Supporting Information for

Global Diastereoconvergence in the Ireland–Claisen Rearrangement of Isomeric Enolates: Synthesis of Tetrasubstituted a*-Amino Acids*

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Computational Details

All quantum mechanical calculations were performed with ORCA version 4.1 and 4.2.[1] The resolution of identity (RI) and chain-of-spheres[2] (keyword = RIJCOSX) approximations were utilized for Coulomb and exchange integrals, respectively. Automatic generation of the auxiliary basis sets was employed (keyword = AutoAux).[3] The finest integration grid settings (Grid7, NoFinalGrid, GridX9) were utilized in all calculations. The values obtained from all quantum mechanical calculations are included in the supporting excel file.

Density functional theory (DFT) calculations

Unless otherwise noted, geometry optimizations were carried out with the B3LYP global hybrid generalized gradient approximation (GGA) functional[4] with Becke–Johnson damped D3 dispersion corrections[5] (henceforth referred to as B3LYP-D3(BJ)) with the 6-31G(d) basis set on all atoms. Thermal corrections at 298.15 K were calculated from the unscaled vibrational frequencies at this level of theory. The Quasi-RRHO method was applied to correct for the breakdown of the harmonic oscillator approximation for low frequency vibrations.[6] All stationary points are characterized by the appropriate number of imaginary vibrational modes (zero for optimized geometries and one for transition states). Intrinsic reaction coordinate (IRC) analyses were carried out to ensure all transition states connect the appropriate starting materials and products.

Triple-ζ quality single point calculations were carried out on all stationary points with the B3LYP-D3(BJ) and M06-2X[7] density functionals with the def2-TZVPP basis set[8] on all atoms. The SMD implicit solvation model[9] for toluene (e = 2.374, r_{probe} = 1.300 Å, Refrac. = 1.330) was employed in these single point calculations. Thermal corrections obtained at the previous level of theory were then applied to these electronic energies to obtain the final DFT Gibbs free energies. Relative free energies are given in kcal/mol and are calculated for a 1 atm standard state at 298.15 K.

Conformer searching was carried out both manually and in Spartan Version 7. Conformers were subsequently optimized at the B3LYP-D3(BJ)/6-31G(d) level of theory. The lowest energy conformers [evaluated at B3LYP-D3(BJ)/def2-TZVPP/SMD(Toluene)//B3LYP-D3(BJ)/6-31G(d)] are reported. Note that for transition states, all conformers were considered in subsequent DFT and DLPNO-CCSD(T) calculations.

DLPNO-CCSD(T) Calculations

Additional single point calculations were performed on key optimized structured with the domain based local pair natural orbital coupled-cluster (DLPNO-CCSD(T)) method as described by Neese and coworkers and as implemented in ORCA.[10] The cc-pVTZ basis set,[11] with the corresponding cc-pVTZ/C and def2/J auxiliary basis sets,[12] are used on all atoms. Gaseous free energies are calculated by applying the thermodynamic corrections obtained at the optimization (DFT) level of theory to the gas phase electronic energies from DLPNO-CCSD(T) single point calculations. A free energy of solvation calculated from DFT (M06-2X/def2-TZVPP/SMD(Toluene)) is added to the gaseous coupled-cluster free energies to afford the final reported coupled-cluster solvated Gibbs free energies as reported in the manuscript:

$$G^{CCSD(T)} = E(el)^{CCSD(T)} + ZPE + E(vib) + E(rot) + E(trans) + k_bT - TS + \Delta G(solv)^{DFT}$$

Similar results are obtained if the SMD for toluene is applied in the DLPNO-CCSD(T) calculations; however, we highlight that the solvent self-consistent reaction field (SCRF) is only optimized self-consistently with respect to the Hartree–Fock reference wavefunction and not with respect to the subsequent optimization of coupled-cluster amplitudes.

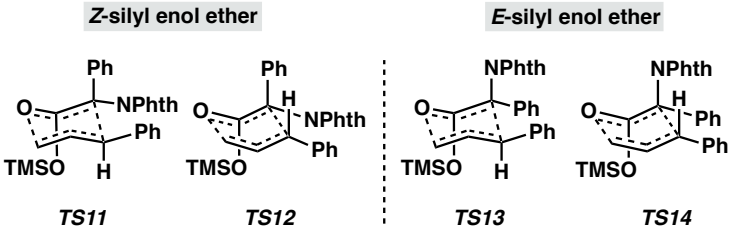
Notes:

- Similar results are obtained with the def2-TZVPP basis set in control experiments, although we elected to employ Dunning's cc-pVnZ family of basis sets for ease of basis set extrapolation with further calculations should the need arise.
- "TightPNO" settings were employed in all calculations.
- "TightPNO": $T_{CutPairs} = 10^{-5}$, $T_{CutDO} = 5x10^{-3}$, $T_{CutPNO} = 1.00x10^{-7}$, $T_{CutMKN} = 10^{-3}$.

Initial Benchmarking/Control Calculations:

Given the importance of non-covalent interactions in controlling the stereochemical outcome of the stereoconvergent Ireland–Claisen reaction, final electronic energies were obtained at the DLPNO-CCSD(T) level of theory. For comparison, DFT single point calculations were carried out with the B3LYP-D3(BJ) and M06-2X functionals. Gratifyingly, the results from the DFT and coupled-cluster computations are in good agreement.

Table S1. Comparison between DFT and DLPNO-CCSD(T) methods.[a]



Method/Basis set	TS11	TS12	TS13	TS14
B3LYP-D3(BJ)/def2-TZVPP/SMD(PhMe)	0.0	4.3	3.8	0.0
M06-2X/def2-TZVPP/SMD(PhMe)	0.0	5.4	3.7	0.0
M06-2X/6-311++G(d,p)/SMD(PhMe)	0.0	5.4	3.7	0.0
DLPNO-CCSD(T)/cc-pVTZ	0.0	5.3	3.6	0.0
DLPNO-CCSD(T)/cc-pVTZ/SMD(PhMe)	0.0	5.5	3.8	0.0

[a] Single point calculations carried out on B3LYP-D3(BJ)/6-31G(d) optimized geometries.

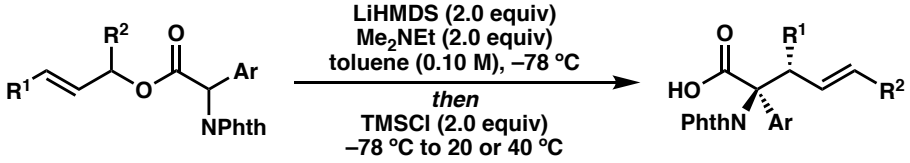
Materials and Methods

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.[13] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. 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 μm) was used for flash chromatography. ^{1}H NMR spectra were recorded on Varian Inova 500 MHz and Bruker 400 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to $CHCl_3$ (δ 77.16 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. 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 or Nicolet 6700 FTIR 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. 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 fast atom bombardment (FAB+). Reagents were purchased from commercial sources and used as received unless otherwise stated.

List of Abbreviations:

TLC – thin-layer chromatography
NPhth – phthalimide
DPPA – Phosphoric acid diphenyl ester azide
LHMDS – lithium bis(trimethylsilyl)amide
THF – tetrahydrofuran
DMF – dimethylformamide
DCC – *N*,*N*′-Dicyclohexylcarbodiimide
DMAP – 4-dimethylaminopyridine
EDC – 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide
TMSCl – trimethylsilyl chloride

General Procedure 1: Ireland–Claisen Rearrangement of α-Phthalidomido Esters



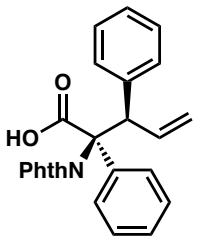
In a nitrogen-filled glovebox, an oven-dried 50 mL round bottom flask was charged with LiHMDS (335.0 mg, 2.00 mmol, 2.0 equiv) and a Teflon-coated stir bar. The flask was then sealed with a septum, removed from the glovebox, and placed under an atmosphere of nitrogen. To the flask was then added toluene (3.0 mL) and *N*,*N*-dimethylethylamine (213 μL, 2.00 mmol, 2.0 equiv). The resulting solution was stirred at 20 °C for 5 min, then the flask was immersed in a –78 °C dry ice/acetone bath. After stirring for 15 min, a solution of the α-phthalidomido ester (1.00 mmol, 1.0 equiv) dissolved in toluene (7.0 mL) was added dropwise over 5 min, resulting in the immediate formation of a dark red/purple opaque reaction mixture. The reaction was maintained at –78 °C for 2 h, after which time TMSCl (254 μL, 2.00 mmol, 2.0 equiv) was added dropwise over 1 min. The reaction flask was then removed from the cooling bath and allowed to warm to 20 °C, typically resulting in an opaque yellow/orange reaction mixture. After consumption of the α-phthalidomido ester was observed by TLC analysis (typically 2–4 h), the reaction was quenched with 1 N HCl (10 mL) and transferred to a separatory funnel with Et_2O (10 mL). As noted below, some compounds required heating to 40 °C for 24 h for full conversion. The layers were separated and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to afford the crude rearrangement product. Depending on the water solubility and/or stability of the product, the reaction was isolated using the following general procedures:

Isolation Procedure 1: The crude reaction mixture was transferred to a 50 mL round bottom flask containing a Teflon-coated stir bar with THF (5 mL) and 2 N HCl (1 mL). The resulting mixture was stirred vigorously at 20 °C for 30 min. THF was then removed via rotary evaporation and the reaction mixture was transferred to a separatory funnel with Et_2O (10 mL) and H_2O (10 mL). The pH of the aqueous layer was adjusted to 12 with sat. aq. Na_2CO_3 and the layers were mixed and separated. The aqueous layer was washed with an additional portion of Et_2O (10 mL), and the combined organic layers were washed with H_2O basified to pH 12 with Na_2CO_3 (5 mL). The

combined aqueous layers were then acidified to pH 3 with 4 N HCl and extracted with Et_2O (2 x 10 mL). The combined organic extracts were then dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to afford the desired rearrangement product.

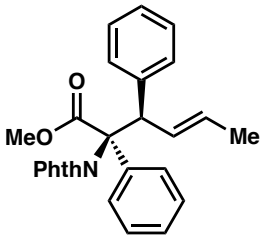
Isolation Procedure 2: The crude reaction mixture was transferred to a flame-dried 25 mL round bottom flask with DMF (3.3 mL). To the stirring solution was then added K_2CO_3 (165.8 mg, 1.20 mmol, 1.2 equiv) and MeI (75 μL, 1.2 mmol, 1.2 equiv). The resulting suspension was stirred rapidly at 20 °C. After consumption of the carboxylic acid rearrangement product was observed by TLC analysis, the reaction mixture was transferred to a separatory funnel with EtOAc (10 mL) and H_2O (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc(2 x 10 mL). The combined organic layers were then washed with brine (10 mL), dried over Na_2SO_4, and concentrated via rotary evaporation. The crude product was then purified by flash column chromatography to afford the desired methyl ester.

Isolation Procedure 3: *Caution! Diazomethane is toxic and explosive; all operations should be carried out in a well-ventilated hood with adequate shielding.* The crude reaction mixture was transferred to a 50 mL round bottom flask with THF (5 mL). The flask was charged with a Teflon-coated stir bar and a blast shield was placed in front of the reaction flask. To the slowly stirring reaction mixture was then added freshly prepared CH_2N_2 (approx. 6 mL of a 0.2 M solution in Et_2O) drop-wise via a flame-polished pipette. After consumption of the carboxylic acid rearrangement product was observed by TLC analysis, acetic acid (2.0 mL) was added dropwise to quench residual CH_2N_2. The reaction mixture was stirred for 20 mins and then transferred to a separatory funnel with EtOAc (10 mL) and sat. aq. $NaHCO_3$ (10 mL). The layers were separated and the aqueous was extracted with EtOAc (2 x 10 mL). The combined organics were dried over Na_2SO_4, filtered, and concentrated via rotary evaporation. The crude product was then purified by flash column chromatography to afford the desired methyl ester.



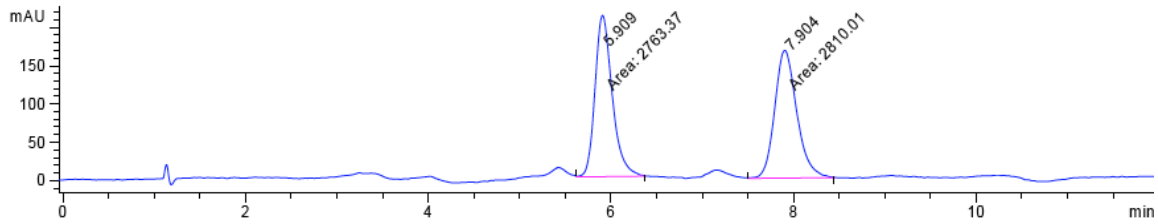
(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2,3-diphenylpent-4-enoic acid (15a)**

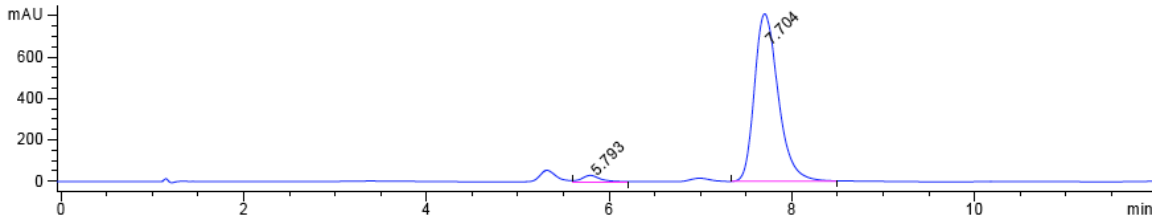
Prepared according to general procedure 1 with isolation procedure 1 and obtained as a white foam (364.5 mg, 0.917 mmol, 92% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.72 (m, 2H), 7.73 – 7.67 (m, 2H), 7.48 – 7.42 (m, 2H), 7.28 – 7.21 (m, 3H), 7.16 – 7.11 (m, 2H), 7.11 – 7.06 (m, 1H), 7.04 – 7.00 (m, 2H), 6.59 (ddd, *J* = 17.2, 10.4, 8.3 Hz, 1H), 5.50 (d, *J* = 8.2 Hz, 1H), 5.24 – 5.02 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.2, 167.9, 139.9, 138.3, 136.1, 134.4, 131.6, 130.6, 128.9, 128.1, 128.0, 127.7, 127.2, 123.6, 118.9, 71.5, 53.1. IR (Neat Film, NaCl) 3061 (br), 1778, 1722, 1497, 1470, 1448, 1369, 1348, 1320, 1265, 1200, 1161, 1110, 1087, 1034, 991, 961, 932, 841, 790, 725, 705, 682, 642 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{20}NO_4$ $[M+H]^+$: 398.1392, found 398.1394.



methyl (2*S*,3*R*,*E*)-2-(1,3-dioxoisoindolin-2-yl)-2,3-diphenylhex-4-enoate (22)

Prepared according to general procedure 1 with isolation procedure 2 with purification by silica gel chromatography (30% EtOAc in hexanes) to afford the desired product as a white solid (365.4 mg, 86% yield over 2 steps, >20:1 dr, 95% ee) $[\alpha]_D^{25}$ +49.5 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 2H), 7.74 – 7.68 (m, 2H), 7.49 – 7.41 (m, 2H), 7.32 – 7.23 (m, 3H), 7.22 – 7.16 (m, 2H), 7.13 – 7.02 (m, 3H), 6.16 (ddd, *J* = 15.3, 8.8, 1.8 Hz, 1H), 5.57 (dq, *J* = 15.6, 6.5 Hz, 1H), 5.48 (d, *J* = 8.8 Hz, 1H), 3.60 (s, 3H), 1.59 (dd, *J* = 6.4, 1.7 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.8, 168.0, 141.2, 136.5, 134.2, 131.7, 131.0, 130.5, 129.6, 128.9, 127.9, 127.7, 127.4, 126.9, 123.4, 71.7, 52.7, 52.3, 18.4; IR (Neat Film, NaCl) 1779, 1722, 1366, 1318, 1222, 1108, 1086, 972, 904, 734, 722; (MM:ESI-APCI+) *m/z* calc'd for $C_{27}H_{24}NO_4$ $[M+H]^+$: 426.1700, found 426.1694; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 5.79, major = 7.70.





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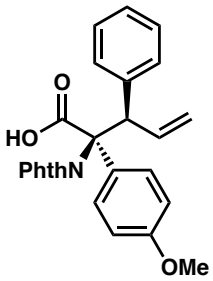
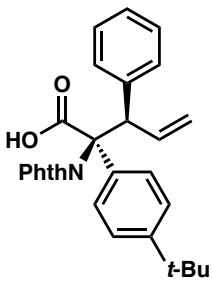


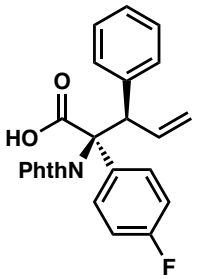
(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-(4-methoxyphenyl)-3-phenylpent-4-enoic acid (23)**

Prepared according to general procedure 1 with isolation procedure 1 and obtained as a white foam (388.7 mg, 0.909 mmol, 91% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.74 (m, 2H), 7.74 – 7.70 (m, 2H), 7.43 – 7.37 (m, 2H), 7.21 – 7.15 (m, 2H), 7.14 – 7.09 (m, 1H), 7.08 – 7.04 (m, 2H), 6.83 – 6.79 (m, 2H), 6.61 (ddd, *J* = 17.1, 10.4, 8.3 Hz, 1H), 5.48 (d, *J* = 8.3 Hz, 1H), 5.21 – 5.09 (m, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.0, 167.9, 159.2, 140.1, 138.4, 134.3, 131.6, 130.6, 130.2, 128.0, 127.9, 127.1, 123.5, 118.7, 113.1, 71.0, 55.3, 53.1; IR (Neat Film, NaCl) 3064 (br), 1776, 1722, 1608, 1512, 1462, 1369, 1347, 1321, 1256, 1180, 1120, 1086, 992, 962, 925, 828, 722, 703, 682 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{26}H_{22}NO_5$ $[M+H]^+$: 428.1498, found 428.1489.



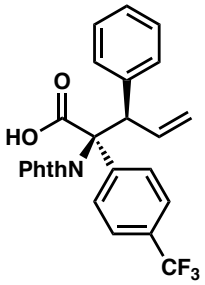
(2*S,3*R**)-2-(4-(*tert*-butyl)phenyl)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpent-4-enoic acid (24)**

Prepared according to general procedure 1 with purification by flash column chromatography (25% EtOAc in hexanes with 2% AcOH) and isolated as a tan amorphous solid (426.7 mg, 0.941 mmol, 94% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.73 (m, 2H), 7.72 – 7.68 (m, 2H), 7.39 – 7.31 (m, 2H), 7.28 – 7.21 (m, 2H), 7.17 – 7.12 (m, 2H), 7.12 – 7.06 (m, 1H), 7.05 – 6.99 (m, 2H), 6.61 (dt, *J* = 17.0, 9.9, 8.2 Hz, 1H), 5.49 (d, *J* = 8.2 Hz, 1H), 5.20 – 5.07 (m, 2H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.1, 167.9, 150.7, 140.0, 138.4, 134.3, 132.7, 131.5, 130.6, 128.5, 127.9, 127.0, 124.6, 123.4, 118.6, 71.3, 52.9, 34.5, 31.3; IR (Neat Film, NaCl) 3062 (br), 2963, 2361, 1778, 1722, 1715, 1652, 1506, 1470, 1506, 1470, 1368, 1348, 1319, 1267, 1204, 1122, 1087, 992, 931, 838, 773, 723, 704, 665 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{29}H_{28}NO_4$ $[M+H]^+$: 454.2018, found 454.2022.



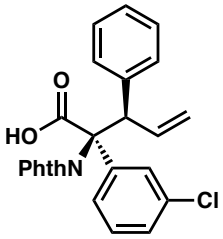
(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-(4-fluorophenyl)-3-phenylpent-4-enoic acid (25)**

Prepared according to general procedure 1 with isolation procedure 1 and obtained as a white foam (404.6 mg, 0.974 mmol, 97% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.76 (m, 2H), 7.77 – 7.72 (m, 2H), 7.45 (t, *J* = 8.4, 5.1 Hz, 2H), 7.16 – 7.10 (m, 3H), 7.11 – 7.04 (m, 2H), 6.95 (t, *J* = 8.5 Hz, 2H), 6.60 (dt, *J* = 17.0, 9.9, 8.8 Hz, 1H), 5.49 (d, *J* = 8.2 Hz, 1H), 5.23 – 5.12 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.1, 167.9, 162.3 (d, J_{C-F} = 247.9 Hz), 139.6, 138.0, 134.5, 131.9 (d, J_{C-F} = 3.5 Hz), 131.5, 130.8 (d, J_{C-F} = 8.1 Hz), 130.6, 128.1, 127.3, 123.6, 119.1, 114.6 (d, J_{C-F} = 21.5 Hz), 71.0, 53.2; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –62.69 – –62.73 (m); IR (Neat Film, NaCl) 3061, 1777, 1722, 1605, 1509, 1470, 1410, 1367, 1348, 1320, 1239, 1164, 1107, 1086, 990, 962, 929, 839, 723, 703 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{19}NO_4F$ $[M+H]^+$: 416.1298, found 416.1282.



(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-3-phenyl-2-(4-(trifluoromethyl)phenyl)pent-4-enoic acid (26)**

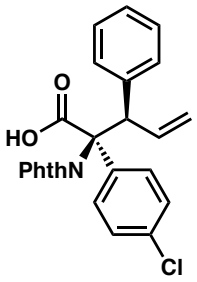
Prepared according to general procedure 1 with isolation procedure 1 with further purification by flash column chromatography (30% EtOAc in hexanes with 2% AcOH) and obtained as a white foam (438.6 mg, 0.942 mmol, 94% yield >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 – 7.77 (m, 2H), 7.77 – 7.73 (m, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.19 – 7.10 (m, 3H), 7.09 – 7.03 (m, 2H), 6.57 (ddd, *J* = 17.1, 10.3, 8.5 Hz, 1H), 5.51 (d, *J* = 8.4 Hz, 1H), 5.24 – 5.15 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.3, 167.9, 140.1, 139.3, 137.7, 134.6, 131.4, 130.5, 130.1 (q, $J_{C–F}$ = 32.6 Hz), 129.4, 128.17, 127.4, 124.6 (q, $J_{C–F}$ = 3.7 Hz), 124.56 (q, $J_{C–F}$ = 272.8 Hz), 123.7, 119.4, 71.3, 53.1; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –62.70; IR (Neat Film, NaCl) 3064 (br), 1778, 1722, 1617, 1470, 1454, 1413, 1370, 1327, 1267, 1170, 1124, 1072, 1017, 990, 963, 836, 724, 704, 656 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{26}H_{19}NO_4F_3$ $[M+H]^+$: 466.1266, found 466.1287.



(2*S,3*R**)-2-(3-chlorophenyl)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpent-4-enoic acid (27)**

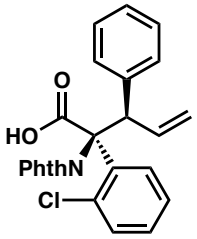
Prepared according to general procedure 1 with isolation procedure 1 and obtained as a white foam (385.0 mg, 0.891 mmol, 89% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.82 – 7.77 (m, 2H), 7.77 – 7.71 (m, 2H), 7.44 (t, *J* = 1.8 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.25 (d, *J* = 1.8 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.16 – 7.11 (m, 3H), 7.10 – 7.03 (m, 2H), 6.58 (ddd, *J* = 17.1, 10.4, 8.4 Hz, 1H), 5.47 (d, *J* = 8.4 Hz, 1H), 5.23 – 5.14 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.1, 167.8, 139.2, 138.1, 137.6, 134.4, 133.5, 131.3, 130.5, 129.3, 128.8, 128.2, 128.0, 127.3,

126.8, 123.6, 119.1, 71.0, 53.0; IR (Neat Film, NaCl) 3066 (br), 1777, 1720, 1470, 1454, 1430, 1370, 1319, 1266, 1121, 1074, 925, 721, 705 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{19}NO_4Cl$ $[M+H]^+$: 432.1003, found 432.1007.



(2*S,3*R**)-2-(4-chlorophenyl)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpent-4-enoic acid (28)**

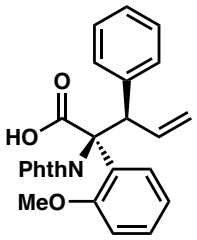
Prepared according to general procedure 1 with isolation procedure 1 and obtained as a white foam (416.7 mg, 0.964 mmol, 96% yield, >20:1 dr); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.74 (m, 2H), 7.74 – 7.71 (m, 2H), 7.43 – 7.35 (m, 2H), 7.26 – 7.20 (m, 3H), 7.16 – 7.08 (m, 3H), 7.08 – 7.02 (m, 2H), 6.55 (ddd, *J* = 17.8, 10.1, 8.7 Hz, 1H), 5.45 (d, *J* = 8.3 Hz, 1H), 5.26 – 5.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 167.9, 139.6, 137.9, 134.8, 134.5, 134.1, 131.4, 130.5, 130.3, 128.1, 127.9, 127.3, 123.6, 119.1, 71.1, 53.0; IR (Neat Film, NaCl) 3062 (br), 1778, 1714, 1494, 1470, 1454, 1371, 1348, 1322, 1266, 1100, 1014, 992, 962, 856, 824, 723, 706, 682 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{19}NO_4Cl$ $[M+H]^+$: 432.1003, found 432.1005.



(2*S*,3*R*)-2-(2-chlorophenyl)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpent-4-enoic acid (29)

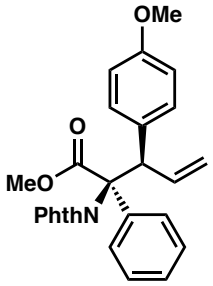
Prepared according to general procedure 1 with heating to 40 ºC with isolation procedure 1 and obtained as a white foam (409.2 mg, 0.948 mmol, 95% yield, >20:1 dr); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.81 (m, 1H), 7.79 – 7.73 (m, 2H), 7.74 – 7.68 (m, 2H), 7.34 – 7.29 (m, 2H), 7.25 – 7.11 (m, 3H), 7.07 – 6.98 (m, 3H), 6.54 (ddd, *J* = 17.5, 10.4, 7.4 Hz, 1H), 5.96 (d, *J* = 7.4 Hz, 1H), 5.18 (d, *J* = 10.5 Hz, 1H), 5.09 (d, *J* = 17.1 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.8, 168.0, 139.2, 138.1, 134.4, 134.3, 132.7, 131.9, 131.6, 131.4, 130.8, 129.1, 127.7,

127.0, 126.1, 123.5, 119.0, 72.4, 51.5; IR (Neat Film, NaCl) 3066 (br), 1777, 1720, 1470, 1454, 1430, 1370, 1319, 1266, 1121, 1074, 925, 721, 705 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{19}NO_4Cl$ $[M+H]^+$: 432.1003, found 432.1019.



(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-(2-methoxyphenyl)-3-phenylpent-4-enoic acid (30)**

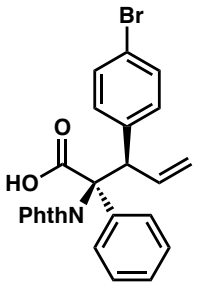
Prepared according to general procedure 1 with heating to 40 ºC with isolation procedure 1 and obtained as a white foam (371.4 mg, 0.869 mmol, 87% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 – 7.73 (m, 2H), 7.76 – 7.68 (m, 2H), 7.69 – 7.62 (m, 1H), 7.36 – 7.29 (m, 3H), 7.12 – 7.02 (m, 3H), 7.04 – 6.94 (m, 1H), 6.91 – 6.83 (m, 1H), 6.59 (ddd, *J* = 17.0, 10.2, 8.0 Hz, 1H), 5.83 – 5.73 (m, 1H), 5.17 (d, *J* = 10.0 Hz, 1H), 5.16 – 5.10 (m, 1H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.1, 167.8, 156.7, 140.3, 138.9, 134.1, 131.6, 130.7, 130.7, 129.6, 127.6, 126.7, 124.7, 123.2, 120.3, 118.0, 111.5, 71.1, 55.6, 51.9; IR (Neat Film, NaCl) 3059 (br), 1776, 1716, 1490, 1463, 1435, 1370, 1319, 1249, 1024, 917, 725, 702 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{26}H_{22}NO_5$ $[M+H]^+$: 428.1498, found 428.1515.



(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-methoxyphenyl)-2-phenylpent-4-enoic acid (31)**

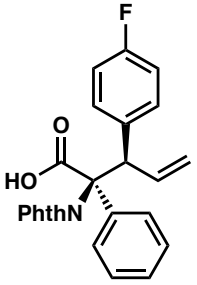
Prepared according to general procedure 1 with isolation procedure 2 with purification by silica gel chromatography (30% EtOAc in hexanes) to afford the desired product as a light yellow oil (206.6 mg, 70% yield over 2 steps, >20:1 dr); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.87 (m, 4H), 7.68 – 7.58 (m, 2H), 7.50 – 7.39 (m, 3H), 7.31 – 7.23 (m, 2H), 6.82 – 6.77 (m, 2H), 6.77 – 6.62 (m, 1H), 5.66 (dd, *J* = 8.2, 1.3 Hz, 1H), 5.35 – 5.26 (m, 2H), 3.88 (s, 3H), 3.79 (s, 3H); ^{13}C

NMR (100 MHz, Chloroform-*d*) δ 169.8, 168.1, 158.5, 138.9, 136.5, 134.3, 132.3, 131.6, 131.5, 128.8, 127.7, 127.6, 123.5, 118.3, 113.3, 71.6, 55.2, 52.7, 52.5; IR (Neat Film, NaCl) 1778, 1716, 1610, 1512, 1468, 1367, 1319, 1228, 1180, 1115, 1035, 908, 846, 730; (MM:ESI-APCI+) *m/z* calc'd for $C_{27}H_{27}N_2O_5$ $[M+NH_4]^+$: 459.1914, found 459.1907.



(2*S,3*R**)-3-(4-bromophenyl)-2-(1,3-dioxoisoindolin-2-yl)-2-phenylpent-4-enoic acid (32)**

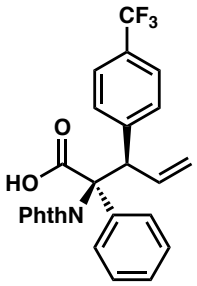
Prepared according to general procedure 1 with isolation procedure 1 to afford the desired product as a light yellow solid (664.9 mg, 93% yield, >20:1 dr); ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.92 – 7.83 (m, 2H), 7.88 – 7.80 (m, 2H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.32 – 7.21 (m, 5H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.42 (ddd, *J* = 17.2, 10.3, 8.7 Hz, 1H), 5.43 (d, *J* = 8.6 Hz, 1H), 5.15 – 5.06 (m, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.5, 167.5, 140.0, 138.5, 136.7, 135.0, 132.3, 130.7, 130.5, 128.7, 127.3, 127.2, 123.3, 119.9, 118.5, 70.5, 51.6; IR (Neat Film, NaCl) 1773, 1715, 1488, 1367, 1348, 1319, 1123, 1074, 1009, 719; (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{22}BrN_2O_4$ $[M+NH_4]^+$: 493.0757, found 493.0792.



(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-3-(4-fluorophenyl)-2-phenylpent-4-enoic acid (33)**

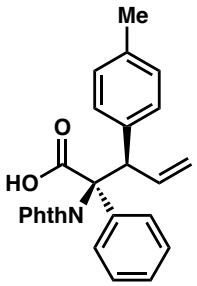
Prepared according to general procedure 1 with isolation procedure 1 to afford the desired product as a white solid (345.6 mg, 83% yield, >20:1 dr); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.75 (m, 2H), 7.79 – 7.69 (m, 2H), 7.53 – 7.44 (m, 2H), 7.32 – 7.25 (m, 3H), 7.18 – 7.08 (m, 2H), 6.79 – 6.71 (m, 2H), 6.58 (ddd, *J* = 17.2, 10.5, 8.0 Hz, 1H), 5.52 (d, *J* = 8.0 Hz, 1H), 5.19 (dt, *J* =

10.4, 1.4 Hz, 1H), 5.12 (dt, J = 17.2, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.2, 168.0, 162.0 (d, $J_{C–F}$ = 245.9 Hz), 138.1, 135.6 (d, $J_{C–F}$ = 3.4 Hz), 134.5, 132.2 (d, $J_{C–F}$ = 8.0 Hz), 131.5, 128.8, 128.2, 127.8, 123.6, 119.0, 115.0, 114.8, 71.4, 52.2; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –115.4 (dddd, J = 13.8, 8.5, 5.3, 1.6 Hz); IR (Neat Film, NaCl) 3070 (br), 1778, 1715, 1601, 1508, 1369, 1319, 1226, 910, 849, 720; (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{22}FN_2O_4$ $[M+NH_4]^+$: 433.1558, found 433.1565.



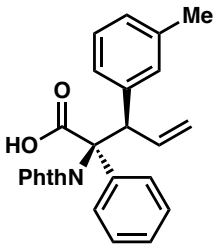
(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-phenyl-3-(4-(trifluoromethyl)phenyl)pent-4-enoic acid (34)**

Prepared according to general procedure 1 with isolation procedure 1 to afford the desired product as a white solid (404.3 mg, 87% yield, >20:1 dr); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 – 7.72 (m, 4H), 7.49 (dd, J = 6.3, 2.8 Hz, 2H), 7.29 (t, J = 4.1 Hz, 7H), 6.61 (ddd, J = 17.2, 10.4, 8.0 Hz, 1H), 5.60 (d, J = 8.0 Hz, 1H), 5.22 (dd, J = 10.5, 0.9 Hz, 1H), 5.14 (dd, J = 17.2, 1.0 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.5, 167.9, 144.1, 137.5, 135.7, 134.6, 131.4, 131.0, 129.3 (q, J = 32.5 Hz), 128.7, 128.3, 127.9, 125.6, 124.8 (q, J = 3.8 Hz), 123.6, 122.9, 119.6, 71.3, 52.7; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –62.6; IR (Neat Film, NaCl) 3077 (br), 1777, 1716, 1368, 1347, 1326, 1166, 1125, 1069, 908, 723 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{19}F_3NO_4$ $[M+H]^+$: 466.1261, found 466.1275.



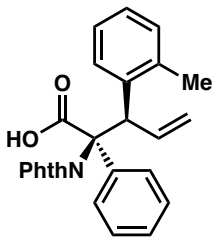
(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-phenyl-3-(*p*-tolyl)pent-4-enoic acid (35)**

Prepared according to general procedure 1 with isolation procedure 1 to afford the desired product as a light yellow solid (364.1 mg, 88% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.81 – 7.76 (m, 2H), 7.75 – 7.68 (m, 2H), 7.51 – 7.46 (m, 2H), 7.26 (dd, *J* = 3.8, 2.7 Hz, 3H), 7.06 – 7.02 (m, 2H), 6.87 (d, *J* = 7.8 Hz, 2H), 6.61 (ddd, *J* = 16.9, 10.5, 8.2 Hz, 1H), 5.50 (d, *J* = 8.3 Hz, 1H), 5.22 – 5.07 (m, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.1, 168.0, 138.4, 136.8, 136.7, 136.3, 134.3, 131.6, 130.4, 128.9, 128.7, 128.0, 127.7, 123.5, 118.6, 71.5, 52.7, 21.2; IR (Neat Film, NaCl) 3424 (br), 1778, 1714, 1514, 1367, 1318, 908, 722; (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{25}N_2O_4$ $[M+NH_4]^+$: 429.1809, found 429.1817.



(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-phenyl-3-(*m*-tolyl)pent-4-enoic acid (36)**

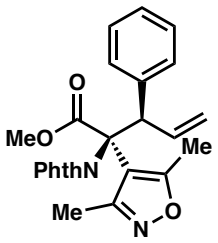
Prepared according to general procedure 1 with isolation procedure 1 to afford the desired product as a white solid (342.4 mg, 0.832 mmol, 83% yield, >20:1 dr); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 – 7.70 (m, 4H), 7.52 – 7.44 (m, 2H), 7.31 – 7.27 (m, 3H), 7.07 (d, *J* = 7.7 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.88 (m, 1H), 6.85 (d, *J* = 1.8 Hz, 1H), 6.57 (ddd, *J* = 16.7, 10.8, 8.4 Hz, 1H), 5.53 – 5.39 (m, 1H), 5.19 – 5.10 (m, 2H), 1.95 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.1, 167.9, 140.1, 138.5, 137.4, 136.0, 134.3, 131.6, 131.2, 129.0, 128.0, 128.0, 127.8, 127.8, 127.7, 123.5, 118.7, 71.4, 53.1, 21.2; IR (Neat Film, NaCl) 1777, 1719, 1367, 1319, 908, 720, 698; (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{22}NO_4$ $[M+H]^+$: 412.1549, found 412.1545.



(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-phenyl-3-(*o*-tolyl)pent-4-enoic acid (37)**

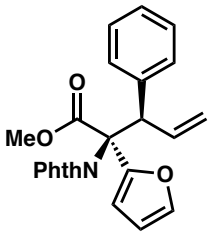
Prepared according to general procedure 1 with isolation procedure 1 to afford the desired product as a white foam (326.6 mg, 0.794 mmol, 79% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-

d) δ 7.96 – 7.88 (m, 2H), 7.87 – 7.74 (m, 2H), 7.41 (d, *J* = 7.7 Hz, 1H), 7.19 (q, *J* = 6.8 Hz, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.72 (ddd, *J* = 17.4, 10.4, 7.3 Hz, 1H), 5.86 (d, *J* = 7.4 Hz, 1H), 5.11 (d, *J* = 10.4 Hz, 1H), 5.03 (d, *J* = 17.0 Hz, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.0, 168.7, 139.1, 138.6, 137.2, 135.5, 134.6, 131.6, 130.4, 129.7, 128.1, 128.0, 127.4, 127.4, 126.2, 123.8, 117.9, 72.6, 48.3, 19.7; IR (Neat Film, NaCl) 3056 (br), 2366, 1774, 1716, 1489, 1418, 1369, 1345, 1318, 1244, 1124, 1086, 90, 909, 876, 794, 726, 698, 660; (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{22}NO_4$ $[M+H]^+$: 412.1549, found 412.1534.



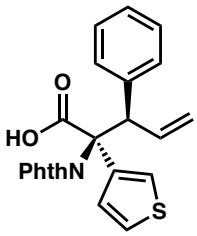
methyl (2*S,3*R**)-2-(3,5-dimethylisoxazol-4-yl)-2-(1,3-dioxoisoindolin-2-yl)-3-phenylpent-4-enoate (38)**

Prepared according to general procedure 1 with isolation procedure 2 and purification by flash column chromatography (20% EtOAc in hexanes) to afford the desired product as an amorphous white solid (171.9 mg, 0.399 mmol, 40% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.74 (s, 4H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.3 Hz, 1H), 7.01 (t, *J* = 7.5 Hz, 2H), 6.82 (ddd, *J* = 17.3, 10.6, 6.5 Hz, 1H), 5.31 (d, *J* = 6.6 Hz, 1H), 5.23 (dt, *J* = 10.8, 1.6 Hz, 1H), 5.04 (dt, *J* = 17.4, 1.3 Hz, 1H), 3.60 (s, 3H), 2.47 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.6, 167.6, 159.0, 140.1, 138.7, 134.6, 131.2, 131.0, 127.9, 127.2, 123.6, 119.6, 111.9, 66.5, 52.9, 52.6, 14.3, 12.6; IR (Neat Film, NaCl) 3474, 3060, 3028, 2950, 2251, 1780, 1743, 1726, 1603, 1467, 1432, 1406, 1365, 1349, 1322, 1258, 1227, 1121, 1087, 1019, 1002, 964, 904, 858, 842, 792, 777, 760, 724, 704, 684, 626 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{23}N_2O_5$ $[M+H]^+$: 431.1607, found 431.1605.



methyl (2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-(furan-2-yl)-3-phenylpent-4-enoate (39)**

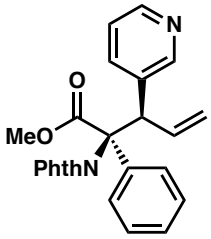
Prepared according to general procedure 1 with isolation procedure 3 and purification by flash column chromatography (10–30% EtOAc in hexanes) to afford the desired product as a white foam (260.3 mg, 0.648 mmol, 65% yield, >20:1 dr); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 – 7.70 (m, 2H), 7.71 – 7.62 (m, 2H), 7.49 – 7.38 (m, 1H), 7.15 (s, 5H), 6.69 – 6.53 (m, 1H), 6.43 (dt, *J* = 3.2, 0.5 Hz, 1H), 6.33 – 6.27 (m, 1H), 5.53 (d, *J* = 7.5 Hz, 1H), 5.24 – 5.10 (m, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.7, 167.6, 148.3, 142.0, 138.7, 137.1, 134.2, 131.6, 130.2, 127.9, 127.3, 123.3, 118.4, 112.0, 110.7, 67.8, 52.9, 52.8; IR (Neat Film, NaCl) 3486, 3063, 3032, 2949, 2365, 1779, 1720, 1653, 1636, 1612, 1495, 1468, 1452, 1435, 1366, 1347, 1316, 1225, 1156, 1124, 1080, 1024, 928, 876, 784, 738, 716, 702, 684 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{24}H_{20}NO_5$ $[M+H]^+$: 402.1341, found 402.1362.



(2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-3-phenyl-2-(thiophen-3-yl)pent-4-enoic acid (40)**

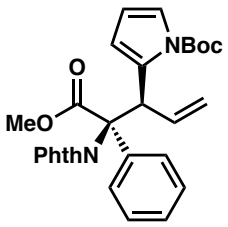
Prepared according to general procedure 1 with isolation procedure 1 and obtained as a tan amorphous solid tan solid with a minor impurity (306.0 mg, 0.758 mmol, 76% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 2H), 7.77 – 7.69 (m, 2H), 7.51 – 7.47 (m, 1H), 7.36 – 7.32 (m, 3H), 7.32 – 7.28 (m, 3H), 7.28 – 7.23 (m, 1H), 6.59 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.16 (s, 1H), 4.93 – 4.82 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.4, 167.9, 138.8, 137.5, 137.2, 134.4, 131.6, 130.6, 128.3, 128.0, 127.4, 125.3, 124.2, 123.6, 118.9, 69.7, 53.9; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 172.4, 167.9, 138.8, 137.5, 137.2, 134.4, 131.6, 130.6, 128.3, 128.0, 127.4, 125.3, 124.2, 123.6, 118.9, 69.7, 53.9; IR (Neat Film, NaCl)

2912 (br), 1774, 1714, 1366, 1343, 1319, 1227, 1169, 1122, 1058, 992, 771, 747, 721, 702, 674 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{23}H_{18}NO_4S$ $[M+H]^+$: 404.0957, found 404.0944.



methyl (2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2-phenyl-3-(pyridin-3-yl)pent-4-enoate (41)**

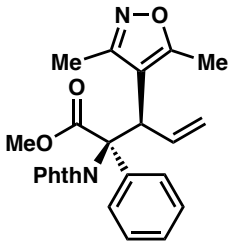
Prepared according to general procedure 1 with isolation procedure 3 and purification by flash column chromatography (10–60% EtOAc in hexanes) to afford the desired product as a white foam (365.5 mg, 0.891 mmol, 89% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.37 (d, *J* = 1.9 Hz, 1H), 8.36 (d, *J* = 1.5 Hz, 1H), 7.81 – 7.69 (m, 4H), 7.64 (dt, *J* = 8.1, 2.0 Hz, 1H), 7.52 – 7.43 (m, 2H), 7.35 – 7.26 (m, 3H), 7.08 (dd, *J* = 8.0, 4.8 Hz, 1H), 6.57 (ddd, *J* = 17.7, 10.5, 7.8 Hz, 1H), 5.56 (d, *J* = 7.8 Hz, 1H), 5.22 (d, *J* = 10.3 Hz, 1H), 5.13 (d, *J* = 17.2 Hz, 1H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.4, 168.0, 151.5, 148.1, 138.1, 137.5, 136.2, 135.8, 134.5, 131.3, 128.5, 128.0, 127.8, 123.6, 122.8, 119.5, 71.1, 52.8, 50.9; IR (Neat Film, NaCl) 3482, 3035, 2950, 1778, 1722, 1610, 1468, 1448, 1426, 1368, 1349, 1321, 1231, 1192, 1112, 1086, 1026, 970, 917, 902, 842, 794, 751, 716, 651 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{21}N_2O_4$ $[M+H]^+$: 413.1501, found 413.1505.



***tert*-butyl 2-((3*R**,4*S**)-4-(1,3-dioxoisoindolin-2-yl)-5-methoxy-5-oxo-4-phenylpent-1-en-3-yl)-1*H*-pyrrole-1-carboxylate (42)**

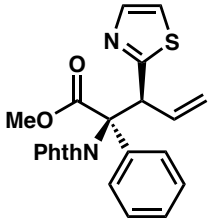
Prepared according to general procedure 1 with isolation procedure 3 and purification by flash column chromatography (20% EtOAc in hexanes) to afford the desired product as a white foam (354.4 mg, 0.708 mmol, 71% yield, 10:1 dr measured by ratio of major δ 3.77 (s, 3H, integral = 2.71) to minor δ 3.73 (s, 3H, integral = 0.27)); ^{1}H NMR (500 MHz, Chloroform-*d*) δ Major: 7.89

– 7.83 (m, 2H), 7.78 – 7.73 (m, 2H), 6.78 (d, J = 7.7 Hz, 1H), 6.47 (ddd, J = 17.5, 10.3, 7.6 Hz, 1H), 6.09 (t, J = 3.4 Hz, 1H), 6.04 – 6.00 (m, 1H), 5.16 (d, J = 17.0 Hz, 1H), 3.77 (s, 3H), Minor: 7.70 – 7.66 (m, 0.2H), 7.60 – 7.56 (m, 0.2H), 7.31 – 7.28 (m, 0.4H), 6.81 (d, J = 7.5 Hz, 0.1H), 6.17 (ddd, J = 17.0, 10.3, 6.8 Hz, 0.1H), 5.92 (t, J = 3.5 Hz, 0.1H), 5.85 (d, J = 3.6 Hz, 0.1H), 5.04 – 4.99 (m, 0.1H), 3.73 (s, 0.3H), Overlapping: 7.23 – 7.14 (m, 4.4H), 7.06 – 7.00 (m, 2.1 H), 5.10 – 5.06 (m, 1.2H), 1.45 (s, 9.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ Major: 169.1, 168.2, 149.4, 137.7, 136.7, 134.4, 131.8, 131.6, 127.8, 127.6, 123.6, 121.9, 117.2, 114.6, 110.0, 84.0, 72.5, 52.5, 44.4, 28.0, Minor: 169.3, 168.1, 149.8, 137.4, 134.1, 131.9, 131.7, 128.2, 127.9, 127.5, 123.3, 121.6, 117.5, 114.8, 109.5, 83.7, 71.6, 52.8, 44.5, 28.1; IR (Neat Film, NaCl) 3484, 2950, 2981, 1778, 1732, 1613, 1470, 1416, 1395, 1369, 1324, 1239, 1165, 1128, 1067, 1000, 942, 924, 854, 817, 772, 725, 701, 665 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{29}H_{29}N_2O_6$ $[M+H]^+$: 501.2026, found 501.2047.



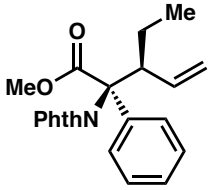
methyl (2*S,3*R**)-3-(3,5-dimethylisoxazol-4-yl)-2-(1,3-dioxoisoindolin-2-yl)-2-phenylpent-4-enoate (43)**

Prepared according to general procedure 1 with isolation procedure 3 and purification by flash column chromatography (30% EtOAc in hexanes) to afford the desired product as a white foam (291.7 mg, 0.678 mmol, 68% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 (dd, J = 5.4, 3.1 Hz, 2H), 7.83 (dd, J = 5.5, 3.1 Hz, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.22 (m, 3H), 6.59 (ddd, J = 16.7, 10.5, 5.6 Hz, 1H), 5.33 (dt, J = 5.4, 1.9 Hz, 1H), 5.22 (dt, J = 10.4, 1.6 Hz, 1H), 5.03 (dt, J = 17.2, 1.3 Hz, 1H), 3.76 (s, 3H), 2.03 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.0, 168.6, 168.1, 160.7, 136.5, 135.5, 134.7, 131.5, 128.1, 128.1, 127.9, 123.8, 117.8, 111.3, 70.9, 52.8, 43.4, 12.4, 10.9; IR (Neat Film, NaCl) 3478, 3061, 2952, 1777, 1747, 1728, 1715, 1614, 1497, 1569, 1446, 1434, 1367, 1349, 1319, 1232, 1175, 1125, 1089, 1006, 967, 924, 794, 720, 701, 666 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{23}N_2O_5$ $[M+H]^+$: 431.1607, found 431.1594.



methyl (2*S,3*S**)-2-(1,3-dioxoisoindolin-2-yl)-2-phenyl-3-(thiazol-2-yl)pent-4-enoate (44)**

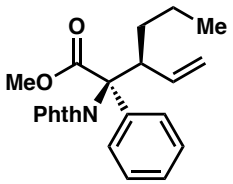
Prepared according to general procedure 1 with isolation procedure 3 and purification by flash column chromatography (30% EtOAc in hexanes) to afford the desired product as a tan amorphous solid (160.2 mg, 0.382 mmol, 38% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 – 7.76 (m, 2H), 7.75 – 7.70 (m, 2H), 7.53 – 7.48 (m, 2H), 7.41 (d, *J* = 3.3 Hz, 1H), 7.35 – 7.27 (m, 3H), 7.22 (d, *J* = 3.3 Hz, 1H), 6.55 – 6.47 (m, 1H), 5.80 (d, *J* = 9.1 Hz, 1H), 5.28 – 5.18 (m, 2H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.5, 168.5, 168.1, 142.2, 136.1, 135.5, 134.2, 131.7, 128.5, 128.0, 127.7, 123.4, 119.7, 119.5, 70.0, 53.1, 51.6; IR (Neat Film, NaCl) 2950, 2339, 1779, 1722, 1490, 1448, 1368, 1348, 1320, 1267, 1232, 1150, 1111, 1086, 1057, 988, 963, 899, 842, 758, 716, 695, 664 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{23}H_{19}N_2O_4S$ $[M+H]^+$: 419.1066, found 419.1064.



methyl (2*S,3*S**)-2-(1,3-dioxoisoindolin-2-yl)-3-ethyl-2-phenylpent-4-enoate (46)**

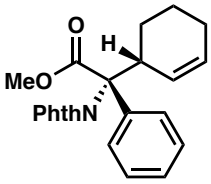
Prepared according to general procedure 1 with isolation procedure 2 with purification by silica gel chromatography (0–30% EtOAc in hexanes) to afford the desired product as white foam (293.9 mg, 0.841 mmol, 84% yield, 3.7:1 dr measured by ratio of major δ 3.78 (s, 3H, integral = 2.85) to minor δ 3.76 (s, 3H, integral = 0.78); ^{1}H NMR (400 MHz, Chloroform-*d*) Major: δ 7.78 – 7.74 (m, 2H), 7.70 – 7.66 (m, 2H), 7.62 – 7.58 (m, 2H), 7.34 – 7.27 (m, 3H), 5.87 (ddd, *J* = 17.1, 10.2, 9.4 Hz, 1H), 5.23 (ddd, *J* = 17.1, 2.1, 0.4 Hz, 1H), 5.18 (dd, *J* = 10.3, 2.1 Hz, 1H), 3.78 (s, 3H), 1.77 – 1.63 (m, 1H), 1.02 – 0.94 (m, 5H), Minor: δ 7.80 – 7.77 (m, 2H), 7.71 – 7.69 (m, 2H), 7.65 – 7.62 (m, 2H), 7.25 – 7.19 (m, 3H), 5.56 (ddd, *J* = 17.1, 10.3, 9.0 Hz, 1H), 5.02 (dd, *J* = 10.3, 1.8 Hz, 1H), 4.94 (ddd, *J* = 17.1, 1.8, 0.7 Hz, 1H), 3.76 (s, 3H), 1.90 (dqd, *J* = 12.8, 7.0, 1.3 Hz, 1H),

1.16 – 1.04 (m, 1H), 0.96 – 0.87 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) Major: δ 169.2, 168.1, 138.0, 136.6, 134.2, 131.7, 128.1, 128.0, 127.9, 123.3, 119.6, 71.1, 52.5, 48.7, 23.6, 12.2, Minor δ 168.9, 168.5, 138.8, 135.9, 134.2, 131.8, 127.9, 127.7, 127.7, 123.4, 119.1, 71.8, 52.3, 50.1, 23.7, 12.2; IR (Neat Film, NaCl) 3476, 3064, 3030, 2967, 2935, 2875, 1777, 1746, 1714, 1722, 1638, 1613, 1498, 1468, 1448, 1456, 1434, 1384, 1367, 1351, 1320, 1267, 1227, 1145, 1111, 1084, 1004, 922, 894, 792, 775, 719, 699, 658 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{22}H_{22}NO_4$ $[M+H]^+$: 364.1549 found 364.1535.



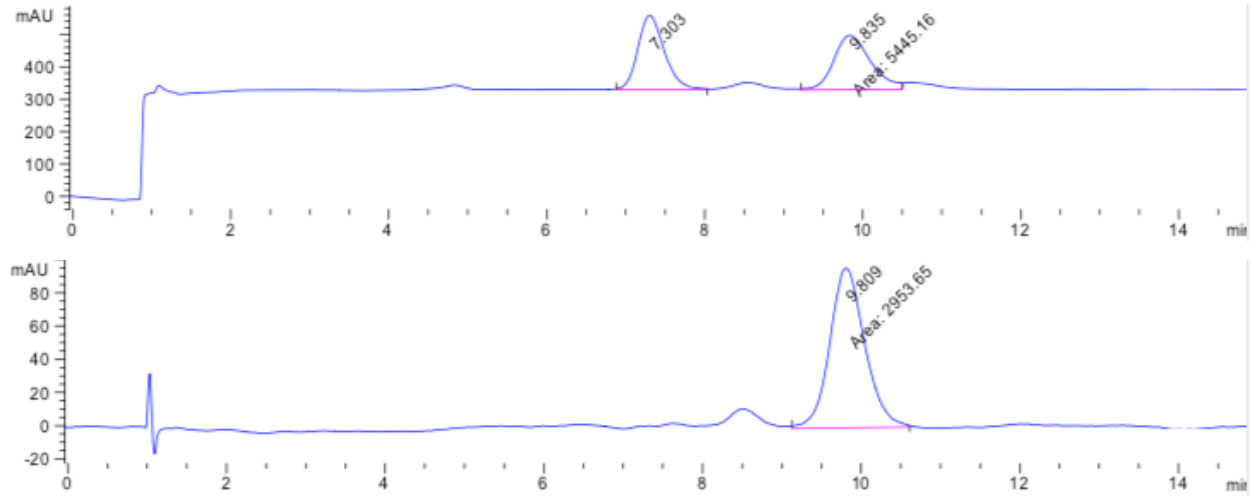
methyl (2*S,3*S**)-2-(1,3-dioxoisoindolin-2-yl)-2-phenyl-3-vinylhexanoate (48)**

Prepared according to general procedure 1 with isolation procedure 2 with purification by silica gel chromatography (0–30% EtOAc in hexanes) to afford the desired product as white foam (304.5 mg, 0.837 mmol, 84% yield, 2.3:1 dr measured by ratio of major δ 3.77 (s, 3H, integral = 2.98) to minor δ 3.73 (s, 3H, integral = 1.28)); ^{1}H NMR (500 MHz, Chloroform-*d*) δ Major: 7.76 – 7.68 (m, 2H), 7.67 – 7.61 (m, 2H), 5.86 (dt, *J* = 17.1, 9.8 Hz, 1H), 5.19 (dd, *J* = 17.1, 1.8 Hz, 1H), 5.12 (dd, *J* = 10.2, 1.9 Hz, 1H), 4.24 (t, *J* = 10.2 Hz, 1H), 3.77 (s, 3H), 1.55 (dt, *J* = 11.8, 5.9 Hz, 1H), 0.86 (t, *J* = 7.2 Hz, 3H); Minor: 7.79 – 7.73 (m, 0.8H), 7.71 – 7.64 (m, 1H), 5.55 (dt, *J* = 17.1, 9.8 Hz, 0.4H), 4.97 (dd, *J* = 10.3, 1.5 Hz, 0.4H), 4.90 (d, *J* = 17.1 Hz, 0.4H), 4.17 (t, *J* = 9.9 Hz, 0.5H), 3.73 (s, 1.3H), 1.77 (td, *J* = 12.1, 6.0 Hz, 0.4H), 1.09 – 1.00 (m, 0.5H), 0.89 (t, *J* = 7.3 Hz, 1.8H); Overlapping: 7.62 – 7.55 (m, 3H), 7.33 – 7.15 (m, 4.8H), 1.50 – 1.27 (m, 3H), 0.98 – 0.89 (m, 2H), ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.0, 167.9, 138.6, 137.9, 136.9, 136.3, 134.1, 134.1, 131.6, 131.6, 128.1, 127.9, 127.8, 127.6, 127.5, 123.3, 123.2, 119.2, 118.7, 71.7, 70.9, 52.3, 52.2, 48.2, 46.3, 32.6, 32.3, 20.8, 20.7, 14.2, 14.0; IR (Neat Film, NaCl) 2953, 1776, 1743, 1718, 1368, 1317, 1222, 994, 934, 718, 700 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{23}H_{24}NO_4$ $[M+H]^+$: 378.1705 found 378.1690.



methyl (*S*)-2-((*S*)-cyclohex-2-en-1-yl)-2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (50)

Prepared according to general procedure 1 with heating to 40 ºC with isolation procedure 2 and purification by flash column chromatography (0–30% EtOAc in hexanes) to afford the desired product as a white amorphous solid (327.0 mg, 0.871 mmol, 87% yield, >20:1 dr, >99% ee); $[\alpha]_D^{25}$ –48.8 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.74 (m, 2H), 7.75 – 7.67 (m, 2H), 7.71 – 7.62 (m, 2H), 7.36 – 7.21 (m, 3H), 5.83 (dp, *J* = 10.4, 1.8 Hz, 1H), 5.76 – 5.66 (m, 1H), 4.46 – 4.34 (m, 1H), 3.69 (s, 3H), 2.06 – 1.56 (m, 5H), 1.28 (tdd, *J* = 12.4, 10.7, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9, 168.3, 134.1, 131.6, 128.8, 128.0, 127.8, 127.7, 127.7, 123.3, 71.4, 52.3, 40.2, 25.2, 25.1, 22.5; IR (Neat Film, NaCl) 3475, 3035, 2930, 2361, 1778, 1738, 1722, 1715, 1614, 1496, 1469, 1446, 1434, 1367, 1348, 1320, 1227, 1194, 1149, 1117, 1084, 1058, 1034, 1008, 940, 910, 792, 753, 719, 696, 682, 665 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{23}H_{22}NO_4$ [M+H]+: 376.1549, found 376.1526. SFC Conditions: 10% IPA, 2.5 mL/min, Chiralpak OB-H column, λ = 210 nm, t_R (min): minor = 7.30, major = 9.80.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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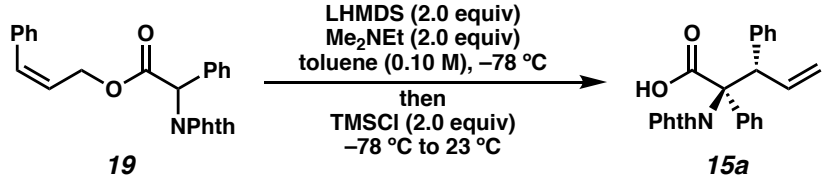
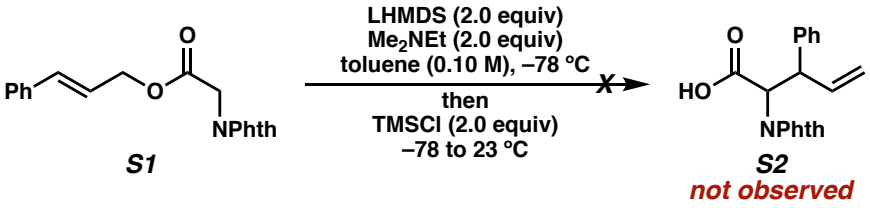
Ireland–Claisen Rearrangement of (*Z*)-3-phenylallyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (19)

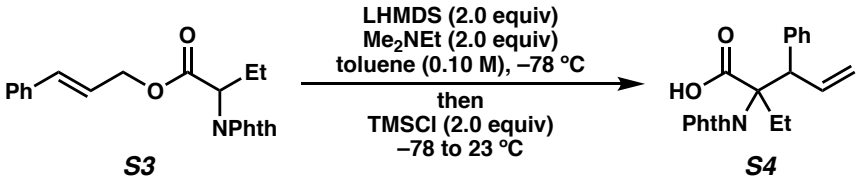


Ireland–Claisen rearrangement of (*Z*)-cinnamyl ester **19** was performed on a 1.00 mmol scale according to general procedure 1 with isolation procedure 1 and to afford product **15a** as a white foam (366.0 mg, 0.921 mmol, 92% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.79 – 7.72 (m, 2H), 7.73 – 7.67 (m, 2H), 7.48 – 7.42 (m, 2H), 7.28 – 7.21 (m, 3H), 7.16 – 7.11 (m, 2H) (d, *J* = 7.6 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.04 – 7.00 (m, 2H), 6.59 (ddd, *J* = 17.2, 10.4, 8.3 Hz, 1H), 5.50 (d, *J* = 8.2 Hz, 1H), 5.24 – 5.02 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.2, 167.9, 139.9, 138.3, 136.1, 134.4, 131.6, 130.6, 128.9, 128.1, 128.0, 127.7, 127.2, 123.6, 118.9, 71.5, 53.1. IR (Neat Film, NaCl) 3061 (br), 1778, 1722, 1497, 1470, 1448, 1369, 1348, 1320, 1265, 1200, 1161, 1110, 1087, 1034, 991, 961, 932, 841, 790, 725, 705, 682, 642 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{20}NO_4$ $[M+H]^+$: 398.1392, found 398.1394.

Ireland–Claisen Rearrangements of Substrates Relevant to Figure 2

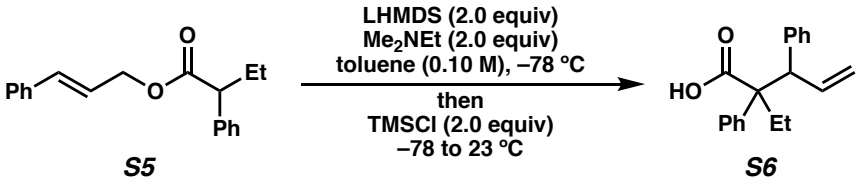


Ireland–Claisen rearrangement of ester **S1** was performed on a 1.00 mmol scale according to general procedure 1. After consumption of α-phthalidomido ester **S1** was observed by TLC analysis (ca. 30 min), the reaction was quenched with 1 N HCl (10 mL) and transferred to a separatory funnel with Et_2O (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. ^{1}H, ^{13}C, and HRMS analysis indicated a complex mixture of products without evidence for the formation of desired product **S2**.



S3 ***S4***

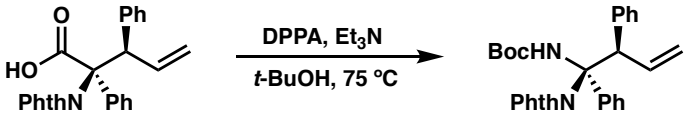
Ireland–Claisen rearrangement of ester **S3** was performed on a 1.00 mmol scale according to general procedure 1. After consumption of the α-phthalidomido ester **S3** was observed by TLC analysis (ca. 4 h), the reaction was quenched with 1 N HCl (10 mL) and transferred to a separatory funnel with Et_2O (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to afford the crude rearrangement product. Purification by silica gel column chromatography (20 to 70% EtOAc in hexanes) afforded the desired product **S4** as an amorphous white solid (241.9 mg, 0.692 mmol, 69% yield, 2.7:1 dr measured by ratio of major 4.87 (d, J = 9.1 Hz, 1H, integral = 1.00) to minor 4.32 (d, J = 9.2 Hz, 1H, integral = 0.37)); ^{1}H NMR (500 MHz, Chloroform-*d*) δ Major: 6.59 (dt, J = 16.8, 9.7 Hz, 1H), 5.17 – 5.10 (m, 2H), 4.87 (d, J = 9.1 Hz, 1H), 2.49 (dq, J = 14.7, 7.4 Hz, 1H), 0.96 (t, J = 7.3 Hz, 3H), Minor: 6.50 (dt, J = 16.7, 9.7 Hz, 0.4H), 5.05 – 4.99 (m, 0.8H), 4.32 (d, J = 9.2 Hz, 0.4H), 2.77 (dq, J = 14.6, 7.3 Hz, 0.4H), 1.00 (t, J = 7.3 Hz, 1.1H), Overlapping: 7.78 – 7.72 (m, 2.6H), 7.72 – 7.65 (m, 2.7H), 7.28 – 7.23 (m, 3.4H), 7.21 – 7.13 (m, 4H), 2.30 (dq, J = 14.6, 7.3 Hz, 1.4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ Major: 175.1, 168.4, 139.3, 137.0, 134.2, 131.5, 129.9, 128.4, 127.3, 123.3, 118.3, 69.9, 53.3, 27.3, 9.2, Minor:175.5, 168.6, 139.3, 137.3, 134.2, 131.4, 130.2, 128.1, 127.2, 123.4, 117.8, 69.7, 55.7, 28.3, 9.8; IR (Neat Film, NaCl) 2943 (br), 2352, 1778, 1714, 1456, 1367, 1352, 1318, 1254, 1157, 1072, 995, 956, 912, 869, 760, 726, 630, 612 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{20}NO_4$ $[M+H]^+$: 350.1392, found 350.1366.



S5 ***S6***

Ireland–Claisen rearrangement of ester **S5** was performed on a 1.00 mmol scale according to general procedure 1 After consumption of the α-phenyl ester was observed by TLC analysis (ca. 4 h), the reaction was quenched with 1 N HCl (10 mL) and transferred to a separatory funnel with Et_2O (10 mL). The layers were separated, and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to afford the crude rearrangement product. Purification by silica gel column chromatography (10 to 50% EtOAc in hexanes) afforded the desired product **S6** as a white foam (244.1 mg, 0.871 mmol, 87% yield, 2.9:1 dr measured by ratio of major 0.87 (t, *J* = 7.3 Hz, 3H, integral = 3.00) to minor 0.93 (t, *J* = 7.3 Hz, 3H, integral =1.05)); ^{1}H NMR (500 MHz, Chloroform-*d*) δ ^{1}H NMR (500 MHz, Chloroform-*d*) δ Major: 6.89 (d, *J* = 7.2 Hz, 2.0H), 5.12 – 5.05 (m, 2.1H), 2.21 – 2.08 (m, *J* = 6.9 Hz, 2H), 0.87 (t, *J* = 7.3 Hz, 3H) Minor: 6.56 (d, *J* = 7.4 Hz, 0.67H), 5.20 – 5.12 (m, 0.6H), Overlapping: 7.33 – 7.21 (m, 4.4H), 7.19 – 7.07 (m, 4.7H),7.07 – 7.01 (m, 2.0H), 6.10 – 5.95 (m, 1.3H), 4.18 – 4.11 (m, 1.3H), 2.01 – 1.94 (m, 0.7H), 0.93 (t, *J* = 7.3 Hz, 1.1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ Major:180.8, 140.7, 137.6, 137.6, 130.1, 129.7, 127.7, 127.4, 127.0, 126.8, 117.5, 60.4, 56.3, 30.3, 9.5, Minor: 181.0, 139.1, 138.6, 136.2, 130.5, 130.0, 127.7, 127.3, 127.2, 127.0, 117.5, 60.7, 57.0, 29.4, 9.5; (MM:FAB+) *m/z* calc'd for $C_{19}H_{21}O_2$ $[M+H]^+$: 281.1542, found 281.1541.

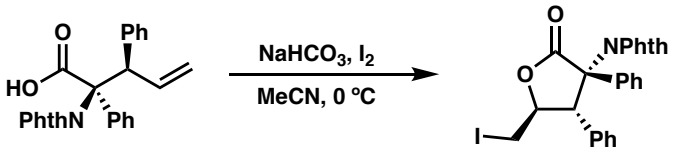
Product Derivatizations



***tert*-butyl ((1*S**,2*R**)-1-(1,3-dioxoisoindolin-2-yl)-1,2-diphenylbut-3-en-1-yl)carbamate (51)**

To a flame-dried 10 mL round bottom flask with a Teflon-coated magnetic stir bar was added carboxylic acid **15a** (79.5 mg, 0.200 mmol, 1.0 equiv), *t*-BuOH (1.0 mL), Et_3N (39 μL, 0.28 mmol, 1.4 equiv), and DPPA (52 μL, 0.24 mmol, 1.2 equiv). The flask was then immersed in a metal heating block at 75 ºC and stirred rapidly. After 20 h, the reaction was complete by TLC analysis. The reaction was cooled to 20 ºC, concentrated by rotary evaporation, and directly purified by silica gel column chromatography (15% Et_2O in hexanes) to afford **51** as a viscous yellow oil (76.8

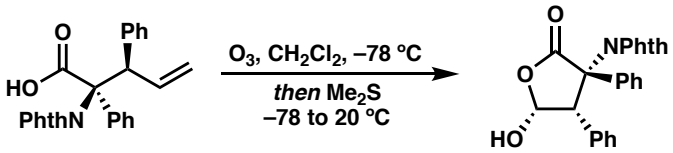
mg, 0.164 mmol, 82% yield); *Note: for ^{1}H and ^{13}C spectra some peak broadening and rotameric peaks are observed.* ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.65 (m, 4H), 7.48 – 7.43 (m, 2H), 7.42 – 7.36 (m, 1H), 7.30 – 7.20 (m, 4H), 7.13 – 7.00 (m, 3H), 6.67 – 6.52 (m, 1H), 5.50 (d, *J* = 8.4 Hz, 1H), 5.20 – 5.05 (m, 2H), 1.20 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.7, 167.4, 140.8, 139.0, 137.0, 134.0, 131.6, 130.5, 130.1, 128.8, 127.7, 127.3, 127.1, 126.8, 126.1, 123.2, 120.3, 120.2, 118.3, 82.4, 72.2, 52.5, 27.4; IR (Neat Film, NaCl) 2976, 2169, 1778, 1721, 1600, 1489 1467, 1367, 1320, 1244, 1157, 1087, 963, 914, 778, 750, 718, 700 cm^{-1};(MM:FAB+) *m/z* calc'd for $C_{28}H_{26}N_2O_4$ $[M–CH_2]^{+\bullet}$: 454.1893, found 454.1905.



2-((3*S,4*S**,5*S**)-5-(iodomethyl)-2-oxo-3,4-diphenyltetrahydrofuran-3-yl)isoindoline-1,3-dione (52)**

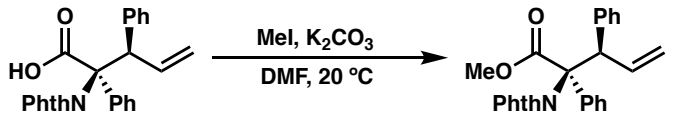
To a flame-dried 1 dram vial with a Teflon-coated magnetic stirring bar was added carboxylic acid **15a** (79.5 mg, 0.200 mmol, 1.0 equiv) and MeCN (700 μL). The heterogeneous reaction mixture was then cooled in a 0 ºC ice bath for 10 min, then $NaHCO_3$ (168.0 mg, 2.00 mmol, 10.0 equiv) was added. After stirring for an additional 5 min, the reaction flask was charged with I_2 (152.3 mg, 0.600 mmol, 3.0 equiv). The resulting orange/black suspension was stirred vigorously at 20 ºC for 3 h, after which time TLC analysis showed full consumption of carboxylic acid **15a**. The reaction mixture was transferred to a separatory funnel with 10 mL Et_2O and 10 mL H_2O. The layers were separated and the aqueous layer was extracted with Et_2O (3 x 5 mL). The combined organic layers were washed with sat. aq. $Na_2S_2O_3$ (5 mL), dried over Na_2SO_4, filtered, and concentrated to afford a white solid. Purification by silica gel column chromatography (25% EtOAc in hexanes) afforded the desired product as an amorphous white solid (94.5 mg, 0.181 mmol, 91% yield, >20:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.79 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.56 – 7.51 (m, 2H), 7.37 – 7.25 (m, 5H), 7.14 (d, *J* = 6.1 Hz, 3H), 5.29 (d, *J* = 4.0 Hz, 1H), 5.12 (ddd, *J* = 9.4, 5.6, 4.2 Hz, 1H), 3.23 (dd, *J* = 10.1, 5.7 Hz, 1H), 2.68 – 2.61 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.1, 167.3, 134.9, 134.0, 132.8, 131.2, 130.4, 130.0, 129.1, 128.6, 128.2, 127.5, 124.0, 80.2, 67.9, 53.8, 0.8; IR (Neat Film, NaCl) 3034, 1790, 1774,

1722, 1498, 1468, 1448, 1364, 1347, 1315, 1266, 1169, 1124, 1084, 1058, 1008, 959, 917, 872, 735, 718, 697 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{19}NO_4I$ $[M+H]^+$: 524.0359, found 524.0360.



2-((3*S,4*S**,5*R**)-5-hydroxy-2-oxo-3,4-diphenyltetrahydrofuran-3-yl)isoindoline-1,3-dione (53)**

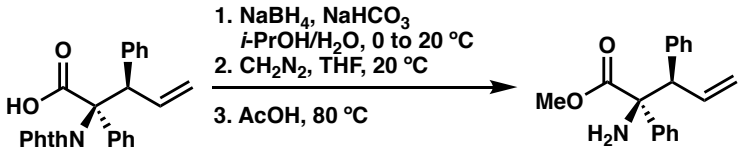
A 10 mL round bottom flask was charged with a Teflon-coated magnetic stir bar, carboxylic acid **15a** (79.5 mg, 0.200 mmol, 1.0 equiv) and CH_2Cl_2 (2 mL). The resulting solution was cooled in a –78 ºC dry ice/acetone bath for 10 min, after which time ozone was bubbled through the solution for 30 min, generating a pale blue solution with TLC analysis indicating full consumption of carboxylic acid **15a**. The reaction was then sparged with O_2 for 10 min, affording a colorless solution to which SMe_2 (44 μL, 0.60 mmol, 3.0 equiv) was then added. The colorless reaction mixture was warmed to 20 ºC and allowed to stir for 2 h, after which time it was loaded directly onto a silica gel column and eluted (0–5% MeOH/CH_2Cl_2) to afford the desired product as a white foam (68.1 mg, 0.171 mmol, 86% yield, 11:1 dr measured by ratio of major δ 5.61 (d, J = 7.0 Hz, 1H, integral = 1.00) to minor δ 5.40 (d, J = 4.5 Hz, 1H, integral = 0.09); ^{1}H NMR (500 MHz, Chloroform-*d*) Major: δ 7.90 – 7.83 (m, 2H), 7.81 – 7.73 (m, 2H), 7.37 – 7.17 (m, 6H), 7.04 (d, J = 7.5 Hz, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.06 (d, J = 6.9 Hz, 1H), 5.61 (d, J = 7.0 Hz, 1H), 4.23 – 4.16 (m, 1H), Minor: 6.27 (dd, J = 10.3, 4.6 Hz, 1H) 5.40 (d, J = 4.5 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 170.9, 168.4, 134.7, 132.9, 131.9, 131.5, 129.5, 128.6, 128.2, 128.2, 128.0, 123.8, 99.4, 71.6, 54.5; IR (Neat Film, NaCl) 3456, 3064 (br), 1770, 1721, 1608, 1500, 1469, 1450, 1378, 1346, 1323, 1265, 1169, 1122, 1087, 1062, 969, 949, 891, 874, 852, 772, 719, 699, 670 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{24}H_{18}NO_5$ $[M+H]^+$: 400.1185, found 400.1194.



methyl (2*S,3*R**)-2-(1,3-dioxoisoindolin-2-yl)-2,3-diphenylpent-4-enoate (54)**

To a flame-dried 10 mL round bottom flask with a Teflon-coated magnetic stir bar was added carboxylic acid **15a** (397.4 mg, 1.00 mmol, 1.0 equiv) and DMF (3.3 mL). To the colorless solution was then added K_2CO_3 (276.4 mg, 2.00 mmol, 2.0 equiv) and MeI (106 μL, 1.70 mmol,

1.7 equiv). The resulting suspension was stirred rapidly at 20 ºC for 30 min, at which time TLC analysis indicated full conversion of carboxylic acid **15a**. The reaction mixture was then transferred to a separatory funnel with EtOAc (10 mL) and H_2O (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 x 5 mL). The combined organics were washed with brine (5 mL), dried over Na_2SO_4, filtered, and concentrated to afford a yellow oil which was purified by silica gel chromatography (30% Et_2O in hexanes) to afford the desired methyl ester as a white foam (372.0 mg, 0.904 mmol, 90% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.80 – 7.69 (m, 4H), 7.48 – 7.43 (m, 2H), 7.31 – 7.24 (m, 3H), 7.22 – 7.18 (m, 2H), 7.14 – 7.03 (m, 3H), 6.58 (ddd, *J* = 17.1, 10.4, 8.3 Hz, 1H), 5.53 (d, *J* = 8.4 Hz, 1H), 5.21 – 5.08 (m, 2H), 3.60 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.7, 168.0, 140.5, 138.7, 136.3, 134.3, 131.6, 130.6, 128.8, 127.9, 127.8, 127.6, 127.0, 123.4, 118.7, 71.5, 53.2, 52.7; IR (Neat Film, NaCl) 3060, 3030, 2951, 1778, 1721, 1611, 1498, 1448, 1348, 1366, 1320, 1270, 1229, 1110, 1087, 1006, 968, 922, 901, 775, 758, 738, 720 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{26}H_{22}NO_4$ $[M+H]^+$: 412.1549, found 412.1524.



To a 100 mL round bottom flask with a Teflon-coated magnetic stirring bar was added carboxylic acid **15a** (397.4 mg, 1.00 mmol, 1.0 equiv), *i*-PrOH (16 mL), and saturated aqueous $NaHCO_3$ solution (1.4 mL). The resulting cloudy reaction mixture was cooled in an ice bath for 5 min. To the cooled reaction was then added $NaBH_4$ (227.0 mg, 6.00 mmol, 6.0 equiv) slowly with vigorous stirring. The ice bath was then removed and the reaction allowed to stir at 20 ºC for 12 h, after which time full consumption of acid **15a** was observed by LC/MS analysis. The reaction mixture was concentrated to dryness, then passed through a 2x4 cm plug of silica gel with 10% MeOH in EtOAc (50 mL). The solution was then concentrated to a yellow foam which was used directly without further purification.

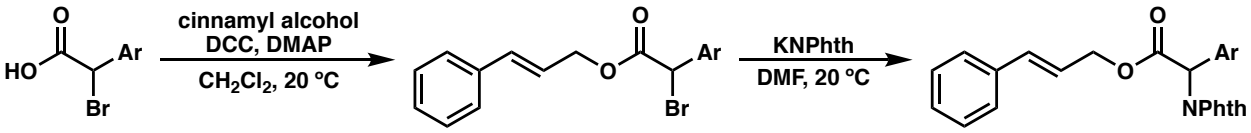
Caution! Diazomethane is toxic and explosive; all operations should be carried out in a well-ventilated hood with adequate shielding. To a 50 mL round bottom flask with a Teflon-coated stirring bar was added the crude product and THF (5 mL). The flask was placed behind a blast shield, and to the slowly stirring reaction mixture was then added freshly prepared CH_2N_2

(approx. 6 mL of a 0.2 M solution in Et_2O) drop-wise via a flame-polished pipette. Acetic acid (2.0 mL) was added dropwise to quench residual CH_2N_2. After stirring an additional 15 min, the reaction mixture was concentrated to a yellow foam.

The flask was sealed with a rubber septum, the purged and evacuated 3x with N_2. To the flask was then added AcOH (2.0 mL) was the reaction mixture was stirred at 80 ºC for 8 h in a heating well. The brown reaction solution was then cooled to 20 ºC and poured into a separatory funnel containing 20 mL sat. aq. $NaHCO_3$ and 20 mL EtOAc. The separatory funnel was shaken and the layers separated. The aqueous layer was extracted 2 x 10 mL EtOAc and the combined organics were dried over Na_2SO_4. Purification by column chromatography (0 to 10% MeOH in CH_2Cl_2) afforded the desired amino acid methyl ester as a white foam (163.5 mg, 0.707 mmol, 71% yield over 3 steps); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.62 (m, 2H), 7.41 – 7.22 (m, 8H), 6.04 (ddd, *J* = 17.1, 10.3, 8.3 Hz, 1H), 4.96 (dq, *J* = 10.4, 1.3 Hz, 1H), 4.86 (dt, *J* = 17.2, 1.3 Hz, 1H), 4.46 (d, *J* = 8.3 Hz, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.8, 140.6, 140.0, 136.3, 129.8, 128.5, 128.3, 127.7, 127.3, 126.6, 118.6, 67.4, 56.9, 52.6; IR (Neat Film, NaCl) 3370, 2919, 2360, 1719, 1597, 1490, 1446, 1227, 1032, 1008, 944, 920, 778, 752, 730, 714, 701, 668 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{20}NO_2$ $[M+H]^+$: 282.1494, found 282.1497.

Preparation of Allyl Esters

General Procedure 2

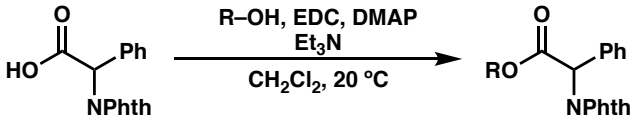


To a flame-dried 100 mL round bottom flask was added commercial or previously reported α-bromo carboxylic acid (10.0 mmol, 1.0 equiv), cinnamyl alcohol (1.74 g, 13.0 mmol, 1.3 equiv), DMAP (122.2 mg, 1.0 mmol, 0.10 equiv) and CH_2Cl_2 (50 mL). The resulting solution was then cooled in a 0 ºC ice/water bath for 10 minutes after which time DCC (2.68 g, 13.0 mmol, 1.3 equiv) was added in a single portion. The resulting solution was vigorously stirred at 20 ºC for 12 h, during which time a white solid precipitates. After the reaction was complete by TLC analysis (typically 12 h), the reaction mixture was concentrated by rotary evaporation and the resulting solid cake was suspended in 30 mL of Et_2O. The mixture was then filtered through a 2 x 5 cm

celite pad with 2 x 20 mL rinses of Et_2O. The resulting solution was concentrated by rotary evaporation and eluted through a 5 x 10 cm plug of silica gel, eluting with 15% Et_2O in hexanes. The crude ester was then used in the next step without further purification.

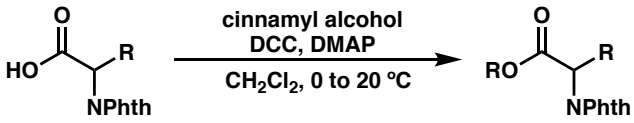
To a flame-dried 100 mL round bottom flask was added the crude α-bromo ester prepared above and DMF (33 mL). To the resulting solution was then added potassium phthalimide (3.70 g, 20.0 mmol, 2.0 equiv) in a single portion. The resulting slurry was then vigorously stirred at 20 ºC. After the reaction was complete by TLC analysis (typically 12 h), the reaction mixture was quenched with 20 mL of H_2O. The reaction mixture was then transferred with 30 mL of EtOAc to a separatory funnel containing 20 mL of brine. The layers were separated and the aqueous was extracted with EtOAc (2 x 20 mL). The combined organics were washed with brine (30 mL), dried over Na_2SO_4, and concentrated. The crude α-phthalimide ester was then purified by column chromatography.

General Procedure 3



To a flame-dried round bottom flask was added the alcohol (2.0 equiv), DMAP (0.10 equiv), the α-phthalimide carboxylic acid (2.0 equiv), CH_2Cl_2 (0.10 M) and Et_3N (2.0 equiv). To the resulting solution was then added the EDC•HCl (2.0 equiv) in a single portion. The resulting solution was vigorously stirred at 20 ºC for 12 h. The reaction mixture was then diluted with CH_2Cl_2 (20 mL) and transferred to a separatory funnel. The organic layer was washed with 0.5 N HCl (20 mL), sat. aq. $NaHCO_3$ (10 mL), and brine (10 mL). The organic layer was then dried over Na_2SO_4, filtered, and concentrated. The resulting crude mixture was then purified by column chromatography to afford the desired α-phthalidomido esters.

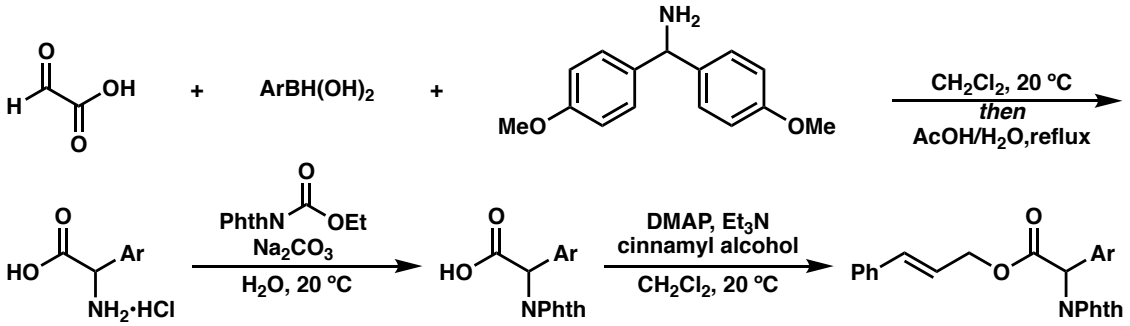
General Procedure 4



To a flame-dried round bottom flask was added cinnamyl alcohol (1.5 equiv), DMAP (0.20 equiv), α-phthalimido carboxylic acid (1.5 equiv), CH_2Cl_2 (0.20 M). The stirring solution was then

cooled in an ice bath and to the resulting solution was then added the DCC (1.5 equiv) in a single portion. The resulting solution was vigorously stirred at 20 ºC for 12 h. To the reaction mixture was then added silica gel (10 g) and the resulting slurry was concentrated to a dry solid which was loaded directly onto a silica gel flash column for purification to afford the corresponding α-phthalimido cinnamyl ester.

General Procedure 5

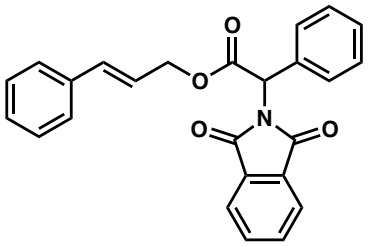


This general procedure was adapted from a procedure reported by Petasis and coworkers.[14] To a 250 mL round bottom flask with a Teflon-coated magnetic stir bar was added glyoxylic acid hydrate (1.4253 g, 15.00 mmol, 1.0 equiv), CH_2Cl_2 (75 mL), and bis(4-methoxyphenyl)methanamine (3.65 g, 15.0 mmol, 1.0 equiv). The resulting heterogeneous reaction mixture was stirred rapidly for 5 min, after which time aryl boronic acid (15.0 mmol, 1.0 equiv) was added in a single portion, causing the precipitation of a white solid. The reaction was stirred vigorously for 16 h, after which time the reaction mixture was concentrated by rotary evaporation. To the flask was then added 70% v/v AcOH/H_2O (75 mL), and the flask was affixed with a reflux condenser. The mixture was then heated to reflux in a metal heating block (preheated to 115 ºC) for 1 h, after which time the mixture became homogeneous. After cooling to 20 ºC, 3 N HCl (32 mL) was then added, the mixture was transferred to a separatory funnel with H_2O (5 mL), and washed with CH_2Cl_2 (3 x 20 mL). The aqueous layer was then partially concentrated to approximately 10 mL total volume, frozen in a dry ice/acetone bath, and lyophilized to afford the crude amino acid hydrochloride which was used without purification.

To a 250 mL round bottom flask with a Teflon-coated magnetic stir bar was added the crude amino acid hydrochloride, H_2O (75 mL), Na_2CO_3 (2.38 g, 22.5 mmol, 1.5 equiv), and *N*-ethoxycarbonylphthalimide (4.93 g, 22.5 mmol, 1.5 equiv). The reaction mixture was stirred vigorously for 3 h, after which time it was transferred to a separatory funnel with H_2O (10 mL).

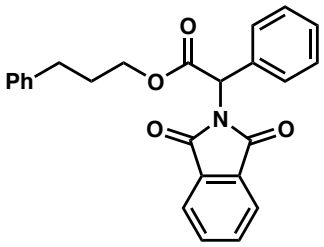
The pH of the aqueous layer was adjusted to 12 with sat. aq. Na_2CO_3 solution, then the aqueous layer was washed with Et_2O (3 x 50 mL). The aqueous layer was then acidified to pH 2 with 2 N HCl and extracted with EtOAc (3 x 50 mL), dried over Na_2SO_4, filtered, and concentrated to afford the desired carboxylic acid which was used without further purification.

To a 500 mL round bottom flask was added the carboxylic acid, CH_2Cl_2 (150 mL), Et_3N (4.2 mL, 30 mmol, 2.0 equiv), DMAP (366.5 mg, 3.00 mmol, 0.20 equiv), and cinnamyl alcohol (4.03 g, 30.0 mmol, 2.0 equiv). To the rapidly stirring solution was then added EDC•HCl (5.75 g, 30.0 mmol, 2.0 equiv) in a single portion. The reaction was stirred until full consumption of the carboxylic acid by TLC analysis, after which time the reaction mixture was diluted with CH_2Cl_2 (100 mL) and transferred to a separatory funnel. The organic layer was washed with 0.5 N HCl (50 mL), sat. aq. $NaHCO_3$ (50 mL), and brine (50 mL). The organic layer was then dried over Na_2SO_4, filtered, and concentrated. The resulting crude mixture was then purified by column chromatography to afford the desired α-phthalidomido esters.



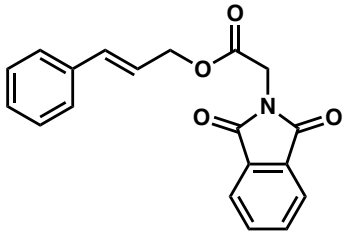
(*E*)-cinnamyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (14)

Performed on a 10.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (50% CH_2Cl_2, 2% EtOAc in hexanes) to afford the desired product as an amorphous white solid (3.59 g, 9.03 mmol, 90% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.74 – 7.69 (m, 2H), 7.61 – 7.55 (m, 2H), 7.41 – 7.28 (m, 7H), 7.28 – 7.23 (m, 1H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.4 Hz, 1H), 6.07 (s, 1H), 4.90 (qdd, *J* = 12.8, 6.4, 1.3 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 167.1, 136.1, 134.7, 134.5, 134.3, 131.8, 129.8, 128.7, 128.6, 128.2, 126.7, 123.7, 122.4, 66.7, 56.0; IR (Neat Film, NaCl) 3476, 3060, 3030, 2929, 1772, 1746, 1721, 1611, 1496, 1468, 1450, 1385, 1337, 1214, 1184, 1111, 1088, 1076, 1020, 968, 894, 842, 790, 777, 720, 697, 661 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{20}NO_4$ $[M+H]^+$: 398.1392, found 398.1368.



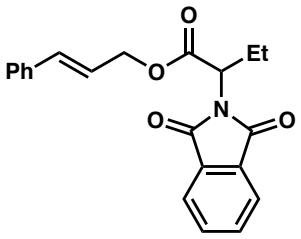
3-phenylpropyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (16)

Performed on a 5.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (20% EtOAc in hexanes) to afford the desired product as a viscous, colorless oil (1.9659 g, 4.92 mmol, 98% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.85 (m, 2H), 7.77 – 7.70 (m, 2H), 7.60 (d, *J* = 7.3 Hz, 2H), 7.38 (dt, *J* = 12.0, 7.0 Hz, 3H), 7.27 (t, *J* = 7.6 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 6.04 (s, 1H), 4.27 (t, *J* = 6.4 Hz, 2H), 2.61 (t, *J* = 7.7 Hz, 2H), 1.97 (p, *J* = 6.8 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 167.2, 141.0, 134.6, 134.3, 131.8, 129.9, 128.7, 128.6, 128.5, 126.1, 123.6, 65.5, 56.0, 32.0, 30.2; IR (Neat Film, NaCl) 3472, 3062, 3028, 2957, 1773, 1746, 1717, 1603, 1515, 1496, 1468, 1454, 1385, 1336, 1215, 1186, 1110, 1076, 1021, 958, 917, 897, 828, 746, 721, 698, 668, 660 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{22}NO_4$ $[M+H]^+$: 400.1549, found 400.1550.



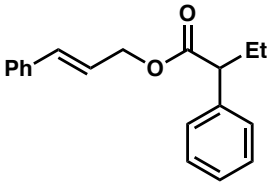
cinnamyl 2-(1,3-dioxoisoindolin-2-yl)acetate (S1)

Performed on a 3.00 mmol scale according to general procedure 4 and purified by silica gel chromatography (50% CH_2Cl_2, 2% EtOAc in hexanes) to afford the desired product as an amorphous white solid (895.0 mg, 2.79 mmol, 93% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.94 – 7.83 (m, 2H), 7.79 – 7.71 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34 – 7.29 (m, 2H), 7.28 – 7.22 (m, 1H), 6.64 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.9, 6.5 Hz, 1H), 4.82 (d, *J* = 6.4 Hz, 2H), 4.49 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.5, 167.2, 136.0, 135.0, 134.3, 132.1, 128.7, 128.3, 126.8, 123.7, 122.3, 66.5, 39.0; IR (Neat Film, NaCl) 2341, 2359, 1716, 1456, 1417, 1391, 1316, 1194, 1112, 956, 759, 734, 711 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{19}N_2O_4$ $[M+NH_4]^+$: 339.1345, found 339.1333.



cinnamyl 2-(1,3-dioxoisoindolin-2-yl)butanoate (S3)

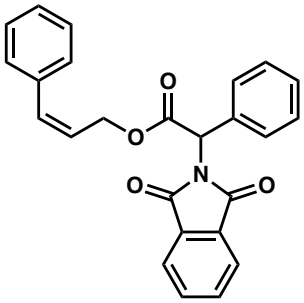
Performed on a 4.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (0 to 20% EtOAc in hexanes) to afford the desired product as a colorless, viscous oil (1.2869 g, 3.68 mmol, 92% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 2H), 7.81 – 7.73 (m, 2H), 7.40 – 7.31 (m, 4H), 7.30 – 7.24 (m, 1H), 6.63 (d, *J* = 15.9 Hz, 1H), 6.25 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.88 – 4.79 (m, 3H), 2.42 – 2.25 (m, 2H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz Chloroform-*d*) δ 169.2, 167.8, 136.1, 134.5, 134.3, 131.9, 128.7, 128.2, 126.7, 123.6, 122.6, 66.3, 53.9, 22.3, 11.1; IR (Neat Film, NaCl) 3476, 3028, 2971, 2879, 1775, 1744, 1716, 1612, 1495, 1467, 1449, 1388, 1290, 1265, 1215, 1149, 1112, 1073, 1041, 967, 898, 743, 720, 693 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{20}NO_4$ $[M+H]^+$: 350.1392, found 350.1404.



cinnamyl 2-phenylbutanoate (S5)

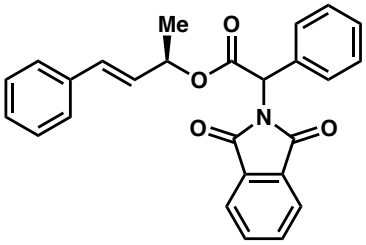
Performed on a 4.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (0 to 20% EtOAc in hexanes) to afford the desired product as a colorless, viscous oil (1.0340 g, 3.69 mmol, 92% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.41 – 7.16 (m, 10H), 6.53 (d, *J* = 15.9 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.1 Hz, 1H), 4.73 (qd, *J* = 13.0, 6.1 Hz, 2H), 3.51 (t, *J* = 7.7 Hz, 1H), 2.14 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.85 (dq, *J* = 14.1, 7.4 Hz, 1H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 139.2, 139.1, 136.4, 136.3, 133.8, 128.7, 128.7, 128.2, 128.1, 128.1, 127.4, 127.3, 126.7, 126.7, 123.3, 123.3, 65.2, 53.6, 26.9, 26.8, 12.3, 12.3; IR (Neat Film, NaCl) 3028, 2965, 2933, 2875, 1733, 1600, 1495, 1453, 1381, 1346, 1266, 1221, 1198,

1164, 1119, 1072, 1028, 965, 731, 696 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{19}H_{21}O_2$ $[M]^{+\bullet}$: 280.1483, found 280.1463.



(*Z*)-3-phenylallyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (19)

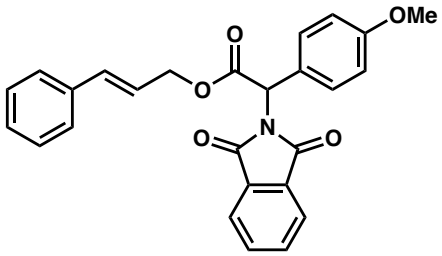
Performed on a 3.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (0–30% EtOAc in hexanes) to afford the desired product as an amorphous white solid (1.056 g, 2.66 mmol, 89% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 – 7.81 (m, 2H), 7.76 – 7.67 (m, 2H), 7.61 – 7.52 (m, 2H), 7.42 – 7.22 (m, 6H), 7.22 – 7.13 (m, 2H), 6.66 (dt, *J* = 11.7, 1.7 Hz, 1H), 6.05 (s, 1H), 5.78 (dt, *J* = 11.7, 6.7 Hz, 1H), 5.00 (dd, *J* = 6.7, 1.6 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 167.2, 135.9, 134.5, 134.3, 133.7, 131.9, 129.9, 128.8, 128.7, 128.7, 128.5, 127.7, 125.1, 123.7, 63.2, 56.0; IR (Neat Film, NaCl) 3045, 1746, 1715, 1682, 1558, 1496, 1468, 1451, 1384, 1337, 1301, 1217, 1109, 1076, 962, 829, 788, 771, 722, 700, 638 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{20}NO_4$ $[M+H]^+$: 398.1392, found 398.1412.



***(R, E)*-4-phenylbut-3-en-2-yl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (21)**

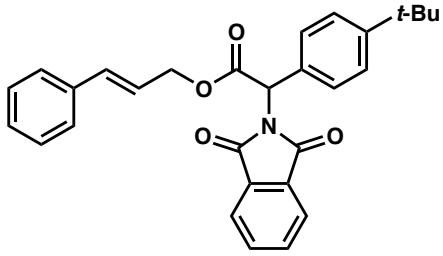
Performed on a 4.83 mmol scale according to general procedure 3 and purified by silica gel chromatography (20% EtOAc in hexanes) to afford a viscous oil (1.8586 g, 4.52 mmol, 94% yield, 1:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (ddd, *J* = 9.8, 5.4, 3.0 Hz, 2H), 7.75 – 7.67 (m, 2H), 7.61 – 7.55 (m, 2H), 7.43 – 7.22 (m, 8H), 6.57 (ddd, *J* = 16.0, 2.9, 1.1 Hz, 1H), 6.15 (dt, *J* = 15.9, 6.7 Hz, 1H), 6.06 (d, *J* = 4.5 Hz, 1H), 5.71 (dpd, *J* = 9.7, 6.5, 1.2 Hz, 1H), 1.46 (d, *J* = 6.5

Hz, 1.5H), 1.43 (d, *J* = 6.5 Hz, 1.5H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.4, 167.4, 167.2, 167.2, 136.3, 136.3, 134.6, 134.3, 134.3, 132.2, 132.2, 131.9, 129.9, 129.9, 128.7, 128.6, 128.6, 128.6, 128.1, 128.1, 128.0, 126.7, 123.7, 123.7, 73.5, 73.4, 56.3, 56.2, 20.4, 20.3; IR (Neat Film, NaCl) 1717, 1384, 1213, 1108, 1076, 1037, 965, 722, 695; (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{25}N_2O_4$ $[M+NH_4]^+$: 429.1809, found 429.1799.



cinnamyl 2-(1,3-dioxoisoindolin-2-yl)-2-(4-methoxyphenyl)acetate (S7)

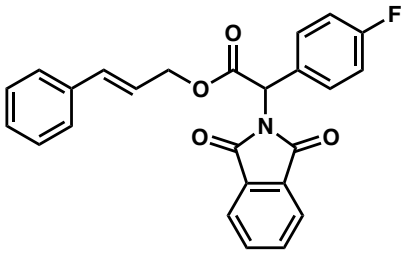
Prepared on a 10.00 mmol scale according to general procedure 2 and purified by column chromatography (30–100% CH_2Cl_2 in hexanes) to provide a white foam (1.63g, 3.81 mmol, 38% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87–7.82 (m, 2H), 7.75–7.67 (m, 2H), 7.53 – 7.47 (m, 2H), 7.36 – 7.28 (m, 4H), 7.23–7.27 (m, 1H), 6.92–6.83 (m, 2H), 6.60 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.24 (dt, *J* = 15.8, 6.4 Hz, 1H), 6.01 (s, 1H), 4.88 (qdd, *J* = 12.8, 6.4, 1.4 Hz, 2H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.3, 167.3, 159.8, 136.2, 134.8, 134.3, 132.0, 131.3, 128.7, 128.3, 126.8, 126.8, 123.7, 122.5, 114.0, 66.8, 55.6, 55.4; IR (Neat Film, NaCl) 3027, 2935, 2838, 2364, 1772, 1746, 1716, 1612, 1515, 1467, 1384, 1336, 1306, 1252, 1214, 1180, 1105, 1032, 966, 910, 834, 793, 738, 716, 694, 645 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{22}NO_5$ $[M+H]^+$: 428.1492, found 428.1507.



cinnamyl 2-(4-(*tert*-butyl)phenyl)-2-(1,3-dioxoisoindolin-2-yl)acetate (S8)

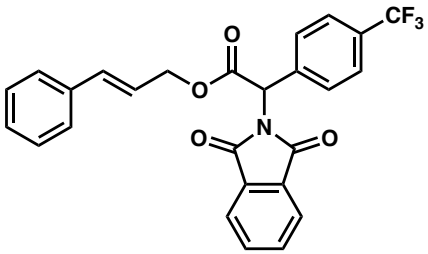
Prepared on a 10.00 mmol scale according to general procedure 2 and purified by column chromatography (30–90% CH_2Cl_2 in hexanes) to provide a white foam (2.73 g, 6.02 mmol, 60%

yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87–7.79 (m, 2H), 7.74–7.68 (m, 2H), 7.52 – 7.46 (m, 2H), 7.40–7.28 (m, 6H), 7.27–7.23 (m, 1H), 6.59 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.25 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.04 (s, 1H), 4.89 (qdd, *J* = 12.8, 6.4, 1.4 Hz, 2H), 1.30 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.2, 167.2, 151.6, 136.2, 134.7, 134.3, 132.0, 131.5, 129.6, 128.7, 128.2, 126.8, 125.7, 123.7, 122.6, 66.8, 55.8, 34.7, 31.4; IR (Neat Film, NaCl) 2960, 1773, 1748, 1717, 1508, 1466, 1384, 1219, 1186, 1108, 966, 910, 842, 721 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{29}H_{28}NO_4$ $[M+H]^+$: 454.2013, found 454.2010.



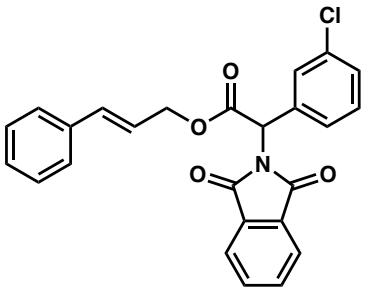
cinnamyl 2-(1,3-dioxoisoindolin-2-yl)-2-(4-fluorophenyl)acetate (S9)

Prepared on a 10.00 mmol scale according to general procedure 2 and purified by column chromatography (35% CH_2Cl_2, 2% EtOAc in hexanes) to provide an amorphous white solid (2.48 g, 5.97 mmol, 60% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.98 – 7.84 (m, 2H), 7.82 – 7.75 (m, 2H), 7.65 – 7.59 (m, 2H), 7.43 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 7.13 – 7.05 (m, 2H), 6.66 (d, *J* = 15.9 Hz, 1H), 6.29 (dt, *J* = 15.8, 6.5 Hz, 1H), 6.08 (s, 1H), 4.94 (qdd, *J* = 12.7, 6.5, 1.4 Hz, 2H).; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 167.2, 162.8 (d, $J_{C–F}$ = 248.1 Hz), 136.1, 135.0, 134.5, 131.9, 131.9 (d, $J_{C–F}$ = 1.7 Hz), 130.5 (d, $J_{C–F}$ = 3.5 Hz), 128.7, 128.3, 126.8, 123.8, 122.3, 115.7 (d, $J_{C–F}$ = 21.7 Hz), 67.0, 55.3; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –112.87 (tt, *J* = 8.5, 5.1 Hz); IR (Neat Film, NaCl) 3045, 2940, 1747, 1716, 1607, 1512, 1469, 1384, 1336, 1224, 1184, 1162, 1112, 1096, 968, 895, 848, 837, 742, 717, 694 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{19}NO_4F$ $[M+H]^+$: 416.1298, found 416.1275.



