Advanced Synthesis & Catalysis

Supporting Information

Palladium-Catalyzed Enantioselective Decarboxylative Allylic Alkylation of Protected Benzoin-Derived Enol Carbonates

Rémi Lavernhe, Eric J. Alexy, Haiming Zhang, and Brian M. Stoltz*

Supporting Information for

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Materials and Methods

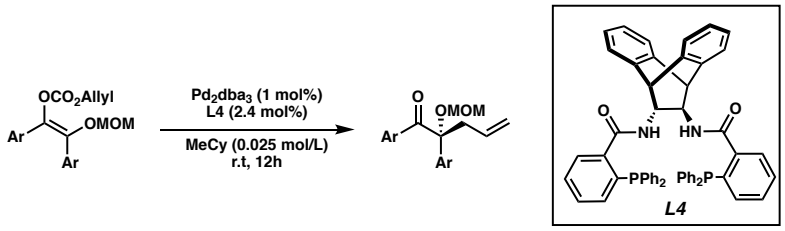
Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Solvents were dried by passage through an activated alumina column under argon.[1] Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. ^{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+). Absolute configuration of **4** was determined by X-ray diffraction, and all other products are assigned by analogy.

Reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Ligand **L4**[2] and Mom-protected benzoins were prepared by known methods unless otherwise described below.[2,3]

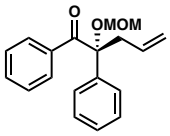
List of Abbreviations:

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

General Procedure for Pd-Catalyzed Allylic Alkylation Reactions

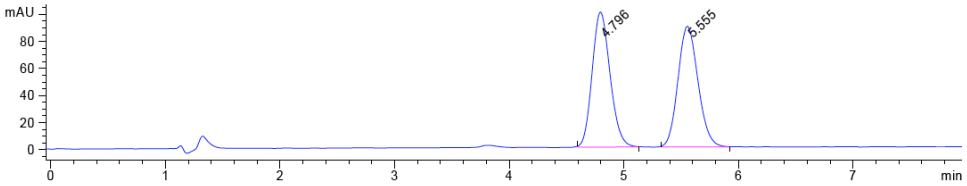


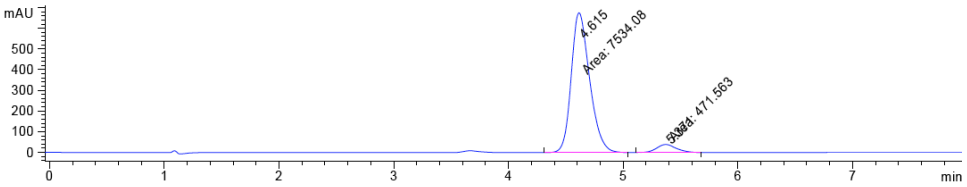
In a nitrogen-filled glovebox, a solution of $Pd_2(dba)_3$ (1.8 mg) and **L4** (3.9 mg) in MeCy (4 mL) was stirred for 30 minutes at 25 °C, then the resulting catalyst solution was added to a vial containing allyl enol carbonate substrate (0.2 mmol) in MeCy (4 mL). The vial was sealed with a Teflon-lined 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-(methoxymethoxy)-1,2-diphenylpent-4-en-1-one (2a)

Purified by column chromatography (10% Et_2O in hexanes) to provide a white solid (58.7 mg, 99% yield); 88% ee, $[\alpha]_D^{25}$ +198.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.78 (m, 2H), 7.40 – 7.35 (m, 2H), 7.34–7.23 (m, 3H), 7.21–7.15 (m, 3H), 5.46 (dddd, *J* = 16.9, 10.6, 7.6, 6.3 Hz, 1H), 4.92 – 4.89 (m, 1H), 4.89 – 4.84 (m, 1H), 4.72 (d, *J* = 6.9 Hz, 1H), 4.66 (d, *J* = 6.9 Hz, 1H), 3.10 (ddt, *J* = 15.5, 7.7, 1.2 Hz, 1H), 3.02 (s, 3H), 2.91 (ddt, *J* = 15.5, 6.4, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 140.7, 135.0, 132.5, 132.4, 130.6, 128.6, 128.0, 127.6, 125.4, 118.5, 93.2, 87.0, 57.1, 40.6; IR (Neat Film, NaCl) 3070, 2926, 1683, 1640, 1597, 1578, 1491, 1446, 1414, 1239, 1182, 1152, 1103, 1078, 1028, 1019, 920, 759, 720, 701, 664 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{24}NO_3$ $[M+NH_4]^+$: 314.1751, found 314.1753; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 4.62, major = 5.37.





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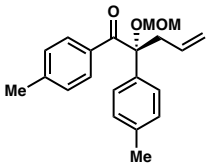
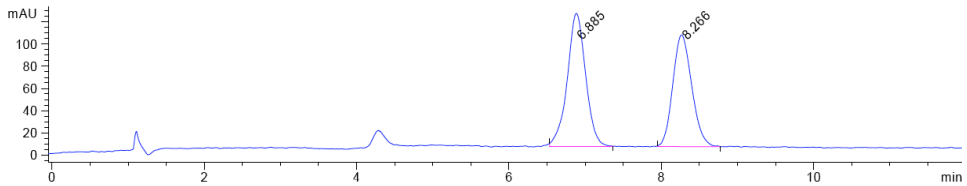
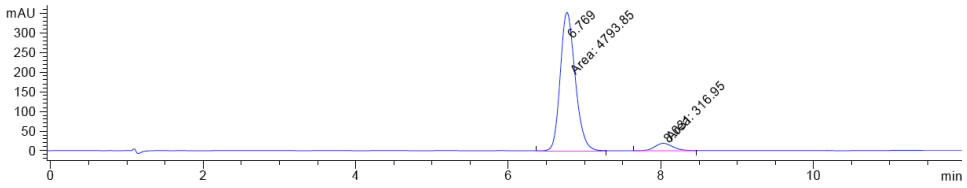
1	4.615	MM	0.1856	7534.07617	676.43915	94.1096
2	5.371	MM	0.2010	471.56253	39.10020	5.8904
Totals :				8005.63870	715.53935	



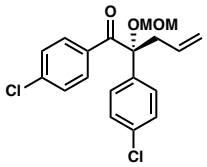
(*S*)-2-(methoxymethoxy)-1,2-di-*p*-tolylpent-4-en-1-one (2b)

Purified by column chromatography (8% Et_2O in hexanes) to provide a colorless oil (64.3 mg, 99% yield); 88% ee, $[\alpha]_D^{25}$ +154.6 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.79 (m, 2H), 7.36 – 7.28 (m, 2H), 7.18 – 7.10 (m, 2H), 7.10 – 7.00 (m, 2H), 5.63 – 5.47 (m, 1H), 4.99 – 4.91 (m, 2H), 4.76 (d, *J* = 6.8 Hz, 1H), 4.72 (d, *J* = 6.8 Hz, 1H), 3.19 – 3.09 (m, 4H), 2.97 (ddt, *J* = 15.4, 6.3, 1.6 Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 143.1, 137.9, 137.1, 132.8, 132.4, 130.8, 129.3, 128.7, 125.3, 118.3, 93.2, 87.0, 57.1, 40.6, 21.7, 21.2; IR (Neat Film, NaCl) 3075, 2922, 2824, 1677, 1640, 1606, 1570, 1511, 1445, 1409, 1242, 1183, 1153, 1101, 1029, 1017, 921, 849, 815, 776, 750 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{28}NO_3$ $[M+NH_4]^+$: 342.2064, found 342.2062; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 6.77, minor = 8.03.



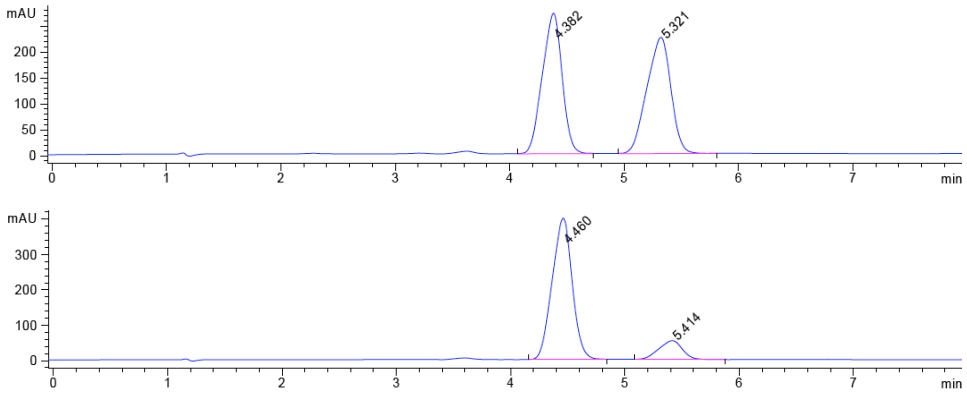


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.769	MM	0.2269	4793.84766	352.09714	93.7984
2	8.031	MM	0.2766	316.94992	19.09983	6.2016
Totals :				5110.79758	371.19697	

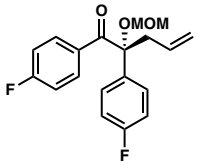


(*S*)-1,2-bis(4-chlorophenyl)-2-(methoxymethoxy)pent-4-en-1-one (2c)

Purified by column chromatography (7% Et_2O in hexanes) to provide a colorless oil (64.7 mg, 89% yield); 73% ee, $[\alpha]_D^{25}$ +112.9 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.78 (m, 2H), 7.34 – 7.26 (m, 4H), 7.26 – 7.19 (m, 2H), 5.46 (dddd, *J* = 17.0, 10.3, 7.4, 6.5 Hz, 1H), 4.99 – 4.87 (m, 2H), 4.80 (d, *J* = 7.0 Hz, 1H), 4.69 (d, *J* = 7.1 Hz, 1H), 3.13 (ddt, *J* = 15.5, 7.5, 1.2 Hz, 1H), 3.08 (s, 3H), 2.88 (ddt, *J* = 15.5, 6.5, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 139.1, 139.0, 133.7, 132.9, 132.1, 131.8, 128.9, 128.5, 126.7, 119.1, 93.3, 86.6, 57.3, 40.2; IR (Neat Film, NaCl) 3077, 2926 (br), 1684, 1639, 1588, 1489, 1400, 1244, 1178, 1154, 1092, 1025, 1012, 922, 849, 815, 757, 748 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}Cl_2NO_3$ $[M+NH_4]^+$: 382.0971, found 382.0981; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 4.46, minor = 5.41.

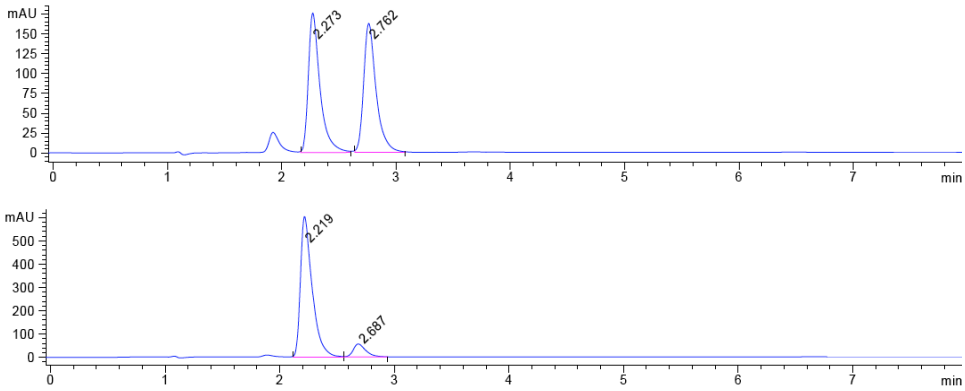


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.460	BB	0.1950	4894.65234	399.41248	86.3796
2	5.414	BB	0.2368	771.79285	53.35695	13.6204
Totals :				5666.44519	452.76942	

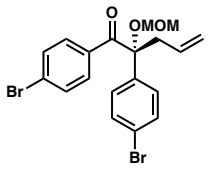


(*S*)-1,2-bis(4-fluorophenyl)-2-(methoxymethoxy)pent-4-en-1-one (2d)

Purified by column chromatography (10% Et_2O in hexanes) to provide a white solid (65.1 mg, 98% yield); 82% ee, $[\alpha]_D^{25}$ +155.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.89 (m, 2H), 7.44 – 7.32 (m, 2H), 7.07 – 6.99 (m, 2H), 6.99 – 6.90 (m, 2H), 5.50 (dddd, *J* = 17.0, 10.4, 7.5, 6.5 Hz, 1H), 5.01 – 4.89 (m, 2H), 4.81 (d, *J* = 7.0 Hz, 1H), 4.72 (d, *J* = 7.0 Hz, 1H), 3.15 (ddt, 15.5, 7.5, 1.3Hz, 1H), 3.11 (s, 3H), 2.92 (ddt, *J* = 15.5, 6.5, 1.6 Hz, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -105.5 (tt, *J* = 8.4, 5.5 Hz), -114.7 (tt, *J* = 8.5, 5.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 165.1 (d, *J* = 255.0 Hz), 162.2 (d, *J* = 246.7 Hz), 136.4 (d, *J* = 3.2 Hz), 133.4 (d, *J* = 9.1 Hz), 132.0, 131.0 (d, *J* = 3.1 Hz), 127.1 (d, *J* = 8.1 Hz), 118.9, 115.6 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.5 Hz), 93.3, 86.6, 57.2, 40.4; IR (Neat Film, NaCl) 3077, 2929 (br), 2848, 2826, 1685, 1640, 1598, 1508, 1445, 1409, 1300, 1237, 1157, 1098, 1024, 1013, 976, 922, 854, 835, 814, 792, 760, 620 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}F_2NO_3$ $[M+NH_4]^+$: 350.1562, found 350.1558; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 2.22, minor = 2.69.

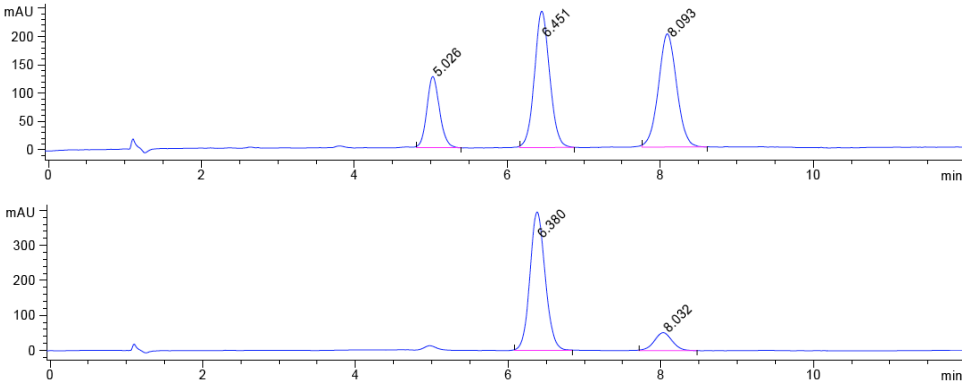


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.219	BV	0.1079	4291.20605	596.60321	90.9403
2	2.687	VB	0.1180	427.49884	55.42331	9.0597
Totals :				4718.70490	652.02652	



(S)-1,2-bis(4-bromophenyl)-2-(methoxymethoxy)pent-4-en-1-one (2e)

Purified by column chromatography (8% Et_2O in hexanes) to provide a colorless oil (91.6 mg, 99% yield); 74% ee, $[\alpha]_D^{25}$ +73.9 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 2H), 7.51 – 7.37 (m, 4H), 7.31 – 7.22 (m, 2H), 5.47 (dddd, *J* = 17.0, 10.4, 7.5, 6.5 Hz, 1H), 5.03 – 4.89 (m, 2H), 4.81 (d, *J* = 7.0 Hz, 1H), 4.70 (d, *J* = 7.0 Hz, 1H), 3.14 (ddt, *J* = 15.7, 7.5, 1.2 Hz, 1H), 3.09 (s, 3H), 2.88 (ddt, *J* = 15.5, 6.5, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.0, 139.6, 133.3, 132.2, 131.9, 131.7, 131.5, 127.9, 127.1, 121.9, 119.1, 93.3, 86.6, 57.3, 40.2; IR (Neat Film, NaCl) 3076, 2928, 1682, 1641, 1583, 1565, 1486, 1445, 1395, 1244, 1178, 1154, 1100, 1072, 1024, 1008, 921, 845, 810, 754, 737 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}Cl_2NO_3$ $[M+NH_4]^+$: 469.9961, found 469.9943; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 210 nm, t_R (min): major = 6.38, minor = 8.03.



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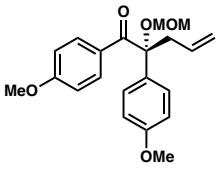
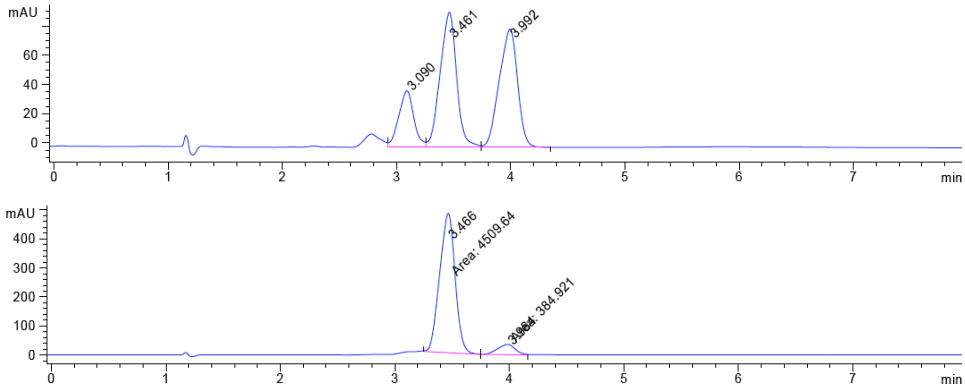
1	6.380	BB	0.2190	5524.54785	395.39938	86.8793
2	8.032	BB	0.2502	834.33191	51.18256	13.1207
Totals :				6358.87976	446.58194	

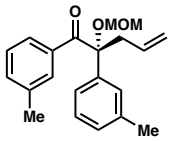


(*S*)-2-(methoxymethoxy)-1,2-bis(4-methoxyphenyl)pent-4-en-1-one (2f)

Reaction carried out 48h instead of 12h. Purified by column chromatography (30% Et_2O in hexanes) to provide a colorless oil (71.2 mg, 99% yield); 84% ee, $[\alpha]_D^{25}$ +129.7 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.37 – 7.29 (m, 2H), 6.91 – 6.80 (m, 2H), 6.80 – 6.70 (m, 2H), 5.55 (dddd, *J* = 16.9, 10.6, 7.5, 6.3 Hz, 1H), 5.00 – 4.90 (m, 2H), 4.75 (d, *J* = 6.8 Hz, 1H), 4.72 (d, *J* = 6.8 Hz, 1H), 3.78 (s, 6H), 3.16 (s, 3H), 3.12 (ddt, *J* = 15.4, 7.6, 1.2 Hz, 1H), 2.94 (ddt, *J* = 15.4, 6.3, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 162.8, 158.9, 133.1, 133.1, 132.8, 127.8, 126.6, 118.3, 113.9, 113.2, 93.2, 86.8, 57.1, 55.4, 55.3, 40.7; IR (Neat Film, NaCl) 3073, 2935br, 2838, 1671, 1640, 1600, 1574, 1510, 1462, 1443, 1419, 1307, 1249, 1172, 1152, 1101, 1027, 1009, 922, 828, 798, 782, 760, 622 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{24}NaO_5$ $[M+Na]^+$: 379.1516, found 379.1525; SFC Conditions: 15% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 3.47, major = 3.98.

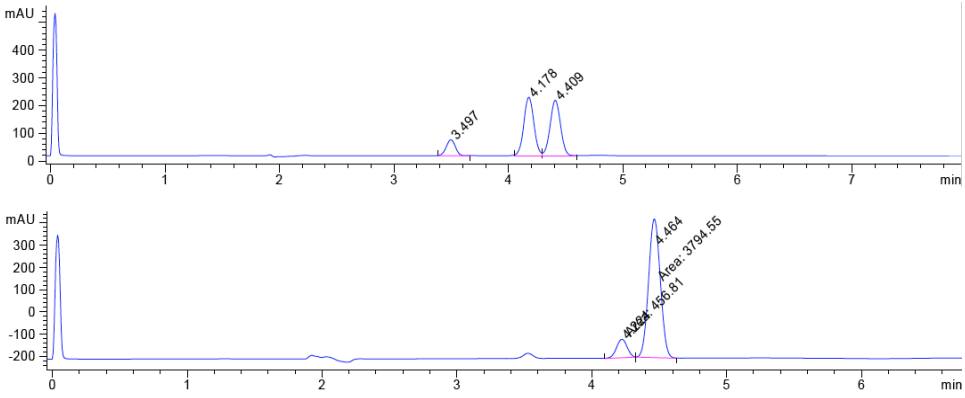


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.465	BV	0.1600	9171.45313	922.15094	92.4204
2	3.983	VB	0.1778	752.17004	67.62103	7.5796
Totals :				9923.62317	989.77197	

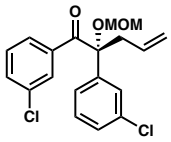


(*S*)-2-(methoxymethoxy)-1,2-di-*m*-tolylpent-4-en-1-one (2g)

Purified by column chromatography (7% Et_2O in hexanes) to provide a colorless oil (63.4 mg, 97% yield); 79% ee, $[\alpha]_D^{25}$ +168.0 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (td, *J* = 1.8, 1.0 Hz, 1H), 7.65 (dq, *J* = 8.0, 1.2 Hz, 1H), 7.30 – 7.17 (m, 4H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.09 – 7.02 (m, 1H), 5.61 – 5.46 (m, 1H), 4.98 (d, *J* = 1.4 Hz, 1H), 4.97 – 4.92 (m, 1H), 4.76 (d, *J* = 6.8 Hz, 1H), 4.71 (d, *J* = 6.9 Hz, 1H), 3.18 – 3.11 (m, 1H), 3.10 (s, 3H), 2.99 (ddt, *J* = 15.5, 6.2, 1.7 Hz, 1H), 2.33 (s, 3H), 2.29 (d, *J* = 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 165.1 (d, *J* = 255.0 Hz), 162.2 (d, *J* = 246.7 Hz), 136.4 (d, *J* = 3.2 Hz), 133.4 (d, *J* = 9.1 Hz), 132.0, 131.0 (d, *J* = 3.1 Hz), 127.1 (d, *J* = 8.1 Hz), 118.9, 115.6 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.5 Hz), 93.3, 86.6, 57.2, 40.4; IR (Neat Film, NaCl) 3077, 2929 (br), 2848, 2826, 1685, 1640, 1598, 1508, 1445, 1409, 1300, 1237, 1157, 1098, 1024, 1013, 976, 922, 854, 835, 814, 792, 760, 620 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}F_2NO_3$ $[M+NH_4]^+$: 350.1562, found 350.1558; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): minor = 4.22, major = 4.64.

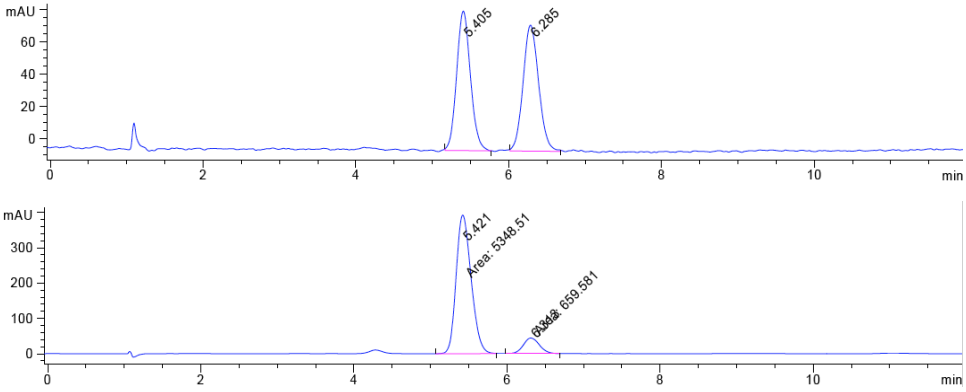


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.224	MM	0.0911	456.81015	83.61755	10.7450
2	4.464	MM	0.1008	3794.54956	627.68188	89.2550
Totals :				4251.35971	711.29943	

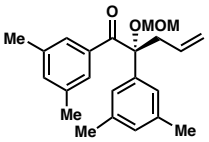


(*S*)-1,2-bis(3-chlorophenyl)-2-(methoxymethoxy)pent-4-en-1-one (2h)

Purified by column chromatography (8% Et2O in hexanes) to provide a colorless oil (64.9 mg, 78% yield); 78% ee, $[\alpha]_D^{25}$ +158.0 (*c* 1.0, CHCl3); 1H NMR (400 MHz, $CDCl_3$) δ 7.90 (ddd, J = 2.1, 1.6, 0.4 Hz, 1H), 7.74 (ddd, J = 7.9, 1.6, 1.0 Hz, 1H), 7.50 (td, J = 1.7, 0.8 Hz, 1H), 7.38 (ddd, J = 8.0, 2.2, 1.1 Hz, 1H), 7.27 – 7.19 (m, 4H), 5.48 (dddd, J = 16.9, 10.4, 7.5, 6.4 Hz, 1H), 5.05 – 4.91 (m, 2H), 4.84 (d, J = 7.1 Hz, 1H), 4.71 (d, J = 7.1 Hz, 1H), 3.16 (ddt, J = 15.6, 7.5, 1.2 Hz, 1H), 3.09 (s, 3H), 2.92 (ddt, J = 15.6, 6.4, 1.6 Hz, 1H); 13C NMR (100 MHz, $CDCl_3$) δ 197.6, 142.5, 136.2, 134.9, 134.4, 132.6, 131.6, 130.5, 130.0, 129.4, 128.8, 128.1, 125.5, 123.5, 119.2, 93.3, 86.6, 57.3, 40.2; IR (Neat Film, NaCl) 3074, 2925, 1686, 1640, 1594, 1570, 1474, 1418, 1278, 1234, 1154, 1079, 1027, 997, 921, 863, 790, 750, 734, 716, 691 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{19}H_{22}Cl_2NO_3$ $[M+NH_4]^+$: 382.0971, found 382.0967; SFC Conditions: 3% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): major = 5.42, minor = 6.31.

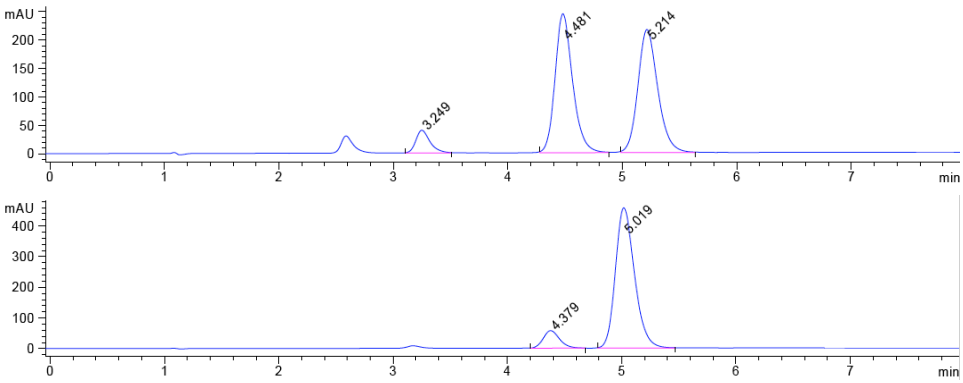


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.421	MM	0.2269	5348.50879	392.88812	89.0218
2	6.313	MM	0.2468	659.58130	44.54468	10.9782
Totals :				6008.09009	437.43280	

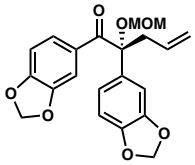


(S)-1,2-bis(3,5-dimethylphenyl)-2-(methoxymethoxy)pent-4-en-1-one (2i)

Purified by column chromatography (10% Et_2O in hexanes) to provide a white solid (70.6 mg, 99% yield); 81% ee, $[\alpha]_D^{25}$ +168.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.30 – 7.17 (m, 4H), 7.12 (t, *J* = 7.7 Hz, 1H), 7.06 (d, 1H), 5.61 – 5.46 (m, 1H), 5.01 – 4.92 (m, 2H), 4.76 (d, *J* = 6.8 Hz, 1H), 4.71 (d, *J* = 6.9 Hz, 1H), 3.14 (ddt, *J* = 15.5, 7.7, 1.3 Hz, 1H), 3.10 (s, 3H), 2.99 (ddt, *J* = 15.5, 6.2, 1.7 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 140.6, 138.2, 137.7, 135.1, 133.2, 132.7, 130.9, 128.4, 128.4, 128.1, 127.8, 125.9, 122.5, 118.3, 93.2, 87.1, 57.0, 40.7, 21.8, 21.5; IR (Neat Film, NaCl) 2921 (br), 1680, 1639, 1602, 1585, 1484, 1444, 1258, 1215, 1182, 1150, 1090, 1030, 921, 766, 741, 708 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_8NO_3$ $[M+NH_4]^+$: 325.1798, found 325.1792; SFC Conditions: 5% IPA, 2.5 mL/min, Chiralpak IC column, λ = 254 nm, t_R (min): minor = 4.38, major = 5.02.

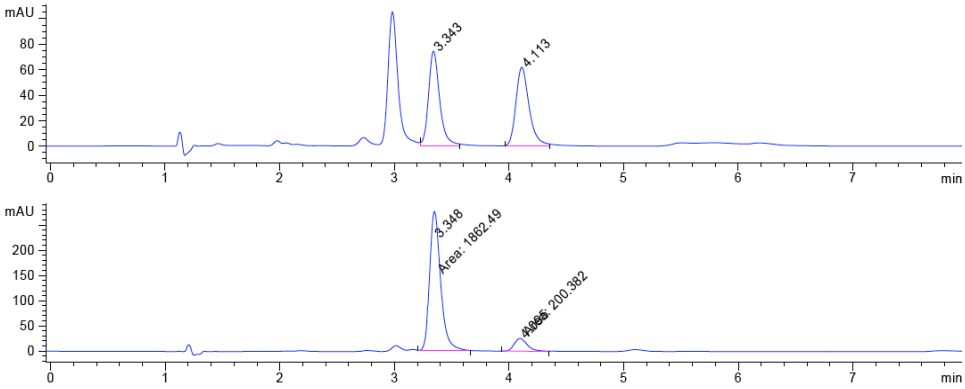


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.379	BB	0.1523	569.48114	57.12303	9.6705
2	5.019	BB	0.1798	5319.38916	456.83295	90.3295
Totals :				5888.87030	513.95598	

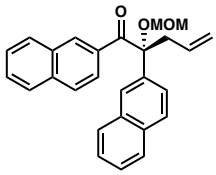


(*S*)-1,2-bis(benzo[*d*][1,3]dioxol-5-yl)-2-(methoxymethoxy)pent-4-en-1-one (2j)

Reaction carried out 48h instead of 12h. Purified by column chromatography (25% Et_2O in hexanes) to provide a colorless oil (56.5 mg, 74% yield); 80% ee, $[\alpha]_D^{25}$ +104.1 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.45 (d, *J* = 1.7 Hz, 1H), 6.96 (d, *J* = 1.8 Hz, 1H), 6.82 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.74 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 5.99 – 5.92 (m, 4H), 5.54 (dddd, *J* = 16.9, 10.5, 7.5, 6.4 Hz, 1H), 5.02 – 4.92 (m, 2H), 4.75 (d, *J* = 6.8 Hz, 1H), 4.71 (d, *J* = 6.8 Hz, 1H), 3.20 (s, 3H), 3.09 (ddt, *J* = 15.5, 7.5, 1.2 Hz, 1H), 2.90 (ddt, *J* = 15.5, 6.5, 1.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 151.1, 148.0, 147.4, 146.9, 135.0, 132.6, 129.2, 127.2, 118.7, 118.4, 110.5, 108.4, 107.7, 106.1, 101.7, 101.3, 93.3, 86.8, 57.2, 40.8; IR (Neat Film, NaCl) 3075, 2898 (br), 2784, 1673, 1640, 1604, 1504, 1487, 1437, 1350, 1254, 1157, 1105, 1039, 934, 814, 793, 756 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{20}NaO_7$ $[M+Na]^+$: 407.1101, found 407.1105; SFC Conditions: 20% IPA, 2.5 mL/min, Chiralpak AD-H column, λ = 254 nm, t_R (min): major = 3.35, minor = 4.10.

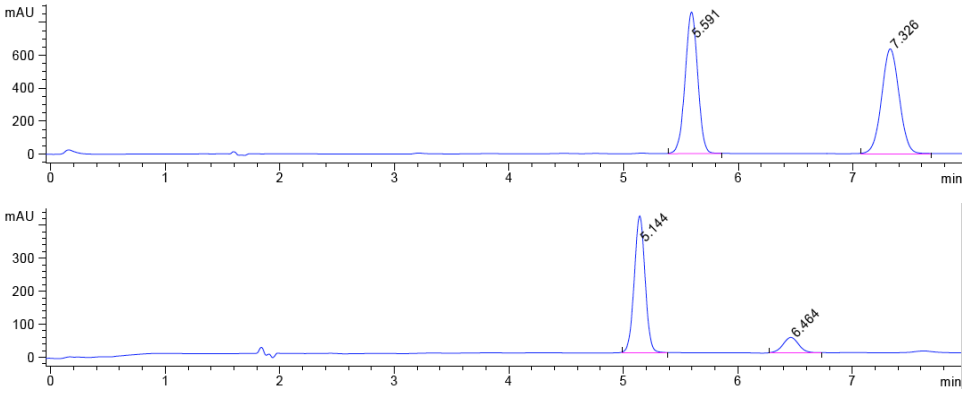


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.348	MM	0.1117	1862.49414	277.88370	90.2863
2	4.095	MM	0.1323	200.38237	25.24171	9.7137
Totals :				2062.87651	303.12540	



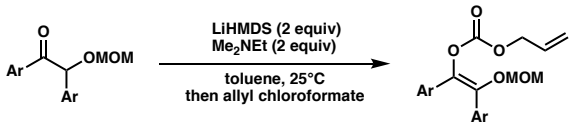
(*S*)-2-(methoxymethoxy)-1,2-di(naphthalen-2-yl)pent-4-en-1-one (2k)

Purified by column chromatography (12% Et_2O in hexanes) to provide a white amorphous solid (79.2 mg, 97% yield); 72% ee, $[\alpha]_D^{25}$ +127.4 (*c* 1.0, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.06 (s, 1H), 8.00 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.84 – 7.78 (m, 2H), 7.77 – 7.70 (m, 2H), 7.67 (d, *J* = 8.7 Hz, 1H), 7.58 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.41 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 5.59 (dddd, *J* = 16.8, 10.4, 7.6, 6.3 Hz, 1H), 5.02 – 4.93 (m, 2H), 4.91 (d, *J* = 7.0 Hz, 1H), 4.84 (d, *J* = 7.0 Hz, 1H), 3.32 (ddt, *J* = 15.5, 7.6, 1.1 Hz, 1H), 3.15 (ddt, *J* = 15.5, 6.3, 1.6 Hz, 1H), 3.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 138.4, 135.1, 133.3, 132.8, 132.7, 132.4, 132.3, 132.3, 129.9, 128.5, 128.4, 127.8, 127.7, 127.6, 126.4, 126.4, 126.3, 126.2, 124.5, 123.3, 118.6, 93.4, 87.4, 57.3, 40.6; IR (Neat Film, NaCl) 3059, 2932 (br), 1679, 1640, 1625, 1596, 1507, 1464, 1436, 1353, 1274, 1220, 1190, 1152, 1130, 1099, 1075, 1027, 999, 921, 859, 821, 774, 757 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{27}H_{24}NaO_3$ $[M+Na]^+$: 419.1618, found 419.1623; SFC Conditions: 2% IPA, 2.5 mL/min, Chiralcel OJ-H column, λ = 254 nm, t_R (min): major = 5.14, minor = 6.46.

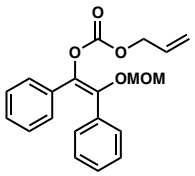


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.144	BB	0.1013	2742.00952	413.65814	86.1900
2	6.464	BB	0.1508	439.34341	46.25590	13.8100
Totals :				3181.35294	459.91404	

General Procedure for Preparation of Allyl Enol Carbonate Substrates

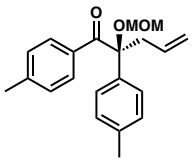


To a flame-dried flask was added LiHMDS (335 mg, 2 mmol) followed by toluene (3.0 mL) and N,N-dimethylethylamine (0.213 mL) and the resulting mixture stirred at 25 °C for 5 minutes. A solution of ketone (1 mmol) in toluene (2.0 mL) was then added, and the reaction stirred at 25 °C for an additional 30 minutes. The flask was then submerged in a room temperature water bath, and allyl chloroformate (0.217 mL, 2 mmol) was added neat, 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. After purification, the major isomer is obtained with a ratio >98:2 (determined by ^1H NMR) unless stated otherwise.



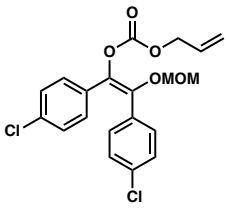
(*Z*)-allyl (2-(methoxymethoxy)-1,2-diphenylvinyl) carbonate (1a)

Run on 5.85 mmol scale. Purified by column chromatography (20% Et_2O in hexanes) to provide a white solid (1.588 g, 80% yield); ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 5H), 7.21 – 7.12 (m, 5H), 5.95 (ddt, J = 17.2, 10.5, 5.7 Hz, 1H), 5.37 (dq, J = 17.2, 1.5 Hz, 1H), 5.27 (dq, J = 10.5, 1.3 Hz, 1H), 4.77 (s, 2H), 4.69 (dt, J = 5.6, 1.4 Hz, 2H), 3.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 144.2, 135.8, 133.8, 132.1, 131.5, 130.4, 129.1, 128.7, 128.6, 128.1, 128.0, 118.9, 94.3, 69.0, 57.0; IR (Neat Film, NaCl) 2954, 1761, 1445, 1364, 1233, 1156, 1130, 1049, 1006, 956, 778, 698 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{20}NaO_5$ $[M+Na]^+$: 363.1203, found 363.1203.



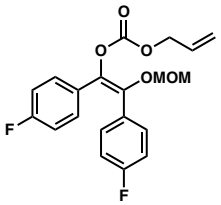
(*Z*)-allyl (2-(methoxymethoxy)-1,2-di-*p*-tolylvinyl) carbonate (1b)

Run on 1.19 mmol scale. Purified by column chromatography (18% Et_2O in hexanes) to provide a colorless oil (389.0 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.16 (m, 2H), 7.11 – 7.03 (m, 4H), 7.00 – 6.92 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.26 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.75 (s, 2H), 4.68 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.54 (s, 3H), 2.32 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.4, 143.8, 139.0, 137.7, 135.6, 131.6, 131.0, 130.2, 129.3, 129.2, 128.9, 128.5, 118.8, 94.3, 69.0, 57.0, 21.5, 21.4; IR (Neat Film, NaCl) 2922 (br), 1762, 1652, 1609, 1558, 1513, 1448 (br), 1364, 1319, 1302, 1235, 1183, 1156, 1131, 1107, 1048, 1026, 1006, 961, 877, 824, 786 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{28}NO_5$ $[M+NH4]^+$: 386.1962, found 386.1970.



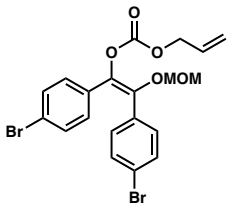
(*Z*)-allyl (1,2-bis(4-chlorophenyl)-2-(methoxymethoxy)vinyl) carbonate (1c)

Run on 0.573 mmol scale. Purified by column chromatography (20% Et_2O in hexanes) to provide a colorless oil (198.3 mg, 85% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.26 – 7.21 (m, 4H), 7.18 – 7.13 (m, 2H), 7.12 – 7.07 (m, 2H), 5.94 (ddt, *J* = 17.3, 10.9, 5.7 Hz, 1H), 5.38 (dq, *J* = 17.1, 1.5 Hz, 1H), 5.29 (dq, *J* = 10.4, 1.4 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.8, 1.5 Hz, 2H), 3.55 (d, *J* = 0.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.1, 143.7, 135.4, 135.3, 134.2, 132.1, 131.6, 131.3, 130.4, 130.0, 129.1, 128.6, 119.2, 94.5, 69.3, 57.1; IR (Neat Film, NaCl) 3088, 2956, 2900, 1763, 1648, 1593, 1490, 1398, 1364, 1317, 1297, 1236, 1157, 1133, 1091, 1049, 1004, 958, 925, 874, 835, 782 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}Cl_2NO_5$ $[M+NH4]^+$: 426.0870, found 426.0854.



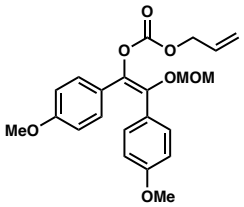
(*Z*)-allyl (1,2-bis(4-fluorophenyl)-2-(methoxymethoxy)vinyl) carbonate (1d)

Run on 1.25 mmol scale. Purified by column chromatography (20% Et_2O in hexanes) to provide a white solid (323.1 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 2H), 7.18 – 7.12 (m, 2H), 7.01 – 6.93 (m, 2H), 6.90 – 6.83 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.2 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.54 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.1 (dddd, *J* = 13.8, 8.7, 5.4, 1.2 Hz), -112.7 (dddd, *J* = 13.9, 8.7, 5.3, 1.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, *J* = 250.0 Hz), 162.4 (d, *J* = 248.5 Hz), 153.2, 143.3, 135.1, 132.3 (d, *J* = 8.3 Hz), 131.4, 130.7 (d, *J* = 8.3 Hz), 129.8 (d, *J* = 3.4 Hz), 128.0 (d, *J* = 3.4 Hz), 119.1, 115.9 (d, *J* = 21.7 Hz), 115.4 (d, *J* = 21.8 Hz), 94.4, 69.2, 57.0; IR (Neat Film, NaCl) 2952, 1762, 1648, 1602, 1508, 1364, 1318, 1298, 1233, 1157, 1131, 1096, 1048, 1006, 959, 880, 841, 817, 780 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}F_2NO_5$ $[M+NH4]^+$: 394.1461, found 394.1450.



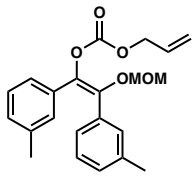
(*Z*)-allyl (1,2-bis(4-bromophenyl)-2-(methoxymethoxy)vinyl) carbonate (1e)

Run on 0.853 mmol scale. Purified by column chromatography (20% Et_2O in hexanes) to provide a white solid (316.2 mg, 74% yield); ^{1}H NMR (400 MHz $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.34 – 7.28 (m, 2H), 7.21 – 7.14 (m, 2H), 7.07 – 7.01 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.5, 5.7 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 143.8, 135.4, 132.6, 132.1, 131.9, 131.6, 131.3, 130.9, 130.3, 123.8, 122.5, 119.2, 94.6, 69.3, 57.1; IR (Neat Film, NaCl) 2953 (br), 1762, 1651, 1586, 1488, 1384, 1363, 1316, 1297, 1234, 1156, 1132, 1100, 1070, 1047, 1001, 958, 872, 830, 778 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}Br_2NO_5$ $[M+NH4]^+$: 513.9859, found 513.9860.



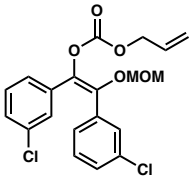
(*Z*)-allyl (2-(methoxymethoxy)-1,2-bis(4-methoxyphenyl)vinyl) carbonate (1f)

Run on 1.08 mmol scale. Purified by column chromatography (40% Et_2O in hexanes) to provide a slightly yellow oil (327.3 mg, 76% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 – 7.21 (m, 2H), 7.15 – 7.09 (m, 2H), 6.82 – 6.76 (m, 2H), 6.72 – 6.67 (m, 2H), 5.94 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H), 3.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 159.1, 153.4, 143.0, 135.1, 131.7, 131.6, 130.0, 126.4, 124.4, 118.8, 114.0, 113.6, 94.2, 68.9, 56.9, 55.3, 55.2; IR (Neat Film, NaCl) 2952 (br), 2838, 1761, 1608, 1511, 1458, 1364, 1319, 1292, 1237, 1175, 1156, 1130, 1107, 1049, 1017, 999, 960, 836 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{28}NO_7$ $[M+NH4]^+$: 418.1860, found 418.1843.



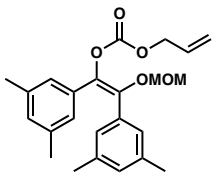
(*Z*)-allyl (2-(methoxymethoxy)-1,2-di-*m*-tolylvinyl) carbonate (1g)

Run on 1.18 mmol scale. Purified by column chromatography (20% Et_2O in hexanes) to provide a colorless oil (250.5 mg, 58% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 – 6.90 (m, 8H), 5.95 (ddt, *J* = 17.2, 10.5, 5.6 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.77 (s, 2H), 4.69 (dt, *J* = 5.6, 1.4 Hz, 2H), 3.56 (s, 3H), 2.27 (s, 2H), 2.20 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 144.2, 138.2, 137.6, 135.8, 133.7, 132.0, 131.6, 130.8, 129.9, 129.0, 128.7, 128.4, 127.9, 127.6, 125.9, 118.9, 94.3, 69.0, 57.0, 21.4, 21.4; IR (Neat Film, NaCl) 2950, 2921, 1763, 1651, 1604, 1584, 1488, 1449, 1381, 1363, 1320, 1239, 1192, 1156, 1127, 1053, 1031, 991, 969, 926, 851, 791, 714, 695 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{28}NO_5$ $[M+NH4]^+$: 386.1962, found 386.1973.



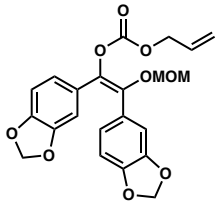
(*Z*)-allyl (1,2-bis(3-chlorophenyl)-2-(methoxymethoxy)vinyl) carbonate (1h)

Run on 0.397 mmol scale. Purified by column chromatography (15% Et_2O in hexanes) to provide a slightly yellow oil (101.9 mg, 63% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (ddd, *J* = 2.0, 1.5, 0.5 Hz, 1H), 7.30 (ddd, *J* = 7.9, 2.1, 1.2 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.16 (dddd, *J* = 5.6, 4.5, 2.3, 1.3 Hz, 2H), 7.08 (td, *J* = 7.9, 0.5 Hz, 1H), 6.99 (ddd, *J* = 7.8, 1.7, 1.1 Hz, 1H), 5.95 (ddt, *J* = 17.1, 10.4, 5.7 Hz, 1H), 5.39 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.30 (dq, *J* = 10.4, 1.2 Hz, 1H), 4.78 (s, 2H), 4.70 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.55 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0, 143.9, 135.3, 135.3, 134.7, 134.2, 133.7, 131.3, 130.1, 130.0, 129.7, 129.5, 128.7, 128.5, 127.1, 119.2, 94.6, 69.3; IR (Neat Film, NaCl) 2958 (br), 1762, 1594, 1566, 1474, 1418, 1363, 1234, 1157, 1136, 1080, 1052, 1018, 966, 792, 682 (br) cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}Cl_2NO_5$ $[M+NH4]^+$: 426.0870, found 426.0859.



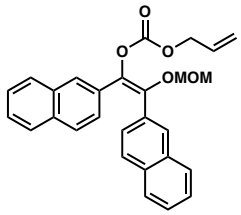
(*Z*)-allyl (1,2-bis(3,5-dimethylphenyl)-2-(methoxymethoxy)vinyl) carbonate (1i)

Run on 1.09 mmol scale. Purified by column chromatography (15% Et_2O in hexanes) to provide a white solid (290.7 mg, 67% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 – 6.87 (m, 3H), 6.87 – 6.69 (m, 3H), 5.96 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H), 5.38 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.76 (s, 2H), 4.69 (dt, *J* = 5.6, 1.5 Hz, 2H), 3.55 (s, 3H), 2.21 (s, 6H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 144.1, 137.9, 137.3, 135.8, 133.6, 131.9, 131.7, 130.7, 129.6, 128.0, 126.2, 118.8, 94.3, 69.0, 56.9, 21.3, 21.3; IR (Neat Film, NaCl) 2950, 2920, 1763, 1648, 1601, 1449, 1379, 1363, 1336, 1307, 1291, 1245, 1222, 1203, 1157, 1129, 1054, 1014, 987, 952, 926, 855, 783, 682 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{24}H_{30}NO_5$ $[M+NH4]^+$: 414.2275, found 414.2260.



