Supporting Information for

Construction of Vicinal Tertiary and All-Carbon Quaternary Stereocenters via Ir-Catalyzed Regio-, Diastereo-, and Enantioselective Allylic Alkylation and Applications in Sequential Pd-Catalysis.

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Materials and Methods

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-LCMS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ^{1}H NMR spectra were recorded on Varian Inova 500 MHz and 600 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm) or C_6HD_5 (δ 7.16 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm) or C_6HD_5 (δ 128.06 ppm). ^{31}P and ^{19}F NMR spectra were recorded on a Varian Mercury 300 MHz (at 121 MHz and 282 MHz, respectively). ^{19}F NMR spectra were reported relative to $CFCl_3$ (δ 0.0 ppm). ^{31}P NMR spectra were reported relative to external H_3PO_4 (δ 0.0 ppm). Data for ^{1}H NMR 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, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet, app = apparent. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell and are reported as: $[\alpha]_D^T$ (concentration in g/100 mL, solvent). Analytical HPLC was performed with an Agilent 1100 Series HPLC utilizing a Chiralpak (AD-H or AS) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained

[1] A. M. Pangborn, M. A. Giardello, R. H. Grubbs, R. K. Rosen and F. J. Timmers, *Organometallics*, **1996**, *15*, 1518.

from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).

Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Ligands **L3**–**L4**,[2] ligands **L5–L8**,[3] allyl carbonates,[4] and β-ketoesters[5] were prepared by known methods.

List of Abbreviations:

ee – enantiomeric excess, dr – diastereomeric ratio, HPLC – high-performance liquid chromatography, SFC – supercritical fluid chromatography, TBAT – tetrabutylammonium triphenyldifluorosilicate, TLC – thin-layer chromatography, THF – tetrahydrofuran, IPA – isopropanol, TBD – 1,5,7-triazabicyclo[4.4.0]dec-5-ene, DABCO – 1,4-diazabicyclo[2.2.2]octane, cod – *cis,cis*-1,5-cyclooctadiene

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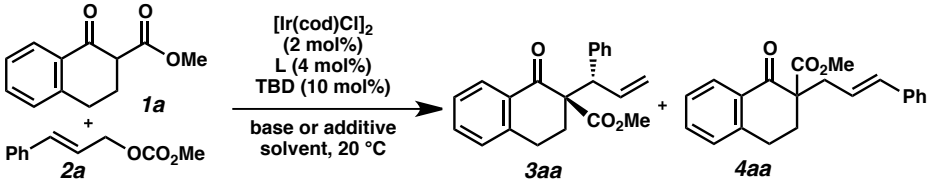
[2] (a) Liu, W.-B.; He, H.; Dai, L.-X.; You, S.-L. *Synthesis*, **2009**, 2076. (b) Liu, W.-B.; Zheng, C.; Zhuo, C.-X.; Dai, L.-X.; You, S.-L. *J. Am. Chem. Soc.* **2012**, *134*, 4812.

[3] McDougal, N. T.; Streuff, J.; Mukherjee, H.; Virgil, S. C.; Stoltz, B. M. *Tetrahedron Lett.* **2010**, *51*, 5550.

[4] (a) Wuts, P. G. M.; Ashford, S. W.; Anderson, A. M.; Atkins, J. R. *Org. Lett.* **2003**, *5*, 1483. (b) Malkov, A. V.; Gouriou, L.; Lloyd-Jones, G. C.; Starý, I.; Langer, V.; Spoor, P.; Vinader, V.; Kočovský, P. *Chem. Eur. J.* **2006**, *12*, 6910.

[5] (a) Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1983**, *24*, 5425. (b) Brown, D. S.; Marples, B. A.; Smith, P.; Walton, L. *Tetrahedron* **1995**, *51*, 3587.

Optimization of Reaction Parameters (Table S1)



entry[a]	*L*	base/additive (equiv)	solvent	*t* (h)	conv (%)[b]	*3aa*:*4aa*[b]	dr of *3aa*[b]	ee of *3aa* (%)[c]
1	*L1*	NaH (2)	THF	24	>95	>95:5	1:1.4	96 (99)[d]
2	*L2*	NaH (2)	THF	60	>95	>95:5	1:1.9	32 (3)[e]
3	*L3*	NaH (2)	THF	12	>95	95:5	>20:1	98
4	*L3*	—	THF	8	>95	80:20	11:1	96
5	*L3*	DABCO (2)	THF	8	>95	72:28	5.0:1	96
6	*L3*	TBD (2)	THF	8	>95	74:26	11:1	95
7	*L3*	Et_3N (2)	THF	8	>95	77:23	11:1	97
8	*L3*	Cs_2CO_3 (2)	THF	12	>95	63:37	6.3:1	93
9	*L3*	K_3PO_4 (2)	THF	12	>95	63:37	4.1:1	90
10	*L3*	NaHMDS (2)	THF	12	>95	75:25	8.3:1	93
11	*L3*	LiHMDS (2)	THF	12	>95	86:14	13:1	96
12	*L3*	LiO*t*-Bu (2)	THF	1	>95	95:5	>20:1	99
13	*L3*	LiCl (1)	THF	1	>95	88:12	14:1	98
14	*L3*	LiBr (1)	THF	1	>95 (98)	95:5	>20:1	>99
15	*L3*	LiI (1)	THF	1	>95	72:28	>20:1	97
16	*L1*	LiBr (1)	THF	60	<5	nd	nd	nd
17	*L2*	LiBr (1)	THF	60	<5	nd	nd	nd
18	*L4*	LiBr (1)	THF	12	>95	80:20	12:1	96
19	*L5*	LiBr (1)	THF	60	60	12:88	nd	nd
20	*L3*	LiBr (1)	*p*-dioxane	1	>95	95:5	>20:1	>99
21	*L3*	LiBr (1)	Et_2O	3	>95	76:24	11:1	96
22	*L3*	LiBr (1)	CH_2Cl_2	60	55	68:32	9.0:1	66
23	*L3*	LiBr (1)	toluene	16	>95	>95:5	>20:1	91
24[f]	*L3*	LiBr (1)	THF	12	>95	95:5	>20:1	99
25[g]	*L3*	LiBr (1)	THF	60	60	92:8	>20:1	94

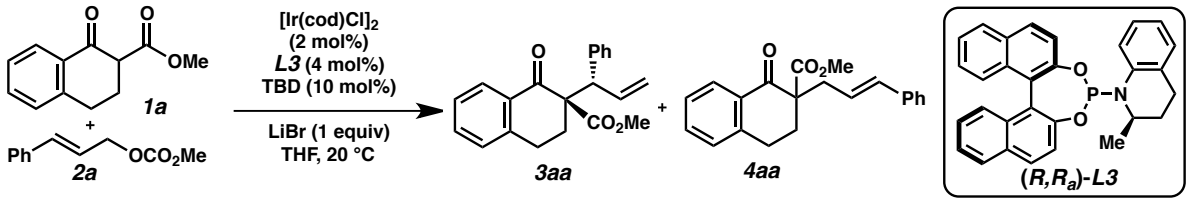
[a] Reactions performed with 0.1 mmol of **2a**, 0.2 mmol of **1a** in 1 mL of solvent. [b] Determined by ^{1}H NMR or UHPLC-MS analysis of the crude reaction mixture. [d] (Ee) of the alternate diasteromer. [e] Measured on the minor isomer and the number in the parenthesis is ee of the major isomer. [f] 1 mol % of $[Ir(cod)Cl]_2$ and 2 mol % of **L3** were used. [g] 0.5 mol % of $[Ir(cod)Cl]_2$ and 1 mol % of **L3** were used.

General Procedure for Optimization Reaction (Table S1): All experiments were preformed in a nitrogen-filled glove box. $[Ir(cod)Cl]_2$ (1.4 mg, 0.002 mmol, 2 mol%), ligand (0.004 mmol, 4 mol%), and TBD (1.4 mg, 0.01 mmol, 10 mol%) were added to a vial equipped with a magnetic stirring bar. The vial was then charged with solvent (0.5 mL) and stirred at 20 °C for 10 min, generating an orange solution. Cinnamyl carbonate **2a** (19.2 mg, 0.1 mmol, 1.0 equiv), β-ketoester **1a** (40.4 mg, 0.2 mmol, 2.0 equiv), base or additive (as indicated below) and another 0.5 mL of solvent were added. The vial was sealed and stirred

at 20 °C until allylic carbonate **2a** was fully consumed, as indicated by TLC or UHPLC-MS anaylsis. The reaction mixture was filtered through a celite pad, rinsed with CH_2Cl_2, and concentrated under reduced pressure. The ratios of constitutional isomers (branched product to linear product: **3aa**:**4aa**) and diastereomers (dr) were determined by ^{1}H NMR or UHPLC-MS.

General Procedure for the Ir-Catalyzed Asymmetric Allylic Alkylation of β-Ketoesters

Please note that the absolute configuration was determined only for compound **3af** via X-ray analysis (vide infra). The absolute configuration for all other products **3** has been inferred by analogy. Isolated yields are reported in Tables 2 and 3 (see manuscript). For respective HPLC or SFC conditions, please refer to Table S2.

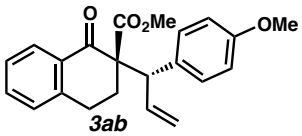


(*R*)-methyl 1-oxo-2-((*S*)-1-phenylallyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3aa). In a nitrogen-filled glove box, $[Ir(cod)Cl]_2$ (2.7 mg, 0.004 mmol, 2 mol%), ligand **L3** (3.7 mg, 0.008 mmol, 4 mol%), and TBD (2.8 mg, 0.02 mmol, 10 mol%) were added to a 2 dram scintillation vial equipped with a magnetic stirring bar. The vial was then charged with THF (1 mL) and stirred at 20 °C for 10 min, generating an orange solution. Cinnamyl carbonate (**2a**) (38.3 mg, 0.2 mmol, 1.0 equiv), LiBr (17.3 mg, 0.2 mmol, 1.0 equiv), β-ketoester **1a** (80.8 mg, 0.4 mmol, 2.0 equiv) and another 1 mL of THF were added. The vial was sealed and stirred at 20 °C until allylic carbonate **2a** was fully consumed, as indicated by TLC or UHPLC-MS analysis. THF was evaporated and the crude mixture was then dissolved in CH_2Cl_2, filtered through a celite pad, rinsed with CH_2Cl_2, and concentrated under reduced pressure. The regioselectivity (branched product to linear product: b:l = 95:5) and diastereoselectivity (dr >20:1) were determined by ^{1}H NMR or UHPLC-MS. The residue was purified by silica gel flash chromatography (gradient elution, 2→5% EtOAc in hexanes) to afford **3aa** and **4aa** (62.6 mg, 98% combined yield). Allylation product **3aa** was isolated as a white solid by silica gel chromatography (gradient elution, 0→2% EtOAc in hexanes). >99% ee, $[\alpha]_D^{25}$ +26.3 (*c* 1.11, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.42– 7.39 (m, 3H), 7.28–7.23 (m, 3H), 7.19–7.13 (m, 2H), 6.36 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.21–5.12 (m, 2H), 4.46 (d, *J* = 10.0 Hz, 1H), 3.56 (s, 3H), 3.23 (ddd, *J* = 17.1, 12.1, 4.7 Hz, 1H), 2.88 (ddd, *J* = 17.6, 5.0,

3.0 Hz, 1H), 2.60 (ddd, *J* = 13.7, 4.7, 3.0 Hz, 1H), 2.10 (ddd, *J* = 13.6, 12.1, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 170.0, 143.1, 139.8, 136.6, 133.6, 132.5, 130.2, 128.8, 128.4, 128.2, 126.9, 126.7, 117.9, 62.7, 53.9, 52.6, 28.8, 26.4; IR (Neat Film, NaCl) 3066, 3028, 2948, 1731, 1685, 1636, 1599, 1491, 1453, 1433, 1358, 1298, 1283, 1238, 1214, 1169, 1108, 1080, 1032, 1001, 980, 926, 892, 808, 743 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{21}O_3$ $[M+H]^+$: 321.1485, found 321.1489; HPLC conditions: 2% IPA, 0.6 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): major = 13.80, minor = 17.89.

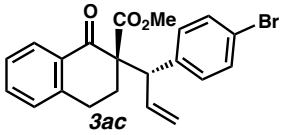
Spectroscopic Data for Ir-Catalyzed Allylic Alkylation Products

(*R*)-methyl 2-((*S*)-1-(4-methoxyphenyl)allyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3ab)



Ketoester **3ab** was isolated by silica gel chromatography (gradient elution, 0→5% EtOAc in hexanes) as a white solid. >99% ee, $[\alpha]_D^{25}$ +38.5 (*c* 0.93, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.41 (td, *J* = 7.5, 1.5 Hz, 1H), 7.37–7.31 (m, 2H), 7.31–7.21 (m, 1H), 7.21–7.12 (m, 1H), 6.86–6.75 (m, 2H), 6.32 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.20–5.09 (m, 2H), 4.41 (d, *J* = 9.9 Hz, 1H), 3.75 (s, 3H), 3.56 (s, 3H), 3.23 (ddd, *J* = 17.1, 12.2, 4.6 Hz, 1H), 2.88 (ddd, *J* = 17.6, 4.9, 2.9 Hz, 1H), 2.58 (ddd, *J* = 13.6, 4.7, 3.0 Hz, 1H), 2.11 (ddd, *J* = 13.6, 12.2, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 170.1, 158.4, 143.2, 136.8, 133.6, 132.5, 131.8, 131.2, 128.8, 128.4, 126.7, 117.6, 113.5, 62.8, 55.3, 53.2, 52.6, 28.7, 26.4; IR (Neat Film, NaCl) 3073, 3003, 2950, 2836, 1732, 1687, 1636, 1608, 1601, 1581, 1511, 1454, 1442, 1435, 1357, 1337, 1303, 1242, 1215, 1181, 1114, 1078, 1033, 1000, 981, 923, 893, 834, 808, 749 cm^{-1}; HRMS (ESI+) *m/z* calc'd for fragment $C_{10}H_{11}O$ $[M\text{-}C_{11}H_{12}O_3+H]^+$: 147.0804, found 147.0807; HPLC conditions: 2% IPA, 0.6 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 27.44, major = 37.29.

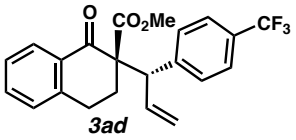
(*R*)-methyl 2-((*S*)-1-(4-bromophenyl)allyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3ac)



Ketoester **3ac** was isolated by silica gel chromatography (gradient elution, 0→3% EtOAc in hexanes) as a colorless oil. 99% ee, $[\alpha]_D^{25}$ +49.1 (*c* 1.18, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.43 (td, *J* = 7.5, 1.5 Hz, 1H), 7.39–7.35 (m, 2H), 7.32–7.27 (m, 2H), 7.27–7.25 (m, 1H), 7.15 (dt, *J* = 7.7, 0.9

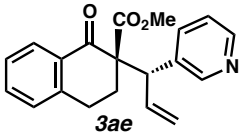
Hz, 1H), 6.29 (dt, *J* = 16.7, 10.0 Hz, 1H), 5.32–5.03 (m, 2H), 4.37 (d, *J* = 9.9 Hz, 1H), 3.54 (s, 3H), 3.29–3.15 (m, 1H), 2.88 (ddd, *J* = 17.5, 4.9, 2.8 Hz, 1H), 2.57 (ddd, *J* = 13.6, 4.7, 2.9 Hz, 1H), 2.09 (ddd, *J* = 13.5, 12.3, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 169.9, 143.0, 139.0, 136.1, 133.8, 132.4, 132.0, 131.2, 128.8, 128.4, 126.8, 121.0, 118.5, 62.5, 53.7, 52.7, 29.1, 26.4; IR (Neat Film, NaCl) 3074, 3025, 2949, 1732, 1687, 1683, 1633, 1601, 1488, 1454, 1435, 1403, 1357, 1297, 1240, 1215, 1170, 1141, 1112, 1075, 1032, 1010, 981, 925, 892, 831, 808, 750, 741 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{20}{}^{79}BrO_3$ $[M+H]^+$: 399.0590, found 399.0585; HPLC conditions: 2% IPA, 0.6 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 19.71, major = 23.59.

(*R*)-methyl 1-oxo-2-((*S*)-1-(4-(trifluoromethyl)phenyl)allyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3ad)



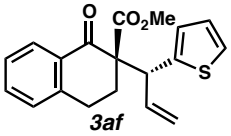
Ketoester **3ad** was isolated by silica gel chromatography (gradient elution, 0→5% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +32.4 (*c* 1.51, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 (t, *J* = 7.5, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.34 (dt, *J* = 16.7, 10.1 Hz, 1H), 5.33–5.08 (m, 2H), 4.45 (d, *J* = 10.0 Hz, 1H), 3.54 (s, 3H), 3.29–3.16 (m, 1H), 2.90 (ddd, *J* = 17.6, 4.9, 2.7 Hz, 1H), 2.60 (ddd, *J* = 13.6, 4.7, 2.8 Hz, 1H), 2.11 (ddd, *J* = 13.5, 12.3, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.1, 169.9, 144.1, 143.0, 135.8, 133.8, 132.4, 130.6, 129.1 (q, $^2J_{CF}$ = 32.4 Hz), 128.8, 128.4, 126.8, 125.0 (q, $^3J_{CF}$ = 3.8 Hz), 124.3 (q, $^1J_{CF}$ = 272.0 Hz), 118.8, 62.5, 54.1, 52.7, 29.3, 26.4; IR (Neat Film, NaCl) 3074, 2952, 1736, 1733, 1689, 1683, 1616, 1601, 1454, 1435, 1413, 1327, 1241, 1217, 1166, 1123, 1070, 1019, 927, 846, 809, 751, 742 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{22}H_{20}{}^{19}F_3O_3$ $[M+H]^+$: 389.1359, found 389.1346; SFC conditions: 5% IPA, 4.0 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 3.38, major = 3.91.

(*R*)-methyl 1-oxo-2-((*S*)-1-(pyridin-3-yl)allyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3ae)



Ketoester **3ae** was isolated by silica gel chromatography (gradient elution 20→50% EtOAc in hexanes) as a white solid. 98% ee, $[\alpha]_D^{25}$ +64.6 (*c* 0.46, $CHCl_3$); R_f = 0.4 (50% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.43 (dd, *J* = 5.0, 1.7 Hz, 1H), 8.02 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.93 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.44 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.23 (dd, *J* = 8.0, 4.8 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.36–6.29 (m, 1H), 5.22–5.18 (m, 2H), 4.31 (d, *J* = 9.8 Hz, 1H), 3.53 (s, 3H), 3.21 (ddd, *J* = 17.2, 12.3, 4.7 Hz, 1H), 2.91 (ddd, *J* = 17.5, 4.9, 2.7 Hz, 1H), 2.60 (ddd, *J* = 13.5, 4.7, 2.8 Hz, 1H), 2.17 (ddd, *J* = 13.4, 12.3, 4.9 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.3, 170.0, 150.9, 147.9, 142.9, 138.4, 136.0, 135.5, 133.9, 132.5, 128.8, 128.4, 126.9, 123.3, 119.2, 62.4, 52.7, 52.5, 29.7, 26.5; IR (Neat Film, NaCl) 3029, 2950, 2848, 1732, 1687, 1599, 1573, 1479, 1454, 1429, 1356, 1295, 1274, 1241, 1216, 1171, 1122, 1077, 1025, 999, 979, 926, 807, 749, 716 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{20}H_{20}NO_3$ $[M+H]^+$: 322.1438, found 322.1442; HPLC conditions: 10% IPA, 1.0 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 13.45, major = 15.72.

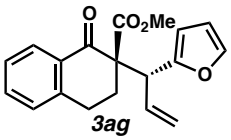
(*R*)-methyl 1-oxo-2-((*R*)-1-(thiophen-2-yl)allyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3af)



Ketoester **3af** was isolated by silica gel chromatography (gradient elution, 0→3% EtOAc in hexanes) as a white solid. 95% ee, $[\alpha]_D^{25}$ –14.2 (*c* 0.86, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 7.14 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.93 (ddd, *J* = 3.6, 1.2, 0.7 Hz, 1H), 6.88 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.23 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.26–5.12 (m, 2H), 4.76 (d, *J* = 10.0 Hz, 1H), 3.59 (s, 3H), 3.25 (ddd, *J* = 17.2,

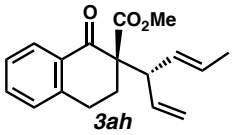
12.0, 4.8 Hz, 1H), 2.89 (ddd, *J* = 17.5, 5.0, 3.1 Hz, 1H), 2.55 (ddd, *J* = 13.7, 4.8, 3.1 Hz, 1H), 2.12 (ddd, *J* = 13.6, 12.0, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.2, 169.7, 143.2, 142.3, 135.9, 133.8, 132.3, 128.9, 128.4, 126.9, 126.8, 126.4, 124.9, 118.3, 62.9, 52.7, 49.5, 28.0, 26.2; IR (Neat Film, NaCl) 3071, 2949, 2925, 2853, 1731, 1686, 1639, 1599, 1484, 1453, 1433, 1354, 1293, 1272, 1240, 1214, 1170, 1119, 1078, 1032, 979, 924, 891, 853, 807, 749 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{19}SO_3$ $[M+H]^+$: 327.1049, found 327.1048; SFC conditions: 10% IPA, 4.0 mL/min, Chiralcel OJ-H column, λ = 254 nm, t_R (min): major = 2.96, minor = 3.63.

(*R*)-methyl 2-((*R*)-1-(furan-2-yl)allyl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3ag)



Ketoester **3ag** was isolated by silica gel chromatography (gradient elution, 0→3% EtOAc in hexanes) as a colorless oil. 95% ee, $[\alpha]_D^{25}$ +22.5 (*c* 1.17, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 (t, *J* = 7.6 Hz, 1H), 7.25 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.17 (d, *J* = 7.7 Hz, 1H), 6.25 (dd, *J* = 3.2, 1.8 Hz, 1H), 6.19–6.09 (m, 2H), 5.26–5.18 (m, 2H), 4.63 (d, *J* = 9.8 Hz, 1H), 3.63 (s, 3H), 3.24 (ddd, *J* = 17.3, 12.2, 4.8 Hz, 1H), 2.88 (ddd, *J* = 17.5, 4.9, 3.1 Hz, 1H), 2.57 (ddd, *J* = 13.8, 4.8, 3.1 Hz, 1H), 1.99 (ddd, *J* = 13.8, 12.1, 5.0 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.7, 169.7, 153.4, 143.3, 141.6, 133.7, 133.6, 132.1, 128.9, 128.4, 126.7, 119.2, 110.3, 108.4, 62.2, 52.7, 47.9, 28.1, 26.1; IR (Neat Film, NaCl) 3116, 3075, 3024, 2950, 2848, 1734, 1731, 1689, 1639, 1600, 1500, 1485, 1453, 1433, 1356, 1293, 1271, 1243, 1216, 1172, 1155, 1120, 1110, 1078, 1012, 981, 965, 928, 905, 892, 806, 745, 736 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{19}H_{19}O_4$ $[M+H]^+$: 311.1278, found 311.1275; SFC conditions: 10% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 5.21, minor = 6.03.

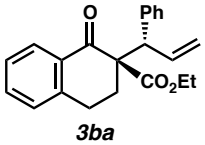
(*R*)-methyl 2-((*S*,*E*)-hexa-1,4-dien-3-yl)-1-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3ah)



3ah

Ketoester **3ah** was isolated by silica gel chromatography (gradient elution, 0→2% EtOAc in hexanes) as a colorless oil. 90% ee, $[\alpha]_D^{25}$ +46.4 (*c* 1.02, $CHCl_3$); R_f = 0.5 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.7 Hz, 1H), 5.98–5.87 (m, 1H), 5.74 (ddd, *J* = 15.3, 8.0, 1.6 Hz, 1H), 5.57–5.48 (m, 1H), 5.08–5.03 (m, 2H), 3.61 (s, 3H), 3.47 (t, *J* = 8.4 Hz, 1H), 3.12 (ddd, *J* = 17.0, 12.0, 4.7 Hz, 1H), 2.91 (dt, *J* = 17.4, 4.1 Hz, 1H), 2.45 (ddd, *J* = 13.7, 4.7, 3.3 Hz, 1H), 2.25 (ddd, *J* = 13.7, 11.9, 4.9 Hz, 1H), 1.65 (ddd, *J* = 6.4, 1.7, 0.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.2, 171.0, 143.1, 136.7, 133.6, 132.8, 129.8, 128.8, 128.2, 128.2, 126.8, 117.6, 62.0, 53.2, 52.4, 29.5, 26.5, 18.2; IR (Neat Film, NaCl) 3075, 3028, 2951, 2854, 1732, 1688, 1600, 1454, 1438, 1356, 1300, 1272, 1235, 1214, 1169, 1122, 1090, 999, 974, 917, 890, 803, 747 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{18}H_{21}O_3$ $[M+H]^+$: 288.1485, found 288.1489; SFC conditions: 2% MeOH, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): minor = 8.23, major = 8.87.

(*R*)-ethyl 1-oxo-2-((*S*)-1-phenylallyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (3ba)

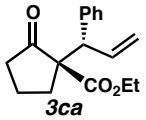


3ba

Ketoester **3ba** was isolated by silica gel chromatography (gradient elution, 0→5% EtOAc in hexanes) as a white solid, >99% ee, $[\alpha]_D^{25}$ +42.7 (*c* 1.09, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.46–7.39 (m, 3H), 7.29–7.23 (m, 3H), 7.20–7.12 (m, 2H), 6.37 (dt, *J* = 16.8, 10.0 Hz, 1H), 5.20–5.07 (m, 2H), 4.40 (d, *J* = 9.9 Hz, 1H), 4.07–3.94 (m, 2H), 3.22 (ddd, *J* = 17.3, 12.2, 4.8 Hz, 1H), 2.88 (ddd, *J* = 17.5, 5.0, 2.9 Hz, 1H), 2.58 (ddd, *J* = 13.6, 4.7, 3.0 Hz, 1H), 2.12 (ddd, *J* = 13.6, 12.1, 5.0 Hz, 1H), 1.06 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.4, 169.7, 143.0, 140.0, 136.7, 133.5, 132.7, 130.3, 128.7, 128.3, 128.1, 126.9, 126.7, 117.9, 62.3, 61.6, 54.1, 29.2, 26.4, 14.0; IR (Neat Film, NaCl) 3063, 3027, 2978, 2934, 1727, 1699,

1689, 1685, 1599, 1490, 1452, 1363, 1298, 1282, 1235, 1212, 1157, 1107, 1080, 1018, 926, 899, 787, 773, 743 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{22}H_{23}O_3$ $[M+H]^+$: 335.1642, found 335.1651; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): minor = 13.82, major = 16.53.

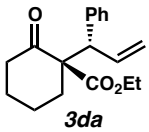
(*R*)-ethyl 2-oxo-1-((*S*)-1-phenylallyl)cyclopentanecarboxylate (3ca)



3ca

Ketoester **3ca** was isolated by silica gel chromatography (gradient elution, 0→5% EtOAc in hexanes) as a colorless oil. 99% ee, $[\alpha]_D^{25}$ –52.5 (*c* 1.04, $CHCl_3$); R_f = 0.3 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.15 (m, 5H), 6.14–6.03 (m, 1H), 5.20–5.10 (m, 2H), 4.37 (d, *J* = 8.9 Hz, 1H), 4.22–4.09 (m, 2H), 2.67 (dddd, *J* = 13.4, 7.1, 3.5, 1.7 Hz, 1H), 2.24–2.14 (m, 1H), 2.13–2.02 (m, 1H), 1.84–1.71 (m, 1H), 1.69–1.59 (m, 1H), 1.59–1.49 (m, 1H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 213.4, 169.2, 139.3, 136.3, 129.9, 128.4, 127.1, 117.8, 65.9, 61.9, 52.8, 38.9, 28.5, 19.7, 14.2; IR (Neat Film, NaCl) 3083, 3062, 3030, 2979, 2891, 1752, 1719, 1639, 1601, 1493, 1465, 1452, 1405, 1365, 1315, 1223, 1138, 1105, 1026, 1003, 923, 864, 826, 757, 707 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{17}H_{21}O_3$ $[M+H]^+$: 273.1485, found 273.1483; HPLC conditions: 2% IPA, 0.6 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): major = 11.23, minor = 12.73.

(*R*)-ethyl 2-oxo-1-((*S*)-1-phenylallyl)cyclohexanecarboxylate (3da)

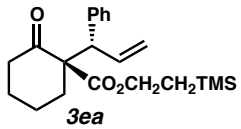


3da

Ketoester **3da** was isolated by silica gel chromatography (gradient elution, 0→5% EtOAc in hexanes) as a white solid. 98% ee, $[\alpha]_D^{25}$ +140.6 (*c* 1.25, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.30 (m, 2H), 7.29–7.22 (m, 2H), 7.21–7.15 (m, 1H), 6.33 (ddd, *J* = 16.9, 10.2, 9.2 Hz, 1H), 5.13–4.99 (m, 2H), 4.11–3.96 (m, 2H), 3.93 (d, *J* = 9.2 Hz, 1H), 2.47–2.39 (m, 2H), 2.36–2.29 (m, 1H), 1.92 (dddd, *J* = 9.5, 4.8, 2.7, 1.5

Hz, 1H), 1.79–1.47 (m, 3H), 1.12 (t, J = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.7, 170.8, 140.0, 137.5, 130.3, 128.0, 126.8, 117.4, 65.5, 61.4, 54.6, 42.1, 35.0, 27.2, 22.8, 14.0; IR (Neat Film, NaCl) 3077, 3028, 2977, 2939, 2865, 1714, 1635, 1600, 1491, 1452, 1388, 1365, 1340, 1309, 1262, 1231, 1204, 1133, 1085, 1020, 1002, 919, 854, 756, 704 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{23}O_3$ $[M+H]^+$: 287.1642, found 287.1639; SFC conditions: 10% IPA, 4.0 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 1.69, major = 1.94.

