Supporting information

Intramolecular Cyclization of *m*-Homoprenylphenols through Oxidative Nucleophilic Aromatic Substitution

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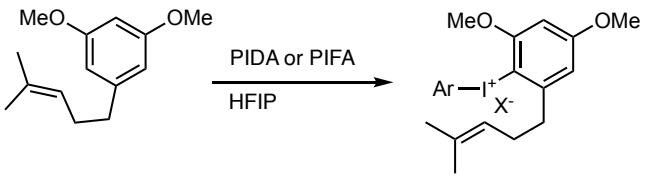
1. General Information

Reagents and solvents for synthesis were commercially purchased and air and/or moisture sensitive reaction were carried out under Ar atmosphere. 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) was distilled from 3Å molecular sieves and stored over 4Å molecular sieves. Ethylenediamine and diisopropylamine were distilled from KOH under Ar atmosphere and stored over 5Å or 4Å molecular sieves, respectively. Silica gel chromatography was performed using Wakosil® C-300 (spherical and neutral; 38-63 μm, 233-01677, FUJIFILM Co.). TLC analysis was performed using Merck Silica gel 60 F_{254}. Preparative TLC was performed using Merck PLC Silica gel 60 F_{254}. Melting points were measured on a Mitamura Riken Kogyo MELTEMP and uncorrected. IR spectra were recorded on a Jasco FT/IR-4700 spectrometer with ATR PRO ONE in ATR mode using diamond prism. ^{1}H and ^{13}C NMR spectra were measured on a Bruker spectrometer at 500 MHz and 125MHz or VARIAN 400-MR spectrometer at 500 MHz or 400 MHz. $CDCl_3$ was used as a solvent and the residual solvent peaks were used as an internal standard (^{1}H NMR: 7.26 ppm; ^{13}C NMR: 77.0 ppm). High resolution (HR) mass spectra (MS) were measured on JEOL JMS-T100LP AccuTOF spectrometer using electrospray method (ESI).

2. Supporting Scheme



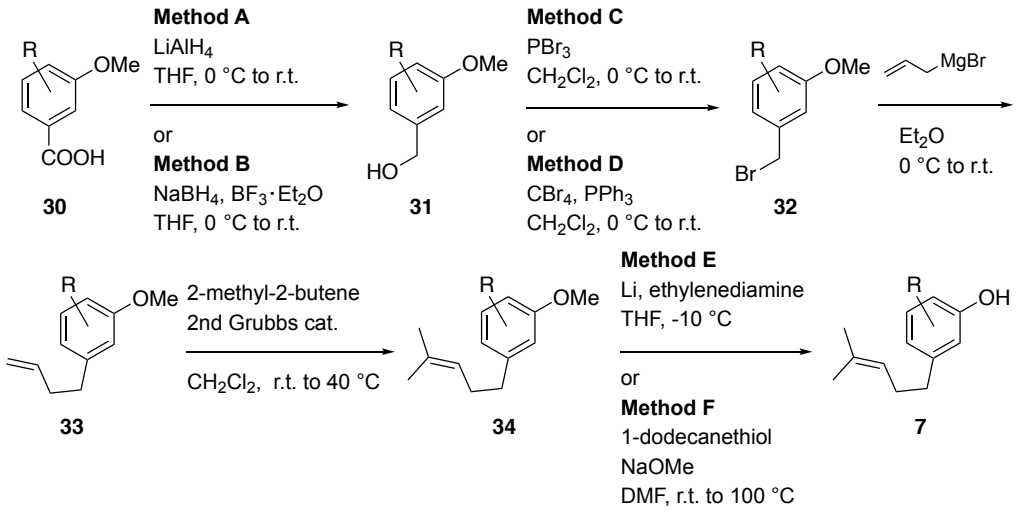
Scheme S1 Reaction of a dimethoxy derivative

Kita *et al.* proposed the reaction mechanism through phenoxyiodine intermediates for phenol coupling in ref. 2f, g. They also reported that the coupling of phenol ethers goes through cation radical intermediates in ref. 2a. In our cyclization, the reaction of a dimethoxy derivative did not afford a cyclized product but diaryliodonium salts (ref. 2c) were formed, which also support our proposed mechanism through phenoxyidodine intermediate **27**.

3. Synthesis and Characterization Data of Compounds

3.1 Synthesis of phenols 7a-m, 23, and 24

Alcohol **31b-m** were prepared by following references (1) and (2). Alkene **34** were prepared from corresponding alkene **33** by following reference (3). Phenol **7a**, **f**, **g**, **j**, **m** were prepared by following reference (4).



General procedure for synthesis of alcohol 31b-m

Method A

To a suspension of lithium aluminum hydride (2.13 g, 56 mmol) in dry THF (70 mL) at 0 °C was added carboxylic acid **30b-m** (28 mmol) in dry THF (120 mL) using a dropping funnel over 2 h under Ar atmosphere. The reaction mixture was warmed up to room temperature and stirred for 5 h. The reaction was quenched by addition of saturated aq. potassium sodium tartrate (50 mL) at 0 °C and the organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure to afford alcohol **31b-m**, which was used for the subsequent reaction without further purification.

Method B

To a solution of carboxylic acid **30b-m** (5.0 mmol) in dry THF (25 mL) at 0 °C was added sodium borohydride (473 mg, 12.5 mmol) in one portion under Ar atmosphere. The reaction mixture was stirred at 0 °C for 30 min and $BF_3 \cdot Et_2O$ (940 μL, 7.5 mmol) was added. The reaction mixture was warmed up to room temperature and stirred for 3 h. The reaction was cooled to 0 °C and quenched by addition of 2 M aq. HCl (7 mL) to pH 1-2 and stirred at 0 °C. To the reaction mixture was added 2 M aq. NaOH (12 mL) to pH 10 and the reaction mixture was concentrated under reduced pressure. The residue was diluted with brine and the organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure to afford alcohol **31**, which was used for the subsequent reaction without further purification.

General procedure for synthesis of benzyl bromide 32

Method C

To a solution of crude alcohol **31** (3.0 mmol) in dry CH_2Cl_2 (14 mL) at 0 °C was added PBr_3 (340 μL, 3.6 mmol) dropwise under Ar atmosphere. The reaction was warmed up to room temperature and stirred for 15 h. The reaction was quenched by addition of saturated aq. $NaHCO_3$ (10 mL) to pH 7 at 0 °C and stirred at room temperature for 1 h. The organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-9/1) to afford benzyl bromide **32**.

Method D

To a solution of crude alcohol **31** (5.0 mmol) in dry CH_2Cl_2 (25 mL) at 0 °C were added CBr_4 (1.66 g, 5.0 mmol) and PPh_3 (1.31 g, 5.0 mmol) portionwise under Ar atmosphere. The reaction was warmed up to room temperature and stirred for 12 h. The reaction mixture was poured into H_2O (20 mL) and the organic materials were extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (1/0-9/1) to afford benzyl bromide **32**.

General procedure for synthesis of alkene 33

To a solution of benzyl bromide **32** (4.0 mmol) in dry Et_2O (20 mL) at 0 °C under Ar atmosphere was added allylmagnesium bromide solution in Et_2O (1.0 M, 6.0 mL, 6.0 mmol). The reaction was warmed up to 35 °C and stirred at 35 °C for 10 h. The reaction was cooled to 0 °C and quenched by addition of saturated aq. NH_4Cl (15 mL) at 0 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (98/2-9/1)to afford alkene **33**.

General procedure for synthesis of alkene 34

To a solution of alkene **33** (3.0 mmol) in dry CH_2Cl_2 (15 mL) at room temperature under Ar atmosphere were added 2-methyl-2-butene (6.4 mL, 60 mmol) and 2nd Grubbs catalyst (127 mg, 0.15 mmol). The reaction was warmed up to 40 °C and stirred at 40 °C for 12 h. The reaction was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with hexane/EtOAc (1/0-19/1) to afford alkene **34**.

General procedure for synthesis of phenol 7

Method E

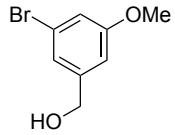
To a solution of alkene **34** (3.5 mmol) in dry THF (8.6 mL) was added dry ethylenediamine (1.6 mL, 24.3 mmol) at room temperature under Ar atmosphere. The mixture was cooled to -10 ℃. To the reaction mixture was added lithium shot (120 mg, 17.3 mmol). The mixture was stirred at -10 °C for 15 h. The reaction was quenched by addition of saturated aq. NH_4Cl (10 mL) at -10 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and

the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-1/1) to afford phenol **7**.

Method F

To a solution of alkene **34** (2.0 mmol) in dry DMF (15 mL) were added 1-dodecanethiol (580 μL, 2.4 mmol) and sodium methoxide (130 mg, 2.4 mmol) at room temperature under Ar atmosphere. The mixture was warmed up to 100 °C and stirred at 100 °C for 9 h. The reaction was quenched by addition of aqueous 2 M aq. HCl (2 mL), H_2O (10 mL) and EtOAc (10 mL) at 0 °C and stirred 0 °C. The organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-1/1) to afford phenol **7**.

(3-Bromo-5-methoxyphenyl)methanol (31b)

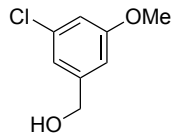


31b was obtained as a colorless oil in 95% yield (1.22 g) by Method B.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10 (1H, d, *J* = 2.0 Hz), 6.97 (1H, dd, *J* = 2.0, 1.8 Hz), 6.85 (1H, d, *J* = 1.8 Hz), 4.65 (2H, s), 3.80 (3H, s) ppm.

Its ^{1}H NMR spectrum was identical with that reported previously.[5]

(3-Chloro-5-methoxyphenyl)methanol (31c)

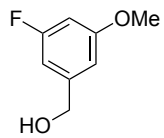


31c was obtained as a colorless oil in 90% yield (1.1 g) by Method B.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (1H, dd, *J* = 1.8, 1.4 Hz), 6.81 (2H, m), 4.65 (2H, s), 3.80 (3H, s) ppm.

Its ^{1}H NMR spectrum was identical with that reported previously.[6]

(3-Fluoro-5-methoxyphenyl)methanol (31d)

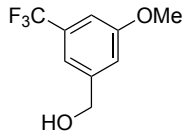


31d was obtained as a colorless oil in 92% yield (965 mg) by Method B.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.66-6.71 (2H, m), 6.53 (1H, ddd, *J* = 10.6, 2.3, 2.3 Hz), 4.66 (2H, s), 3.80 (3H, s) ppm.

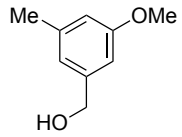
Its ^{1}H NMR spectrum was identical with that reported previously.[7]

(3-Methoxy-5-(trifluoromethyl)phenyl)methanol (31e)



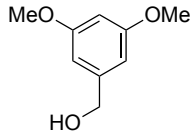
31e was obtained as a yellow oil in 92% yield (1.81 g) by Method B.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (1H, s), 7.10 (1H, s), 7.05 (1H, s), 4.74 (2H, s), 3.86 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[6]

(3-Methoxy-5-methylphenyl)methanol (31f)



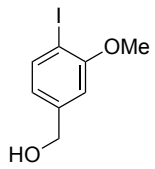
31f was obtained as a yellow oil in 95% yield (1.94 g) by Method B.
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.77 (1H, s), 6.73 (1H, s), 6.66 (1H, s), 4.63 (2H, s), 3.80 (3H, s), 2.33 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[8]

(3,5-Dimethoxyphenyl)methanol (31g)



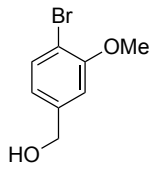
31g was obtained as a colorless oil in 90% yield (1.54 g) by Method A.
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.53 (2H, d, J = 2.3 Hz), 6.39 (1H, t, J = 2.3 Hz), 4.64 (2H, s), 3.80 (6H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[1]

(4-Iodo-3-methoxyphenyl)methanol (31h)



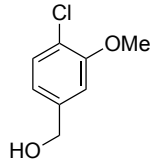
31h was obtained as a yellow oil in 93% yield (940 mg) by Method B.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.76 (1H, d, J = 7.9 Hz), 6.90 (1H, d, J = 1.7 Hz), 6.73 (1H, dd, J = 7.9, 1.7Hz), 4.70 (2H, s), 3.92 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[9]

(4-Bromo-3-methoxyphenyl)methanol (31i)



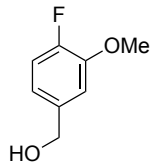
31i was obtained as a yellow oil in 93% yield (1.76 g) by Method B.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (1H, d, *J* = 8.0 Hz), 6.96 (1H, d, *J* = 2.0 Hz), 6.81 (1H, ddd, *J* = 8.0, 2.0, 0.8 Hz), 4.67 (2H, s), 3.91 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[10]

(4-Chloro-3-methoxyphenyl)methanol (31j)



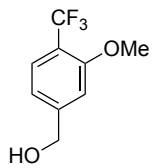
31j was obtained as a yellow oil in 97% yield (992 mg) by Method B.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (1H, d, *J* = 8.0 Hz), 6.99 (1H, d, *J* = 1.8 Hz), 6.87 (1H, dd, *J* = 8.0, 1.8 Hz), 4.68 (2H, s), 3.92 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[11]

(4-Fluoro-3-methoxyphenyl)methanol (31k)



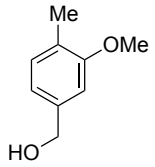
31k was obtained as a yellow oil in 95% yield (940 mg) by Method B.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.05 (1H, dd, *J* = 11.2, 8.2 Hz), 7.01 (1H, dd *J* = 8.2, 2.0 Hz), 6.86 (1H, ddd, *J* = 8.2, 4.3, 2.0 Hz), 4.66 (2H, d, *J* = 0.4 Hz), 3.90 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[12]

(3-Methoxy-4-(trifluoromethyl)phenyl)methanol (31l)



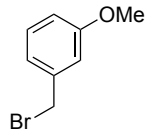
31l was obtained as a white solid in 90% yield (1.62 g) by Method B.
Mp. : 46.2 °C. IR (ATR) : ν 3263, 2921, 2849, 1620, 1417, 1308, 1266, 1121, 1040, 1025, 919, 810, 737 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.54 (1H, d, *J* = 7.9 Hz), 7.06 (1H, s), 6.97 (1H, s, *J* = 7.9 Hz), 4.75 (2H, s), 3.92 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 146.8, 127.4, 127.3, 123.2 (q, *J* = 272.1 Hz), 117.9, 110.1, 64.8, 56.1 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_9H_9F_3O_2Na$: 229.0452, found: 229.0458.

(3-Methoxy-4-methylphenyl)methanol (31m)



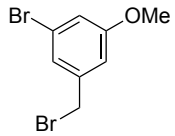
31m was obtained as a yellow oil in 93% yield (980 mg) by Method B.
^1H NMR (400 MHz, $CDCl_3$): δ 7.11 (1H, d, *J* = 7.6 Hz), 6.87 (1H, d *J* = 1.2 Hz), 6.84 (1H, dd, *J* = 7.6, 1.2 Hz), 4.66 (2H, s), 3.85 (3H, s), 2.21 (3H, s) ppm.
Its ^1H NMR spectrum was identical with that reported previously.[13]

1-(Bromomethyl)-3-methoxybenzene (32a)



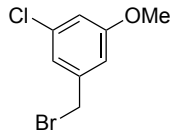
32a was obtained as a colorless oil in 93% yield (1.86 g) by Method D.
^1H NMR (400 MHz, $CDCl_3$): δ 7.26 (1H, dd, *J* = 8.2, 7.8 Hz), 6.98 (1H, dd, *J* = 7.8, 1.8 Hz), 6.93 (1H, dd, *J* = 2.2, 1.8 Hz), 6.84 (1H, ddd, *J* = 8.2, 2.2, 0.6 Hz), 4.47 (2H, s), 3.82 (3H, s) ppm.
Its ^1H NMR spectrum was identical with that reported previously.[14]

1-Bromo-3-(bromomethyl)-5-methoxybenzene (32b)



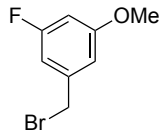
32b was obtained as a white solid in 93% yield (1.75 g) by Method D.
^1H NMR (400 MHz, $CDCl_3$): δ 7.13 (1H, dd, *J* = 1.8, 1.7 Hz), 6.98 (1H, dd, *J* = 2.0, 1.8 Hz), 6.85 (1H, dd, *J* = 2.0, 1.7 Hz), 4.38 (2H, s), 3.80 (3H, s) ppm.
Its ^1H NMR spectrum was identical with that reported previously.[15]

1-(Bromomethyl)-3-chloro-5-methoxybenzene (32c)



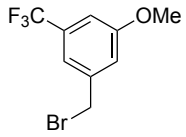
32c was obtained as a white solid in 97% yield (1.36 g) by Method D.
Mp. : 78.5 °C. IR (ATR) : ν 3006, 2966, 2940, 2837, 1576, 1462, 1276, 1054, 842, 764, 750, 688 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.98 (1H, dd, *J* = 1.9, 1.6 Hz), 6.83 (1H, dd, *J* = 2.2, 1.9 Hz), 6.81 (1H, dd, *J* = 2.2, 1.6 Hz), 4.39 (2H, s), 3.81 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.5, 140.4, 135.2, 121.5, 114.5, 113.4, 55.7, 32.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_8H_8{}^{79}BrClONa$: 256.9344, found: 256.9330.

1-(Bromomethyl)-3-fluoro-5-methoxybenzene (32d)



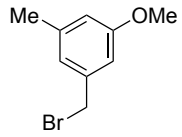
32d was obtained as a white solid in 93% yield (1.86 g) by Method D.
Mp. : 32.1 °C. IR (ATR) : ν 3081, 2967, 2840, 1611, 1454, 1133, 1055, 987, 842, 689 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.69-6.72 (2H, m), 6.55 (1H, ddd, *J* = 10.5, 2.3, 2.3 Hz), 4.40 (2H, s), 3.80 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6 (d, *J* = 245.5 Hz), 161.1 (d, *J* = 11.7 Hz), 140.5 (d, *J* = 10.0 Hz), 110.7 (d, *J* = 2.7 Hz), 108.4 (d, *J* = 22.4 Hz), 101.8 (d, *J* = 25.2 Hz), 55.8, 32.6 (d, *J* = 3.3 Hz) ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_8H_8{}^{79}BrFONa$: 240.9640, found: 240.9644.

1-(Bromomethyl)-3-methoxy-5-(trifluoromethyl)benzene (32e)



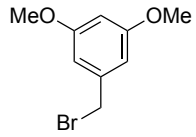
32e was obtained as a colorless oil in 94% yield (1.28 g) by Method D.
^1H NMR (500 MHz, $CDCl_3$): δ 7.23 (1H, s), 7.09 (1H, s), 7.06 (1H, s), 4.46 (2H, s), 3.86 (3H, s) ppm.
Its ^1H NMR spectrum was identical with that reported previously.[6]

1-(Bromomethyl)-3-methoxy-5-methylbenzene (32f)



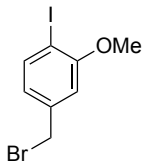
32f was obtained as a colorless oil in 90% yield (1.27 g) by Method D.
^1H NMR (500 MHz, $CDCl_3$): δ 6.80 (1H, s), 6.73 (1H, s), 6.66 (1H, s), 4.43 (2H, s), 3.80 (3H, s), 2.32 (3H, s) ppm.
Its ^1H NMR spectrum was identical with that reported previously.[16]

1-(Bromomethyl)-3,5-dimethoxybenzene (32g)



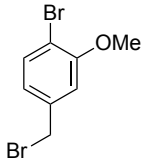
32g was obtained as a white solid in 92% yield (1.52 g) by Method C.
^{1}H NMR (500 MHz, $CDCl_3$): δ 6.54 (2H, d, *J* = 2.3 Hz), 6.39 (1H, t, *J* = 2.3 Hz), 4.42 (2H, s), 3.80 (6H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[17]

4-(Bromomethyl)-1-iodo-2-methoxybenzene (32h)



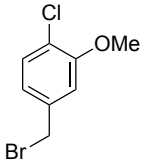
32h was obtained as a brown oil in 92% yield (1.19 g) by Method D.
IR (ATR) : ν 3002, 2963, 2922, 2853, 1585, 1463, 1404, 1278, 1038, 850, 810, 765, 750, 651 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72 (1H, d, *J* = 7.9 Hz), 6.84 (1H, d, *J* = 1.9 Hz), 6.75 (1H, dd, *J* = 7.9, 1.9 Hz), 4.44 (2H, s), 3.90 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.5, 139.9, 139.7, 123.1, 111.6, 86.3, 56.5, 33.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_8H_8{}^{79}BrIONa$: 348.8700, found: 348.8717.