(*Z*)-allyl (1,2-bis(benzo[*d*][1,3]dioxol-5-yl)-2-(methoxymethoxy)vinyl) carbonate (1j)

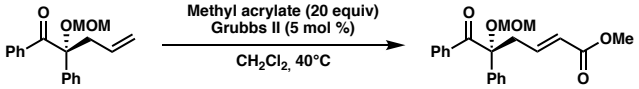
Run on 0.44 mmol scale. Purified by column chromatography (35% Et_2O in hexanes) to provide a colorless oil (188.2 mg, 99% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.60 (m, 6H), 6.01 – 5.87 (m, 5H), 5.37 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.27 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.76 (s, 2H), 4.68 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 148.3, 147.9, 147.4, 143.2, 135.2, 131.5, 127.8, 125.8, 124.7, 123.0, 119.0, 110.2, 109.1, 108.6, 108.2, 101.4, 101.2, 94.3, 69.1, 57.0; IR (Neat Film, NaCl) 2897, 1759, 1503, 1489, 1439, 1364, 1341, 1300, 1239, 1225, 1154, 1101, 1082, 1039, 1008, 968, 932, 884, 870, 812 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{22}H_{24}NO_9$ $[M+NH4]^+$: 446.1446, found 446.1452.



(*Z*)-allyl (2-(methoxymethoxy)-1,2-di(naphthalen-2-yl)vinyl) carbonate (1k)

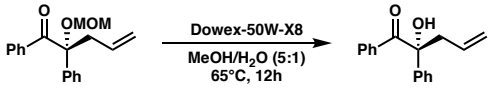
Run on 0.988 mmol scale. Purified by column chromatography (20% Et_2O in hexanes) to provide a beige oil (345.8 mg, 79% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 1H), 7.86 – 7.83 (m, 1H), 7.81 – 7.76 (m, 1H), 7.74 – 7.63 (m, 4H), 7.52 – 7.36 (m, 6H), 7.15 (dd, *J* = 8.6, 1.8 Hz, 1H), 5.96 (ddt, *J* = 17.2, 10.4, 5.7 Hz, 1H), 5.39 (dq, *J* = 17.2, 1.5 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.3 Hz, 1H), 4.85 (s, 2H), 4.71 (dt, *J* = 5.7, 1.4 Hz, 2H), 3.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.4, 144.6, 136.5, 133.5, 133.2, 133.1, 132.9, 131.5, 131.4, 130.2, 129.7, 128.5, 128.4, 128.4, 127.8, 127.8, 127.7, 127.6, 127.4, 127.0, 126.5, 126.5, 126.2, 119.0, 94.7, 69.2, 57.2; IR (Neat Film, NaCl) 3058, 2952, 1761, 1648, 1506, 1457, 1362, 1298, 1244, 1224, 1192, 1156, 1118, 1049, 1012, 974, 948, 862, 823, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{28}H_{28}NO_5$ $[M+NH4]^+$: 458.1962, found 458.1980.

Derivatization of Alkylation Products



methyl (*R*,*E*)-5-(methoxymethoxy)-6-oxo-5,6-diphenylhex-2-enoate (3)

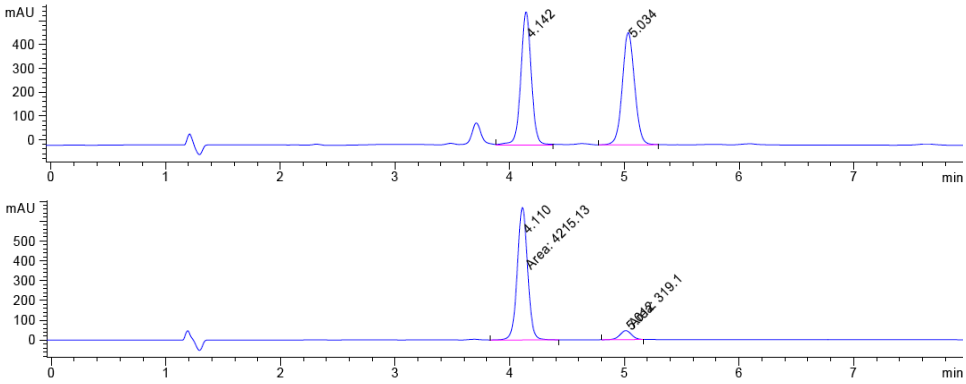
To an oven dried vial was added the alpha-tertiary benzoin (0.1 mmol) followed by CH_2Cl_2 (1 mL) and methyl acrylate (2.0 mmol, 180 μL). The resulting solution was stirred for five minutes at ambient temperature then treated with a solution of Grubbs' second generation catalyst (4.2 mg) in 500 μL CH_2Cl_2. The reaction was then heated to 40 °C and stirred overnight. The crude reaction mixture was directly concentrated and then purified by silica gel flash chromatography (10% EtOAc in hexanes) to provide a colorless oil (32.0 mg, 93% yield; $[\alpha]_D^{25}$ +164.54 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.81 (m, 2H), 7.46 – 7.31 (m, 5H), 7.30 – 7.22 (m, 3H), 6.71 (ddd, *J* = 15.8, 7.8, 6.8 Hz, 1H), 5.72 (dt, *J* = 15.7, 1.5 Hz, 1H), 4.73 (s, 2H), 3.66 (s, 3H), 3.30 (ddd, *J* = 15.7, 7.7, 1.4 Hz, 1H), 3.15 (s, 3H), 3.14 – 3.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.0, 166.7, 143.7, 139.9, 134.5, 132.7, 130.7, 128.9, 128.2, 128.0, 125.1, 124.3, 93.6, 87.3, 57.1, 51.5, 39.7; IR (Neat Film, NaCl) 2949 (br), 1723, 1681, 1597, 1463, 1447, 1272, 1238, 1199, 1153, 1079, 1025, 926, 734, 702, 682 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_5$ $[M+NH_4]^+$: 372.1805, found 372.1796.



(*S*)-2-hydroxy-1,2-diphenylpent-4-en-1-one (4)

Dowex-50W-X8 resin (H+ form, 170 mg) and the corresponding ketone **2a** (0.111 mmol) were added to a 1-dram vial containing 1.6 mL of MeOH and 0.32 ml of H_2O. The vial was sealed with a cap containing a PTFE-lined silicone-septum. The solution was heated and stirred at 65 °C for 12 h. The crude mixture was filtered through a short Celite plug to remove the solids (eluting with 1:1 hexanes:EtOAc). The resulting solution was concentrated under reduced pressure and the residue was purified by column chromatography (20% Et_2O in hexanes) to provide a white solid (27.8 mg, 99% yield); 86% ee, $[\alpha]_D^{25}$ +54.5 (*c* 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.53 – 7.48 (m, 2H), 7.46 – 7.42 (m, 1H), 7.41 – 7.36 (m, 2H), 7.34 – 7.27 (m, 3H), 5.74 (dddd, *J* = 17.1, 10.2, 7.5, 6.9 Hz, 1H), 5.12 (ddt, *J* = 10.2, 1.9, 0.9 Hz, 1H), 5.02 (ddt, *J* = 17.2, 2.0, 1.3 Hz, 1H), 4.19 (s, 1H), 3.15 (ddt, *J* = 13.8, 7.5, 1.0 Hz,

1H), 2.98 (ddt, *J* = 13.7, 6.9, 1.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.9, 141.9, 134.6, 132.9, 132.4, 130.3, 129.0, 128.3, 128.2, 125.8, 120.5, 81.5, 44.1; IR (Neat Film, NaCl) 3459 (Br), 3062, 2924, 1674, 1597, 1578, 1491, 1447, 1364, 1230, 1181, 1140, 1096, 1068, 1035, 1001, 976, 922, 762, 724, 699, 678, 632 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{17}H_{15}O$ $[M\text{-}OH]^+$: 235.1117, found 235.1118; SFC Conditions: 10% IPA, 2.5 mL/min, Chiralcel OD-H column, λ = 210 nm, t_R (min): major = 4.11, minor = 5.01.



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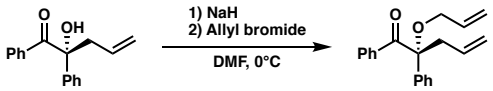
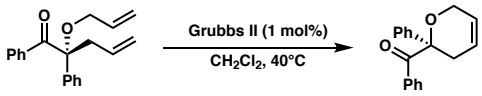
2	5.012	MM	0.1165	319.09998	45.64754	7.0376



(*R*)-2-(allyloxy)-1,2-diphenylpent-4-en-1-one (SI1)

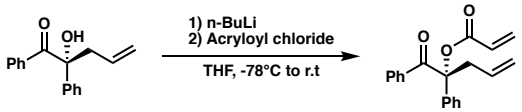
To a solution of **4** in DMF (3 mL) was added NaH (0.6 mmol) at 0 °C. The mixture was stirred for 30 min at 0 °C then allyl bromide (0.39 mmol) was added dropwise and the reaction was allowed to warm-up to room temperature. After completion of the reaction showed by TLC, NH_4Cl (aq) was added and the mixture was extracted with EtOAc three times. The combined organic layers were washed with water, brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by silica gel flash chromatography (2% EtOAc in hexanes) to afford the desired product as a colorless oil (77.2 mg, 88% yield); $[\alpha]_D^{25}$ +52.3 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.52 – 7.45 (m, 2H), 7.44 – 7.37 (m, 1H), 7.36 – 7.30 (m, 2H), 7.29 – 7.21 (m, 3H), 5.75 (dddd, *J* = 17.2, 10.5, 5.6, 5.0 Hz, 1H), 5.60 – 5.47 (m, 1H), 5.22 (dq, *J* = 17.2, 1.7 Hz, 1H), 5.08 (dq, *J* = 10.4, 1.5 Hz, 1H), 5.01 – 4.98 (m, 1H), 4.98 – 4.91 (m, 1H), 4.16 (ddt, *J* = 11.9, 5.6, 1.5 Hz, 1H), 3.72 (ddt, *J* = 11.9, 5.0, 1.6 Hz, 1H), 3.16 (ddt, *J* = 15.4, 7.6, 1.2 Hz, 1H), 2.91 (ddt, *J* = 15.4, 6.4, 1.6 Hz, 1H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 200.9, 140.7, 135.0, 134.1, 132.8, 132.4, 130.3, 128.5, 128.1, 127.6, 125.5, 118.3, 116.8, 87.6, 65.4, 40.0; IR (Neat Film, NaCl) 3072, 2935, 1681, 1647, 1596, 1447, 1238, 1120, 1072, 1028, 994, 918, 827, 730, 701, 681, 667 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{20}O_2Na$ $[M+Na]^+$: 315.1356, found 315.1343.



(*R*)-phenyl(2-phenyl-3,6-dihydro-2*H*-pyran-2-yl)methanone (5)

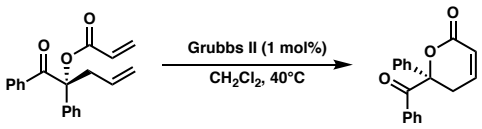
To an oven dried vial was added **5** (0.24 mmol) followed by CH_2Cl_2 (3 mL). The resulting solution was treated with a solution of Grubbs' second-generation catalyst (2 mg) in CH_2Cl_2 (1.5 mL). The reaction was then heated to 40 °C and stirred overnight. The crude reaction mixture was directly concentrated and then purified by silica gel flash chromatography (3% EtOAc in hexanes) to provide a colorless oil (64.2 mg, 99% yield); $[\alpha]_D^{25}$ +222.8 (*c* 1.00, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.55 – 7.49 (m, 2H), 7.47 – 7.40 (m, 1H), 7.39 – 7.33 (m, 2H), 7.33 – 7.26 (m, 3H), 5.92 (ddq, *J* = 10.2, 5.7, 2.2 Hz, 1H), 5.70 – 5.59 (m, 1H), 4.33 (dtdd, *J* = 17.2, 3.2, 2.2, 1.0 Hz, 1H), 4.05 (dddt, *J* = 17.2, 4.1, 3.0, 2.1 Hz, 1H), 3.27 – 3.15 (m, 1H), 2.23 (ddtd, *J* = 17.3, 4.1, 3.0, 2.2 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.6, 142.4, 135.1, 132.8, 130.0, 128.9, 128.2, 127.6, 124.5, 124.4, 124.2, 84.2, 63.7, 35.0; IR (Neat Film, NaCl) 3059, 3037, 2931, 2900, 2840, 1682, 1597, 1579, 1492, 1447, 1417, 1386, 1327, 1258, 1226, 1210, 1180, 1089, 1024, 978, 960, 942, 793, 754, 700, 657 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{17}O_2$ $[M+H]^+$: 265.1223, found 265.1224.



(*R*)-1-oxo-1,2-diphenylpent-4-en-2-yl acrylate (SI2)

To a solution of **4** (0.147 mmol) in THF (1.5 mL) was added dropwise *n*-BuLi (0.127 mL, 2.3M solution in hexane, 0.294 mmol, 2 equiv) at –78 °C. The resulting yellow solution was stirred for 30 min at -78 °C. Acryloyl chloride (0.735 mmol) was then added dropwise and the reaction was allowed to warm-up to room temperature overnight. Water was added and the reaction was extracted three times with EtOAc. The combined organic layers were washed with 1N NaOH (aq), brine, dried over Na_2SO_4, filtered and concentrated. The crude product was purified by

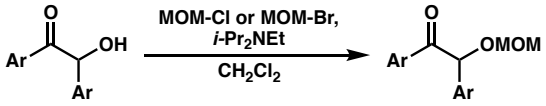
silica gel flash chromatography (5% EtOAc in hexanes) to afford the desired product as a colorless oil (42.2 mg, 94% yield); $[\alpha]_D^{25}$ +140.6 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.60 – 7.54 (m, 2H), 7.45 – 7.38 (m, 2H), 7.38 – 7.29 (m, 2H), 7.23 (ddt, *J* = 8.0, 6.7, 1.2 Hz, 2H), 6.40 (dd, *J* = 17.3, 1.3 Hz, 1H), 6.12 (dd, *J* = 17.3, 10.5 Hz, 1H), 5.83 (dd, *J* = 10.4, 1.3 Hz, 1H), 5.46 (dddd, *J* = 17.0, 10.3, 8.8, 5.9 Hz, 1H), 5.02 – 4.87 (m, 2H), 3.60 – 3.41 (m, 1H), 3.13 (ddt, *J* = 14.8, 5.9, 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 164.2, 137.8, 135.1, 132.3, 132.0, 131.6, 129.2, 129.0, 128.2, 128.2, 128.0, 125.0, 119.4, 88.3, 41.9; IR (Neat Film, NaCl) 3060, 2929, 1727, 1687, 1634, 1598, 1491, 1447, 1404, 1295, 1243, 1173, 1121, 1061, 1028, 986, 919, 828, 809, 760, 736, 701, 688, 681 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{22}NO_3$ $[M+NH_4]^+$: 324.1594, found 324.1597.



(*R*)-6-benzoyl-6-phenyl-5,6-dihydro-2*H*-pyran-2-one (6)

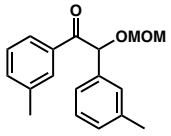
In an oven dried vial, a solution of **7** (0.078 mmol) in CH_2Cl_2 (1.1 mL) was treated with a solution of Grubbs' second-generation catalyst (0.6 mg) in CH_2Cl_2 (0.5 mL). The reaction was then heated to 40 °C and stirred overnight. The crude reaction mixture was directly concentrated and then purified by silica gel flash chromatography (10% EtOAc in hexanes) to provide a colorless oil (21.5 mg, 99% yield); $[\alpha]_D^{25}$ +344.7 (*c* 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.87 (m, 2H), 7.61 – 7.56 (m, 2H), 7.48 – 7.38 (m, 3H), 7.38 – 7.28 (m, 3H), 6.95 (ddd, *J* = 9.9, 5.9, 2.5 Hz, 1H), 5.97 (ddd, *J* = 9.9, 2.7, 0.9 Hz, 1H), 3.65 (ddd, *J* = 18.2, 5.9, 1.0 Hz, 1H), 2.70 (dt, *J* = 18.2, 2.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 162.3, 146.3, 138.4, 134.0, 133.5, 130.7, 129.3, 128.8, 128.5, 124.4, 120.9, 90.4, 34.9; IR (Neat Film, NaCl) 3061, 2924, 2854, 1744, 1682, 1596, 1579, 1491, 1448, 1409, 1378, 1319, 1244, 1222, 1184, 1158, 1100, 1056, 1002, 951, 909, 868, 815, 784, 755, 736, 699 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{18}NO_3$ $[M+NH_4]^+$: 296.1281, found 296.1280.

Mom protection of benzoin derivatives



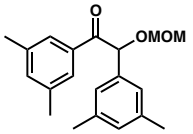
Method A: At room temperature, MOM-Br (4 equiv) was added to a solution of corresponding benzoin (1 equiv) and *i*-Pr_2NEt (5 equiv) in CH_2Cl_2 (0.25 mol/L). The reaction was stirred overnight at 40 °C. The crude reaction mixture was quenched with the addition of a 2 M NaOH solution. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic layers were washed with a 1 M HCl solution, dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel flash chromatography to afford the desired Mom protected benzoin.

Method B: At 0 °C, MOM-Cl (4 equiv) was added to a solution of corresponding benzoin (1 equiv) and *i*-Pr_2NEt (5 equiv) in CH_2Cl_2 (0.25 mol/L). The reaction was stirred overnight at room temperature. The crude reaction mixture was quenched with the addition of a 2 M NaOH solution. The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 twice. The combined organic layers were washed with a 1 M HCl solution, dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel flash chromatography to afford the desired Mom protected benzoin.



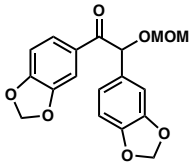
2-(methoxymethoxy)-1,2-di-*m*-tolylethan-1-one (SI3)

Method A. Run on 2.31 mmol scale. Purified by column chromatography (20% Et_2O in hexanes) to provide a colorless oil (415.3 mg, 75% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (s, 1H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.19 (m, 5H), 7.08 (d, *J* = 7.4 Hz, 1H), 5.97 (s, 1H), 4.74 (s, 2H), 3.36 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 138.9, 138.5, 135.9, 135.3, 134.2, 129.6, 129.6, 128.9, 128.7, 128.5, 126.4, 125.4, 95.1, 79.9, 56.1, 21.5, 21.5; IR (Neat Film, NaCl) 2926 (br), 1694, 1604, 1586, 1487, 1457, 1254, 1213, 1167, 1149, 1108, 1034, 964, 918, 773, 700 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{21}O_3$ $[M+H]^+$: 285.1485, found 285.1484.



1,2-bis(3,5-dimethylphenyl)-2-(methoxymethoxy)ethan-1-one (SI4)

Method A. Run on 1.49 mmol scale. Purified by column chromatography (20% Et_2O in hexanes) to provide a colorless oil (411.1 mg, 88% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 2H), 7.13 (s, 1H), 7.07 (s, 2H), 6.92 (s, 1H), 5.96 (s, 1H), 4.76 – 4.72 (m, 2H), 3.39 (s, 3H), 2.32 (s, 6H), 2.28 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 138.6, 138.2, 135.8, 135.4, 135.0, 130.5, 126.8, 126.0, 95.0, 79.6, 56.1, 21.4, 21.3; IR (Neat Film, NaCl) 2920 (br), 1691, 1606, 1457 br, 1305, 1184, 1149, 1107, 1043, 1017, 918, 848, 792 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{20}H_{25}O_3$ $[M+H]^+$: 313.1798, found 313.1804.



1,2-bis(benzo[*d*][1,3]dioxol-5-yl)-2-(methoxymethoxy)ethan-1-one (SI5)

Method B. Run on 1.73 mmol scale. Purified by column chromatography (50% Et_2O in hexanes) to provide a beige amorphous solid (571.3 mg, 96% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (ddd, J = 8.2, 1.8, 0.6 Hz, 1H), 7.44 (d, J = 1.7 Hz, 1H), 6.94 – 6.89 (m, 2H), 6.82 – 6.73 (m, 2H), 6.00 (s, 2H), 5.94 – 5.92 (m, 2H), 5.83 (s, 1H), 4.72 (s, 2H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 194.4, 152.0, 148.3, 148.2, 148.1, 130.0, 129.8, 125.5, 122.1, 108.9, 108.7, 108.3, 108.1, 102.0, 101.4, 94.9, 79.3, 56.1; IR (Neat Film, NaCl) 2896, 1684, 1604, 1503, 1489, 1443, 1358, 1251, 1150, 1099, 1037, 931, 798 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{18}H_{17}O_7$ $[M+H]^+$: 345.0969, found 345.0963.

X-Ray Crystal Structure for 4

A crystal of compound ***4*** was grown by slow evaporation of EtOAc/Hexanes.

Figure S1. X-Ray Coordinate of compound 4

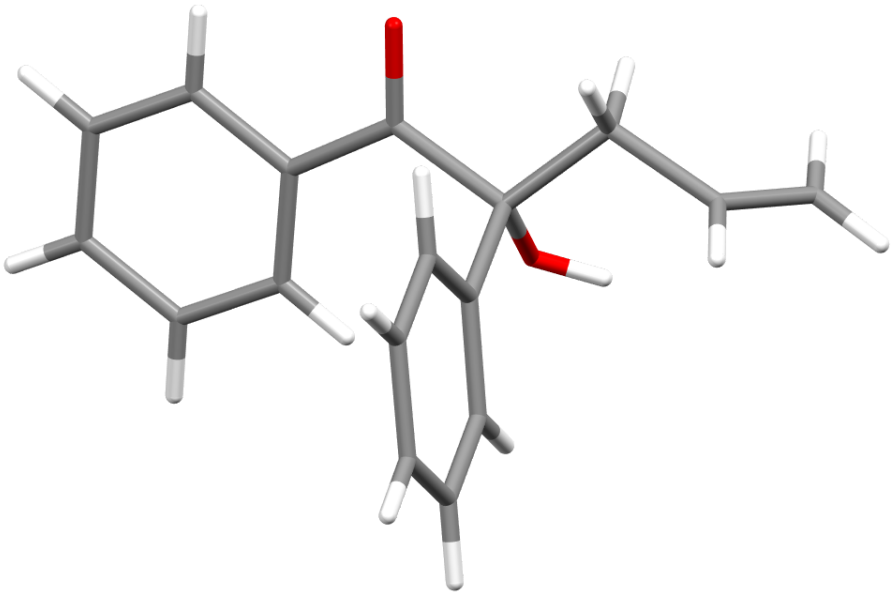


Table 1. Crystal data and structure refinement for v19245.

Identification code	v19245	
Empirical formula	C17 H16 O2	
Formula weight	252.30	
Temperature	100 K	
Wavelength	1.54178 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 6.0838(9) Å	a= 104.527(6)°
	b = 7.2384(11) Å	b= 95.732(7)°
	c = 8.3465(12) Å	g = 105.236(7)°
Volume	337.85(9) $Å^3$	
Z	1	
Density (calculated)	1.240 g/cm^3	
Absorption coefficient	0.635 mm^{-1}	
F(000)	134	
Crystal size	0.23 x 0.22 x 0.09 mm^3	
Theta range for data collection	5.564 to 79.408°.	

Index ranges	-7<=h<=7,-9<=k<=9,-10<=l<=10
Reflections collected	15392
Independent reflections	2730 [R(int) = 0.0394]
Completeness to theta = 67.679°	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.8971
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2730 / 3 / 173
Goodness-of-fit on F^2	1.124
Final R indices [I>2sigma(I)]	R1 = 0.0347, wR2 = 0.1003
R indices (all data)	R1 = 0.0350, wR2 = 0.1008
Absolute structure parameter [Flack]	-0.08(12)
Extinction coefficient	n/a
Largest diff. peak and hole	0.237 and -0.195 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for v19245. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
O(1)	1929(3)	6639(2)	3788(2)	28(1)
O(2)	7109(2)	5729(2)	3722(2)	18(1)
C(1)	3498(4)	2012(3)	2629(3)	19(1)
C(2)	2477(4)	21(3)	1703(3)	23(1)
C(3)	196(4)	-625(4)	867(3)	25(1)
C(4)	-1054(4)	738(4)	941(3)	26(1)
C(5)	-46(4)	2728(3)	1848(3)	21(1)
C(6)	2246(4)	3391(3)	2708(3)	18(1)
C(7)	3157(4)	5550(3)	3727(3)	17(1)
C(8)	5633(3)	6424(3)	4782(3)	16(1)
C(9)	5597(4)	5646(3)	6333(3)	17(1)
C(10)	7086(4)	4584(3)	6704(3)	18(1)
C(11)	7052(4)	3930(3)	8137(3)	22(1)
C(12)	5520(4)	4327(4)	9212(3)	25(1)
C(13)	4017(4)	5365(4)	8842(3)	24(1)
C(14)	4053(4)	6033(3)	7417(3)	20(1)
C(15)	6325(4)	8725(3)	5307(3)	20(1)
C(16)	8745(4)	9622(3)	6294(3)	20(1)
C(17)	10493(4)	10636(4)	5752(3)	27(1)

Table 3. Bond lengths [Å] and angles [°] for v19245.

O(1)-C(7)	1.216(3)
O(2)-H(2W)	0.8400
O(2)-C(8)	1.420(3)
C(1)-H(1)	0.9500
C(1)-C(2)	1.391(3)
C(1)-C(6)	1.399(3)
C(2)-H(2)	0.9500
C(2)-C(3)	1.390(3)
C(3)-H(3)	0.9500
C(3)-C(4)	1.389(4)
C(4)-H(4)	0.9500
C(4)-C(5)	1.386(3)
C(5)-H(5)	0.9500
C(5)-C(6)	1.402(3)
C(6)-C(7)	1.502(3)
C(7)-C(8)	1.549(3)
C(8)-C(9)	1.535(3)
C(8)-C(15)	1.540(3)
C(9)-C(10)	1.392(3)
C(9)-C(14)	1.401(3)
C(10)-H(10)	0.9500
C(10)-C(11)	1.393(3)
C(11)-H(11)	0.9500
C(11)-C(12)	1.391(4)
C(12)-H(12)	0.9500
C(12)-C(13)	1.384(4)
C(13)-H(13)	0.9500
C(13)-C(14)	1.392(3)
C(14)-H(14)	0.9500
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(15)-C(16)	1.502(3)
C(16)-H(16)	0.9500
C(16)-C(17)	1.314(3)

C(17)-H(17A)	0.9500
C(17)-H(17B)	0.9500

C(8)-O(2)-H(2W)	109.5
C(2)-C(1)-H(1)	119.9
C(2)-C(1)-C(6)	120.2(2)
C(6)-C(1)-H(1)	119.9
C(1)-C(2)-H(2)	119.8
C(3)-C(2)-C(1)	120.5(2)
C(3)-C(2)-H(2)	119.8
C(2)-C(3)-H(3)	120.2
C(4)-C(3)-C(2)	119.5(2)
C(4)-C(3)-H(3)	120.2
C(3)-C(4)-H(4)	119.8
C(5)-C(4)-C(3)	120.4(2)
C(5)-C(4)-H(4)	119.8
C(4)-C(5)-H(5)	119.8
C(4)-C(5)-C(6)	120.5(2)
C(6)-C(5)-H(5)	119.8
C(1)-C(6)-C(5)	118.9(2)
C(1)-C(6)-C(7)	124.26(18)
C(5)-C(6)-C(7)	116.77(19)
O(1)-C(7)-C(6)	120.41(19)
O(1)-C(7)-C(8)	118.4(2)
C(6)-C(7)-C(8)	121.18(17)
O(2)-C(8)-C(7)	106.12(16)
O(2)-C(8)-C(9)	112.43(17)
O(2)-C(8)-C(15)	110.40(17)
C(9)-C(8)-C(7)	107.21(17)
C(9)-C(8)-C(15)	110.82(17)
C(15)-C(8)-C(7)	109.68(16)
C(10)-C(9)-C(8)	121.64(19)
C(10)-C(9)-C(14)	118.92(19)
C(14)-C(9)-C(8)	119.43(19)
C(9)-C(10)-H(10)	119.7
C(9)-C(10)-C(11)	120.5(2)

C(11)-C(10)-H(10)	119.7
C(10)-C(11)-H(11)	119.9
C(12)-C(11)-C(10)	120.3(2)
C(12)-C(11)-H(11)	119.9
C(11)-C(12)-H(12)	120.2
C(13)-C(12)-C(11)	119.6(2)
C(13)-C(12)-H(12)	120.2
C(12)-C(13)-H(13)	119.8
C(12)-C(13)-C(14)	120.4(2)
C(14)-C(13)-H(13)	119.8
C(9)-C(14)-H(14)	119.9
C(13)-C(14)-C(9)	120.3(2)
C(13)-C(14)-H(14)	119.9
C(8)-C(15)-H(15A)	109.4
C(8)-C(15)-H(15B)	109.4
H(15A)-C(15)-H(15B)	108.0
C(16)-C(15)-C(8)	111.06(18)
C(16)-C(15)-H(15A)	109.4
C(16)-C(15)-H(15B)	109.4
C(15)-C(16)-H(16)	118.0
C(17)-C(16)-C(15)	124.1(2)
C(17)-C(16)-H(16)	118.0
C(16)-C(17)-H(17A)	120.0
C(16)-C(17)-H(17B)	120.0
H(17A)-C(17)-H(17B)	120.0

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for v19245. 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)	16(1)	22(1)	44(1)	7(1)	1(1)	8(1)
O(2)	13(1)	22(1)	19(1)	4(1)	6(1)	4(1)
C(1)	18(1)	18(1)	18(1)	6(1)	3(1)	4(1)
C(2)	26(1)	21(1)	22(1)	6(1)	5(1)	9(1)
C(3)	28(1)	21(1)	21(1)	0(1)	4(1)	3(1)
C(4)	18(1)	31(1)	21(1)	1(1)	-1(1)	3(1)
C(5)	18(1)	26(1)	20(1)	4(1)	2(1)	8(1)
C(6)	16(1)	22(1)	15(1)	7(1)	4(1)	5(1)
C(7)	14(1)	18(1)	22(1)	10(1)	5(1)	4(1)
C(8)	14(1)	17(1)	19(1)	6(1)	6(1)	6(1)
C(9)	16(1)	15(1)	18(1)	3(1)	3(1)	2(1)
C(10)	18(1)	19(1)	19(1)	4(1)	3(1)	7(1)
C(11)	24(1)	18(1)	21(1)	4(1)	-1(1)	6(1)
C(12)	28(1)	25(1)	16(1)	5(1)	1(1)	2(1)
C(13)	25(1)	23(1)	19(1)	2(1)	9(1)	3(1)
C(14)	20(1)	19(1)	22(1)	4(1)	5(1)	6(1)
C(15)	18(1)	17(1)	25(1)	7(1)	4(1)	5(1)
C(16)	23(1)	18(1)	18(1)	4(1)	3(1)	6(1)
C(17)	21(1)	24(1)	27(1)	1(1)	4(1)	1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for v19245.

	x	y	z	U(eq)
H(2W)	8466	6502	4056	28
H(1)	5051	2437	3210	22
H(2)	3344	-903	1642	27
H(3)	-502	-1990	248	31
H(4)	-2611	303	366	31
H(5)	-913	3650	1887	26
H(10)	8134	4303	5974	22
H(11)	8078	3209	8381	26
H(12)	5506	3889	10194	30
H(13)	2955	5622	9566	28
H(14)	3025	6755	7179	24
H(15A)	6221	9189	4291	23
H(15B)	5234	9184	5999	23
H(16)	9030	9446	7378	24
H(17A)	10264	10838	4674	32
H(17B)	11985	11166	6438	32

Table 6. Torsion angles [°] for v19245.

O(1)-C(7)-C(8)-O(2)	-136.5(2)
O(1)-C(7)-C(8)-C(9)	103.2(2)
O(1)-C(7)-C(8)-C(15)	-17.2(3)
O(2)-C(8)-C(9)-C(10)	7.1(3)
O(2)-C(8)-C(9)-C(14)	-173.72(18)
O(2)-C(8)-C(15)-C(16)	-61.9(2)
C(1)-C(2)-C(3)-C(4)	0.9(4)
C(1)-C(6)-C(7)-O(1)	-176.9(2)
C(1)-C(6)-C(7)-C(8)	0.5(3)
C(2)-C(1)-C(6)-C(5)	0.3(3)
C(2)-C(1)-C(6)-C(7)	177.4(2)
C(2)-C(3)-C(4)-C(5)	-0.3(4)
C(3)-C(4)-C(5)-C(6)	-0.2(3)
C(4)-C(5)-C(6)-C(1)	0.3(3)
C(4)-C(5)-C(6)-C(7)	-177.1(2)
C(5)-C(6)-C(7)-O(1)	0.3(3)
C(5)-C(6)-C(7)-C(8)	177.67(19)
C(6)-C(1)-C(2)-C(3)	-0.9(3)
C(6)-C(7)-C(8)-O(2)	46.1(2)
C(6)-C(7)-C(8)-C(9)	-74.3(2)
C(6)-C(7)-C(8)-C(15)	165.33(18)
C(7)-C(8)-C(9)-C(10)	123.4(2)
C(7)-C(8)-C(9)-C(14)	-57.5(2)
C(7)-C(8)-C(15)-C(16)	-178.45(18)
C(8)-C(9)-C(10)-C(11)	178.69(19)
C(8)-C(9)-C(14)-C(13)	-179.09(19)
C(8)-C(15)-C(16)-C(17)	112.5(2)
C(9)-C(8)-C(15)-C(16)	63.4(2)
C(9)-C(10)-C(11)-C(12)	0.2(3)
C(10)-C(9)-C(14)-C(13)	0.1(3)
C(10)-C(11)-C(12)-C(13)	0.5(3)
C(11)-C(12)-C(13)-C(14)	-0.9(3)
C(12)-C(13)-C(14)-C(9)	0.6(3)
C(14)-C(9)-C(10)-C(11)	-0.5(3)

C(15)-C(8)-C(9)-C(10)	-117.0(2)
C(15)-C(8)-C(9)-C(14)	62.2(2)

Table 7. Hydrogen bonds for v19245 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2)-H(2W)...O(1)#1	0.84	2.12	2.823(2)	141.1

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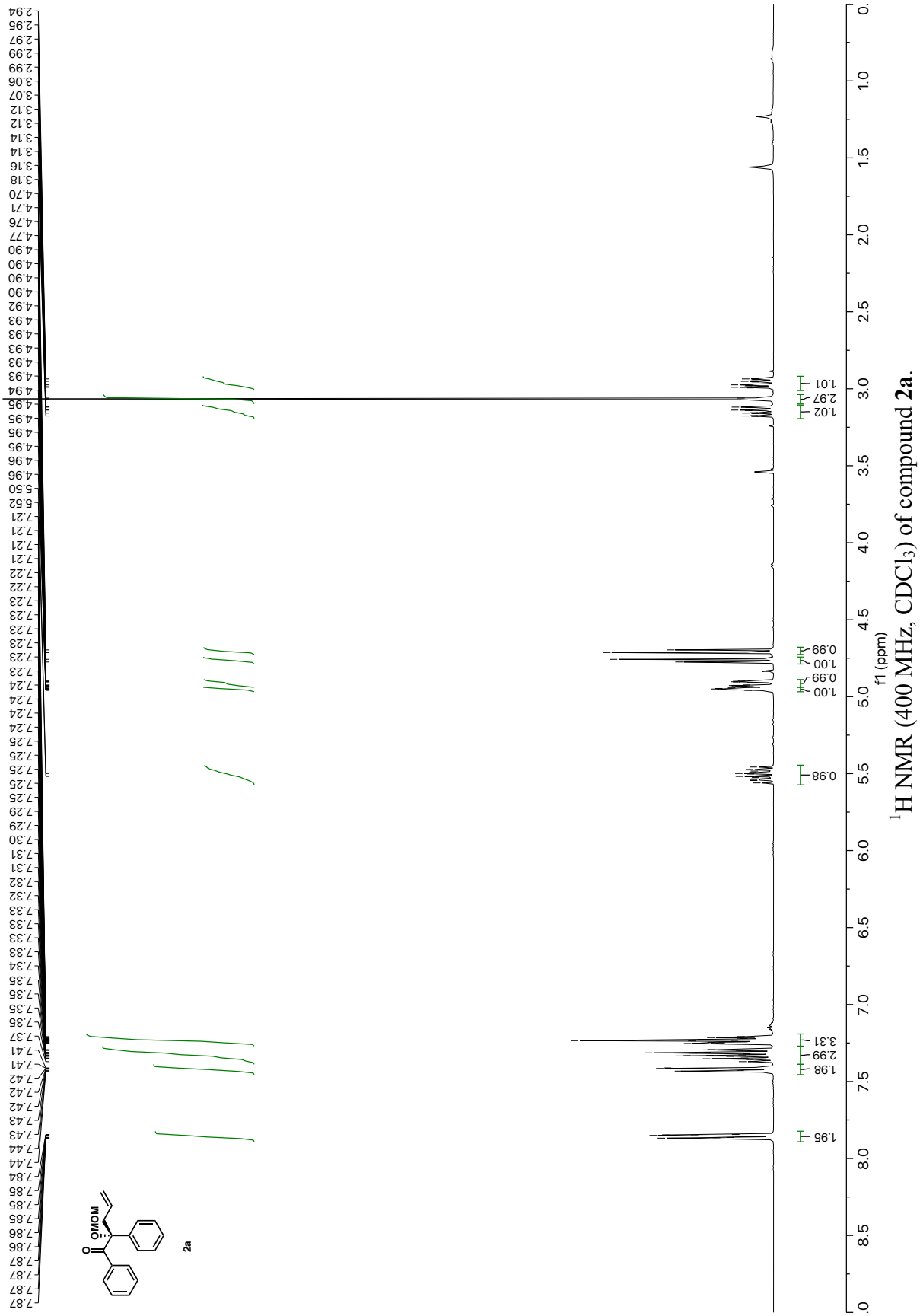
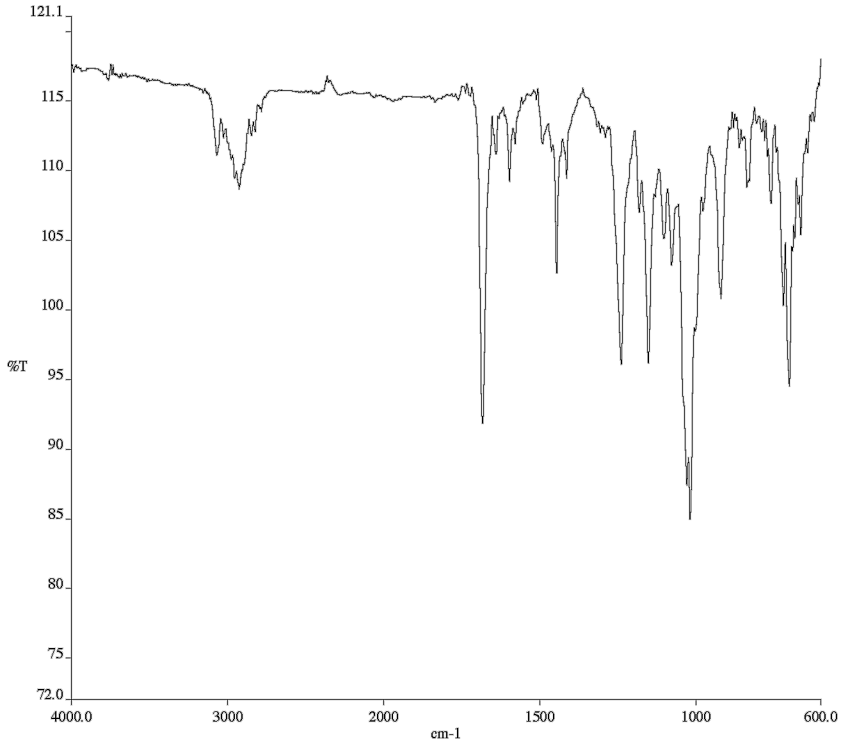
(2) Trost, B. M.; Van Vranken, D. L.; Bingel, C. *J. Am. Chem. Soc*. **1992**, *114*, 9327–9343.

(3) Meng, J.; Gao, M.; Lv, H.; Zhang, X. *Org. Lett*. **2015**, *178*, 1842-1845

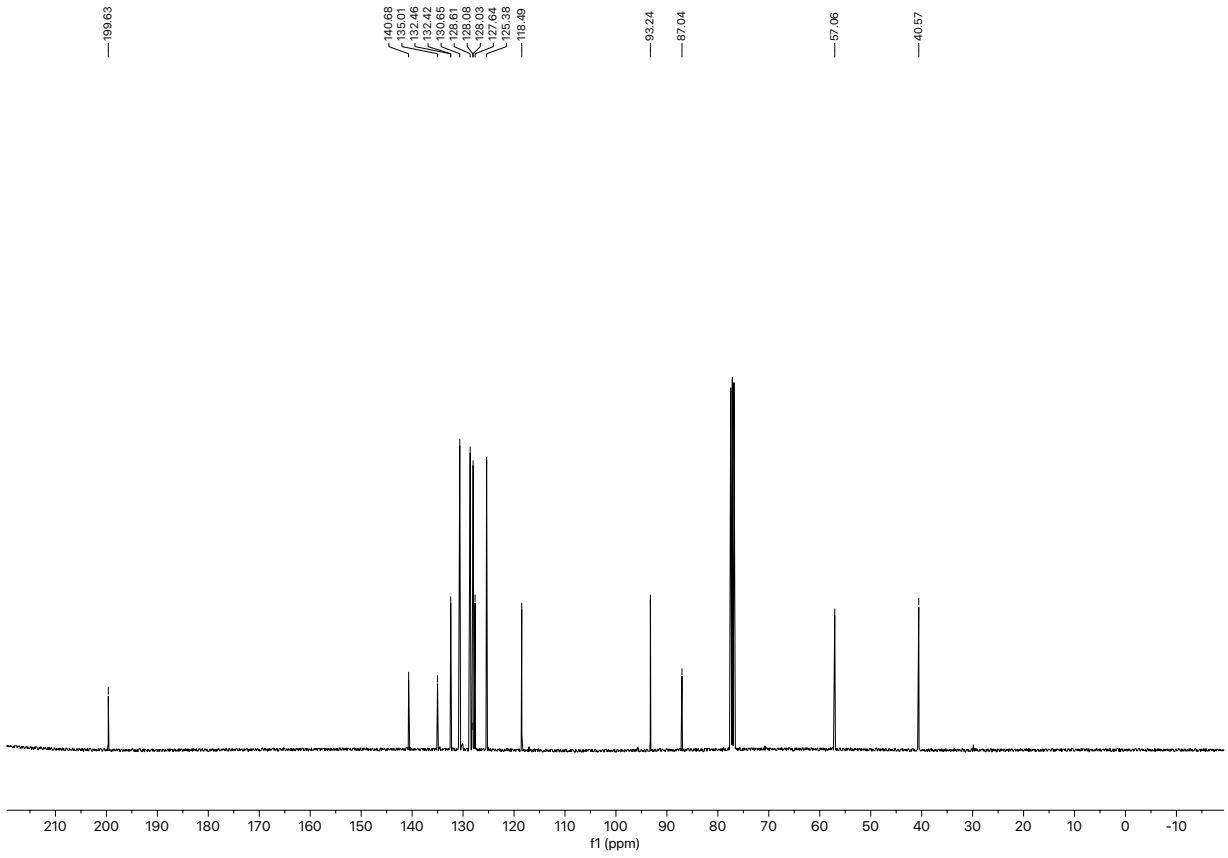
NMR and IR Spectra of New Compounds



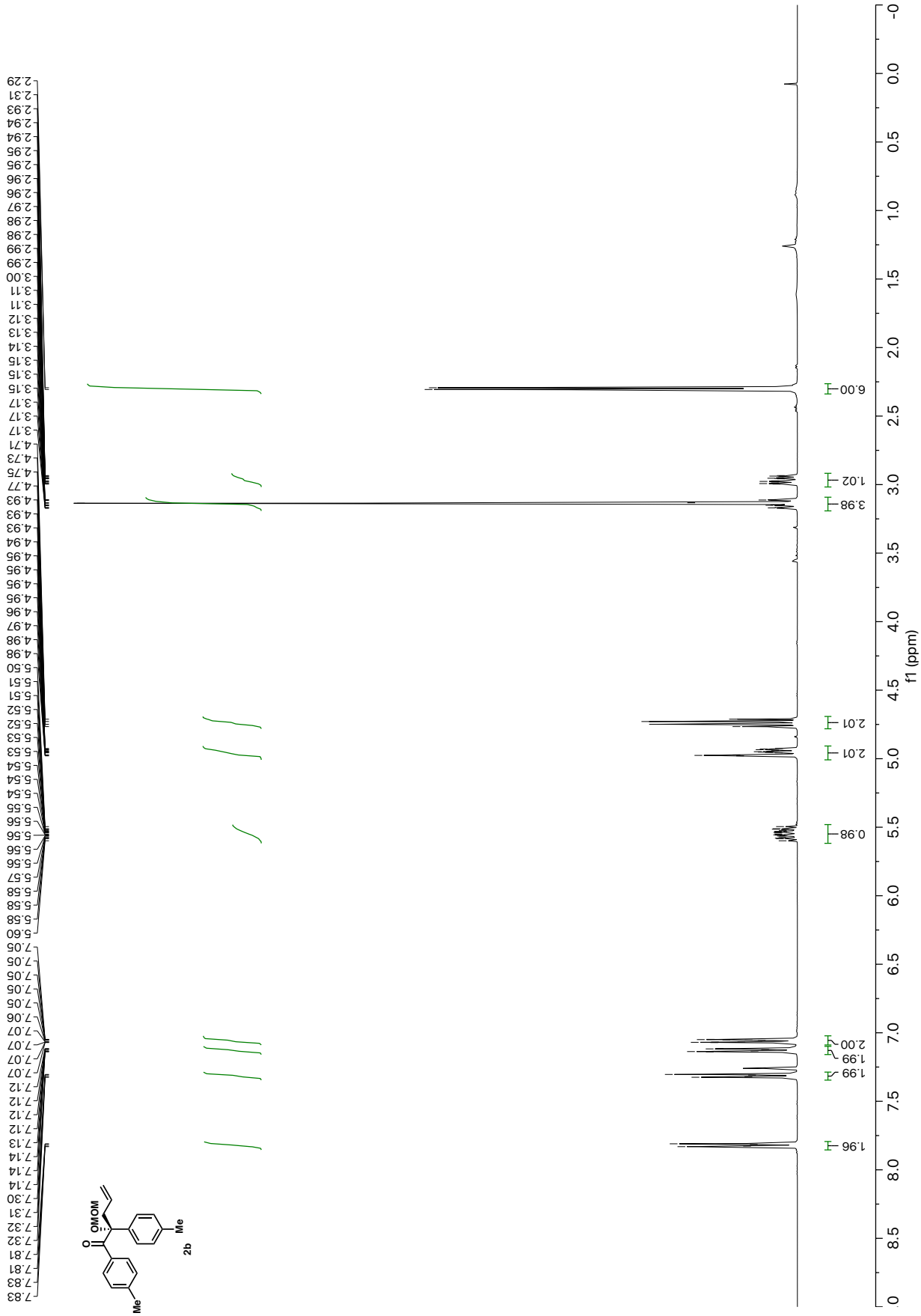
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



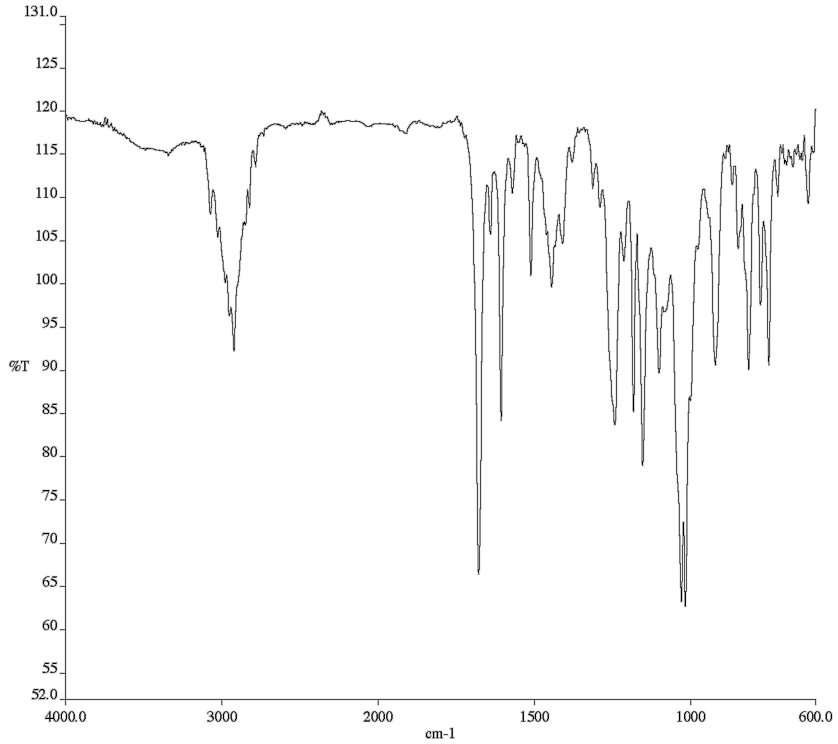
Infrared spectrum (Thin Film, NaCl) of compound **2a**.



