Supporting Information for

Stereospecific Overman Rearrangement of Substituted Cyclic Vinyl Bromides: Access to Fully-Substituted α-Amino Ketones

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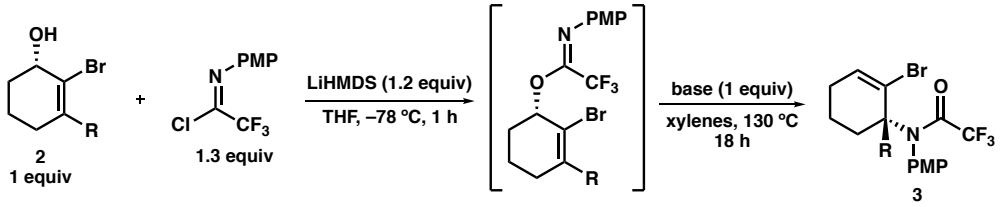
Materials and Methods

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. Reaction progress was monitored by thin-layer chromatography (TLC) or Agilent 1290 UHPLC-MS. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, *p*-anisaldehyde, or $KMnO_4$ staining. Silicycle Silia*Flash*® P60 Academic Silica gel (particle size 40–63 nm) was used for flash chromatography. The (*Z*)-enol carbonates were purified by preparative LC on a Teledyne Isco ACCQPrep HP125; column: C–18, 100 Å, 5 μm, ID 20 mm. ^{1}H NMR spectra were recorded on Varian Inova 500 MHz and Bruker 400 MHz spectrometers and are reported relative to residual $CHCl_3$ (δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Inova 500 MHz spectrometer (125 MHz) and Bruker 400 MHz spectrometers (100 MHz) and are reported relative to $CHCl_3$ (δ 77.16 ppm). Data for ^{1}H NMR are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration). Multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d = broad doublet. Data for ^{13}C NMR are reported in terms of chemical shifts (δ ppm). IR spectra were obtained by use of a Perkin Elmer Spectrum BXII spectrometer or Nicolet 6700 FTIR spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm^{-1}). Optical rotations were measured with a Jasco P-2000 polarimeter operating on the sodium D-line (589 nm), using a 100 mm path-length cell. High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+). Reagents were purchased from commercial sources and used as received unless otherwise stated.

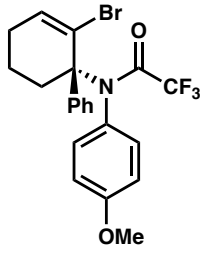
List of Abbreviations:

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

General Procedure for Overman Rearrangement



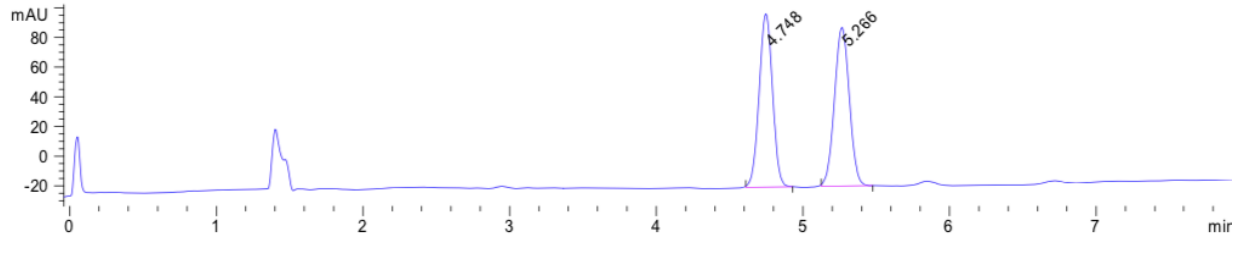
To a stirred solution of the alcohol **2** (0.2 mmol, 1.0 equiv) in THF (1 mL) at –78 ºC under a nitrogen atmosphere was added slowly a solution of LiHMDS (40 mg, 0.24 mmol, 1.2 equiv) in THF (1 mL). The mixture was stirred at –78 °C for 30 min before adding a solution of (*E*)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetimidoyl chloride[1] (62 mg, 0.26 mmol, 1.3 equiv) in THF (1 mL). The reaction was allowed to reach room temperature and stirred for 30 min. The reaction was then filtered through a silica plug (pretreated with Et_3N) eluting with 10% Et_3N in Et_2O. Following solvent removal in vacuo the crude residue was dissolved in 2 mL of xylenes and K_2CO_3 (28 mg, 0.2 mmol, 1.0 equiv) was added. The reaction was then heated to 130 ºC for 18 h, allowed to cool to ambient temperature, and directly purified by silica gel column chromatography to provide the desired product.

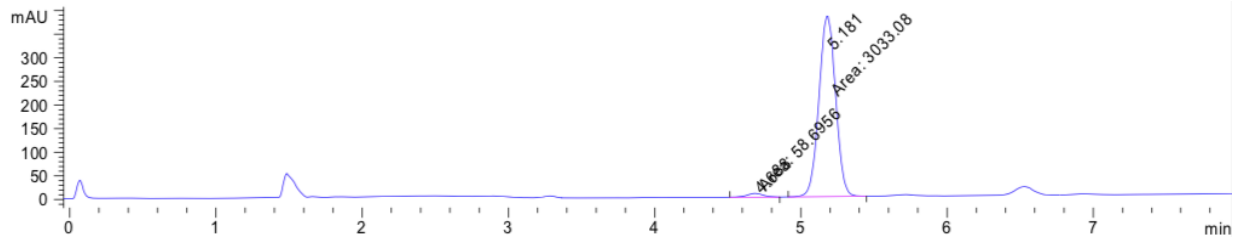


(*S*)-*N*-(6-bromo-3,4-dihydro-[1,1'-biphenyl]-1(2*H*)-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3a)

Purified by column chromatography (10% EtOAc in Hexanes) to provide the desired product as an amorphous white solid (41 mg, 45% yield); 96% ee, $[\alpha]_D^{25}$ 181.7 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.21 (m, 6H), 7.00 (dd, J = 8.9, 2.6 Hz, 1H), 6.80 (dd, J = 8.7, 3.0 Hz, 1H), 6.60 (dd, J = 8.8, 3.0 Hz, 1H), 6.51 (dd, J = 4.9, 3.1 Hz, 1H), 3.77 (s, 3H), 2.88 (d, J = 12.0 Hz, 1H), 2.35 (d, J = 10.1 Hz, 1H), 2.28 – 2.17 (m, 1H), 2.12 – 2.01 (m, 1H), 1.66 – 1.56 (m, 1H), 1.31 – 1.18 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 159.7, 156.6 (q, *J* = 34.5 Hz), 139.7, 136.0, 132.4, 132.4, 129.6, 128.3, 127.7, 127.2, 124.1, 116.3 (q, *J* = 289.8 Hz), 113.6, 112.8, 73.1, 55.4, 35.5, 27.62, 18.5; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.1; IR (Neat film, NaCl) 3443, 2931, 1697, 1509, 1250, 1200, 1177, 1035, 760, 732, 698 cm^{-1}; HRMS (MM:

ESI-APCI+) *m/z* calc'd for $C_{21}H_{20}BrF_3NO_2$ $[M+H]^+$: 454.0629, found 454.0605; SFC conditions: 10% IPA, Chiralpak OJ-H column, λ=210 nm, t_R (min): minor = 4.68, major = 5.18.





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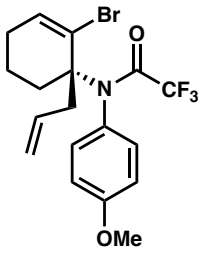
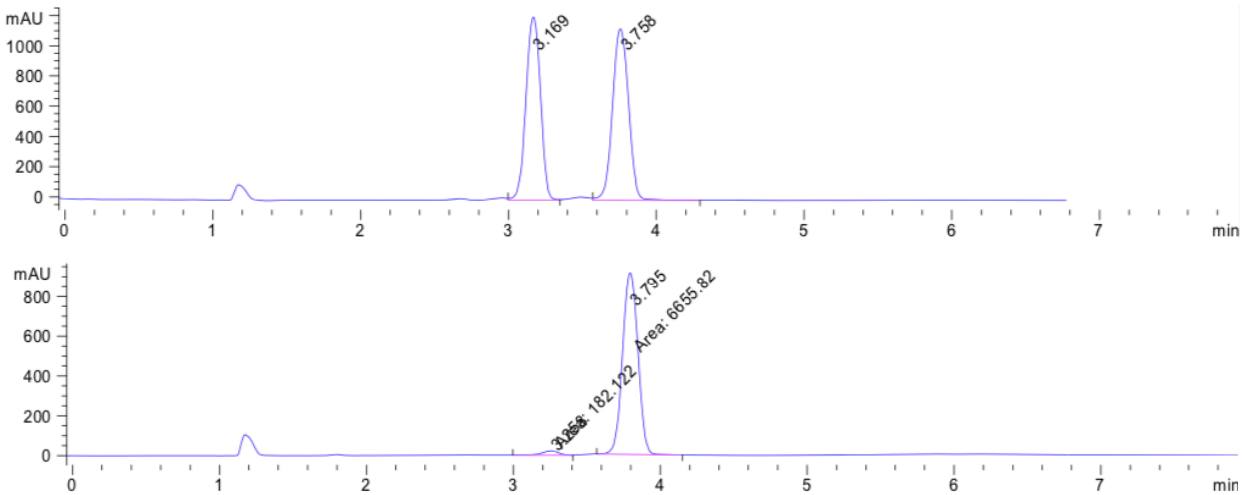


(*S*)-*N*-(1-allyl-2-bromocyclohex-2-en-1-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3b)

Purified by column chromatography (5% Et_2O in hexanes) to provide the desired product as a yellow solid (63 mg, 75% yield); 95% ee, $[\alpha]_D^{25}$ 124.0 (c 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.8 Hz, 1H), 7.10 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.88 (ddd, *J* = 22.0, 8.7, 3.0 Hz, 2H), 6.37 (dd, *J* = 5.8, 2.9 Hz, 1H), 5.53 – 5.39 (m, 1H), 5.00 – 4.92 (m, 2H), 3.85 (s, 3H), 2.79 – 2.67 (m, 1H), 2.48 (dd, *J* = 13.7, 5.6 Hz, 1H), 2.41 – 2.25 (m, 1H), 2.19 – 2.02 (m, 2H), 1.95 – 1.74 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.2, 156.0 (q, *J* = 34.3 Hz), 134.5, 133.0, 132.7, 132.3, 128.4, 124.9, 118.5, 116.1 (q, *J* = 289.5 Hz), 113.7, 113.5, 67.4, 55.5, 44.0, 33.0, 26.9, 20.5; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.4; IR (Neat film, NaCl) 3076, 2937, 3838, 1703, 1310, 1444, 1252, 1201, 1152, 1032, 922, 838, 739 cm^{-1}; HRMS (MM: ESI-

APCI+) *m/z* calc'd for $C_{18}H_{20}BrF_3NO_2$ $[M+H]^+$: 418.0629, found 418.0609 ; SFC conditions: 5% IPA, Chiralpak OJ-H column, λ=210 nm, t_R (min): minor = 3.26, major = 3.79.



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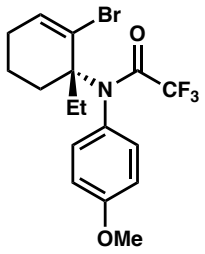
2	3.795	MM	0.1214	6655.81982	913.72266	97.3366

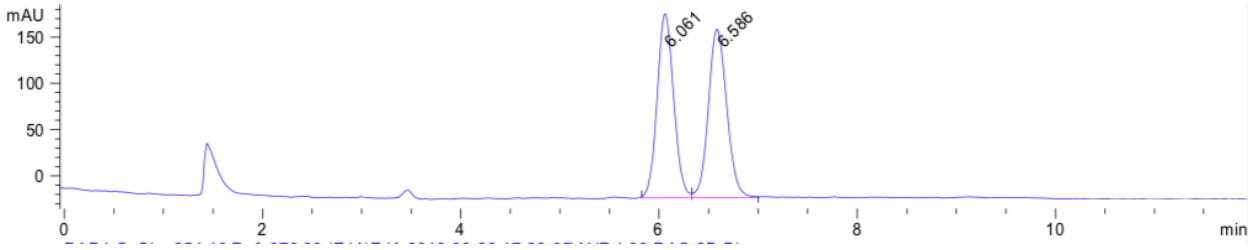
Procedure for Preparatory Scale Preparation of 3b

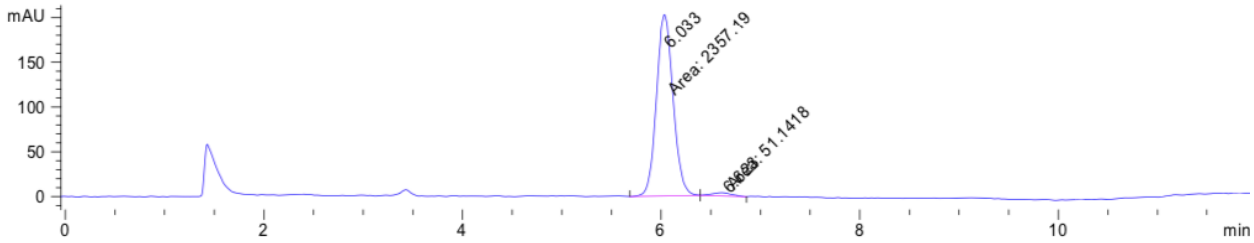
A solution of alcohol **2b** (4.62 mmol, 1.0 g) dissolved in 23 mL of THF was cooled to –78 °C in a dry-ice/acetone bath. A solution of LiHMDS (6.06 mmol, 1.440 g) in 20 mL THF was then added slowly, and the resulting mixture stirred at –78 °C for 30 min. A solution of (*E*)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetimidoyl chloride in 10 mL of THF was then added slowly, and the reaction allowed to slowly warm to room temperature and continued for 30 min. The crude reaction mixture was then filtered through a short silica plug (pretreated with Et_3N) eluting 10% Et_3N in Et_2O. Following solvent removal in vacuo, the crude residue was redissolved in 20 mL xylenes and K_2CO_3 (4.62 mmol, 637 mg) was added. The reaction was then heated to 130 °C for 18 h, allowed to cool to ambient temperature, and directly purified by silica gel column chromatography (5% Et_2O in hexanes) to provide the desired product as a yellow solid (1.6 g, 83% yield)



(*R*)-*N*-(2-bromo-1-ethylcyclohex-2-en-1-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3c)

Purified by column chromatography (10% Et_2O in hexanes) to provide the desired product as a brown oil (69 mg, 85% yield); 96% ee, $[\alpha]_D^{25}$ 137.3 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.44 (ddd, *J* = 8.8, 2.6, 1.2 Hz, 1H), 7.08 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.89 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.83 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.40 (dd, *J* = 5.6, 3.1 Hz, 1H), 3.84 (s, 3H), 2.73 (dddd, *J* = 13.2, 11.8, 4.6, 1.2 Hz, 1H), 2.42 – 2.33 (m, 1H), 2.16 – 2.05 (m, 2H), 1.91 (dp, *J* = 14.1, 5.0 Hz, 1H), 1.81 – 1.60 (m, 2H), 1.27 – 1.17 (m, 1H), 0.75 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.0, 156.1 (q, *J* = 34.2 Hz), 135.0, 132.8, 132.3, 128.5, 125.0, 116.2 (q, *J* = 289.8 Hz), 113.6, 113.2, 68.2, 55.4, 32.8, 32.5, 26.9, 21.2, 9.4; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.3; IR (Neat film, NaCl) 3390, 2970, 2941, 2838, 1703, 1697, 1505, 1252, 1200, 1179, 1166, 1033, 839, 800, 736, 680, 625 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{17}H_{20}BrF_3NO_2$ $[M+H]^+$: 406.0629, found 406.0632; SFC conditions: 3% IPA, Chiralpak AD-H column, λ=210 nm, t_R (min): minor = 6.03, major = 6.58.





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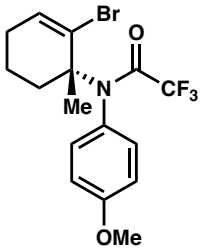
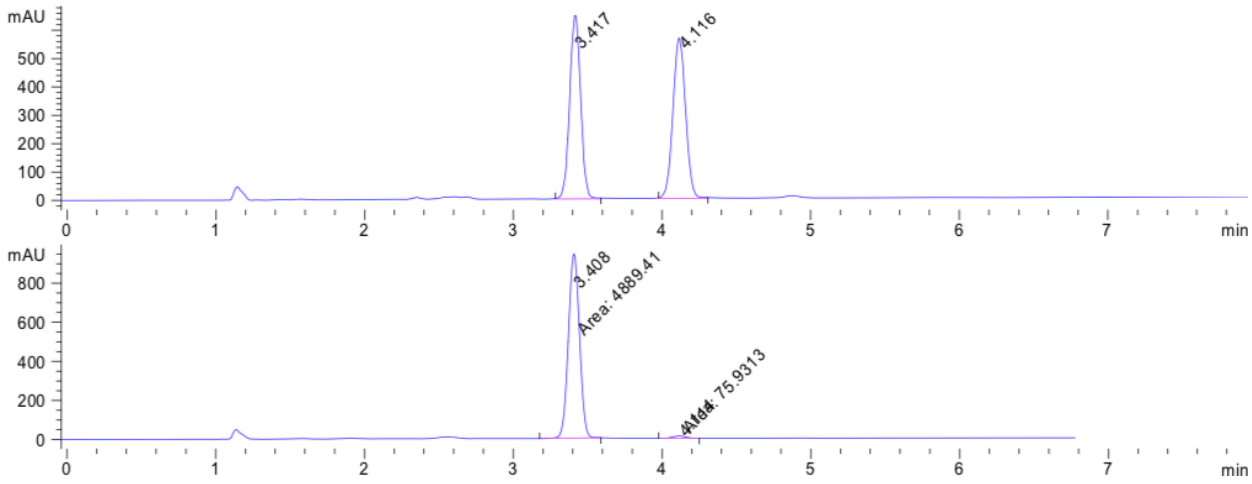


(*R*)-*N*-(2-bromo-1-methylcyclohex-2-en-1-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3d)

Purified by column chromatography (10% Et_2O in hexanes) to provide the desired product as a colorless oil (75 mg, 95% yield); 97% ee, $[\alpha]_D^{25}$ 77.1 (c 0.50, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.51 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.05 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.91 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.85 (dd, *J* = 8.6, 3.0 Hz, 1H), 6.18 (dd, *J* = 6.5, 2.1 Hz, 1H), 3.84 (s, 3H), 2.86 – 2.75 (m, 1H), 2.34 (dddd, *J* = 17.4, 11.8, 5.6, 2.4 Hz, 1H), 2.14 – 2.06 (m, 1H), 1.97 (dtd, *J* = 12.4, 3.4, 1.6 Hz, 1H), 1.87 (dt, *J* = 10.0, 4.8 Hz, 1H), 1.80 – 1.67 (m, 1H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.0, 155.8 (q, *J* = 34.6 Hz), 132.4, 131.7, 131.1, 128.7, 127.2, 116.1 (q, *J* = 289.4 Hz), 113.7, 113.5, 66.3, 56.8, 33.5, 27.1, 26.1; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.7; IR (Neat film, NaCl) 3435m 2941, 2838, 1697, 1510, 1201, 1182, 1149, 1032, 840, 738, 687 cm^{-1}. HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{18}BrF_3NO_2$ $[M+H]^+$: 392.0473, found 392.0450 ; SFC conditions: 10% IPA, Chiralpak OJ-H column, λ=210 nm, t_R (min): minor = 3.41, major = 4.11.



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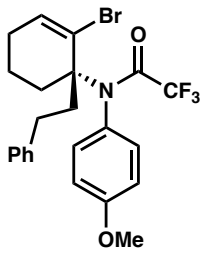
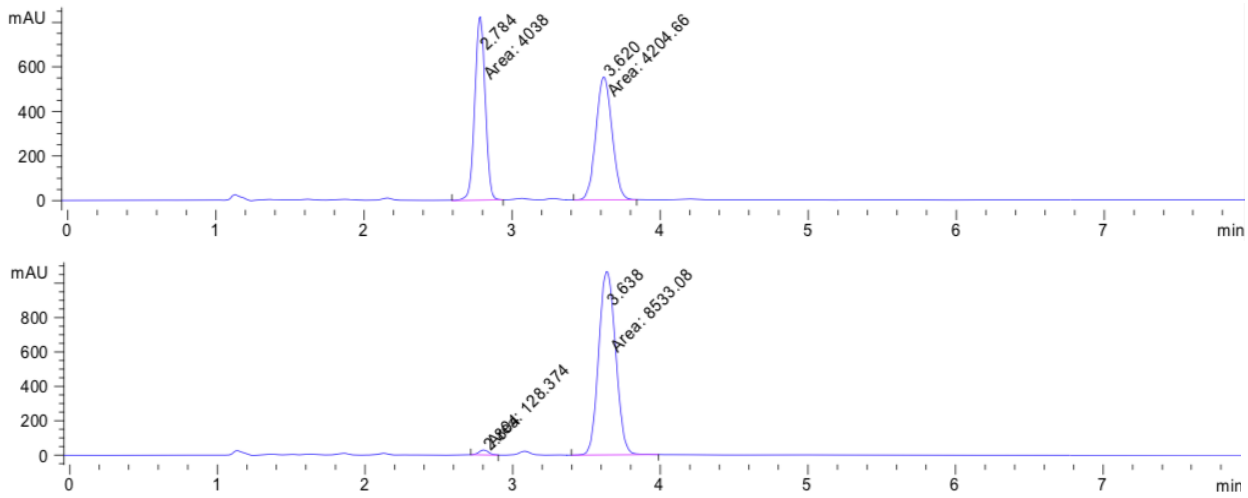


(*S*)-*N*-(2-bromo-1-phenethylcyclohex-2-en-1-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3e)

Purified by column chromatography (Et_2O 10% in hexanes) to provide the desired product as a yellow foam (68 mg, 70% yield); 97 % ee, $[\alpha]_D^{25}$ 123.2 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.24 – 7.18 (m, 2H), 7.18 – 7.10 (m, 2H), 7.00 – 6.94 (m, 2H), 6.93 – 6.86 (m, 1H), 6.83 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.41 (dd, *J* = 5.5, 3.1 Hz, 1H), 3.83 (s, 3H), 2.95 – 2.84 (m, 1H), 2.54 (td, *J* = 12.9, 3.8 Hz, 1H), 2.42 (dddd, *J* = 18.0, 9.1, 5.8, 3.1 Hz, 1H), 2.31 – 2.13 (m, 4H), 1.96 (td, *J* = 13.4, 3.9 Hz, 2H), 1.90 – 1.70 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.1, 156.2 (q, *J* = 34.4 Hz), 141.3, 134.9, 132.7, 132.6, 128.4, 128.3, 126.0, 125.4, 116.2 (q, *J* = 289.8 Hz), 113.8, 113.3, 68.0, 55.5, 41.2, 32.2, 31.3, 27.1, 20.8; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.2; IR (Neat film, NaCl) 3437, 2937, 1697, 1667, 1643, 1509, 1454, 1251, 1201, 1178, 1165, 1149, 1031, 738, 690 cm^{-1}; HRMS (MM: ESI-

APCI+) *m/z* calc'd for $C_{23}H_{24}BrF_3NO_2$ $[M+H]^+$: 482.0942, found 482.0953; SFC conditions: 20% IPA, Chiralpak OJ-H column, λ=210 nm, t_R (min): minor = 2.80, major = 3.64.



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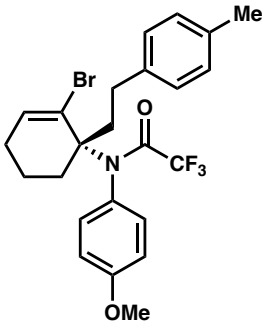
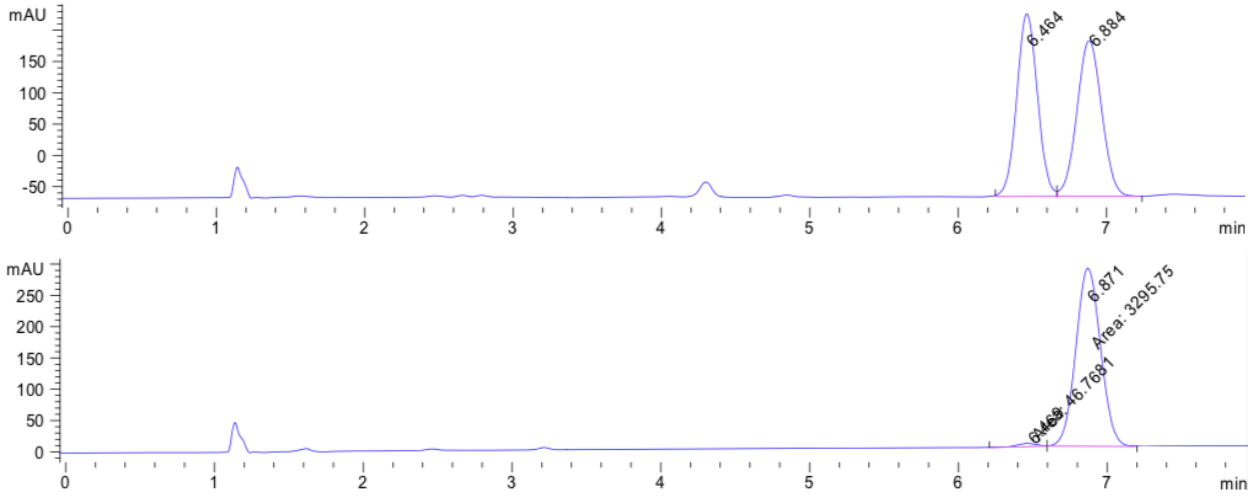
2	3.638	MM	0.1330	8533.08398	1069.05469	98.5179



(*S*)-*N*-(2-bromo-1-(4-methylphenethyl)cyclohex-2-en-1-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3f)

Purified by column chromatography (Et_2O 10% in hexanes) to provide the desired product as a off-white solid (70 mg, 70% yield); 97% ee, $[\alpha]_D^{25}$ 222.3 (c 0.70, $CHCl_3$); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.43 (ddd, *J* = 8.8, 2.7, 1.1 Hz, 1H), 7.13 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.02 (d, *J* = 7.7 Hz, 2H), 6.90 – 6.81 (m, 4H), 6.40 (dd, *J* = 5.5, 3.1 Hz, 1H), 3.83 (s, 3H), 2.92 – 2.84 (m, 1H), 2.54 – 2.37 (m, 2H), 2.29 (s, 3H), 2.26 – 2.14 (m, 3H), 2.01 – 1.69 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.1, 156.2 (q, *J* = 34.3 Hz), 138.3, 135.5, 134.8, 132.8, 132.6, 129.1, 128.4, 128.2, 125.4, 116.2 (q, *J* = 289.8 Hz), 113.8, 113.3, 68.0, 55.5, 41.3, 32.2, 30.8, 27.1,

20.8; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.2; IR (Neat film, NaCl) 3444, 2937, 1697, 1509, 1198, 1178, 1151, 1164, 1033, 839, 736, 624 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{24}H_{26}BrF_3NO_2$ $[M+H]^+$: 496.1099, found 496.1118; SFC conditions: 10% IPA, Chiralpak OJ-H column, λ = 210 nm, t_R (min): minor = 6.47, major = 6.87.



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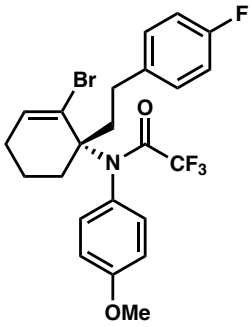
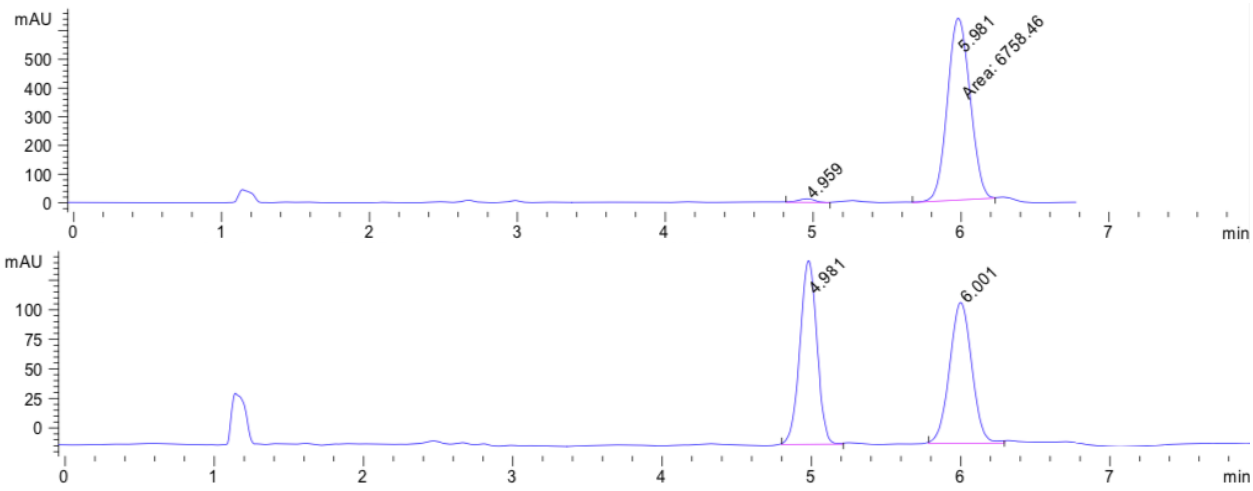


(*S*)-*N*-(2-bromo-1-(4-fluorophenethyl)cyclohex-2-en-1-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3g)

Purified by column chromatography (Et_2O 10% in hexanes) to provide the desired product as an amorphous solid (75 mg, 75% yield); 97% ee, $[\alpha]_D^{25}$ 118.3 (c 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.13 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.95 – 6.78 (m, 6H), 6.41 (dd, *J* = 5.5, 3.1 Hz, 1H), 3.82 (s, 3H), 2.89 (ddd, *J* = 13.2, 11.4, 4.2 Hz, 1H), 2.57 – 2.35 (m, 2H), 2.31 – 2.11 (m, 3H), 2.02 – 1.66 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.5, 160.1, 160.1, 156.2 (q, *J* = 34.3 Hz), 137.0, 136.9, 135.1, 132.7, 132.6, 129.7, 129.6,

128.3, 116.2 (q, J = 289.7 Hz), 115.3, 115.1, 113.8, 113.3, 68.0, 55.5, 41.4, 32.2, 30.5, 27.1, 20.7; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.2, -116.1 – -118.8 (m); IR (Neat film, NaCl) 3443, 2936, 1698, 1509, 1252, 1201, 1179, 1154, 1032, 970, 834, 736 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{23}BrF_4NO_2$ $[M+H]^+$: 500.0848, found 500.0846; SFC conditions: 10% IPA, Chiralpak OJ-H column, λ = 210 nm, t_R (min): minor = 4.96, major = 5.98.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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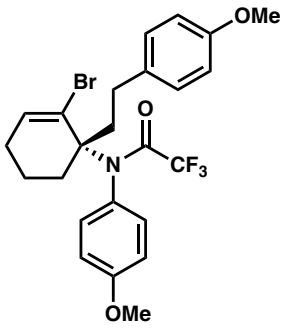
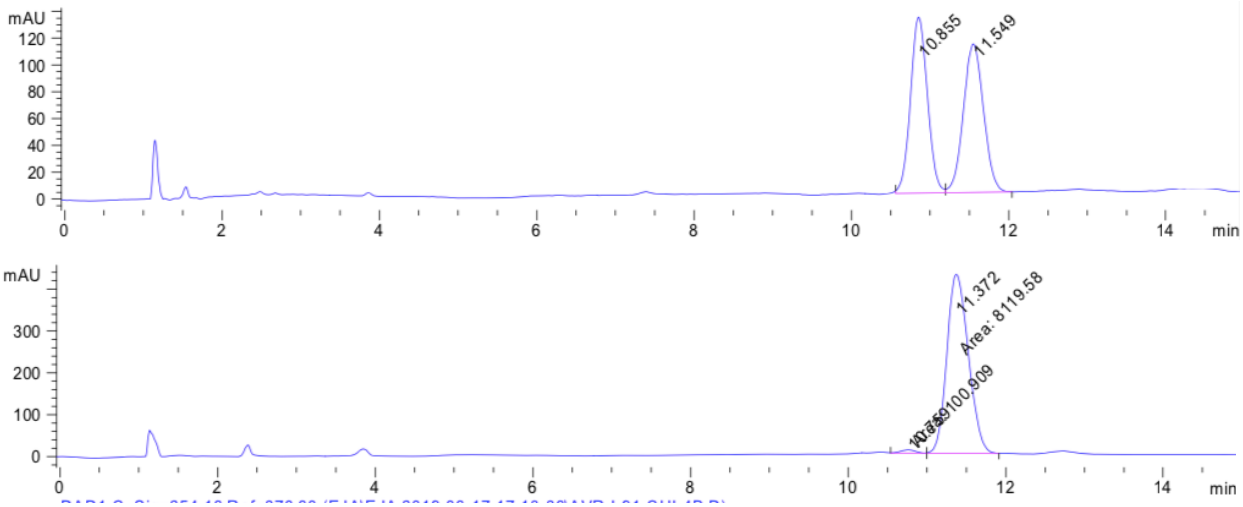
2	5.981	MM	0.1776	6758.46289	634.31512	98.5714



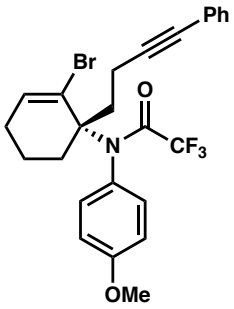
(*S*)-*N*-(2-bromo-1-(4-methoxyphenethyl)cyclohex-2-en-1-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3h)

Purified by column chromatography (CH_2Cl_2 50% in hexanes) to provide the desired product as a colorless oil (62mg, 60% yield); 98% ee, $[\alpha]_D^{25}$ 85.2 (c 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, J = 8.8, 1.5 Hz, 1H), 7.12 (dd, J = 8.7, 2.7 Hz, 1H), 6.94 – 6.79 (m, 4H), 6.79 – 6.70 (m, 2H), 6.40 (dd, J = 5.5, 3.0 Hz, 1H), 3.82 (s, 3H), 3.75 (s, 3H), 2.94 – 2.80

(m, 1H), 2.54 – 2.34 (m, 2H), 2.25 – 2.09 (m, 3H), 2.02 – 1.77 (m, 3H), 1.70 (td, J = 13.2, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 160.1, 157.9, 156.2 (q, J = 34.4 Hz), 134.8, 133.4, 132.8, 132.6, 129.2, 128.4, 125.4, 116.2 (q, J = 289.8 Hz), 113.8, 113.3, 68.0, 55.5, 41.5, 30.4, 20.8; ^{19}F NMR (282 MHz, Chloroform-*d*) δ -67.2; IR (Neat film, NaCl) 3386, 2934, 2836, 1697, 1513, 1249, 1201, 1178, 1151, 1034, 824, 737 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{24}H_{26}BrF_3NO_3$ $[M+H]^+$: 512.1048, found 512.1056; SFC conditions: 10% IPA, Chiralpak OJ-H column, λ = 210 nm, t_R (min): minor = 10.76, major = 11.37.



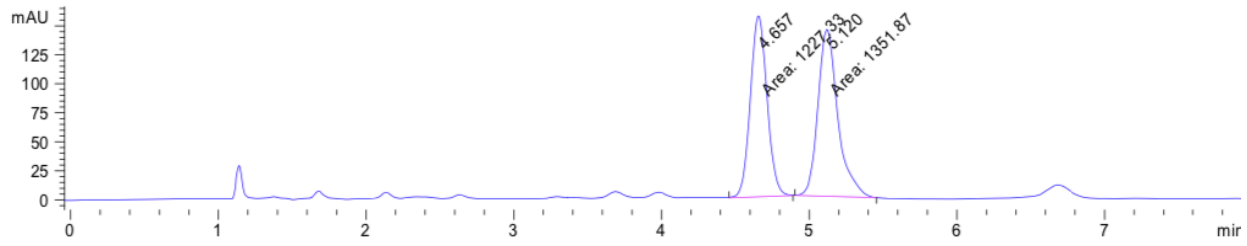
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.759	MM	0.2117	100.90923	7.94563	1.2275
2	11.372	MM	0.3163	8119.58154	427.83438	98.7725



(*S*)-*N*-(2-bromo-1-(4-phenylbut-3-yn-1-yl)cyclohex-2-en-1-yl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (3i)

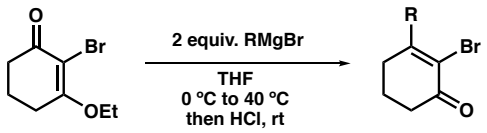
Purified by column chromatography (15% Et_2O in Hexanes) to provide the desired product as a colorless oil (51 mg, 50% yield); 92% ee, $[\alpha]_D^{25}$ 181.7 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.47 (ddd, J = 8.8, 3.0, 1.4 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.27 (tq, J = 3.9, 2.1

Hz, 3H), 7.14 (dd, *J* = 8.7, 2.7 Hz, 1H), 6.94 (dd, *J* = 8.8, 3.0 Hz, 1H), 6.87 (dd, *J* = 8.7, 3.0 Hz, 1H), 6.43 (dd, *J* = 5.5, 3.2 Hz, 1H), 3.86 (s, 3H), 2.84 (ddd, *J* = 13.4, 11.5, 4.4 Hz, 1H), 2.46 – 2.30 (m, 2H), 2.24 – 2.12 (m, 3H), 2.06 (ddd, *J* = 13.5, 10.6, 5.1 Hz, 1H), 2.02 – 1.92 (m, 1H), 1.92 – 1.70 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 156.2 (q, *J* = 34.4 Hz), 135.5, 132.7, 132.4, 131.5, 128.2, 127.8, 124.5, 123.5, 116.2 (q, *J* = 289.7 Hz), 113.9, 113.5, 88.9, 80.8, 67.5, 55.5, 55.4, 38.1, 32.3, 27.0, 20.7, 15.3; ^{19}F NMR (282 MHz, Chloroform-*d*) δ -67.2; IR (Neat film, NaCl) 3441, 2937, 2839, 1703, 1698, 1510, 1300, 1252, 1200, 1179, 1152, 1032, 972, 756, 690 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{25}H_{24}BrF_3NO_2$ $[M+H]^+$: 506.0942, found 506.0962; SFC conditions: 15% IPA, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 4.51, major =4.98.



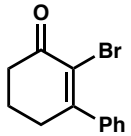
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.509	MM	0.1439	4042.40601	468.30676	96.2630
2	4.979	MM	0.1402	156.92706	18.65687	3.7370

General procedure A for the synthesis of the 2-bromo-enones



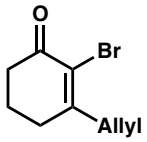
To a solution of 2-bromo-3-ethoxycyclohex-2-en-1-one[2] (1.09 g, 5 mmol, 1.0 equiv) in THF (0.1 M) at 0 ºC was added slowly the corresponding Grignard (2.0 equiv). The reaction was then

heated to 40 °C and continued until no starting material remained as seen by TLC. The reaction was then quenched with 2M HCl (2.0 equiv) and stirred at room temperature for 2 hours. The reaction was diluted with water and extracted with Et_2O, and the combined organic phases dried over anhydrous Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography to yield the desired product.



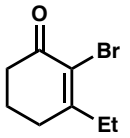
2-bromo-5,6-dihydro-[1,1'-biphenyl]-3(4*H*)-one (1a)

Purified by column chromatography (10% AcOEt in Hexanes) to provide a white-off solid (1 g, 80% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.29 (m, 5H), 2.79 (t, *J* = 6.0 Hz, 2H), 2.75 – 2.69 (m, 2H), 2.21 – 2.13 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.7, 160.8, 140.8, 128.9, 128.4, 126.9, 122.5, 37.8, 35.1, 22.4; IR (Neat film NaCl) 3056, 2957, 2867, 1681, 1588, 1265, 1182, 1130, 983, 785, 755, 700 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{12}H_{12}BrO$ $[M+H]^+$: 251.0071, found 251.0069.



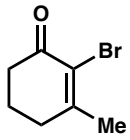
3-allyl-2-bromocyclohex-2-en-1-one (1b)

Purified by column chromatography (20% AcOEt in Hexanes) to provide a colorless oil (1.020 g, 95% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 5.78 (td, *J* = 16.8, 16.0, 7.4 Hz, 1H), 5.22 – 5.14 (m, 2H), 3.24 (d, *J* = 6.7 Hz, 2H), 2.59 (t, *J* = 6.6 Hz, 2H), 2.50 (t, *J* = 6.0 Hz, 2H), 1.99 (p, *J* = 5.9 Hz, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.3, 161.0, 131.6, 123.1, 118.4, 43.4, 37.8, 32.1, 21.9; IR (Neat film NaCl) 3079, 2949, 2888, 1693, 1598, 1453, 1427, 1416, 1273, 1183, 985, 920, 794 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_9H_{12}BrO$ $[M+H]^+$: 215.0071, found 215.0059.



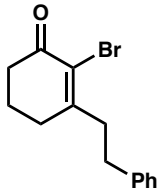
2-bromo-3-ethylcyclohex-2-en-1-one (1c)

Purified by column chromatography (10% AcOEt in Hexanes) to provide a red oil (707 mg, 70% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 2.60 – 2.54 (m, 2H), 2.54 – 2.41 (m, 4H), 2.04 – 1.95 (m, 2H), 1.13 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.4, 165.3, 122.0, 37.8, 32.5, 31.9, 22.0, 11.0; IR (Neat film NaCl) 3436, 2936, 2875, 1693, 1598, 1455k 1461, 1282, 1191, 1170, 1133, 984, 886, 801 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_8H_{12}BrO$ $[M+H]^+$: 203.0071, found 203.0060.



2-bromo-3-methylcyclohex-2-en-1-one (1d)

Purified by column chromatography (10% AcOEt in Hexanes) to provide the desired product a colorless oil (750 mg, 80% yield); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.58 – 2.45 (m, 4H), 2.14 (t, *J* = 0.9 Hz, 3H), 2.02 – 1.90 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 191.0, 160.6, 122.7, 37.6, 34.2, 25.9, 21.8; IR (Neat film NaCl) 2946, 2869, 1681, 1605, 1452, 1426, 1371, 1269, 1194, 1172, 1269, 1194, 1172, 1134, 1039, 978, 909, 793 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_7H_{10}BrO$ $[M+H]^+$: 188.9915, found 188.9907.

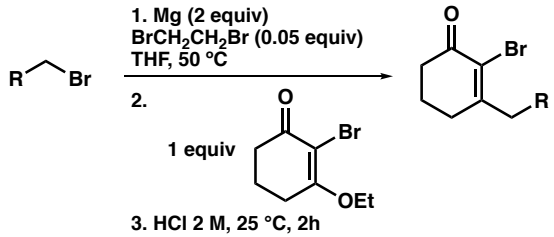


2-bromo-3-phenethylcyclohex-2-en-1-one (1e)

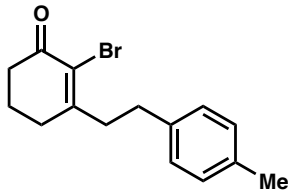
Purified by column chromatography (20% AcOEt in Hexanes) to provide the desired product as a white solid (1.110 g, 80% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.21 (m, 3H), 2.92 – 2.85 (m, 2H), 2.83 – 2.74 (m, 2H), 2.62 – 2.53 (m, 2H), 2.39 (t, *J* = 6.1 Hz, 2H), 1.99 – 1.87 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.3, 163.1, 140.5,

128.7, 128.5, 126.6, 123.3, 41.3, 37.8, 33.2, 32.9, 22.0; IR (Neat film NaCl) 2932, 2865, 1681, 1598, 1495, 1454, 1269, 1175, 978, 795, 749, 700 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{16}BrO$ $[M+H]^+$: 279.0384, found 279.0370.

General procedure B for the synthesis of the 2-bromo-enones



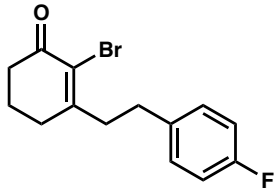
A flame-dried flask under nitrogen was charged with magnesium turnings (260 mg, 20 mmol, 2.0 equiv,), the bromo derivative (2 mmol, 0.2 equiv), dibromoethane (0.2 mmol, 0.01 equiv) and 5 mL of THF. The reaction was heated to 50 ºC to initiate the Grignard reagent formation. Then, a solution of the bromo derivative (18 mmol, 1.8 equiv) in 15 mL of THF was added to the reaction and the resulting mixture was heated for 30 min. The reaction was then cooled to room temperature and a solution of 2-bromo-3-ethoxycyclohex-2-en-1-one (2.20 g, 10 mmol, 1.0 equiv) in THF (15 mL) was added slowly. The reaction was heated at 50 ºC until no starting material remained by TLC. The reaction was allowed to cool to ambient temperature, then quenched with 2M HCl and stirred for 2 h. The reaction was diluted with water and extracted with Et_2O. The combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was purified by silica gel column chromatography to provide the desired product.



2-bromo-3-(4-methylphenethyl)cyclohex-2-en-1-one (1f)

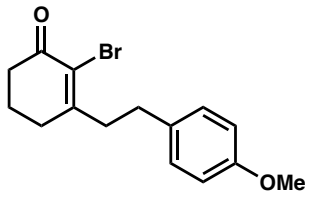
Purified by column chromatography (20% AcOEt in Hexanes) provide the desired product as a white solid (2.248 g, 77% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.11 (s, 4H), 2.87 – 2.72 (m, 4H), 2.60 – 2.54 (m, 2H), 2.40 (t, *J* = 6.0 Hz, 2H), 2.34 (s, 3H), 1.99 – 1.90 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.2, 163.2, 137.3, 136.0, 129.3, 128.3, 123.1, 41.3, 37.8, 33.1, 32.4, 21.9, 21.1; IR (Neat film NaCl) 2925, 2866, 1681, 1596, 1514, 1454, 1425, 1269,

1174, 1127, 978, 808 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}BrO$ $[M+H]^+$: 293.0541, found 293.0546.



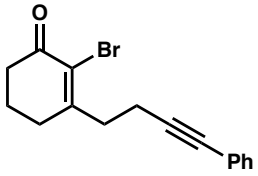
2-bromo-3-(4-fluorophenethyl)cyclohex-2-en-1-one (1g)

Purified by column chromatography (20% AcOEt in Hexanes) to provide the desired product as white solid (2.368 g, 80% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.22 – 7.12 (m, 2H), 7.03 – 6.93 (m, 2H), 2.85 (dd, *J* = 9.6, 6.6 Hz, 2H), 2.79 – 2.70 (m, 2H), 2.62 – 2.50 (m, 2H), 2.39 (t, *J* = 6.0 Hz, 2H), 1.98 – 1.89 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.1, 162.6, 161.6 (d, *J* = 244.3 Hz), 136.0 (d, *J* = 3.2 Hz), 129.8 (d, *J* = 7.8 Hz), 123.3, 115.4 (d, *J* = 21.2 Hz), 41.2, 37.7, 33.1, 31.9, 21.9; ^{19}F NMR (282 MHz, Chloroform-*d*) δ -116.56 (tt, *J* = 8.7, 5.4 Hz); IR (Neat Film NaCl) 2932, 2868, 1693, 1681, 1599, 1512, 1505, 1222, 979, 824, 805, 771 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{15}BrFO$ $[M+H]^+$: 297.0290, found 297.0304.



2-bromo-3-(4-methoxyphenethyl)cyclohex-2-en-1-one (1h)

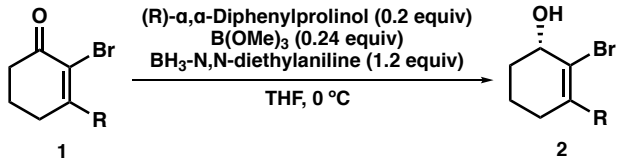
Purified by column chromatography (25% AcOEt in Hexanes) to provide the desired product as a white solid (3.0 g, 65% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.18 – 7.09 (m, 2H), 6.90 – 6.74 (m, 2H), 3.80 (s, 3H), 2.86 – 2.80 (m, 2H), 2.75 (ddd, *J* = 8.6, 6.6, 1.3 Hz, 2H), 2.60 – 2.54 (m, 2H), 2.38 (t, *J* = 6.0 Hz, 2H), 1.99 – 1.89 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.23, 163.23, 158.22, 132.41, 129.32, 123.09, 113.97, 55.30, 41.42, 37.75, 33.12, 31.91, 21.93; IR (Neat film NaCl) 2933, 2834, 1681, 1597, 1513,1454, 1426, 1246, 1176, 1034, 978, 822, 801 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}BrO_2$ $[M+H]^+$: 309.0490, found 309.0500.



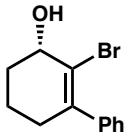
2-bromo-3-(4-phenylbut-3-yn-1-yl)cyclohex-2-en-1-one (1i)[3]

Purified by column chromatography (20% AcOEt in Hexanes) to provide the desired product as a colorless oil (1.5 g, 50% yield); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.35 (qd, *J* = 3.8, 1.6 Hz, 2H), 7.29 – 7.24 (m, 3H), 2.78 (dd, *J* = 7.5, 5.7 Hz, 2H), 2.71 (td, *J* = 6.8, 1.4 Hz, 2H), 2.63 (t, *J* = 6.0 Hz, 2H), 2.58 (dd, *J* = 7.4, 6.0 Hz, 2H), 2.06 – 1.96 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.1, 162.0, 131.5, 128.3, 128.0, 123.7, 123.3, 87.8, 81.9, 37.8, 37.8, 33.2, 21.9, 17.0; IR (Neat film NaCl) 2942, 2866, 1681, 1597, 1441, 1271, 1175, 978, 757, 689 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{16}BrO$ $[M+H]^+$: 303.0384, found 303.0387

General procedure for CBS reduction of ketones

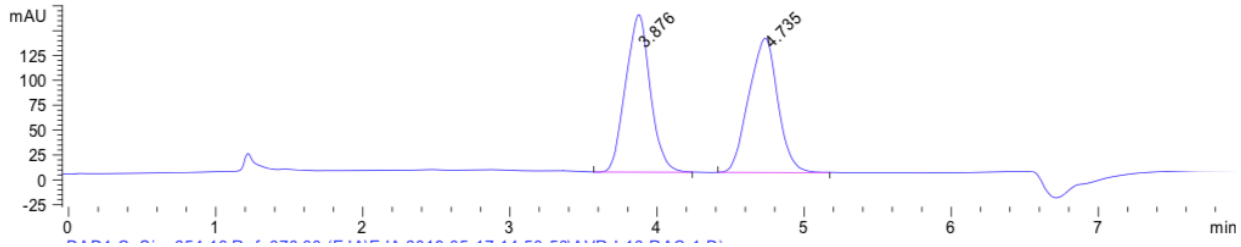


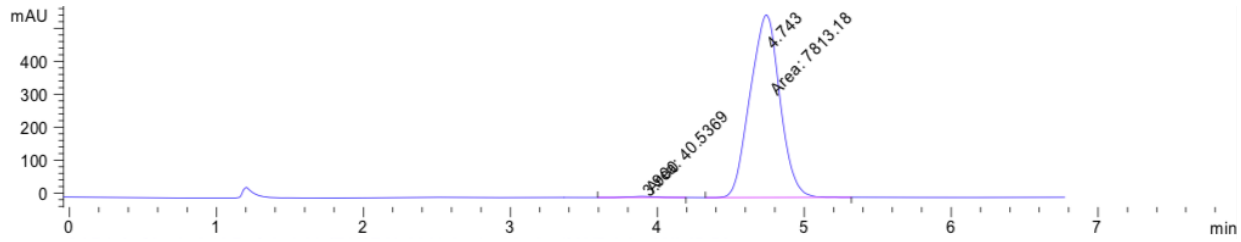
To a stirred solution of (R)-α,α-Diphenylprolinol (0.2 equiv) in THF (0.1 M) was added trimethyl borate (0.24 equiv) and the resulting mixture was stirred for 1 h at room temperature. Then, borane N,N-diethylaniline complex (1.2 equiv) was added and the reaction was cooled to 0 ºC. After 10 min of stirring at this temperature, a solution of **1** in THF (0.5 M) was added slowly over 3 hours. Following completion of the addition, the reaction was quenched with 2 M HCl and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude mixture was purified by column chromatography to provide the desired alcohol.



(*S*)-2-bromo-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-ol (2a)

Purified by column chromatography (20% EtOAc in Hexanes) to provide the desired product as a white solid (250 mg, 99% yield); 99% ee, $[\alpha]_D^{25}$ -61.8 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.38 (tt, *J* = 7.6, 1.4 Hz, 2H), 7.34 – 7.29 (m, 1H), 7.26 – 7.22 (m, 2H), 4.44 (ddt, *J* = 4.8, 2.8, 1.5 Hz, 1H), 2.68 (s, 1H), 2.51 – 2.33 (m, 2H), 2.08 – 1.89 (m, 3H), 1.85 – 1.73 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.3, 141.7, 128.3, 127.7, 127.5, 123.6, 71.1, 34.5, 31.8, 18.6; IR (Neat film NaCl) 3382, 2930, 1489, 1441, 1331, 1064, 990, 756, 697 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{12}H_{14}BrO$ $[M\text{-}OH]^+$: 235.0117, found 235.0125; SFC conditions: 15% IPA, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 3.90, major = 4.74.





Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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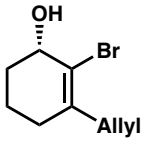
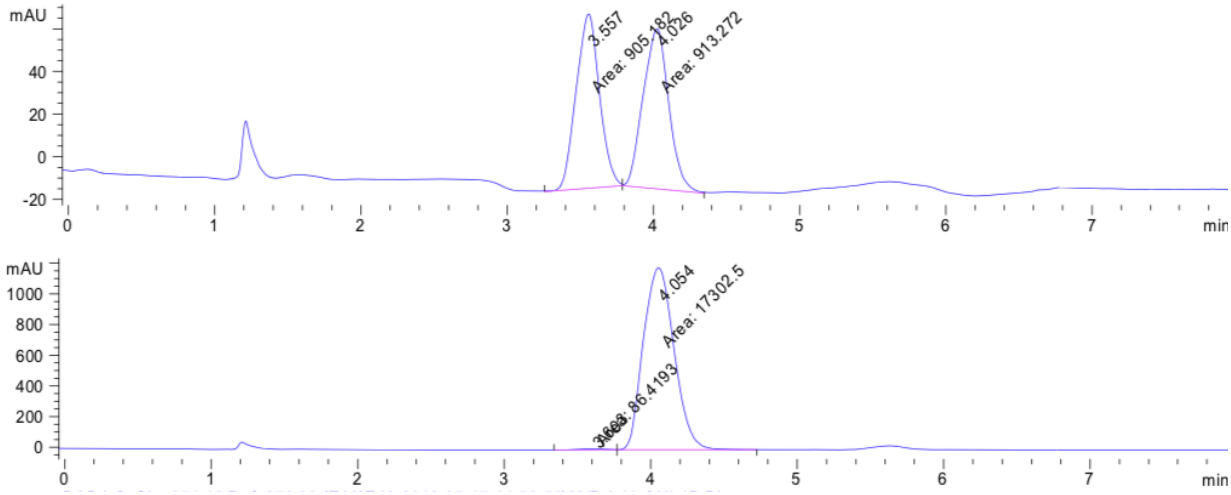
2	4.743	MM	0.2349	7813.18457	554.47266	99.4839



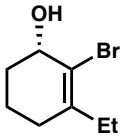
(*S*)-3-allyl-2-bromocyclohex-2-en-1-ol (2b)

Purified by column chromatography (20% EtOAc in Hexanes) to provide the desired product as a colorless oil (195 mg, 90% yield); 97% ee, $[\alpha]_D^{25}$ -102.1 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz,

Chloroform-*d*) δ 5.75 (ddt, *J* = 16.8, 10.0, 6.7 Hz, 1H), 5.18 – 5.00 (m, 2H), 4.28 (t, *J* = 4.6 Hz, 1H), 2.96 (ddtd, *J* = 6.7, 4.7, 1.5, 0.7 Hz, 2H), 2.21 – 2.02 (m, 2H), 1.95 – 1.84 (m, 2H), 1.83 – 1.72 (m, 1H), 1.69 – 1.53 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.5, 133.6, 123.6, 116.7, 71.1, 41.6, 32.0, 31.3, 18.3; IR (Neat film, NaCl) 3382, 2932, 1636, 1447, 1335, 1170, 1075, 993, 971, 917, 798, 699 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_9H_{12}Br$ [M-OH]$^+$: 199.0117, found 199.0126; SFC conditions: 10% IPA, Chiralpak IC column, λ = 210 nm, t_R (min): minor = 3.60, major = 4.05.



