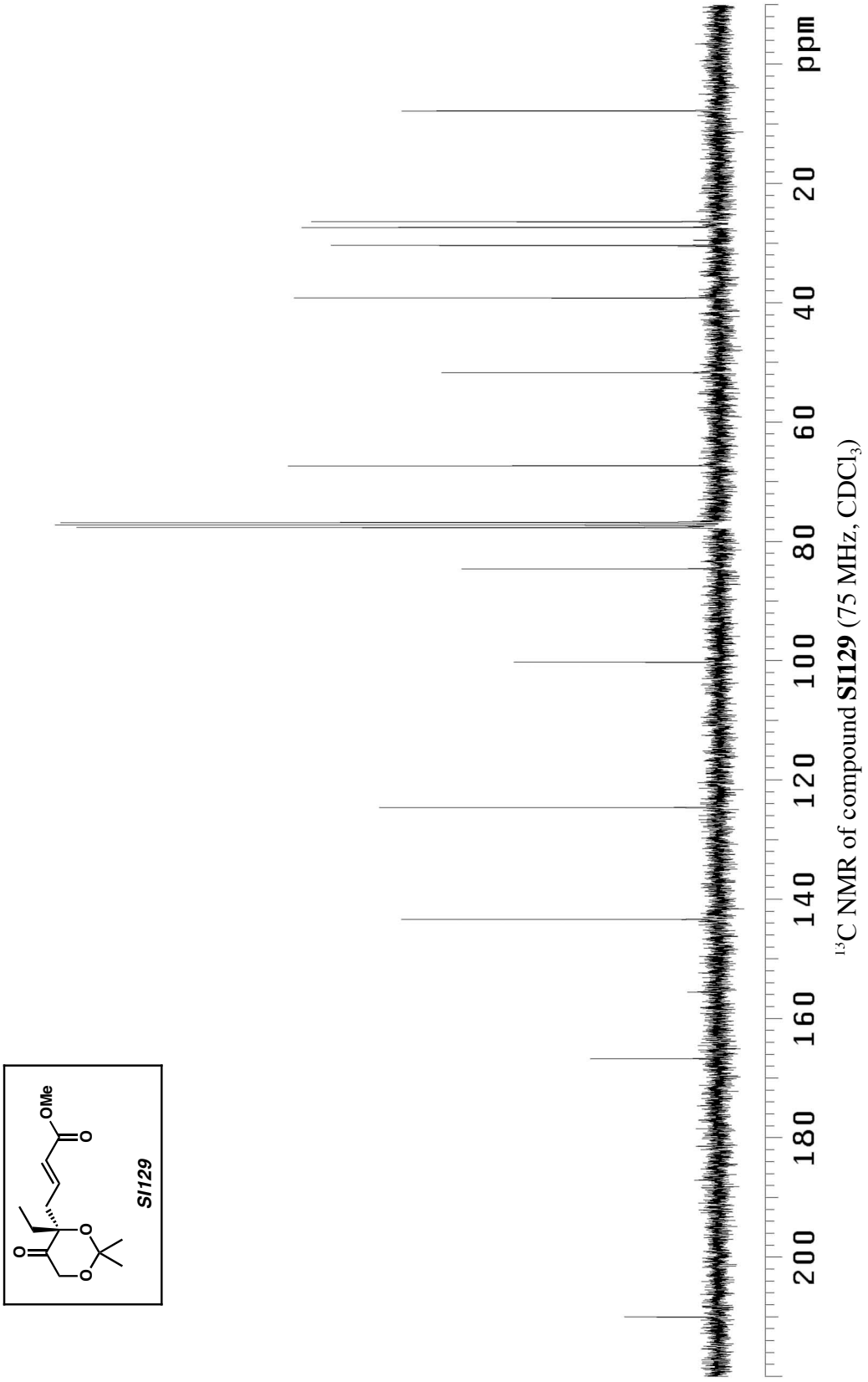
^{1}H NMR of compound **SI128** (300 MHz, $CDCl_3$)



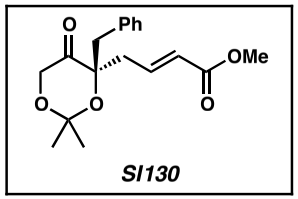
^{13}C NMR of compound **Si128** (75 MHz, $CDCl_3$)



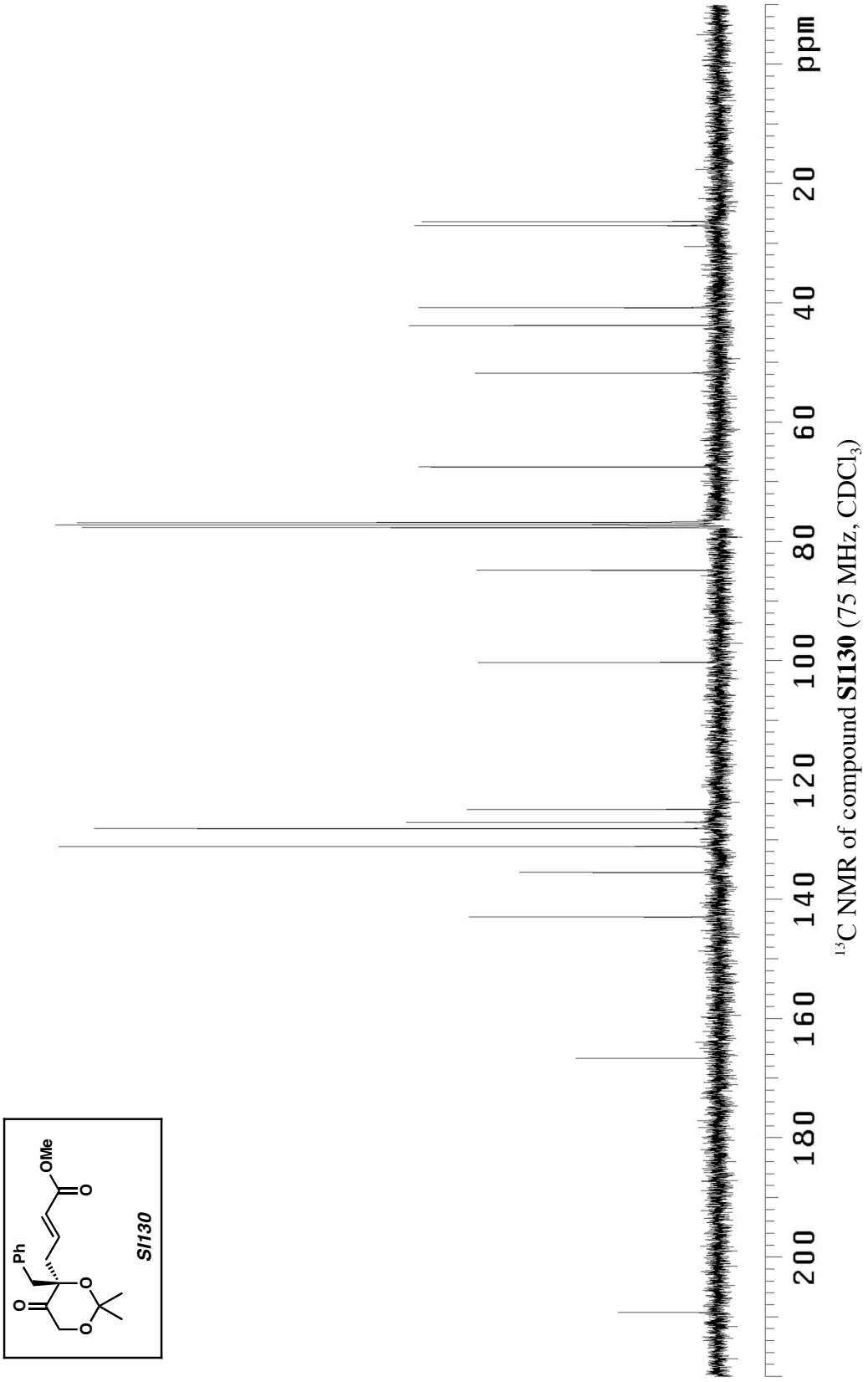
^{1}H NMR of compound **SI129** (300 MHz, $CDCl_3$)



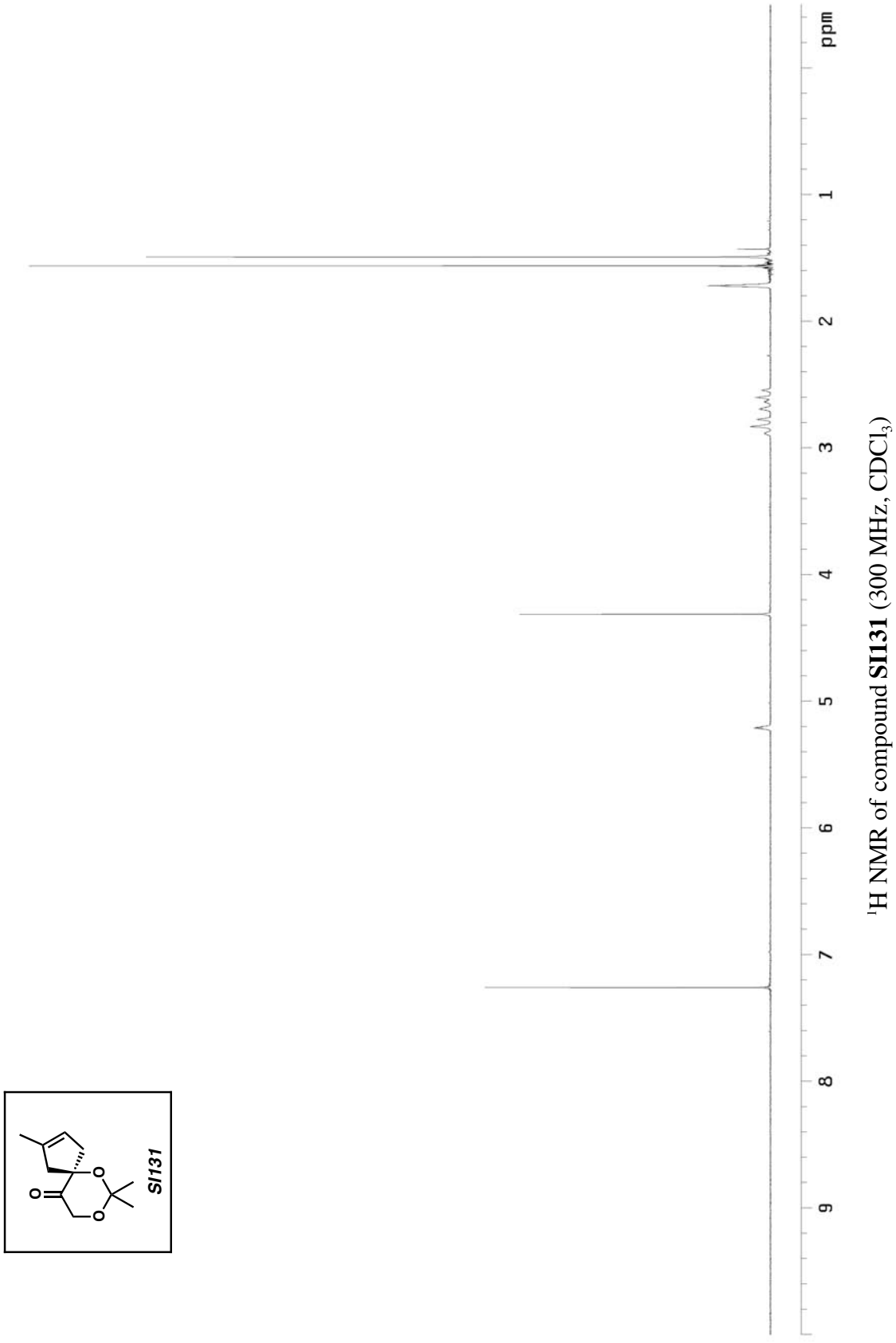
^{13}C NMR of compound **SI129** (75 MHz, $CDCl_3$)



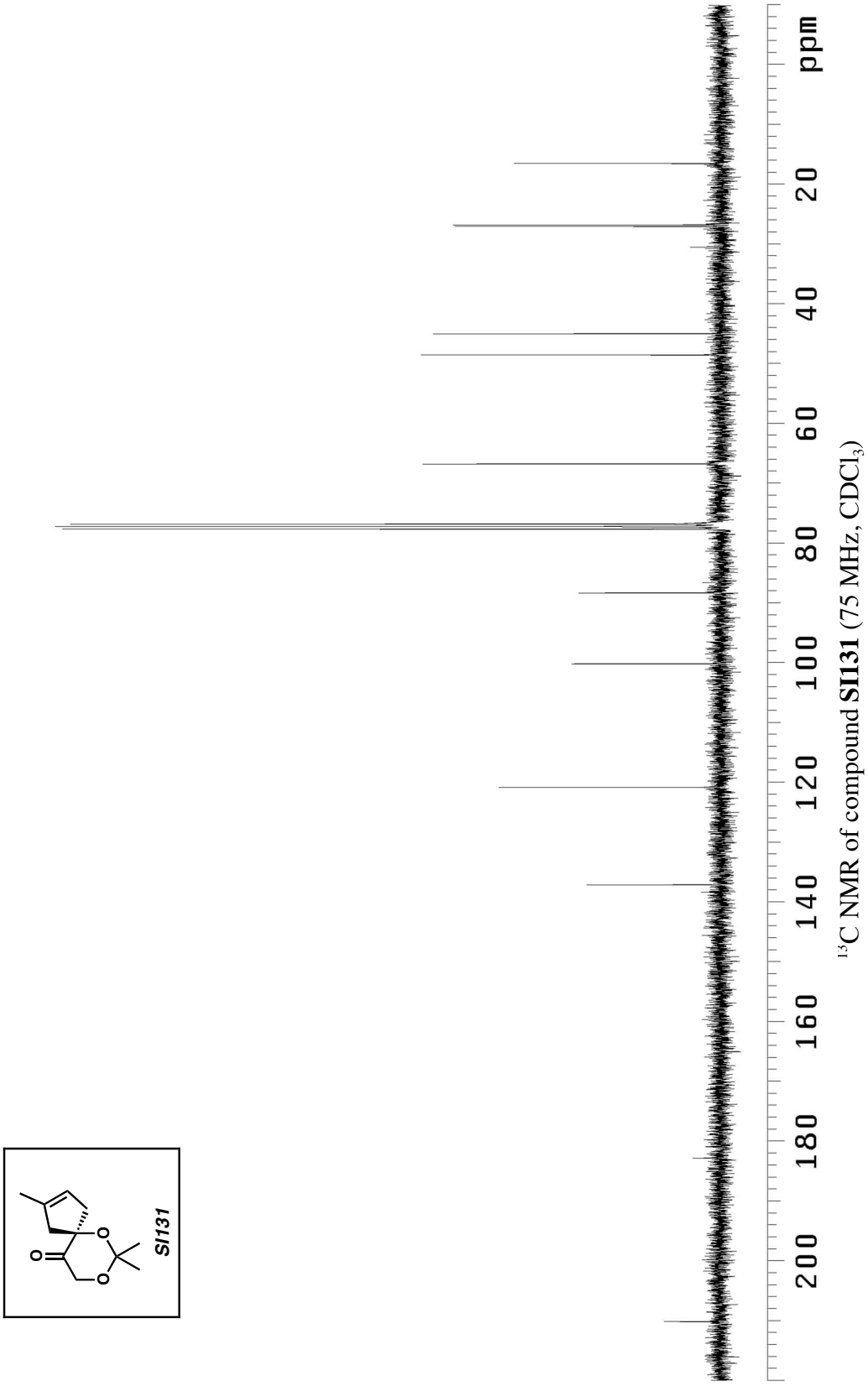
^{1}H NMR of compound **SI130** (300 MHz, $CDCl_3$)



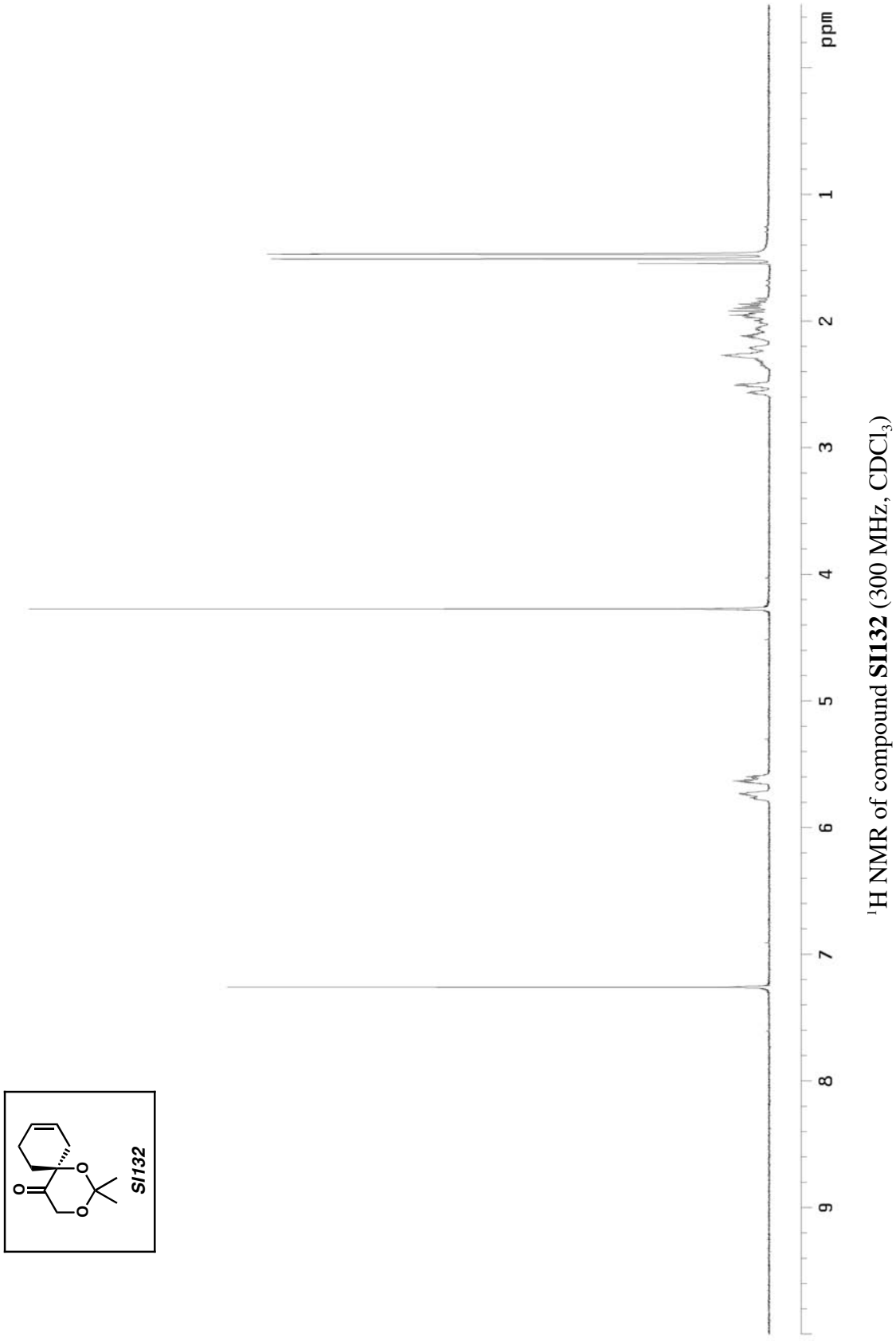
^{13}C NMR of compound **SI130** (75 MHz, $CDCl_3$)



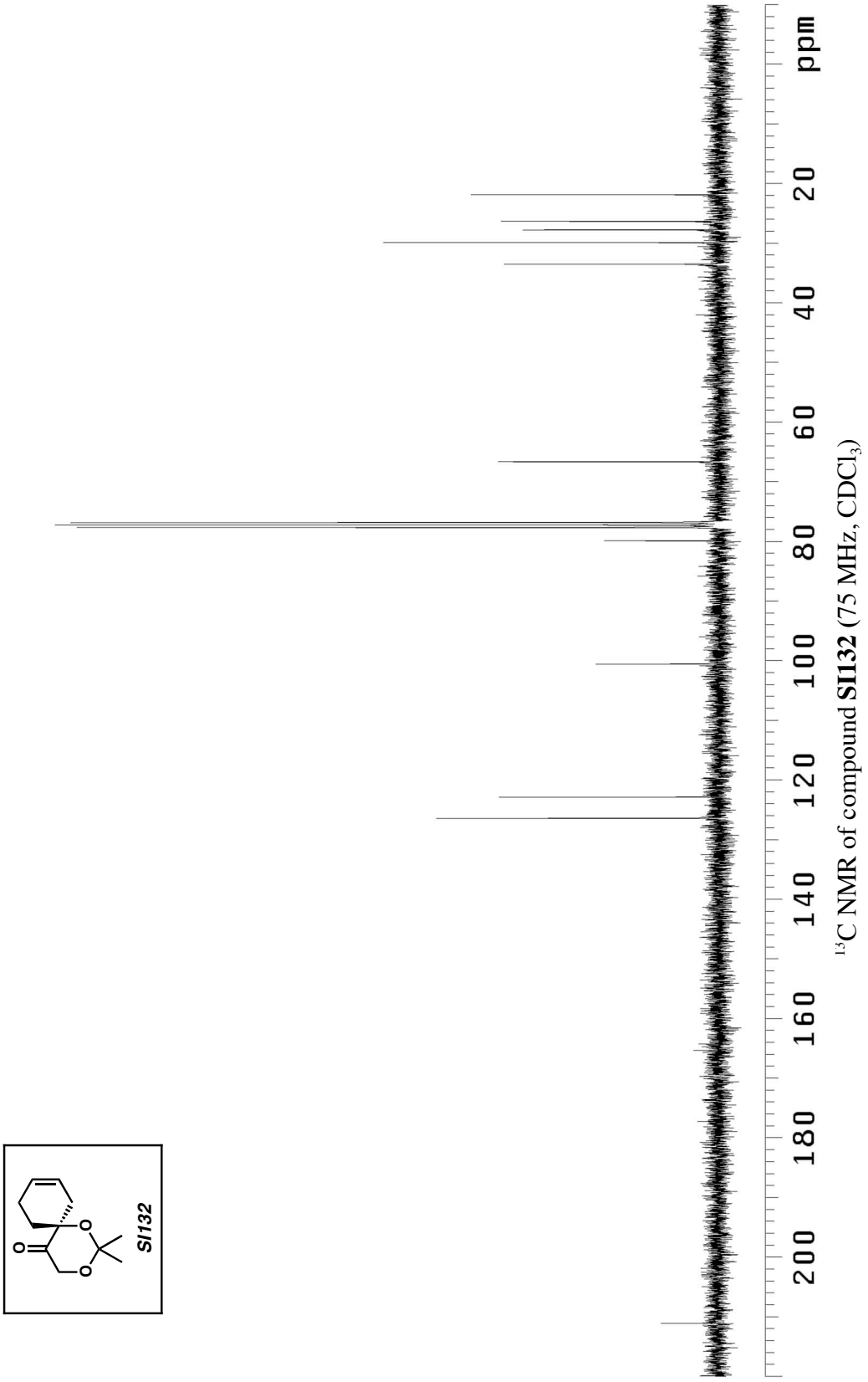
^{1}H NMR of compound **SI131** (300 MHz, $CDCl_3$)