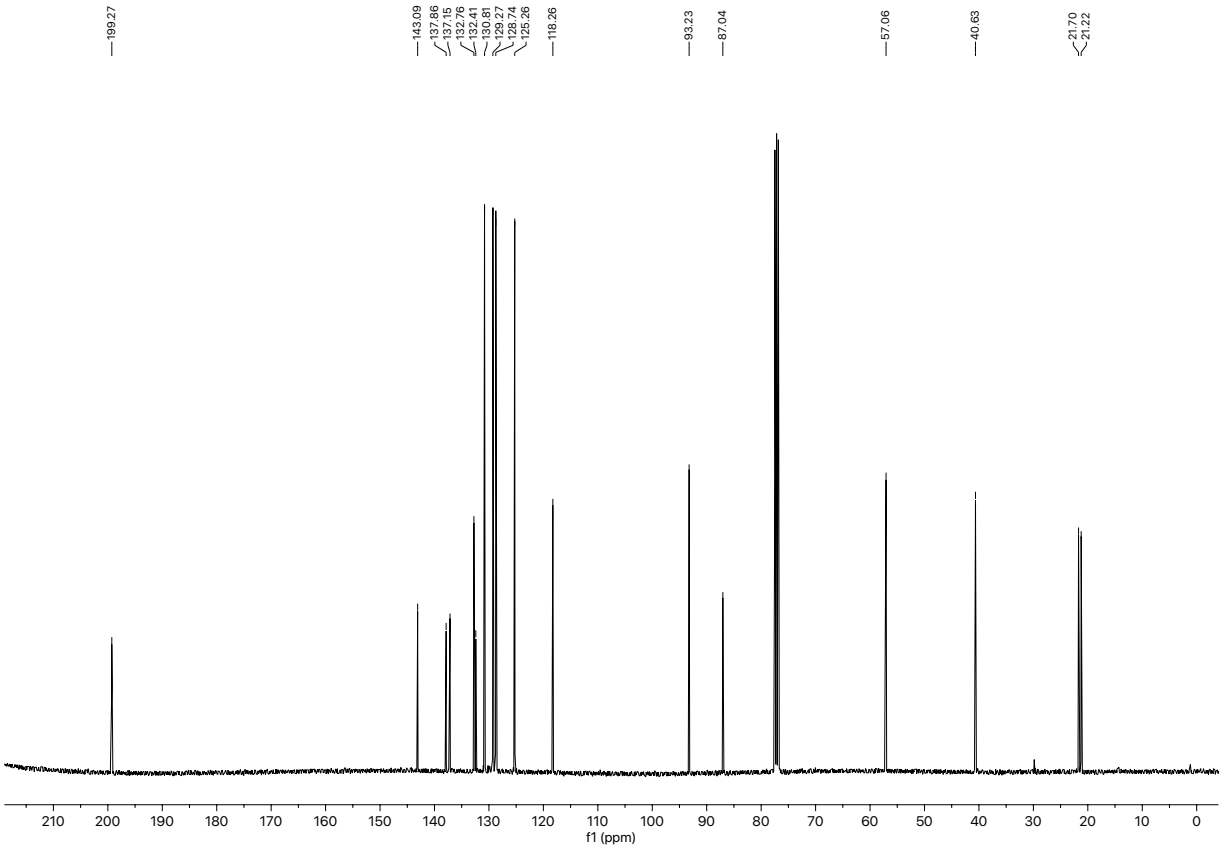
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.



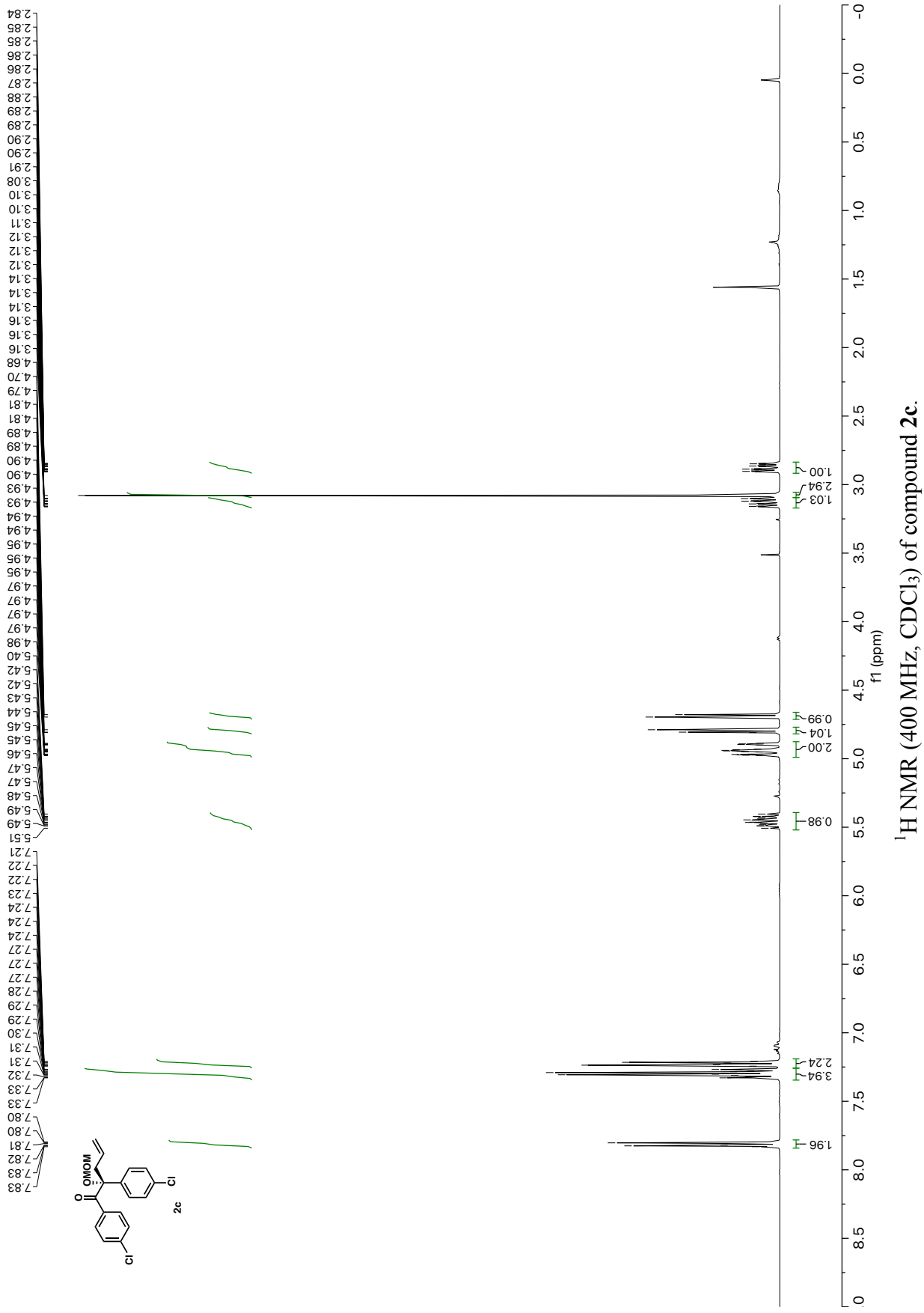
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**.



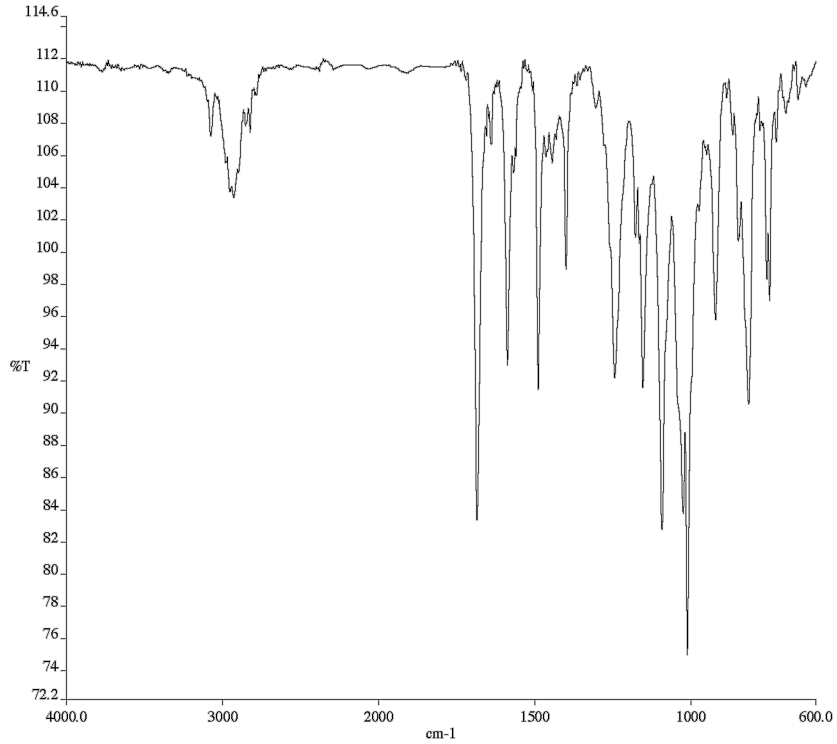
Infrared spectrum (Thin Film, NaCl) of compound **2b**.



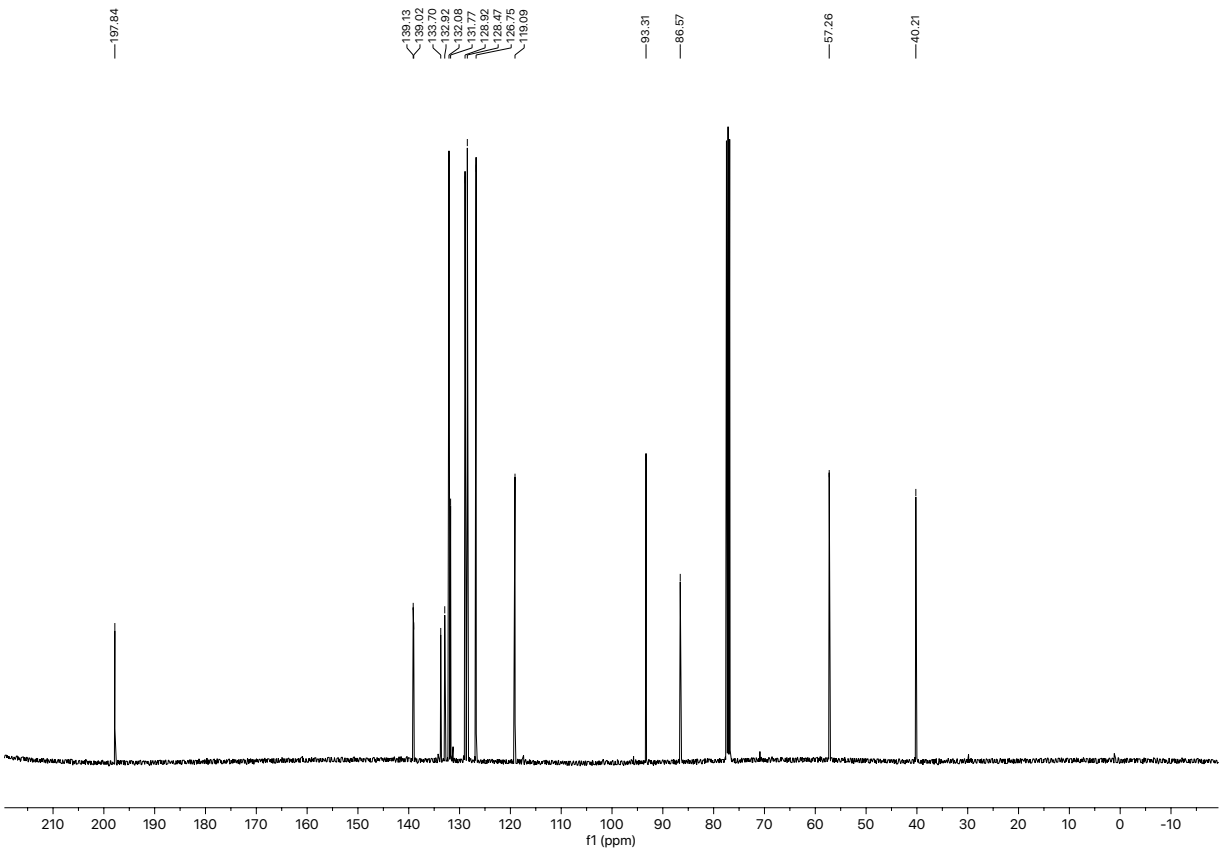
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**.



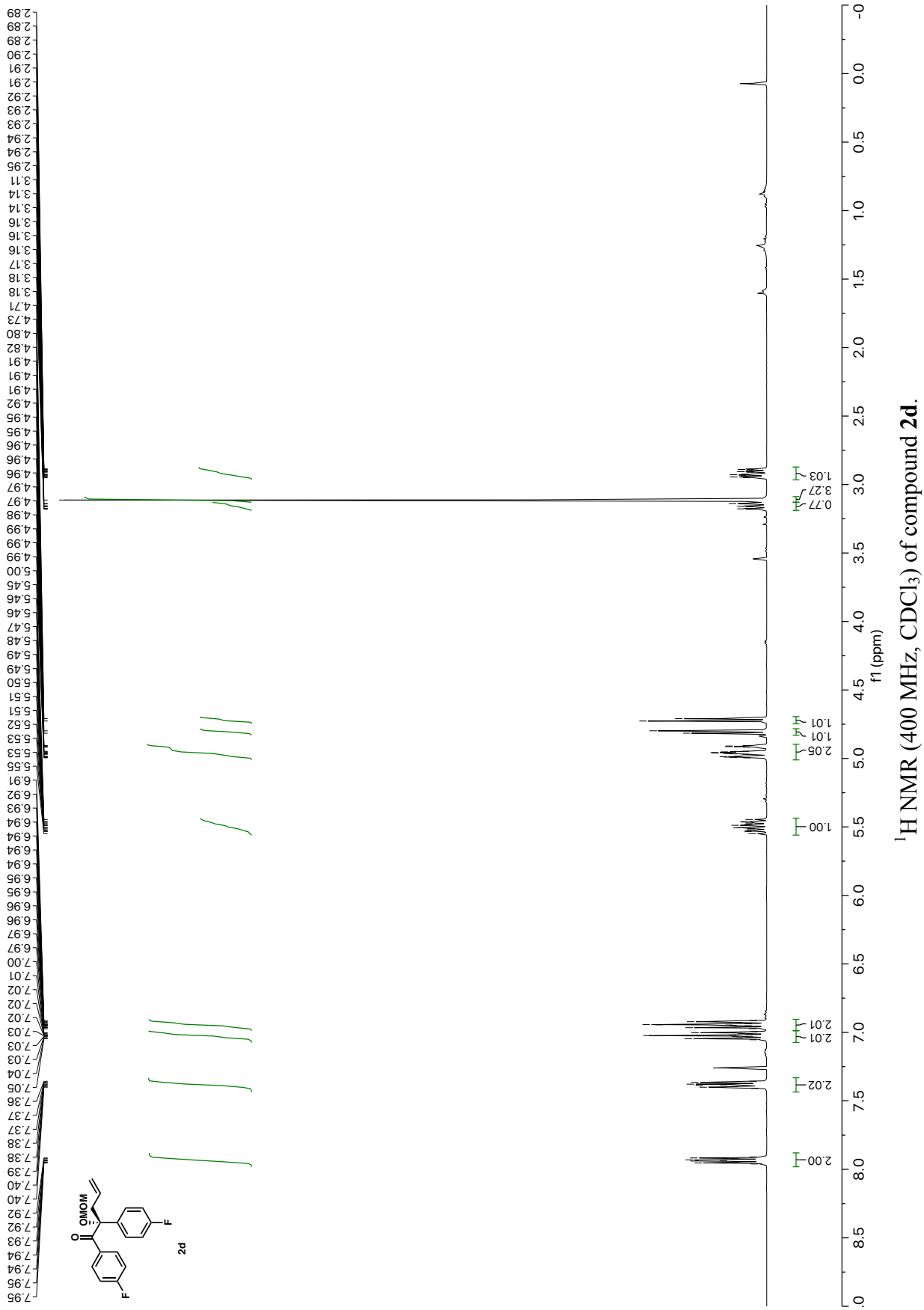
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2c**.



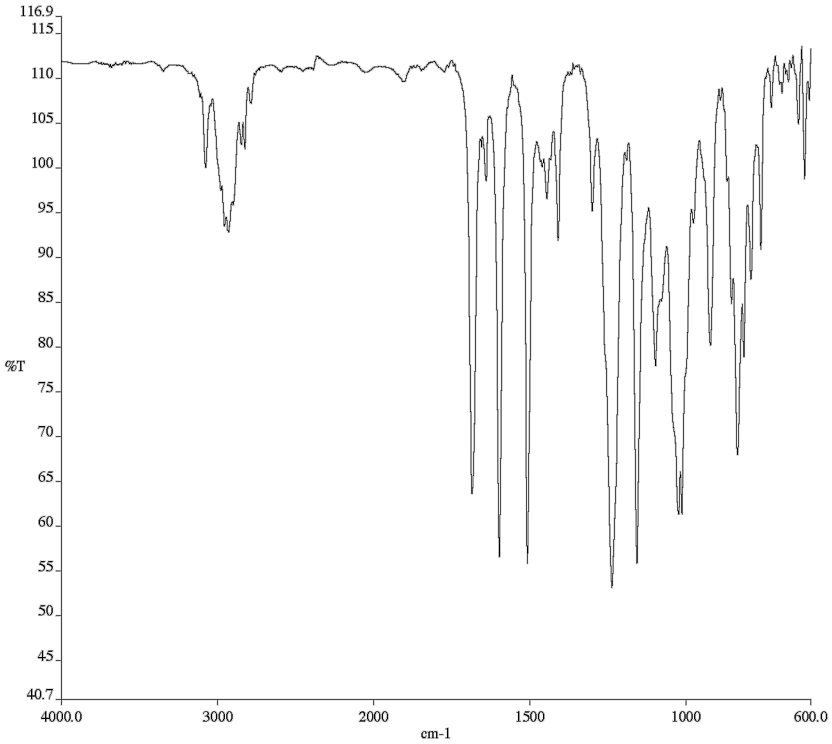
Infrared spectrum (Thin Film, NaCl) of compound **2c**.



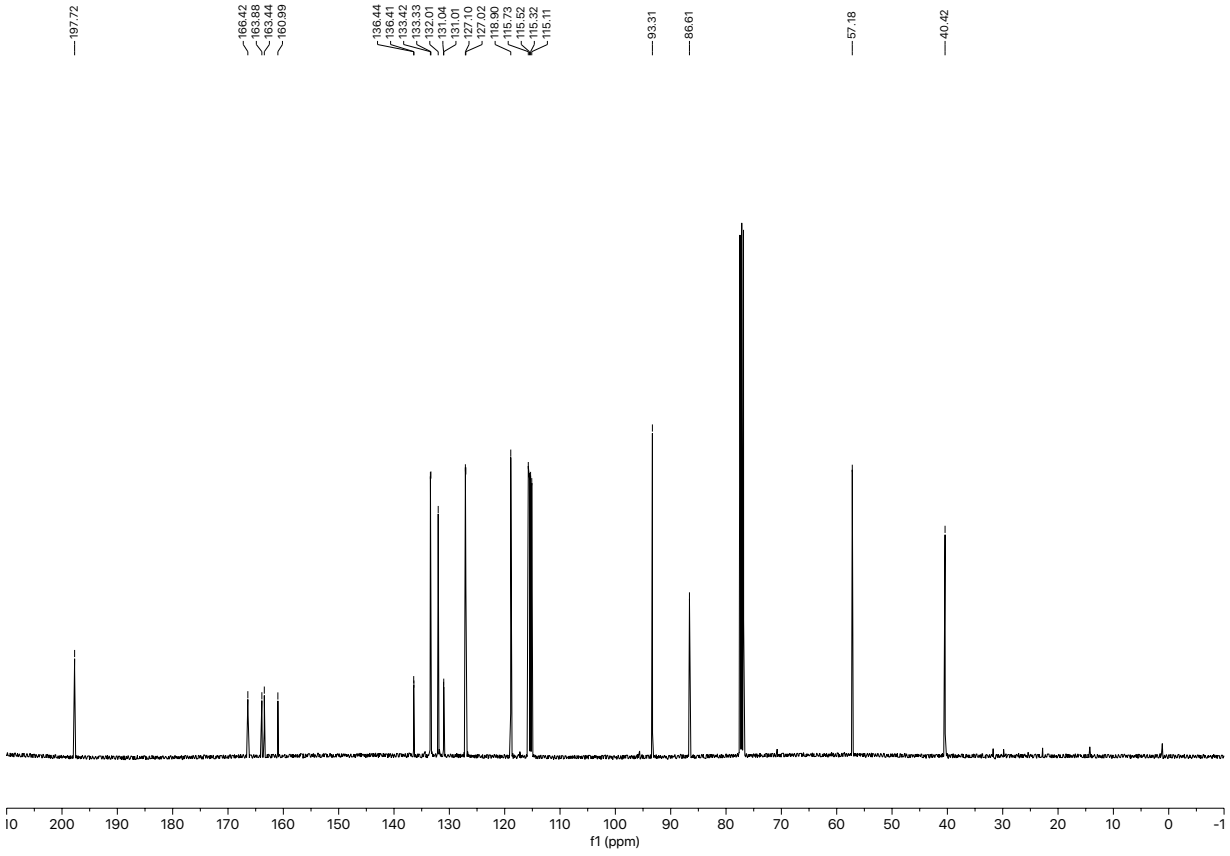
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2c**.



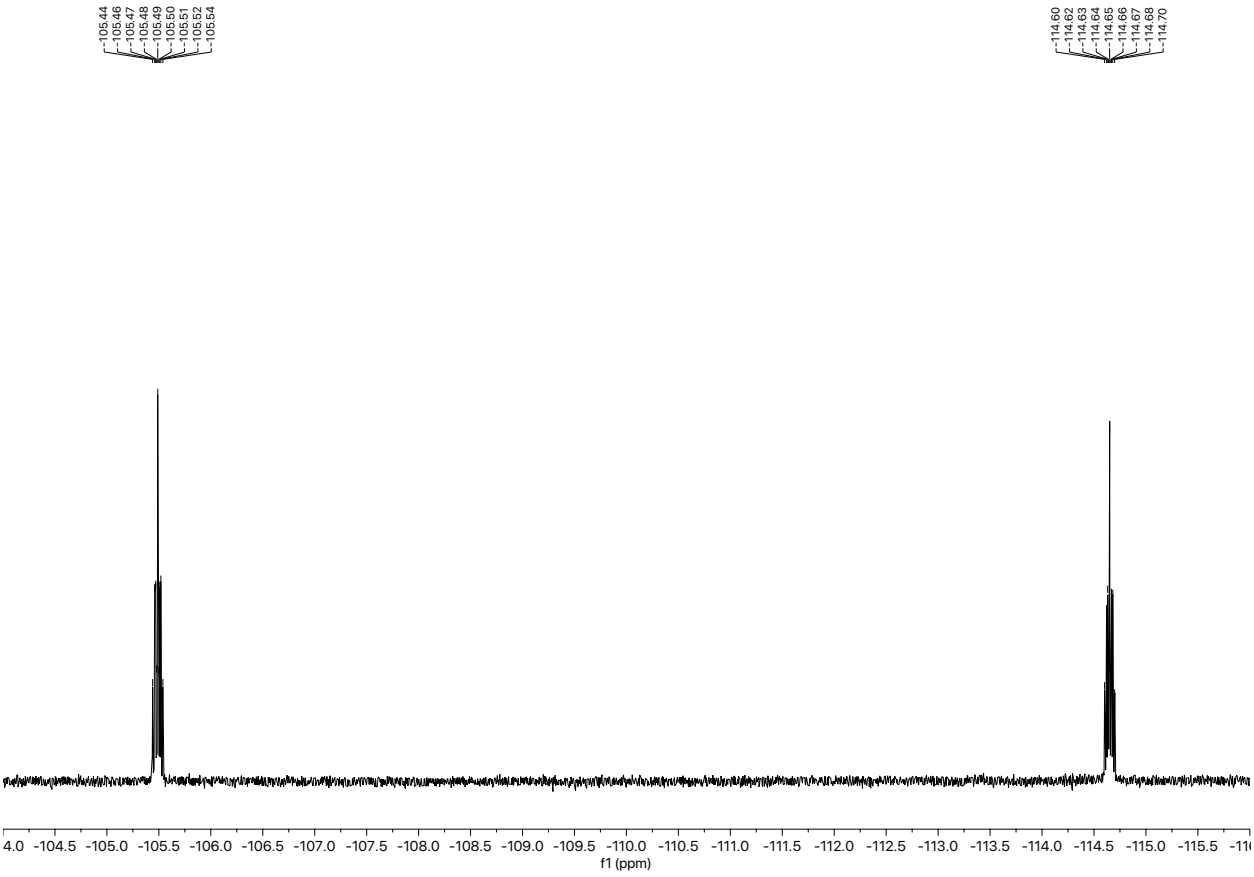
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2d**.



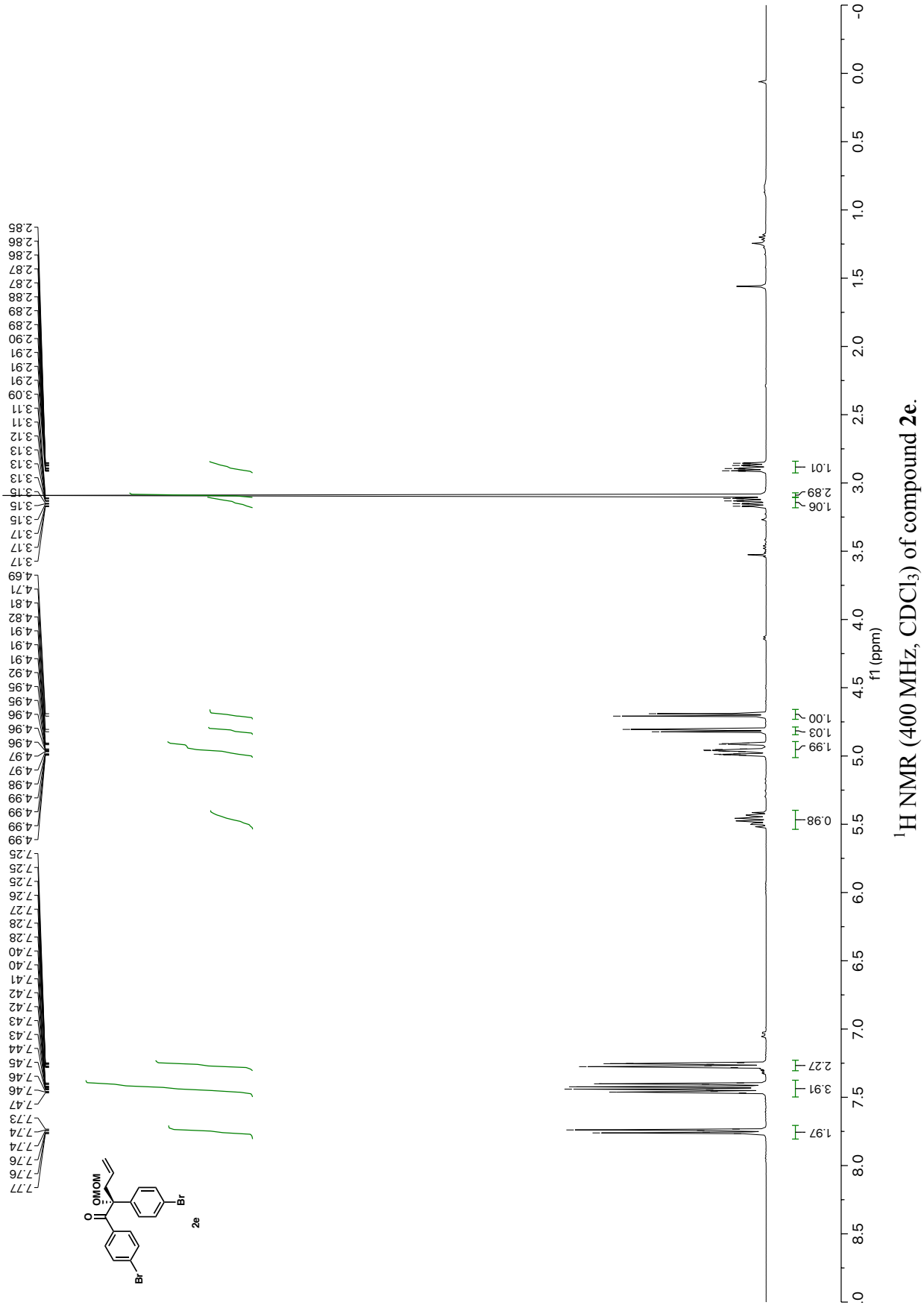
Infrared spectrum (Thin Film, NaCl) of compound **2d**.



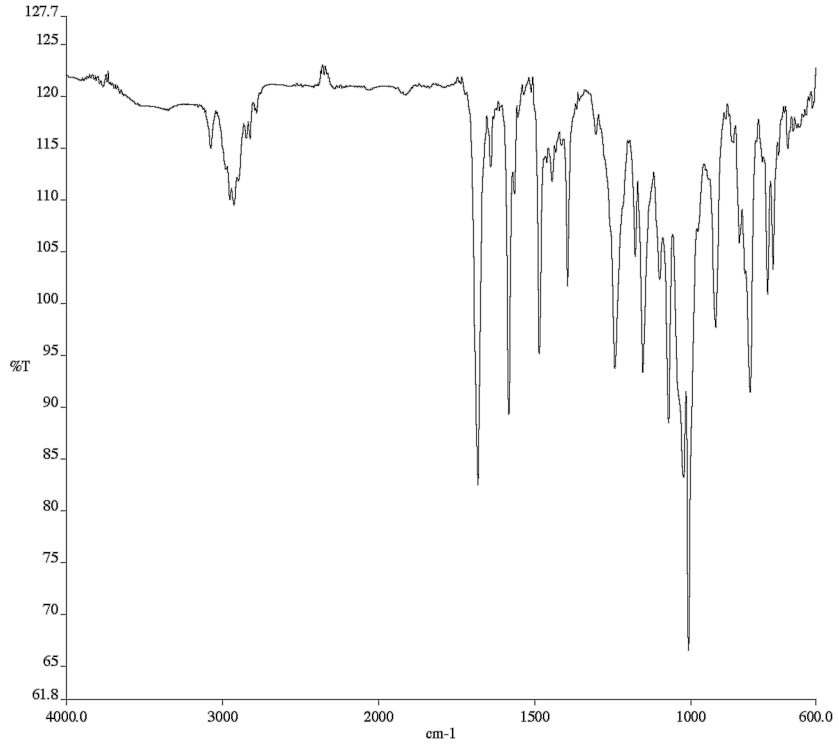
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2d**.



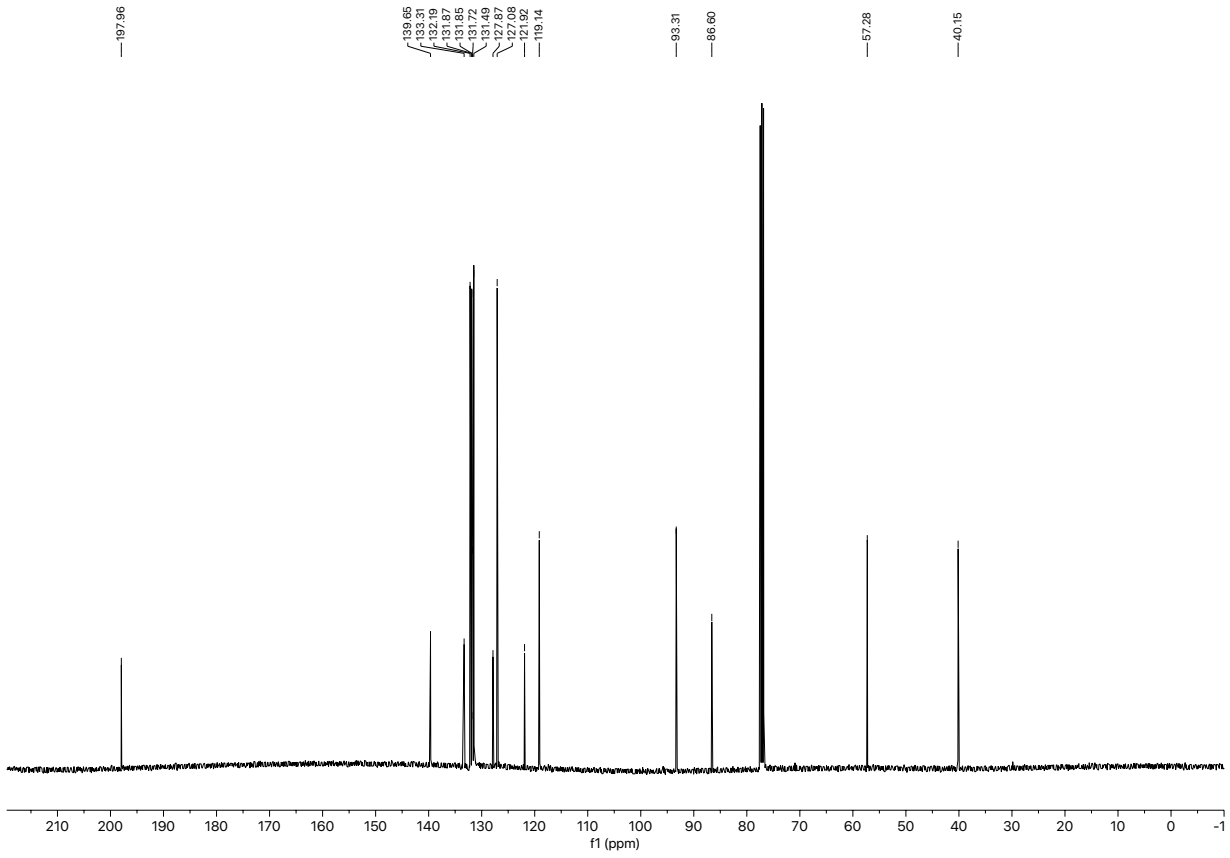
^{19}F NMR (282 MHz, $CDCl_3$) of compound **2d**.



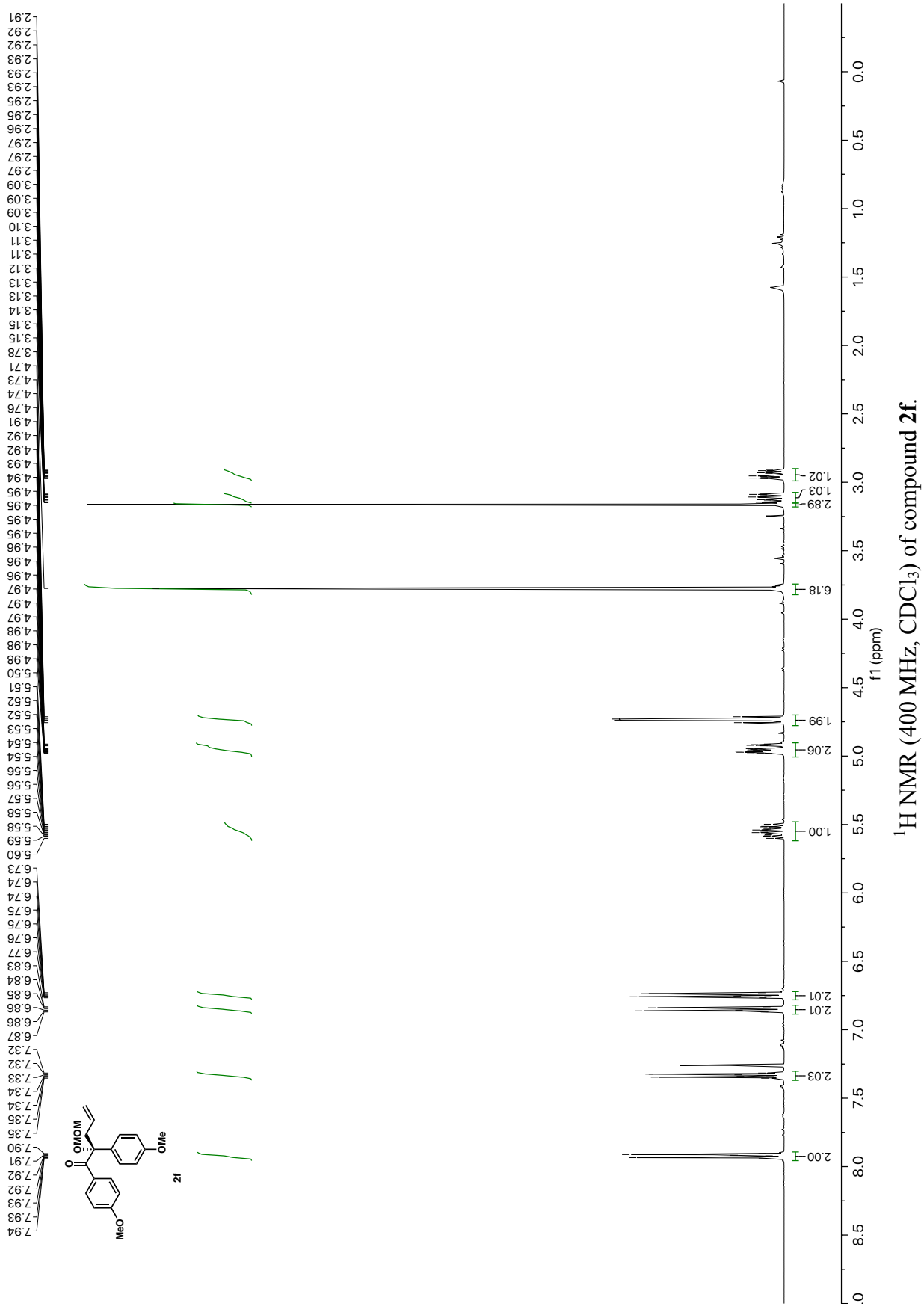
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2e**.



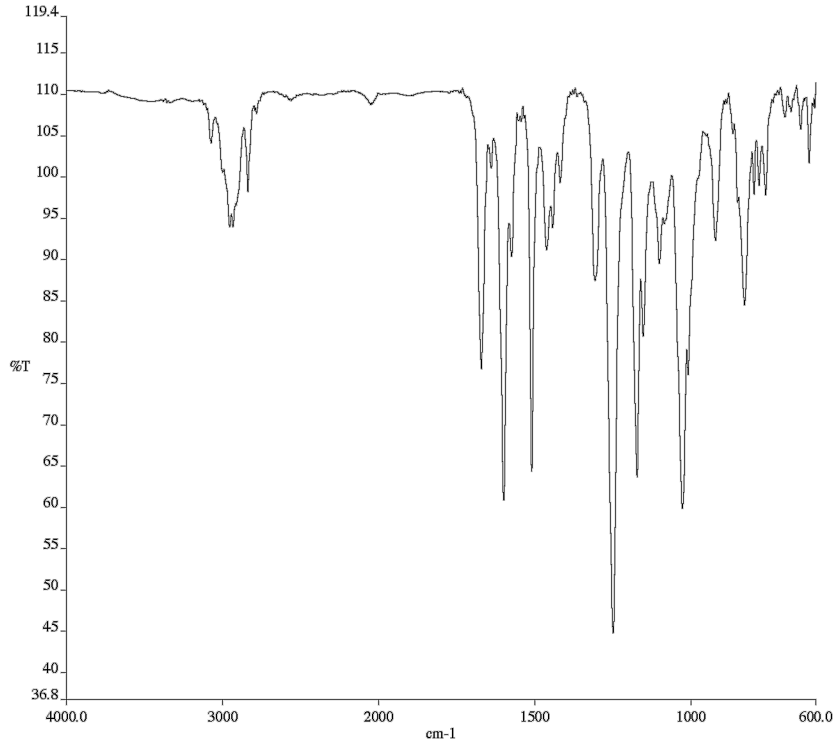
Infrared spectrum (Thin Film, NaCl) of compound **2e**.



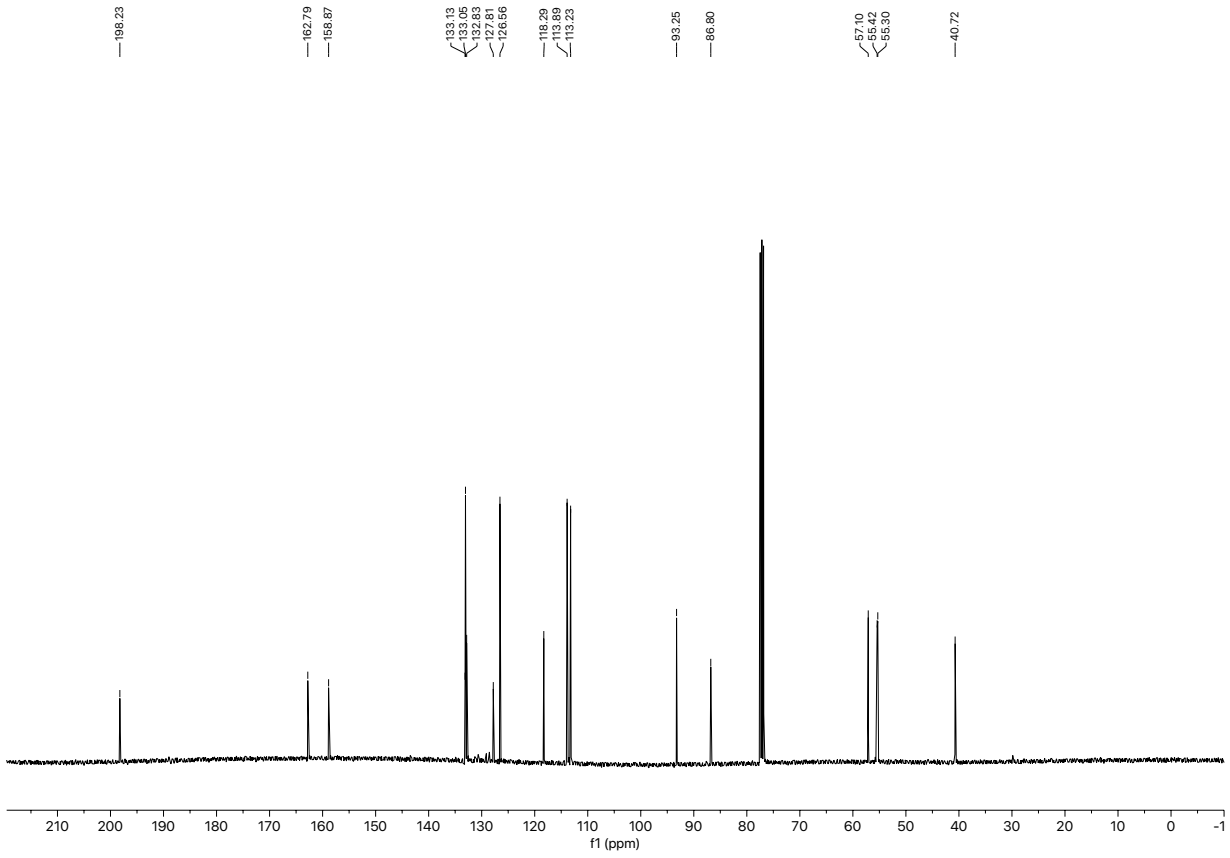
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2e**.



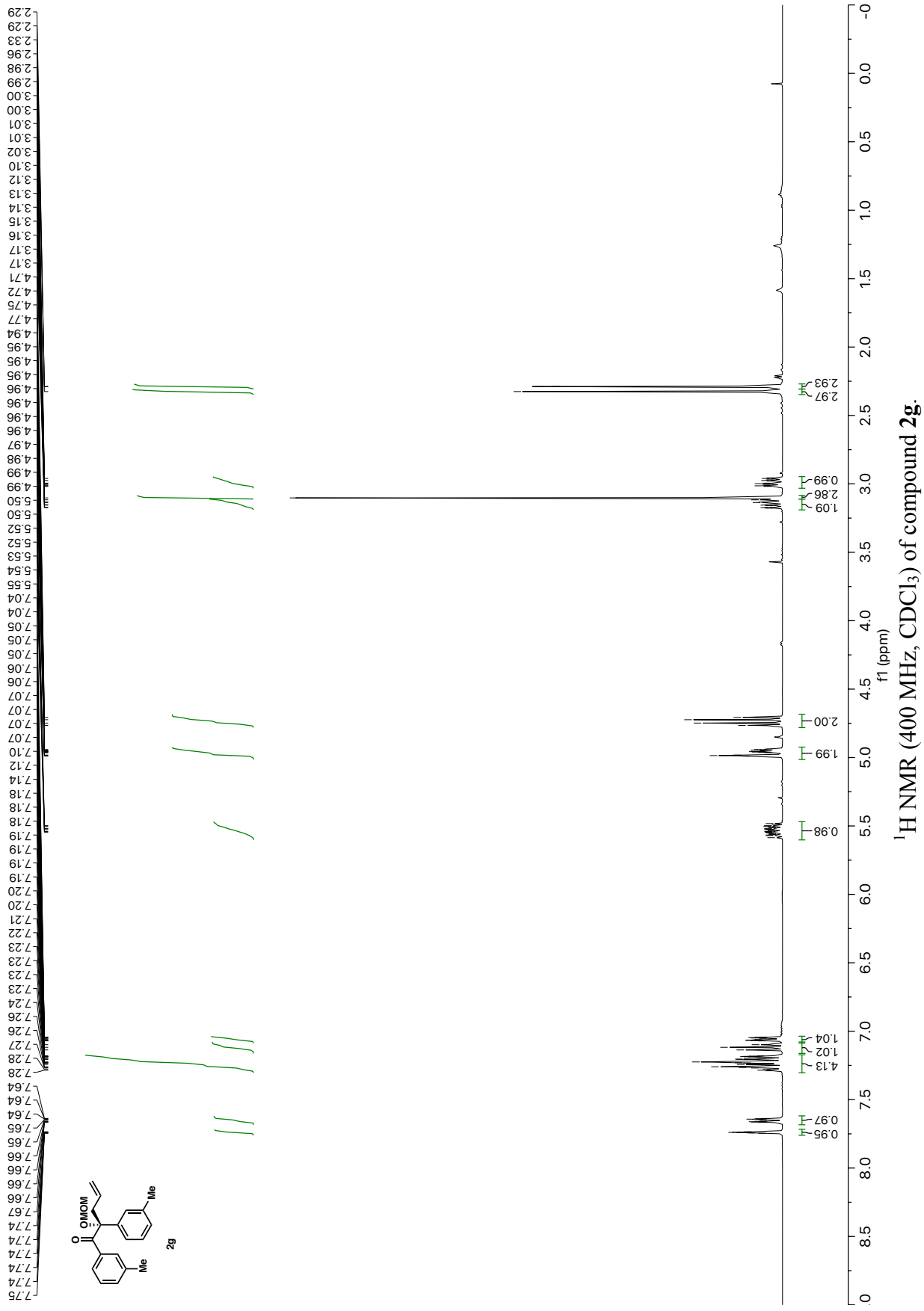
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2f**.



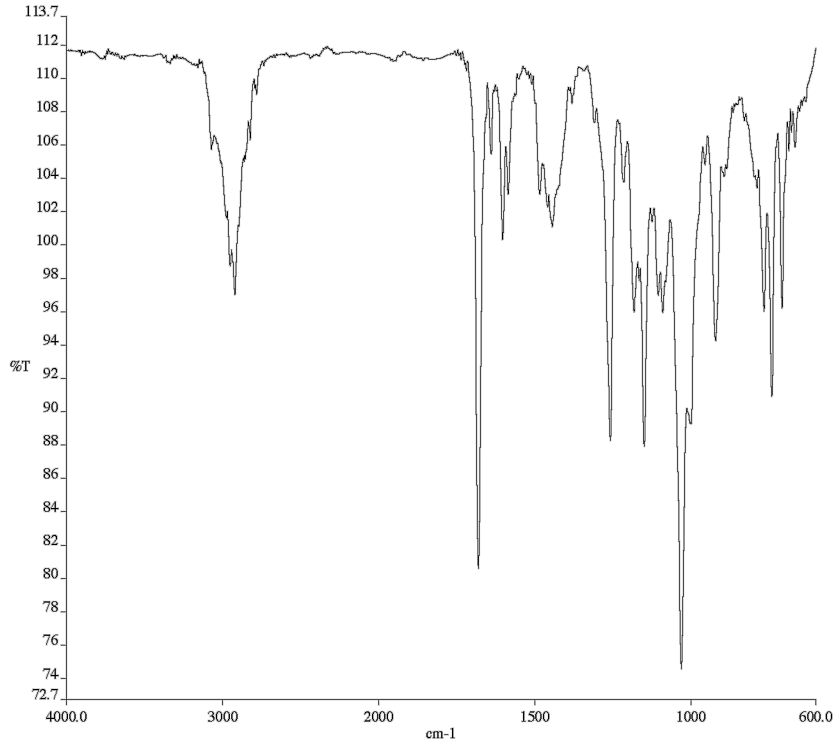
Infrared spectrum (Thin Film, NaCl) of compound **2f**.