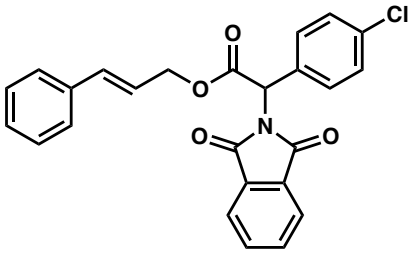
cinnamyl 2-(1,3-dioxoisoindolin-2-yl)-2-(4-(trifluoromethyl)phenyl)acetate (S10)

Prepared on a 10.00 mmol scale according to general procedure 2 and purified by column chromatography (27% CH_2Cl_2, 3% EtOAc in hexanes) to provide an amorphous white solid (2.76 g, 6.30 mmol, 63% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 – 7.84 (m, 2H), 7.77 – 7.72 (m, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.29 (m, 4H), 7.29 – 7.23 (m, 1H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.5 Hz, 1H), 6.09 (s, 1H), 4.90 (dddd, *J* = 20.5, 12.8, 6.5, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.3, 167.1, 138.3, 136.0, 135.1, 134.5, 131.7, 130.8 (q, $J_{C–F}$ = 32.6 Hz), 130.3, 128.7, 128.3, 126.8, 125.6 (q, $J_{C–F}$ = 3.7 Hz), 124.0 (q, $J_{C–F}$ = 272.3 Hz), 123.9, 122.1, 67.1, 55.4; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –62.7; IR (Neat Film, NaCl) 3486, 3044, 2938, 2116, 1774, 1747, 1720, 1620, 1495, 1469, 1449, 1422, 1385, 1326, 1385, 1326, 1216, 1170, 1125, 1105, 1069, 966, 909, 847, 745, 719 cm$^{–1}$; (MM:FAB+) *m/z* calc'd for $C_{26}H_{19}NO_4F_3$ $[M+H]^+$: 466.1266, found 466.1255.



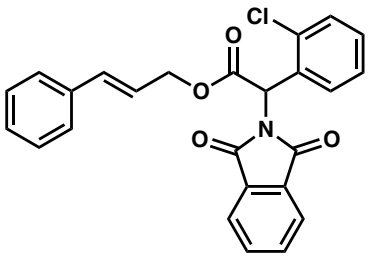
cinnamyl 2-(3-chlorophenyl)-2-(1,3-dioxoisoindolin-2-yl)acetate (S11)

Prepared on a 10.00 mmol scale according to general procedure 2 and purified by column chromatography (35% CH_2Cl_2, 2% EtOAc in hexanes) to provide an amorphous white solid (2.66 g, 6.16 mmol, 62% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 7.59 – 7.54 (m, 1H), 7.46 (dt, *J* = 6.6, 2.0 Hz, 1H), 7.37 – 7.29 (m, 6H), 7.29 – 7.22 (m, 1H), 6.60 (d, *J* = 15.8 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.4 Hz, 1H), 6.00 (s, 1H), 4.88 (tdd, *J* = 13.1, 6.4, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.4, 167.1, 136.3, 136.1, 135.0, 134.5, 134.5, 131.8, 130.0, 129.9, 129.0, 128.7, 128.3, 128.1, 126.8, 123.9, 122.2, 67.0, 55.4; IR (Neat Film, NaCl) 3044, 1775, 1746, 1721, 1610, 1469, 1447, 1382, 1312, 1256, 1216, 1188, 1104, 967, 912, 738, 722, 710 cm$^{–1}$; (MM:FAB+) *m/z* calc'd for $C_{25}H_{19}NO_4Cl$ $[M+H]^+$: 432.1003, found 432.1024.



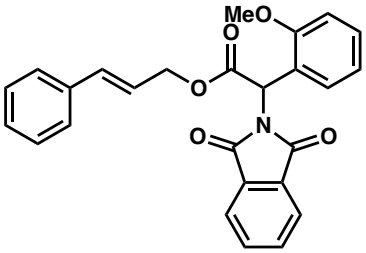
cinnamyl 2-(4-chlorophenyl)-2-(1,3-dioxoisoindolin-2-yl)acetate (S12)

Prepared on a 10.00 mmol scale according to general procedure 2 and purified by column chromatography (35% CH_2Cl_2, 2% EtOAc in hexanes) to provide a white foam (2.60 g, 6.02 mmol, 60% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.76 – 7.70 (m, 2H), 7.53 – 7.48 (m, 2H), 7.37 – 7.29 (m, 6H), 7.28 – 7.22 (m, 1H), 6.60 (dd, *J* = 15.9, 1.5 Hz, 1H), 6.23 (dt, *J* = 15.8, 6.5 Hz, 1H), 6.02 (s, 1H), 4.94 – 4.80 (m, 2H); ^{13}C NMR (100 MHz Chloroform-*d*) δ 167.6, 167.1, 136.1, 135.1, 134.8, 134.5, 133.0, 131.8, 131.3, 128.9, 128.7, 128.3, 126.8, 123.84, 122.2, 67.0, 55.3; IR (Neat Film, NaCl) 3024, 1773, 1745, 1717, 1493, 1467, 1384, 1216, 1186, 1090, 963, 911, 737, 723, 7103 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{25}H_{19}NO_4Cl$ $[M+H]^+$: 432.1003, found 432.1018.



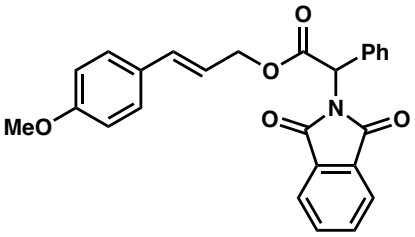
cinnamyl 2-(2-chlorophenyl)-2-(1,3-dioxoisoindolin-2-yl)acetate (S13)

Prepared on a 10.00 mmol scale according to general procedure 2 and purified by column chromatography (10–90% CH_2Cl_2 in hexanes) to provide a white foam (2.72 g, 6.30 mmol, 63% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.77 – 7.71 (m, 2H), 7.69 – 7.63 (m, 1H), 7.44 – 7.37 (m, 1H), 7.37 – 7.23 (m, 7H), 6.60 (d, *J* = 15.9 Hz, 1H), 6.56 (d, *J* = 1.7 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.4 Hz, 1H), 4.94 – 4.86 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.6, 167.2, 136.1, 134.9, 134.5, 134.4, 131.9, 131.8, 131.6, 130.1, 129.6, 128.7, 128.3, 126.8, 123.8, 122.2, 66.9, 53.5.; IR (Neat Film, NaCl) 3024, 1773, 1746, 1717, 1493, 1384, 1216, 1186, 1090, 963, 737, 723, 710 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{19}ClNO_4$ $[M+H]^+$: 432.0997, found 432.0984.



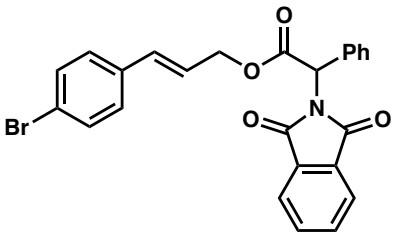
cinnamyl 2-(1,3-dioxoisoindolin-2-yl)-2-(2-methoxyphenyl)acetate (S14)

Prepared on a 10.00 mmol scale according to general procedure 2 and purified by column chromatography (50% CH_2Cl_2, 2% EtOAc in hexanes) to provide a white amorphous solid (2.67 g, 6.25 mmol, 63% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.67 (m, 2H), 7.56 – 7.50 (m, 1H), 7.36 – 7.28 (m, 5H), 7.27 – 7.23 (m, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.64 – 6.54 (m, 2H), 6.25 (dt, *J* = 15.9, 6.3 Hz, 1H), 4.88 (d, *J* = 6.2 Hz, 2H), 3.84 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.5, 167.3, 157.3, 136.2, 134.4, 134.2, 131.9, 130.6, 130.0, 128.6, 128.1, 126.7, 123.5, 122.6, 122.3, 120.3, 110.7, 66.5, 55.8, 50.3; IR (Neat Film, NaCl) 1841, 1720, 1602, 1494, 1466, 1384, 1251, 1216, 1097, 1026, 963, 902, 748, 718 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{26}H_{22}NO_5$ $[M+H]^+$: 428.1498, found 428.1500.



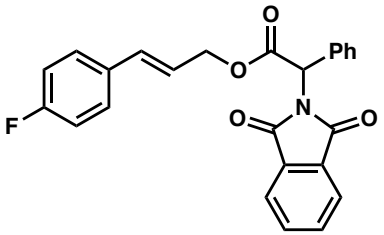
(*E*)-3-(4-methoxyphenyl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S15)

Performed on a 2.72 mmol scale according to general procedure 3 and purified by silica gel chromatography (30% EtOAc in hexanes) to afford a viscous yellow oil (1.10 g, 2.57 mmol, 95% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.81 (m, 2H), 7.75 – 7.68 (m, 2H), 7.61 – 7.53 (m, 2H), 7.39 – 7.31 (m, 3H), 7.30 – 7.27 (m, 2H), 6.87 – 6.80 (m, 2H), 6.59 – 6.50 (m, 1H), 6.11 (dt, *J* = 15.8, 6.6 Hz, 1H), 6.06 (s, 1H), 4.87 (qdd, *J* = 12.6, 6.6, 1.3 Hz, 2H), 3.81 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 167.2, 159.7, 134.6, 134.5, 134.3, 131.9, 129.9, 128.9, 128.7, 128.6, 128.0, 123.7, 120.1, 114.1, 67.1, 56.1, 55.4; IR (Neat Film, NaCl) 1772, 1746, 1716, 1607, 1512, 1384, 1337, 1250, 1220, 1175, 1113, 1033, 966, 906, 895, 838, 721, 699; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{25}N_2O_5$ $[M+NH_4]^+$: 445.1758, found 445.1748.



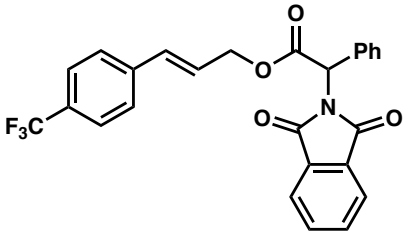
(*E*)-3-(4-bromophenyl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S16)

Performed on a 2.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (20% EtOAc, in hexanes) to afford a viscous colorless oil (897.1 mg, 1.88 mmol, 94% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.74 – 7.67 (m, 2H), 7.63 – 7.54 (m, 2H), 7.46 – 7.31 (m, 5H), 7.23 – 7.16 (m, 2H), 6.55 – 6.47 (m, 1H), 6.23 (dt, *J* = 15.9, 6.3 Hz, 1H), 6.08 (s, 1H), 4.99 – 4.81 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 167.1, 135.1, 134.5, 134.3, 133.4, 131.8, 131.8, 129.8, 128.8, 128.7, 128.2, 123.7, 123.3, 122.0, 66.5, 56.0; IR (Neat Film, NaCl) 1772, 1748, 1717, 1487, 1384, 1214, 1185, 1109, 1073, 1008, 965, 721, 699; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{22}BrN_2O_4$ $[M+NH_4]^+$: 493.0757, found 493.0748.



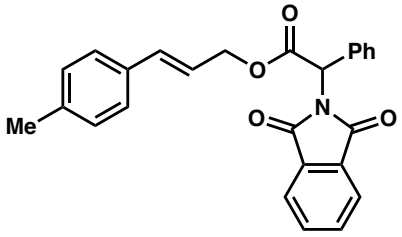
(*E*)-3-(4-fluorophenyl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S17)

Performed on a 2.79 mmol scale according to general procedure 3 and purified by silica gel chromatography (20% EtOAc in hexanes) to afford a viscous yellow oil (1.0238 g, 2.46 mmol, 88% yield); ^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.72 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.62 – 7.52 (m, 2H), 7.43 – 7.27 (m, 5H), 7.05 – 6.91 (m, 2H), 6.56 (dd, *J* = 15.9, 1.4 Hz, 1H), 6.16 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.06 (s, 1H), 4.96 – 4.79 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 167.1, 162.7 (d, *J* = 247.6 Hz), 134.5, 134.3, 133.6, 132.3 (d, *J* = 3.3 Hz), 131.8, 129.8, 128.7, 128.6, 128.3 (d, *J* = 8.1 Hz), 123.7, 122.2 (d, *J* = 2.2 Hz), 115.6 (d, *J* = 21.7 Hz), 66.6, 56.0; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –113.5 (tt, *J* = 8.6, 5.4 Hz); IR (Neat Film, NaCl) 1773, 1748, 1716, 1601, 1508, 1385, 1227, 1185, 1112, 968, 908, 722, 700; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{22}FN_2O_4$ $[M+NH_4]^+$: 433.1558, found 433.1544.



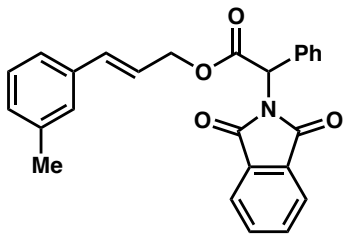
(*E*)-3-(4-(trifluoromethyl)phenyl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S18)

Performed on a 2.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (25% EtOAc in hexanes) to afford a viscous colorless oil (799.2 mg, 1.72 mmol, 86% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 – 7.81 (m, 2H), 7.77 – 7.68 (m, 2H), 7.64 – 7.53 (m, 4H), 7.46 – 7.31 (m, 5H), 6.66 – 6.57 (m, 1H), 6.34 (dt, *J* = 15.9, 6.0 Hz, 1H), 6.10 (s, 1H), 4.98 – 4.85 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 167.2, 139.6 (d, *J* = 1.5 Hz), 134.5, 134.4, 132.8, 131.8, 129.9 (q, *J* = 32.5) 129.8, 128.8, 128.7, 126.9, 125.6 (q, *J* = 3.8 Hz), 125.2, 123.9 (q, *J* = 271.8) 123.7, 66.2, 56.0; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –62.5; IR (Neat Film, NaCl) 1773, 1750, 1719, 1615, 1385, 1326, 1214, 1168, 1120, 1068, 720, 698; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{22}N_2O_4$ $[M+NH_4]^+$: 483.1526, found 483.1512.



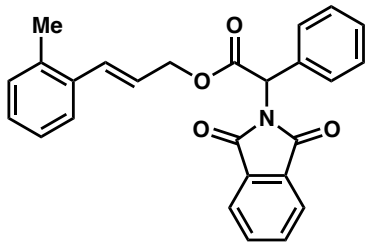
(*E*)-3-(*p*-tolyl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S19)

Performed on a 2.72 mmol scale according to general procedure 3 and purified by silica gel chromatography (20% EtOAc in hexanes) to afford a viscous yellow oil (1.0574 g, 2.57 mmol, 94% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.91 – 7.82 (m, 2H), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.41 – 7.31 (m, 3H), 7.28 – 7.22 (m, 3H), 7.16 – 7.08 (m, 2H), 6.57 (dd, *J* = 15.9, 1.3 Hz, 1H), 6.19 (dt, *J* = 15.8, 6.5 Hz, 1H), 6.06 (s, 1H), 4.88 (qdd, *J* = 12.7, 6.5, 1.3 Hz, 2H), 2.34 (s, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 167.2, 138.2, 134.8, 134.5, 134.3, 133.3, 131.9, 129.9, 129.4, 128.7, 128.7, 126.7, 123.7, 121.3, 67.0, 56.1, 21.3; IR (Neat Film, NaCl) 1772, 1748, 1716, 1384, 1222, 1182, 1108, 1076, 966, 906, 719, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{25}N_2O_4$ $[M+NH_4]^+$: 429.1809, found 429.1818.



(*E*)-3-(*m*-tolyl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S20)

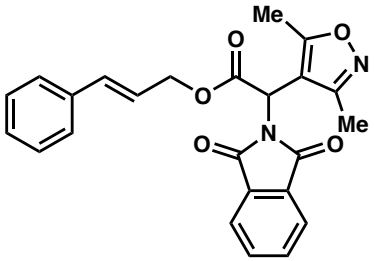
Performed on a 2.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (20% EtOAc in hexanes) to afford a viscous oil (779 mg, 1.89 mmol, 95% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 5.4, 3.1 Hz, 2H), 7.71 (dd, *J* = 5.5, 3.0 Hz, 2H), 7.63 – 7.56 (m, 2H), 7.42 – 7.32 (m, 3H), 7.23 – 7.13 (m, 3H), 7.08 (d, *J* = 7.4 Hz, 1H), 6.62 – 6.54 (m, 1H), 6.25 (dt, *J* = 15.8, 6.4 Hz, 1H), 6.09 (s, 1H), 4.90 (qdd, *J* = 12.8, 6.4, 1.4 Hz, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 167.1, 138.2, 136.0, 134.9, 134.5, 134.3, 131.8, 129.9, 129.0, 128.7, 128.6, 128.5, 127.4, 123.9, 123.7, 122.2, 66.8, 56.0, 21.4; IR (Neat film, NaCl) 1772, 1747, 1715, 1605, 1468, 1456, 1385, 1214, 1186, 1111, 1076, 966, 908, 776, 721, 697; (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{25}N_2O_4$ $[M+NH_4]^+$: 429.1809, found 429.1791.



(*E*)-3-(*o*-tolyl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S21)

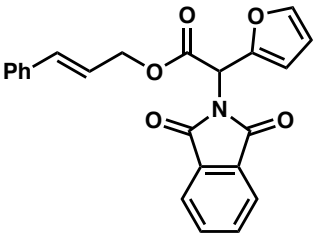
Performed on a 3.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (0–30% EtOAc in hexanes) to afford a viscous, colorless oil (716.0 mg, 1.74 mmol, 58% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.75 – 7.67 (m, 2H), 7.63 – 7.56 (m, 2H), 7.45 – 7.31 (m, 4H), 7.20 – 7.08 (m, 3H), 6.82 (d, *J* = 15.7 Hz, 1H), 6.14 (dt, *J* = 15.8, 6.3 Hz, 1H), 6.08 (s, 1H), 4.98 – 4.86 (m, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 167.1, 135.8, 135.3, 134.5, 134.3, 132.4, 131.9, 130.4, 129.9, 128.7, 128.7, 128.1, 126.2, 125.9, 123.7, 66.9, 56.1, 19.8; IR (Neat Film, NaCl) 3477, 3065, 3030, 2948, 2358, 2258, 1772, 1747, 1716, 1636, 1614, 1496, 1485, 1468, 1456, 1385, 1358, 1337, 1216, 1186, 1112,

1076, 966, 909, 720, 699 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{22}NO_4$ $[M+H]^+$: 412.1549, found 412.1549.



cinnamyl 2-(3,5-dimethylisoxazol-4-yl)-2-(1,3-dioxoisoindolin-2-yl)acetate (S22)

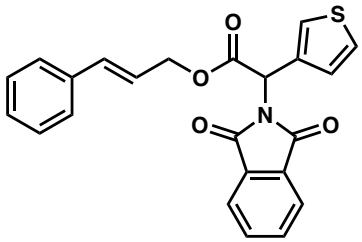
Performed according to general procedure 5 and purified by column chromatography (0–30% EtOAc in hexanes) to afford an amorphous white solid (1.2173 g, 2.92 mmol, 19% yield over 4 steps); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 – 7.83 (m, 2H), 7.78 – 7.72 (m, 2H), 7.38 – 7.25 (m, 5H), 6.65 (d, *J* = 15.8 Hz, 1H), 6.25 (dt, *J* = 15.8, 6.7 Hz, 1H), 5.98 (s, 1H), 4.89 (d, *J* = 6.6 Hz, 2H), 2.49 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 169.3, 166.9, 166.6, 159.5, 135.7, 135.6, 134.4, 131.5, 128.6, 128.3, 126.7, 123.7, 121.6, 108.2, 67.2, 45.7, 12.2, 10.5; IR (Neat Film, NaCl) 3509, 2935, 1726, 1677, 1430, 1364, 1340, 1299, 1240, 1175, 1114, 1050, 1002, 925, 839, 816, 754, 694 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{24}H_{21}N_2O_5$ $[M+H]^+$: 417.1450, found 417.1469.



cinnamyl 2-(1,3-dioxoisoindolin-2-yl)-2-(furan-2-yl)acetate (S23)

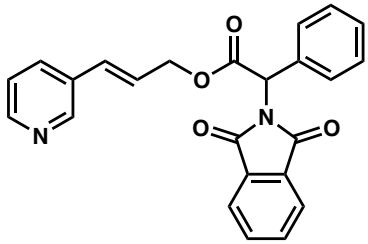
Performed according to general procedure 5 and purified by column chromatography (0–30% EtOAc in hexanes) to afford an amorphous white solid (1.7335 g, 4.47 mmol, 30% yield over 4 steps); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.82 (m, 2H), 7.80 – 7.69 (m, 2H), 7.42 – 7.37 (m, 1H), 7.37 – 7.28 (m, 4H), 7.28 – 7.22 (m, 1H), 6.65 – 6.57 (m, 2H), 6.38 (dd, *J* = 3.1, 1.8 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.18 (s, 1H), 4.94 – 4.84 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.8, 166.2, 146.8, 142.7, 136.1, 134.9, 134.4, 131.9, 128.7, 128.3, 126.8, 123.8,

122.1, 110.9, 110.7, 67.1, 49.5; IR (Neat Film, NaCl) 3838, 3472, 3027, 1750, 1721, 1662, 1646, 1493, 1467, 1449, 1426, 1384, 1336, 1300, 1221, 1192, 1110, 1089, 1073, 1014, 964, 933, 906, 886, 833, 734, 715, 70, 692 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{23}H_{18}NO_5$ $[M+H]^+$: 388.1185, found 388.1206.



cinnamyl 2-(1,3-dioxoisoindolin-2-yl)-2-(thiophen-3-yl)acetate (S24)

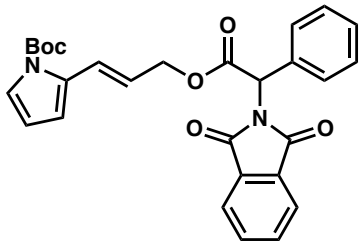
Performed according to general procedure 5 and purified by column chromatography (0–30% EtOAc in hexanes) to afford an amorphous white solid with a minor, inseparable impurity (1.7355 g, 4.30 mmol, 29% yield over 4 steps); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.92 – 7.87 (m, 2H), 7.79 – 7.73 (m, 2H), 7.54 – 7.51 (m, 1H), 7.40 – 7.31 (m, 6H), 7.31 – 7.26 (m, 1H), 6.62 (d, *J* = 15.8 Hz, 1H), 6.27 (dt, *J* = 15.9, 6.4 Hz, 1H), 6.20 (s, 1H), 4.91 (qd, *J* = 12.8, 6.3 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.7, 167.0, 136.1, 134.7, 134.3, 131.8, 128.7, 128.6, 128.2, 126.7, 126.0, 125.9, 123.7, 122.3, 66.8, 51.0; IR (Neat Film, NaCl) 3474, 3102, 3060, 3027, 2933, 2699, 2482, 2296, 2258, 1948, 1888, 1770, 1747, 1722, 1714, 1613, 1550, 1513, 1494, 1469 1456, 1449, 1384, 1337, 1298, 1220, 1179, 1108, 1088, 1020, 968, 910, 886, 838, 800, 732, 711, 693, 668 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{23}H_{18}NO_4S$ $[M+H]^+$: 404.0957, found 404.0968.



(*E*)-3-(pyridin-3-yl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S25)

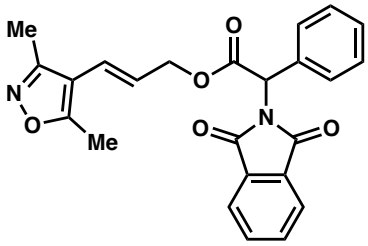
Performed on a 4.75 mmol scale according to general procedure 3 and purified by silica gel chromatography (30–100% EtOAc in hexanes) to afford the desired product as an amorphous white solid (1.5260 g, 3.83 mmol, 81% yield);^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.53 (s, 1H), 8.51 – 8.44 (m, 1H), 7.94 – 7.81 (m, 2H), 7.77 – 7.67 (m, 2H), 7.72 – 7.66 (m, 1H), 7.62 – 7.54

(m, 2H), 7.45 – 7.32 (m, 3H), 7.31 – 7.21 (m, 1H), 6.56 (d, *J* = 16.0 Hz, 1H), 6.32 (dt, *J* = 15.9, 6.1 Hz, 1H), 6.07 (s, 1H), 5.00 – 4.82 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.8, 167.0, 148.8, 148.2, 134.3, 134.3, 133.2, 131.8, 131.7, 130.4, 129.7, 128.7, 128.6, 124.9, 123.6, 123.5, 66.0, 55.9; IR (Neat Film, NaCl) 3471, 3033, 2938, 1771, 1747, 1716, 1613, 1385, 1337, 1264, 1222, 1186, 1111, 1088, 1076, 970, 895, 721, 700 cm^{-1} ;(MM:FAB+) *m/z* calc'd for $C_{24}H_{19}N_2O_4$ $[M+H]^+$: 399.1345, found 399.1358.



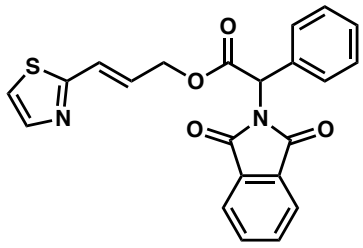
***tert*-butyl (*E*)-2-(3-(2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetoxy)prop-1-en-1-yl)-1*H*-pyrrole-1-carboxylate (S26)**

Performed on a 4.48 mmol scale according to general procedure 3 and purified by silica gel chromatography (20% EtOAc in hexanes) to afford the desired product as an amorphous white solid (1.9915g, 4.09 mmol, 91% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.85 (dt, *J* = 7.5, 3.8 Hz, 2H), 7.71 (dq, *J* = 7.3, 4.0 Hz, 2H), 7.55 (d, *J* = 7.5 Hz, 2H), 7.34 (dq, *J* = 9.7, 6.9 Hz, 4H), 7.23 – 7.17 (m, 1H), 6.41 (d, *J* = 3.4 Hz, 1H), 6.13 (t, *J* = 3.4 Hz, 1H), 6.08 – 5.99 (m, 1H), 6.04 (s, 1H), 4.93 – 4.78 (m, 2H), 1.58 (s, 9H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 167.1, 149.2, 134.5, 134.2, 132.5, 131.8, 129.8, 128.6, 128.6, 126.3, 123.6, 122.3, 121.8, 111.9, 110.9, 84.0, 67.0, 56.0, 28.0; IR (Neat Film, NaCl) 3476, 3064, 2982, 2940, 1738, 1722, 1716, 1613, 1496, 1469, 1456, 1385, 1372, 1323, 1247, 1214, 1183, 1172, 1165, 1128, 1069, 962, 892, 847, 721, 699 cm^{-1};(MM:FAB+) *m/z* calc'd for $C_{28}H_{26}N_2O_6$ $[M]^{+\bullet}$: 486.1791, found 486.1808.



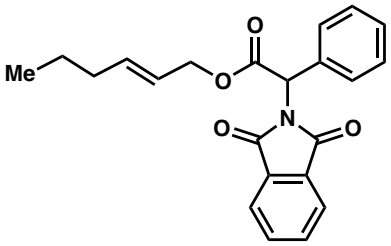
(*E*)-3-(3,5-dimethylisoxazol-4-yl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S27)

Performed on a 6.20 mmol scale according to general procedure 3 and purified by silica gel chromatography (30% EtOAc in hexanes) to afford the desired product as an amorphous white solid (2.0168 g, 4.84 mmol, 78% yield);^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 – 7.81 (m, 2H), 7.77 – 7.70 (m, 2H), 7.60 – 7.53 (m, 2H), 7.40 – 7.30 (m, 3H), 6.29 (d, *J* = 16.3 Hz, 1H), 6.05 (s, 1H), 5.92 (dt, *J* = 16.2, 6.2 Hz, 1H), 4.90 – 4.80 (m, 2H), 2.38 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.8, 167.0, 166.2, 158.2, 134.4, 134.3, 131.7, 129.7, 128.7, 128.6, 123.6, 123.5, 122.4, 111.8, 66.6, 55.9, 11.6, 11.4; IR (Neat Film, NaCl) 3044, 1747, 1716, 1676, 1610, 1430, 1385, 1337, 1213, 1110, 1076, 962, 893, 721, 699, 682 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{24}H_{21}N_2O_5$ [M+H]+: 417.1450, found 417.1478.



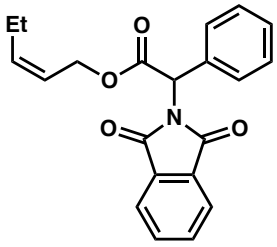
(*E*)-3-(thiazol-2-yl)allyl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (S28)

Performed on a 6.28 mmol scale according to general procedure 3 and purified by silica gel chromatography (30% EtOAc in hexanes) to afford the desired product as an viscous, colorless semisolid (1.32 g, 3.24 mmol, 52% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.89 – 7.84 (m, 2H), 7.77 (d, *J* = 3.2 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.59 – 7.54 (m, 2H), 7.40 – 7.32 (m, 3H), 7.26 (d, *J* = 3.2 Hz, 1H), 6.78 (dt, *J* = 15.9, 1.4 Hz, 1H), 6.61 (dt, *J* = 15.9, 5.9 Hz, 1H), 6.07 (s, 1H), 4.99 – 4.86 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.9, 167.2, 165.5, 143.6, 134.4, 134.4, 131.9, 129.8, 128.9, 128.7, 128.6, 126.7, 123.8, 119.0, 65.5, 56.0; IR (Neat Film, NaCl) 3476. 3060, 1772, 1750, 1716, 1610, 1487, 1467, 1456, 1385, 1336, 1216, 1186, 1110, 1076, 960, 894, 787, 772, 760, 719, 699, 638 cm^{-1} ;(MM:FAB+) *m/z* calc'd for $C_{22}H_{17}N_2O_4S$ [M+H]$^{+}$: 405.0909, found 405.0899.



(*E*)-hex-2-en-1-yl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (45)

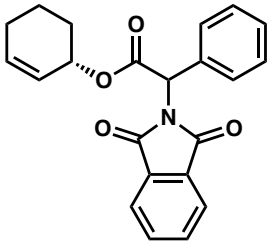
Performed on a 3.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (0–25% EtOAc in hexanes) to afford the desired product as a colorless oil (784.8 mg, 2.16 mmol, 72% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.90 – 7.80 (m, 2H), 7.75 – 7.68 (m, 2H), 7.58 – 7.51 (m, 2H), 7.41 – 7.28 (m, 3H), 6.02 (s, 1H), 5.73 (dt, *J* = 13.9, 6.8 Hz, 1H), 5.56 – 5.49 (m, 1H), 4.67 (qd, *J* = 12.2, 6.5 Hz, 2H), 2.00 (q, *J* = 7.1 Hz, 2H), 1.37 (h, *J* = 7.3 Hz, 2H), 0.87 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 167.2, 137.3, 134.6, 134.3, 131.9, 129.9, 128.7, 128.6, 123.7, 123.3, 67.0, 56.1, 34.3, 22.1, 13.7; IR (Neat Film, NaCl) 3838, 3472, 2956, 2932, 1773, 1745, 1719, 1610, 1498, 1467, 1457, 1426, 1384, 1338, 1302, 1216, 1186, 1116, 1089, 1076, 1016, 996, 970, 906, 894, 835, 776, 760, 768, 719, 699, 661, 645 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{22}NO_4$ $[M+H]^+$: 364.1549, found 364.1572.



(*Z*)-pent-2-en-1-yl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (47)

Performed on a 3.00 mmol scale according to general procedure 3 and purified by silica gel chromatography (0–25% EtOAc in hexanes) to afford the desired product as a colorless oil (903.9 mg, 2.59 mmol, 86% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.75 – 7.68 (m, 2H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.28 (m, 3H), 6.02 (s, 1H), 5.63 (dt, *J* = 10.6, 7.5 Hz, 1H), 5.51 – 5.41 (m, 1H), 4.83 – 4.73 (m, 2H), 2.10 (p, *J* = 7.5 Hz, 2H), 0.95 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 168.0, 167.2, 137.8, 134.6, 134.3, 131.9, 129.9, 128.7, 128.6, 123.7, 122.0, 62.0, 56.0, 21.0, 14.1; IR (Neat Film, NaCl 3473, 3025, 2964, 2935, 1772, 1747, 1718, 1649, 1498, 1467, 1458, 1384, 1266, 1214, 1186, 1108, 1088, 1076, 1020, 996, 976,

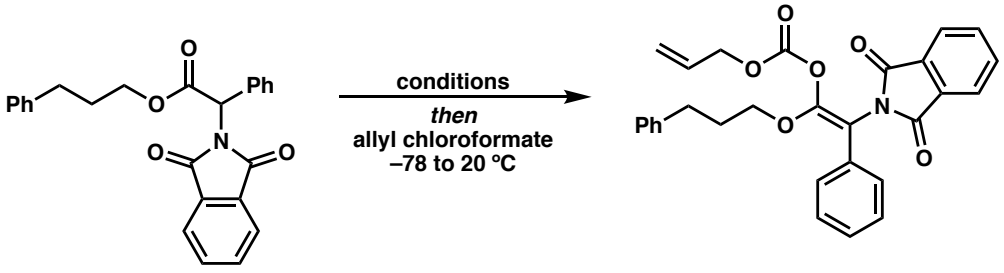
906, 893, 842, 719, 699 cm^{-1}; (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{20}NO_4$ $[M+H]^+$: 350.1392, found 350.1422.



(*S*)-cyclohex-2-en-1-yl 2-(1,3-dioxoisoindolin-2-yl)-2-phenylacetate (49)

Performed on a 3.00 mmol scale and purified by silica gel chromatography (0–30% EtOAc in hexanes) to afford the desired product as an amorphous white solid (953.4 mg, 2.64 mmol, 66% yield, 1:1 dr); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.84 (q, *J* = 5.5, 4.6 Hz, 2H), 7.71 (dt, *J* = 5.5, 2.6 Hz, 2H), 7.54 (dd, *J* = 7.8, 2.3 Hz, 2H), 7.38 – 7.29 (m, 3H), 6.01 (s, 0.5H), 6.00 (s, 0.5H), 5.93 (tt, *J* = 13.2, 3.8 Hz, 1H), 5.79 – 5.72 (m, 0.5H), 5.72 – 5.65 (m, 0.5H), 5.49 – 5.38 (m, 1H), 2.06 – 1.83 (m, 3H), 1.81 – 1.70 (m, 1H), 1.58 (dp, *J* = 13.1, 6.6 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.7, 167.7, 167.2, 134.7, 134.3, 134.3, 133.4, 133.2, 131.9, 129.9, 129.8, 128.6, 128.5, 125.1, 125.1, 123.6, 70.4, 70.4, 56.2, 56.1, 28.2, 28.1, 24.9, 24.8, 18.8, 18.7; IR (Neat Film, NaCl) 3472, 3034, 2935, 2866, 2831, 1773, 1741, 1734, 1718, 1650, 1612, 1550, 1497, 1467, 1455, 1426, 1385, 1360, 1337, 1231, 1214, 1187, 1161, 1112, 1089, 1076, 1051, 1018, 1006, 961, 909, 855, 844, 834, 816, 785, 778, 760, 767, 719, 699, 682, 661 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{22}H_{20}NO_4$ $[M+H]^+$: 362.1392, found 362.1408.

Investigation of Enolization Selectivity



16 ***enol carbonates A and B geometries not assigned***

entry	enolization conditions	% yield isomer A	% yield isomer B
1	LiHMDS (2.0 equiv), Me_2NEt (2.0 equiv), PhMe (0.10 M), – 78 °C, 2 h	16	23
2	LiHMDS (2.0 equiv), PhMe (0.10 M), – 78 °C, 2 h	43	27
3	KHMDS (2.0 equiv), PhMe (0.10 M), – 78 °C, 2 h	55	24

In a nitrogen-filled glovebox, an oven-dried 50 mL round bottom flask was charged with LiHMDS (335.0 mg, 2.00 mmol, 2.0 equiv) *or* KHMDS (399.0 mg, 2.00 mmol, 2.0 equiv) and a Teflon-coated stir bar. The flask was then sealed with a septum, removed from the glovebox, and placed under an atmosphere of nitrogen. To the flask was then added toluene (3.0 mL) and for entry 1, *N*,*N*-dimethylethylamine (213 μL, 2.00 mmol, 2.0 equiv). The resulting solution was stirred at 20 °C for 5 min, then the flask was immersed in a –78 °C dry ice/acetone bath. After stirring for 15 min, a solution of the α-phthalidomido ester **16** (1.00 mmol, 1.0 equiv) dissolved in toluene (7.0 mL) was added dropwise over 5 min, resulting in the immediate formation of a dark red/purple opaque reaction mixture. The reaction was maintained at –78 °C for 2 h, after which time allyl chloroformate (217 μL, 2.00 mmol, 2.0 equiv) was added dropwise over 1 min. The reaction flask was then removed from the cooling bath and allowed to warm to 20 °C. After 30 min, the reaction was quenched with 1 N HCl (10 mL) and transferred to a separatory funnel with Et_2O (10 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to afford the crude allyl enol carbonates. Due to substantial NMR overlap of enol carbonates A and B, the crude reaction mixtures were purified directly by silica gel chromatography (0–30% EtOAc in hexanes). Enol carbonate olefin geometries were not assigned unambiguously, therefore the higher R_f enol carbonate by TLC analysis (30% EtOAc) is designated

enol carbonate A and the lower R_f enol carbonate by TLC analysis (30% EtOAc) is designated enol carbonate B.

Entry 1: 76.6 mg, 0.158 mmol, 16% yield of enol carbonate A; 112.2 mg, 0.232 mmol, 23% yield enol carbonate B

Entry 2: 209.3 mg, 0.433 mmol, 43% yield of enol carbonate A; 131.7 mg, 0.272 mmol, 27% yield enol carbonate B

Entry 3: 266.4 mg, 0.551 mmol, 55% yield of enol carbonate A; 116.3 mg, 0.241 mmol, 24% yield enol carbonate B

Enol carbonate A: colorless, viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.76 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.61 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.29 – 7.24 (m, 2H), 7.20 – 7.13 (m, 2H), 7.13 – 7.03 (m, 3H), 7.03 – 6.97 (m, 1H), 6.93 – 6.86 (m, 2H), 5.68 (ddt, *J* = 17.1, 10.5, 5.8 Hz, 1H), 5.17 (dq, *J* = 17.2, 1.3 Hz, 1H), 5.11 (dq, *J* = 10.5, 1.1 Hz, 1H), 4.49 (dt, *J* = 5.7, 1.2 Hz, 2H), 3.88 (t, *J* = 6.3 Hz, 2H), 2.41 (dd, *J* = 8.5, 7.0 Hz, 2H), 1.81 – 1.68 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.2, 150.8, 141.1, 134.3, 133.1, 132.2, 130.5, 128.6, 128.4, 127.9, 127.6, 126.0, 123.8, 119.9, 103.4, 69.9, 69.8, 31.8, 30.9; IR (Neat Film, NaCl) 3069, 3026, 2955, 1777, 1725, 1680, 1604, 1496, 1468, 1446, 1420, 1383, 1264, 1201, 1173, 1113, 1088, 1071, 1020, 975, 941, 913, 883, 766, 753, 721, 699 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{29}H_{26}NO_6$ $[M+H]^+$: 484.1760, found 484.1739.

Enol carbonate B: colorless, viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 2H), 7.64 – 7.56 (m, 2H), 7.39 – 7.31 (m, 2H), 7.20 – 7.12 (m, 2H), 7.12 – 7.06 (m, 3H), 7.05 – 7.00 (m, 1H), 6.98 – 6.94 (m, 2H), 5.62 (ddt, *J* = 17.1, 10.4, 5.8 Hz, 1H), 5.09 (dq, *J* = 17.2, 1.4 Hz, 1H), 4.99 (dq, *J* = 10.5, 1.1 Hz, 1H), 4.45 (dt, *J* = 5.8, 1.3 Hz, 2H), 3.92 (t, *J* = 6.3 Hz, 2H), 2.50 (dd, *J* = 8.3, 7.0 Hz, 2H), 1.92 – 1.80 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.9, 151.3, 150.8, 141.1, 134.4, 132.7, 132.1, 130.6, 128.6, 128.5, 128.5, 127.9, 127.5, 126.1, 123.9, 119.8, 103.5, 71.2, 69.8, 31.9, 30.9; IR (Neat Film, NaCl) 3059, 3026, 2955, 1777, 1725, 1672, 1604, 1496, 1468, 1445, 1424, 1385, 1300, 1250, 1203, 1165, 1110, 1088, 1071, 996, 948, 882, 760, 748, 721, 700 cm^{-1}; (MM:FAB+) *m/z* calc'd for $C_{29}H_{26}NO_6$ $[M+H]^+$: 484.1760, found 484.1740.

X-Ray Crystal Structure for Ireland–Claisen Rearrangement Product 15a (V19143)

An X-ray quality crystal of Ireland–Claisen rearrangement product **15a** (compound V18448) was grown by slow cooling of a solution in toluene (approx. 50 mg/600 μL). Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Mo K_α radiation (λ = 0.71073 Å) from an IμS micro-source for the structure of compound V19143. The structure was solved by direct methods using SHELXS[15] and refined against F^2 on all data by full-matrix least squares with SHELXL-2017[16] using established refinement techniques.[17] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U value of the atoms they are linked to (1.5 times for methyl groups). Compound V19143 crystallizes in the triclinic space group P–1 with one molecule in the asymmetric unit. The coordinates for the hydrogen atom bound to O1 were located in the difference Fourier synthesis and refined semi-freely with the help of a restraint on the O–H distance (0.84(4) Å).

Figure S1. X-Ray Coordinate of Ireland–Claisen Rearrangement Product 15a (V19143)

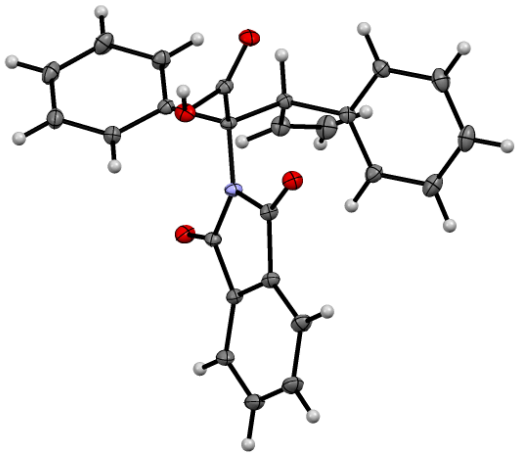


Table S2. Crystal data and structure refinement for V19143.

Identification code	V19143

Empirical formula	C25 H19 N O4	
Formula weight	397.41	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.645(2) Å	a= 93.927(13)°.
	b = 10.036(3) Å	b= 96.322(12)°.
	c = 12.230(3) Å	g = 113.900(15)°.
Volume	956.8(4) $Å^3$	
Z	2	
Density (calculated)	1.379 Mg/m^3	
Absorption coefficient	0.094 mm^{-1}	
F(000)	416	
Crystal size	0.450 x 0.250 x 0.150 mm^3	
Theta range for data collection	2.636 to 36.329°.	
Index ranges	-14<=h<=14, -16<=k<=16, -20<=l<=20	
Reflections collected	47728	
Independent reflections	9254 [R(int) = 0.0600]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7389 and 0.6940	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9254 / 1 / 274	
Goodness-of-fit on F^2	1.035	
Final R indices [I>2sigma(I)]	R1 = 0.0449, wR2 = 0.1207	
R indices (all data)	R1 = 0.0555, wR2 = 0.1309	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.586 and -0.297 $e.Å^{-3}$	

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for V19143. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5924(1)	5535(1)	1870(1)	13(1)
O(1)	6544(1)	6036(1)	955(1)	17(1)
O(2)	5608(1)	4314(1)	2102(1)	18(1)
C(2)	5878(1)	6774(1)	2682(1)	11(1)
N(1)	5163(1)	7649(1)	2043(1)	12(1)
C(6)	3796(1)	7005(1)	1165(1)	13(1)
O(3)	3204(1)	5730(1)	752(1)	16(1)
C(7)	3264(1)	8171(1)	849(1)	14(1)
C(8)	1938(1)	8087(1)	62(1)	18(1)
C(9)	1782(1)	9400(1)	-82(1)	21(1)
C(10)	2917(1)	10728(1)	539(1)	21(1)
C(11)	4220(1)	10785(1)	1356(1)	18(1)
C(12)	4354(1)	9476(1)	1498(1)	14(1)
C(13)	5526(1)	9155(1)	2317(1)	13(1)
O(4)	6555(1)	9979(1)	3080(1)	19(1)
C(21)	7800(1)	7664(1)	3141(1)	13(1)
C(22)	8882(1)	8605(1)	2491(1)	16(1)
C(23)	10631(1)	9341(1)	2856(1)	20(1)
C(24)	11337(1)	9147(1)	3877(1)	20(1)
C(25)	10286(1)	8199(1)	4523(1)	21(1)
C(26)	8526(1)	7451(1)	4155(1)	17(1)
C(3)	4787(1)	6121(1)	3610(1)	13(1)
C(31)	2887(1)	5214(1)	3199(1)	13(1)
C(32)	2197(1)	3682(1)	3091(1)	17(1)
C(33)	434(1)	2859(1)	2804(1)	22(1)
C(34)	-653(1)	3553(1)	2607(1)	23(1)
C(35)	26(1)	5073(1)	2685(1)	21(1)
C(36)	1777(1)	5896(1)	2992(1)	17(1)
C(4)	5062(1)	7322(1)	4541(1)	16(1)
C(5)	4064(1)	7193(1)	5313(1)	22(1)

Table S4. Bond lengths [Å] and angles [°] for V19143.

C(1)-O(2)	1.2038(9)
C(1)-O(1)	1.3352(10)
C(1)-C(2)	1.5532(10)
O(1)-H(1O)	0.850(12)
C(2)-N(1)	1.4807(9)
C(2)-C(21)	1.5486(11)
C(2)-C(3)	1.5626(11)
N(1)-C(6)	1.4053(10)
N(1)-C(13)	1.4201(10)
C(6)-O(3)	1.2155(9)
C(6)-C(7)	1.4797(11)
C(7)-C(8)	1.3841(11)
C(7)-C(12)	1.3884(11)
C(8)-C(9)	1.3989(13)
C(8)-H(8)	0.9500
C(9)-C(10)	1.3971(14)
C(9)-H(9)	0.9500
C(10)-C(11)	1.4008(12)
C(10)-H(10)	0.9500
C(11)-C(12)	1.3857(11)
C(11)-H(11)	0.9500
C(12)-C(13)	1.4899(11)
C(13)-O(4)	1.2081(10)
C(21)-C(22)	1.3963(11)
C(21)-C(26)	1.3966(11)
C(22)-C(23)	1.3904(12)
C(22)-H(22)	0.9500
C(23)-C(24)	1.3902(14)
C(23)-H(23)	0.9500
C(24)-C(25)	1.3842(14)
C(24)-H(24)	0.9500
C(25)-C(26)	1.3988(12)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500

C(3)-C(31)	1.5244(11)
C(3)-C(4)	1.5249(11)
C(3)-H(3)	1.0000
C(31)-C(32)	1.3956(11)
C(31)-C(36)	1.3990(11)
C(32)-C(33)	1.3967(12)
C(32)-H(32)	0.9500
C(33)-C(34)	1.3894(14)
C(33)-H(33)	0.9500
C(34)-C(35)	1.3869(14)
C(34)-H(34)	0.9500
C(35)-C(36)	1.3908(12)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(4)-C(5)	1.3264(12)
C(4)-H(4)	0.9500
C(5)-H(5A)	0.9500
C(5)-H(5B)	0.9500

O(2)-C(1)-O(1)	124.51(7)
O(2)-C(1)-C(2)	123.19(7)
O(1)-C(1)-C(2)	111.85(6)
C(1)-O(1)-H(1O)	109.9(9)
N(1)-C(2)-C(21)	111.86(6)
N(1)-C(2)-C(1)	108.70(6)
C(21)-C(2)-C(1)	101.80(6)
N(1)-C(2)-C(3)	110.60(6)
C(21)-C(2)-C(3)	112.53(6)
C(1)-C(2)-C(3)	111.00(6)
C(6)-N(1)-C(13)	110.41(6)
C(6)-N(1)-C(2)	122.40(6)
C(13)-N(1)-C(2)	126.44(6)
O(3)-C(6)-N(1)	125.27(7)
O(3)-C(6)-C(7)	127.79(7)
N(1)-C(6)-C(7)	106.94(6)
C(8)-C(7)-C(12)	122.17(7)

C(8)-C(7)-C(6)	129.64(7)
C(12)-C(7)-C(6)	108.19(7)
C(7)-C(8)-C(9)	116.69(8)
C(7)-C(8)-H(8)	121.7
C(9)-C(8)-H(8)	121.7
C(10)-C(9)-C(8)	121.37(8)
C(10)-C(9)-H(9)	119.3
C(8)-C(9)-H(9)	119.3
C(9)-C(10)-C(11)	121.18(8)
C(9)-C(10)-H(10)	119.4
C(11)-C(10)-H(10)	119.4
C(12)-C(11)-C(10)	116.97(8)
C(12)-C(11)-H(11)	121.5
C(10)-C(11)-H(11)	121.5
C(11)-C(12)-C(7)	121.54(7)
C(11)-C(12)-C(13)	130.16(7)
C(7)-C(12)-C(13)	108.27(6)
O(4)-C(13)-N(1)	126.09(7)
O(4)-C(13)-C(12)	127.95(7)
N(1)-C(13)-C(12)	105.94(6)
C(22)-C(21)-C(26)	118.31(7)
C(22)-C(21)-C(2)	119.86(7)
C(26)-C(21)-C(2)	121.55(7)
C(23)-C(22)-C(21)	120.88(8)
C(23)-C(22)-H(22)	119.6
C(21)-C(22)-H(22)	119.6
C(24)-C(23)-C(22)	120.38(8)
C(24)-C(23)-H(23)	119.8
C(22)-C(23)-H(23)	119.8
C(25)-C(24)-C(23)	119.40(8)
C(25)-C(24)-H(24)	120.3
C(23)-C(24)-H(24)	120.3
C(24)-C(25)-C(26)	120.31(8)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(21)-C(26)-C(25)	120.68(8)

C(21)-C(26)-H(26)	119.7
C(25)-C(26)-H(26)	119.7
C(31)-C(3)-C(4)	111.16(6)
C(31)-C(3)-C(2)	114.66(6)
C(4)-C(3)-C(2)	110.84(6)
C(31)-C(3)-H(3)	106.6
C(4)-C(3)-H(3)	106.6
C(2)-C(3)-H(3)	106.6
C(32)-C(31)-C(36)	118.46(7)
C(32)-C(31)-C(3)	120.66(7)
C(36)-C(31)-C(3)	120.76(7)
C(31)-C(32)-C(33)	120.41(8)
C(31)-C(32)-H(32)	119.8
C(33)-C(32)-H(32)	119.8
C(34)-C(33)-C(32)	120.47(8)
C(34)-C(33)-H(33)	119.8
C(32)-C(33)-H(33)	119.8
C(35)-C(34)-C(33)	119.50(8)
C(35)-C(34)-H(34)	120.3
C(33)-C(34)-H(34)	120.3
C(34)-C(35)-C(36)	120.13(8)
C(34)-C(35)-H(35)	119.9
C(36)-C(35)-H(35)	119.9
C(35)-C(36)-C(31)	121.00(8)
C(35)-C(36)-H(36)	119.5
C(31)-C(36)-H(36)	119.5
C(5)-C(4)-C(3)	125.11(8)
C(5)-C(4)-H(4)	117.4
C(3)-C(4)-H(4)	117.4
C(4)-C(5)-H(5A)	120.0
C(4)-C(5)-H(5B)	120.0
H(5A)-C(5)-H(5B)	120.0

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for V19143. 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}
C(1)	14(1)	12(1)	14(1)	-1(1)	1(1)	6(1)
O(1)	23(1)	16(1)	14(1)	-1(1)	5(1)	10(1)
O(2)	22(1)	12(1)	22(1)	1(1)	4(1)	9(1)
C(2)	12(1)	10(1)	12(1)	0(1)	1(1)	6(1)
N(1)	14(1)	10(1)	12(1)	0(1)	0(1)	6(1)
C(6)	14(1)	13(1)	11(1)	0(1)	1(1)	6(1)
O(3)	19(1)	14(1)	14(1)	-3(1)	0(1)	7(1)
C(7)	16(1)	15(1)	13(1)	2(1)	2(1)	8(1)
C(8)	19(1)	22(1)	16(1)	4(1)	0(1)	10(1)
C(9)	22(1)	27(1)	21(1)	9(1)	2(1)	14(1)
C(10)	22(1)	22(1)	25(1)	11(1)	7(1)	14(1)
C(11)	17(1)	14(1)	24(1)	6(1)	6(1)	9(1)
C(12)	14(1)	13(1)	16(1)	3(1)	3(1)	7(1)
C(13)	14(1)	10(1)	17(1)	1(1)	2(1)	6(1)
O(4)	18(1)	13(1)	23(1)	-4(1)	-2(1)	6(1)
C(21)	12(1)	12(1)	13(1)	0(1)	1(1)	5(1)
C(22)	14(1)	17(1)	18(1)	4(1)	3(1)	6(1)
C(23)	14(1)	18(1)	26(1)	2(1)	5(1)	5(1)
C(24)	13(1)	20(1)	26(1)	-5(1)	-1(1)	5(1)
C(25)	17(1)	26(1)	18(1)	-2(1)	-3(1)	9(1)
C(26)	15(1)	20(1)	14(1)	1(1)	-1(1)	7(1)
C(3)	13(1)	12(1)	13(1)	1(1)	2(1)	5(1)
C(31)	13(1)	13(1)	13(1)	1(1)	2(1)	5(1)
C(32)	17(1)	13(1)	18(1)	1(1)	2(1)	5(1)
C(33)	19(1)	16(1)	23(1)	-1(1)	3(1)	1(1)
C(34)	14(1)	26(1)	22(1)	-4(1)	1(1)	4(1)
C(35)	15(1)	26(1)	22(1)	-2(1)	1(1)	10(1)
C(36)	15(1)	17(1)	19(1)	1(1)	2(1)	9(1)
C(4)	18(1)	17(1)	14(1)	-2(1)	2(1)	7(1)
C(5)	24(1)	25(1)	17(1)	-1(1)	6(1)	10(1)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for V19143.

	x	y	z	U(eq)
H(1O)	6581(17)	5342(14)	536(11)	20
H(8)	1171	7182	-360	22
H(9)	886	9390	-612	26
H(10)	2803	11607	404	25
H(11)	4978	11681	1792	21
H(22)	8416	8744	1790	20
H(23)	11348	9980	2404	24
H(24)	12531	9660	4129	25
H(25)	10761	8055	5219	25
H(26)	7818	6792	4600	21
H(3)	5237	5440	3940	15
H(32)	2931	3197	3213	20
H(33)	-25	1818	2744	26
H(34)	-1853	2990	2420	28
H(35)	-707	5553	2529	25
H(36)	2226	6938	3063	20
H(4)	6025	8233	4570	20
H(5A)	3089	6298	5312	27
H(5B)	4323	7994	5867	27

Table S7. Torsion angles [°] for V19143.

O(2)-C(1)-C(2)-N(1)	-141.93(7)
O(1)-C(1)-C(2)-N(1)	45.42(8)
O(2)-C(1)-C(2)-C(21)	99.90(8)
O(1)-C(1)-C(2)-C(21)	-72.76(7)
O(2)-C(1)-C(2)-C(3)	-20.06(10)
O(1)-C(1)-C(2)-C(3)	167.28(6)
C(21)-C(2)-N(1)-C(6)	150.72(7)
C(1)-C(2)-N(1)-C(6)	39.11(9)
C(3)-C(2)-N(1)-C(6)	-82.99(8)
C(21)-C(2)-N(1)-C(13)	-40.15(9)
C(1)-C(2)-N(1)-C(13)	-151.76(7)
C(3)-C(2)-N(1)-C(13)	86.14(8)
C(13)-N(1)-C(6)-O(3)	179.89(7)
C(2)-N(1)-C(6)-O(3)	-9.42(12)
C(13)-N(1)-C(6)-C(7)	0.68(8)
C(2)-N(1)-C(6)-C(7)	171.37(6)
O(3)-C(6)-C(7)-C(8)	3.61(14)
N(1)-C(6)-C(7)-C(8)	-177.21(8)
O(3)-C(6)-C(7)-C(12)	-176.58(8)
N(1)-C(6)-C(7)-C(12)	2.61(8)
C(12)-C(7)-C(8)-C(9)	2.43(12)
C(6)-C(7)-C(8)-C(9)	-177.78(8)
C(7)-C(8)-C(9)-C(10)	0.21(13)
C(8)-C(9)-C(10)-C(11)	-2.21(14)
C(9)-C(10)-C(11)-C(12)	1.53(13)
C(10)-C(11)-C(12)-C(7)	1.08(12)
C(10)-C(11)-C(12)-C(13)	-176.79(8)
C(8)-C(7)-C(12)-C(11)	-3.16(12)
C(6)-C(7)-C(12)-C(11)	177.01(7)
C(8)-C(7)-C(12)-C(13)	175.13(7)
C(6)-C(7)-C(12)-C(13)	-4.71(8)
C(6)-N(1)-C(13)-O(4)	175.02(8)
C(2)-N(1)-C(13)-O(4)	4.80(12)
C(6)-N(1)-C(13)-C(12)	-3.45(8)

C(2)-N(1)-C(13)-C(12)	-173.67(6)
C(11)-C(12)-C(13)-O(4)	4.72(14)
C(7)-C(12)-C(13)-O(4)	-173.36(8)
C(11)-C(12)-C(13)-N(1)	-176.84(8)
C(7)-C(12)-C(13)-N(1)	5.07(8)
N(1)-C(2)-C(21)-C(22)	-39.46(9)
C(1)-C(2)-C(21)-C(22)	76.44(8)
C(3)-C(2)-C(21)-C(22)	-164.69(6)
N(1)-C(2)-C(21)-C(26)	146.64(7)
C(1)-C(2)-C(21)-C(26)	-97.46(8)
C(3)-C(2)-C(21)-C(26)	21.42(9)
C(26)-C(21)-C(22)-C(23)	-1.64(11)
C(2)-C(21)-C(22)-C(23)	-175.73(7)
C(21)-C(22)-C(23)-C(24)	0.28(12)
C(22)-C(23)-C(24)-C(25)	0.79(13)
C(23)-C(24)-C(25)-C(26)	-0.46(13)
C(22)-C(21)-C(26)-C(25)	1.96(12)
C(2)-C(21)-C(26)-C(25)	175.95(7)
C(24)-C(25)-C(26)-C(21)	-0.93(13)
N(1)-C(2)-C(3)-C(31)	54.99(8)
C(21)-C(2)-C(3)-C(31)	-179.10(6)
C(1)-C(2)-C(3)-C(31)	-65.76(8)
N(1)-C(2)-C(3)-C(4)	-71.86(7)
C(21)-C(2)-C(3)-C(4)	54.05(8)
C(1)-C(2)-C(3)-C(4)	167.39(6)
C(4)-C(3)-C(31)-C(32)	-130.31(8)
C(2)-C(3)-C(31)-C(32)	103.00(8)
C(4)-C(3)-C(31)-C(36)	45.45(9)
C(2)-C(3)-C(31)-C(36)	-81.24(9)
C(36)-C(31)-C(32)-C(33)	-1.27(12)
C(3)-C(31)-C(32)-C(33)	174.58(7)
C(31)-C(32)-C(33)-C(34)	0.99(13)
C(32)-C(33)-C(34)-C(35)	0.63(14)
C(33)-C(34)-C(35)-C(36)	-1.94(14)
C(34)-C(35)-C(36)-C(31)	1.67(13)
C(32)-C(31)-C(36)-C(35)	-0.05(12)

C(3)-C(31)-C(36)-C(35)	-175.90(7)
C(31)-C(3)-C(4)-C(5)	35.57(11)
C(2)-C(3)-C(4)-C(5)	164.33(8)

Symmetry transformations used to generate equivalent atoms:

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1)-H(1O)...O(3)#1	0.850(12)	1.915(12)	2.7303(10)	160.5(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z

X-Ray Crystal Structure for Ireland–Claisen Rearrangement Product 50 (V20078)

An X-ray quality crystal of Ireland–Claisen Rearrangement Product **50** (compound V20078) was grown by slow cooling of a solution in *i*-PrOH (approx. 20 mg/300 μL). Low-temperature diffraction data (ϕ-and ω-scans) were collected on a Bruker AXS D8 VENTURE KAPPA diffractometer coupled to a PHOTON II CPAD detector with Cu K_α radiation (λ = 1.54178 Å) from an IμS micro-source for the structure of compound V20078. The structure was solved by direct methods using SHELXS[15] and refined against F^2 on all data by full-matrix least squares with SHELXL-2018[16] using established refinement techniques.[17] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were included into the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the *U* value of the atoms they are linked to (1.5 times for methyl groups). All disordered atoms were refined with the help of similarity restraints on the 1,2- and 1,3-distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. Compound V20078 crystallizes in the triclinic space group *P*1 with two molecules in the asymmetric unit.

Figure S2. X-Ray Coordinate of Ireland–Claisen Rearrangement Product 50 (V20078)

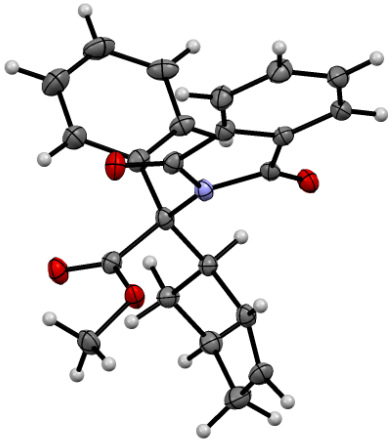


Table S8. Crystal data and structure refinement for V20078.

Identification code	V20078
Empirical formula	C23 H21 N O4

Formula weight	375.41	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 8.7657(4) Å	a= 79.3918(12)°.
	b = 9.6615(5) Å	b= 89.6083(13)°.
	c = 11.4746(6) Å	g = 82.2116(12)°.
Volume	946.20(8) $Å^3$	
Z	2	
Density (calculated)	1.318 Mg/m^3	
Absorption coefficient	0.734 mm^{-1}	
F(000)	396	
Crystal size	0.200 x 0.150 x 0.100 mm^3	
Theta range for data collection	3.920 to 74.662°.	
Index ranges	-10<=h<=10, -10<=k<=12, -14<=l<=14	
Reflections collected	43609	
Independent reflections	7033 [R(int) = 0.0302]	
Completeness to theta = 67.679°	99.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7538 and 0.6661	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	7033 / 3 / 507	
Goodness-of-fit on F^2	1.048	
Final R indices [I>2sigma(I)]	R1 = 0.0387, wR2 = 0.1032	
R indices (all data)	R1 = 0.0391, wR2 = 0.1041	
Absolute structure parameter	-0.22(12)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.241 and -0.220 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for V20078. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	6288(3)	4066(3)	7505(2)	15(1)
N(1)	7046(2)	3211(2)	8607(2)	16(1)
C(11)	6637(3)	1885(3)	9145(2)	17(1)
O(1)	5602(2)	1330(2)	8815(2)	22(1)
C(12)	7725(3)	1332(3)	10165(2)	19(1)
C(13)	7807(4)	85(3)	10991(3)	26(1)
C(14)	8981(4)	-143(3)	11854(3)	31(1)
C(15)	9998(4)	828(3)	11880(3)	30(1)
C(16)	9900(3)	2087(3)	11050(3)	24(1)
C(17)	8741(3)	2309(3)	10190(2)	19(1)
C(18)	8348(3)	3509(3)	9178(2)	17(1)
O(2)	8995(2)	4543(2)	8885(2)	20(1)
C(21)	4566(3)	3871(3)	7493(2)	17(1)
O(3)	3880(2)	3729(2)	6632(2)	24(1)
O(4)	3906(2)	4037(2)	8520(2)	19(1)
C(22)	2246(3)	4092(3)	8512(3)	22(1)
C(31)	6200(3)	5679(3)	7504(2)	16(1)
C(32)	5942(3)	6199(3)	8557(3)	19(1)
C(33)	5778(3)	7649(3)	8550(3)	23(1)
C(34)	5824(3)	8606(3)	7485(3)	26(1)
C(35)	6048(4)	8095(3)	6443(3)	25(1)
C(36)	6243(3)	6644(3)	6444(3)	20(1)
C(41)	7091(3)	3625(3)	6391(2)	16(1)
C(42)	8729(3)	3958(3)	6304(2)	18(1)
C(43)	9846(3)	3209(3)	5799(3)	22(1)
C(44)	9616(3)	1979(3)	5221(3)	25(1)
C(45)	7929(3)	1766(3)	5176(3)	24(1)
C(46)	7076(3)	2066(3)	6297(2)	19(1)
C(101)	3411(3)	5804(3)	2643(2)	19(1)
N(101)	2805(3)	6625(2)	1479(2)	18(1)
C(111)	3232(3)	7972(3)	1031(2)	20(1)

O(101)	4204(3)	8496(2)	1477(2)	27(1)
C(112)	2251(3)	8578(3)	-41(3)	21(1)
C(113)	2232(4)	9844(3)	-827(3)	26(1)
C(114)	1131(4)	10127(3)	-1740(3)	29(1)
C(115)	118(4)	9166(3)	-1858(3)	28(1)
C(116)	152(3)	7890(3)	-1066(3)	23(1)
C(117)	1233(3)	7624(3)	-154(3)	20(1)
C(118)	1513(3)	6402(3)	845(2)	18(1)
O(102)	777(2)	5420(2)	1086(2)	24(1)
C(121)	5160(3)	5846(3)	2700(2)	20(1)
O(103)	5883(2)	5842(2)	3591(2)	26(1)
O(104)	5815(2)	5729(2)	1656(2)	23(1)
C(122)	7473(3)	5659(4)	1663(3)	28(1)
C(131)	2488(3)	6488(3)	3593(3)	22(1)
C(132)	3062(4)	7422(4)	4217(3)	31(1)
C(133)	2126(5)	8068(4)	5001(4)	43(1)
C(134)	623(4)	7830(4)	5161(3)	35(1)
C(135)	22(4)	6929(3)	4534(3)	29(1)
C(136)	957(3)	6266(3)	3755(3)	23(1)
C(141)	3225(3)	4186(3)	2761(2)	19(1)
C(142)	3830(3)	3512(3)	1735(3)	22(1)
C(143)	4396(4)	2147(3)	1864(3)	27(1)
C(144)	4603(4)	1142(3)	3034(3)	32(1)
C(145)	3726(4)	1755(3)	4008(3)	25(1)
C(146)	3895(4)	3318(3)	3935(3)	24(1)

Table S10. Bond lengths [Å] and angles [°] for V20078.

C(1)-N(1)	1.484(3)
C(1)-C(21)	1.547(4)
C(1)-C(31)	1.550(4)
C(1)-C(41)	1.555(4)
N(1)-C(11)	1.408(3)
N(1)-C(18)	1.409(3)
C(11)-O(1)	1.210(3)
C(11)-C(12)	1.487(4)
C(12)-C(13)	1.383(4)
C(12)-C(17)	1.387(4)
C(13)-C(14)	1.400(5)
C(13)-H(13)	0.9500
C(14)-C(15)	1.383(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.393(4)
C(15)-H(15)	0.9500
C(16)-C(17)	1.389(4)
C(16)-H(16)	0.9500
C(17)-C(18)	1.487(4)
C(18)-O(2)	1.208(3)
C(21)-O(3)	1.199(3)
C(21)-O(4)	1.335(3)
O(4)-C(22)	1.449(3)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(31)-C(36)	1.393(4)
C(31)-C(32)	1.397(4)
C(32)-C(33)	1.387(4)
C(32)-H(32)	0.9500
C(33)-C(34)	1.394(4)
C(33)-H(33)	0.9500
C(34)-C(35)	1.378(5)
C(34)-H(34)	0.9500

C(35)-C(36)	1.389(4)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500
C(41)-C(42)	1.512(4)
C(41)-C(46)	1.532(4)
C(41)-H(41)	1.0000
C(42)-C(43)	1.331(4)
C(42)-H(42)	0.9500
C(43)-C(44)	1.500(4)
C(43)-H(43)	0.9500
C(44)-C(45)	1.523(4)
C(44)-H(44A)	0.9900
C(44)-H(44B)	0.9900
C(45)-C(46)	1.537(4)
C(45)-H(45A)	0.9900
C(45)-H(45B)	0.9900
C(46)-H(46A)	0.9900
C(46)-H(46B)	0.9900
C(101)-N(101)	1.483(4)
C(101)-C(121)	1.541(4)
C(101)-C(131)	1.545(4)
C(101)-C(141)	1.575(4)
N(101)-C(111)	1.408(4)
N(101)-C(118)	1.412(4)
C(111)-O(101)	1.209(4)
C(111)-C(112)	1.486(4)
C(112)-C(113)	1.378(4)
C(112)-C(117)	1.390(4)
C(113)-C(114)	1.394(4)
C(113)-H(113)	0.9500
C(114)-C(115)	1.393(5)
C(114)-H(114)	0.9500
C(115)-C(116)	1.387(5)
C(115)-H(115)	0.9500
C(116)-C(117)	1.381(4)
C(116)-H(116)	0.9500

C(117)-C(118)	1.481(4)
C(118)-O(102)	1.209(3)
C(121)-O(103)	1.206(4)
C(121)-O(104)	1.342(4)
O(104)-C(122)	1.446(4)
C(122)-H(12A)	0.9800
C(122)-H(12B)	0.9800
C(122)-H(12C)	0.9800
C(131)-C(136)	1.394(4)
C(131)-C(132)	1.396(4)
C(132)-C(133)	1.389(5)
C(132)-H(132)	0.9500
C(133)-C(134)	1.373(6)
C(133)-H(133)	0.9500
C(134)-C(135)	1.383(5)
C(134)-H(134)	0.9500
C(135)-C(136)	1.392(4)
C(135)-H(135)	0.9500
C(136)-H(136)	0.9500
C(141)-C(142)	1.507(4)
C(141)-C(146)	1.524(4)
C(141)-H(141)	1.0000
C(142)-C(143)	1.327(4)
C(142)-H(142)	0.9500
C(143)-C(144)	1.502(5)
C(143)-H(143)	0.9500
C(144)-C(145)	1.516(4)
C(144)-H(14A)	0.9900
C(144)-H(14B)	0.9900
C(145)-C(146)	1.524(4)
C(145)-H(14C)	0.9900
C(145)-H(14D)	0.9900
C(146)-H(14E)	0.9900
C(146)-H(14F)	0.9900

N(1)-C(1)-C(21)	109.5(2)

N(1)-C(1)-C(31)	111.1(2)
C(21)-C(1)-C(31)	101.9(2)
N(1)-C(1)-C(41)	110.8(2)
C(21)-C(1)-C(41)	110.4(2)
C(31)-C(1)-C(41)	112.7(2)
C(11)-N(1)-C(18)	110.8(2)
C(11)-N(1)-C(1)	122.8(2)
C(18)-N(1)-C(1)	126.0(2)
O(1)-C(11)-N(1)	125.4(3)
O(1)-C(11)-C(12)	128.2(3)
N(1)-C(11)-C(12)	106.4(2)
C(13)-C(12)-C(17)	122.0(3)
C(13)-C(12)-C(11)	129.7(3)
C(17)-C(12)-C(11)	108.2(2)
C(12)-C(13)-C(14)	116.3(3)
C(12)-C(13)-H(13)	121.9
C(14)-C(13)-H(13)	121.9
C(15)-C(14)-C(13)	121.8(3)
C(15)-C(14)-H(14)	119.1
C(13)-C(14)-H(14)	119.1
C(14)-C(15)-C(16)	121.6(3)
C(14)-C(15)-H(15)	119.2
C(16)-C(15)-H(15)	119.2
C(17)-C(16)-C(15)	116.6(3)
C(17)-C(16)-H(16)	121.7
C(15)-C(16)-H(16)	121.7
C(12)-C(17)-C(16)	121.7(3)
C(12)-C(17)-C(18)	108.3(2)
C(16)-C(17)-C(18)	130.0(3)
O(2)-C(18)-N(1)	125.7(3)
O(2)-C(18)-C(17)	128.0(3)
N(1)-C(18)-C(17)	106.3(2)
O(3)-C(21)-O(4)	124.2(2)
O(3)-C(21)-C(1)	123.9(2)
O(4)-C(21)-C(1)	111.5(2)
C(21)-O(4)-C(22)	114.6(2)

O(4)-C(22)-H(22A)	109.5
O(4)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
O(4)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(36)-C(31)-C(32)	118.8(3)
C(36)-C(31)-C(1)	120.6(2)
C(32)-C(31)-C(1)	120.3(2)
C(33)-C(32)-C(31)	120.5(3)
C(33)-C(32)-H(32)	119.7
C(31)-C(32)-H(32)	119.7
C(32)-C(33)-C(34)	120.3(3)
C(32)-C(33)-H(33)	119.9
C(34)-C(33)-H(33)	119.9
C(35)-C(34)-C(33)	119.3(3)
C(35)-C(34)-H(34)	120.4
C(33)-C(34)-H(34)	120.4
C(34)-C(35)-C(36)	120.9(3)
C(34)-C(35)-H(35)	119.6
C(36)-C(35)-H(35)	119.6
C(35)-C(36)-C(31)	120.3(3)
C(35)-C(36)-H(36)	119.9
C(31)-C(36)-H(36)	119.9
C(42)-C(41)-C(46)	109.3(2)
C(42)-C(41)-C(1)	111.7(2)
C(46)-C(41)-C(1)	114.6(2)
C(42)-C(41)-H(41)	107.0
C(46)-C(41)-H(41)	107.0
C(1)-C(41)-H(41)	107.0
C(43)-C(42)-C(41)	123.3(3)
C(43)-C(42)-H(42)	118.3
C(41)-C(42)-H(42)	118.3
C(42)-C(43)-C(44)	124.1(3)
C(42)-C(43)-H(43)	117.9
C(44)-C(43)-H(43)	117.9

C(43)-C(44)-C(45)	112.2(2)
C(43)-C(44)-H(44A)	109.2
C(45)-C(44)-H(44A)	109.2
C(43)-C(44)-H(44B)	109.2
C(45)-C(44)-H(44B)	109.2
H(44A)-C(44)-H(44B)	107.9
C(44)-C(45)-C(46)	112.0(2)
C(44)-C(45)-H(45A)	109.2
C(46)-C(45)-H(45A)	109.2
C(44)-C(45)-H(45B)	109.2
C(46)-C(45)-H(45B)	109.2
H(45A)-C(45)-H(45B)	107.9
C(41)-C(46)-C(45)	109.2(2)
C(41)-C(46)-H(46A)	109.8
C(45)-C(46)-H(46A)	109.8
C(41)-C(46)-H(46B)	109.8
C(45)-C(46)-H(46B)	109.8
H(46A)-C(46)-H(46B)	108.3
N(101)-C(101)-C(121)	108.4(2)
N(101)-C(101)-C(131)	106.1(2)
C(121)-C(101)-C(131)	114.3(2)
N(101)-C(101)-C(141)	110.9(2)
C(121)-C(101)-C(141)	105.5(2)
C(131)-C(101)-C(141)	111.6(2)
C(111)-N(101)-C(118)	110.4(2)
C(111)-N(101)-C(101)	120.8(2)
C(118)-N(101)-C(101)	126.9(2)
O(101)-C(111)-N(101)	124.5(3)
O(101)-C(111)-C(112)	128.9(3)
N(101)-C(111)-C(112)	106.7(2)
C(113)-C(112)-C(117)	121.9(3)
C(113)-C(112)-C(111)	130.4(3)
C(117)-C(112)-C(111)	107.7(3)
C(112)-C(113)-C(114)	116.6(3)
C(112)-C(113)-H(113)	121.7
C(114)-C(113)-H(113)	121.7

C(115)-C(114)-C(113)	121.5(3)
C(115)-C(114)-H(114)	119.3
C(113)-C(114)-H(114)	119.3
C(116)-C(115)-C(114)	121.5(3)
C(116)-C(115)-H(115)	119.2
C(114)-C(115)-H(115)	119.2
C(117)-C(116)-C(115)	116.8(3)
C(117)-C(116)-H(116)	121.6
C(115)-C(116)-H(116)	121.6
C(116)-C(117)-C(112)	121.8(3)
C(116)-C(117)-C(118)	129.6(3)
C(112)-C(117)-C(118)	108.7(2)
O(102)-C(118)-N(101)	126.5(3)
O(102)-C(118)-C(117)	127.3(3)
N(101)-C(118)-C(117)	106.1(2)
O(103)-C(121)-O(104)	123.4(3)
O(103)-C(121)-C(101)	124.8(3)
O(104)-C(121)-C(101)	111.4(2)
C(121)-O(104)-C(122)	114.6(2)
O(104)-C(122)-H(12A)	109.5
O(104)-C(122)-H(12B)	109.5
H(12A)-C(122)-H(12B)	109.5
O(104)-C(122)-H(12C)	109.5
H(12A)-C(122)-H(12C)	109.5
H(12B)-C(122)-H(12C)	109.5
C(136)-C(131)-C(132)	118.1(3)
C(136)-C(131)-C(101)	118.3(3)
C(132)-C(131)-C(101)	123.3(3)
C(133)-C(132)-C(131)	120.0(3)
C(133)-C(132)-H(132)	120.0
C(131)-C(132)-H(132)	120.0
C(134)-C(133)-C(132)	121.3(3)
C(134)-C(133)-H(133)	119.4
C(132)-C(133)-H(133)	119.4
C(133)-C(134)-C(135)	119.7(3)
C(133)-C(134)-H(134)	120.2

C(135)-C(134)-H(134)	120.2
C(134)-C(135)-C(136)	119.4(3)
C(134)-C(135)-H(135)	120.3
C(136)-C(135)-H(135)	120.3
C(135)-C(136)-C(131)	121.5(3)
C(135)-C(136)-H(136)	119.2
C(131)-C(136)-H(136)	119.2
C(142)-C(141)-C(146)	110.9(2)
C(142)-C(141)-C(101)	114.9(2)
C(146)-C(141)-C(101)	111.6(2)
C(142)-C(141)-H(141)	106.3
C(146)-C(141)-H(141)	106.3
C(101)-C(141)-H(141)	106.3
C(143)-C(142)-C(141)	122.5(3)
C(143)-C(142)-H(142)	118.8
C(141)-C(142)-H(142)	118.8
C(142)-C(143)-C(144)	124.4(3)
C(142)-C(143)-H(143)	117.8
C(144)-C(143)-H(143)	117.8
C(143)-C(144)-C(145)	111.7(3)
C(143)-C(144)-H(14A)	109.3
C(145)-C(144)-H(14A)	109.3
C(143)-C(144)-H(14B)	109.3
C(145)-C(144)-H(14B)	109.3
H(14A)-C(144)-H(14B)	107.9
C(144)-C(145)-C(146)	111.4(3)
C(144)-C(145)-H(14C)	109.3
C(146)-C(145)-H(14C)	109.3
C(144)-C(145)-H(14D)	109.3
C(146)-C(145)-H(14D)	109.3
H(14C)-C(145)-H(14D)	108.0
C(145)-C(146)-C(141)	110.2(2)
C(145)-C(146)-H(14E)	109.6
C(141)-C(146)-H(14E)	109.6
C(145)-C(146)-H(14F)	109.6
C(141)-C(146)-H(14F)	109.6

H(14E)-C(146)-H(14F) 108.1

Symmetry transformations used to generate equivalent atoms:

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for V20078. 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}
C(1)	16(1)	15(1)	13(1)	-2(1)	0(1)	-2(1)
N(1)	13(1)	18(1)	16(1)	-1(1)	0(1)	-3(1)
C(11)	19(1)	18(1)	15(1)	-2(1)	4(1)	-3(1)
O(1)	24(1)	22(1)	21(1)	-4(1)	-2(1)	-7(1)
C(12)	21(1)	21(1)	15(1)	-4(1)	2(1)	0(1)
C(13)	32(2)	20(1)	22(2)	-1(1)	0(1)	-2(1)
C(14)	41(2)	25(2)	20(2)	3(1)	-5(1)	7(1)
C(15)	30(2)	31(2)	25(2)	-5(1)	-11(1)	8(1)
C(16)	22(1)	28(2)	23(2)	-7(1)	-4(1)	2(1)
C(17)	17(1)	22(1)	18(1)	-6(1)	0(1)	2(1)
C(18)	14(1)	23(1)	15(1)	-6(1)	1(1)	1(1)
O(2)	16(1)	24(1)	22(1)	-4(1)	0(1)	-6(1)
C(21)	17(1)	17(1)	16(1)	-3(1)	0(1)	-2(1)
O(3)	19(1)	36(1)	19(1)	-9(1)	-1(1)	-5(1)
O(4)	13(1)	29(1)	18(1)	-8(1)	1(1)	-3(1)
C(22)	13(1)	31(2)	23(2)	-8(1)	2(1)	-4(1)
C(31)	12(1)	18(1)	19(1)	-4(1)	0(1)	-2(1)
C(32)	15(1)	22(1)	21(1)	-6(1)	1(1)	-2(1)
C(33)	21(1)	25(1)	27(2)	-12(1)	1(1)	-2(1)
C(34)	26(2)	18(1)	36(2)	-8(1)	0(1)	-3(1)
C(35)	28(2)	19(1)	27(2)	1(1)	-1(1)	-4(1)
C(36)	20(1)	22(1)	19(1)	-5(1)	1(1)	-2(1)
C(41)	18(1)	18(1)	13(1)	-3(1)	2(1)	-1(1)
C(42)	20(1)	18(1)	16(1)	-2(1)	1(1)	-2(1)
C(43)	18(1)	26(1)	21(1)	-1(1)	3(1)	-3(1)
C(44)	21(2)	29(2)	24(2)	-7(1)	5(1)	5(1)
C(45)	22(2)	27(2)	24(2)	-11(1)	2(1)	0(1)
C(46)	20(1)	18(1)	21(1)	-5(1)	2(1)	-2(1)
C(101)	19(1)	25(1)	15(1)	-4(1)	-1(1)	-3(1)
N(101)	17(1)	23(1)	16(1)	-4(1)	0(1)	-4(1)
C(111)	21(1)	22(1)	18(1)	-7(1)	3(1)	-5(1)

O(101)	30(1)	29(1)	23(1)	-6(1)	-4(1)	-11(1)
C(112)	21(1)	24(2)	19(1)	-8(1)	-1(1)	-2(1)
C(113)	30(2)	24(2)	24(2)	-5(1)	-3(1)	-4(1)
C(114)	38(2)	22(2)	24(2)	-3(1)	-4(1)	0(1)
C(115)	30(2)	28(2)	25(2)	-9(1)	-9(1)	5(1)
C(116)	19(1)	25(2)	27(2)	-10(1)	-3(1)	1(1)
C(117)	20(1)	21(1)	20(1)	-8(1)	1(1)	0(1)
C(118)	13(1)	23(1)	19(1)	-8(1)	2(1)	-2(1)
O(102)	18(1)	26(1)	27(1)	-4(1)	-2(1)	-5(1)
C(121)	23(1)	22(1)	17(1)	-4(1)	1(1)	-4(1)
O(103)	24(1)	35(1)	18(1)	-5(1)	-4(1)	-5(1)
O(104)	17(1)	36(1)	19(1)	-10(1)	1(1)	-6(1)
C(122)	16(1)	39(2)	31(2)	-10(1)	1(1)	-5(1)
C(131)	26(2)	22(1)	17(1)	-3(1)	1(1)	-2(1)
C(132)	28(2)	36(2)	31(2)	-15(1)	-1(1)	-1(1)
C(133)	44(2)	44(2)	46(2)	-28(2)	1(2)	-2(2)
C(134)	41(2)	34(2)	30(2)	-14(1)	9(1)	6(1)
C(135)	29(2)	24(2)	30(2)	-2(1)	10(1)	2(1)
C(136)	26(2)	21(1)	22(1)	-5(1)	6(1)	-2(1)
C(141)	20(1)	20(1)	16(1)	-5(1)	-2(1)	-2(1)
C(142)	19(1)	28(2)	18(1)	-6(1)	0(1)	-3(1)
C(143)	26(2)	31(2)	26(2)	-14(1)	3(1)	-1(1)
C(144)	37(2)	25(2)	35(2)	-10(1)	0(1)	1(1)
C(145)	28(2)	25(2)	20(2)	-2(1)	-3(1)	0(1)
C(146)	27(2)	25(2)	18(1)	-6(1)	-3(1)	4(1)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for V20078.

	x	y	z	U(eq)
H(13)	7106	-580	10974	31
H(14)	9082	-988	12438	37
H(15)	10783	632	12477	36
H(16)	10590	2761	11072	29
H(22A)	1972	3208	8321	33
H(22B)	1788	4899	7915	33
H(22C)	1854	4206	9296	33
H(32)	5878	5555	9283	23
H(33)	5635	7991	9273	28
H(34)	5702	9600	7477	31
H(35)	6068	8744	5714	30
H(36)	6408	6308	5720	24
H(41)	6513	4214	5682	19
H(42)	8973	4741	6625	22
H(43)	10852	3471	5804	26
H(44A)	10218	1103	5667	30
H(44B)	10011	2144	4404	30
H(45A)	7863	775	5088	29
H(45B)	7420	2407	4473	29
H(46A)	6000	1869	6256	23
H(46B)	7586	1438	7007	23
H(113)	2934	10492	-749	31
H(114)	1070	10995	-2295	35
H(115)	-612	9388	-2496	34
H(116)	-535	7232	-1146	28
H(12A)	7927	4817	2227	42
H(12B)	7760	6515	1900	42
H(12C)	7856	5597	867	42
H(132)	4092	7617	4106	37
H(133)	2533	8686	5435	51

H(134)	-1	8281	5700	42
H(135)	-1019	6765	4633	34
H(136)	541	5649	3325	28
H(141)	2093	4137	2781	23
H(142)	3804	4087	967	26
H(143)	4690	1781	1169	32
H(14A)	5712	934	3253	39
H(14B)	4238	236	2958	39
H(14C)	4117	1212	4790	30
H(14D)	2622	1657	3939	30
H(14E)	4997	3421	4002	28
H(14F)	3350	3677	4601	28

Table S13. Torsion angles [°] for V20078.

C(21)-C(1)-N(1)-C(11)	34.9(3)
C(31)-C(1)-N(1)-C(11)	146.7(2)
C(41)-C(1)-N(1)-C(11)	-87.2(3)
C(21)-C(1)-N(1)-C(18)	-152.7(2)
C(31)-C(1)-N(1)-C(18)	-40.9(3)
C(41)-C(1)-N(1)-C(18)	85.3(3)
C(18)-N(1)-C(11)-O(1)	-177.1(3)
C(1)-N(1)-C(11)-O(1)	-3.6(4)
C(18)-N(1)-C(11)-C(12)	2.5(3)
C(1)-N(1)-C(11)-C(12)	176.0(2)
O(1)-C(11)-C(12)-C(13)	-1.5(5)
N(1)-C(11)-C(12)-C(13)	178.9(3)
O(1)-C(11)-C(12)-C(17)	178.5(3)
N(1)-C(11)-C(12)-C(17)	-1.1(3)
C(17)-C(12)-C(13)-C(14)	-0.3(4)
C(11)-C(12)-C(13)-C(14)	179.7(3)
C(12)-C(13)-C(14)-C(15)	0.2(5)
C(13)-C(14)-C(15)-C(16)	0.3(5)
C(14)-C(15)-C(16)-C(17)	-0.7(5)
C(13)-C(12)-C(17)-C(16)	-0.1(4)
C(11)-C(12)-C(17)-C(16)	179.9(3)
C(13)-C(12)-C(17)-C(18)	179.3(3)
C(11)-C(12)-C(17)-C(18)	-0.7(3)
C(15)-C(16)-C(17)-C(12)	0.6(4)
C(15)-C(16)-C(17)-C(18)	-178.7(3)
C(11)-N(1)-C(18)-O(2)	177.0(3)
C(1)-N(1)-C(18)-O(2)	3.8(4)
C(11)-N(1)-C(18)-C(17)	-2.9(3)
C(1)-N(1)-C(18)-C(17)	-176.1(2)
C(12)-C(17)-C(18)-O(2)	-177.8(3)
C(16)-C(17)-C(18)-O(2)	1.6(5)
C(12)-C(17)-C(18)-N(1)	2.2(3)
C(16)-C(17)-C(18)-N(1)	-178.5(3)
N(1)-C(1)-C(21)-O(3)	-138.4(3)

C(31)-C(1)-C(21)-O(3)	103.8(3)
C(41)-C(1)-C(21)-O(3)	-16.2(4)
N(1)-C(1)-C(21)-O(4)	48.3(3)
C(31)-C(1)-C(21)-O(4)	-69.4(3)
C(41)-C(1)-C(21)-O(4)	170.6(2)
O(3)-C(21)-O(4)-C(22)	-2.4(4)
C(1)-C(21)-O(4)-C(22)	170.8(2)
N(1)-C(1)-C(31)-C(36)	149.3(2)
C(21)-C(1)-C(31)-C(36)	-94.1(3)
C(41)-C(1)-C(31)-C(36)	24.3(3)
N(1)-C(1)-C(31)-C(32)	-36.2(3)
C(21)-C(1)-C(31)-C(32)	80.4(3)
C(41)-C(1)-C(31)-C(32)	-161.3(2)
C(36)-C(31)-C(32)-C(33)	-1.9(4)
C(1)-C(31)-C(32)-C(33)	-176.5(2)
C(31)-C(32)-C(33)-C(34)	1.9(4)
C(32)-C(33)-C(34)-C(35)	-0.6(4)
C(33)-C(34)-C(35)-C(36)	-0.7(5)
C(34)-C(35)-C(36)-C(31)	0.7(5)
C(32)-C(31)-C(36)-C(35)	0.6(4)
C(1)-C(31)-C(36)-C(35)	175.2(3)
N(1)-C(1)-C(41)-C(42)	-64.9(3)
C(21)-C(1)-C(41)-C(42)	173.6(2)
C(31)-C(1)-C(41)-C(42)	60.3(3)
N(1)-C(1)-C(41)-C(46)	60.0(3)
C(21)-C(1)-C(41)-C(46)	-61.5(3)
C(31)-C(1)-C(41)-C(46)	-174.7(2)
C(46)-C(41)-C(42)-C(43)	22.5(4)
C(1)-C(41)-C(42)-C(43)	150.3(3)
C(41)-C(42)-C(43)-C(44)	2.0(4)
C(42)-C(43)-C(44)-C(45)	5.3(4)
C(43)-C(44)-C(45)-C(46)	-37.2(4)
C(42)-C(41)-C(46)-C(45)	-52.7(3)
C(1)-C(41)-C(46)-C(45)	-178.9(2)
C(44)-C(45)-C(46)-C(41)	62.4(3)
C(121)-C(101)-N(101)-C(111)	-46.2(3)

C(131)-C(101)-N(101)-C(111)	77.1(3)
C(141)-C(101)-N(101)-C(111)	-161.5(2)
C(121)-C(101)-N(101)-C(118)	151.2(3)
C(131)-C(101)-N(101)-C(118)	-85.6(3)
C(141)-C(101)-N(101)-C(118)	35.8(4)
C(118)-N(101)-C(111)-O(101)	172.7(3)
C(101)-N(101)-C(111)-O(101)	7.4(4)
C(118)-N(101)-C(111)-C(112)	-6.4(3)
C(101)-N(101)-C(111)-C(112)	-171.7(2)
O(101)-C(111)-C(112)-C(113)	3.1(5)
N(101)-C(111)-C(112)-C(113)	-177.9(3)
O(101)-C(111)-C(112)-C(117)	-175.7(3)
N(101)-C(111)-C(112)-C(117)	3.3(3)
C(117)-C(112)-C(113)-C(114)	0.4(4)
C(111)-C(112)-C(113)-C(114)	-178.4(3)
C(112)-C(113)-C(114)-C(115)	-0.9(5)
C(113)-C(114)-C(115)-C(116)	0.6(5)
C(114)-C(115)-C(116)-C(117)	0.2(5)
C(115)-C(116)-C(117)-C(112)	-0.7(4)
C(115)-C(116)-C(117)-C(118)	177.4(3)
C(113)-C(112)-C(117)-C(116)	0.4(4)
C(111)-C(112)-C(117)-C(116)	179.4(3)
C(113)-C(112)-C(117)-C(118)	-178.1(3)
C(111)-C(112)-C(117)-C(118)	0.9(3)
C(111)-N(101)-C(118)-O(102)	-172.1(3)
C(101)-N(101)-C(118)-O(102)	-7.9(5)
C(111)-N(101)-C(118)-C(117)	6.9(3)
C(101)-N(101)-C(118)-C(117)	171.1(2)
C(116)-C(117)-C(118)-O(102)	-4.1(5)
C(112)-C(117)-C(118)-O(102)	174.2(3)
C(116)-C(117)-C(118)-N(101)	176.9(3)
C(112)-C(117)-C(118)-N(101)	-4.7(3)
N(101)-C(101)-C(121)-O(103)	147.3(3)
C(131)-C(101)-C(121)-O(103)	29.2(4)
C(141)-C(101)-C(121)-O(103)	-93.8(3)
N(101)-C(101)-C(121)-O(104)	-39.5(3)

C(131)-C(101)-C(121)-O(104)	-157.7(2)
C(141)-C(101)-C(121)-O(104)	79.4(3)
O(103)-C(121)-O(104)-C(122)	-2.6(4)
C(101)-C(121)-O(104)-C(122)	-175.8(2)
N(101)-C(101)-C(131)-C(136)	72.4(3)
C(121)-C(101)-C(131)-C(136)	-168.1(3)
C(141)-C(101)-C(131)-C(136)	-48.5(3)
N(101)-C(101)-C(131)-C(132)	-101.4(3)
C(121)-C(101)-C(131)-C(132)	18.1(4)
C(141)-C(101)-C(131)-C(132)	137.7(3)
C(136)-C(131)-C(132)-C(133)	1.9(5)
C(101)-C(131)-C(132)-C(133)	175.7(3)
C(131)-C(132)-C(133)-C(134)	-1.4(6)
C(132)-C(133)-C(134)-C(135)	0.1(6)
C(133)-C(134)-C(135)-C(136)	0.6(5)
C(134)-C(135)-C(136)-C(131)	0.0(5)
C(132)-C(131)-C(136)-C(135)	-1.3(5)
C(101)-C(131)-C(136)-C(135)	-175.4(3)
N(101)-C(101)-C(141)-C(142)	50.6(3)
C(121)-C(101)-C(141)-C(142)	-66.6(3)
C(131)-C(101)-C(141)-C(142)	168.7(2)
N(101)-C(101)-C(141)-C(146)	178.0(2)
C(121)-C(101)-C(141)-C(146)	60.8(3)
C(131)-C(101)-C(141)-C(146)	-63.9(3)
C(146)-C(141)-C(142)-C(143)	21.9(4)
C(101)-C(141)-C(142)-C(143)	149.6(3)
C(141)-C(142)-C(143)-C(144)	-4.3(5)
C(142)-C(143)-C(144)-C(145)	14.7(4)
C(143)-C(144)-C(145)-C(146)	-42.7(4)
C(144)-C(145)-C(146)-C(141)	61.8(3)
C(142)-C(141)-C(146)-C(145)	-49.4(3)
C(101)-C(141)-C(146)-C(145)	-178.8(2)

Symmetry transformations used to generate equivalent atoms:

X-Ray Crystal Structure for Iodolactonization Product 52 (D19152)

An X-ray quality crystal of Iodolactonization product **52** (compound D19152) was grown by slow cooling of a solution in toluene (approx. 50 mg/600 μL). Low temperature (100K) X-ray data were collected with a Bruker AXS KAPPA APEX II diffractometer diffractometer running at 50 kV and 30 mA (Mo K_α = 0.71073 Å; PHOTON 100 CMOS detector with TRIUMPH graphite monochromator). All diffractometer manipulations, including data collection, integration, and scaling were carried out using the Bruker APEX3 software. An absorption correction was applied using SADABS. The space group was determined and the structure solved by intrinsic phasing using XT. Refinement was full-matrix least squares on F^2 using XL. All non-hydrogen atoms were refined using anisotropic displacement parameters. Hydrogen atoms were placed in idealized positions and the coordinates refined. The isotropic displacement parameters of all hydrogen atoms were fixed at 1.2 times the U_{eq} value of the bonded atom. Compound D19152 crystallizes in the monoclinic space group $P2_1/n$ (#14) with one molecule in the asymmetric unit.

Figure S3. X-Ray Coordinate of Iodolactonization Product 52 (D19152)

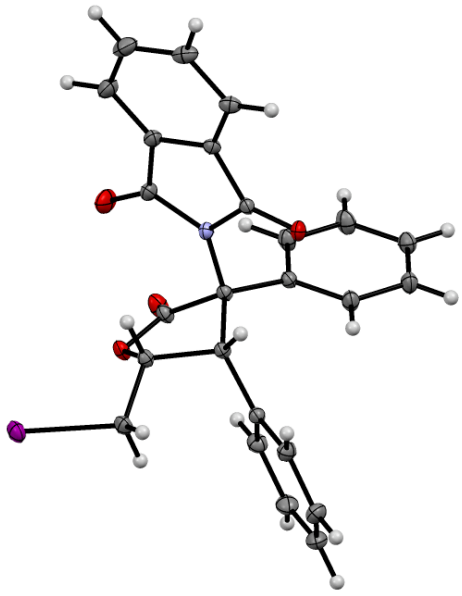


Table S14. Crystal data and structure refinement for d19152.

Identification code	d19152
Empirical formula	C25 H18 I N O4
Formula weight	523.30

Temperature	100 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 10.564(3) Å	a= 90°
	b = 11.245(3) Å	b= 99.605(14)°
	c = 18.024(4) Å	g = 90°
Volume	2111.0(9) $Å^3$	
Z	4	
Density (calculated)	1.647 g/cm^3	
Absorption coefficient	1.550 mm^{-1}	
F(000)	1040	
Crystal size	0.38 x 0.28 x 0.23 mm^3	
Theta range for data collection	2.095 to 39.457°.	
Index ranges	-18 £ h £ 18, -19 £ k £ 19, -32 £ l £ 31	
Reflections collected	116544	
Independent reflections	12393 [R(int) = 0.0317]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.0000 and 0.9003	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12393 / 0 / 280	
Goodness-of-fit on F^2	1.045	
Final R indices [I>2sigma(I)]	R1 = 0.0235, wR2 = 0.0543	
R indices (all data)	R1 = 0.0321, wR2 = 0.0572	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.582 and -1.257 $e.Å^{-3}$	

Table S15. Atomic coordinates (x 10^5), equivalent isotropic displacement parameters ($Å^2$x 10^4), and population for d19152. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)	pop
I(1)	69462(2)	42397(2)	2320(2)	183(1)	1
O(1)	91487(8)	27284(8)	29620(5)	262(2)	1
O(2)	70094(6)	57024(6)	39843(4)	153(1)	1
O(3)	66878(7)	29559(6)	18651(3)	146(1)	1
O(4)	66269(8)	14619(6)	26660(4)	197(1)	1
N(1)	77648(7)	40606(7)	34013(4)	123(1)	1
C(1)	64824(8)	35589(7)	31003(4)	116(1)	1
C(2)	58040(8)	44885(7)	25247(4)	117(1)	1
C(3)	65422(8)	42399(8)	18656(5)	126(1)	1
C(4)	66452(9)	25118(8)	25523(5)	139(1)	1
C(5)	89720(8)	36292(9)	32989(5)	159(1)	1
C(6)	99316(8)	44973(9)	36764(5)	153(1)	1
C(7)	112555(9)	45394(11)	37153(6)	212(2)	1
C(8)	118931(9)	55061(11)	40936(6)	232(2)	1
C(9)	112402(9)	63773(10)	44307(6)	204(2)	1
C(10)	99104(9)	63219(9)	43919(5)	164(1)	1
C(11)	92837(8)	53747(8)	40017(4)	128(1)	1
C(12)	78907(8)	51282(8)	38246(4)	119(1)	1
C(13)	58413(8)	31854(8)	37607(4)	125(1)	1
C(14)	62680(10)	21628(9)	41678(5)	174(2)	1
C(15)	57814(10)	18590(9)	48140(5)	204(2)	1
C(16)	48741(9)	25774(10)	50691(5)	188(2)	1
C(17)	44428(10)	35903(10)	46649(5)	199(2)	1
C(18)	49211(9)	38934(9)	40158(5)	176(2)	1
C(19)	43592(8)	43835(8)	22863(5)	129(1)	1
C(20)	36645(9)	54402(9)	21319(5)	165(1)	1
C(21)	23455(9)	54181(10)	18704(6)	206(2)	1
C(22)	17004(9)	43390(10)	17649(6)	215(2)	1
C(23)	23815(10)	32842(10)	19149(6)	207(2)	1
C(24)	37016(9)	33017(9)	21724(5)	169(1)	1
C(25)	58542(9)	46312(9)	11081(5)	164(1)	1

Table 16. Bond lengths [Å] and angles [°] for d19152.

