Supporting Information for

Palladium catalyzed α,β-dehydrogenation of acyclic ester equivalents promoted by a novel electron deficient phosphinooxazoline ligand.

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Table of Contents:

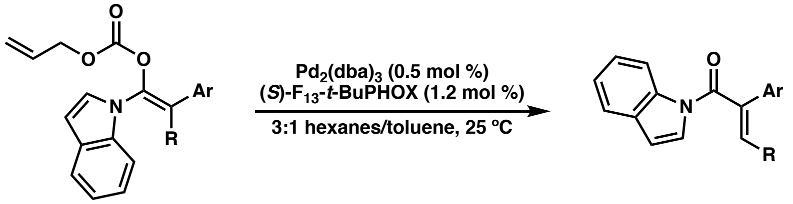
Materials and Methods

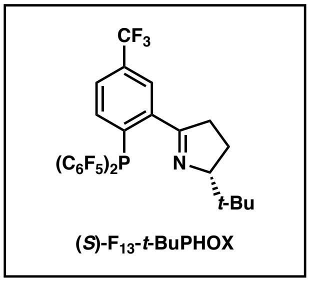
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-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 nm) was used for flash chromatography. The (*Z*)-enol carbonates were purified by preparative LC on a Teledyne Isco ACCQPrep HP125; column: C–18, 100 Å, 5 µm, ID 20 mm. ^{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 mixed ionization mode (MM: ESI-APCI+). Reagents were purchased from commercial sources and used as received unless otherwise stated.

List of Abbreviations:

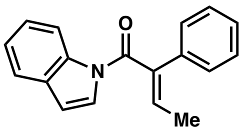
TLC – thin-layer chromatography
alloCl – allyl chloroformate

General Procedure for Pd-catalyzed Dehydrogenation Reactions



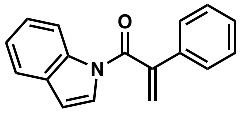


In a nitrogen-filled glovebox, a solution of $Pd_2(dba)_3$ (1.8 mg/mL) and (*S*)-F_{13}-*t*-BuPHOX (2.8 mg/mL) in toluene was stirred for 30 min at 25 °C, then 0.5 mL of the resulting catalyst solution was added to a one dram vial containing allyl enol carbonate substrate (0.2 mmol) dissolved in hexanes (1.5 mL). The vial was sealed with a Teflon-lined cap, removed from the glovebox, and stirred at 25 °C for 16 h unless noted otherwise. The crude reaction mixture was concentrated then purified by silica gel flash chromatography to provide the desired dehydrogenation product.



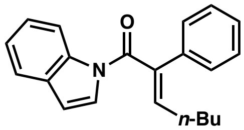
(*E*)-1-(1*H*-indol-1-yl)-2-phenylbut-2-en-1-one (3a)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (52.1 mg, 0.199 mmol, >99% yield, 10:1 *E*/*Z*); ^1H NMR (400 MHz, $CDCl_3$) δ 8.47 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.54 (dq, *J* = 7.6, 0.8 Hz, 1H), 7.43–7.27 (m, 8H), 6.50 (dd, *J* = 3.8, 0.7 Hz, 1H), 6.46 (q, *J* = 7.2 Hz, 1H), 1.99 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 138.0, 136.0, 134.9, 134.6, 130.8, 129.1, 128.8, 128.2, 127.2, 125.6, 125.0, 123.9, 120.9, 116.7, 108.5, 15.3; IR (Neat Film, NaCl) 3054, 2918, 2854, 1682, 1585, 1535, 1495, 1472, 1451, 1385, 1359, 1331, 1240, 1204, 1158, 1144, 1079, 1016, 946, 881, 815, 752, 703 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{16}NO$ $[M+H]^+$: 262.1226, found 262.1222.



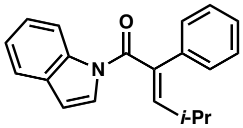
1-(1*H*-indol-1-yl)-2-phenylprop-2-en-1-one (3b)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (41.4 mg, 0.167 mmol, 84% yield);^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57–8.54 (m, 1H), 7.57 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.51–7.45 (m, 2H), 7.43–7.28 (m, 6H), 6.54 (d, *J* = 3.7 Hz, 1H), 6.08 (s, 1H), 5.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 144.5, 135.7, 135.4, 131.0, 129.2, 129.2, 127.1, 126.2, 125.3, 124.3, 121.0, 118.6, 116.8, 109.3; IR (Neat Film, NaCl) 3055, 2926, 1692, 1535, 1496, 1471, 1450, 1378, 1348, 1293, 1205, 1156, 1072, 1016, 931, 880, 752, 696 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{14}NO$ [M+H]$^+$: 248.1070, found 248.1063.



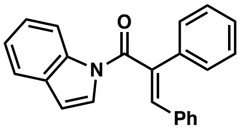
(*E*)-1-(1*H*-indol-1-yl)-2-phenylhept-2-en-1-one (3c)

Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (58.9 mg, 0.194 mmol, 97% yield, 14:1 *E*/*Z*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 8.3 Hz, 1H), 7.54 (dd, *J* = 7.5, 0.9 Hz, 1H), 7.42 – 7.26 (m, 7H), 6.57–6.48 (m, 2H), 6.33 (t, *J* = 7.5 Hz, 1H), 2.36 (q, *J* = 7.5 Hz, 2H), 1.50 (tt, *J* = 8.2, 6.9 Hz, 2H), 1.37 (dq, *J* = 14.4, 7.2 Hz, 2H), 0.89 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 140.2, 136.8, 136.0, 135.2, 130.8, 129.0, 128.8, 128.2, 127.2, 125.0, 123.9, 120.9, 116.7, 108.5, 31.5, 28.9, 22.6, 14.0; IR (Neat Film, NaCl) 3053, 2957, 2928, 2858, 1688, 1636, 1600, 1585, 1534, 1494, 1472, 1450, 1379, 1333, 1205, 1157, 1143, 1113, 1078, 1016, 938, 882, 816, 769, 752, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{22}NO$ [M+H]$^+$: 304.1696, found 304.1688.



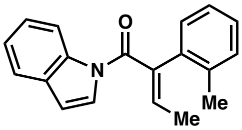
(*E*)-1-(1*H*-indol-1-yl)-4-methyl-2-phenylpent-2-en-1-one (3d)

Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (44.3 mg, 0.153 mmol, 77% yield, >20:1 *E*/*Z*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.55 (ddd, *J* = 7.7, 1.3, 0.7 Hz, 1H), 7.42–7.27 (m, 8H), 6.54 (d, *J* = 3.8 Hz, 1H), 6.10 (d, *J* = 10.5 Hz, 1H), 2.80 (dhept, *J* = 10.5, 6.6 Hz, 1H), 1.11 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 146.6, 136.0, 135.3, 134.5, 130.9, 128.9, 128.8, 128.8, 127.2, 125.0, 123.9, 120.9, 116.7, 108.5, 28.3, 22.7; IR (Neat Film, NaCl) 3054, 2962, 2868, 1687, 1534, 1494, 1450, 1377, 1334, 1238, 1201, 1112, 1078, 1017, 882, 795, 769, 752, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{20}NO$ [M+H]$^+$: 290.1539, found 290.1528.



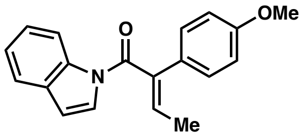
(*E*)-1-(1*H*-indol-1-yl)-2,3-diphenylprop-2-en-1-one (3e)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (48.3 mg, 0.149 mmol, 75% yield, 6:1 *E*/*Z*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.2 Hz, 1H), 7.70 (dd, *J* = 11.3, 7.5 Hz, 2H), 7.65 (d, *J* = 3.8 Hz, 1H), 7.59–7.44 (m, 7H), 7.44–7.30 (m, 5H), 6.71 (d, *J* = 3.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 136.4, 136.1, 135.3, 134.6, 130.9, 130.0, 129.3, 129.2, 128.9, 128.7, 128.5, 127.1, 126.0, 125.1, 124.1, 121.0, 116.8, 108.9.; IR (Neat Film, NaCl) 3053, 3026, 2923, 1684, 1535, 1492, 1472, 1450, 1381, 1333, 1235, 1206, 1155, 1141, 1112, 1077, 1016, 908, 882, 862, 753, 721, 694 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{18}NO$ [M+H]$^+$: 324.1383, found 324.1380.



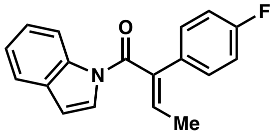
(*E*)-1-(1*H*-indol-1-yl)-2-(*o*-tolyl)but-2-en-1-one (3f)

Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (50.1 mg, 0.182 mmol, 91% yield, 12:1 *E*/*Z*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 8.2 Hz, 1H), 7.46 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.31–7.26 (m, 1H), 7.25 (d, *J* = 3.8 Hz, 1H), 7.22–7.16 (m, 3H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 3.8 Hz, 1H), 6.35 (q, *J* = 7.2 Hz, 1H), 2.28 (s, 3H), 1.91 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.4, 138.0, 137.9, 135.9, 134.0, 131.9, 130.8, 129.7, 129.5, 128.9, 127.2, 125.5, 124.9, 123.9, 120.8, 116.7, 108.4, 21.4, 15.3; IR (Neat Film, NaCl) 3027, 2919, 2856, 1688, 1533, 1513, 1472, 1450, 1384, 1329, 1239, 1206, 1157, 1143, 1113, 1080, 1017, 946, 882, 828, 770, 753, 723 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{18}NO$ [M+H]$^+$: 276.1383, found 276.1375.



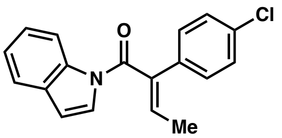
(*E*)-1-(1*H*-indol-1-yl)-2-(4-methoxyphenyl)but-2-en-1-one (3g)

Purified by column chromatography (8% Et_2O in hexanes) to provide a colorless oil (55.0 mg, 0.189 mmol, 94% yield, 19:1 *E/Z*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.41–7.24 (m, 5H), 6.96–6.87 (m, 2H), 6.50 (d, *J* = 3.8 Hz, 1H), 6.40 (q, *J* = 7.1 Hz, 1H), 3.81 (s, 3H), 1.99 (d, *J* = 7.1 Hz, 3H).;^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 159.4, 137.6, 135.9, 133.6, 130.8, 130.3, 127.3, 127.2, 124.9, 123.9, 120.8, 116.7, 114.2, 108.4, 55.4, 15.3; IR (Neat Film, NaCl) 2934, 2361, 1684, 1607, 1511, 1450, 1328, 1292, 1250, 1202, 1178, 1110, 1079, 1032, 948, 881, 838, 815, 770, 753 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{18}NO_2$ [M+H]$^+$: 292.1332, found 292.1340.



(*E*)-2-(4-fluorophenyl)-1-(1*H*-indol-1-yl)but-2-en-1-one (3h)

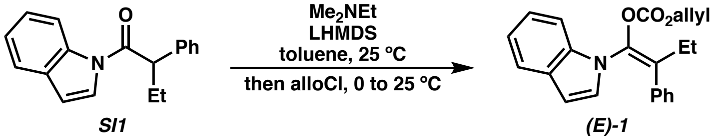
Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (49.8 mg, 0.178 mmol, 89% yield, 13:1 *E/Z*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.2 Hz, 1H), 7.55 (dt, *J* = 7.7, 0.9 Hz, 1H), 7.40–7.32 (m, 4H), 7.32–7.26 (m, 1H), 7.13–7.06 (m, 2H), 6.53 (d, *J* = 3.8 Hz, 1H), 6.45 (q, *J* = 7.1 Hz, 1H), 1.96 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.0, 162.45 (d, $J_{C\text{–}F}$ = 248.2 Hz), 136.9, 135.9, 134.9, 130.9, 130.8, 127.0, 125.1, 124.0, 120.9, 116.6, 116.0, 115.7, 108.7, 15.2; ^{19}F NMR (282 MHz, $CDCl_3$) δ –113.18 (dtq, *J* = 10.8, 5.3, 2.3 Hz). IR (Neat Film, NaCl) 3051, 2917, 1685, 1602, 1534, 1509, 1472, 1450, 1385, 1331, 1224, 1202, 1160, 1101, 1080, 1016, 948, 881, 842, 786, 770, 754 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{15}FNO$ [M+H]$^+$: 280.1132, found 280.1137.



(*E*)-2-(4-chlorophenyl)-1-(1*H*-indol-1-yl)but-2-en-1-one (3i)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (46.7 mg, 0.158 mmol, 79% yield, 8:1 *E*/*Z*); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.1 Hz, 1H), 7.59–7.51 (m, 1H), 7.40–7.26 (m, 7H), 6.53 (d, *J* = 3.7 Hz, 1H), 6.46 (q, *J* = 7.2 Hz, 1H), 1.97 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 136.9, 135.9, 135.3, 134.2, 133.2, 130.4, 129.2, 129.0, 127.0, 125.1, 124.1, 120.9, 116.6, 108.8, 15.3; IR (Neat Film, NaCl) 3051, 2916, 1688, 1534, 1491, 1472, 1451, 1384, 1330, 1204, 1143, 1089, 1016, 947, 881, 838, 802, 770, 754 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{15}ClNO$ [M+H]$^+$: 296.0837, found 296.0835.

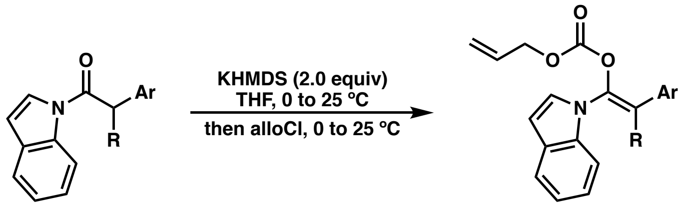
Enolization of *N*-Acyl Indole Substrates



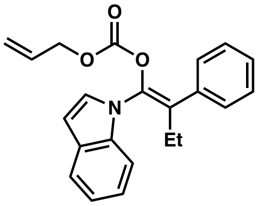
(*E*)-1-(1*H*-indol-1-yl)-2-phenylbut-1-en-1-yl allyl carbonate ((*E*)-1)

To a flame-dried flask was added LHMDS (2.68 g, 16.0 mmol) followed by toluene (24.0 mL) and *N*,*N*-dimethylethylamine (1.7 mL, 16.0 mmol, 2.0 equiv), and the resulting mixture stirred at 25 °C for 5 min. A solution of **SI1** (2.11 g, 8.00 mmol, 1.0 equiv) in toluene (16.0 mL) was then added, and the reaction stirred at 25 °C for an additional 2 hours. The flask was then submerged in a room temperature water bath, and allyl chloroformate (1.7 mL, 16 mmol, 2.0 equiv) was added neat, and the reaction continued until no starting material remained by TLC (typically less than 30 min). The crude reaction mixture was diluted with Et_2O and quenched with water. The layers were separated, and the aqueous layer was extracted with Et_2O twice. The combined organic layers were dried over Na_2SO_4 and concentrated. Purified by column chromatography (5% Et_2O in hexanes) to provide **(*E*)-1** as a colorless oil (>98:2 *E*/*Z*, 2.08 g, 75% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.43 (m, 2H), 7.24–7.18 (m, 1H), 7.15–7.06 (m, 4H), 7.02–6.94 (m, 2H), 6.89 (d, *J* = 3.3 Hz, 1H), 6.35 (dd, *J* = 0.9, 3.4 Hz, 1H), 5.88 (ddt, *J* = 5.8, 10.4, 17.1 Hz, 1H), 5.37–5.23 (m, 2H), 4.61 (dt, *J* = 1.4, 5.8 Hz, 2H), 2.68 (q, *J* = 7.5 Hz, 2H), 1.09 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 136.2, 135.0, 130.8, 130.2, 129.0, 128.4, 128.2, 127.5, 127.5, 122.6, 120.7, 119.4, 111.2, 103.9, 69.3, 24.9, 12.6; IR (Neat Film, NaCl) 3056, 2974, 1766, 1682, 1519, 1456, 1333, 1259, 1238, 1209, 1143, 1119, 1094, 1042, 968, 946, 913, 765, 743, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.1594, found 348.1588.

General Procedure for the Enolization of *N*-Acyl Indole Substrates



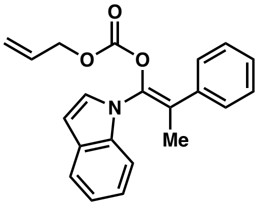
To a flame-dried flask was added KHMDS (2.0 equiv) followed by THF (0.20 M) and the resulting mixture stirred at 0 °C for 5 min. A solution of *N*-acyl indole (1.0 equiv) in THF (0.50 M) was then added dropwise, and the reaction stirred at 0 °C for 10 min then at 20 ºC for 3 h. The flask was then submerged in a room temperature water bath, and allyl chloroformate (2.0 equiv) was added neat, and the reaction continued until no starting material remained by TLC (typically less than 30 min). The crude reaction mixture was diluted with Et_2O and quenched with water. The layers were separated, and the aqueous layer was extracted with Et_2O twice. The combined organic layers were dried over Na_2SO_4 and concentrated. The (*Z*)-enol carbonates were purified by preparative LC on a Teledyne Isco ACCQPrep HP125; column: C–18, 100 Å, 5 μm, ID 20 mm, gradient 50 to 100% MeCN/H_2O (0.25% AcOH).



(*Z*)-1-(1*H*-indol-1-yl)-2-phenylbut-1-en-1-yl allyl carbonate ((*Z*)-1)

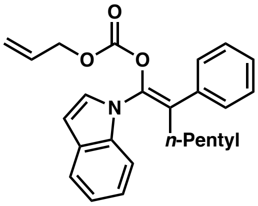
Isolated as a viscous, colorless oil (168.2 mg, 0.484 mmol, 48% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 0.9 Hz, 1H), 7.57–7.53 (m, 1H), 7.46–7.38 (m, 4H), 7.34 (dd, *J* = 8.5, 2.9 Hz, 2H), 7.31–7.27 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 5.68 (ddt, *J* = 17.1, 10.6, 5.6 Hz, 1H), 5.18–5.02 (m, 2H), 4.43 (dt, *J* = 5.6, 1.4 Hz, 2H), 2.20 (q, *J* = 7.5 Hz, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 136.7, 136.2, 133.7, 132.6, 130.8, 128.8, 128.5, 128.5, 128.1, 127.9, 122.9, 121.0, 118.8, 111.1, 104.0, 69.0, 25.4, 12.7; IR

(Neat Film, NaCl) 3054, 2972, 2356, 1761, 1684, 1518, 1456, 1331, 1296, 1241, 1211, 1140, 1117, 1038, 961, 824, 765, 744, 702 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.1594, found 348.1586.



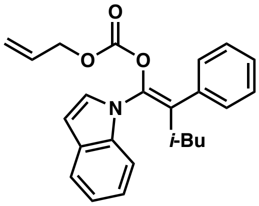
(*Z*)-1-(1*H*-indol-1-yl)-2-phenylprop-1-en-1-yl allyl carbonate (1b)

Isolated as a viscous, colorless oil (145.4 mg, 0.436 mmol, 44% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 7.8, 0.8 Hz, 1H), 7.56–7.48 (m, 1H), 7.51–7.43 (m, 2H), 7.46–7.36 (m, 2H), 7.40–7.30 (m, 2H), 7.29 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.24–7.15 (m, 1H), 6.64 (d, *J* = 3.1 Hz, 1H), 5.80–5.57 (m, 1H), 5.20–5.04 (m, 2H), 4.46 (dt, *J* = 5.6, 1.4 Hz, 2H), 1.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 137.8, 136.4, 134.1, 130.8, 128.6, 128.4, 128.2, 128.0, 127.7, 125.5, 122.9, 121.0, 121.0, 118.9, 111.3, 104.3, 69.1, 18.8; IR (Neat Film, NaCl) 3055, 1763, 1684, 1518, 1474, 1456, 1328, 1295, 1278, 1242, 1213, 1141, 1118, 1078, 1027, 950, 764, 744, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{20}NO_3$ $[M+H]^+$: 334.1438, found 334.1447.



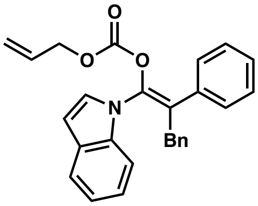
(*Z*)-1-(1H-indol-1-yl)-2-phenylhept-1-en-1-yl allyl carbonate (1c)

Isolated as a viscous, colorless oil (152.7 mg, 0.436 mmol, 44% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 7.8, 0.7 Hz, 1H), 7.54 (dq, *J* = 8.1, 0.7 Hz, 1H), 7.40 (d, *J* = 3.5 Hz, 4H), 7.34 (p, *J* = 4.0 Hz, 2H), 7.30–7.25 (m, 1H), 7.19 (ddd, *J* = 8.0, 7.3, 1.1 Hz, 1H), 6.62 (d, *J* = 3.2 Hz, 1H), 5.68 (ddt, *J* = 17.2, 10.7, 5.6 Hz, 1H), 5.20–4.98 (m, 2H), 4.43 (dt, *J* = 5.6, 1.5 Hz, 2H), 2.26–2.08 (m, 2H), 1.21 (ddt, *J* = 12.6, 8.9, 4.6 Hz, 2H), 1.14–0.97 (m, 4H), 0.78–0.63 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 136.7, 136.5, 134.1, 131.5, 130.9, 129.0, 128.5, 128.5, 128.1, 127.9, 122.8, 121.0, 118.9, 111.2, 104.0, 69.0, 32.0, 31.3, 27.3, 22.3, 13.9; IR (Neat Film, NaCl) 3055, 2955, 2928, 1762, 1682, 1518, 1456, 1326, 1296, 1242, 1212, 1140, 1120, 988, 952, 765, 743, 718, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{28}NO_3$ $[M+H]^+$: 390.2064, found 390.2060.



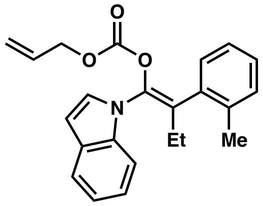
(*Z*)-1-(1*H*-indol-1-yl)-4-methyl-2-phenylpent-1-en-1-yl allyl carbonate (1d)

Isolated as a viscous, colorless oil (137.2 mg, 0.365 mmol, 37% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 8.1 Hz, 1H), 7.45–7.38 (m, 4H), 7.38–7.31 (m, 2H), 7.31–7.26 (m, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 3.3 Hz, 1H), 5.78–5.47 (m, 1H), 5.18–4.97 (m, 2H), 4.42 (dt, *J* = 5.5, 1.3 Hz, 2H), 2.08 (d, *J* = 7.3 Hz, 2H), 1.42 (dh, *J* = 13.7, 6.8 Hz, 1H), 0.73 (d, *J* = 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 135.9, 135.8, 135.7, 135.6, 130.9, 130.2, 129.7, 129.0, 128.9, 128.4, 127.6, 125.5, 122.5, 120.8, 120.7, 119.6, 111.4, 103.4, 69.5, 25.5, 19.7, 12.1; IR (Neat Film, NaCl) 3057, 3030, 2956, 1766, 1682, 1611, 1518, 1456, 1384, 1366, 1347, 1326, 1296, 1278, 1244, 1210, 1140, 1117, 1066, 971, 946, 888, 766, 743, 718, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{26}NO_3$ $[M+H]^+$: 376.1907, found 376.1910.



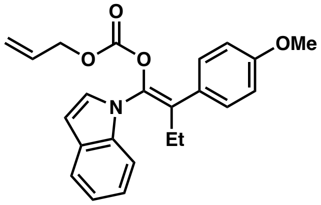
(*Z*)-1-(1*H*-indol-1-yl)-2,3-diphenylprop-1-en-1-yl allyl carbonate (1e)

Isolated as a viscous, colorless oil (129.2 mg, 0.316 mmol, 32% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.63–7.55 (m, 1H), 7.38 (d, *J* = 3.4 Hz, 1H), 7.33–7.27 (m, 6H), 7.21 (ddd, *J* = 8.1, 7.1, 1.1 Hz, 1H), 7.16–7.08 (m, 3H), 6.95–6.87 (m, 2H), 6.67–6.53 (m, 1H), 5.68 (ddt, *J* = 17.3, 10.6, 5.6 Hz, 1H), 5.17–5.02 (m, 2H), 4.45 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.55 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 137.6, 136.7, 136.2, 135.4, 130.8, 129.6, 128.8, 128.6, 128.4, 128.4, 128.0, 126.4, 123.0, 121.2, 121.1, 119.0, 111.2, 104.4, 69.1, 38.3; IR (Neat Film, NaCl) 3060, 3027, 1763, 1683, 1518, 1494, 1474, 1456, 1328, 1294, 1278, 1242, 1214, 1139, 1113, 1068, 987, 939, 766, 744, 712, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{27}H_{24}NO_3$ [M+H]$^+$: 410.1751, found 410.1732.



(*Z*)-1-(1H-indol-1-yl)-2-(o-tolyl)but-1-en-1-yl allyl carbonate (1f)

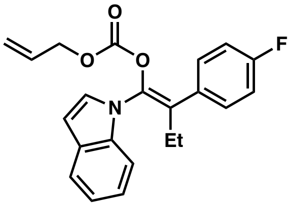
Isolated as a viscous, colorless oil (117.4 mg, 0.324 mmol, 32% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (dq, *J* = 8.1, 0.7 Hz, 1H), 7.51–7.44 (m, 1H), 7.22 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.14–7.08 (m, 1H), 7.08–6.97 (m, 4H), 6.85 (d, *J* = 3.3 Hz, 1H), 6.27 (d, *J* = 3.3 Hz, 1H), 5.90 (ddt, *J* = 17.3, 10.4, 5.8 Hz, 1H), 5.42–5.13 (m, 2H), 4.69–4.57 (m, 2H), 2.60 (ddt, *J* = 59.4, 13.8, 6.9 Hz, 2H), 2.17 (s, 3H), 1.09 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.8, 136.8, 136.5, 134.6, 131.1, 130.9, 129.1, 128.5, 128.5, 128.4, 128.2 (overlapping), 127.9, 122.8, 121.0, 118.8, 111.3, 104.0, 69.0, 40.8, 25.9, 22.3; IR (Neat Film, NaCl) 2934, 2361, 1684, 1607, 1511, 1450, 1328, 1292, 1250, 1202, 1178, 1110, 1079, 1032, 948, 881, 838, 815, 770, 753 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO_3$ [M+H]$^+$: 362.1751, found 362.1749.



(*Z*)-1-(1*H*-indol-1-yl)-2-(4-methoxyphenyl)but-1-en-1-yl allyl carbonate (1g)

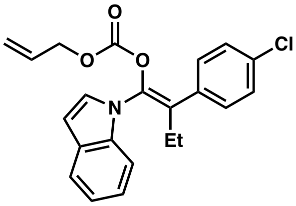
Isolated as a viscous, colorless oil (168.6 mg, 0.447 mmol, 45% yield); ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.55–7.51 (m, 1H), 7.37–7.30 (m, 3H), 7.30–7.24 (m, 1H), 7.21–7.14 (m, 1H), 6.98–6.91 (m, 2H), 6.61 (dd, *J* = 3.3, 1.0 Hz, 1H), 5.82–5.57 (m, 1H), 5.21–5.02 (m, 2H), 4.45 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.85 (s, 3H), 2.17 (q, *J* = 7.5 Hz, 2H), 0.84 (t, *J* = 7.5 Hz, 3H);^{13}C NMR (100 MHz, CDCl$_3$) δ 159.3, 152.9, 136.7, 133.5, 132.2, 130.9, 129.4, 128.9, 128.4, 128.3, 122.8, 121.0, 120.9, 118.9, 113.9, 111.2, 103.9, 69.0, 55.3, 25.4, 12.9; IR

(Neat Film, NaCl) 2972, 1765, 1687, 1519, 1456, 1333, 1259, 1238, 1210, 1144, 1115, 1088, 1039, 969, 945, 763, 743 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO_4$ $[M+H]^+$: 378.1700, found 378.1713.



(*Z*)-allyl (2-(4-fluorophenyl)-1-(1*H*-indol-1-yl)but-1-en-1-yl) carbonate (1h)

Isolated as a viscous, colorless oil (225.1 mg, 0.616 mmol, 31% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.55 (ddd, *J* = 8.2, 1.7, 0.6 Hz, 1H), 7.44–7.37 (m, 2H), 7.34 (d, *J* = 3.3 Hz, 1H), 7.33–7.29 (m, 1H), 7.22 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 7.17–7.10 (m, 2H), 6.65 (dd, *J* = 3.2, 0.8 Hz, 1H), 5.72 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.24–5.08 (m, 2H), 4.46 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.21 (q, *J* = 7.5 Hz, 2H), 0.86 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.41 (d, $J_{C\text{–}F}$ = 246.9 Hz), 152.8, 136.7, 134.1, 132.1 (d, $J_{C\text{–}F}$ = 3.5 Hz), 131.6, 130.8, 130.0 (d, $J_{C\text{–}F}$ = 8.2 Hz), 128.7, 128.5, 122.9, 121.0, 119.1, 115.7, 115.5, 111.1, 104.2, 69.1, 25.5, 12.7**;**^{19}F NMR (282 MHz, $CDCl_3$) δ –113.98 – –114.11 (m);.IR (Neat Film, NaCl) 3052, 2973, 1763, 1685, 1604, 1510, 1456, 1331, 1296, 1242, 1211, 1160, 1140, 1117, 1066, 1037, 1012, 960, 846, 767, 745 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{21}FNO_3$ $[M+H]^+$: 366.1500, found 366.1496.

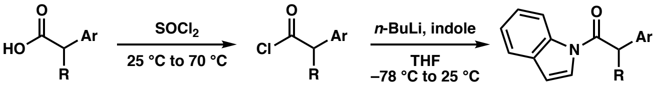


(*Z*)-allyl (2-(4-chlorophenyl)-1-(1*H*-indol-1-yl)but-1-en-1-yl) carbonate (1i)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (dt, *J* = 7.8, 0.9 Hz, 1H), 7.57–7.50 (m, 1H), 7.43–7.34 (m, 4H), 7.32 (d, *J* = 3.3 Hz, 1H), 7.34–7.25 (m, 1H), 7.20 (td, *J* = 7.5, 7.1, 1.0 Hz, 1H), 6.64 (d, *J* = 3.2 Hz, 1H), 5.71 (ddt, *J* = 17.1, 10.5, 5.7 Hz, 1H), 5.21–5.08 (m, 2H), 4.45 (dt, *J* = 5.7, 1.5 Hz, 2H), 2.20 (q, *J* = 7.5 Hz, 2H), 0.85 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 136.6, 134.7, 134.2, 133.9, 131.3, 130.7, 129.6, 128.8, 128.7, 128.5, 123.0, 121.1, 121.1, 119.2, 111.1, 104.3, 69.2, 25.3, 12.7; IR (Neat Film, NaCl) 2972, 1762, 1681, 1491, 1474, 1455, 1241, 1209, 1140, 1111, 1014, 960, 816, 765, 744 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{21}ClNO$ [M+H]$^+$: 382.1204, found 382.1189.

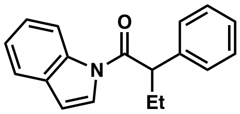
Preparation of *N*-Acyl Indoles

General Procedure 1



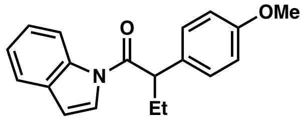
To an oven-dried vial containing α-aryl carboxylic acid (1.2 equiv) was added $SOCl_2$ neat (2.4 equiv) and the resuting mixture stirred at 25 °C for 20 min then 70 °: effluent gas flow is bubbled through a glass tube packed with powdered NaOH). The reaction was then concentrated in vacuo to afford the crude acid chloride, which was used in the next step without further purification.

A flame-dried flask containing indole (1.0 equiv) in THF (500 mM) was cooled to 0 °C in an ice bath and *n*-BuLi (1.05 equiv) was added dropwise. The mixture was stirred at 0 °C for 15 min then cooled to –78 °C in a dry-ice acetone bath. The crude acid chloride dissolved in THF is then added quickly, and the resulting mixture allowed to slowly warm to room temperature. Then reaction was then quenched with water and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and the desired *N*-acyl indole isolated by silica gel flash chromatography.



1-(1*H*-indol-1-yl)-2-phenylbutan-1-one (SI1)

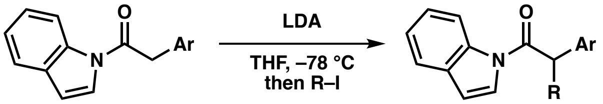
Prepared according to general procedure 1. Purified by column chromatography (3% Et_2O in hexanes) to provide the desired product as a white solid (428.2 mg, 81% yield); ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.54 (d, *J* = 8.3, 1H), 7.51–7.42 (m, 2H), 7.38–7.13 (m, 7H), 6.48 (d, *J* = 3.8 Hz, 1H), 4.10 (t, *J* = 7.2 Hz, 1H), 2.35–2.18 (m, 1H), 1.89 (dt, *J* = 13.7, 7.2 Hz, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 171.9, 139.1, 136.0, 130.3, 129.1, 127.7, 127.5, 125.2, 124.9, 123.8, 120.8, 117.0, 109.1, 53.7, 27.9, 12.3; IR (Neat Film, NaCl) 3063, 2967, 2943, 2874, 1704, 1602, 1584, 1539, 1472, 1451, 1384, 1355, 1328, 1304, 1222, 1208, 1181, 1154, 1082, 1017, 903, 880, 825, 807, 766, 749, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{18}NO$ [M+H]$^+$: 264.1383, found 264.1377.



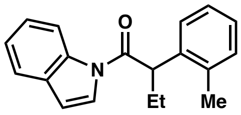
1-(1*H*-indol-1-yl)-2-(4-methoxyphenyl)butan-1-one (SI2)

Prepared according to general procedure 1. Purified by column chromatography (3% Et_2O in hexanes) to provide the desired product as a yellow oil containing minor impurities (1.2439 g, 85% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dq, *J* = 8.3, 0.9 Hz, 1H), 7.53–7.48 (m, 2H), 7.35 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.30–7.22 (m, 3H), 6.89–6.82 (m, 2H), 6.53 (dd, *J* = 3.8, 0.7 Hz, 1H), 4.10 (t, *J* = 7.3 Hz, 1H), 3.76 (s, 3H), 2.37–2.20 (m, 1H), 1.90 (m, 1H), 0.97 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2, 158.9, 135.9, 131.1, 130.3, 128.7, 125.1, 124.9, 123.7, 120.7, 116.9, 114.4, 108.9, 55.1, 52.8, 27.8, 12.2; IR (Neat Film, NaCl) 2964, 2933, 1702, 1610, 1540, 1511, 1450, 1384, 1354, 1324, 1302, 1252, 1222, 1207, 1179, 1154, 1033, 904, 820, 788, 766, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}NO_2$ [M+H]$^+$: 294.1489, found 294.1494.

General Procedure 2

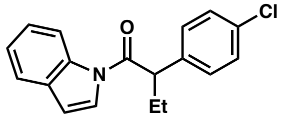


A flame-dried round bottom flask was charged with *i*-Pr_2NH (367 μL, 2.60 mmol, 1.3 equiv) and THF (18.0 mL). The solution was then cooled in a 0 ºC ice bath for 10 min and a 2.40 M solution of *n*-BuLi (996 μL, 2.40 mmol, 1.2 equiv) was added dropwise. After stirring for 15 min, the solution was cooled in a –78 ºC acetone/dry ice bath for 15 min, after which time a solution of acyl indole (498.6 mg, 2.00 mmol, 1.0 equiv) in THF (4.0 mL) was added dropwise over 5 min. After stirring at –78 ºC for 1 h, neat ethyl iodide (193 μL, 2.40 mmol, 1.2 equiv) was then added dropwise. The reaction mixture was allowed to slowly warm to 20 ºC, and then heated to 65 ºC and stirred for 16 h, after which time the reaction was quenched with the slow addition of 10 mL H_2O. The mixture was then transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted 3 x 10 mL Et_2O and the combined organics were dried over Na_2SO_4, filtered, and concentrated. The desired *N*-acyl indole was isolated by silica gel flash chromatography.



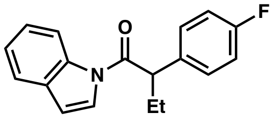
1-(1*H*-indol-1-yl)-2-(*o*-tolyl)butan-1-one (SI3)

Prepared according to General Procedure 2 with (623.3 mg, 2.50 mmol, 1.0 equiv) of acyl indole. Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as an amorphous white solid (458.8 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.3 Hz, 1H), 7.50 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.36 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.29–7.21 (m, 3H), 7.19 (d, *J* = 3.8 Hz, 1H), 7.13 (pd, *J* = 7.3, 1.8 Hz, 2H), 6.48 (d, *J* = 3.7 Hz, 1H), 4.34 (dd, *J* = 8.5, 5.4 Hz, 1H), 2.51 (s, 3H), 2.30 (ddq, *J* = 14.4, 8.7, 7.4 Hz, 1H), 1.81 (dqd, *J* = 14.7, 7.4, 5.4 Hz, 1H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3, 138.1, 136.1, 134.5, 131.1, 130.3, 127.4, 127.1, 126.9, 125.2, 124.5, 123.8, 120.8, 117.0, 109.2, 49.9, 27.3, 19.8, 12.9; IR (Neat Film, NaCl) 2966, 2876, 1703, 1539, 1450, 1383, 1354, 1327, 1306, 1222, 1207, 1156, 1107, 1080, 1017, 903, 830, 750, 712 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539, found 278.1547.



2-(4-chlorophenyl)-1-(1*H*-indol-1-yl)butan-1-one (SI4)

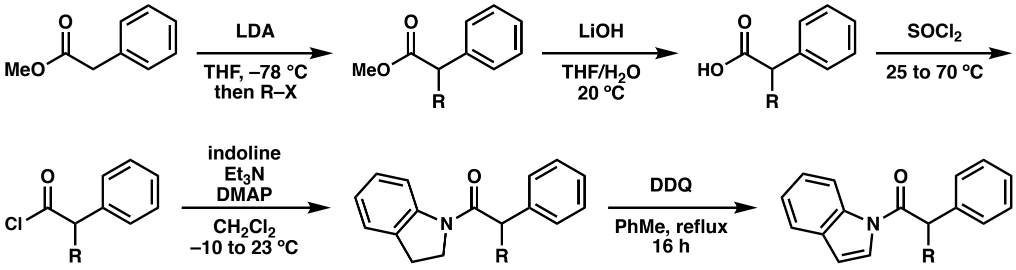
Prepared according to General Procedure 2 with (539.5 mg, 2.00 mmol, 1.0 equiv) of acyl indole. Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a light yellow oil (373.8 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.52 (dt, *J* = 7.7, 1.1 Hz, 1H), 7.44 (d, *J* = 3.8 Hz, 1H), 7.36 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.30 (s, 4H), 7.28–7.24 (m, 1H), 6.56 (dd, *J* = 3.9, 0.8 Hz, 1H), 4.13 (t, *J* = 7.3 Hz, 1H), 2.29 (dt, *J* = 13.8, 7.3 Hz, 1H), 2.03–1.76 (m, 1H), 0.97 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 137.6, 136.0, 133.5, 130.4, 129.4, 129.2, 125.4, 124.6, 124.0, 120.9, 117.0, 109.5, 53.1, 27.9, 12.3; IR (Neat Film, NaCl) 2967, 2361, 1700, 1540, 1491, 1451, 1384, 1354, 1328, 1302, 1221, 1207, 1094, 1015, 904, 814, 794, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{17}ClNO$ $[M+H]^+$: 298.0993, found 298.0984.



2-(4-fluorophenyl)-1-(1*H*-indol-1-yl)butan-1-one (SI5)

Prepared according to General Procedure 2 with (506.6 mg, 2.00 mmol, 1.0 equiv) of acyl indole. Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (360.4 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.3 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.46 (d, *J* = 3.8 Hz, 1H), 7.39–7.29 (m, 3H), 7.30–7.22 (m, 1H), 7.07–6.97 (m, 2H), 6.56 (dd, *J* = 3.8, 0.6 Hz, 1H), 4.15 (t, *J* = 7.3 Hz, 1H), 2.30 (dt, *J* = 13.8, 7.3 Hz, 1H), 1.92 (dq, *J* = 14.1, 7.3 Hz, 1H), 0.98 (t, *J* = 7.3 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ –114.9 (tt, *J* = 8.5, 5.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 162.1 (d, $J_{C–F}$ = 246.2 Hz), 136.0, 134.8 (d, $J_{C–F}$ = 3.3 Hz), 130.3, 129.4 (d, $J_{C–F}$ = 8.0 Hz), 125.3, 124.7, 123.9, 120.9, 117.0, 116.0 (d, $J_{C–F}$ = 21.5 Hz), 109.3, 52.8, 27.9, 12.2; IR (Neat Film, NaCl) 3074, 2967, 2934, 2873, 1702, 1603, 1508, 1450, 1384, 1354, 1327, 1301, 1222, 1207, 1158, 818, 792, 752, 714 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{17}FNO$ $[M+H]^+$: 282.1289, found 282.1286.

General Procedure 3



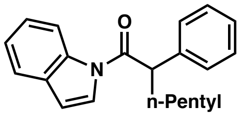
A flame-dried round bottom flask was charged with *i*-Pr_2NH (1.82 mL, 13.0 mmol, 1.3 equiv) and THF (15 mL). The solution was then cooled in a 0 ºC ice bath for 10 min and a 2.40 M solution of *n*-BuLi (5.0 mL, 12.0 mmol, 1.2 equiv) was added dropwise. After stirring for 15 min, the solution was cooled in a –78 ºC acetone/dry ice bath for 15 min, after which time a solution of methyl phenyl acetate (1.41 mL, 10.0 mmol, 1.0 equiv) in THF (29 mL) was added dropwise over 10 min. After stirring at –78 ºC for 1 h, the appropriate electrophile (1.5 equiv) was then added neat dropwise. The reaction mixture was allowed to slowly warm to 20 ºC and stirred for 16 h after which time the reaction was quenched with the slow addition of 30 mL of sat. aq. NH_4Cl. The mixture was then transferred to a separatory funnel and the layers were separated. The aqueous layer was extracted 3 x 20 mL EtOAc and the combined organics were dried over Na_2SO_4, filtered, and concentrated.

The crude material was then transferred to a round bottom flask and dissolved in THF (28 mL) and H_2O (20 mL). To the solution was then added LiOH (479.0 mg, 20.0 mmol, 2.0 equiv) and the resulting reaction mixture was stirred at 20 ºC for 16 h. The mixture was then transferred to a separatory funnel and washed with 2 x 5 mL Et_2O. The aqueous layer was then slowly acidified to pH 1 with 2.0 N HCl and extracted 2 x 10 mL Et_2O. The combined organics were dried over Na_2SO_4, filtered, and concentrated. The crude acid was used in the next step without further purification.

To an oven-dried flask containing α-aryl carboxylic acid (5.0 mmol, 1.0 equiv) was added $SOCl_2$ neat (620 µL, 1.7 equiv) and the resulting mixture stirred at 25 °C for 20 min then 70 °C for 2 h (note: effluent gas flow is bubbled through a glass tube packed with powdered NaOH). The reaction was then concentrated in vacuo to afford the crude acid chloride, which was used in the next step without further purification.

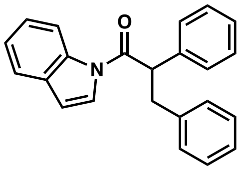
A separate flame-dried flask containing freshly distilled indoline (4.20 mmol, 1.0 equiv), Et_3N (1.17 mL, 8.40 mmol, 2.0 equiv), and DMAP (25.7 mg, 0.21 mmol, 0.05 equiv) in CH_2Cl_2 (42 mL) was cooled to –10 °C in an acetone/ice bath and the crude acid chloride (5.0 mmol, 1.2 equiv) dissolved in CH_2Cl_2 (21 mL) was added dropwise via cannula transfer. The mixture was stirred at –10 °C for 15 min then warmed to 23 ºC and stirred for 18 h. The reaction mixture was quenched with saturated $NaHCO_3$ (20 mL) and transferred to a separatory funnel. The layers were separated and the aqueous layer was extracted twice with CH_2Cl_2 (20 mL). The combined organics were washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated to afford the crude amide which was used in the next step without further purification.

The crude amide prepared above was transferred to a round bottom flask affixed with a reflux condenser. Dry toluene (42 mL) and DDQ (2,3-Dichloro-5,6-dicyano-1,4-benzoquinone) (1.14 g, 5.0 mmol, 1.2 equiv) were then added and the resulting dark red reaction solution was heated to reflux for 16 h. The crude reaction mixture was then filtered through a pad of celite with toluene, concentrated, and purified via flash column chromatography to afford the desired acyl indole.