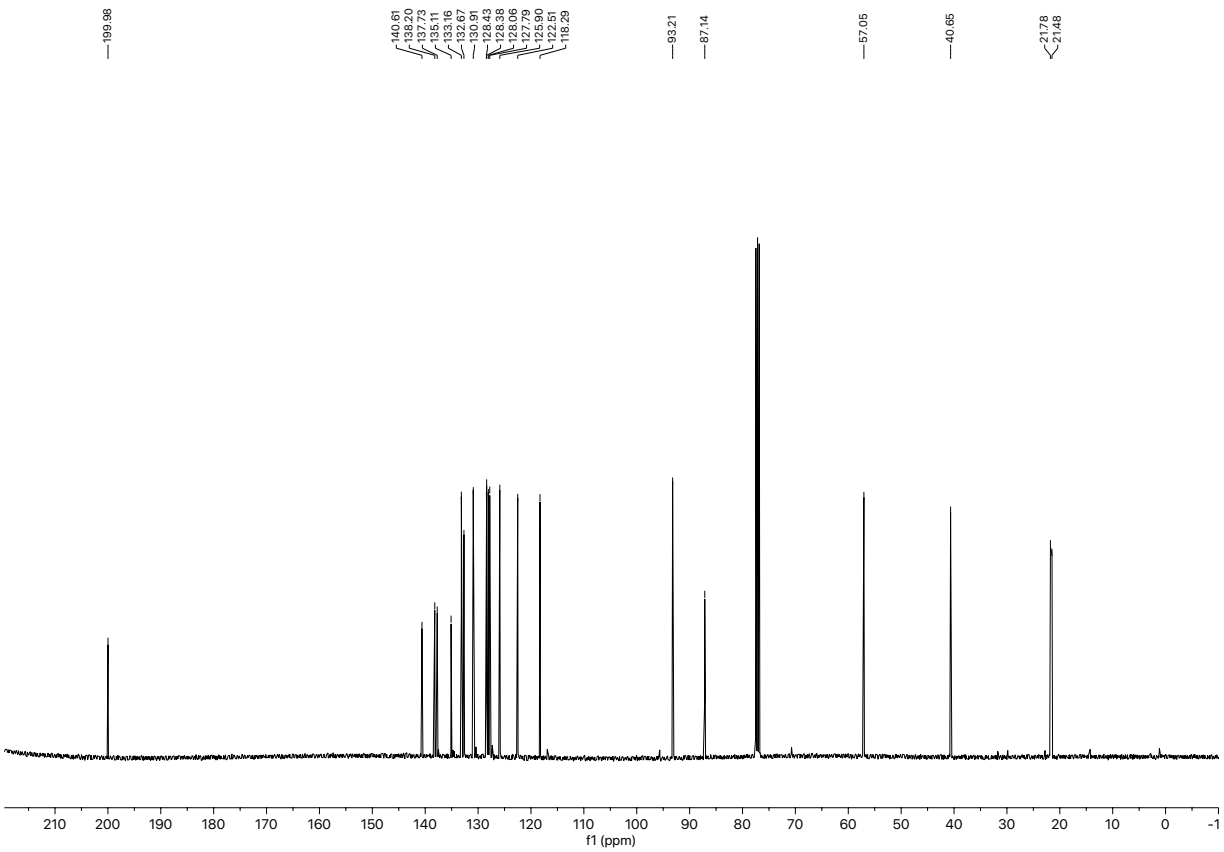
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2f**.



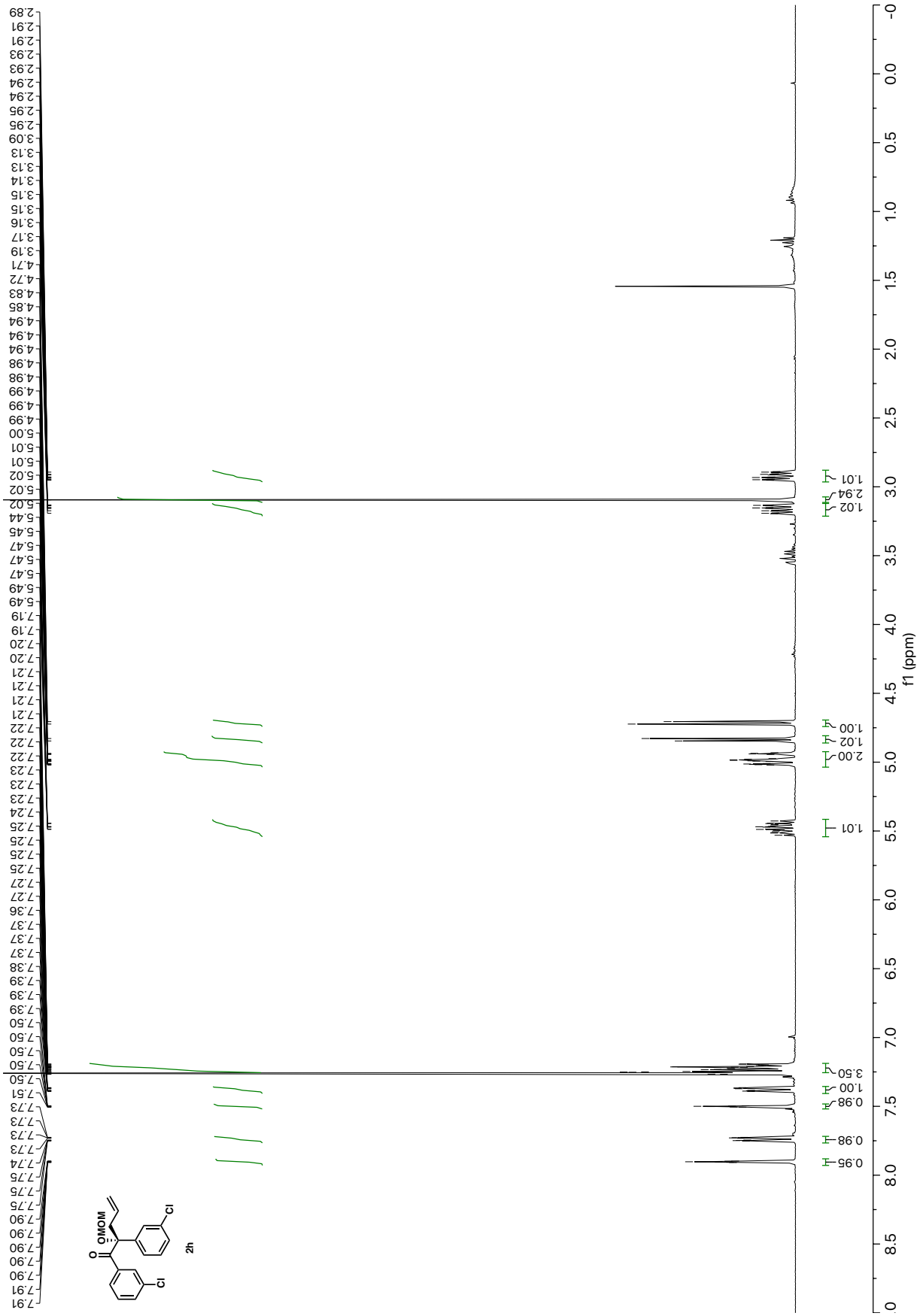
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2g**.



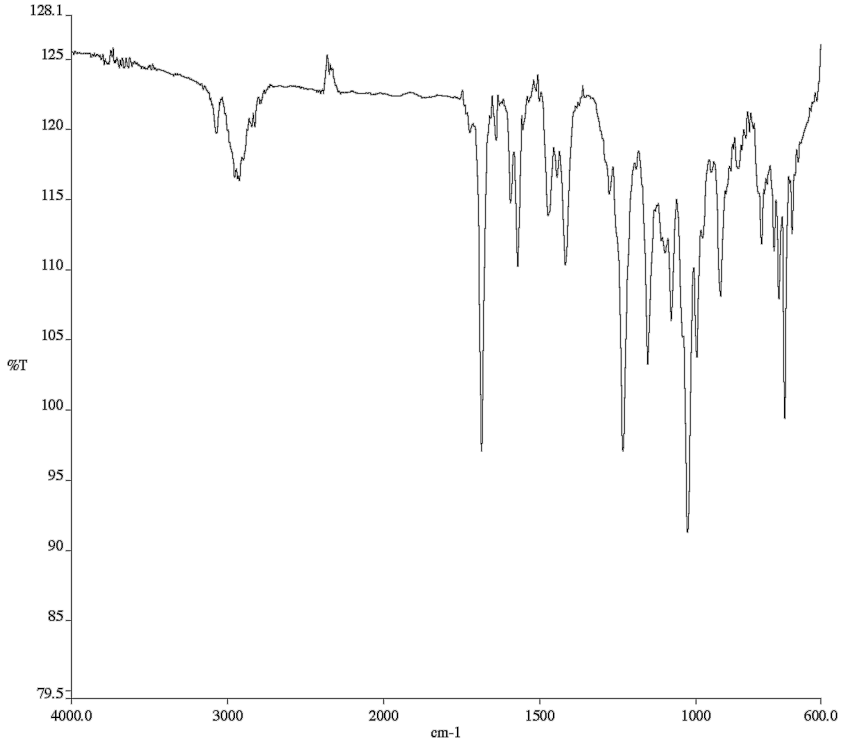
Infrared spectrum (Thin Film, NaCl) of compound **2g**.



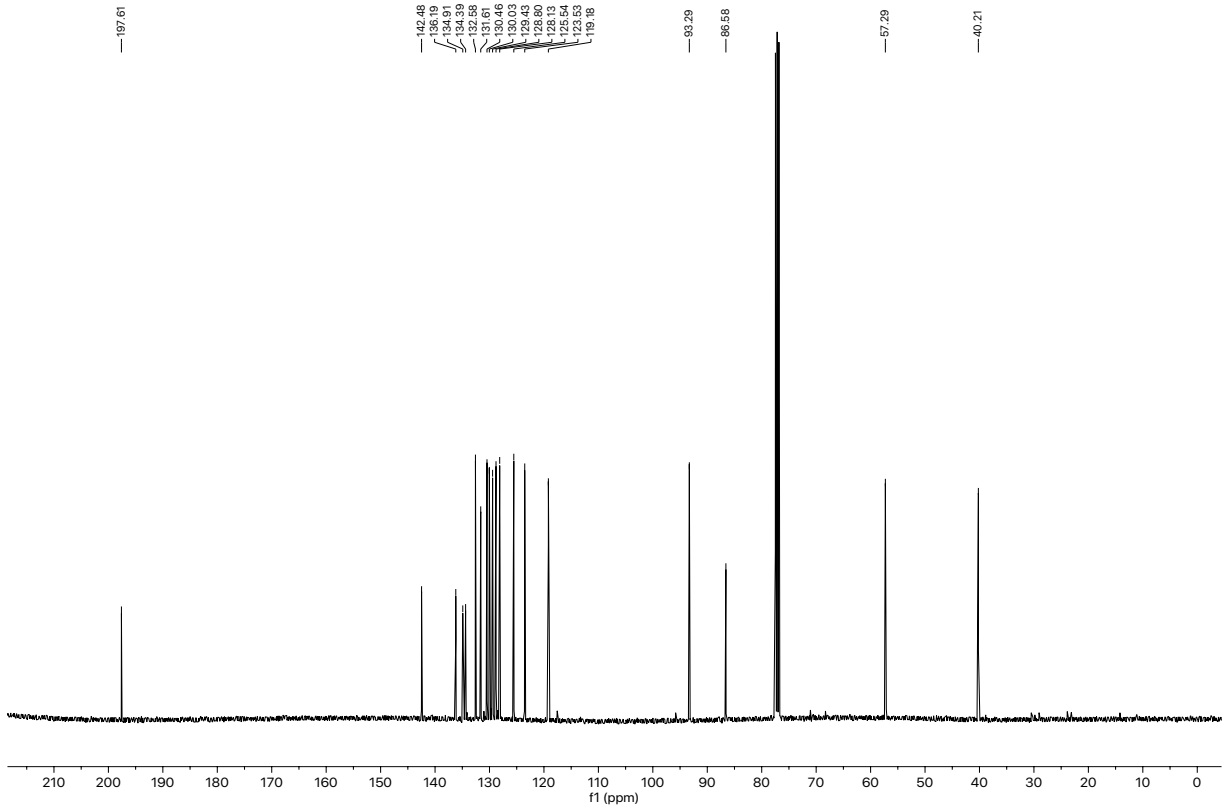
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2g**.



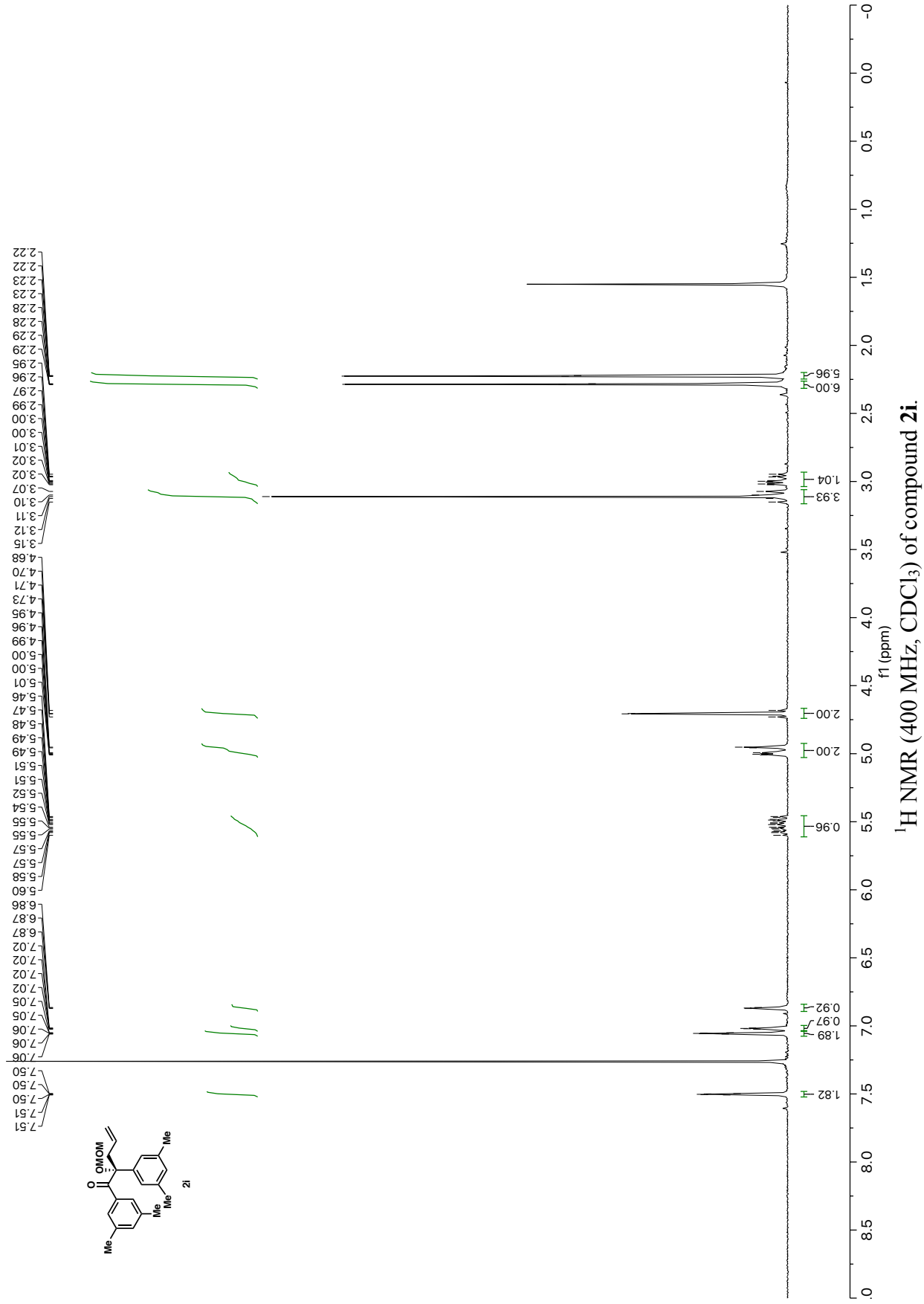
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2h**.



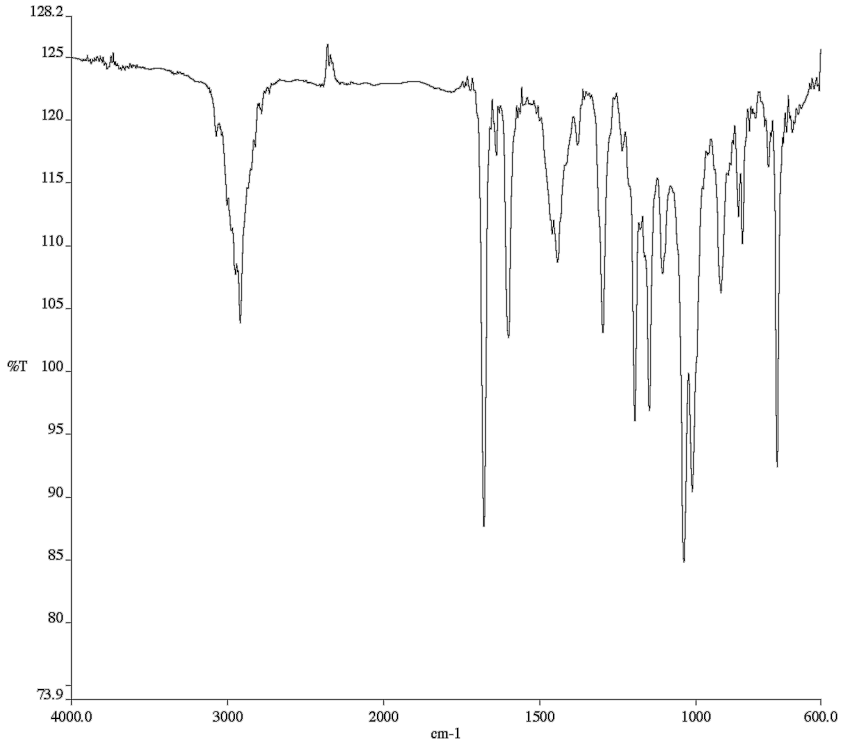
Infrared spectrum (Thin Film, NaCl) of compound **2h**.



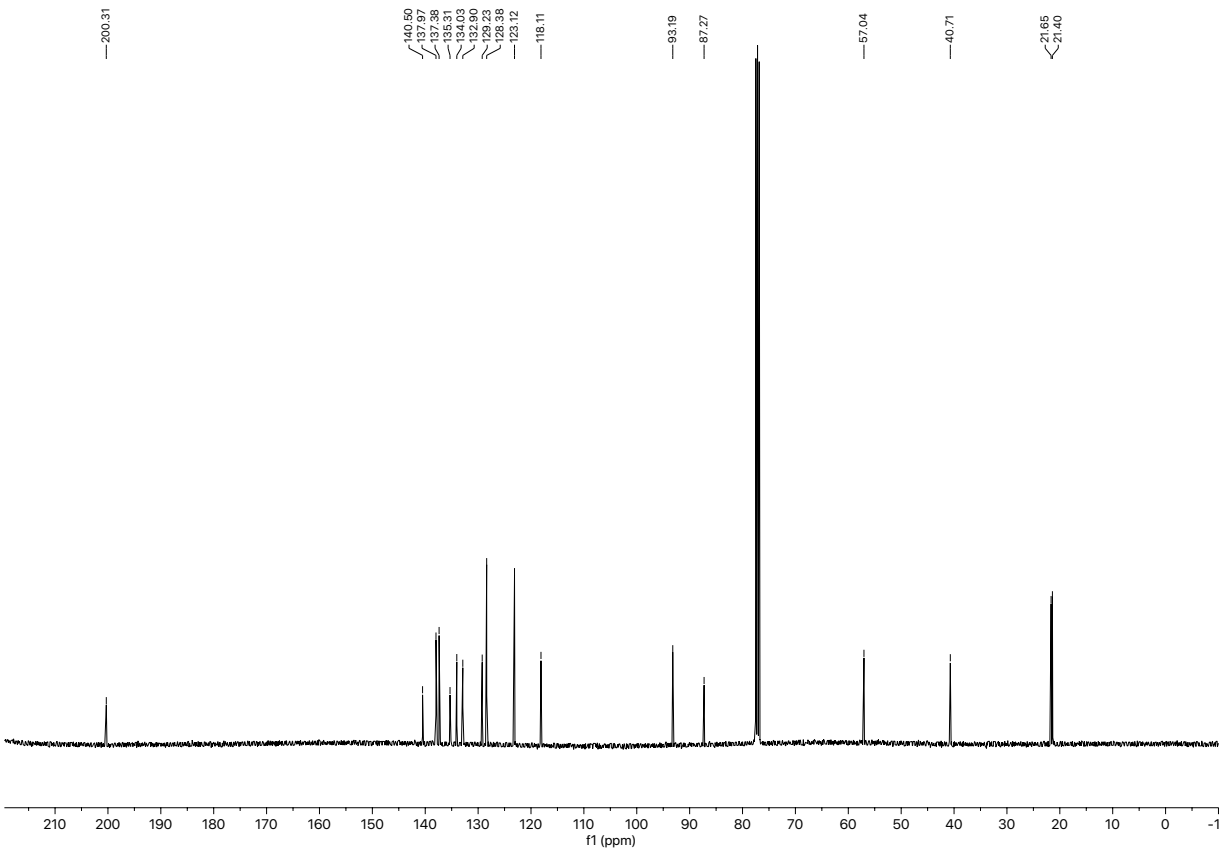
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2h**.



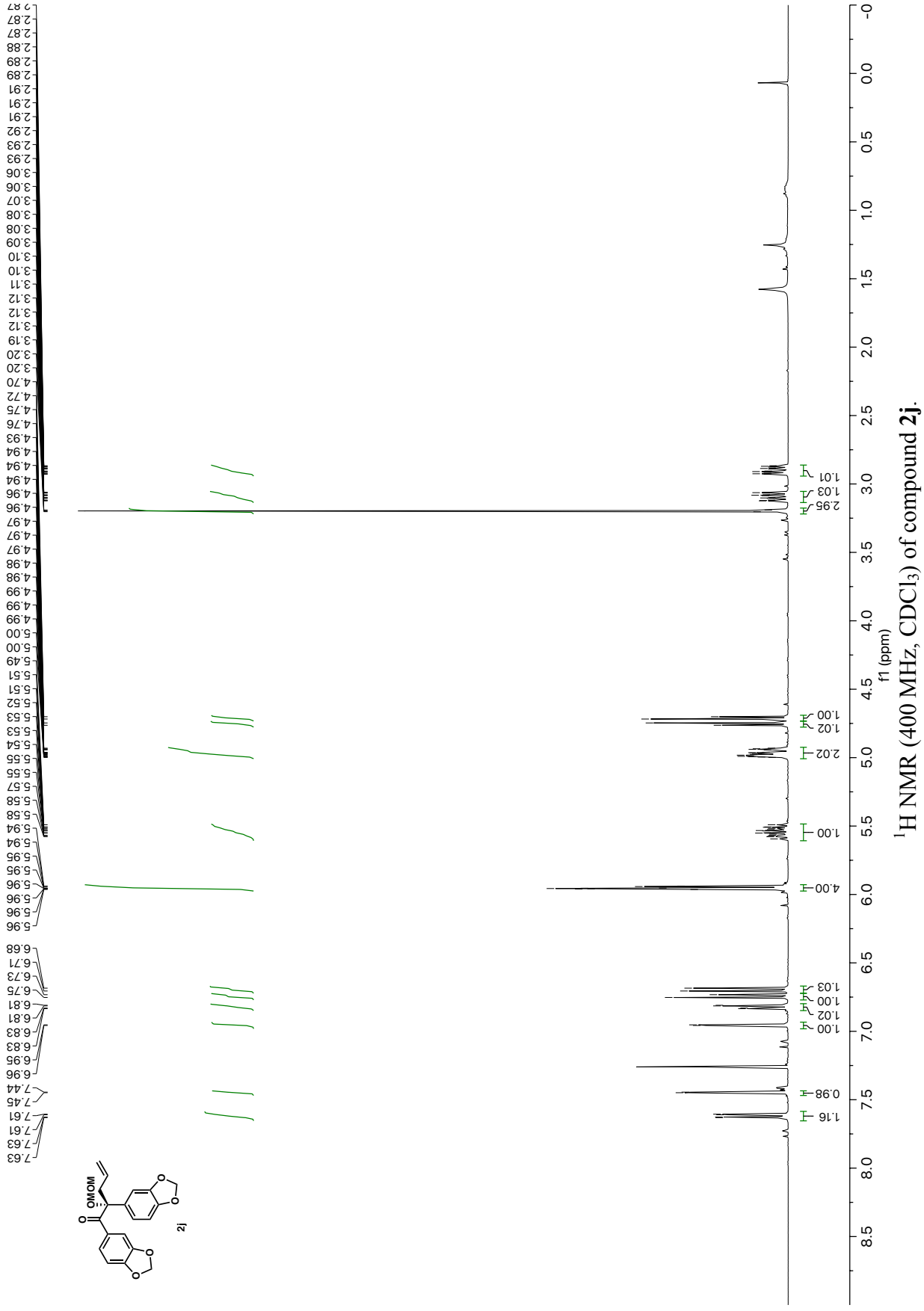
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2i**.



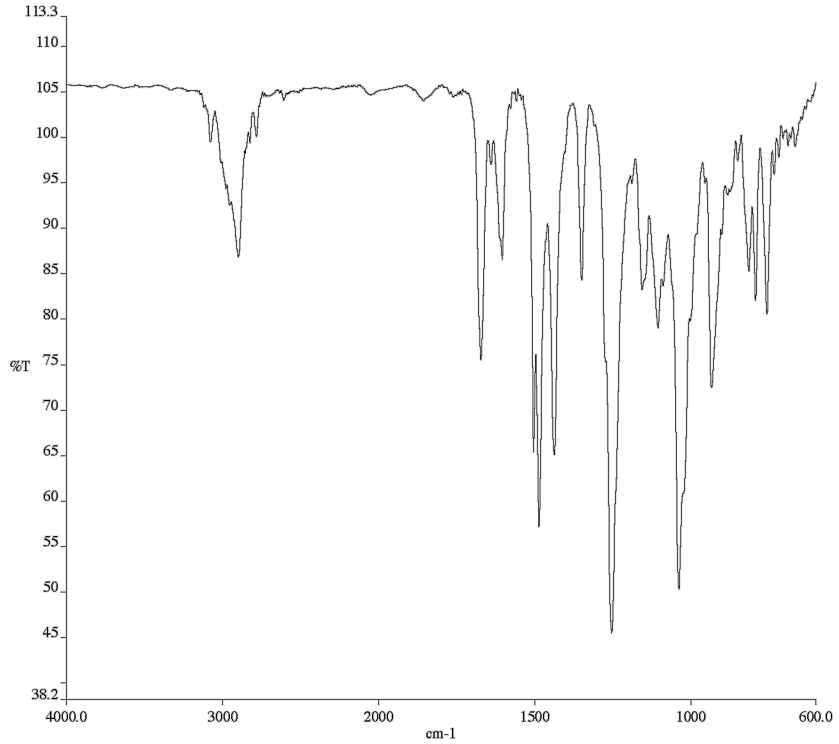
Infrared spectrum (Thin Film, NaCl) of compound **2i**.



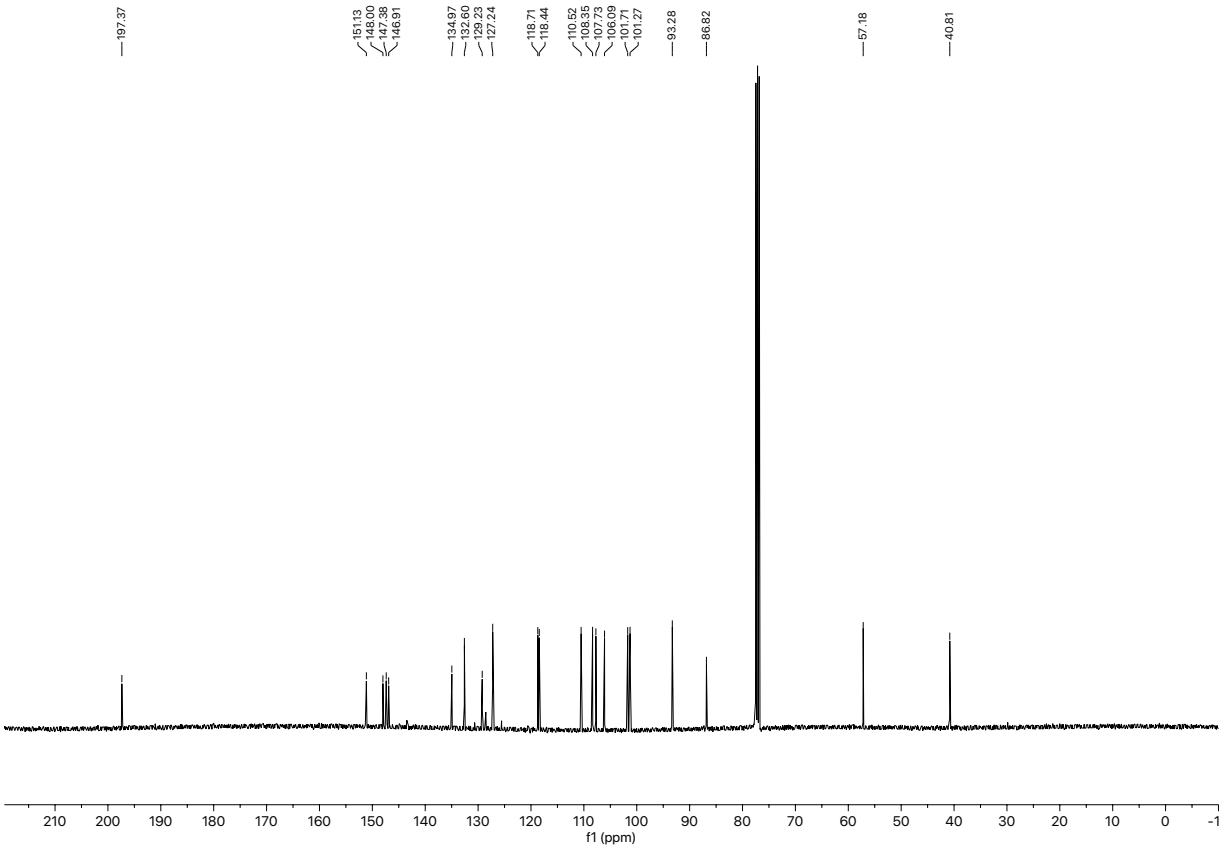
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2i**.



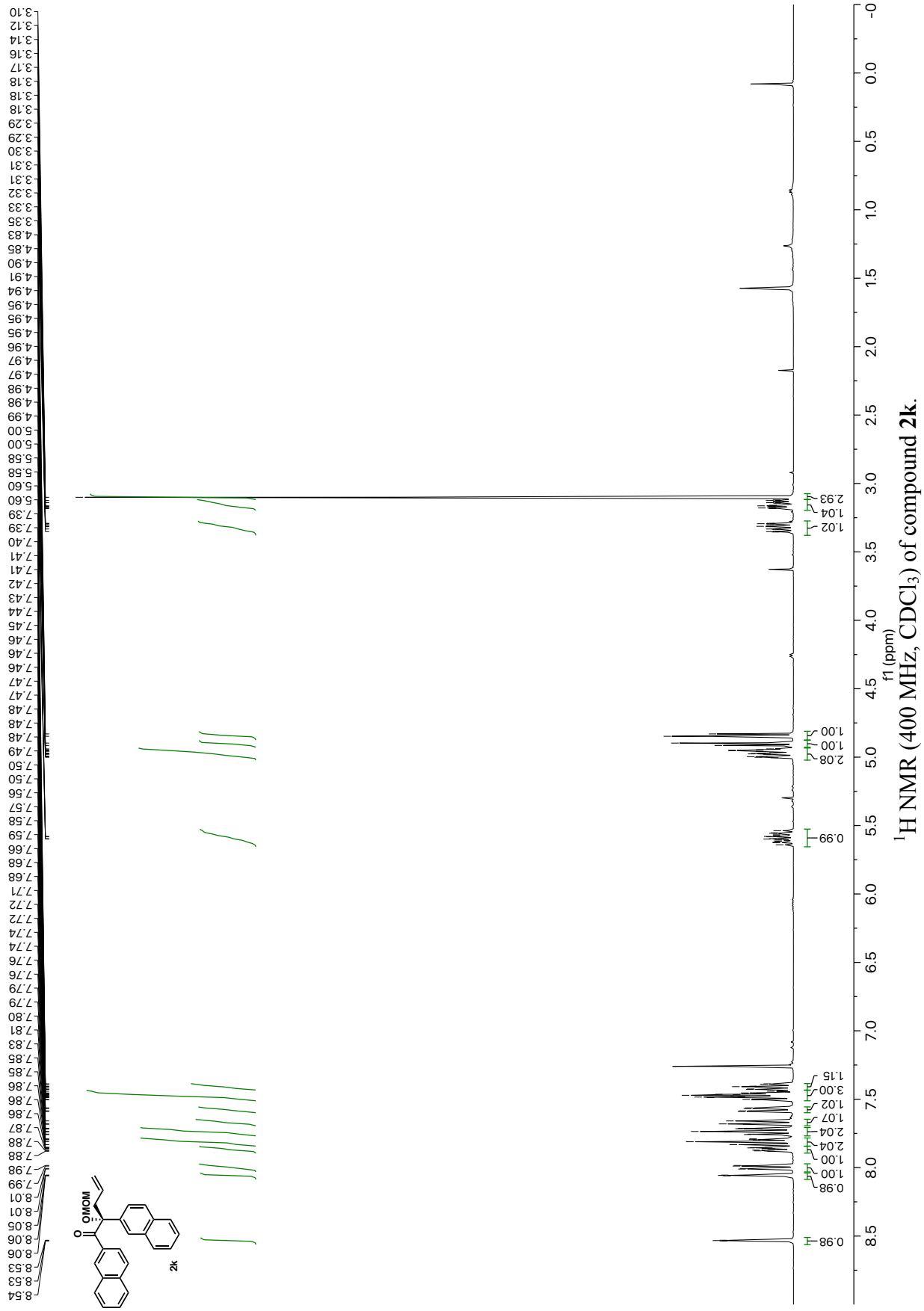
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2j**.



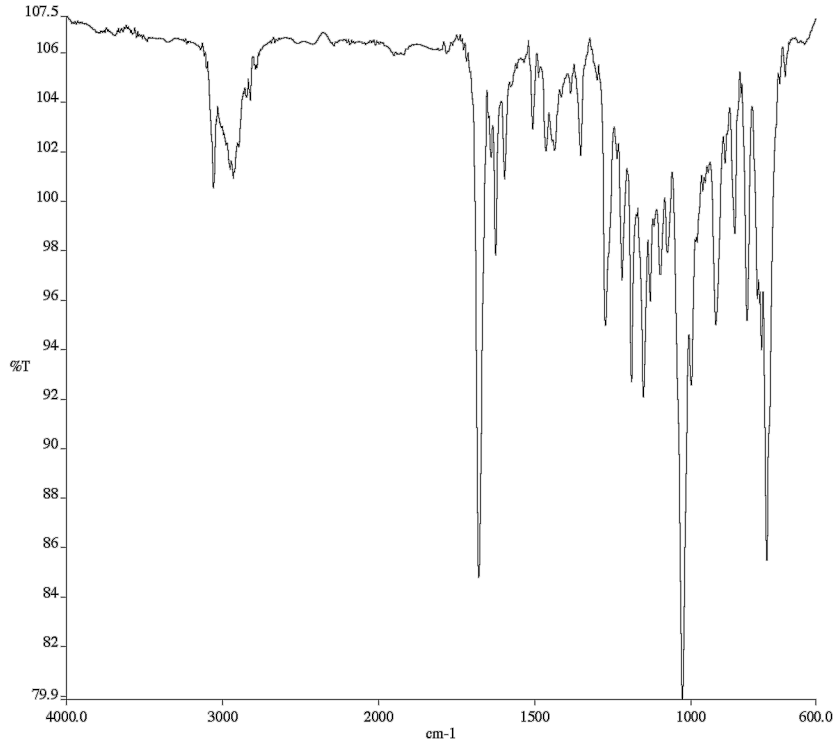
Infrared spectrum (Thin Film, NaCl) of compound **2j**.



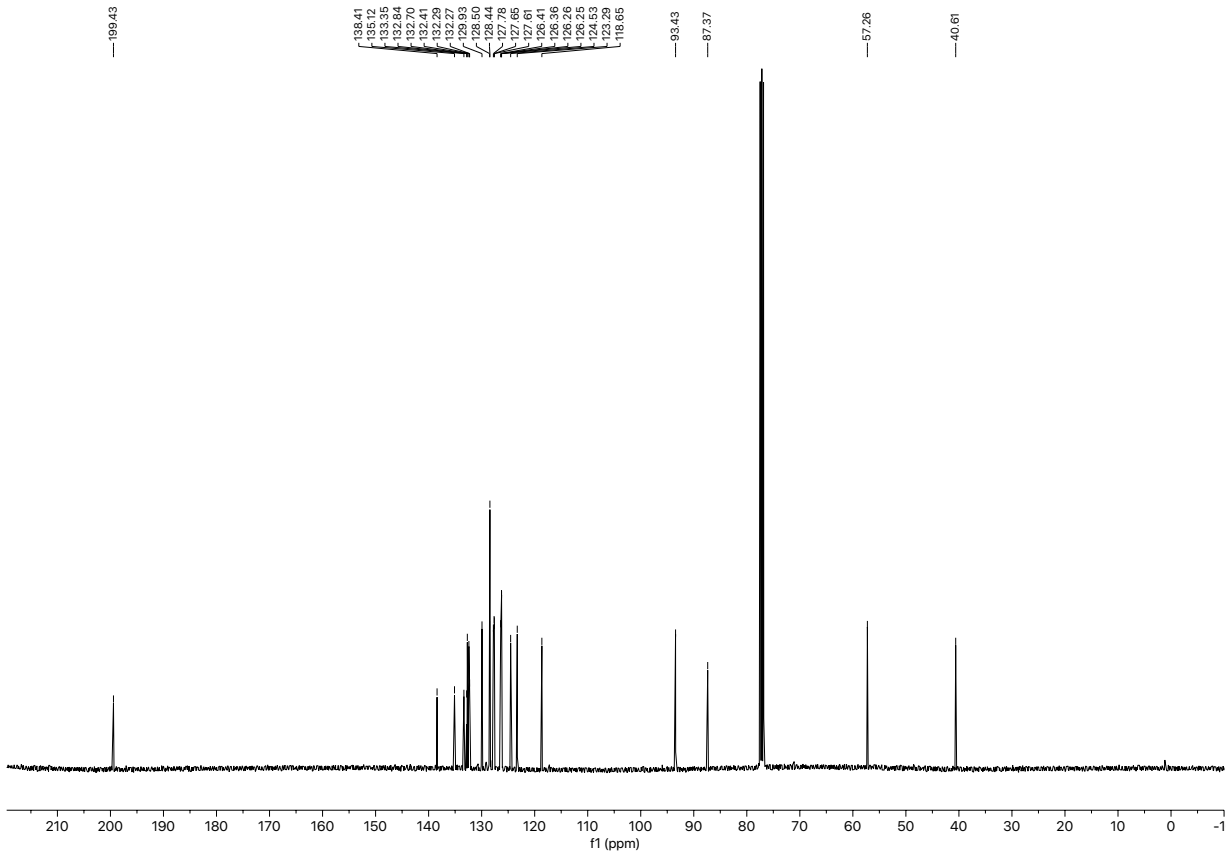
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2j**.



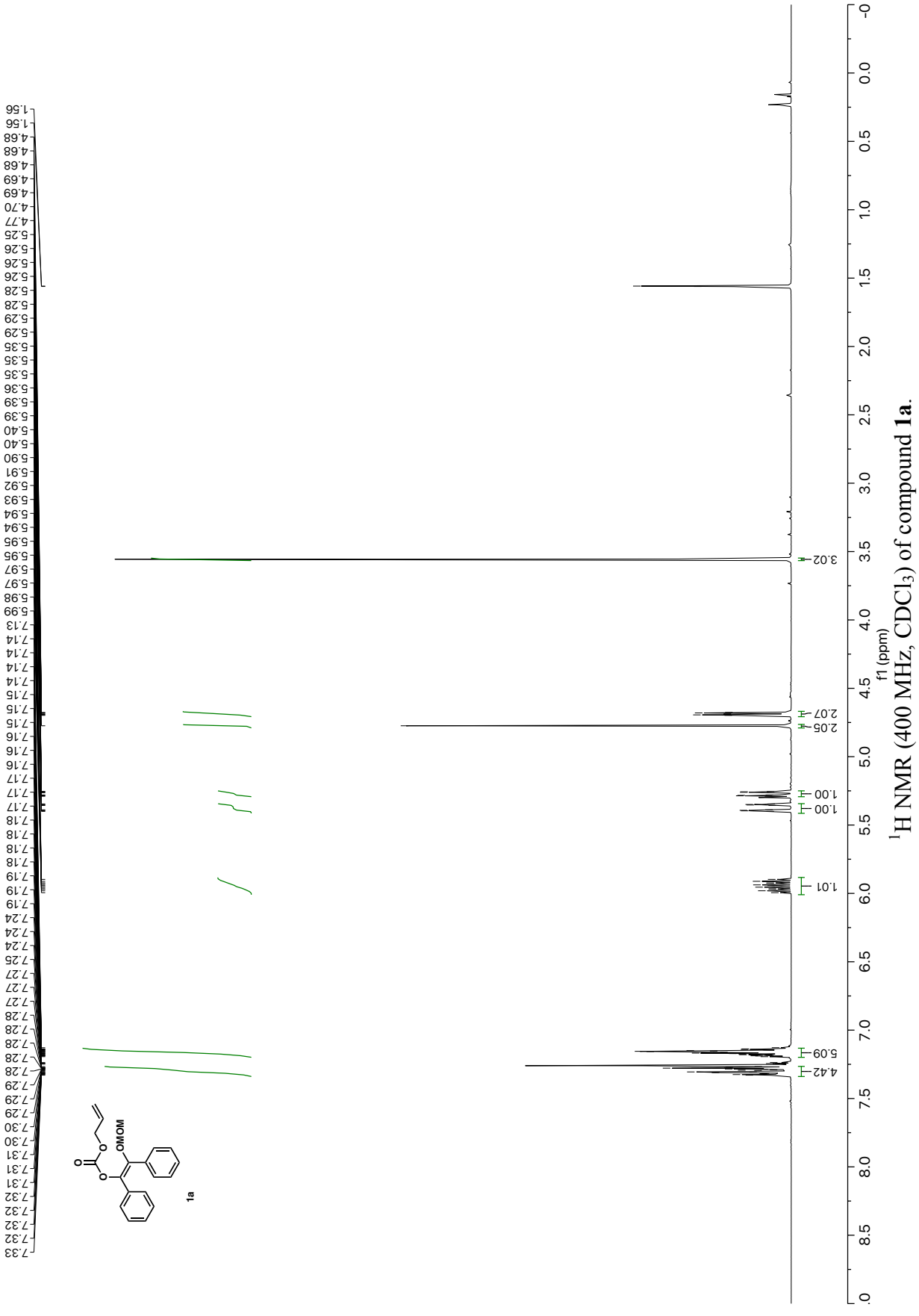
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2k**.



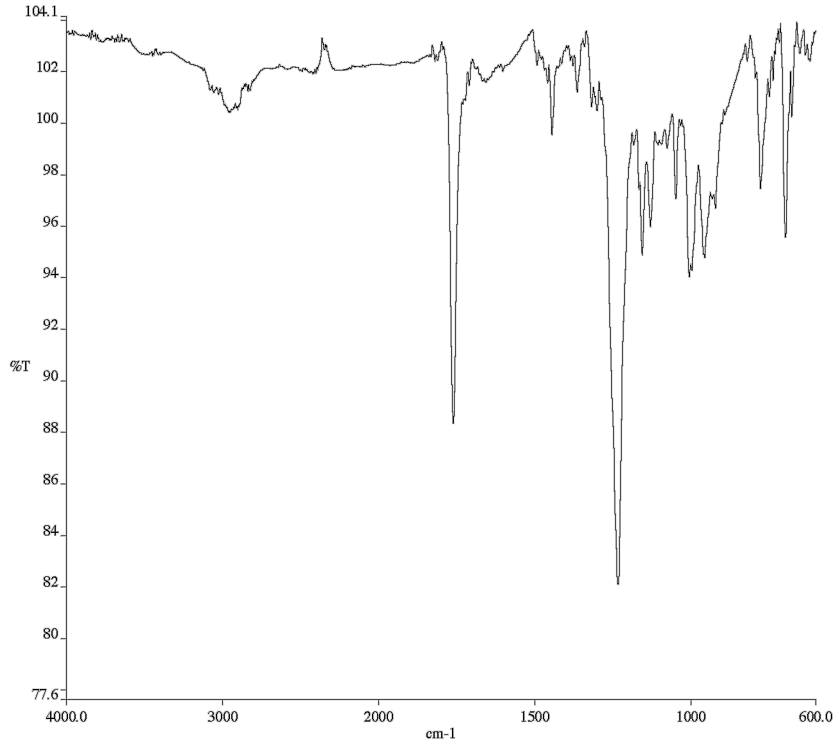
Infrared spectrum (Thin Film, NaCl) of compound **2k**.



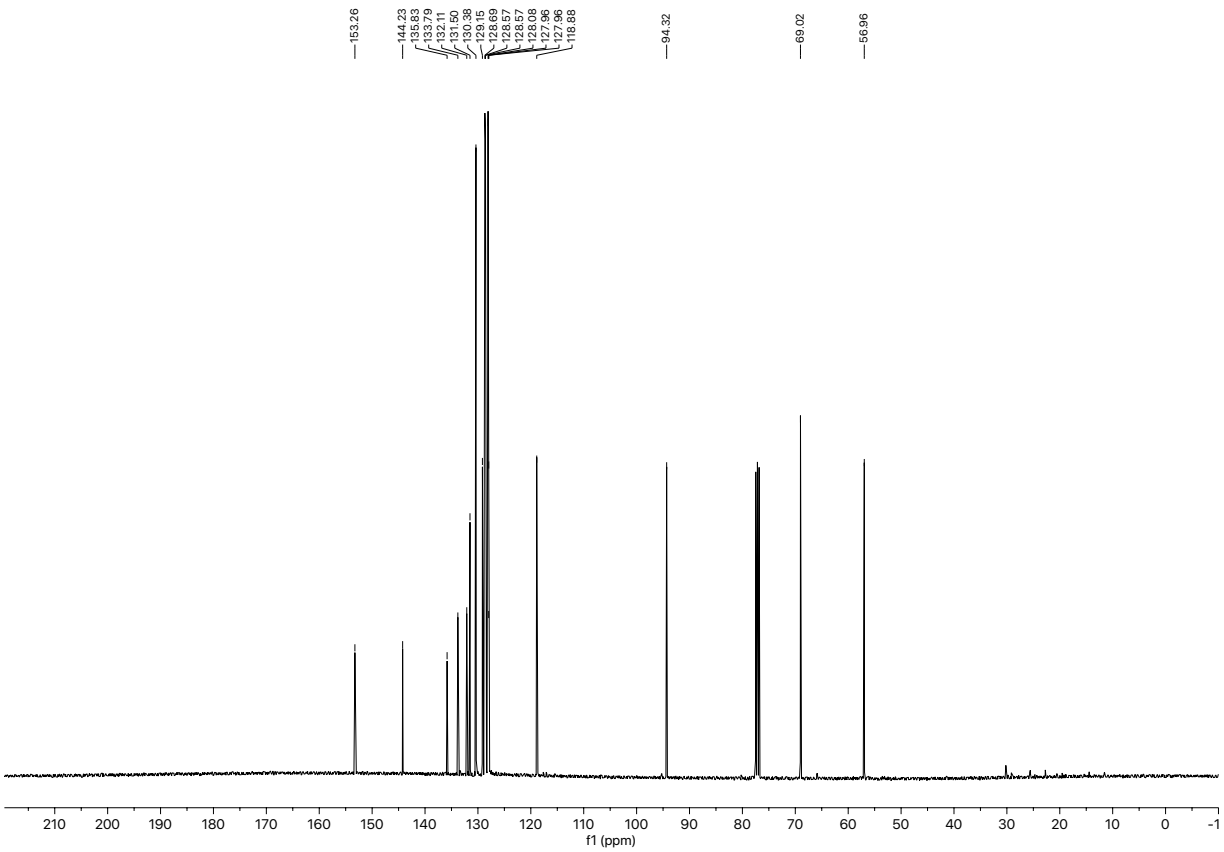
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2k**.



