Supporting Information for

Palladium-Catalyzed Enantioselective Decarboxylative Allylic Alkylation of Acyclic α-N-Pyrrolyl/Indolyl Ketones.

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Table of Contents:

Materials and Methods.....**SI 2**

List of Abbreviations .....**SI 3**

General Procedure for Pd-Catalyzed Allylic Alkylation Reactions .....**SI 3**

General Procedure for Preparation of Allyl Enol Carbonate Substrates.....**SI 21**

Synthesis of α-pyrrolyl-acetophenone derivatives.....**SI 31**

Synthesis of α-indolyl-acetophenone derivatives .....**SI 35**

Alkylation of α-pyrrolyl-acetophenone and α-indolyl-acetophenone derivatives .....**SI 37**

Derivatization of alkylation products.....**SI 46**

X-ray crystal structure info for **2e**.....**SI 49**

References .....**SI 60**

NMR and IR Spectra of New Compounds .....**SI 61**

Materials and Methods

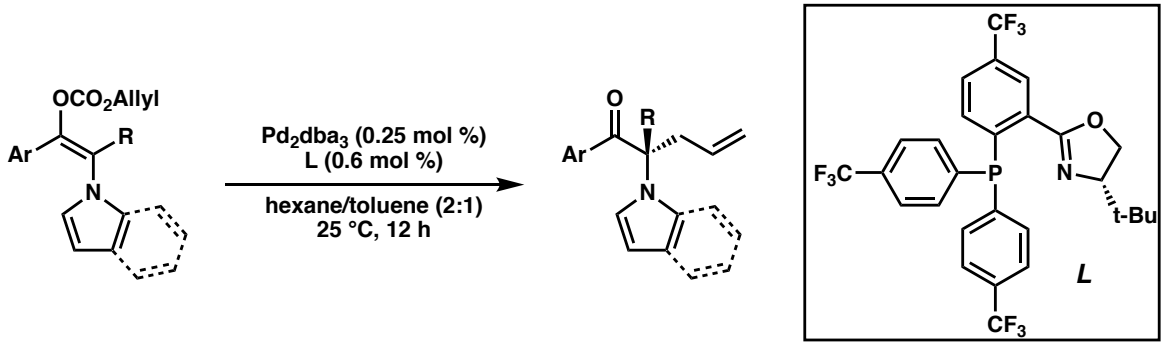
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 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 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. Analytical SFC was performed with a Mettler SFC supercritical CO_2 analytical chromatography system utilizing Chiralpak (AD-H, AS-H or IC) or Chiralcel (OD-H, OJ-H, or OB-H) columns (4.6 mm x 25 cm) obtained from Daicel Chemical Industries, Ltd. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).

Reagents were purchased from Sigma-Aldrich, Combi-Blocks, or Strem and used as received unless otherwise stated. Ligands[2] and bromoacetophenone derivatives[3] were prepared by known methods. Ketones **SI-1**[4], **SI-6**[5] and **SI-10**[4] are all known compounds. ^{1}H-NMR spectral data matched those reported in the literature.

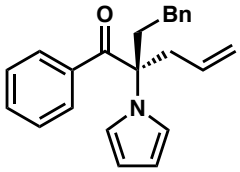
List of Abbreviations:

ee – enantiomeric excess, SFC – supercritical fluid chromatography, TLC – thin-layer chromatography, IPA – isopropanol

General Procedure for Pd-Catalyzed Allylic Alkylation Reactions



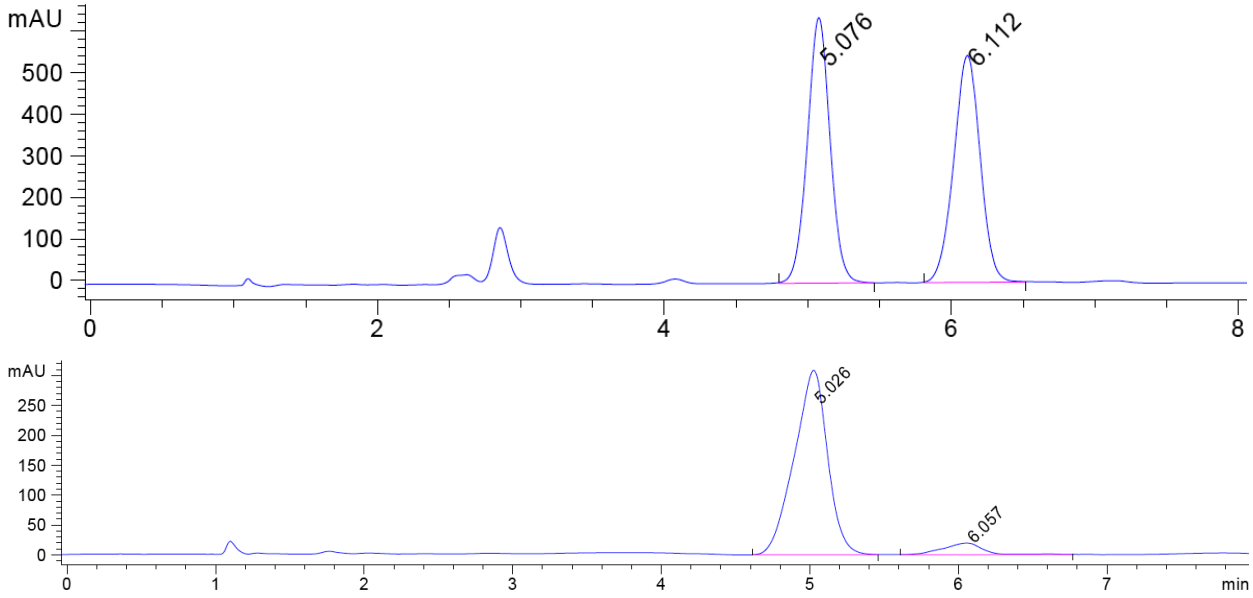
In a nitrogen-filled glovebox, a solution of $Pd_2(dba)_3$ (0.69 mg/mL) and **L** (1.06 mg/mL) in toluene was stirred for 30 minutes at 25 °C, then 0.67 mL of the resulting catalyst solution was transferred to a one dram vial containing allyl enol carbonate substrate (0.2 mmol) dissolved in hexanes (1.33 mL). The vial was sealed with a Teflon-lined cap, removed from the glovebox, and stirred at 25 °C for 12 h. The crude reaction mixture was concentrated then purified by silica gel flash chromatography to provide the desired alkylation product.



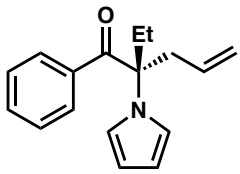
(*S*)-2-phenethyl-1-phenyl-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2a)

Purified by column chromatography (2% Et_2O in hexanes) to provide a beige solid (65.8 mg, 96% yield); 86% ee, $[\alpha]_D^{25}$ –50.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 1H), 7.32 – 7.25 (m, 2H), 7.25 – 7.13 (m, 5H), 7.00 – 6.92 (m, 2H), 6.80 (t, *J* = 2.2 Hz, 2H), 6.29 – 6.23 (m, 2H), 5.42 (dddd, *J* = 16.9, 10.3, 7.8, 6.7 Hz, 1H), 5.17 – 5.06 (m, 2H), 3.08 – 2.95 (m, 2H), 2.60 – 2.27 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 141.1, 136.0, 132.8, 131.5, 128.7, 128.7, 128.6, 128.4, 126.3, 119.9, 118.9, 109.6, 69.9, 39.7, 36.9, 29.6 ; IR (Neat Film, NaCl) 3065, 3024, 2962, 1682, 1646, 1596, 1483, 1455, 1250, 1220, 1181, 1097, 975, 923, 724, 698, 662 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO$ $[M+H]^+$: 330.1852, found

330.1856; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 5.03, minor = 6.06.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.026	BB	0.2263	4823.49268	308.68088	93.0100
2	6.057	BB	0.2677	362.50104	19.24629	6.9900
Totals :				5185.99371	327.92716	

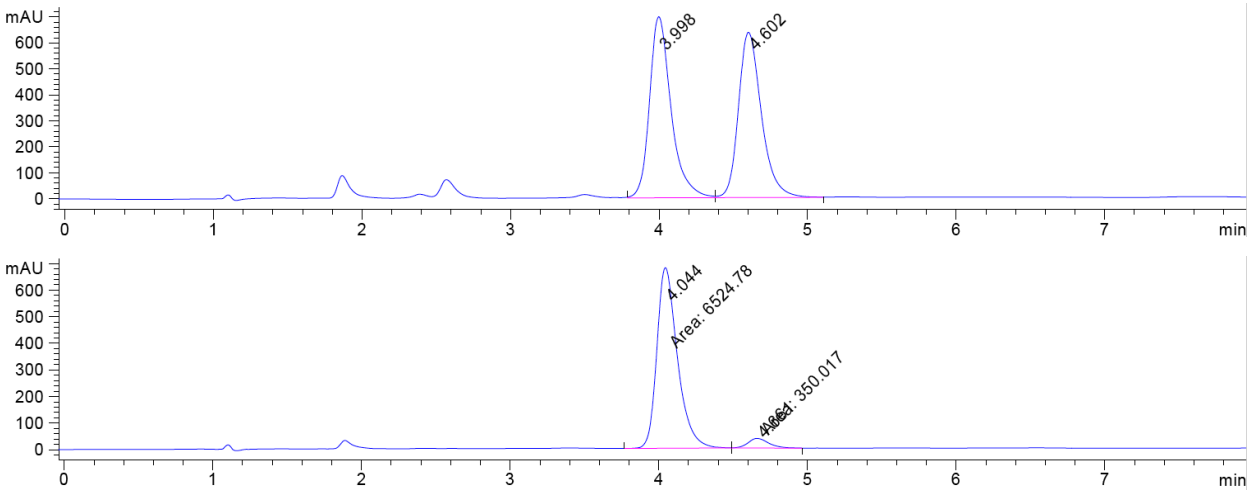


(*S*)-2-ethyl-1-phenyl-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2b)

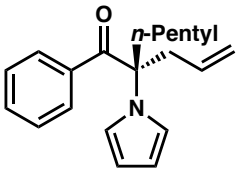
Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (49.6 mg, 98% yield); 90% ee, $[\alpha]_D^{25}$ –97.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 1H), 7.29 – 7.22 (m, 2H), 7.19 – 7.13 (m, 2H), 6.77 (t, *J* = 2.2 Hz, 2H), 6.25 (t, *J* = 2.2 Hz, 2H), 5.34 (dddd, *J* = 16.9, 10.2, 7.8, 6.7 Hz, 1H), 5.09 – 4.96 (m, 2H), 2.90 (dq, *J* = 7.7, 1.3 Hz, 2H), 2.36 – 2.10 (m, 2H), 0.75 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 136.0, 132.6, 131.6, 128.7, 128.6, 119.6, 118.9, 109.4, 70.5, 39.0, 27.2, 7.6; IR (Neat Film, NaCl) 3070, 2976, 1683, 1641, 1596, 1484, 1464, 1446, 1266, 1228, 1186, 1048, 1093, 1075, 1003, 976, 922, 722, 692 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{20}NO$ $[M+H]^+$: 254.1539, found

254.1540; SFC Conditions:* 10% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 4.04, minor = 4.66.

*SFC performed on cross-metathesis product of **2b** with methyl acrylate with Grubbs II



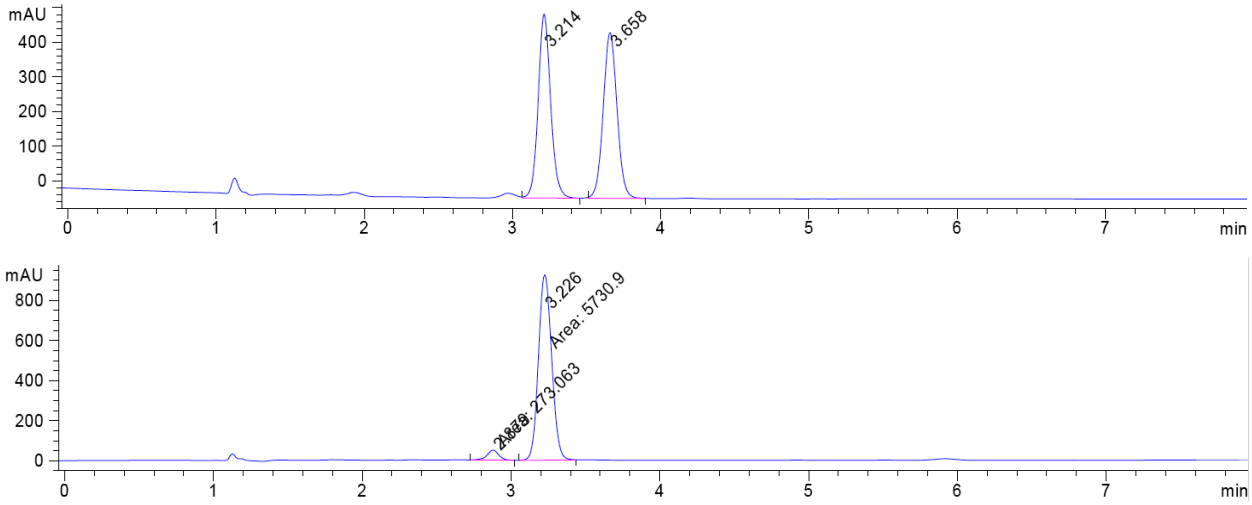
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.044	MM	0.1599	6524.78076	680.14410	94.9087
2	4.661	MM	0.1614	350.01682	36.13647	5.0913
Totals :				6874.79758	716.28058	



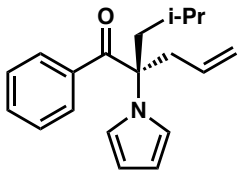
(*S*)-2-allyl-1-phenyl-2-(1*H*-pyrrol-1-yl)heptan-1-one (2c)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (57.9 mg, 98% yield); 91% ee, $[\alpha]_D^{25}$ –96.0 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 1H), 7.29 – 7.23 (m, 2H), 7.19 – 7.14 (m, 2H), 6.76 (t, *J* = 2.2 Hz, 2H), 6.24 (t, *J* = 2.2 Hz, 2H), 5.35 (dddd, *J* = 16.7, 10.2, 8.1, 6.4 Hz, 1H), 5.06 (ddt, *J* = 10.2, 2.0, 1.0 Hz, 1H), 5.00 (ddt, *J* = 16.9, 2.1, 1.3 Hz, 1H), 3.00 – 2.81 (m, 2H), 2.22 (ddd, *J* = 13.3, 12.2, 4.0 Hz, 1H), 2.16 – 2.04 (m, 1H), 1.24 – 1.08 (m, 5H), 1.08 – 0.95 (m, 1H), 0.78 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 136.0, 132.6, 131.7, 128.7, 128.5, 119.6, 118.9, 109.3, 70.1, 39.8, 34.2, 32.0, 22.7, 22.3, 14.0; IR (Neat Film, NaCl) 3102, 3069, 2956, 2931, 2870, 1682, 1641, 1596, 1578, 1483, 1467, 1446, 1418, 1379, 1268, 1252, 1219, 1203, 1185, 1150, 1095, 1073, 1002, 971, 920, 867, 783, 725, 692, 665 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{26}NO$ $[M+H]^+$:

296.2009, found 296.2022; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralcel AD-H column, λ = 210 nm, t_R (min): minor = 2.88, major = 3.23.

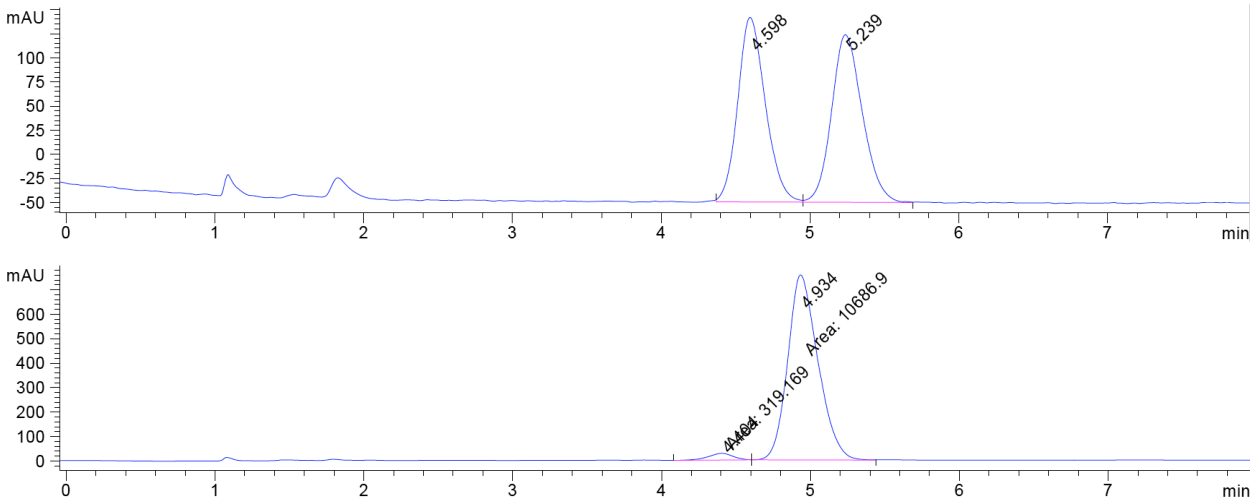


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.879	MM	0.0916	273.06308	49.70215	4.5480
2	3.226	MM	0.1031	5730.90332	926.10498	95.4520
Totals :				6003.96640	975.80713	

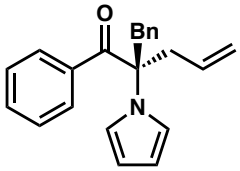


(*S*)-2-isobutyl-1-phenyl-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2d)

Purified by column chromatography (2% Et_2O in hexanes) to provide a white solid (55.1 mg, 99% yield); 94% ee, $[\alpha]_D^{25}$ –33.1 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.38 (m, 1H), 7.28 – 7.22 (m, 2H), 7.21 – 7.16 (m, 2H), 6.78 – 6.73 (m, 2H), 6.25 – 6.20 (m, 2H), 5.36 (dddd, *J* = 16.8, 10.2, 7.8, 6.5 Hz, 1H), 5.06 (ddt, *J* = 10.2, 2.0, 1.0 Hz, 1H), 4.97 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.07 – 2.91 (m, 2H), 2.25 – 2.06 (m, 2H), 1.68 – 1.57 (m, 1H), 0.74 (d, *J* = 1.3 Hz, 3H), 0.72 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.9, 136.1, 132.5, 131.5, 128.7, 128.4, 119.8, 118.7, 109.2, 70.1, 42.8, 40.0, 24.4, 23.9, 23.6; IR (Neat Film, NaCl) 3070, 2957, 2870, 1682, 1642, 1596, 1483, 1470, 1446, 1388, 1367, 1273, 1258, 1219, 1186, 1148, 1095, 1026, 1002, 921, 900, 724, 691, 666 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{24}NO$ $[M+H]^+$: 282.1852, found 252.1857; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 4.40, major = 4.93.

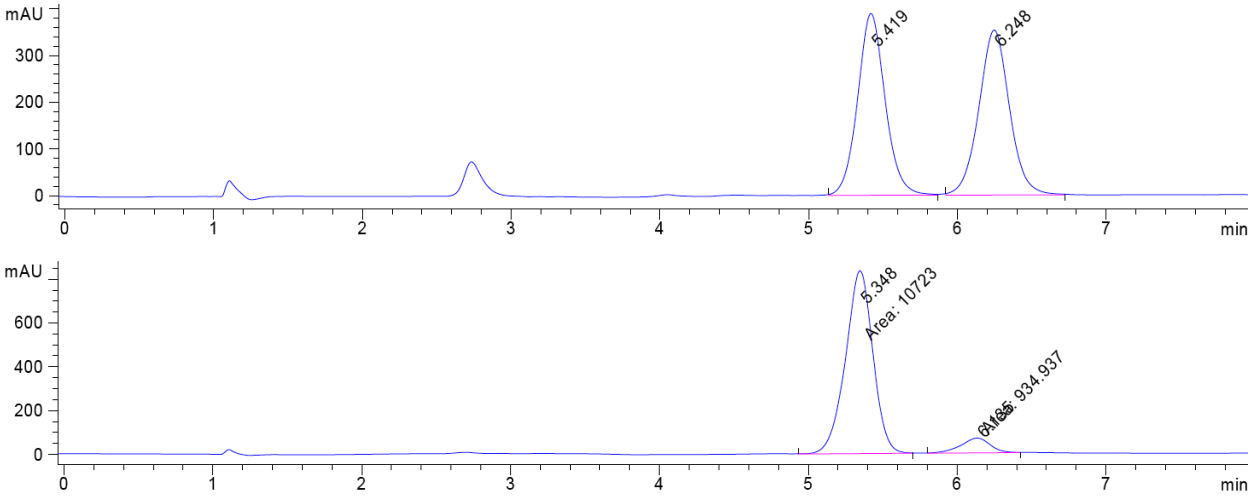


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.404	MM	0.1918	319.16907	27.73673	2.8999
2	4.934	MM	0.2356	1.06869e4	755.98010	97.1001
Totals :				1.10061e4	783.71684	

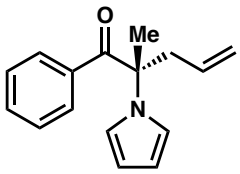


(*R*)-2-benzyl-1-phenyl-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2e)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (61.8 mg, 98% yield); 84% ee, $[\alpha]_D^{25}$ +82.353 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (ddt, *J* = 8.6, 6.8, 1.5 Hz, 1H), 7.31 – 7.12 (m, 7H), 6.66 (t, *J* = 2.2 Hz, 2H), 6.63 – 6.56 (m, 2H), 6.24 (t, *J* = 2.2 Hz, 2H), 5.61 (ddt, *J* = 17.3, 10.2, 7.1 Hz, 1H), 5.13 (dq, *J* = 10.2, 1.3 Hz, 1H), 4.93 (dq, *J* = 17.0, 1.6 Hz, 1H), 3.43 (s, 2H), 2.88 – 2.75 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.1, 136.0, 135.5, 132.8, 130.8, 130.5, 129.0, 128.6, 128.1, 127.0, 120.7, 119.1, 109.6, 70.4, 41.7, 38.4; IR (Neat Film, NaCl) 3064, 1686, 1645, 1487, 1443, 1276, 1256, 1214, 1188, 1141, 1100, 1027, 1000, 934, 905, 808, 756, 737, 701, 692, 667, 643 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{22}NO$ $[M+H]^+$: 316.1696, found 316.1696; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 5.35, minor = 6.14.



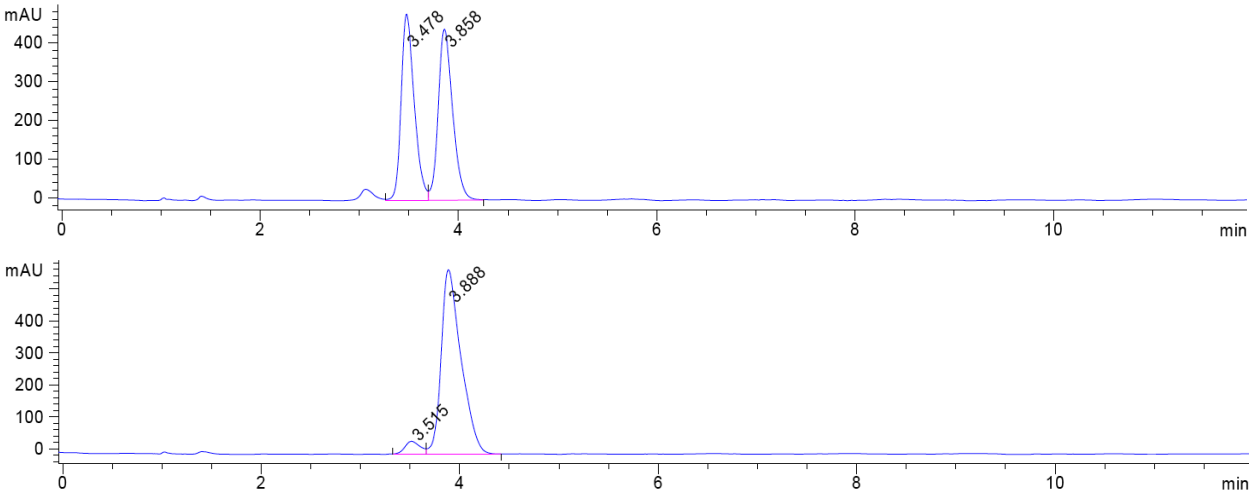
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.348	MM	0.2137	1.07230e4	836.14789	91.9803
2	6.135	MM	0.2283	934.93744	68.24573	8.0197



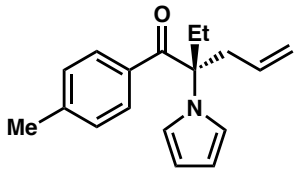
(*S*)-2-methyl-1-phenyl-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2f)

Purified by column chromatography (2% Et_2O in hexanes) to provide a white solid (47.0 mg, 98% yield); 90% ee, $[\alpha]_D^{25}$ –163.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 1H), 7.29 – 7.19 (m, 4H), 6.74 (d, *J* = 2.2 Hz, 2H), 6.23 (t, *J* = 2.2 Hz, 2H), 5.40 (dddd, *J* = 16.7, 10.3, 8.2, 6.3 Hz, 1H), 5.10 – 5.00 (m, 2H), 2.97 – 2.89 (m, 1H), 2.83 (ddt, *J* = 13.9, 8.2, 1.0 Hz, 1H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 135.5, 132.7, 132.1, 128.8, 128.5, 119.9, 118.8, 109.5, 67.2, 43.9, 23.4; IR (Neat Film, NaCl) 3070, 2982, 1682, 1641, 1596, 1484, 1446, 1378, 1280, 1255, 1152, 1092, 1073, 974, 951, 922, 794, 719, 693 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{16}H_{17}NONa$ $[M+Na]^+$: 262.1202, found 262.1210; SFC Conditions: 0.5% IPA, 2.5 mL/min, Chiralcel OB-H column, λ = 210 nm, t_R (min): minor = 3.52, major = 3.89.

Substrate rerun on 5.08 mmol scale to provide **2f** (1.14 g, 94% yield) in 90% ee.

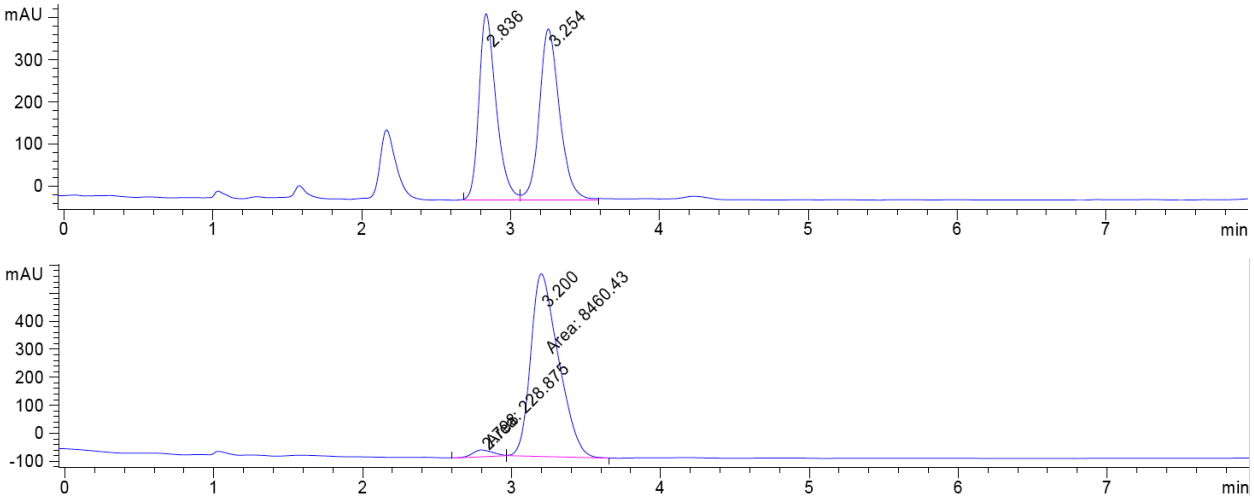


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.515	BV	0.1615	432.60568	40.23061	5.1137
2	3.888	VB	0.2028	8027.13574	575.27679	94.8863



(*S*)-2-ethyl-2-(1*H*-pyrrol-1-yl)-1-(*p*-tolyl)pent-4-en-1-one (2g)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (50.4 mg, 95% yield); 95% ee, $[\alpha]_D^{25}$ –90.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.09 (m, 2H), 7.10 – 7.02 (m, 2H), 6.75 (t, *J* = 2.2 Hz, 2H), 6.23 (t, *J* = 2.2 Hz, 2H), 5.41 – 5.27 (m, 1H), 5.09 – 4.97 (m, 2H), 2.90 (dt, *J* = 7.7, 1.2 Hz, 2H), 2.31 (s, 3H), 2.30 – 2.14 (m, 2H), 0.74 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.4, 143.4, 133.3, 131.8, 129.3, 128.9, 119.5, 118.9, 109.2, 70.5, 39.2, 27.4, 21.6, 7.6; IR (Neat Film, NaCl) 3070, 2976, 2881, 1681, 1641, 1606, 1484, 1459, 1265, 1236, 1187, 1149, 1093, 1075, 1003, 917, 846, 827, 792, 756, 724 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1696, found 268.1693; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralcel OB-H column, λ = 210 nm, t_R (min): minor = 2.80, major = 3.20.



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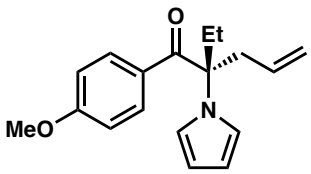
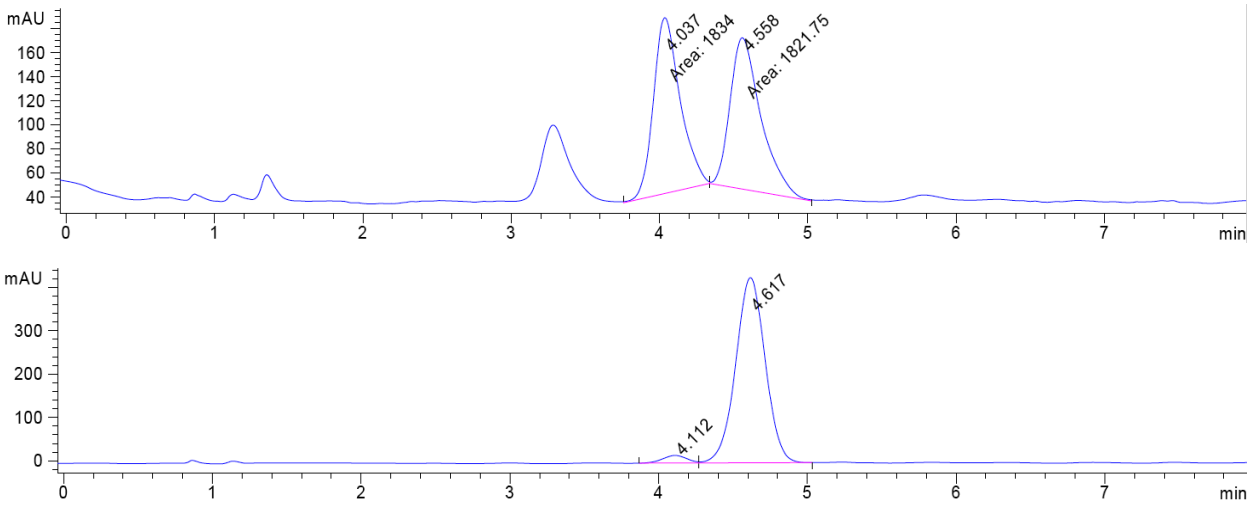
1	2.798	MM	0.1571	228.87466	24.28337	2.6340
2	3.200	MM	0.2163	8460.42578	651.76965	97.3660
Totals :				8689.30045	676.05302	

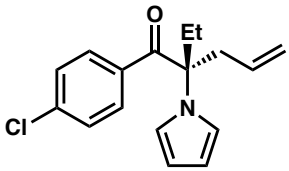


(*S*)-2-ethyl-1-(4-methoxyphenyl)-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2h)

Purified by column chromatography (5% Et_2O in hexanes) to provide a colorless oil (55.9 mg, 99% yield); 94% ee, $[\alpha]_D^{25}$ –80.0 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.22 (m, 2H), 6.76 – 6.70 (m, 4H), 6.22 (t, *J* = 2.2 Hz, 2H), 5.33 (dddd, *J* = 16.8, 10.3, 7.9, 6.6 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.78 (s, 3H), 2.95 – 2.81 (m, 2H), 2.35 – 2.12 (m, 2H), 0.74 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 163.1, 131.9, 131.2, 128.6, 119.5, 118.9, 113.7, 109.2, 70.6, 55.5, 39.4, 27.7, 7.7; IR (Neat Film, NaCl) 3076, 2974, 2839, 1673, 1645, 1600, 1574, 1508, 1484, 1459, 1418, 1306, 1263, 1242, 1178, 1149, 1092, 1074, 1032, 917, 847, 726 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{22}NO_2$ $[M+H]^+$: 284.1645, found 284.1644; SFC Conditions: 1% IPA, 2.5 mL/min, Chiralcel OB-H column, λ = 210 nm, t_R (min): minor = 4.11, major = 4.62.

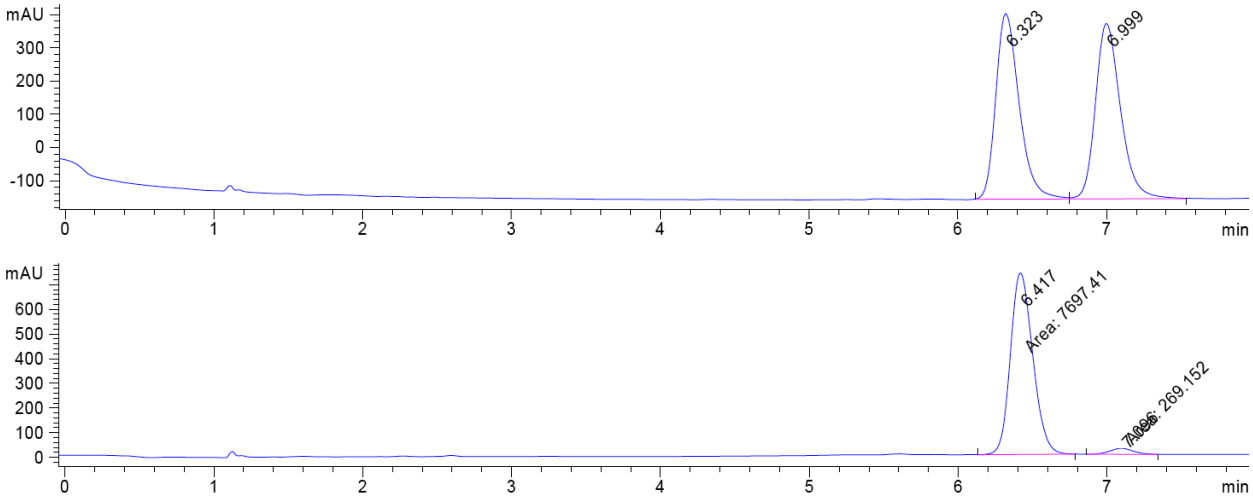


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.112	BV	0.1731	196.70833	17.50358	3.2291
2	4.617	VB	0.2133	5894.96680	426.44641	96.7709
Totals :				6091.67513	443.94999	

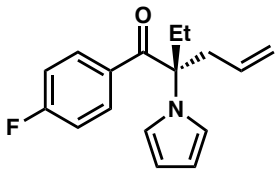


(*S*)-1-(4-chlorophenyl)-2-ethyl-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2i)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (54.8 mg, 95% yield); 93% ee, $[\alpha]_D^{25}$ –86.8 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.20 (m, 2H), 7.12 – 7.06 (m, 2H), 6.74 (t, *J* = 2.2 Hz, 2H), 6.26 – 6.23 (m, 2H), 5.33 (dddd, *J* = 16.8, 10.3, 7.9, 6.5 Hz, 1H), 5.14 – 4.94 (m, 2H), 2.97 – 2.79 (m, 2H), 2.28 (dq, *J* = 13.6, 7.5 Hz, 1H), 2.14 (dqd, *J* = 13.7, 7.4, 0.8 Hz, 1H), 0.74 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 139.1, 134.2, 131.4, 130.2, 128.9, 119.8, 118.9, 109.6, 70.6, 39.0, 27.3, 7.6; IR (Neat Film, NaCl) 3074, 2980, 1682, 1644, 1586, 1486, 1398, 1280, 1266, 1224, 1184, 1147, 1116, 1093, 1075, 1003, 926, 914, 845, 824, 750, 726, 707 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{19}ClNO$ $[M+H]^+$: 288.1150, found 288.1150; SFC Conditions: 3% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 6.42, major = 7.10.

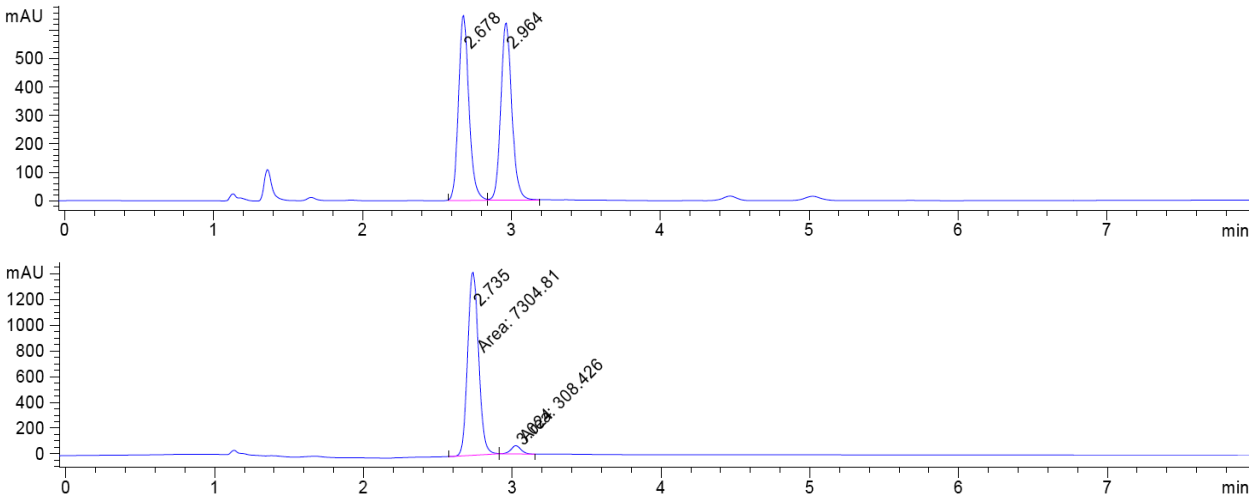


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.417	MM	0.1743	7697.41455	735.88245	96.6215
2	7.096	MM	0.1838	269.15225	24.41217	3.3785
Totals :				7966.56680	760.29461	

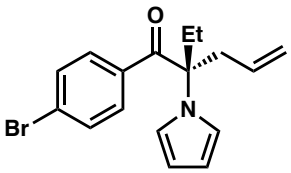


(*S*)-2-ethyl-1-(4-fluorophenyl)-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2j)

Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (53.9 mg, 99% yield); 92% ee, $[\alpha]_D^{25}$ –93.7 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 6.96 – 6.89 (m, 2H), 6.74 (t, *J* = 2.2 Hz, 2H), 6.25 (t, *J* = 2.2 Hz, 2H), 5.34 (dddd, *J* = 16.9, 10.2, 7.8, 6.6 Hz, 1H), 5.07 (ddt, *J* = 10.1, 1.9, 1.0 Hz, 1H), 5.01 (dq, *J* = 16.9, 1.5 Hz, 1H), 2.89 (ddt, *J* = 7.9, 2.3, 1.1 Hz, 2H), 2.29 (dq, *J* = 13.6, 7.5 Hz, 1H), 2.22 – 2.11 (m, 1H), 0.75 (t, *J* = 7.4 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.6 – -105.7 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 165.3 (d, *J* = 254.7 Hz), 132.3 (d, *J* = 3.6 Hz), 131.5 (d, *J* = 9.5 Hz), 131.5, 119.7, 118.9, 115.6 (d, *J* = 21.5 Hz), 109.5, 70.6, 39.1, 27.4, 7.6; IR (Neat Film, NaCl) 3078, 2977, 2882, 1682, 1642, 1598, 1504, 1484, 1463, 1266, 1235, 1161, 1093, 1075, 1006, 921, 853, 841, 759, 726cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{19}FNO$ $[M+H]^+$: 272.1445, found 272.1446; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 2.74, minor = 3.02.

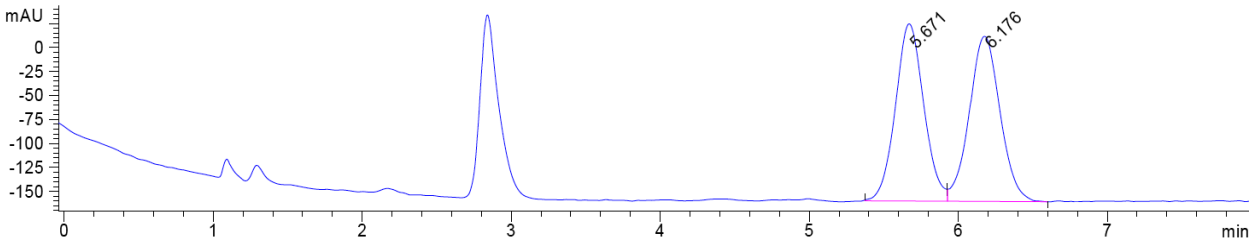


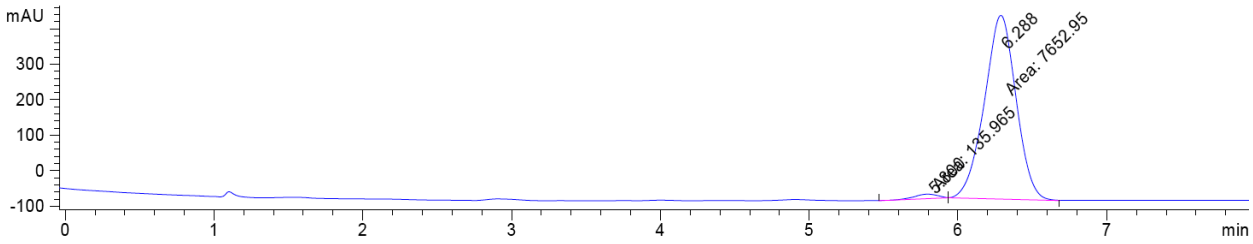
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.735	MM	0.0852	7304.81494	1429.49524	95.9488
2	3.024	MM	0.0803	308.42645	64.02464	4.0512
Totals :				7613.24139	1493.51988	



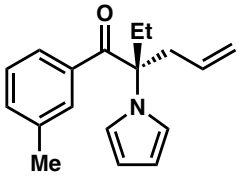
(*S*)-1-(4-bromophenyl)-2-ethyl-2-(1*H*-pyrrol-1-yl)pent-4-en-1-one (2k)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (60.0 mg, 90% yield); 97% ee, $[\alpha]_D^{25}$ –73.6 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.04 – 6.97 (m, 2H), 6.73 (t, *J* = 2.2 Hz, 2H), 6.24 (t, *J* = 2.2 Hz, 2H), 5.33 (dddd, *J* = 16.8, 10.2, 8.0, 6.5 Hz, 1H), 5.06 (ddt, *J* = 10.2, 2.0, 1.0 Hz, 1H), 5.04 – 4.98 (m, 1H), 2.95 – 2.79 (m, 2H), 2.27 (dq, *J* = 13.6, 7.6 Hz, 1H), 2.19 – 2.08 (m, 1H), 0.74 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 134.6, 131.9, 131.3, 130.3, 127.9, 119.8, 118.9, 109.6, 70.6, 38.9, 27.2, 7.6; IR (Neat Film, NaCl) 3074, 2975, 1682, 1642, 1582, 1483, 1462, 1394, 1266, 1227, 1384, 1150, 1093, 1074, 1004, 979, 918, 844, 818, 751, 725 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{19}BrNO$ $[M+H]^+$: 332.0645, found 332.0640; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 5.80, major = 6.29.



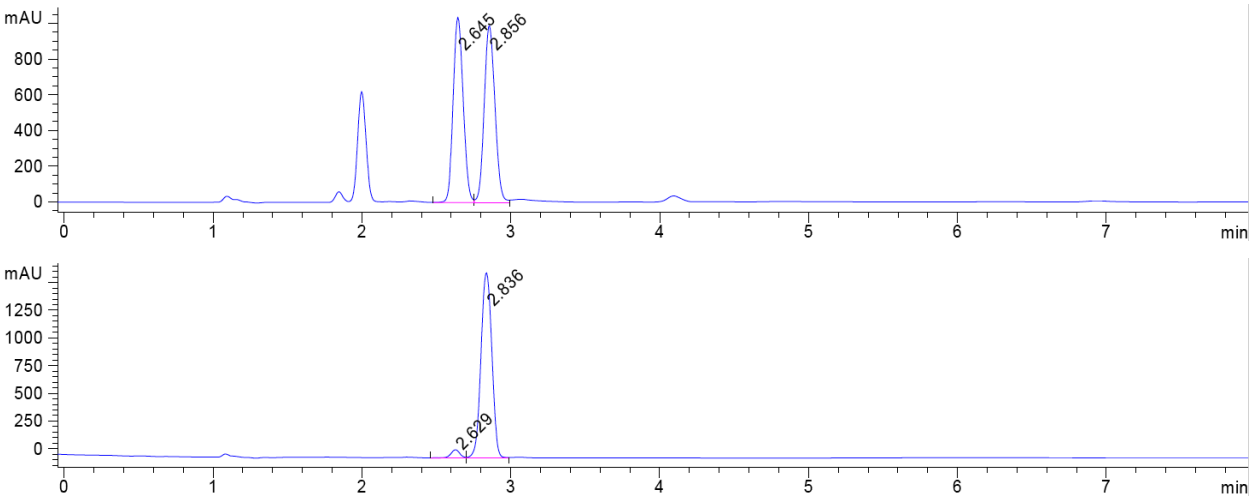


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.800	MM	0.1766	135.96484	12.83426	1.7456
2	6.288	MM	0.2465	7652.95068	517.45605	98.2544
Totals :				7788.91553	530.29031	

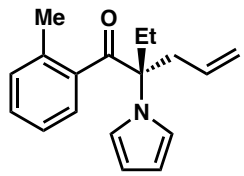


(*S*)-2-ethyl-2-(1*H*-pyrrol-1-yl)-1-(*m*-tolyl)pent-4-en-1-one (2l)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (53.4 mg, 99% yield); 93% ee, $[\alpha]_D^{25}$ –96.6 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.24 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 7.04 (s, 1H), 6.86 (dt, *J* = 7.9, 1.3 Hz, 1H), 6.76 (t, *J* = 2.2 Hz, 2H), 6.24 (t, *J* = 2.2 Hz, 2H), 5.35 (ddt, *J* = 17.2, 10.2, 7.3 Hz, 1H), 5.11 – 4.97 (m, 2H), 2.94 – 2.84 (m, 2H), 2.26 (s, 3H), 2.32 – 2.12 (m, 2H), 0.75 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 138.2, 136.0, 133.3, 131.7, 129.4, 128.4, 125.6, 119.5, 118.9, 109.3, 70.5, 39.0, 27.2, 21.4, 7.6; IR (Neat Film, NaCl) 3067, 2977, 2942, 2882, 1682, 1642, 1601, 1584, 1484, 1462, 1266, 1251, 1190, 1140, 1093, 923, 790, 724, 694 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1696, found 268.1699; SFC Conditions: 3% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 210 nm, t_R (min): minor = 2.63, major = 2.84.

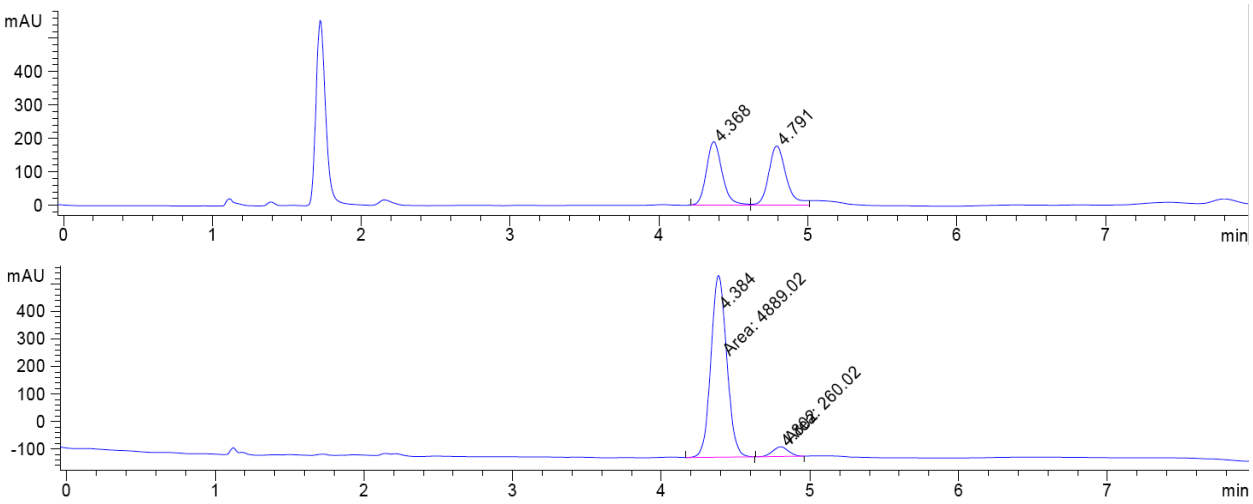


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.629	VV	0.0706	318.11304	73.27620	3.5998
2	2.836	VV	0.0837	8518.83301	1663.66541	96.4002

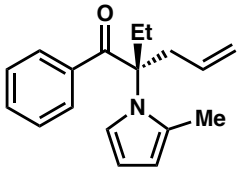


(*S*)-2-ethyl-2-(1*H*-pyrrol-1-yl)-1-(*o*-tolyl)pent-4-en-1-one (2m)

Purified by column chromatography (2% Et_2O in hexanes) to provide a white solid (45.6 mg, 85% yield); 90% ee, $[\alpha]_D^{25}$ –67.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.17 (m, 2H), 6.96 – 6.89 (m, 1H), 6.79 (t, *J* = 2.2 Hz, 2H), 6.23 (t, *J* = 2.2 Hz, 2H), 6.12 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.44 (dddd, *J* = 16.7, 10.3, 8.0, 6.3 Hz, 1H), 5.12 – 5.00 (m, 2H), 2.98 (ddq, *J* = 14.4, 6.3, 1.3 Hz, 1H), 2.92 – 2.83 (m, 1H), 2.36 (s, 3H), 2.31 – 2.21 (m, 1H), 2.20 – 2.09 (m, 1H), 0.80 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 138.1, 136.5, 131.8, 131.7, 130.6, 126.6, 125.5, 119.6, 118.8, 109.3, 70.4, 38.3, 26.9, 21.1, 7.4; IR (Neat Film, NaCl) 3071, 2972, 2932, 2875, 1688, 1645, 1485, 1456, 1383, 1318, 1289, 1262, 1121, 1084, 999, 965, 917, 755, 748, 723 cm^1; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{22}NO$ $[M+H]^+$: 268.1696, found 268.1705; SFC Conditions: 3% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): major = 4.38, minor = 4.80.

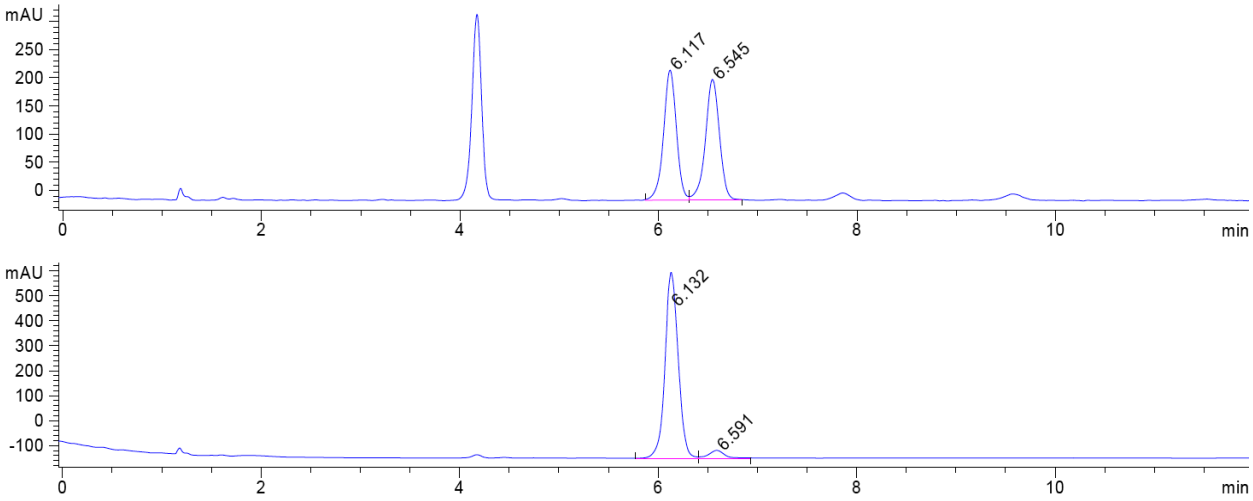


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.384	MM	0.1231	4889.02344	661.80304	94.9501
2	4.802	MM	0.1219	260.02014	35.56029	5.0499
Totals :				5149.04358	697.36333	

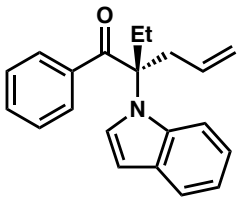


(*S*)-2-ethyl-2-(2-methyl-1*H*-pyrrol-1-yl)-1-phenylpent-4-en-1-one (2n)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (48.7 mg, 91% yield); 90% ee, $[\alpha]_D^{25}$ –105.4 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 1H), 7.30 – 7.21 (m, 4H), 6.93 (dd, *J* = 3.1, 1.9 Hz, 1H), 6.16 (t, *J* = 3.2 Hz, 1H), 5.91 (ddq, *J* = 3.6, 1.8, 0.9 Hz, 1H), 5.30 (dddd, *J* = 16.6, 10.2, 8.3, 6.1 Hz, 1H), 5.11 – 4.97 (m, 2H), 3.03 – 2.93 (m, 1H), 2.89 (ddt, *J* = 14.3, 8.3, 0.9 Hz, 1H), 2.39 – 2.27 (m, 1H), 2.17 (dqd, *J* = 13.5, 7.4, 1.2 Hz, 1H), 1.98 (s, 3H), 0.71 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 135.7, 132.9, 131.8, 129.5, 129.2, 128.7, 119.6, 118.0, 110.4, 107.6, 70.6, 37.8, 27.2, 14.0, 7.6; IR (Neat Film, NaCl) 3070, 2977, 1683, 1596, 1446, 1417, 1268, 1228, 1146, 1085, 1006, 920, 840, 780, 724, 692 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{21}NONa$ $[M+Na]^+$: 290.1515, found 290.1516; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): major = 6.13, minor = 6.59.



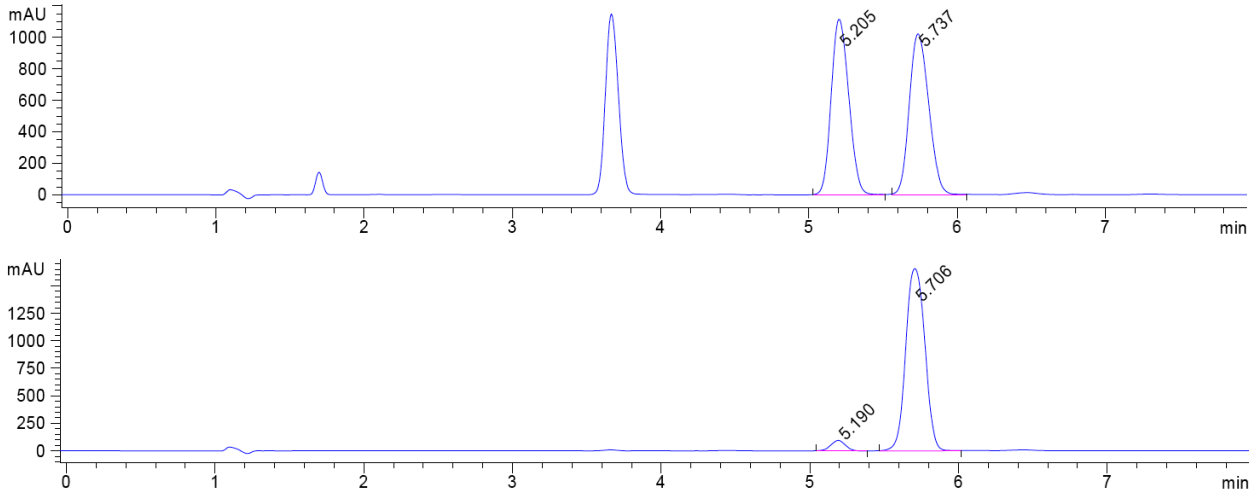
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.132	VV	0.1417	6879.79932	745.57166	95.1164
2	6.591	VB	0.1632	353.23019	31.90499	4.8836
Totals :				7233.02951	777.47664	



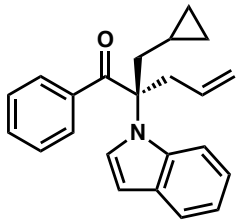
(*S*)-2-ethyl-2-(1*H*-indol-1-yl)-1-phenylpent-4-en-1-one (2o)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (54.1 mg, 89% yield); 92% ee, $[\alpha]_D^{25}$ –115.2 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 1H), 7.48 (d, *J* = 3.4 Hz, 1H), 7.33 (ddt, *J* = 8.6, 7.0, 1.3 Hz, 1H), 7.29 – 7.26 (m, 2H), 7.21 – 7.11 (m, 3H), 7.07 – 6.97 (m, 2H), 6.68 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.23 (dddd, *J* = 16.5, 10.1, 8.5, 6.0 Hz, 1H), 5.02 (ddd, *J* = 10.2, 2.3, 1.1 Hz, 1H), 4.96 (ddt, *J* = 16.9, 1.9, 1.2 Hz, 1H), 3.29 (ddq, *J* = 14.3, 6.0, 1.4 Hz, 1H), 3.00 (dd, *J* = 14.3, 8.4 Hz, 1H), 2.57 (dq, *J* = 13.3, 7.5 Hz, 1H), 2.31 (dqd, *J* = 13.4, 7.4, 1.3 Hz, 1H), 0.76 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 135.8, 135.7, 132.9, 131.5, 129.7, 128.6, 128.6, 124.5, 122.2, 121.3, 120.1, 119.8, 111.8, 102.8, 70.6, 36.7, 26.8, 7.6; IR (Neat Film, NaCl) 3069, 2980, 1681, 1596, 1512, 1457, 1311, 1296, 1226, 1185, 1142, 1005, 925, 742, 721, 691 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for

$C_{21}H_{22}NO$ $[M+H]^+$: 304.1696, found 304.1706; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 210 nm, t_R (min): minor = 5.19, major = 5.71.



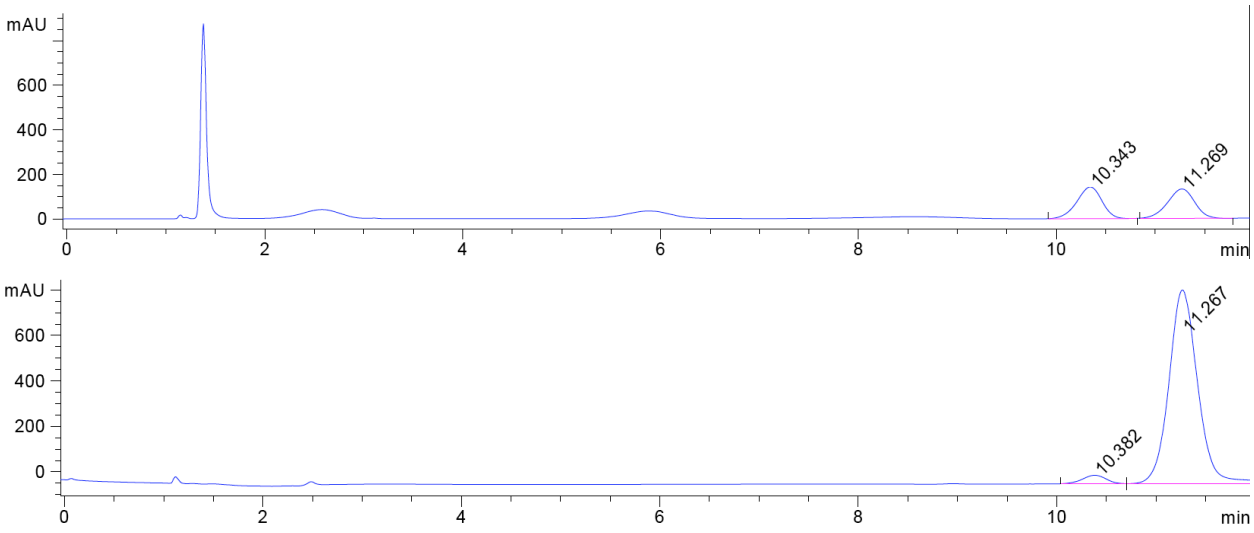
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.190	BB	0.1079	650.85986	95.01244	4.1949
2	5.706	BB	0.1448	1.48648e4	1655.23389	95.8051



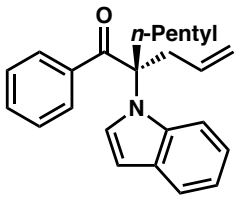
(*R*)-2-(cyclopropylmethyl)-2-(1*H*-indol-1-yl)-1-phenylpent-4-en-1-one (2p)

Performed on 0.1 mmol scale. Purified by column chromatography (4% Et_2O in hexanes) to provide a colorless oil (33.1 mg, 94% yield); 92% ee, $[\alpha]_D^{25}$ –49.9 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.47 (d, *J* = 3.4 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.20 – 7.11 (m, 3H), 7.06 – 6.97 (m, 2H), 6.68 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.29 (q, *J* = 9.1, 8.2 Hz, 1H), 5.10 – 4.92 (m, 2H), 3.50 (dd, *J* = 14.1, 6.0 Hz, 1H), 3.21 (dd, *J* = 14.0, 8.2 Hz, 1H), 2.54 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.23 (dd, *J* = 13.8, 6.7 Hz, 1H), 0.53 – 0.27 (m, 3H), –0.10 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 135.8, 135.6, 132.9, 131.6, 129.6, 128.7, 128.5, 124.4, 122.2, 121.2, 120.1, 120.0, 111.8, 102.8, 71.0, 38.3, 38.2, 5.4, 5.0, 4.0; IR (Neat Film, NaCl) 3076, 3003, 2362, 2341, 1678, 1595, 1457, 1309, 1229, 1019, 922, 764, 743, 724, 692 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO$ $[M+H]^+$: 330.1858, found 330.1861; SFC

Conditions: 5% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 10.38, major = 11.27.



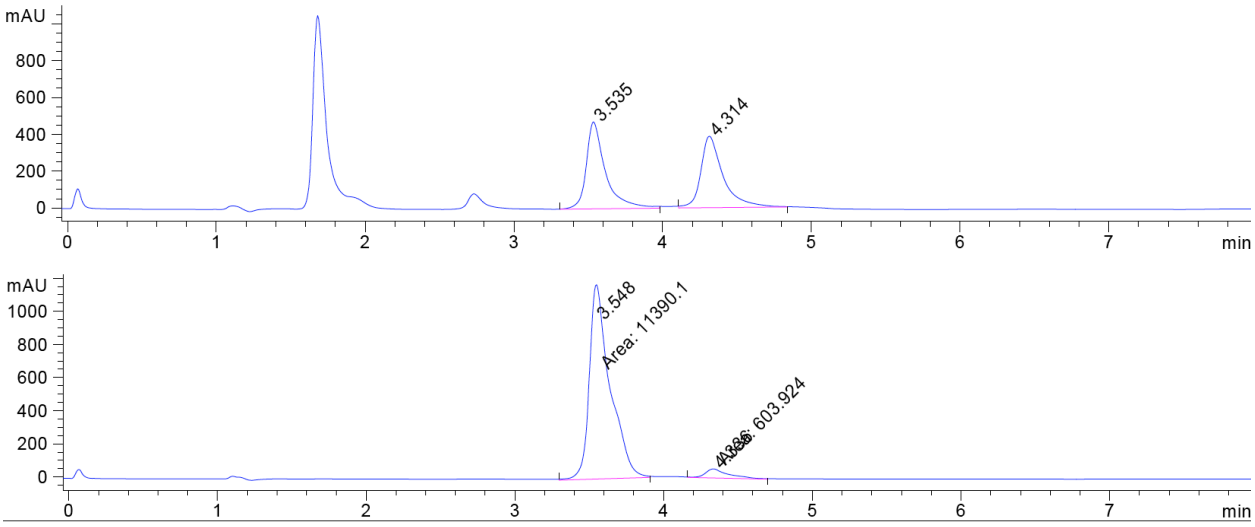
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.382	BV	0.2582	651.16205	38.33008	3.6644
2	11.267	VBA	0.3060	1.71187e4	853.42157	96.3356



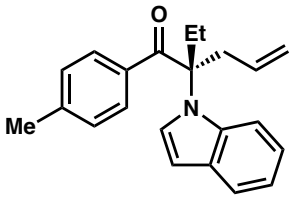
(*S*)-2-allyl-2-(1*H*-indol-1-yl)-1-phenylheptan-1-one (2q)

Purified by column chromatography (2% Et_2O in hexanes) to provide a colorless oil (48.6 mg, 70% yield); 90% ee, $[\alpha]_D^{25}$ –94.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 – 7.59 (m, 1H), 7.50 (d, *J* = 3.3 Hz, 1H), 7.33 (tt, *J* = 7.3, 1.3 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.21 (dq, *J* = 7.1, 1.1 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.03 (tt, *J* = 7.1, 5.5 Hz, 2H), 6.69 (dd, *J* = 3.4, 0.9 Hz, 1H), 5.23 (ddd, *J* = 16.3, 9.6, 4.6 Hz, 1H), 5.13 – 4.91 (m, 2H), 3.38 – 3.25 (m, 1H), 3.02 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.52 (td, *J* = 13.1, 3.9 Hz, 1H), 2.33 – 2.18 (m, 1H), 1.26 – 1.02 (m, 6H), 0.89 – 0.77 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 135.7, 135.6, 132.8, 131.7, 129.7, 128.5, 124.4, 122.2, 121.2, 120.1, 119.7, 111.8, 102.8, 70.2, 37.4, 33.9, 32.0, 22.7, 22.3, 14.0; IR (Neat Film, NaCl) 2956, 2929, 2870, 1679, 1596, 1457, 1313, 1225, 922, 764, 743, 692 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{28}NO$ $[M+H]^+$: 346.2171, found 346.2168; SFC

Conditions: 5% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 210 nm, t_R (min): major = 3.55, minor = 4.34.



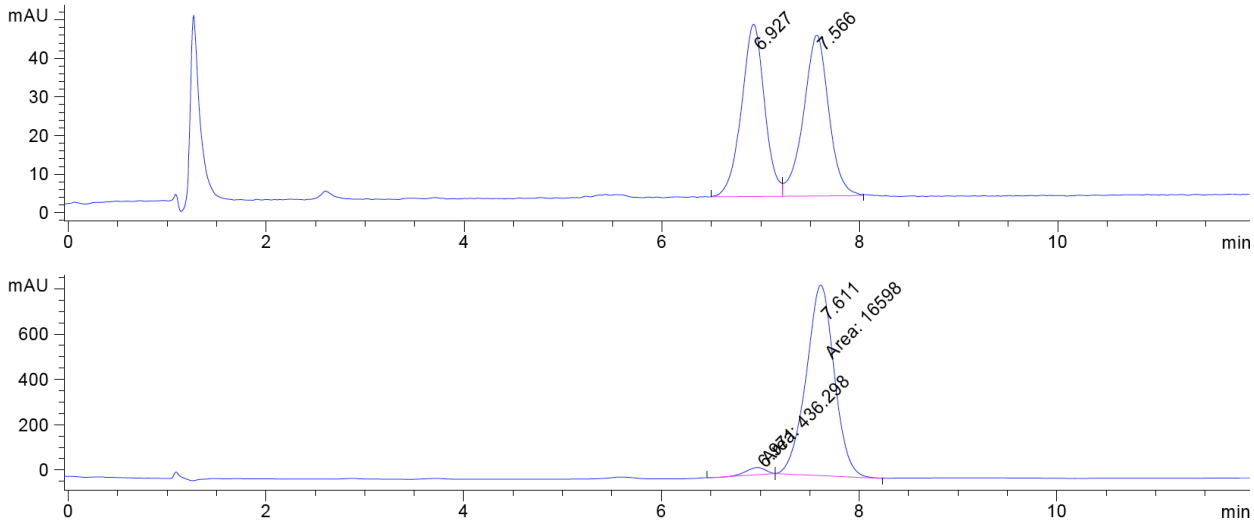
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.548	MM	0.1615	1.13901e4	1175.29565	94.9648
2	4.336	MM	0.1845	603.92371	54.56400	5.0352



(*S*)-2-ethyl-2-(1*H*-indol-1-yl)-1-(*p*-tolyl)pent-4-en-1-one (2r)

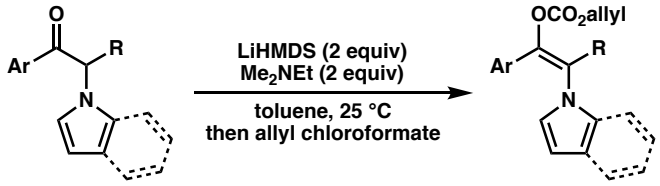
Performed on 0.107 mmol scale. Purified by column chromatography (3% Et_2O in hexanes) to provide a colorless oil (23.3 mg, 73% yield); 95% ee, $[\alpha]_D^{25}$ –87.8 (*c* 1.00, $CHCl_3$); ^1H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.58 (m, 1H), 7.49 (d, *J* = 3.4 Hz, 1H), 7.24 – 7.16 (m, 3H), 7.02 (tt, *J* = 7.0, 5.5 Hz, 2H), 6.95 (d, *J* = 8.1 Hz, 2H), 6.68 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.23 (dq, *J* = 16.6, 8.5 Hz, 1H), 5.08 – 4.90 (m, 2H), 3.38 – 3.23 (m, 1H), 3.02 (dd, *J* = 14.2, 8.5 Hz, 1H), 2.58 (dq, *J* = 13.3, 7.5 Hz, 1H), 2.33 (dtd, *J* = 14.6, 8.6, 8.0, 6.8 Hz, 1H), 2.23 (s, 3H), 0.78 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 143.7, 135.6, 133.1, 131.7, 129.6, 129.3, 128.7, 124.4, 122.1, 121.2, 120.0, 119.6, 111.8, 102.7, 70.6, 36.8, 27.0, 21.6, 7.7; IR (Neat Film, NaCl) 2978, 2360, 1674, 1605, 1457, 1295, 1226, 1186, 1142, 922, 742 cm^{-1}; HRMS (MM:ESI-

APCI+) *m/z* calc'd for $C_{22}H_{24}NO$ $[M+H]^+$: 318.1858, found 318.1845; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 6.97, major = 7.61.



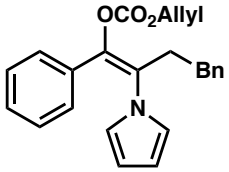
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.971	MM	0.2267	436.29816	32.07634	2.5613
2	7.611	MM	0.3288	1.65980e4	841.31396	97.4387

General Procedure for Preparation of Allyl Enol Carbonate Substrates



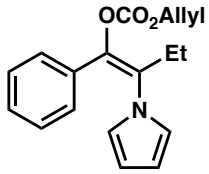
To a flame-dried flask was added LiHMDS (335 mg, 2 mmol) followed by toluene (3.0 mL) and N,N-dimethylethylamine (0.213 mL), and the resulting mixture stirred at 25 °C for 5 minutes. A solution of ketone (1 mmol) in toluene (2.0 mL) was then added, and the reaction continued at 25 °C for an additional 30 minutes. The flask was then submerged in a room temperature water bath and allyl chloroformate (0.217 mL, 2 mmol) was added slowly, and the reaction continued until no starting material remained by TLC (typically less than 30 minutes). 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 crude product was purified by silica gel flash chromatography to

afford the desired enol carbonate. The *E/Z* ratio of enol carbonates was determined by ^{1}H NMR and is >95:5 unless stated otherwise.



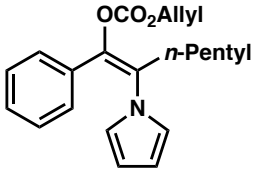
(*E*)-allyl (1,4-diphenyl-2-(1*H*-pyrrol-1-yl)but-1-en-1-yl) carbonate (1a)

Run on 1.0 mmol scale. Purified by column chromatography (10% Et_2O in hexanes) to provide a yellow oil (363.1 mg, 97% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.23 – 7.16 (m, 6H), 6.99 – 6.95 (m, 2H), 6.50 (t, *J* = 2.1 Hz, 2H), 6.16 (t, *J* = 2.2 Hz, 2H), 5.92 (ddt, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.29 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.65 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.93 – 2.84 (m, 2H), 2.78 – 2.63 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.0, 142.7, 140.9, 133.0, 131.6, 131.1, 128.7, 128.5, 128.5, 128.4, 127.1, 126.3, 121.1, 119.6, 109.8, 69.4, 33.9, 32.7; IR (Neat Film, NaCl) 1762, 1482, 1348, 1228, 1138, 1080, 1040, 942, 729, 696 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{24}NO_3$ $[M+H]^+$: 374.1751, found 374.1745.



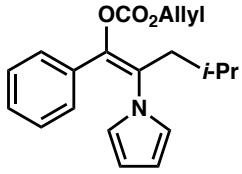
(*E*)-allyl (1-phenyl-2-(1*H*-pyrrol-1-yl)but-1-en-1-yl) carbonate (1b)

Run on a 1.47 mmol scale. Purified by column chromatography (10% Et_2O in hexanes) to provide a colorless oil (380.2 mg, 87% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 3H), 7.04 – 6.95 (m, 2H), 6.52 (t, *J* = 2.1 Hz, 2H), 6.16 (t, *J* = 2.2 Hz, 2H), 5.94 (ddt, *J* = 17.4, 10.5, 5.8 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.30 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.67 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.61 (q, *J* = 7.5 Hz, 2H), 1.00 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 141.9, 133.7, 133.1, 131.1, 128.6, 128.3, 127.0, 121.2, 119.6, 109.6, 69.4, 25.2, 11.1; IR (Neat Film, NaCl) 3060, 2977, 2938, 2877, 1766, 1494, 1483, 1458, 1446, 1364, 1347, 1320, 1292, 1260, 1224, 1145, 1121, 1085, 1039, 990, 946, 922, 901, 843, 775, 730, 696 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{20}NO_3$ $[M+H]^+$: 298.1438, found 298.1442.



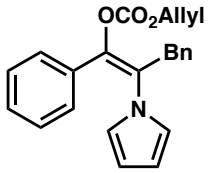
(*E*)-allyl (1-phenyl-2-(1*H*-pyrrol-1-yl)hept-1-en-1-yl) carbonate (1c)

Run on a 1.31 mmol scale. Purified by column chromatography (5% Et_2O in hexanes) to provide a slightly brown oil (421.4 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 3H), 7.02 – 6.94 (m, 2H), 6.51 (t, *J* = 2.1 Hz, 2H), 6.14 (t, *J* = 2.2 Hz, 2H), 5.93 (ddt, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.30 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.66 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.56 (dd, *J* = 8.0, 6.5 Hz, 2H), 1.44 – 1.22 (m, 5H), 0.92 – 0.83 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 142.4, 133.2, 132.6, 131.2, 128.6, 128.3, 127.1, 121.1, 119.5, 109.5, 69.3, 31.8, 31.5, 26.1, 22.5, 14.1; IR (Neat Film, NaCl) 3061, 3026, 2957, 2931, 2861, 1767, 1494, 1483, 1446, 1380, 1363, 1347, 1292, 1229 (br), 1144, 1125, 1087, 1071, 1040, 988, 944, 862, 774, 729, 696 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_3$ $[M+H]^+$: 340.1907, found 340.1893.



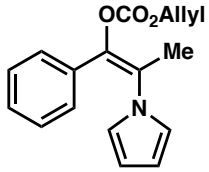
(*E*)-allyl (4-methyl-1-phenyl-2-(1*H*-pyrrol-1-yl)pent-1-en-1-yl) carbonate (1d)

Run on a 1.22 mmol scale. Purified by column chromatography (7% Et_2O in hexanes) to provide a white solid (324.2 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.16 (m, 3H), 7.03 – 6.95 (m, 2H), 6.50 (t, *J* = 2.2 Hz, 2H), 6.12 (t, *J* = 2.1 Hz, 2H), 5.91 (ddt, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.35 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.64 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.46 (d, *J* = 7.2 Hz, 2H), 1.62 – 1.51 (m, 1H), 0.94 (s, 3H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.0, 143.0, 133.3, 131.7, 131.2, 128.6, 128.3, 127.1, 121.1, 119.5, 109.5, 69.3, 40.5, 26.0, 22.4; IR (Neat Film, NaCl) 2959, 2367, 1753, 1541, 1226, 1068, 1039, 785, 730 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{23}NO_3Na$ $[M+Na]^+$: 348.1570, found 348.1564.



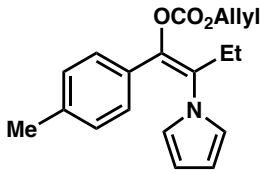
(*E*)-allyl (1,3-diphenyl-2-(1*H*-pyrrol-1-yl)prop-1-en-1-yl) carbonate (1e)

Run on a 1.58 mmol scale. Purified by column chromatography (8% Et_2O in hexanes) to provide a white solid (461.7 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.13 (m, 8H), 7.06 – 6.97 (m, 2H), 6.38 (t, *J* = 2.2 Hz, 2H), 6.05 (t, *J* = 2.2 Hz, 2H), 5.91 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.36 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.29 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.65 (dt, *J* = 5.8, 1.4 Hz, 2H), 3.89 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 143.1, 137.0, 132.9, 131.1, 130.9, 128.9, 128.9, 128.7, 128.4, 127.1, 126.8, 121.3, 119.7, 109.6, 69.5, 38.3; IR (Neat Film, NaCl) 3028, 1763, 1481, 1454, 1346, 1230, 1136, 1070, 1038, 987, 937, 772, 729, 696 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1594, found 360.1589.



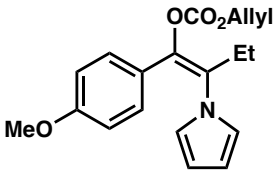
(*E*)-allyl (1-phenyl-2-(1*H*-pyrrol-1-yl)prop-1-en-1-yl) carbonate (1f)

Run on a 1.36 mmol scale. Purified by column chromatography (10% Et_2O in hexanes) to provide a colorless oil (372.2 mg, 97% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.18 (m, 3H), 7.02 – 6.96 (m, 2H), 6.54 (t, *J* = 2.2 Hz, 2H), 6.14 (t, *J* = 2.2 Hz, 2H), 5.94 (ddt, *J* = 17.1, 10.3, 5.7 Hz, 1H), 5.38 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.34 – 5.27 (m, 1H), 4.67 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 141.9, 133.1, 131.1, 128.6, 128.4, 128.3, 127.2, 120.8, 119.5, 109.6, 69.4, 18.4; IR (Neat Film, NaCl) 3060, 2951, 1763, 1484, 1446, 1381, 1364, 1345, 1316, 1292, 1230, 1143, 1118, 1081, 1037, 998, 978, 940, 773, 729, 697, 623 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{18}NO_3$ $[M+H]^+$: 284.1281, found 284.1285.



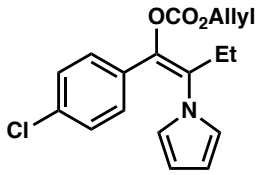
(*E*)-2-(1*H*-pyrrol-1-yl)-1-(*p*-tolyl)but-1-en-1-yl allyl carbonate (1g)

Run on a 0.736 mmol scale. Purified by column chromatography (7% EtOAc in hexanes) to provide a yellow oil (196.0 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 – 6.97 (m, 2H), 6.89 – 6.83 (m, 2H), 6.53 (t, *J* = 2.2 Hz, 2H), 6.16 (t, *J* = 2.1 Hz, 2H), 5.94 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.38 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.30 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.66 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.58 (q, *J* = 7.5 Hz, 2H), 2.27 (s, 3H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.1, 142.1, 138.6, 133.0, 131.2, 130.2, 129.1, 126.9, 121.2, 119.5, 109.5, 69.3, 25.3, 21.4, 11.1; IR (Neat Film, NaCl) 3028, 2976, 2938, 2878, 1766, 1651, 1613, 1513, 1484, 1456, 1363, 1346, 1320, 1292, 1228, 1188, 1146, 1119, 1084, 1057, 1040, 990, 945, 903, 848, 824, 795, 782, 727 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594, found 312.1578.



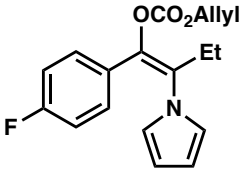
(*E*)-allyl (1-(4-methoxyphenyl)-2-(1*H*-pyrrol-1-yl)but-1-en-1-yl) carbonate (1h)

Run on a 0.955 mmol scale. Reaction washed three times with 1M HCl beforehand to remove an overlapping by-product resulting from the addition of LHMDS onto allyl chloroformate. Purified by column chromatography (10% EtOAc in hexanes) to provide a beige oil (253.8 mg, 81% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 – 6.86 (m, 2H), 6.75 – 6.67 (m, 2H), 6.53 (t, *J* = 2.1 Hz, 2H), 6.16 (t, *J* = 2.1 Hz, 2H), 5.94 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.30 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.66 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.75 (s, 3H), 2.57 (q, *J* = 7.4 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.6, 153.1, 142.0, 132.3, 131.2, 128.4, 125.5, 121.2, 119.5, 113.8, 109.5, 69.3, 55.2, 25.2, 11.2; IR (Neat Film, NaCl) 2972, 2938, 2838, 1763, 1608, 1576, 1540, 1512, 1483, 1459, 1364, 1345, 1297, 1254, 1227, 1179, 1146, 1120, 1084, 1038, 990, 942, 836, 783, 730 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}NO_4$ $[M+H]^+$: 328.1543, found 328.1535.



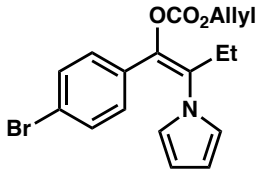
(*E*)-allyl (1-(4-chlorophenyl)-2-(1*H*-pyrrol-1-yl)but-1-en-1-yl) carbonate (1i)

Run on a 0.758 mmol scale. Purified by column chromatography (6% EtOAc in hexanes) to provide a yellow oil (227.8 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 – 7.12 (m, 2H), 6.94 – 6.84 (m, 2H), 6.50 (t, *J* = 2.2 Hz, 2H), 6.17 (t, *J* = 2.2 Hz, 2H), 5.93 (ddt, *J* = 17.1, 10.4, 5.8 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.31 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.66 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.58 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 141.0, 134.4, 134.3, 131.7, 131.0, 128.7, 128.3, 121.0, 119.8, 109.9, 69.5, 25.2, 11.0; IR (Neat Film, NaCl) 3101, 2977, 2938, 2878, 1765, 1594, 1490, 1482, 1458, 1364, 1346, 1319, 1255, 1224, 1146, 1120, 1092, 1057, 1039, 1014, 990, 944, 903, 836, 785, 728 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{19}ClNO_3$ $[M+H]^+$: 332.1048, found 332.1044.



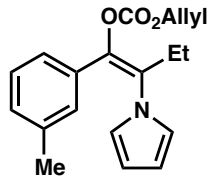
(*E*)-allyl (1-(4-fluorophenyl)-2-(1*H*-pyrrol-1-yl)but-1-en-1-yl) carbonate (1j)

Run on a 0.902 mmol scale. Purified by column chromatography (6% EtOAc in hexanes) to provide a slightly yellow oil (258.8 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 – 6.81 (m, 4H), 6.50 (t, *J* = 2.2 Hz, 2H), 6.16 (t, *J* = 2.2 Hz, 2H), 5.93 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.31 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.66 (dt, *J* = 5.8, 1.3 Hz, 2H), 2.58 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -112.1 (dddd, *J* = 13.9, 8.4, 5.6, 1.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, *J* = 249.1 Hz), 152.9, 141.0, 133.6, 130.9, 129.1 (d, *J* = 3.5 Hz), 128.9 (d, *J* = 8.2 Hz), 120.9, 119.6, 115.4 (d, *J* = 21.7 Hz), 109.7, 69.4, 25.1, 11.0; IR (Neat Film, NaCl) 2976, 1764, 1604, 1509, 1483, 1460, 1364, 1346, 1293, 1256, 1226, 1162, 1145, 1120, 1084, 1039, 990, 945, 904, 842, 780, 727 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{19}FNO_3$ $[M+H]^+$: 316.1343, found 316.1346.



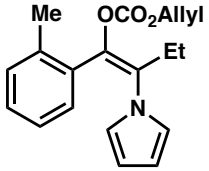
(*E*)-allyl (1-(4-bromophenyl)-2-(1*H*-pyrrol-1-yl)but-1-en-1-yl) carbonate (1k)

Run on a 0.669 mmol scale. Purified by column chromatography (6% EtOAc in hexanes) to provide a yellow oil (195.7 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 2H), 6.86 – 6.78 (m, 2H), 6.50 (t, *J* = 2.2 Hz, 2H), 6.17 (t, *J* = 2.1 Hz, 2H), 5.93 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.31 (dq, *J* = 10.1, 1.0 Hz, 1H), 4.66 (dt, *J* = 5.8, 1.3 Hz, 2H), 2.58 (q, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 141.0, 134.4, 132.1, 131.6, 131.0, 128.6, 122.8, 121.0, 119.8, 110.0, 69.5, 25.3, 11.0; IR (Neat Film, NaCl) 2977, 2937, 1765, 1588, 1483, 1460, 1364, 1346, 1254, 1225, 1145, 1120, 1084, 1072, 1039, 990, 945, 902, 831, 784, 729 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{19}BrNO_3$ $[M+NH_4]^+$: 376.0543, found 376.0540.



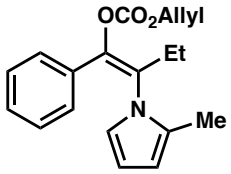
(*E*)-2-(1*H*-pyrrol-1-yl)-1-(*m*-tolyl)but-1-en-1-yl allyl carbonate (1l)

Run on a 1.0 mmol scale. Purified by column chromatography (6% EtOAc in hexanes) to provide a yellow oil (294.0 mg, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 6.96 (m, 2H), 6.81 – 6.75 (m, 2H), 6.51 (t, *J* = 2.2 Hz, 2H), 6.15 (t, *J* = 2.2 Hz, 2H), 5.94 (ddt, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.34 – 5.27 (m, 1H), 4.67 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.59 (q, *J* = 7.5 Hz, 2H), 2.21 (s, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 142.1, 137.9, 133.5, 132.9, 131.2, 129.4, 128.1, 127.6, 124.1, 121.2, 119.5, 109.5, 69.3, 25.2, 21.5, 11.1; IR (Neat Film, NaCl) 2975, 1764, 1484, 1364, 1346, 1234, 1190, 1120, 1085, 1040, 988, 942, 874, 784, 727, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594, found 312.1593.



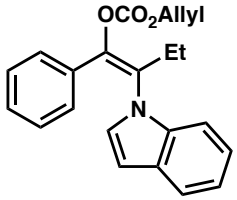
(E)-2-(1*H*-pyrrol-1-yl)-1-(*o*-tolyl)but-1-en-1-yl allyl carbonate (1m)

Run on a 0.546 mmol scale. Purified by column chromatography (6% EtOAc in hexanes) to provide a colorless oil (138.7 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.22 (m, 1H), 7.19 – 7.14 (m, 1H), 7.12 – 7.06 (m, 2H), 6.42 (t, *J* = 2.2 Hz, 2H), 6.01 (t, *J* = 2.2 Hz, 2H), 5.89 (ddt, *J* = 17.2, 10.5, 5.8 Hz, 1H), 5.33 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.60 (dt, *J* = 5.8, 1.3 Hz, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 2.08 (s, 3H), 1.03 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 140.2, 137.9, 134.7, 132.8, 131.2, 130.1, 129.8, 129.0, 125.7, 121.0, 119.5, 109.0, 69.2, 24.3, 19.5, 11.7; IR (Neat Film, NaCl) 2974, 1761, 1482, 1458, 1346, 1292, 1254, 1225, 1147, 1122, 1084, 1038, 990, 945, 725 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594, found 312.1601.



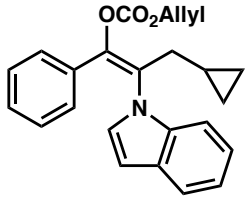
(*E*)-allyl (2-(2-methyl-1*H*-pyrrol-1-yl)-1-phenylbut-1-en-1-yl) carbonate (1n)

Run on a 0.532 mmol scale. Purified by column chromatography (7% EtOAc in hexanes) to provide a colorless oil (156.6 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 – 7.13 (m, 3H), 6.91 – 6.84 (m, 2H), 6.56 (dd, *J* = 2.9, 1.7 Hz, 1H), 6.15 (t, *J* = 3.1 Hz, 1H), 5.95 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.86 (ddq, *J* = 3.5, 1.8, 0.9 Hz, 1H), 5.39 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.31 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.69 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.57 (q, *J* = 7.5 Hz, 2H), 1.89 (d, *J* = 0.9 Hz, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 144.0, 133.0, 132.1, 131.1, 129.2, 128.6, 128.4, 126.7, 119.6, 119.6, 109.1, 107.9, 69.4, 25.8, 12.1, 10.7; IR (Neat Film, NaCl) 2976, 2940, 1764, 1481, 1445, 1420, 1363, 1343, 1260, 1224, 1183, 1132, 1110, 1042, 988, 947, 776, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}NO_3$ $[M+H]^+$: 312.1594, found 312.1597.



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

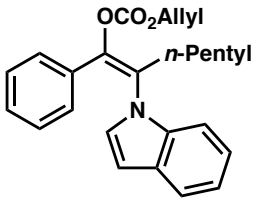
Run on a 0.647 mmol scale. Purified by column chromatography (8% EtOAc in hexanes) to provide a beige oil (213.9 mg, 95% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (dt, *J* = 7.5, 0.9 Hz, 1H), 7.28 (dt, *J* = 8.1, 1.0 Hz, 1H), 7.15 – 7.05 (m, 5H), 6.99 – 6.94 (m, 3H), 6.56 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.98 (ddt, *J* = 17.1, 10.4, 5.8 Hz, 1H), 5.43 (dq, *J* = 17.1, 1.4 Hz, 1H), 5.34 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.73 (dt, *J* = 5.8, 1.4 Hz, 2H), 2.74 (q, *J* = 7.5 Hz, 2H), 0.94 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.2, 145.0, 136.2, 133.1, 131.8, 131.3, 128.9, 128.9, 128.4, 128.0, 126.8, 122.4, 121.0, 120.3, 119.7, 111.1, 103.9, 69.6, 24.7, 11.2; IR (Neat Film, NaCl) 3058, 2976, 2940, 1764, 1513, 1494, 1474, 1458, 1363, 1335, 1292, 1260, 1224, 1144, 1012, 988, 946, 846, 764, 743, 694 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{22}NO_3$ $[M+H]^+$: 348.1594, found 348.1601.



(*E*)-allyl (3-cyclopropyl-2-(1*H*-indol-1-yl)-1-phenylprop-1-en-1-yl) carbonate (1p)

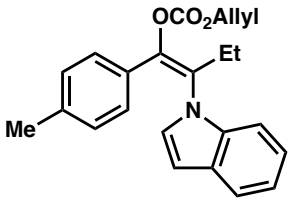
Run on a 0.514 mmol scale. Purified by column chromatography (7% EtOAc in hexanes) to provide a brown oil (164.8 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.28 (dq, *J* = 8.4, 0.9 Hz, 1H), 7.15 – 7.04 (m, 5H), 7.03 – 6.97 (m, 3H), 6.54 (dd, *J* = 3.2, 0.9 Hz, 1H), 5.96 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.40 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.32 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.71 (dt, *J* = 5.7, 1.4 Hz, 2H), 2.57 (d, *J* = 7.0 Hz, 2H), 0.72 – 0.56 (m, 1H), 0.35 – 0.25 (m, 2H), -0.03 (dt, *J* = 6.0, 4.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 145.3, 136.1, 132.9, 131.1, 130.5, 128.8, 128.8, 128.3, 128.1, 126.8, 122.2, 120.9, 120.1, 119.6, 111.0, 103.6, 69.5, 35.7, 8.7, 4.3; IR (Neat Film, NaCl) 3081, 3004, 2956, 1766, 1514, 1494, 1475, 1459, 1426, 1383, 1362, 1335, 1293, 1249, 1223, 1158, 1132, 1020, 966, 946, 831, 763,

743, 721, 695 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{24}NO_3$ $[M+H]^+$: 374.1751, found 374.1748.



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

Run on a 0.89 mmol scale. Purified by column chromatography (7% EtOAc in hexanes) to provide a beige oil (325.5 mg, 94% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 1H), 7.30 – 7.20 (m, 1H), 7.17 – 7.00 (m, 5H), 7.00 – 6.90 (m, 3H), 6.59 – 6.50 (m, 1H), 5.97 (ddt, *J* = 16.5, 11.0, 5.7 Hz, 1H), 5.41 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.33 (dt, *J* = 10.5, 1.3 Hz, 1H), 4.75 – 4.66 (m, 2H), 2.74 – 2.64 (m, 2H), 1.28 (ddt, *J* = 20.1, 13.5, 6.0 Hz, 6H), 0.83 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.1, 145.2, 136.0, 133.0, 131.2, 130.8, 128.8, 128.7, 128.3, 127.9, 126.8, 122.3, 120.9, 120.1, 119.5, 111.0, 103.8, 69.4, 31.6, 31.2, 26.2, 22.4, 14.0; IR (Neat Film, NaCl) 3057, 2957, 2929, 2860, 1764, 1513, 1494, 1475, 1458, 1381, 1363, 1334, 1293, 1225, 1158, 1143, 1130, 1012, 992, 958, 764, 742, 696 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{25}H_{28}NO_3$ $[M+H]^+$: 390.2064, found 390.2064.



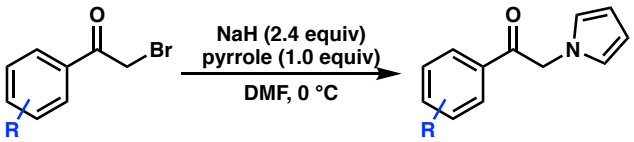
(*E*)-2-(1*H*-indol-1-yl)-1-(*p*-tolyl)but-1-en-1-yl allyl carbonate (1r)

Run on a 0.14 mmol scale. Purified by column chromatography (10% EtOAc in hexanes) to provide a brown oil (51.0 mg, 99% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.54 (m, 1H), 7.28 (dd, J = 8.2, 1.1 Hz, 1H), 7.16 – 7.05 (m, 2H), 6.93 (d, J = 3.3 Hz, 1H), 6.90 – 6.81 (m, 4H), 6.54 (dd, J = 3.2, 0.9 Hz, 1H), 5.97 (ddt, J = 17.2, 10.4, 5.8 Hz, 1H), 5.41 (dq, J = 17.2, 1.5 Hz, 1H), 5.33 (dq, J = 10.5, 1.2 Hz, 1H), 4.71 (dt, J = 5.8, 1.4 Hz, 2H), 2.70 (q, J = 7.5 Hz, 2H), 2.17 (s, 3H), 0.90 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 145.0, 138.8, 136.1,

131.2, 131.0, 130.0, 129.1, 128.8, 128.1, 126.6, 122.3, 120.9, 120.1, 119.6, 111.0, 103.6, 69.4, 24.6, 21.3, 11.2; IR (Neat Film, NaCl) 2976, 1764, 1610, 1512, 1475, 1459, 1381, 1361, 1335, 1293, 1259, 1226, 1187, 1145, 1013, 989, 946, 822, 764, 742 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}NO_3$ $[M+H]^+$: 362.1752, found 362.1749.