1-Bromo-4-(bromomethyl)-2-methoxybenzene (32i)



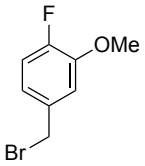
32i was obtained as a colorless oil in 89% yield (1.18 g) by Method D.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (1H, d, *J* = 8.1 Hz), 6.92 (1H, d, *J* = 1.9 Hz), 6.87 (1H, dd, *J* = 8.1, 1.9 Hz), 4.45 (2H, s), 3.92 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[18]

4-(Bromomethyl)-1-chloro-2-methoxybenzene (32j)



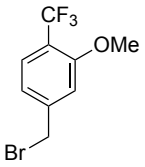
32j was obtained as a colorless oil in 93% yield (1.26 g) by Method D.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (1H, d, *J* = 8.0 Hz), 6.95 (1H, d, *J* = 2.0 Hz), 6.92 (1H, dd, *J* = 8.0, 2.0 Hz), 4.46 (2H, s), 3.92 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[19]

4-(Bromomethyl)-1-fluoro-2-methoxybenzene (32k)



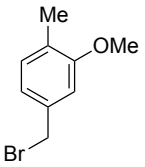
32k was obtained as a white solid in 96% yield (1.06 g) by Method D.
Mp. : 50.3 °C. IR (ATR) : ν 3006, 2986, 1609, 1518, 1276, 1154, 1023, 823, 765, 750, 653 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (1H, dd, *J* = 11.0, 8.2 Hz), 7.00 (1H, dd, *J* = 8.0, 2.2 Hz), 6.91 (1H, ddd, *J* = 8.2, 4.2, 2.2 Hz), 4.46 (2H, d, *J* = 1.0 Hz), 3.91 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4 (d, *J* = 247.8 Hz), 147.8 (q, *J* = 11.0 Hz), 134.2 (d, *J* = 3.8 Hz), 121.6 (q, *J* = 7.1 Hz) 116.3 (d, *J* = 18.6 Hz), 114.3 (d, *J* = 1.9 Hz), 56.4, 33.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_8H_8{}^{79}BrFONa$: 240.9640, found: 240.9626.

4-(Bromomethyl)-2-methoxy-1-(trifluoromethyl)benzene (32l)



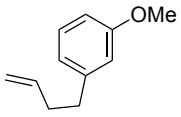
32l was obtained as a white solid in 95% yield (1.13 g) by Method D.
Mp. : 57.1 °C. IR (ATR) : ν 3008, 2986, 2948, 1613, 1419, 1326, 1260, 1109, 764, 750, 670 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (1H, d, *J* = 8.3 Hz), 7.01-7.02 (2H, m), 4.47 (2H, s), 3.93 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.8, 143.4, 127.7. 127.6, 123.5 (q, *J* = 272.2 Hz), 120.5, 112.6, 56.1, 32.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_8H_8{}^{79}BrF_3ONa$: 290.9608, found: 290.9621.

4-(Bromomethyl)-2-methoxy-1-methylbenzene (32m)



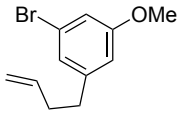
32m was obtained as a white solid in 96% yield (1.30 g) by Method D.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (1H, dd, *J* = 7.4, 0.6 Hz), 6.89 (1H, dd, *J* = 7.4, 1.6 Hz), 6.85 (1H, d, *J* = 1.6 Hz), 4.50 (2H, s), 3.85 (3H, s), 2.21 (3H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[20]

1-(But-3-en-1-yl)-3-methoxybenzene (33a)



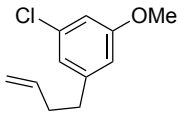
33a was obtained as a colorless oil in 90% yield (1.22 g).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20 (1H, ddd, *J* = 7.4, 1.4, 1.4 Hz), 6.76 (3H, m), 5.82-5.90 (1H, m), 5.03-5.07 (1H, m), 4.97-5.00 (1H, m), 3.80 (3H, s), 2.69 (2H, t, *J* = 7.8 Hz), 2.35-2.40 (2H, m) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[21]

1-Bromo-3-(but-3-en-1-yl)-5-methoxybenzene (33b)



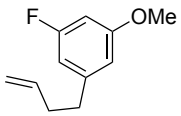
33b was obtained as a yellow oil in 93% yield (760 mg).
IR (ATR) : ν 3076, 3001, 2935, 2834, 1568, 1457, 1270, 1151, 1054, 914, 822, 687 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.94 (1H, dd, *J* = 2.0, 1.6 Hz), 6.88 (1H, dd, *J* = 2.1, 2.0 Hz), 6.66 (1H, dd, *J* = 2.1, 1.6 Hz), 5.78-5.87 (1H, m), 5.02-5.07 (1H, m), 4.98-5.01 (1H, m), 3.78 (3H, s), 2.65 (2H, t, *J* = 7.8 Hz), 2.32-2.37 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.4, 145.2, 137.6, 124.1, 122.7, 115.5, 114.5, 113.7, 55.6, 35.3, 35.2 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{11}H_{13}{}^{79}BrONa$: 263.0047, found: 263.0056.

1-(But-3-en-1-yl)-3-chloro-5-methoxybenzene (33c)



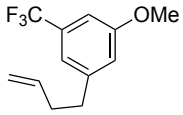
33c was obtained as a colorless oil in 91% yield (936 mg).
IR (ATR) : ν 2989, 2938, 1576, 1458, 1276, 1260, 1151, 1056, 914, 847, 764, 750, 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.78 (1H, dd, *J* = 2.2, 1.6 Hz), 6.73 (1H, dd, *J* = 2.2, 2.0 Hz), 6.62 (1H, dd, *J* = 2.0, 1.6 Hz), 5.79-5.87 (1H, m), 5.02-5.07 (1H, m), 4.98-5.00 (1H, m), 3.78 (3H, s), 2.65 (2H, t, *J* = 7.8 Hz), 2.33-2.38 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.4, 144.8, 137.7, 134.7, 121.1, 115.4, 113.1, 111.7, 55.6, 35.3, 35.2 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{11}H_{13}ClONa$: 219.0552, found: 219.0531.

1-(But-3-en-1-yl)-3-fluoro-5-methoxybenzene (33d)



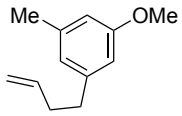
33d was obtained as a colorless oil in 90% yield (738 mg).
IR (ATR) : ν 3005, 2928, 2840, 1613, 1590, 1276, 1147, 1129, 1057, 840, 764, 750, 690 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.49-6.52 (2H, m), 6.45 (1H, ddd, *J* = 10.7, 2.3, 2.3 Hz), 5.79-5.87 (1H, m), 5.02-5.06 (1H, m), 4.97-5.00 (1H, m), 3.78 (3H, s), 2.66 (2H, t, *J* = 7.8 Hz), 2.33-2.38 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7 (d, *J* = 244.2 Hz), 160.9 (d, *J* = 11.6 Hz), 145.1 (d, *J* = 9.1 Hz), 137.7, 115.4, 110.2 (d, *J* = 2.3 Hz), 107.7 (d, *J* = 21.3 Hz), 99.1 (d, *J* = 25.3 Hz), 55.6, 35.5 (d, *J* = 2.0 Hz), 35.2 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{11}H_{13}FONa$: 203.0848, found: 203.0833.

1-(But-3-en-1-yl)-3-methoxy-5-(trifluoromethyl)benzene (33e)



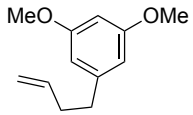
33e was obtained as a colorless oil in 96% yield (837 mg).
IR (ATR) : ν 2931, 2846, 1604, 1466, 1356, 1245, 1167, 1119, 1054, 914, 853, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.04 (1H, s), 6.95 (1H, m), 6.89 (1H, m), 5.79-5.87 (1H, m), 5.03-5.07 (1H, m), 4.99-5.02 (1H, m), 3.83 (3H, s), 2.73 (2H, t, *J* = 7.8 Hz), 2.36-2.41 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 144.5, 137.5, 131.7 (q, *J* = 34.0, Hz), 124.2 (q, *J* = 272.4, Hz), 117.9, 117.7 (d, *J* = 3.7, Hz), 115.6, 108.6 (d, *J* = 4.1, Hz), 55.6, 35.4, 35.2 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}F3ONa$: 253.0816, found: 253.0810.

1-(But-3-en-1-yl)-3-methoxy-5-methylbenzene (33f)



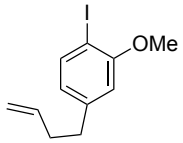
33f was obtained as a colorless oil in 90% yield (1.12 g).
IR (ATR) : ν 3004, 2920, 2836, 1595, 1461, 1276, 1151, 1067, 913, 835, 765, 750, 699 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.62 (1H, s), 6.56 (2H, s), 5.82-5.90 (1H, m), 5.04-5.08 (1H, m), 4.97-4.99 (1H, m), 3.78 (3H, s), 2.64 (2H, t, *J* = 7.8 Hz), 2.34-2.39 (2H, m), 2.31 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 143.5, 139.3, 138.3, 121.9, 114.9, 112.1, 111.3, 55.2, 35.6, 21.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{16}ONa$: 199.1098, found: 199.1105.

1-(But-3-en-1-yl)-3,5-dimethoxybenzene (33g)



33g was obtained as a colorless oil in 93% yield (1.51 g).
^1H NMR (500 MHz, $CDCl_3$): δ 6.36 (2H, d, *J* = 2.3 Hz), 6.31 (1H, t, *J* = 2.3 Hz), 5.82-5.90 (1H, m), 5.03-5.07 (1H, m), 4.97-5.00 (1H, m), 3.78 (3H, s), 2.64-2.67 (2H, t, *J* = 7.8 Hz), 2.34-2.39 (2H, m) ppm. Its ^1H NMR spectrum was identical with that reported previously.[22]

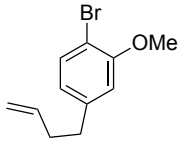
4-(But-3-en-1-yl)-1-iodo-2-methoxybenzene (33h)



33h was obtained as a yellow oil in 82% yield (705 mg).
IR (ATR) : ν 2923, 2852, 142, 1405, 1276, 1261, 1043, 913, 764, 749, 704 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.65 (1H, d, *J* = 7.9 Hz), 6.66 (1H, d, *J* = 1.8 Hz), 6.57 (1H, dd, *J* = 7.9, 1.8 Hz), 5.80-5.88 (1H,

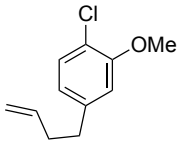
m), 5.02-5.07 (1H, m), 4.98-5.01 (1H, m), 3.87 (3H, s), 2.68 (2H, t, *J* = 7.8 Hz), 2.34-2.39 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.1, 144.1, 139.2, 137.8, 122.9, 115.4, 111.6, 82.6, 56.4, 35.4, 35.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{11}H_{13}IONa$: 310.9908, found: 310.9925.

1-Bromo-4-(but-3-en-1-yl)-2-methoxybenzene (33i)



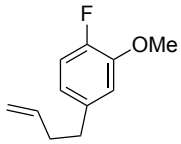
33i was obtained as a colorless oil in 91% yield (901 mg).
IR (ATR) : ν 3004, 2936, 2858, 1590, 1483, 1407, 1276, 1171, 1046, 911, 764, 750, 634 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42 (1H, d, *J* = 8.0 Hz), 6.73 (1H, d, *J* = 1.8 Hz), 6.67 (1H, dd, *J* = 8.0, 1.8 Hz), 5.80-5.88 (1H, m), 5.02-5.07 (1H, m), 4.98-5.01 (1H, m), 3.89 (3H, s), 2.68 (2H, t, *J* = 7.8 Hz), 2.34-2.39 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 143.0, 137.8, 133.1, 122.0, 115.4, 112.5, 118.9, 56.3, 35.5, 35.4 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{11}H_{13}{}^{79}BrONa$: 263.0047, found: 263.0034.

4-(But-3-en-1-yl)-1-chloro-2-methoxybenzene (33j)



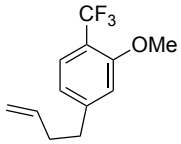
33j was obtained as a colorless oil in 91% yield (779 mg).
IR (ATR) : ν 2922, 2848, 1723, 1696, 1581, 1465, 1413, 1281, 1257, 1173, 1064, 1030, 853, 764, 747, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27 (1H, d, *J* = 8.0 Hz), 6.77 (1H, t, *J* = 1.8 Hz), 6.74 (1H, dd, *J* = 8.0, 1.8 Hz), 5.81-5.90 (1H, m), 5.04-5.08 (1H, m), 5.00-5.02 (1H, m), 3.91 (3H, s), 2.70 (2H, t, *J* = 7.8 Hz), 2.36-2.41 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.9, 142.1, 137.8, 130.0, 121.4, 119.9, 115.4, 112.6, 56.2, 35.5, 35.4 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{11}H_{13}ClONa$: 219.0552, found: 219.0573.

4-(But-3-en-1-yl)-1-fluoro-2-methoxybenzene (33k)



33k was obtained as a colorless oil in 87% yield (810 mg).
IR (ATR) : ν 2954, 2918, 2849, 1609, 1518, 1464, 1280, 1217, 1152, 1037, 912, 811, 765, 747 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.97 (1H, dd, *J* = 11.3, 8.2 Hz), 6.78 (1H, dd, *J* = 8.2, 2.1 Hz), 6.69 (1H, ddd, *J* = 8.2, 4.3, 2.1 Hz), 5.80-5.88 (1H, m), 5.00-5.06 (1H, m), 4.98-5.00 (1H, m), 3.88 (3H, s), 2.67 (2H, t, *J* = 7.8 Hz), 2.33-2.38 (2H, m) ppm.^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0 (d, *J* = 242.5, Hz), 147.4 (d, *J* = 10.5 Hz), 138.2 (d, *J* = 4.0, Hz), 137.9, 120.5 (d, *J* = 6.5, Hz), 115.8 (d, *J* = 18.1, Hz), 115.3, 113.8, 111.3, 56.3, 35.7, 35.2 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{11}H_{13}FONa$: 203.0848, found: 203.0832.

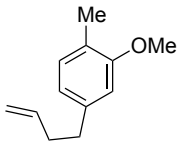
4-(But-3-en-1-yl)-2-methoxy-1-(trifluoromethyl)benzene (33l)



33l was obtained as a colorless oil in 93% yield (865 mg).

IR (ATR) : ν 2932, 2850, 1616, 1584, 1510, 1465, 1419, 1313, 1276, 1173, 1122, 1048, 915, 823, 764, 748 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (1H, d, *J* = 7.7 Hz), 6.82 (2H, m), 5.80-5.88 (1H, m), 5.04-5.08 (1H, m), 4.99-5.02 (1H, m), 3.90 (3H, s), 2.75 (2H, t, *J* = 7.8 Hz), 2.37-2.42 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 148.0, 137.5, 127.1 (q, *J* = 5.3, Hz), 124.0 (q, *J* = 271.5, Hz), 120.1, 116.5 (q, *J* = 30.8, Hz), 115.6, 112.3, 56.0, 35.7, 35.2 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}F_3ONa$: 253.0816, found: 253.0836.

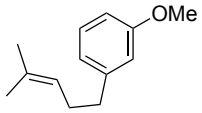
4-(But-3-en-1-yl)-2-methoxy-1-methylbenzene (33m)



33m was obtained as a colorless oil in 98% yield (1.00 g).

IR (ATR) : ν 2956, 2921, 2851, 1463, 1276, 1260, 1040, 897, 764, 750 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$): δ 7.04 (1H, d, *J* = 7.5 Hz), 6.70 (1H, dd, *J* =7.5, 1.3 Hz), 6.67 (1H, d, *J* = 1.3 Hz), 5.83-5.91 (1H, m), 5.04-5.08 (1H, m), 4.97-5.00 (1H, m), 3.82 (3H, s), 2.69 (2H, t, *J* = 7.8 Hz), 2.35-2.40 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 140.9, 138.4, 130.5, 124.1, 120.2, 114.9, 110.4, 55.3, 35.8, 35.5, 16.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{16}ONa$: 199.1098, found: 199.1112.

1-Methoxy-3-(4-methylpent-3-en-1-yl)benzene (34a)

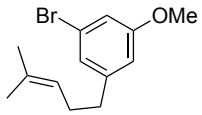


34a was obtained as a colorless oil in 90% yield (1.13 g).

^1H NMR (500 MHz, $CDCl_3$): δ 7.20 (1H, dd, *J* = 7.8, 7.7 Hz), 6.72-6.80 (3H, m), 5.16-5.19 (1H, m), 3.80 (3H, s), 2.61 (2H, t, *J* = 7.9 Hz), 2.29 (2H, dd, *J* = 7.9, 0.9 Hz), 1.69 (3H, d, *J* = 0.9 Hz), 1.58 (3H, s) ppm.

Its ^1H NMR spectrum was identical with that reported previously.[23]

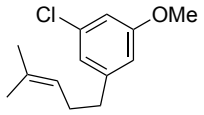
1-Bromo-3-methoxy-5-(4-methylpent-3-en-1-yl)benzene (34b)



IR (ATR) : ν 2962, 2928, 2856, 1597, 1568, 1457, 1270, 1151, 1053, 991, 828, 807, 732, 688 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.94 (1H, dd, *J* = 1.9, 1.5 Hz), 6.87 (1H, dd, *J* = 2.1, 1.9 Hz), 6.66 (1H, dd, *J*

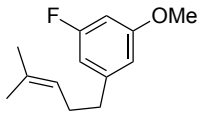
= 2.1, 1.5 Hz), 5.11-5.15 (1H, m), 3.78 (3H, s), 2.56 (2H, t, *J* = 7.8 Hz), 2.24-2.29 (2H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.57 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.3, 145.7, 132.7, 124.1, 123.3, 122.6, 114.4, 113.6, 55.6, 36.0, 29.8, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{17}{}^{79}BrONa$: 291.0360, found: 291.0348.

1-Chloro-3-methoxy-5-(4-methylpent-3-en-1-yl)benzene (34c)



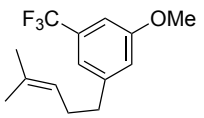
34c was obtained as a colorless oil in 88% yield (483 mg).
IR (ATR) : ν 2964, 2935, 2836, 1706, 1598, 1576, 1459, 1431, 1315, 1273, 1151, 1054, 849, 788, 691 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.62 (1H, d, *J* = 7.5 Hz), 6.56 (2H, m), 5.16-5.19 (1H, m), 3.78 (3H, s), 2.55-2.58 (2H, m), 2.25-2.29 (5H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 144.0, 139.3, 132.2, 124.0, 121.9, 112.0, 111.3, 55.2, 36.3, 30.1, 25.8, 21.7, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{17}ClONa$: 247.0865, found: 247.0849.

1-Fluoro-3-methoxy-5-(4-methylpent-3-en-1-yl)benzene (34d)



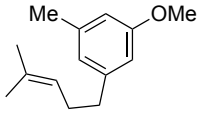
34d was obtained as a colorless oil in 88% yield (390 mg).
IR (ATR) : ν 2960, 2917, 2848, 1614, 1591, 1457, 1276, 1260, 1147, 1130, 1059, 841, 765, 750, 691 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.49-6.52 (2H, m), 6.44 (1H, ddd, *J* = 10.7, 4.6, 2.3 Hz), 5.12-5.16 (1H, m), 3.78 (3H, s), 2.58 (2H, t, *J* = 7.8 Hz), 2.25-2.30 (2H, m), 1.69 (3H, d, *J* = 1.0 Hz),1.57 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7 (d, *J* = 244.2, Hz), 160.8 (d, *J* = 11.7 Hz), 145.6 (d, *J* = 9.1, Hz), 132.6, 123.4, 110.2 (d, *J* = 2.7, Hz), 107.7 (d, *J* = 21.0, Hz), 98.9 (d, *J* = 25.0, Hz), 55.6, 36.2 (d, *J* = 1.7, Hz), 29.7, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{17}FONa$: 231.1161, found: 231.1136.

1-Methoxy-3-(4-methylpent-3-en-1-yl)-5-(trifluoromethyl)benzene (34e)



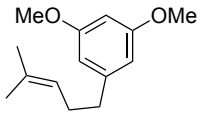
34e was obtained as a colorless oil in 93% yield (361 mg).
IR (ATR) : ν 2966, 2931, 2858, 1604, 1465, 1353, 1316, 1245, 1167, 1119, 1055, 853, 748, 701 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (1H, s), 6.94 (1H, s), 6.89 (1H, s), 5.12-5.16 (1H, m), 3.83 (3H, s), 2.65 (2H, t, *J* = 7.7 Hz), 2.27-2.32 (2H, m), 1.68 (3H, d, *J* = 1.0 Hz), 1.53 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 145.0, 132.9, 131.6 (q, *J* = 32.1 Hz), 123.2 (q, *J* = 272.6 Hz), 123.2, 117.9, 117.8 (q, *J* = 3.7 Hz), 107.9 (q, *J* = 3.8 Hz), 55.6, 36.1, 29.7, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{17}F_3ONa$: 281.1129, found: 281.1115.