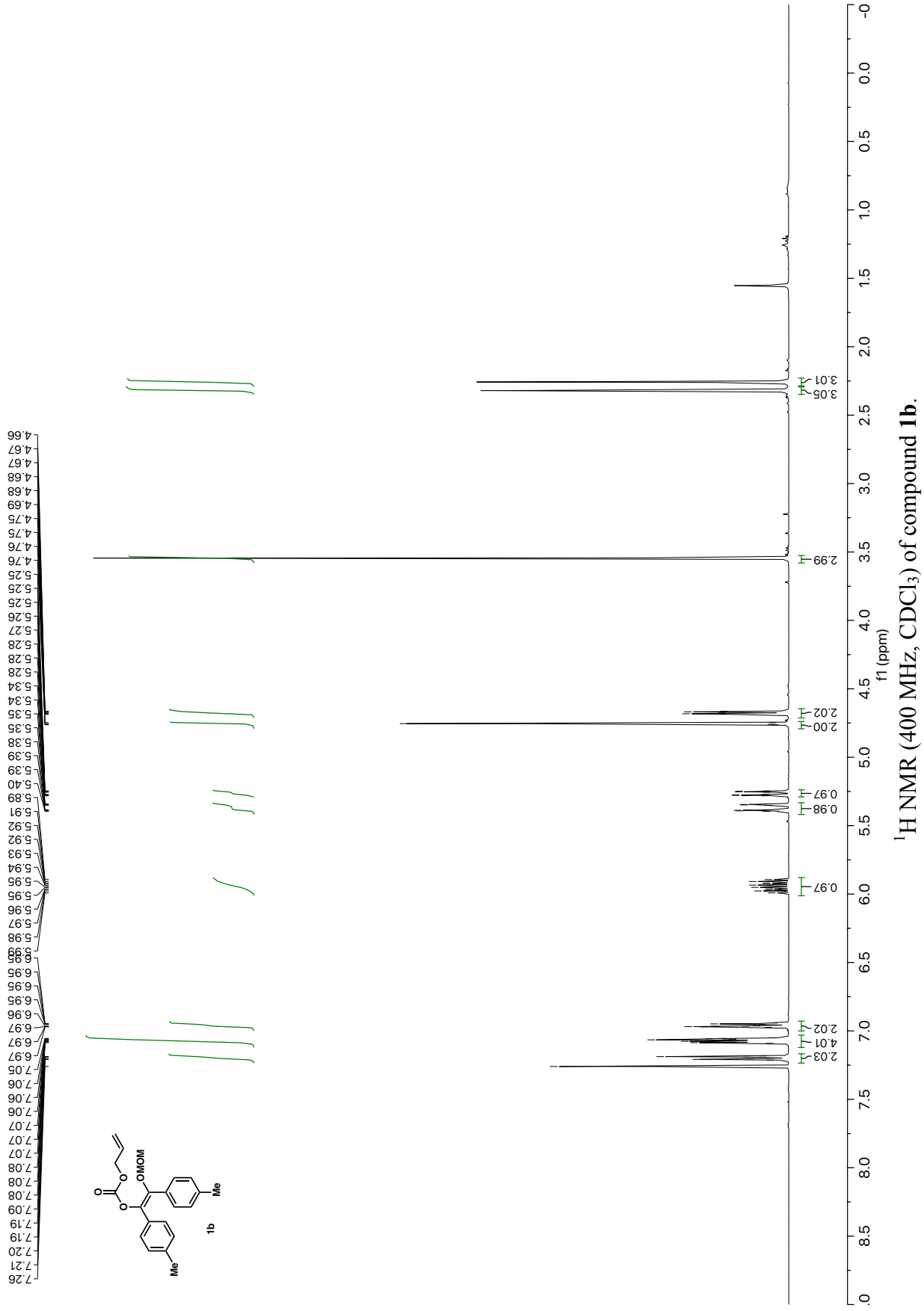
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1a**.



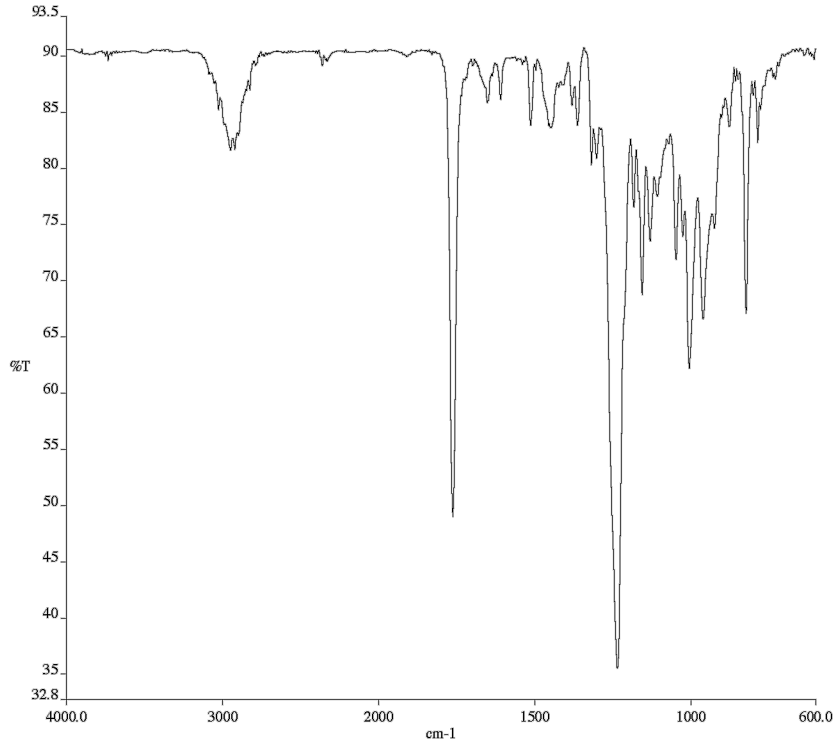
Infrared spectrum (Thin Film, NaCl) of compound **1a**.



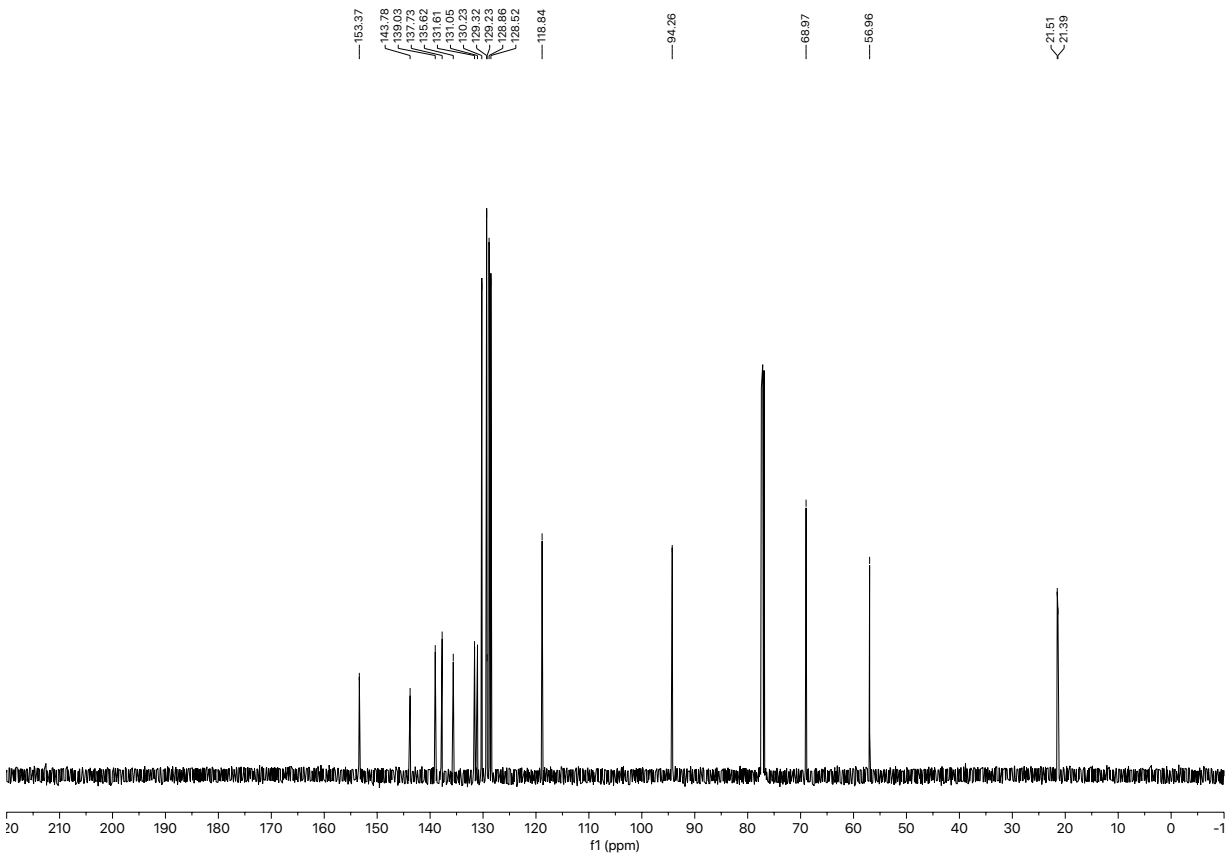
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1a**.



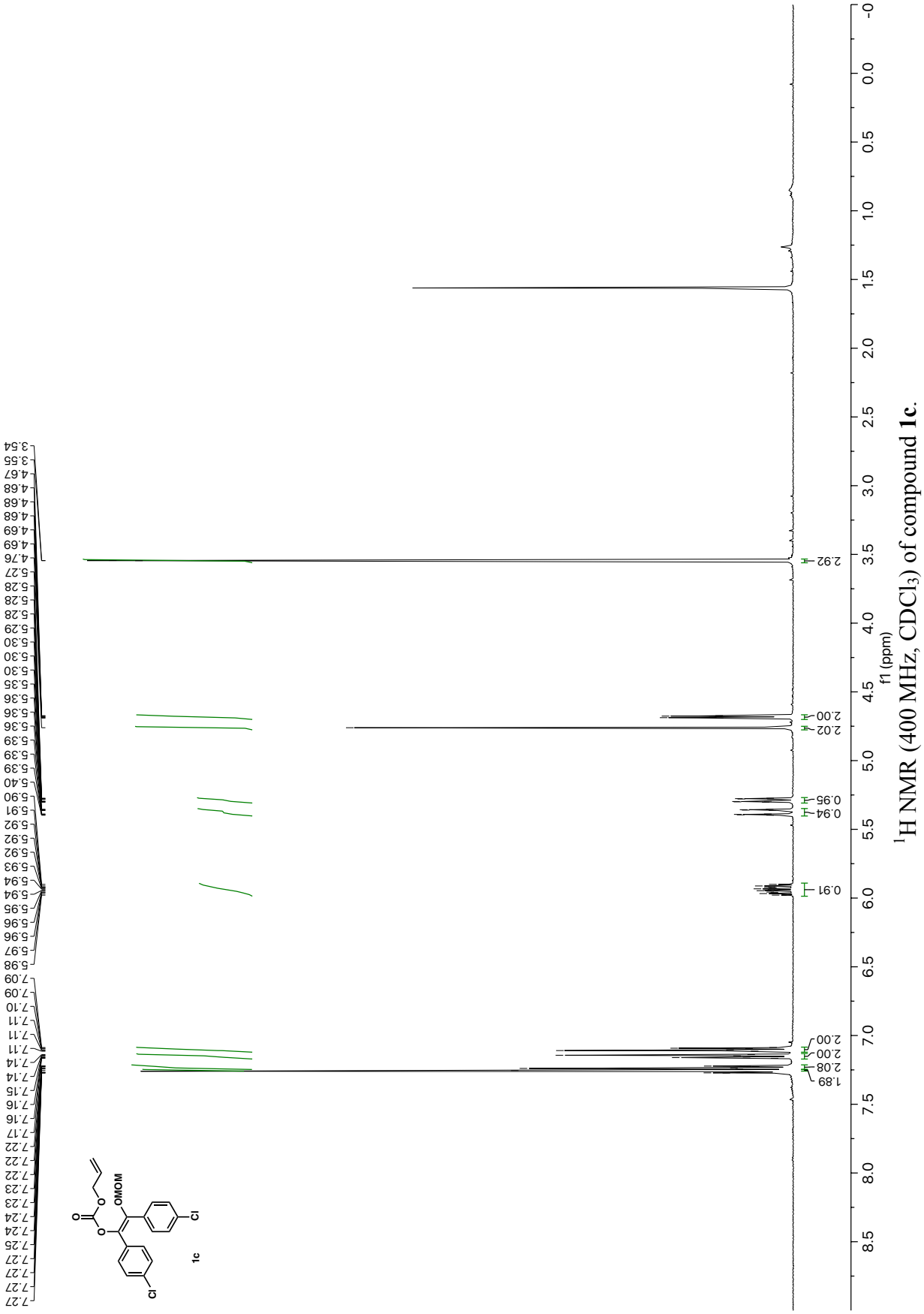
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1b**.



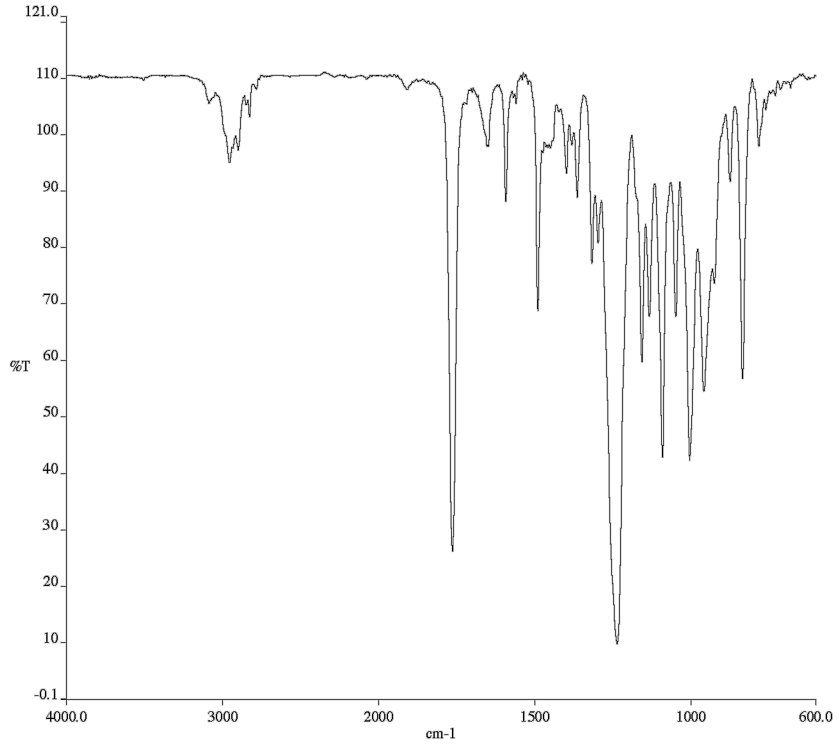
Infrared spectrum (Thin Film, NaCl) of compound **1b**.



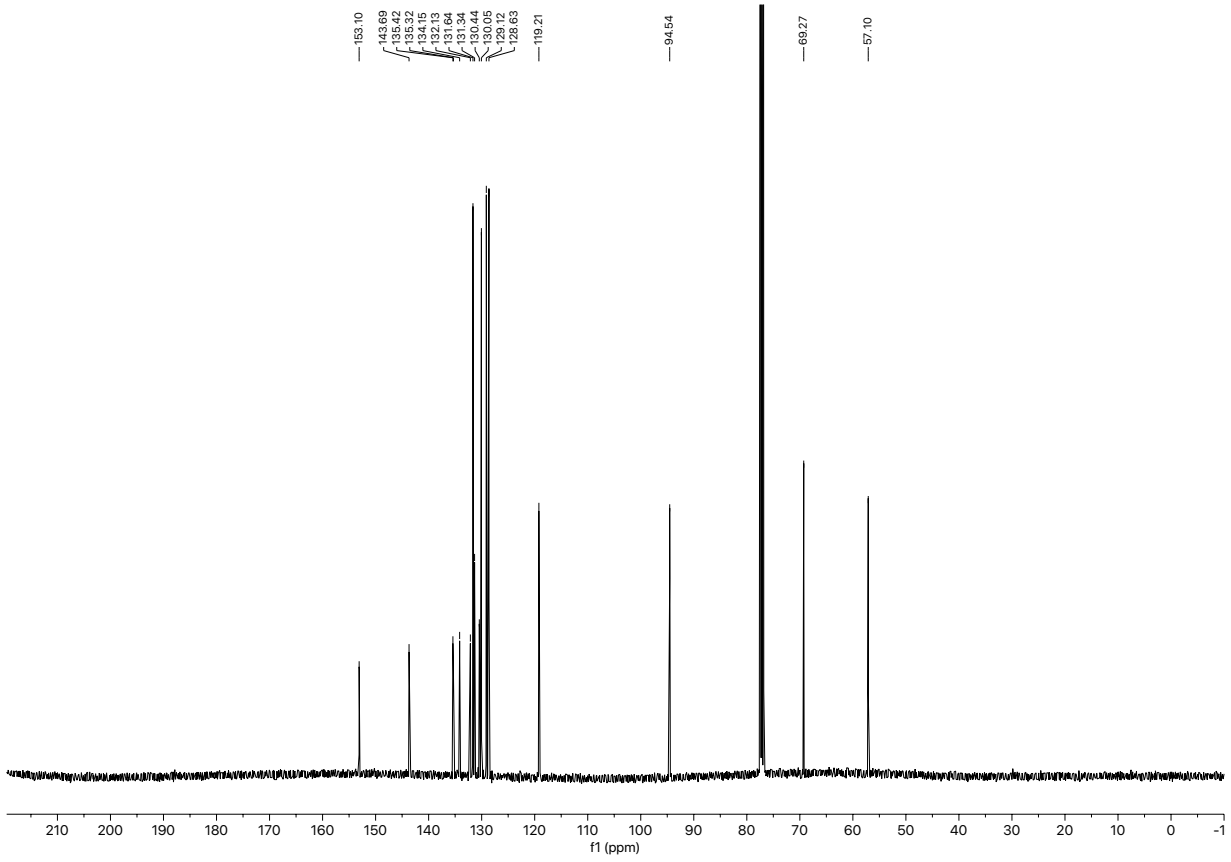
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1b**.



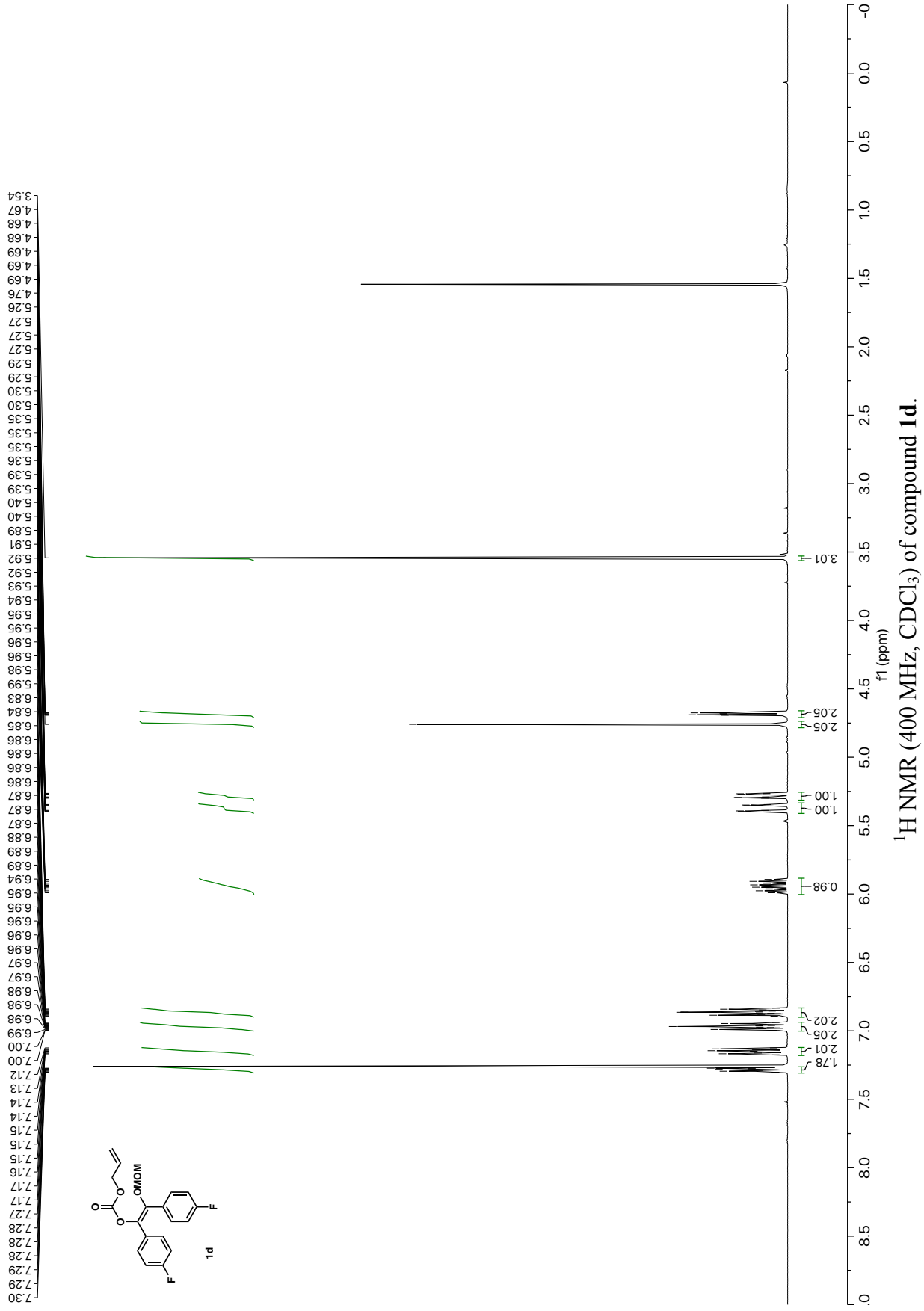
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1c**.



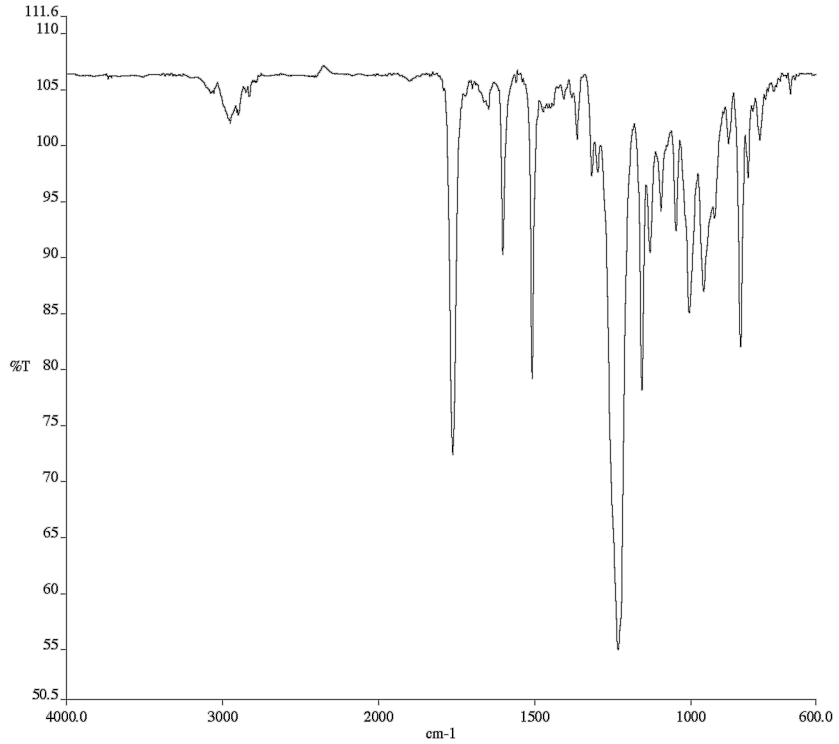
Infrared spectrum (Thin Film, NaCl) of compound **1c**.



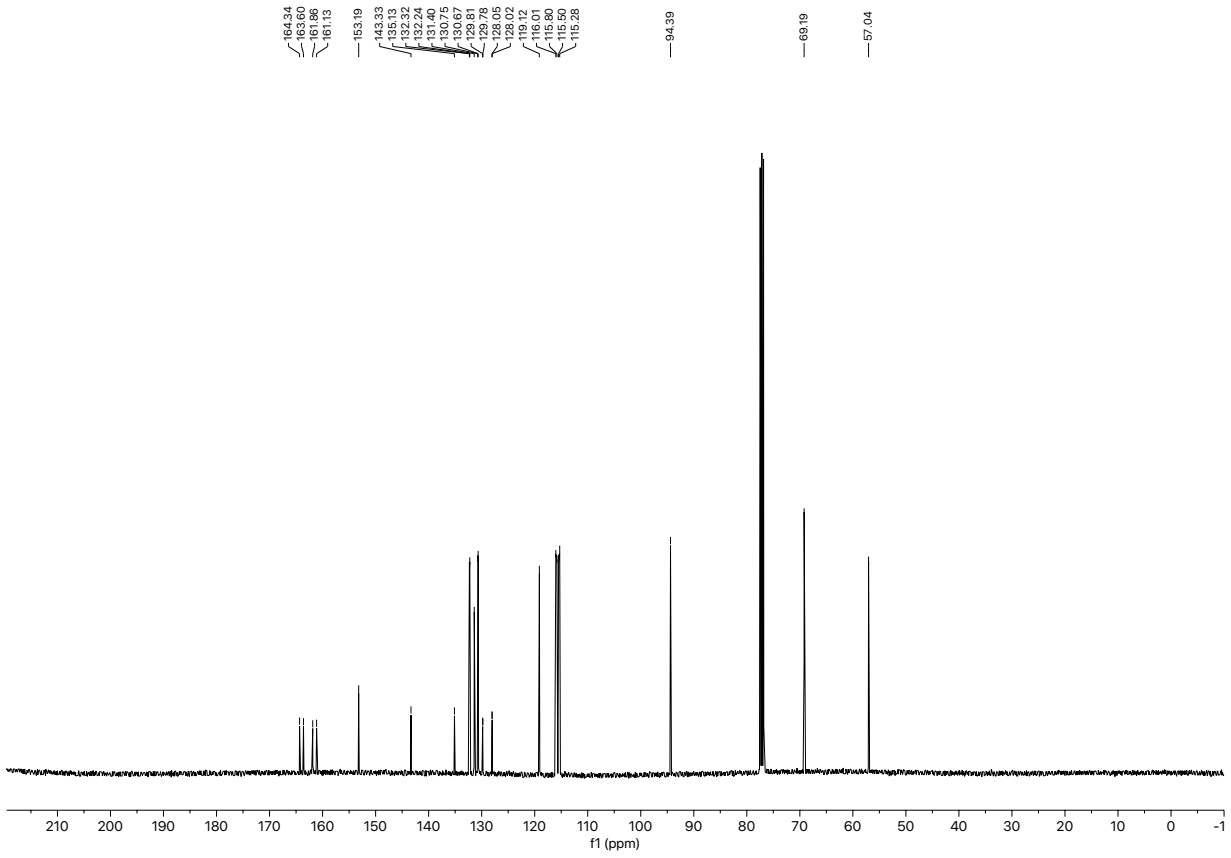
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1c**.



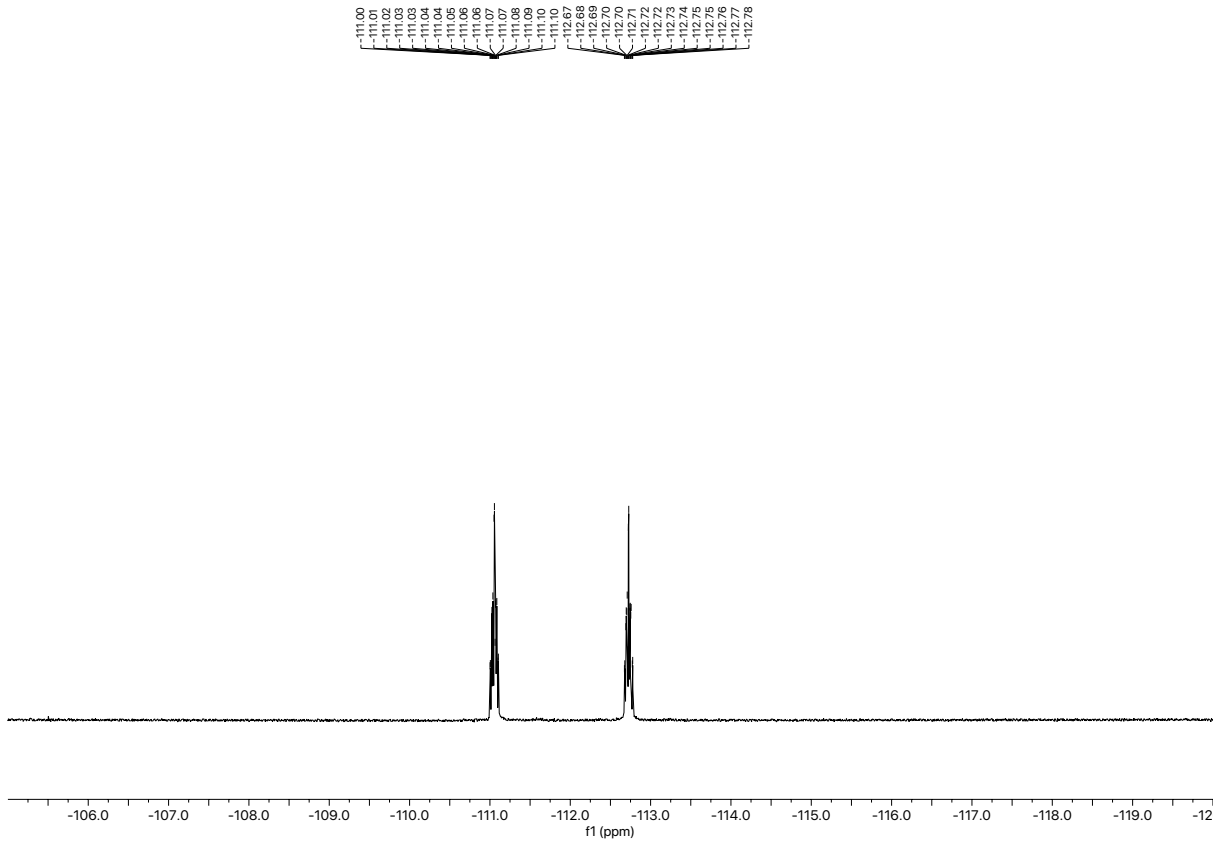
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1d**.



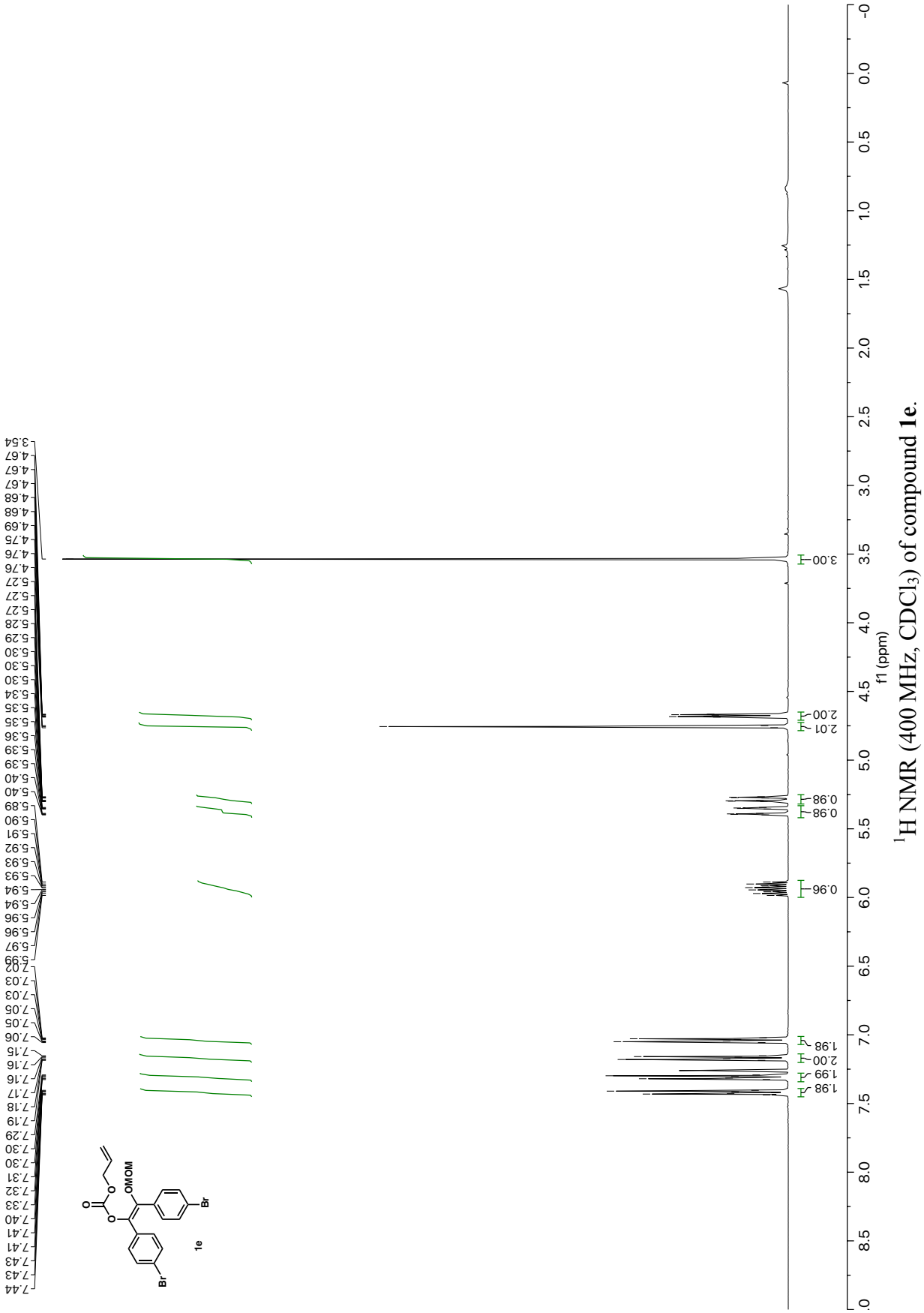
Infrared spectrum (Thin Film, NaCl) of compound **1d**.



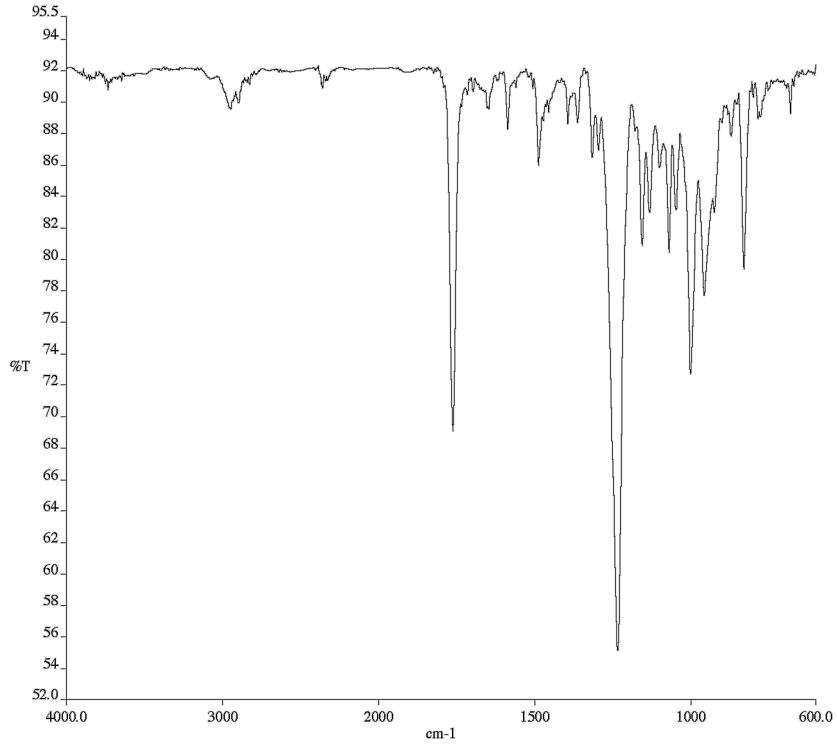
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1d**.



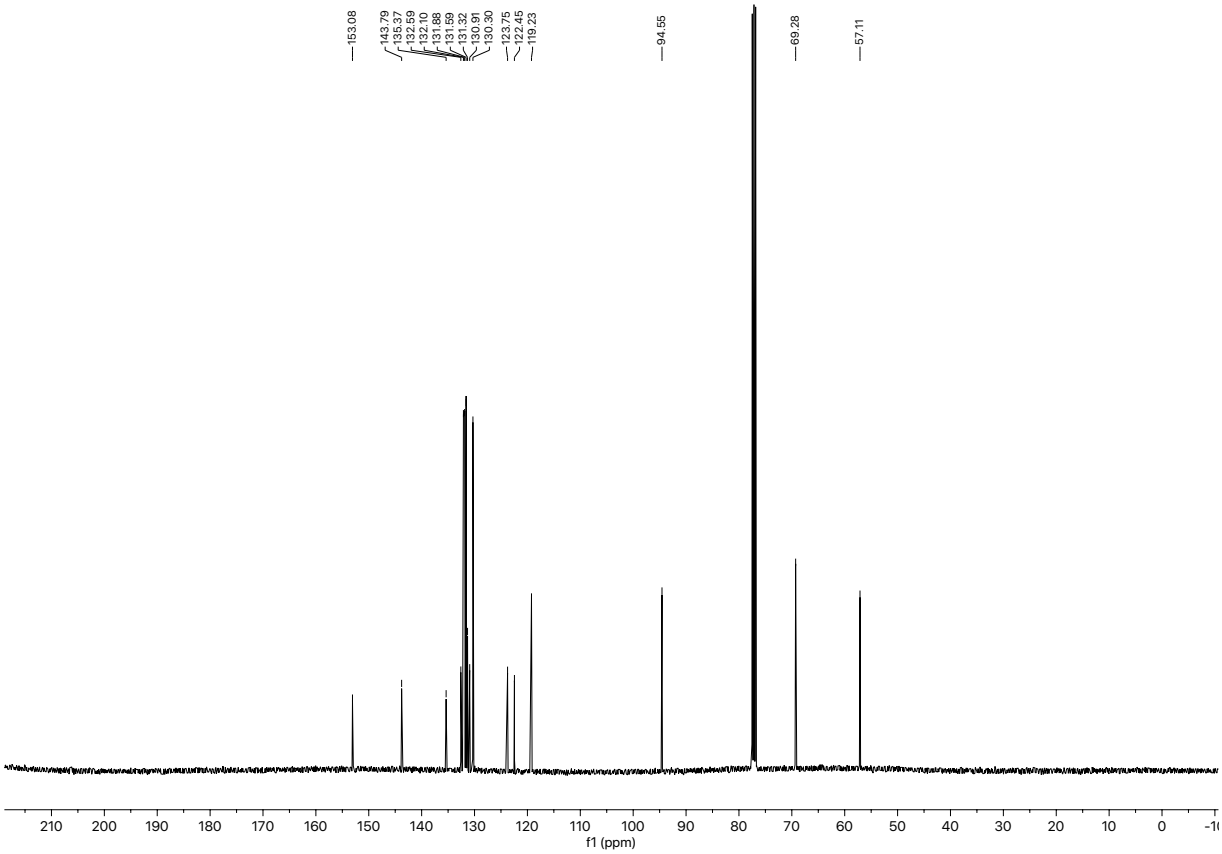
^{19}F NMR (282 MHz, $CDCl_3$) of compound **1d**.



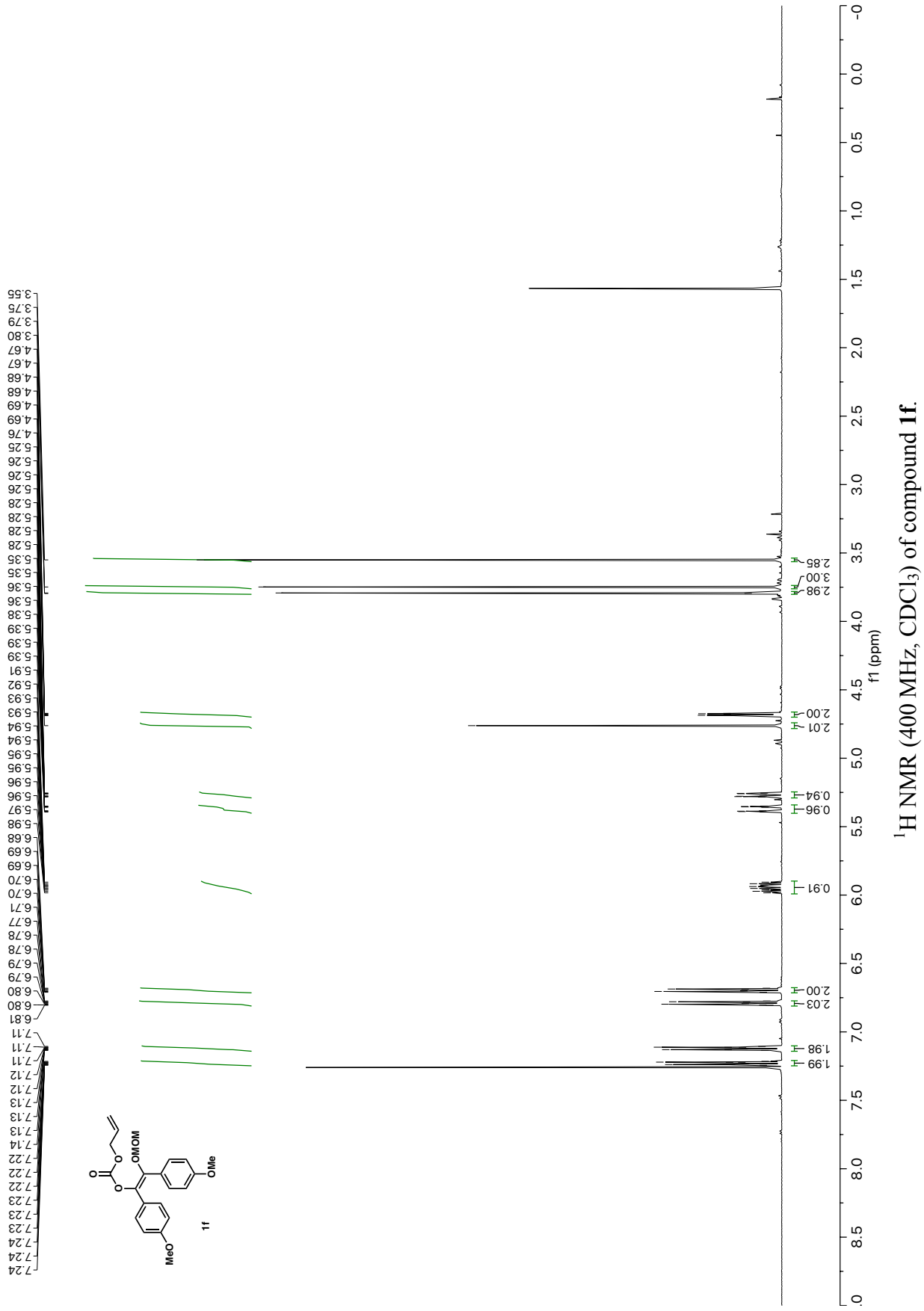
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1e**.



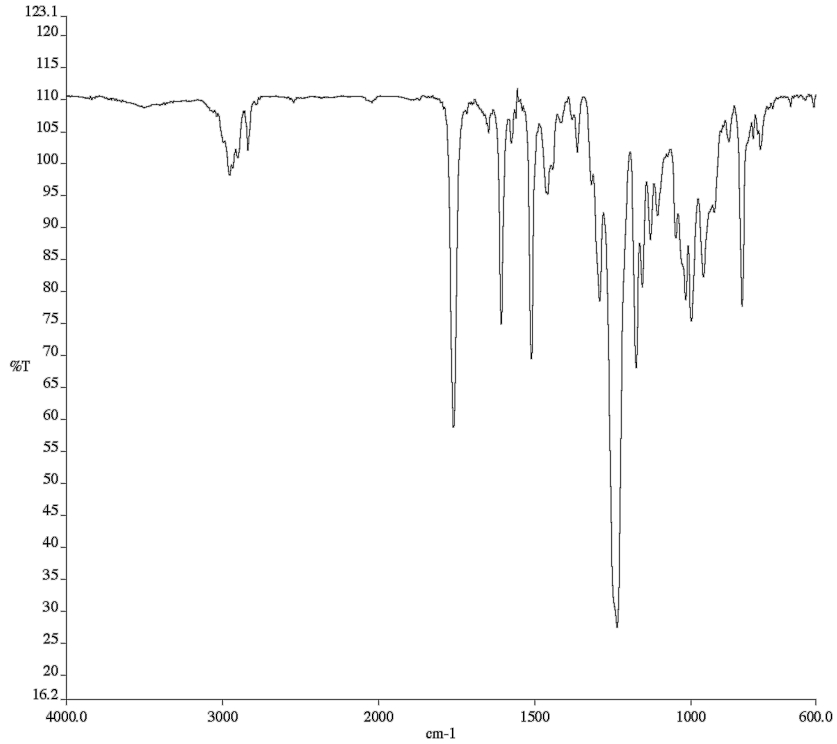
Infrared spectrum (Thin Film, NaCl) of compound **1e**.



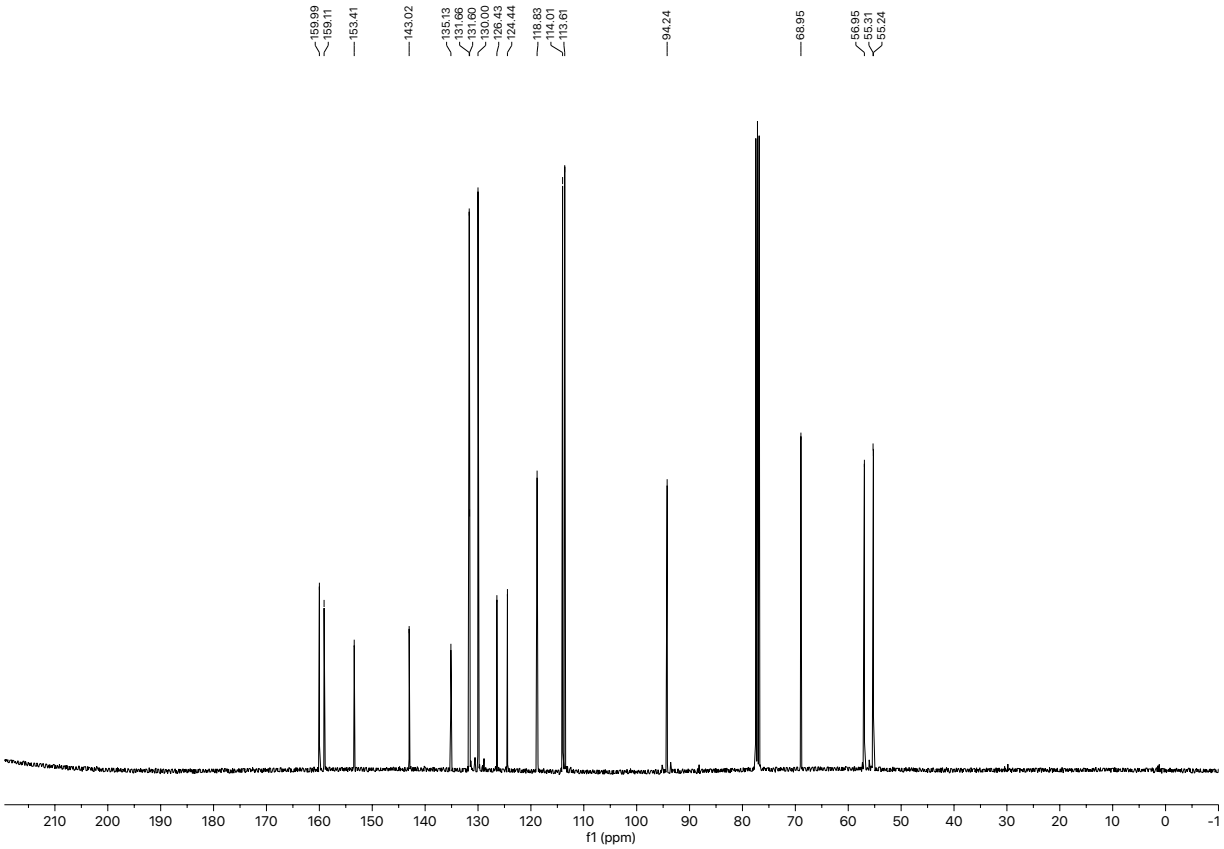
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1e**.