I(1)-C(25)	2.1507(10)
O(1)-C(5)	1.2114(12)
O(2)-C(12)	1.2066(10)
O(3)-C(3)	1.4520(11)
O(3)-C(4)	1.3433(11)
O(4)-C(4)	1.1989(11)
N(1)-C(1)	1.4841(12)
N(1)-C(5)	1.4051(12)
N(1)-C(12)	1.4167(11)
C(1)-C(2)	1.5603(12)
C(1)-C(4)	1.5646(12)
C(1)-C(13)	1.5234(12)
C(2)-H(2)	1.0000
C(2)-C(3)	1.5512(12)
C(2)-C(19)	1.5196(13)
C(3)-H(3)	1.0000
C(3)-C(25)	1.5015(12)
C(5)-C(6)	1.4878(14)
C(6)-C(7)	1.3894(14)
C(6)-C(11)	1.3854(13)
C(7)-H(7)	0.9500
C(7)-C(8)	1.3953(17)
C(8)-H(8)	0.9500
C(8)-C(9)	1.3944(17)
C(9)-H(9)	0.9500
C(9)-C(10)	1.3962(14)
C(10)-H(10)	0.9500
C(10)-C(11)	1.3828(13)
C(11)-C(12)	1.4790(12)
C(13)-C(14)	1.3977(13)
C(13)-C(18)	1.3926(13)
C(14)-H(14)	0.9500
C(14)-C(15)	1.3918(13)
C(15)-H(15)	0.9500

C(15)-C(16)	1.3891(14)
C(16)-H(16)	0.9500
C(16)-C(17)	1.3874(15)
C(17)-H(17)	0.9500
C(17)-C(18)	1.3919(13)
C(18)-H(18)	0.9500
C(19)-C(20)	1.3999(13)
C(19)-C(24)	1.3990(13)
C(20)-H(20)	0.9500
C(20)-C(21)	1.3945(14)
C(21)-H(21)	0.9500
C(21)-C(22)	1.3892(16)
C(22)-H(22)	0.9500
C(22)-C(23)	1.3902(16)
C(23)-H(23)	0.9500
C(23)-C(24)	1.3944(14)
C(24)-H(24)	0.9500
C(25)-H(25A)	0.9900
C(25)-H(25B)	0.9900

C(4)-O(3)-C(3)	110.44(6)
C(5)-N(1)-C(1)	127.87(7)
C(5)-N(1)-C(12)	110.96(7)
C(12)-N(1)-C(1)	121.12(7)
N(1)-C(1)-C(2)	106.16(7)
N(1)-C(1)-C(4)	109.09(7)
N(1)-C(1)-C(13)	108.47(7)
C(2)-C(1)-C(4)	99.85(6)
C(13)-C(1)-C(2)	119.31(7)
C(13)-C(1)-C(4)	113.31(7)
C(1)-C(2)-H(2)	109.2
C(3)-C(2)-C(1)	98.90(6)
C(3)-C(2)-H(2)	109.2
C(19)-C(2)-C(1)	117.65(7)
C(19)-C(2)-H(2)	109.2
C(19)-C(2)-C(3)	112.27(7)

O(3)-C(3)-C(2)	104.27(6)
O(3)-C(3)-H(3)	109.6
O(3)-C(3)-C(25)	109.03(7)
C(2)-C(3)-H(3)	109.6
C(25)-C(3)-C(2)	114.49(7)
C(25)-C(3)-H(3)	109.6
O(3)-C(4)-C(1)	109.05(7)
O(4)-C(4)-O(3)	121.84(8)
O(4)-C(4)-C(1)	128.80(8)
O(1)-C(5)-N(1)	125.01(9)
O(1)-C(5)-C(6)	128.89(9)
N(1)-C(5)-C(6)	106.10(8)
C(7)-C(6)-C(5)	130.44(9)
C(11)-C(6)-C(5)	108.29(8)
C(11)-C(6)-C(7)	121.24(9)
C(6)-C(7)-H(7)	121.6
C(6)-C(7)-C(8)	116.80(10)
C(8)-C(7)-H(7)	121.6
C(7)-C(8)-H(8)	119.1
C(9)-C(8)-C(7)	121.79(9)
C(9)-C(8)-H(8)	119.1
C(8)-C(9)-H(9)	119.6
C(8)-C(9)-C(10)	120.90(10)
C(10)-C(9)-H(9)	119.6
C(9)-C(10)-H(10)	121.6
C(11)-C(10)-C(9)	116.88(9)
C(11)-C(10)-H(10)	121.6
C(6)-C(11)-C(12)	108.61(8)
C(10)-C(11)-C(6)	122.37(8)
C(10)-C(11)-C(12)	128.96(8)
O(2)-C(12)-N(1)	125.11(8)
O(2)-C(12)-C(11)	128.88(8)
N(1)-C(12)-C(11)	106.00(7)
C(14)-C(13)-C(1)	119.38(7)
C(18)-C(13)-C(1)	121.75(8)
C(18)-C(13)-C(14)	118.60(8)

C(13)-C(14)-H(14)	119.7
C(15)-C(14)-C(13)	120.63(9)
C(15)-C(14)-H(14)	119.7
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-C(14)	120.38(9)
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-H(16)	120.4
C(17)-C(16)-C(15)	119.20(8)
C(17)-C(16)-H(16)	120.4
C(16)-C(17)-H(17)	119.7
C(16)-C(17)-C(18)	120.60(9)
C(18)-C(17)-H(17)	119.7
C(13)-C(18)-H(18)	119.7
C(17)-C(18)-C(13)	120.58(9)
C(17)-C(18)-H(18)	119.7
C(20)-C(19)-C(2)	117.30(8)
C(24)-C(19)-C(2)	124.04(8)
C(24)-C(19)-C(20)	118.55(8)
C(19)-C(20)-H(20)	119.6
C(21)-C(20)-C(19)	120.87(9)
C(21)-C(20)-H(20)	119.6
C(20)-C(21)-H(21)	120.0
C(22)-C(21)-C(20)	120.09(10)
C(22)-C(21)-H(21)	120.0
C(21)-C(22)-H(22)	120.2
C(21)-C(22)-C(23)	119.51(9)
C(23)-C(22)-H(22)	120.2
C(22)-C(23)-H(23)	119.7
C(22)-C(23)-C(24)	120.60(10)
C(24)-C(23)-H(23)	119.7
C(19)-C(24)-H(24)	119.8
C(23)-C(24)-C(19)	120.37(9)
C(23)-C(24)-H(24)	119.8
I(1)-C(25)-H(25A)	109.3
I(1)-C(25)-H(25B)	109.3
C(3)-C(25)-I(1)	111.72(6)

C(3)-C(25)-H(25A)	109.3
C(3)-C(25)-H(25B)	109.3
H(25A)-C(25)-H(25B)	107.9

Symmetry transformations used to generate equivalent atoms:

Table S17. Anisotropic displacement parameters ($Å^2 x\ 10^4$) for d19152. 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}
I(1)	216(1)	219(1)	125(1)	11(1)	63(1)	-14(1)
O(1)	219(3)	257(4)	304(4)	-124(3)	27(3)	92(3)
O(2)	148(2)	167(3)	153(3)	-29(2)	49(2)	28(2)
O(3)	213(3)	127(3)	102(2)	-8(2)	39(2)	22(2)
O(4)	326(4)	114(3)	154(3)	-5(2)	45(2)	30(2)
N(1)	127(3)	132(3)	114(2)	-17(2)	27(2)	25(2)
C(1)	140(3)	111(3)	99(3)	-3(2)	22(2)	14(2)
C(2)	138(3)	108(3)	106(3)	2(2)	22(2)	11(2)
C(3)	149(3)	121(3)	109(3)	5(2)	26(2)	11(2)
C(4)	186(3)	125(3)	107(3)	-12(2)	24(2)	21(3)
C(5)	149(3)	182(4)	144(3)	-12(3)	21(2)	57(3)
C(6)	133(3)	189(4)	135(3)	17(3)	19(2)	40(3)
C(7)	142(3)	276(5)	218(4)	26(3)	34(3)	56(3)
C(8)	128(3)	295(5)	264(4)	75(4)	7(3)	13(3)
C(9)	163(4)	218(4)	212(4)	57(3)	-27(3)	-22(3)
C(10)	169(3)	160(4)	150(3)	22(3)	-9(3)	1(3)
C(11)	127(3)	147(3)	108(3)	24(2)	11(2)	19(2)
C(12)	136(3)	129(3)	95(3)	0(2)	27(2)	17(2)
C(13)	141(3)	133(3)	102(3)	0(2)	23(2)	4(2)
C(14)	223(4)	165(4)	143(3)	31(3)	61(3)	43(3)
C(15)	273(4)	192(4)	161(3)	52(3)	78(3)	25(3)
C(16)	189(4)	243(4)	143(3)	24(3)	57(3)	-16(3)
C(17)	190(4)	271(5)	151(3)	21(3)	71(3)	53(3)
C(18)	198(4)	199(4)	140(3)	22(3)	59(3)	57(3)
C(19)	141(3)	135(3)	110(3)	-5(2)	22(2)	7(2)
C(20)	156(3)	158(3)	179(3)	-9(3)	25(3)	23(3)
C(21)	160(4)	240(4)	212(4)	-13(3)	16(3)	53(3)
C(22)	145(3)	304(5)	191(4)	-46(3)	11(3)	-5(3)
C(23)	182(4)	236(4)	198(4)	-39(3)	19(3)	-46(3)
C(24)	178(3)	161(4)	167(3)	-14(3)	23(3)	-18(3)
C(25)	182(3)	197(4)	115(3)	26(3)	33(2)	25(3)

Table S18. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{-3}) for d19152.

	x	y	z	U(eq)
H(2)	6017	5308	2723	14
H(3)	7407	4624	1972	15
H(7)	11705	3939	3495	25
H(8)	12796	5573	4122	28
H(9)	11707	7017	4690	25
H(10)	9457	6908	4623	20
H(14)	6896	1670	4002	21
H(15)	6071	1156	5082	24
H(16)	4553	2378	5515	23
H(17)	3815	4081	4833	24
H(18)	4617	4589	3744	21
H(20)	4097	6182	2206	20
H(21)	1888	6142	1764	25
H(22)	801	4322	1592	26
H(23)	1944	2545	1841	25
H(24)	4157	2575	2271	20
H(25A)	5693	5498	1118	20
H(25B)	5013	4224	997	20

Table S19. Torsion angles [°] for d19152.

O(1)-C(5)-C(6)-C(7)	3.25(18)
O(1)-C(5)-C(6)-C(11)	-178.70(10)
O(3)-C(3)-C(25)-I(1)	-63.31(8)
N(1)-C(1)-C(2)-C(3)	75.39(7)
N(1)-C(1)-C(2)-C(19)	-163.61(7)
N(1)-C(1)-C(4)-O(3)	-84.86(8)
N(1)-C(1)-C(4)-O(4)	101.48(11)
N(1)-C(1)-C(13)-C(14)	-73.89(10)
N(1)-C(1)-C(13)-C(18)	100.01(9)
N(1)-C(5)-C(6)-C(7)	-176.34(10)
N(1)-C(5)-C(6)-C(11)	1.71(10)
C(1)-N(1)-C(5)-O(1)	-3.07(15)
C(1)-N(1)-C(5)-C(6)	176.54(8)
C(1)-N(1)-C(12)-O(2)	1.01(13)
C(1)-N(1)-C(12)-C(11)	-177.87(7)
C(1)-C(2)-C(3)-O(3)	39.31(8)
C(1)-C(2)-C(3)-C(25)	158.36(7)
C(1)-C(2)-C(19)-C(20)	146.36(8)
C(1)-C(2)-C(19)-C(24)	-37.39(11)
C(1)-C(13)-C(14)-C(15)	174.16(9)
C(1)-C(13)-C(18)-C(17)	-173.61(9)
C(2)-C(1)-C(4)-O(3)	26.18(9)
C(2)-C(1)-C(4)-O(4)	-147.47(10)
C(2)-C(1)-C(13)-C(14)	164.51(8)
C(2)-C(1)-C(13)-C(18)	-21.60(12)
C(2)-C(3)-C(25)-I(1)	-179.65(6)
C(2)-C(19)-C(20)-C(21)	176.48(8)
C(2)-C(19)-C(24)-C(23)	-176.58(8)
C(3)-O(3)-C(4)-O(4)	172.99(9)
C(3)-O(3)-C(4)-C(1)	-1.18(9)
C(3)-C(2)-C(19)-C(20)	-99.86(9)
C(3)-C(2)-C(19)-C(24)	76.39(10)
C(4)-O(3)-C(3)-C(2)	-24.90(9)
C(4)-O(3)-C(3)-C(25)	-147.60(7)

C(4)-C(1)-C(2)-C(3)	-37.94(7)
C(4)-C(1)-C(2)-C(19)	83.06(8)
C(4)-C(1)-C(13)-C(14)	47.40(11)
C(4)-C(1)-C(13)-C(18)	-138.70(9)
C(5)-N(1)-C(1)-C(2)	-113.25(9)
C(5)-N(1)-C(1)-C(4)	-6.46(11)
C(5)-N(1)-C(1)-C(13)	117.40(9)
C(5)-N(1)-C(12)-O(2)	178.57(8)
C(5)-N(1)-C(12)-C(11)	-0.31(9)
C(5)-C(6)-C(7)-C(8)	177.59(10)
C(5)-C(6)-C(11)-C(10)	-179.47(8)
C(5)-C(6)-C(11)-C(12)	-1.92(10)
C(6)-C(7)-C(8)-C(9)	1.29(16)
C(6)-C(11)-C(12)-O(2)	-177.41(9)
C(6)-C(11)-C(12)-N(1)	1.42(9)
C(7)-C(6)-C(11)-C(10)	-1.20(14)
C(7)-C(6)-C(11)-C(12)	176.35(8)
C(7)-C(8)-C(9)-C(10)	-0.95(16)
C(8)-C(9)-C(10)-C(11)	-0.47(14)
C(9)-C(10)-C(11)-C(6)	1.54(13)
C(9)-C(10)-C(11)-C(12)	-175.48(8)
C(10)-C(11)-C(12)-O(2)	-0.07(15)
C(10)-C(11)-C(12)-N(1)	178.75(8)
C(11)-C(6)-C(7)-C(8)	-0.24(14)
C(12)-N(1)-C(1)-C(2)	63.87(9)
C(12)-N(1)-C(1)-C(4)	170.66(7)
C(12)-N(1)-C(1)-C(13)	-65.49(9)
C(12)-N(1)-C(5)-O(1)	179.57(10)
C(12)-N(1)-C(5)-C(6)	-0.82(9)
C(13)-C(1)-C(2)-C(3)	-161.86(7)
C(13)-C(1)-C(2)-C(19)	-40.86(10)
C(13)-C(1)-C(4)-O(3)	154.19(7)
C(13)-C(1)-C(4)-O(4)	-19.46(13)
C(13)-C(14)-C(15)-C(16)	-0.79(16)
C(14)-C(13)-C(18)-C(17)	0.33(14)
C(14)-C(15)-C(16)-C(17)	1.09(16)

C(15)-C(16)-C(17)-C(18)	-0.70(16)
C(16)-C(17)-C(18)-C(13)	-0.01(16)
C(18)-C(13)-C(14)-C(15)	0.07(14)
C(19)-C(2)-C(3)-O(3)	-85.56(8)
C(19)-C(2)-C(3)-C(25)	33.49(10)
C(19)-C(20)-C(21)-C(22)	0.48(15)
C(20)-C(19)-C(24)-C(23)	-0.38(13)
C(20)-C(21)-C(22)-C(23)	-0.61(16)
C(21)-C(22)-C(23)-C(24)	0.25(16)
C(22)-C(23)-C(24)-C(19)	0.25(15)
C(24)-C(19)-C(20)-C(21)	0.02(13)

Symmetry transformations used to generate equivalent atoms:

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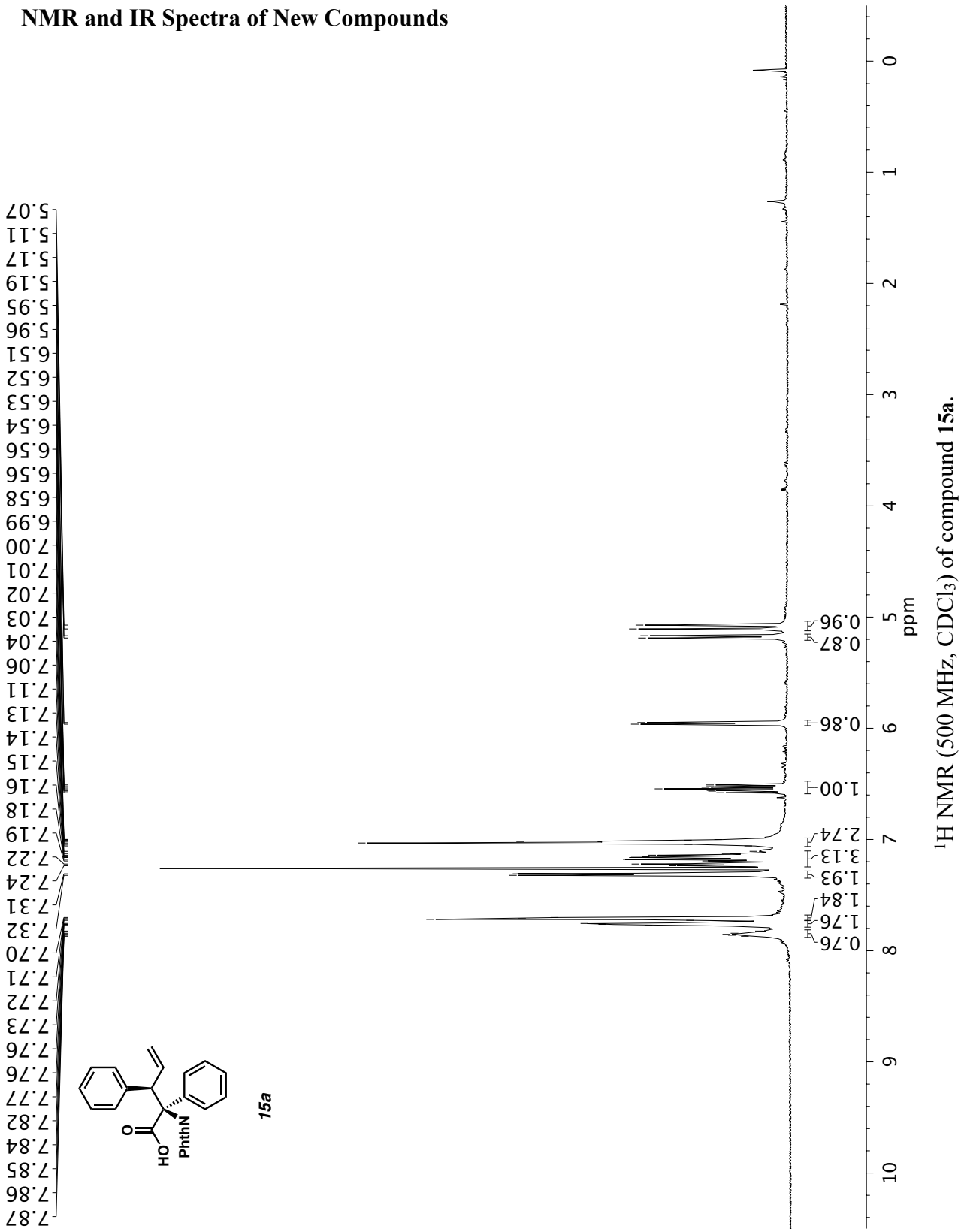
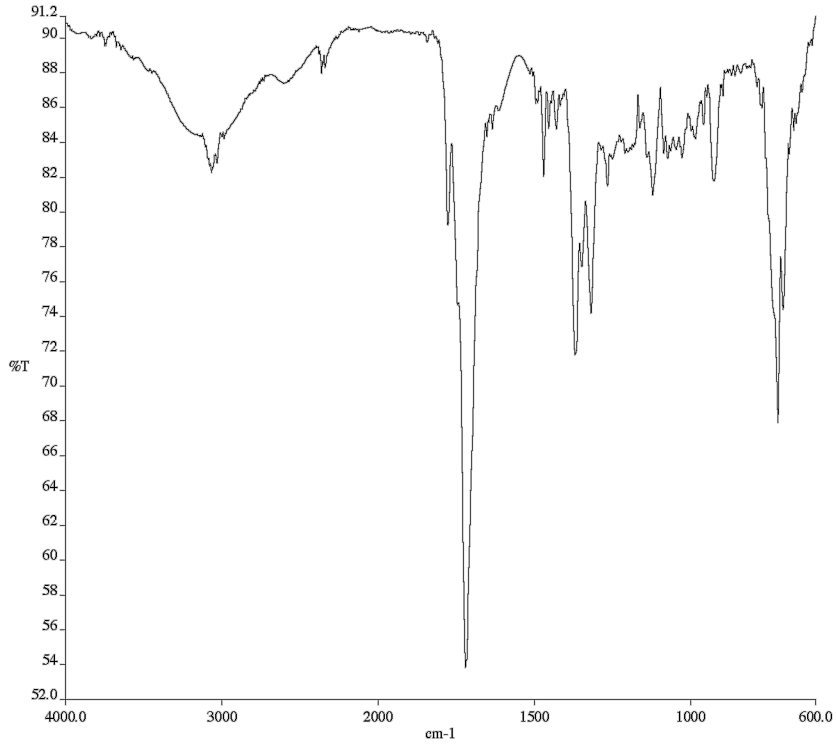
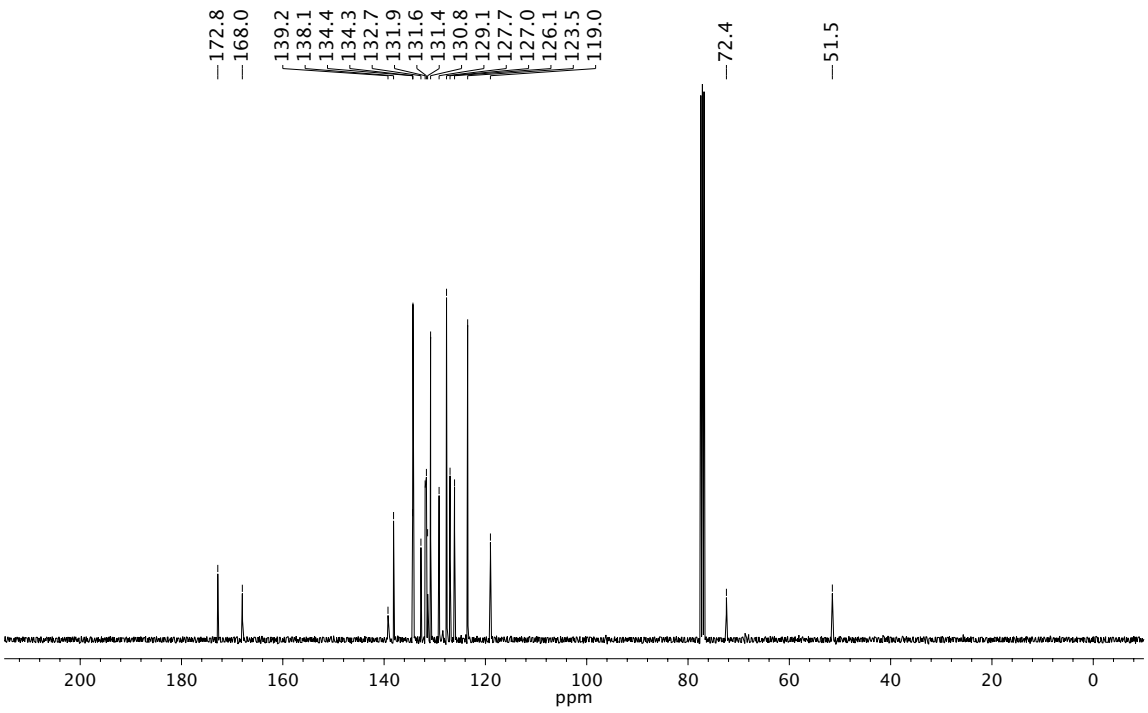
NMR and IR Spectra of New Compounds



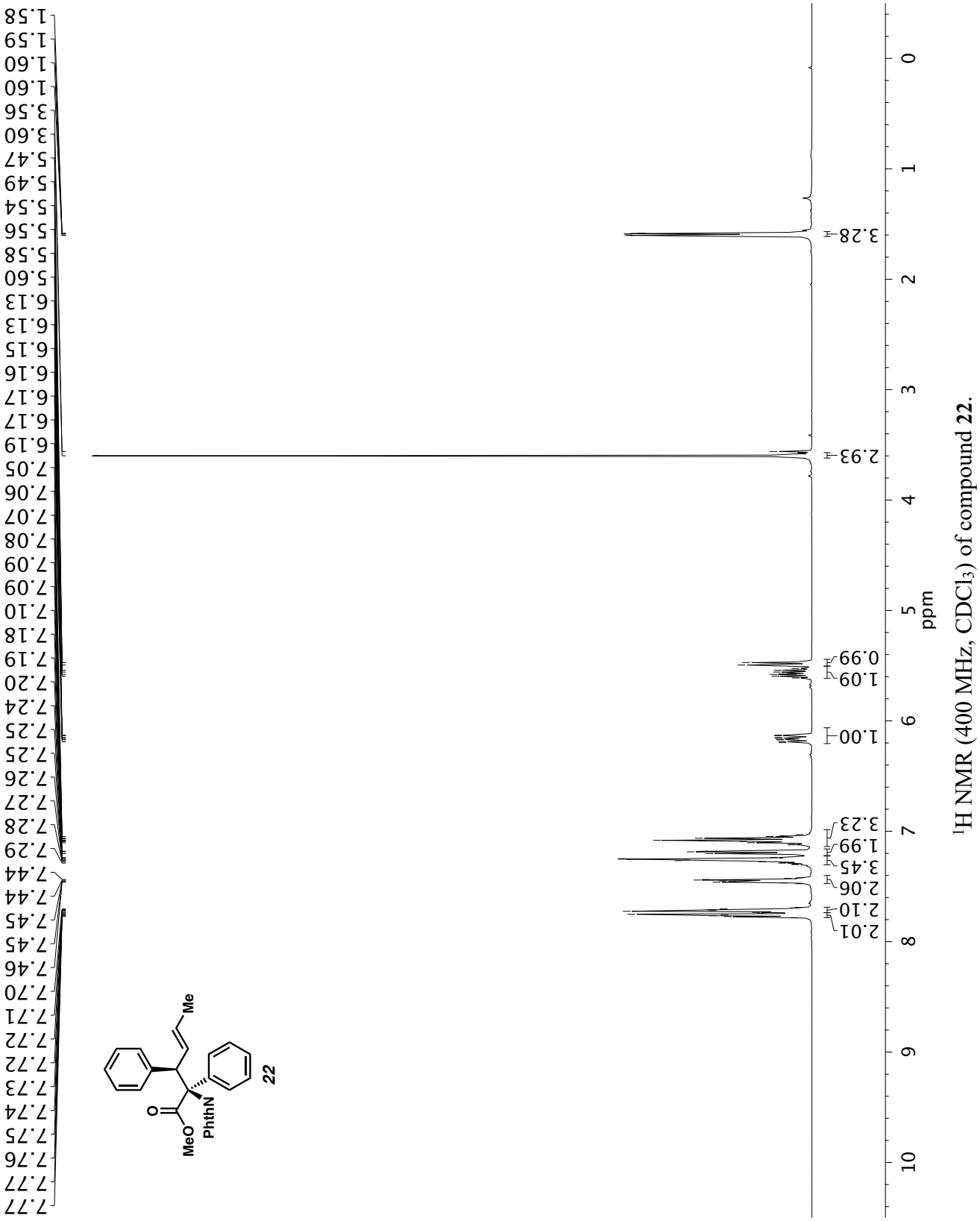
^{1}H NMR (500 MHz, $CDCl_3$) of compound **15a**.



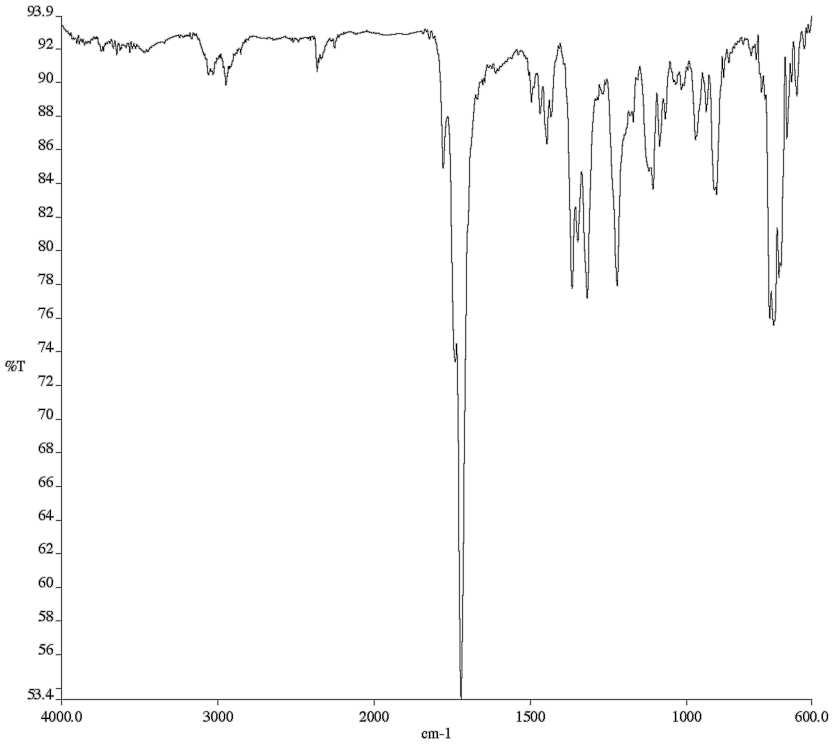
Infrared spectrum (Thin Film, NaCl) of compound **15a**.



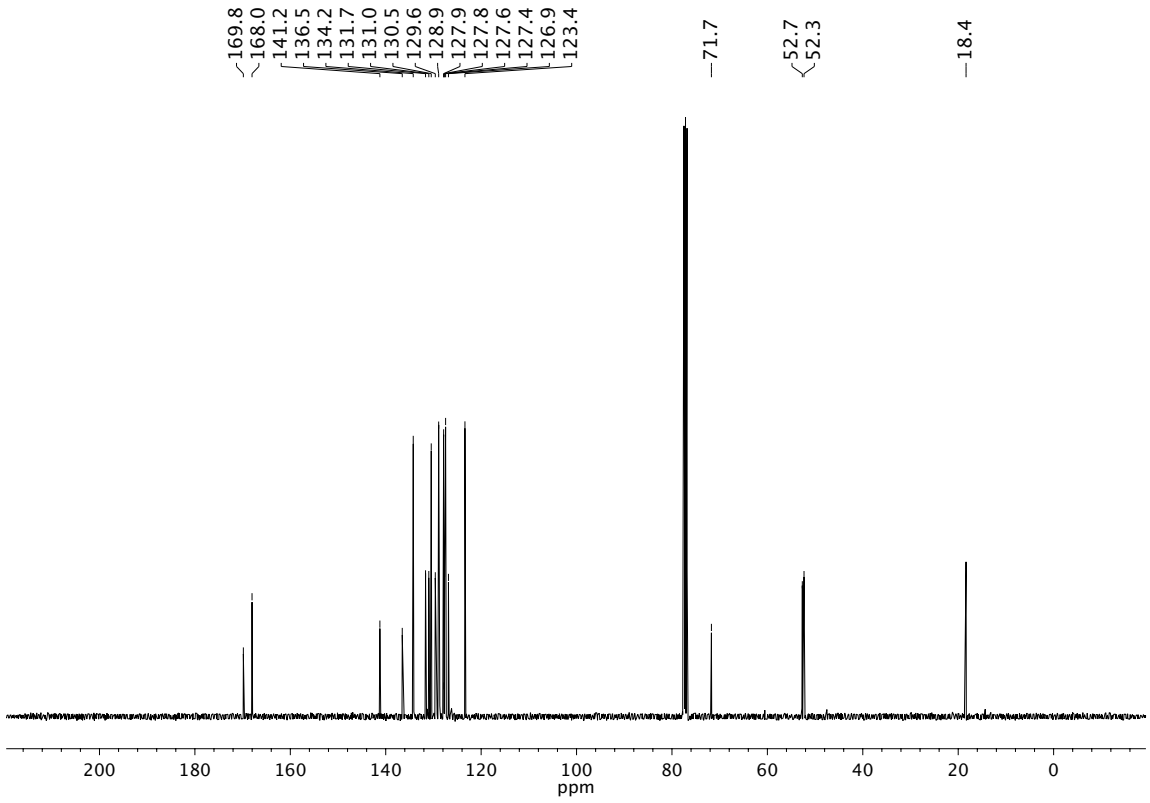
^{13}C NMR (100 MHz, $CDCl_3$) of compound **15a**.



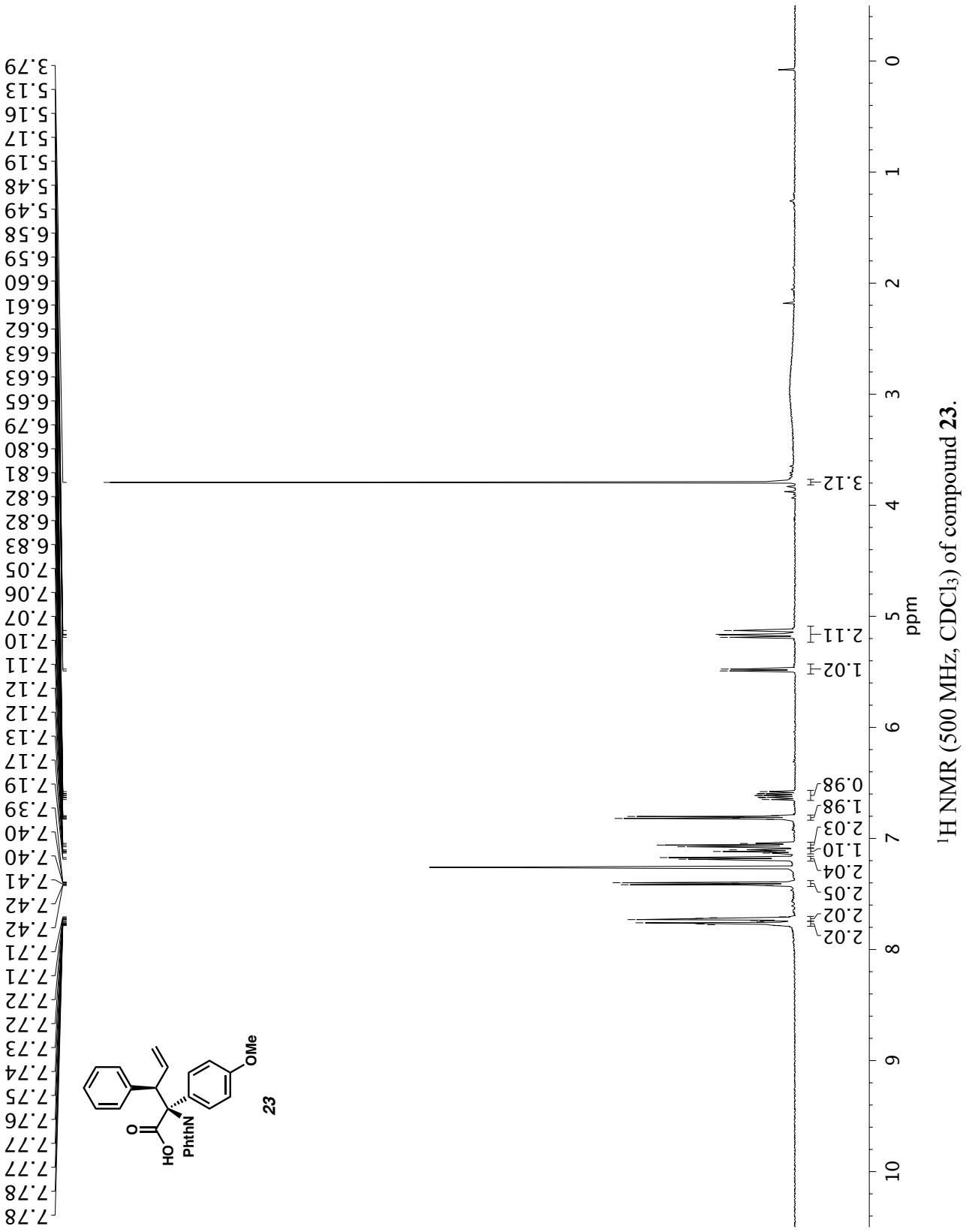
^{1}H NMR (400 MHz, $CDCl_3$) of compound **22**.



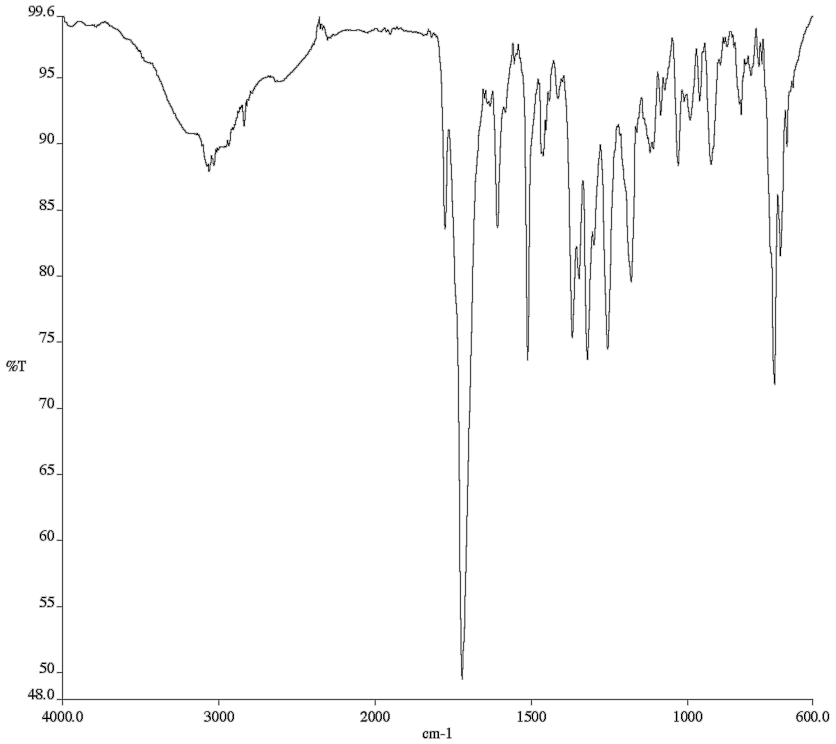
Infrared spectrum (Thin Film, NaCl) of compound **22**.



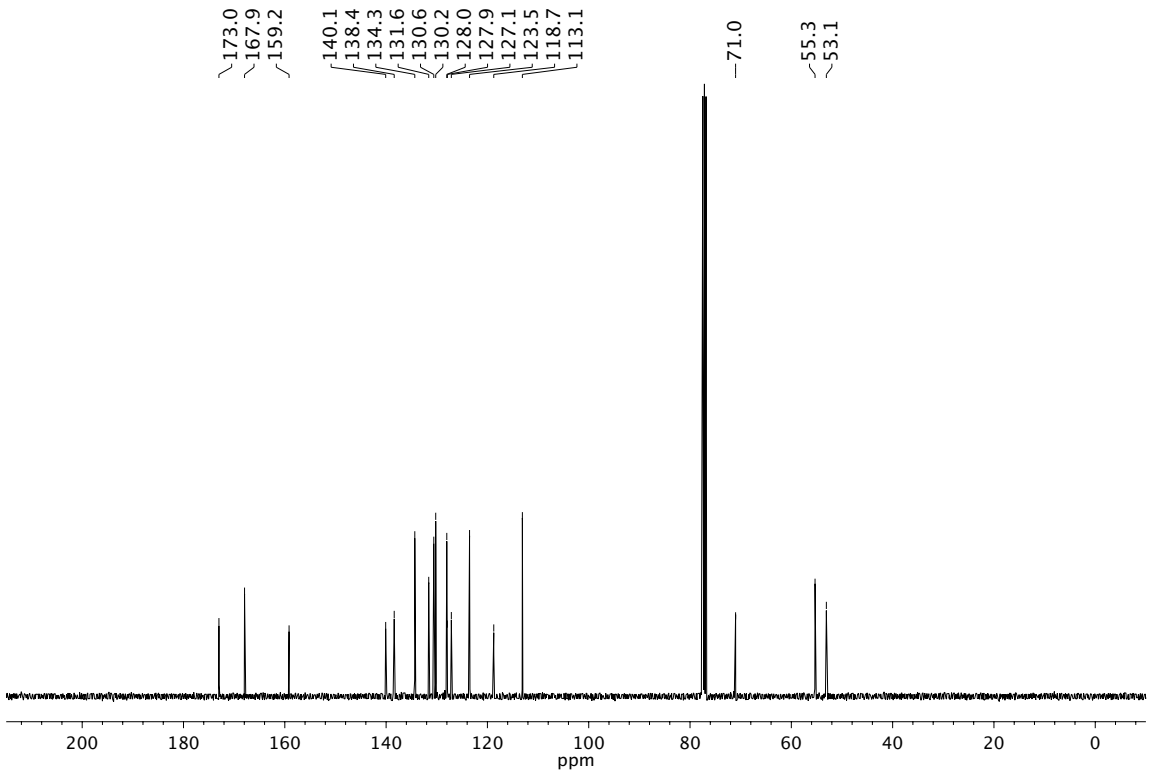
^{13}C NMR (100 MHz, $CDCl_3$) of compound **22**.



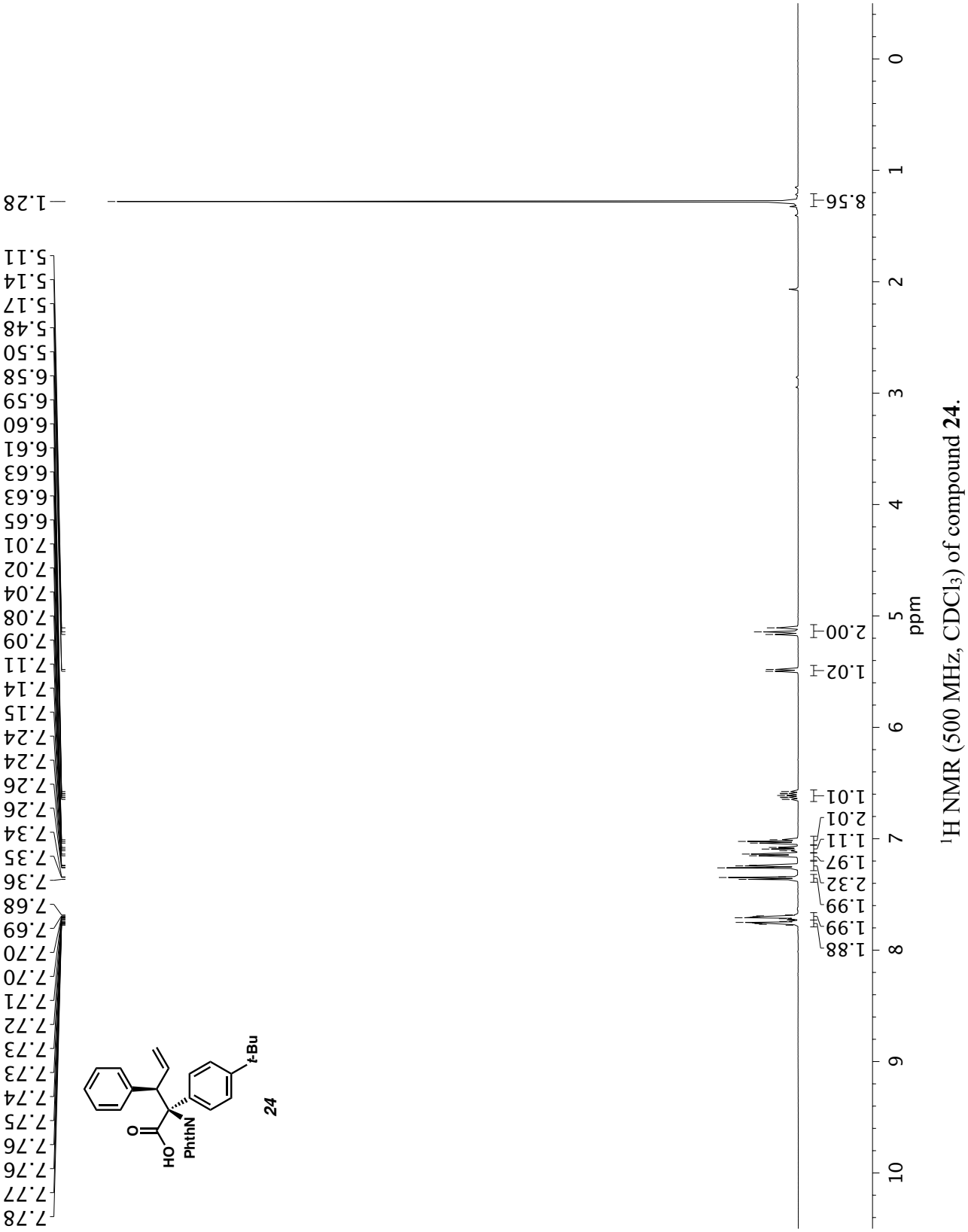
^{1}H NMR (500 MHz, $CDCl_3$) of compound **23**.



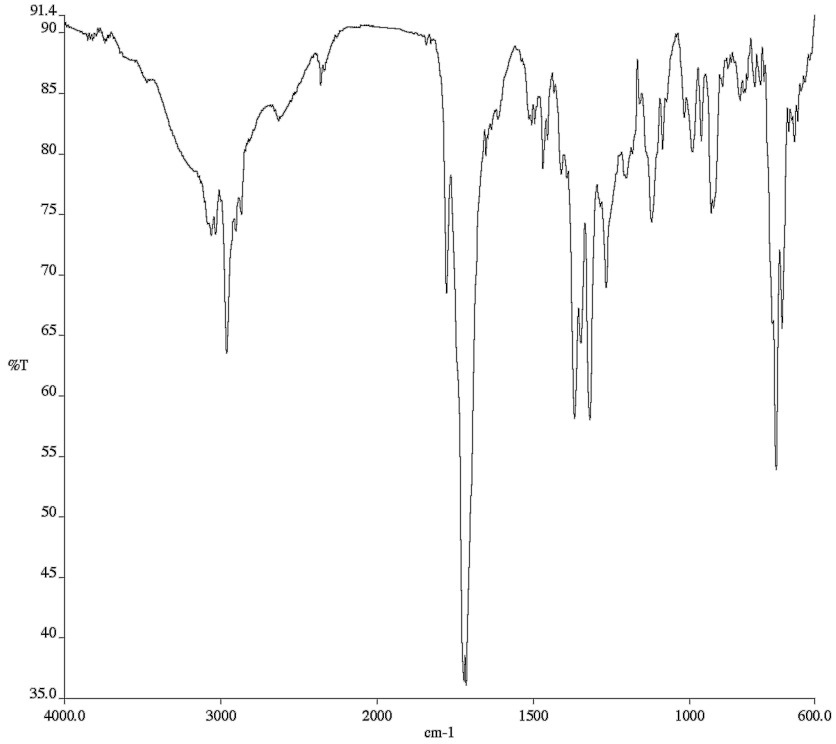
Infrared spectrum (Thin Film, NaCl) of compound **23**.



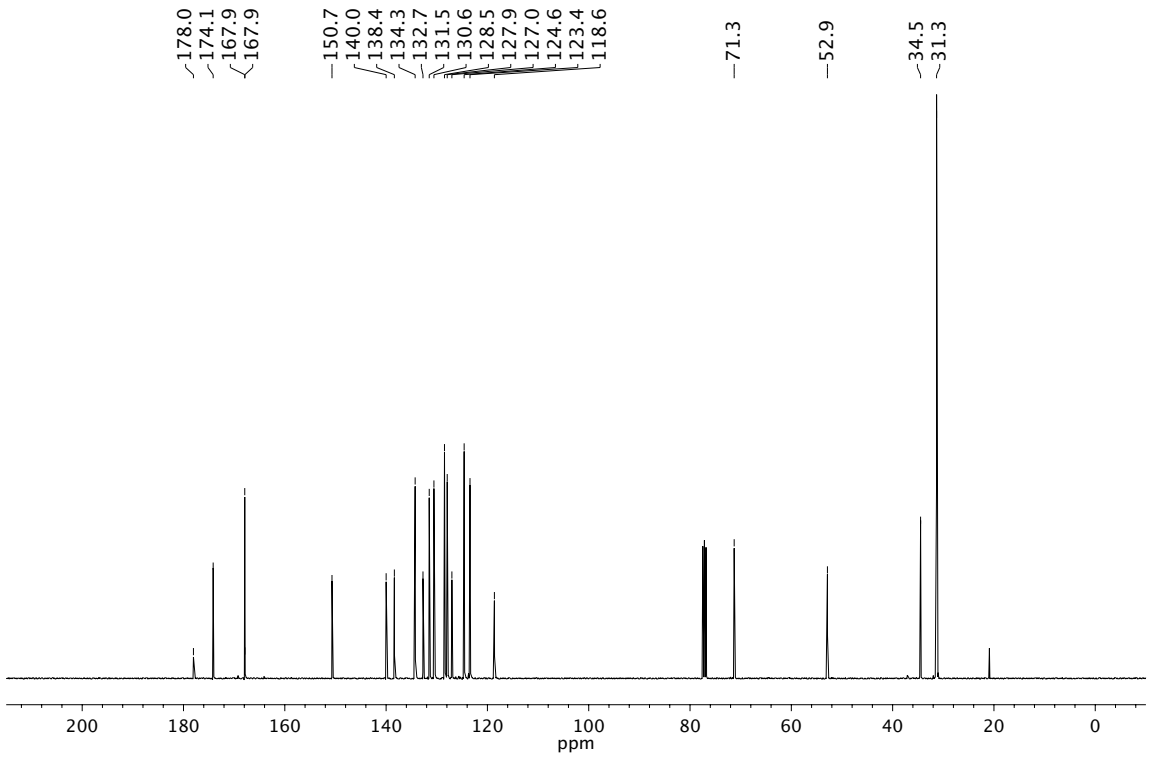
^{13}C NMR (100 MHz, $CDCl_3$) of compound **23**.



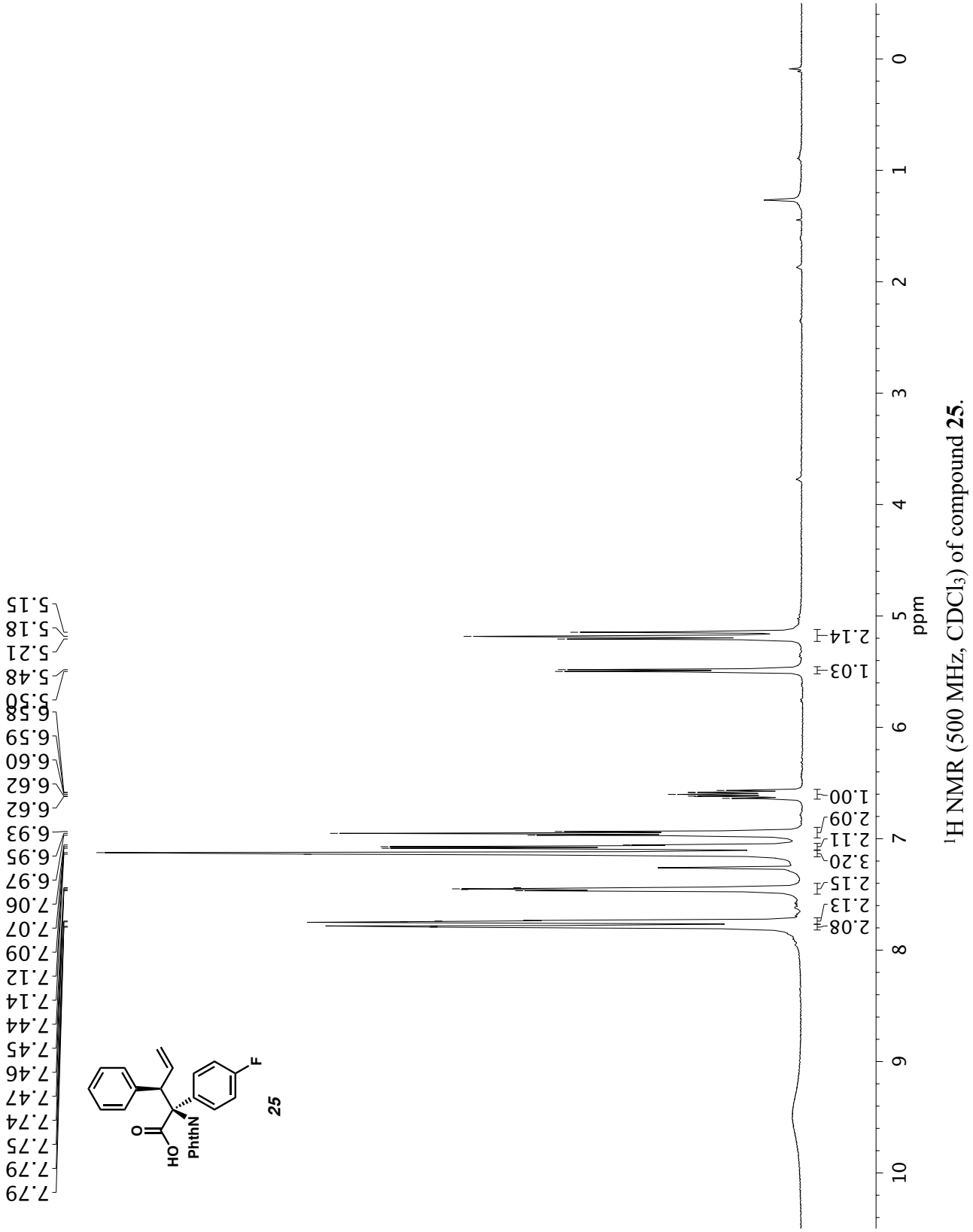
^{1}H NMR (500 MHz, $CDCl_3$) of compound **24**.



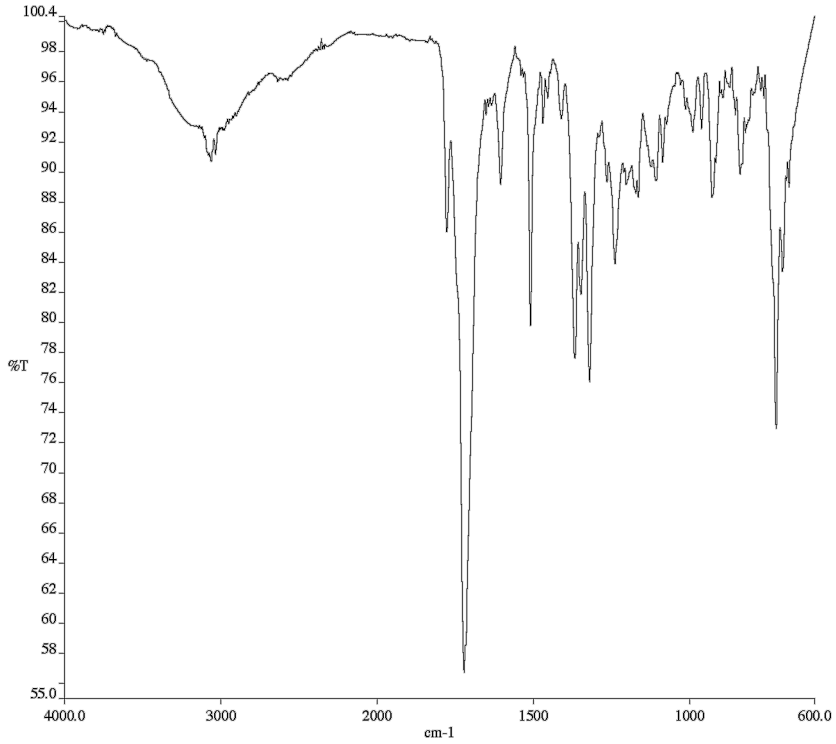
Infrared spectrum (Thin Film, NaCl) of compound **24**.



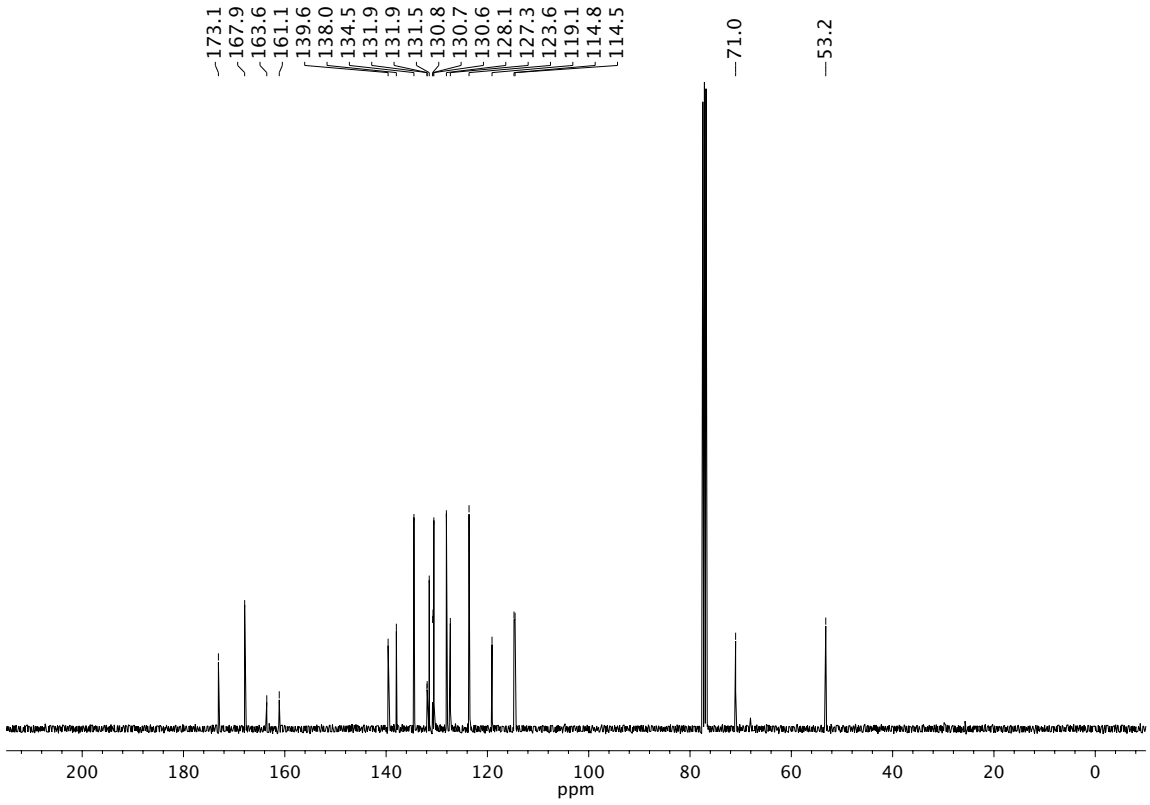
^{13}C NMR (100 MHz, $CDCl_3$) of compound **24**.



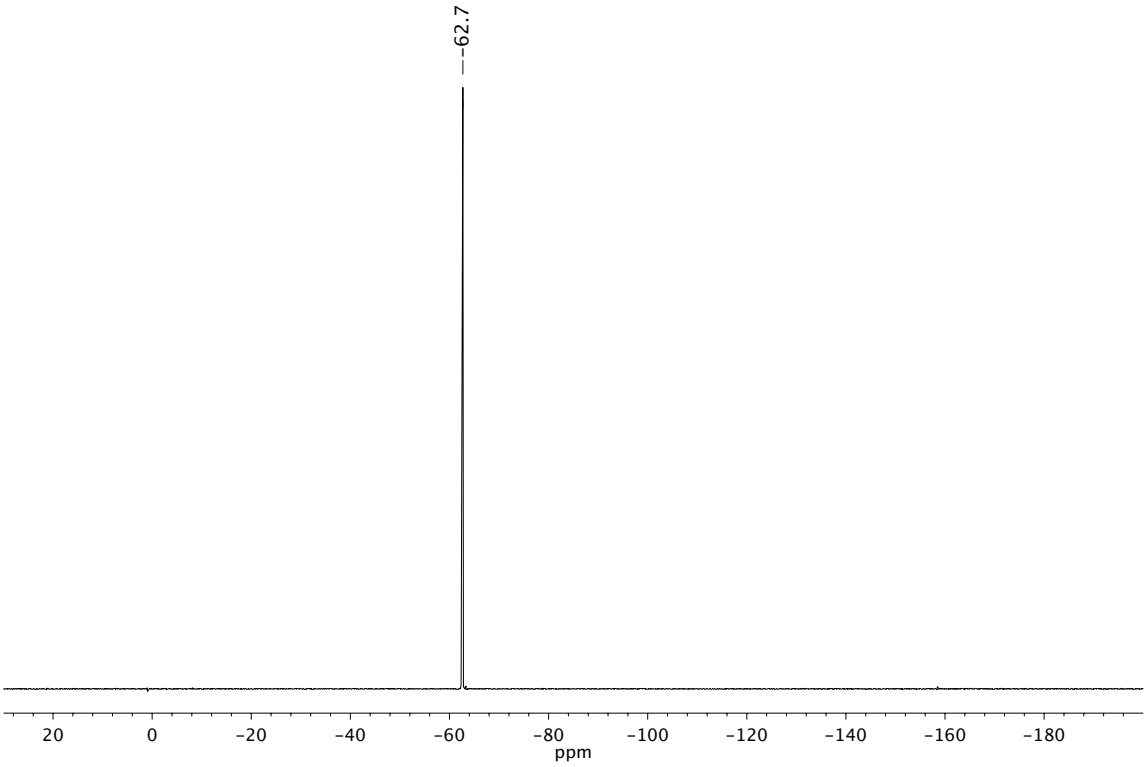
^{1}H NMR (500 MHz, $CDCl_3$) of compound **25**.



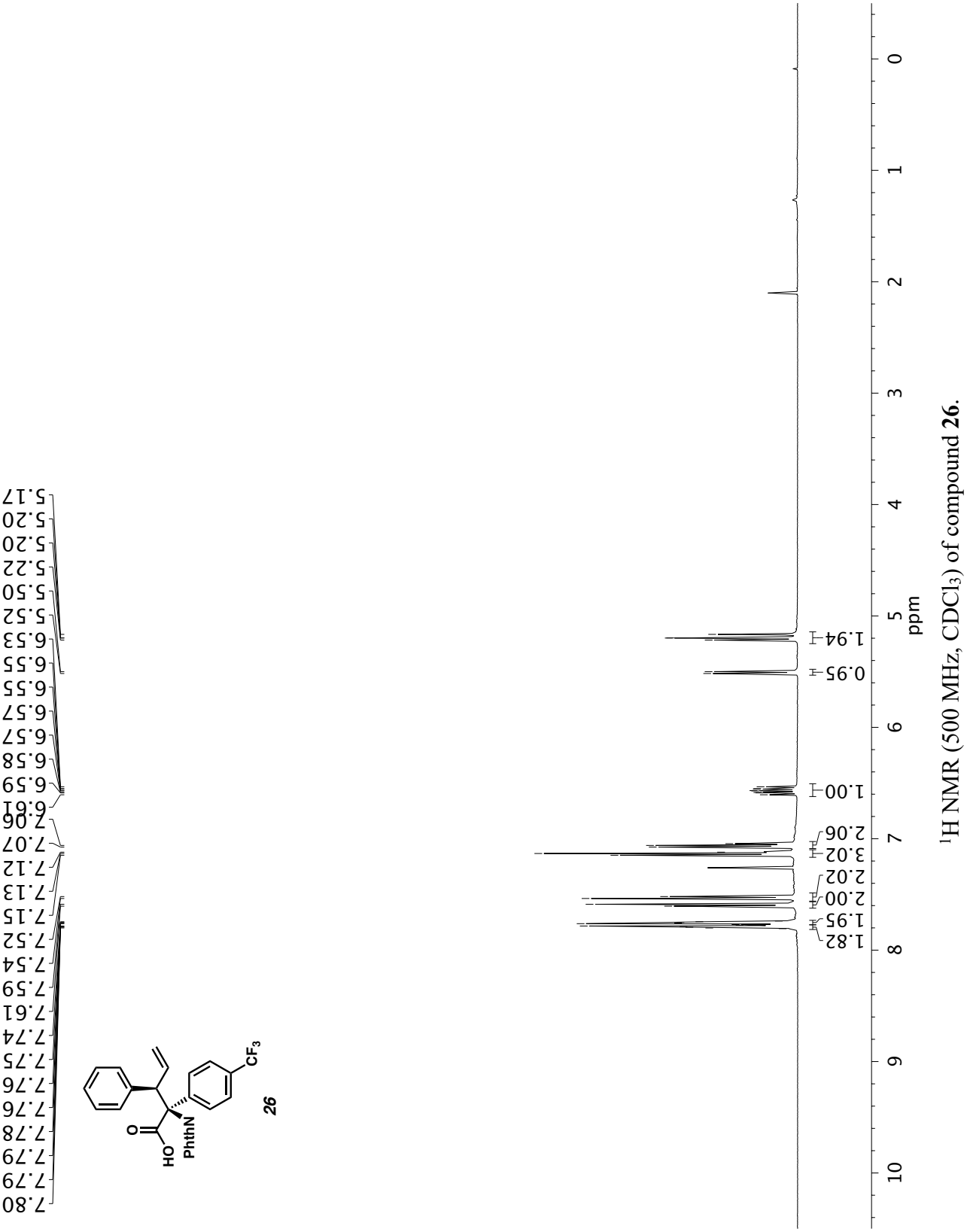
Infrared spectrum (Thin Film, NaCl) of compound **25**.



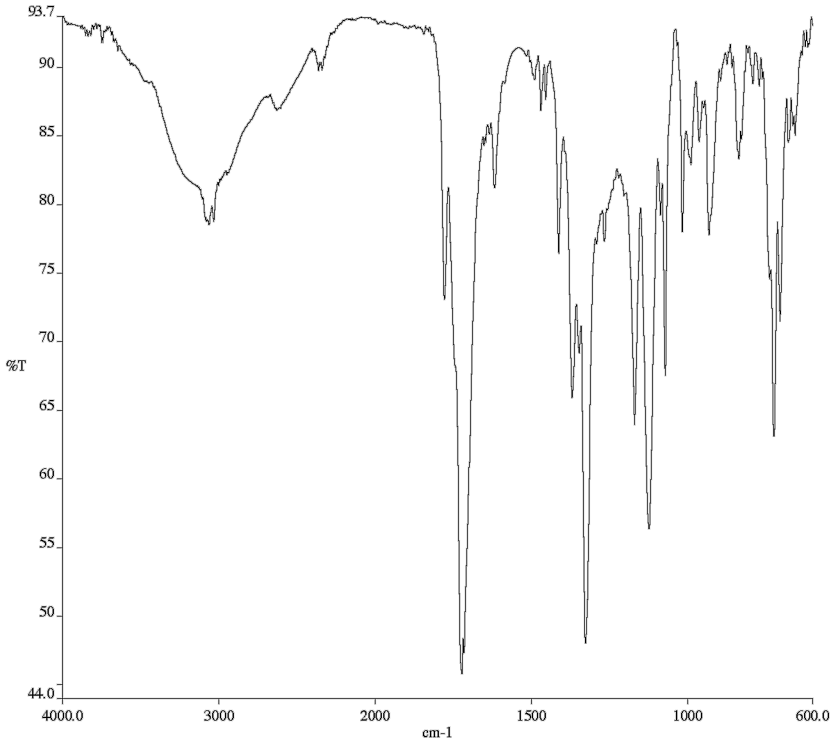
^{13}C NMR (100 MHz, $CDCl_3$) of compound **25**.



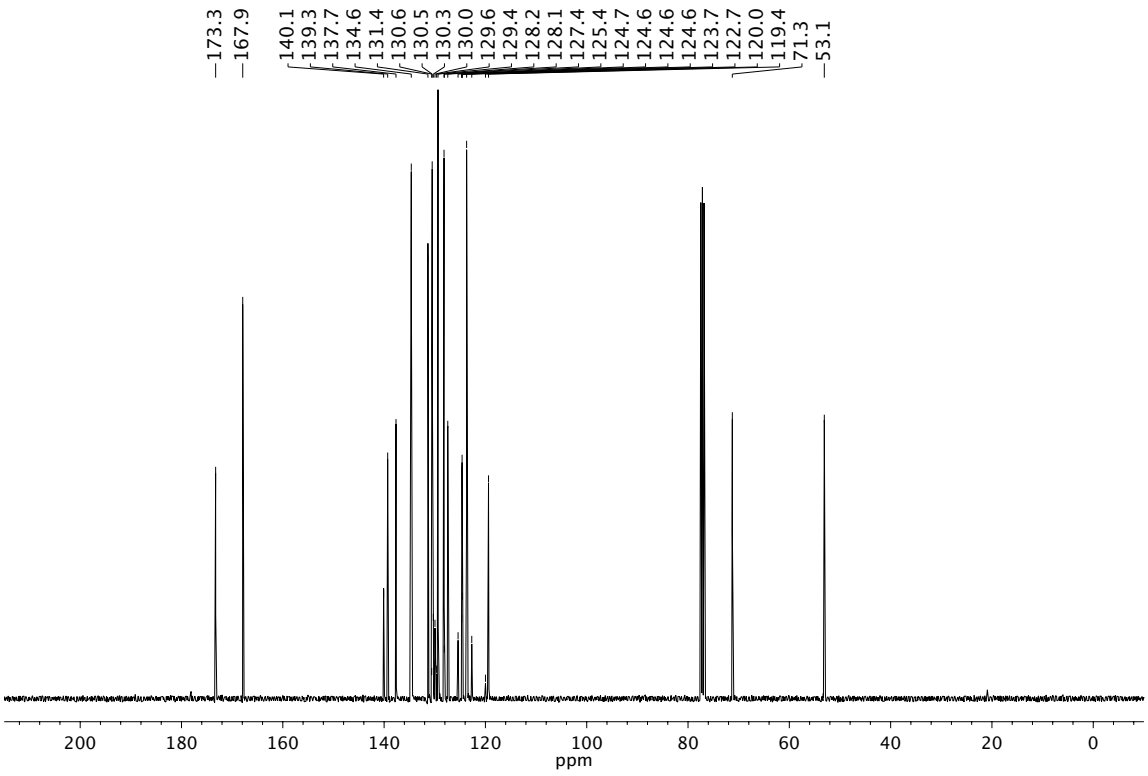
^{19}F NMR (282 MHz, $CDCl_3$) of compound **25**.



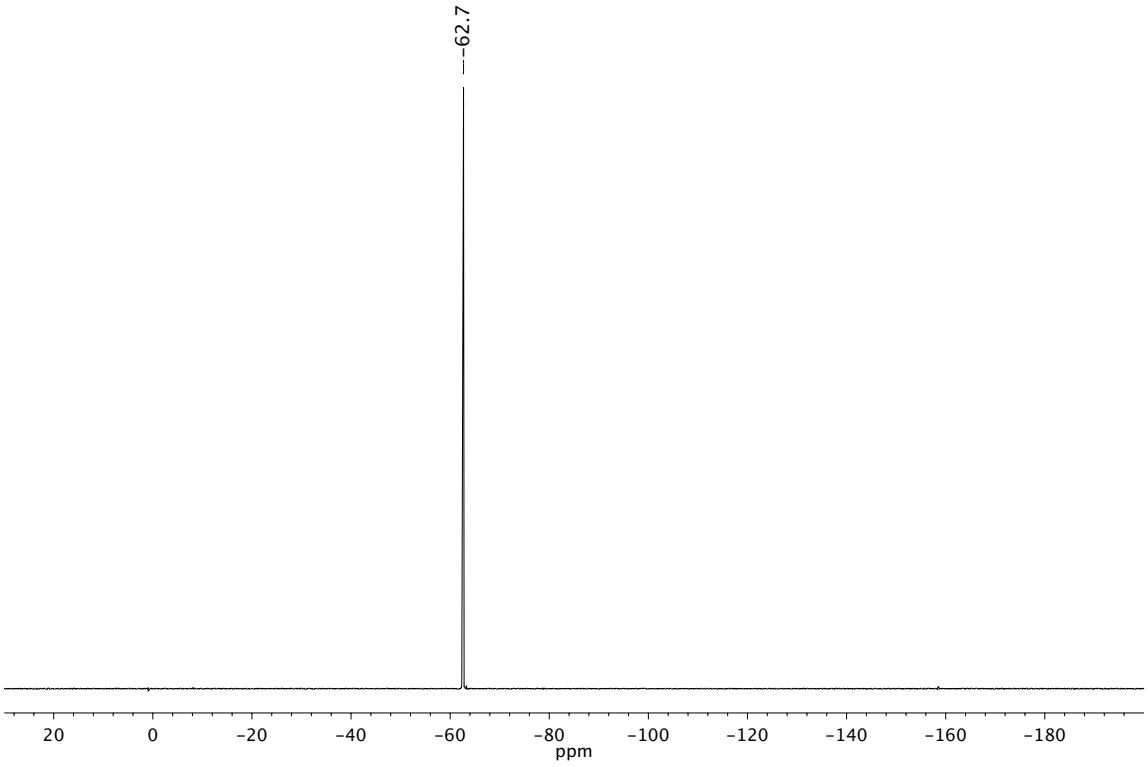
^{1}H NMR (500 MHz, $CDCl_3$) of compound **26**.



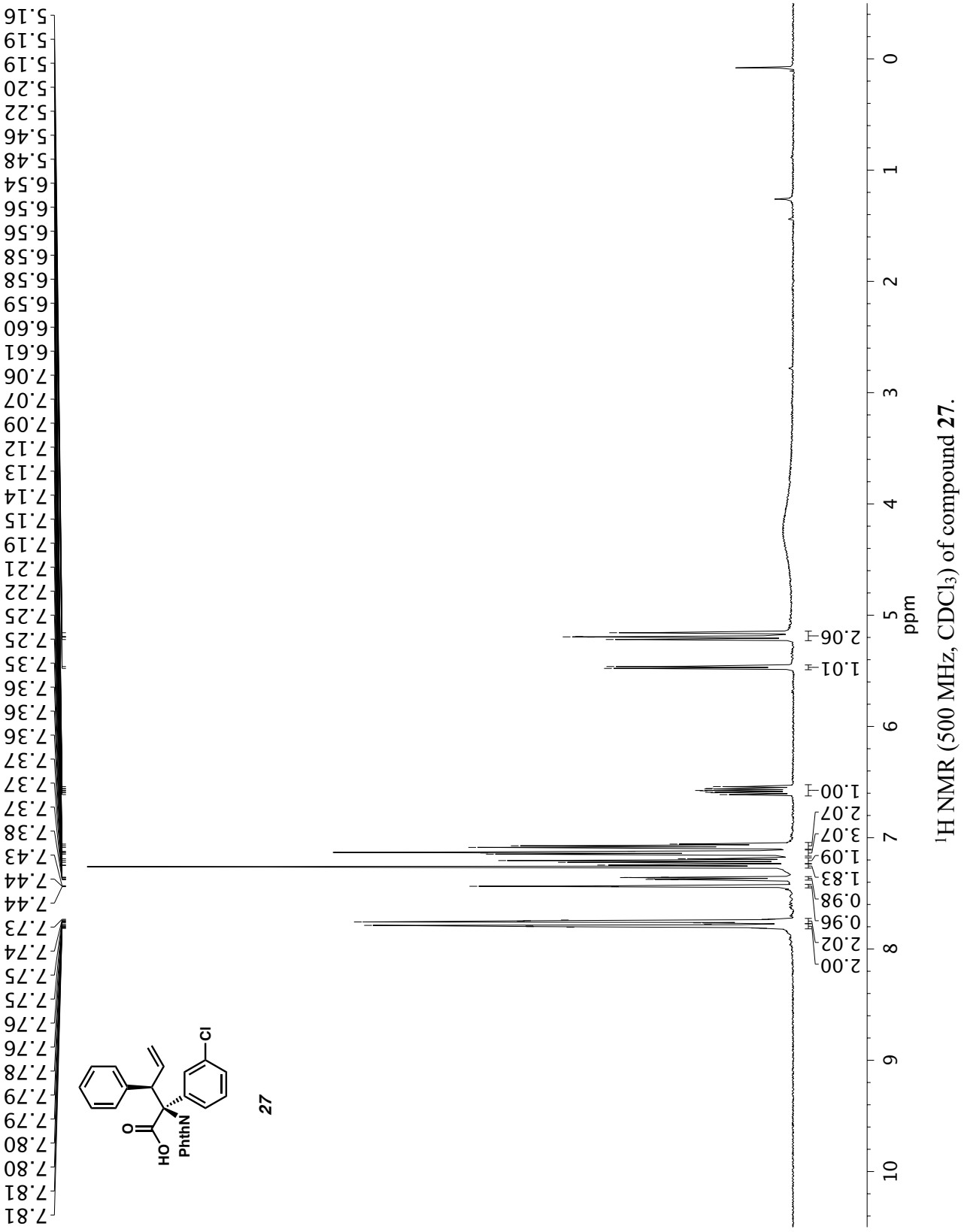
Infrared spectrum (Thin Film, NaCl) of compound **26**.



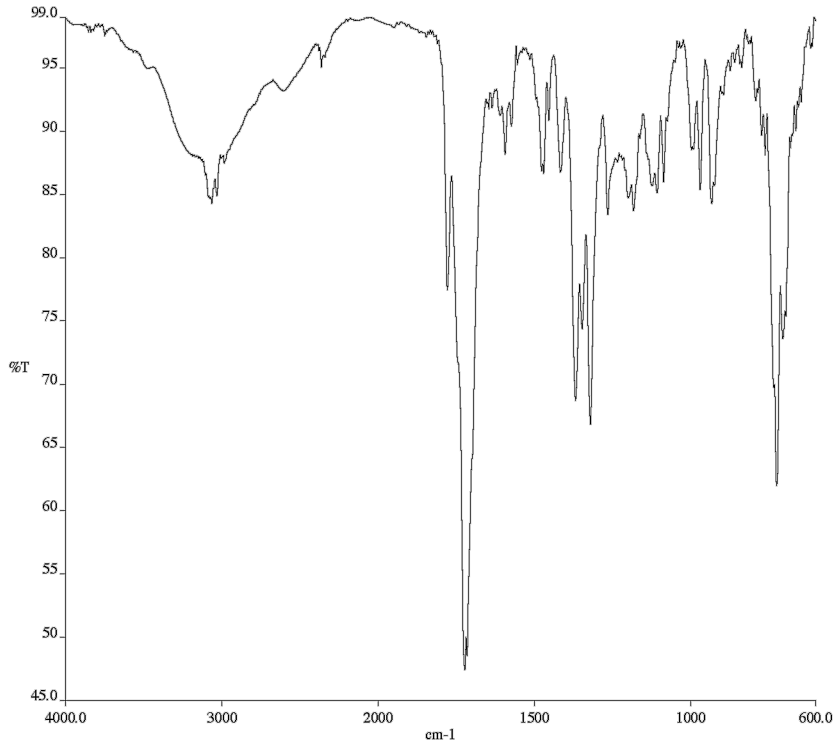
^{13}C NMR (100 MHz, $CDCl_3$) of compound **26**.



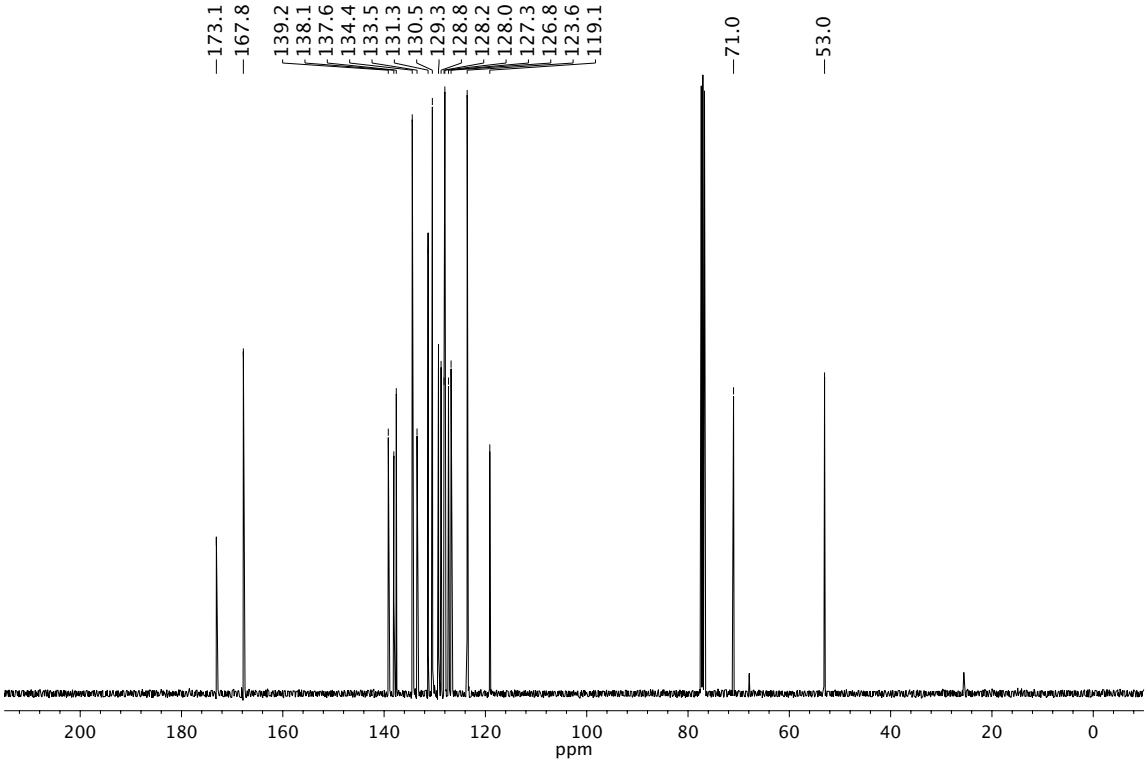
^{19}F NMR (282 MHz, $CDCl_3$) of compound **26**.



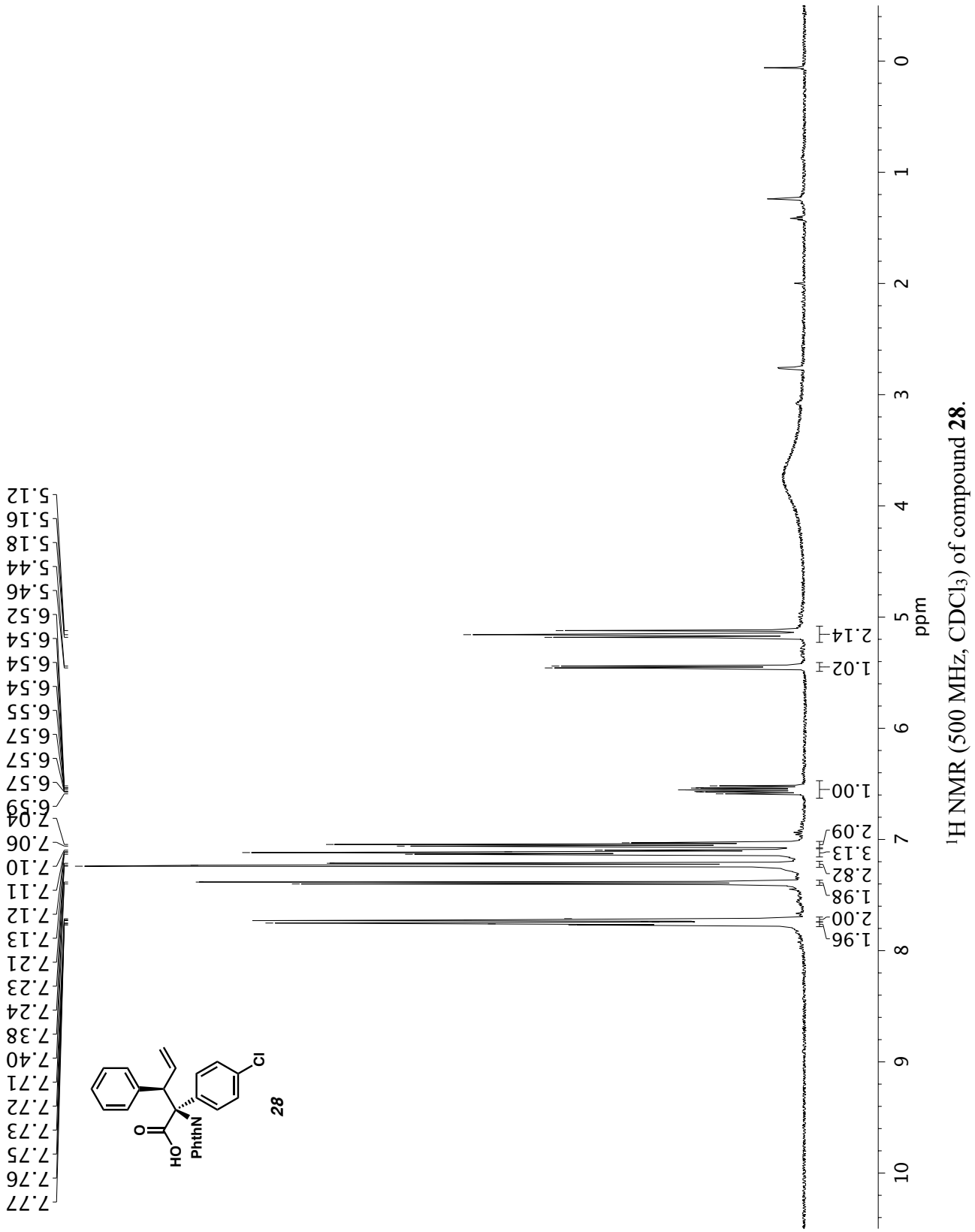
^{1}H NMR (500 MHz, $CDCl_3$) of compound **27**.



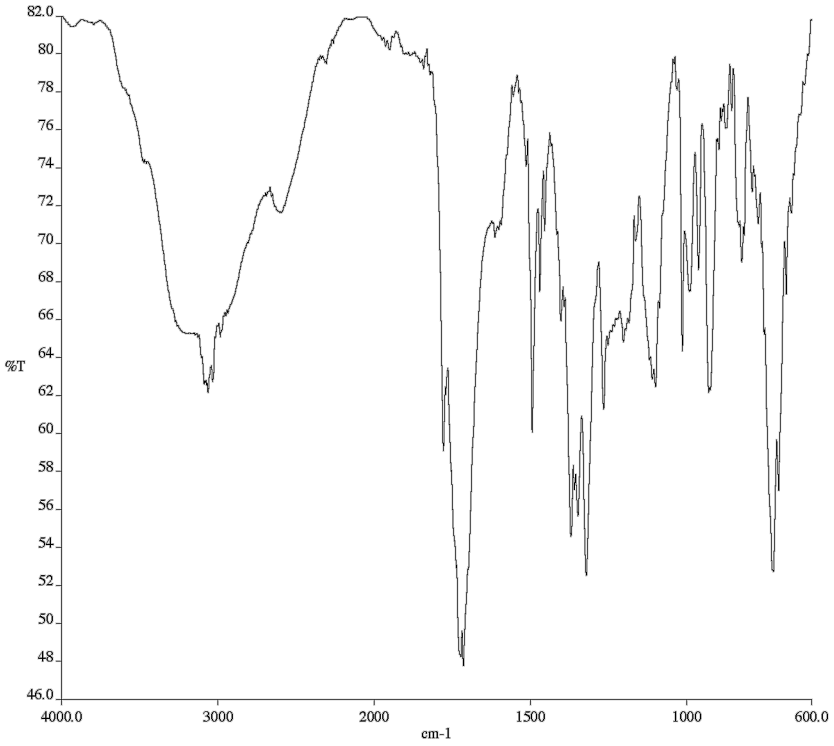
Infrared spectrum (Thin Film, NaCl) of compound **27**.



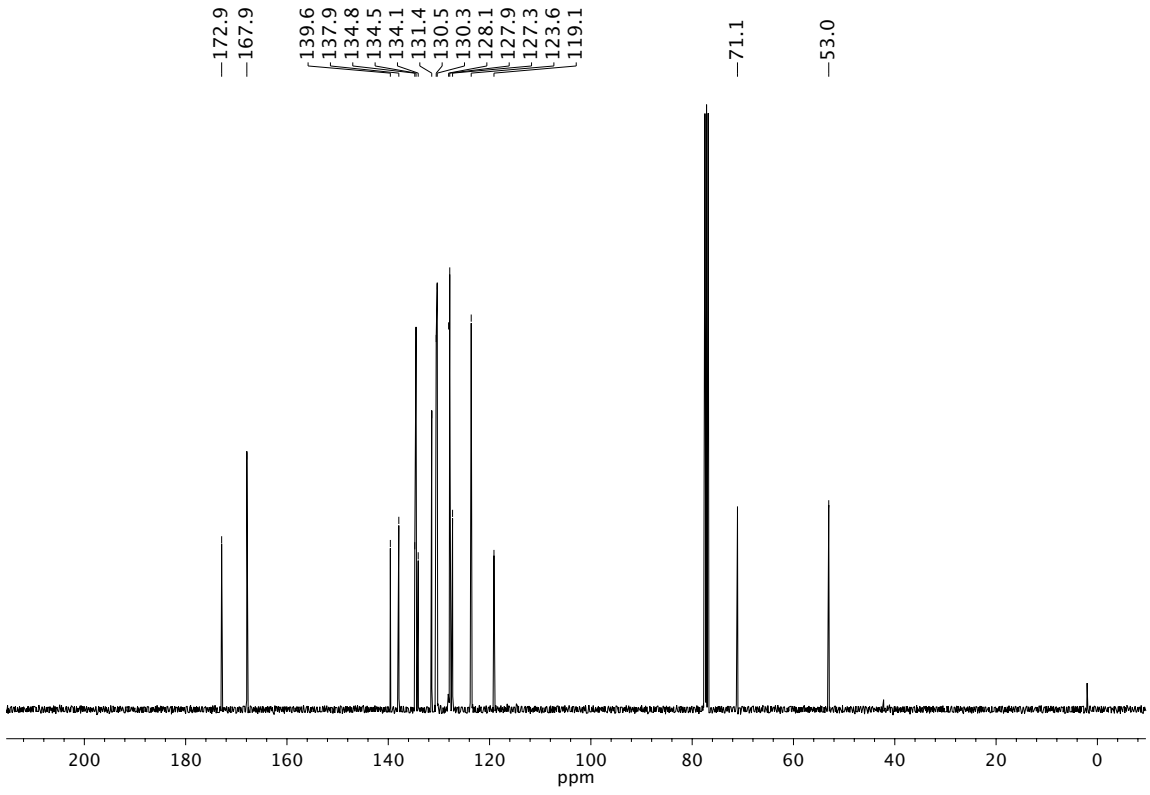
^{13}C NMR (100 MHz, $CDCl_3$) of compound **27**.



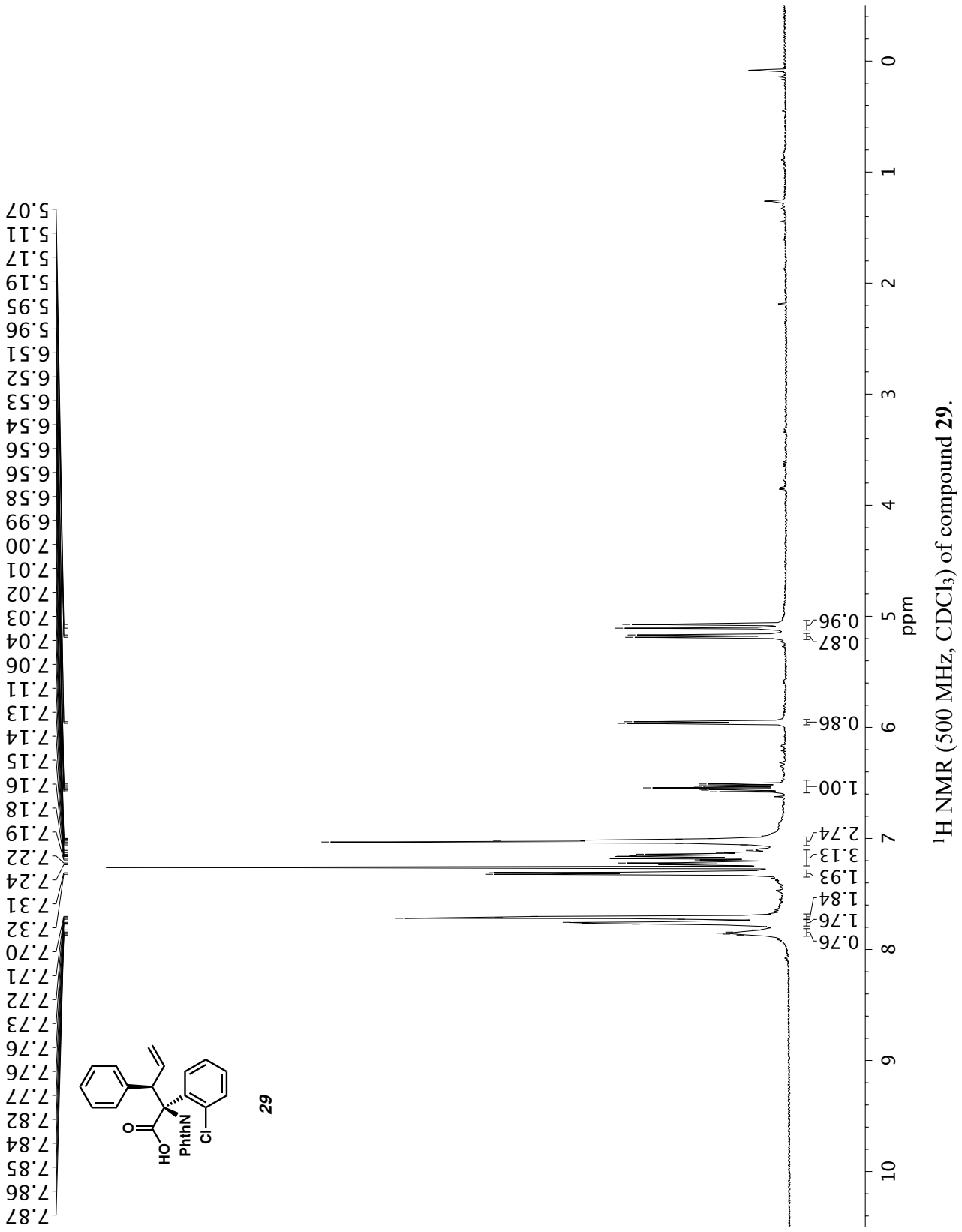
^{1}H NMR (500 MHz, $CDCl_3$) of compound **28**.



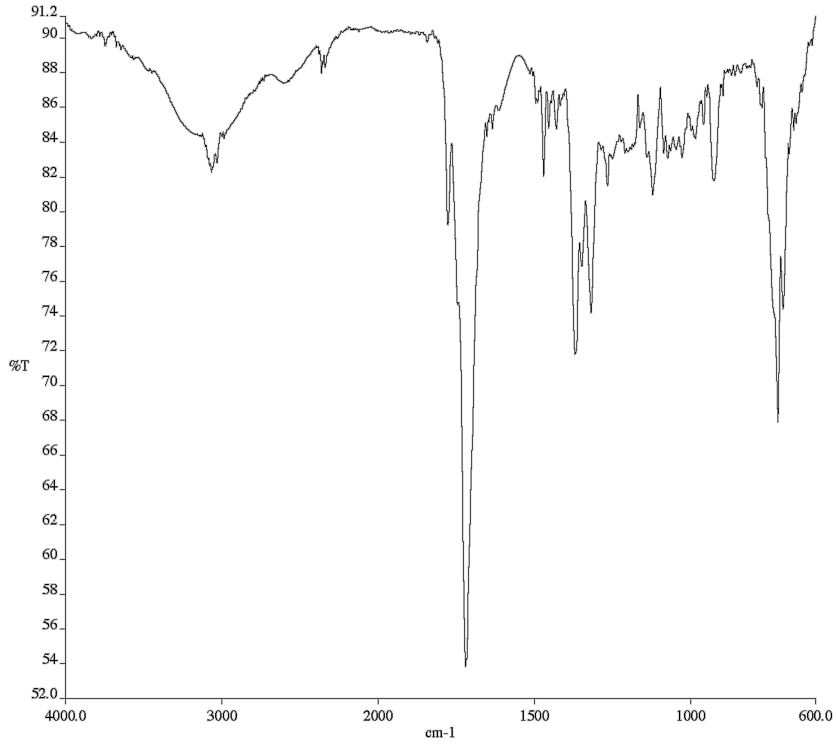
Infrared spectrum (Thin Film, NaCl) of compound **28**.



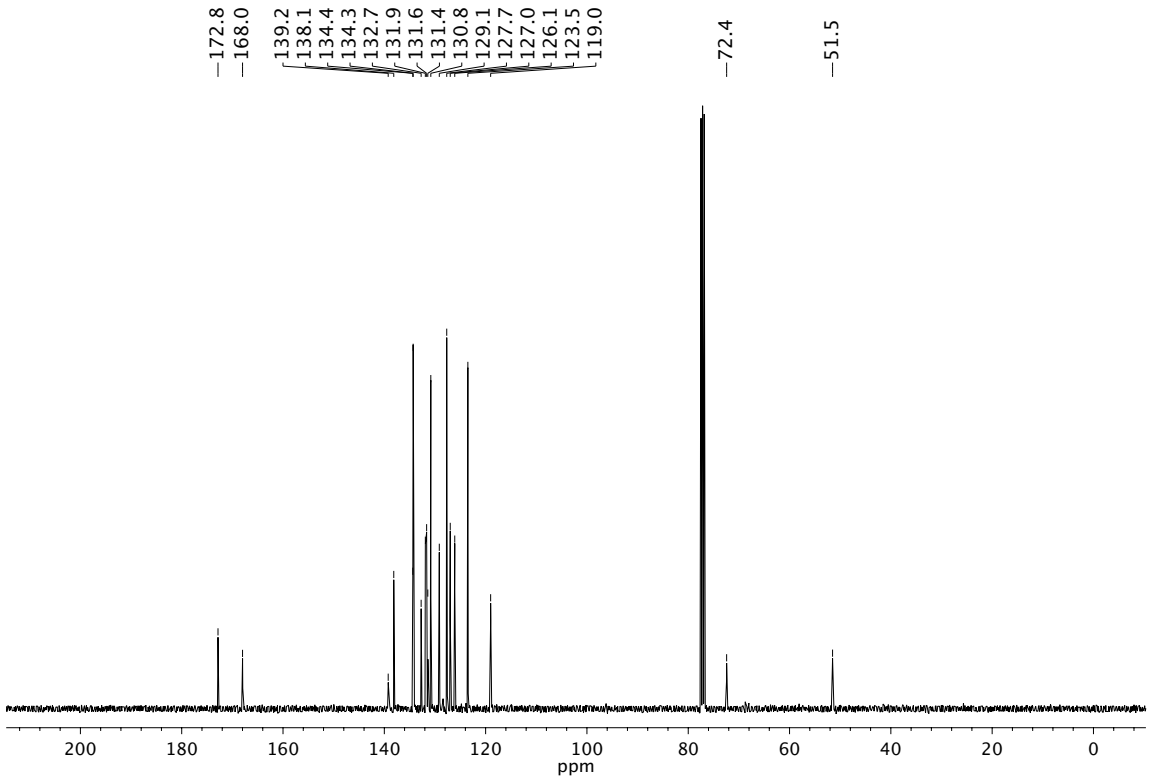
^{13}C NMR (100 MHz, $CDCl_3$) of compound **28**.



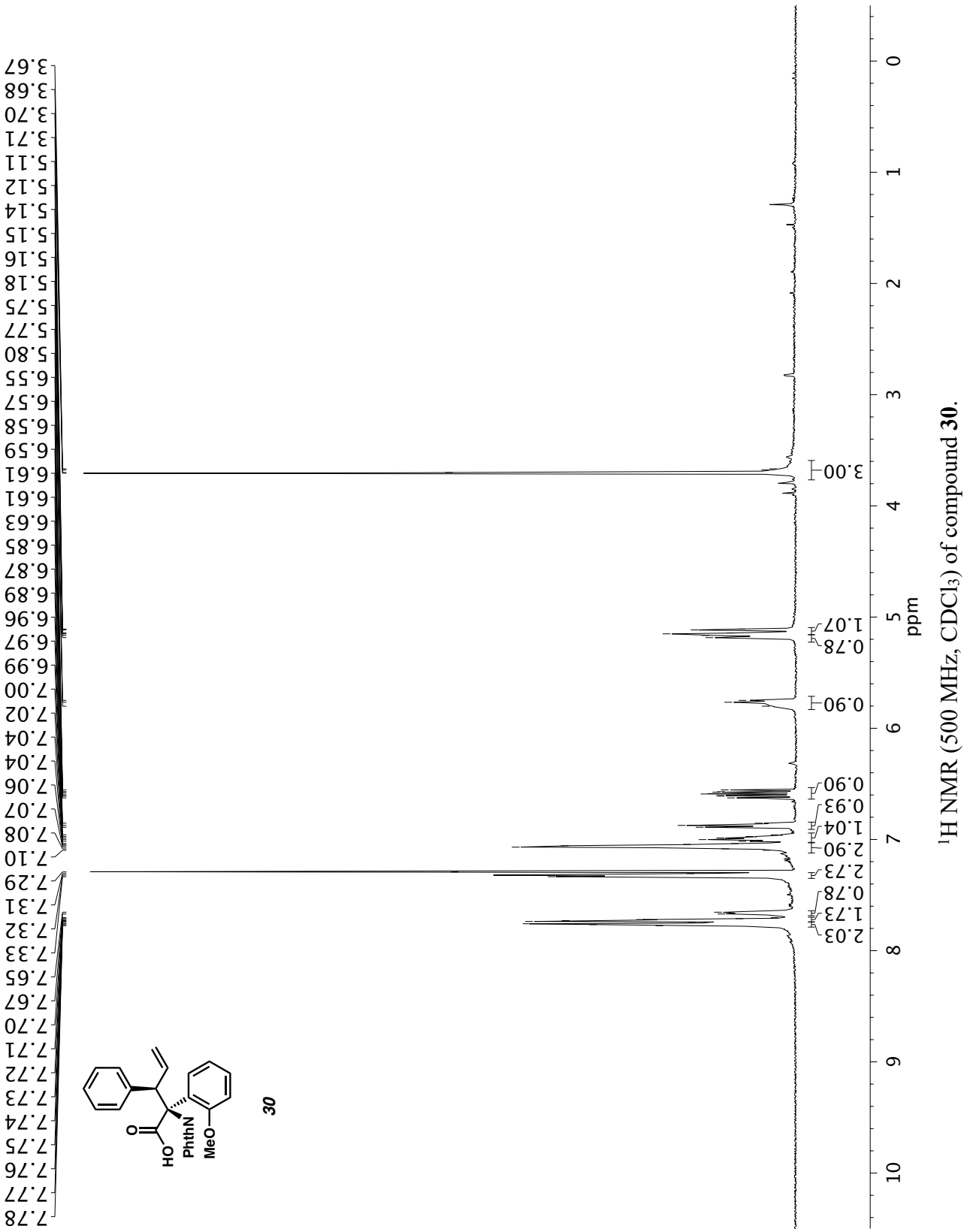
^{1}H NMR (500 MHz, $CDCl_3$) of compound **29**.



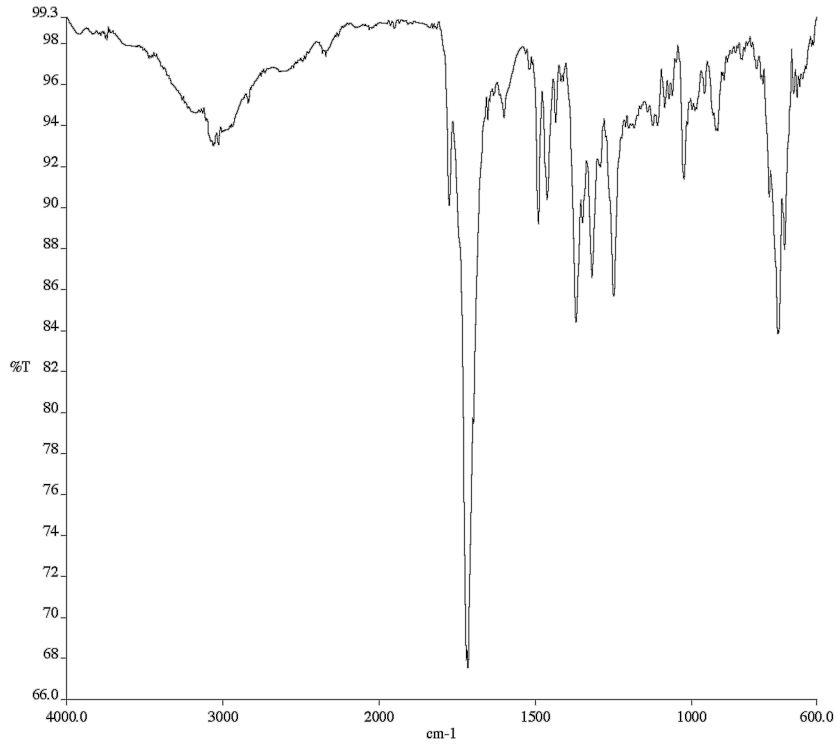
Infrared spectrum (Thin Film, NaCl) of compound **29**.



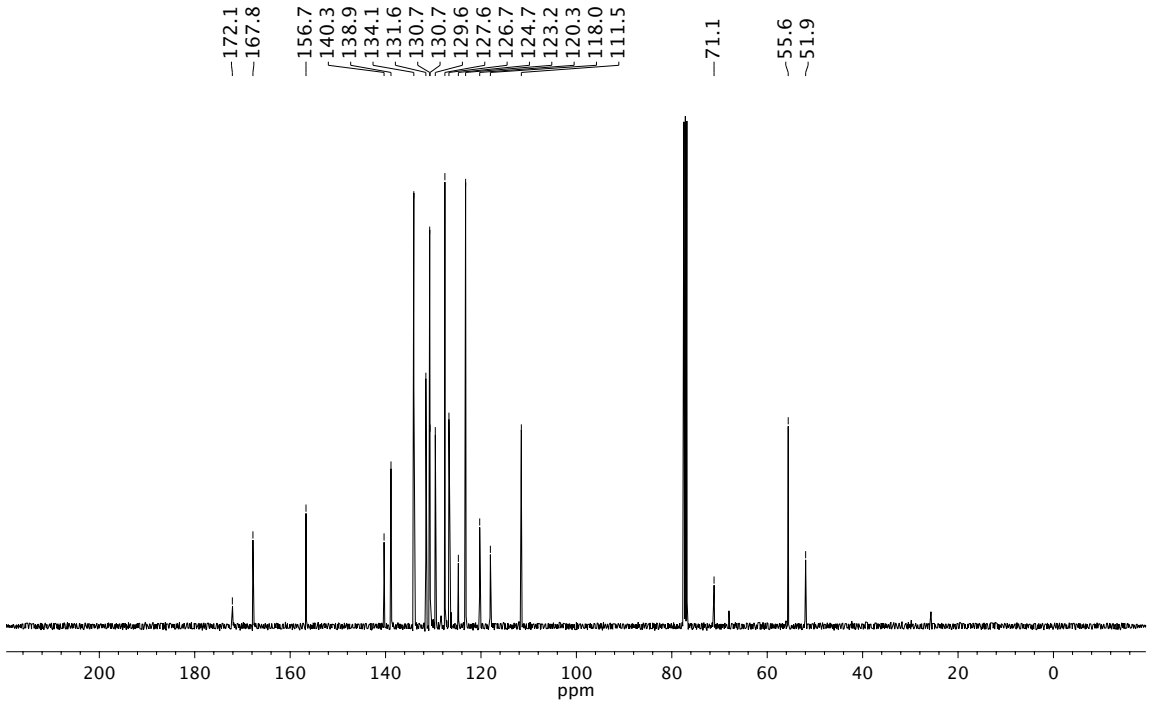
^{13}C NMR (100 MHz, $CDCl_3$) of compound **29**.