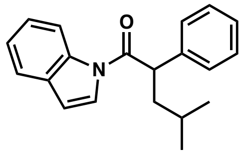
1-(1*H*-indol-1-yl)-2-phenylheptan-1-one (SI6)

Prepared according to General Procedure 3 with *n*-pentyl iodide (1.96 mL, 15.0 mmol, 1.5 equiv). Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a colorless oil (319.5 mg, 25% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.54–7.48 (m, 2H), 7.39–7.30 (m, 5H), 7.30–7.21 (m, 2H), 6.54 (dd, *J* = 3.8, 0.8 Hz, 1H), 4.25 (t, *J* = 7.2 Hz, 1H), 2.34–2.25 (m, 1H), 1.90 (tdd, *J* = 12.9, 8.5, 5.7 Hz, 1H), 1.46–1.25 (m, 6H), 0.91–0.84 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 139.4, 136.0, 130.3, 129.2, 127.7, 127.5, 125.2, 124.8, 123.8, 120.7, 117.0, 109.1, 52.1, 34.7, 31.8, 27.4, 22.6, 14.1; IR (Neat Film, NaCl) 3063, 3029, 2954, 2928, 2858, 1704, 1602, 1584, 1539, 1451, 1384, 1353, 1311, 1207, 1154, 1102, 941, 919, 880, 766, 749, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{24}NO$ $[M+H]^+$: 306.1846, found 306.1846.



1-(1*H*-indol-1-yl)-2,3-diphenylpropan-1-one (SI7)

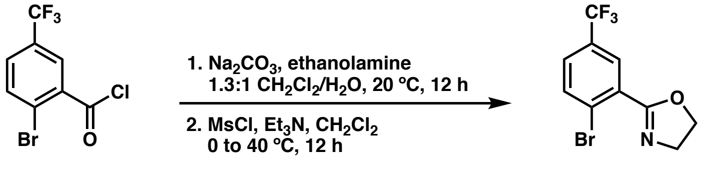
Prepared according to General Procedure 3 with BnBr (1.78 mL, 15.0 mmol, 1.5 equiv). Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (830.7 mg, 61% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.48 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.39 (d, *J* = 3.8 Hz, 1H), 7.34 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 7.32–7.27 (m, 4H), 7.26–7.10 (m, 7H), 6.48 (dd, *J* = 3.9, 0.7 Hz, 1H), 4.51 (t, *J* = 7.2 Hz, 1H), 3.67 (dd, *J* = 13.7, 7.6 Hz, 1H), 3.14 (dd, *J* = 13.8, 6.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 139.1, 138.7, 136.0, 130.3, 129.3, 129.2, 128.5, 127.8, 127.7, 126.6, 125.3, 124.8, 123.9, 120.8, 117.0, 109.3, 54.4, 40.8; IR (Neat Film, NaCl) 3155, 3062, 3029, 2927, 1950, 1805, 1698, 1601, 1585, 1539, 1495, 1472, 1453, 1385, 1354, 1319, 1300, 1221, 1207, 1108, 1074, 911, 898, 766, 749, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{20}NO$ [M+H]$^+$: 326.1539, found 326.1536.



1-(1*H*-indol-1-yl)-4-methyl-2-phenylpentan-1-one (SI8)

Prepared according to General Procedure 3 with *i*-butyl iodide (1.73 mL, 15.0 mmol, 1.5 equiv). Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a white solid (1.2177 g, 99% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 3.8 Hz, 1H), 7.52–7.50 (m, 1H), 7.39–7.29 (m, 5H), 7.27–7.22 (m, 2H), 6.55 (dd, *J* = 3.8, 0.7 Hz, 1H), 4.37 (t, *J* = 7.3 Hz, 1H), 2.22 (dt, *J* = 13.6 Hz, 7.4 Hz, 1H), 1.79 (dt, *J* = 13.7, 6.9 Hz, 1H), 1.61 (dp, *J* = 13.5, 6.8 Hz, 1H), 0.97 (dd, *J* = 27.5, 6.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 139.5, 136.1, 130.4, 129.3, 127.8, 127.5, 125.3, 124.8, 123.9, 120.9, 117.1, 109.3, 49.8, 43.8, 25.9, 22.9, 22.7; IR (Neat Film, NaCl) 3386, 3154, 3063, 3029, 2956, 2868, 1703, 1602, 1585 1538, 1493, 1471, 1451, 1385, 1344, 1332, 1308, 1295, 1222, 1207, 1103, 1084, 1018, 943, 886, 766, 748, 670 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}NO$ [M+H]$^+$: 292.1696, found 292.1696.

Ligand Synthesis

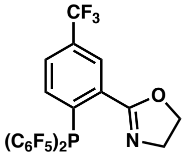


SI9

2-(2-bromo-5-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (SI9)

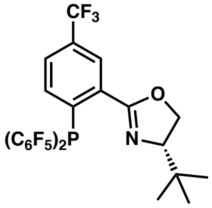
To a 500 mL round bottomed flask charged with a magnetic stirring bar and ethanolamine (1.35 mL, 22.31 mmol, 1.20 equiv) was added CH_2Cl_2 (62 mL). To the mixture was added a solution of Na_2CO_3 (5.91 g, 55.77 mmol, 3.0 equiv) in water (46 mL). The biphasic mixture is vigorously stirred at 20 ºC. To the mixture was added 2-bromo-5-(trifluoromethyl)benzoyl chloride[2] (5.34 g, 18.59 mmol, 1.00 equiv) dropwise over 10 min. The reaction mixture was vigorously stirred at 20 ºC for 14 h. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (4 x 50 mL). The combined organic layers were washed with brine, dried over sodium sulfate, and concentrated to afford an amorphous white solid which was used in the next step without further purification.

To a 250 mL round bottomed flask charged with a stir bar and a reflux condenser was added the crude alcohol prepared above. To the flask was added CH_2Cl_2 (120 mL) and Et_3N (7.3 mL, 52.2 mmol, 2.8 equiv). The flask was cooled in a 0 ºC ice/water bath for 10 min, then MsCl (2.02 mL, 26.1 mmol, 1.4 equiv) was added dropwise over 2 min. The reaction was stirred at 0 ºC for 20 min then heated in an oil bath at 40 ºC for 8 h. The flask was then cooled to 20 ºC and the reaction mixture diluted with CH_2Cl_2 (50 mL) and transferred to a separatory funnel. The organic layer was washed with water (2 x 50 mL) and brine (50 mL), then dried over Na_2SO_4, filtered, and concentrated to an orange oil. Purification by column chromatography (15 to 25% EtOAc/hexanes) provided the product as a colorless oil (3.1182 g, 10.6 mmol, 57% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J = 2.3 Hz, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.53 (dd, J = 8.4, 2.2 Hz, 1H), 4.49 (t, J = 9.6 Hz, 2H), 4.15 (t, J = 9.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, J = 3.7 Hz), 134.8, 130.5, 130.0 (q, $J_{C–F}$ = 35.3, 33.6 Hz), 128.3 (d, $J_{C–F}$ = 37.9 Hz), 126.0, 123.7 (q, $J_{C–F}$ = 272.4 Hz), 68.0, 55.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.93; IR (Neat Film, NaCl) 2977, 1652, 1609, 1580, 1474, 1426, 1403, 1337, 1312, 1263, 1242, 1173, 1133, 1077, 1027, 976, 947, 908, 831, 736, 712 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{10}H_8BrF_3NO$ [M+H]$^+$: 293.9736, found 293.9740.



2-(2-(bis(perfluorophenyl)phosphaneyl)-5-(trifluoromethyl)phenyl)-4,5-dihydrooxazole (F_{13}-glyPHOX)

To a 100 mL Schlenk tube charged with a stir bar was added **SI9** (320.5 mg, 1.09 mmol, 1.0 equiv) and Et_2O (22 mL). The resulting solution was cooled to –78 ºC in an acetone/dry ice bath for 30 min, then a 1.26 M solution of *sec*-BuLi in hexanes (1.04 mL, 1.31 mmol, 1.2 equiv) was added dropwise over 5 min. The resulting dark red solution was stirred for 30 min at –78 ºC, then TMEDA (200 μL, 1.32 mmol, 1.21 equiv) was added. After stirring for 15 min at –78 ºC, a solution of $PCl(C_6F_5)_2$[3] (530.0 mg, 1.32 mmol, 1.21 equiv) in Et_2O (11 mL) was added dropwise, resulting in an immediate color change to light red. After 1 h at –78 ºC, the reaction mixture was warmed to 0 ºC and quenched with water (10 mL). The mixture was transferred to a separatory funnel and diluted with 5 mL brine before being separated. The aqueous layer was then extracted with Et_2O (2 x 10 mL) and the combined organic layers dried over Na_2SO_4, filtered, and concentrated to yield a yellow oil. Purification by column chromatography (3% Et_2O/hexanes) provided F_{13}-glyPHOX as an amorphous white solid (128.7 mg, 0.222 mmol, 20% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 4.6, 1.9 Hz, 1H), 7.65 (dt, *J* = 8.4, 1.1 Hz, 1H), 7.36 (dd, *J* = 8.4, 3.1 Hz, 1H), 4.45 (t, *J* = 9.6 Hz, 2H), 3.96 (t, *J* = 9.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.7 (d, *J* = 5.7 Hz), 149.5–145.9 (m), 144.2–140.8 (m), 139.2–136.0 (m), 137.4 (d, *J* = 28.6 Hz), 133.1, 131.9 (q, *J* = 33.6 Hz), 131.6 (d, *J* = 21.7 Hz), 127.1 (d, *J* = 4.0 Hz), 126.4 (d, *J* = 4.1 Hz), 123.5 (q, *J* = 272.6 Hz), 111.5 – 109.3 (m), 68.2, 55.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ –62.09 – –65.06 (m), –128.89 – –130.15 (m), –149.89 (tt, *J* = 20.8, 3.8 Hz), –160.33 (tt, *J* = 20.8, 5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ –55.11 (p, *J* = 36.4 Hz); IR (Neat Film, NaCl) 1656, 1517, 1475, 1366, 1338, 1318, 1289, 1252, 1179, 1134, 1083, 1041, 977, 949 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_8F_{13}NOP$ $[M+H]^+$: 580.0130, found 580.0138.



(*S*)-2-(2-(bis(perfluorophenyl)phosphaneyl)-5-(trifluoromethyl)phenyl)-4-(*tert*-butyl)-4,5-dihydrooxazole ((*S*)-F_{13}-glyPHOX)

To a 100 mL Schlenk tube charged with a stir bar was added (*S*)-2-(2-bromo-5-(trifluoromethyl)phenyl)-4-(*tert*-butyl)-4,5-dihydrooxazole[4] (289.2 mg, 0.826 mmol, 1.0 equiv) and Et_2O (16.5 mL). The resulting solution was cooled to –78 ºC in an acetone/dry ice bath for 30 min, then a 1.26 M solution of *sec*-BuLi in hexanes (794 μL, 1.00 mmol, 1.2 equiv) was added dropwise over 5 min. The resulting dark red solution was stirred for 30 min at –78 ºC, then TMEDA (150 μL, 1.00 mmol, 1.2 equiv) was added. After stirring for 15 min at –78 ºC, a solution of $PCl(C_6F_5)_2$[3] (400.0 mg, 1.00 mmol, 1.2 equiv) in Et_2O (8.3 mL) was added dropwise, resulting in an immediate color change to light red. After 1 h at –78 ºC, the reaction mixture was warmed to 0 ºC and quenched with water (10 mL). The mixture was transferred to a separatory funnel and diluted with 5 mL brine before being separated. The aqueous layer was then extracted with Et_2O (2 x 10 mL) and the combined organic layers dried over Na_2SO_4, filtered, and concentrated to yield a yellow oil. Purification by column chromatography (10% CH_2Cl_2/hexanes); ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 4.6, 1.9 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.31 (dd, *J* = 8.2, 3.0 Hz, 1H), 4.39 (dd, *J* = 10.2, 8.7 Hz, 1H), 4.22 (t, *J* = 8.7 Hz, 1H), 3.95 (dd, *J* = 10.1, 8.7 Hz, 1H), 0.77 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.5 (d, *J* = 5.4 Hz), 149.5 – 145.5 (m), 144.5 – 140.2 (m), 139.7 – 135.4 (m), 137.3 (d, *J* = 28.9 Hz), 133.0, 132.5 – 131.3 (m), 131.9, 127.1 (q, *J* = 3.6 Hz), 126.4 (q, *J* = 4.1 Hz), 123.6 (q, *J* = 272.6 Hz), 111.95 – 110.41 (m), 69.44, 33.63, 25.63; ^{19}F NMR (282 MHz, $CDCl_3$) δ –61.9 – –64.6 (m), –127.5 – –132.1 (m), –150.3 (dtt, *J* = 213.8, 20.6, 3.8 Hz), –158.50 – –162.90 (m); ^{31}P NMR (162 MHz, $CDCl_3$) δ –55.79 (p, *J* = 38.0 Hz); IR (Neat Film, NaCl) 2962, 1654, 1517, 1473, 1362, 1327, 1306, 1287, 1179, 1135, 1085, 978, 834 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{26}H_{16}F_{13}NOP$ $[M+H]^+$: 636.0756, found 636.0750.

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2. Tani, K.; Behenna, D. C.; McFadden, R. M.; Stoltz, B. M. *Org. Lett.* **2007**, *9*, 2529–2531.
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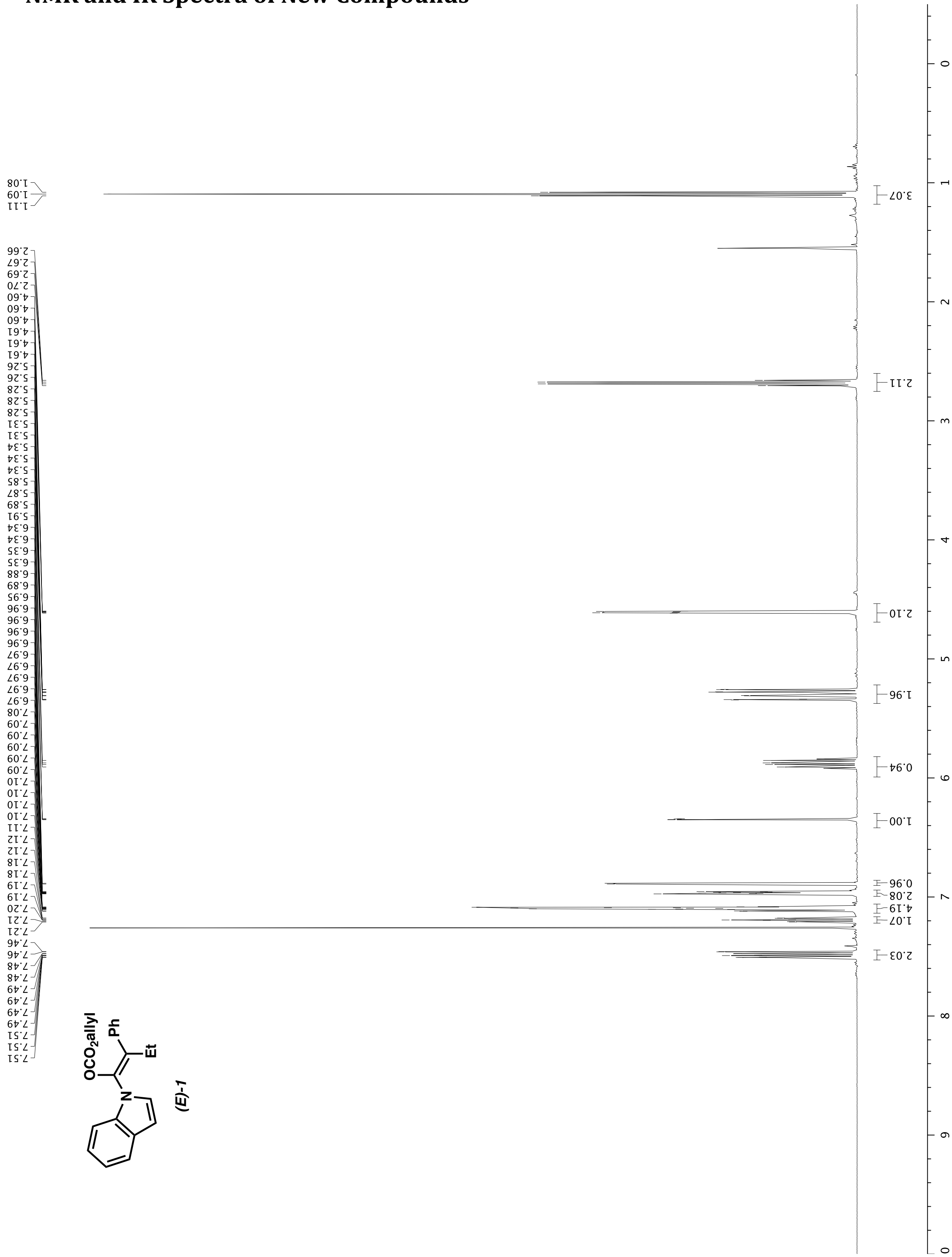
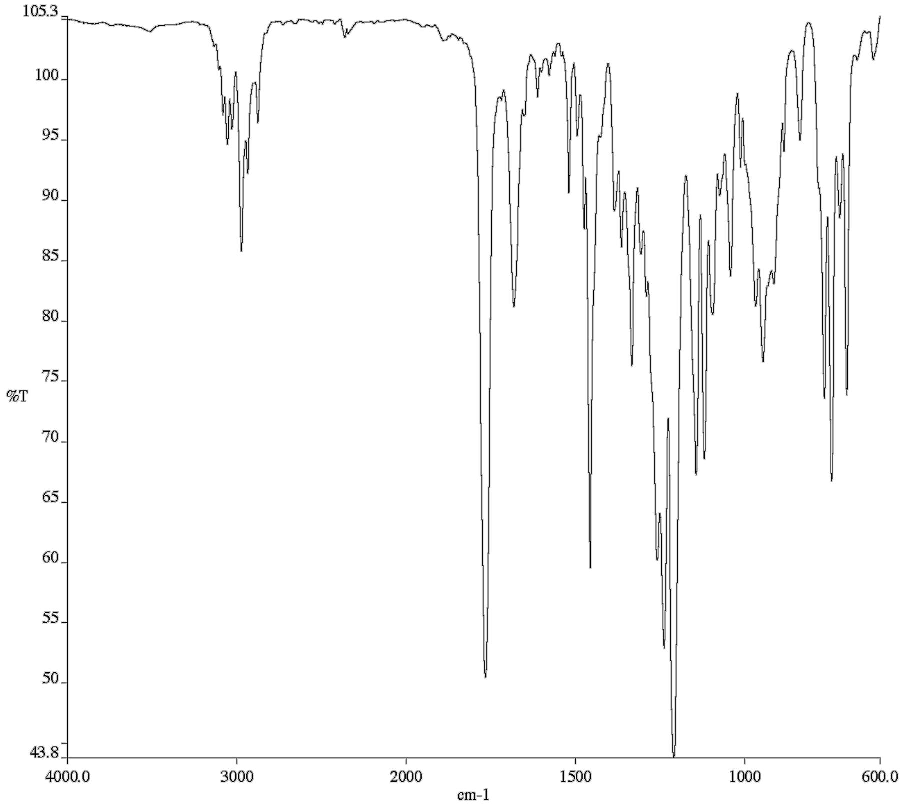
4. McDougal, N. T.; Streuff, J.; Mukherjee, H.; Virgil, S. C.; Stoltz, B. M. *Tetrahedron Lett.* **2010**, *51*, 5550–5554.

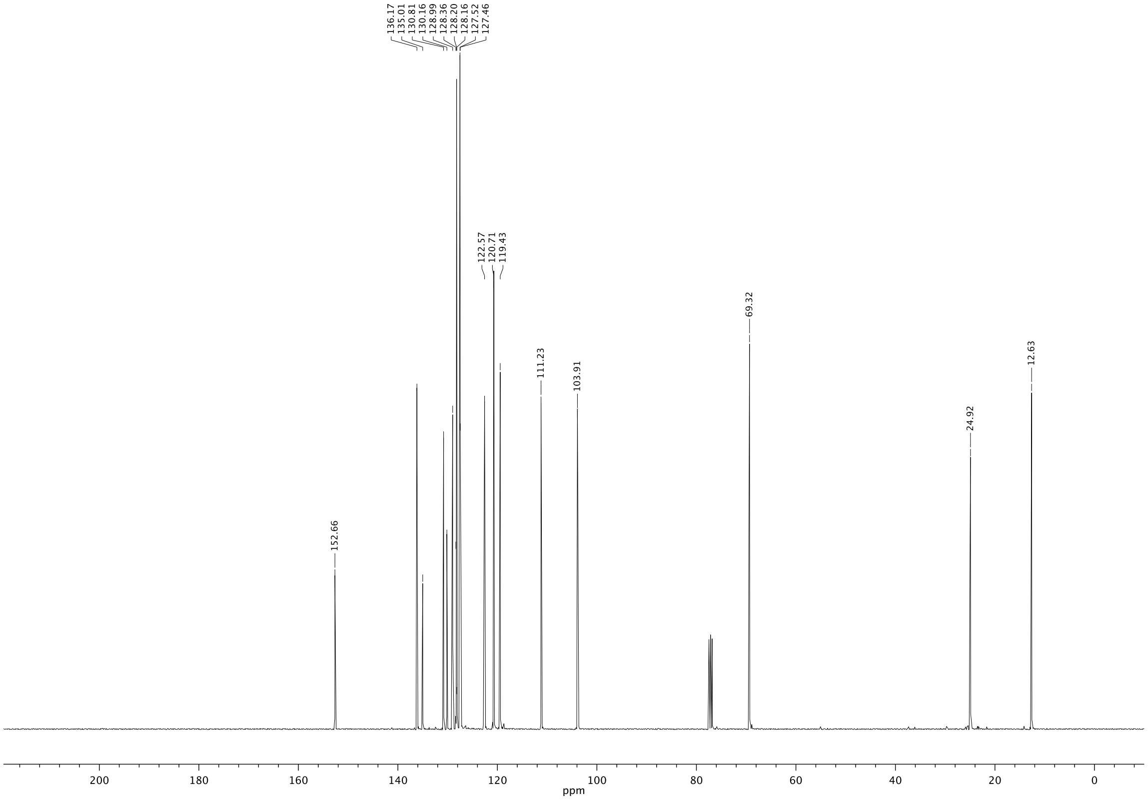
NMR and IR Spectra of New Compounds



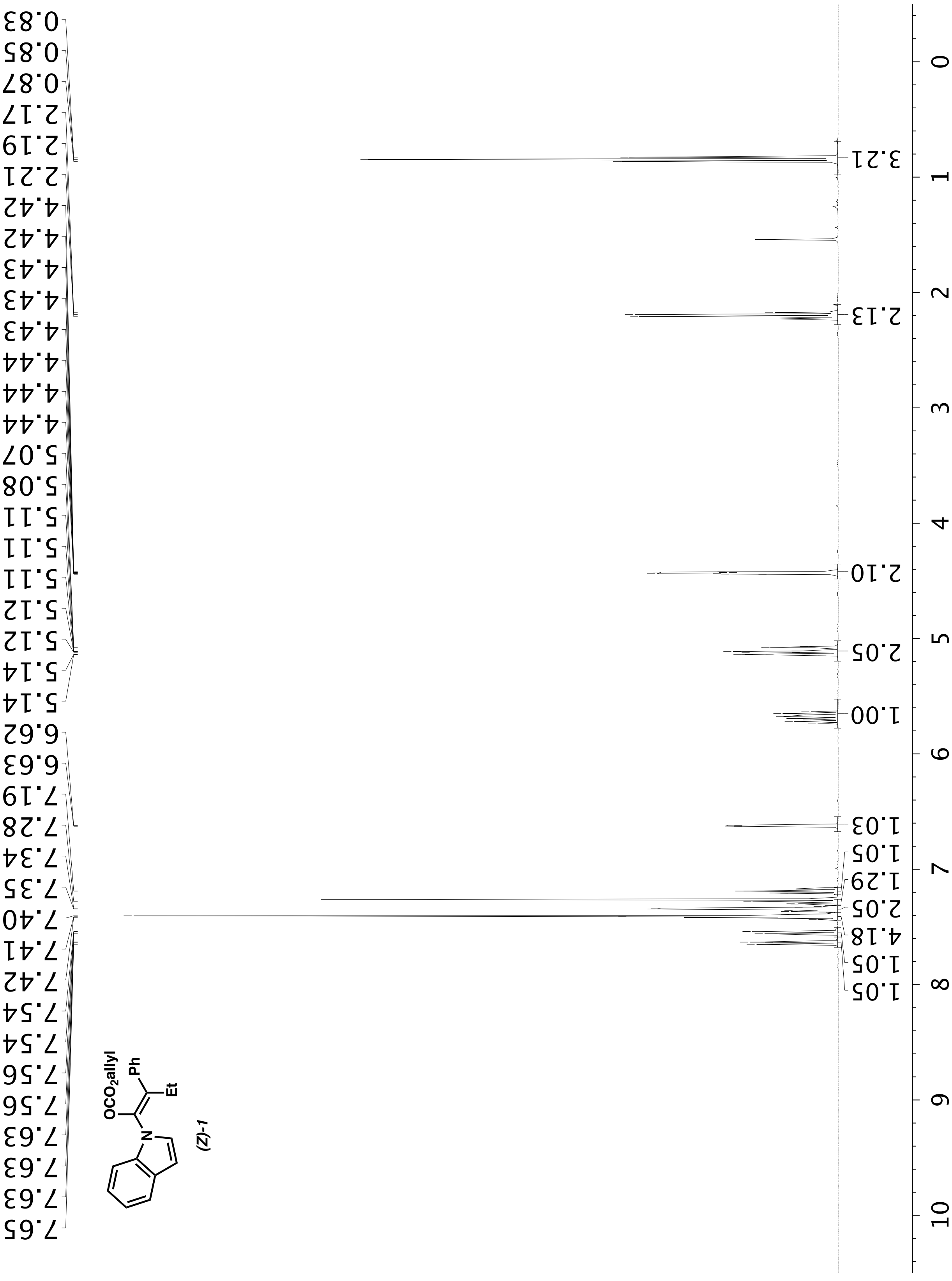
^{1}H NMR (500 MHz, CDCl$_3$) of compound **(*E*)-1**.



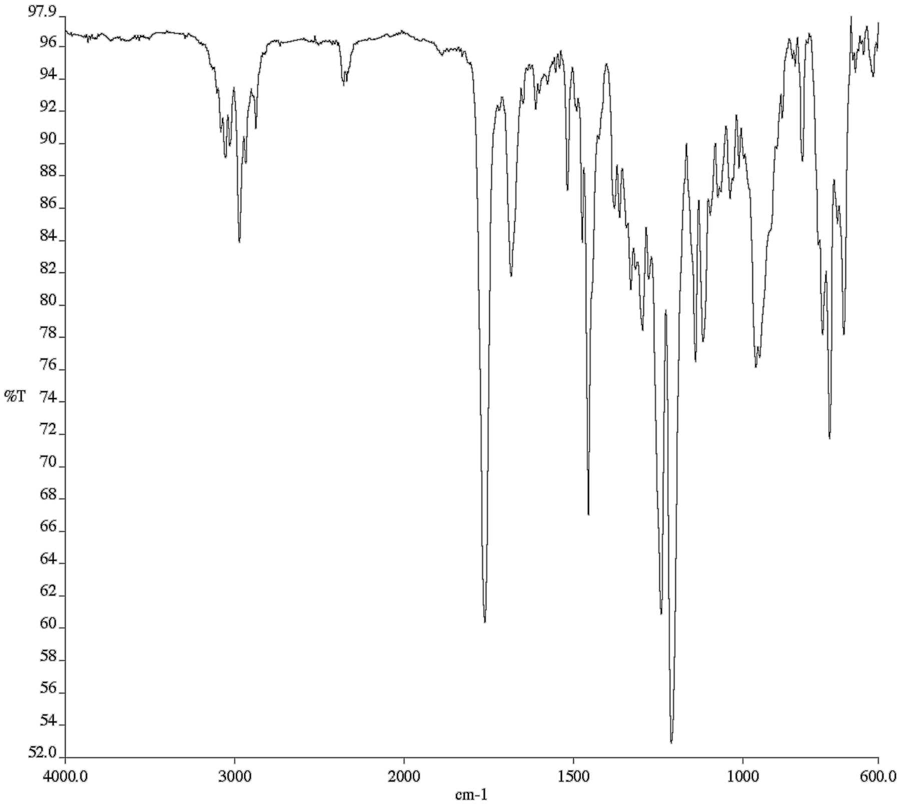
Infrared spectrum (Thin Film, NaCl) of compound **(*E*)-1**.



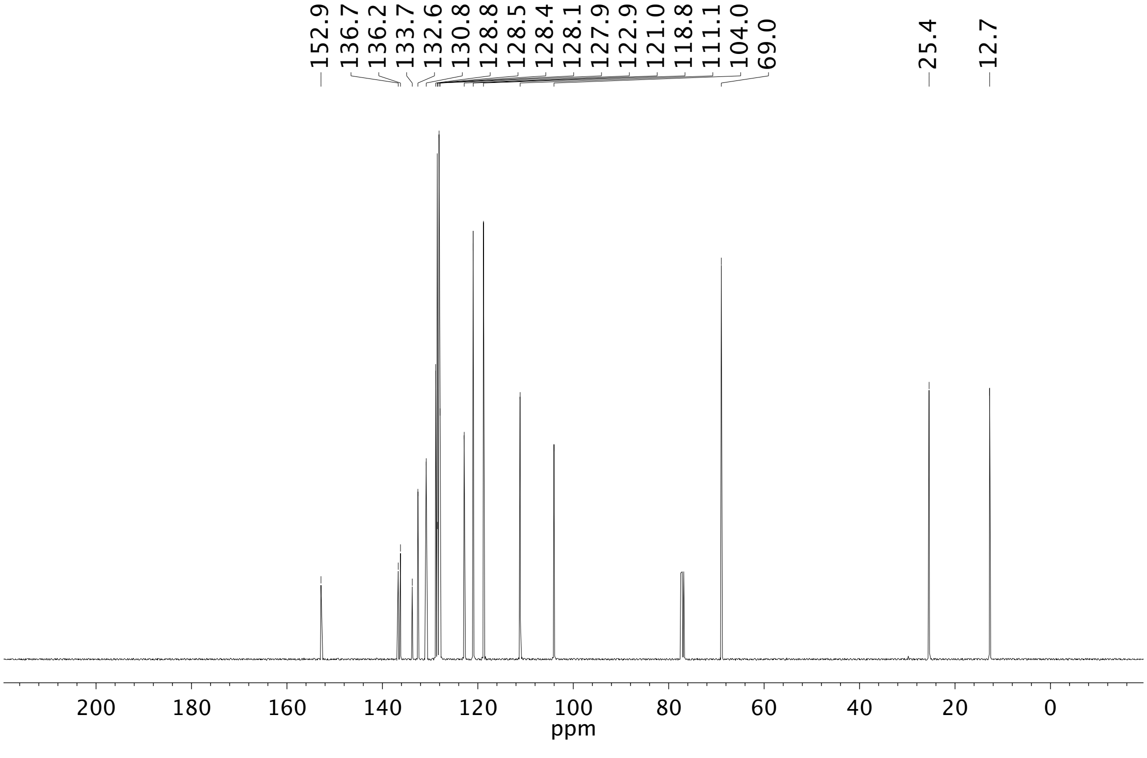
^{13}C NMR (100 MHz, CDCl$_3$) of compound **(*E*)-1**.



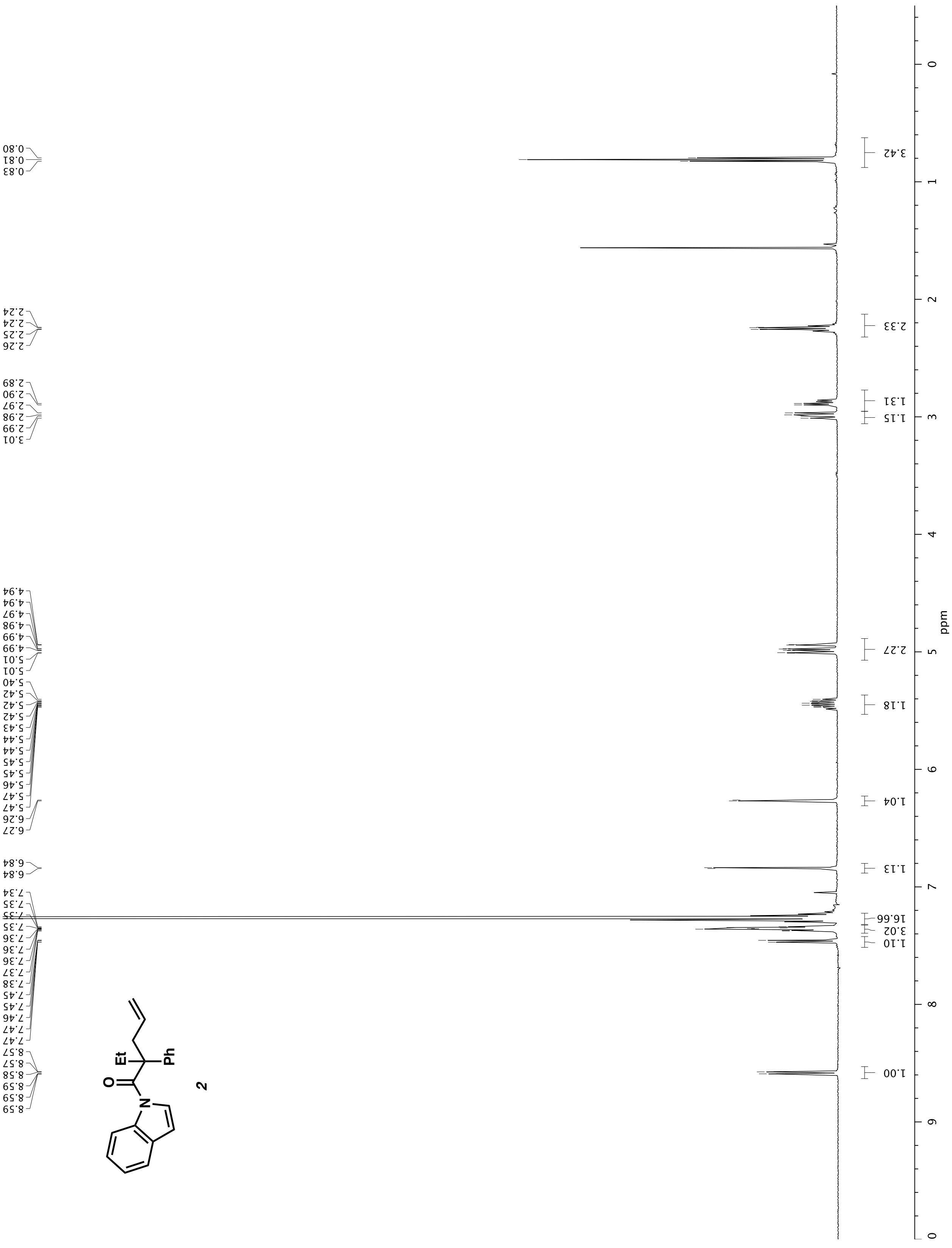
^{1}H NMR (400 MHz, CDCl$_3$) of compound **(*Z*)-1**.



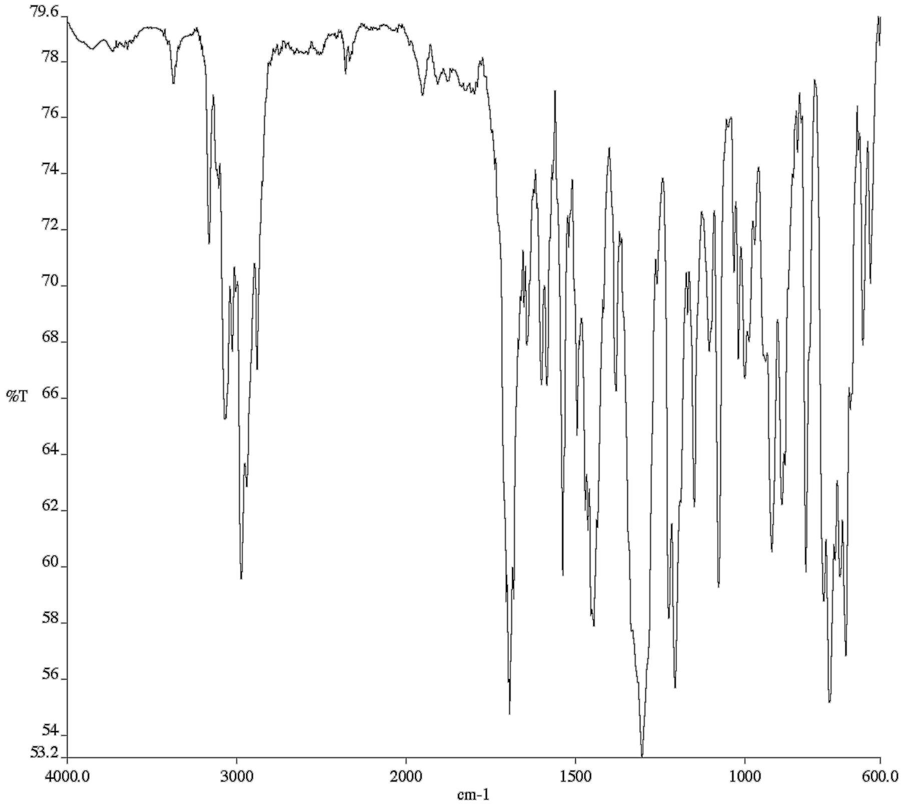
Infrared spectrum (Thin Film, NaCl) of compound **(*Z*)-1**.



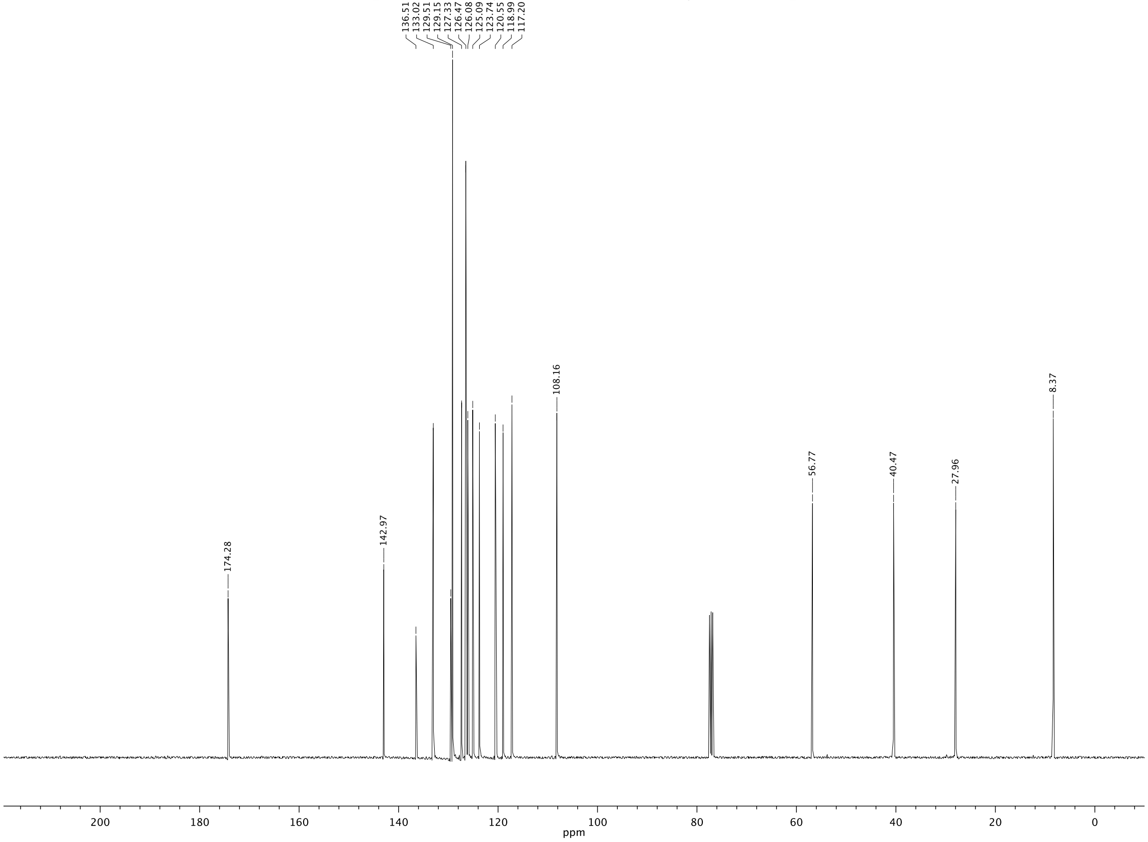
^{13}C NMR (100 MHz, CDCl$_3$) of compound **(*Z*)-1**.



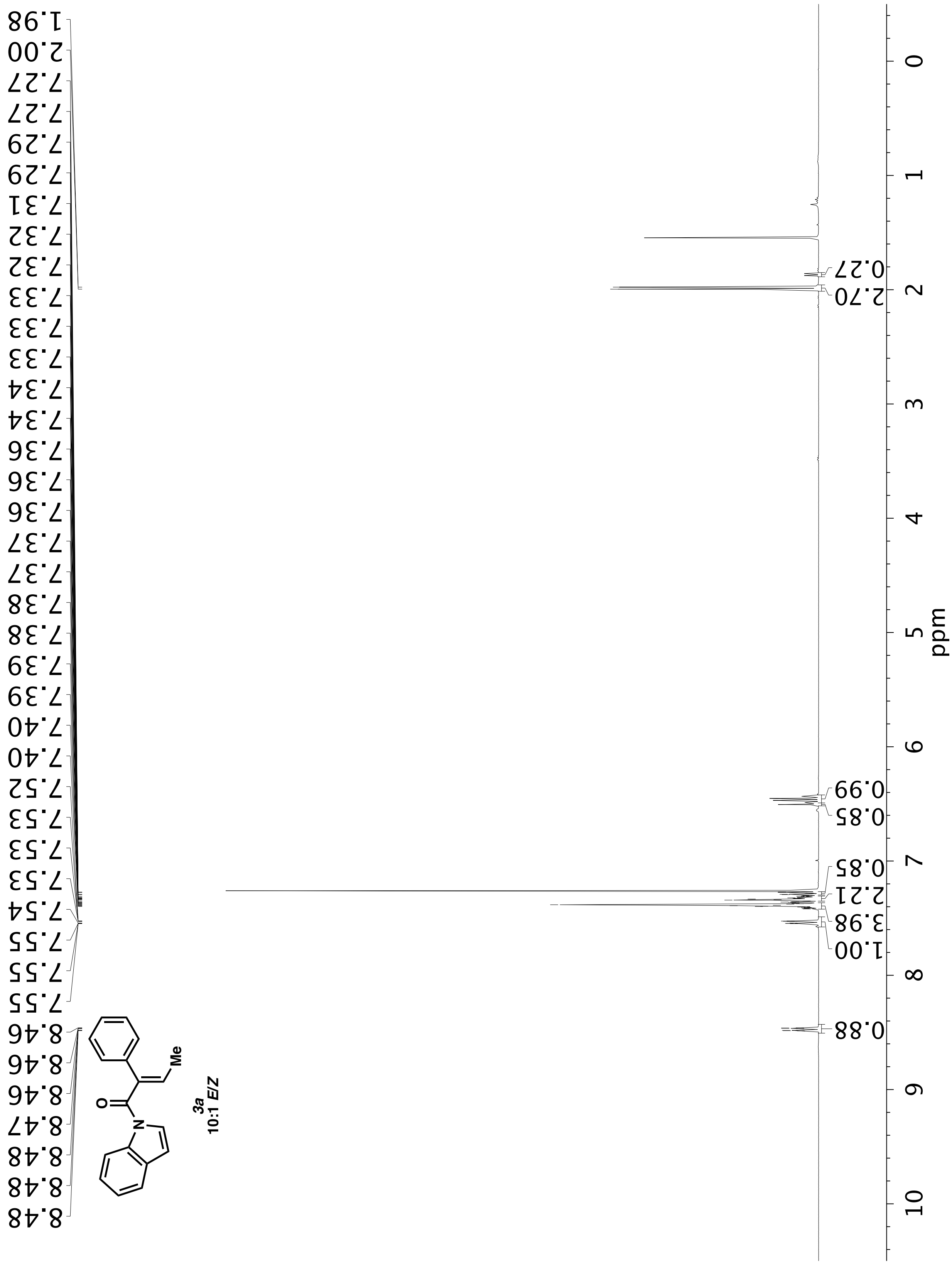
^{1}H NMR (400 MHz, CDCl$_3$) of compound **2.**



Infrared spectrum (Thin Film, NaCl) of compound **2**.

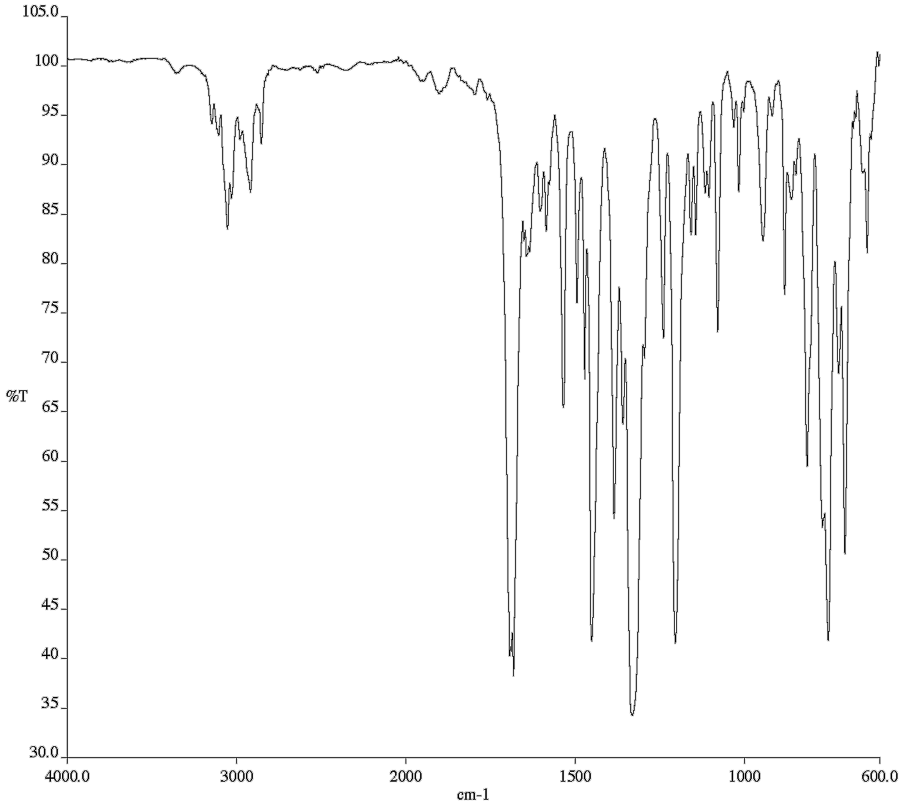


^{13}C NMR (100 MHz, $CDCl_3$) of compound **2**.