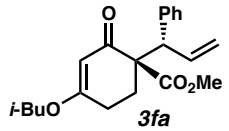
(*R*)-2-(trimethylsilyl)ethyl 2-oxo-1-((*S*)-1-phenylallyl)cyclohexanecarboxylate (3ea)



3ea

Ketoester **3ea** was isolated by silica gel chromatography (gradient elution, 0→2% i-BuOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +91.6 (*c* 0.45, $CHCl_3$); R_f = 0.4 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.32 (m, 2H), 7.24 (ddd, J = 8.2, 6.9, 1.4 Hz, 2H), 7.21–7.15 (m, 1H), 6.34 (ddd, J = 16.9, 10.2, 9.2 Hz, 1H), 5.21–4.86 (m, 2H), 4.05 (dddd, J = 58.0, 11.8, 10.8, 5.9 Hz, 2H), 3.92 (d, J = 9.2 Hz, 1H), 2.46–2.40 (m, 2H), 2.38–2.28 (m, 1H), 1.98–1.87 (m, 1H), 1.80–1.71 (m, 1H), 1.72–1.47 (m, 3H), 0.82 (qdd, J = 13.6, 11.7, 5.7 Hz, 2H), 0.01 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 206.6, 170.9, 139.9, 137.4, 130.2, 127.9, 126.7, 117.3, 65.4, 63.7, 54.5, 42.0, 34.9, 27.0, 22.7, 17.2, –1.6; IR (Neat Film, NaCl) 2950, 1712, 1452, 1250, 1231, 1133, 921, 859, 837 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{30}NaO_3Si$ $[M+Na]^+$: 381.1856, found 381.1865; SFC conditions: 3% IPA, 2.5 mL/min, Chiralcel OJ–H column, λ = 210 nm, t_R (min): minor = 1.93, major = 2.24.

(*R*)-methyl 4-isobutoxy-2-oxo-1-((*S*)-1-phenylallyl)cyclohex-3-enecarboxylate (3fa)

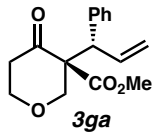


3fa

Ketoester **3fa** was isolated by silica gel chromatography (gradient elution, 0→10% EtOAc in hexanes) as a colorless oil. >99% ee, $[\alpha]_D^{25}$ +31.5 (*c* 1.88, $CHCl_3$); R_f = 0.4 (10% EtOAc

in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.29 (m, 2H), 7.27–7.20 (m, 2H), 7.20–7.13 (m, 1H), 6.24 (dt, *J* = 16.7, 10.2 Hz, 1H), 5.28 (s, 1H), 5.18 (ddd, *J* = 16.8, 1.9, 0.8 Hz, 1H), 5.12 (dd, *J* = 10.0, 1.8 Hz, 1H), 4.62 (d, *J* = 10.4 Hz, 1H), 3.64 (s, 3H), 3.53–3.45 (m, 2H), 2.79 (dddd, *J* = 18.3, 11.8, 5.1, 1.6 Hz, 1H), 2.43 (ddd, *J* = 13.4, 5.1, 2.4 Hz, 1H), 2.26 (ddd, *J* = 18.2, 5.5, 2.4 Hz, 1H), 1.94 (dt, *J* = 13.3, 6.7 Hz, 1H), 1.83 (ddd, *J* = 13.4, 11.8, 5.5 Hz, 1H), 0.91 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 192.8, 177.2, 170.0, 139.7, 136.1, 130.2, 128.1, 126.8, 118.0, 102.9, 74.9, 61.1, 52.6, 52.1, 27.7, 26.7, 25.2, 19.11, 19.08; IR (Neat Film, NaCl) 3073, 3029, 2958, 2874, 1727, 1664, 1607, 1582, 1491, 1470, 1452, 1443, 1431, 1406, 1384, 1369, 1316, 1298, 1231, 1193, 1177, 1140, 1116, 1079, 1012, 987, 921, 903, 844, 817, 788, 764, 724 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{27}O_4$ $[M+H]^+$: 343.1904, found 343.1905; SFC conditions: 10% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 254 nm, t_R (min): major = 3.71, minor = 6.24.

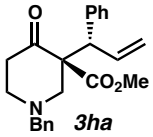
(*S*)-methyl 4-oxo-3-((*S*)-1-phenylallyl)tetrahydro-2*H*-pyran-3-carboxylate (3ga)



3ga

Ketoester **3ge** was isolated by silica gel chromatography (gradient elution, 5→10% EtOAc in hexanes) as a colorless oil. 98% ee, $[\alpha]_D^{25}$ +71.1 (*c* 0.88, $CHCl_3$); R_f = 0.2 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.30 (m, 2H), 7.31–7.25 (m, 2H), 7.24–7.19 (m, 1H), 6.43 (ddd, *J* = 16.9, 10.2, 9.4 Hz, 1H), 5.19–5.03 (m, 2H), 4.28 (dd, *J* = 11.9, 1.2 Hz, 1H), 4.03 (dddd, *J* = 11.1, 6.2, 4.9, 1.3 Hz, 1H), 3.98 (d, *J* = 9.4 Hz, 1H), 3.82 (dddd, *J* = 11.3, 9.0, 4.5, 0.6 Hz, 1H), 3.67 (d, *J* = 11.8 Hz, 1H), 3.61 (s, 3H), 2.70 (ddd, *J* = 14.5, 8.9, 6.2 Hz, 1H), 2.57 (dt, *J* = 14.5, 4.7 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 202.8, 169.7, 138.6, 136.7, 129.8, 128.4, 127.4, 118.0, 73.2, 68.6, 67.1, 52.4, 51.6, 41.9; IR (Neat Film, NaCl) 3063, 3029, 2973, 2951, 2863, 1746, 1716, 1635, 1600, 1492, 1472, 1454, 1433, 1378, 1360, 1310, 1290, 1229, 1212, 1176, 1140, 1112, 1085, 1033, 1001, 978, 925, 826, 763, 741 cm^{-1}; HRMS (ESI+) *m/z* calc'd for $C_{16}H_{19}O_4$ $[M+H]^+$: 275.1278, found 275.1282; SFC conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.65, major = 4.95.

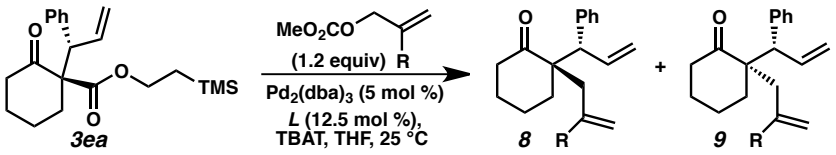
(*S*)-methyl 1-benzyl-4-oxo-3-((*S*)-1-phenylallyl)piperidine-3-carboxylate (3ha)



3ha

Ketoester **3ha** was isolated by silica gel chromatography (gradient elution, 5→10% EtOAc in hexanes) as a colorless oil. 97% ee, $[\alpha]_D^{25}$ +34.3 (*c* 0.87, $CHCl_3$); R_f = 0.3 (10% EtOAc in hexanes); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.29 (m, 5H), 7.28–7.24 (m, 2H), 7.24–7.14 (m, 3H), 6.44 (ddd, *J* = 16.9, 10.2, 9.3 Hz, 1H), 5.12–5.04 (m, 2H), 4.03 (d, *J* = 9.4 Hz, 1H), 3.59 (s, 3H), 3.64–3.54 (m, 2H), 3.15 (dd, *J* = 11.9, 2.0 Hz, 1H), 2.82–2.75 (m, 1H), 2.71 (ddd, *J* = 14.1, 8.5, 5.7 Hz, 1H), 2.65–2.56 (m, 2H), 2.53 (ddd, *J* = 13.9, 5.4, 4.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.3, 170.6, 139.4, 138.0, 137.4, 129.9, 129.2, 128.5, 128.2, 127.5, 127.1, 117.6, 66.1, 62.0, 60.2, 53.4, 53.0, 52.0, 40.9; IR (Neat Film, NaCl) 3060, 3027, 2949, 2811, 2765, 1718, 1631, 1600, 1584, 1493, 1468, 1452, 1432, 1364, 1345, 1310, 1286, 1228, 1194, 1138, 1073, 1047, 1028, 1001, 973, 922, 821, 740 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{26}NO_3$ $[M+H]^+$: 364.1907, found 364.1908; SFC conditions: 10% IPA, 4.0 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 2.49, minor = 2.94.

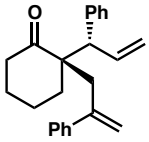
General Procedure for Pd-Catalyzed Allylic Alkylation



(*R*)-2-allyl-2-((*S*)-1-phenylallyl)cyclohexanone (8a). To a 0.5 dram scintillation vial equipped with a magnetic stir bar were added $Pd_2(dba)_3$ (1.3 mg, 0.0014 mmol), **L6** (1.2 mg, 0.0035 mmol), TBAT (16.6 mg, 0.031 mmol) and THF (0.9 mL) in a nitrogen-filled glove box. The dark purple mixture was stirred at ambient glove box temperature (ca. 30 °C) for 35 minutes at which point the mixture had become red-orange. Ketoester **3ea** (10.0 mg, 0.028 mmol) and allyl methylcarbonate (4.1 mg, 0.035 mmol) were then added neat to the reaction mixture. The resulting yellow-green reaction mixture was stirred at 20 °C until full conversion of the starting material was indicated by TLC analysis (reaction times typically ranged from 24 to 36 hours). The vial was removed from the glove box, uncapped and diluted with 2 ml of hexanes. Filtration through a celite pad afforded the crude residue, which was concentrated *in vacuo* and analyzed by ^{1}H NMR to determine the diastereomeric ratio of **8a** and **9a** (2:1). The residue was purified by silica gel flash chromatography (gradient elution, 0→2% EtOAc in hexanes) to afford **8a** and **9a** (6.5 mg, 91% combined yield) as a colorless oil. 99% ee (The enantiomeric excesses of the products **8a** and **9a** are inferred from the corresponding Ir-catalyzed allylic alkylation products (**3ea**)). Spectroscopic data for compound **8a** is as follows: $[\alpha]_D^{25}$ –1.9 (*c* 0.48, $CHCl_3$); R_f = 0.3 (0.4% EtOAc in hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.25–7.20 (m, 3H), 6.20 (dt, *J* = 16.8, 10.1 Hz, 1H), 5.68 (dddd, *J* = 17.1, 10.1, 8.8, 5.4 Hz, 1H), 5.09 (ddd, *J* = 10.1, 1.6, 0.4 Hz, 1H), 5.08 (ddd, *J* = 16.7, 1.7, 0.8 Hz, 1H), 4.98 (dddd, *J* = 10.2, 2.3, 1.3, 0.7 Hz, 1H), 4.92–4.86 (m, 1H), 3.92 (d, *J* = 9.9 Hz, 1H), 2.75 (dd, *J* = 13.7, 5.4 Hz, 1H), 2.56–2.10 (m, 2H), 2.11–1.59 (m, 7H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.9, 140.1, 136.3, 134.9, 130.0, 128.1, 126.8, 117.9, 117.4, 55.7, 52.8, 40.5, 37.6, 31.9, 26.2, 21.1; IR (Neat Film, NaCl) 3073, 3028, 2937, 2864, 1833, 1701, 1636, 1600, 1452, 1432, 1313,

1219, 1125, 1056, 1002, 916, 849, 787, 765 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{18}H_{23}O$ $[M+H]^+$: 255.1754; found 255.1743.

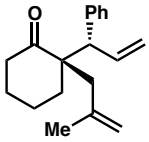
(*R*)-2-((*S*)-1-phenylallyl)-2-(2-phenylallyl)cyclohexanone



8b

Ketone **8b** was isolated by silica gel chromatography (gradient elution, 0→1% Et_2O in hexanes) as a colorless oil. $[\alpha]_D^{25}$ –50.9 (*c* 0.22, $CHCl_3$); R_f = 0.5 (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.13 (m, 10H), 6.24 (dt, *J* = 16.8, 10.1 Hz, 1H), 5.29 (d, *J* = 1.8 Hz, 1H), 5.22–5.02 (m, 3H), 3.92 (d, *J* = 10.0 Hz, 1H), 2.95 (ddd, *J* = 377.8, 13.8, 0.9 Hz, 2H), 2.15–2.00 (m, 2H), 1.76–1.57 (m, 4H), 1.54–1.43 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.8, 145.6, 142.8, 140.3, 136.2, 129.9, 128.1, 128.0, 127.0, 126.7, 126.5, 118.2, 117.7, 56.6, 54.4, 40.6, 37.6, 30.6, 24.8, 21.4; IR (Neat Film, NaCl) 2937, 2859, 1701, 1624, 1597, 1451, 1310, 1256, 1207, 1125 910, 779 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{24}H_{26}O$ $[M+H]^+$: 331.2056, found 331.2065.

(*R*)-2-(2-methylallyl)-2-((*S*)-1-phenylallyl)cyclohexanone



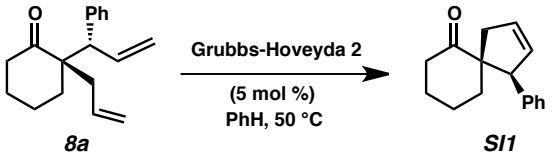
8c

Ketone **8c** was isolated by silica gel chromatography (gradient elution, 0→2% EtOAc in hexanes) as a colorless oil. $[\alpha]_D^{25}$ –41.7 (*c* 0.46, $CHCl_3$); R_f = 0.4 (5% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.33–7.28 (m, 2H), 7.25–7.19 (m, 3H), 6.19 (dt, *J* = 16.8, 10.1 Hz, 1H), 5.08 (dd, *J* = 10.2, 1.6 Hz, 1H), 5.03 (ddd, *J* = 16.8, 1.6, 0.8 Hz, 1H), 4.74 (ddt, *J* = 2.7, 1.8, 0.9 Hz, 1H), 4.52 (ddt, *J* = 2.4, 1.6, 0.9 Hz, 1H), 3.86 (d, *J* = 10.0 Hz, 1H), 2.90 (d, *J* = 13.1 Hz, 1H), 2.37 (dtd, *J* = 16.2, 4.9, 1.6 Hz, 1H), 2.25 (ddd, *J* = 15.9, 11.3, 6.0 Hz, 1H), 2.00 (d, *J* = 13.7 Hz, 1H), 1.93–1.78 (m, 2H), 1.74–1.63 (m, 4H), 1.59 (dt, *J* = 1.4, 0.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.8, 143.0, 140.3, 136.5, 130.1, 128.2, 126.9, 117.4, 115.3, 55.5, 54.2, 40.7, 40.2, 30.8, 25.5, 25.1, 21.4; IR (Neat Film, NaCl) 3071, 3030,

2940, 2865, 1704, 1637, 1599, 1452, 1375, 1314, 1209, 1124, 994, 916, 893, 756 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{19}H_{25}O$ $[M+H]^+$: 269.1920; found 269.1920.

Determination of the Relative Configuration of Compound 8a

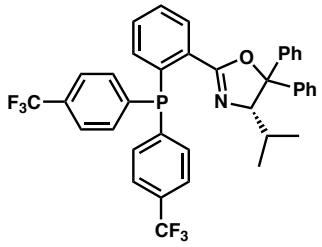
The relative configuration of compound **8a** was determined via NOE analysis of the corresponding spirocycle, **SI1**, obtained via ring-closing metathesis. The experimental procedure by which **SI1** was generated is as follows:



(1*S*,5*R*)-1-phenylspiro[4.5]dec-2-en-6-one (SI1). To a flask charged with Grubbs-Hoveyda second generation catalyst (1.85 mg, 0.0030 mmol) under an atmosphere of argon was added a solution of cyclohexanone **8a** (15.0 mg, 0.059 mmol) in 6 mL benzene. The reaction mixture was heated to 50 °C and stirred for 4 hours, at which point the reaction was determined to be complete by TLC analysis. The reaction vessel was cooled to 25 °C and 0.5 mL of ethyl vinyl ether was added. After 30 minutes of stirring, the crude mixture was purified directly by silica gel chromatography (gradient elution, 0→3% EtOAc in hexanes) to afford spirocycle **SI1** (12.7 mg, 0.056 mmol, 94% yield) as a colorless oil. $[\alpha]_D^{25}$ –133.6 (*c* 0.25, $CHCl_3$); R_f = 0.5 (10% EtOAc in hexanes); ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.24 (m, 2H), 7.24–7.18 (m, 1H), 7.18–7.12 (m, 2H), 6.01–5.52 (m, 1H), 4.75 (p, *J* = 2.1 Hz, 1H), 2.66–2.56 (m, 2H), 2.56–2.44 (m, 2H), 1.95–1.85 (m, 1H), 1.64–1.49 (m, 3H), 1.42 (dtd, *J* = 14.66, 3.6, 2.3 Hz, 1H), 1.35–0.72 (m, 1H), 1.01 (ddd, *J* = 13.9, 11.3, 4.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 212.9, 140.6, 133.8, 129.3, 128.0, 127.4, 126.4, 59.8, 53.7, 42.8, 39.6, 35.5, 26.8, 22.2; IR (Neat Film, NaCl) 3944, 3693, 3053, 2986, 2941, 2866, 2685, 2305, 1698, 1422, 1264, 1129, 896, 756 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{19}O$ $[M+H]^+$: 227.1430; found 227.1431.

Spectroscopic Data for New Phosphinooxazoline Ligands

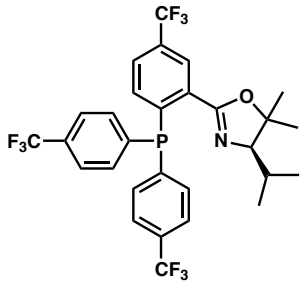
(*S*)-2-(2-(bis(4-(trifluoromethyl)phenyl)phosphino)phenyl)-4-isopropyl-5,5-diphenyl-4,5-dihydrooxazole (*L7*)



L7

$[\alpha]_D^{25}$ –163.33 (*c* 0.75, $CHCl_3$,); R_f = 0.3 (4:1 hexanes in dichloromethane); ^{1}H NMR (500 MHz, C_6D_6) δ 8.22 (ddd, *J* = 7.8, 3.9, 1.4 Hz, 1H), 7.29 (ddd, *J* = 49.4, 8.4, 1.4 Hz, 4H), 7.21–7.14 (m, 5H), 7.10–7.02 (m, 7H), 7.02–6.94 (m, 3H), 6.89 (td, *J* = 7.6, 1.4 Hz, 1H), 6.81 (ddd, *J* = 7.9, 3.4, 1.3 Hz, 1H), 4.66 (d, *J* = 4.5 Hz, 1H), 1.74 (td, *J* = 6.6, 4.6 Hz, 1H), 0.83 (d, *J* = 6.7 Hz, 3H), 0.59 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 160.1 (d, J_{CP} = 3.2 Hz), 145.8 , 144.4–143.9 (m) 141.2 , 137.9 (d, J_{CP} = 27.4 Hz), 134.9, 134.5 (dd, J_{CP} = 70.9, 20.8 Hz), 132.6 (d, J_{CP} = 21.4 HZ), 131.3 , 130.6 (dd, J_{CP} = 32.3, 18.4 Hz), 130.3 (d, J_{CP} = 3.2 Hz), 129.1, 127.5 (d, J_{CF} = 11.2 Hz), 126.8, 125.3 (ddt, J_{CF} = 14.7, 7.6, 3.8 Hz), 124.8 (d, J_{CF} = 273.5 Hz), 93.1, 81.1 (d J_{CP} = 2.0 Hz), 30.60, 22.0; ^{19}F NMR (282 MHz, C_6D_6) δ –62.44, –62.53; ^{31}P NMR (121MHz, C_6D_6) δ –7.59; IR (Neat Film, NaCl) 3060, 2961, 1654, 1605, 1493, 1470, 1448, 1396, 1323, 1166, 1127, 1060, 1016, 954, 832, 756 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{28}H_{30}{}^{19}F_6NOP$ $[M+H]^+$: 662.2042, found 662.2080.

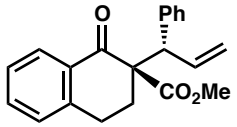
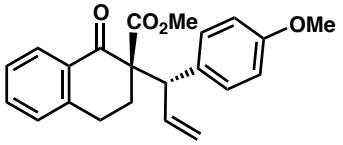
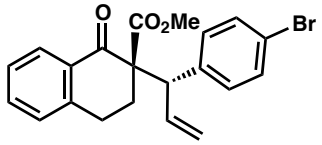
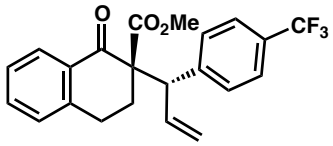
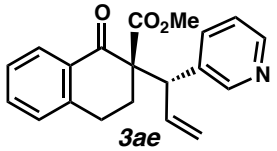
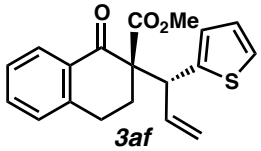
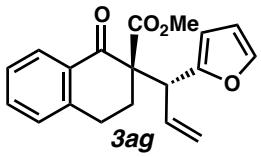
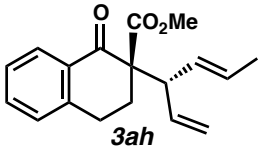
(*R*)-2-(2-(bis(4-(trifluoromethyl)phenyl)phosphino)-5-(trifluoromethyl)phenyl)-4-isopropyl-5,5-dimethyl-4,5-dihydrooxazole (*L8*)

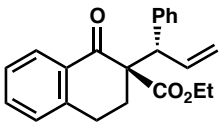
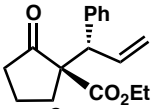
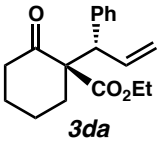
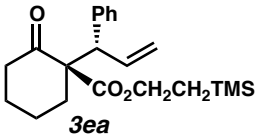
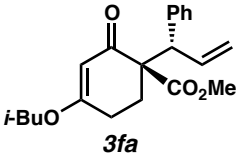
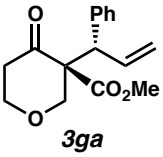
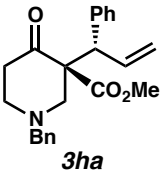


L8

$[\alpha]_D^{25}$ +9.45 (*c* 3.20, $CHCl_3$,); R_f = 0.3 (4:1 hexanes in dichloromethane); ^{1}H NMR (500 MHz, C_6D_6) δ 8.57 (dd, *J* = 3.3, 2.0 Hz, 1H), 7.41–7.36 (m, 4H), 7.21–7.15 (m, 4H), 7.10 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.78 (dd, *J* = 8.0, 3.0 Hz, 1H), 3.22 (d, *J* = 8.4 Hz, 1H), 1.55 (ddt, *J* = 13.0, 8.3, 6.5 Hz, 1H), 1.21 (s, 3H), 1.08 (s, 3H), 0.99 (d, J = 6.5 Hz, 3H), 0.75 (d, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, C_6D_6) δ 159.1 (d, J_{CP} = 4.0 Hz), 143.5 (t, J_{CP} = 14.8 Hz), 142.7 (d, J_{CP} = 30.6 Hz), 134.5 (dd, J_{CP} = 21.3, 15.7 Hz), 133.7 (d, J_{CP} = 19.5 Hz), 131.1 (q, J_{CF} = 3.6 Hz), 126.4–126.1 (m), 125.9 (d, J_{CF} = 3.2 Hz), 126.5–125.0 (m), 123.8 (d, J_{CF} = 3.3 Hz), 123.3, 87.2, 81.7 (d, J_{CP} = 1.5 Hz), 29.1, 28.8, 21.1, 20.8, 20.8 (d, J_{CP} = 1.8 Hz); ^{19}F NMR (282 MHz, C_6D_6) δ –62.63, –62.85; ^{31}P NMR (121MHz, C_6D_6) δ –7.10; IR (Neat Film, NaCl) 2974, 1652, 1397, 1323, 1165, 1128, 1060, 1017, 832, 756 cm^{-1}; HRMS (FAB+) *m/z* calc'd for $C_{29}H_{26}O^{19}F_9NP$ $[M+H]^+$: 606.1608, found 606.1585.

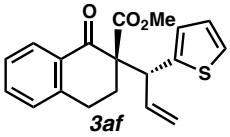
Determination of Enantiomeric Excess (Table S2)

entry	compound	analytic conditions	ee (%)
1	 ***3aa***	**HPLC** **Chiralcel OD-H, λ = 254 nm** **2% IPA/hexanes, 0.6 mL/min** **t_R (min): major 13.80, minor 17.89**	**>99**
2	 ***3ab***	**HPLC** **Chiralpak AD-H, λ = 254 nm** **2% IPA/hexanes, 0.6 mL/min** **t_R (min): minor 27.44, major 37.29**	**>99**
3	 ***3ac***	**HPLC** **Chiralpak AD-H, λ = 254 nm** **2% IPA/hexanes, 0.6 mL/min** **t_R (min): minor 19.71, major 23.59**	**99**
4	 ***3ad***	**SFC** **Chiralpak AD-H, λ = 254 nm** **5% IPA/CO_2, 4.0 mL/min** **t_R (min): minor 3.38, major 3.91**	**>99**
5	 ***3ae***	**HPLC** **Chiralpak AD-H, λ = 254 nm** **90% IPA/hexanes, 1.0 mL/min** **t_R (min): minor 13.45, major 15.72**	**98**
6	 ***3af***	**SFC** **Chiralcel OJ-H, λ = 254 nm** **10% IPA/CO_2, 4.0 mL/min,** **t_R (min): major 2.96, minor 3.63**	**95**
7	 ***3ag***	**SFC** **Chiralpak AD-H, λ = 254 nm** **10% IPA/CO_2, 2.5 mL/min,** **t_R (min): major 5.21, minor 6.03**	**95**
8	 ***3ah***	**SFC** **Chiralpak IC, λ = 254 nm** **2% MeOH/CO_2, 2.5 mL/min,** **t_R (min): minor 8.23, major 8.87**	**90**

entry	compound	analytic conditions	ee (%)
9	 ***3ba***	**SFC** **Chiralpak AD-H, λ = 254 nm** **5% IPA/CO_2, 2.5 mL/min,** **t_R (min): minor 13.82, major 16.53**	**>99**
10	 ***3ca***	**HPLC** **Chiralcel OD-H, λ = 220 nm** **2% IPA/hexanes, 0.6 mL/min** **t_R(min): major 11.23, minor 12.73**	**99**
11	 ***3da***	**SFC** **Chiralpak IC, λ= 210 nm** **10% IPA/CO_2, 4.0 mL/min** **t_R (min): minor 1.69, major 1.94**	**98**
12	 ***3ea***	**SFC** **Chiralcel OJ-H, λ= 210 nm** **3% IPA/CO_2, 2.5 mL/min** **t_R (min): minor 1.93, major 2.24**	**>99**
13	 ***3fa***	**SFC** **Chiralcel OD-H, λ = 254 nm** **10% IPA/CO_2, 2.5 mL/min** **t_R (min): major 3.71, minor 6.24**	**>99**
14	 ***3ga***	**SFC** **Chiralpak AD-H, λ = 210 nm** **5% IPA/CO_2, 2.5 mL/min** **t_R (min): minor 4.65, major 4.95**	**98**
15	 ***3ha***	**SFC** **Chiralpak AD-H, λ = 210 nm** **10% IPA/CO_2, 4.0 mL/min** **t_R (min): major 2.49, minor 2.94**	**97**

Crystal Structure Analysis of Ketoester 3af

The allylation ketoester **3af** (>99% ee) was recrystallized from *i*-PrOH/hexanes (liquid/liquid diffusion) to provide suitable crystals for X-ray analysis, mp = 98-99 °C.



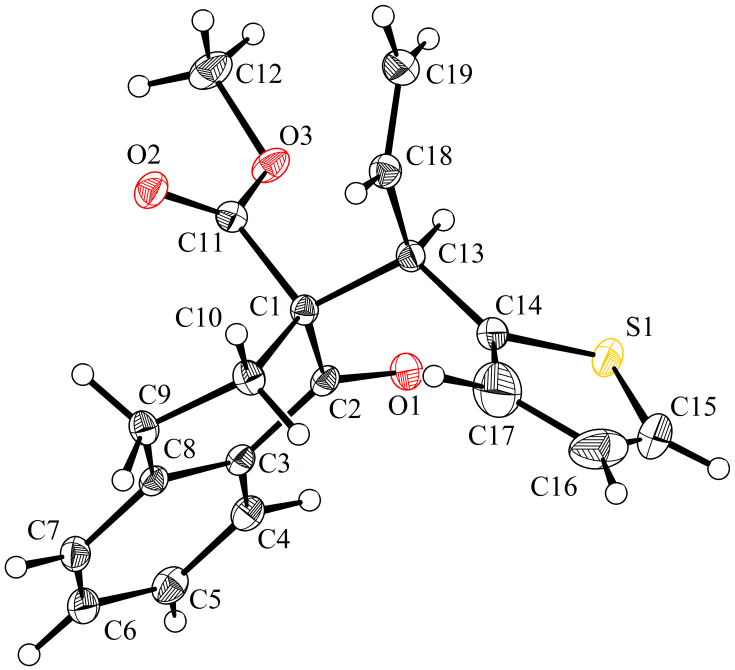


Table S3: Crystal Data and Structure Analysis Details for allylation ketoester 3af (CCDC 939243).

Empirical formula	C19 H18 O3 S
Formula weight	326.39
Crystallization solvent	*i*-PrOH/hexanes
Crystal shape	block
Crystal color	colourless
Crystal size	0.13 x 0.23 x 0.29 mm

Data Collection

Preliminary photograph(s)	rotation
Type of diffractometer	Bruker SMART 1000 ccd
Wavelength	0.71073 Å MoK
Data collection temperature	100 K

Theta range for 9849 reflections used		
in lattice determination	2.30 to 30.92°	
Unit cell dimensions	a = 8.4853(3) Å	a= 90°
	b = 10.8613(4) Å	b= 90°
	c = 17.6979(6) Å	g = 90°
Volume	1631.06(10) $Å^3$	
Z	4	
Crystal system	orthorhombic	
Space group	P 21 21 21 (# 19)	
Density (calculated)	1.329 g/cm^3	
F(000)	688	
Theta range for data collection	2.2 to 36.7°	
Completeness to theta = 25.000°	99.9%	
Index ranges	-14 £ h £ 14, -18 £ k £ 18, -29 £ l £ 29	
Data collection scan type	and scans	
Reflections collected	49310	
Independent reflections	7841 [R_{int}= 0.0476]	
Reflections > 2s(I)	6228	
Average s(I)/(net I)	0.0436	
Absorption coefficient	0.21 mm^{-1}	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9025	

Structure Solution and Refinement

Primary solution method	dual
Secondary solution method	?
Hydrogen placement	difmap
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7841 / 0 / 303
Treatment of hydrogen atoms	refall
Goodness-of-fit on F^2	1.55
Final R indices [I>2s(I), 6228 reflections]	R1 = 0.0483, wR2 = 0.0806
R indices (all data)	R1 = 0.0694, wR2 = 0.0846
Type of weighting scheme used	calc
Weighting scheme used	
Max shift/error	0.000

Average shift/error	0.000
Absolute structure parameter	0.01(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.37 and -0.24 e·Å^{-3}

_refine_ls_abs_structure_details;
Flack x determined using 2400 quotients [(I+)-(I-)]/[(I+)+(I-)];
(Parsons and Flack (2004), Acta Cryst. A60, s61).
_refine_ls_abs_structure_Flack 0.01(3)
_refine_ls_abs_structure_Hooft 0.02(3)

Programs Used

Cell refinement	SAINT V8.27B (Bruker-AXS, 2007)
Data collection	Bruker SMART v5.054 (Bruker-AXS, 2007)
Data reduction	SAINT V8.27B (Bruker-AXS, 2007)
Structure solution	SHELXT (Sheldrick, 2012)
Structure refinement	SHELXL-2013/2 (Sheldrick, 2013)
Graphics	DIAMOND 3 (Crystal Impact, 1999)

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 3af. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U_{eq}
S(1)	9499(4)	3027(2)	9424(2)	26(1)
S(1A)	7396(4)	1194(2)	8920(1)	26(1)
O(1)	10909(1)	3864(1)	7769(1)	20(1)
O(2)	6712(1)	3819(1)	6298(1)	22(1)
O(3)	8198(1)	5196(1)	6915(1)	20(1)
C(1)	8415(2)	3108(1)	7316(1)	14(1)
C(2)	10216(2)	3266(1)	7292(1)	14(1)
C(3)	11064(2)	2667(1)	6651(1)	14(1)
C(4)	12665(2)	2961(1)	6537(1)	18(1)
C(5)	13491(2)	2453(2)	5941(1)	21(1)
C(6)	12737(2)	1641(2)	5451(1)	21(1)
C(7)	11165(2)	1346(1)	5556(1)	18(1)

C(8)	10300(2)	1842(1)	6161(1)	14(1)
C(9)	8605(2)	1477(1)	6273(1)	16(1)
C(10)	7999(2)	1793(1)	7062(1)	17(1)
C(11)	7676(2)	4054(1)	6775(1)	15(1)
C(12)	7433(2)	6145(2)	6468(1)	27(1)
C(13)	7740(2)	3432(1)	8120(1)	16(1)
C(14)	8255(2)	2565(1)	8741(1)	19(1)
C(15)	9443(3)	1759(2)	9876(1)	44(1)
C(16)	8455(3)	892(2)	9630(1)	42(1)
C(17)	7757(14)	1354(11)	8921(7)	51(4)
C(17A)	9366(19)	2793(11)	9301(7)	45(3)
C(18)	5962(2)	3506(2)	8090(1)	18(1)
C(19)	5128(2)	4517(2)	8192(1)	25(1)

Table S4. Bond lengths [Å] and angles [°] for 3af.