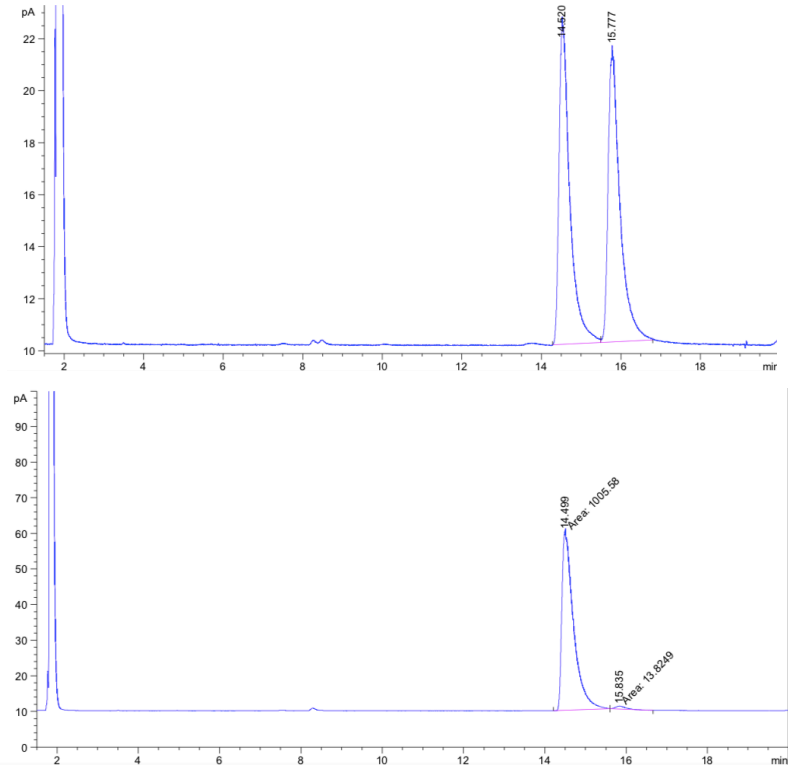
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.603	MM	0.1798	86.41930	8.01077	0.4970
2	4.054	MM	0.2430	1.73025e4	1186.70422	99.5030



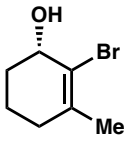
(*S*)-2-bromo-3-ethylcyclohex-2-en-1-ol (2c)

Purified by column chromatography (20% EtOAc in Hexanes) to provide the desired product as a white solid (203 mg, 99% yield); 97% ee, $[\alpha]_D^{25}$ -90.2 (c 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.23 (t, *J* = 4.6 Hz, 1H), 2.42 (s, 1H), 2.22 – 2.04 (m, 4H), 1.88 – 1.82 (m, 2H), 1.81 – 1.68 (m, 1H), 1.65 – 1.56 (m, 1H), 0.99 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.1, 122.0, 71.1, 32.1, 30.9, 30.4, 18.4, 11.4; IR (Neat film, NaCl) 3366, 2934, 2872, 1651, 1455, 1337, 1166, 1077, 978, 914, 801, 725 cm^{-1}; HRMS (MM: ESI-APCI+)

m/z calc'd for $C_8H_{12}Br$ $[M\text{-}OH]^+$: 187.0117, found 187.0123; Chiral GC: 120 ºC Isotherm, GTA column, FID detector, t_R (min): minor = 14.52, major = 15.77.

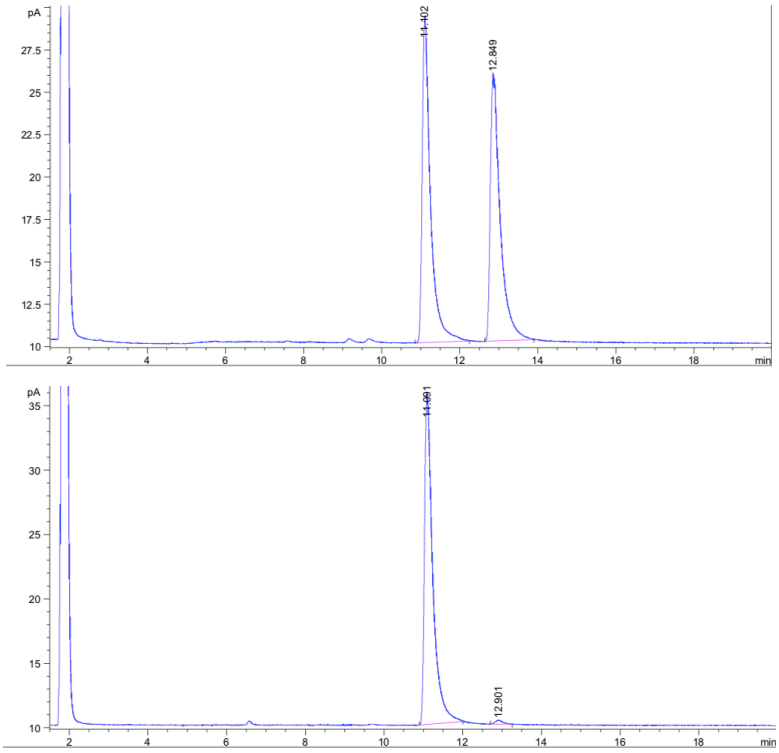


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	14.499	MM	0.3335	1005.58484	50.25248	98.64383
2	15.835	MM	0.2787	13.82488	8.26666e-1	1.35617

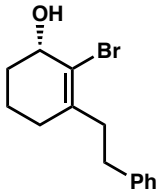


(*S*)-2-bromo-3-methylcyclohex-2-en-1-ol (2d)

Purified by column chromatography (20% EtOAc in Hexanes) to provide the desired product as a white solid (189 mg, 99% yield); 98% ee, $[\alpha]_D^{25}$ -100.5 (c 0.70, $CHCl_3$); ^1H NMR (500 MHz, Chloroform-*d*) δ 4.27 (tq, *J* = 4.6, 1.3 Hz, 1H), 2.25 – 2.03 (m, 3H), 1.92 – 1.86 (m, 2H), 1.86 – 1.83 (m, 3H), 1.83 – 1.75 (m, 1H), 1.67 – 1.60 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 137.1, 122.5, 71.0, 33.3, 32.0, 23.5, 18.2; IR (Neat film, NaCl) 3334, 2936, 2864, 1654, 1438, 1337, 1166, 1078, 1010, 978, 794 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_7H_{10}Br$ $[M\text{-}OH]^+$: 172.9960, found 172.9965; Chiral GC: 120 ºC Isotherm, GTA column, FID detector, t_R (min): minor = 11.10, major = 12.84.

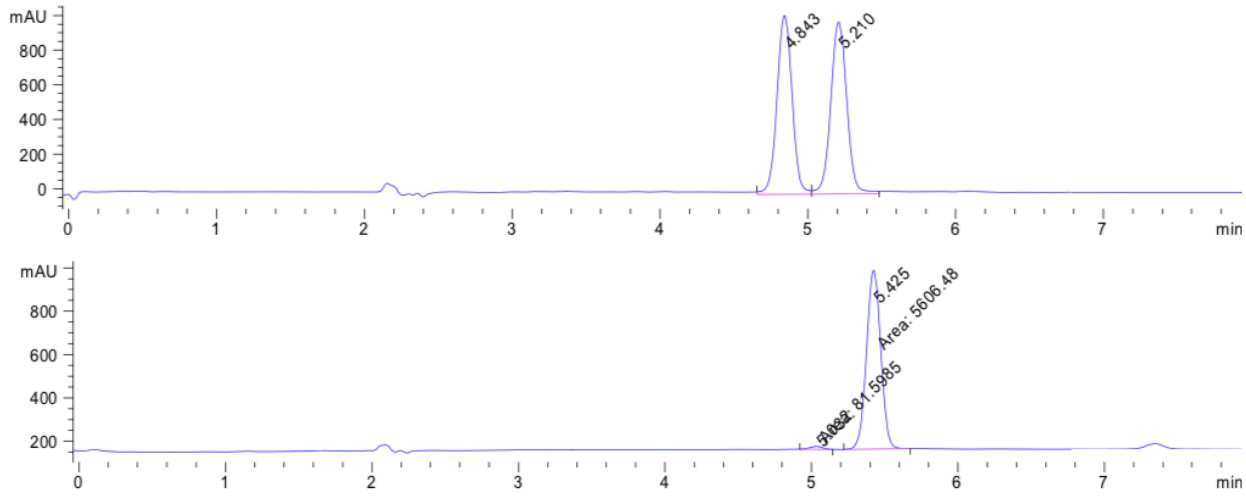


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	11.091	BB	0.1957	376.59824	25.59542	98.88320
2	12.901	BB	0.1603	4.25337	3.17541e-1	1.11680



(*S*)-2-bromo-3-phenethylcyclohex-2-en-1-ol (2e)

Purified by column chromatography (20% EtOAc in Hexanes) to provide the desired product as a white solid (278 mg, 99% yield); 97% ee, $[\alpha]_D^{25}$ -50.2 (c 0.70, $CHCl_3$); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 8.0, 3.1 Hz, 3H), 4.31 – 4.26 (m, 1H), 2.80 – 2.73 (m, 2H), 2.49 (ddt, *J* = 13.6, 7.3, 3.4 Hz, 2H), 2.35 (s, 1H), 2.20 – 2.02 (m, 2H), 1.88 (dd, *J* = 7.9, 4.5 Hz, 2H), 1.83 – 1.71 (m, 1H), 1.63 (dt, *J* = 13.6, 5.1 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.4, 140.2, 128.4, 128.4, 126.1, 123.5, 71.1, 39.3, 33.3, 32.0, 31.9, 18.3; IR (Neat film, NaCl) 3390, 2934, 2863, 1495, 1454, 1335, 1077, 972, 748, 699cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{16}Br$ $[M\text{-}OH]^+$: 263.0430, found 263.0420; SFC conditions: 15% IPA, Chiralpak OJ-H column, λ = 210 nm, t_R (min): minor = 5.03, major = 5.43.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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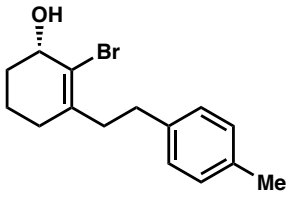
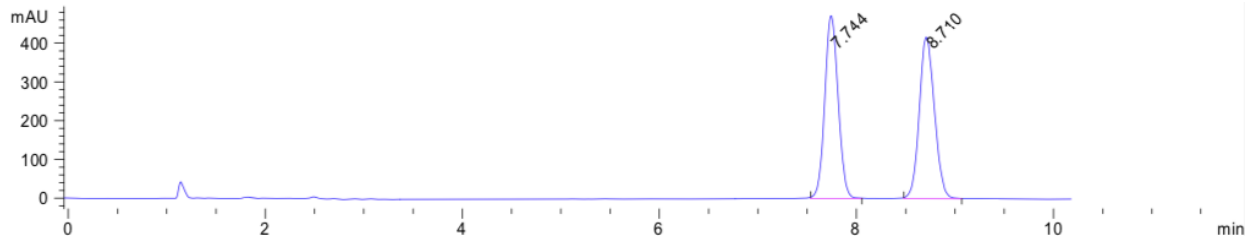
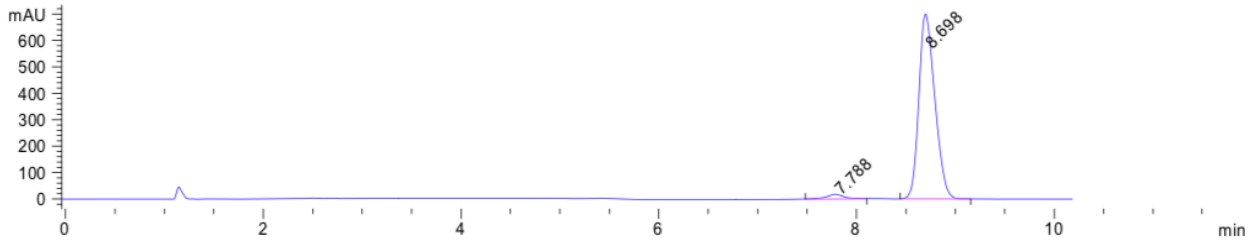
2	5.425	MM	0.1130	5606.47754	826.75659	98.5654



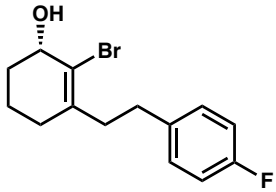
(*S*)-2-bromo-3-(4-methylphenethyl)cyclohex-2-en-1-ol (2f)

Purified by column chromatography (20% EtOAc in Hexanes) to provide the desired product as a white solid (292 mg, 99% yield); 94% ee, $[\alpha]_D^{25}$ -59.4 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 (s, 3H), 4.35 (t, *J* = 4.6 Hz, 1H), 2.86 – 2.71 (m, 2H), 2.55 (tdq, *J* = 11.3, 7.8, 3.5 Hz, 3H), 2.41 (s, 3H), 2.30 – 2.07 (m, 2H), 2.01 – 1.89 (m, 2H), 1.84 (dddd, *J* = 14.1, 10.4, 8.5, 5.3 Hz, 1H), 1.75 – 1.65 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.3, 138.4, 135.5, 129.1, 128.3, 123.4, 71.2, 39.5, 32.9, 32.1, 31.9, 21.1, 18.4; IR (Neat film, NaCl) 3392, 2932, 2863, 1514, 1454, 1334, 1249, 1163, 1076, 806, 610 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}Br$ $[M\text{-}OH]^+$: 277.0586, found 277.0574; SFC conditions: 10% IPA, Chiralpak OJ-H column, λ = 210 nm, t_R (min): minor = 7.79, major = 8.70.



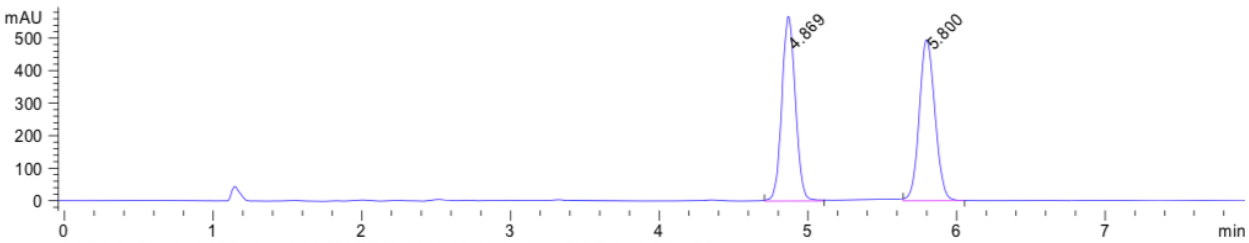


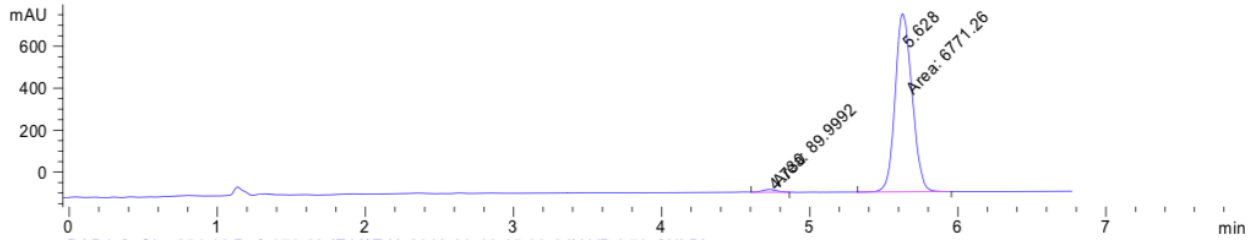
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.788	BB	0.1804	227.66461	18.14277	2.8211
2	8.698	BB	0.1728	7842.54199	699.57501	97.1789



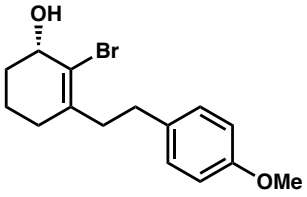
(*S*)-2-bromo-3-(4-fluorophenethyl)cyclohex-2-en-1-ol (2g)

Purified by column chromatography (20% AcOEt in Hexanes) to provide the desired product as a white solid (296 mg, 99% yield); 97% ee, $[\alpha]_D^{25}$ -59.9 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 – 7.13 (m, 2H), 7.00 – 6.94 (m, 2H), 4.27 (t, *J* = 4.7 Hz, 1H), 2.72 (ddd, *J* = 9.0, 6.9, 2.5 Hz, 2H), 2.53 – 2.39 (m, 2H), 2.26 (s, 1H), 2.18 – 1.99 (m, 2H), 1.92 – 1.83 (m, 2H), 1.76 (dtt, *J* = 16.7, 8.4, 5.4 Hz, 1H), 1.70 – 1.54 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4 (d, *J* = 243.7 Hz), 139.9, 136.9 (d, *J* = 3.3 Hz), 129.8 (d, *J* = 7.8 Hz), 123.7, 115.1 (d, *J* = 21.2 Hz), 71.1, 39.3, 32.4, 31.9, 31.9, 18.3; ^{19}F NMR (282 MHz, Chloroform-*d*) δ -117.34 (tt, *J* = 8.9, 5.4 Hz); IR (Neat film, NaCl) 3392, 2932, 2864, 1600, 1509, 1221, 1157, 1076, 973, 825 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{14}H_{15}BrF$ $[M\text{-}OH]^+$: 281.0336, found 281.0327; SFC conditions: 10% IPA, Chiralpak OJ-H column, λ=210, t_R (min): minor = 4.73, major = 5.63.



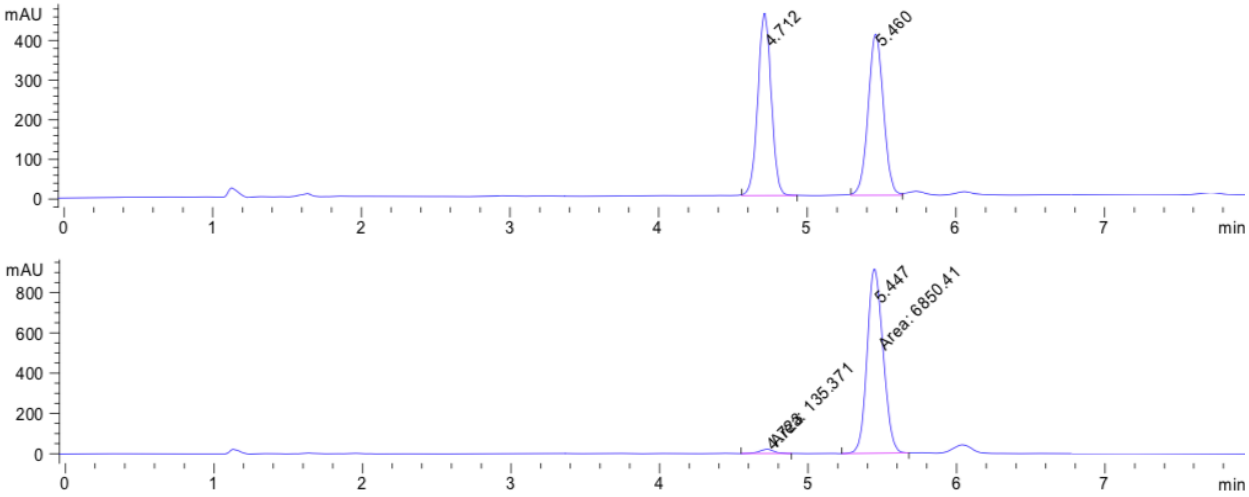


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.730	MM	0.1080	89.99923	13.88285	1.3117
2	5.628	MM	0.1327	6771.25830	850.20990	98.6883

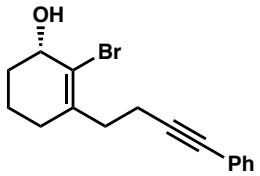


(*S*)-2-bromo-3-(4-methoxyphenethyl)cyclohex-2-en-1-ol (2h)

Purified by column chromatography (20% AcOEt in Hexanes) to provide the desired product as a white solid (308 mg, 99% yield); 96% ee, $[\alpha]_D^{25}$ -59.9 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.19 – 7.08 (m, 2H), 6.91 – 6.67 (m, 2H), 4.27 (t, *J* = 4.6 Hz, 1H), 3.80 (s, 3H), 2.75 – 2.67 (m, 2H), 2.50 – 2.40 (m, 2H), 2.35 (s, 1H), 2.19 – 2.00 (m, 2H), 1.92 – 1.84 (m, 2H), 1.76 (dtt, *J* = 19.6, 8.7, 5.3 Hz, 1H), 1.68 – 1.56 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.0, 140.3, 133.5, 129.4, 123.5, 113.9, 71.2, 55.4, 39.6, 32.5, 32.1, 32.0, 18.4; IR (Neat film, NaCl) 3380, 2935, 2863, 1611, 1511, 1454, 1243, 1174, 1033, 972, 818, 728 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{15}H_{18}BrO$ $[M\text{-}OH]^+$: 293.0535, found 293.0527; SFC conditions: 20 % IPA, Chiralpak OJ-H column, λ = 210 nm, t_R (min): minor = 4.72, major = 5.45.

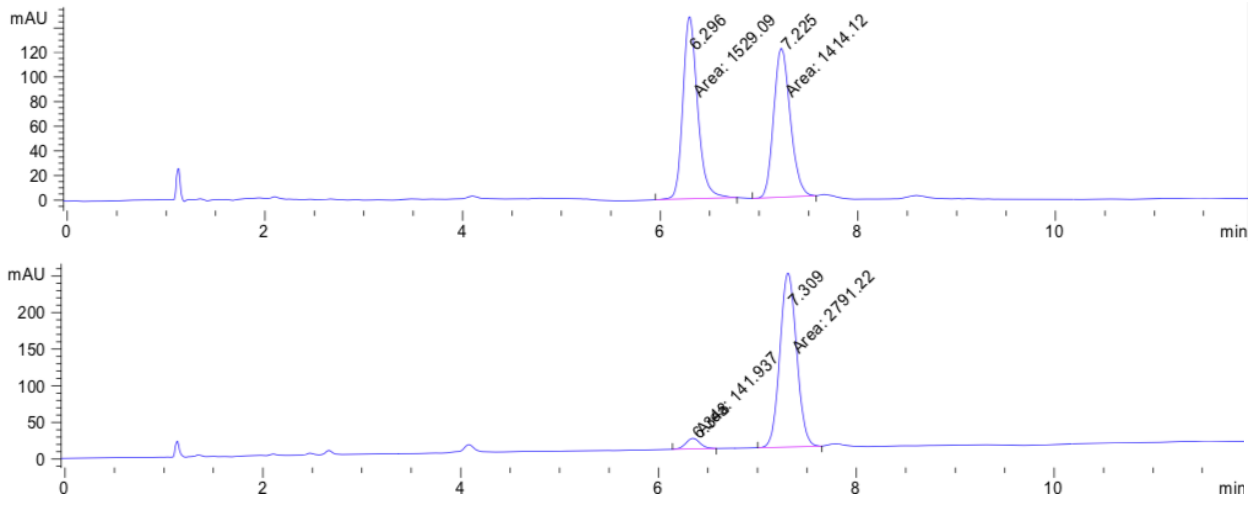


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.723	MM	0.1043	135.37074	21.64034	1.9378
2	5.447	MM	0.1246	6850.41064	916.15576	98.0622



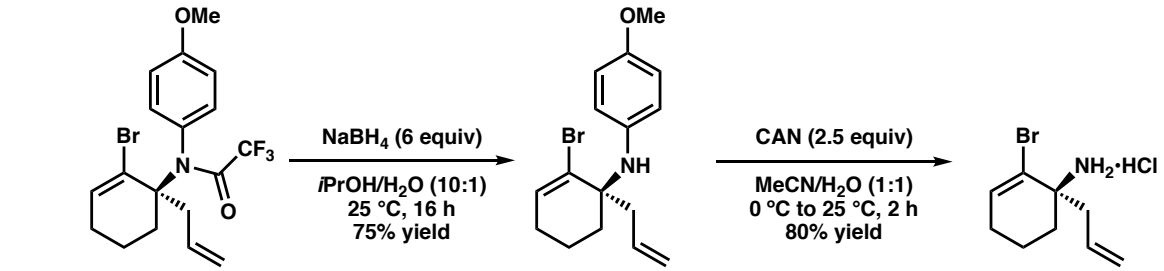
(*S*)-2-bromo-3-(4-phenylbut-3-yn-1-yl)cyclohex-2-en-1-ol (2i)

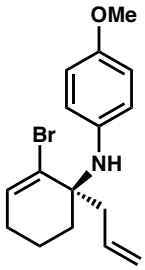
Purified by column chromatography (20% Et_2O in Hexanes) to provide the desired product as a brown oil (213 mg, 70% yield); 91% ee, $[\alpha]_D^{25}$ -62.8 (c 0.70, $CHCl_3$); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.42 – 7.36 (m, 2H), 7.31 – 7.26 (m, 3H), 4.29 (t, *J* = 4.7 Hz, 1H), 2.59 (ddd, *J* = 7.1, 6.3, 3.1 Hz, 2H), 2.52 (dd, *J* = 8.7, 7.0 Hz, 2H), 2.30 (dtd, *J* = 17.2, 5.1, 1.2 Hz, 2H), 2.25 – 2.19 (m, 1H), 1.91 (dt, *J* = 9.5, 4.6 Hz, 2H), 1.87 – 1.76 (m, 1H), 1.71 – 1.61 (m, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 139.3, 131.5, 128.3, 127.7, 124.2, 123.7, 89.0, 81.2, 71.1, 36.2, 32.0, 32.0, 18.3, 17.3; IR (Neat film, NaCl) 3432, 2933, 2864, 2364, 1681, 1597, 1489, 1442, 1335, 1272, 1175, 1076, 977, 757, 692 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{16}Br$ $[M\text{-}OH]^+$: 287.0430, found 287.0437; SFC conditions: 20% IPA, Chiralpak AD-H column, λ = 210 nm, t_R (min): minor = 6.35, major = 7.31.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.348	MM	0.1645	141.93741	14.37658	4.8391
2	7.309	MM	0.1956	2791.22119	237.77579	95.1609

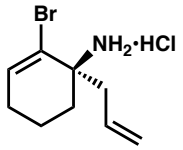
Product Derivatization





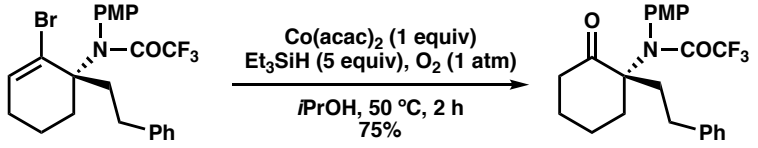
(*S*)-*N*-(1-allyl-2-bromocyclohex-2-en-1-yl)-4-methoxyaniline (4)[4]

To a stirred solution of **3b** (209 mg, 0.5 mmol) in 10:1 *i*PrOH/H_2O (2.5 mL) was added $NaBH_4$ (115 mg, 3 mmol) and the resulting mixture stirred for 16 h at 25 °C. The crude reaction was diluted with H_2O and extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried with $MgSO_4$ and concentrated. The crude product was purified by silica gel column chromatography (2:1 CH_2Cl_2/hexanes) to afford the desired product as a brown oil (120 mg, 75% yield). $[\alpha]_D^{25}$ -18.1 (c 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.81 – 6.72 (m, 4H), 6.31 (dd, *J* = 4.9, 3.5 Hz, 1H), 5.88 (dddd, *J* = 16.5, 10.2, 8.7, 6.1 Hz, 1H), 5.29 – 5.18 (m, 2H), 3.75 (s, 3H), 3.57 (d, *J* = 7.5 Hz, 1H), 2.61 – 2.42 (m, 2H), 2.26 – 1.99 (m, 3H), 1.89 – 1.51 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 153.5, 138.9, 133.3, 132.9, 119.8, 119.7, 114.4, 59.5, 55.6, 44.5, 30.8, 27.6, 19.7; IR (Neat film, NaCl) 3493, 2621, 1636, 1512, 1258, 937, 738 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{16}H_{21}BrNO$ $[M+H]^+$ 322.0801, found 322.0794.



(*S*)-1-allyl-2-bromocyclohex-2-en-1-aminium Chloride (5)[4]

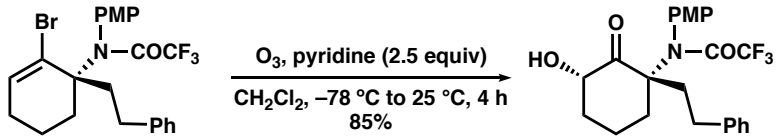
A solution of PMP-protected amine **4** (65 mg, 0.2 mmol) in 6.0 mL MeCN was cooled in an ice-bath and treated with a solution of CAN (275 mg, 0.5 mmol, 2.5 equiv) in water (6 mL) dropwise. The reaction allowed to warm to 25 °C and stirred for 3 h. The crude reaction was diluted with water, washed with Et_2O, and the organic layer discarded. The aqueous layer was basified to pH 10 with a saturated Na_2CO_3 solution and extracted with Et_2O. The combined organic layers were dried with $MgSO_4$ and treated with a 1 M HCl solution in Et_2O, and concentrated to afford the hydrochloride salt of the product as a white solid (40 mg, 80% yield). $[\alpha]_D^{25}$ 51.0 (c 0.70, $CHCl_3$); ^{1}H NMR (500 MHz, Methanol-d_4) δ 6.51 (t, J = 4.1 Hz, 1H), 5.73 (dddd, J = 16.6, 10.1, 8.1, 6.3 Hz, 1H), 5.33 – 5.20 (m, 2H), 2.69 (dd, J = 14.0, 6.3 Hz, 1H), 2.56 (dd, J = 14.0, 8.1 Hz, 1H), 2.26 – 2.04 (m, 3H), 2.04 – 1.91 (m, 2H), 1.84 – 1.67 (m, 2H); ^{13}C NMR (100 MHz, Methanol-d_4) δ 138.3, 129.9, 121.3, 120.7, 58.2, 41.6, 32.2, 27.2, 17.2; IR (Neat film, NaCl) 2933, 2863, 1603 1515, 1447, 361, 984, 925, 761, 681 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_9H_{15}BrN$ $[M\text{-}Cl]^+$, 216.0382, found 216.0372.



(*S*)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)-*N*-(2-oxo-1-phenethylcyclohexyl)acetamide (6)[5]

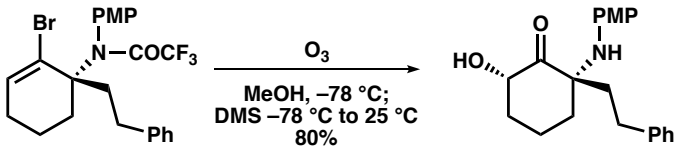
A vial was charged with $Co(acac)_2$ (90 mg, 0.35 mmol, 1.00 equiv) and the vial was evacuated and backfilled with oxygen three times. Isopropanol was then added (2 mL) followed by starting material **3e** (170 mg, 0.35 mmol, 1.00 equiv) and Et_3SiH (280 μL, 1.75 mmol, 5 equiv). The resulting mixture was heated to 50 °C for 2 h under a balloon of oxygen. The crude reaction mixture was directly concentrated and purified by silica gel column chromatography (20% EtOAc/hexanes) to provide the desired product as a colorless oil (110 mg, 75% yield). $[\alpha]_D^{25}$ 72.1 (c 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.43 (m, 1H), 7.30 – 7.09 (m, 4H), 6.95 (ddd, J = 13.1, 8.7, 2.9 Hz, 2H), 6.81 (dt, J = 6.3, 1.4 Hz, 2H), 3.86 (s, 3H), 2.73 (dtd,

J = 15.9, 4.5, 1.8 Hz, 1H), 2.51 – 2.34 (m, 2H), 2.33 – 1.85 (m, 8H), 1.85 – 1.58 (m, 3H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.0, 160.4, 157.3 (q, *J* = 35.1 Hz), 140.9, 132.4, 131.8, 128.5, 128.1, 127.7, 126.2, 122.3, 116.3 (q, *J* = 288.3 Hz), 114.0, 113.9, 72.0, 55.6, 40.1, 36.5, 36.1, 30.4, 25.1, 22.6; IR (Neat film, NaCl) 2945, 1720, 1962, 1510, 1300, 1252, 1185, 1203, 1155, 1032, 737, 703 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{25}F_3NO_3$ $[M+H]^+$: 420.1786, found 420.1796.



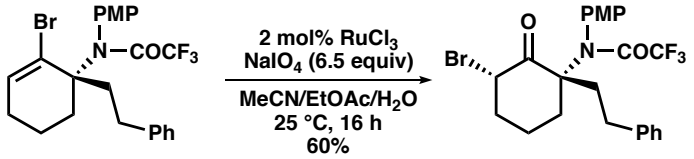
2,2,2-trifluoro-*N*-((1*S*,3*S*)-3-hydroxy-2-oxo-1-phenethylcyclohexyl)-*N*-(4-methoxyphenyl)acetamide (7)

To a solution of **3e** (96 mg, 0.2 mmol, 1 equiv) in wet CH_2Cl_2 (0.1 M) was added pyridine (40 μL, 0.5 mmol, 2.5 equiv). This solution was then cooled to –78 ºC and O_3 was bubbled through until no starting material remained by TLC (~ 1 h). O_2 was then bubbled through the solution for 10 min and the reaction was allowed to warm up to 25 °C. After 3 h at 25 °C, the product was purified by column chromatography (20% to 50% EtOAc/hexanes) to provide the desired product as a white foam (75 mg, 85% yield). $[\alpha]_D^{25}$ 88.3 (c 1, $CHCl_3$); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.6 Hz, 1H), 7.18 (dt, *J* = 14.1, 7.8 Hz, 4H), 7.02 – 6.89 (m, 2H), 6.87 – 6.67 (m, 2H), 4.23 (dd, *J* = 11.9, 6.3 Hz, 1H), 3.86 (s, 3H), 3.60 (s, 1H), 2.50 – 2.29 (m, 3H), 2.16 (d, *J* = 34.0 Hz, 2H), 2.04 (d, *J* = 12.2 Hz, 1H), 2.00 – 1.73 (m, 4H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.4, 160.5, 157.2 (q, *J* = 35.1 Hz), 140.2, 132.5, 132.1, 128.5, 128.0, 126.3, 116.2 (q, *J* = 288.5 Hz), 114.1, 113.9, 74.2, 72.5, 55.5, 36.4, 35.3, 30.2, 19.7; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.4; IR (Neat film, NaCl) 3469, 2939, 1723, 1693, 1509, 1455, 1251, 1201, 1184, 1154, 1030, 759, 701 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{23}H_{25}F_3NO_4$ $[M+H]^+$: 436.1735, found 436.1733.



(2*S*,6*S*)-6-hydroxy-2-((4-methoxyphenyl)amino)-2-phenethylcyclohexan-1-one (8)

A solution of **3e** (96 mg, 0.2 mmol, 1.00 equiv) in wet MeOH (0.1 M) was cooled to –78 ºC and O_3 was bubbled through until no starting material remained by TLC (~30 min). O_2 was then bubbled through for 10 min and DMS (55 μL, 0.6 mmol, 3 equiv) was added. The reaction was allowed to warm up to 25 °C and stirred overnight. The reaction was washed with a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The crude product was purified by column chromatography (20% to 50% EtOAc/hexanes) to provide the desired product as an amorphous brown solid (55 mg, 80% yield). $[\alpha]_D^{25}$ 50.2 (c 1, $CHCl_3$); ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.25 – 7.21 (m, 2H), 7.19 – 7.14 (m, 1H), 6.98 – 6.93 (m, 2H), 6.82 – 6.74 (m, 4H), 4.47 (dd, *J* = 12.3, 6.8 Hz, 1H), 3.78 (s, 3H), 2.73 – 2.62 (m, 1H), 2.57 – 2.44 (m, 2H), 2.32 (ddd, *J* = 14.2, 12.2, 4.6 Hz, 1H), 2.25 – 2.08 (m, 2H), 1.89 – 1.77 (m, 3H), 1.55 (dddd, *J* = 12.6, 10.6, 8.7, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 212.1, 153.5, 141.0, 138.1, 128.5, 128.3, 126.2, 120.1, 114.6, 72.9, 66.9, 55.7, 40.9, 37.1, 37.0, 29.5, 19.2; IR (Neat film, NaCl) 3374, 2948, 1711, 1510, 1454, 1237, 1035, 826, 700 cm^{-1}; HRMS (MM: ESI-APCI+) *m/z* calc'd for $C_{21}H_{26}NO_3$ $[M+H]^+$: 340.1912, found 340.1923.



***N*-((1*S*,3*S*)-3-bromo-2-oxo-1-phenethylcyclohexyl)-2,2,2-trifluoro-*N*-(4-methoxyphenyl)acetamide (9)**

To a solution of **3e** (96 mg, 0.2 mmol, 1.00 equiv) in H_2O (0.55 mL), acetonitrile (1.25 mL), and EtOAc (1.25 mL) was added sodium periodate ($NaIO_4$, 274 mg, 1.28 mmol, 6.40 equiv) and ruthenium(III) trichloride ($RuCl_3$, 4 μL, 0.1 M solution in H_2O, 0.02 equiv). The reaction mixture was then stirred at room temperature for 18 h, at which time consumption of starting material was complete as determined by TLC analysis. The crude reaction mixture was washed with a saturated solution of $NaHCO_3$, and the aqueous layer extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The crude

product was purified by column chromatography (20% EtOAc/hexanes) to provide the desired product as a white foam (60 mg, 60% yield). $[\alpha]_D^{25}$ 50.2 (c 1.0, $CHCl_3$); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.55 (ddd, *J* = 8.7, 2.7, 1.1 Hz, 1H), 7.23 – 7.10 (m, 4H), 6.99 (ddd, *J* = 21.4, 8.7, 3.0 Hz, 2H), 6.85 – 6.74 (m, 2H), 4.80 (d, *J* = 1.3 Hz, 1H), 3.89 (s, 3H), 2.69 (ddq, *J* = 14.5, 10.7, 3.5 Hz, 1H), 2.49 – 2.36 (m, 2H), 2.31 – 2.16 (m, 3H), 2.02 (dtt, *J* = 13.9, 8.3, 2.8 Hz, 2H), 1.85 (s, 1H), 1.80 (ddd, *J* = 15.3, 10.8, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, Chloroform-*d*) δ 196.6, 160.6, 157.6 (q, *J* = 35.8 Hz), 141.0, 132.4, 131.4, 128.4, 128.2, 126.8, 126.1, 116.1 (q, *J* = 287.9 Hz), 114.3, 113.9, 71.3, 55.7, 51.3, 38.7, 37.2, 34.3, 30.5, 18.9; ^{19}F NMR (282 MHz, Chloroform-*d*) δ –67.5; IR (Neat film, NaCl) 3493, 2942, 1716, 1682, 1509, 1455, 1254, 1206, 1184, 1165, 1031, 752 cm^{-1}; HRMS (MM:ESI-APCI+) *m/z* calc'd for $C_{23}H_{24}BrF_3NO_3$ $[M+H]^+$: 498.0891, found 498.0891.

X-Ray Crystal Structure for 8 (V19265)

An X-ray crystal structure of compound ***8*** (V19265) was grown by vapor diffusion.

Figure S1. X-Ray Coordinate of compound 8 (V19265)

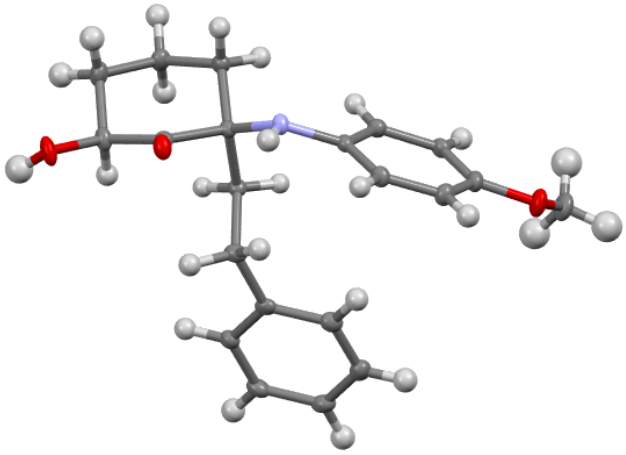


Table 1. Crystal data and structure refinement for V19265.

Empirical formula	C21 H25 N O3
Formula weight	339.42
Temperature	100(2) K
Wavelength	1.54178 Å

Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 5.9218(7) Å	a= 90°.
	b = 7.5604(10) Å	b= 90°.
	c = 41.115(6) Å	g = 90°.
Volume	1840.8(4) $Å^3$	
Z	4	
Density (calculated)	1.225 Mg/m^3	
Absorption coefficient	0.650 mm^{-1}	
F(000)	728	
Crystal size	0.300 x 0.100 x 0.100 mm^3	
Theta range for data collection	4.301 to 79.710°.	
Index ranges	-5<=h<=7, -8<=k<=9, -51<=l<=50	
Reflections collected	19853	
Independent reflections	3921 [R(int) = 0.0518]	
Completeness to theta = 67.679°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7451 and 0.6491	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3921 / 2 / 233	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0714	
R indices (all data)	R1 = 0.0340, wR2 = 0.0731	
Absolute structure parameter	-0.02(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.184 and -0.169 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 104) and equivalent isotropic displacement parameters (Å2x 103) for V19265. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
N(1)	2984(2)	4882(2)	3921(1)	16(1)
C(1)	4851(2)	5030(2)	4154(1)	14(1)
C(2)	3912(3)	5870(2)	4466(1)	15(1)
O(1)	1984(2)	6407(2)	4486(1)	20(1)
C(3)	5573(3)	5965(2)	4746(1)	19(1)
O(2)	4536(2)	6809(2)	5013(1)	24(1)
C(4)	6395(3)	4103(2)	4829(1)	23(1)
C(5)	7396(3)	3169(2)	4532(1)	21(1)
C(6)	5718(3)	3171(2)	4249(1)	18(1)
C(7)	3311(2)	4934(2)	3581(1)	15(1)
C(8)	5057(3)	4034(2)	3423(1)	17(1)
C(9)	5305(3)	4126(2)	3086(1)	18(1)
C(10)	3762(3)	5069(2)	2900(1)	19(1)
O(3)	3866(2)	5233(2)	2566(1)	26(1)
C(13)	5968(3)	4833(3)	2416(1)	29(1)
C(11)	1965(3)	5913(2)	3053(1)	20(1)
C(12)	1766(3)	5864(2)	3389(1)	18(1)
C(14)	6760(2)	6244(2)	4026(1)	15(1)
C(15)	5972(3)	8156(2)	3974(1)	19(1)
C(16)	7559(3)	9143(2)	3752(1)	17(1)
C(17)	7148(3)	9212(2)	3419(1)	20(1)
C(18)	8634(3)	10088(2)	3211(1)	22(1)
C(19)	10541(3)	10910(2)	3336(1)	22(1)
C(20)	10992(3)	10823(2)	3668(1)	22(1)
C(21)	9512(3)	9938(2)	3874(1)	19(1)

Table 3. Bond lengths [Å] and angles [°] for V19265.

N(1)-C(7)	1.4128(18)
N(1)-C(1)	1.4668(19)
N(1)-H(1N)	0.894(18)
C(1)-C(2)	1.534(2)
C(1)-C(6)	1.546(2)
C(1)-C(14)	1.548(2)
C(2)-O(1)	1.214(2)
C(2)-C(3)	1.518(2)
C(3)-O(2)	1.4111(19)
C(3)-C(4)	1.528(2)
C(3)-H(3)	1.0000
O(2)-H(2O)	0.87(2)
C(4)-C(5)	1.529(2)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.532(2)
C(5)-H(5A)	0.9900
C(5)-H(5B)	0.9900
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.398(2)
C(7)-C(12)	1.399(2)
C(8)-C(9)	1.396(2)
C(8)-H(8)	0.9500
C(9)-C(10)	1.388(2)
C(9)-H(9)	0.9500
C(10)-O(3)	1.3786(18)
C(10)-C(11)	1.392(2)
O(3)-C(13)	1.421(2)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(11)-C(12)	1.387(2)
C(11)-H(11)	0.9500

C(12)-H(12)	0.9500
C(14)-C(15)	1.535(2)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(16)	1.507(2)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.395(2)
C(16)-C(21)	1.396(2)
C(17)-C(18)	1.394(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.388(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.389(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.392(2)
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500

C(7)-N(1)-C(1)	122.78(12)
C(7)-N(1)-H(1N)	110.0(13)
C(1)-N(1)-H(1N)	111.4(14)
N(1)-C(1)-C(2)	107.64(12)
N(1)-C(1)-C(6)	110.24(12)
C(2)-C(1)-C(6)	106.67(12)
N(1)-C(1)-C(14)	111.97(12)
C(2)-C(1)-C(14)	107.59(12)
C(6)-C(1)-C(14)	112.43(12)
O(1)-C(2)-C(3)	122.75(14)
O(1)-C(2)-C(1)	122.50(13)
C(3)-C(2)-C(1)	114.75(13)
O(2)-C(3)-C(2)	109.31(13)
O(2)-C(3)-C(4)	112.41(13)
C(2)-C(3)-C(4)	109.45(13)
O(2)-C(3)-H(3)	108.5
C(2)-C(3)-H(3)	108.5

C(4)-C(3)-H(3)	108.5
C(3)-O(2)-H(2O)	107.7(17)
C(3)-C(4)-C(5)	111.77(13)
C(3)-C(4)-H(4A)	109.3
C(5)-C(4)-H(4A)	109.3
C(3)-C(4)-H(4B)	109.3
C(5)-C(4)-H(4B)	109.3
H(4A)-C(4)-H(4B)	107.9
C(4)-C(5)-C(6)	110.78(13)
C(4)-C(5)-H(5A)	109.5
C(6)-C(5)-H(5A)	109.5
C(4)-C(5)-H(5B)	109.5
C(6)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	108.1
C(5)-C(6)-C(1)	114.11(13)
C(5)-C(6)-H(6A)	108.7
C(1)-C(6)-H(6A)	108.7
C(5)-C(6)-H(6B)	108.7
C(1)-C(6)-H(6B)	108.7
H(6A)-C(6)-H(6B)	107.6
C(8)-C(7)-C(12)	117.76(13)
C(8)-C(7)-N(1)	123.25(14)
C(12)-C(7)-N(1)	118.93(13)
C(9)-C(8)-C(7)	121.04(14)
C(9)-C(8)-H(8)	119.5
C(7)-C(8)-H(8)	119.5
C(10)-C(9)-C(8)	120.19(14)
C(10)-C(9)-H(9)	119.9
C(8)-C(9)-H(9)	119.9
O(3)-C(10)-C(9)	124.37(15)
O(3)-C(10)-C(11)	116.30(14)
C(9)-C(10)-C(11)	119.34(14)
C(10)-O(3)-C(13)	116.80(13)
O(3)-C(13)-H(13A)	109.5
O(3)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5

O(3)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(12)-C(11)-C(10)	120.21(15)
C(12)-C(11)-H(11)	119.9
C(10)-C(11)-H(11)	119.9
C(11)-C(12)-C(7)	121.38(14)
C(11)-C(12)-H(12)	119.3
C(7)-C(12)-H(12)	119.3
C(15)-C(14)-C(1)	112.59(12)
C(15)-C(14)-H(14A)	109.1
C(1)-C(14)-H(14A)	109.1
C(15)-C(14)-H(14B)	109.1
C(1)-C(14)-H(14B)	109.1
H(14A)-C(14)-H(14B)	107.8
C(16)-C(15)-C(14)	111.21(12)
C(16)-C(15)-H(15A)	109.4
C(14)-C(15)-H(15A)	109.4
C(16)-C(15)-H(15B)	109.4
C(14)-C(15)-H(15B)	109.4
H(15A)-C(15)-H(15B)	108.0
C(17)-C(16)-C(21)	118.79(14)
C(17)-C(16)-C(15)	120.31(14)
C(21)-C(16)-C(15)	120.85(14)
C(18)-C(17)-C(16)	120.69(15)
C(18)-C(17)-H(17)	119.7
C(16)-C(17)-H(17)	119.7
C(19)-C(18)-C(17)	119.91(15)
C(19)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0
C(18)-C(19)-C(20)	119.96(15)
C(18)-C(19)-H(19)	120.0
C(20)-C(19)-H(19)	120.0
C(19)-C(20)-C(21)	120.02(15)
C(19)-C(20)-H(20)	120.0
C(21)-C(20)-H(20)	120.0

C(20)-C(21)-C(16)	120.60(14)
C(20)-C(21)-H(21)	119.7
C(16)-C(21)-H(21)	119.7

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for V19265. 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}
N(1)	13(1)	20(1)	14(1)	-2(1)	1(1)	-1(1)
C(1)	13(1)	15(1)	14(1)	-1(1)	0(1)	-1(1)
C(2)	15(1)	15(1)	16(1)	0(1)	2(1)	-4(1)
O(1)	14(1)	28(1)	17(1)	-5(1)	1(1)	1(1)
C(3)	16(1)	25(1)	15(1)	-6(1)	1(1)	1(1)
O(2)	18(1)	36(1)	18(1)	-14(1)	-1(1)	0(1)
C(4)	27(1)	28(1)	15(1)	-1(1)	-2(1)	4(1)
C(5)	24(1)	21(1)	18(1)	1(1)	-3(1)	4(1)
C(6)	22(1)	16(1)	16(1)	-1(1)	0(1)	1(1)
C(7)	17(1)	15(1)	14(1)	-1(1)	1(1)	-2(1)
C(8)	17(1)	16(1)	18(1)	0(1)	0(1)	1(1)
C(9)	20(1)	16(1)	18(1)	-3(1)	3(1)	1(1)
C(10)	22(1)	22(1)	13(1)	-1(1)	1(1)	-3(1)
O(3)	28(1)	37(1)	13(1)	0(1)	2(1)	4(1)
C(13)	32(1)	38(1)	16(1)	0(1)	7(1)	2(1)
C(11)	20(1)	23(1)	18(1)	2(1)	-1(1)	2(1)
C(12)	14(1)	20(1)	18(1)	-2(1)	2(1)	1(1)
C(14)	12(1)	15(1)	16(1)	0(1)	1(1)	-2(1)
C(15)	16(1)	16(1)	25(1)	0(1)	4(1)	0(1)
C(16)	18(1)	12(1)	22(1)	0(1)	4(1)	2(1)
C(17)	18(1)	18(1)	25(1)	0(1)	-2(1)	0(1)
C(18)	26(1)	20(1)	20(1)	2(1)	-1(1)	3(1)
C(19)	24(1)	16(1)	27(1)	2(1)	7(1)	0(1)
C(20)	21(1)	17(1)	28(1)	-3(1)	1(1)	-4(1)
C(21)	21(1)	16(1)	19(1)	-2(1)	1(1)	-1(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for V19265.

	x	y	z	U(eq)
H(1N)	1830(30)	5580(30)	3977(5)	24
H(3)	6901	6689	4676	22
H(2O)	5590(40)	7310(30)	5127(6)	36
H(4A)	5114	3399	4914	28
H(4B)	7554	4176	5002	28
H(5A)	7782	1934	4590	25
H(5B)	8802	3777	4466	25
H(6A)	4409	2423	4308	21
H(6B)	6454	2630	4057	21
H(8)	6091	3350	3547	20
H(9)	6533	3541	2983	22
H(13A)	7164	5541	2517	43
H(13B)	5885	5108	2184	43
H(13C)	6305	3573	2445	43
H(11)	870	6524	2927	24
H(12)	555	6475	3491	21
H(14A)	8024	6237	4184	18
H(14B)	7333	5765	3818	18
H(15A)	4439	8152	3878	23
H(15B)	5891	8770	4186	23
H(17)	5840	8657	3332	24
H(18)	8343	10122	2984	27
H(19)	11536	11532	3196	27
H(20)	12310	11368	3753	26
H(21)	9834	9875	4100	22

—

Table 6. Torsion angles [°] for V19265.