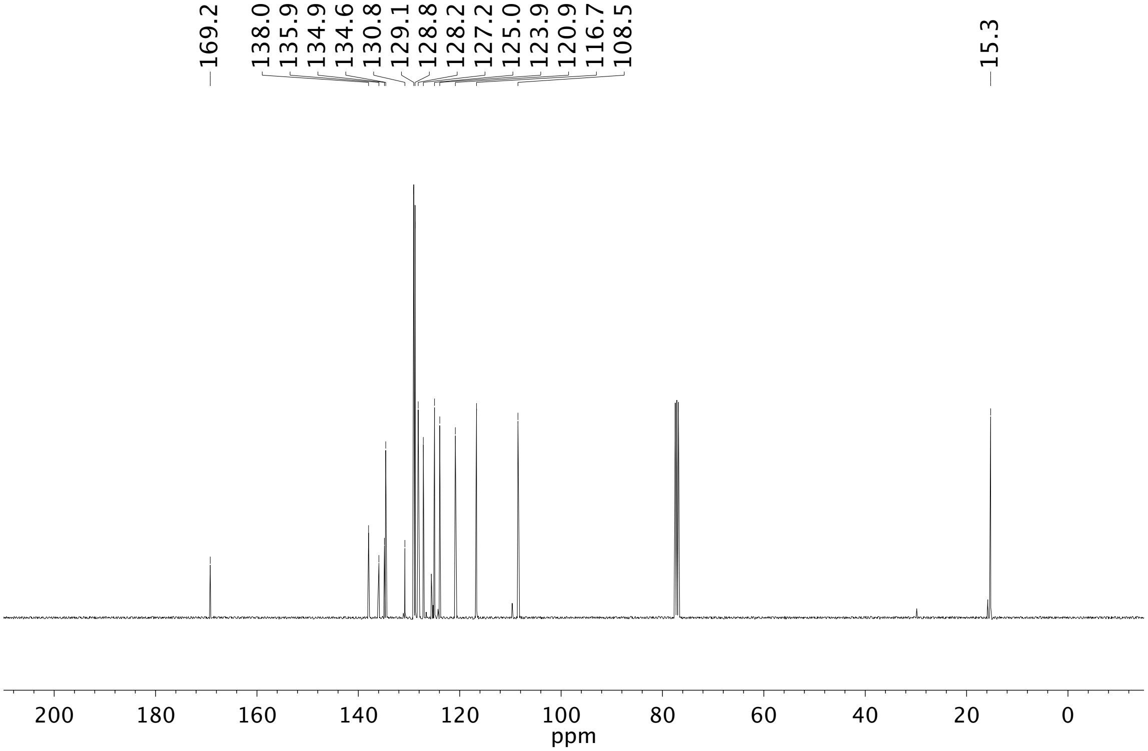


3a
10:1 *E*/*Z*

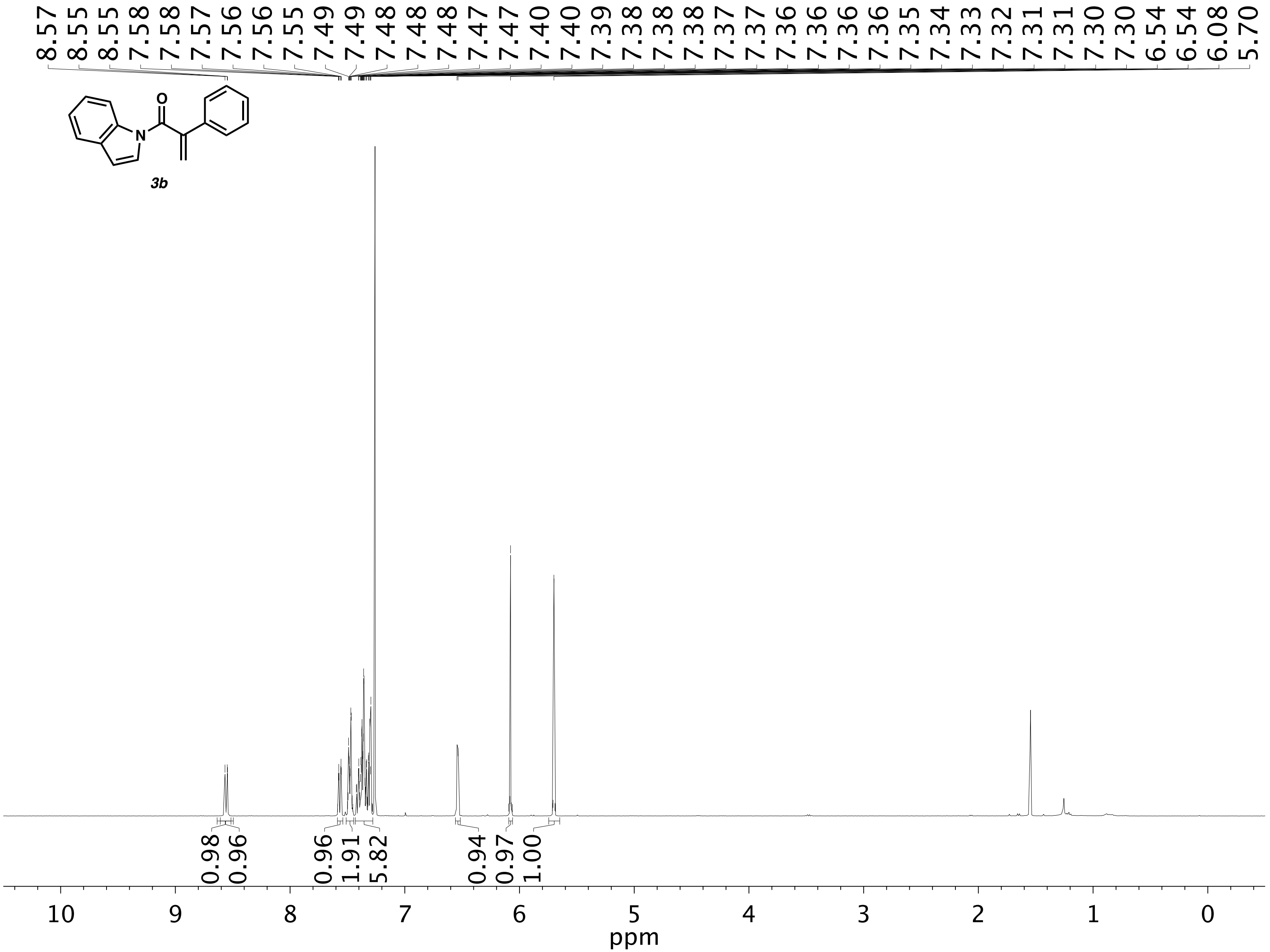
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3a.**



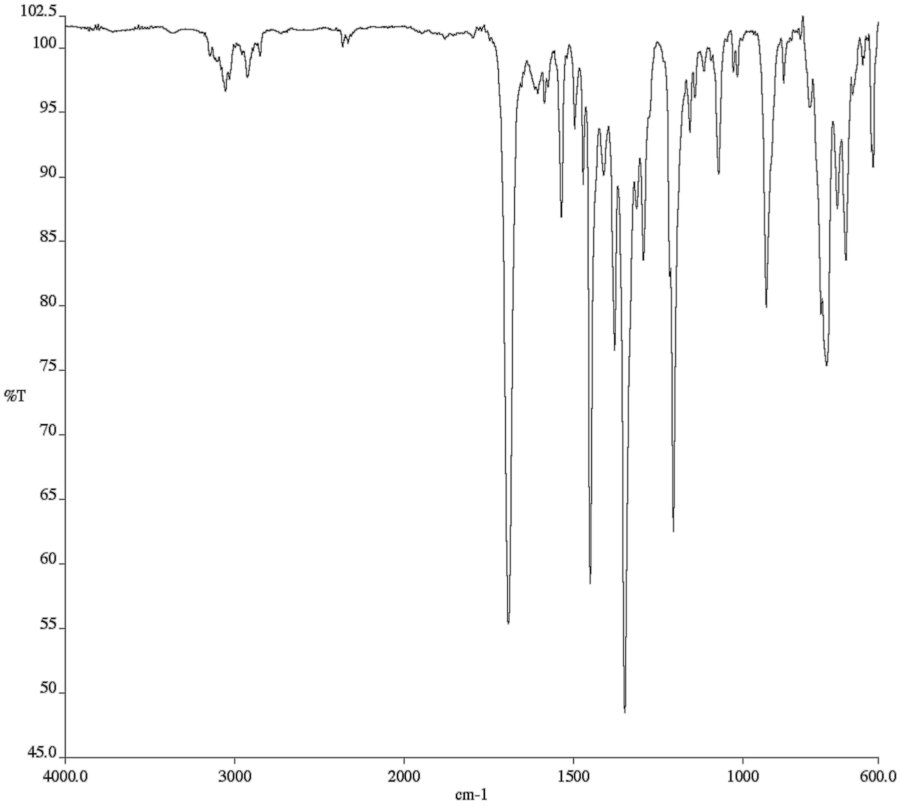
Infrared spectrum (Thin Film, NaCl) of compound **3a**.



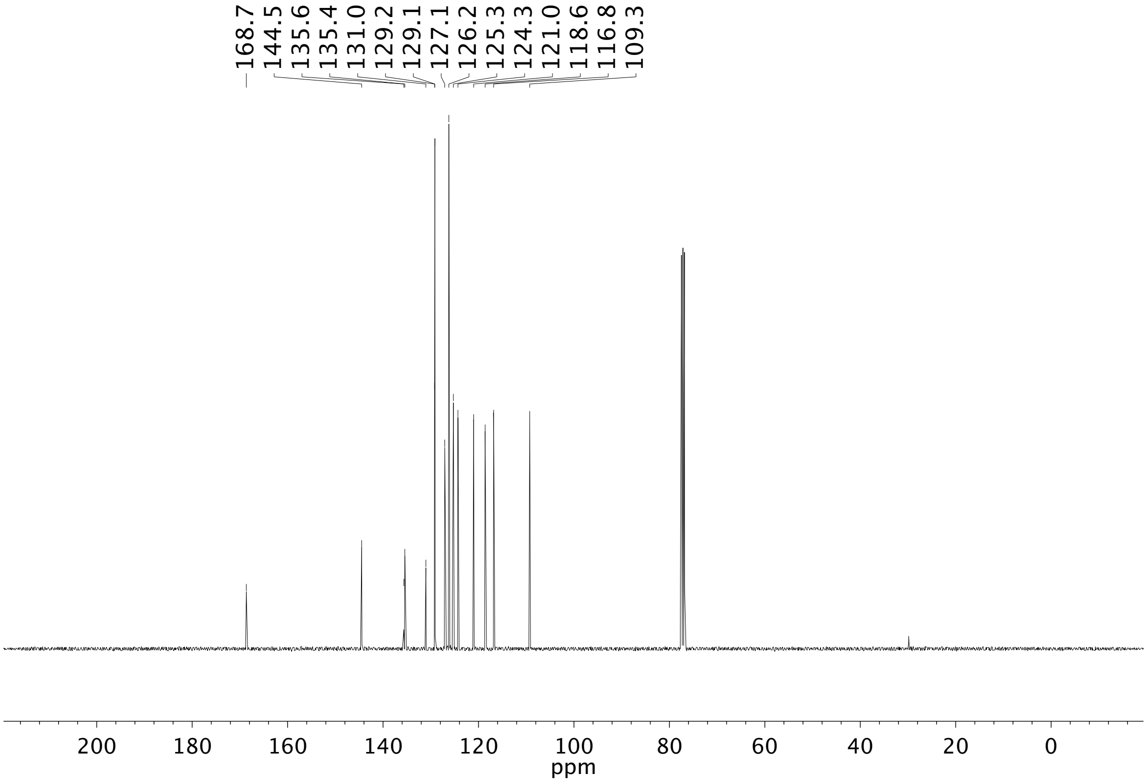
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**.



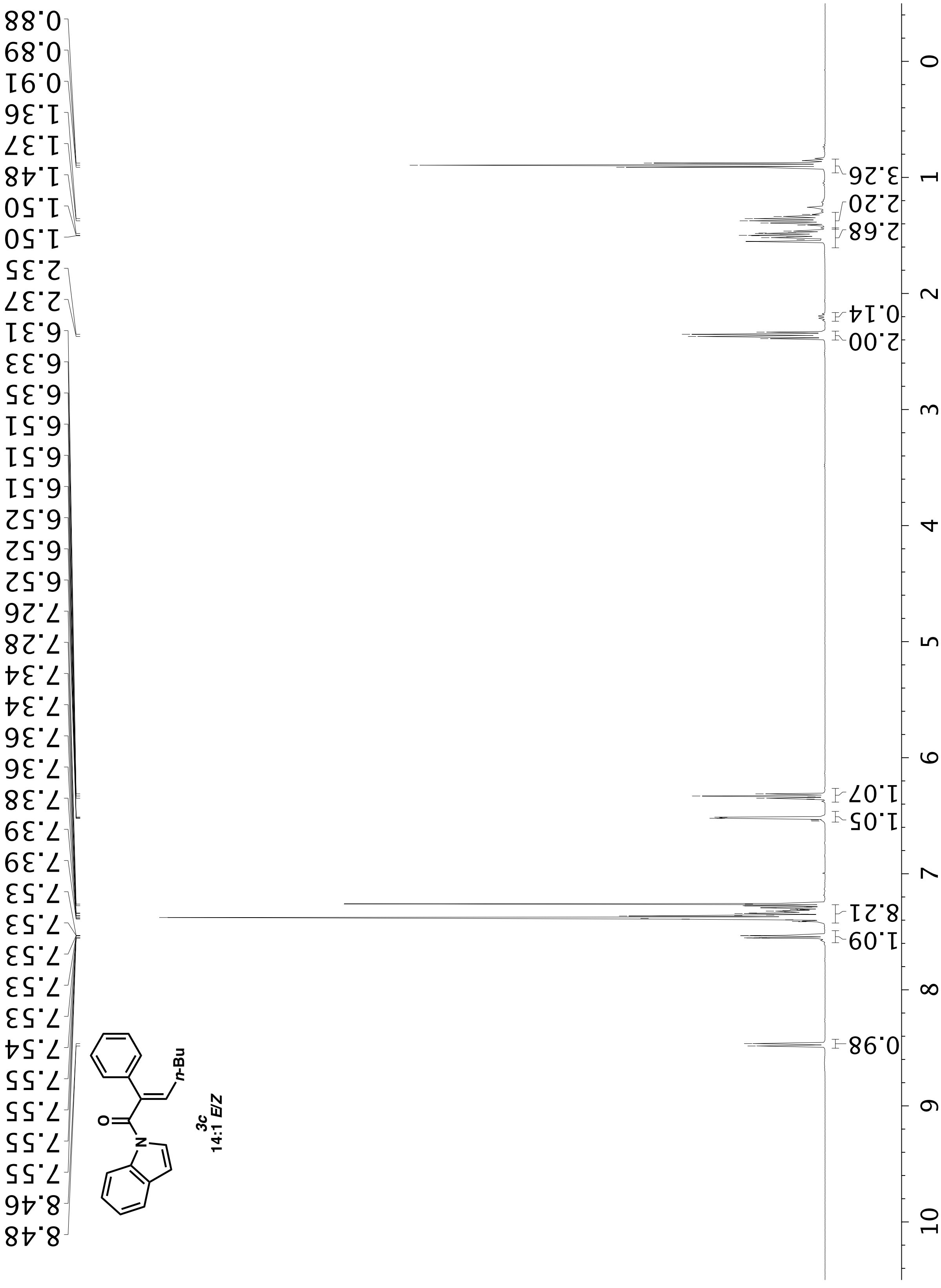
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b.**



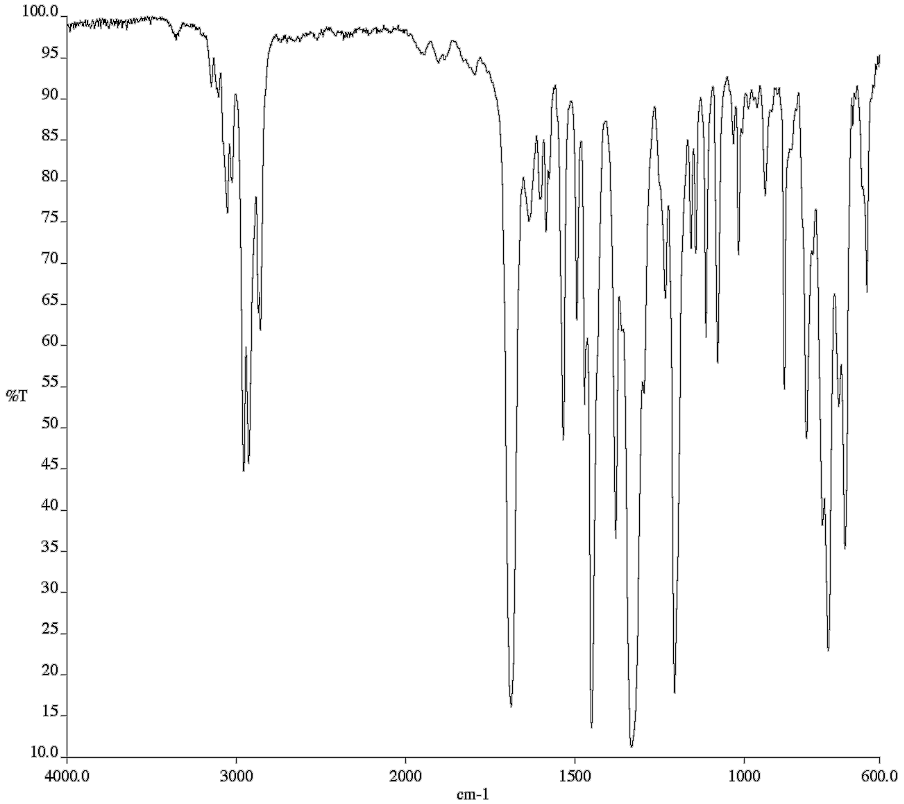
Infrared spectrum (Thin Film, NaCl) of compound **3b**.



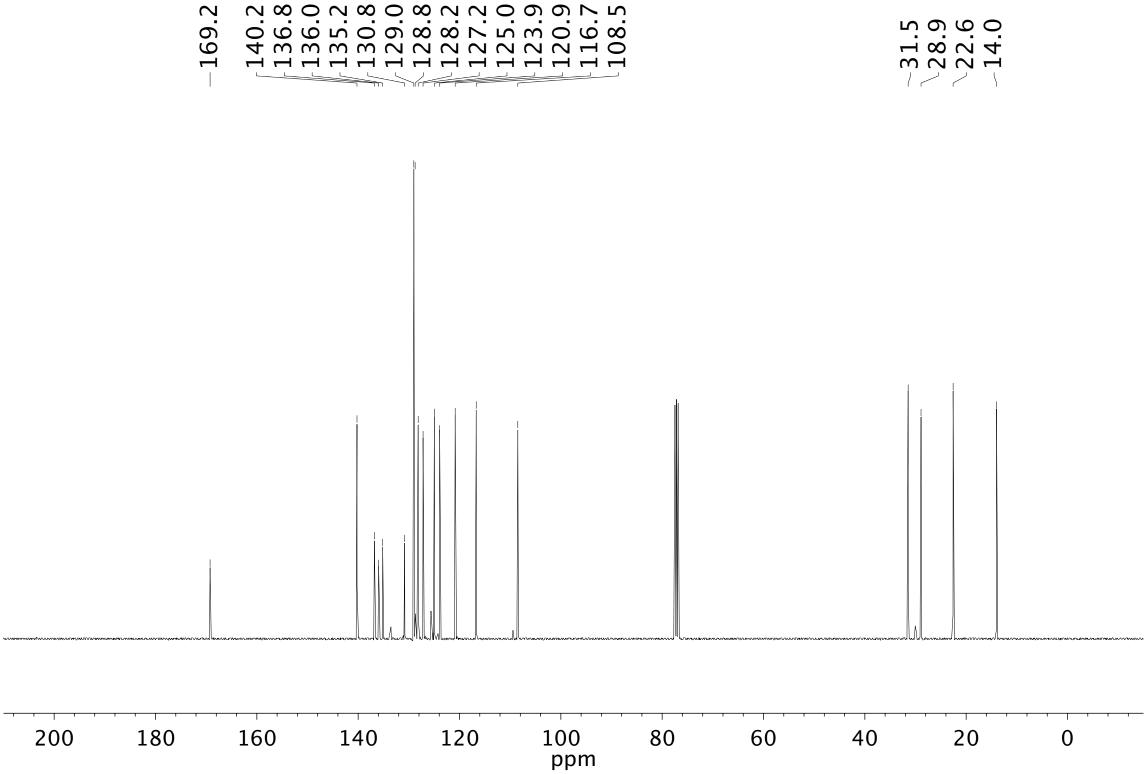
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3b**.



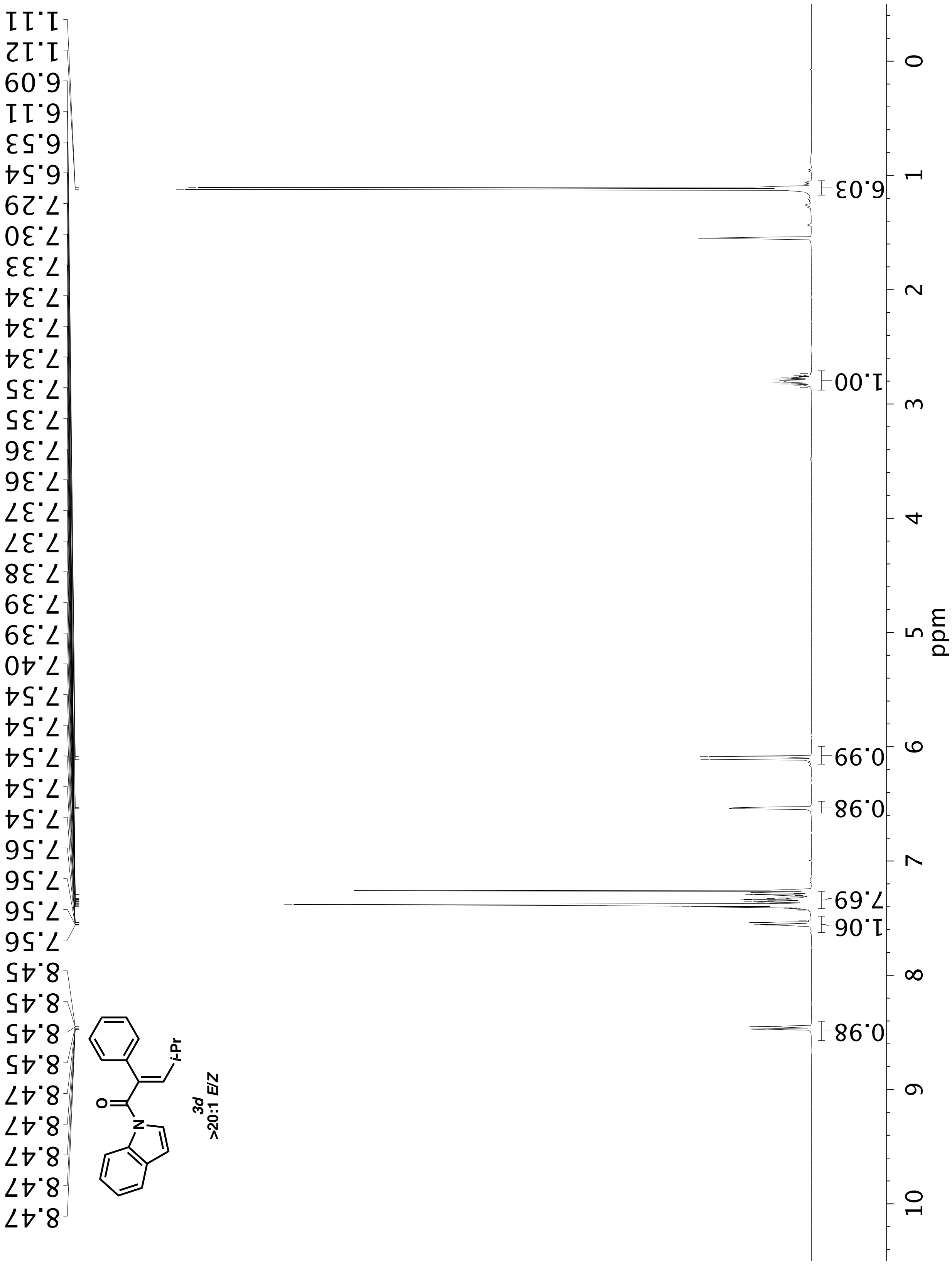
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3c.**



Infrared spectrum (Thin Film, NaCl) of compound **3c**.

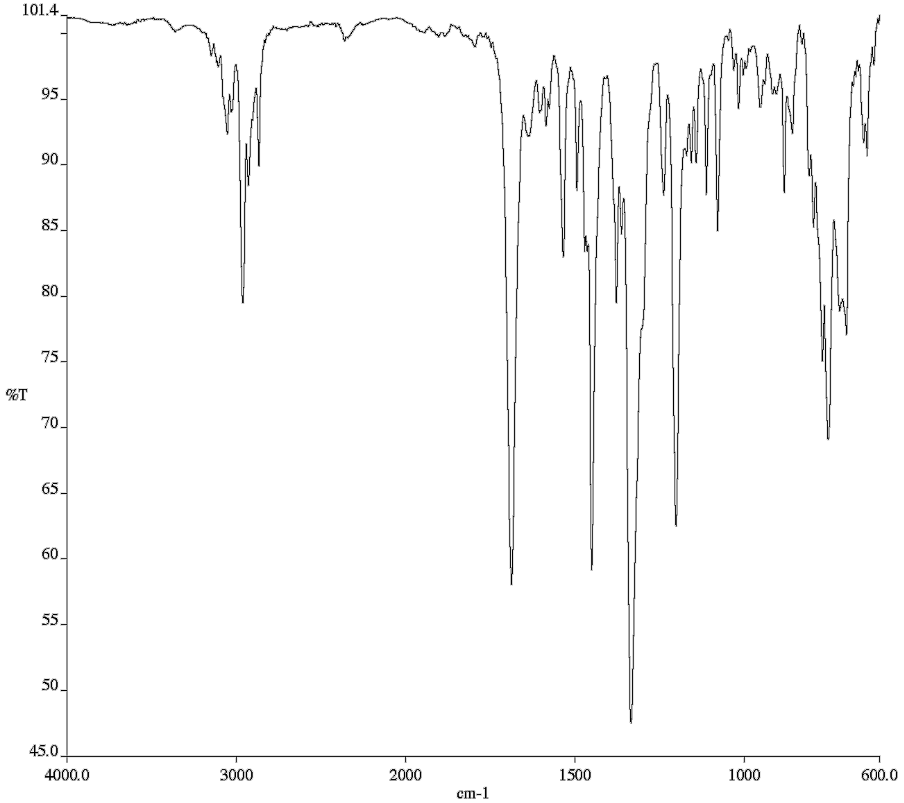


^{13}C NMR (100 MHz, CDCl$_3$) of compound **3c**.

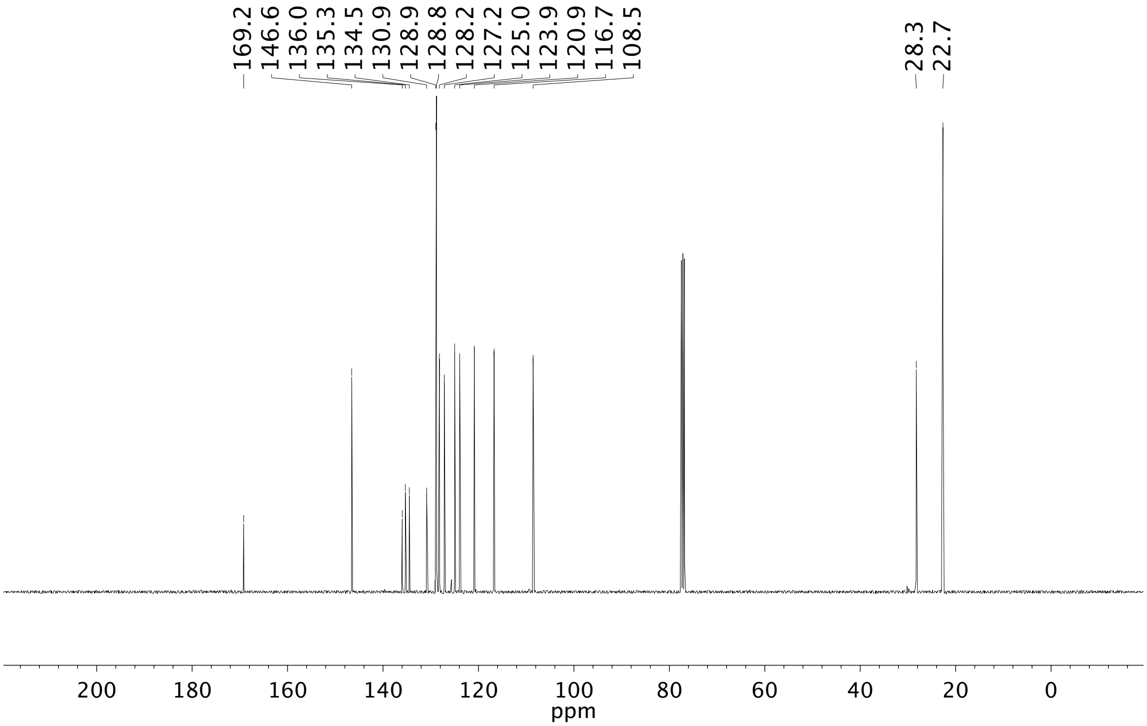


3d
>20:1 *E/Z*

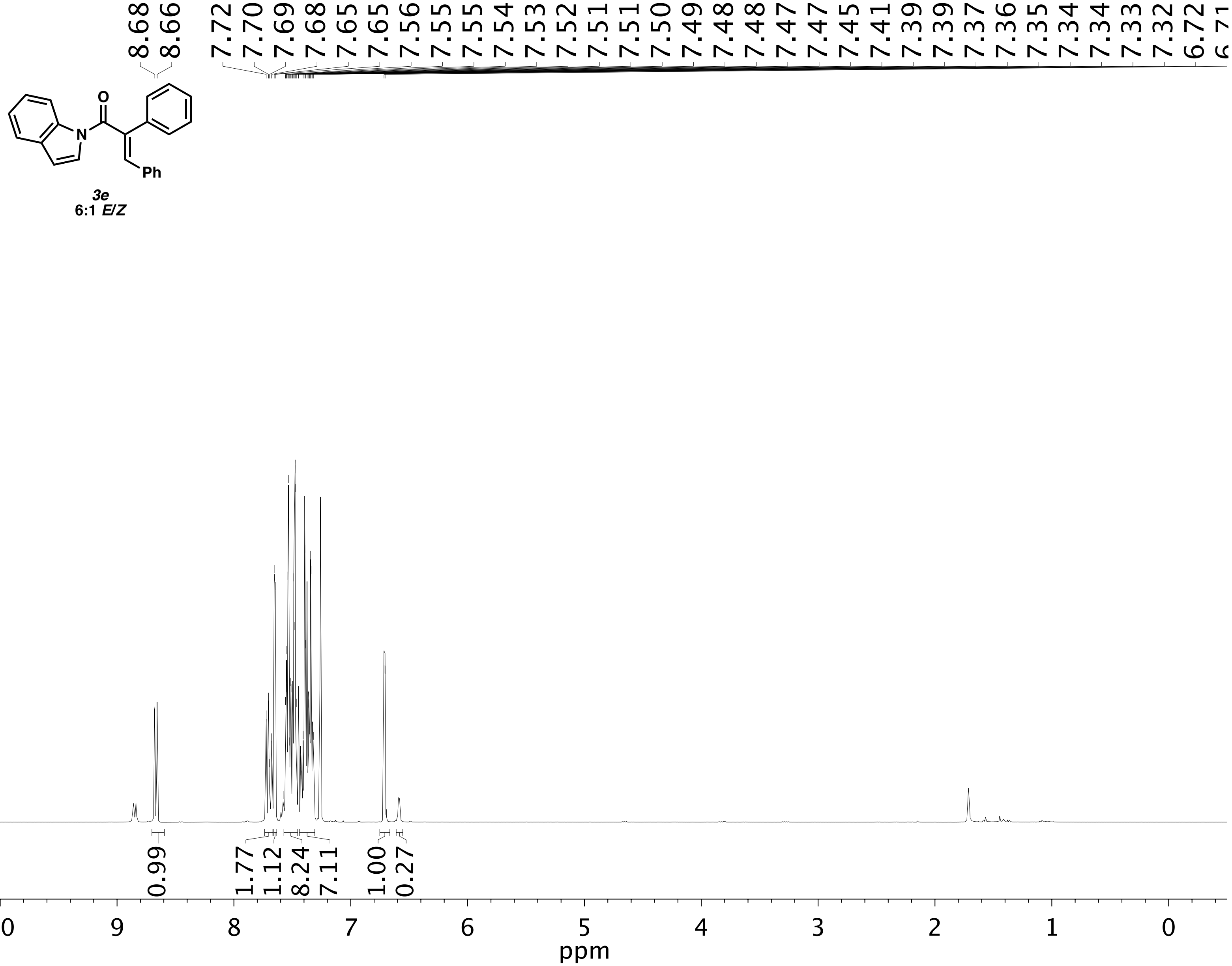
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3d.**



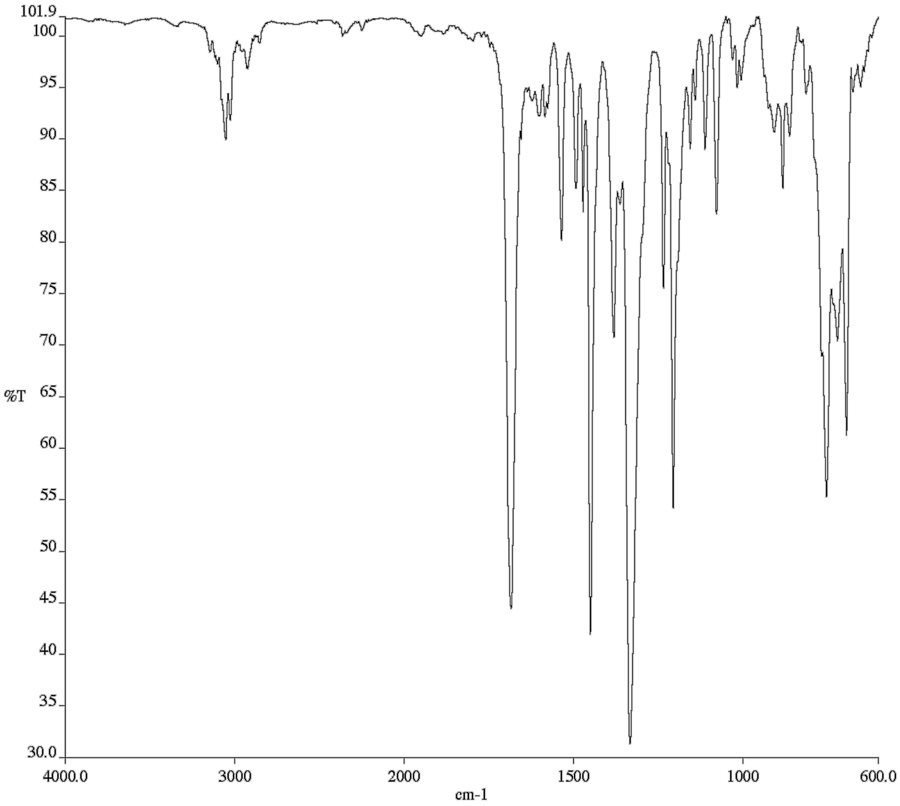
Infrared spectrum (Thin Film, NaCl) of compound **3d**.



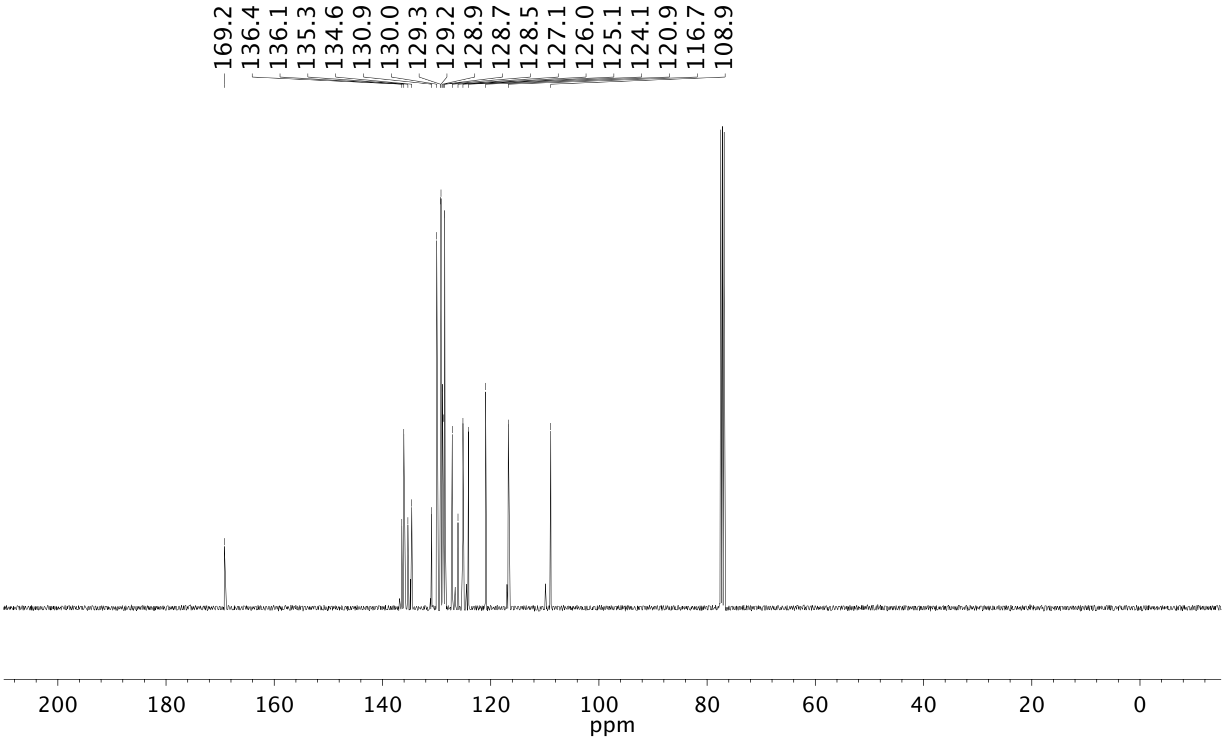
^{13}C NMR (100 MHz, CDCl$_3$) of compound **3d**.



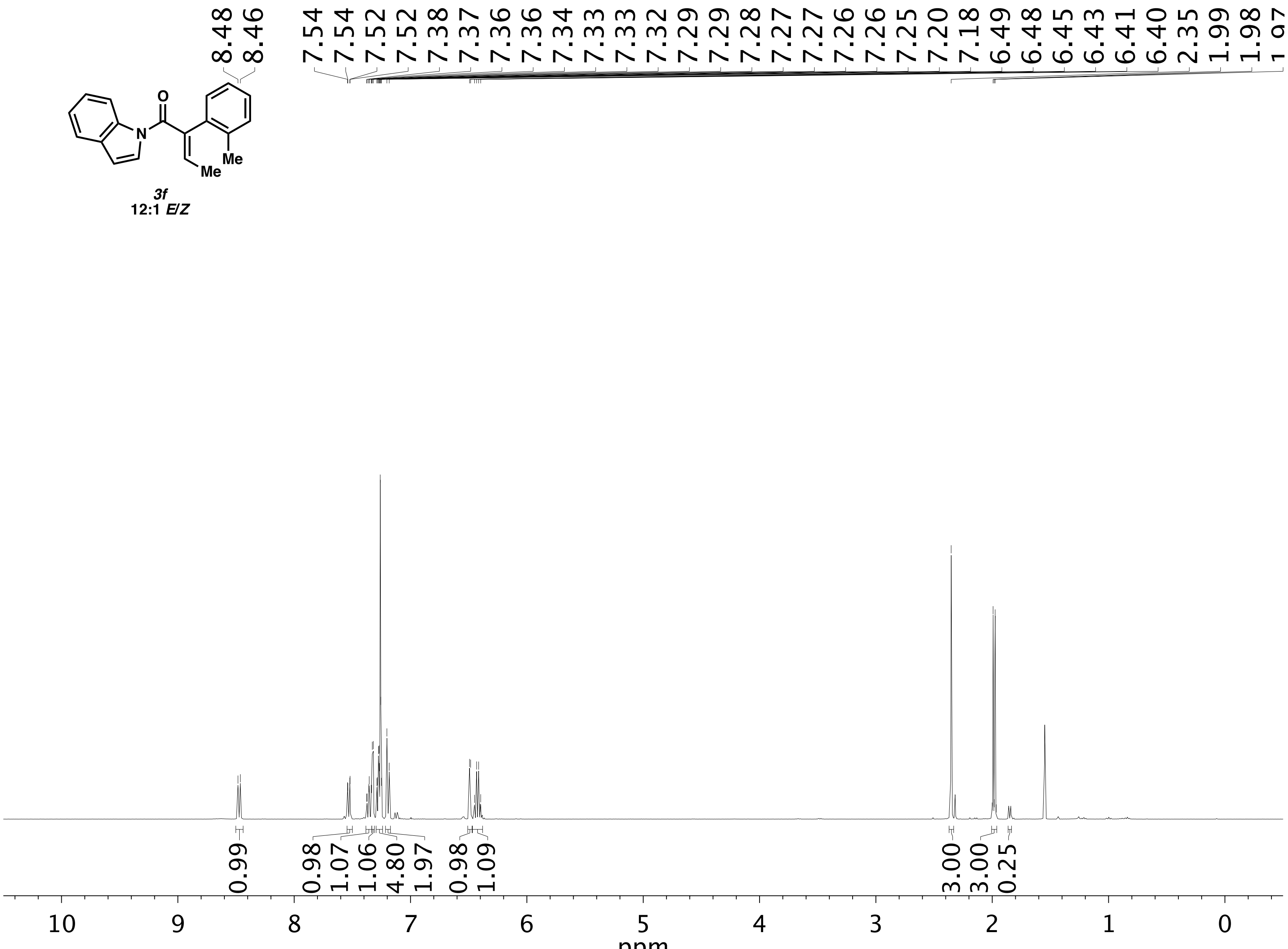
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3e.**



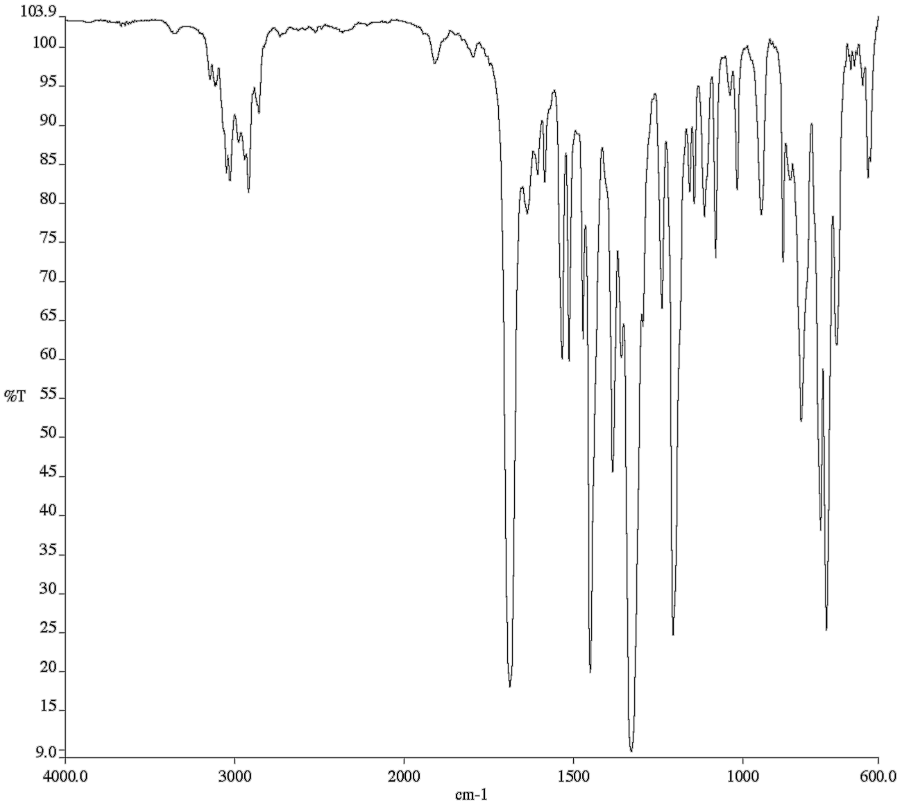
Infrared spectrum (Thin Film, NaCl) of compound **3e**.