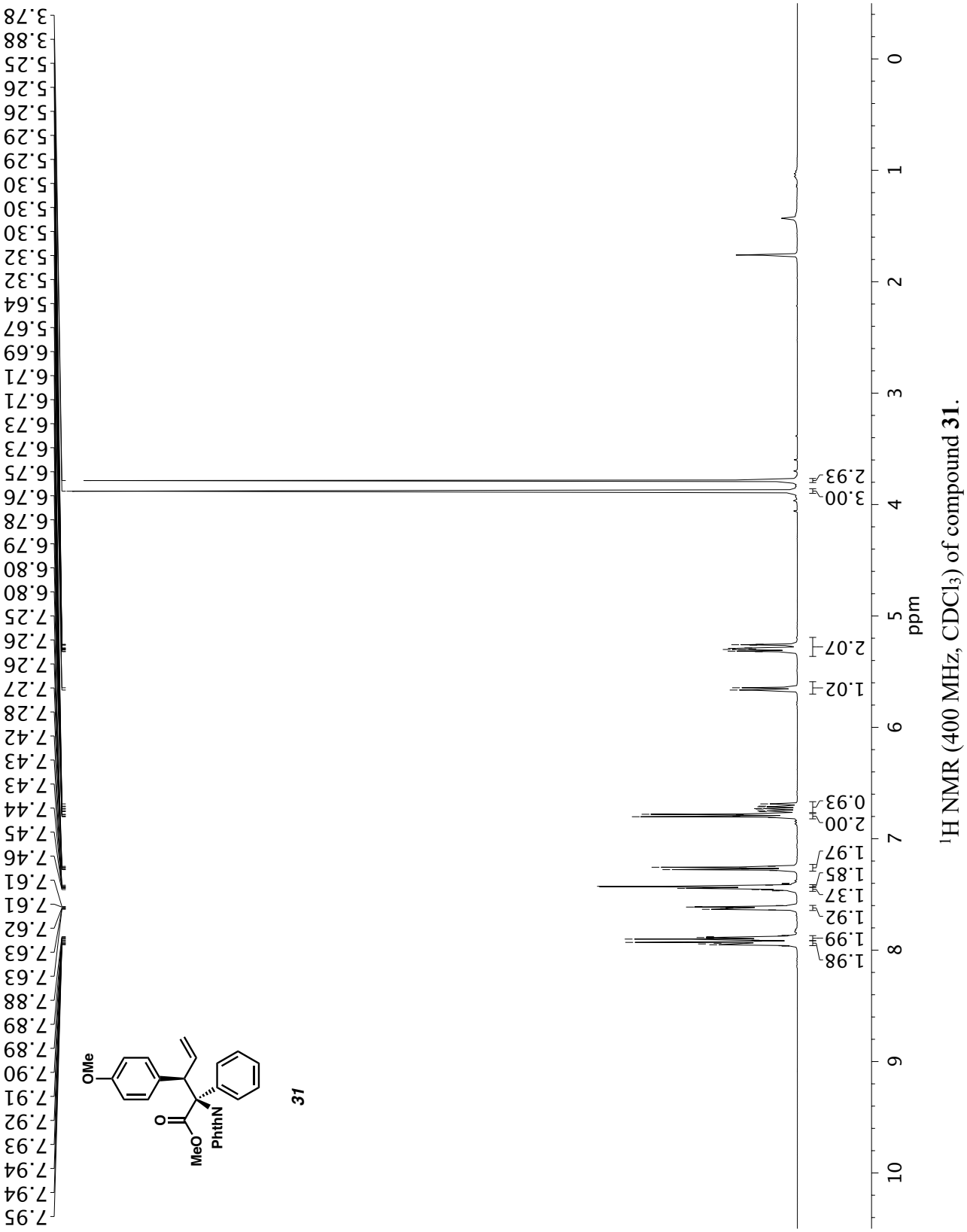
^{1}H NMR (500 MHz, $CDCl_3$) of compound **30**.



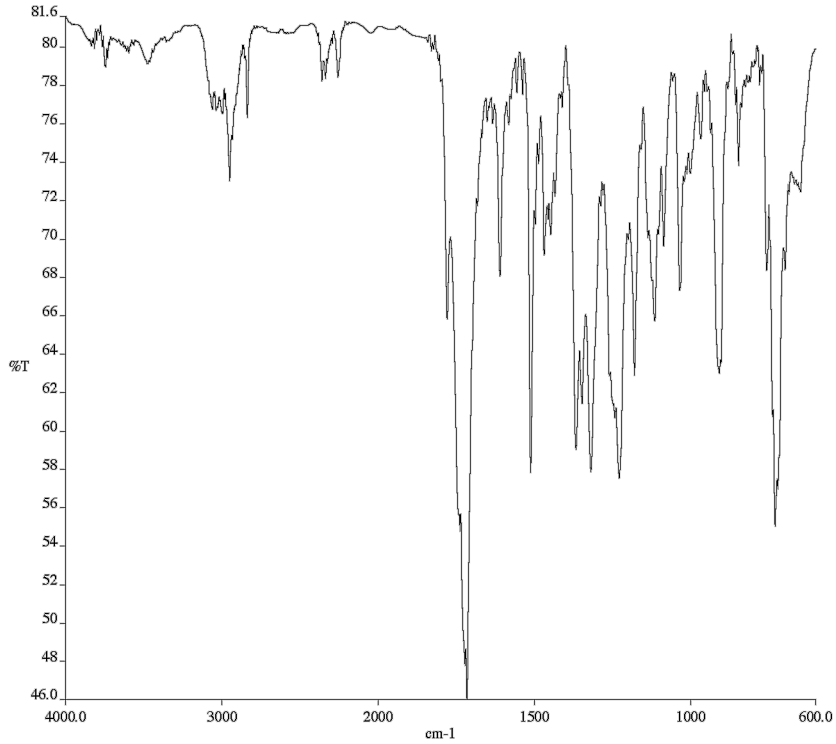
Infrared spectrum (Thin Film, NaCl) of compound **30**.



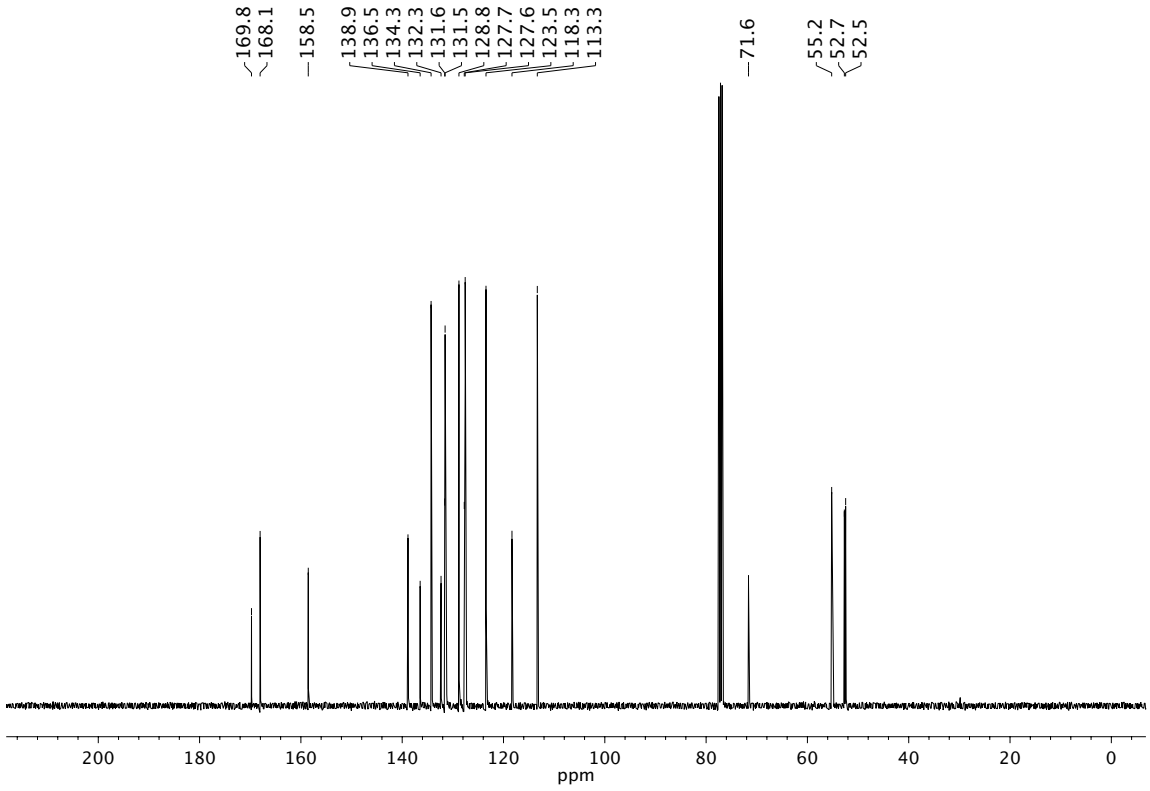
^{13}C NMR (100 MHz, $CDCl_3$) of compound **30**.



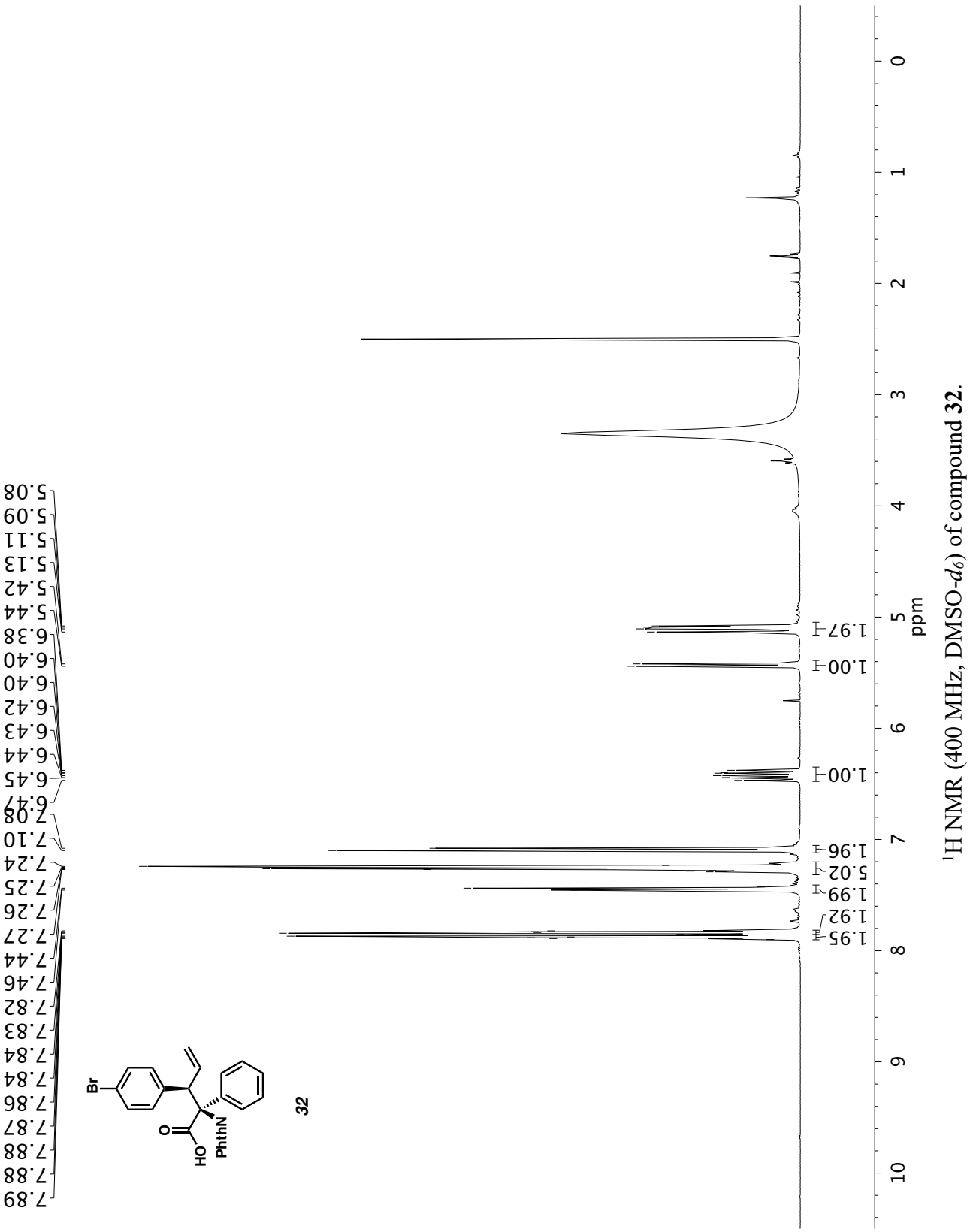
^{1}H NMR (400 MHz, $CDCl_3$) of compound **31**.



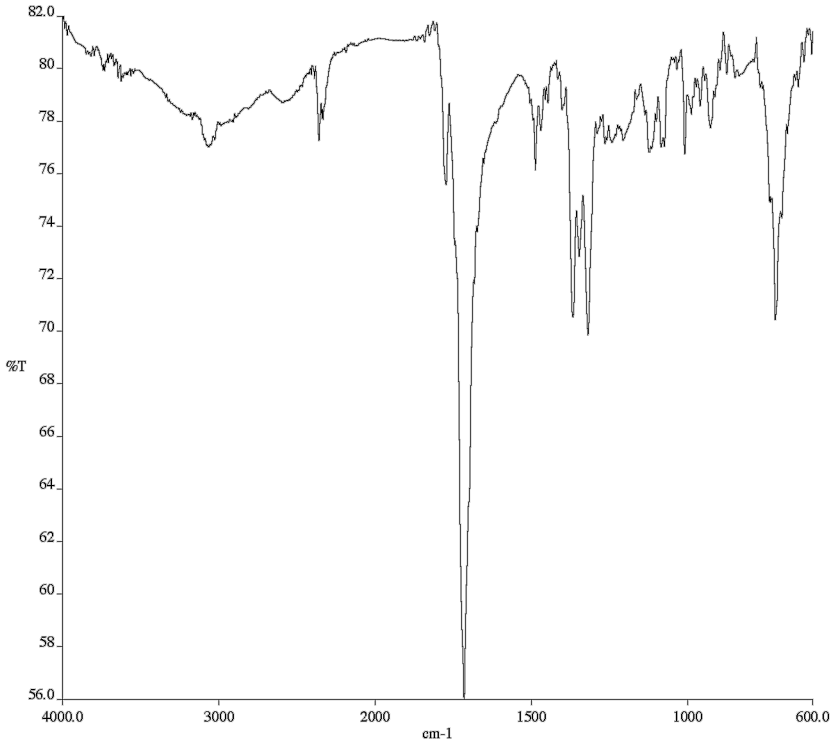
Infrared spectrum (Thin Film, NaCl) of compound **31**.



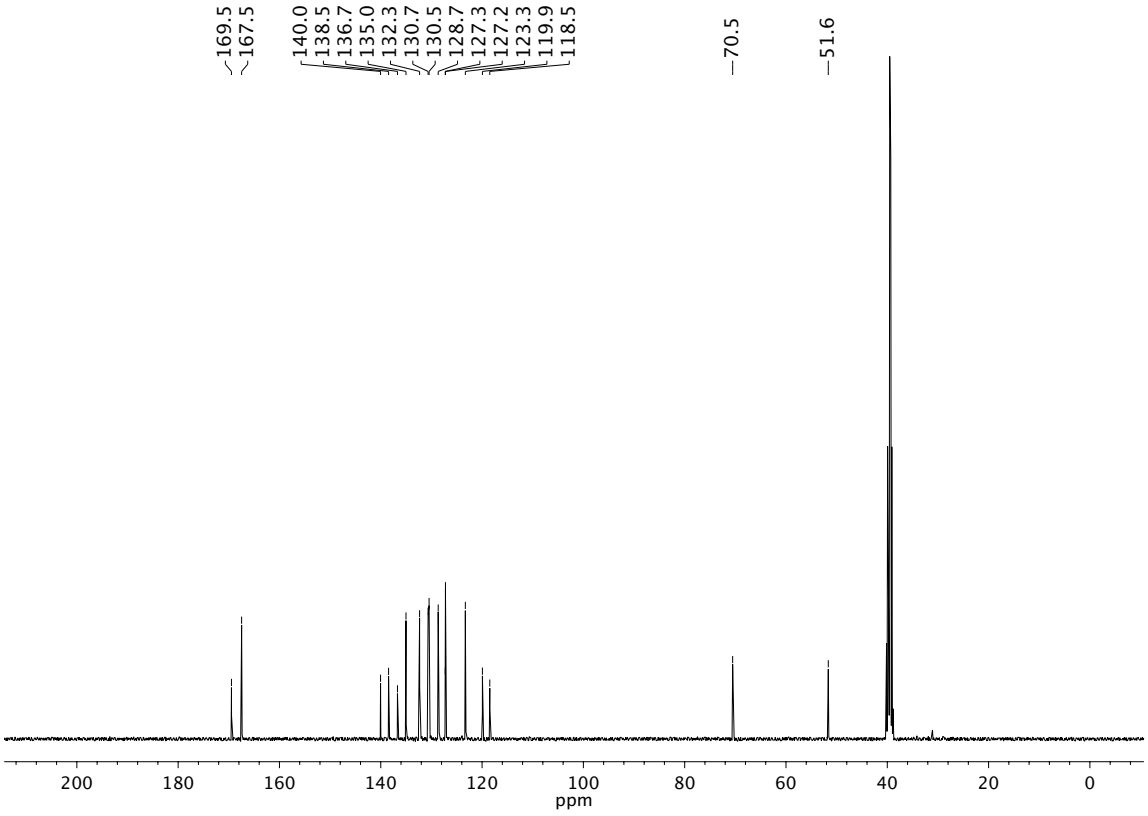
^{13}C NMR (100 MHz, $CDCl_3$) of compound **31**.



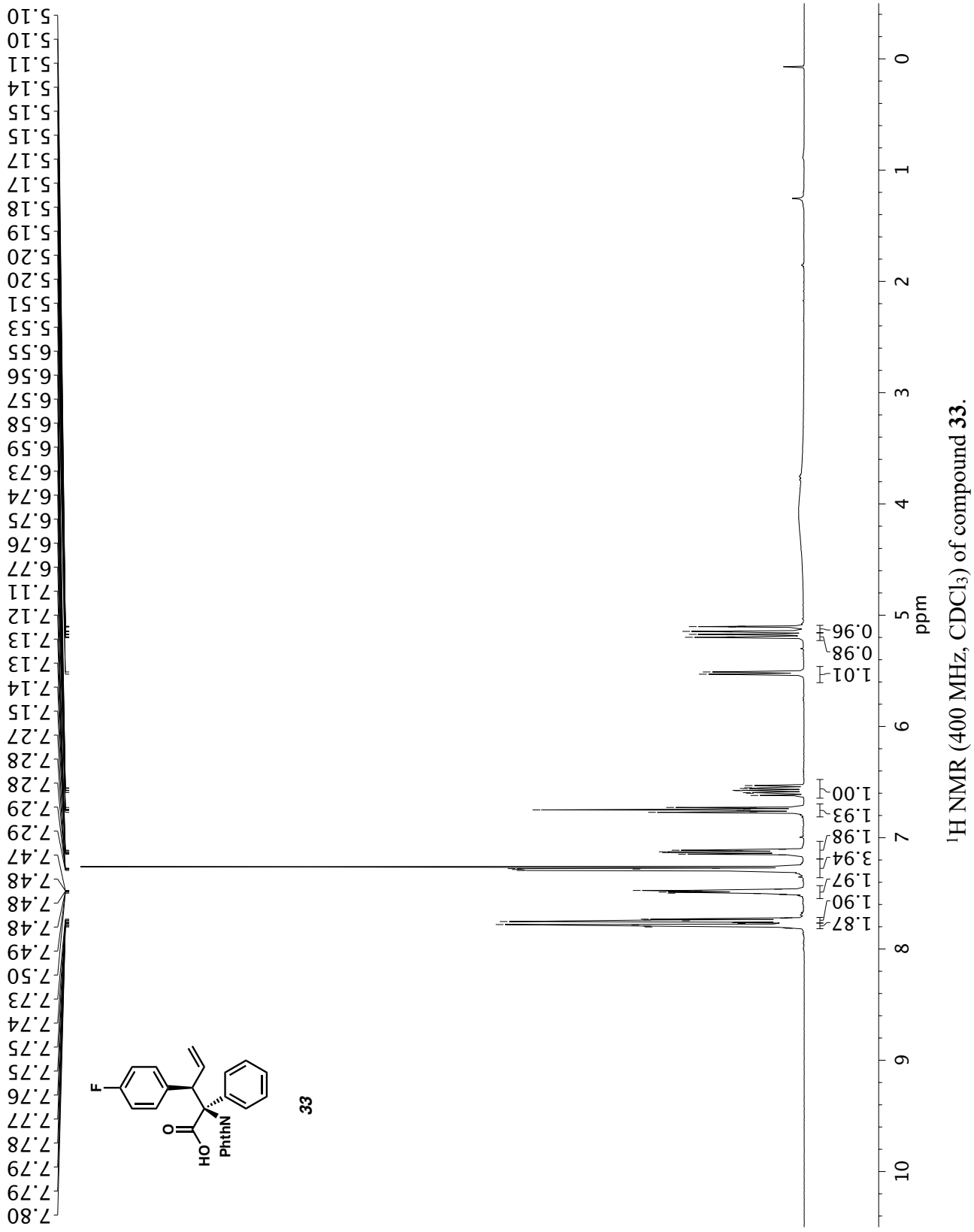
^{1}H NMR (400 MHz, DMSO-d_6) of compound **32**.



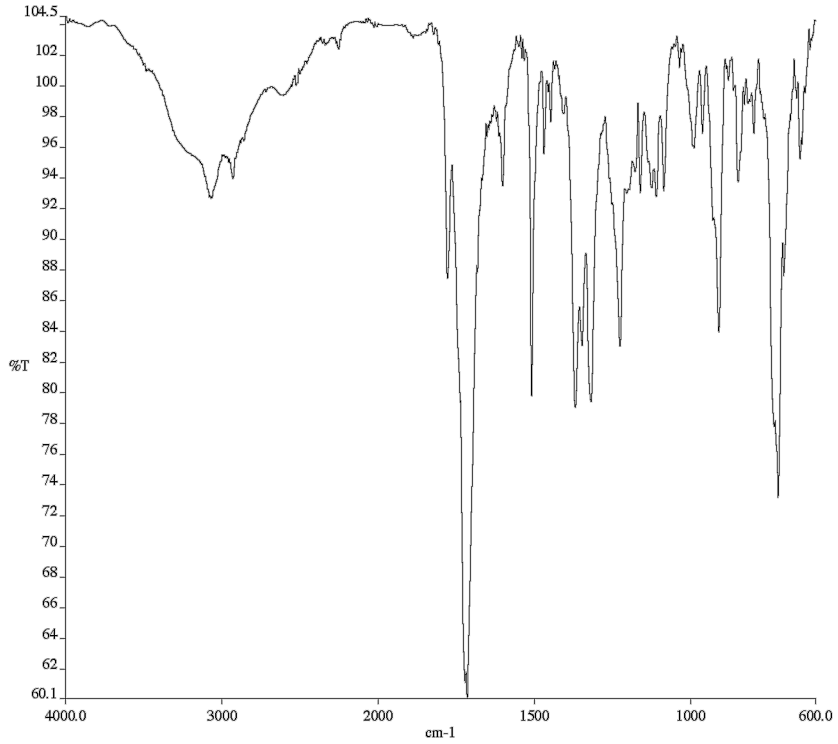
Infrared spectrum (Thin Film, NaCl) of compound **32**.



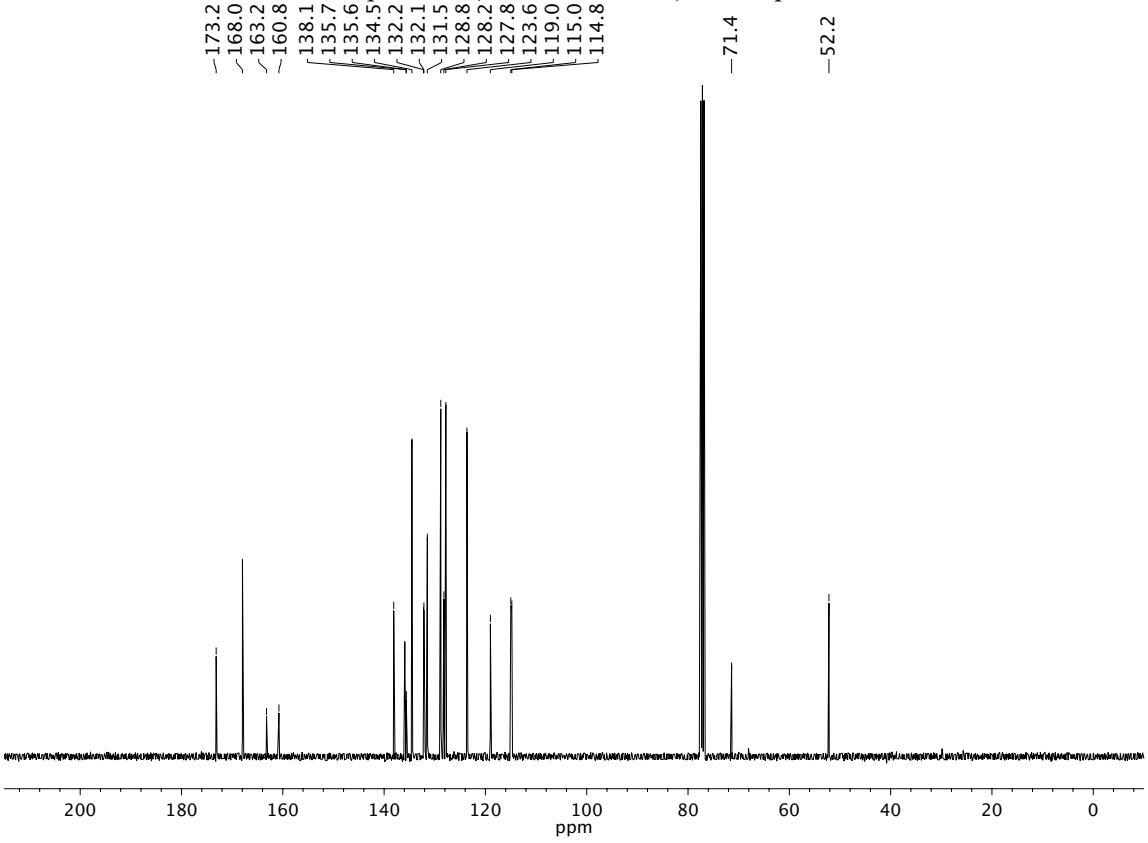
^{13}C NMR (100 MHz, $CDCl_3$) of compound **32**.



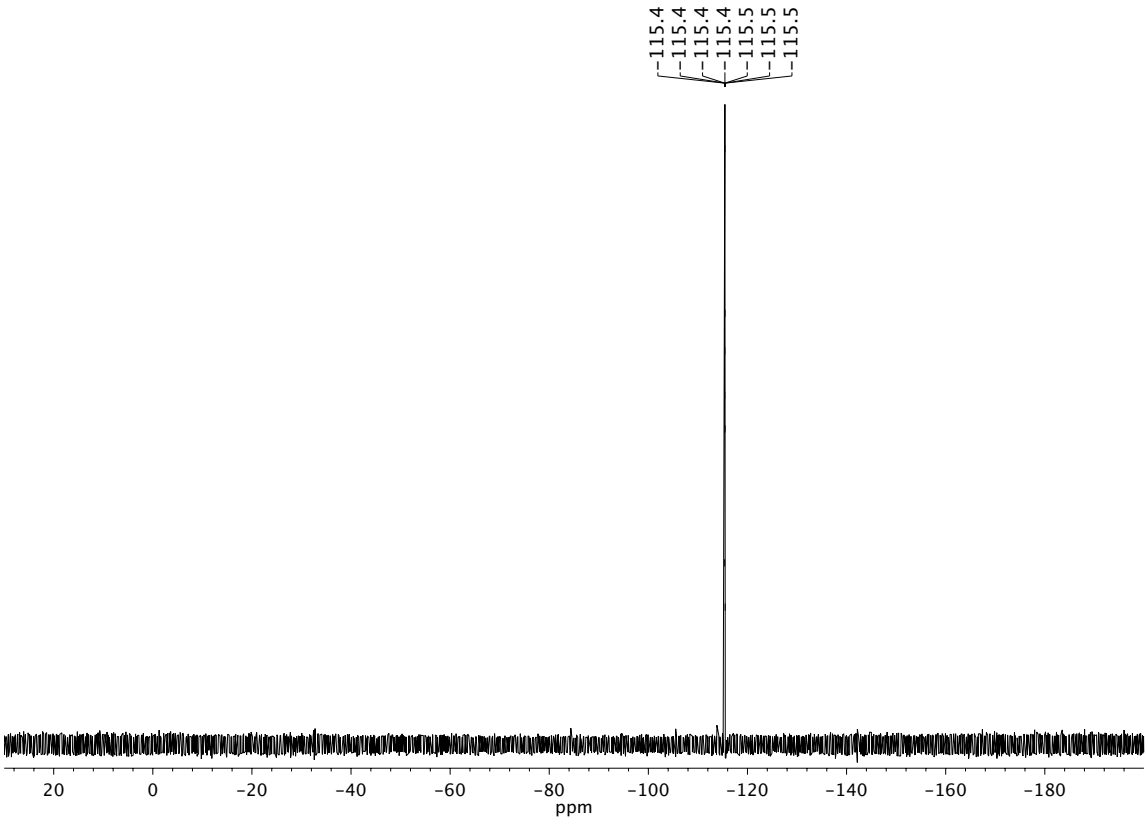
^{1}H NMR (400 MHz, $CDCl_3$) of compound **33**.



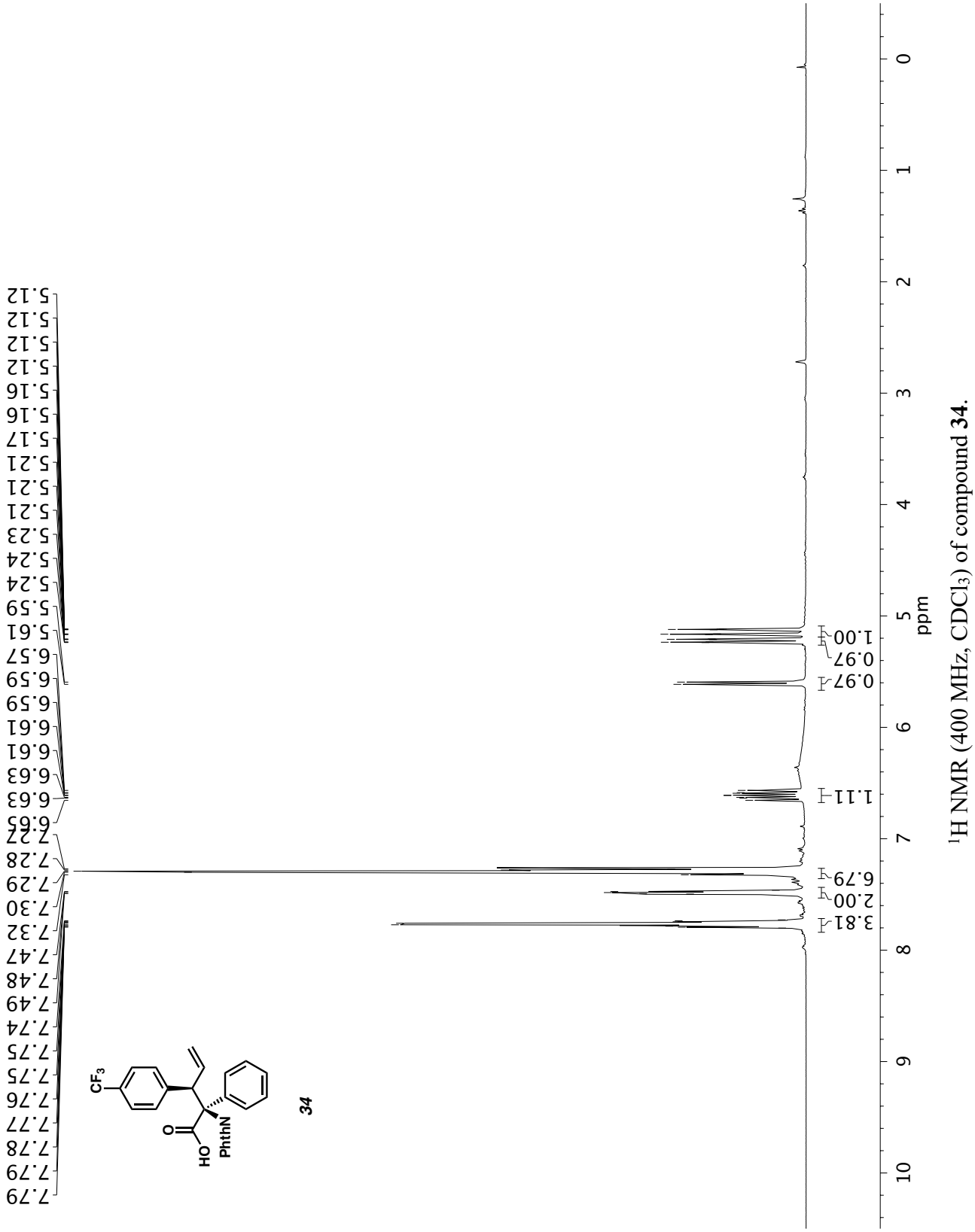
Infrared spectrum (Thin Film, NaCl) of compound **33**.



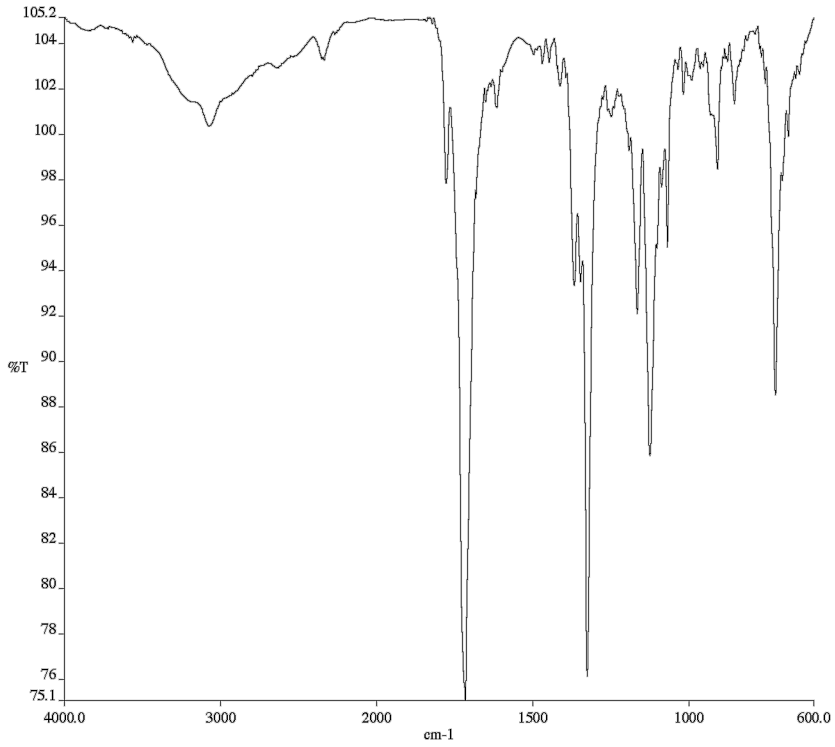
^{13}C NMR (100 MHz, $CDCl_3$) of compound **33**.



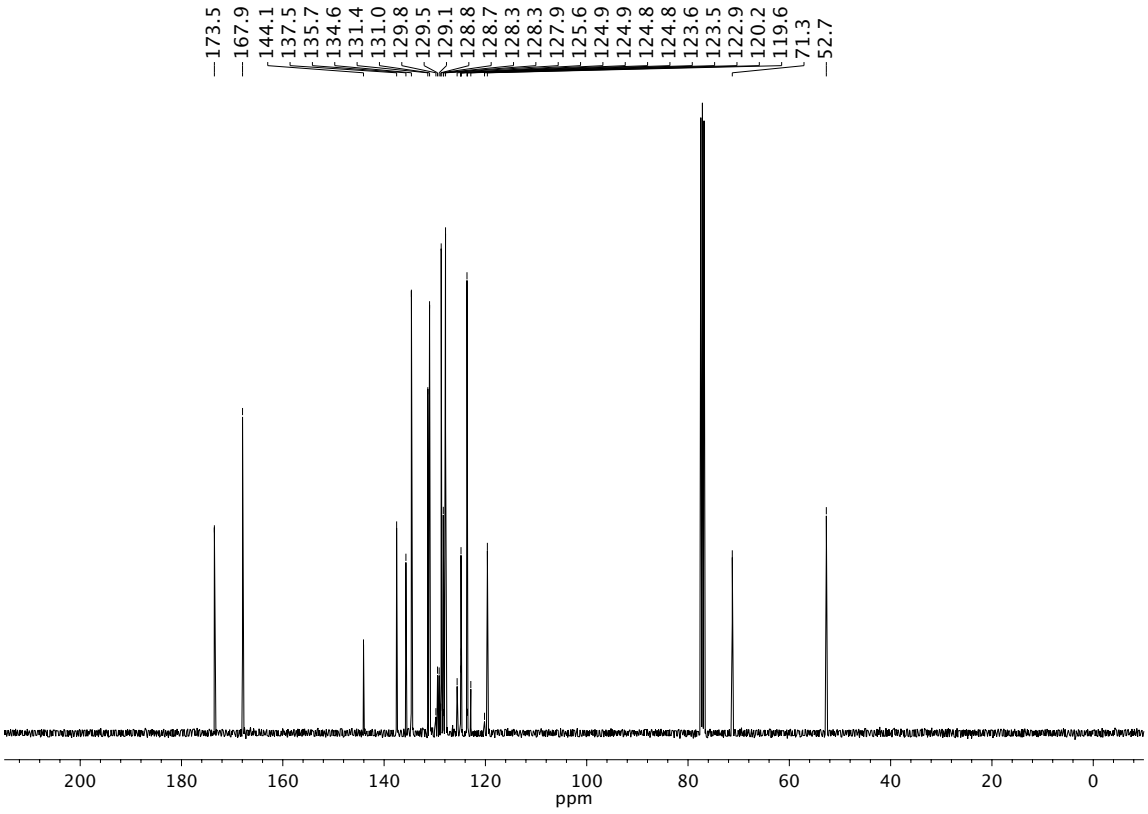
^{19}F NMR (282 MHz, $CDCl_3$) of compound **33**.



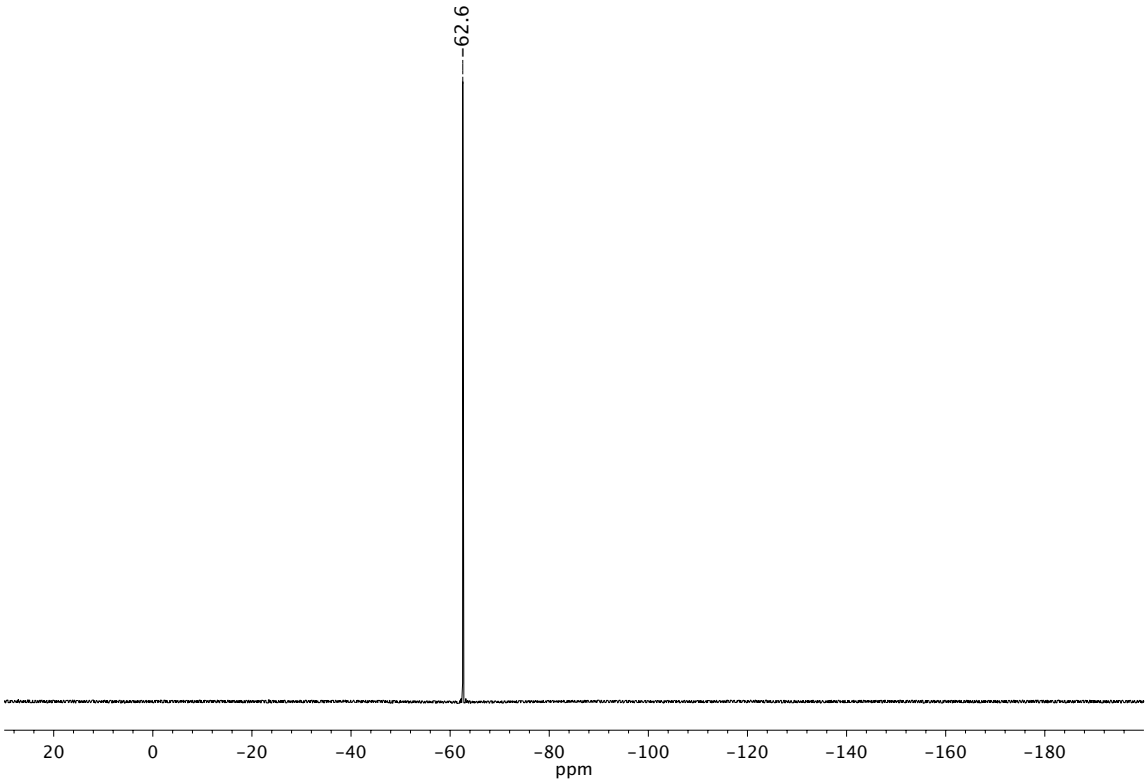
^{1}H NMR (400 MHz, $CDCl_3$) of compound **34**.



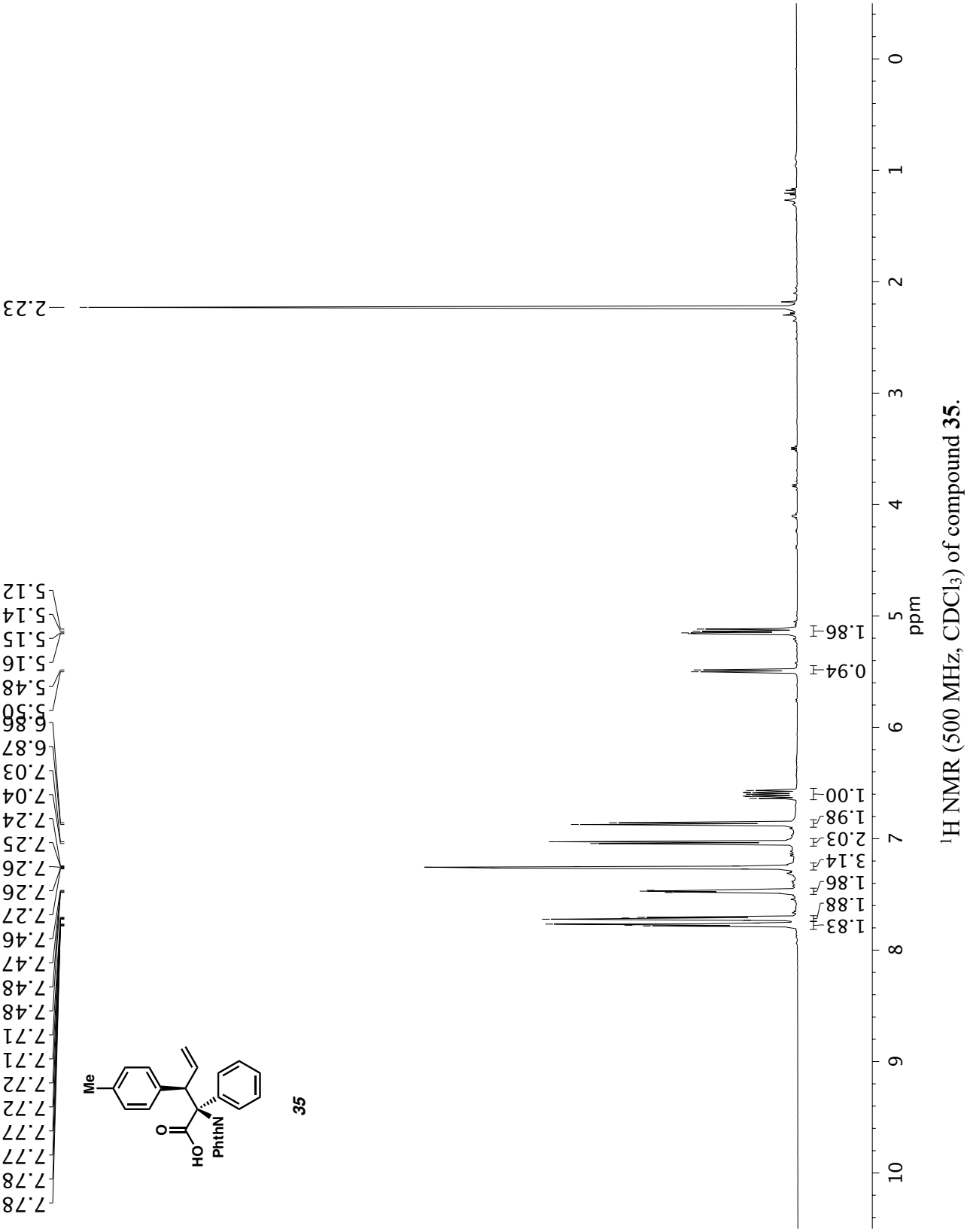
Infrared spectrum (Thin Film, NaCl) of compound **34**.



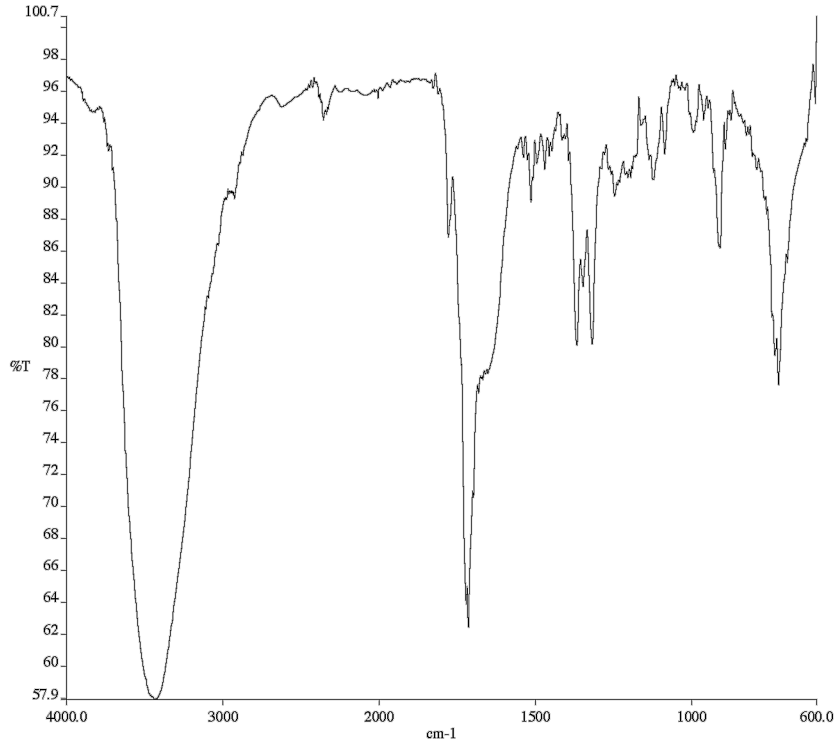
^{13}C NMR (100 MHz, $CDCl_3$) of compound **34**.



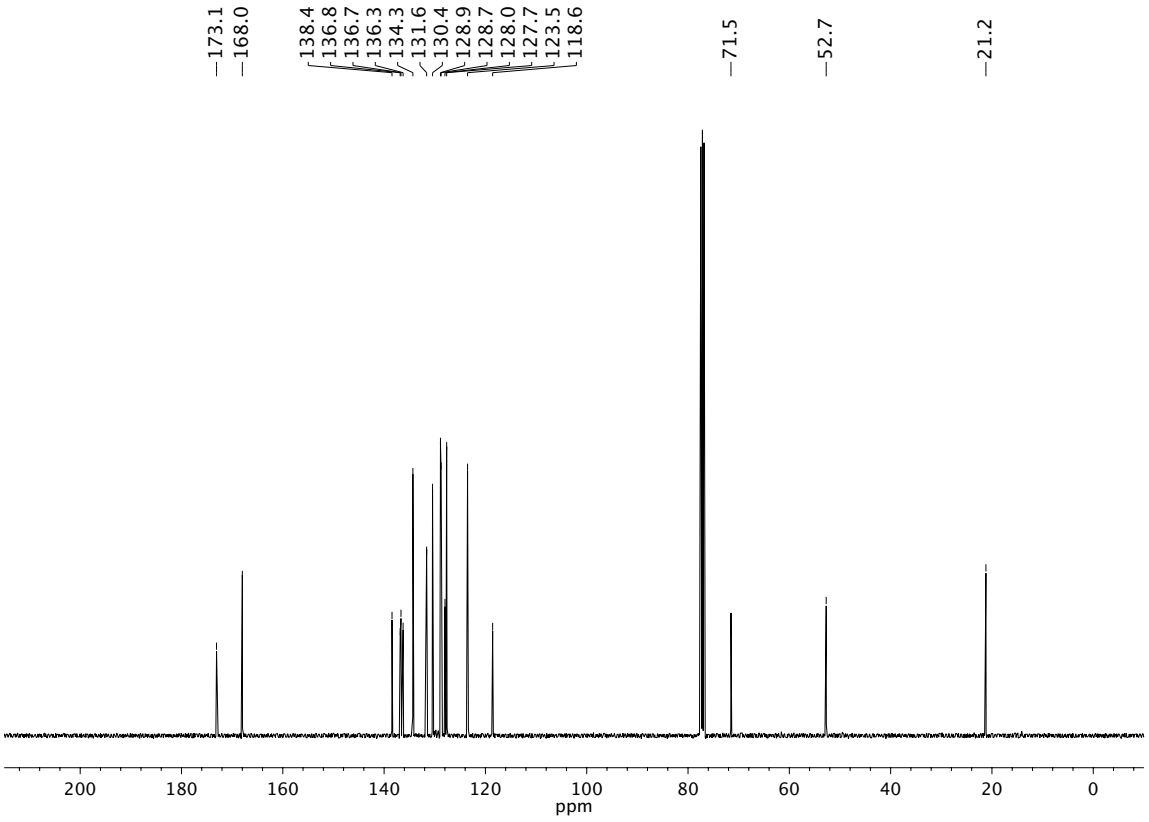
^{19}F NMR (282 MHz, $CDCl_3$) of compound **34**.



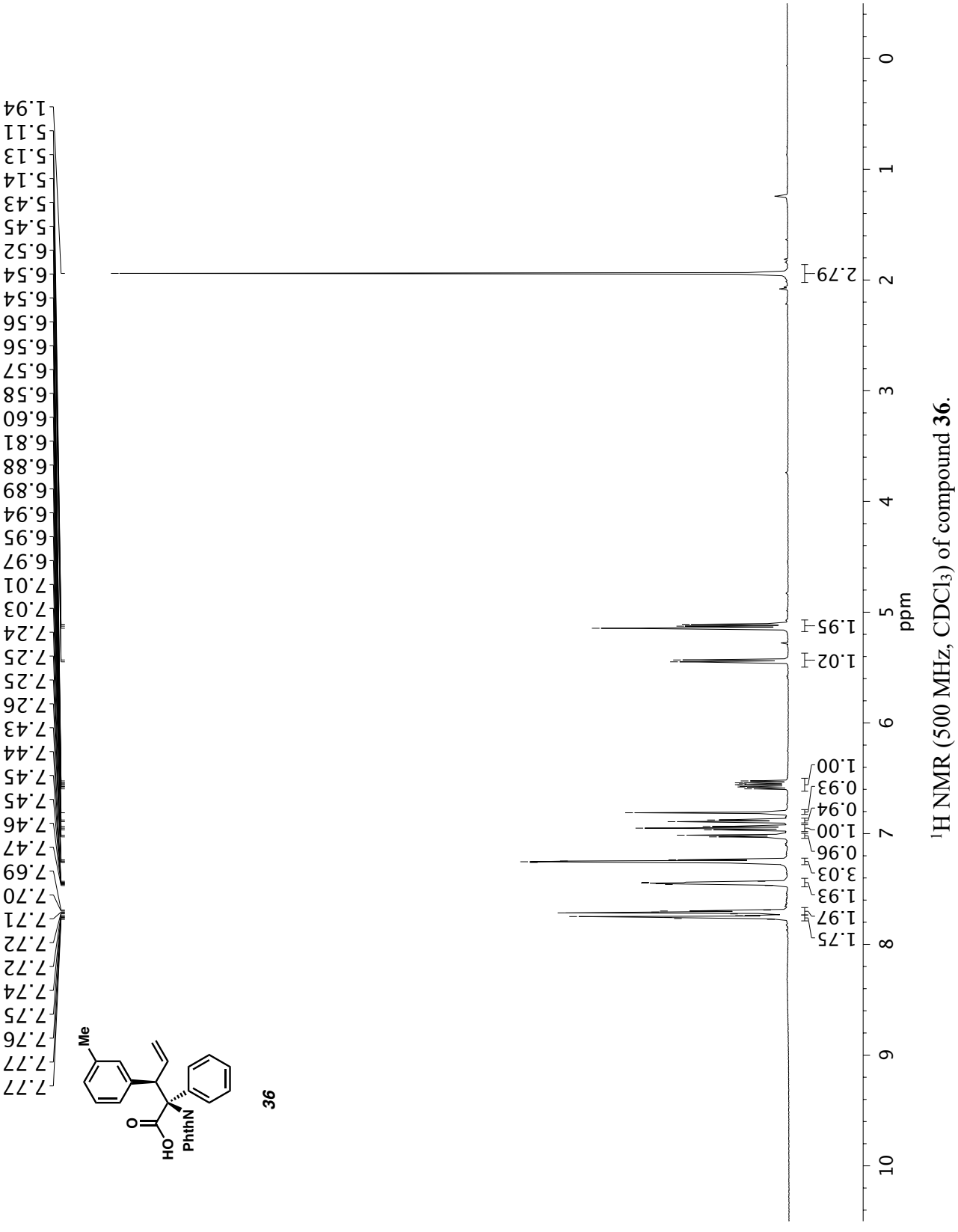
^{1}H NMR (500 MHz, $CDCl_3$) of compound **35**.



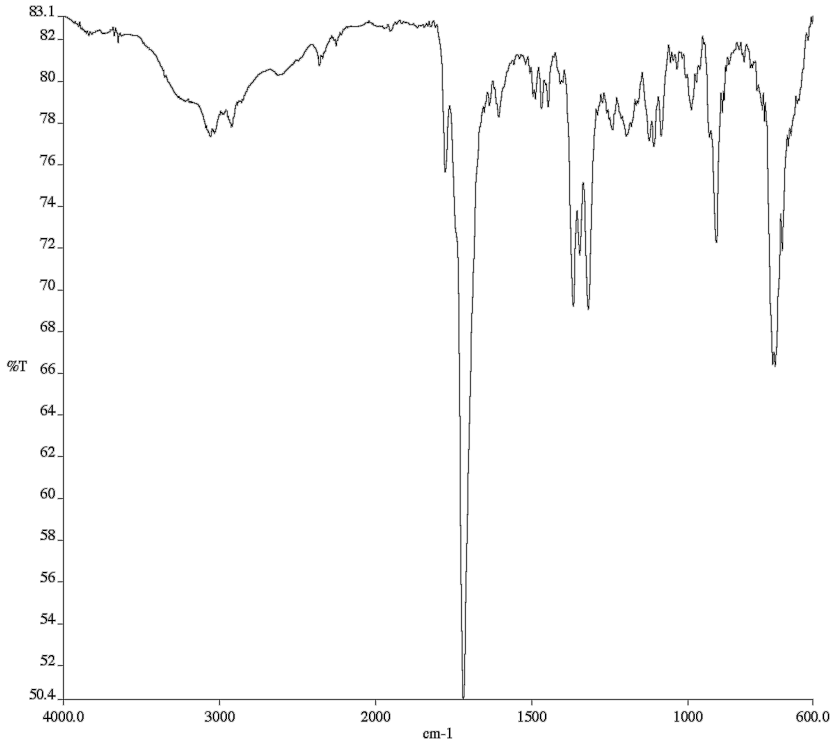
Infrared spectrum (Thin Film, NaCl) of compound **35**.



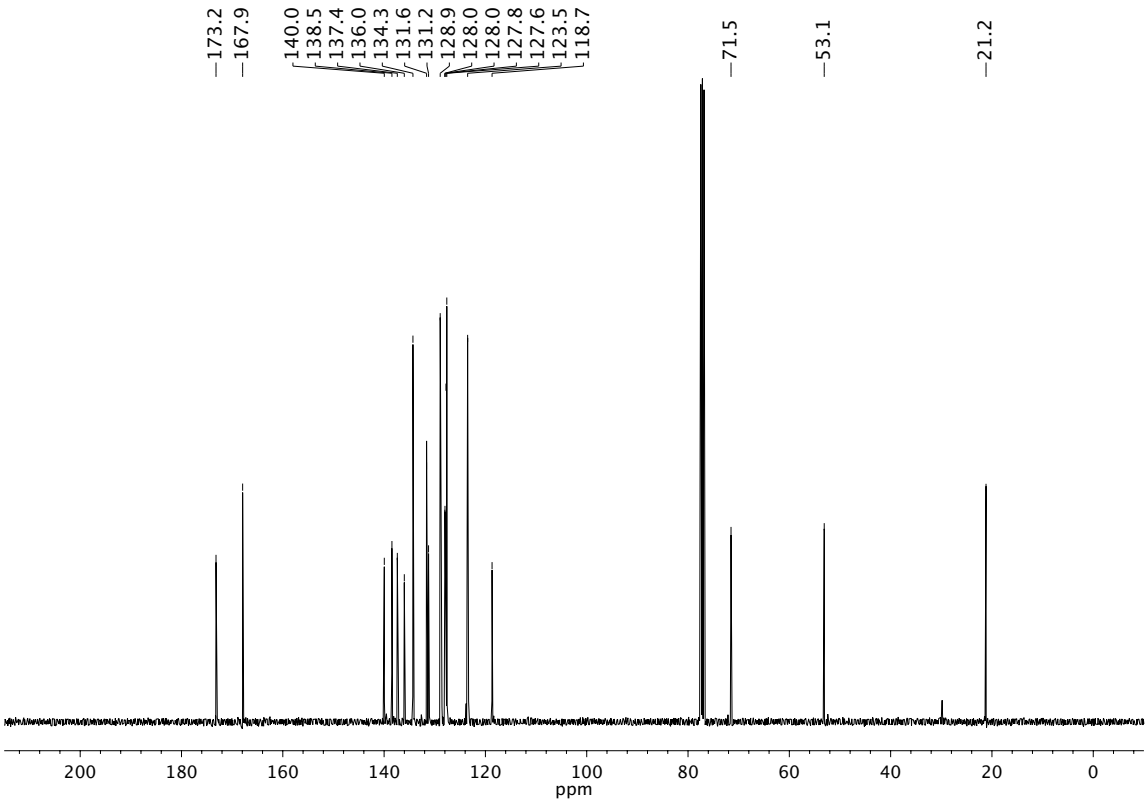
^{13}C NMR (100 MHz, $CDCl_3$) of compound **35**.



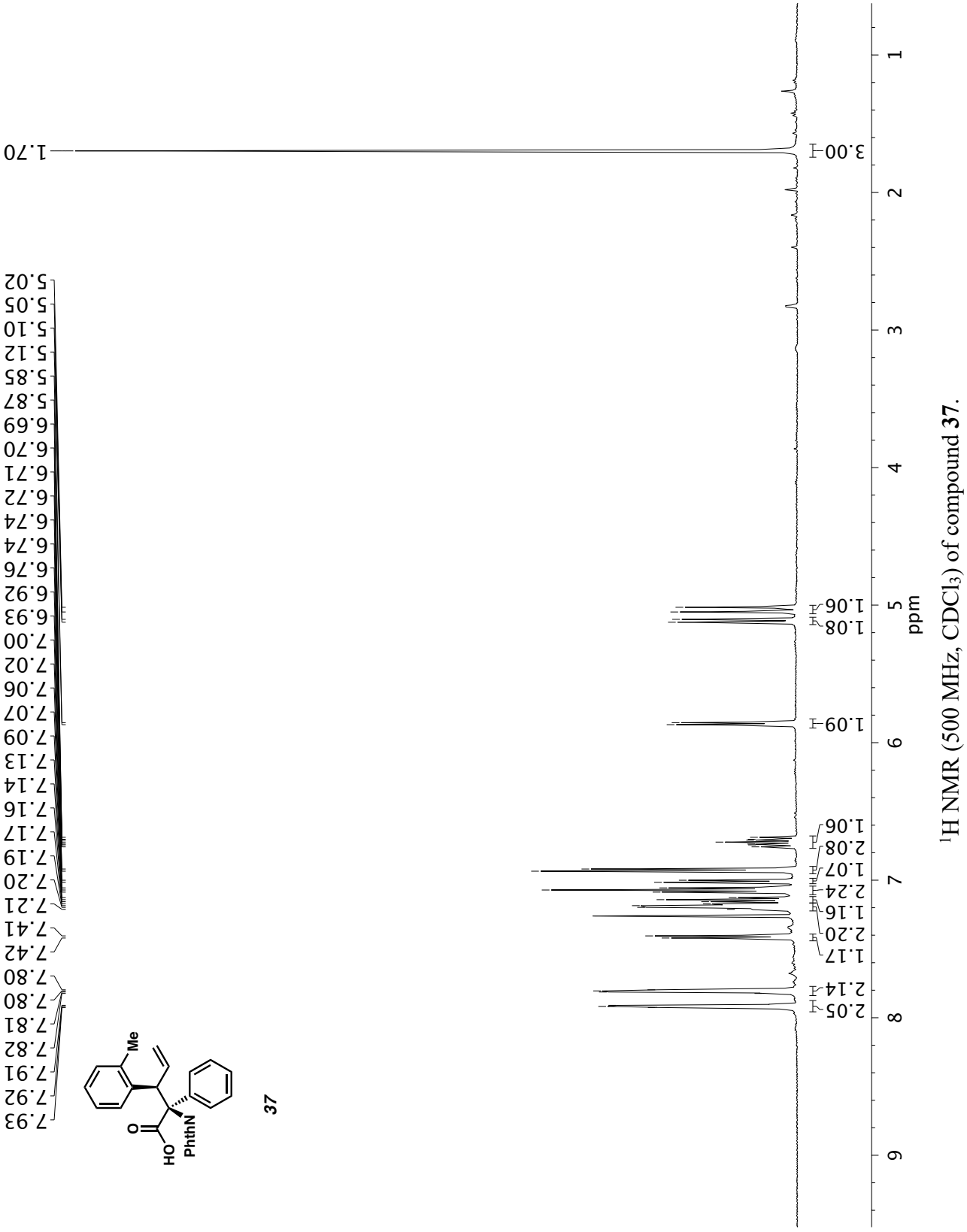
^{1}H NMR (500 MHz, $CDCl_3$) of compound **36**.



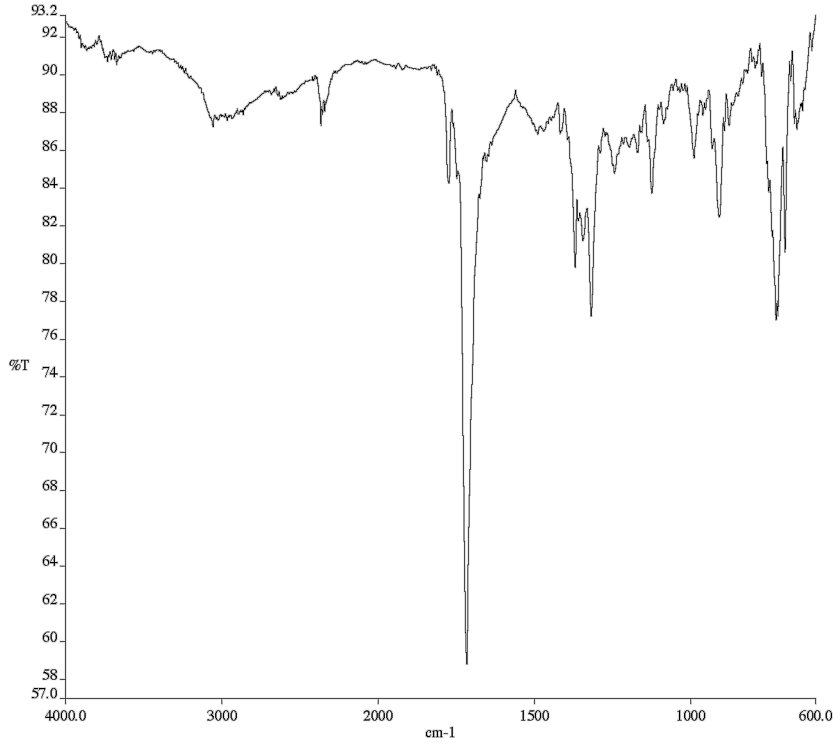
Infrared spectrum (Thin Film, NaCl) of compound **36**.



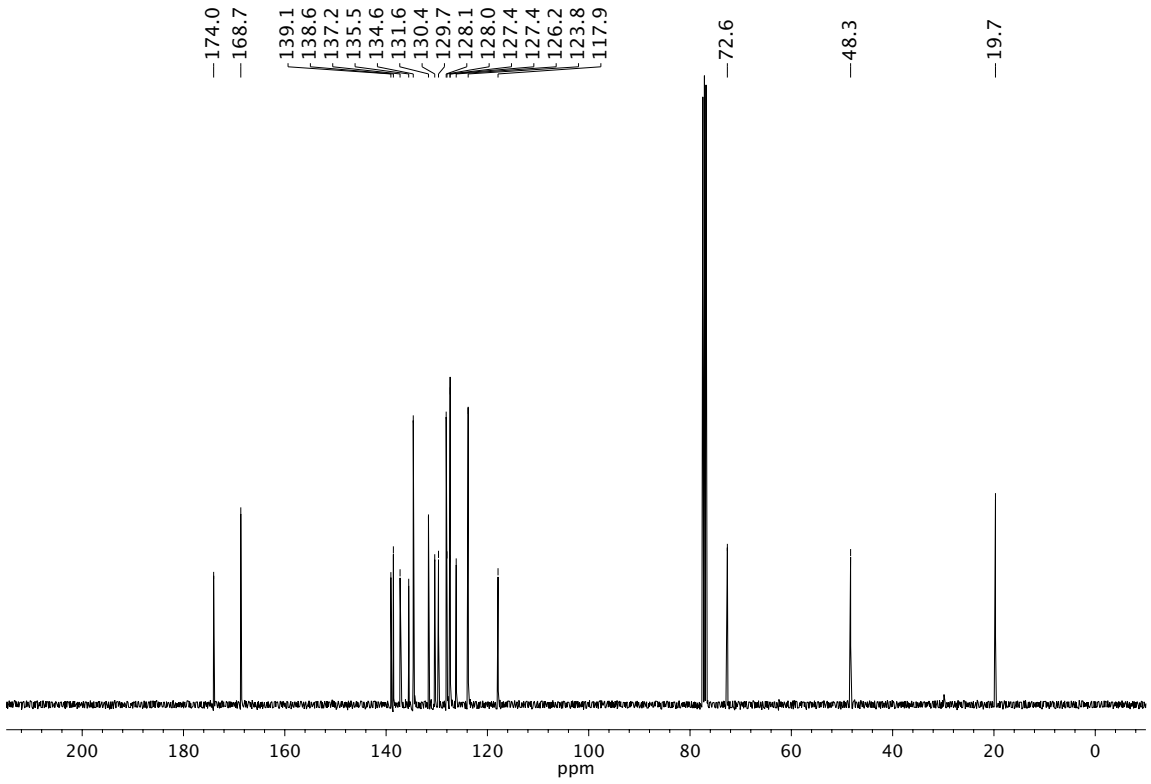
^{13}C NMR (100 MHz, $CDCl_3$) of compound **36**.



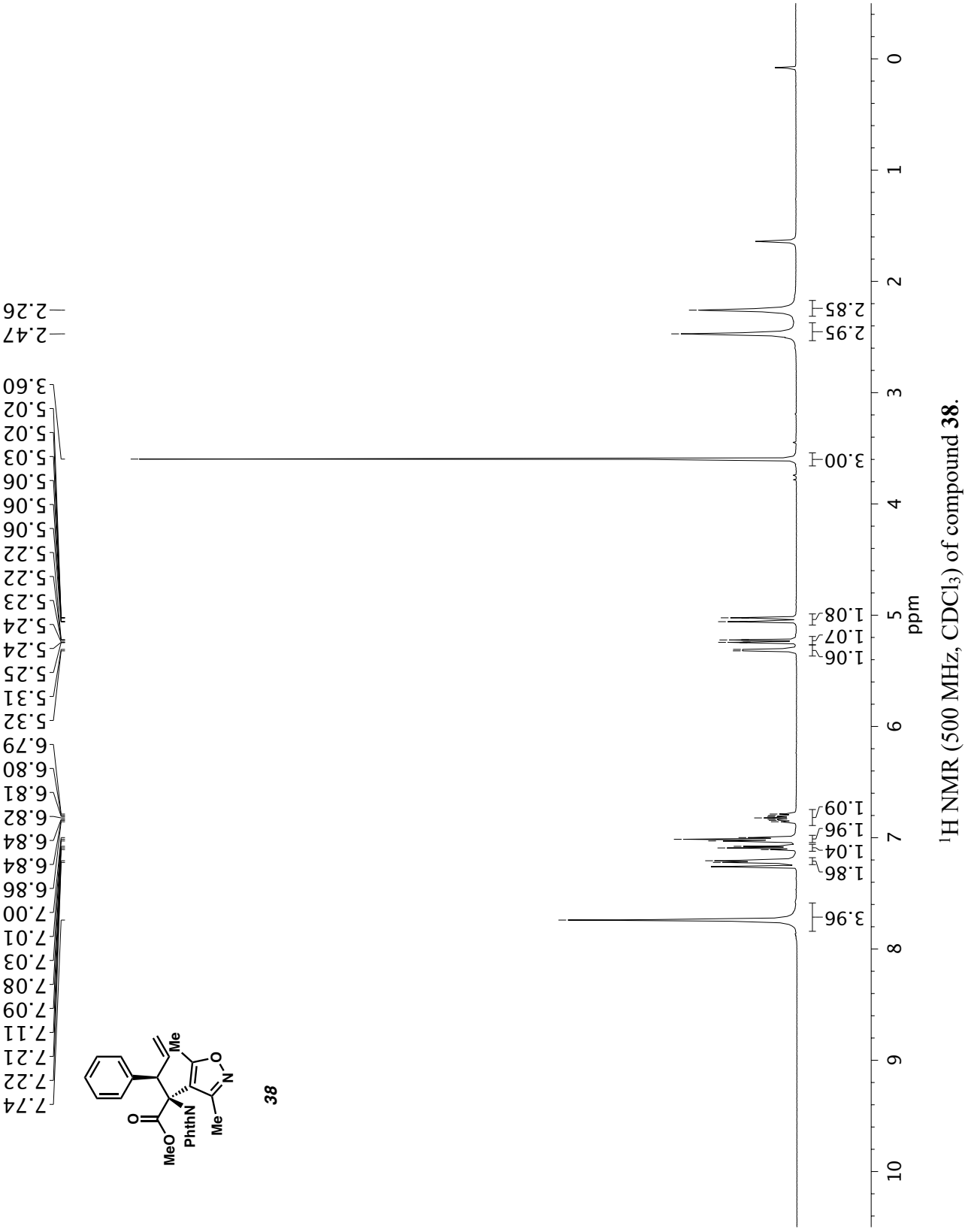
^{1}H NMR (500 MHz, $CDCl_3$) of compound **37**.



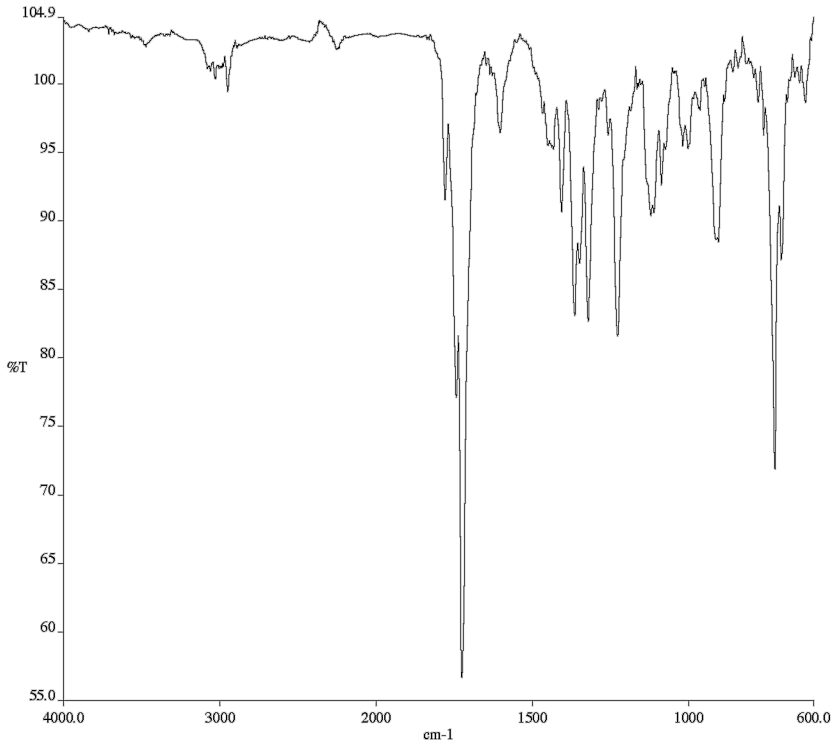
Infrared spectrum (Thin Film, NaCl) of compound **37**.



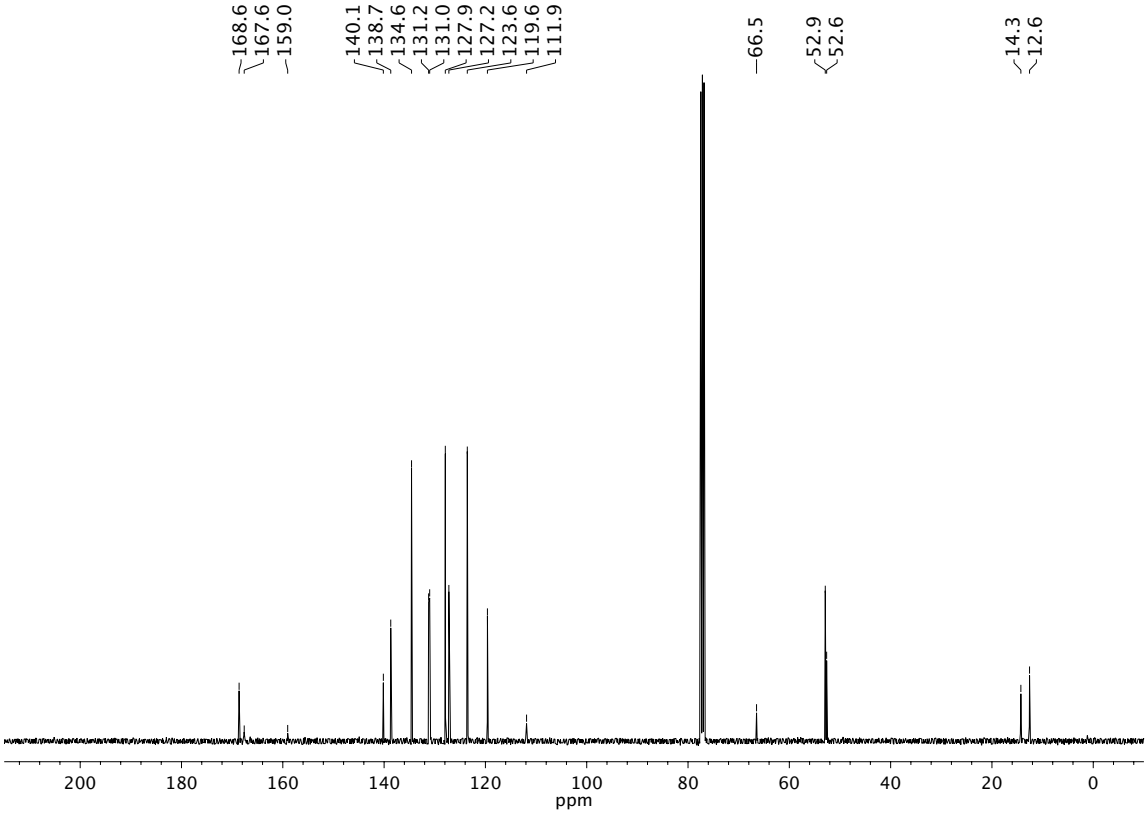
^{13}C NMR (100 MHz, $CDCl_3$) of compound **37**.



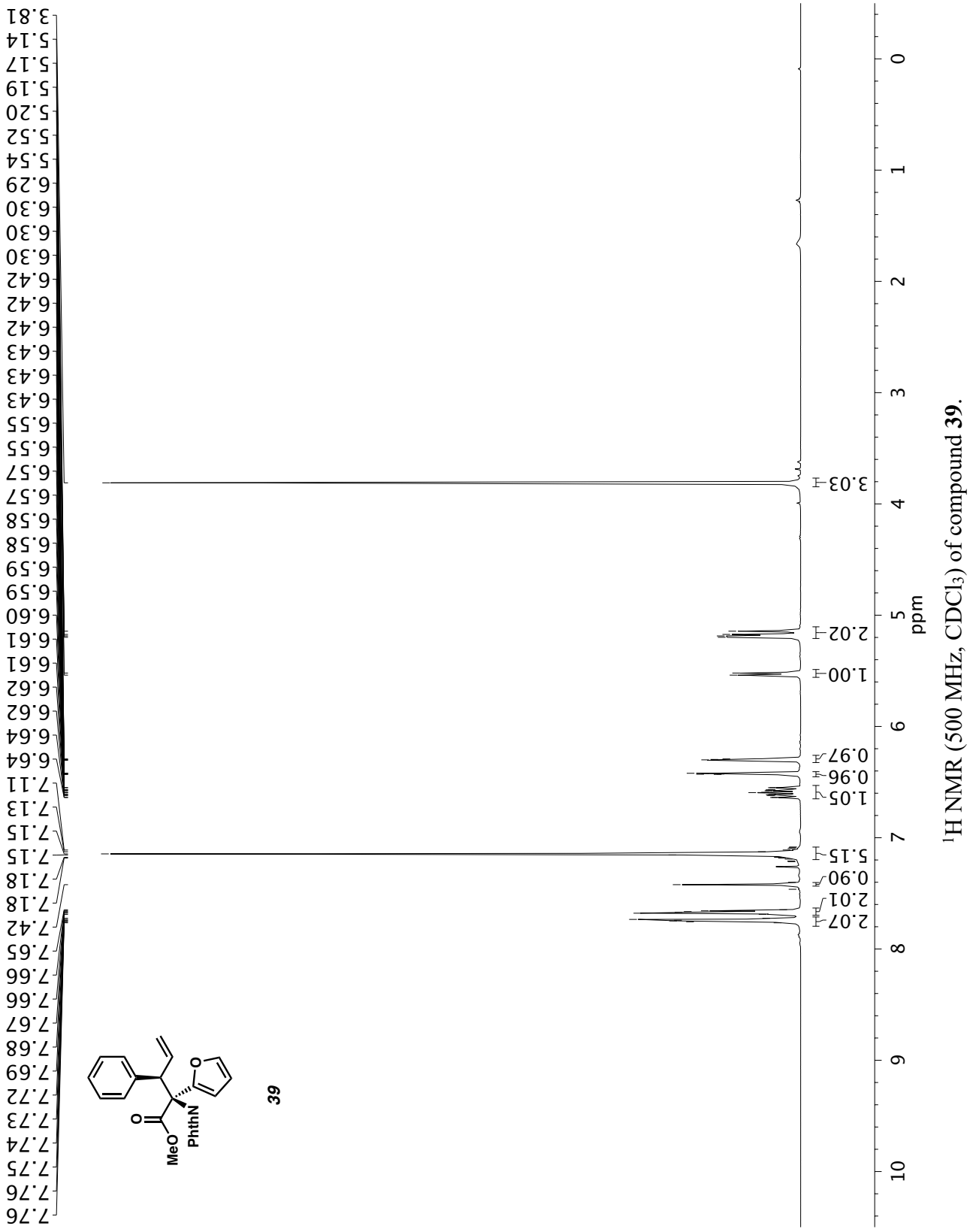
^{1}H NMR (500 MHz, $CDCl_3$) of compound **38**.



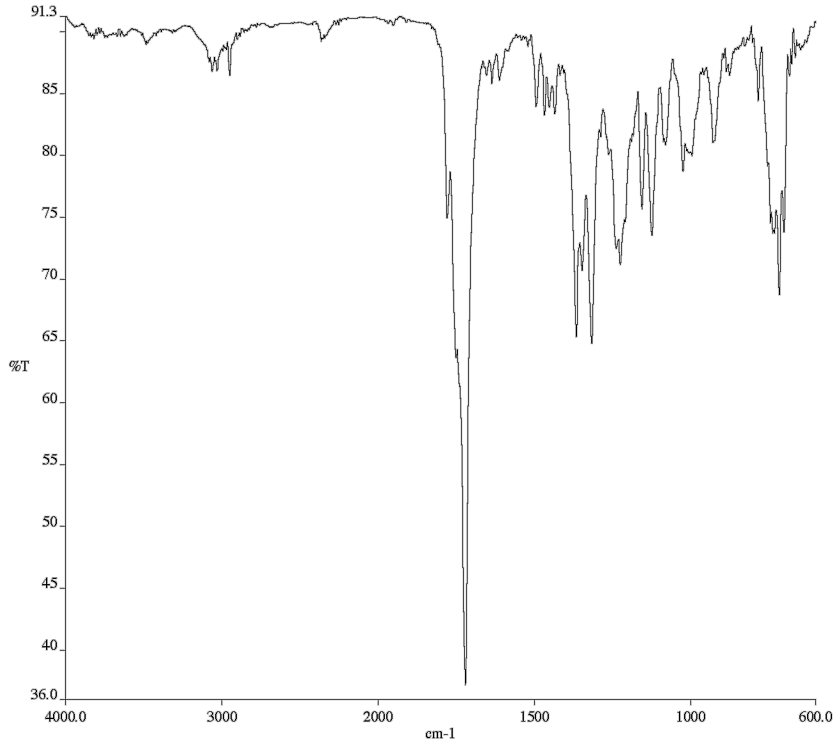
Infrared spectrum (Thin Film, NaCl) of compound **38**.



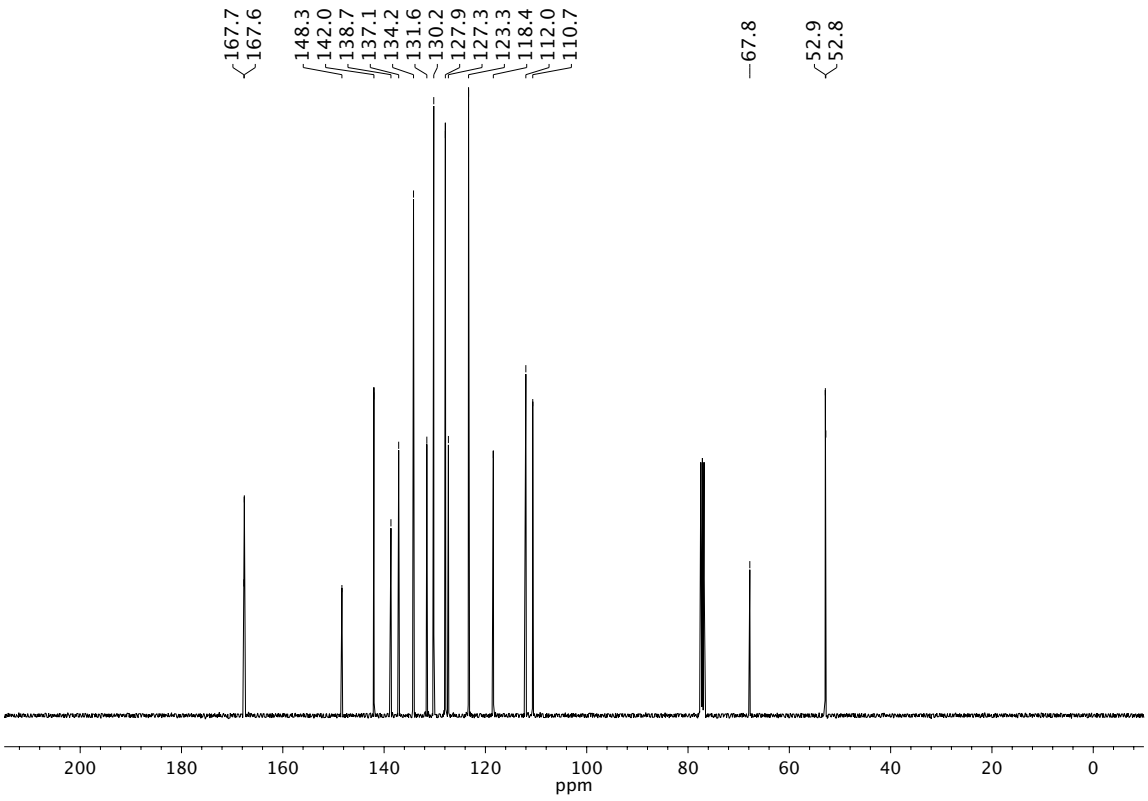
^{13}C NMR (100 MHz, $CDCl_3$) of compound **38**.



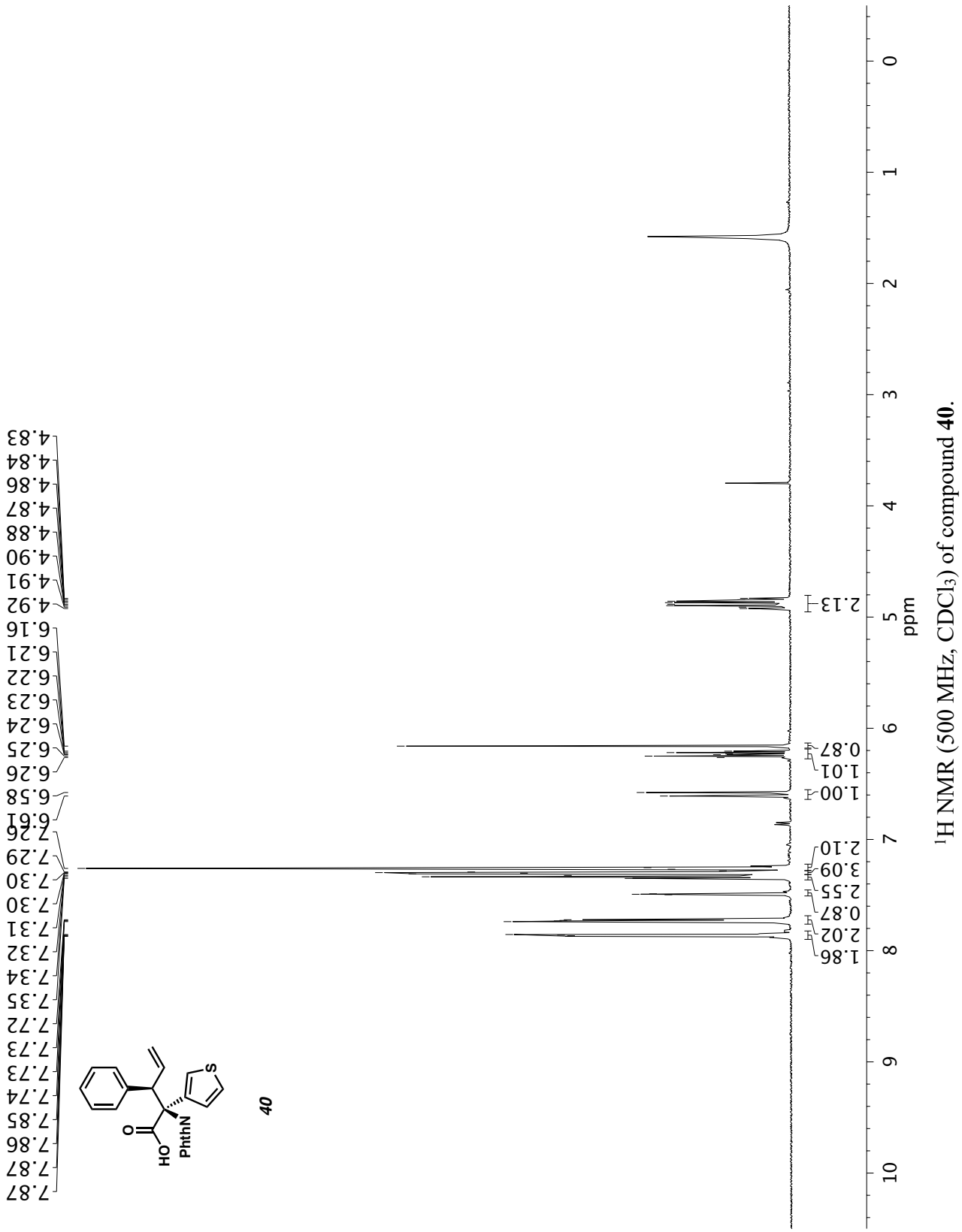
^{1}H NMR (500 MHz, $CDCl_3$) of compound **39**.



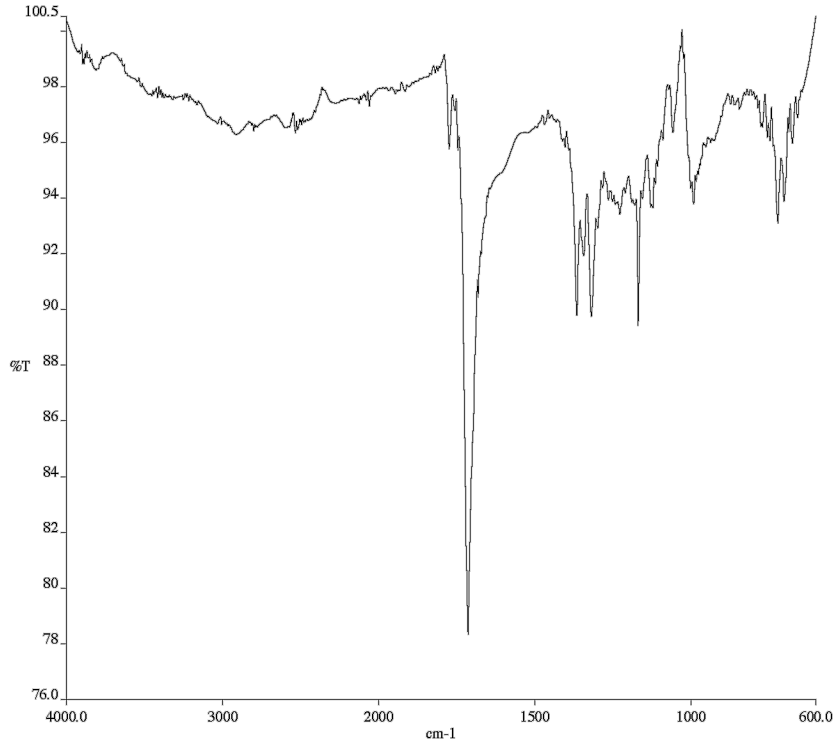
Infrared spectrum (Thin Film, NaCl) of compound **39**.



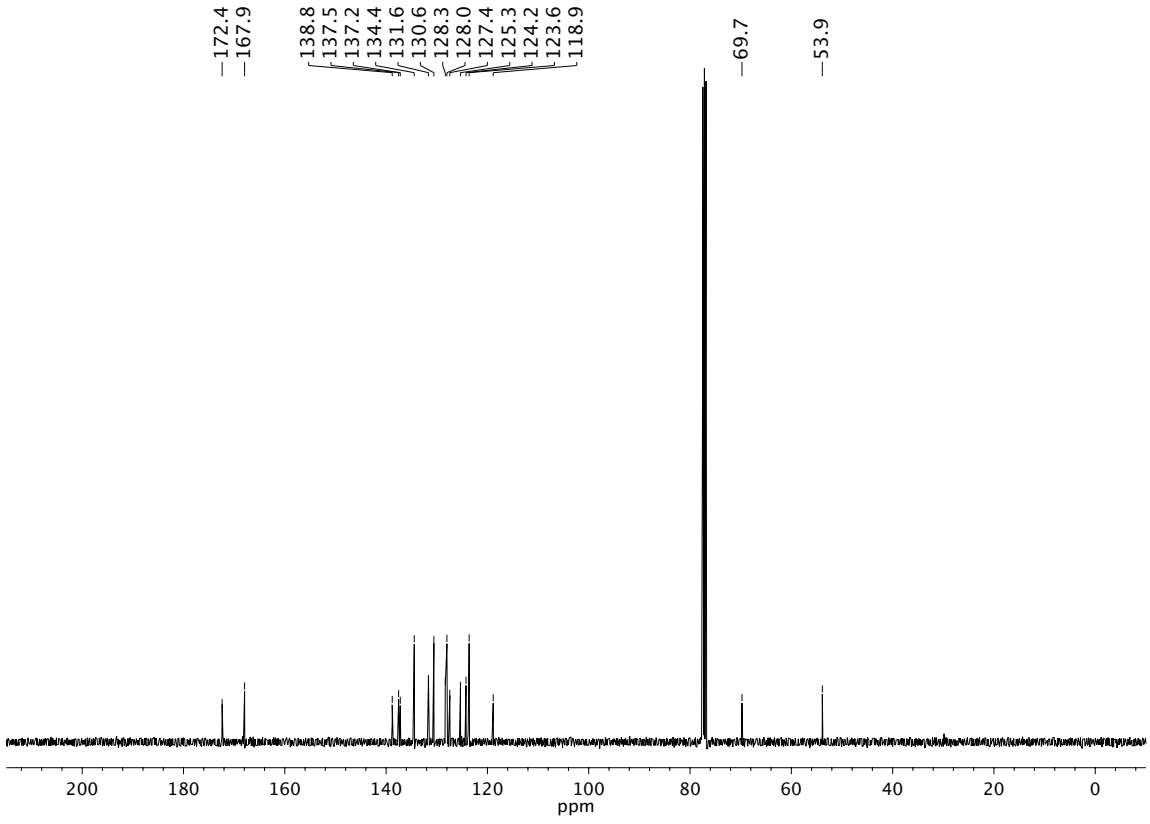
^{13}C NMR (100 MHz, $CDCl_3$) of compound **39**.



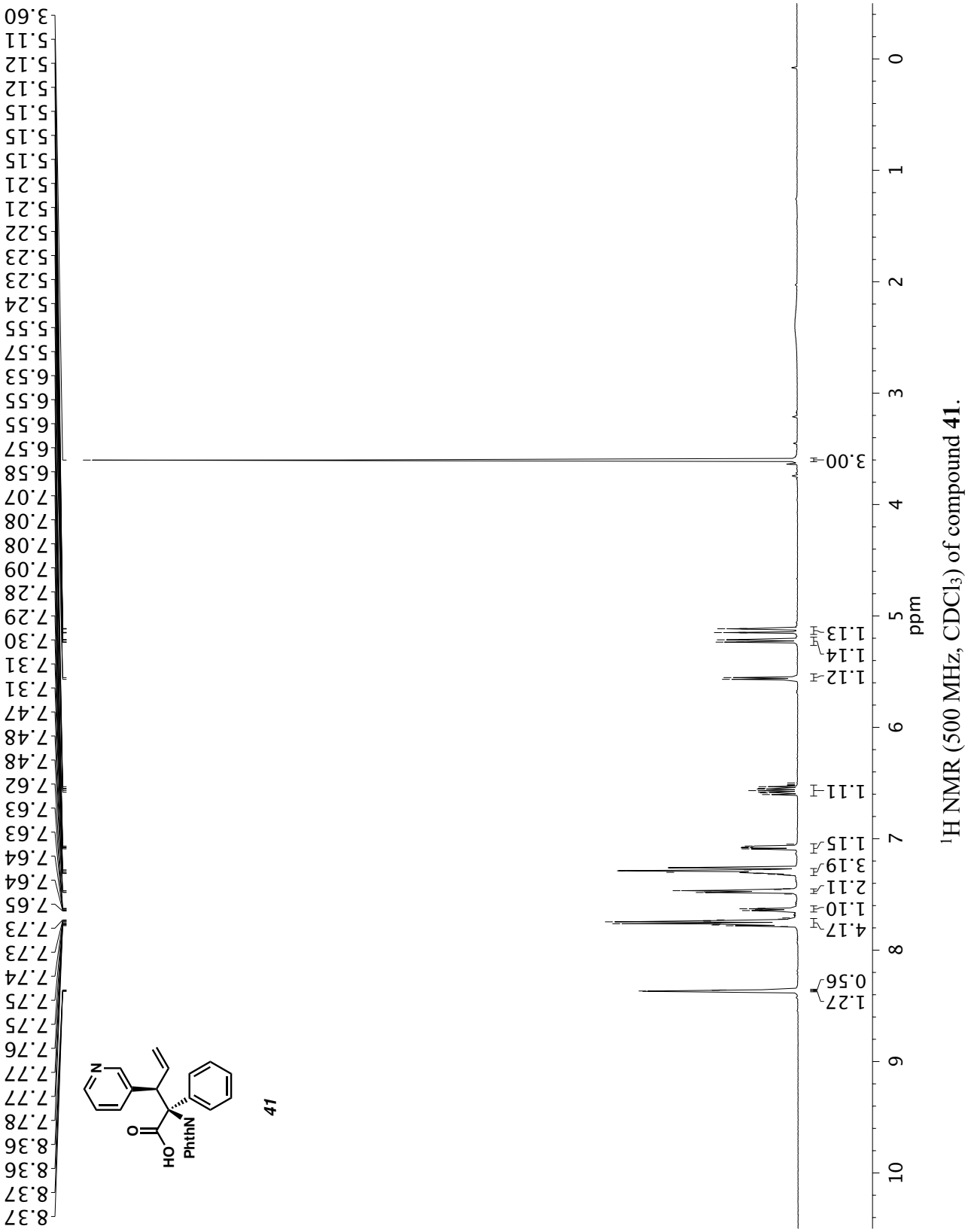
^{1}H NMR (500 MHz, $CDCl_3$) of compound **40**.



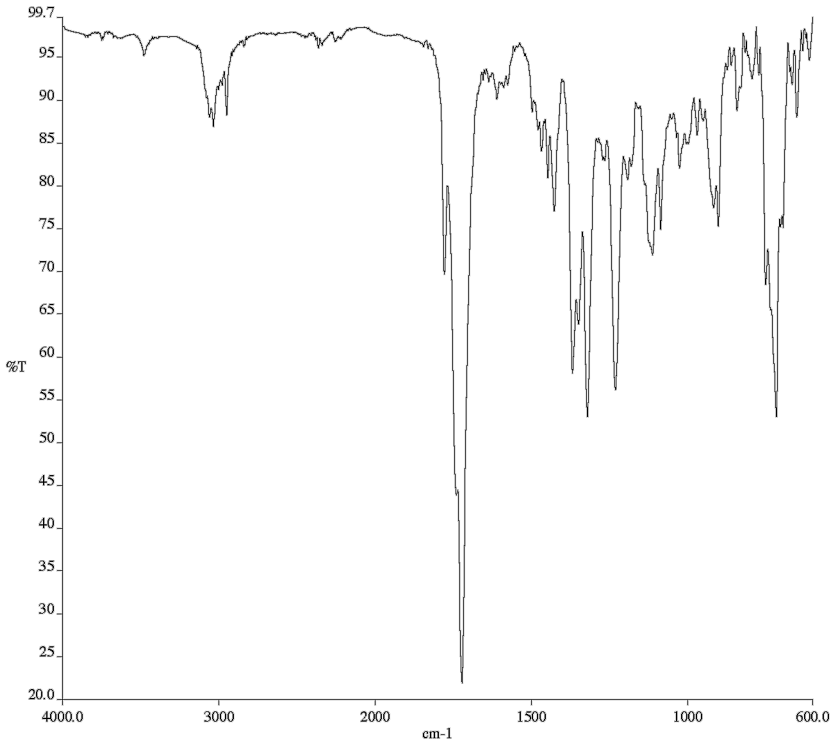
Infrared spectrum (Thin Film, NaCl) of compound **40**.



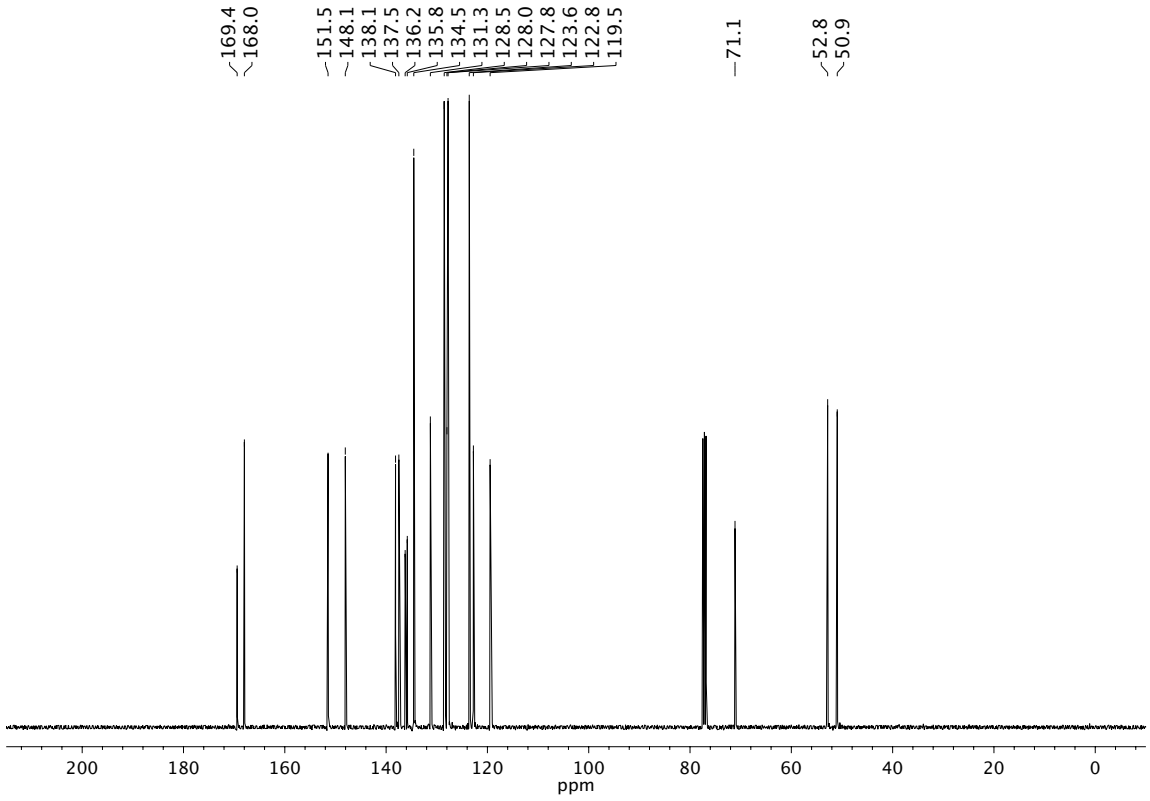
^{13}C NMR (100 MHz, $CDCl_3$) of compound **40**.