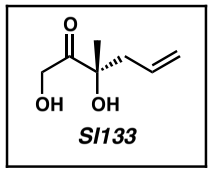
^{13}C NMR of compound **SI131** (75 MHz, $CDCl_3$)



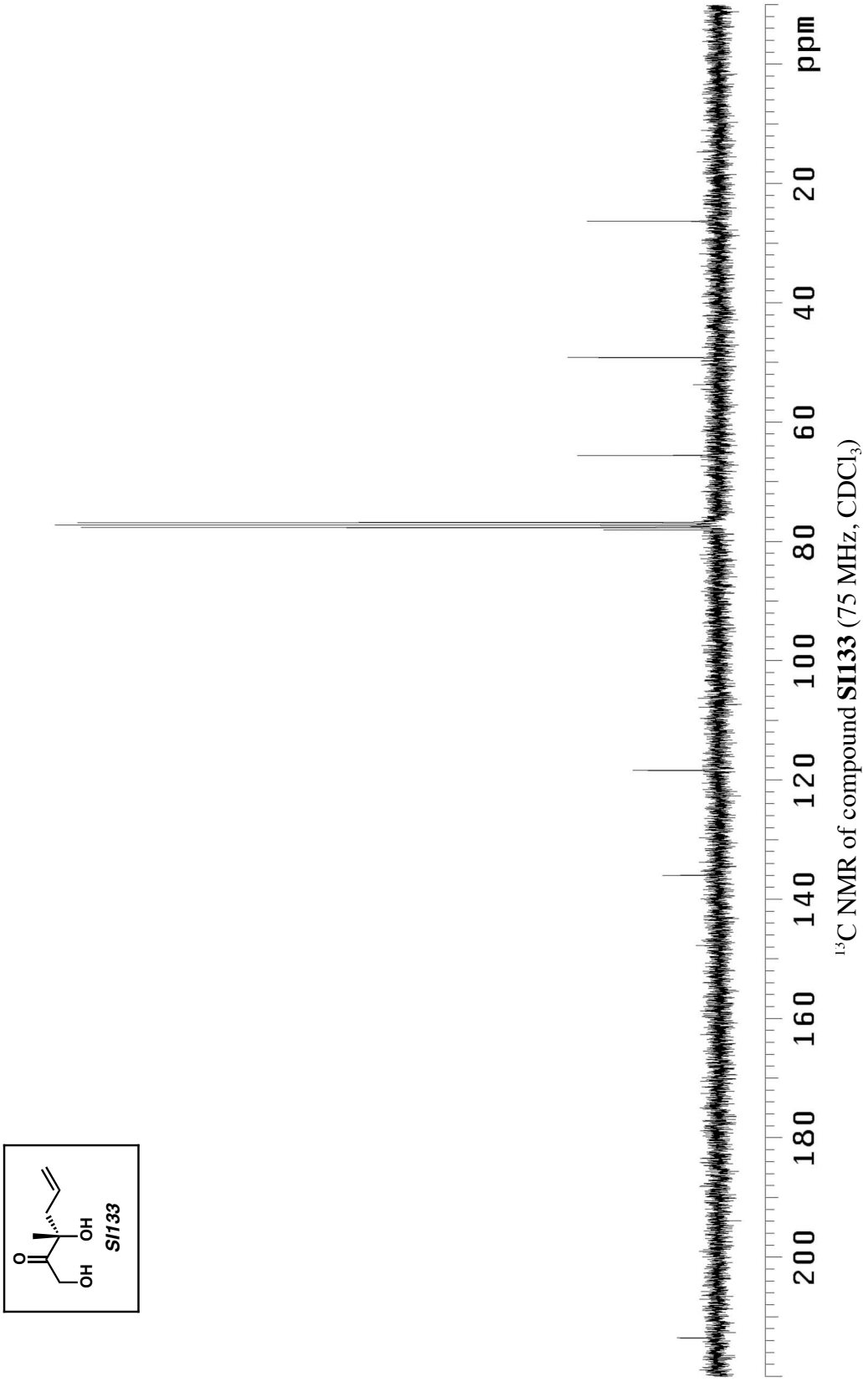
^{1}H NMR of compound **SI132** (300 MHz, $CDCl_3$)



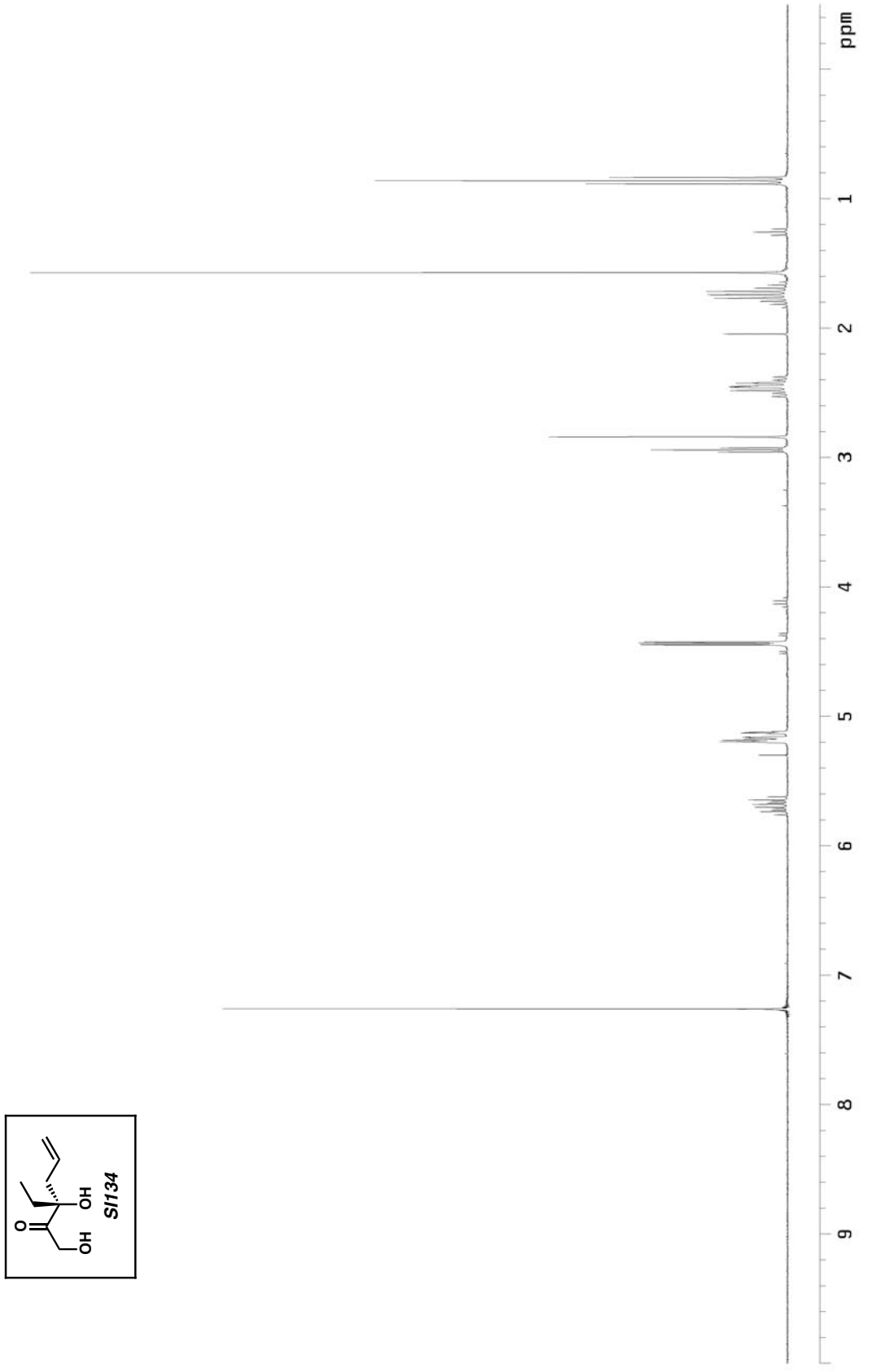
^{13}C NMR of compound **SI132** (75 MHz, $CDCl_3$)



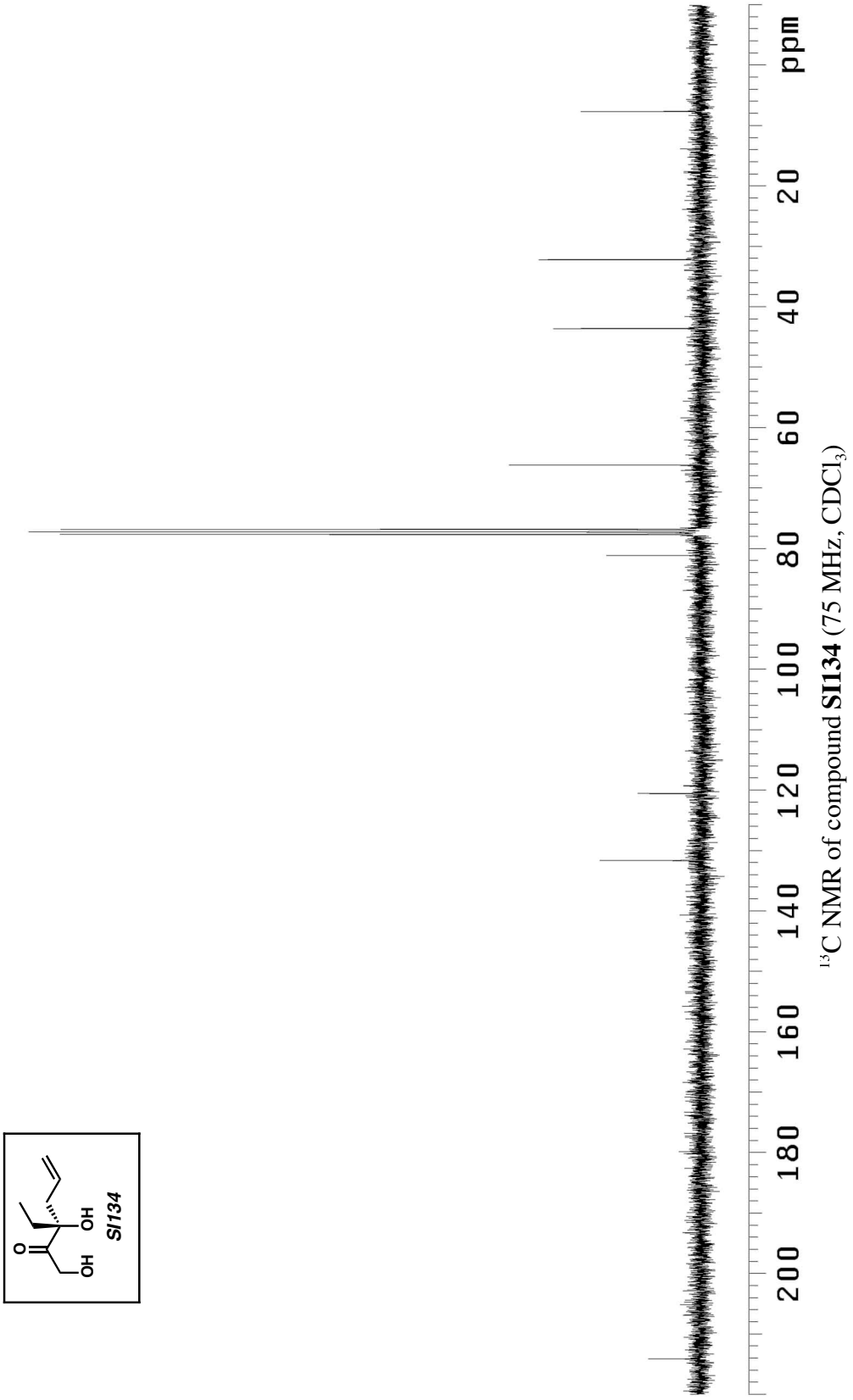
^{1}H NMR of compound **SI133** (300 MHz, $CDCl_3$)



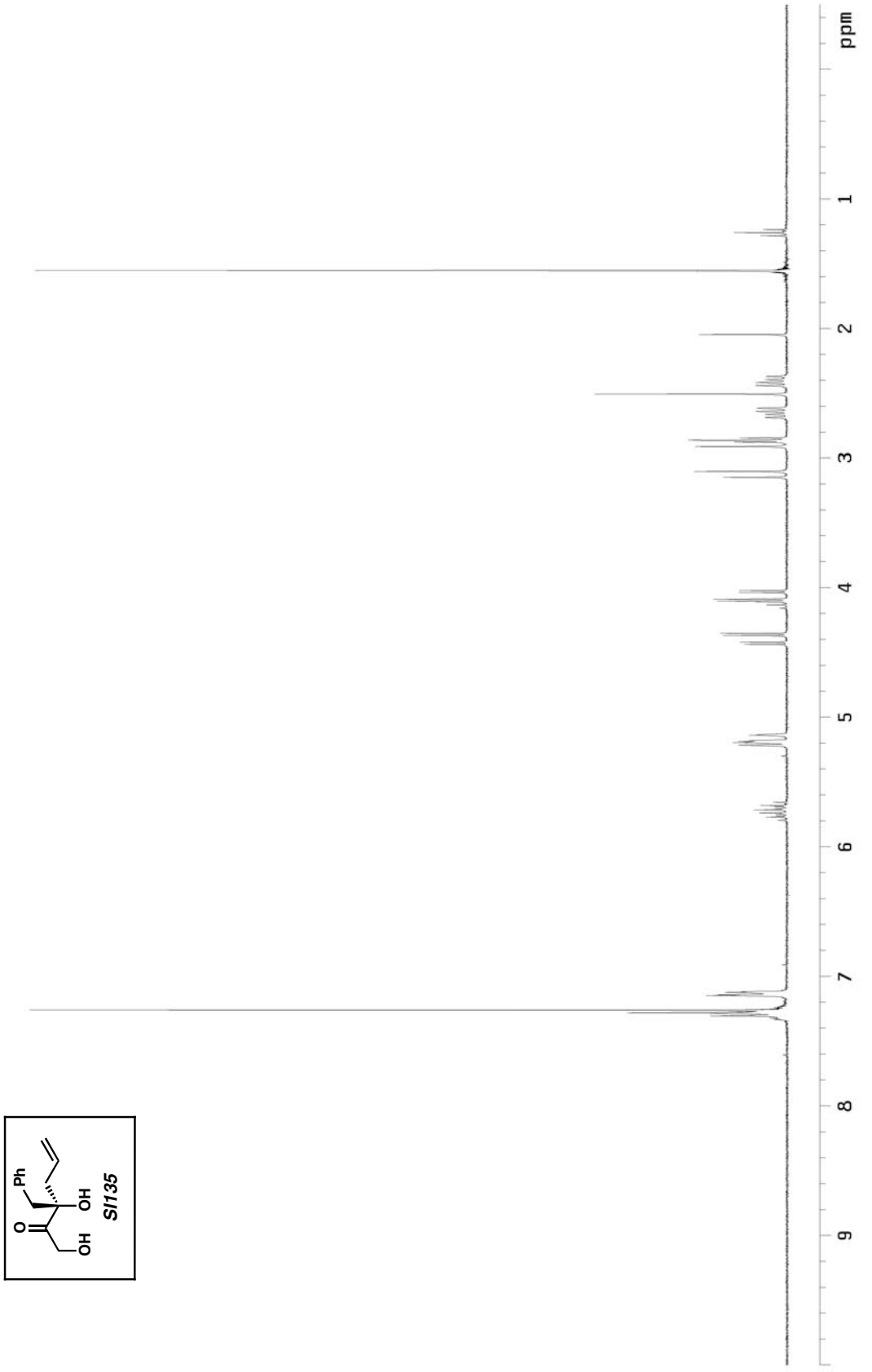
^{13}C NMR of compound **SI133** (75 MHz, $CDCl_3$)



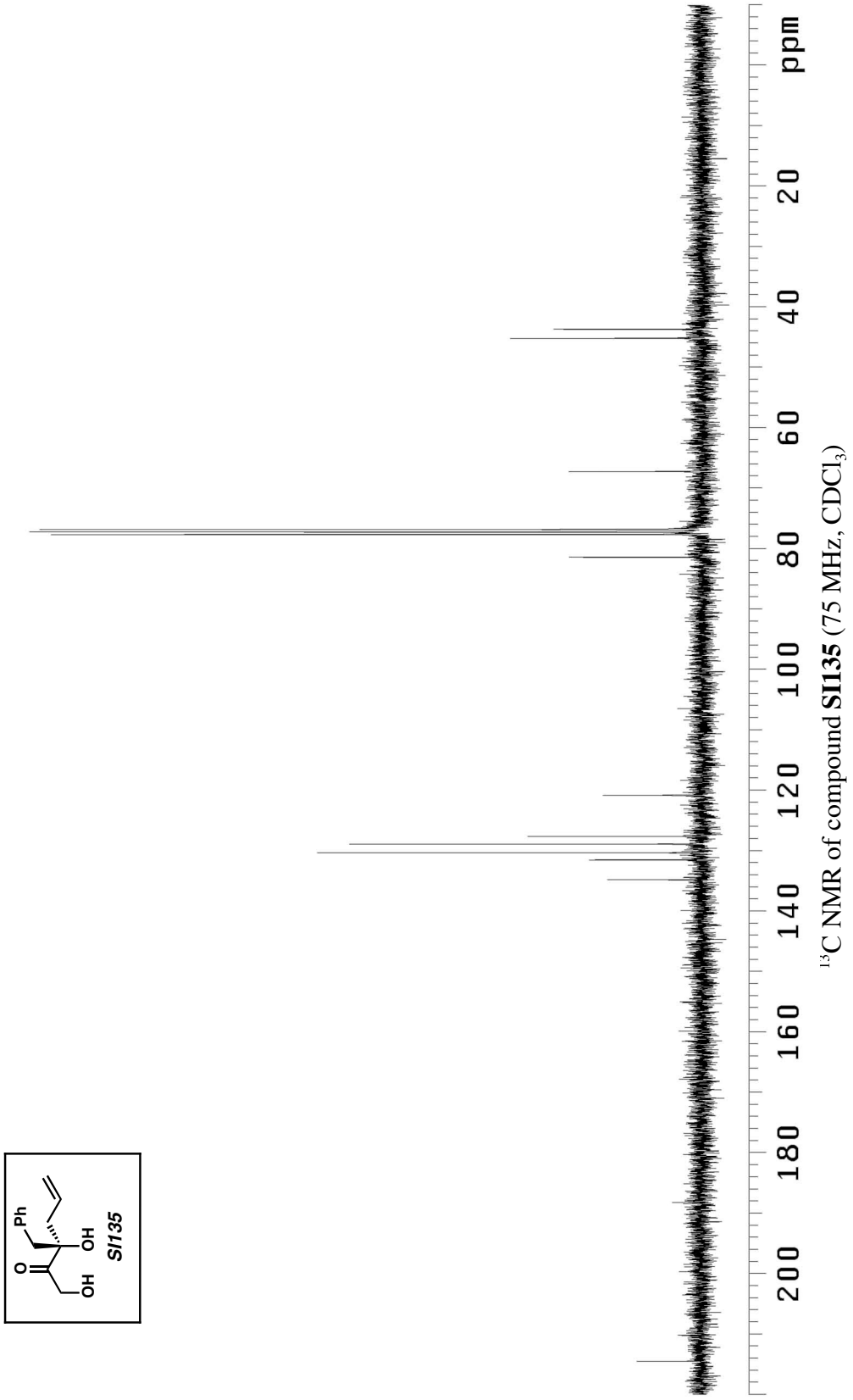
^{1}H NMR of compound **SI134** (300 MHz, $CDCl_3$)