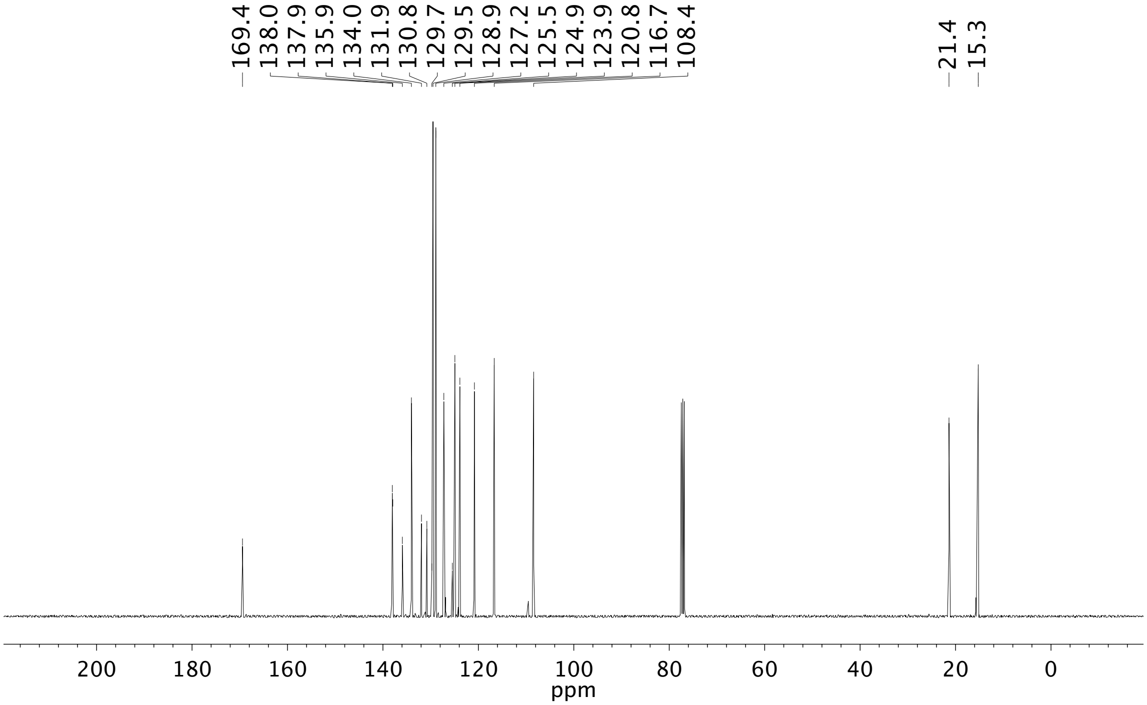
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3e**.



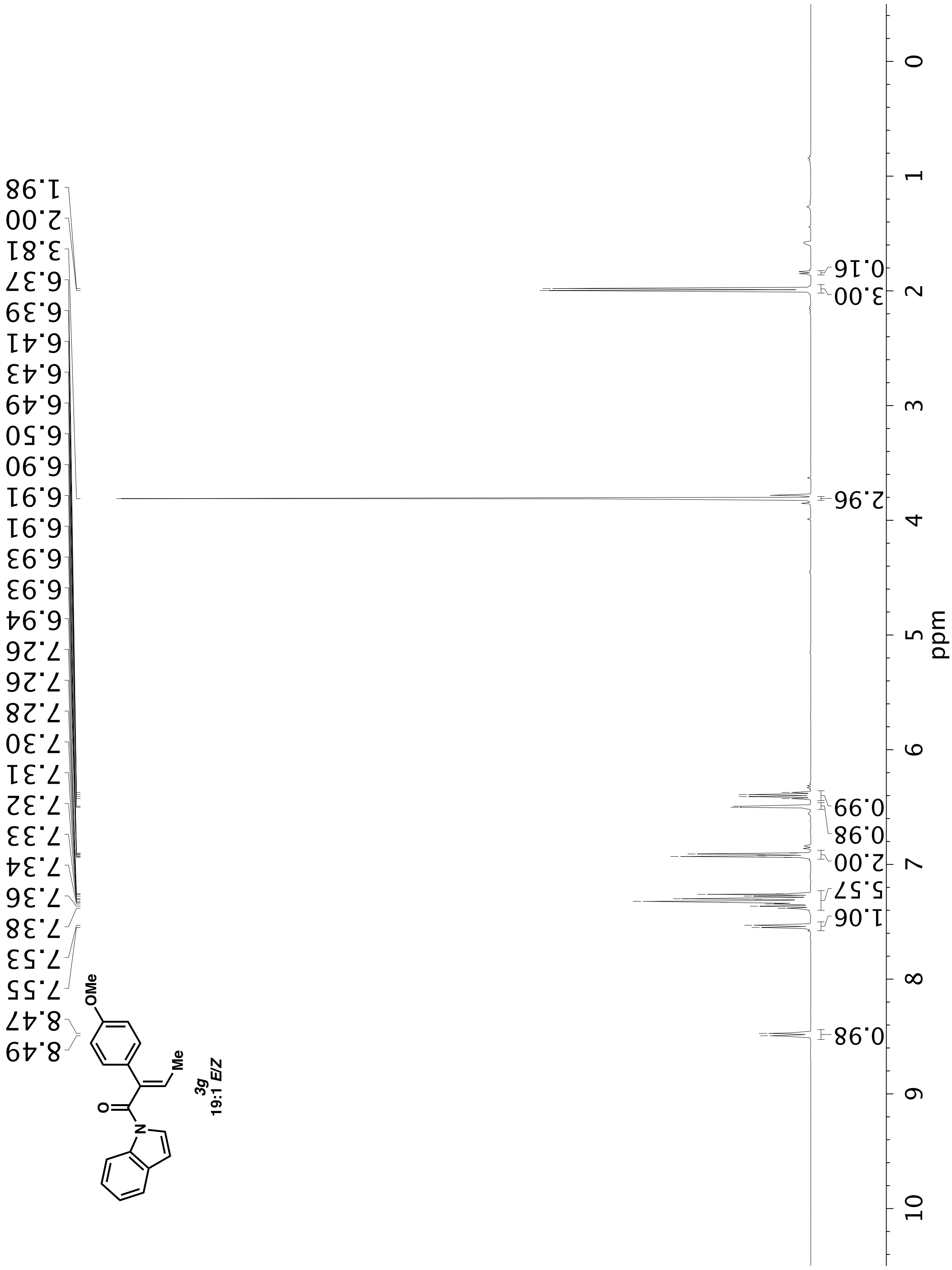
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3f.**



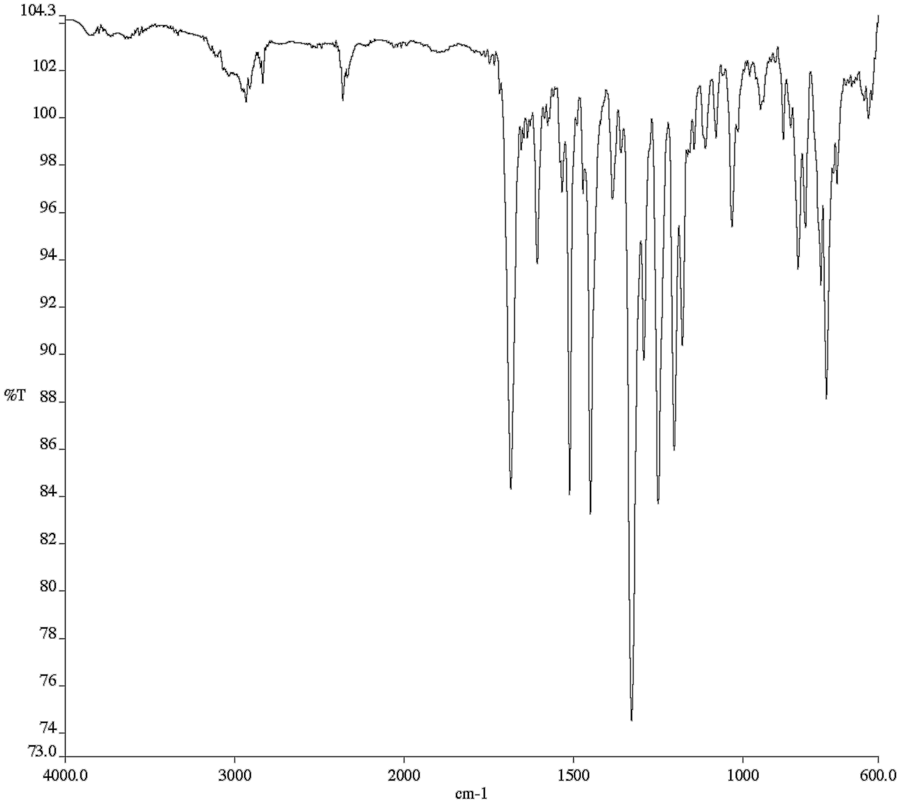
Infrared spectrum (Thin Film, NaCl) of compound **3f**.



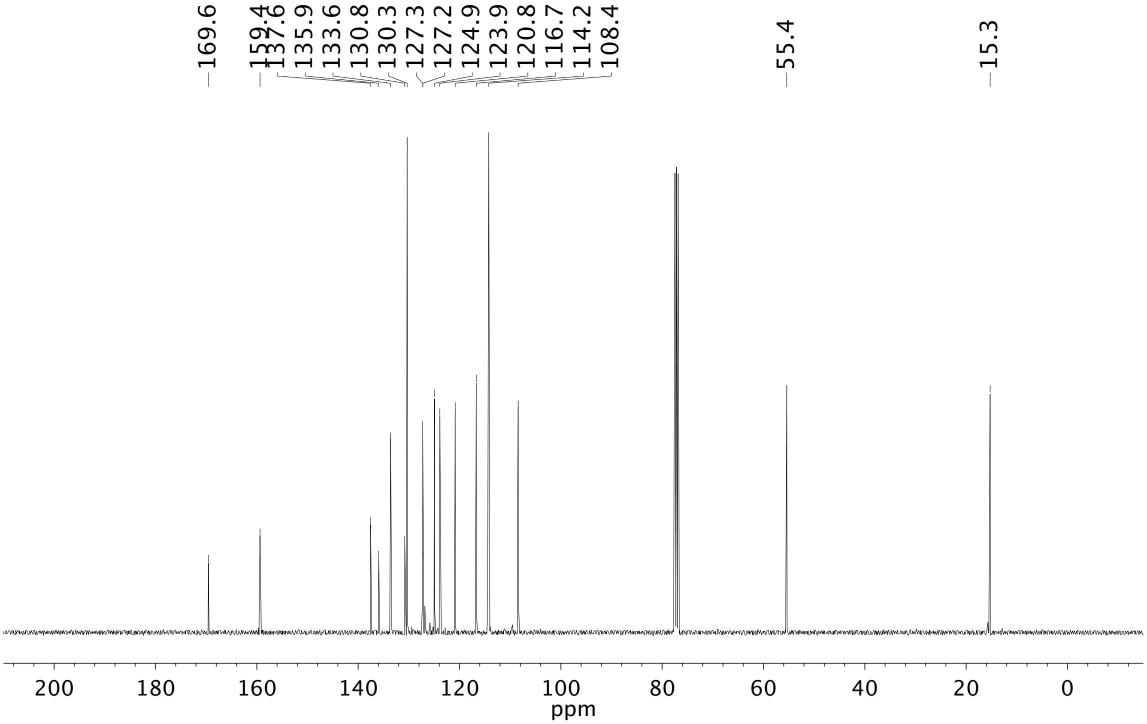
^{13}C NMR (100 MHz, CDCl$_3$) of compound **3f**.



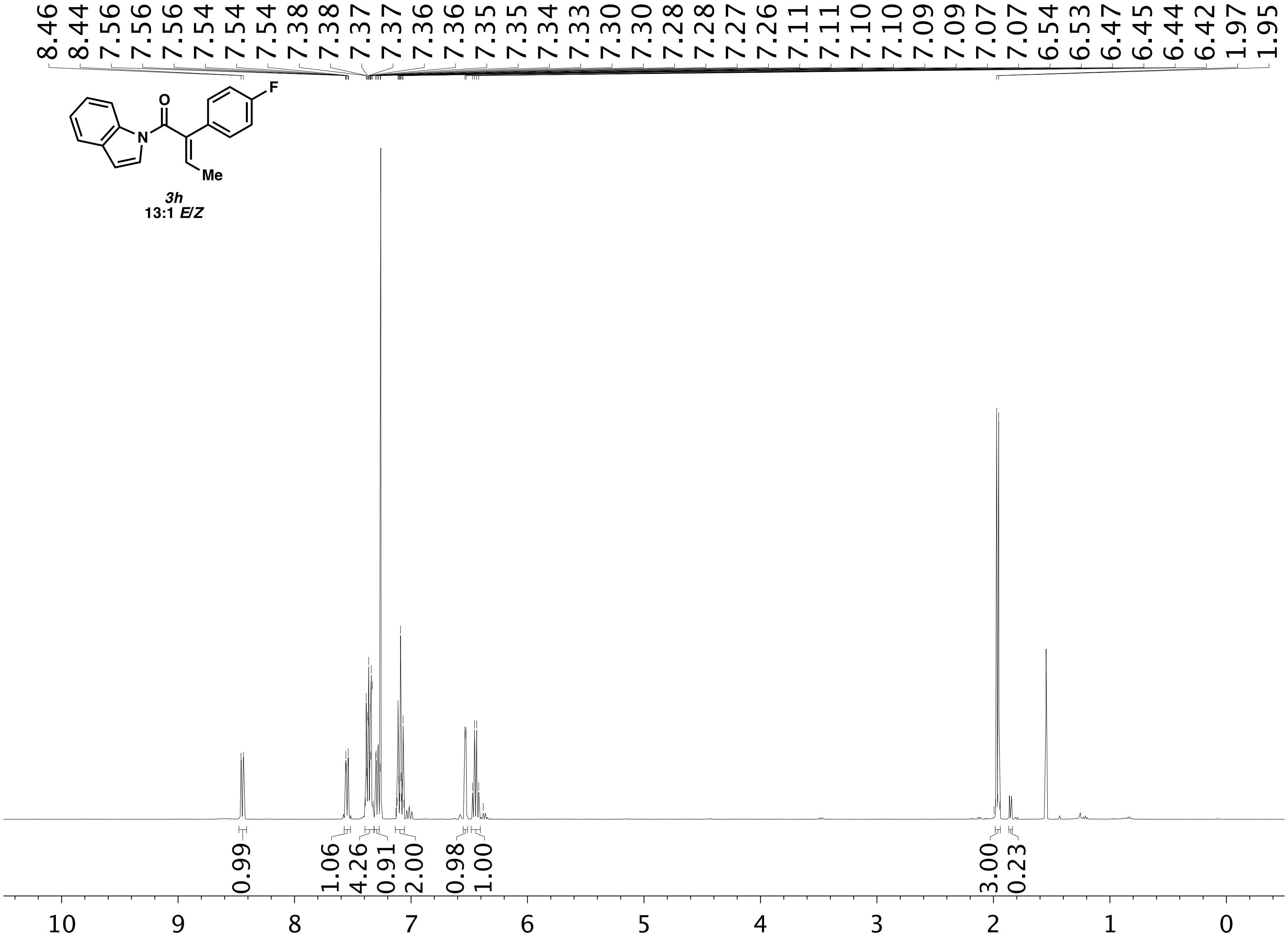
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3g.**



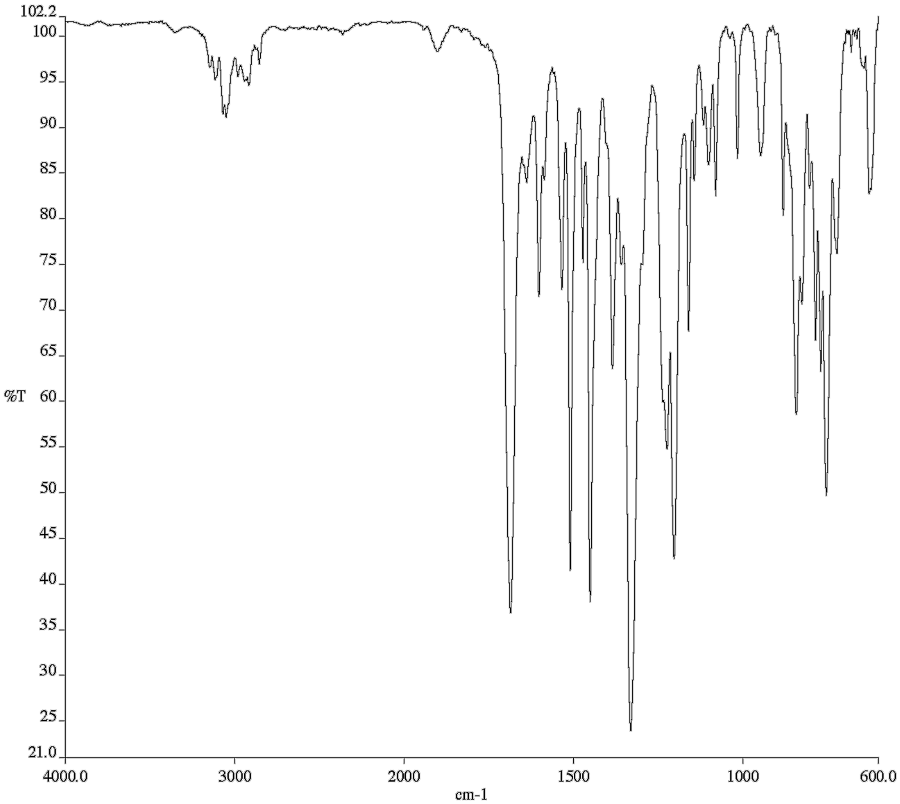
Infrared spectrum (Thin Film, NaCl) of compound **3g**.



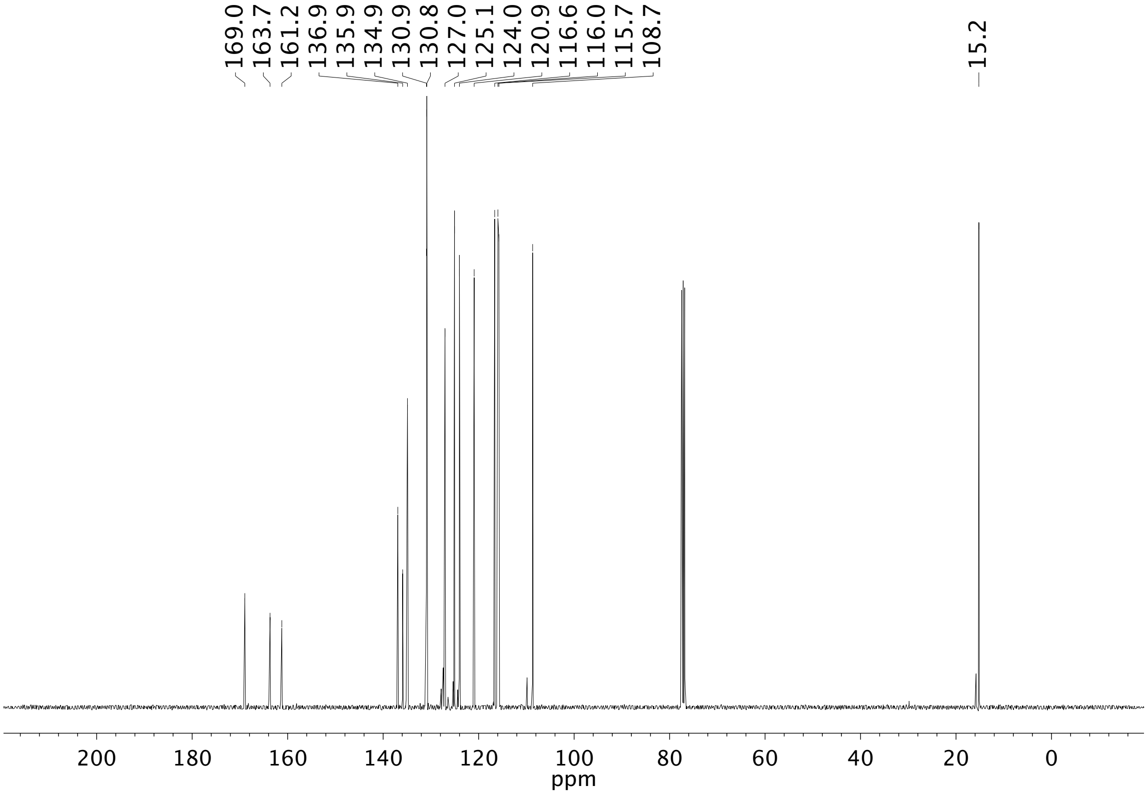
^{13}C NMR (100 MHz, CDCl$_3$) of compound **3g.**



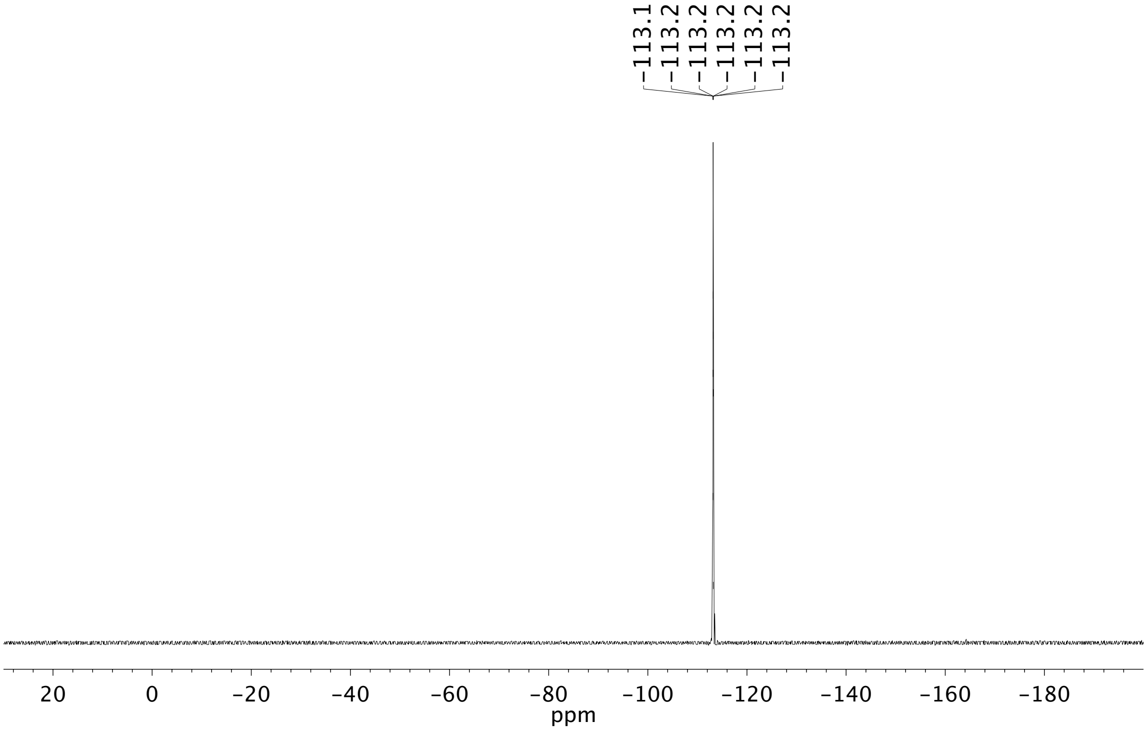
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3h.**



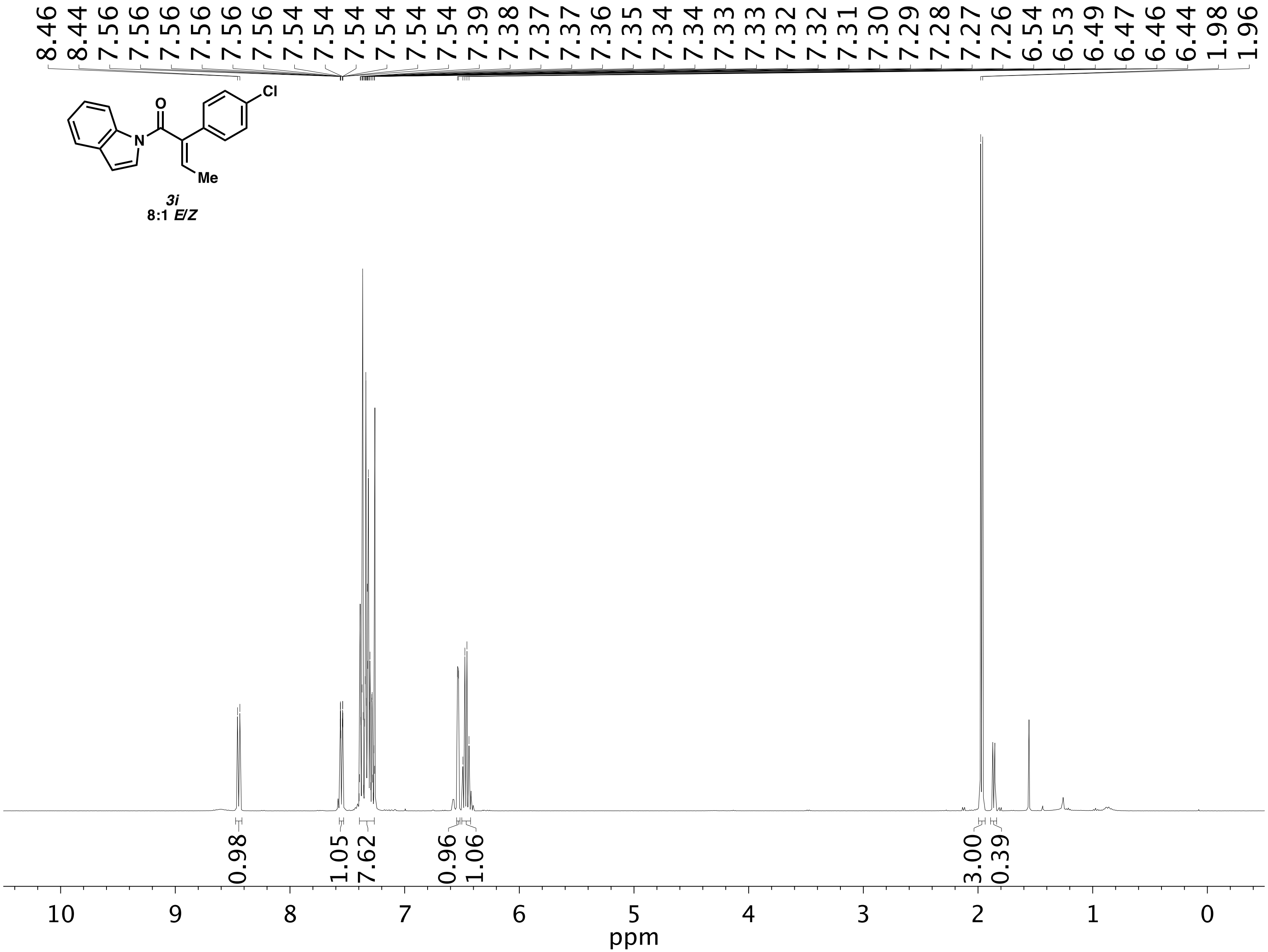
Infrared spectrum (Thin Film, NaCl) of compound **3h**.



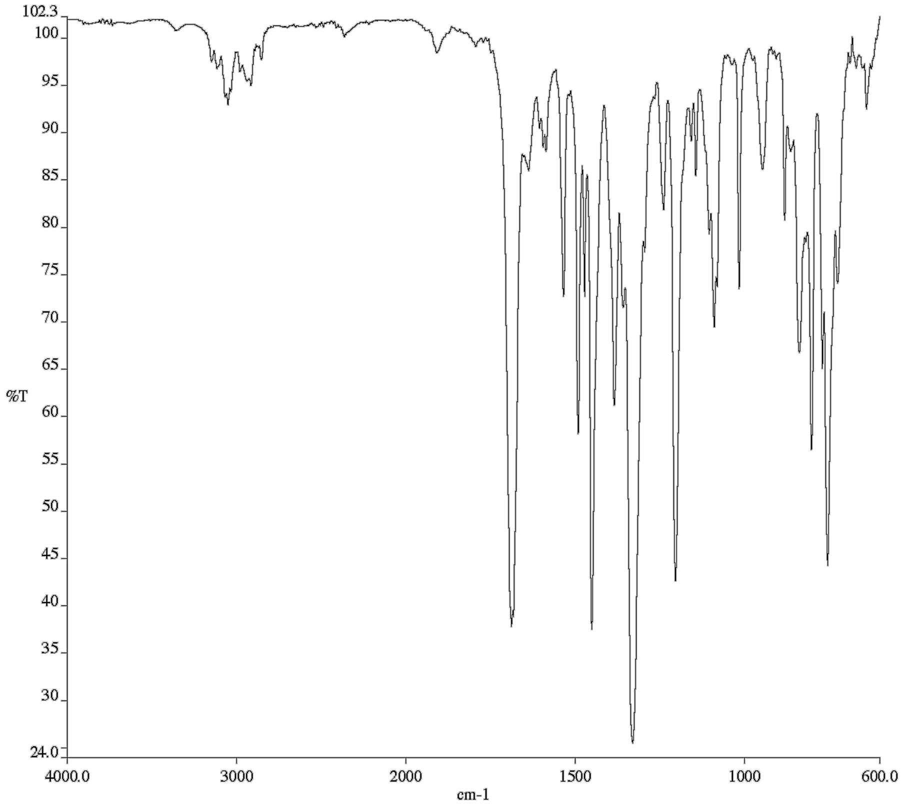
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3h**.



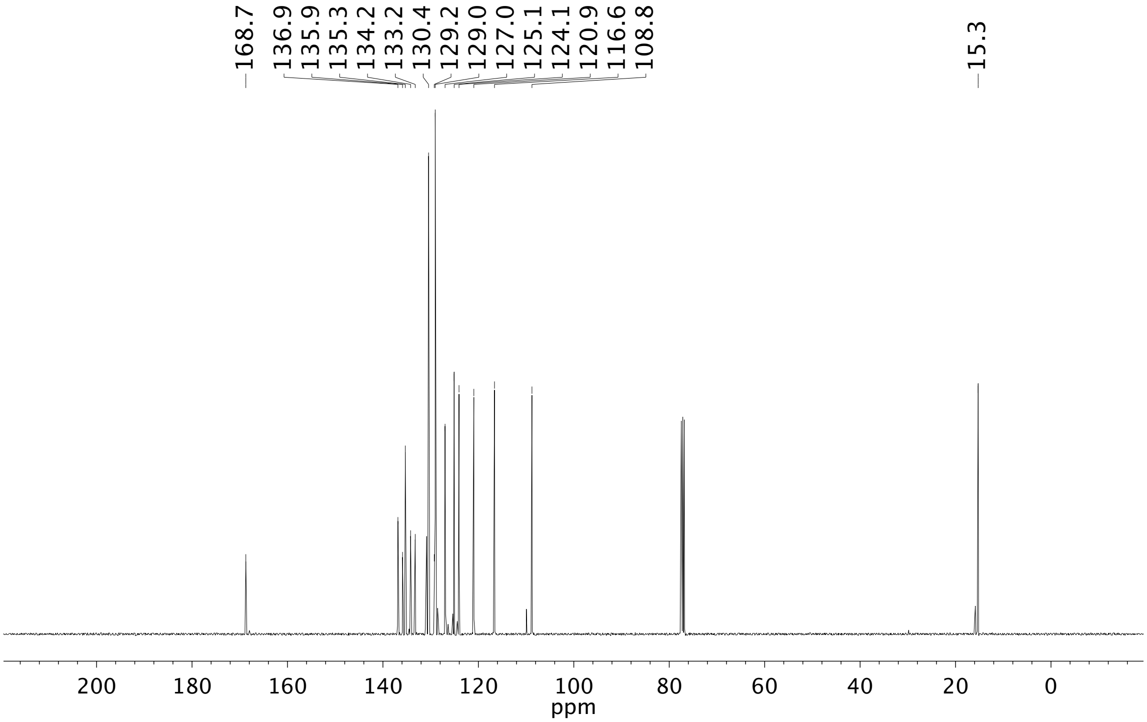
^{19}F NMR (282 MHz, CDCl$_3$) of compound **3h**.



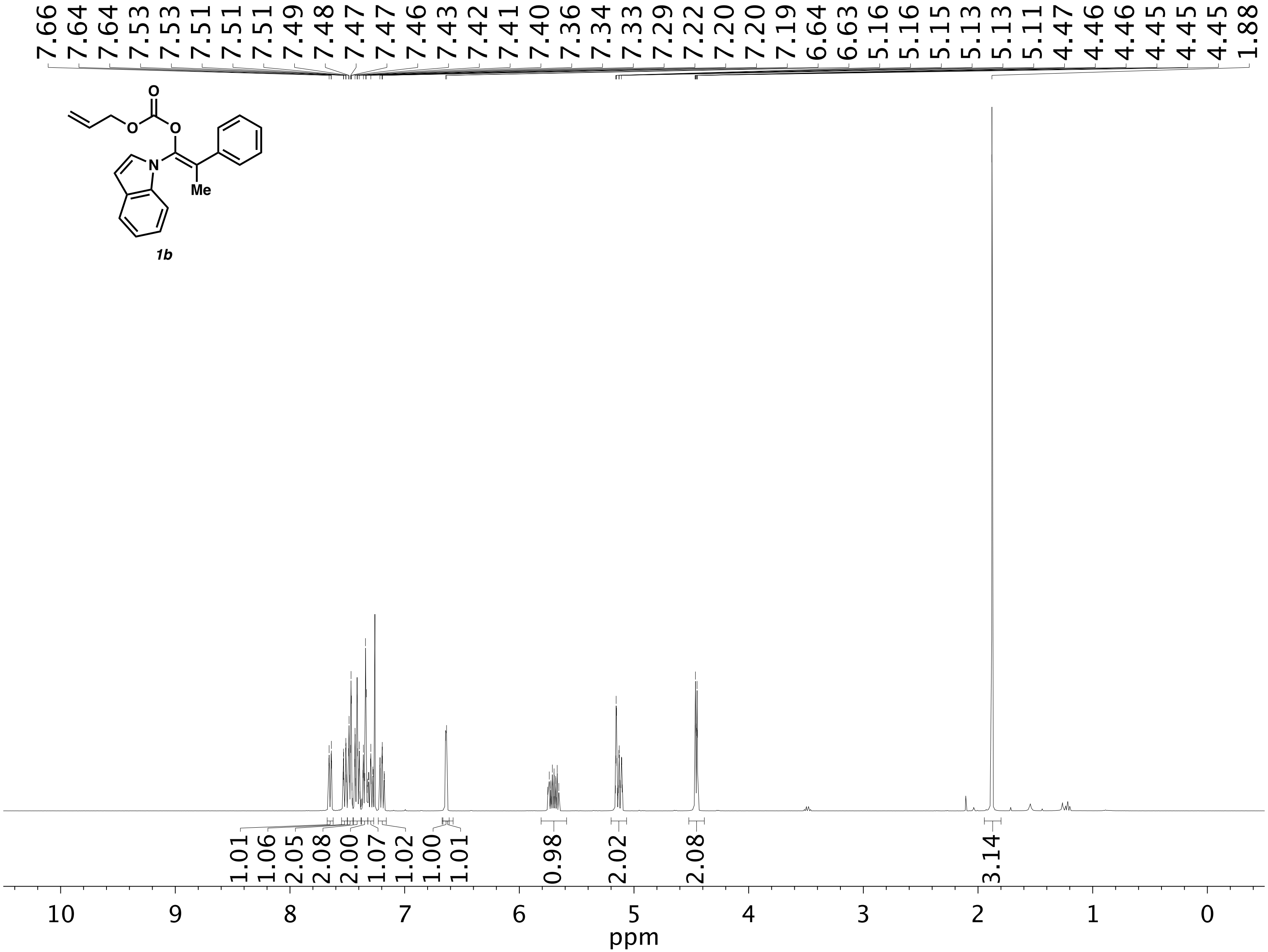
^{1}H NMR (400 MHz, CDCl$_3$) of compound **3i.**



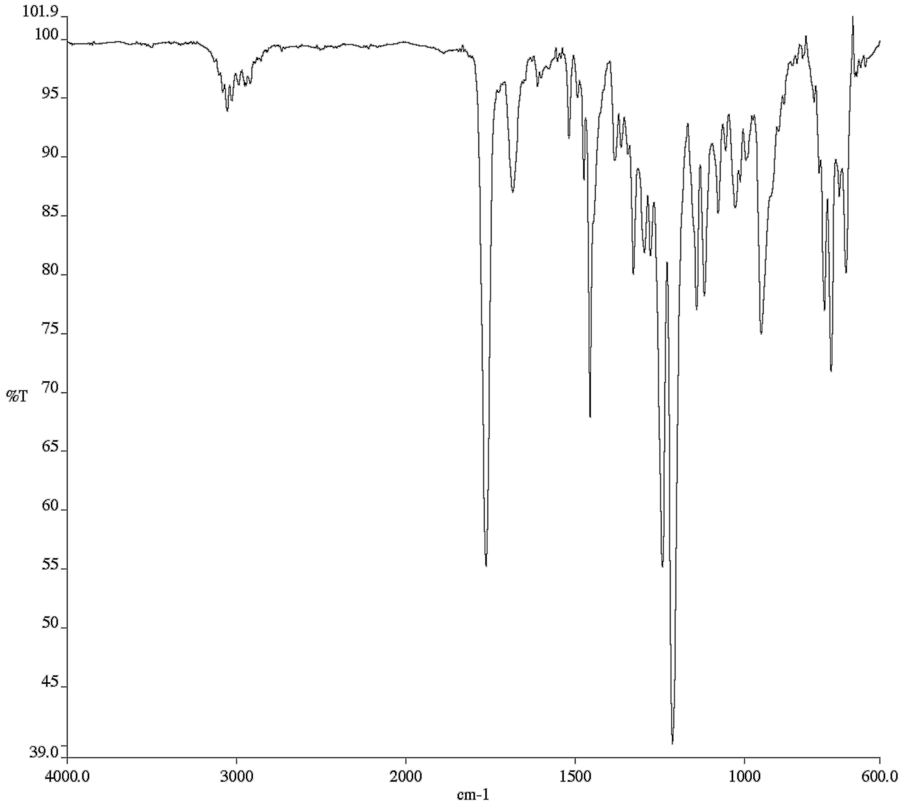
Infrared spectrum (Thin Film, NaCl) of compound **3i**.



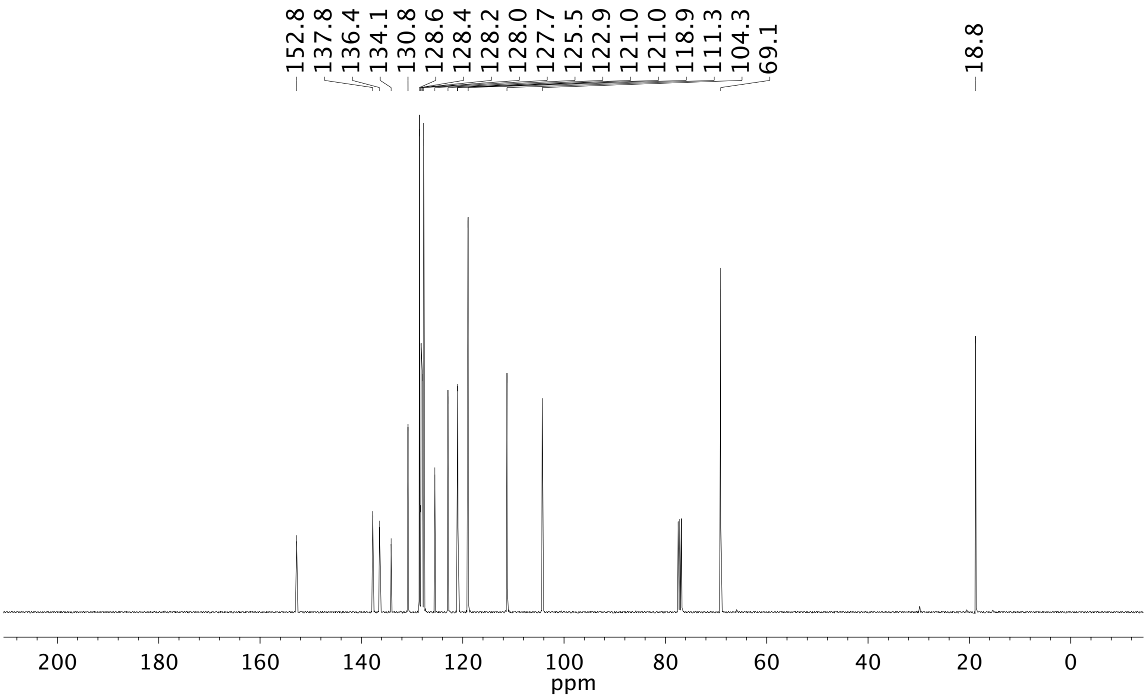
^{13}C NMR (100 MHz, CDCl$_3$) of compound **3i**.



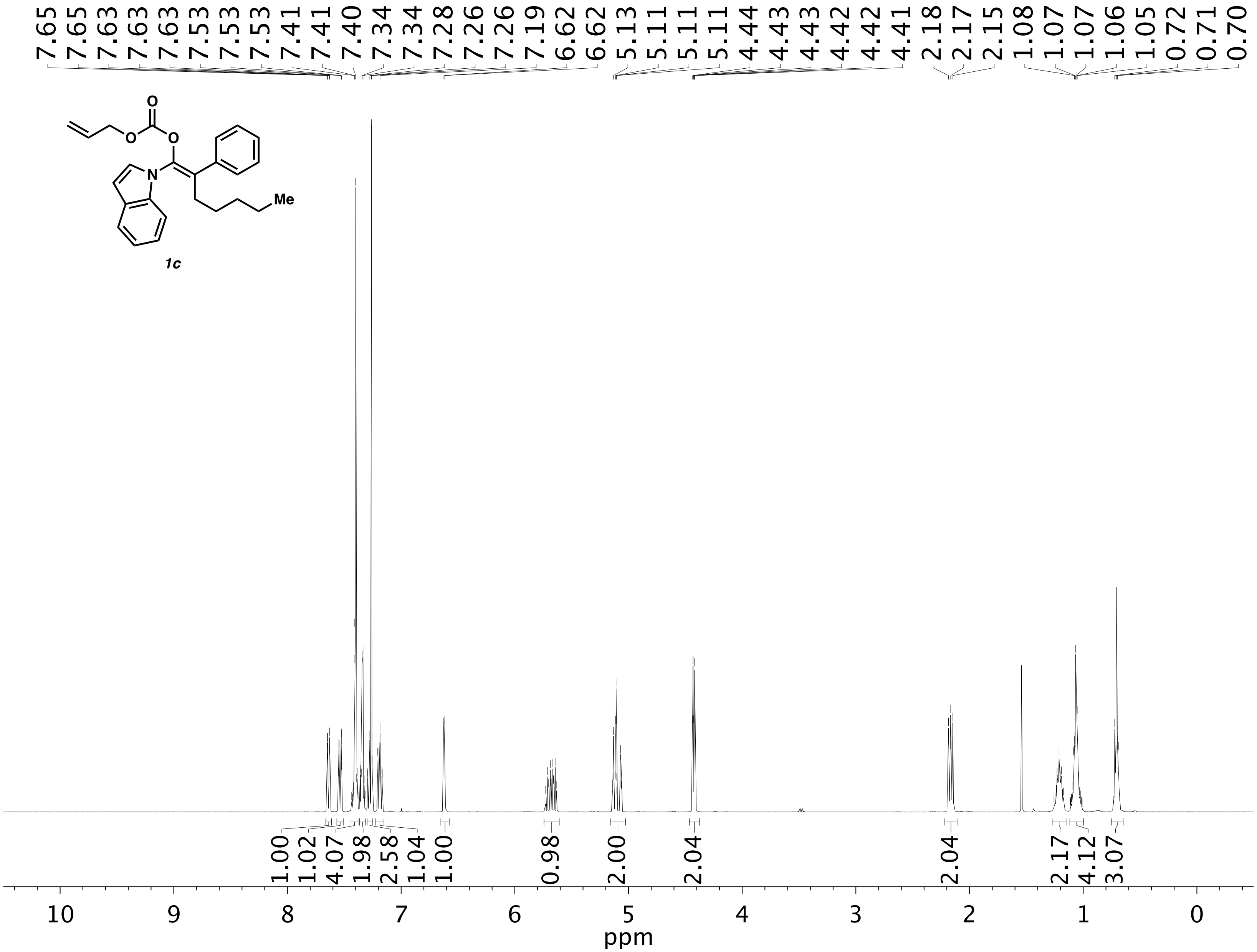
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1b.**



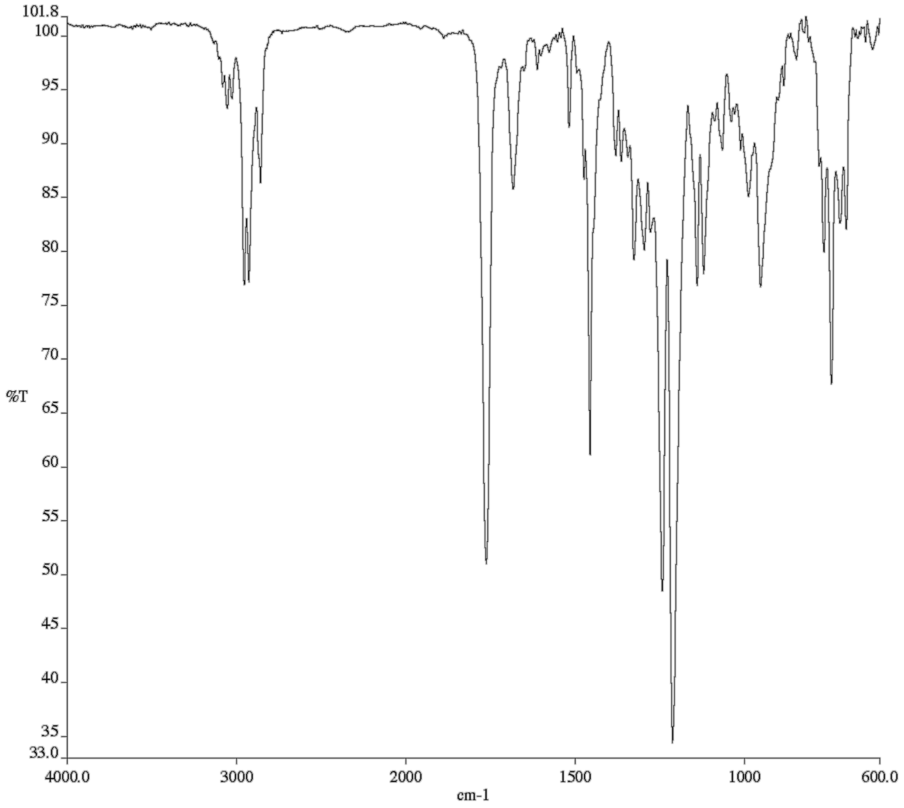
Infrared spectrum (Thin Film, NaCl) of compound **1b**.