C(7)-N(1)-C(1)-C(2)	150.99(14)
C(7)-N(1)-C(1)-C(6)	-93.03(17)
C(7)-N(1)-C(1)-C(14)	32.94(19)
N(1)-C(1)-C(2)-O(1)	-5.1(2)
C(6)-C(1)-C(2)-O(1)	-123.39(16)
C(14)-C(1)-C(2)-O(1)	115.76(16)
N(1)-C(1)-C(2)-C(3)	174.48(13)
C(6)-C(1)-C(2)-C(3)	56.17(16)
C(14)-C(1)-C(2)-C(3)	-64.68(16)
O(1)-C(2)-C(3)-O(2)	-2.2(2)
C(1)-C(2)-C(3)-O(2)	178.20(13)
O(1)-C(2)-C(3)-C(4)	121.28(17)
C(1)-C(2)-C(3)-C(4)	-58.28(17)
O(2)-C(3)-C(4)-C(5)	176.86(14)
C(2)-C(3)-C(4)-C(5)	55.20(17)
C(3)-C(4)-C(5)-C(6)	-54.08(18)
C(4)-C(5)-C(6)-C(1)	54.73(18)
N(1)-C(1)-C(6)-C(5)	-170.37(12)
C(2)-C(1)-C(6)-C(5)	-53.78(16)
C(14)-C(1)-C(6)-C(5)	63.92(16)
C(1)-N(1)-C(7)-C(8)	43.0(2)
C(1)-N(1)-C(7)-C(12)	-139.76(15)
C(12)-C(7)-C(8)-C(9)	2.7(2)
N(1)-C(7)-C(8)-C(9)	179.92(14)
C(7)-C(8)-C(9)-C(10)	-2.3(2)
C(8)-C(9)-C(10)-O(3)	-179.95(15)
C(8)-C(9)-C(10)-C(11)	-0.3(2)
C(9)-C(10)-O(3)-C(13)	-17.7(2)
C(11)-C(10)-O(3)-C(13)	162.65(16)
O(3)-C(10)-C(11)-C(12)	-178.00(15)
C(9)-C(10)-C(11)-C(12)	2.3(3)
C(10)-C(11)-C(12)-C(7)	-1.9(3)
C(8)-C(7)-C(12)-C(11)	-0.7(2)
N(1)-C(7)-C(12)-C(11)	-178.00(15)

N(1)-C(1)-C(14)-C(15)	62.65(16)
C(2)-C(1)-C(14)-C(15)	-55.43(16)
C(6)-C(1)-C(14)-C(15)	-172.59(12)
C(1)-C(14)-C(15)-C(16)	-161.29(12)
C(14)-C(15)-C(16)-C(17)	93.17(17)
C(14)-C(15)-C(16)-C(21)	-84.11(18)
C(21)-C(16)-C(17)-C(18)	-1.2(2)
C(15)-C(16)-C(17)-C(18)	-178.53(15)
C(16)-C(17)-C(18)-C(19)	-0.4(2)
C(17)-C(18)-C(19)-C(20)	1.5(3)
C(18)-C(19)-C(20)-C(21)	-1.1(3)
C(19)-C(20)-C(21)-C(16)	-0.5(2)
C(17)-C(16)-C(21)-C(20)	1.6(2)
C(15)-C(16)-C(21)-C(20)	178.93(15)

Table 7. Hydrogen bonds for V19265 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)	0.894(18)	2.19(2)	2.6591(16)	112.5(16)
C(3)-H(3)...O(2)#1	1.00	2.31	3.053(2)	129.9
O(2)-H(2O)...O(1)#1	0.87(2)	2.04(2)	2.8566(16)	157(2)
O(2)-H(2O)...O(2)#1	0.87(2)	2.50(2)	3.1420(10)	132(2)
C(13)-H(13C)...O(3)#2	0.98	2.53	3.480(3)	163.8
C(14)-H(14A)...O(1)#3	0.99	2.66	3.6265(19)	166.6

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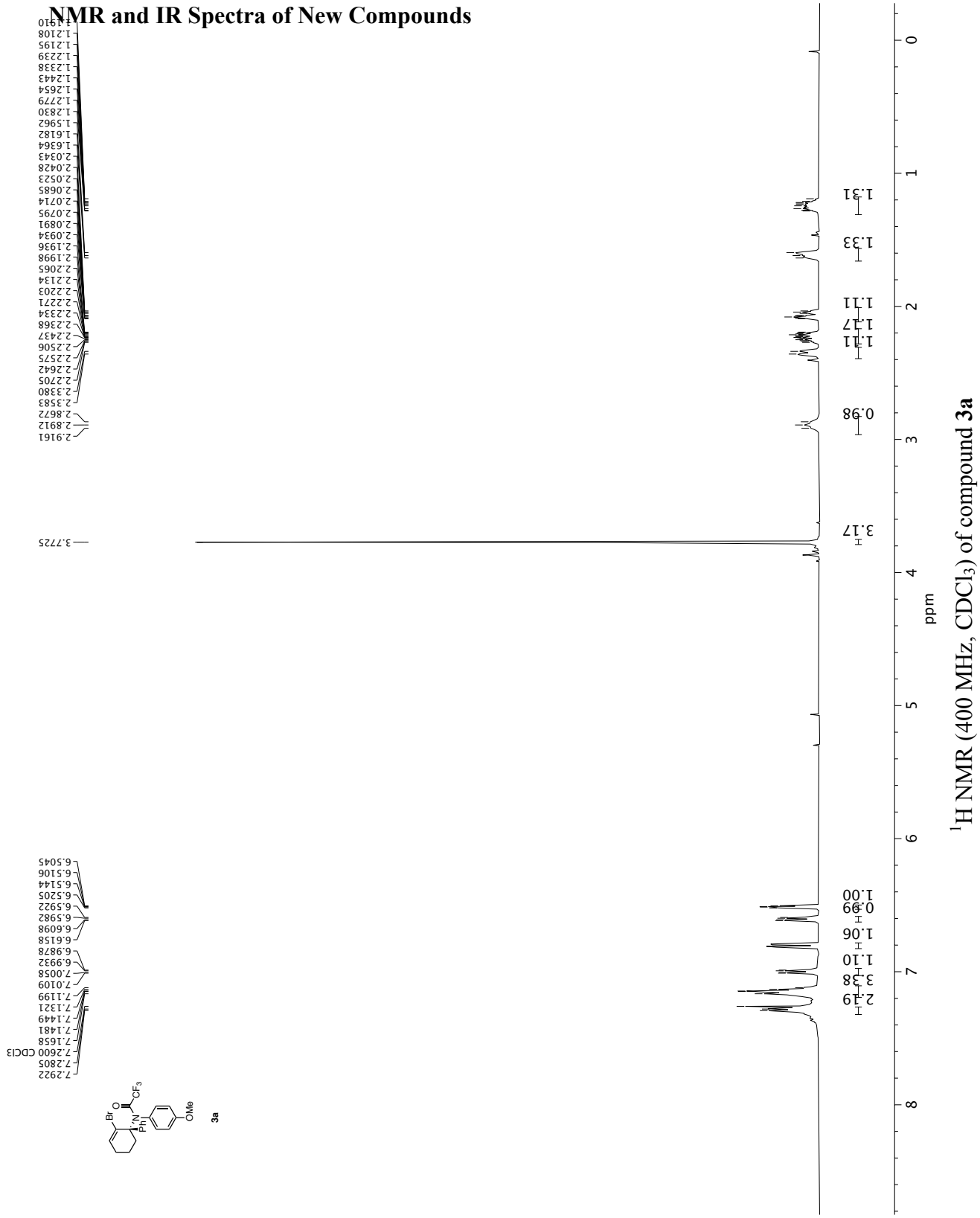
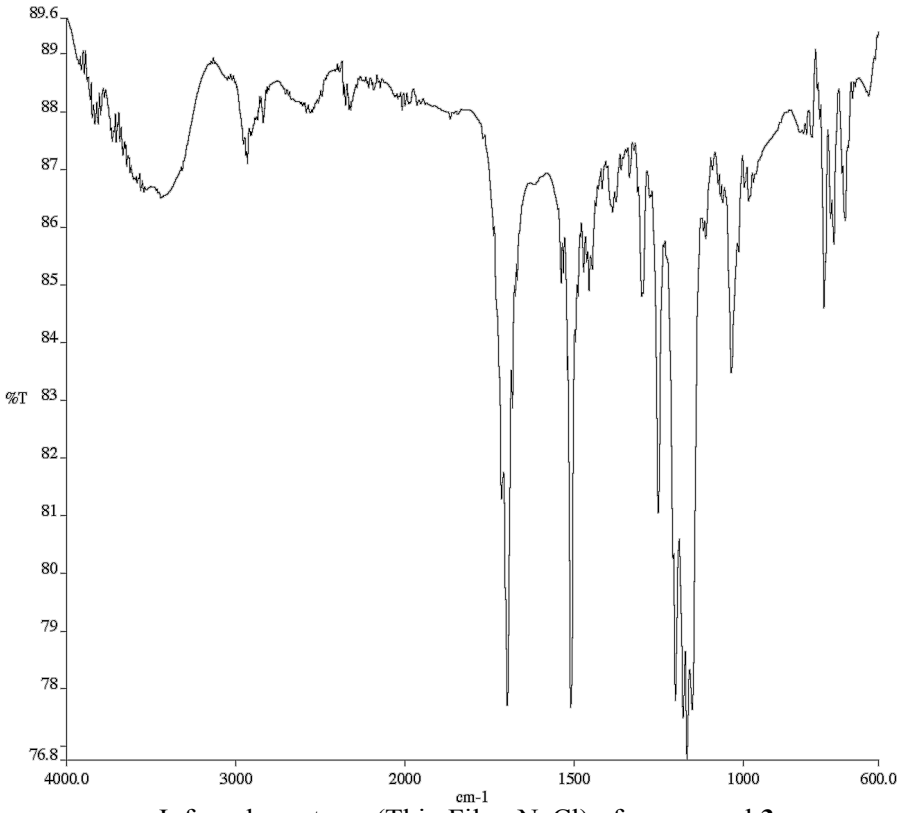
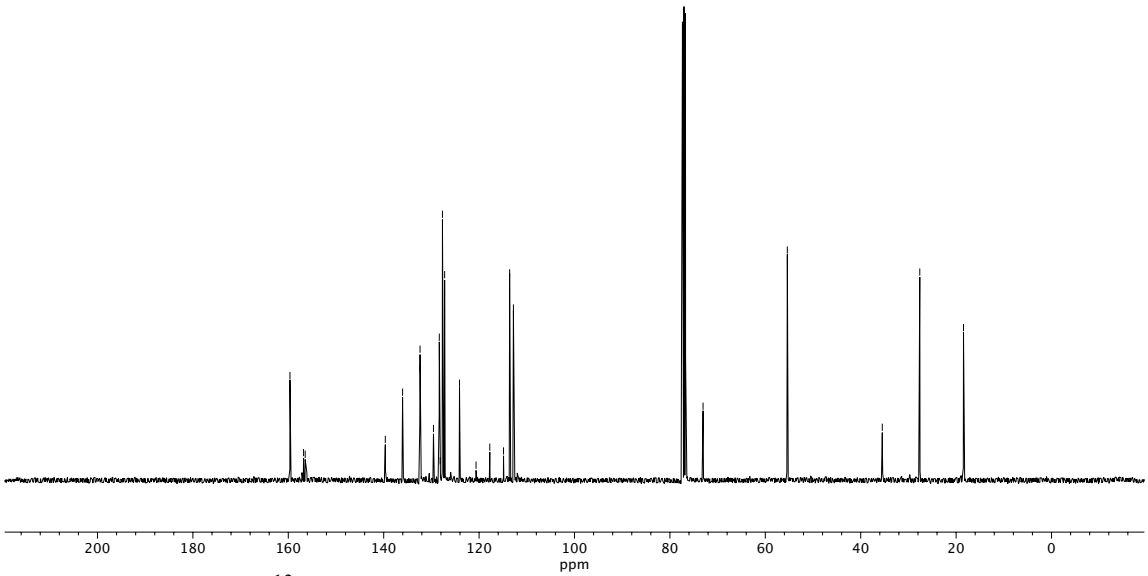
NMR and IR Spectra of New Compounds



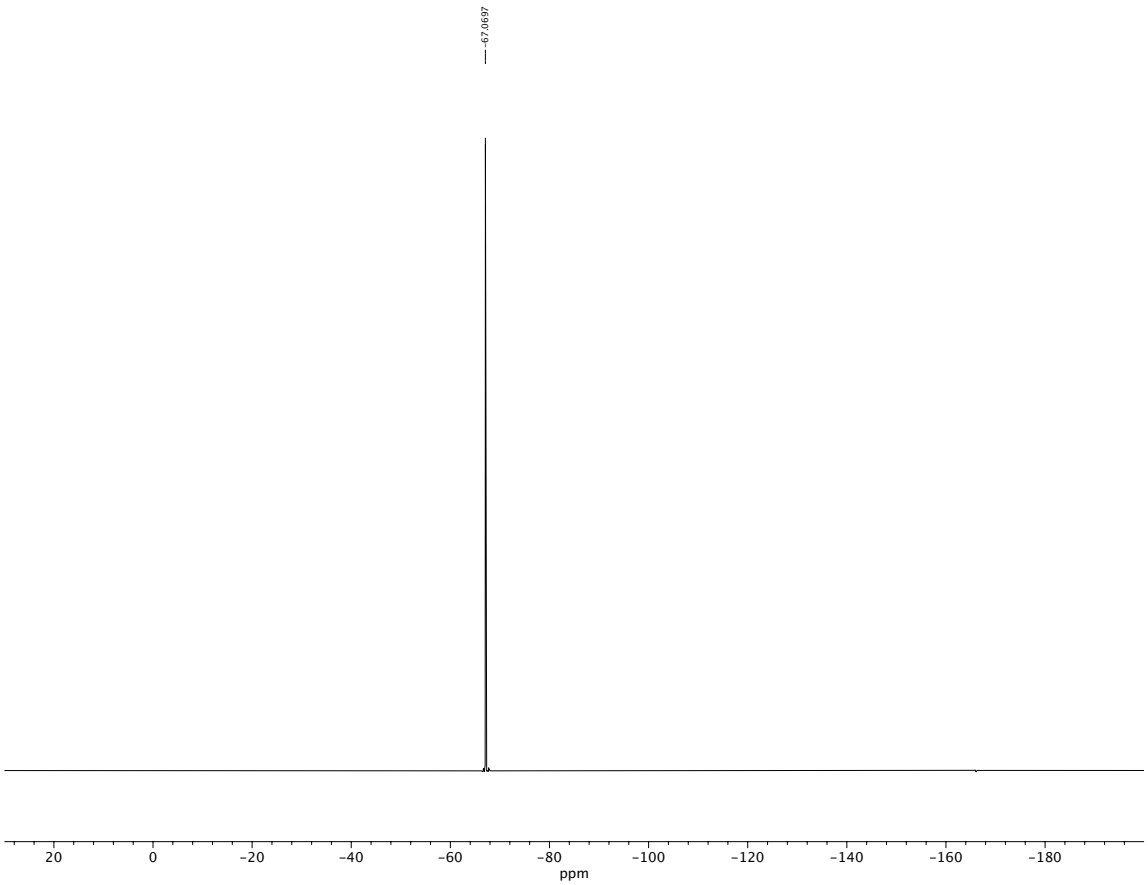
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**



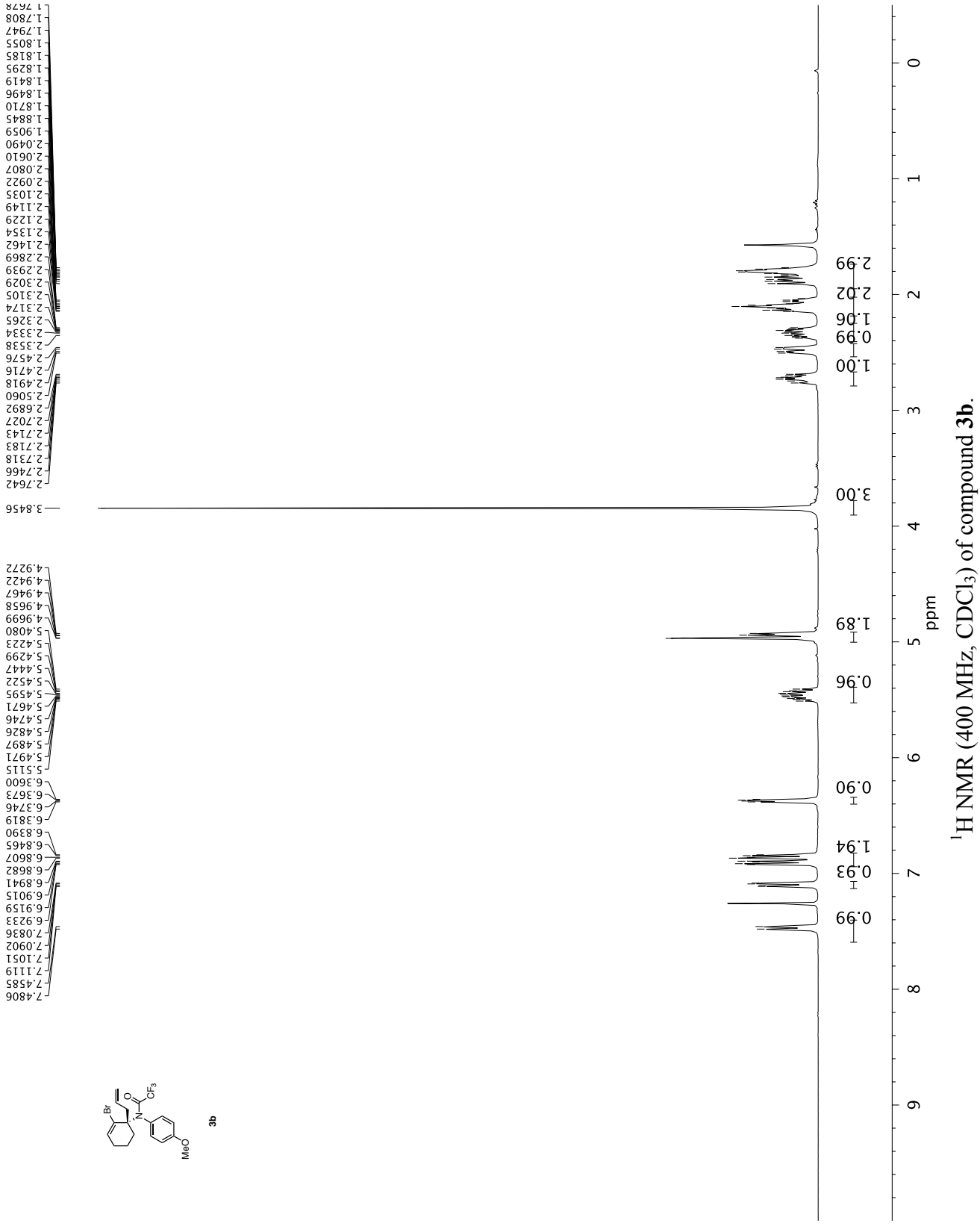
Infrared spectrum (Thin Film, NaCl) of compound **3a**.



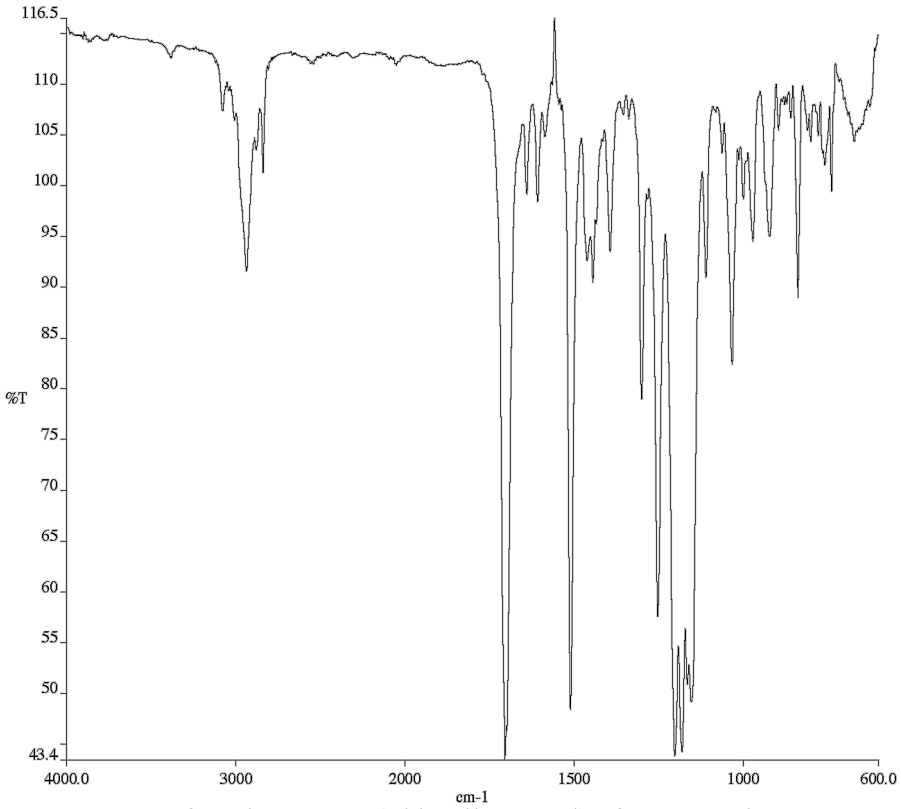
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**.



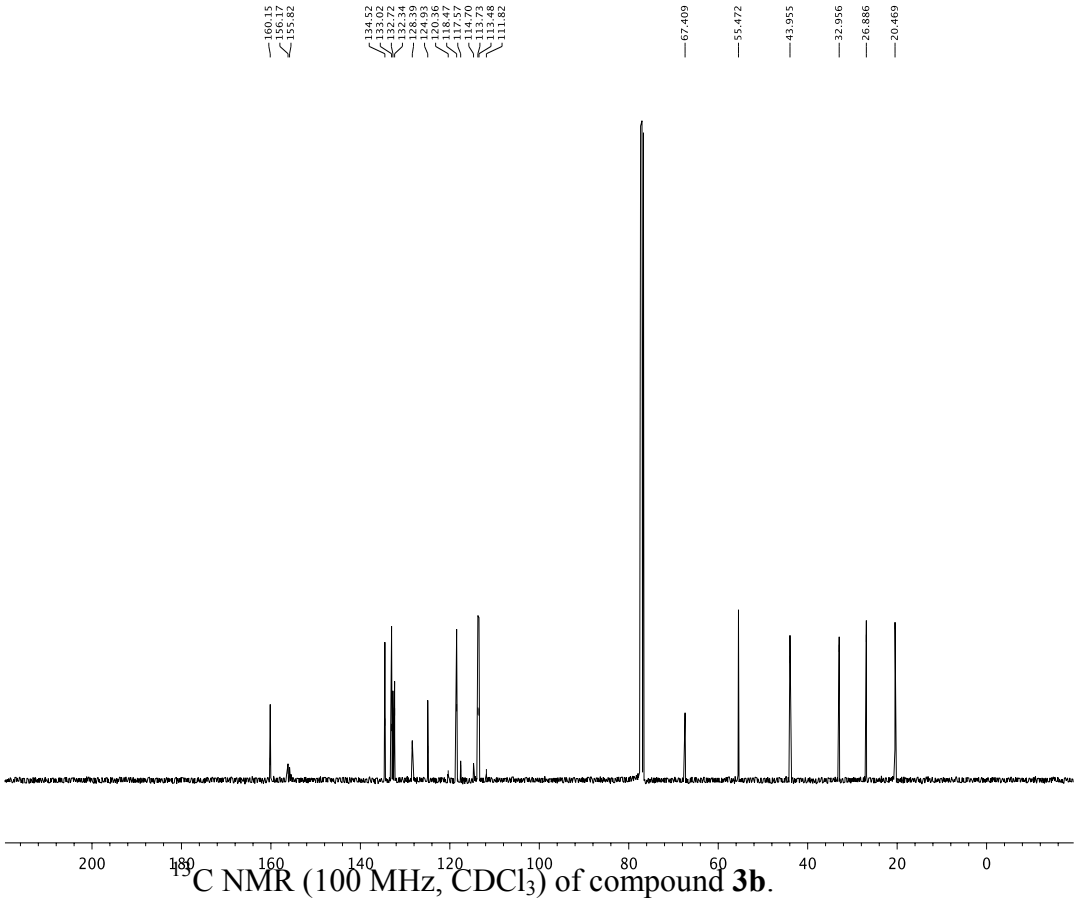
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3a**.



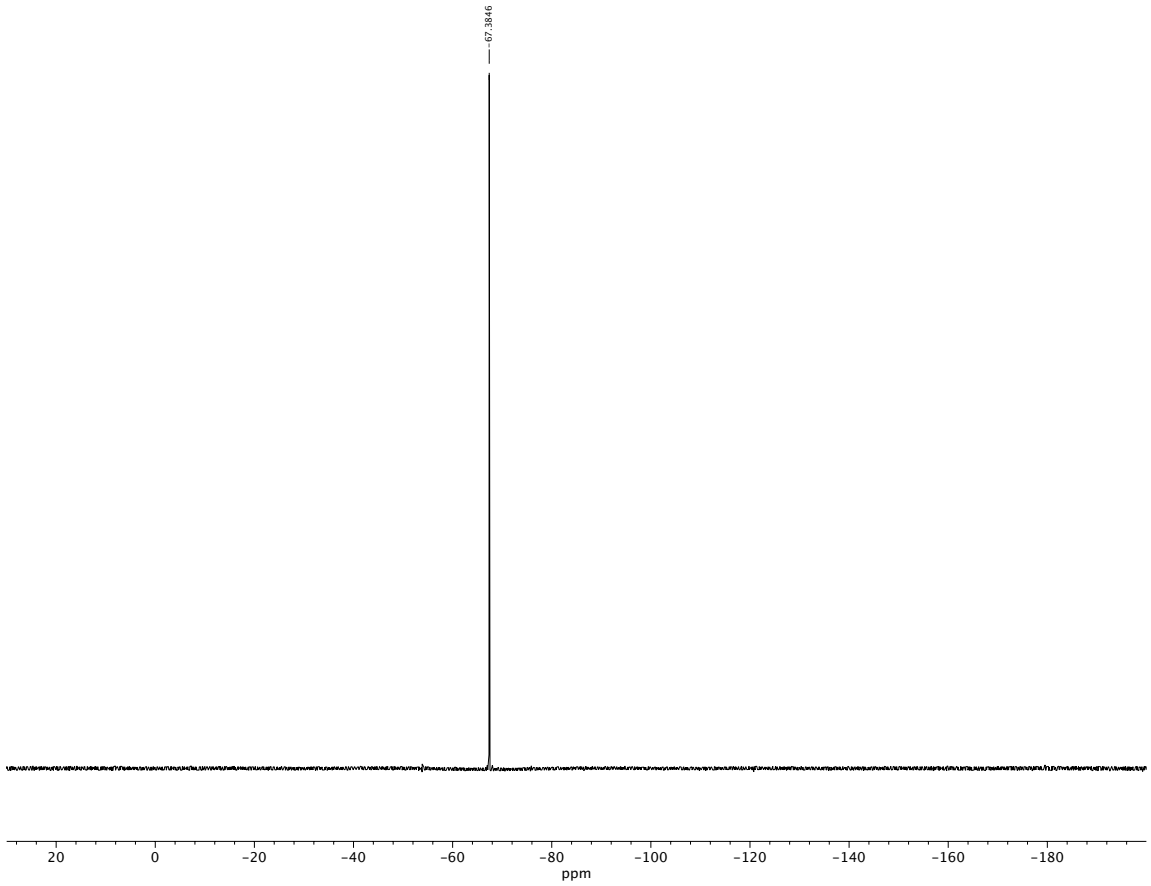
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**.



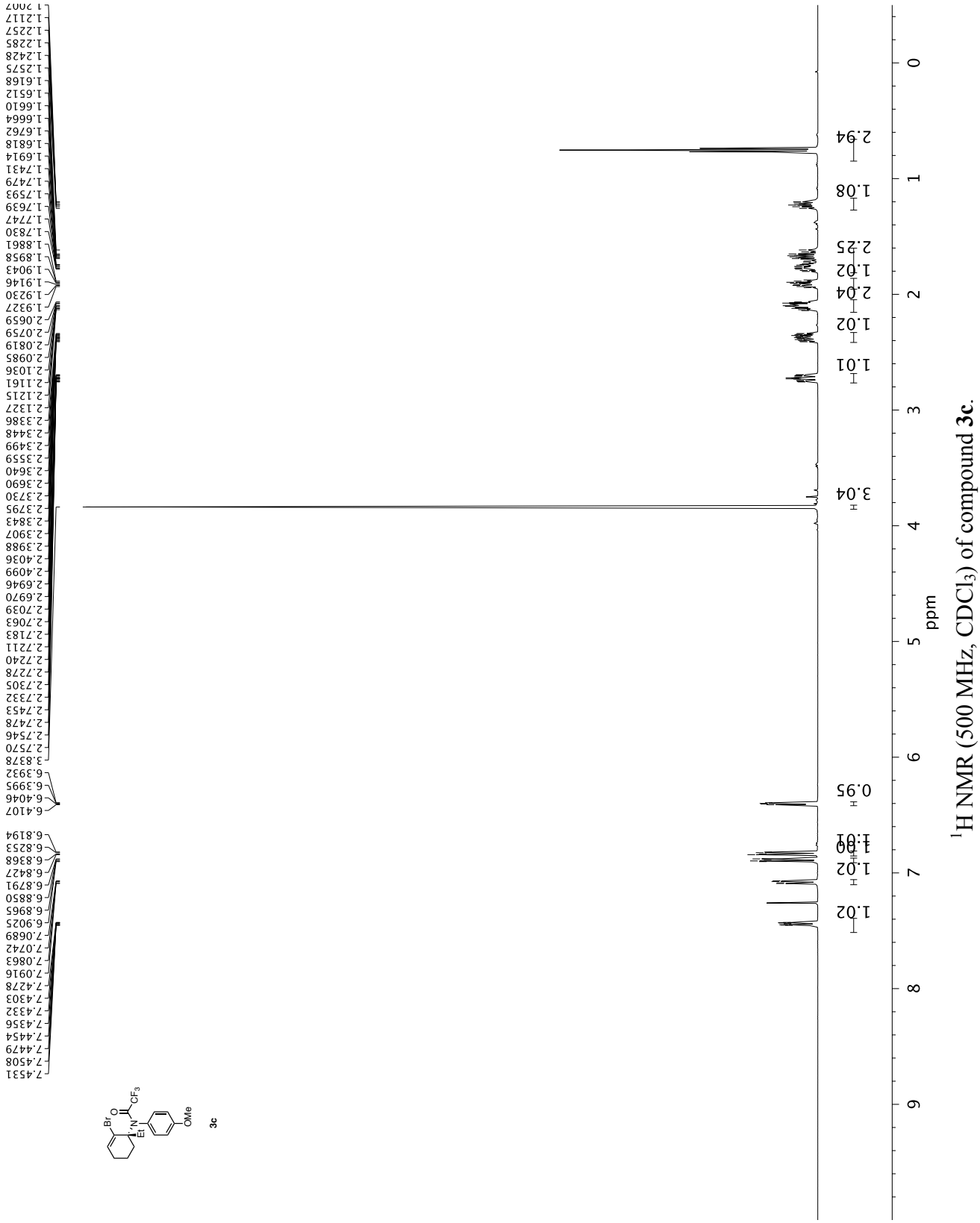
Infrared spectrum (Thin Film, NaCl) of compound **3b**.



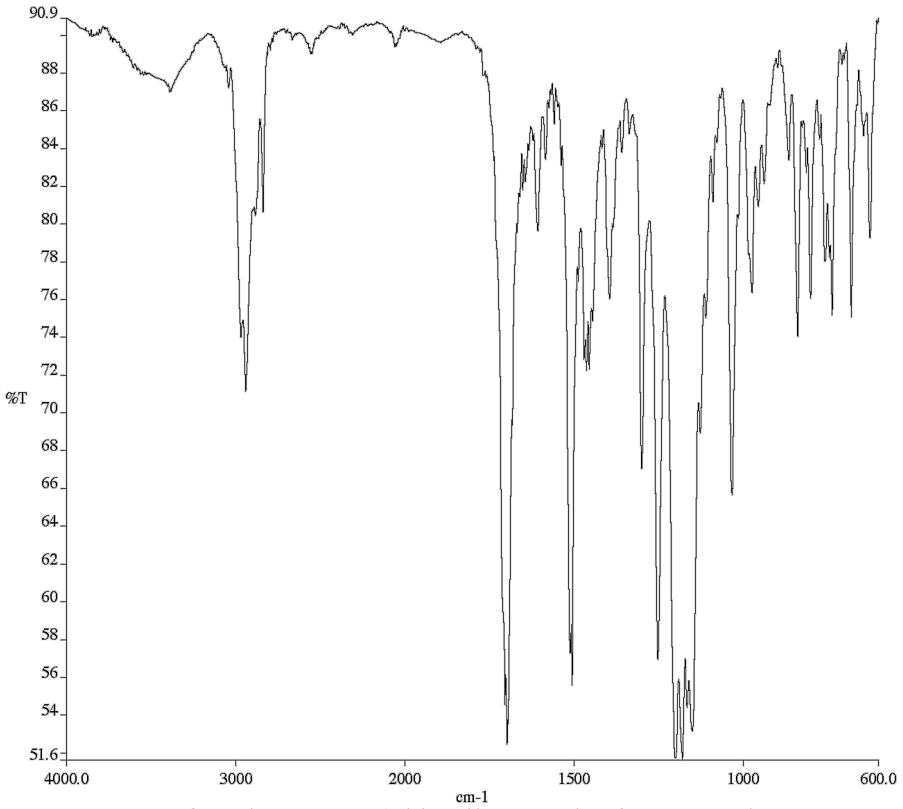
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3b**.



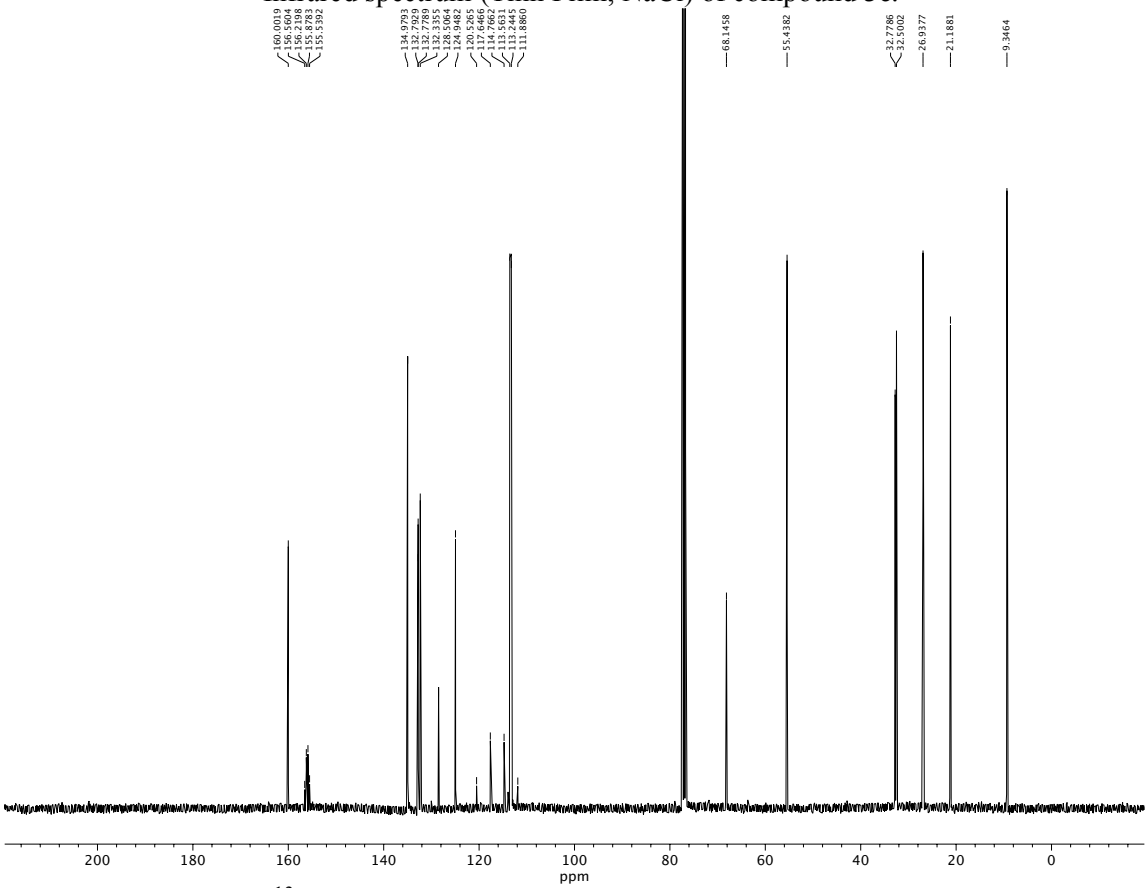
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3b**.



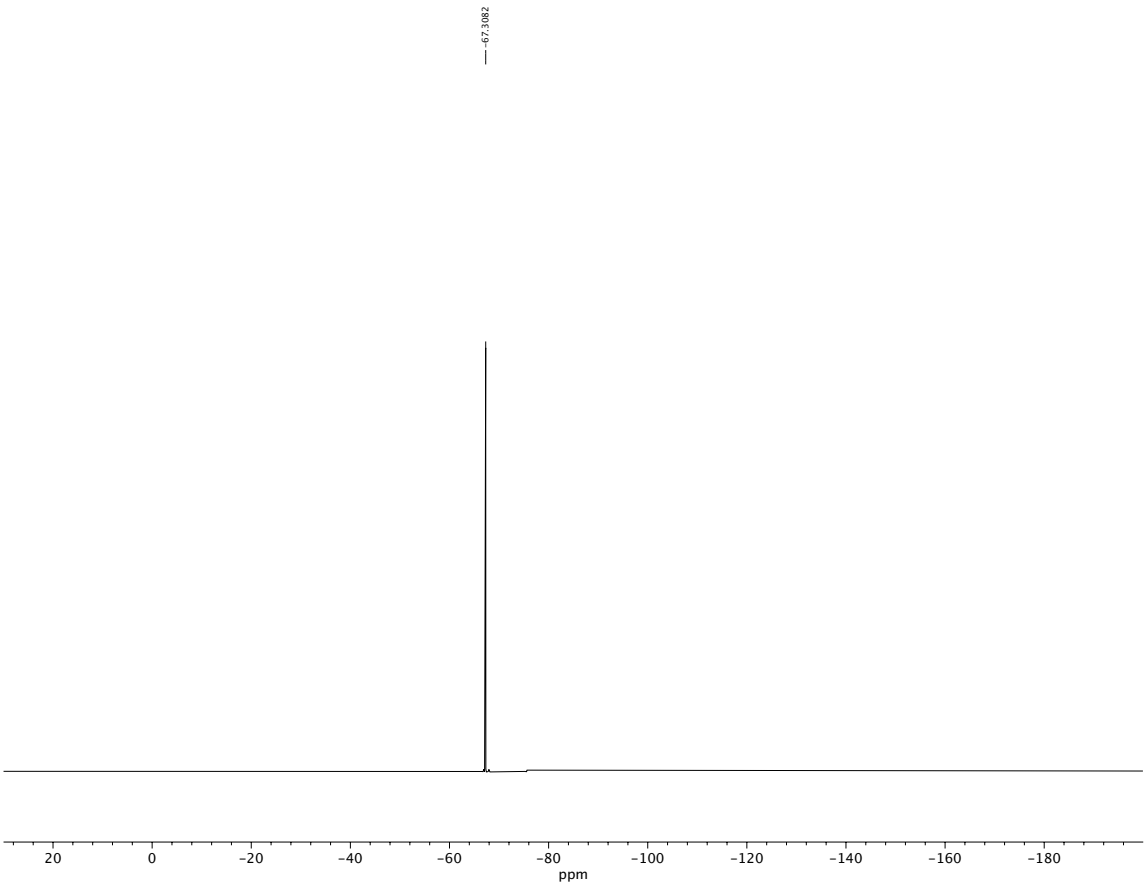
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3c**.



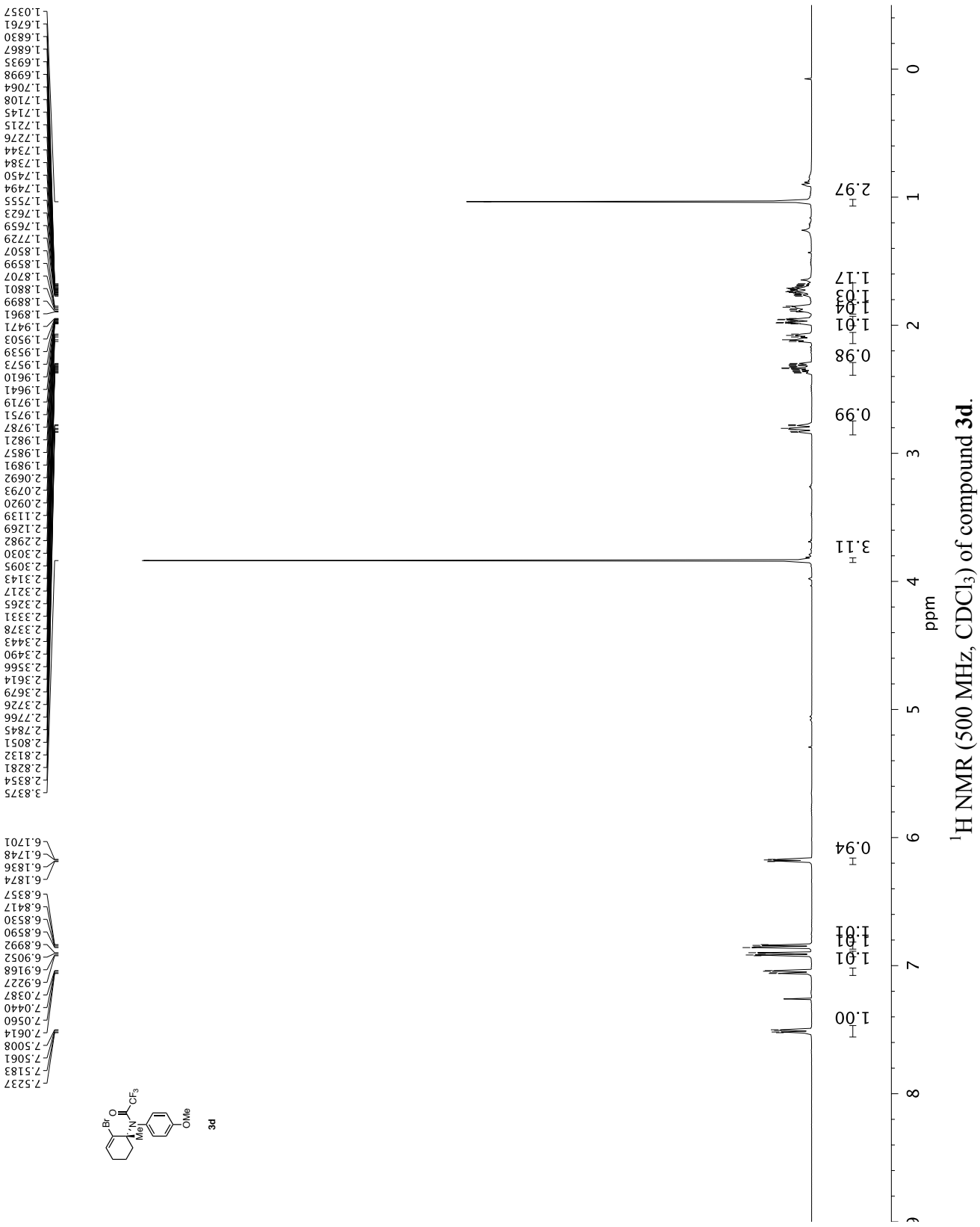
Infrared spectrum (Thin Film, NaCl) of compound **3c**.



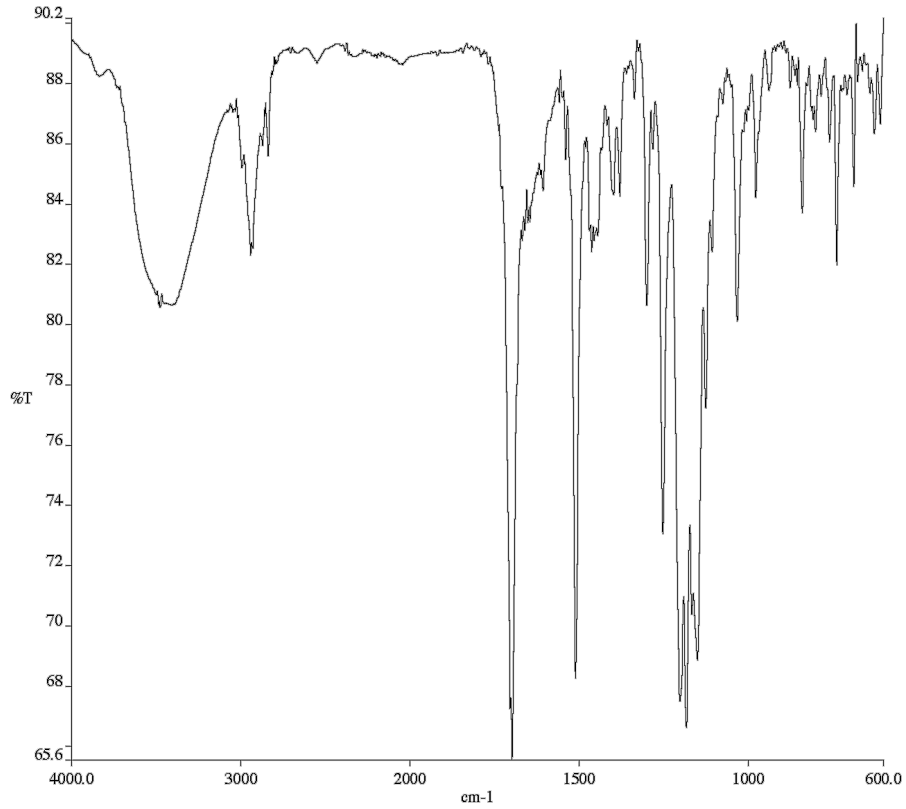
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3c**.



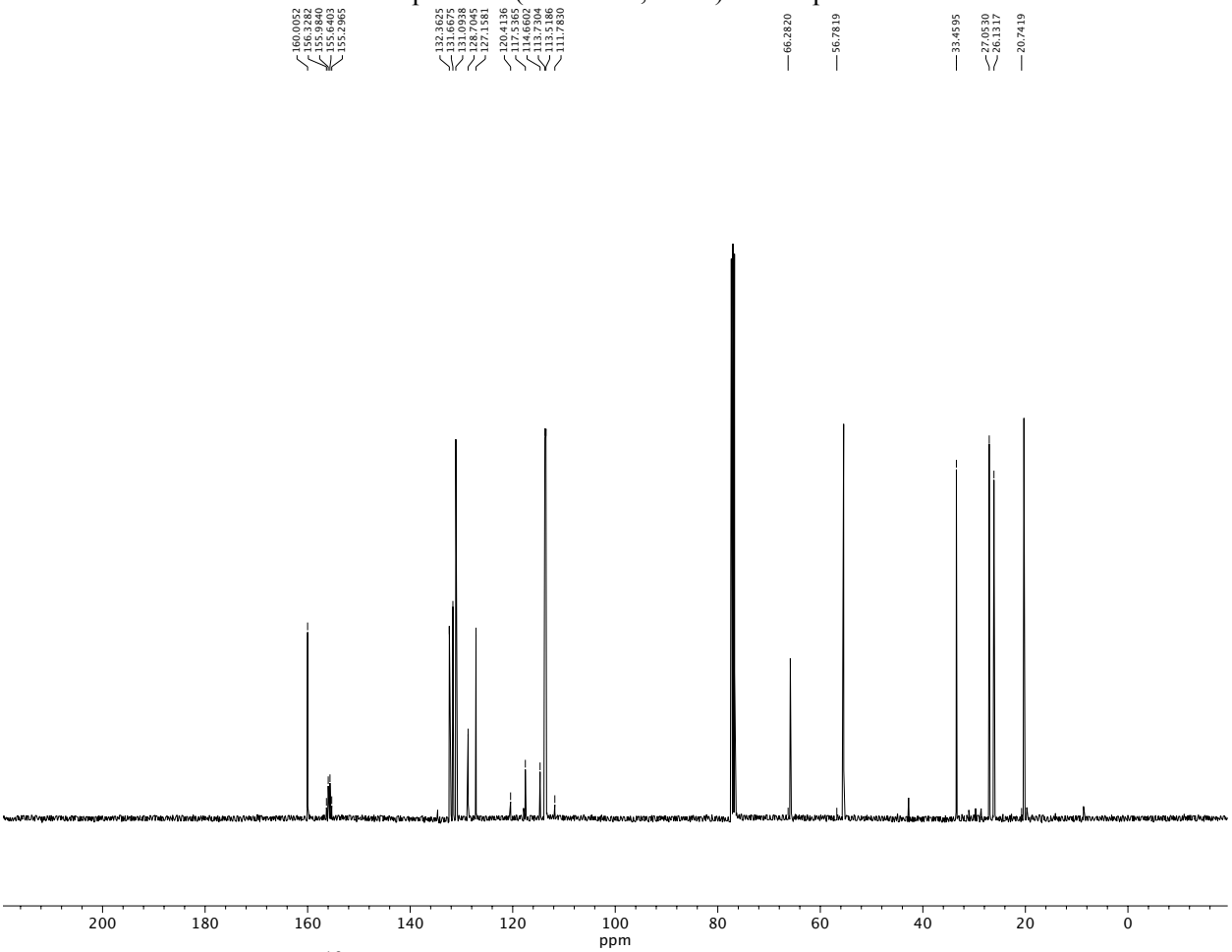
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3c**.



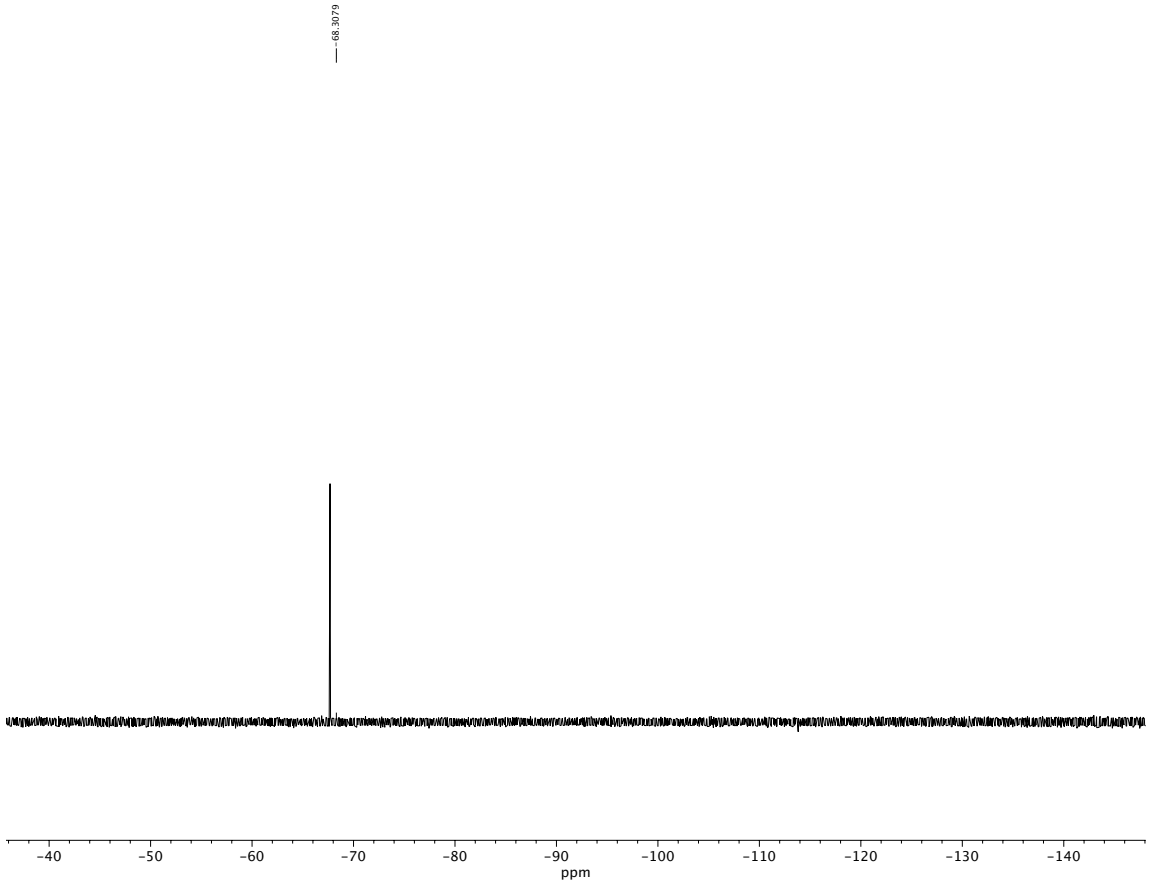
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3d**.



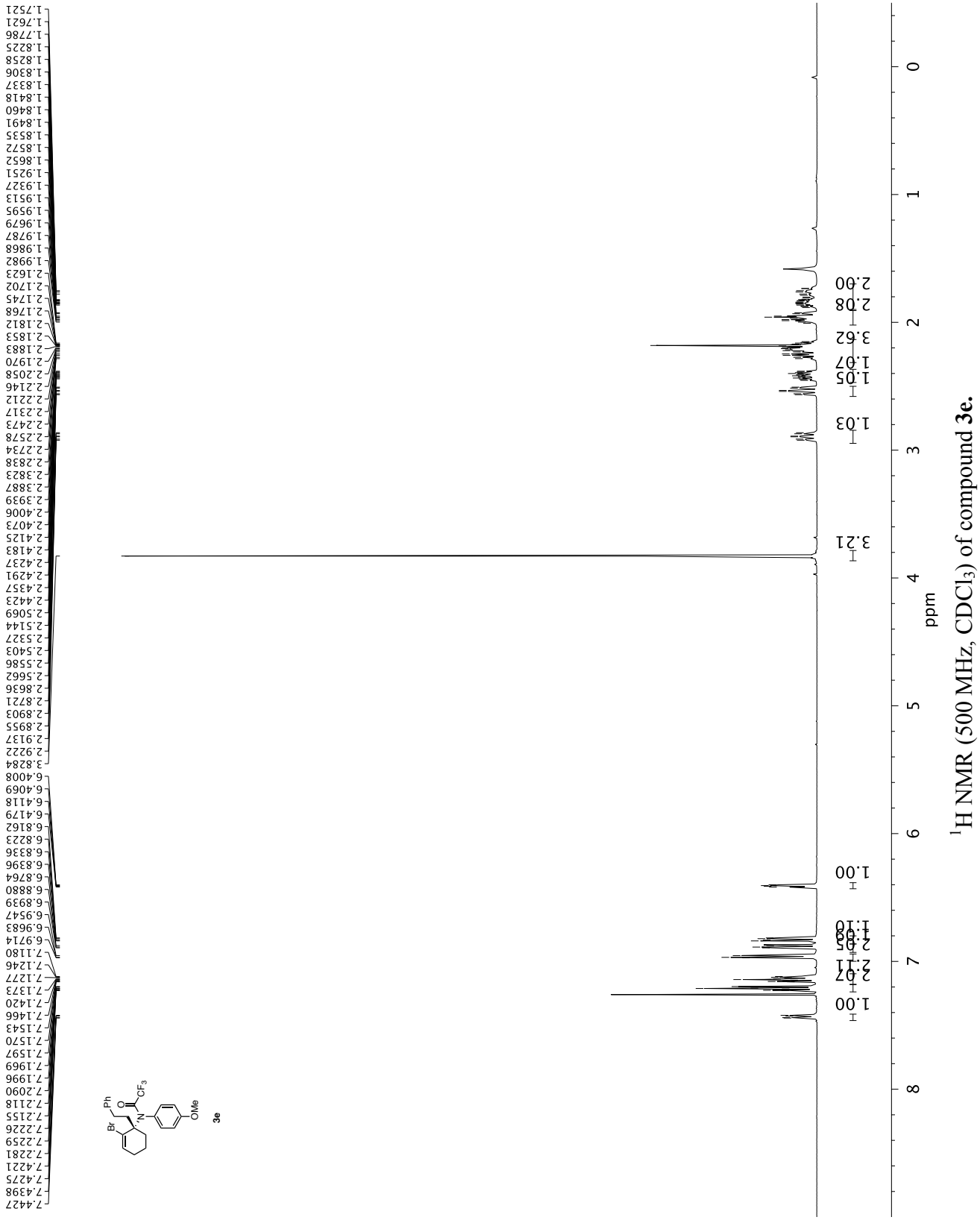
Infrared spectrum (Thin Film, NaCl) of compound **3d**.



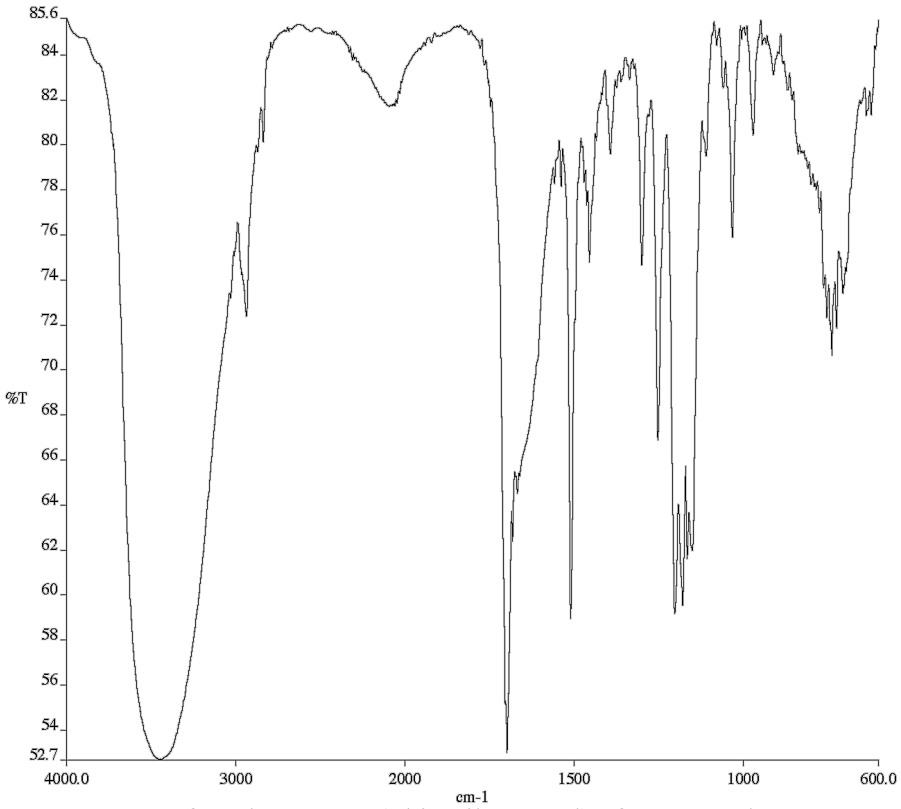
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3d**.



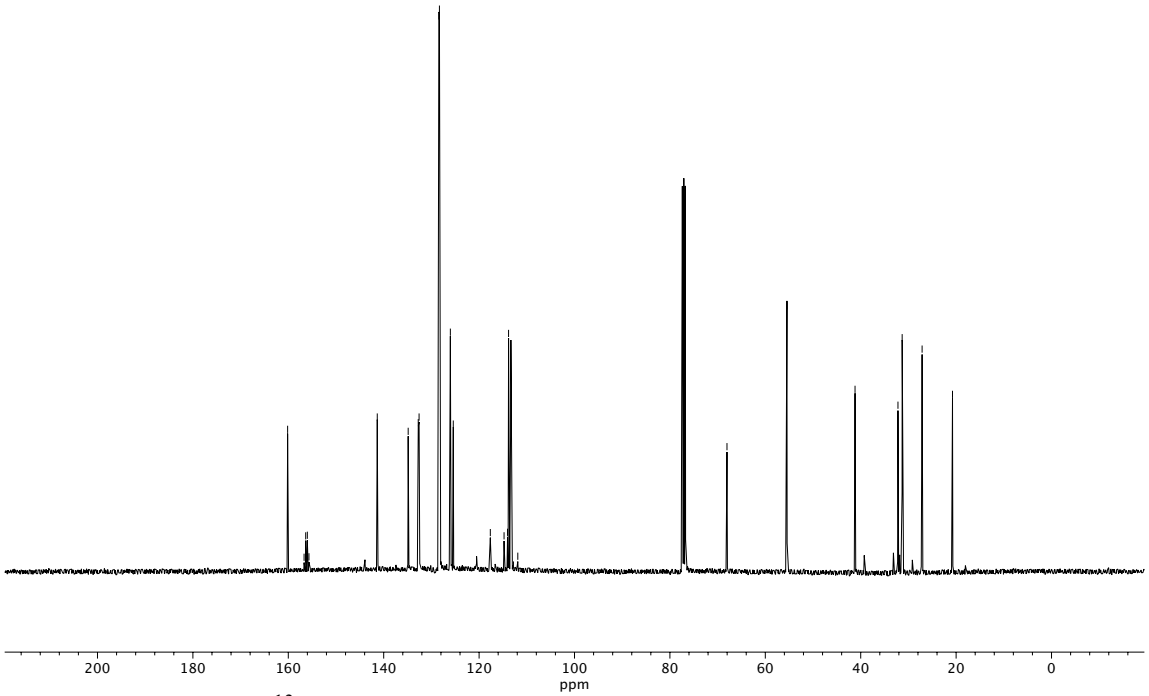
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3d**.