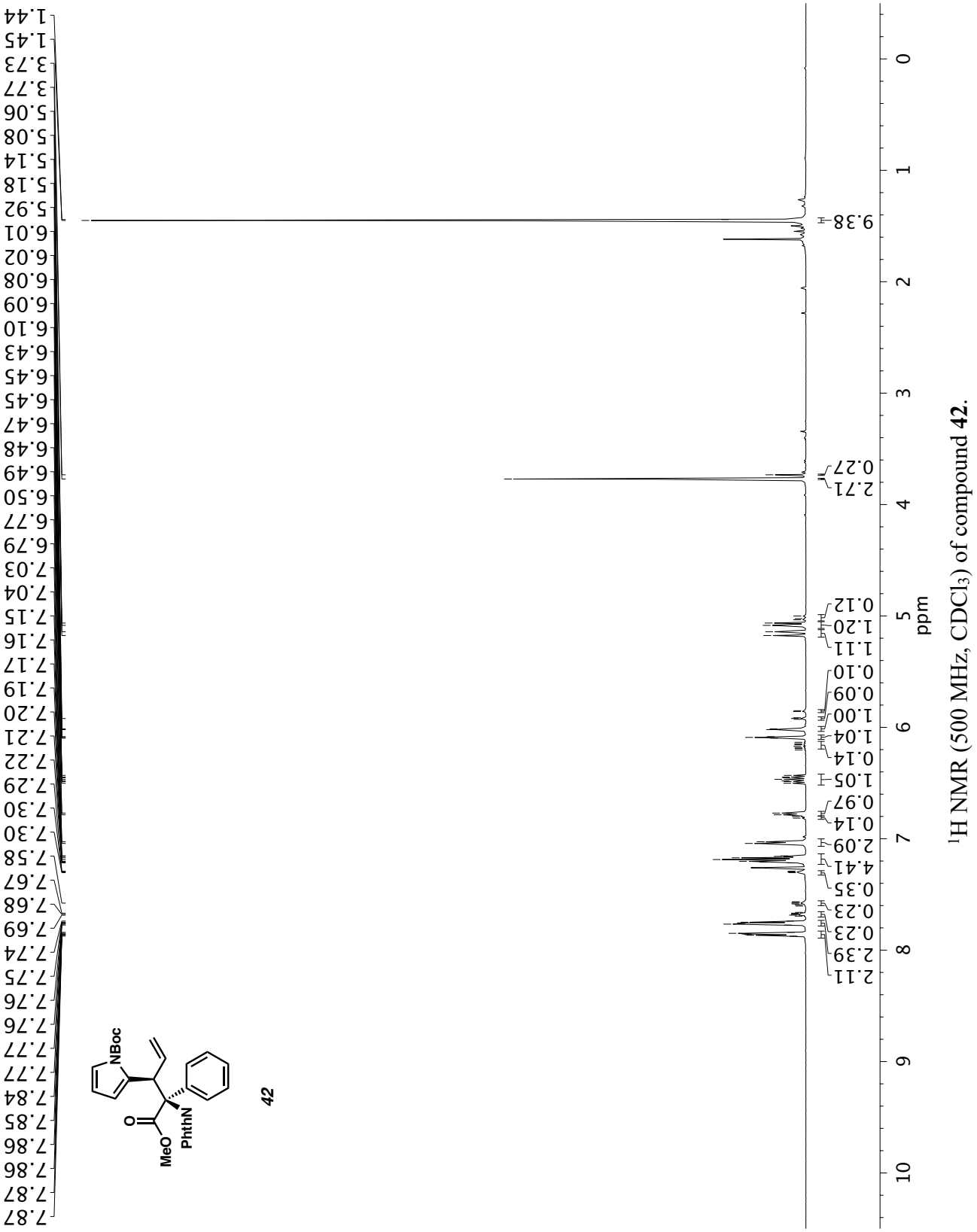
^{1}H NMR (500 MHz, $CDCl_3$) of compound **41**.



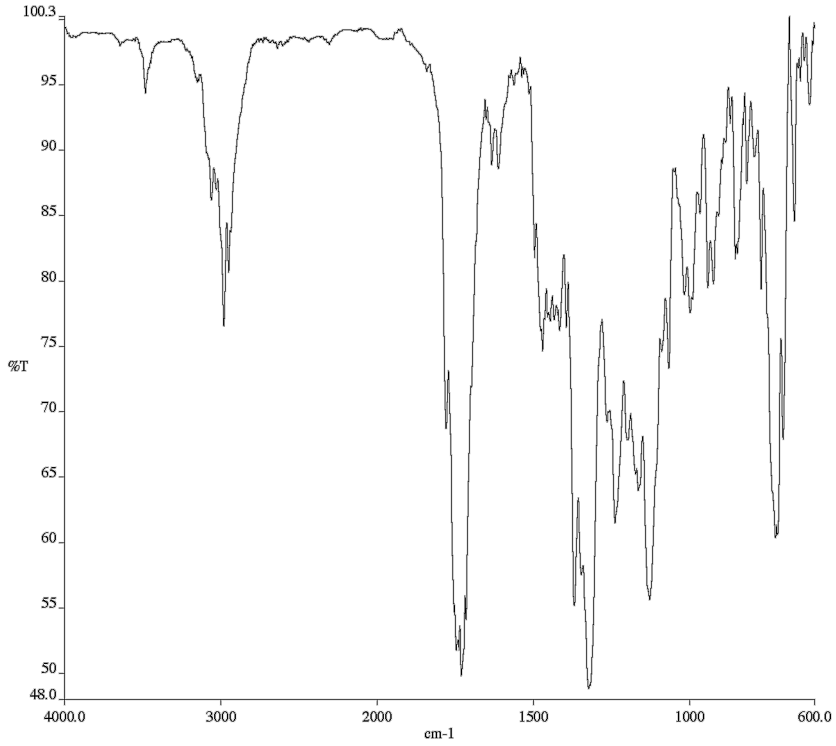
Infrared spectrum (Thin Film, NaCl) of compound **41**.



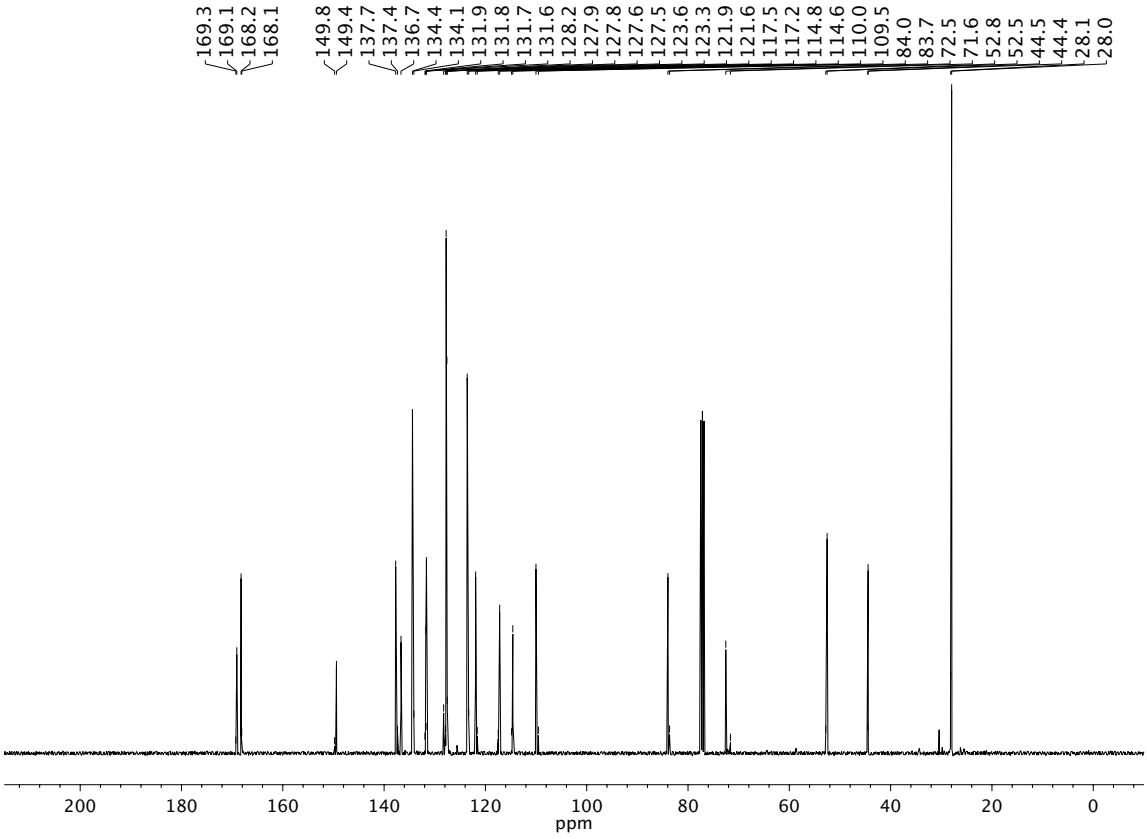
^{13}C NMR (100 MHz, $CDCl_3$) of compound **41**.



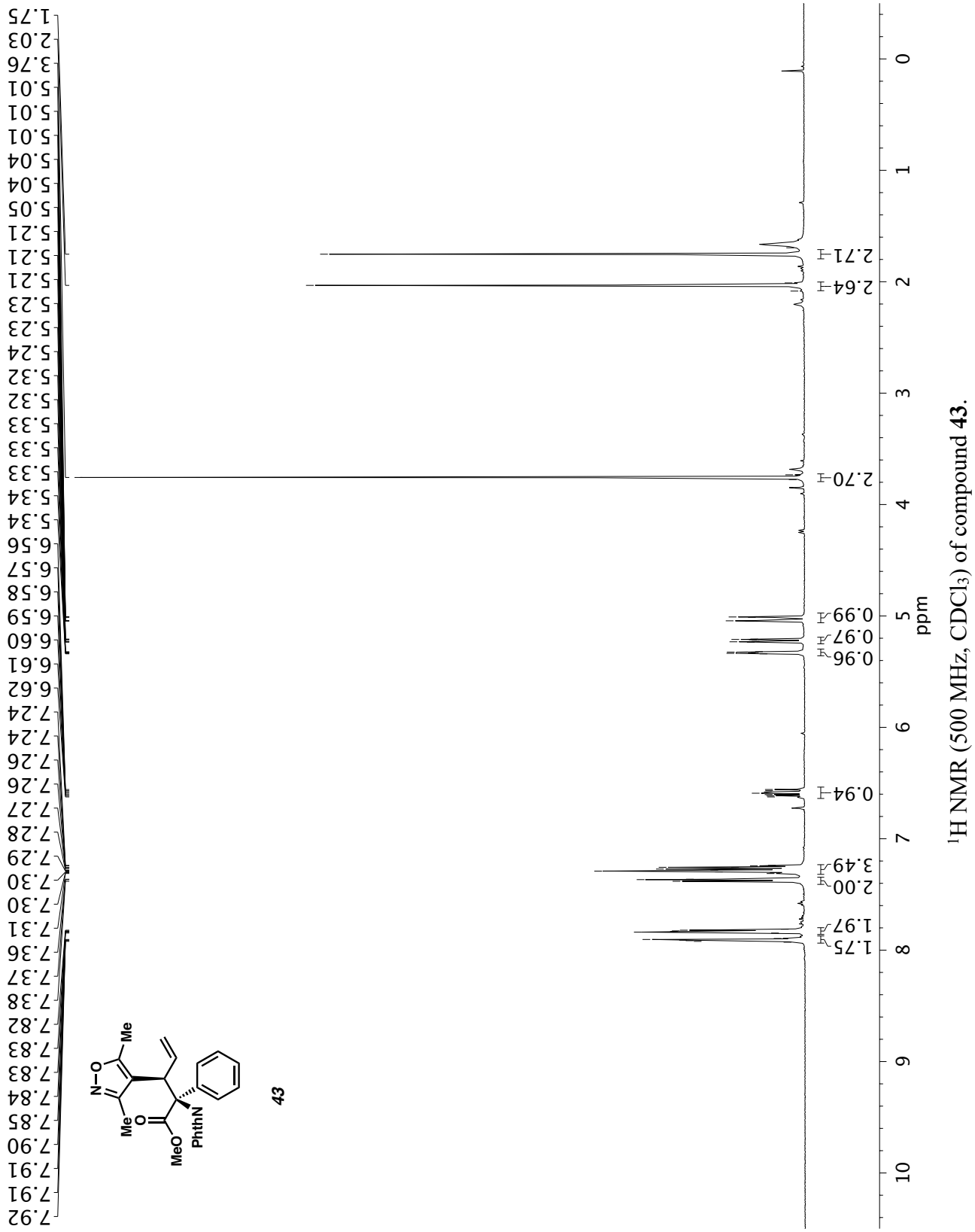
^{1}H NMR (500 MHz, $CDCl_3$) of compound **42**.



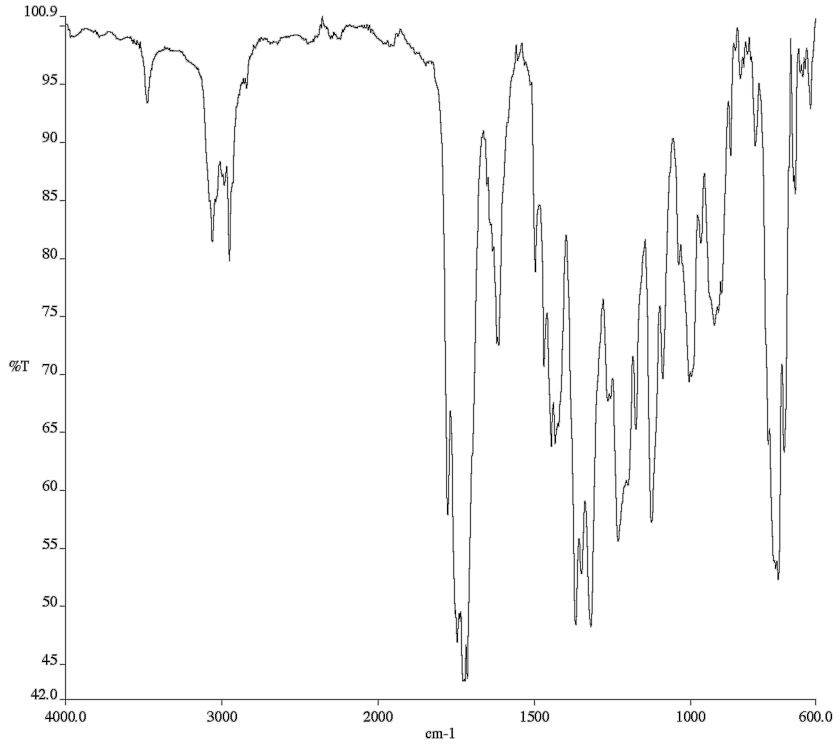
Infrared spectrum (Thin Film, NaCl) of compound **42**.



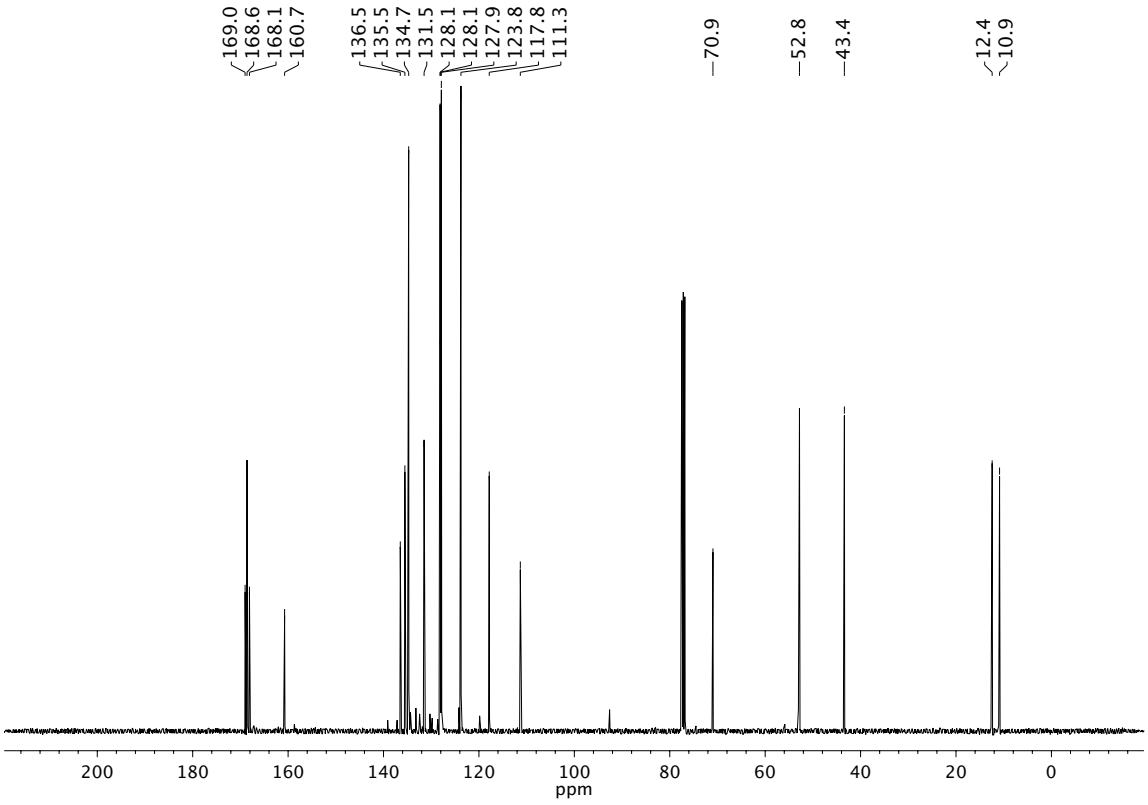
^{13}C NMR (100 MHz, $CDCl_3$) of compound **42**.



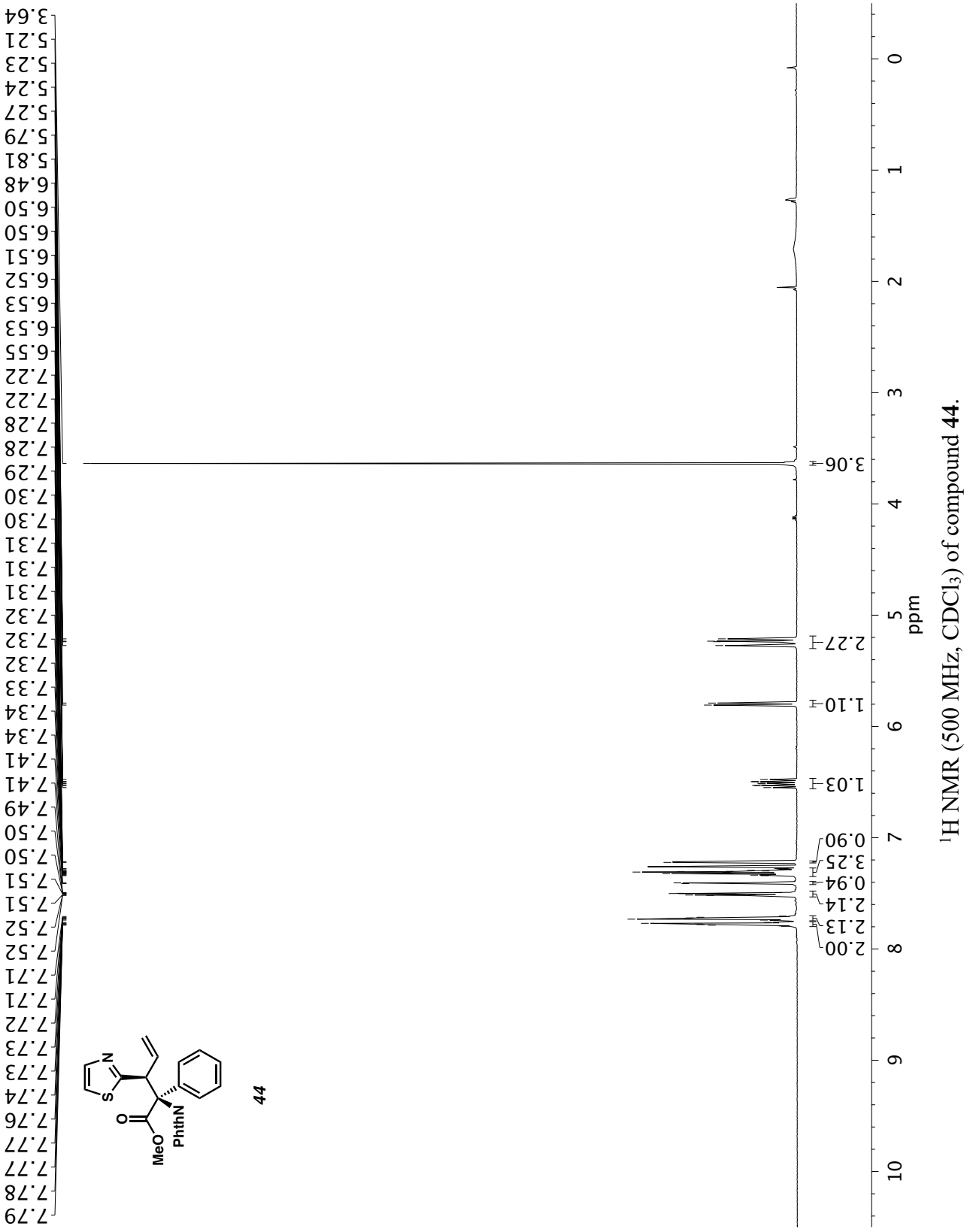
^{1}H NMR (500 MHz, $CDCl_3$) of compound **43**.



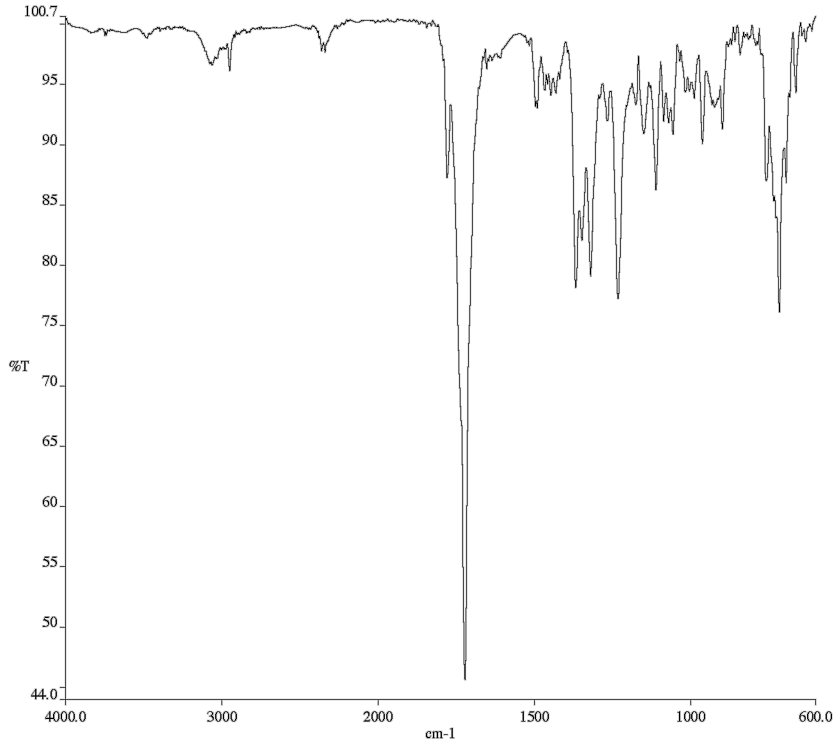
Infrared spectrum (Thin Film, NaCl) of compound **43**.



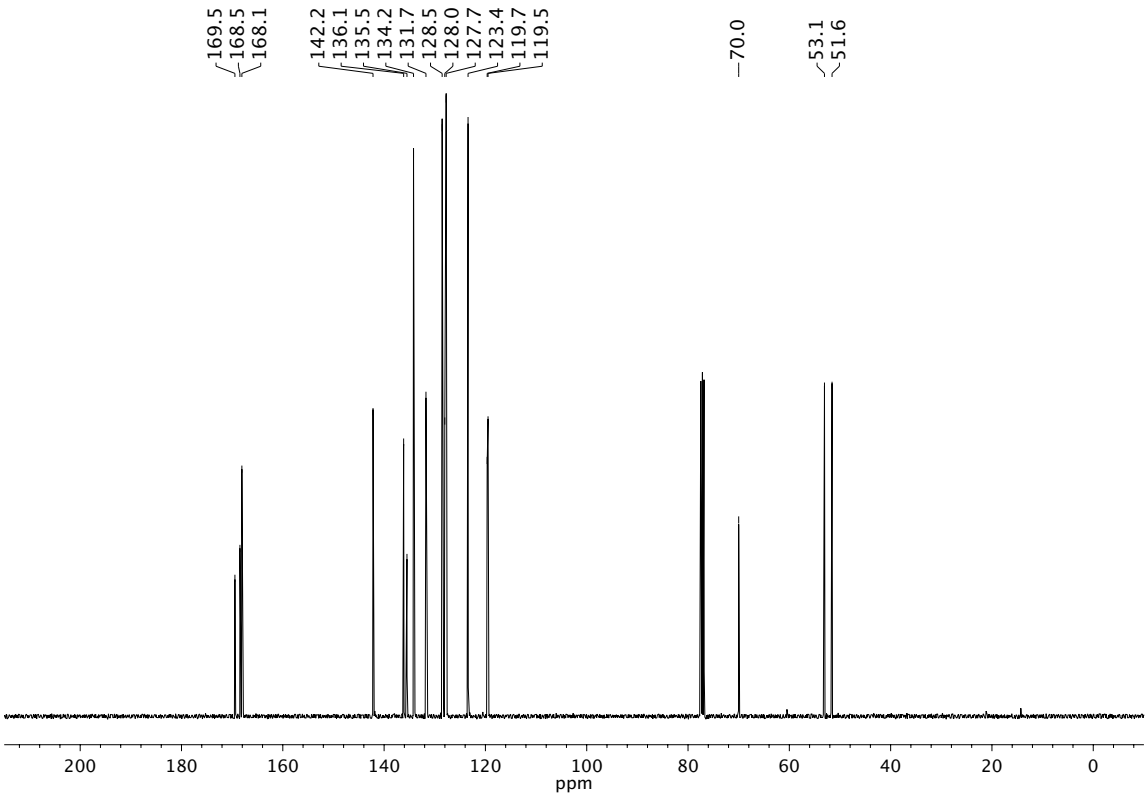
^{13}C NMR (100 MHz, $CDCl_3$) of compound **43**.



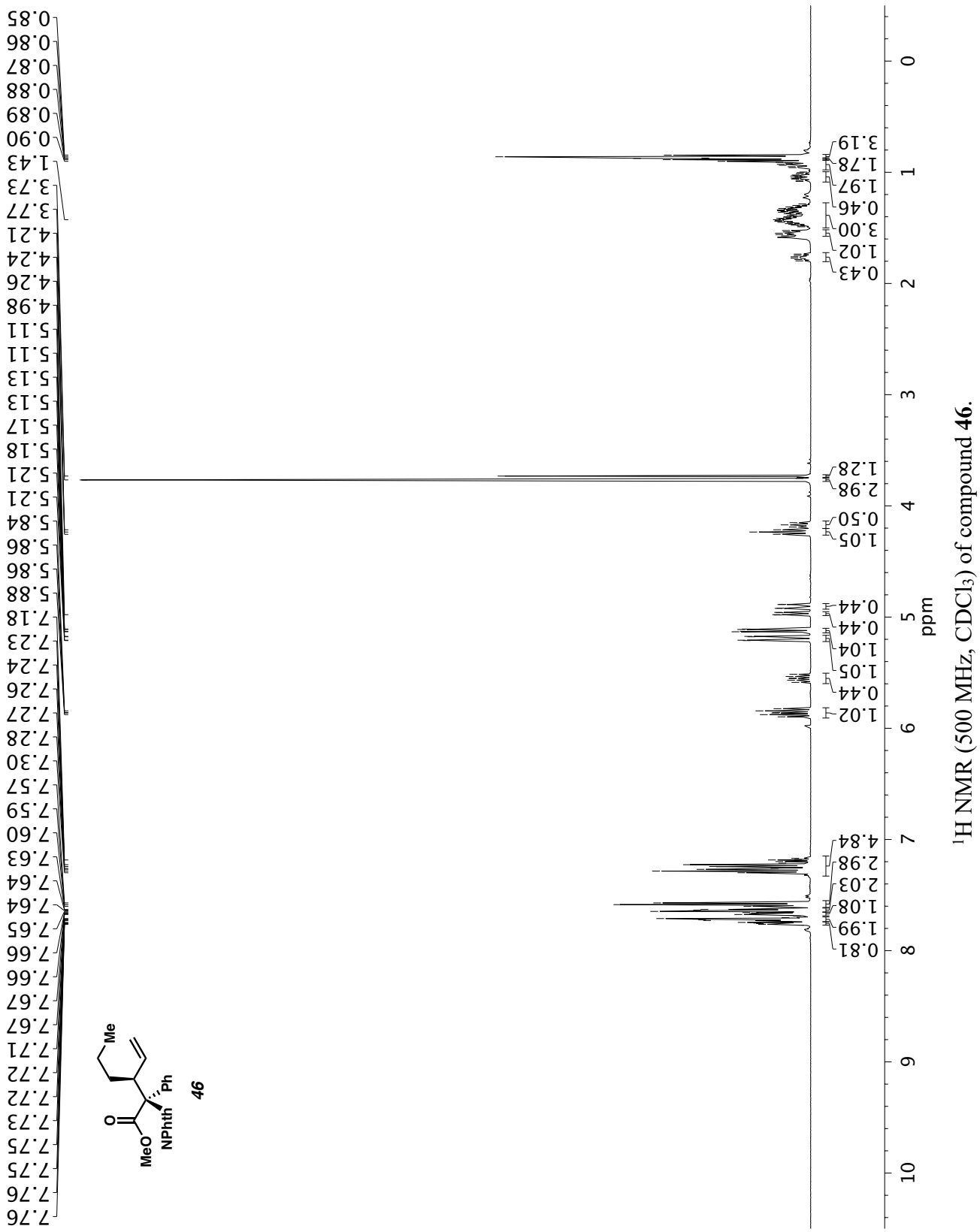
^{1}H NMR (500 MHz, $CDCl_3$) of compound **44**.



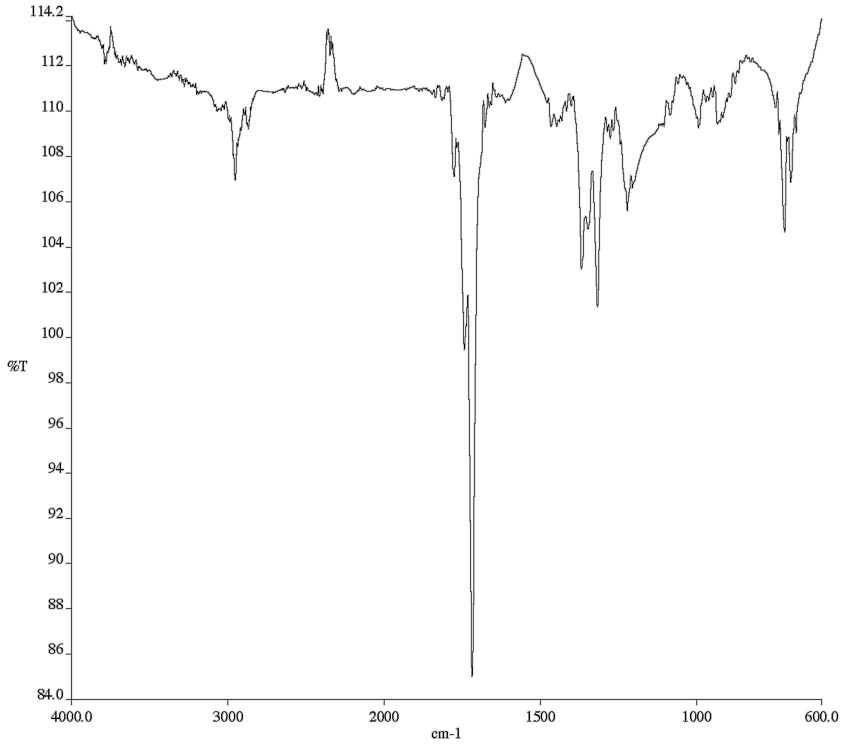
Infrared spectrum (Thin Film, NaCl) of compound **44**.



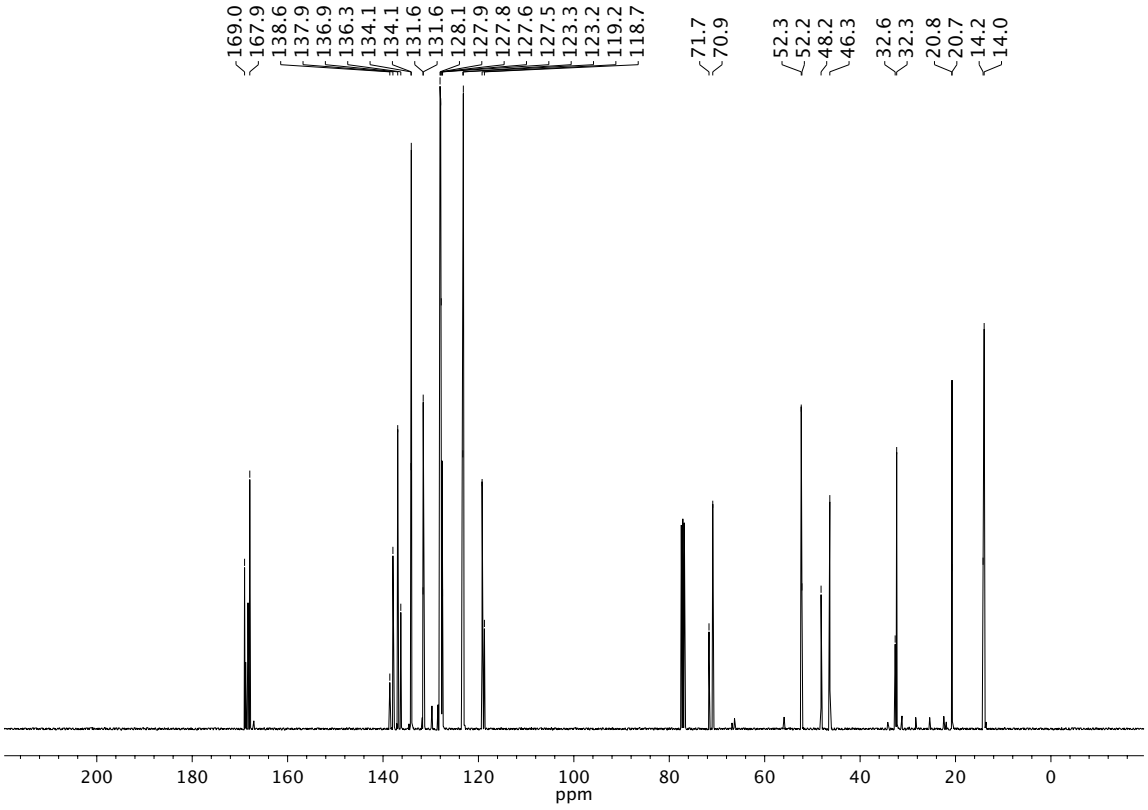
^{13}C NMR (100 MHz, $CDCl_3$) of compound **44**.



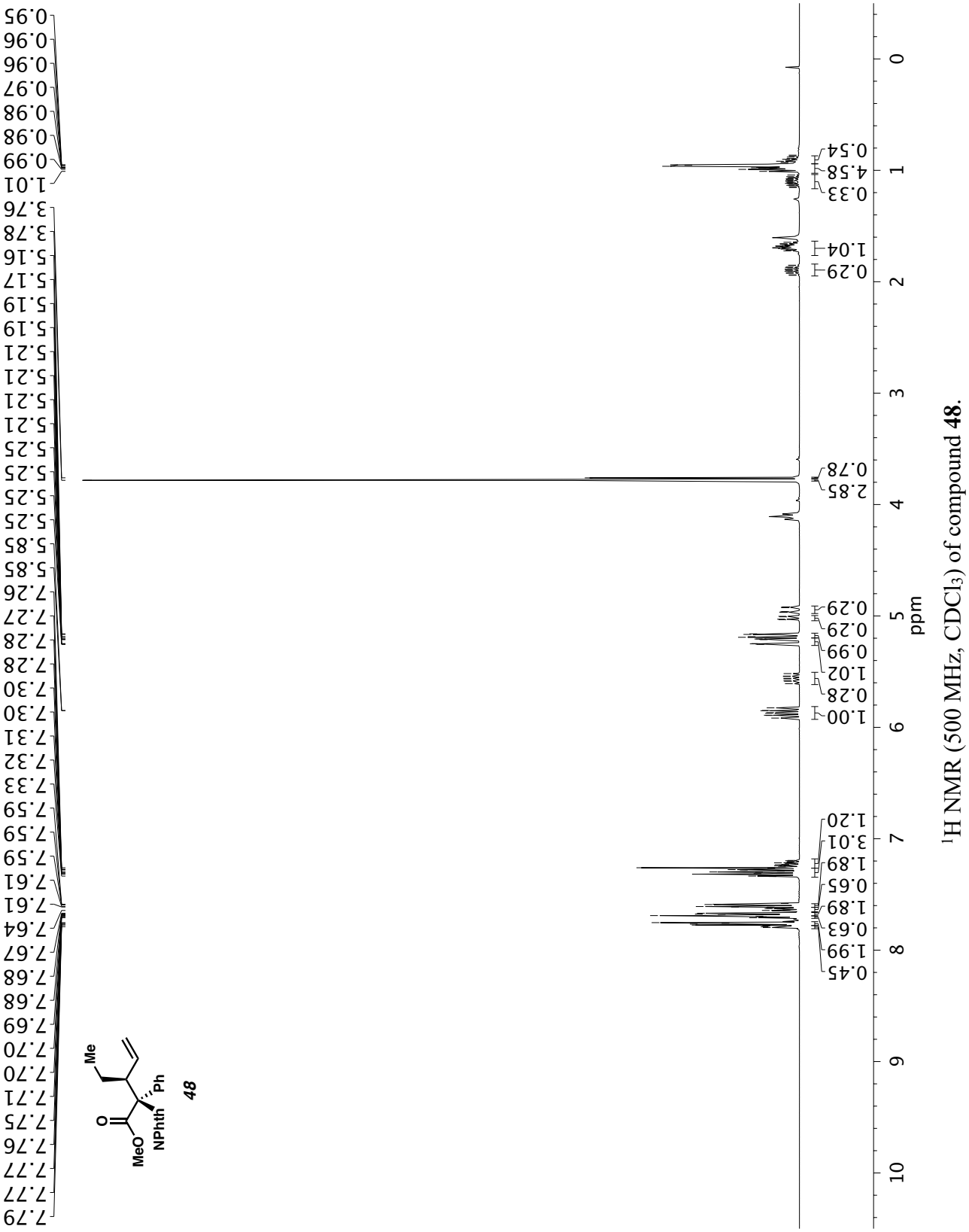
^{1}H NMR (500 MHz, $CDCl_3$) of compound **46**.



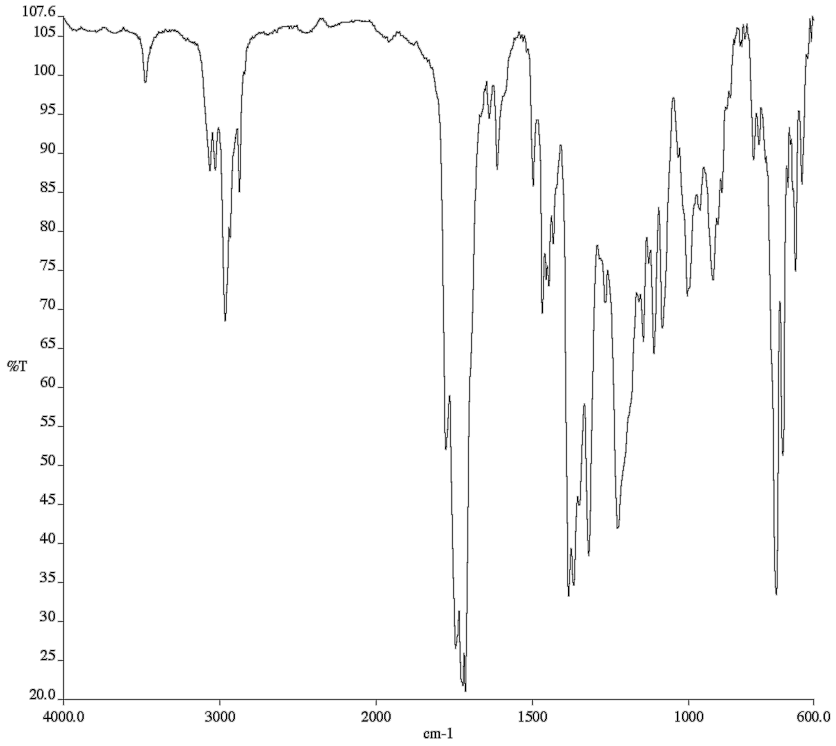
Infrared spectrum (Thin Film, NaCl) of compound **46**.



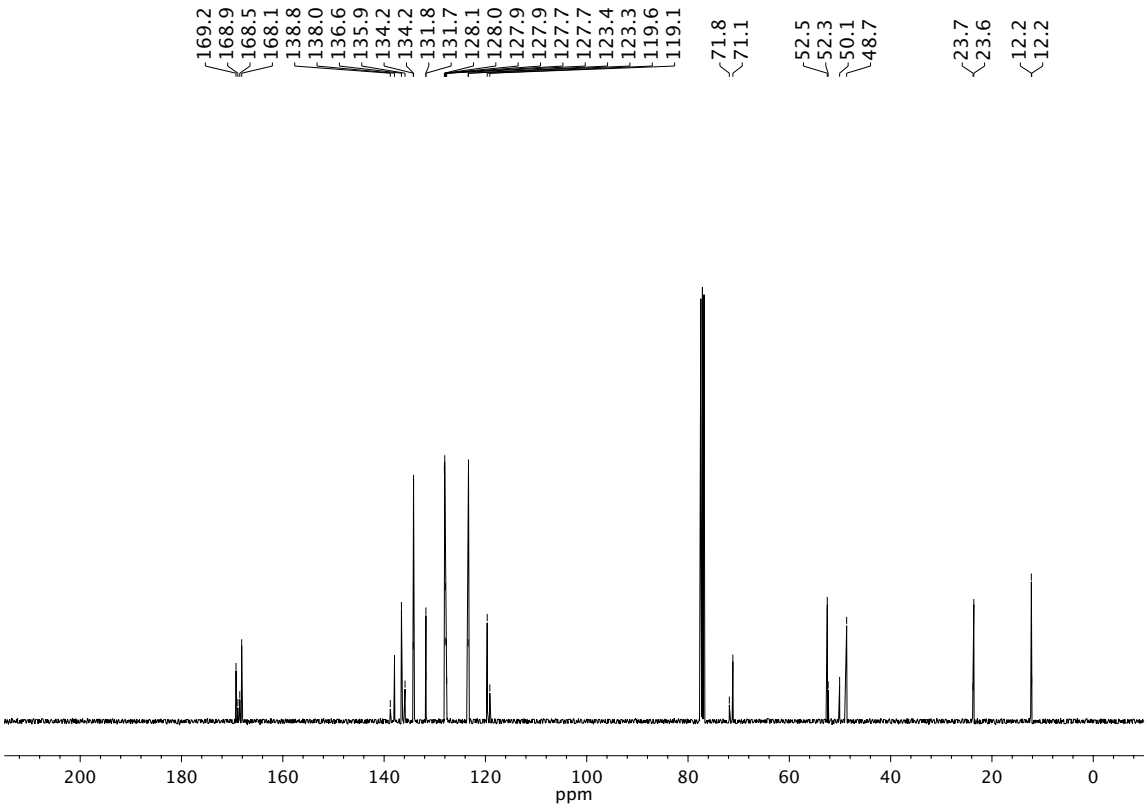
^{13}C NMR (100 MHz, $CDCl_3$) of compound **46**.



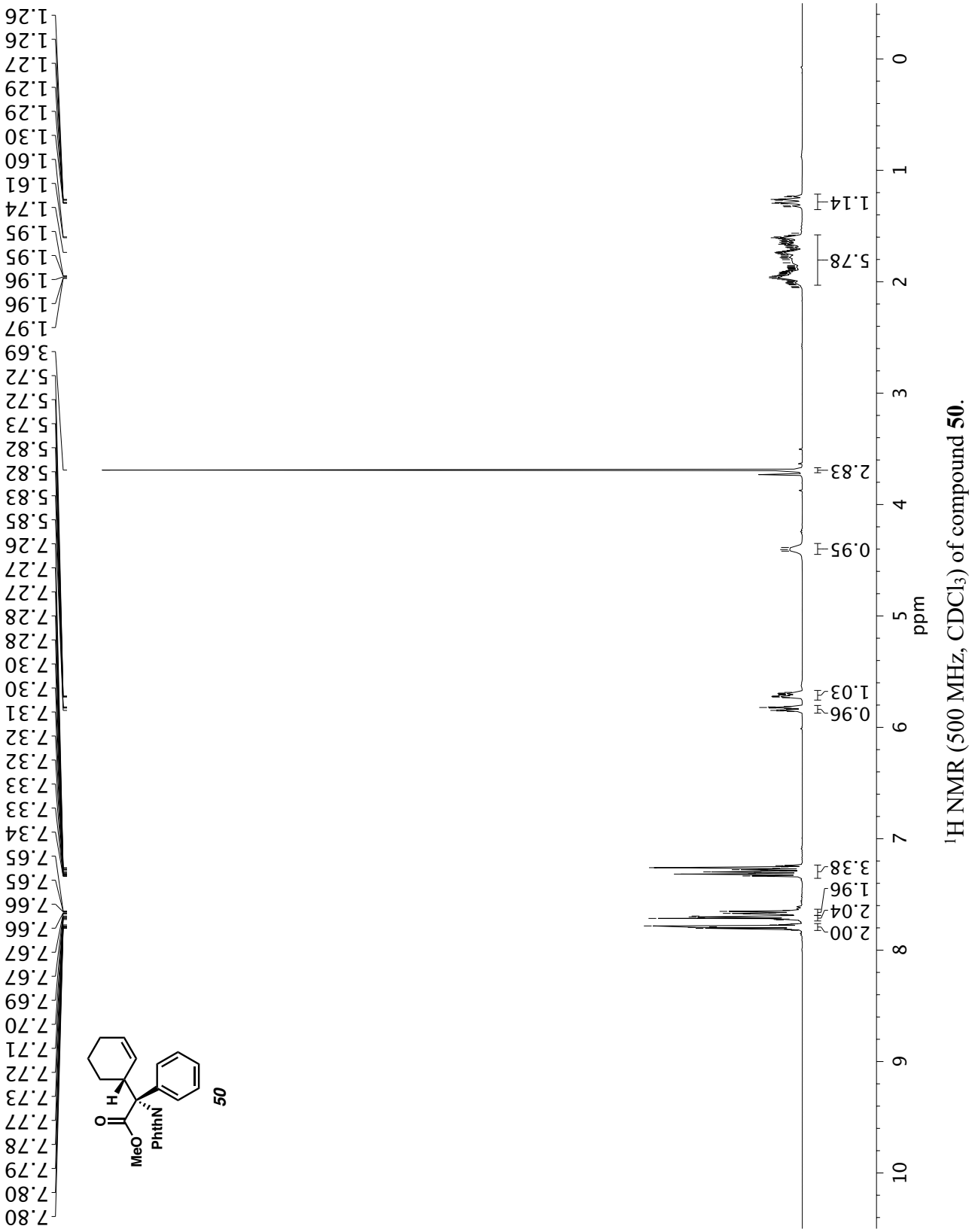
^{1}H NMR (500 MHz, $CDCl_3$) of compound **48**.



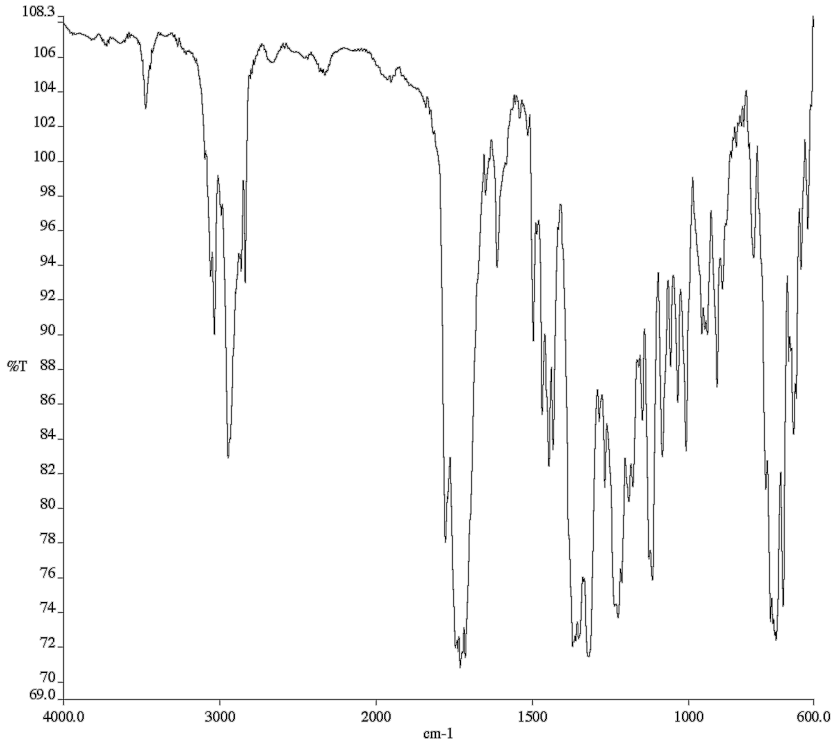
Infrared spectrum (Thin Film, NaCl) of compound **48**.



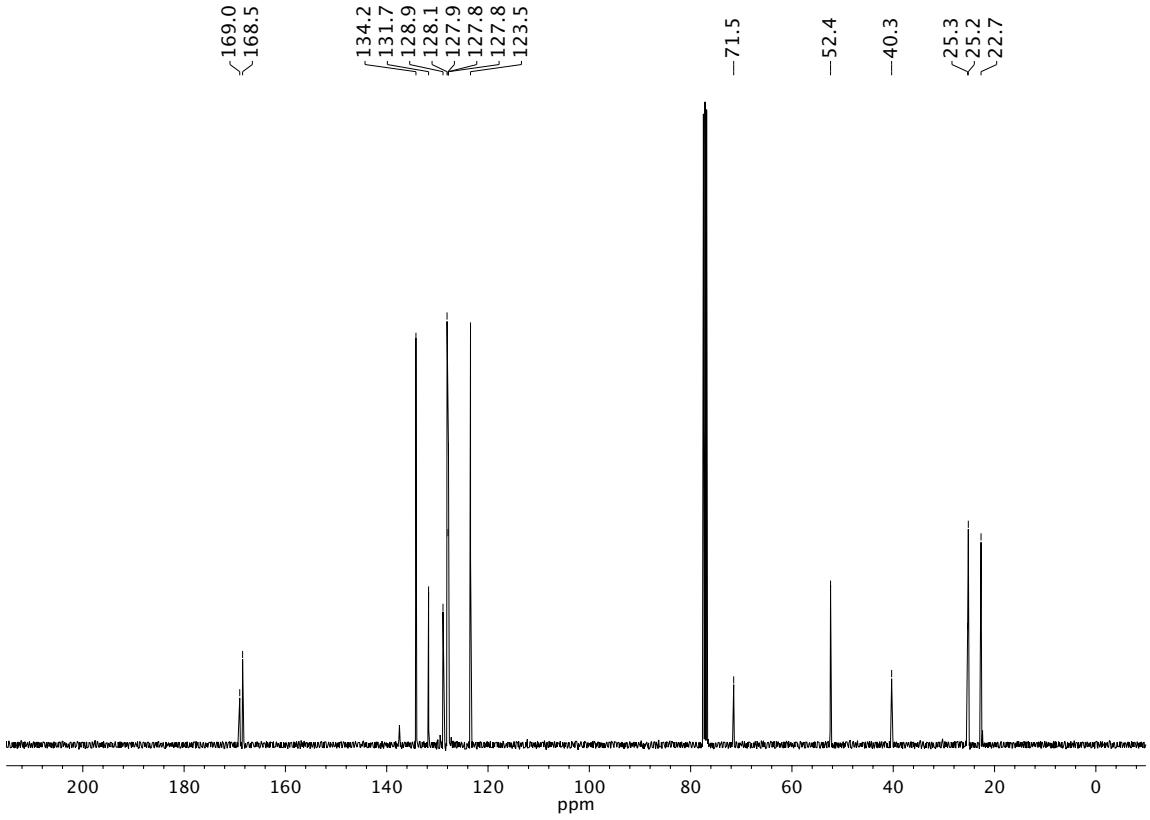
^{13}C NMR (100 MHz, $CDCl_3$) of compound **48**.



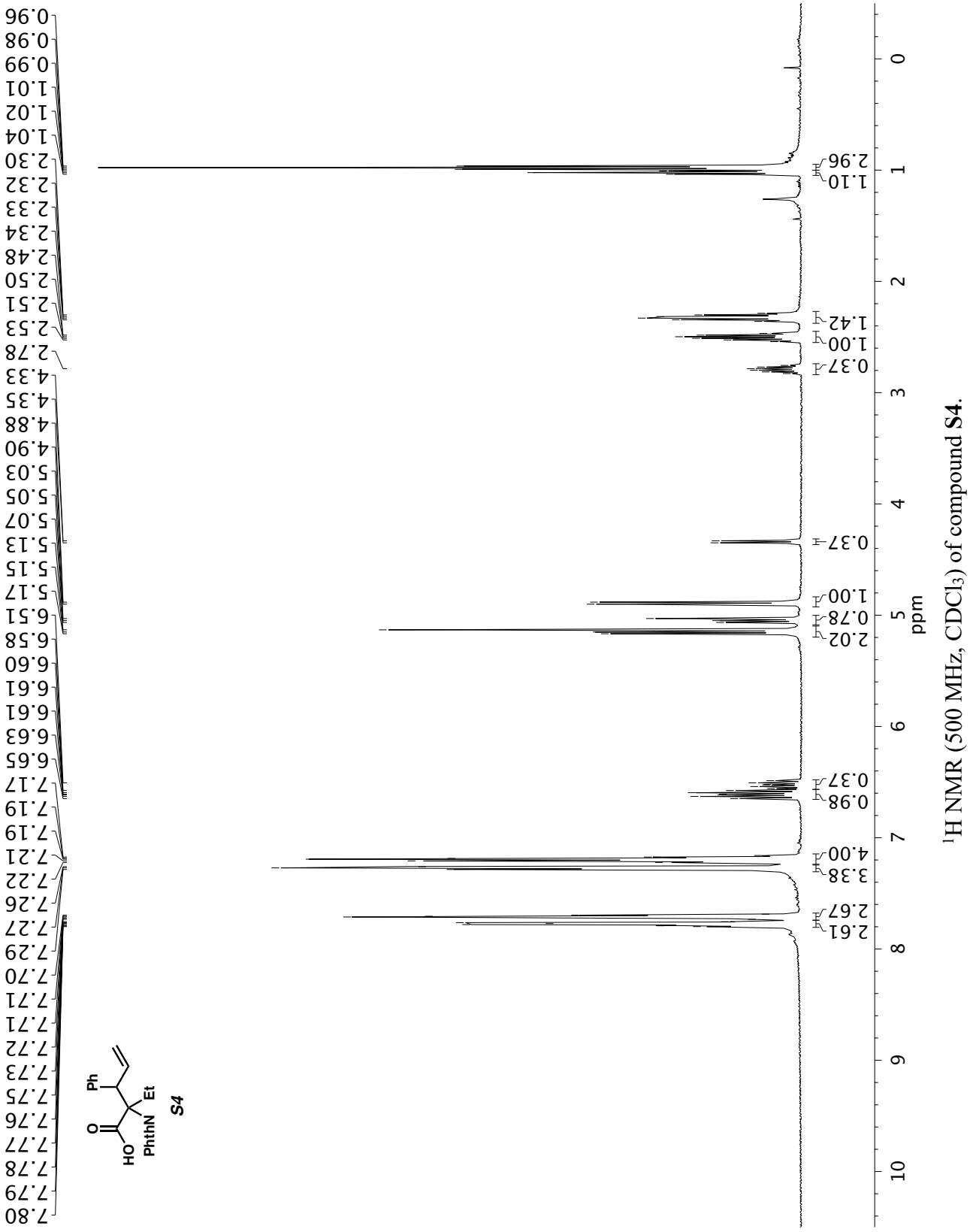
^{1}H NMR (500 MHz, $CDCl_3$) of compound **50**.



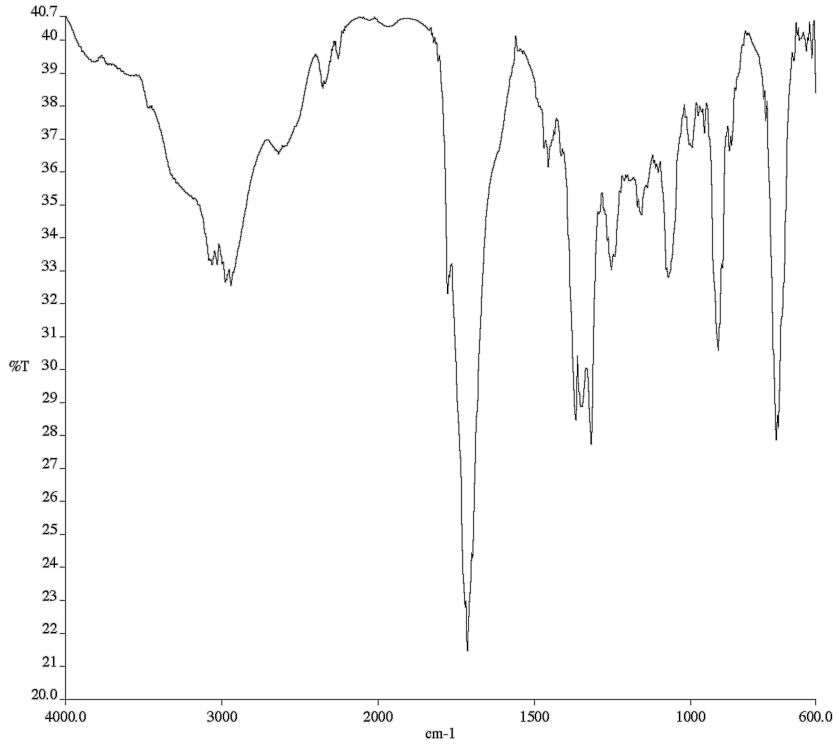
Infrared spectrum (Thin Film, NaCl) of compound **50**.



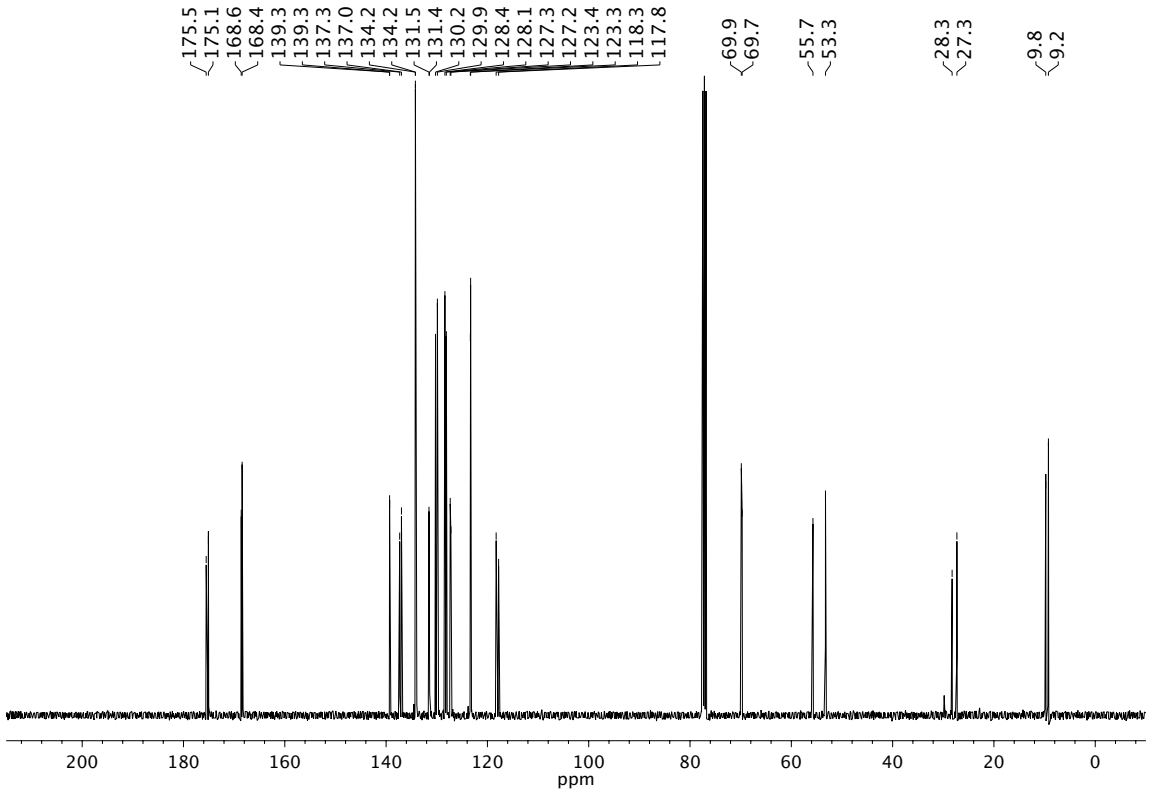
^{13}C NMR (100 MHz, $CDCl_3$) of compound **50**.



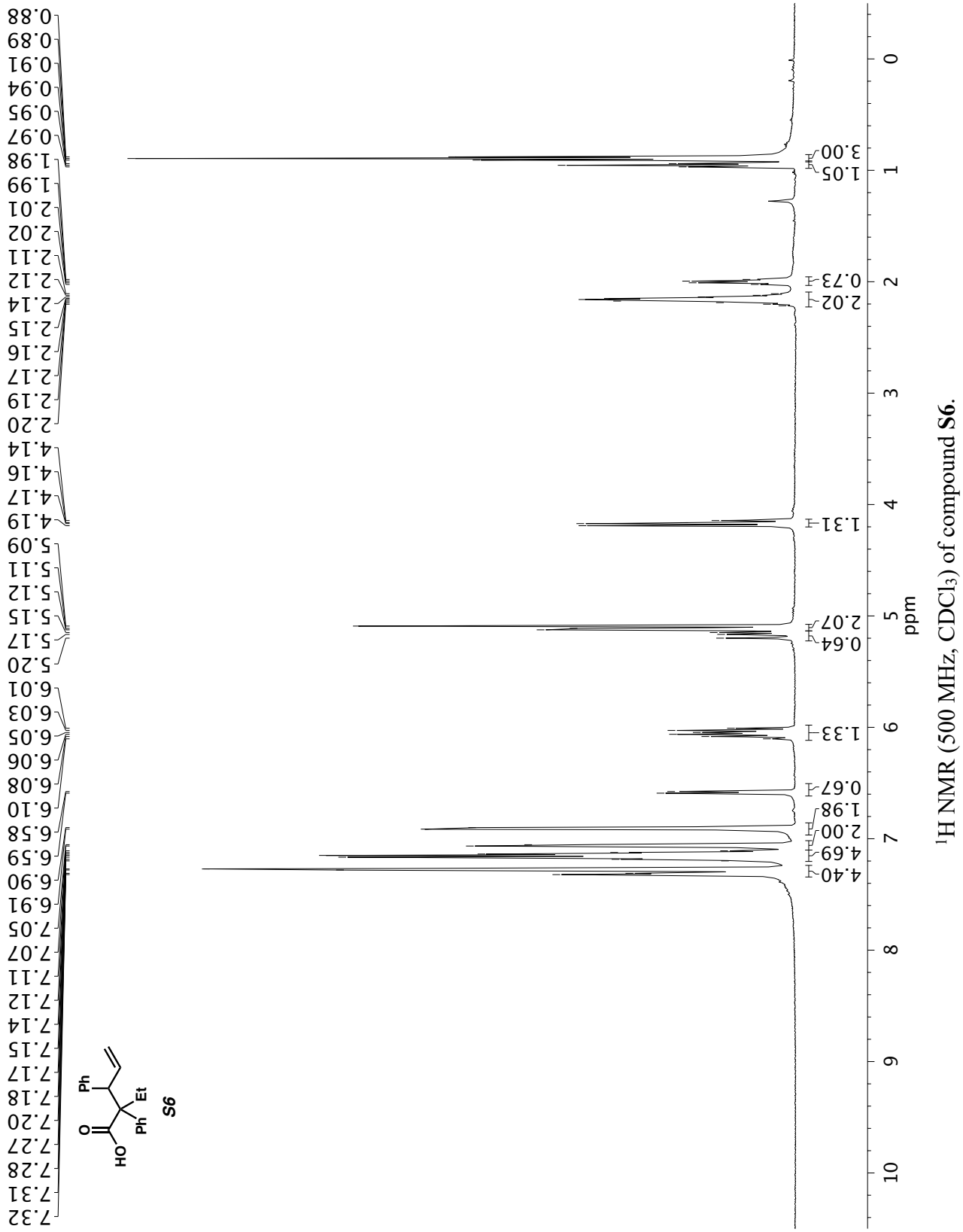
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S4**.



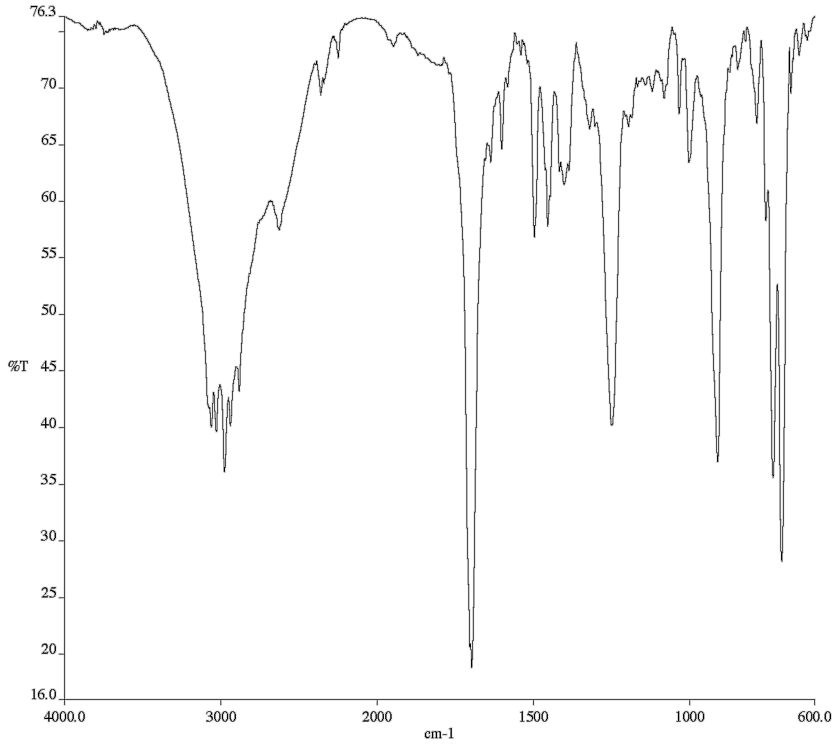
Infrared spectrum (Thin Film, NaCl) of compound **S4**.



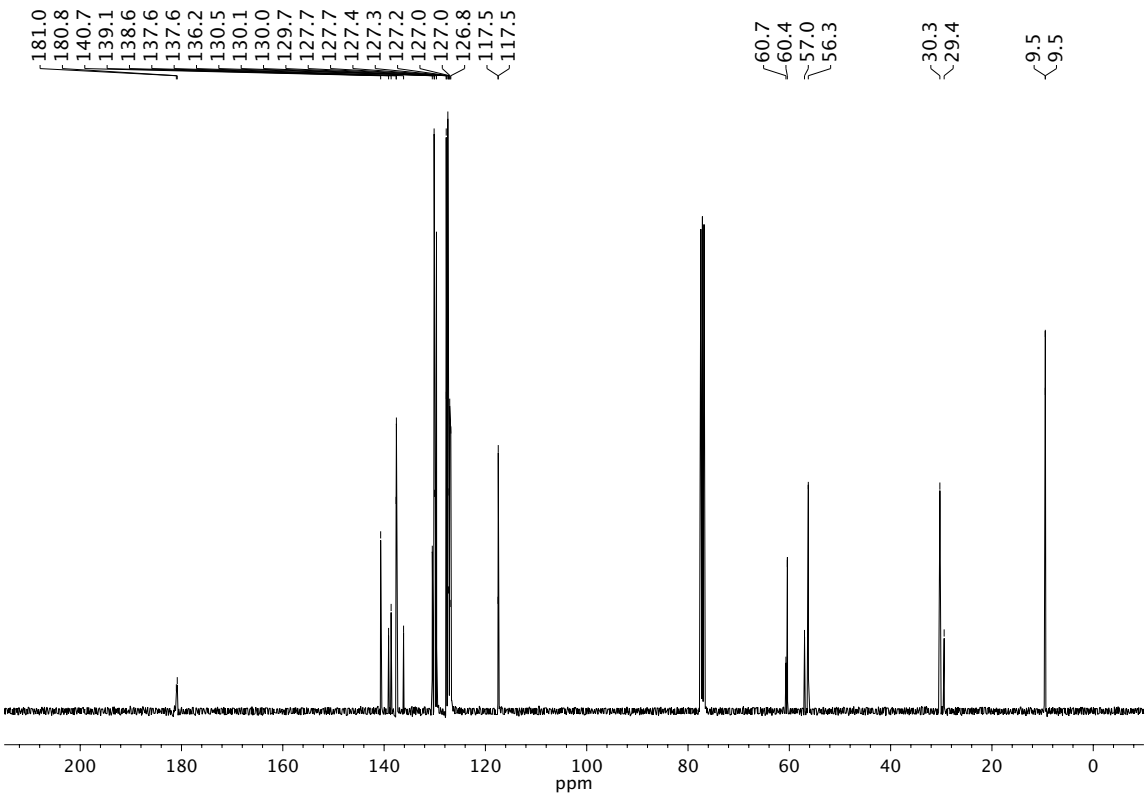
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S4**.



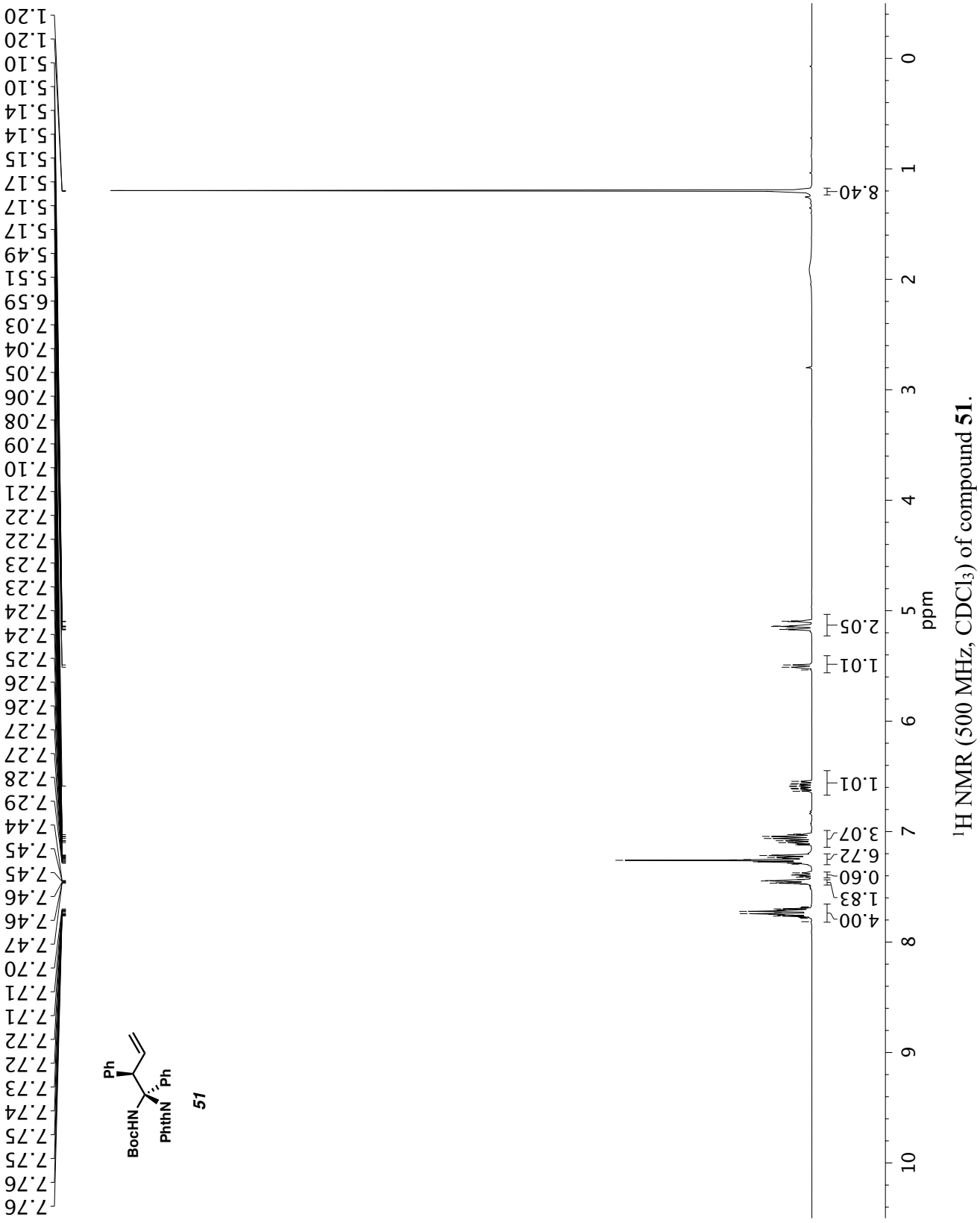
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S6**.



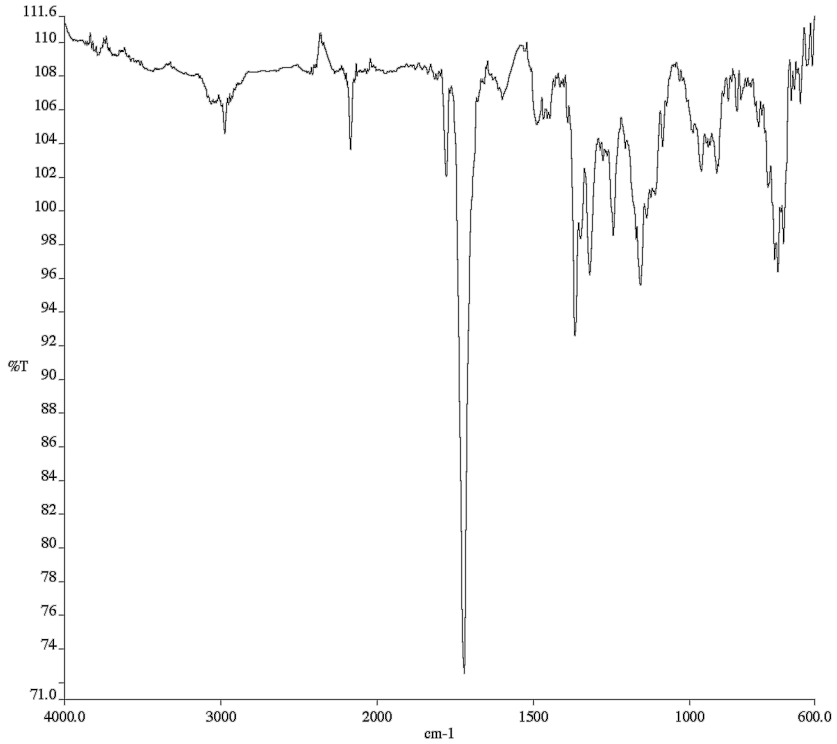
Infrared spectrum (Thin Film, NaCl) of compound **S6**.



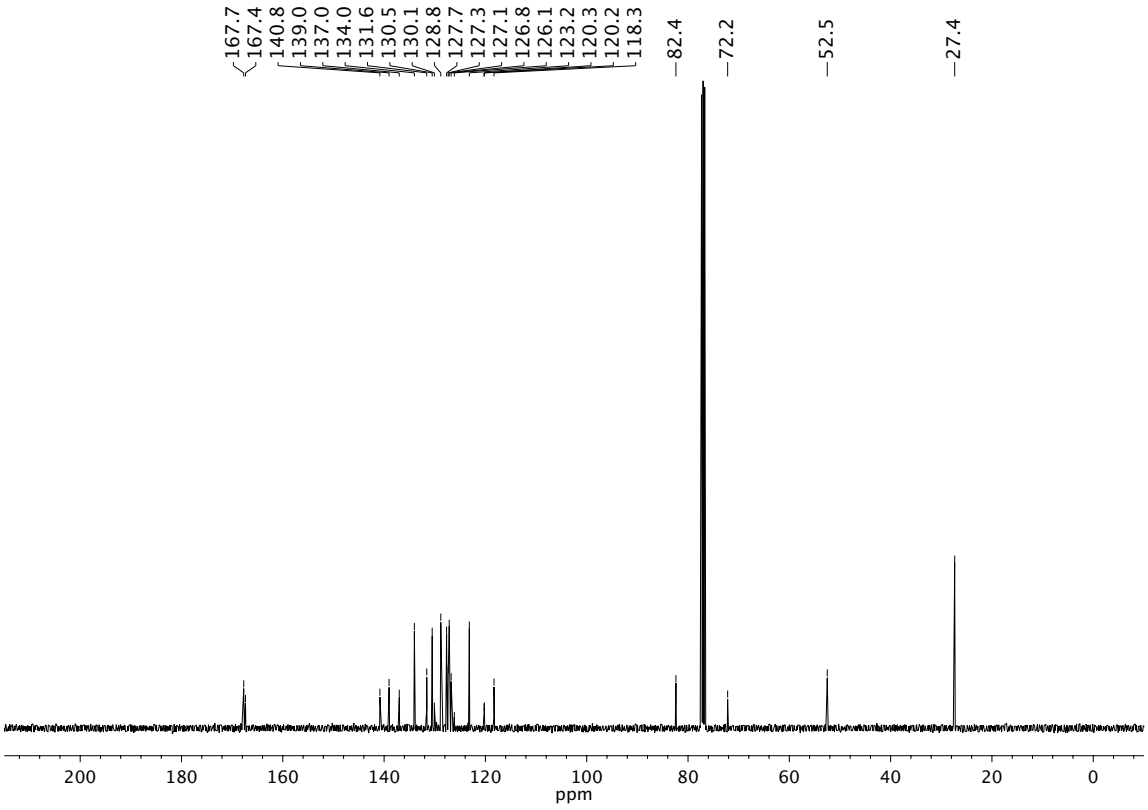
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S6**.



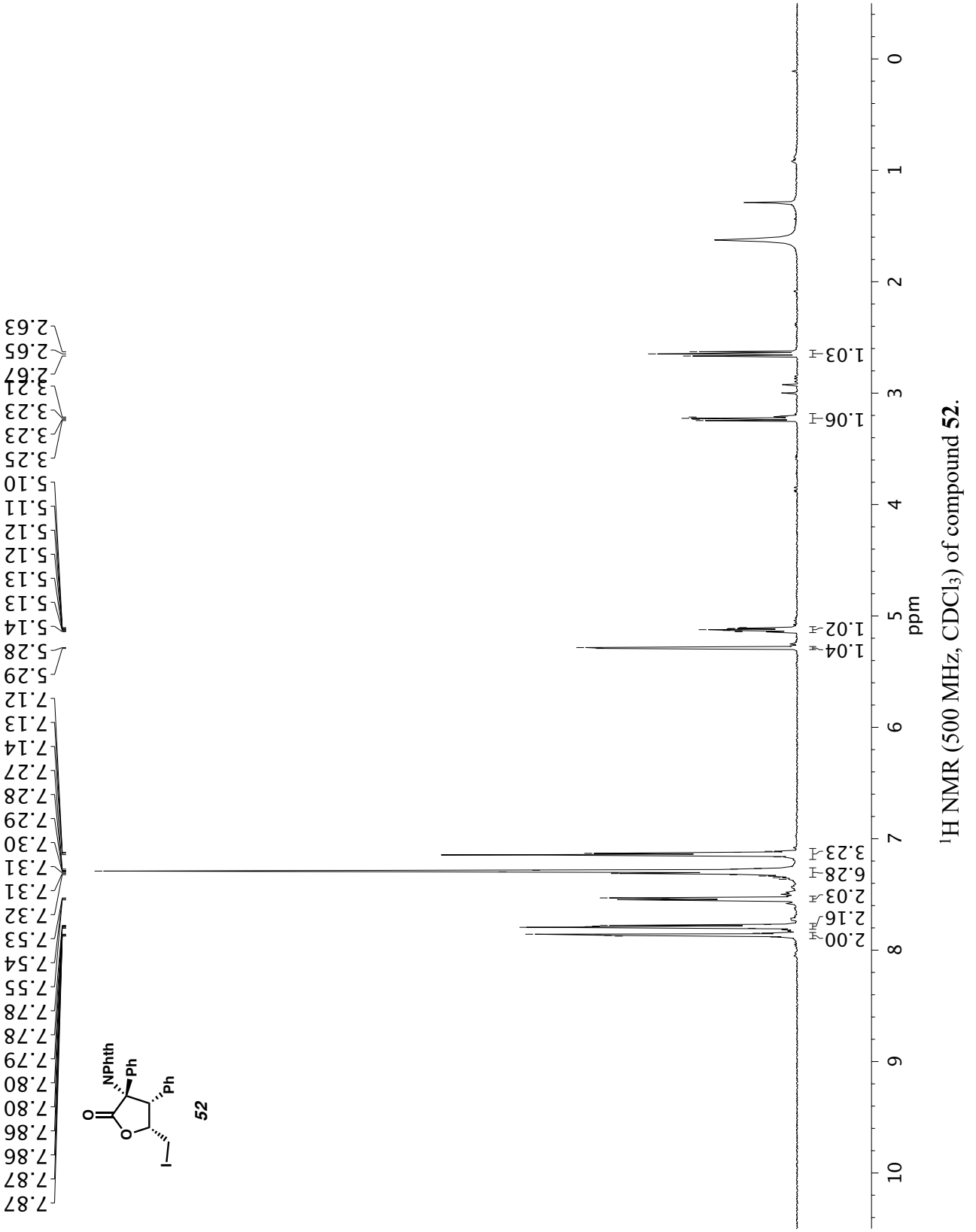
^{1}H NMR (500 MHz, $CDCl_3$) of compound **51**.



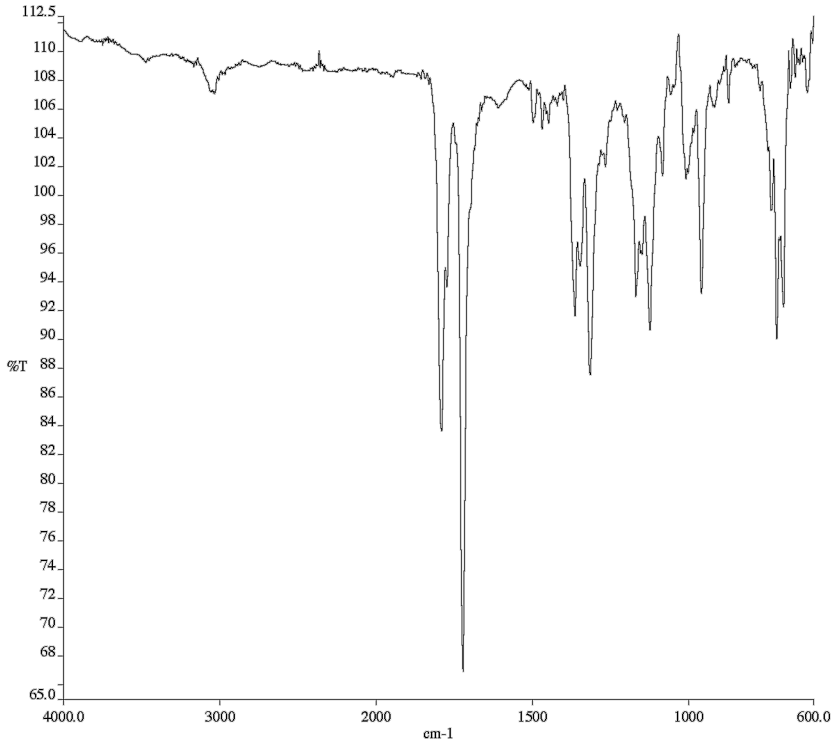
Infrared spectrum (Thin Film, NaCl) of compound **51**.



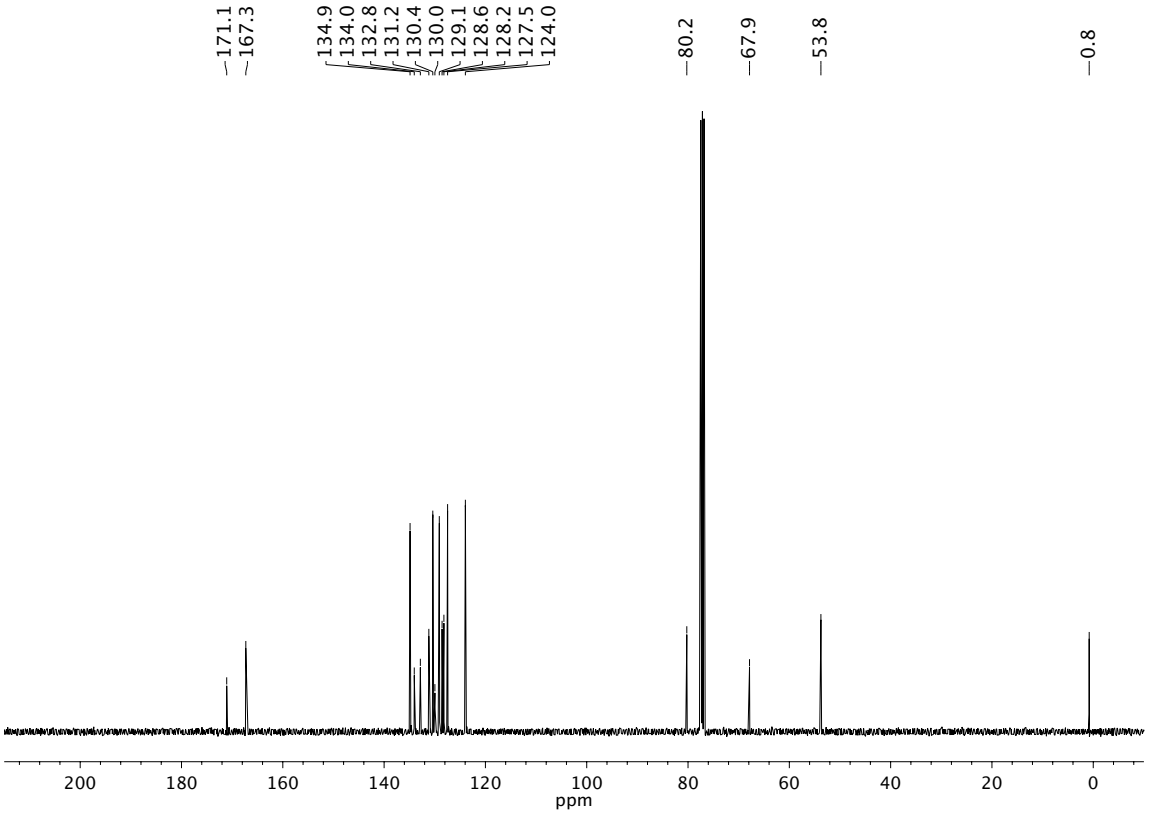
^{13}C NMR (100 MHz, $CDCl_3$) of compound **51**.



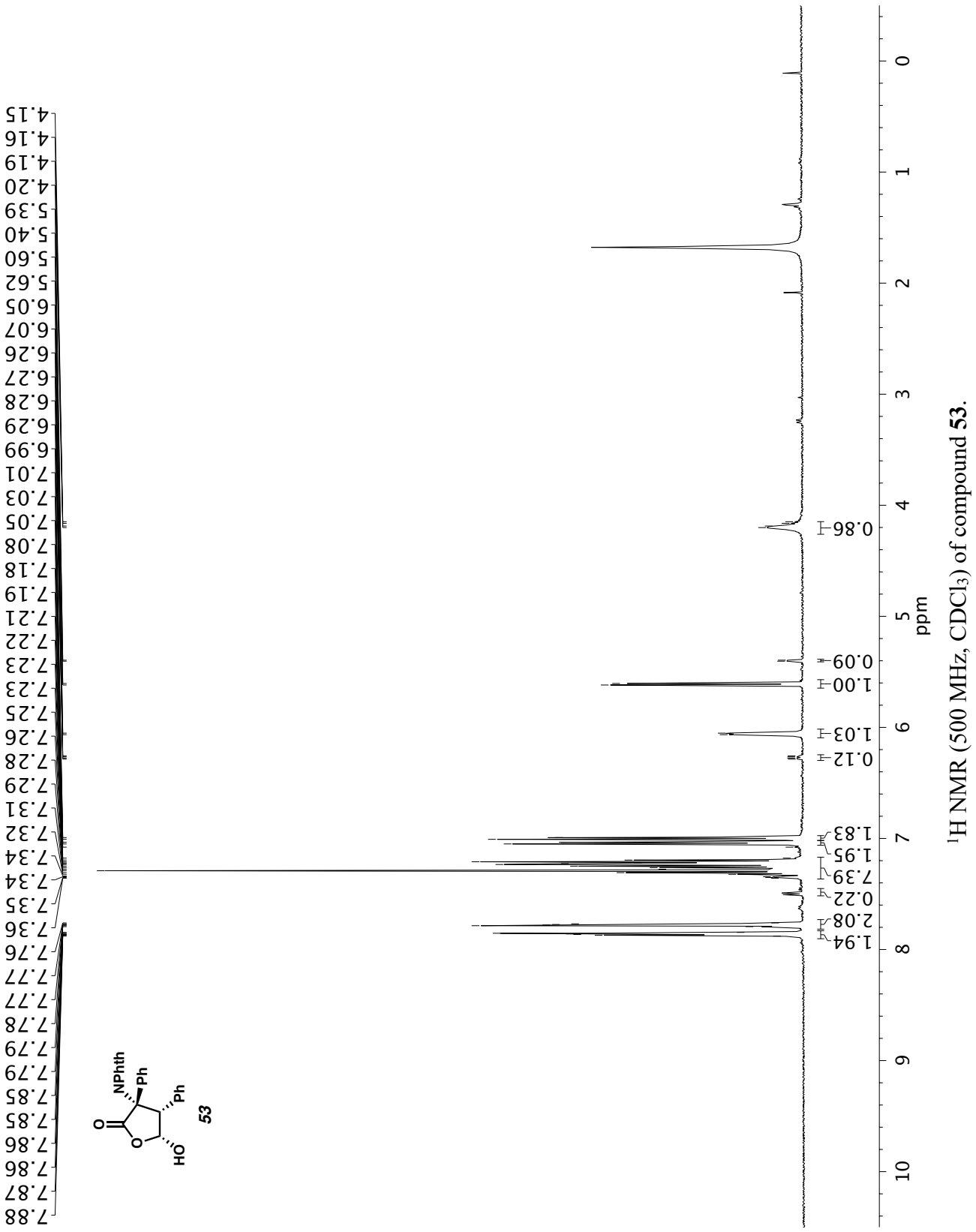
^{1}H NMR (500 MHz, $CDCl_3$) of compound **52**.



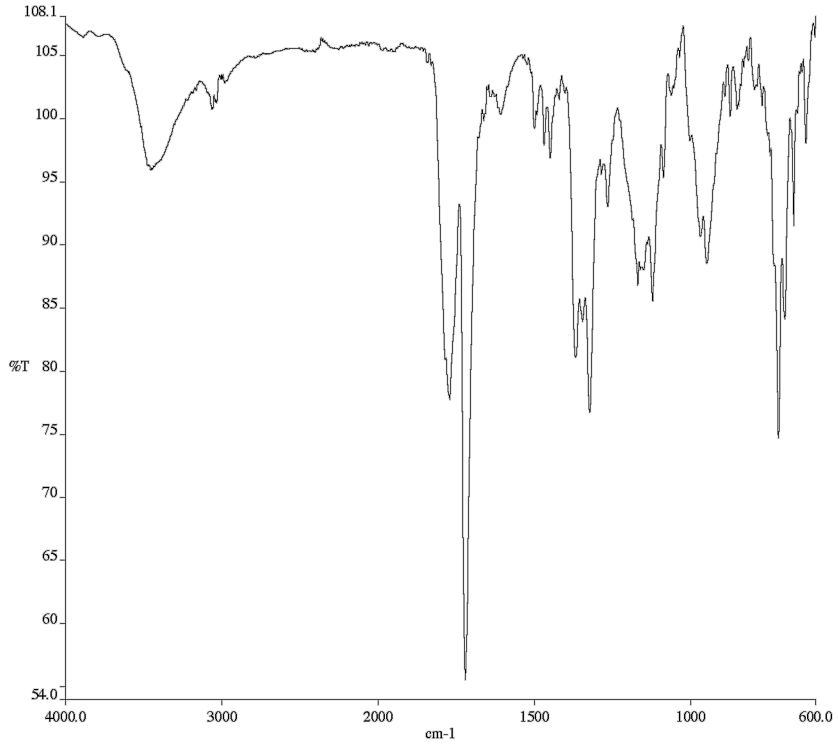
Infrared spectrum (Thin Film, NaCl) of compound **52**.



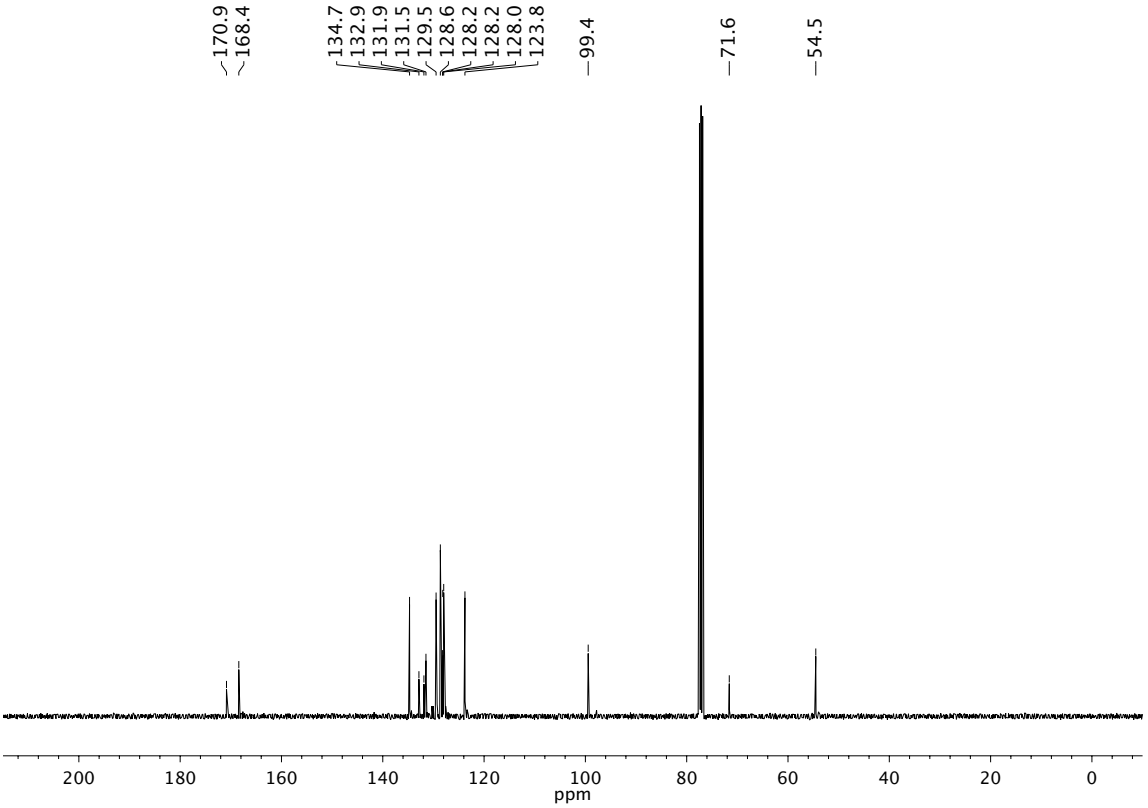
^{13}C NMR (100 MHz, $CDCl_3$) of compound **52**.



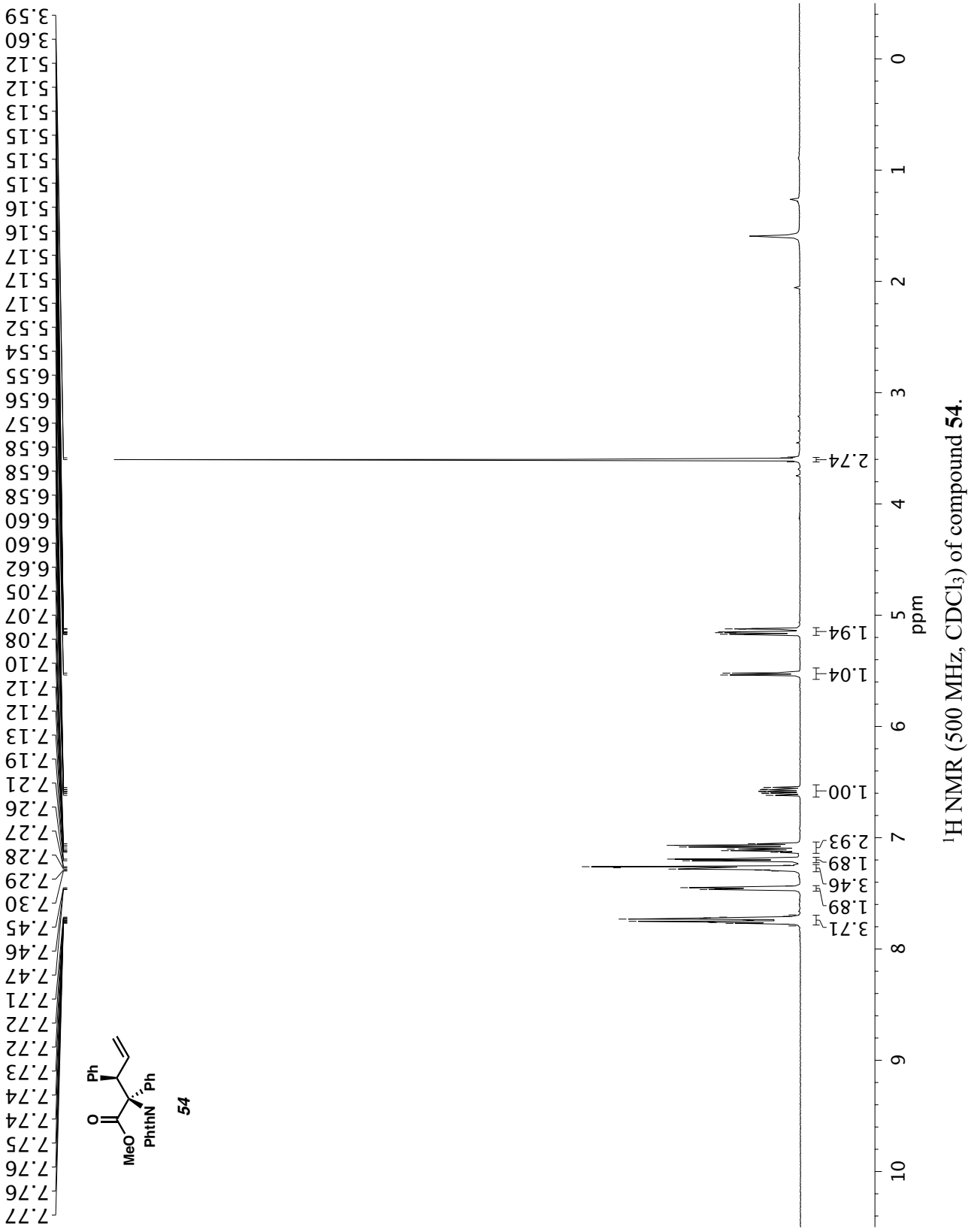
^{1}H NMR (500 MHz, $CDCl_3$) of compound **53**.



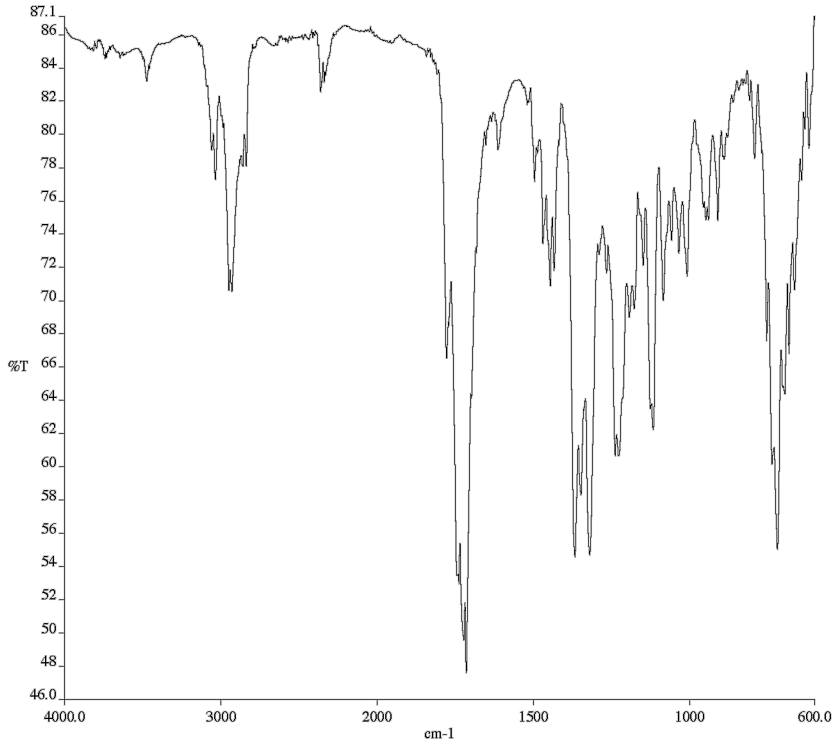
Infrared spectrum (Thin Film, NaCl) of compound **53**.



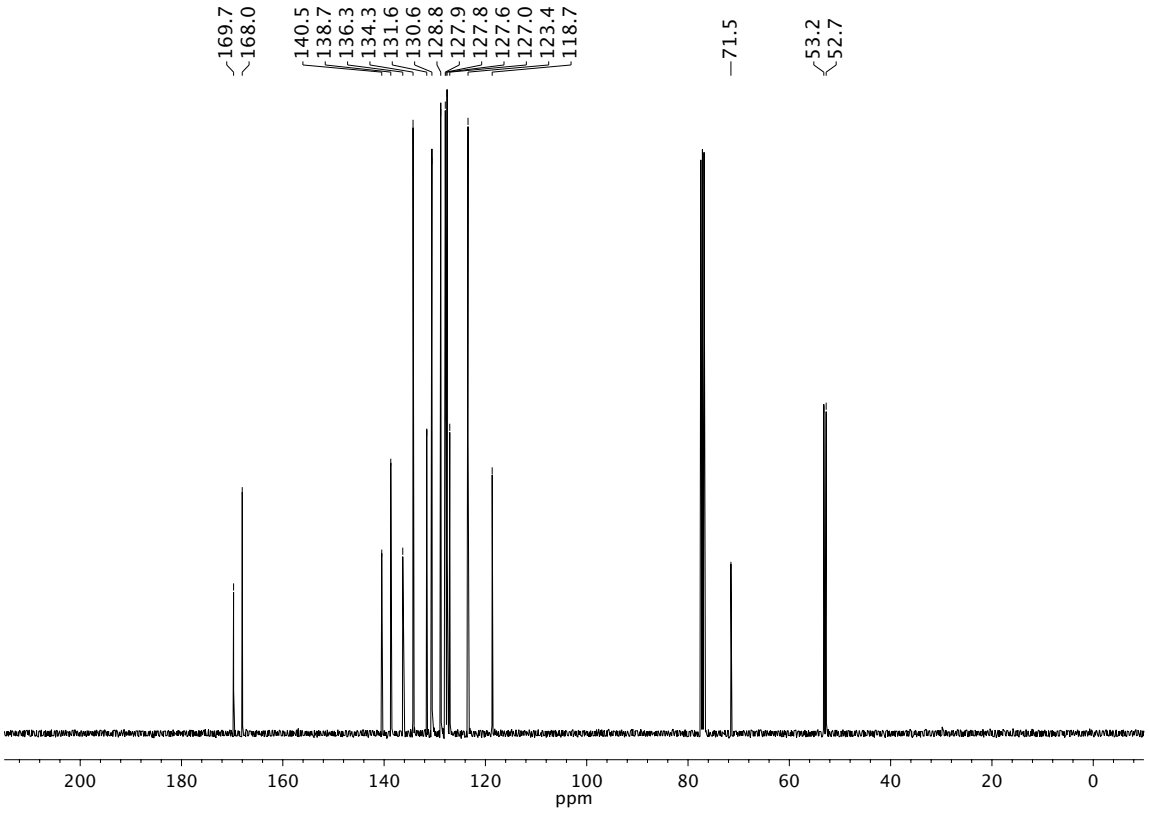
^{13}C NMR (100 MHz, $CDCl_3$) of compound **53**.