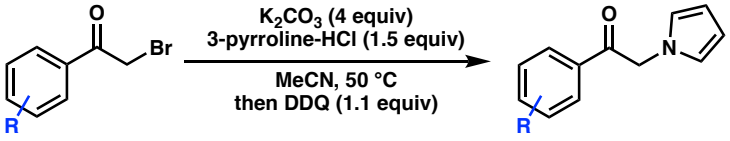
Synthesis of α-pyrrolyl-acetophenone derivatives:

Method A:



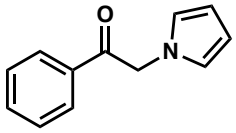
To a flame-dried flask was added freshly distilled pyrrole (2.0 mmol, 1 equiv) and DMF (8 mL), and the resulting mixture was stirred at room temperature for 5 minutes. Then, NaH (4.8 mmol, 2.4 equiv) was slowly added at 0 °C with vigorous stirring until no hydrogen evolution was observed. Afterwards, the bromoacetophenone derivative (2.0 mmol, 1 equiv) was added and the suspension was allowed to warm to room temperature and continued overnight. The reaction was quenched with aqueous NH_4Cl and extracted with Et_2O. The combined organic layers were washed with brine, dried with Na_2SO_4, and filtered. Following concentration, the crude residue was purified by silica gel column chromatography.

Method B:



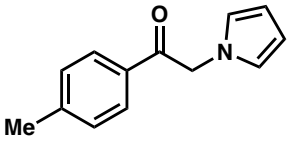
To a solution of the bromoacetophenone derivative (2.0 mmol) and K_2CO_3 (8.0 mmol, 4 equiv) in MeCN (16 mL) was added 3-pyrroline hydrochloride (2.4 mmol, 1.2 equiv), and the mixture was heated to 50 °C via an oil bath and stirred until TLC analysis showed complete consumption of the starting material. DDQ was then added (2.2 mmol, 1.1 equiv) and the resulting mixture was stirred at the same temperature overnight. The crude reaction mixture was filtered through

celite (using CH_2Cl_2 as eluent), concentrated and then purified by silica gel flash chromatography to obtain the desired product.



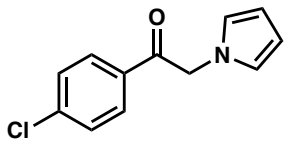
1-phenyl-2-(1*H*-pyrrol-1-yl)ethan-1-one (SI1)

Method A run on a 20.1 mmol scale. Purified by column chromatography (30% Et_2O in hexanes) to provide an orange solid (920 mg, 25% yield); 1H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.67 – 7.60 (m, 1H), 7.54 – 7.48 (m, 2H), 6.68 (t, J = 2.1 Hz, 2H), 6.25 (t, J = 2.1 Hz, 2H), 5.32 (s, 2H). Characterization data matched those reported in the literature.[4]



2-(1*H*-indol-1-yl)-1-phenylethan-1-one (SI2)

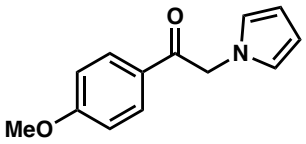
Method A run on a 2.35 mmol scale. Purified by column chromatography (30% CH_2Cl_2 in hexanes) to provide a slightly yellow solid (127.0 mg, 28% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 2H), 7.33 – 7.27 (m, 2H), 6.67 (t, *J* = 2.1 Hz, 2H), 6.25 (t, *J* = 2.1 Hz, 2H), 5.29 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.1, 145.1, 132.4, 129.7, 128.2, 122.1, 109.1, 55.4, 21.9; IR (Neat Film, NaCl) 3122, 3091, 1703, 1540, 1358, 1065, 815, 745, 734, 712 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1070, found 200.1070.



1-(4-chlorophenyl)-2-(1*H*-pyrrol-1-yl)ethan-1-one (SI3)

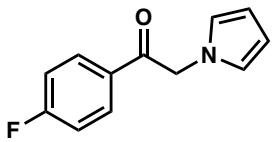
Method A run on a 4.92 mmol scale. Purified by column chromatography (60% CH_2Cl_2 in hexanes) to provide a yellow solid (248.7 mg, 23% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.52 – 7.44 (m, 2H), 6.66 (t, *J* = 2.1 Hz, 2H), 6.25 (t, *J* = 2.1 Hz, 2H), 5.28 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 140.6, 133.1, 129.5, 129.4, 122.0, 109.4, 55.6; IR (Neat

Film, NaCl) 1703, 1401, 1358, 1065, 816, 736, 704 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{12}H_{11}ClNO$ $[M+H]^+$: 220.0524, found 220.0520.



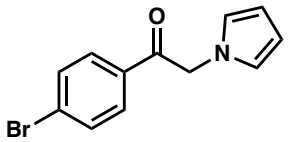
1-(4-methoxyphenyl)-2-(1*H*-pyrrol-1-yl)ethan-1-one (SI4)

Method B run on a 3.0 mmol scale. In this case, displacement by chloride counter-anion happened first and addition of Et_3N (12.0 mmol) led to the correct product. Purified by column chromatography (20% EtOAc in hexanes) to provide a brown solid (325.5 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 6.99 – 6.93 (m, 2H), 6.67 (t, *J* = 2.1 Hz, 2H), 6.24 (t, *J* = 2.1 Hz, 2H), 5.26 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 164.2, 130.5, 127.9, 122.1, 114.2, 109.1, 55.7, 55.3; IR (Neat Film, NaCl) 1685, 1601, 1574, 1500, 1420, 1356, 1318, 1293, 1266, 1234, 1186, 1167, 1116, 1092, 1020, 993, 738 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{13}H_{14}NO_2$ $[M+H]^+$: 216.1019, found 216.1028.



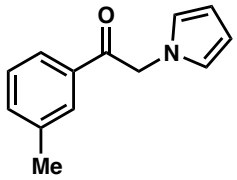
1-(4-fluorophenyl)-2-(1*H*-pyrrol-1-yl)ethan-1-one (SI5)

Method B run on a 2.0 mmol scale. Purified by column chromatography (10% to 20% EtOAc in hexanes) to provide a beige solid (196.8 mg, 46% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 2H), 7.23 – 7.10 (m, 2H), 6.67 (t, *J* = 2.1 Hz, 2H), 6.25 (t, *J* = 2.1 Hz, 2H), 5.28 (s, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -103.3 (tt, *J* = 8.4, 5.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.0, 166.3 (d, *J* = 256.3 Hz), 131.3 (d, *J* = 3.0 Hz), 130.8 (d, *J* = 9.4 Hz), 122.0, 116.3 (d, *J* = 22.0 Hz), 109.3, 55.5; IR (Neat Film, NaCl) 3098, 1702, 1678, 1598, 1408, 1359, 1097, 1066, 832, 742, 719 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{12}H_{11}FNO$ $[M+H]^+$: 204.0819, found 204.0821.



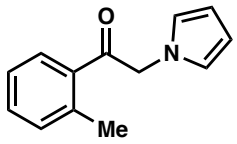
1-(4-bromophenyl)-2-(1*H*-pyrrol-1-yl)ethan-1-one (SI6)

Method B run on a 1.0 mmol scale. Purified by column chromatography (10% EtOAc in hexanes) to provide a white solid (196.8 mg, 46% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 6.66 (t, *J* = 2.1 Hz, 2H), 6.25 (t, *J* = 2.1 Hz, 2H), 5.28 (s, 2H). Characterization data matched those reported in the literature.[5]



2-(1*H*-pyrrol-1-yl)-1-(*m*-tolyl)ethan-1-one (SI7)

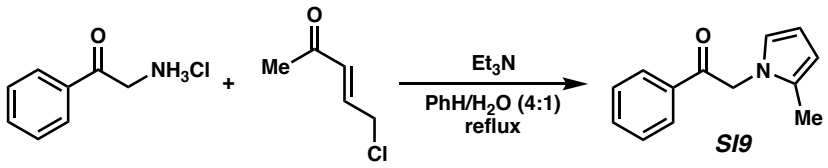
Method B run on a 2.0 mmol scale. Purified by column chromatography (10% EtOAc in hexanes) to provide a beige solid (174.8 mg, 44% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.72 (m, 2H), 7.47 – 7.35 (m, 2H), 6.67 (t, *J* = 2.1 Hz, 2H), 6.25 (t, *J* = 2.1 Hz, 2H), 5.31 (s, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 139.0, 134.9, 134.9, 128.9, 128.6, 125.3, 122.1, 109.2, 55.6, 21.5; IR (Neat Film, NaCl) 3106, 3094, 2923, 1693, 1588, 1488, 1417, 1356, 1297, 1257, 1192, 1096, 1066, 834, 788, 733, 711, 687, 649 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1070, found 200.1065.



2-(1*H*-pyrrol-1-yl)-1-(*o*-tolyl)ethan-1-one (SI8)

Method B run on a 2.0 mmol scale. Purified by column chromatography (10% EtOAc in hexanes) to provide a low melting point brown solid (164.0 mg, 41% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.44 (td, *J* = 7.4, 1.4 Hz, 1H), 7.31 (dddt, *J* = 7.9, 7.3, 1.4, 0.7 Hz, 2H), 6.66 (t, *J* = 2.1 Hz, 2H), 6.24 (t, *J* = 2.1 Hz, 2H), 5.21 (s, 2H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 139.6, 134.8, 132.6, 132.4, 128.3, 126.0, 122.0, 109.2, 57.2,

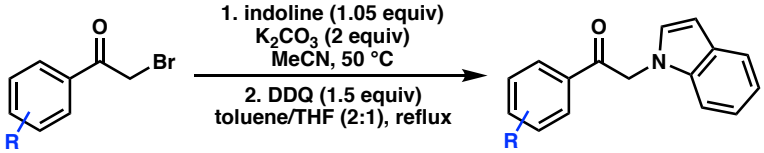
21.7; IR (Neat Film, NaCl) 3094, 2924, 1696, 1458, 1351, 1290, 1065, 758, 746, 737, 718 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1070, found 200.1067.



(2-methyl-1*H*-pyrrol-1-yl)-1-phenylethan-1-one (SI9)

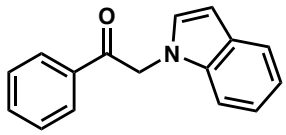
2-Aminoacetophenone hydrochloride (789.5 mg, 4.60 mmol) and Et_3N (2.56 mL, 18.4 mmol) were added to a mixture of benzene (5 mL) and water (2.5 mL). A solution of 5-chloropent-3-en-2-one (4.60 mmol) in benzene (2.5 mL) and then added, and the mixture heated to reflux via an oil bath and stirred for 5 h. Upon completion, the crude reaction mixture was allowed to cool to room temperature, and diluted with EtOAc and water. The layers were separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with 1M HCl and brine, then dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography (10% EtOAc in hexanes) to provide a light brown solid (110.0 mg, 12% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.68 – 7.59 (m, 1H), 7.57 – 7.47 (m, 2H), 6.57 (dd, *J* = 2.9, 1.8 Hz, 1H), 6.15 (t, *J* = 3.1 Hz, 1H), 5.98 (ddq, *J* = 3.6, 1.8, 0.9 Hz, 1H), 5.24 (s, 2H), 2.14 (d, *J* = 0.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.6, 134.9, 134.1, 129.3, 129.1, 128.1, 121.3, 107.9, 107.6, 53.2, 12.0; IR (Neat Film, NaCl) 2914, 1698, 1596, 1489, 1450, 1425, 1354, 1303, 1223, 1078, 1016, 990, 752, 710, 624 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1070, found 200.1063.

Synthesis of α-indolyl-acetophenone derivatives:



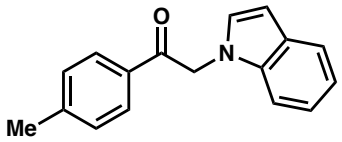
To a solution of the bromoacetophenone derivative (2.0 mmol) and K_2CO_3 (4.0 mmol) in MeCN (20 mL) was added indoline (2.1 mmol), and the mixture was heated to 50 °C via oil bath and stirred until TLC analysis showed complete consumption of the starting material. The mixture was filtered through celite and concentrated. The crude residue was redissolved in toluene (26

mL) and THF (14 mL) and treated with DDQ (2.2 mmol). The resulting mixture was heated to reflux via oil bath and stirred overnight. Following completion, the crude reaction was allowed to cool to room temperature and filtered through celite and concentrated. The crude residue was purified by silica gel flash chromatography to obtain the desired product.



2-(1*H*-indol-1-yl)-1-phenylethan-1-one (SI10)

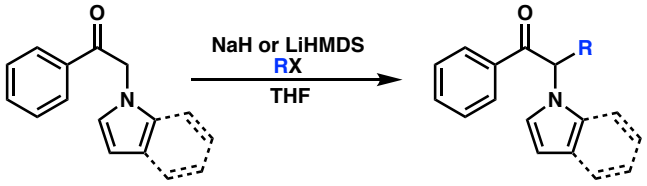
Run on a 2.0 mmol scale. Purified by column chromatography (15% EtOAc in hexanes) to provide a beige solid (144.1 mg, 31% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.98 (m, 2H), 7.71 – 7.60 (m, 2H), 7.57 – 7.49 (m, 2H), 7.22 – 7.18 (m, 2H), 7.17 – 7.10 (m, 2H), 6.62 (d, *J* = 3.2 Hz, 1H), 5.53 (s, 1H). Characterization data matched those reported in the literature.[5]



2-(1*H*-indol-1-yl)-1-(*p*-tolyl)ethan-1-one (SI11)

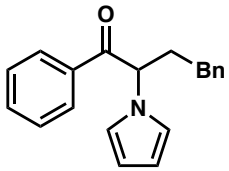
Run on a 2.0 mmol scale. Purified by column chromatography (15% EtOAc in hexanes) to provide a beige solid (90.0 mg, 18% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.89 (m, 2H), 7.66 (dt, J = 7.8, 1.0 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.19 (dt, J = 3.9, 1.0 Hz, 2H), 7.14 – 7.09 (m, 2H), 6.61 (dd, J = 3.2, 0.5 Hz, 1H), 5.50 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.8, 145.2, 136.8, 132.4, 129.8, 128.8, 128.8, 128.3, 122.1, 121.3, 119.8, 109.1, 102.6, 52.3, 21.9; IR (Neat Film, NaCl) 3054, 2968, 2934, 2877, 1682, 1607, 1574, 1514, 1459, 1307, 1260, 1200, 1183, 763, 739, 720 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{16}NO$ $[M+H]^+$: 250.1226, found 250.1227.

Alkylation of α-pyrrolyl-acetophenone and α-indolyl-acetophenone derivatives:



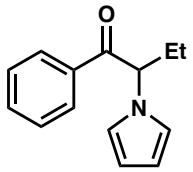
Method A: A flame-dried round bottom flask was charged with NaH (2.4 mmol, 1.2 equiv) and THF (7.5 mL). The suspension was then cooled in a 0 °C ice bath and a solution of ketone (2.0 mmol) in THF (2.5 mL) was added dropwise. The reaction was allowed to warm to room temperature and continued until no more H_2 evolution was observed. The mixture was then treated with the appropriate electrophil (2.4 mmol, 1.2 equiv) and the resulting mixture heated to 50 °C via oil bath and stirred overnight. Following completion, the reaction was allowed to cool to room temperature and then quenched by slow addition of saturated aqueous NH_4Cl and extracted with CH_2Cl_2. The combined organic layers were dried with Na_2SO_4 and concentrated. The crude residue was purified by silica gel flash chromatography to afford the desired alkylated product.

Method B: A flame-dried round bottom flask was charged with LiHMDS (2.2 mmol, 1.1 equiv) and THF (7.5 mL). The solution was then cooled in a 0 °C ice bath for 10 min and a solution of ketone (2.0 mmol) in THF (2.5 mL) was added dropwise. After stirring for 15 min, the electrophile (2.4 mmol, 1.2 equiv) was added dropwise and the reaction heated to 60 °C via oil bath and continued overnight. Following completion, the reaction was allowed to cool to room temperature and then quenched with a slow addition of saturated aqueous NH_4Cl and extracted with EtOAc. The combined organics were dried over Na_2SO_4 and concentrated. The crude residue was purified by silica gel flash chromatography to afford the alkylated product.



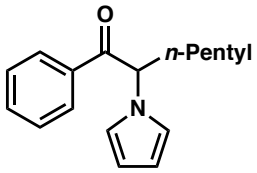
1,4-diphenyl-2-(1*H*-pyrrol-1-yl)butan-1-one (SI12)

Method A run on a 2.16 mmol scale. Purified by column chromatography (10% Et_2O in hexanes) to provide a yellow solid (314.7 mg, 50% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.74 (m, 2H), 7.53 (ddt, *J* = 7.9, 6.9, 1.3 Hz, 1H), 7.44 – 7.36 (m, 2H), 7.36 – 7.29 (m, 2H), 7.28 – 7.21 (m, 1H), 7.20 – 7.15 (m, 2H), 6.78 (t, *J* = 2.1 Hz, 2H), 6.21 (t, *J* = 2.1 Hz, 2H), 5.38 (dd, *J* = 9.3, 5.0 Hz, 1H), 2.73 – 2.61 (m, 1H), 2.57 – 2.35 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 140.5, 135.2, 133.7, 128.9, 128.8, 128.7, 128.5, 126.5, 120.3, 109.1, 61.5, 34.2, 31.9; IR (Neat Film, NaCl) 3025, 2923, 1687, 1597, 1580, 1488, 1259, 1214, 1092, 1070, 788, 723, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{19}NONa$ $[M+Na]^+$: 312.1359, found 312.1357.



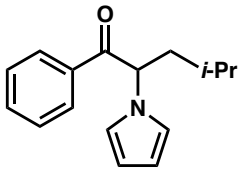
1-phenyl-2-(1*H*-pyrrol-1-yl)butan-1-one (SI13)

Method A run on a 2.16 mmol scale. Purified by column chromatography (10% Et_2O in hexanes) to provide a yellow solid (315.6 mg, 69% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.55 (ddt, *J* = 7.8, 6.9, 1.3 Hz, 1H), 7.49 – 7.40 (m, 2H), 6.76 (t, *J* = 2.1 Hz, 2H), 6.17 (t, *J* = 2.2 Hz, 2H), 5.34 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.25 – 2.13 (m, 1H), 2.07 (ddq, *J* = 14.6, 9.3, 7.4 Hz, 1H), 0.93 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 135.7, 133.6, 128.9, 128.5, 120.2, 109.0, 64.3, 26.2, 10.7; IR (Neat Film, NaCl) 3100, 3061, 2970, 2934, 2876, 1688, 1597, 1579, 1488, 1458, 1448, 1273, 1263, 1208, 1183, 1095, 1082, 1068, 1002, 988, 902, 813, 725, 688 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{14}H_{16}NO$ $[M+H]^+$: 214.1226, found 214.1235.



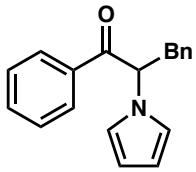
1-phenyl-2-(1*H*-pyrrol-1-yl)heptan-1-one (SI14)

Method A run on a 2.16 mmol scale. Purified by column chromatography (10% Et_2O in hexanes) to provide a brown solid (358.5 mg, 65% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.42 (m, 2H), 6.76 (t, *J* = 2.1 Hz, 2H), 6.17 (t, *J* = 2.1 Hz, 2H), 5.44 (dd, *J* = 9.3, 5.5 Hz, 1H), 2.18 – 1.97 (m, 2H), 1.43 – 1.18 (m, 6H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.1, 135.5, 133.7, 128.9, 128.5, 120.1, 108.9, 62.8, 32.8, 31.5, 25.8, 22.5, 14.1; IR (Neat Film, NaCl) 3064, 2956, 2929, 2859, 1690, 1597, 1580, 1487, 1448, 1267, 1206, 1182, 1090, 1069, 966, 723, 688 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{22}NO$ $[M+H]^+$: 256.1696, found 256.1705.



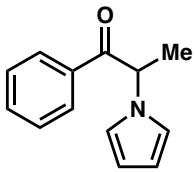
4-methyl-1-phenyl-2-(1*H*-pyrrol-1-yl)pentan-1-one (SI15)

Method A run on a 2.16 mmol scale. Purified by column chromatography (10% Et_2O in hexanes) to provide a brown solid (335.7 mg, 64% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.89 (m, 2H), 7.60 – 7.53 (m, 1H), 7.49 – 7.42 (m, 2H), 6.77 (t, *J* = 2.1 Hz, 2H), 6.17 (t, *J* = 2.1 Hz, 2H), 5.57 (dd, *J* = 10.0, 5.0 Hz, 1H), 2.03 (ddd, *J* = 14.1, 10.0, 4.9 Hz, 1H), 1.91 (ddd, *J* = 14.1, 8.9, 5.0 Hz, 1H), 1.47 (dddd, *J* = 13.3, 11.5, 8.9, 6.5 Hz, 1H), 1.03 (d, *J* = 6.6 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.2, 135.4, 133.7, 129.0, 128.5, 120.2, 108.9, 60.9, 41.6, 24.8, 23.2, 21.9; IR (Neat Film, NaCl) 2956, 2929, 2869, 1690, 1596, 1579, 1488, 1448, 1386, 1368, 1279, 1204, 1182, 1091, 1069, 1002, 861, 775, 723, 688 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{16}H_{20}NO$ $[M+H]^+$: 242.1539, found 242.1547.



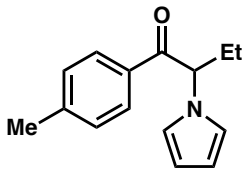
1,3-diphenyl-2-(1*H*-pyrrol-1-yl)propan-1-one (SI16)

Method A run on a 2.16 mmol scale. Reaction complete after 1 h at room temperature, no additional heating required. Purified by column chromatography (10% Et_2O in hexanes) to provide a white solid (566.5 mg, 95% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.84 (m, 2H), 7.57 – 7.48 (m, 1H), 7.45 – 7.34 (m, 2H), 7.25 – 7.16 (m, 3H), 7.05 – 6.95 (m, 2H), 6.66 (t, *J* = 2.2 Hz, 2H), 6.12 (t, *J* = 2.2 Hz, 2H), 5.57 (dd, *J* = 8.8, 5.7 Hz, 1H), 3.47 (dd, *J* = 13.9, 5.7 Hz, 1H), 3.28 (dd, *J* = 13.9, 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 137.3, 135.4, 133.8, 129.2, 128.9, 128.6, 128.6, 126.9, 120.1, 109.3, 64.3, 39.3; IR (Neat Film, NaCl) 3027, 2922, 1687, 1596, 1487, 1448, 1271, 1202, 1090, 1070, 967, 874, 725, 700, 688, 665 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{18}NO$ $[M+H]^+$: 276.1383, found 276.1371.



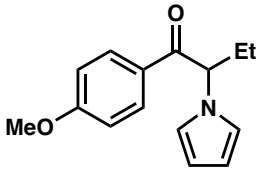
1-phenyl-2-(1*H*-pyrrol-1-yl)propan-1-one (SI17)

Method A run on a 2.16 mmol scale. Reaction done after 45 min at room temperature, no additional heating required. Purified by column chromatography (8% Et_2O in hexanes) to provide a white solid (320.2 mg, 74% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 7.61 – 7.52 (m, 1H), 7.50 – 7.40 (m, 2H), 6.77 (t, *J* = 2.1 Hz, 2H), 6.19 (t, *J* = 2.2 Hz, 2H), 5.65 (q, *J* = 7.0 Hz, 1H), 1.74 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 135.0, 133.7, 128.9, 128.5, 119.8, 109.1, 58.4, 18.8; IR (Neat Film, NaCl) 3097, 2988, 2937, 1693, 1596, 1488, 1449, 1374, 1275, 1250, 1214, 1183, 1093, 1070, 1000, 964, 938, 726, 687, 646 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{13}H_{14}NO$ $[M+H]^+$: 200.1070, found 200.1073.



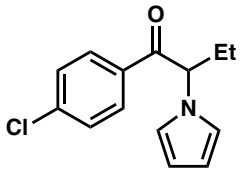
2-(1*H*-pyrrol-1-yl)-1-(*p*-tolyl)butan-1-one (SI18)

Method B run on a 1.30 mmol scale. Purified by column chromatography (8% EtOAc in hexanes) to provide a white solid (213.6 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.77 (m, 2H), 7.25 – 7.21 (m, 2H), 6.76 (t, *J* = 2.1 Hz, 2H), 6.16 (t, *J* = 2.1 Hz, 2H), 5.31 (dd, *J* = 9.1, 5.7 Hz, 1H), 2.39 (s, 3H), 2.23 – 1.97 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.6, 144.6, 133.0, 129.6, 128.7, 120.2, 108.8, 64.1, 26.2, 21.8, 10.8; IR (Neat Film, NaCl) 3097, 2969, 2931, 2876, 1684, 1606, 1573, 1488, 1459, 1406, 1263, 1205, 1183, 1096, 1068, 982, 901, 860, 779, 725 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}NO$ $[M+H]^+$: 228.1383, found 228.1392.



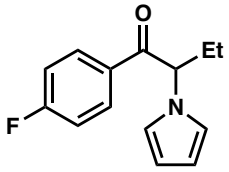
1-(4-methoxyphenyl)-2-(1*H*-pyrrol-1-yl)butan-1-one (SI19)

Method B run on a 1.51 mmol scale. Purified by column chromatography (10% EtOAc in hexanes) to provide a yellow oil (264.7 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.87 (m, 2H), 6.96 – 6.85 (m, 2H), 6.77 (t, *J* = 2.2 Hz, 2H), 6.17 (t, *J* = 2.1 Hz, 2H), 5.30 (dd, *J* = 9.0, 5.8 Hz, 1H), 3.85 (s, 3H), 2.26 – 1.94 (m, 2H), 0.91 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 163.9, 130.9, 128.5, 120.1, 114.1, 108.8, 63.9, 55.6, 26.3, 10.8; IR (Neat Film, NaCl) 2968, 1681, 1600, 1574, 1509, 1488, 1456, 1421, 1312, 1260, 1212, 1170, 1095, 1027, 988, 860, 839, 724 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}NO_2$ $[M+H]^+$: 244.1332, found 244.1331.



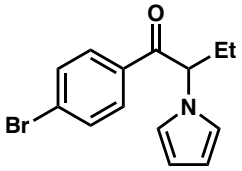
1-(4-chlorophenyl)-2-(1*H*-pyrrol-1-yl)butan-1-one (SI20)

Method B run on a 1.11 mmol scale. Purified by column chromatography (5% EtOAc in hexanes) to provide a yellow oil (212.3 mg, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.79 (m, 2H), 7.43 – 7.36 (m, 2H), 6.72 (t, *J* = 2.2 Hz, 2H), 6.17 (t, *J* = 2.1 Hz, 2H), 5.25 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.22 – 1.99 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.8, 140.1, 133.9, 129.9, 129.2, 120.1, 109.2, 64.4, 26.0, 10.7; IR (Neat Film, NaCl) 3101, 2970, 2935, 2877, 1688, 1588, 1570, 1488, 1462, 1400, 1307, 1274, 1262, 1230, 1207, 1180, 1094, 1069, 1012, 990, 965, 902, 862, 832, 806, 726, 626 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{14}H_{15}ClNO$ $[M+H]^+$: 248.0837, found 248.0842.



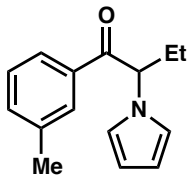
11-(4-fluorophenyl)-2-(1*H*-pyrrol-1-yl)butan-1-one (SI21)

Method B run on a 1.34 mmol scale. Purified by column chromatography (5% EtOAc in hexanes) to provide a yellow oil (231.2 mg, 75% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.87 (m, 1H), 7.15 – 7.05 (m, 1H), 6.74 (t, *J* = 2.2 Hz, 1H), 6.17 (t, *J* = 2.2 Hz, 1H), 5.27 (dd, *J* = 9.1, 5.7 Hz, 1H), 2.24 – 1.98 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 2H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -104.0 (ttd, *J* = 8.2, 5.4, 2.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 166.0 (d, *J* = 256.0 Hz), 132.0 (d, *J* = 3.1 Hz), 131.2 (d, *J* = 9.4 Hz), 120.1, 116.1 (d, *J* = 22.0 Hz), 109.2, 64.3, 26.1, 10.7; IR (Neat Film, NaCl) 3104, 2971, 2936, 2878, 1688, 1598, 1506, 1488, 1458, 1410, 1302, 1274, 1263, 1231, 1208, 1159, 1096, 1069, 1010, 991, 964, 903, 864, 843, 792, 726 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{14}H_{15}FNO$ $[M+H]^+$: 232.1132, found 232.1144.



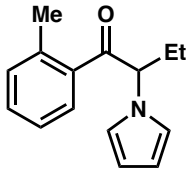
1-(4-bromophenyl)-2-(1*H*-pyrrol-1-yl)butan-1-one (SI22)

Method B run on a 0.912 mmol scale. Purified by column chromatography (7% EtOAc in hexanes) to provide an orange solid (204.6 mg, 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.71 (m, 2H), 7.61 – 7.53 (m, 2H), 6.72 (t, *J* = 2.1 Hz, 2H), 6.17 (t, *J* = 2.1 Hz, 2H), 5.24 (dd, *J* = 9.1, 5.6 Hz, 1H), 2.23 – 1.99 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.0, 134.3, 132.3, 130.0, 128.9, 120.1, 109.3, 64.4, 26.0, 10.7; IR (Neat Film, NaCl) 2971, 2936, 1693, 1584, 1553, 1485, 1462, 1396, 1263, 1206, 1180, 1095, 1071, 1007, 989, 902, 862, 806, 727 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{14}H_{15}BrNO$ $[M+H]^+$: 292.0332, found 292.0335.



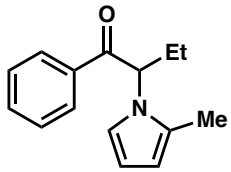
2-(1*H*-pyrrol-1-yl)-1-(*m*-tolyl)butan-1-one (SI23)

Method B run on a 1.46 mmol scale. Purified by column chromatography (5% EtOAc in hexanes) to provide a yellow oil (259.4 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.68 (m, 2H), 7.41 – 7.29 (m, 2H), 6.78 (t, *J* = 2.1 Hz, 2H), 6.18 (t, *J* = 2.1 Hz, 2H), 5.35 (dd, *J* = 9.2, 5.7 Hz, 1H), 2.40 (s, 3H), 2.25 – 1.99 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 138.7, 135.6, 134.4, 129.1, 128.7, 125.6, 120.1, 108.8, 64.2, 26.2, 21.5, 10.7; IR (Neat Film, NaCl) 3099, 2970, 2933, 2876, 1686, 1602, 1585, 1487, 1460, 1381, 1265, 1240, 1164, 1096, 1068, 964, 773, 724, 687 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}NO$ $[M+H]^+$: 228.1383, found 228.1383.



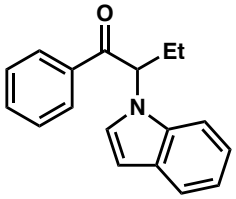
2-(1*H*-pyrrol-1-yl)-1-(*o*-tolyl)butan-1-one (SI24)

Method B run on a 0.76 mmol scale. Purified by column chromatography (5% EtOAc in hexanes) to provide a yellow oil (139.5 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.35 (td, *J* = 7.5, 1.4 Hz, 1H), 7.25 – 7.20 (m, 2H), 6.72 (t, *J* = 2.2 Hz, 2H), 6.16 (t, *J* = 2.2 Hz, 2H), 5.16 (dd, *J* = 9.3, 5.6 Hz, 1H), 2.40 (s, 3H), 2.18 (dqd, *J* = 14.7, 7.4, 5.6 Hz, 1H), 2.03 (ddq, *J* = 14.5, 9.3, 7.3 Hz, 1H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 138.6, 136.9, 132.0, 131.6, 127.5, 125.7, 120.1, 108.9, 66.8, 25.6, 20.9, 10.8; IR (Neat Film, NaCl) 3100, 3064, 3022, 2967, 2932, 2876, 1695, 1600, 1570, 1487, 1457, 1382, 1272, 1261, 1228, 1210, 1197, 1095, 1082, 1068, 980, 965, 904, 850, 821, 780, 758, 723, 656 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}NO$ $[M+H]^+$: 228.1383, found 228.1384.



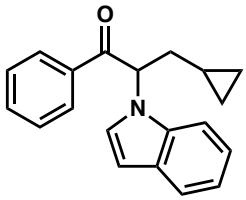
2-(2-methyl-1*H*-pyrrol-1-yl)-1-phenylbutan-1-one (SI25)

Method B run on a 0.872 mmol scale. Purified by column chromatography (5% EtOAc in hexanes) to provide a yellow oil (134.8 mg, 68% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m, 2H), 7.59 – 7.50 (m, 1H), 7.48 – 7.39 (m, 2H), 6.65 (dd, *J* = 3.0, 1.8 Hz, 1H), 6.07 (t, *J* = 3.2 Hz, 1H), 5.91 (ddq, *J* = 3.5, 1.7, 0.9 Hz, 1H), 5.32 (dd, *J* = 8.8, 5.8 Hz, 1H), 2.30 (d, *J* = 0.9 Hz, 3H), 2.28 – 2.16 (m, 1H), 2.08 – 1.95 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 135.9, 133.5, 128.9, 128.4, 128.1, 118.5, 107.9, 107.7, 61.3, 26.0, 12.6, 10.9; IR (Neat Film, NaCl) 2970, 2936, 1689, 1597, 1486, 1448, 1418, 1291, 1211, 1182, 1147, 1068, 964, 907, 815, 773, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}NO$ $[M+H]^+$: 228.1383, found 228.1385.



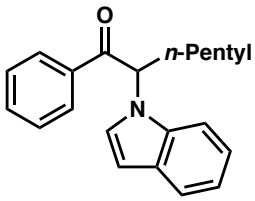
2-(1*H*-indol-1-yl)-1-phenylbutan-1-one (SI26)

Method B run for 36h on a 0.594 mmol scale. Purified by column chromatography (6% EtOAc in hexanes) to provide a beige solid (130.3 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.88 (m, 2H), 7.63 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.54 – 7.49 (m, 1H), 7.46 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.39 (ddt, *J* = 7.9, 6.7, 1.2 Hz, 2H), 7.27 – 7.21 (m, 2H), 7.13 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 6.55 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.76 (dd, *J* = 9.0, 5.7 Hz, 1H), 2.38 – 2.25 (m, 1H), 2.25 – 2.12 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 136.2, 135.6, 133.7, 129.0, 128.9, 128.4, 126.0, 122.0, 121.4, 120.0, 109.1, 103.0, 60.8, 25.4, 11.0; IR (Neat Film, NaCl) 3052, 2969, 1685, 1596, 1512, 1475, 1458, 1307, 1202, 1014, 902, 812, 762, 741, 722 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{18}NO$ $[M+H]^+$: 264.1383, found 264.1388.



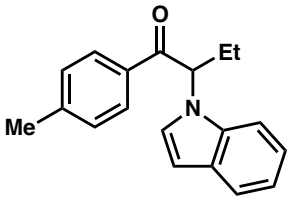
3-cyclopropyl-2-(1*H*-indol-1-yl)-1-phenylpropan-1-one (SI27)

Method B run for 36 h with 1.5 equivalent of electrophile on a 1.28 mmol scale. Purified by column chromatography (5% EtOAc in hexanes) to provide a yellow oil (184.1 mg, 49% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 2H), 7.62 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.43 – 7.34 (m, 2H), 7.30 – 7.20 (m, 2H), 7.13 (ddd, *J* = 7.9, 7.0, 0.9 Hz, 1H), 6.55 (dd, *J* = 3.3, 0.9 Hz, 1H), 5.96 (dd, *J* = 8.7, 5.7 Hz, 1H), 2.18 (ddd, *J* = 14.7, 8.7, 6.3 Hz, 1H), 2.03 (ddd, *J* = 14.0, 7.8, 5.7 Hz, 1H), 0.56 (qdt, *J* = 7.9, 6.3, 4.9 Hz, 1H), 0.49 – 0.39 (m, 1H), 0.36 (dddd, *J* = 9.3, 7.9, 5.4, 4.3 Hz, 1H), 0.15 (dtd, *J* = 9.2, 5.2, 4.2 Hz, 1H), 0.03 (dtd, *J* = 9.4, 5.3, 4.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.5, 136.2, 135.7, 133.7, 129.0, 128.9, 128.4, 126.0, 122.0, 121.4, 119.9, 109.2, 103.0, 59.7, 37.1, 8.2, 4.8, 4.8; IR (Neat Film, NaCl) 3056, 2999, 1686, 1596, 1513, 1476, 1458, 1308, 1275, 1249, 1210, 1163, 1015, 926, 763, 739, 691 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{20}NO$ $[M+H]^+$: 290.1539, found 290.1529.



2-(1*H*-indol-1-yl)-1-phenylheptan-1-one (SI28)

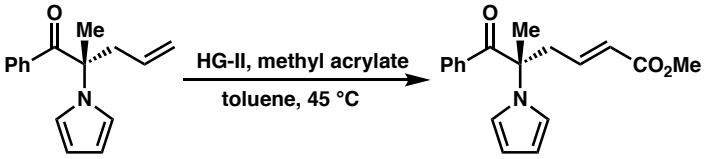
Method B run for 36h with 1.5 equivalent of electrophile on a 1.28 mmol scale. Purified by column chromatography (5% EtOAc in hexanes) to provide a beige oil (299.7 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.88 (m, 2H), 7.62 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.56 – 7.48 (m, 1H), 7.47 – 7.36 (m, 3H), 7.28 – 7.19 (m, 2H), 7.12 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 6.55 (dd, *J* = 3.3, 0.8 Hz, 1H), 5.85 (dd, *J* = 9.1, 5.6 Hz, 1H), 2.26 (ddt, *J* = 14.0, 11.0, 5.5 Hz, 1H), 2.20 – 2.08 (m, 1H), 1.40 – 1.18 (m, 6H), 0.83 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 136.2, 135.6, 133.7, 129.0, 128.9, 128.4, 126.0, 122.0, 121.4, 119.9, 109.1, 102.9, 59.2, 32.0, 31.6, 26.0, 22.5, 14.1; IR (Neat Film, NaCl) 3054, 2955, 2929, 2860, 1688, 1596, 1513, 1478, 1460, 1309, 1227, 1198, 1014, 957, 763, 738, 718, 690 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{24}NO$ $[M+H]^+$: 306.1852, found 306.1857.



2-(1*H*-indol-1-yl)-1-(*p*-tolyl)butan-1-one (SI29)

Run on a 0.22 mmol scale. Purified by column chromatography (8% EtOAc in hexanes) to provide a brown oil (43.0 mg, 78% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.81 (m, 2H), 7.62 (dt, J = 7.8, 1.0 Hz, 1H), 7.46 (dd, J = 8.4, 1.0 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.21 – 7.16 (m, 2H), 7.12 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.55 (dd, J = 3.3, 0.8 Hz, 1H), 5.74 (dd, J = 8.9, 5.7 Hz, 1H), 2.35 (s, 3H), 2.29 (dtd, J = 14.8, 7.3, 5.7 Hz, 1H), 2.17 (ddq, J = 14.6, 9.0, 7.3 Hz, 1H), 0.92 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 144.7, 136.2, 133.1, 129.6, 128.9, 128.5, 126.0, 122.0, 121.3, 119.9, 109.1, 102.8, 60.6, 25.4, 21.8, 11.0; IR (Neat Film, NaCl) 3054, 2968, 2934, 2877, 1682, 1607, 1574, 1514, 1459, 1307, 1260, 1200, 1183, 763, 739, 720 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{20}NO$ $[M+H]^+$: 278.1539, found 278.1542.

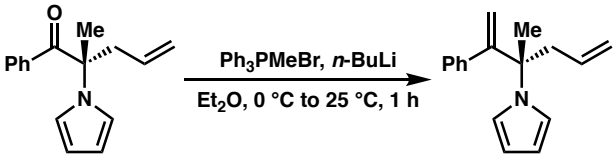
Derivatization of Alkylation Products



3

methyl (*S*,*E*)-5-methyl-6-oxo-6-phenyl-5-(1*H*-pyrrol-1-yl)hex-2-enoate (3)

To an oven-dried 1 dram vial was added α-pyrrolo ketone **2f** (23.9 mg, 0.1 mmol), Hoveyda-Grubbs 2nd generation catalyst (3.2 mg, 0.005 mmol), and toluene (1.0 mL). The resulting mixture was stirred till all solids dissolved, then trated with methyl acrylate (90 μL, 1 mmol) and heated to 45 °C in a metal heating block for 12 h. Following completion, the reaction was allowed to cool to room temperature and concentrated to a crude oil. The crude mixture was purified by column chromatogprahy (10 to 20% Et_2O in hexanes) to afford the desired product as a colorless oil (28.4 mg, 95% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (tt, *J* = 7.0, 1.5 Hz, 1H), 7.31 – 7.21 (m, 6H), 6.72 (t, *J* = 2.2 Hz, 2H), 6.60 (ddd, *J* = 15.4, 8.3, 6.9 Hz, 1H), 6.25 (t, *J* = 2.1 Hz, 2H), 5.80 (dt, *J* = 15.5, 1.4 Hz, 1H), 3.70 (s, 4H), 3.08 – 2.91 (m, 2H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 166.4, 142.6, 134.9, 132.9, 128.9, 128.6, 125.3, 118.7, 110.0, 67.0, 51.6, 42.7, 23.2; IR (Neat Film, NaCl) 3068, 2994, 2950, 1723, 1682, 1659, 1595, 1484, 1436, 1381, 1335, 1278, 1221, 1177, 1132, 1091, 1040, 974, 726 cm $^{-1}$; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{20}NO_3$ $[M+H]^+$: 298.1438, found 298.1442.

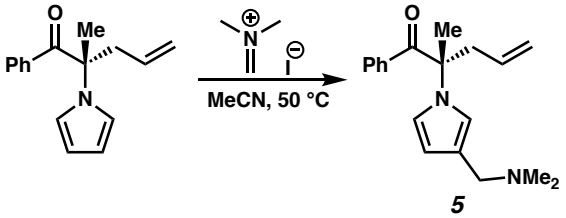


4

(*S*)-1-(3-methyl-2-phenylhexa-1,5-dien-3-yl)-1*H*-pyrrole (4)

To an oven-dried 1 dram vial was added methyltriphenylphosphonium bromide (53.6 mg, 0.15 mmol) and Et_2O (0.75 mL). The resulting suspension was cooled in an ice-bath and *n*-BuLi (58 μL, 0.14 mmol, 2.4 M) added dropwise. After stirring for an additional 30 min, a solution of α-pyrrolo ketone **2f** (23.9 mg, 0.1 mmol) in Et_2O (0.75 mL) was added, and the ice-bath removed. The reaction was allowed to warm to room temperature and continued for 1 h. Following completion, the reaction was diluted with H_2O and extracted with Et_2O. The combined organics

were washed with brine, dried with $MgSO_4$, then concentrated. The crude product was purified by column chromatography (0 to 5% Et_2O in hexanes) to afford the desired product as a colorless oil (20.0 mg, 84% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.15 (m, 3H), 6.85 (t, *J* = 2.2 Hz, 2H), 6.59 (dt, *J* = 7.0, 1.5 Hz, 2H), 6.22 (t, *J* = 2.2 Hz, 2H), 5.51 (ddt, *J* = 16.1, 10.9, 7.1 Hz, 1H), 5.39 (s, 1H), 5.22 (s, 1H), 5.14 – 5.02 (m, 2H), 2.89 (dd, *J* = 13.7, 6.6 Hz, 1H), 2.66 (dd, *J* = 13.6, 7.4 Hz, 1H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8, 140.9, 133.1, 128.4, 128.0, 127.4, 119.0, 118.9, 115.4, 108.1, 61.9, 44.3, 25.2; IR (Neat Film, NaCl) 3079, 2981, 1492, 1483, 1442, 1376, 1266, 1243, 1092, 1072, 918, 778, 723, 701 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{20}N$ $[M+H]^+$: 238.1590, found 238.1584.



5

(*S*)-2-(3-((dimethylamino)methyl)-1*H*-pyrrol-1-yl)-2-methyl-1-phenylpent-4-en-1-one (5)

To an oven-dried 1 dram vial was added α-pyrrolo ketone **2f** (23.9 mg, 0.1 mmol), Escehnmoser's salt (27.8 mg, 0.15 mmol), and MeCN (1.0 mL). The resulting mixture was heated to 55 °C in a metal heating block and stirred for 2 h. Following completion, the reaction was diluted with EtOAc and washed with saturated $NaHCO_3$ and brine. Following drying with $MgSO_4$ and concentration, the desired product was obtained as a light-yellow foam (28.1 mg, 93% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (tt, *J* = 6.8, 1.9 Hz, 1H), 7.29 – 7.20 (m, 4H), 6.68 (dt, *J* = 15.4, 2.3 Hz, 2H), 6.19 (t, *J* = 2.2 Hz, 1H), 5.39 (dddd, *J* = 16.6, 10.1, 8.1, 6.2 Hz, 1H), 5.14 – 4.96 (m, 2H), 3.55 – 3.36 (m, 2H), 2.95 – 2.72 (m, 2H), 2.24 (s, 6H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 135.3, 132.7, 131.9, 128.7, 128.5, 119.9, 119.4, 119.1, 119.1, 111.0, 67.3, 56.0, 44.0, 43.7, 23.2; IR (Neat Film, NaCl) 3069, 2977, 2938, 2854, 2811, 2761, 1682, 1488, 1456, 1446, 1320, 1255, 1179, 1166, 968, 924, 774, 718, 692 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{25}N_2O$ $[M+H]^+$: 297.1961, found 297.1972.

X-ray crystal structure info for 2e

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 V19435. The structure was solved by direct methods using SHELXS[6] and refined against F^2 on all data by full-matrix least squares with SHELXL-2017[7] using established refinement techniques.[8] 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 crystallizes in the hexagonal space group $P6_122$ with one molecule in the asymmetric unit. Sample was prepared via slow evaporation from $CHCl_3$.

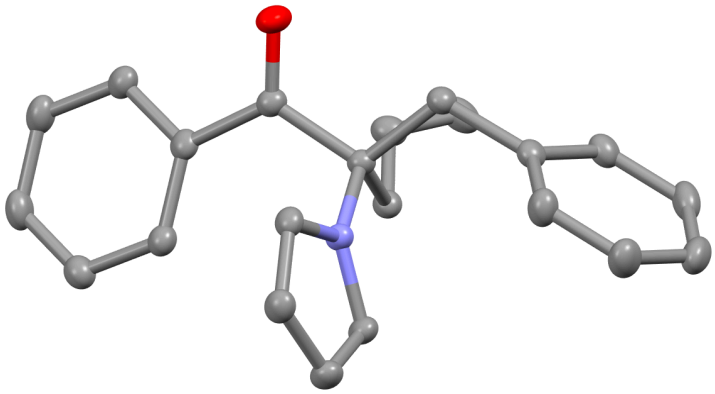


Table 1. Crystal data and structure refinement for 2e, ellipsoid contour at 50% probability.

Identification code	V19435	
Empirical formula	C22 H21 N O	
Formula weight	315.40	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Hexagonal	
Space group	$P6_122$	
Unit cell dimensions	a = 10.0004(9) Å	a= 90°.
	b = 10.0004(9) Å	b= 90°.
	c = 60.021(9) Å	g = 120°.
Volume	5198.4(12) Å^3	

Z	12
Density (calculated)	1.209 Mg/m^3
Absorption coefficient	0.570 mm^{-1}
F(000)	2016
Crystal size	0.400 x 0.300 x 0.250 mm^3
Theta range for data collection	4.420 to 74.784°.
Index ranges	-12<=h<=12, -12<=k<=12, -74<=l<=74
Reflections collected	52855
Independent reflections	3574 [R(int) = 0.0580]
Completeness to theta = 67.679°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7538 and 0.6512
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3574 / 0 / 217
Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0324, wR2 = 0.0766
R indices (all data)	R1 = 0.0336, wR2 = 0.0774
Absolute structure parameter	0.07(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.107 and -0.172 $e.Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for V19435. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	3640(1)	3587(2)	799(1)	25(1)
C(1)	3750(2)	3710(2)	597(1)	18(1)
C(11)	2319(2)	3021(2)	456(1)	18(1)
C(12)	962(2)	2749(2)	562(1)	21(1)
C(13)	-416(2)	2128(2)	444(1)	25(1)
C(14)	-453(2)	1771(2)	220(1)	26(1)
C(15)	883(2)	2023(2)	113(1)	24(1)
C(16)	2270(2)	2652(2)	229(1)	20(1)
C(2)	5368(2)	4675(2)	489(1)	16(1)
N(1)	5602(2)	3635(2)	343(1)	16(1)
C(17)	5208(2)	2152(2)	402(1)	19(1)
C(18)	5550(2)	1500(2)	227(1)	22(1)
C(19)	6183(2)	2621(2)	56(1)	23(1)
C(20)	6214(2)	3928(2)	132(1)	20(1)
C(3)	5384(2)	6001(2)	354(1)	18(1)
C(4)	4800(2)	6877(2)	487(1)	23(1)
C(5)	5550(2)	8380(2)	518(1)	29(1)
C(6)	6621(2)	5322(2)	674(1)	19(1)
C(21)	8244(2)	6227(2)	584(1)	19(1)
C(22)	9002(2)	5484(2)	502(1)	26(1)
C(23)	10486(2)	6322(2)	415(1)	31(1)
C(24)	11236(2)	7919(2)	410(1)	31(1)
C(25)	10506(2)	8677(2)	494(1)	28(1)
C(26)	9019(2)	7834(2)	580(1)	23(1)

Table 3. Bond lengths [Å] and angles [°] for V19435.

O(1)-C(1)	1.2169(18)
C(1)-C(11)	1.503(2)
C(1)-C(2)	1.551(2)
C(11)-C(12)	1.397(2)
C(11)-C(16)	1.403(2)
C(12)-C(13)	1.388(2)
C(12)-H(12)	0.9500
C(13)-C(14)	1.390(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.386(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.390(2)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(2)-N(1)	1.4668(19)
C(2)-C(3)	1.547(2)
C(2)-C(6)	1.549(2)
N(1)-C(20)	1.3745(19)
N(1)-C(17)	1.377(2)
C(17)-C(18)	1.369(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.415(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.371(2)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(3)-C(4)	1.504(2)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.314(3)
C(4)-H(4)	0.9500
C(5)-H(5A)	0.9500
C(5)-H(5B)	0.9500
C(6)-C(21)	1.509(2)

C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(21)-C(22)	1.390(2)
C(21)-C(26)	1.392(2)
C(22)-C(23)	1.392(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.384(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.385(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.391(2)
C(25)-H(25)	0.9500
C(26)-H(26)	0.9500

O(1)-C(1)-C(11)	119.94(14)
O(1)-C(1)-C(2)	119.47(14)
C(11)-C(1)-C(2)	120.46(12)
C(12)-C(11)-C(16)	119.18(15)
C(12)-C(11)-C(1)	116.18(13)
C(16)-C(11)-C(1)	124.64(14)
C(13)-C(12)-C(11)	120.43(15)
C(13)-C(12)-H(12)	119.8
C(11)-C(12)-H(12)	119.8
C(12)-C(13)-C(14)	120.01(16)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
C(15)-C(14)-C(13)	120.07(16)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.29(15)
C(14)-C(15)-H(15)	119.9
C(16)-C(15)-H(15)	119.9
C(15)-C(16)-C(11)	120.02(15)
C(15)-C(16)-H(16)	120.0
C(11)-C(16)-H(16)	120.0
N(1)-C(2)-C(3)	110.92(11)

N(1)-C(2)-C(6)	109.91(12)
C(3)-C(2)-C(6)	110.88(13)
N(1)-C(2)-C(1)	107.15(12)
C(3)-C(2)-C(1)	108.26(12)
C(6)-C(2)-C(1)	109.63(12)
C(20)-N(1)-C(17)	109.05(13)
C(20)-N(1)-C(2)	127.78(13)
C(17)-N(1)-C(2)	123.17(12)
C(18)-C(17)-N(1)	107.93(14)
C(18)-C(17)-H(17)	126.0
N(1)-C(17)-H(17)	126.0
C(17)-C(18)-C(19)	107.53(15)
C(17)-C(18)-H(18)	126.2
C(19)-C(18)-H(18)	126.2
C(20)-C(19)-C(18)	107.53(14)
C(20)-C(19)-H(19)	126.2
C(18)-C(19)-H(19)	126.2
C(19)-C(20)-N(1)	107.95(14)
C(19)-C(20)-H(20)	126.0
N(1)-C(20)-H(20)	126.0
C(4)-C(3)-C(2)	112.32(12)
C(4)-C(3)-H(3A)	109.1
C(2)-C(3)-H(3A)	109.1
C(4)-C(3)-H(3B)	109.1
C(2)-C(3)-H(3B)	109.1
H(3A)-C(3)-H(3B)	107.9
C(5)-C(4)-C(3)	125.02(17)
C(5)-C(4)-H(4)	117.5
C(3)-C(4)-H(4)	117.5
C(4)-C(5)-H(5A)	120.0
C(4)-C(5)-H(5B)	120.0
H(5A)-C(5)-H(5B)	120.0
C(21)-C(6)-C(2)	113.48(12)
C(21)-C(6)-H(6A)	108.9
C(2)-C(6)-H(6A)	108.9
C(21)-C(6)-H(6B)	108.9

C(2)-C(6)-H(6B)	108.9
H(6A)-C(6)-H(6B)	107.7
C(22)-C(21)-C(26)	118.29(16)
C(22)-C(21)-C(6)	121.09(15)
C(26)-C(21)-C(6)	120.62(15)
C(21)-C(22)-C(23)	120.91(17)
C(21)-C(22)-H(22)	119.5
C(23)-C(22)-H(22)	119.5
C(24)-C(23)-C(22)	120.16(17)
C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9
C(23)-C(24)-C(25)	119.61(16)
C(23)-C(24)-H(24)	120.2
C(25)-C(24)-H(24)	120.2
C(24)-C(25)-C(26)	120.00(17)
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-H(25)	120.0
C(25)-C(26)-C(21)	121.01(16)
C(25)-C(26)-H(26)	119.5
C(21)-C(26)-H(26)	119.5

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for V19435. 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}
O(1)	24(1)	35(1)	17(1)	4(1)	3(1)	15(1)
C(1)	20(1)	18(1)	18(1)	2(1)	2(1)	11(1)
C(11)	18(1)	15(1)	21(1)	4(1)	1(1)	8(1)
C(12)	20(1)	17(1)	25(1)	2(1)	4(1)	9(1)
C(13)	18(1)	20(1)	36(1)	1(1)	2(1)	9(1)
C(14)	18(1)	22(1)	36(1)	-2(1)	-5(1)	9(1)
C(15)	25(1)	22(1)	24(1)	0(1)	-3(1)	11(1)
C(16)	18(1)	19(1)	22(1)	3(1)	1(1)	9(1)
C(2)	18(1)	18(1)	15(1)	0(1)	1(1)	10(1)
N(1)	18(1)	16(1)	16(1)	1(1)	1(1)	9(1)
C(17)	19(1)	17(1)	20(1)	3(1)	1(1)	8(1)
C(18)	23(1)	17(1)	27(1)	-1(1)	2(1)	10(1)
C(19)	24(1)	24(1)	21(1)	-1(1)	5(1)	11(1)
C(20)	20(1)	19(1)	18(1)	2(1)	4(1)	8(1)
C(3)	20(1)	17(1)	17(1)	2(1)	0(1)	9(1)
C(4)	30(1)	24(1)	20(1)	1(1)	-1(1)	17(1)
C(5)	39(1)	26(1)	27(1)	-6(1)	-9(1)	20(1)
C(6)	19(1)	21(1)	16(1)	0(1)	-1(1)	11(1)
C(21)	19(1)	21(1)	17(1)	0(1)	-3(1)	10(1)
C(22)	21(1)	21(1)	34(1)	-1(1)	0(1)	10(1)
C(23)	21(1)	33(1)	37(1)	-4(1)	2(1)	13(1)
C(24)	19(1)	34(1)	31(1)	4(1)	1(1)	6(1)
C(25)	24(1)	19(1)	31(1)	2(1)	-7(1)	4(1)
C(26)	24(1)	21(1)	23(1)	-2(1)	-6(1)	11(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for V19435.

	x	y	z	U(eq)
H(12)	983	2990	715	25
H(13)	-1334	1947	517	30
H(14)	-1396	1353	139	31
H(15)	851	1765	-40	29
H(16)	3185	2833	155	24
H(17)	4775	1668	541	23
H(18)	5392	482	221	27
H(19)	6525	2490	-86	28
H(20)	6591	4871	52	24
H(3A)	6453	6722	304	21
H(3B)	4734	5566	220	21
H(4)	3813	6299	555	28
H(5A)	6541	8997	453	35
H(5B)	5102	8849	604	35
H(6A)	6429	5997	773	23
H(6B)	6527	4451	764	23
H(22)	8499	4389	505	31
H(23)	10987	5797	358	37
H(24)	12245	8491	349	37
H(25)	11021	9773	494	34
H(26)	8525	8362	638	27

Table 6. Torsion angles [°] for V19435.

O(1)-C(1)-C(11)-C(12)	21.4(2)
C(2)-C(1)-C(11)-C(12)	-154.28(14)
O(1)-C(1)-C(11)-C(16)	-158.82(15)
C(2)-C(1)-C(11)-C(16)	25.5(2)
C(16)-C(11)-C(12)-C(13)	-0.3(2)
C(1)-C(11)-C(12)-C(13)	179.47(14)
C(11)-C(12)-C(13)-C(14)	0.1(3)
C(12)-C(13)-C(14)-C(15)	0.5(3)
C(13)-C(14)-C(15)-C(16)	-0.8(3)
C(14)-C(15)-C(16)-C(11)	0.6(3)
C(12)-C(11)-C(16)-C(15)	0.0(2)
C(1)-C(11)-C(16)-C(15)	-179.78(15)
O(1)-C(1)-C(2)-N(1)	120.14(15)
C(11)-C(1)-C(2)-N(1)	-64.12(17)
O(1)-C(1)-C(2)-C(3)	-120.17(15)
C(11)-C(1)-C(2)-C(3)	55.57(17)
O(1)-C(1)-C(2)-C(6)	0.9(2)
C(11)-C(1)-C(2)-C(6)	176.64(13)
C(3)-C(2)-N(1)-C(20)	18.9(2)
C(6)-C(2)-N(1)-C(20)	-104.03(17)
C(1)-C(2)-N(1)-C(20)	136.92(15)
C(3)-C(2)-N(1)-C(17)	-160.68(14)
C(6)-C(2)-N(1)-C(17)	76.34(18)
C(1)-C(2)-N(1)-C(17)	-42.71(18)
C(20)-N(1)-C(17)-C(18)	-0.91(18)
C(2)-N(1)-C(17)-C(18)	178.78(14)
N(1)-C(17)-C(18)-C(19)	0.46(19)
C(17)-C(18)-C(19)-C(20)	0.1(2)
C(18)-C(19)-C(20)-N(1)	-0.70(19)
C(17)-N(1)-C(20)-C(19)	1.00(18)
C(2)-N(1)-C(20)-C(19)	-178.67(15)
N(1)-C(2)-C(3)-C(4)	167.14(13)
C(6)-C(2)-C(3)-C(4)	-70.45(17)
C(1)-C(2)-C(3)-C(4)	49.85(17)

C(2)-C(3)-C(4)-C(5)	126.00(17)
N(1)-C(2)-C(6)-C(21)	60.14(17)
C(3)-C(2)-C(6)-C(21)	-62.85(17)
C(1)-C(2)-C(6)-C(21)	177.66(13)
C(2)-C(6)-C(21)-C(22)	-79.89(18)
C(2)-C(6)-C(21)-C(26)	99.92(17)
C(26)-C(21)-C(22)-C(23)	-1.2(2)
C(6)-C(21)-C(22)-C(23)	178.60(15)
C(21)-C(22)-C(23)-C(24)	0.4(3)
C(22)-C(23)-C(24)-C(25)	0.7(3)
C(23)-C(24)-C(25)-C(26)	-1.0(3)
C(24)-C(25)-C(26)-C(21)	0.2(2)
C(22)-C(21)-C(26)-C(25)	0.9(2)
C(6)-C(21)-C(26)-C(25)	-178.88(14)

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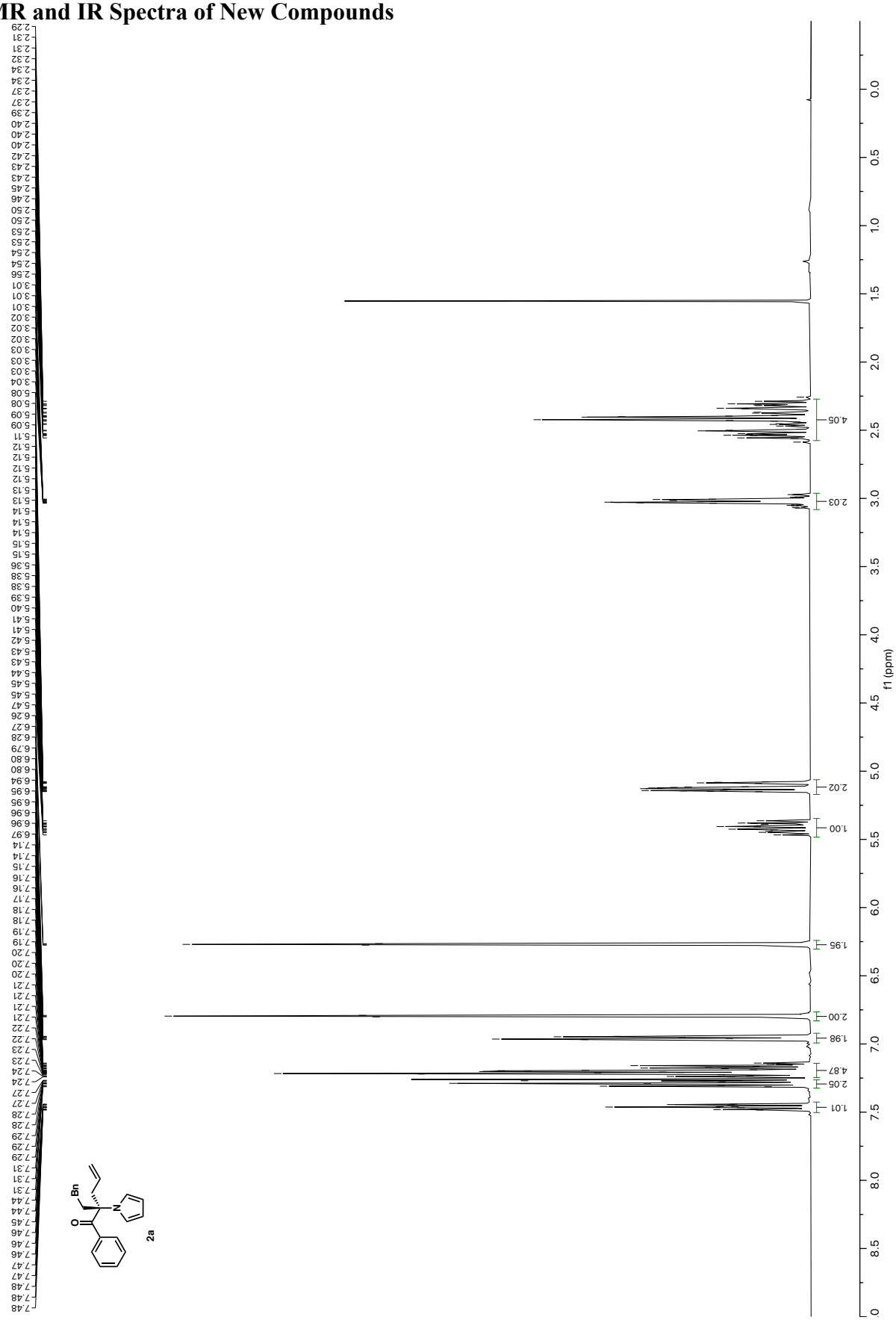
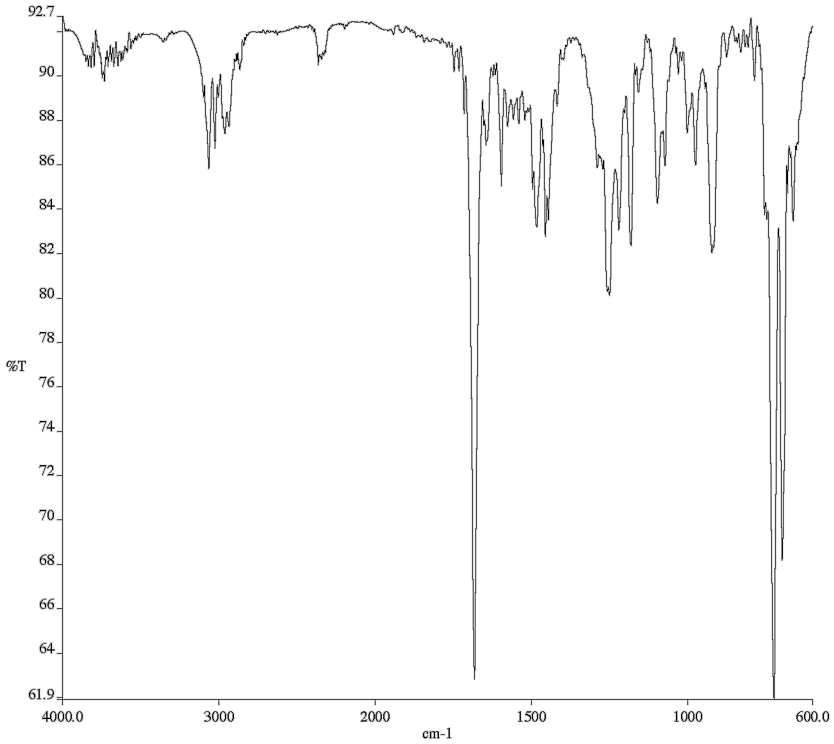
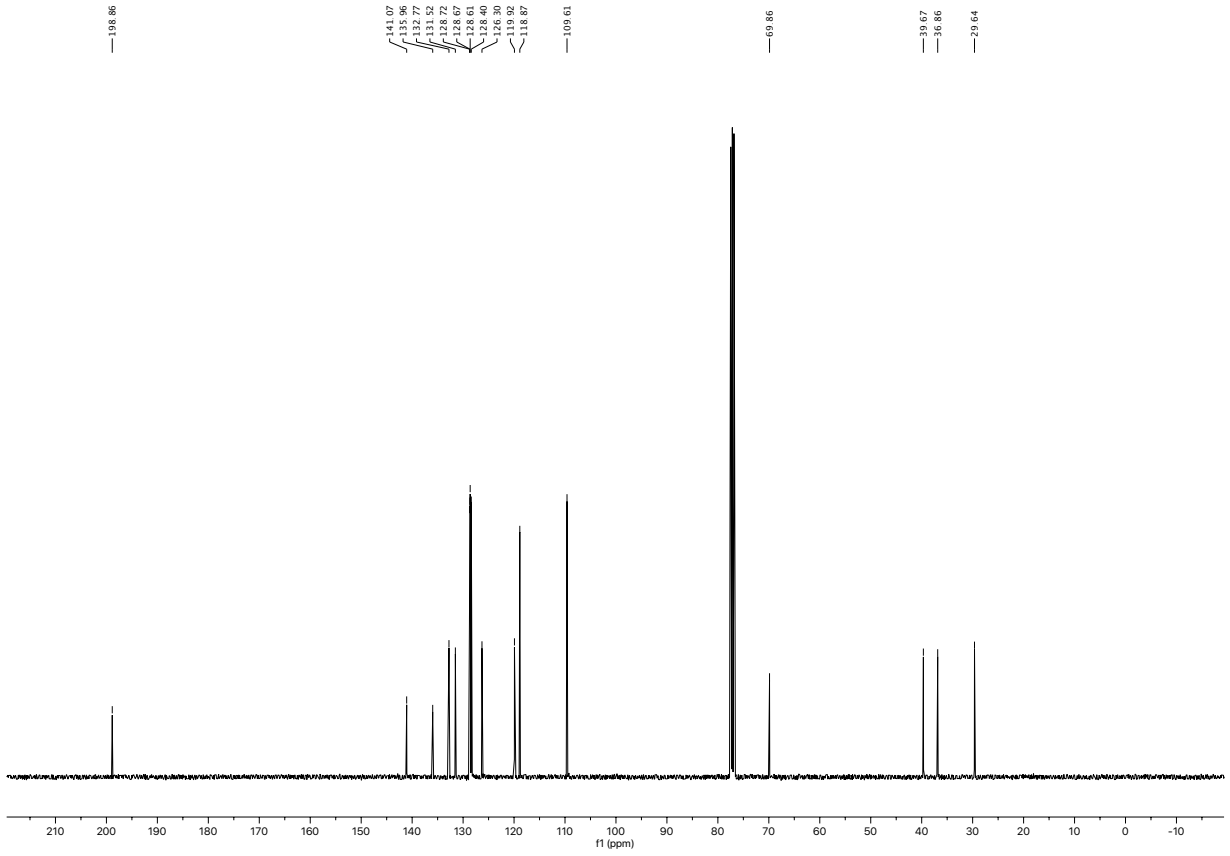
NMR and IR Spectra of New Compounds



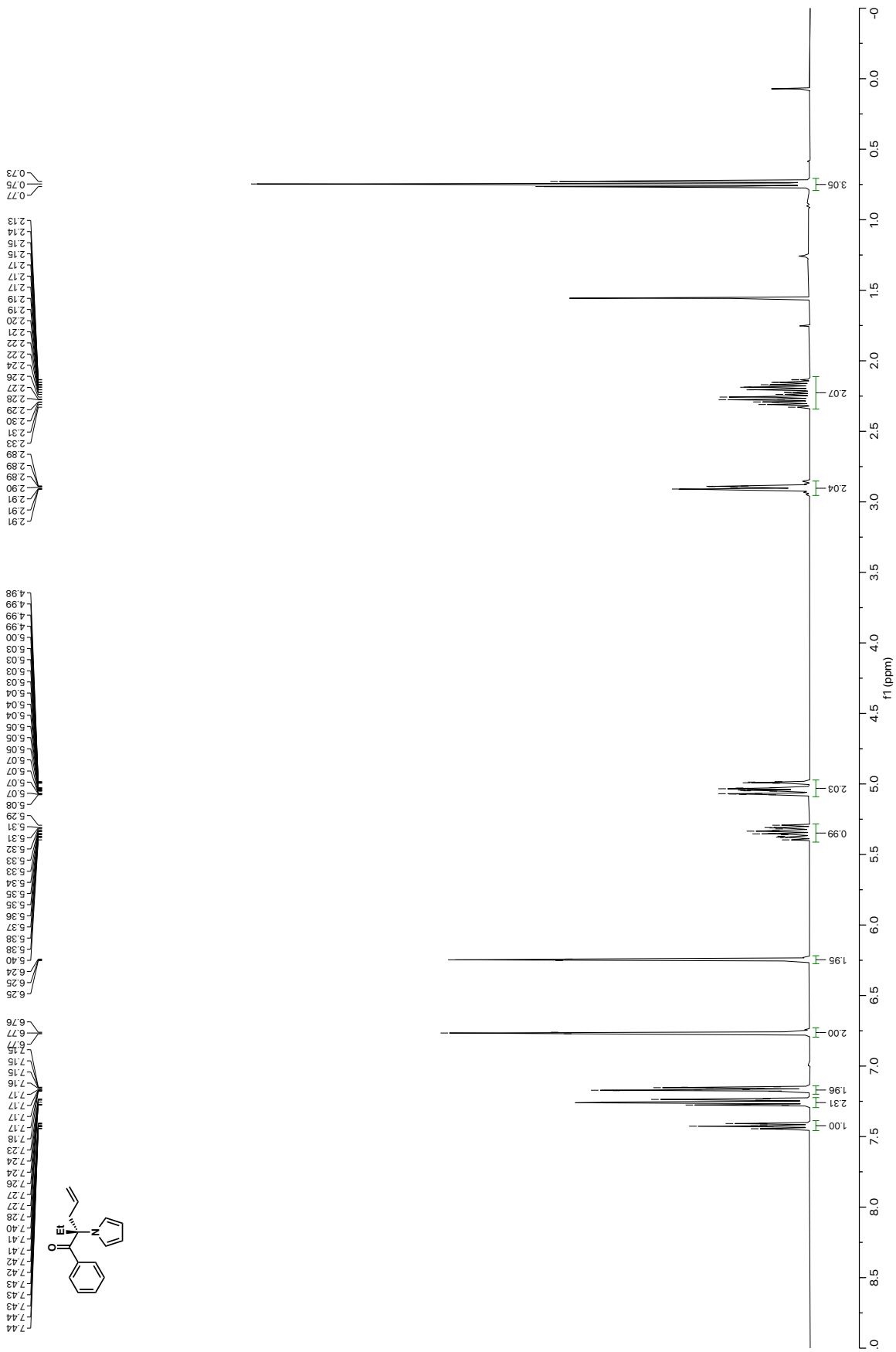
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



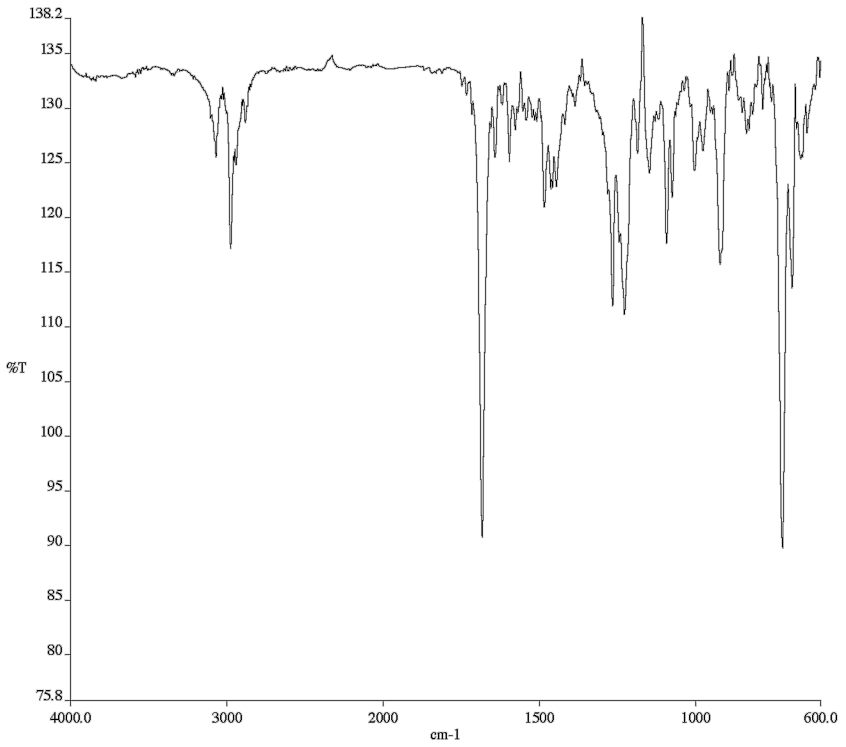
Infrared spectrum (Thin Film, NaCl) of compound **2a**.



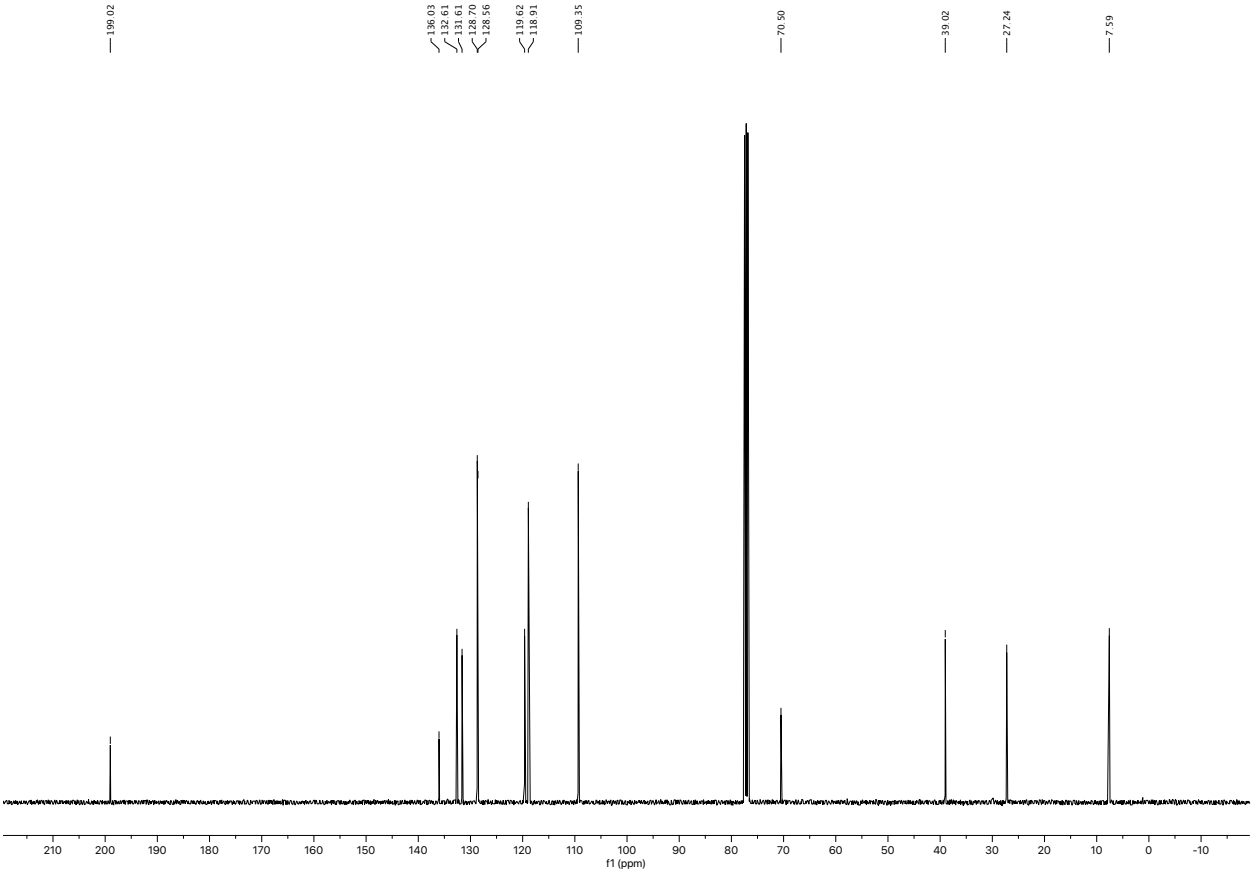
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.



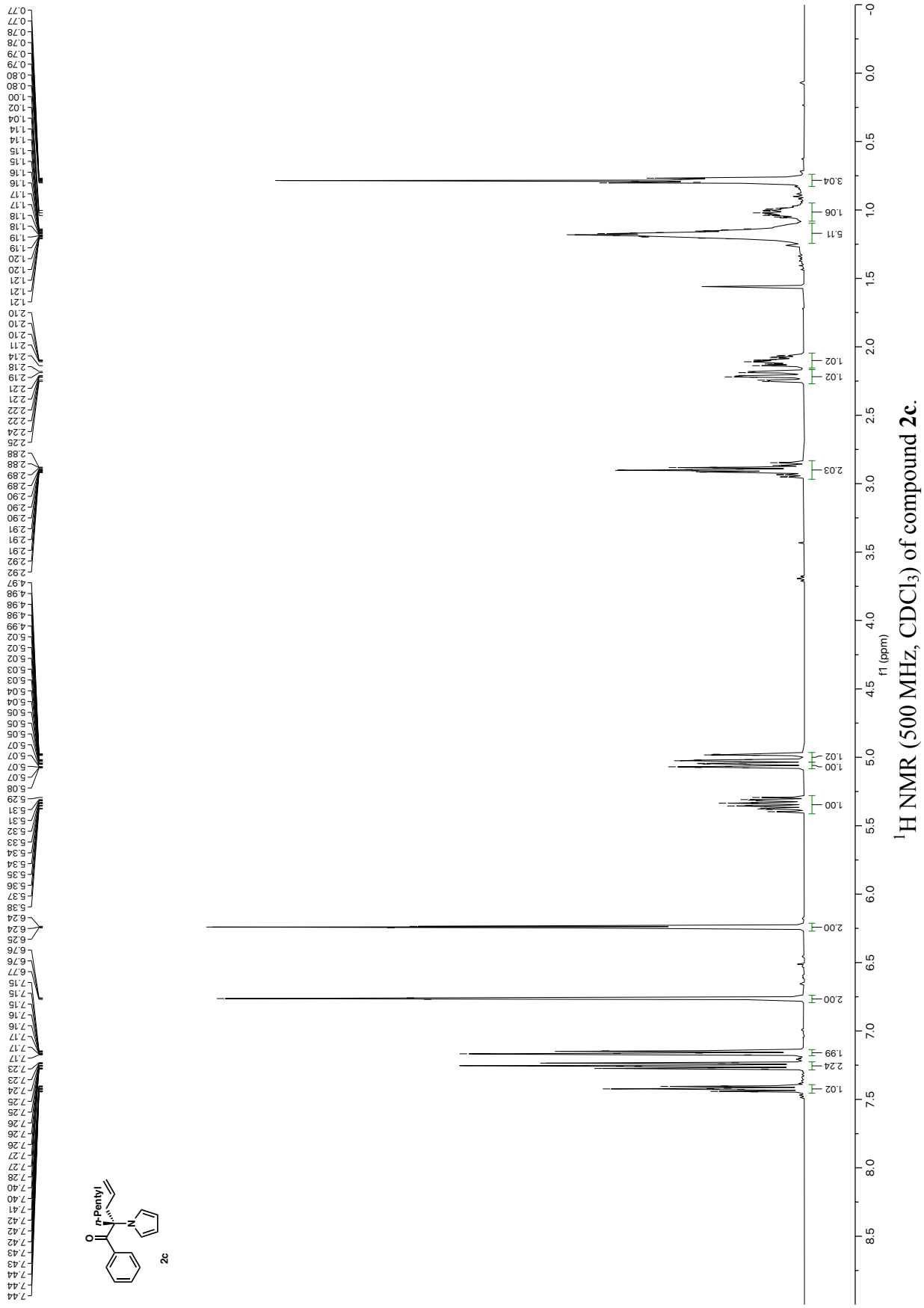
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**.



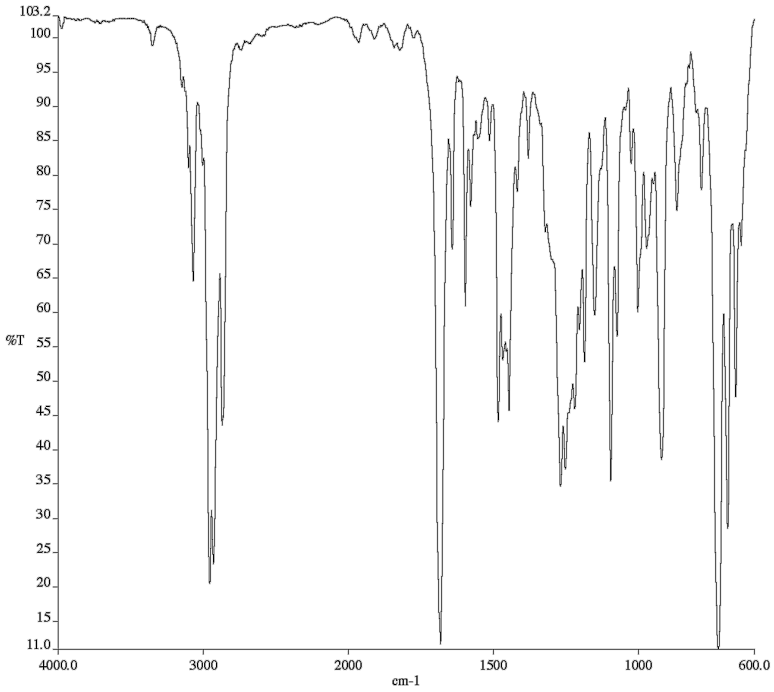
Infrared spectrum (Thin Film, NaCl) of compound **2b**.



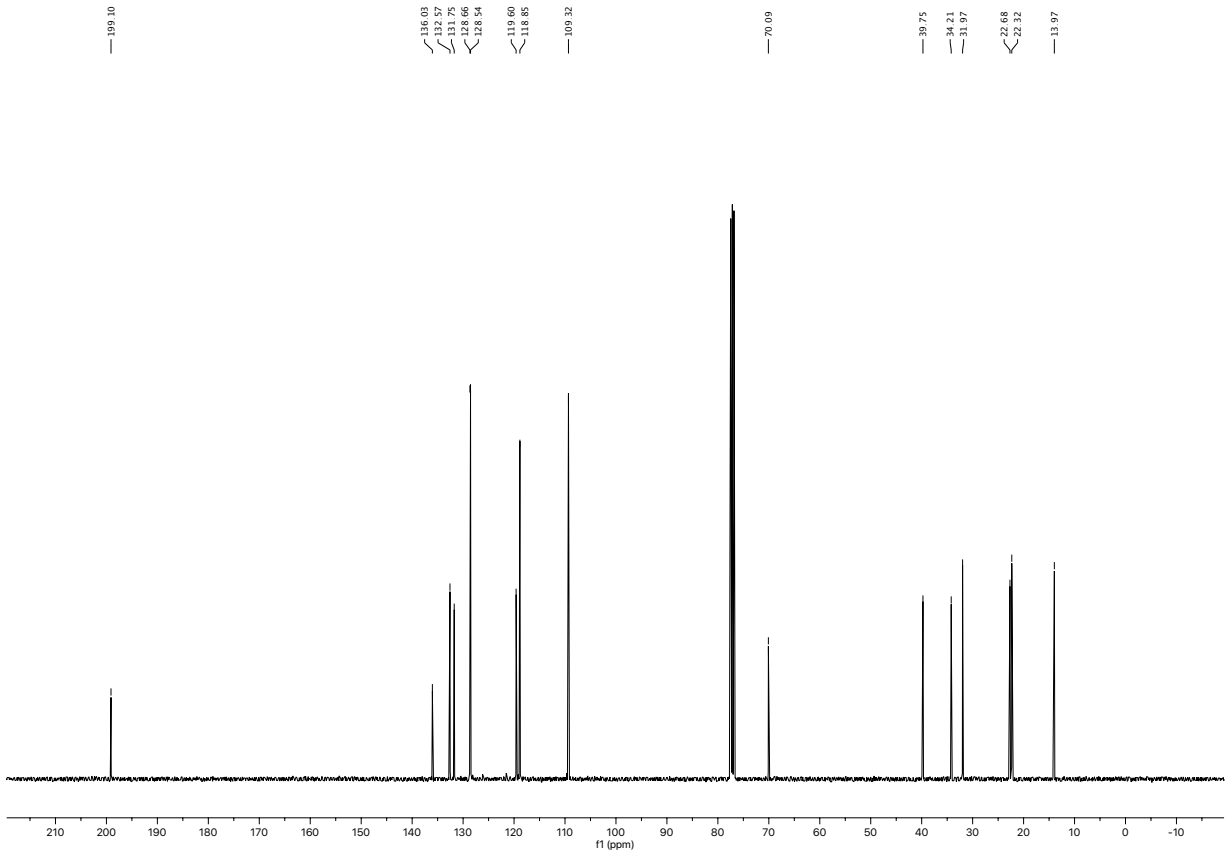
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **2c**.



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



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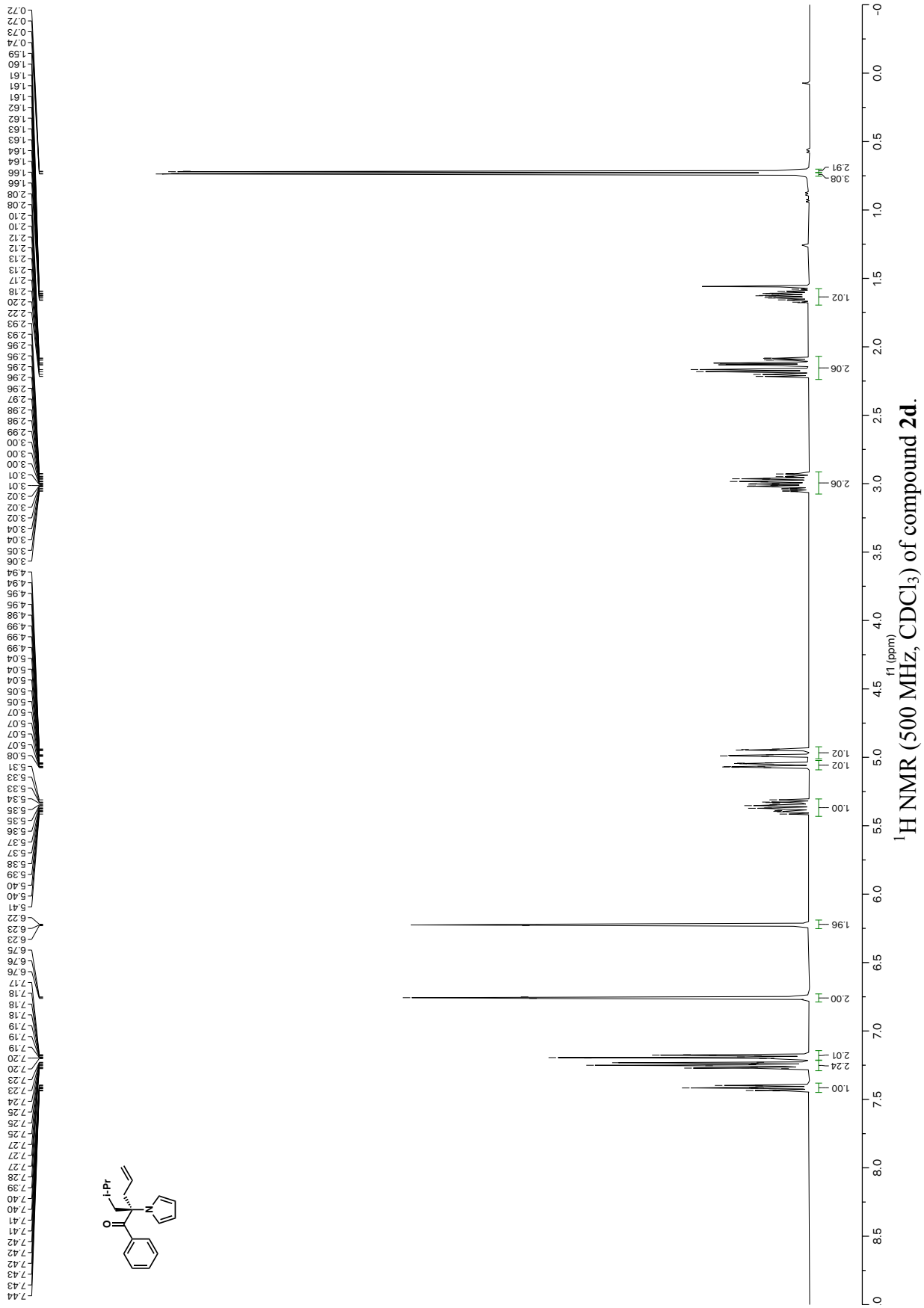
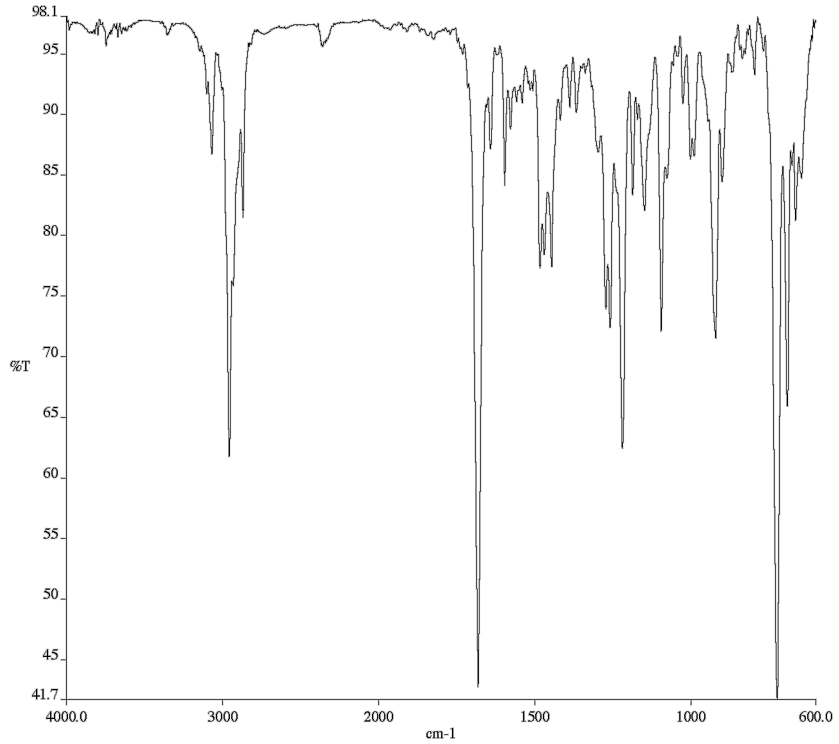
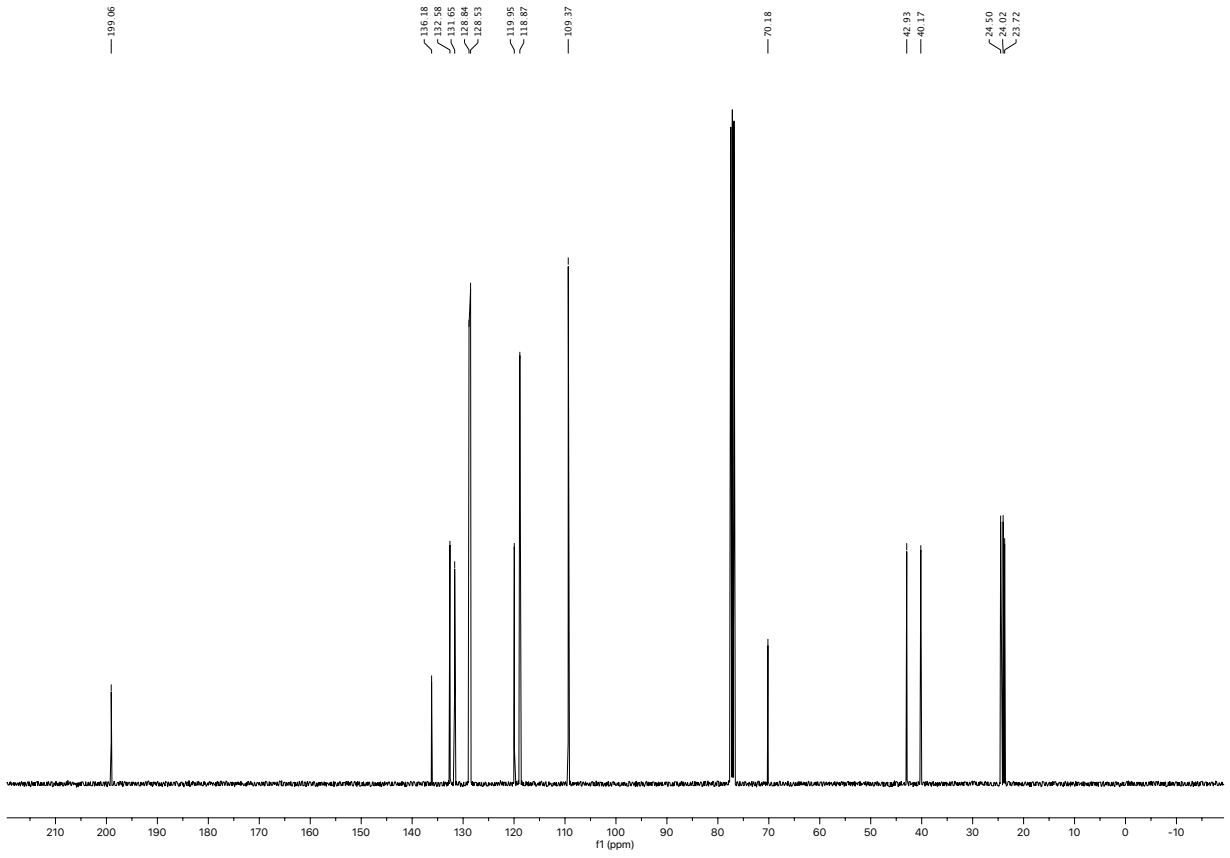


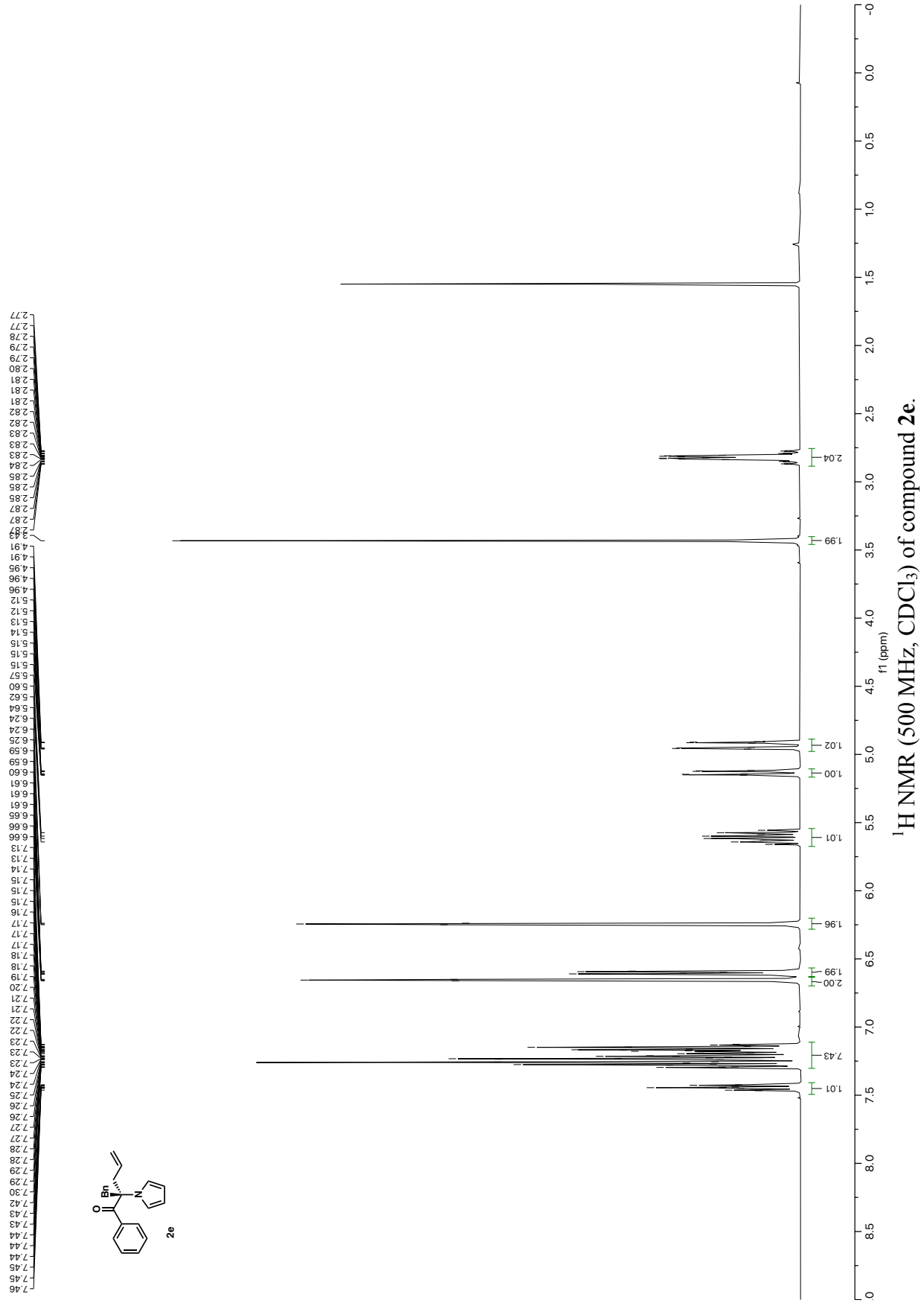
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2d**.