1-Methoxy-3-methyl-5-(4-methylpent-3-en-1-yl)benzene (34f)



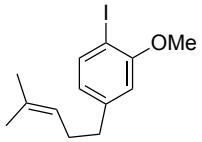
34f was obtained as a colorless oil in 91% yield (517 mg).
IR (ATR) : ν 2960, 2923, 2855, 1613, 1584, 1509, 1412, 1259, 1153, 1132, 1043, 909, 849, 733 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.62 (1H, d, *J* = 7.5 Hz), 6.56 (2H, m), 5.16-5.19 (1H, m), 3.78 (3H, s), 2.55-2.58 (2H, m), 2.25-2.29 (5H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 144.0, 139.3, 132.2, 124.0, 121.9, 112.0, 111.3, 55.2, 36.3, 30.1, 25.8, 21.7, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{20}ONa$: 247.1411, found: 247.1389.

1,3-Dimethoxy-5-(4-methylpent-3-en-1-yl)benzene (34g)



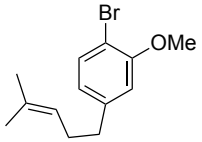
34g was obtained as a colorless oil in 93% yield (679 mg).
IR (ATR) : ν 2925, 2853, 2837, 1596, 1462, 1428, 1346, 1314, 1293, 1205, 1153, 1069, 926, 829, 692 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.36 (2H, d, *J* = 2.3 Hz), 6.31 (1H, t, *J* = 2.3 Hz), 5.15-5.19 (1H, m), 3.78 (6H, s), 2.56-2.59 (2H, m), 2.26-2.31 (2H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.8, 145.0, 132.3, 123.8, 106.6, 97.8, 55.4, 36.6, 29.9, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{20}O_2Na$: 243.2971, found: 243.2969.

1-Iodo-2-methoxy-4-(4-methylpent-3-en-1-yl)benzene (34h)



34h was obtained as a yellow oil in 88% yield (310 mg).
IR (ATR) : ν 2963, 2932, 2855, 1703, 1462, 1404, 1277, 1170, 1041, 764 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64 (1H, d, *J* = 8.0 Hz), 6.66 (1H, d, *J* = 1.8 Hz), 6.57 (1H, dd, *J* = 8.0, 1.8 Hz), 5.12-5.15 (1H, m), 3.87 (3H, s), 2.60 (2H, d, *J* = 7.8 Hz), 2.26-2.30 (2H, m), 1.68 (3H, d, *J* = 1.0 Hz), 1.56 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 139.1, 132.6, 123.5, 122.9, 111.7, 82.4, 56.4, 36.1, 29.9, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{17}IONa$: 339.0221, found: 339.0205.

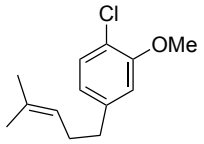
1-Bromo-2-methoxy-4-(4-methylpent-3-en-1-yl)benzene (34i)



34i was obtained as a yellow oil in 83% yield (390 mg).

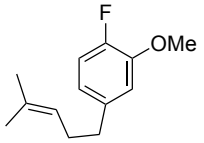
IR (ATR) : ν 2924, 2852, 1704, 1577, 1481, 1420, 1257, 1198, 1160, 1031, 804, 764, 748, 645 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.41 (1H, d, *J* = 8.0 Hz), 6.72 (1H, d, *J* = 1.9 Hz), 6.67 (1H, dd, *J* = 8.0, 1.9 Hz), 5.12-5.16 (1H, m), 3.88 (3H, s), 2.60 (2H, d, *J* = 7.8 Hz), 2.26-2.31 (2H, m), 1.68 (3H, d, *J* = 1.0 Hz), 1.56 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 143.5, 133.0, 132.6, 123.4, 122.0, 112.5, 108.7, 56.2, 36.1, 29.9, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{17}{}^{79}BrONa$: 291.0360, found: 291.0377.

1-Chloro-2-methoxy-4-(4-methylpent-3-en-1-yl)benzene (34j)



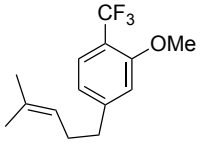
34j was obtained as a colorless oil in 87% yield (352 mg).
IR (ATR) : ν 2965, 2925, 2856, 1595, 1580, 1490, 1410, 1276, 1260, 1064, 1032, 810, 765, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.25 (1H, d, *J* = 8.0 Hz), 6.71-6.75 (2H, m), 5.12-5.16 (1H, m), 3.89 (3H, s), 2.61 (2H, t, *J* = 7.7 Hz), 2.26-2.30 (2H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.55 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8, 142.7, 132.6, 129.9, 123.4, 121.5, 119.7, 112.6, 56.2, 36.1, 30.0, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{17}ClONa$: 247.0865, found: 247.0852.

1-Fluoro-2-methoxy-4-(4-methylpent-3-en-1-yl)benzene (34k)



34k was obtained as a colorless oil in 91% yield (287 mg).
IR (ATR) : ν 2987, 2921, 2850, 1609, 1517, 1276, 1261, 1033, 812, 764, 749 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.96 (1H, dd, *J* = 11.4, 8.2 Hz), 6.78 (1H, dd, *J* = 8.2, 2.0 Hz), 6.69 (1H, ddd, *J* = 8.2, 4.3, 2.0 Hz), 5.13-5.16 (1H, m), 3.88 (3H, s), 2.59 (2H, t, *J* = 7.8 Hz), 2.25-2.29 (2H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.55 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.9 (d, *J* = 242.6 Hz), 147.3, 138.8 (d, *J* = 3.9 Hz), 132.5, 123.5, 120.6 (d, *J* = 6.8 Hz), 115.7 (d, *J* = 22.0 Hz), 113.8 (d, *J* = 1.6 Hz), 56.3, 35.9, 30.2, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{17}FONa$: 231.1161, found: 231.1155.

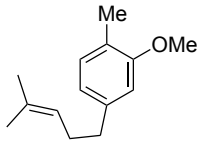
2-Methoxy-4-(4-methylpent-3-en-1-yl)-1-(trifluoromethyl)benzene (34l)



34l was obtained as a colorless oil in 90% yield (345 mg).
IR (ATR) : ν 2970, 2936, 2858, 1615, 1419, 1312, 1117, 1045, 823, 748 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.45 (1H, d, *J* = 7.8 Hz), 6.80-6.83 (2H, m), 5.13-5.16 (1H, m), 3.89 (3H, s), 2.66 (2H, t, *J* = 7.7 Hz), 2.29-2.33 (2H, m), 1.69 (3H, d, *J* = 0.9 Hz), 1.56 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 148.6, 133.9 (q, *J* = 19.6 Hz), 132.9, 129.0, 128.7 (q, *J* = 6.9 Hz), 127.1 (q, *J* = 5.3 Hz),

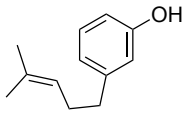
123.2 (q, J = 32.0 Hz), 121.9 (q, J = 271.4 Hz), 120.2, 112.3, 56.0, 36.4, 29.7, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{17}F_3ONa$: 281.1129, found: 281.1113.

2-Methoxy-1-methyl-4-(4-methylpent-3-en-1-yl)benzene (34m)



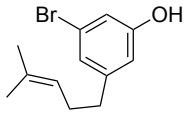
34m was obtained as a yellow oil in 88% yield (478 mg).
IR (ATR) : ν 2961, 2922, 2855, 1509, 1464, 1412, 1259, 1132, 1042, 813, 749 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.03 (1H, d, J = 7.5 Hz), 6.67-6.71 (2H, m), 5.17-5.20 (1H, m), 3.83 (3H, s), 2.61 (2H, t, J = 7.9 Hz), 2.27-2.32 (2H, m), 1.70 (3H, s), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 141.4 132.2, 130.5, 124.0, 123.9, 120.2, 110.5, 55.3, 36.3, 30.3, 25.8, 17.8, 16.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{20}ONa$: 247.1411, found: 247.1420.

3-(4-Methylpent-3-en-1-yl)phenol (7a)



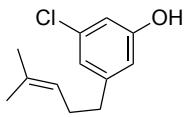
7a was obtained as a colorless oil in 94% yield (1.02 g) by Method E.
IR (ATR) : ν 3354, 2965, 2918, 2855, 1588, 1455, 1272, 1246, 1155, 938, 782, 694 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.15 (1H, dd, J = 7.8, 7.8 Hz), 6.78 (1H, d, J = 7.8 Hz), 6.66 (2H, m), 5.15-5.18 (1H, m), 4.68 (1h, brs), 2.59 (2H, t, J = 7.9 Hz), 2.26-2.31 (2H, m), 1.69 (3H, d, J = 0.8 Hz), 1.58 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.5, 144.6, 132.3, 129.5, 123.7, 121.1, 115.5, 112.7, 36.1, 30.0, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{16}ONa$: 199.1098, found 199.1091.

3-Bromo-5-(4-methylpent-3-en-1-yl)phenol (7b)



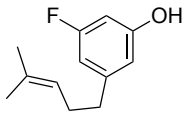
7b was obtained as a colorless oil in 93% yield (180 mg) by Method F.
IR (ATR) : ν 3338, 2926, 2856, 1592, 1573, 1442, 1275, 1154, 994, 840, 748, 688 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.91-6.92 (1H, m), 6.83-6.84 (1H, m), 6.59-6.60 (1H, m), 5.40 (1H, brs), 5.11-5.14 (1H, m), 4.73 (1H, brs), 2.54 (2H, t, J = 7.8 Hz), 2.23-2.28 (2H, m), 1.69 (3H, d, J = 1.0 Hz), 1.57 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.2, 146.1, 132.8, 124.3, 123.2, 122.6, 116.2, 114.5, 35.8, 29.7, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{15}{}^{79}BrONa$: 277.0204, found 277.0227.

3-Chloro-5-(4-methylpent-3-en-1-yl)phenol (7c)



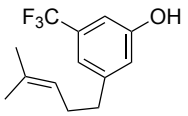
7c was obtained as a yellow oil in 89% yield (202 mg) by Method F.
IR (ATR) : ν 3345, 2967, 2926, 2855, 1595, 1579, 1446, 1276, 1153, 996, 871, 846, 748, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.78 (1H, s), 6.68 (1H, dd, *J* = 2.1, 1.9 Hz), 6.59-6.60 (1H, s), 5.11-5.14 (1H, m), 4.74 (1H, brs), 2.54 (2H, t, *J* = 7.8 Hz), 2.24-2.28 (2H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.57 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.2, 145.8, 134.7, 132.8, 123.3, 121.4, 114.1, 113.4, 35.9, 29.7, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{15}ClONa$: 233.0709, found 233.0715.

3-Fluoro-5-(4-methylpent-3-en-1-yl)phenol (7d)



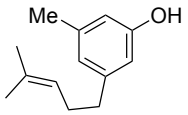
7d was obtained as a colorless oil in 66% yield (175 mg) by Method F.
IR (ATR) : ν 3358, 2965, 2927, 2857, 1618, 1593, 1462, 1445, 1276, 1148, 1125, 984, 842, 750, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.48-6.50 (1H, m), 6.43-6.44 (1H, m), 6.37-6.40 (1H, m), 5.11-5.15 (1H, m), 4.70 (1H, brs), 2.58 (2H, t, *J* = 7.8 Hz), 2.24-2.29 (2H, m), 1.69 (3H, d, *J* = 1.1 Hz),1.57 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6 (d, *J* = 245.0 Hz), 156.6 (d, *J* = 1.9 Hz), 146.1 (d, *J* = 9.1 Hz), 132.7, 123.3, 111.3 (d, *J* = 2.3 Hz), 108.0 (d, *J* = 21.1 Hz), 100.7 (d, *J* = 24.6 Hz), 36.0 (d, *J* = 1.7 Hz), 29.6, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{15}FONa$: 217.1004, found 217.0993.

3-(4-Methylpent-3-en-1-yl)-5-(trifluoromethyl)phenol (7e)



7e was obtained as a yellow oil in 80% yield (157 mg) by Method F.
IR (ATR) : ν 3353, 2977, 2933, 1606, 1457, 1354, 1251, 1170, 1122, 866, 747, 703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.48-6.50 (1H, m), 6.43-6.44 (1H, m), 6.37-6.40 (1H, m), 5.11-5.15 (1H, m), 4.70 (1H, brs), 2.58 (2H, t, *J* = 7.8 Hz), 2.24-2.29 (2H, m), 1.69 (3H, d, *J* = 1.1 Hz),1.57 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.6 (d, *J* = 245.0 Hz), 156.6 (d, *J* = 1.9 Hz), 146.1 (d, *J* = 9.1 Hz), 132.7, 123.3, 111.3 (d, *J* = 2.3 Hz), 108.0 (d, *J* = 21.1 Hz), 100.7 (d, *J* = 24.6 Hz), 36.0 (d, *J* = 1.7 Hz), 29.6, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{15}F_3ONa$: 267.0972, found 267.0988.

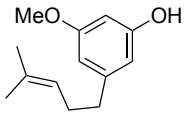
3-Methyl-5-(4-methylpent-3-en-1-yl)phenol (7f)



7f was obtained as a yellow oil in 91% yield (380 mg) by Method E.
IR (ATR) : ν 3365, 2964, 2920, 2855, 1595, 1455, 1299, 1277, 1152, 956, 841, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.60 (1H, s), 6.48 (2H, m), 5.15-5.18 (1H, m), 2.52-2.55 (2H, m), 2.24-2.28 (5H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 144.3, 139.6, 32.5,

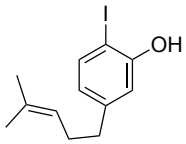
123.9, 122.0, 1113.5, 112.5, 36.1, 30.0, 25.8, 21.4, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{18}ONa$: 213.1255, found 213.1239.

3-Methoxy-5-(4-methylpent-3-en-1-yl)phenol (7g)



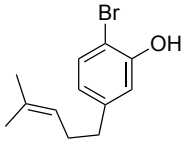
7g was obtained as a colorless oil in 91% yield (603 mg) by Method E.
IR (ATR): ν 3389, 2920, 2852, 1596, 1461, 1455, 1438, 1342, 1299, 1195, 1148, 1063, 985, 835, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.35 (1H, dd, *J* = 2.1, 2.1 Hz), 6.28 (1H, dd, *J* = 2.1, 2.1 Hz), 6.25 (1H, dd, *J* = 2.1, 2.1 Hz), 5.14-5.17 (1H, m), 4.86 (1H, s), 3.77 (3H, s), 2.53-2.56 (2H, m), 2.25-2.29 (2H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.8, 156.4, 145.2, 132.2, 123.6, 107.9, 106.8, 98.8, 55.2, 36.2, 29.7, 25.6, 17.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{18}O_2Na$: 229.2705, found: 229.2706.

2-Iodo-5-(4-methylpent-3-en-1-yl)phenol (7h)



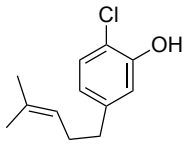
7h was obtained as a yellow oil in 91% yield (280 mg) by Method F.
IR (ATR): ν 3480, 2923, 2852, 1702, 1586, 1415, 1292, 1197, 1016, 802, 731 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.52 (1H, d, *J* = 8.1 Hz), 6.84 (1H, d, *J* = 2.0 Hz), 6.53 (1H, d, *J* = 8.1, 2.0 Hz), 5.17 (1H, brs), 5.11-5.15 (1H, m), 2.56 (2H, t, *J* = 7.8 Hz), 2.24-2.28 (2H, m), 1.68 (3H, d, *J* = 1.1 Hz), 1.56 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.7, 145.5, 137.9, 132.7, 123.4, 115.4, 82.2, 35.7, 29.8, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{15}IONa$: 325.0065, found 325.0091.

2-Bromo-5-(4-methylpent-3-en-1-yl)phenol (7i)



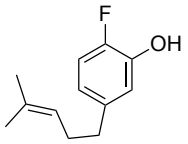
7i was obtained as a colorless oil in 89% yield (201 mg) by Method F.
IR (ATR) : ν 3503, 2925, 2855, 1577, 1481, 1419, 1276, 1159, 1030, 866, 806, 750 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.33 (1H, d, *J* = 8.2 Hz), 6.86 (1H, d, *J* = 2.0 Hz), 6.65 (1H, dd, *J* = 8.2, 2.0 Hz), 5.40 (1H, brs), 5.11-5.15 (1H, m), 2.56 (2H, t, *J* = 7.8 Hz), 2.24-2.29 (2H, m), 1.68 (3H, d, *J* = 1.0 Hz), 1.56 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 144.3, 132.6, 131.6, 123.4, 122.3, 116.2, 107.3, 35.7, 29.8, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{15}{}^{79}BrONa$: 277.0204, found 277.0188.

2-Chloro-5-(4-methylpent-3-en-1-yl)phenol (7j)



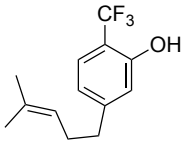
7j was obtained as a yellow oil in 79% yield (167 mg) by Method E.
IR (ATR) : ν 3346, 2927, 2856, 1605, 1458, 1361, 1124, 1053, 866, 808, 703 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.19 (1H, d, *J* = 8.2 Hz), 6.86 (1H, d, *J* = 2.0 Hz), 6.70 (1H, dd, *J* = 8.2, 2.0 Hz), 5.43 (1H, brs), 5.11-5.15 (1H, m), 2.56 (2H, t, *J* = 7.8 Hz), 2.24-2.28 (2H, m), 1.68 (3H, d, *J* = 1.0 Hz), 1.56 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.1, 143.5, 132.6, 128.6, 123.4, 121.7, 117.1, 116.3, 35.7, 29.8, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{15}ClONa$: 233.0709, found 233.0695.

2-Fluoro-5-(4-methylpent-3-en-1-yl)phenol (7k)



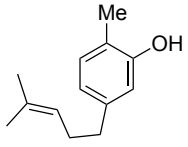
7k was obtained as a yellow oil in 57% yield (177 mg) by Method F.
IR (ATR) : ν 3361, 2925, 2855, 1702, 1607, 1508, 1434, 1274, 1191, 1112, 904, 876, 810, 750 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.96 (1H, dd, *J* = 10.5, 8.5 Hz), 6.83 (1H, dd, *J* = 8.5, 2.2 Hz), 6.65 (1H, ddd, *J* = 7.6, 4.6, 2.2 Hz), 5.11-5.15 (1H, m), 4.98 (1H, brs), 2.55 (2H, t, *J* = 7.8 Hz), 2.23-2.27 (2H, m), 1.68 (3H, d, *J* = 1.1 Hz), 1.56 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.5 (d, *J* = 234.6, Hz), 143.2 (d, *J* = 14.2, Hz), 139.5 (d, *J* = 3.7, Hz), 132.5, 123.5, 120.7 (d, *J* = 6.4 Hz), 117.2 (d, *J* = 1.4 Hz), 115.1 (d, *J* = 17.9 Hz), 35.6, 30.1, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{15}FONa$: 217.1004, found 217.1022.

5-(4-Methylpent-3-en-1-yl)-2-(trifluoromethyl)phenol (7l)

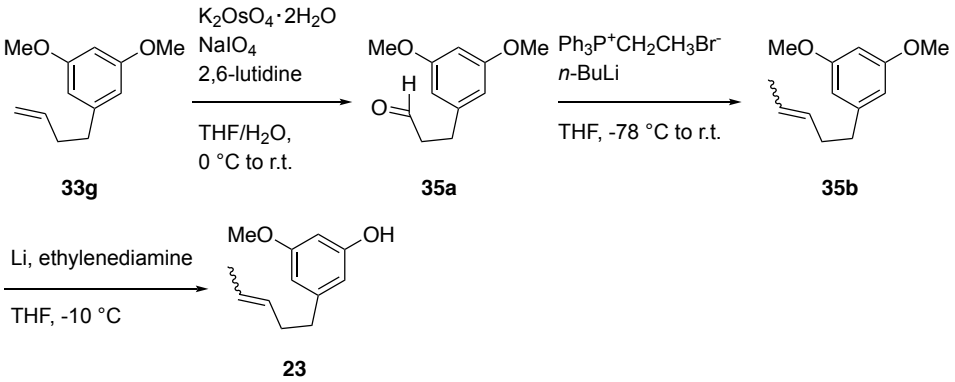


7l was obtained as a yellow oil in 60% yield (197 mg) by Method F.
IR (ATR) : ν 3465, 2930, 1657, 1528, 1400, 1305, 1118, 965, 830, 748 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.40 (1H, d, *J* = 8.0 Hz), 6.82-6.84 (1H, m), 6.78 (1H, s), 5.38 (1H, brs), 5.11-5.15 (1H, m), 2.62 (2H, t, *J* = 7.8 Hz), 2.26-2.31 (2H, m), 1.69 (3H, d, *J* = 1.0 Hz), 1.56 (3H, s) ppm. ^{113}C NMR (125 MHz, $CDCl_3$): δ 156.6, 148.6, 133.9 (q, *J* = 19.6 Hz), 133.5, 129.0, 128.8 (q, *J* = 7.1 Hz), 127.6 (q, *J* = 5.0 Hz), 126.1 (q, *J* = 32.0 Hz), 122.7 (q, *J* = 271.4 Hz), 120.8, 112.3, 36.9, 29.8, 25.9, 17.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{15}F_3ONa$: 267.0972, found 267.0994.