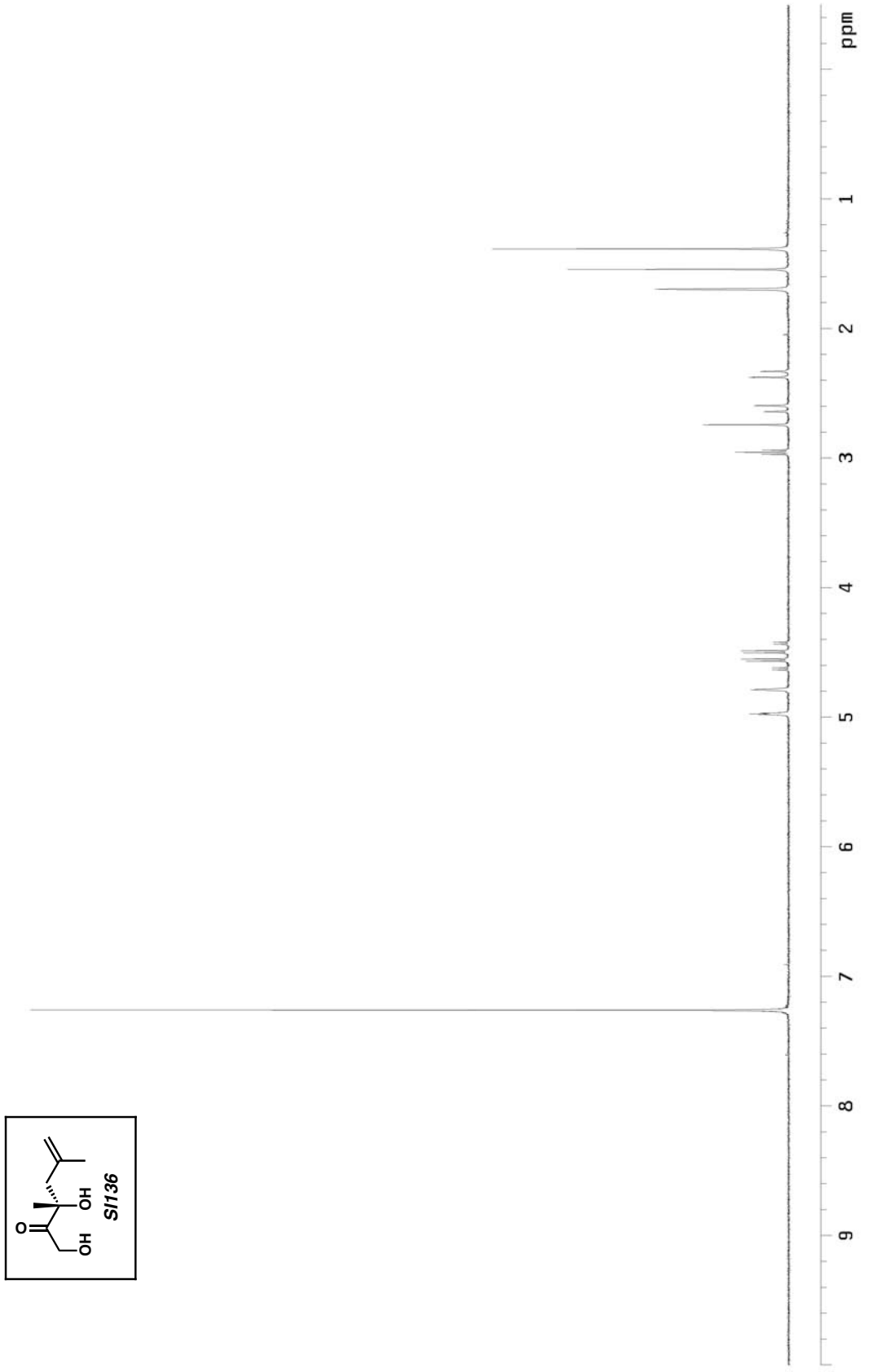
^{13}C NMR of compound **SI134** (75 MHz, $CDCl_3$)



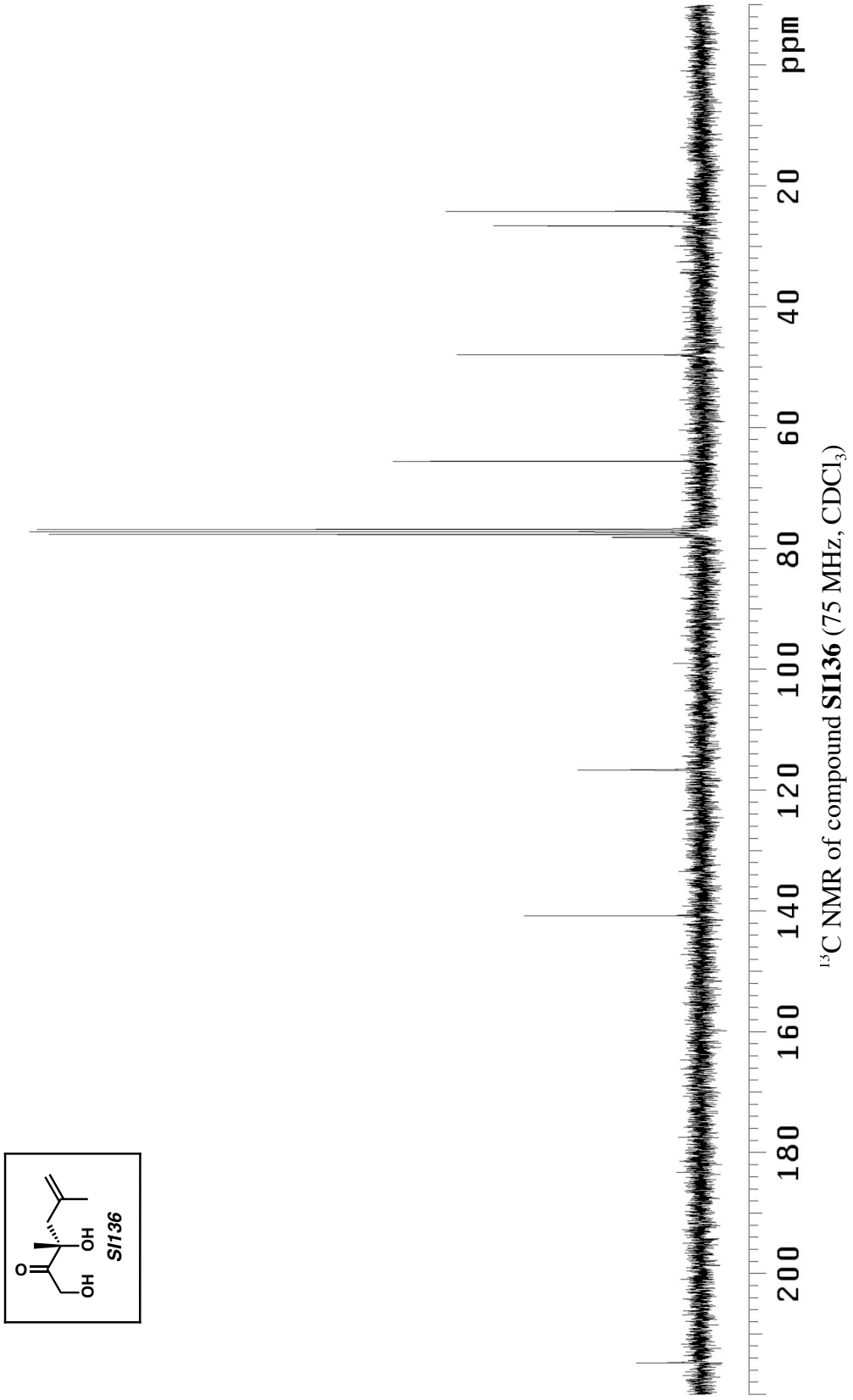
^{1}H NMR of compound **SI135** (300 MHz, $CDCl_3$)



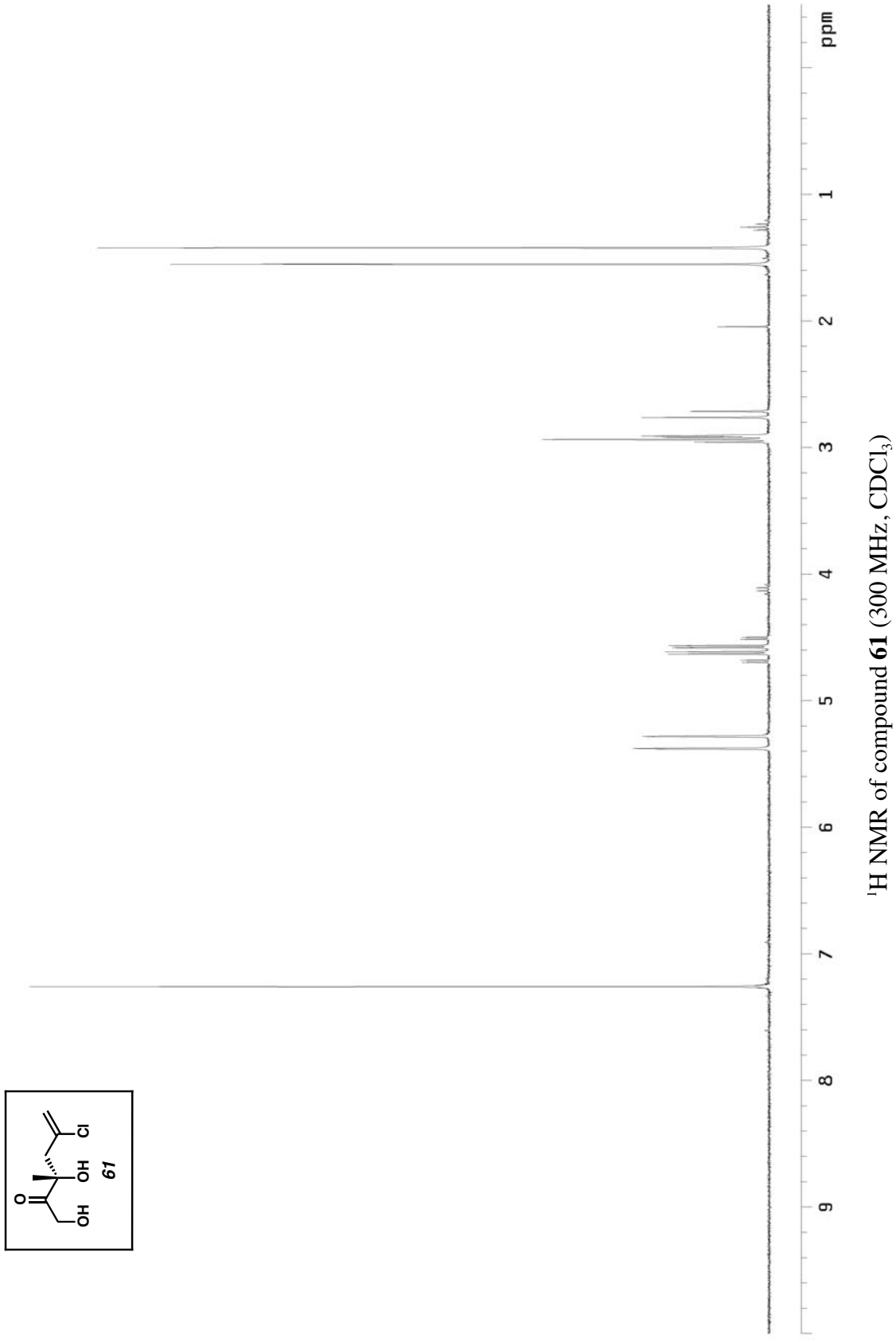
^{13}C NMR of compound **SI135** (75 MHz, $CDCl_3$)



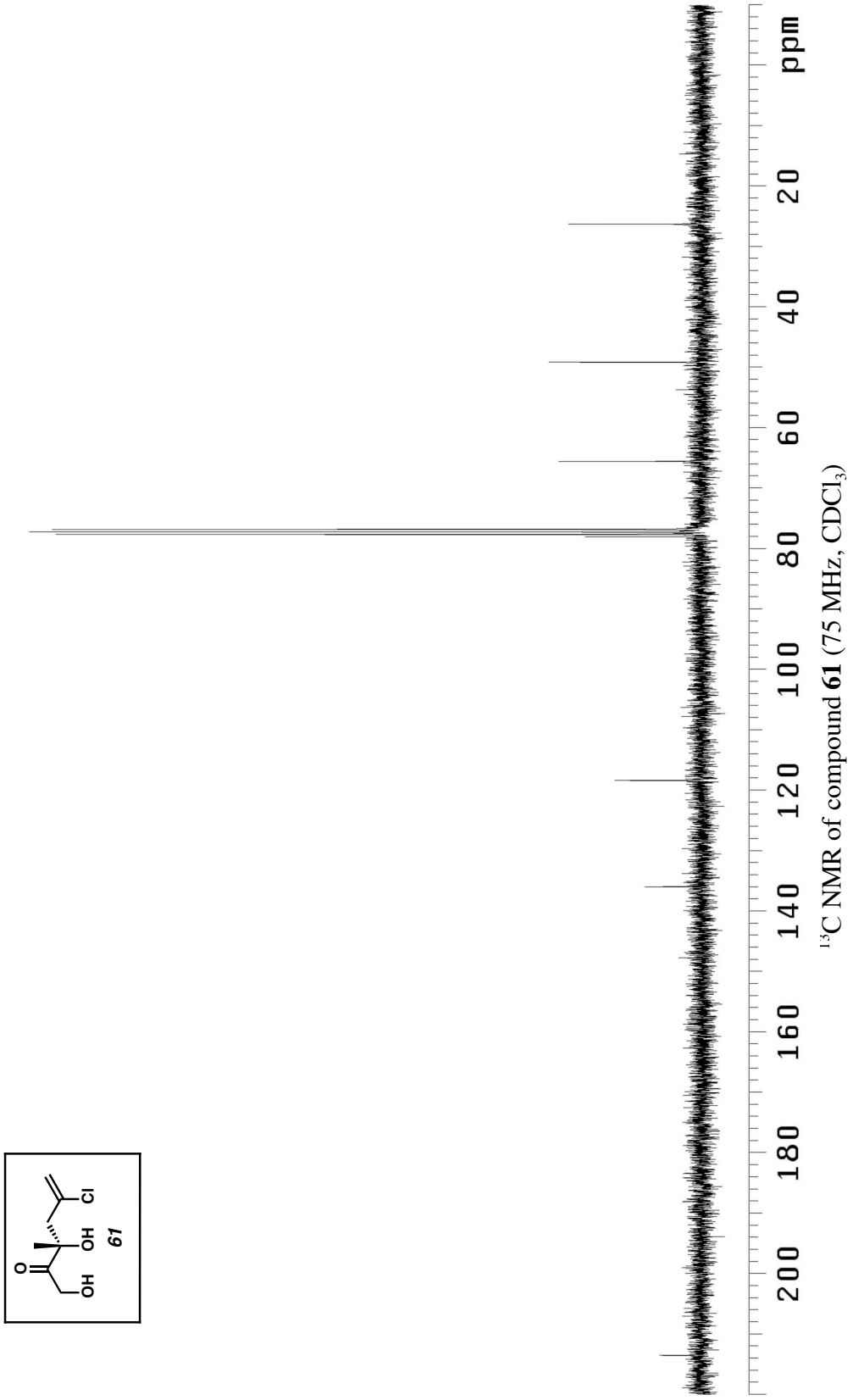
^{1}H NMR of compound **SI136** (300 MHz, $CDCl_3$)



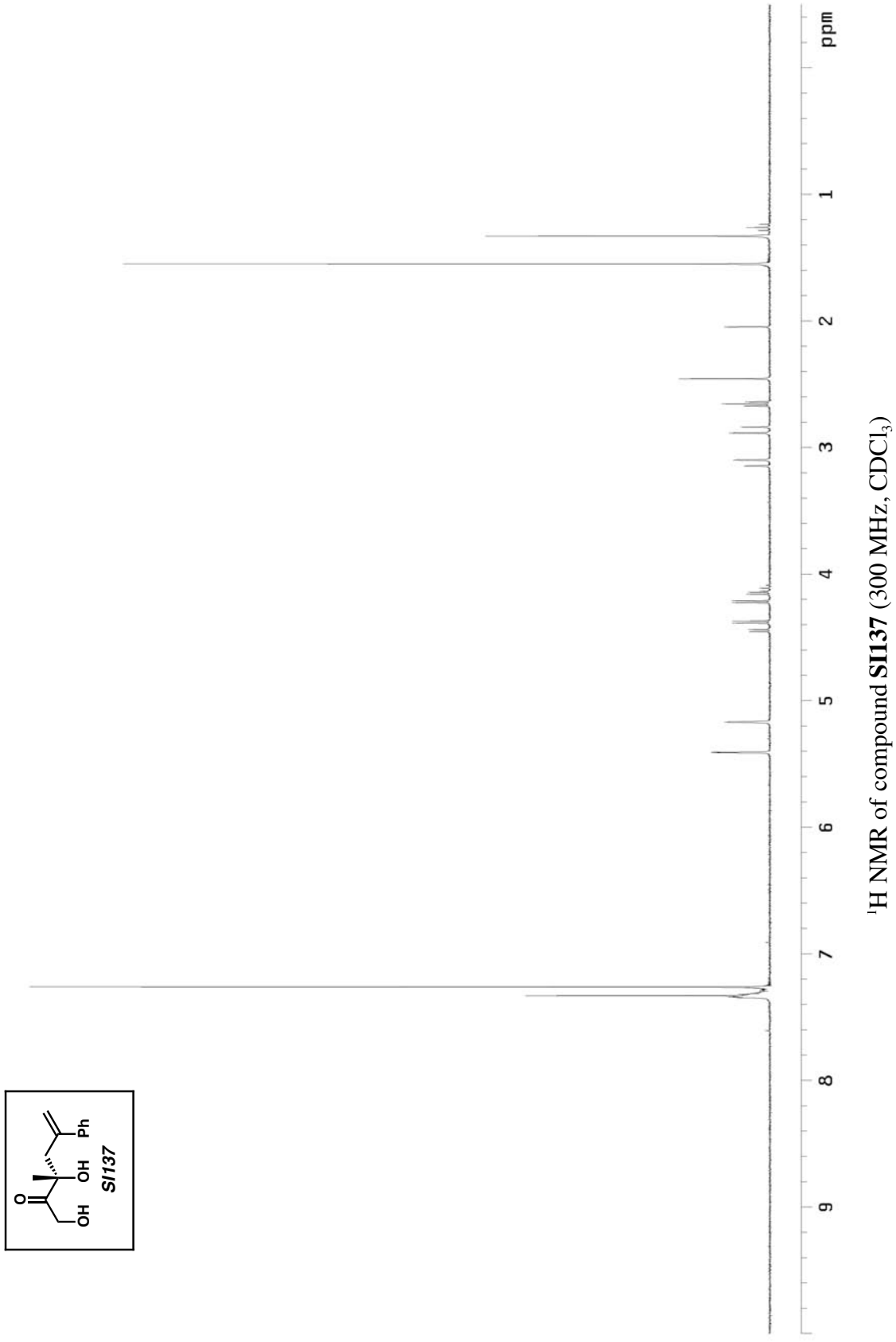
^{13}C NMR of compound **SI136** (75 MHz, $CDCl_3$)



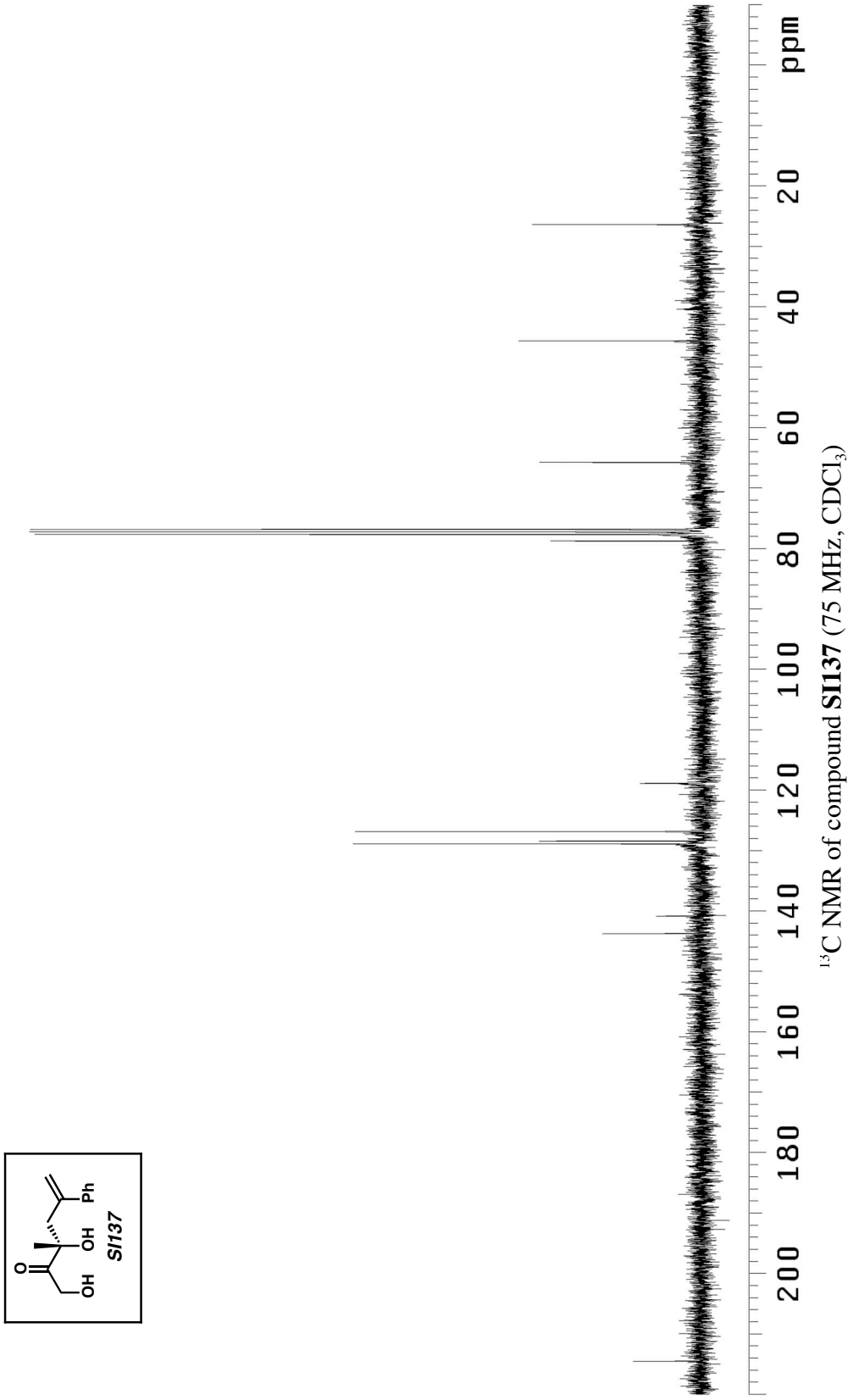
^{1}H NMR of compound **61** (300 MHz, $CDCl_3$)