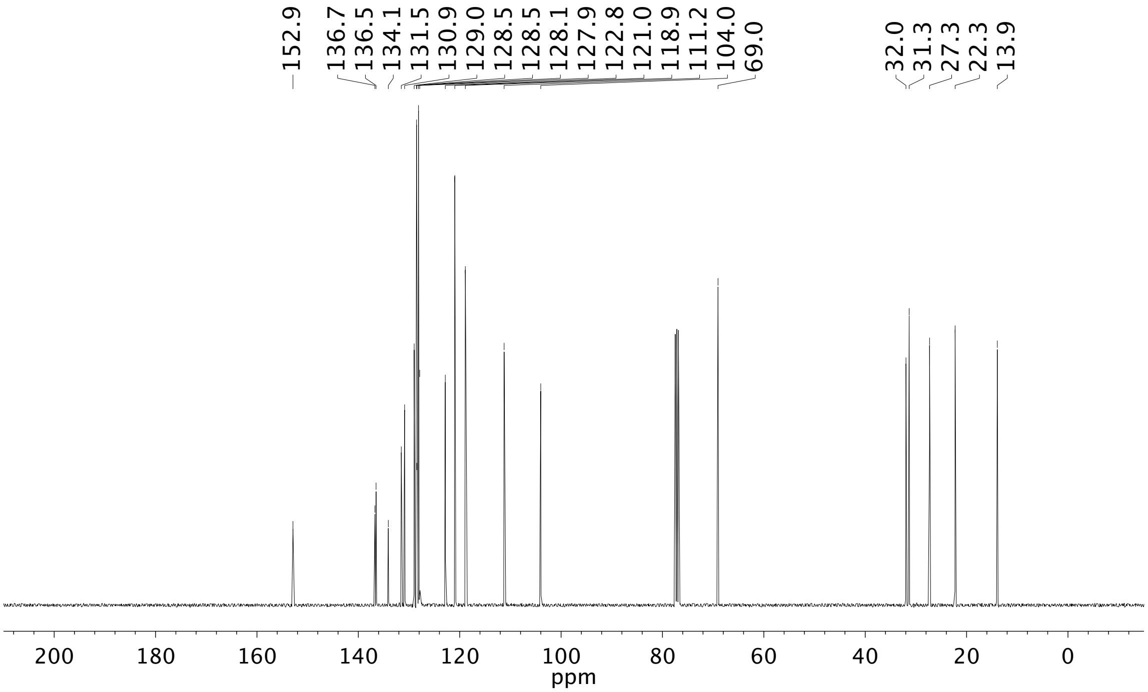
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1b**.



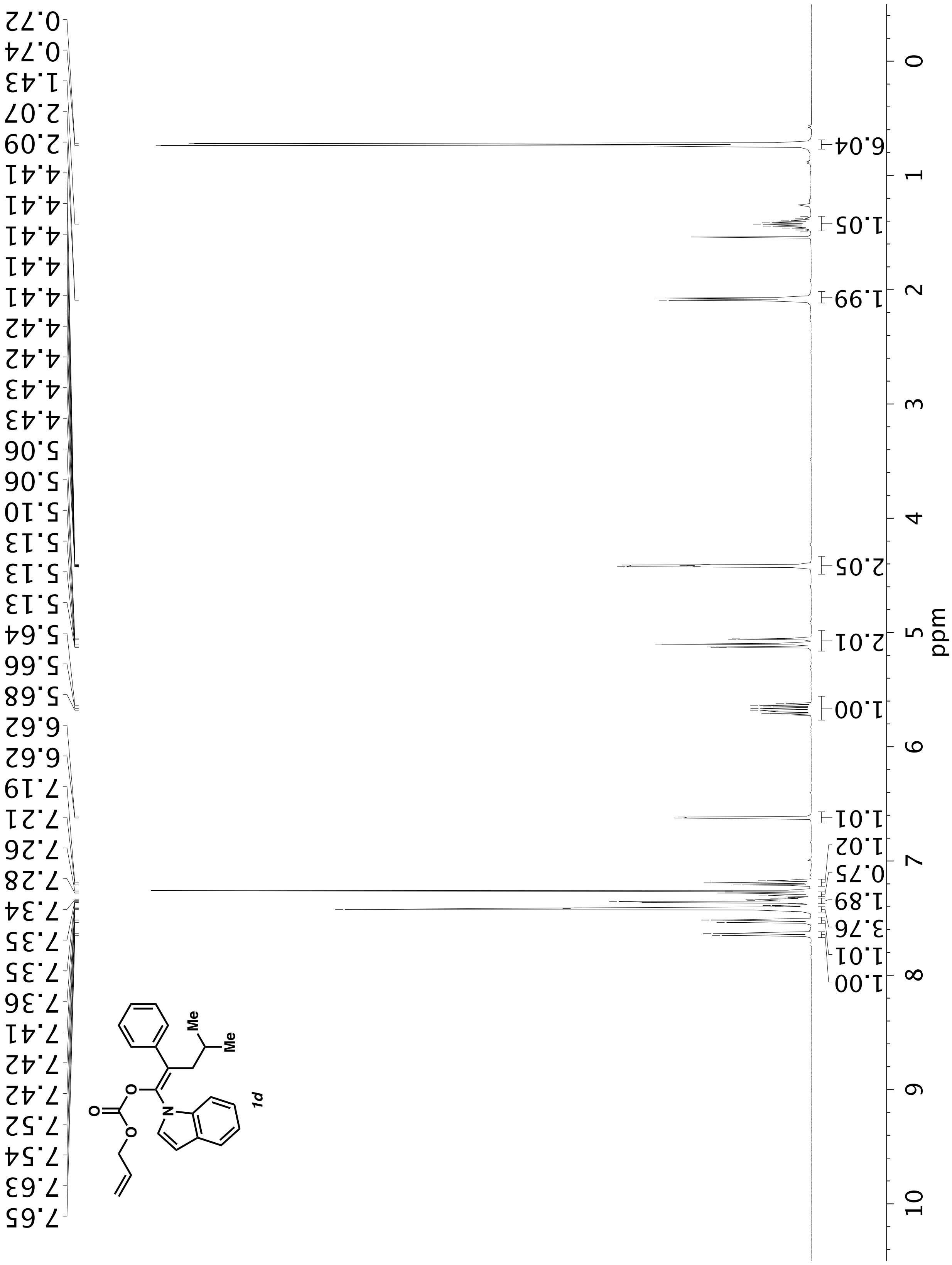
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1c.**



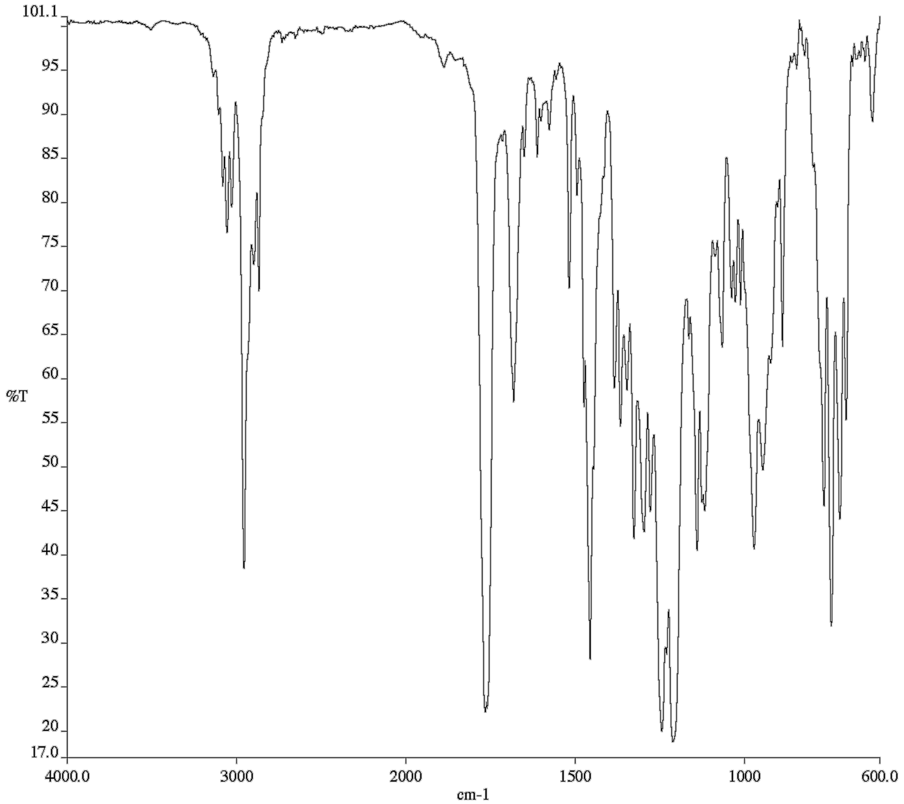
Infrared spectrum (Thin Film, NaCl) of compound **1c**.



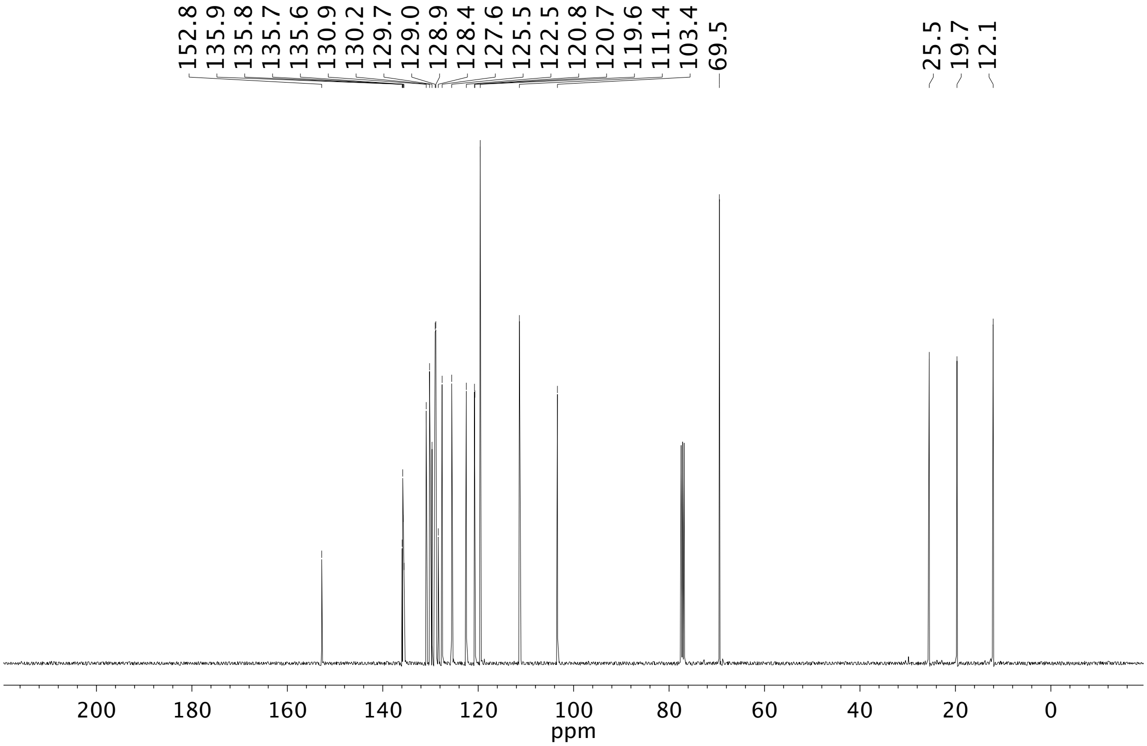
^{13}C NMR (100 MHz, CDCl$_3$) of compound **1c**.



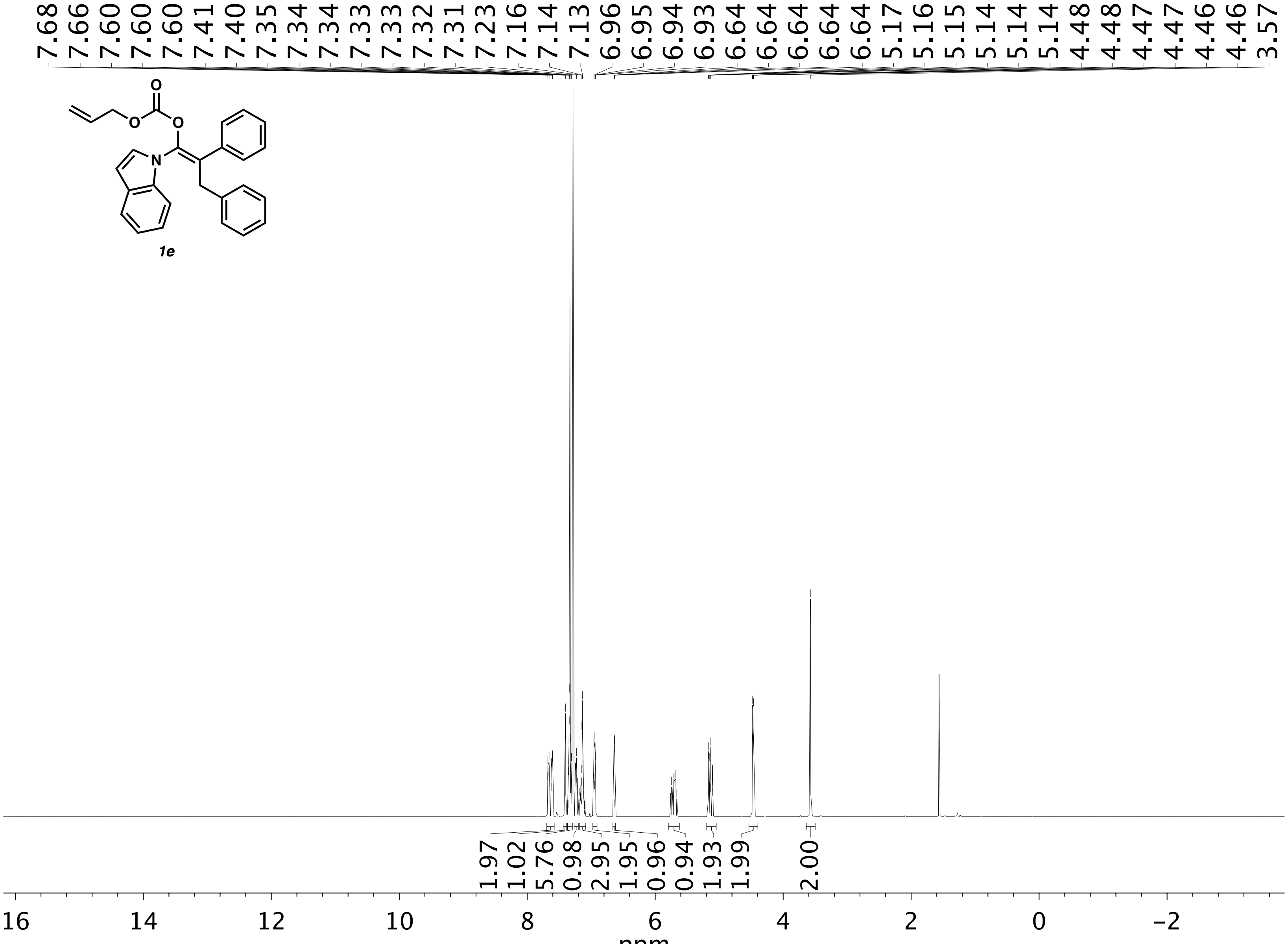
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1d.**



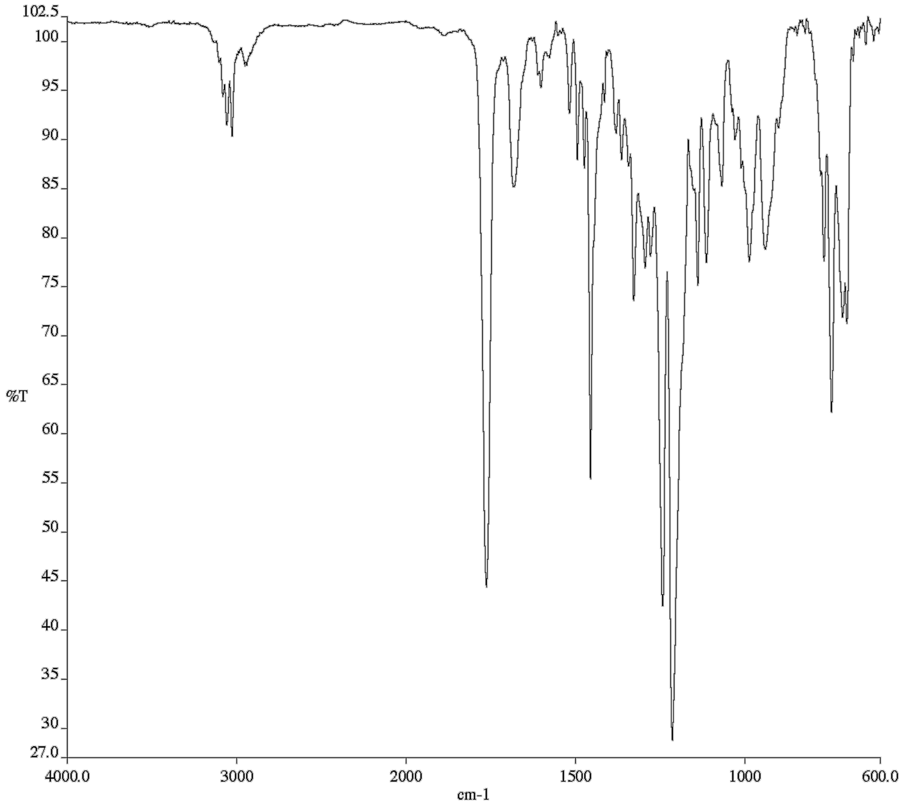
Infrared spectrum (Thin Film, NaCl) of compound **1d**.



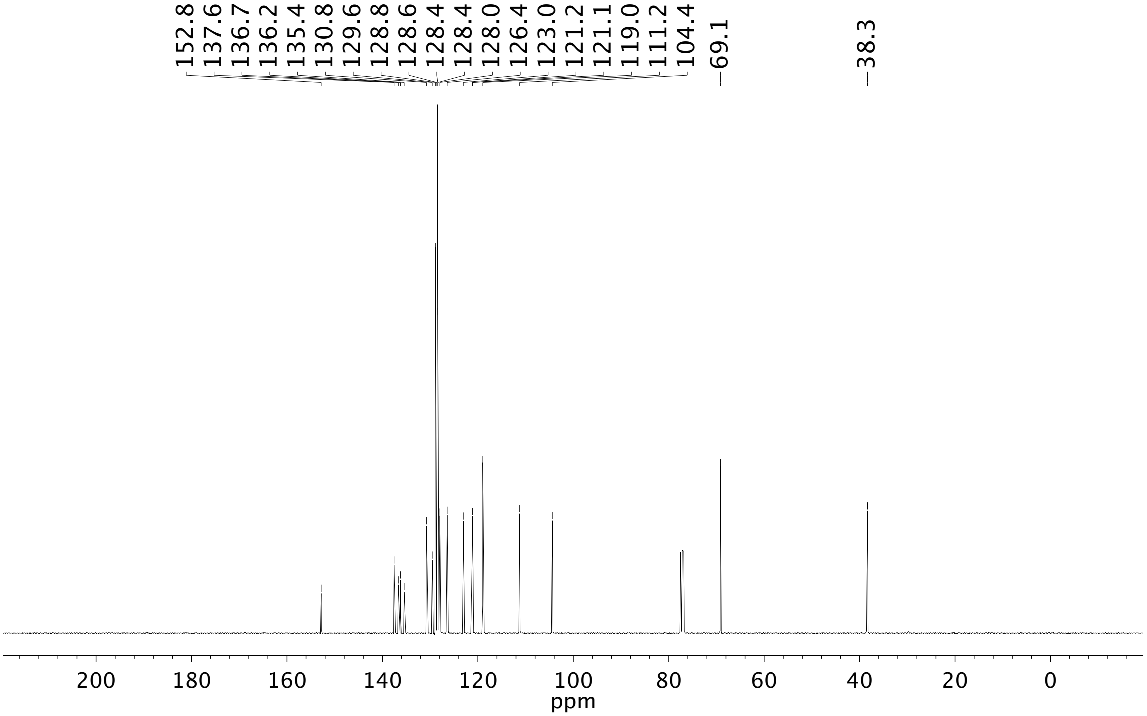
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1d**.



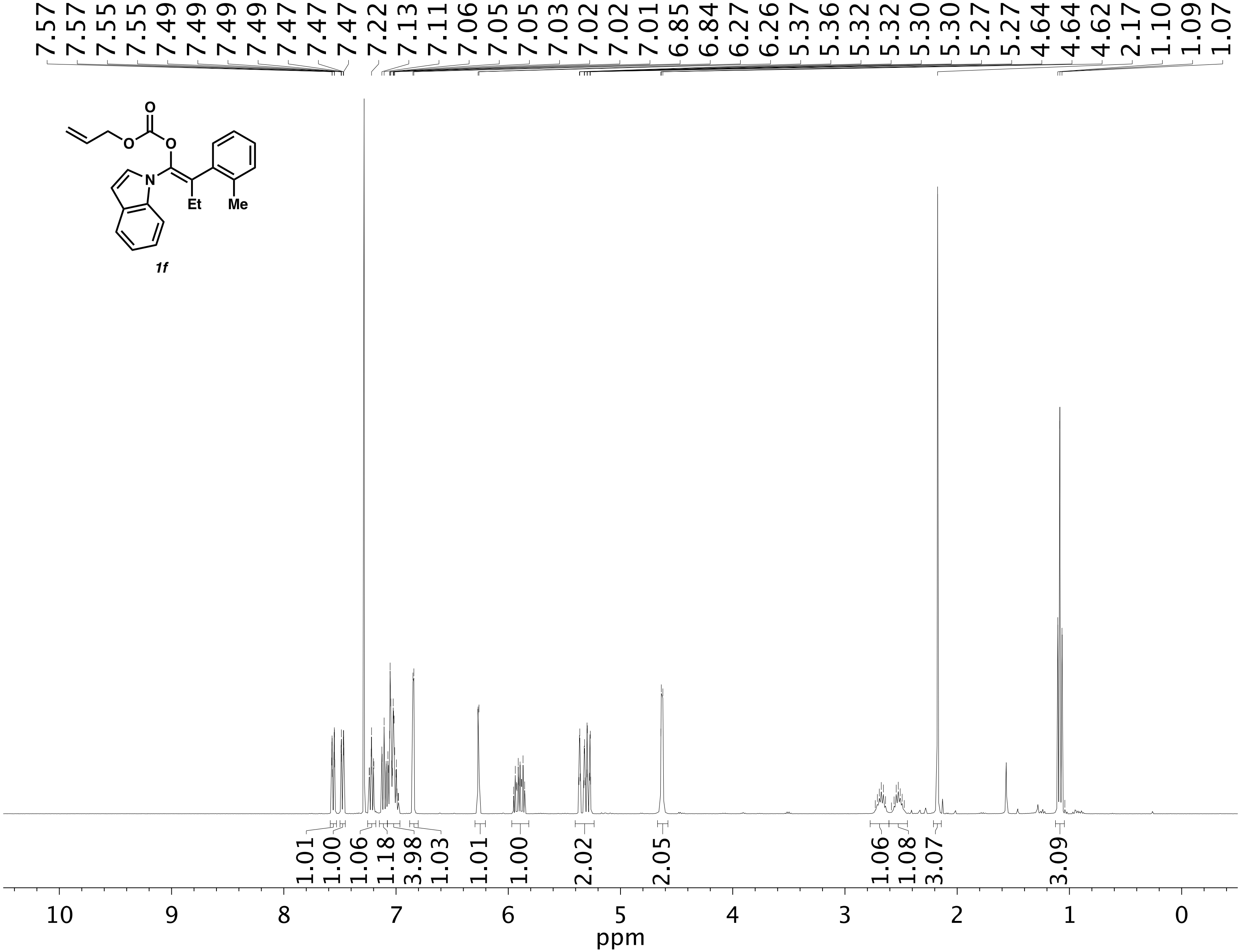
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1e.**



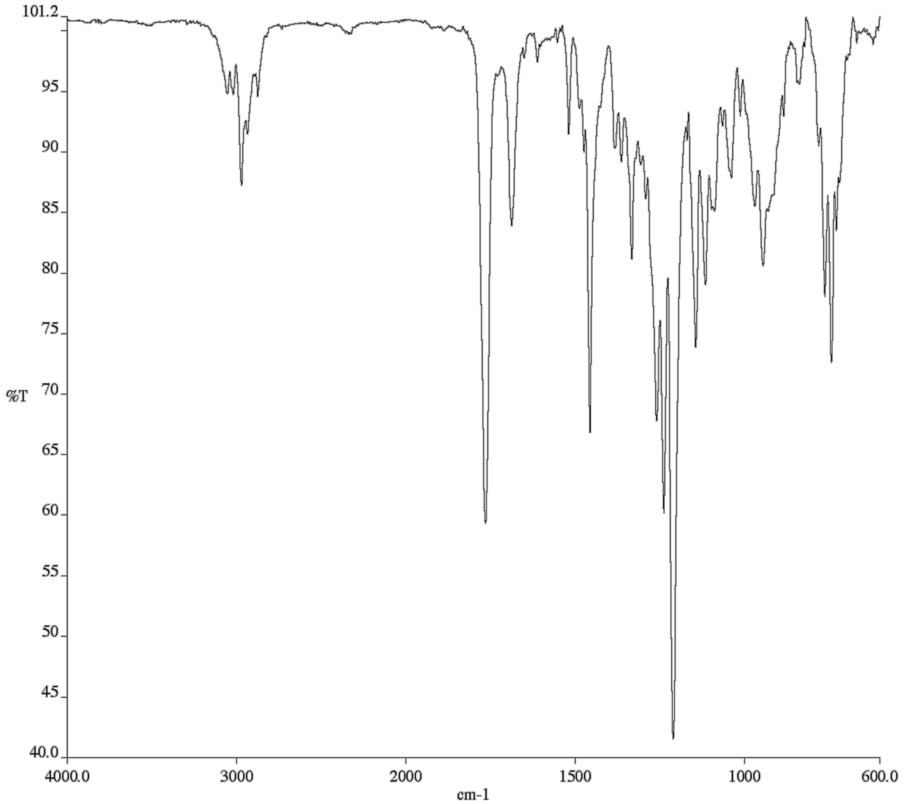
Infrared spectrum (Thin Film, NaCl) of compound **1e**.



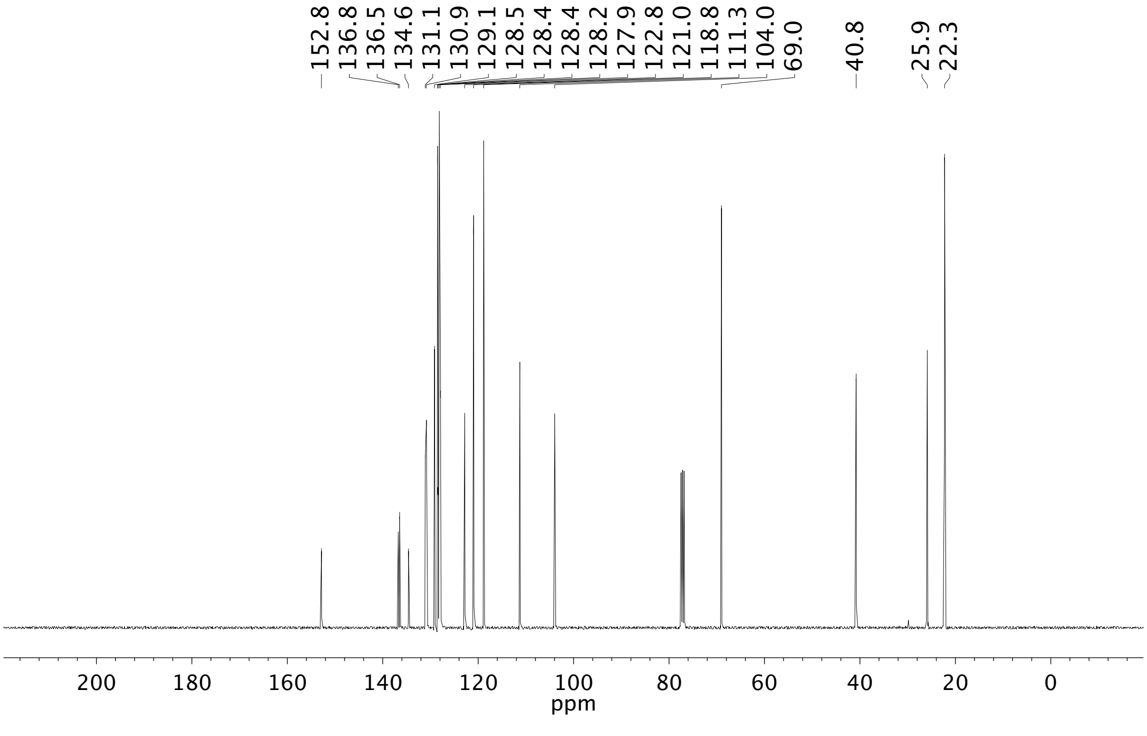
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1e**.



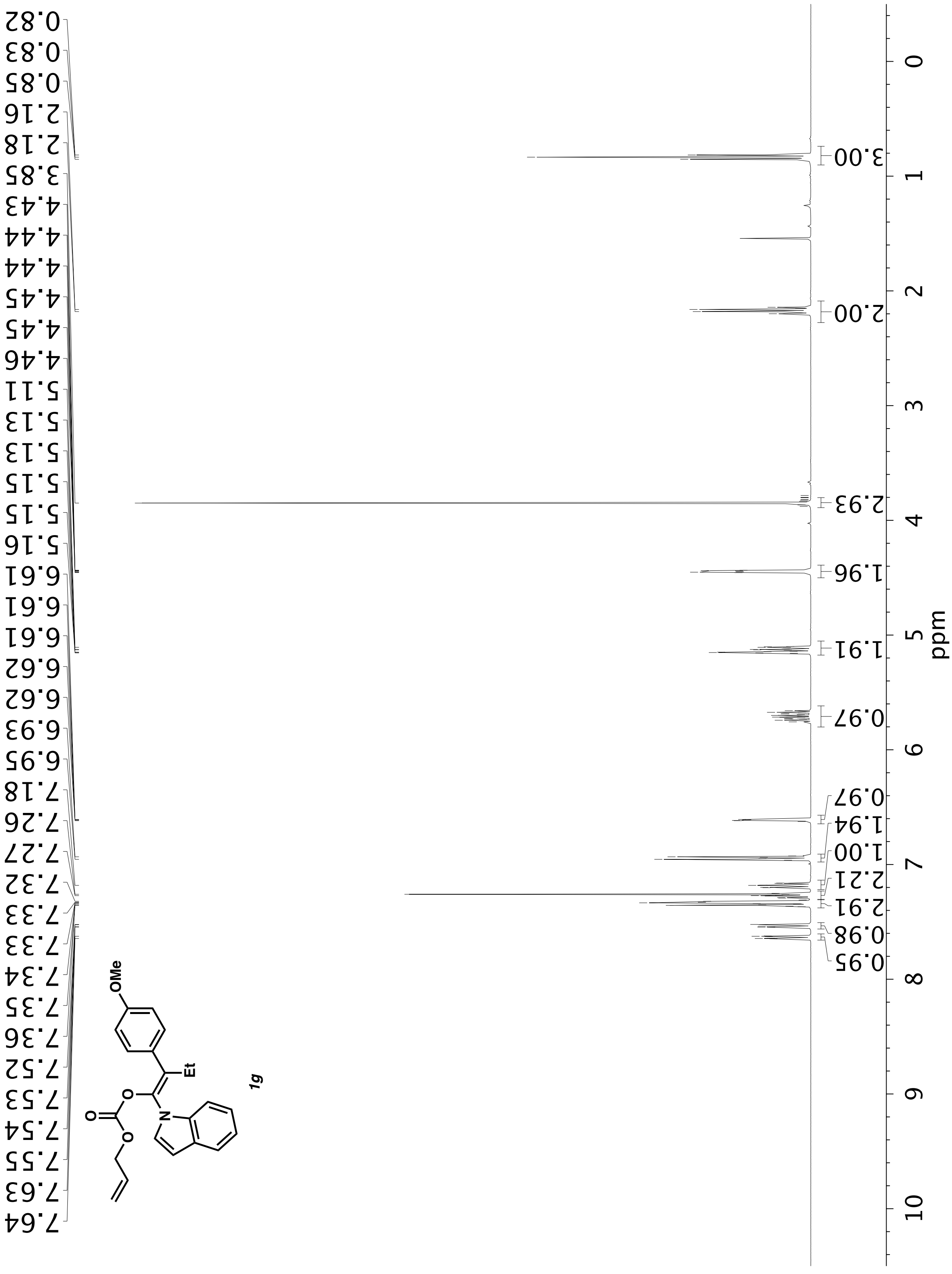
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1f.**



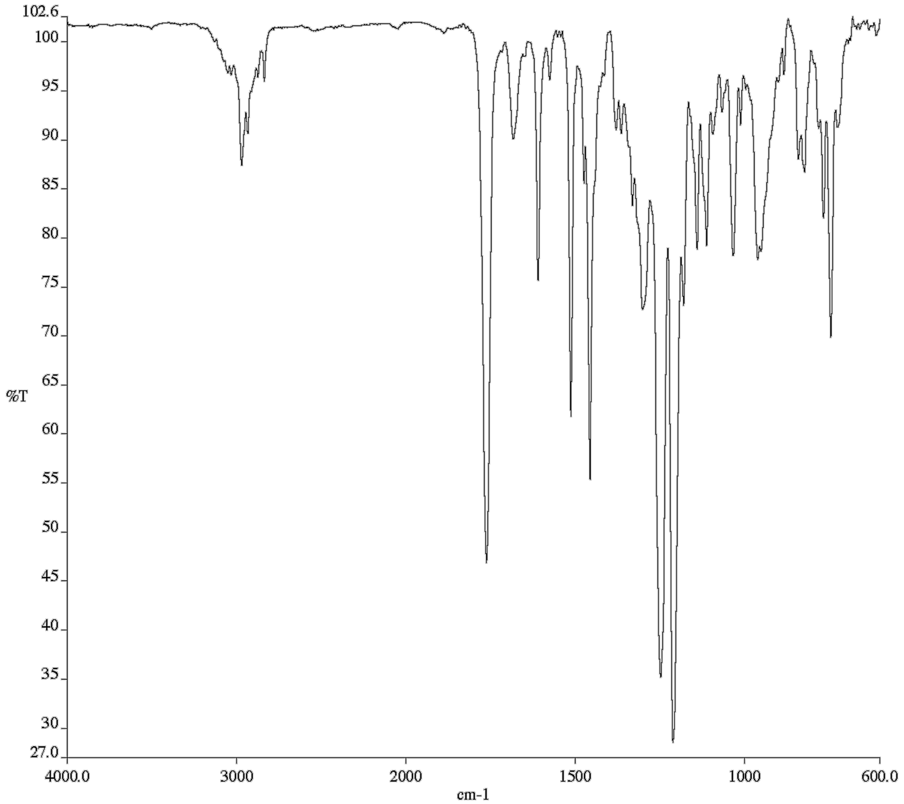
Infrared spectrum (Thin Film, NaCl) of compound **1f**.



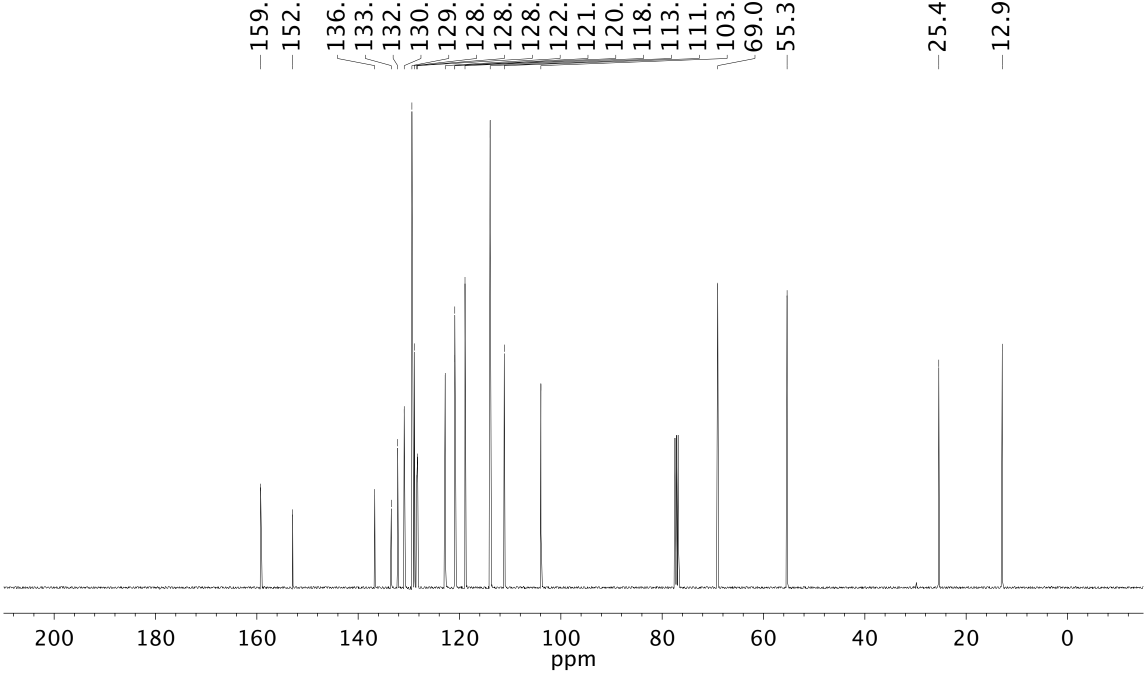
^{13}C NMR (100 MHz, CDCl$_3$) of compound **1f**.



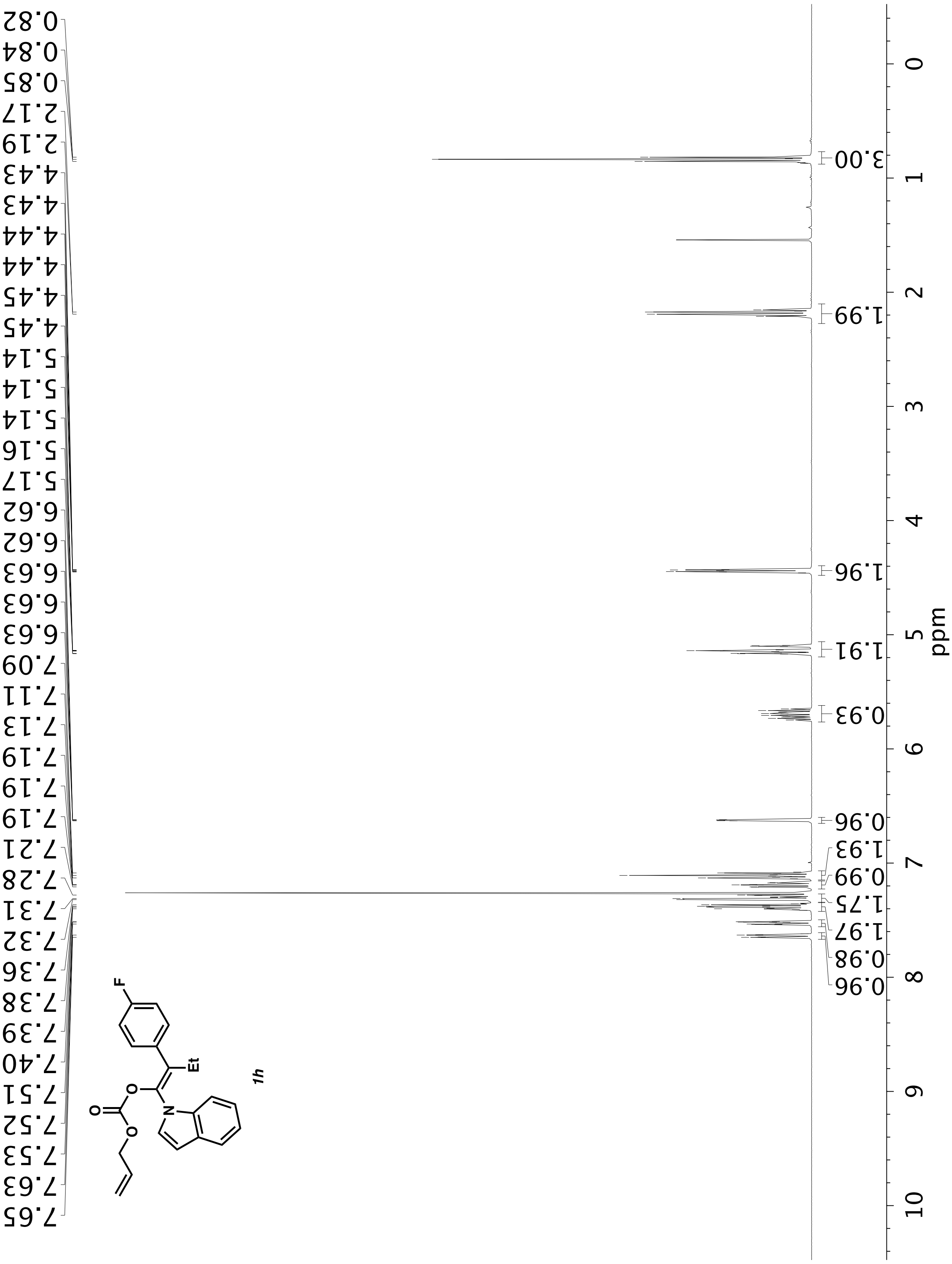
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1g.**



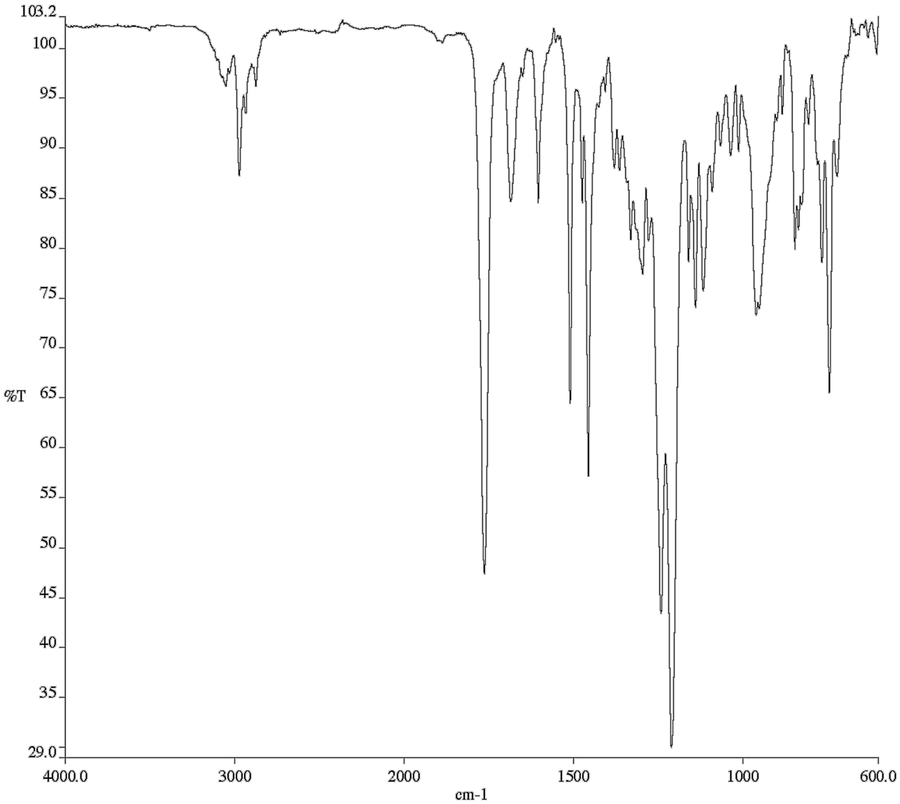
Infrared spectrum (Thin Film, NaCl) of compound **1g**.