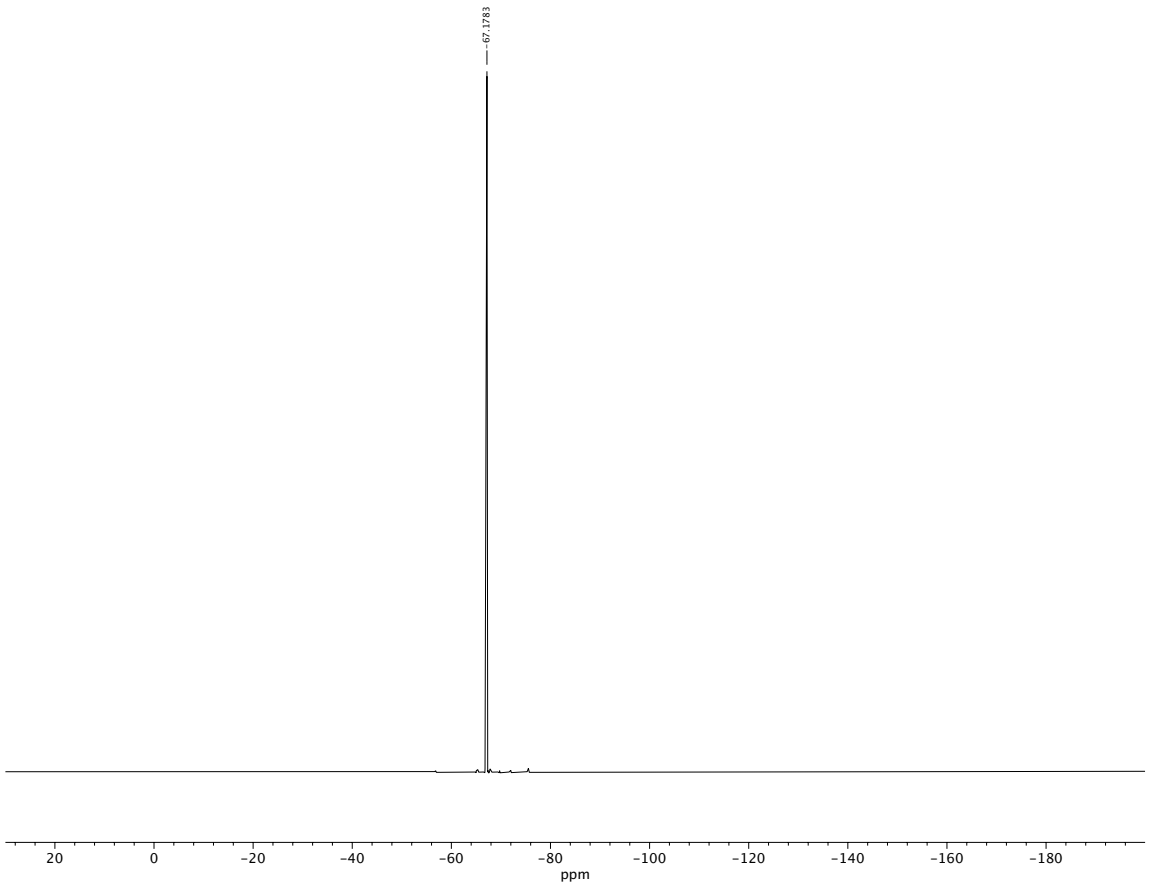
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3e.**



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



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



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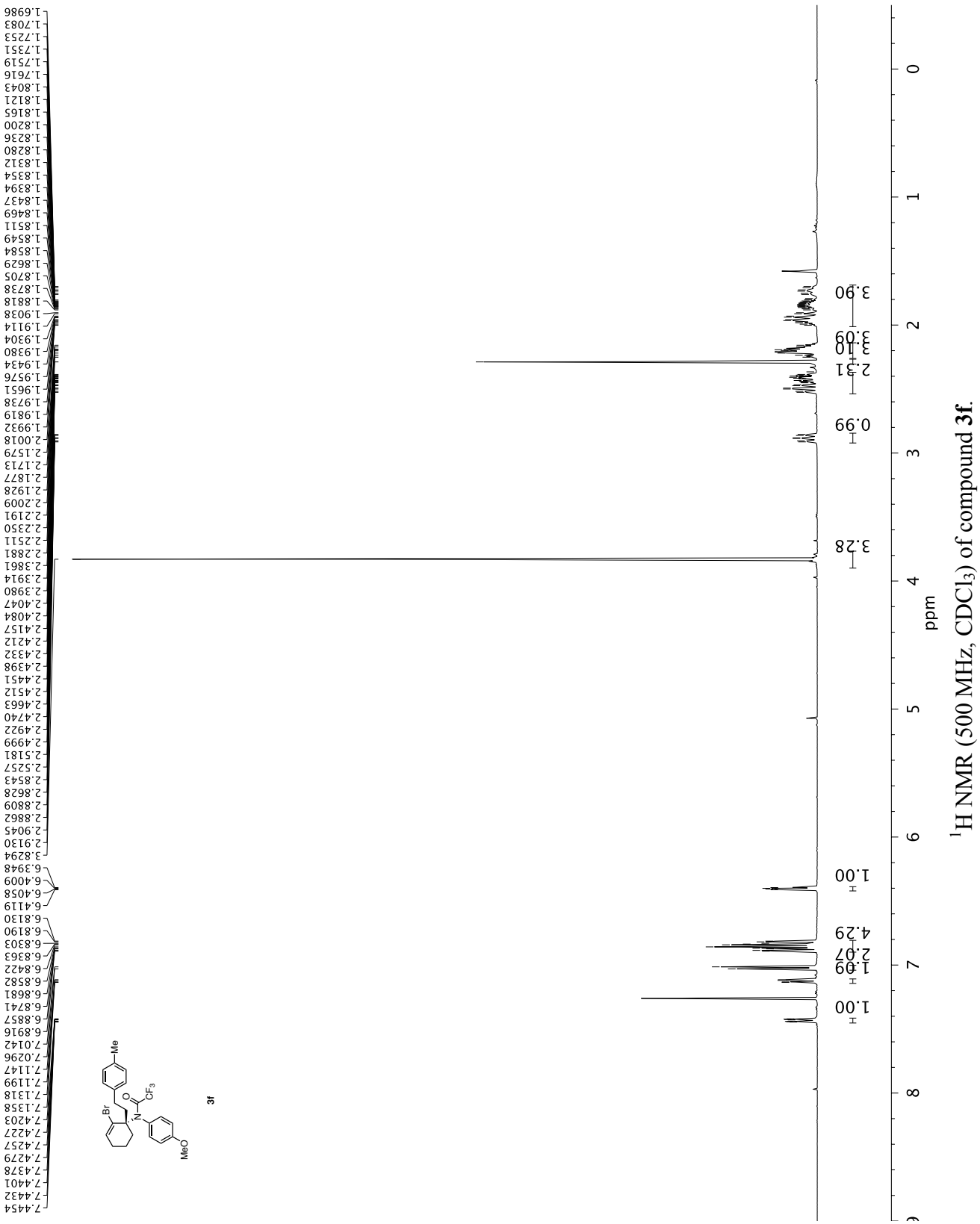
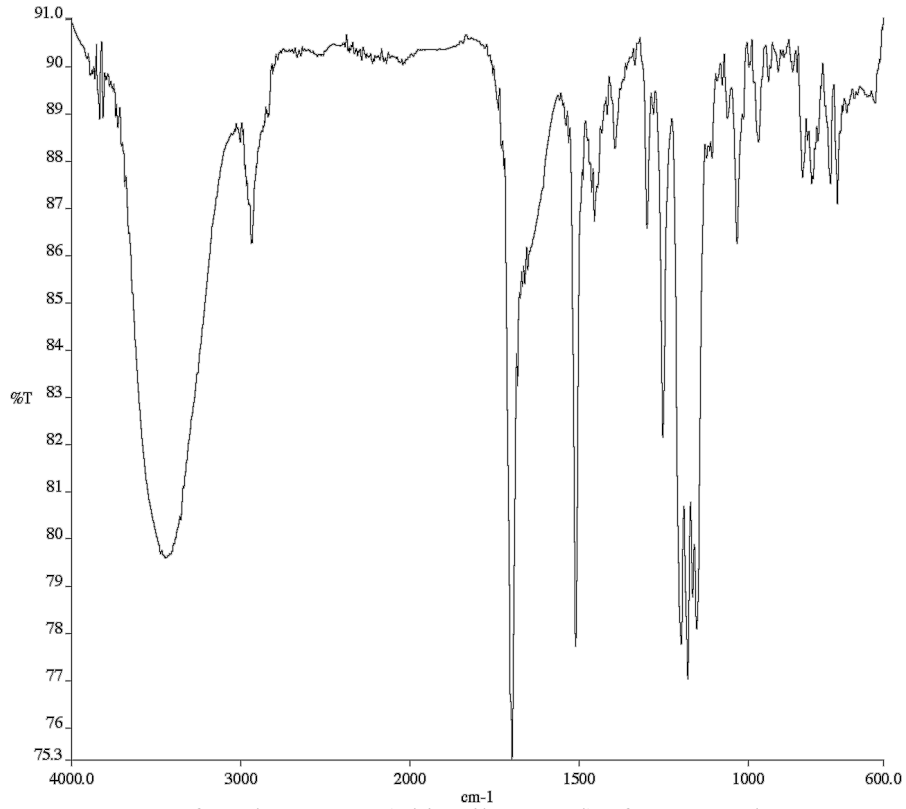
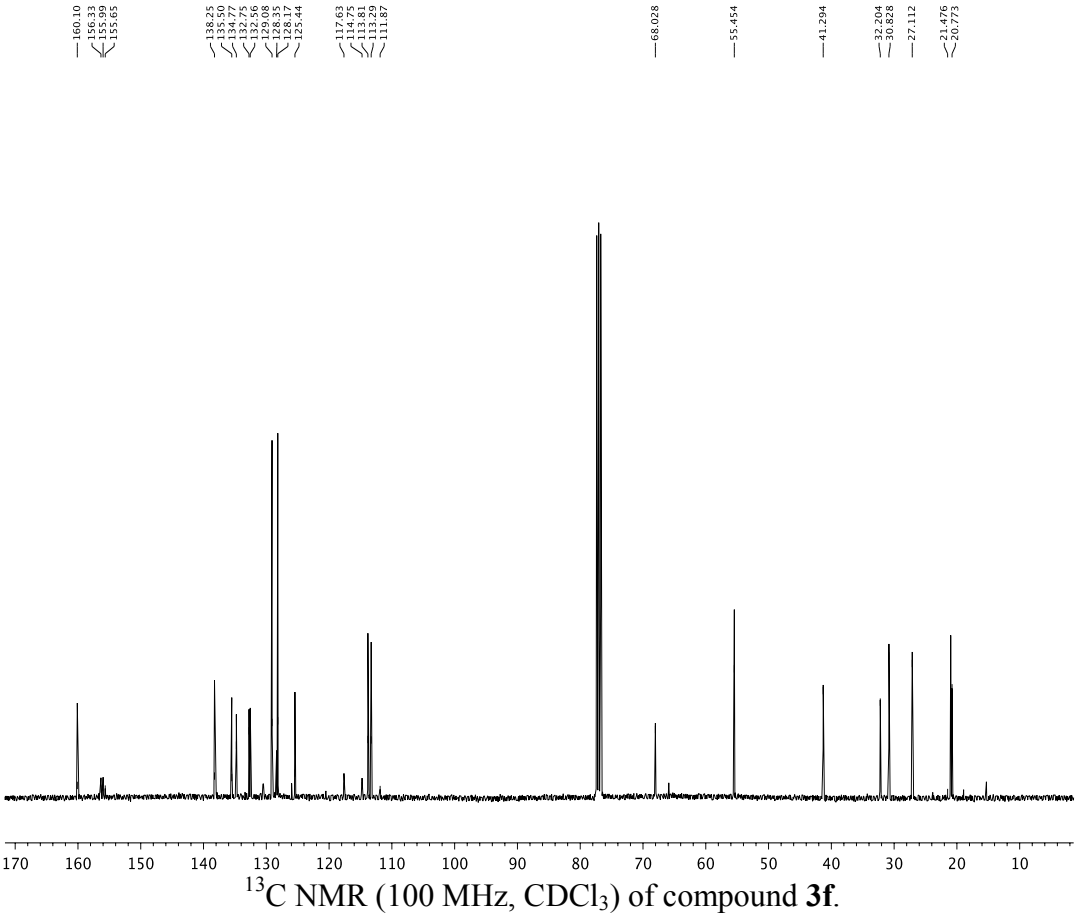


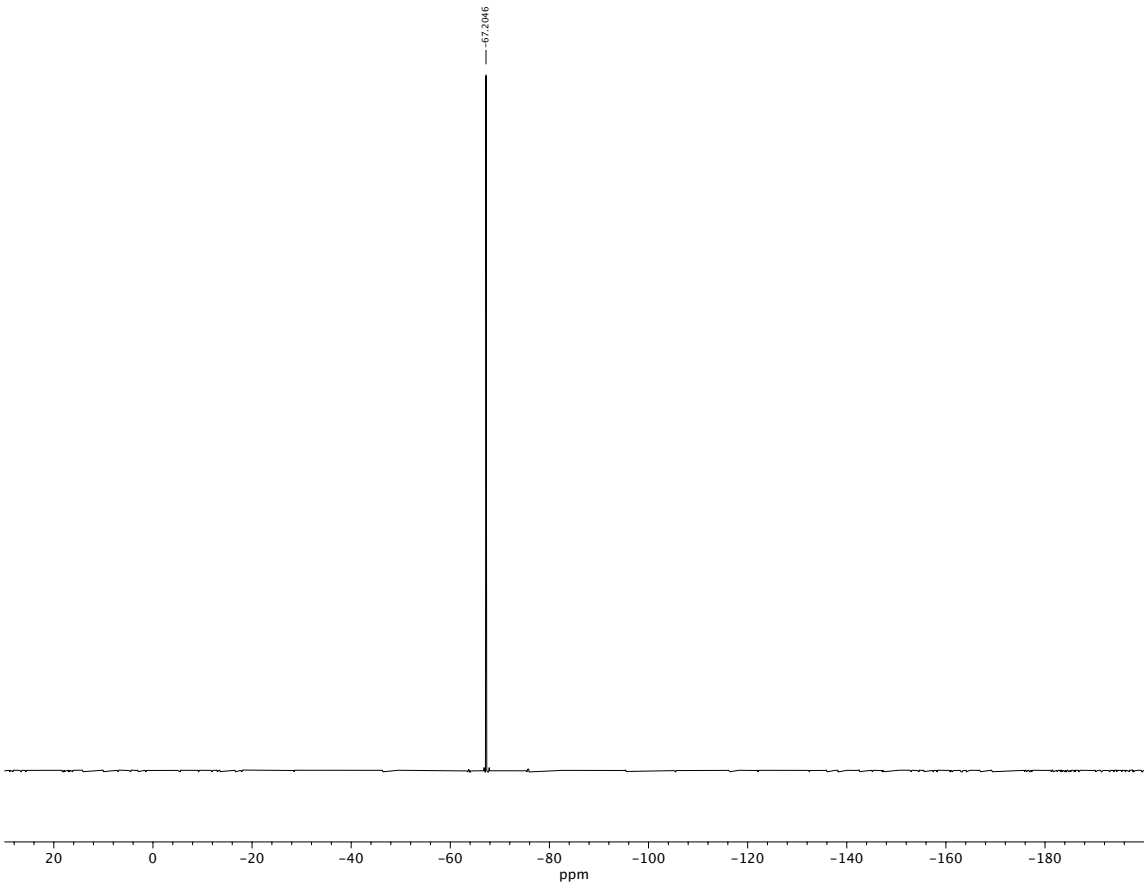
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3f**.



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



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



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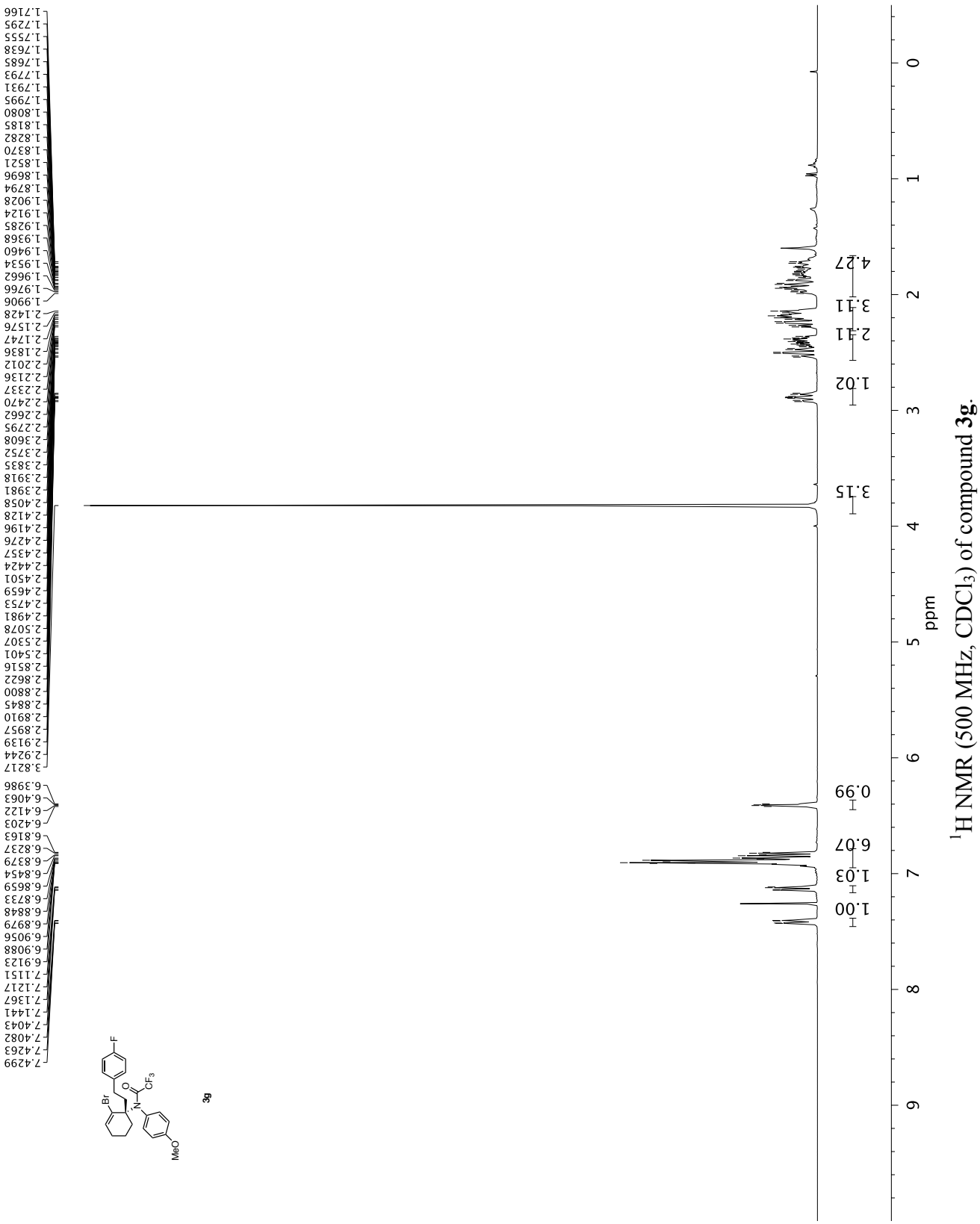
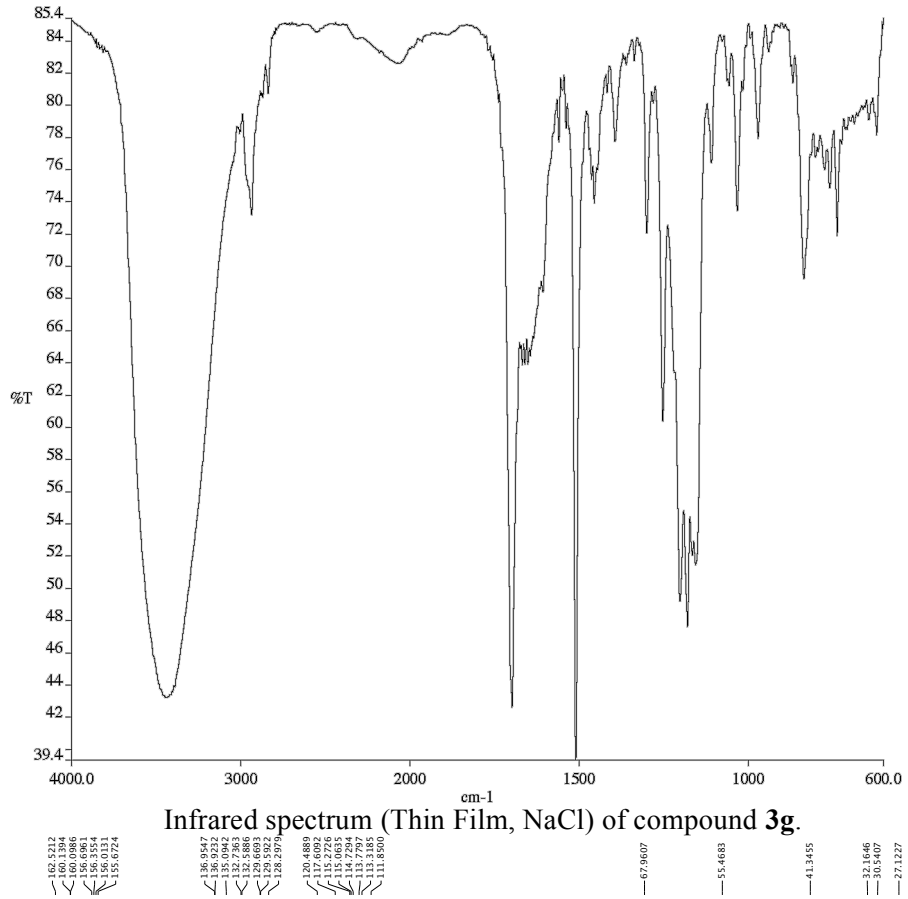
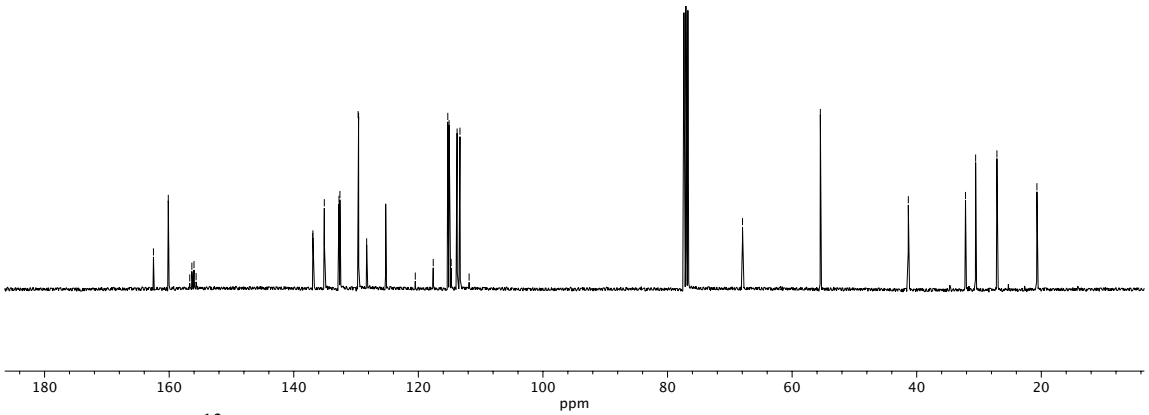


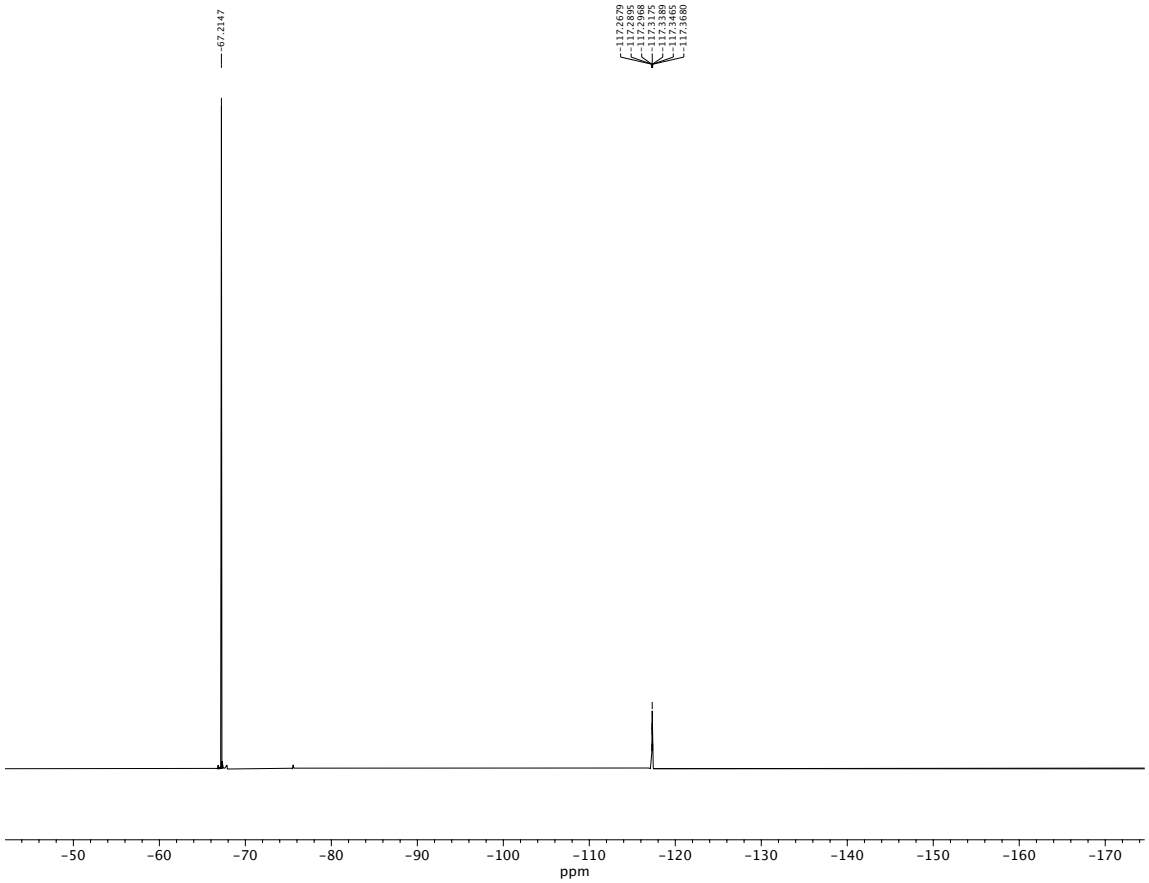
^{1}H NMR (500 MHz, $CDCl_3$) of compound **3g**.



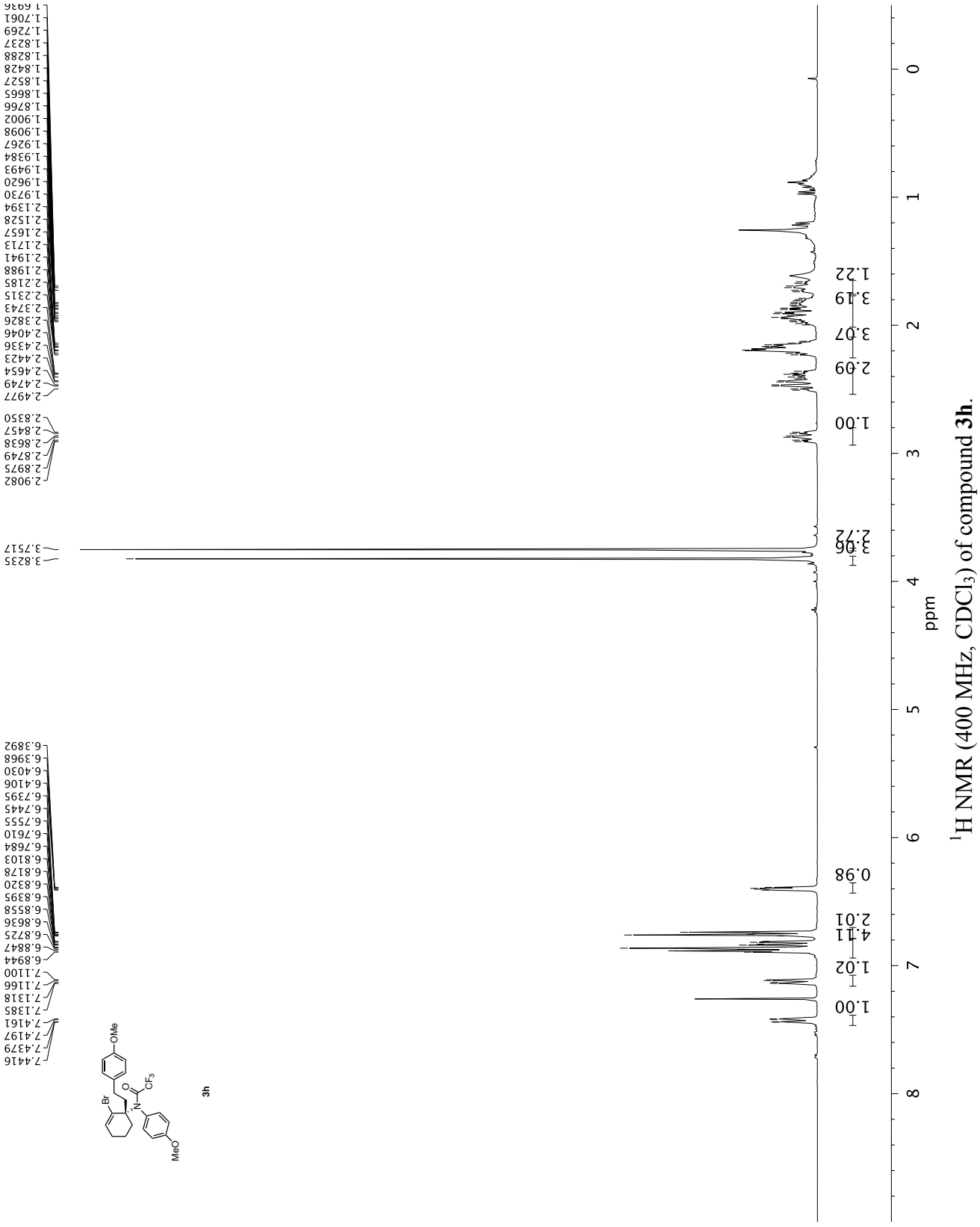
Infrared spectrum (Thin Film, NaCl) of compound **3g**.



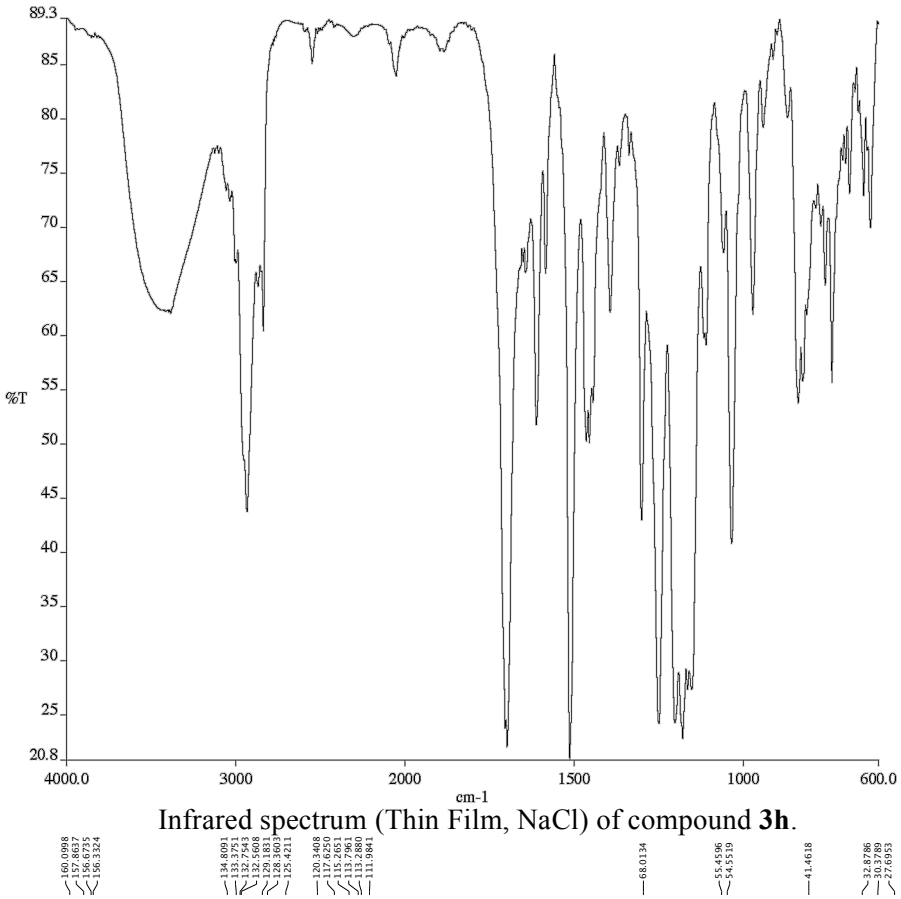
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3g**.



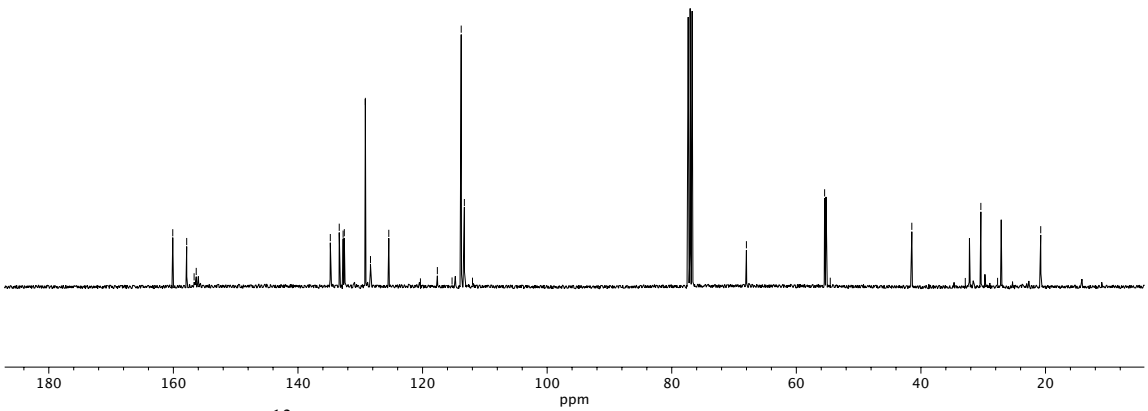
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3g**.



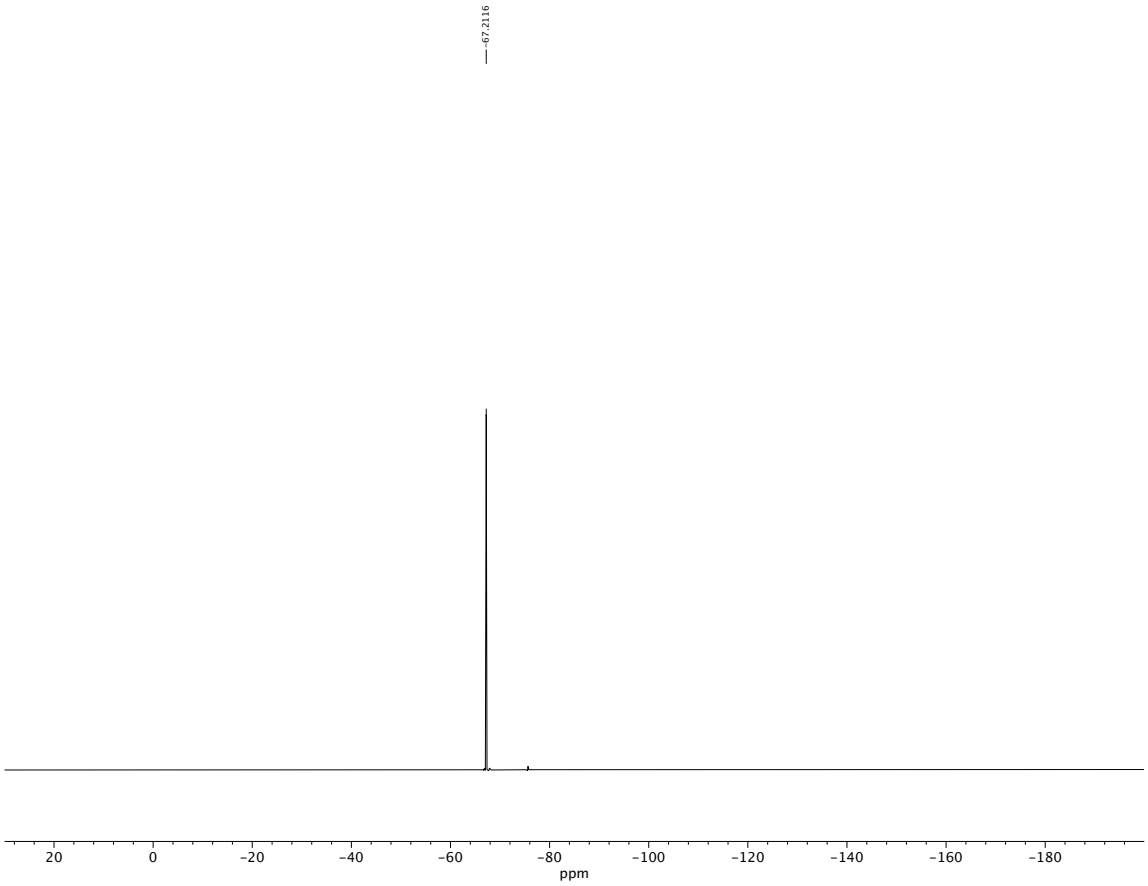
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3h**.



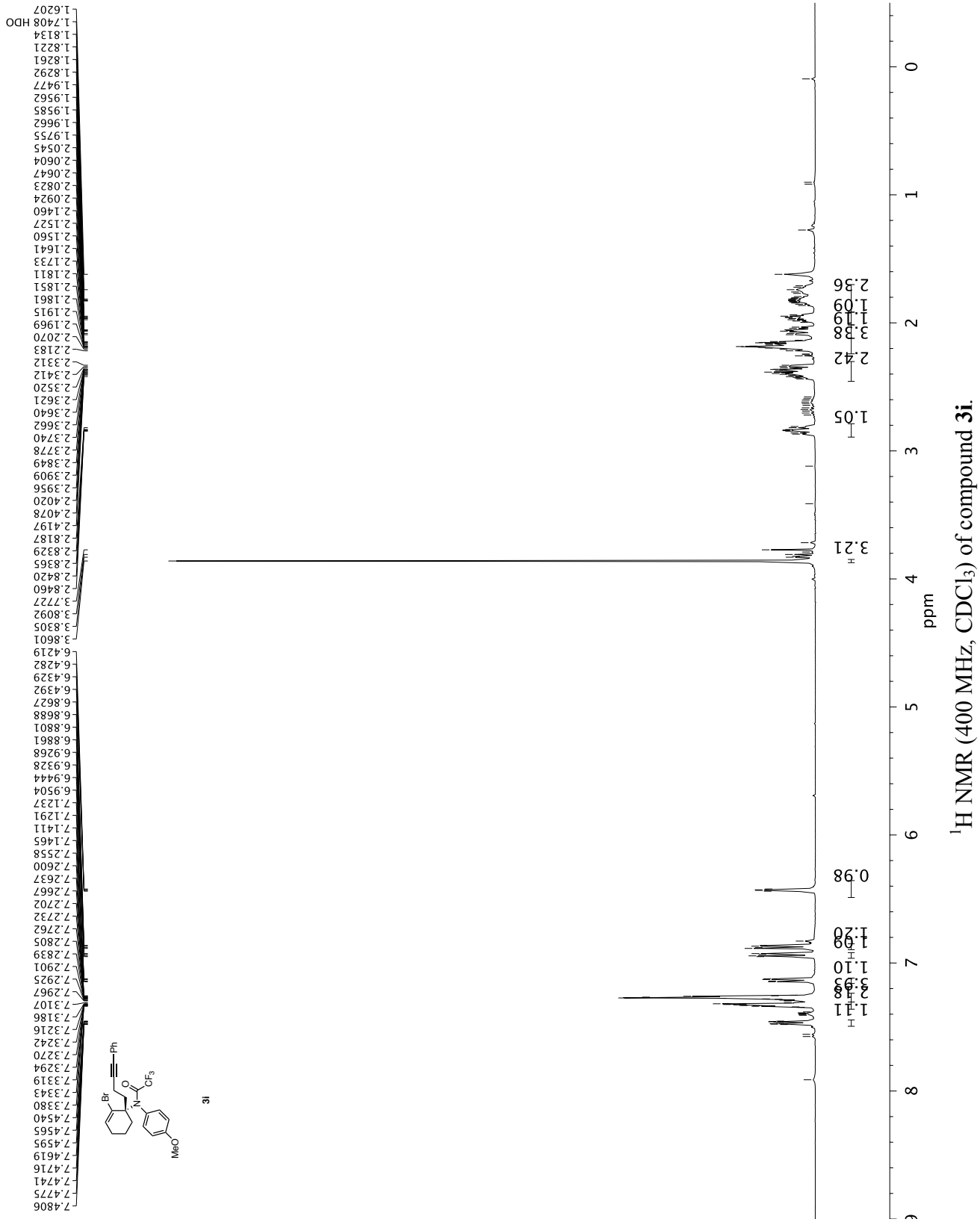
Infrared spectrum (Thin Film, NaCl) of compound **3h**.



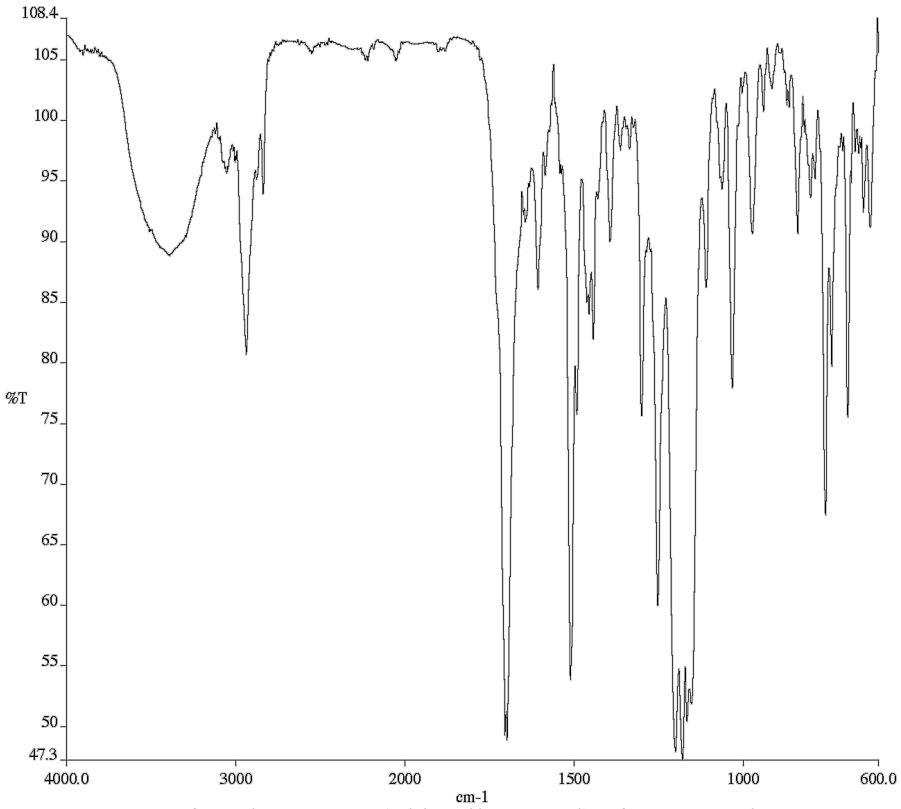
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3h**.



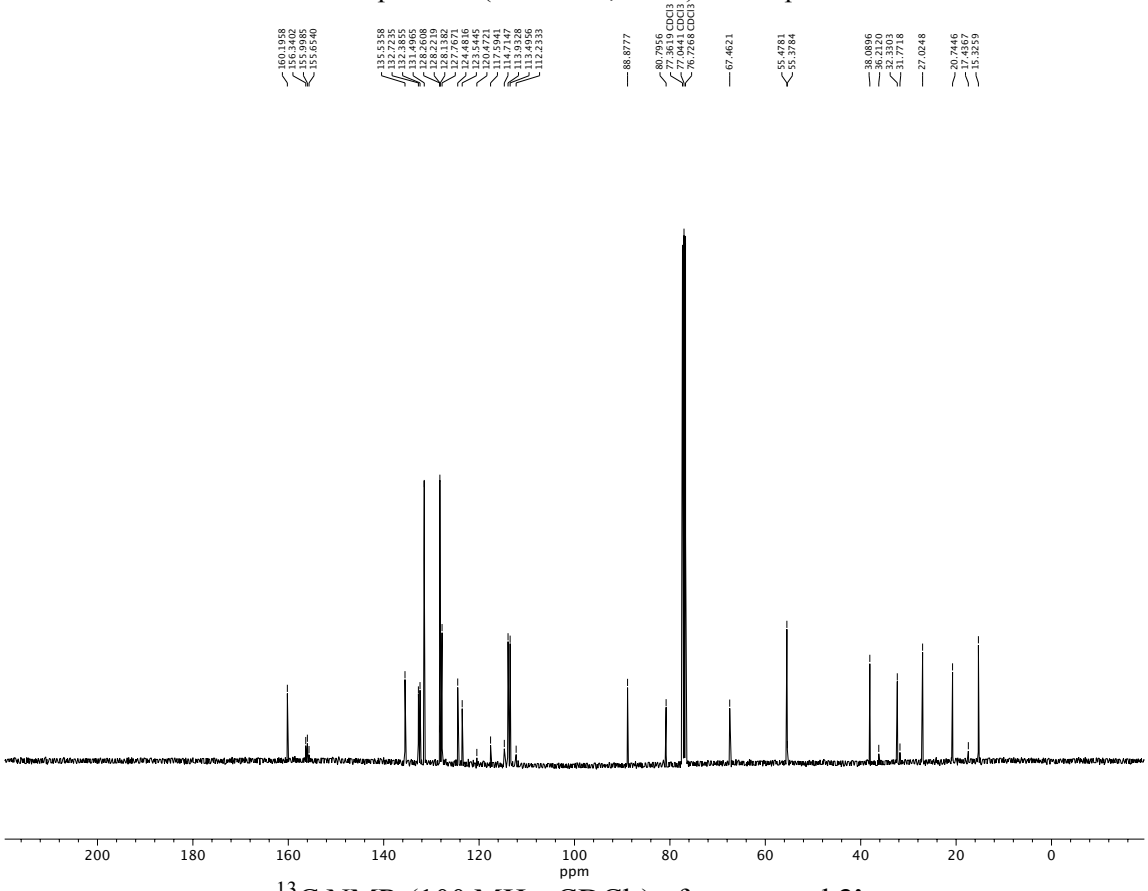
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3h**.



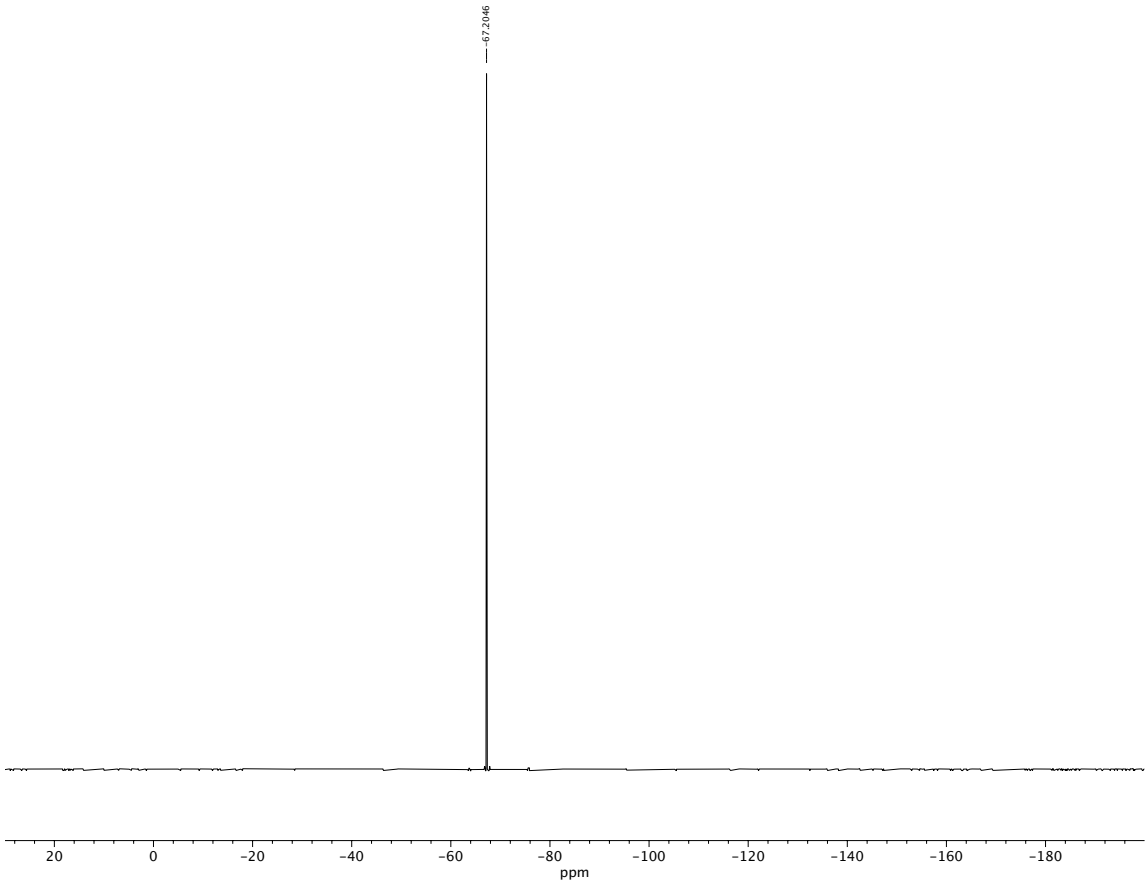
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3i**.



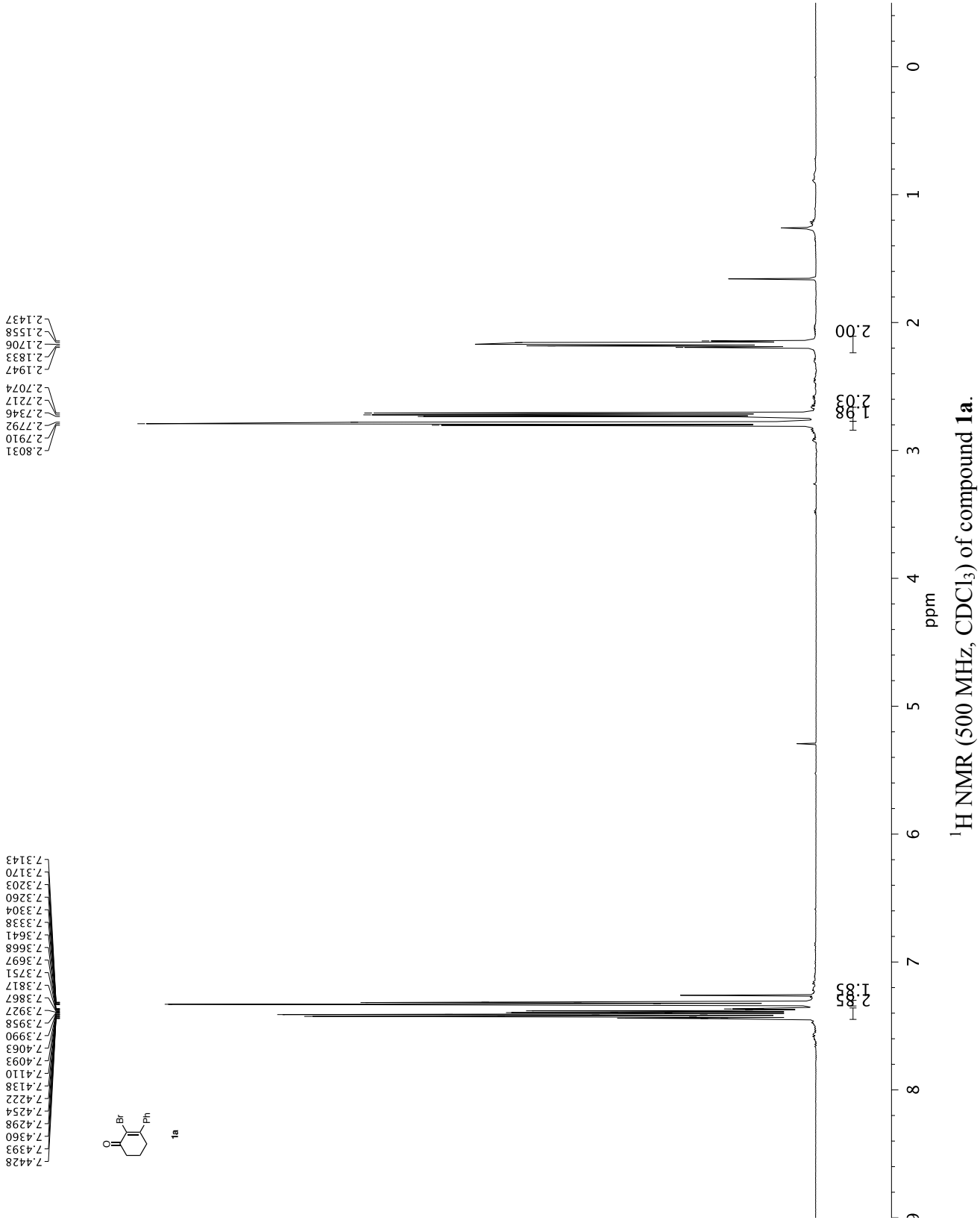
Infrared spectrum (Thin Film, NaCl) of compound **3i**.



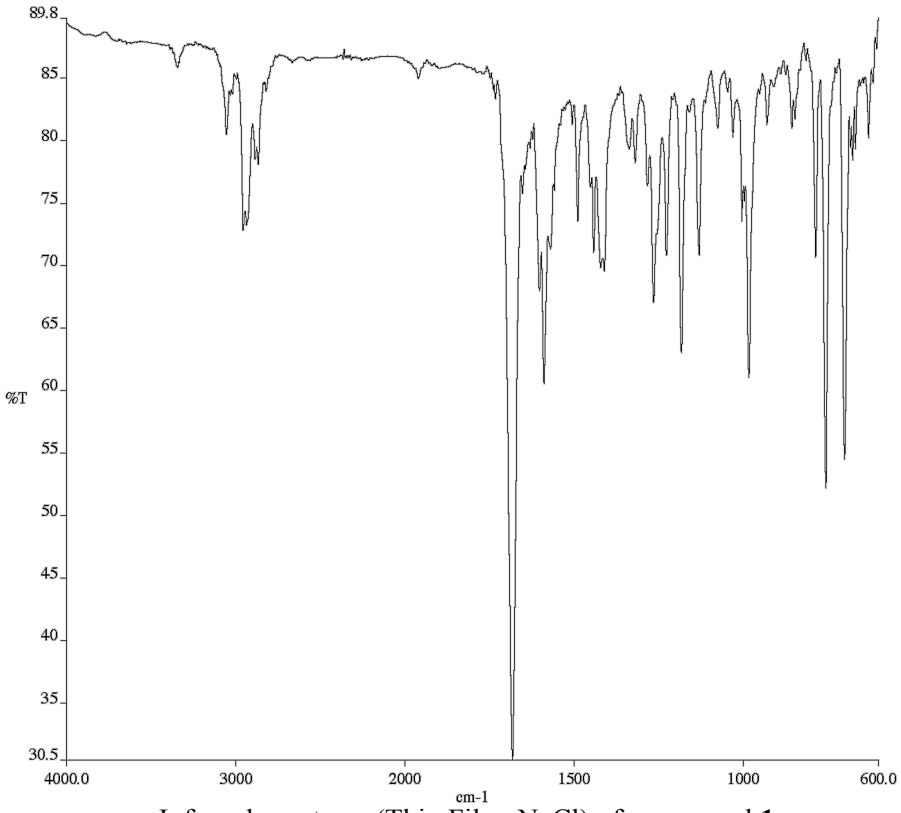
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3i**.