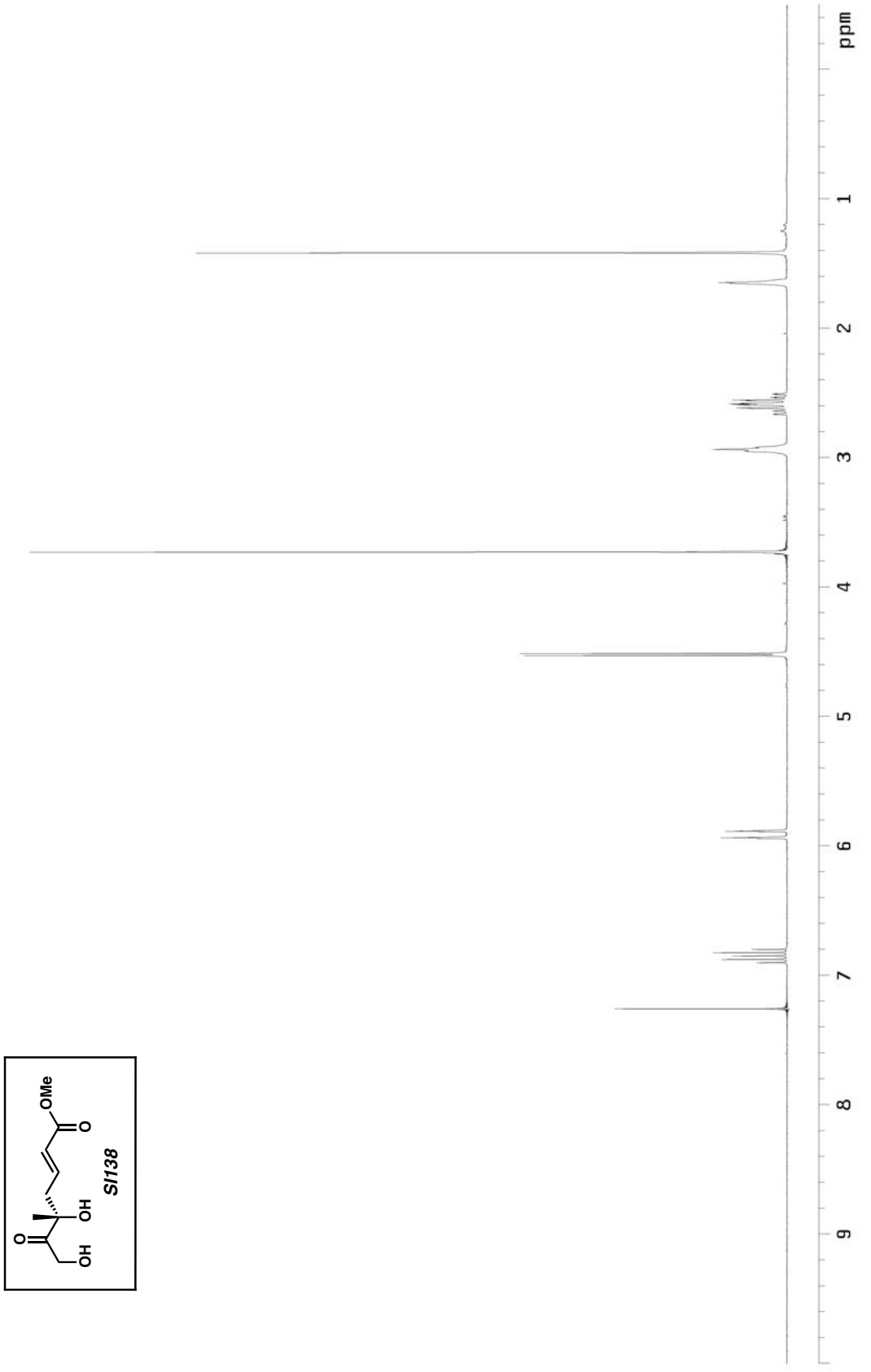
^{13}C NMR of compound **61** (75 MHz, $CDCl_3$)



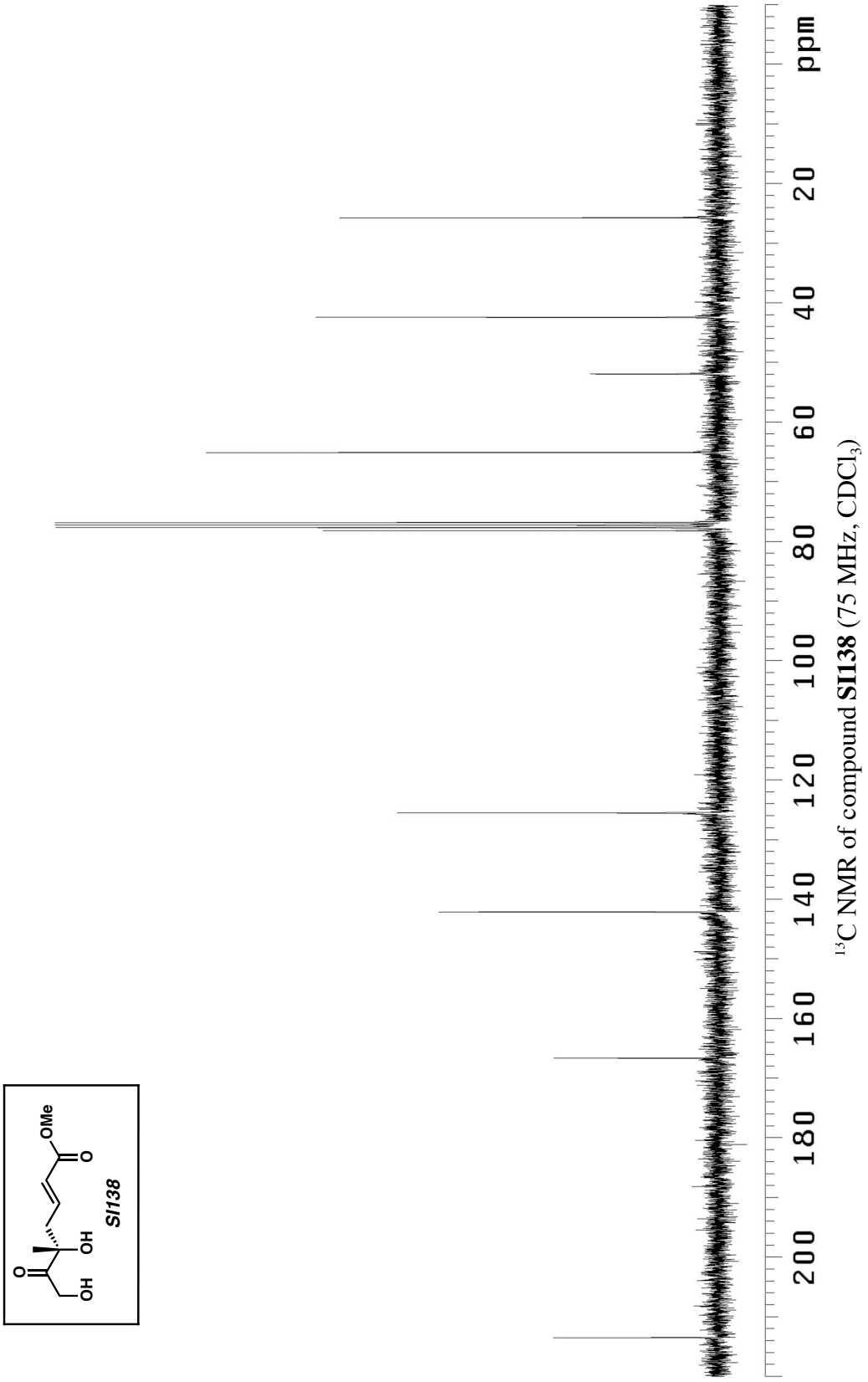
^{1}H NMR of compound **SI137** (300 MHz, $CDCl_3$)



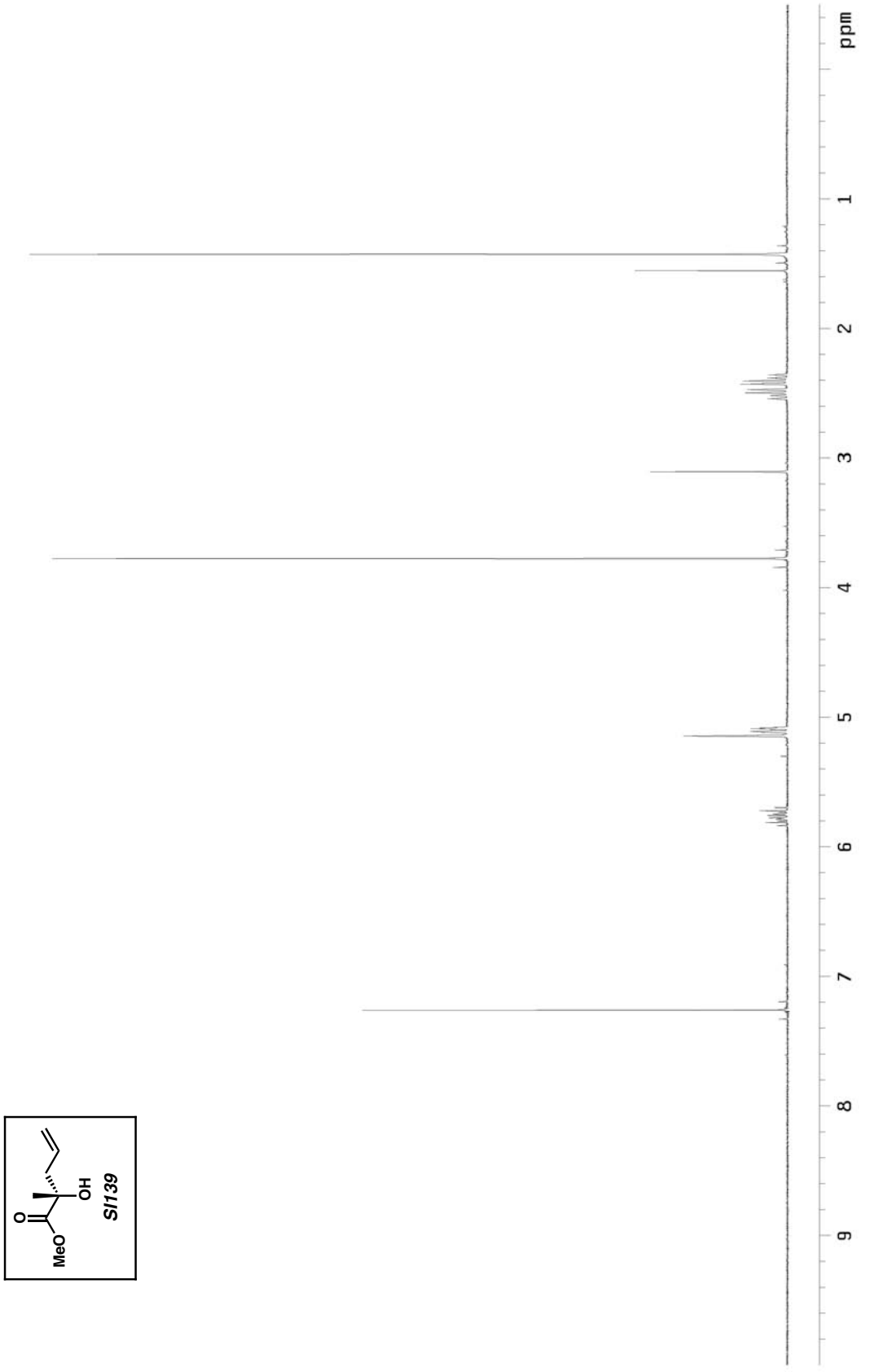
^{13}C NMR of compound **SI137** (75 MHz, $CDCl_3$)



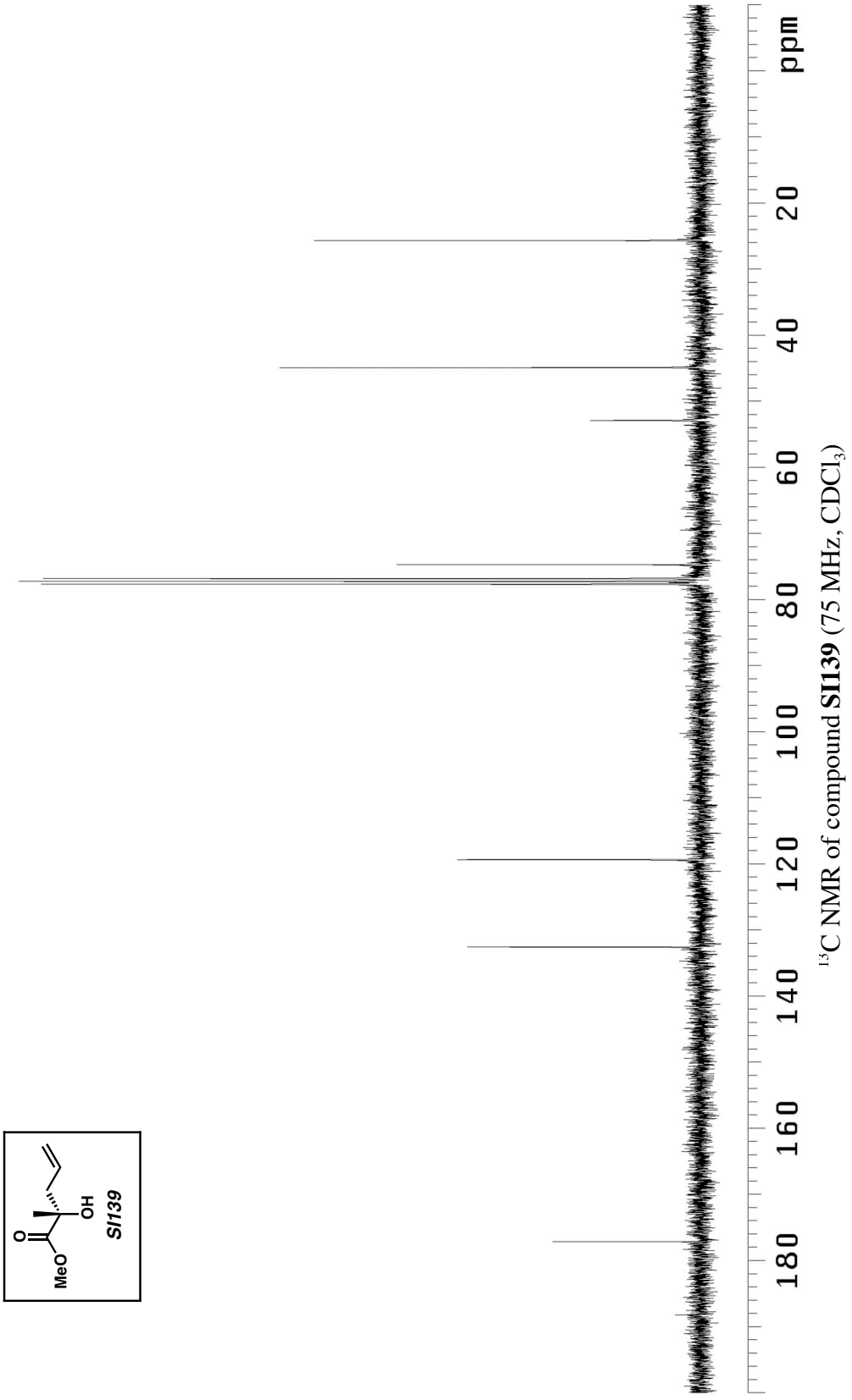
^{1}H NMR of compound **SI138** (300 MHz, $CDCl_3$)



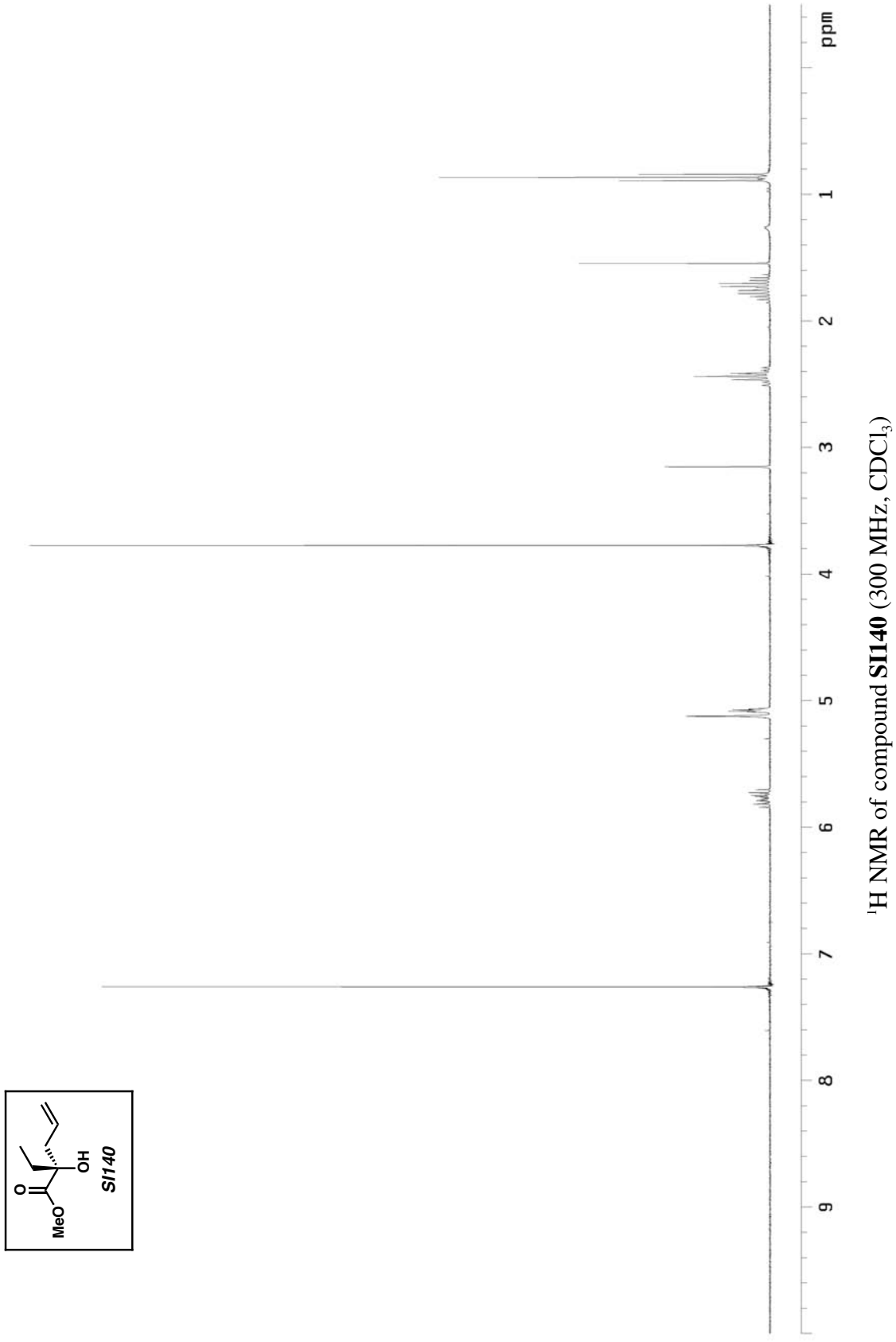
^{13}C NMR of compound **SI138** (75 MHz, $CDCl_3$)



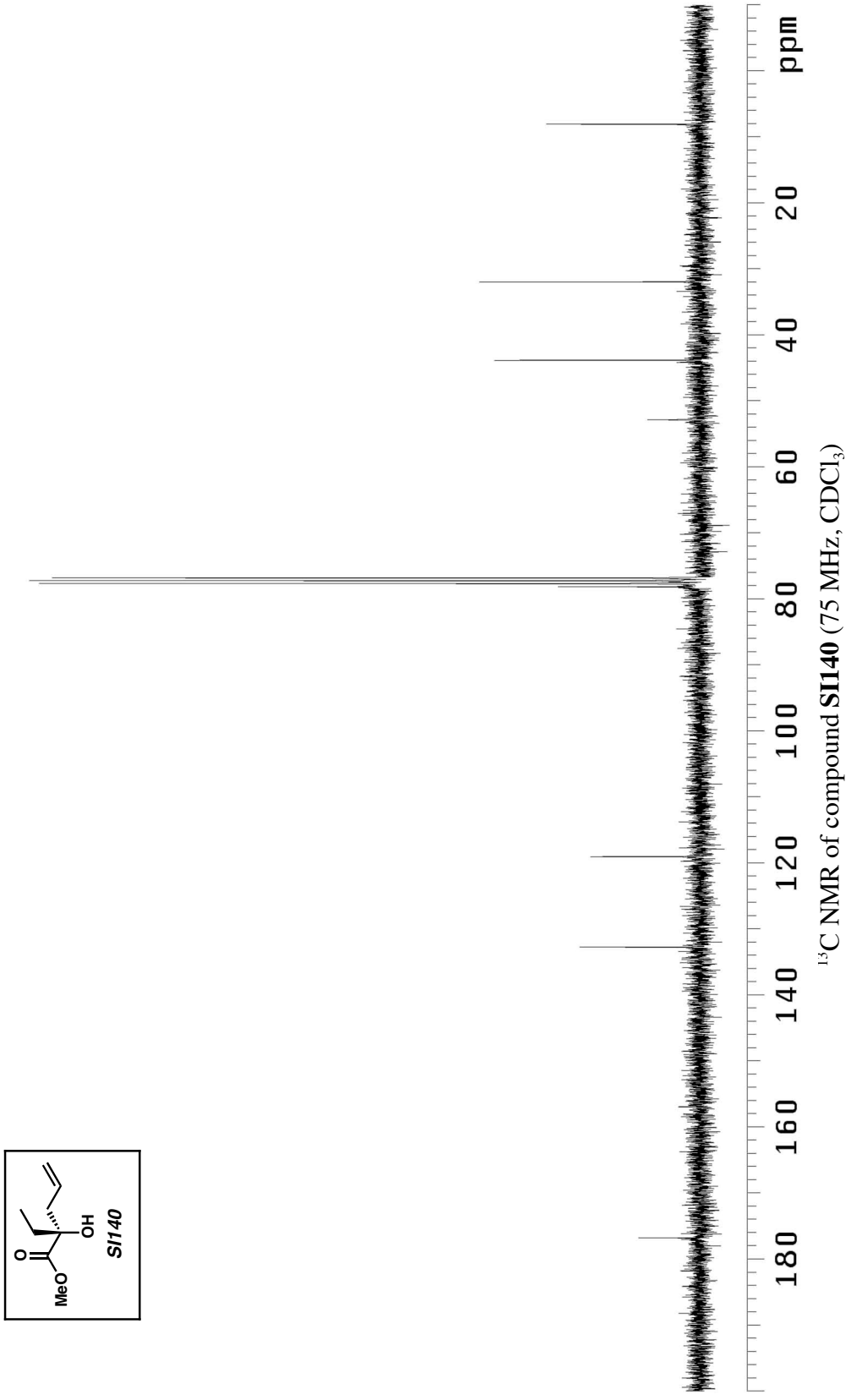
^{1}H NMR of compound **SI139** (300 MHz, $CDCl_3$)