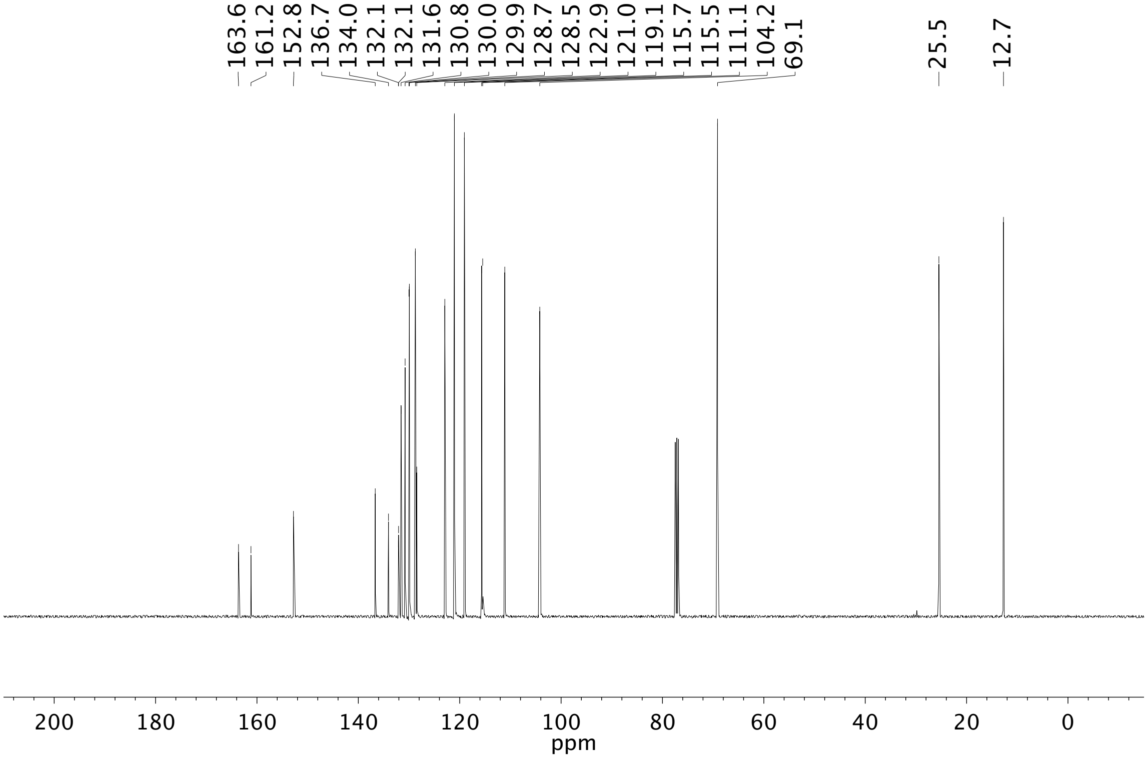
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1g.**



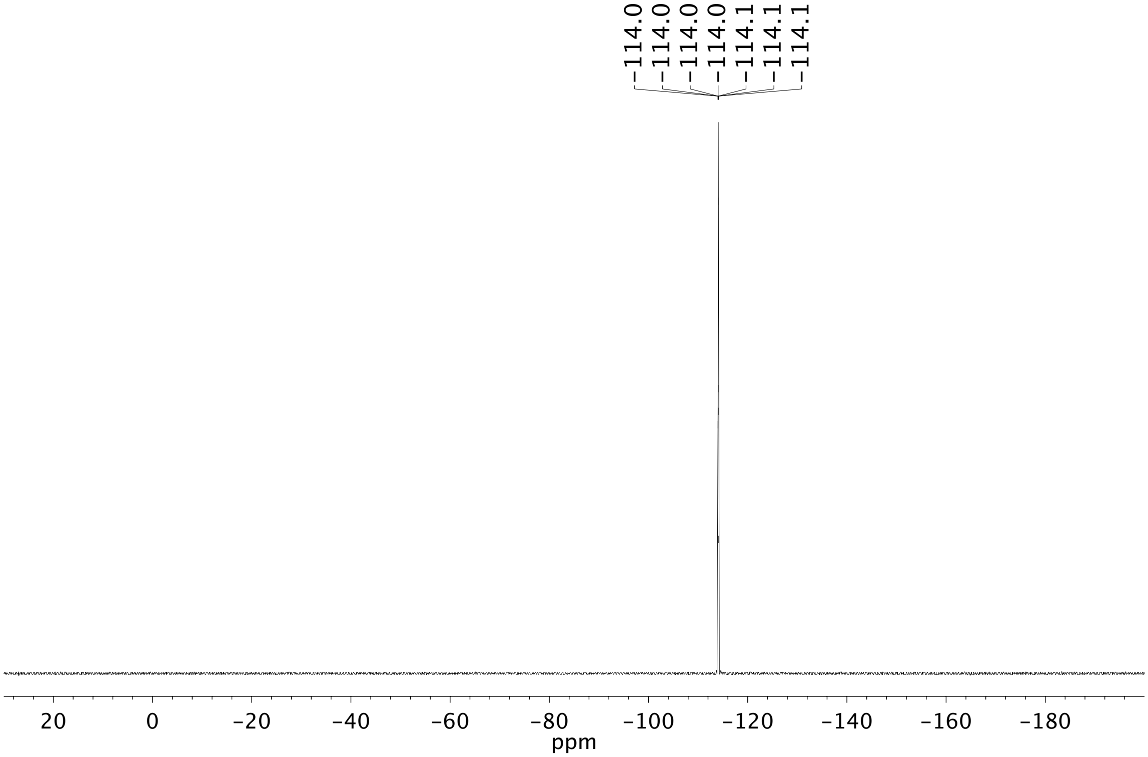
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1h.**



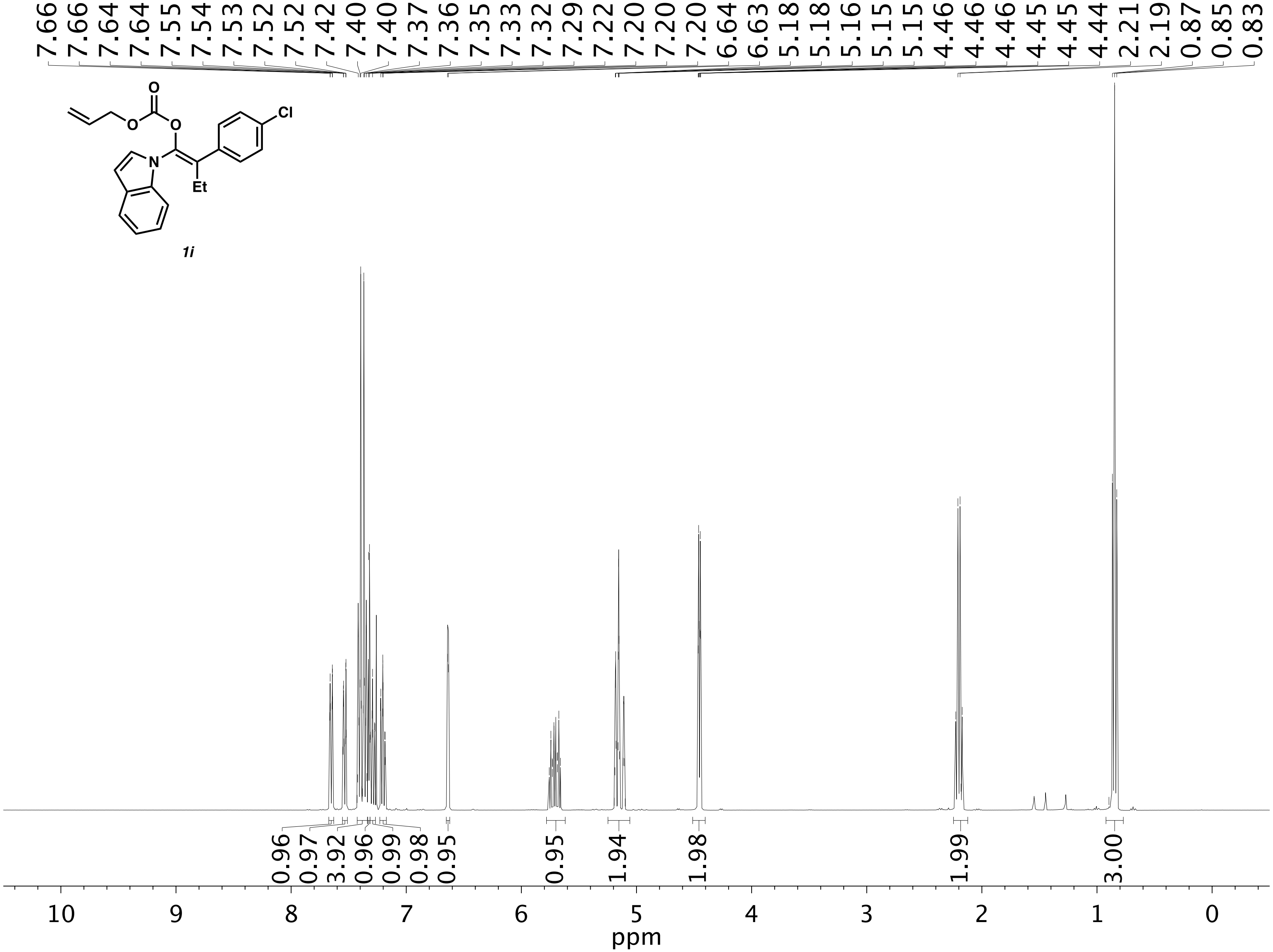
Infrared spectrum (Thin Film, NaCl) of compound **1h**.



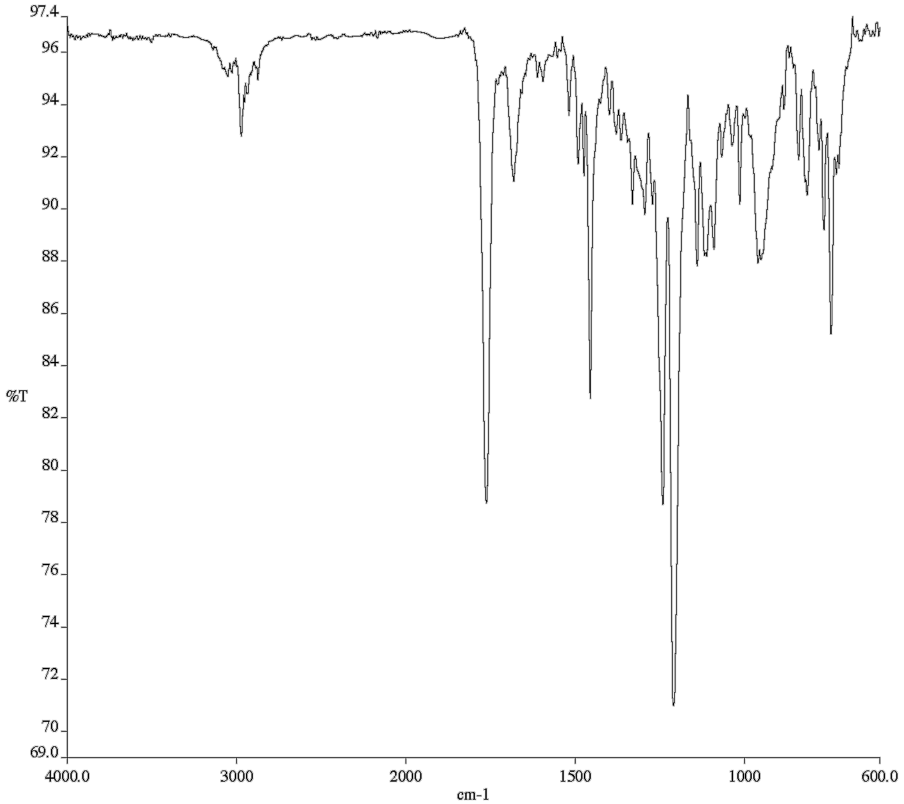
^{13}C NMR (100 MHz, CDCl$_3$) of compound **1h**.



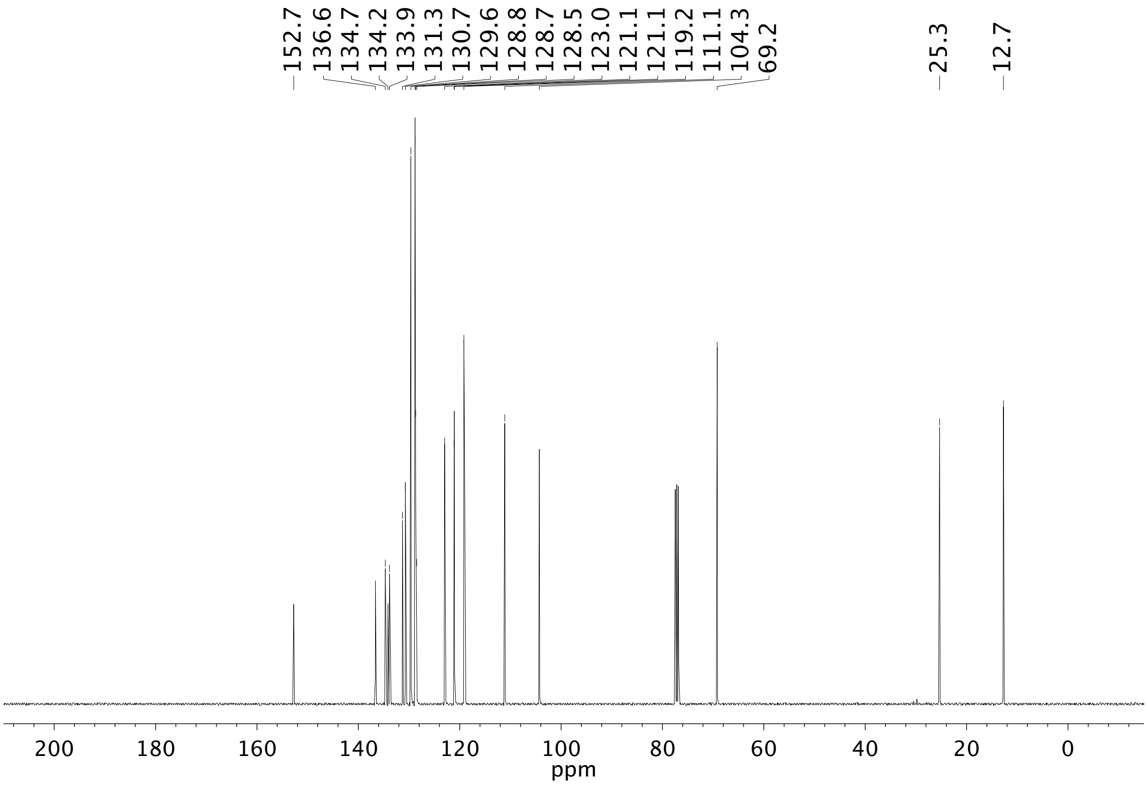
^{19}F NMR (282 MHz, CDCl$_3$) of compound **1h**.



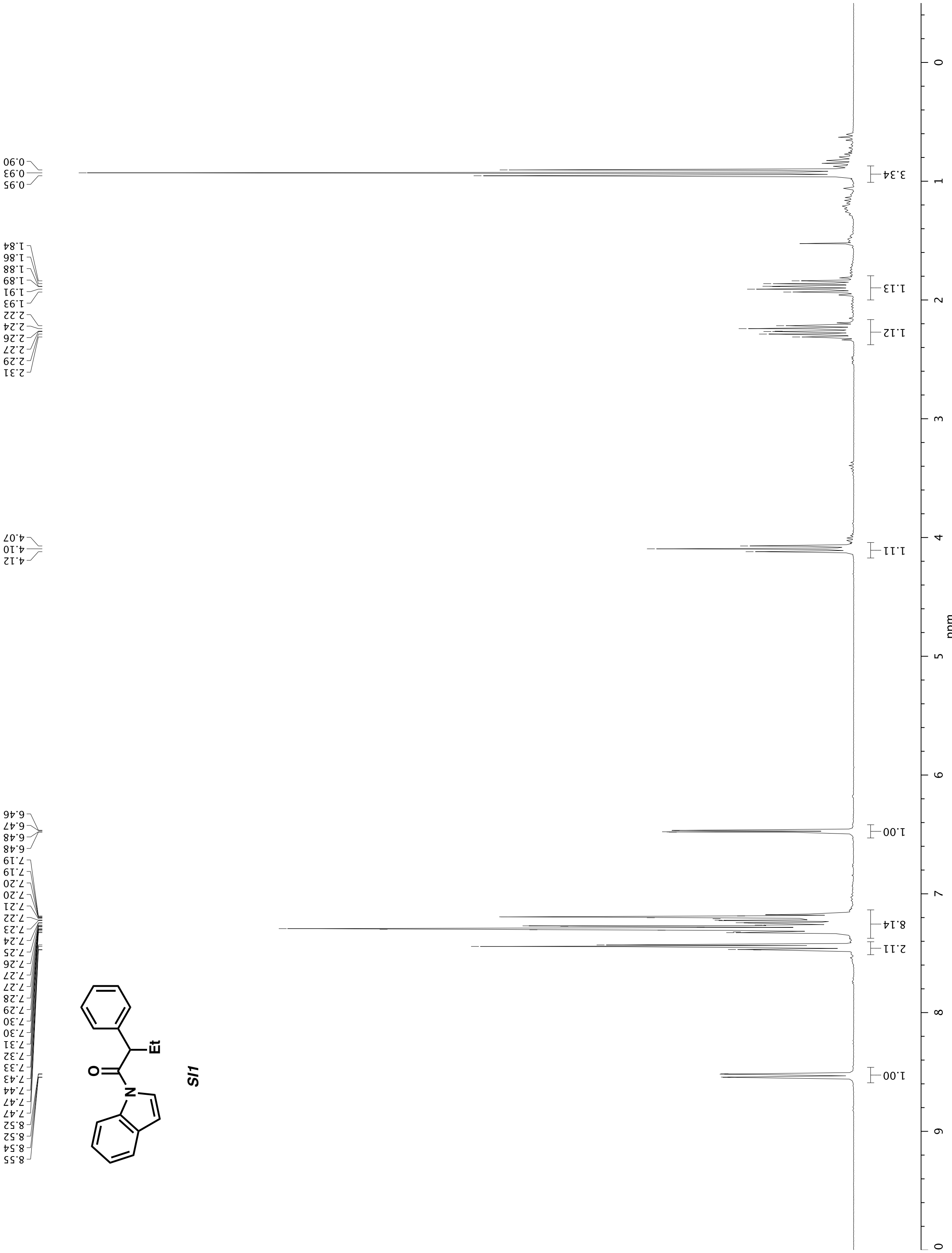
^{1}H NMR (400 MHz, CDCl$_3$) of compound **1i.**



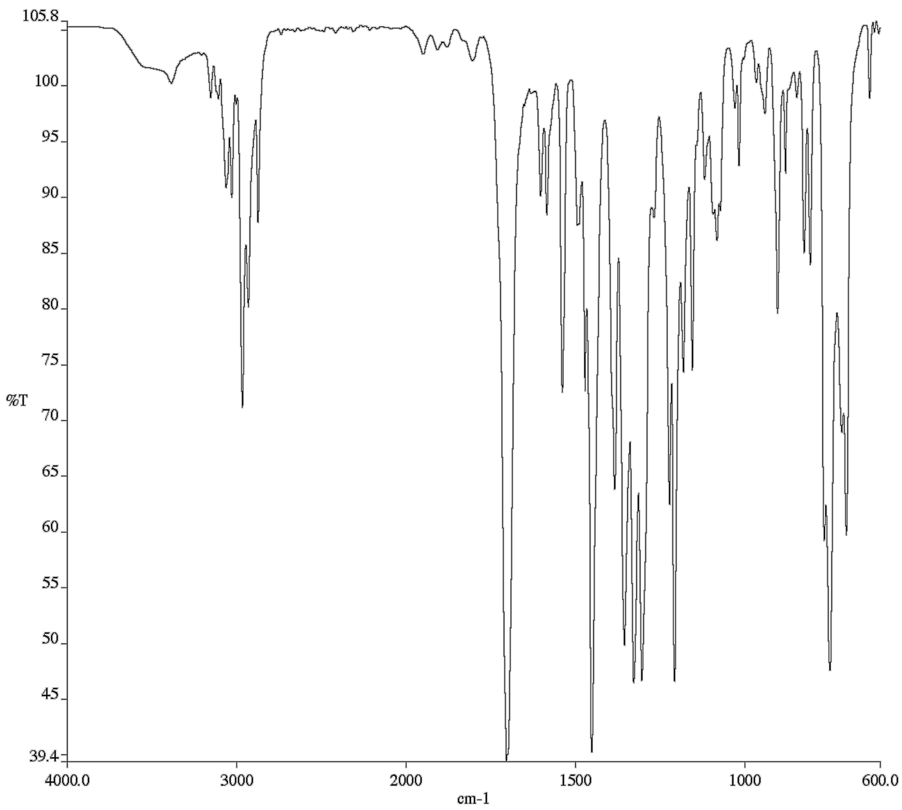
Infrared spectrum (Thin Film, NaCl) of compound **1i**.



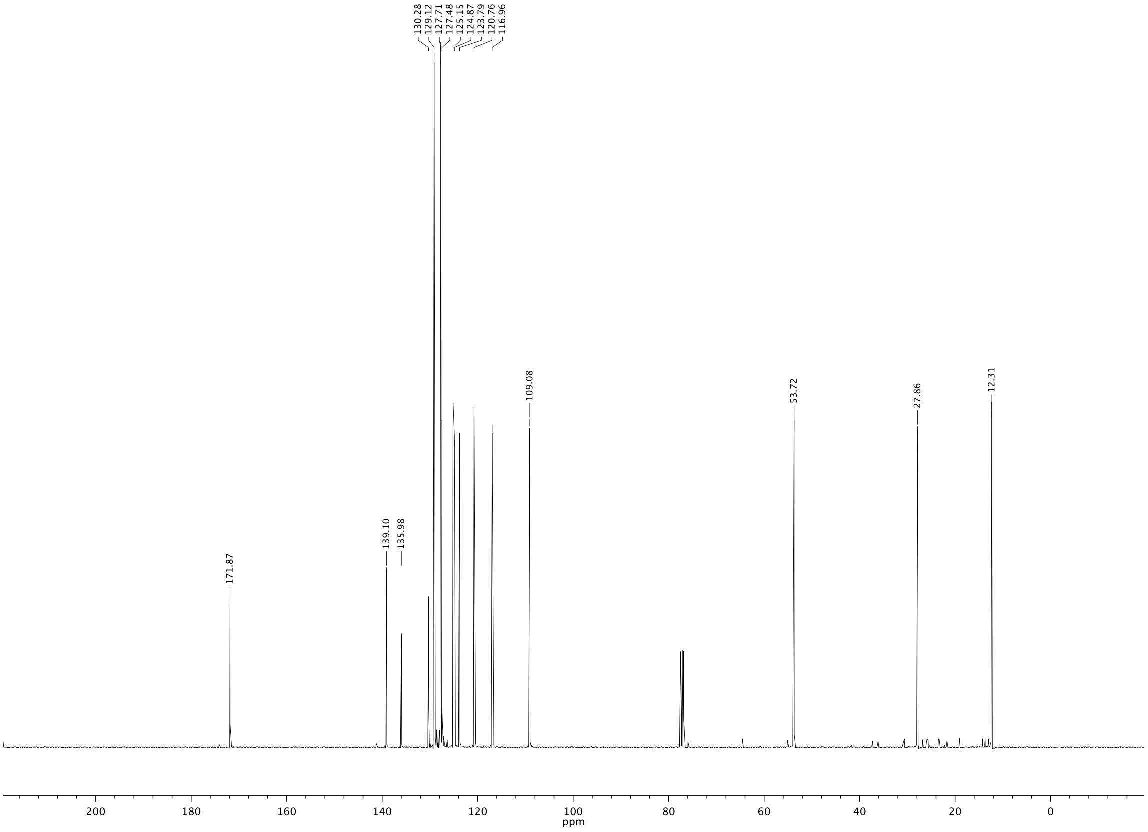
^{13}C NMR (100 MHz, CDCl$_3$) of compound **1i**.



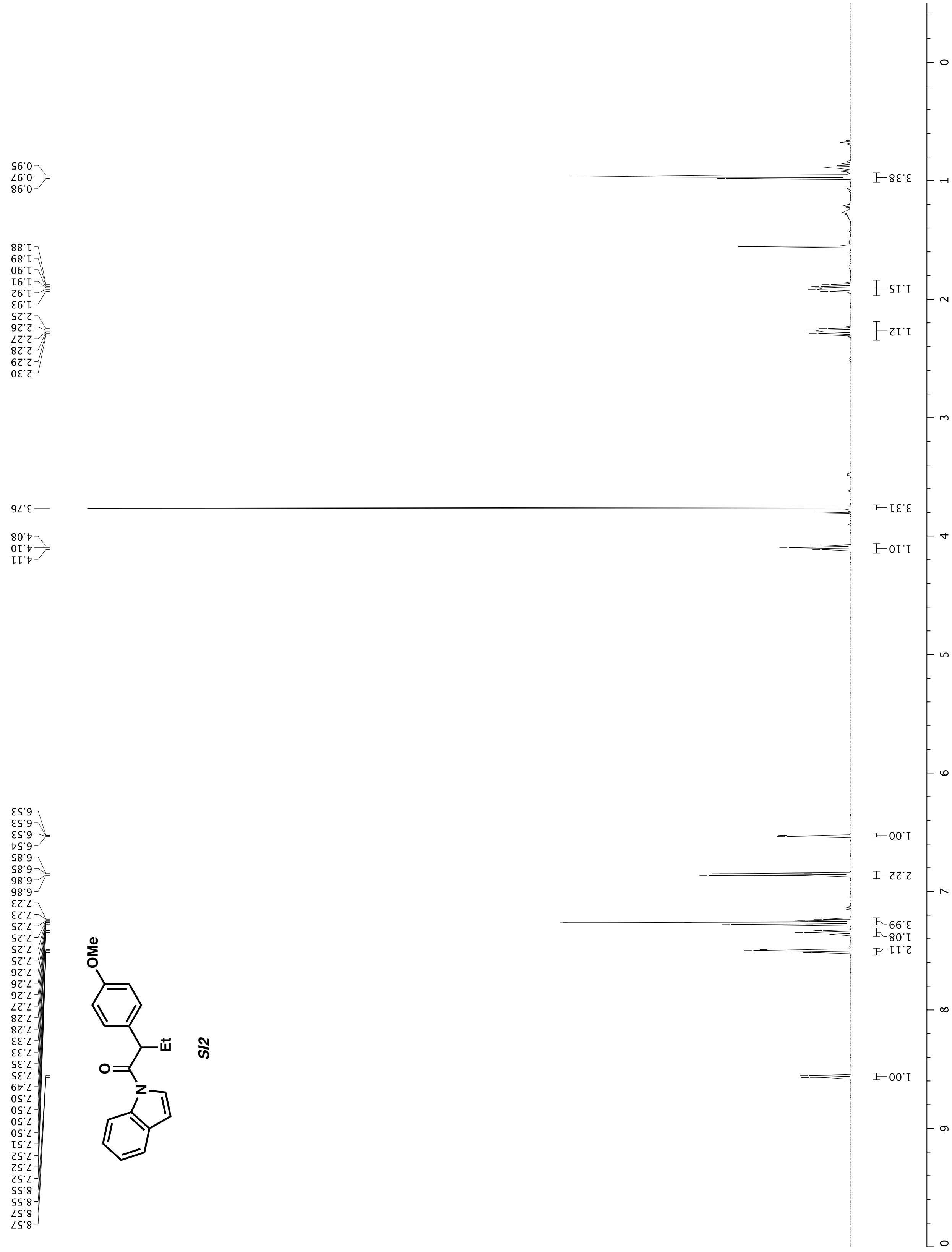
^{1}H NMR (300 MHz, CDCl$_3$) of compound **SI1.**



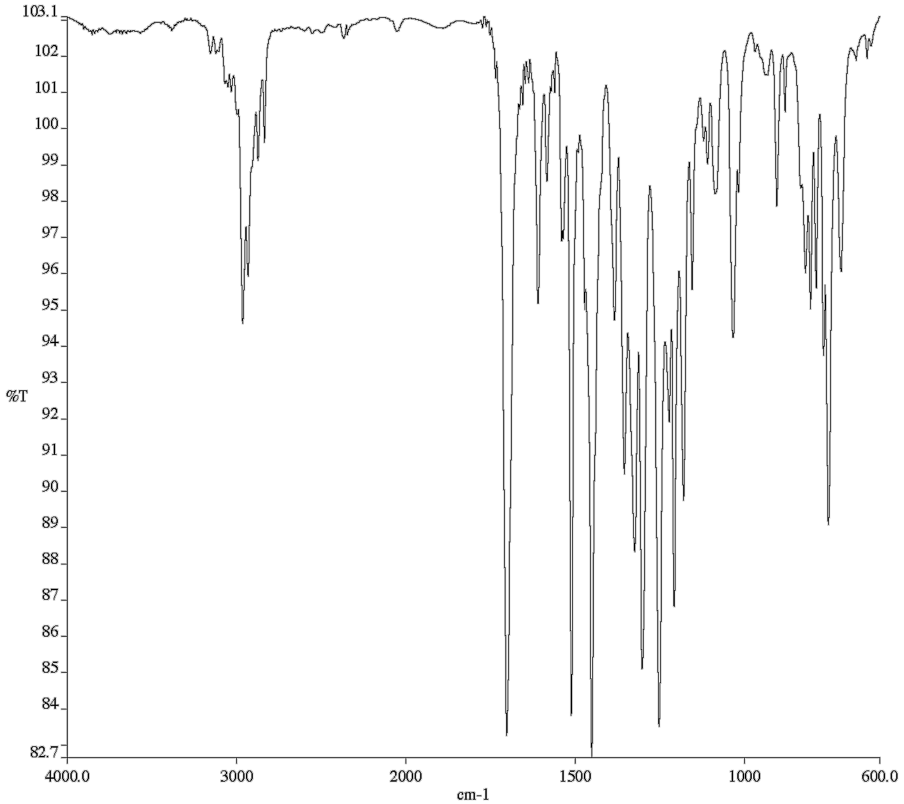
Infrared spectrum (Thin Film, NaCl) of compound **SI1**.



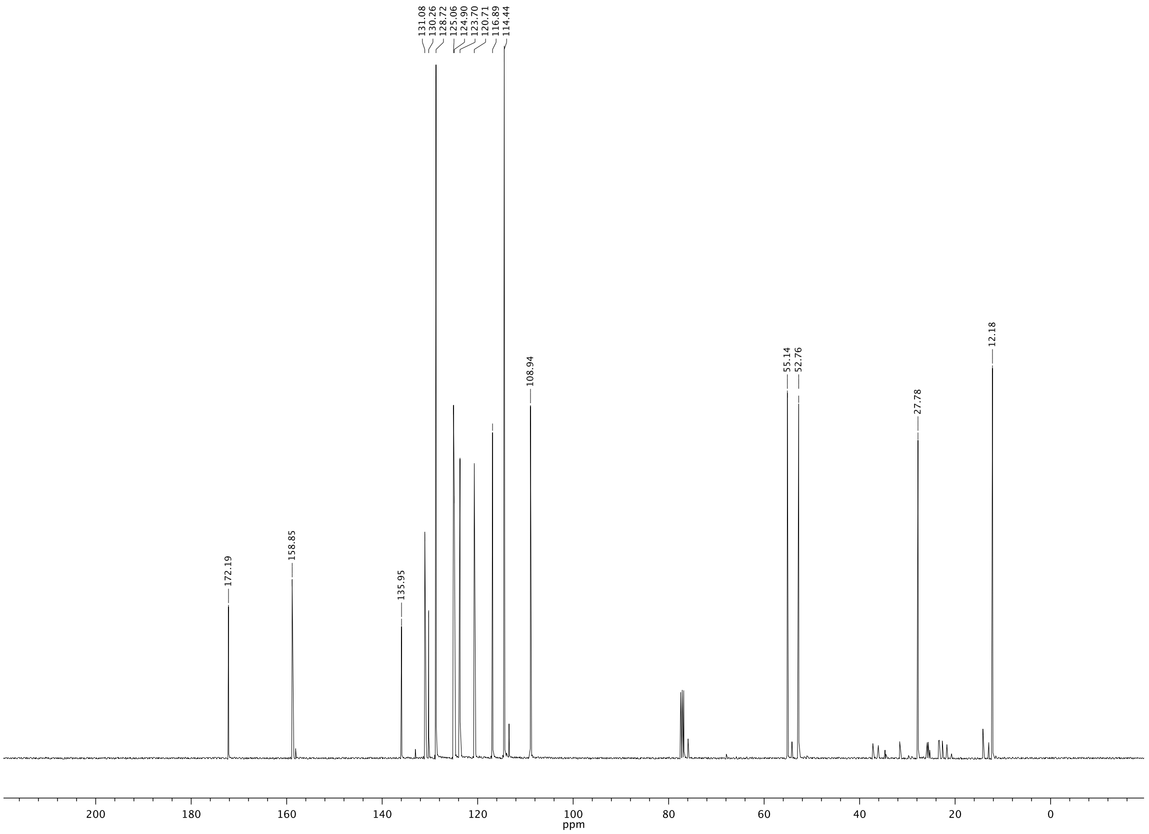
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI1**.



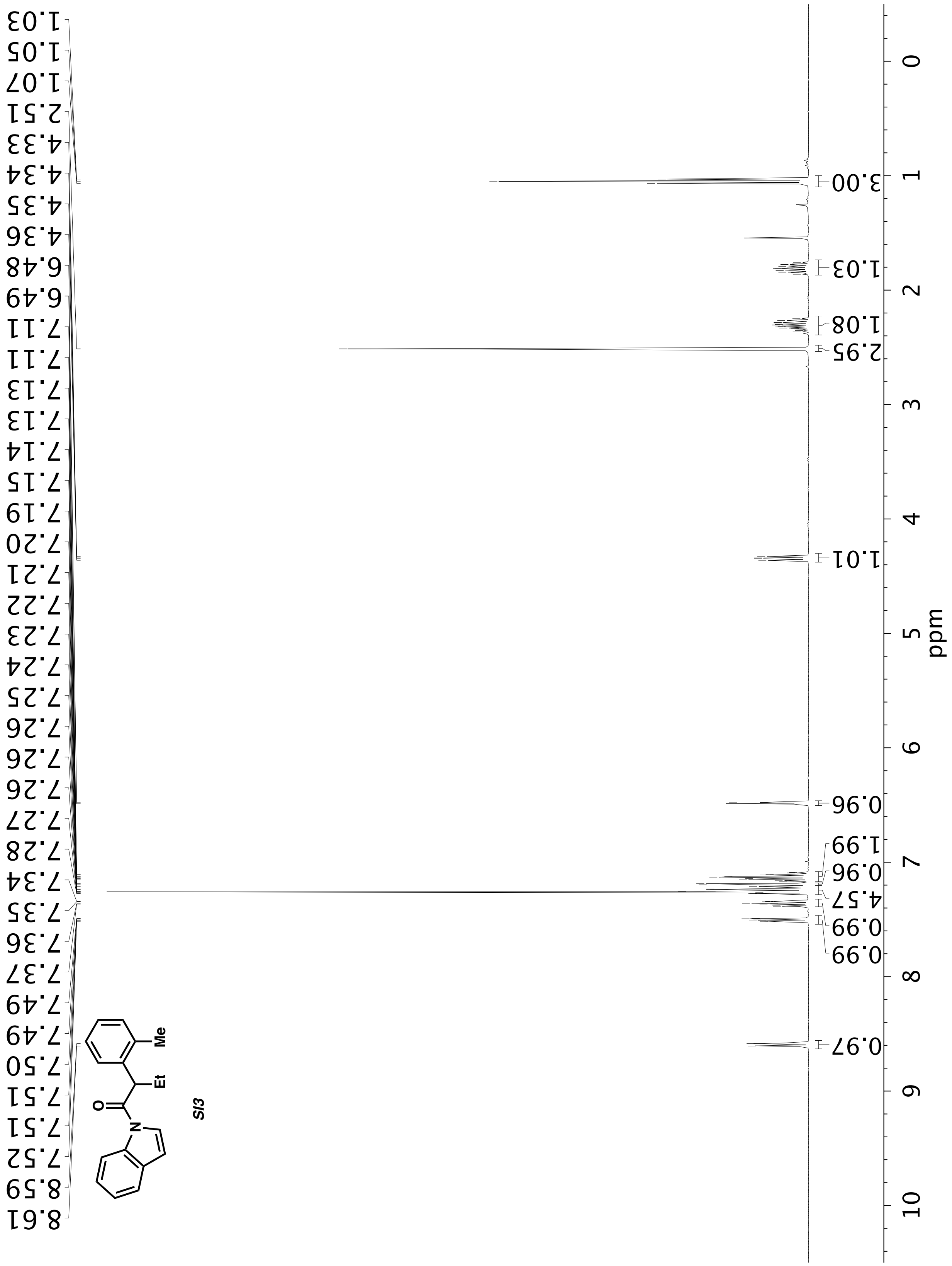
^{1}H NMR (500 MHz, CDCl$_3$) of compound **SI2.**



Infrared spectrum (Thin Film, NaCl) of compound **SI2**.

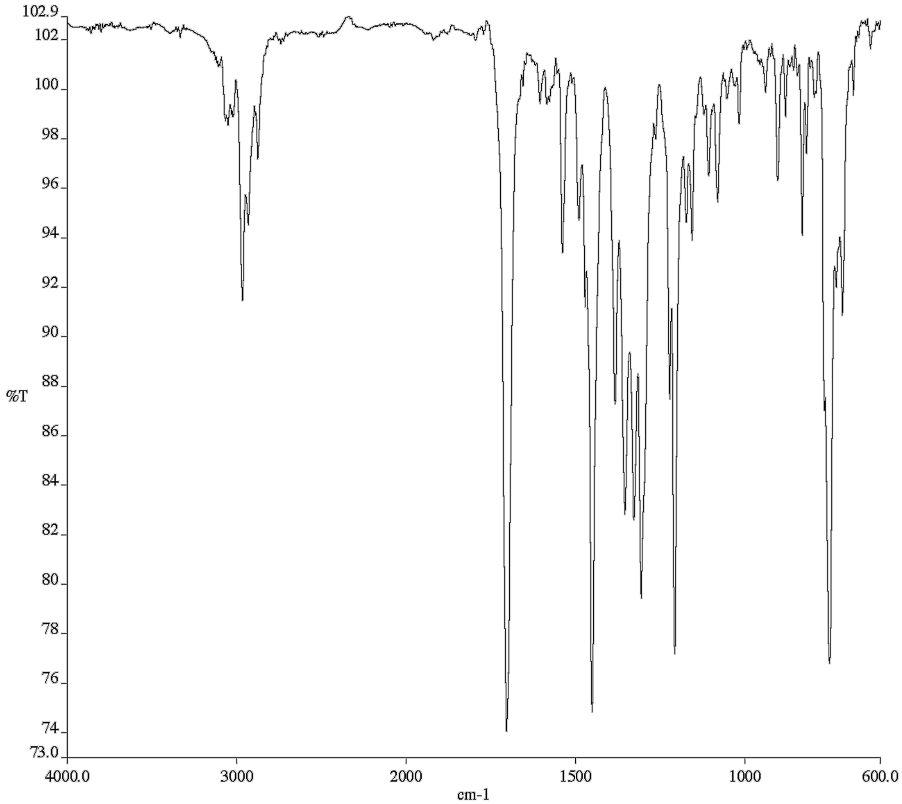


^{13}C NMR (100 MHz, CDCl$_3$) of compound **SI2**.

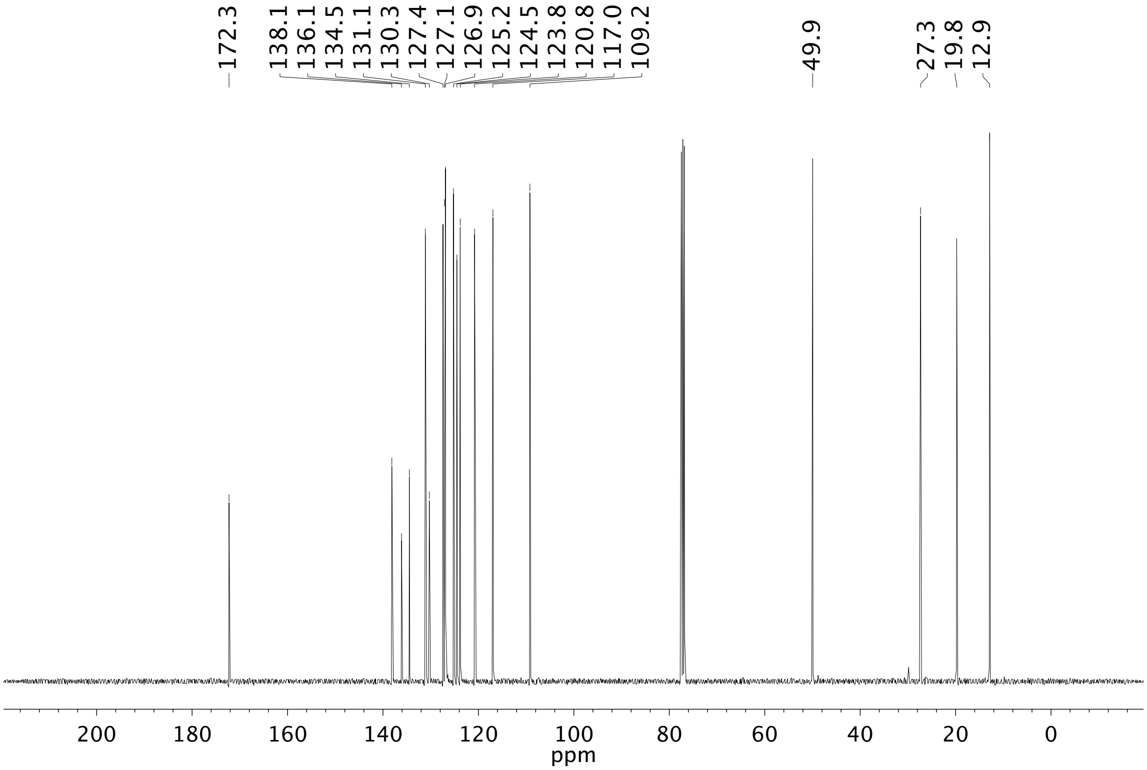


SI3

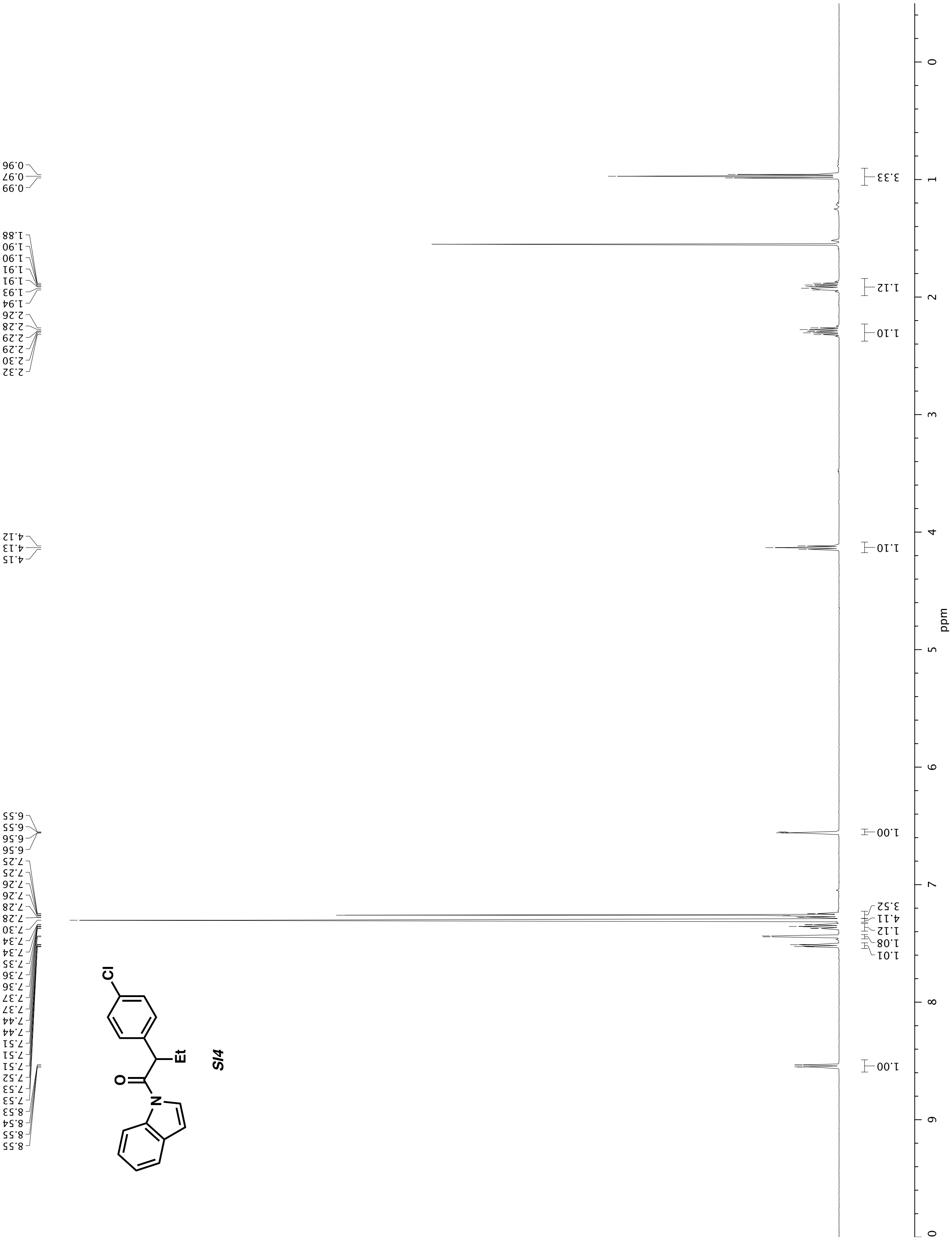
^{1}H NMR (400 MHz, CDCl$_3$) of compound **SI3**.