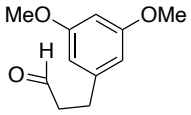
2-Methyl-5-(4-methylpent-3-en-1-yl)phenol (7m)



7m was obtained as a yellow oil in 90% yield (229 mg) by Method E.
IR (ATR) : ν 3402, 2965, 2923, 2855, 1621, 1587, 1454, 1420, 1230, 1114, 998, 859, 811, 634 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.02 (1H, d, *J* = 7.6 Hz), 6.69 (1H, dd, *J* = 7.6, 1.5 Hz), 6.62 (1H, d, *J* = 1.5 Hz), 5.15-5.18 (1H, m), 4.57 (1h, brs), 2.55 (2H, t, *J* = 7.9 Hz), 2.24-2.29 (2H, m), 2.22 (3H, s), 1.69 (3H, d, *J* = 0.9 Hz), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7, 141.9, 132.2, 130.9, 123.9, 120.9, 120.8, 115.1, 35.8, 30.1, 25.8, 17.8 15.4 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{18}ONa$: 213.1255, found 213.1240.

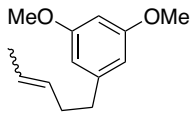


3-(3,5-Dimethoxyphenyl)propanal (35a)



To a solution of **33g** (330 mg, 1.7 mmol) in H_2O/THF (10 mL/9 mL) were added 2,6-lutidine (410 μL, 3.5 mmol), K_2OsO_4•$2H_2O$ (13 mg, 0.035 mmol), and sodium periodate (1.82 g, 8.5 mmol) at room temperature. The mixture was stirred at room temperature for 3 h. The reaction was diluted by addition of H_2O (28 mL) and CH_2Cl_2 (28 mL) and the organic materials were extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (6/1-0/1) to afford **35a** in 80% yield (265 mg) as a colorless oil.
^1H NMR (500 MHz, $CDCl_3$): δ 9.82 (1H, t, *J* = 1.4 Hz), 6.35 (2H, d, *J* = 2.2 Hz), 6.32 (1H, t, *J* = 2.2 Hz), 3.78 (6H, s), 2.89-2.92 (2H, t, *J* = 7.5 Hz), 2.75-2.79 (2H, m) ppm.
Its ^1H NMR spectrum was identical with that reported previously.[24]

1-(Hex-4-en-1-yl)-3,5-dimethoxybenzene (35b)

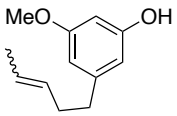


To a solution of ethyltriphenylphosphonium bromide (2.3 g, 6.36 mmol) in dry THF (20 mL) was added *n*-BuLi solution in hexene (1.5 M, 3.9 mL, 5.9 mmol) at -78 °C under Ar atmosphere. The mixture was warmed up to room temperature and stirred at room temperature for 30 min. The reaction was cooled to -78 °C and **35a** (820 mg, 4.2 mmol) in THF (20 mL) was added at -78 °C and the mixture was stirred at

room temperature for 6 h. The reaction was quenched by addition of saturated aq. NH_4Cl (50 mL) at 0 °C and the organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (10/1-1/1) to afford **35b** in 96% yield (840 mg, *E*/*Z* = 3/1) as a colorless oil.

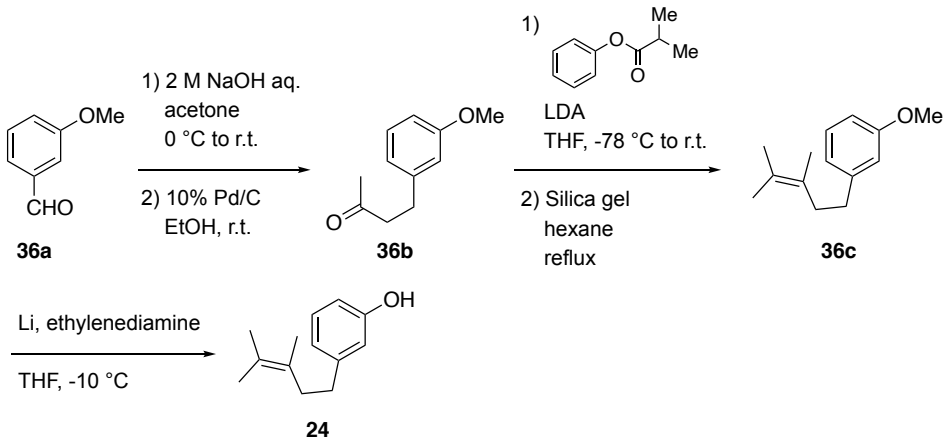
IR (ATR): ν 3000, 2929, 2852, 2837, 1596, 1462, 1428, 1348, 1293, 1205, 1153, 1067, 966, 926, 830, 693 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.37 (3/2H, d, *J* = 2.2 Hz), 6.35 (1/2H, d, *J* = 2.2 Hz), 6.31 (1H, t, *J* = 2.2 Hz), 5.40-5.51 (2H, m), 3.79 (6H, s), 2.61 (2H, t, *J* = 7.8 Hz), 2.34-2.38 (3/2H, m), 2.27-2.30 (1/2H, m), 1.65 (3/4H, d, *J* = 2.1 Hz), 1.58 (9/4H, dd, *J* = 6.8, 0.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) (*E*)-**35b**: δ 160.8, 144.6, 129.7, 124.7, 106.6, 97.9, 55.4, 36.2, 28.7, 12.9 ppm. (*Z*)-**35b**: δ 160.8, 144.6, 130.7, 125.6, 106.6, 97.9, 55.4, 36.6, 34.4, 18.1 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{18}O_2Na$: 229.2705, found: 229.2706.

3-(Hex-4-en-1-yl)-5-methoxyphenol (23)

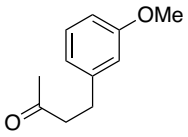


To a solution of **35b** (420 mg, 2.1 mmol) in dry THF (5.1 mL) was added dry ethylenediamine (960 μL, 14.4 mmol) at room temperature under Ar atmosphere. The mixture was cooled to -10 °C. To the reaction mixture was added lithium shot (71 mg, 10.3 mmol). The mixture was stirred at -10 °C for 3 h. The reaction was quenched by addition of saturated aq. NH_4Cl (5 mL) at -10 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-1/1) to afford **23** in 81% yield (320 mg, *E*/*Z* = 3/1) as a colorless oil.

IR (ATR): ν 3404, 3077, 2918, 2851, 2839, 1597, 1462, 1453, 1435, 1344, 1297, 1196, 1148, 1061, 913, 837, 690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.35 (1H, dd, *J* = 2.4, 2.4 Hz), 6.28 (1H, dd, *J* = 2.0, 1.2 Hz), 6.24 (1H, dd, *J* = 2.4, 2.4 Hz), 5.41-5.49 (2H, m), 4.67 (1H, s), 3.77 (3H, s), 2.57 (2H, t, *J* = 7.4 Hz), 2.31-2.36 (3/2H, m), 2.24-2.28 (1/2H, m), 1.64 (3/4H, m), 1.58 (9/4H, d, *J* = 6.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) (*E*)-**23**: δ 160.9, 156.6, 145.1, 129.6, 124.7, 108.1, 107.0, 99.0, 55.4, 36.0, 28.6, 12.9 ppm. (*Z*)-**23**: δ 160.9, 156.6, 145.1, 130.5, 125.5, 108.1, 107.0, 99.0, 55.4, 36.3, 34.0, 18.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{16}O_2Na$: 215.2240, found: 215.2238.



4-(3-Methoxyphenyl)butan-2-one (36b)

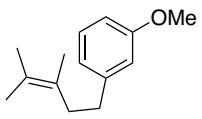


To a solution of aldehyde **36a** (5.48 g, 40.3 mmol) in acetone (30 mL) was added aq. 2 M NaOH (40.3 mL, 80.6 mmol) dropwise at 0 ℃. The mixture was warmed up to room temperature and stirred at room temperature for 3 h. The reaction was quenched by addition of saturated aq. 6 M HCl (14 mL) to pH 1-2 at 0 °C and the organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure to afford corresponding enone (8.05 g) as a colorless oil. To a solution of the crude material in EtOH (66 mL) were added 10% Pd/C (705 mg) and AcOH (70 μL, 1.2 mmol) at room temperature under Ar atmosphere. The atmosphere was replaced by H_2 and the mixture was stirred at room temperature for 14 h. The reaction mixture was filtered through a pad of Celite® and washed with EtOH. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (98/2-3/1) to afford **36b** in 68% yield (4.88 g) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.22 (1H, m), 6.73-6.78 (3H, m), 3.79 (3H, s), 2.87 (2H, t, J = 7.5 Hz), 2.76 (2H, t, J = 7.5 Hz), 2.14 (3H, s) ppm.

Its ^{1}H NMR spectrum was identical with that reported previously.[25]

1-Methoxy-3-(4-methylpent-3-en-1-yl)benzene (36c)

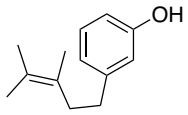


To a solution of diisopropylamine (1.6 mL, 11.1 mmol) in dry THF (30 mL) was added *n*-BuLi solution in hexene (1.5 M, 7.3 mL, 11.1 mmol) at -78 °C under Ar atmosphere. The mixture was warmed up to 0 °C and stirred at 0 °C for 30 min. The reaction was cooled to -78 °C and phenyl isobutylate (1.65 mL, 10.2 mmol) in THF (3 mL) was added at -78 °C and the mixture was stirred at -78 °C for additional 30 min. Ketone **36b** (1.82 g, 10.2 mmol) in THF (3 mL) was added to the reaction mixture at -78 °C and

stirred at -78 °C for 3 h. The reaction was warmed up to room temperature and stirred at room temperature for 18 h. The reaction mixture was concentrated under reduced pressure and the residue was diluted with Et_2O (20 mL) and H_2O (20 mL). The organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure to afford oxetanone as a colorless oil. The crude material was dissolved in dry hexane (8 mL) and silica gel (40-64 mesh, 1.8 g) was added at room temperature. The mixture was warmed up to 85 °C and stirred at 85 °C for 3 h. The mixture was cooled to room temperature and the reaction mixture was filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (98/2-9/1) to afford **36c** in 50% yield (1.05 g) as a colorless oil.

IR (ATR) : ν 2991, 2916, 2859, 2834, 1601, 1489, 1260, 1152, 1051, 765, 694 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.18-7.21 (1H, m), 6.79 (1H, d, *J* = 7.6 Hz), 6.72-6.74 (2H, m), 3.80 (3H, s), 2.60-2.63 (2H, m), 2.29-2.33 (2H, m), 1.69 (3H, m), 1.65 (3H, m), 1.60 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 144.5, 129.3, 127.1, 125.0, 121.0, 114.3, 111.0, 55.3, 36.9, 34.8. 20.7, 20.1, 18.6 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{20}ONa$: 227.1411, found: 227.1428.

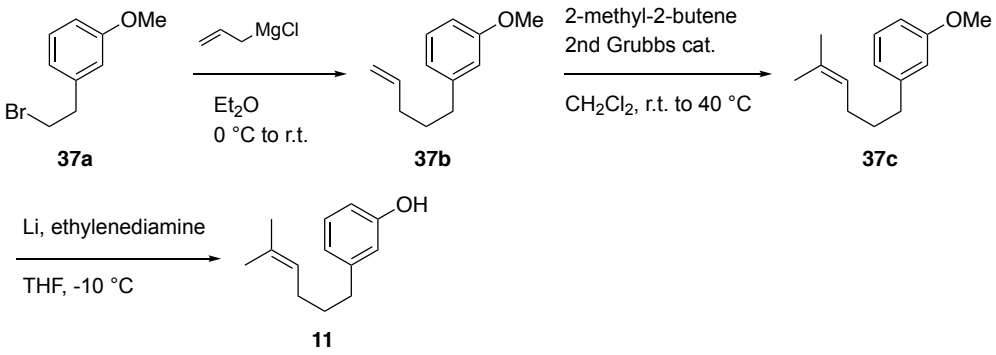
3-(4-Methylpent-3-en-1-yl)phenol (24)



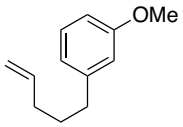
To a solution of methoxybenzene **36c** (605 mg, 3.0 mmol) in dry THF (7.5 mL) was added dry ethylenediamine (1.4 mL, 21.0 mmol) at room temperature under Ar atmosphere. The mixture was cooled to -10 ℃. To the reaction mixture was added lithium shot (103 mg, 14.8 mmol) and the mixture was stirred at -10 °C for 15 h. The reaction was quenched by addition of saturated aq. NH_4Cl (5 mL) at -10 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (98/2-3/1) to afford **24** in 89% yield (502 mg) as a colorless oil.

IR (ATR) : ν 3327, 2984, 2918, 2859, 1588, 1455, 1275, 1154, 939, 782, 764, 750, 693 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.14 (1H, dd, *J* = 7.8, 7.7 Hz), 6.77 (1H, d, *J* = 7.7 Hz), 6.64-6.67 (2H, m), 4.59 (1H, s), 2.58-2.61 (2H, m), 2.28-2.31 (2H, m), 1.68 (3H, dd, *J* = 1.3, 1.0 Hz), 1.65 (3H, m), 1.60 (3H, d, *J* = 1.0 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 144.9, 129.5, 127.0, 125.0, 121.1, 115.4, 112.6, 36.8, 34.6, 20.7, 20.1, 18.6 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{18}ONa$: 213,1255, found: 213.1237.

3.2 Synthesis of phenols 11 and 12



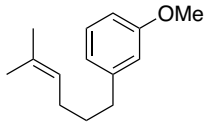
1-Methoxy-3-(pent-4-en-1-yl)benzene (37b)



To a solution of bromide **37a** (4.89 g, 22.8 mmol) in dry Et_2O (93 mL) at 0 °C under Ar atmosphere was added allylmagnesium chloride solution in Et_2O (2.0 M, 17 mL, 34.0 mmol). The reaction was warmed up to 35 °C and stirred for 1 h at 35 °C. The reaction was cooled to 0 °C and quenched by addition of saturated aq. NH_4Cl at 0 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure to afford alkene **37b** in 93% yield (3.73 g) as a colorless oil.

IR (ATR) : ν 3075, 2998, 2933, 2834, 1639, 1584, 1488, 1455, 1259, 1152, 1045, 911, 765, 749, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.18-7.22 (1H, m), 6.73-6.79 (3H, m), 5.80-5.88 (1H, m), 5.01-5.05 (1H, m), 4.97-4.99 (1H, m), 3.80 (3H, s), 2.61 (2H, t, J = 7.8 Hz), 2.08-2.12 (2H, m), 1.70-1.76 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 144.2, 138.7, 129.3, 121.0, 114.8, 114.3, 110.1, 55.2, 35.5, 33.4, 30.6 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{16}ONa$: 199.1098, found: 199.1080.

1-Methoxy-3-(5-methylhex-4-en-1-yl)benzene (37c)

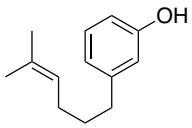


To a solution of alkene **37b** (420 mg, 2.4 mmol) in dry CH_2Cl_2 (12 mL) at room temperature under Ar atmosphere were added 2-methyl-2-butene (5.0 mL, 47.2 mmol) and 2nd Grubbs catalyst (74.6 mg, 0.12 mmol). The reaction was warmed up to 40 °C and stirred at 40 °C for 17 h. The reaction mixture was cooled to room temperature and concentrated under reduced pressure. The residue was purified by silica gel column chromatography with hexane/EtOAc (1/0-19/1) to afford alkene **37c** in 82% yield (400 mg) as a colorless oil.

IR (ATR) : ν 3318, 2984, 2927, 1580, 1502, 1284, 1249, 1012, 778, 748, 702 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.17-7.21 (1H, m), 6.71-6.78 (3H, m), 5.12-5.16 (1H, m), 3.80 (3H, s), 2.59 (2H, t, J = 7.8 Hz), 2.00-2.04 (2H, m), 1.70 (3H, d, J = 1.1 Hz), 1.62-1.69 (2H, m), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz,

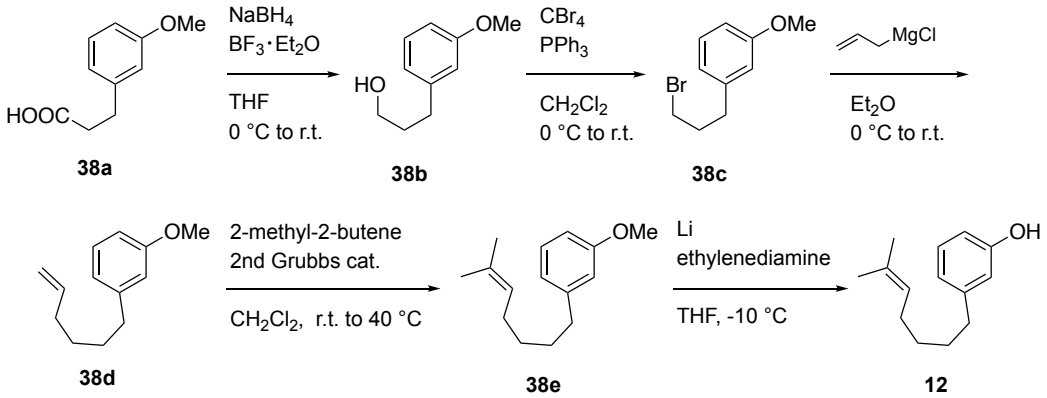
$CDCl_3$): δ 159.7, 144.5, 131.9, 129.3, 124.5, 121.0, 114.3, 111.0, 55.3, 35.7, 31.6, 27.8, 25.9, 17.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{20}ONa$: 227.1411, found: 227.1432.

3-(5-Methylhex-4-en-1-yl)phenol (11)

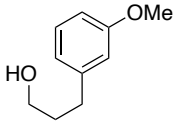


To a solution of alkene **37c** (254 mg, 1.24 mmol) in dry THF (3.1 mL) was added dry ethylenediamine (580 μL, 8.71 mmol) at room temperature under Ar atmosphere. The mixture was cooled to -10 °C. To the reaction mixture was added lithium shot (43.2 mg, 6.22 mmol). The mixture was stirred at -10 °C. The reaction was quenched by addition of saturated aq. NH_4Cl at -10 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-1/1) to afford phenol **11** in 88% yield (208 mg) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.14 (1H, d, J = 7.7, 7.7 Hz), 6.63-6.76 (4H, m), 5.12-5.16 (1H, m), 2.56 (2H, t, J = 7.8 Hz), 1.99-2.03 (2H, m), 1.70 (3H, d, J = 1.1 Hz), 1.61-1.67 (2H, m), 1.59 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.5, 144.9, 132.0, 129.5, 124.4, 121.2, 115.4, 112.6, 35.5, 31.5, 27.7, 25.9, 17.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{18}ONa$: 213.1255, found: 213.1278.