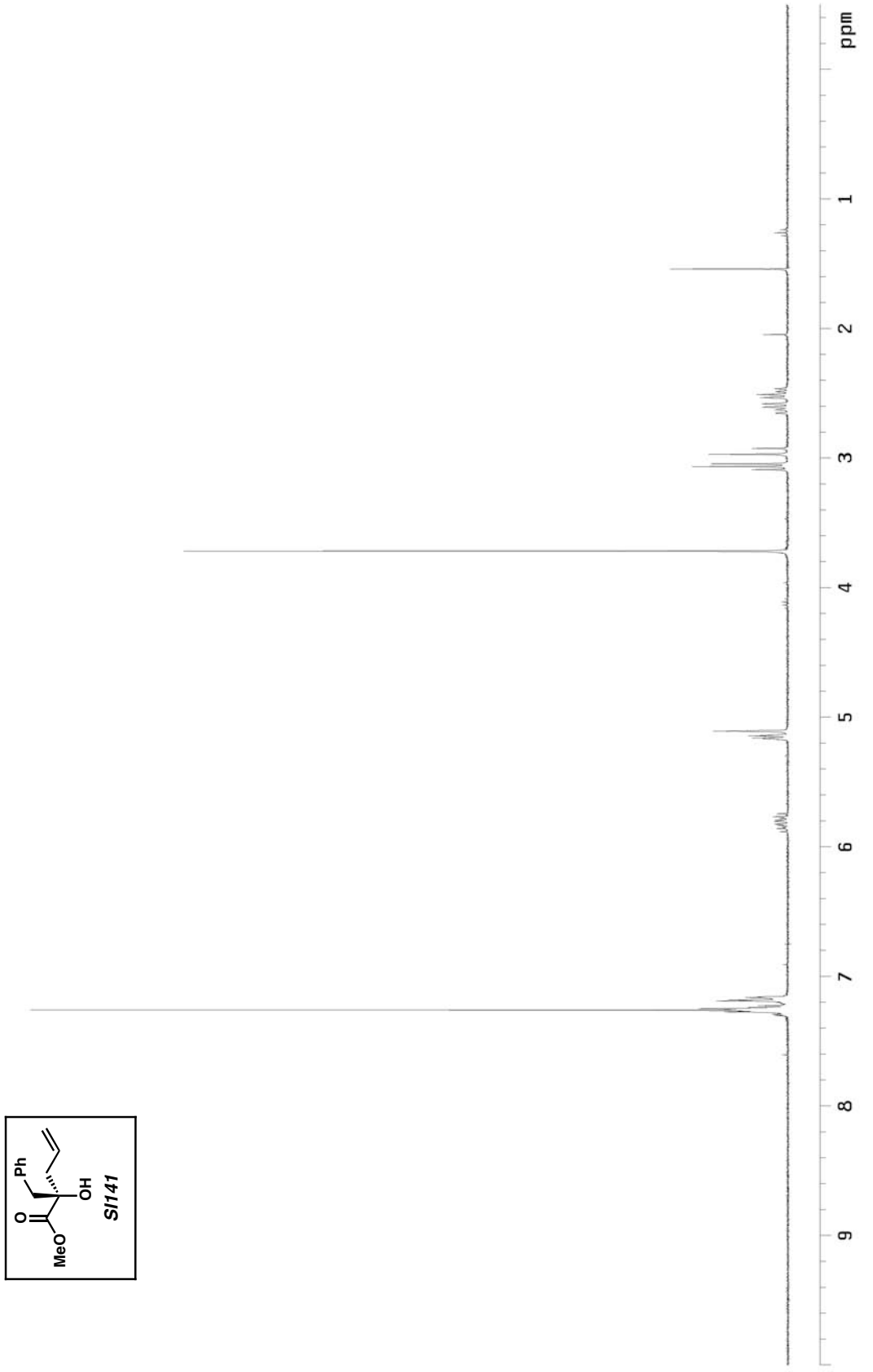
^{13}C NMR of compound **SI139** (75 MHz, $CDCl_3$)



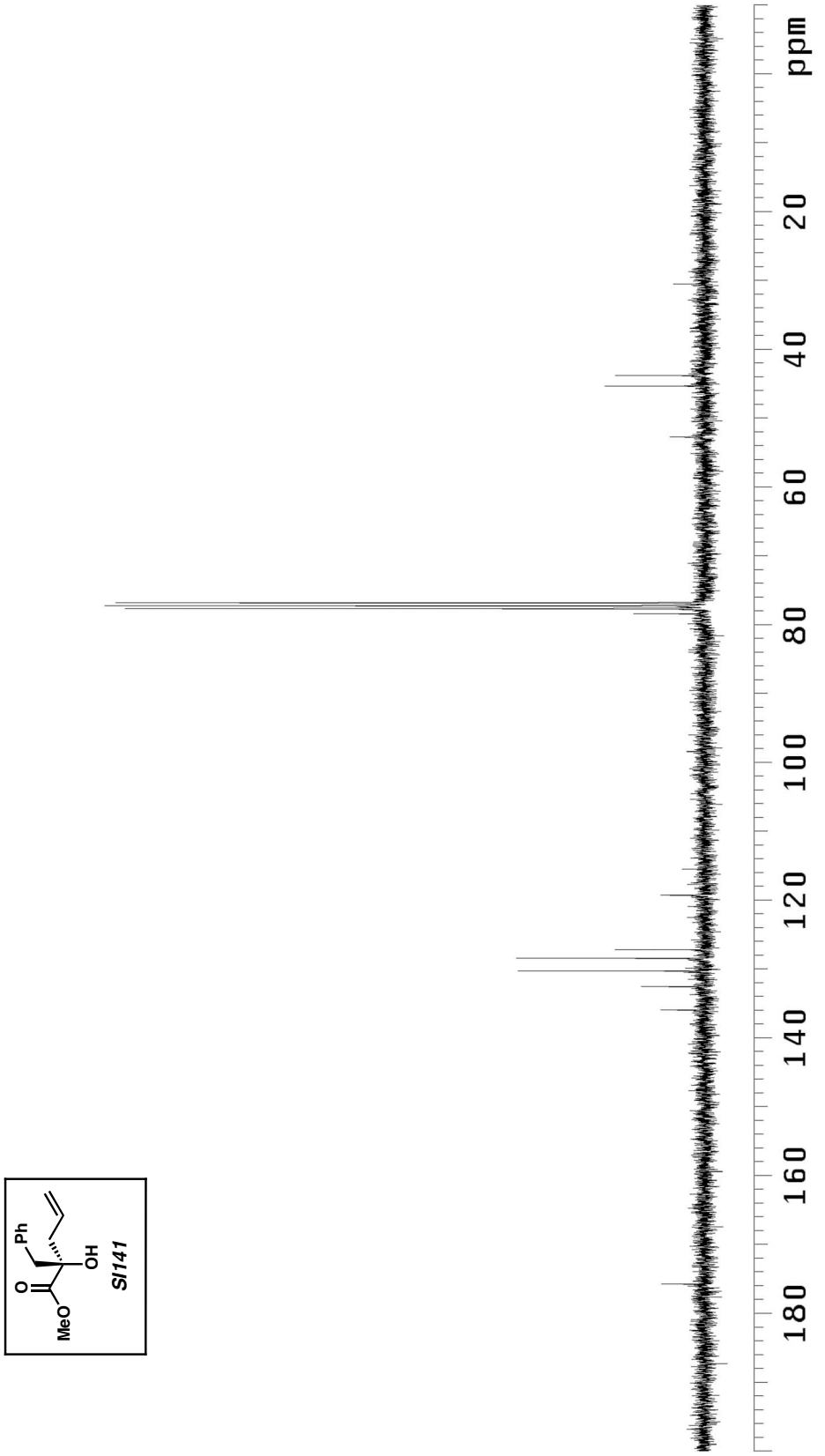
^{1}H NMR of compound **SI140** (300 MHz, $CDCl_3$)



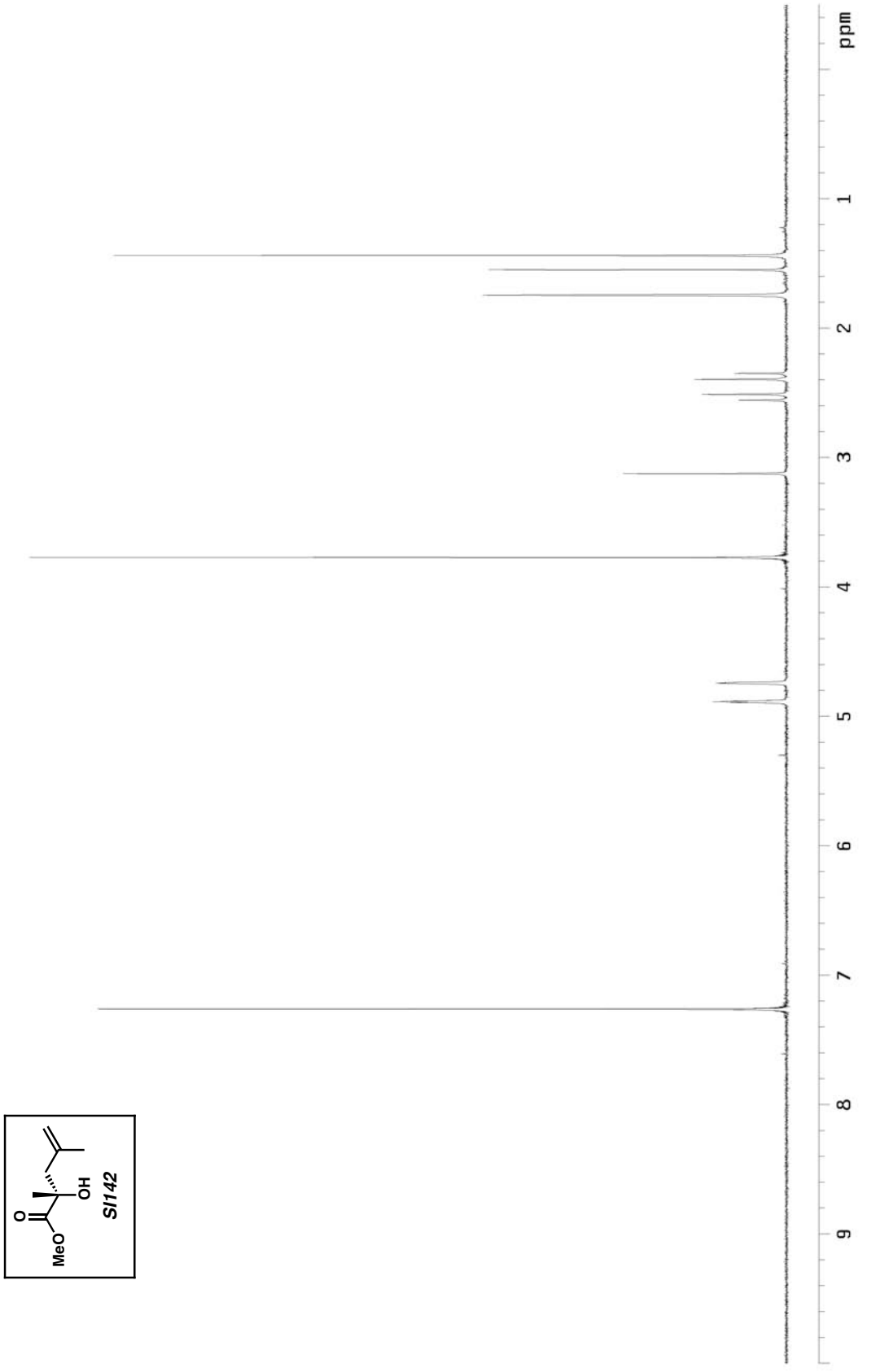
^{13}C NMR of compound **SI140** (75 MHz, $CDCl_3$)



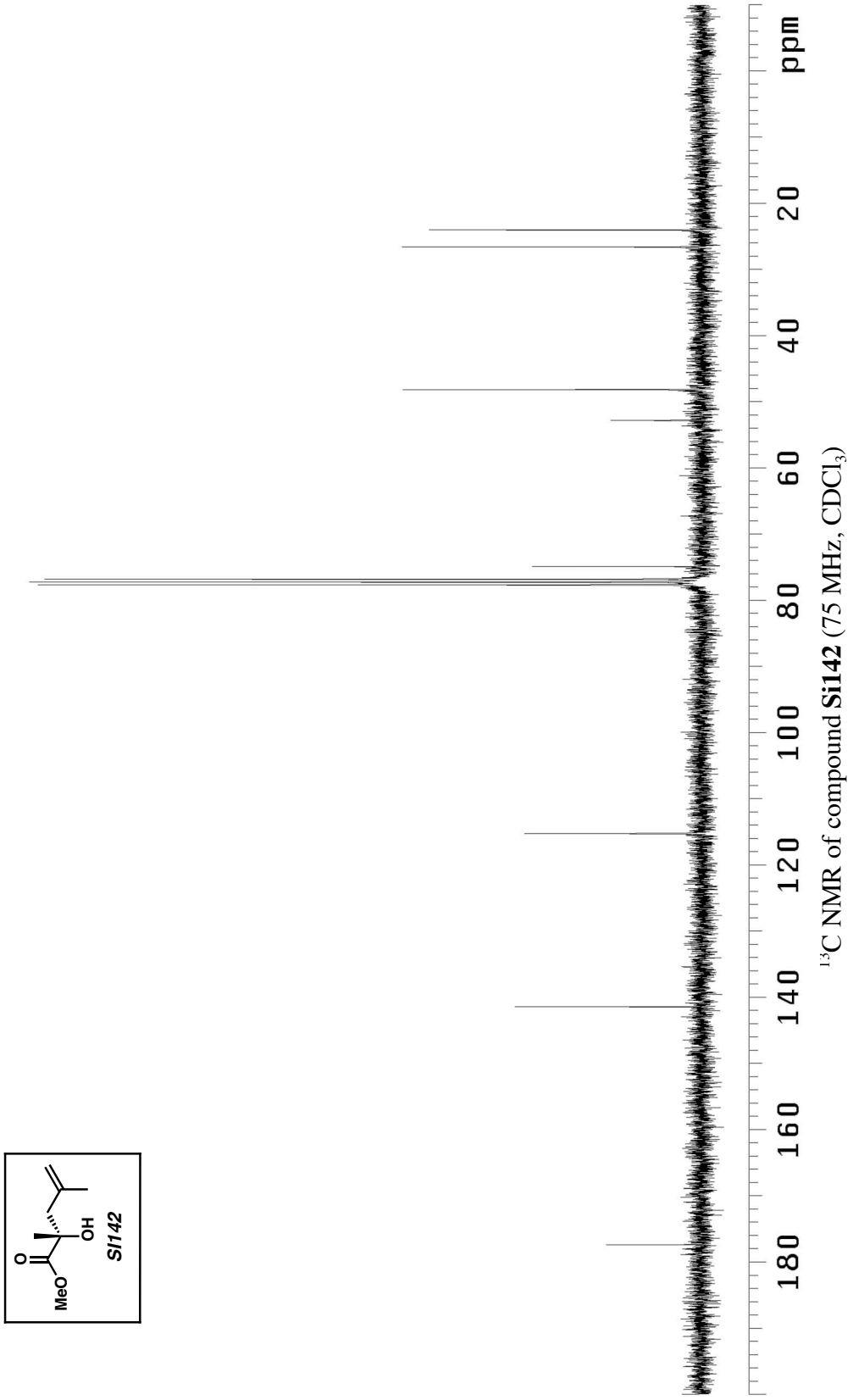
^{1}H NMR of compound **SI141** (300 MHz, $CDCl_3$)



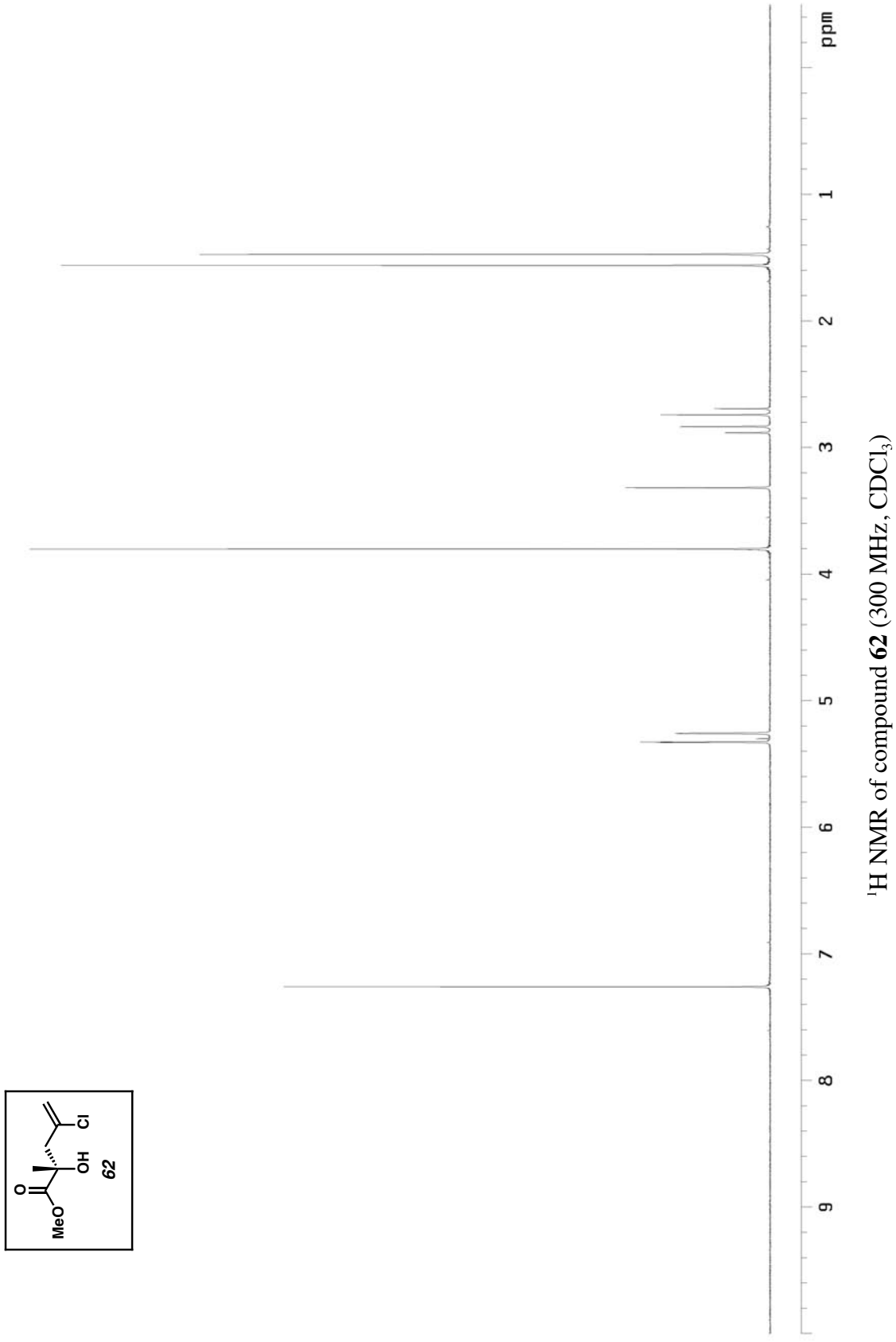
^{13}C NMR of compound **SI141** (75 MHz, $CDCl_3$)