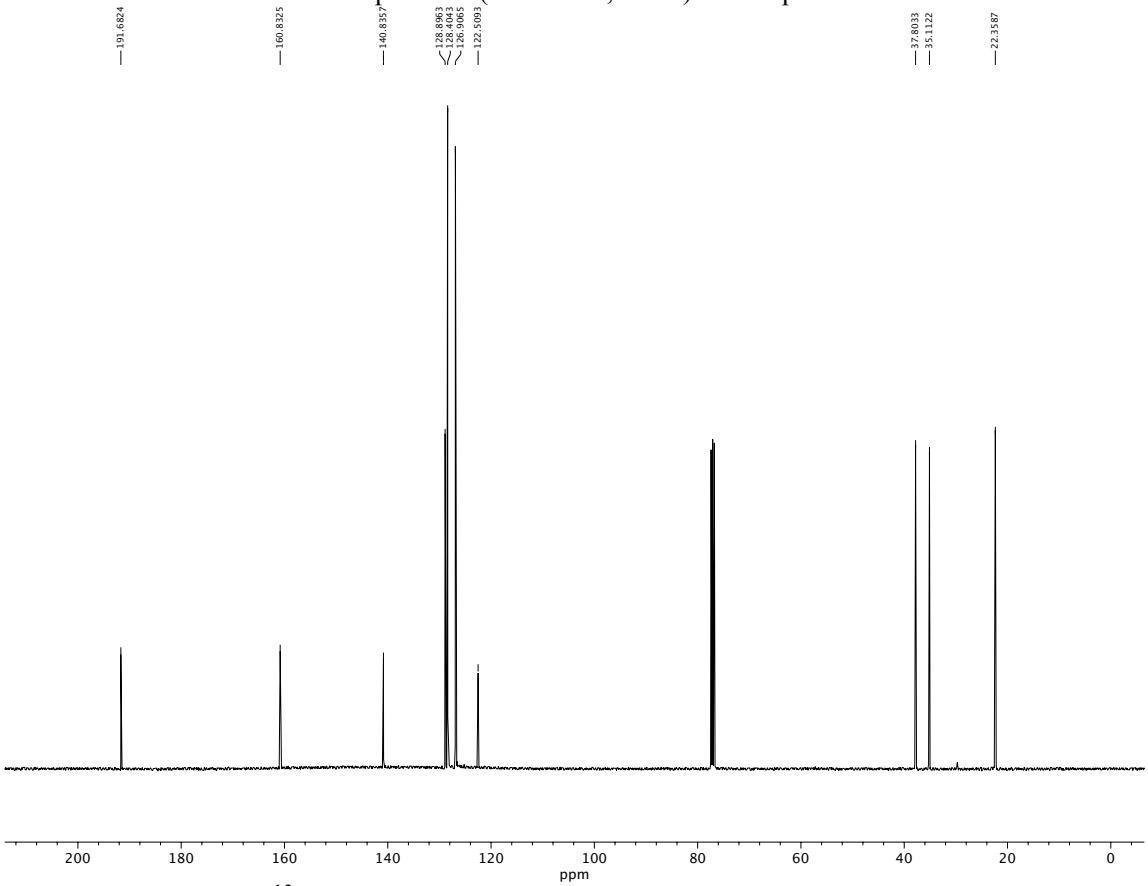
^{19}F NMR (282 MHz, $CDCl_3$) of compound **3i**.



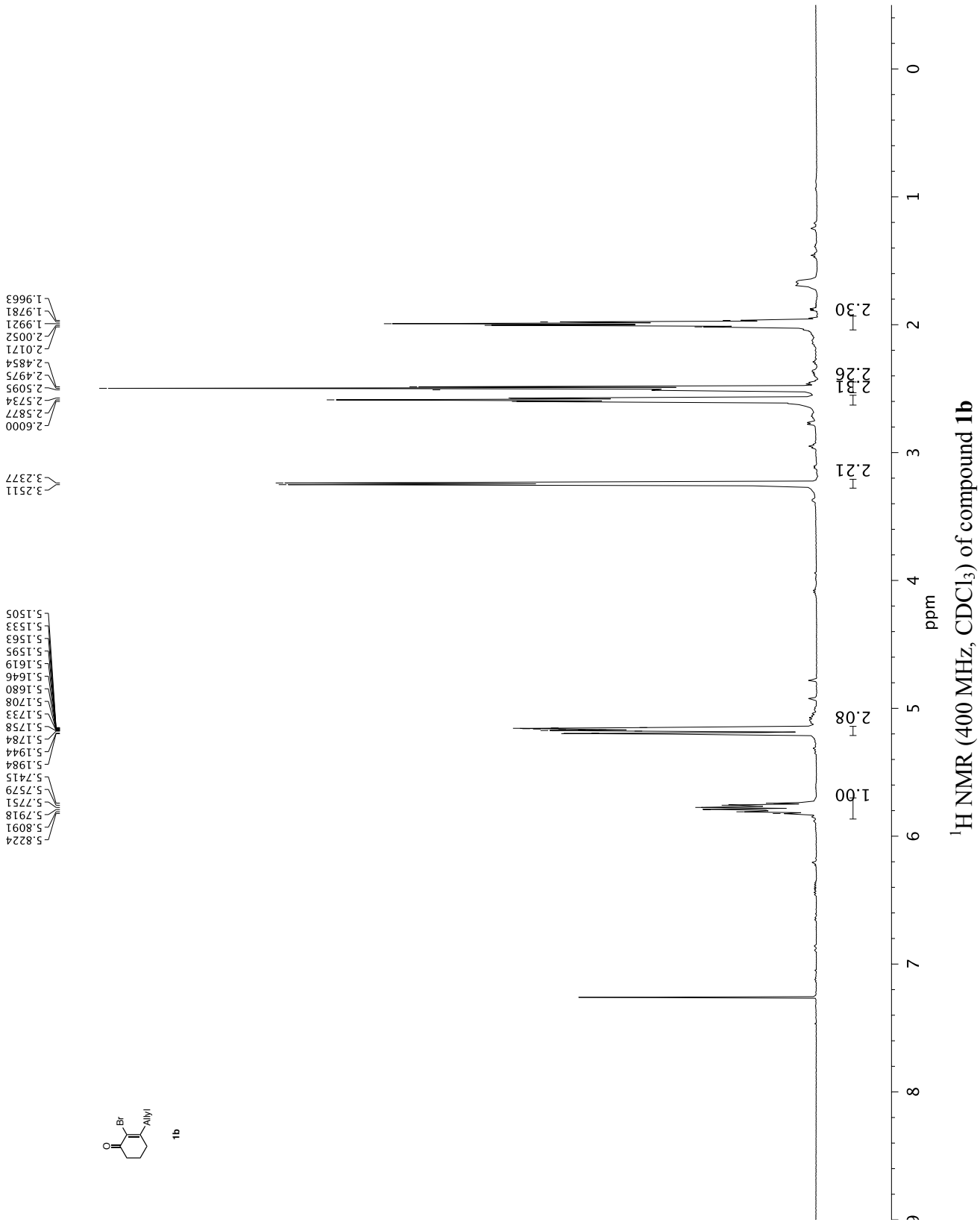
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1a**.



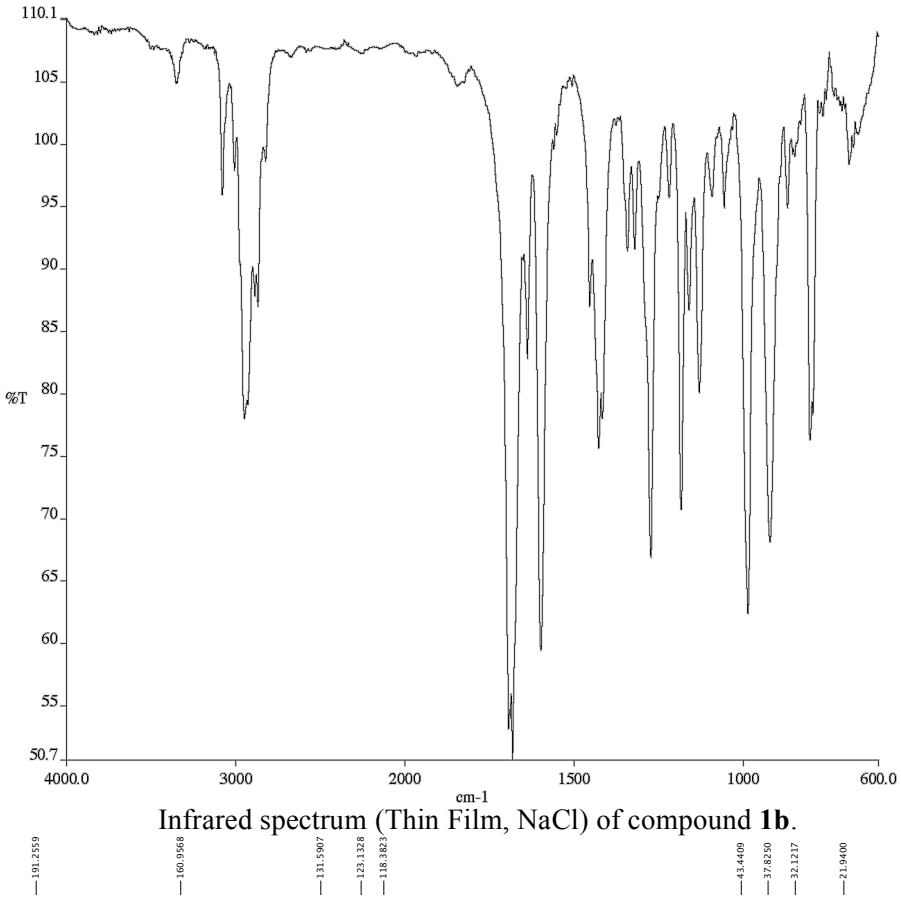
Infrared spectrum (Thin Film, NaCl) of compound **1a**.



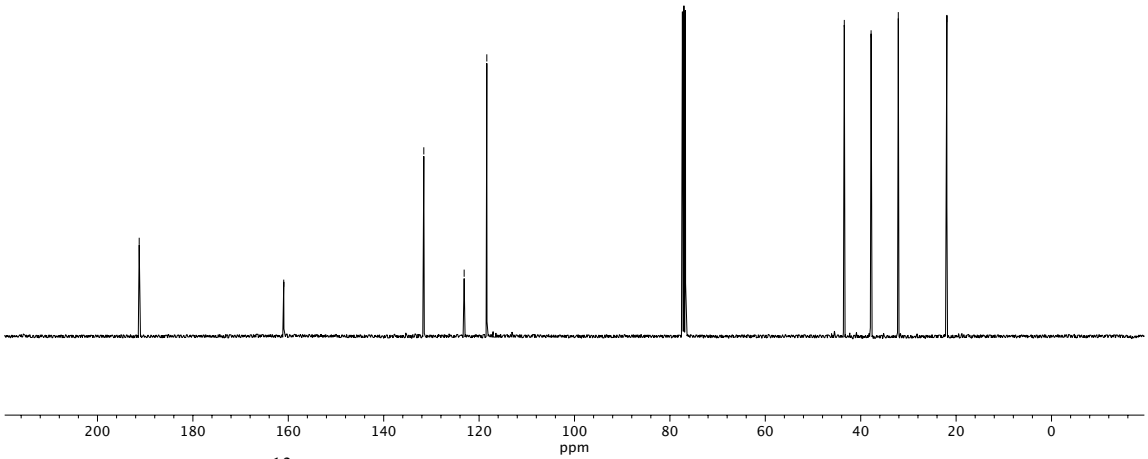
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1a**.



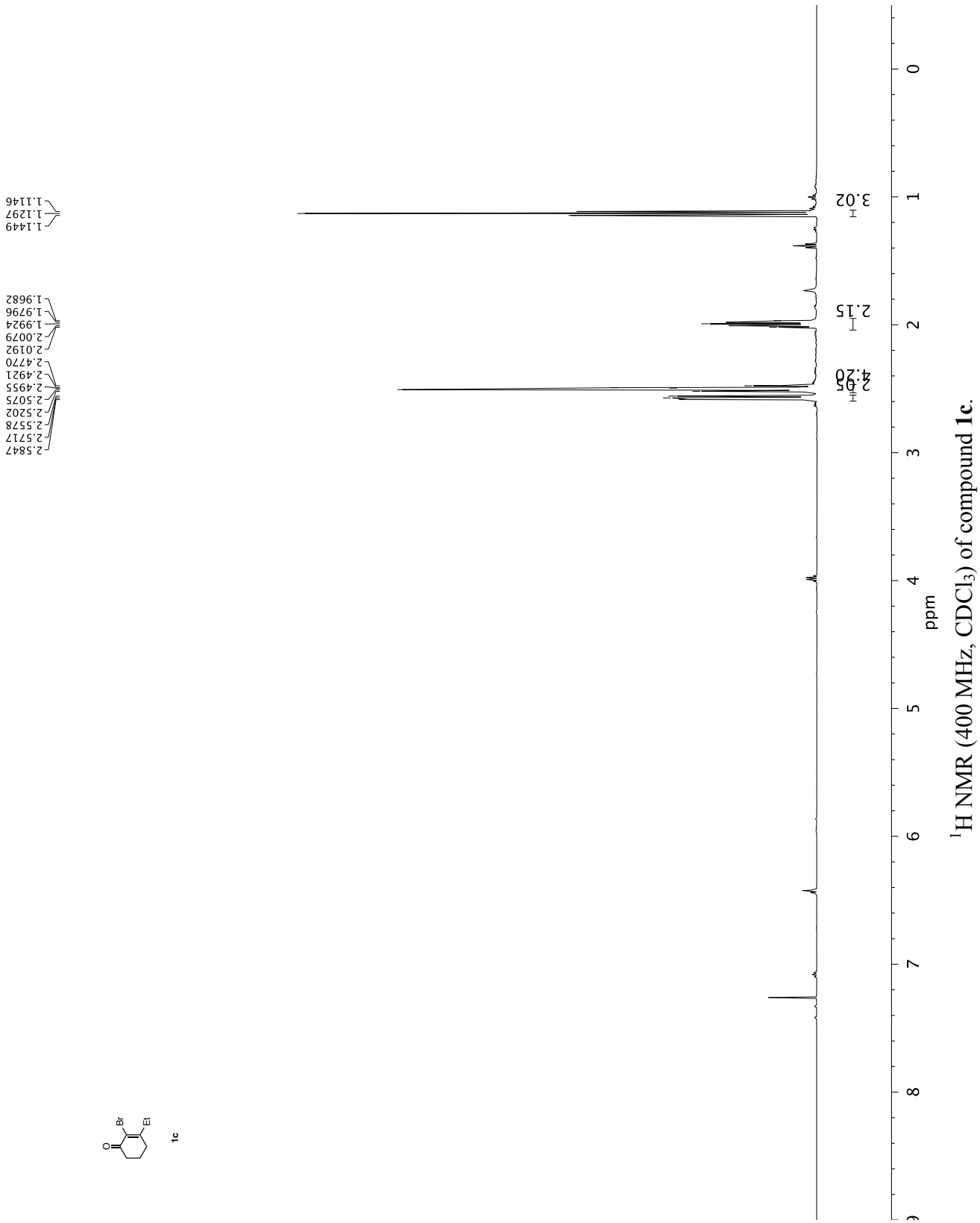
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1b**



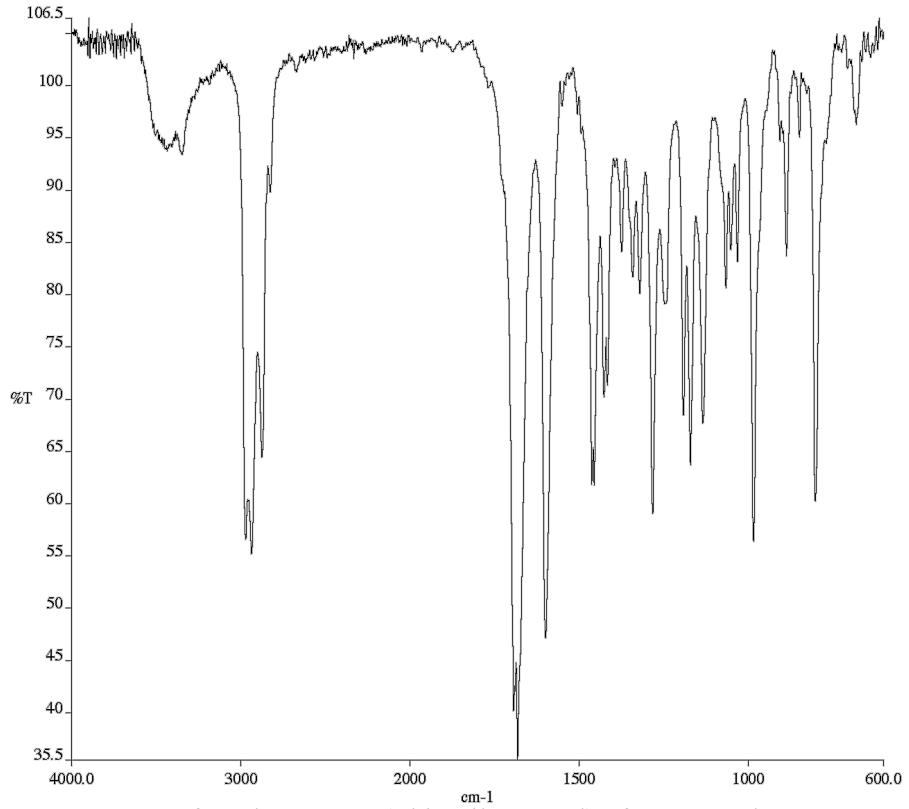
Infrared spectrum (Thin Film, NaCl) of compound **1b**.



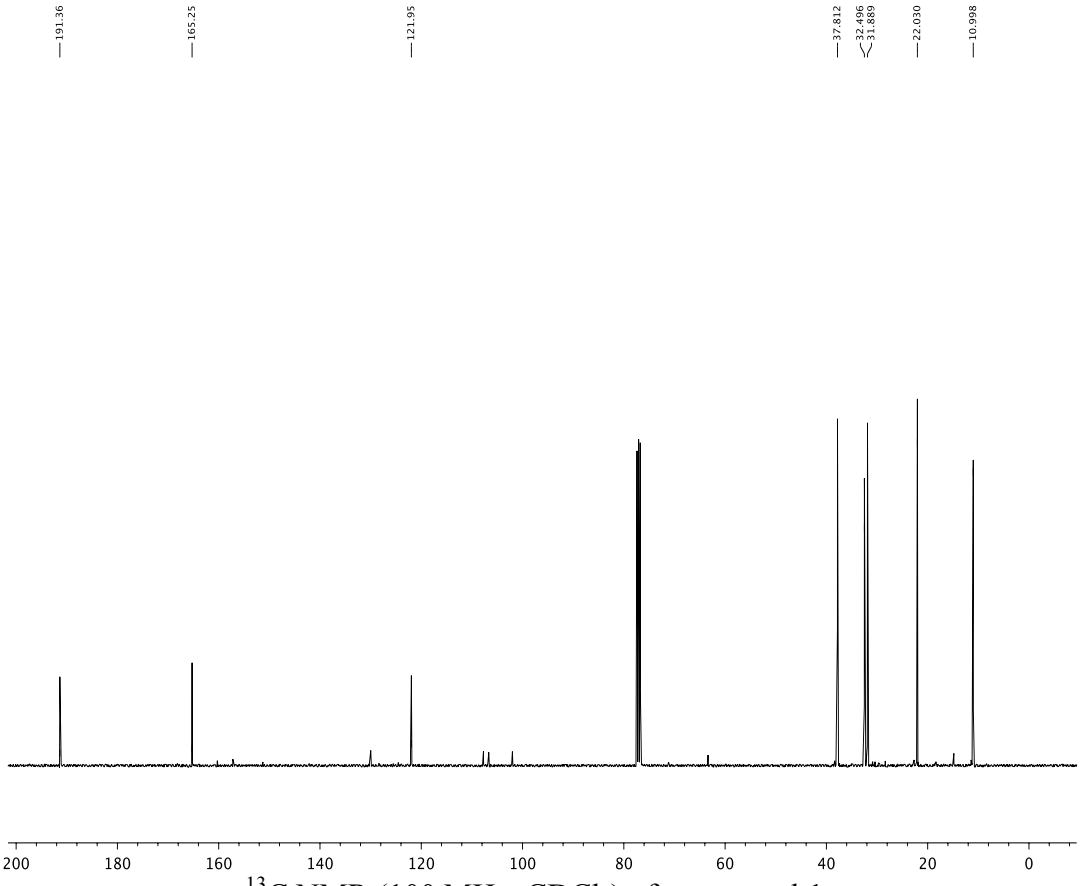
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1b**.



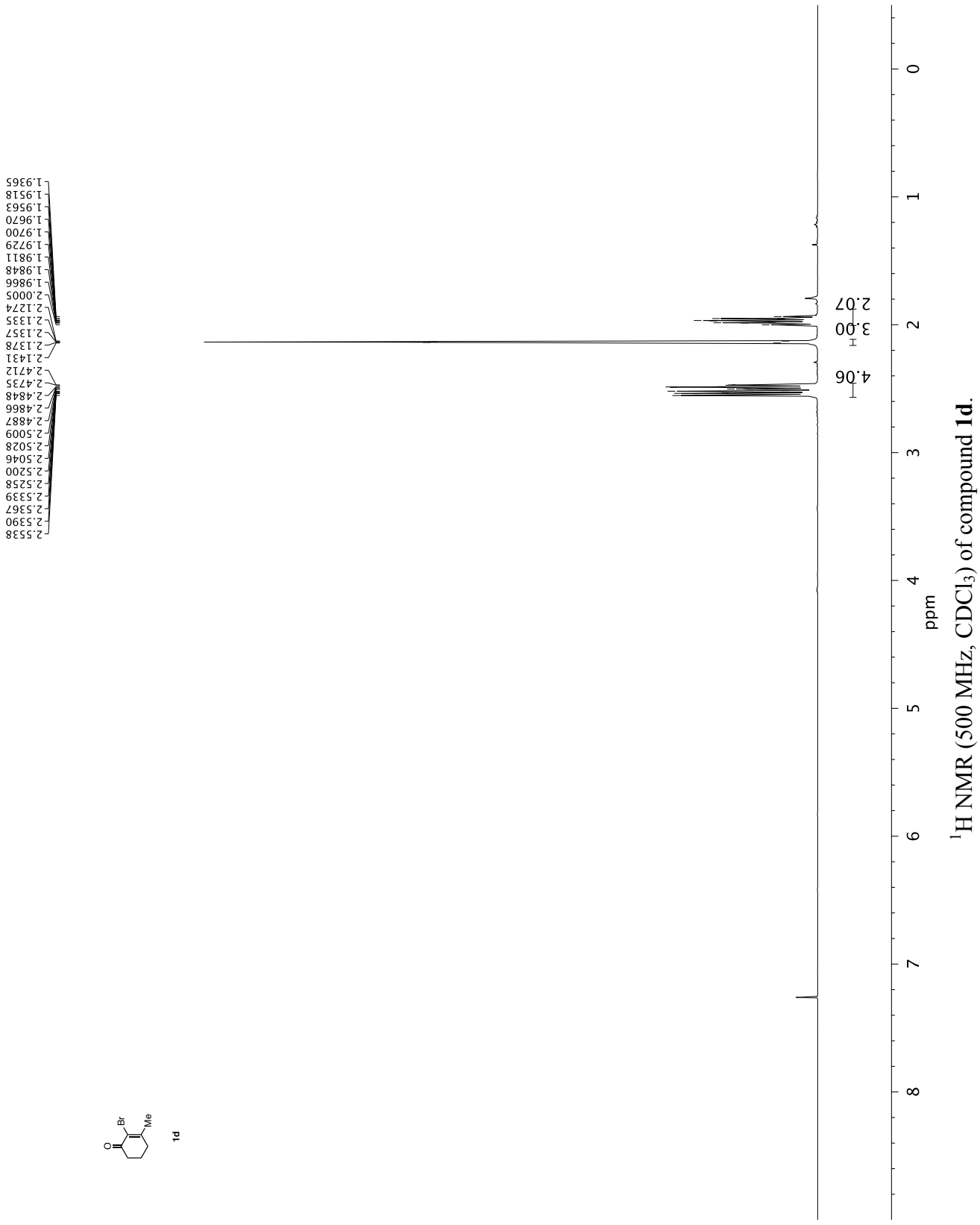
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1c**.



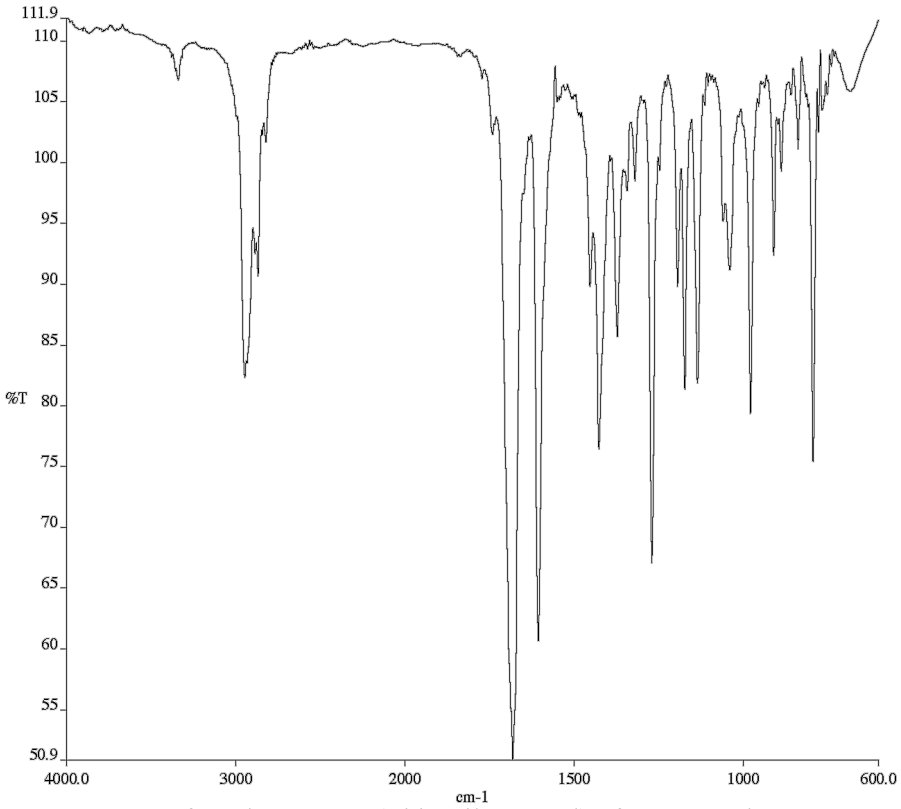
Infrared spectrum (Thin Film, NaCl) of compound **1c**.



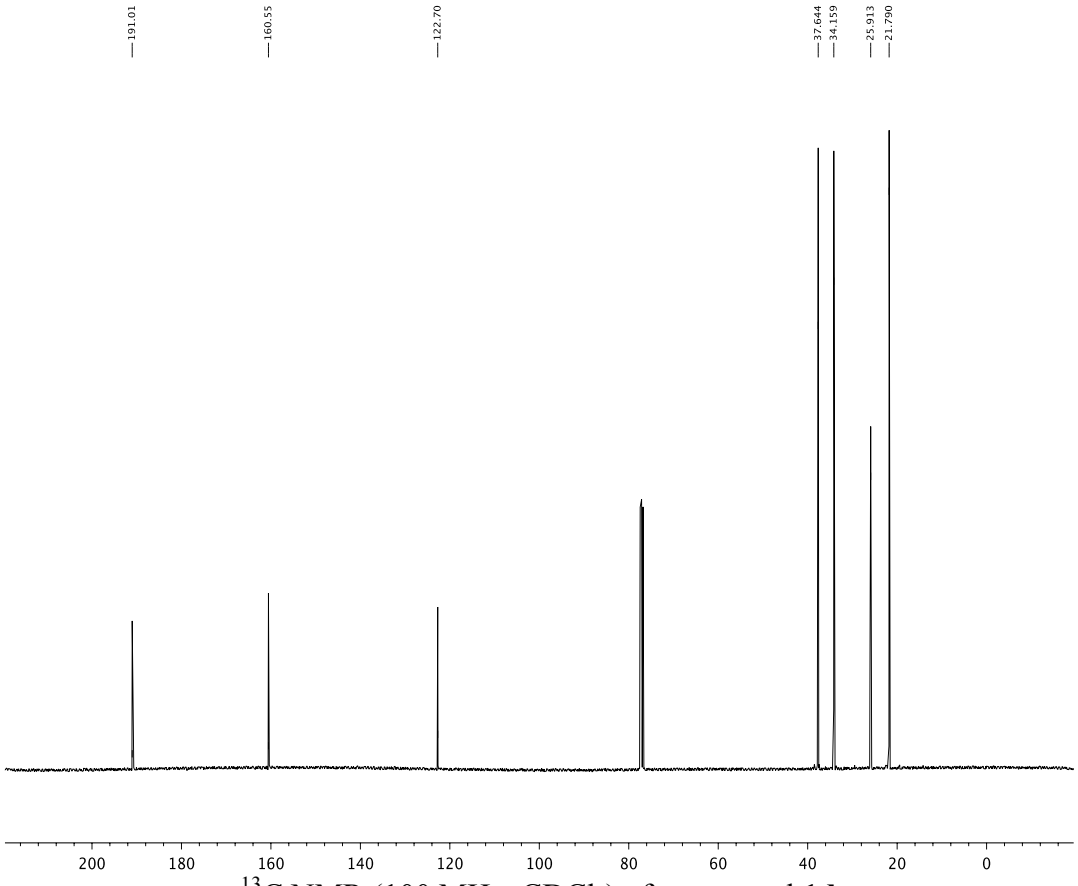
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1c**.



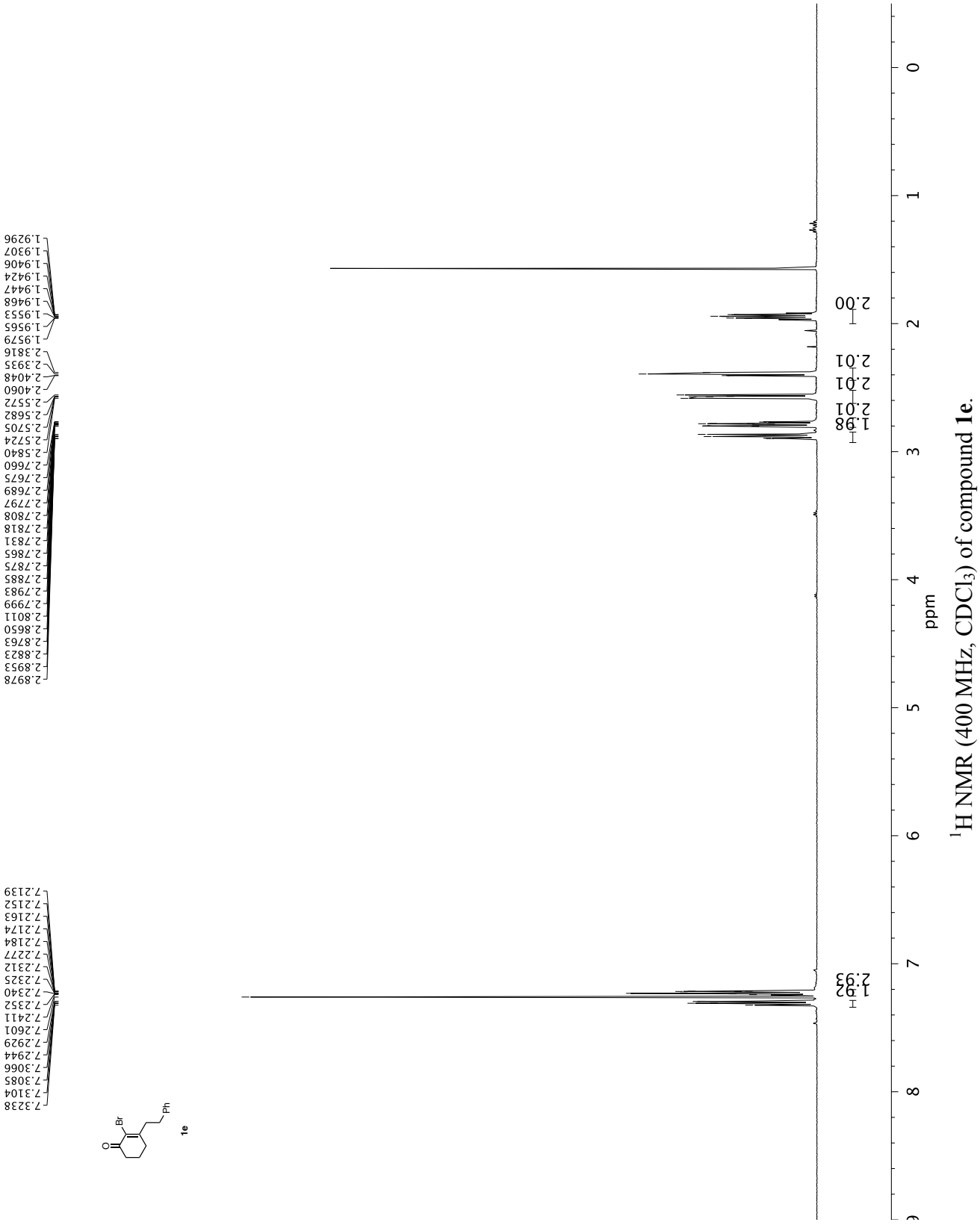
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1d**.



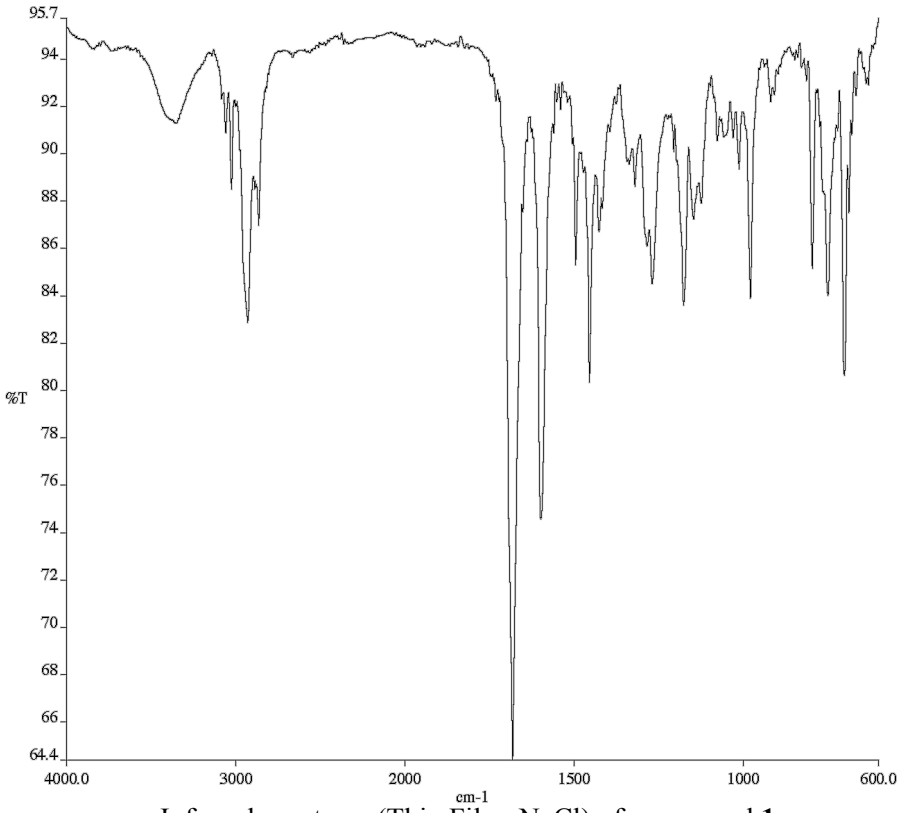
Infrared spectrum (Thin Film, NaCl) of compound **1d**.



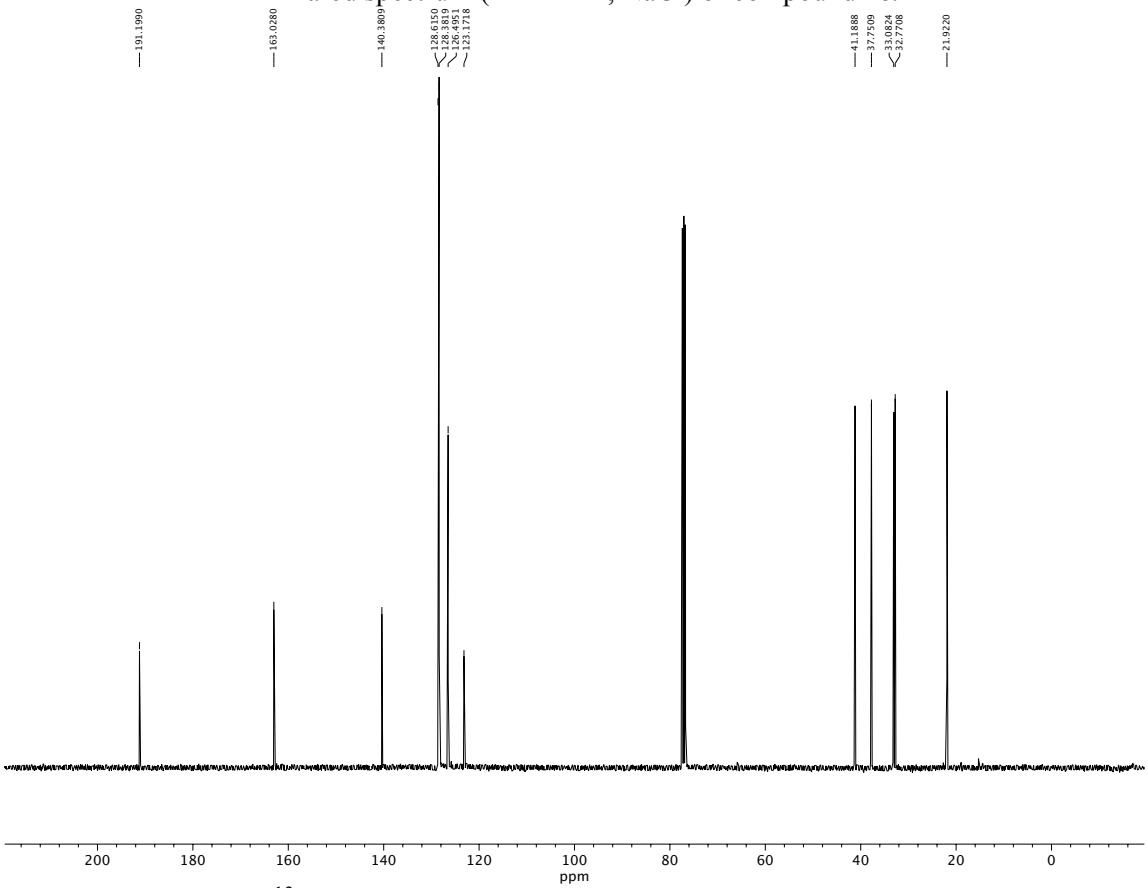
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1d**.



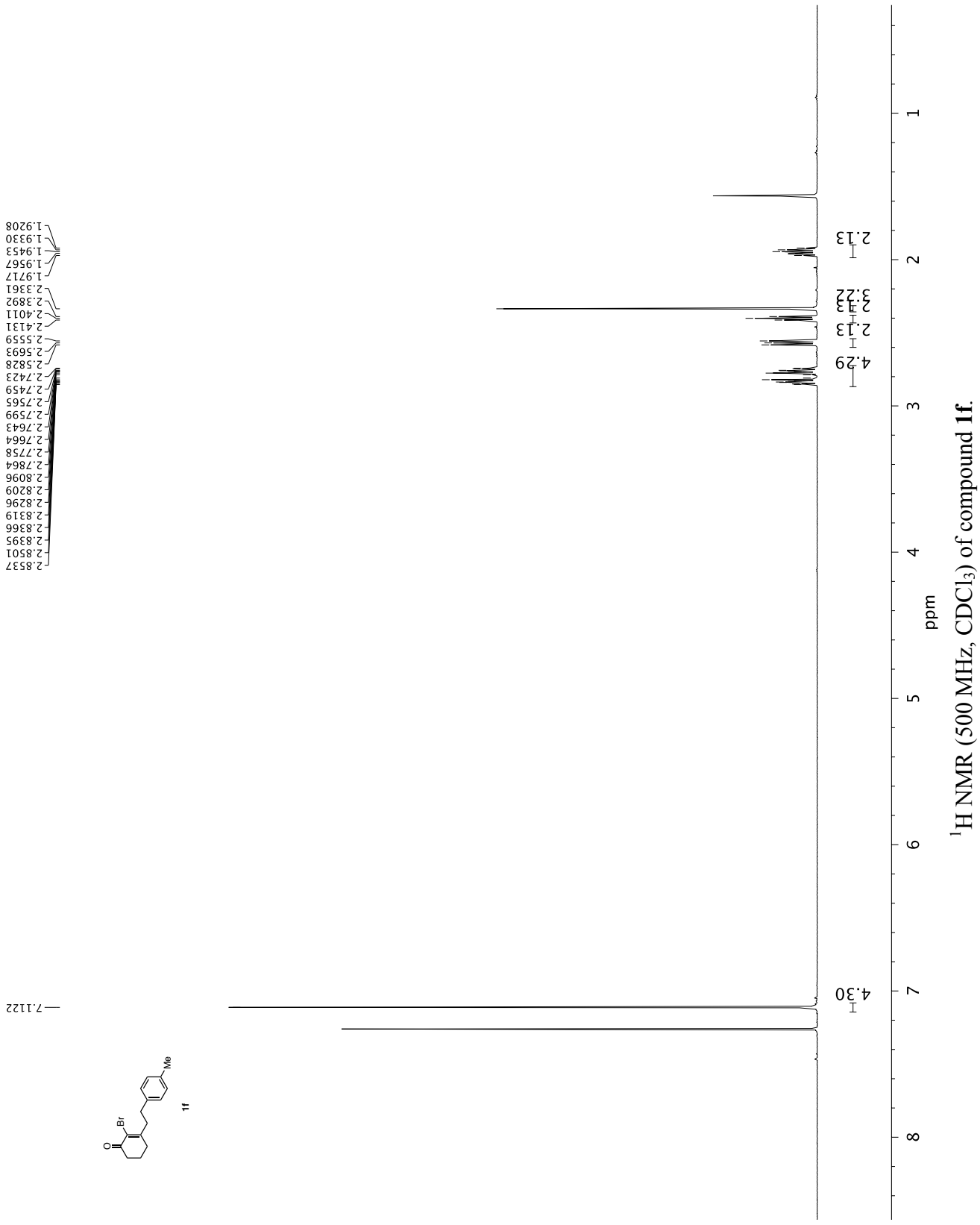
^{1}H NMR (400 MHz, $CDCl_3$) of compound **1e**.



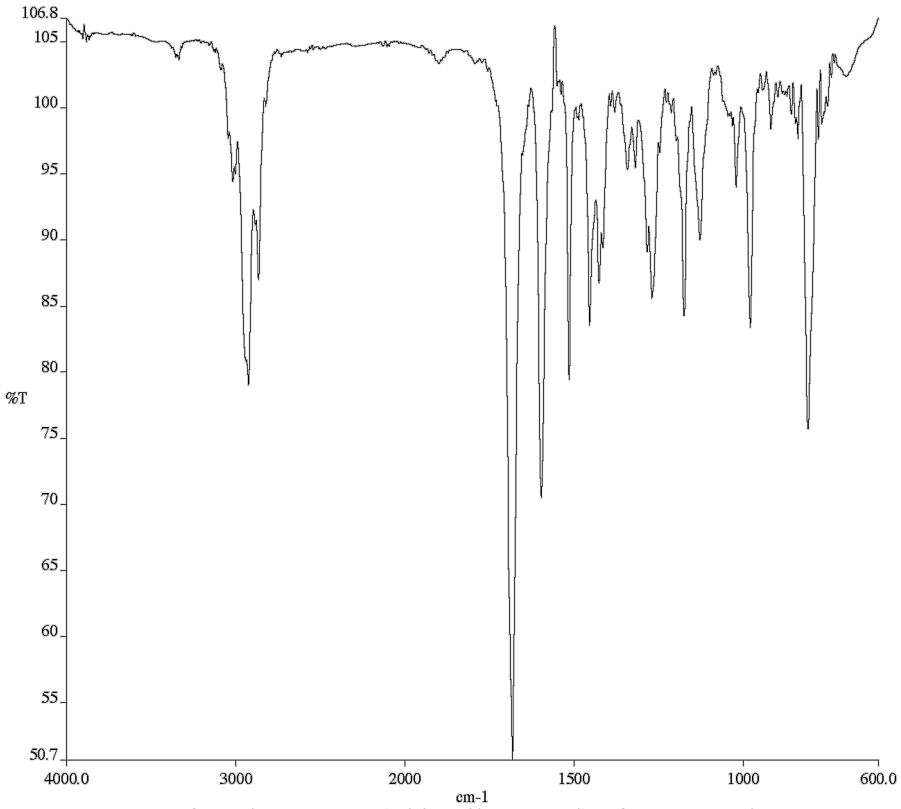
Infrared spectrum (Thin Film, NaCl) of compound **1e**.



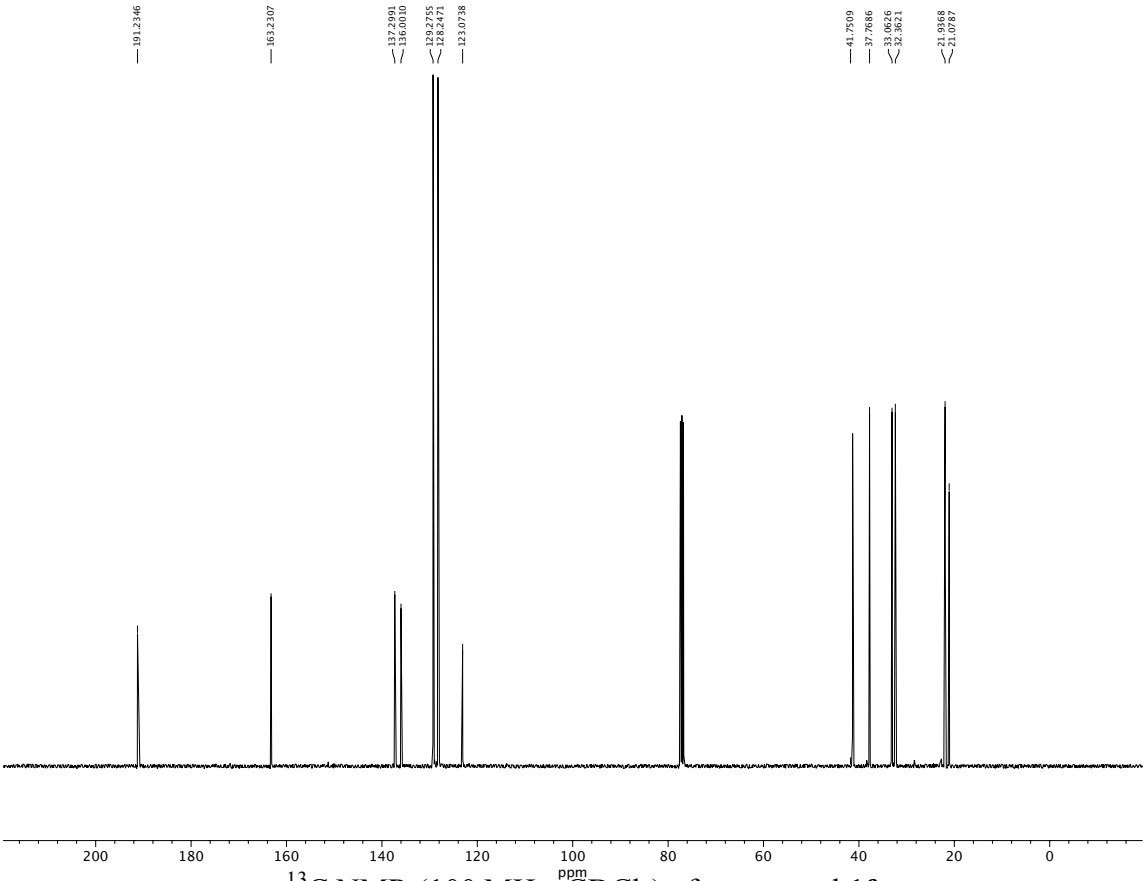
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1e**.



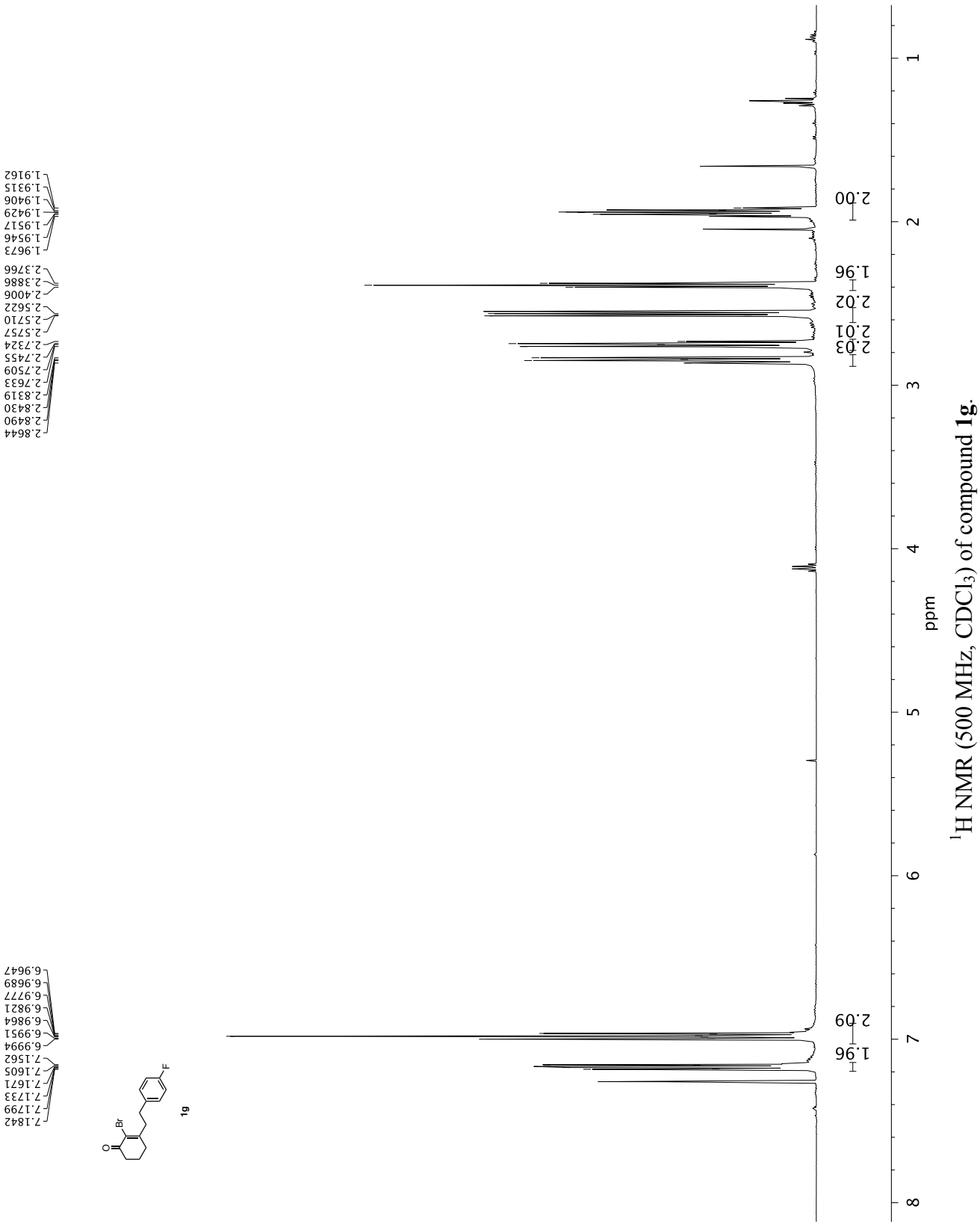
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1f**.



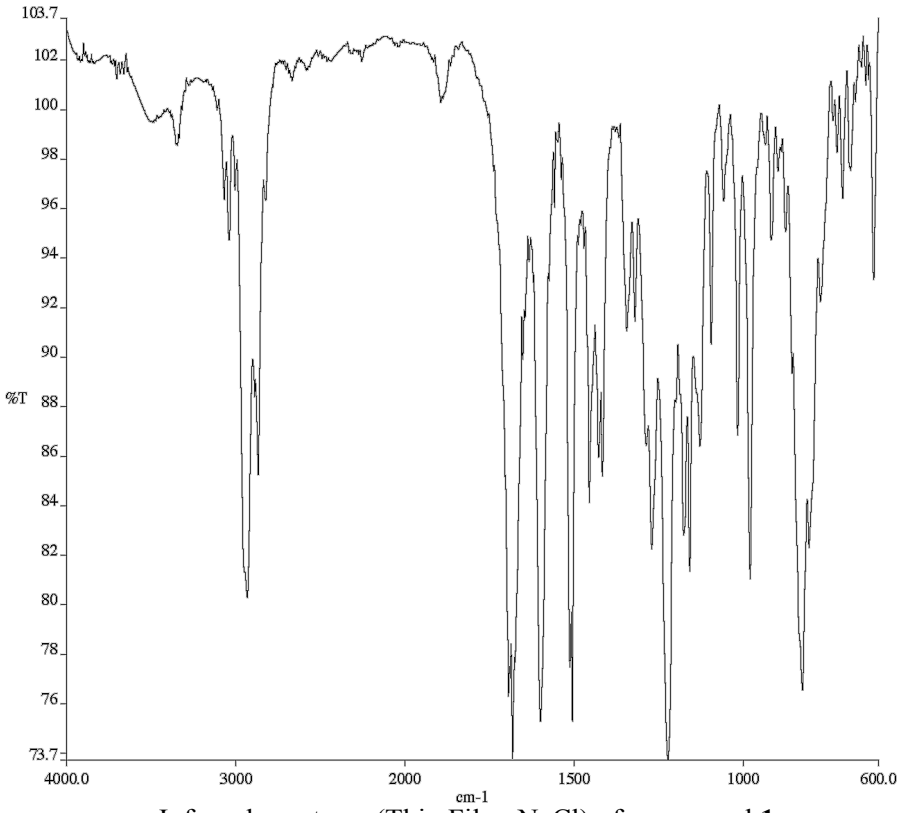
Infrared spectrum (Thin Film, NaCl) of compound **1f**.