S(1)-C(14)	1.681(3)
S(1)-C(15)	1.594(4)
S(1A)-C(14)	1.688(3)
S(1A)-C(16)	1.579(3)
O(1)-C(2)	1.2177(17)
O(2)-C(11)	1.2030(18)
O(3)-C(11)	1.3403(17)
O(3)-C(12)	1.452(2)
C(1)-C(2)	1.538(2)
C(1)-C(10)	1.539(2)
C(1)-C(11)	1.539(2)
C(1)-C(13)	1.5733(19)
C(2)-C(3)	1.492(2)
C(3)-C(4)	1.409(2)
C(3)-C(8)	1.406(2)
C(4)-H(4)	0.967(17)
C(4)-C(5)	1.380(2)
C(5)-H(5)	0.950(19)
C(5)-C(6)	1.394(2)
C(6)-H(6)	0.958(18)
C(6)-C(7)	1.385(2)

C(7)-H(7)	0.963(16)
C(7)-C(8)	1.405(2)
C(8)-C(9)	1.505(2)
C(9)-H(9A)	0.942(17)
C(9)-H(9B)	1.013(17)
C(9)-C(10)	1.527(2)
C(10)-H(10A)	0.977(17)
C(10)-H(10B)	0.966(18)
C(12)-H(12A)	0.96(2)
C(12)-H(12B)	1.03(2)
C(12)-H(12C)	1.02(2)
C(13)-H(13)	0.996(18)
C(13)-C(14)	1.511(2)
C(13)-C(18)	1.511(2)
C(14)-C(17)	1.418(11)
C(14)-C(17A)	1.391(12)
C(15)-H(15)	0.90(3)
C(15)-C(16)	1.334(3)
C(15)-C(17A)	1.517(15)
C(16)-H(16)	0.98(3)
C(16)-C(17)	1.476(12)
C(17)-H(17)	1.04(4)
C(17A)-H(17A)	0.97(5)
C(18)-H(18)	0.950(18)
C(18)-C(19)	1.319(2)
C(19)-H(19A)	0.97(2)
C(19)-H(19B)	1.01(2)

C(15)-S(1)-C(14)	94.87(18)
C(16)-S(1A)-C(14)	95.02(18)
C(11)-O(3)-C(12)	114.07(12)
C(2)-C(1)-C(10)	108.86(12)
C(2)-C(1)-C(11)	108.20(11)
C(2)-C(1)-C(13)	111.27(11)
C(10)-C(1)-C(13)	112.89(12)
C(11)-C(1)-C(10)	110.12(12)
C(11)-C(1)-C(13)	105.36(11)

O(1)-C(2)-C(1)	121.30(13)
O(1)-C(2)-C(3)	121.79(13)
C(3)-C(2)-C(1)	116.91(12)
C(4)-C(3)-C(2)	118.41(13)
C(8)-C(3)-C(2)	121.60(13)
C(8)-C(3)-C(4)	119.98(13)
C(3)-C(4)-H(4)	118.7(10)
C(5)-C(4)-C(3)	120.59(14)
C(5)-C(4)-H(4)	120.7(10)
C(4)-C(5)-H(5)	120.4(11)
C(4)-C(5)-C(6)	119.70(15)
C(6)-C(5)-H(5)	119.9(11)
C(5)-C(6)-H(6)	119.0(11)
C(7)-C(6)-C(5)	120.27(15)
C(7)-C(6)-H(6)	120.7(11)
C(6)-C(7)-H(7)	121.4(10)
C(6)-C(7)-C(8)	121.19(15)
C(8)-C(7)-H(7)	117.4(10)
C(3)-C(8)-C(9)	121.84(13)
C(7)-C(8)-C(3)	118.25(13)
C(7)-C(8)-C(9)	119.90(13)
C(8)-C(9)-H(9A)	108.3(10)
C(8)-C(9)-H(9B)	109.8(10)
C(8)-C(9)-C(10)	112.49(12)
H(9A)-C(9)-H(9B)	104.7(14)
C(10)-C(9)-H(9A)	108.8(10)
C(10)-C(9)-H(9B)	112.4(9)
C(1)-C(10)-H(10A)	107.6(10)
C(1)-C(10)-H(10B)	109.6(10)
C(9)-C(10)-C(1)	113.53(12)
C(9)-C(10)-H(10A)	109.2(10)
C(9)-C(10)-H(10B)	109.8(10)
H(10A)-C(10)-H(10B)	106.8(14)
O(2)-C(11)-O(3)	123.43(13)
O(2)-C(11)-C(1)	124.93(13)
O(3)-C(11)-C(1)	111.60(12)
O(3)-C(12)-H(12A)	113.2(14)

O(3)-C(12)-H(12B)	106.2(11)
O(3)-C(12)-H(12C)	110.2(11)
H(12A)-C(12)-H(12B)	109.9(18)
H(12A)-C(12)-H(12C)	106.8(18)
H(12B)-C(12)-H(12C)	110.5(16)
C(1)-C(13)-H(13)	106.6(10)
C(14)-C(13)-C(1)	114.33(12)
C(14)-C(13)-H(13)	107.1(10)
C(18)-C(13)-C(1)	110.12(12)
C(18)-C(13)-H(13)	108.2(10)
C(18)-C(13)-C(14)	110.28(13)
C(13)-C(14)-S(1)	121.21(15)
C(13)-C(14)-S(1A)	124.16(14)
C(17)-C(14)-S(1)	107.6(5)
C(17)-C(14)-C(13)	131.0(5)
C(17A)-C(14)-S(1A)	108.4(6)
C(17A)-C(14)-C(13)	127.1(6)
S(1)-C(15)-H(15)	120.9(19)
C(16)-C(15)-S(1)	117.68(19)
C(16)-C(15)-H(15)	121.4(19)
C(16)-C(15)-C(17A)	106.1(5)
C(17A)-C(15)-H(15)	132(2)
S(1A)-C(16)-H(16)	113.9(17)
C(15)-C(16)-S(1A)	118.07(19)
C(15)-C(16)-H(16)	128.0(17)
C(15)-C(16)-C(17)	106.8(5)
C(17)-C(16)-H(16)	125.0(17)
C(14)-C(17)-C(16)	112.8(8)
C(14)-C(17)-H(17)	116(2)
C(16)-C(17)-H(17)	131(2)
C(14)-C(17A)-C(15)	112.1(9)
C(14)-C(17A)-H(17A)	124(3)
C(15)-C(17A)-H(17A)	124(3)
C(13)-C(18)-H(18)	118.4(11)
C(19)-C(18)-C(13)	125.07(16)
C(19)-C(18)-H(18)	116.5(11)
C(18)-C(19)-H(19A)	121.1(14)

C(18)-C(19)-H(19B)	119.8(11)
H(19A)-C(19)-H(19B)	119.1(17)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for 3af. The anisotropic displacement factor exponent takes the form: $-2p^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	360(9)	243(10)	173(5)	5(6)	-83(5)	58(8)
S(1A)	335(10)	229(6)	231(7)	93(6)	-46(6)	-2(6)
O(1)	198(5)	189(5)	197(5)	-39(4)	-40(4)	-28(4)
O(2)	242(6)	202(5)	213(5)	-7(4)	-87(5)	5(4)
O(3)	220(6)	136(5)	253(6)	36(4)	-82(5)	-16(4)
C(1)	145(6)	132(6)	130(6)	-2(5)	-6(5)	-11(5)
C(2)	168(7)	127(6)	140(6)	26(5)	-27(5)	-4(5)
C(3)	151(6)	139(6)	138(6)	19(5)	-17(5)	-6(5)
C(4)	166(7)	188(7)	188(7)	24(5)	-23(6)	-20(6)
C(5)	160(7)	267(8)	204(7)	46(6)	-2(6)	-6(6)
C(6)	232(8)	258(8)	146(7)	24(6)	23(6)	39(6)
C(7)	223(8)	188(7)	143(6)	4(5)	-6(6)	3(6)
C(8)	168(7)	131(6)	136(6)	23(5)	-18(5)	4(5)
C(9)	185(7)	142(6)	153(6)	-24(5)	-2(5)	-32(5)
C(10)	191(7)	139(7)	170(7)	-10(5)	10(5)	-36(5)
C(11)	149(7)	150(6)	157(6)	4(5)	14(5)	-6(5)
C(12)	330(10)	151(7)	333(9)	58(7)	-107(8)	5(7)
C(13)	197(7)	140(6)	136(6)	-6(5)	-7(5)	4(5)
C(14)	215(7)	198(7)	152(7)	4(5)	7(6)	34(6)
C(15)	537(14)	571(14)	214(9)	-26(9)	-113(9)	224(12)
C(16)	451(13)	329(11)	469(12)	186(9)	150(10)	127(10)
C(17)	480(60)	540(60)	500(50)	-210(40)	-180(40)	20(40)
C(17A)	510(50)	330(50)	510(70)	90(40)	70(50)	-90(40)
C(18)	185(7)	194(7)	163(7)	6(6)	6(6)	-3(6)

C(19)	262(9)	251(9)	244(8)	-56(7)	-34(7)	49(7)

Table S6. Hydrogen coordinates (x 10^3) and isotropic displacement parameters ($Å^2$x 10^3) for 3af.

	x	y	z	U_{iso}
H(4)	1318(2)	350(2)	689(1)	11(4)
H(5)	1457(2)	265(2)	587(1)	23(5)
H(6)	1331(2)	131(2)	503(1)	18(4)
H(7)	1063(2)	79(1)	522(1)	12(4)
H(9A)	852(2)	62(2)	620(1)	14(4)
H(9B)	793(2)	185(2)	586(1)	14(4)
H(10A)	846(2)	122(2)	743(1)	14(4)
H(10B)	687(2)	168(2)	708(1)	17(4)
H(12A)	766(3)	608(2)	594(1)	44(6)
H(12B)	784(2)	697(2)	667(1)	32(5)
H(12C)	624(3)	608(2)	652(1)	32(5)
H(13)	815(2)	426(2)	825(1)	17(4)
H(15)	1003(3)	165(3)	1030(2)	72(8)
H(16)	827(3)	7(3)	985(2)	80(9)
H(17)	689(4)	98(3)	857(2)	10(8)
H(17A)	1003(5)	352(4)	932(2)	9(11)
H(18)	539(2)	277(2)	799(1)	20(4)
H(19A)	564(3)	531(2)	828(1)	40(6)
H(19B)	394(2)	448(2)	818(1)	27(5)

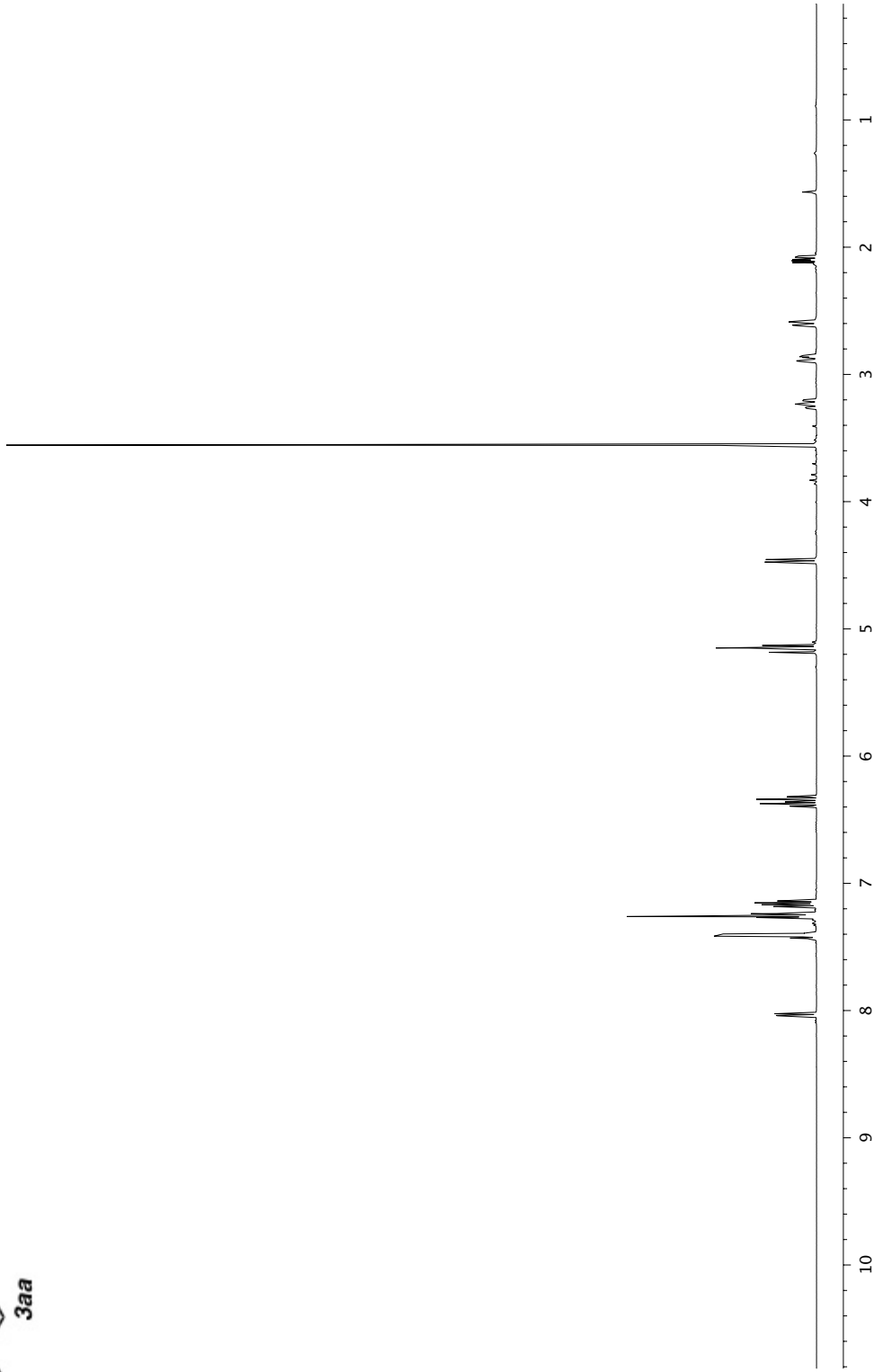
Table S7. Hydrogen bonds for 3af [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(12)-H(12B)...O(1)#1	1.03(2)	2.52(2)	3.539(2)	173.4(16)

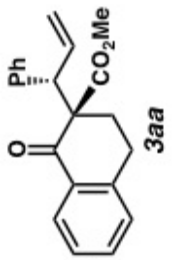
Symmetry transformations used to generate equivalent atoms:

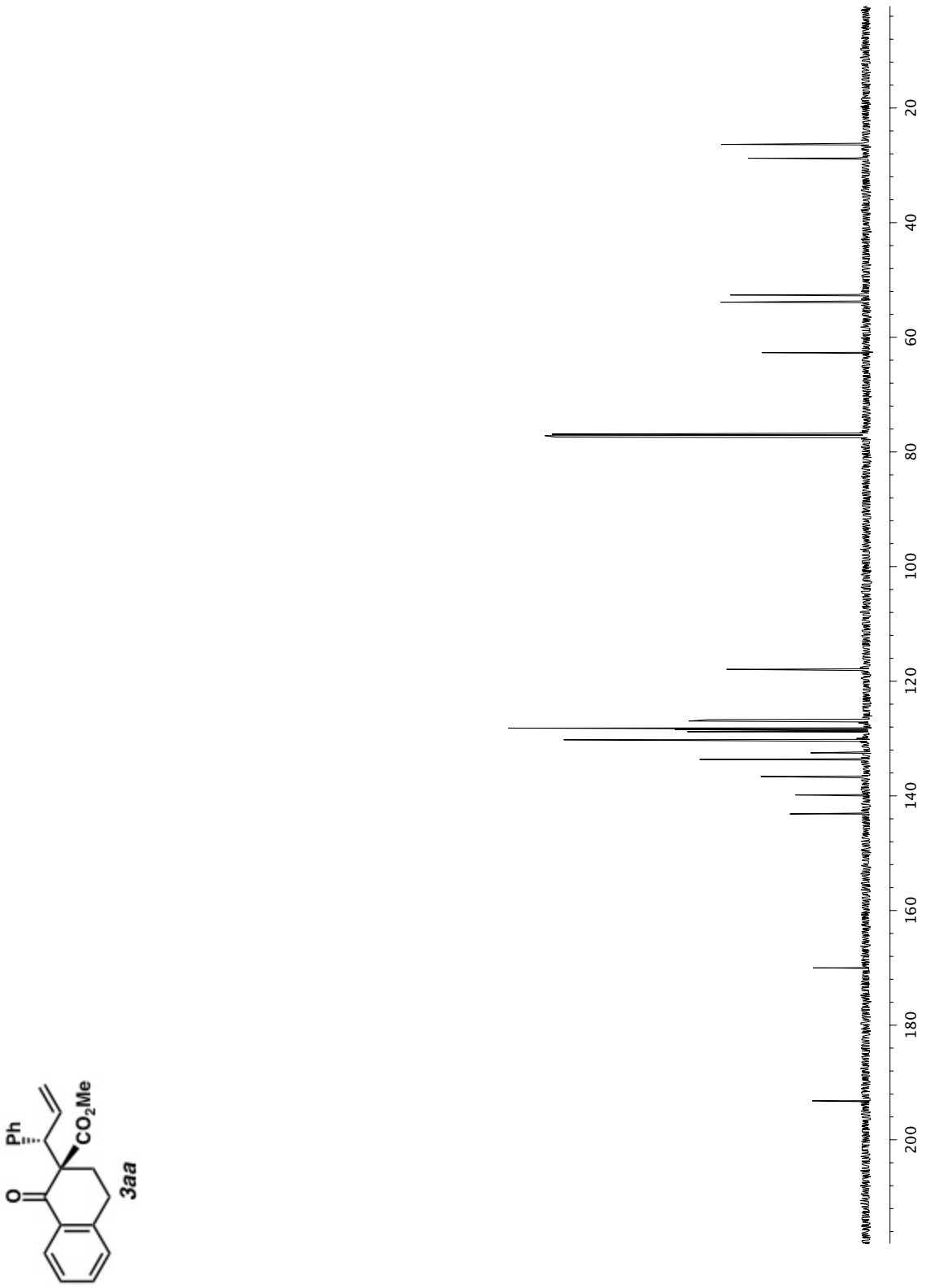
#1 -x+2,y+1/2,-z+3/2

^{1}H NMR and ^{13}C NMR Spectra

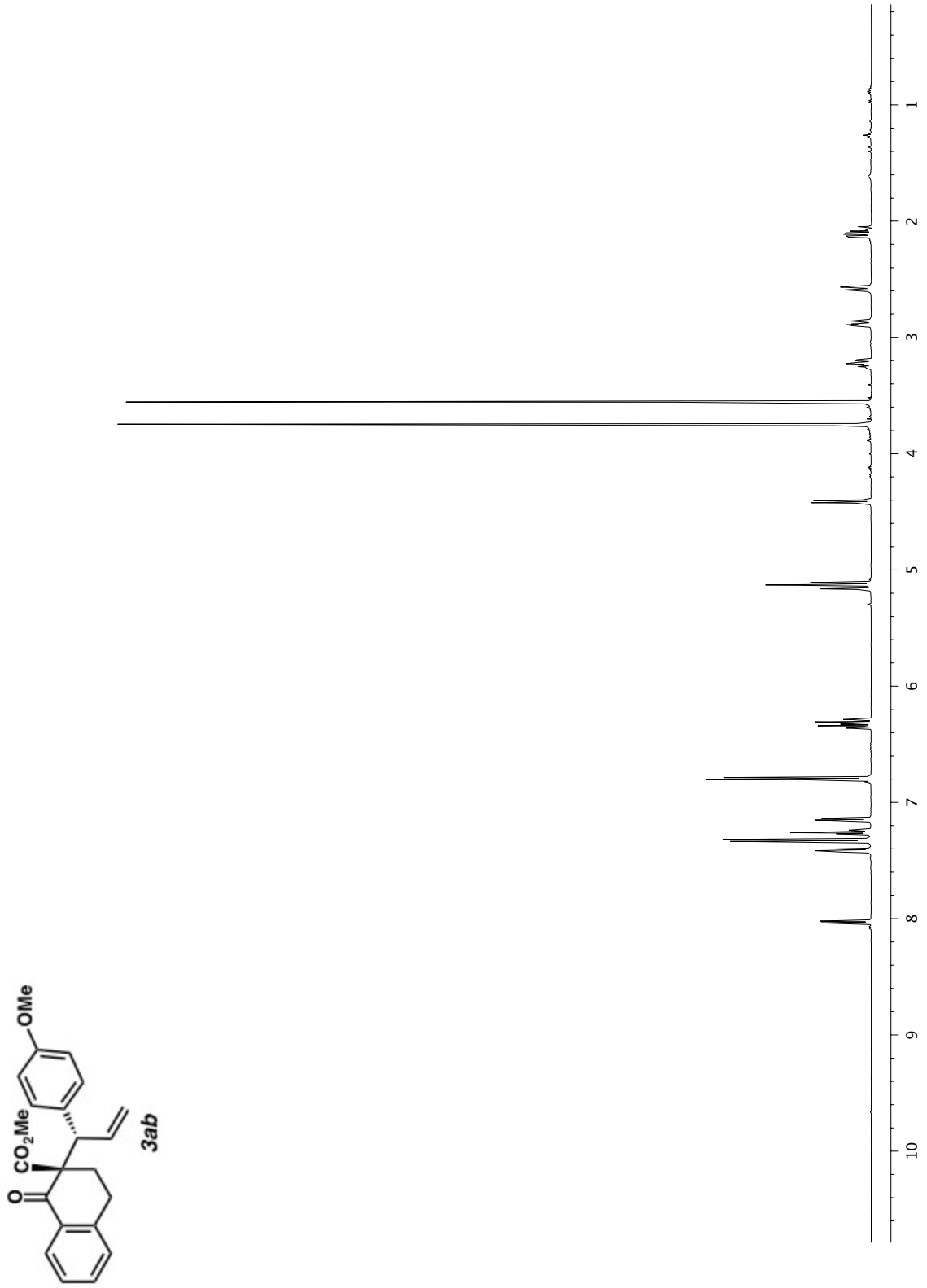


^{1}H NMR (500 MHz, $CDCl_3$) of compound **3aa**.

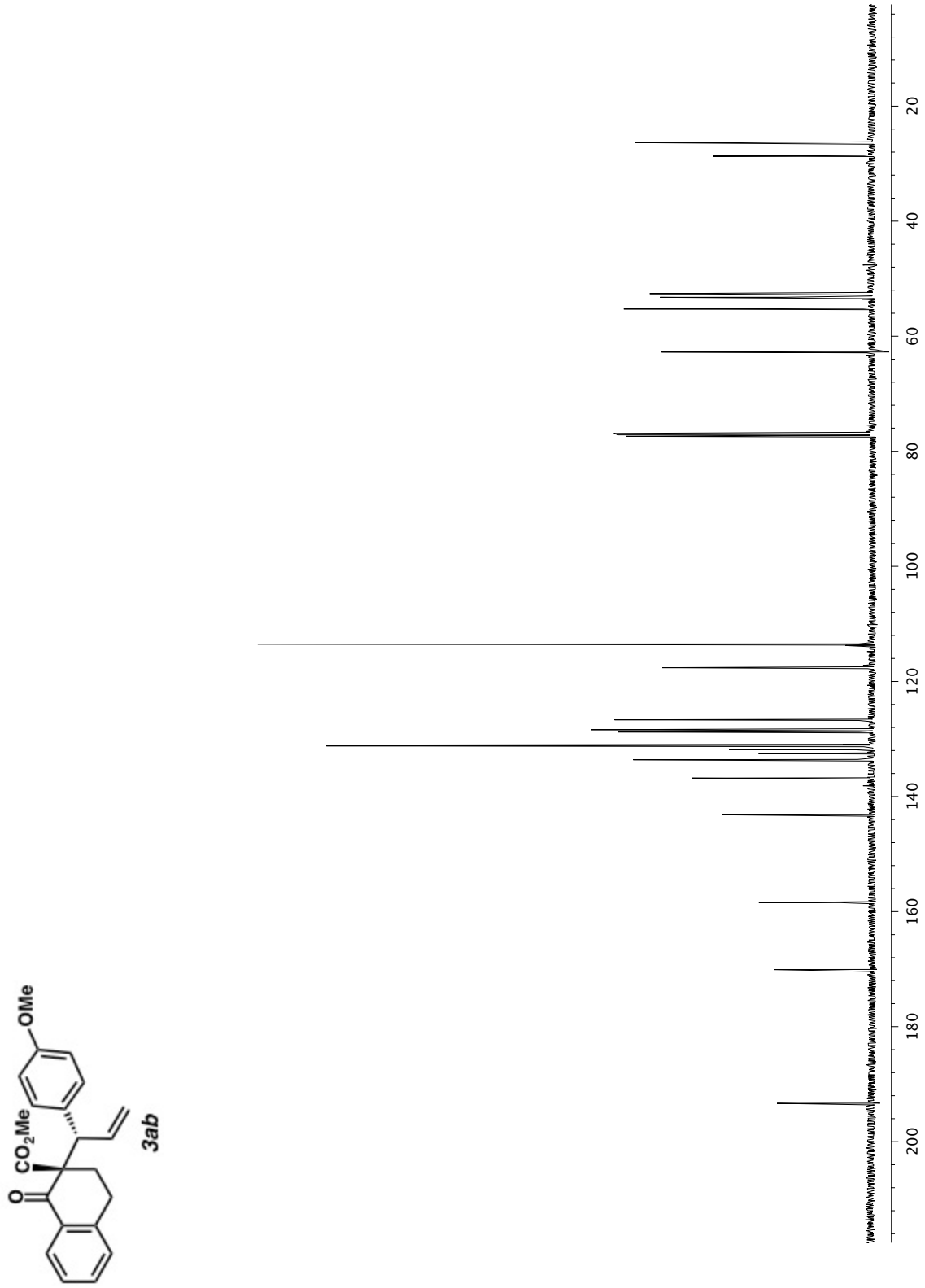




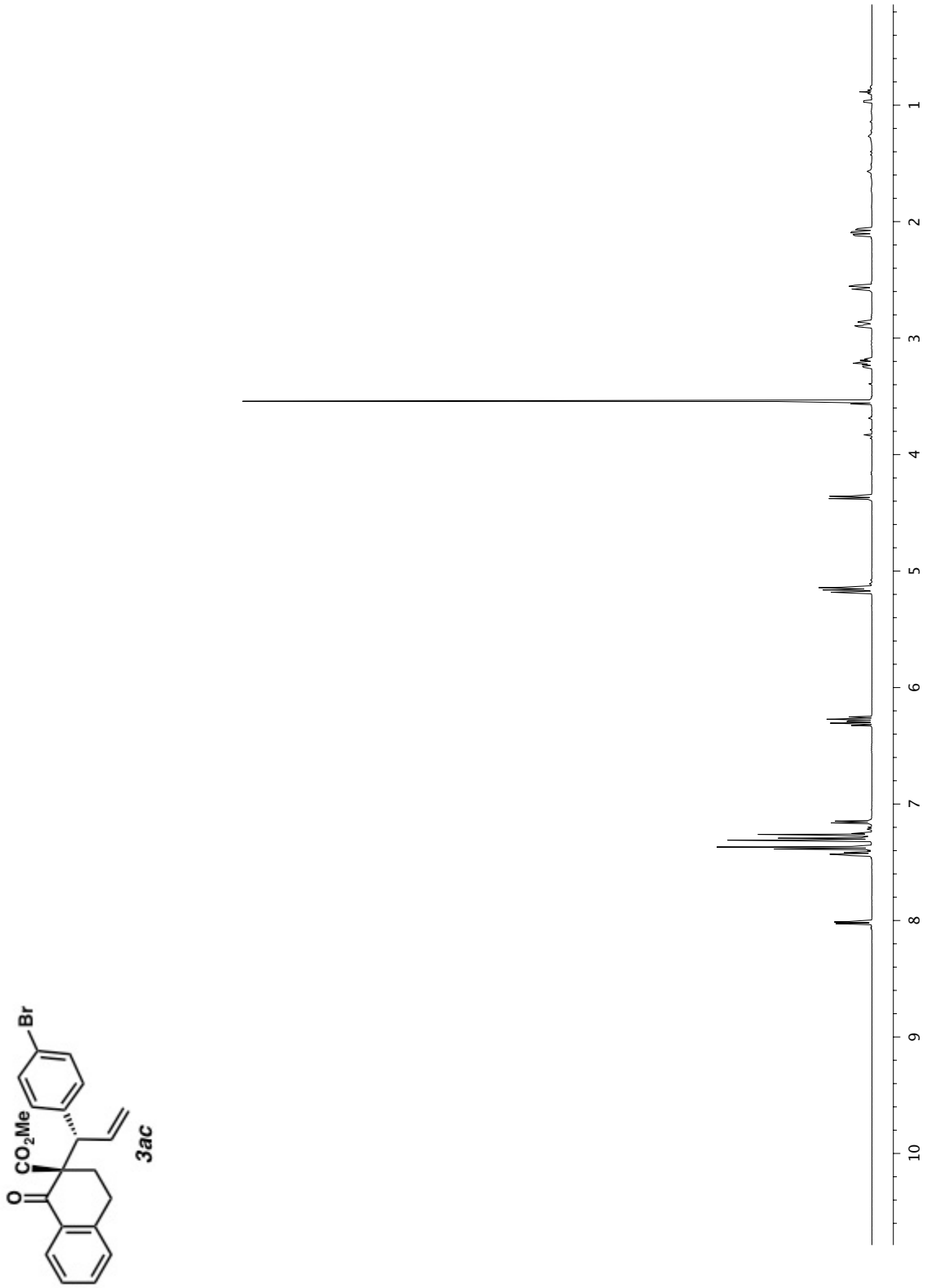
^{13}C NMR (500 MHz, $CDCl_3$) of compound **3aa**.