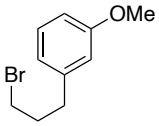
3-(3-Methoxyphenyl)propan-1-ol (38b)



To a solution of carboxylic acid **38a** (2.11g, 11.7 mmol) in dry THF (60 mL) at 0 °C was added sodium borohydride (1.11g, 29.3 mmol) in one portion under Ar atmosphere. The reaction mixture was stirred at 0 °C for 15 min and BF_3·Et_2O (2.2 mL, 16.5 mmol) was added. The reaction mixture was warmed up to room temperature and stirred for 14 h. The reaction was cooled to 0 °C and quenched by addition of 2 M aq. HCl (6 mL) to pH 1-2 and stirred at 0 °C. To the reaction mixture was 2 M aq. NaOH (8 mL) to pH 10 and the reaction mixture was concentrated under reduced pressure. The solution was diluted with brine and the organic materials were extracted with EtOAc three times. The combined organic layers were

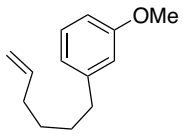
washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure to afford alcohol **38b** as a colorless oil (1.91 g), which was used for the subsequent reaction without further purification.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (1H, ddd, *J* = 7.7, 7.4, 1.0 Hz), 6.80 (1H, d, *J* = 7.7, Hz), 6.73-6.76 (2H, m), 3.80 (1H, s), 3.68 (2H, t, *J* = 6.4 Hz), 2.69 (2H, t, *J* = 7.8 Hz), 1.90 (2H, tt, *J* = 7.8, 6.4 Hz) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[26]

1-(3-Bromopropyl)-3-methoxybenzene (38c)



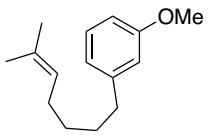
To a solution of crude material **38b** in dry CH_2Cl_2 (27 mL) at 0 °C were added CBr_4 (3.88 g, 11.7 mmol) and PPh_3 (3.07 g, 11.7 mmol) portionwise under Ar atmosphere. The reaction was warmed up to room temperature and stirred for 13 h. The reaction mixture was poured into H_2O (20 mL) and the organic materials were extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (1/0-9/1) to afford bromide **38c** in 80% yield over 2 steps from **38a** (2.14 g) as a colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (1H, ddd, *J* = 7.8, 7.4, 2.0 Hz), 6.75-6.83 (3H, m), 3.80 (1H, s), 3.34 (2H, t, *J* = 6.6 Hz), 2.76 (2H, t, *J* = 7.4 Hz), 2.17 (2H, tt, *J* = 7.4, 6.6 Hz) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[27]

1-(Hex-5-en-1-yl)-3-methoxybenzene (38d)



To a solution of bromide **38c** (921 mg, 4.0 mmol) in dry Et_2O at 0 °C under Ar atmosphere was added allylmagnesium choloride solution in Et_2O (1.0 M, 6.0 mL, 6.0 mmol). The reaction was warmed up to 35 °C and stirred at 35 °C for 17 h. The reaction was cooled to 0 °C and quenched by addition of saturated aq. NH_4Cl (6 mL) at 0 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (1/0-19/1) to afford alkene **38d** in 76% yield (581 mg) as a colorless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.18-7.21 (1H, m), 6.72-6.78 (3H, m), 5.77-5.85 (1H, m), 4.98-5.02 (1H, m), 4.93-4.95 (1H, m), 3.80 (3H, s), 2.59 (2H, t, *J* = 7.7 Hz), 2.06-2.10 (2H, m) 1.61-1.67 (2H, m), 1.41-1.47 (2H, m) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[28]

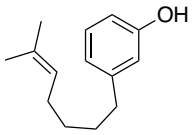
1-Methoxy-3-(6-methylhept-5-en-1-yl)benzene (38e)



To a solution of alkene **38d** (523 mg, 2.75 mmol) in dry CH_2Cl_2 (16 mL) at room temperature under Ar atmosphere were added 2-methyl-2-butene (5.8 mL, 55 mmol) and 2nd Grubbs catalyst (117 mg, 0.14 mmol). The reaction was warmed up to 40 °C and stirred at 40 °C for 13 h. The reaction was cooled to room temperature and the reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (1/0-19/1) to afford tri-substituted alkene **38e** in 94% yield (561 mg) as a colorless oil.

IR (ATR) : ν 2942, 2866, 1462, 1246, 1080, 1048, 996, 883, 779, 677. 653 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.18-7.21 (1H, m), 6.72-6.79 (3H, m), 5.09-5.13 (1H, m), 3.80 (3H, s), 2.59 (2H, t, J = 7.8 Hz), 1.98-2.02 (2H, m), 1.59-1.69 (8H, m), 1.61-1.67 (2H, m), 1.35-1.41 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 144.7, 131.5, 129.3, 124.8, 121.0, 114.4, 111.0, 55.3, 36.1, 31.2, 29.7, 28.0, 25.9, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{15}H_{20}ONa$: 241.1569, found: 241.1550.

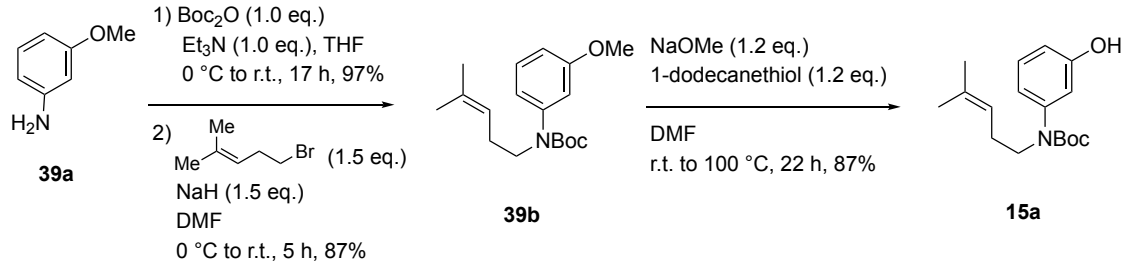
3-(6-Methylhept-5-en-1-yl)phenol (12)



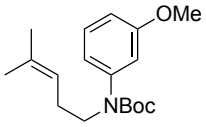
To a solution of alkene **38e** (420 mg, 1.92 mmol) in dry THF (4.8 mL) was added dry ethylenediamine (900 μL, 13.4 mmol) at room temperature under Ar atmosphere. The mixture was cooled to -10 °C. To the reaction mixture was added lithium shot (66.6 mg, 9.6 mmol). The mixture was stirred at -10 °C for 22 h. The reaction was quenched by addition of saturated aq. NH_4Cl (5 mL) at -10 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-1/1) to afford phenol **12** in 77% yield (304 mg) as a colorless oil.

IR (ATR) : ν 3310, 2950, 2849, 1488, 1407, 1230, 1139, 1040, 1008, 946, 880, 792, 653 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$): δ 7.12-7.15 (1H, m), 6.75-6.76 (1H, m), 6.63-6.66 (2H, m), 5.06-5.13 (1H, m), 4.58 (1H, brs), 2.56 (2H, t, J = 7.8 Hz), 1.95-2.04 (2H, m), 1.57-1.70 (8H, m), 1.33-1.40 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 143.6, 132.8, 131.1, 126.5, 118.7, 111.2, 107.9, 33.8, 28.7, 27.0, 25.7, 23.2, 15.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{20}ONa$: : 227.1411, found: 227.1401.

3.3 Synthesis of phenols 15-18

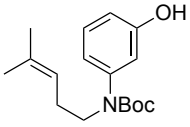


***tert*-Butyl (3-methoxyphenyl)(4-methylpent-3-en-1-yl)carbamate (39b)**



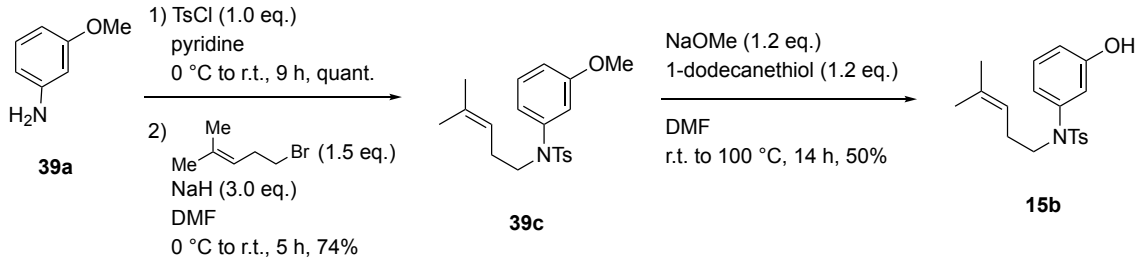
To a solution of amine **39a** (2.44 g, 19.8 mmol) in dry THF (45 mL) were added triethylamine (2.8 mL, 19.8 mmol) and Boc_2O (4.55 mL, 19.8 mmol) at 0 °C under Ar atmosphere. The mixture was warmed up to room temperature and stirred at room temperature for 17 h. The reaction was quenched by addition of H_2O (30 mL) at 0 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (5/1-2/1) to afford carbamate in 97% yield (4.30 g) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.17 (1H, dd, J = 8.2, 8.2 Hz), 7.10 (1H, s), 6.83 (1H, d, J = 7.3 Hz), 6.59 (1H, dd, J = 8.2, 1.7 Hz), 6.45 (1H, s), 3.80 (3H, m), 2.21-2.27 (2H, m), 1.52 (9H, s) ppm.
Its ^{1}H NMR spectrum was identical with that reported previously.[29]
To a solution of carbamate (1.36 g, 6.11 mmol) in dry DMF (30 mL) was added sodium hydride (366 mg, 9.16 mmol) at 0 °C under Ar atmosphere and stirred for 1.5 h. To reaction mixture was added 5-bromo-2-methyl-2-pentene (1.23 mL, 9.17 mmol) at 0 °C. The mixture was warmed up to room temperature and stirred for 5 h. The reaction was quenched by addition of H_2O (30 mL) at 0 °C and the organic materials were extracted with Et_2O three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (30/1-20/1) to afford alkene **39b** in 87% yield (1.56 g) as a colorless oil.
IR (ATR) : ν 3002, 2974, 2929, 2836, 1697, 1602, 1490, 1277, 1159, 1046, 883, 765, 698 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (1H, dd, J = 8.1, 8.1 Hz), 6.74-6.79 (3H, m), 5.04-5.09 (1H, m), 3.80 (3H, m), 3.56-3.60 (2H, m), 2.21-2.27 (2H, m), 1.67 (3H, d, J = 1.0 Hz), 1.58 (3H, s), 1.44 (9H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 154.8, 144.0, 133.9, 129.3, 121.0, 119.7, 113.2, 115.6, 80.1, 55.4, 50.1, 28.5, 27.6, 25.9, 17.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{18}H_{27}NO_3Na$: 328.1888, found: 328.1864.

***tert*-Butyl (3-hydroxyphenyl)(4-methylpent-3-en-1-yl)carbamate (15a)**

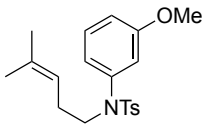


To a solution of alkene **39b** (384 mg, 1.32 mmol) in dry DMF (9 mL) were added 1-dodecanethiol (380 μL, 1.58 mmol) and sodium methoxide (71 mg, 1.58 mmol) at room temperature under Ar atmosphere. The mixture was warmed up to 100 °C and stirred at 100 °C for 22 h. The reaction was quenched by addition of 2 M aq. HCl (3 mL), H_2O (20 mL) and EtOAc (20 mL) at 0 °C and stirred at 0 °C. The organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-1/1) to afford phenol **15a** in 87% yield (334 mg) as a colorless oil.

IR (ATR) : ν 3320, 3006, 2978, 2929, 1661, 1590, 1401, 1276, 1260, 1162, 906, 869, 700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.17 (1H, dd, *J* = 8.3, 7.8 Hz), 6.74 (1H, d, *J* = 7.8 Hz), 6.65-6.68 (2H, m), 5.23 (1H, brs), 5.04-5.07 (1H, m), 3.54-3.58 (2H, m), 2.20-2.26 (2H, m), 1.67 (3H, s), 1.58 (3H, s), 1.45 (9H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 143.8, 134.0, 129.6, 120.8, 119.3, 115.0, 114.7, 113.4, 80.4, 50.1, 28.5, 27.6, 25.9, 17.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{25}NO_3Na$: 314.1732, found: 314.1754.



***N*-(3-Methoxyphenyl)-4-methyl-*N*-(4-methylpent-3-en-1-yl)benzenesulfonamide (39c)**



To a solution of amine **39a** (2.42 g, 19.6 mmol) in dry pyridine (100 mL) was added TsCl (4.11 g, 19.6 mmol) at 0 °C under Ar atmosphere. The mixture was warmed up to room temperature and stirred at room temperature for 9 h. The reaction mixture was concentrated under reduced pressure. The solution was poured into H_2O (30 mL) and the organic materials were extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (5/1-1/1) to afford amide in quantitative yield (5.30 g) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$): δ 7.67 (1H, d, *J* = 8.4 Hz), 7.23 (1H, d, *J* = 8.4 Hz), 7.11 (1H, dd, *J* = 8.2, 8.1 Hz), 6.68 (1H, dd, *J* = 2.2, 2.1 Hz), 6.58-6.65 (3H, m), 3.74 (3H, s), 2.38 (3H, s) ppm.

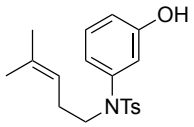
Its ^1H NMR spectrum was identical with that reported previously.[30]

To a solution of amide (1.51 g, 5.46 mmol) in dry DMF (30 mL) was added sodium hydride (328 mg, 8.19 mmol) at 0 °C under Ar atmosphere and stirred for 1.5 h. To reaction mixture was added 5-bromo-2-methyl-2-pentene (1.1 mL, 8.19 mmol) at 0 ℃. The mixture was warmed up to room temperature and stirred for 5 h. The reaction was quenched by addition of H_2O (30 mL) at 0 °C and the organic materials were extracted with Et_2O five times. The combined organic layers were washed with

brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-10/1) to afford alkene **39c** in 74% yield (1.44 g) as a colorless oil.

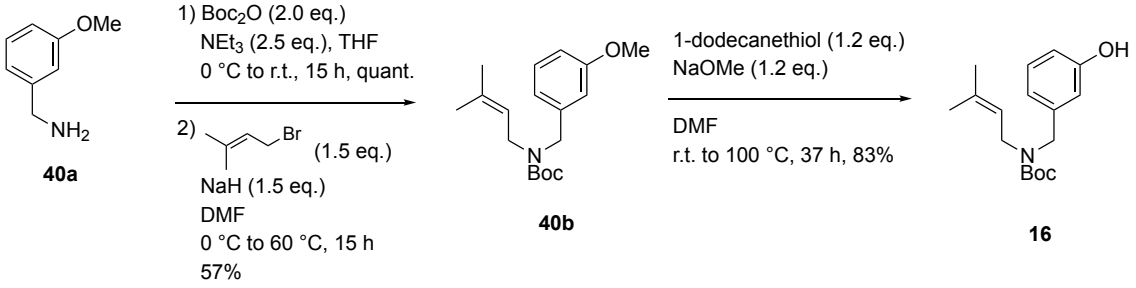
IR (ATR) : ν 3005, 2968, 2919, 2870, 2836, 1600, 1486, 1347, 1277, 1160, 1092, 1041, 941, 815, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (1H, d, *J* = 8.2 Hz), 7.24 (1H, d, *J* = 8.2 Hz), 7.19 (1H, dd, *J* = 8.2, 8.0 Hz), 6.83 (1H, ddd, *J* = 8.2, 2.2, 1.0 Hz), 6.64 (1H, dd, *J* = 2.2, 2.2 Hz), 6.58 (1H, ddd, *J* = 8.0, 2.2, 1.0 Hz), 5.01-5.05 (1H, m), 3.75 (3H, s), 3.45-3.49 (2H, m), 2.42 (3H, s), 2.08-2.14 (2H, m), 1.65 (3H, d, *J* = 1.0 Hz), 1.47 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 143.4, 140.5, 135.6, 134.4, 129.5 (2C), 127.9, 120.8, 120.2, 115.0, 113.9, 55.5, 50.6, 27.5, 25.8, 21.7, 17.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{20}H_{25}NO_3SNa$: 382.1452, found: 382.1461.

***N*-(3-hydroxyphenyl)-4-methyl-*N*-(4-methylpent-3-en-1-yl)benzenesulfonamide (15b)**

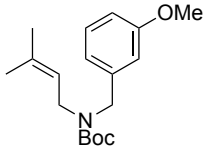


To a solution of alkene **39c** (472 mg, 1.3 mmol) in dry DMF (9 mL) were added 1-dodecanethiol (380 µL, 1.6 mmol) and sodium methoxide (85 mg, 1.6 mmol) at room temperature under Ar atmosphere. The mixture was warmed up to 100 °C and stirred at 100 °C for 14 h. The reaction was quenched by addition of 2 M aq. HCl (3 mL) , H_2O (20 mL) and EtOAc (20 mL) at 0 °C and stirred 0 °C. The organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-3/1) to afford **15b** in 50% yield (225 mg) as a yellow oil.

IR (ATR) : ν 3423, 2973, 2922, 2870, 1594, 1483, 1454, 1335, 1151, 1090, 954, 813, 692, 657, 578, 550 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (1H, d, *J* = 7.8 Hz), 7.24 (1H, d, *J* = 7.8 Hz), 7.14 (1H, dd, *J* = 8.0, 8.0 Hz), 6.77 (1H, ddd, *J* = 7.4, 2.4, 1.6 Hz), 6.62 (1H, dd, *J* = 2.4, 2.2 Hz), 6.55 (1H, ddd, *J* = 7.4, 2.2, 1.6 Hz), 5.01-5.04 (1H, m), 4.99 (1H, s), 3.45-3.48 (2H, m), 2.42 (3H, s), 2.08-2.14 (2H, m), 1.65 (3H, d, *J* = 0.8 Hz), 1.47 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 143.5, 140.5, 135.5, 129.8, 129.5, 127.9, 120.8, 120.7, 120.1, 116.6, 115.1, 50.5, 27.5, 25.8, 21.7, 17.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{19}H_{23}NO_3SNa$: 368.1296, found: 368.1280.



***tert*-Butyl (3-methoxybenzyl)(3-methylbut-2-en-1-yl)carbamate (40b)**



To a solution of amine **40a** (1.38 g, 10.1 mmol) in dry CH_2Cl_2 (30 mL) were added triethylamine (3.5 mL, 25.2 mmol) and Boc_2O (4.65 mL, 20.2 mmol) at 0 °C under Ar atmosphere. The mixture was warmed up to room temperature and stirred at room temperature for 15 h. The reaction was quenched by addition of saturated aq. $NaHCO_3$ solution (15 mL) at 0 °C and the organic materials were extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (98/2-2/1) to afford carbamate in quantitative yield (2.76 g) as a colorless oil.

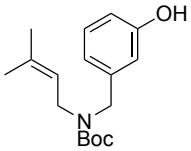
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (1H, dd, *J* = 7.9, 7.9 Hz), 6.86 (1H, d, *J* = 7.9 Hz), 6.79-6.83 (2H, m), 4.82 (1H, brs), 4.29 (1H, d, *J* = 5.6 Hz), 3.80 (3H, s), 1.46 (9H, s) ppm.

Its ^{1}H NMR spectrum was identical with that reported previously.[31]

To a solution of carbamate (1.21 g, 5.1 mmol) in dry DMF (25 mL) was added sodium hydride (306 mg, 7.7 mmol) at 0 °C under Ar atmosphere and stirred for 30 min. To reaction mixture was added prenyl bromide (900 μL, 7.7 mmol) at 0 °C. The mixture was warmed up to 60 °C and stirred at 60 °C for 15 h. The reaction was quenched by addition of H_2O (15 mL) at 0 °C and the organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-3/1) to afford alkene **40b** in 57% yield (891 mg) as a yellow oil.

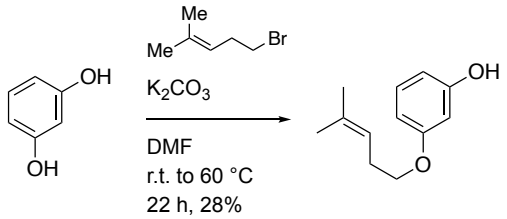
IR (ATR) : ν 3004, 2972, 2925, 2856, 1691, 1601, 1454, 1410, 1364, 1260, 1160, 1112, 1047, 877, 694 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.22 (1H, dd, *J* = 8.4, 7.6 Hz), 6.78-6.80 (3H, m), 5.16 (1H, brs), 4.35 (2H, brs), 3.77-3.82 (5H, m), 1.71 (3H, d, *J* = 0.8 Hz), 1.56 (3H, s), 1.47 (9H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.9, 155.8, 140.4, 135.8, 129.5, 120.6, 119.8, 113.0, 112.7, 79.7, 55.3, 49.4, 43.9, 28.6, 25.9, 18.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{18}H_{27}NO_3Na$: 328.1888, found: 328.1904.

***Tert*-butyl (3-hydroxybenzyl)(3-methylbut-2-en-1-yl)carbamate (16)**



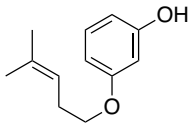
To a solution of alkene **40b** (660 mg, 2.16 mmol) in dry DMF (14 mL) were added 1-dodecanethiol (630 μL, 2.59 mmol) and sodium methoxide (140 mg, 2.59 mmol) at room temperature under Ar atmosphere. The mixture was warmed up to 100 °C and stirred at 100 °C for 37 h. The reaction was quenched by addition of 2 M aq. HCl (4 mL), H_2O (25 mL) and EtOAc (25 mL) at 0 °C and stirred 0 °C. The organic materials were extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (98/2-3/1) to afford phenol **16** in 83% yield (523 mg) as a yellow oil.