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



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



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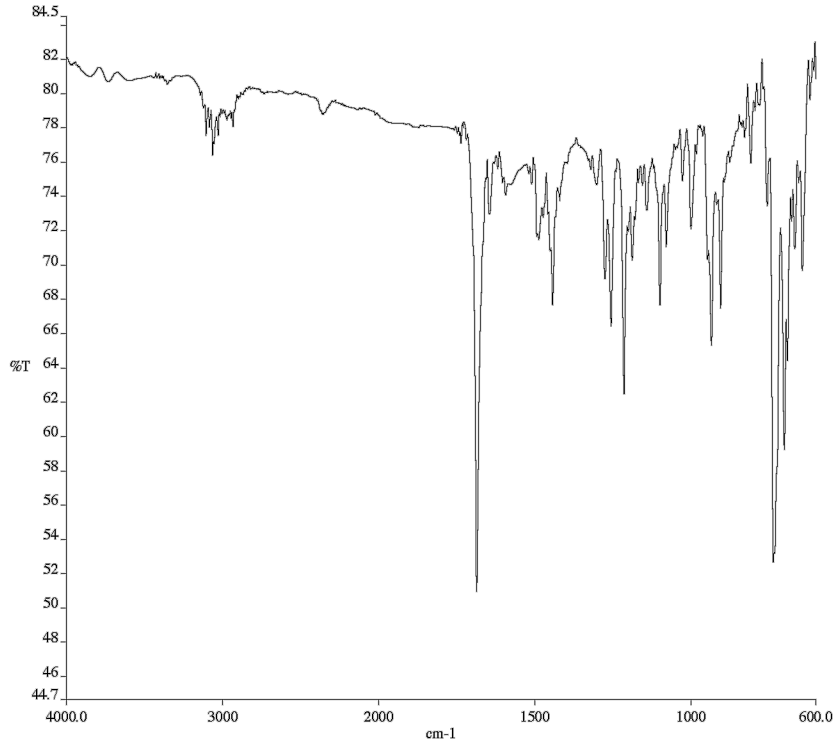
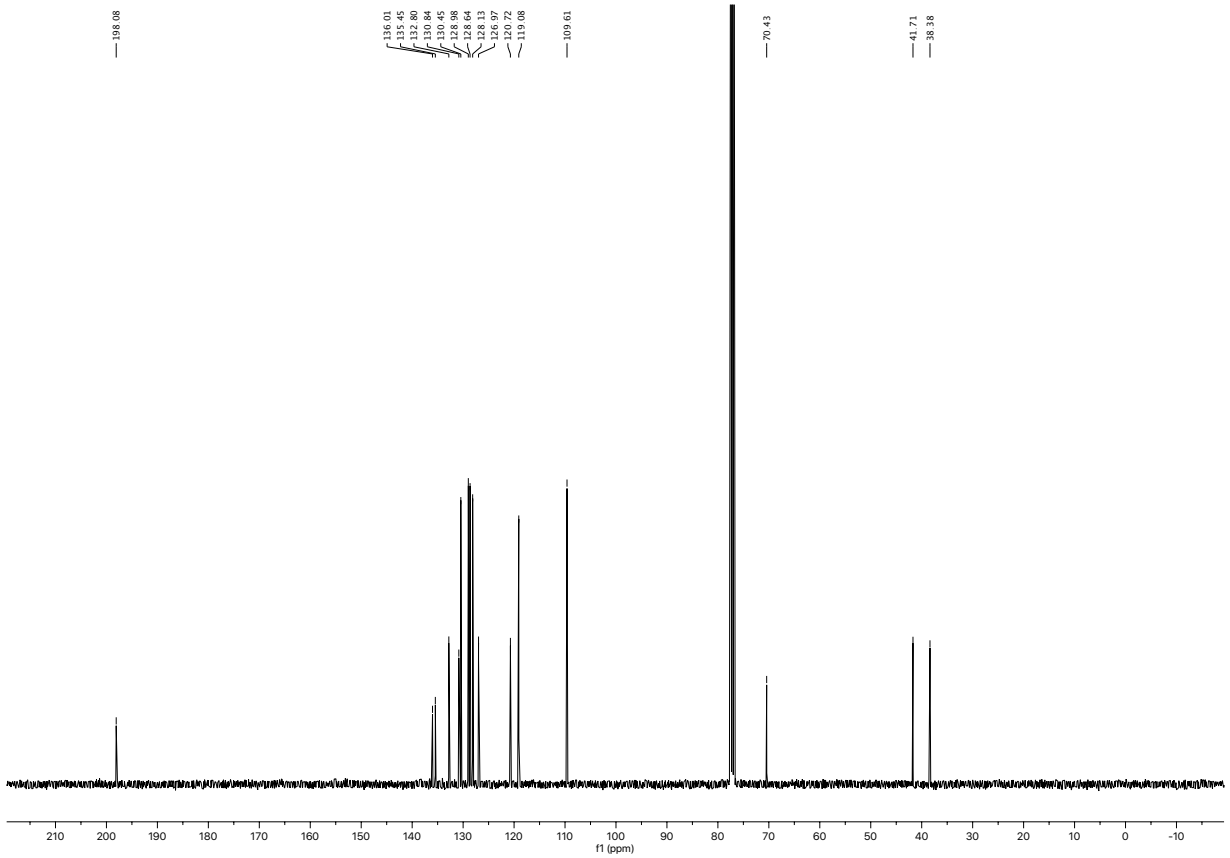
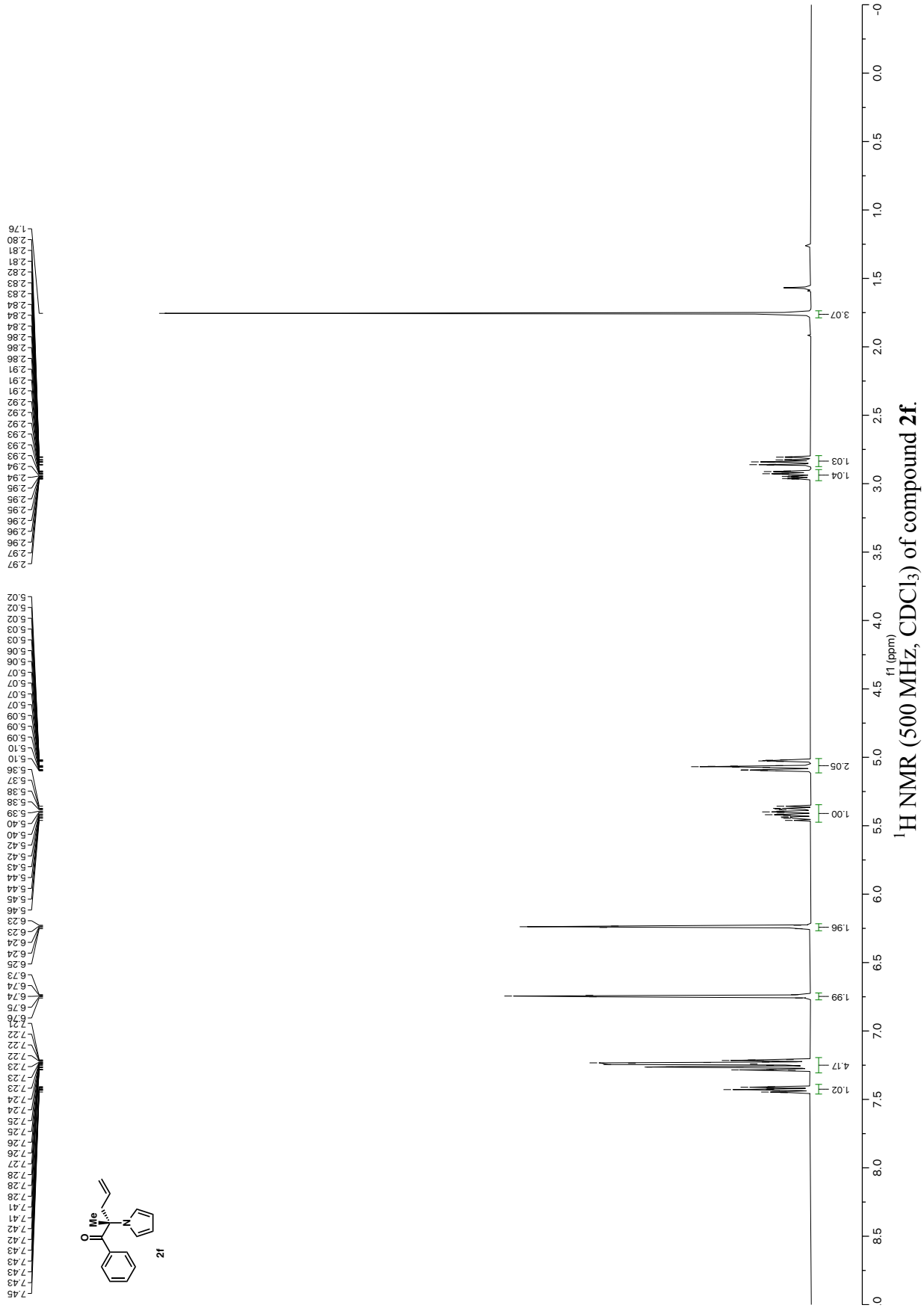


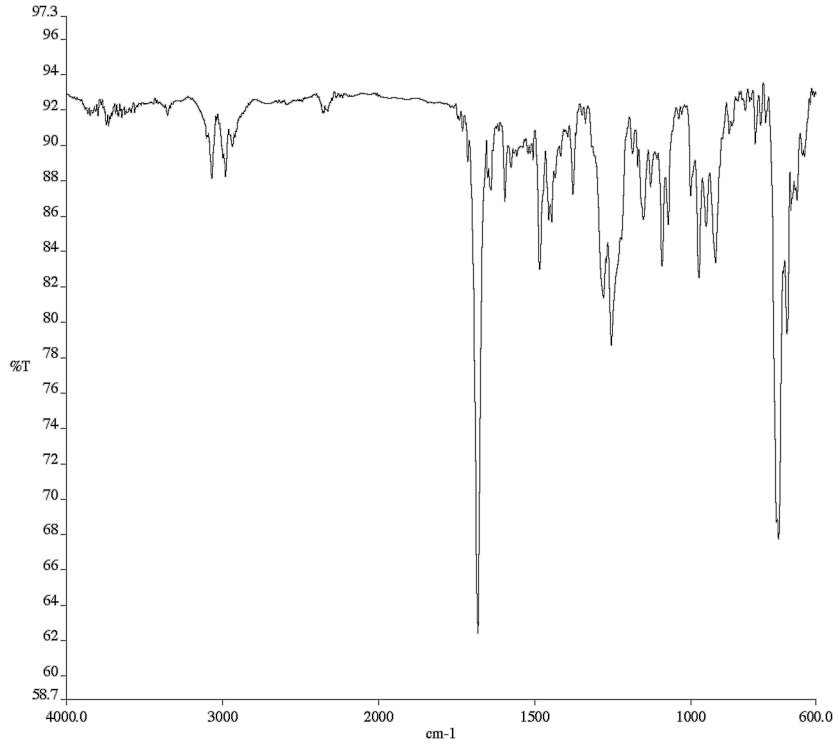
Infrared spectrum (Thin Film, NaCl) of compound **2e**.



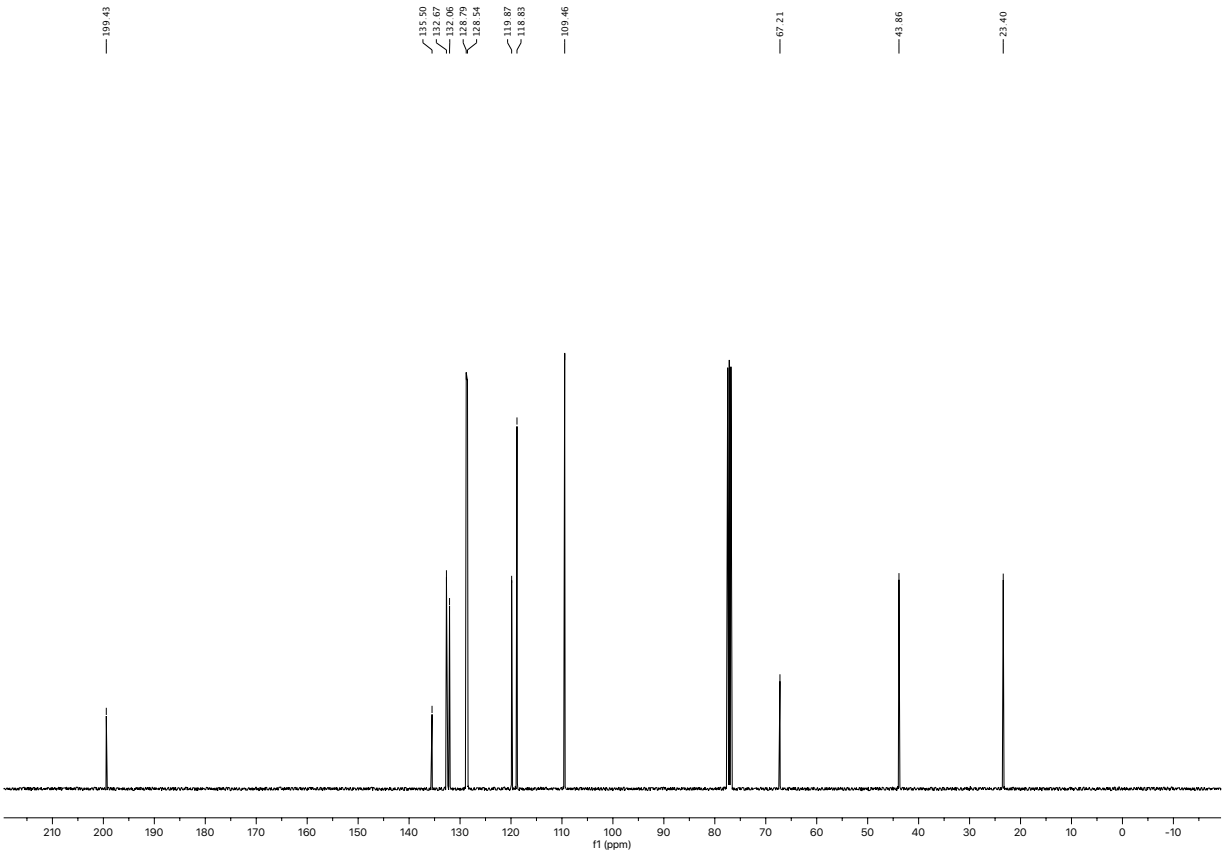
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2e**.



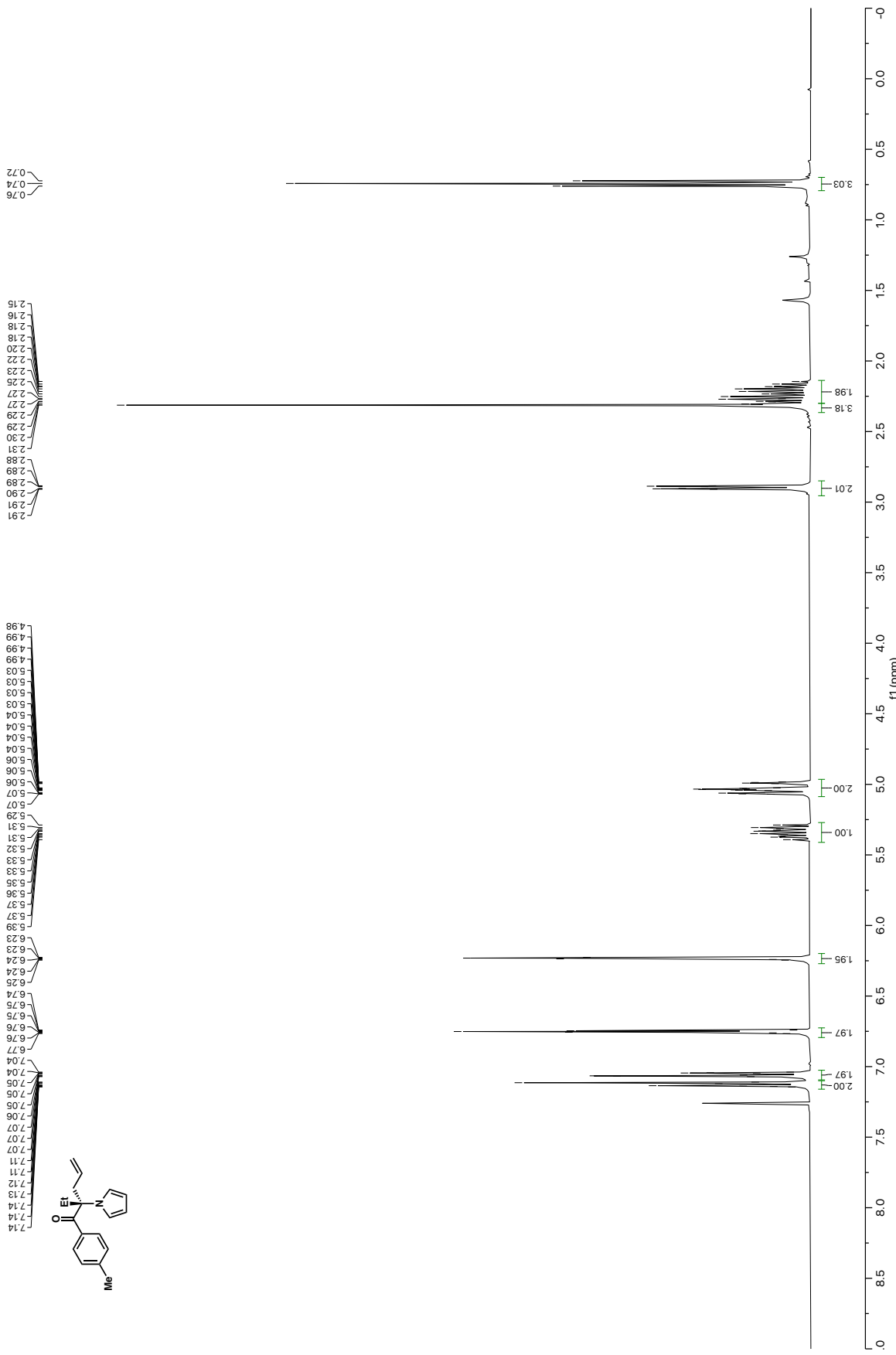
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2f**.



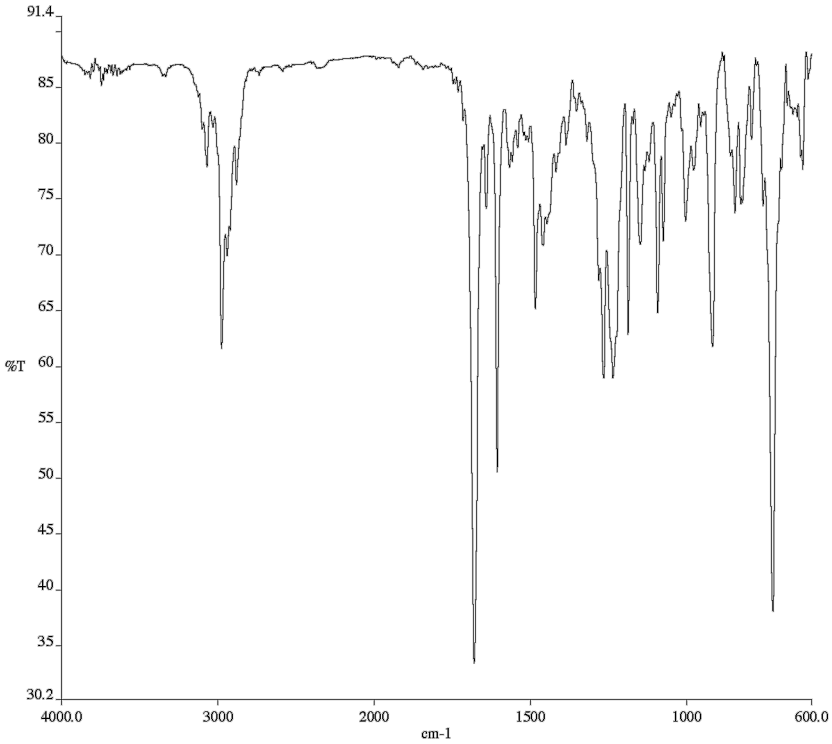
Infrared spectrum (Thin Film, NaCl) of compound **2f**.



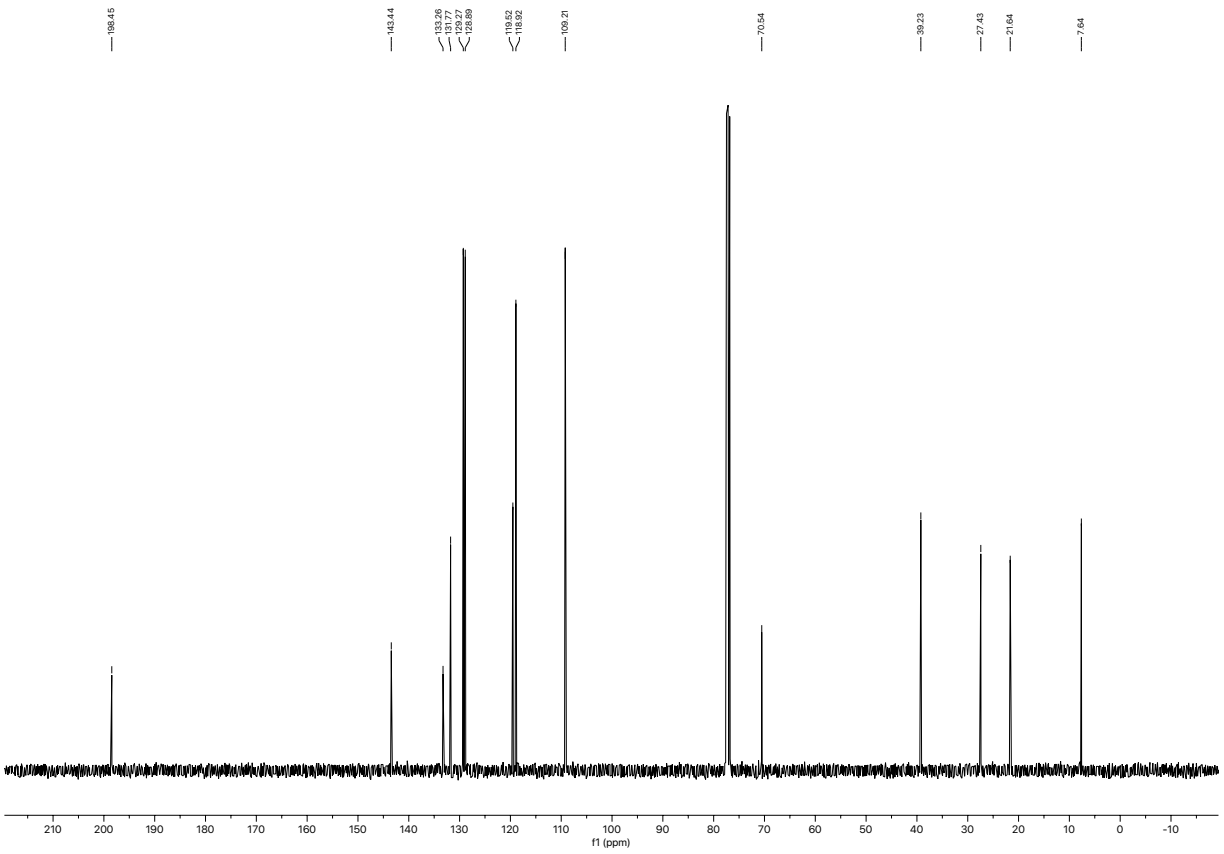
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2f**.



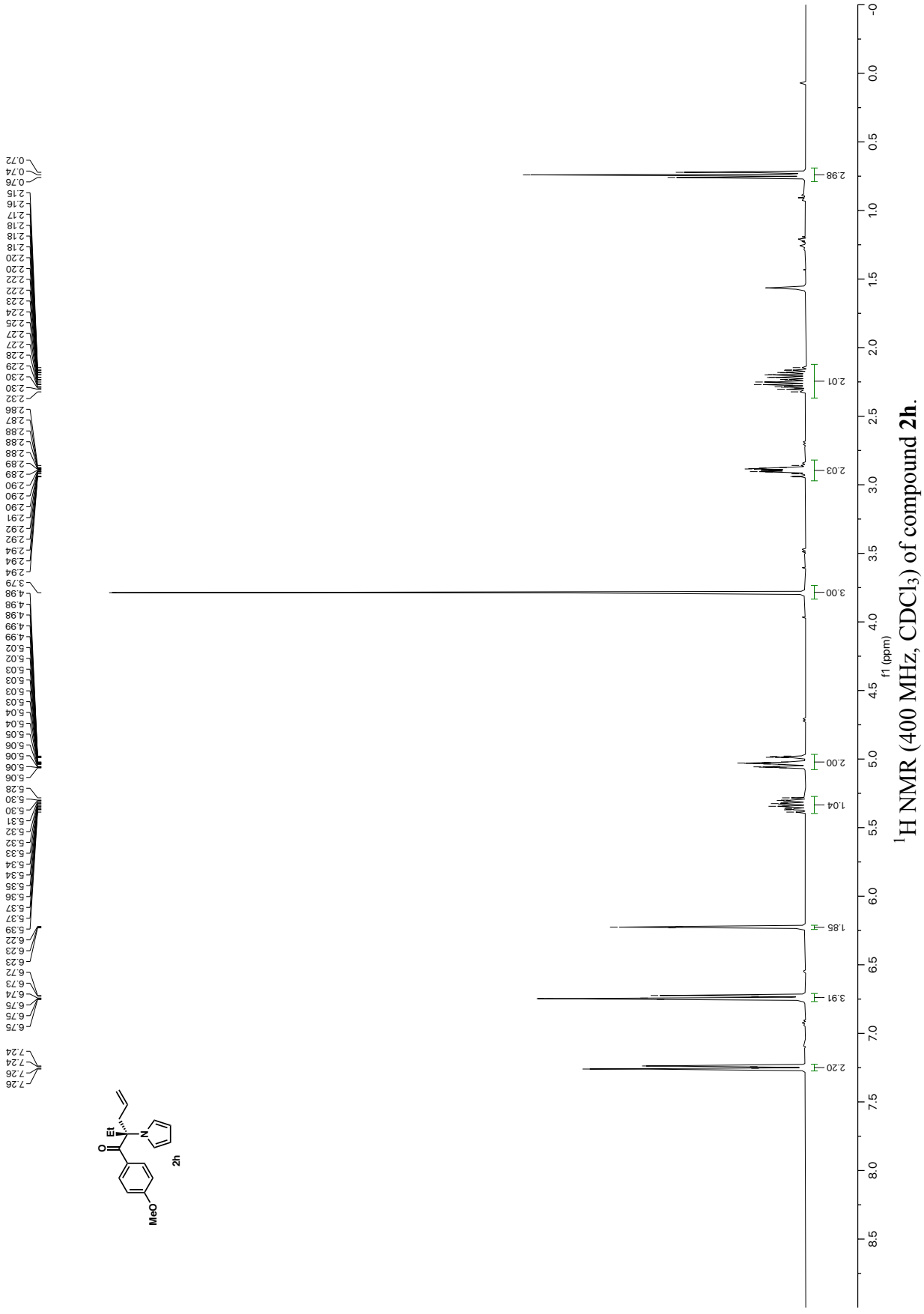
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2g**.



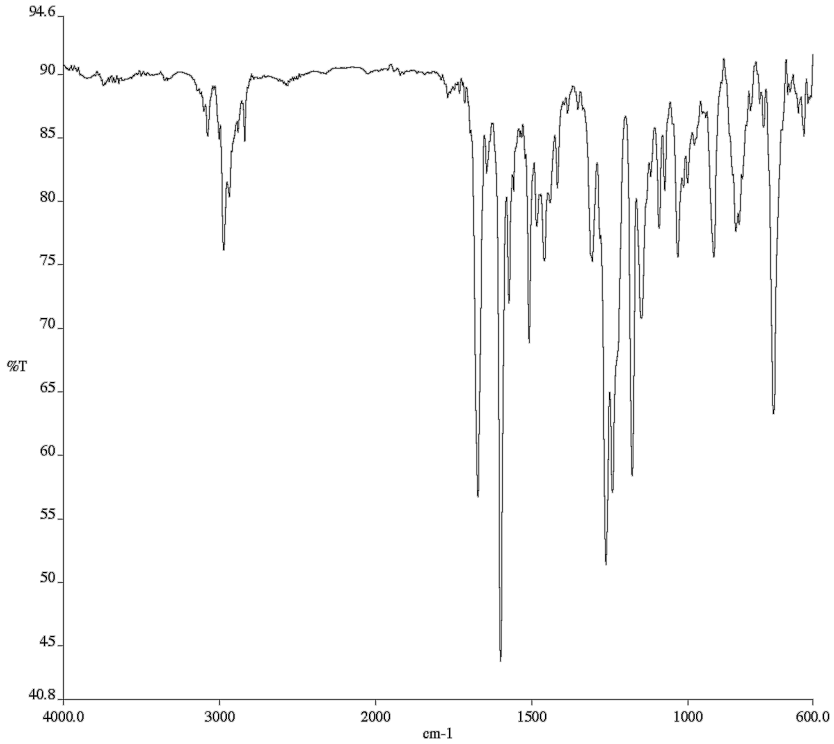
Infrared spectrum (Thin Film, NaCl) of compound **2g**.



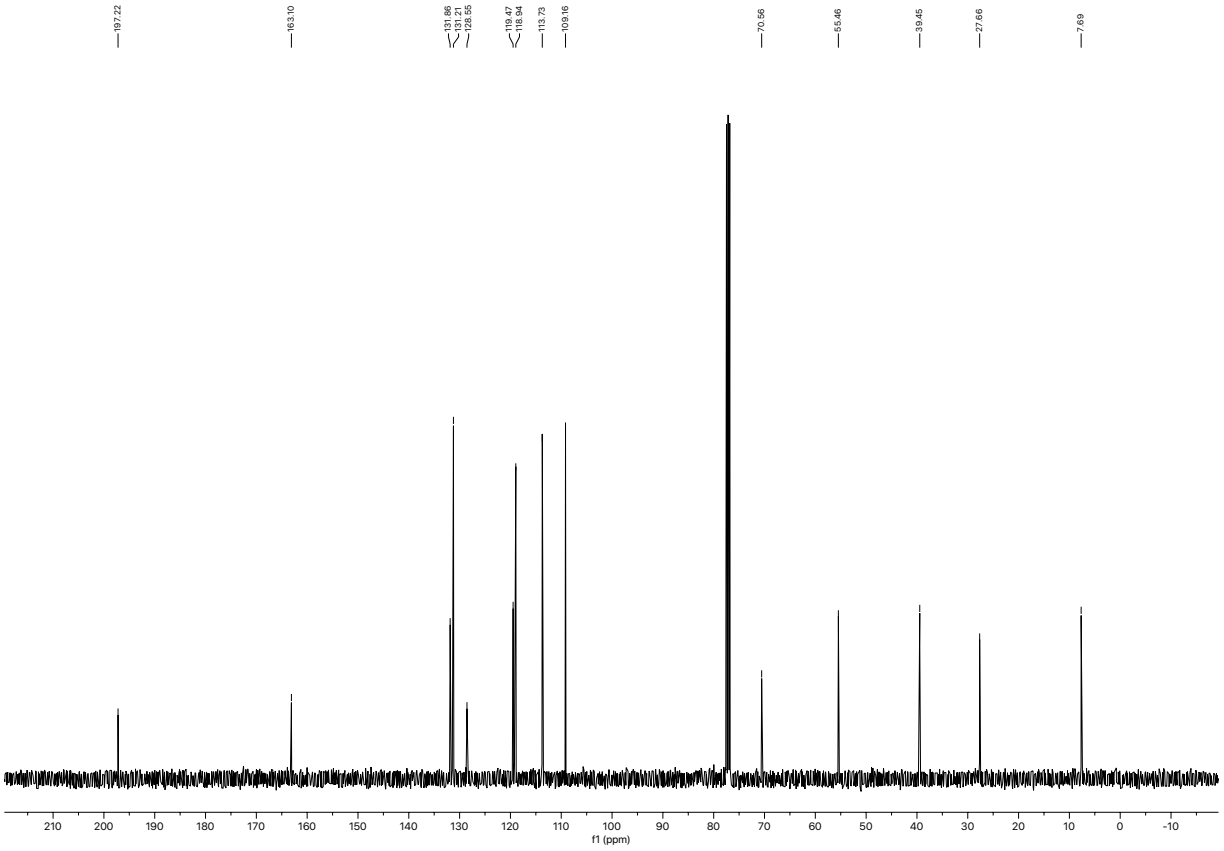
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2g**.



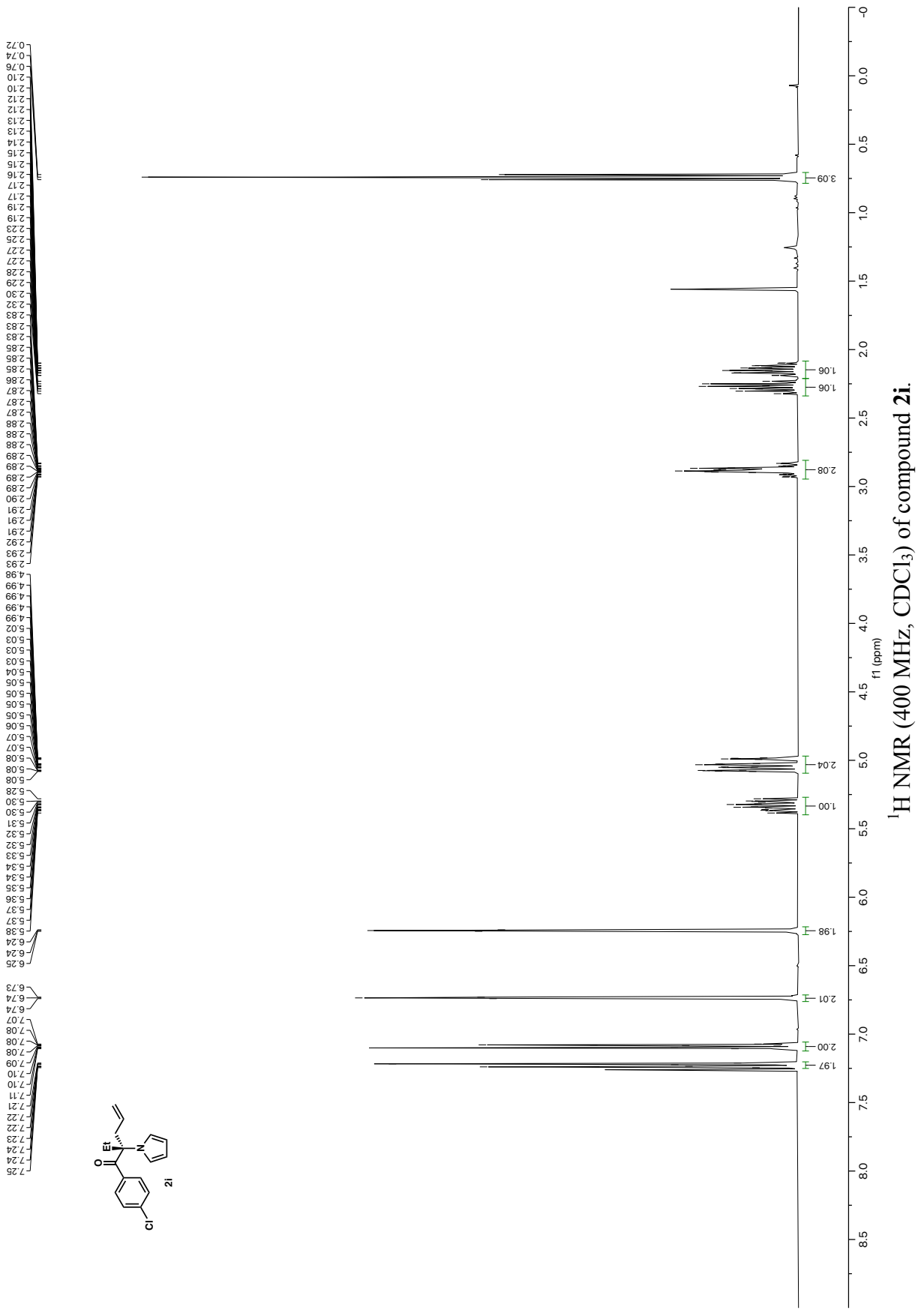
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2h**.



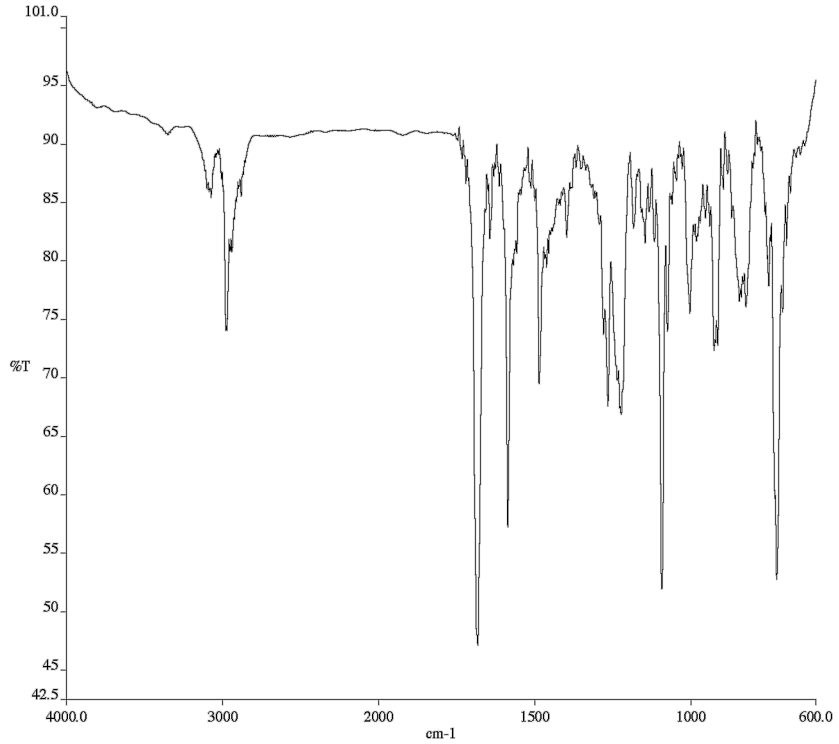
Infrared spectrum (Thin Film, NaCl) of compound **2h**.



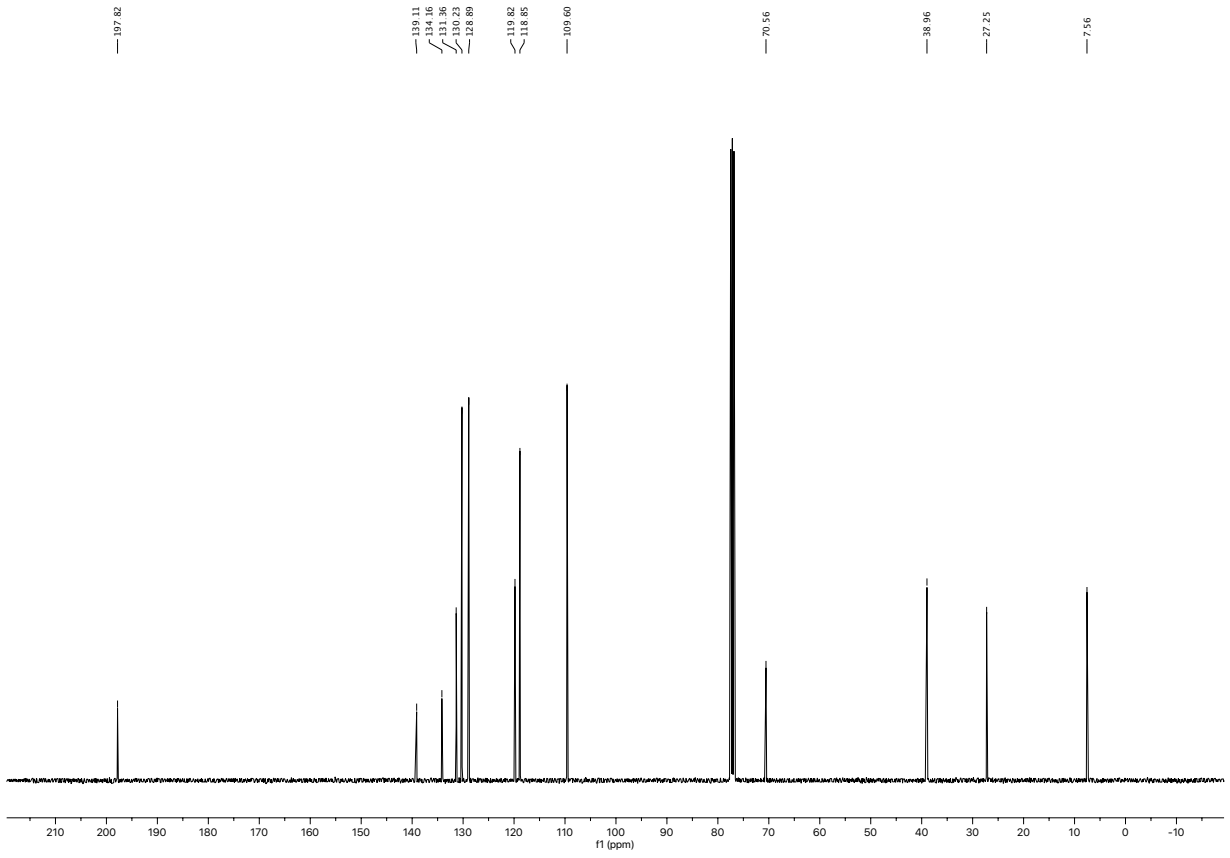
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2h**.



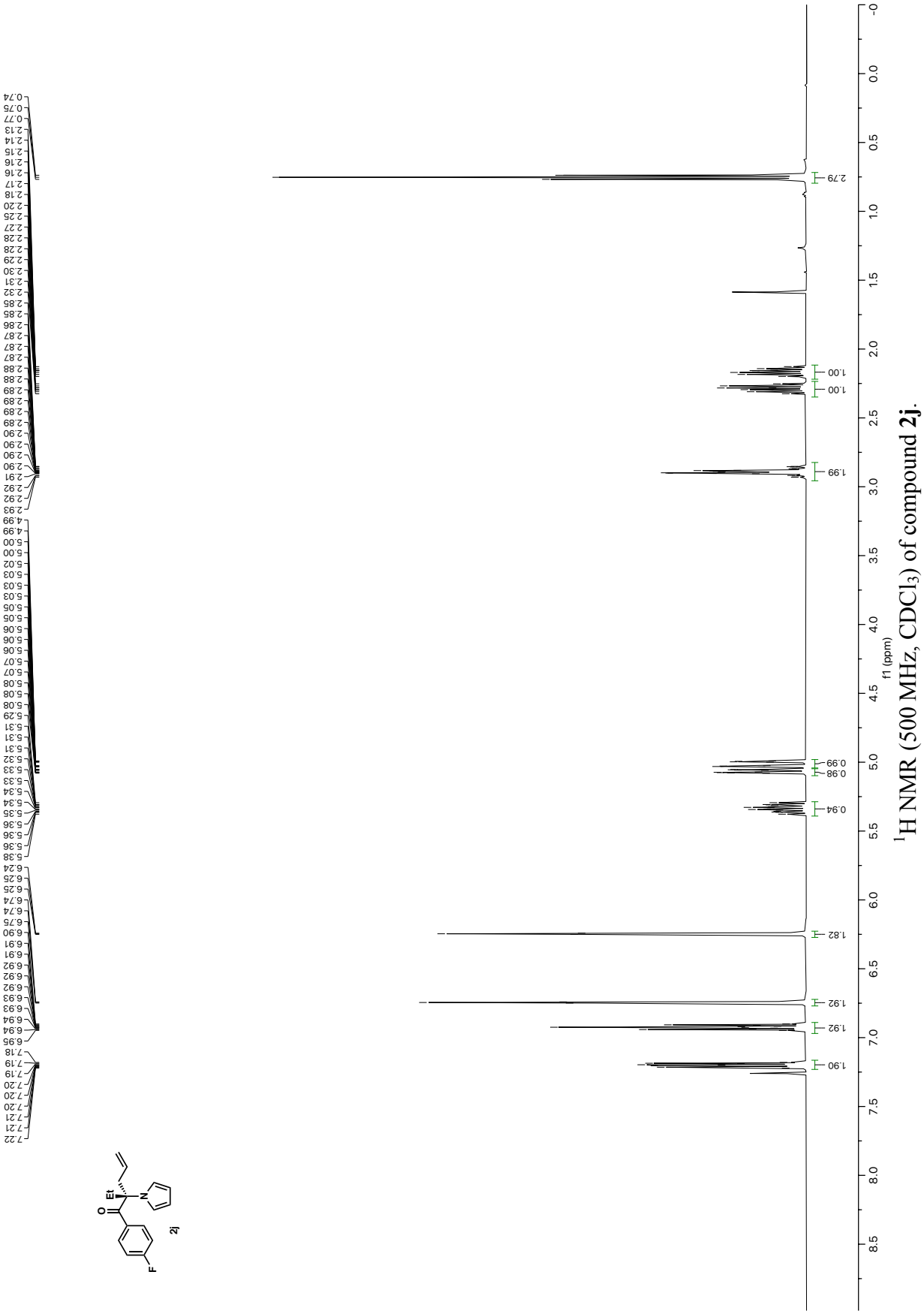
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2i**.



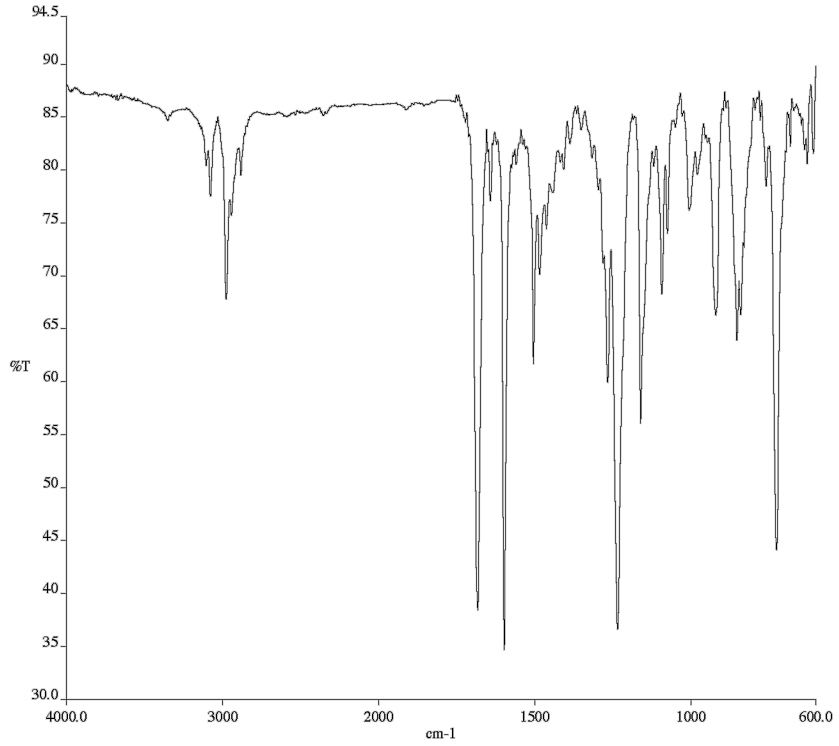
Infrared spectrum (Thin Film, NaCl) of compound **2i**.



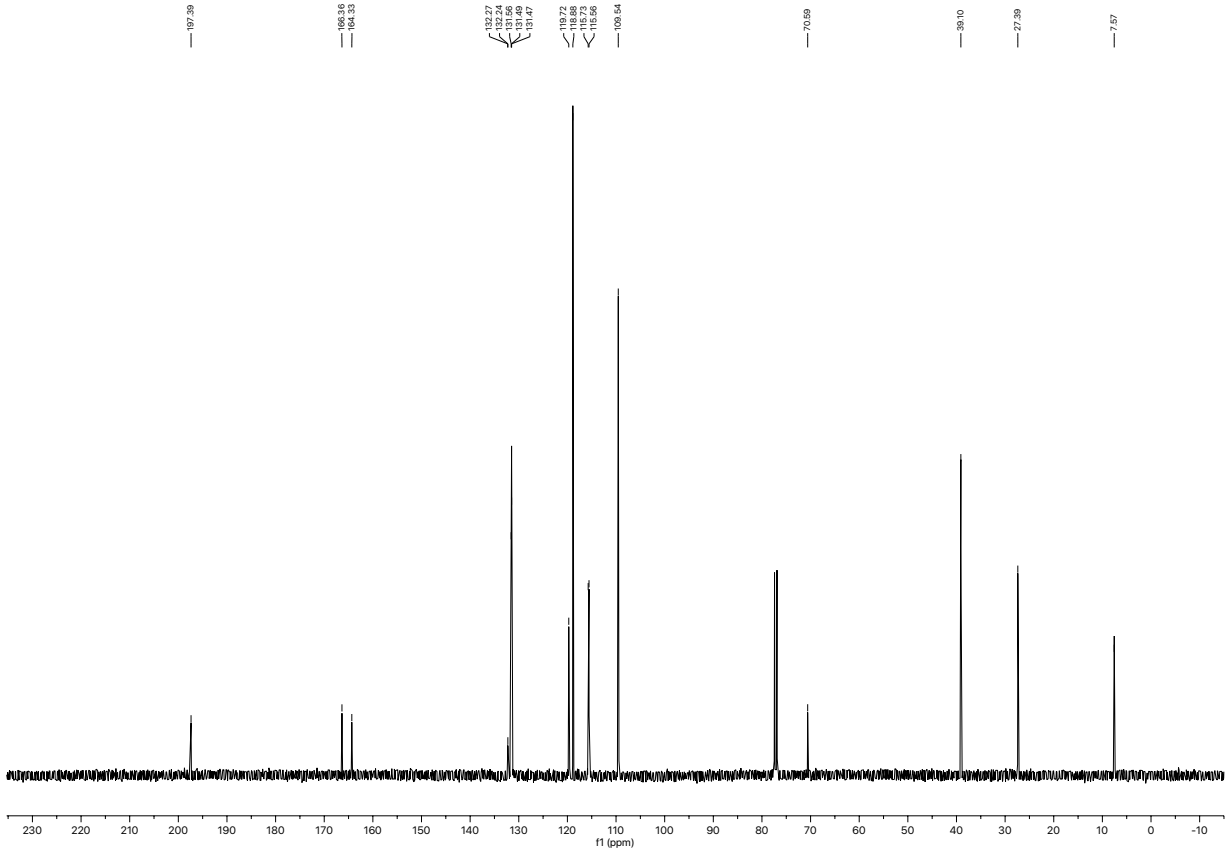
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2i**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **2j**.



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



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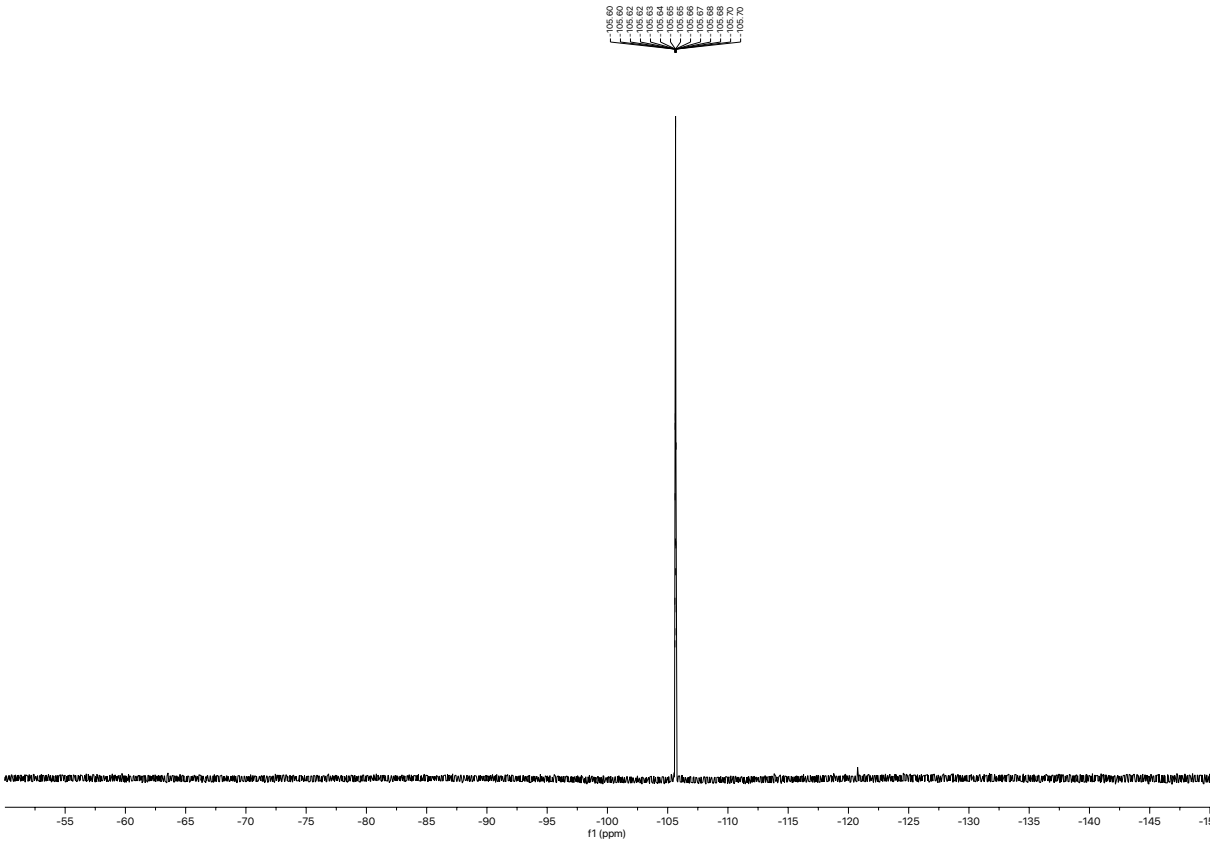
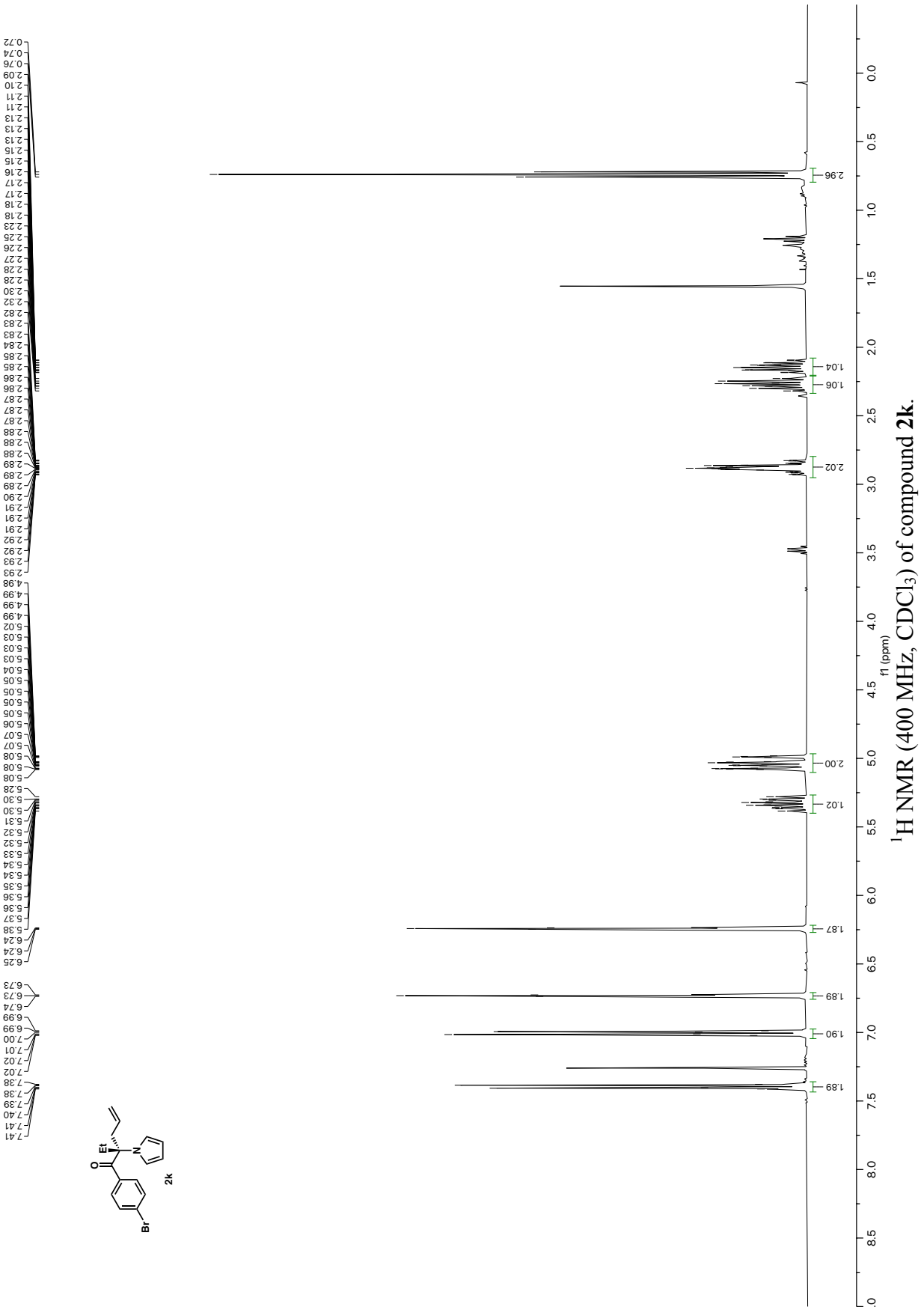
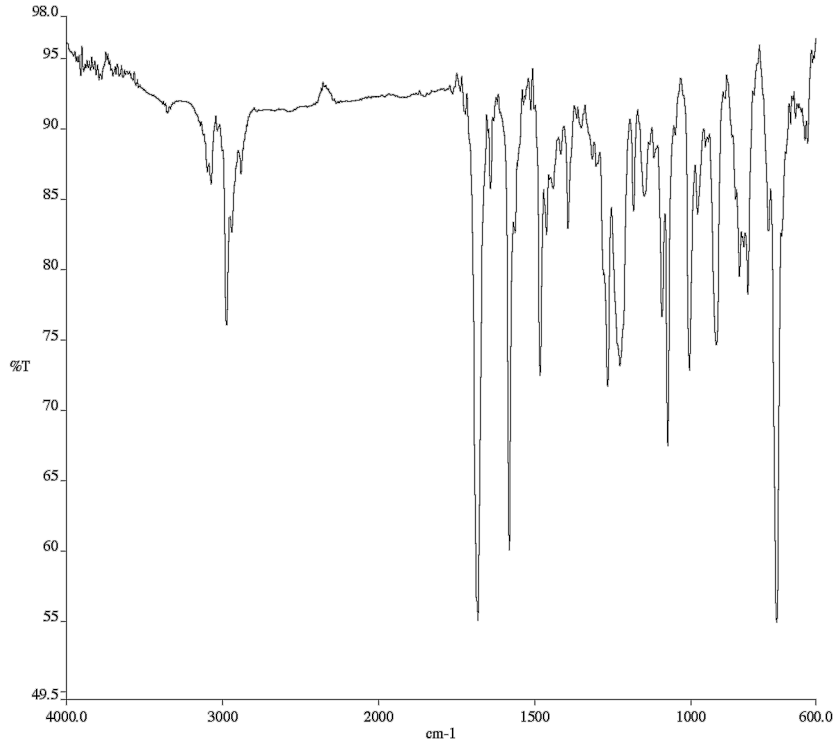


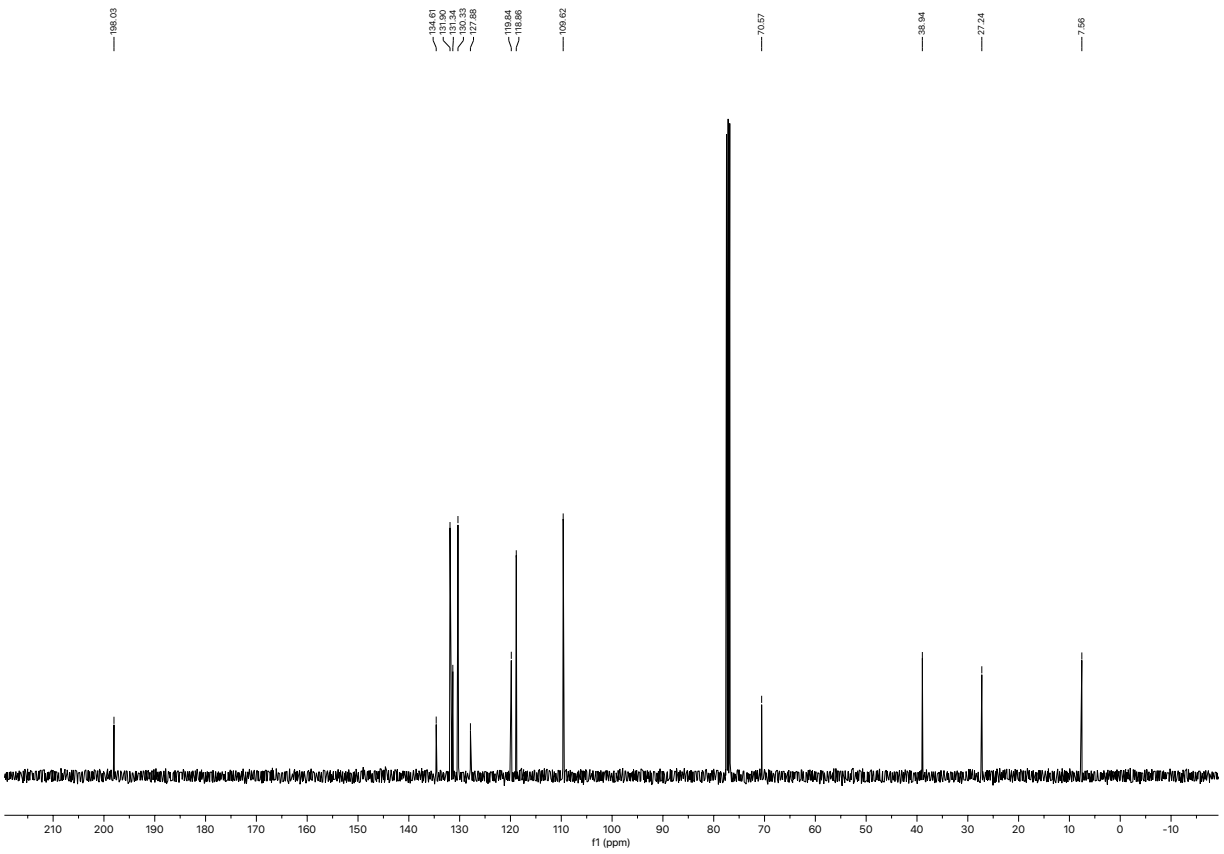
^{19}F NMR (282 MHz, $CDCl_3$) of compound **2j**.



^{1}H NMR (400 MHz, $CDCl_3$) of compound **2k**.



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



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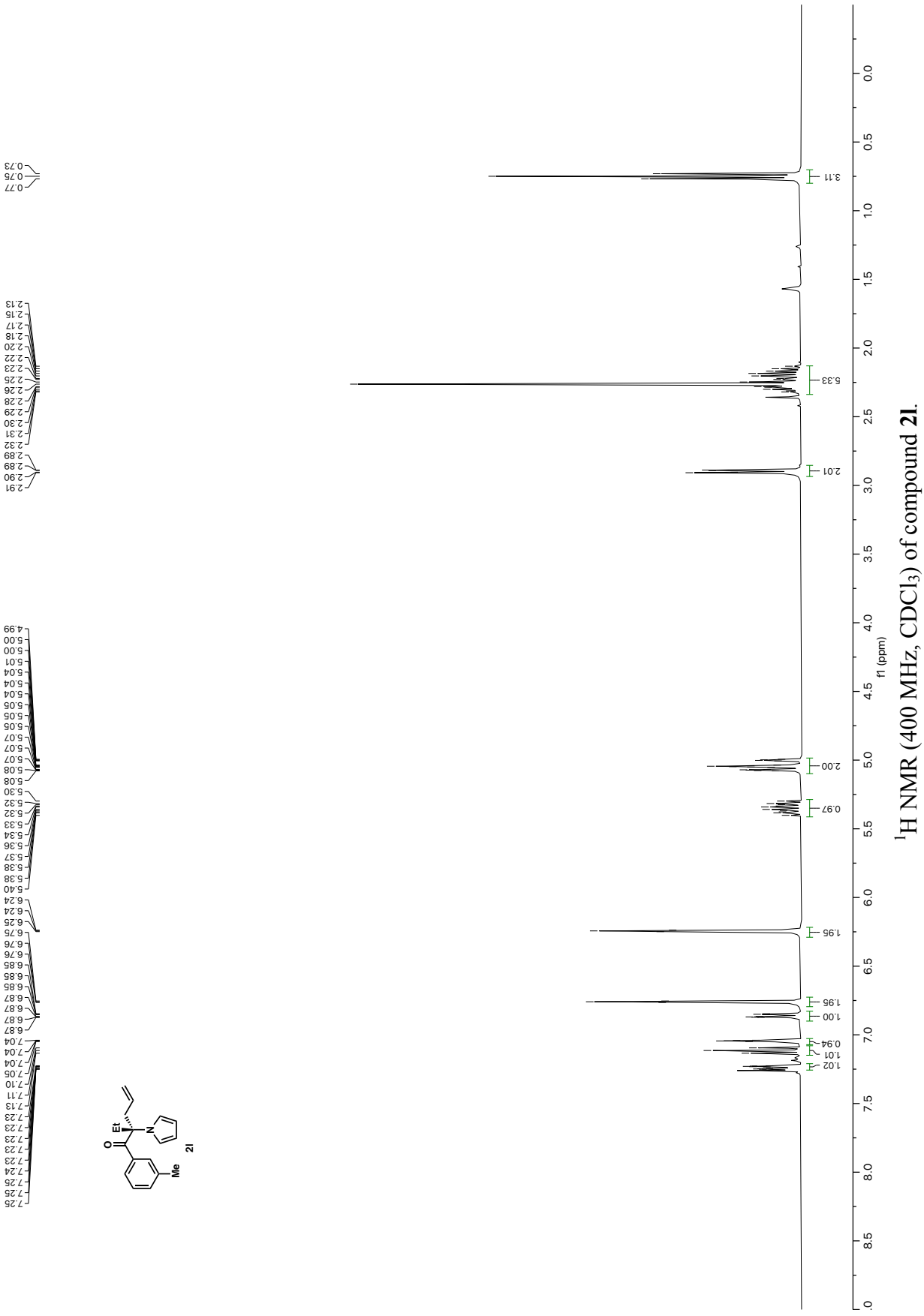

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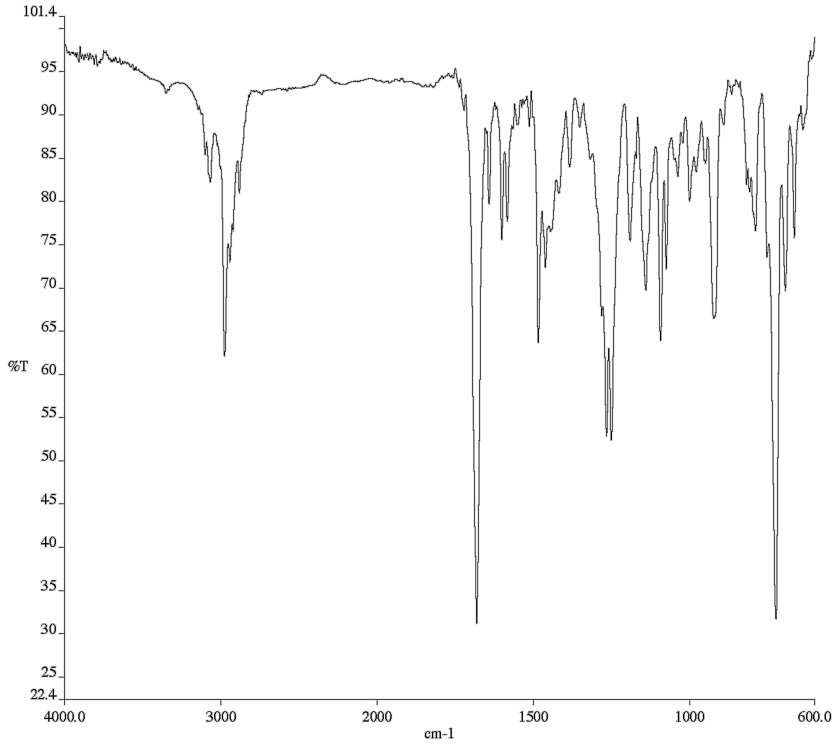
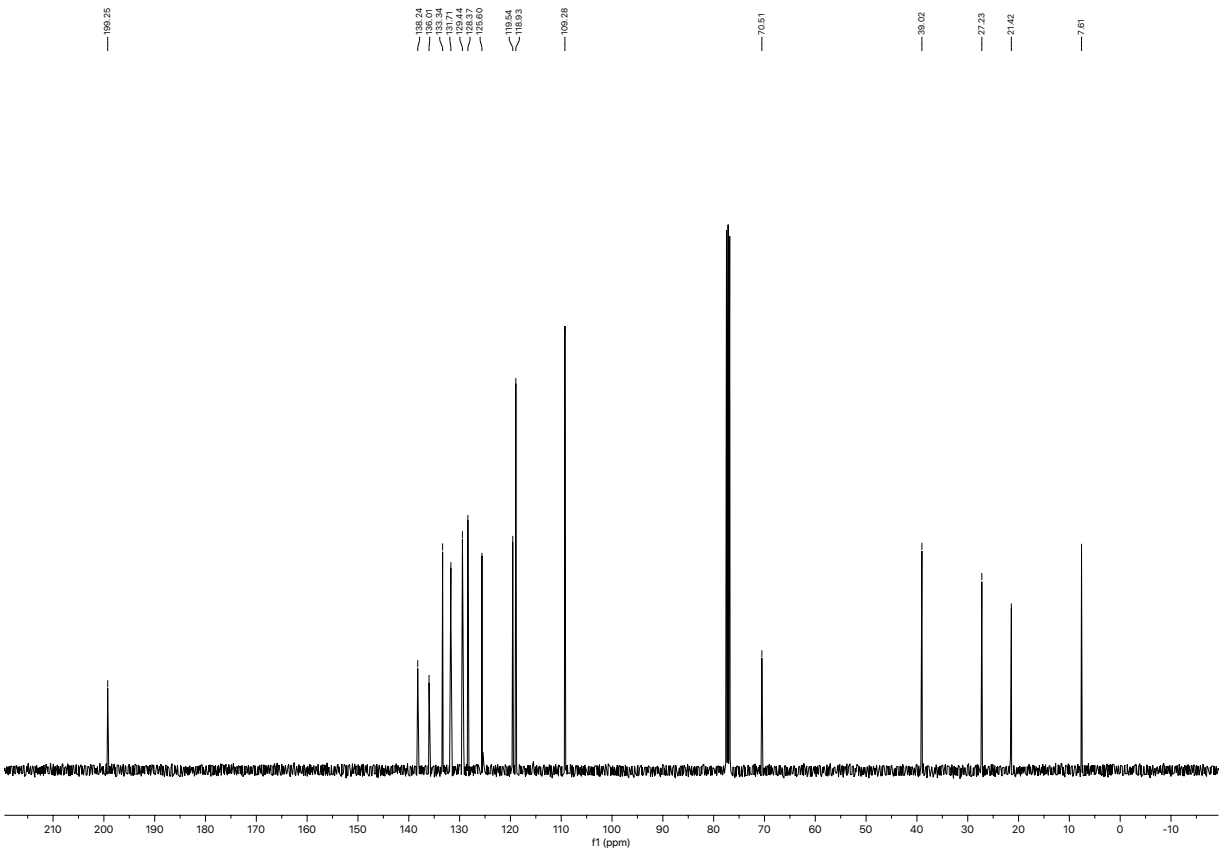
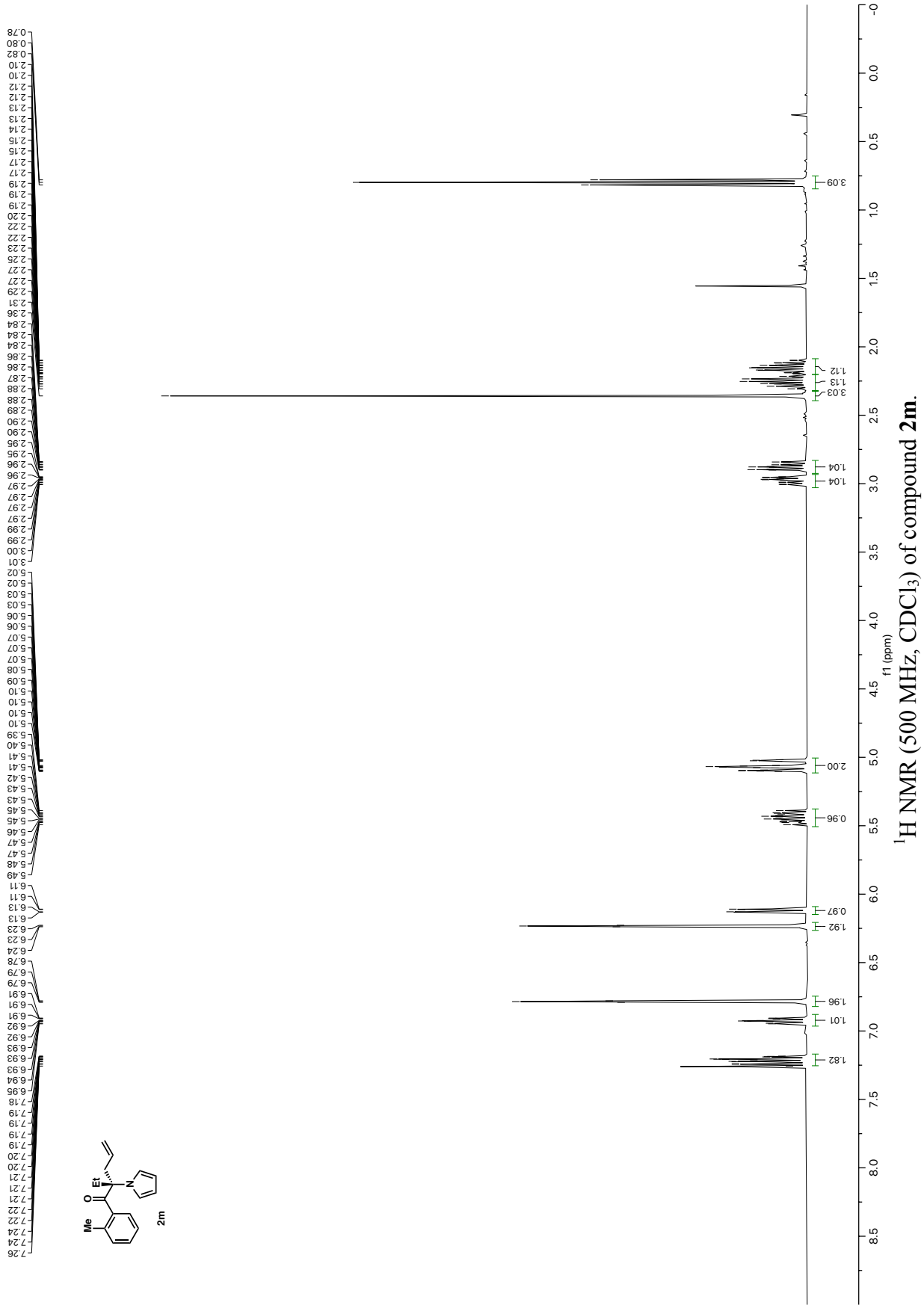


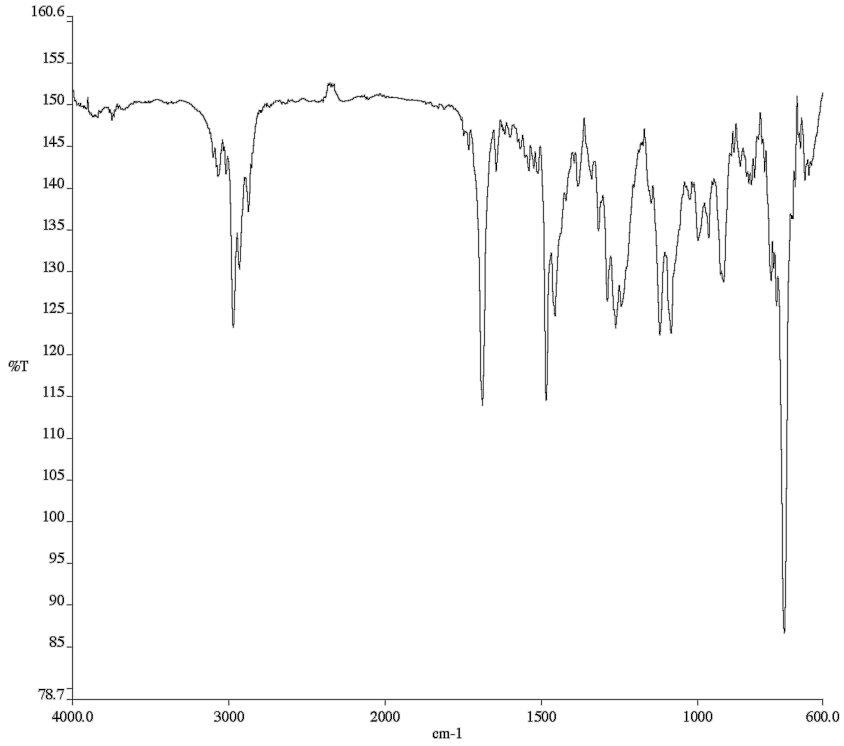
Infrared spectrum (Thin Film, NaCl) of compound **2l**.



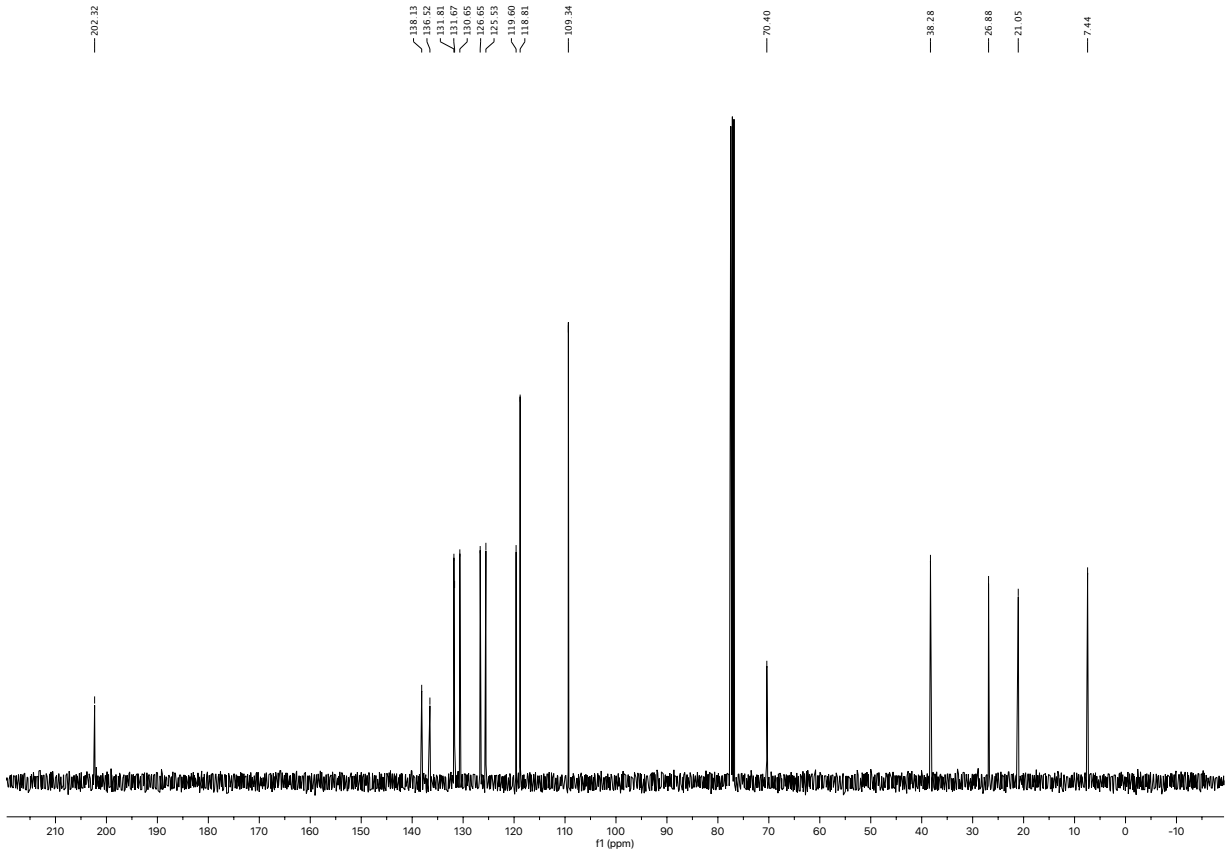
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2l**.



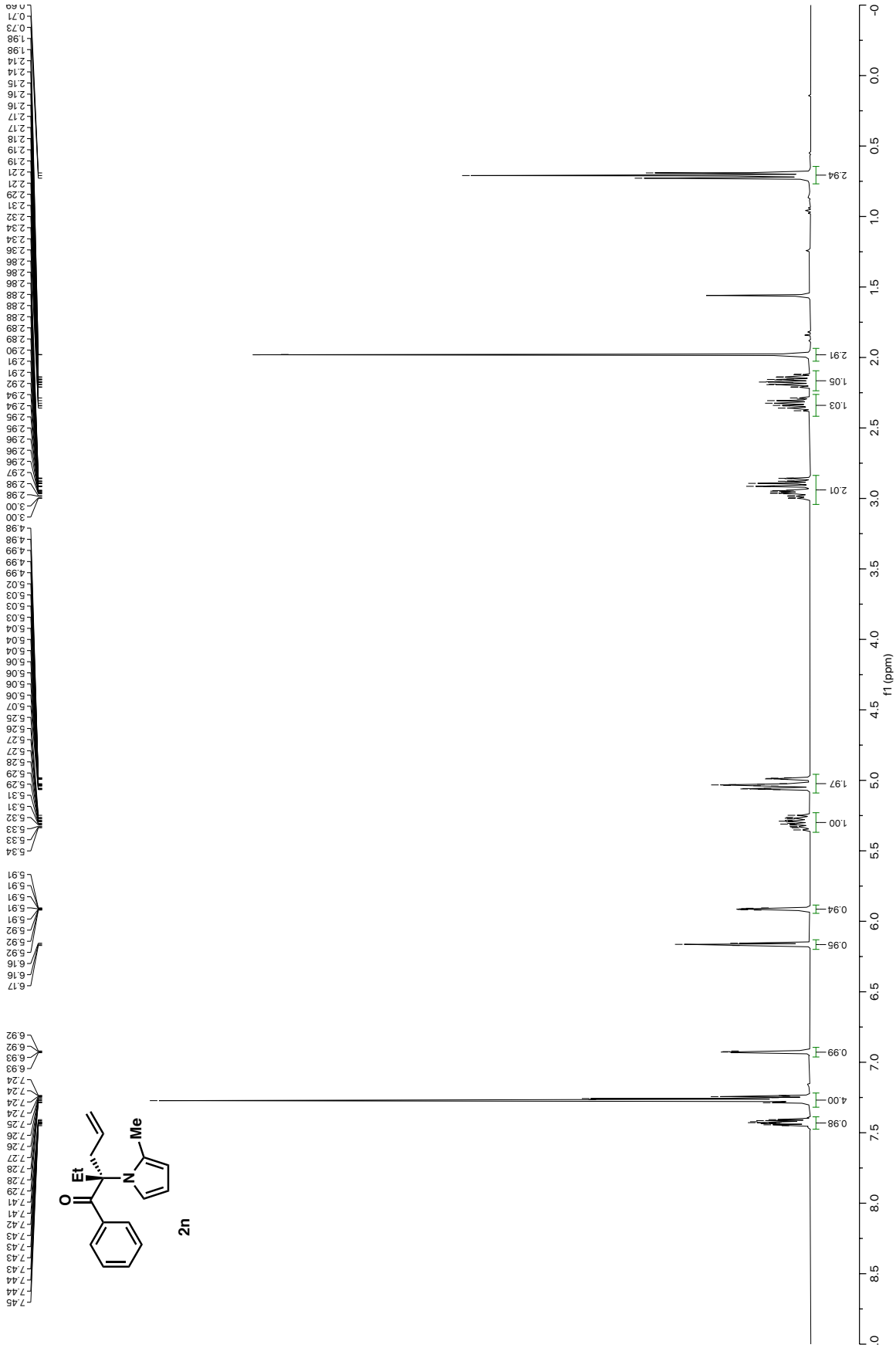
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2m**.



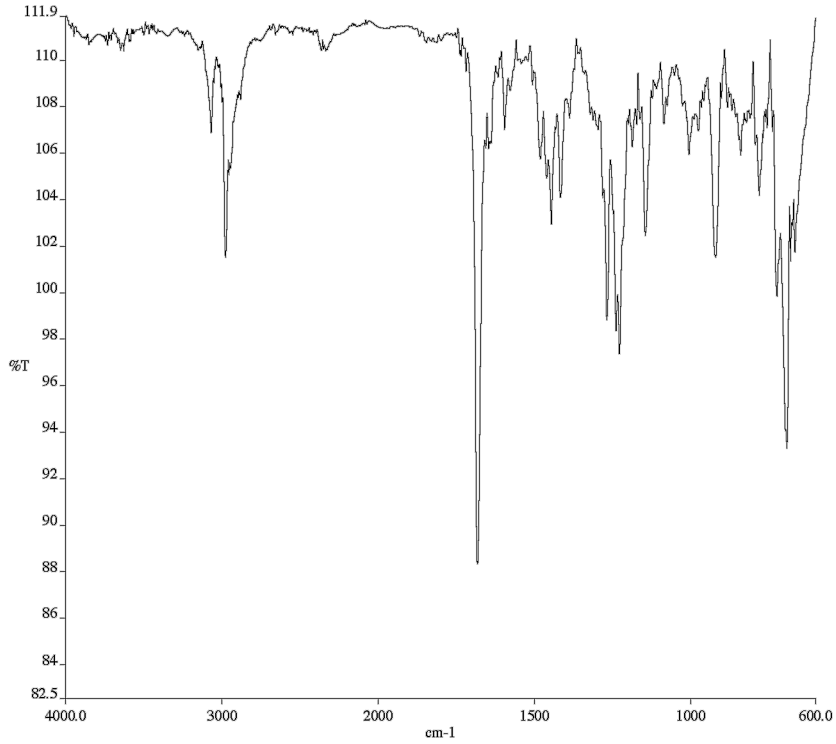
Infrared spectrum (Thin Film, NaCl) of compound **2m**.



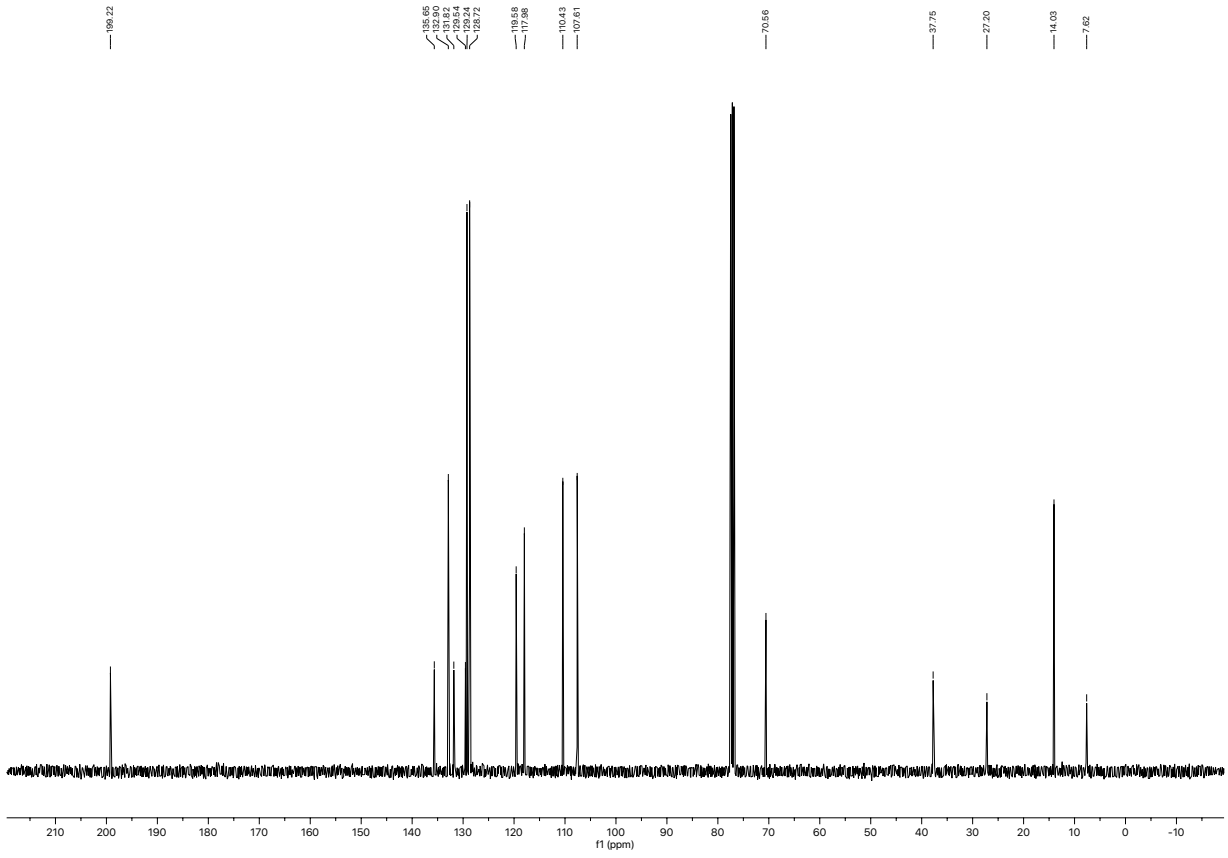
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2m**.



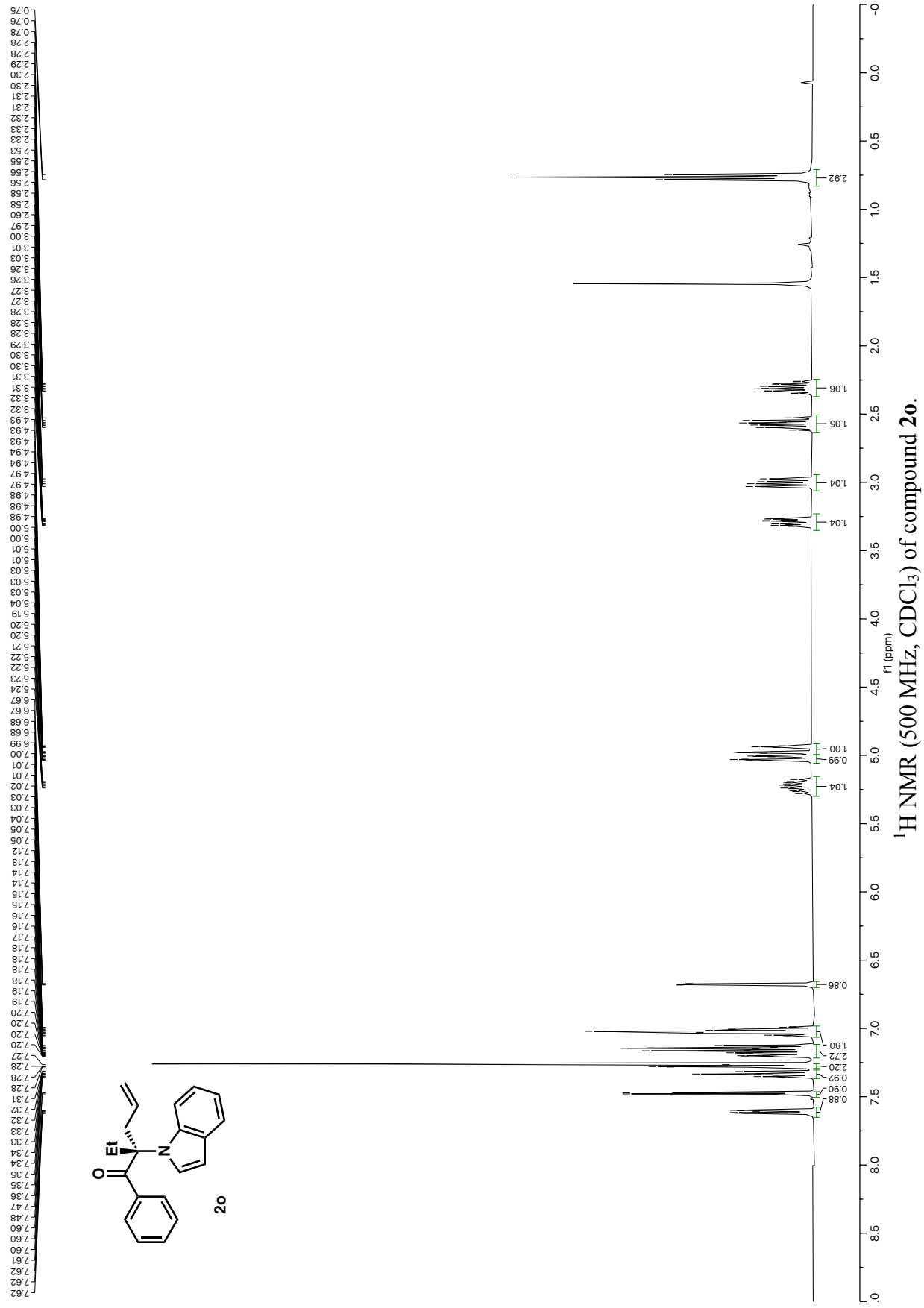
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2n**.