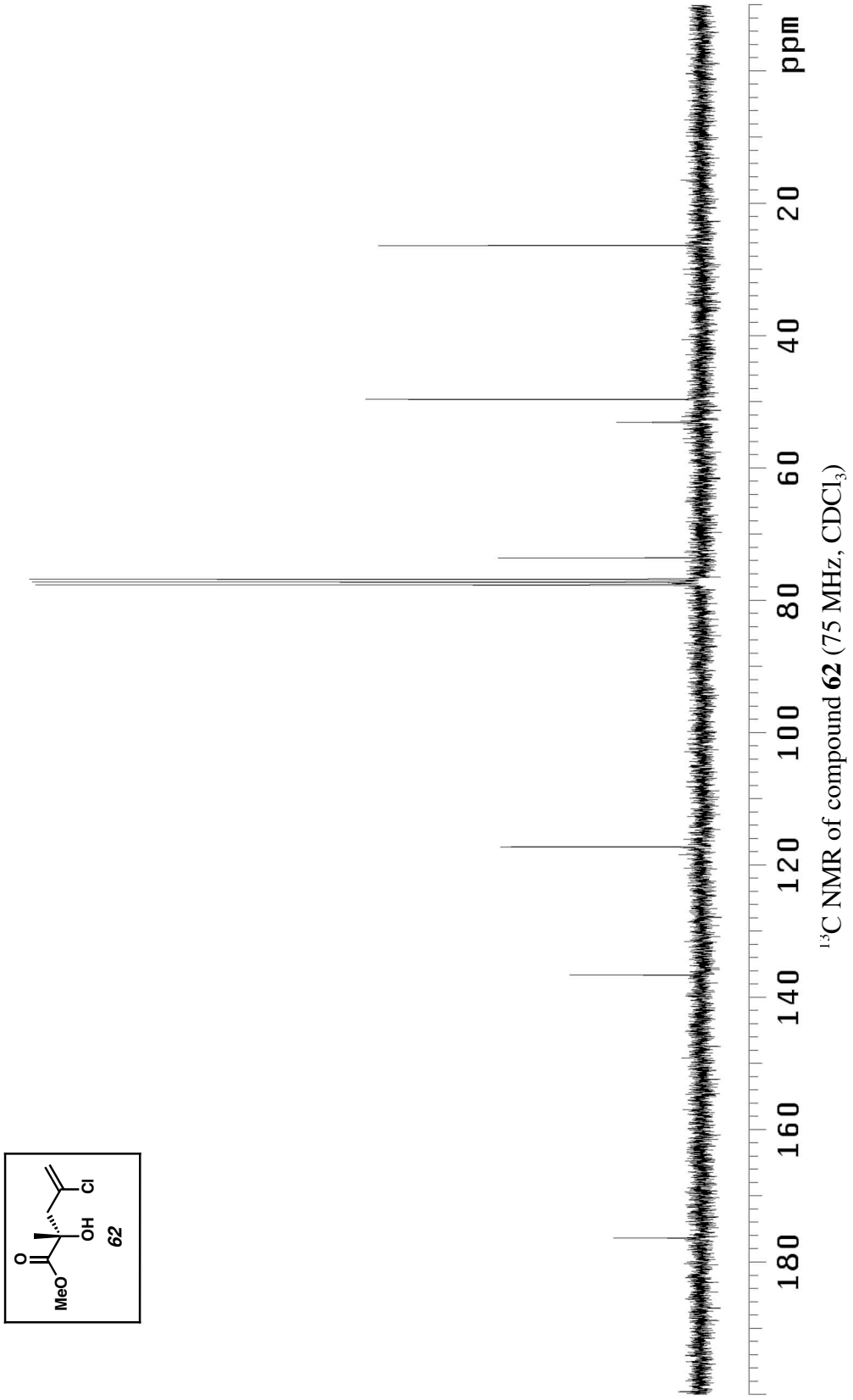
^{1}H NMR of compound **SI142** (300 MHz, $CDCl_3$)



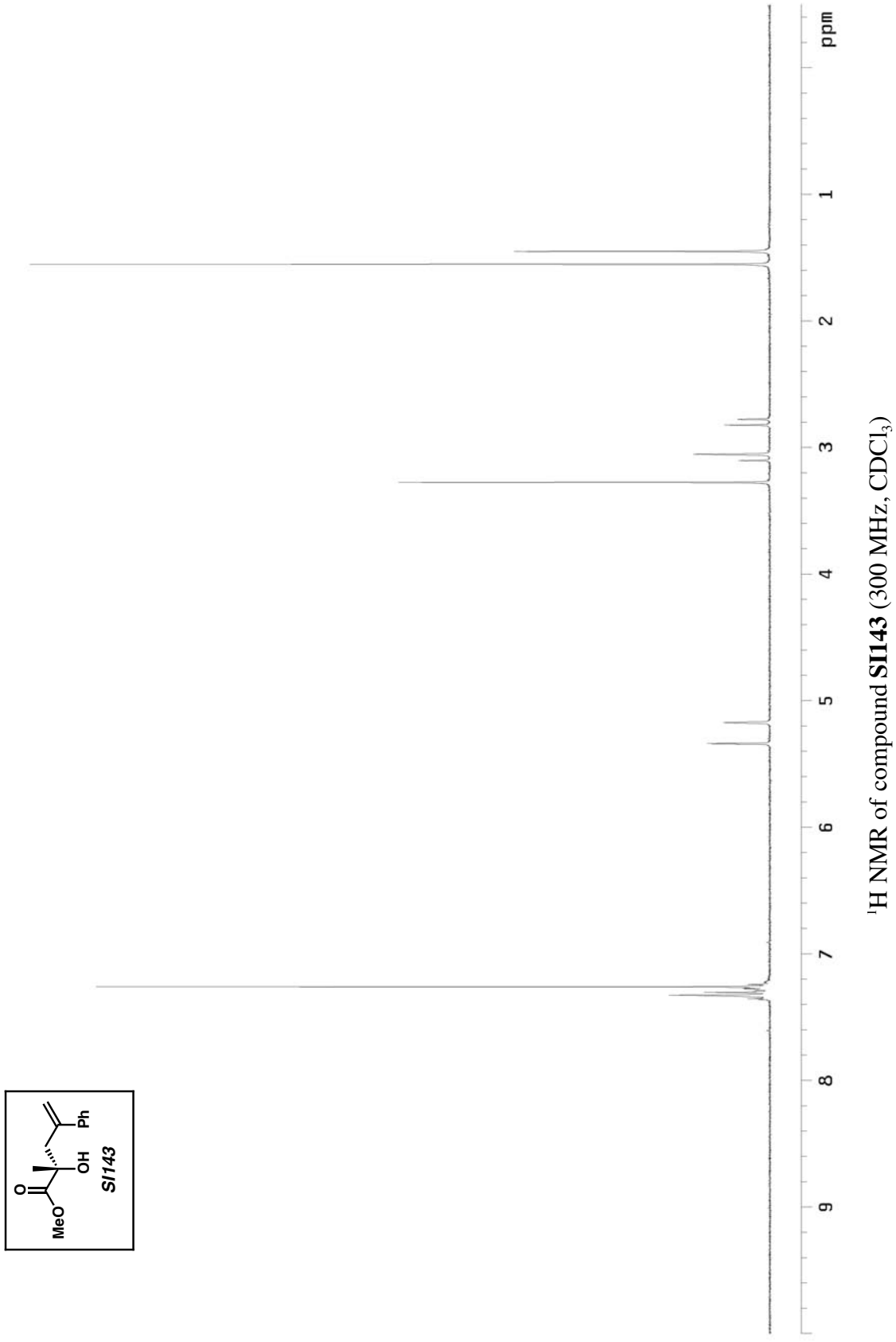
^{13}C NMR of compound **Si142** (75 MHz, $CDCl_3$)



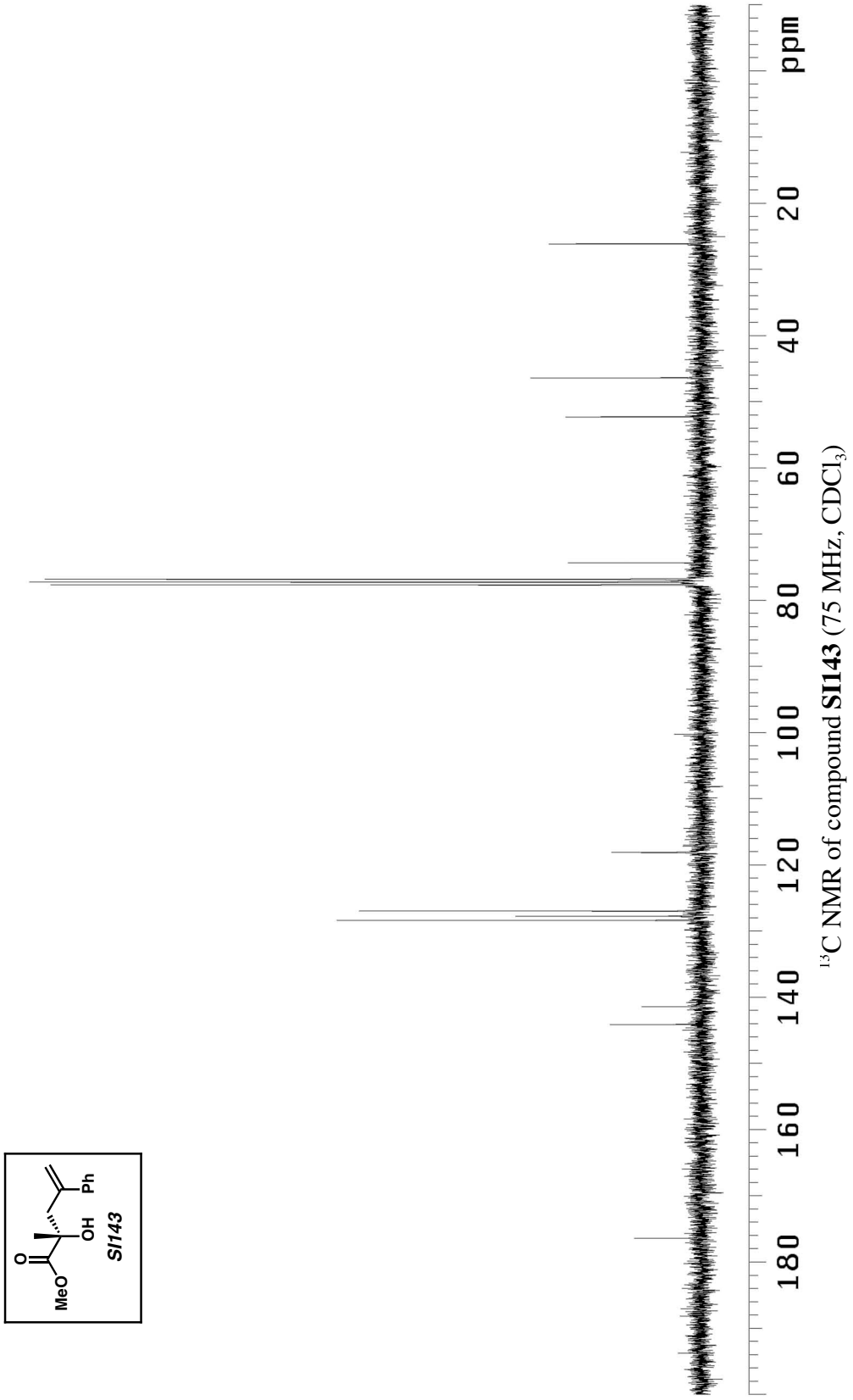
^{1}H NMR of compound **62** (300 MHz, $CDCl_3$)



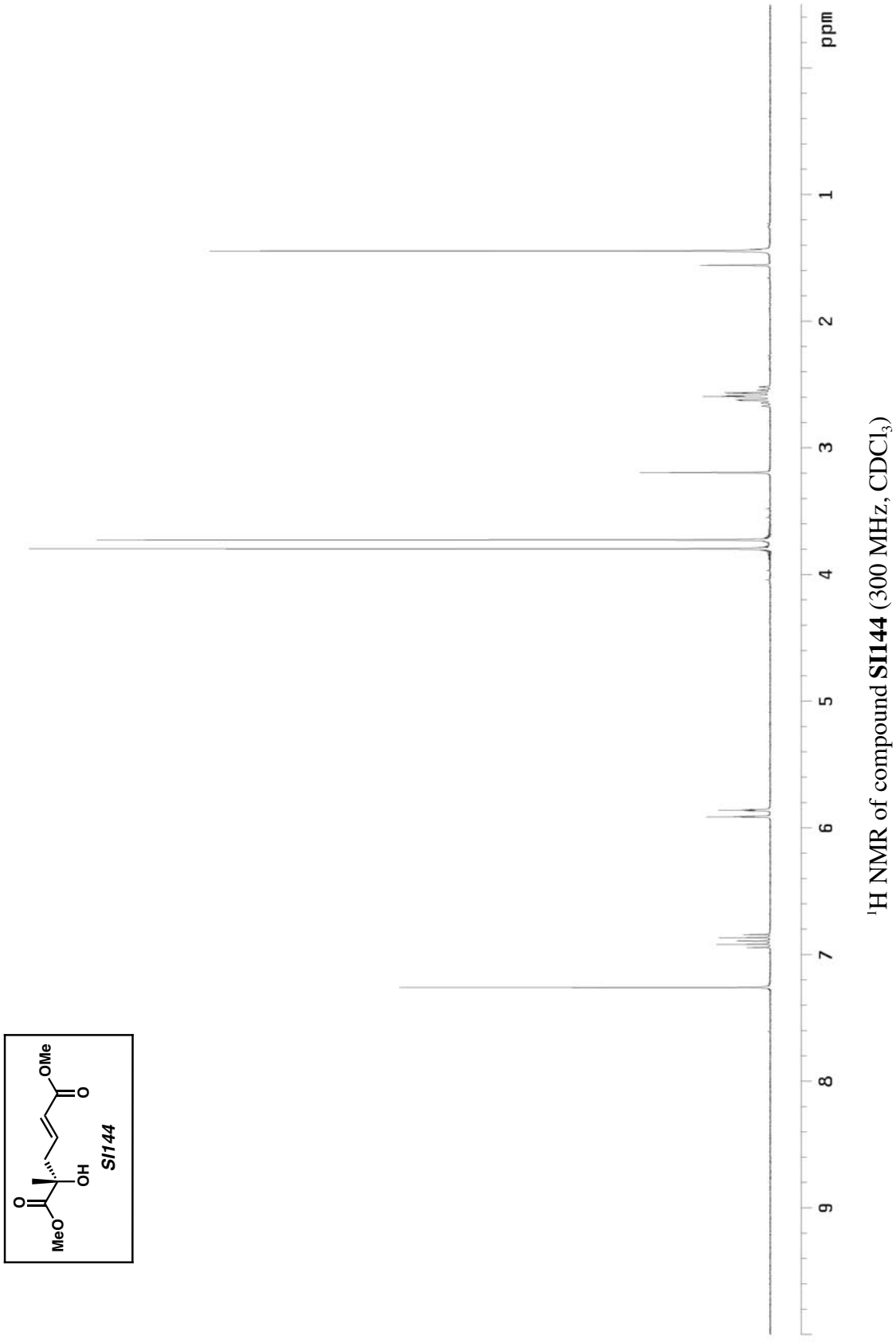
^{13}C NMR of compound **62** (75 MHz, $CDCl_3$)



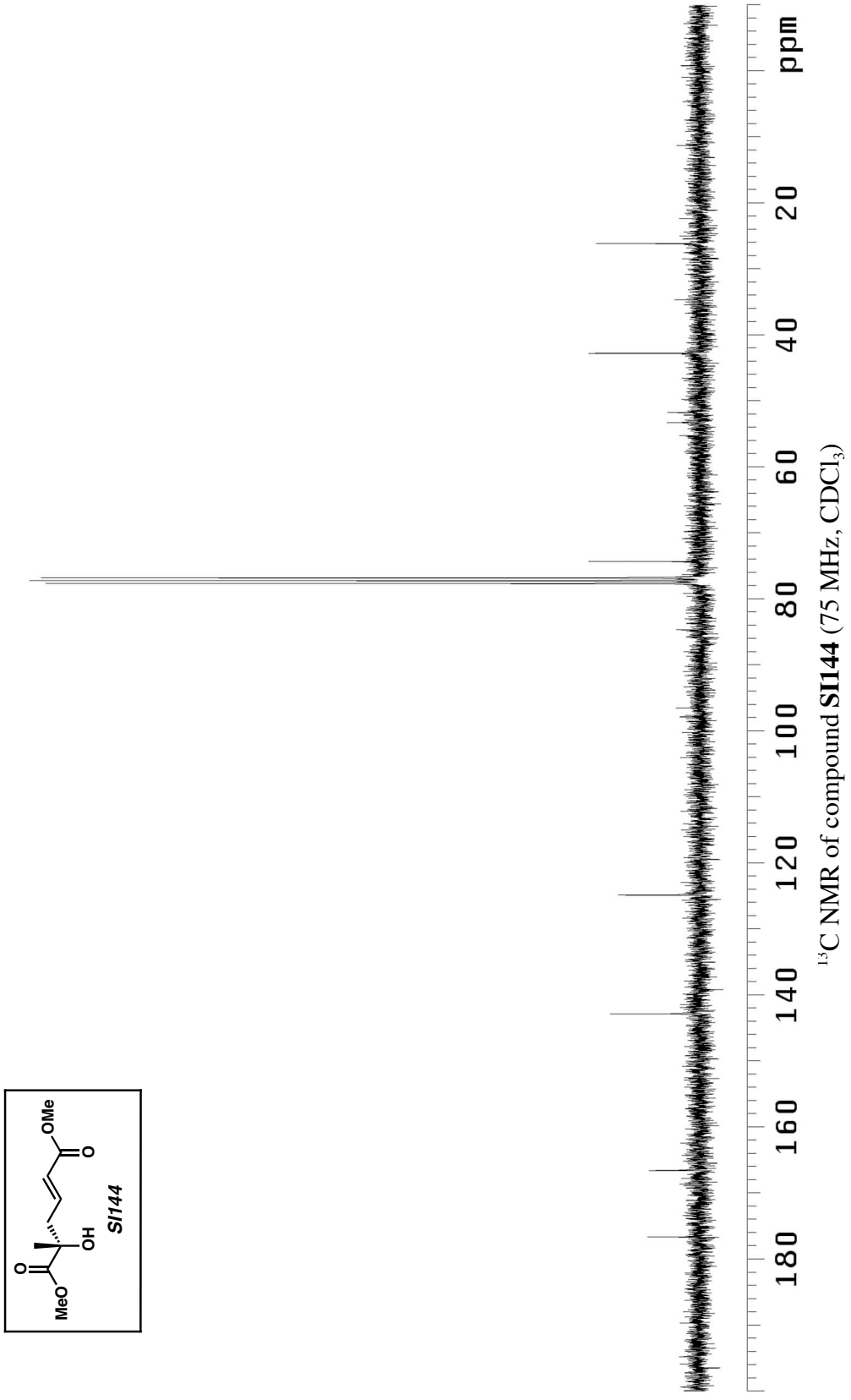
^{1}H NMR of compound **SI143** (300 MHz, $CDCl_3$)



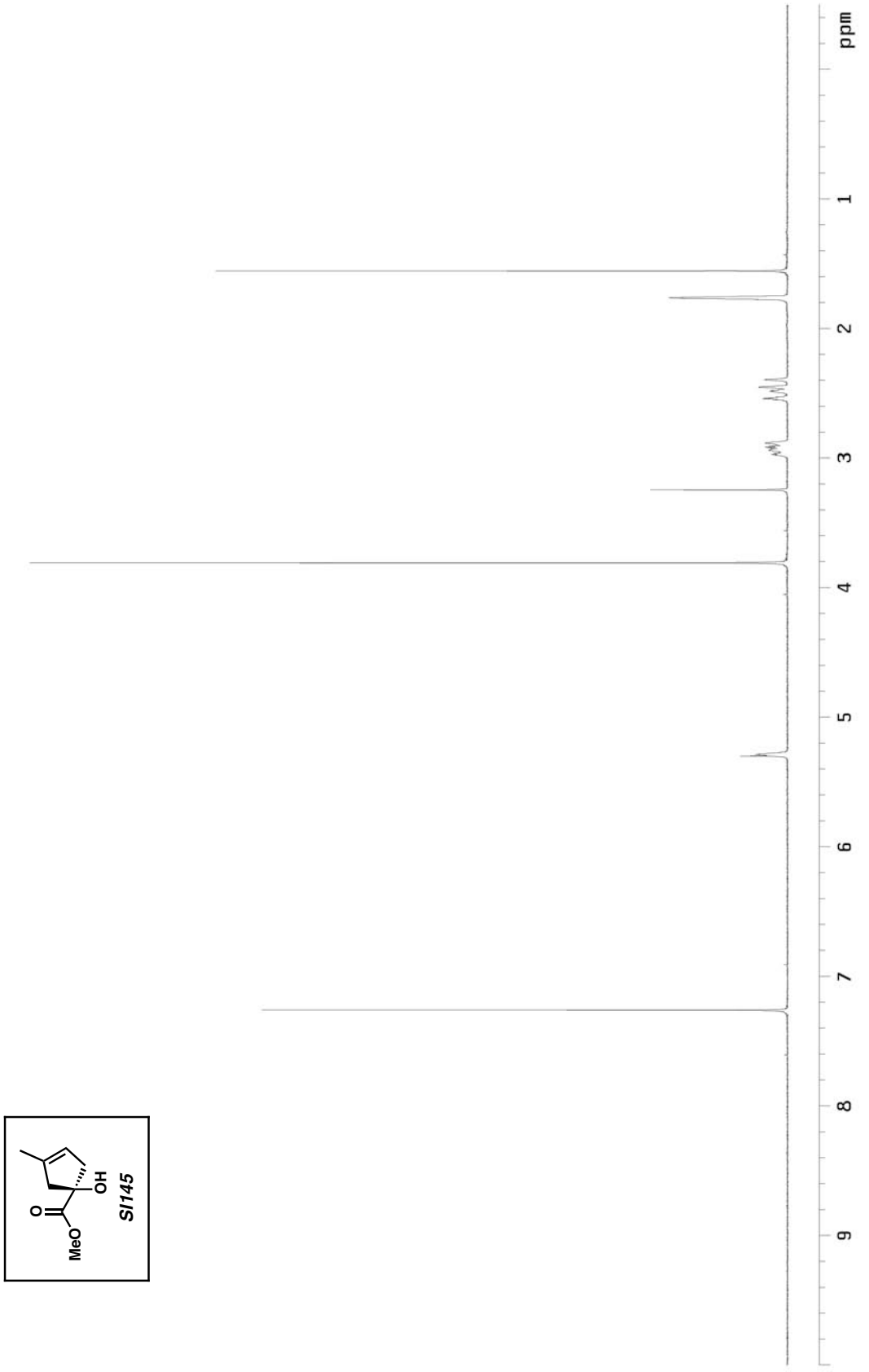
^{13}C NMR of compound **SI143** (75 MHz, $CDCl_3$)