IR (ATR) : ν 3325, 2975, 2929, 1656, 1590, 1455, 1417, 1365, 1260, 1158, 1117, 877, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.17 (1H, dd, *J* = 8.2, 7.8 Hz), 6.71-6.78 (3H, m), 5.15 (1H, brs), 4.33 (2H, s), 3.76 (2H, brs), 1.71 (3H, d, *J* = 0.9 Hz), 1.56 (3H, m), 1.47 (9H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 149.0, 132.9, 126.8, 125.6, 123.5, 123.1, 121.1, 117.7, 77.7, 35.9, 29.5, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{25}NO_3Na$: 317.1732, found: 317.1715



41 **17**

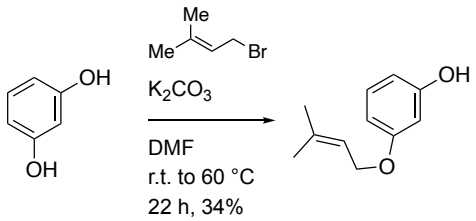
3-((4-Methylpent-3-en-1-yl)oxy)phenol (17)



To a solution of resorcinol **(41)** (640 mg, 5.81 mmol) in dry DMF (29 mL) was added potassium carbonate (2.41 g, 17.4 mmol) at room temperature under Ar atmosphere. The mixture was warmed up to 60 °C and stirred at 60 °C for 30 min. The reaction was cooled to room temperature and 5-bromo-2-methyl-2-pentene (780 μL, 6.97 mmol) was added. The mixture was re-warmed up to 60 °C and stirred at 60 °C for 22 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and poured into H_2O (20 mL) directly and the organic materials were extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-2/1) to afford **17** in 28% yield (312 mg) as a colorless oil.

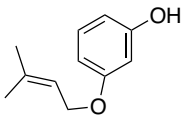
^1H NMR (500 MHz, $CDCl_3$): δ 7.09-7.14 (1H, m), 6.49 (1H, ddd, *J* = 8.2, 2.3, 1.0 Hz), 6.49 (1H, ddd, *J* = 8.2, 2.3, 1.0 Hz), 6.39-6.42 (2H, m), 5.18-5.22 (1H, m), 4.79 (1H, s), 3.90 (1H, t, *J* = 7.0 Hz), 2.44-2.49 (2H, m), 1.73 (3H, d, *J* = 1.0 Hz) 1.66 (3H, s) ppm.

Its ^1H NMR spectrum was identical with that reported previously.[32]



41 **18**

3-((3-Methylbut-2-en-1-yl)oxy)phenol (18)



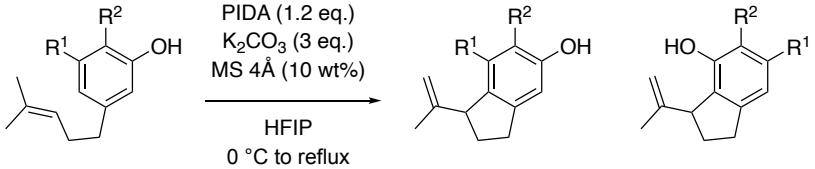
To a solution of resorcinol **(41)** (613 mg, 5.57 mmol) in dry DMF (28 mL) was added potassium carbonate (2.31 g, 16.7 mmol) at room temperature under Ar atmosphere. The mixture was warmed up to 60 °C and stirred at 60 °C for 30 min. The reaction was cooled to room temperature and prenyl bromide (770 μL, 6.68 mmol) was added. The mixture was re-warmed up to 60 °C and stirred at 60 °C for 22 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and poured into H_2O (20 mL) directly and the organic materials were extracted with CH_2Cl_2 three times. The combined organic layers were washed with brine, dried over Na_2SO_4 and filtered through a pad of Celite®. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (20/1-2/1) to afford **18** in 34% yield (338 mg) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.12 (1H, ddd, *J* = 8.4, 8.4, 2.1 Hz), 6.51 (1H, ddd, *J* = 8.4, 2.1, 1.5 Hz), 6.40-6.43 (2H, m), 5.47-5.51 (1H, m), 4.83 (1H, brs), 4.83 (1H, brs), 4.48 (1H, d, *J* = 6.6 Hz), 1.79 (3H, d, *J* = 1.0 Hz), 1.74 (3H, s) ppm.

Its ^{1}H NMR spectrum was identical with that reported previously.[33]

3.4 Cyclization of phenols

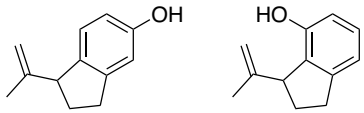
General procedure of cyclization of 7



7 **8x** **8y**

To a solution of **7** (0.30 mmol) in dry HFIP (15 mL) were added potassium carbonate (124 mg, 0.90 mmol) and molecular sieve 4Å (10 wt%) at room temperature under Ar atmosphere. The mixture was cooled to 0 °C and phenyliodine diacetate (PIDA) (116 mg, 0.36 mmol) was added. After stirring at 0 °C for 10 min, the reaction mixture was warmed up to 60 °C and stirred for 3 h. The reaction was quenched by addition of Et_2O (20 mL) and saturated aq. NH_4Cl solution (5 mL) at 0 °C. The organic materials were extracted with Et_2O (20 mL × 2). The combined organic layer was dried over Na_2SO_4, and filtered through a pad of Celite®. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (30/1-1/1) to afford a mixture of **8x** and **8y**. Regioisomers **8x** and **8y** were separated by preparative TLC with hexane/EtOAc (1/1). Regioisomers **x** and **y** of **8**, **13**, **14**, **19**-**22**, **25**, **26** were assigned by ^{1}H-^{1}H coupling constants of aromatic protons in ^{1}H NMR spectra. **8b**-**8g** were determined by nOe between a vinyl proton and MeO or Me groups of **8f**, **8g**, and methyl ether derivatives of **8b**-**e**.

1-(Prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8ax)
3-(Prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8ay)

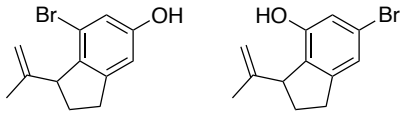


K_2CO_3 (415 mg, 3.0 mmol) was used as a base. **8ax** and **8ay** (1:1) were obtained as a colorless oil in 84% yield (43.2 mg).

8ax: IR (ATR): ν 3378, 2960, 2843, 1598, 1445, 1182, 1036, 980, 802, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.99 (1H, d, *J* = 8.1 Hz), 6.78 (1H, d, *J* = 2.4 Hz), 6.72 (1H, dd, *J* = 8.1, 2.4 Hz), 4.79-4.81 (2H, m), 4.53 (1H, s), 3.77 (1H, t, *J* = 7.9 Hz), 2.91 (1H, ddd, *J* = 16.0, 8.7, 4.0 Hz), 2.83 (1H, ddd, *J* = 16.6, 8.3, 4.7 Hz), 2.27 (1H, dddd, *J* = 16.6, 8.3, 7.6, 4.7 Hz), 1.95 (1H, dddd, *J* = 16.3, 8.7, 7.6, 4.0 Hz), 1.63 (3H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 147.3, 146.5, 137.7, 121.6, 120.4, 115.2, 110.5, 52.6, 32.6, 31.5, 21.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{14}ONa$: 197.0943, found:197.0966.

8ay: IR (ATR): ν 3465, 2944, 2833, 1606, 1590, 1468, 1177, 1028, 946, 794, 691 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.10 (1H, dd, *J* = 8.0, 8.0 Hz), 6.80 (1H, d, *J* = 8.0 Hz), 6.65 (1H, d, *J* = 8.0 Hz), 5.38 (1H, s), 5.07 (1H, dd, *J* = 1.4, 0.7 Hz), 4.97 (1H, dd, *J* = 1.4, 1.4 Hz), 4.00 (1H, t, *J* = 8.0 Hz), 2.99 (1H, ddd, *J* = 15.7, 8.9, 4.3 Hz), 2.90 (1H, ddd, *J* = 15.7, 8.6, 3.8 Hz), 2.30 (1H, dddd, *J* = 16.7, 8.6, 7.8, 4.3 Hz), 1.97 (1H, dddd, *J* = 16.7, 8.9, 7.8, 3.8 Hz), 1.73 (3H, dd, *J* = 1.3, 0.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.7, 148.6, 146.4, 129.0, 116.9, 113.5, 112.9, 51.4, 32.3, 31.0, 19.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{14}ONa$: 197.0943, found: 197.0956.

7-Bromo-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8bx)
6-Bromo-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8by)

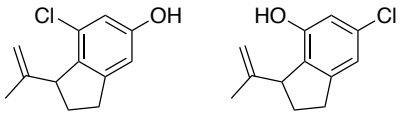


8bx and **8by** (9:2) were obtained as a yellow oil in 65% yield (50.9 mg).

8bx: IR (ATR): ν 3384, 2930, 2361, 1606, 1574, 1444, 1267, 1090, 1043, 824, 770 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.83 (1H, m), 6.65 (1H, m), 4.85 (1H, brs), 4.74-4.75 (1H, m), 4.40-4.41 (1H, m), 3.74-3.76 (1H, m), 2.97-3.04 (1H, m), 2.79-2.85 (1H, m), 2.26-2.34 (1H, m), 1.93-1.99 (1H, m), 1.74 (3H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.5, 147.9, 146.4, 137.5, 120.8, 117.1, 110.8, 110.7, 52.9, 32.6, 31.5, 21.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}{}^{79}BrONa$: 275.0049, found: 275.0022.

8by: IR (ATR): ν 3460, 2967, 2850, 1613, 1478, 1280, 1152, 1009, 965, 790, 692 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 6.95 (1H, s), 6.82 (1H, s), 5.47 (1H, s), 5.05-5.06 (1H, m), 4.97-4.99 (1H, m), 3.93 (1H, t, *J* = 7.9 Hz), 2.94-3.00 (1H, m), 2.84-2.92 (1H, m), 2.27-2.35 (1H, m), 1.92-1.98 (1H, m), 1.72 (3H, dd, *J* = 1.4, 0.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.1, 147.3, 137.2, 131.5, 120.8, 116.8, 110.9, 110.5, 50.8, 31.4, 28.7, 21.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}{}^{79}BrONa$: 275.0049, found: 275.0026.

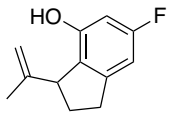
7-Chloro-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8cx)
6-Chloro-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8cy)



8cx and **8cy** (3:1) were obtained as a colorless oil in 62% yield (39.0 mg).
8cx: IR (ATR): ν 3358, 2917, 2376, 1640, 1583, 1259, 1048, 997, 859, 794 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.77 (1H, s), 6.64 (1H, s), 4.70-4.77 (2H, m), 4.70 (1H, s), 3.67 (1H, t, *J* = 7.8 Hz), 2.85-2.92 (1H, m), 2.72-2.80 (1H, m), 2.17-2.23 (1H, m), 1.94-2.00 (1H, m), 1.64 (3H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 148.1, 146.5, 135.4, 131.9, 114.2, 110.5, 110.2, 51.4, 32.8, 31.6, 21.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}ClONa$: 231.0554, found: 231.0535.

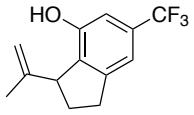
8cy: IR (ATR): ν 3449, 2955, 2919, 2856, 1708, 1649, 1455, 1248, 1166, 990, 812, 701 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.81 (1H, d, *J* = 2.2 Hz), 6.63 (1H, d, *J* = 2.2 Hz), 5.03 (1H, s), 4.66-4.69 (1H, m), 4.32-4.34 (1H, m), 3.71 (1H, t, *J* = 7.8 Hz), 2.93-2.99 (1H, m), 2.75-2.80 (1H, m), 2.19-2.27 (1H, m), 1.87-1.92 (1H, m), 1.67 (3H, dd, *J* = 1.4, 0.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 147.3, 144.8, 135.2, 131.6, 114.2, 110.7, 109.4, 51.2, 31.6, 30.8, 20.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}FONa$: 231.0554, found: 231.0529.

6-Fluoro-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8dy)



8dy was obtained as a yellow oil in 32% yield (18.3mg).
IR (ATR): ν 3269, 2921, 2851, 2356, 1977, 1939, 1291, 1059, 990, 805, 758cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.51 (1H, dd, *J* = 8.6, 2.1 Hz), 6.39 (1H, dd, *J* = 10.5, 2.1 Hz), 5.50 (1H, d, *J* = 8.6, 1.4 Hz), 5.07 (1H, dd, *J* = 1.4, 0.7 Hz), 4.97 (1H, dd, *J* = 1.4, 1.4 Hz), 3.94 (1H, t, *J* = 7.9 Hz), 2.96 (1H, ddd, *J* = 15.7, 8.8, 4.0 Hz), 2.86 (1H, ddd, *J* = 15.7, 7.9, 3.7 Hz), 2.33 (1H, dddd, *J* = 16.7, 8.0, 7.9, 4.0 Hz), 1.98 (1H, dddd, *J* = 16.7, 8.8, 7.6, 3.7 Hz), 1.72 (3H, dd, *J* = 1.4, 0.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.7 (d, *J* = 243.4 Hz), 154.2, 148.4, 147.5 (d, *J* = 10.1 Hz), 124.3, 113.2, 104.0 (d, *J* = 22.6 Hz), 101.3 (d, *J* = 25.7 Hz), 50.8, 32.6 (d, *J* = 2.5 Hz), 31.2, 18.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}FONa$: 215.0848, found: 215.0866.

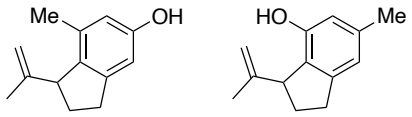
3-(Prop-1-en-2-yl)-6-(trifluoromethyl)-2,3-dihydro-1*H*-inden-4-ol (8ey)



8ey was obtained as a yellow oil in 79% yield (57.3 mg).
IR (ATR) : ν 3412, 2970, 2925, 1708, 1644, 1428, 1354, 1220, 1166, 1043, 998, 890, 695 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.02 (1H, s), 6.84 (1H, s), 5.05 (1H, m), 4.71 (1H, m), 3.97 (1H, t, *J* = 7.9 Hz),

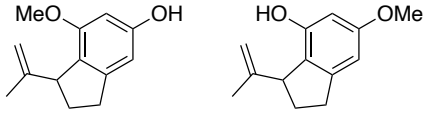
2.92-3.03 (1H, m), 2.74-2.82 (1H, m), 2.18-2.27 (1H, m), 1.83-1.91 (1H, m), 1.68 (3H, dd, *J* = 1.4, 0.6 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.3. (d, *J* = 234.8, Hz), 142.7 (d, *J* = 11.6, Hz), 139.5, 133.3, 124.0, 119.6, 116.8, 114.7 (d, *J* = 18.0 Hz), 53.7, 36.0, 29.2, 17.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{13}F_3ONa$: 265.0817, found: 265.0840.

7-Methyl-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8fx)
6-Methyl-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8fy)



8fx and **8fy** (2:1) were obtained as a yellow oil in 64% yield (36.2 mg).
8fx: IR (ATR) : ν 3437, 2925, 2908, 1716, 1667, 1410, 1218, 1190, 1031, 986, 895, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.53 (1H, d, *J* = 1.7 Hz), 6.44 (1H, d, *J* = 1.7 Hz), 4.57 (1H, brs), 4.67-4.69 (1H, m), 4.47-4.48 (1H, m), 3.73 (1H, m), 2.89-2.96 (1H, m), 2.73-2.83 (1H, m), 2.24-2.32 (1H, m), 2.13 (3H, s), 1.90-1.96 (1H, m), 1.66 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8, 147.6, 146.1, 136.1, 135.9, 114.5, 110.1, 108.5, 51.0, 31.7, 29.7, 20.4, 18.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$: 211.1099, found: 211.1127.
8fy: IR (ATR) : ν 3490, 2967, 2905, 2217, 1740, 1687, 1436, 1220, 1203, 1018, 970, 896, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.63 (1H, s), 6.48 (1H, s), 5.29 (1H, s), 5.06 (1H, dd, *J* = 1.4, 0.7 Hz), 4.95 (1H, dd, *J* = 1.4, 1.4 Hz), 3.95 (1H, t, *J* = 7.8 Hz), 2.91-2.97 (1H, m), 2.81-2.89 (1H, m), 2.26-2.33 (5H, m), 1.92-1.99 (1H, m), 1.72 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.2, 148.9, 146.3, 139.0, 125.8, 117.8, 114.1, 112.6, 51.0, 32.1, 31.1, 21.2, 18.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$: 211.1099, found: 211.1115.

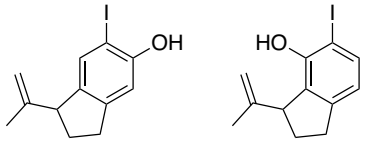
7-Methoxy-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8gx)
6-Methoxy-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8gy)



8gx and **8gy** (1:1) were obtained as a colorless oil in 49% yield (30.1 mg).
8gx: IR (ATR): ν 3410, 2978, 2860, 1707, 1594, 1501, 1470, 1250, 1026, 935, 800, 742, 698 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.30 (1H, d, *J* = 2.0 Hz), 6.22 (1H, d, *J* = 2.0 Hz), 4.56-4.77 (2H, m), 4.49-4.50 (1H, m), 3.81 (1H, m), 3.75 (3H, s), 2.87-2.94 (1H, m), 2.70-2.76 (1H, m), 2.21-2.29 (1H, m), 1.89-1.95 (1H, m), 1.70 (3H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.1, 148.1, 147.7, 134.4, 134.0, 109.2, 103.3, 97.0, 55.5, 49.5, 32.1, 29.9, 22.8, 20.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}O_2Na$: 227.2547, found: 227.2523.
8gy: IR (ATR): ν 3492, 2942, 2871, 2841, 1621, 1607, 1592, 1488, 1466, 1455, 1440, 1337, 1273, 1194, 1143, 1040, 938, 793, 742, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.39 (1H, d, *J* = 2.2 Hz), 6.25 (1H, d, *J* = 2.2 Hz), 5.37 (1H, s), 5.06 (1H, dd, *J* = 1.4, 0.7 Hz), 4.95 (1H, dd, *J* = 1.4, 1.4 Hz), 3.93 (1H, t, *J* = 7.9 Hz), 3.76 (3H, s), 2.94 (1H, ddd, *J* = 15.7, 9.2, 4.3 Hz), 2.85 (1H, ddd, *J* = 15.7, 8.6, 3.8 Hz), 2.30 (1H, dddd, *J* = 16.6, 8.7, 8.6, 4.3 Hz), 1.96 (1H, dddd, *J* = 16.6, 9.1, 8.7, 3.8 Hz), 1.72 (3H, dd, *J* = 1.4, 0.7 Hz)

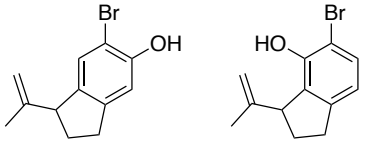
ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0, 153.9, 148.8, 147.1, 121.0, 112.6, 102.7, 99.5, 55.4, 50.7, 33.2, 32.5, 18.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}O_2Na$: 227.2547, found: 227.2550.

6-Iodo-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8hx)
5-Iodo-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8hy)



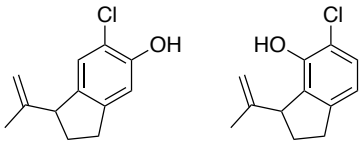
8hx and **8hy** (1:2) were obtained as a yellow oil in 60% yield (53.8 mg).
8hx: IR (ATR): ν 3475, 2956, 2888, 2854, 1720, 1571, 1426, 1298, 1190, 1026, 959, 844, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (1H, s), 6.71 (1H, s), 4.77-4.82 (2H, m), 3.78 (1H, t, *J* = 7.9 Hz), 2.92-3.01 (1H, m), 2.74-2.81 (1H, m), 2.19-2.27 (1H, m), 1.83-1.91 (1H, m), 1.65 (3H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2, 149.4, 140.2, 136.0, 112.5, 111.8, 82.5, 52.1, 32.8, 30.4, 18.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}IONa$: 322.9909, found: 322.9920.
8hy: IR (ATR): ν 3469 2955, 2922, 2852, 1713, 1463, 1194, 1018, 793, 751 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70 (1H, d, *J* = 8.0 Hz), 6.79 (1H, d, *J* = 8.0 Hz), 5.01-5.22 (2H, m), 4.67-4.68 (1H, m), 4.02 (1H, t, *J* = 7.7 Hz), 2.91-2.98 (1H, m), 2.73-2.80 (1H, m), 2.20-2.28 (1H, m), 1.87-1.92 (1H, m), 1.67 (3H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 148.8, 135.2, 130.6, 121.2, 116.0, 113.8, 109.5, 81.2, 54.8, 29.9, 26.7, 20.5 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}IONa$: 322.9909, found: 322.9898.