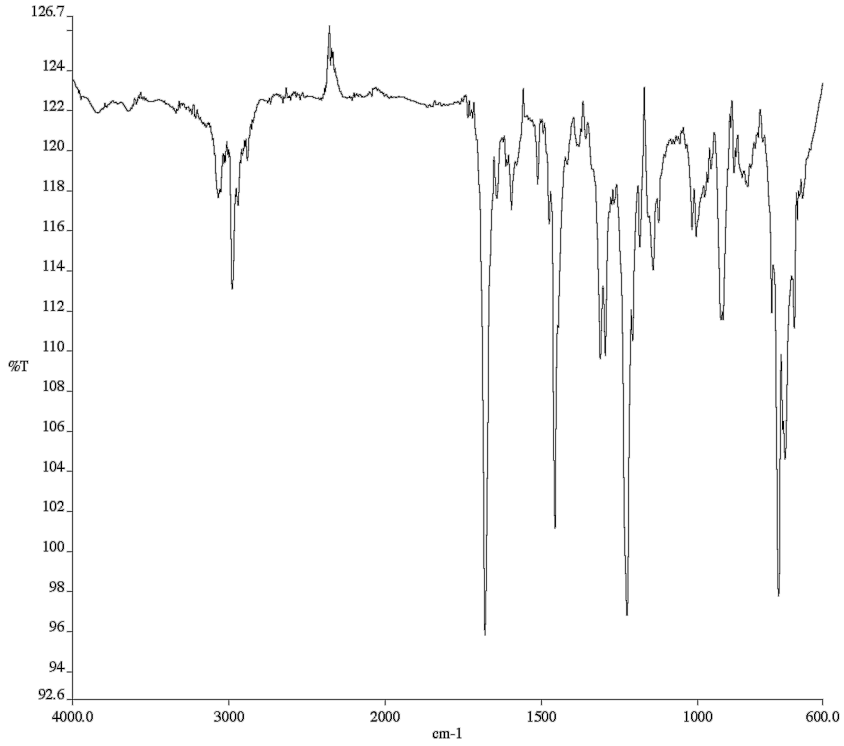
Infrared spectrum (Thin Film, NaCl) of compound **2n**.



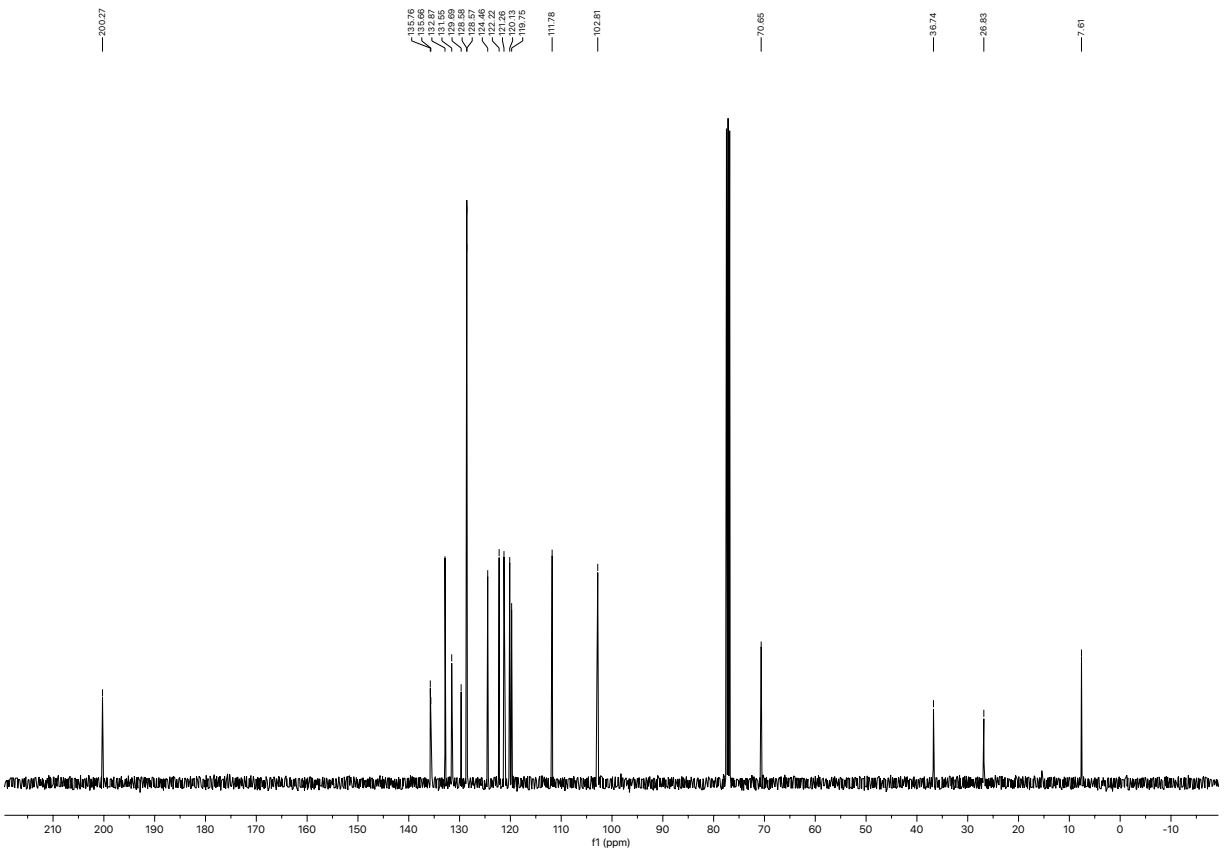
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2n**.



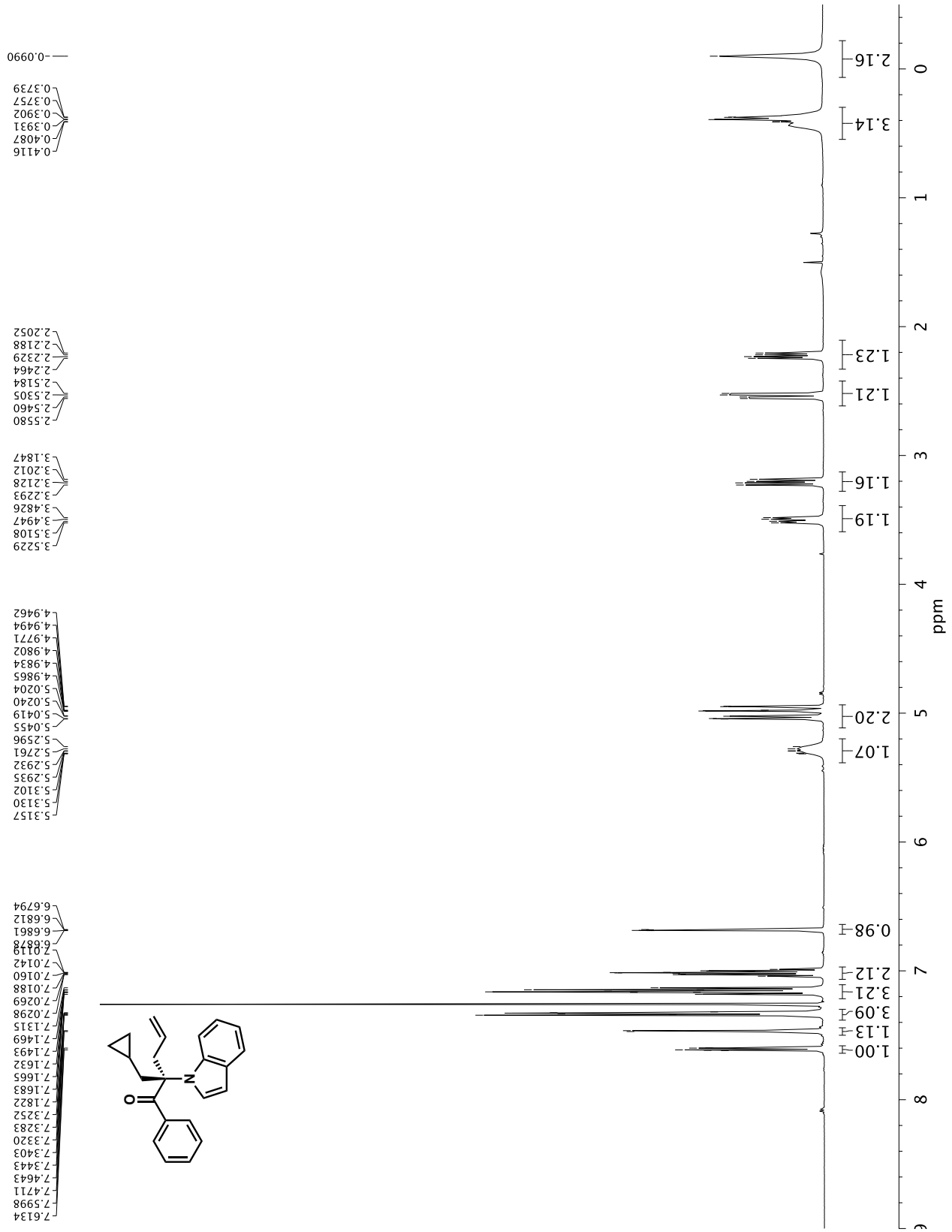
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2o**.



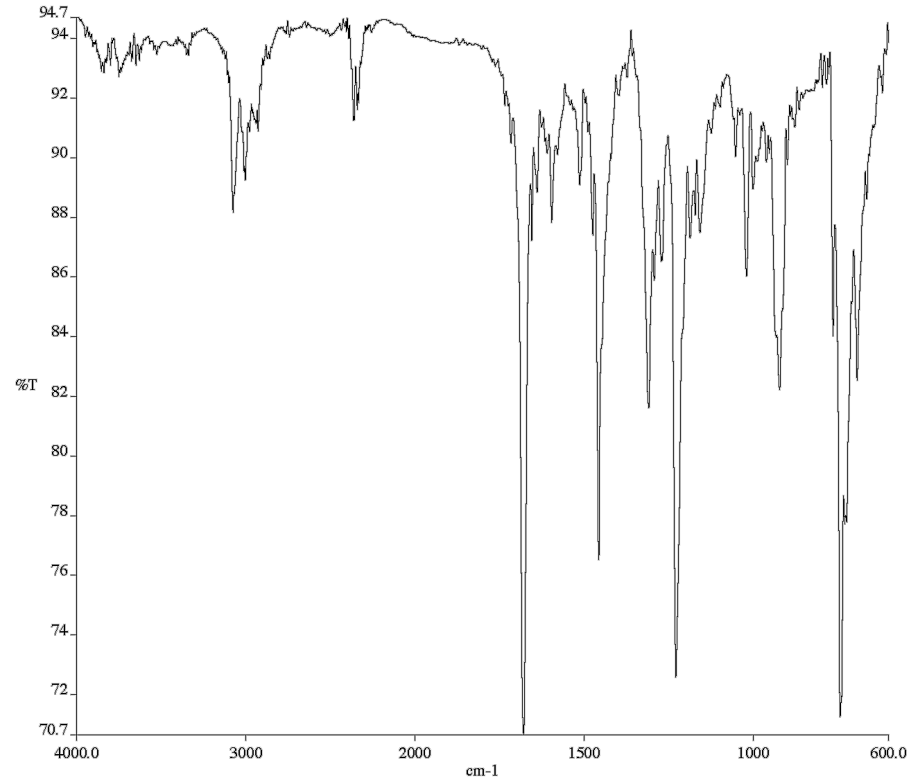
Infrared spectrum (Thin Film, NaCl) of compound **2o**.



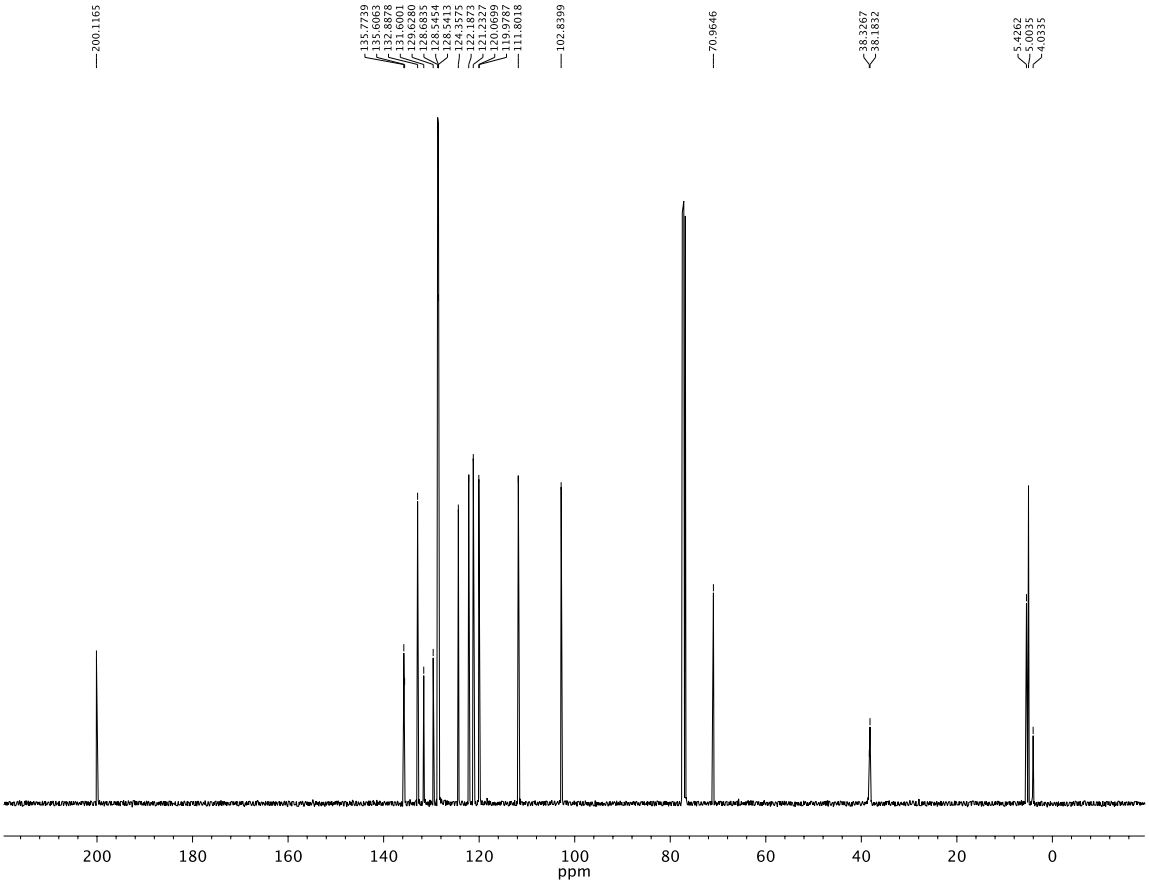
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2o**.



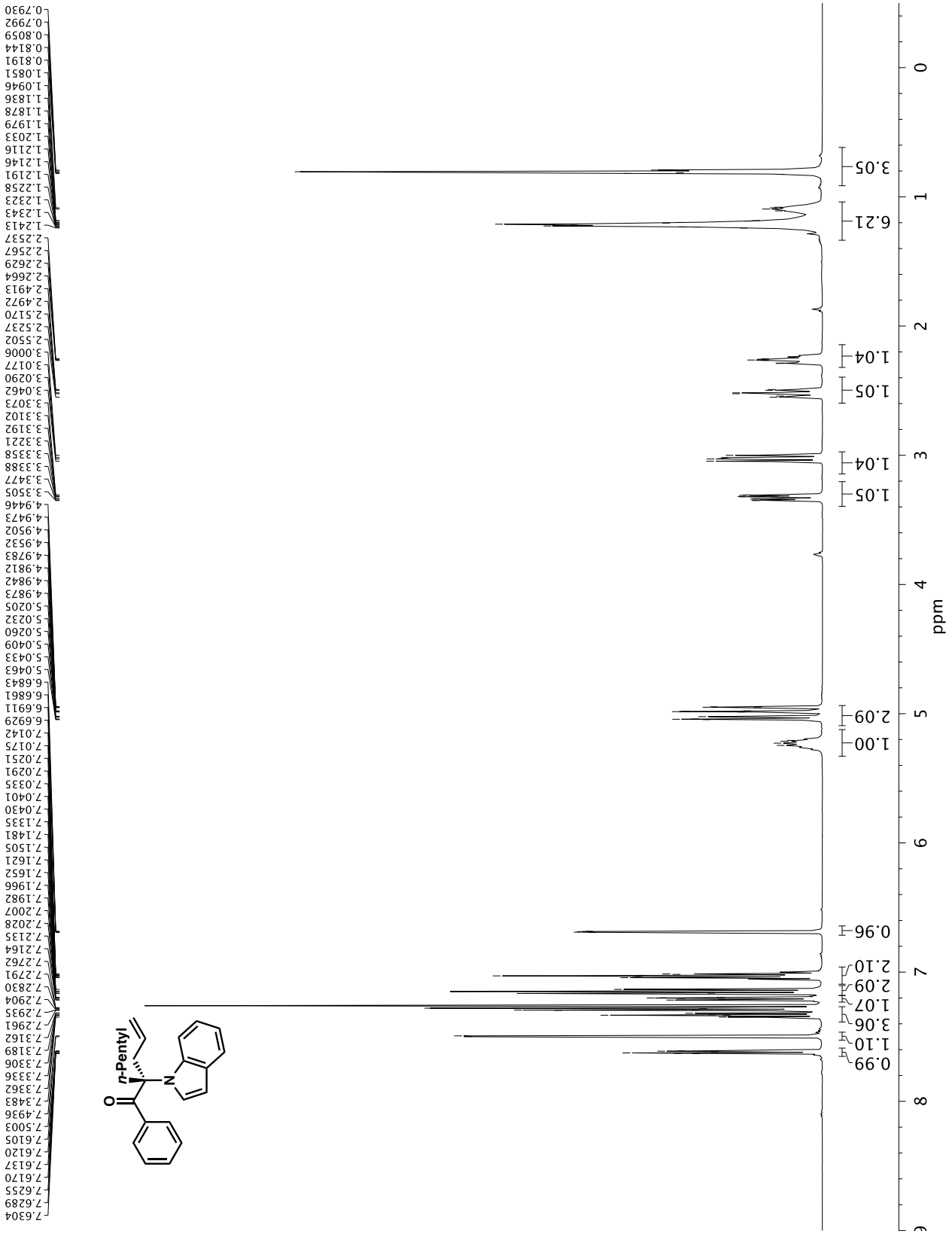
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2p**.



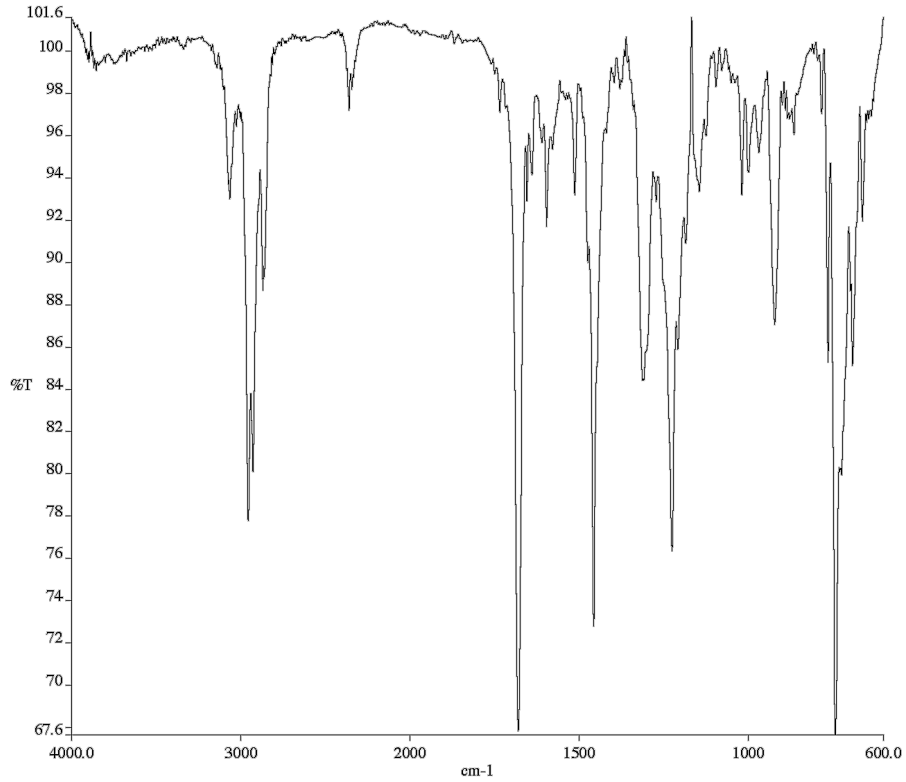
Infrared spectrum (Thin Film, NaCl) of compound **2p**.



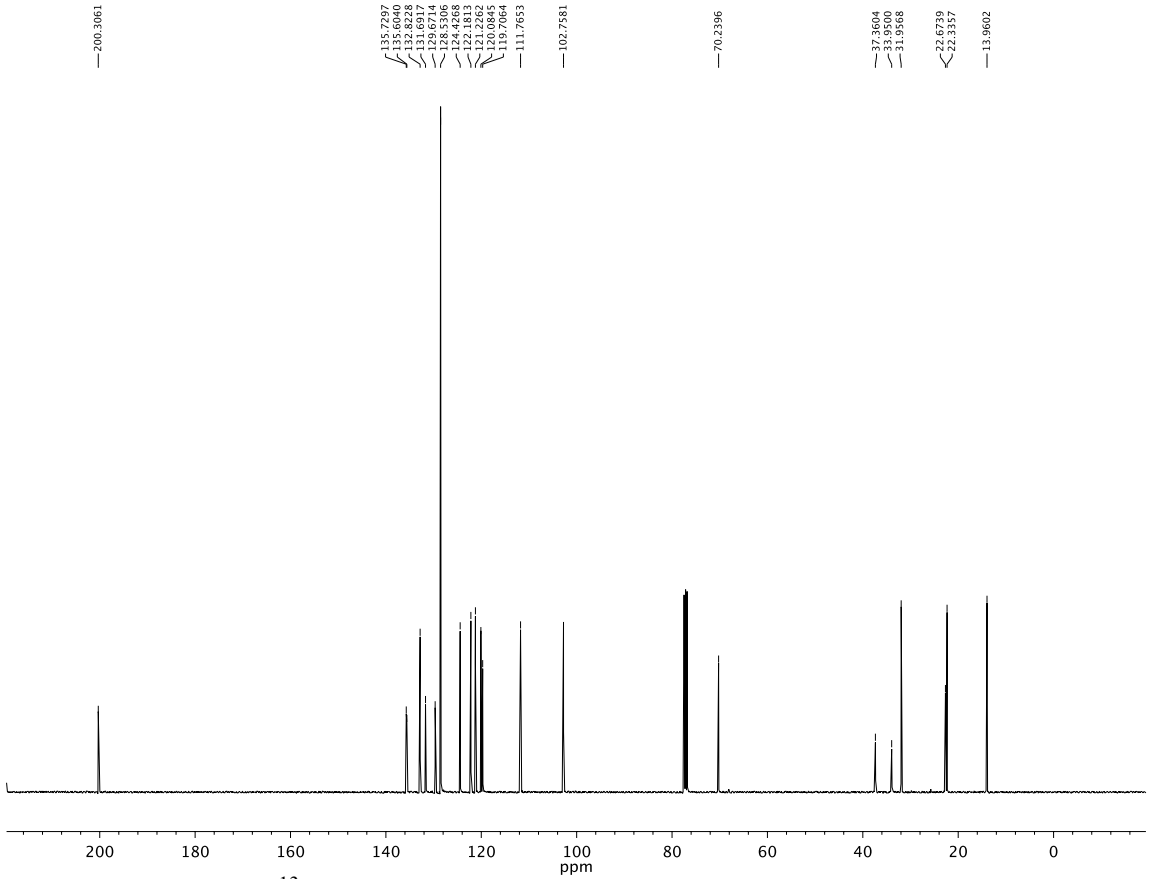
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2p**.



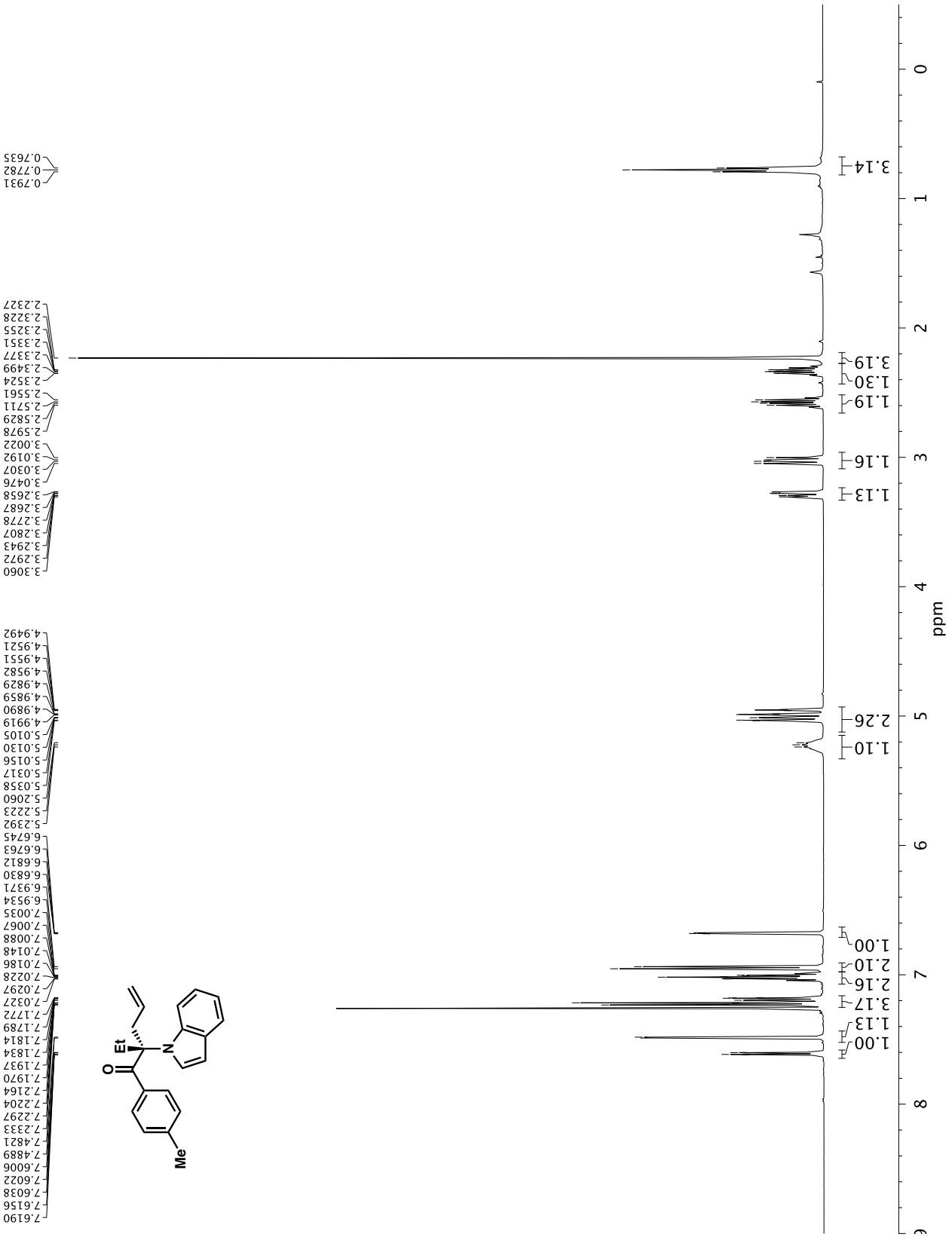
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2q**.



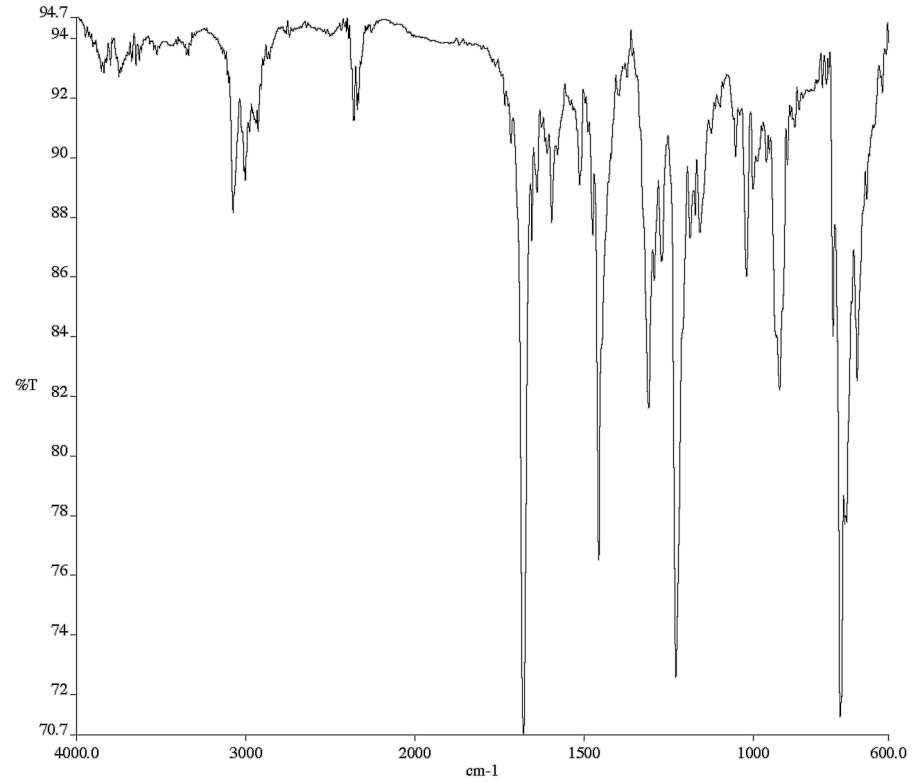
Infrared spectrum (Thin Film, NaCl) of compound **2q**.



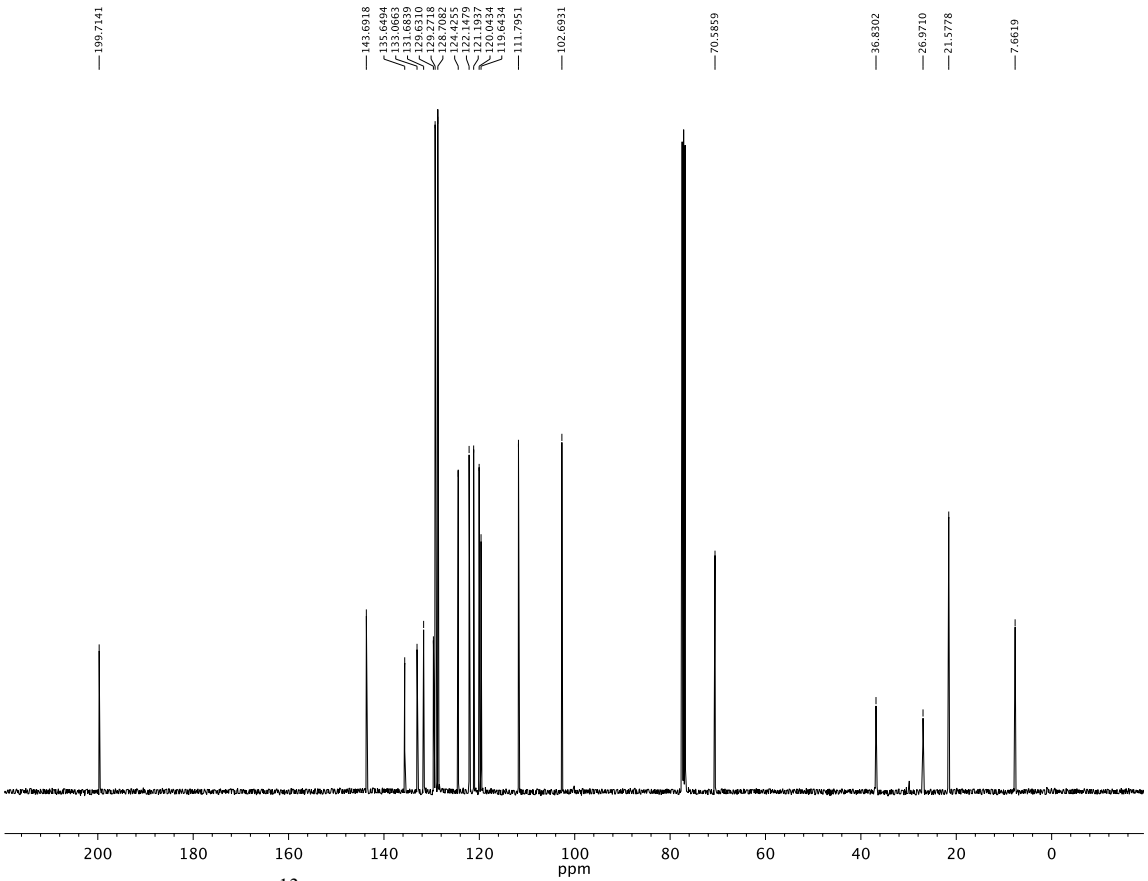
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2q**.



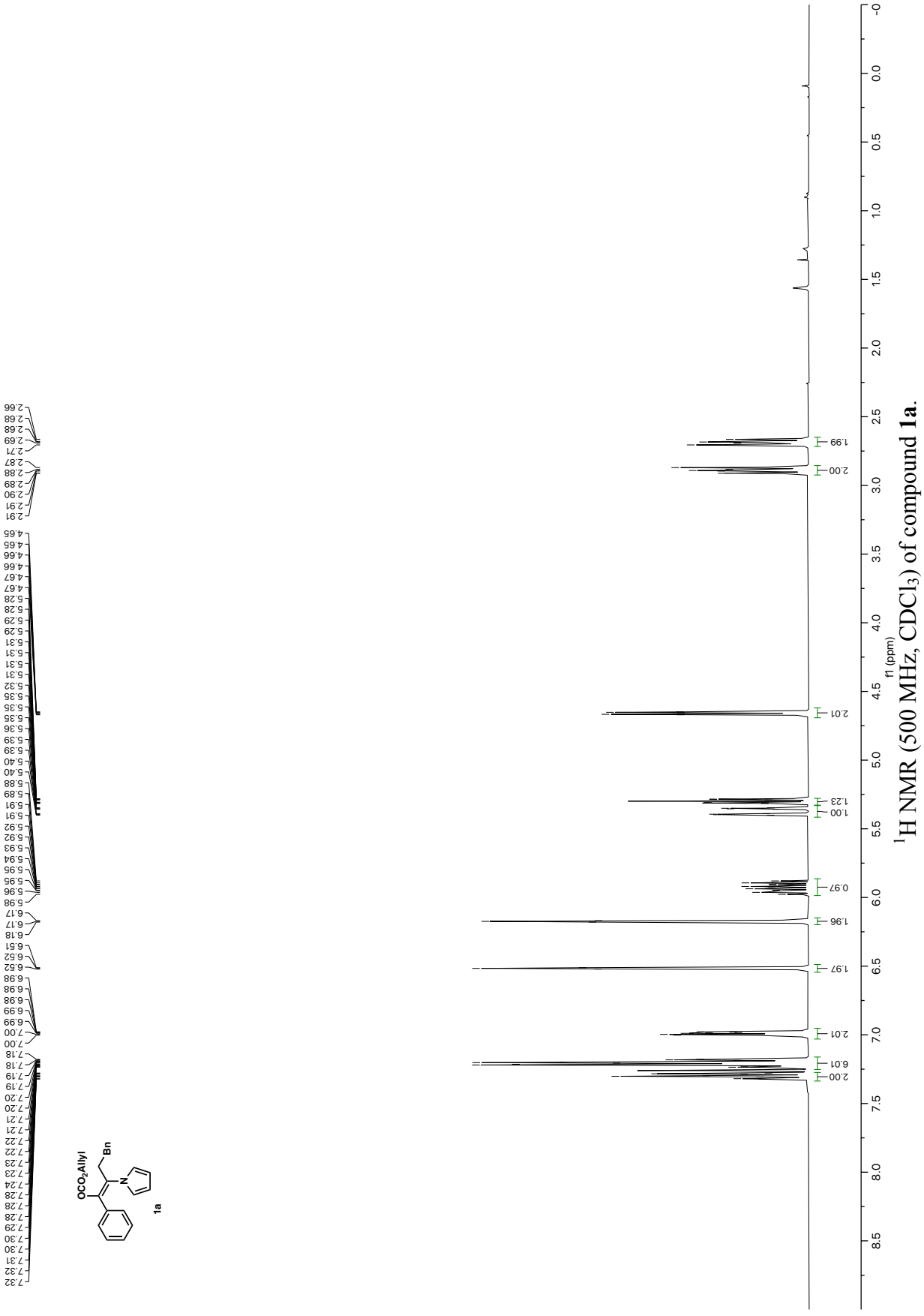
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2r**.



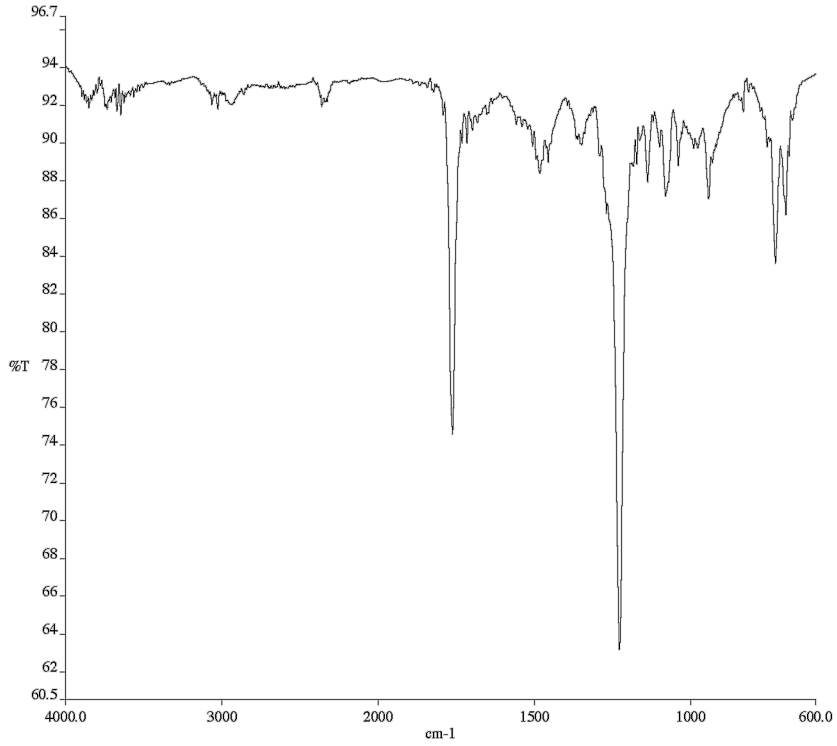
Infrared spectrum (Thin Film, NaCl) of compound **2r**.



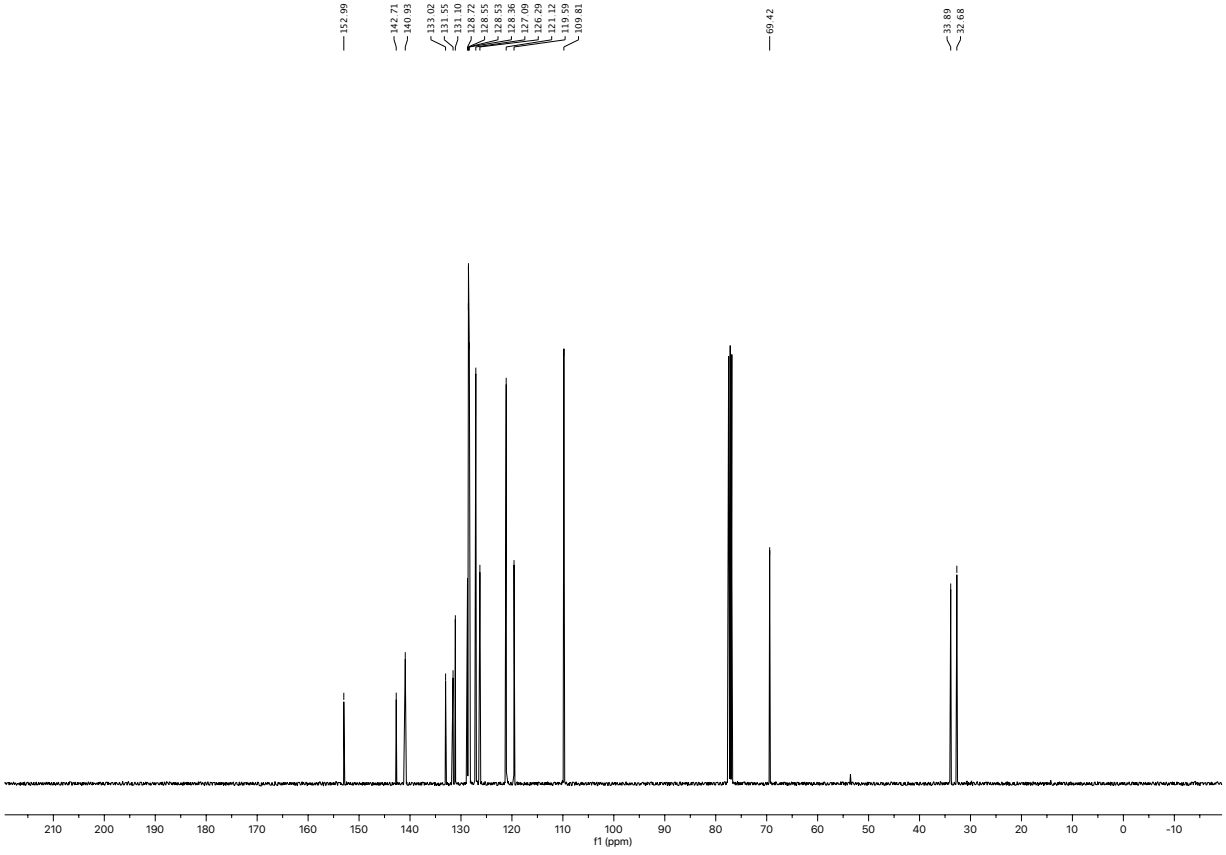
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2r**.



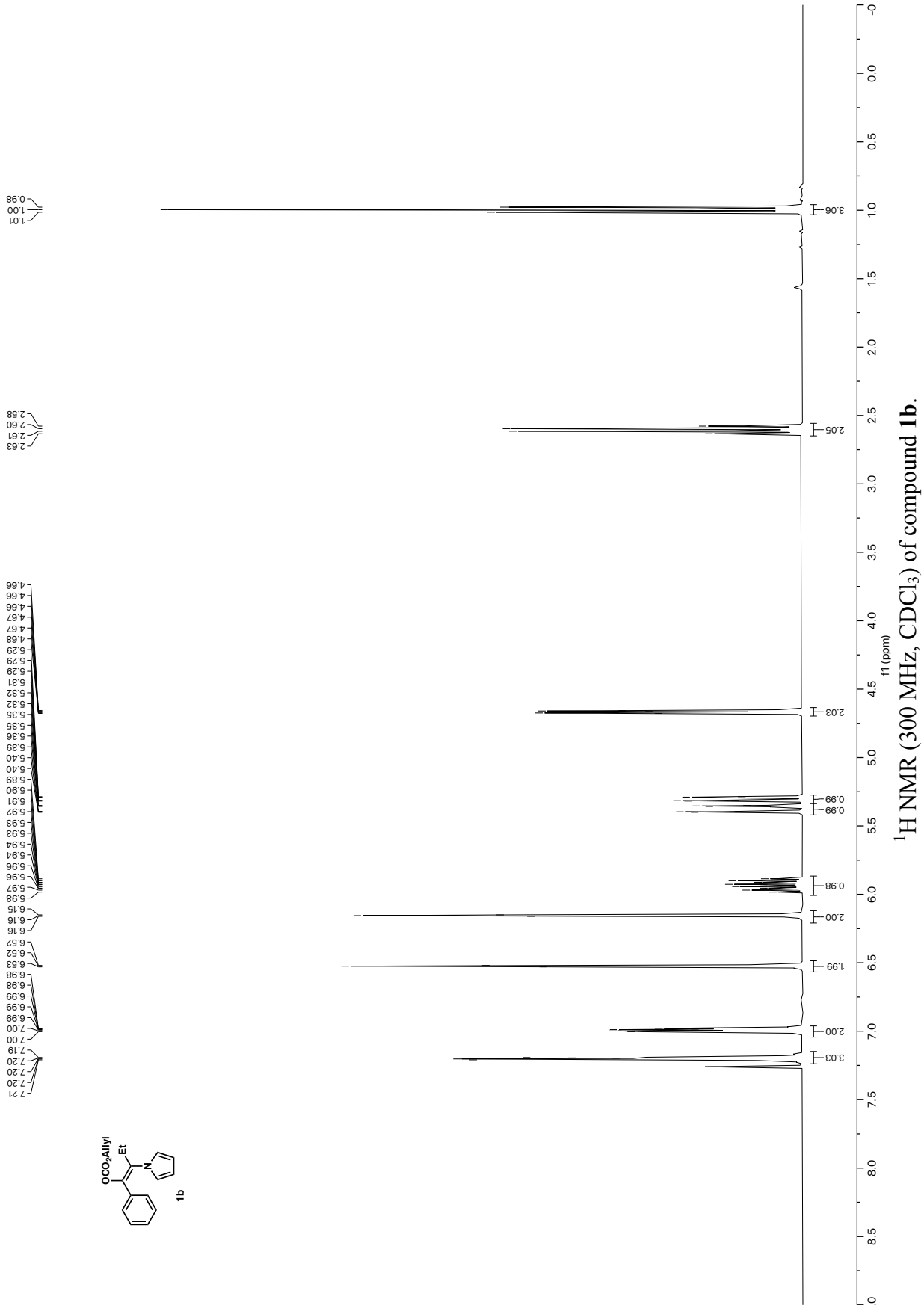
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1a**.



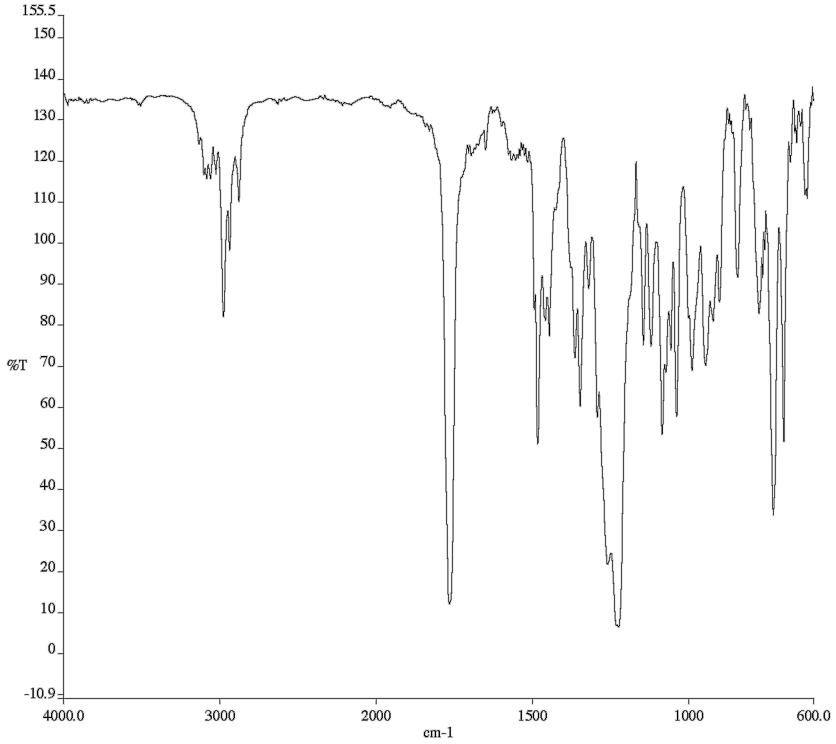
Infrared spectrum (Thin Film, NaCl) of compound **1a**.



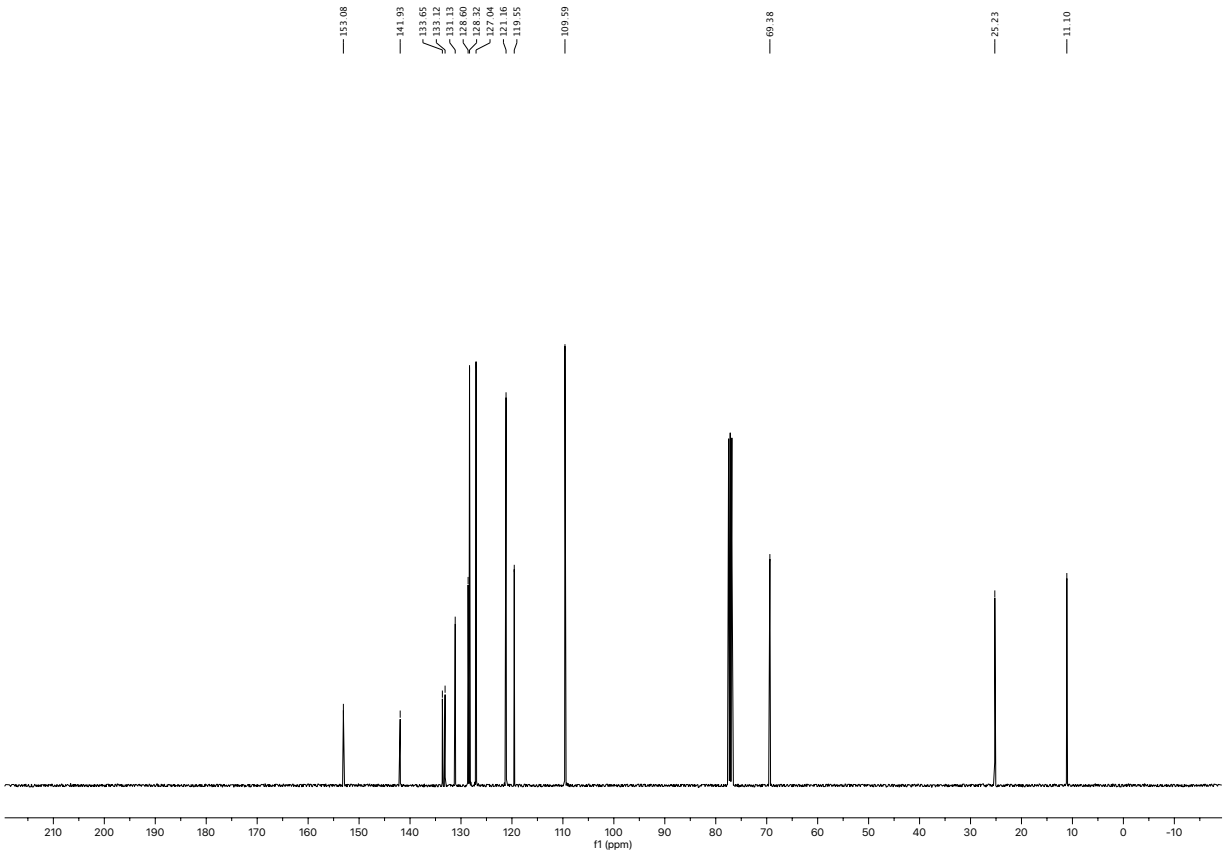
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1a**.



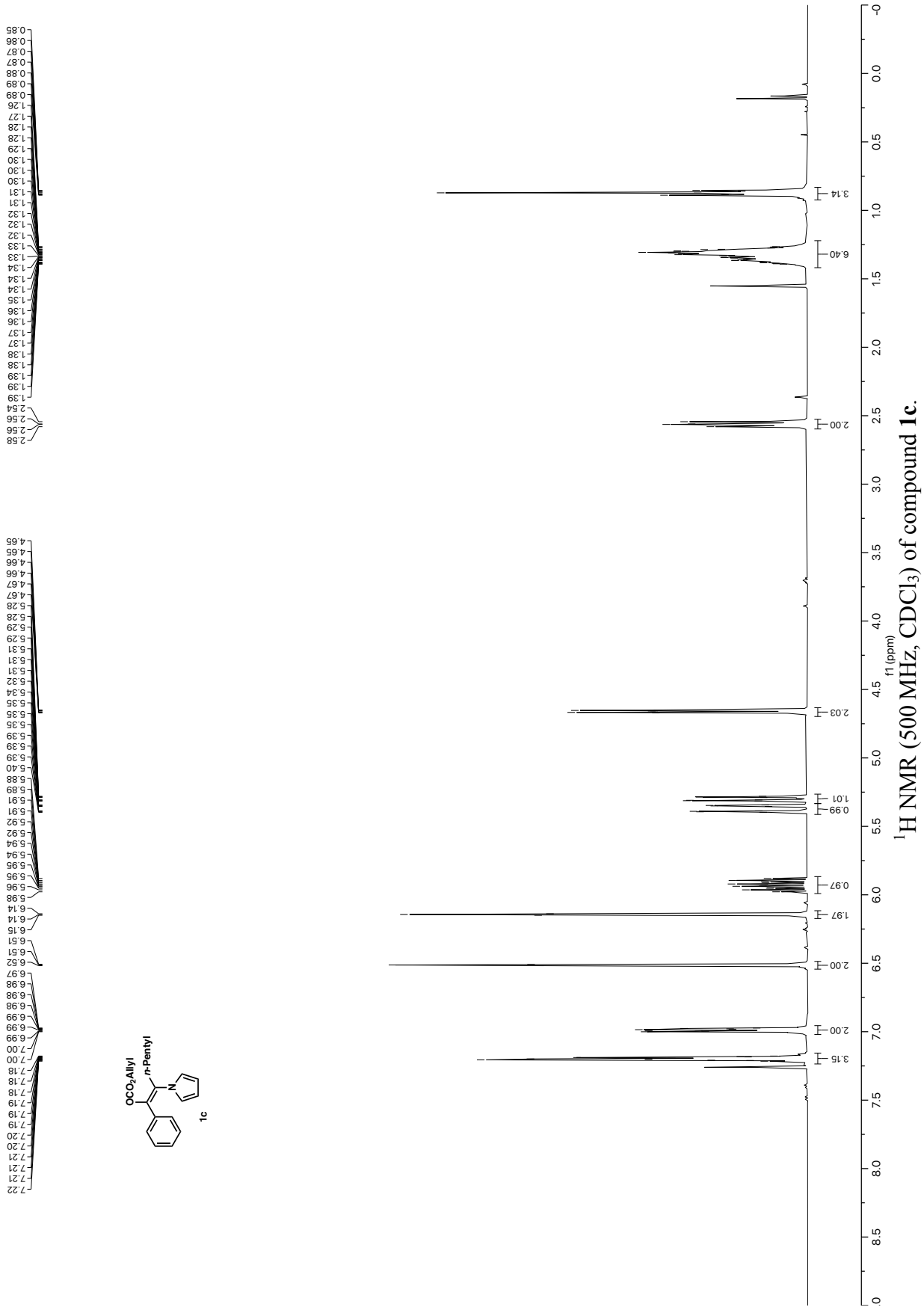
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1b**.



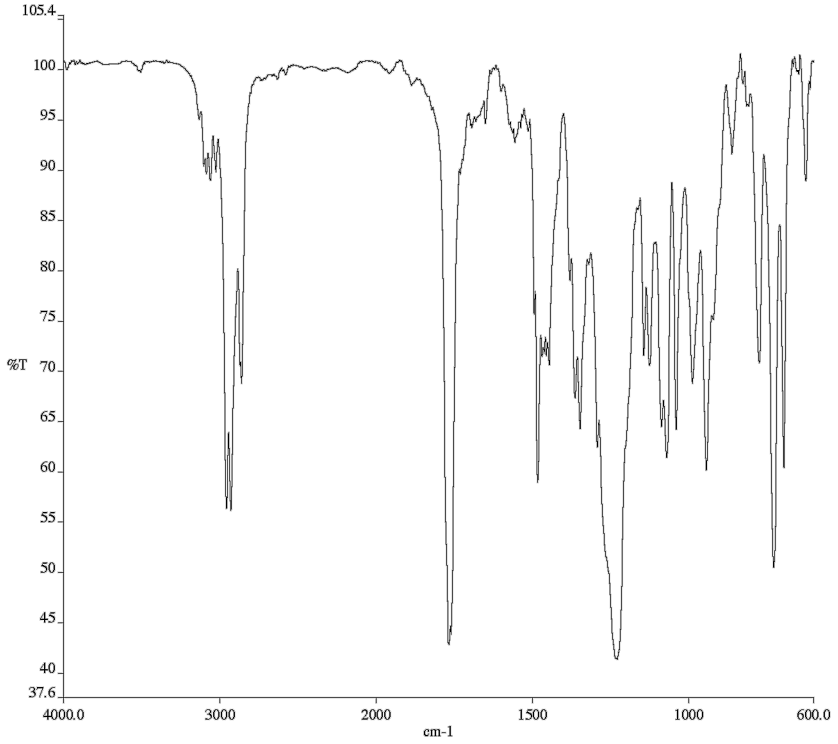
Infrared spectrum (Thin Film, NaCl) of compound **1b**.



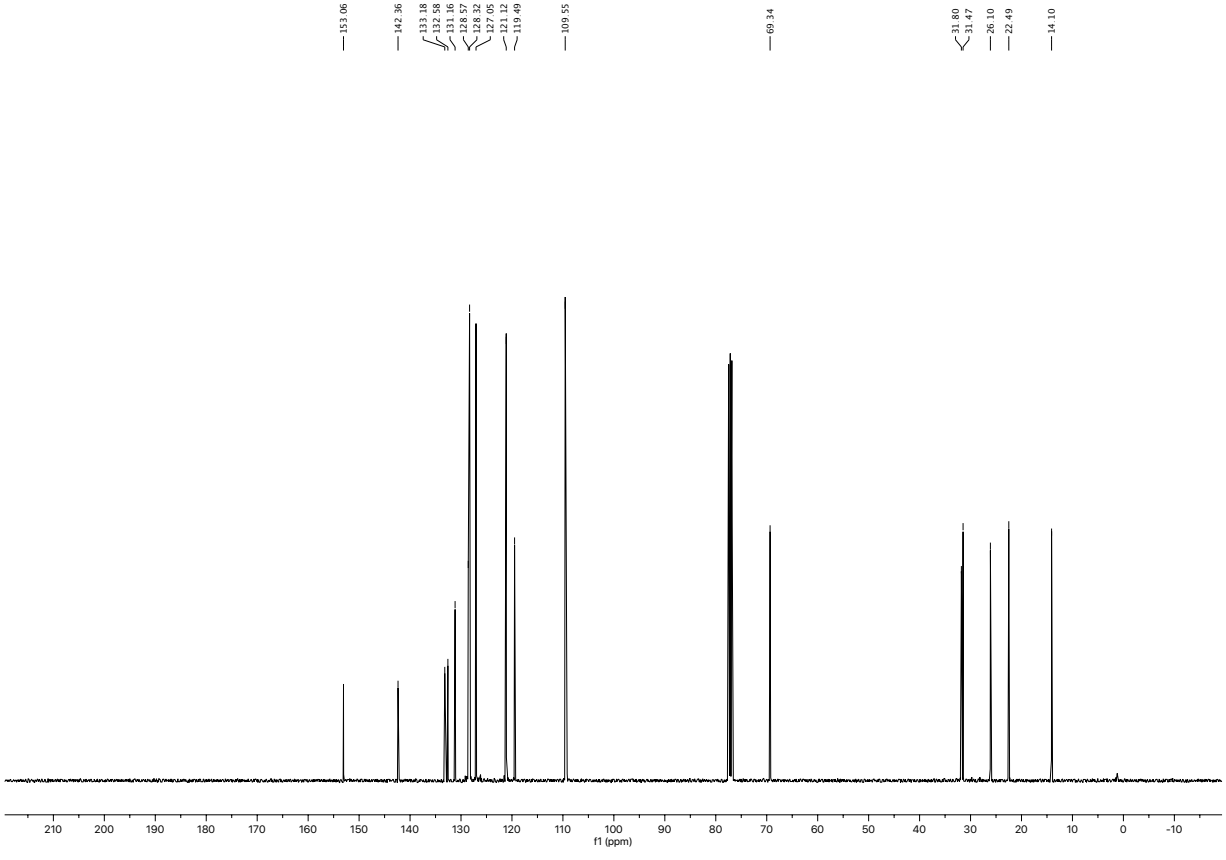
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1b**.



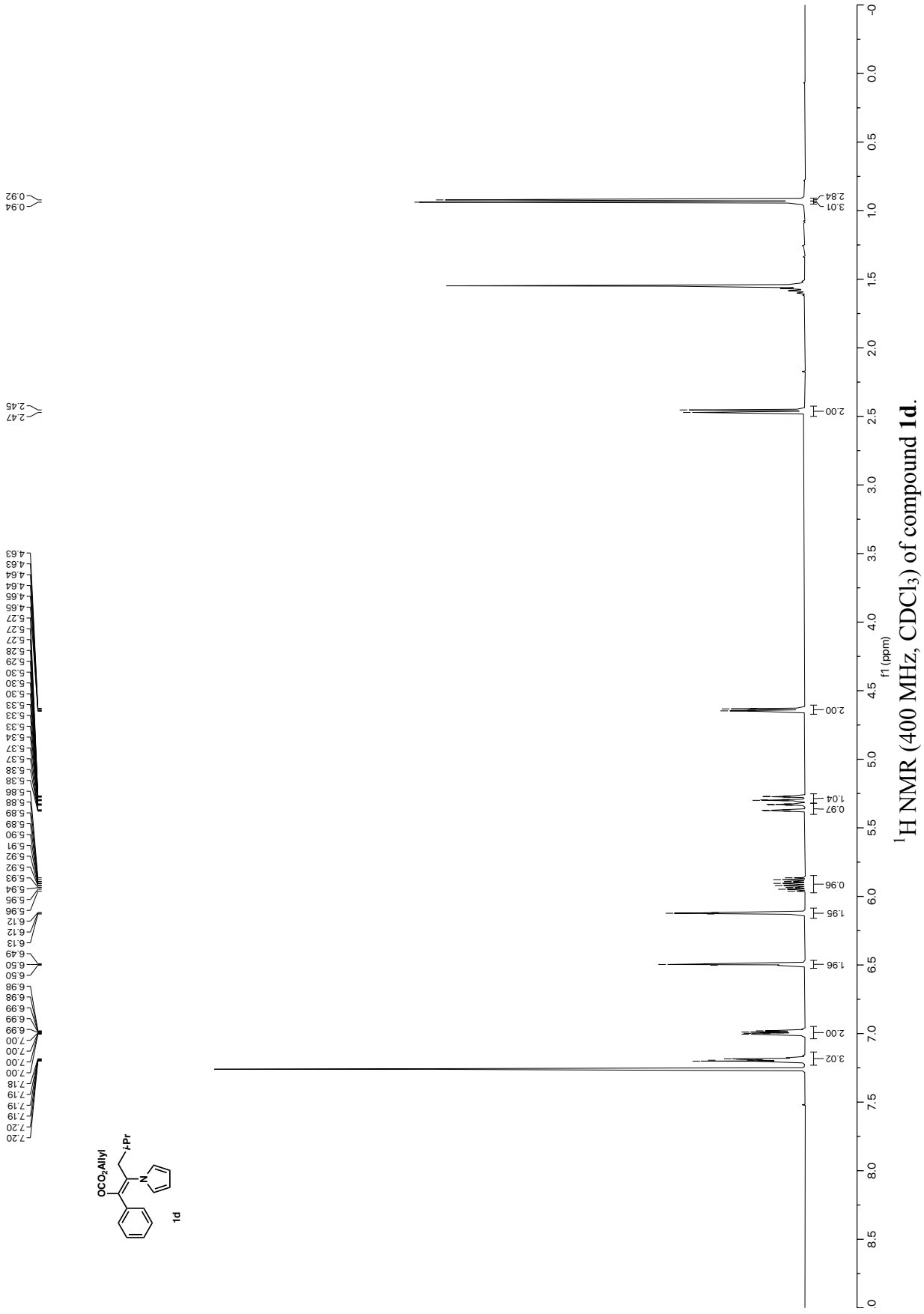
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1c**.



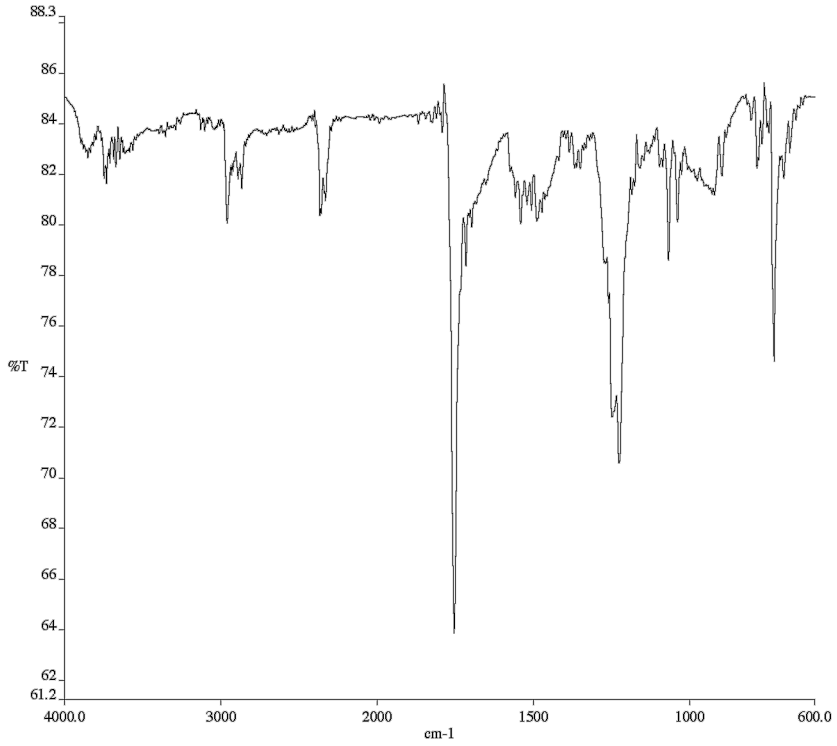
Infrared spectrum (Thin Film, NaCl) of compound **1c**.



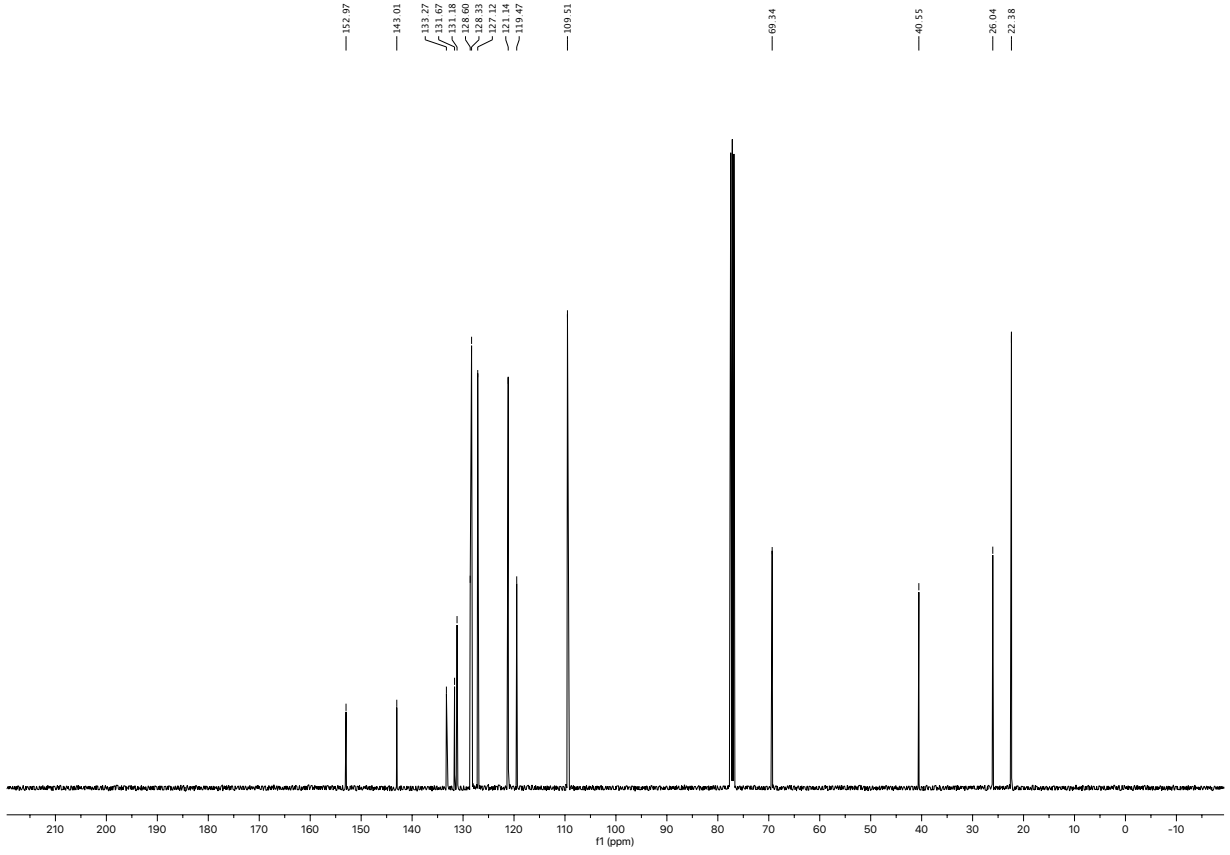
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1c**.



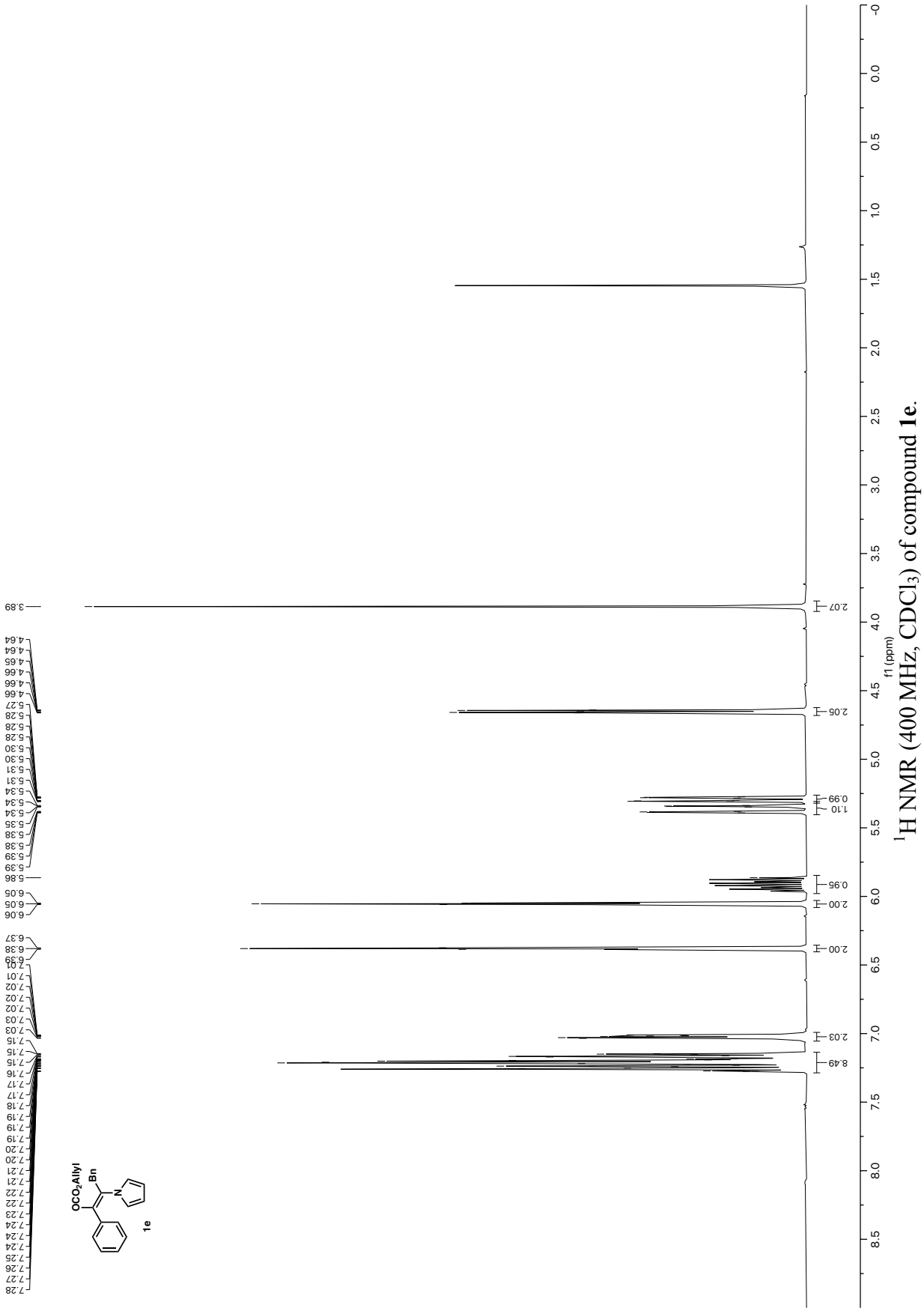
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1d**.



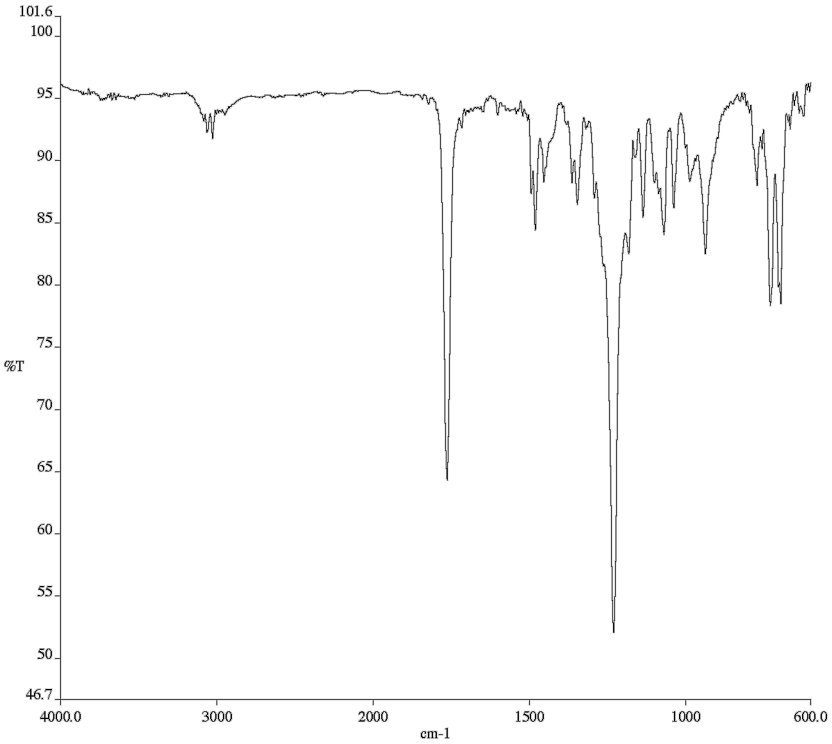
Infrared spectrum (Thin Film, NaCl) of compound **1d**.



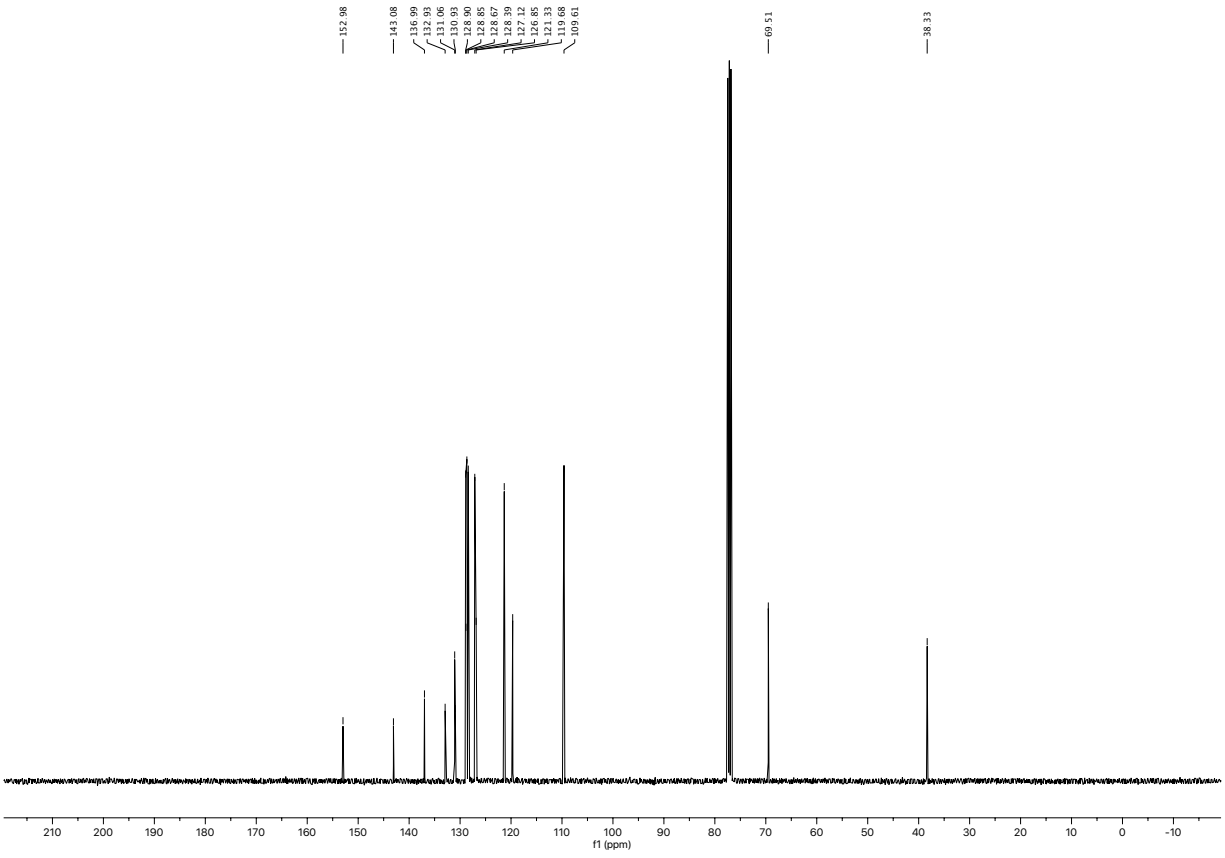
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1d**.



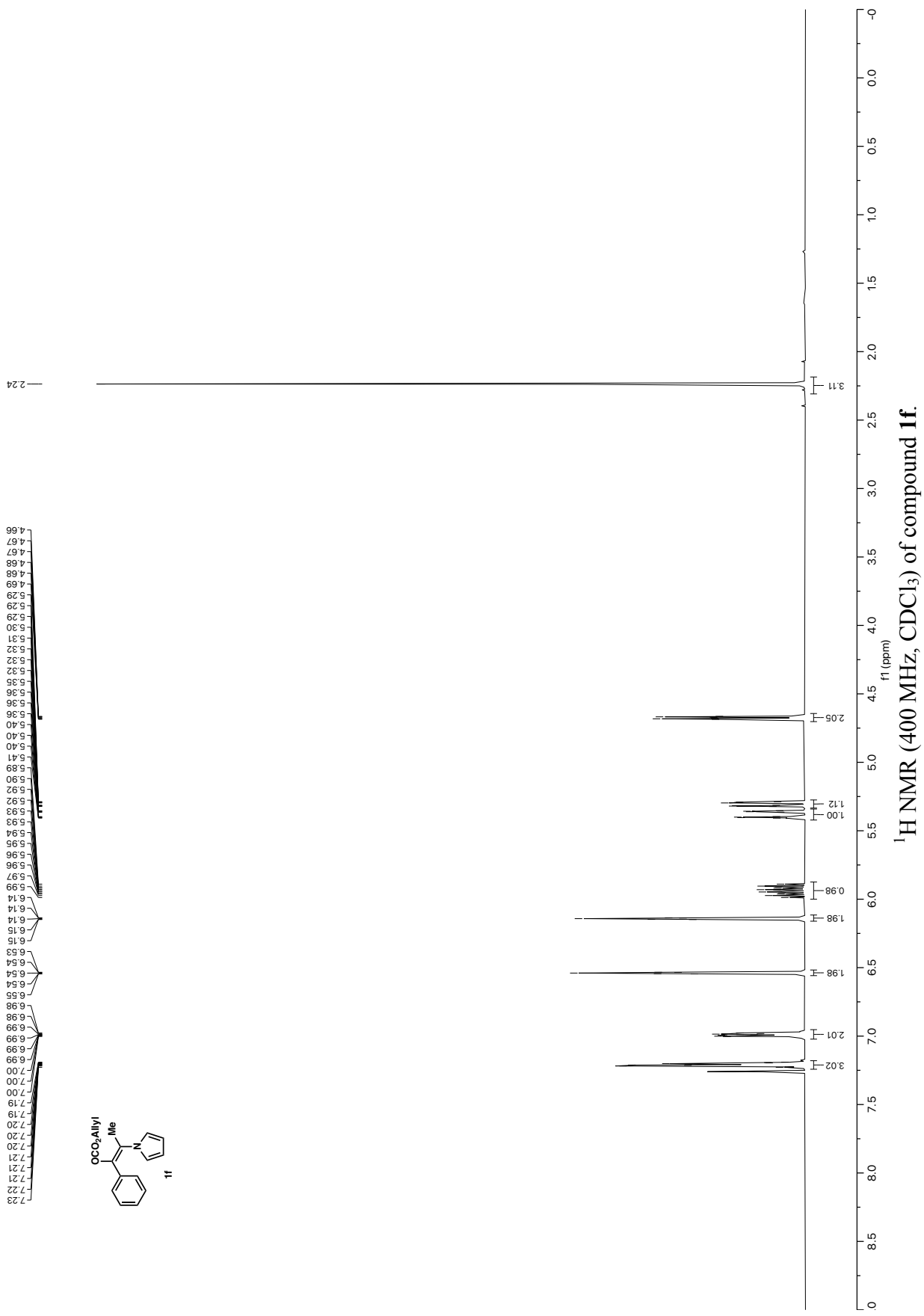
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1e**.



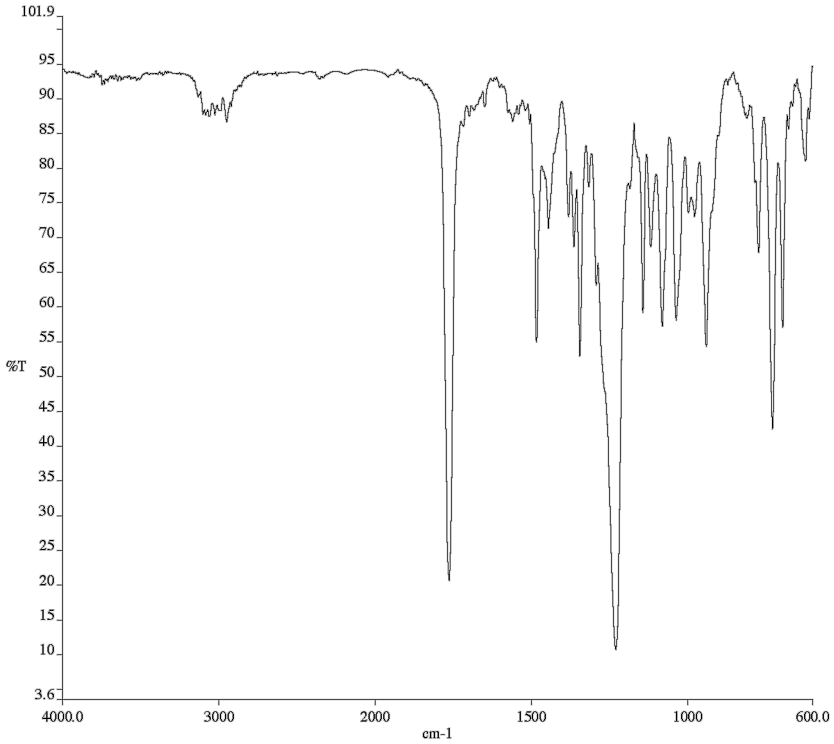
Infrared spectrum (Thin Film, NaCl) of compound **1e**.



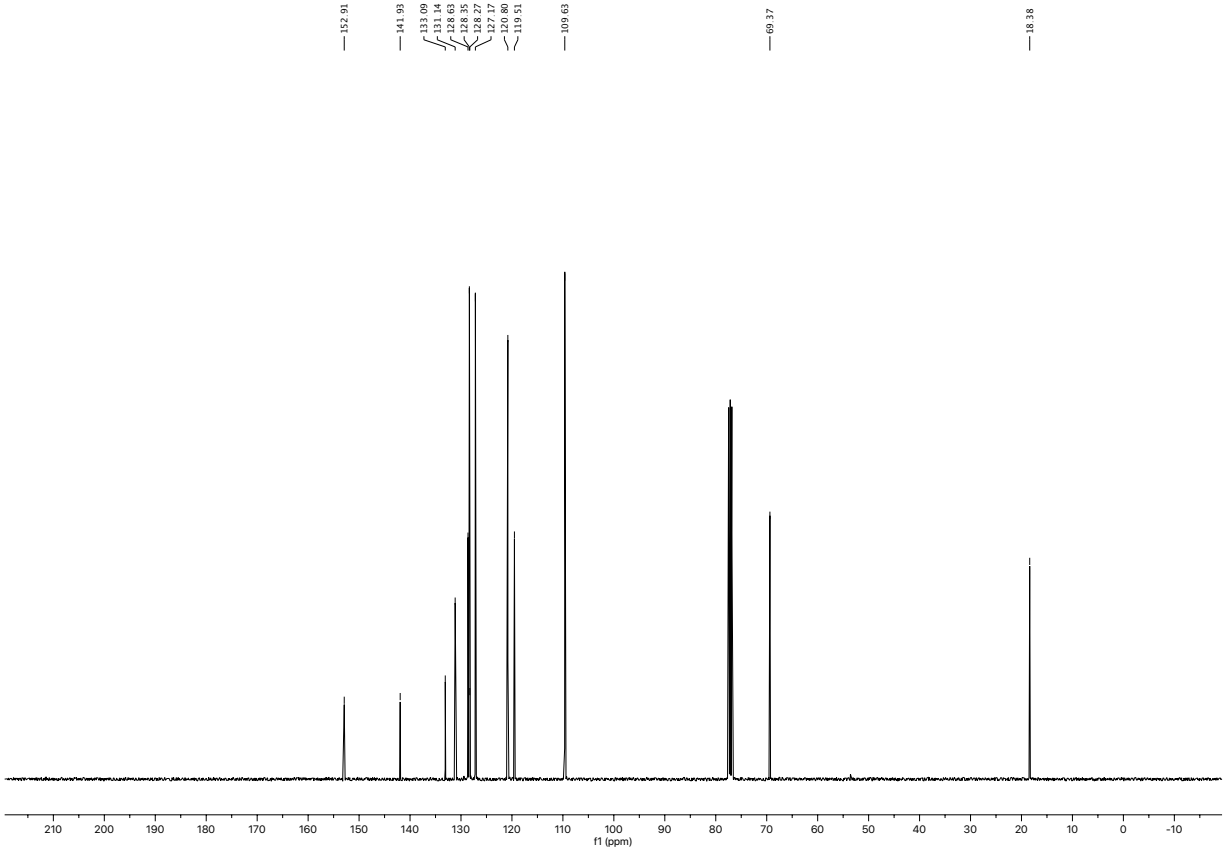
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1e**.



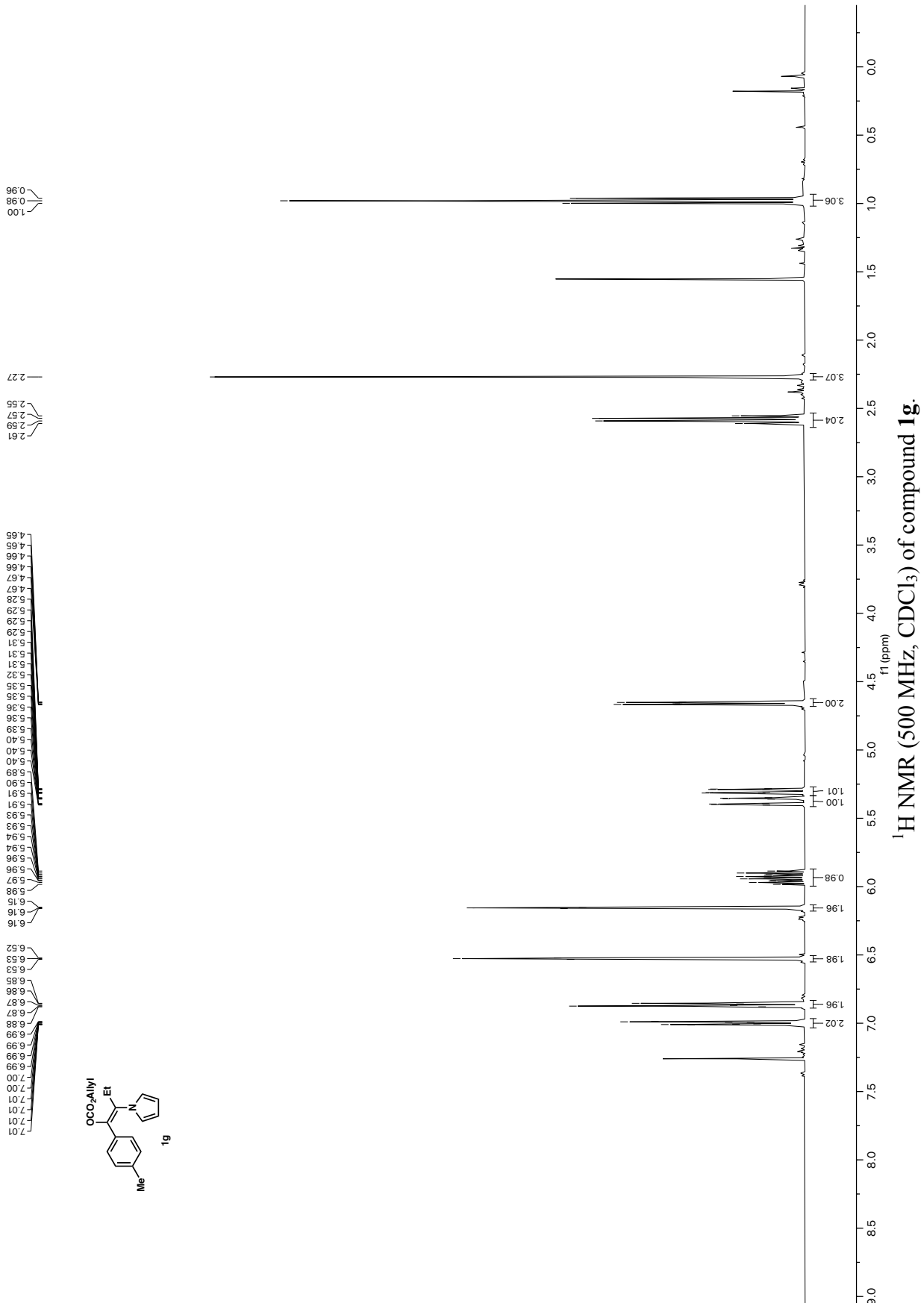
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1f**.



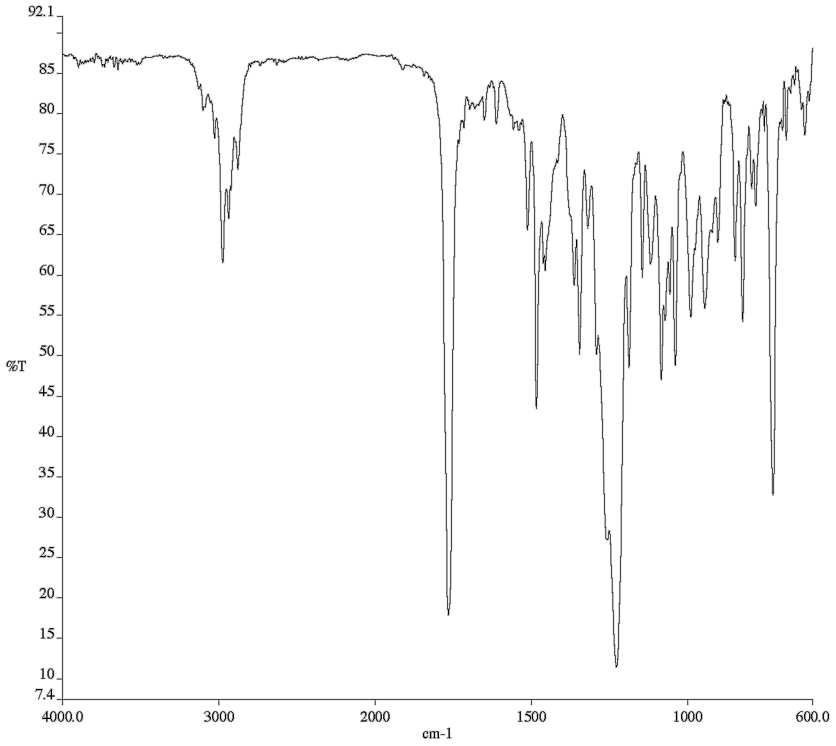
Infrared spectrum (Thin Film, NaCl) of compound **1f**.



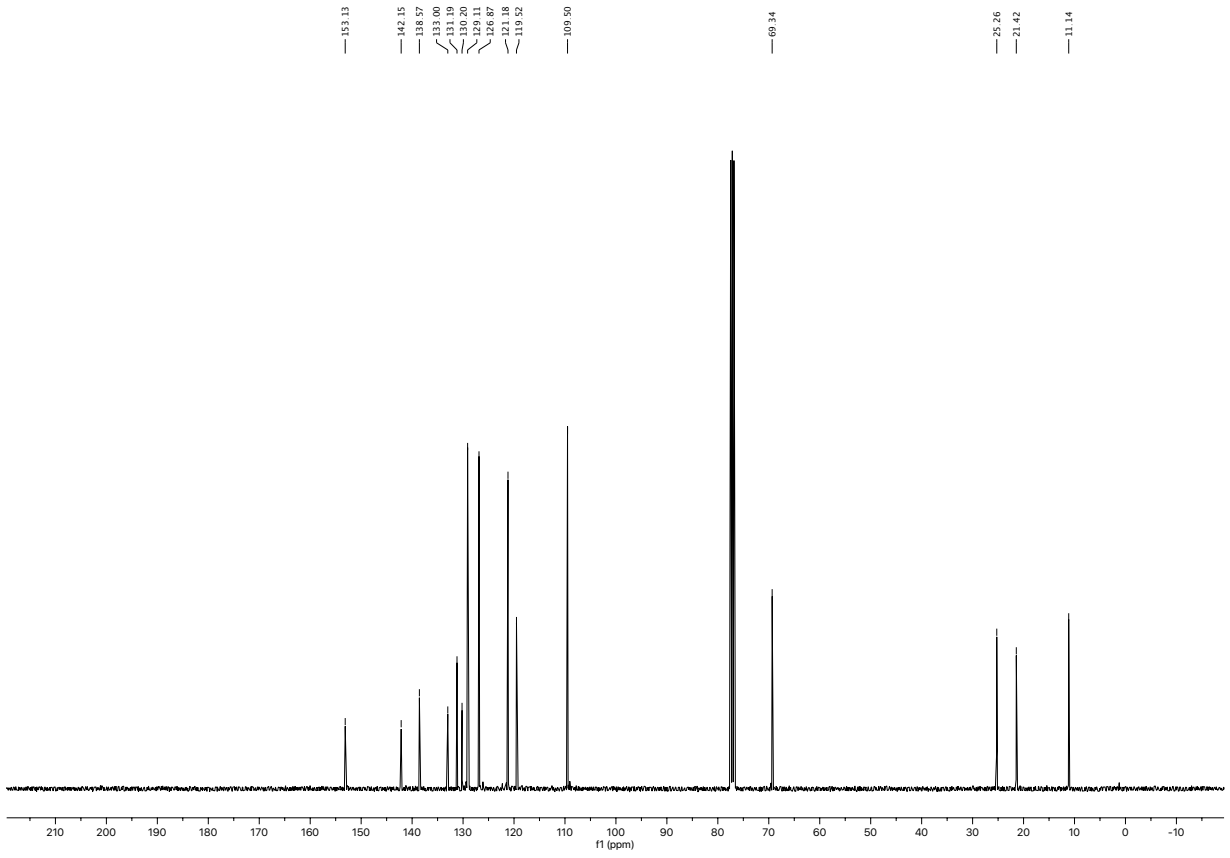
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1f**.