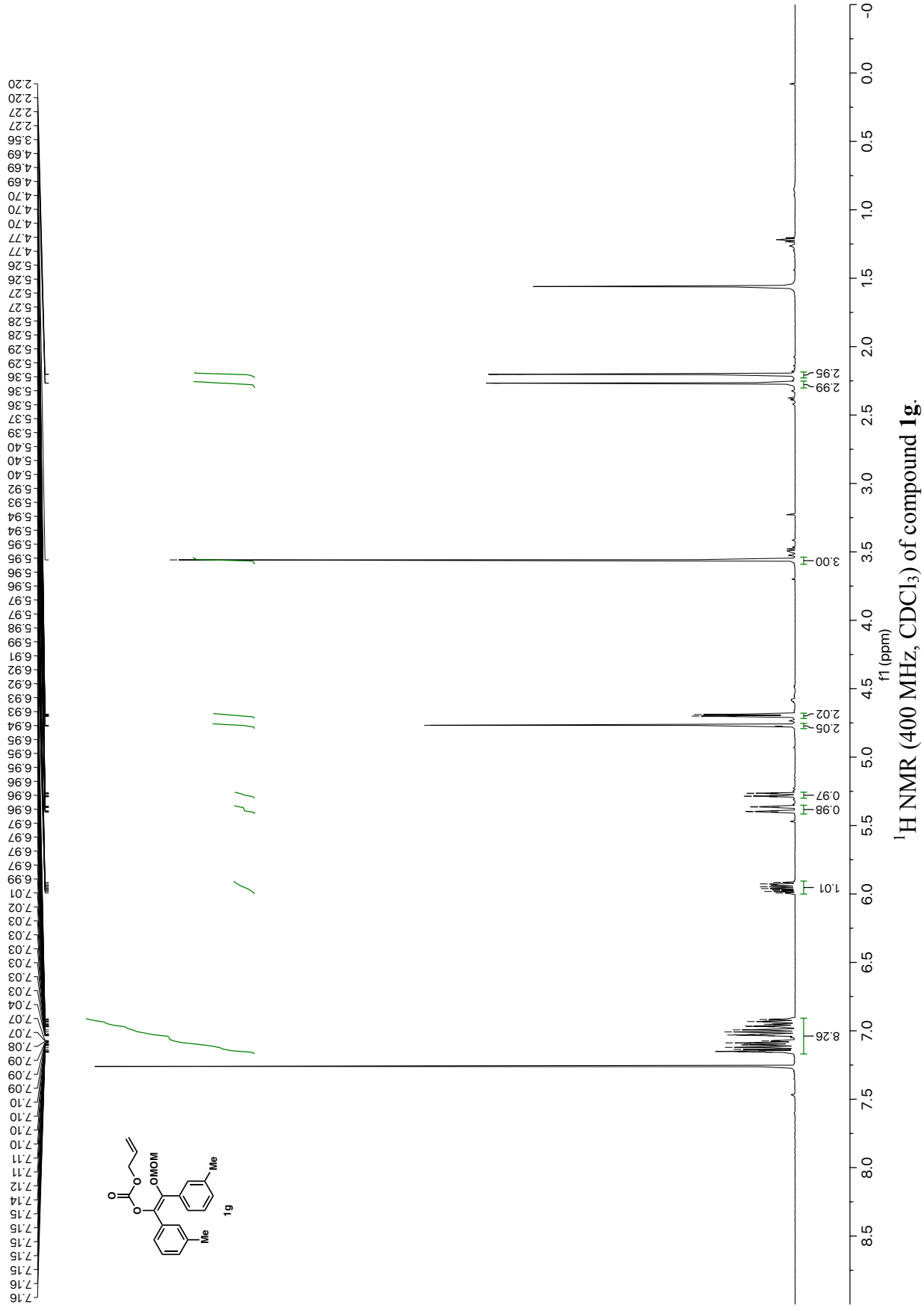
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1f**.



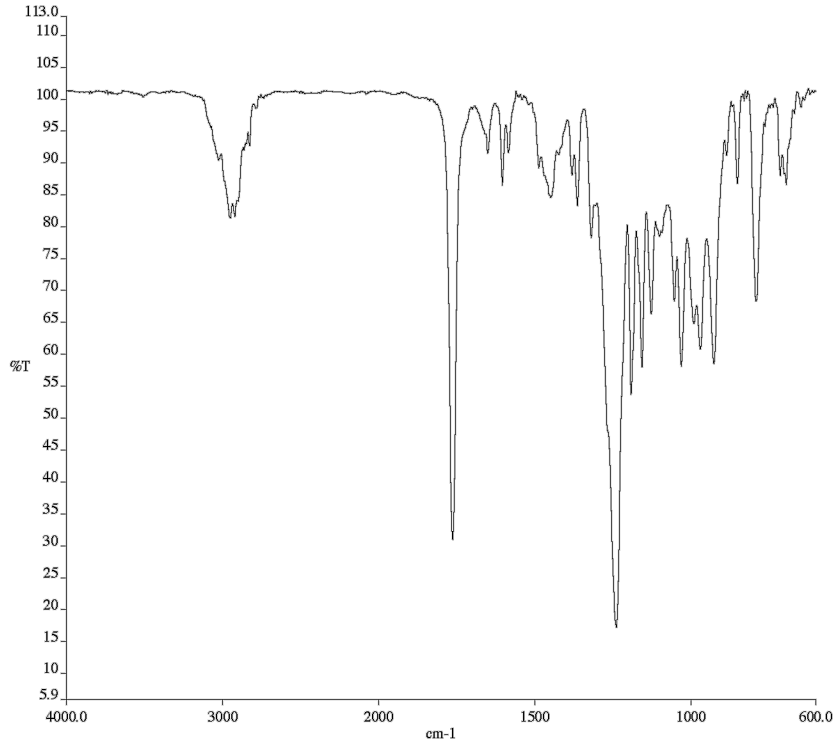
Infrared spectrum (Thin Film, NaCl) of compound **1f**.



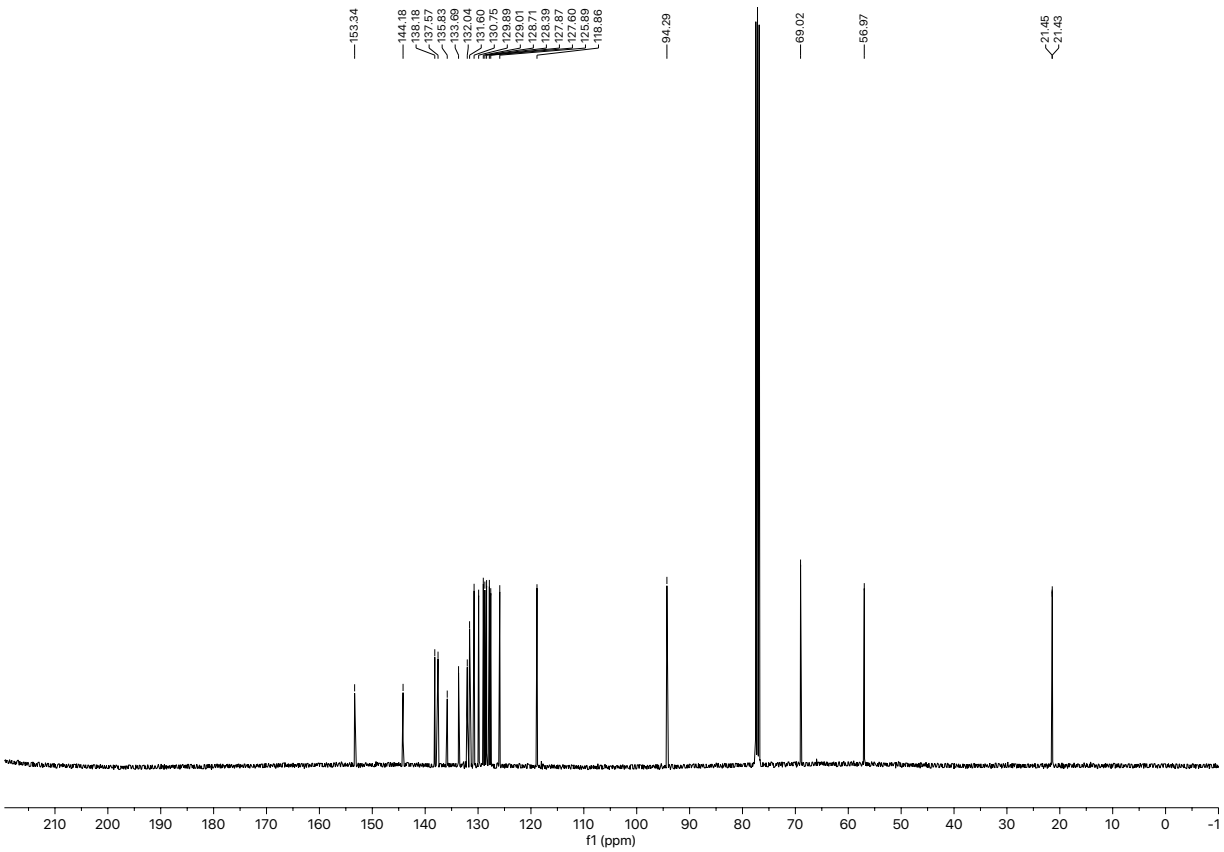
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1f**.



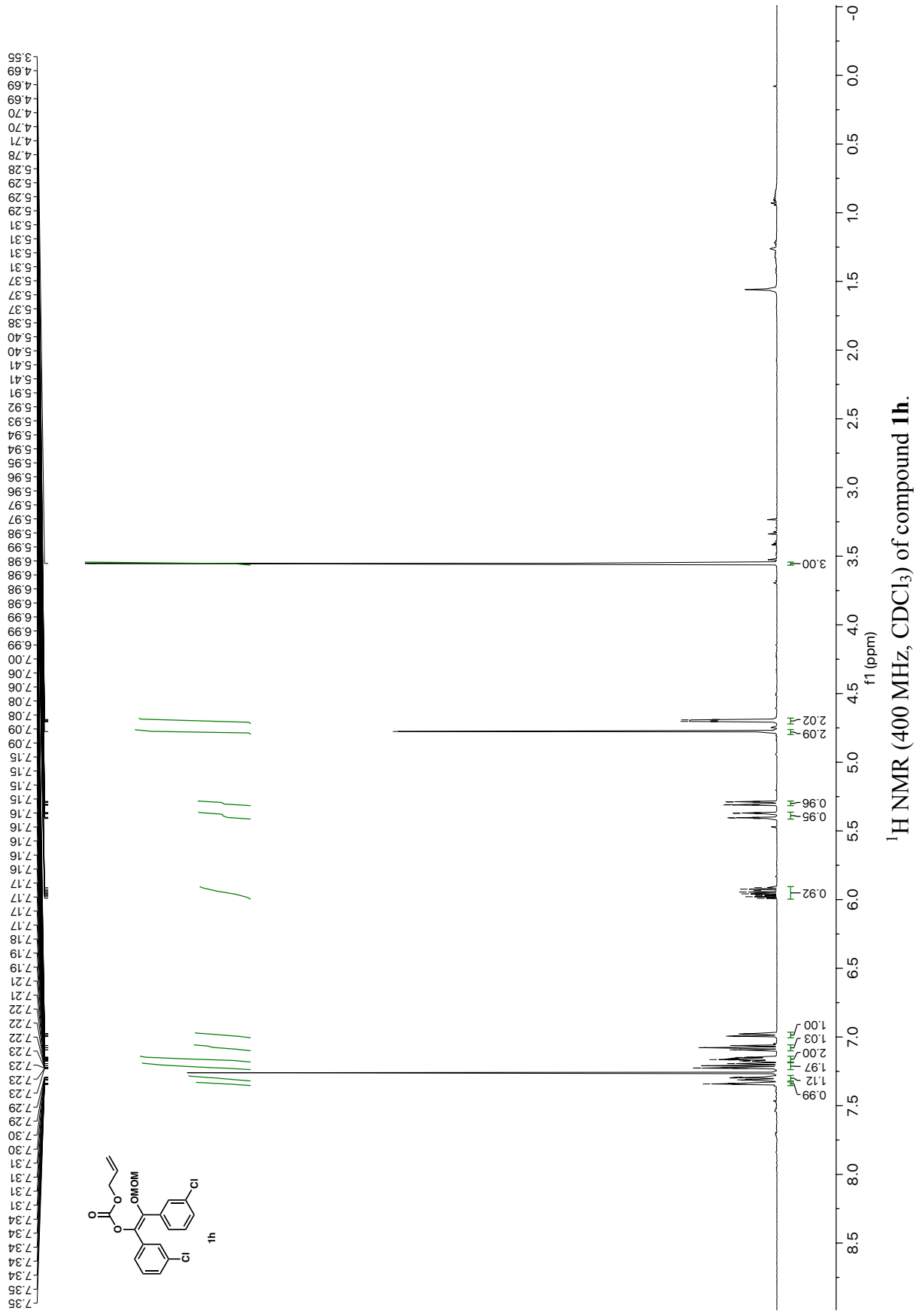
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1g**.



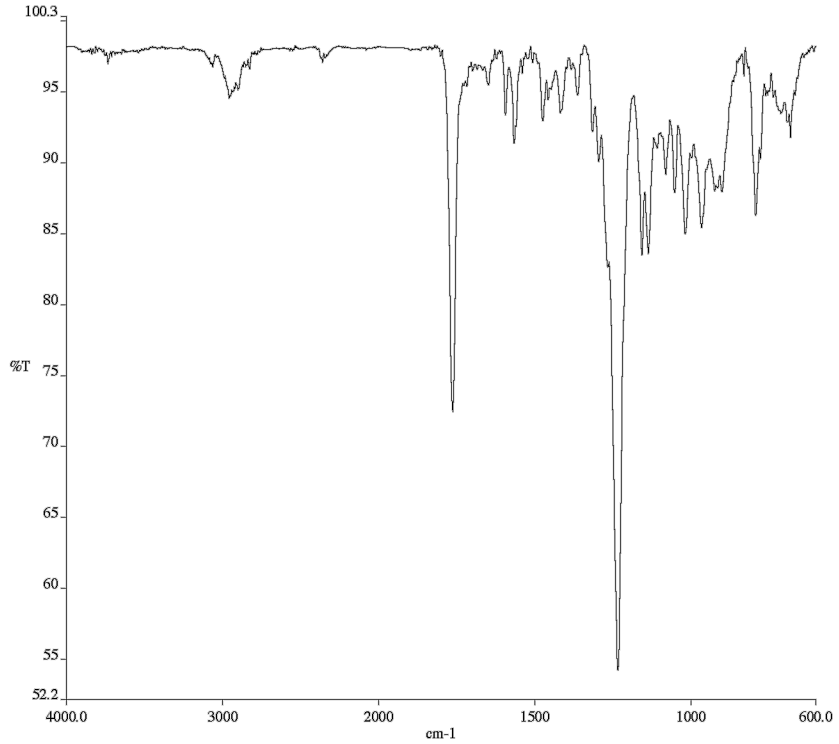
Infrared spectrum (Thin Film, NaCl) of compound **1g**.



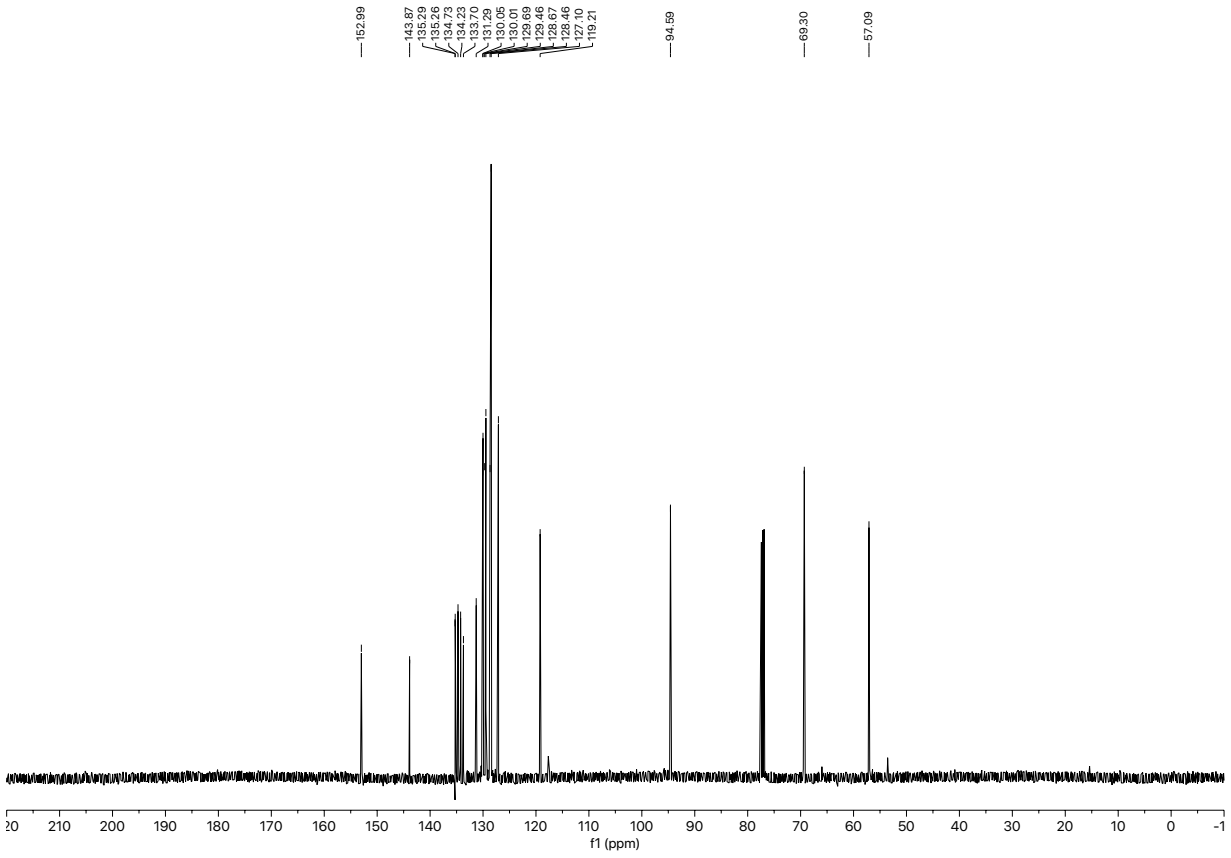
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1g**.



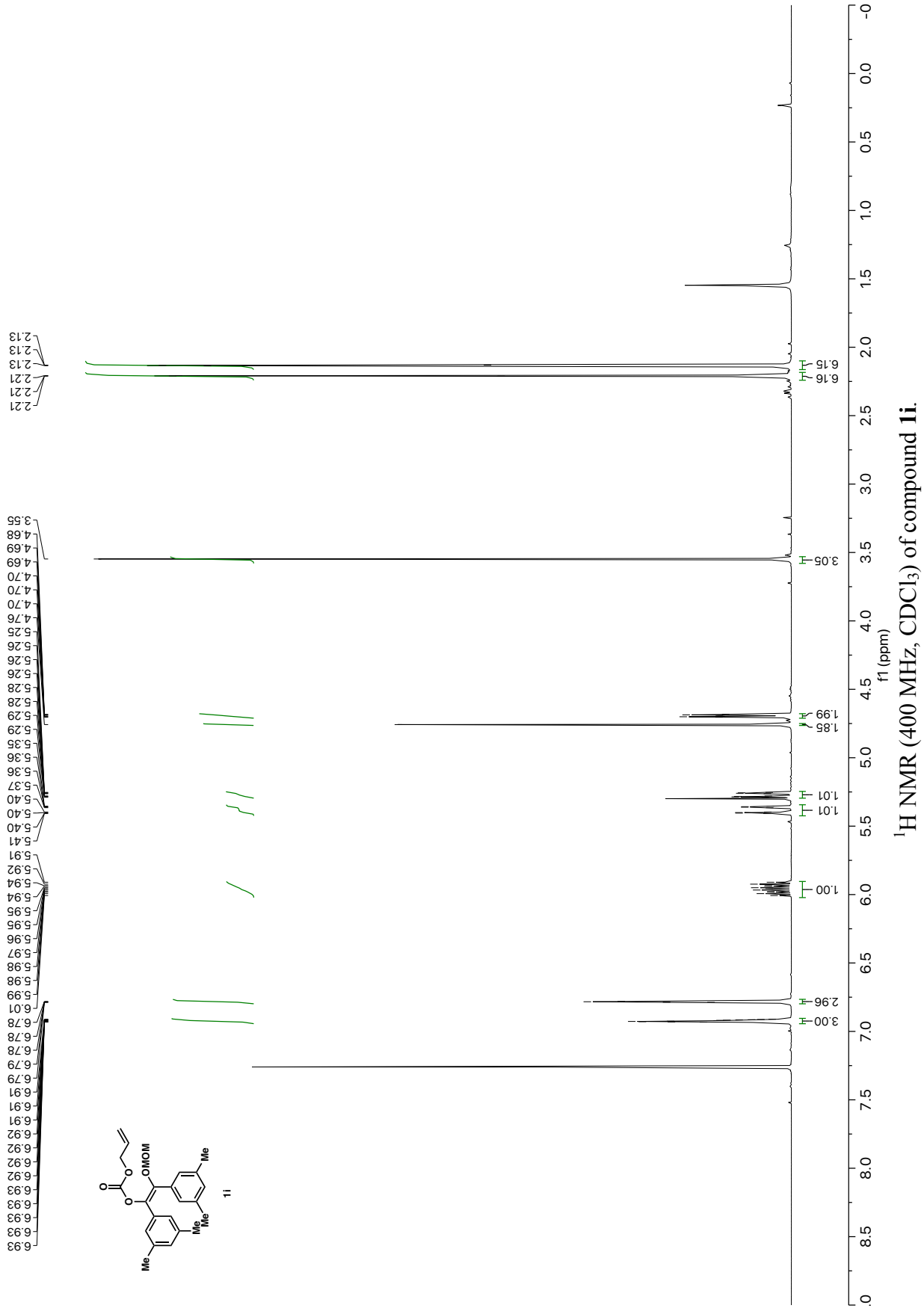
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1h**.



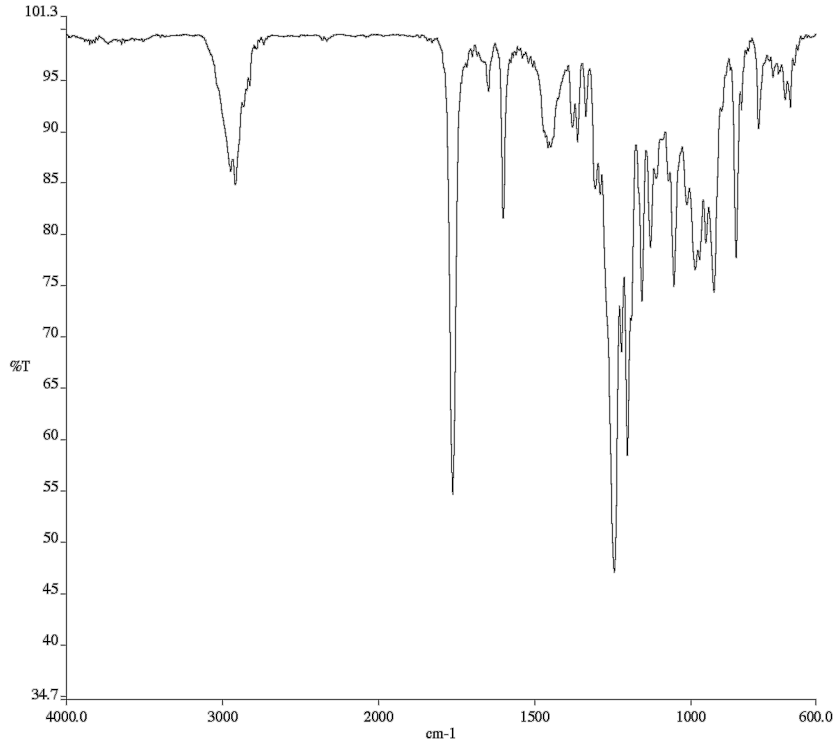
Infrared spectrum (Thin Film, NaCl) of compound **1h**.



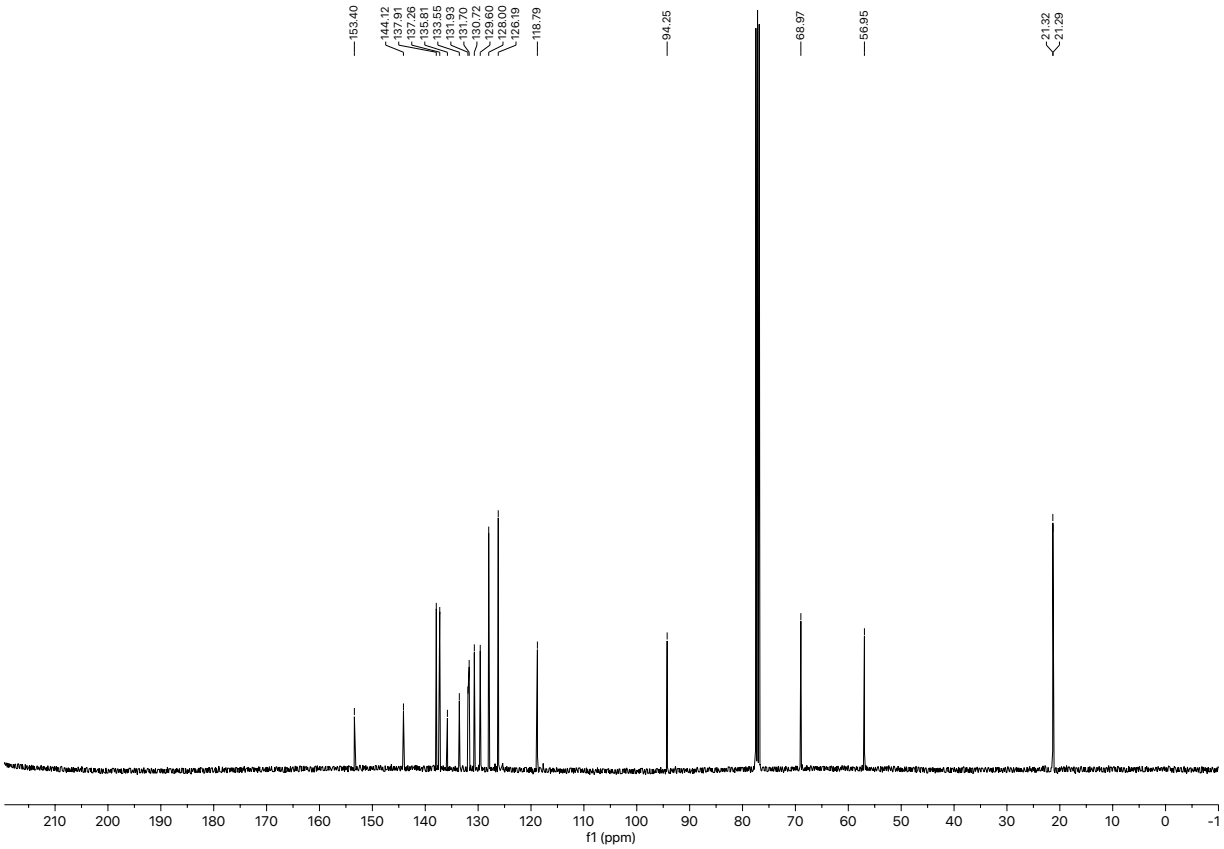
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1h**.



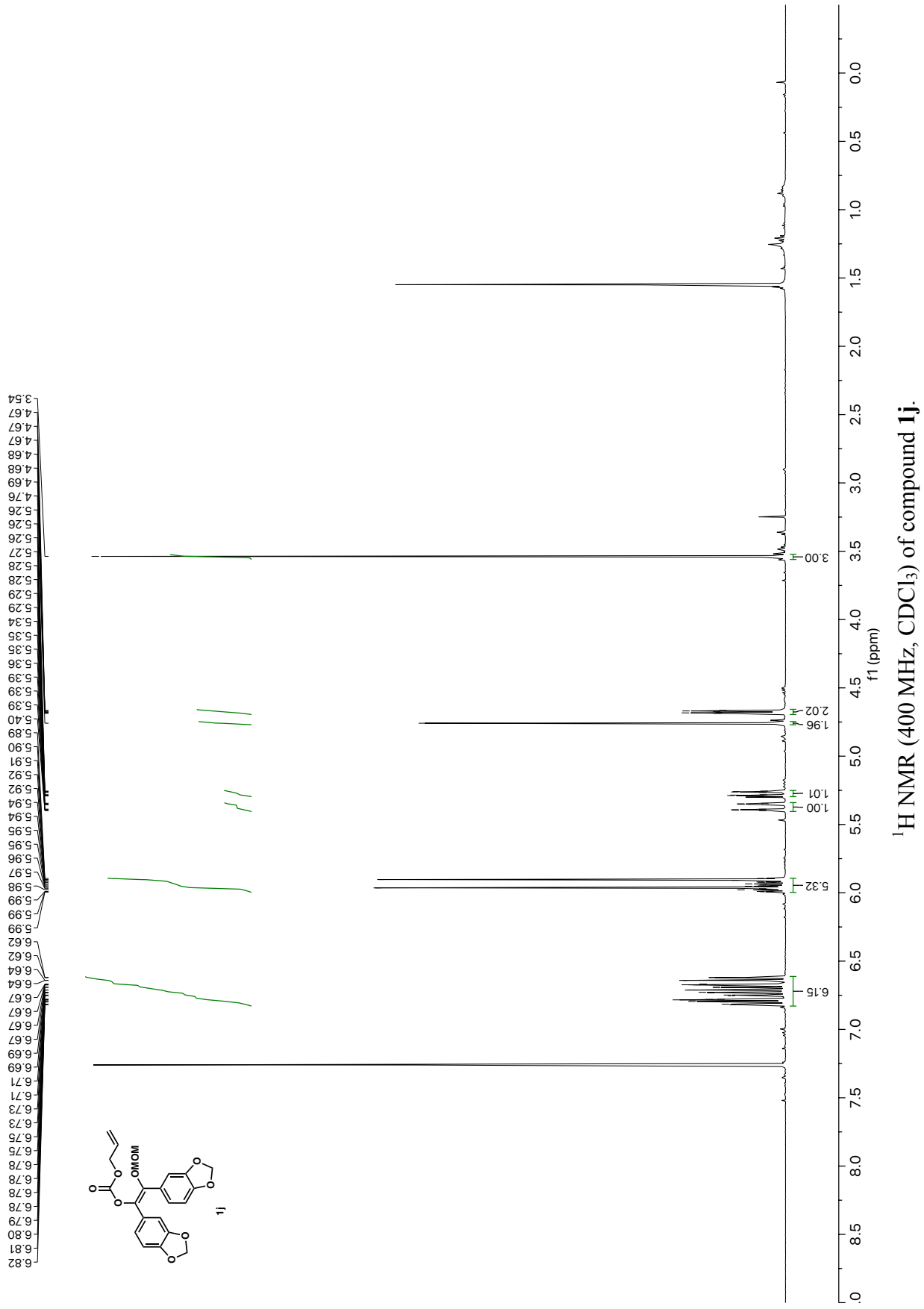
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1i**.



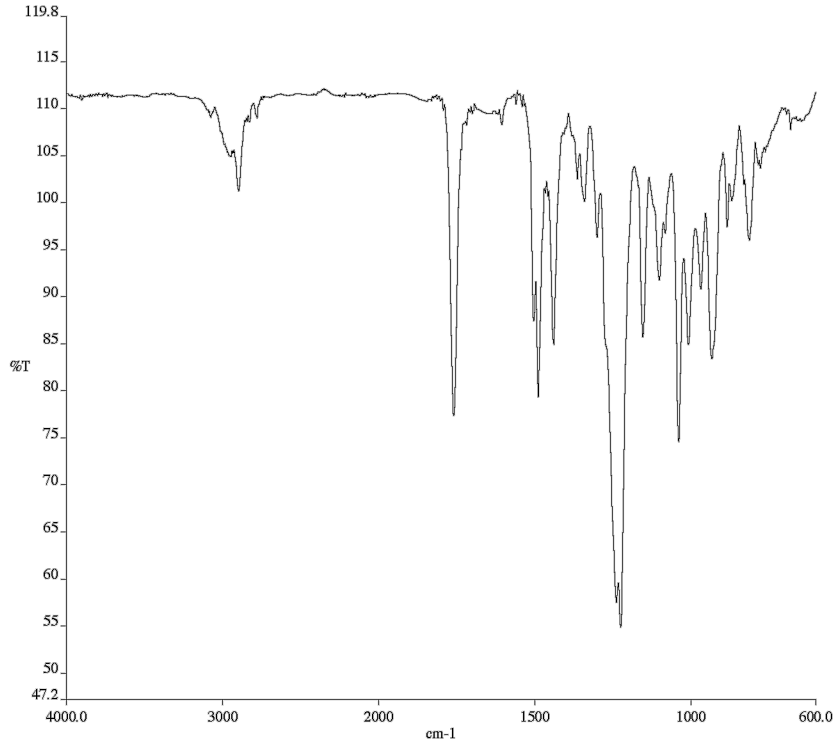
Infrared spectrum (Thin Film, NaCl) of compound **1i**.



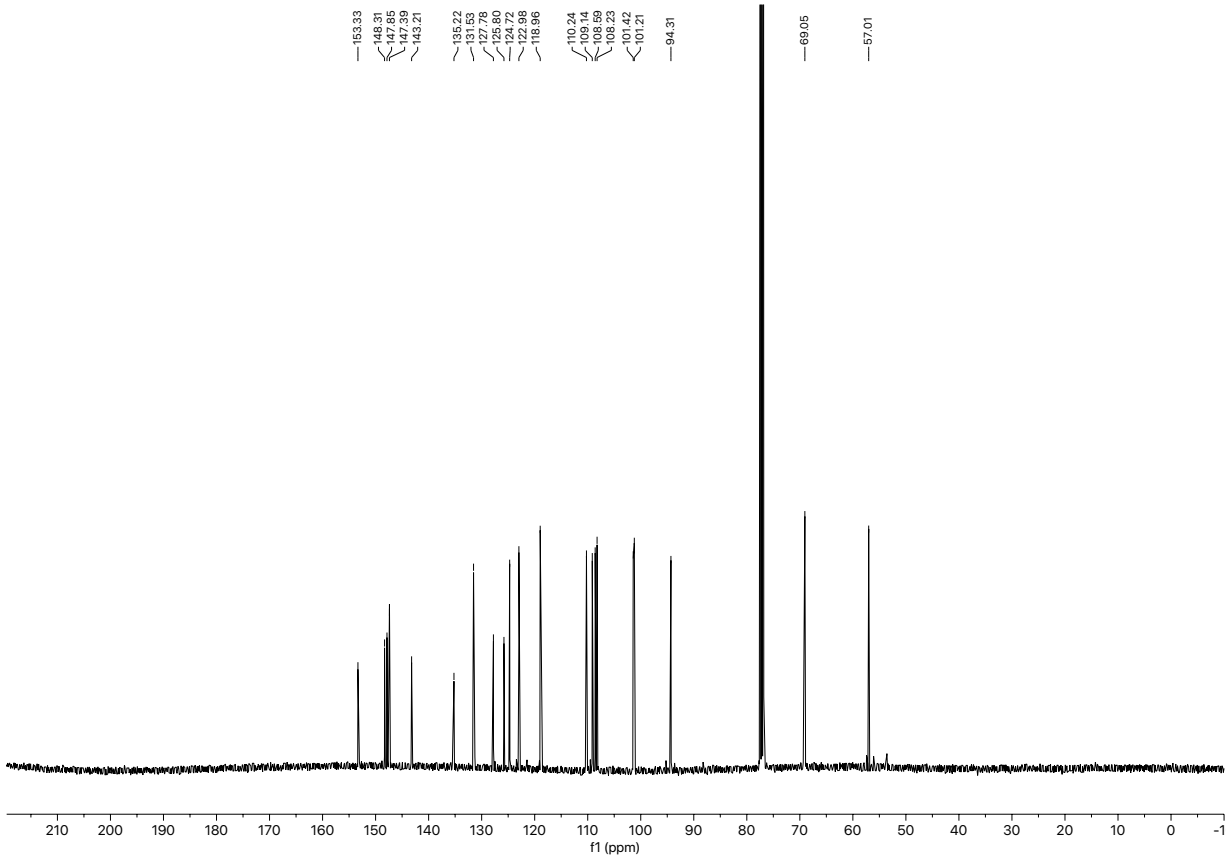
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1i**.



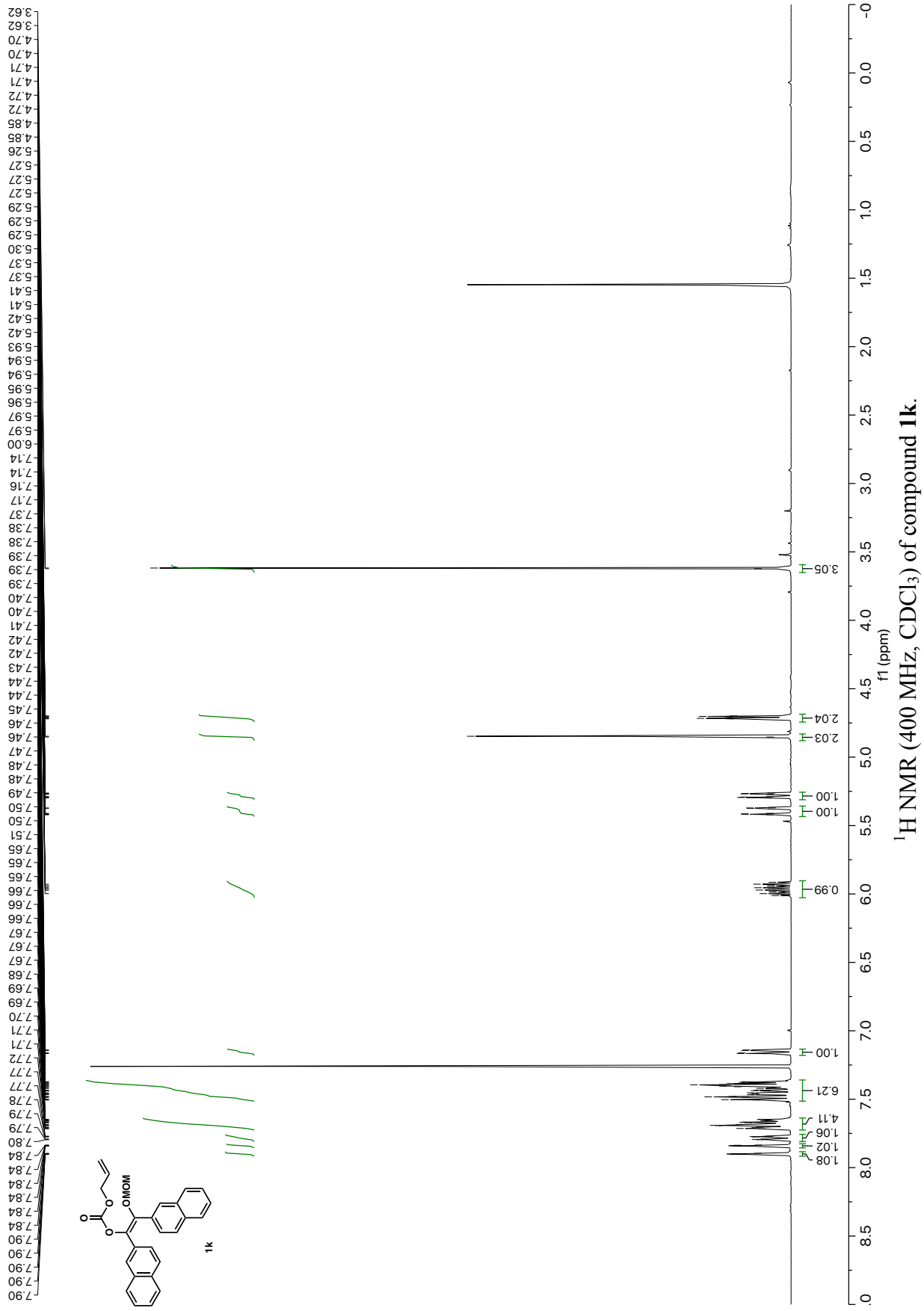
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1j**.



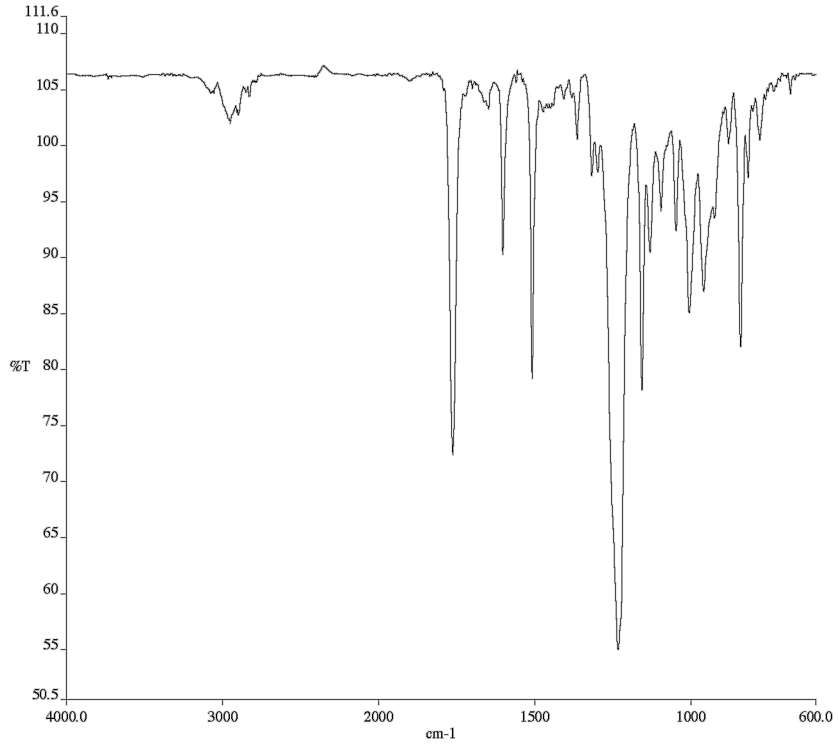
Infrared spectrum (Thin Film, NaCl) of compound **1j**.



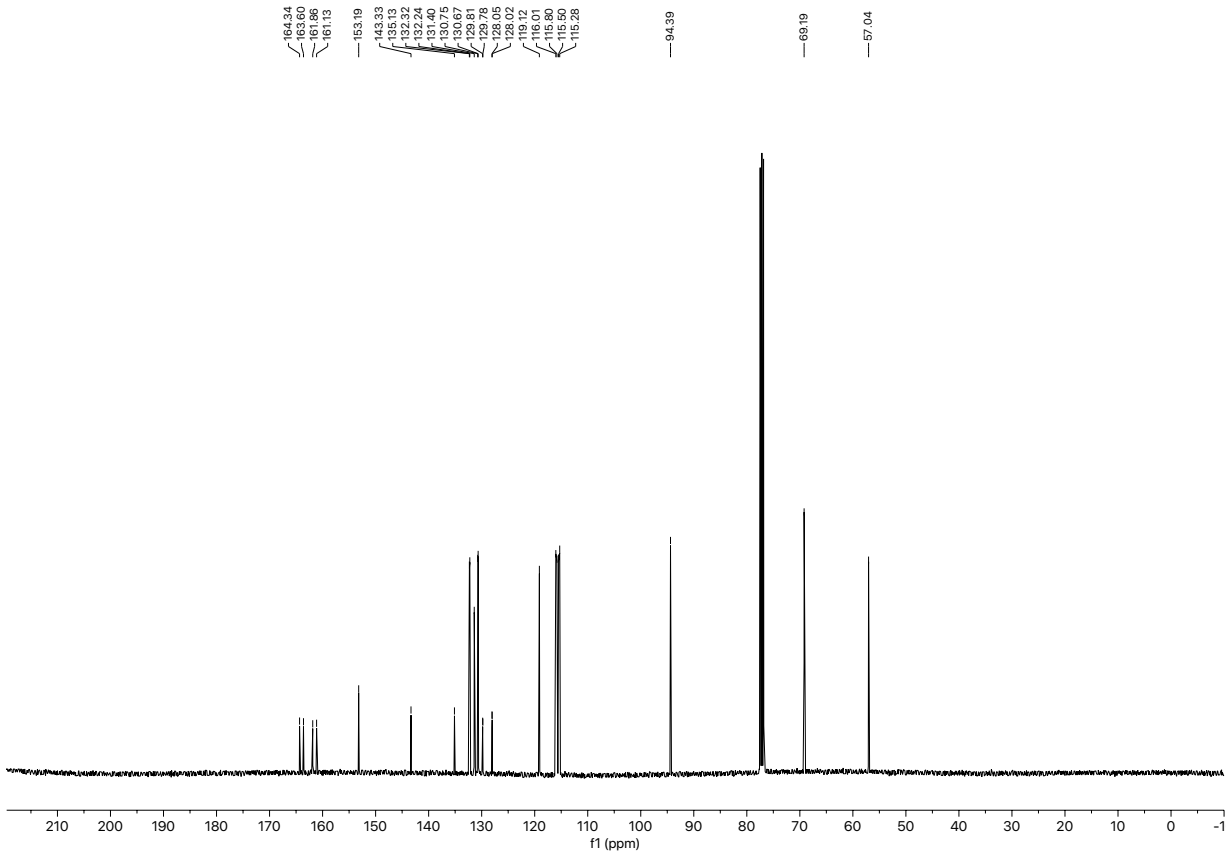
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1j**.



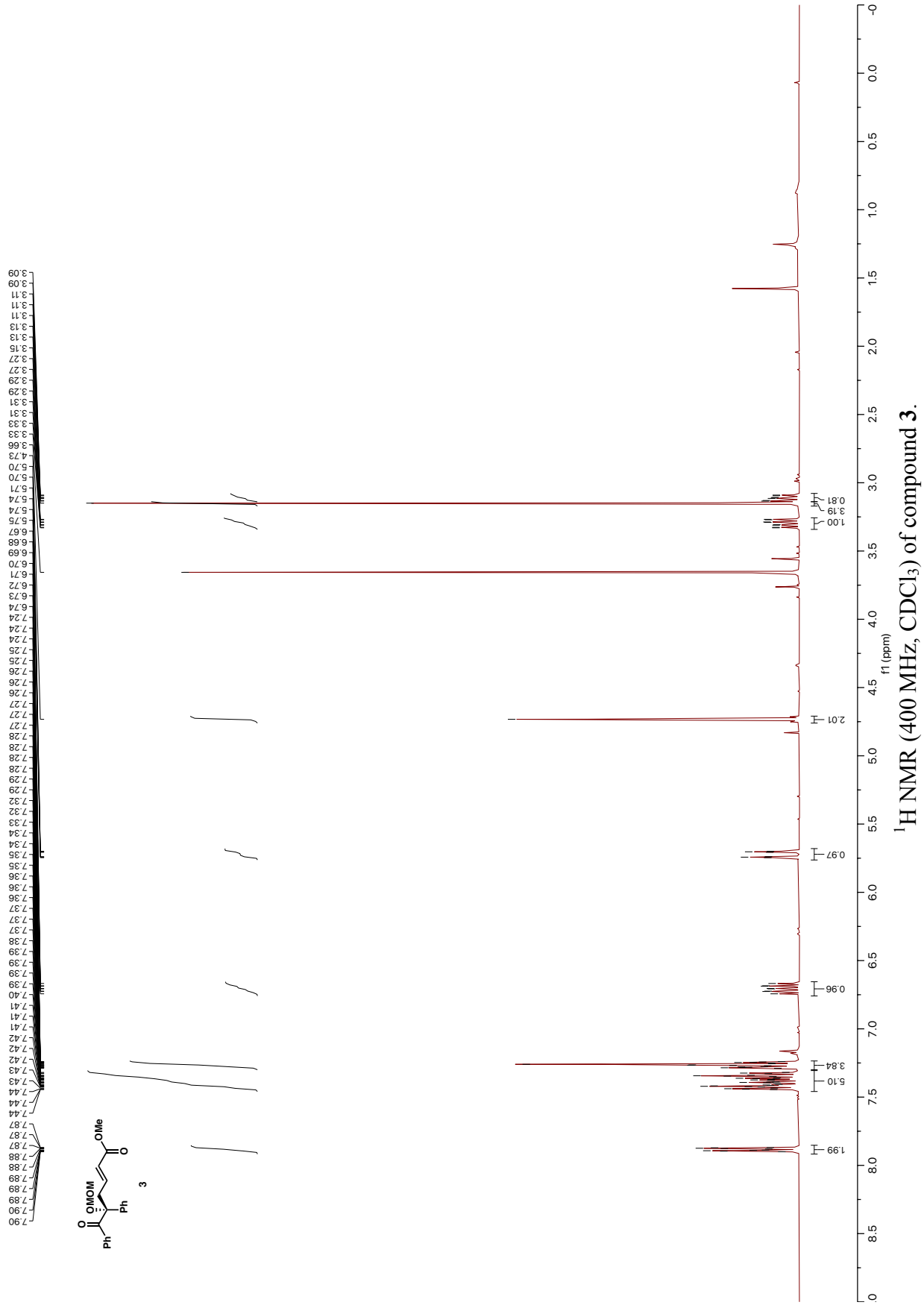
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1k**.