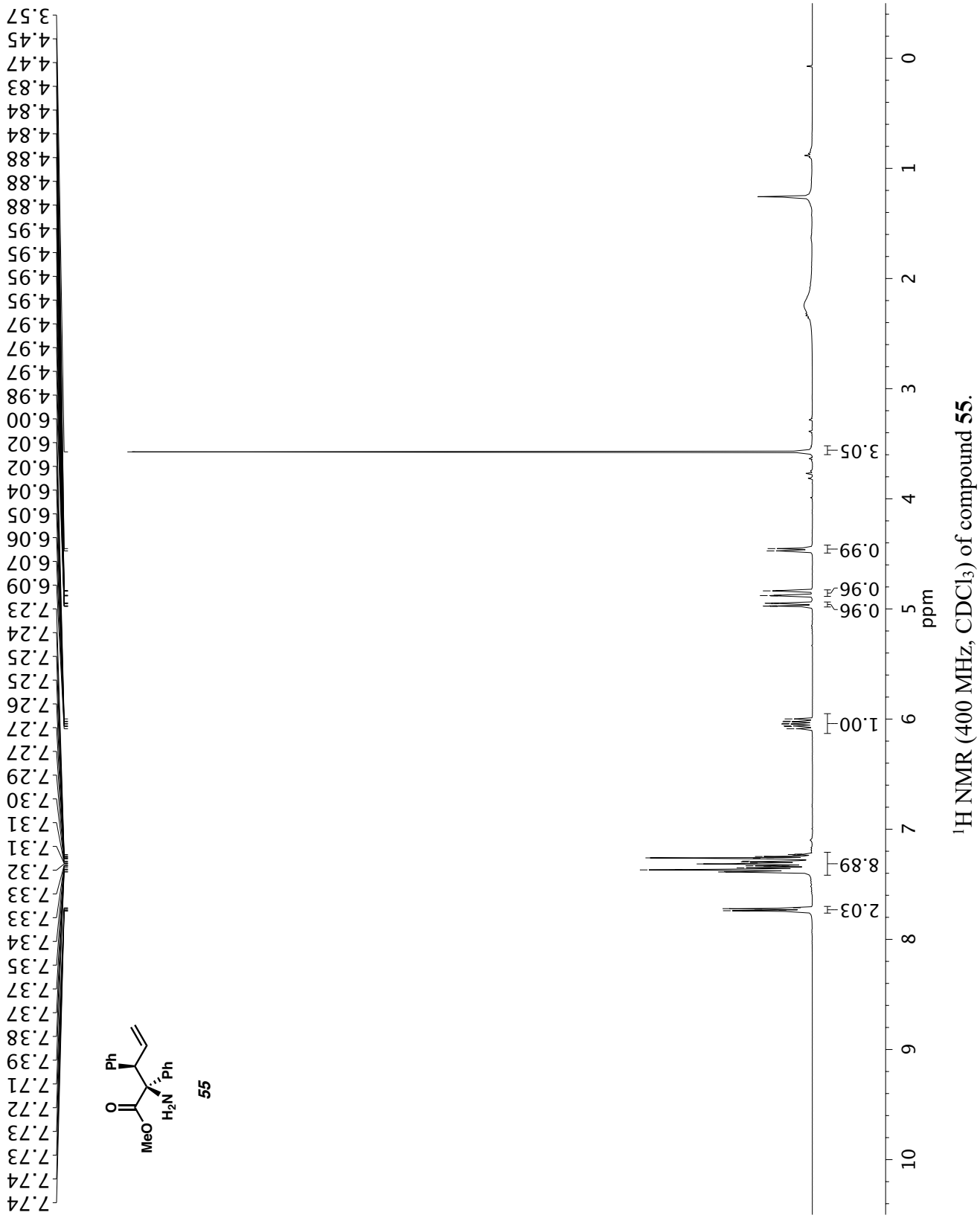
^{1}H NMR (500 MHz, $CDCl_3$) of compound **54**.



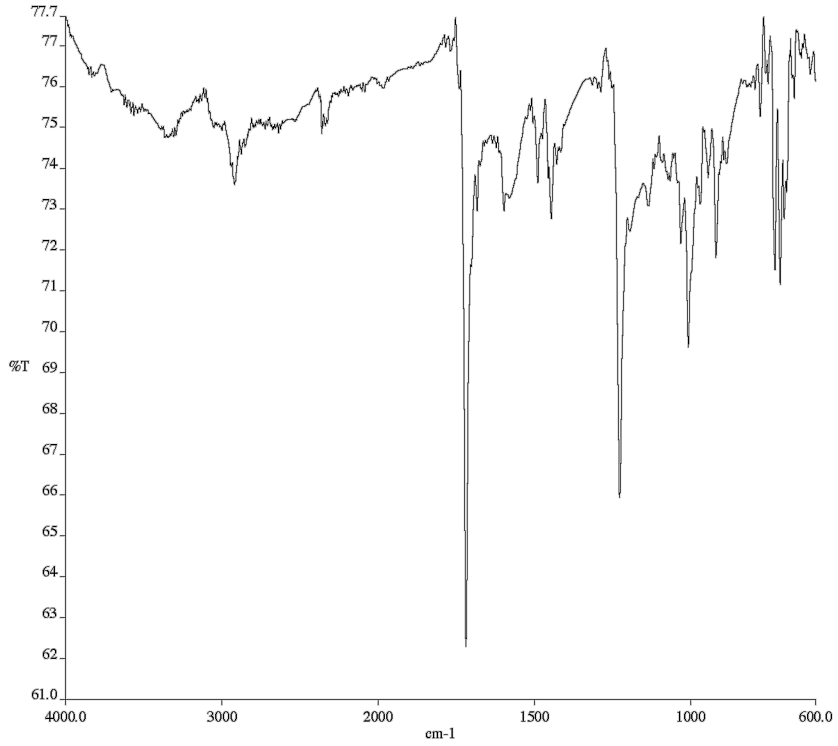
Infrared spectrum (Thin Film, NaCl) of compound **54**.



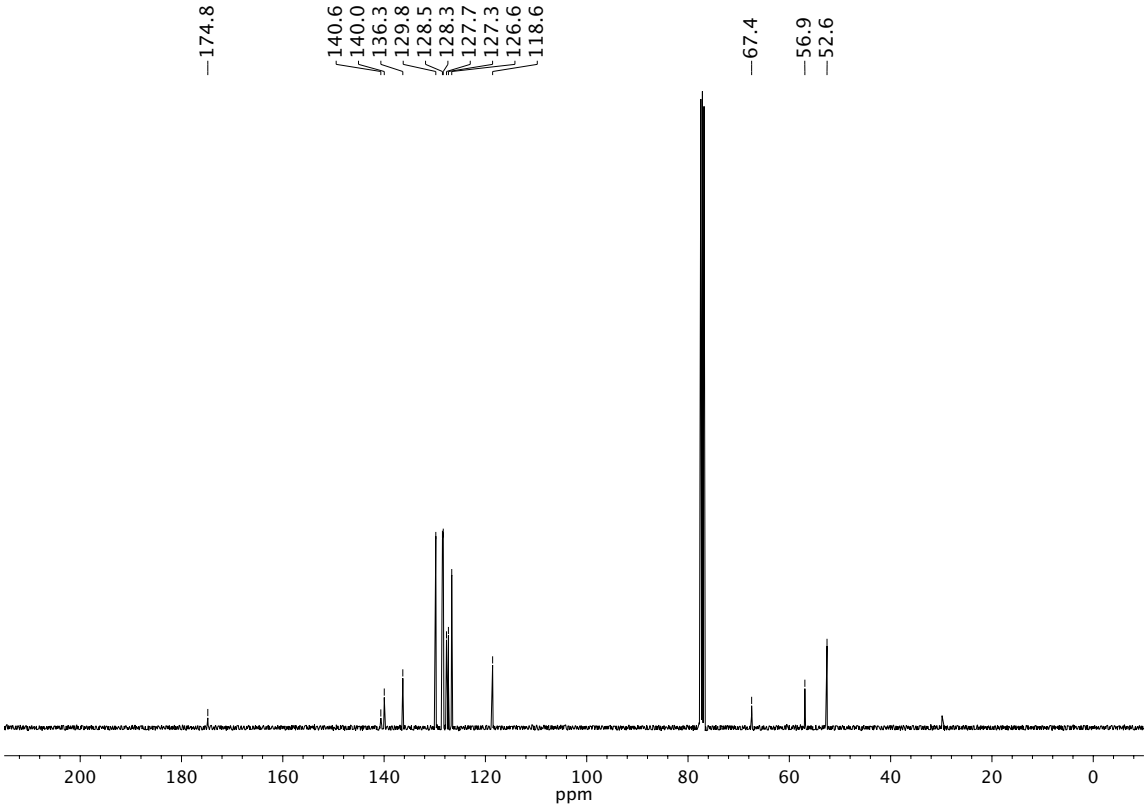
^{13}C NMR (100 MHz, $CDCl_3$) of compound **54**.



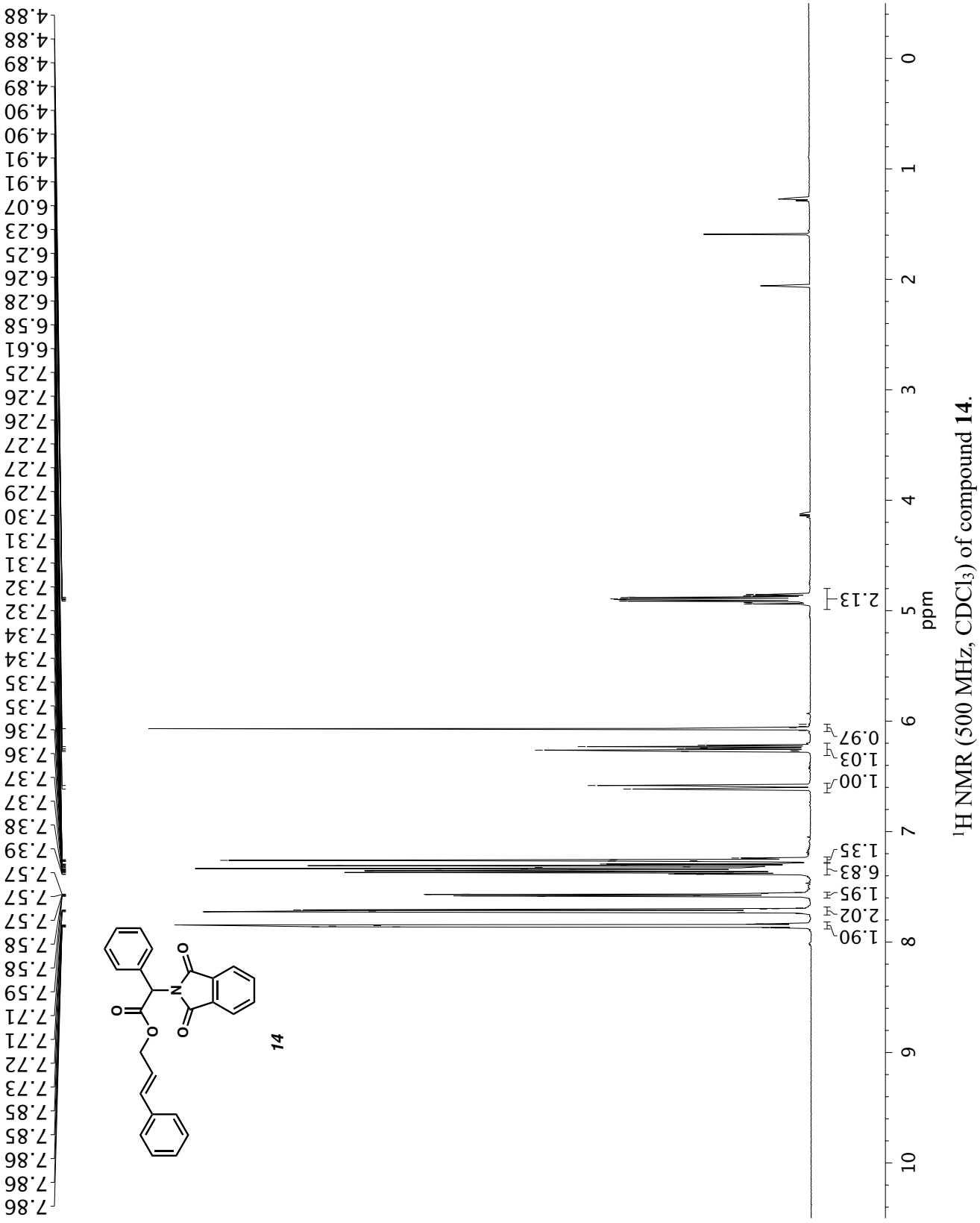
^{1}H NMR (400 MHz, $CDCl_3$) of compound **55**.



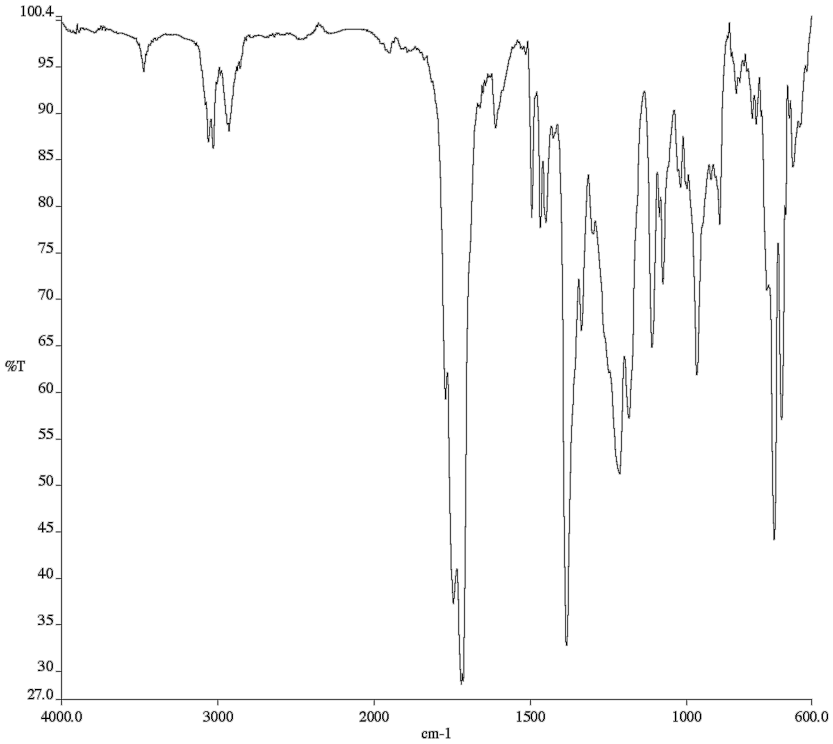
Infrared spectrum (Thin Film, NaCl) of compound **55**.



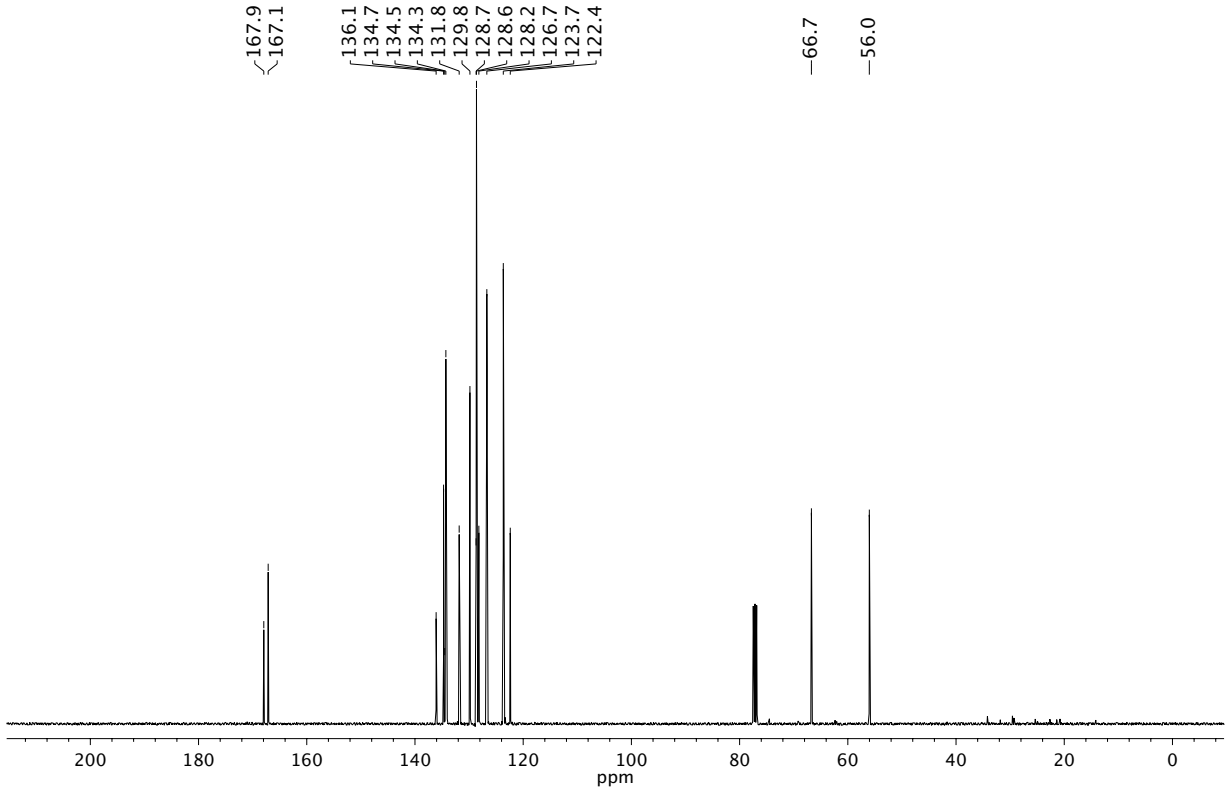
^{13}C NMR (100 MHz, $CDCl_3$) of compound **55**.



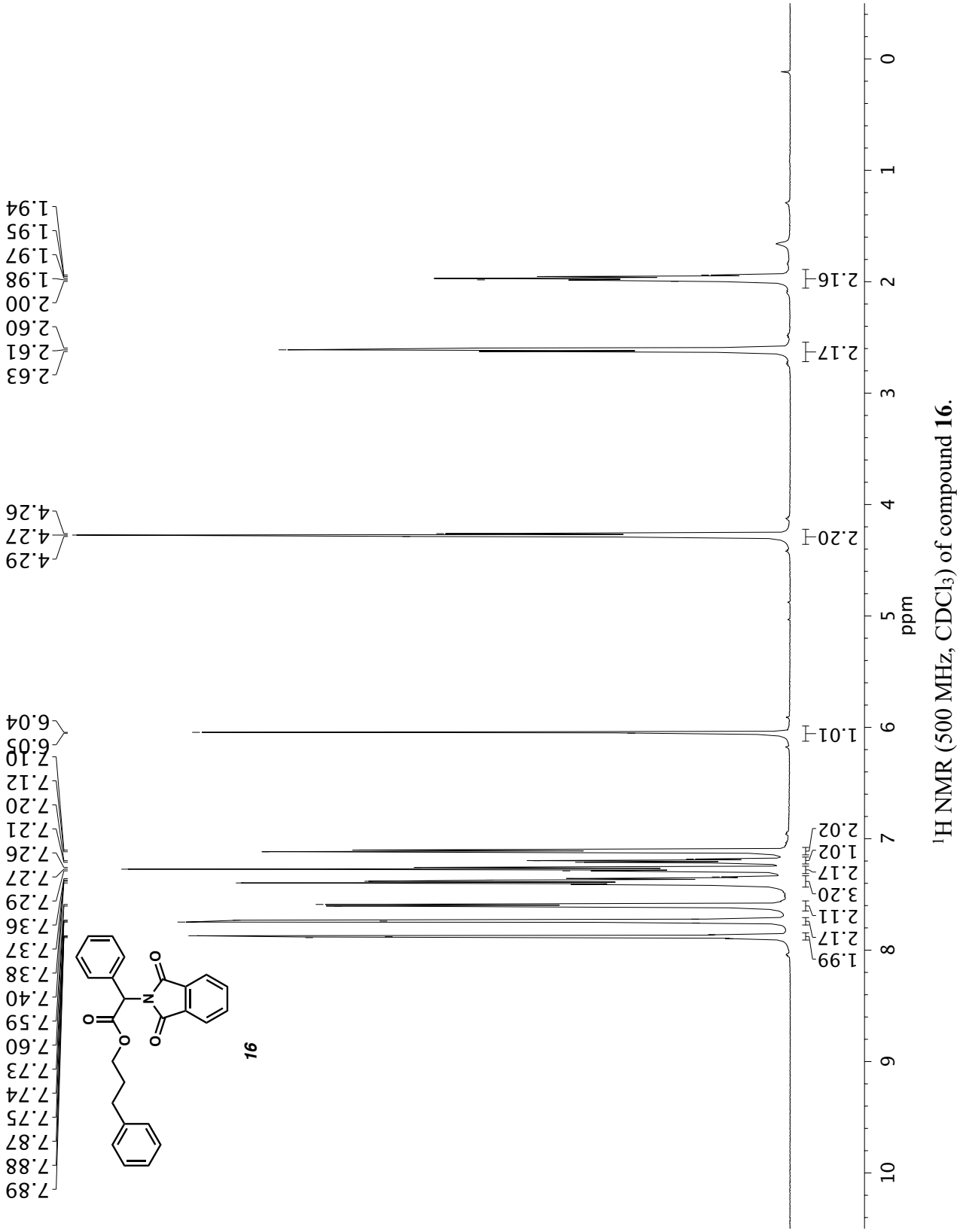
^{1}H NMR (500 MHz, $CDCl_3$) of compound **14**.



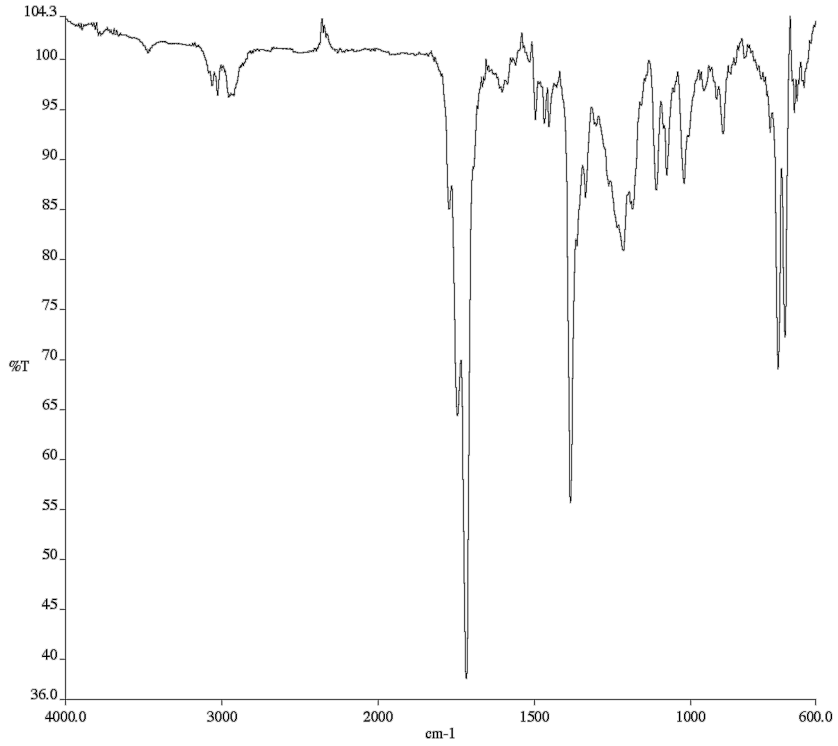
Infrared spectrum (Thin Film, NaCl) of compound **14**.



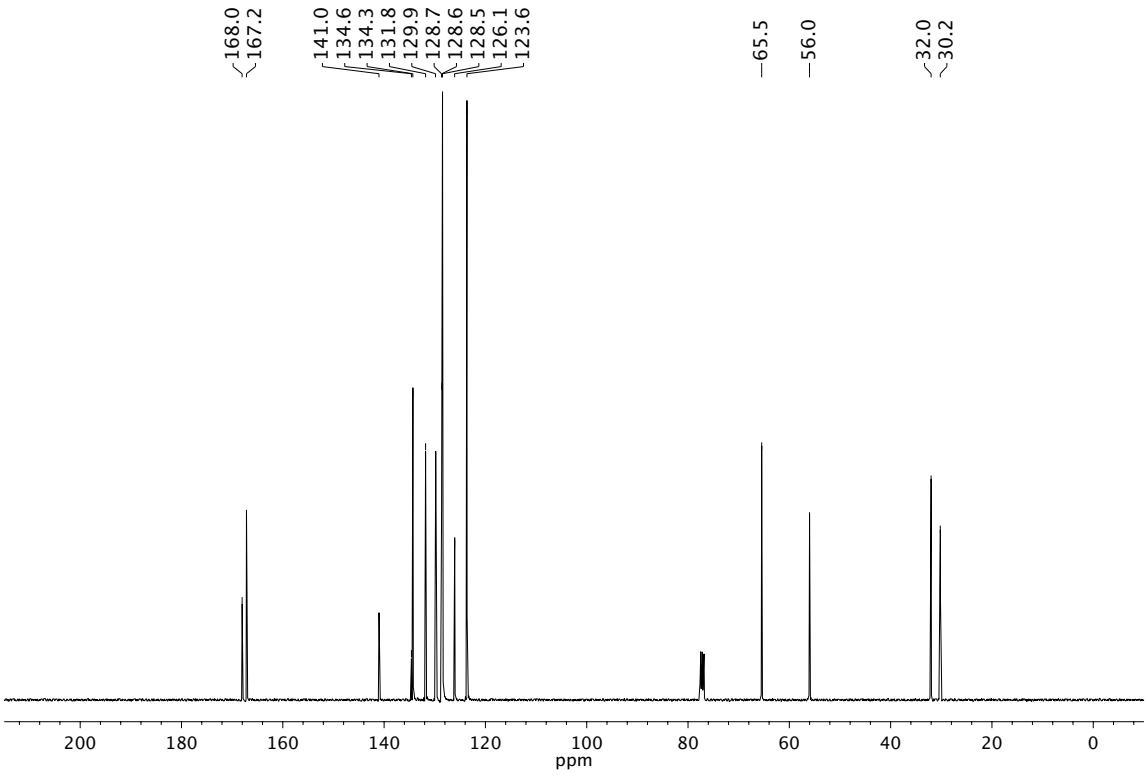
^{13}C NMR (100 MHz, $CDCl_3$) of compound **14**.



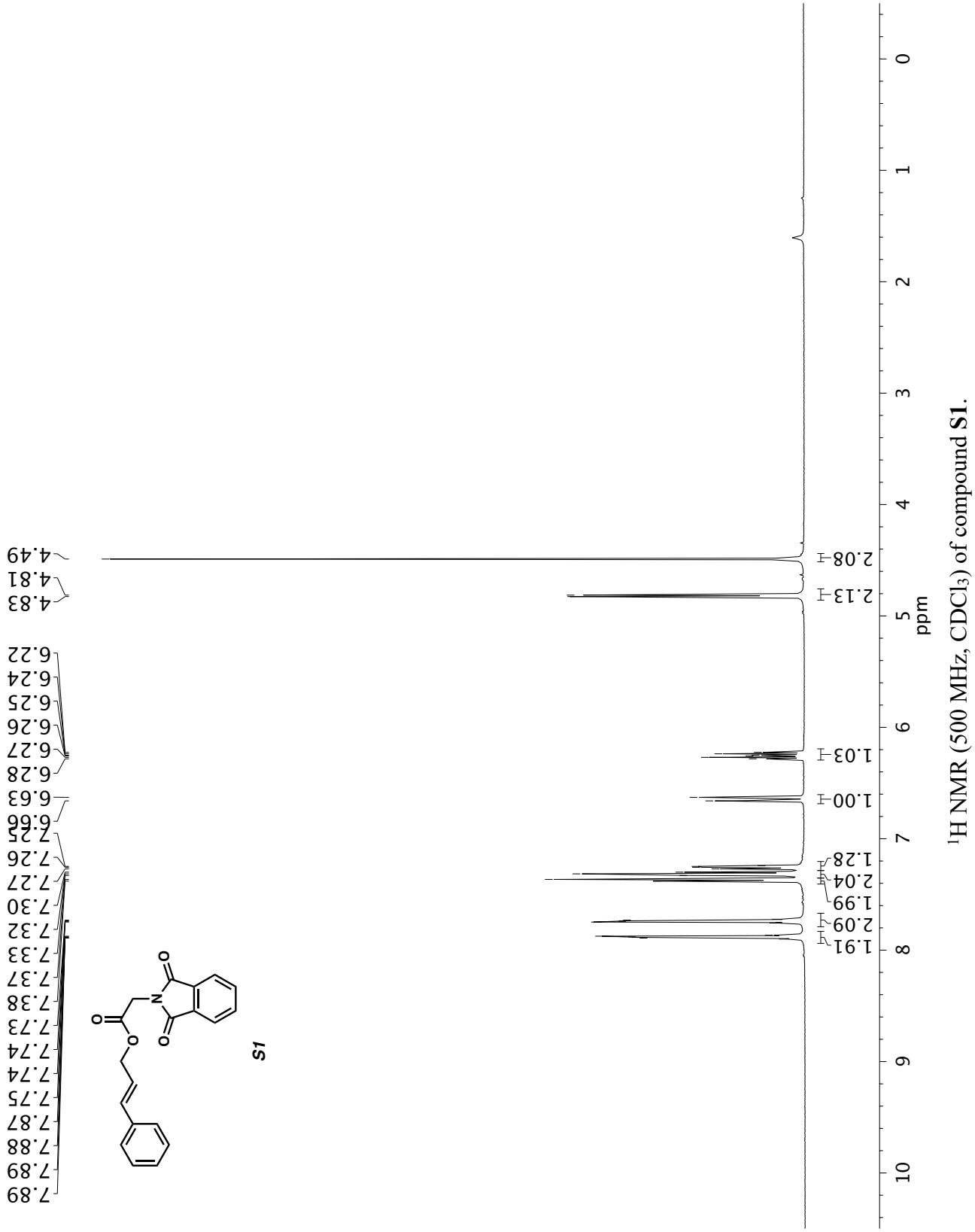
^{1}H NMR (500 MHz, $CDCl_3$) of compound **16**.



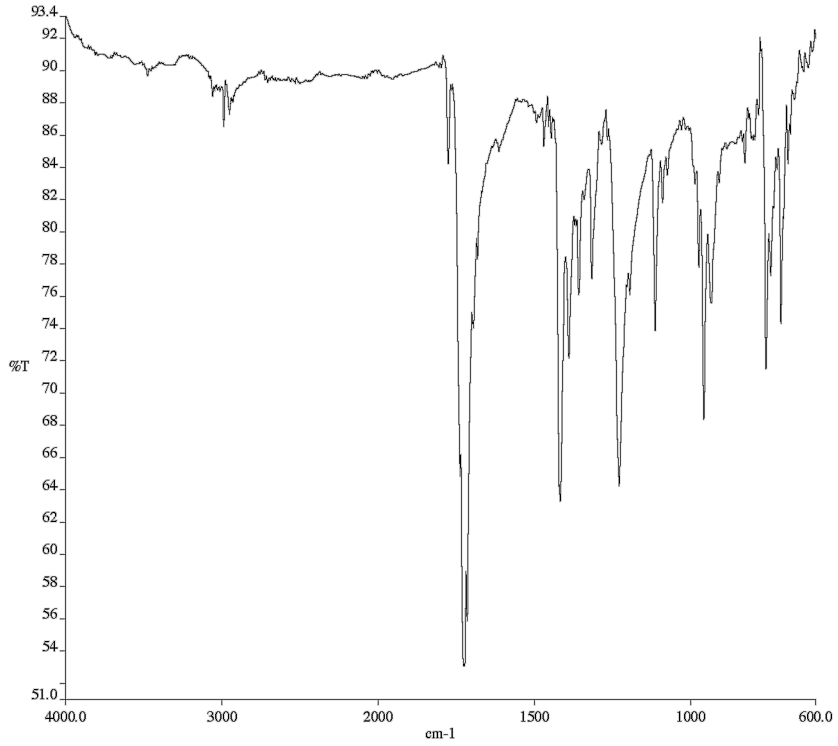
Infrared spectrum (Thin Film, NaCl) of compound **16**.



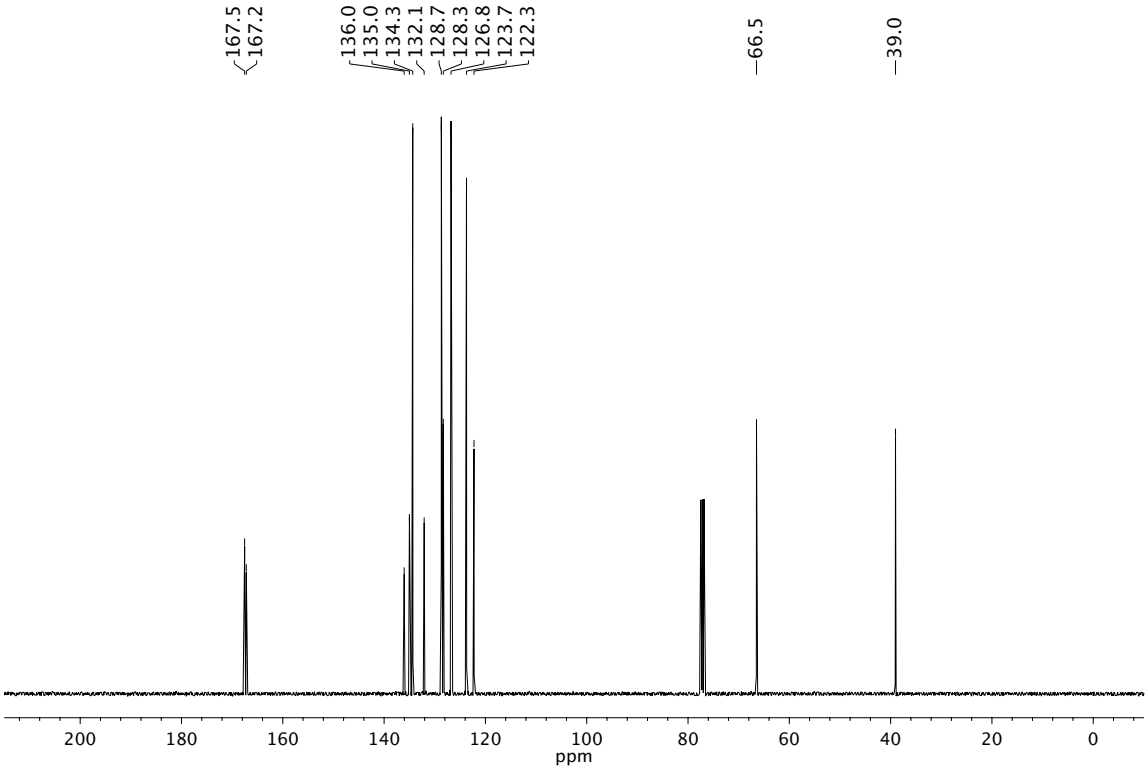
^{13}C NMR (100 MHz, $CDCl_3$) of compound **16**.



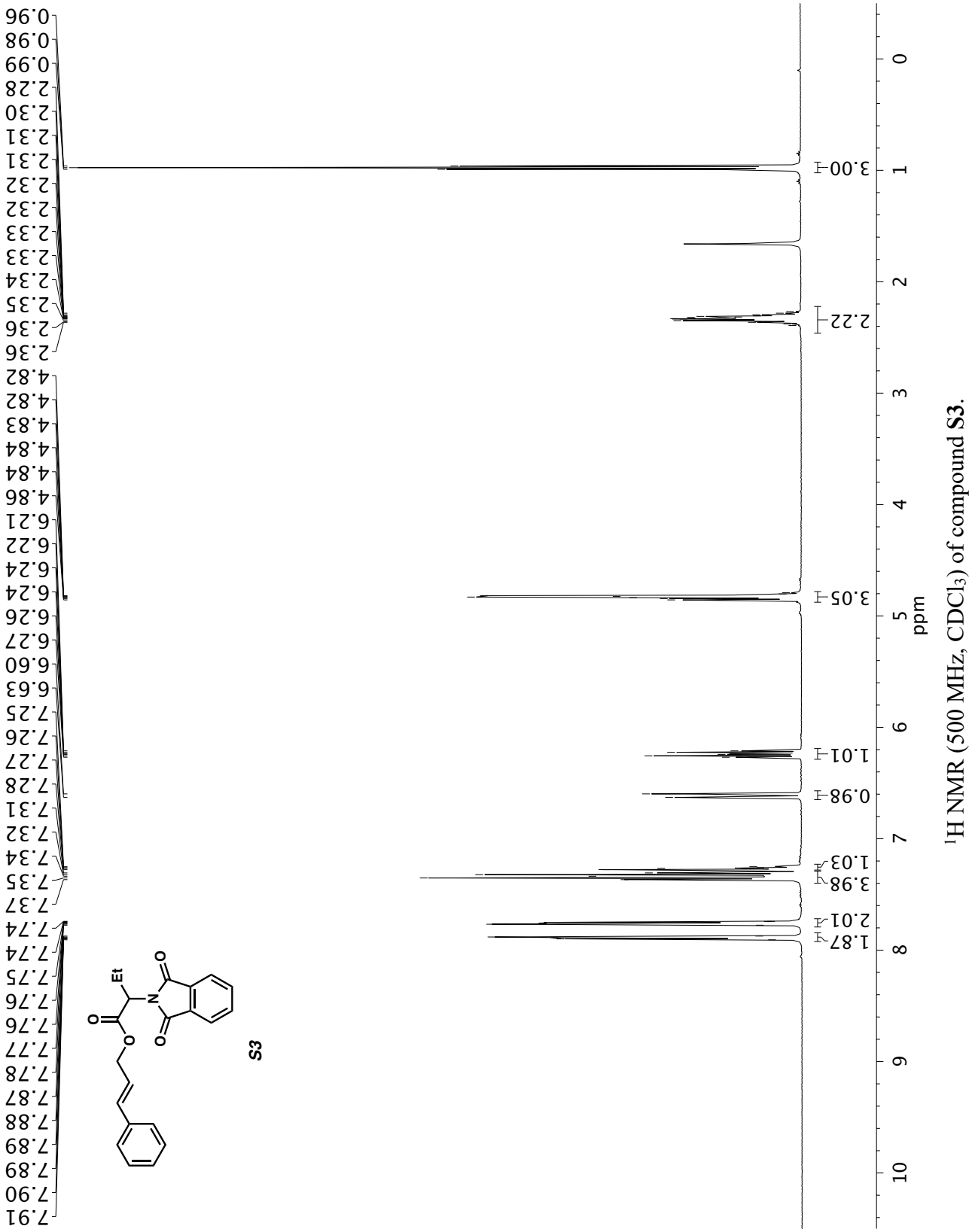
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S1**.



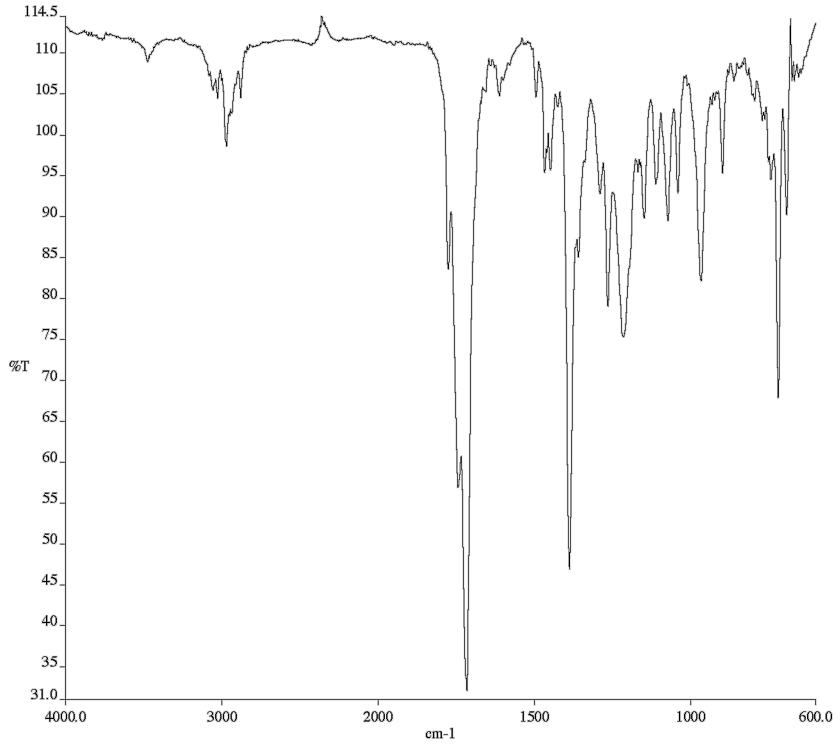
Infrared spectrum (Thin Film, NaCl) of compound **S1**.



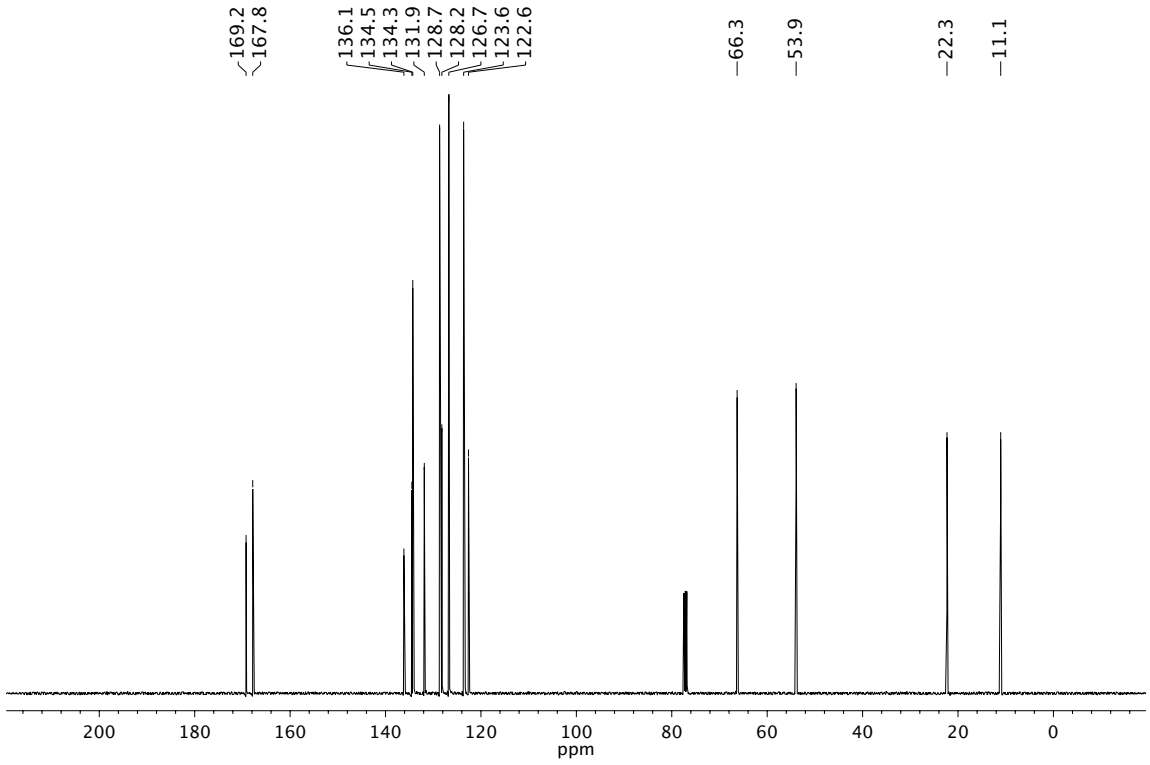
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S1**.



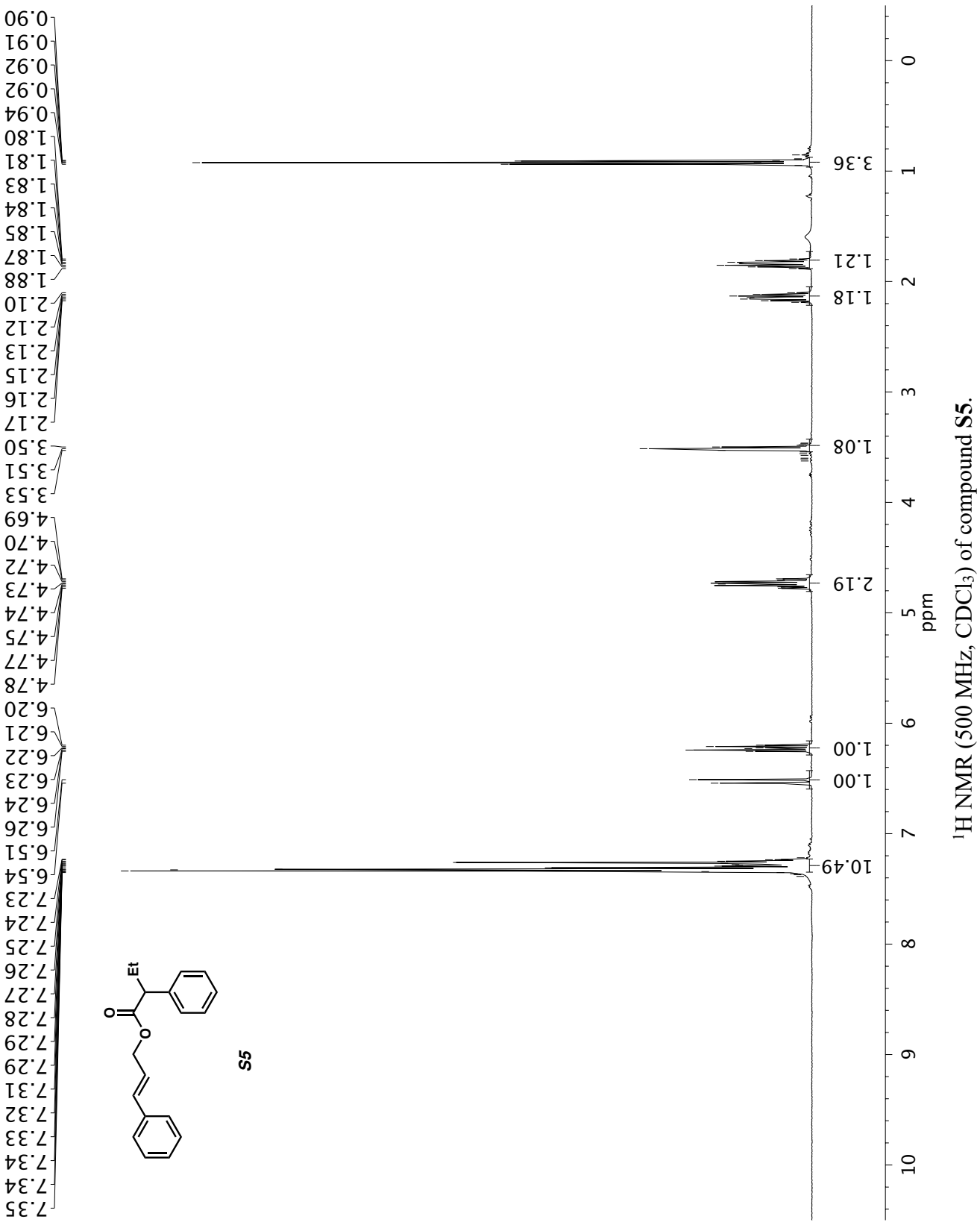
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S3**.



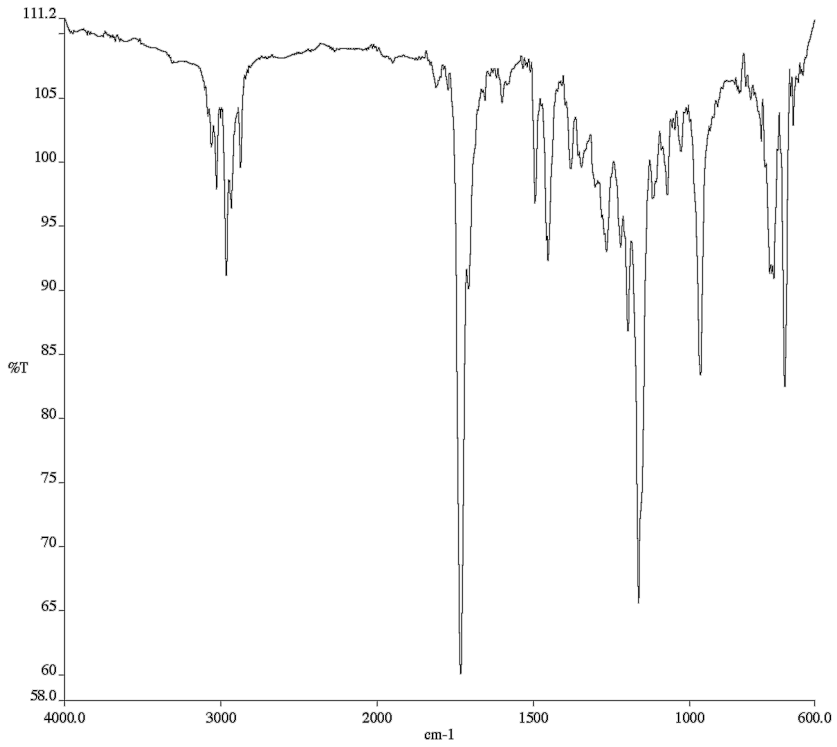
Infrared spectrum (Thin Film, NaCl) of compound **S3**.



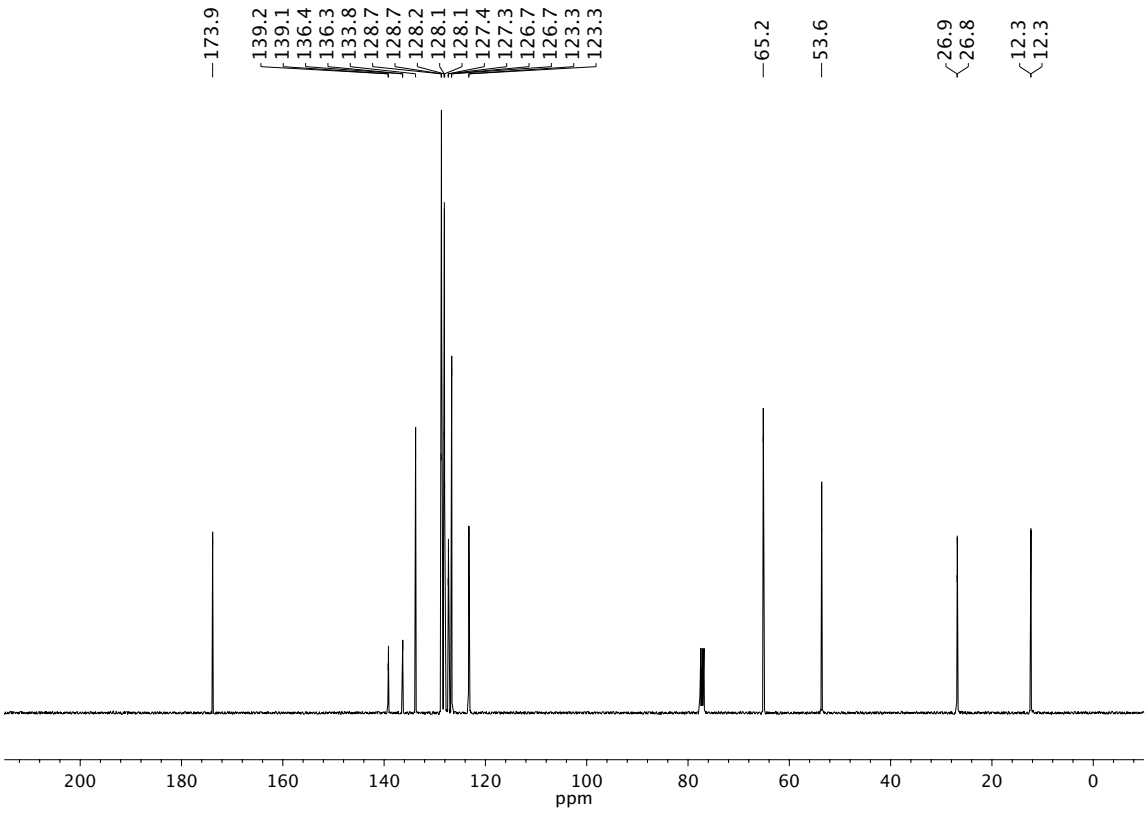
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S3**.



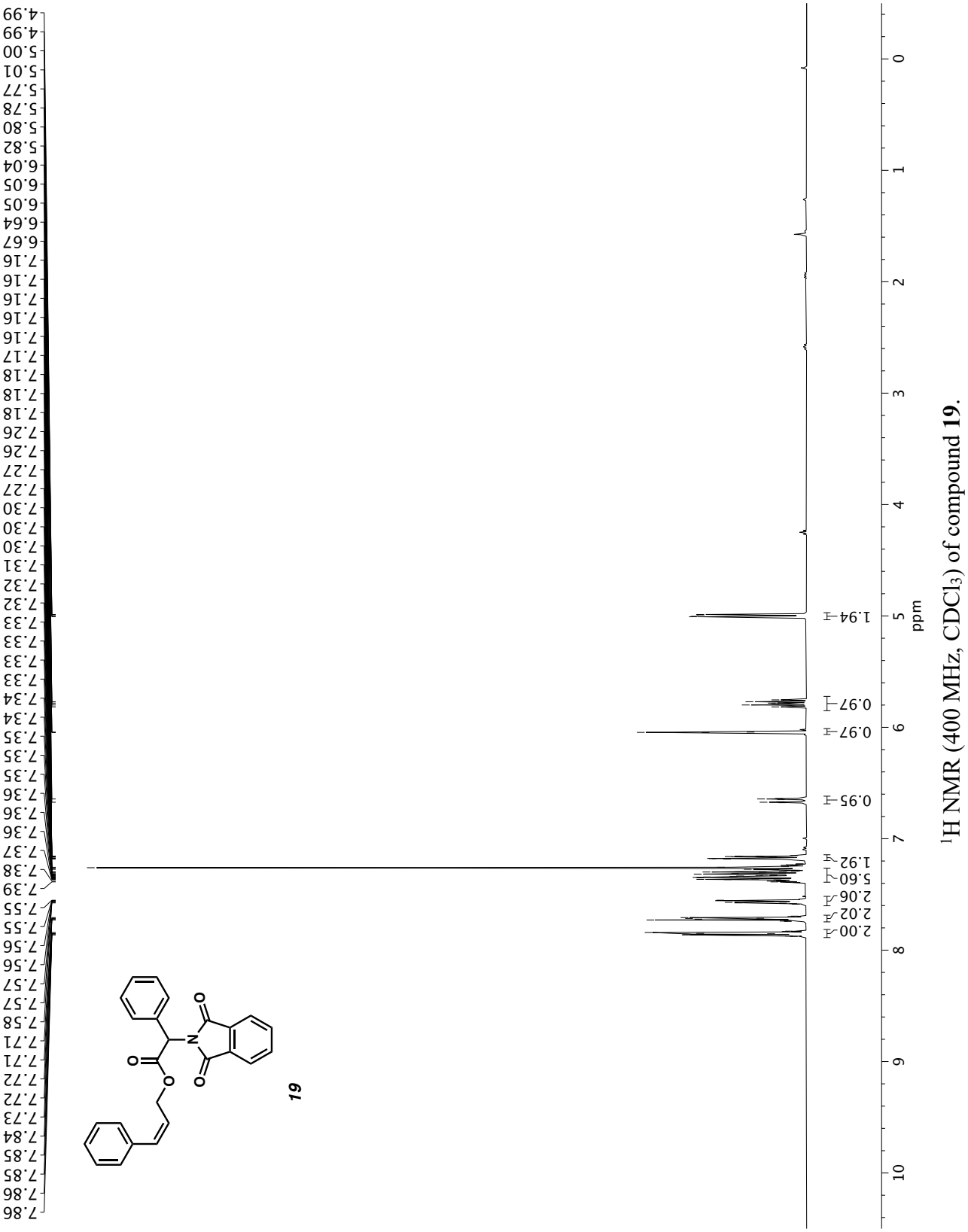
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S5**.



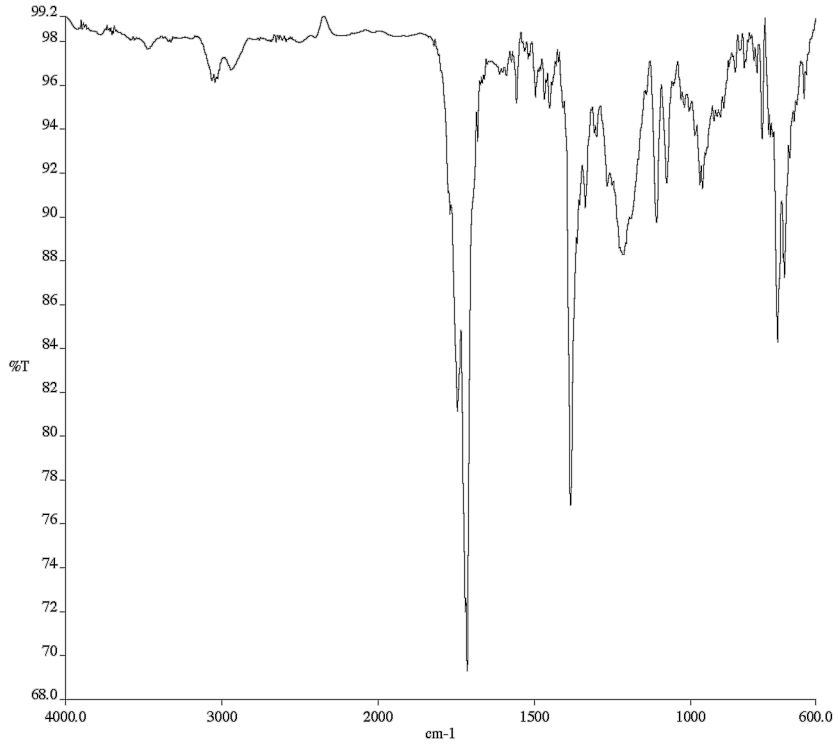
Infrared spectrum (Thin Film, NaCl) of compound **S5**.



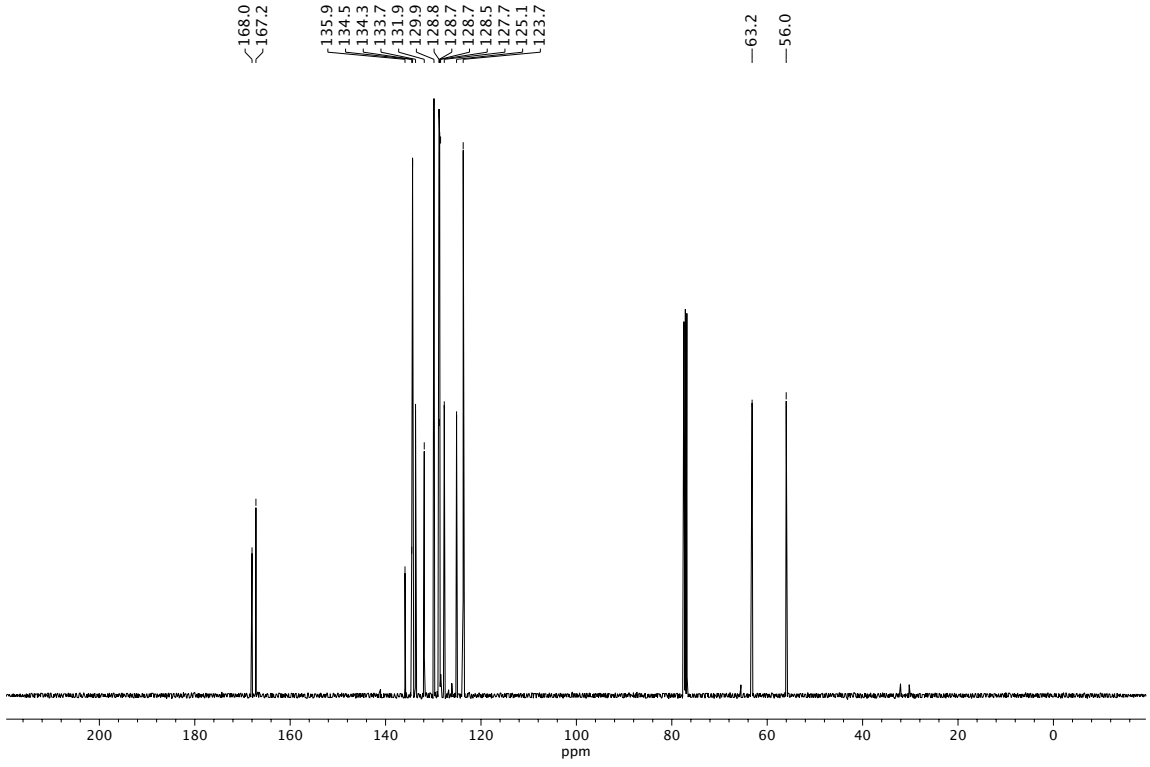
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S5**.



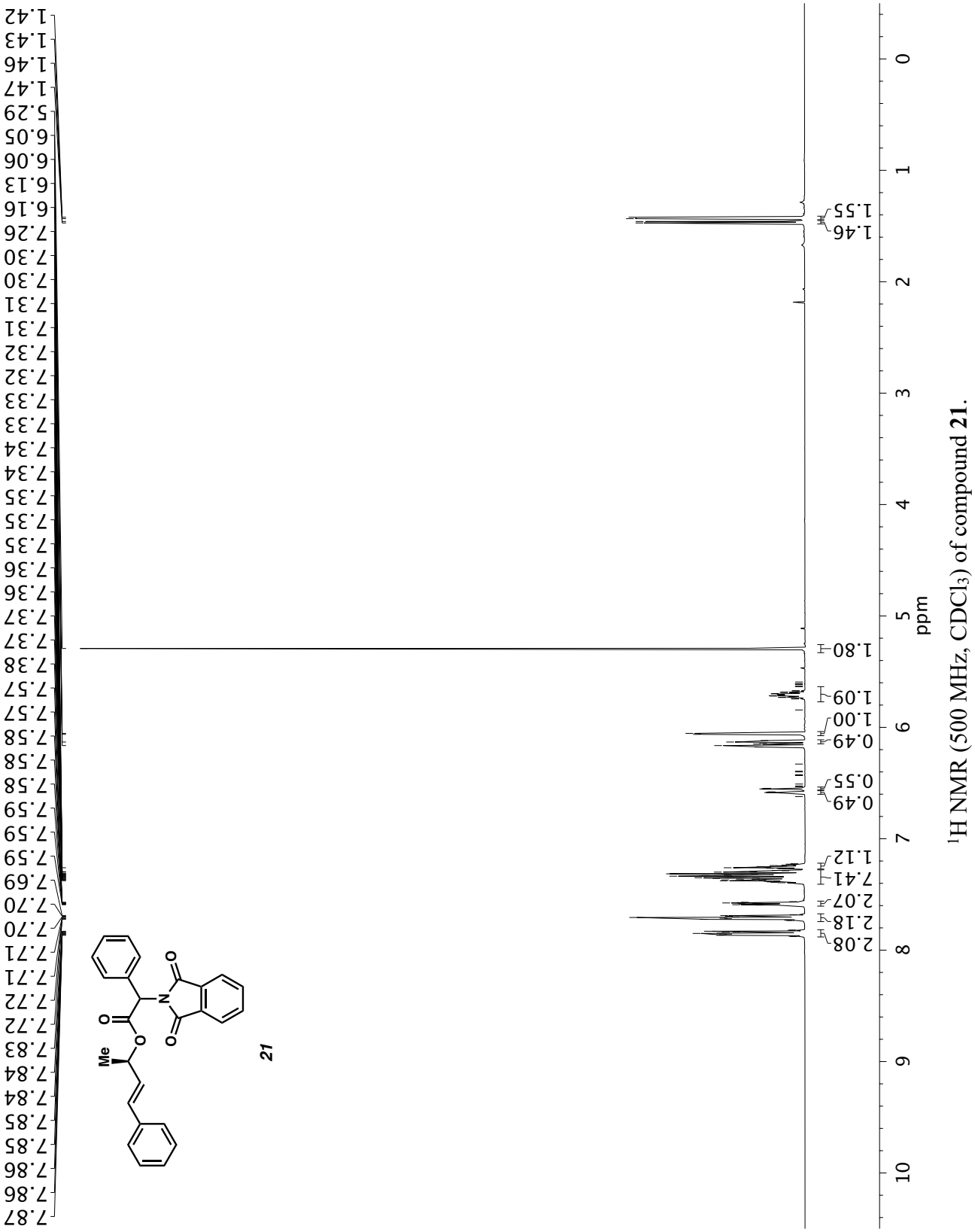
^{1}H NMR (400 MHz, $CDCl_3$) of compound **19**.



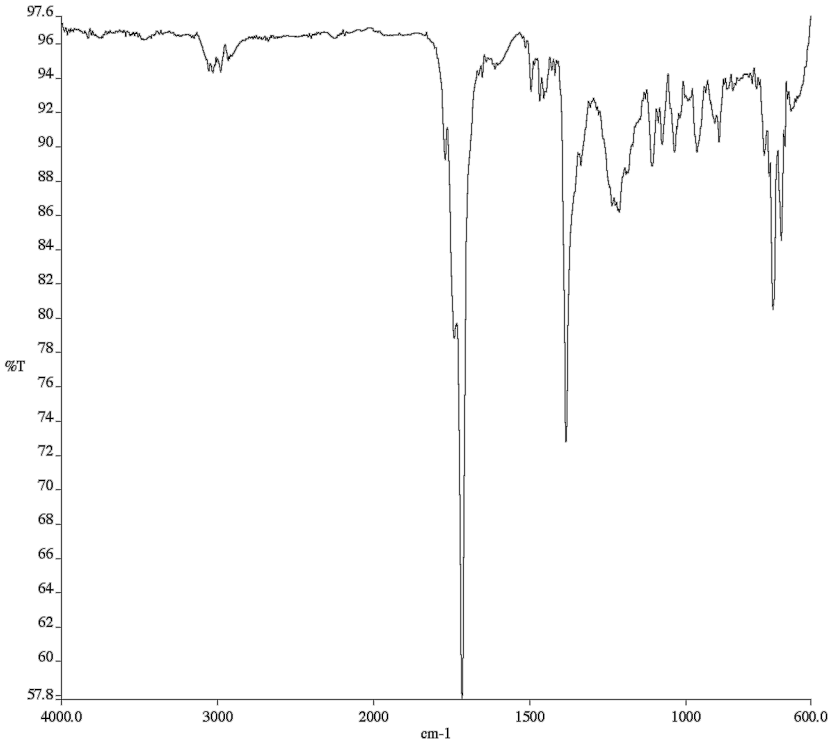
Infrared spectrum (Thin Film, NaCl) of compound **19**.



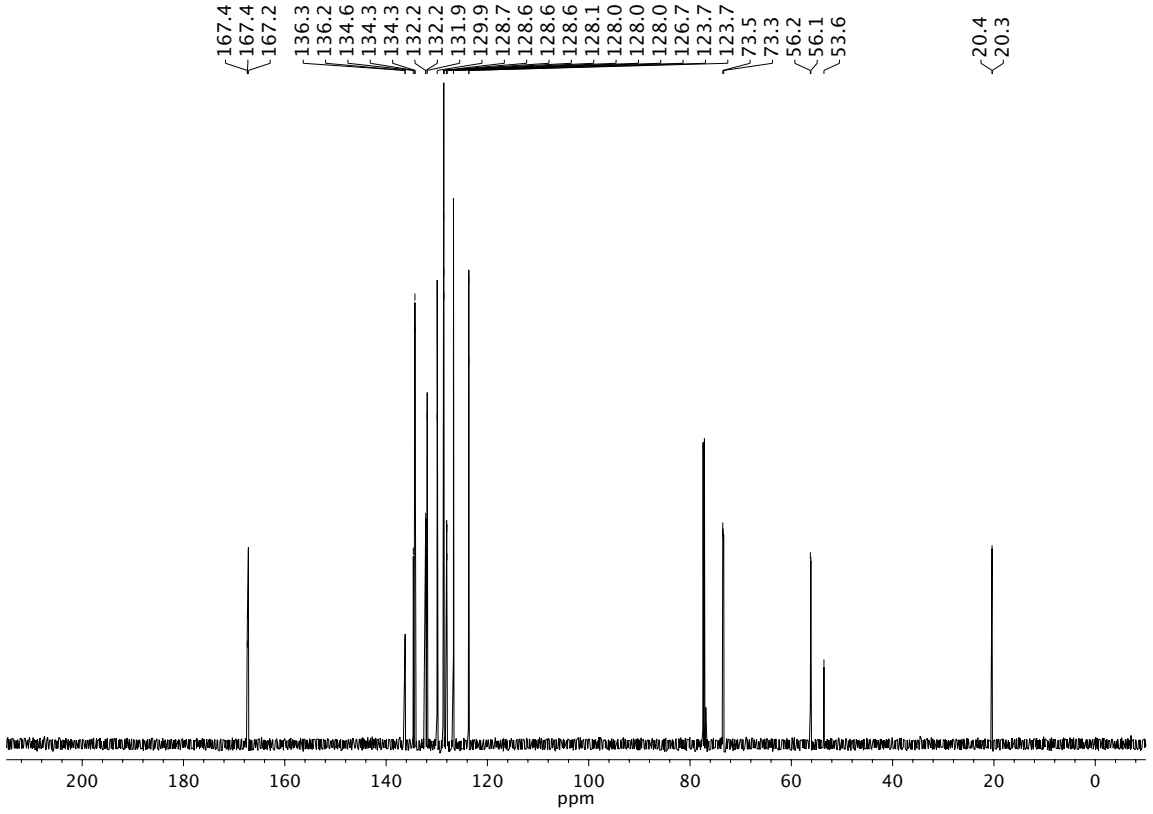
^{13}C NMR (100 MHz, $CDCl_3$) of compound **19**.



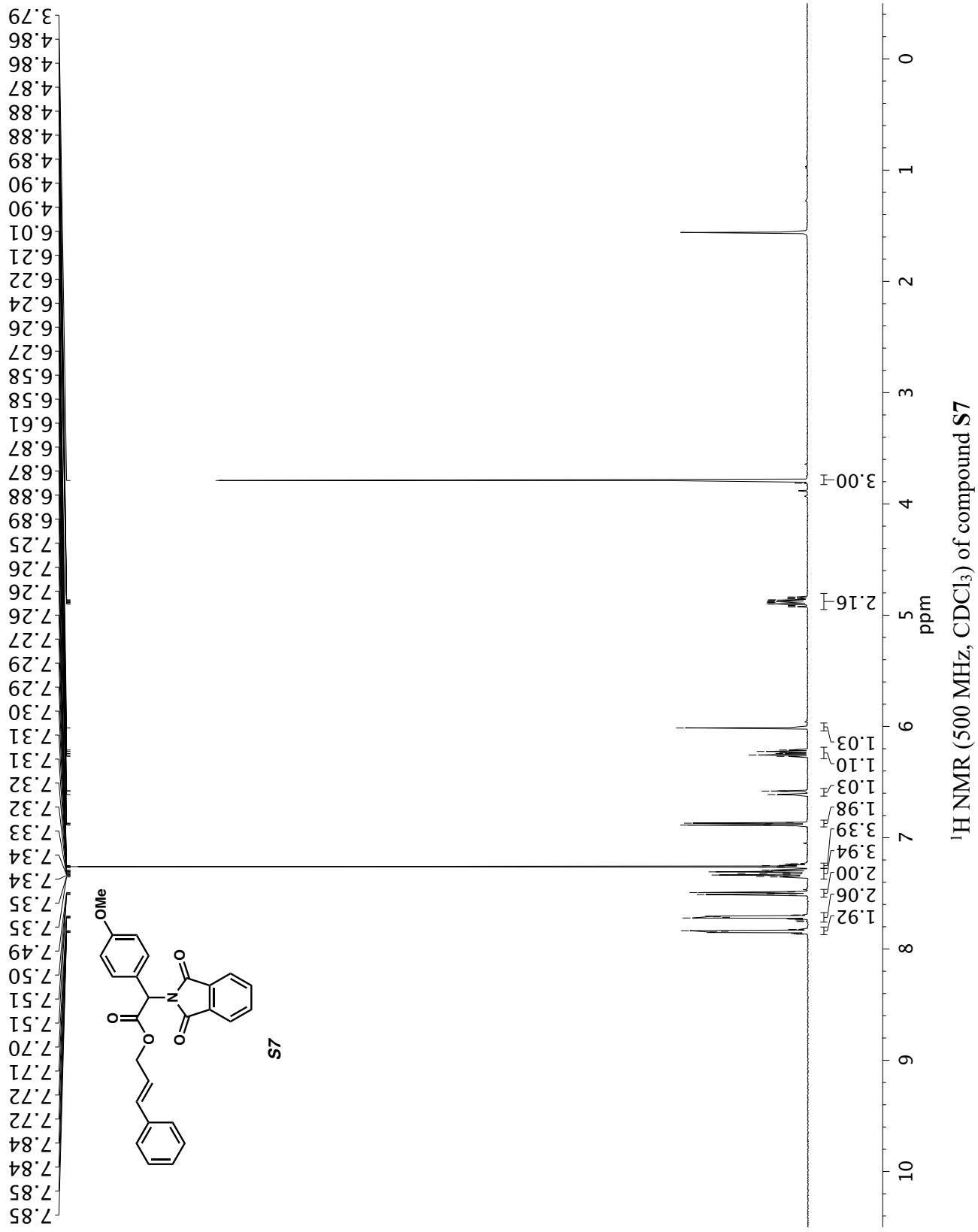
^{1}H NMR (500 MHz, $CDCl_3$) of compound **21**.



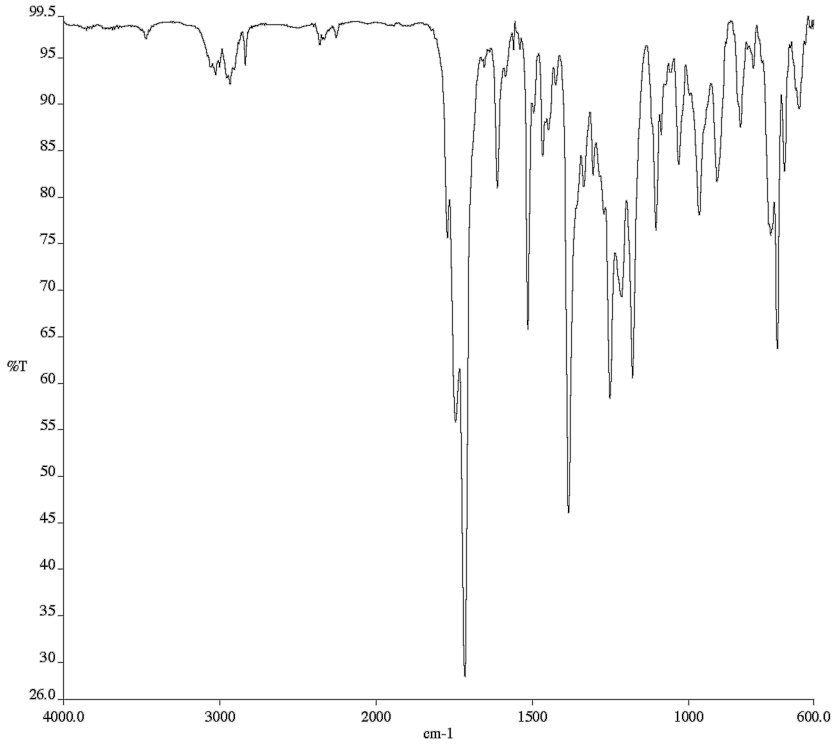
Infrared spectrum (Thin Film, NaCl) of compound **21**.



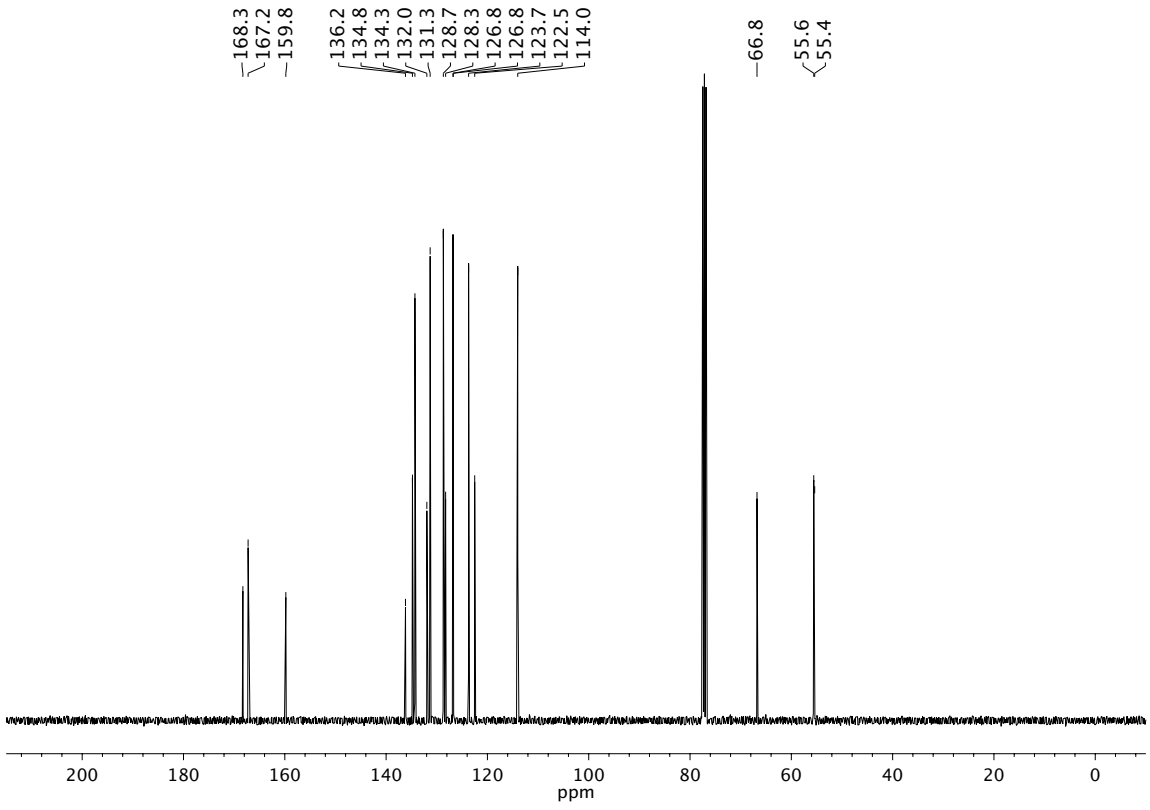
^{13}C NMR (100 MHz, $CDCl_3$) of compound **21**.



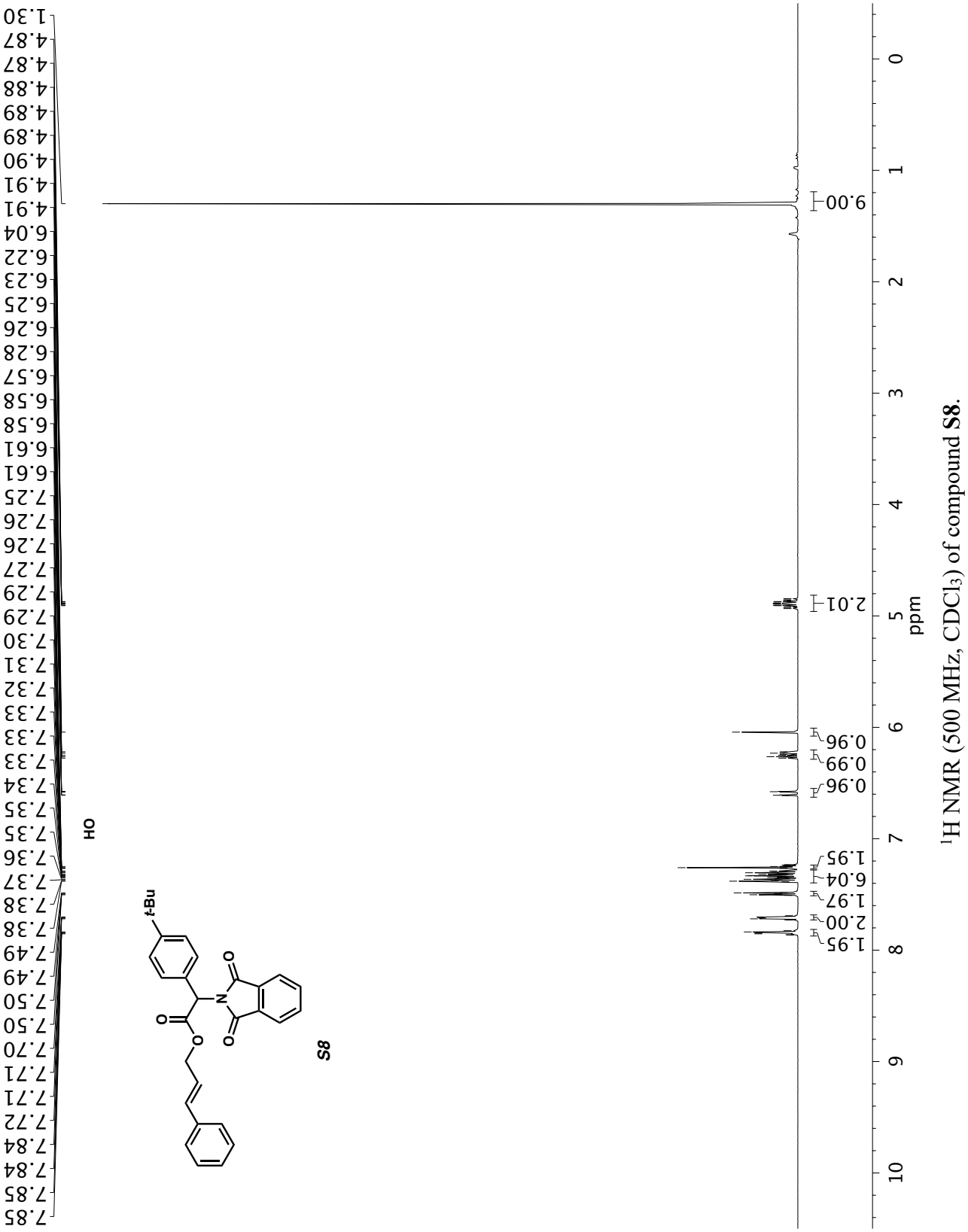
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S7**



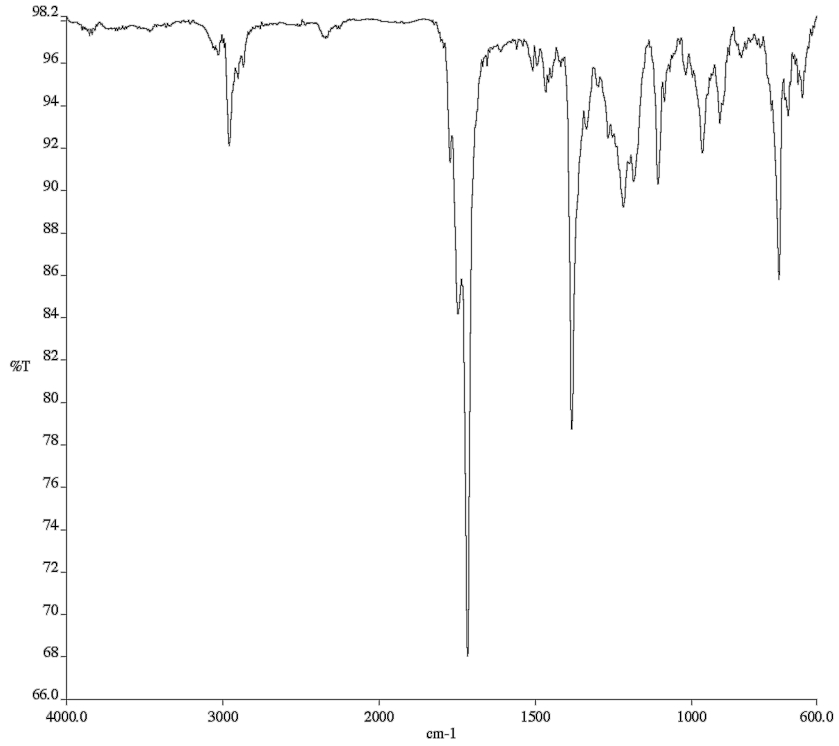
Infrared spectrum (Thin Film, NaCl) of compound **S7**.



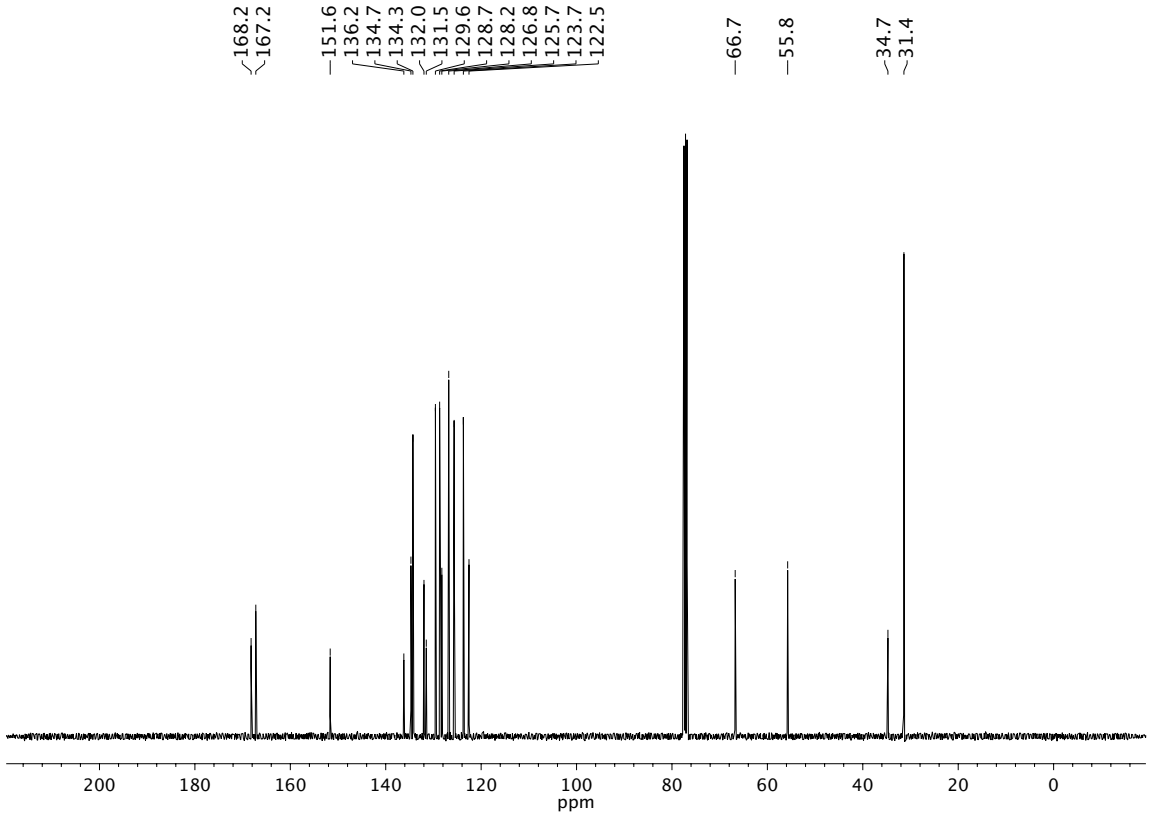
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S7**.



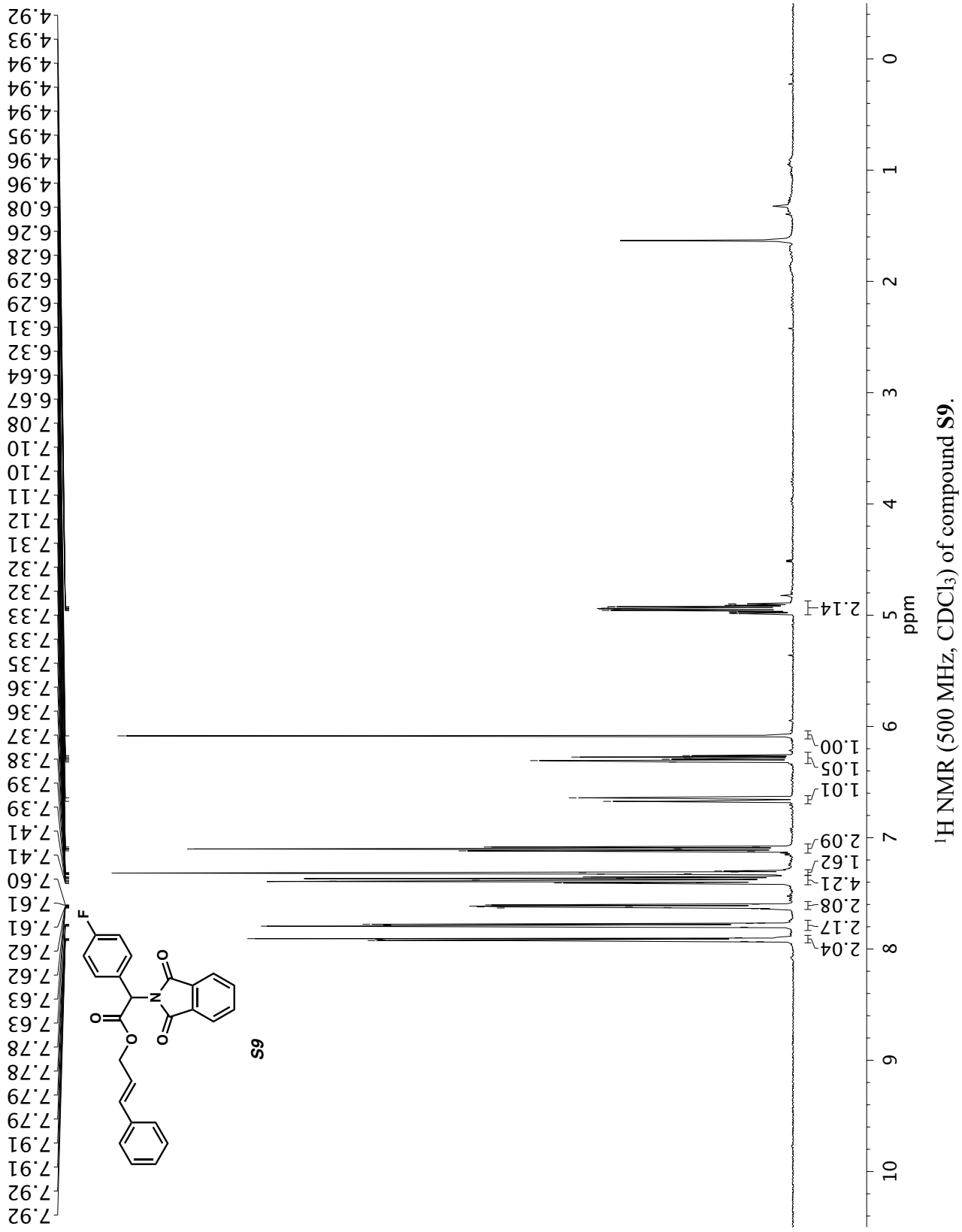
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S8**.



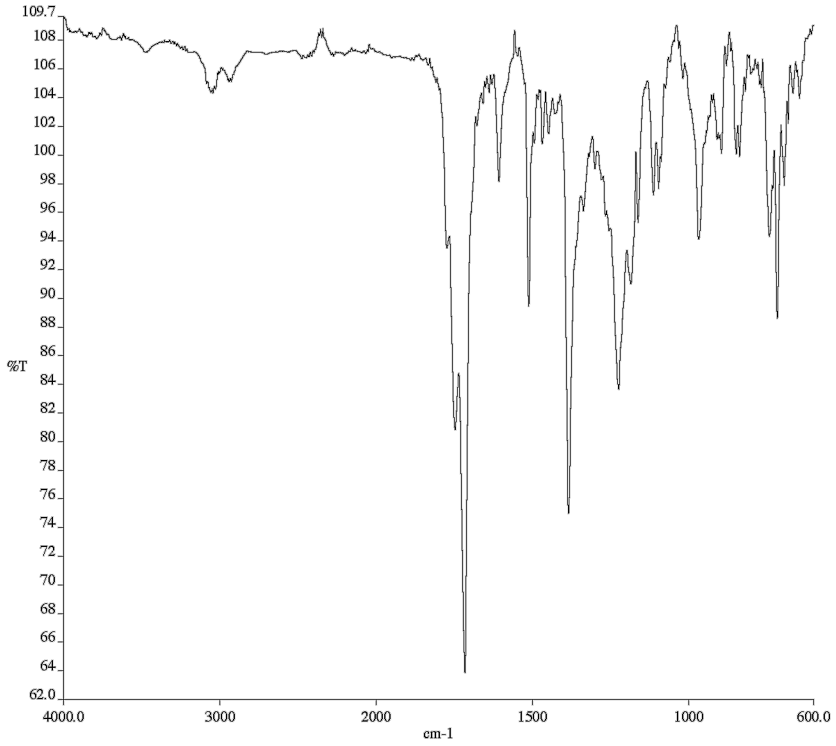
Infrared spectrum (Thin Film, NaCl) of compound **S8**.



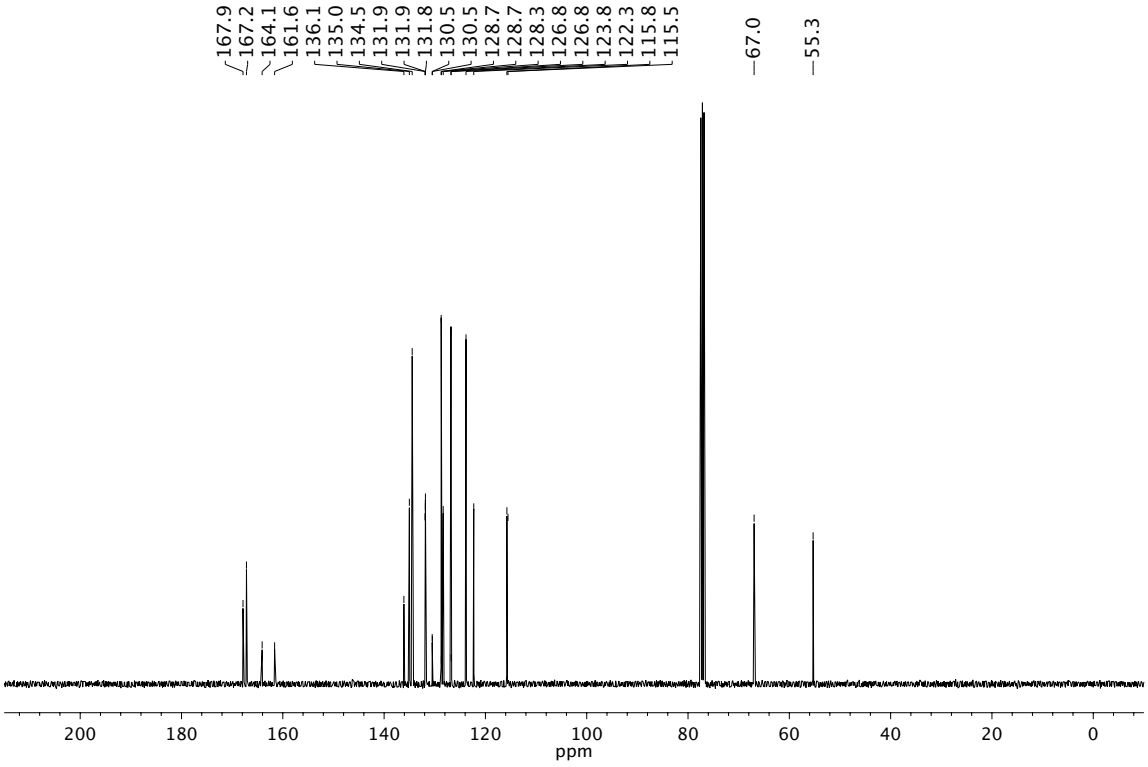
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S8**.



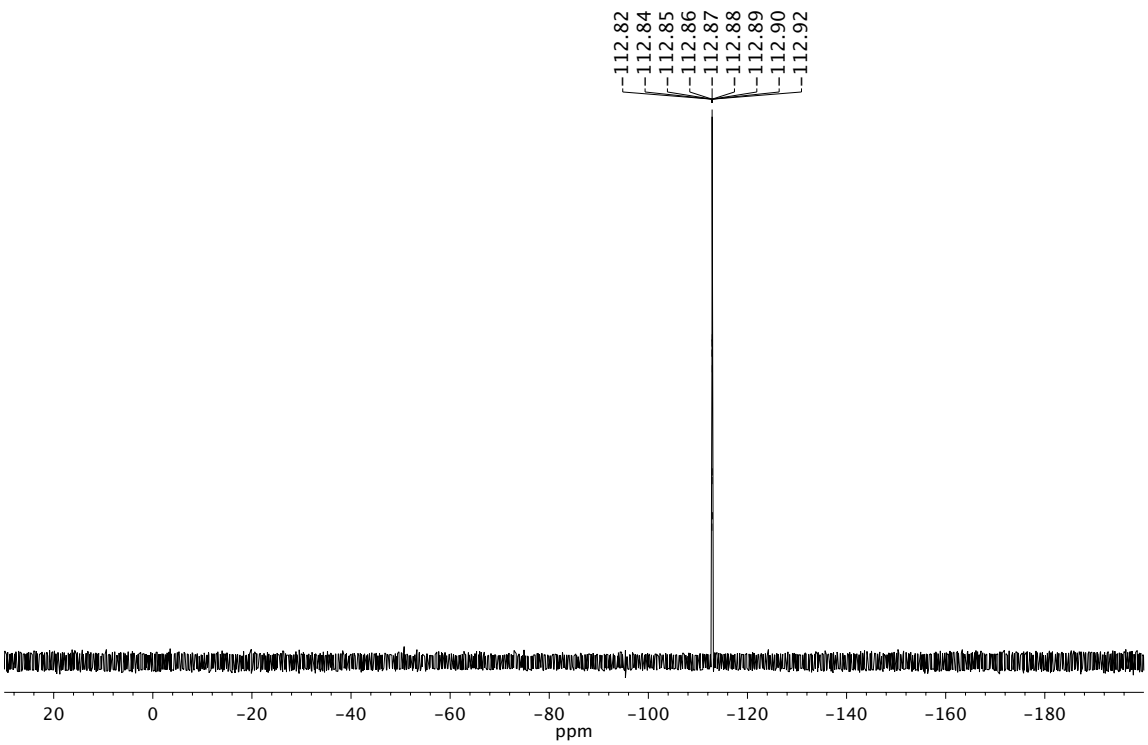
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S9**.



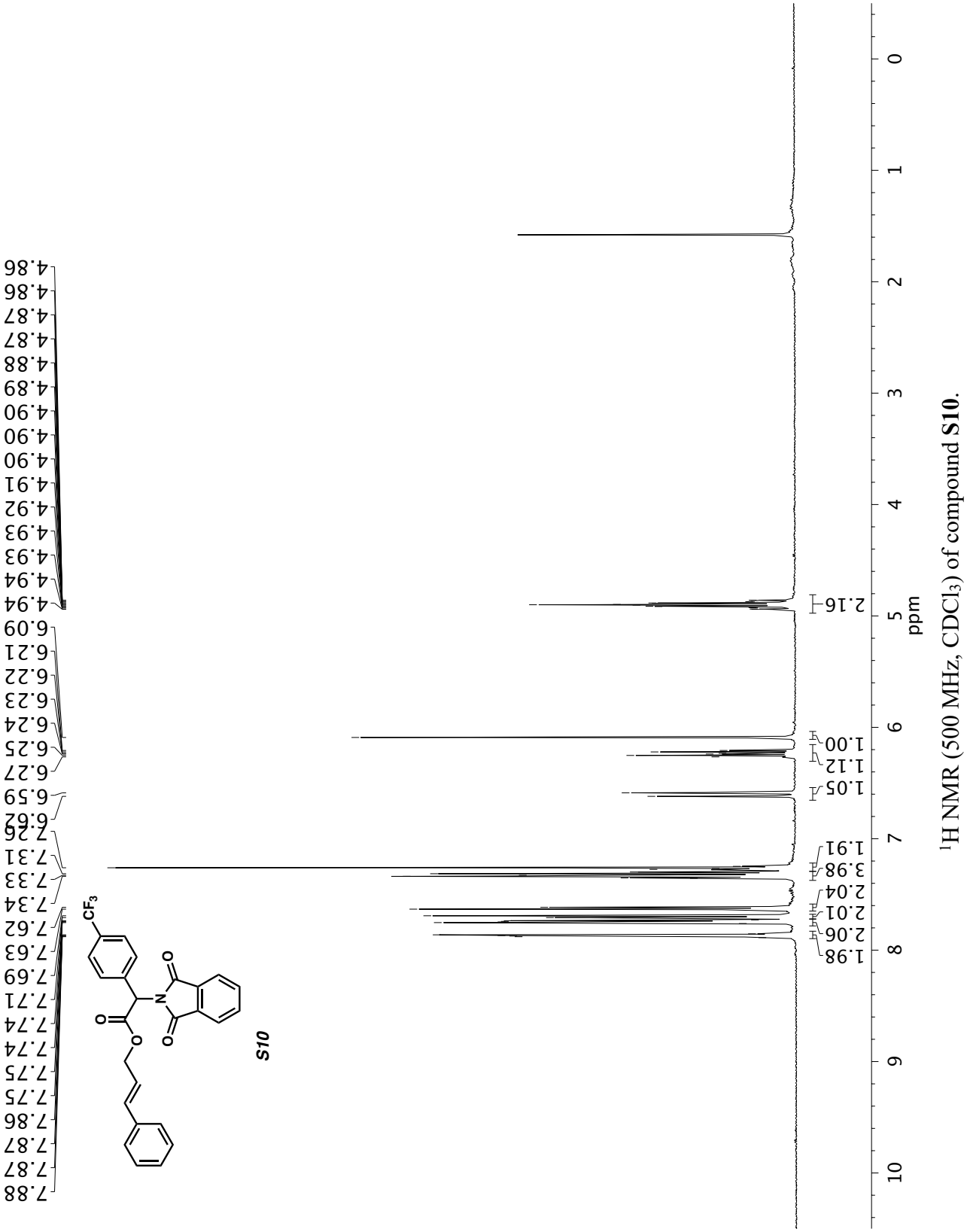
Infrared spectrum (Thin Film, NaCl) of compound **S9**.