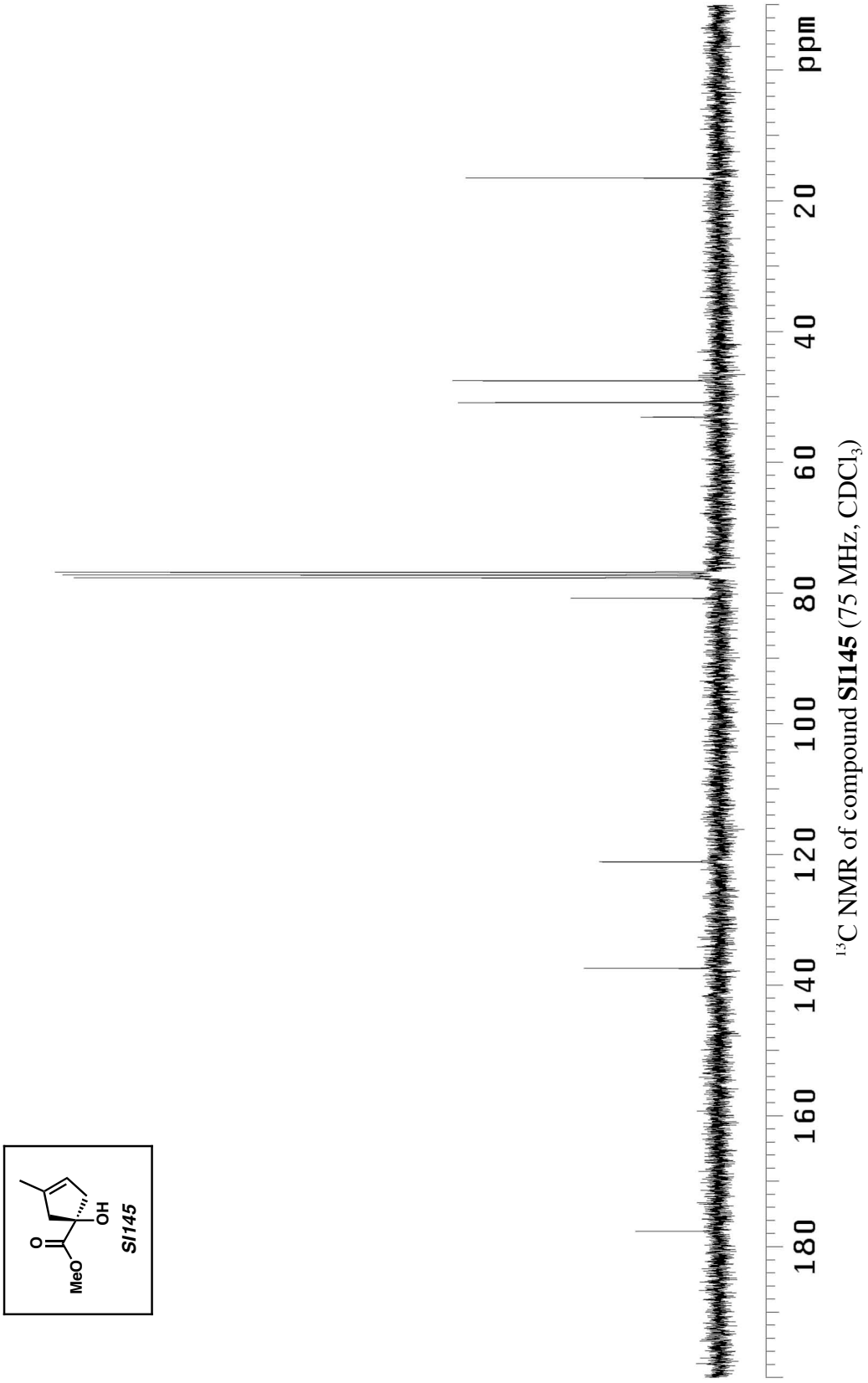
^{1}H NMR of compound **SI144** (300 MHz, $CDCl_3$)



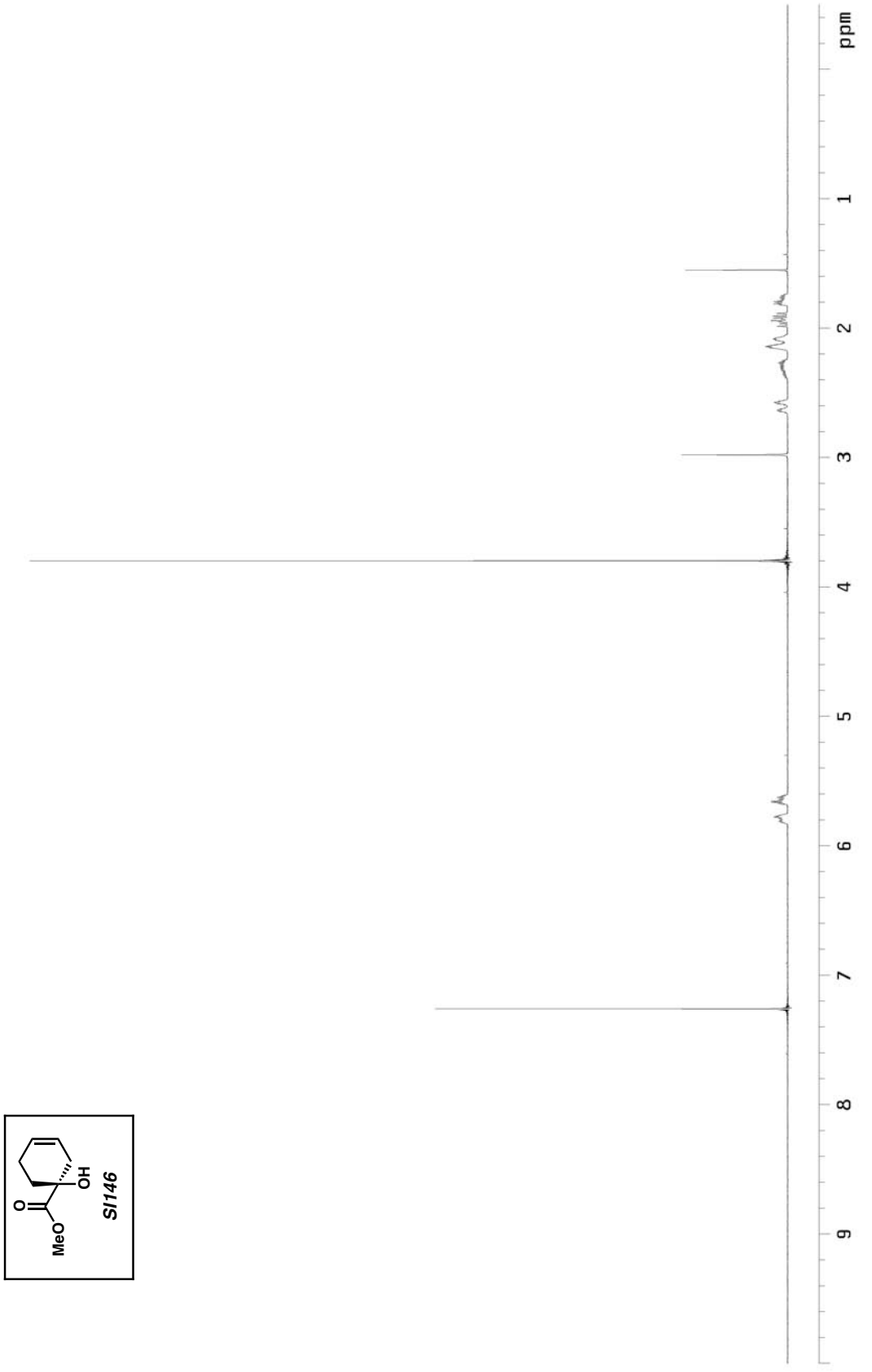
^{13}C NMR of compound **SI144** (75 MHz, $CDCl_3$)



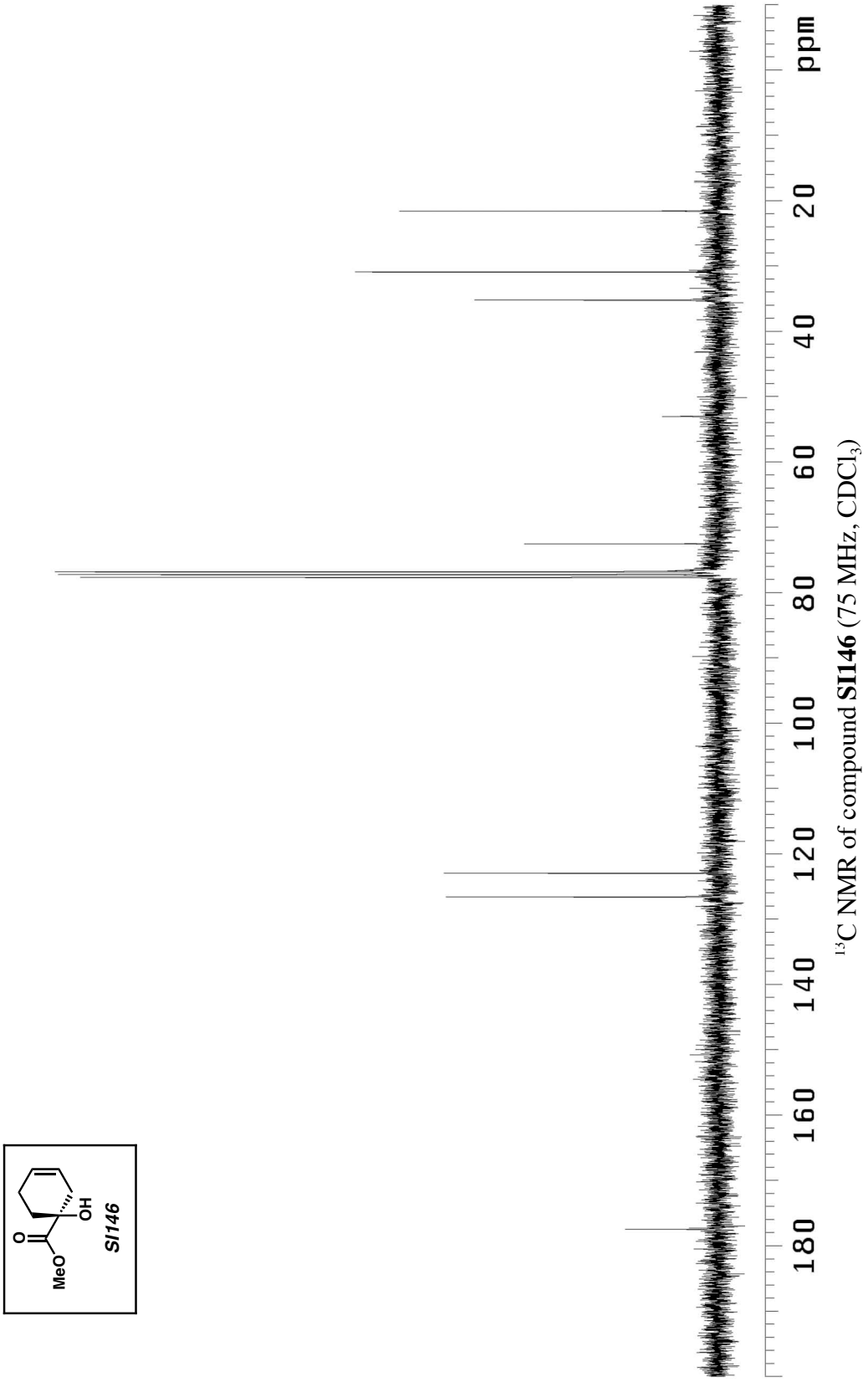
^{1}H NMR of compound **SI145** (300 MHz, $CDCl_3$)



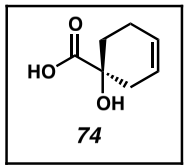
^{13}C NMR of compound **SI145** (75 MHz, $CDCl_3$)



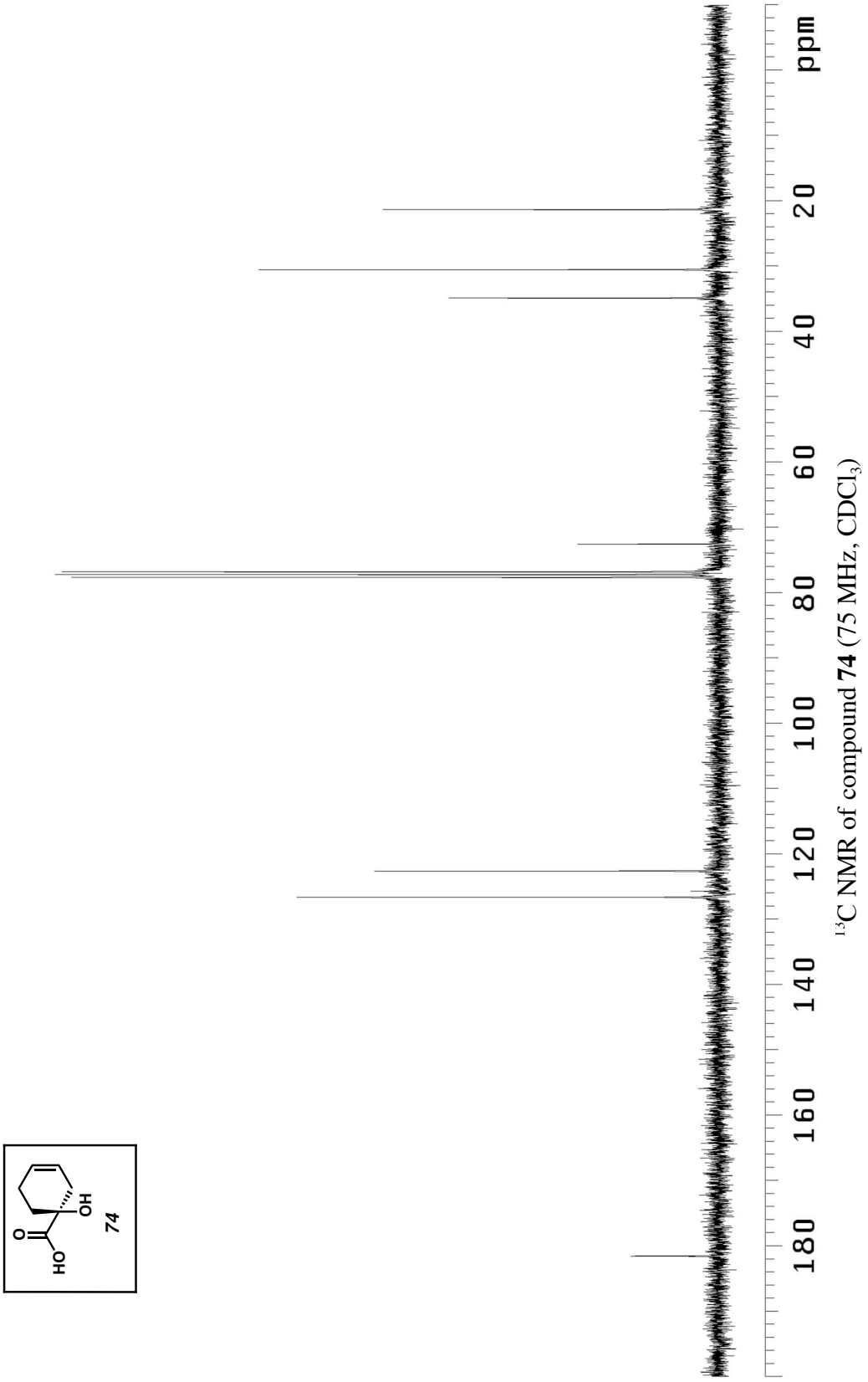
^{1}H NMR of compound **SI146** (300 MHz, $CDCl_3$)



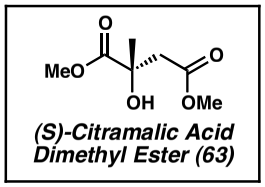
^{13}C NMR of compound **SI146** (75 MHz, $CDCl_3$)



^{1}H NMR of compound **74** (300 MHz, $CDCl_3$)

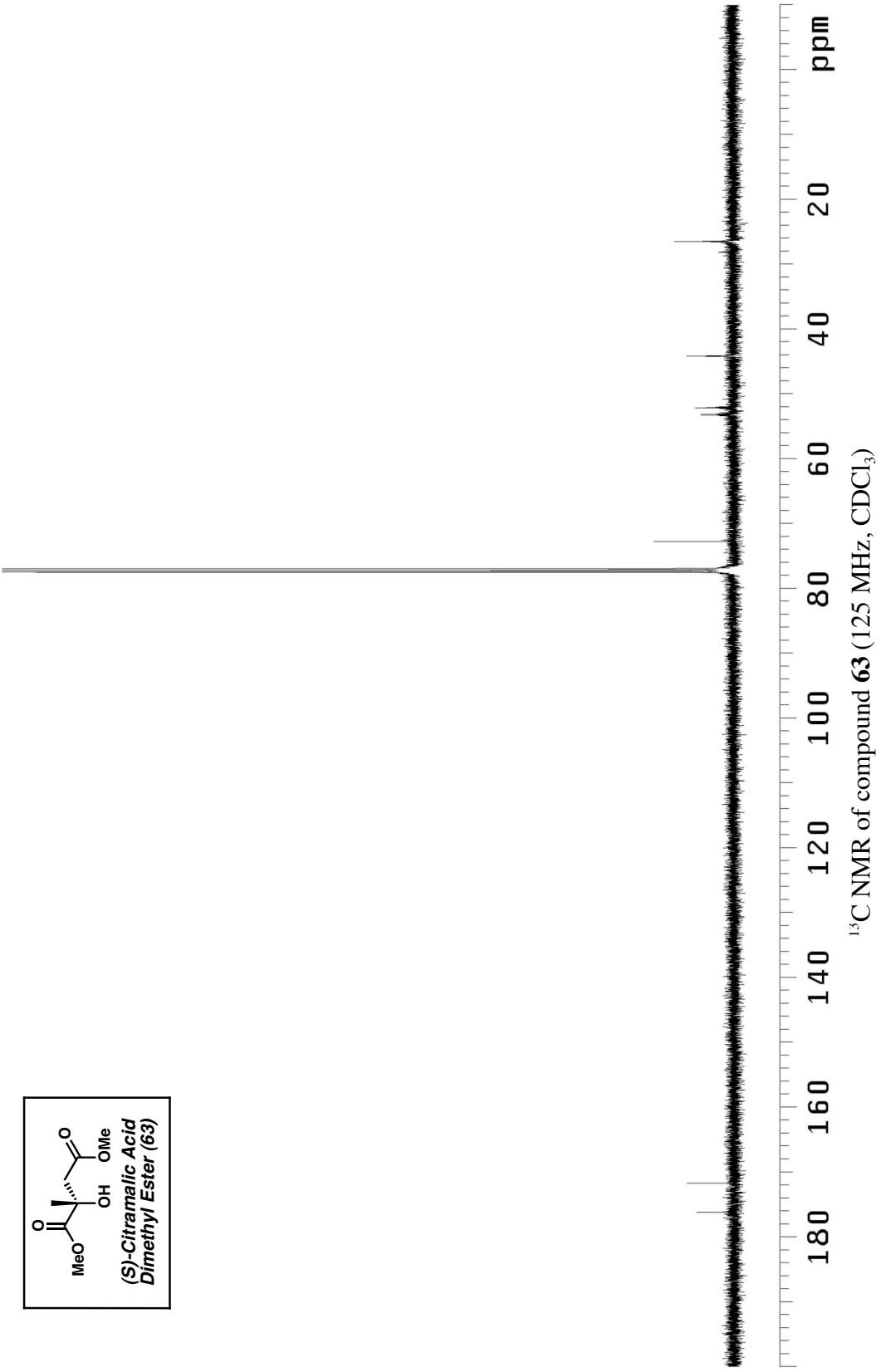


^{13}C NMR of compound **74** (75 MHz, $CDCl_3$)

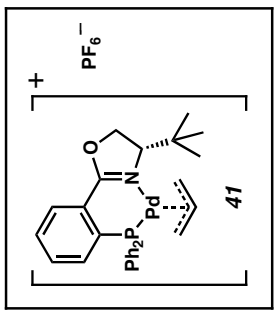


(S)-Citramalic Acid Dimethyl Ester (63)