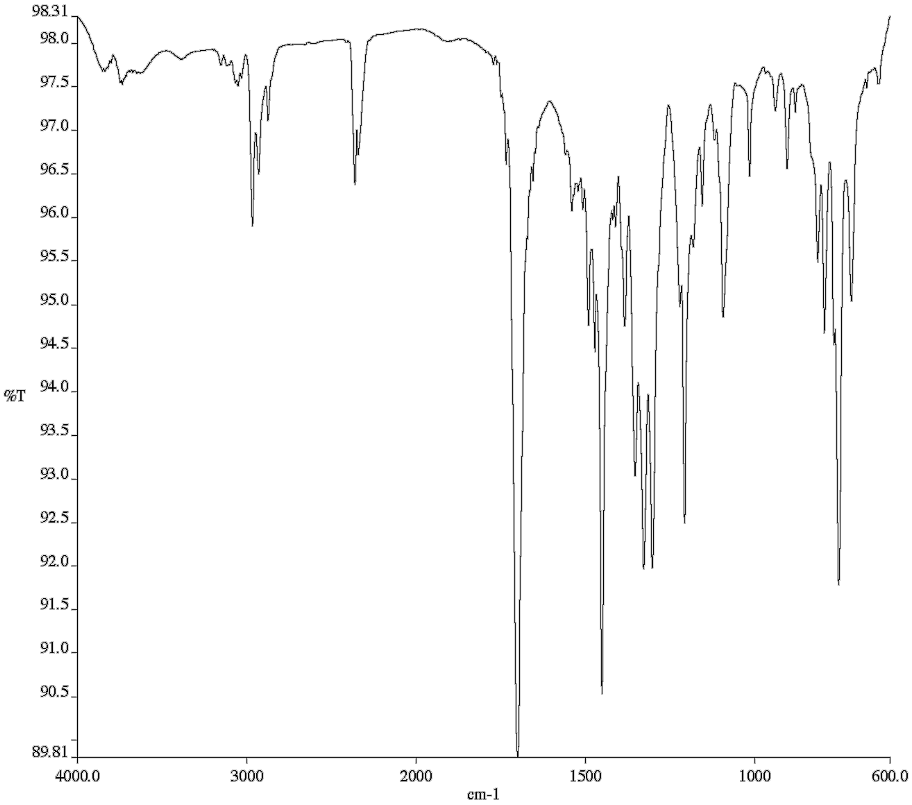
Infrared spectrum (Thin Film, NaCl) of compound **SI3**.



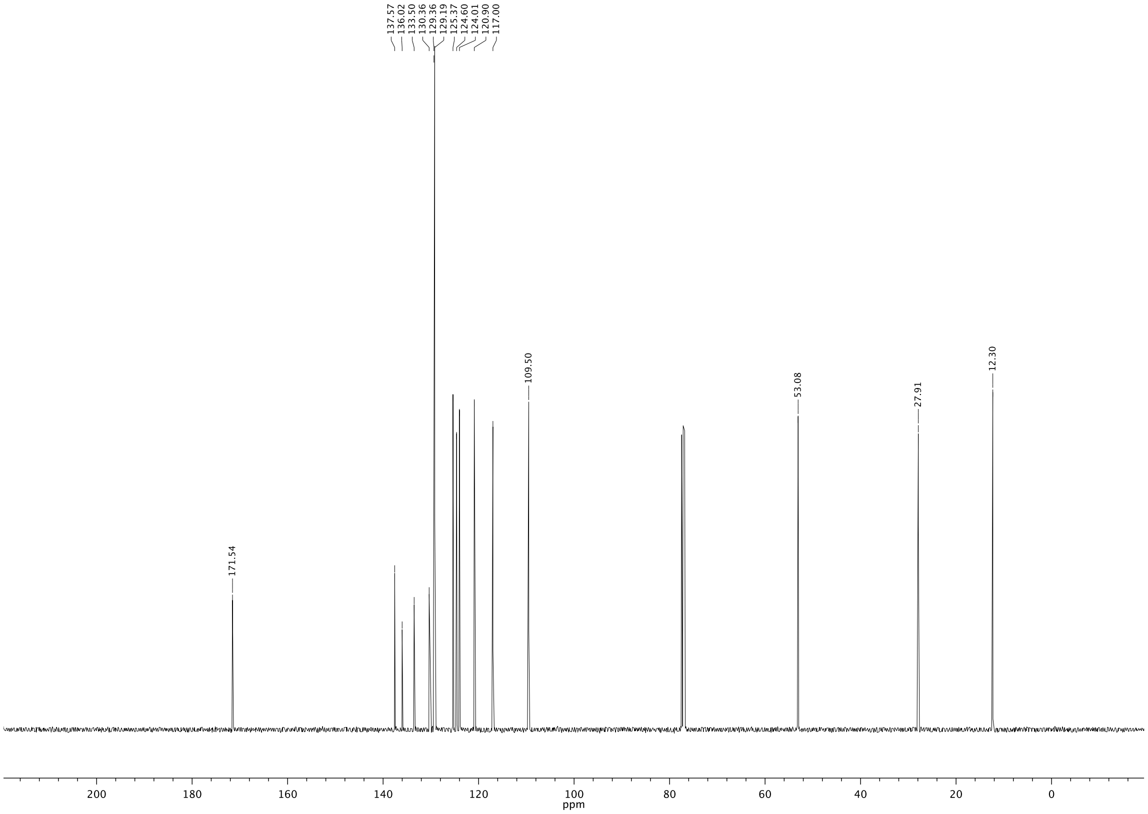
^{13}C NMR (100 MHz, CDCl$_3$) of compound **SI3**.



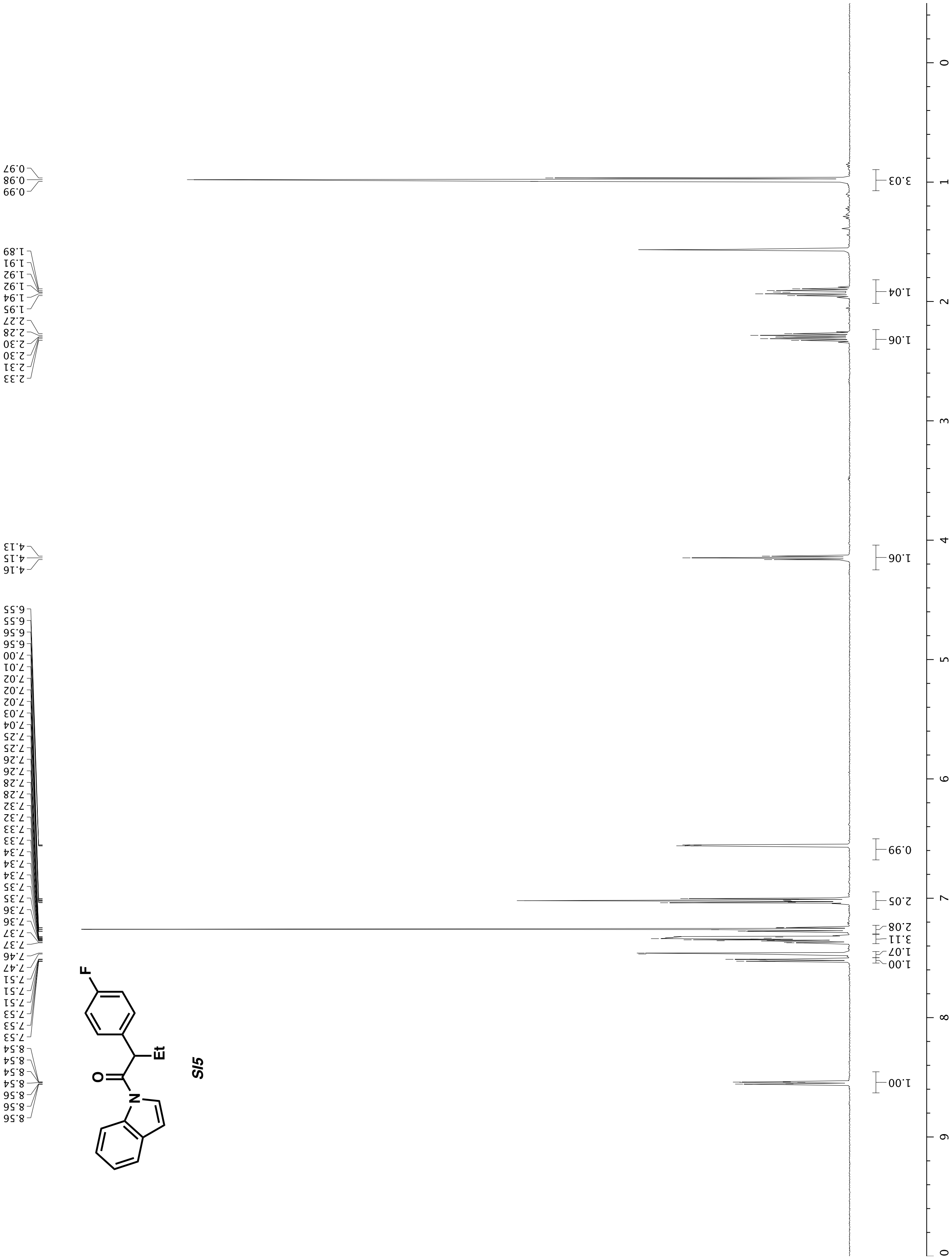
^{1}H NMR (500 MHz, CDCl$_3$) of compound **SI4**.



Infrared spectrum (Thin Film, NaCl) of compound **SI4**.

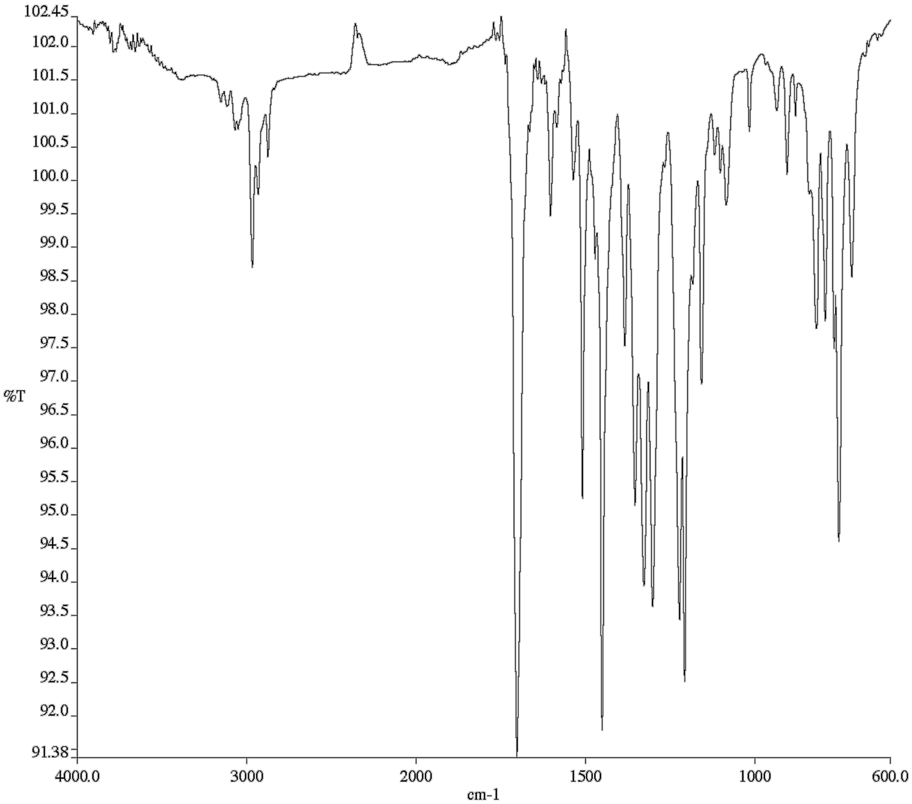


^{13}C NMR (100 MHz, CDCl$_3$) of compound **SI4**.

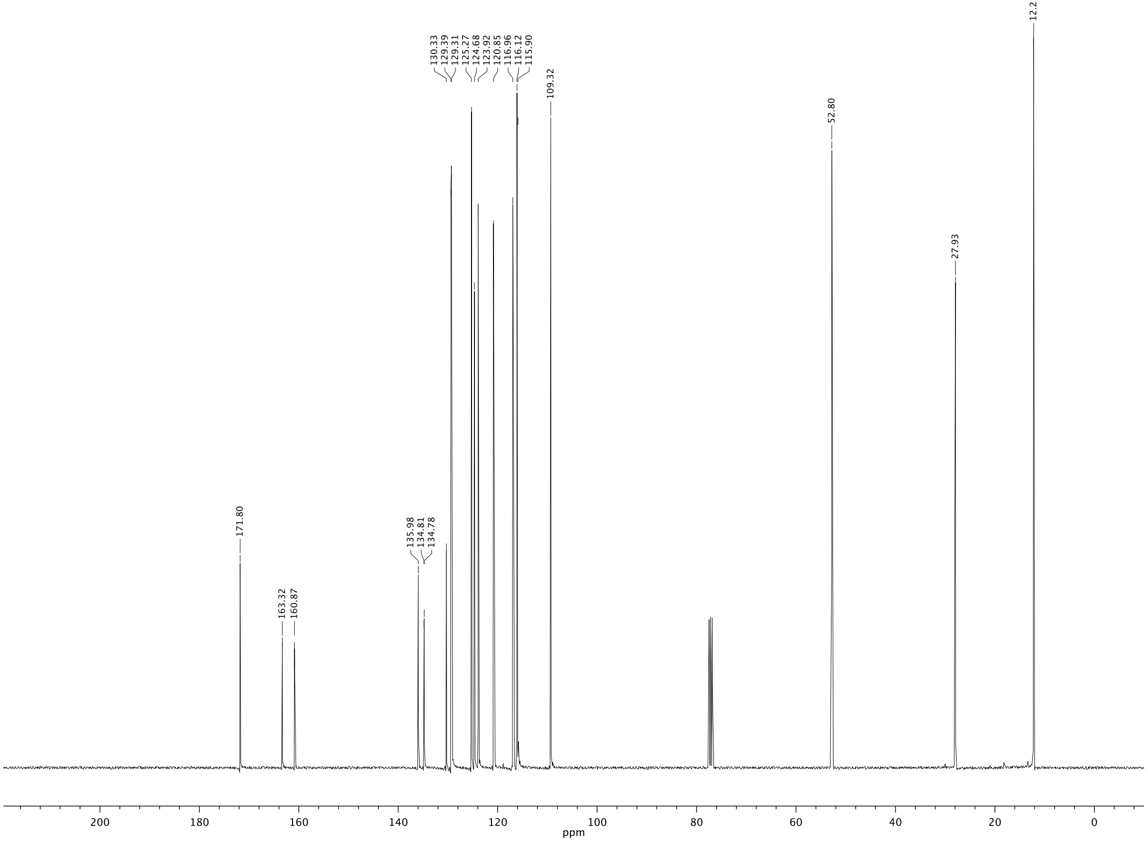


SI5

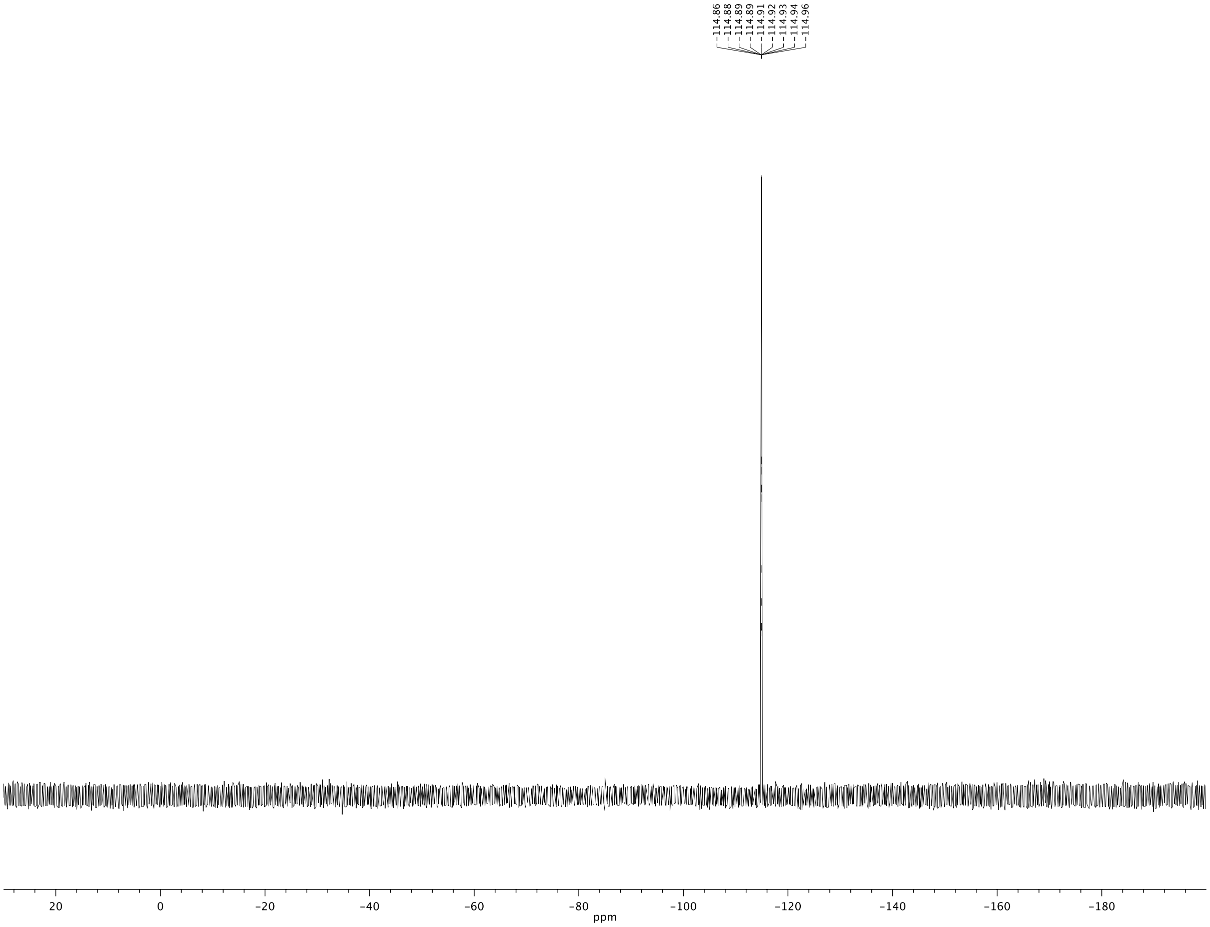
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI5.**



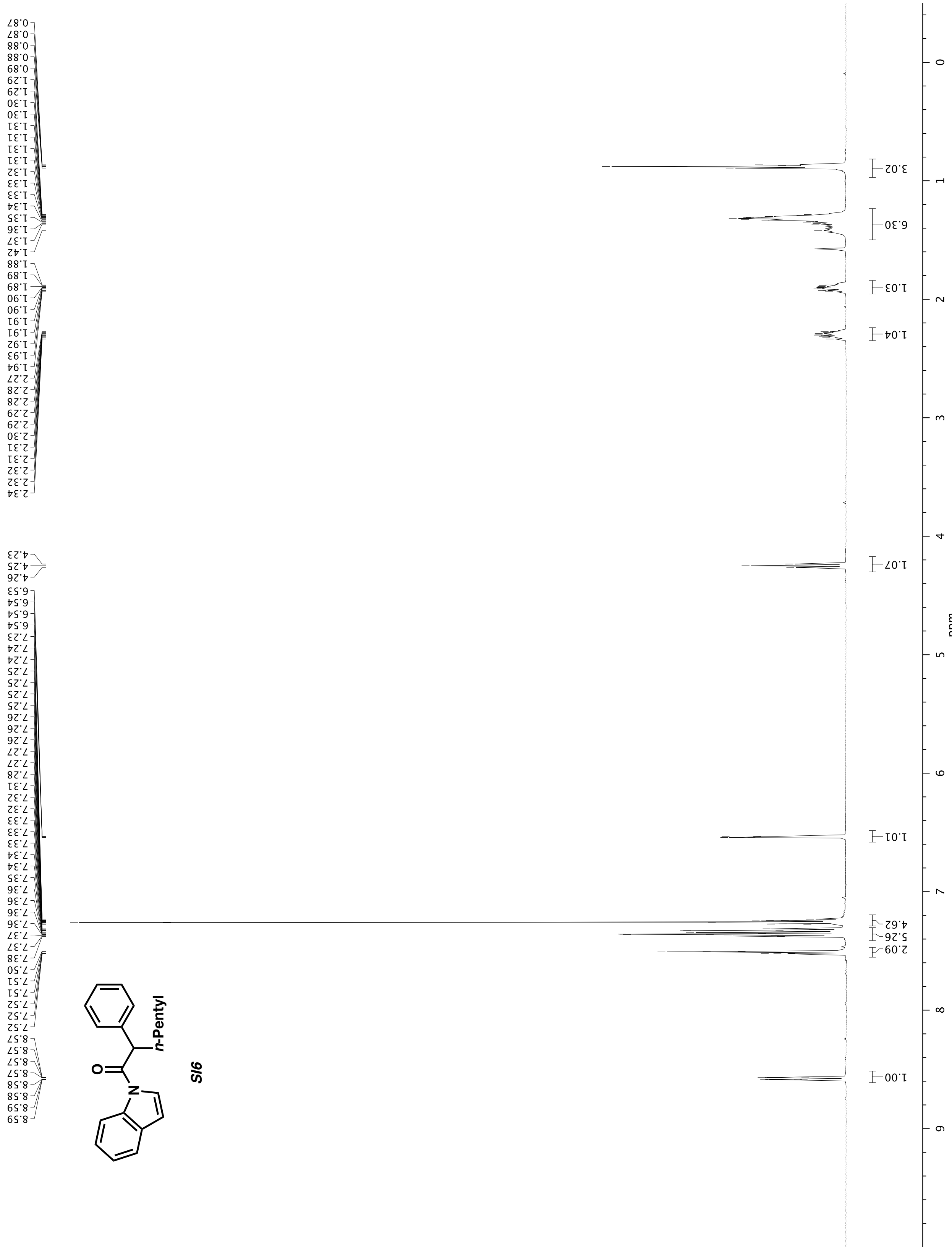
Infrared spectrum (Thin Film, NaCl) of compound **SI5**.



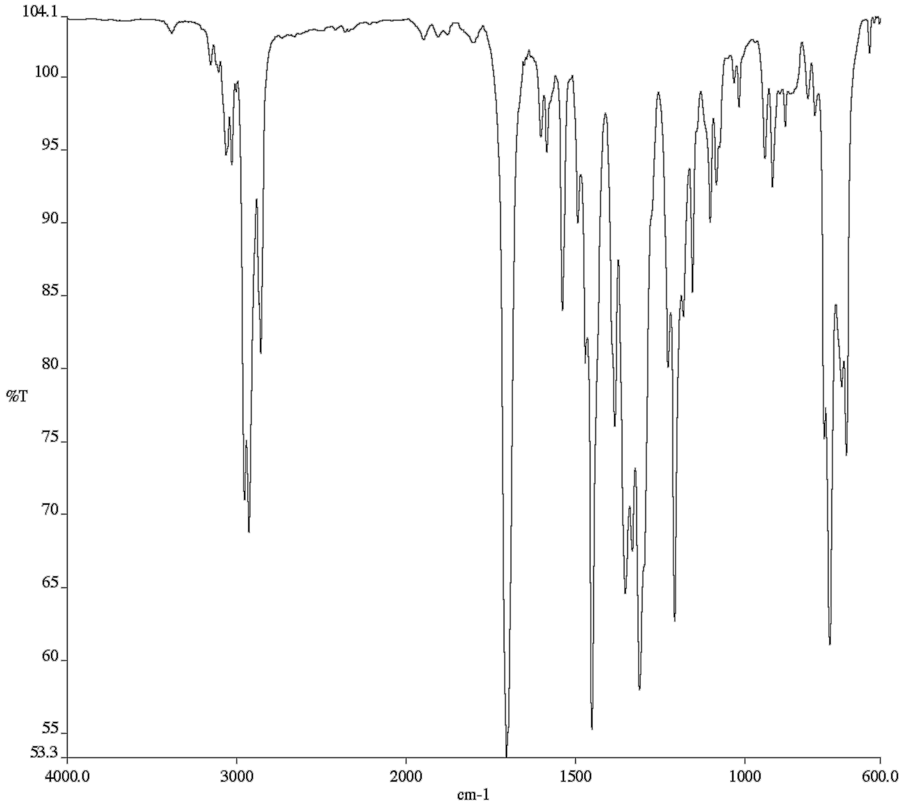
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI5**.



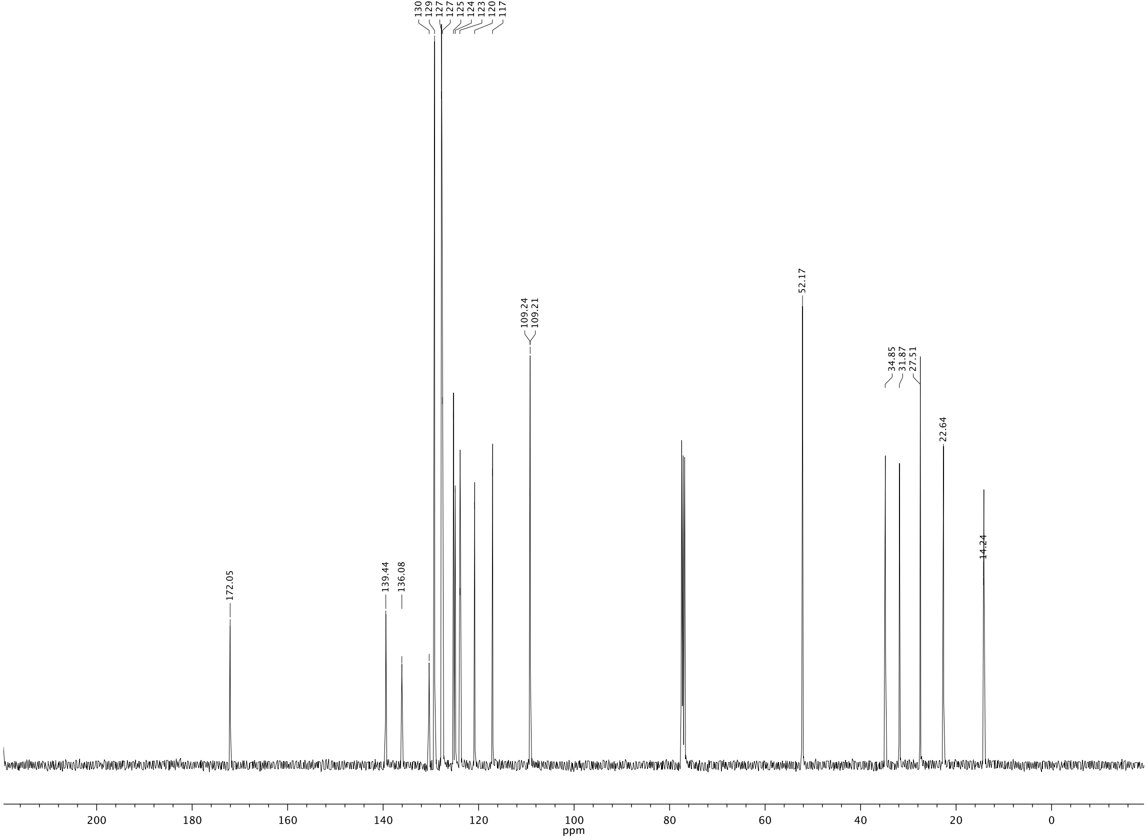
^{19}F NMR (282 MHz, CDCl$_3$) of compound **SI5.**



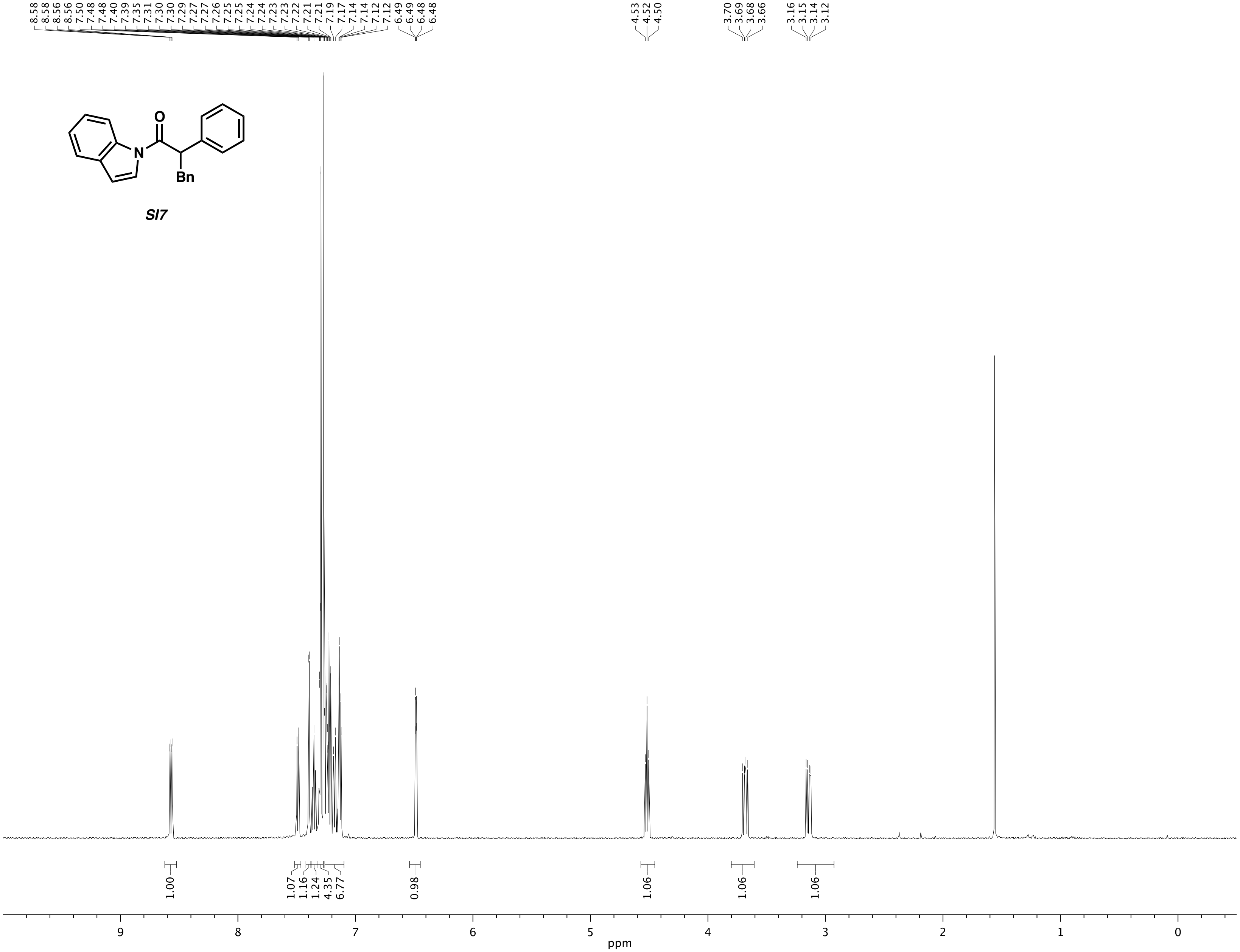
^{1}H NMR (400 MHz, CDCl$_3$) of compound **SI6.**
]



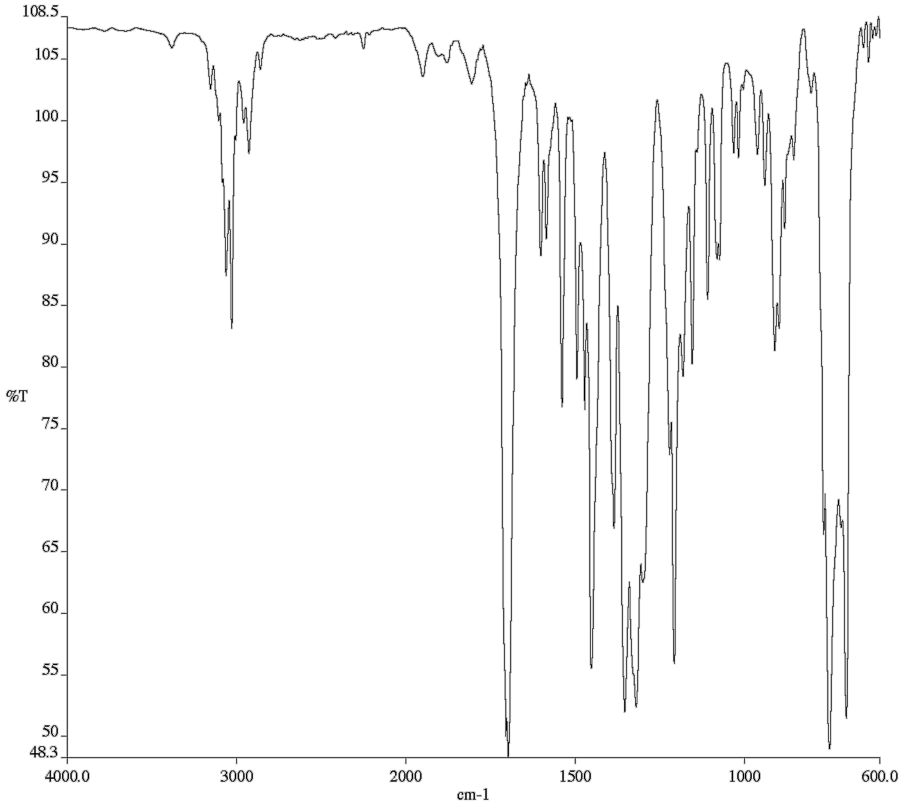
Infrared spectrum (Thin Film, NaCl) of compound **SI6**.



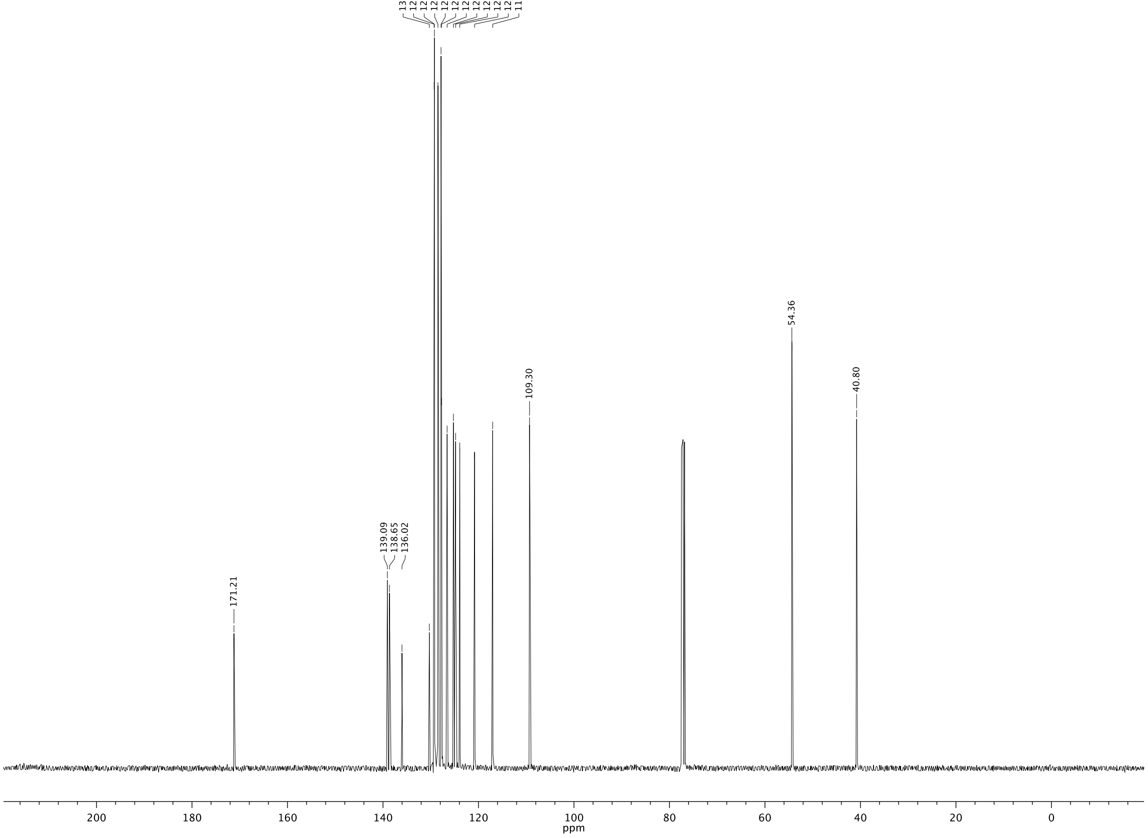
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI6**.



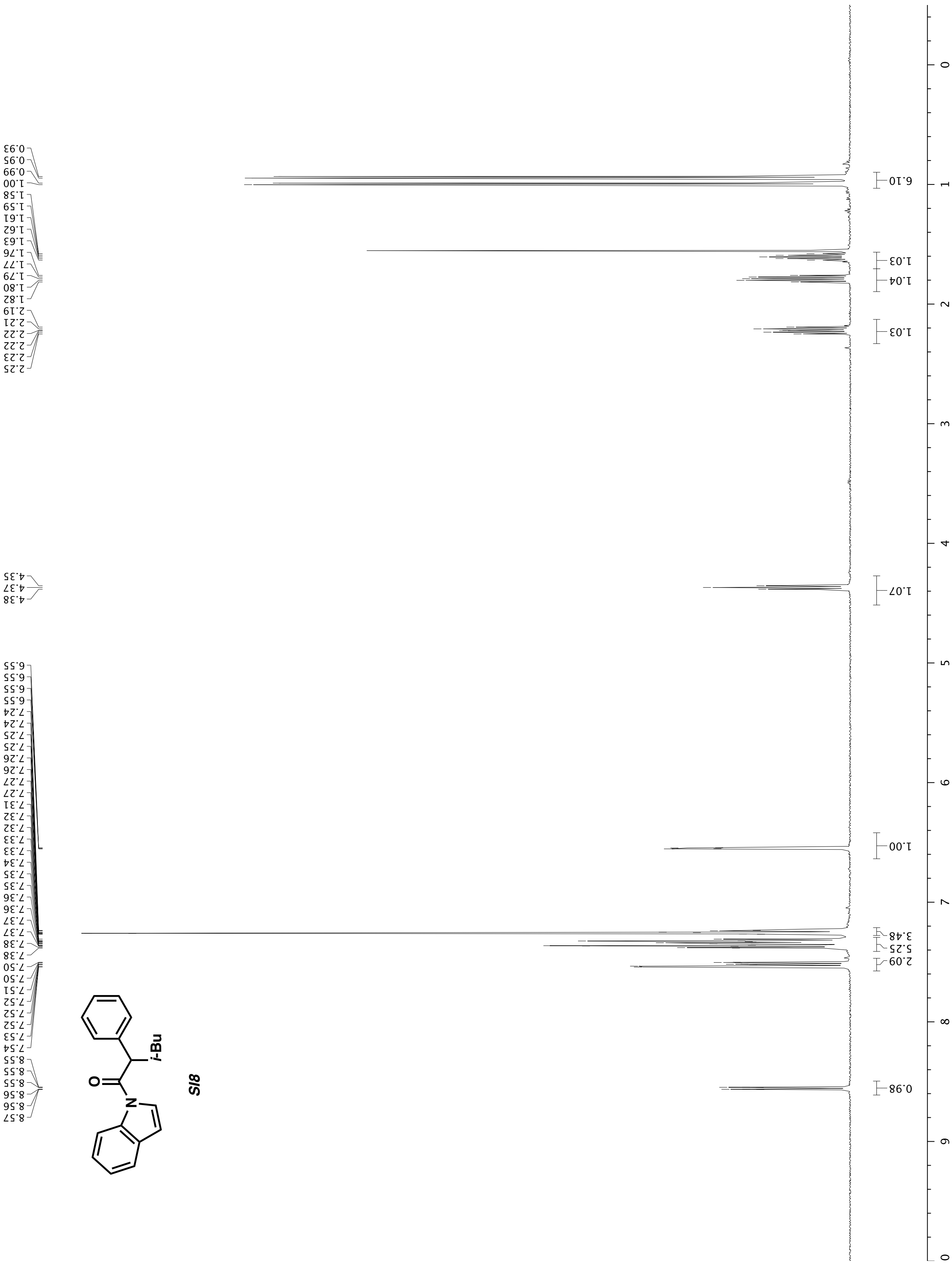
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI7**.



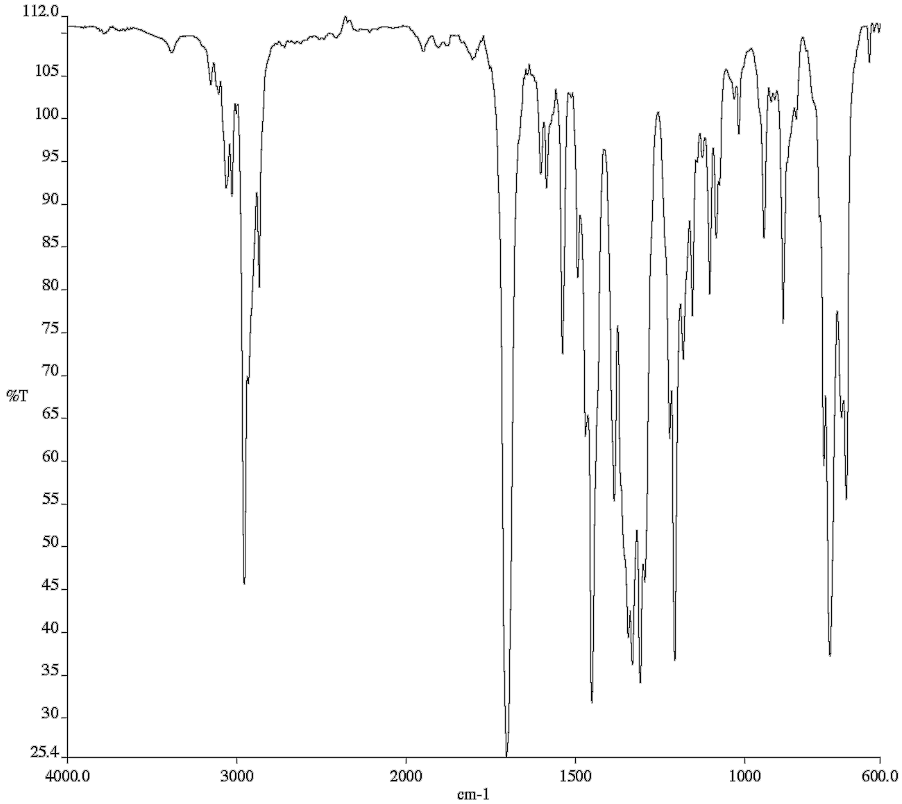
Infrared spectrum (Thin Film, NaCl) of compound **SI7**.