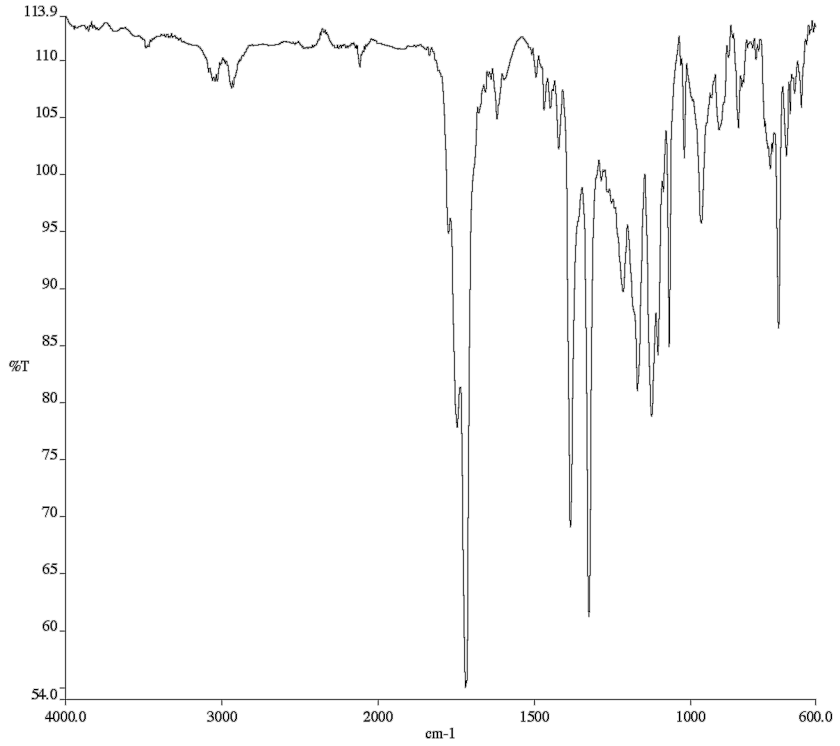
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S9**.



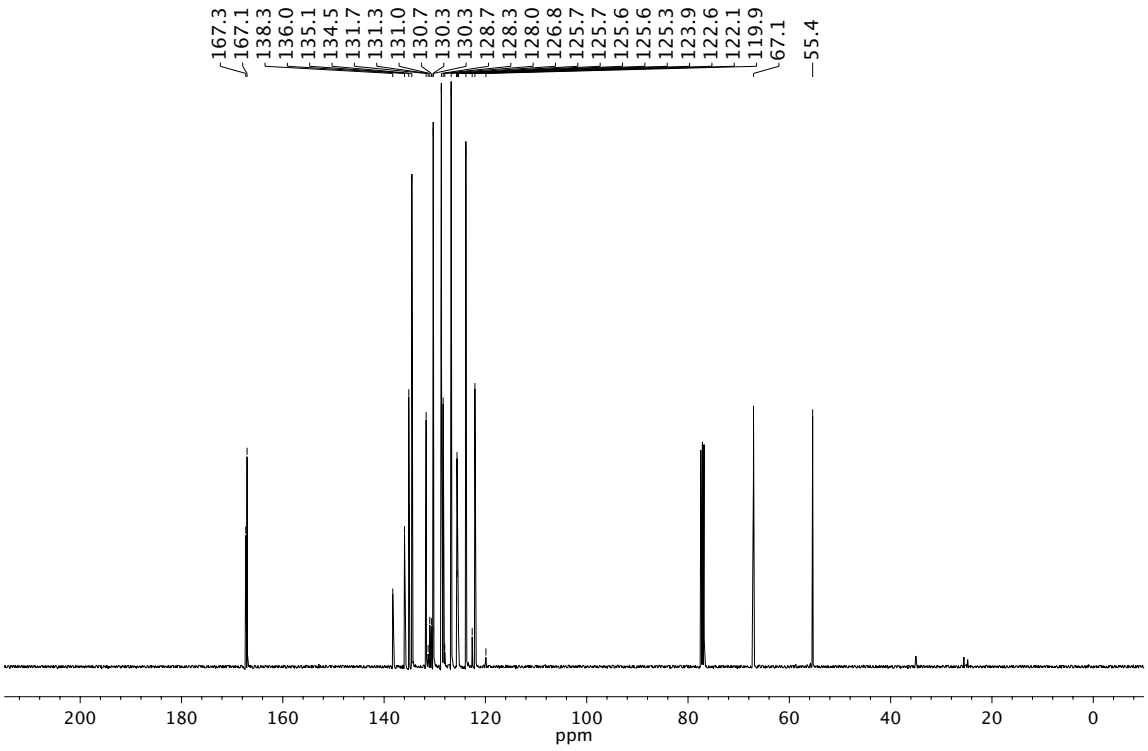
^{19}F NMR (282 MHz, $CDCl_3$) of compound **S9**.



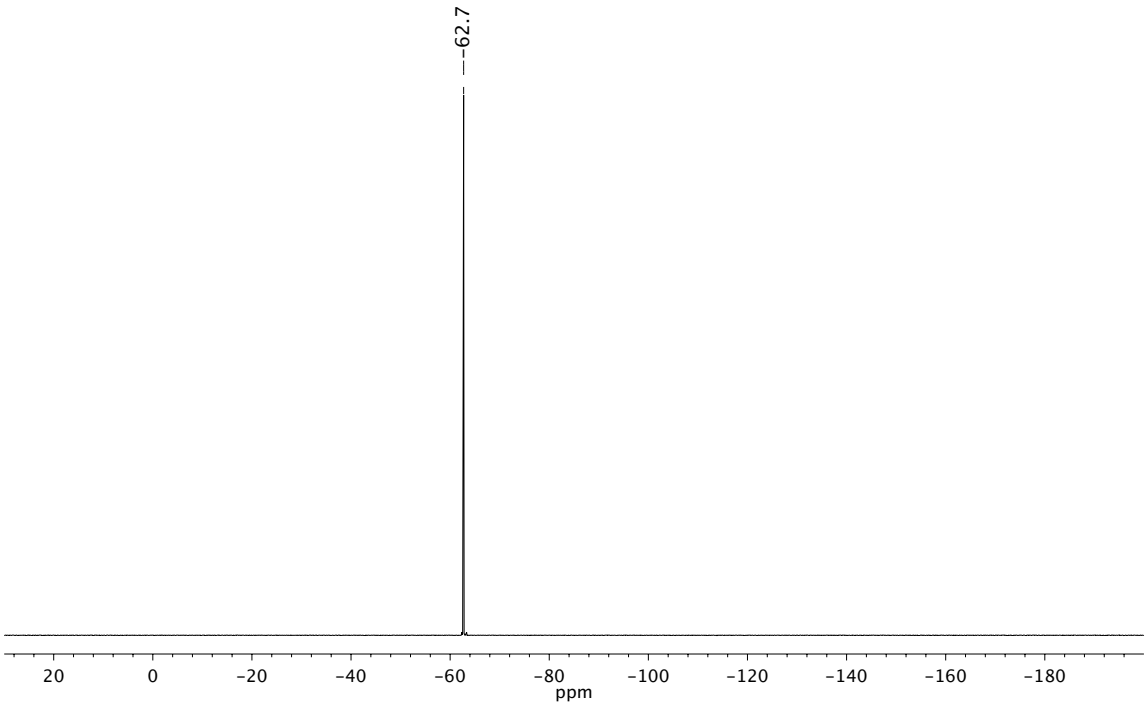
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S10**.



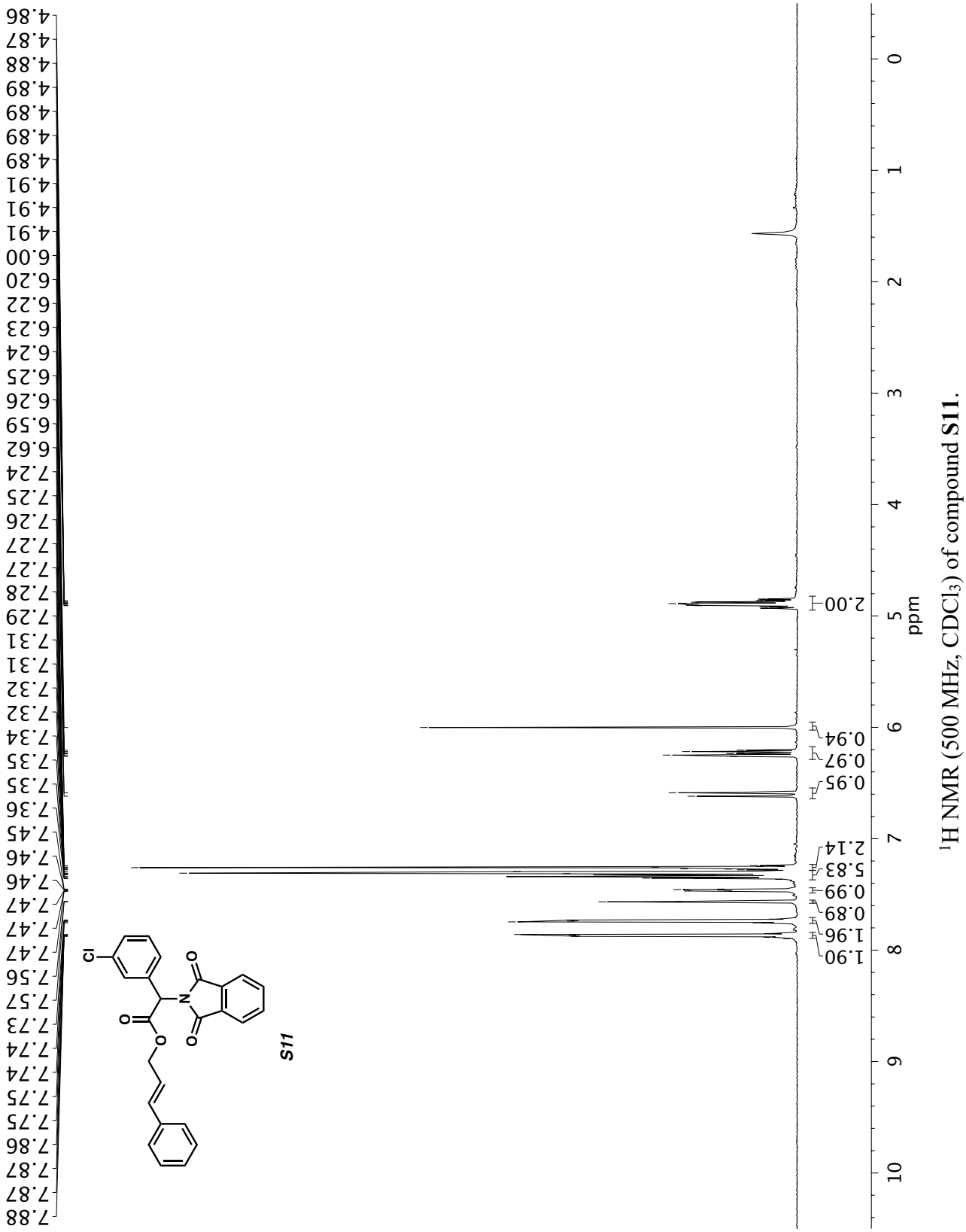
Infrared spectrum (Thin Film, NaCl) of compound **S10**.



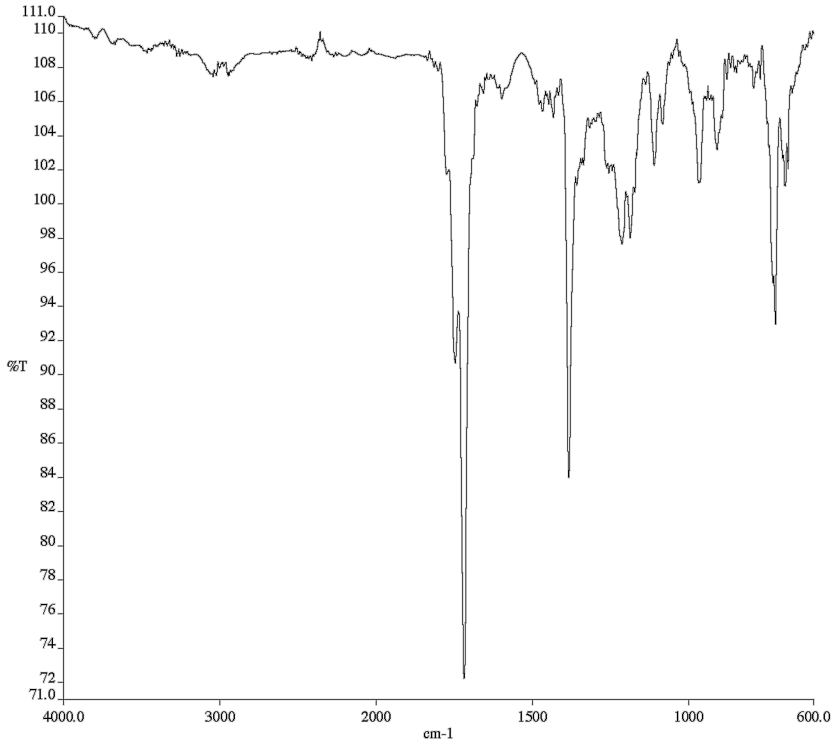
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S10**.



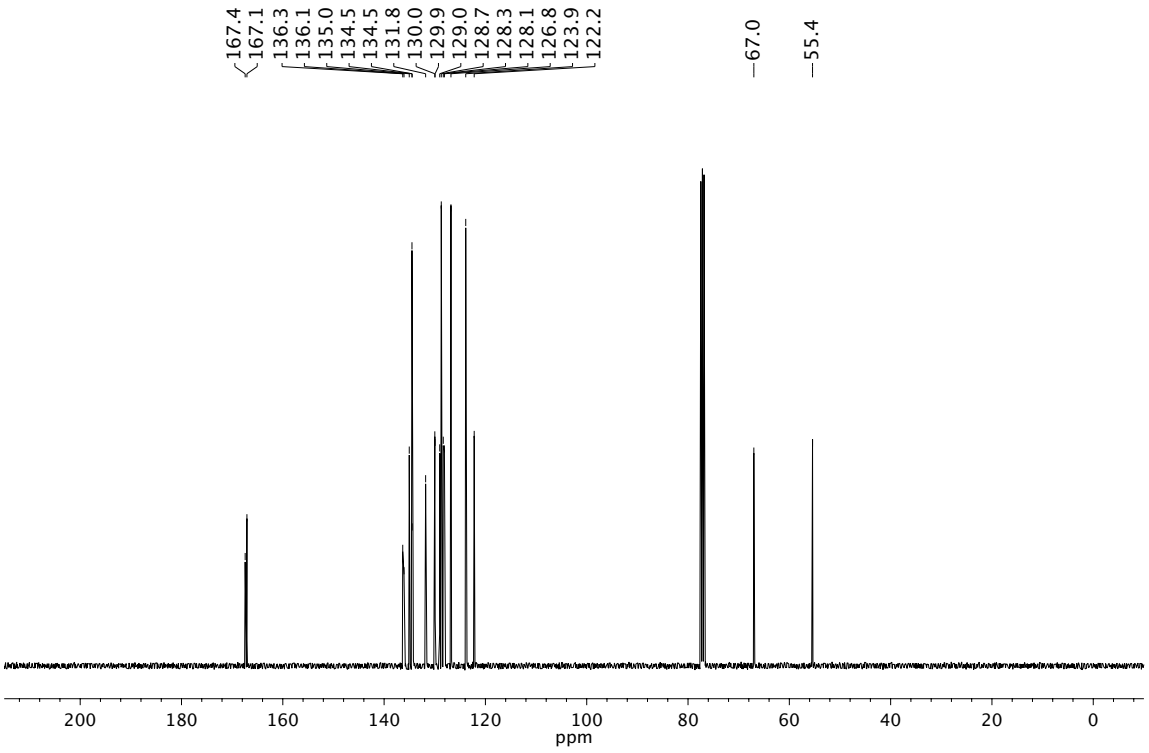
^{19}F NMR (282 MHz, $CDCl_3$) of compound **S10**.



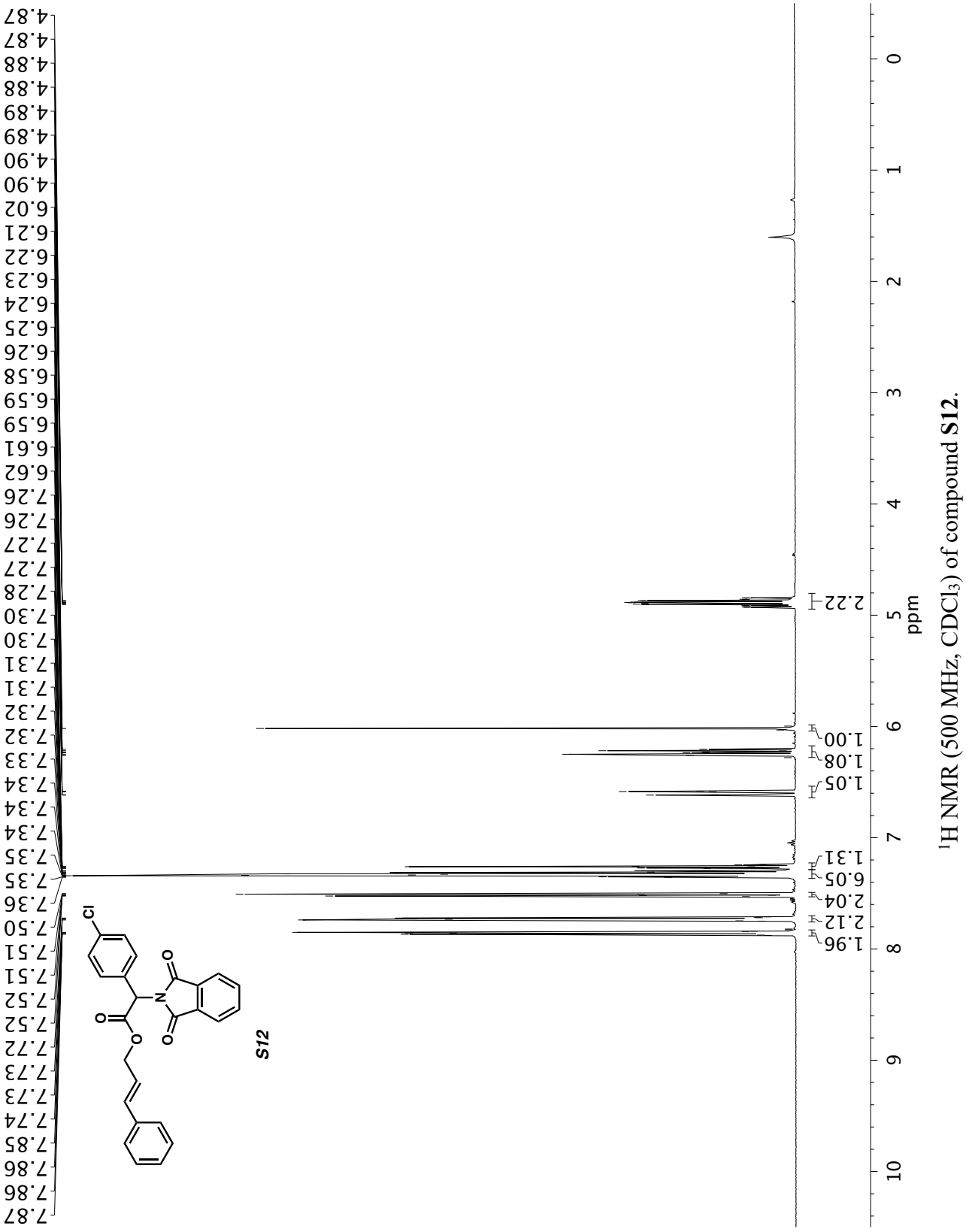
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S11**.



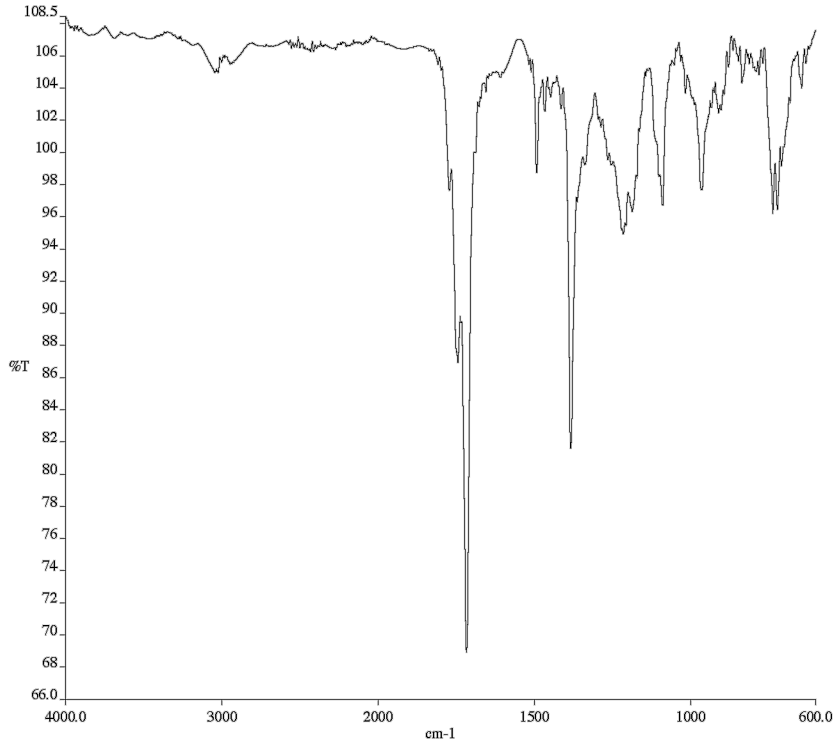
Infrared spectrum (Thin Film, NaCl) of compound **S11**.



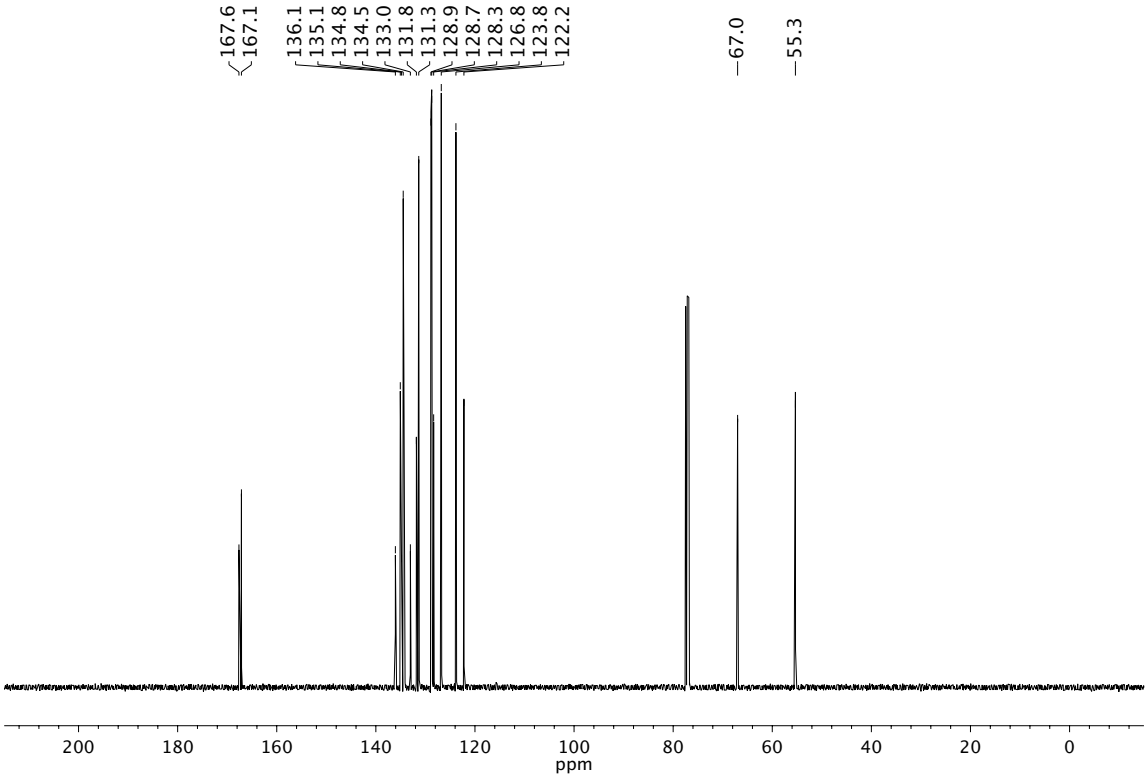
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S11**.



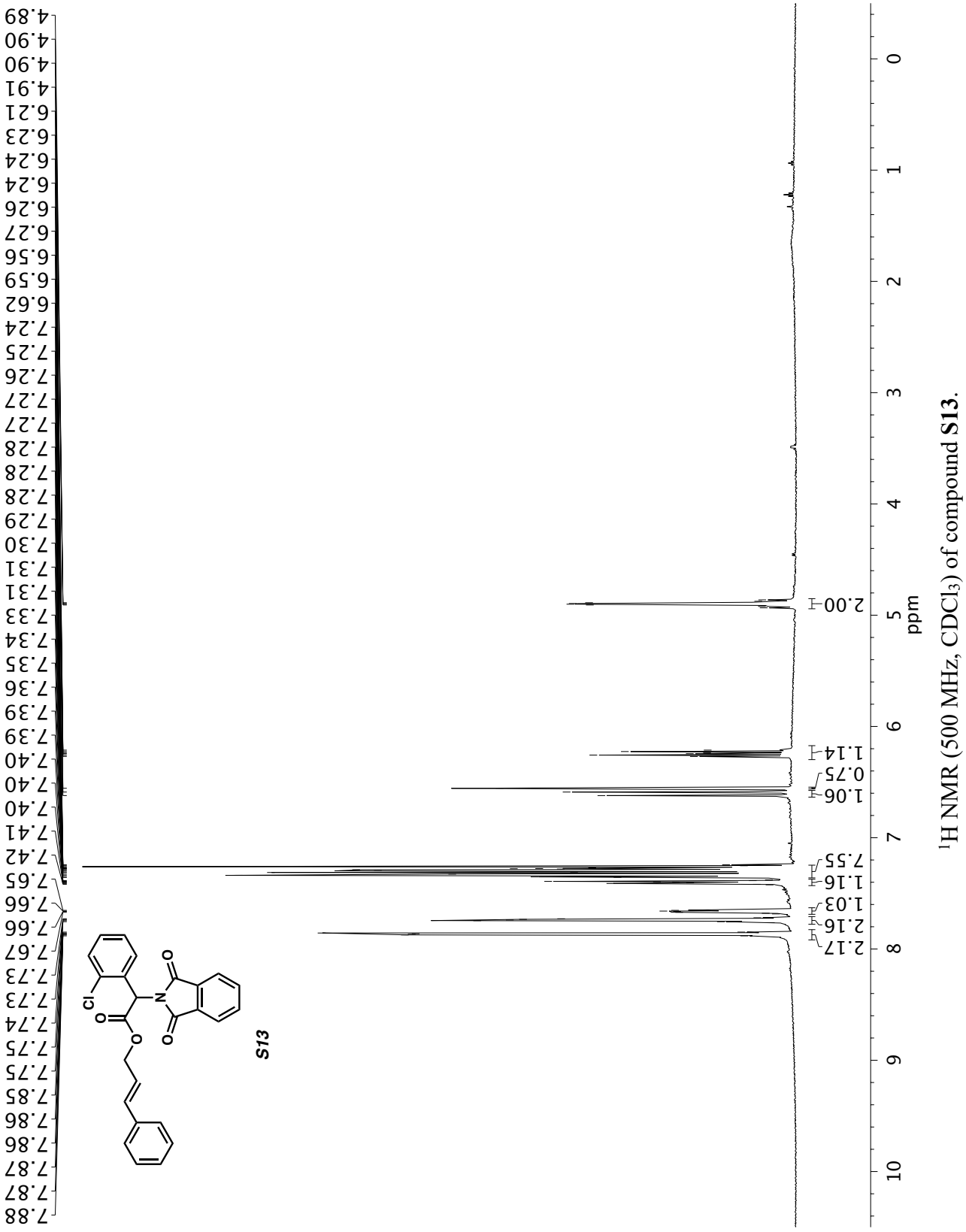
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S12**.



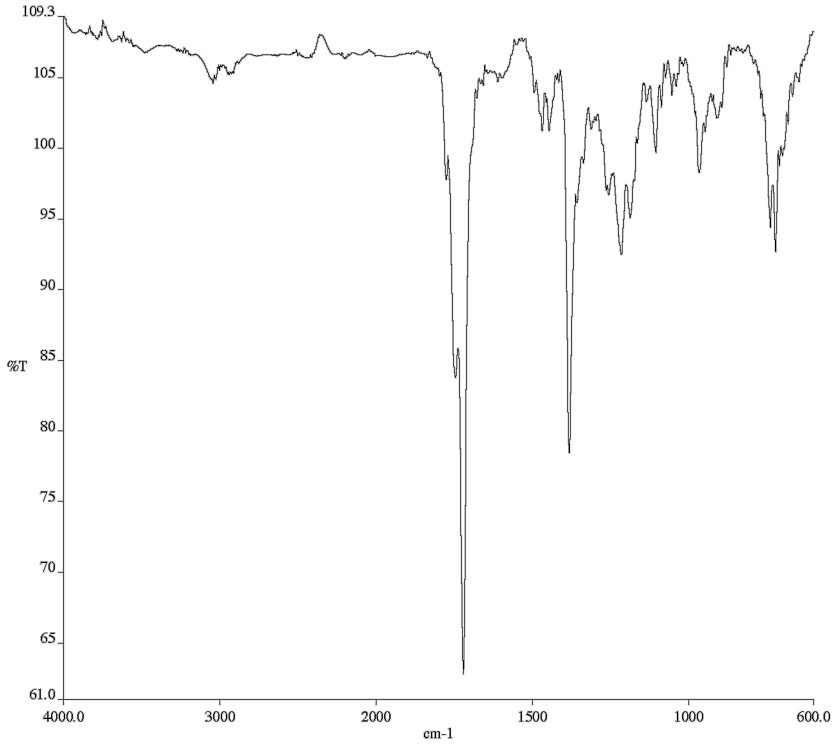
Infrared spectrum (Thin Film, NaCl) of compound **S12**.



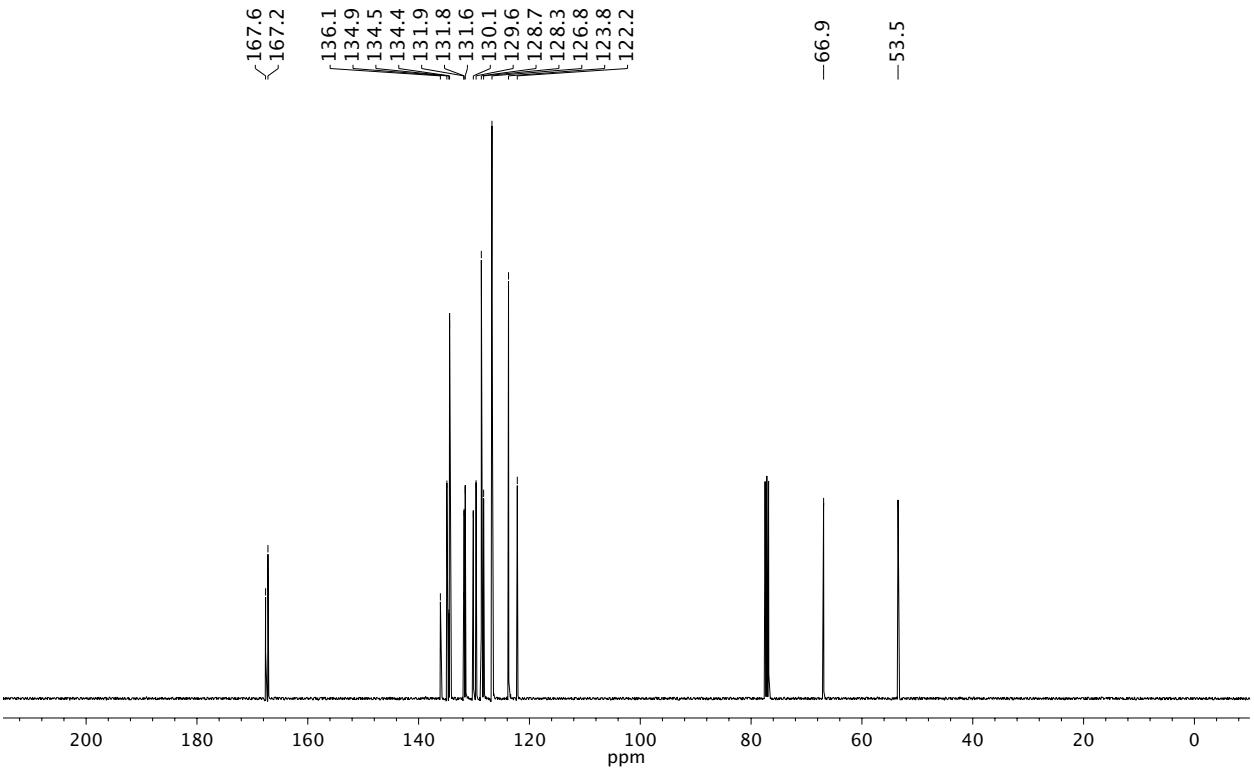
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S12**.



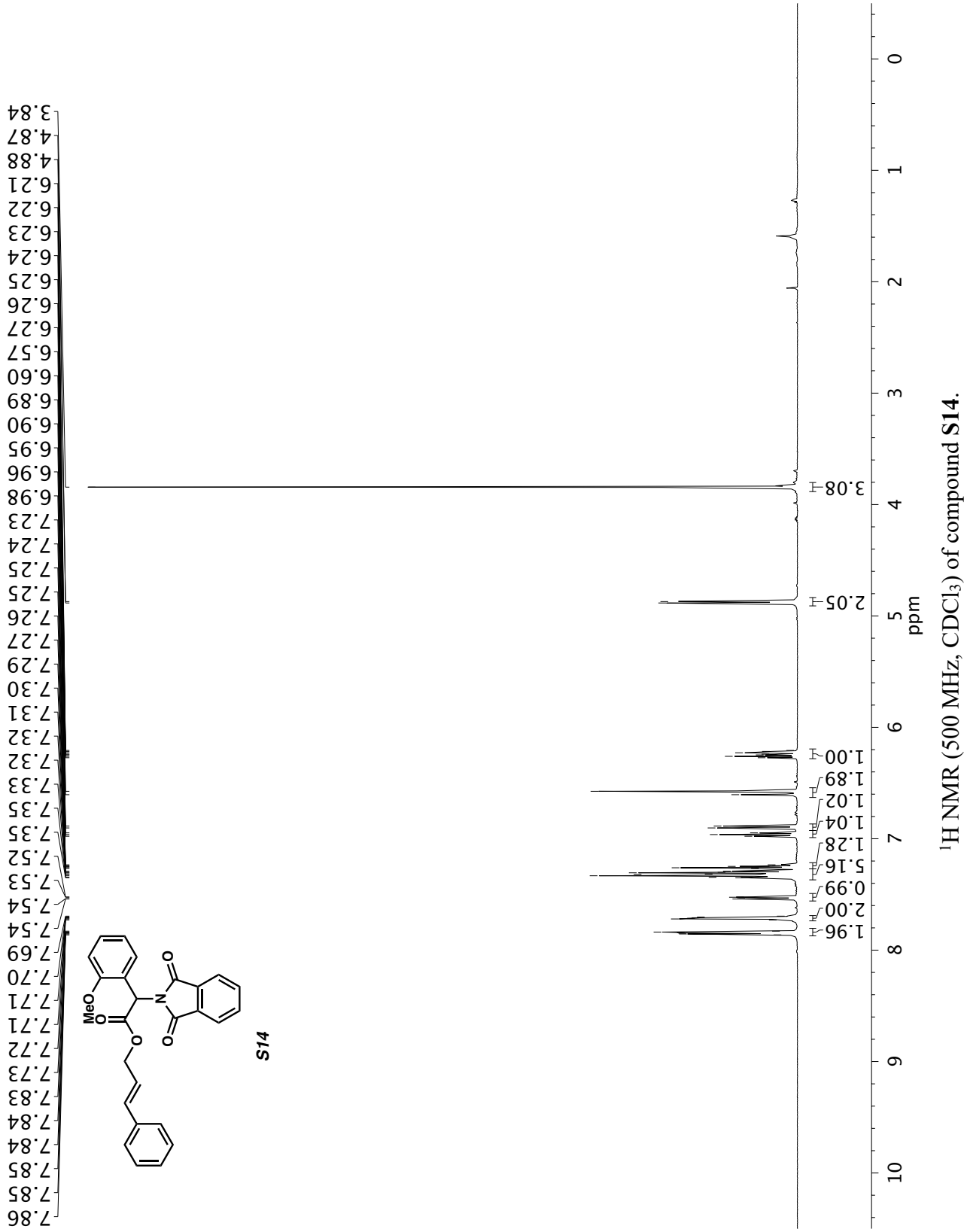
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S13**.



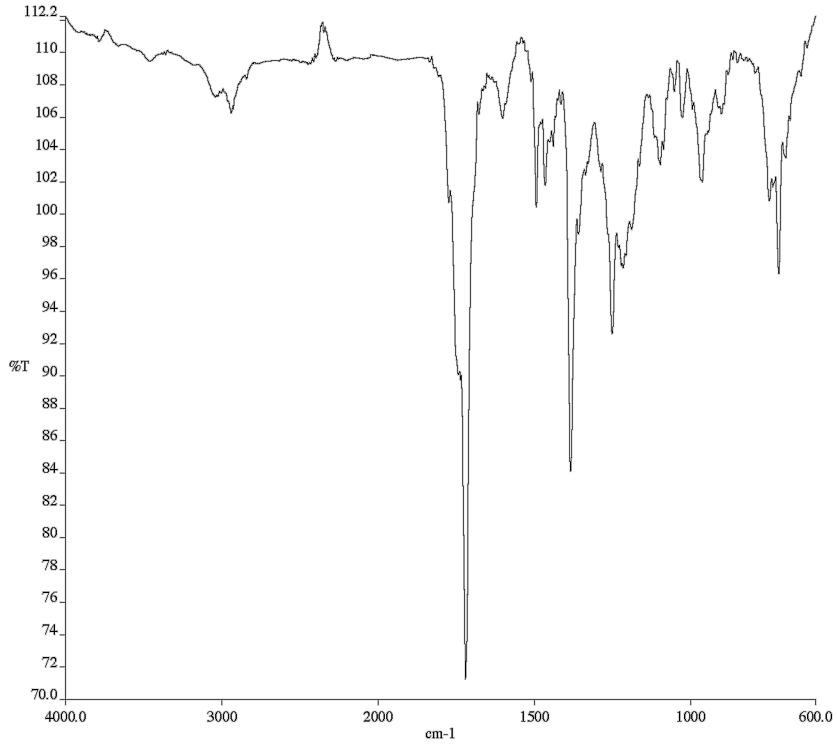
Infrared spectrum (Thin Film, NaCl) of compound **S13**.



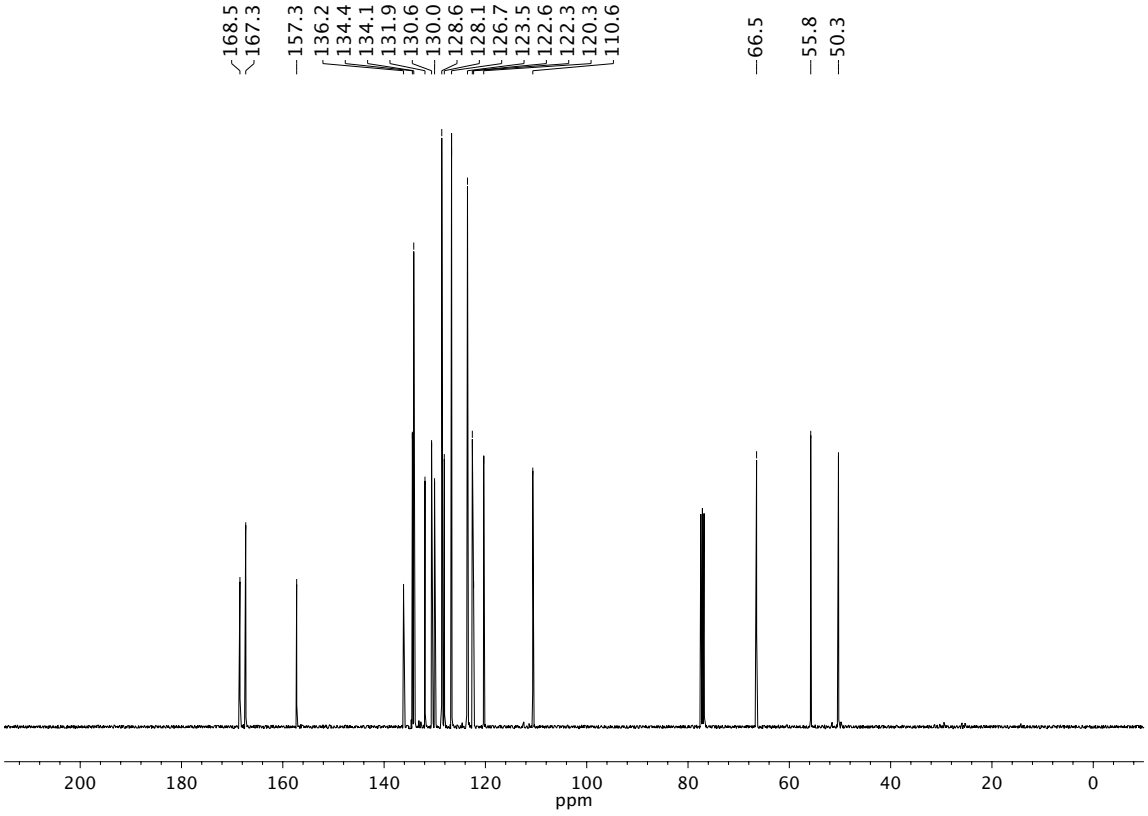
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S13**.



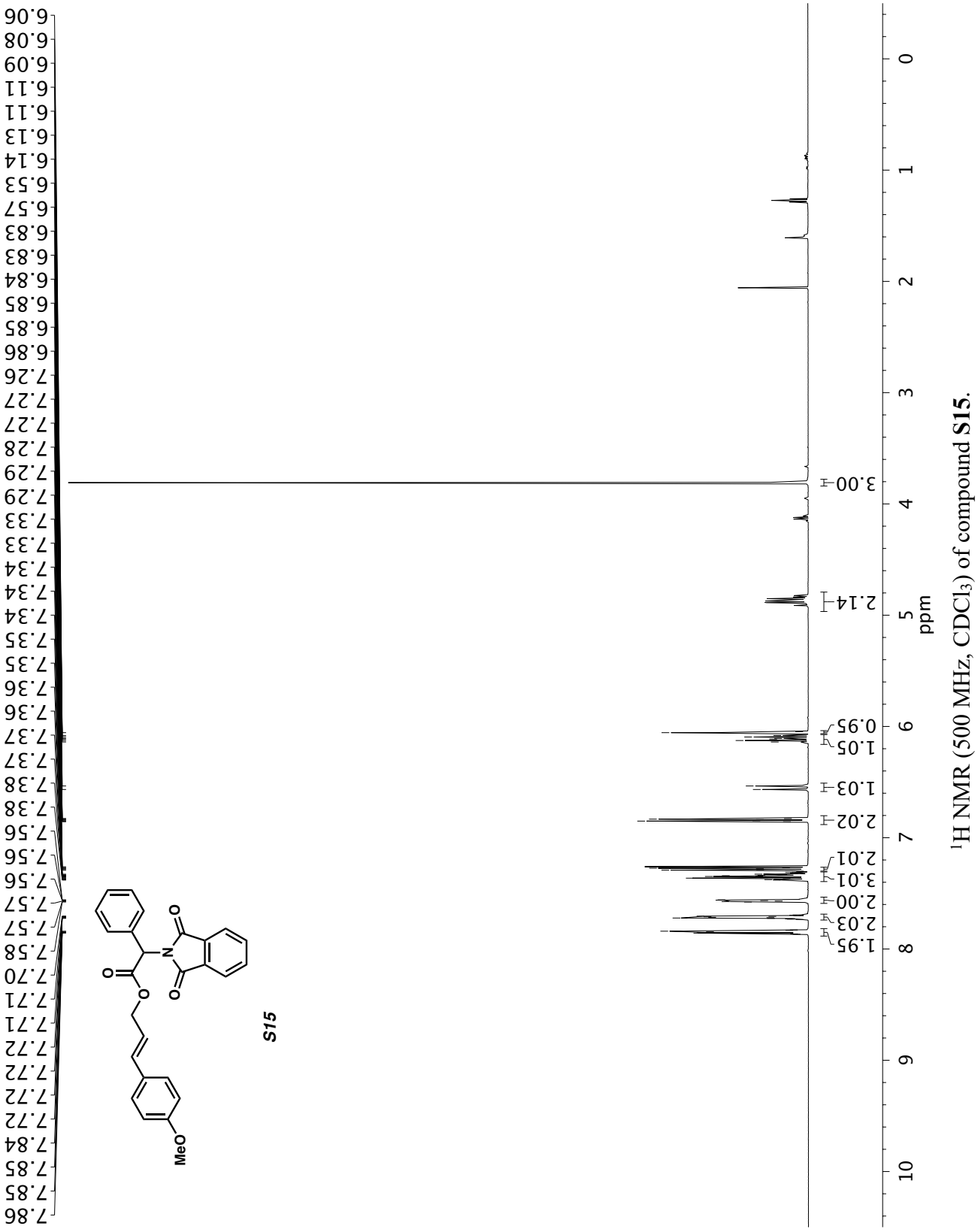
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S14**.



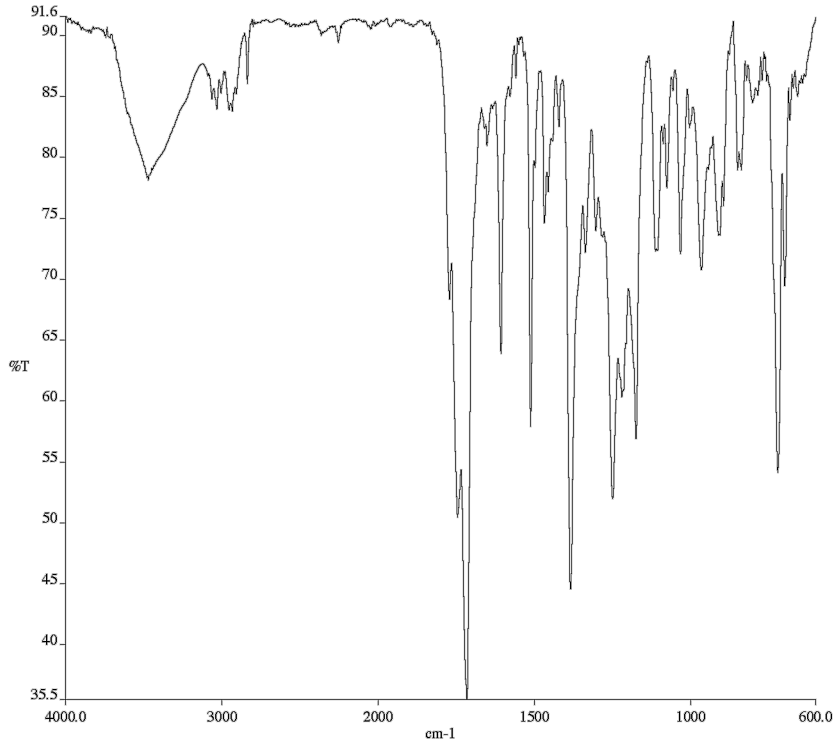
Infrared spectrum (Thin Film, NaCl) of compound **S14**.



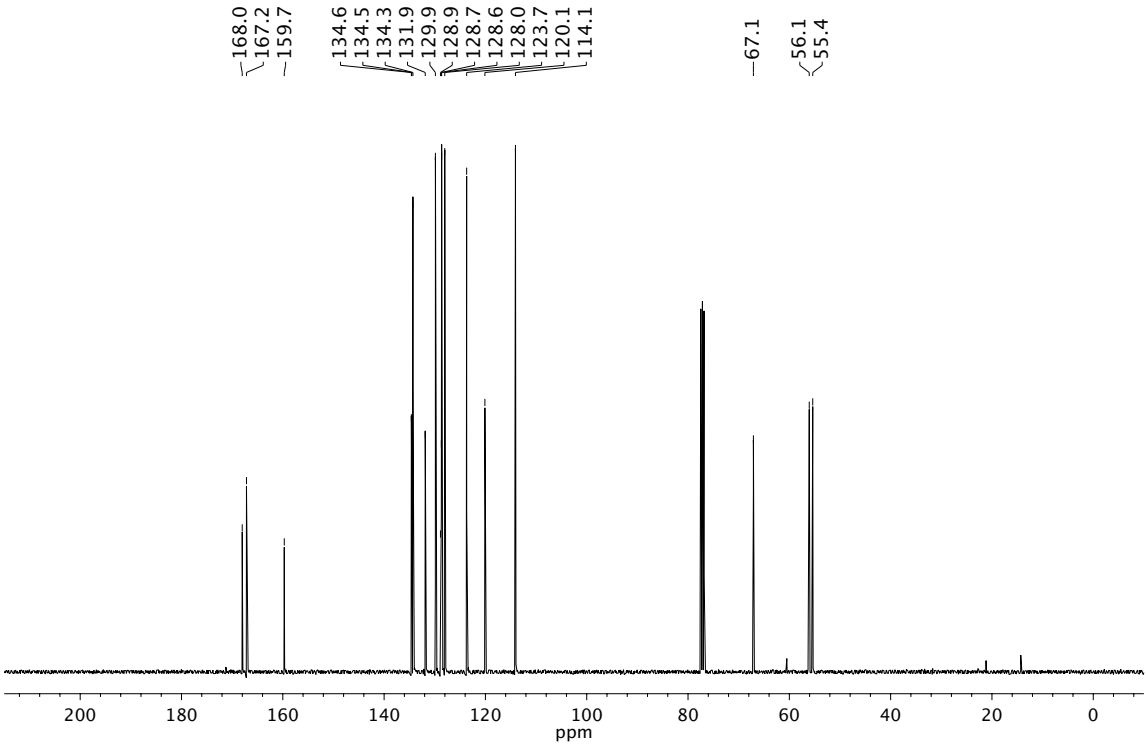
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S14**.



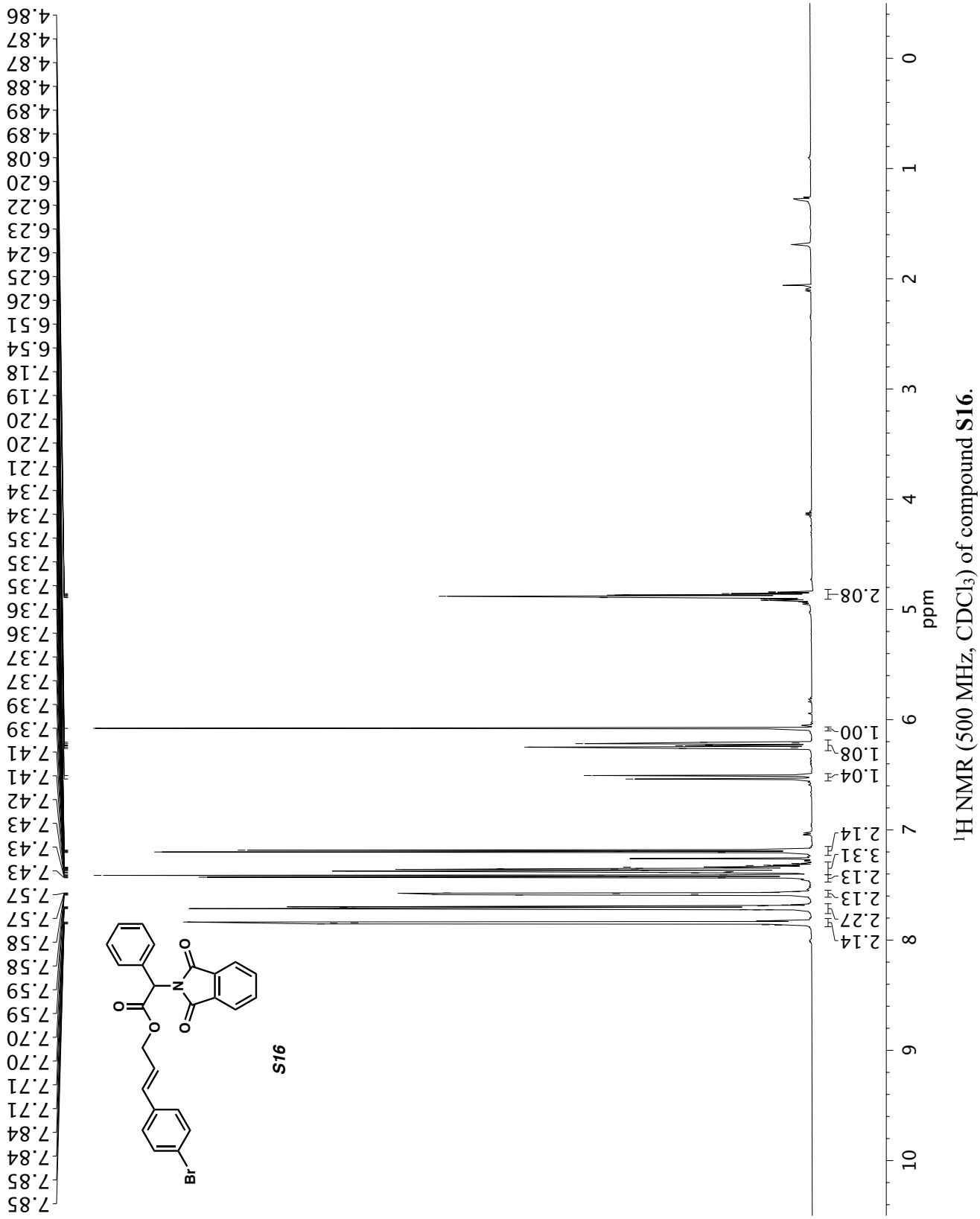
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S15**.



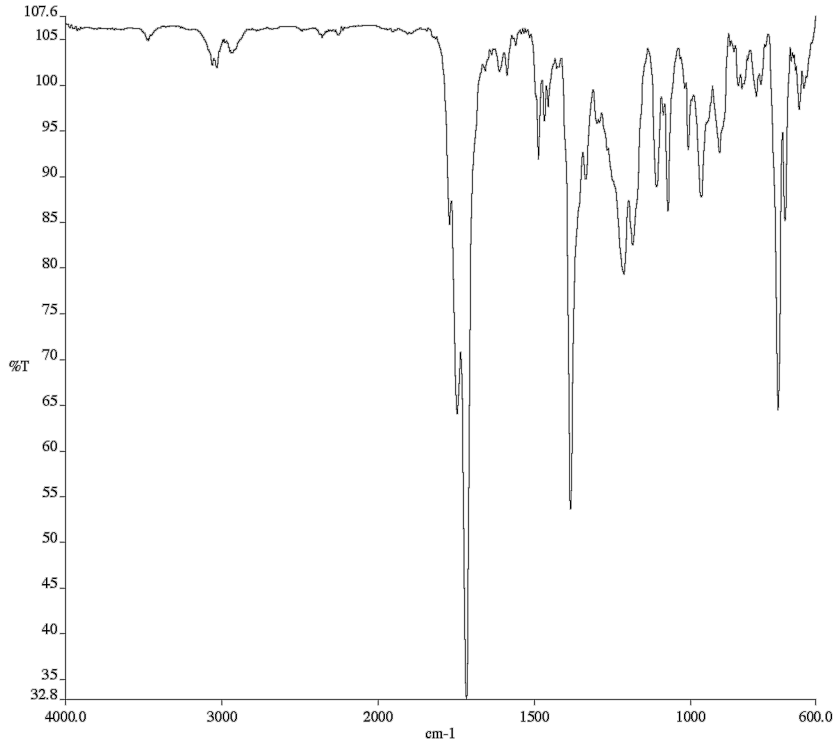
Infrared spectrum (Thin Film, NaCl) of compound **S15**.



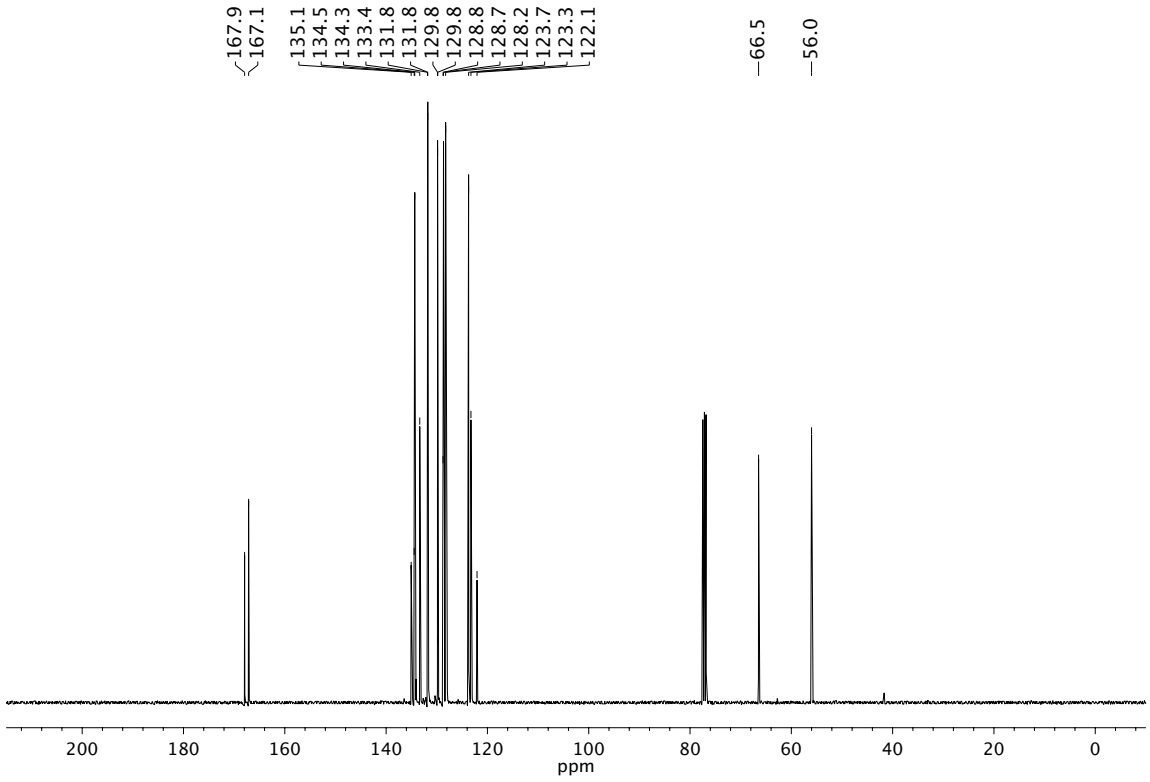
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S15**.



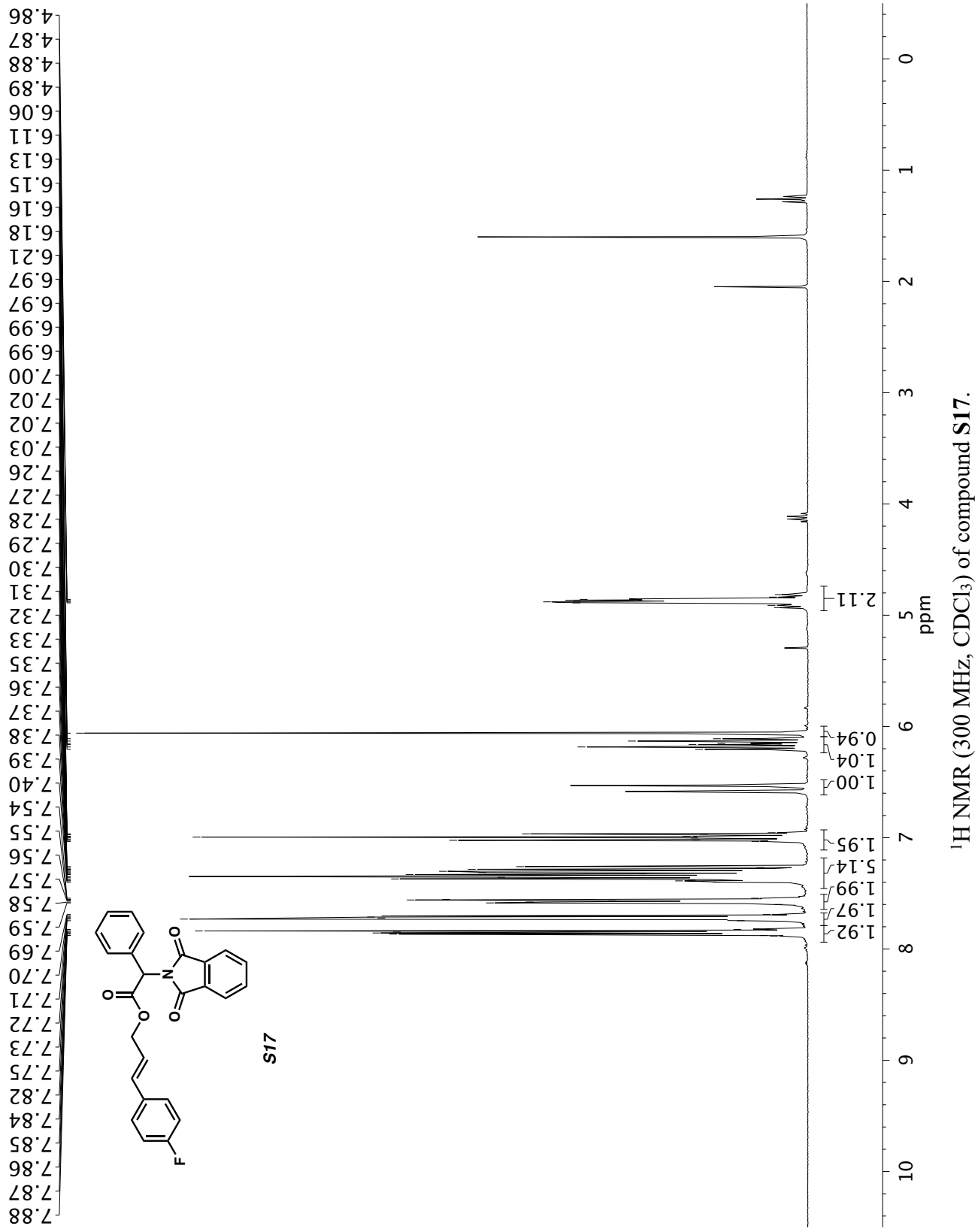
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S16**.



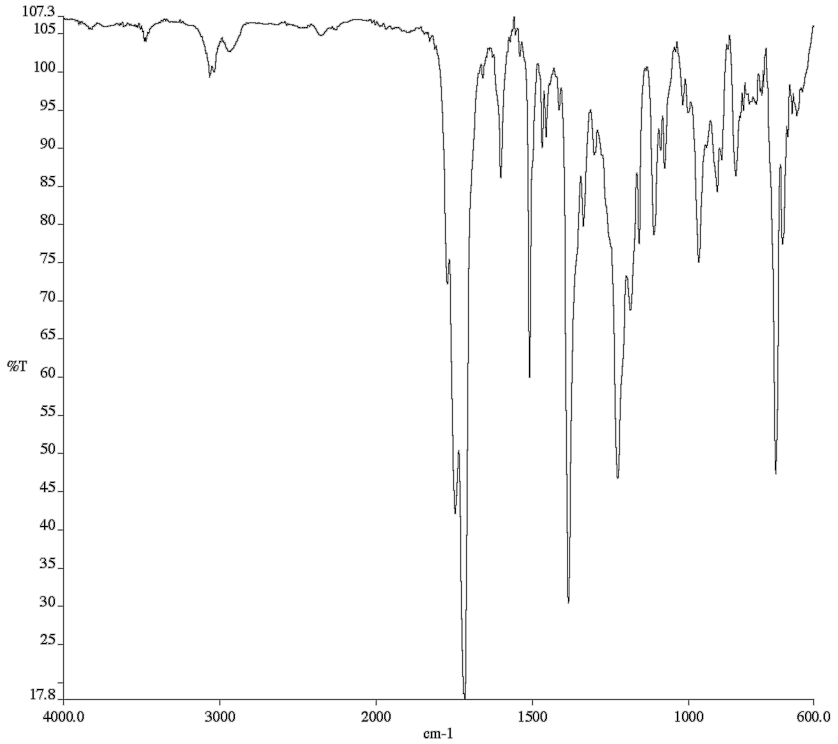
Infrared spectrum (Thin Film, NaCl) of compound **S16**.



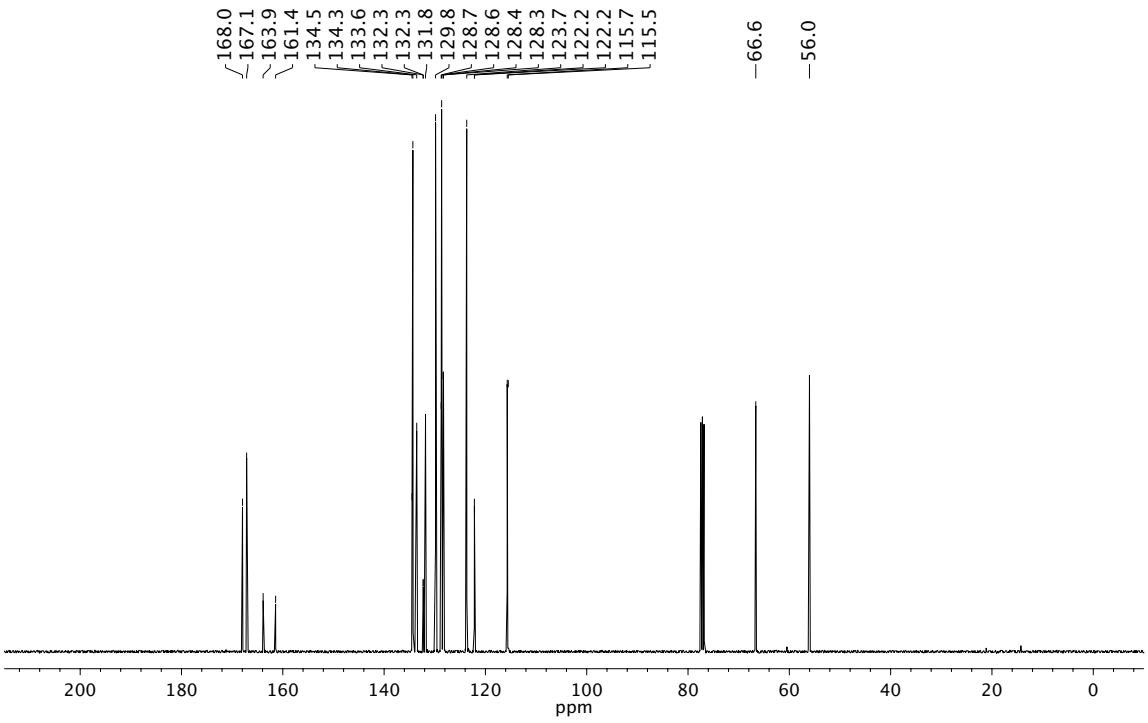
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S16**.



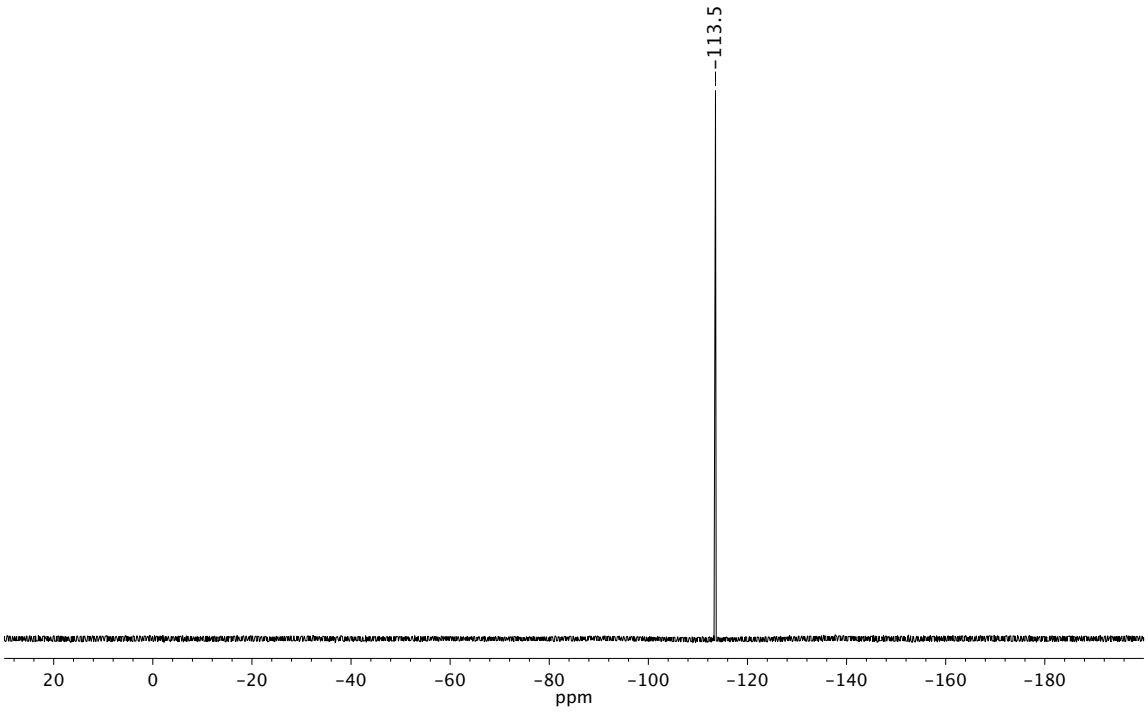
^{1}H NMR (300 MHz, $CDCl_3$) of compound **S17**.



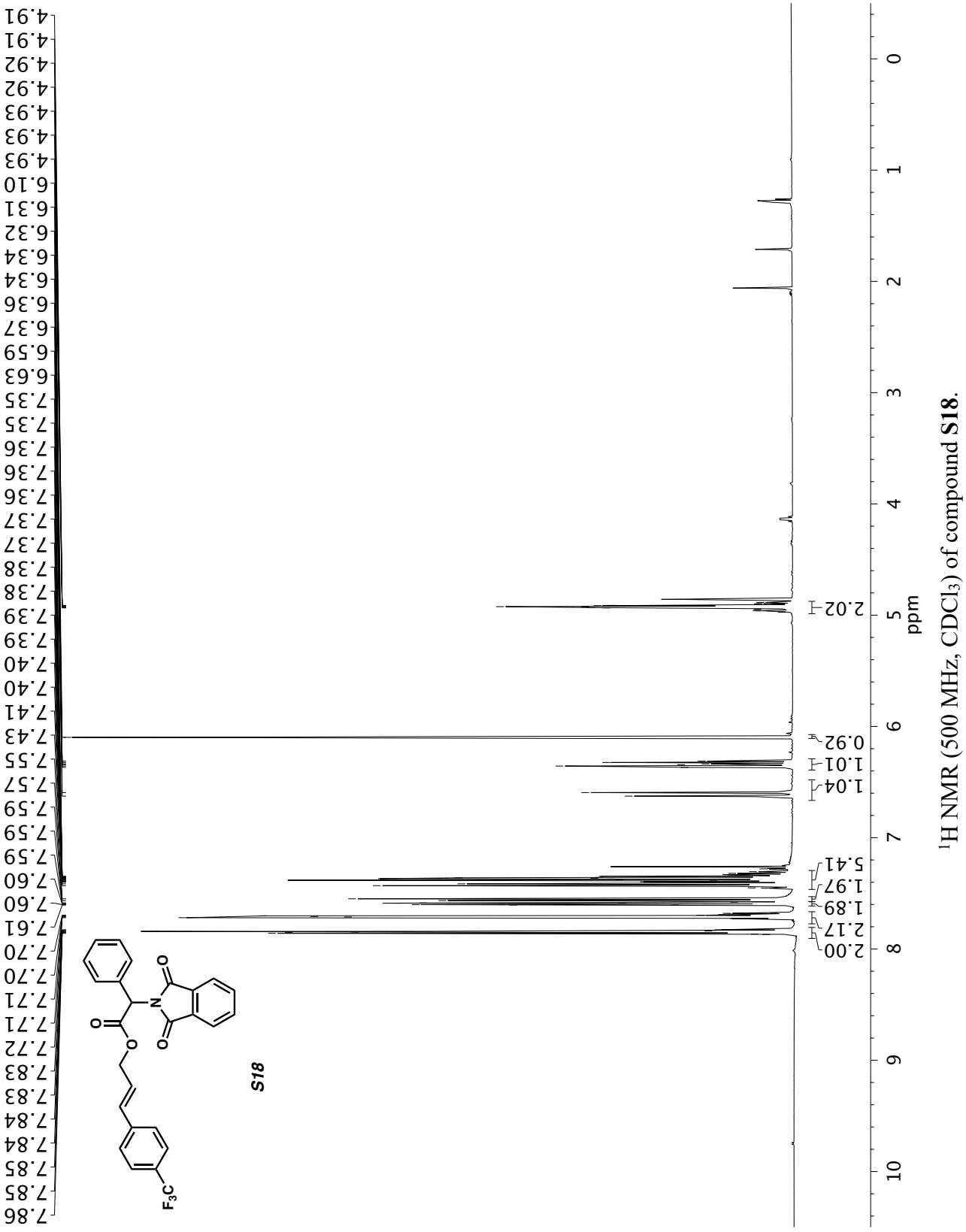
Infrared spectrum (Thin Film, NaCl) of compound **S17**.



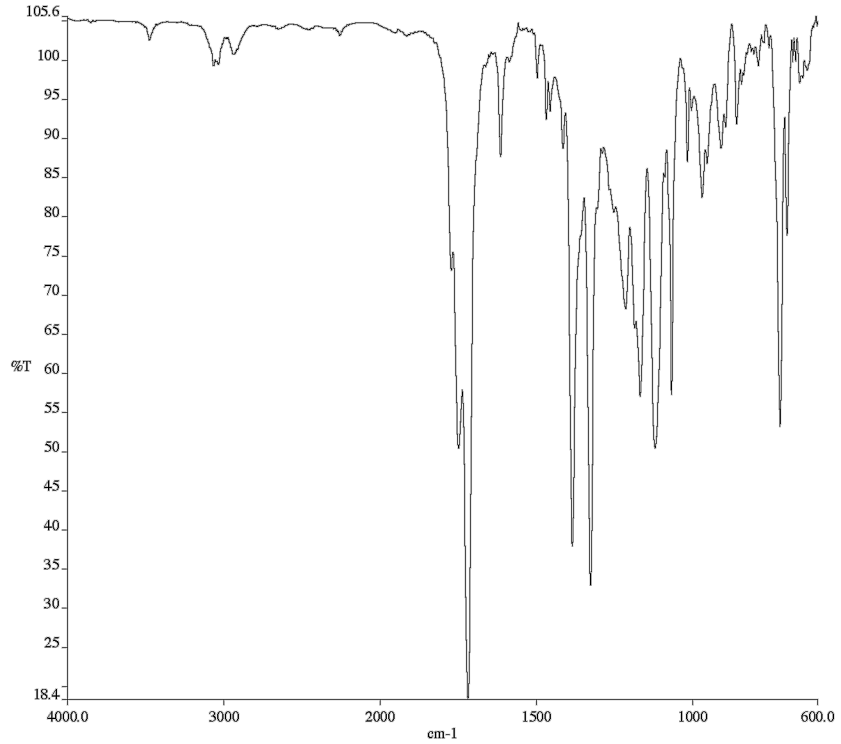
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S17**.



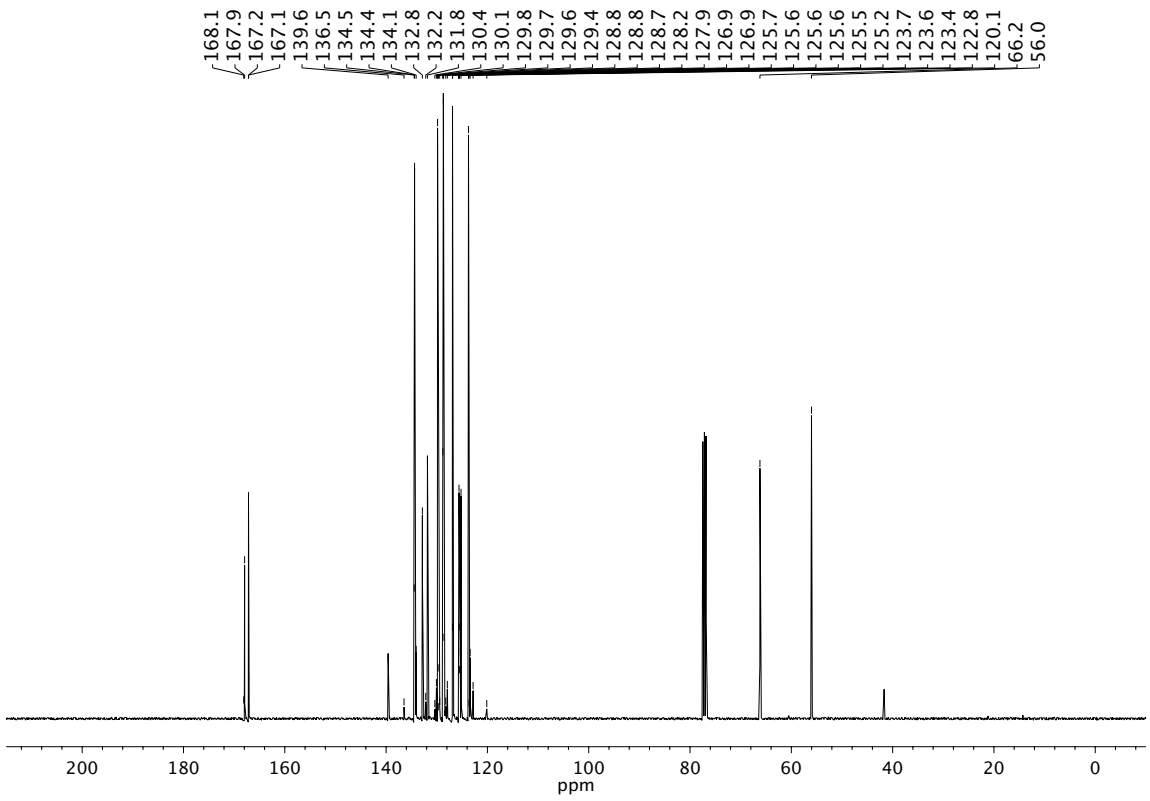
^{19}F NMR (282 MHz, $CDCl_3$) of compound **S17**.



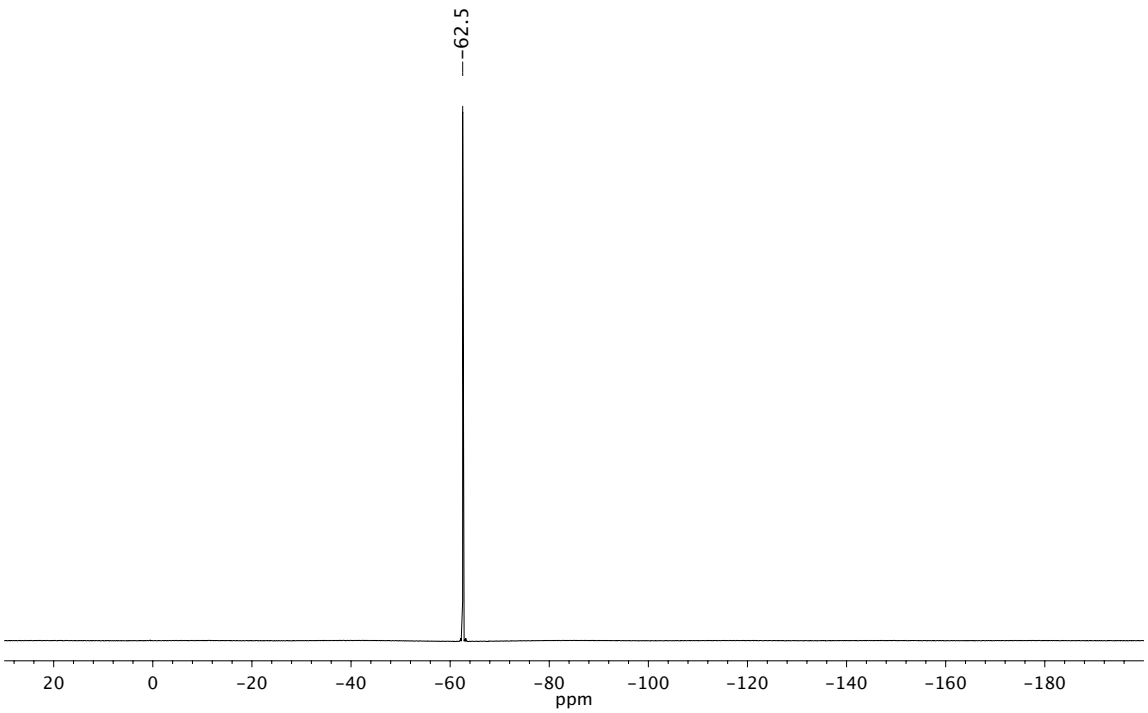
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S18**.



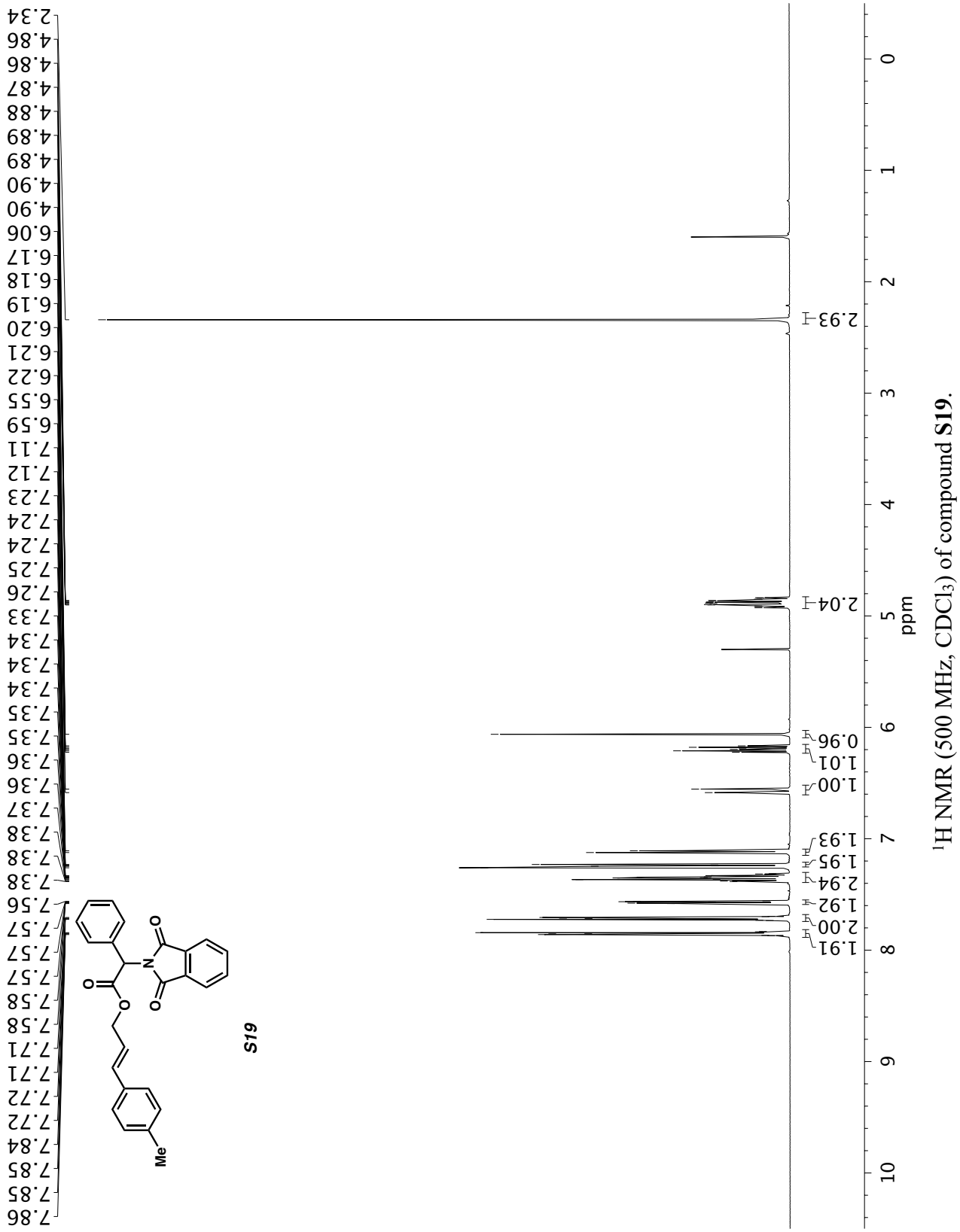
Infrared spectrum (Thin Film, NaCl) of compound **S18**.



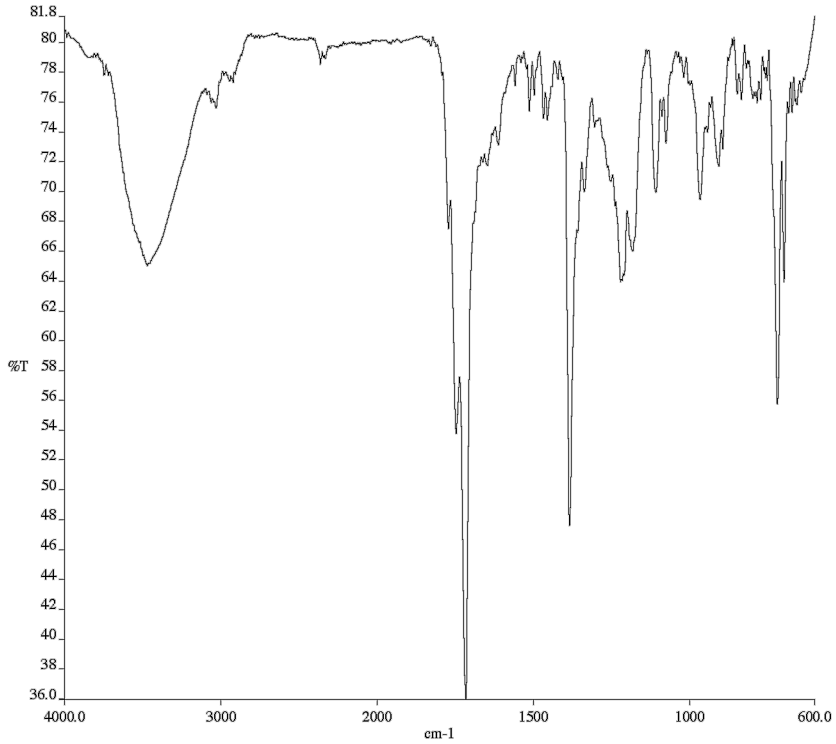
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S18**.



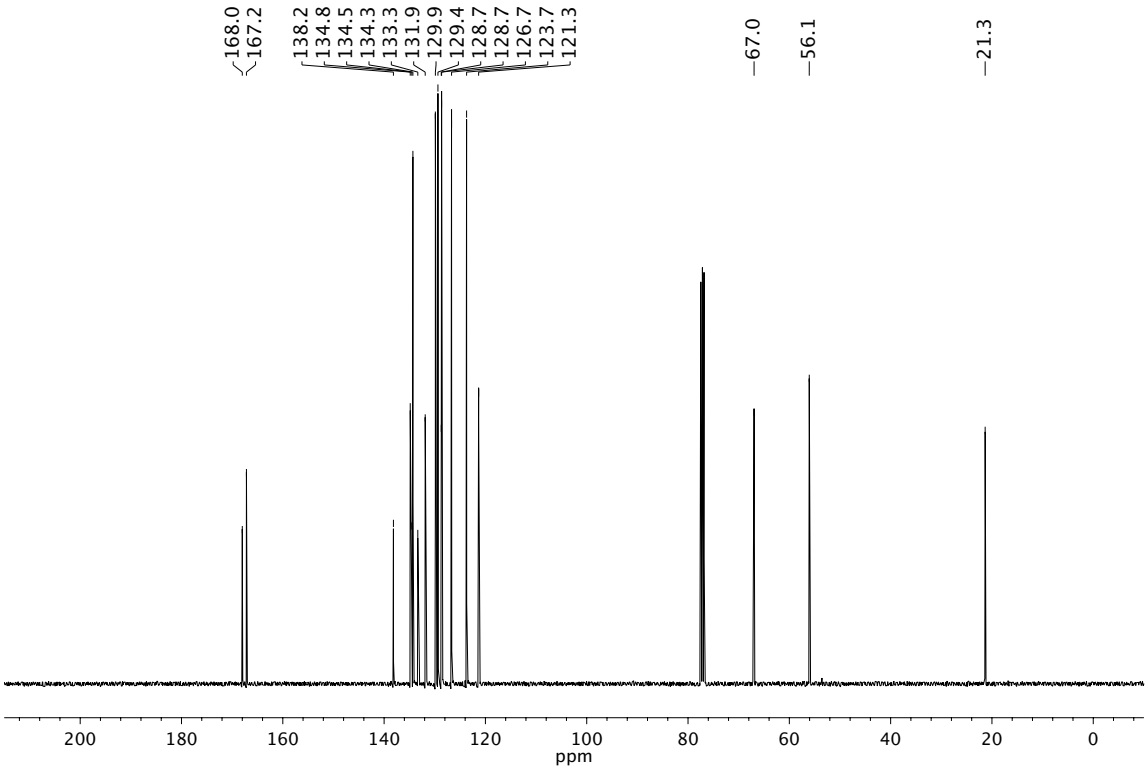
^{19}F NMR (282 MHz, $CDCl_3$) of compound **S18**.



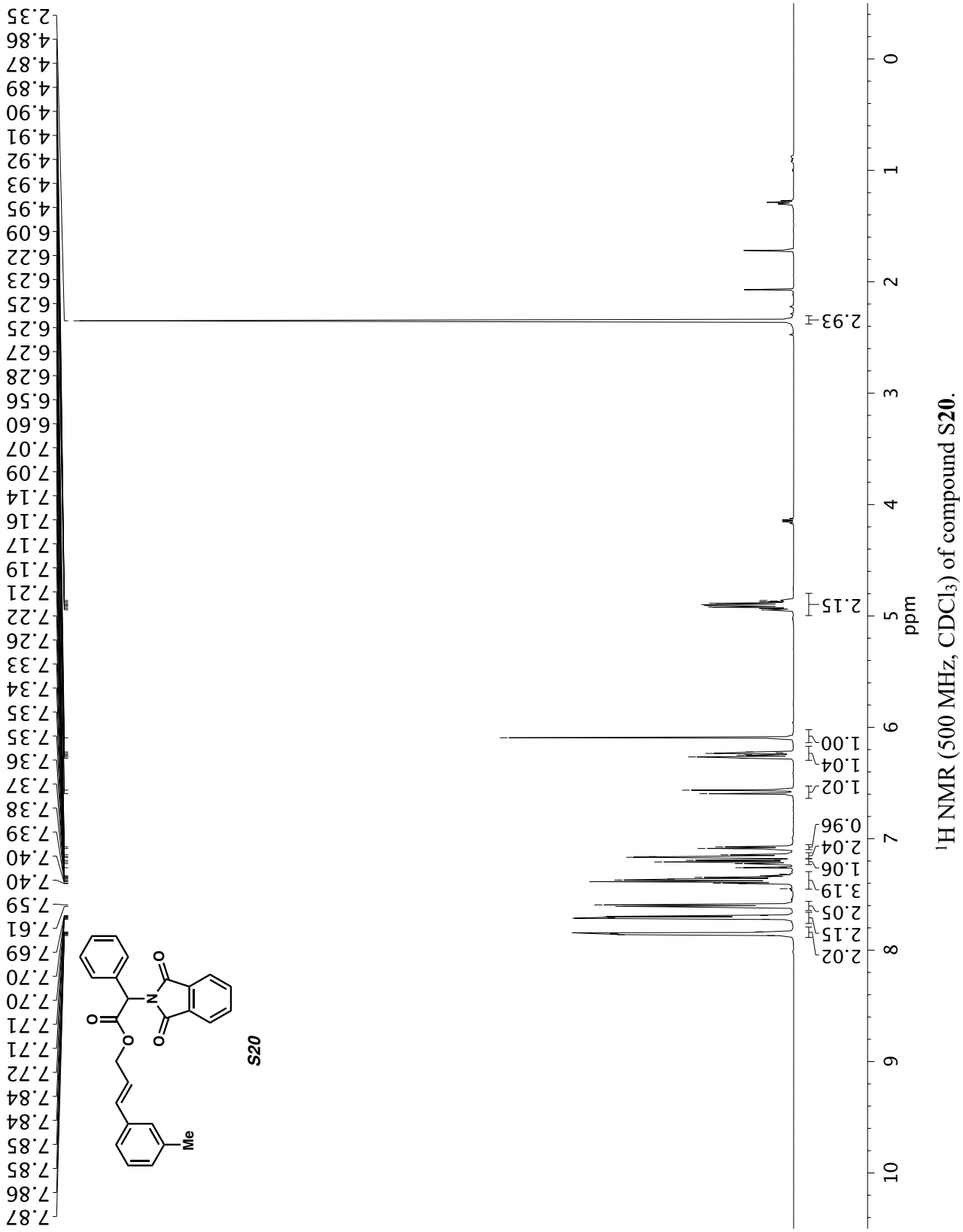
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S19**.



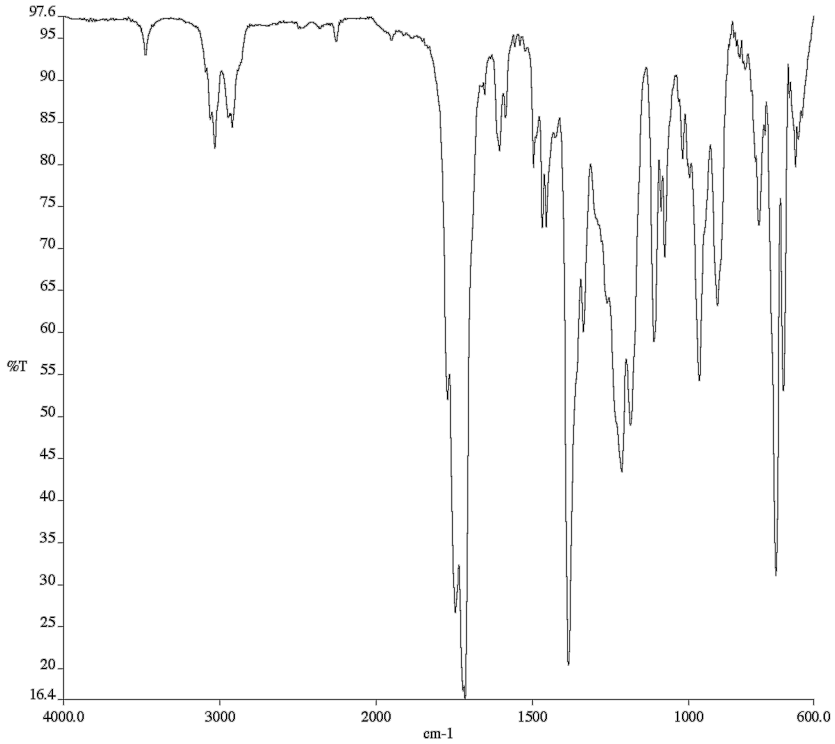
Infrared spectrum (Thin Film, NaCl) of compound **S19**.



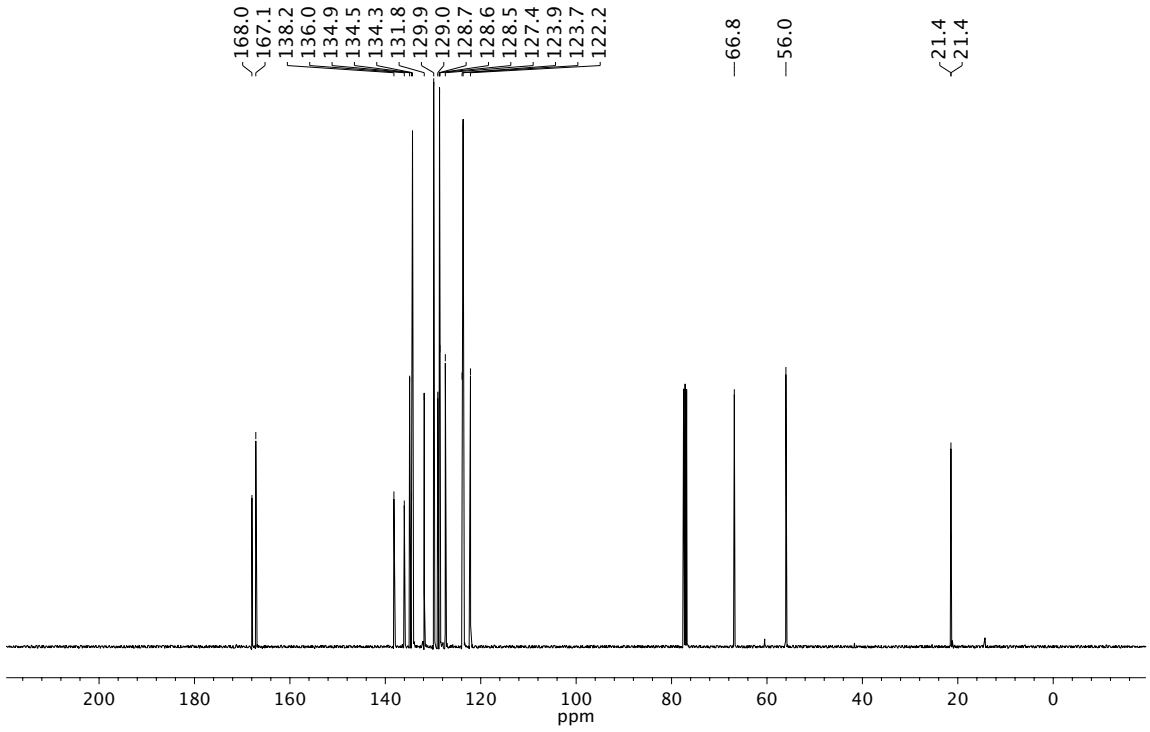
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S19**.



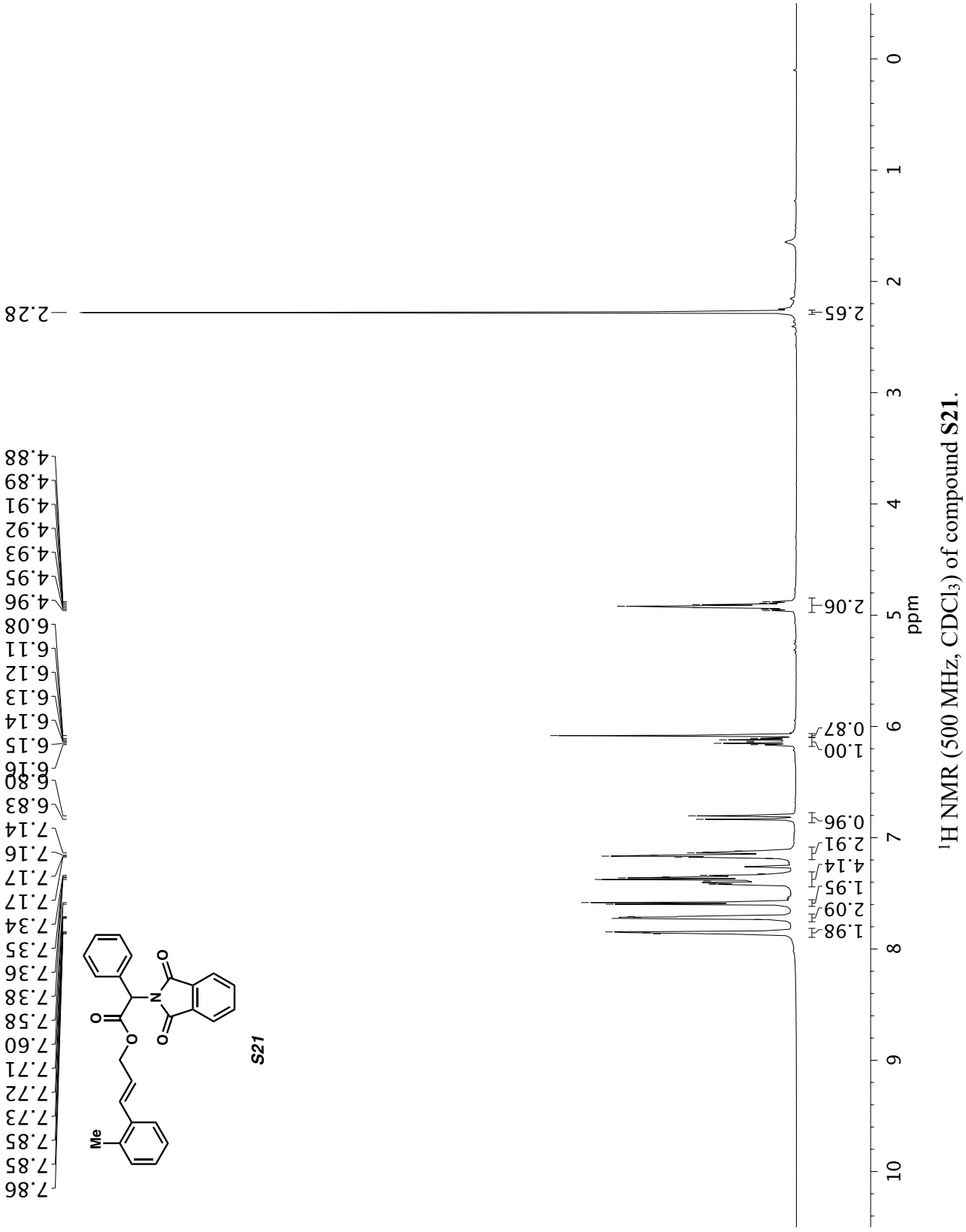
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S20**.



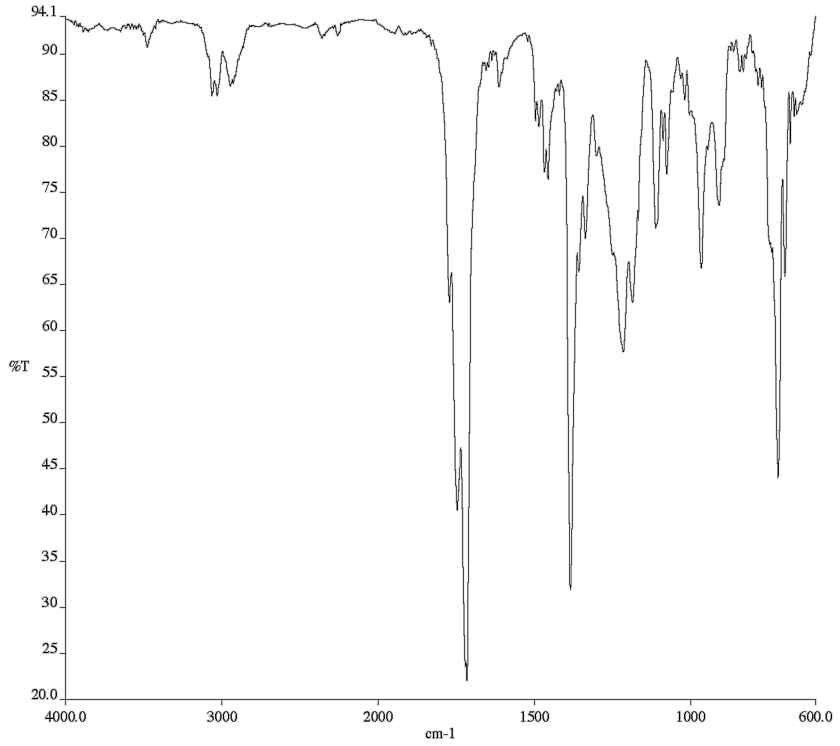
Infrared spectrum (Thin Film, NaCl) of compound **S20**.