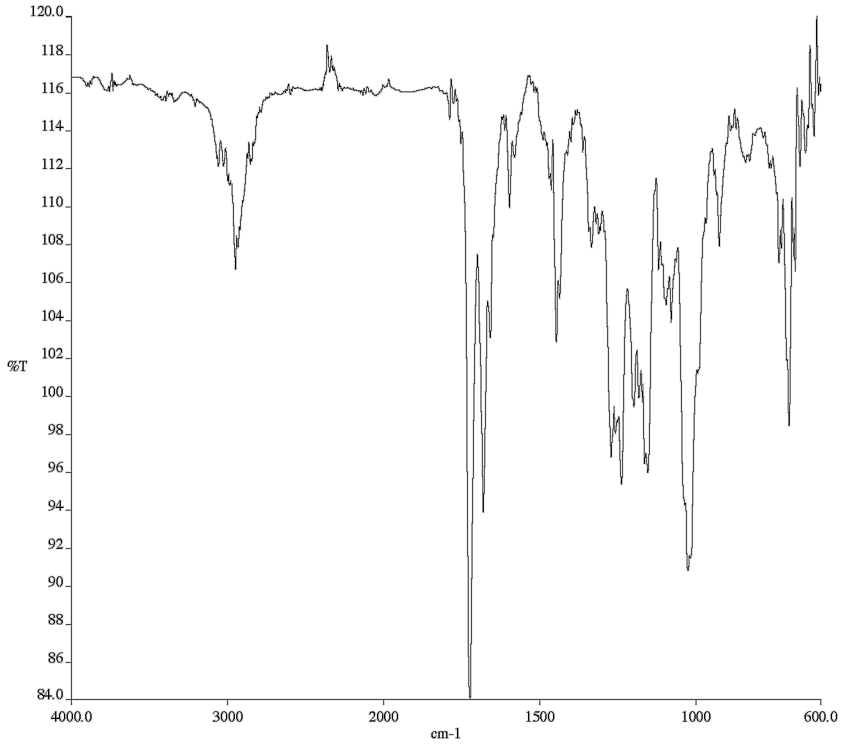
Infrared spectrum (Thin Film, NaCl) of compound **1k**.



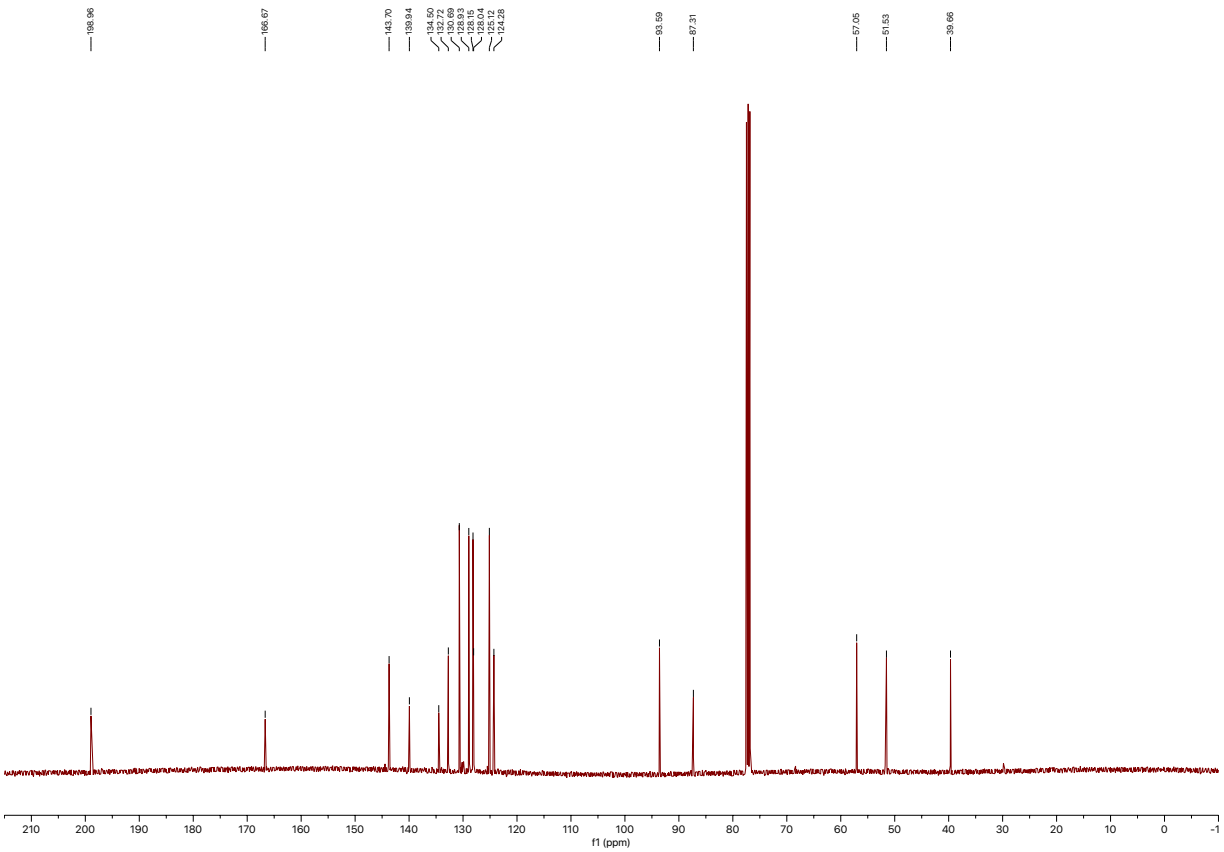
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1k**.



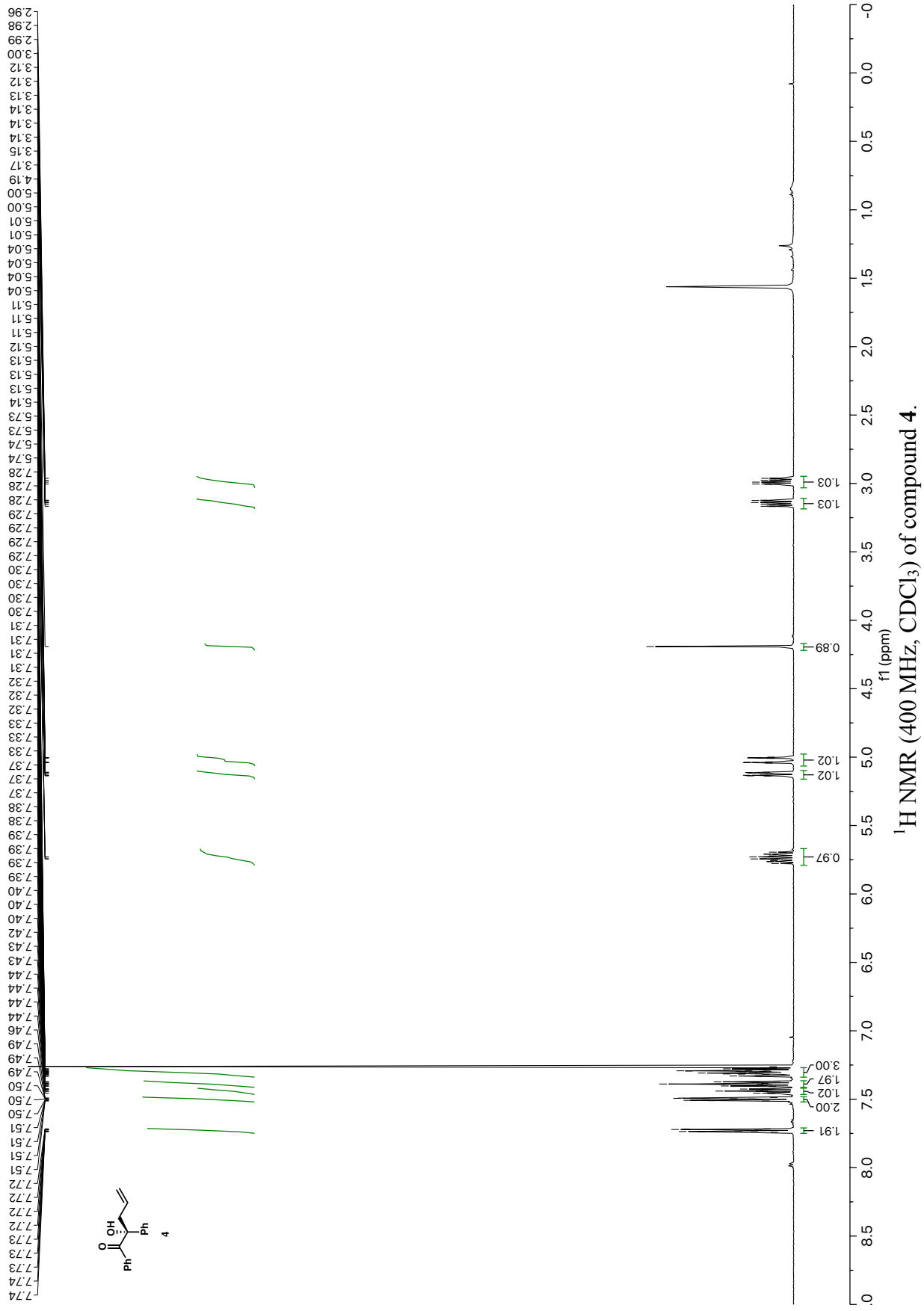
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3**.



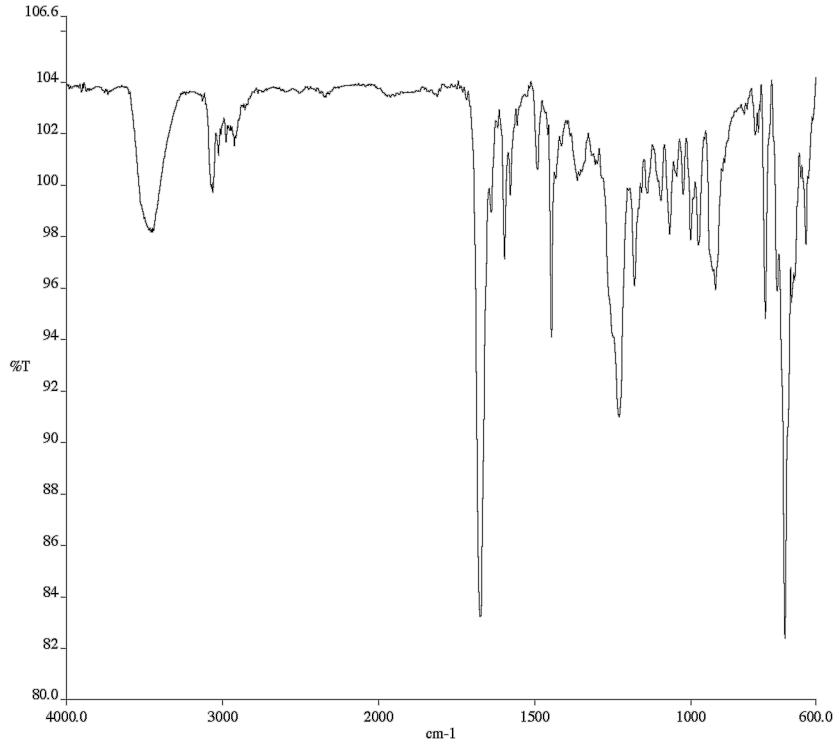
Infrared spectrum (Thin Film, NaCl) of compound **3**.



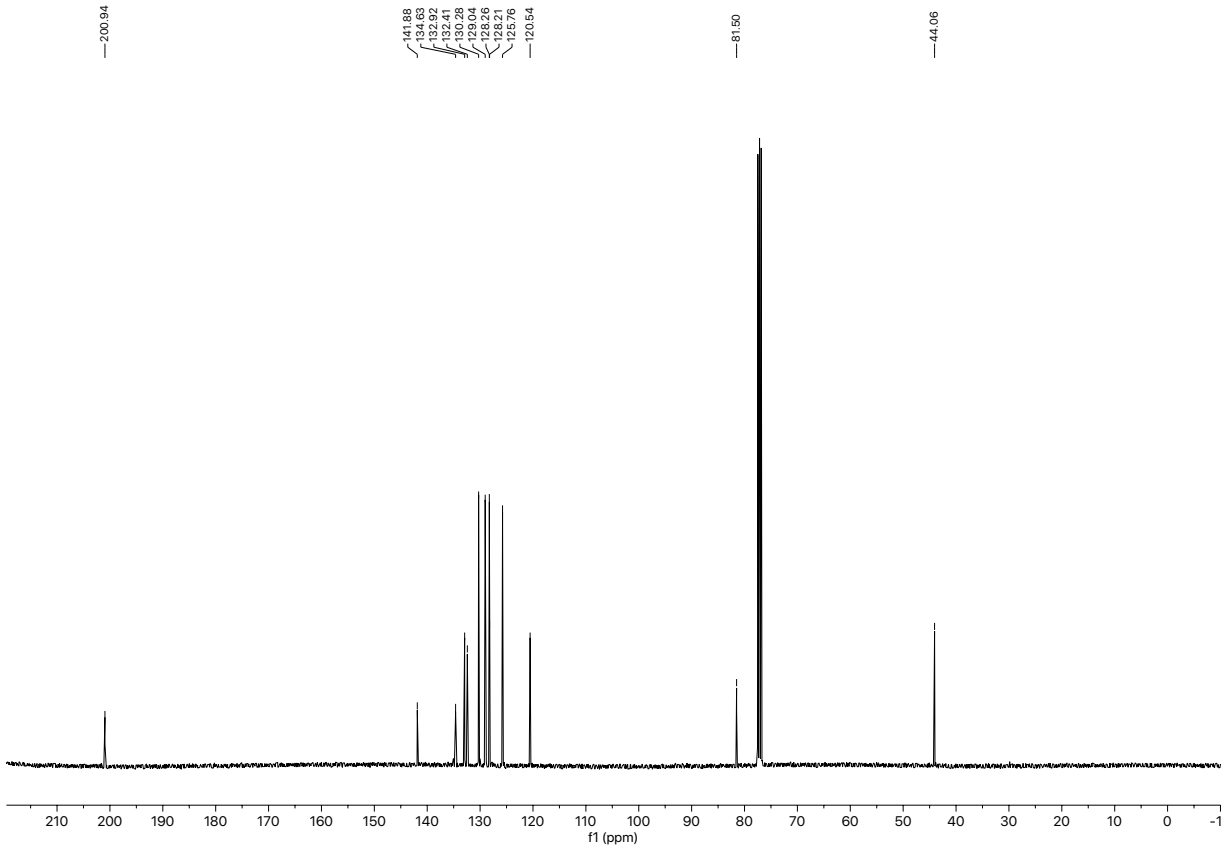
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3**.



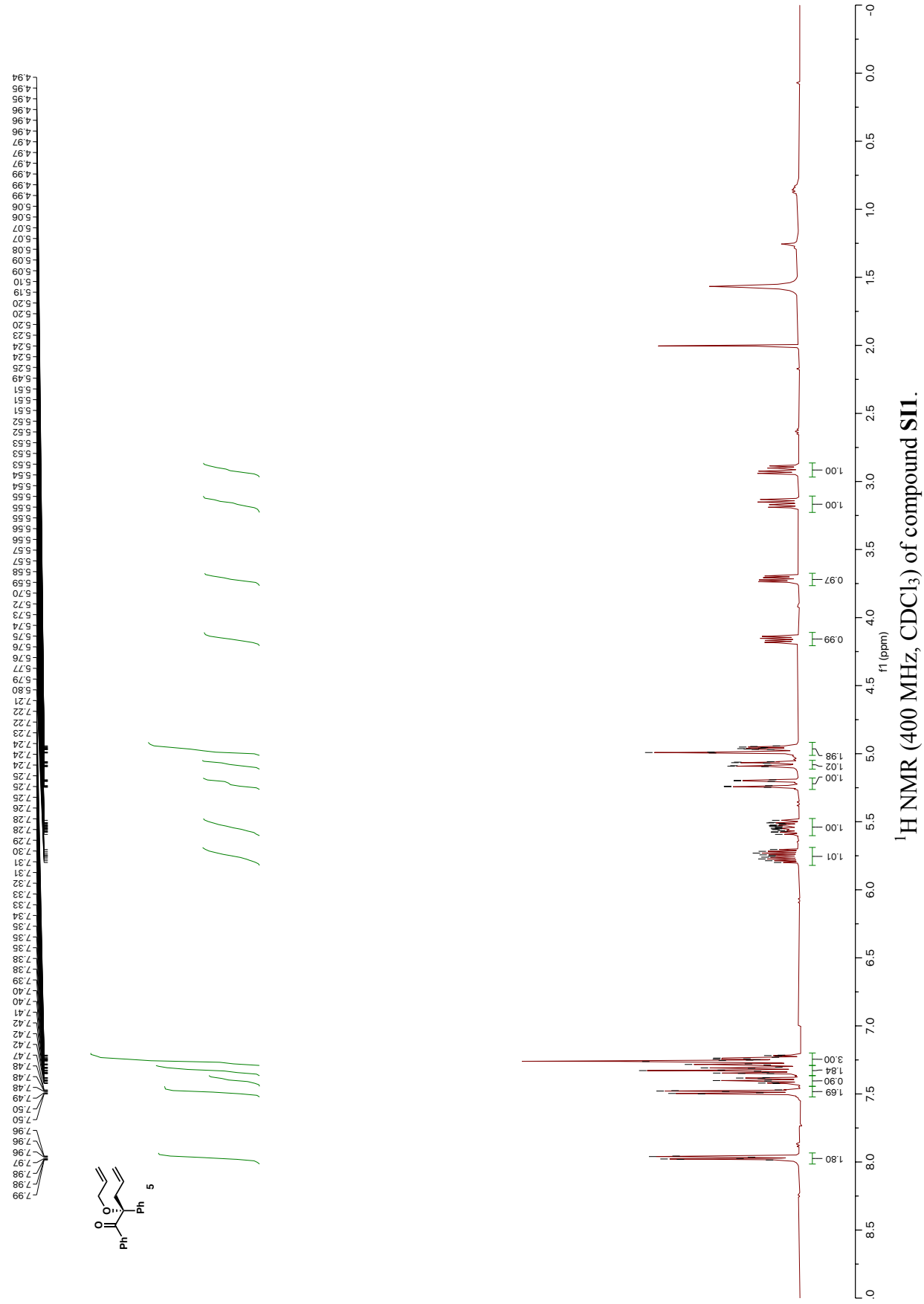
^{1}H NMR (400 MHz, $CDCl_3$) of compound **4**.



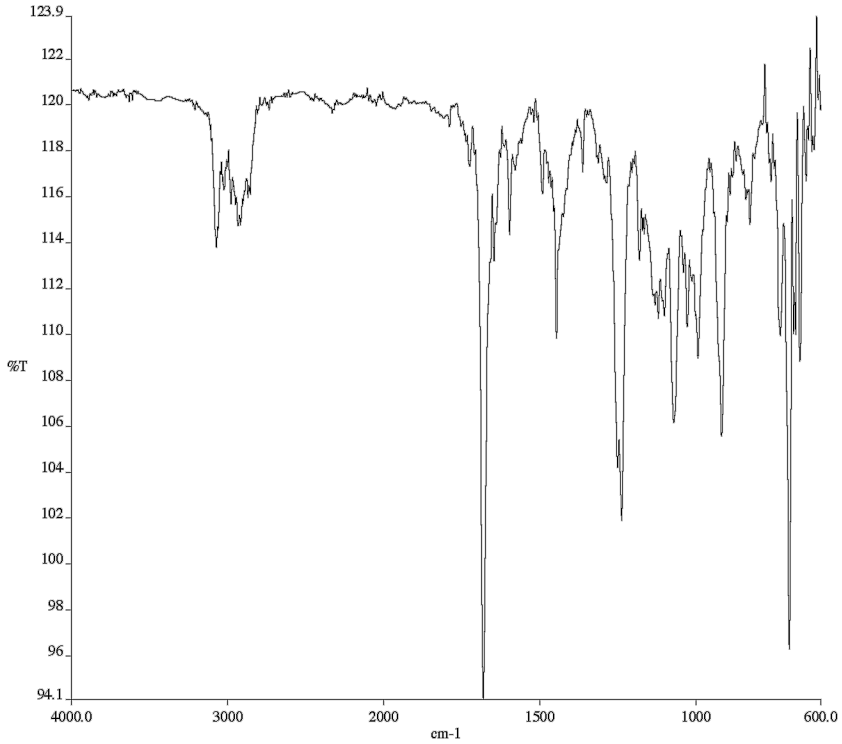
Infrared spectrum (Thin Film, NaCl) of compound **4**.



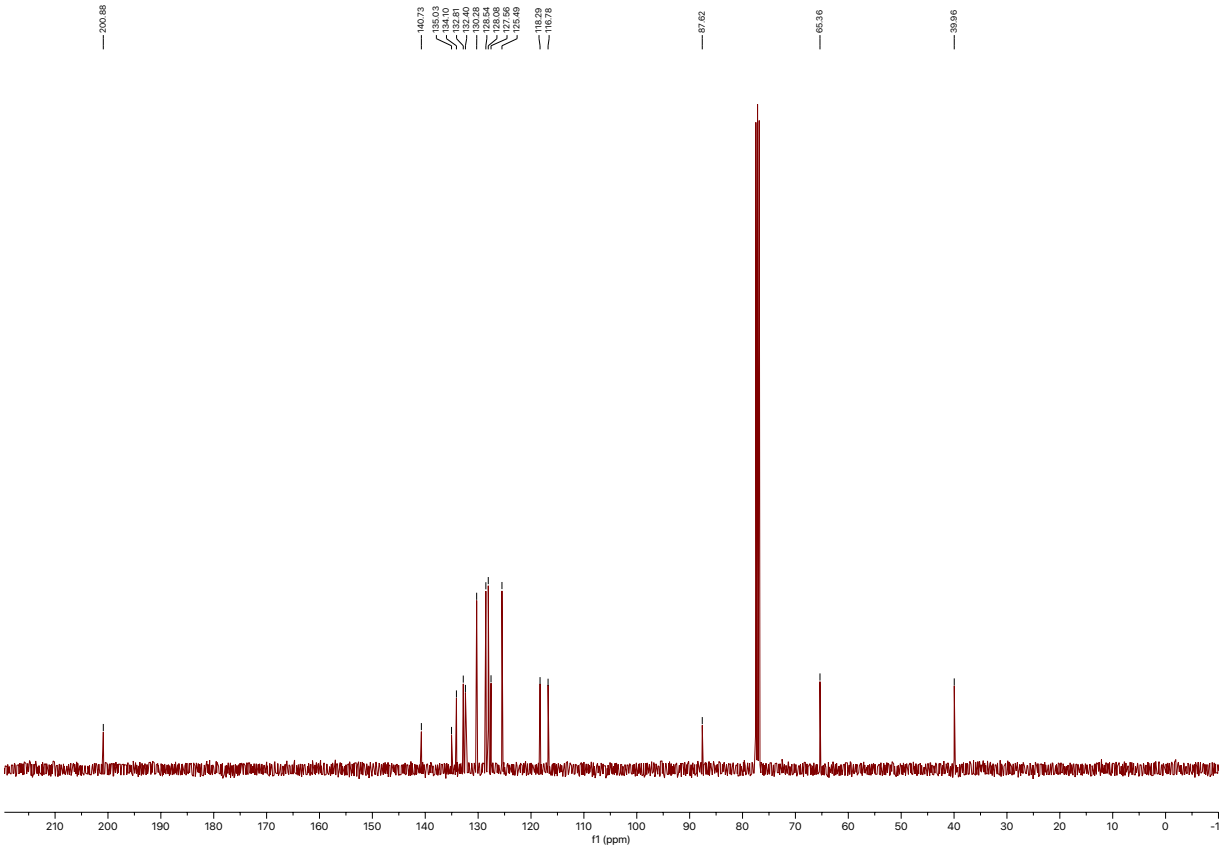
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4**.



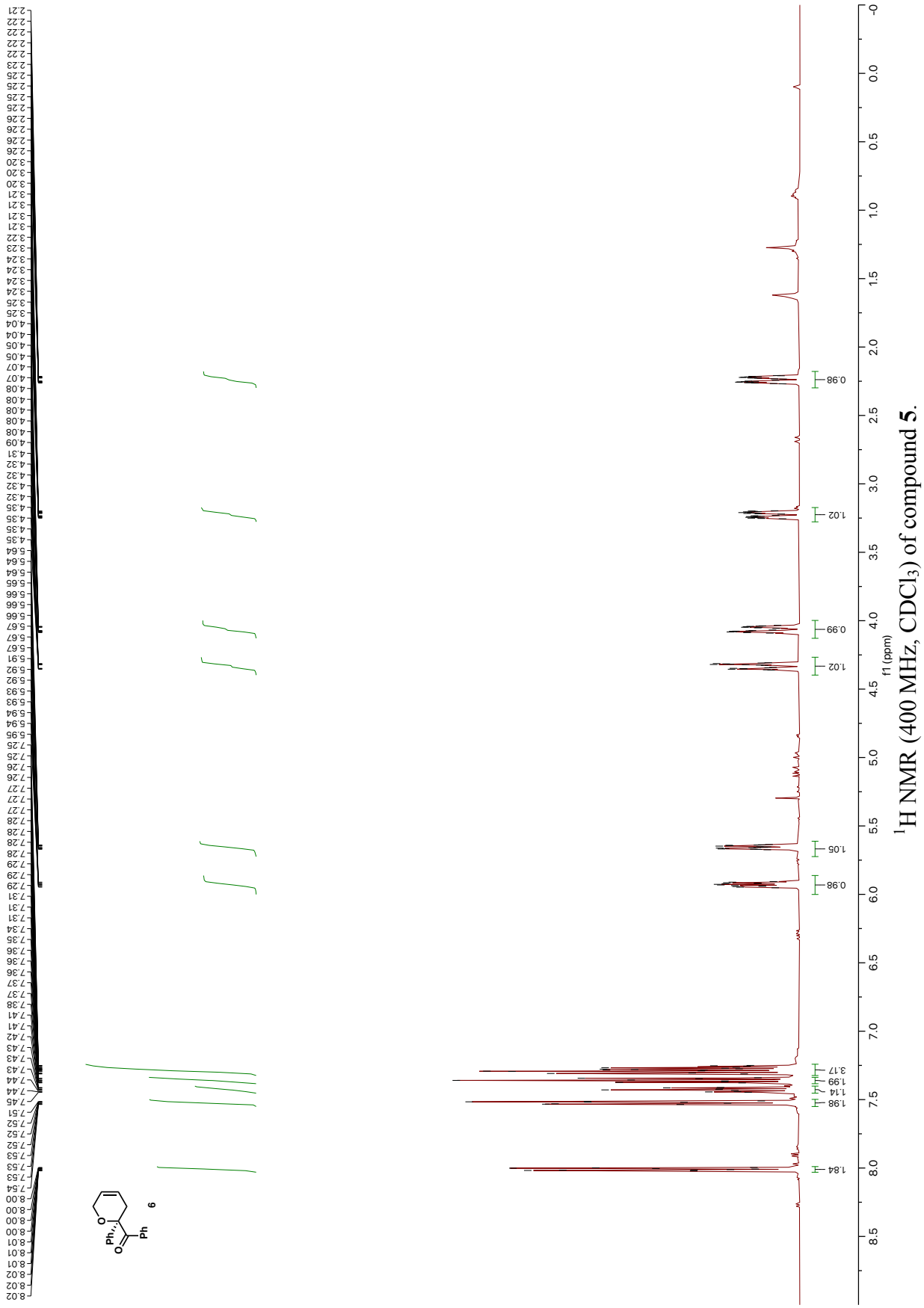
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI1**.



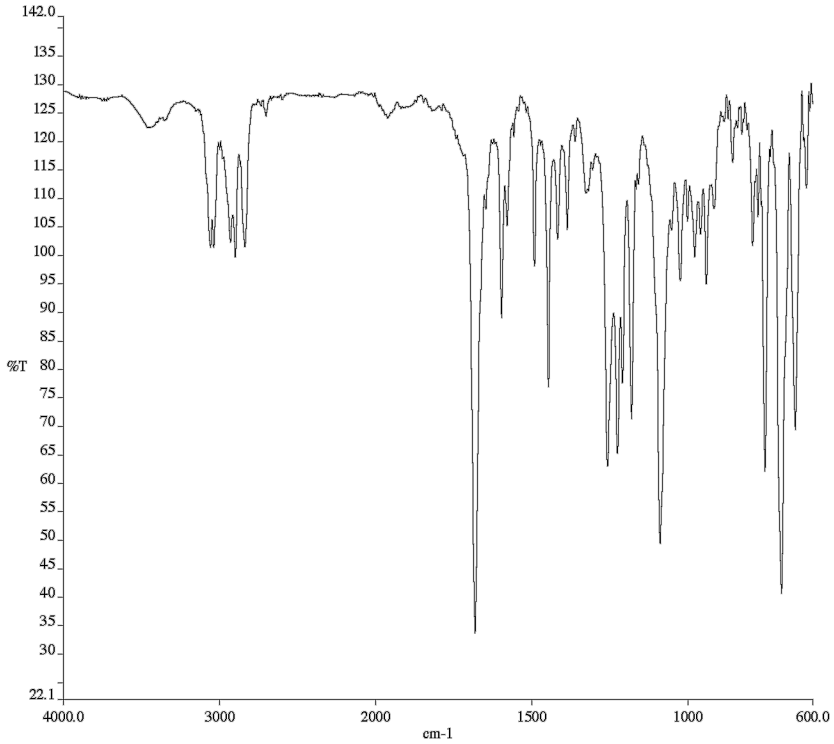
Infrared spectrum (Thin Film, NaCl) of compound **SI1**.



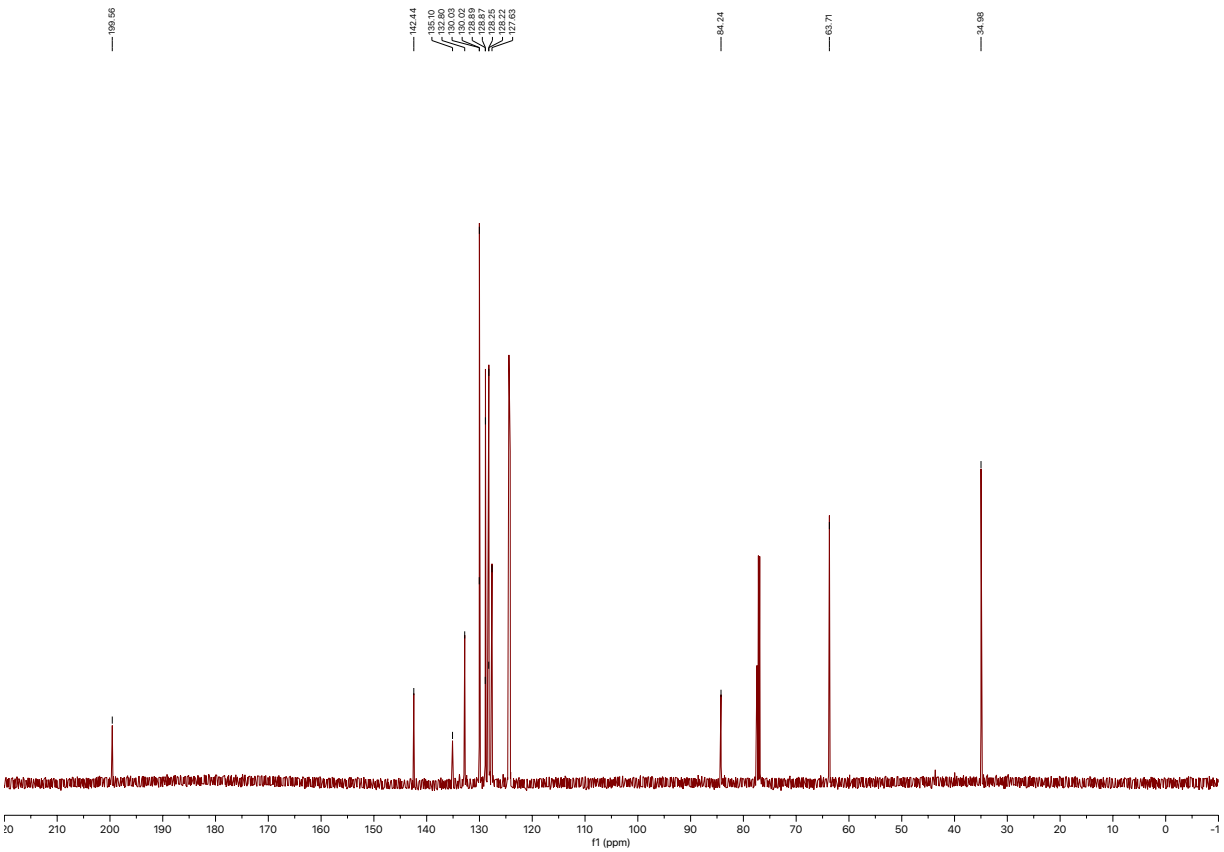
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI1**.



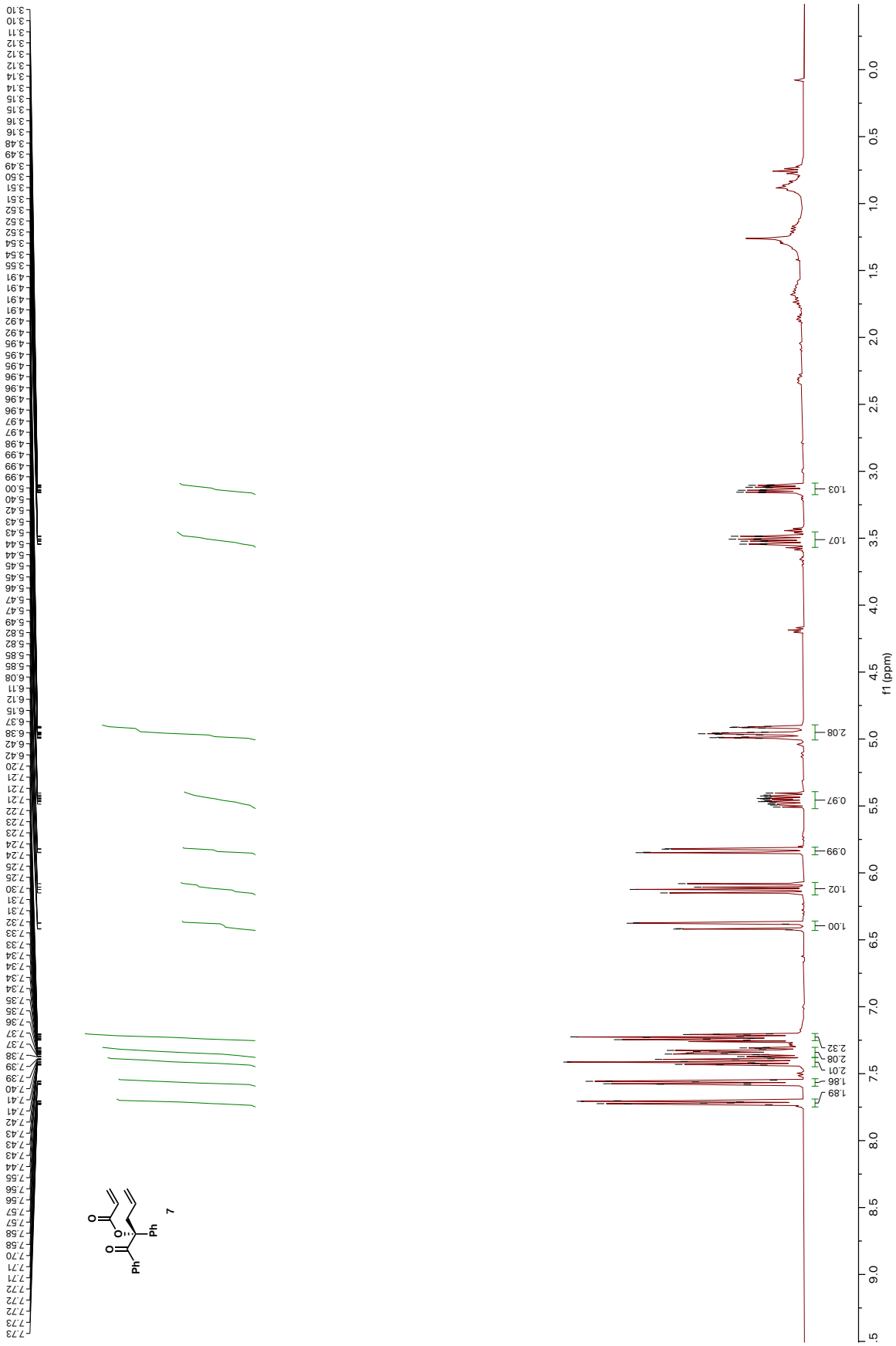
^{1}H NMR (400 MHz, $CDCl_3$) of compound **5**.



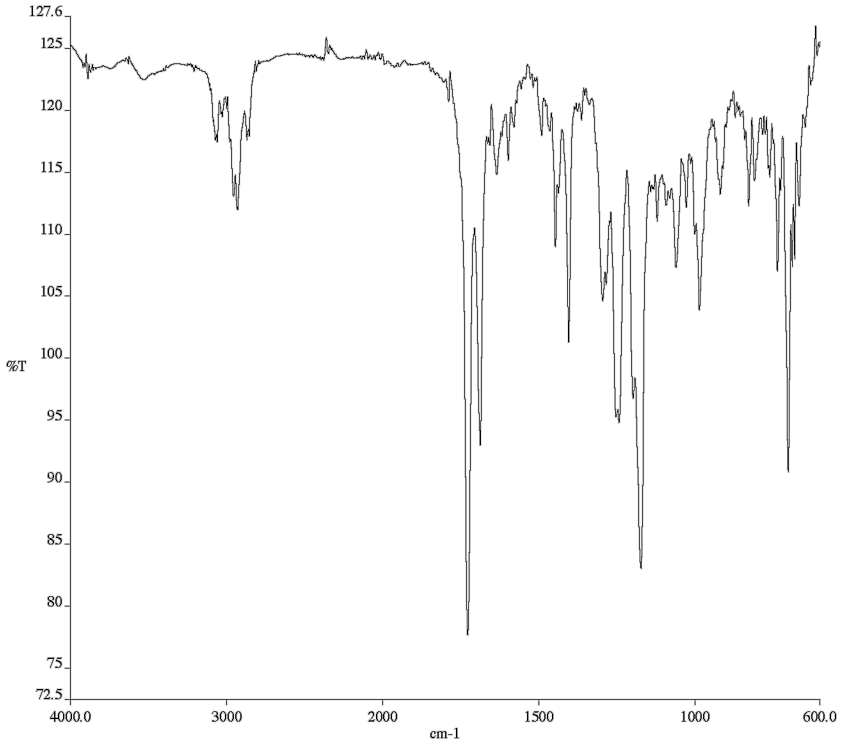
Infrared spectrum (Thin Film, NaCl) of compound **5**.



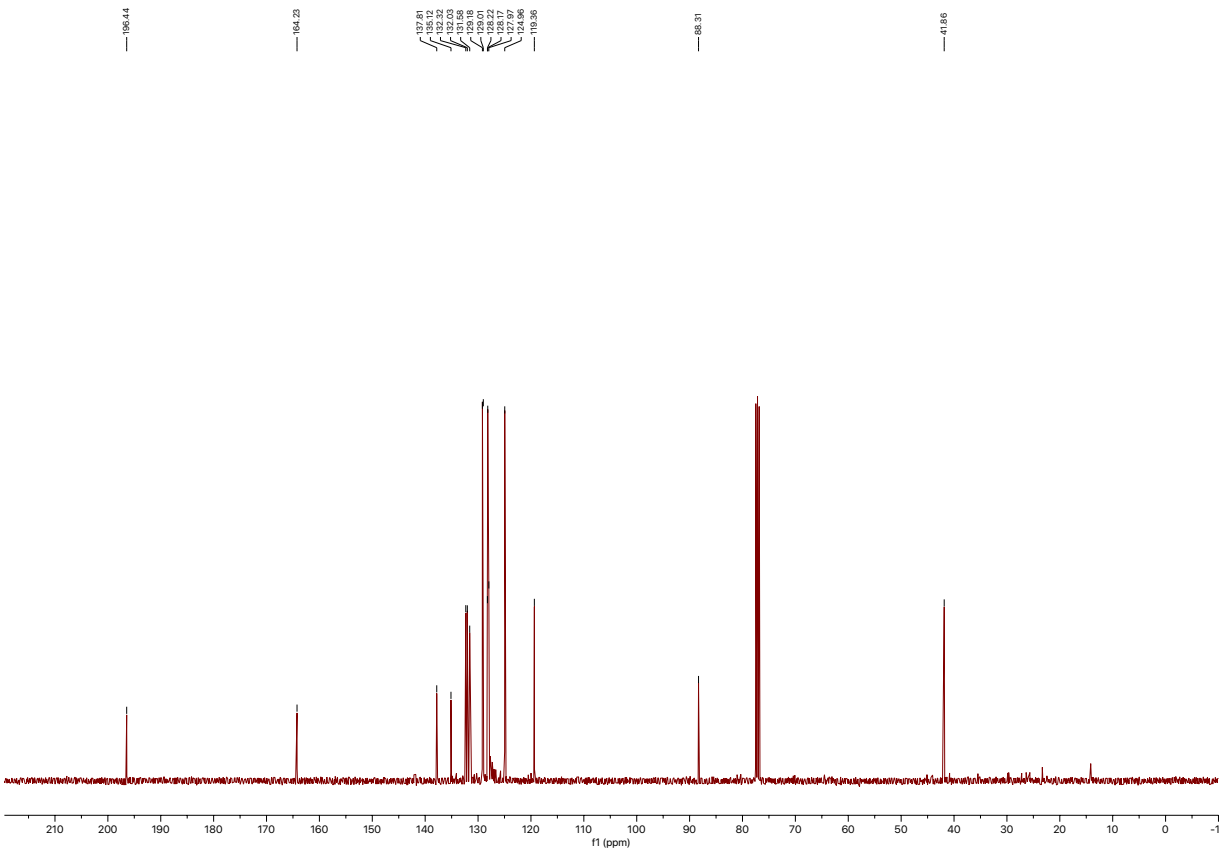
^{13}C NMR (100 MHz, $CDCl_3$) of compound **5**.



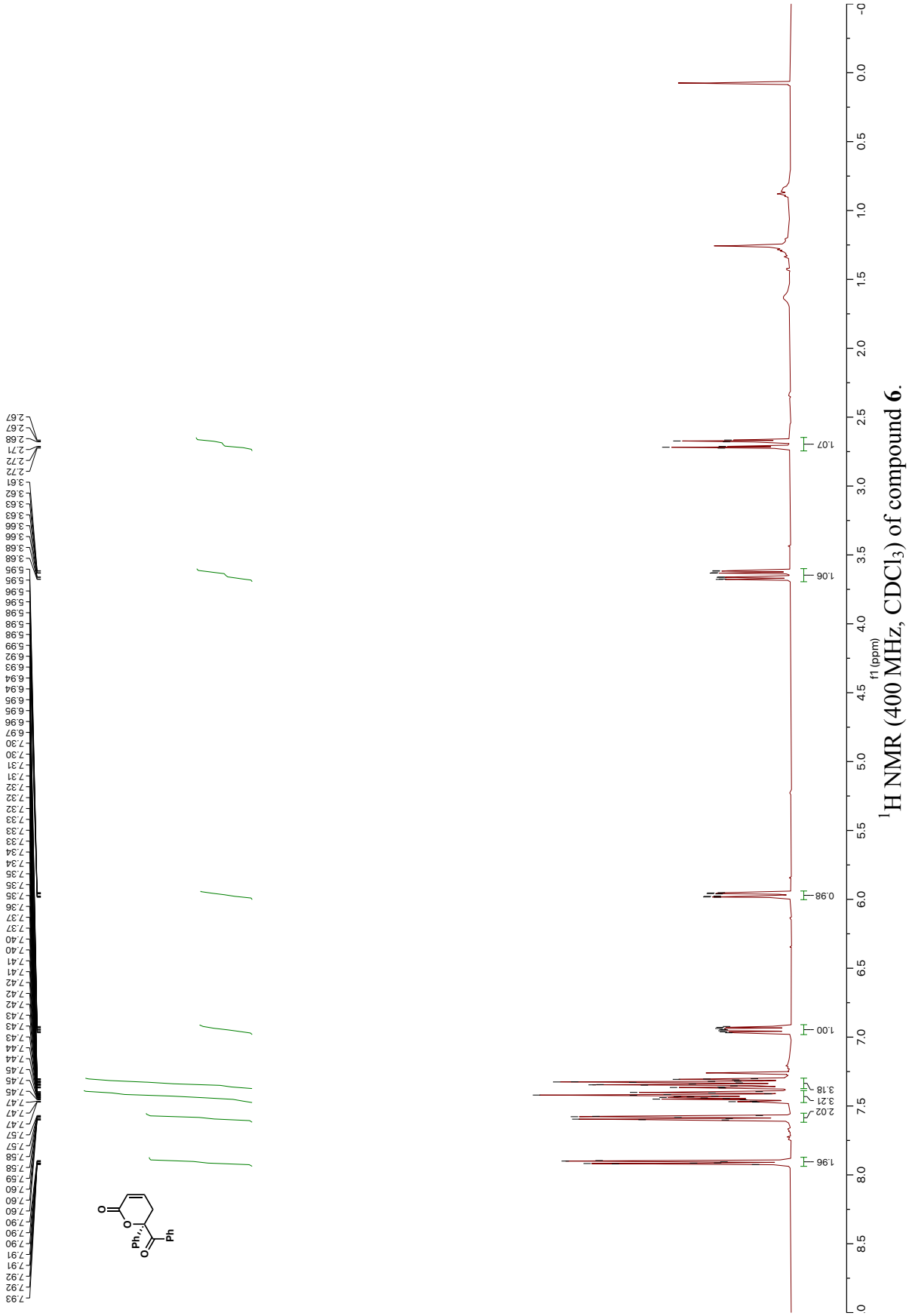
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI2**.



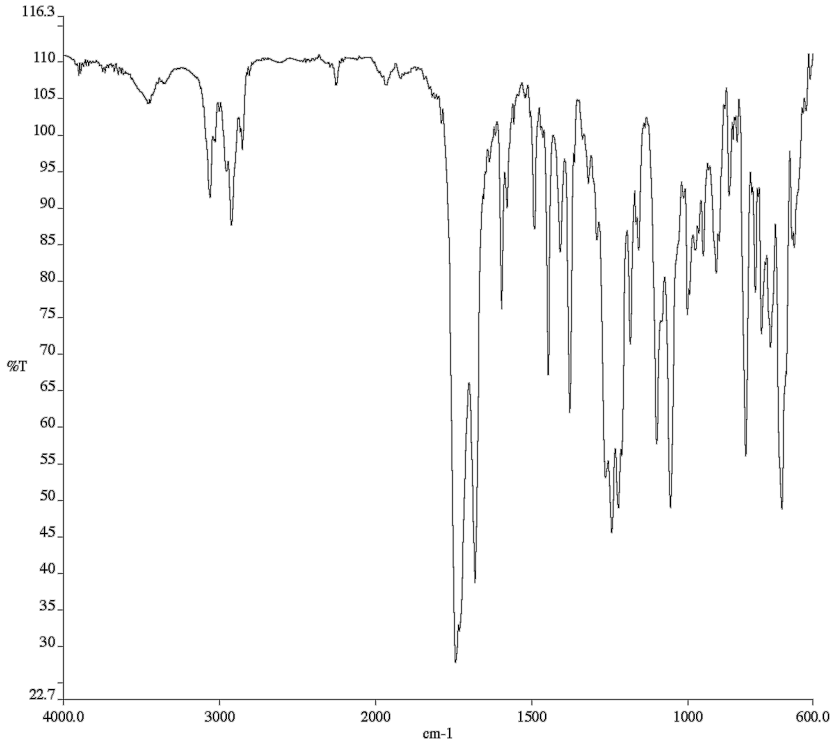
Infrared spectrum (Thin Film, NaCl) of compound **SI2**.