6-Bromo-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8ix)
5-Bromo-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8iy)



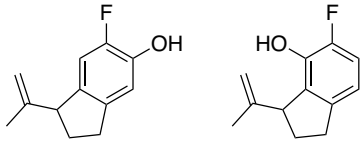
8ix and **8iy** (3:2) were obtained as a yellow oil in 40% yield (30.4 mg).
8ix: IR (ATR) : ν 3490, 2966, 2820, 1720, 1508, 1484, 1283, 1014, 898, 775, 694 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.72 (1H, s), 6.64 (1H, s), 4.78 (1H, s), 4.66-4.73 (1H, m), 4.45-4.47 (1H, m), 3.82 (1H, t, *J* = 7.9 Hz), 2.92-3.01 (1H, m), 2.72-2.80 (1H, m), 2.19-2.26 (1H, m), 1.89-1.97 (1H, m), 1.63 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.4, 147.2, 145.8, 134.8, 130.6, 112.6, 111.9, 109.0, 51.2, 33.4, 30.8, 20.5 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}{}^{79}BrONa$: 275.0049, found: 275.0060.
8iy: IR (ATR): ν 3210, 2955, 2922, 2852, 2359, 2342, 2308, 1463, 1289, 1198, 792, 752, 668 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29 (1H, d, *J* = 8.0 Hz), 6.79 (1H, d, *J* = 8.0 Hz), 5.72 (1H, s), 4.88 (1H, m), 4.84 (1H, m), 4.00 (1H, dd, *J* = 8.7, 5.8 Hz), 2.92-2.98 (1H, m), 2.79-2.85 (1H, m), 2.28-2.35 (1H, m), 1.97-2.03 (1H, m), 1.73 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 149.5, 147.7, 146.4, 131.4, 128.4, 118.0, 111.9, 111.9, 51.4, 32.0, 31.7, 19.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}{}^{79}BrONa$: 275.0049, found: 275.0067.

6-Chloro-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8jx)
5-Chloro-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8jy)



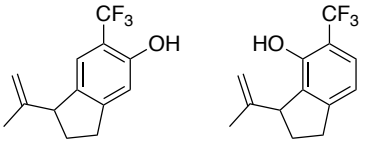
8jx and **8jy** (2:1) were obtained as a yellow oil in 45% yield (28.0 mg).
8jx: IR (ATR): ν 3320, 2956, 2840, 1640, 1522, 1218, 996, 802, 690 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.92 (1H, d, *J* = 2.2 Hz), 6.82 (1H, d, *J* = 2.2 Hz), 5.40 (1H, s), 4.78-4.83 (2H, m), 3.90 (1H, t, *J* = 7.8 Hz), 2.93-2.98 (1H, m), 2.83-2.90 (1H, m), 2.25-2.34 (1H, m), 1.96-2.02 (1H, m), 1.64 (3H, d, *J* = 1.4, 0.8 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.5, 140.7, 132.8, 127.5, 123.3, 122.1, 120.1, 113.7, 51.2, 28.3, 25.8, 17.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}ClONa$: 231.0554, found: 231.0528.
8jy: IR (ATR): ν 3172, 2922, 2852, 1979, 1463, 1198, 1027, 793, 751cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.15 (1H, d, *J* = 8.0 Hz), 6.74 (1H, d, *J* = 8.0 Hz), 5.67 (1H, s), 4.87 (1H, m), 4.82 (1H, m), 3.99 (1H, dd, *J* = 8.8, 5.5 Hz), 2.93-2.99 (1H, m), 2.80-2.86 (1H, m), 2.29-2.36 (1H, m), 1.97-2.04 (1H, m), 1.74 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.6, 147.6, 145.6, 131.3, 128.4, 117.8, 117.3, 111.8, 51.2, 32.0, 31.8, 19.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}ClONa$: 231.0554, found: 231.0541

6-Fluoro-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8kx)
5-Fluoro-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8ky)



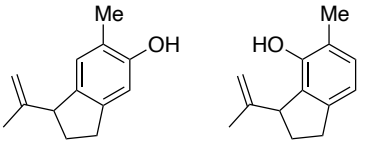
8kx and **8ky** (1:1) were obtained as a yellow oil in 24% yield (13.7 mg).
8kx: IR (ATR): ν 3460, 2960, 2829, 1920, 1517, 1228, 1009, 799, 698 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.37 (1H, dd, *J* = 8.6, 2.0 Hz), 6.26 (1H, dd, *J* = 10.5, 2.0 Hz), 5.38 (1H, m), 4.93-4.94 (1H, m), 4.83-4.85 (1H, m), 3.80 (1H, t, *J* = 7.8 Hz), 2.79-2.86 (1H, m), 2.69-2.76 (1H, m), 2.17-2.24 (1H, m), 1.81-1.92 (1H, m), 1.58 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 150.2 (d, *J* = 243.0 Hz), 144.8, 133.2, 128.7, 124.6, 123.5, 121.7, 114.8 (d, *J* = 22.6 Hz), 52.2, 28.9, 26.4, 17.6 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}FONa$: 215.0848, found: 215.0833.
8ky: IR (ATR): ν 3520, 2987, 2805, 1832, 1529, 1225, 980, 802, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.95 (1H, dd, *J* = 10.5, 8.6 Hz), 6.76 (1H, dd, *J* = 8.6, 2.1 Hz), 5.53 (1H, s), 5.21-5.29 (1H, m), 5.14-5.19 (1H, m), 4.15 (1H, t, *J* = 7.8 Hz), 3.12-3.22 (1H, m), 3.03-3.10 (1H, m), 2.47-2.53 (1H, m), 2.12-2.19 (1H, m), 1.87 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.7 (d, *J* = 243.2 Hz), 143.2, 139.5, 132.5, 123.5, 120.7, 117.2, 115.1, 51.2, 30.1, 25.8, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{13}FONa$: 215.0848, found: 215.0836.

1-(Prop-1-en-2-yl)-6-(trifluoromethyl)-2,3-dihydro-1*H*-inden-5-ol (8lx)
3-(Prop-1-en-2-yl)-5-(trifluoromethyl)-2,3-dihydro-1*H*-inden-4-ol (8ly)



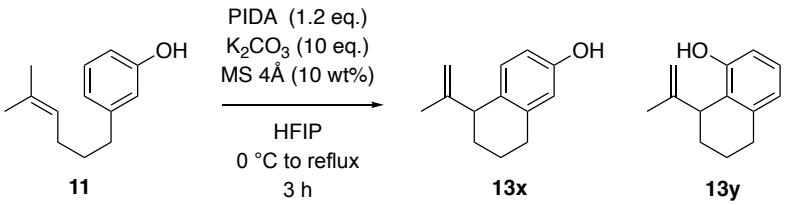
8lx and **8ly** (1:1) were obtained as a yellow oil in 64% yield (46.5 mg).
8lx: IR (ATR): ν 3612, 2980, 2774, 2018, 1956, 1610, 1217, 1002, 860, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.46 (1H, s), 6.64 (1H, s), 5.52 (1H, s), 5.42-5.43 (1H, m), 5.07-5.10 (1H, m), 3.77 (1H, t, *J* = 7.8 Hz), 2.97-3.05 (1H, m), 2.76-2.85 (1H, m), 2.25-2.33 (1H, m), 1.93-1.99 (1H, m), 1.73 (3H, dd, *J* = 1.3, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 145.4, 133.3. 131.7, 125.2 (q, *J* = 234.8, Hz), 121.4, 117.5, 106.5, 48.8, 29.6, 25.4, 17.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{13}F_3ONa$: 265.0817, found: 265.0806.
8ly: IR (ATR): ν 3151, 2977, 2936, 2818, 2289, 1643, 1287, 1202, 1084, 917, 870 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.87 (1H, s), 6.70 (1H, s), 4.71-4.73 (1H, m), 4.51-4.52 (1H, m), 3.91 (1H, m), 2.97-3.03 (1H, m), 2.82-2.86 (1H, m), 2.25-2.32 (1H, m), 1.95-2.01 (1H, m), 1.74 (3H, dd, *J* = 1.4, 0.6 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.2, 147.5, 133.8, 131.4, 124.7 (q, *J* = 243.2 Hz), 118.8, 108.5, 54.2, 29.6, 26.0, 18.2 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{13}F_3ONa$: 265.0817, found: 265.0823.

6-Methyl-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (8mx)
5-Methyl-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (8my)



8mx and **8my** (1:1) were obtained as a yellow oil in 45% yield (25.5 mg).
8mx: IR (ATR): ν 3229, 2970, 2886, 2267, 1659, 1226, 1188, 1015, 989, 821, 699 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.84 (1H, s), 6.65 (1H, s), 4.80-4.81 (2H, m), 4.50 (1H, s), 3.76 (1H, t, *J* = 7.8 Hz), 2.85-2.90 (1H, m), 2.76-2.82 (1H, m), 2.21-2.27 (1H, m), 2.21 (3H, s), 1.89-1.97 (1H, m), 1.72 (3H, dd, *J* = 1.2, 0.9 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.8, 148.0, 143.5, 137.5, 126.6, 121.5, 111.3, 110.9, 52.8, 31.7, 30.1, 19.2, 16.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$: 211.1099, found: 211.1120.
8my: IR (ATR): ν 3378, 2964, 2880, 2117, 1654, 1238, 1180, 986, 805, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.96 (1H, d, *J* = 7.6 Hz), 6.70 (1H, t, *J* = 7.8 Hz), 5.46 (1H, s), 5.09 (1H, dd, *J* = 1.4, 0.7 Hz), 4.97 (1H, dd, *J* = 1.4, 1.4 Hz), 3.99 (1H, t, *J* = 8.0 Hz), 2.92-2.98 (1H, m), 2.82-2.88 (1H, m), 2.28-2.34 (1H, m), 2.19 (3H, s), 1.94-2.02 (1H, m), 1.72 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 147.2, 145.9, 129.2, 128.7, 126.9, 116.5, 113.4, 52.8, 32.4, 31.6, 30.7, 23.1 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$: 211.1099, found: 211.1083.

Cyclization of 11, 12, 23, 24



11 **13x** **13y**

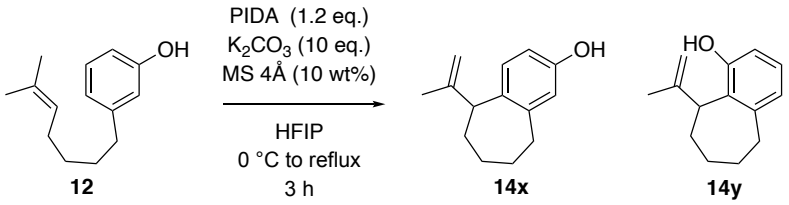
To a solution of **11** (57.2 mg, 0.30 mmol) in dry HFIP (15 mL) was added potassium carbonate (416 mg, 0.90 mmol) and molecular sieve 4A (6 mg, 10 wt%) at room temperature under Ar atmosphere. The mixture was cooled to 0 °C. To the reaction mixture was added phenyliodine diacetate (PIDA) (116 mg, 0.36 mmol) at 0 ℃. The mixture was stirred at 0 °C for 10 min. The reaction mixture was warmed up to 60 °C and stirred for 3 h. The reaction was quenched by addition of Et_2O (20 mL) and saturated aq. NH_4Cl solution (5 mL) at 0 °C. The organic materials were extracted with Et_2O (20 mL × 2). The combined organic layer was dried over Na_2SO_4, and filtered through a pad of Celite®. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (30/1-1/1) to afford mixture of **13x** and **13y** (2:1) in 60 % yield (33.6 mg) as a colorless oil. Regioisomers **13x** and **13y** were separated by preparative TLC with hexane/EtOAc. (1/1).

8-(Prop-1-en-2-yl)-5,6,7,8-tetrahydronaphthalen-1-ol (13x)

IR (ATR): ν 3420, 2998, 2850, 2218, 1678, 1245, 996, 810, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.97 (1H, d, *J* = 8.4 Hz), 6.60 (1H, dd, *J* = 8.4, 2.7 Hz), 6.54 (1H, d, *J* = 2.7 Hz), 4.87-4.90 (1H, m), 4.66-4.67 (1H, m), 4.57 (1H, brs), 3.46 (1H, m), 2.67-2.74 (2H, m), 1.83-1.90 (2H, m), 1.65-1.77 (2H, m) 1.62 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.5, 149.4, 139.1, 130.6, 130.4, 115.1, 113.5, 113.1, 47.0, 30.1, 28.7, 21.4, 19.6 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$: 211.1099, found: 211.1104.

5-(Prop-1-en-2-yl)-5,6,7,8-tetrahydronaphthalen-2-ol (13y)

IR (ATR): ν 3518, 2916, 2821, 2336, 2219, 1648, 1331, 1078, 925, 786, 701 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$): δ 6.96 (1H, d, *J* = 8.2 Hz), 6.61 (1H, dd, *J* = 8.2, 8.0 Hz), 6.54 (1H, d, *J* = 8.0 Hz), 4.85-4.88 (1H, m), 4.64-4.68 (1H, m), 4.60 (1H, s), 3.44 (1H, t, *J* = 7.9 Hz), 2.61-2.78 (2H, m), 1.82-1.91 (2H, m), 1.63-1.77 (2H, m) 1.63 (3H, dd, *J* = 1.3, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.8, 159.0, 127.8, 120.5, 119.5, 112.8, 109.4, 104.2, 54.8, 36.9, 24.8, 21.7, 18.2 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$: 211.1099, found: 211.1127.



12 **14x** **14y**

To a solution of **12** (61.6 mg, 0.30 mmol) in dry HFIP (15 mL) were added potassium carbonate (418 mg, 3.0 mmol) and molecular sieve 4A (6 mg, 10 wt%) at room temperature under Ar atmosphere. The mixture was cooled to 0 °C. To the reaction mixture was added phenyliodine diacetate (PIDA) (117 mg, 0.36 mmol) at 0 ℃. The mixture was stirred at 0 °C for 10 min. The reaction mixture was warmed up to

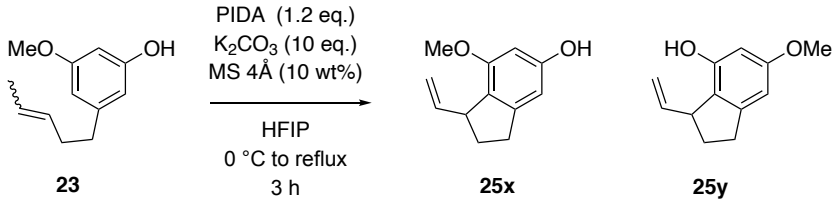
60 °C and stirred for 3 h. The reaction was quenched by addition of Et_2O (20 mL) and saturated aq. NH_4Cl solution (5 mL) at 0 °C. The organic materials were extracted with Et_2O (20 mL × 2). The combined organic layer was dried over Na_2SO_4, and filtered through a pad of Celite®. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (30/1-1/1) to afford mixture of **14x** and **14y** (5:2) in 79 % yield (48.0 mg) as a yellow oil. Regioisomers **14x** and **14y** were separated by preparative TLC with hexane/EtOAc. (1/1)

5-(Prop-1-en-2-yl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-2-ol (14x)

IR (ATR) : ν 3318, 2980, 2873, 1578, 1437, 1328, 1024, 970, 692 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.31 (1H, d, *J* = 8.4 Hz), 6.70 (1H, dd, *J* = 8.4, 2.6 Hz), 6.65 (1H, dd, *J* = 2.6 Hz), 5.06-5.08 (1H, m), 4.66-4.68 (1H, m), 3.62 (1H, t, *J* = 7.9 Hz), 2.73-2.85 (2H, m), 1.97-2.10 (2H, m), 1.82-1.89 (1H, m), 1.81 (3H, dd, *J* = 1.4, 0.7 Hz), 1.62-1.76 (3H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.1, 154.1, 149.0, 147.3, 121.2, 112.8, 102.8, 99.7, 55.6, 50.8, 32.6, 31.3, 27.2, 18.9 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{18}ONa$: 225.1255, found: 226.1277.

9-(Prop-1-en-2-yl)-6,7,8,9-tetrahydro-5*H*-benzo[7]annulen-1-ol (14y)

IR (ATR) : ν 3470, 2922, 2816, 1548, 1446, 1338, 1151, 1090, 820, 689 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$): δ 7.18 (1H, dd, *J* = 8.0, 8.0 Hz), 6.87 (1H, d, *J* = 8.0 Hz), 6.70 (1H, d, *J* = 8.0 Hz), 4.70-4.72 (1H, m), 4.50-4.51 (1H, m), 3.87-3.93 (1H, m), 2.85-2.98 (2H, m), 2.09-2.22 (2H, m), 1.92-2.02 (5H, m), 1.78-1.88 (2H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 148.3, 146.1, 135.6, 125.2, 115.0, 112.9, 110.7, 49.3, 43.7, 33.8, 31.5, 23.7, 17.8 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{14}H_{18}ONa$: 225.1255, found: 226.1238.



23 **25x** **25y**

To a solution of **23** (57.2 mg, 0.30 mmol) in dry HFIP (15 mL) were added potassium carbonate (415 mg, 3.0 mmol) and molecular sieve 4A (6 mg, 10 wt%) at room temperature under Ar atmosphere. The mixture was cooled to 0 °C. To the reaction mixture was added phenyliodine diacetate (PIDA) (115 mg, 0.36 mmol) at 0 ℃. The mixture was stirred at 0 °C for 10 min. The reaction mixture was warmed up to 60 °C and stirred for 3 h. The reaction was quenched by addition of Et_2O (20 mL) and saturated aq. NH_4Cl solution (5 mL) at 0 °C. The organic materials were extracted with Et_2O (20 mL × 2). The combined organic layer was dried over Na_2SO_4, and filtered through a pad of Celite®. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (30/1-1/1) to afford mixture of **25x** and **25y** (2:1) in 35 % yield (19.4 mg) as a yellow oil. Regioisomers **25x** and **25y** were separated by preparative TLC with hexane/EtOAc. (1/1).

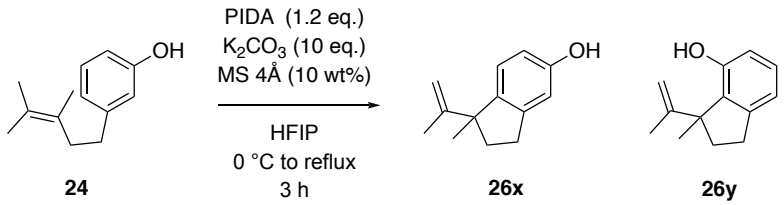
1-Vinyl-2,3-dihydro-1*H*-inden-5-ol (25x)

IR (ATR) : ν 3410, 2967, 2856, 1610, 1228, 1004, 810, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.34 (1H, d, *J* = 2.2 Hz), 6.26 (1H, d, *J* = 2.2 Hz), 5.80-5.88 (1H, m), 5.04-5.11 (1H, m), 4.95-5.01 (1H, m), 3.94 (1H, t, *J* = 7.8 Hz), 3.76 (3H, s), 2.91-2.98 (1H, m), 2.77-2.84 (1H, m), 2.23-2.32 (1H, m), 1.88-1.97

(1H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 151.2, 145.8, 144.1, 121.2, 114.7, 103.6, 100.5, 56.9, 43.8, 42.4, 27.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{14}O_2Na$: 213.0892, found: 213.0884.

3-Vinyl-2,3-dihydro-1*H*-inden-4-ol (25y)

IR (ATR) : ν 3519, 2980, 2847, 1619, 1554, 1226, 1015, 885, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.52 (1H, d, *J* = 2.1 Hz), 6.39 (1H, d, *J* = 2.1 Hz), 5.77-5.85 (1H, m), 5.51 (1H, s), 5.01-5.08 (1H, m), 4.94-5.00 (1H, m), 4.07 (1H, t, *J* = 7.9 Hz), 3.77 (3H, s), 2.95-3.08 (2H, m), 2.41-2.47 (1H, m), 2.05-2.13 (1H, m) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.4, 147.8, 146.2, 137.4, 120.7, 117.0, 110.7, 110.5, 52.7, 40.8, 38.5, 28.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{14}O_2Na$: 213.0892, found: 213.0866.