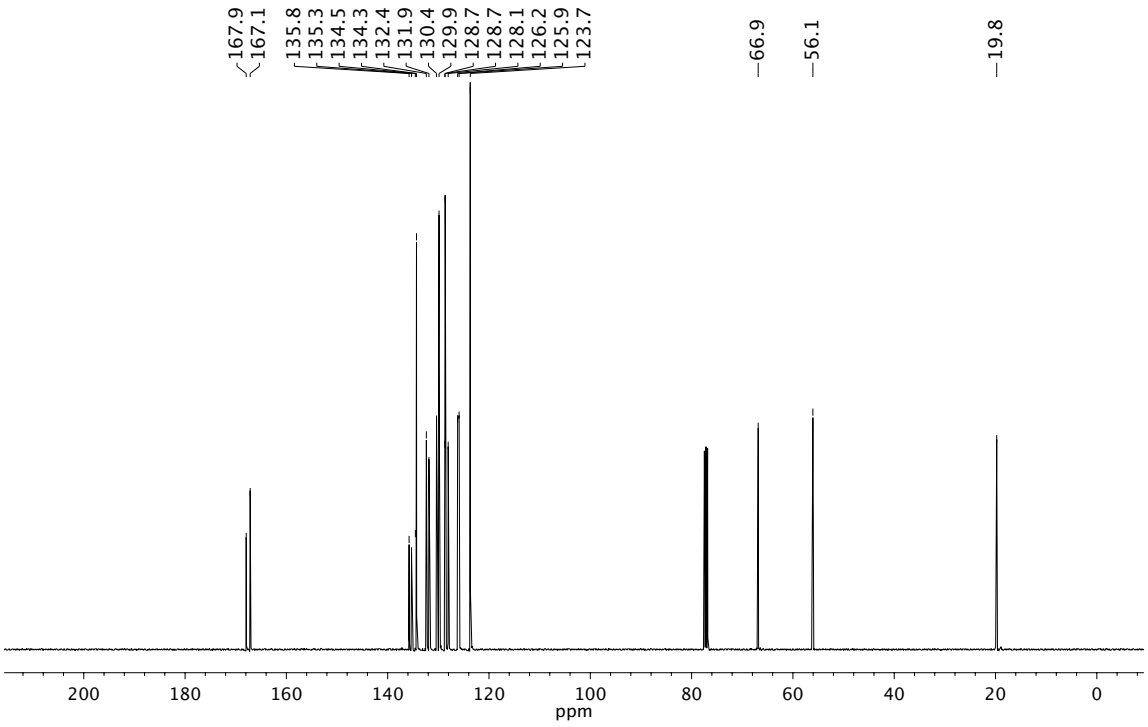
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S20**.



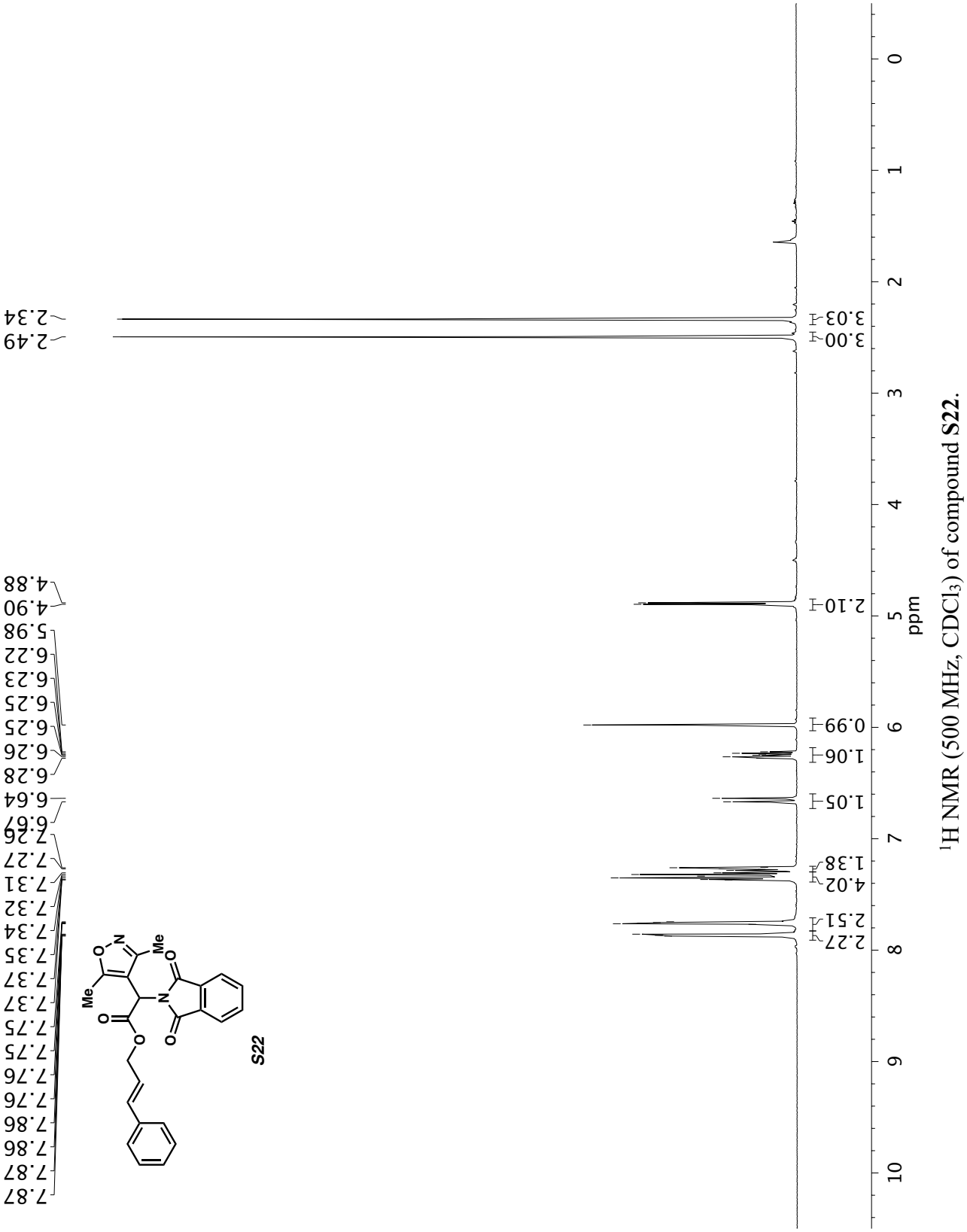
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S21**.



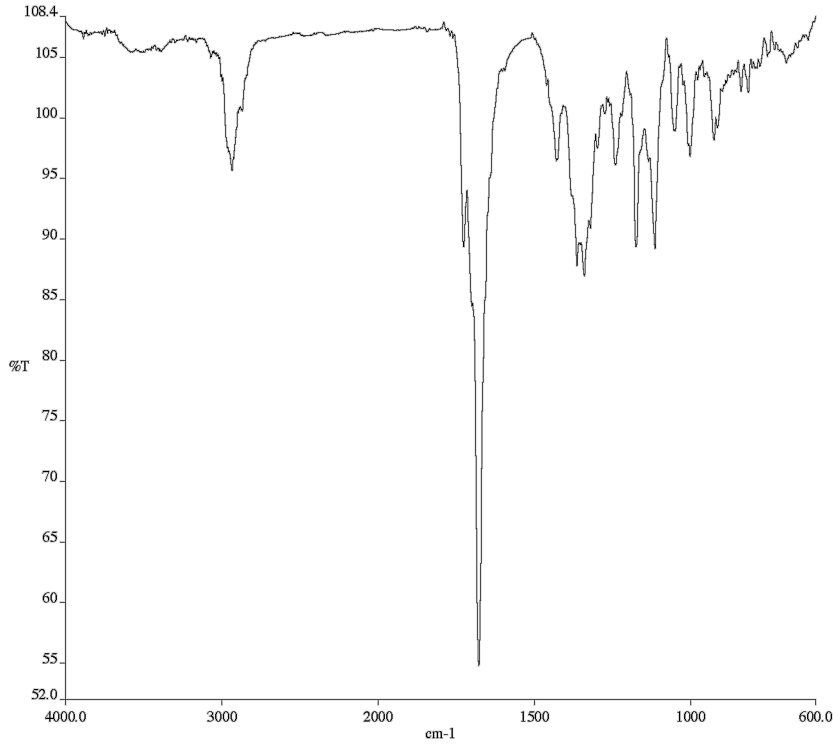
Infrared spectrum (Thin Film, NaCl) of compound **S21**.



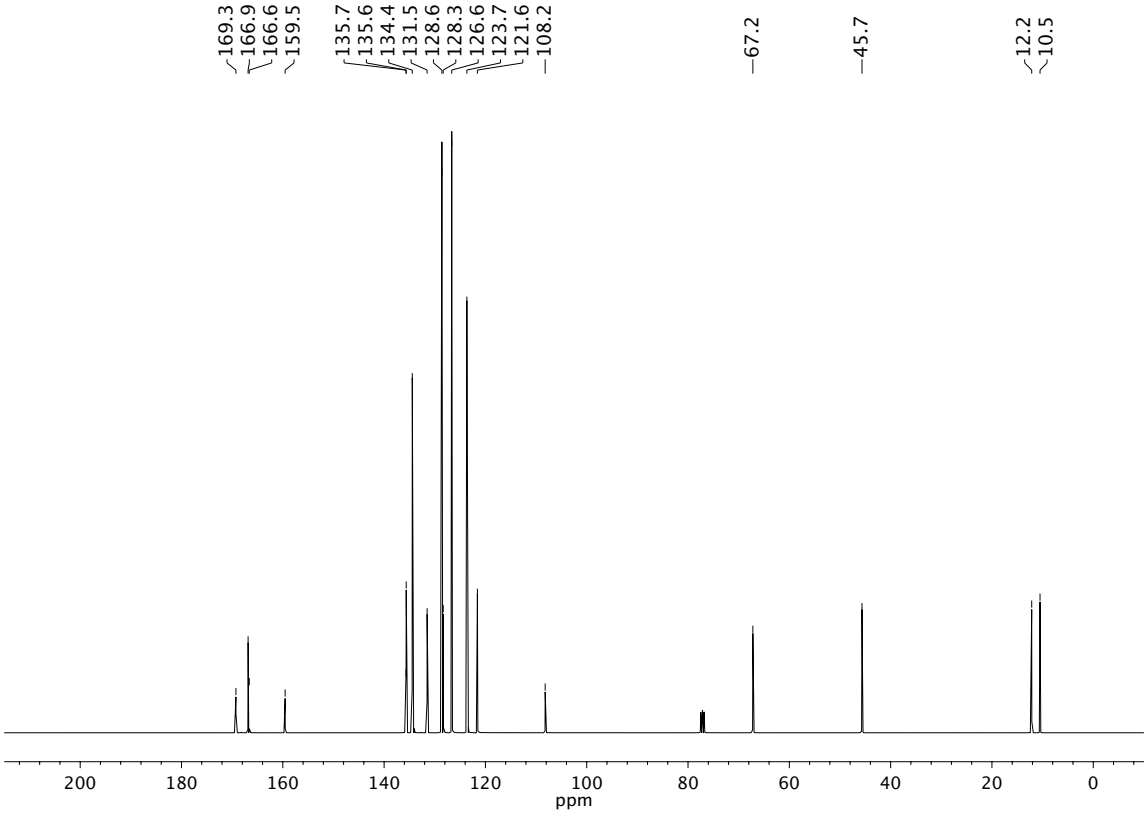
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S21**.



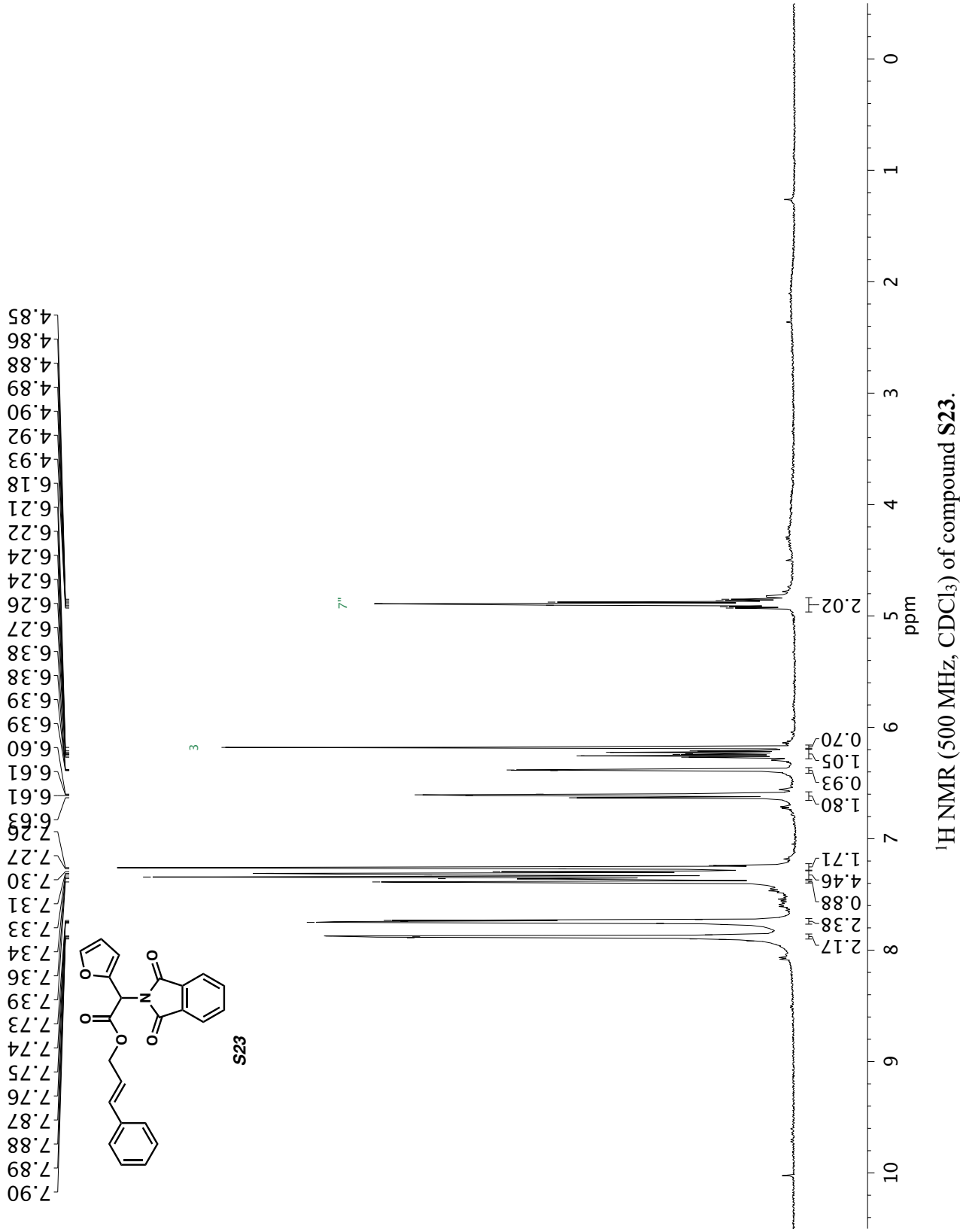
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S22**.



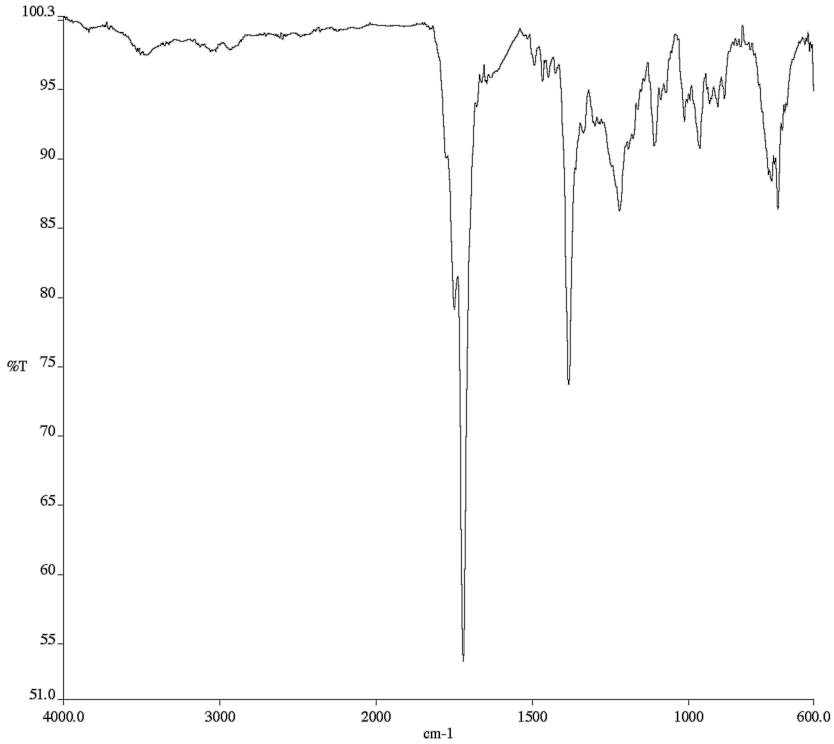
Infrared spectrum (Thin Film, NaCl) of compound **S22**.



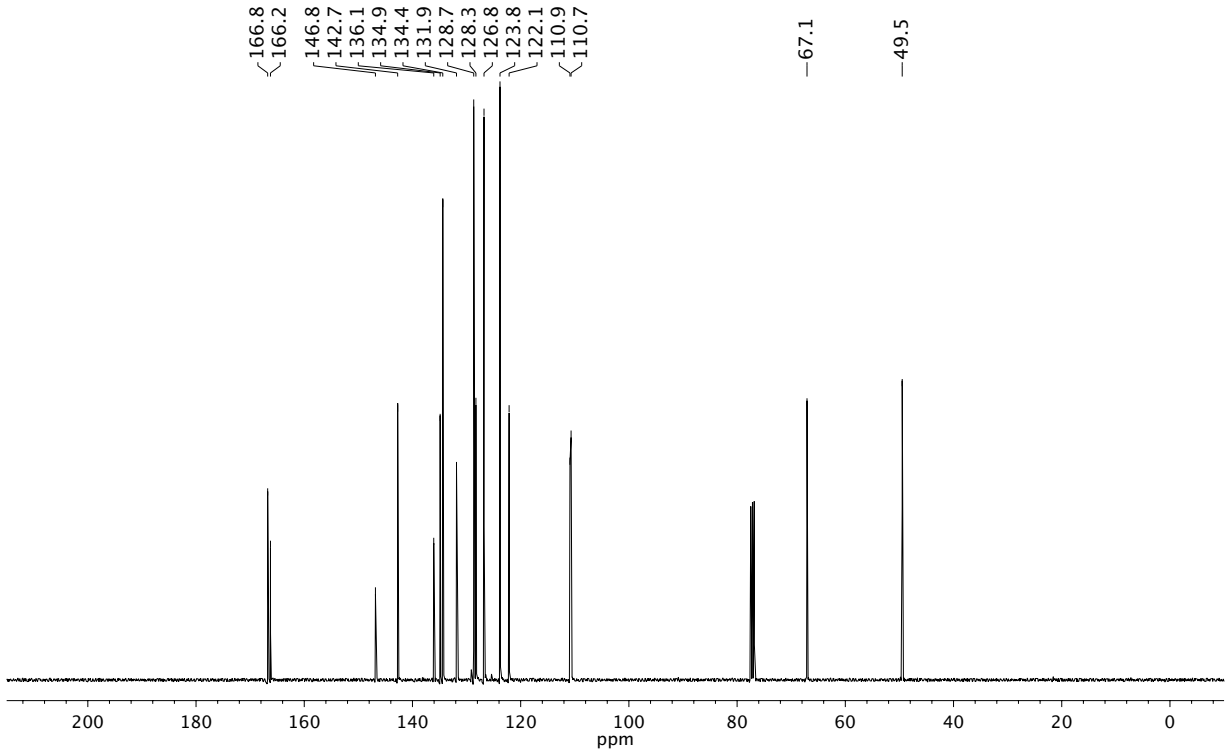
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S22**.



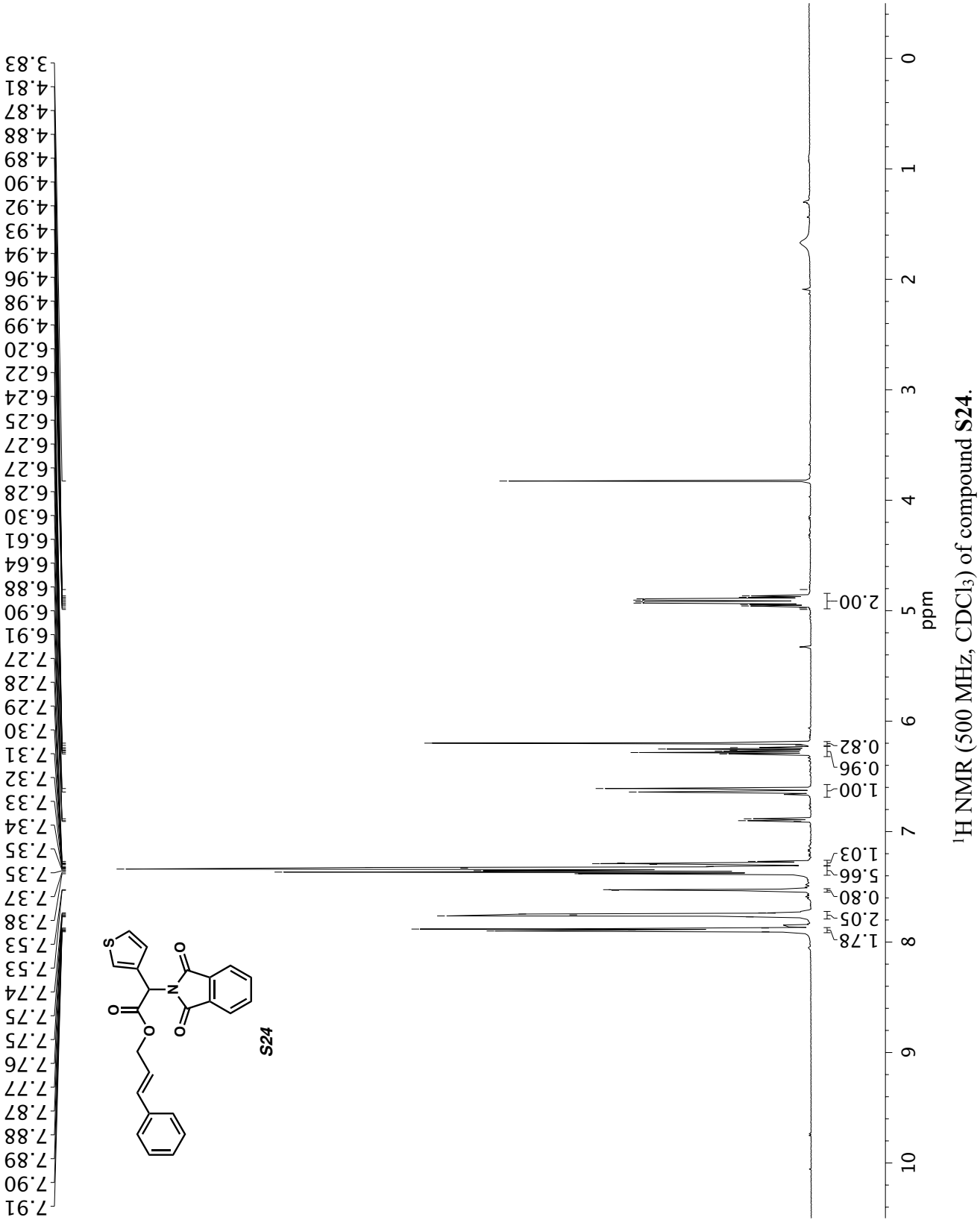
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S23**.



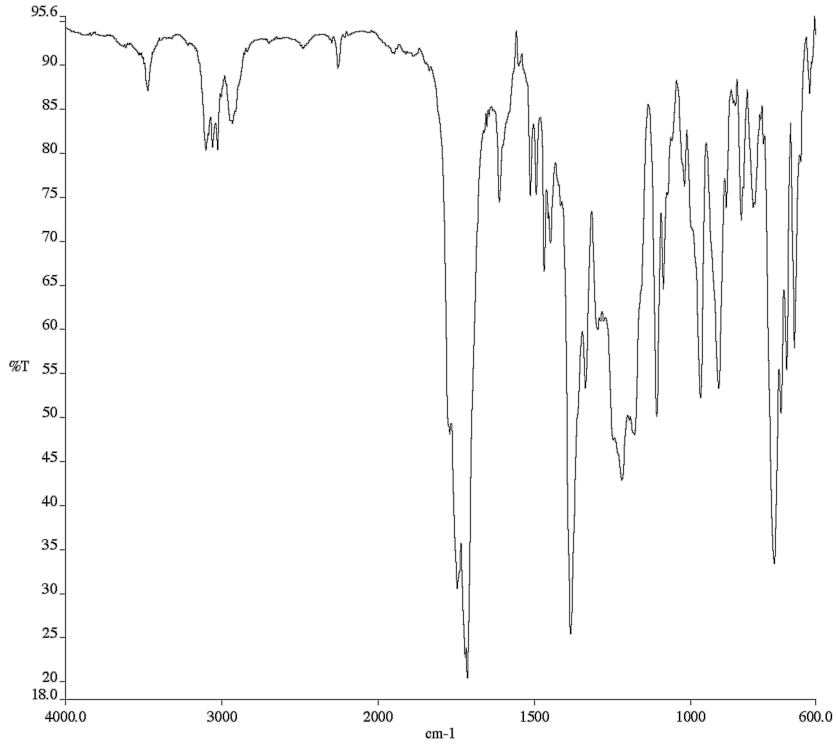
Infrared spectrum (Thin Film, NaCl) of compound **S23**.



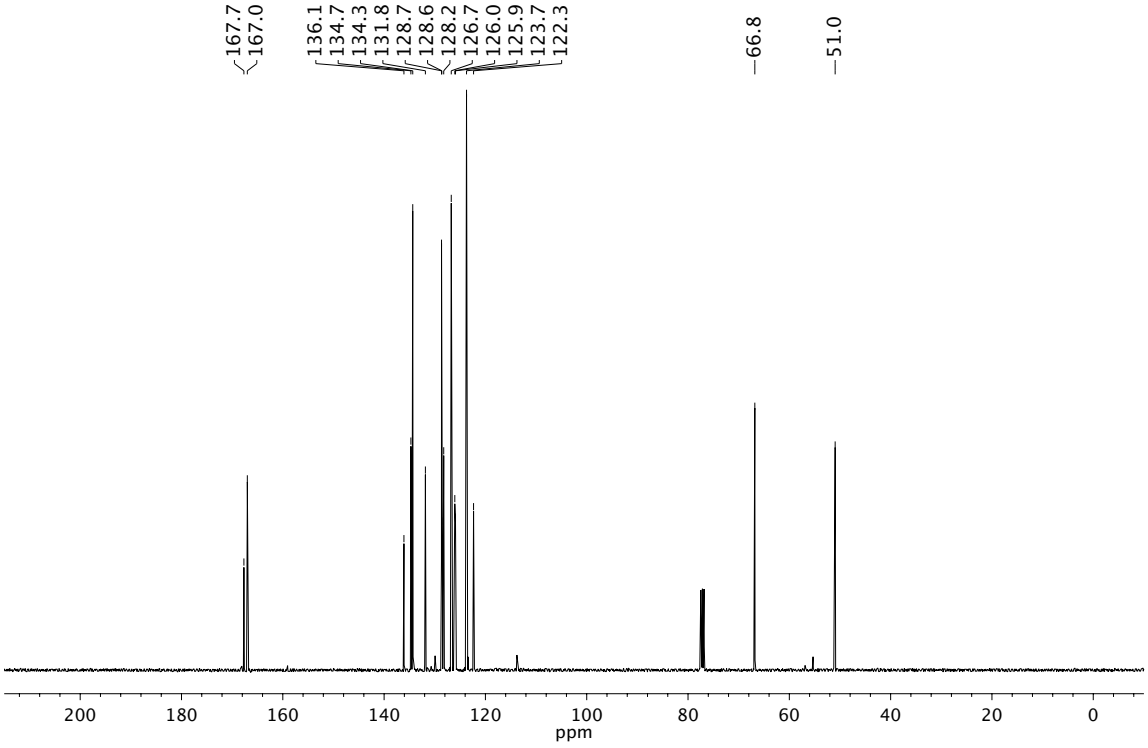
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S23**.



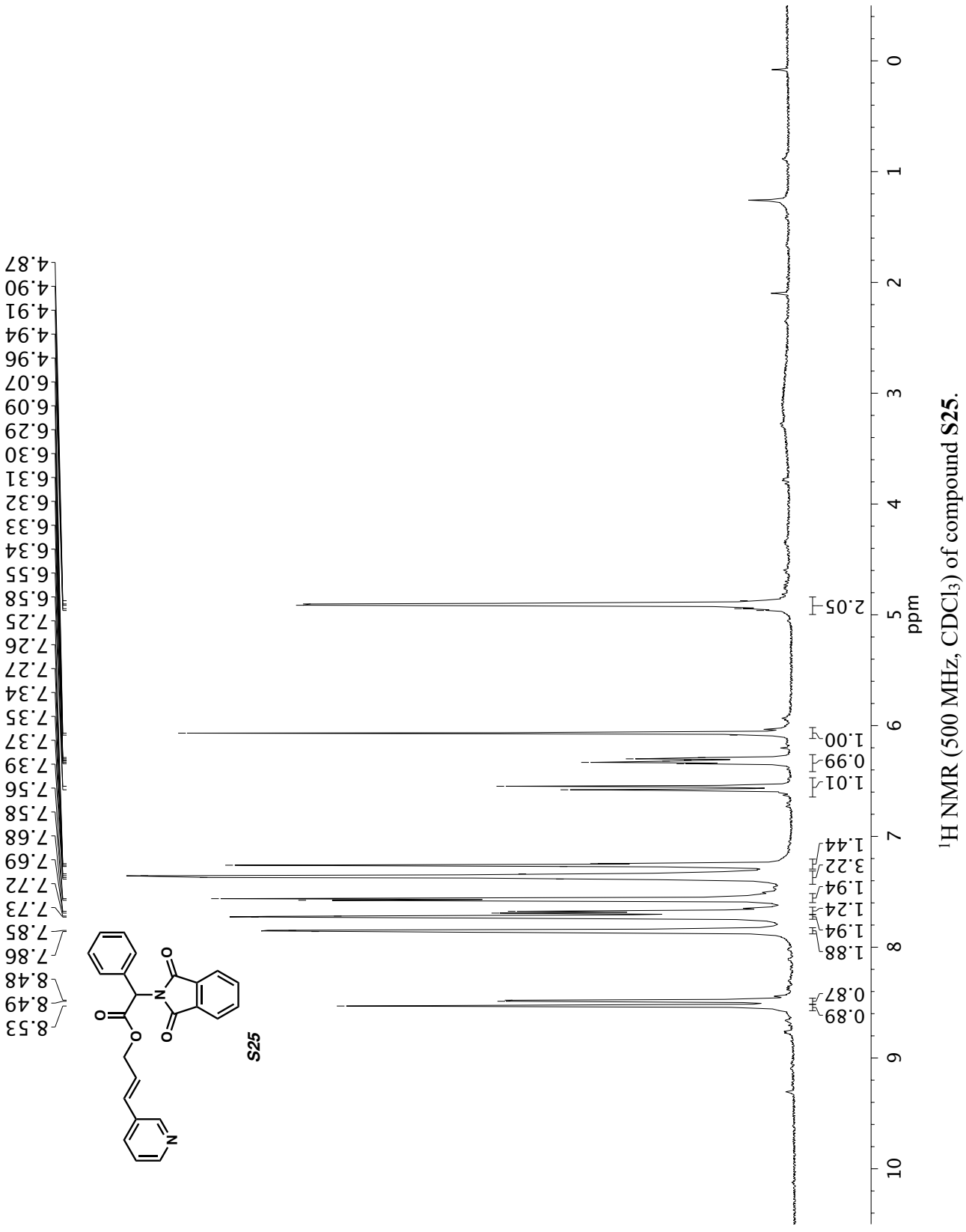
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S24**.



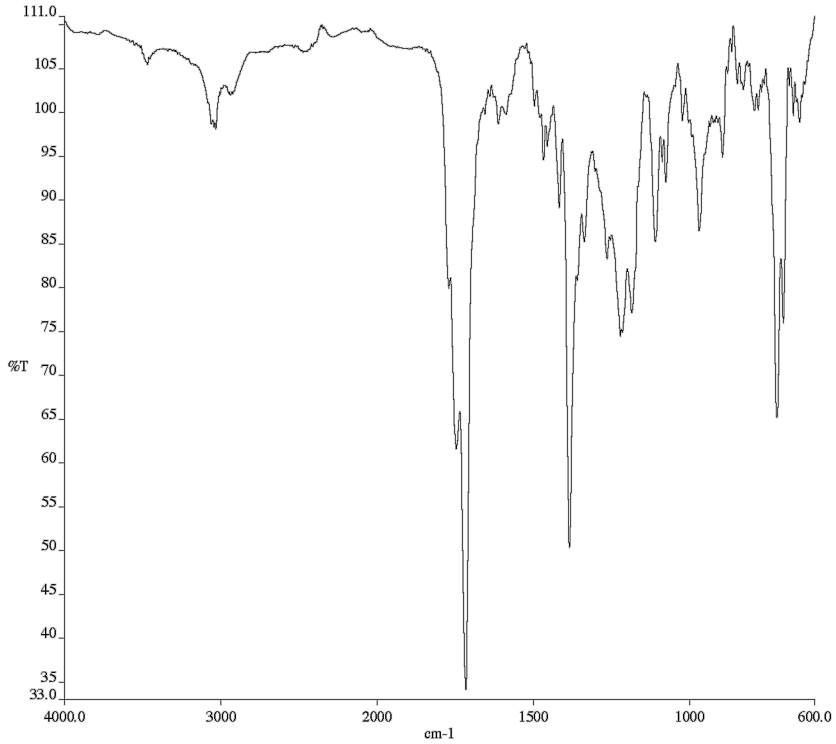
Infrared spectrum (Thin Film, NaCl) of compound **S24**.



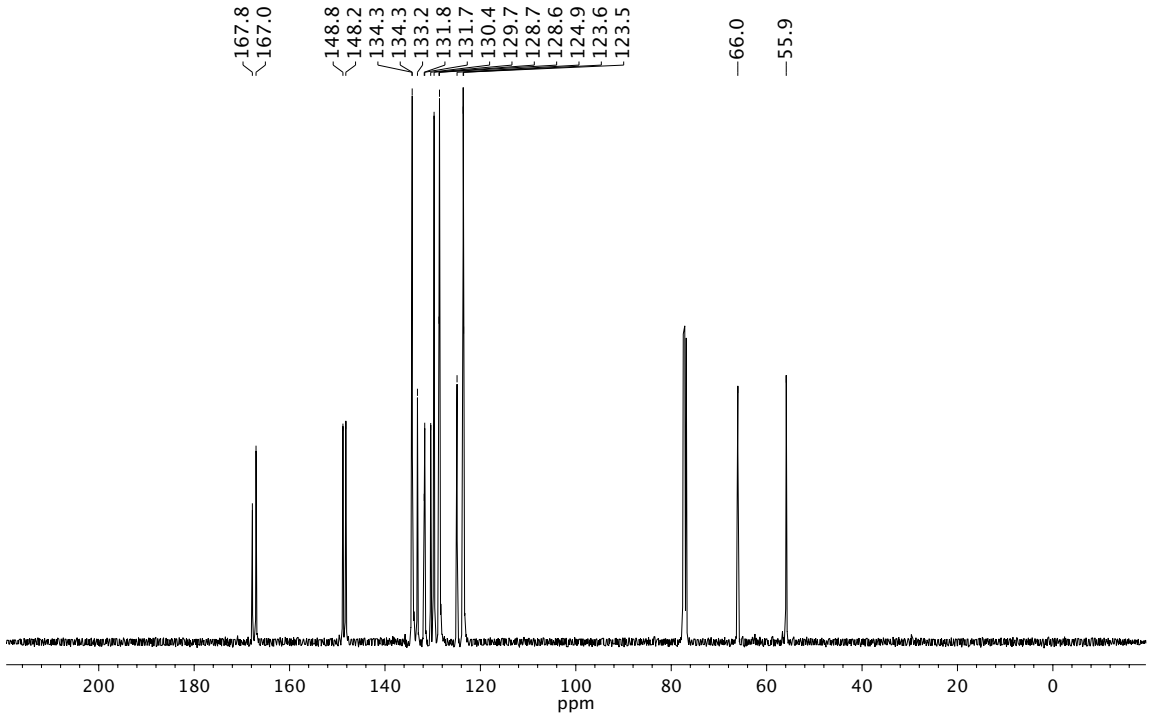
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S24**.



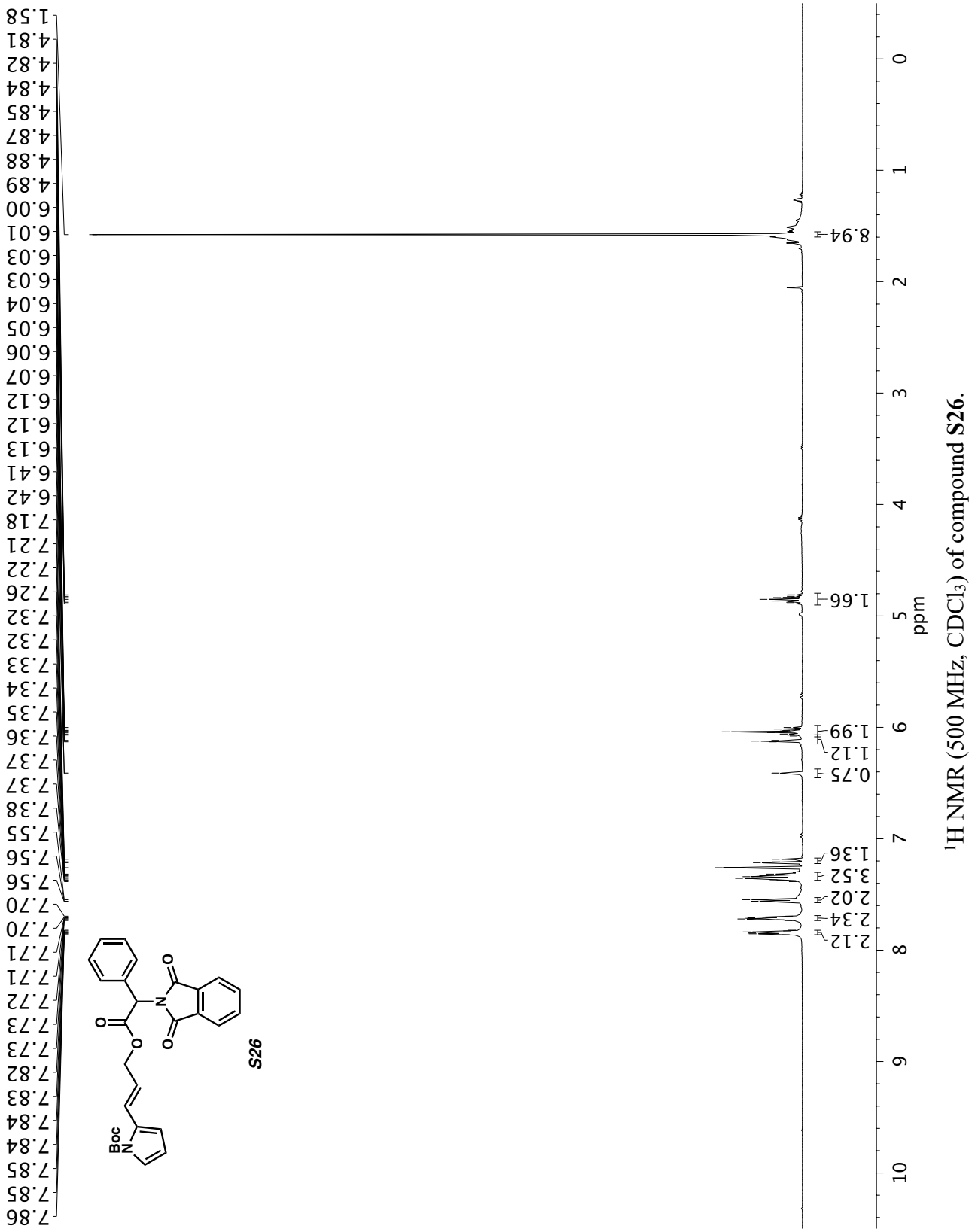
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S25**.



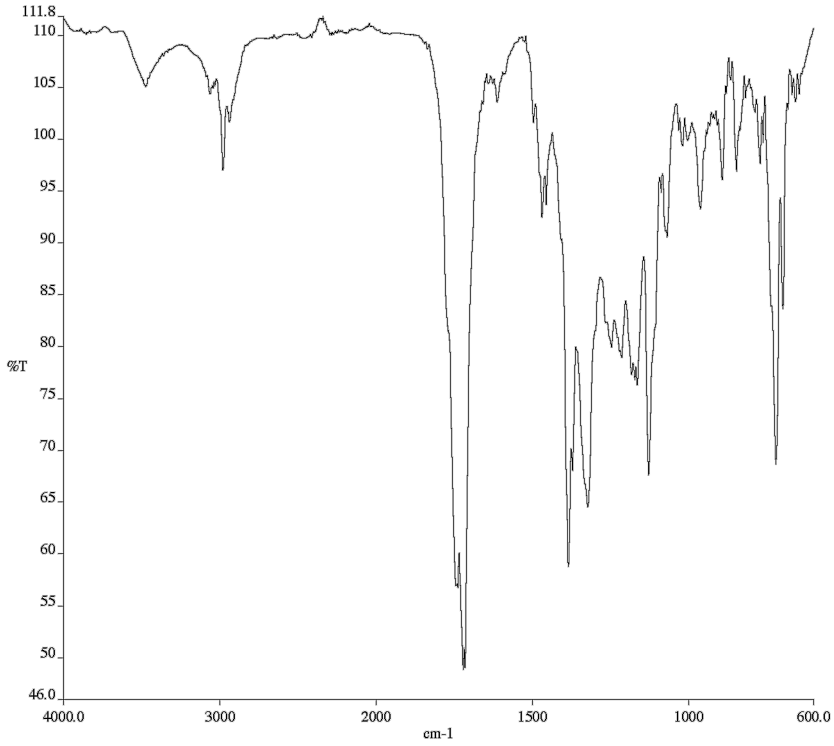
Infrared spectrum (Thin Film, NaCl) of compound **S25**.



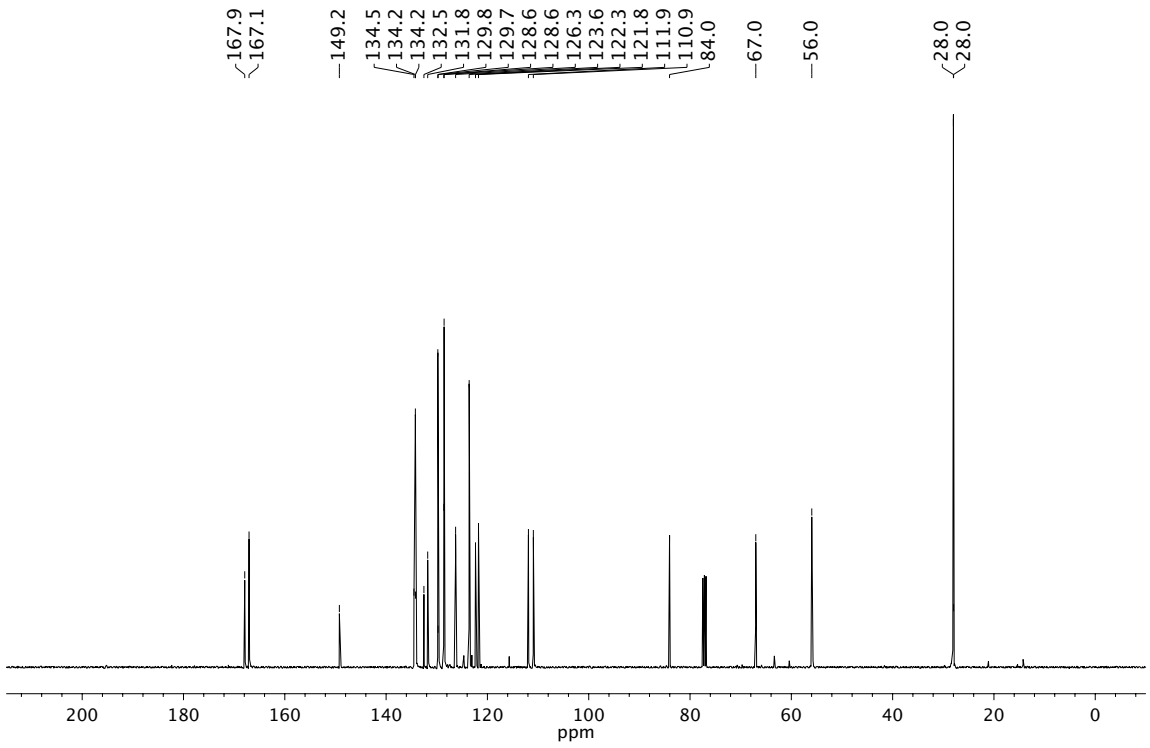
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S25**.



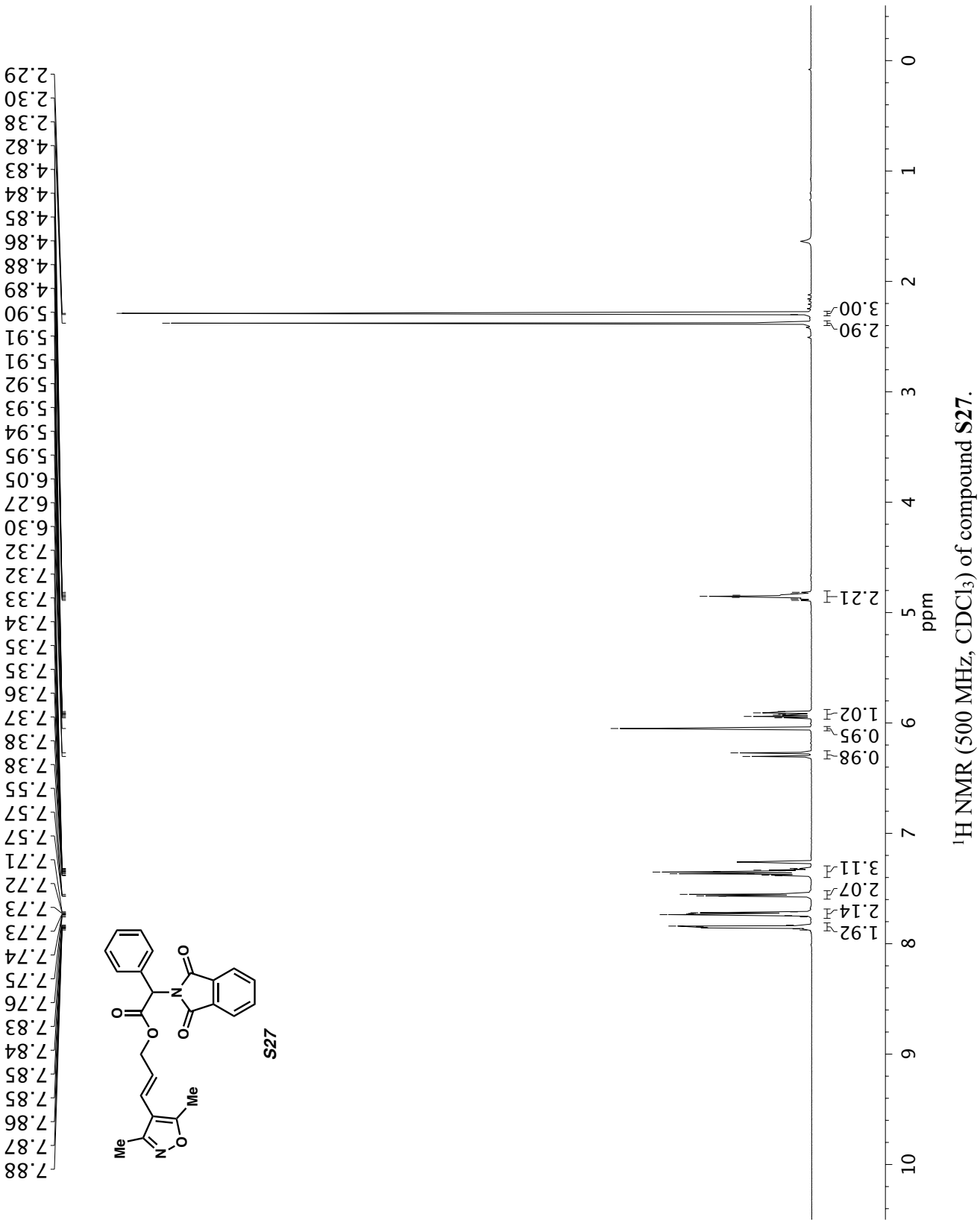
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S26**.



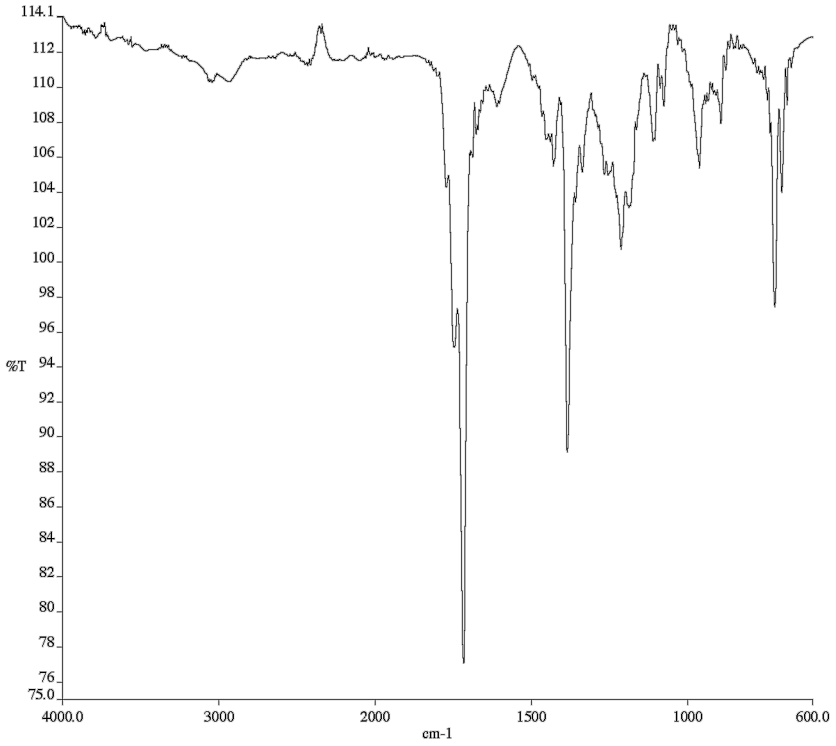
Infrared spectrum (Thin Film, NaCl) of compound **S26**.



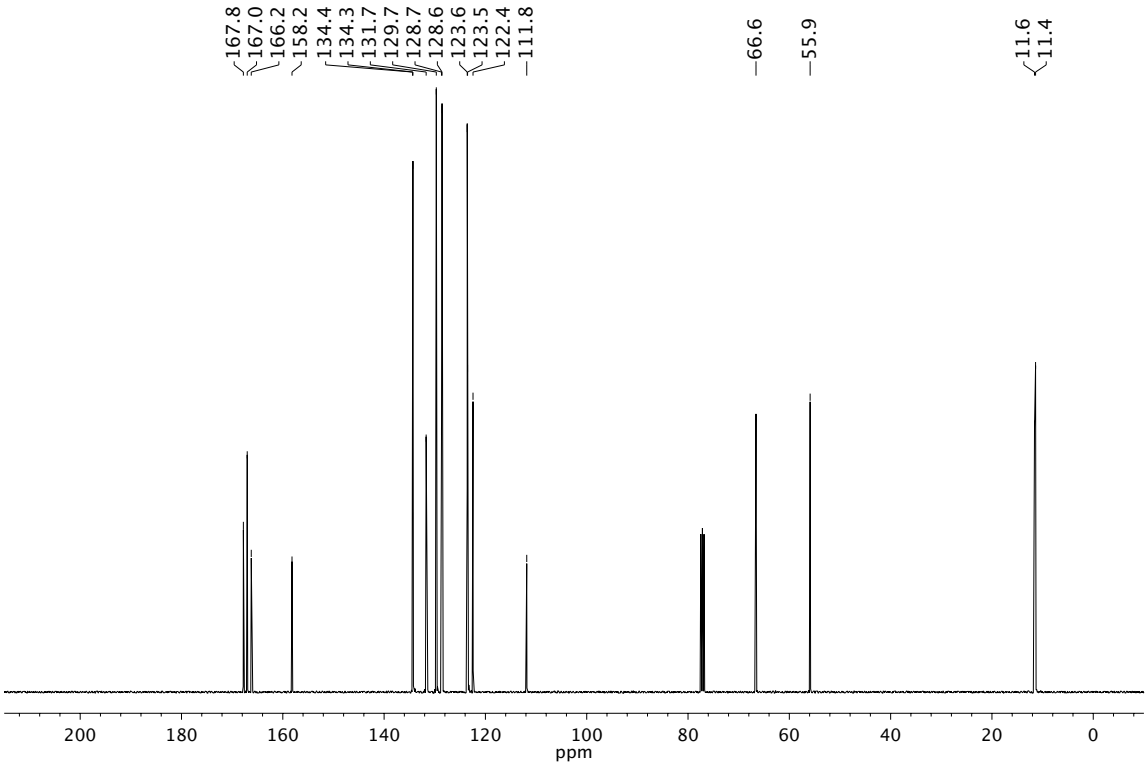
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S26**.



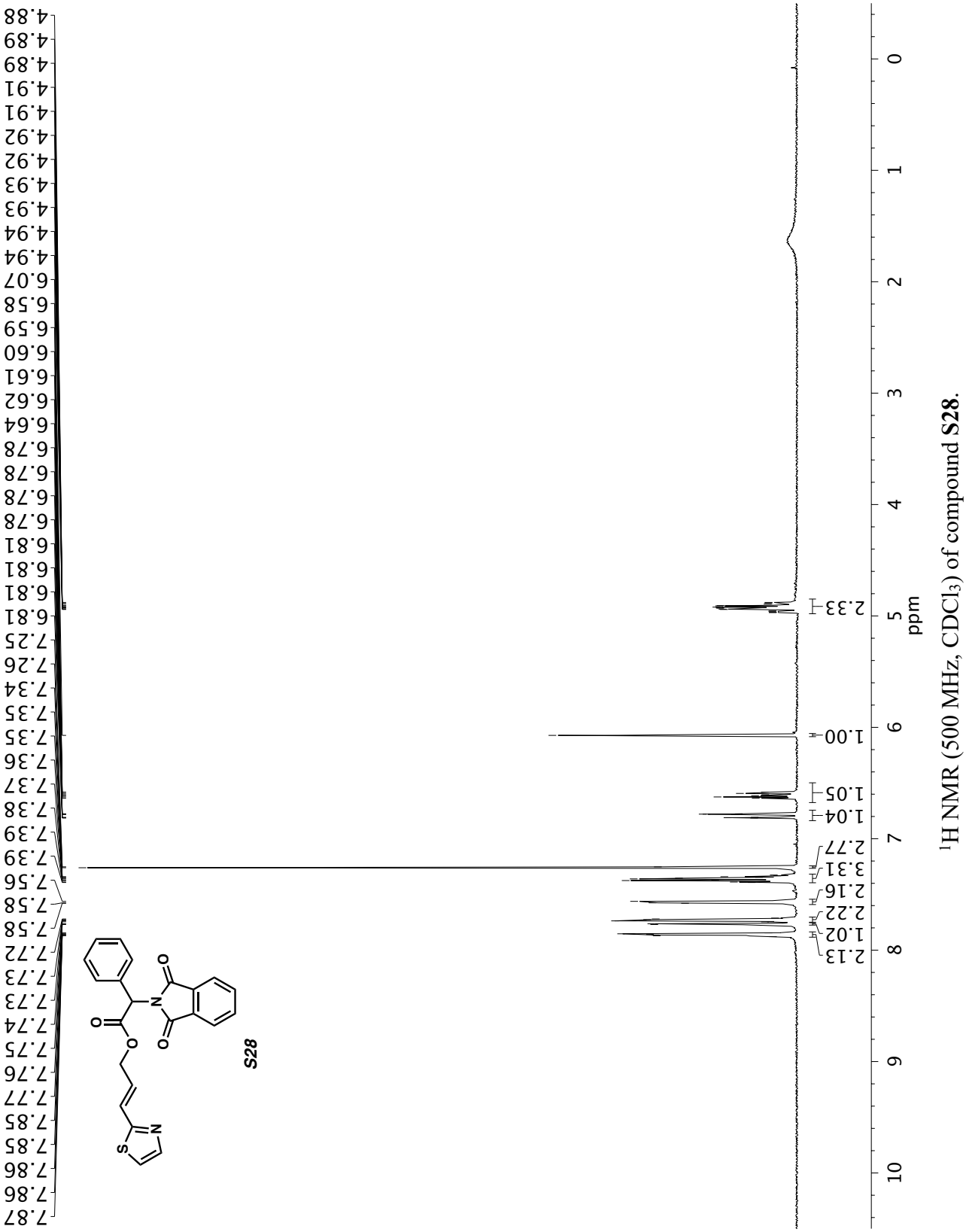
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S27**.



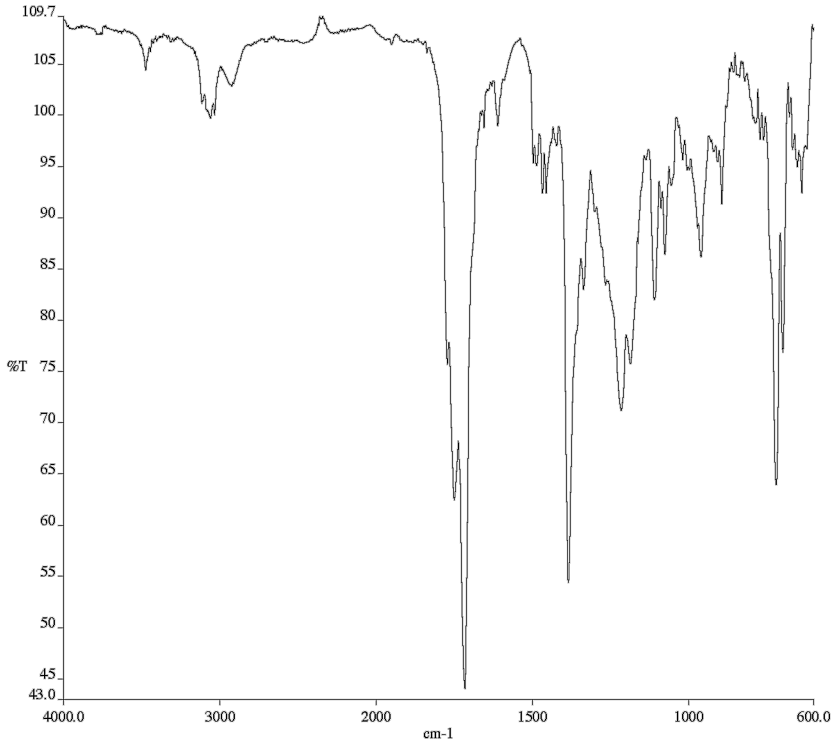
Infrared spectrum (Thin Film, NaCl) of compound **S27**.



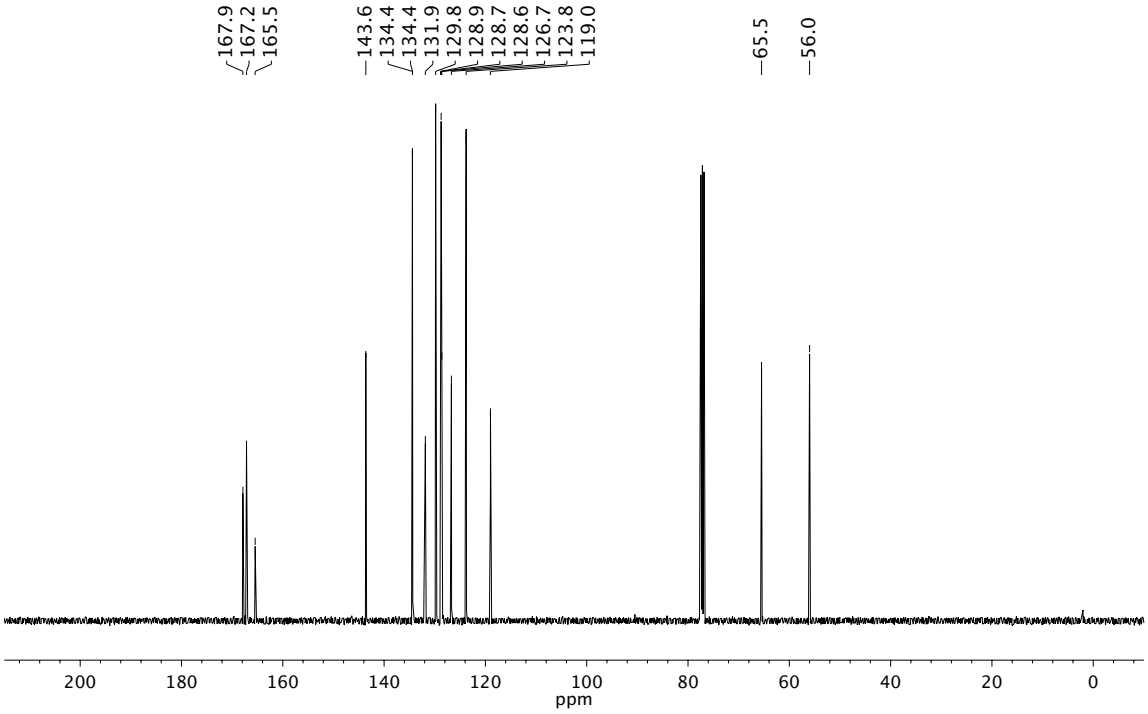
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S27**.



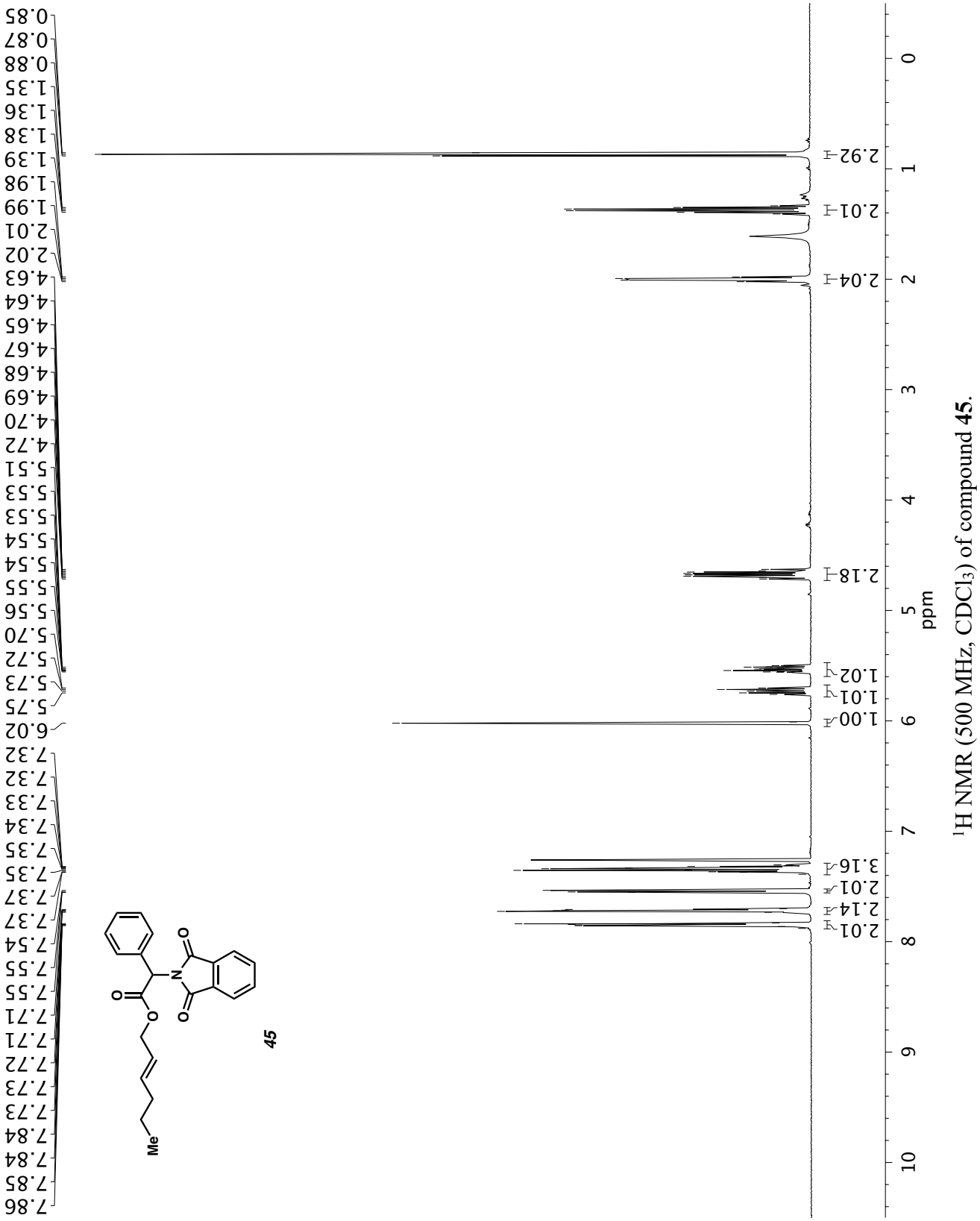
^{1}H NMR (500 MHz, $CDCl_3$) of compound **S28**.



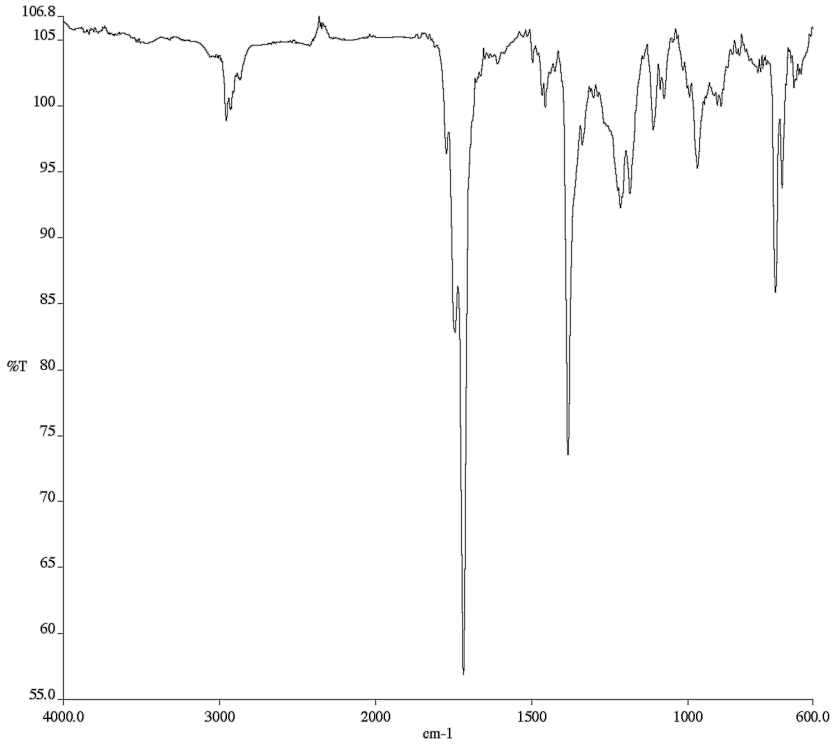
Infrared spectrum (Thin Film, NaCl) of compound **S28**.



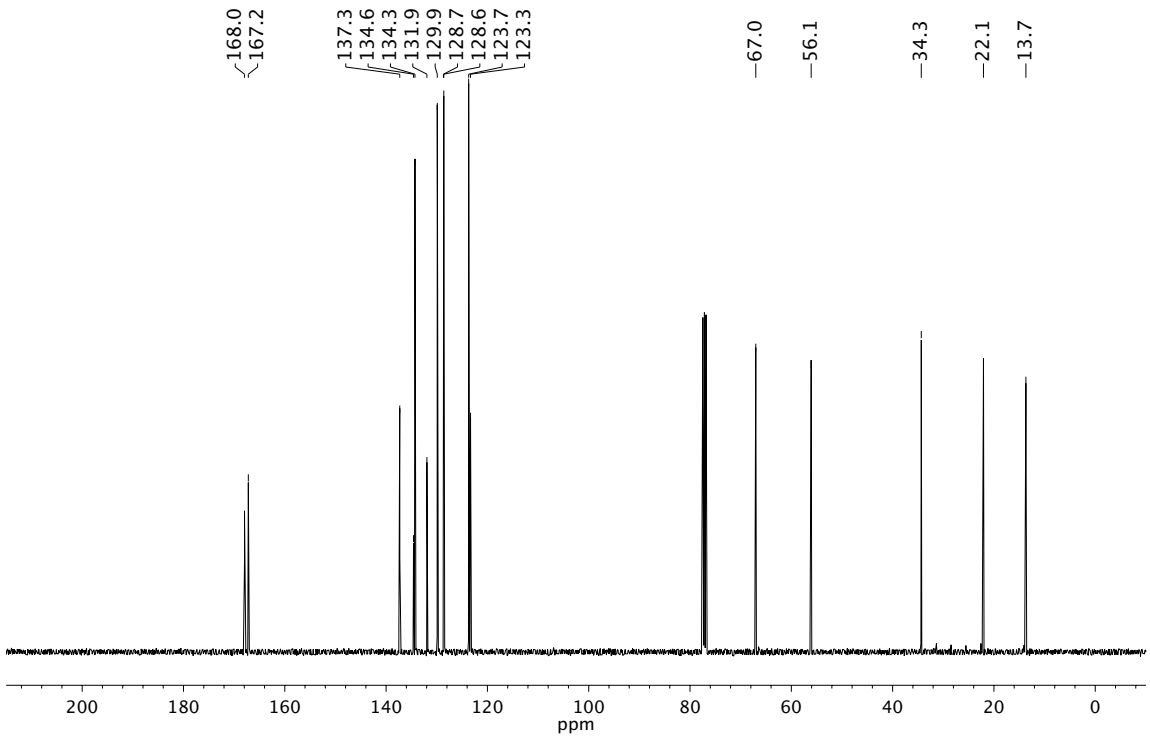
^{13}C NMR (100 MHz, $CDCl_3$) of compound **S28**.



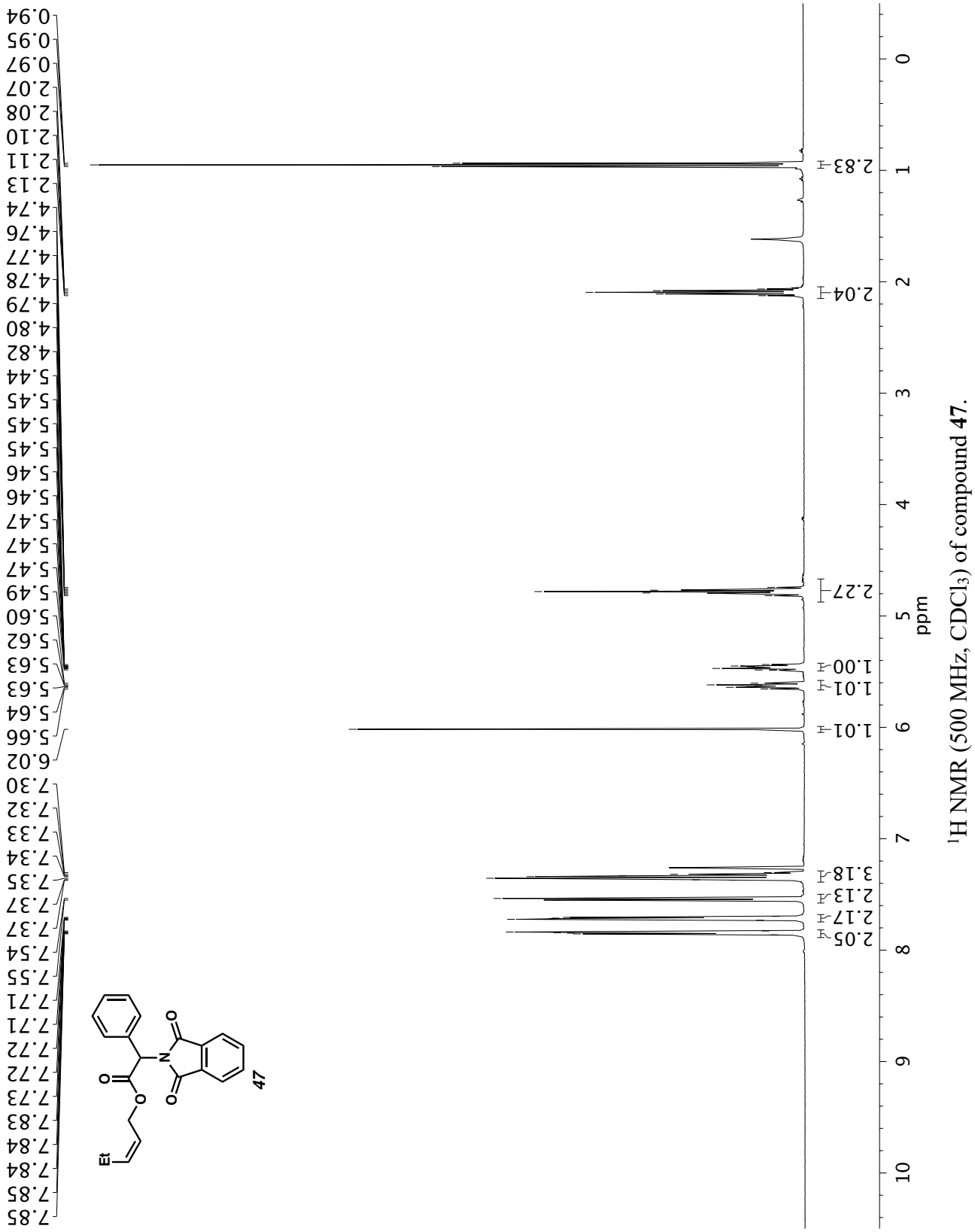
^{1}H NMR (500 MHz, $CDCl_3$) of compound **45**.



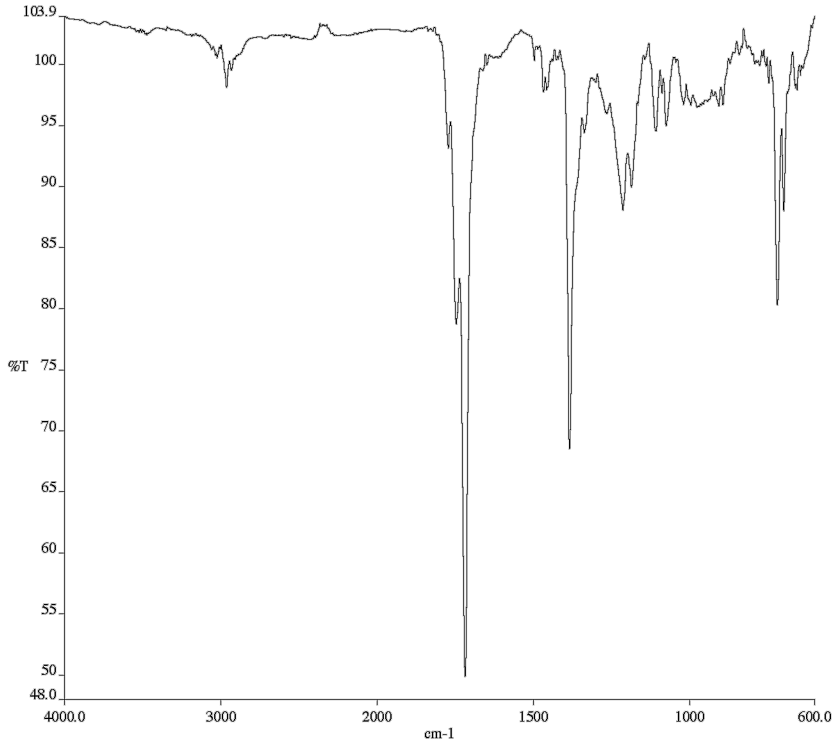
Infrared spectrum (Thin Film, NaCl) of compound **45**.



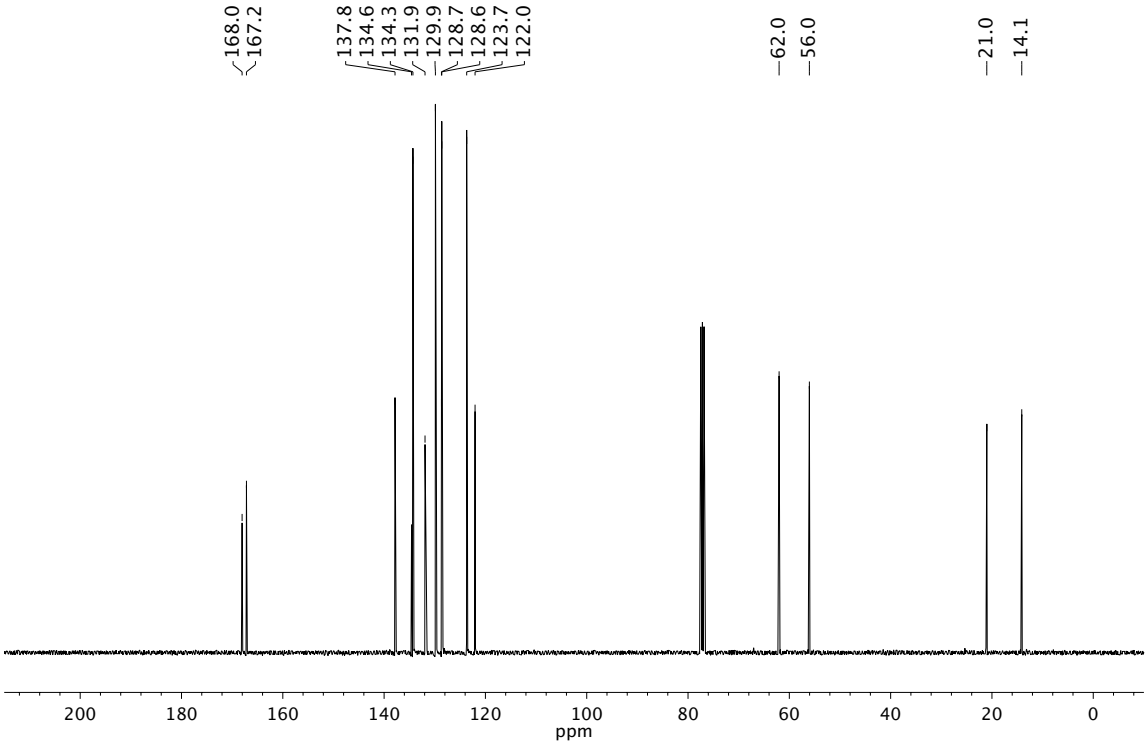
^{13}C NMR (100 MHz, $CDCl_3$) of compound **45**.



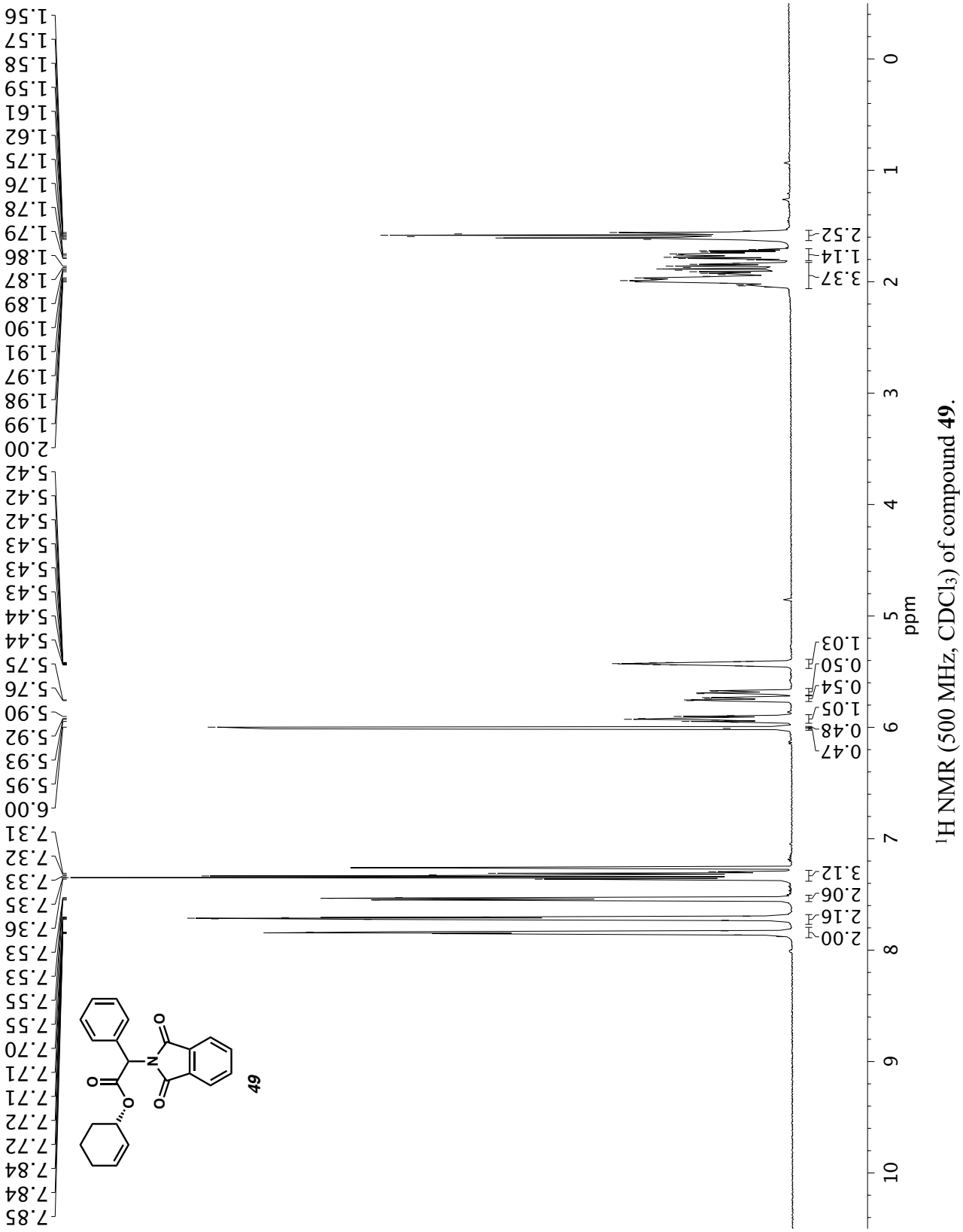
^{1}H NMR (500 MHz, $CDCl_3$) of compound **47**.



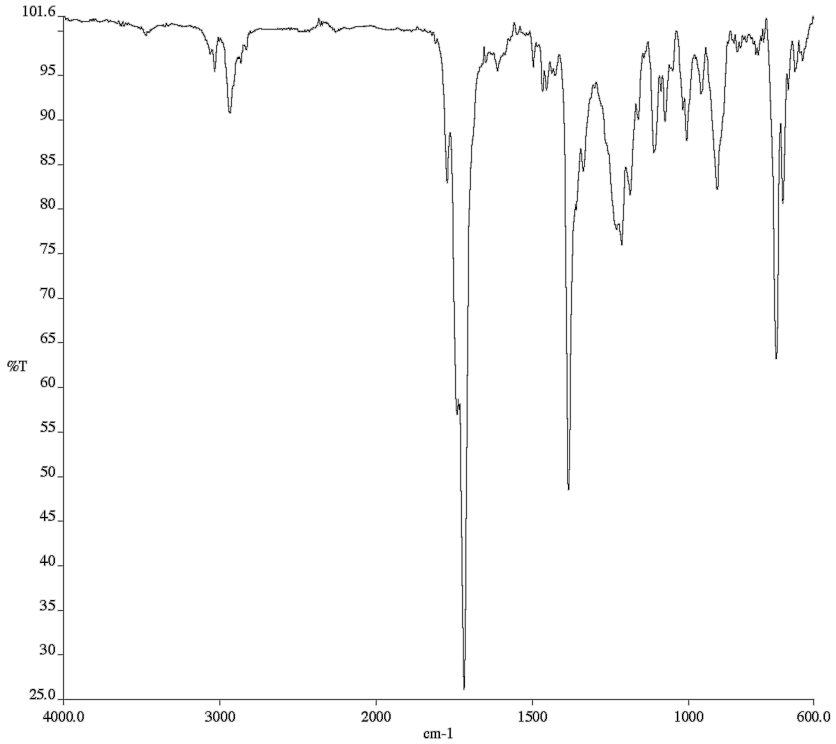
Infrared spectrum (Thin Film, NaCl) of compound **47**.



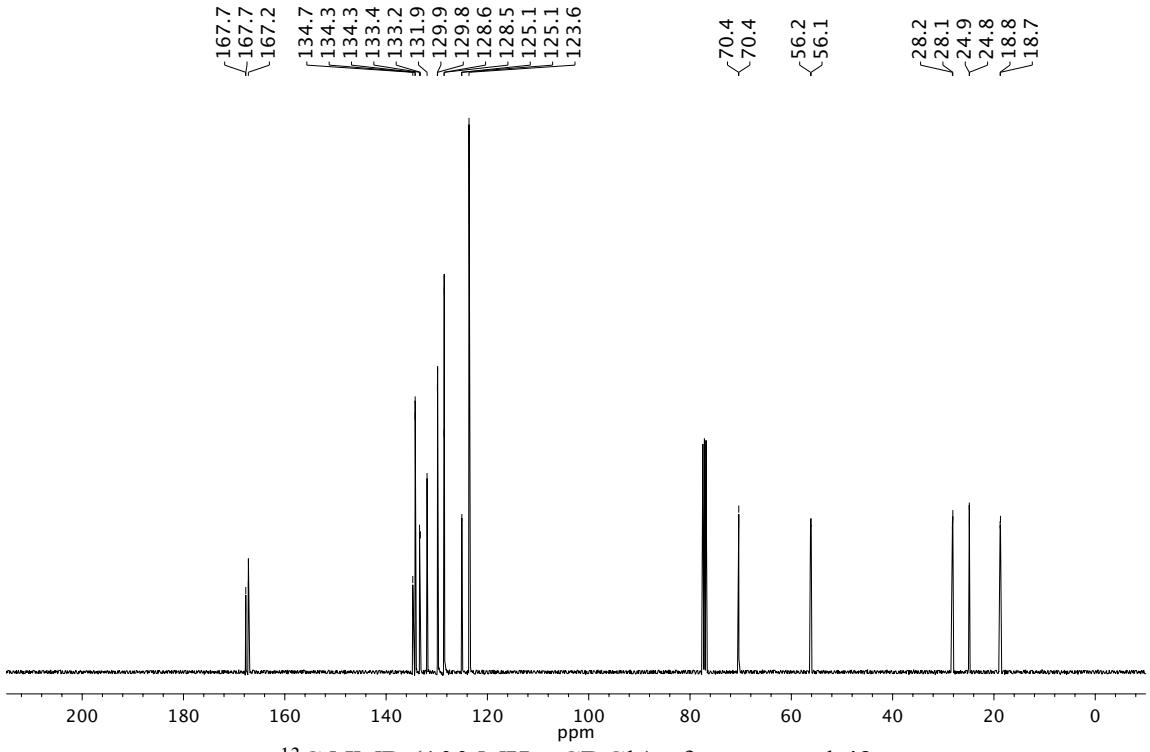
^{13}C NMR (100 MHz, $CDCl_3$) of compound **47**.



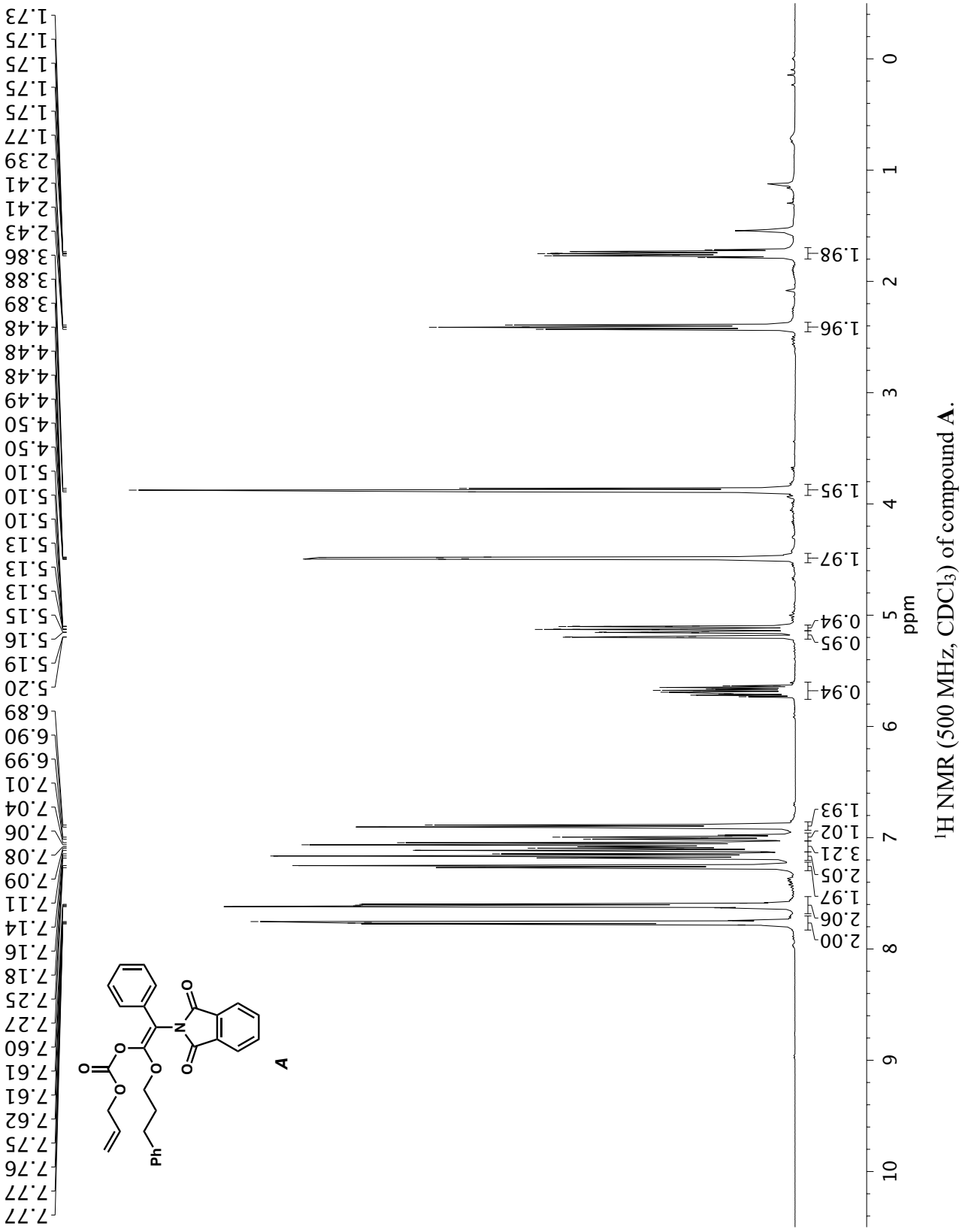
^{1}H NMR (500 MHz, $CDCl_3$) of compound **49**.



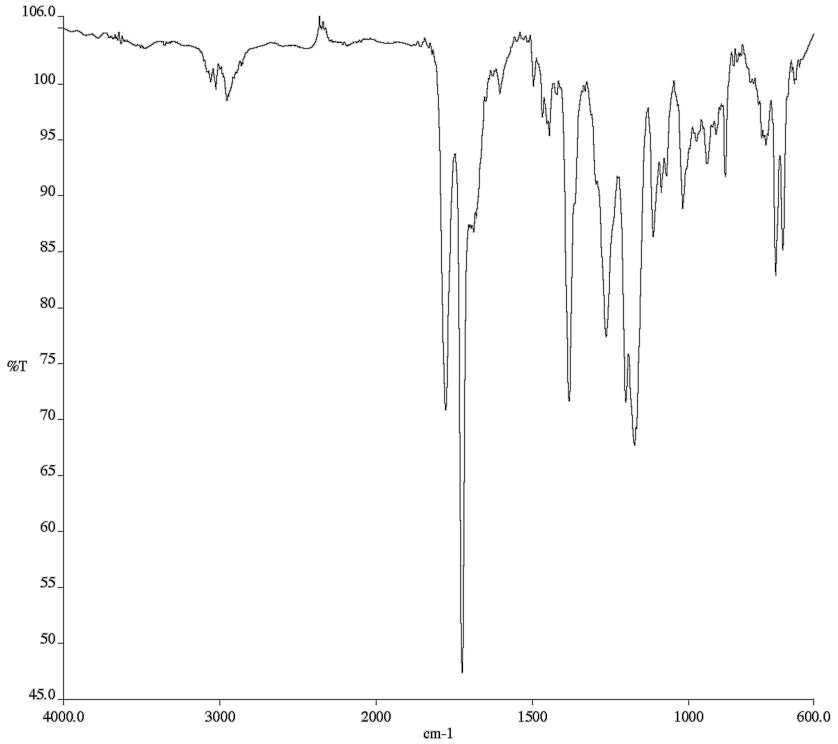
Infrared spectrum (Thin Film, NaCl) of compound **49**.



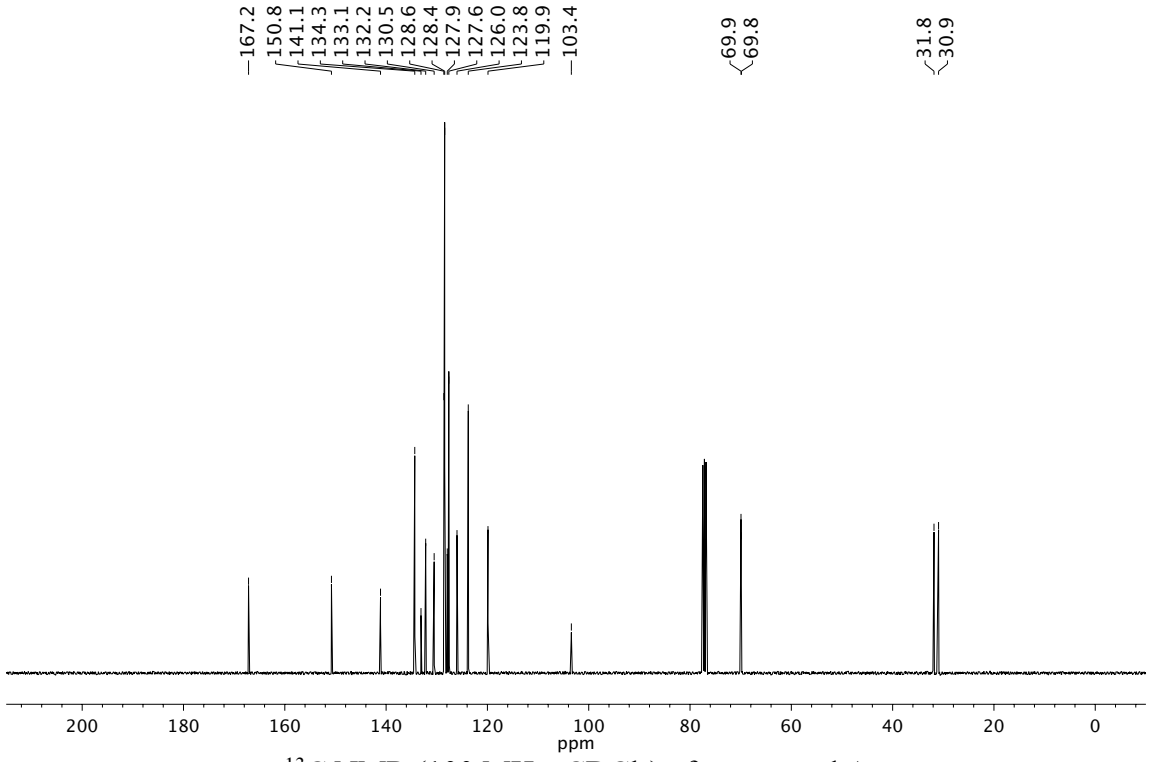
^{13}C NMR (100 MHz, $CDCl_3$) of compound **49**.



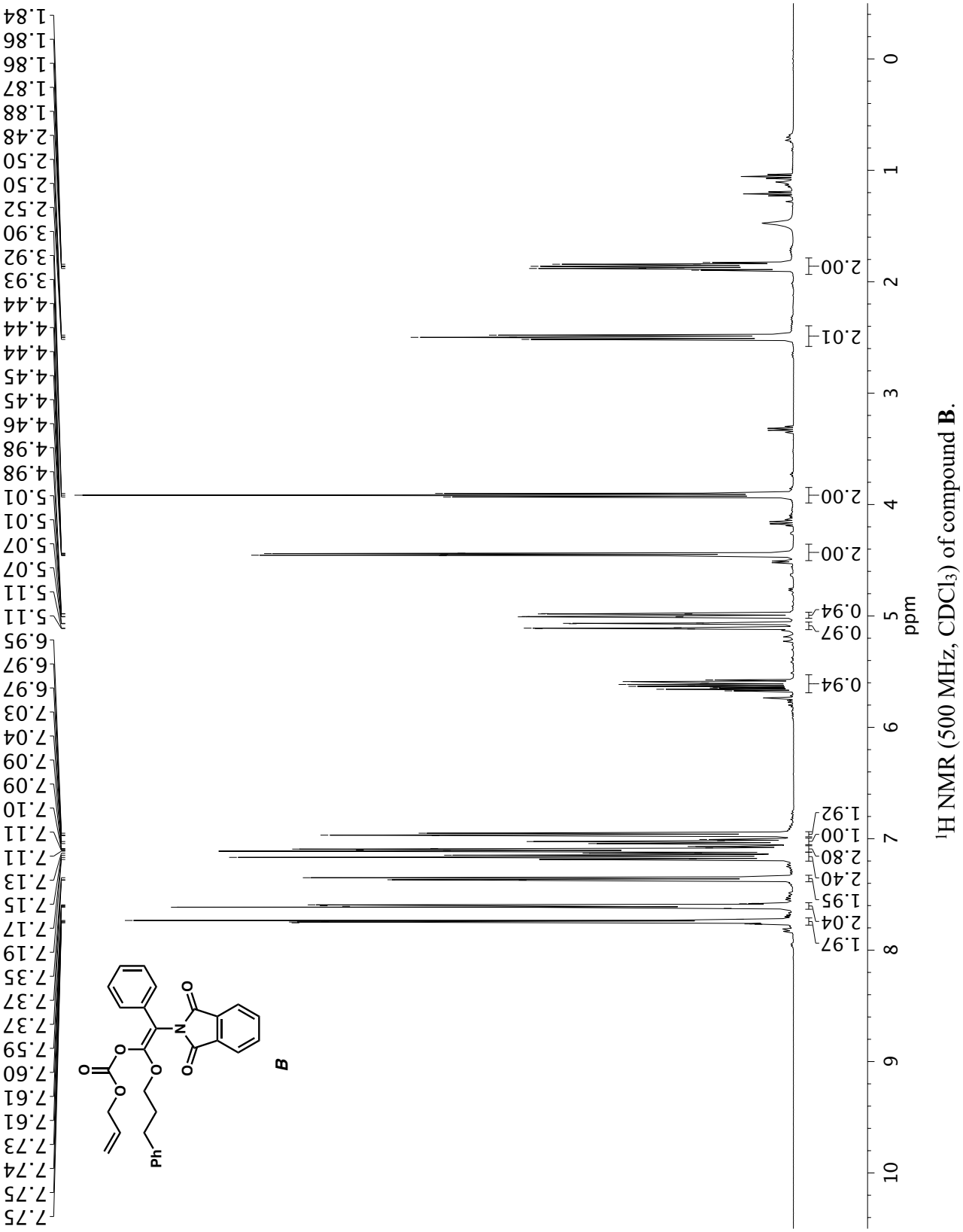
^{1}H NMR (500 MHz, $CDCl_3$) of compound **A**.



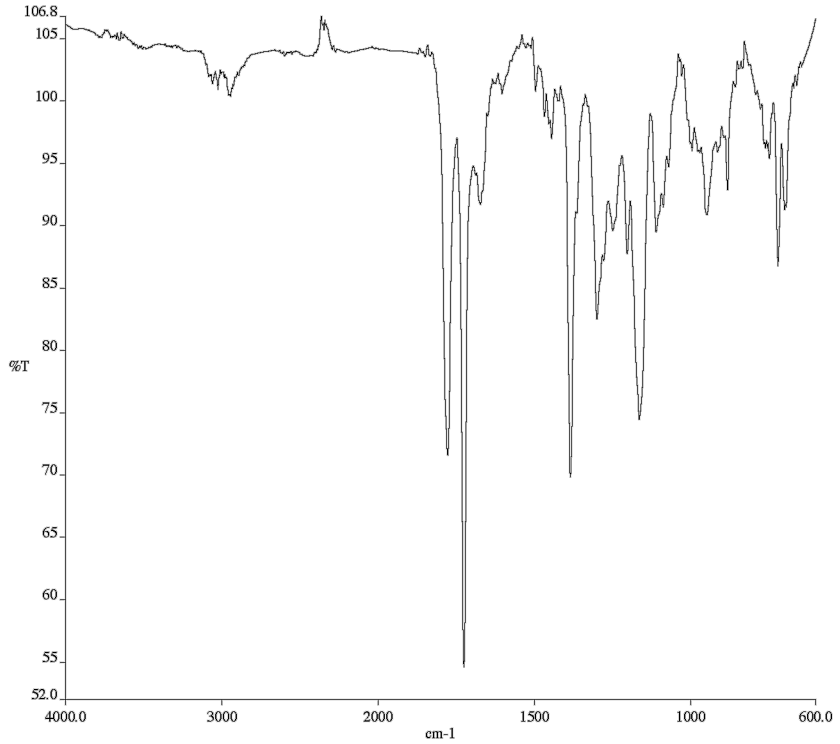
Infrared spectrum (Thin Film, NaCl) of compound **A**.



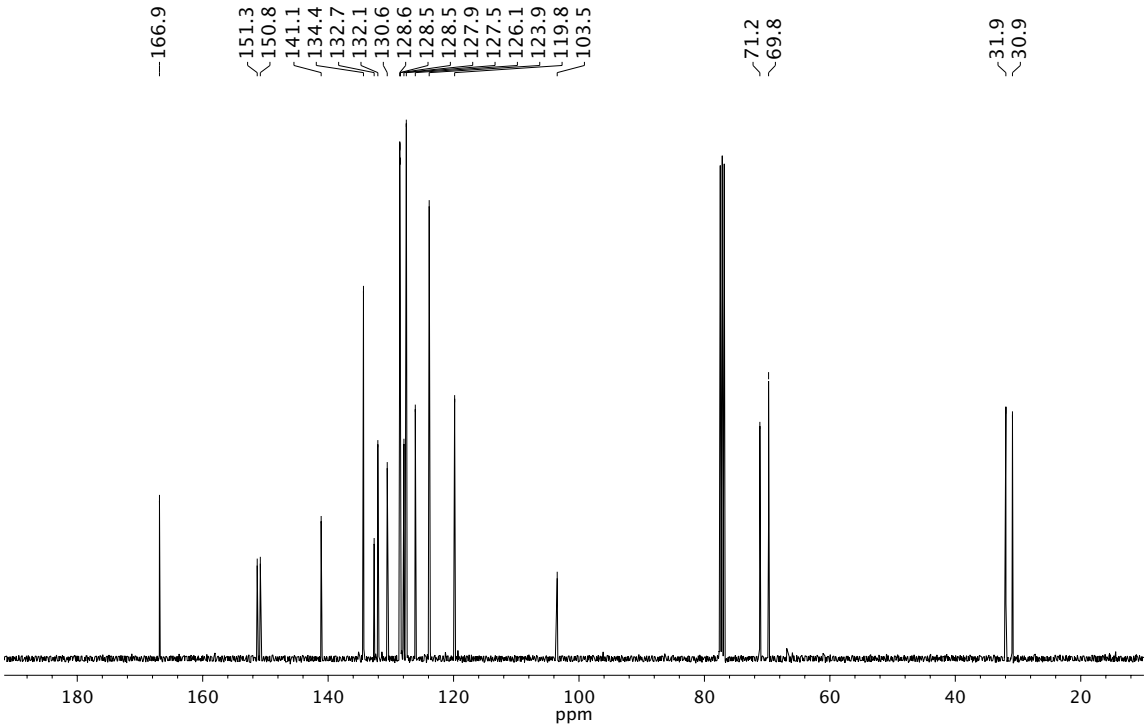
^{13}C NMR (100 MHz, $CDCl_3$) of compound **A**.



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



Infrared spectrum (Thin Film, NaCl) of compound **B**.



^{13}C NMR (100 MHz, $CDCl_3$) of compound **B**.