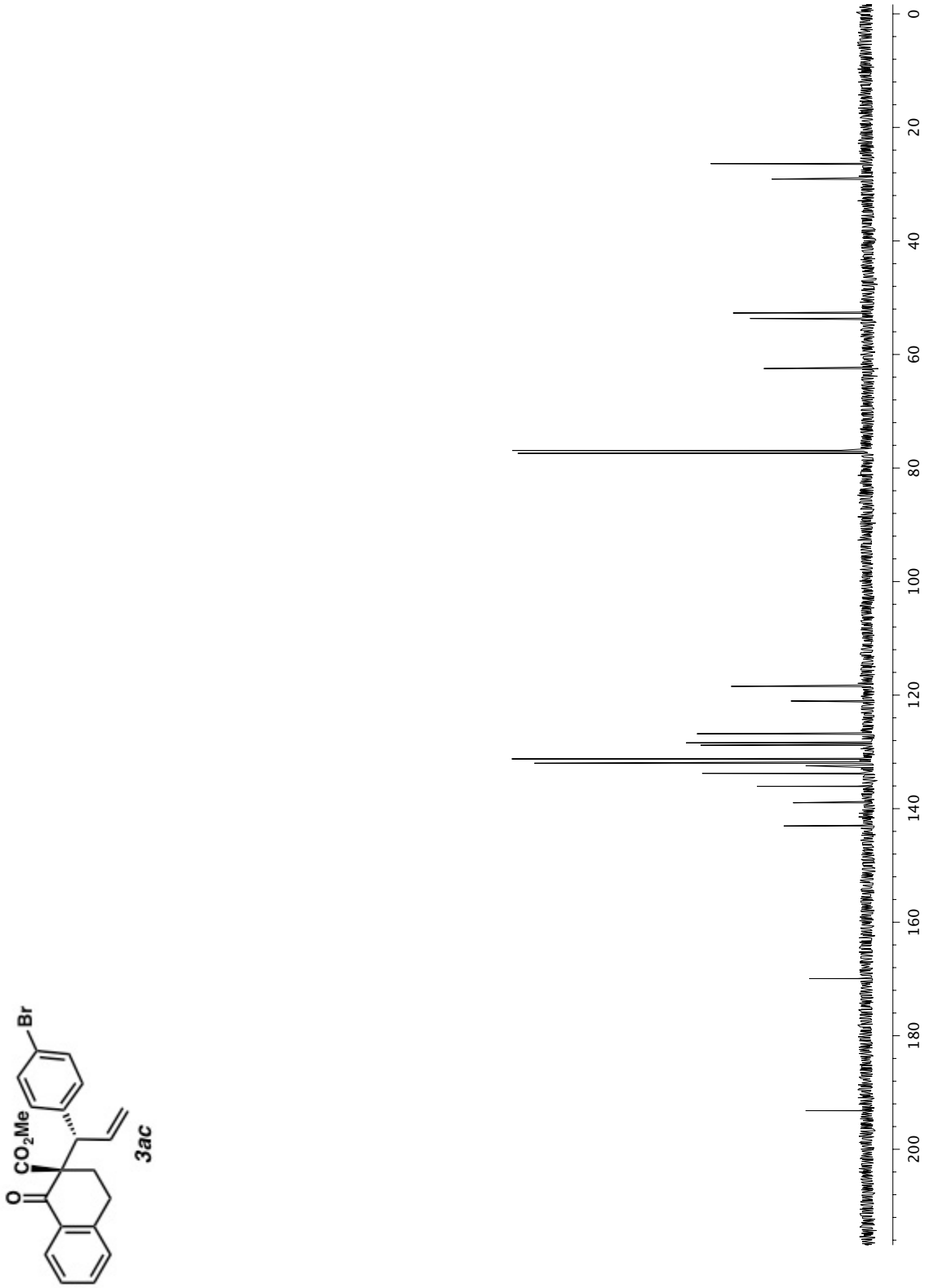
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ab**.



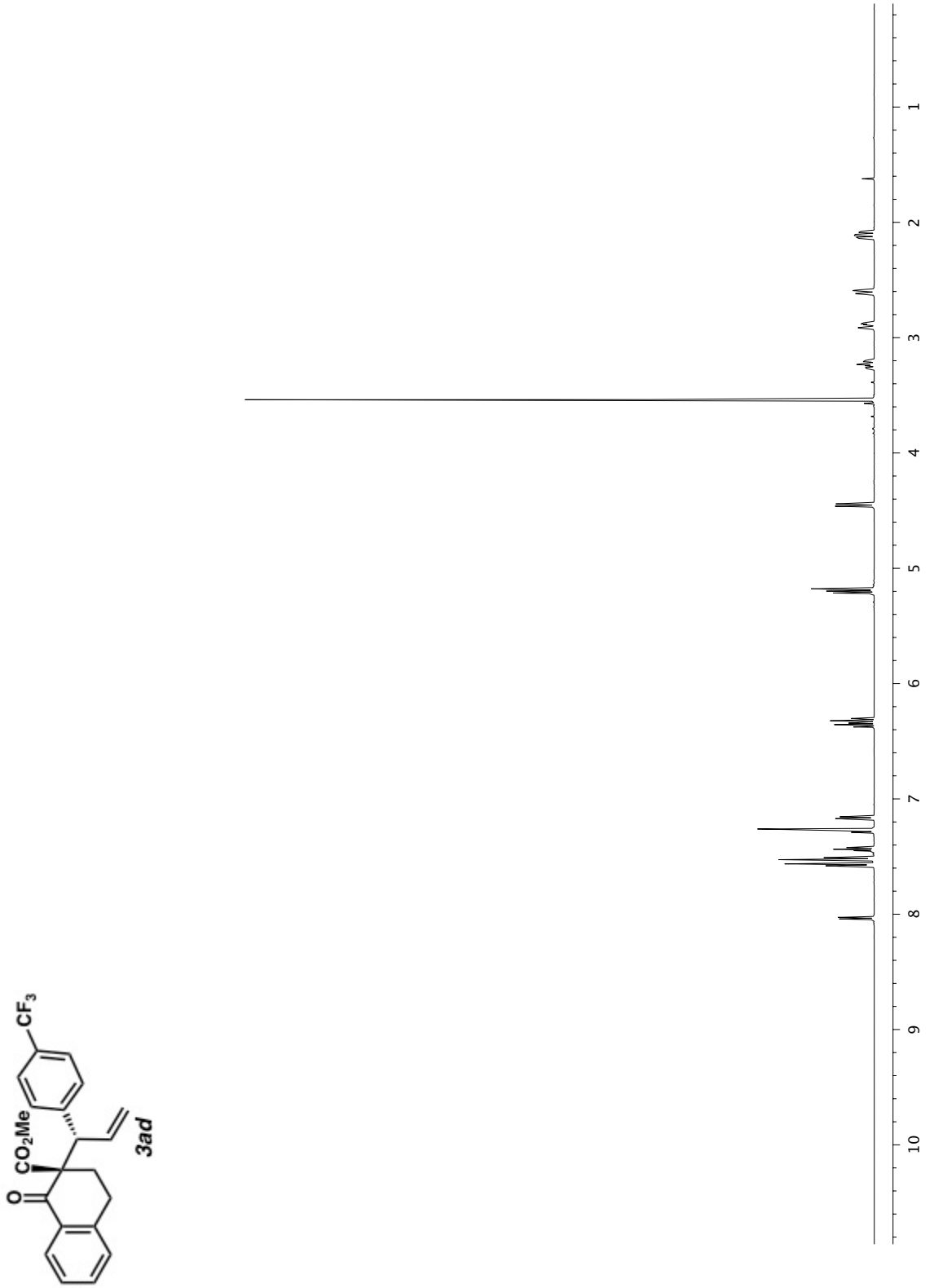
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ab**.



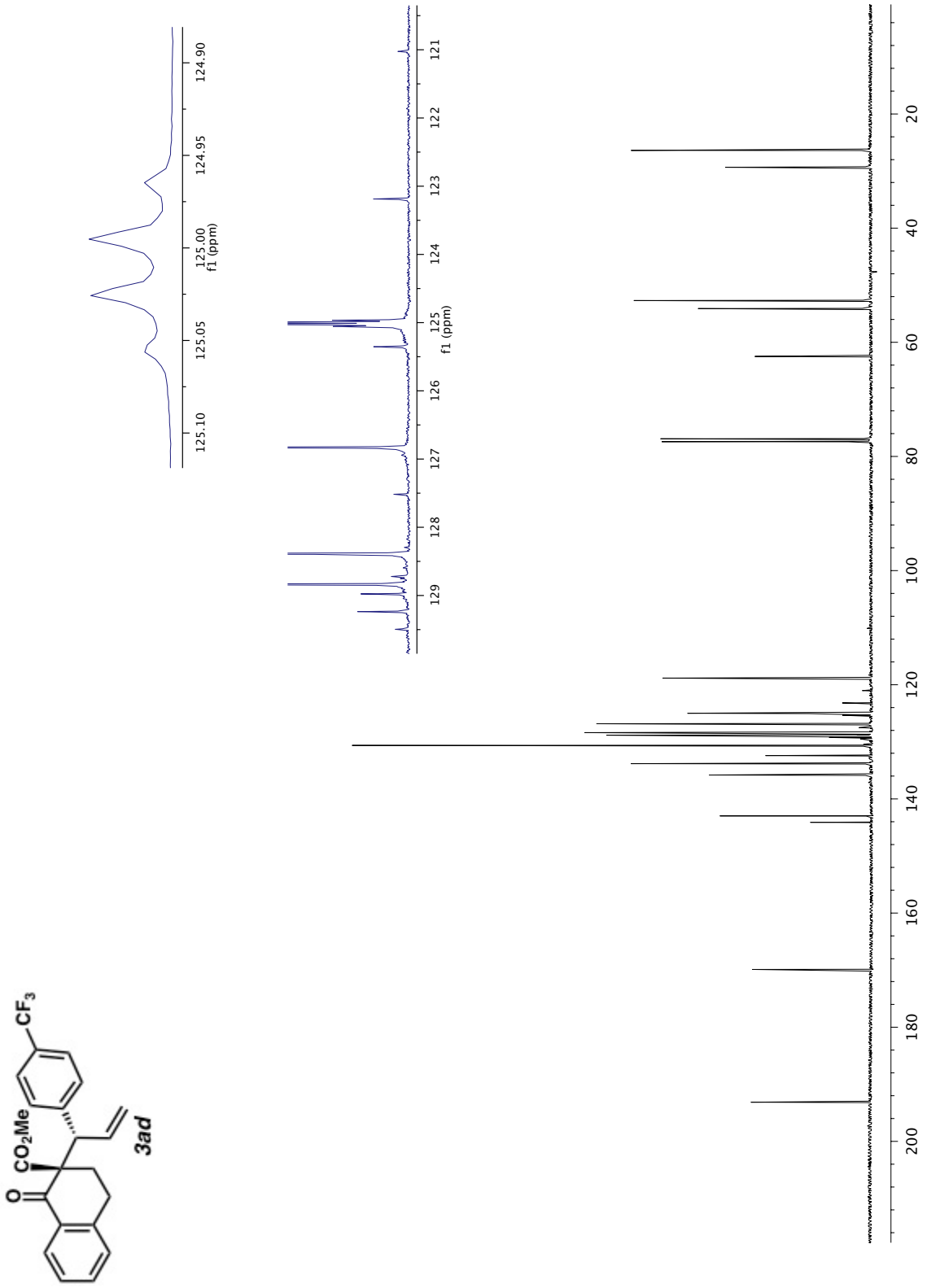
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ac**.



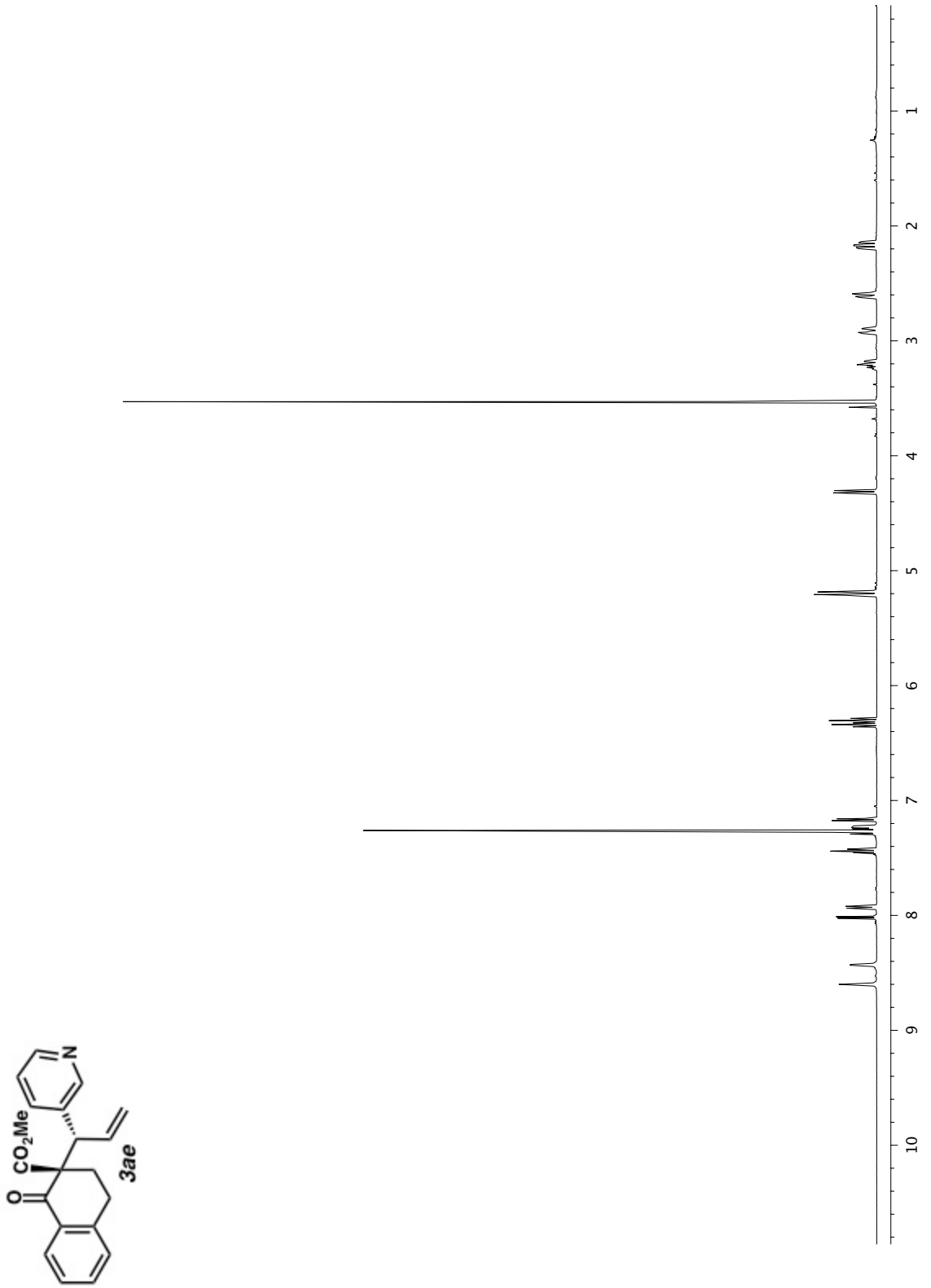
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ac**.



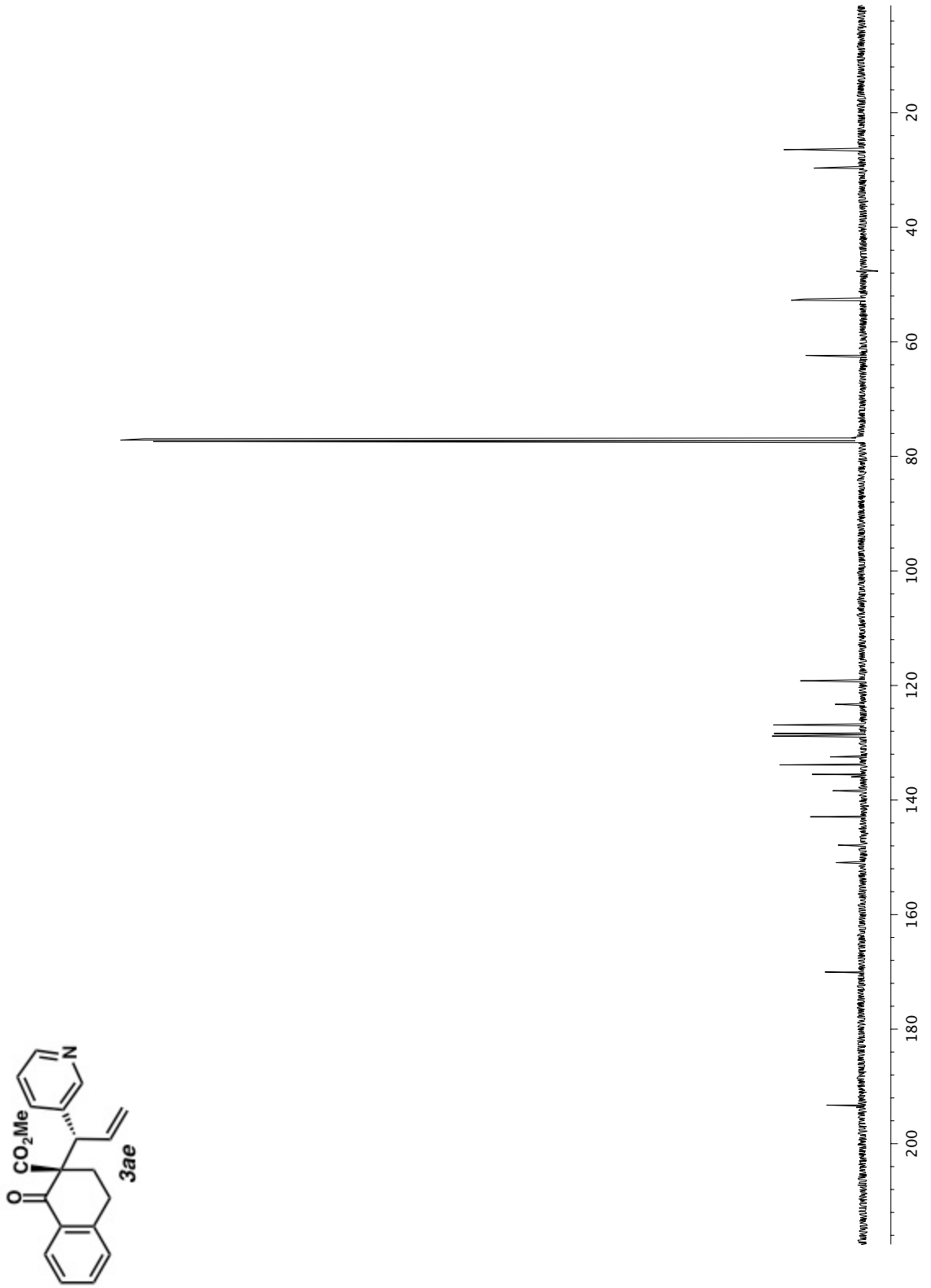
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ad**.



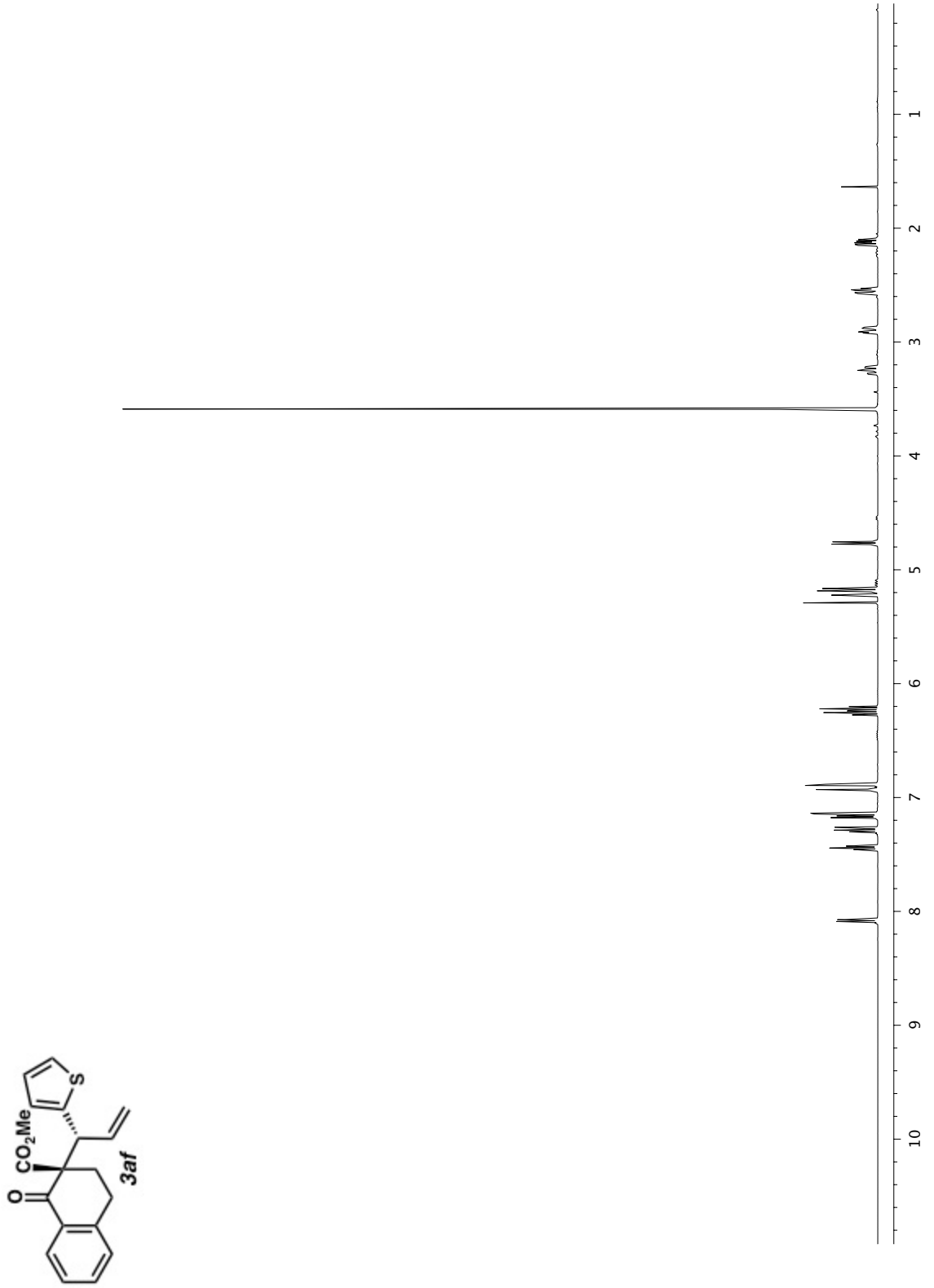
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ad**.



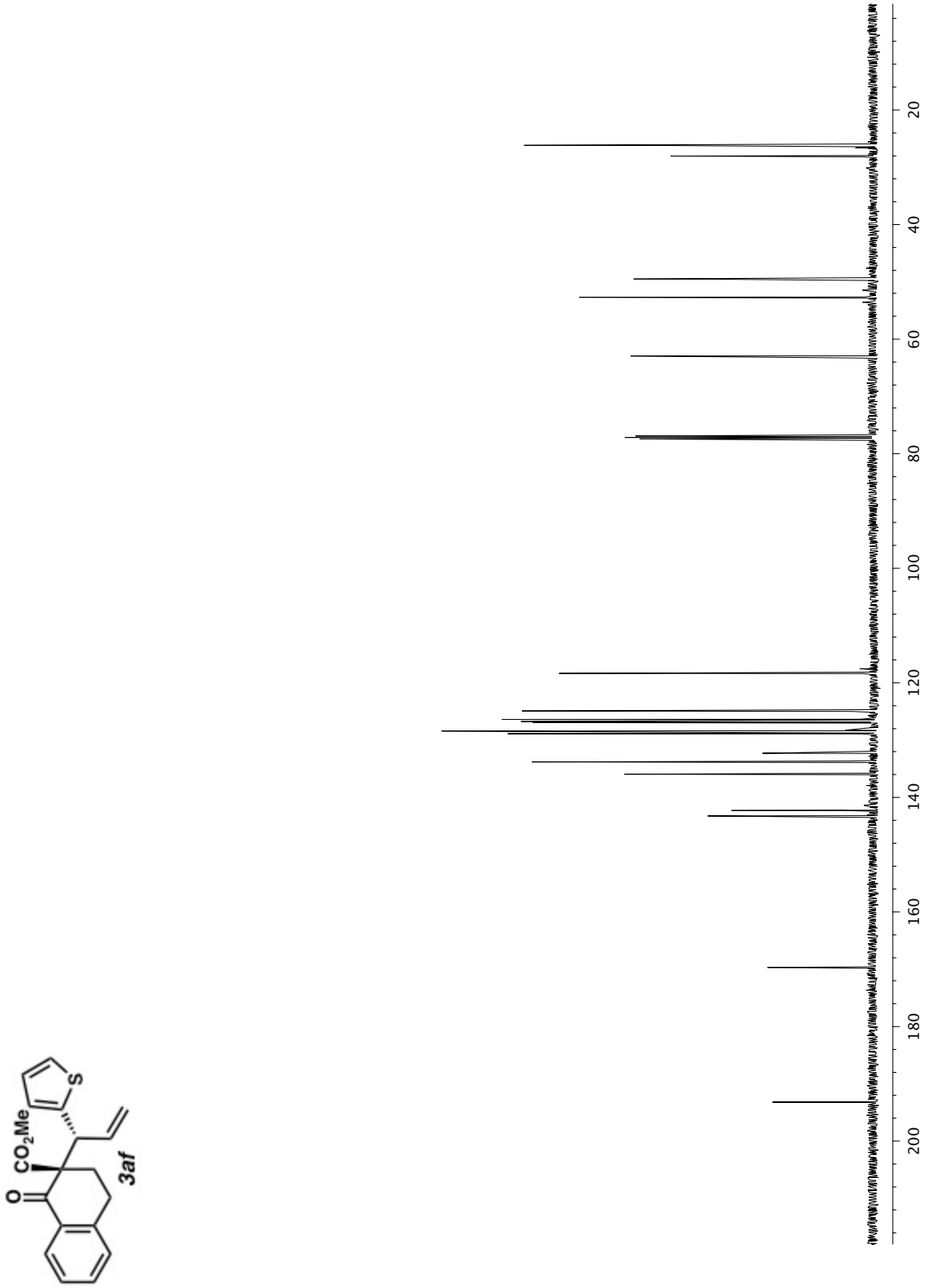
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ae**.



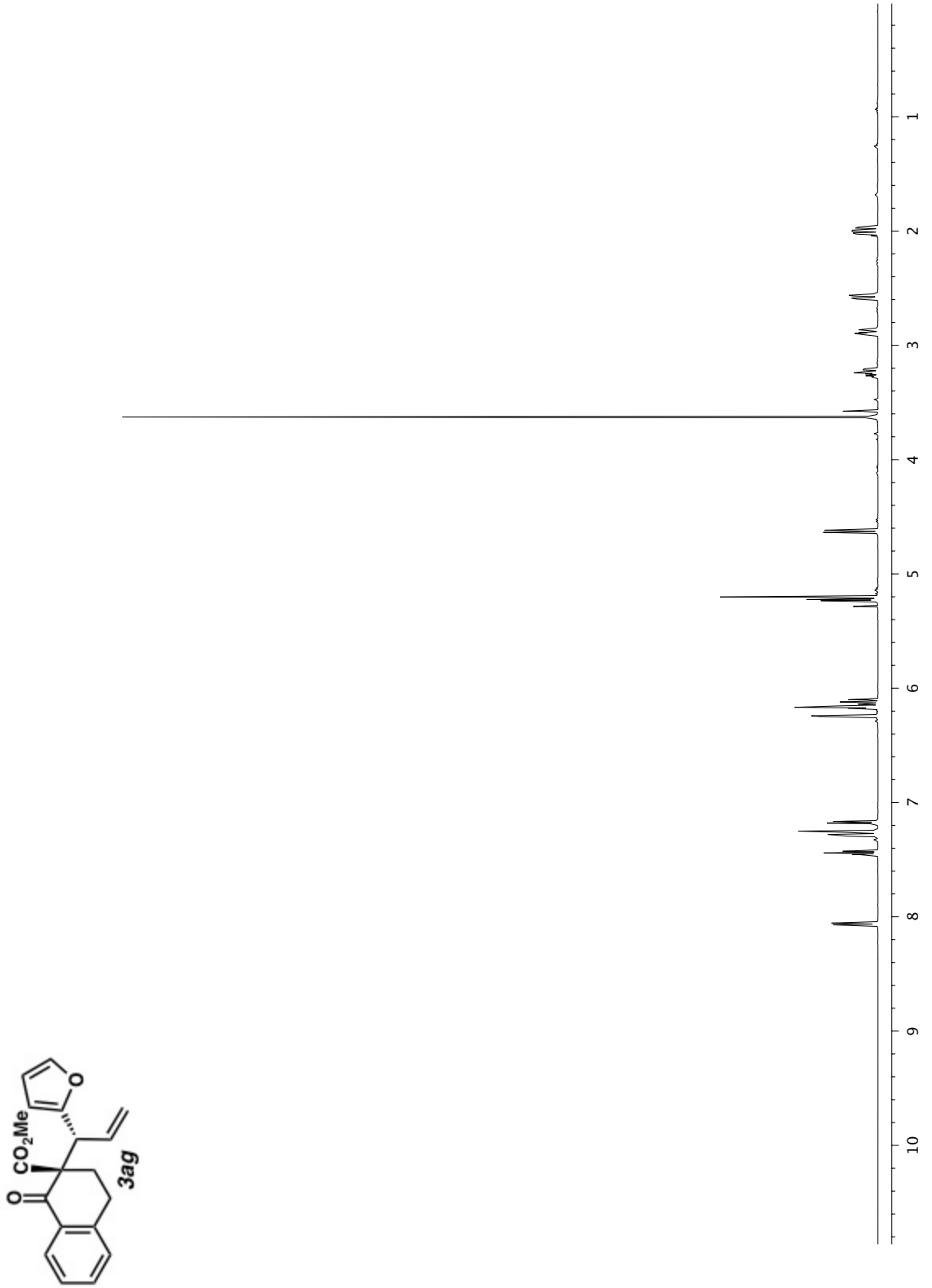
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ae**.