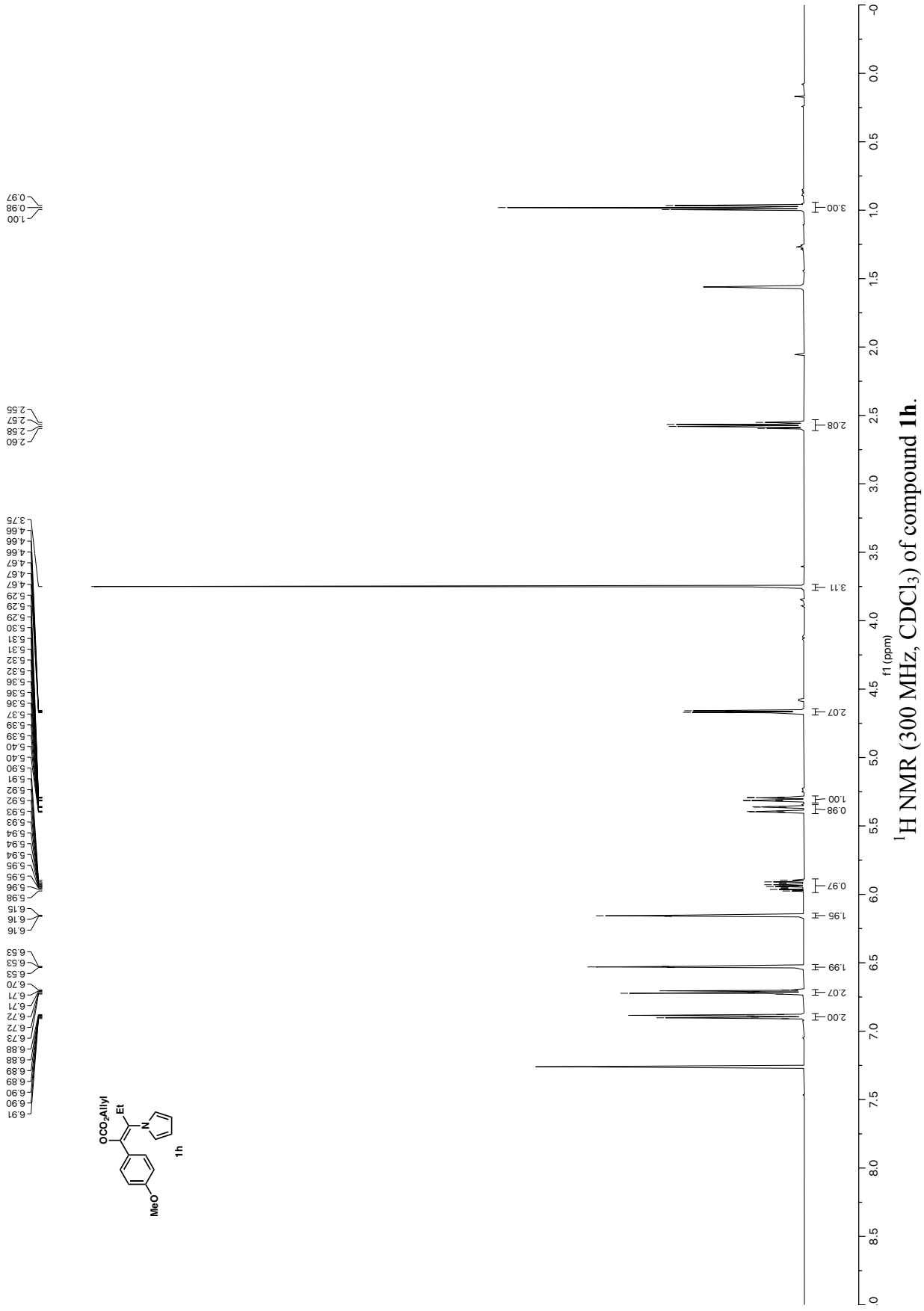
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1g**.



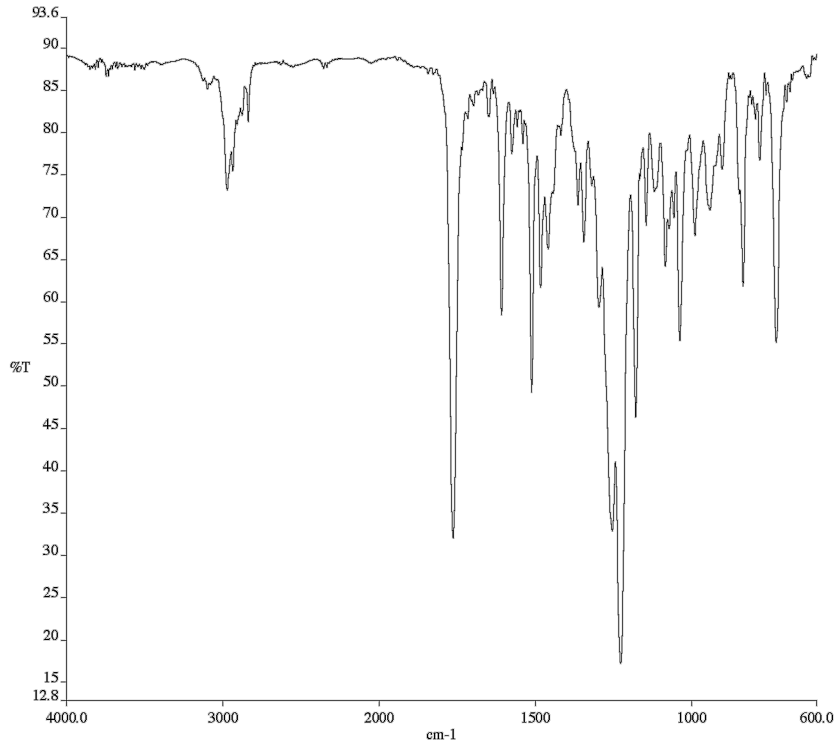
Infrared spectrum (Thin Film, NaCl) of compound **1g**.



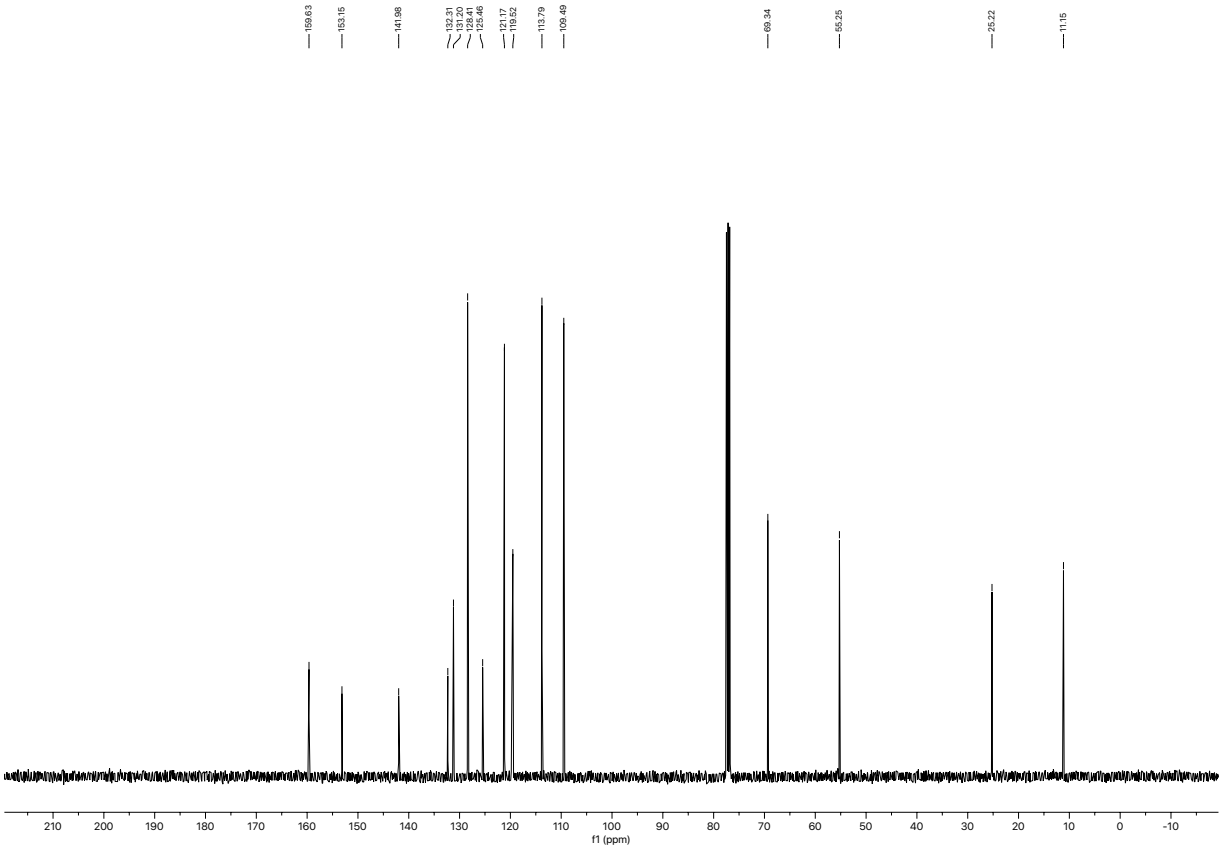
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1g**.



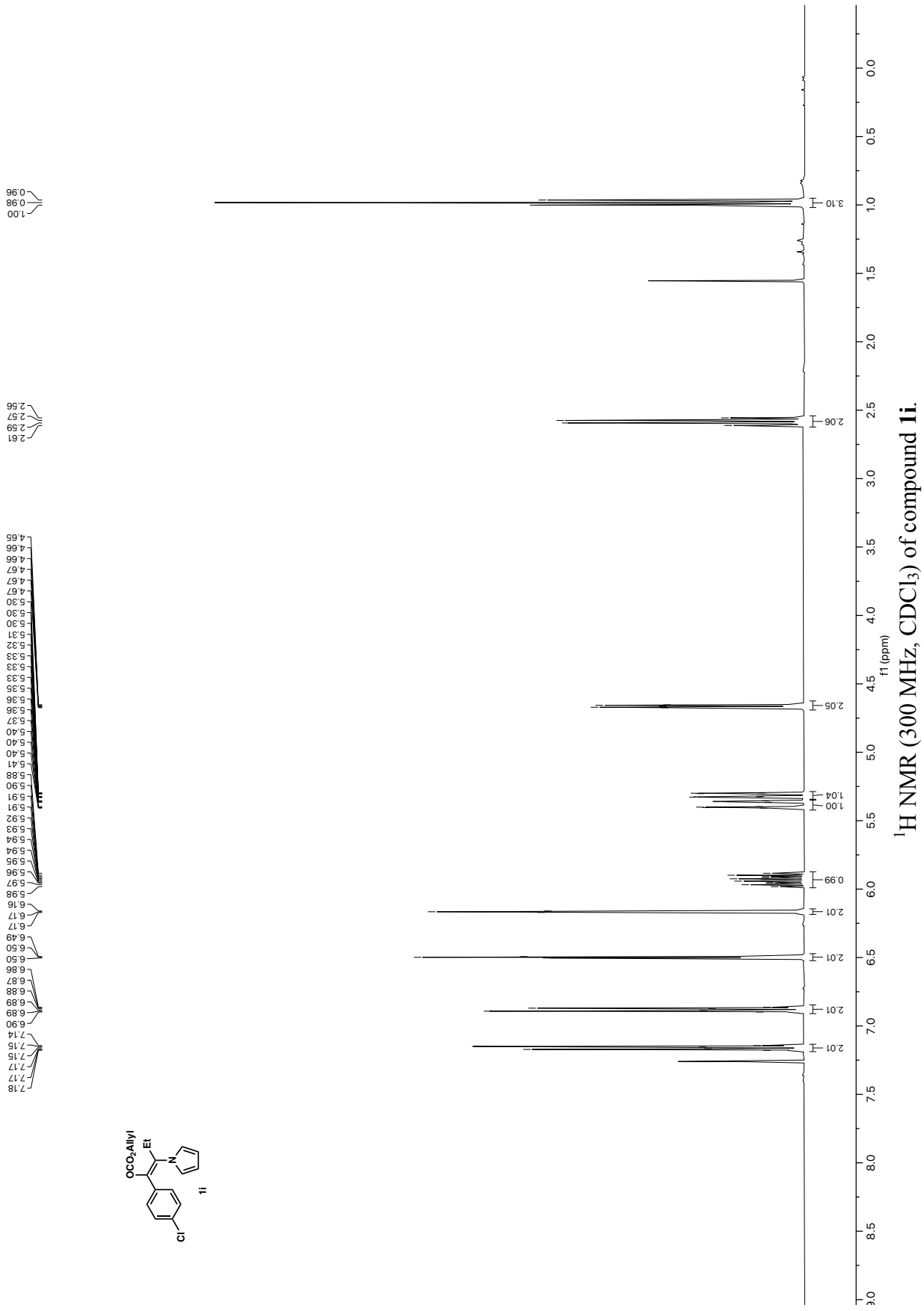
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1h**.



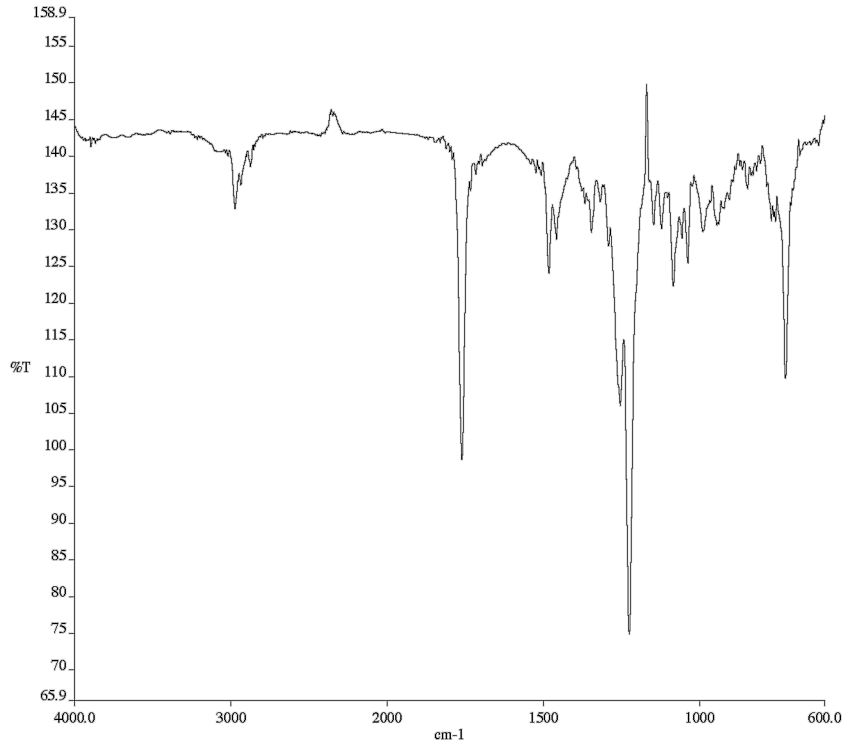
Infrared spectrum (Thin Film, NaCl) of compound **1h**.



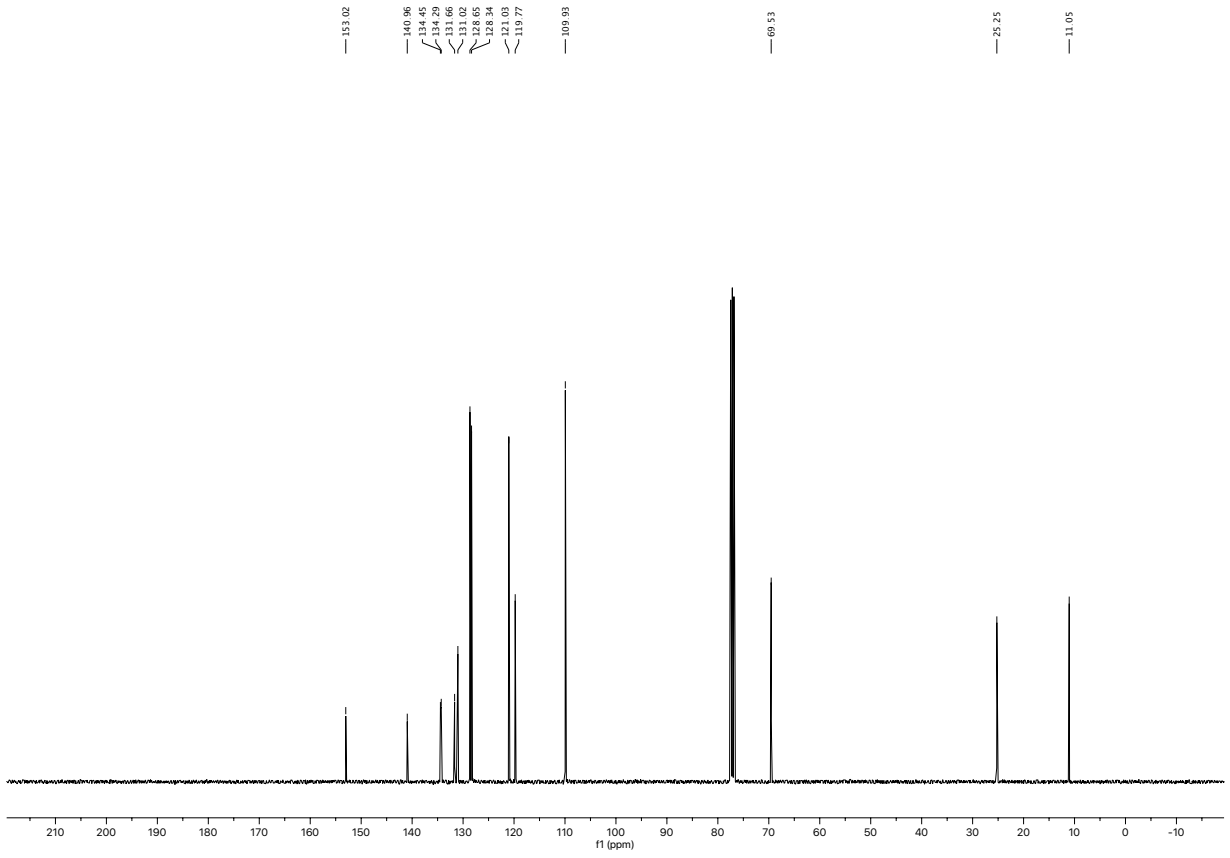
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1h**.



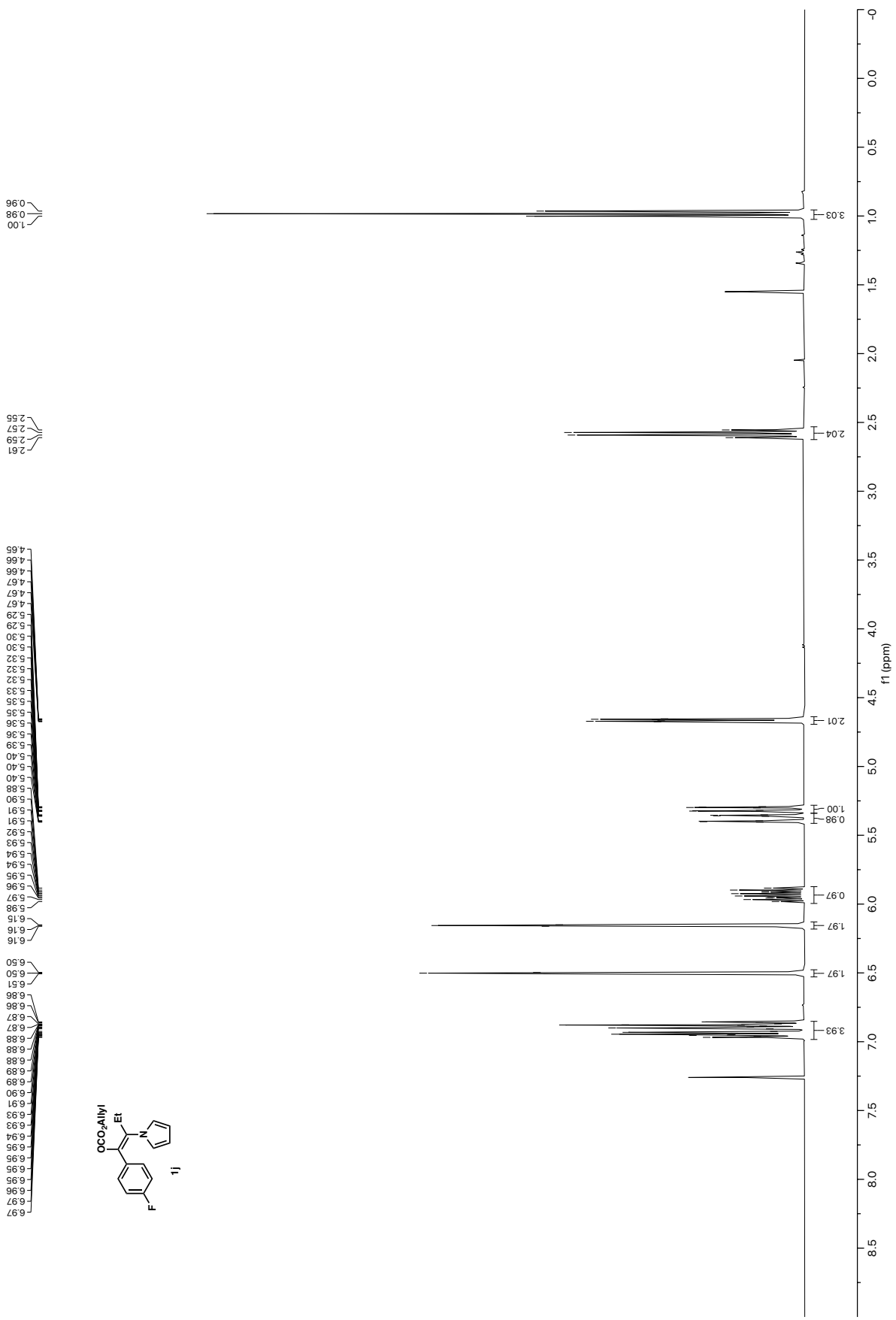
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1i**.



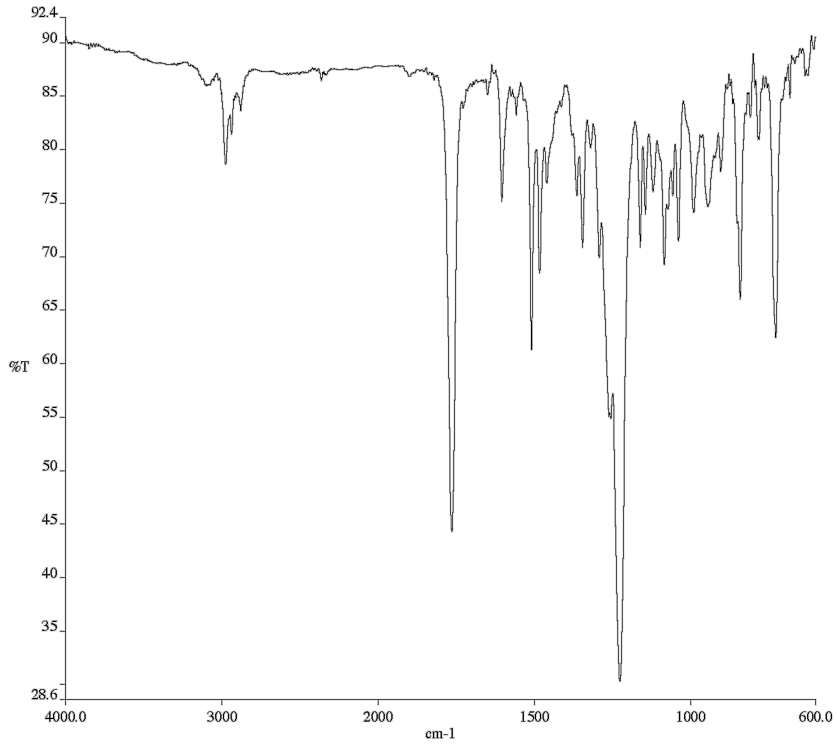
Infrared spectrum (Thin Film, NaCl) of compound **1i**.



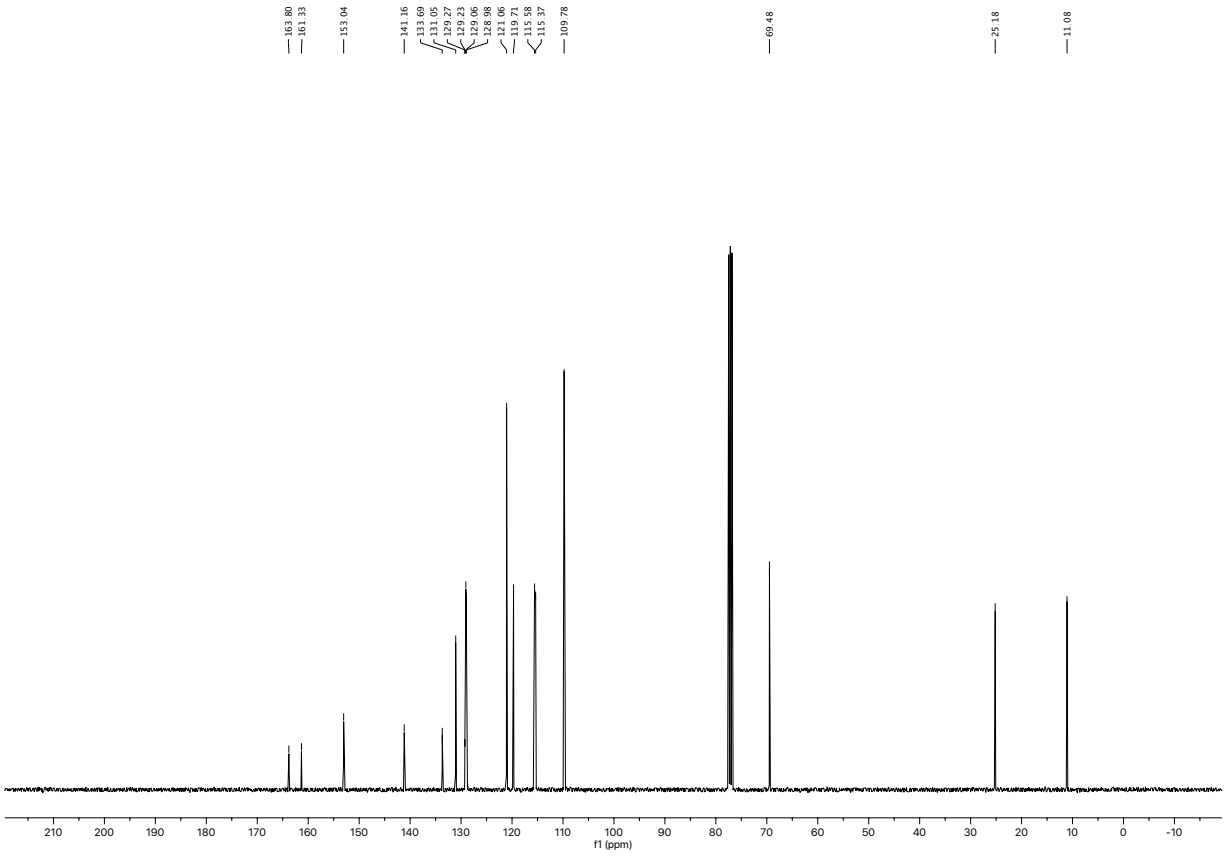
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1i**.



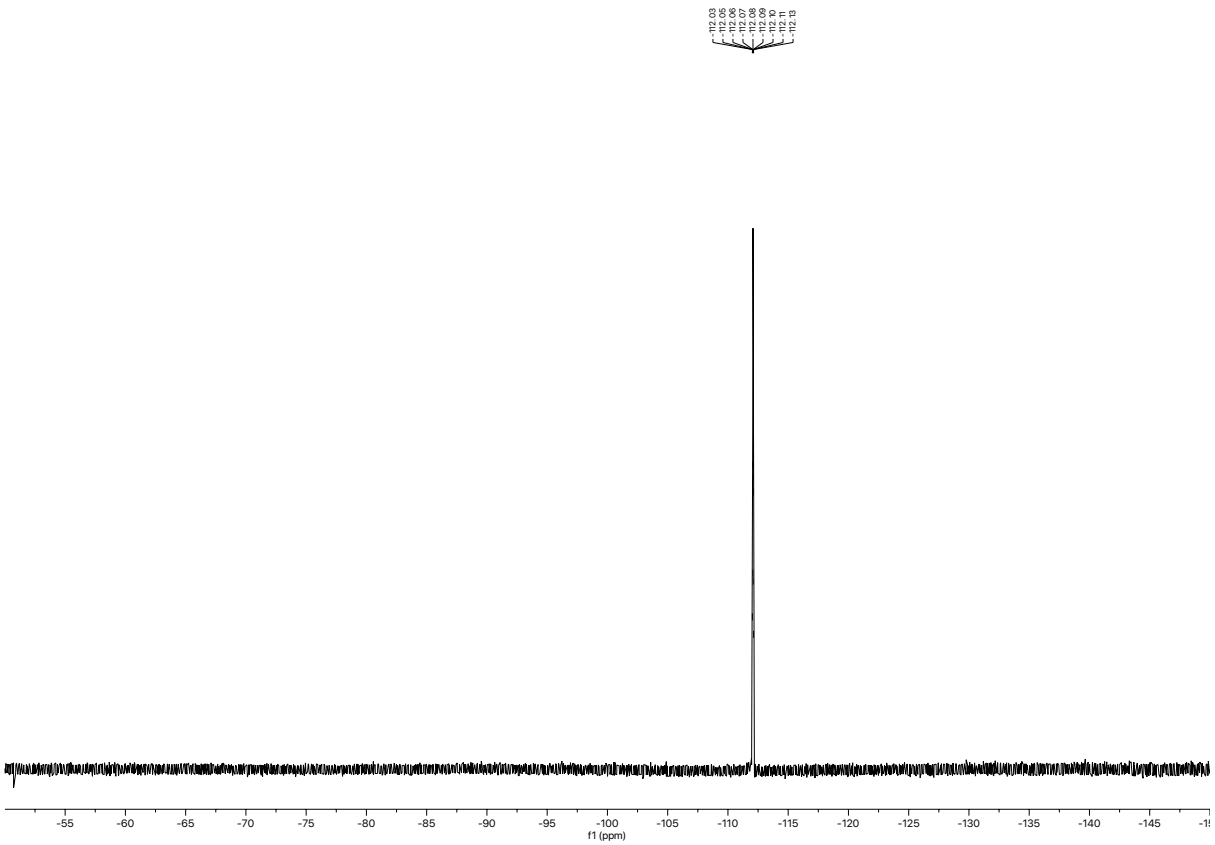
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1j**.



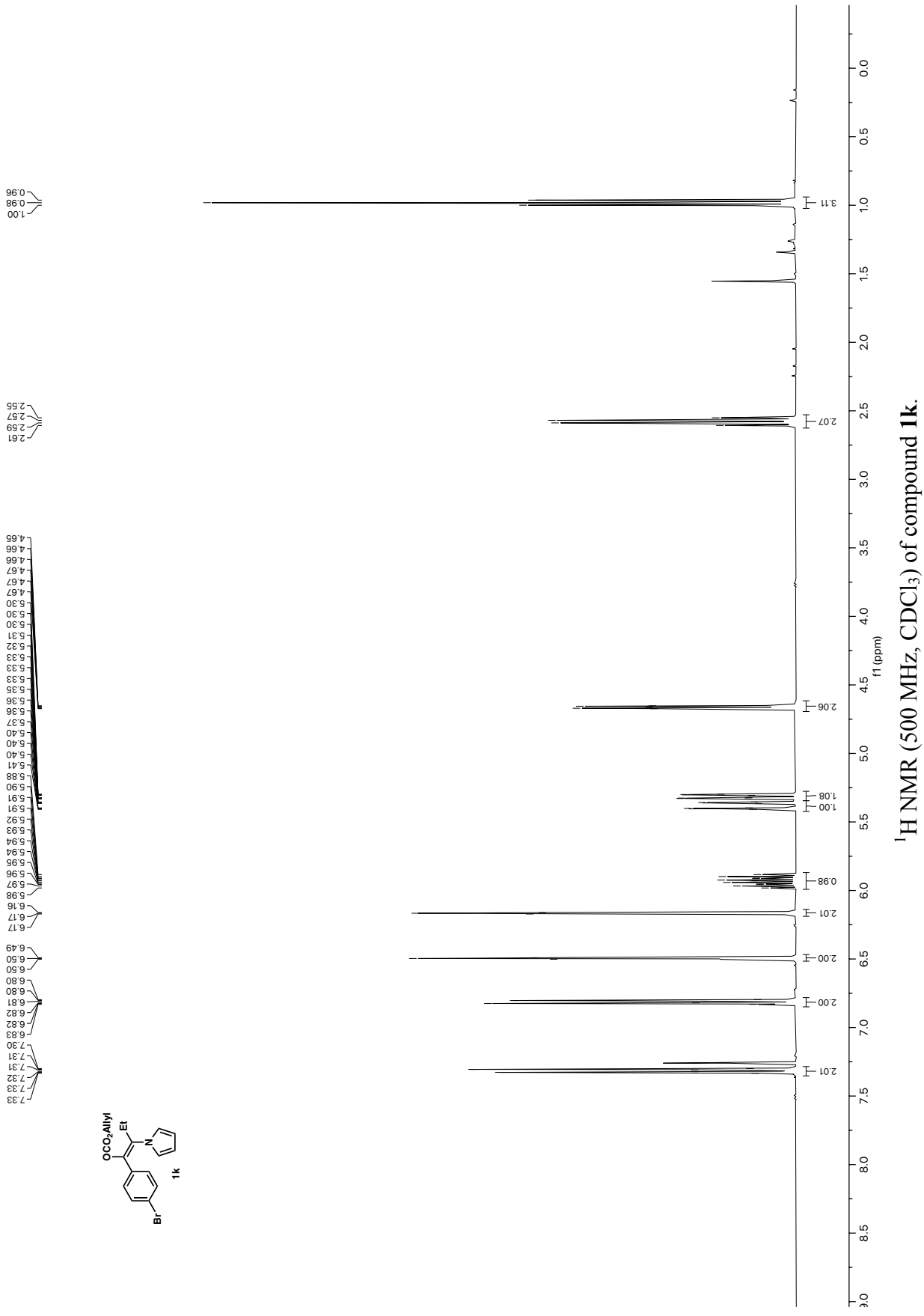
Infrared spectrum (Thin Film, NaCl) of compound **1j**.



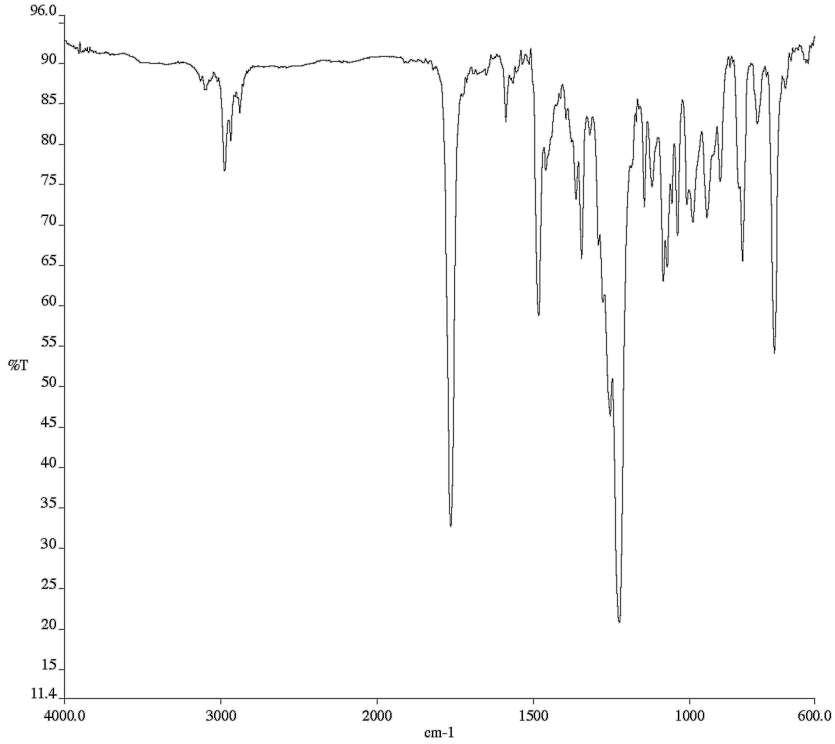
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1j**.



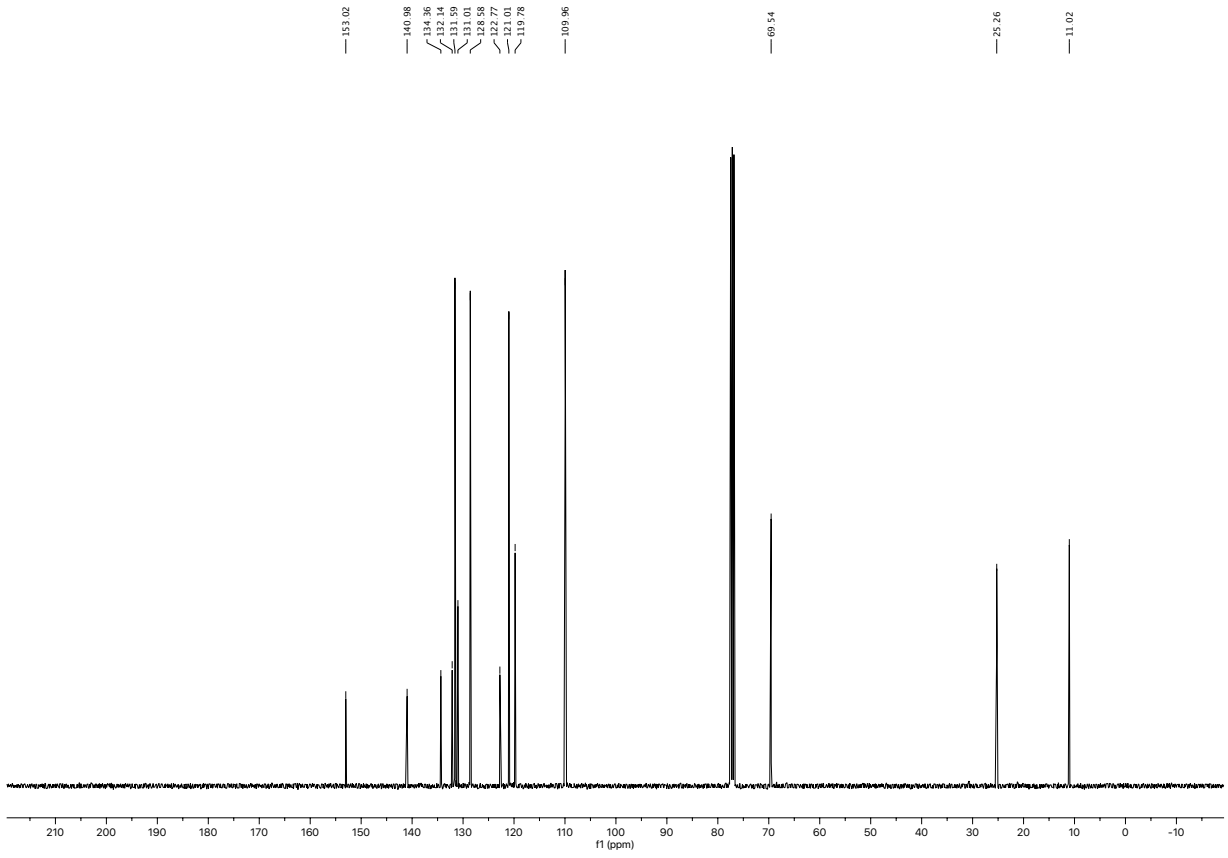
^{19}F NMR (282 MHz, $CDCl_3$) of compound **1k**.



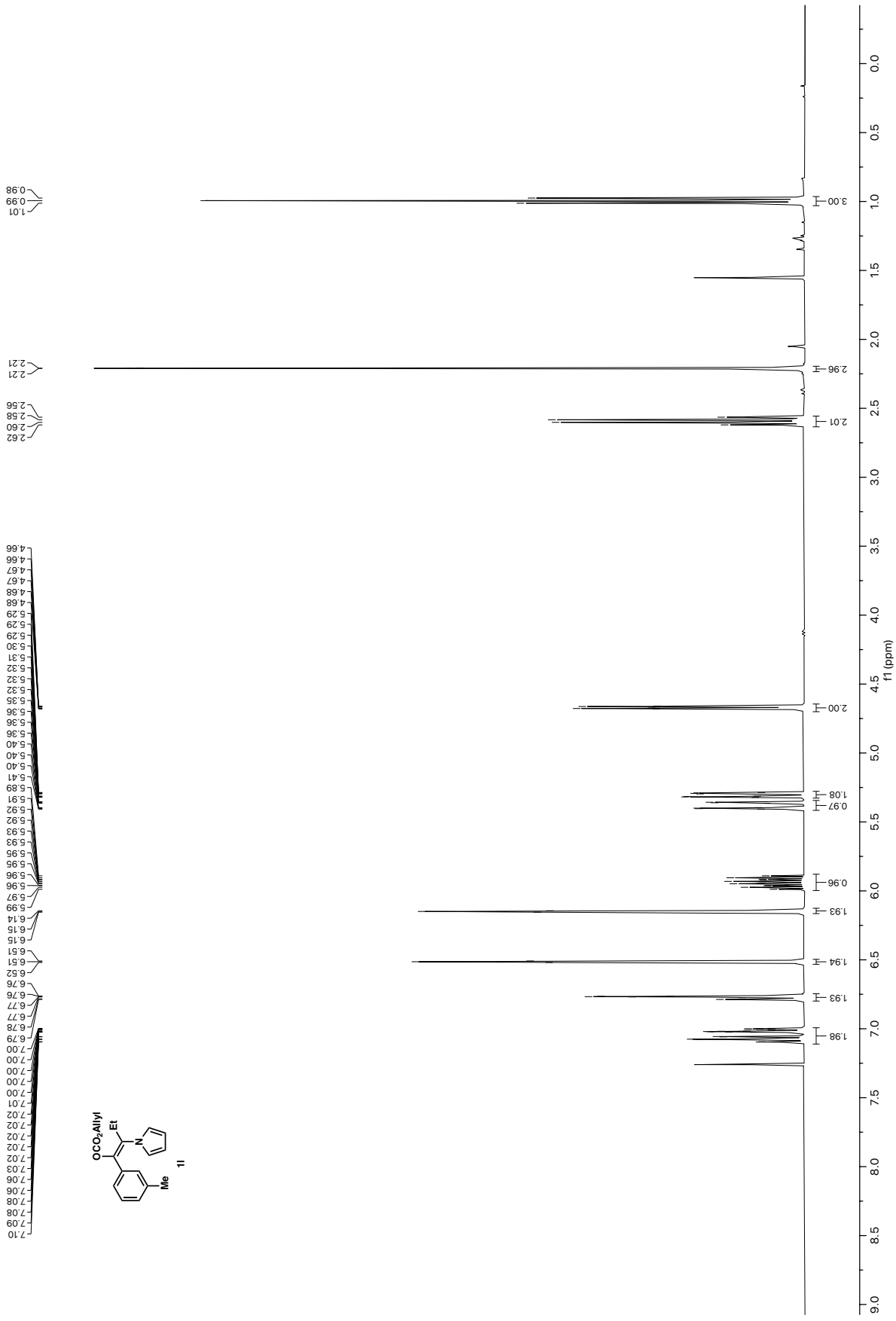
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1k**.



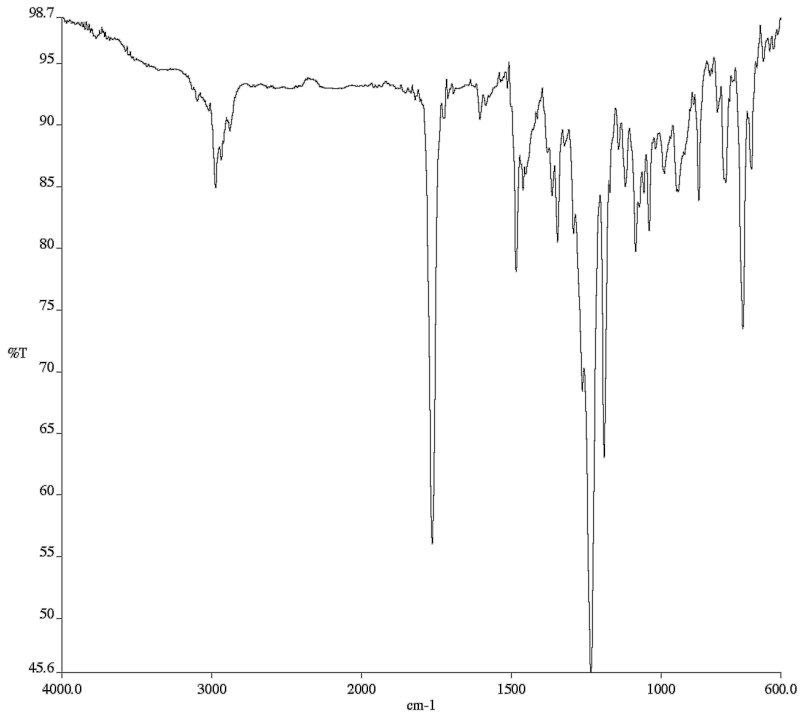
Infrared spectrum (Thin Film, NaCl) of compound **1k**.



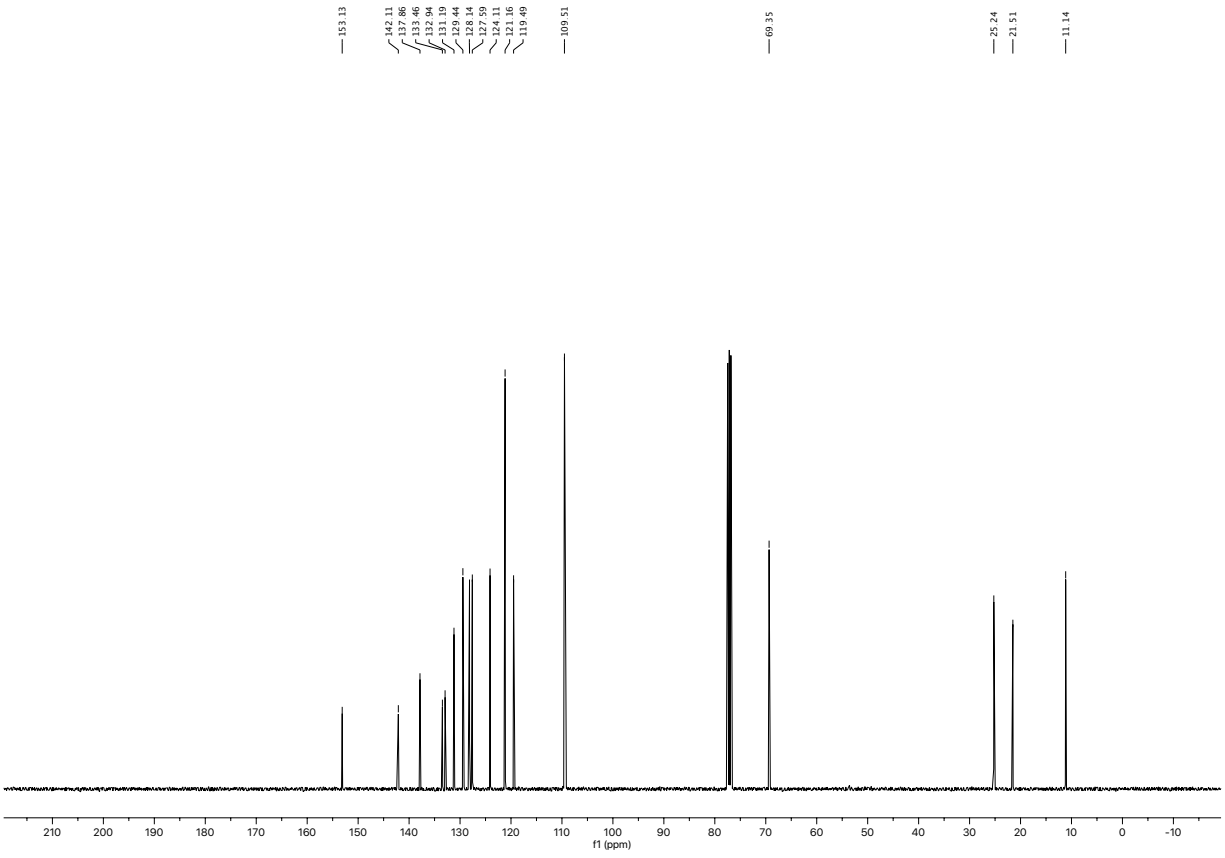
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1k**.



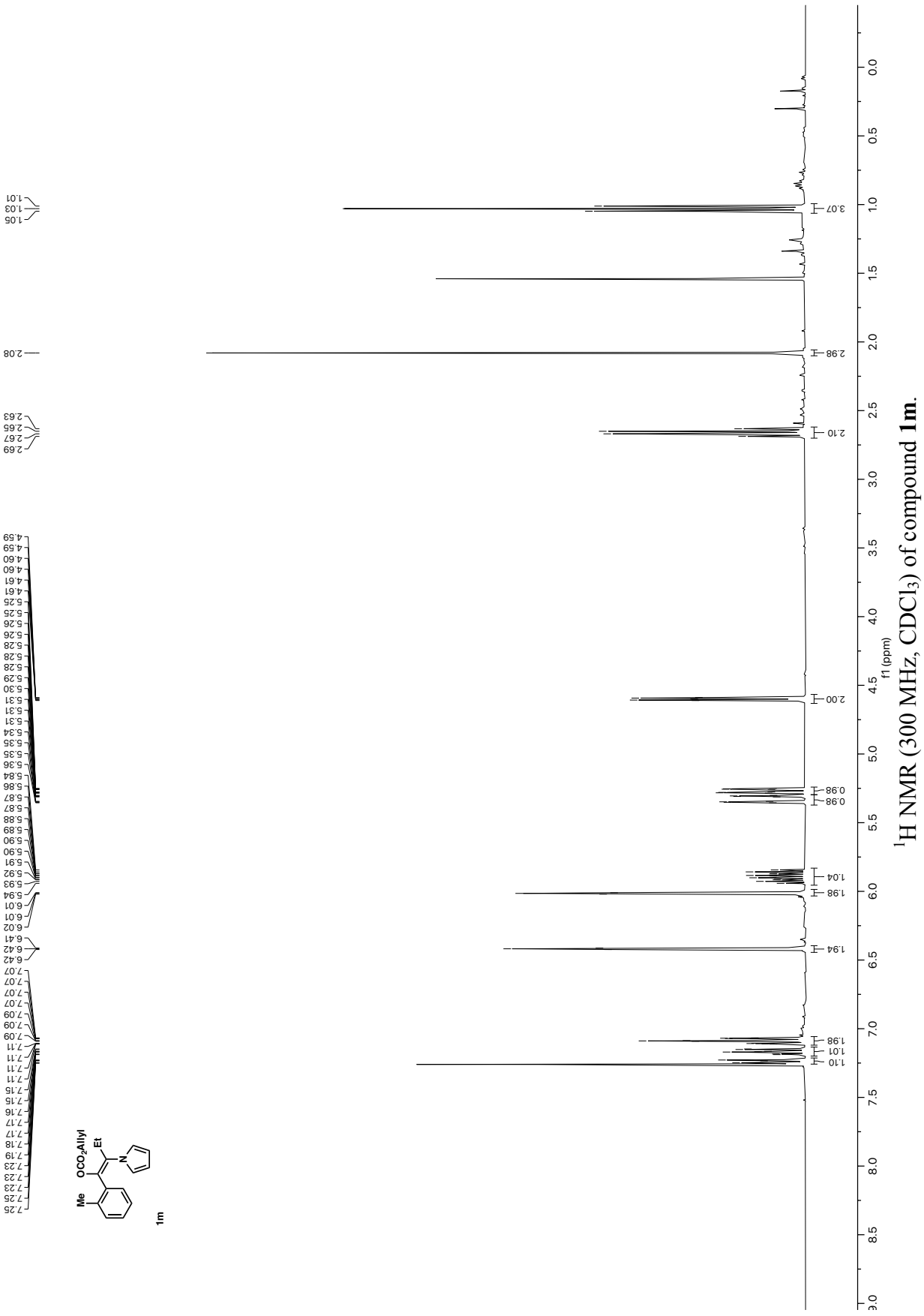
^{1}H NMR (300 MHz, $CDCl_3$) of compound **11**.



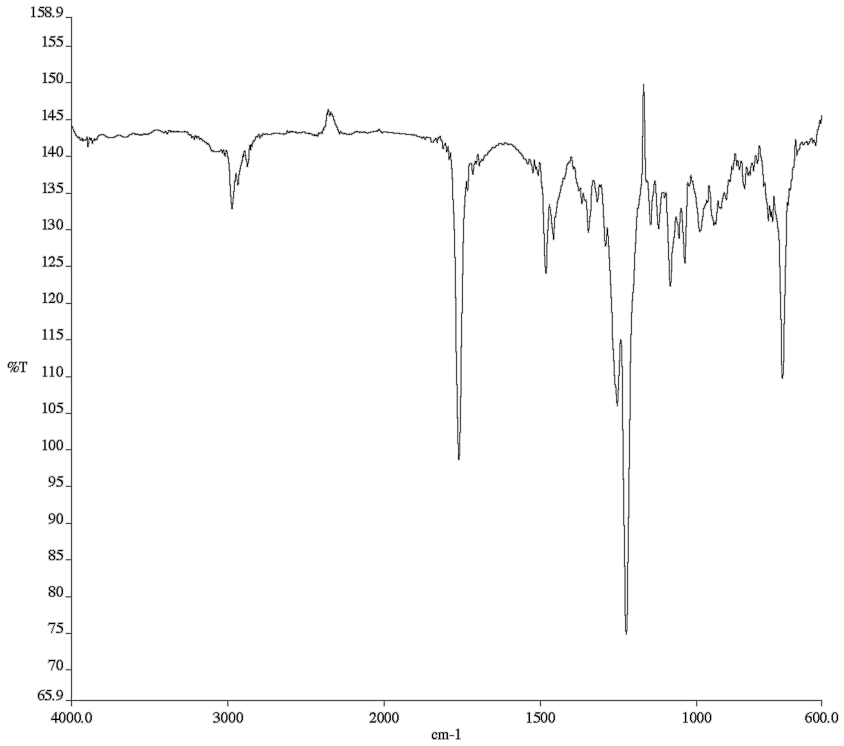
Infrared spectrum (Thin Film, NaCl) of compound **11**.



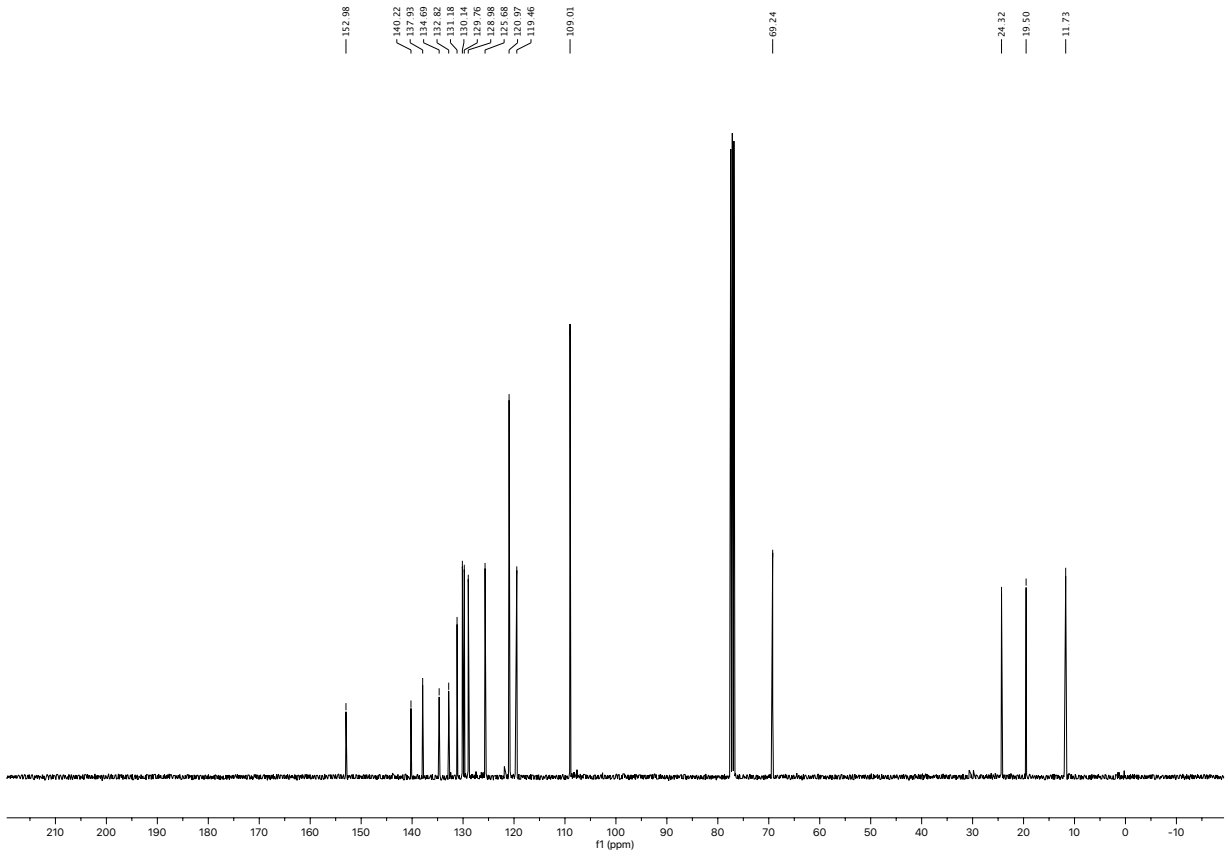
^{13}C NMR (100 MHz, $CDCl_3$) of compound **11**.



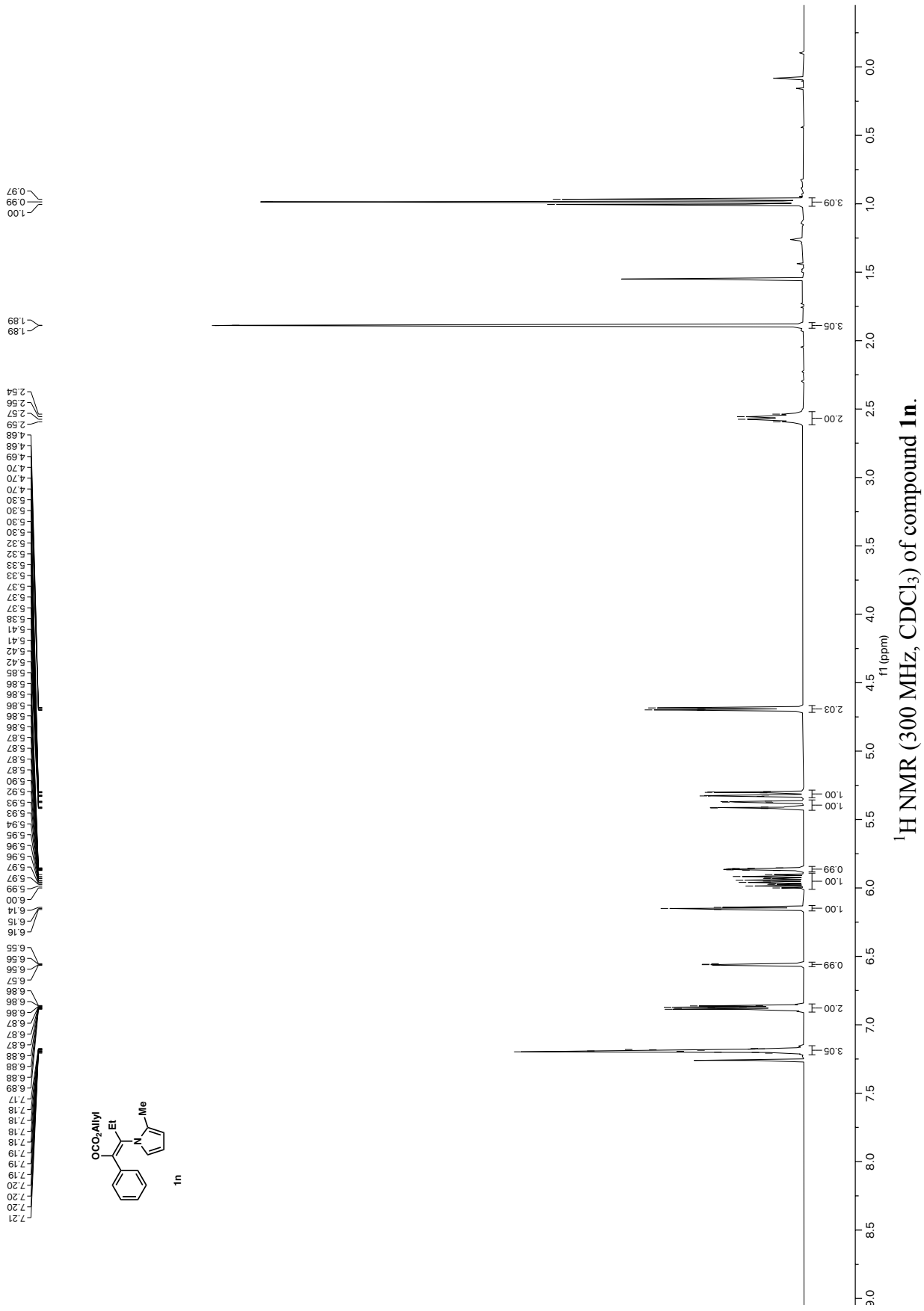
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1m**.



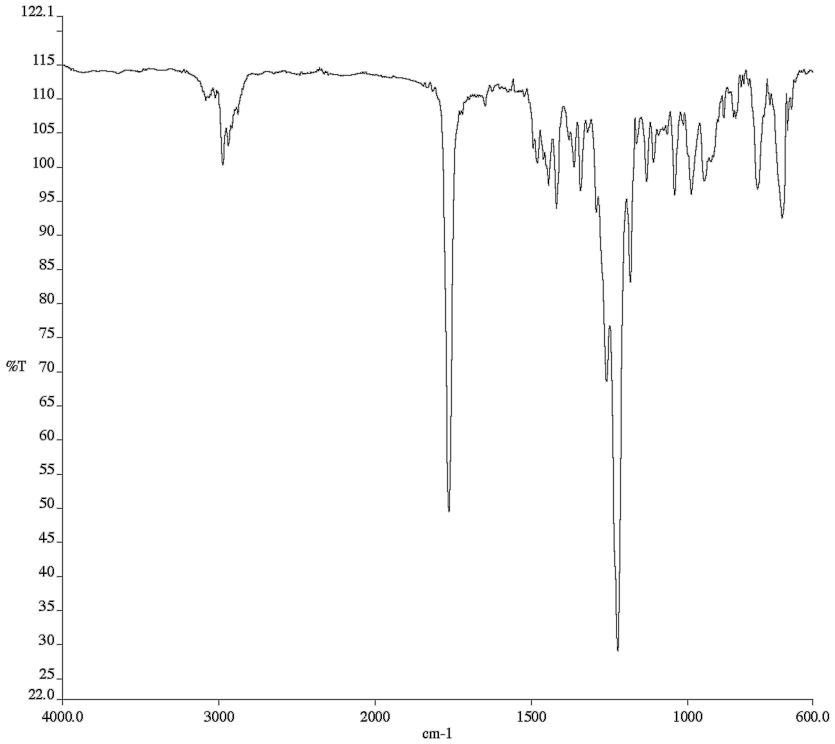
Infrared spectrum (Thin Film, NaCl) of compound **1m**.



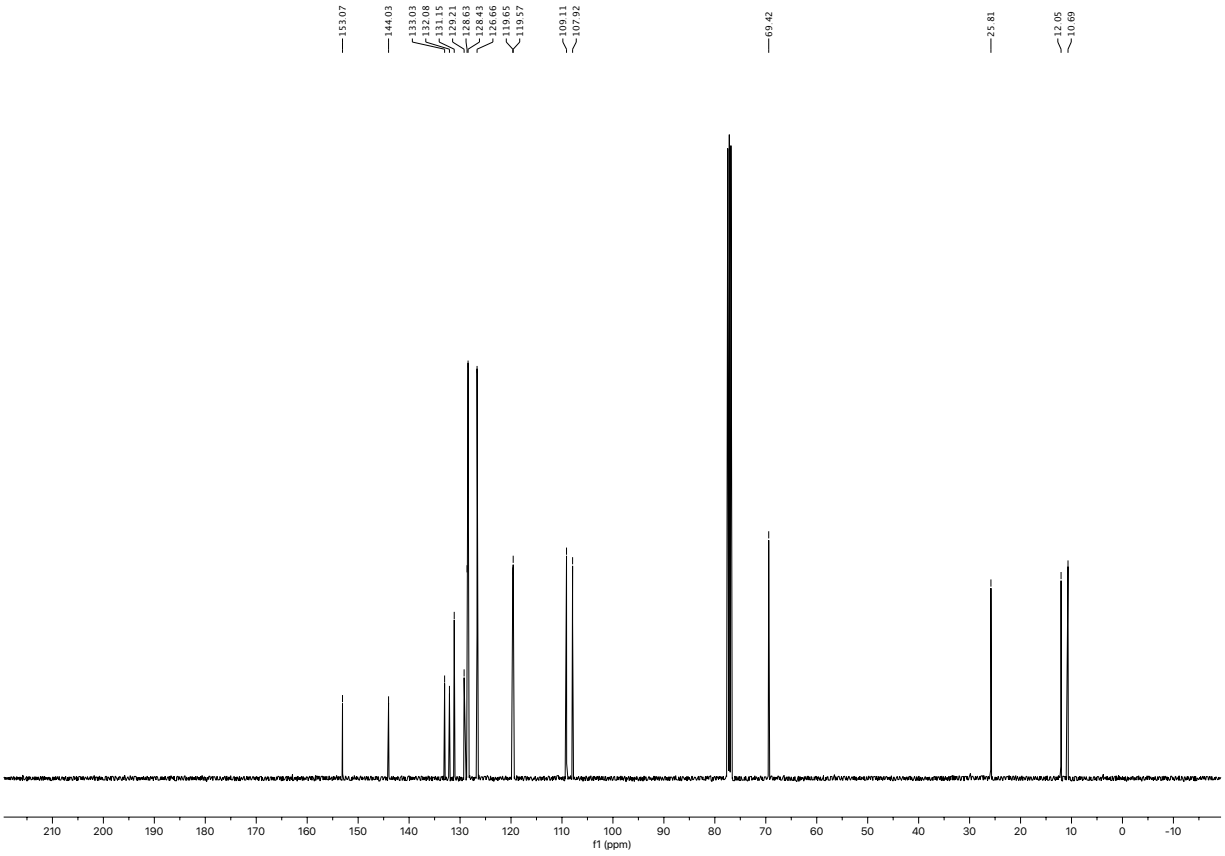
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1m**.



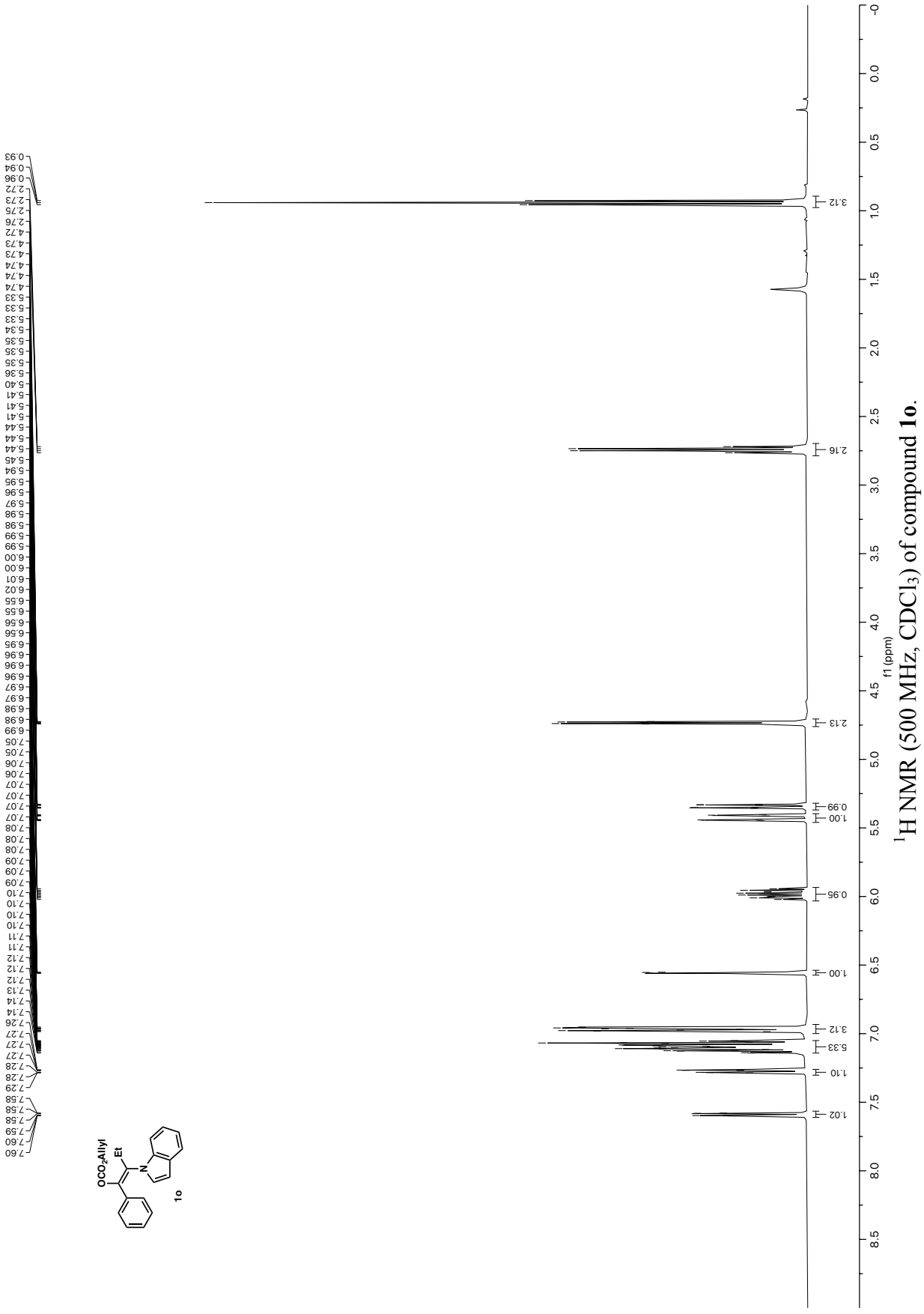
^{1}H NMR (300 MHz, $CDCl_3$) of compound **1n**.



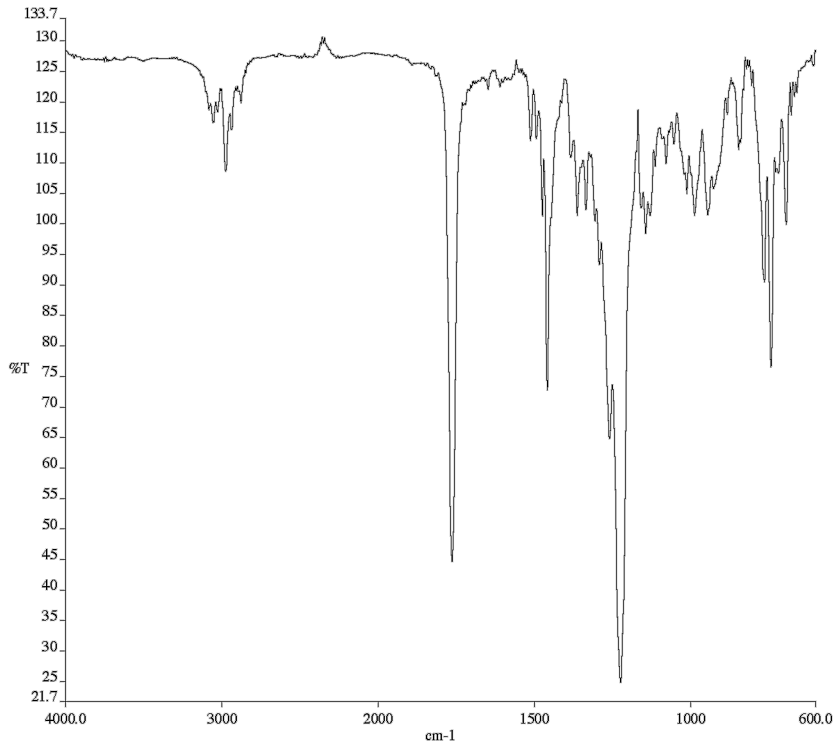
Infrared spectrum (Thin Film, NaCl) of compound **1n**.



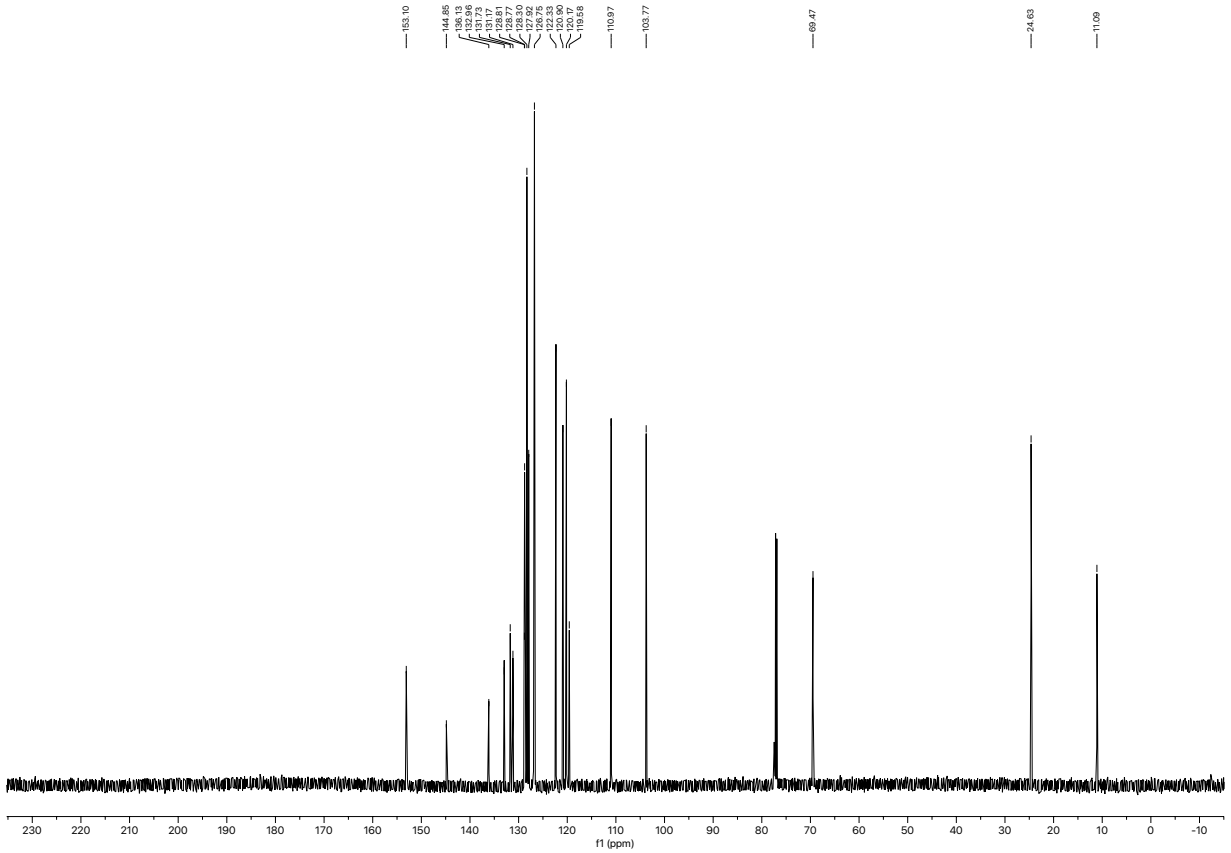
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1n**.



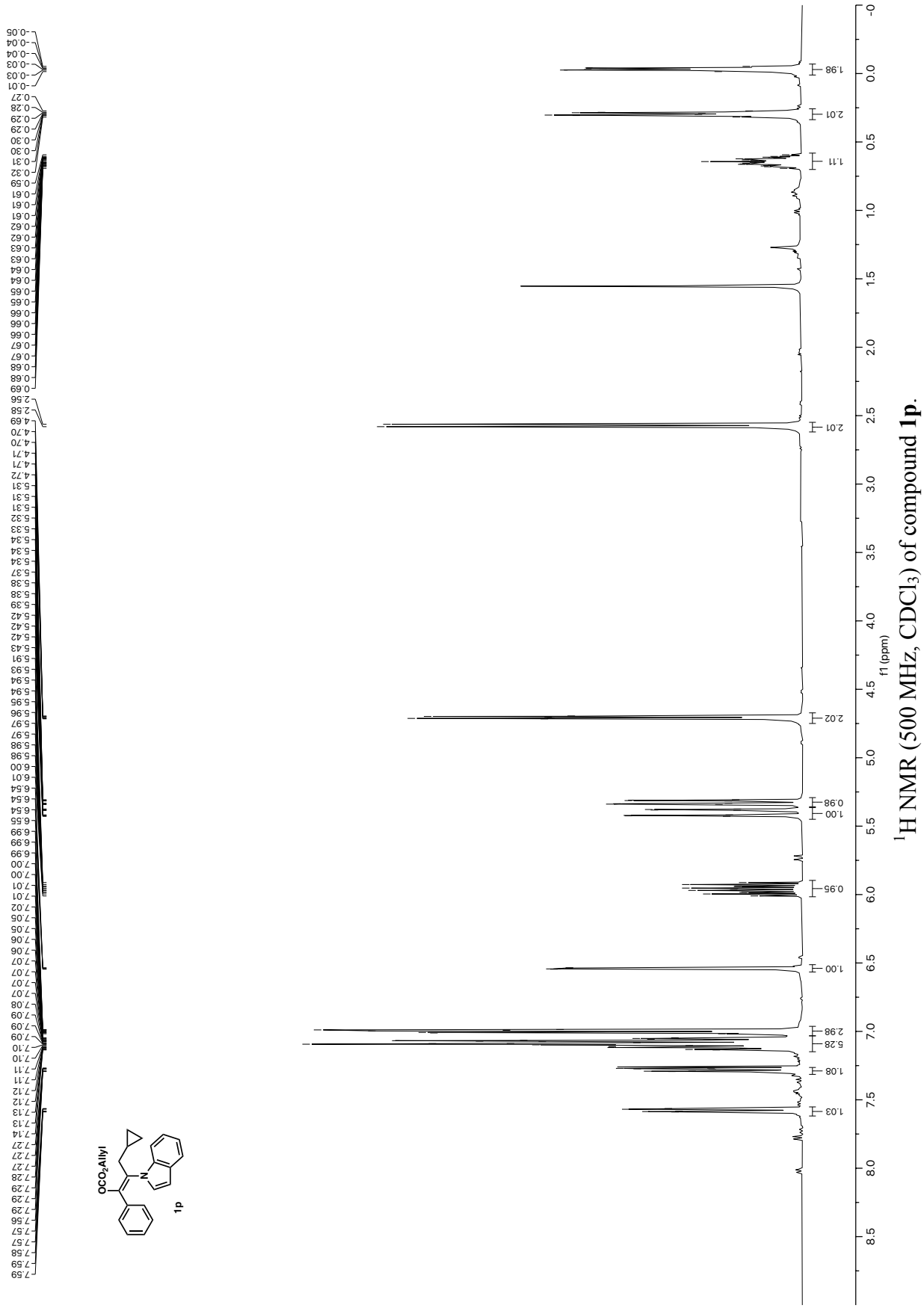
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1o**.



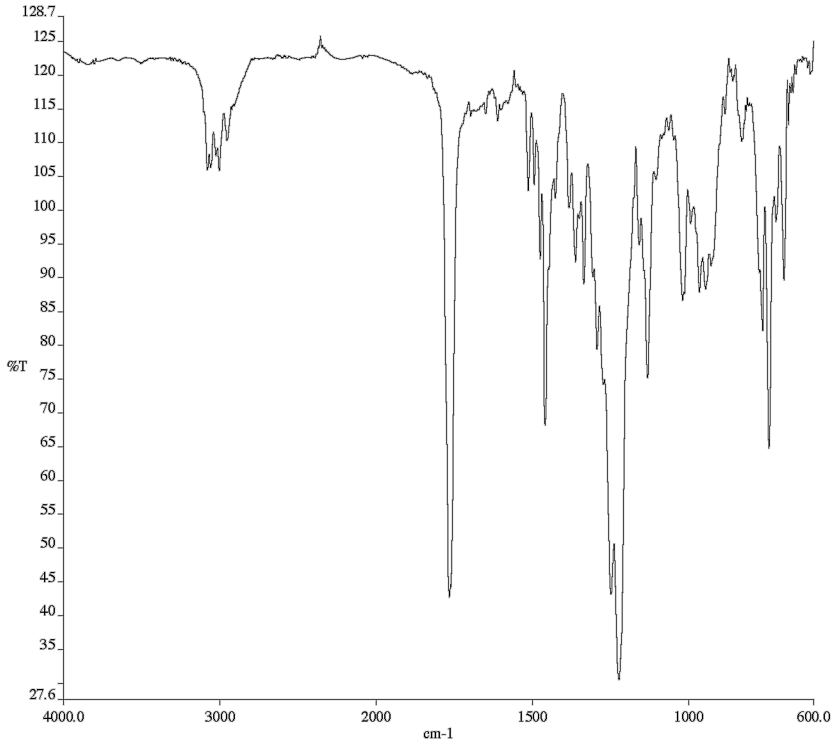
Infrared spectrum (Thin Film, NaCl) of compound **1o**.



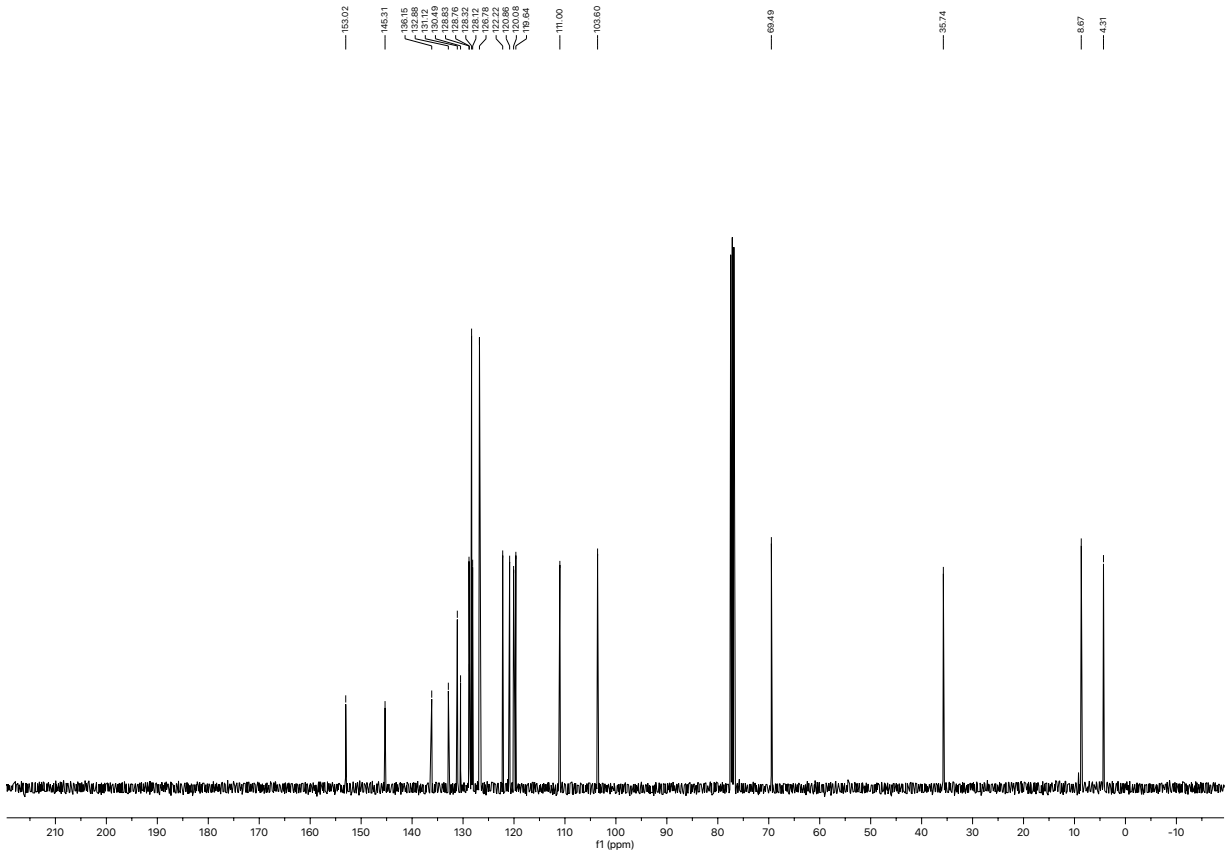
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1o**.



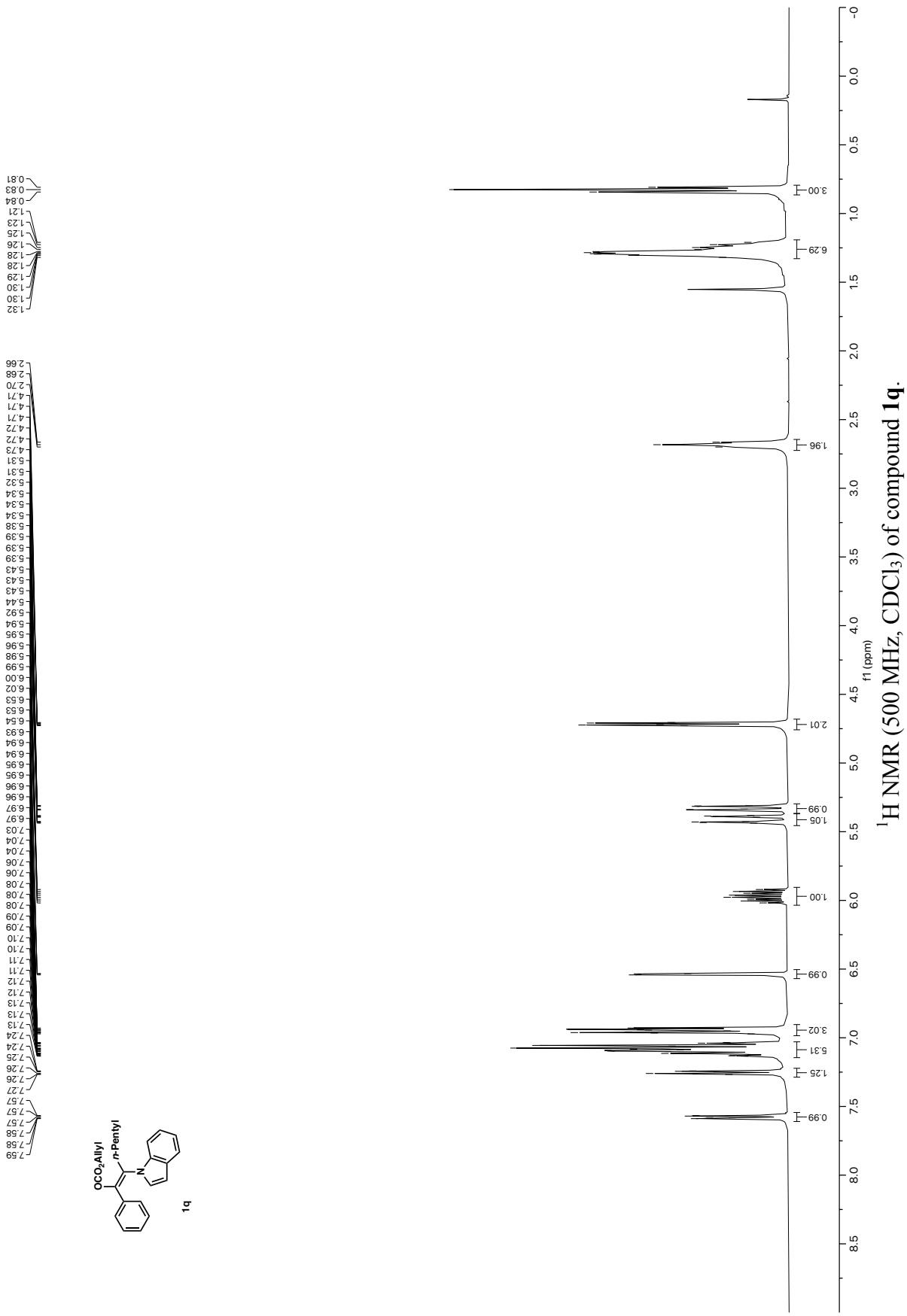
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1p**.



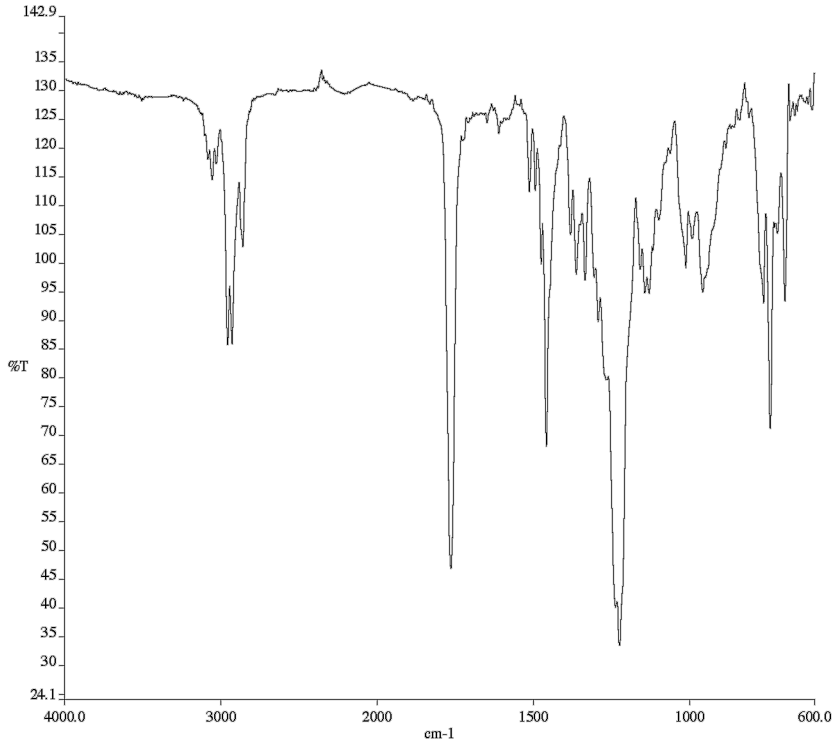
Infrared spectrum (Thin Film, NaCl) of compound **1p**.



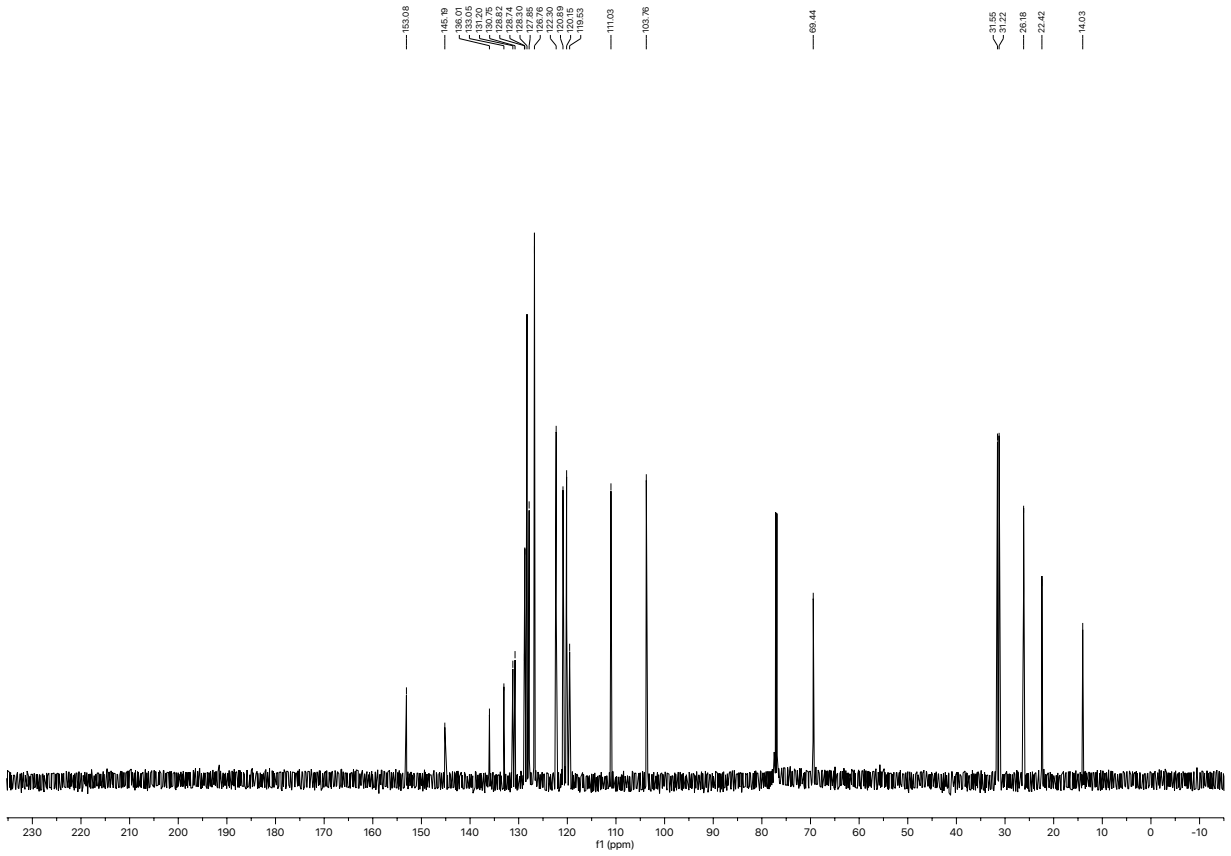
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1p**.



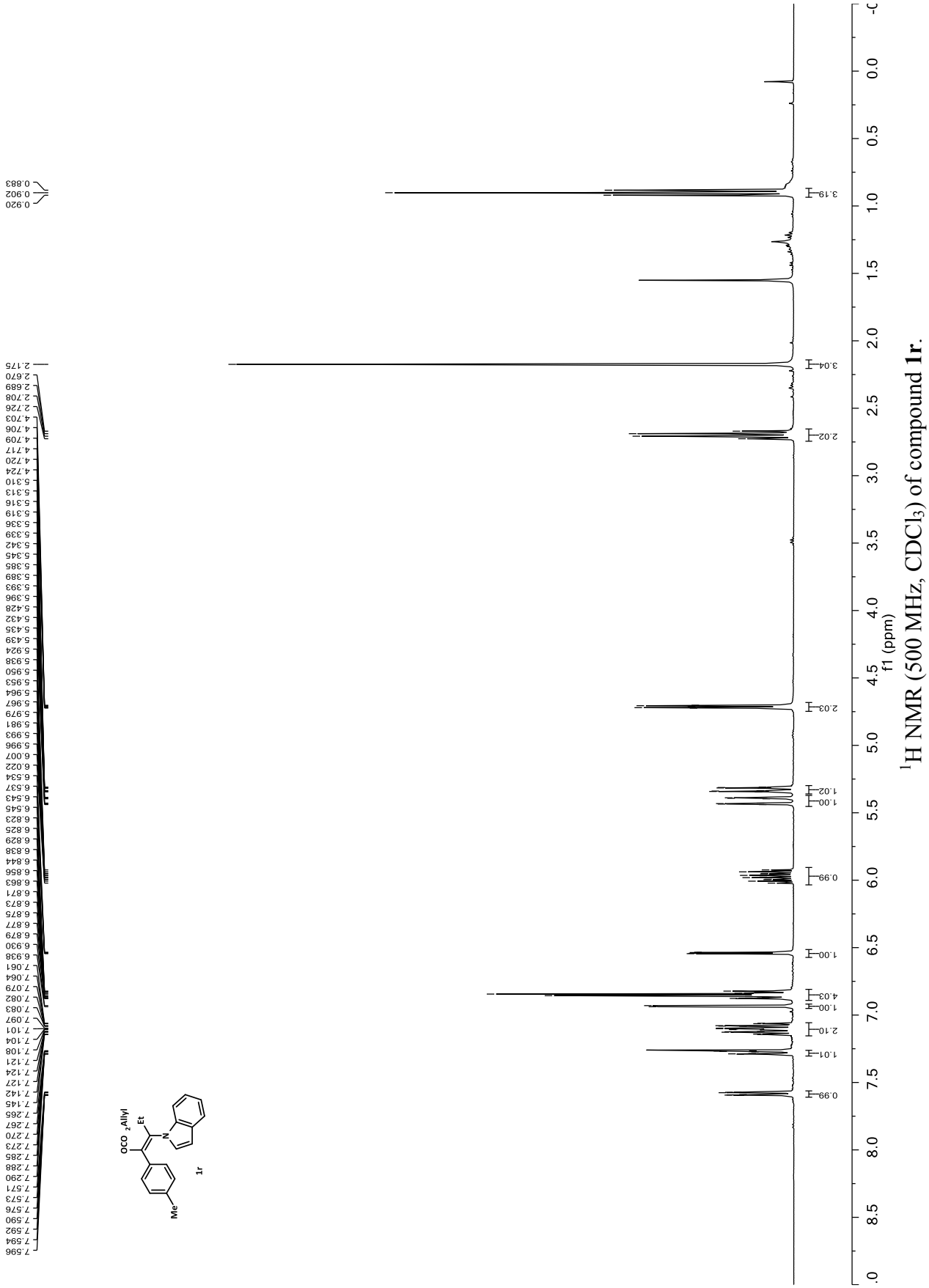
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1q**.