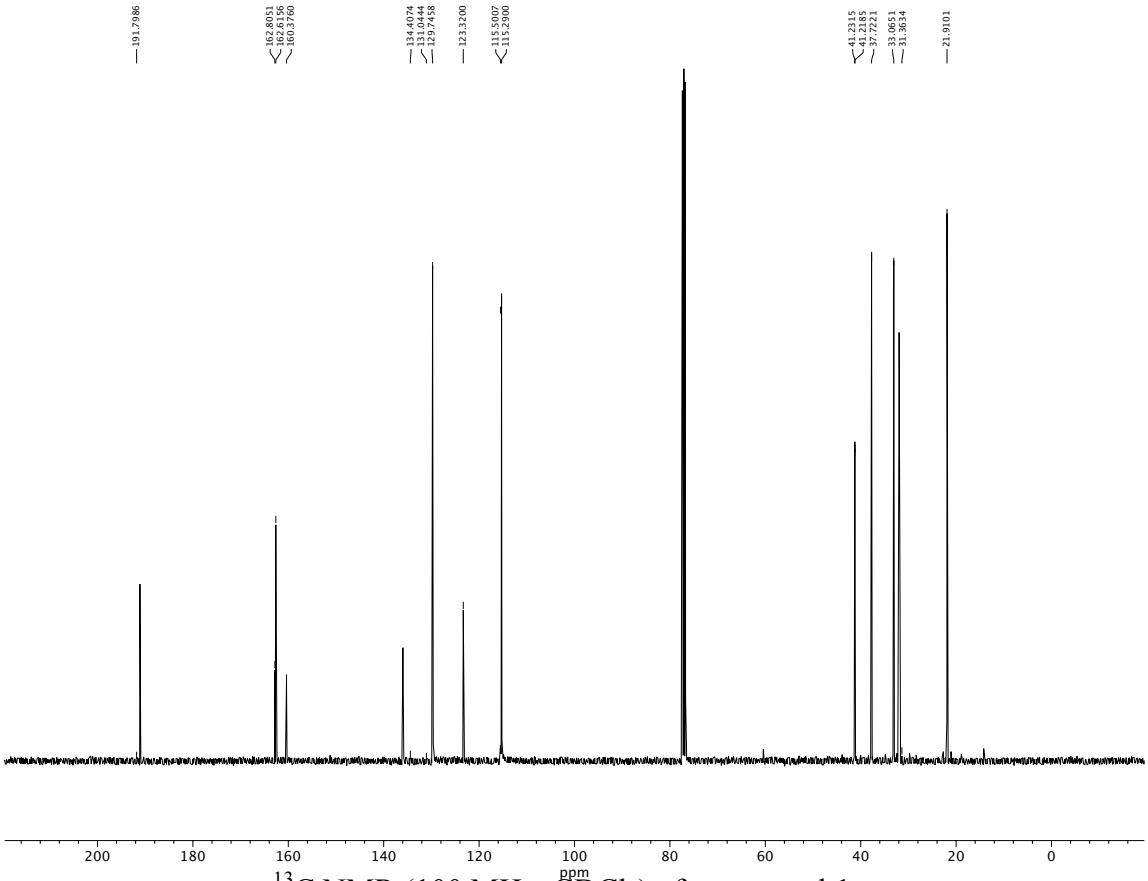
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1f**.



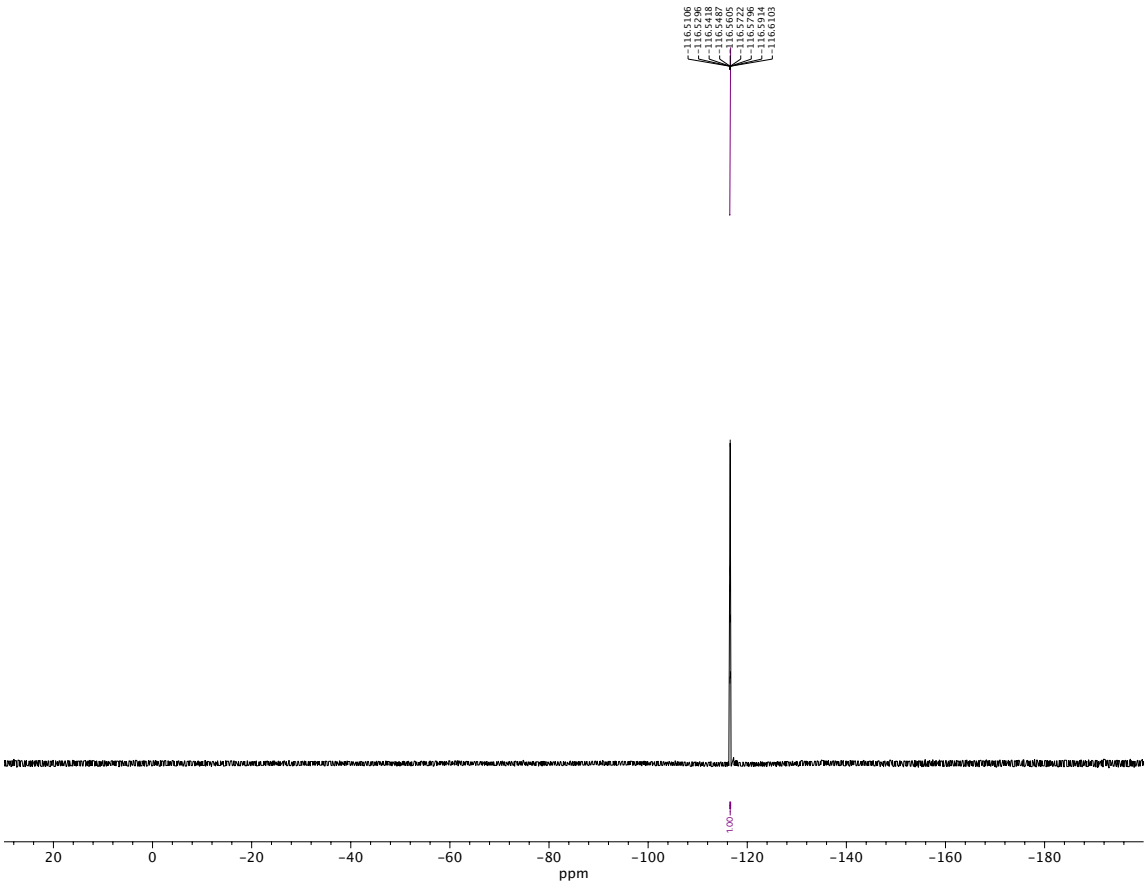
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1g**.



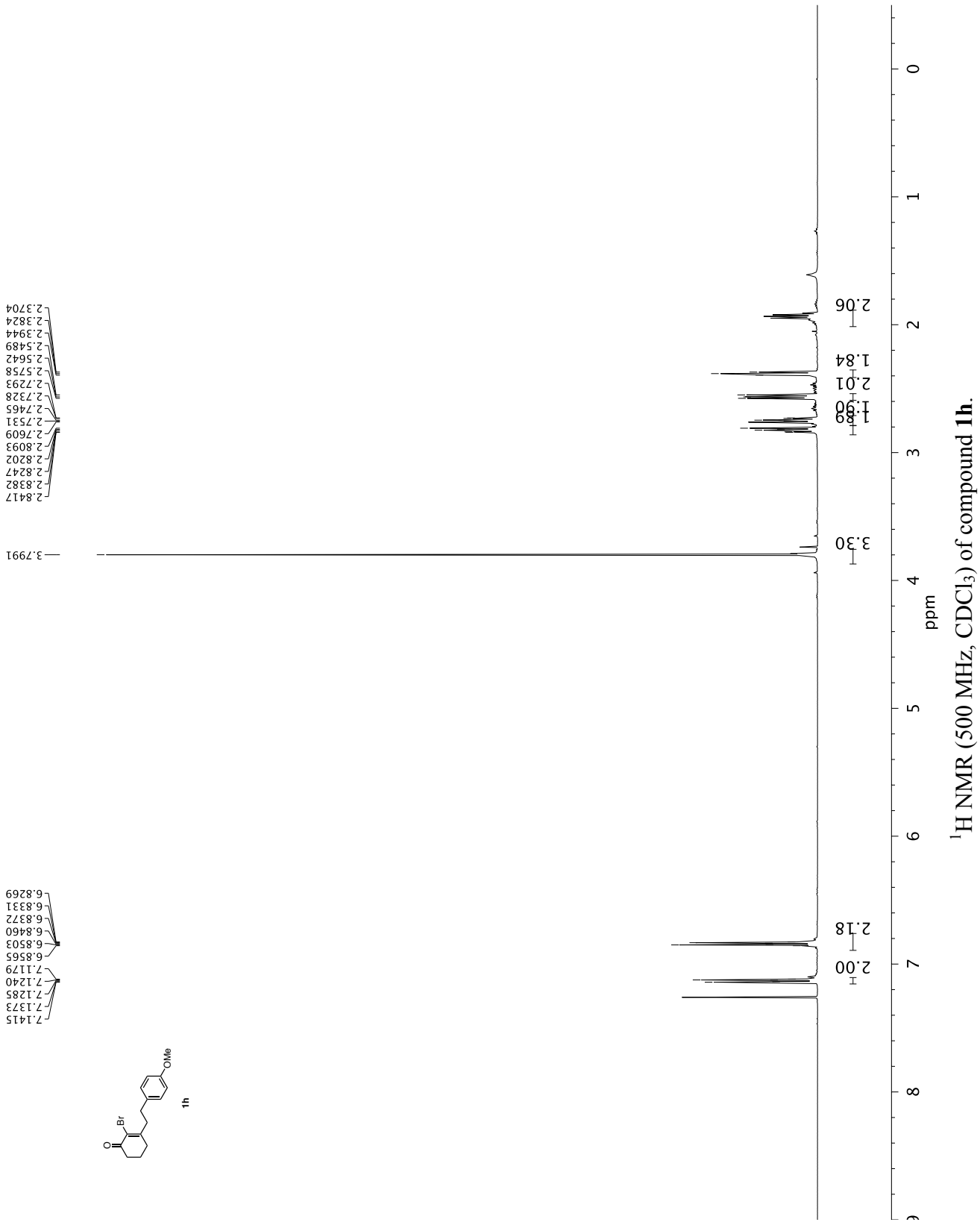
Infrared spectrum (Thin Film, NaCl) of compound **1g**.



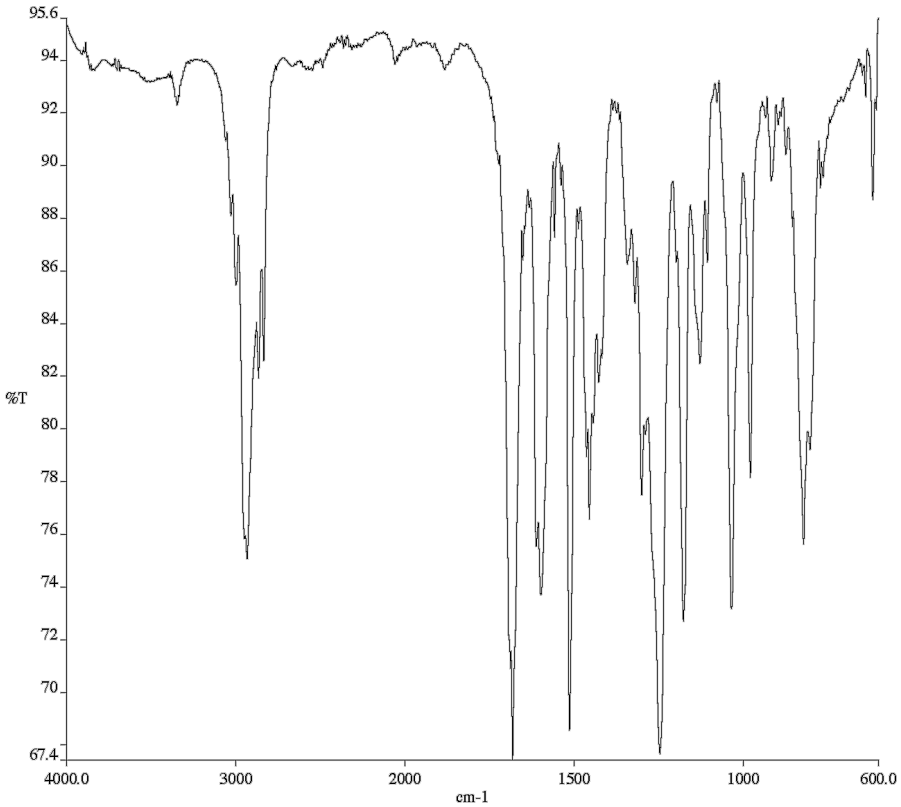
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1g**.



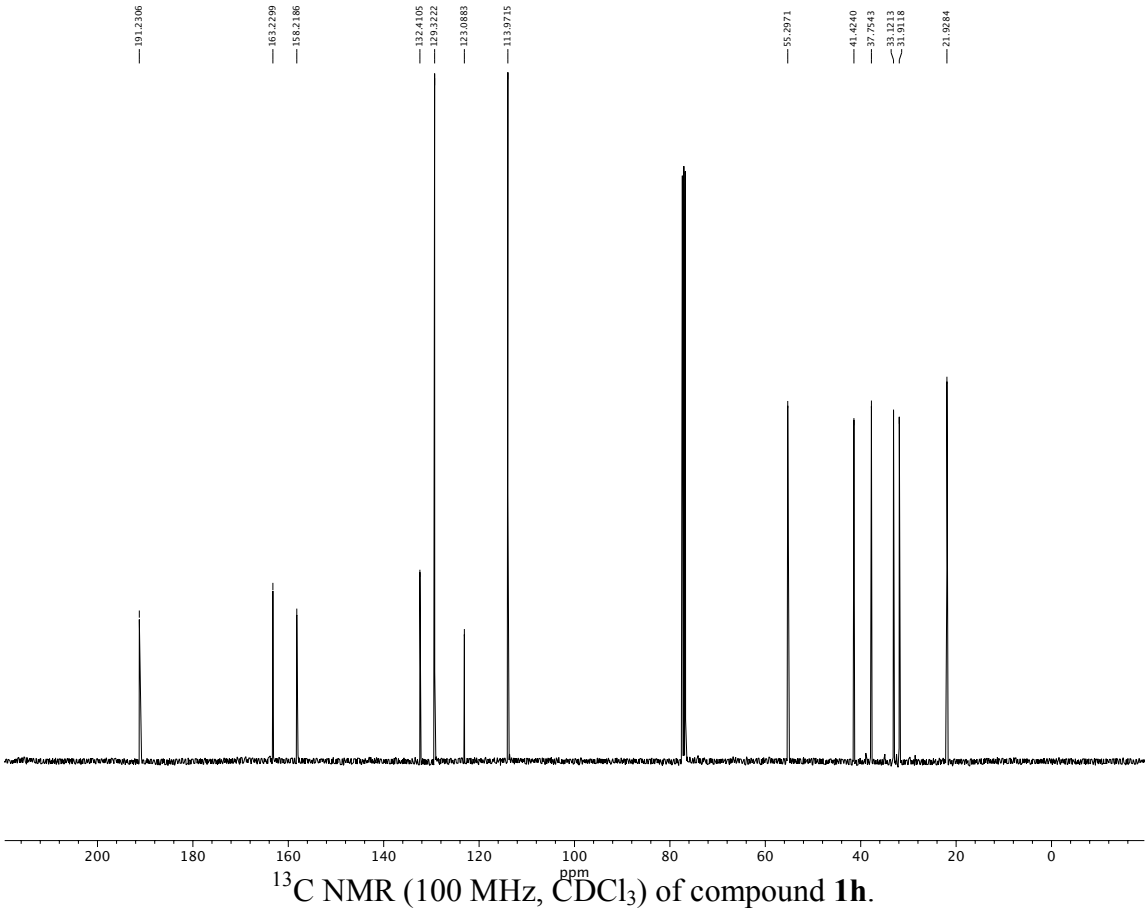
^{19}F NMR (282 MHz, $CDCl_3$) of compound **1g**.



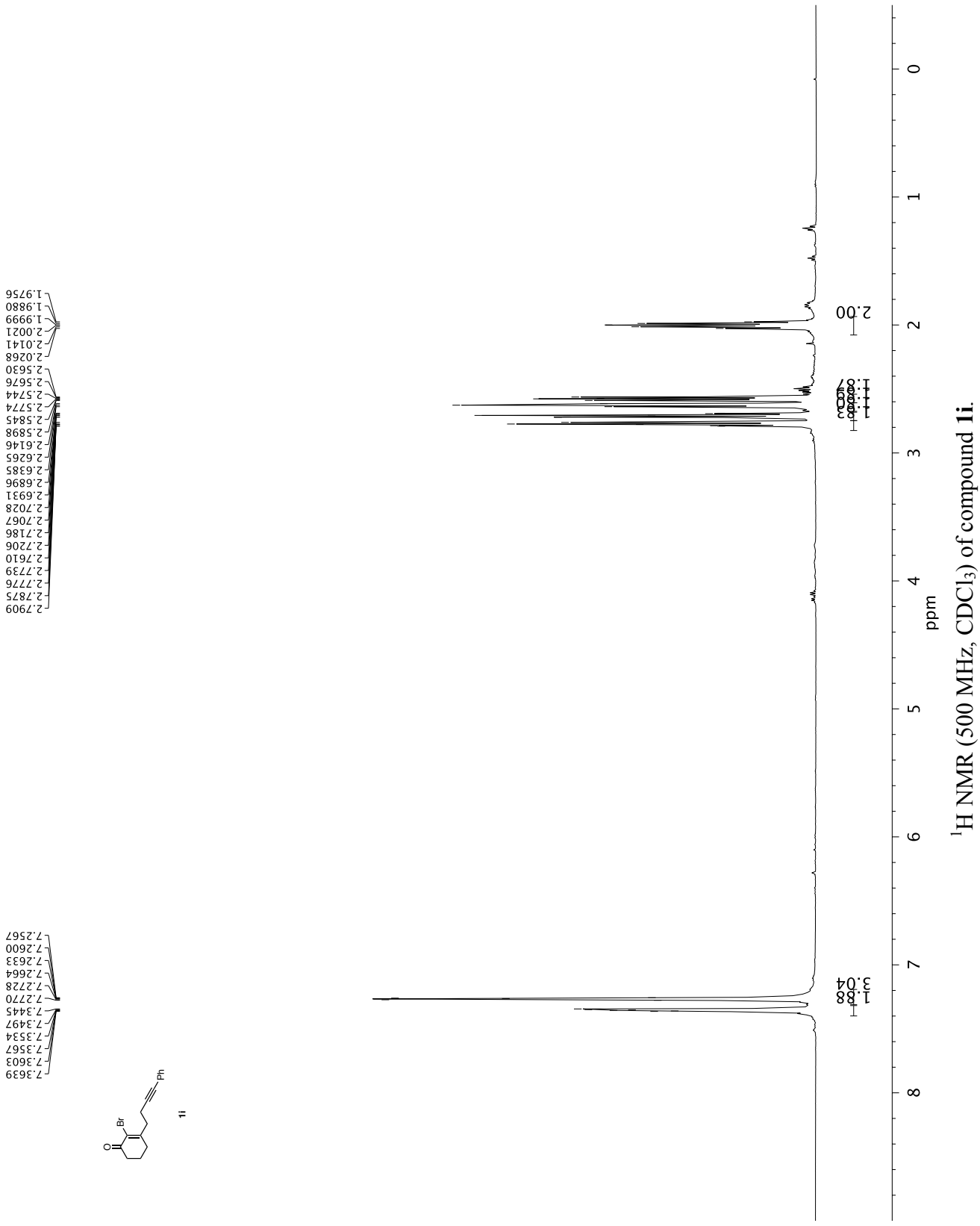
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1h**.



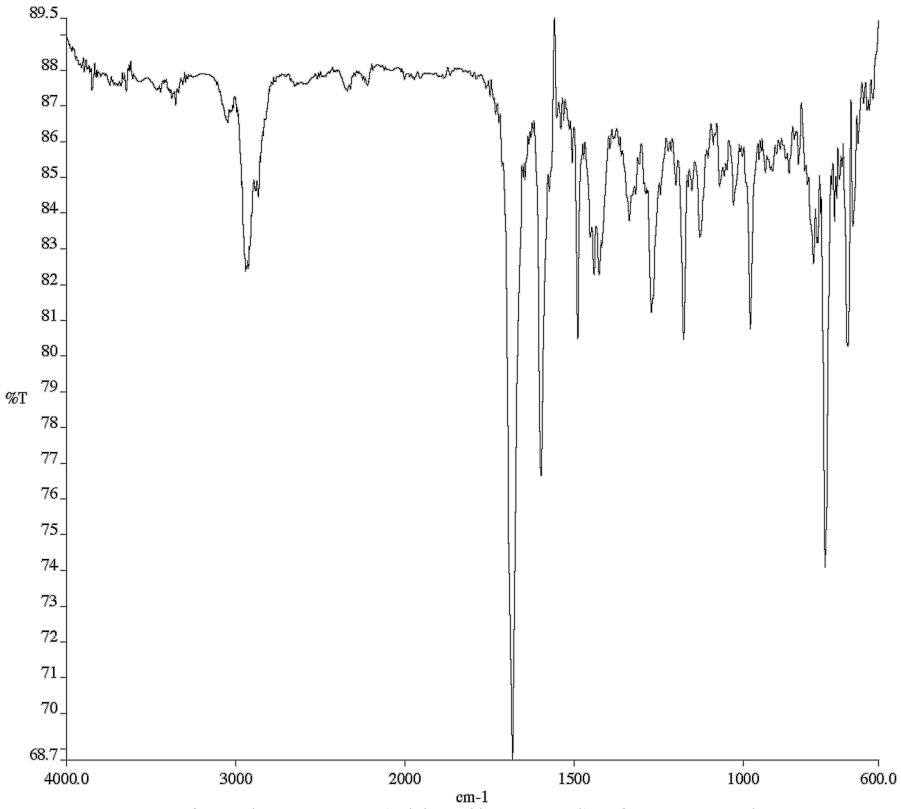
Infrared spectrum (Thin Film, NaCl) of compound **1h**.



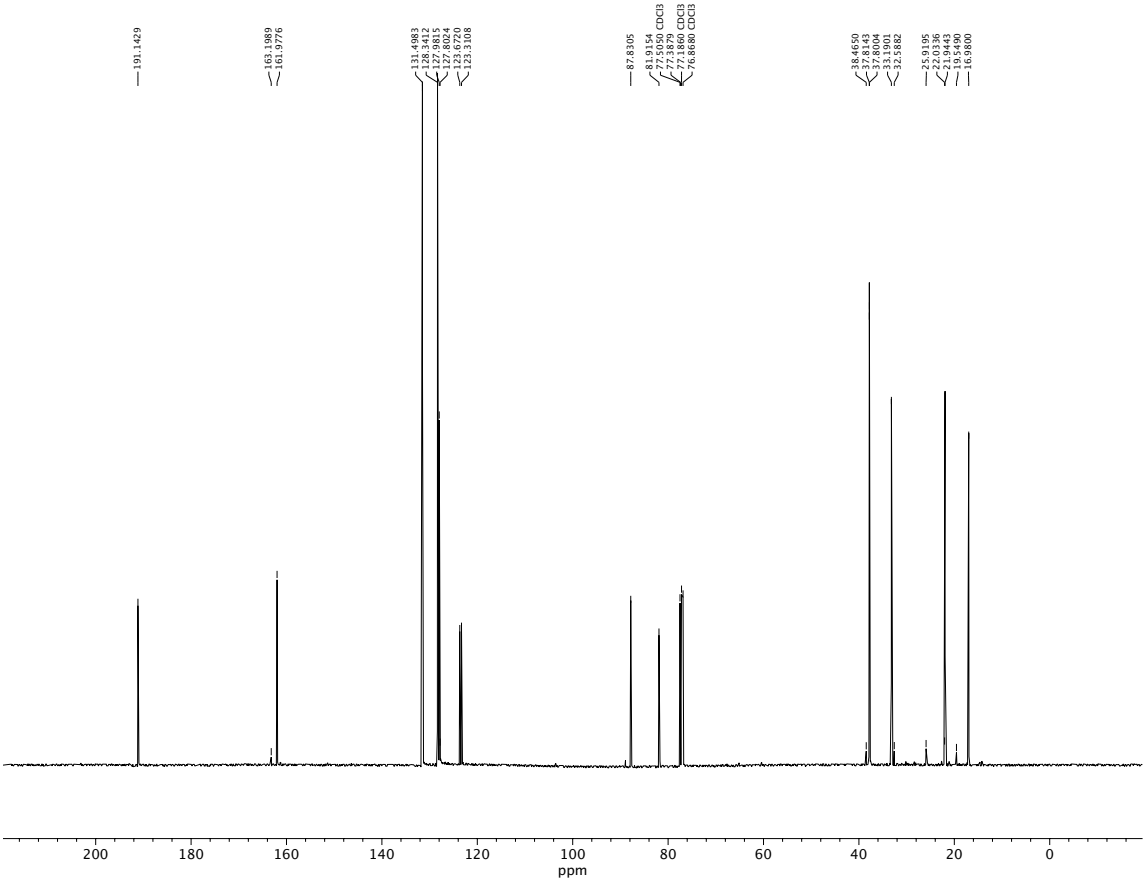
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1h**.



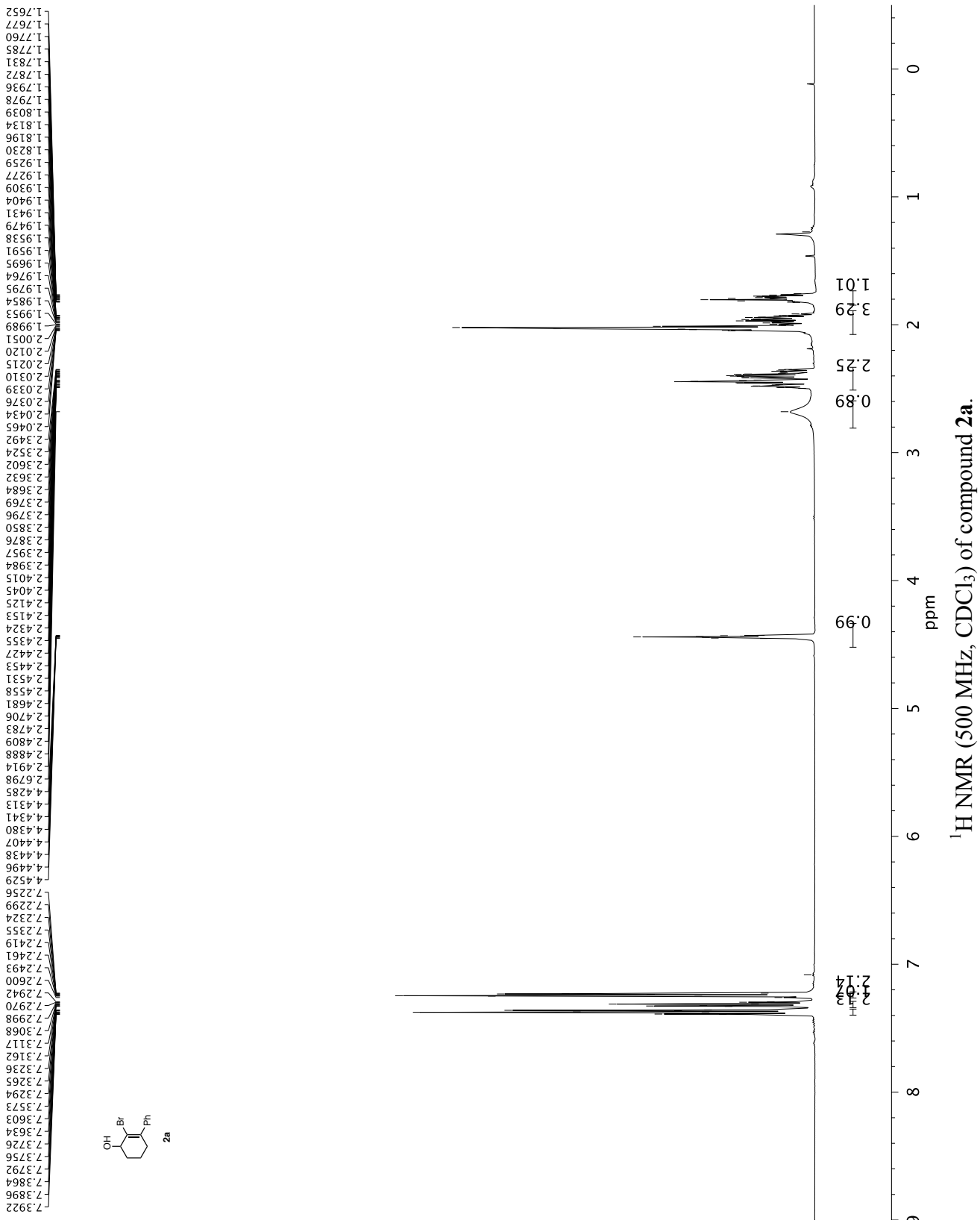
^{1}H NMR (500 MHz, $CDCl_3$) of compound **1i**.



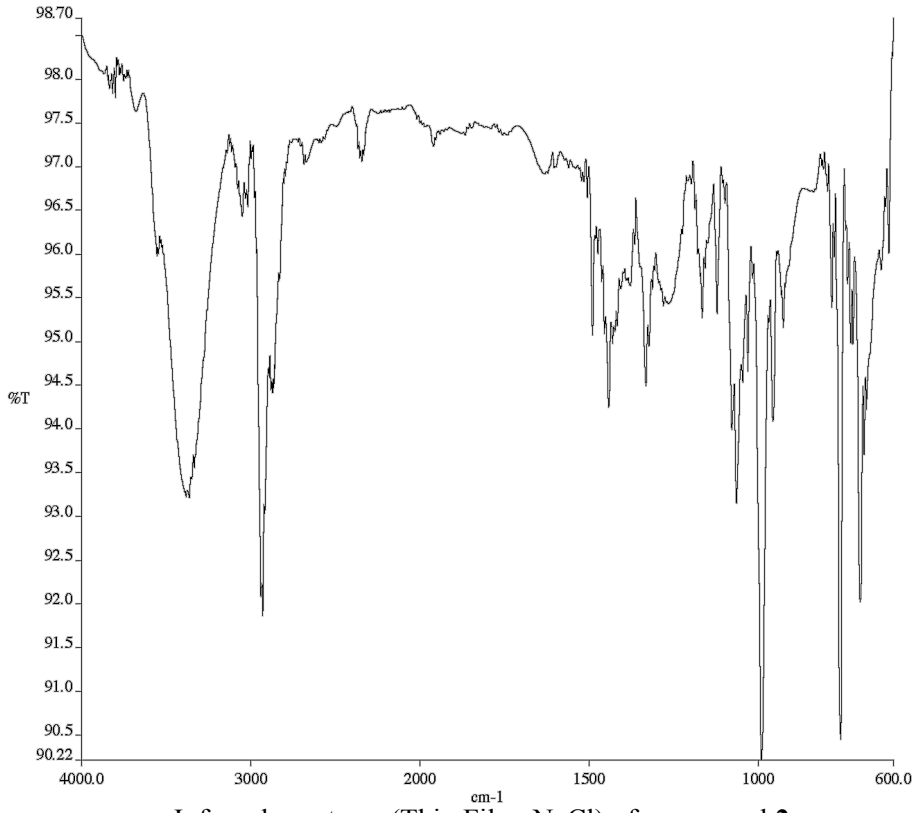
Infrared spectrum (Thin Film, NaCl) of compound **1i**.



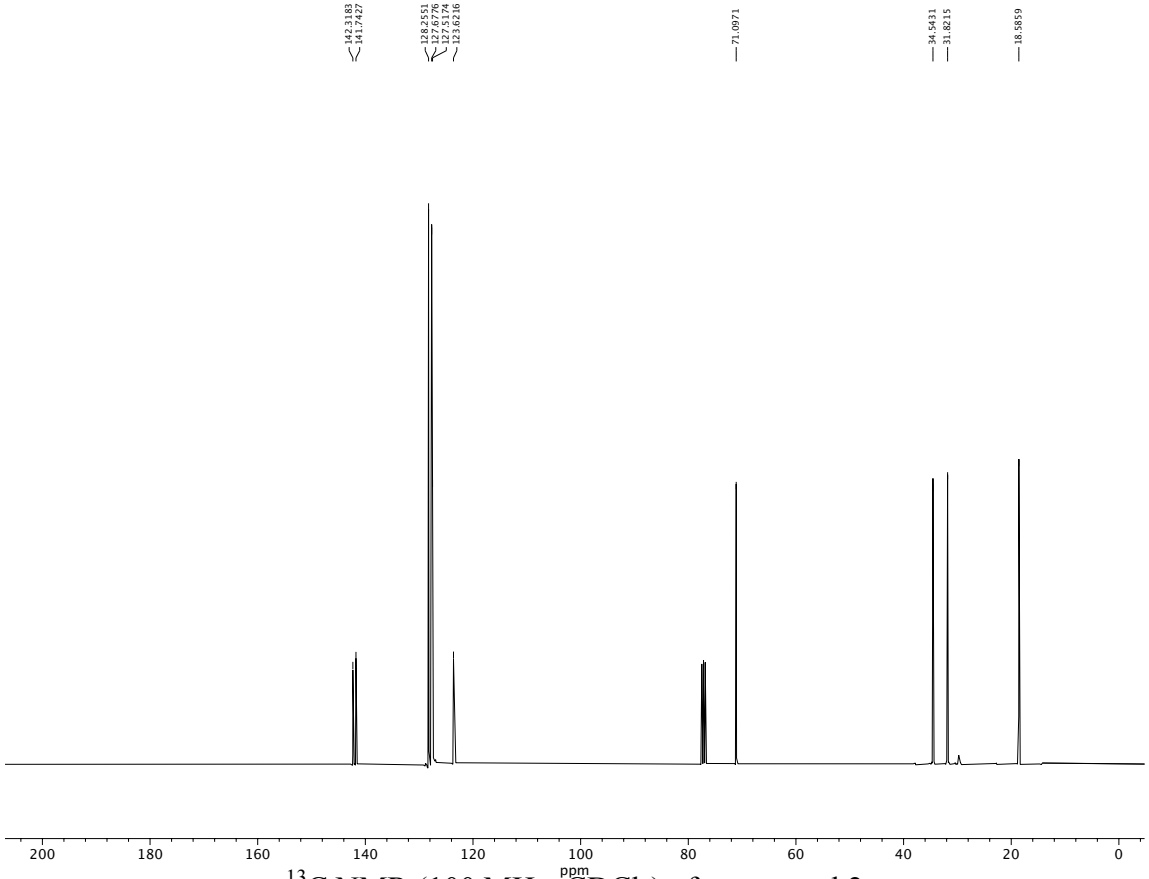
^{13}C NMR (100 MHz, $CDCl_3$) of compound **1i**.



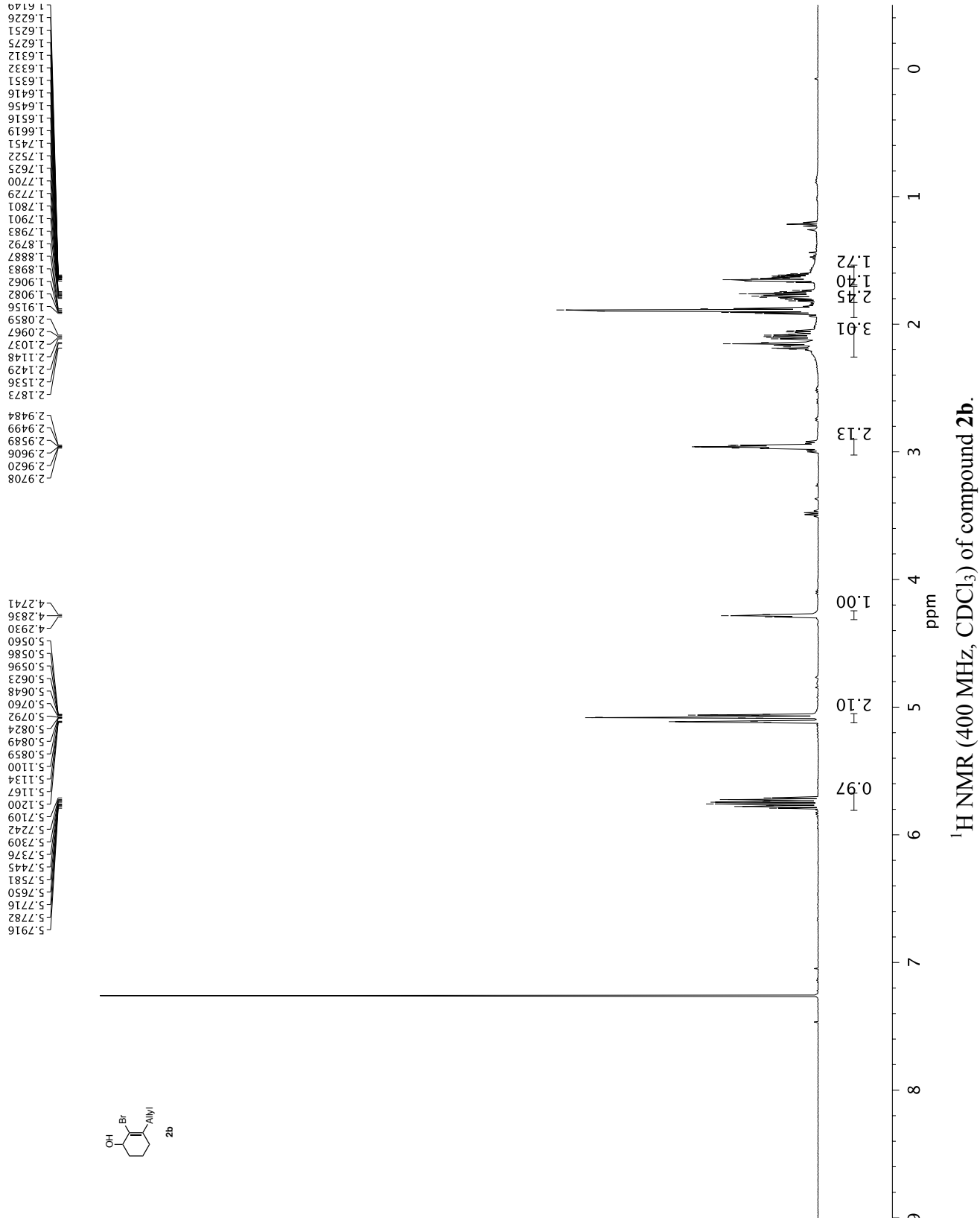
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2a**.



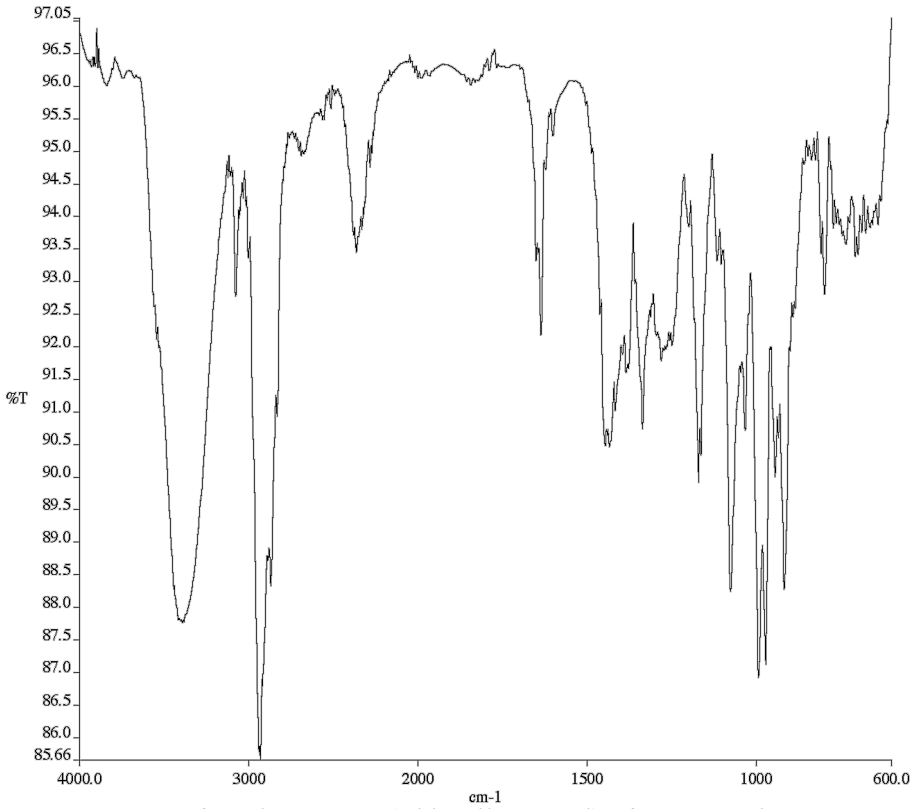
Infrared spectrum (Thin Film, NaCl) of compound **2a**.



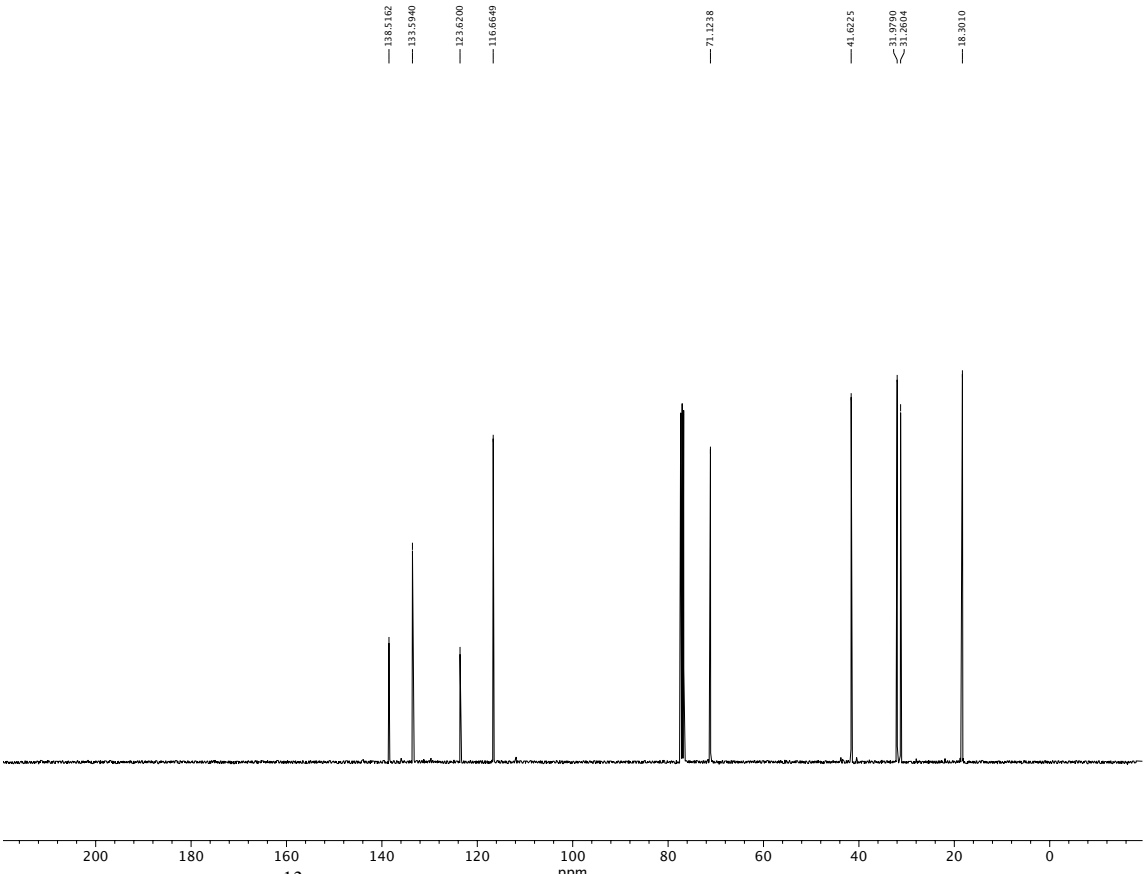
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.



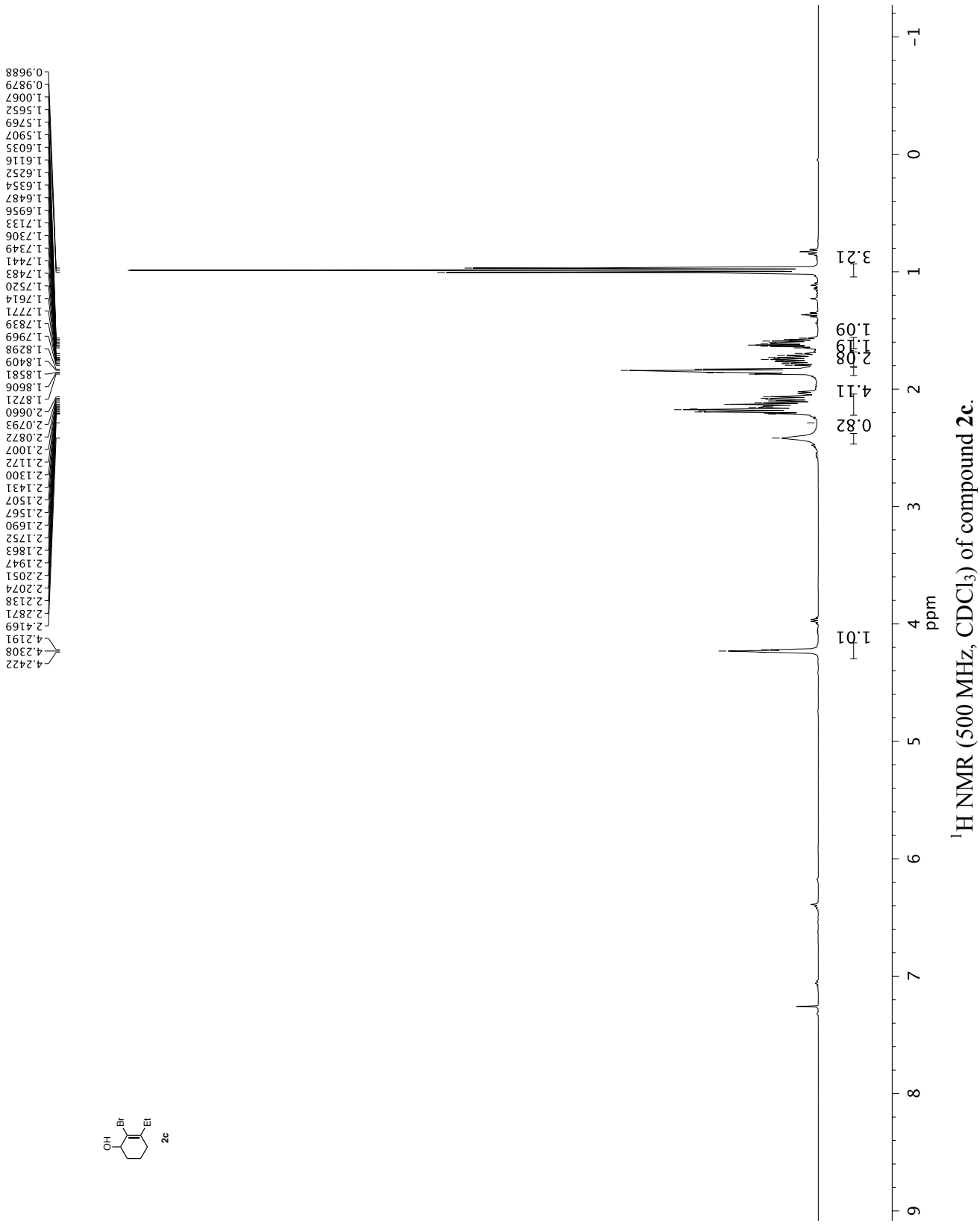
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**.



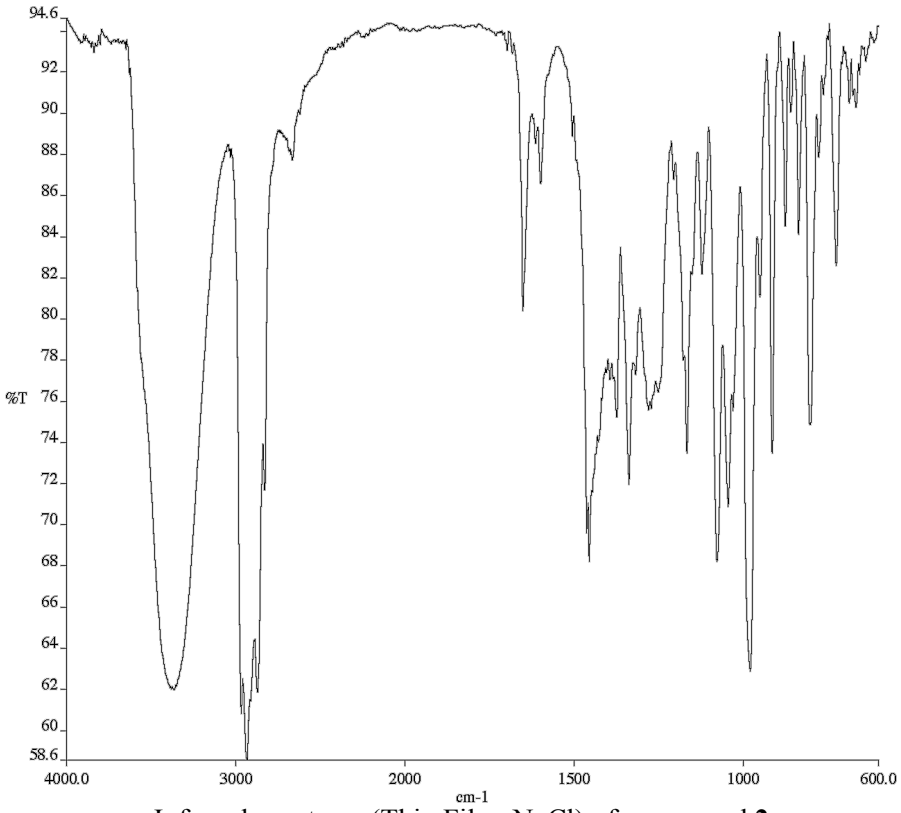
Infrared spectrum (Thin Film, NaCl) of compound **2b**.



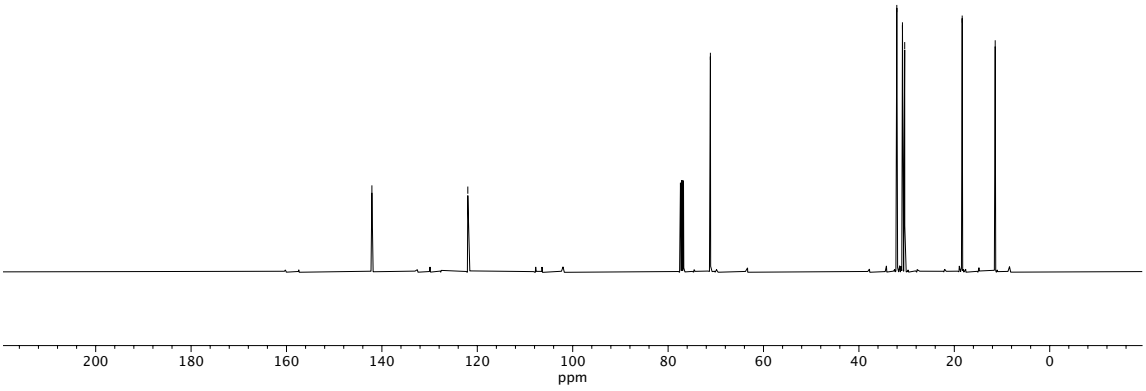
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**.



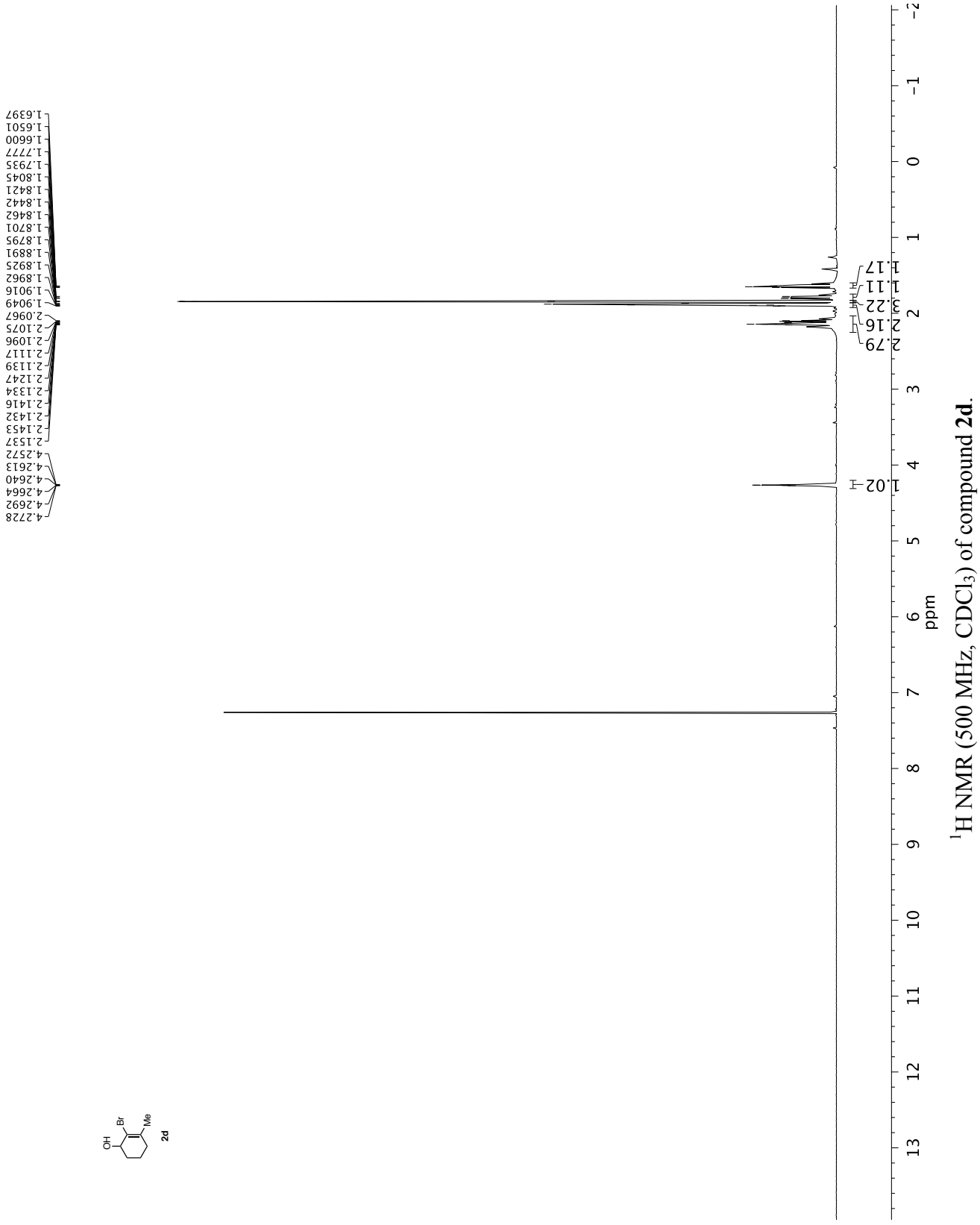
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2c**.



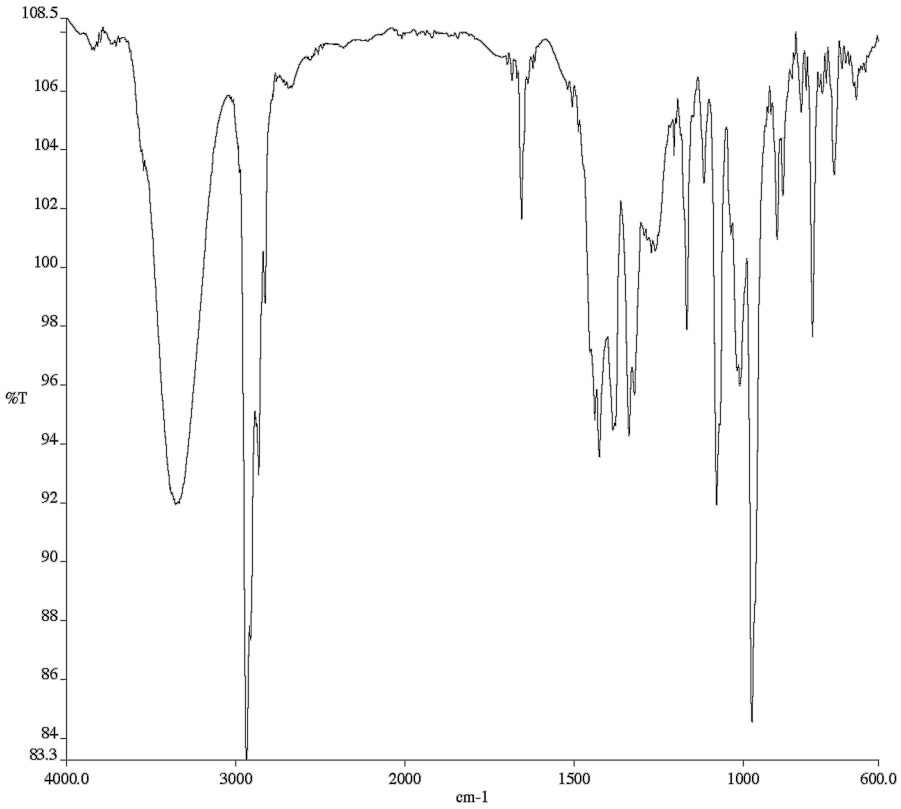
Infrared spectrum (Thin Film, NaCl) of compound **2c**.