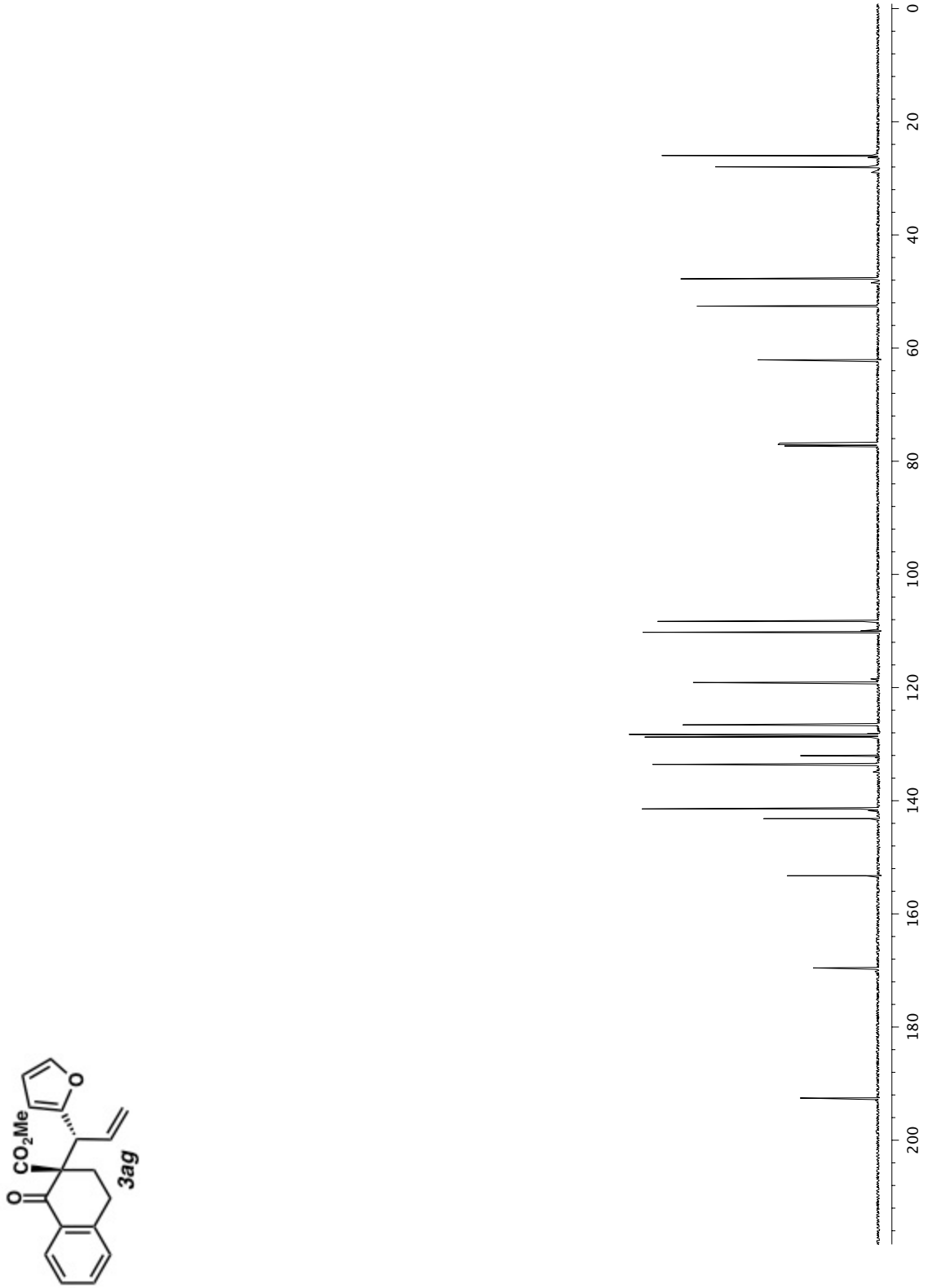
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3af**.



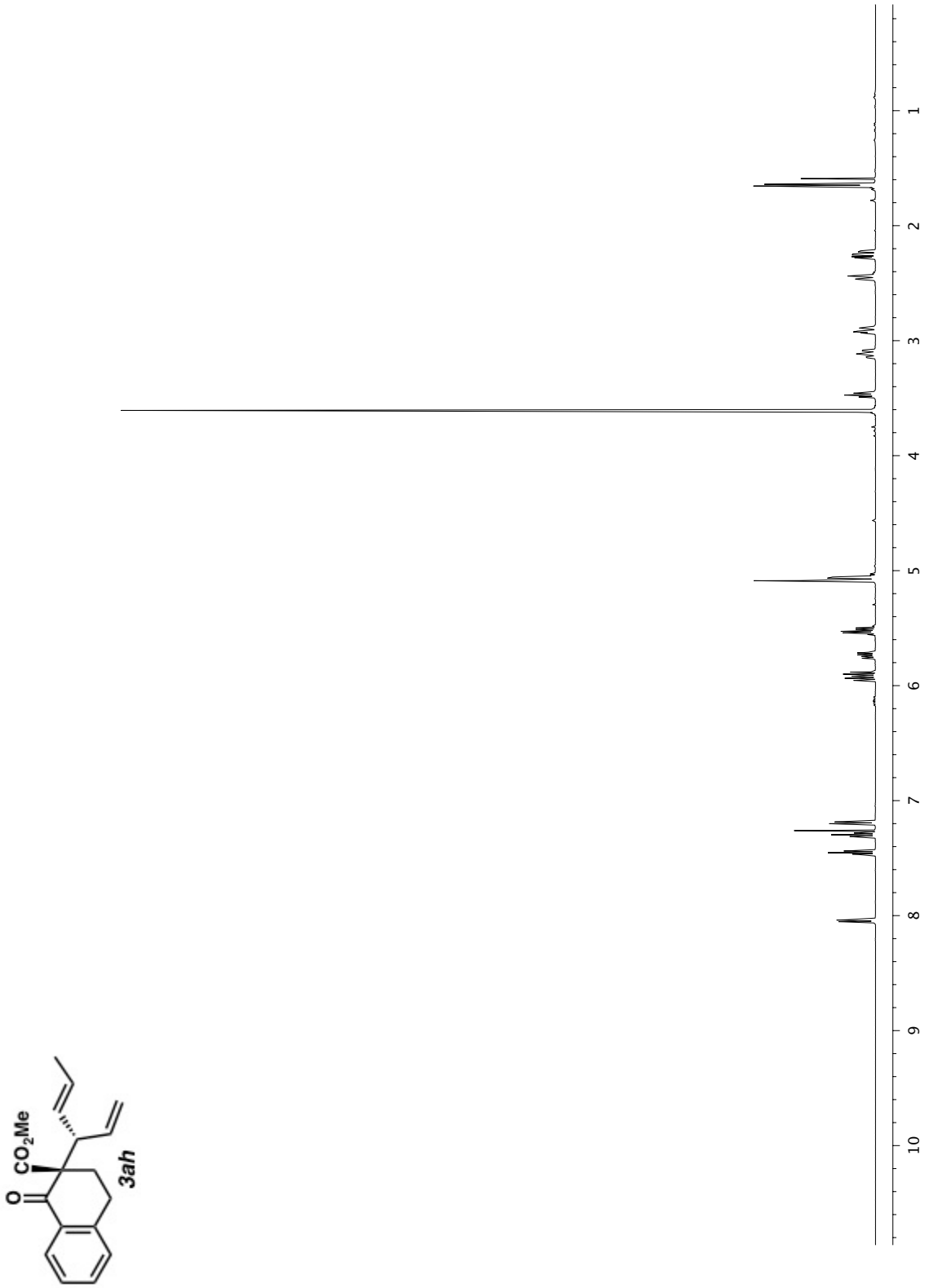
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3af**.



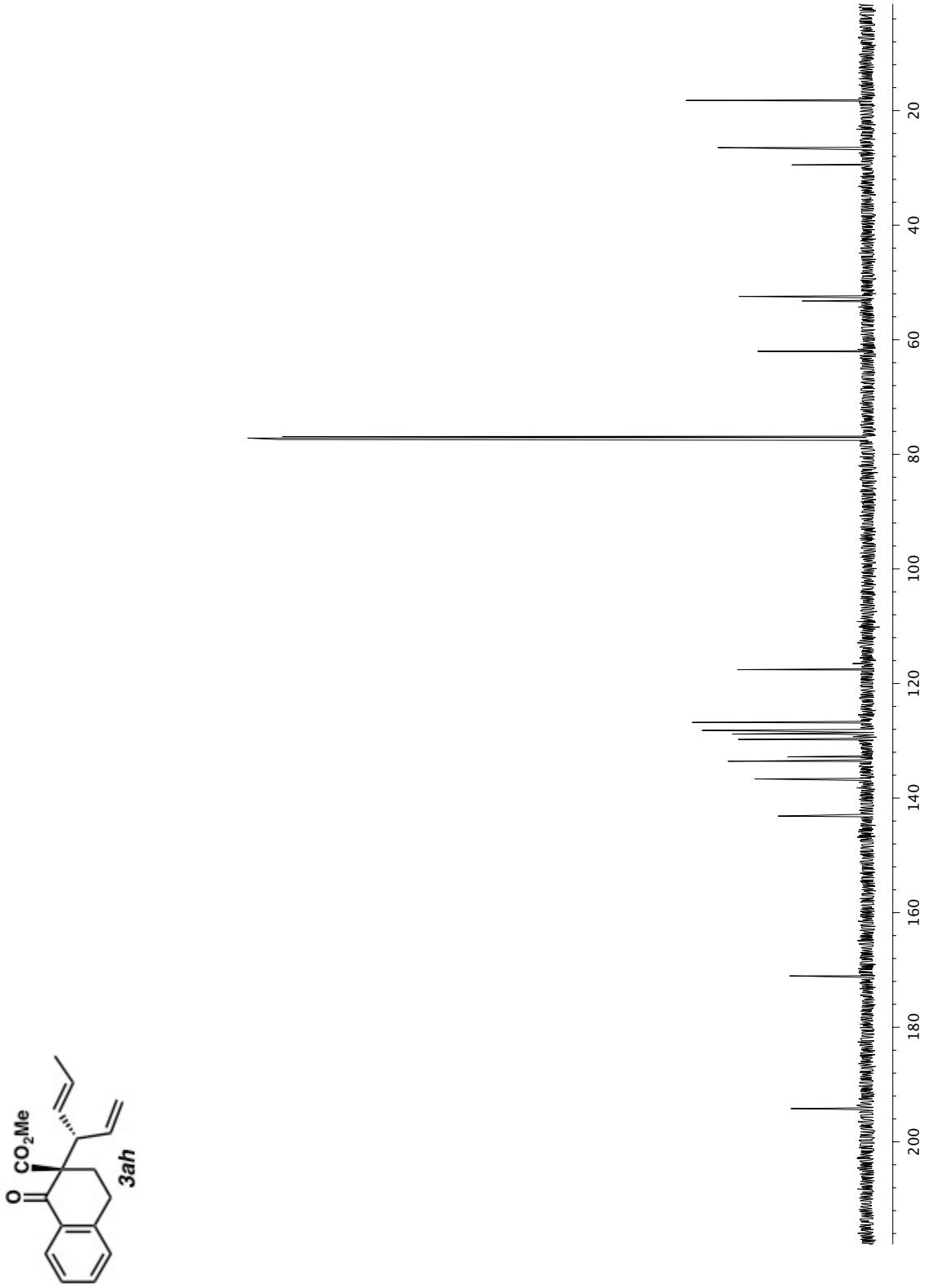
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ag**.



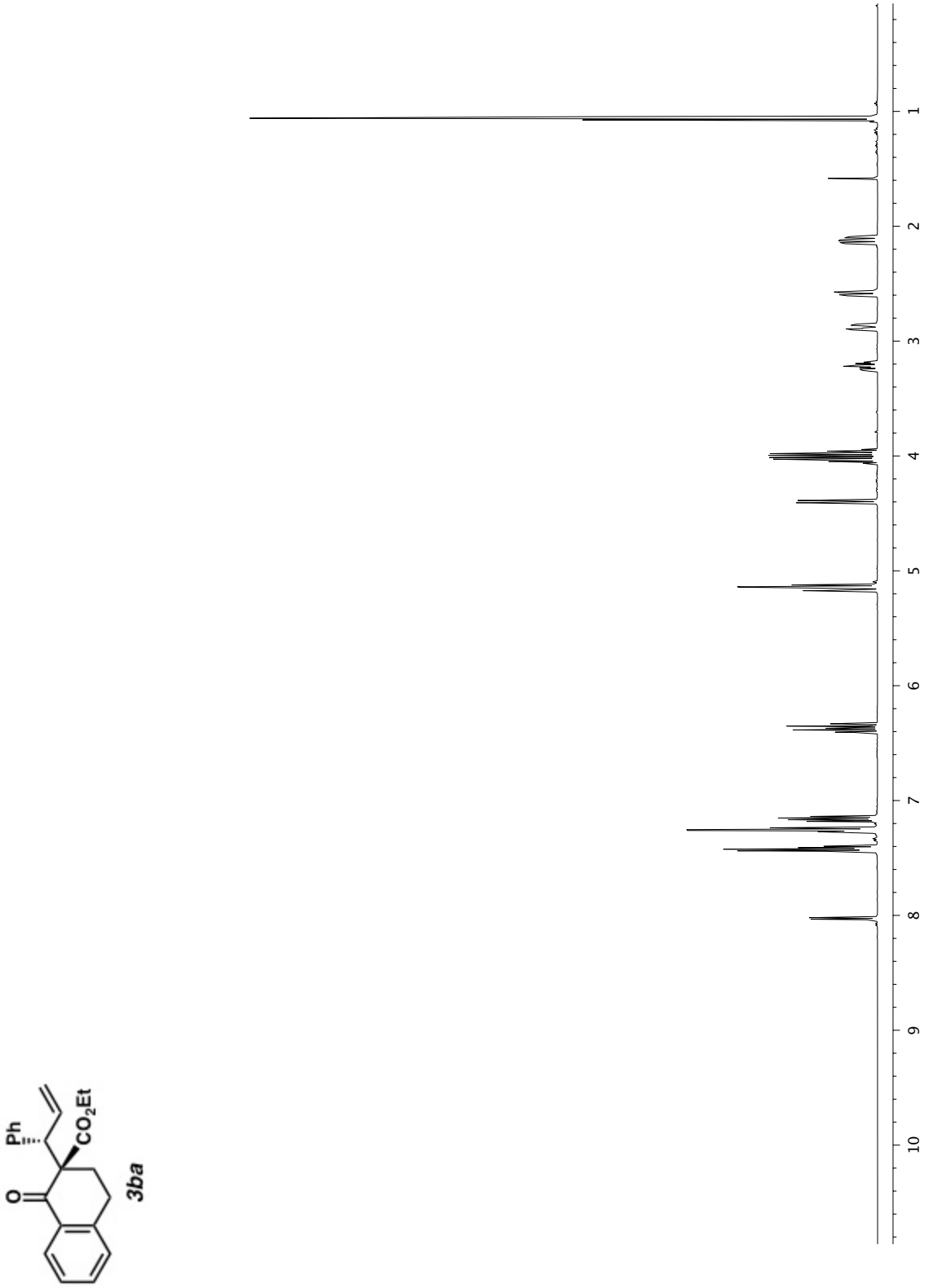
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ag**.



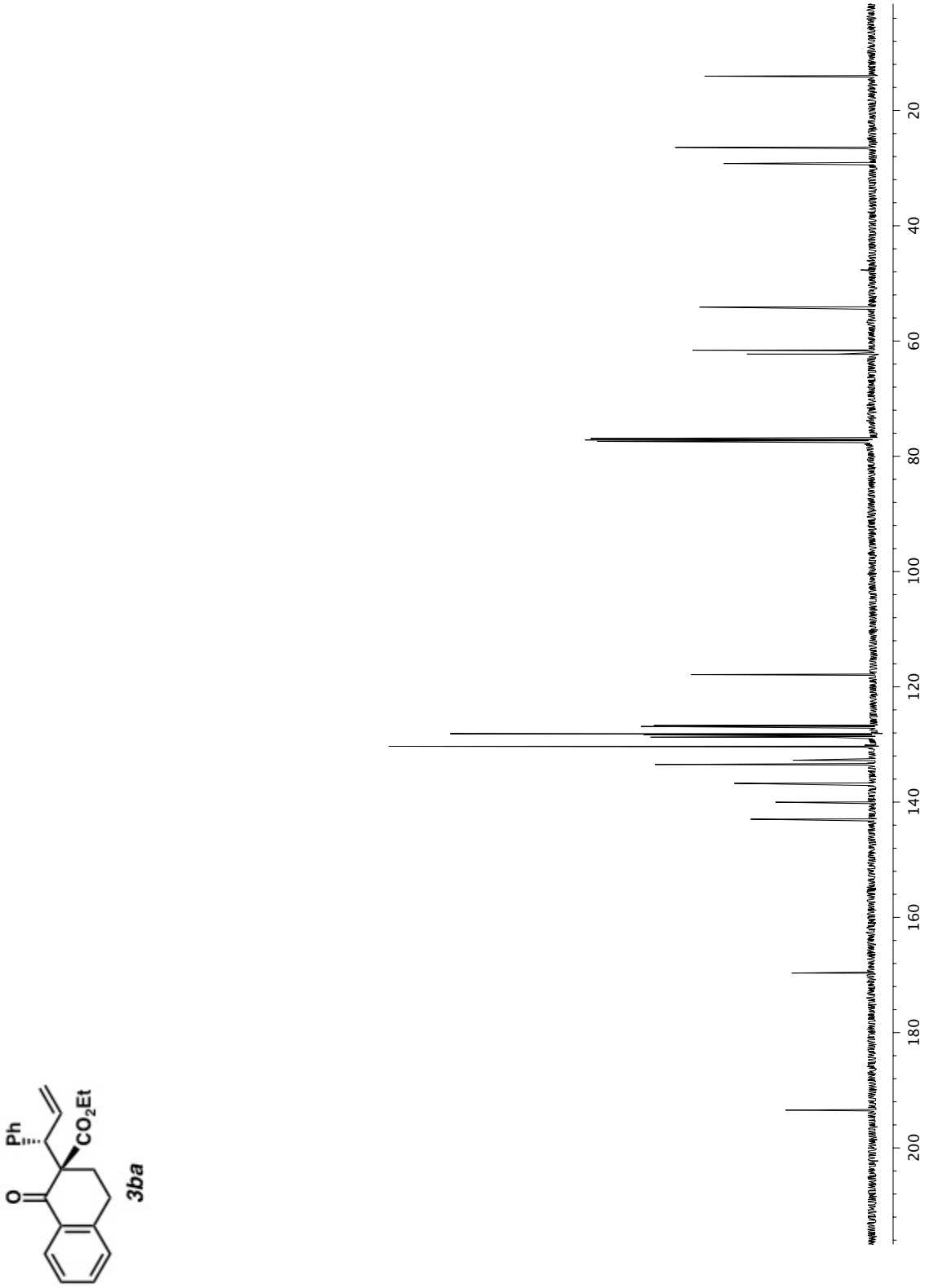
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ah**.



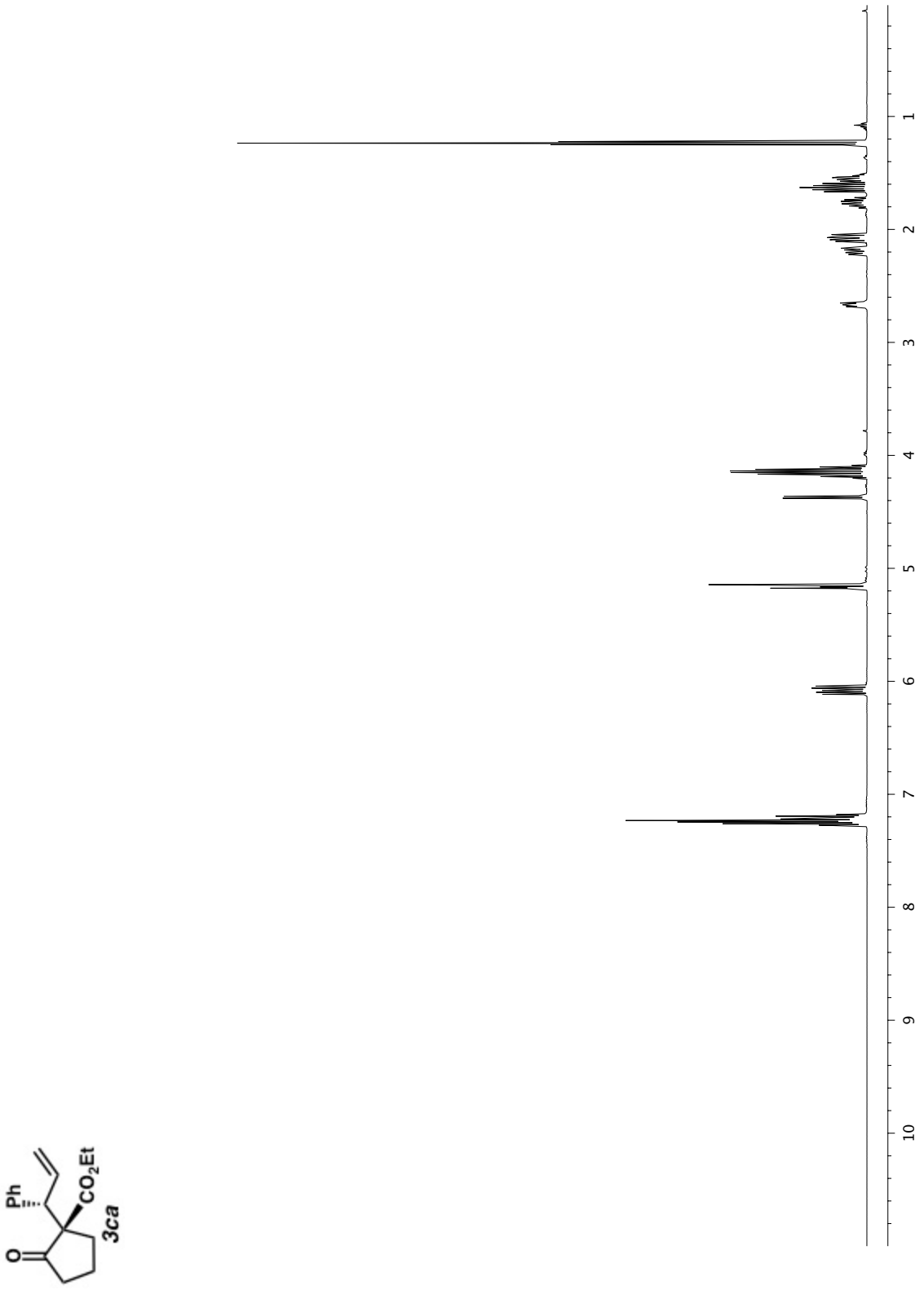
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ah**.



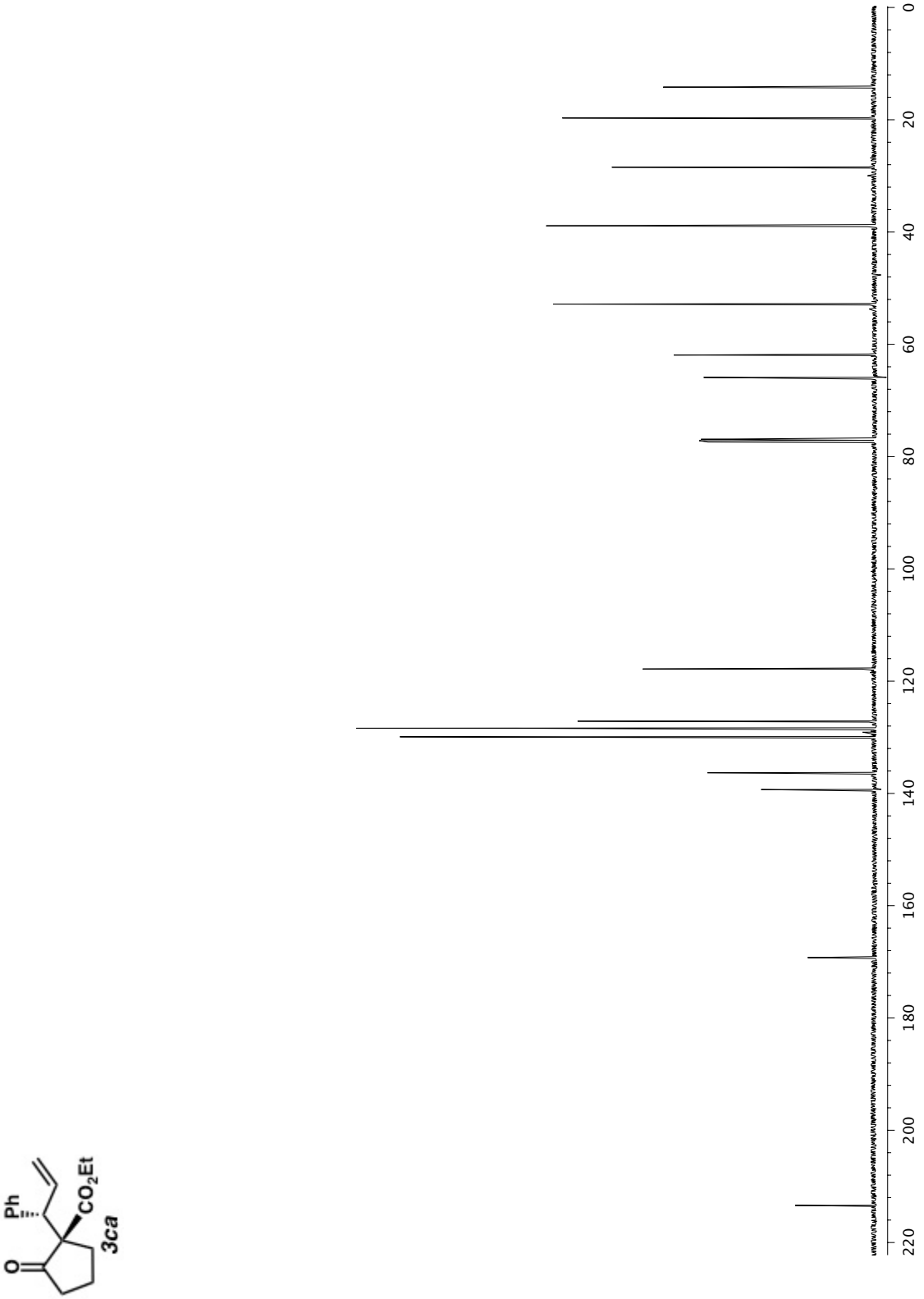
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ba**.



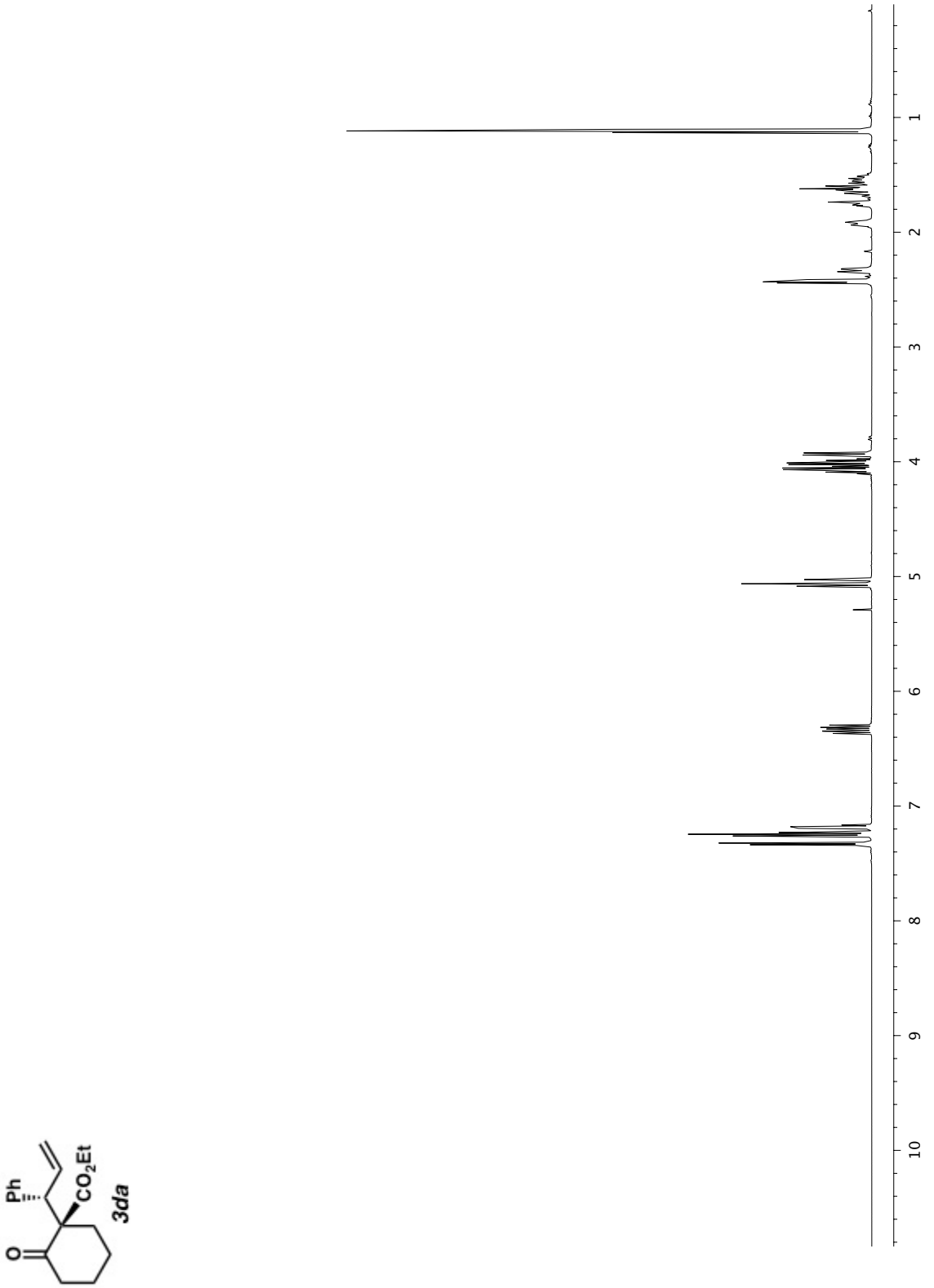
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ba**.