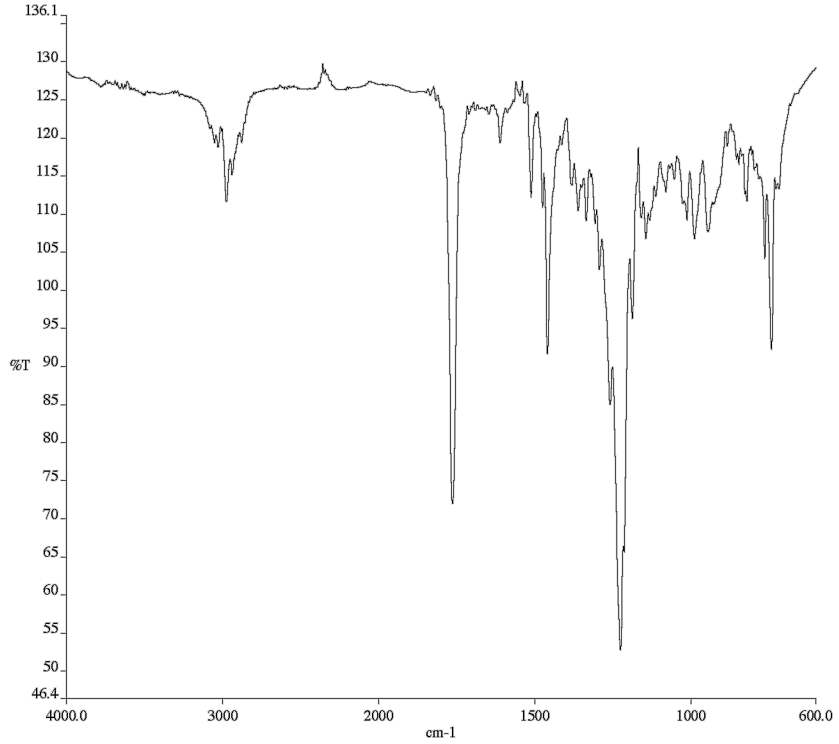
Infrared spectrum (Thin Film, NaCl) of compound **1q**.



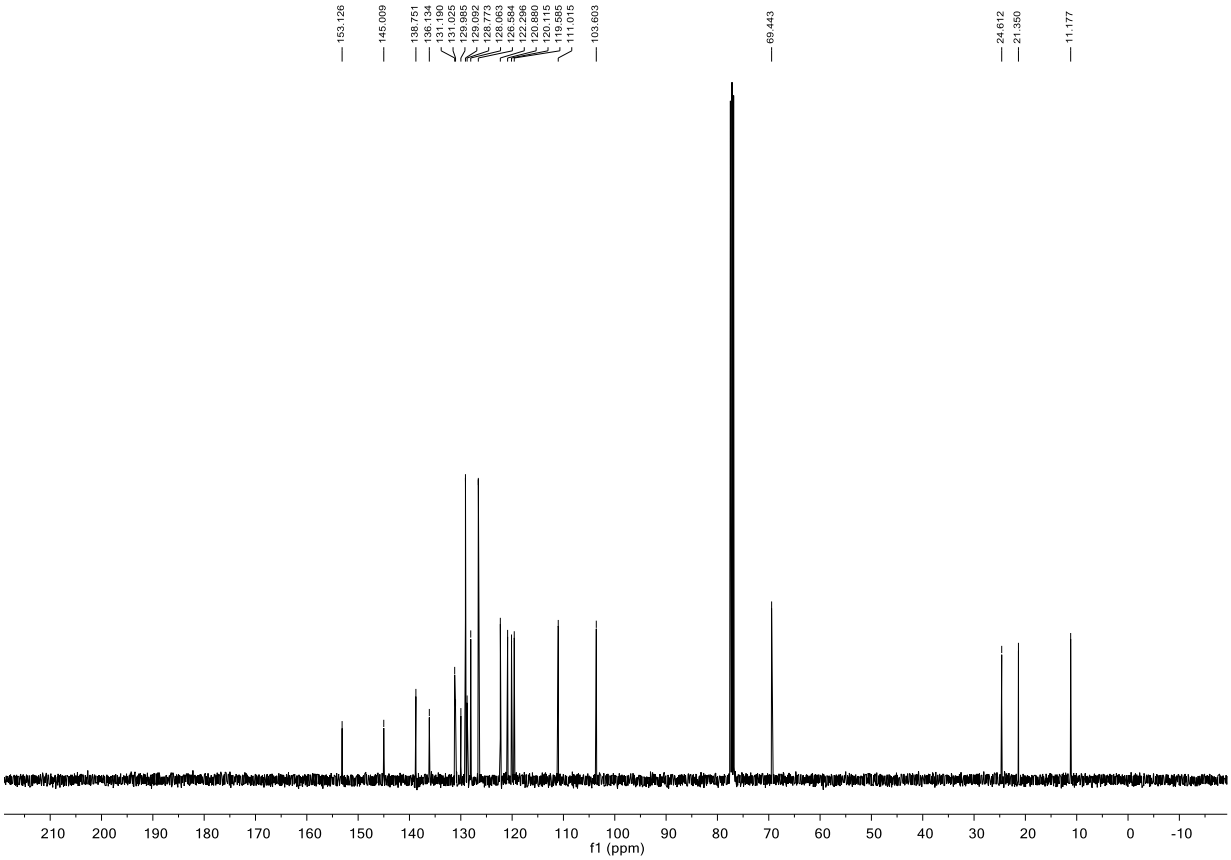
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1q**.



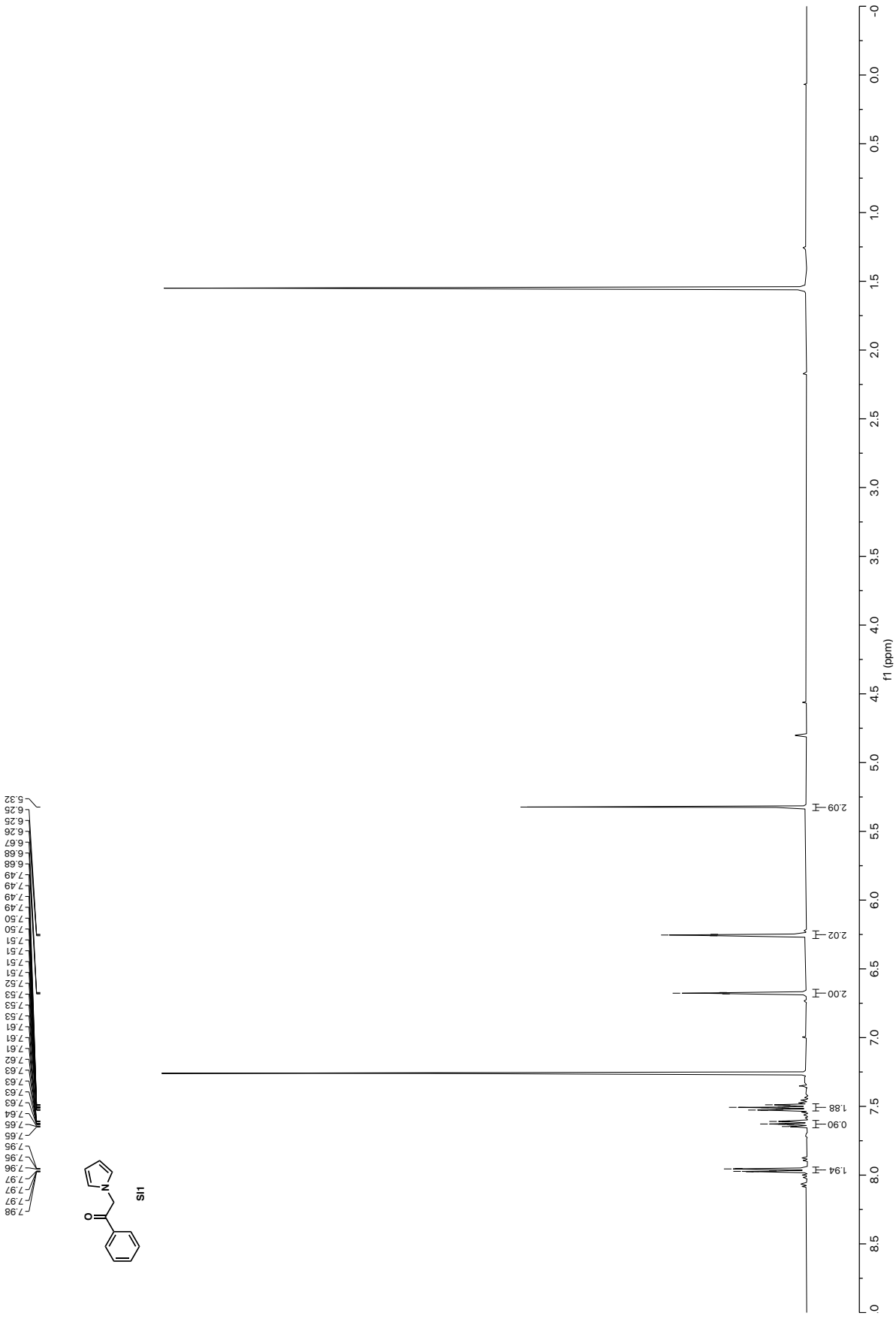
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1r**.



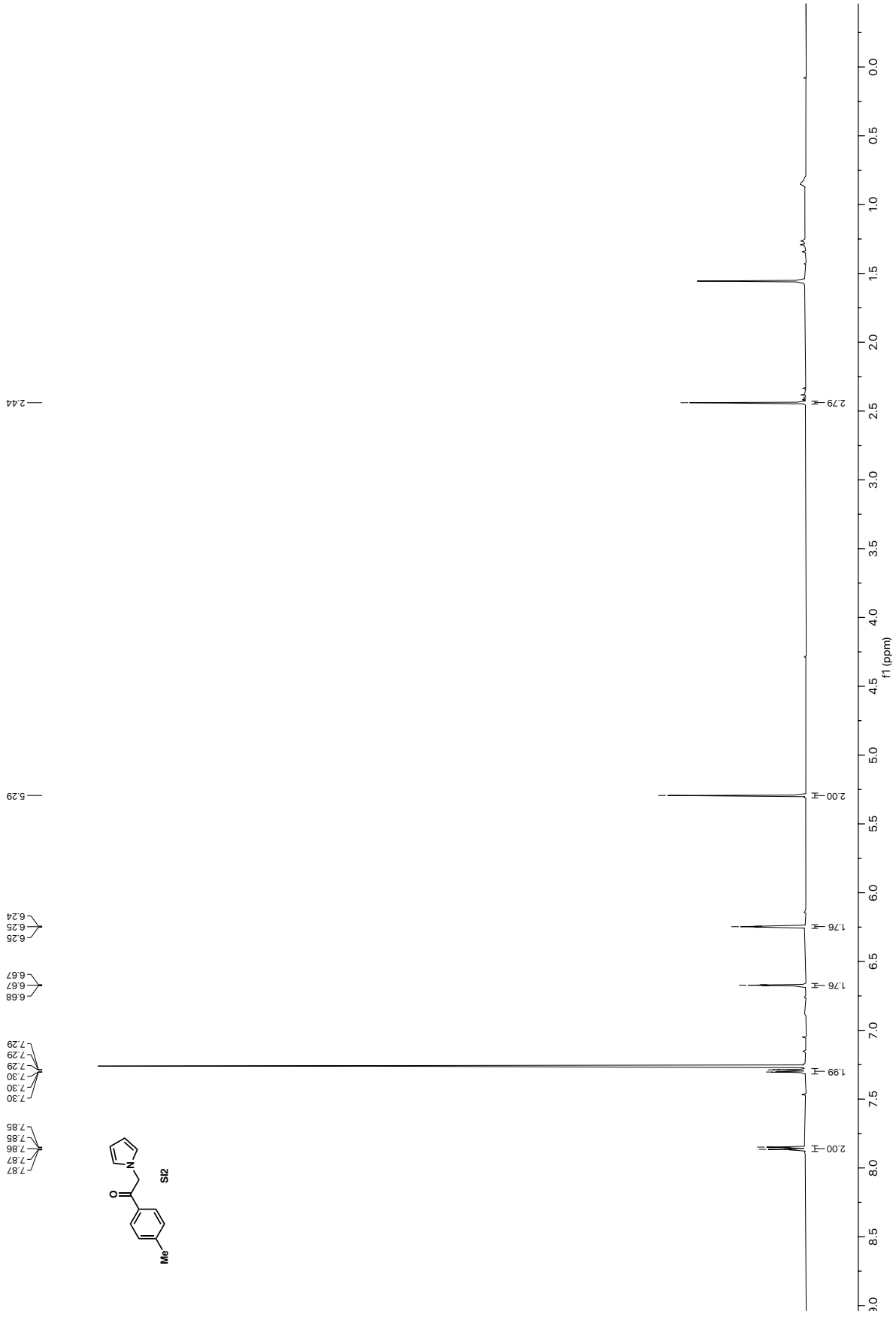
Infrared spectrum (Thin Film, NaCl) of compound **1r**.



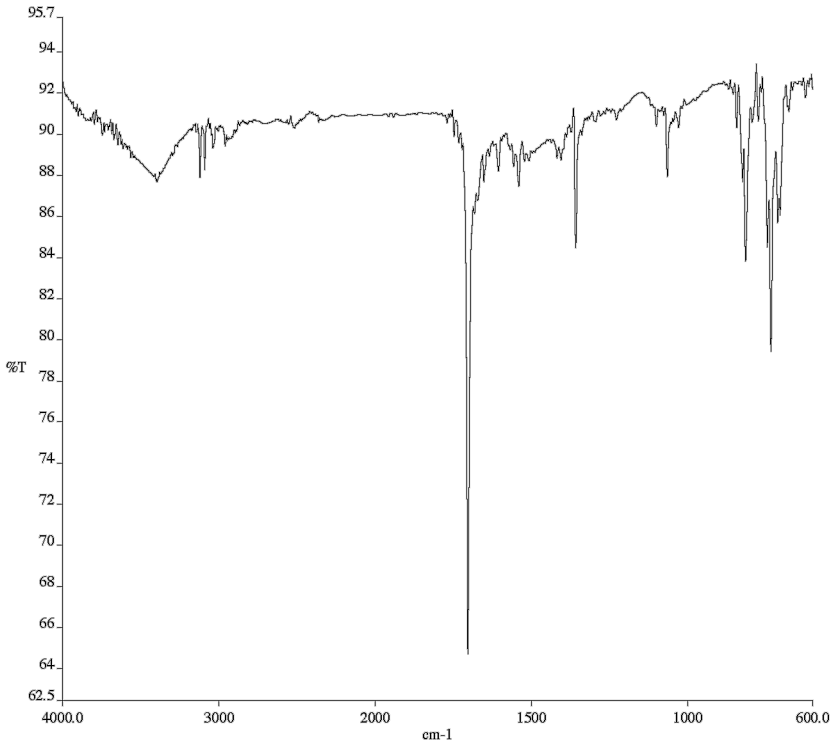
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1r**.



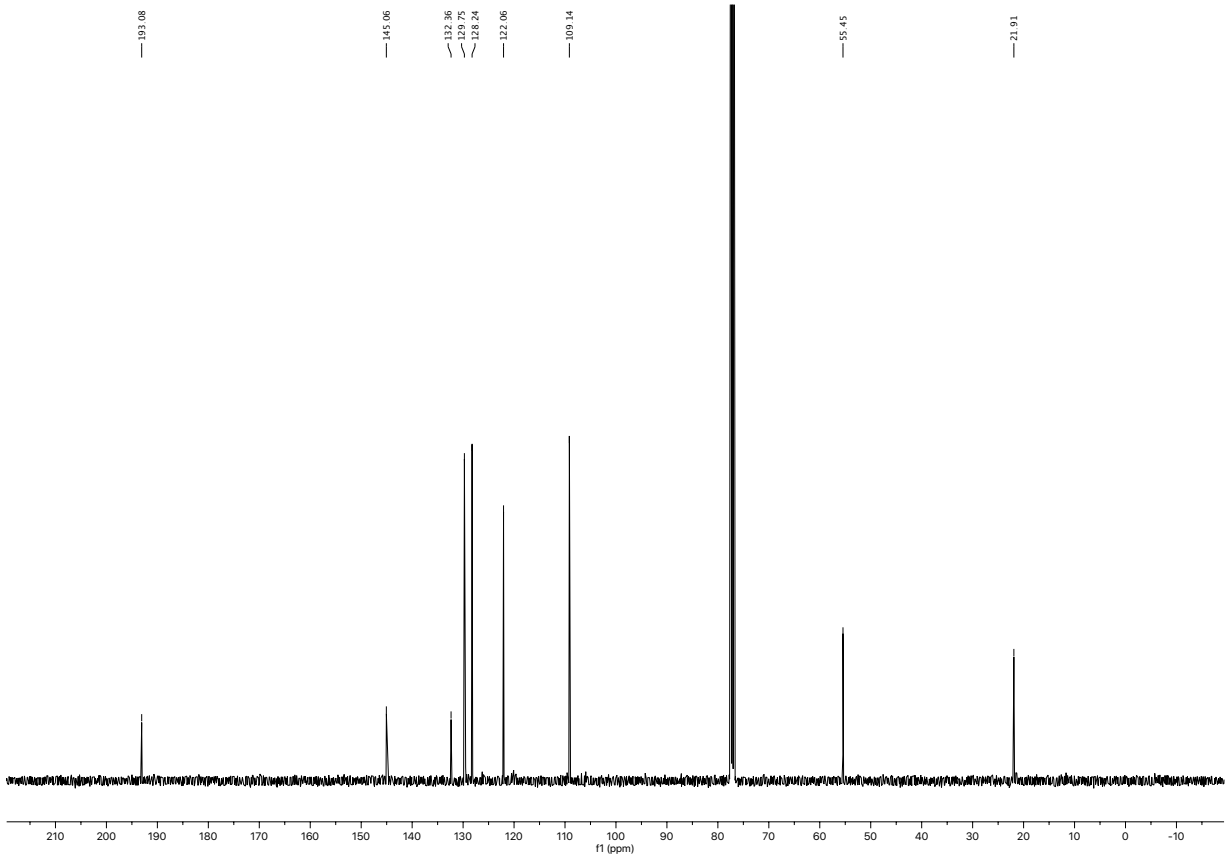
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI1**.



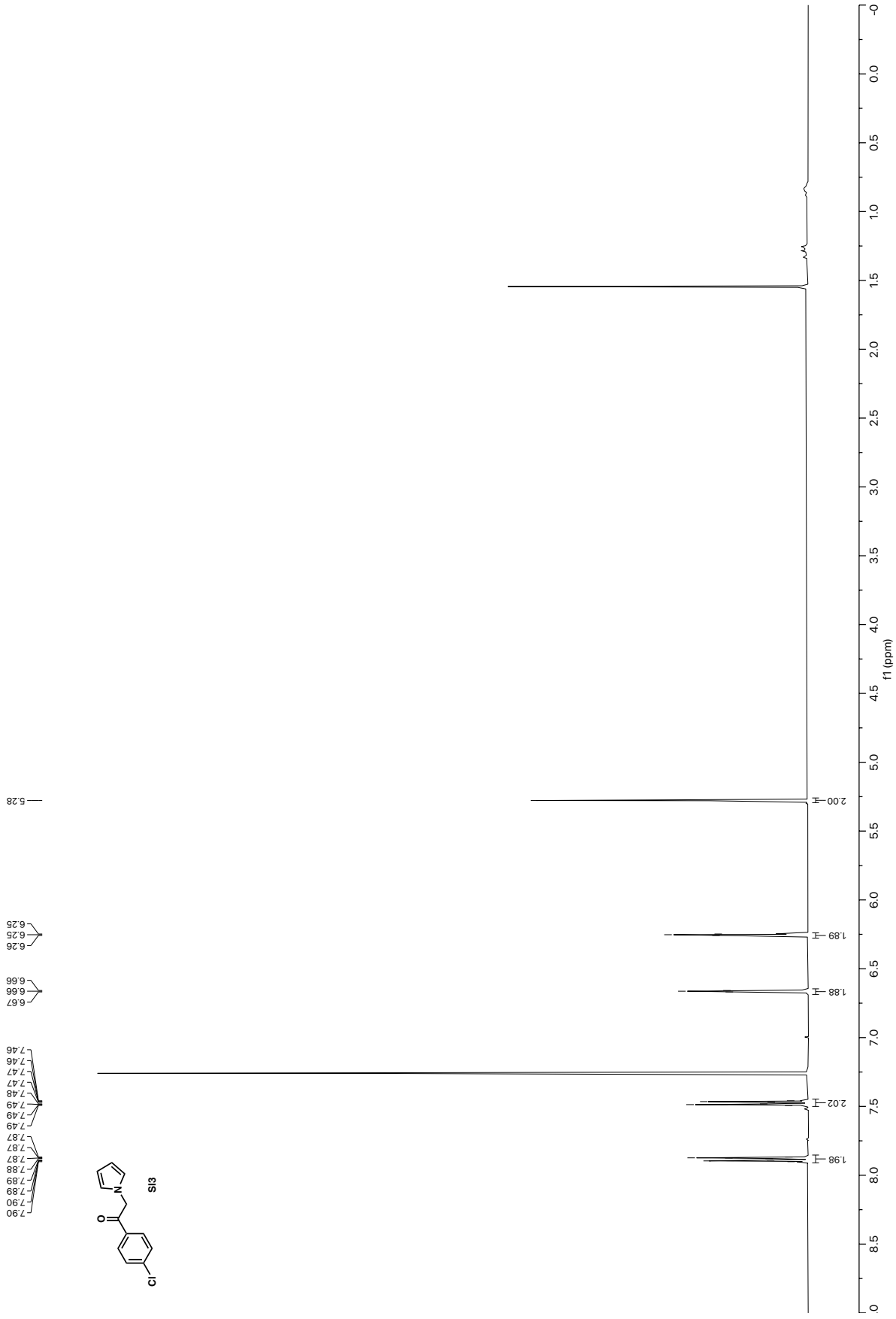
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI2**.



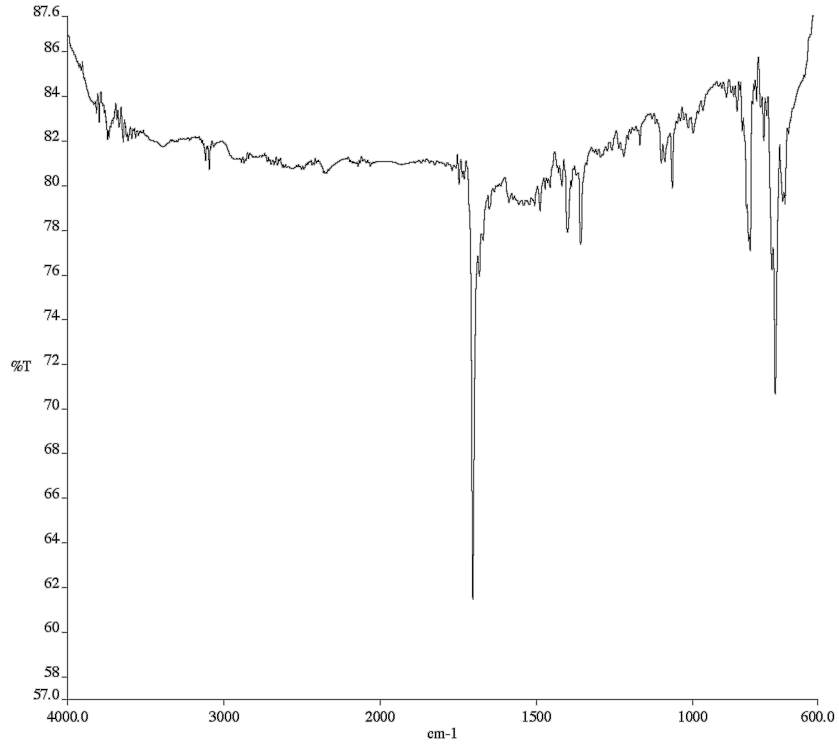
Infrared spectrum (Thin Film, NaCl) of compound **SI2**.



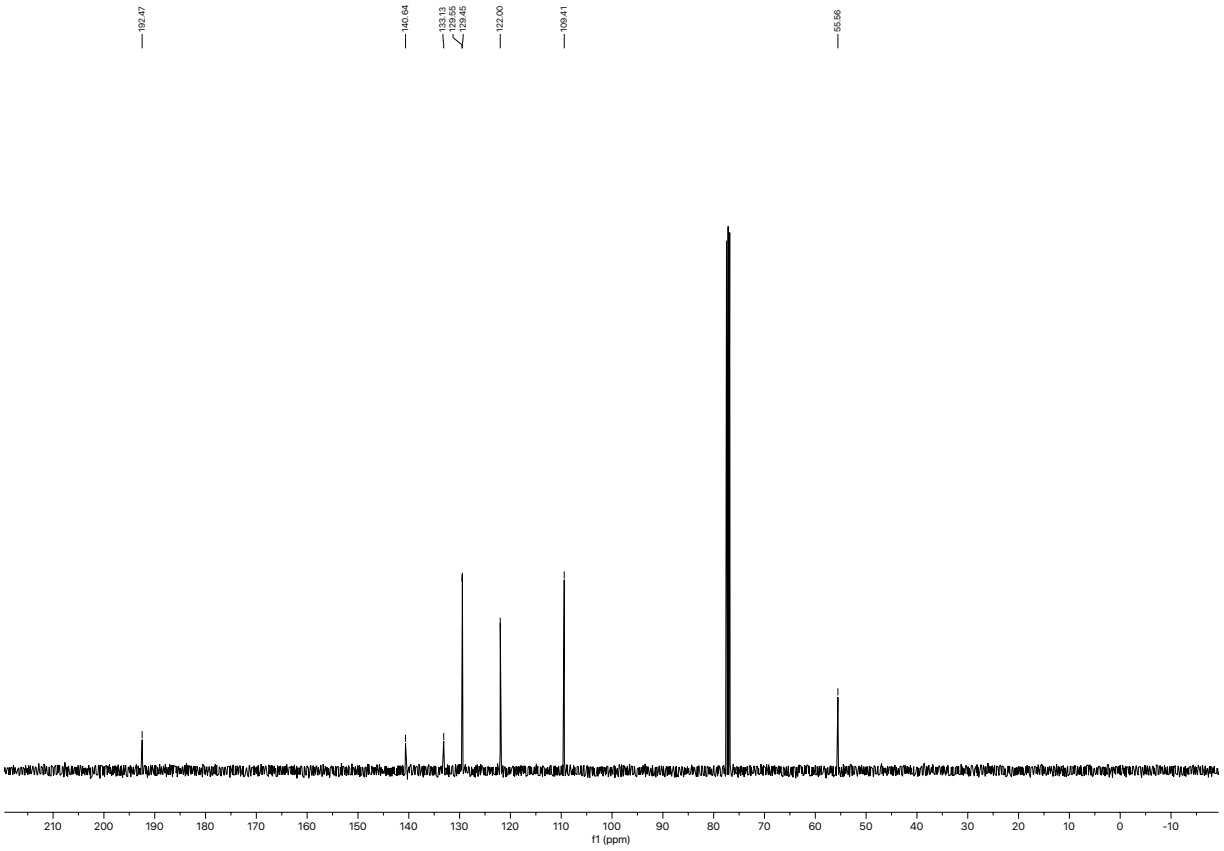
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI2**.



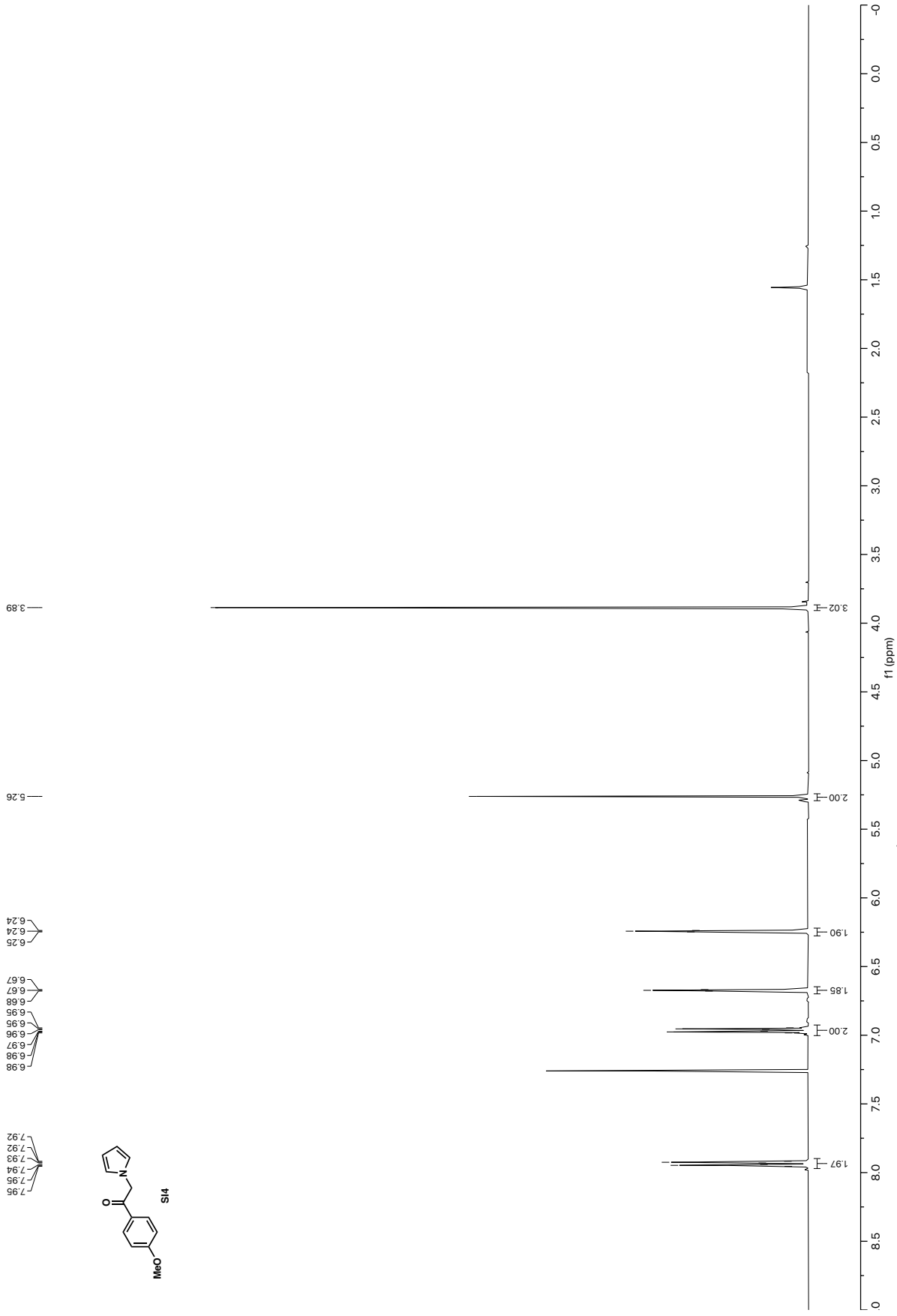
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI3.**



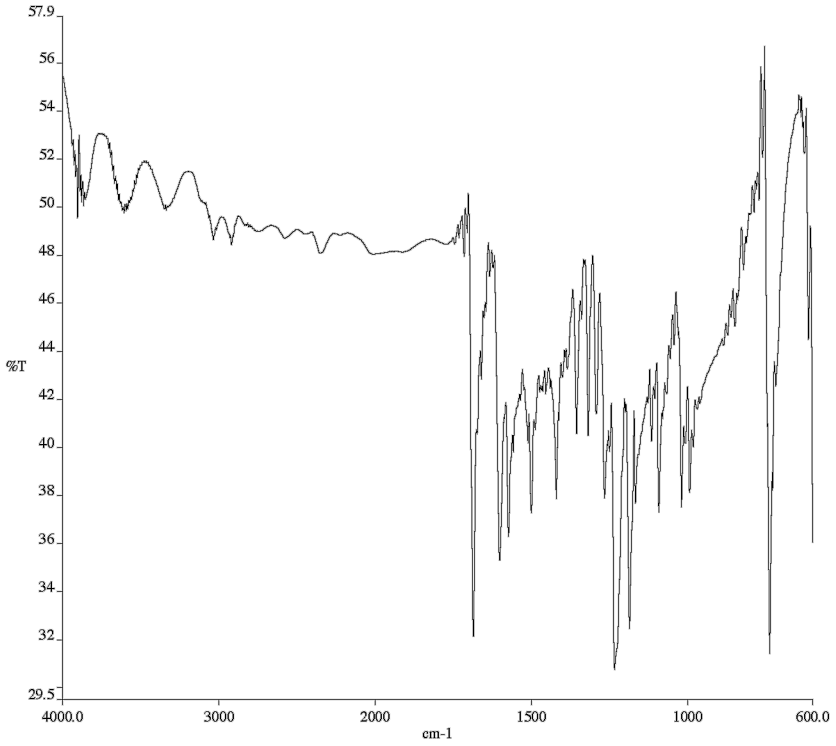
Infrared spectrum (Thin Film, NaCl) of compound **SI3**.



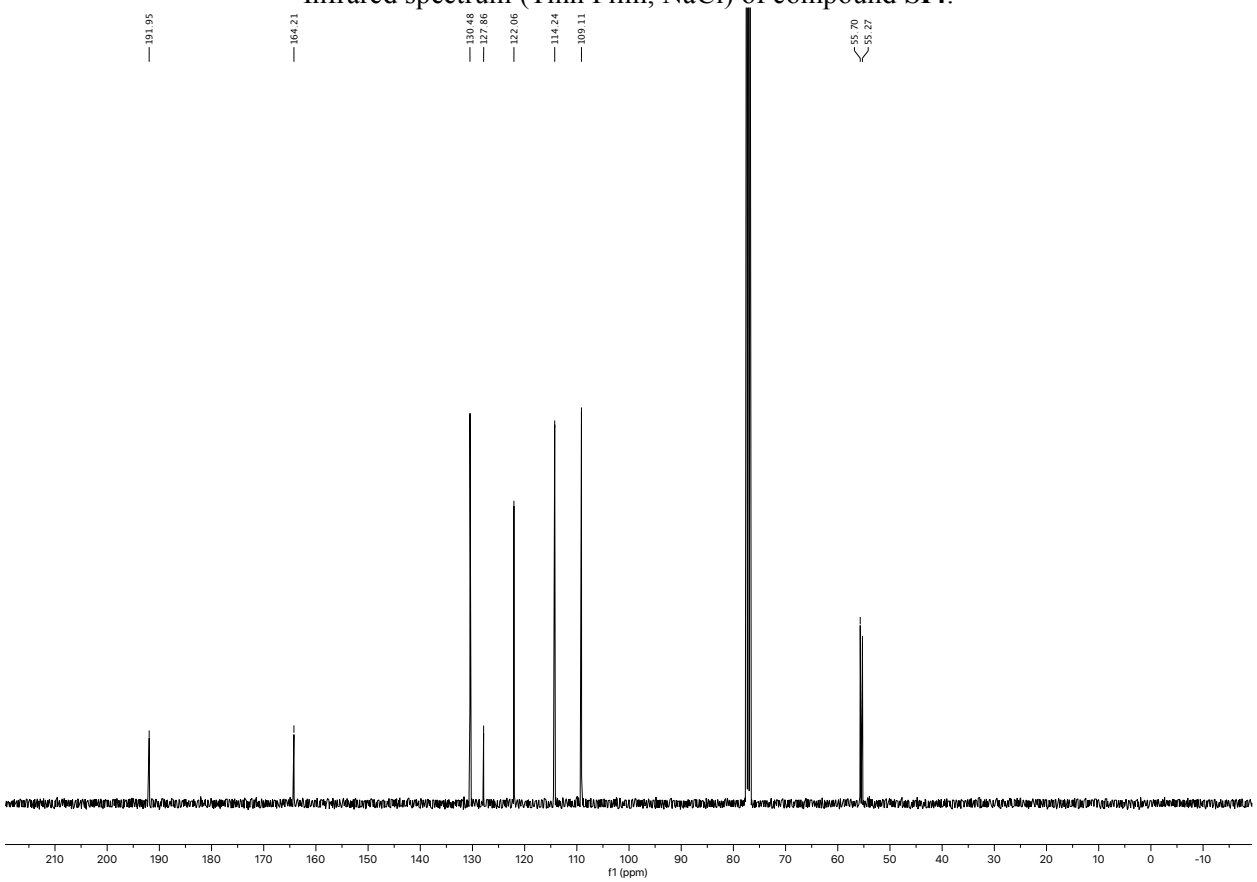
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI3**.



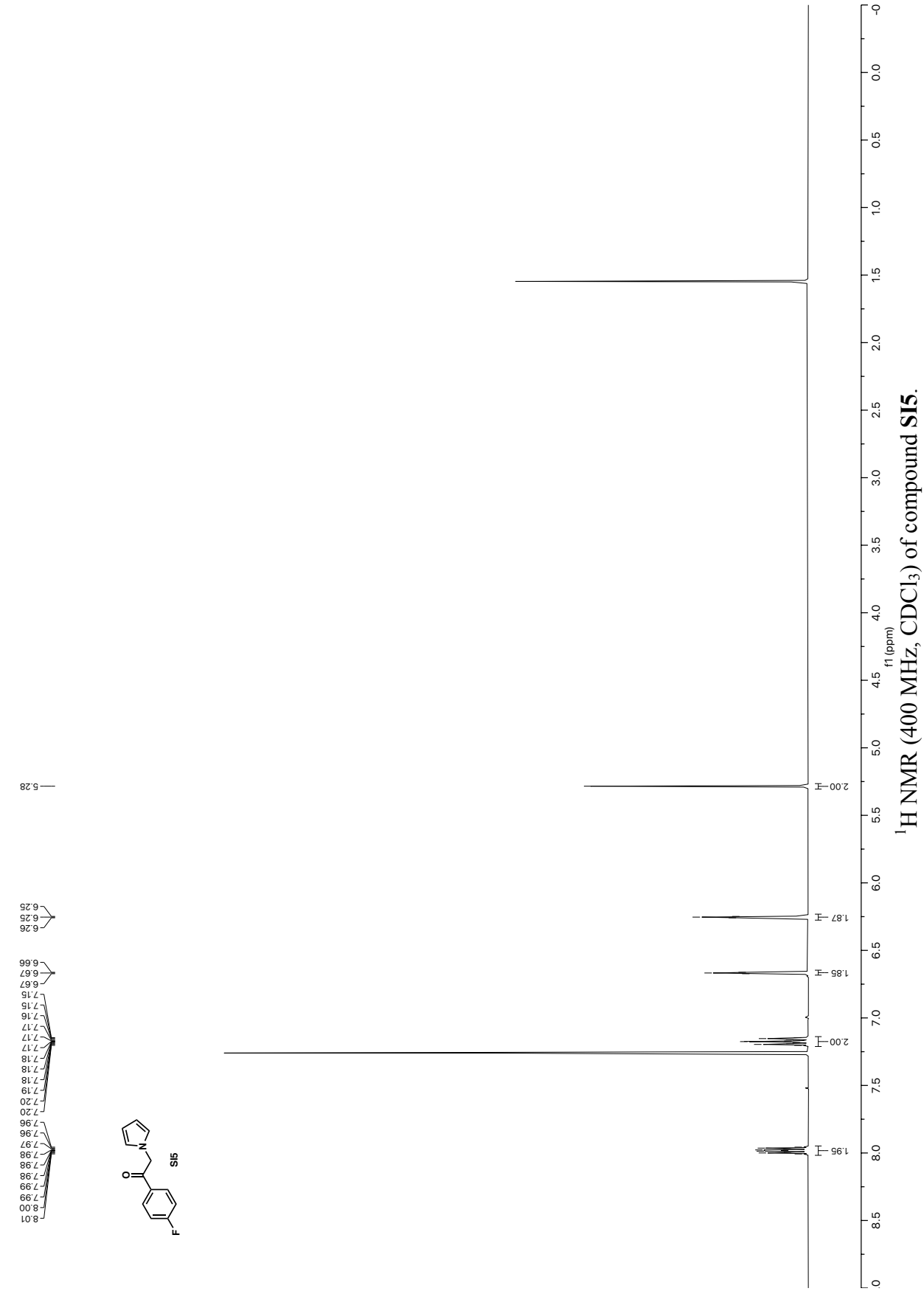
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI4**.



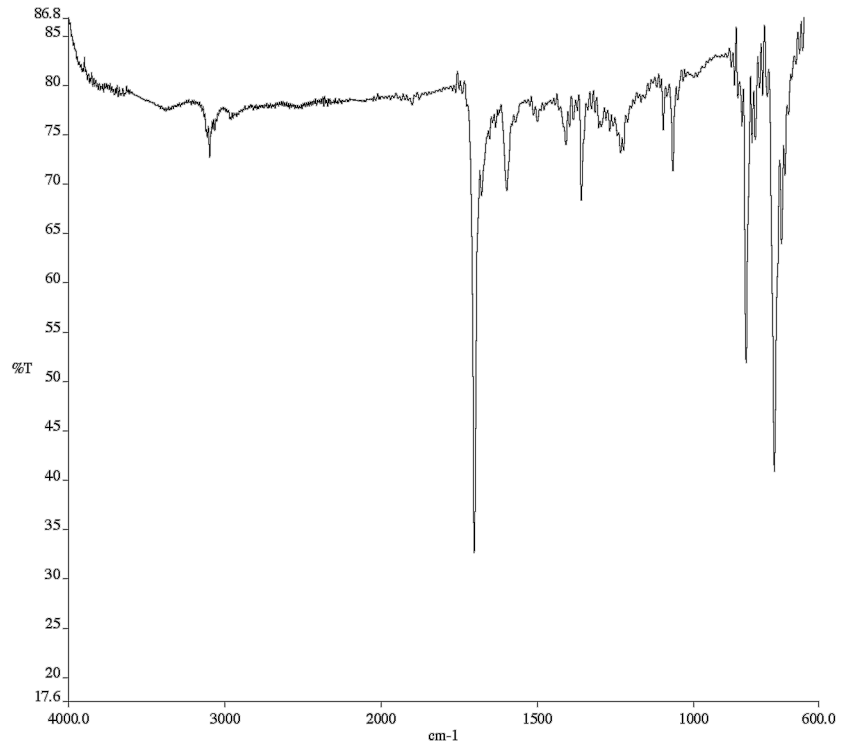
Infrared spectrum (Thin Film, NaCl) of compound **SI4**.



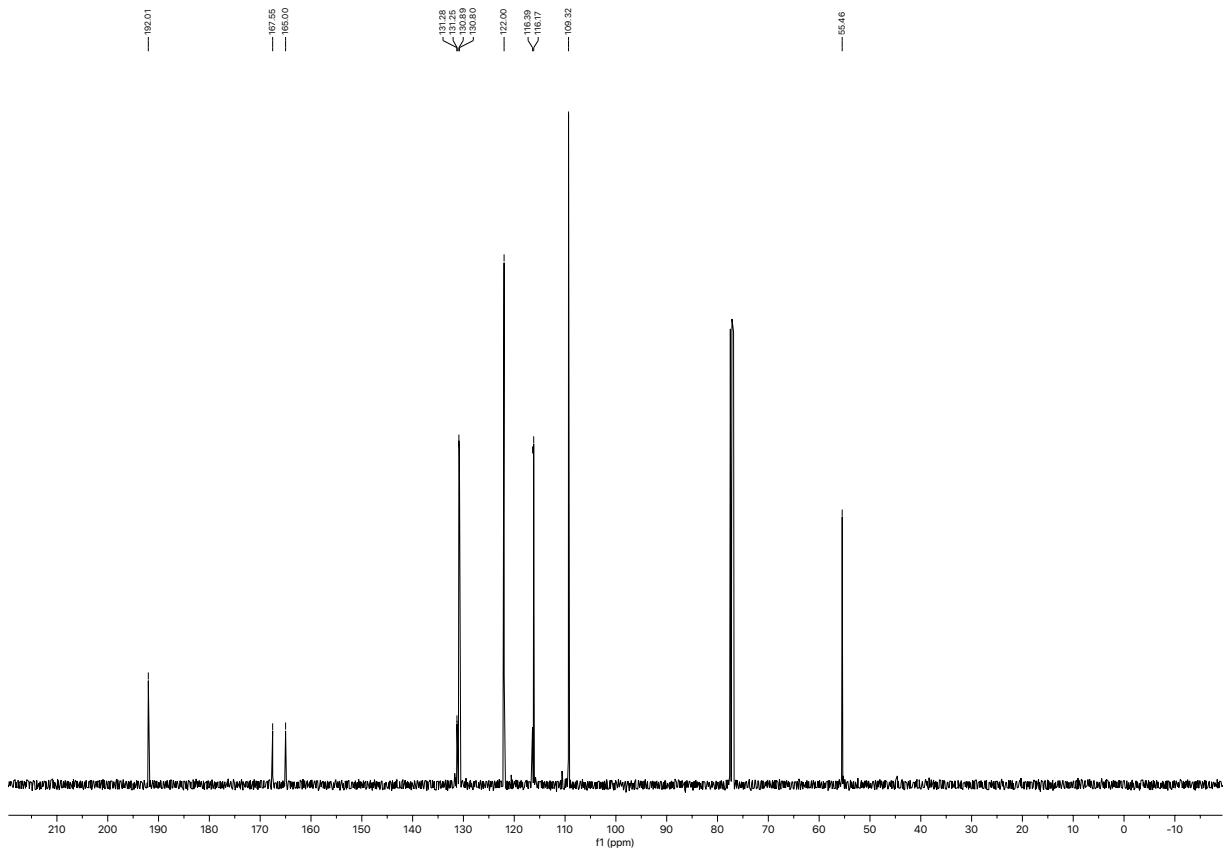
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI4**.



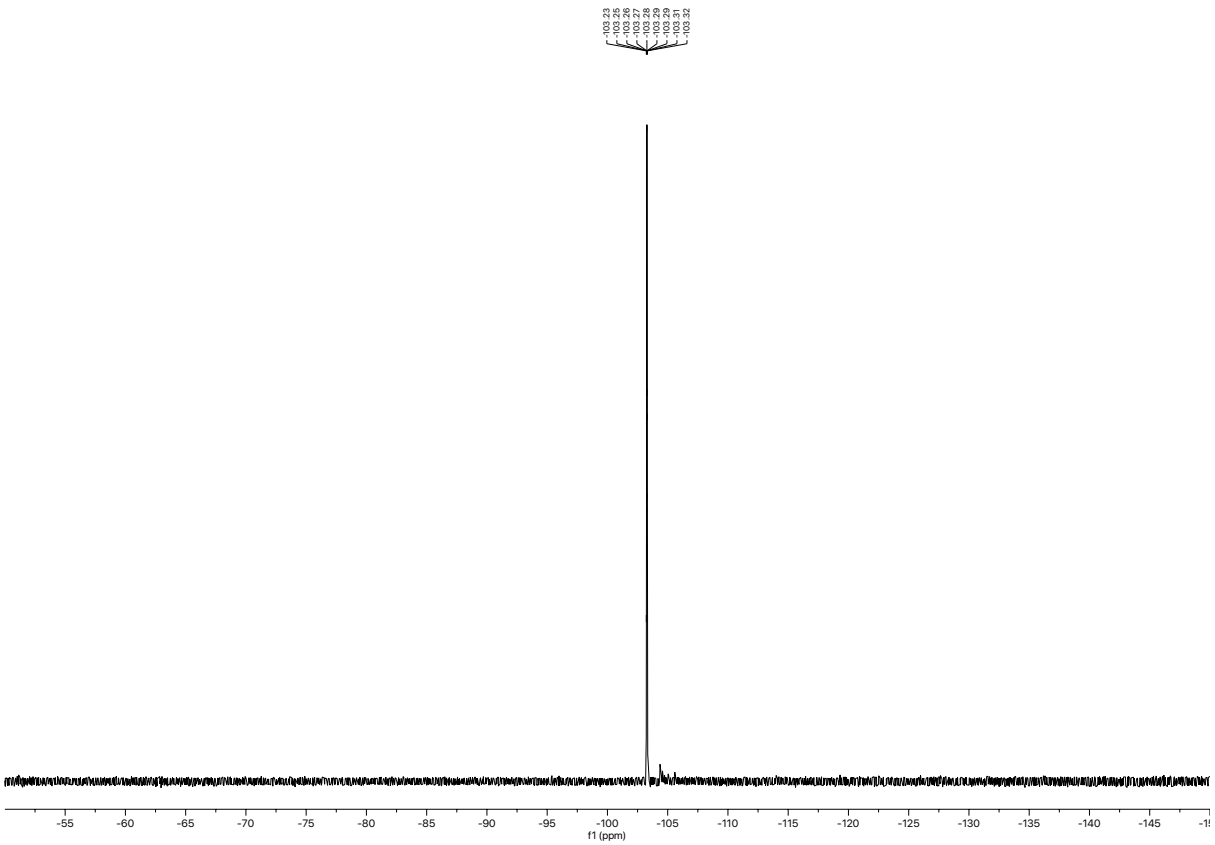
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI5**.



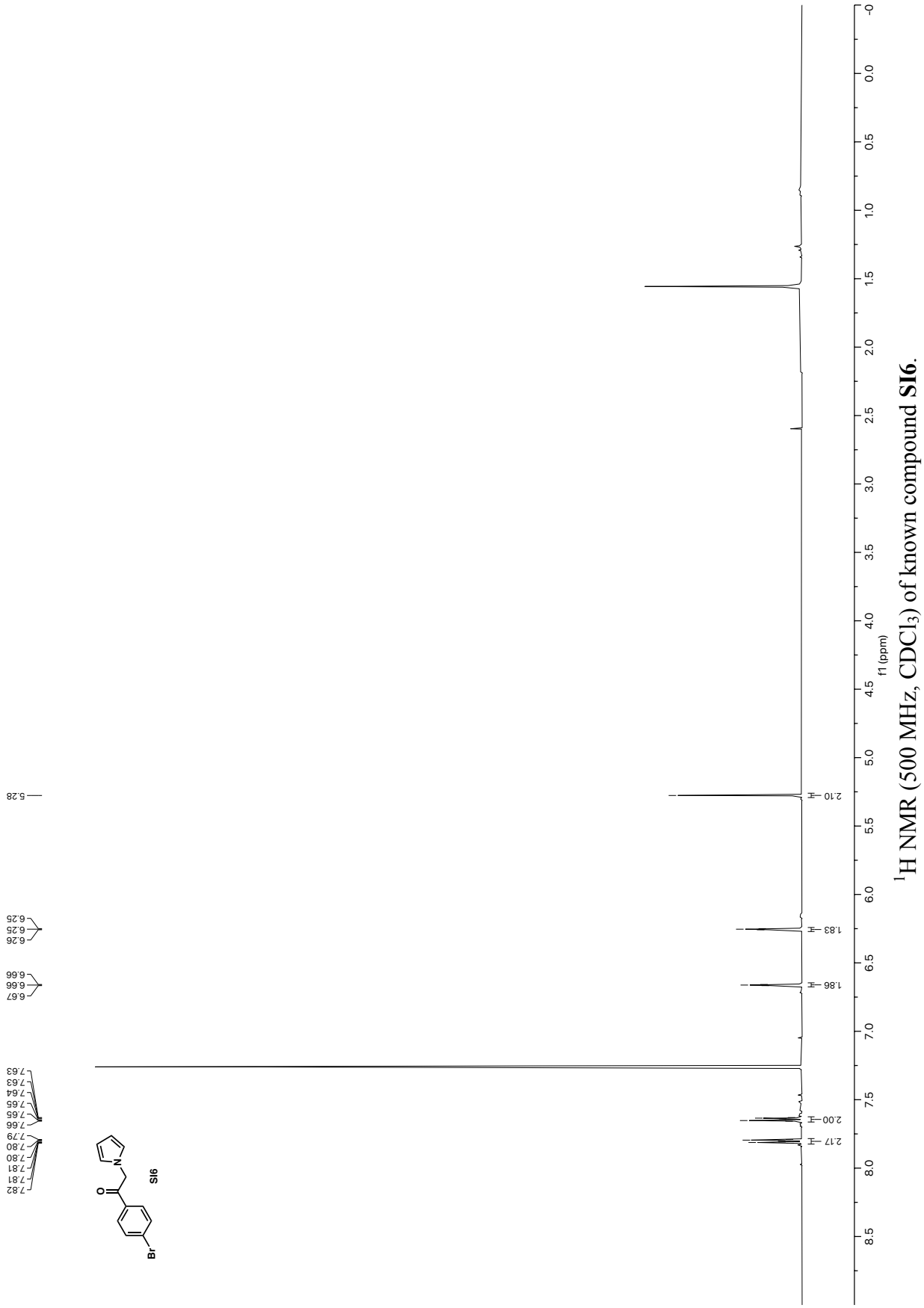
Infrared spectrum (Thin Film, NaCl) of compound **SI5**.



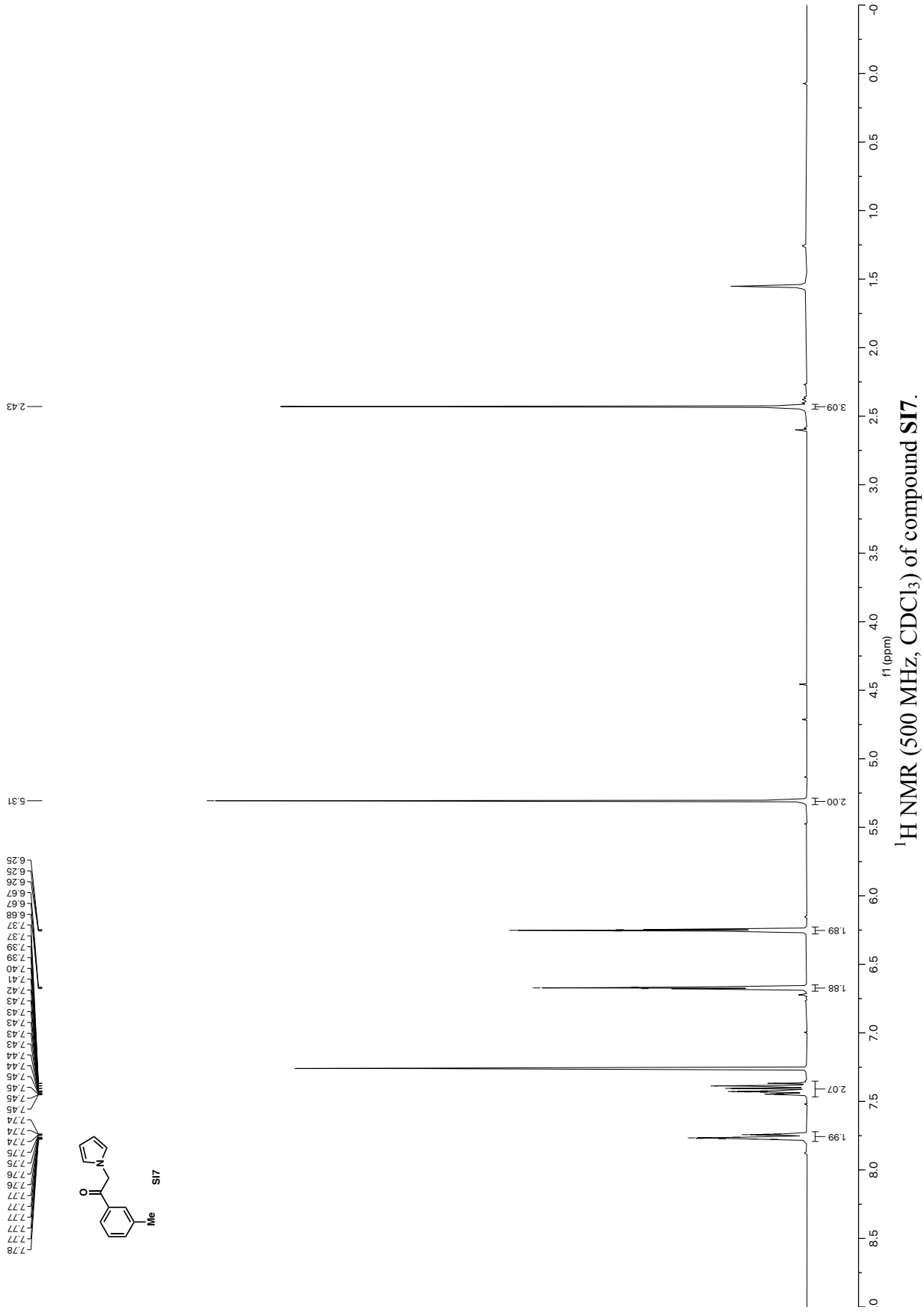
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI5**.



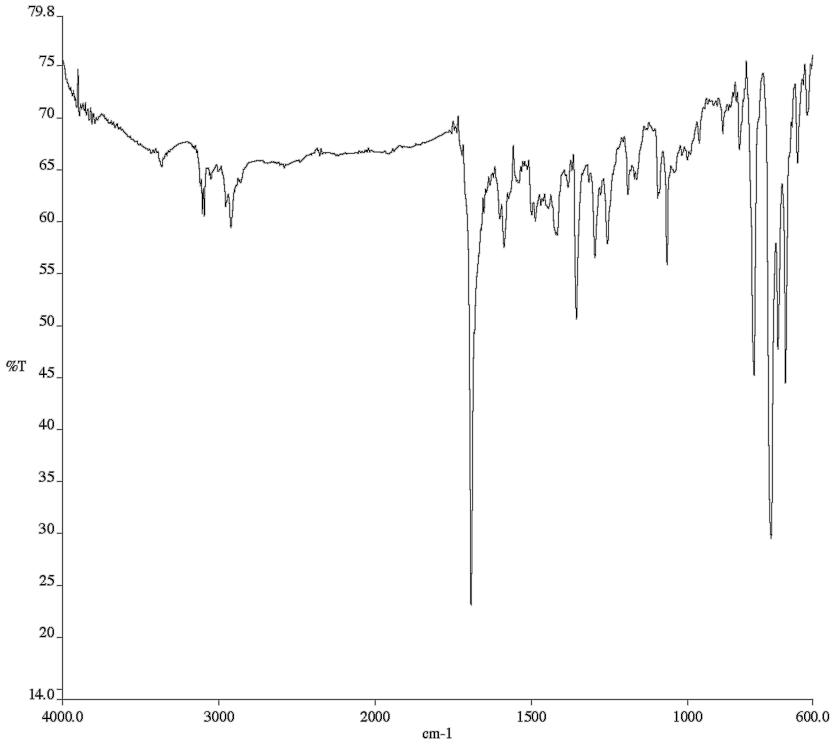
^{19}F NMR (282 MHz, $CDCl_3$) of compound **SI5.**



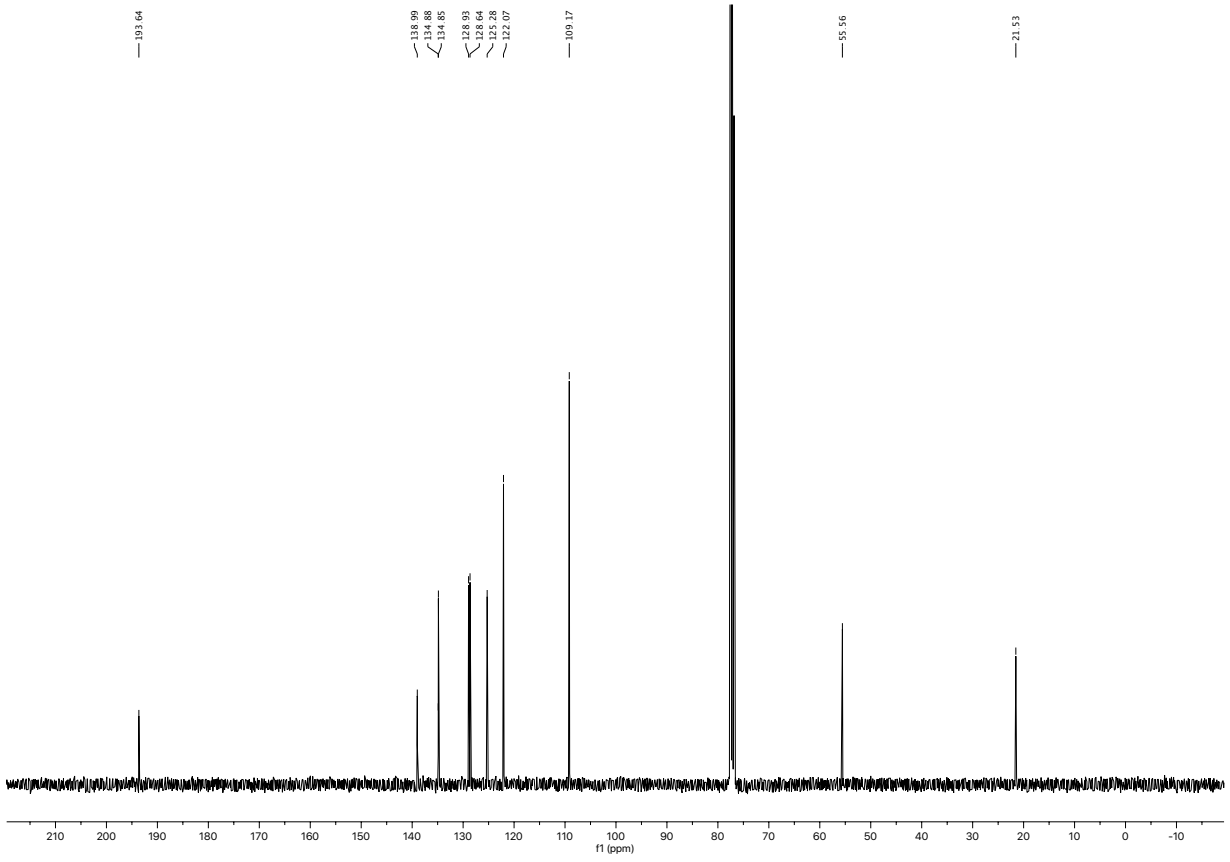
^{1}H NMR (500 MHz, $CDCl_3$) of known compound **SI6**.



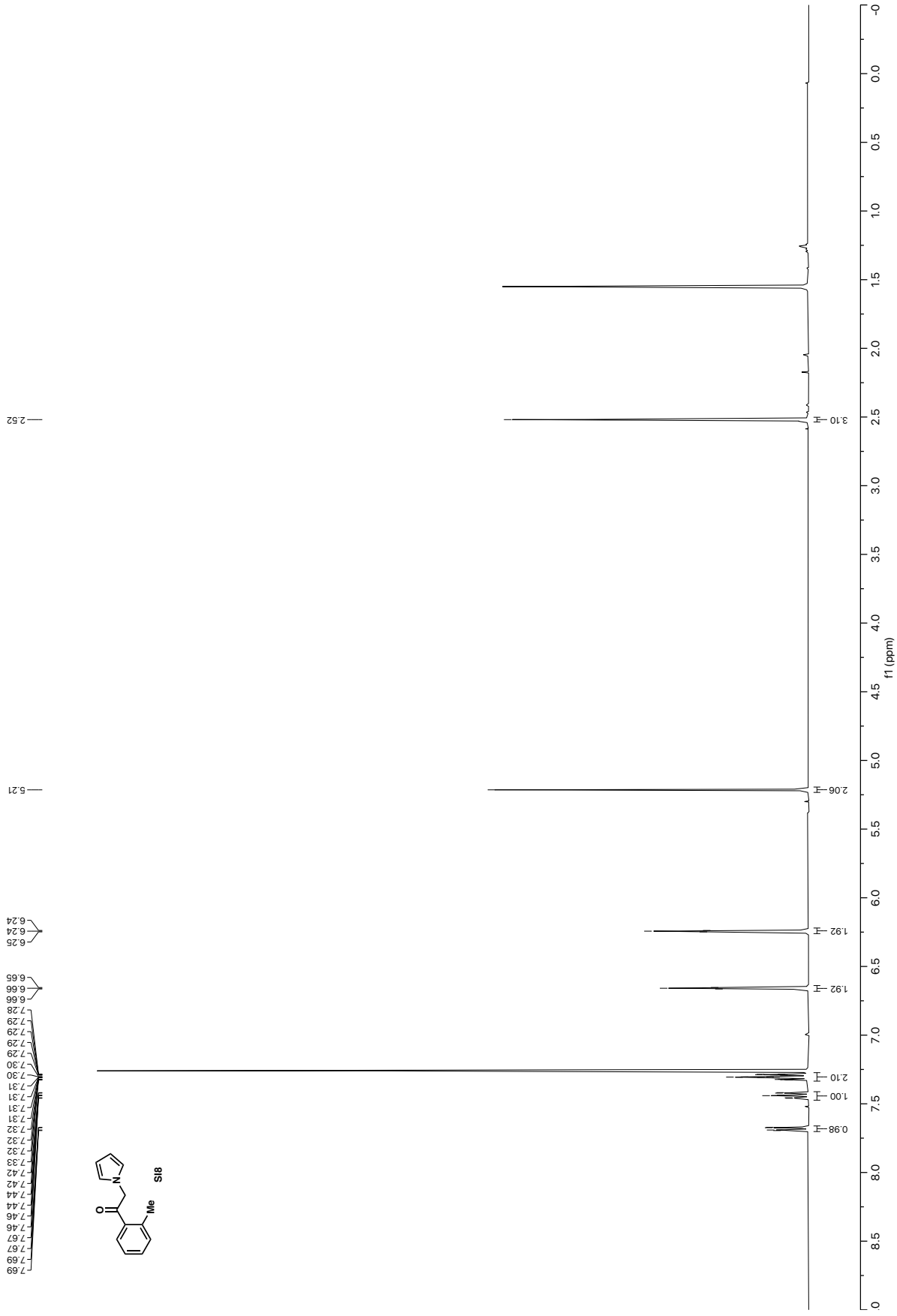
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI7**.



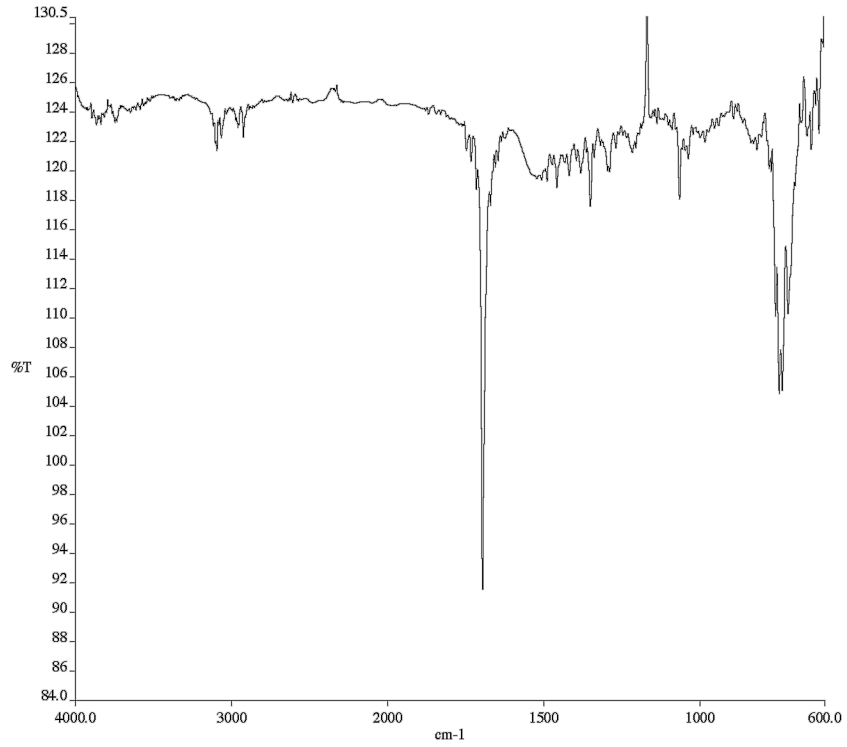
Infrared spectrum (Thin Film, NaCl) of compound **SI7**.



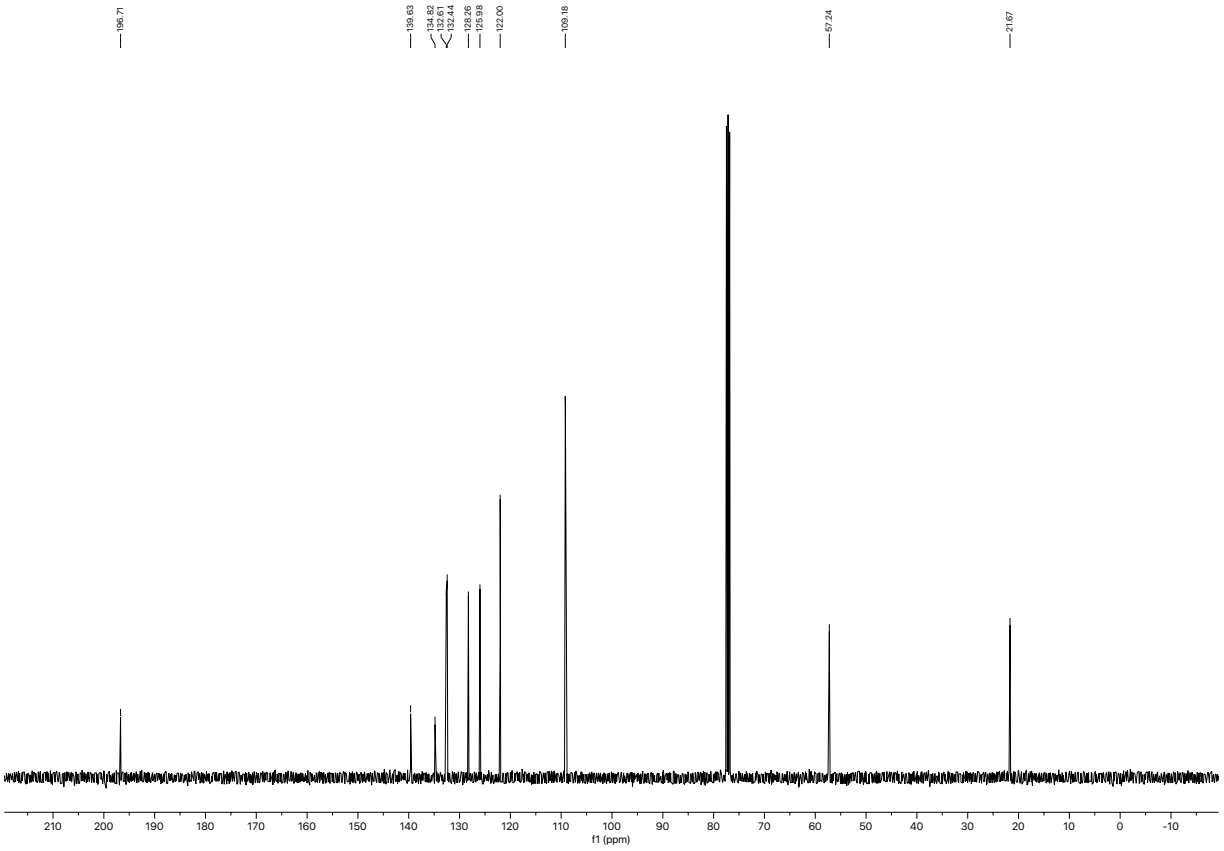
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI7**.



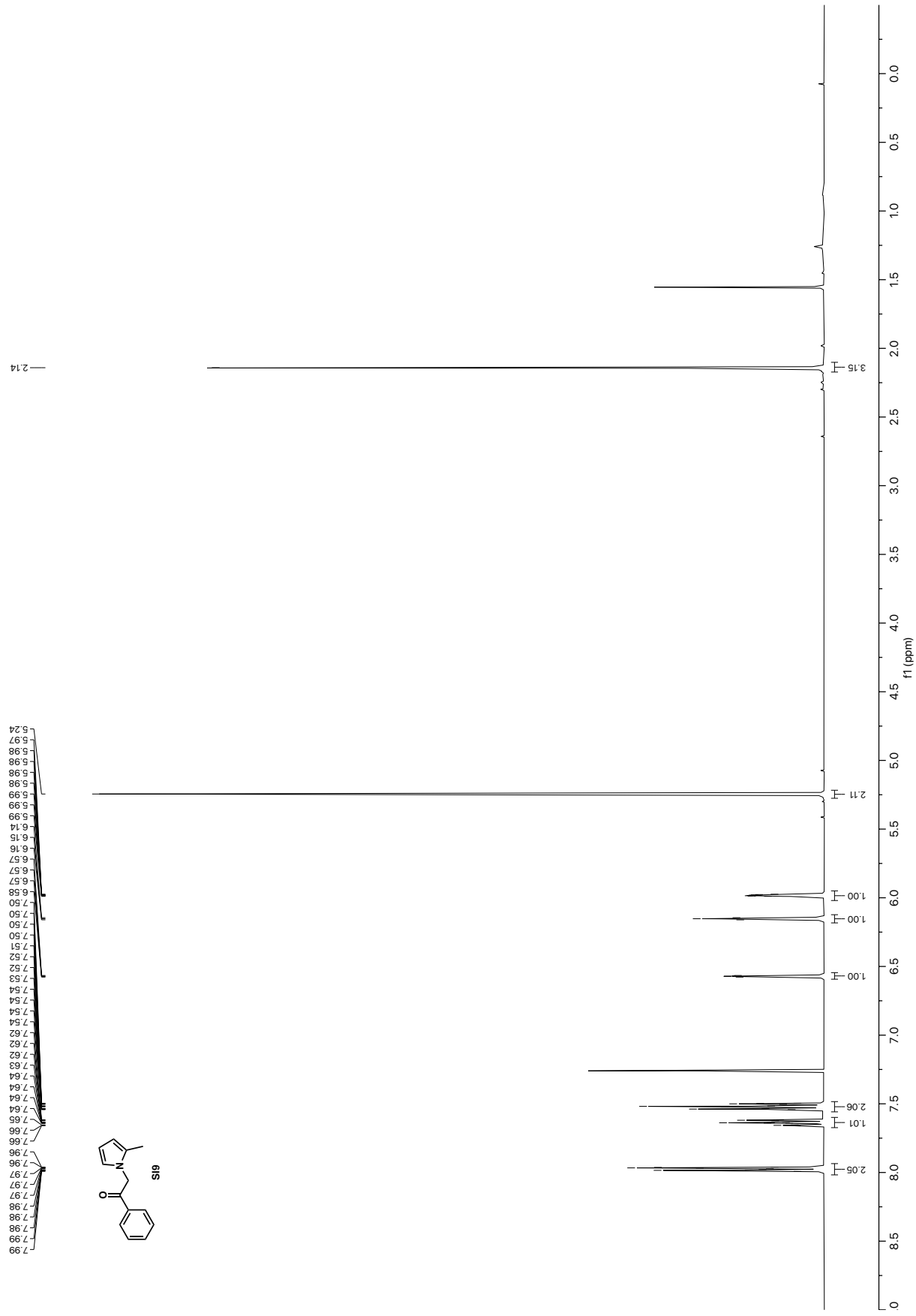
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI8**.



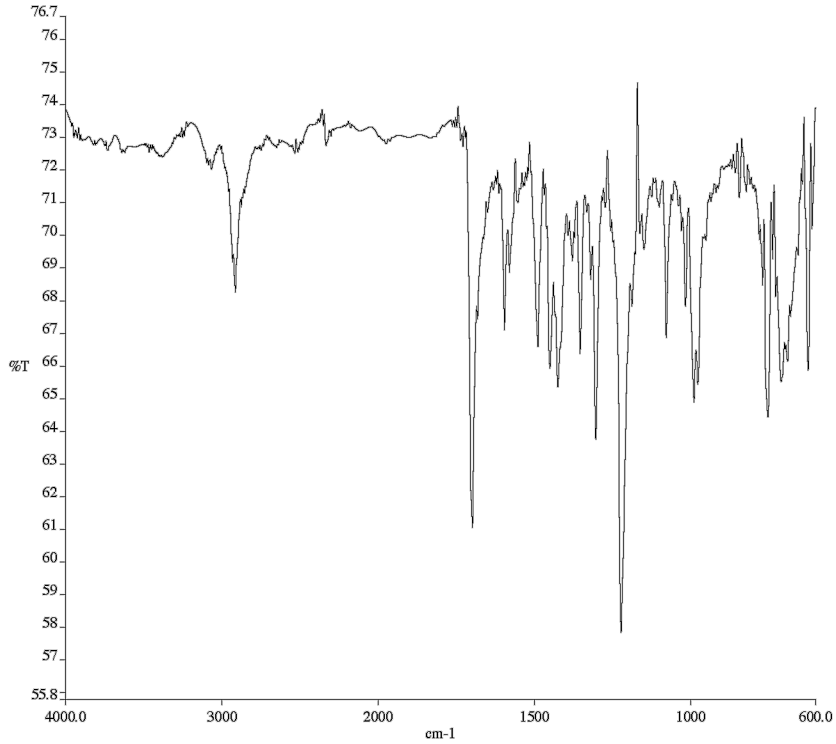
Infrared spectrum (Thin Film, NaCl) of compound **SI8**.



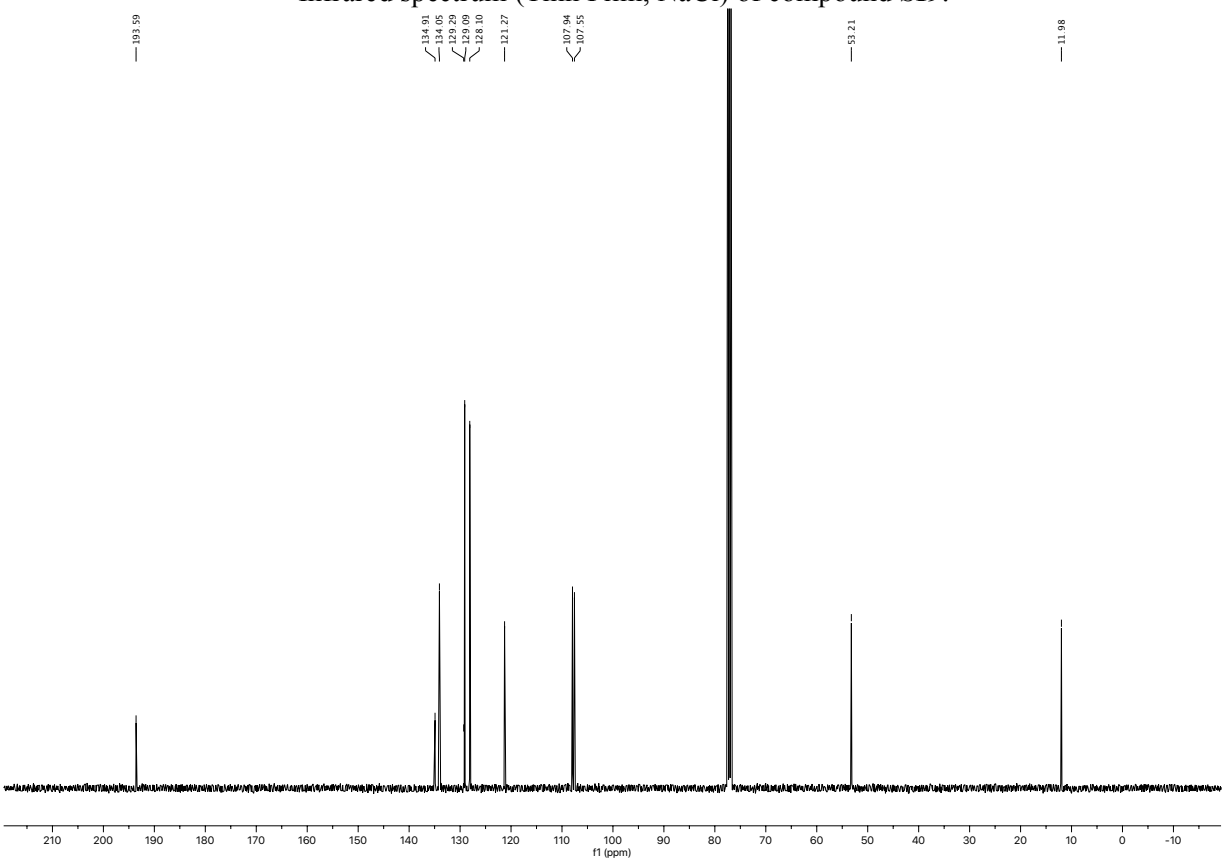
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI8**.



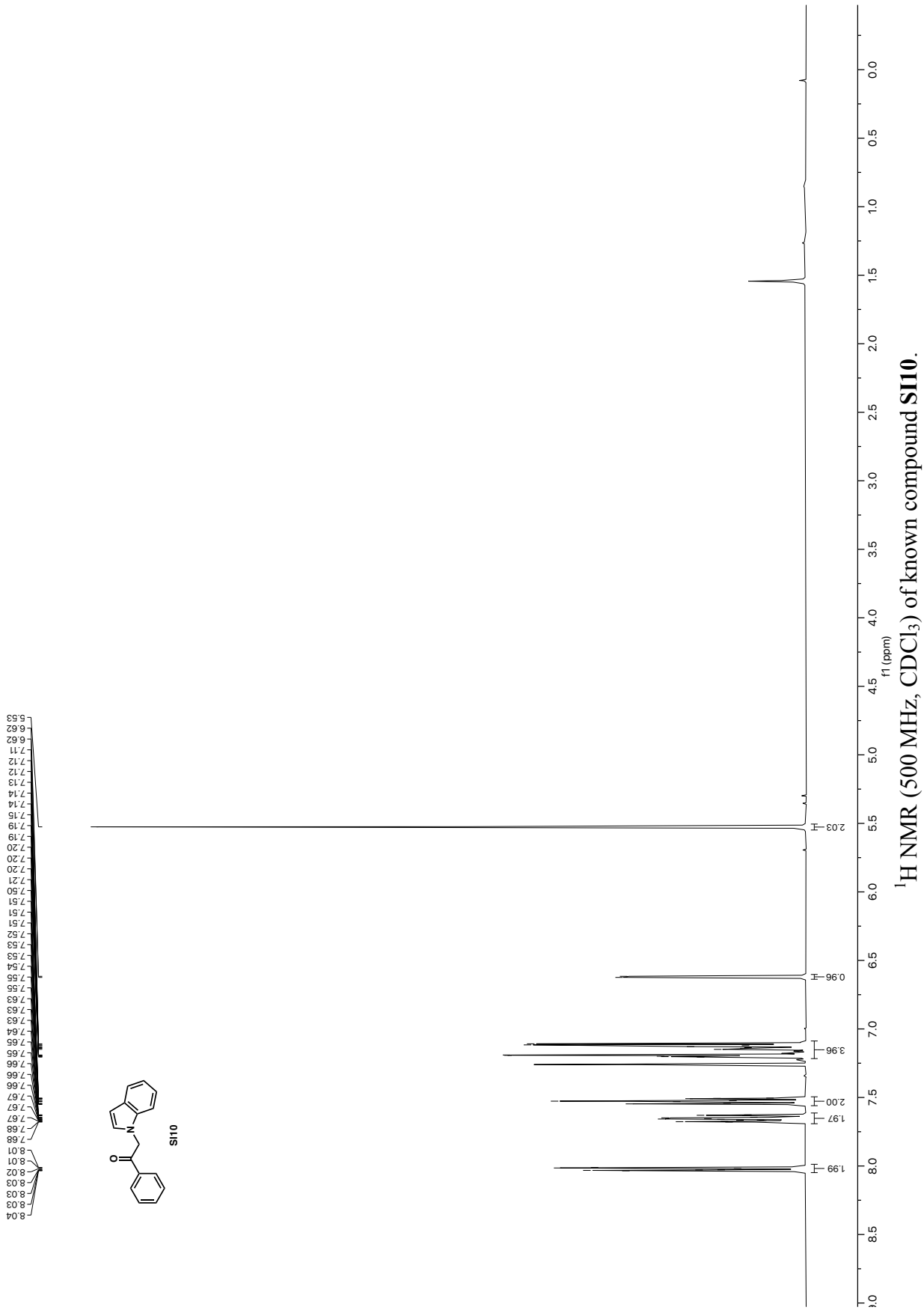
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI9**.



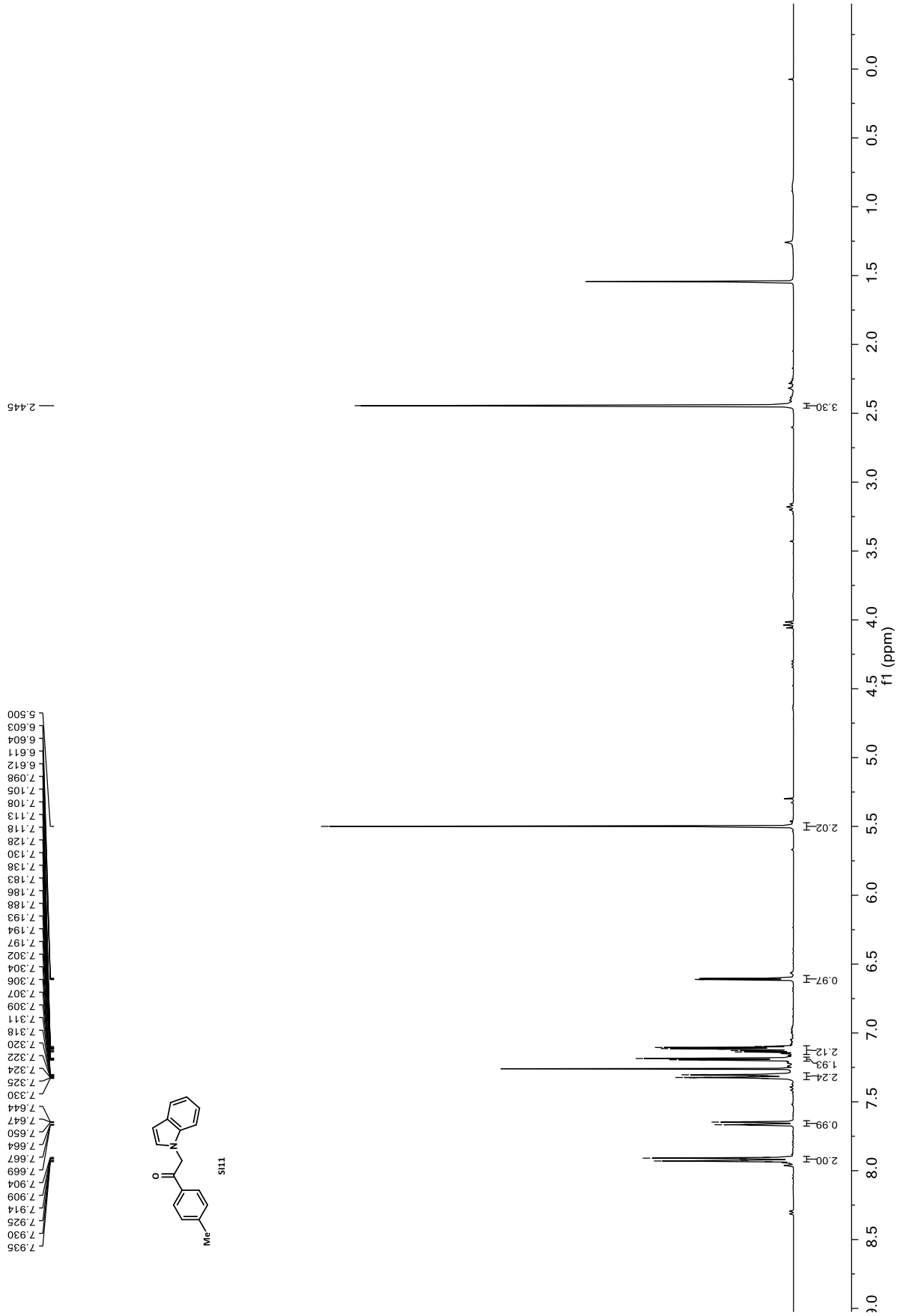
Infrared spectrum (Thin Film, NaCl) of compound **SI9**.



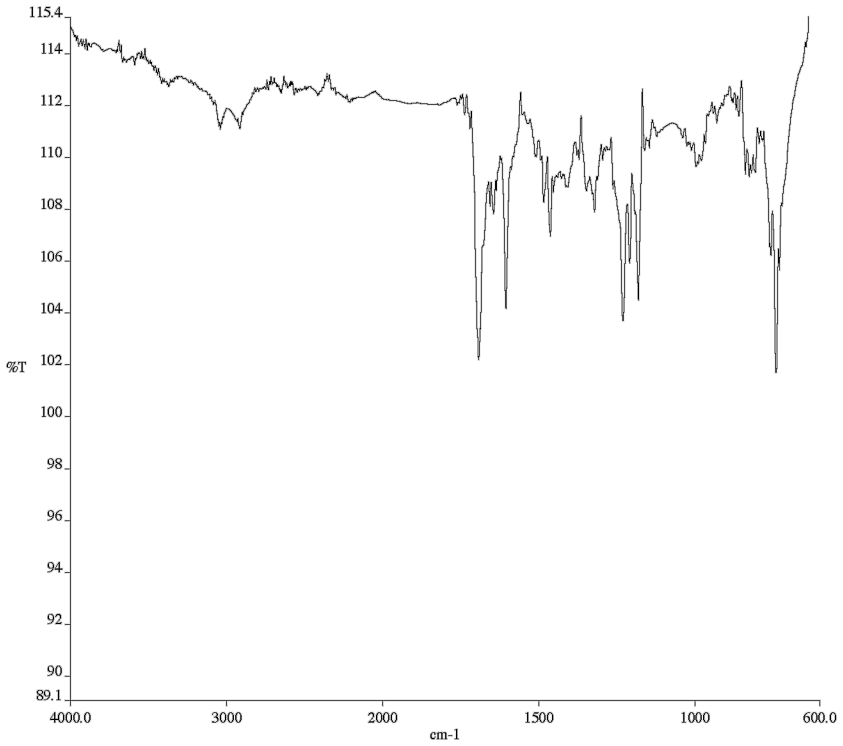
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI9**.



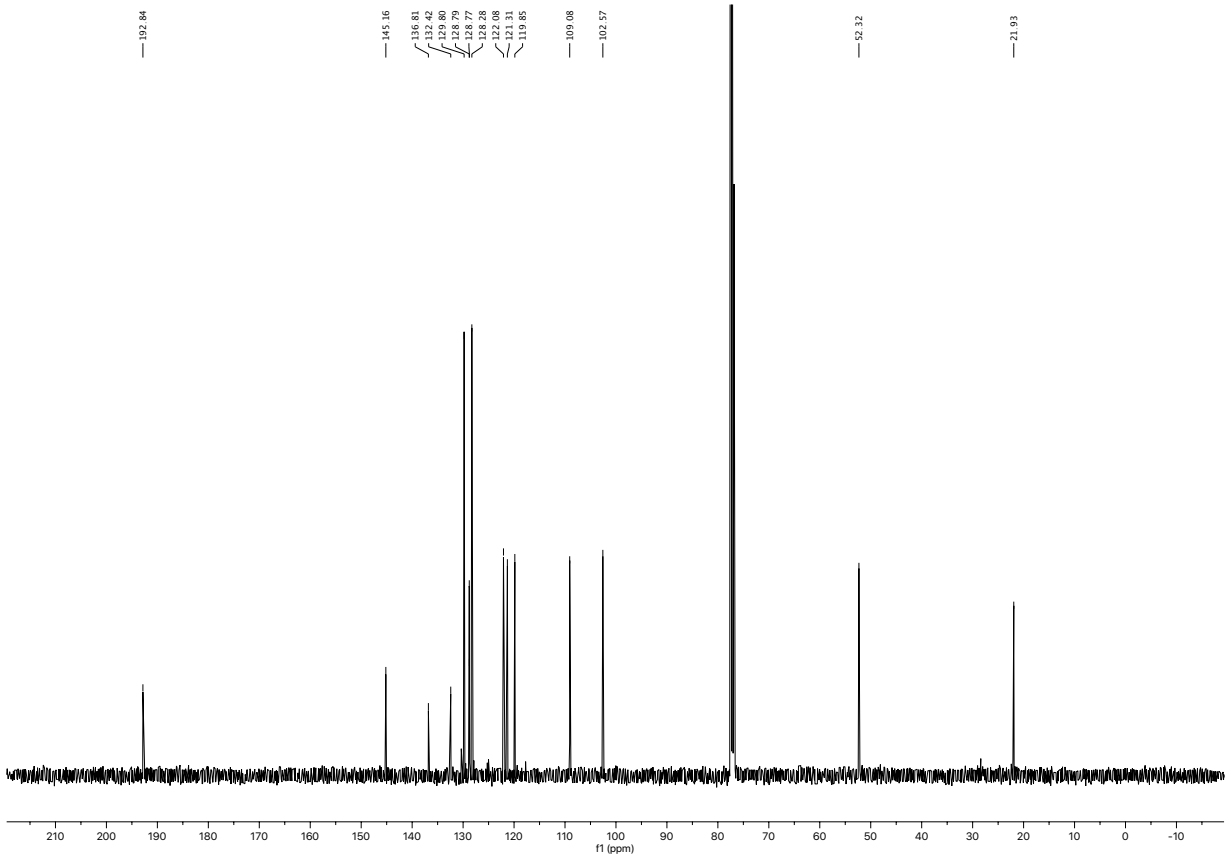
^{1}H NMR (500 MHz, $CDCl_3$) of known compound **SI10**.



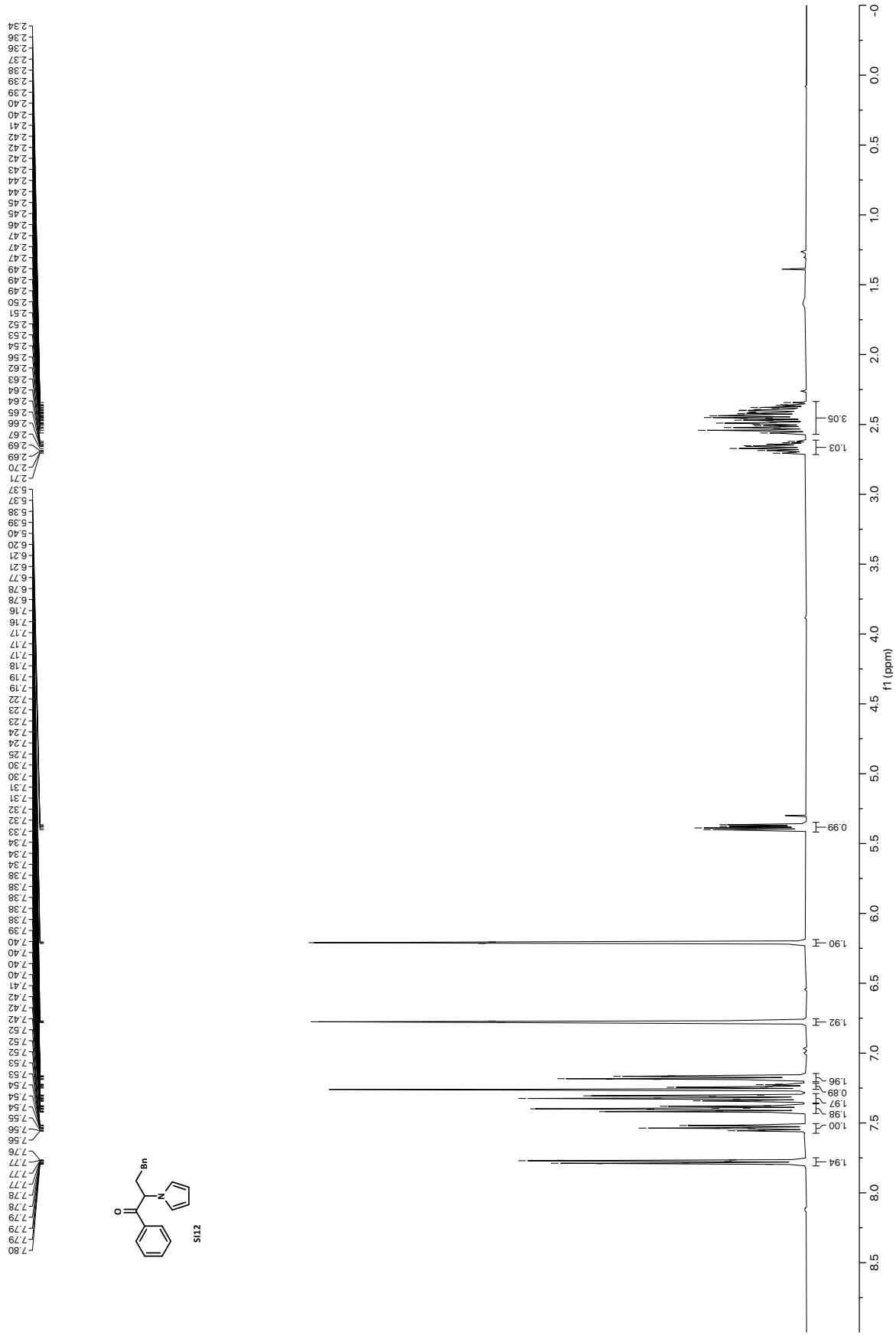
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI11**.