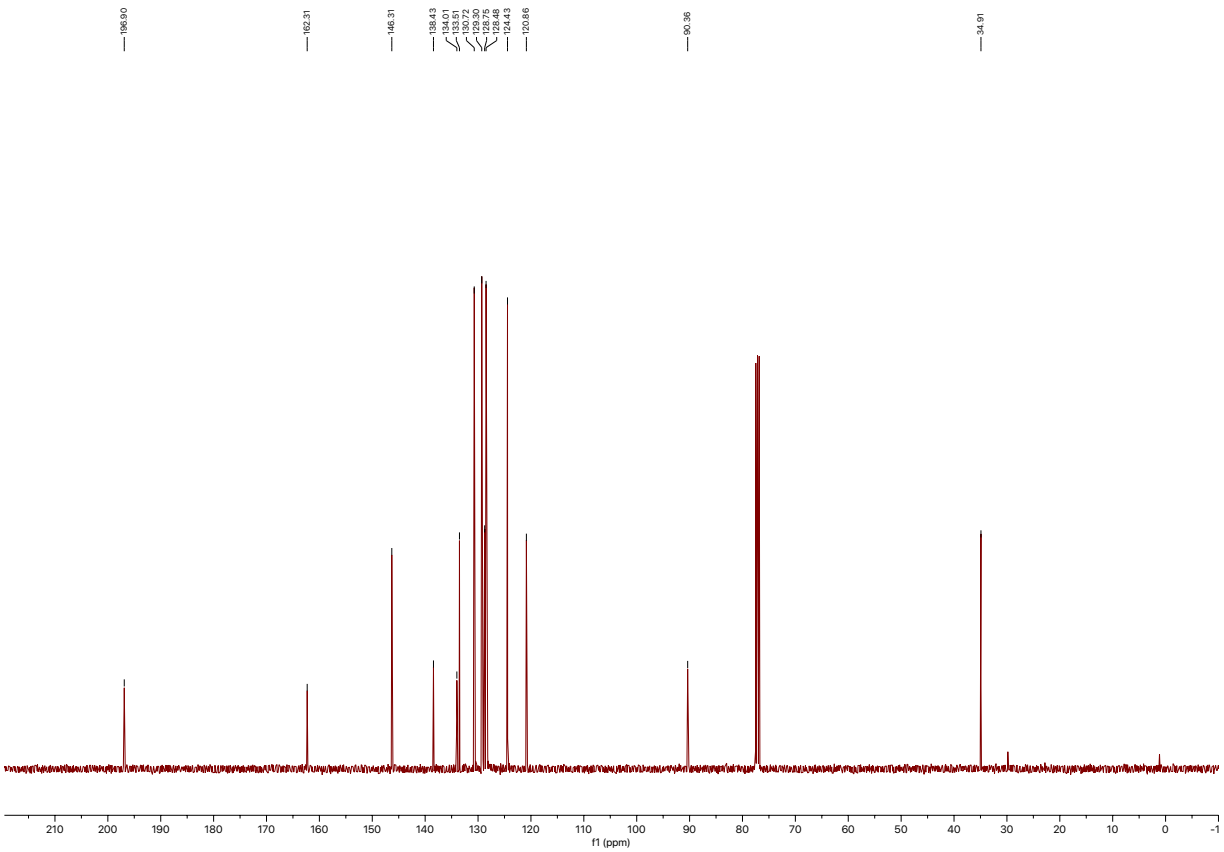
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI2**.



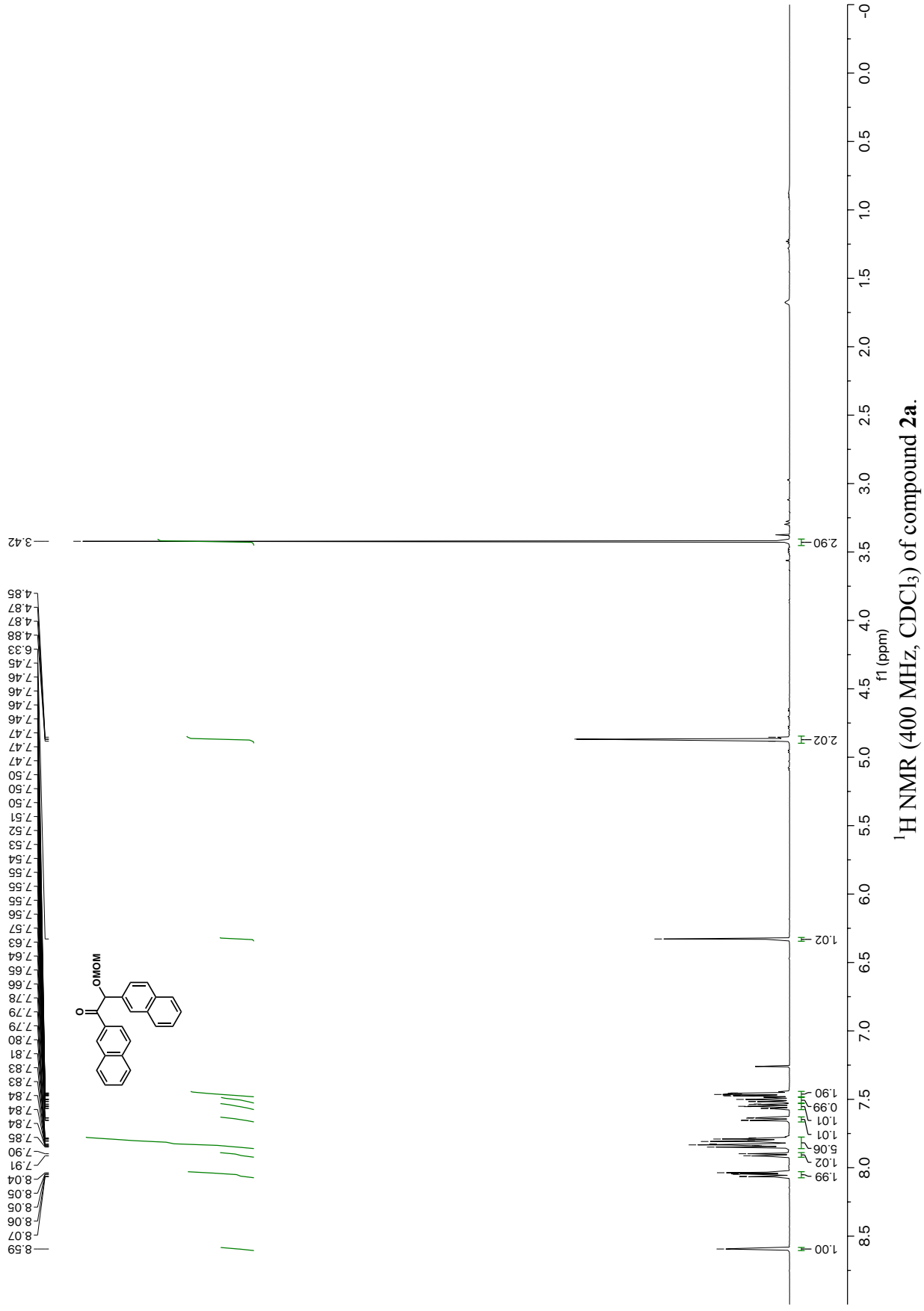
^{1}H NMR (400 MHz, $CDCl_3$) of compound **6**.



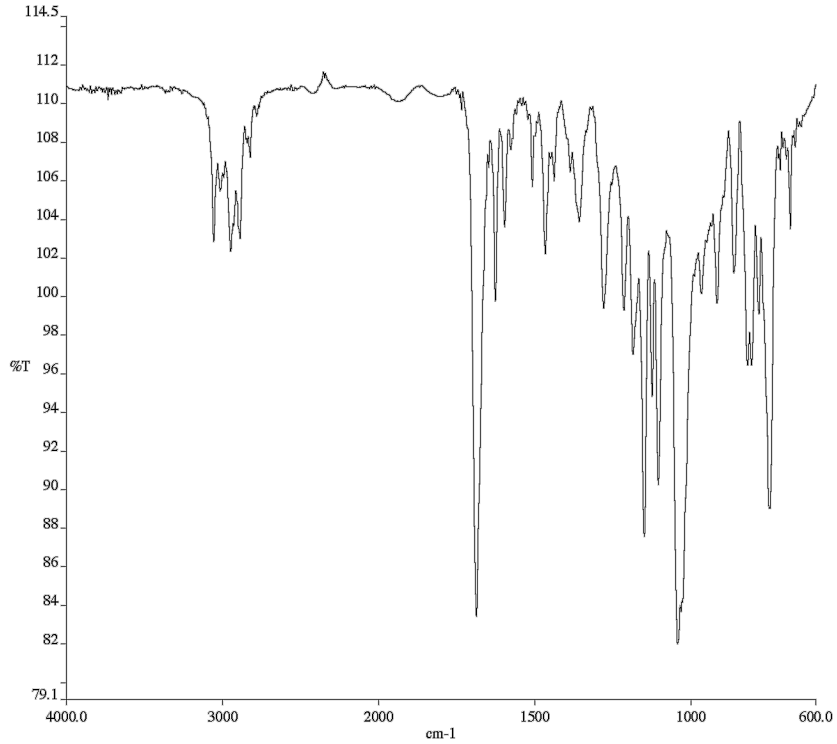
Infrared spectrum (Thin Film, NaCl) of compound **6**.



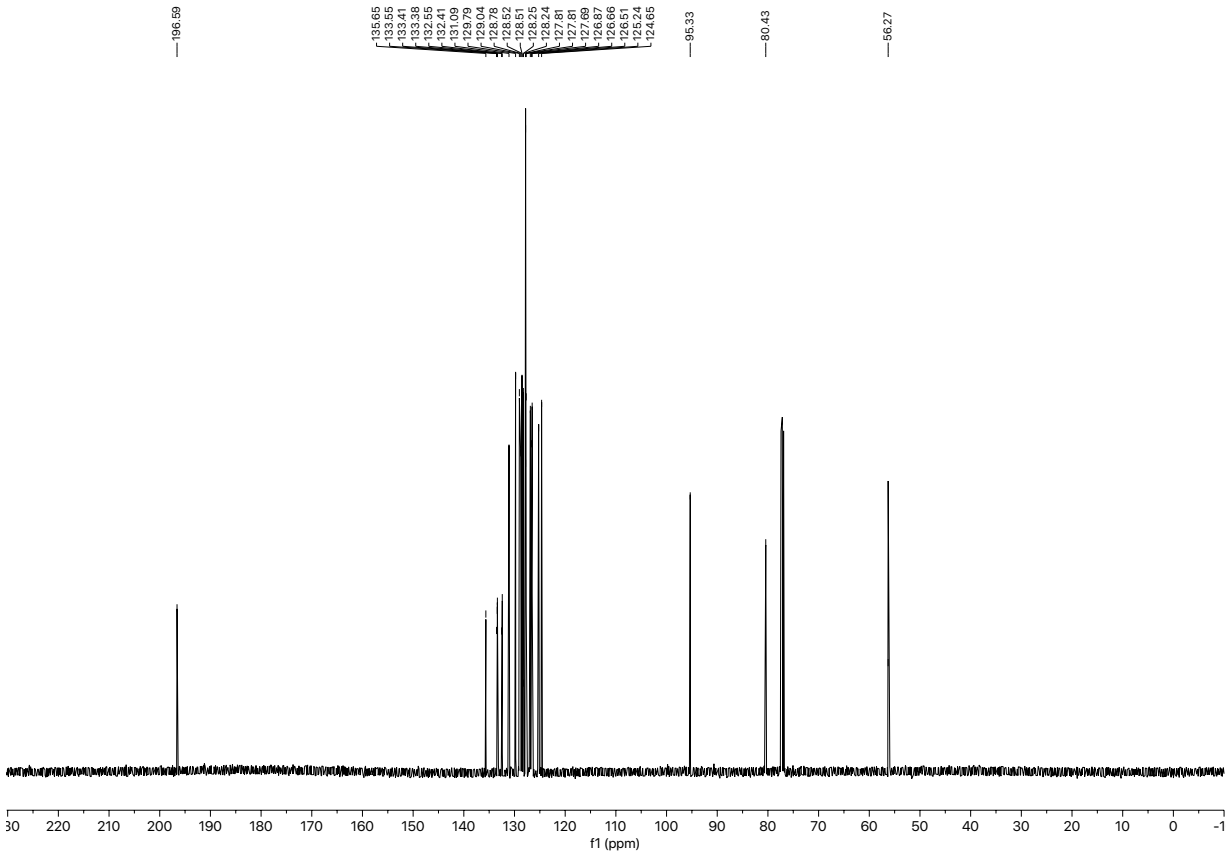
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6**.



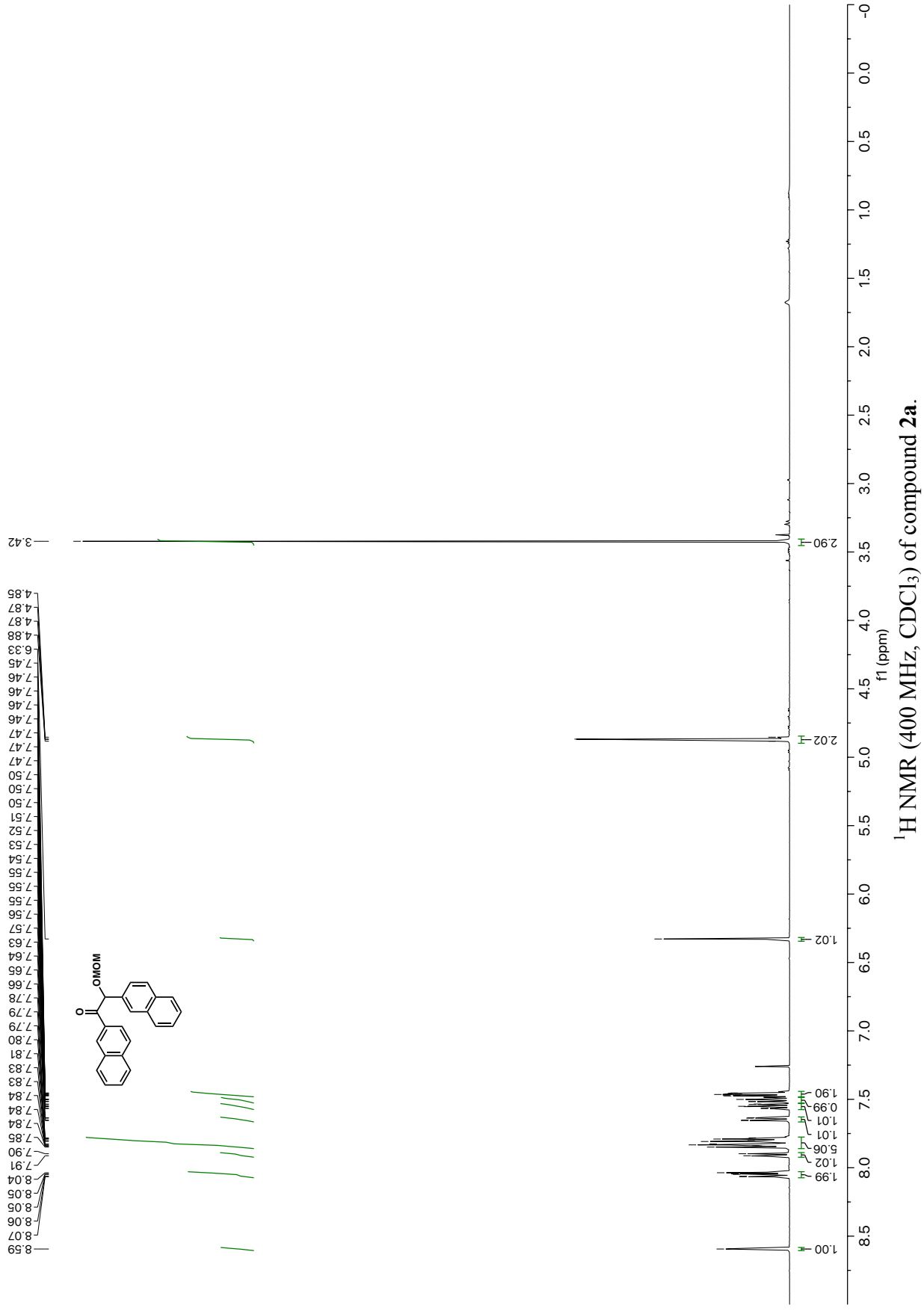
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



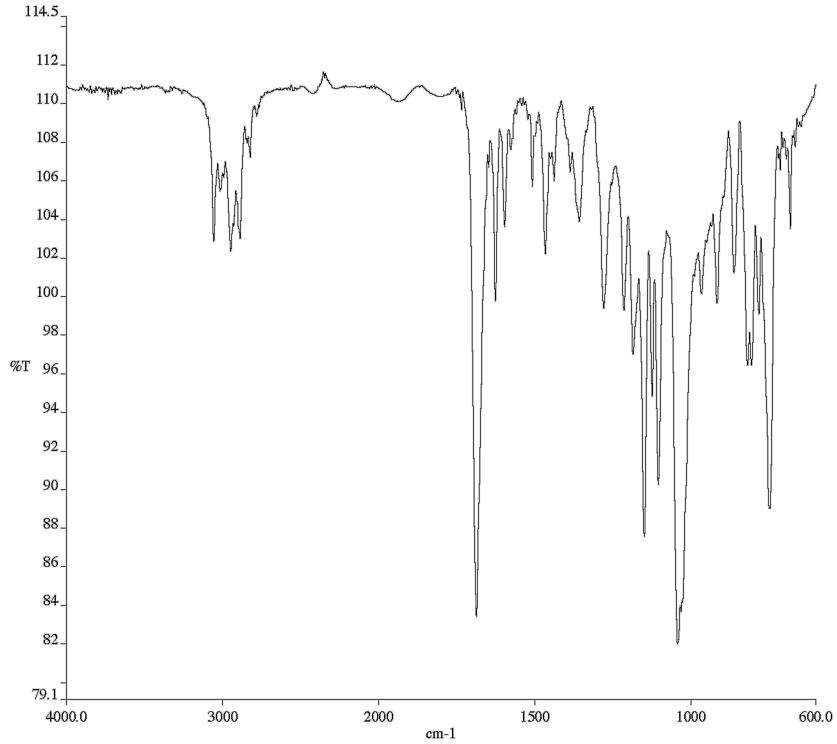
Infrared spectrum (Thin Film, NaCl) of compound **2a**.



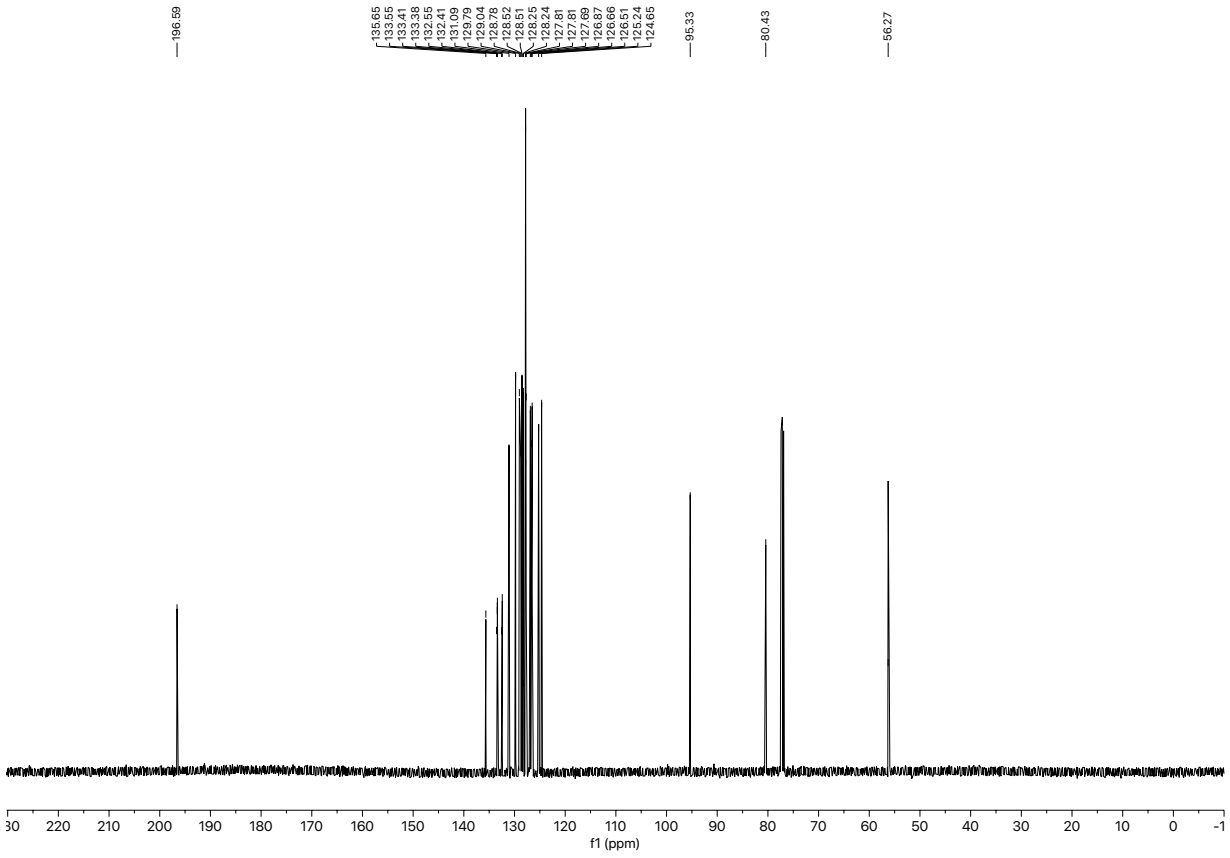
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.



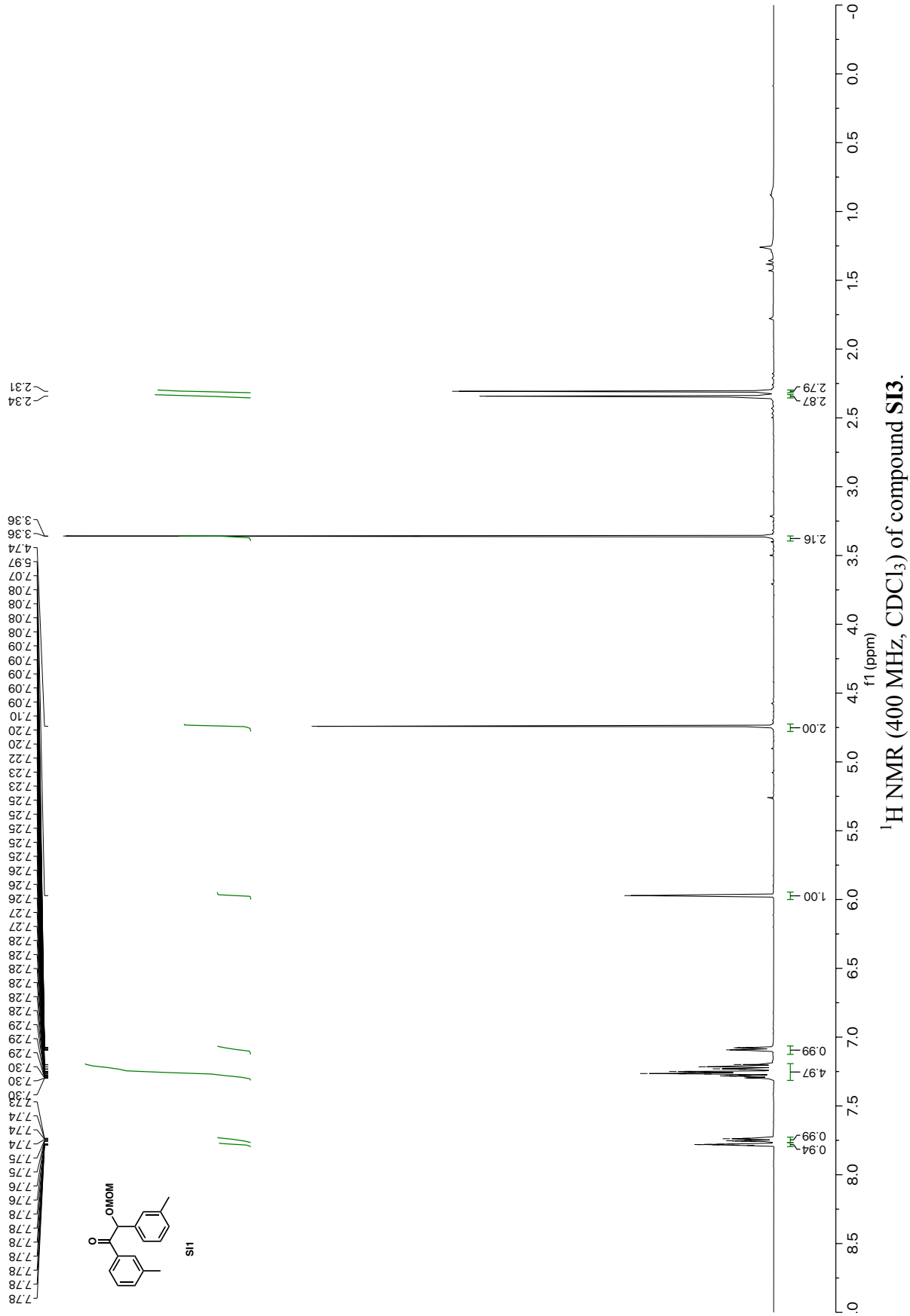
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



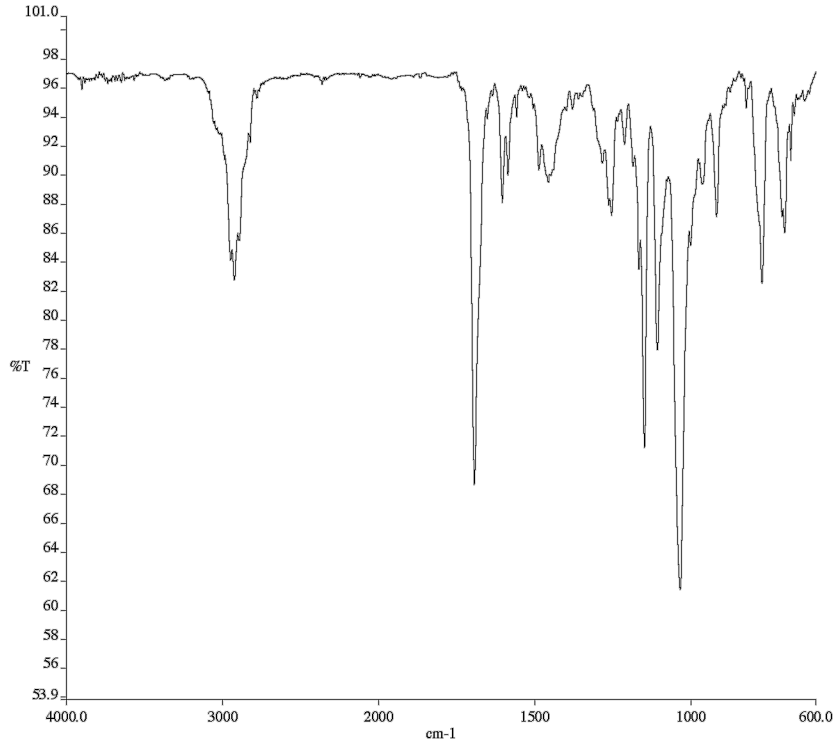
Infrared spectrum (Thin Film, NaCl) of compound **2a**.



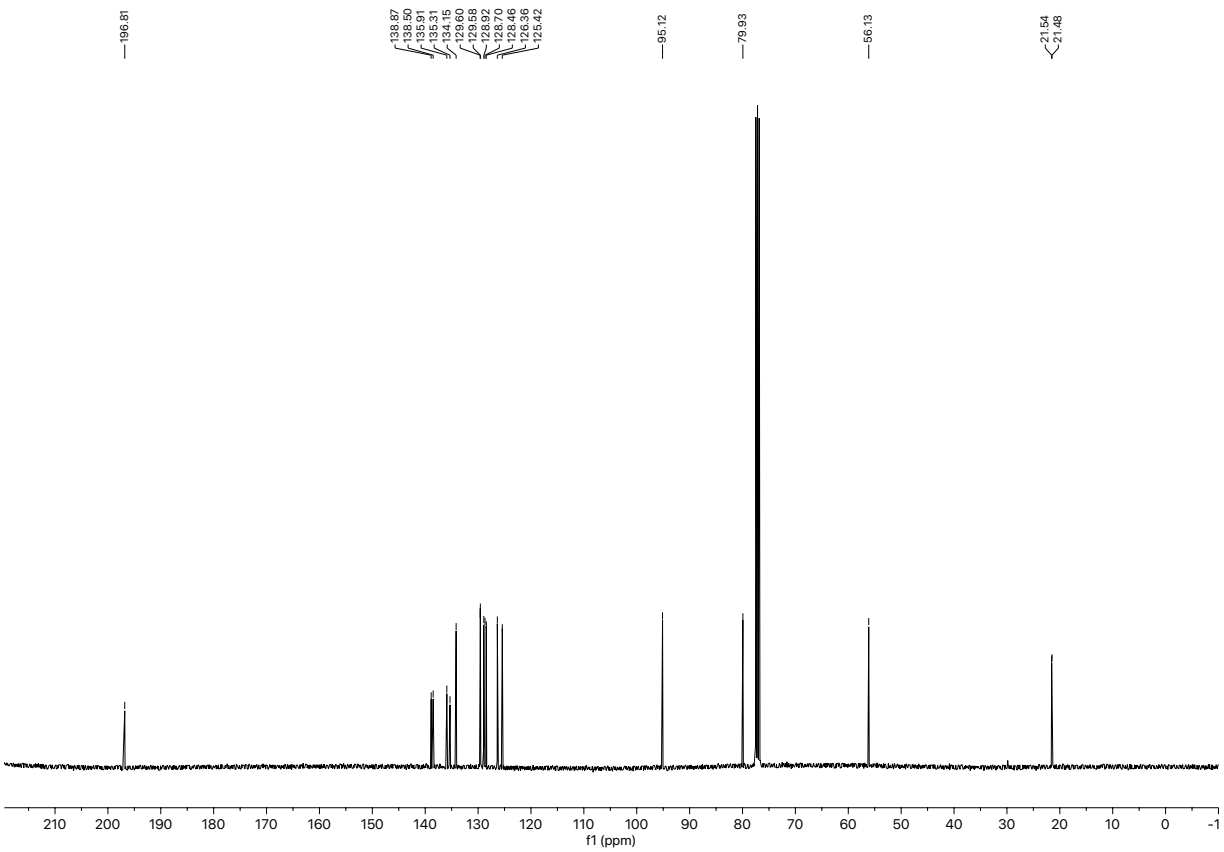
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.



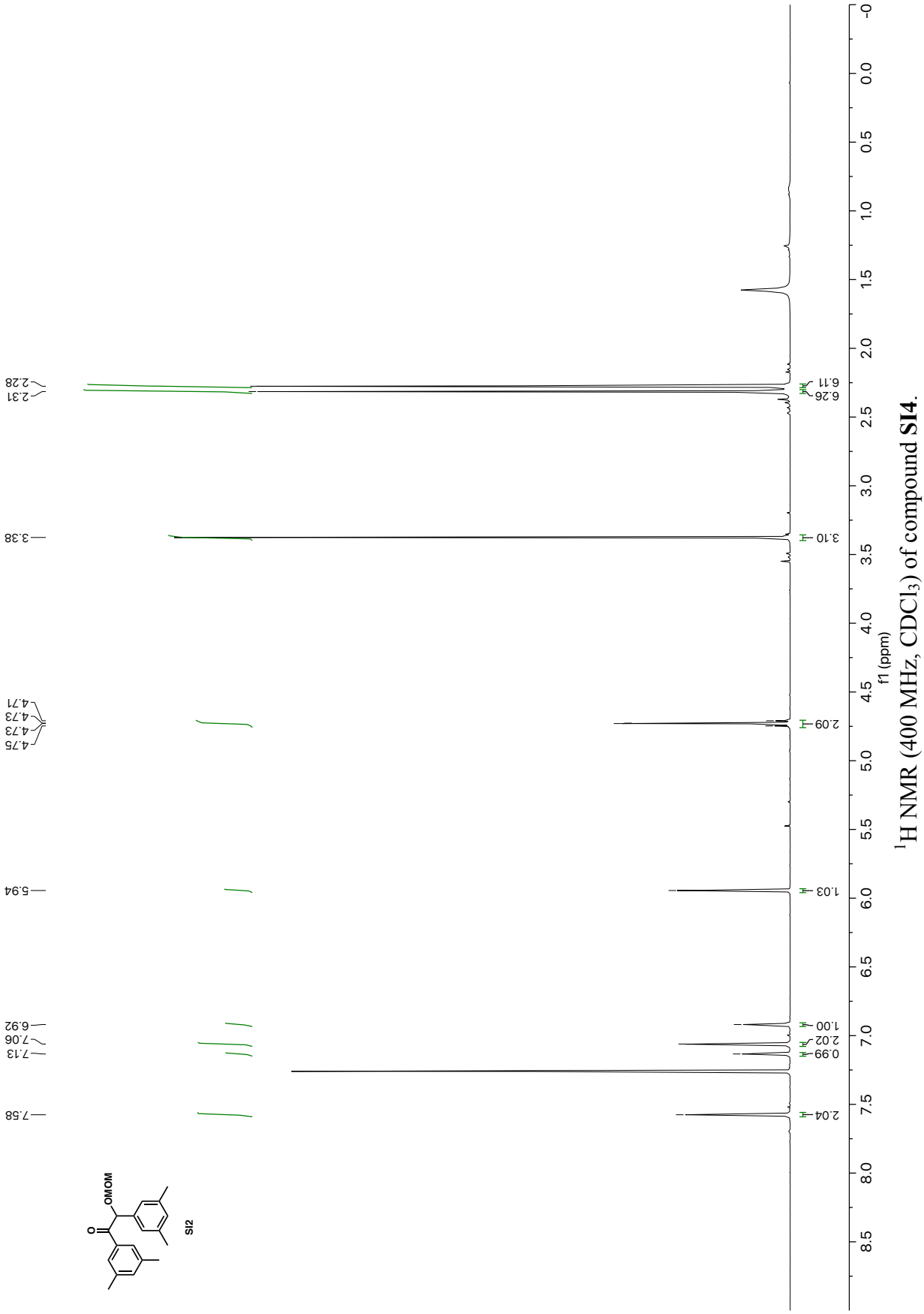
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI3**.



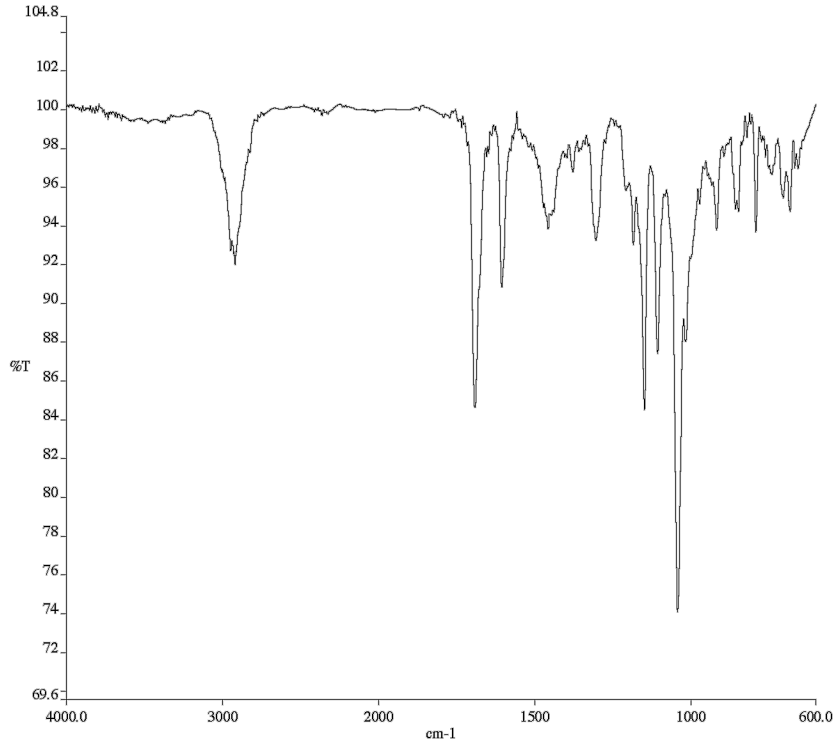
Infrared spectrum (Thin Film, NaCl) of compound **SI3**.



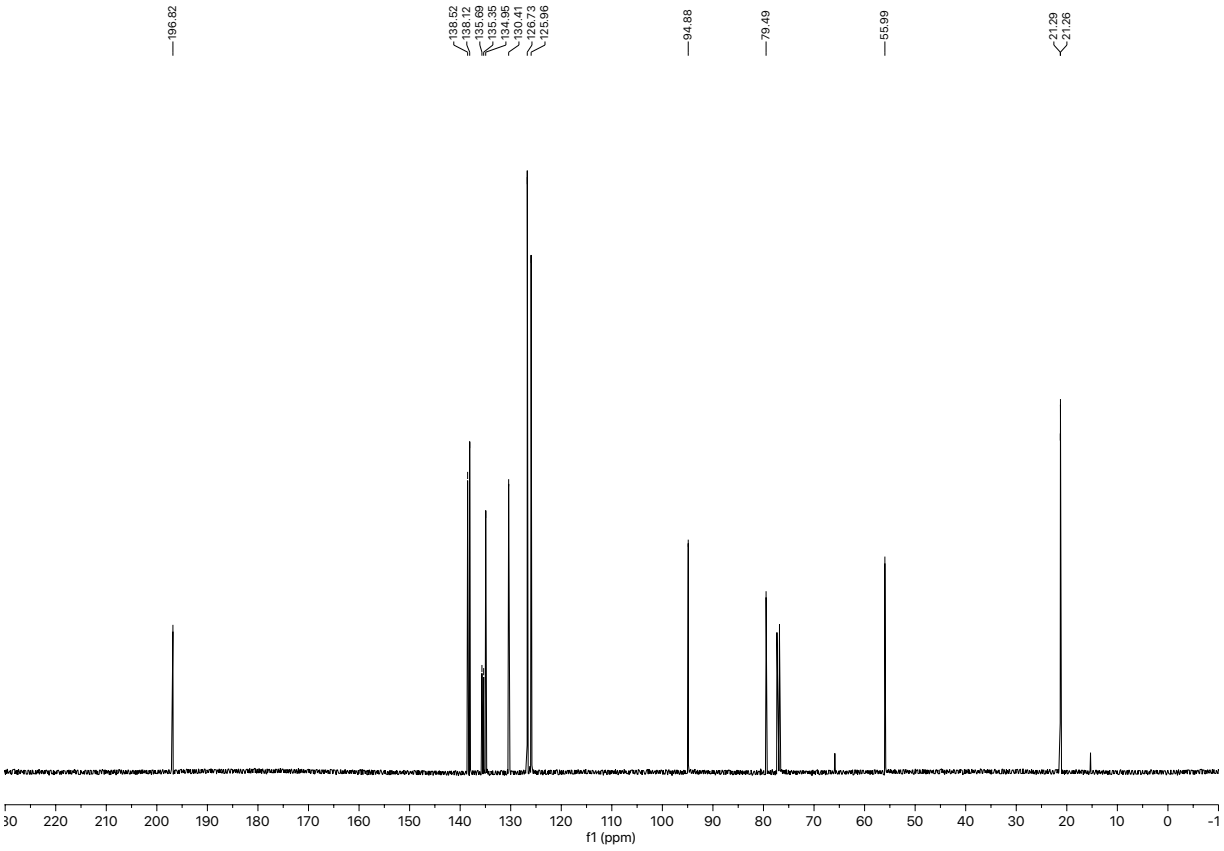
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI3**.



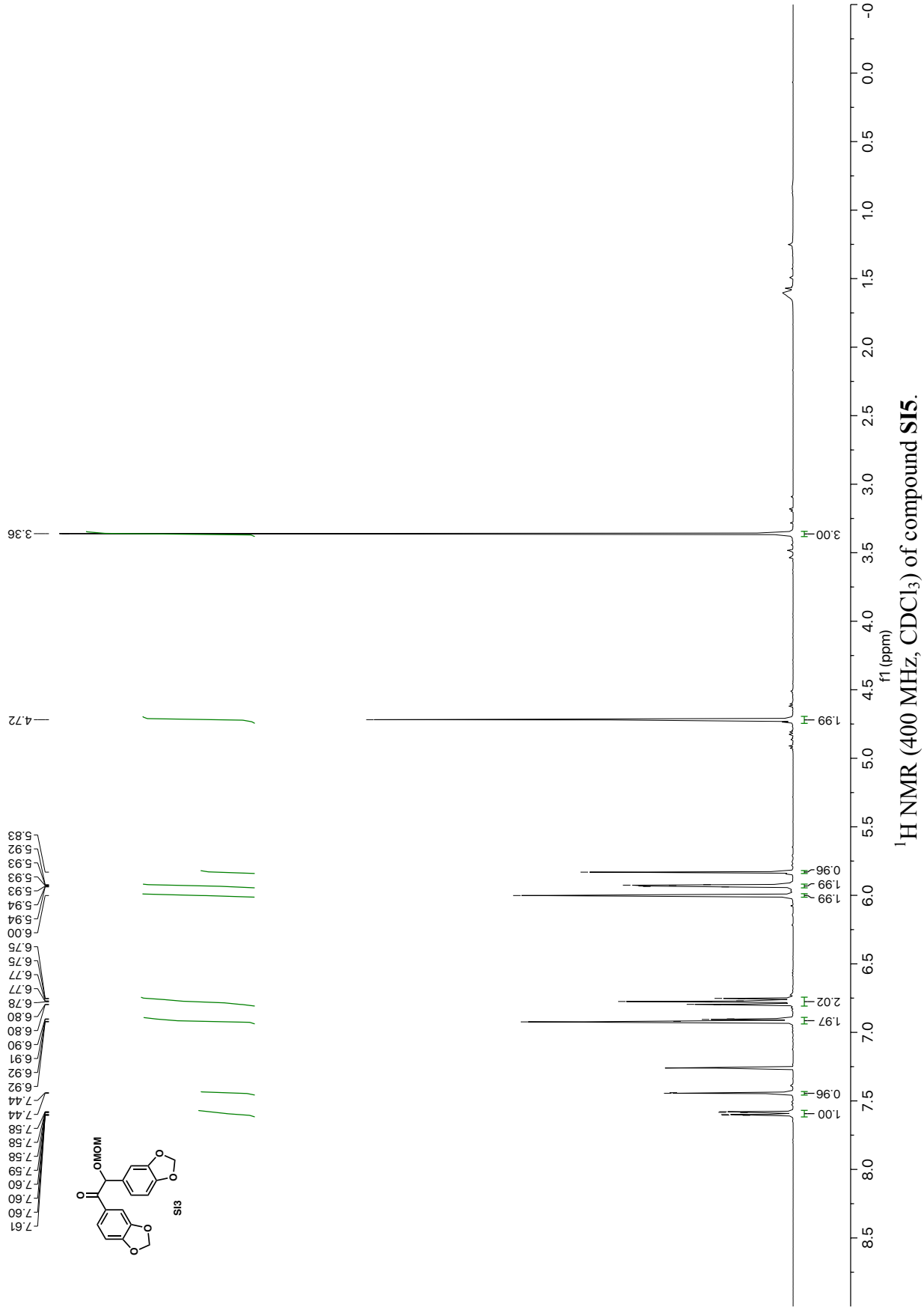
^{1}H NMR (400 MHz, $CDCl_3$) of compound **SI4**.



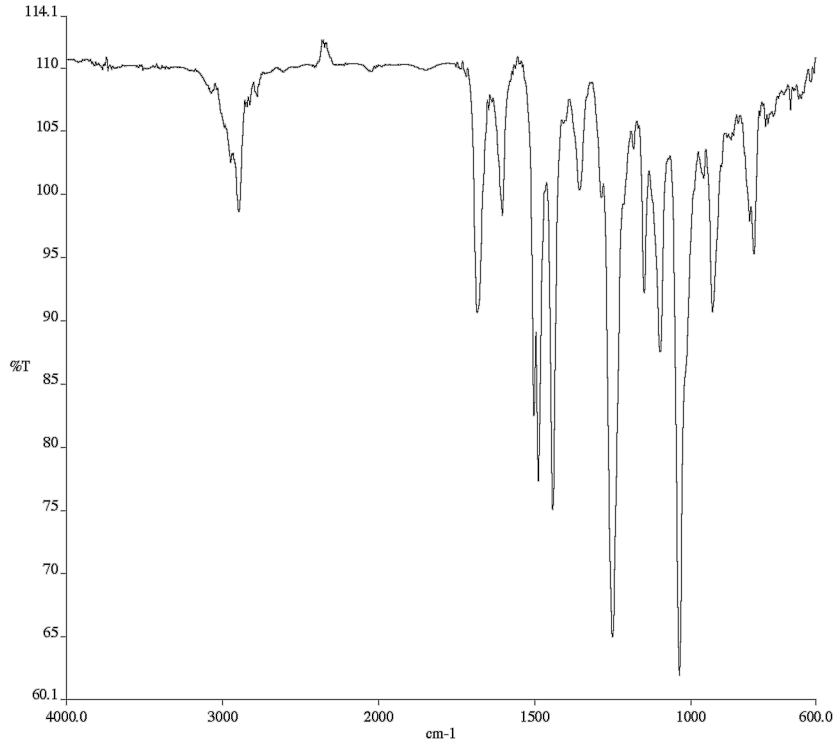
Infrared spectrum (Thin Film, NaCl) of compound **SI4**.



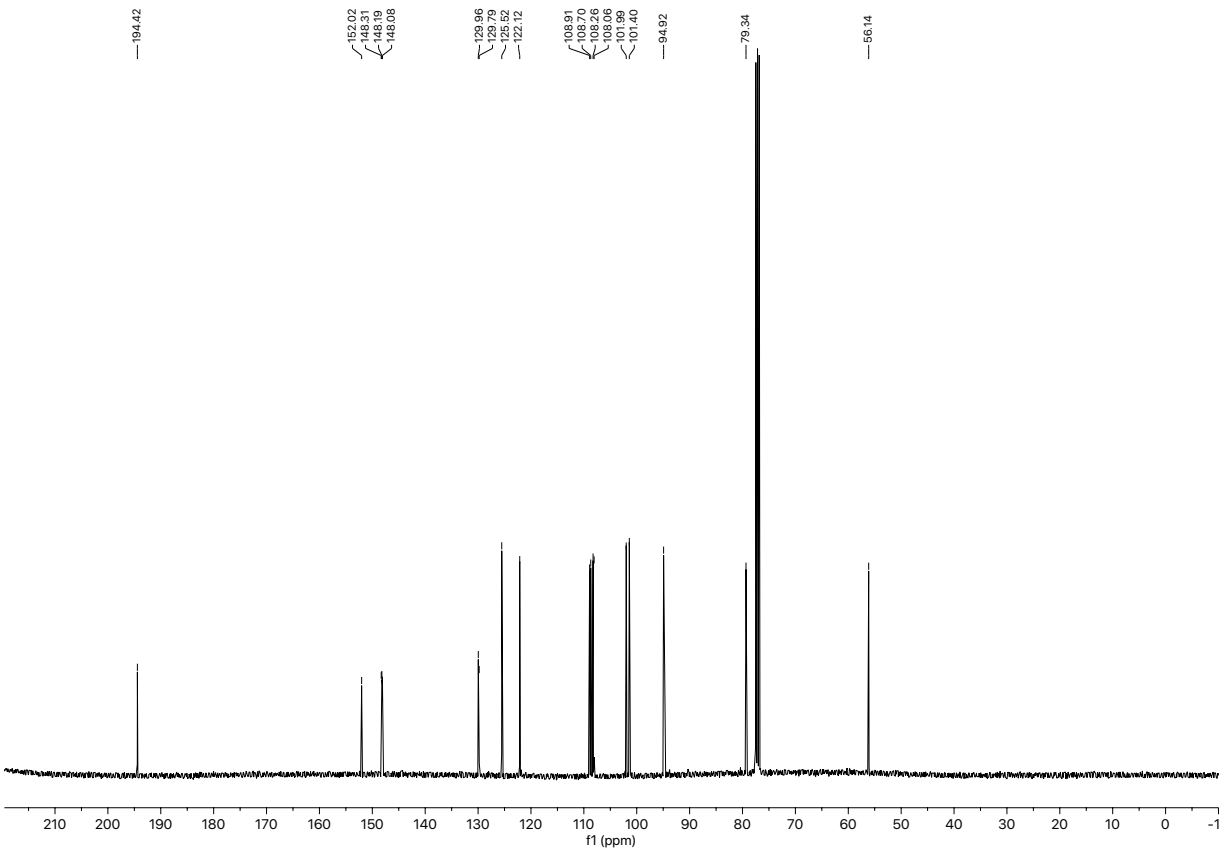
^{13}C NMR (100 MHz, $CDCl_3$) of compound **SI4**.



^{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**.