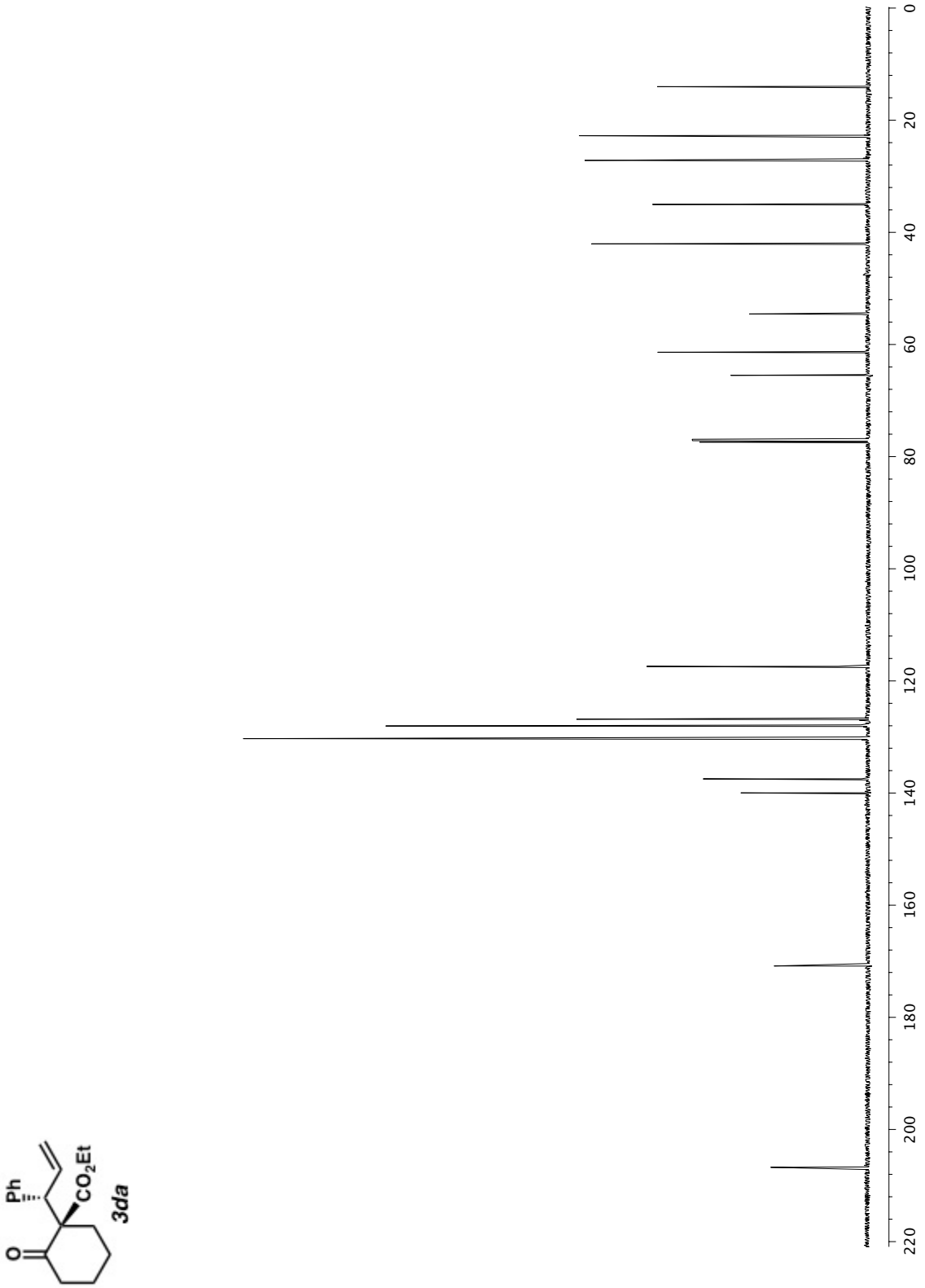
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ca**.



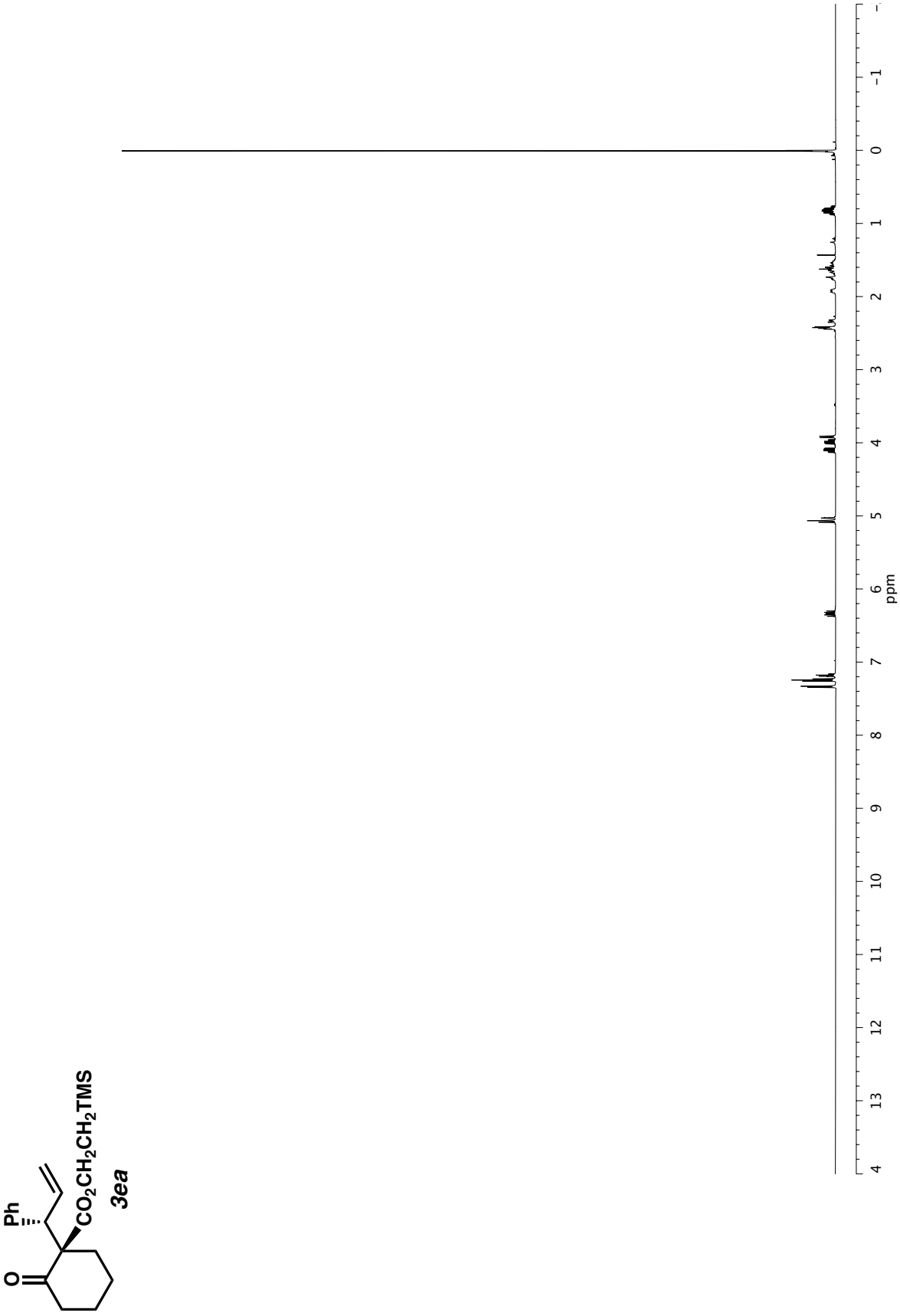
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ca**.



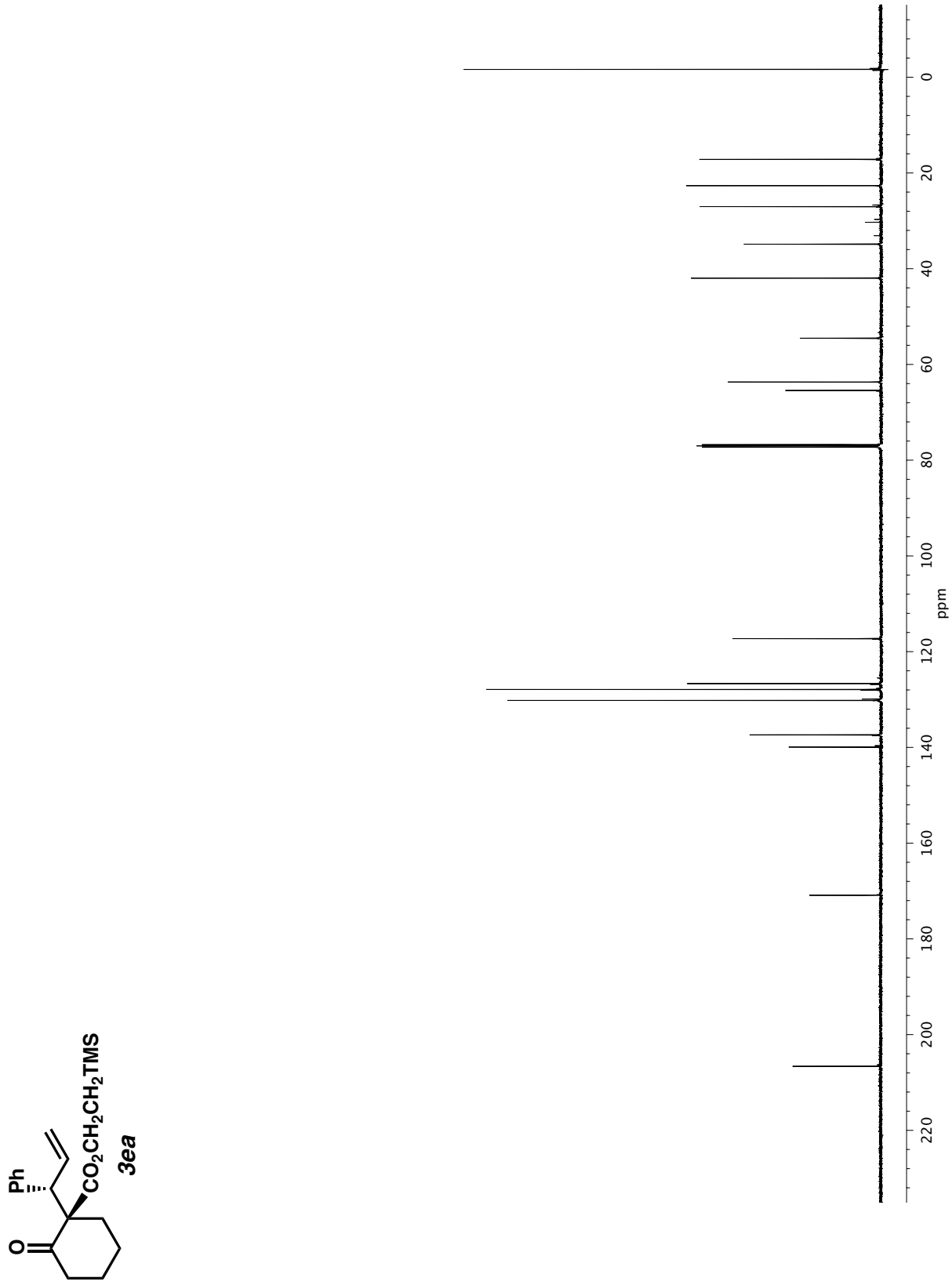
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3da**.



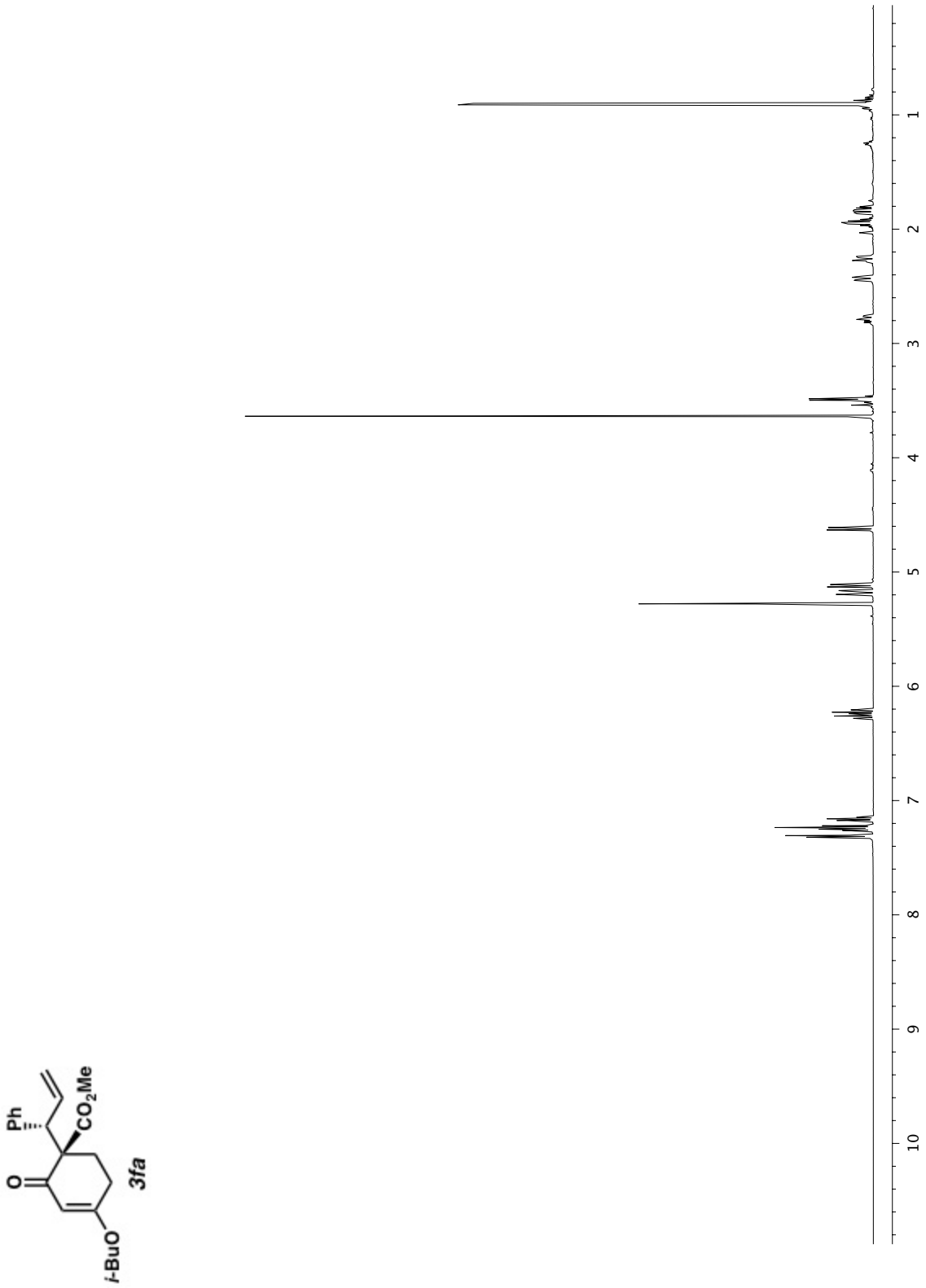
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3da**.



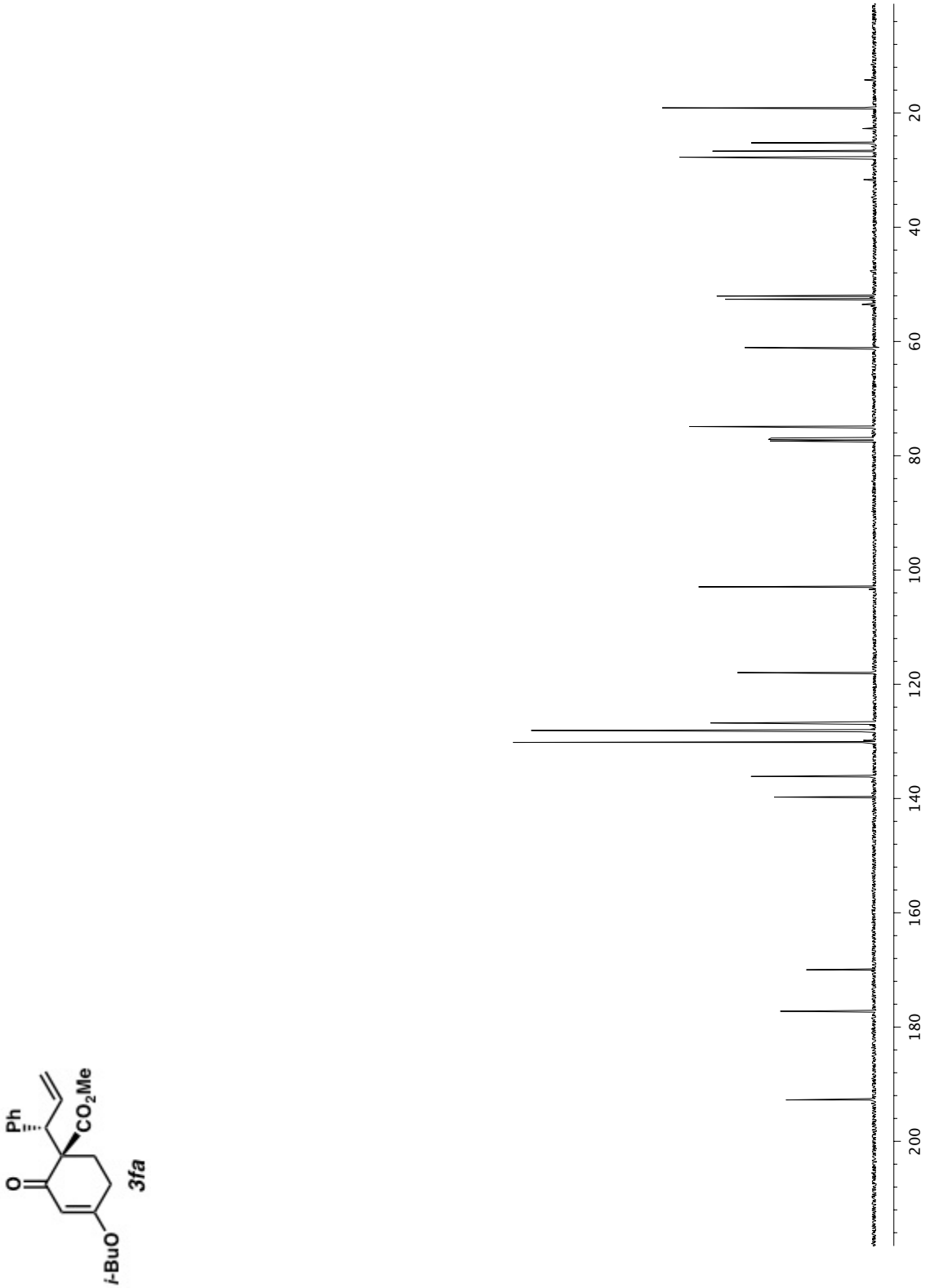
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ea**.



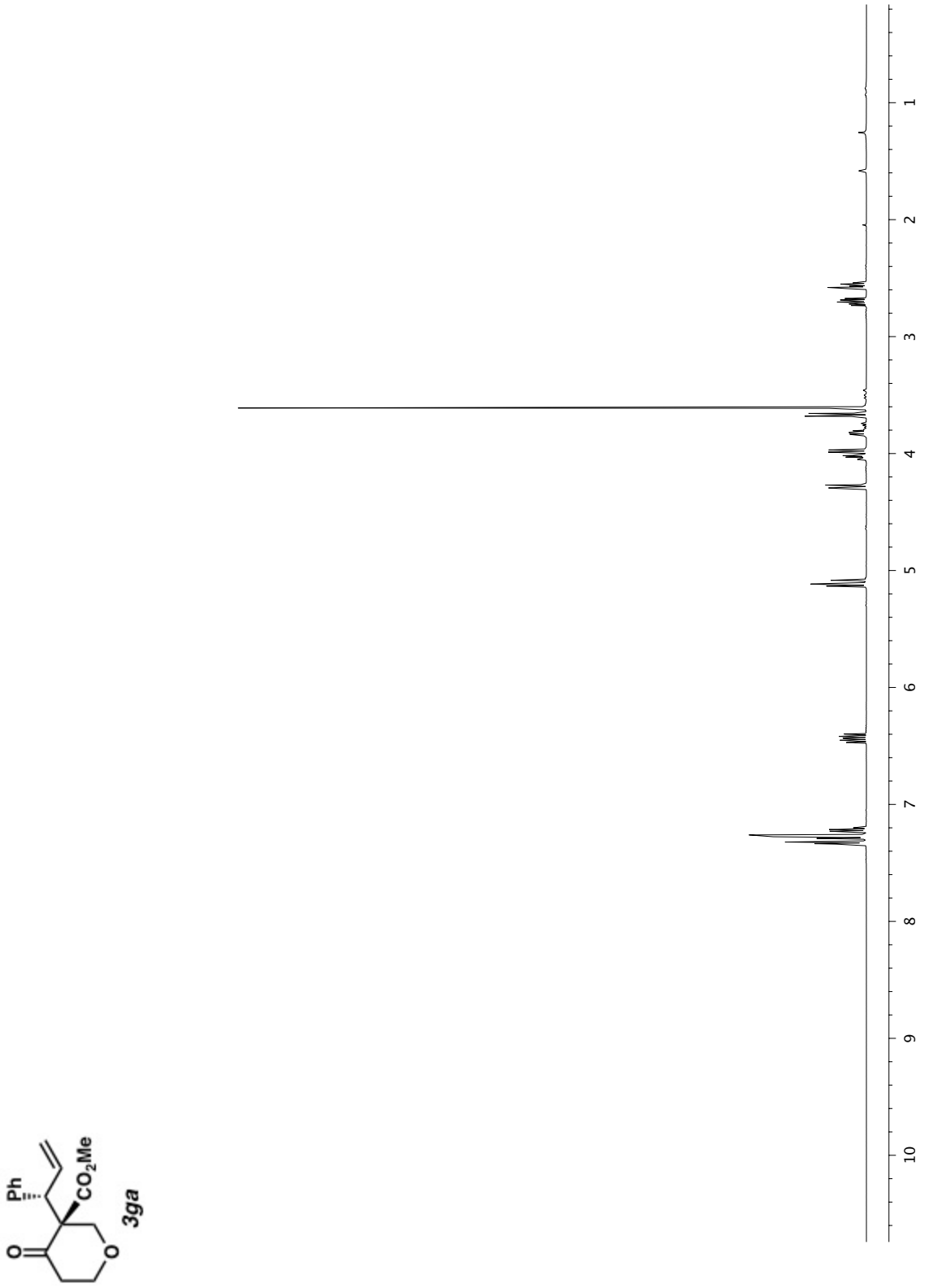
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ea**.



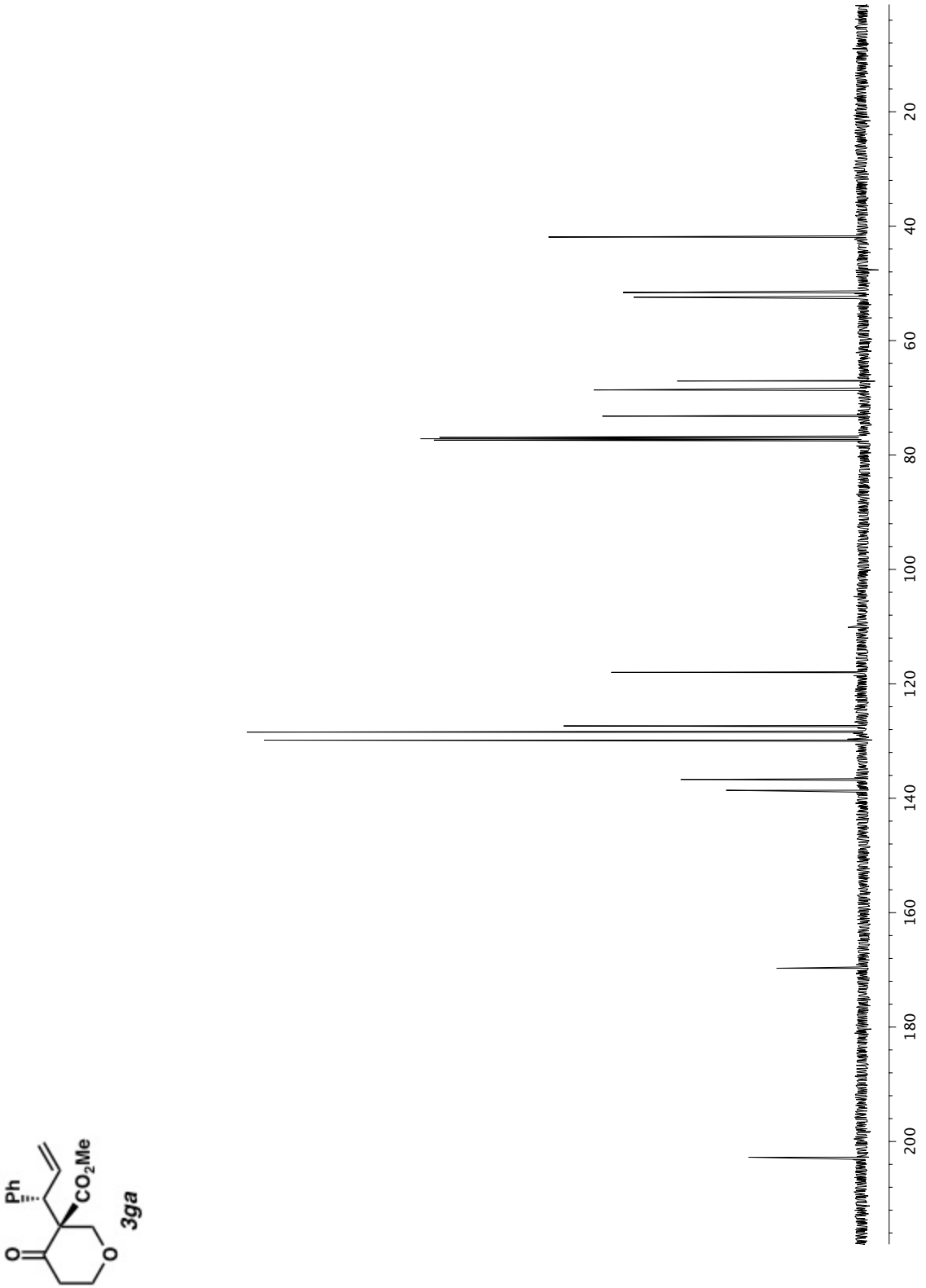
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3fa**.



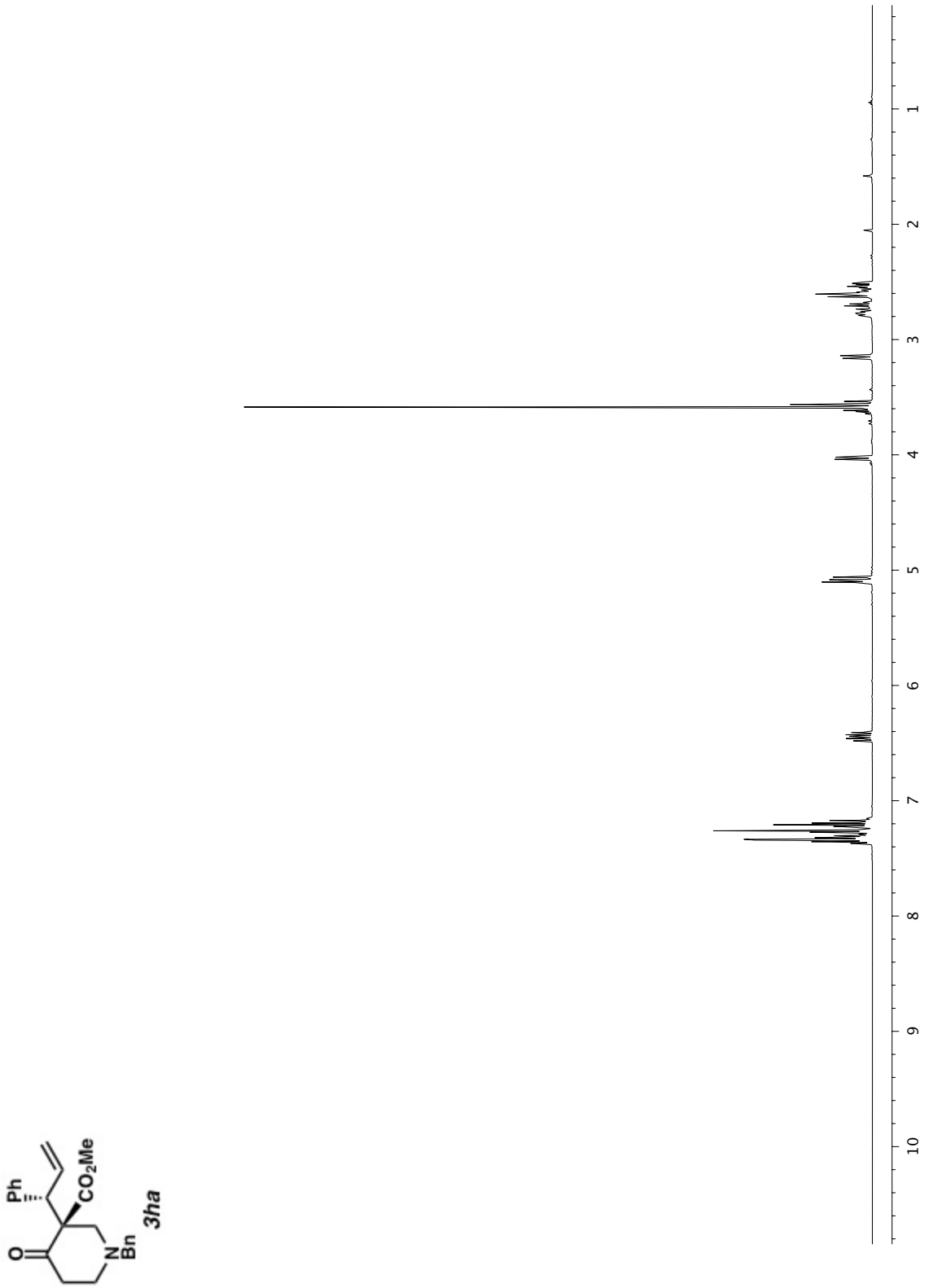
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3fa**.