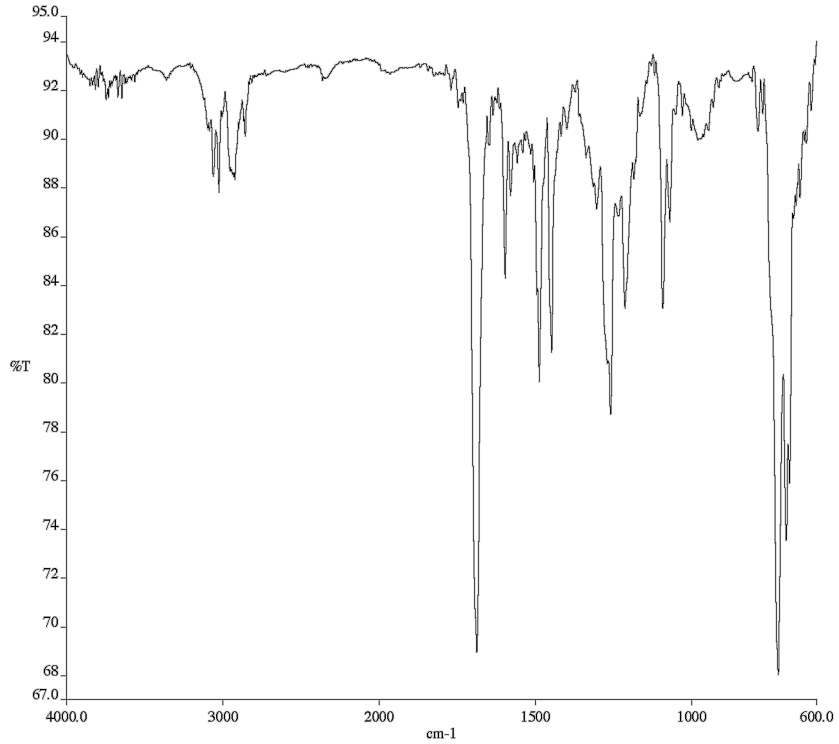
Infrared spectrum (Thin Film, NaCl) of compound **SI11**.



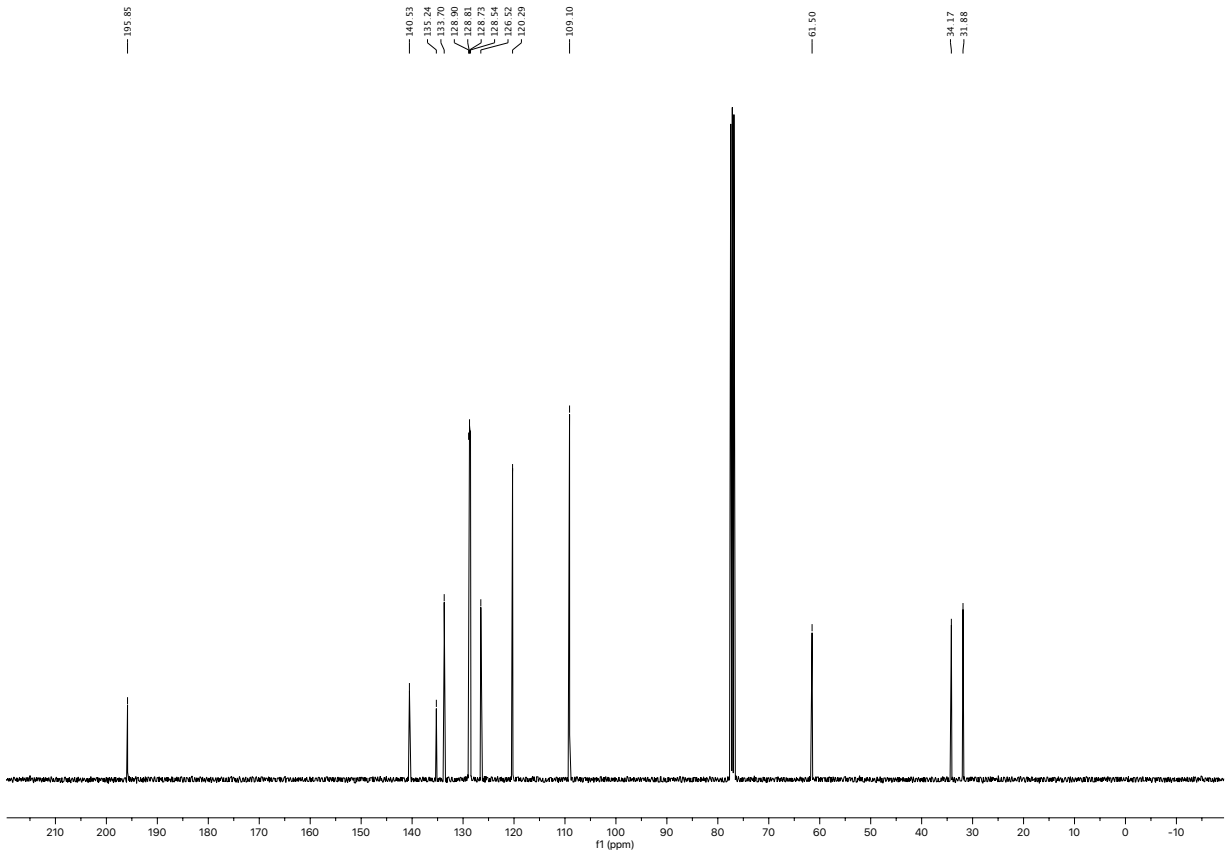
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI11**.



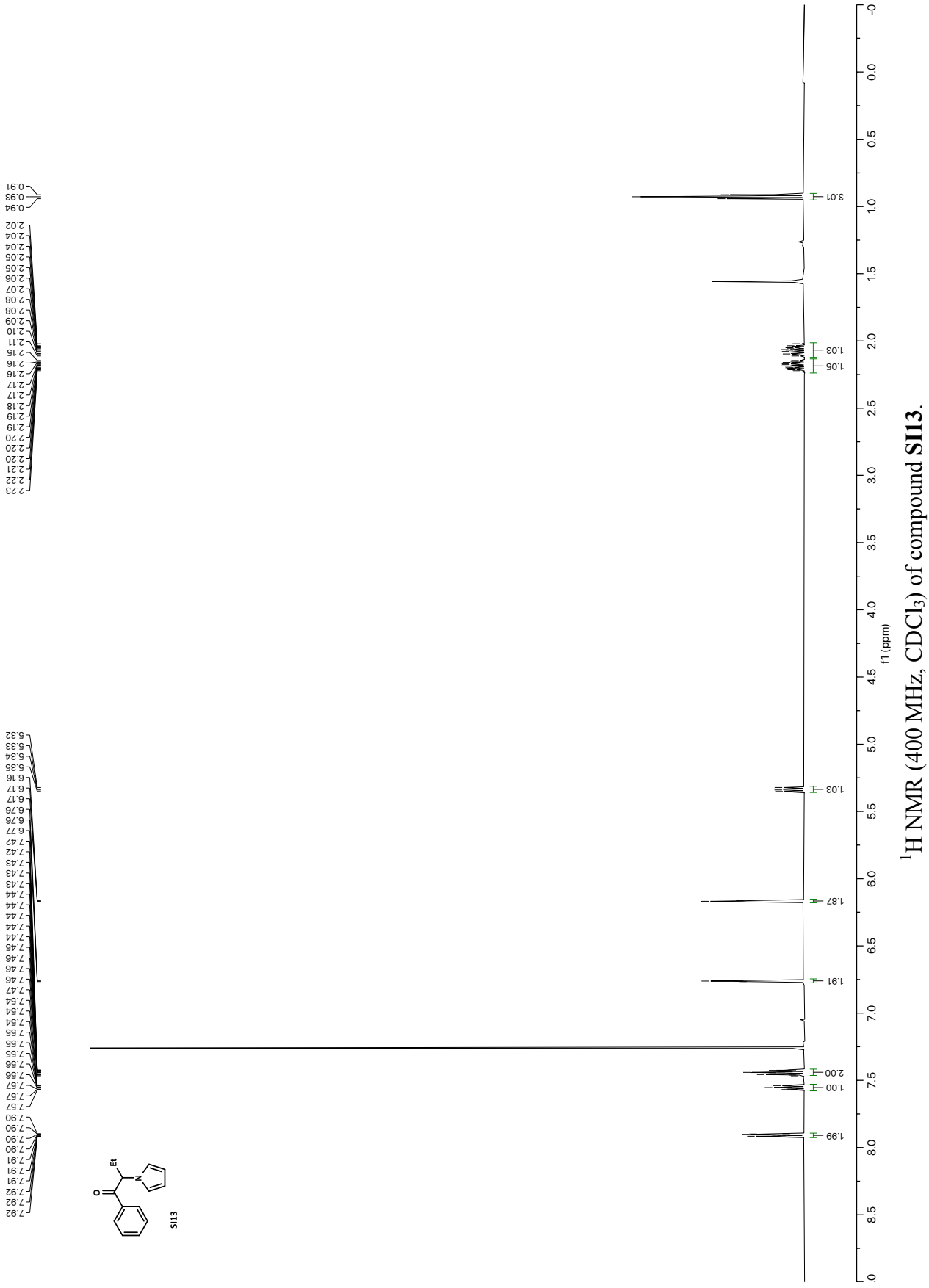
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI12**.



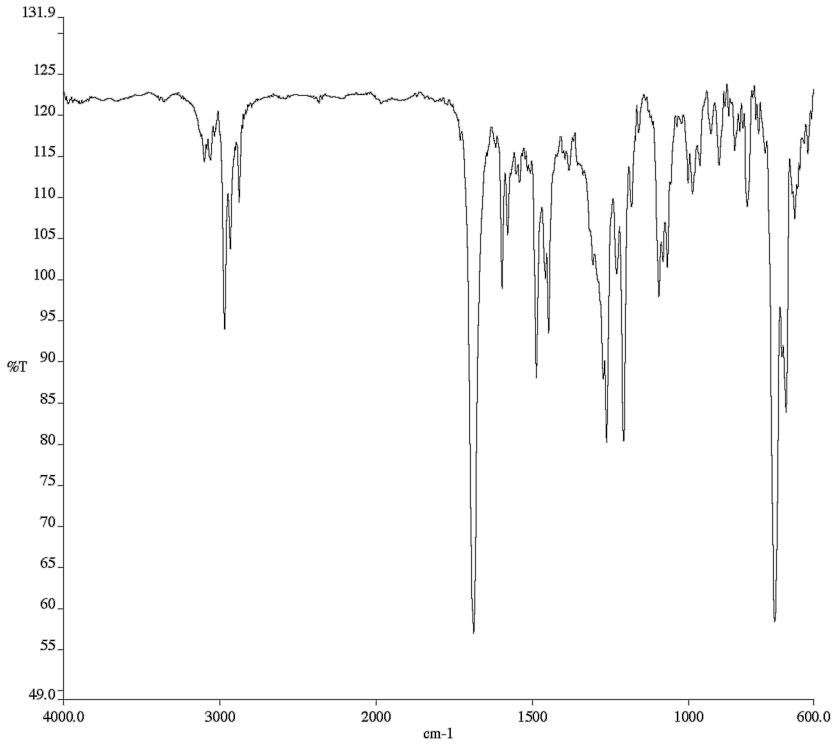
Infrared spectrum (Thin Film, NaCl) of compound **SI12**.



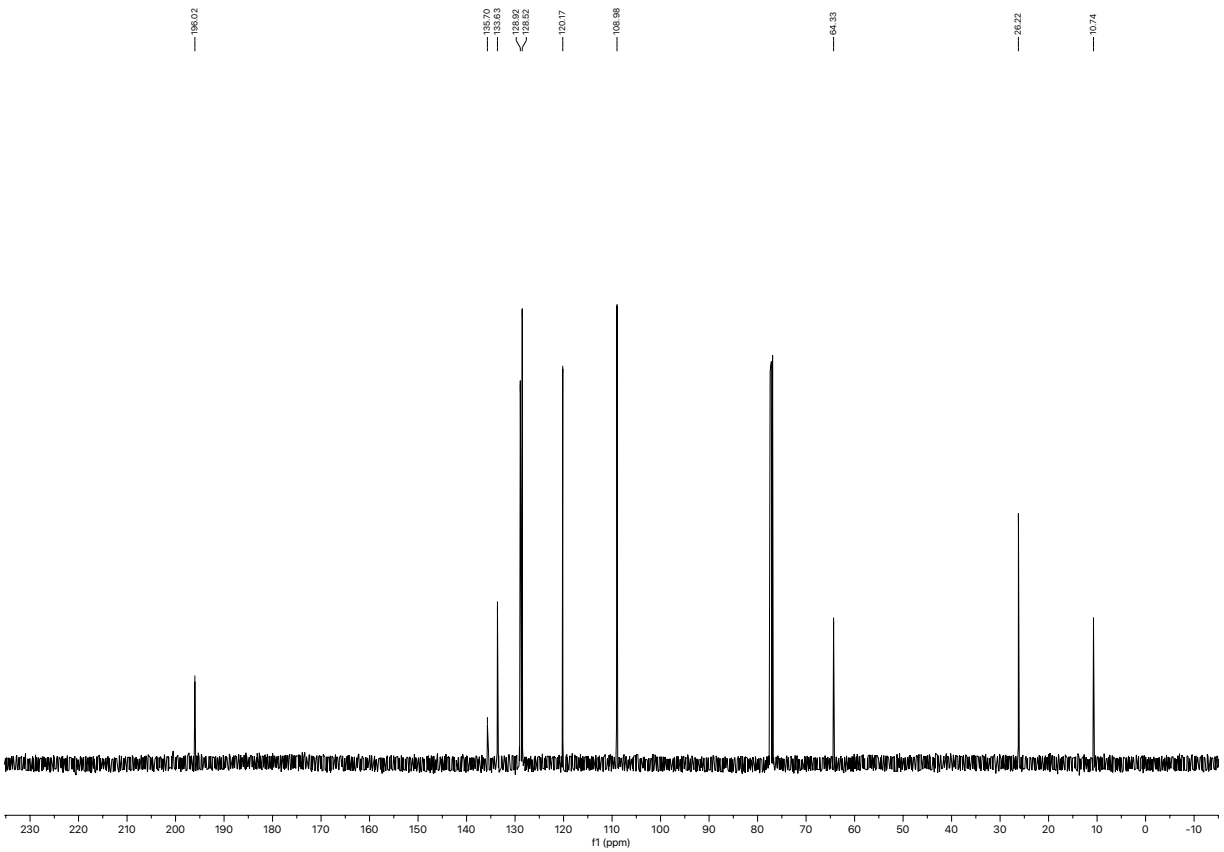
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI12**.



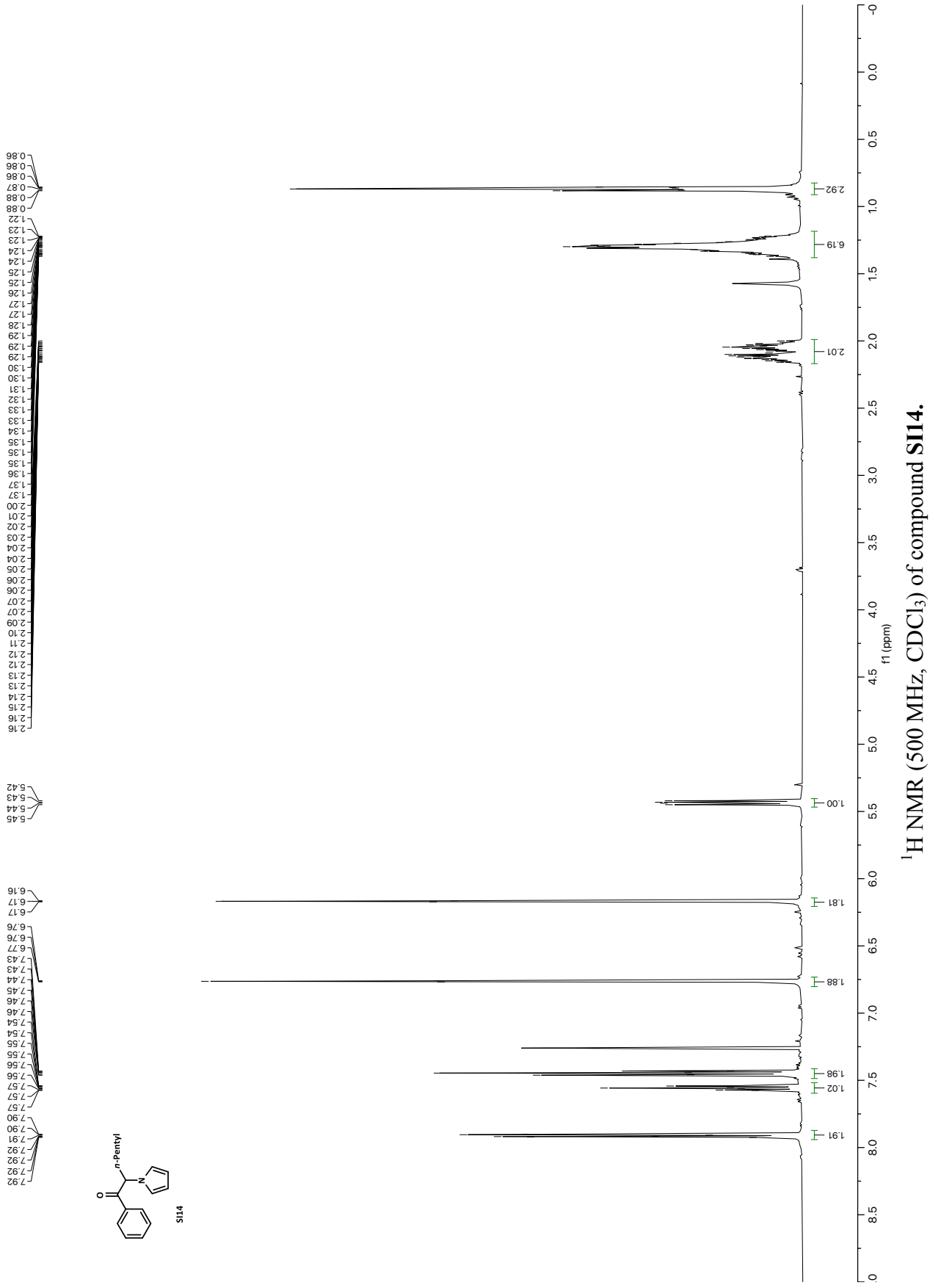
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI13**.



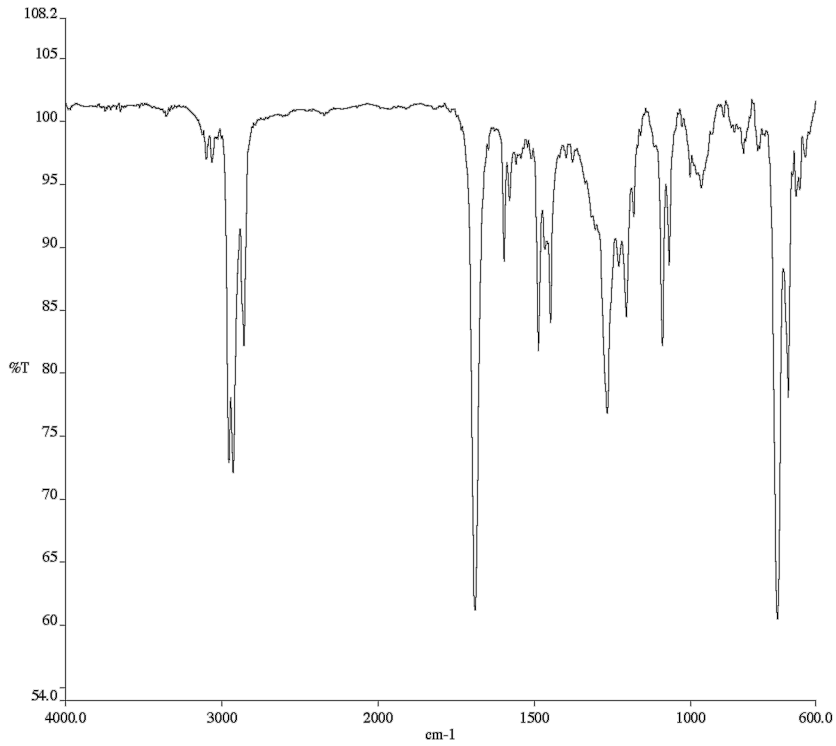
Infrared spectrum (Thin Film, NaCl) of compound **SI13**.



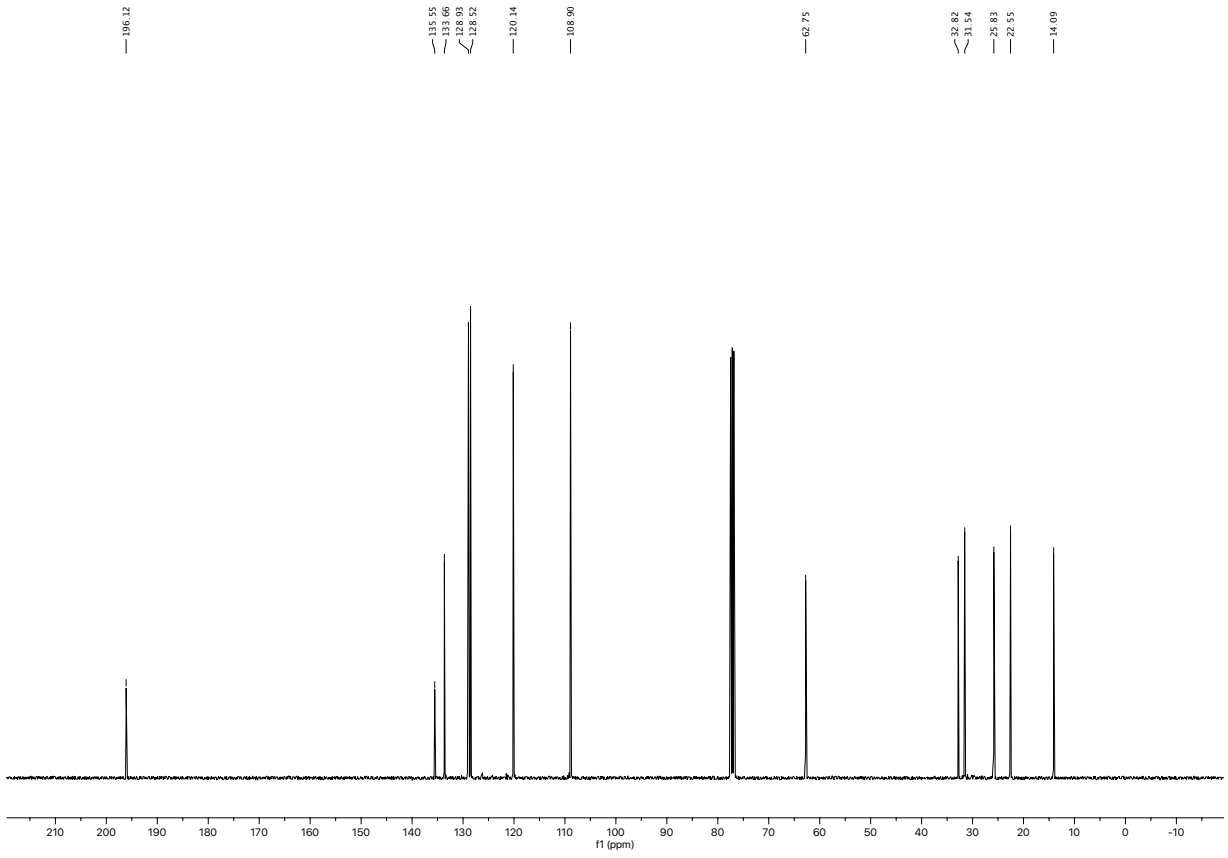
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI13**.



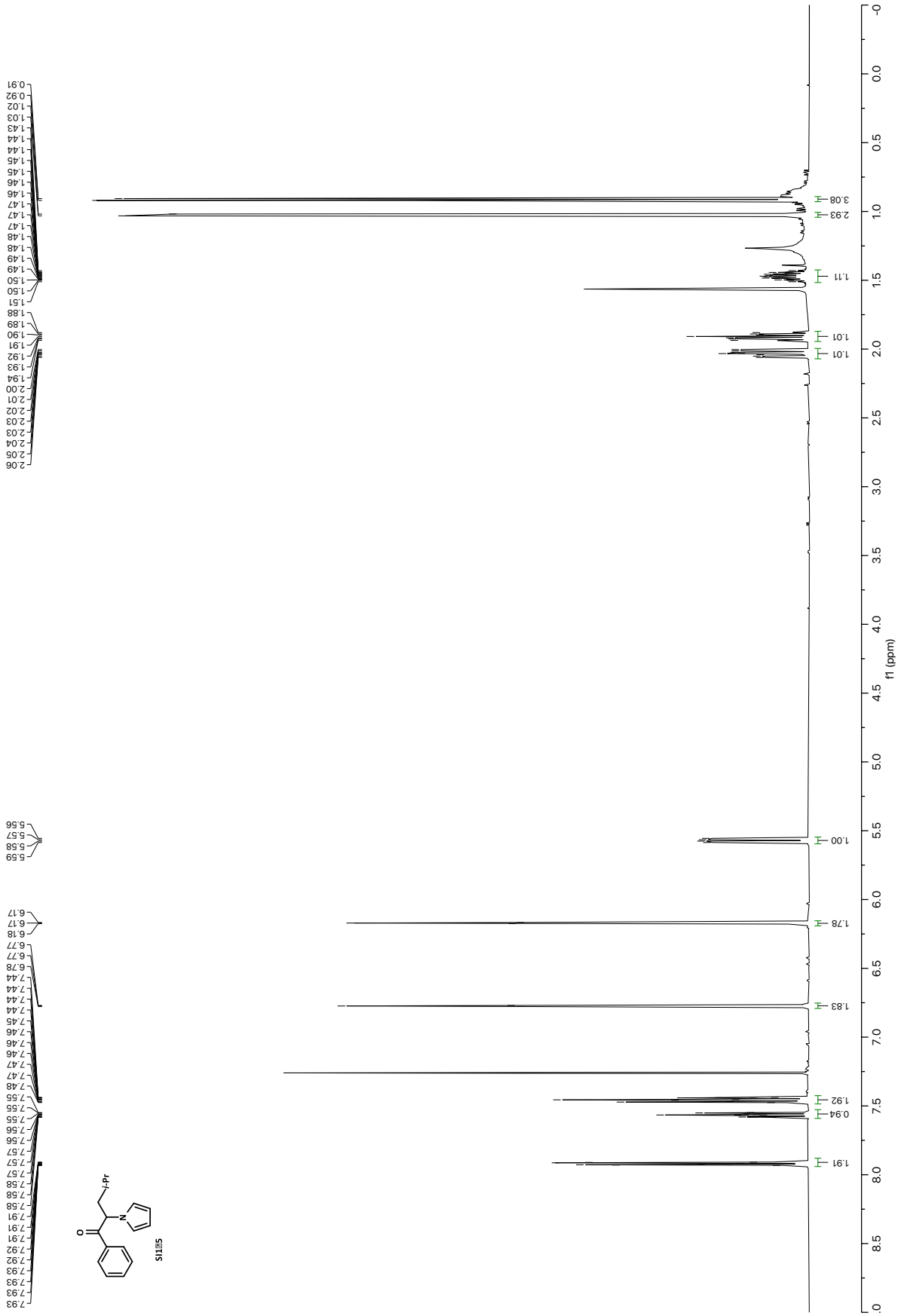
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI14.**



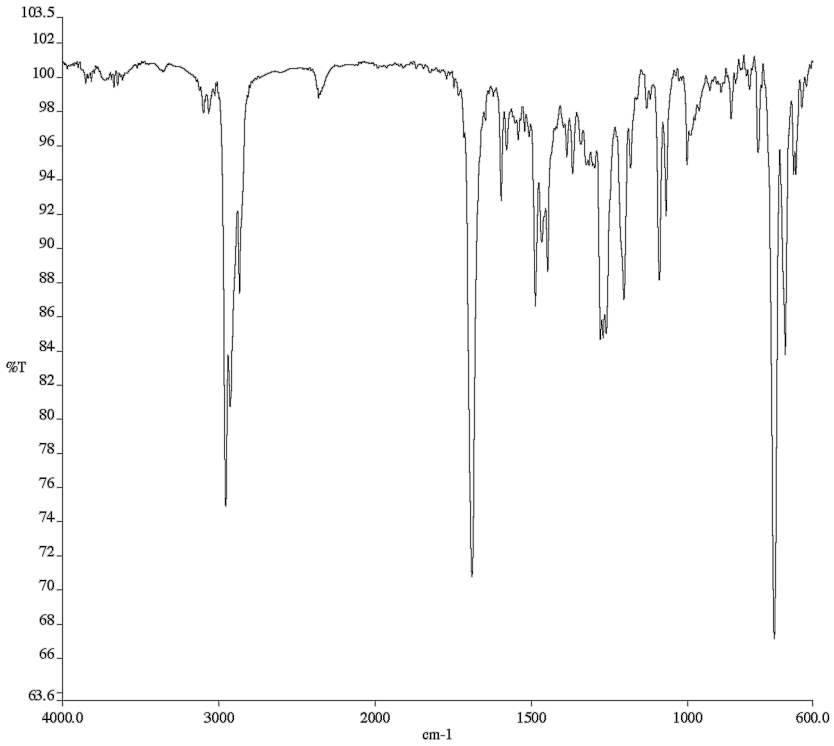
Infrared spectrum (Thin Film, NaCl) of compound **SI14**.



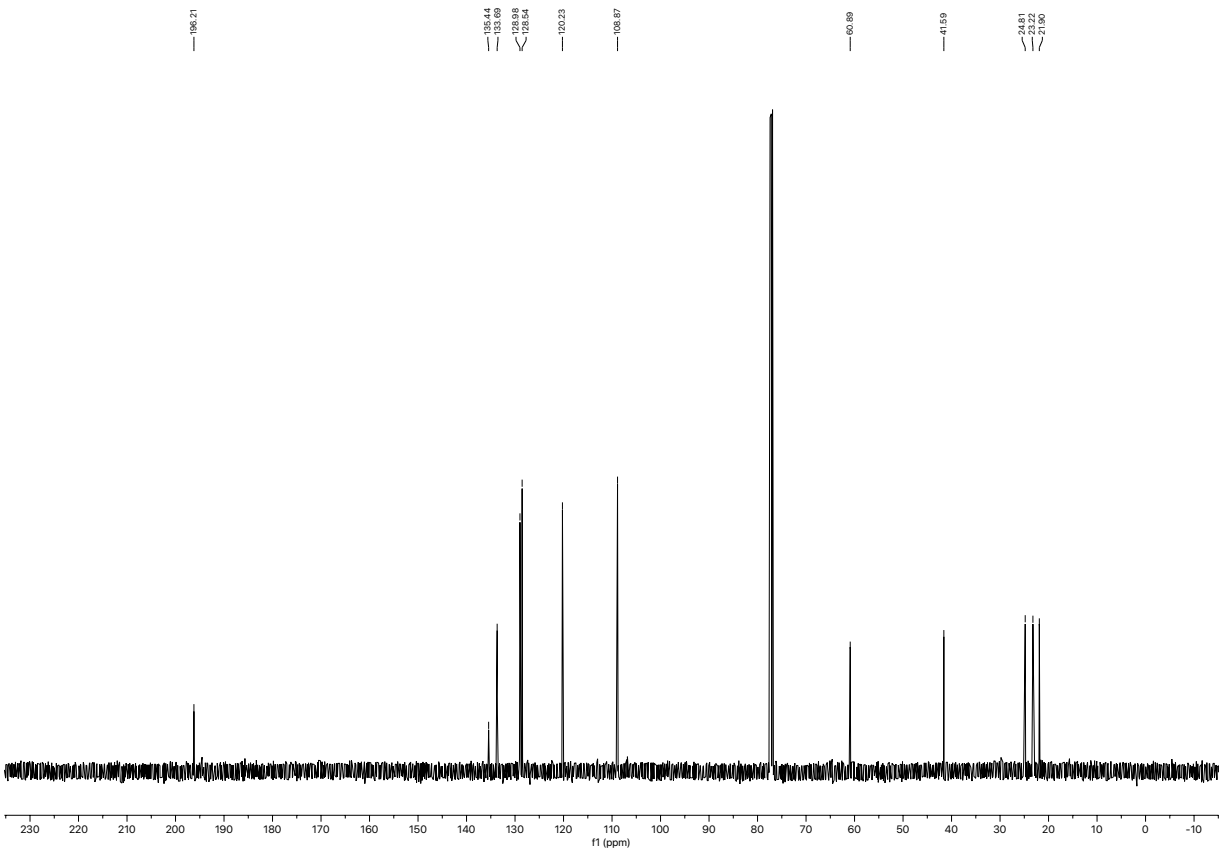
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI14**.



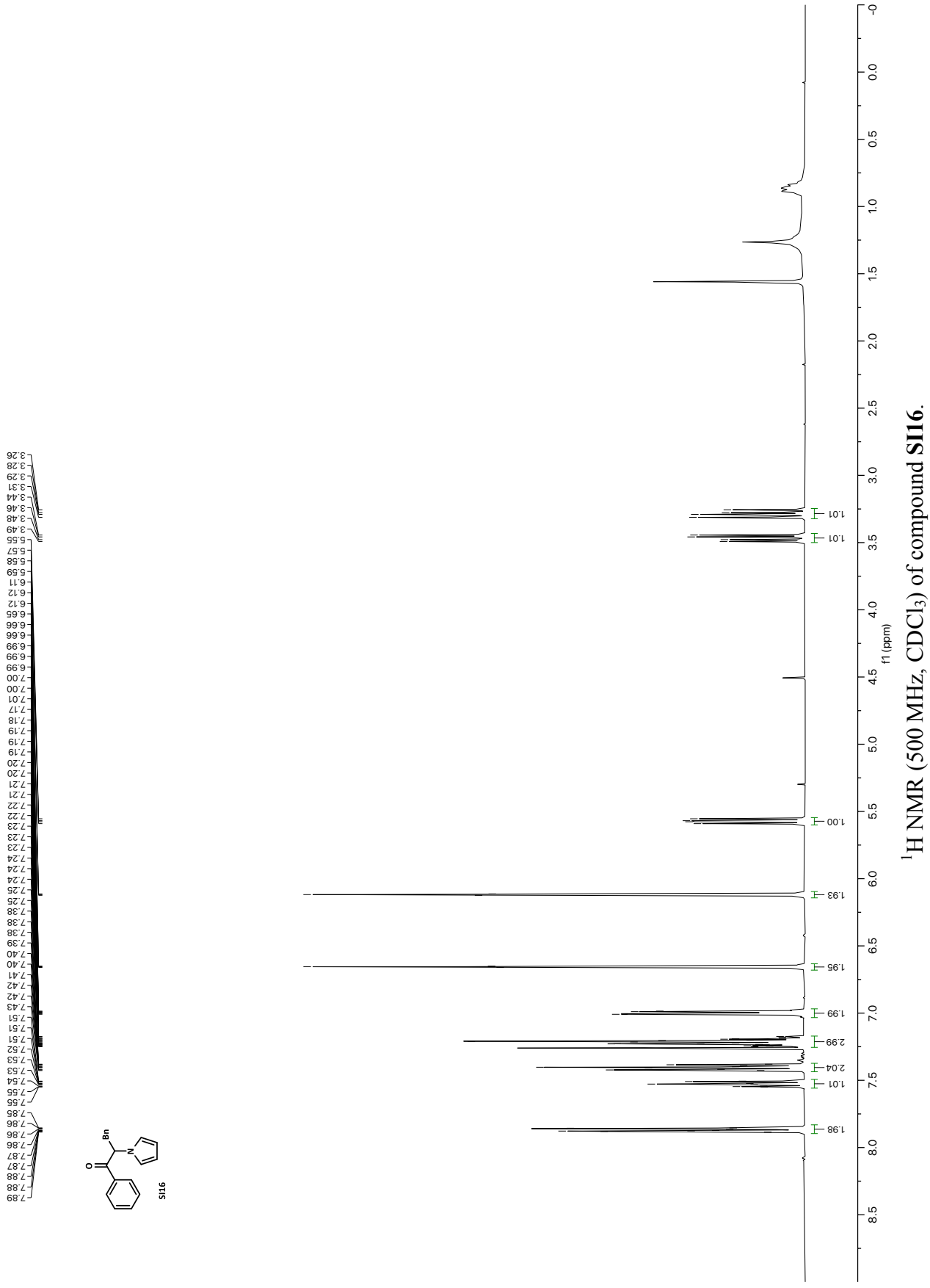
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI15**.



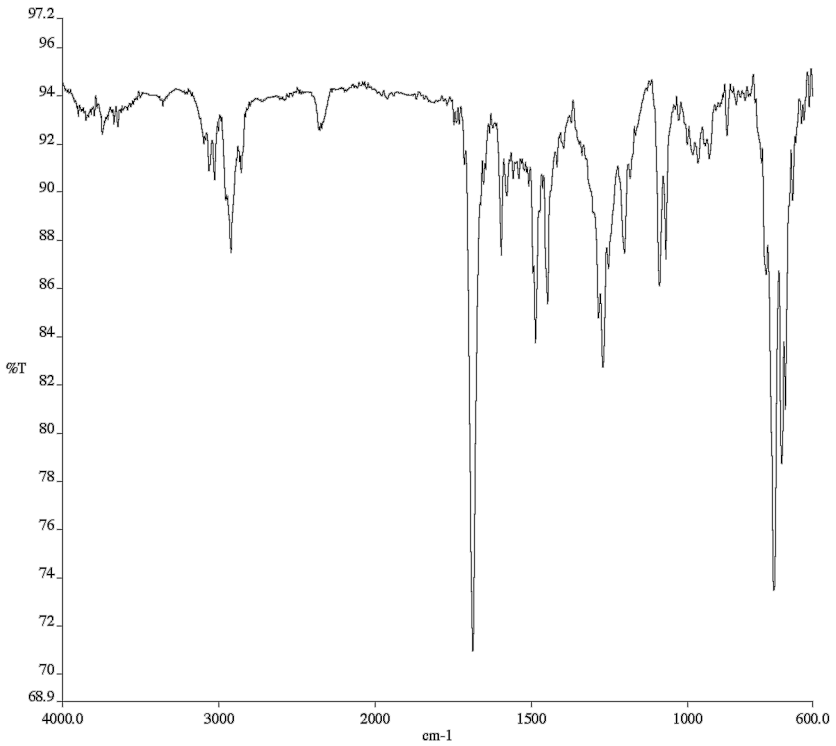
Infrared spectrum (Thin Film, NaCl) of compound **SI15**.



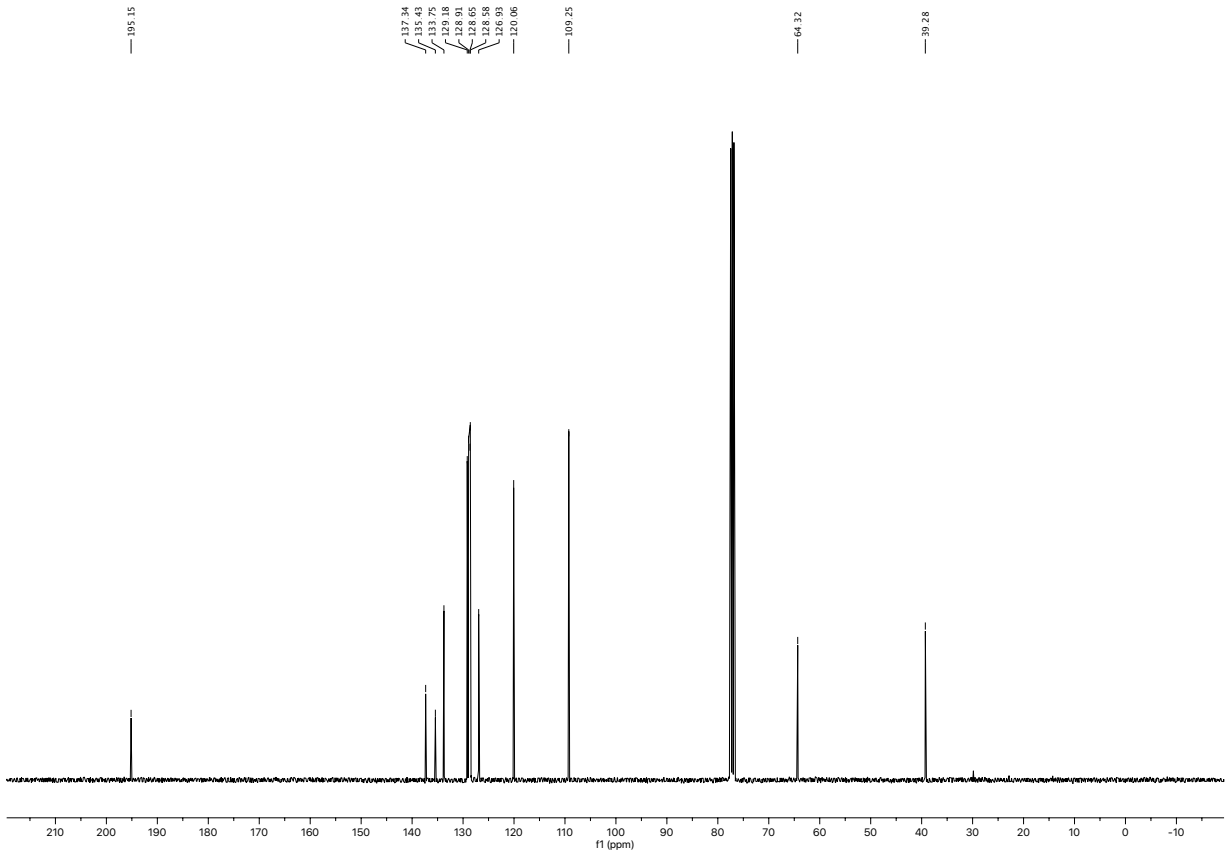
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI15**.



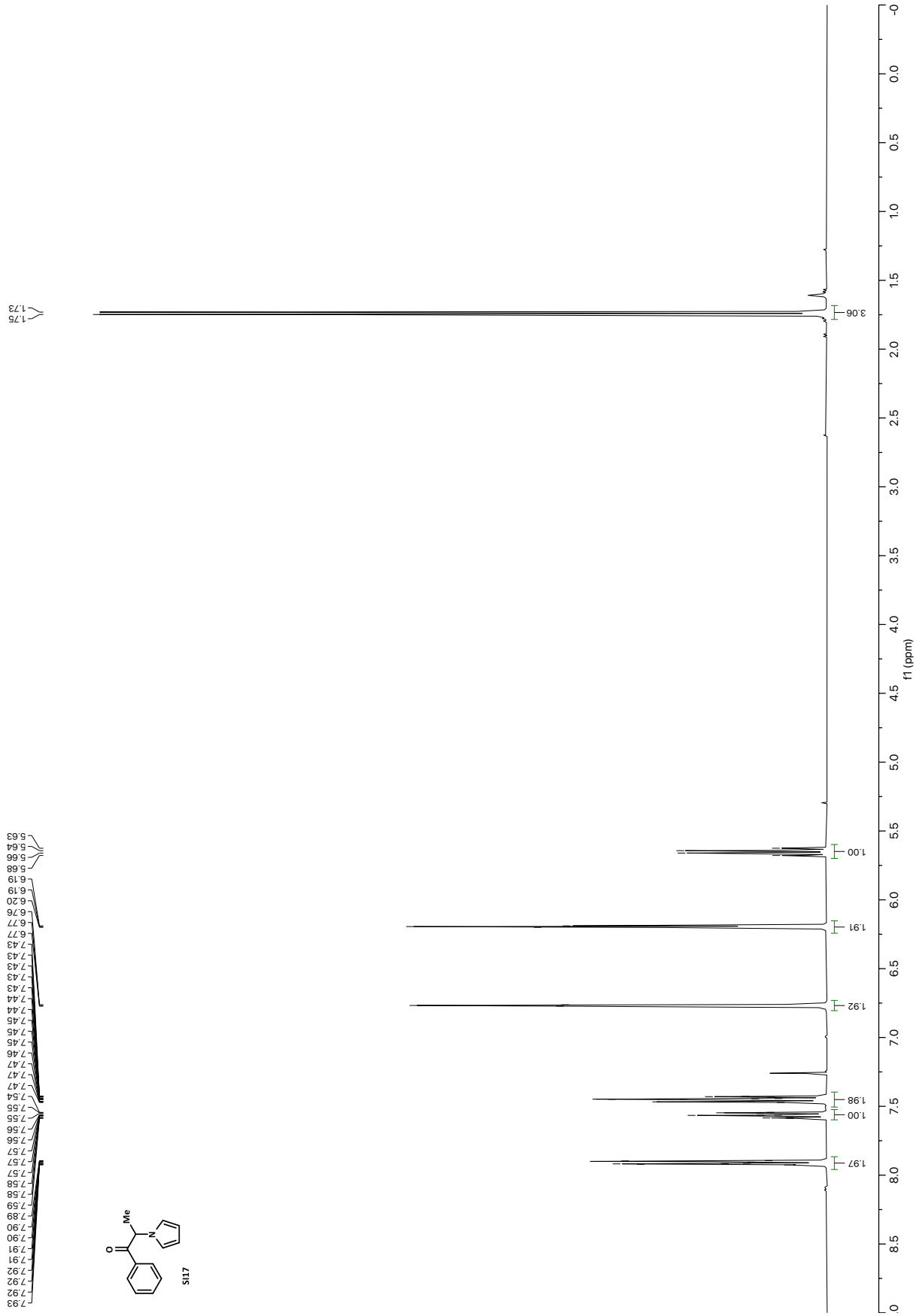
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI16**.



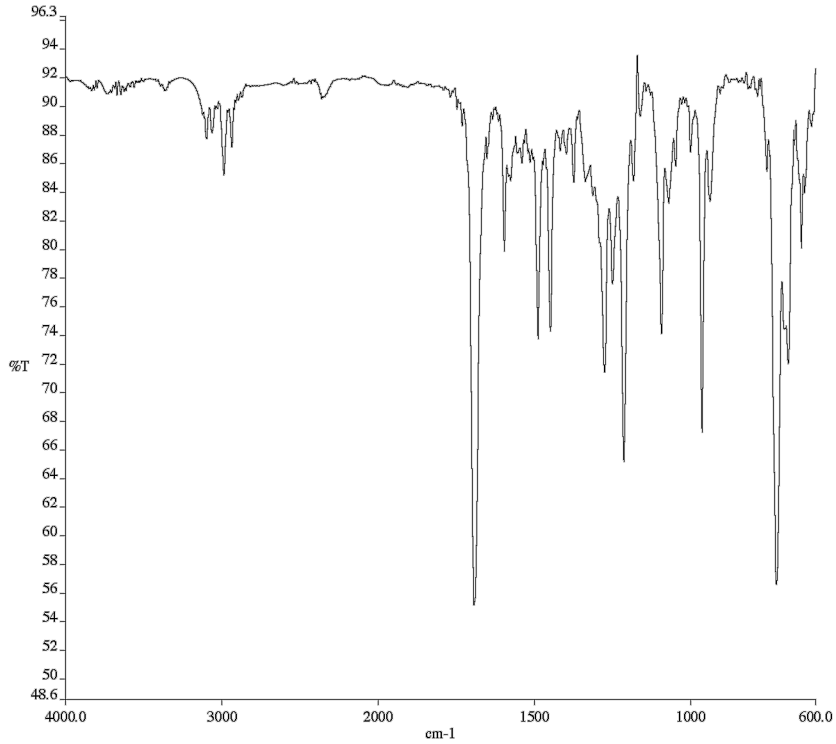
Infrared spectrum (Thin Film, NaCl) of compound **SI16**.



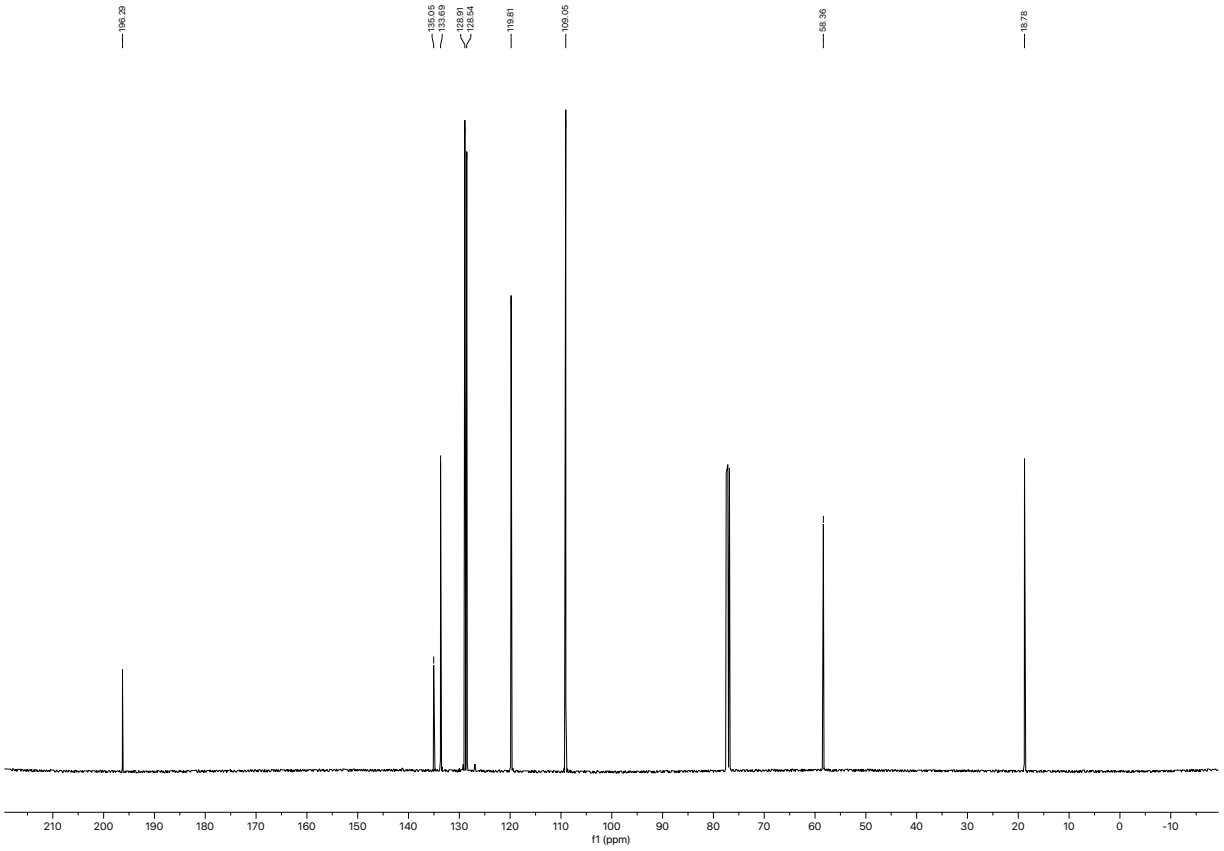
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI16**.



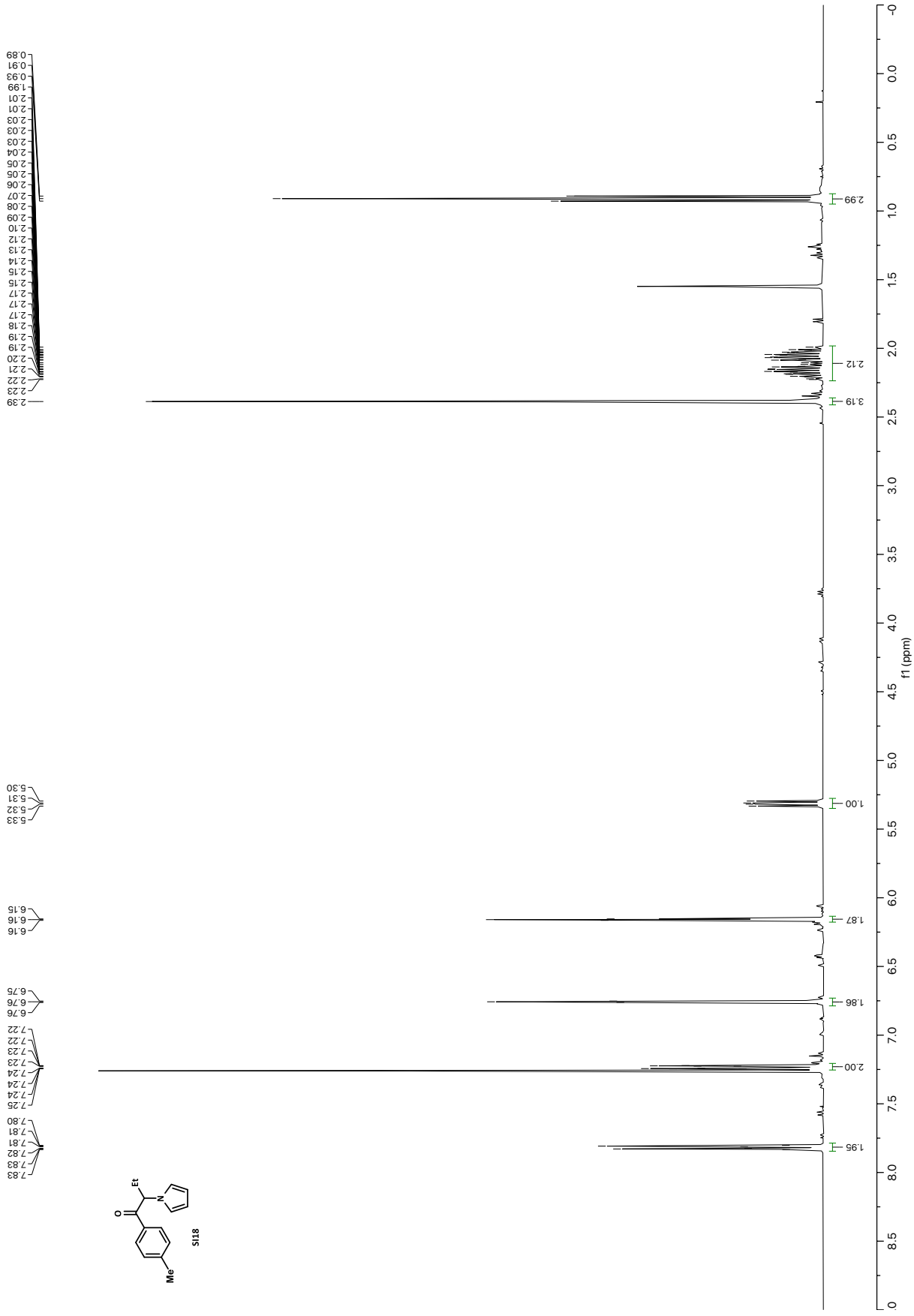
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI17**.



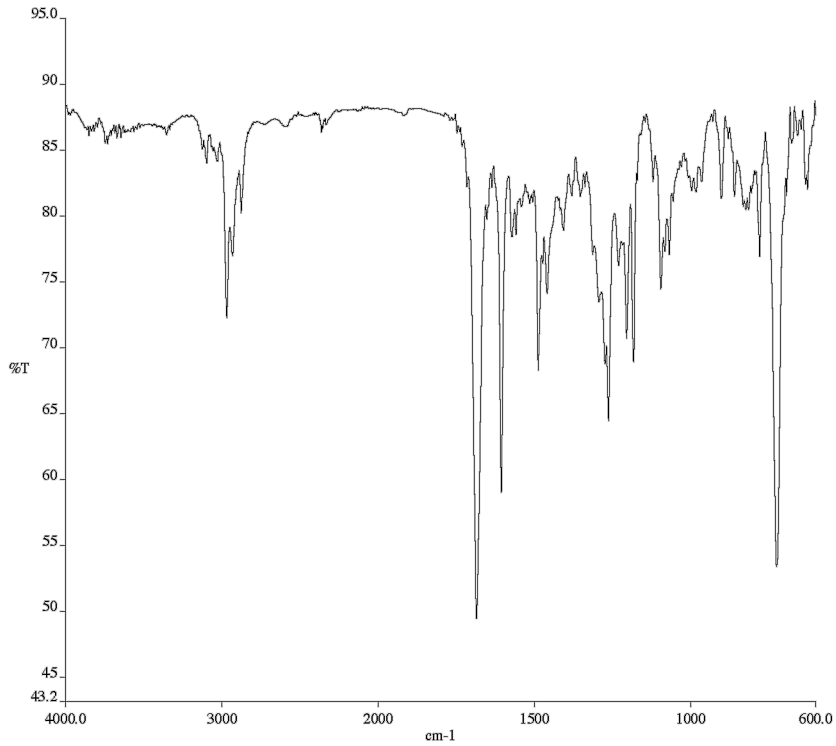
Infrared spectrum (Thin Film, NaCl) of compound **SI17**.



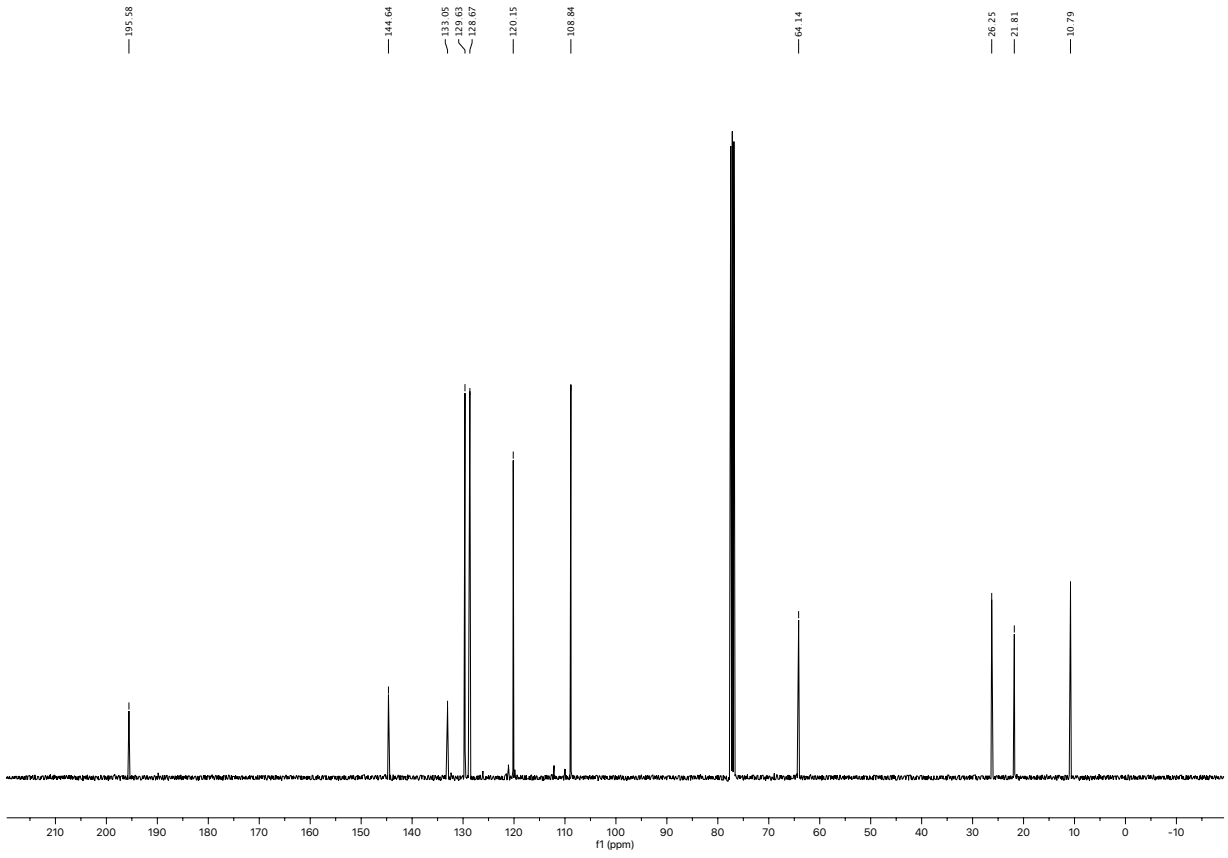
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI17**.



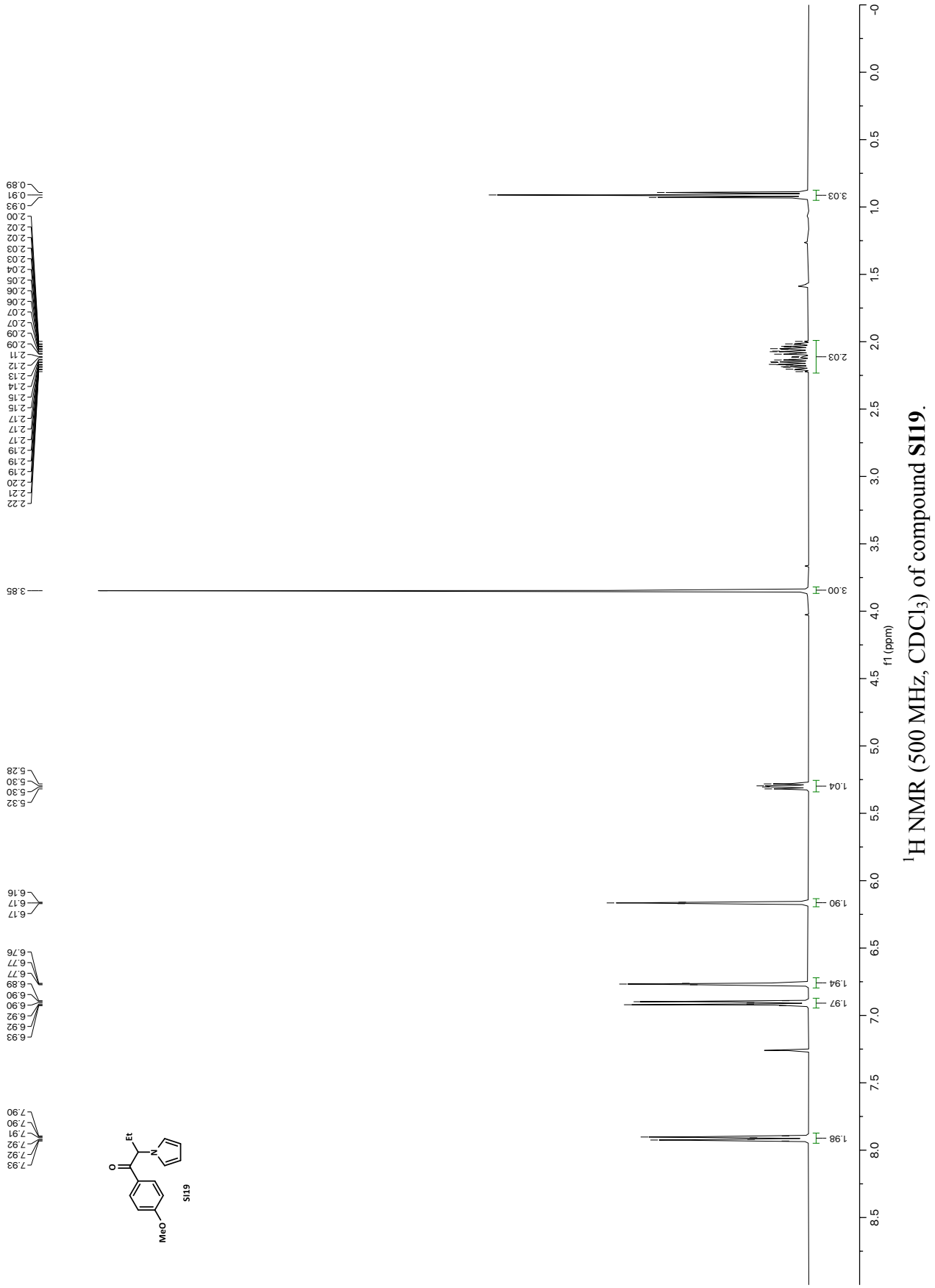
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI18**.



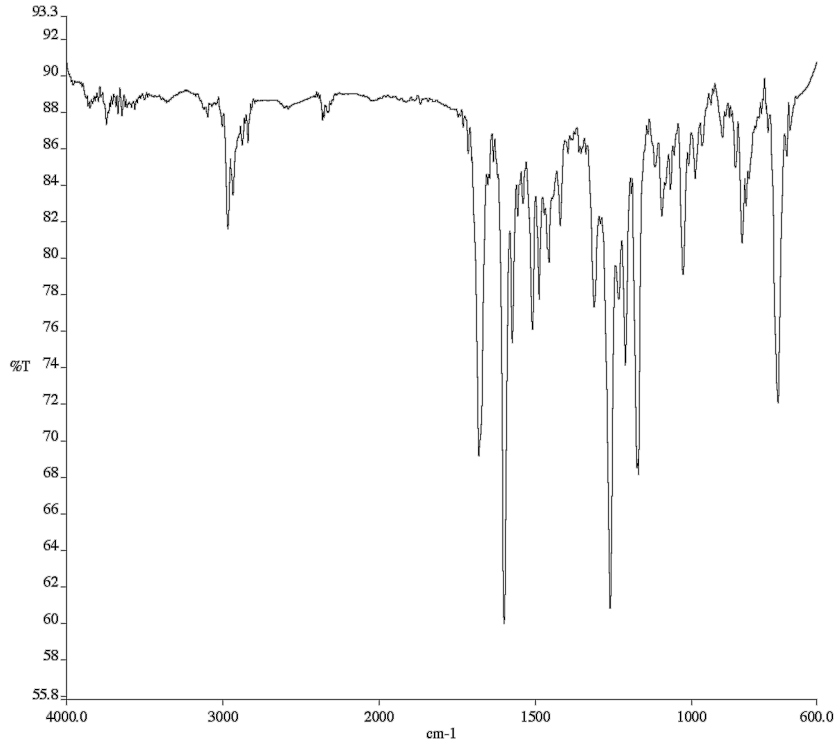
Infrared spectrum (Thin Film, NaCl) of compound **SI18**.



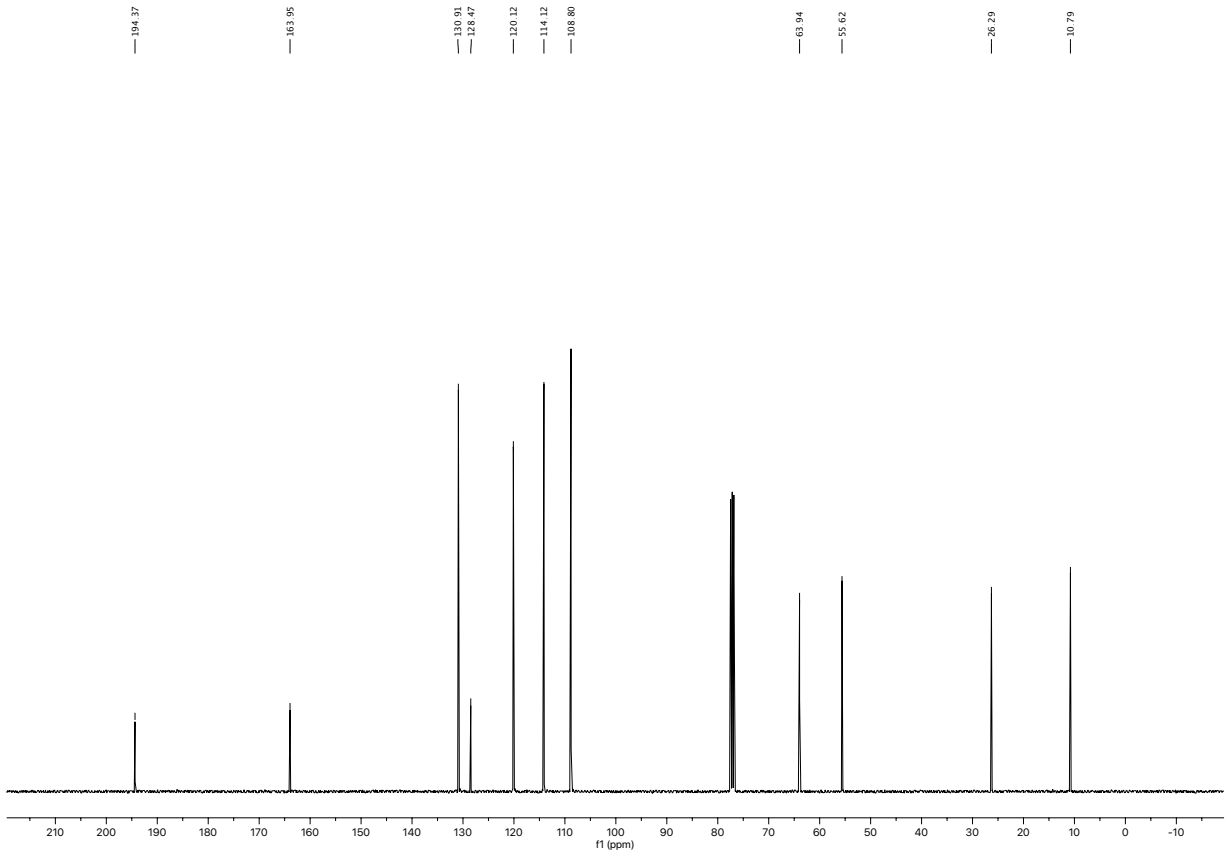
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI18**.



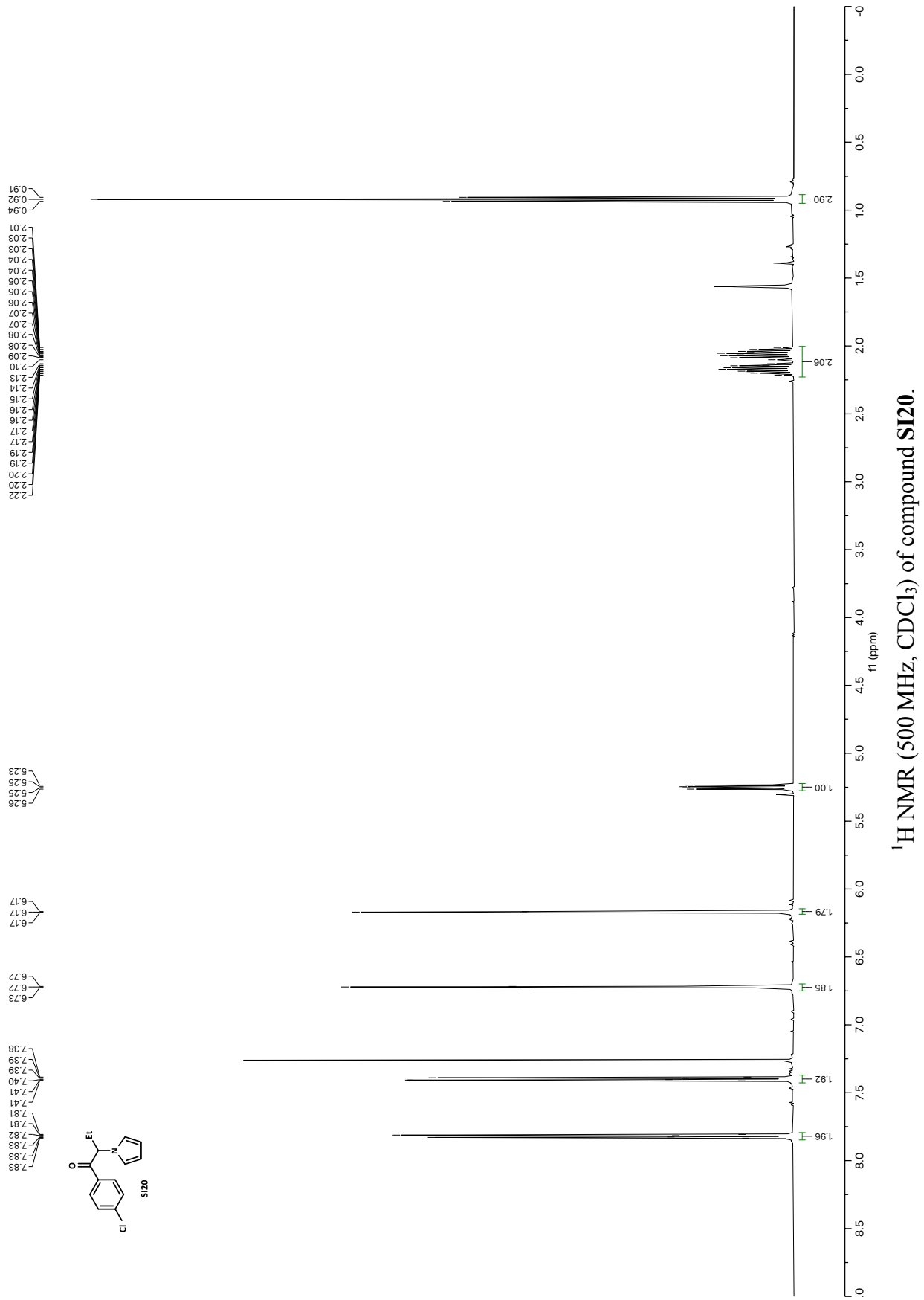
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI19**.



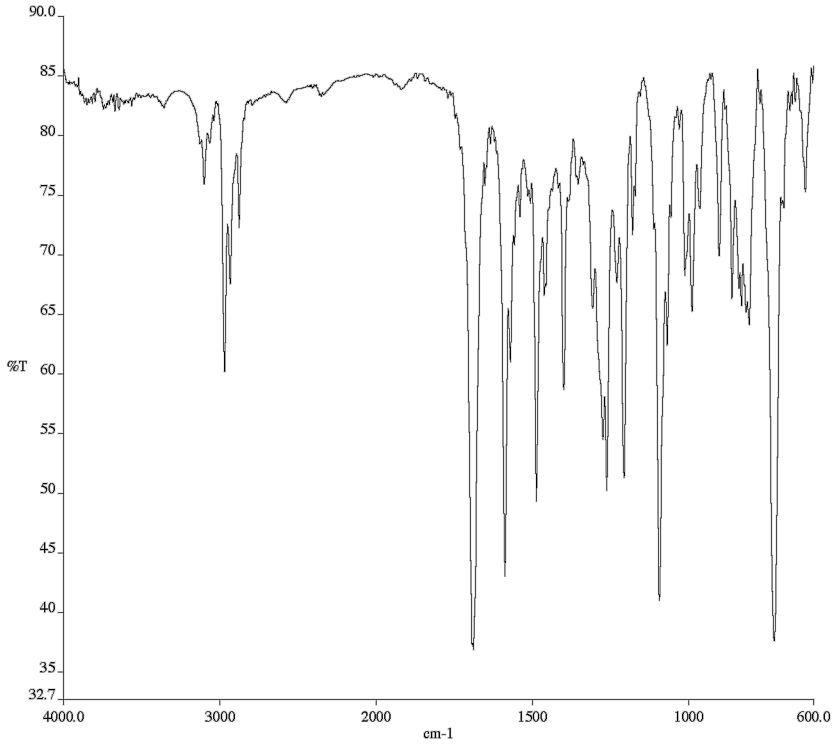
Infrared spectrum (Thin Film, NaCl) of compound **SI19**.



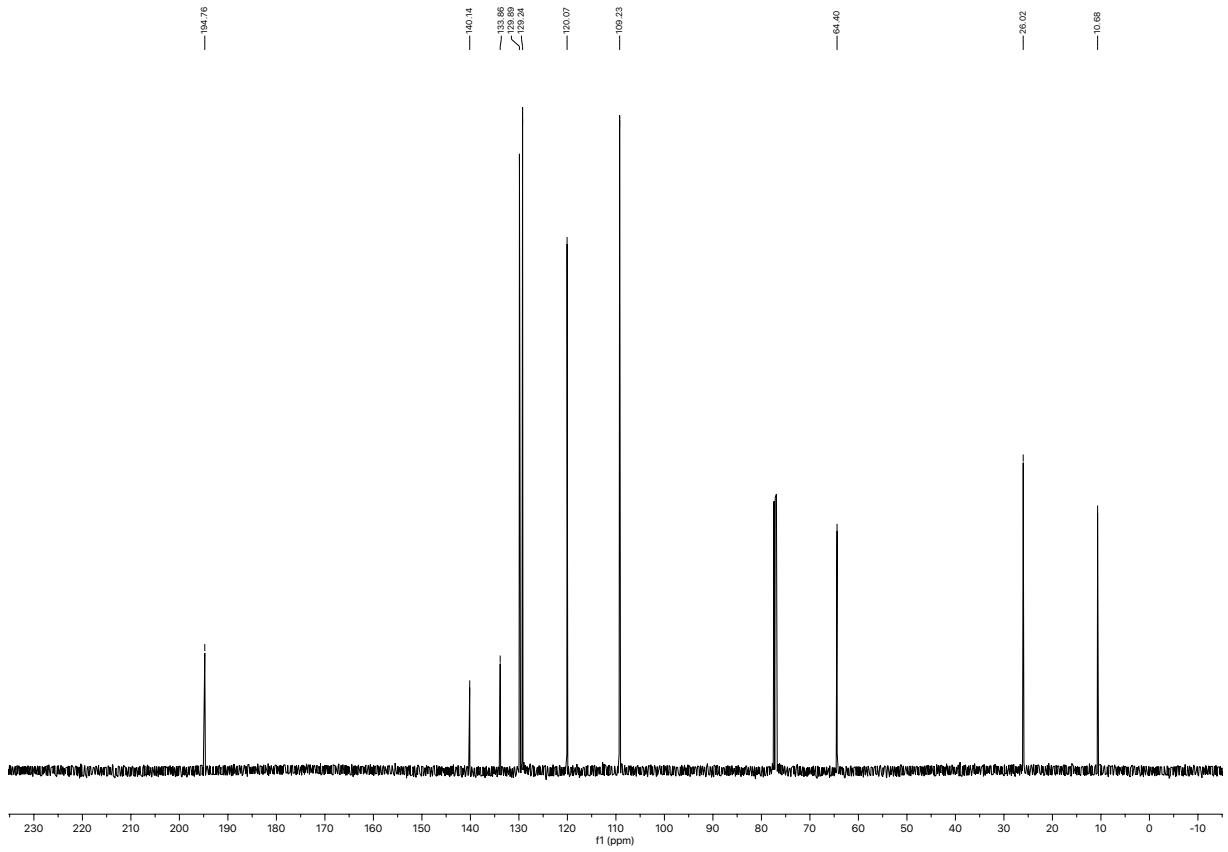
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI19**.



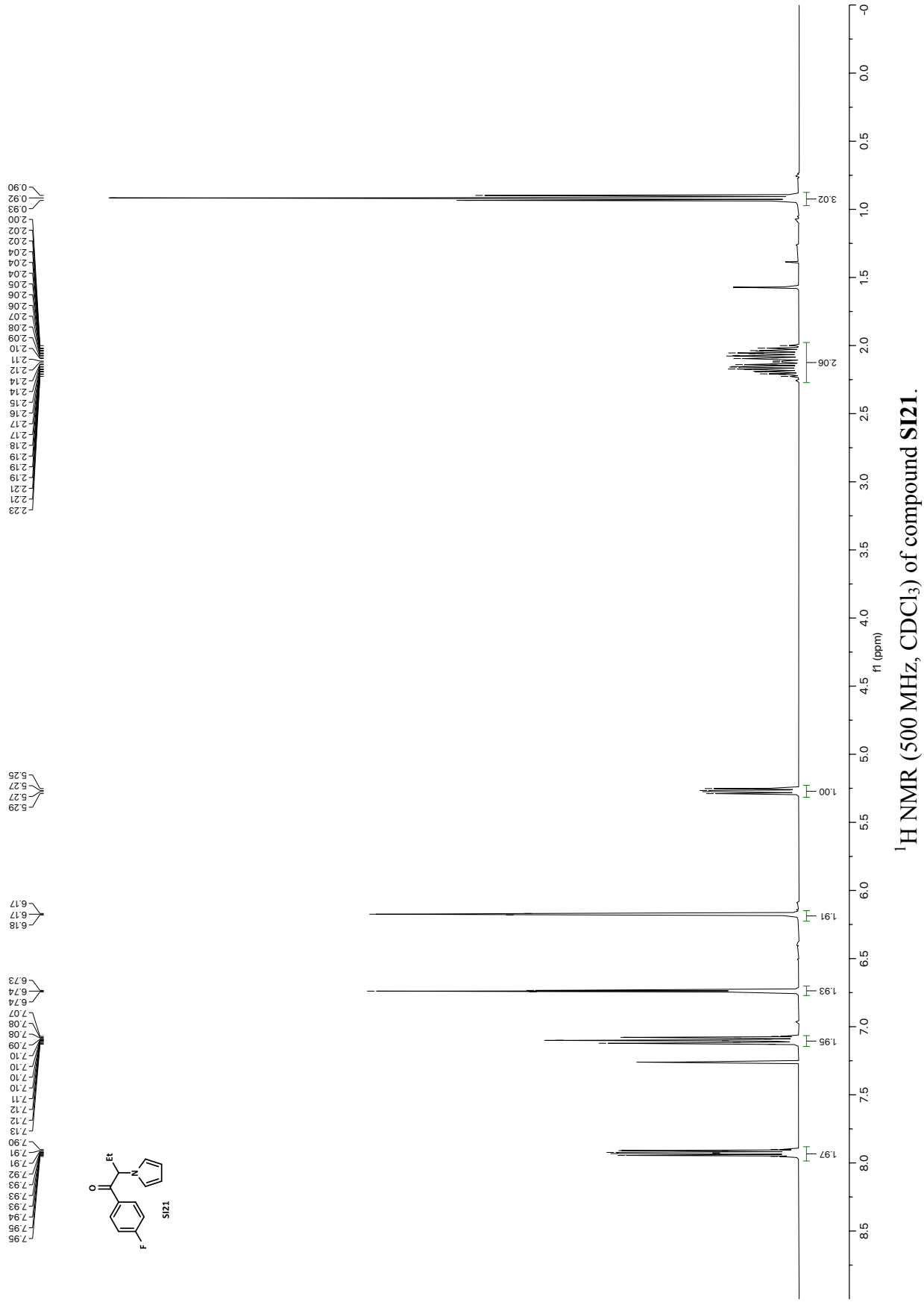
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI20**.



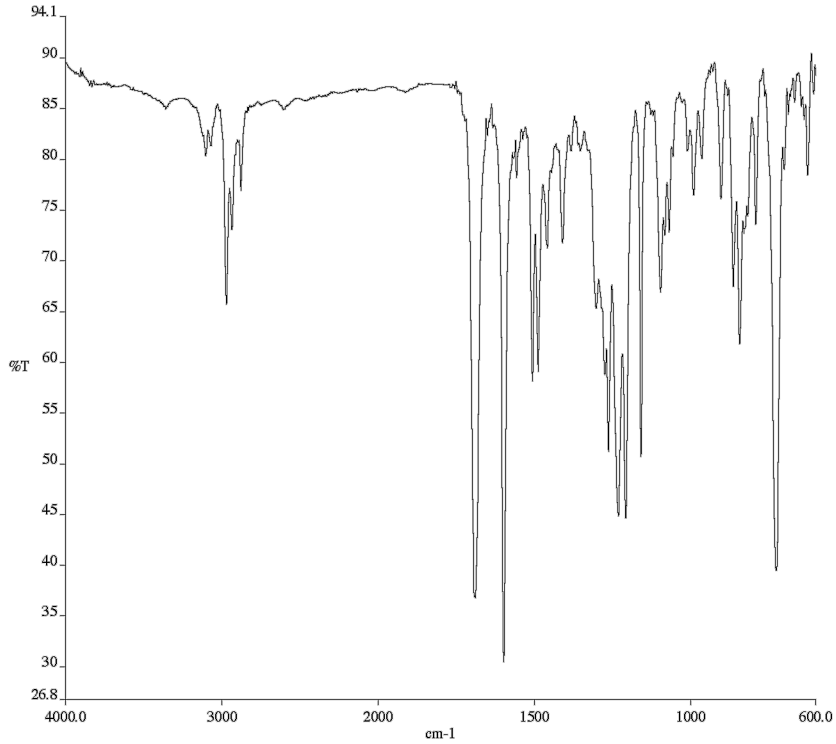
Infrared spectrum (Thin Film, NaCl) of compound **SI20**.



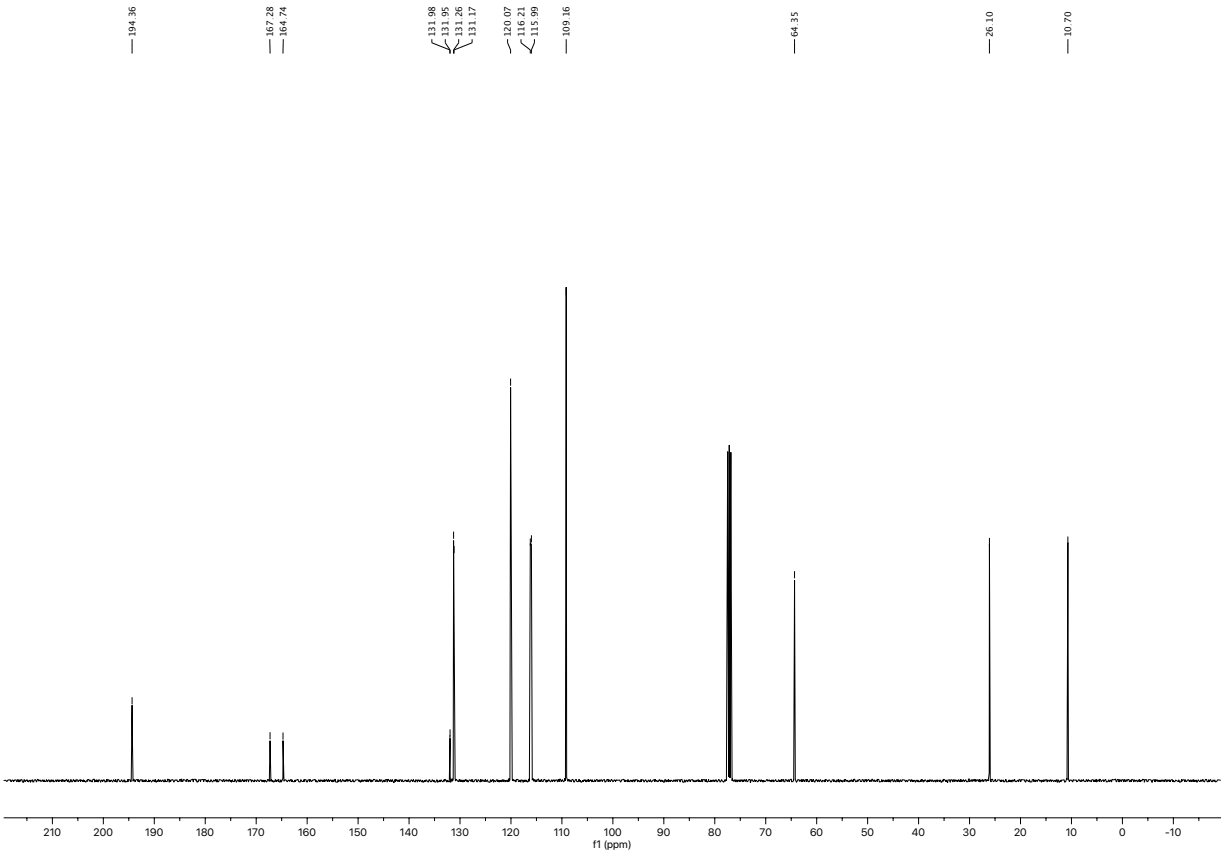
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI20**.



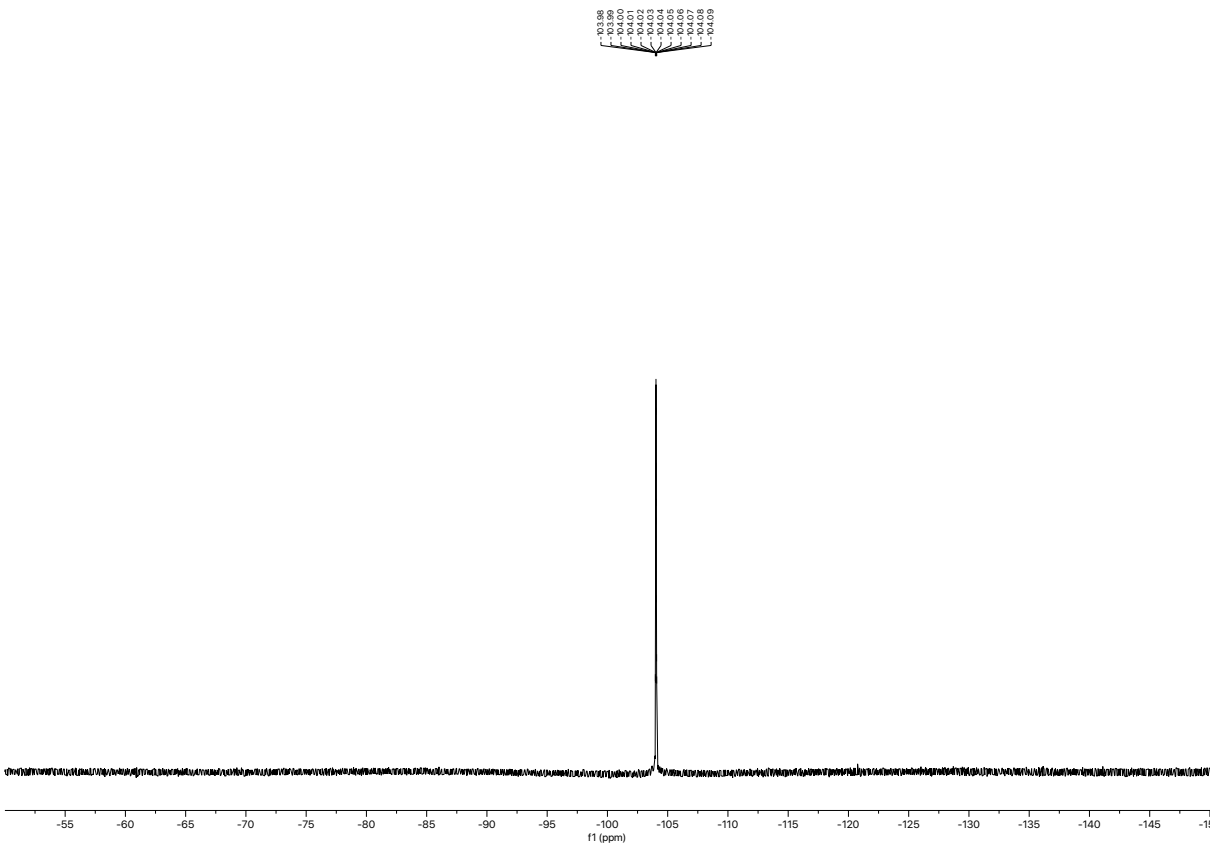
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI21**.



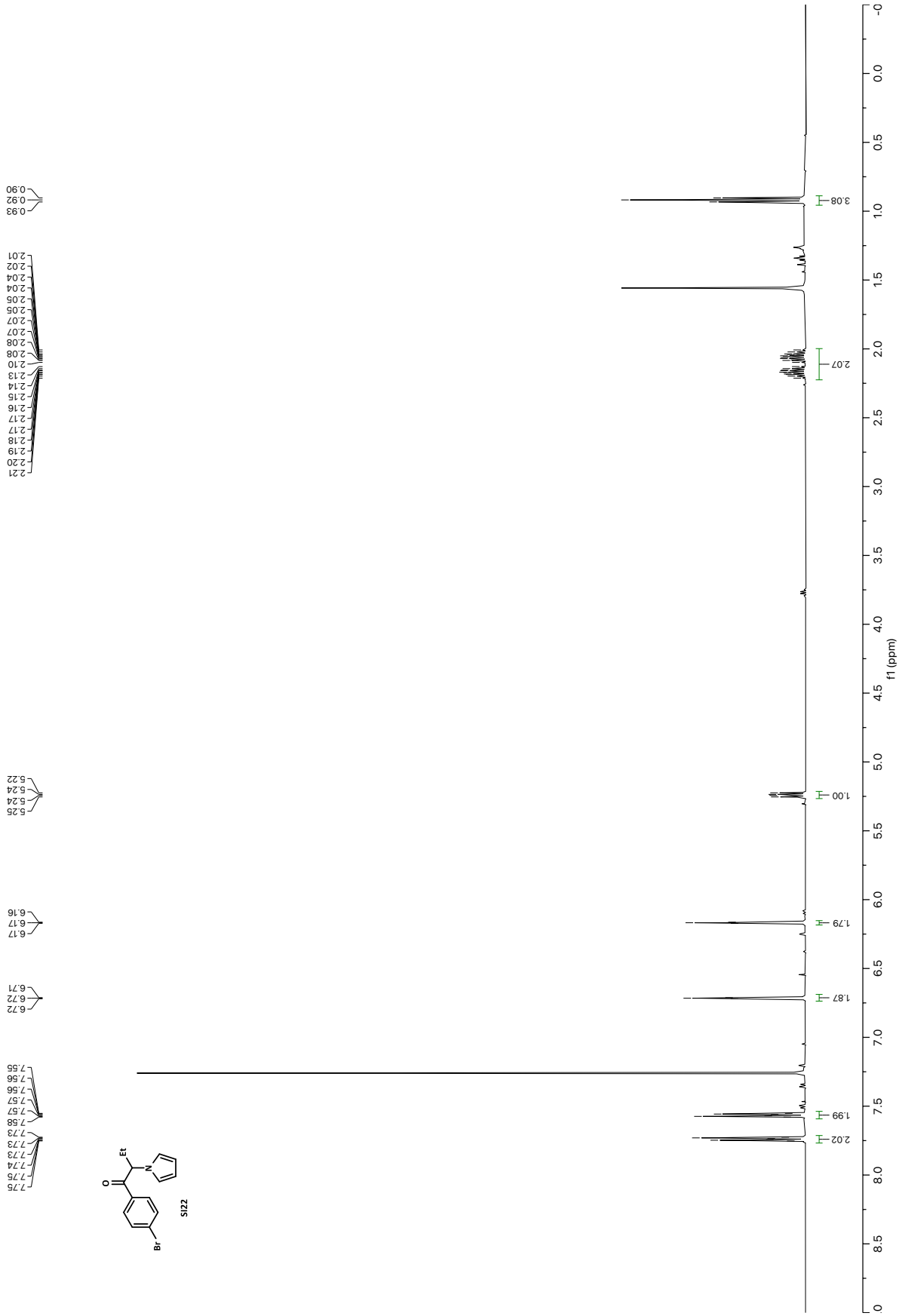
Infrared spectrum (Thin Film, NaCl) of compound **SI21**.



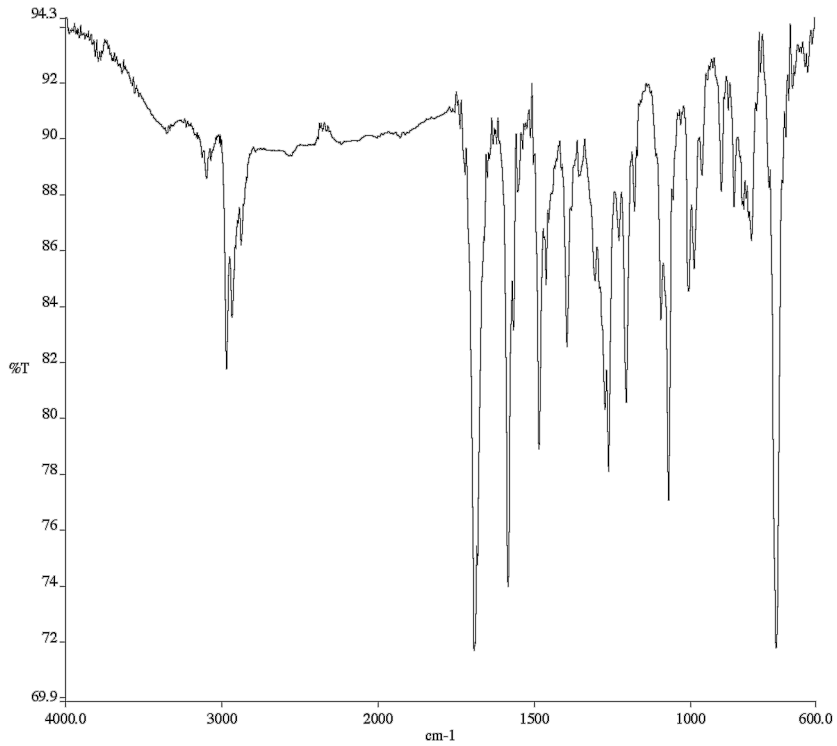
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI21**.