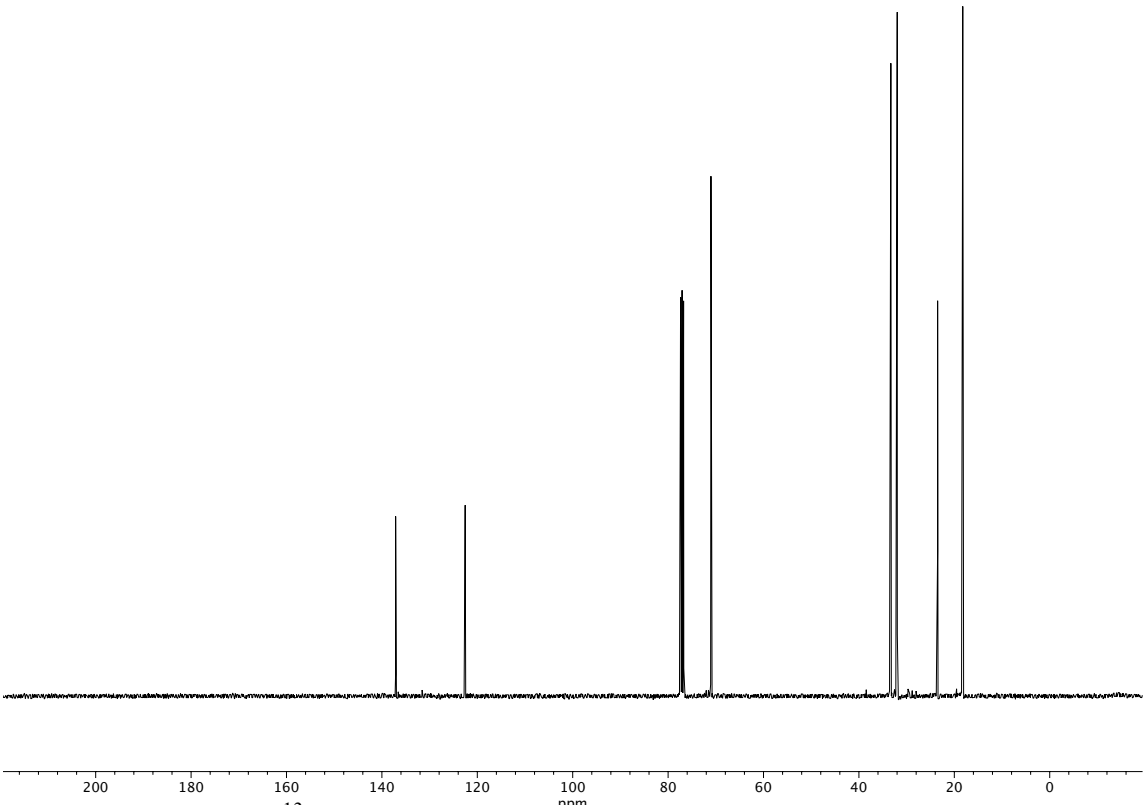
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2c**.



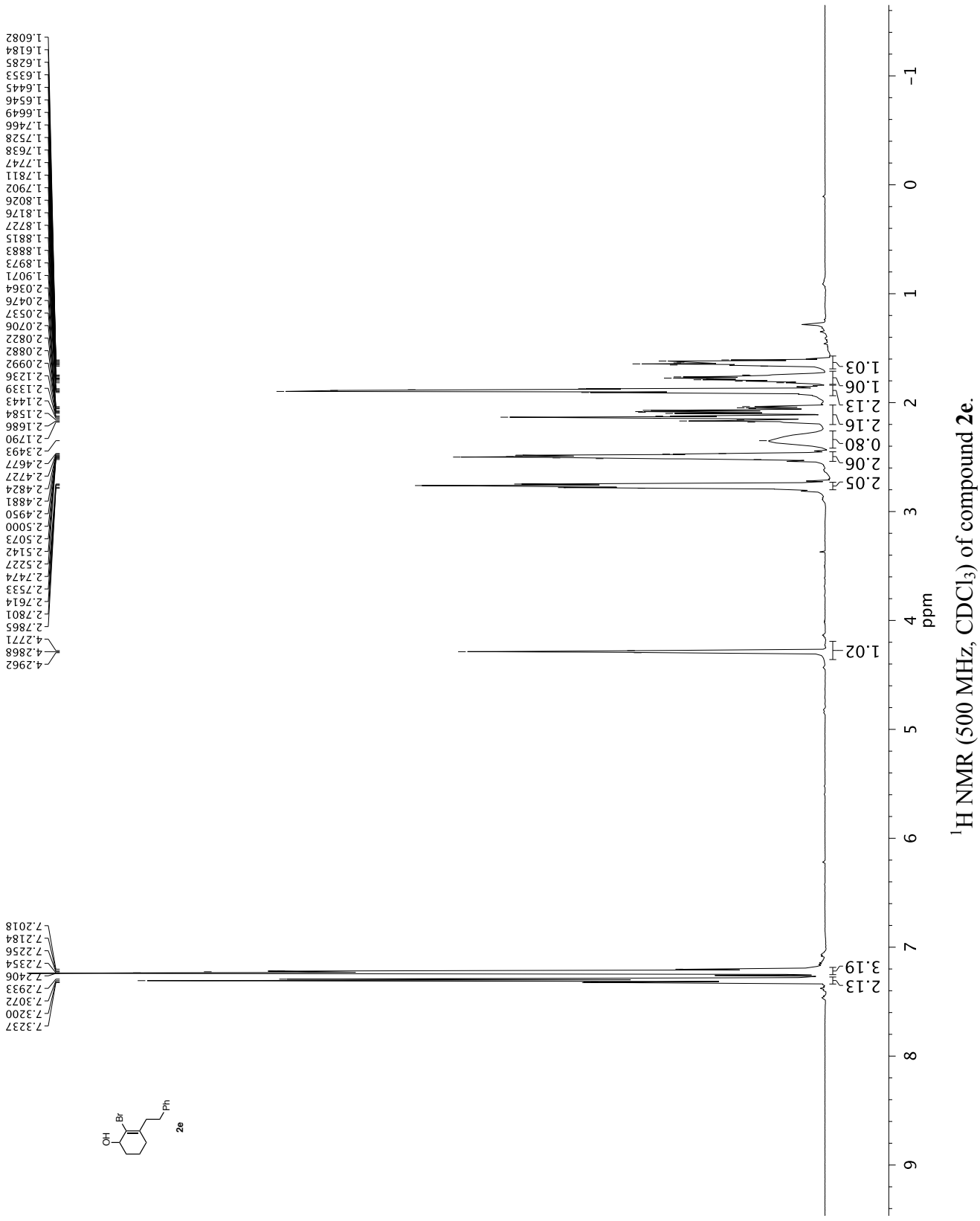
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2d**.



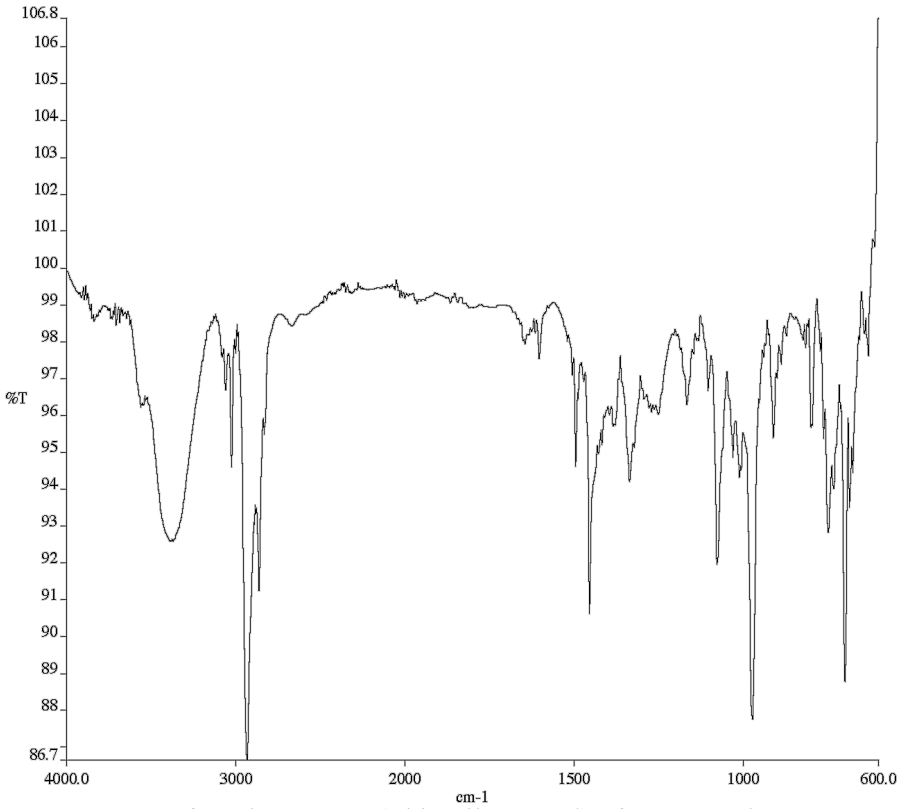
Infrared spectrum (Thin Film, NaCl) of compound **2d**.



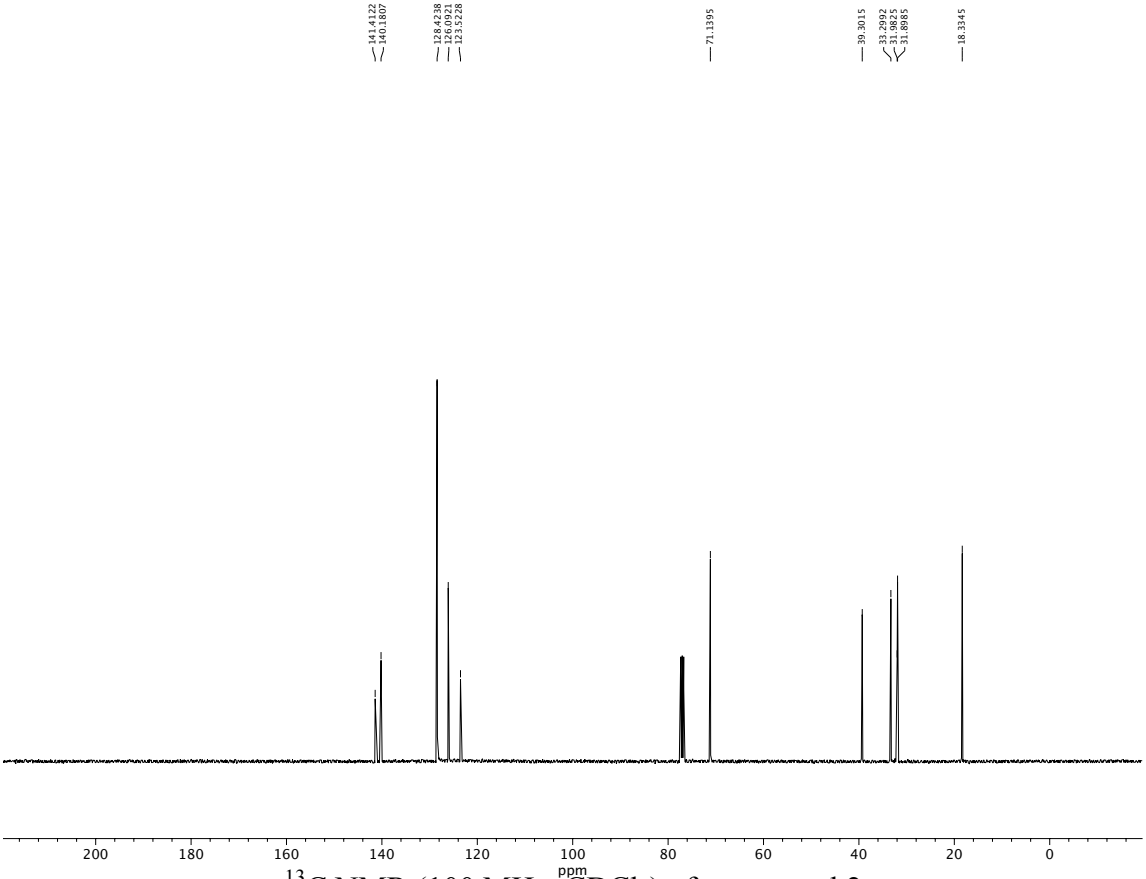
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2d**.



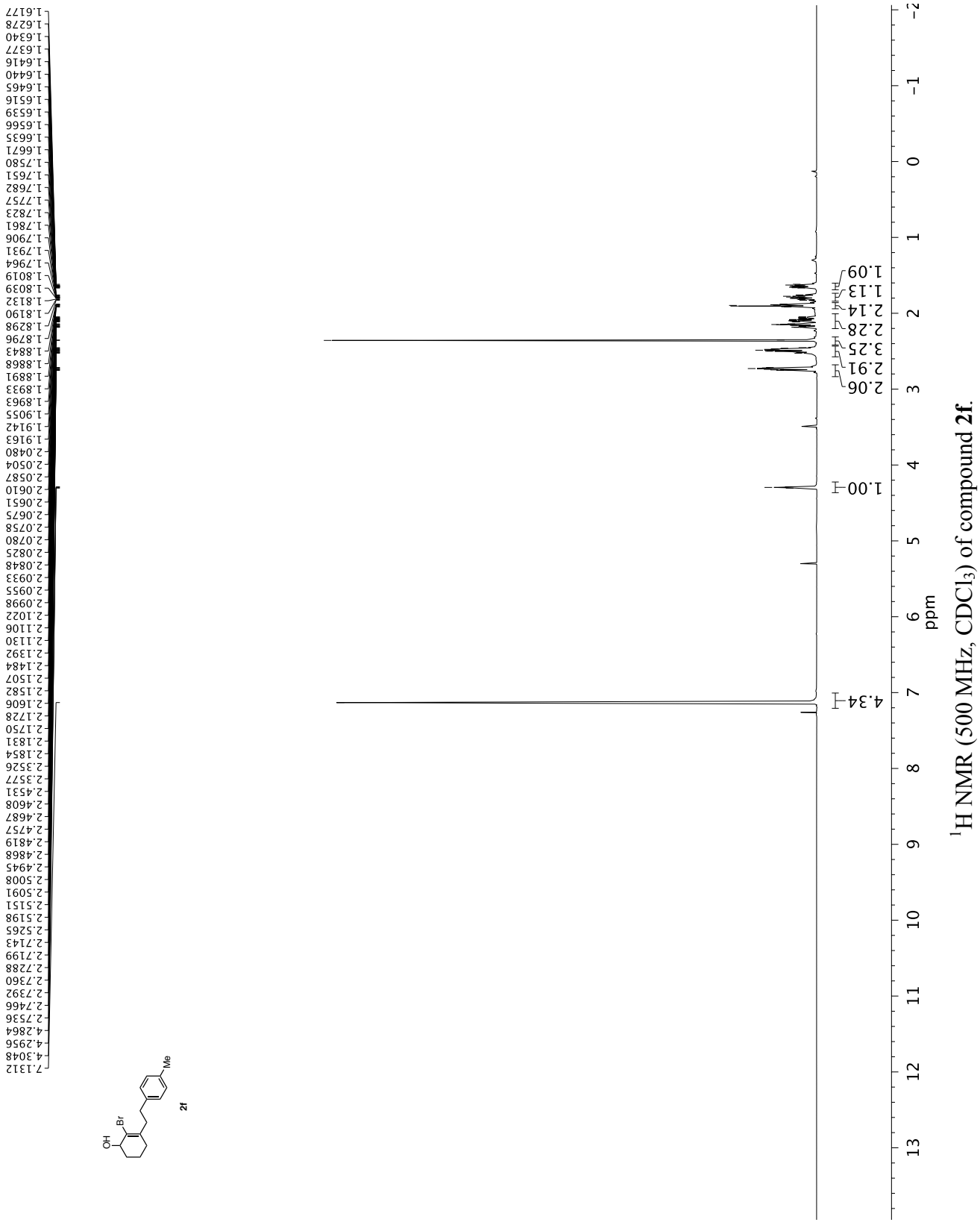
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2e**.



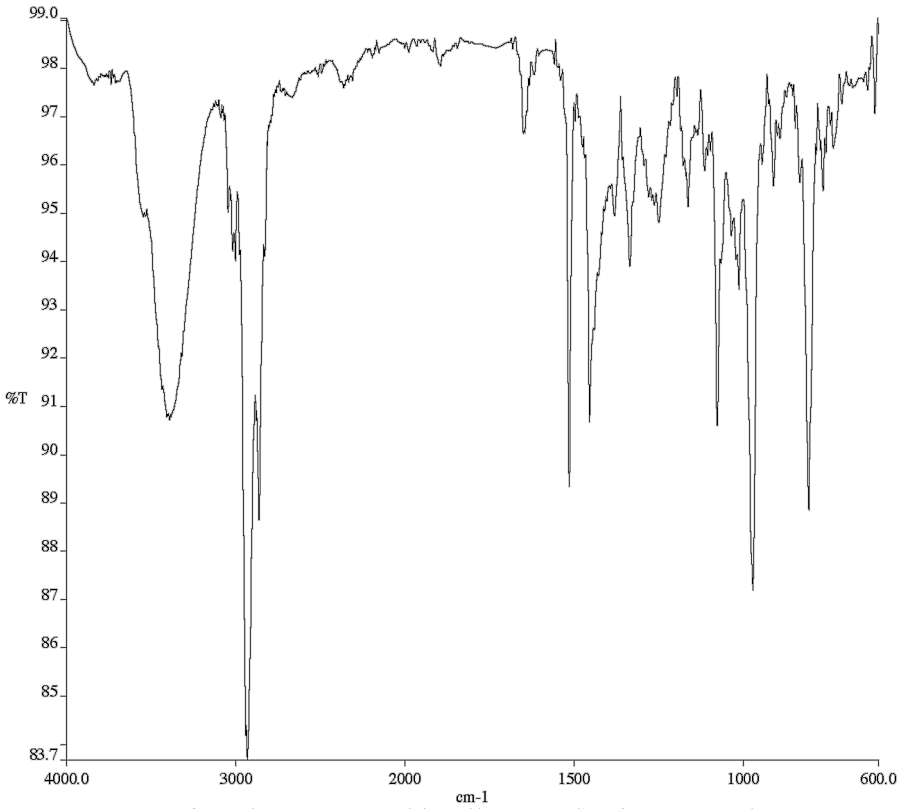
Infrared spectrum (Thin Film, NaCl) of compound **2e**.



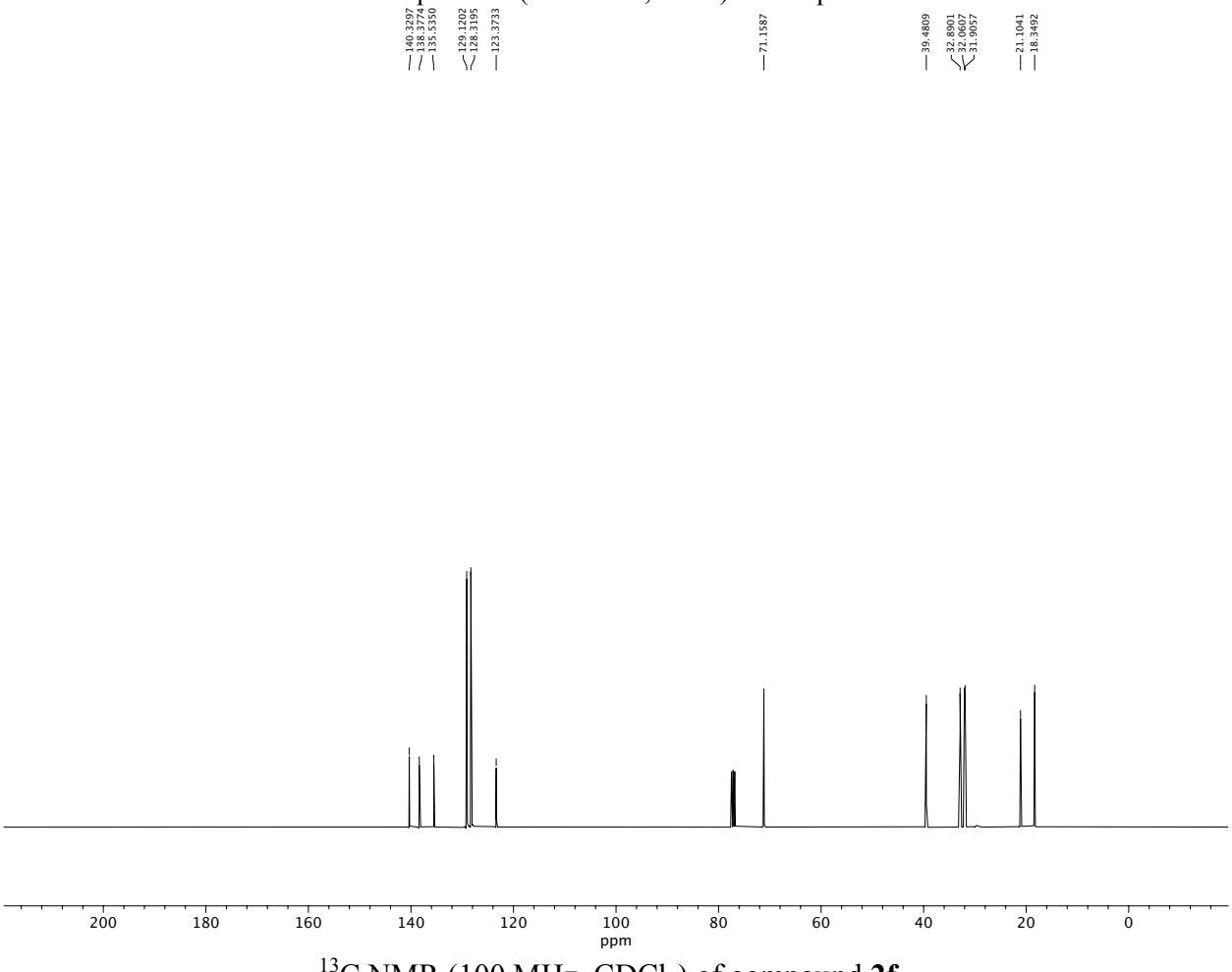
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2e**.



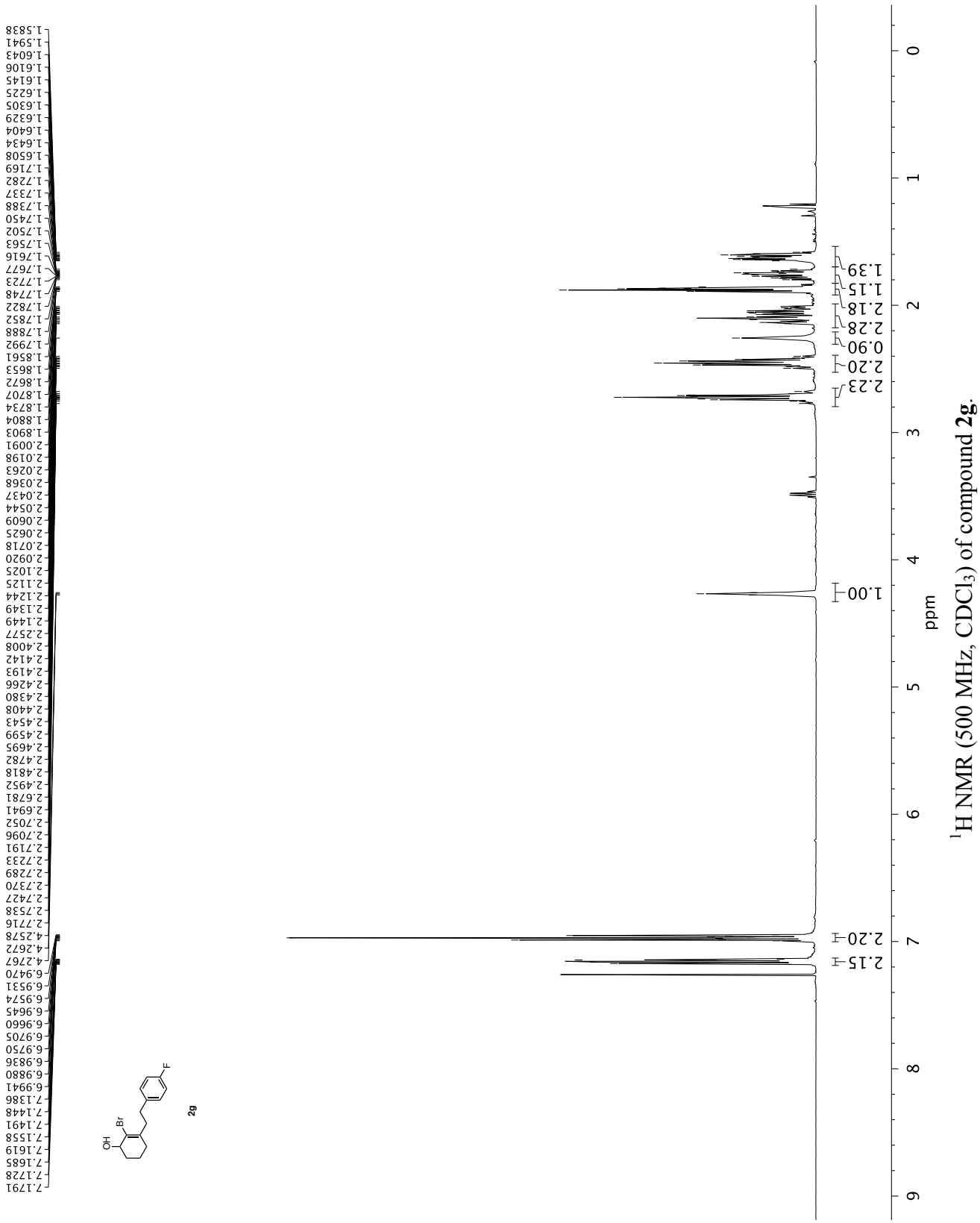
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2f**.



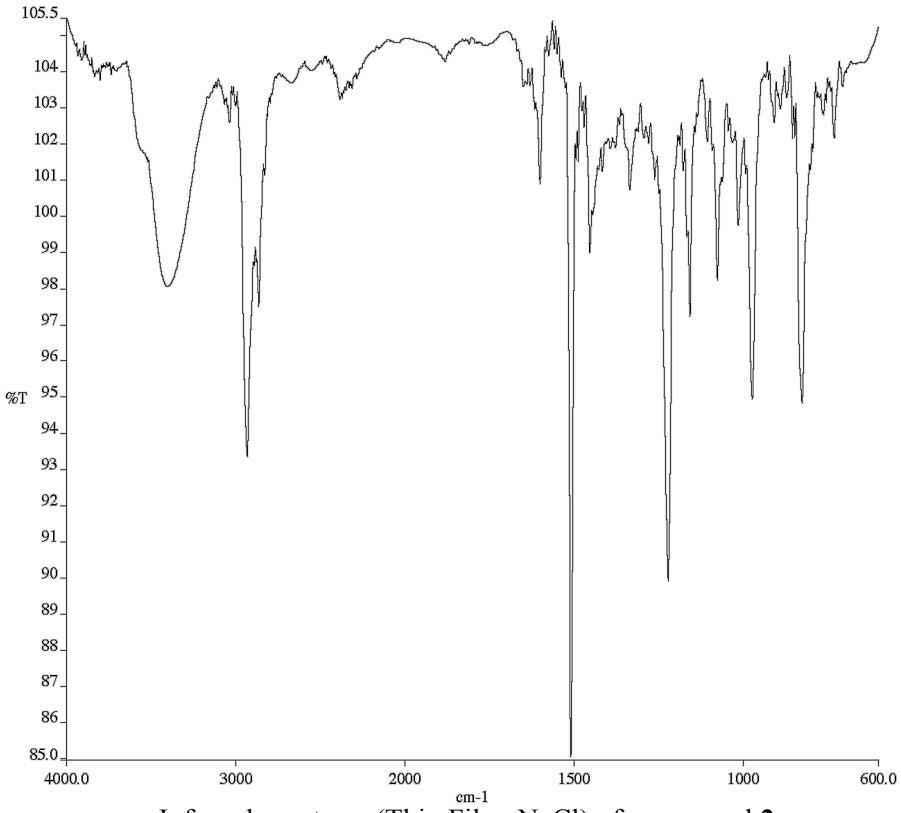
Infrared spectrum (Thin Film, NaCl) of compound **2f**.



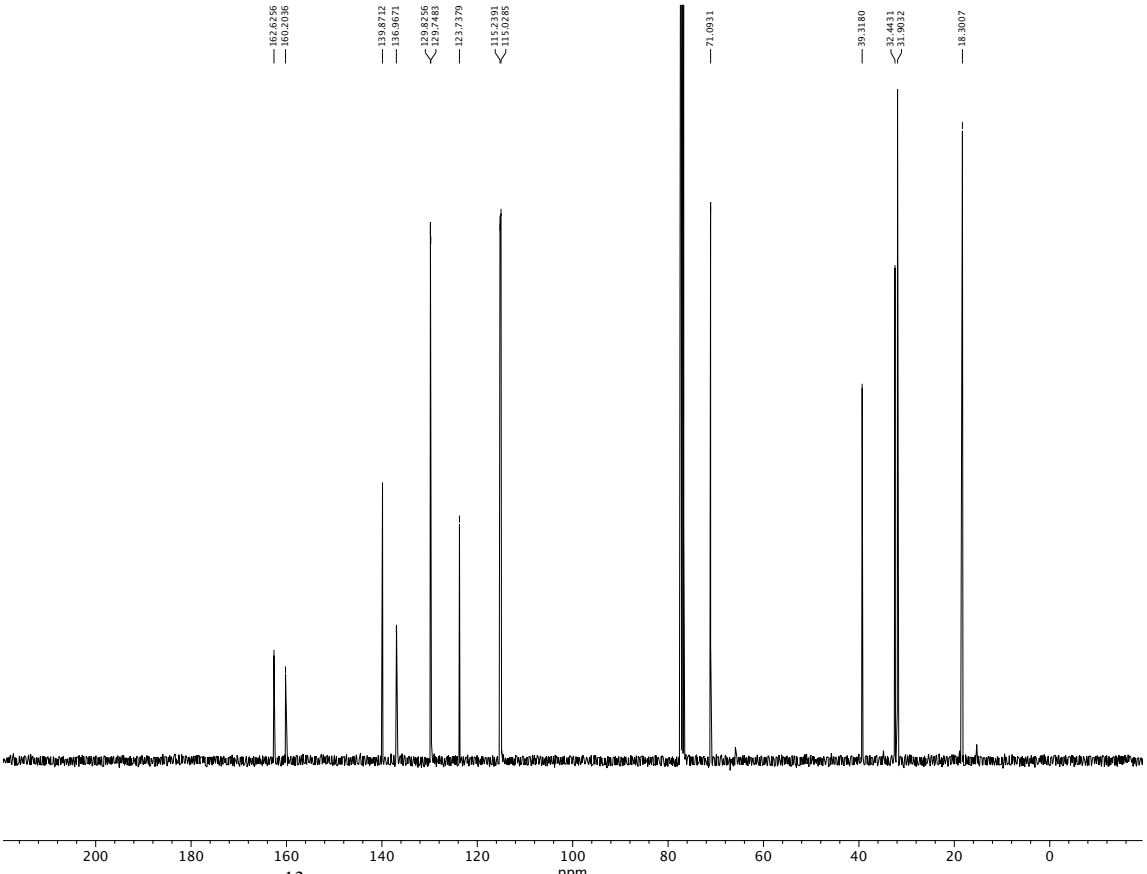
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2f**.



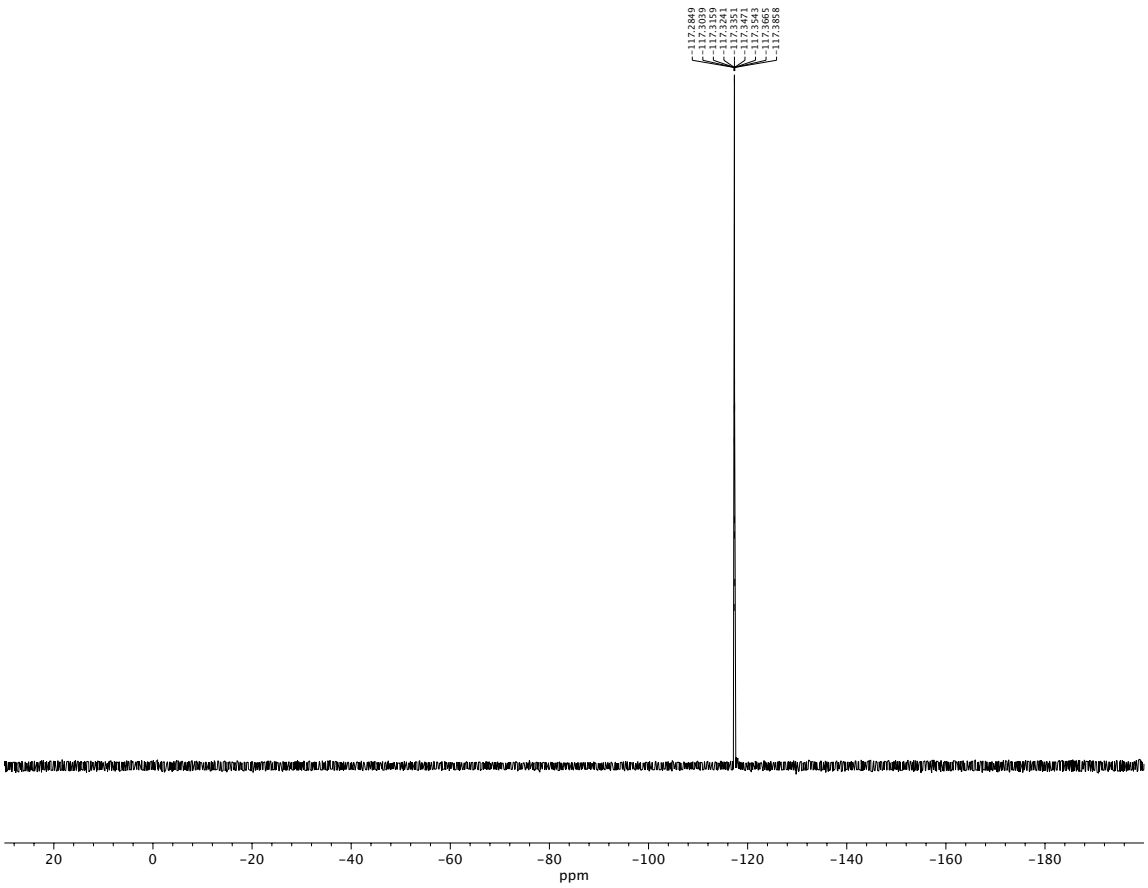
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2g**.



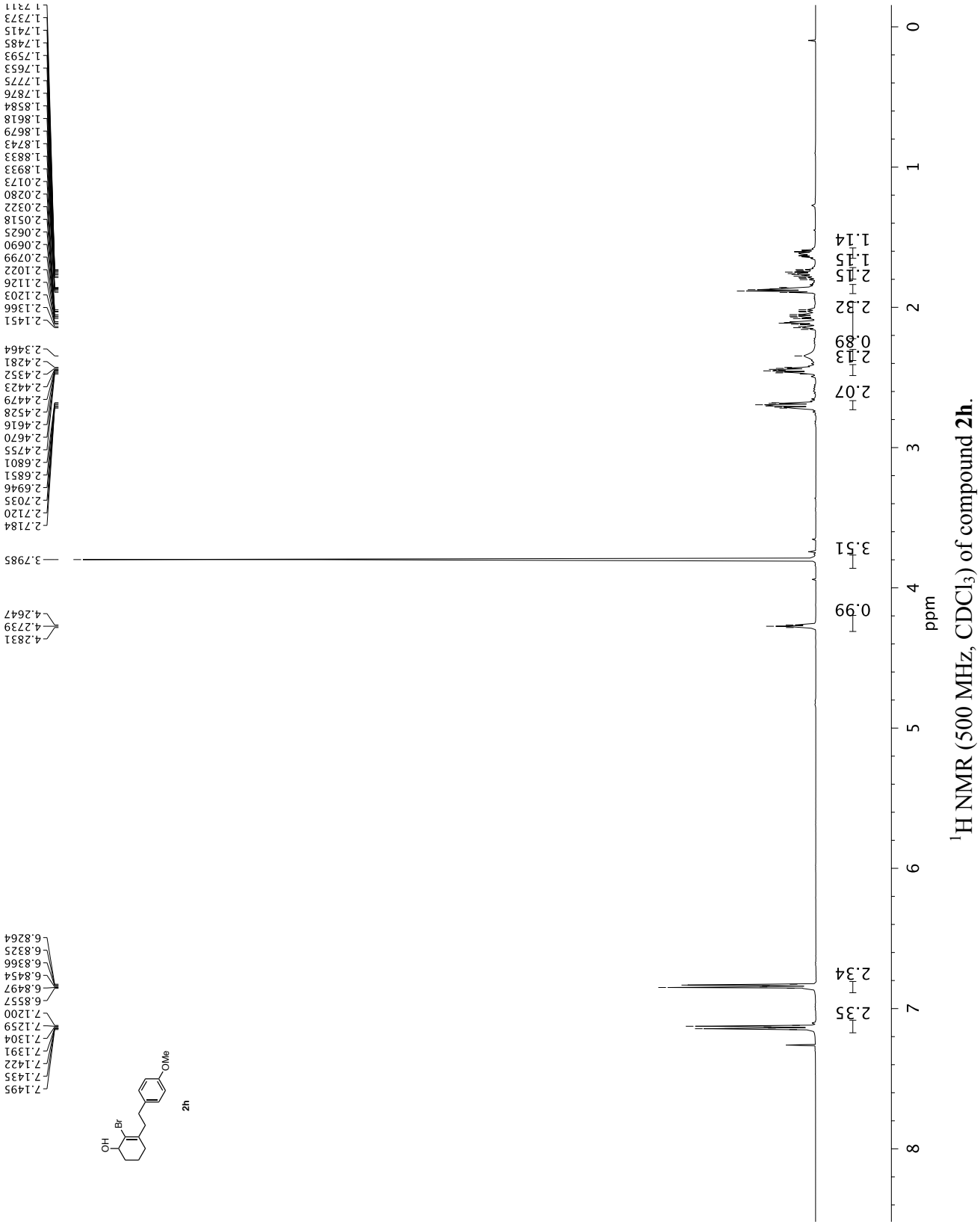
Infrared spectrum (Thin Film, NaCl) of compound **2g**.



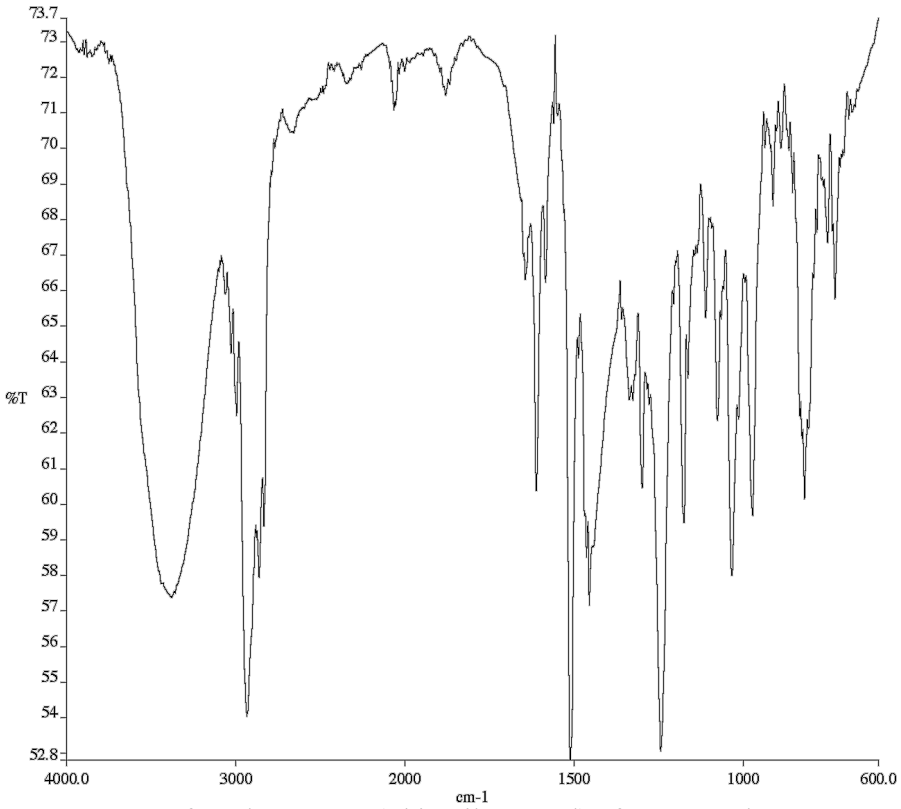
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2g**.



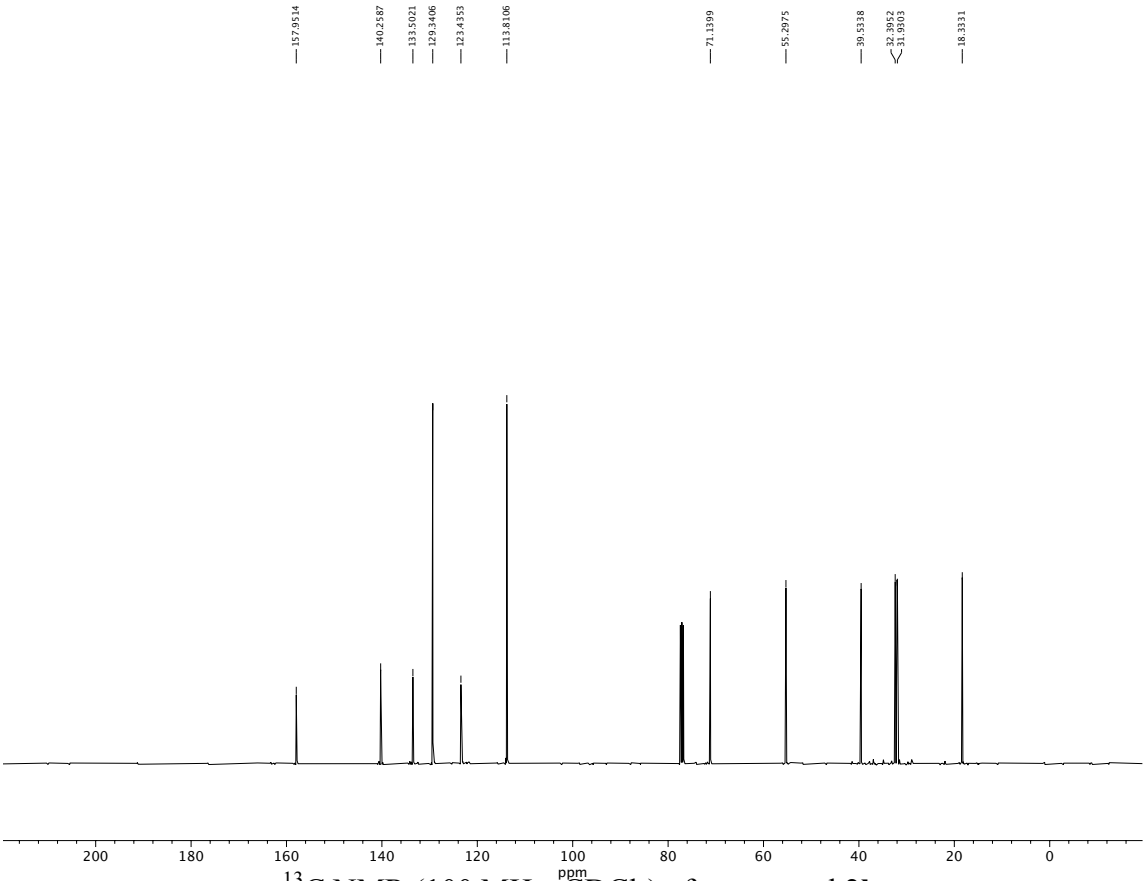
^{19}F NMR (282 MHz, $CDCl_3$) of compound **2g**.



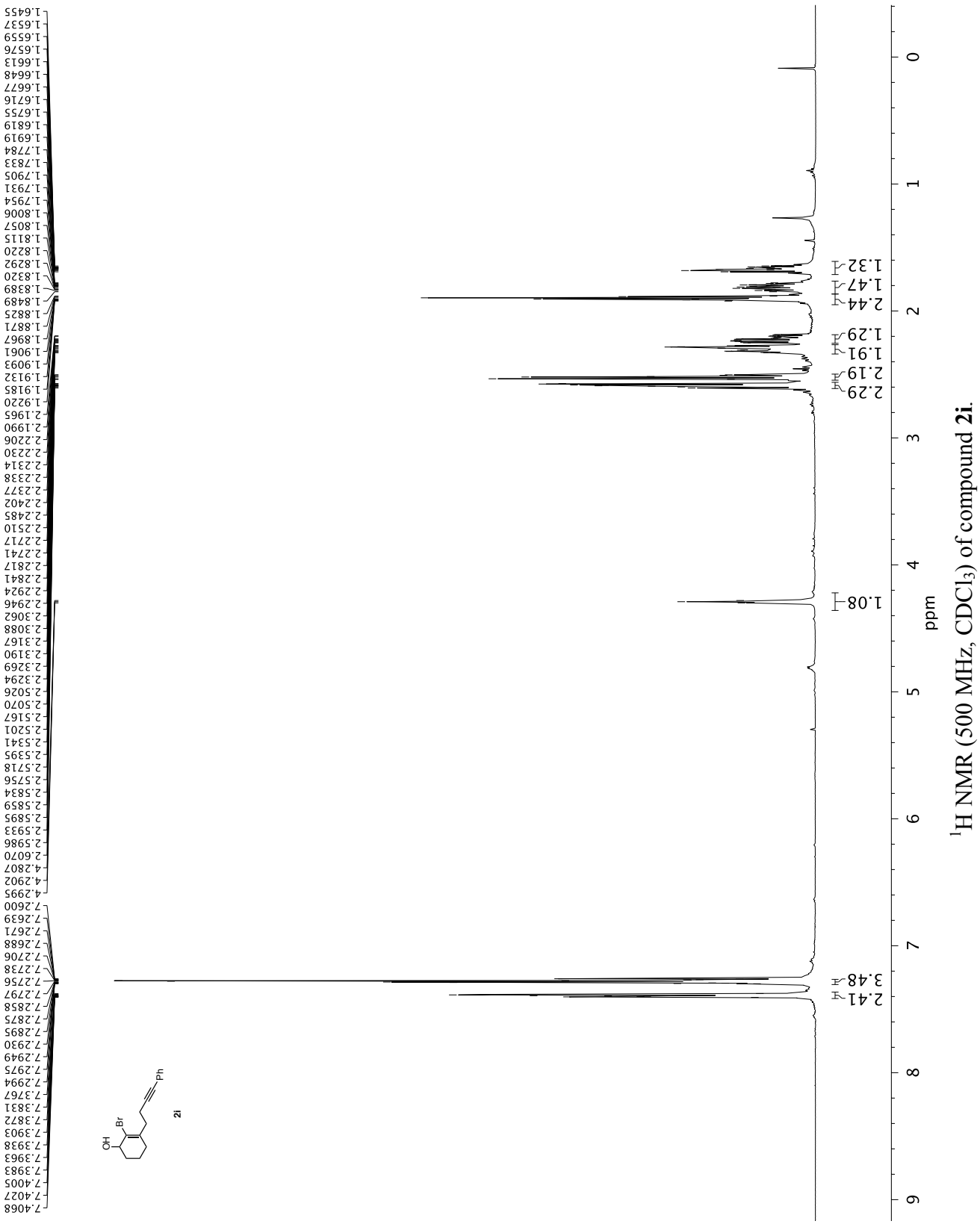
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2h**.



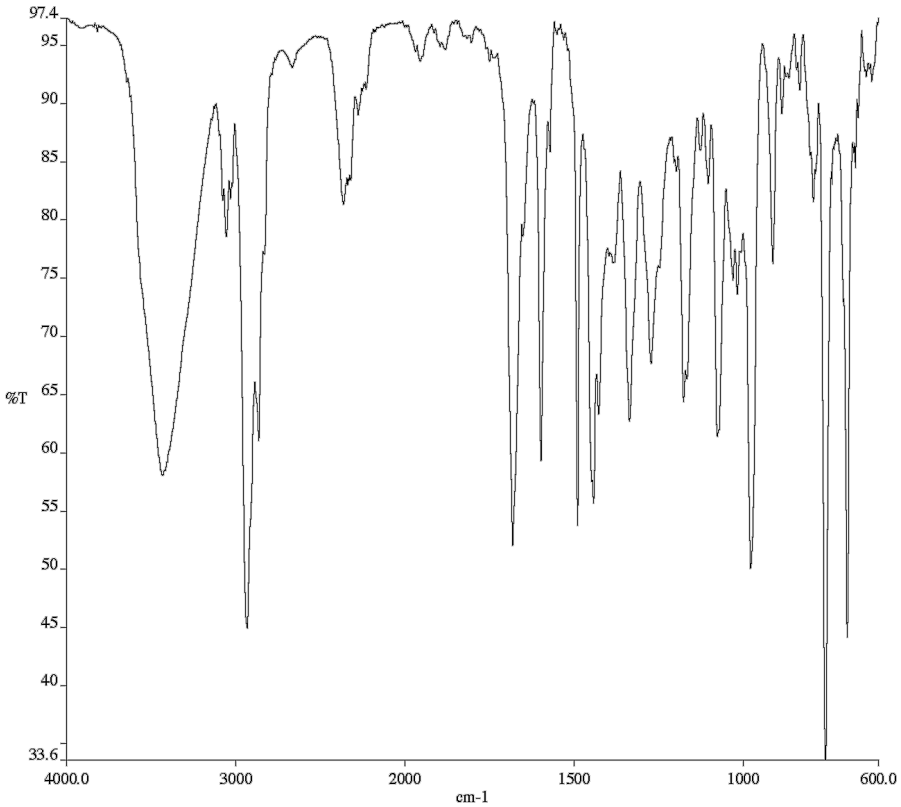
Infrared spectrum (Thin Film, NaCl) of compound **2h**.



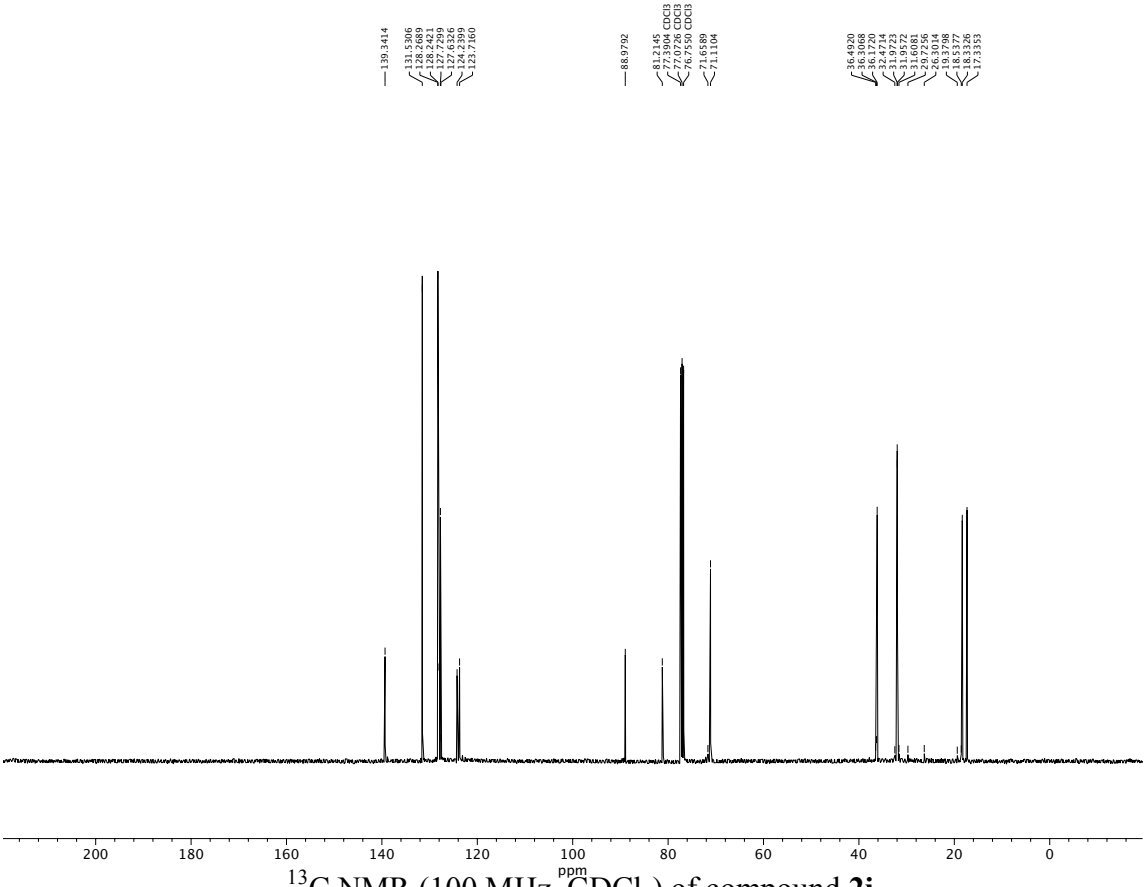
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2h**.



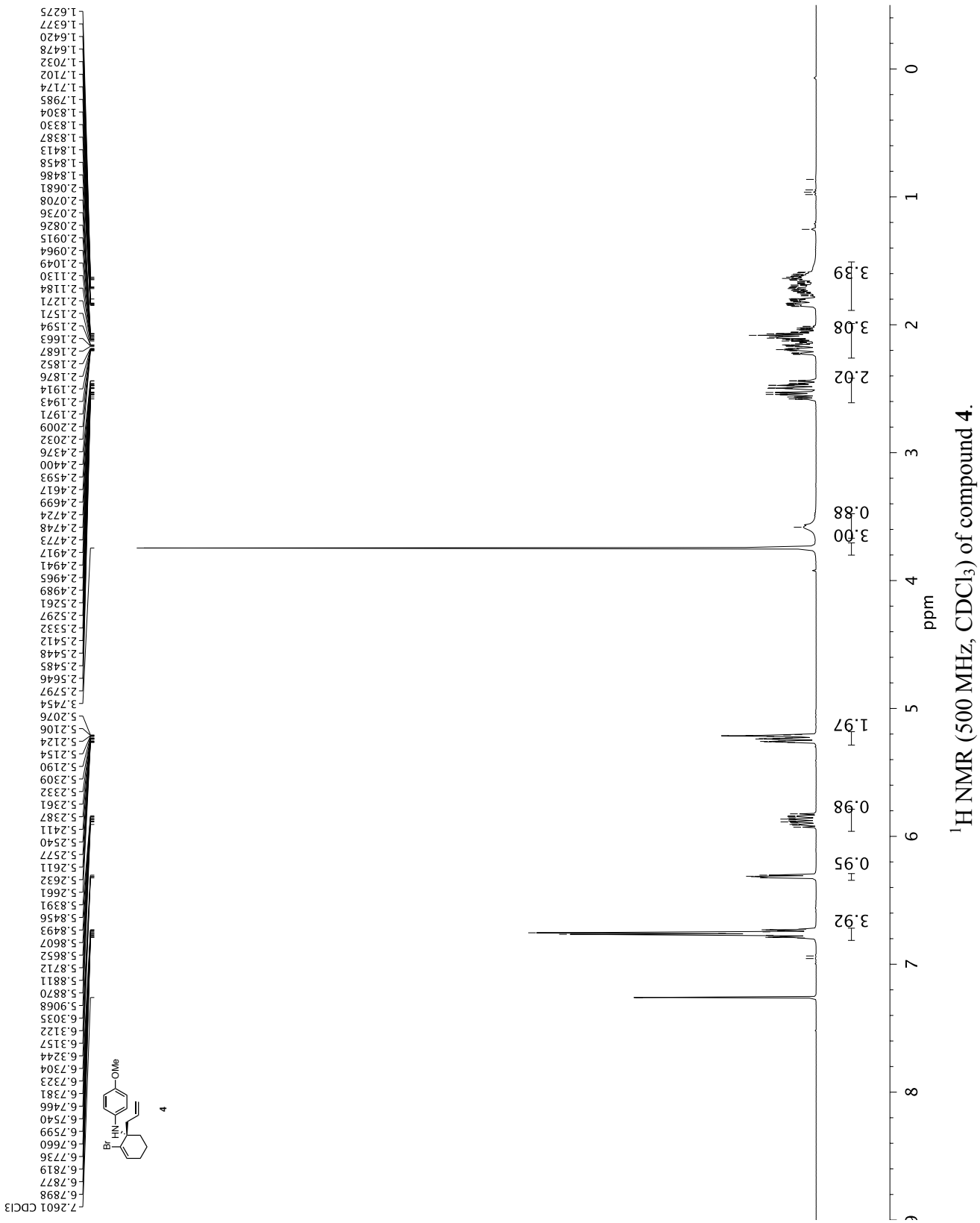
^{1}H NMR (500 MHz, $CDCl_3$) of compound **2i**.