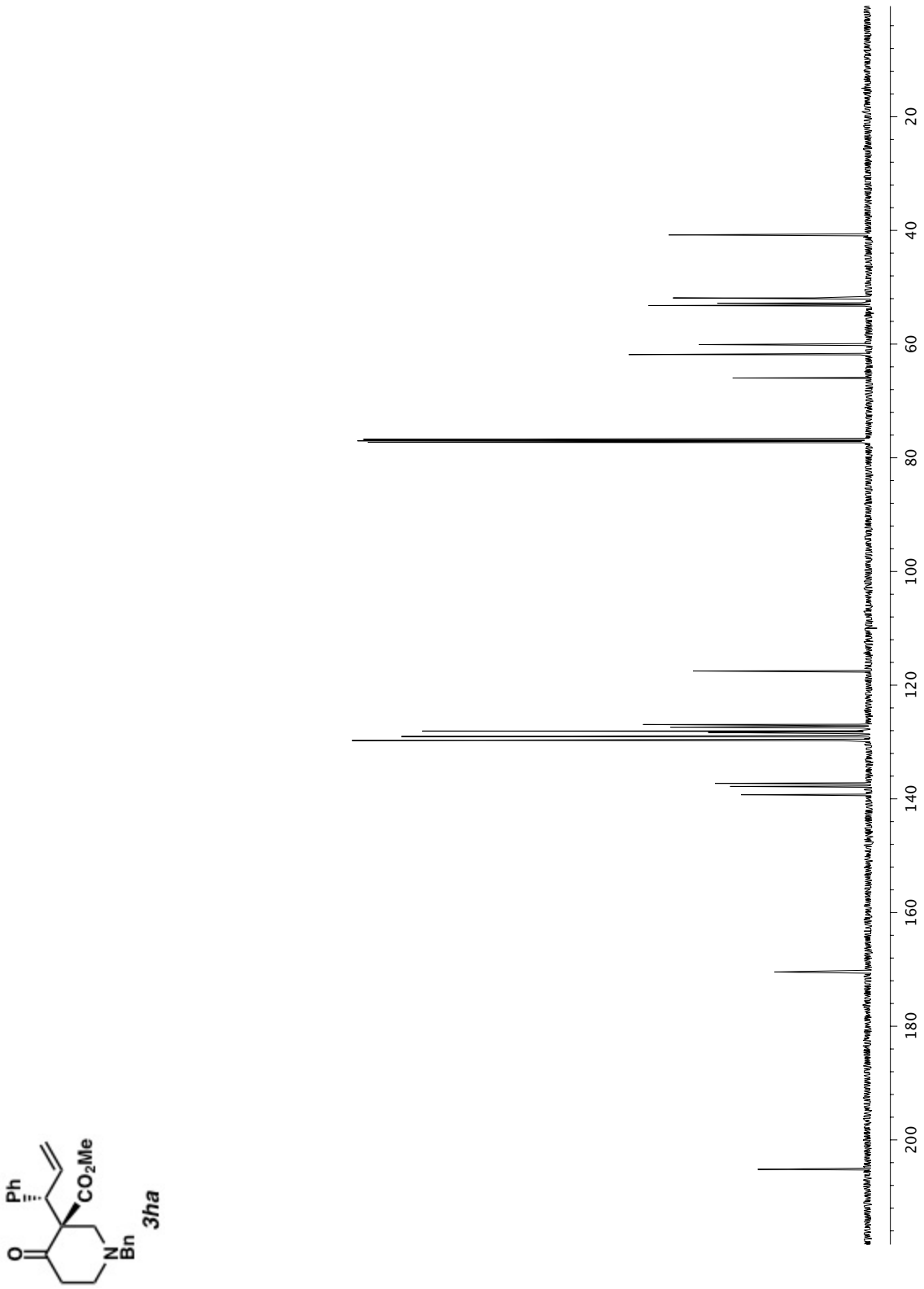
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ga**.



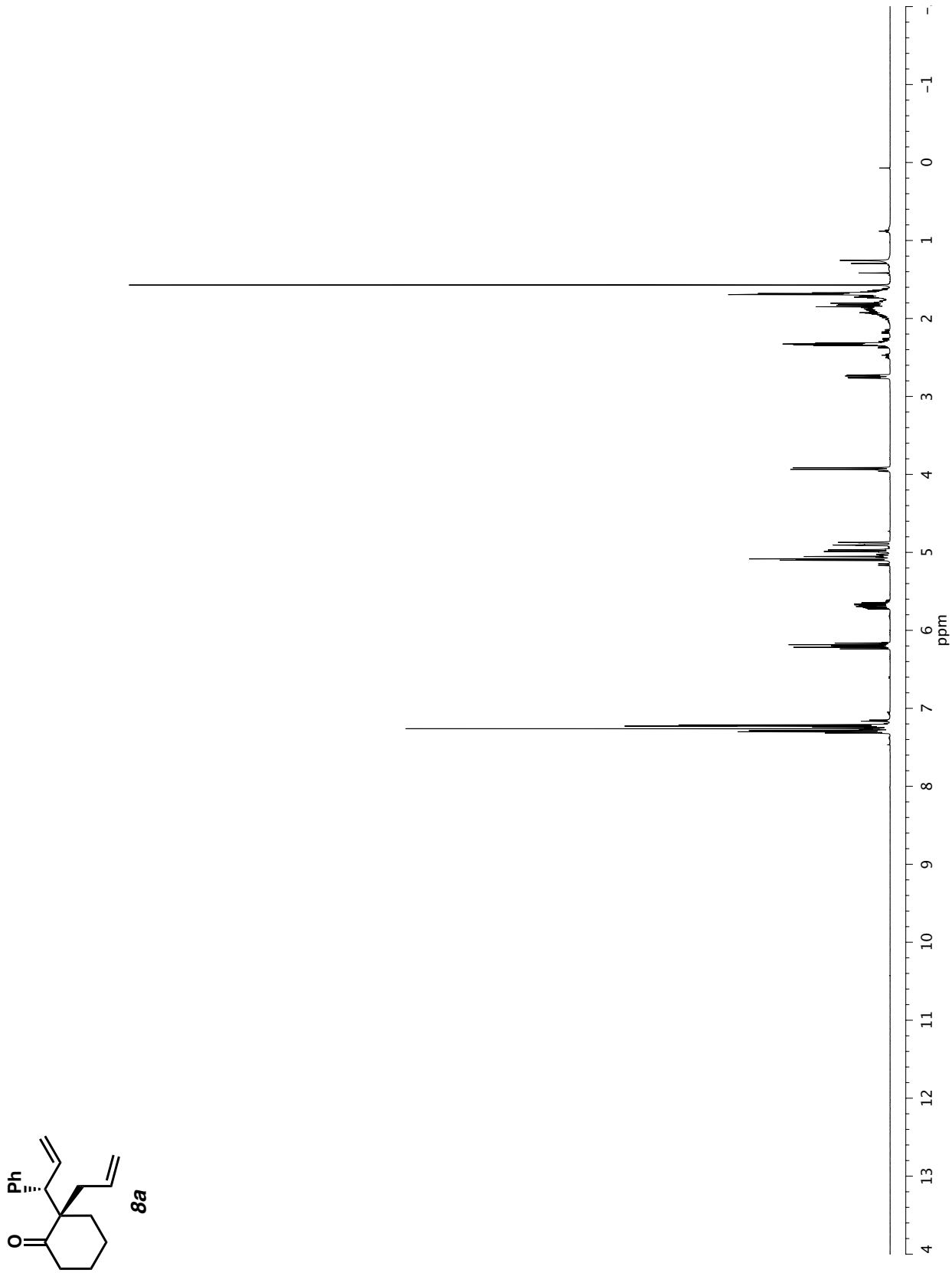
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ga**.



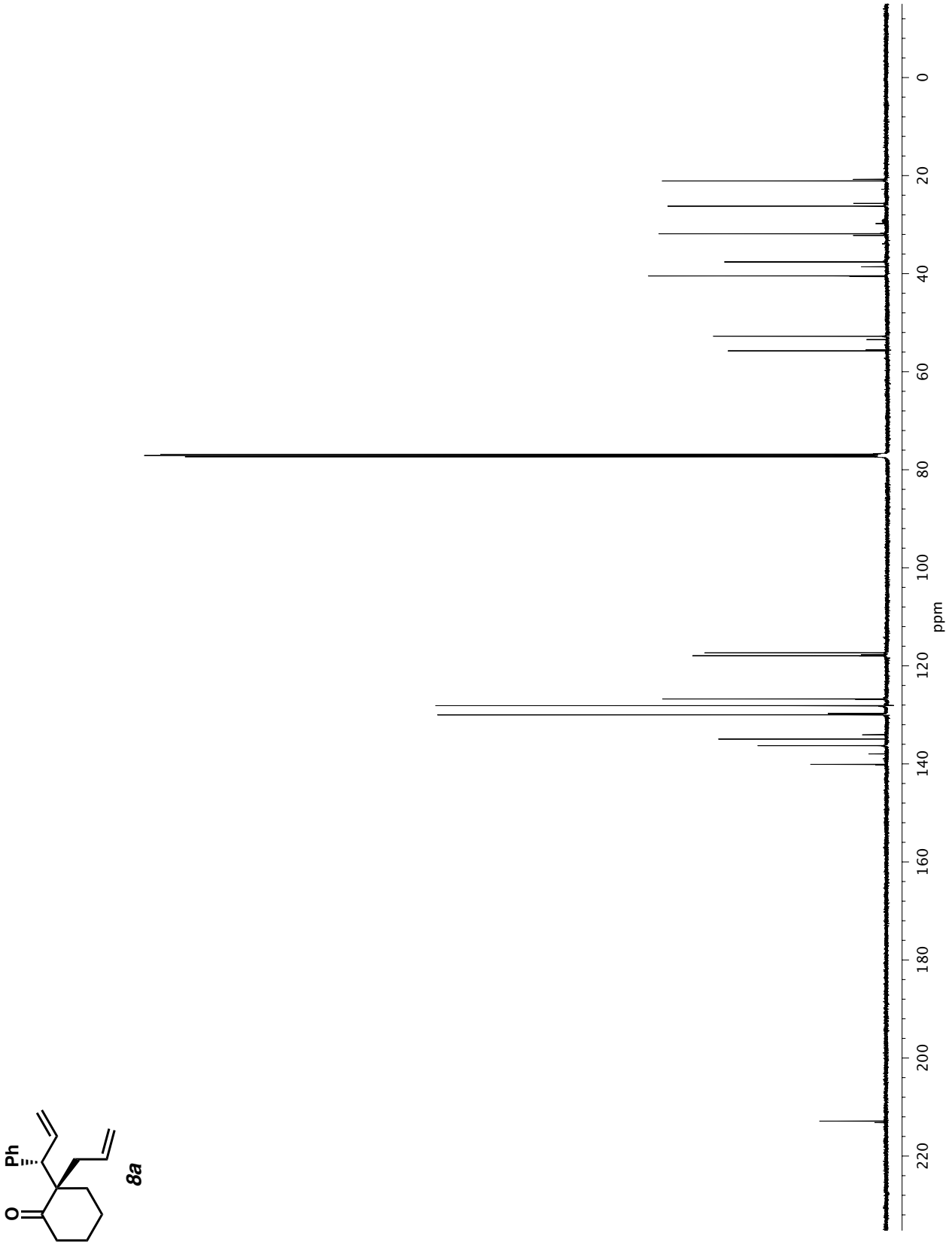
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3ha**.



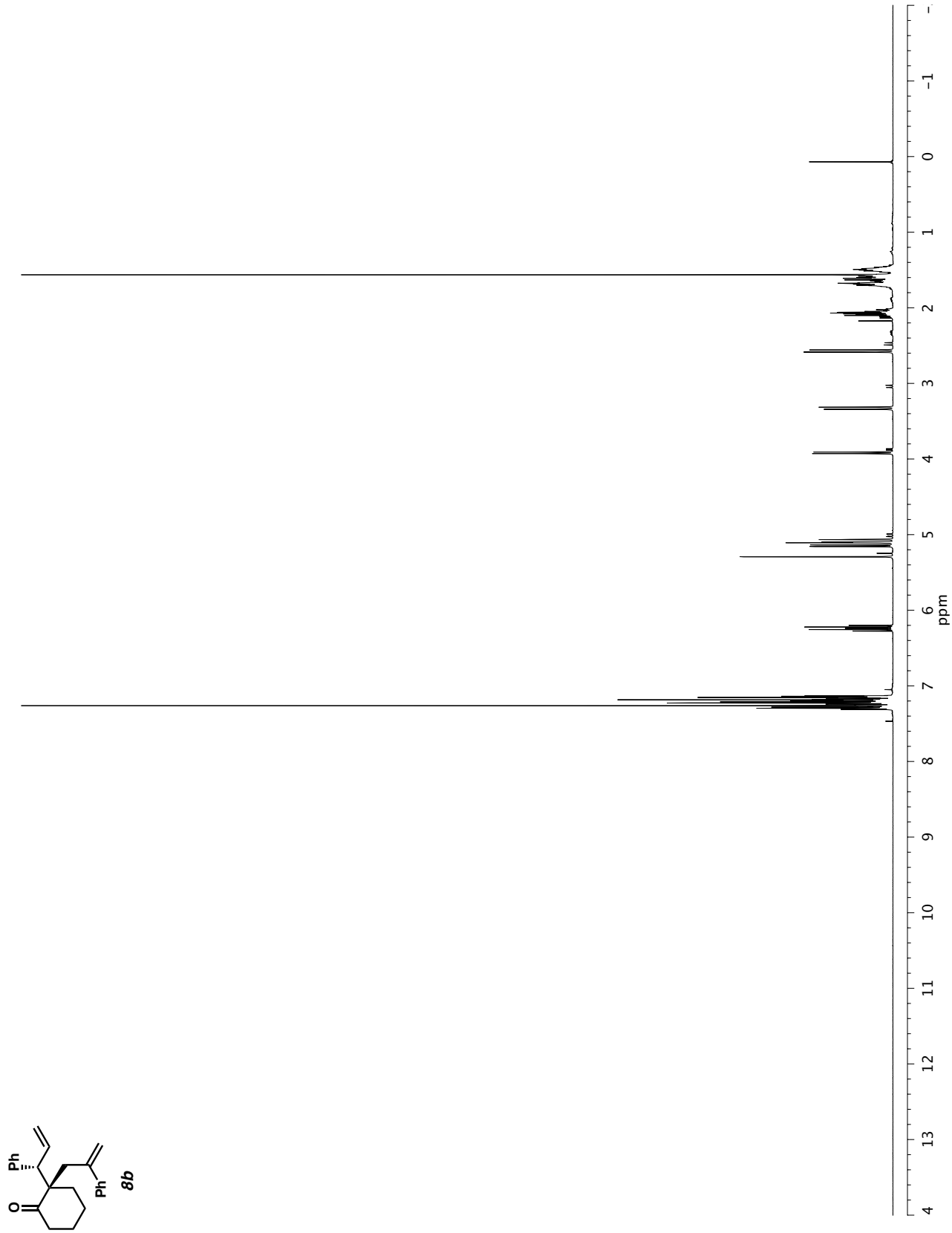
^{13}C NMR (126 MHz, $CDCl_3$) of compound **3ha**.



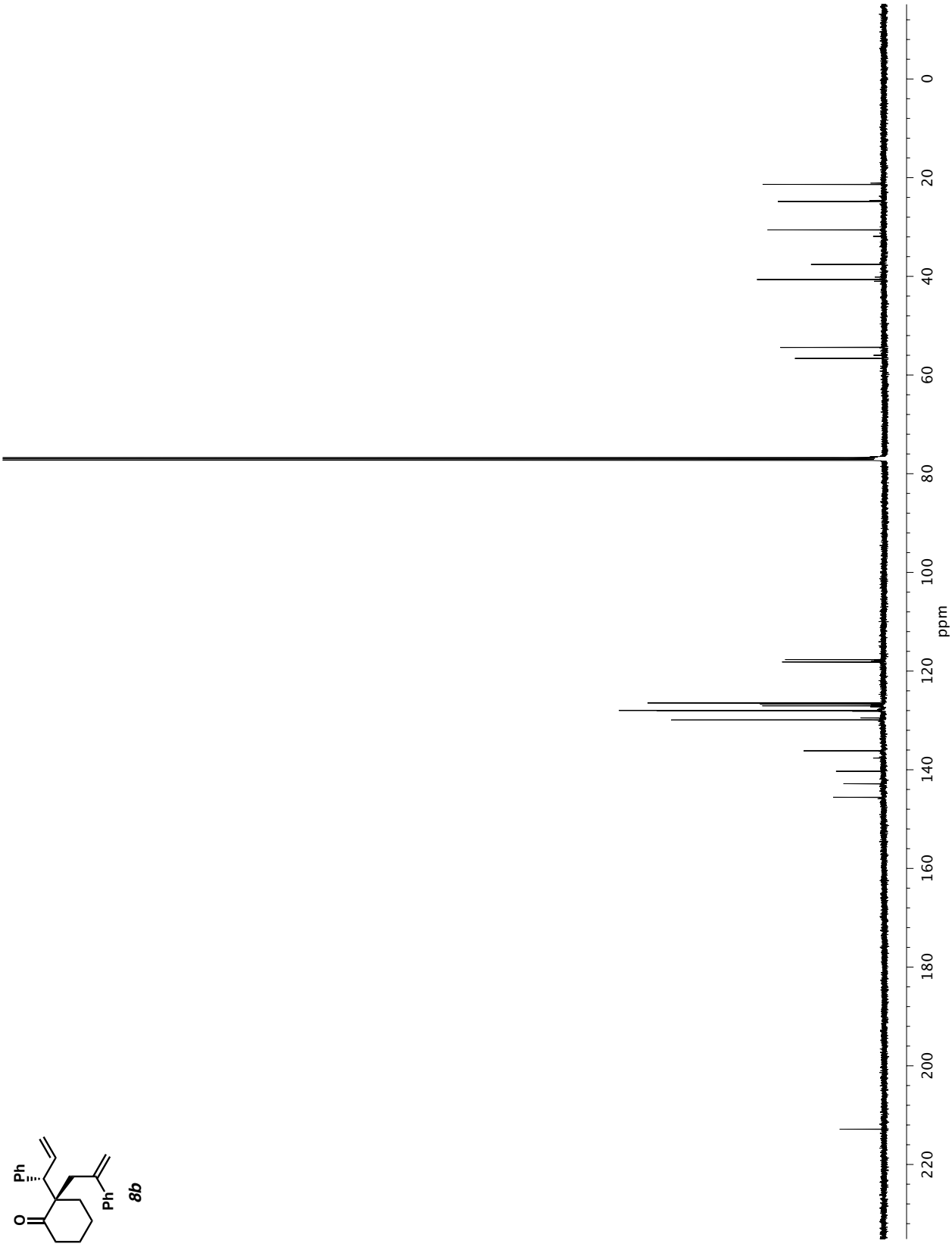
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8a**.



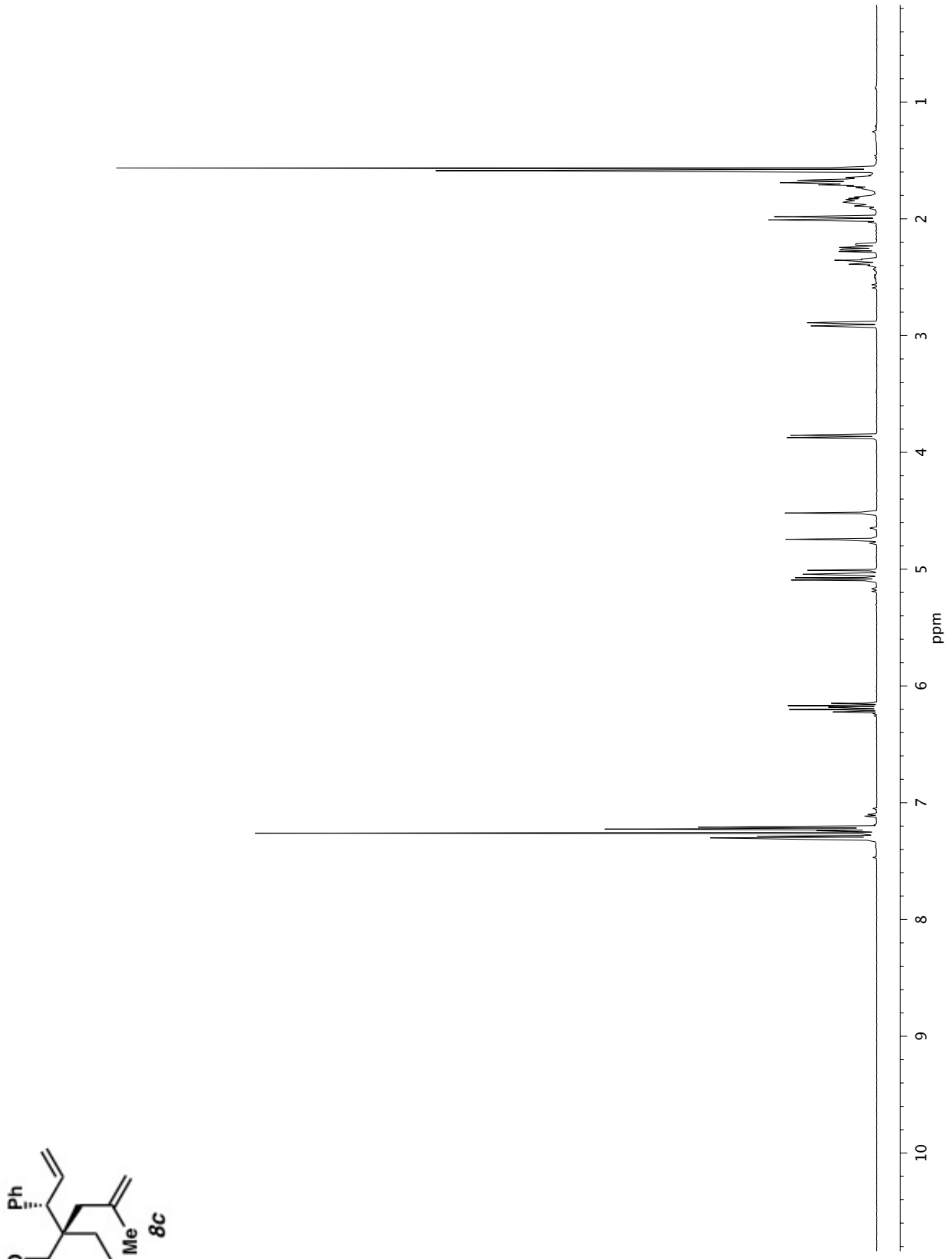
^{13}C NMR (126 MHz, $CDCl_3$) of compound **8a**.



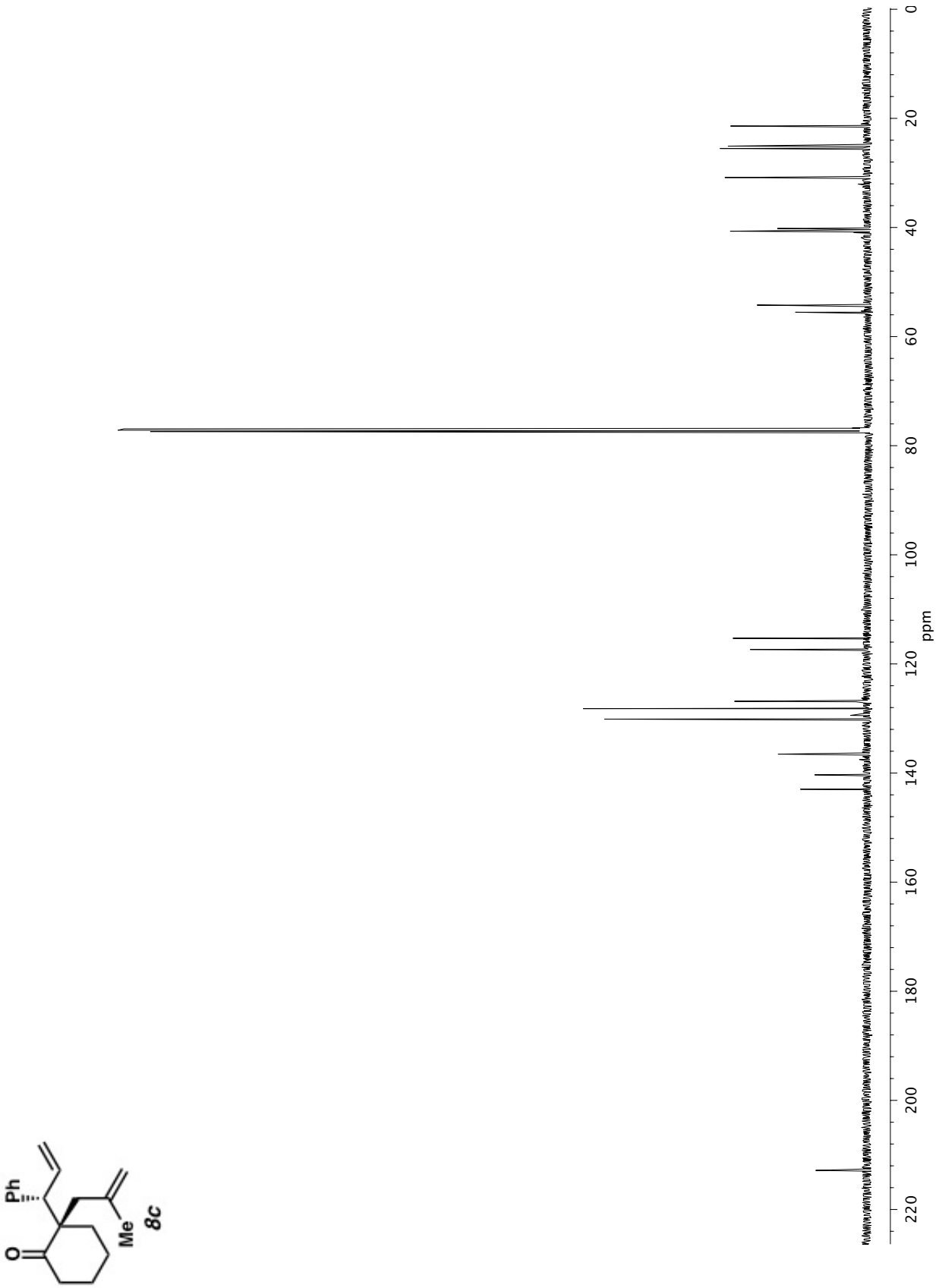
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8b**.



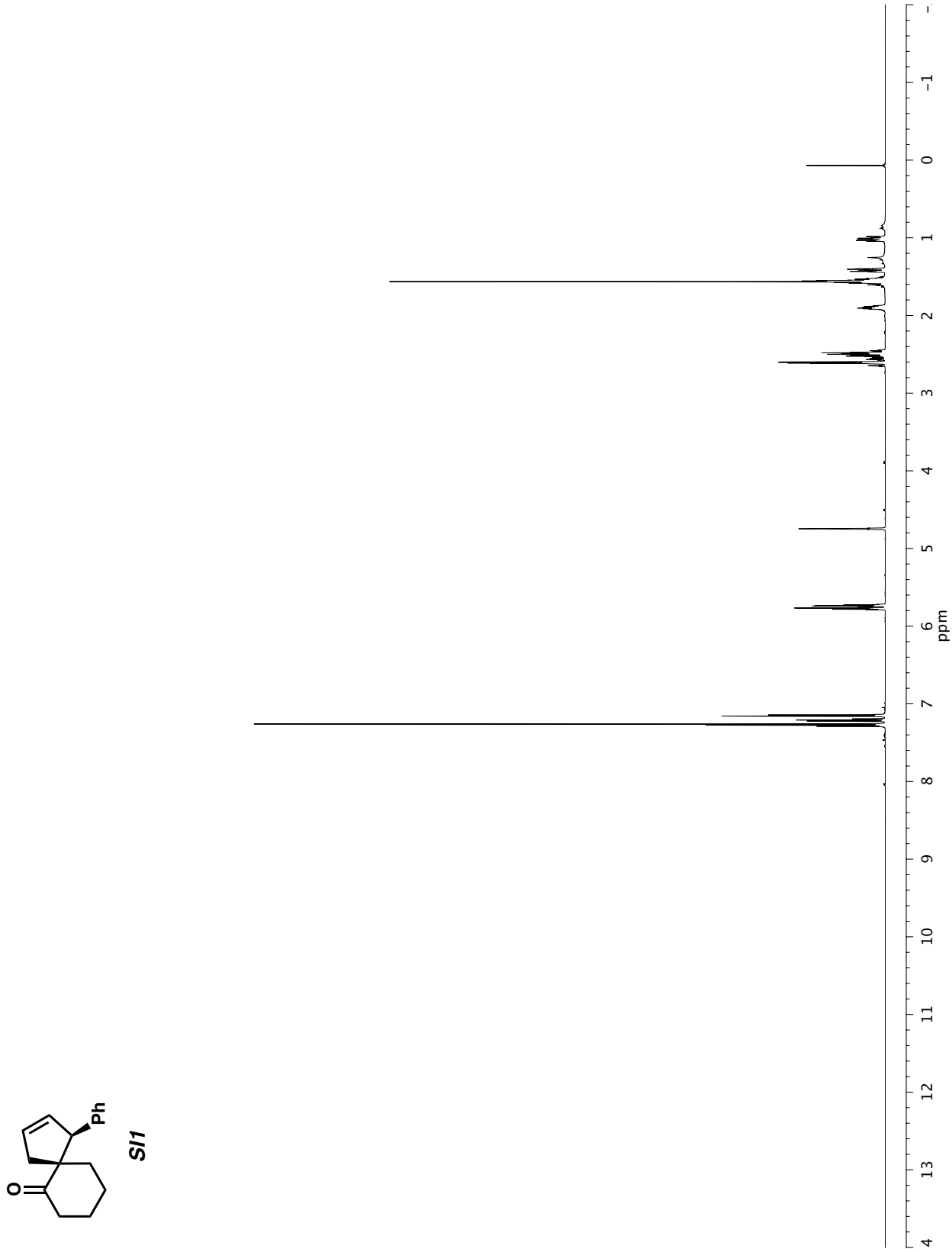
^{13}C NMR (126 MHz, $CDCl_3$) of compound **8b**.