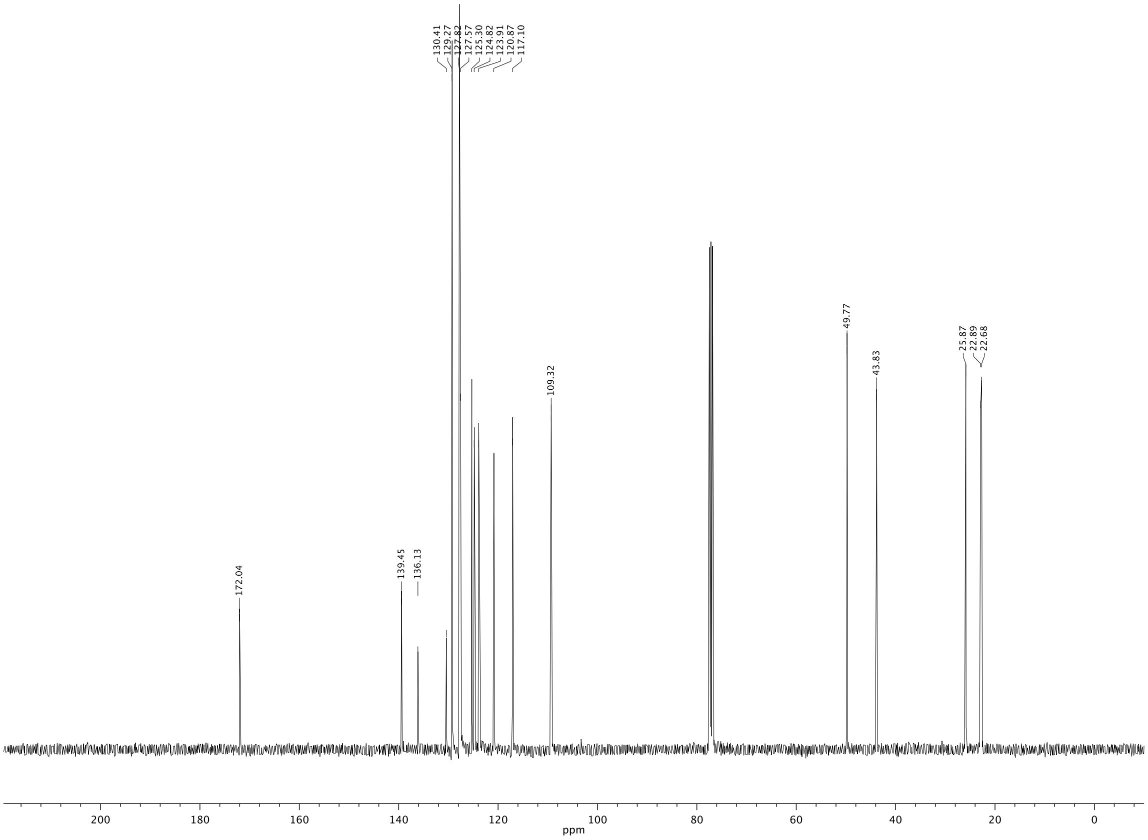
^{13}C NMR (100 MHz, CDCl$_3$) of compound **SI7**.



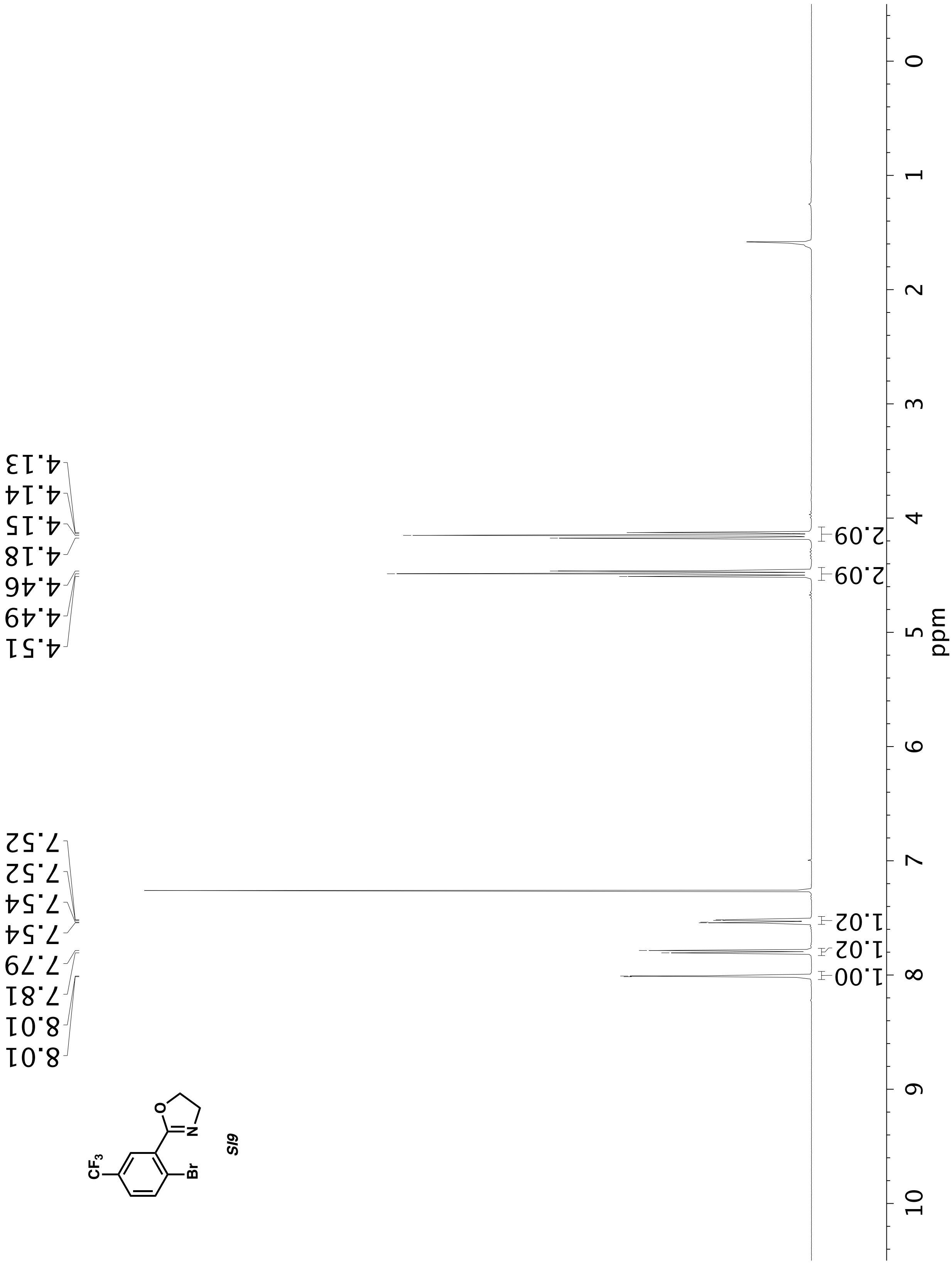
^{1}H NMR (500 MHz, CDCl$_3$) of compound **SI8.**



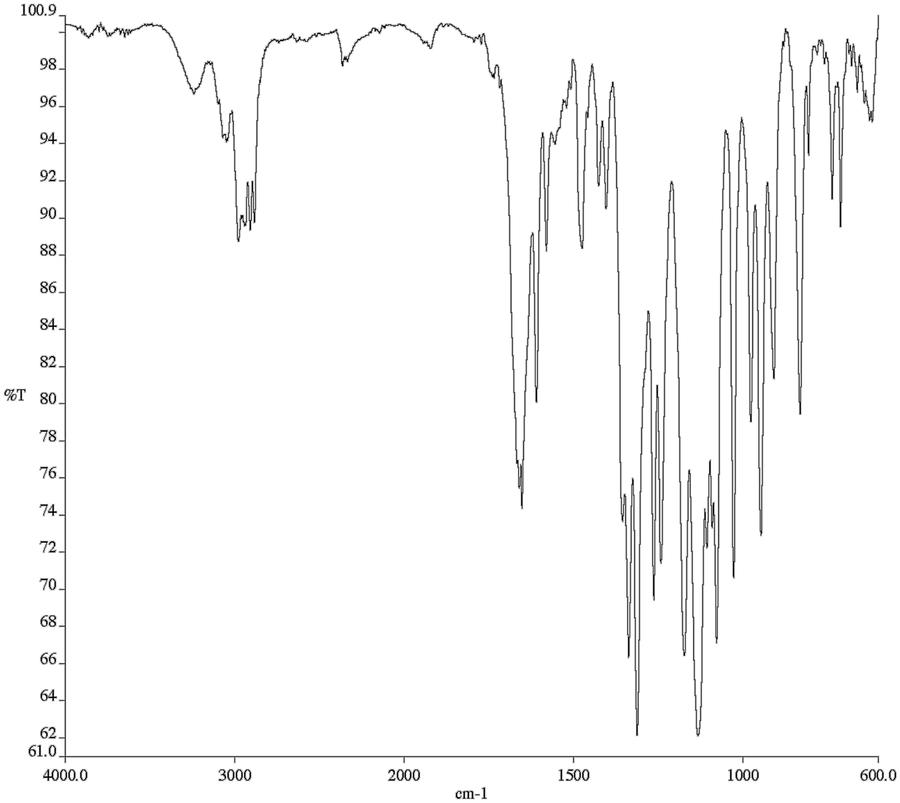
Infrared spectrum (Thin Film, NaCl) of compound **SI8**.



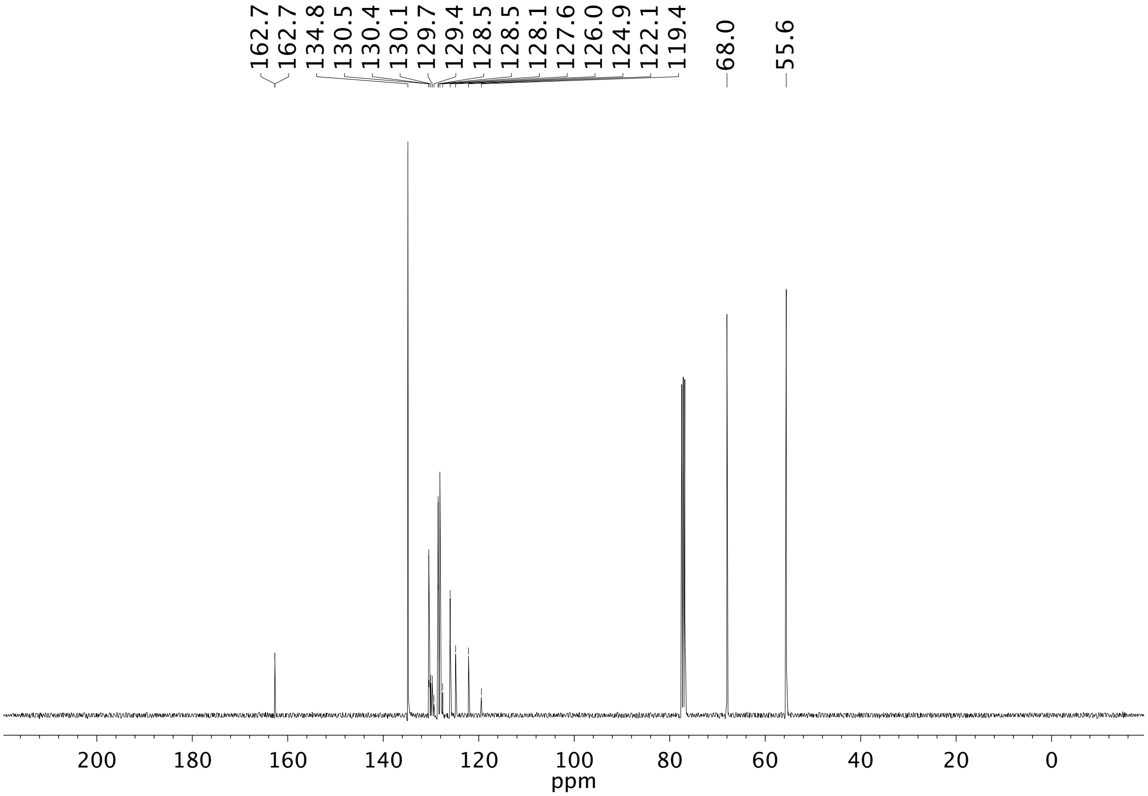
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI8**.



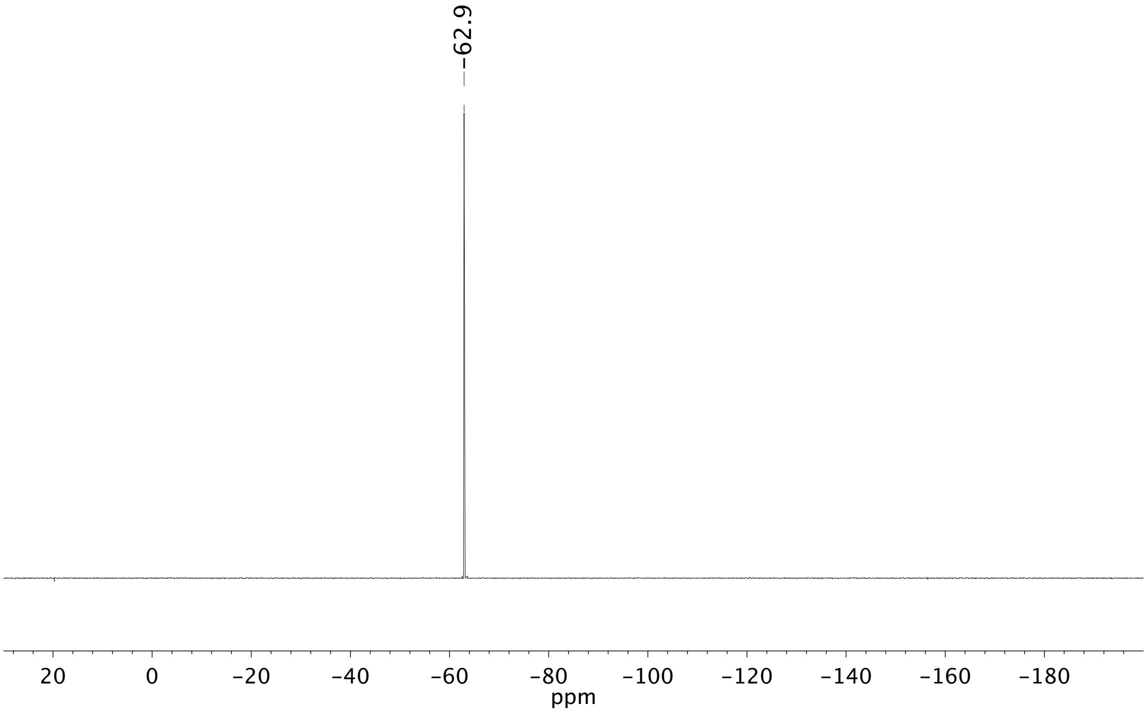
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI9**.



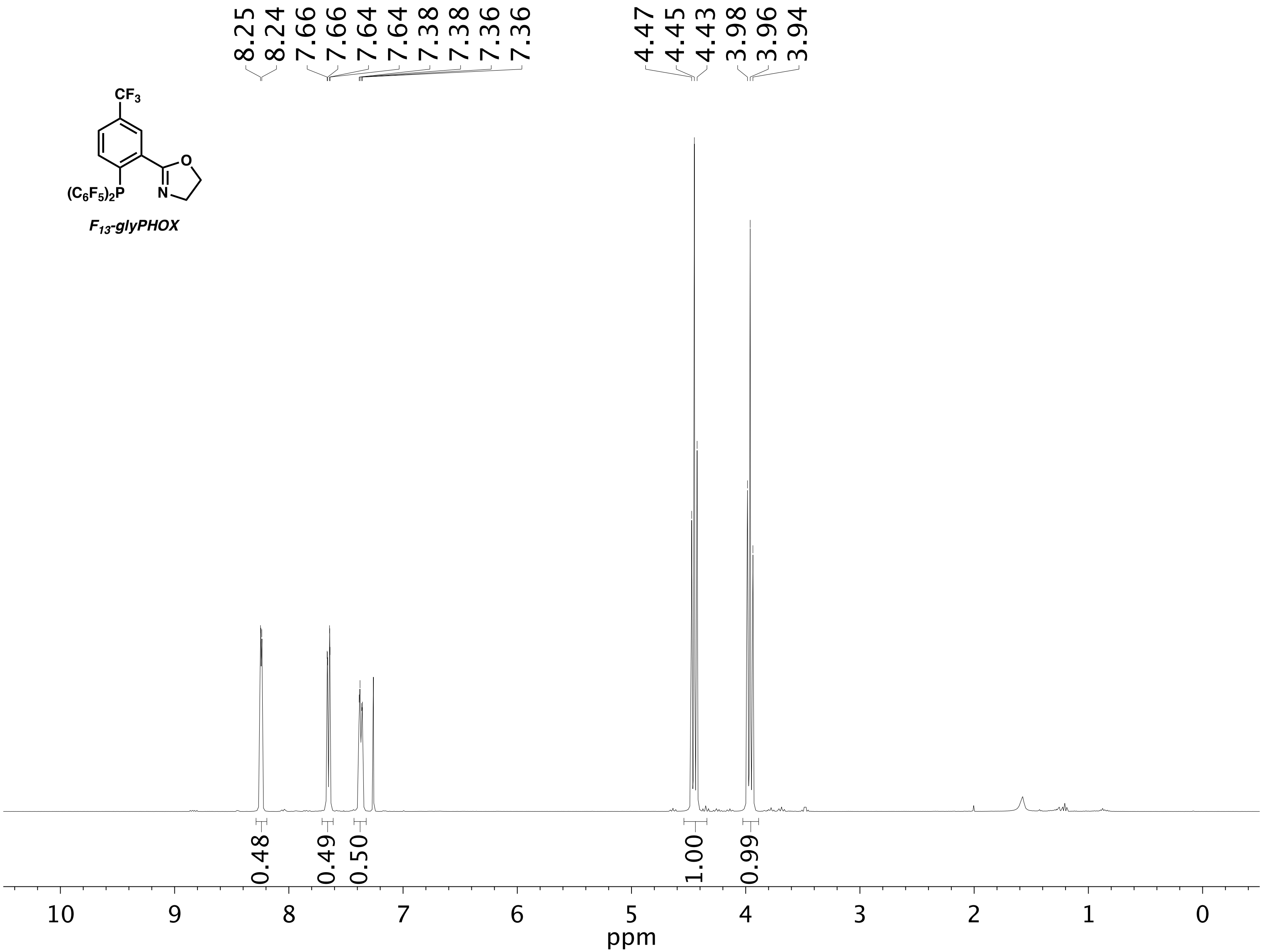
Infrared spectrum (Thin Film, NaCl) of compound **SI9**.



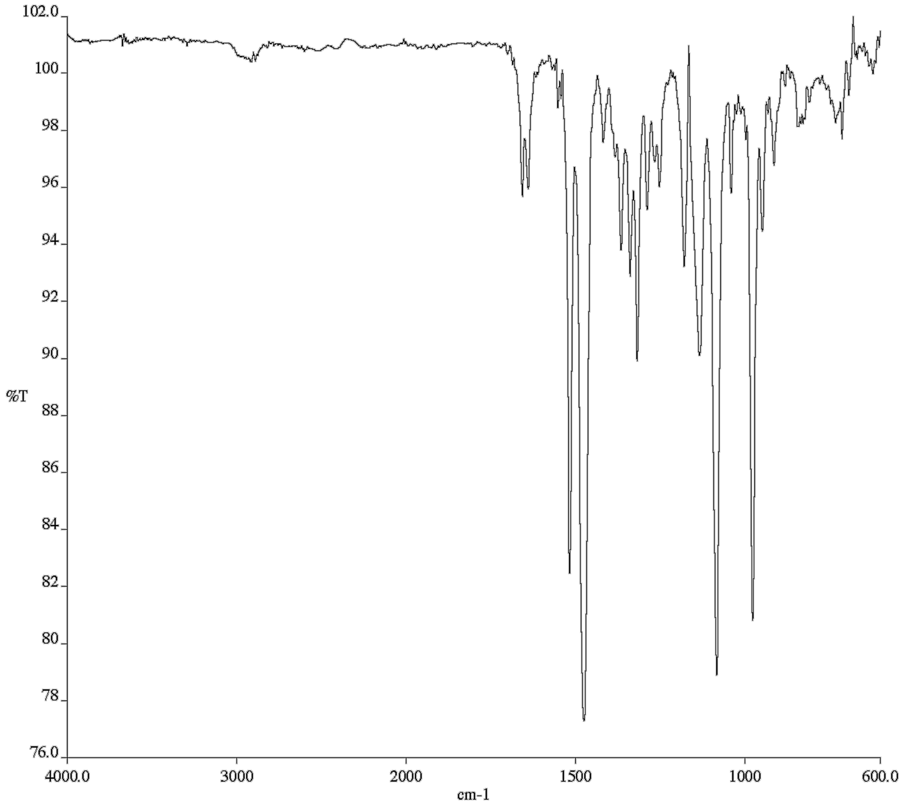
^{13}C NMR (100 MHz, CDCl$_3$) of compound **SI9**.



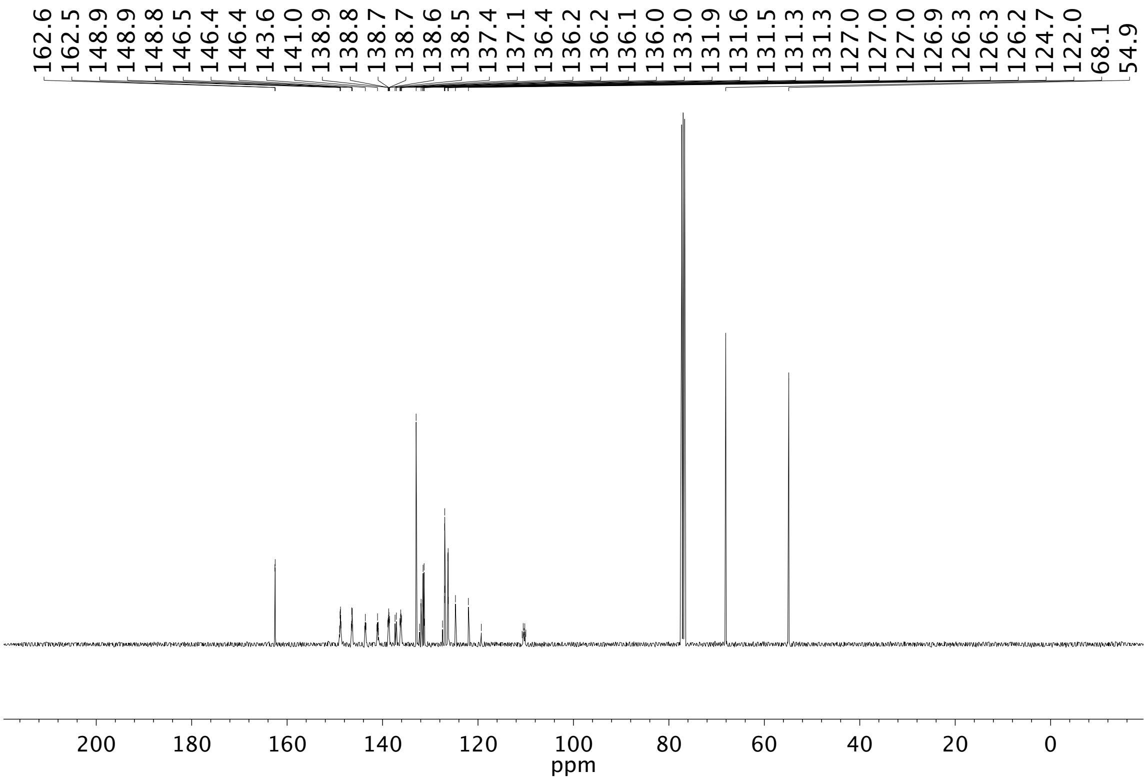
^{19}F NMR (282 MHz, $CDCl_3$) of compound **SI9**.



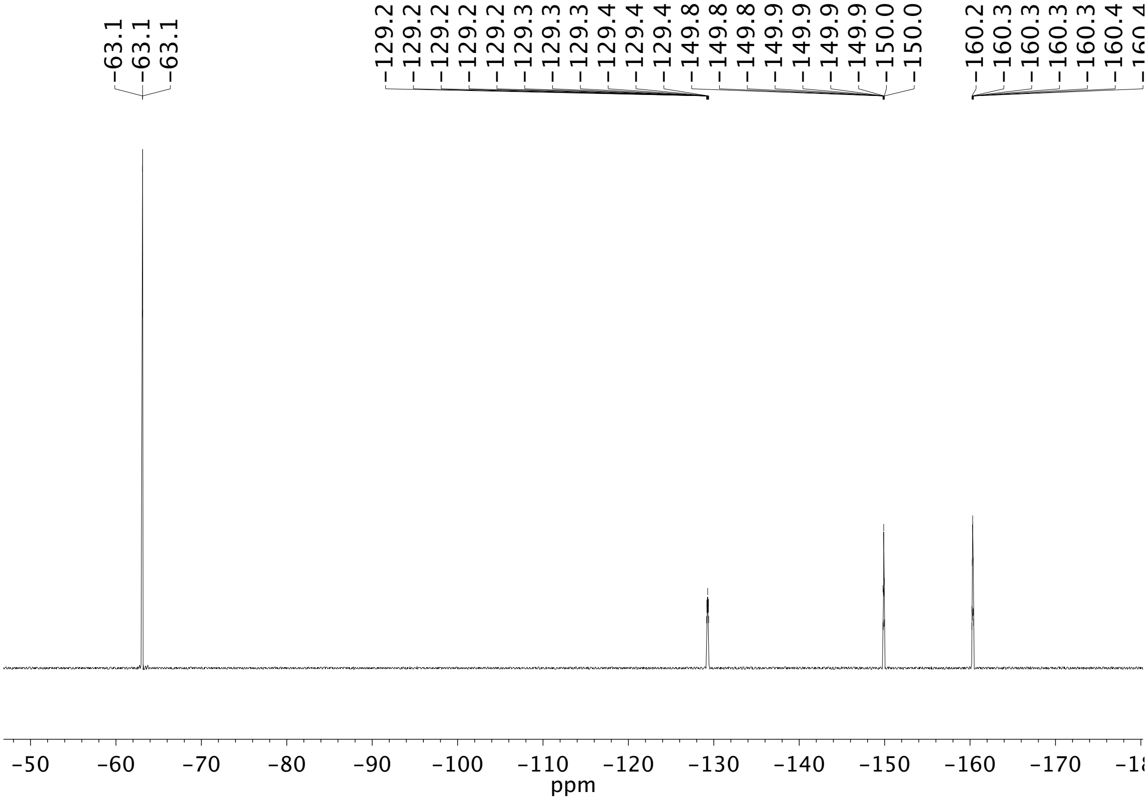
^{1}H NMR (400 MHz, $CDCl_3$) of compound **F_{13}-glyPHOX**.



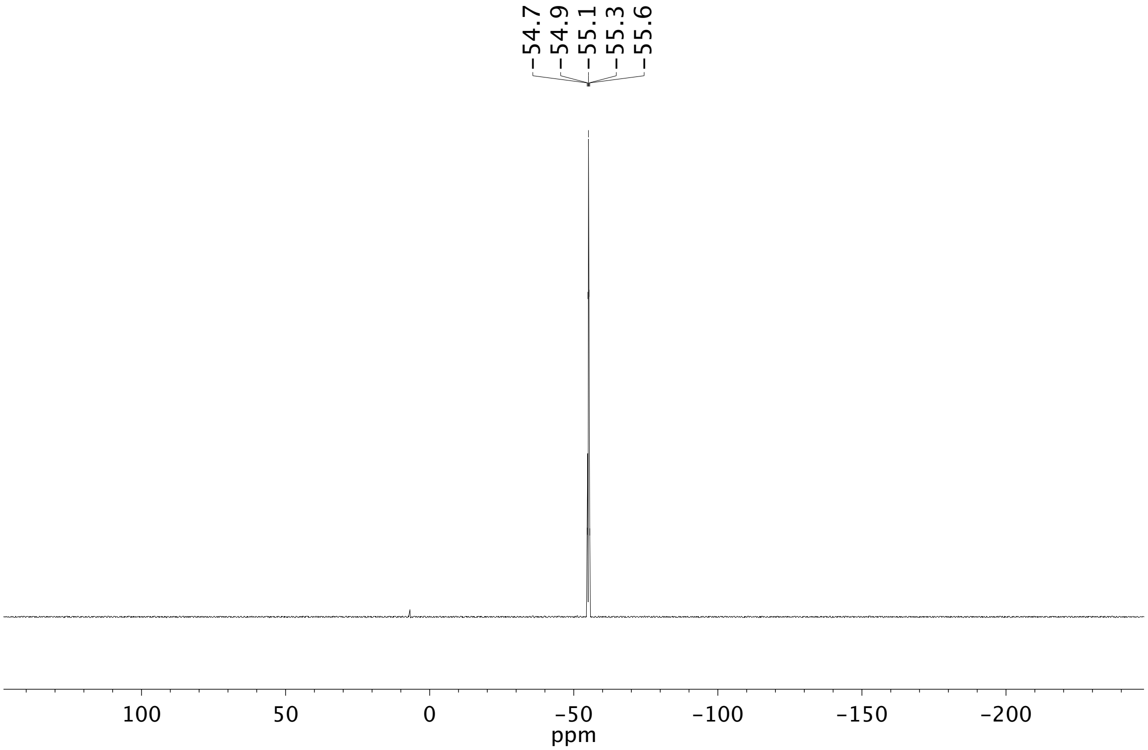
Infrared spectrum (Thin Film, NaCl) of compound **F_{13}-glyPHOX**.



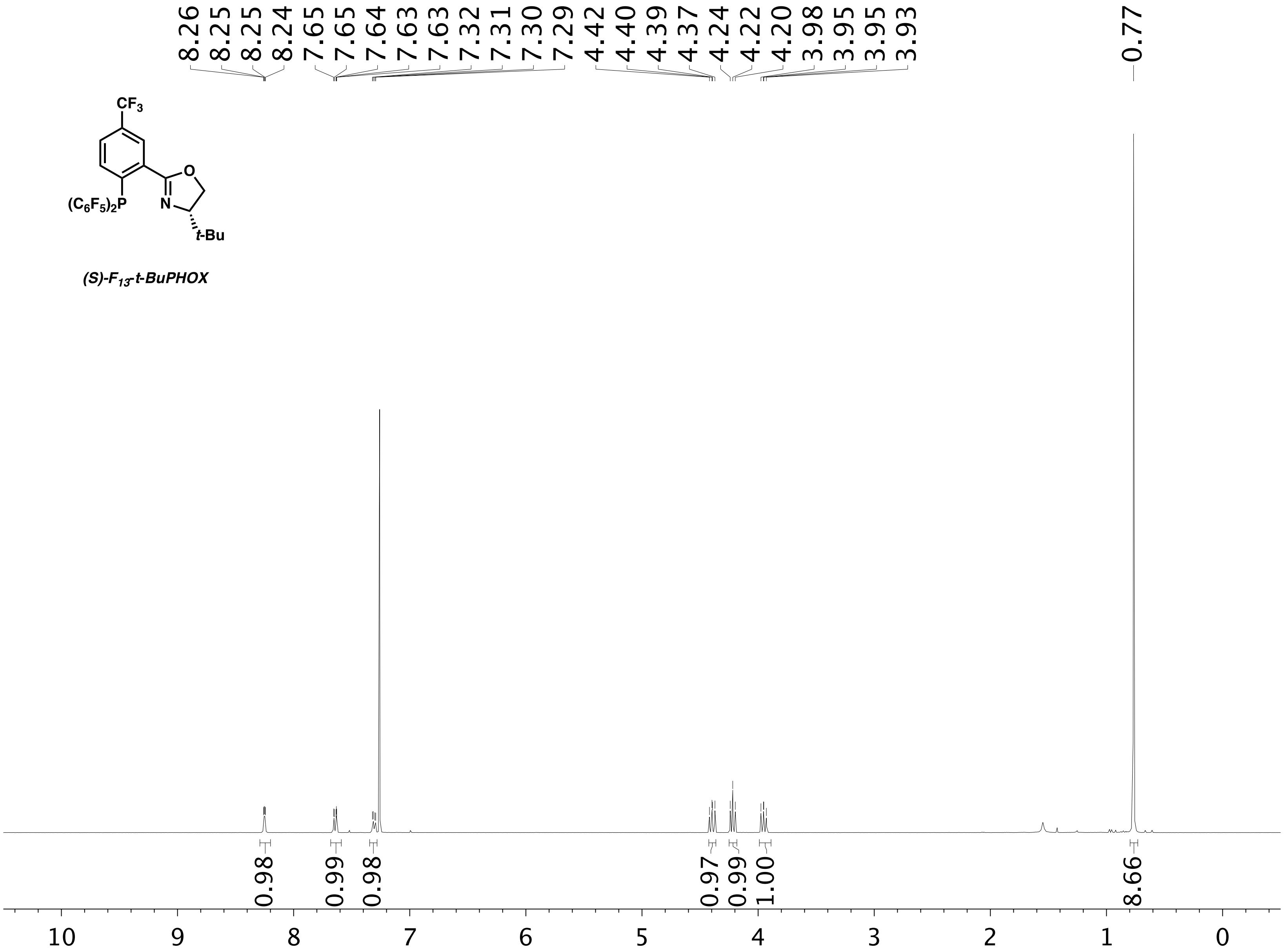
^{13}C NMR (100 MHz, $CDCl_3$) of compound **F_{13}-glyPHOX**.



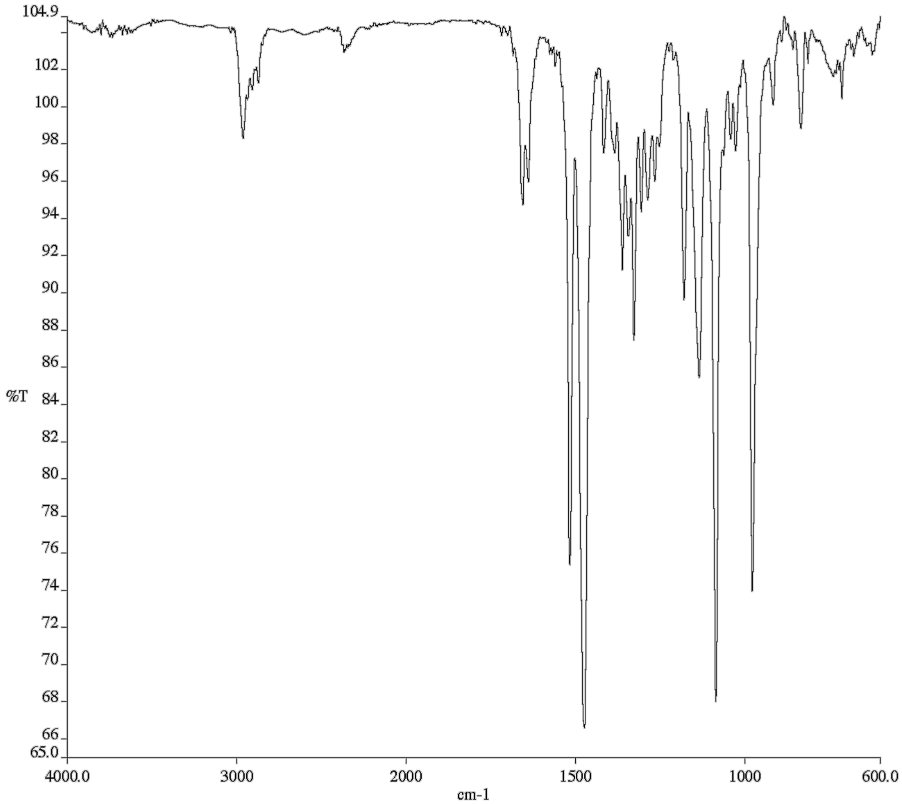
^{19}F NMR (282 MHz, CDCl$_3$) of compound **F$_{13}$-glyPHOX**.



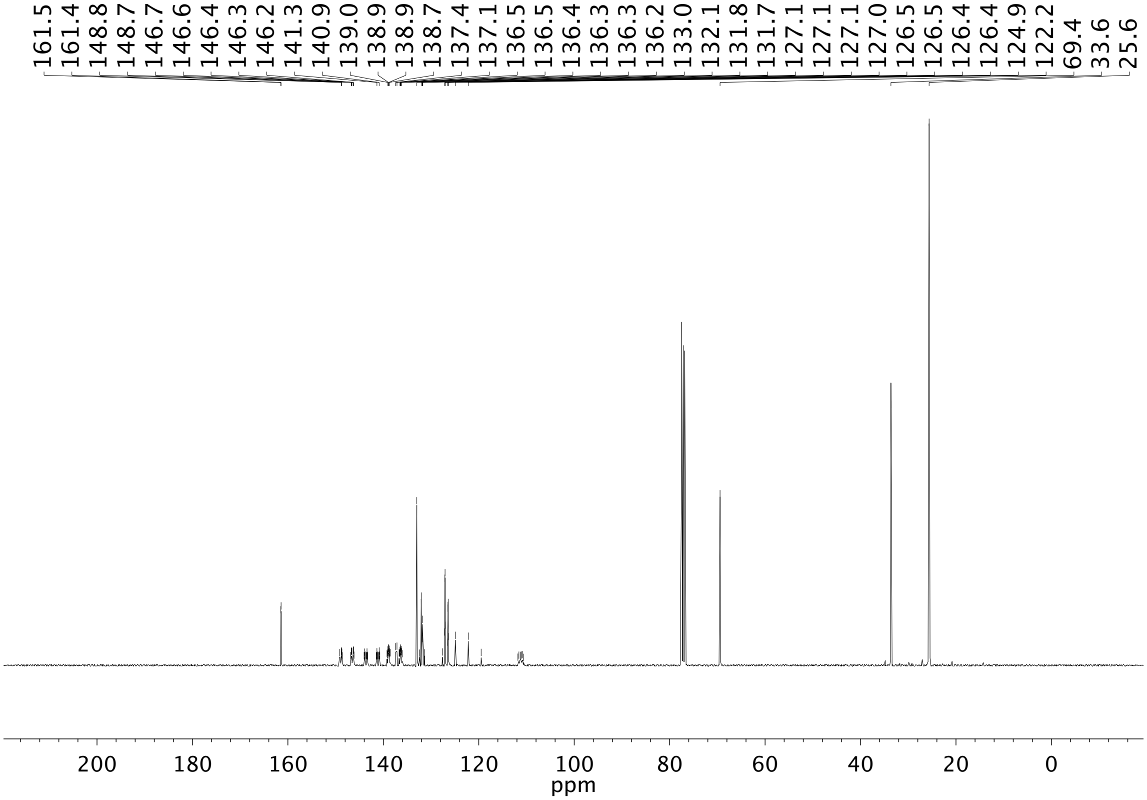
^{31}P NMR (162 MHz, CDCl$_3$) of compound **F$_{13}$-glyPHOX**.



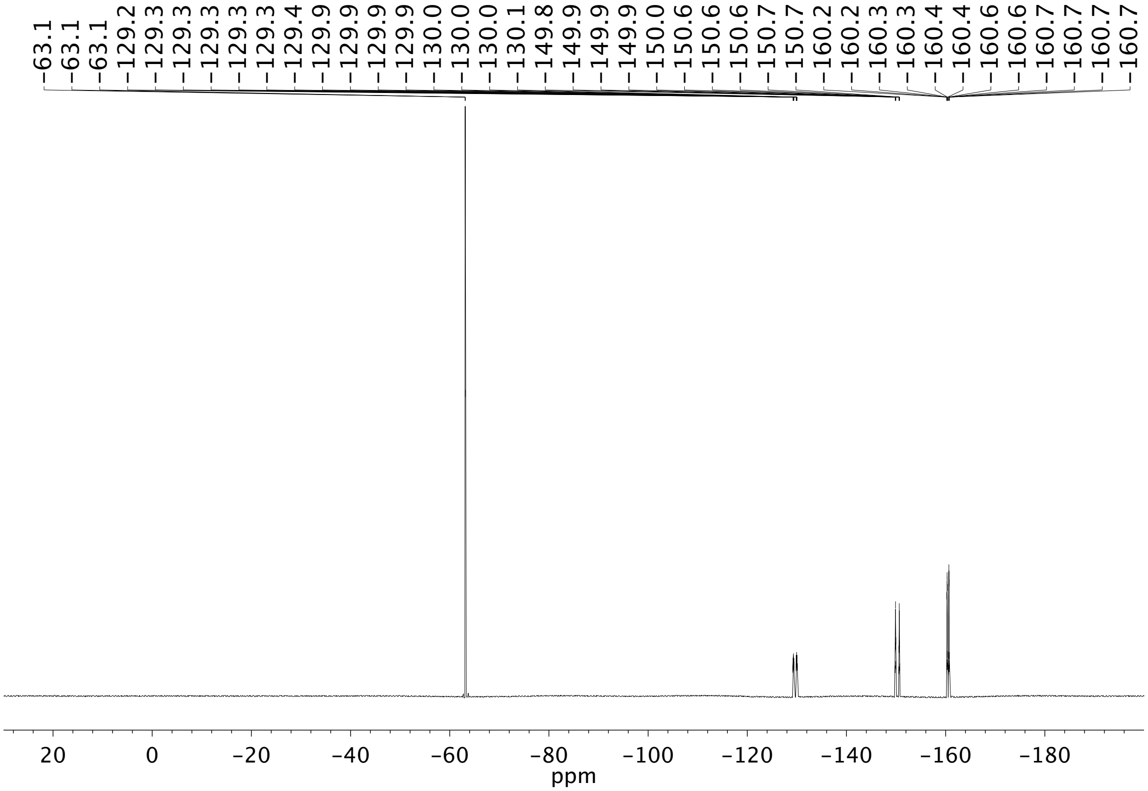
^{1}H NMR (400 MHz, CDCl$_3$) of compound **(*S*)-F$_{13}$-*t*-BuPHOX**.



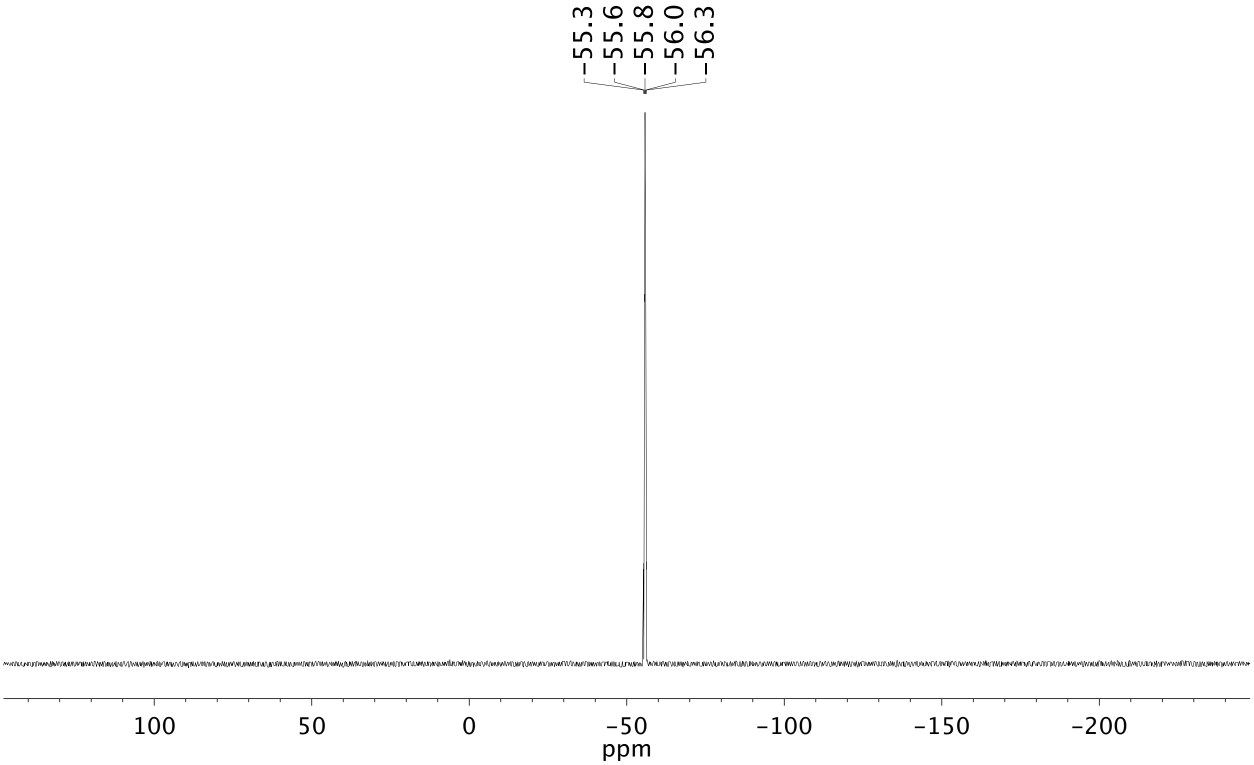
Infrared spectrum (Thin Film, NaCl) of compound **(*S*)-F$_{13}$-*t*-BuPHOX**..



^{13}C NMR (100 MHz, CDCl$_3$) of compound **(*S*)-F$_{13}$-*t*-BuPHOX**.



^{19}F NMR (282 MHz, CDCl$_3$) of compound **(*S*)-F$_{13}$-*t*-BuPHOX**.



^{31}P NMR (162 MHz, CDCl$_3$) of compound **(*S*)-F$_{13}$-*t*-BuPHOX.**