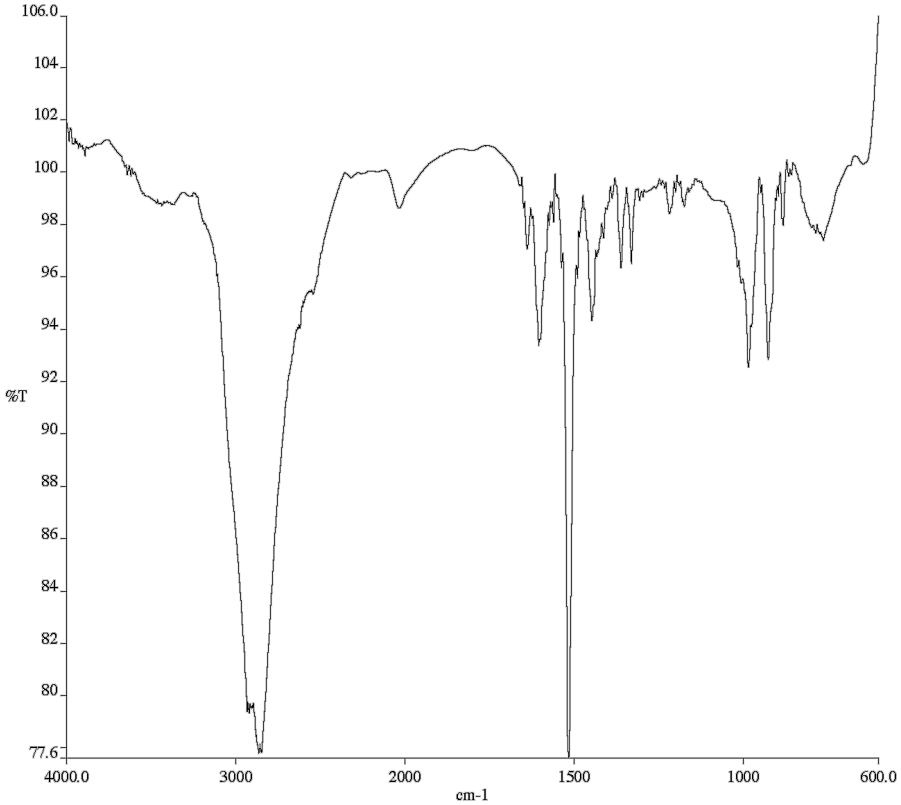
Infrared spectrum (Thin Film, NaCl) of compound **2i**.



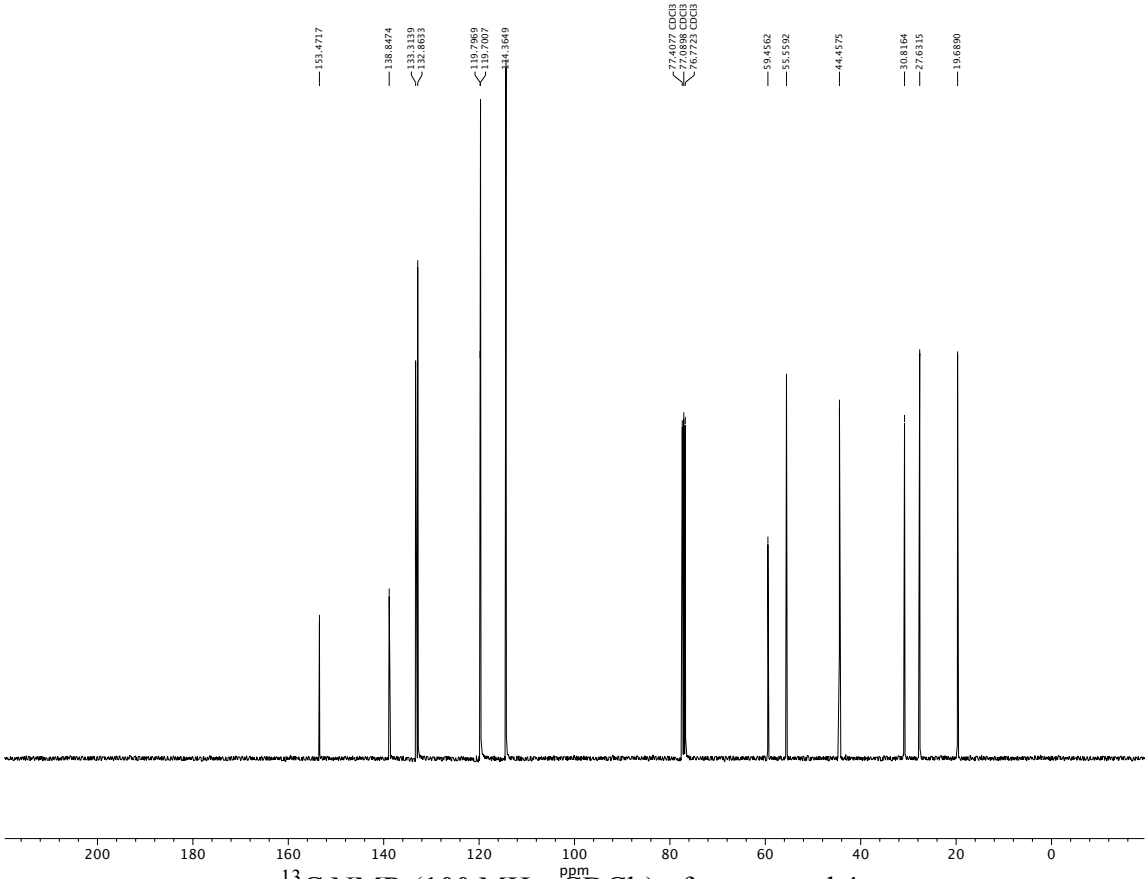
^{13}C NMR (100 MHz, $CDCl_3$) of compound **2i**.



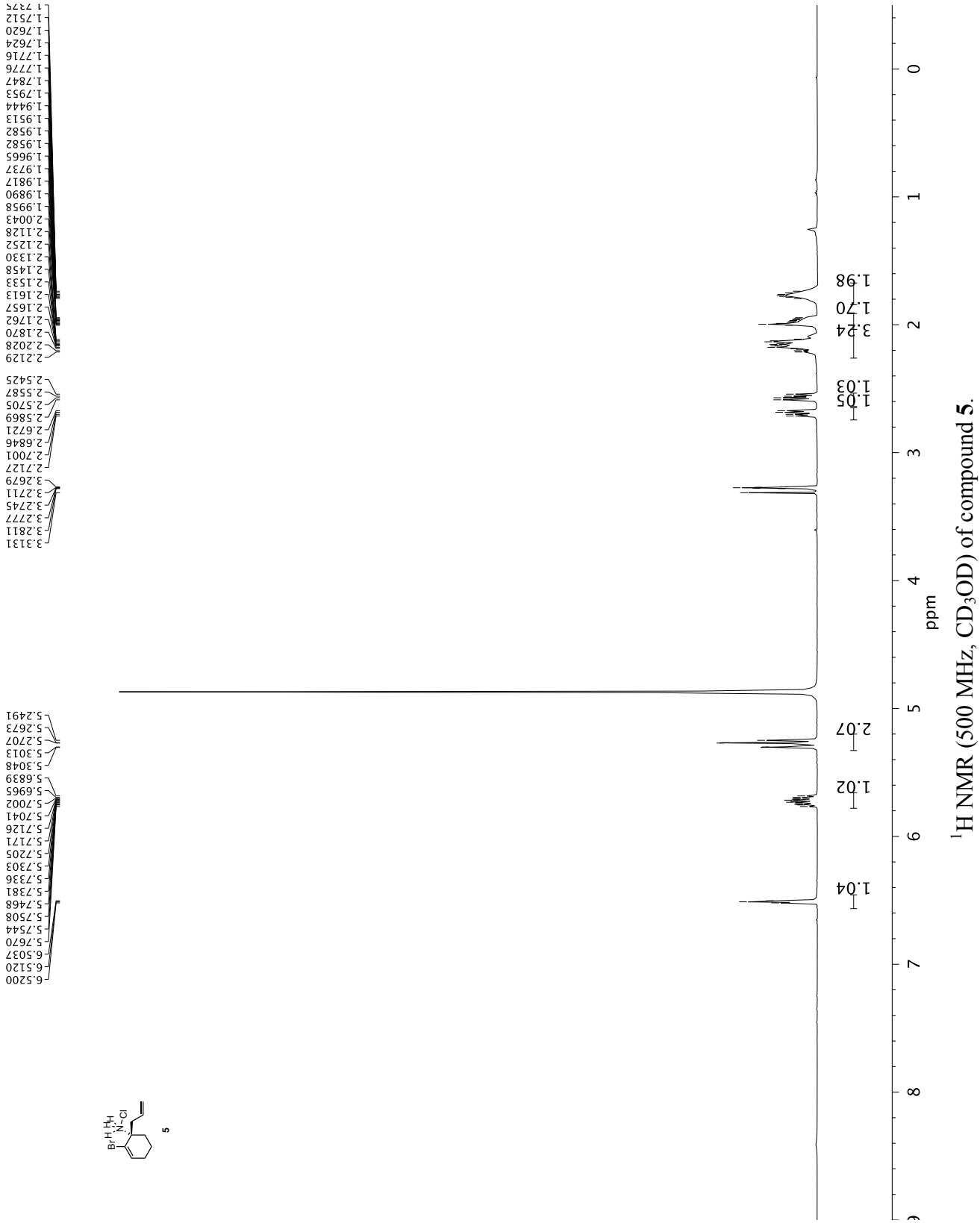
^{1}H NMR (500 MHz, $CDCl_3$) of compound **4**.



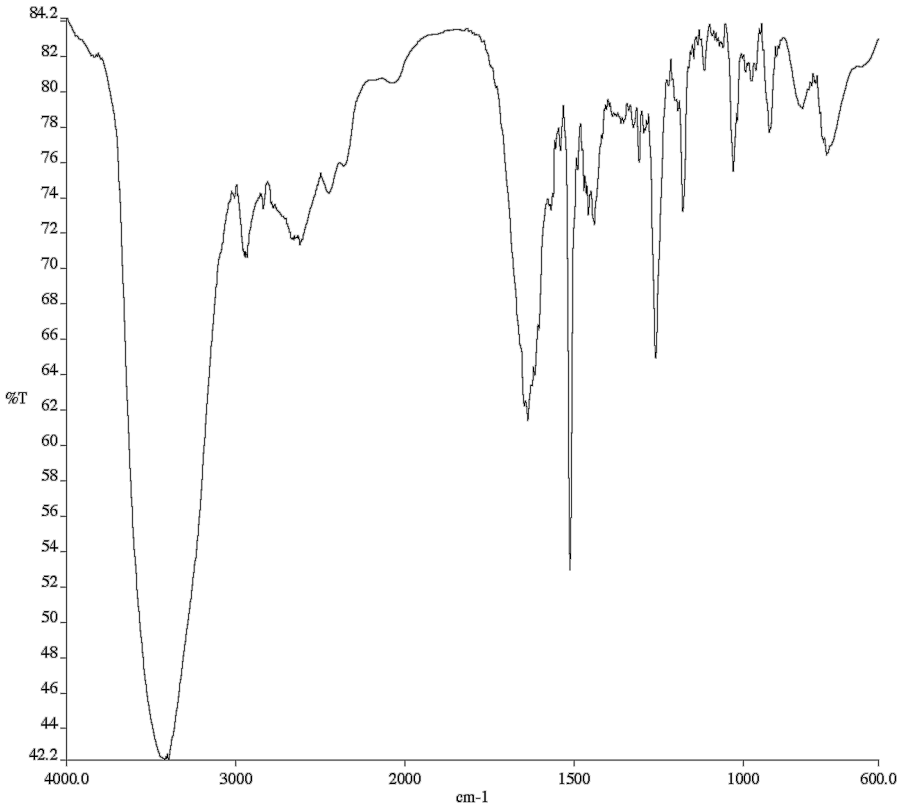
Infrared spectrum (Thin Film, NaCl) of compound **4**.



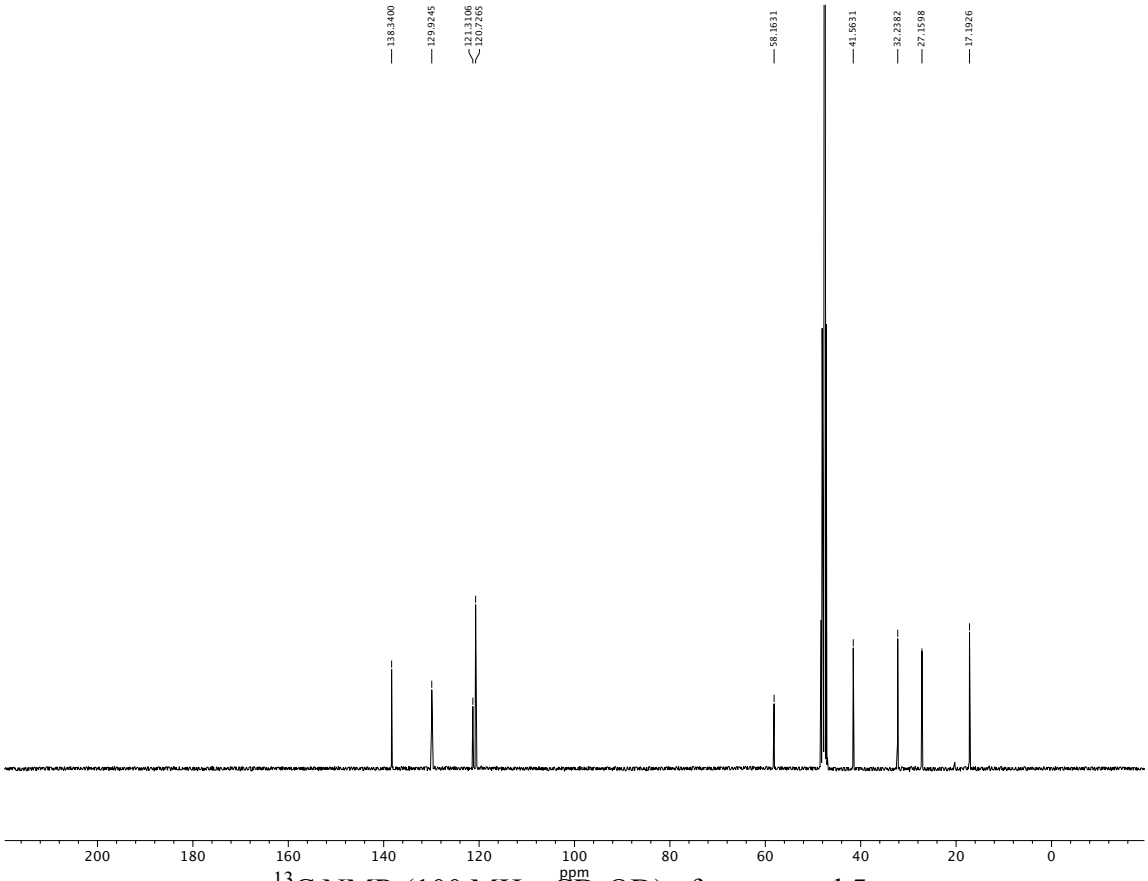
^{13}C NMR (100 MHz, $CDCl_3$) of compound **4**.



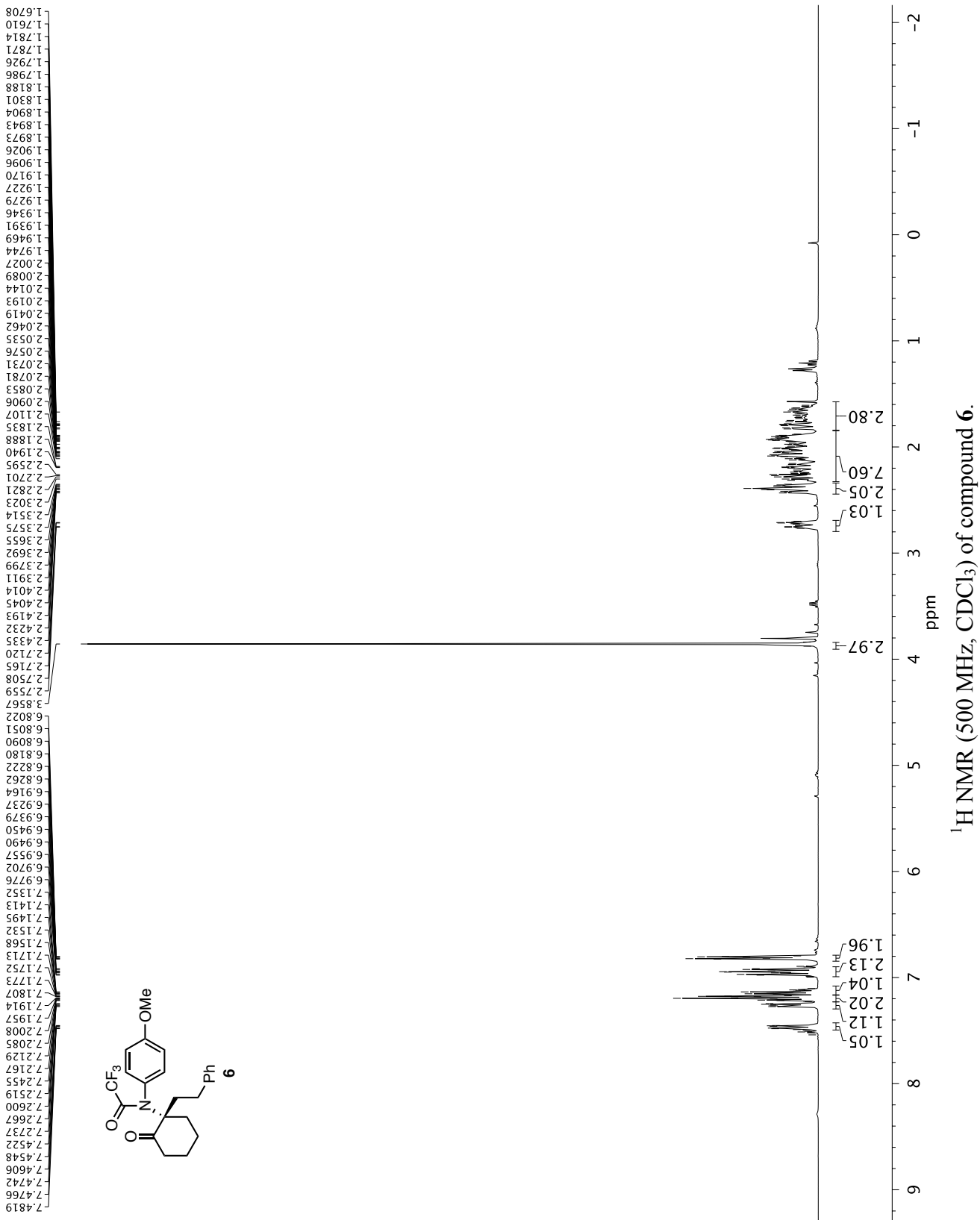
^{1}H NMR (500 MHz, CD_3OD) of compound **5**.



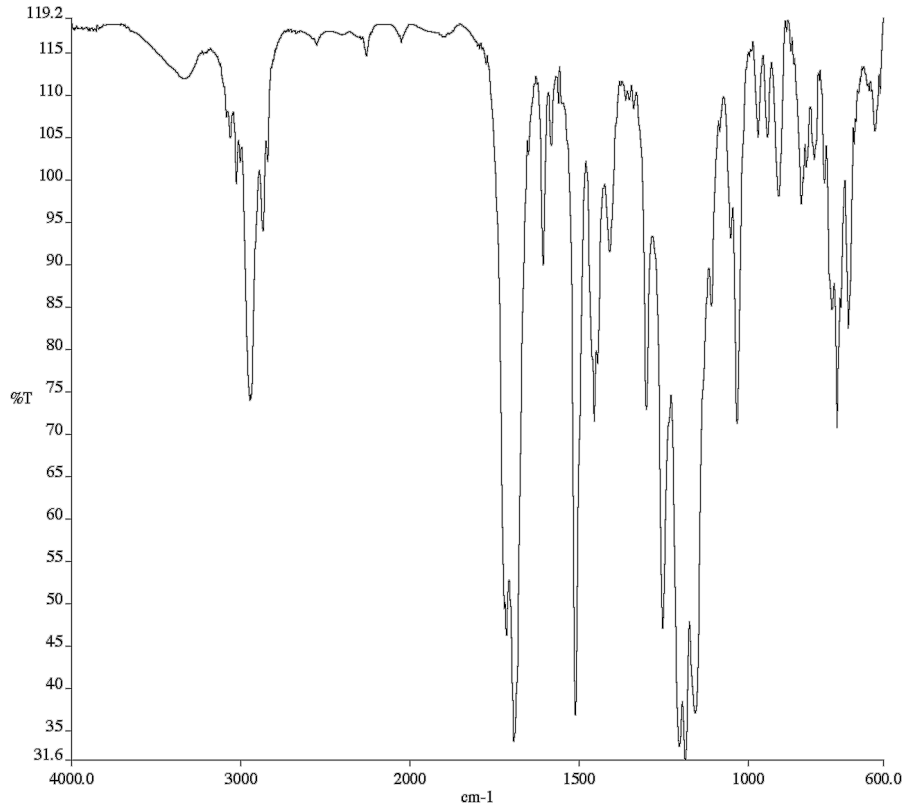
Infrared spectrum (Thin Film, NaCl) of compound **5**.



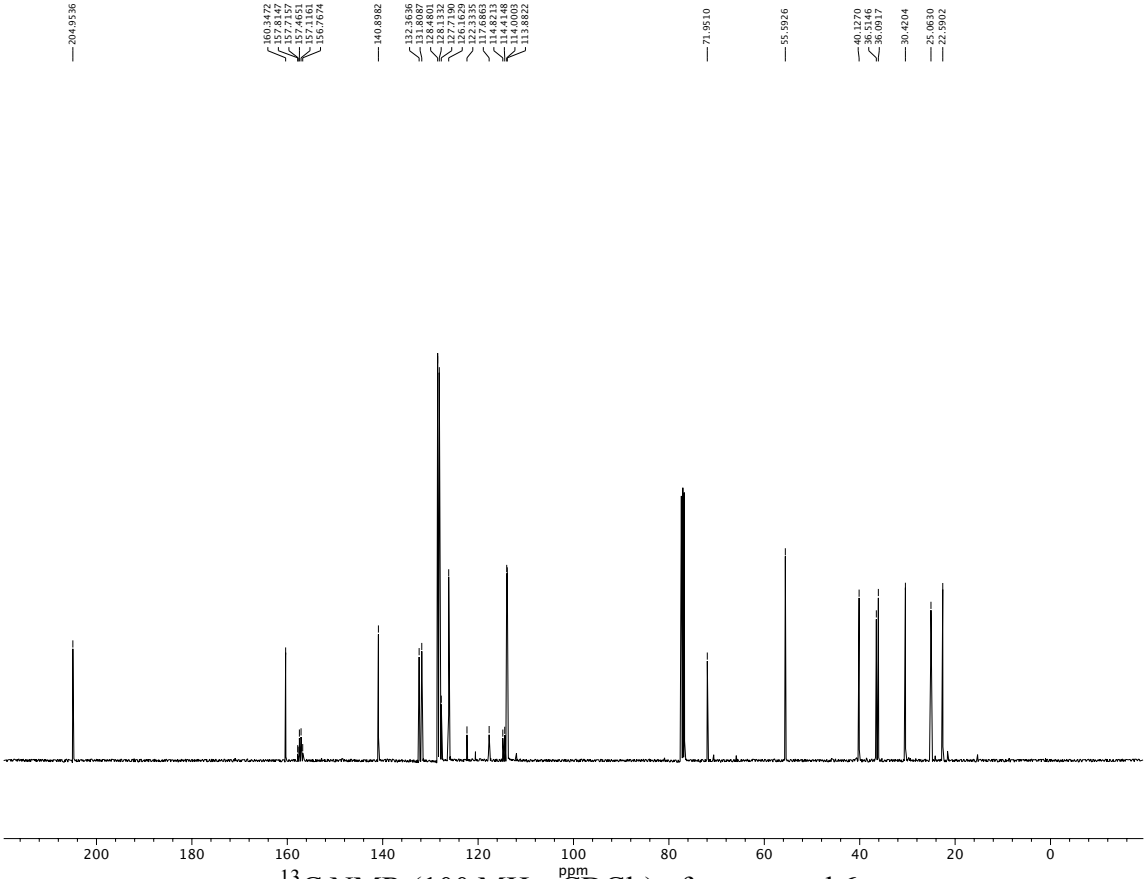
^{13}C NMR (100 MHz, CD_3OD) of compound **5**.



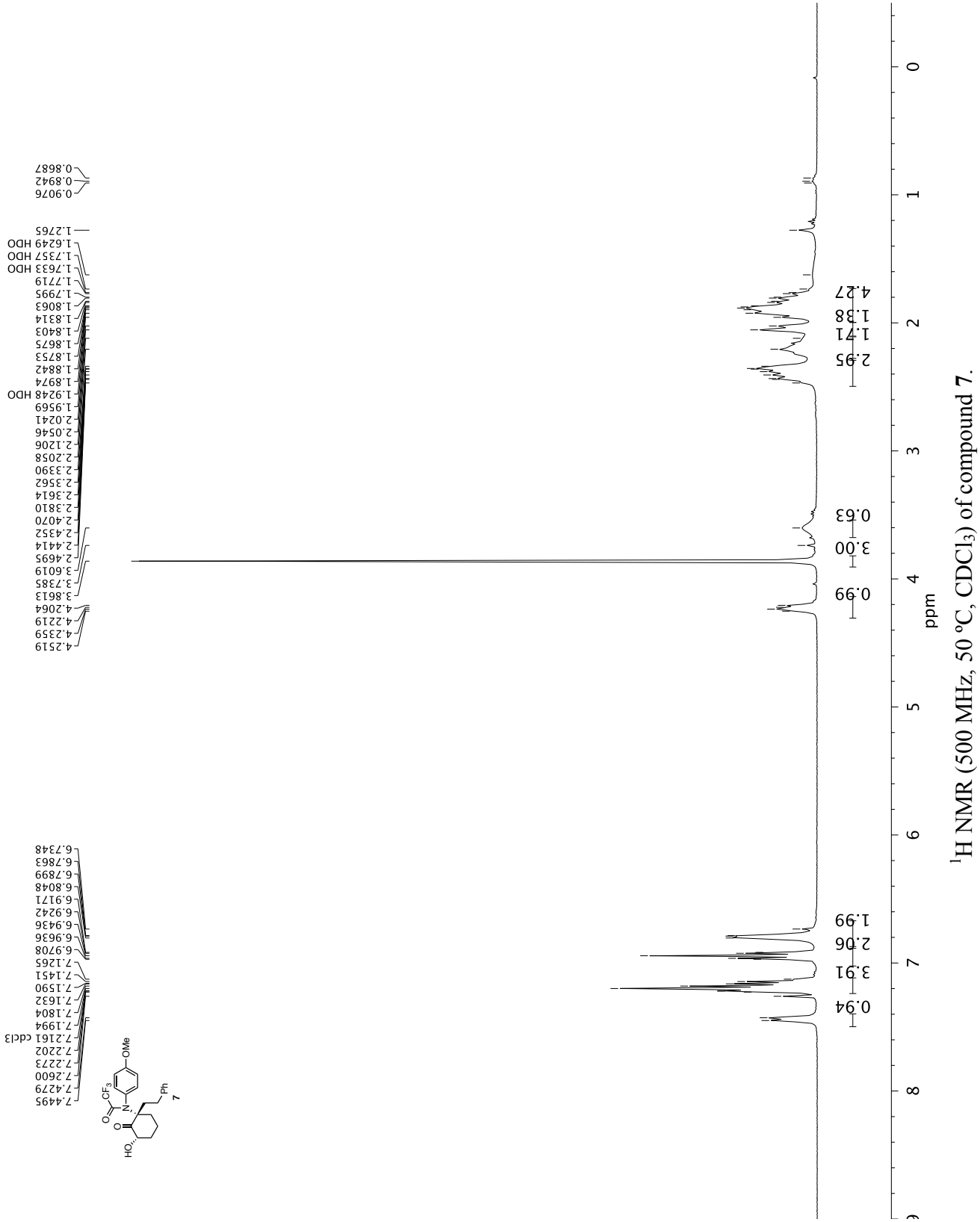
^{1}H NMR (500 MHz, $CDCl_3$) of compound **6**.



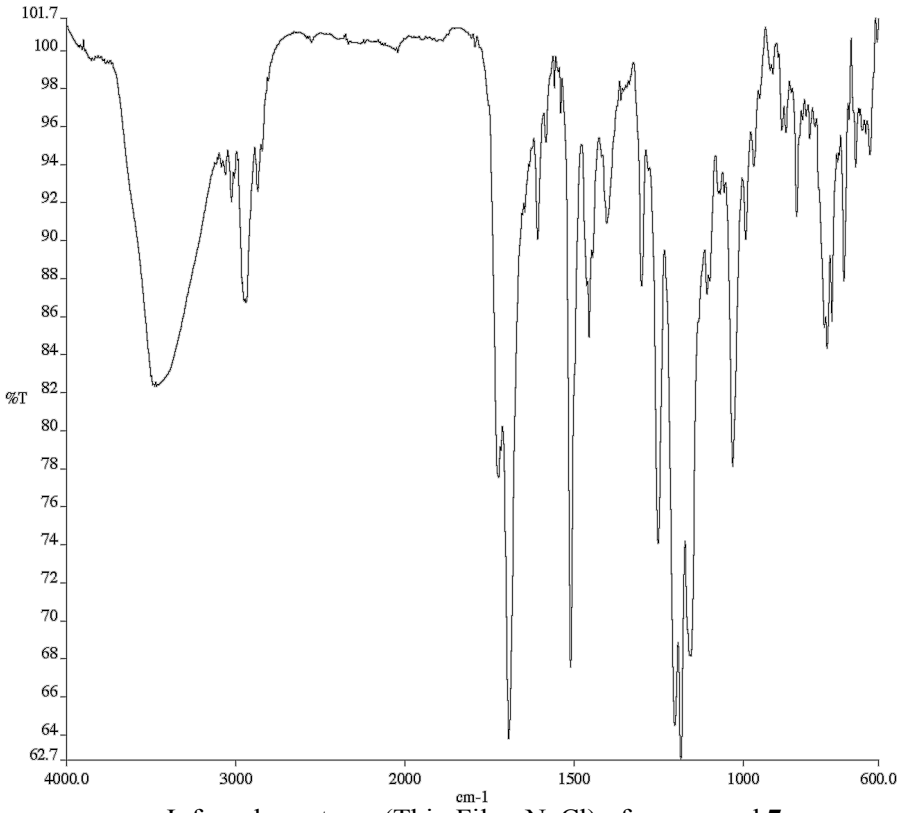
Infrared spectrum (Thin Film, NaCl) of compound **6**.



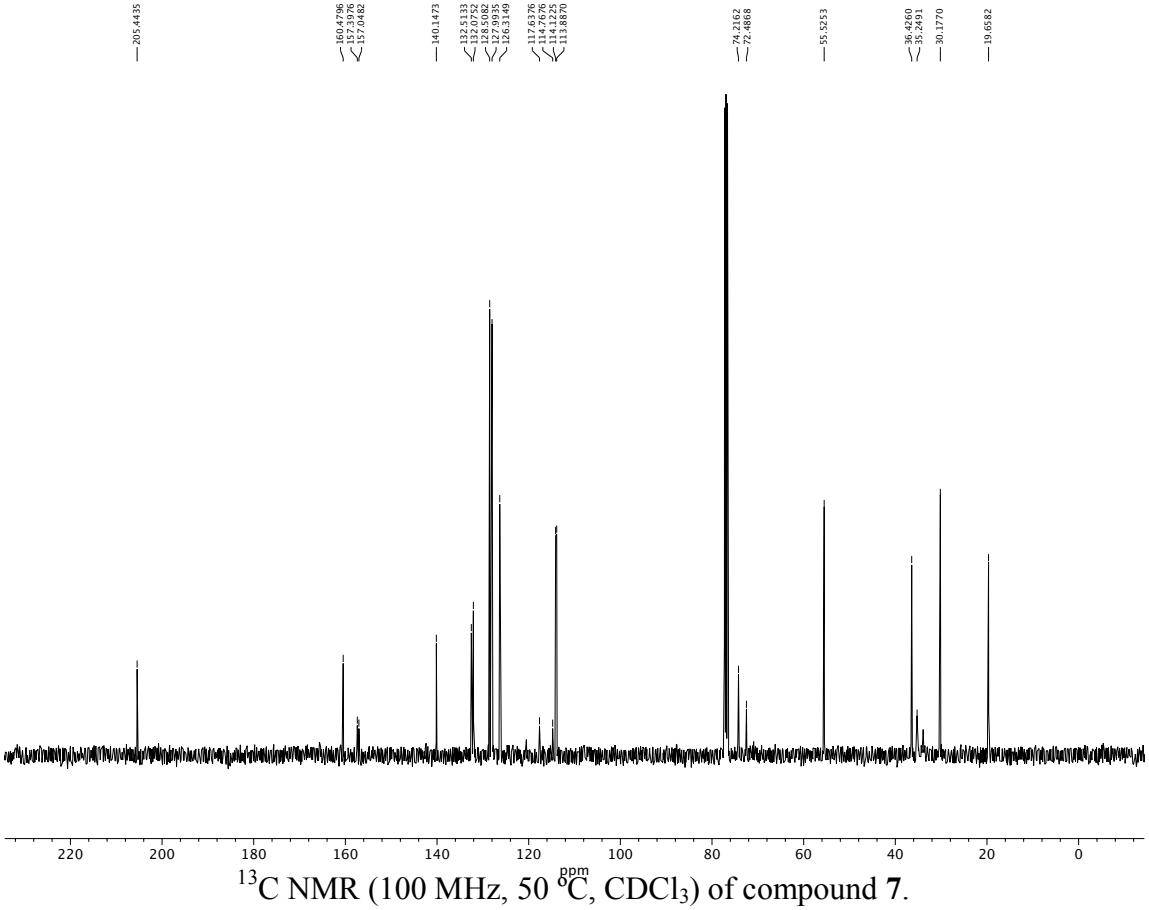
^{13}C NMR (100 MHz, $CDCl_3$) of compound **6**.



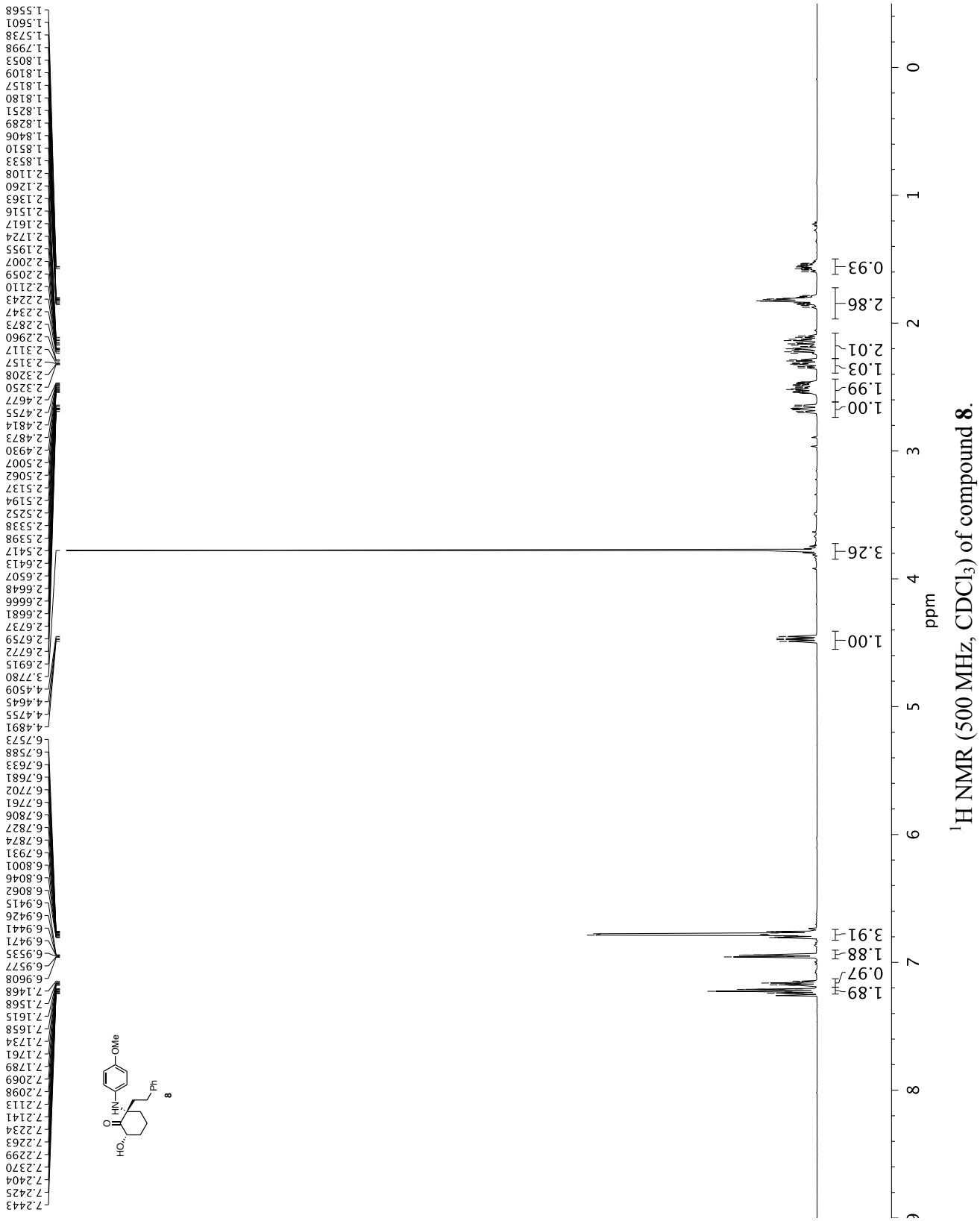
^{1}H NMR (500 MHz, 50 °C, $CDCl_3$) of compound **7**.



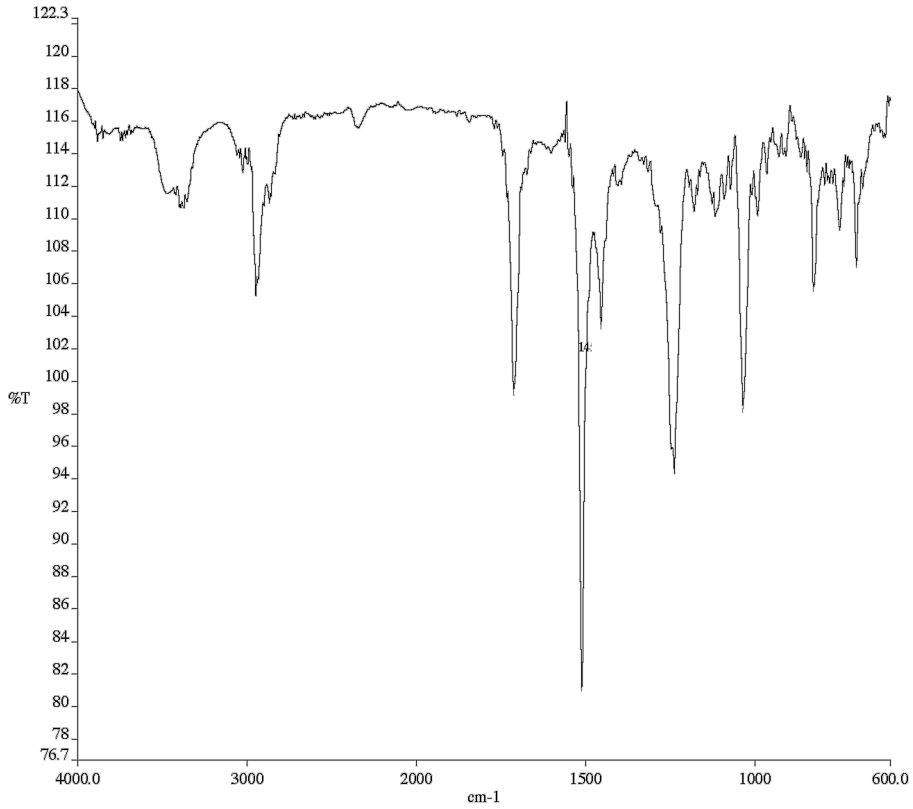
Infrared spectrum (Thin Film, NaCl) of compound **7**.



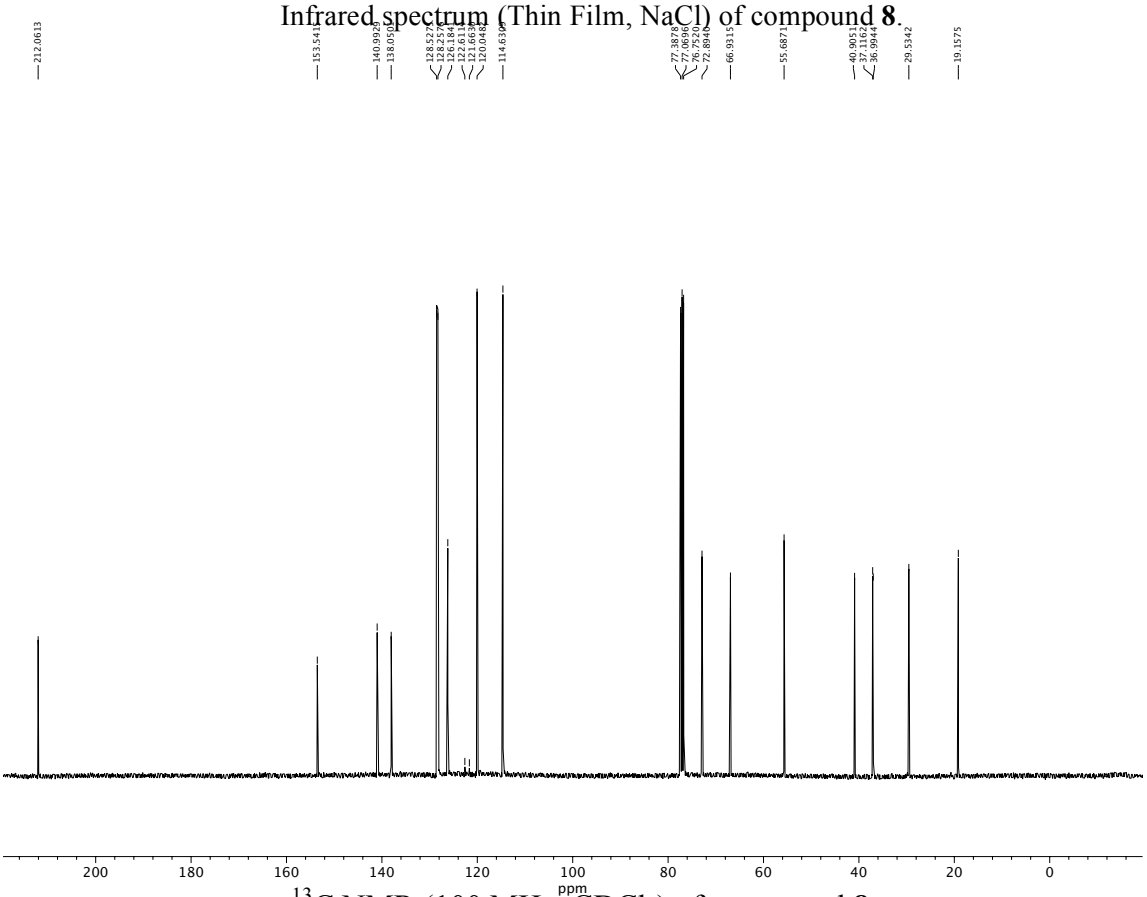
^{13}C NMR (100 MHz, 50 °C, $CDCl_3$) of compound **7**.



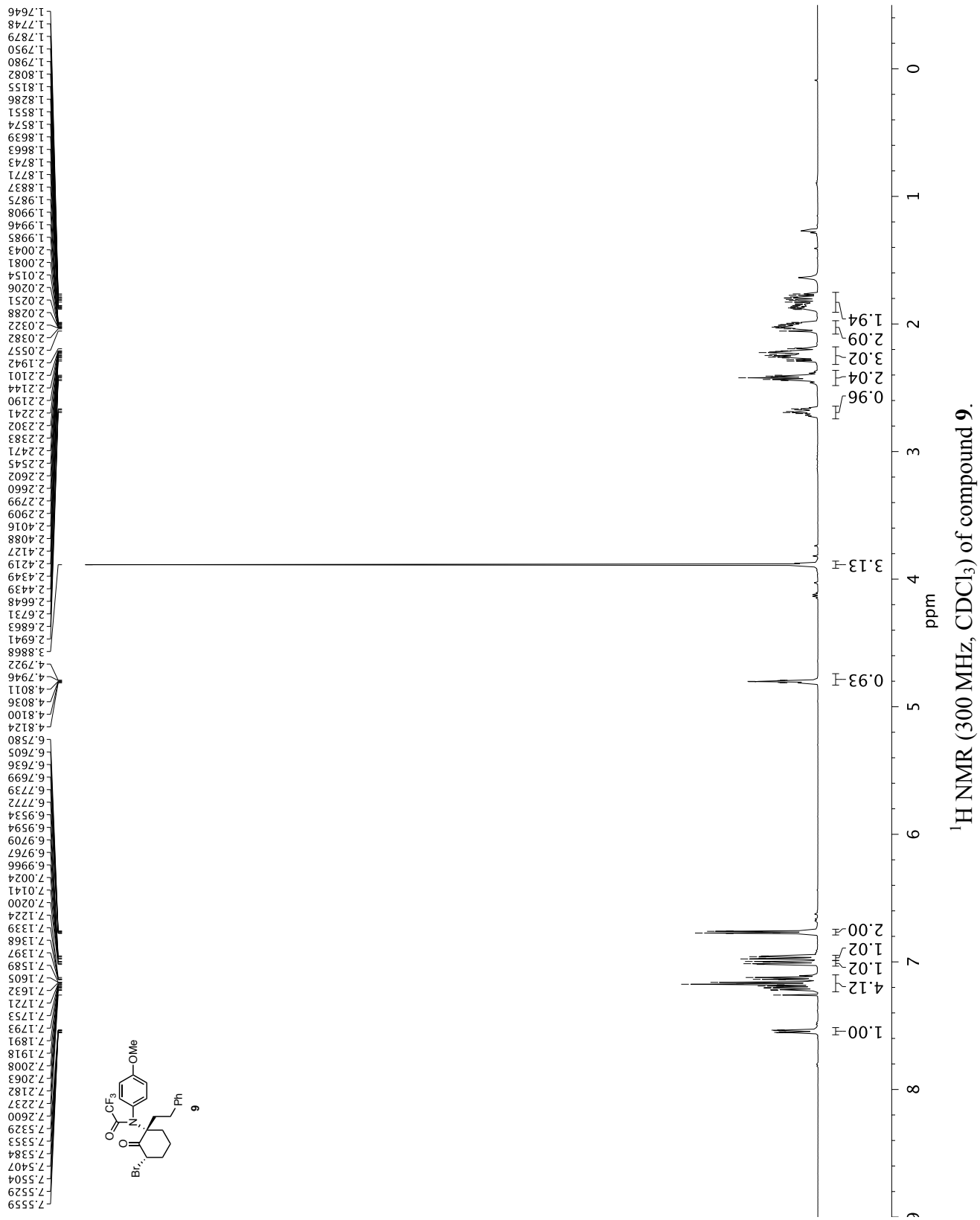
^{1}H NMR (500 MHz, $CDCl_3$) of compound **8**.



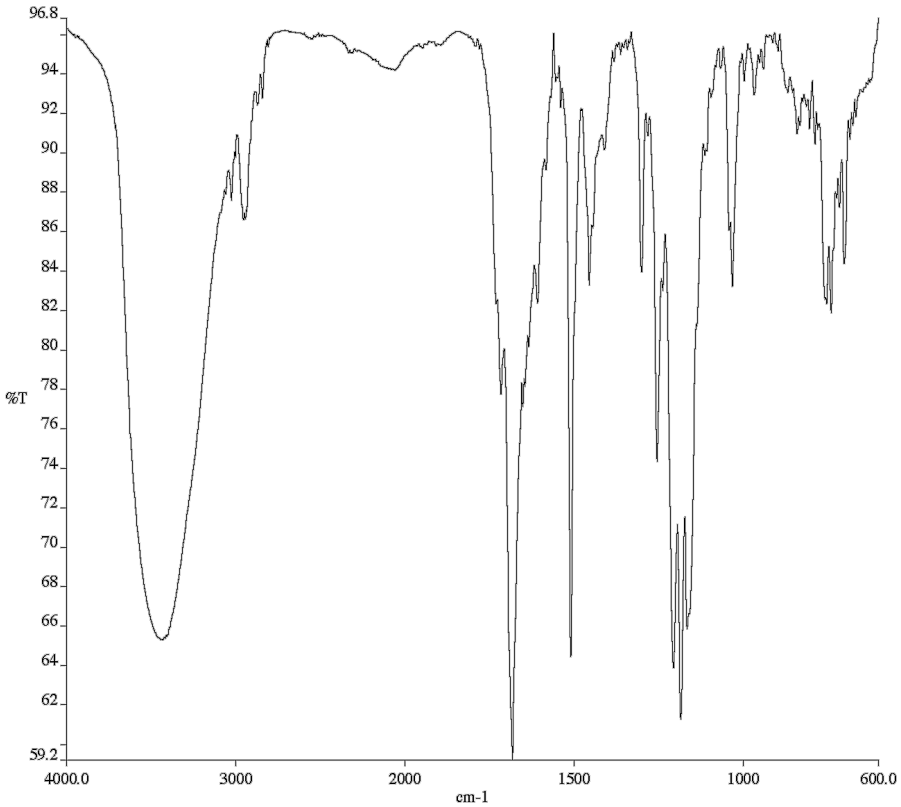
Infrared spectrum (Thin Film, NaCl) of compound **8**.



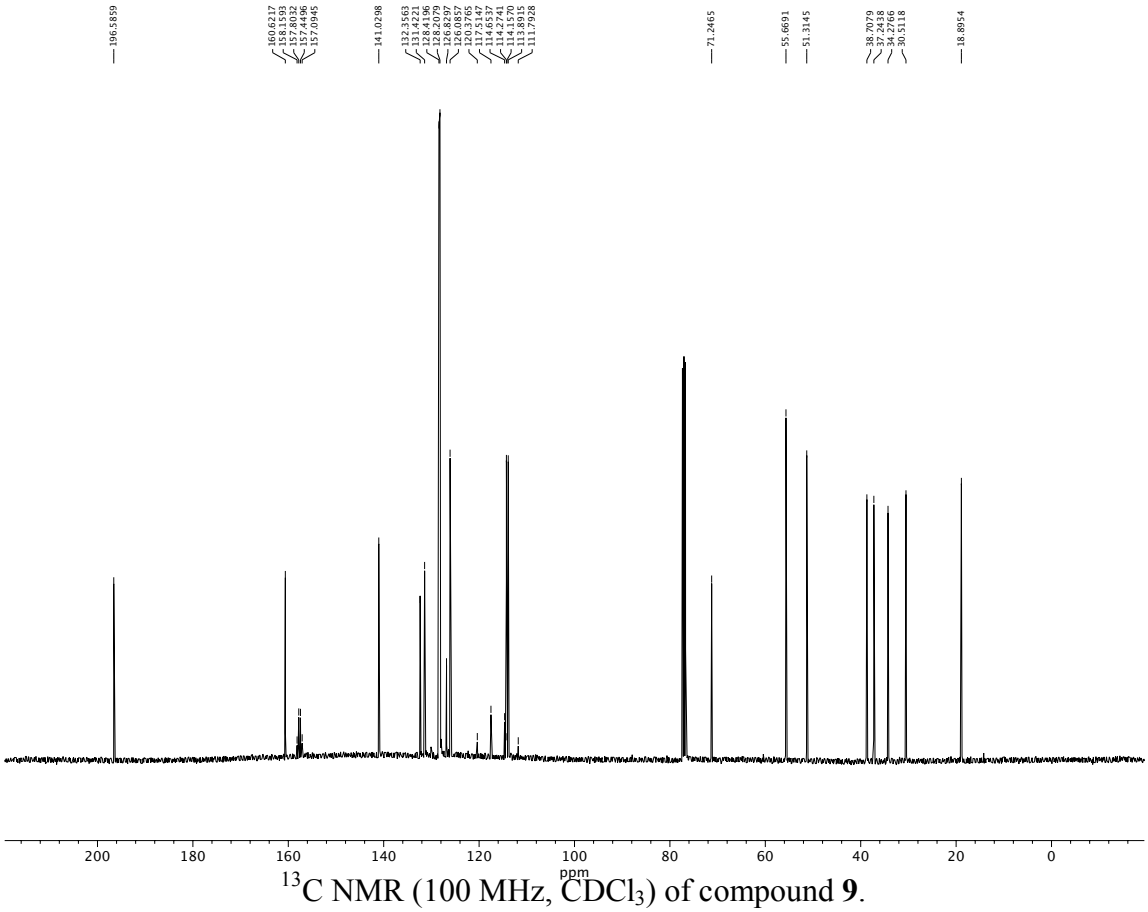
^{13}C NMR (100 MHz, $CDCl_3$) of compound **8**.



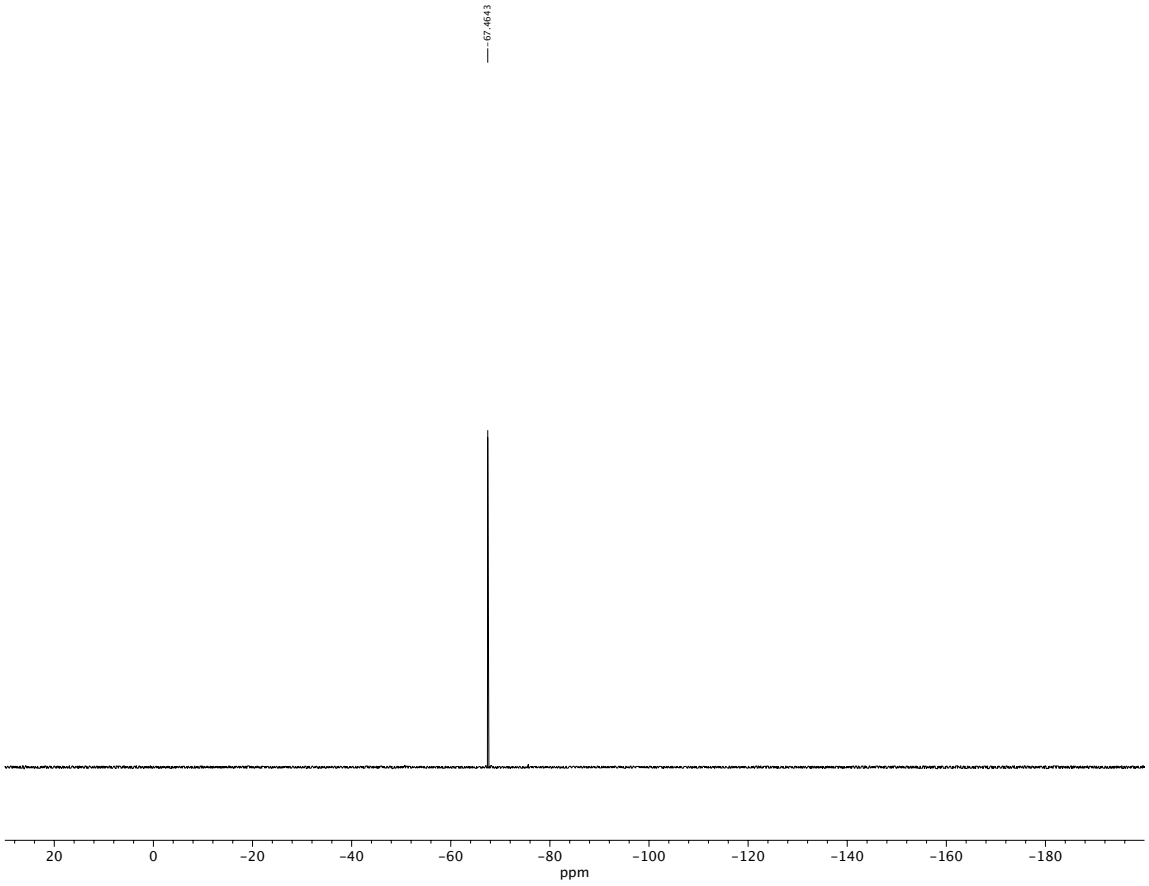
^{1}H NMR (300 MHz, $CDCl_3$) of compound **9**.



Infrared spectrum (Thin Film, NaCl) of compound **9**.



^{13}C NMR (100 MHz, $CDCl_3$) of compound **9**.



^{19}F NMR (100 MHz, $CDCl_3$) of compound **9**.