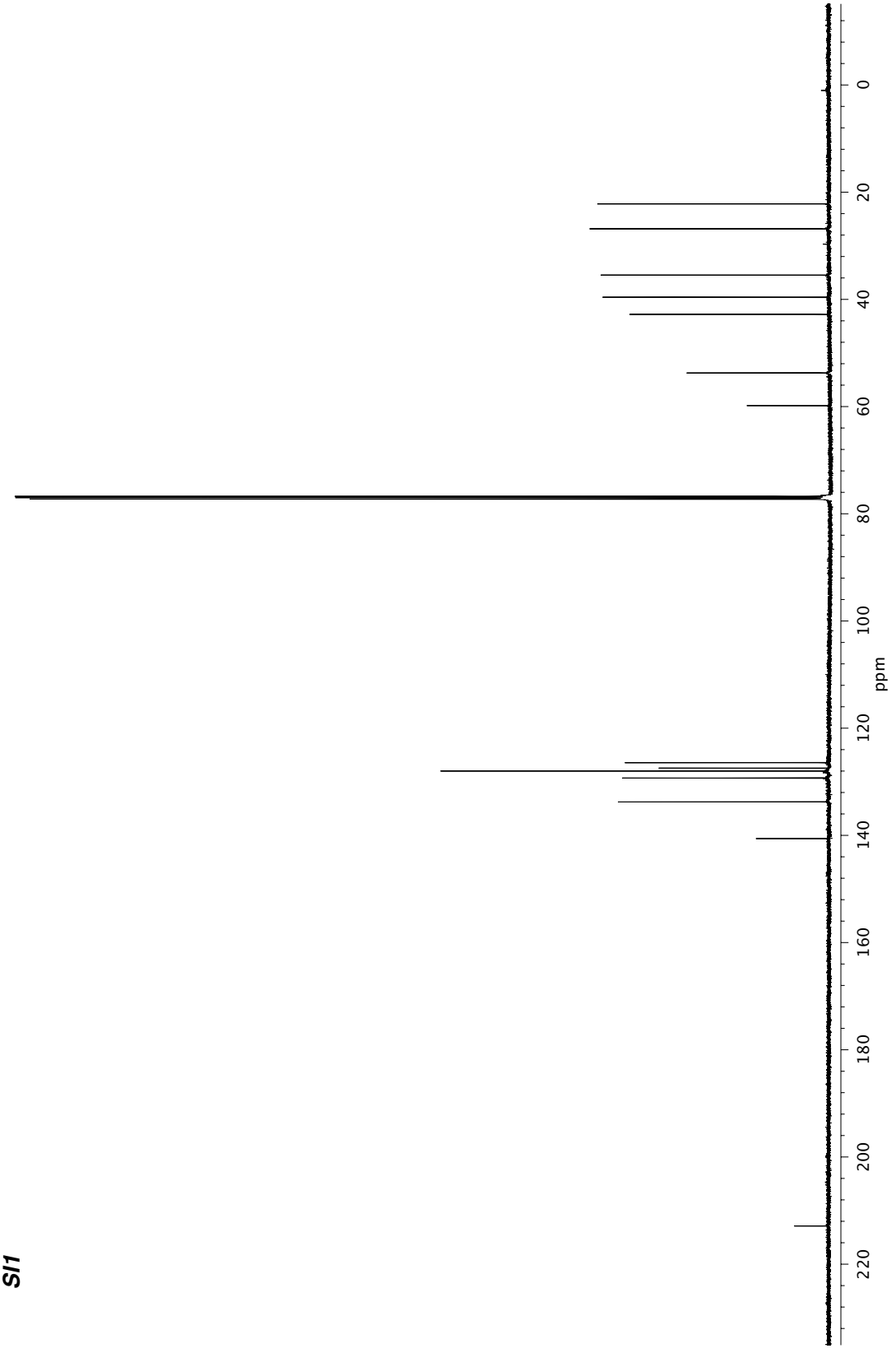
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8c**.



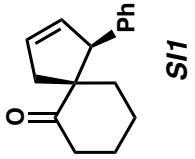
^{13}C NMR (126 MHz, $CDCl_3$) of compound **8a**.



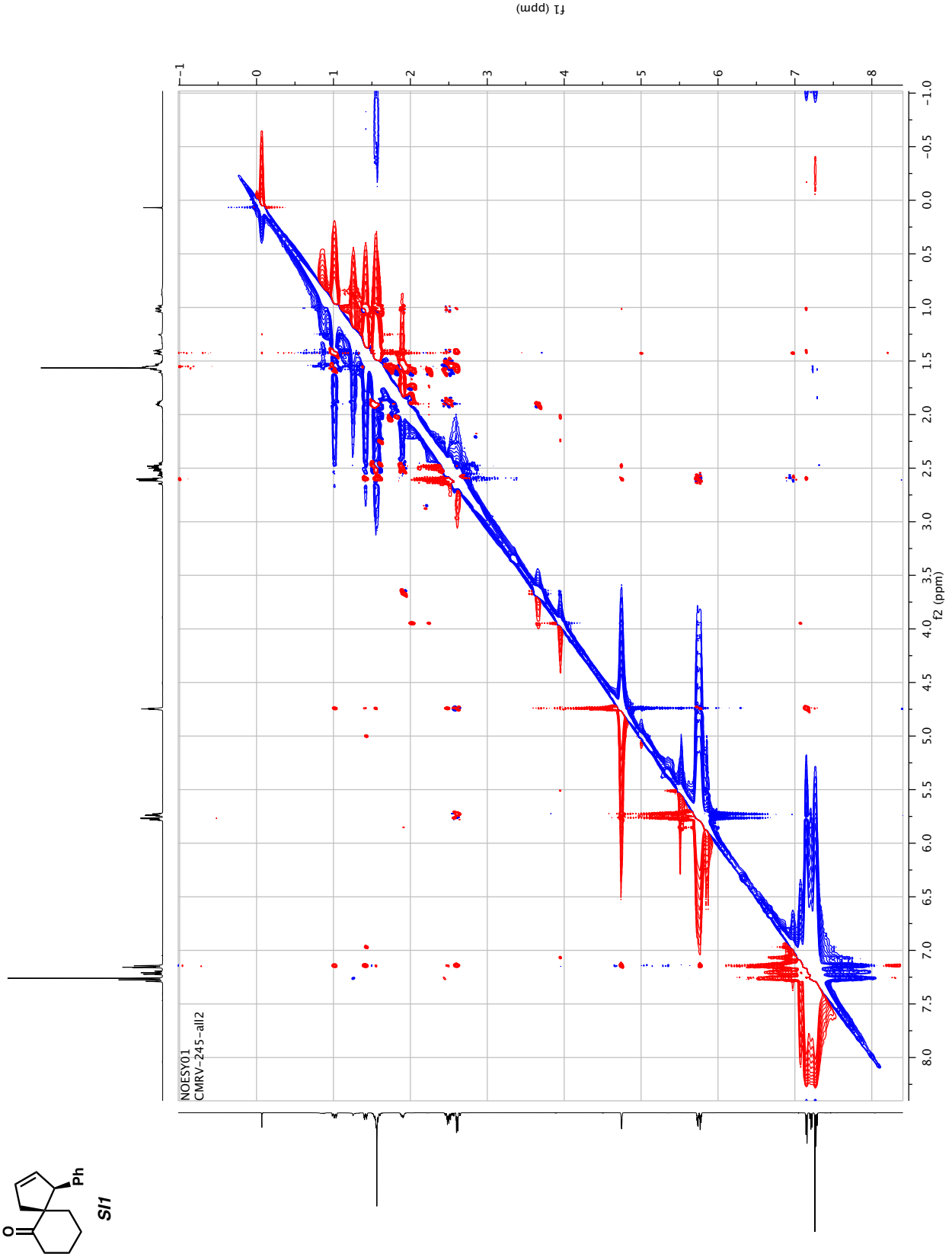
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI1**.



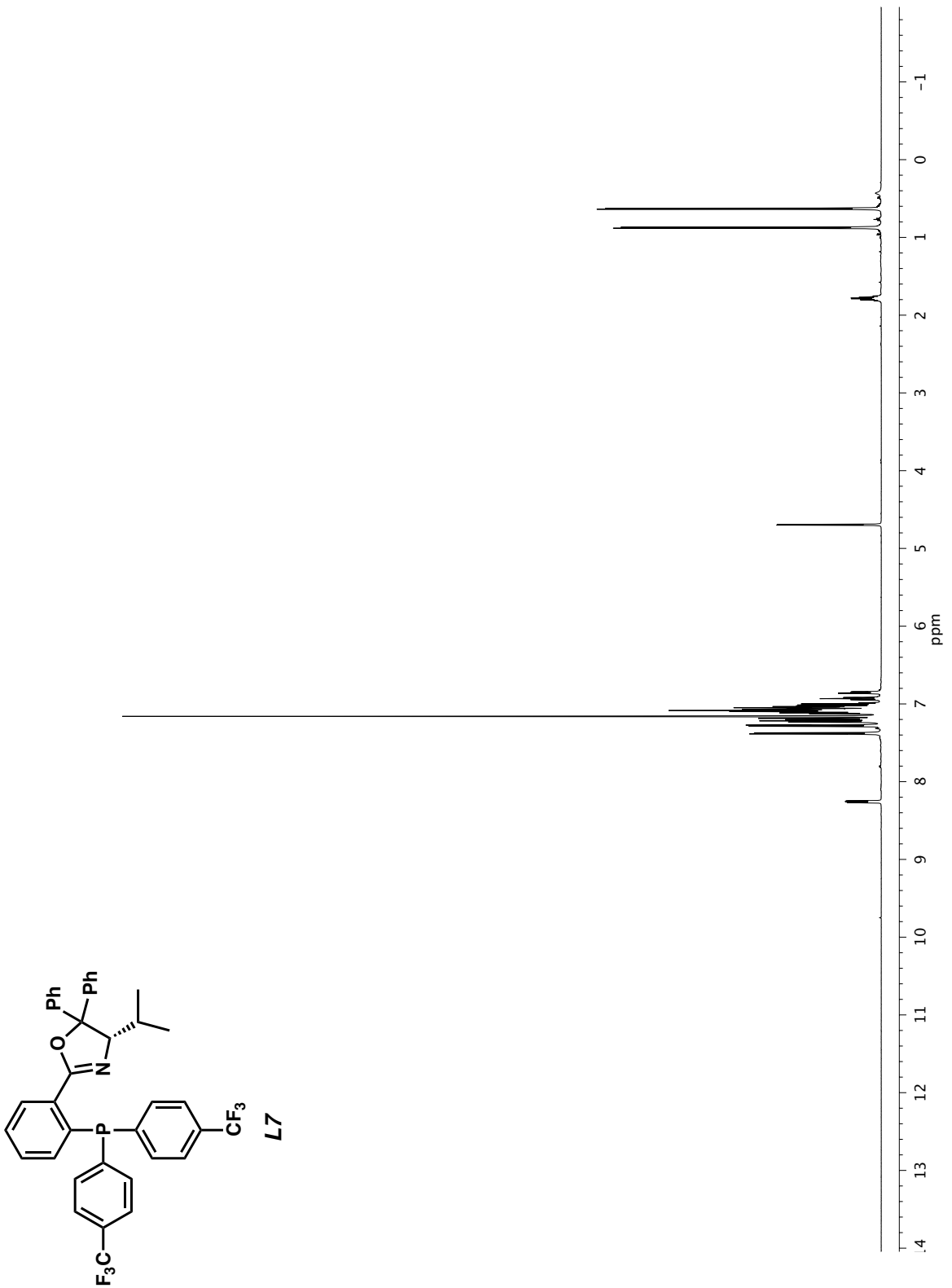
^{13}C NMR (126 MHz, $CDCl_3$) of compound **SI1**.



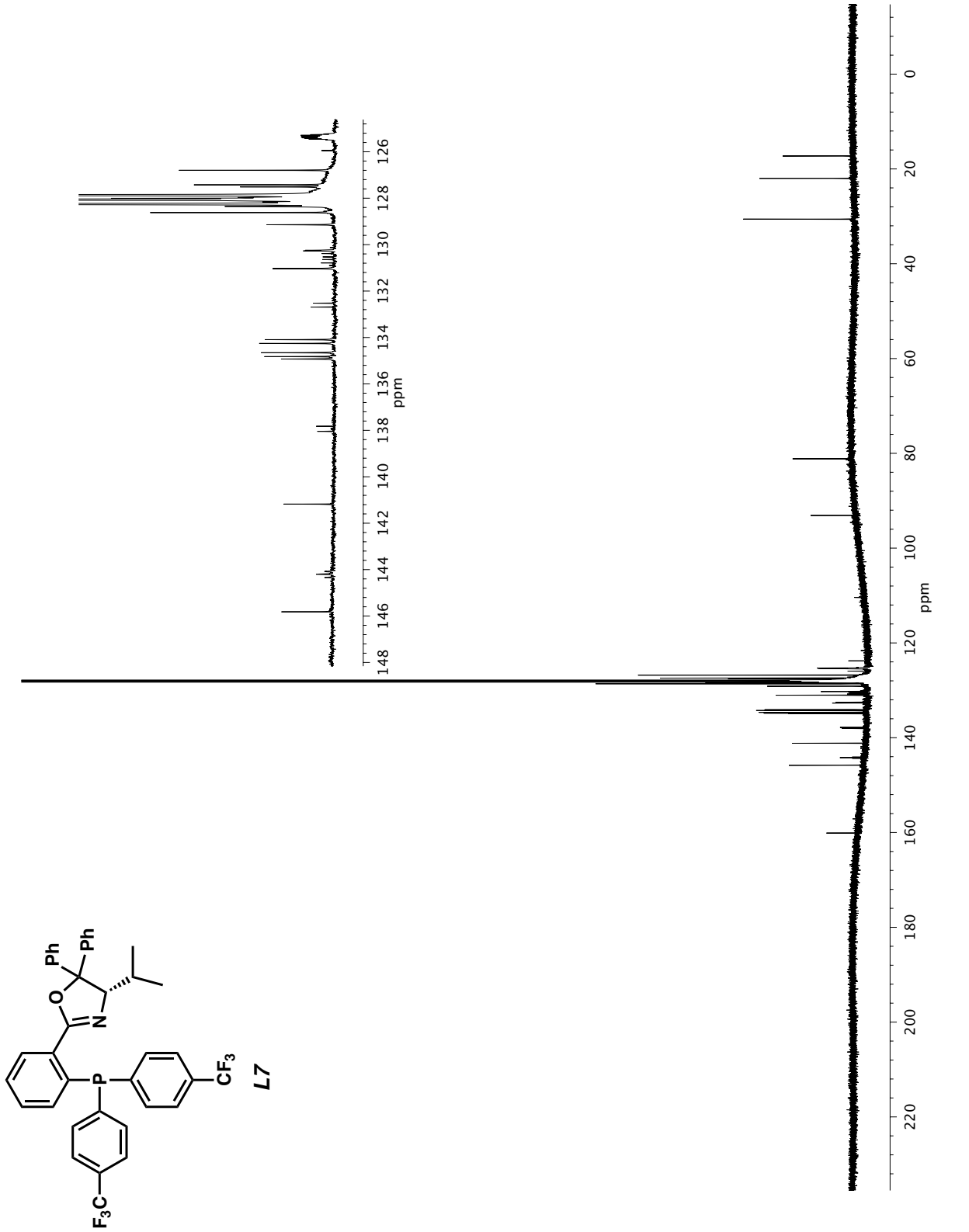
SI1



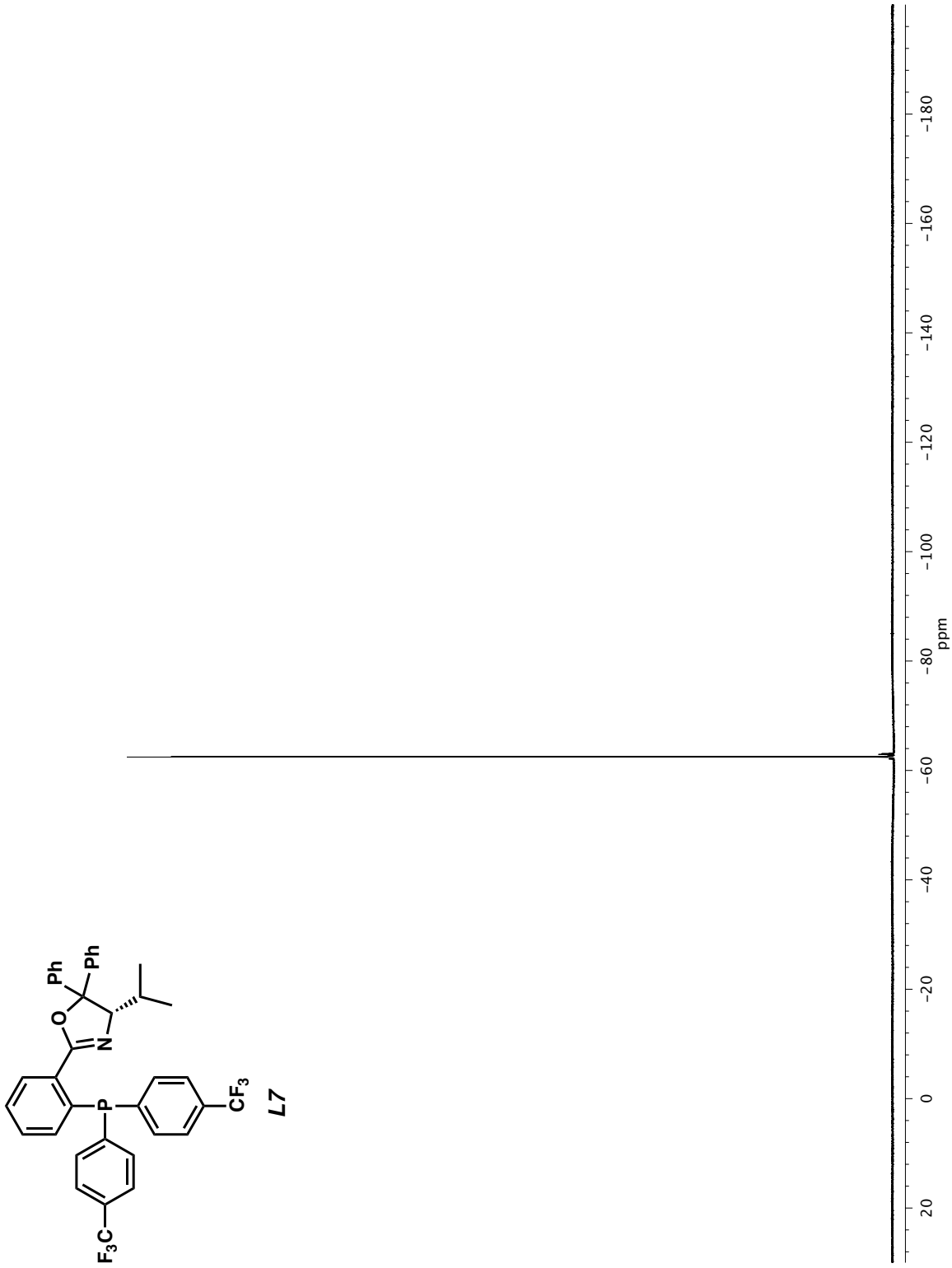
^{1}H NOSEY NMR (600 MHz, $CDCl_3$) of compound **SI1**.



^{1}H NMR (500 MHz, C_6D_6) of compound **L7**.

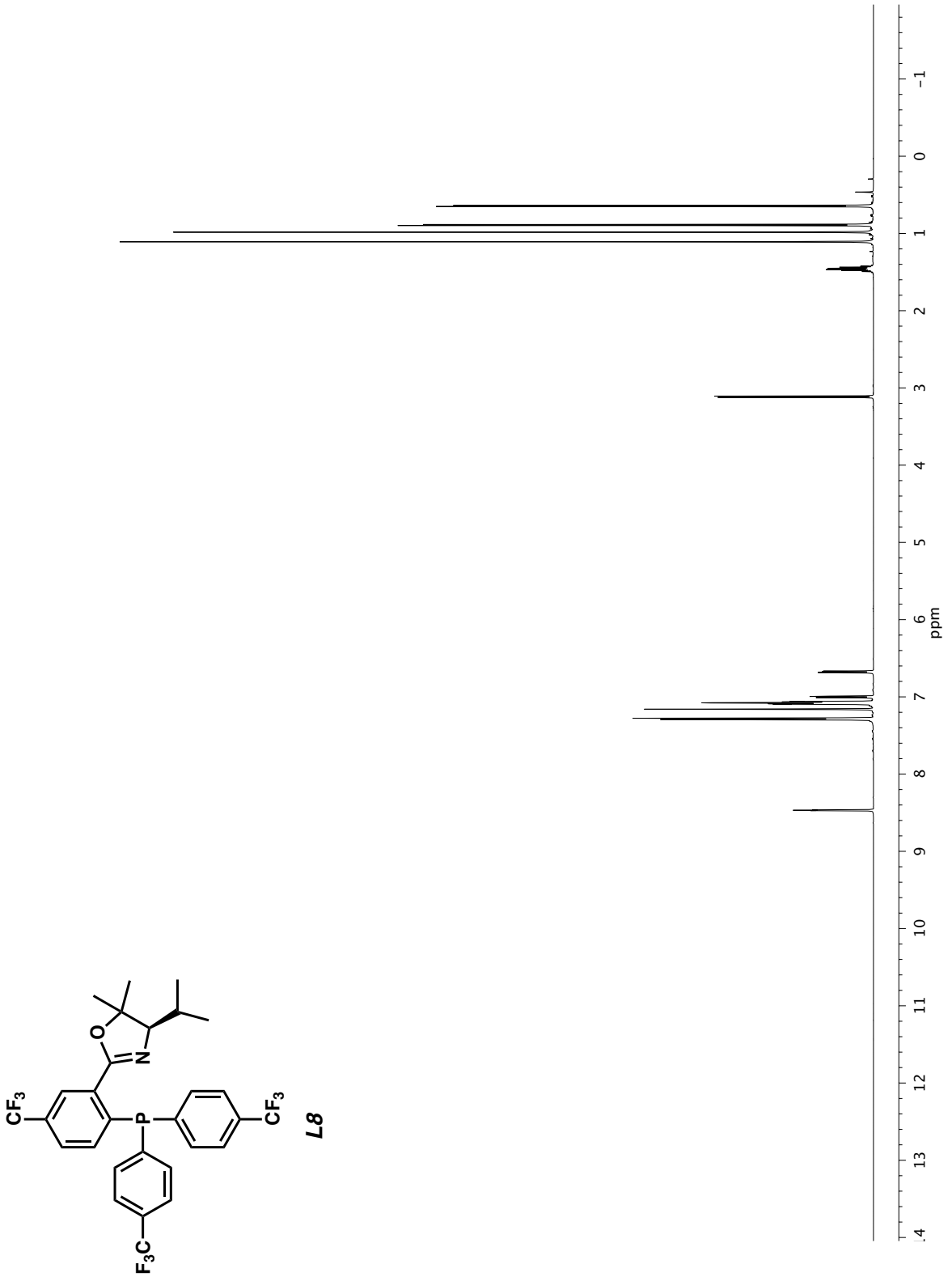


^{13}C NMR (126 MHz, C_6D_6) of compound **L7**.

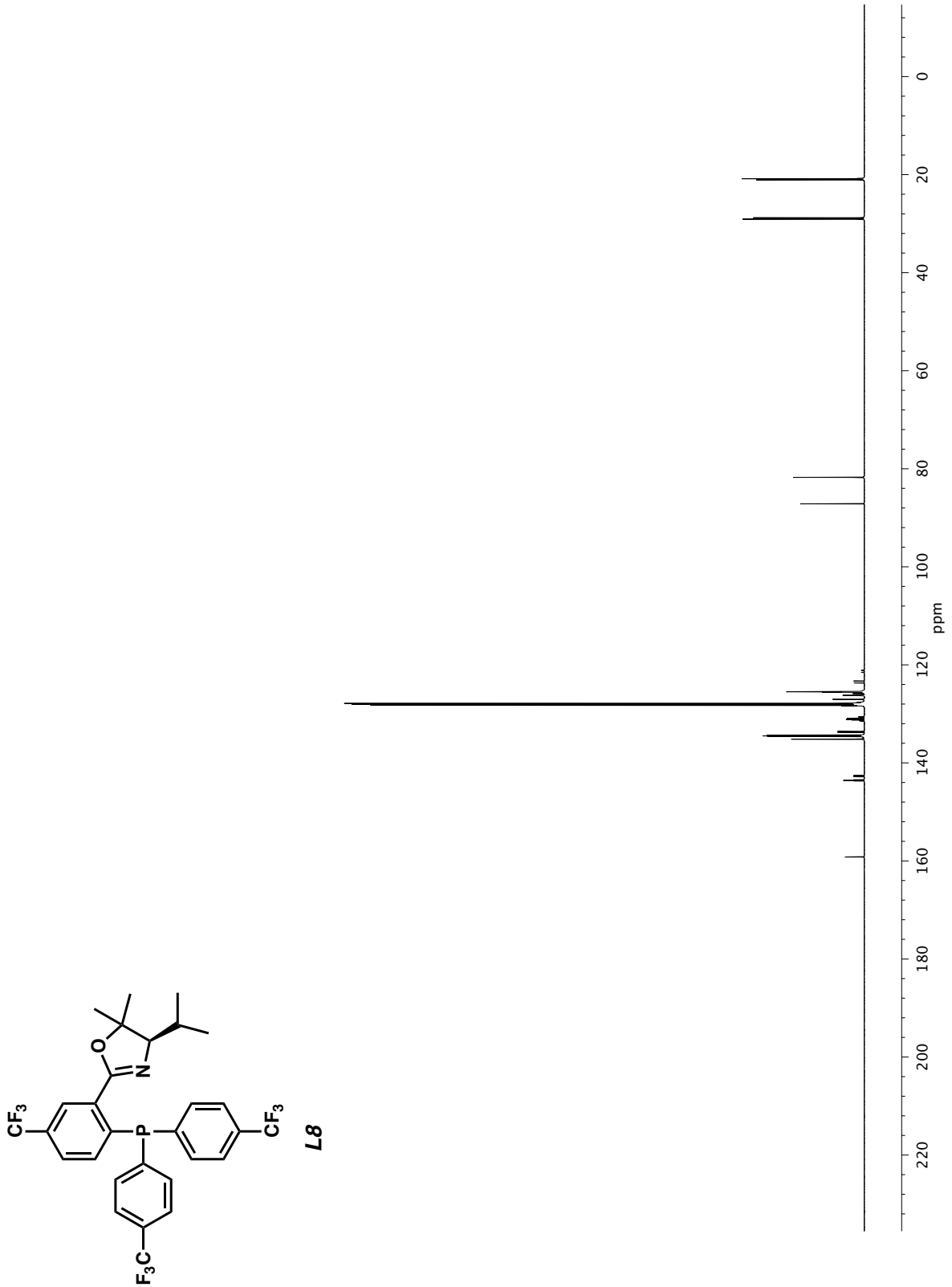


^{19}F NMR (282 MHz, C_6D_6) of compound **L7**.

^{31}P NMR (121 MHz, C_6D_6) of compound **L7**.



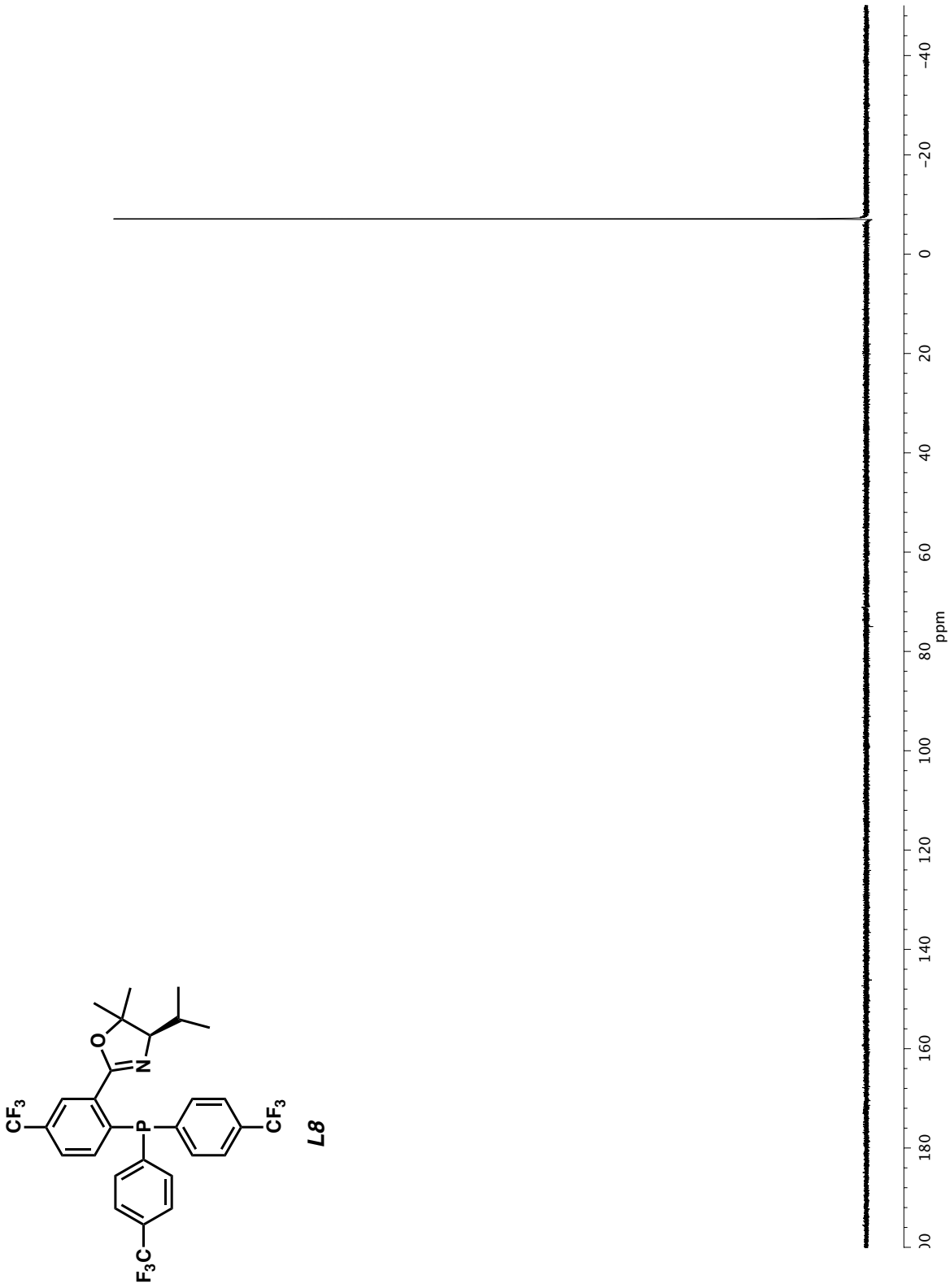
^{1}H NMR (500 MHz, C_6D_6) of compound **L8**.



^{13}C NMR (126 MHz, C_6D_6) of compound **L8**.

^{19}F NMR (282 MHz, C_6D_6) of compound **L8**.

L8



L8

^{31}P NMR (121 MHz, C_6D_6) of compound **L8**.