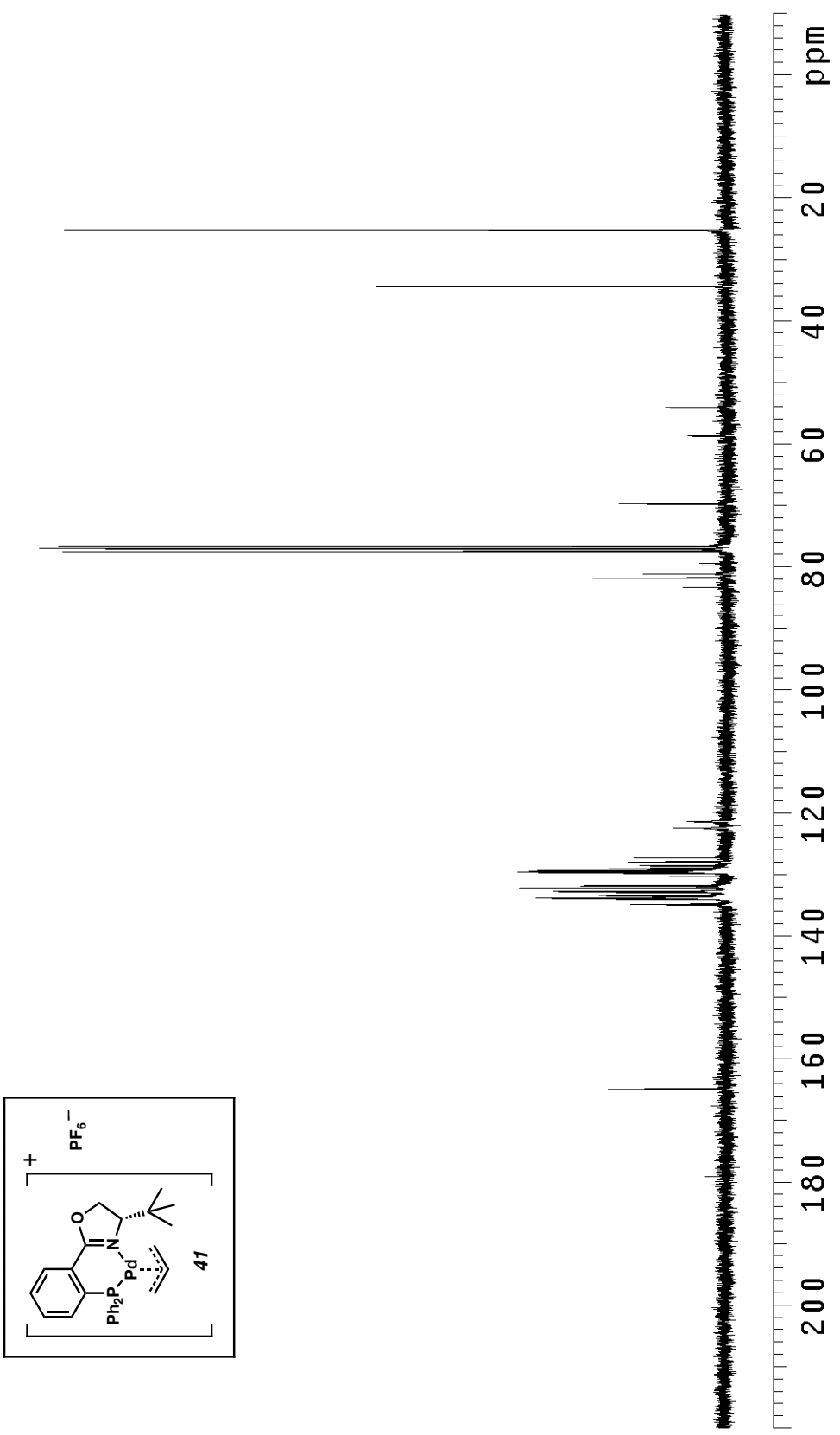
^{1}H NMR of compound **63** (500 MHz, $CDCl_3$)



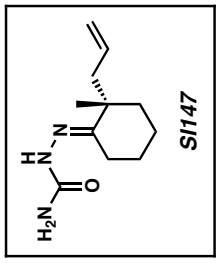
^{13}C NMR of compound **63** (125 MHz, $CDCl_3$)



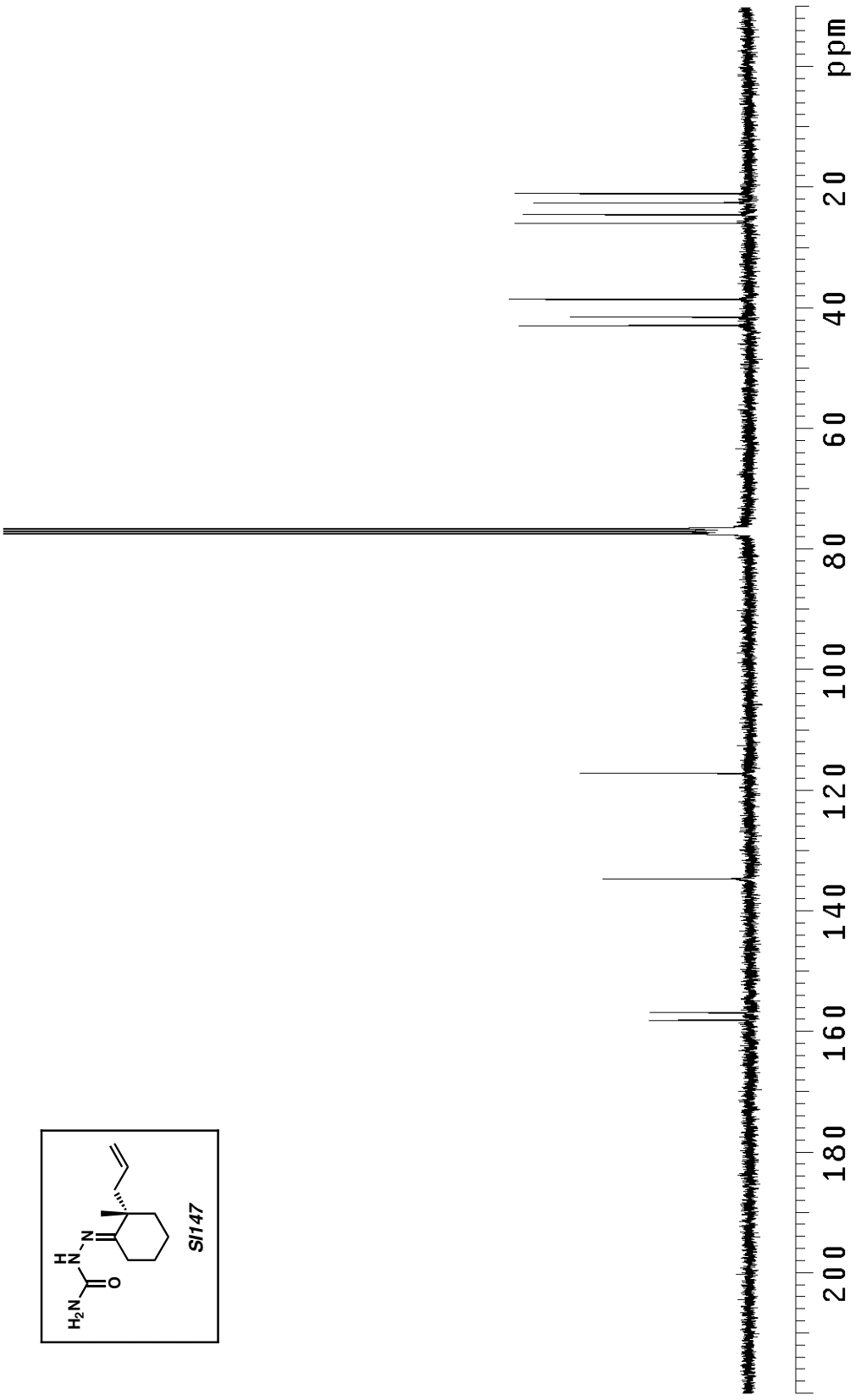
^{1}H NMR of compound **41** (300 MHz, $CDCl_3$)



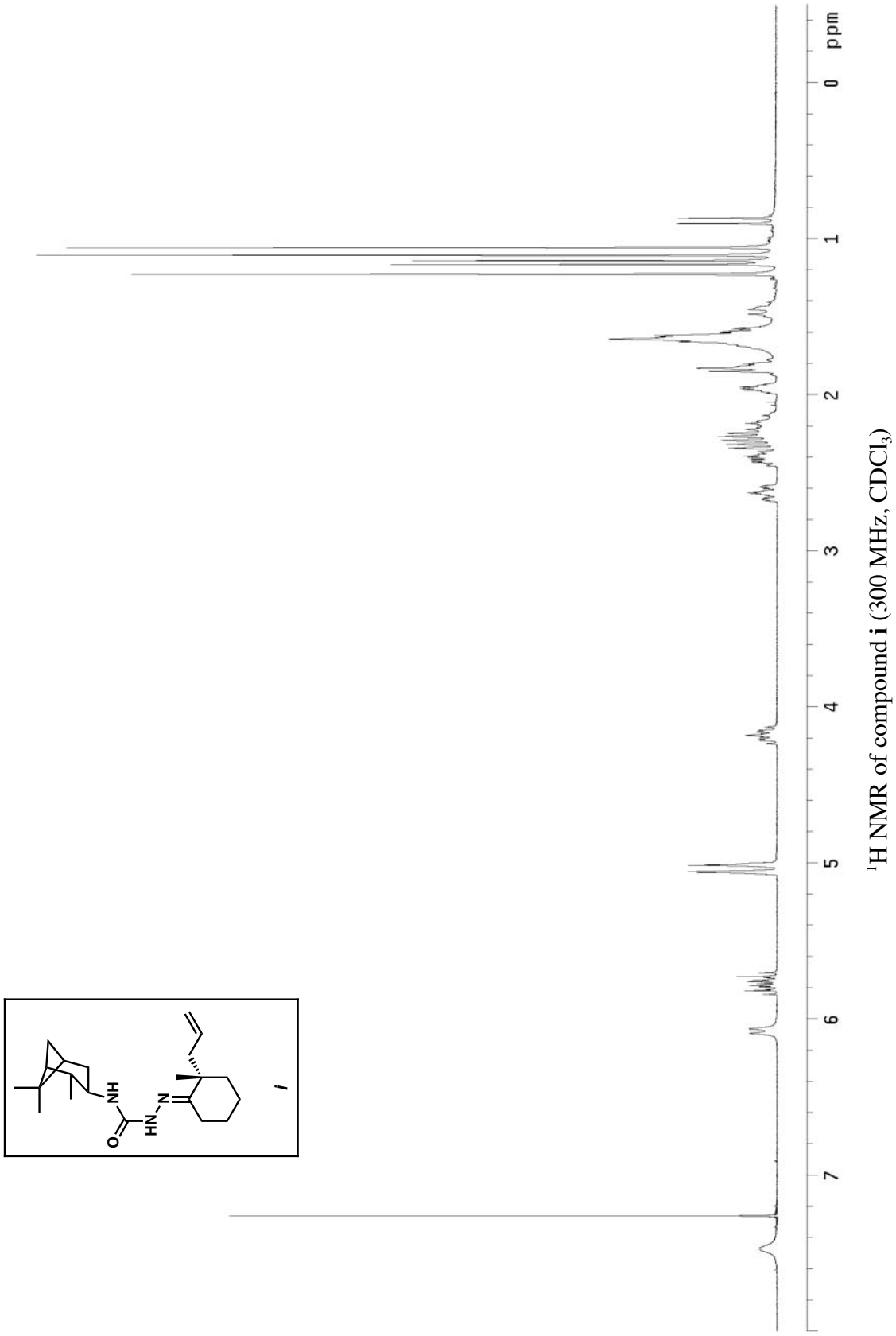
^{13}C NMR of compound **41** (75 MHz, $CDCl_3$)



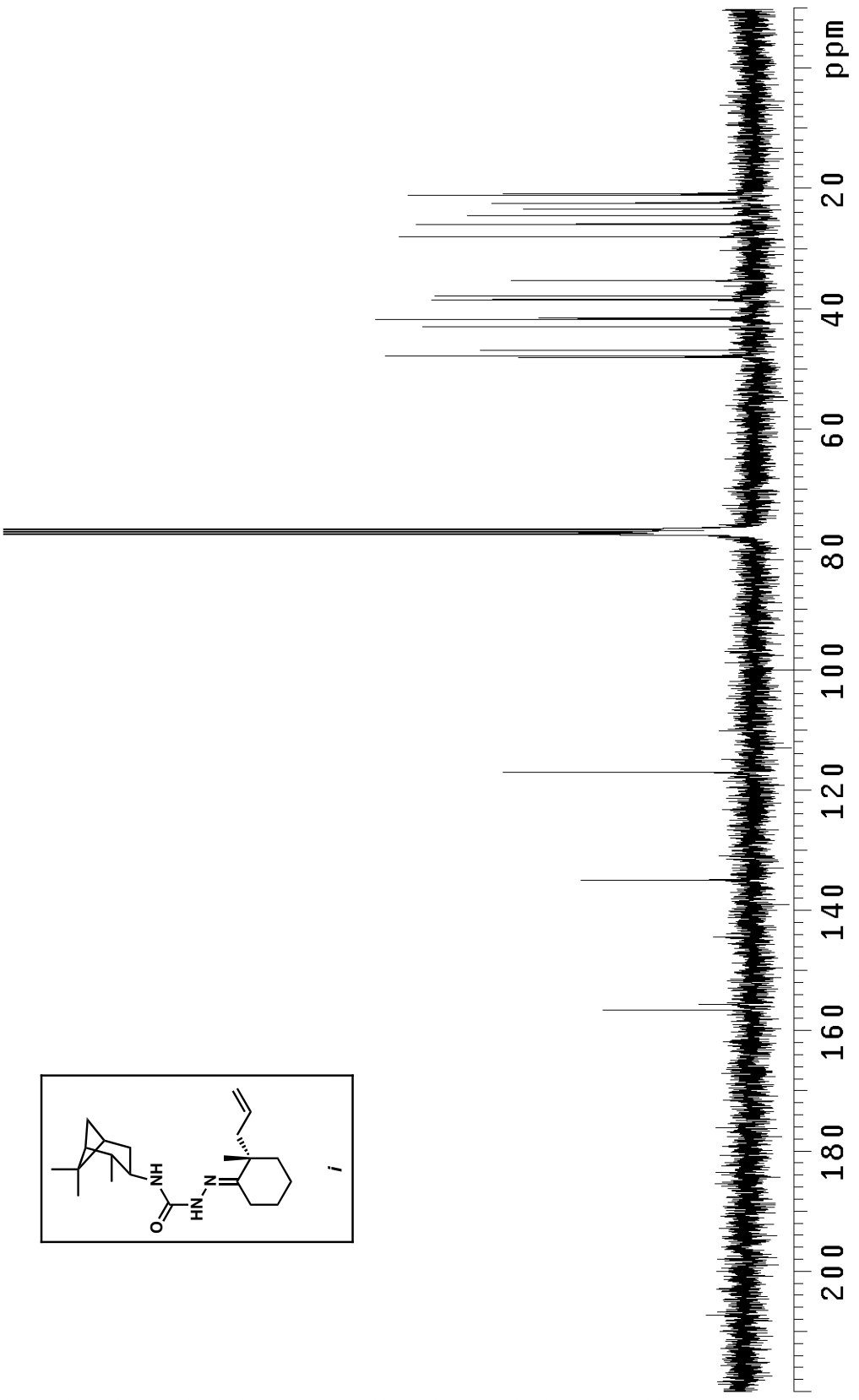
^{1}H NMR of compound **SI147** (300 MHz, $CDCl_3$)



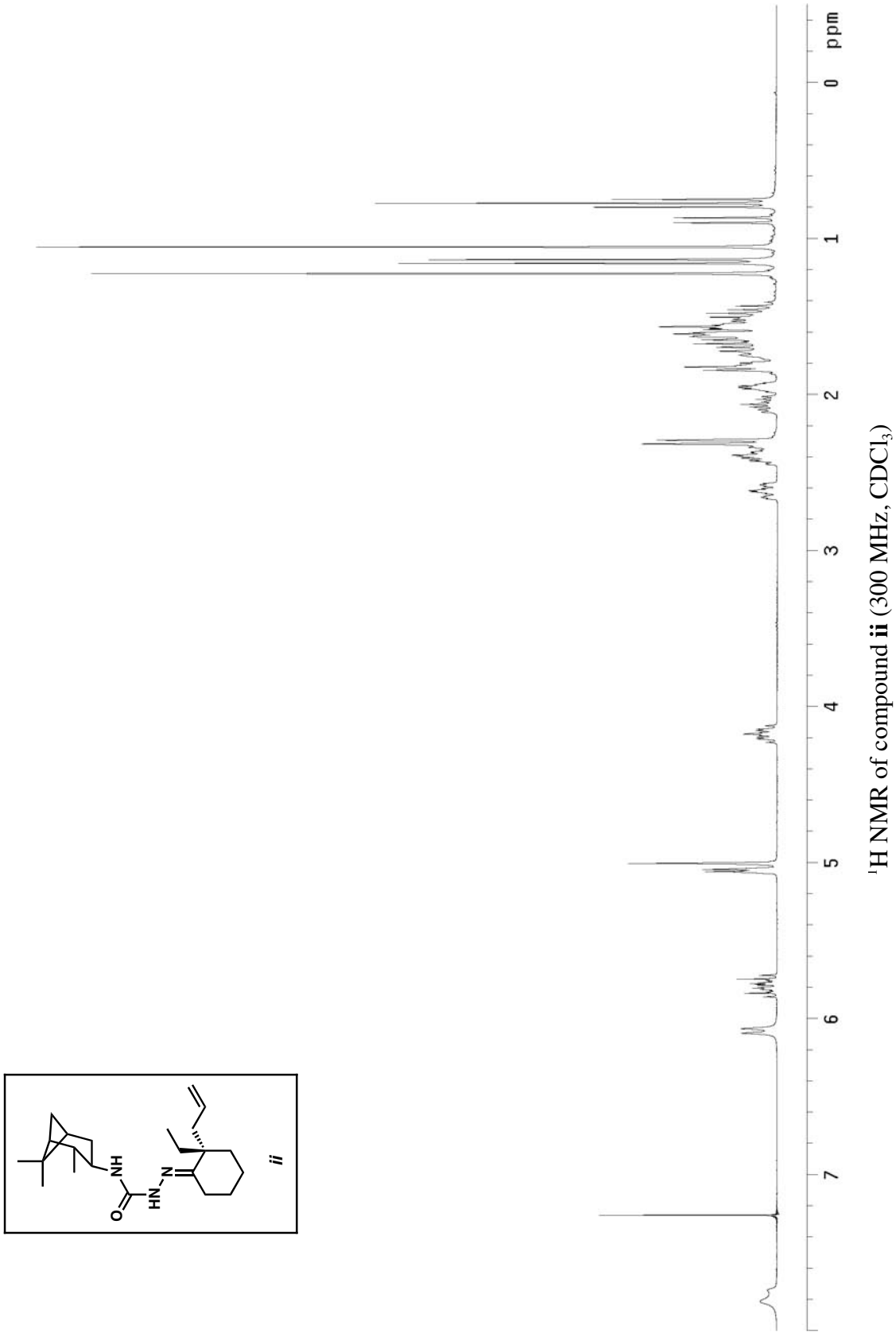
^{13}C NMR of compound **SI147** (75 MHz, $CDCl_3$)



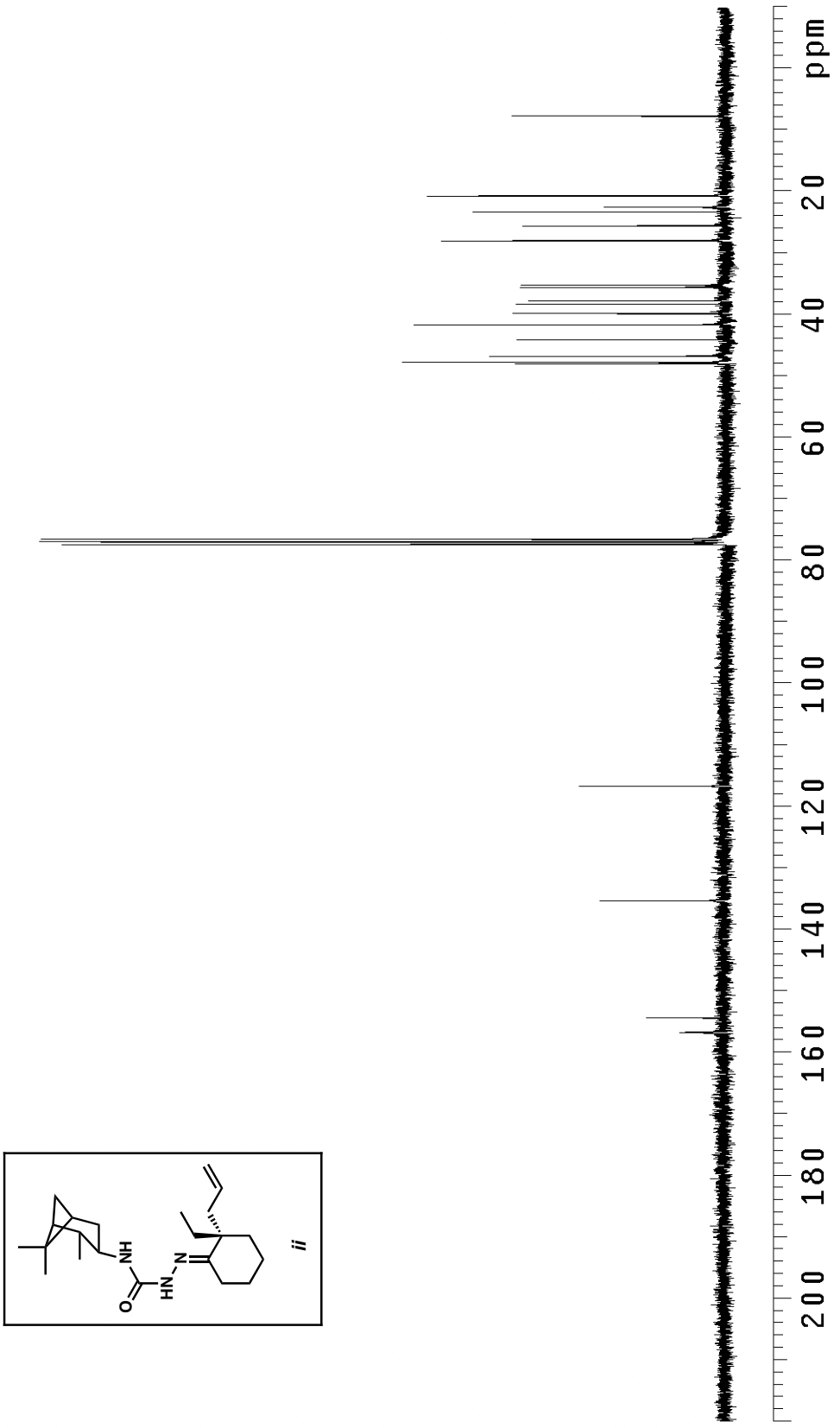
^{1}H NMR of compound **i** (300 MHz, $CDCl_3$)



^{13}C NMR of compound **i** (75 MHz, $CDCl_3$)



^{1}H NMR of compound **ii** (300 MHz, $CDCl_3$)



^{13}C NMR of compound **ii** (75 MHz, $CDCl_3$)