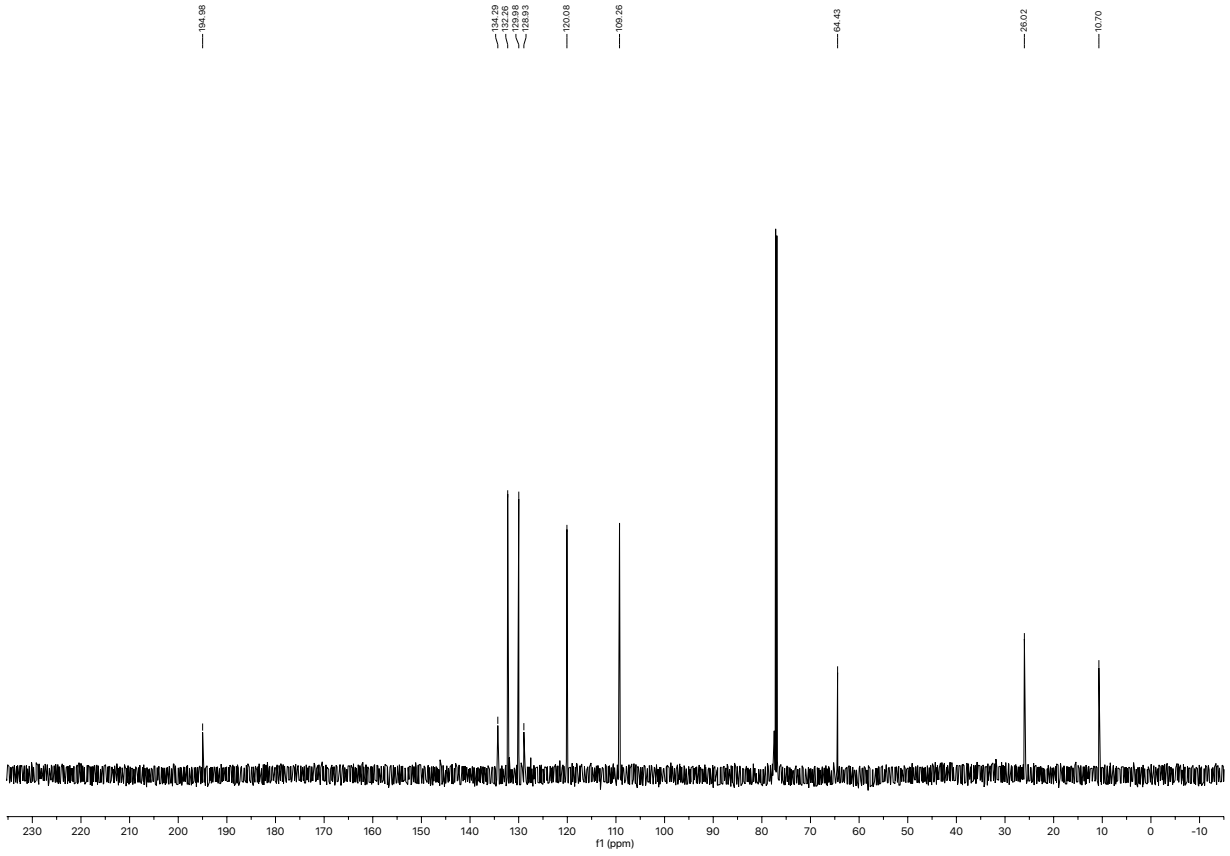
^{19}F NMR (282 MHz, $CDCl_3$) of compound **SI21.**



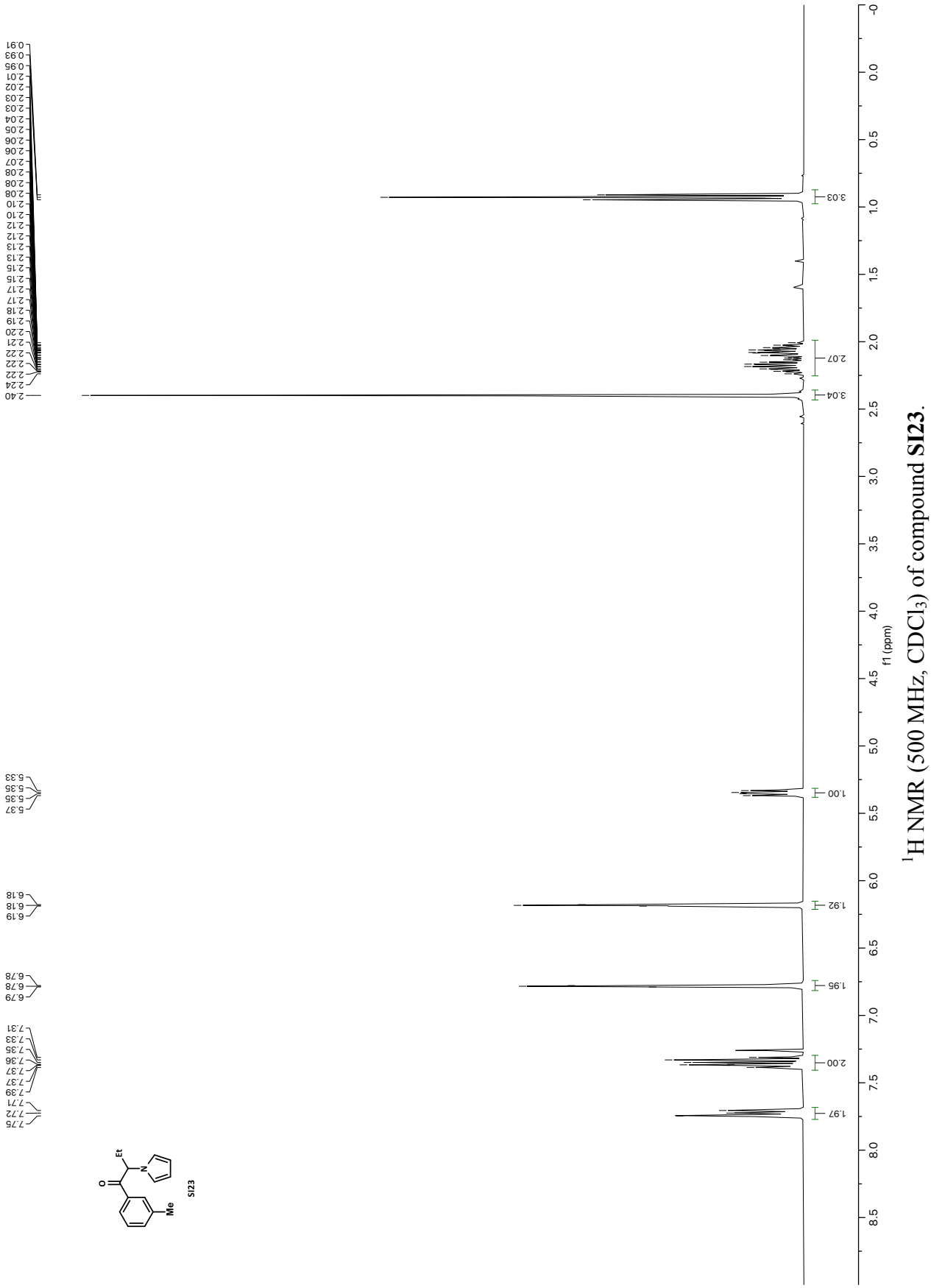
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI22**.



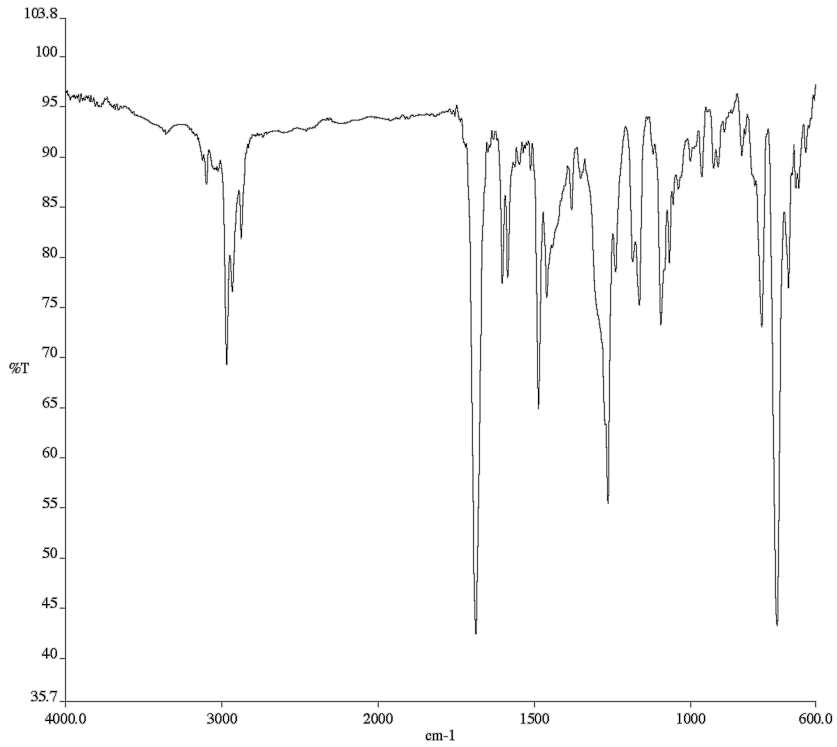
Infrared spectrum (Thin Film, NaCl) of compound **SI22**.



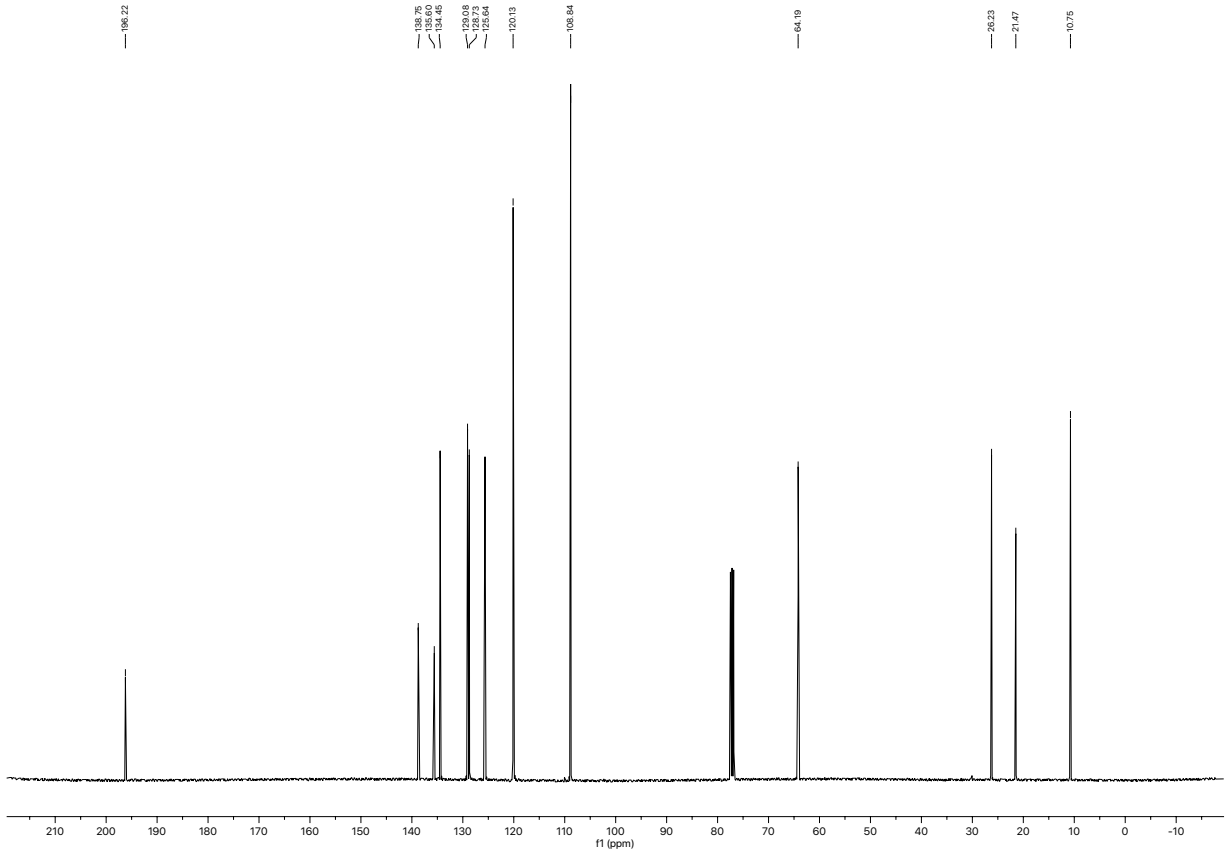
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI22**.



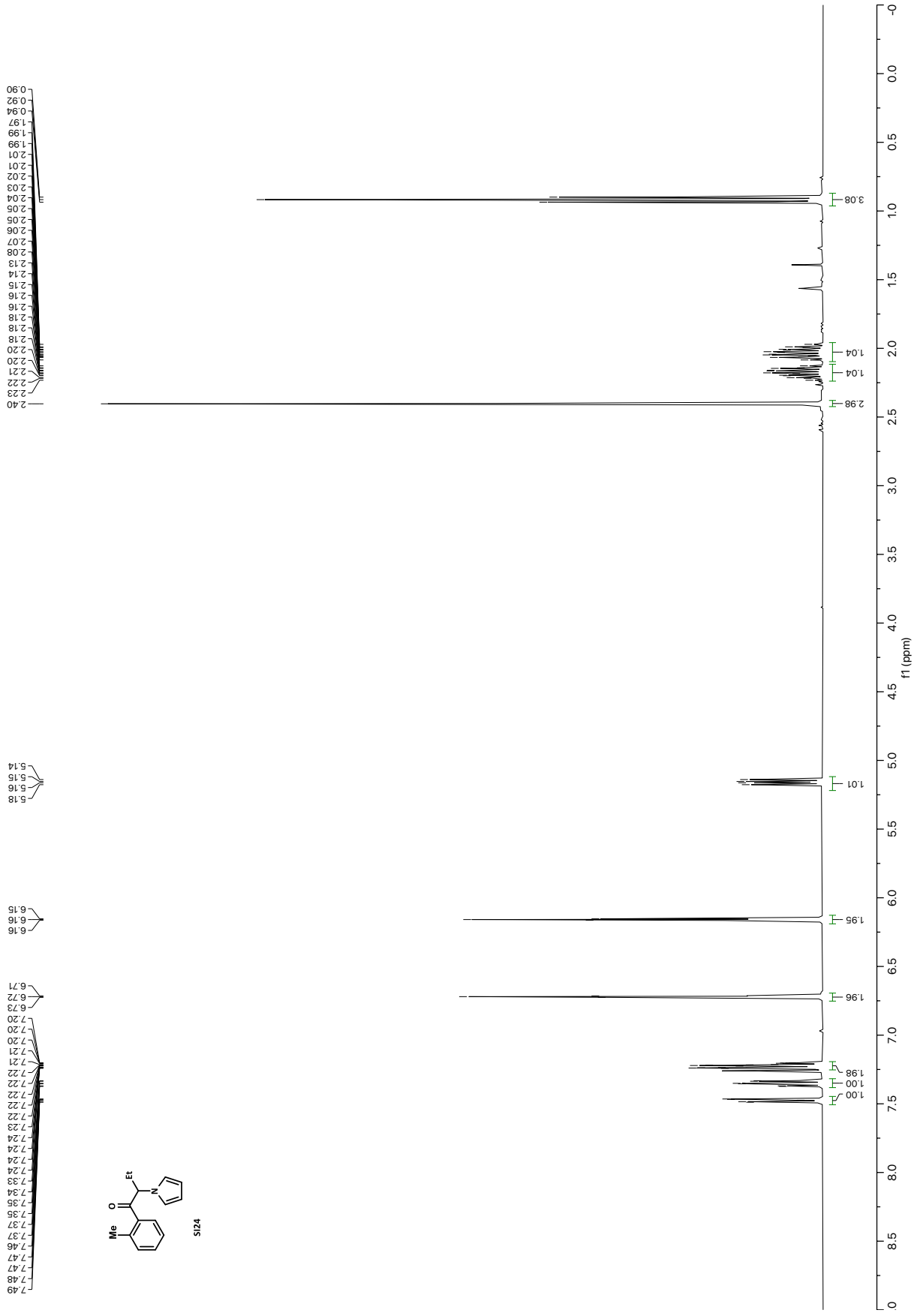
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI23**.



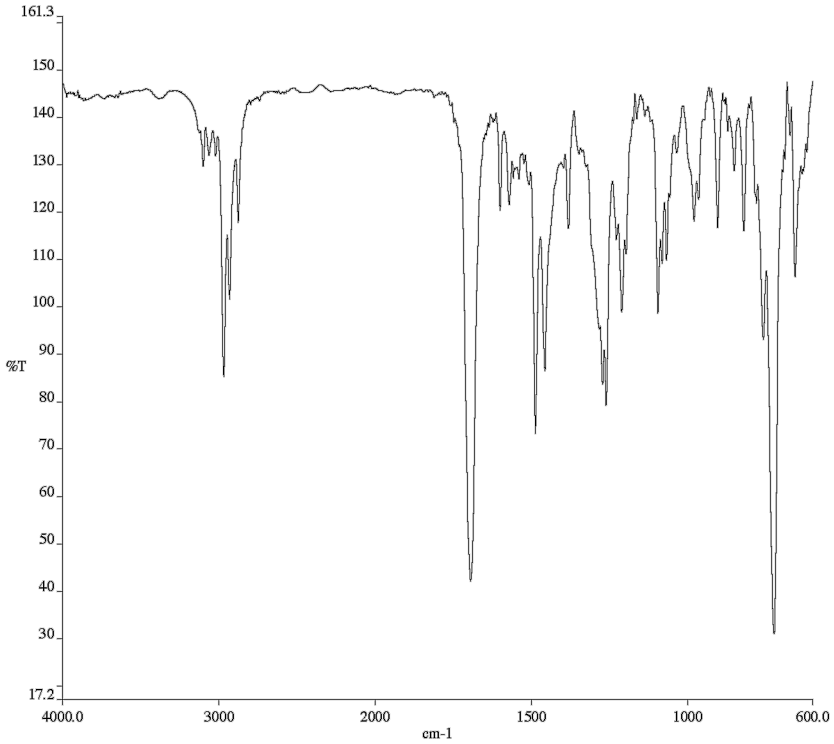
Infrared spectrum (Thin Film, NaCl) of compound **SI23**.



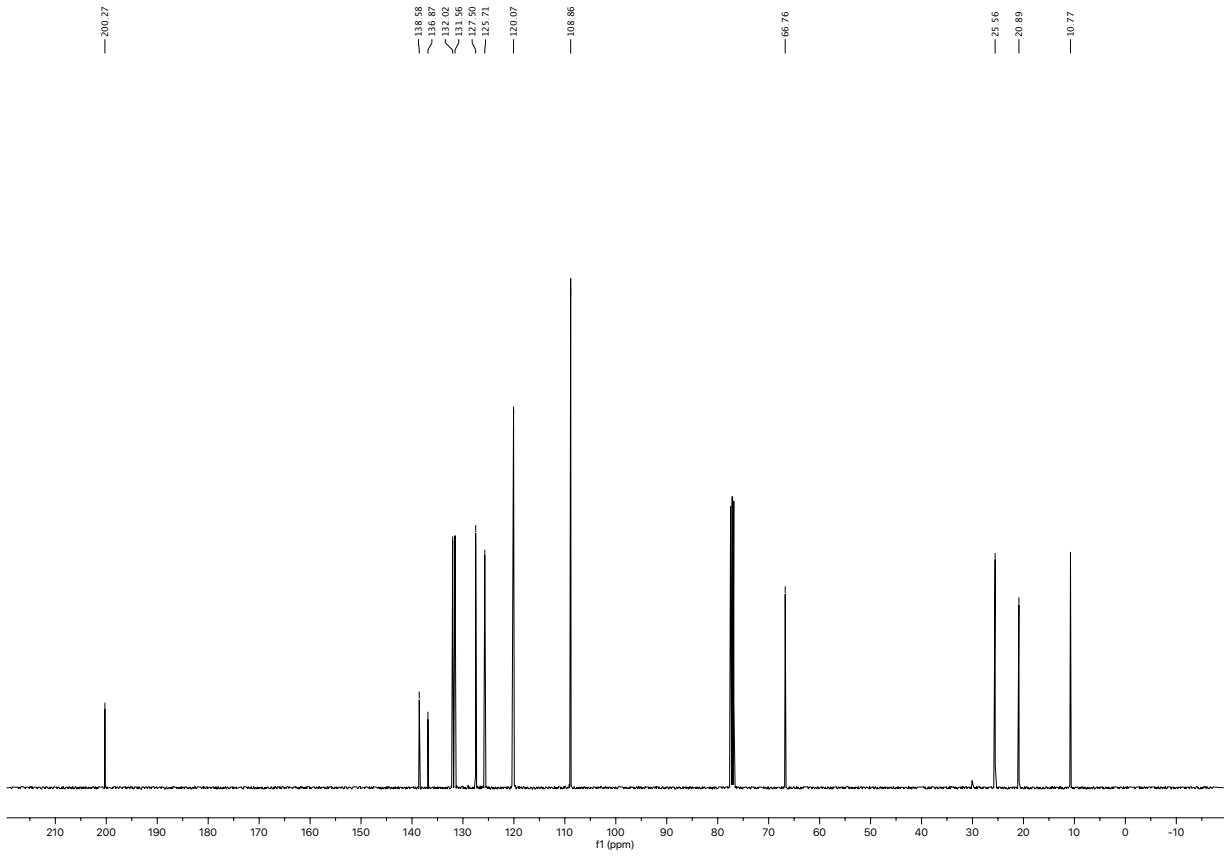
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI23**.



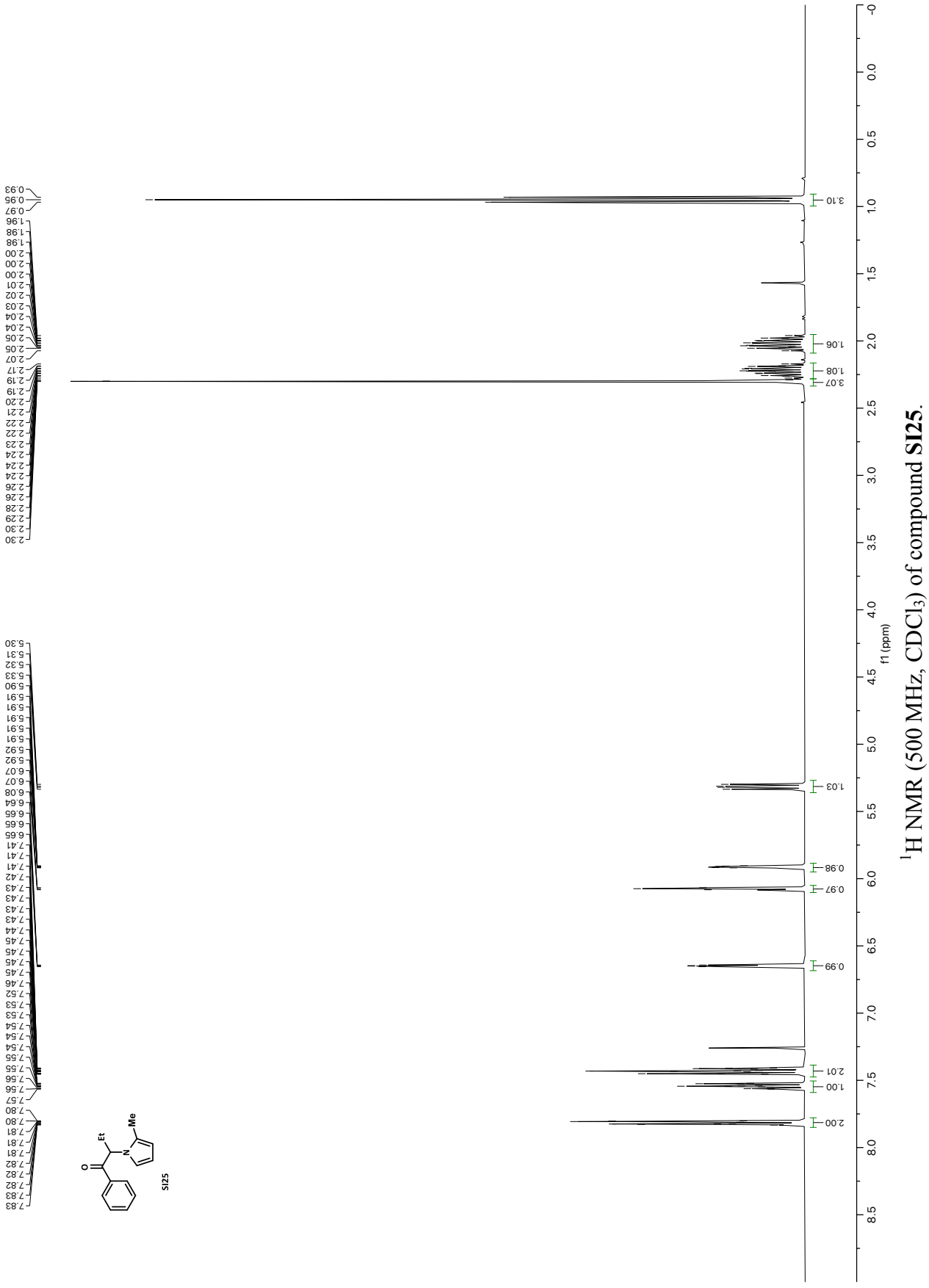
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI24**.



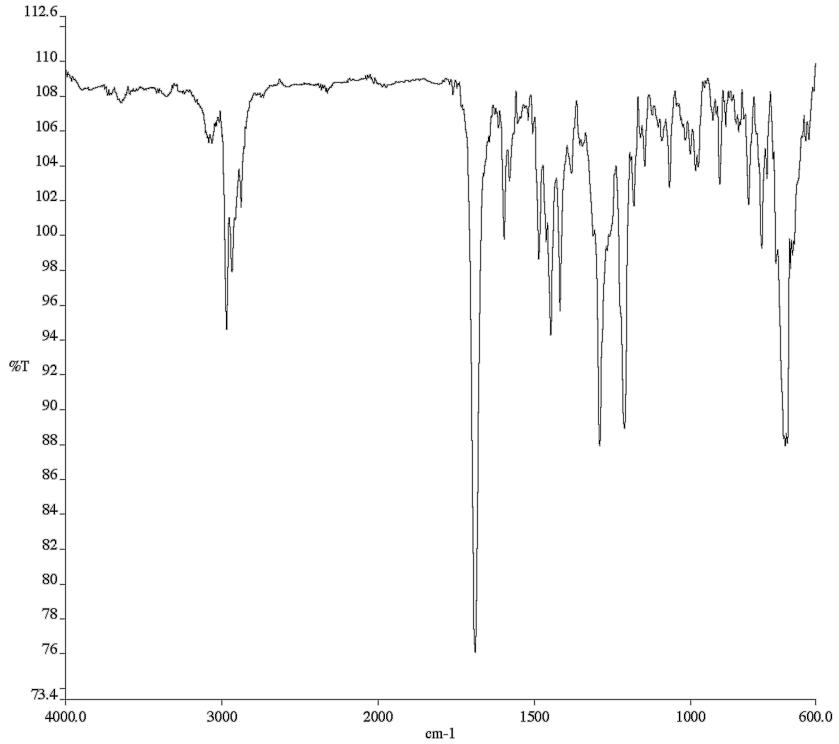
Infrared spectrum (Thin Film, NaCl) of compound **SI24**.



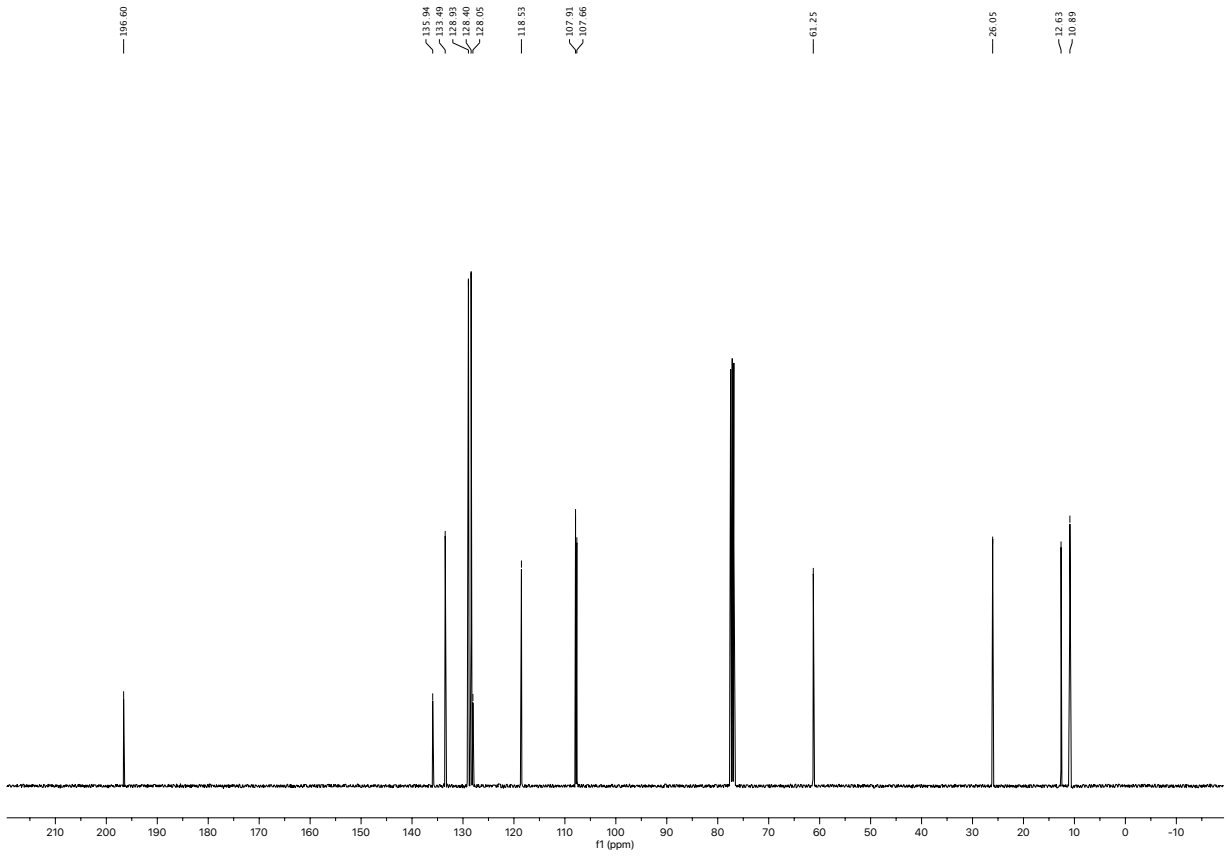
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI24**.



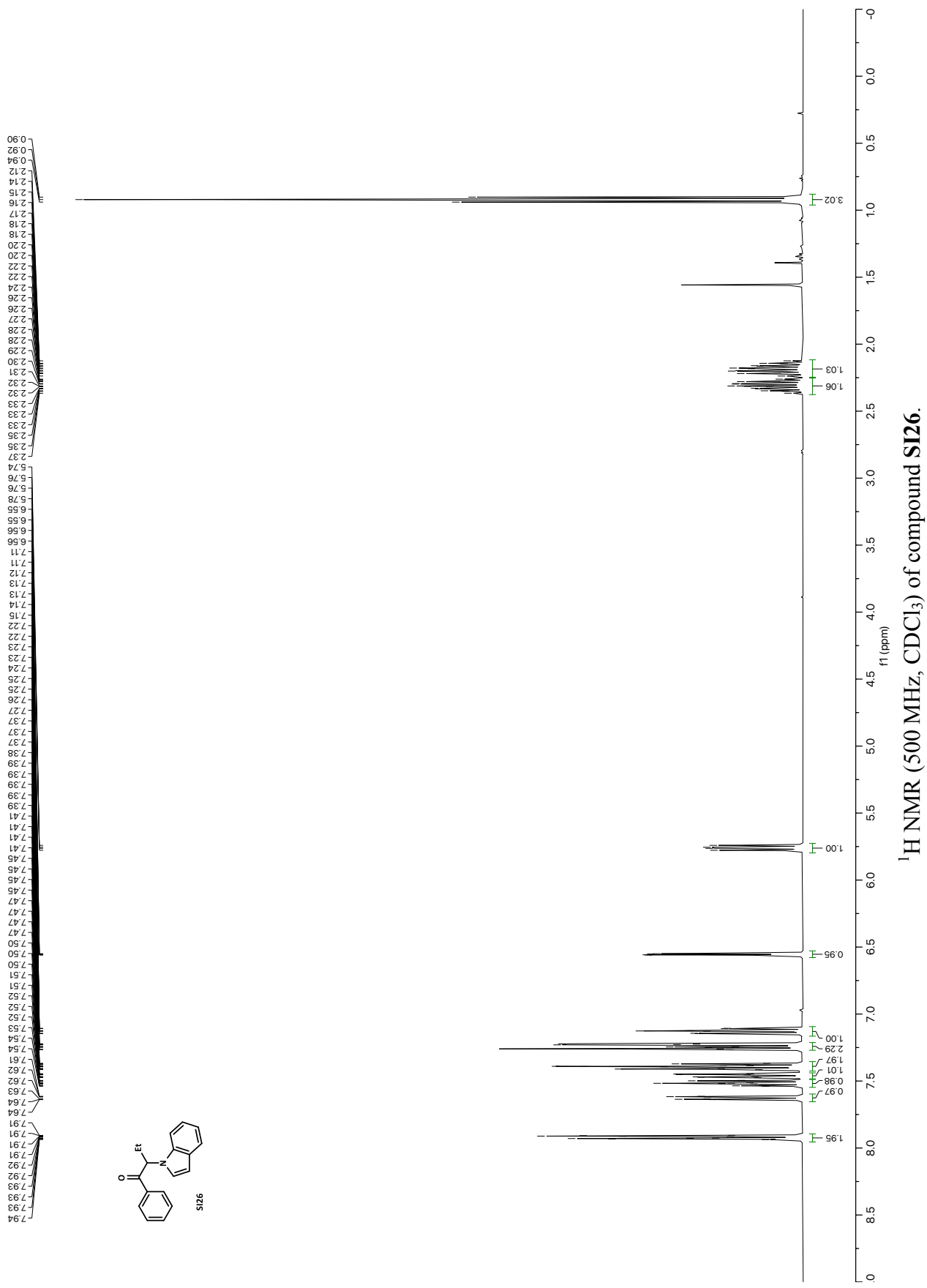
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI25**.



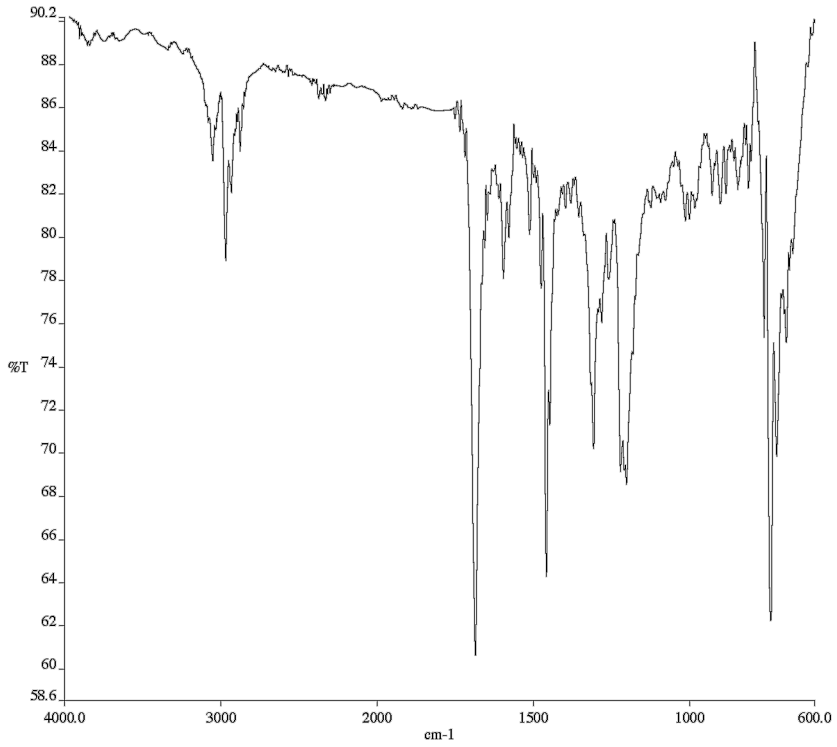
Infrared spectrum (Thin Film, NaCl) of compound **SI25**.



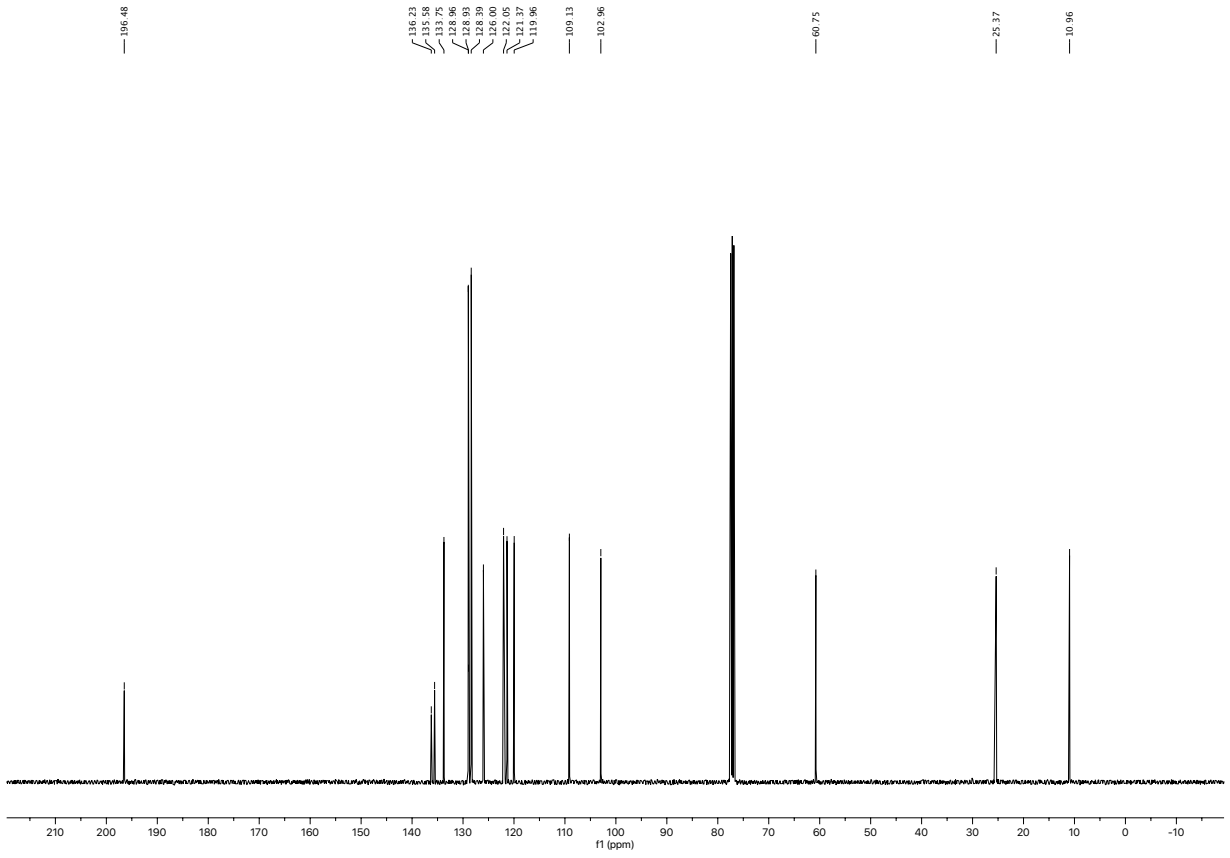
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI25**.



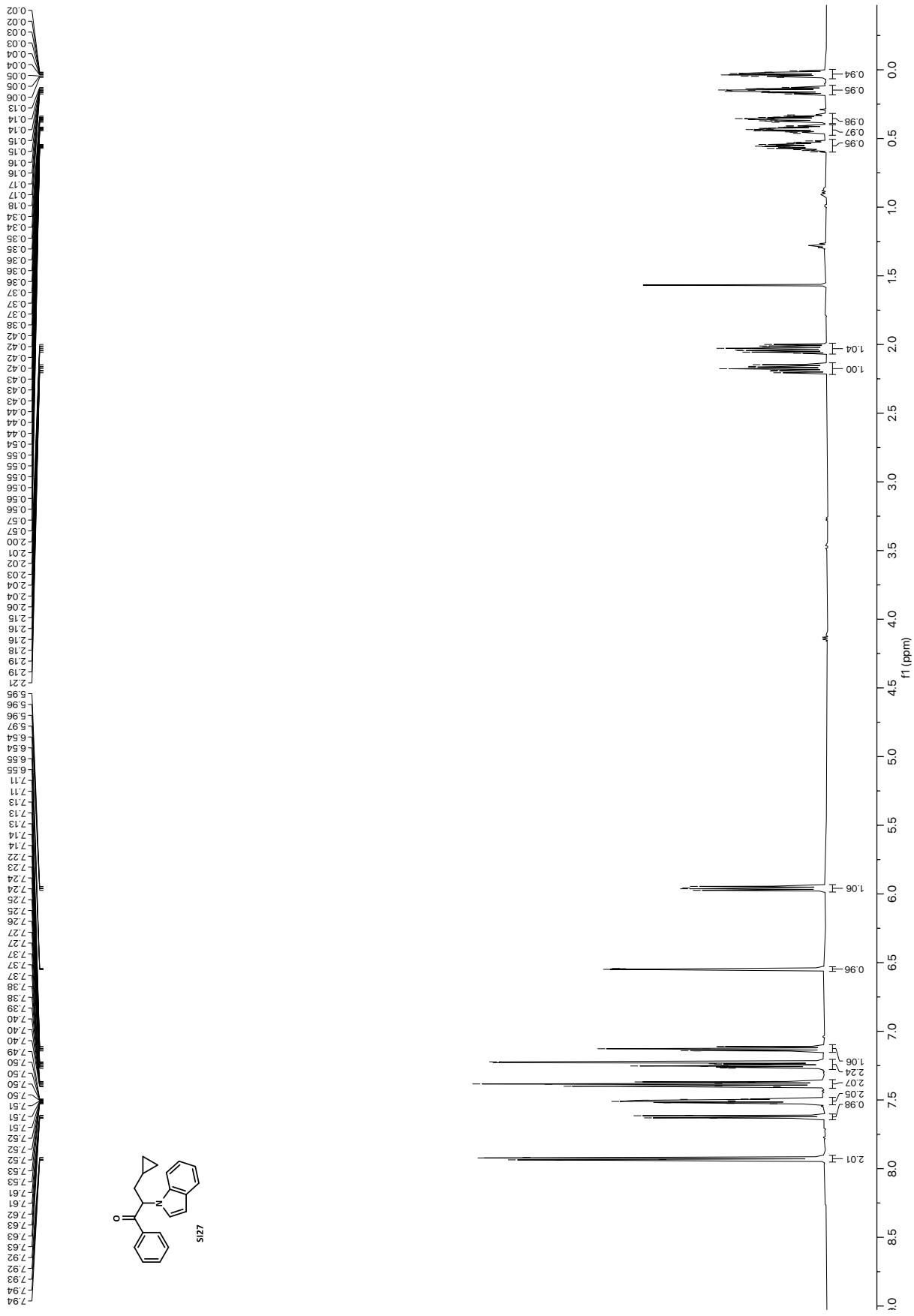
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI26**.



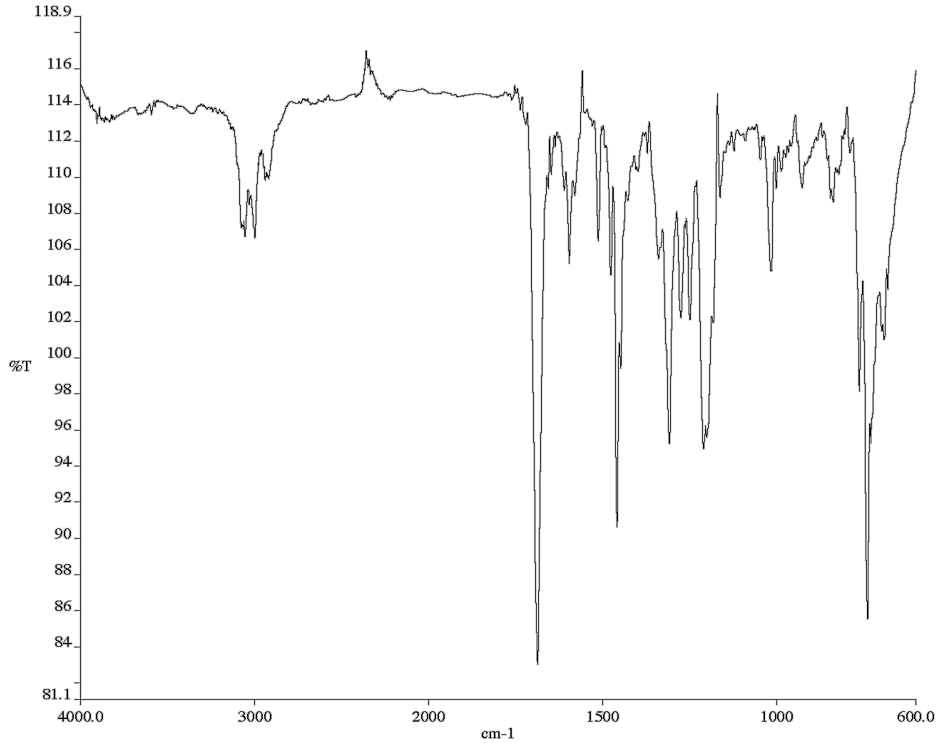
Infrared spectrum (Thin Film, NaCl) of compound **SI26**.



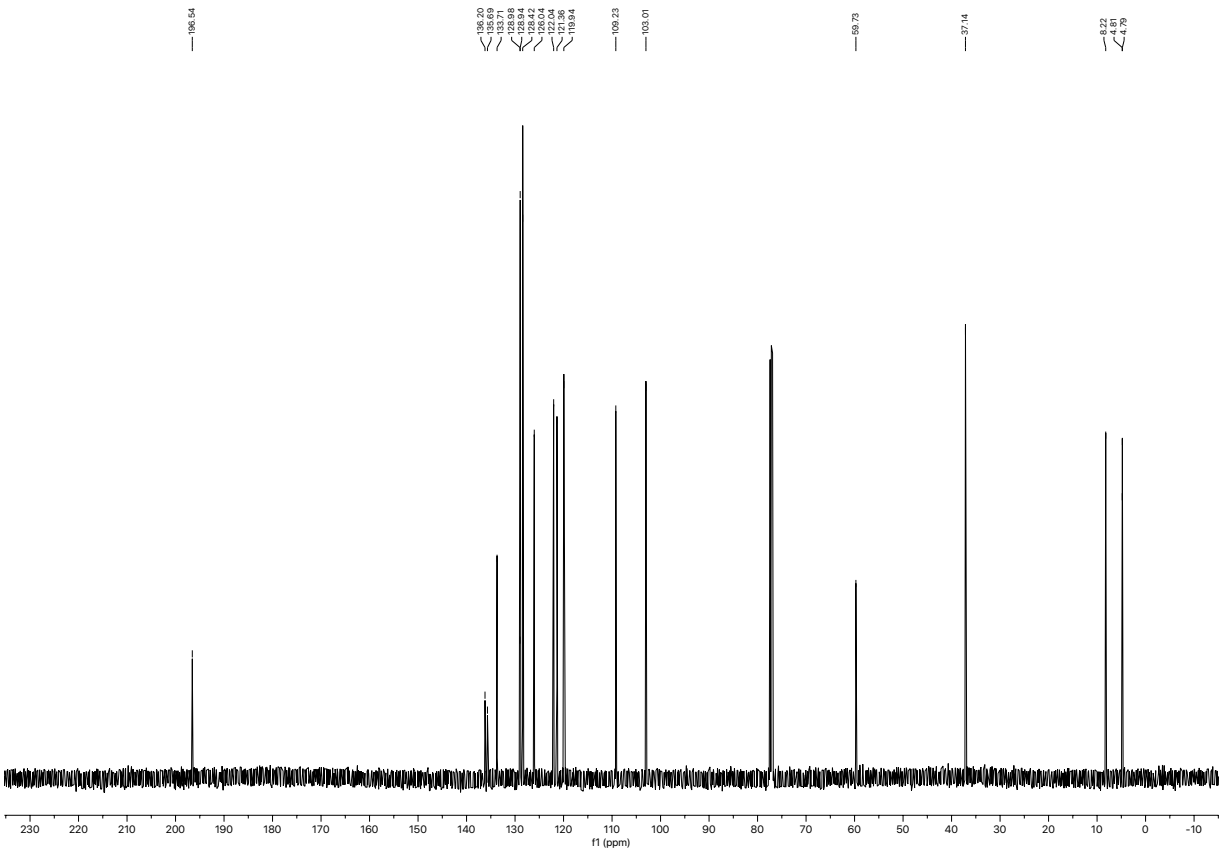
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI26**.



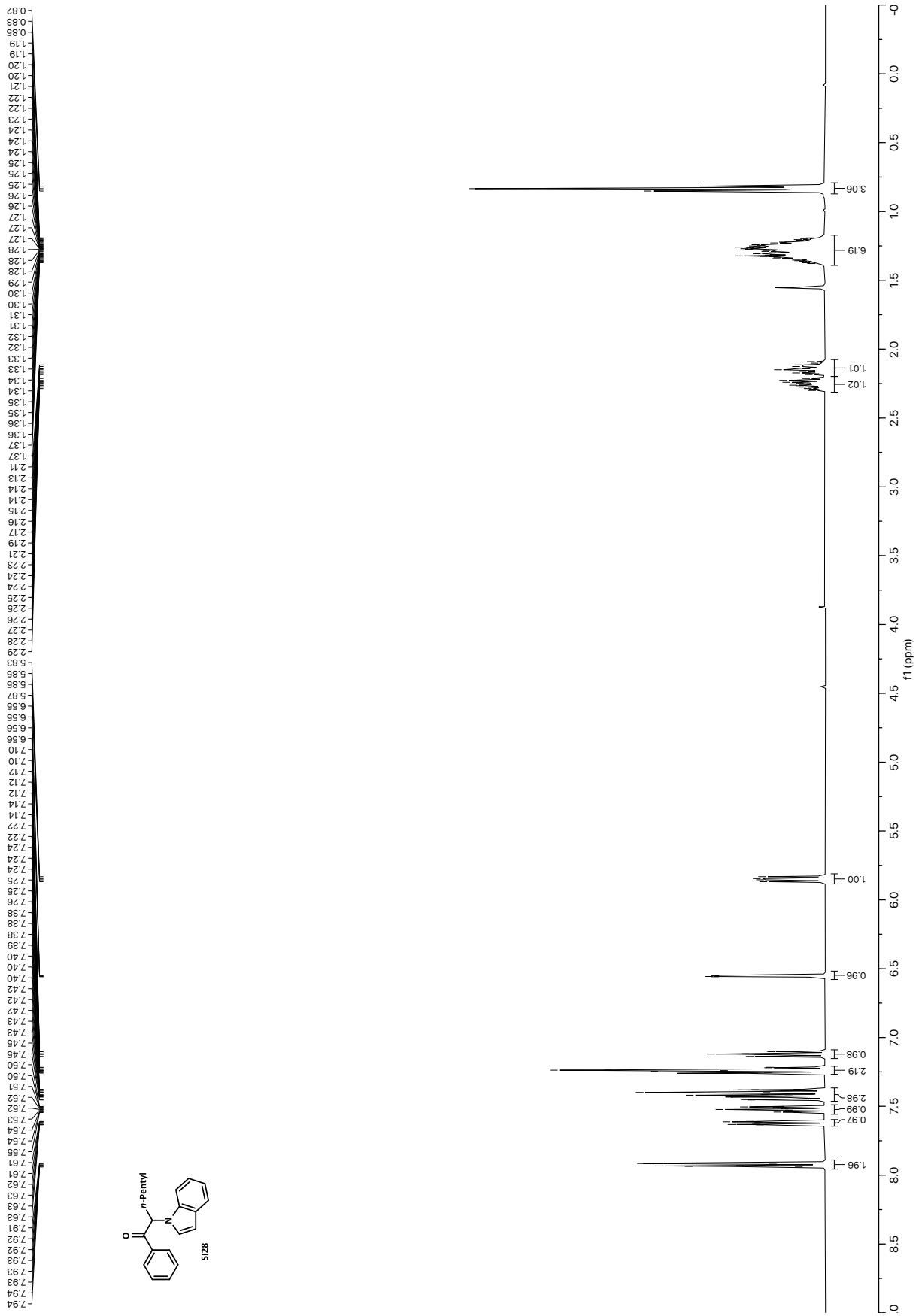
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI27**.



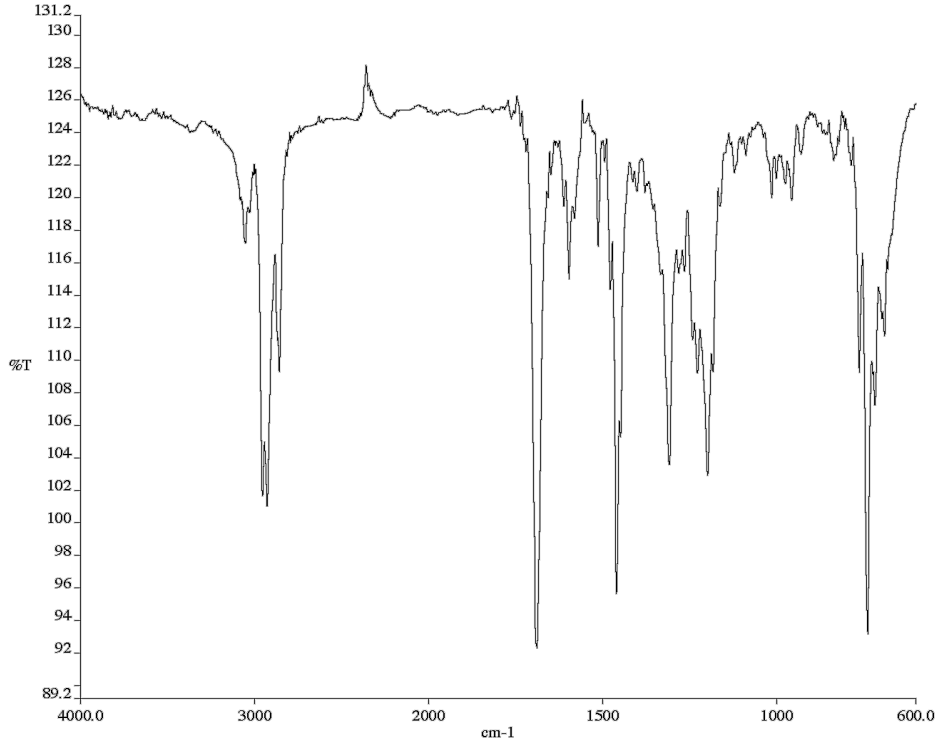
Infrared spectrum (Thin Film, NaCl) of compound **SI27**.



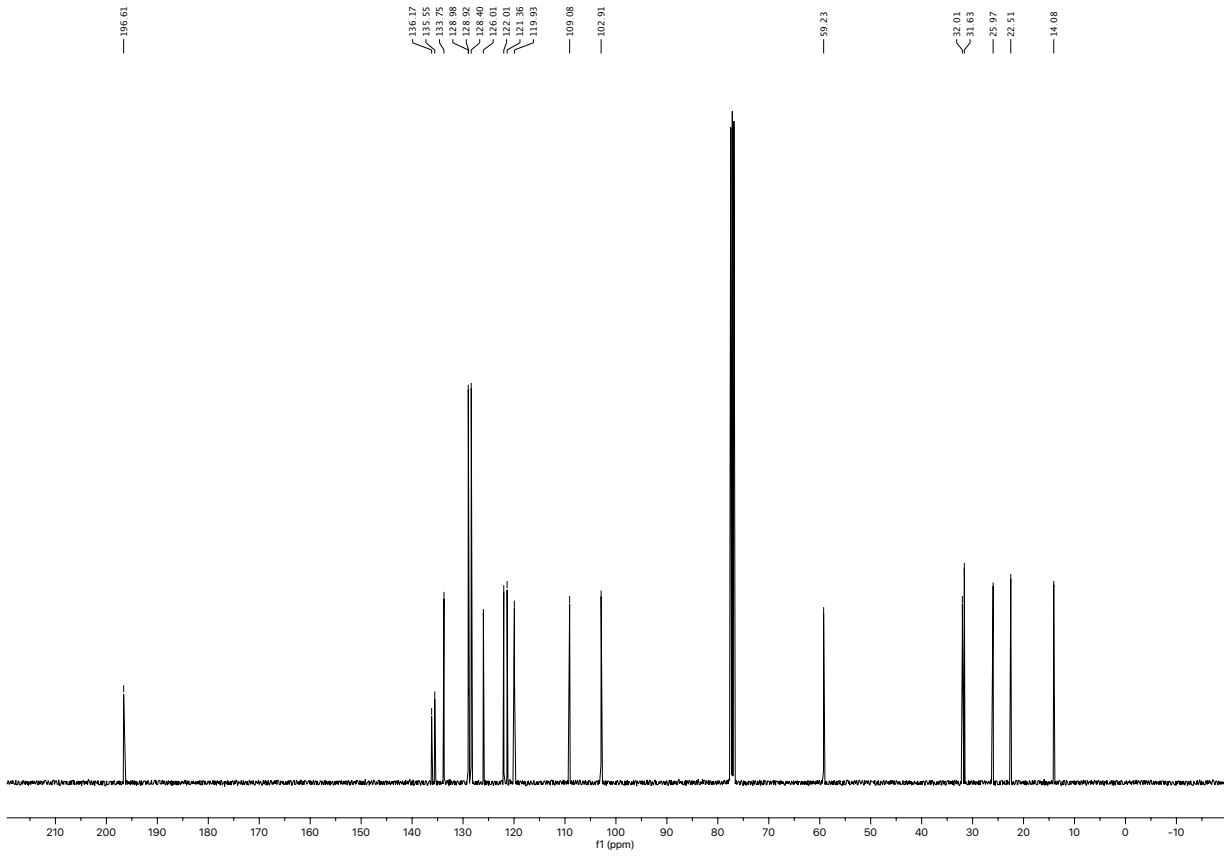
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI27**.



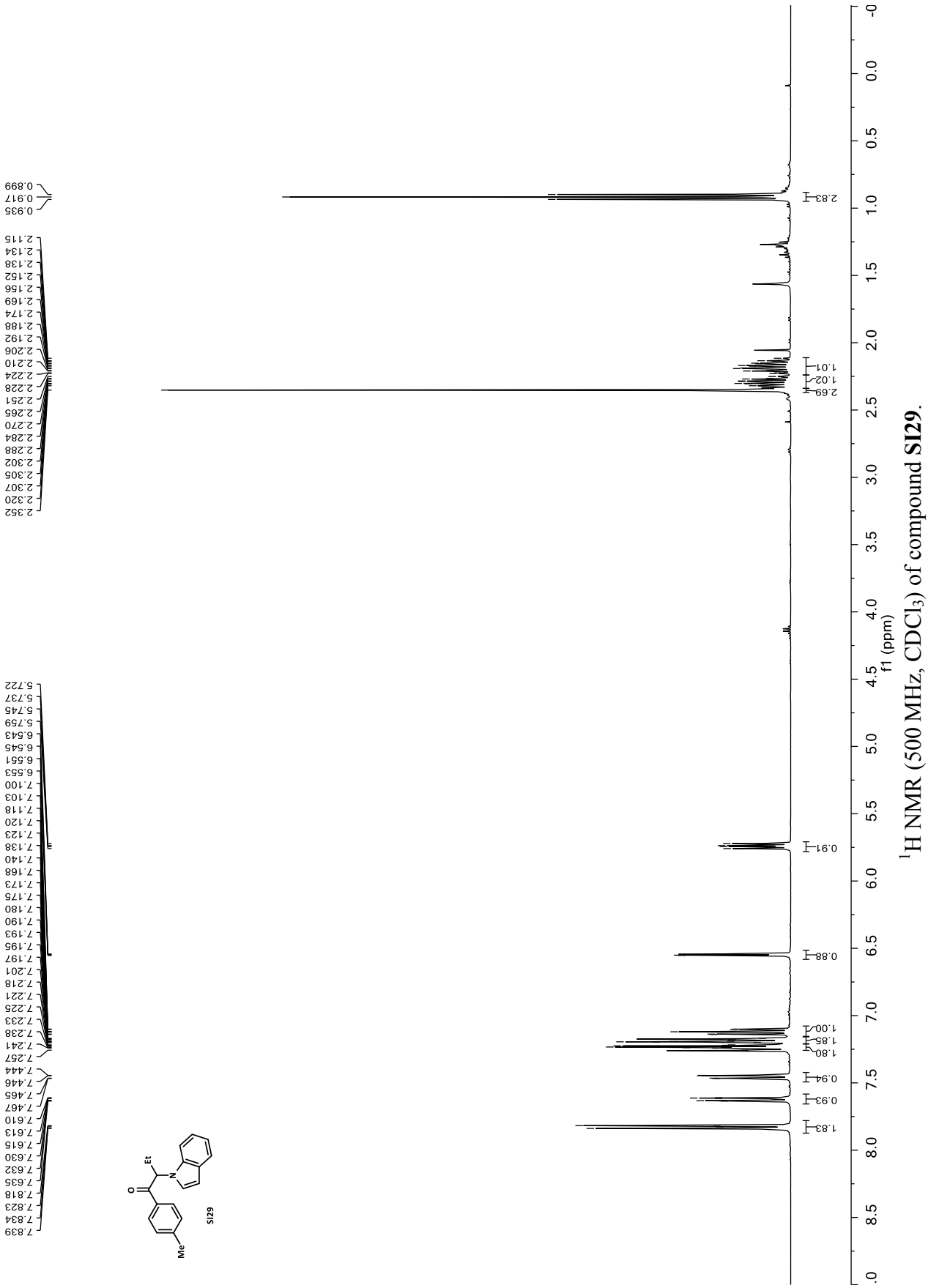
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI28**.



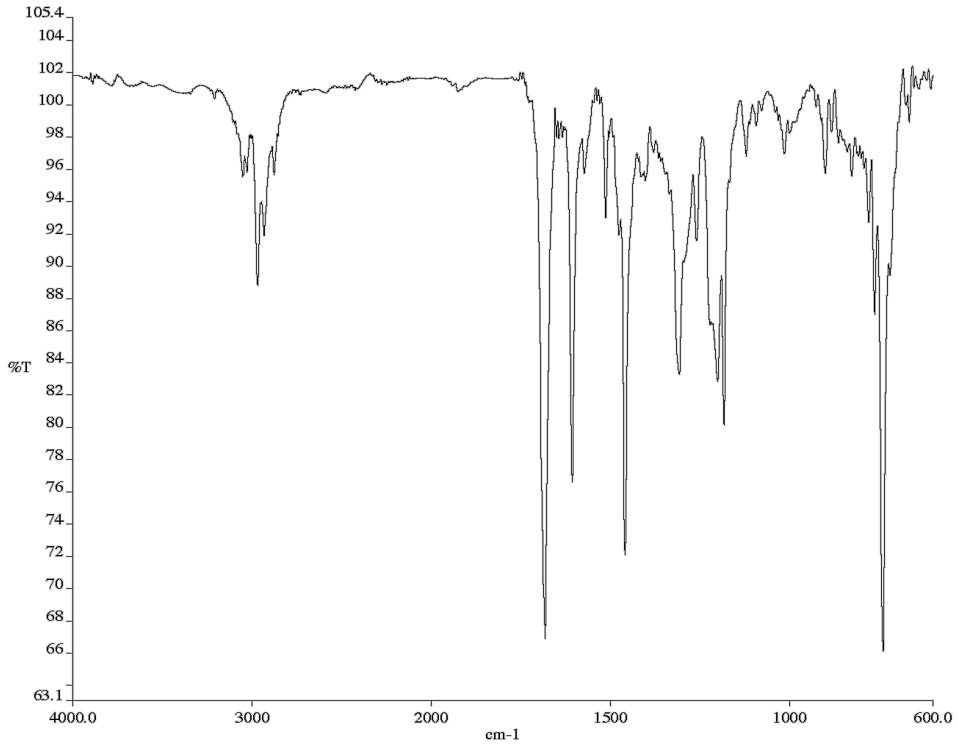
Infrared spectrum (Thin Film, NaCl) of compound **SI28**.



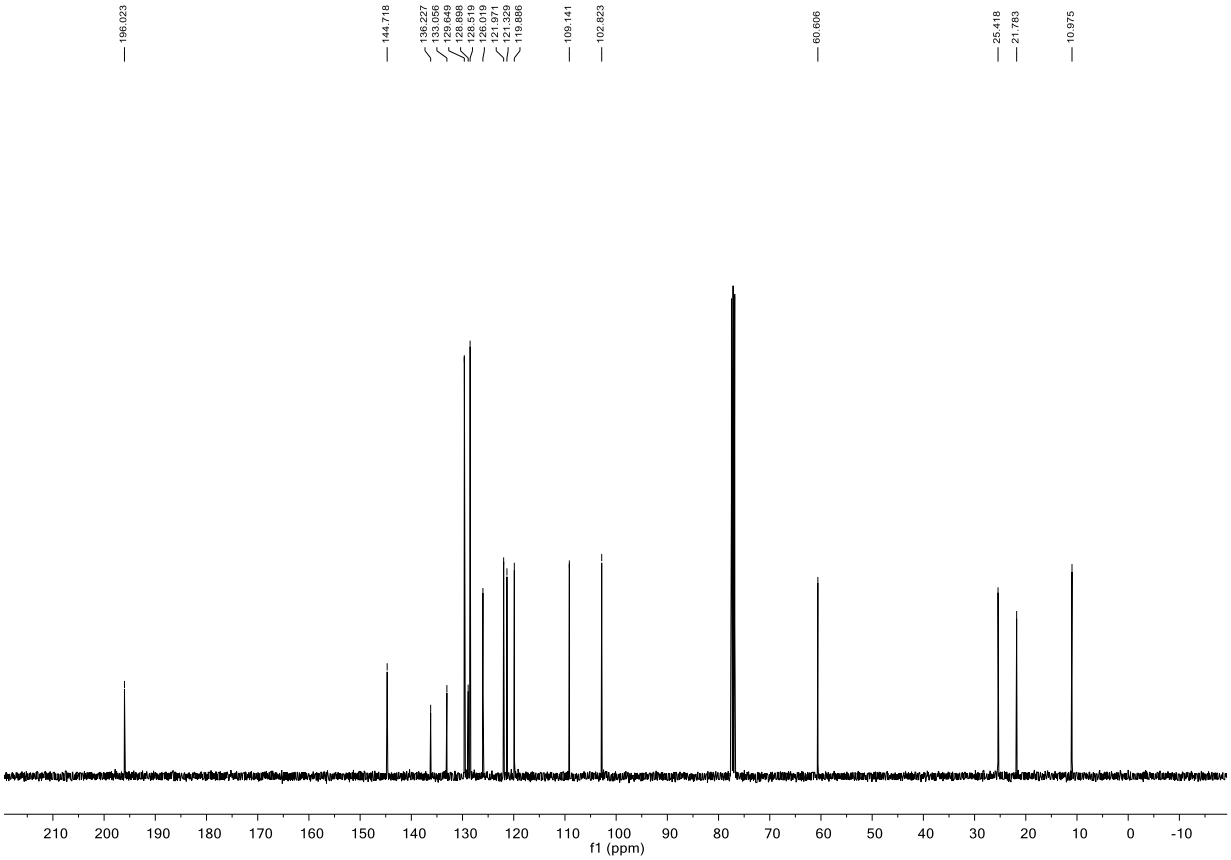
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI28**.



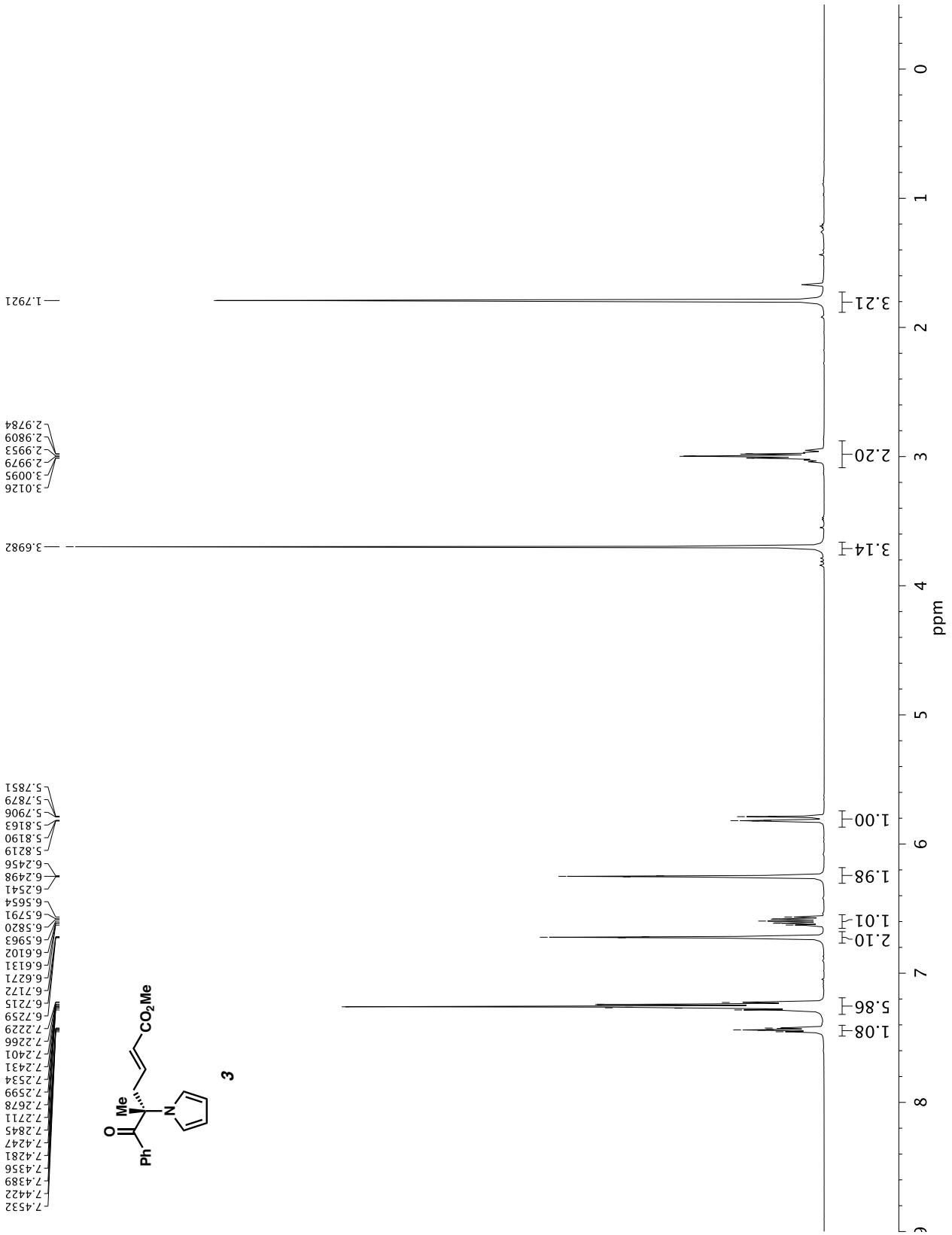
^{1}H NMR (500 MHz, $CDCl_3$) of compound **SI29**.



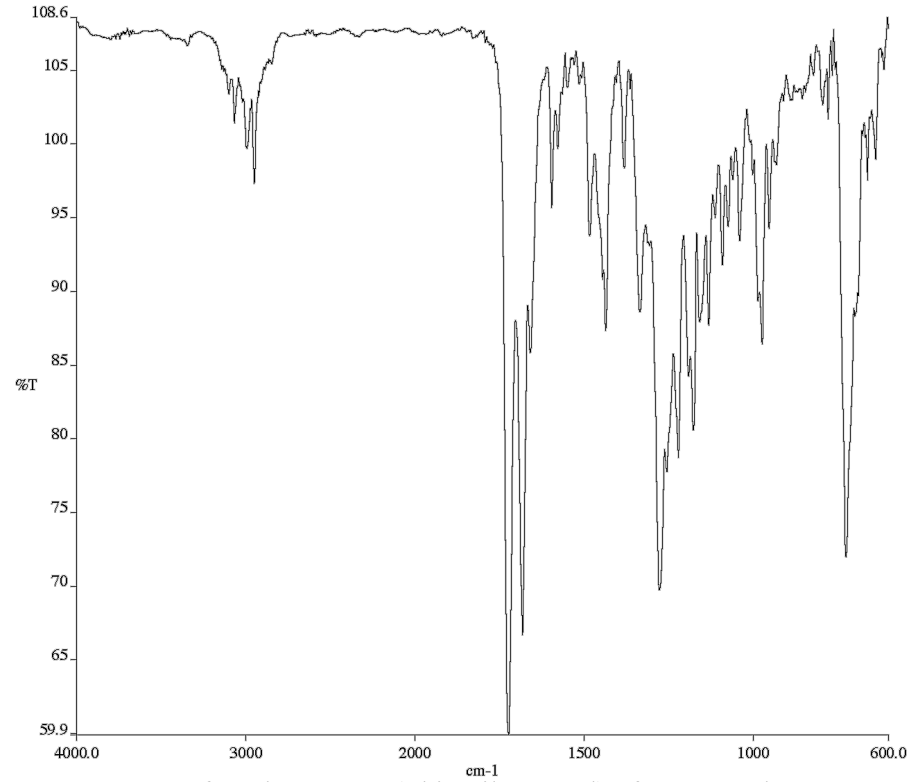
Infrared spectrum (Thin Film, NaCl) of compound **SI29**.



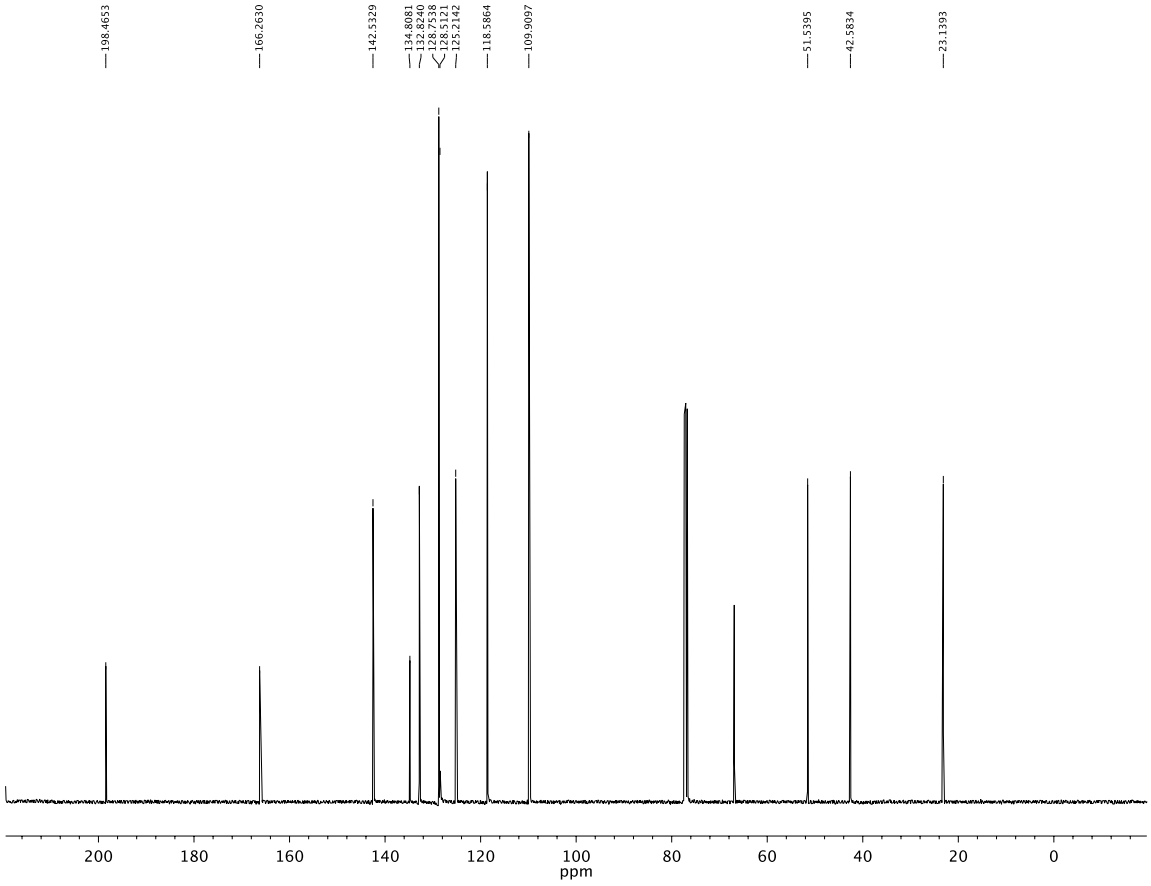
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI29**.



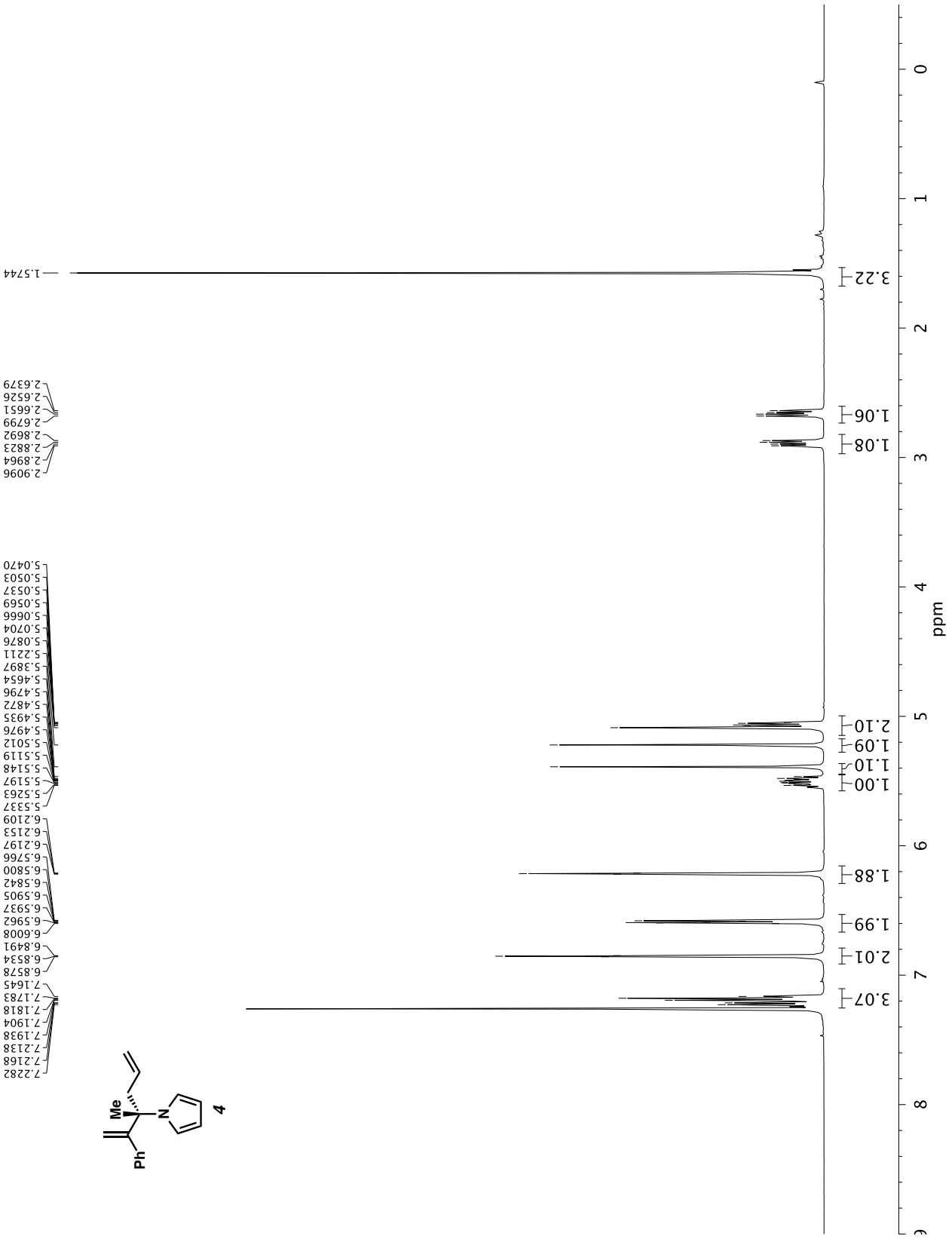
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3**.



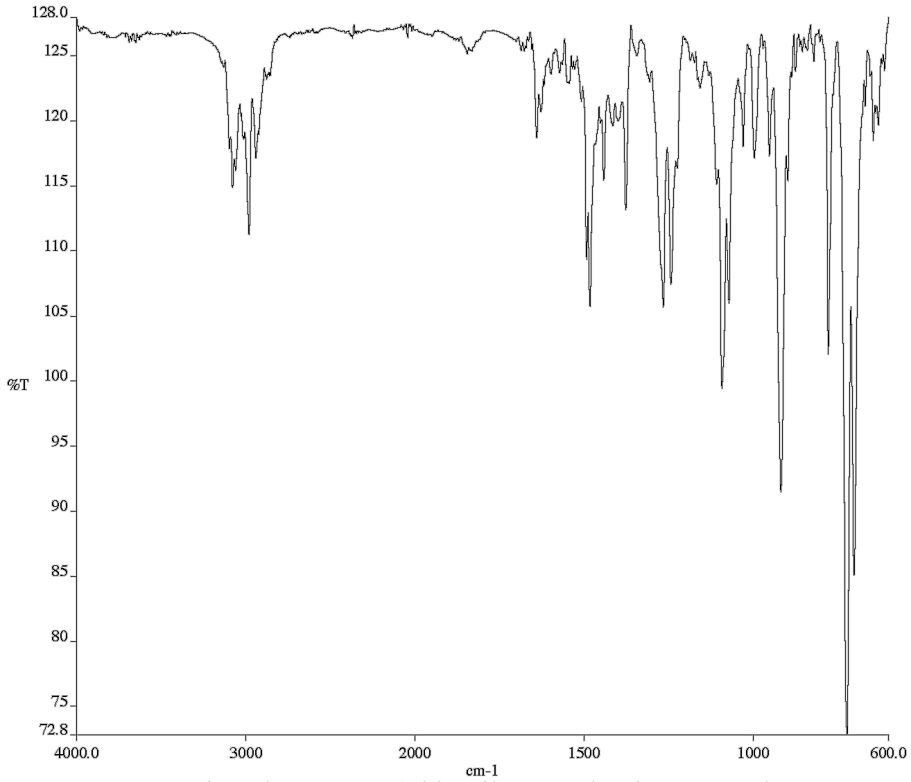
Infrared spectrum (Thin Film, NaCl) of compound **3**.



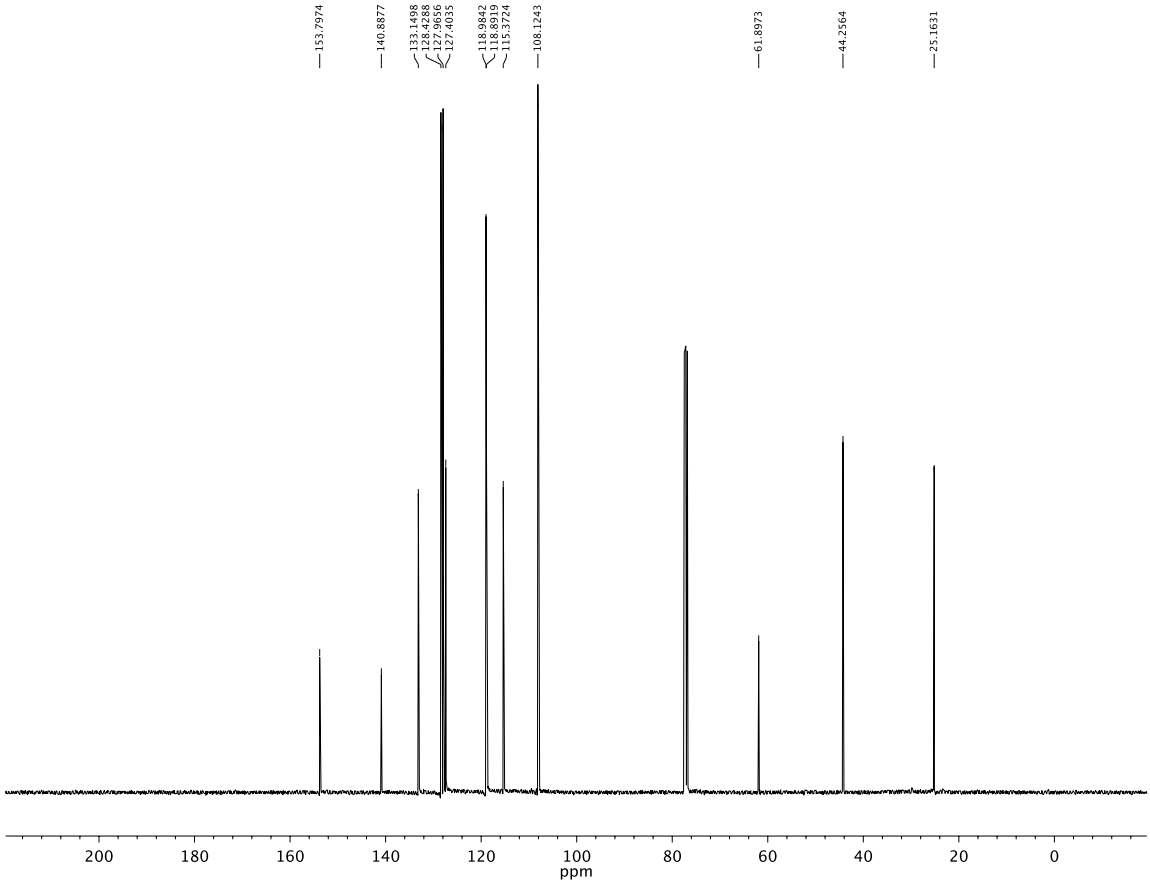
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3**.



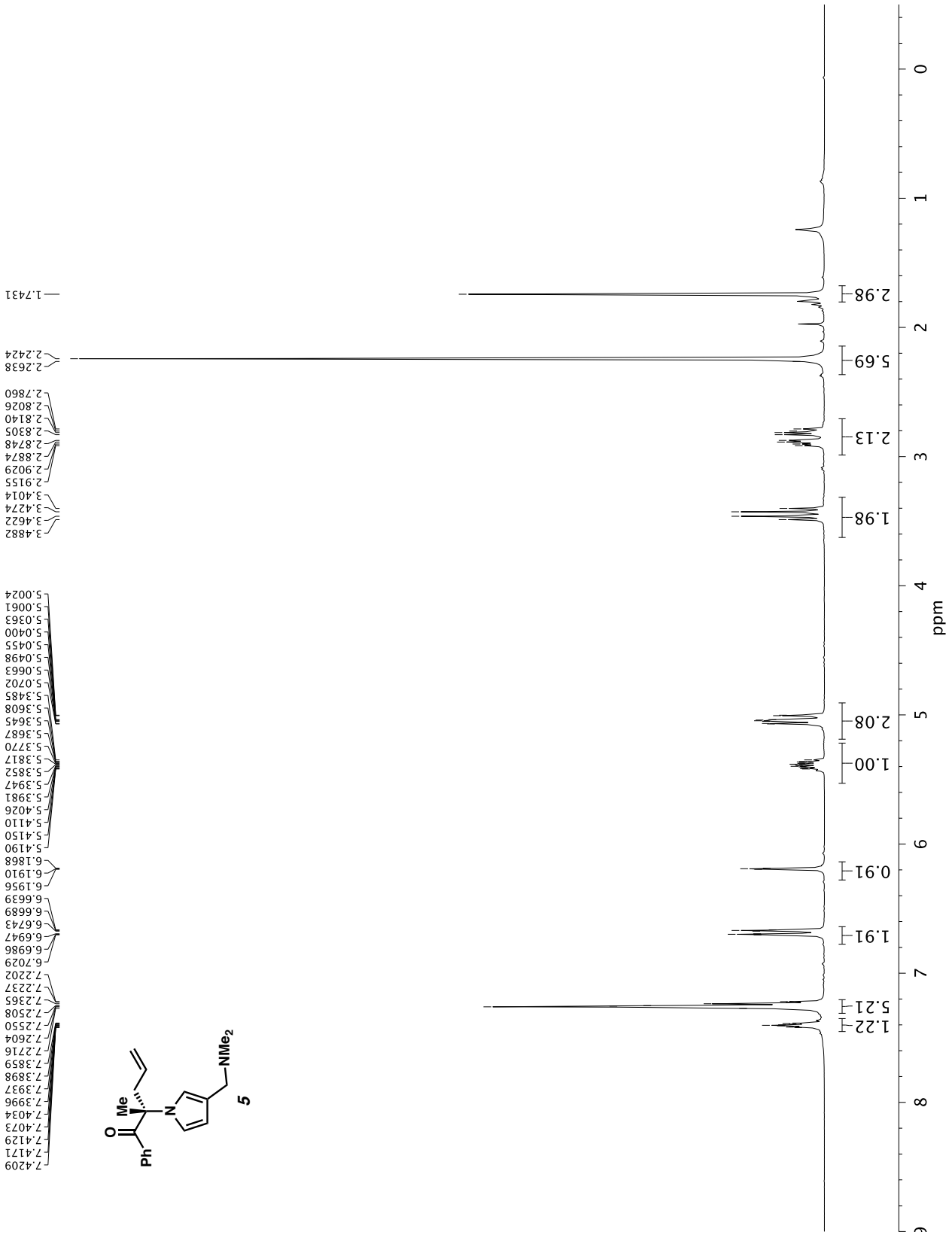
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4**.



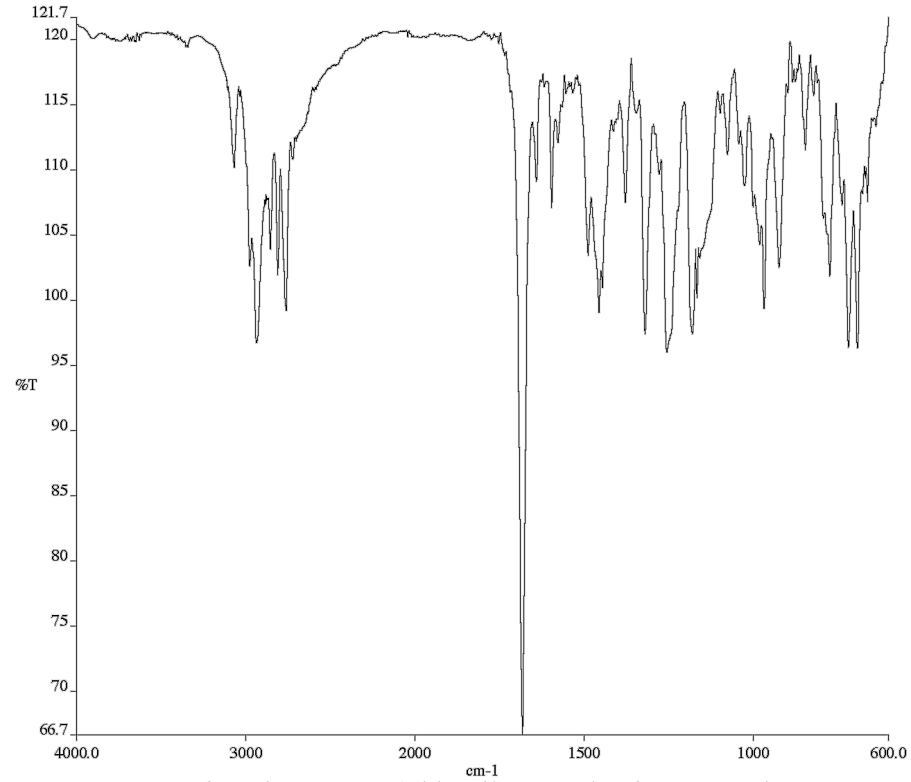
Infrared spectrum (Thin Film, NaCl) of compound **4**.



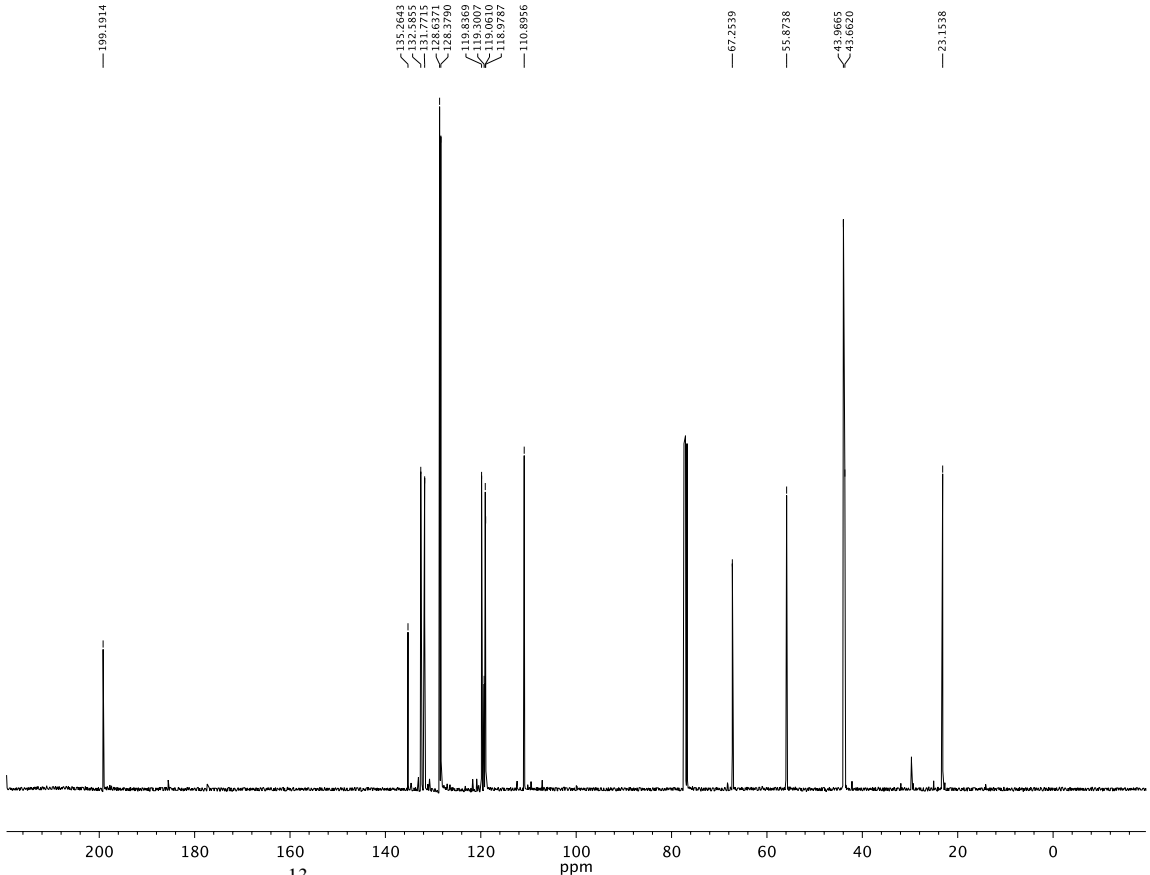
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4**.



^{1}H NMR (500 MHz, $CDCl_3$) of compound **5**.



Infrared spectrum (Thin Film, NaCl) of compound **5**.



^{13}C NMR (100 MHz, $CDCl_3$) of compound **5**.