To a solution of **24** (57.2 mg, 0.30 mmol) in dry HFIP (15 mL) were added potassium carbonate (417 mg, 3.0 mmol) and molecular sieve 4A (6 mg, 10 wt%) at room temperature under Ar atmosphere. The mixture was cooled to 0 °C. To the reaction mixture was added phenyliodine diacetate (PIDA) (117 mg, 0.36 mmol) at 0 ℃. The mixture was stirred at 0 °C for 10 min. The reaction mixture was warmed up to 60 °C and stirred for 3 h. The reaction was quenched by addition of Et_2O (20 mL) and saturated aqueous NH_4Cl solution (5 mL) at 0 °C. The organic materials were extracted with Et_2O (20 mL × 2). The combined organic layer was dried over Na_2SO_4, and filtered through a pad of Celite®. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (30/1-1/1) to afford mixture of **26x** and **26y** (1:1) in 14 % yield (7.9 mg) as colorless oil. Regioisomers **26x** and **26y** were separated by preparative TLC with hexane/EtOAc. (1/1).

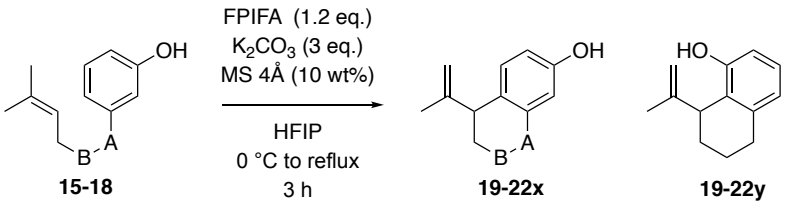
1-Methyl-1-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-5-ol (26x)

IR (ATR) : ν 3386, 2915, 1573, 1440, 1218, 1053, 932, 712 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.89 (1H, d, *J* = 8.1 Hz), 6.67 (1H, d, *J* = 2.1 Hz), 6.64 (1H, dd, *J* = 8.1, 2.1 Hz), 4.76-4.77 (1H, m), 4.57-4.61 (2H, m), 2.82-2.84 (2H, m), 2.24-2.29 (1H, m), 1.81-1.87 (1H, m), 1.68 (3H, d, *J* = 0.7 Hz), 1.37 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.0, 154.6, 151.0, 145.4, 124.5, 113.4, 111.4, 110.2, 52.6, 39.2, 30.6, 26.3, 20.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$: 211.1099, found: 211.1090.

3-Methyl-3-(prop-1-en-2-yl)-2,3-dihydro-1*H*-inden-4-ol (26y)

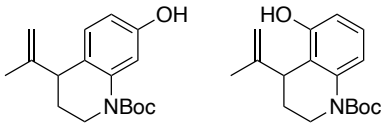
IR (ATR) : ν 3418, 2943, 1656, 1501, 1229, 1053, 990, 801 cm^{-1}.^{1}H NMR (500 MHz, $CDCl_3$): δ 7.07 (1H, dd, *J* = 8.0, 8.0 Hz), 6.73 (1H, dd, *J* = 8.0, 2.2 Hz), 6.60 (1H, dd, *J* = 8.0, 2.2 Hz), 4.65-4.66 (1H, m), 4.46-4.47 (1H, m), 2.77-2.80 (2H, m), 2.08-2.13 (1H, m), 1.71-1.77 (1H, m), 1.63 (3H, d, m), 1.43 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9, 150.7, 145.9, 136.7, 128.3, 125.7, 117.2, 108.9, 53.5, 40.1, 31.1, 24.6, 20.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{13}H_{16}ONa$: 211.1099, found: 211.1076.

Cyclization of 15-18



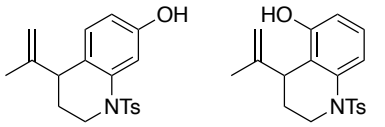
To a solution of **15-18** (0.30 mmol) in dry HFIP (15 mL) were added potassium carbonate (125 mg, 0.90 mmol) and molecular sieve 4A (10 wt%) at room temperature under Ar atmosphere. The mixture was cooled to 0 °C. To the reaction mixture was added pentafluorophenyliodine ditrifluoroacetate (FPIFA) (187 mg, 0.36 mmol) at 0 ℃. The mixture was stirred at 0 °C for 10 min. The reaction mixture was warmed up to 60 °C and stirred for 3 h. The reaction was quenched by addition of Et_2O (20 mL) and saturated aq. NH_4Cl solution (5 mL) at 0 °C. The organic materials were extracted with Et_2O (20 mL × 2). The combined organic layer was dried over Na_2SO_4, and filtered through a pad of Celite®. The reaction mixture was concentrated under reduced pressure and the residue was purified by silica gel column chromatography with hexane/EtOAc (30/1-1/1) to afford mixture of **19-22x** and **19-22y**. Regioisomers **19-22x** and **19-22y** were separated by preparative TLC with hexane/EtOAc. (1/1).

***Tert*-butyl 7-hydroxy-4-(prop-1-en-2-yl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (19ax)**
***Tert*-butyl 5-hydroxy-4-(prop-1-en-2-yl)-3,4-dihydroquinoline-1(2*H*)-carboxylate (19ay)**



19ax and **19ay** (3:1) were obtained as a yellow oil in 41% yield (35.5 mg).
19ax: IR (ATR) : ν 3228, 2970, 2848, 1701, 1648, 1435, 1328, 1260, 1047, 910, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.81 (1H, d, *J* = 8.0 Hz), 6.33 (1H, dd, *J* = 8.0, 2.2 Hz), 6.08 (1H, d, *J* = 2.2 Hz), 5.25-5.26 (1H, m), 5.02-5.04 (1H, m), 4.18-4.23 (1H, m), 4.12 (1H, t, *J* = 7.8 Hz), 3.44-3.49 (1H, m), 2.12-2.18 (1H, m), 1.77-1.81 (1H, m), 1.58 (3H, dd, *J* = 1.4, 0.7 Hz), 1.53 (9H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 146.8, 142.1, 140.8, 135.3, 130.7, 123.7, 120.5, 116.6, 80.2, 50.1, 41.4, 26.7, 20.8, 17.0 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{23}NO_3Na$: 312.1576, found: 312.1592.
19ay: IR (ATR) : ν 3306, 2995, 2816, 1716, 1640, 1398, 1041, 996, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.17 (1H, dd, *J* = 8.0, 8.0 Hz), 6.65 (1H, dd, *J* = 8.0, 2.2 Hz), 6.62 (1H, dd, *J* = 8.0, 2.2 Hz), 4.81-4.82 (2H, m), 4.04 (1H, brs), 3.95-4.00 (1H, m), 3.72 (1H, t, *J* = 7.8 Hz), 3.42-3.47 (1H, m), 1.93-2.01 (2H, m), 1.61 (3H, dd, *J* = 1.4, 0.7 Hz), 1.50 (9H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.2, 152.7, 142.8, 139.5, 138.8, 129.7, 126.2, 121.5, 115.5, 109.9, 81.2, 54.9, 42.7, 28.8, 22.9, 20.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{23}NO_3Na$: 312.1576, found: 312.1555.

4-(Prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-7-ol (19bx)
4-(Prop-1-en-2-yl)-1-tosyl-1,2,3,4-tetrahydroquinolin-5-ol (19by)

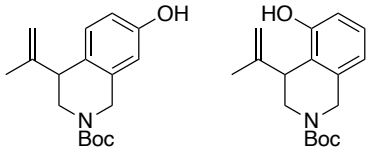


19bx and **19by** (5:2) were obtained as a yellow oil in 28% yield (29.0 mg).

19bx: IR (ATR) : ν 3423, 2956, 2908, 2817, 1601, 1467, 1332, 1148, 1025, 990, 810, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.32-7.37 (3H, m), 7.05 (2H, m), 7.12-7.16 (3H, m), 6.99 (1H, d, *J* = 8.0 Hz), 6.75 (1H, dd, *J* = 8.0, 2.2 Hz), 5.15-5.17 (1H, m), 4.82-4.85 (1H, m), 4.17-4.22 (1H, m), 3.70-3.77 (1H, m), 3.46 (1H, t, *J* = 7.9 Hz), 2.48 (3H, s), 1.82-1.91 (2H, m), 1.63 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.7, 143.8, 142.7, 136.5, 136.2, 128.8, 127.1, 126.6, 115.7, 104.0, 101.8, 100.6, 51.8, 45.5, 37.3, 23.2, 17.5 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{19}H_{23}NO_3SNa$: 366.1140, found: 366.1148.

19by: IR (ATR) : ν 3510, 2944, 2896, 2804, 1614, 1510, 1127, 1005, 977, 820, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.62 (2H, m), 7.57 (1H, dd, *J* = 8.0, 2.2 Hz), 7.18-7.22 (3H, m), 6.67 (1H, dd, *J* = 8.0, 2.2 Hz), 4.63-4.64 (1H, m), 4.52-4.53 (1H, m), 4.05-4.10 (1H, m), 3.65-3.70 (1H, m), 3.32 (1H, t, *J* = 7.9 Hz), 2.35 (3H, s), 1.69-1.73 (2H, m), 1.26 (3H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 143.3, 142.2, 136.8, 136.5, 129.1, 127.5, 126.6, 126.1, 116.8, 115.5, 113.1, 112.2, 55.6, 45.4, 21.9, 21.4, 21.3 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{19}H_{23}NO_3SNa$: 366.1140, found: 366.1155.

***Tert*-butyl 7-hydroxy-4-(prop-1-en-2-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (20x)**
***Tert*-butyl 5-hydroxy-4-(prop-1-en-2-yl)-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (20y)**

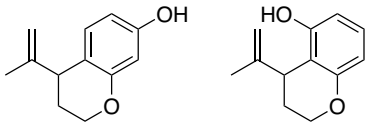


20x and **20y** (1:1) were obtained as a yellow oil in 48% yield (41.8 mg).

20x: IR (ATR) : ν 3217, 2956, 2845, 1710, 1580, 1435, 1332, 1248, 1003, 890, 695 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.32 (1H, dd, *J* = 8.2, 2.0 Hz), 7.15 (1H, dd, *J* = 8.2, 8.2 Hz), 6.66 (1H, dd, *J* = 8.2, 2.0 Hz), 4.73-4.77 (2H, m), 4.17 (2H, s), 3.75 (1H, t, *J* = 7.8 Hz), 3.27-3.30 (1H, m), 2.85-2.90 (1H, m), 1.63 (3H, dd, *J* = 1.4, 0.7 Hz), 1.54 (9H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.0, 148.3, 146.7, 137.7, 120.5, 117.7, 110.3, 109.8, 81.2, 53.1, 47.7, 46.8, 29.1, 18.6 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{23}NO_3Na$: 312.1576, found: 312.1558.

20y: IR (ATR) : ν 3456, 2879, 1720, 1468, 1402, 1367, 1128, 990, 821, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.20 (1H, dd, *J* = 8.0, 8.0 Hz), 6.23-6.27 (2H, m), 5.04-5.11 (2H, m), 4.08 (2H, s), 3.71 (1H, t, *J* = 7.9 Hz), 3.30-3.35 (1H, m), 3.20-3.25 (1H, m), 1.67 (3H, dd, *J* = 1.4, 0.7 Hz), 1.55 (9H, s) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.8, 142.3, 132.1, 130.0, 123.8, 121.8, 118.9, 113.5, 67.7, 56.2, 49.1, 35.8, 29.8, 26.2, 16.5 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{17}H_{23}NO_3Na$: 312.1576, found: 312.1584.

4-(Prop-1-en-2-yl)chroman-7-ol (21x)
4-(Prop-1-en-2-yl)chroman-5-ol (21y)

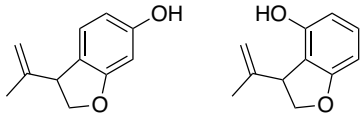


21x and **21y** (2:1) were obtained as a yellow oil in 38% yield (21.6 mg).

21x: IR (ATR) : ν 3210, 2950, 1532, 1438, 1260, 1034, 906, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 6.87 (1H, d, *J* = 8.4 Hz), 6.36 (1H, dd, *J* = 8.4, 2.6 Hz), 6.30 (1H, d, *J* = 2.6 Hz), 4.96-4.97 (1H, m), 4.69-4.70 (1H, m), 4.17-4.22 (1H, m), 4.08-4.12 (1H, m), 3.48 (1H, t, *J* = 6.7 Hz), 1.96-1.99 (2H, m), 1.67 (3H, dd, *J* = 1.3, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 155.2, 147.7, 130.8, 116.2, 114.8, 108.1, 103.2, 64.4, 42.5, 27.1, 19.5 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{14}O_2Na$: 213.0892, found: 213.0907.

21y: IR (ATR) : ν 3473, 2914, 2286, 1630, 1302, 1165, 1002, 984, 710 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$): δ 6.98 (1H, dd, *J* = 8.2, 8.0 Hz), 6.47 (1H, dd, *J* = 8.2, 2.4 Hz), 6.36 (1H, dd, *J* = 8.0, 2.4 Hz), 4.93-4.95 (1H, m), 4.69-4.70 (1H, m), 4.64 (1H, m), 4.54 (1H, s), 4.12-4.16 (1H, m), 4.03-4.08 (1H, m), 3.60 (1H, t, *J* = 6.6 Hz), 2.04-2.16 (2H, m), 1.82 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 156.0, 146.4, 135.4, 121.6, 118.4, 112.7, 106.2, 65.1, 42.3, 36.5, 20.6 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{14}O_2Na$: 213.0892, found: 213.0883.

3-(Prop-1-en-2-yl)-2,3-dihydrobenzofuran-6-ol (22x)
3-(Prop-1-en-2-yl)-2,3-dihydrobenzofuran-4-ol (22y)



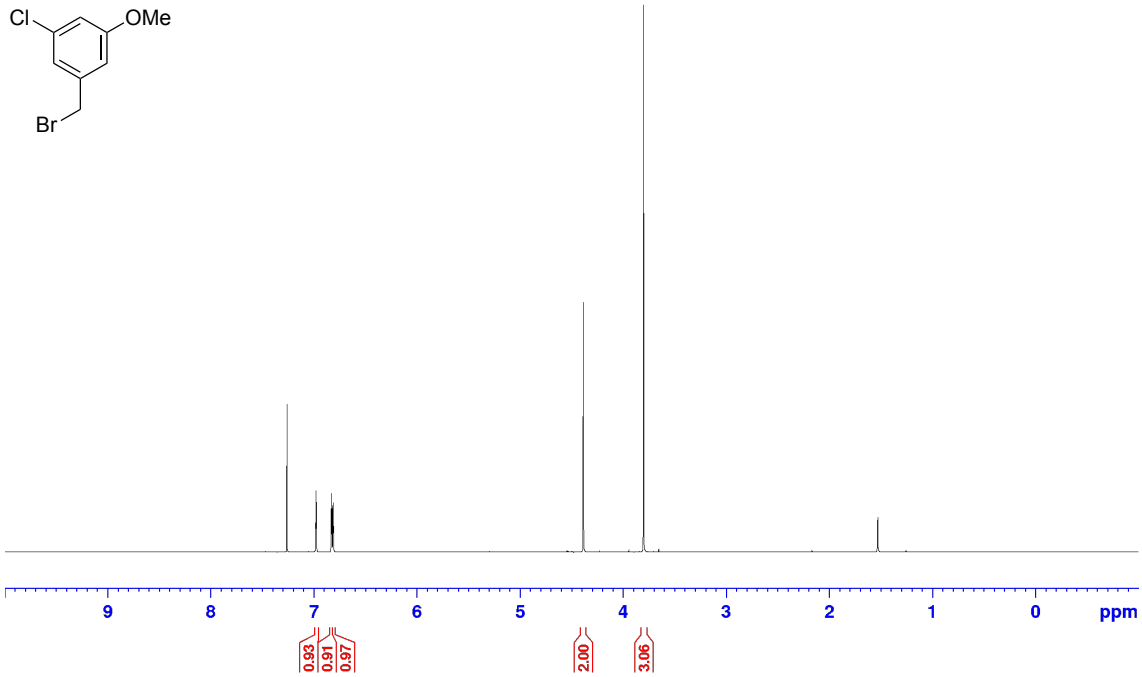
22x and **22y** (3:2) were obtained as a yellow oil in 38% yield (19.9 mg).

22x: IR (ATR) : ν 3179, 2920, 2245, 1670, 1338, 1221, 1018, 902, 850 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 7.11 (1H, d, *J* = 8.0 Hz), 6.42-6.46 (2H, m), 5.22-5.23 (1H, m), 4.97-4.99 (1H, m), 4.15-4.19 (1H, m), 4.00-4.03 (1H, m), 3.75 (1H, t, *J* = 6.6 Hz), 1.72 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6, 157.2, 147.1, 121.3, 117.0, 110.2, 109.9, 101.3, 68.5, 52.8, 14.6 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{12}O_2Na$: 199.0736, found: 199.0748.

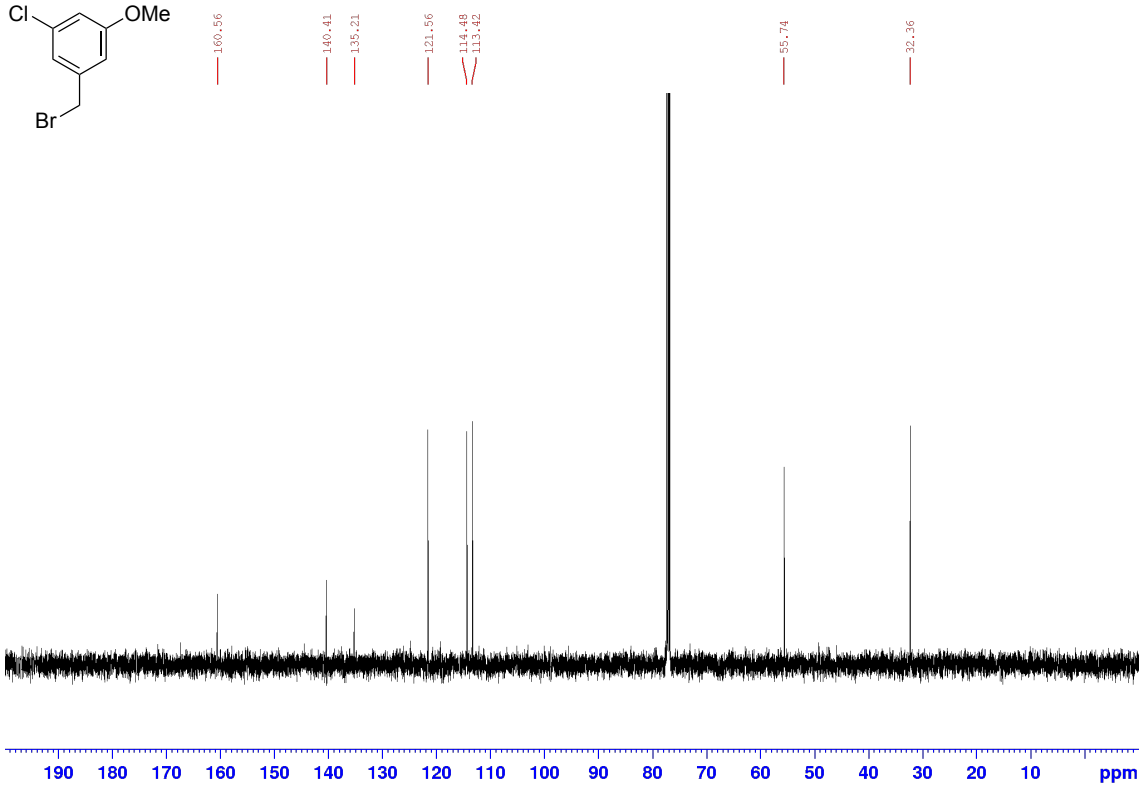
22y: IR (ATR) : ν 3370, 2978, 2218, 1725, 1560, 1285, 1039, 910, 802, 699 cm^{-1}.^1H NMR (500 MHz, $CDCl_3$): δ 7.12 (1H, dd, *J* = 8.2, 8.0 Hz), 6.45 (1H, dd, *J* = 8.2, 2.3 Hz), 6.42 (1H, dd, *J* = 8.0, 2.3 Hz), 5.42-5.51 (2H, m), 5.09-5.11 (1H, m), 4.78-4.82 (1H, m), 4.38 (1H, t, *J* = 7.8 Hz), 4.14-4.17 (1H, m), 1.73 (3H, dd, *J* = 1.4, 0.7 Hz) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.6, 156.0, 147.4, 137.5, 120.8, 117.7, 110.3, 100.8, 69.2, 53.8, 20.7 ppm. HRMS (ESI) $[M+Na]^+$ calculated for $C_{12}H_{12}O_2Na$: 199.0736, found: 199.0751.

4. NMR Spectra

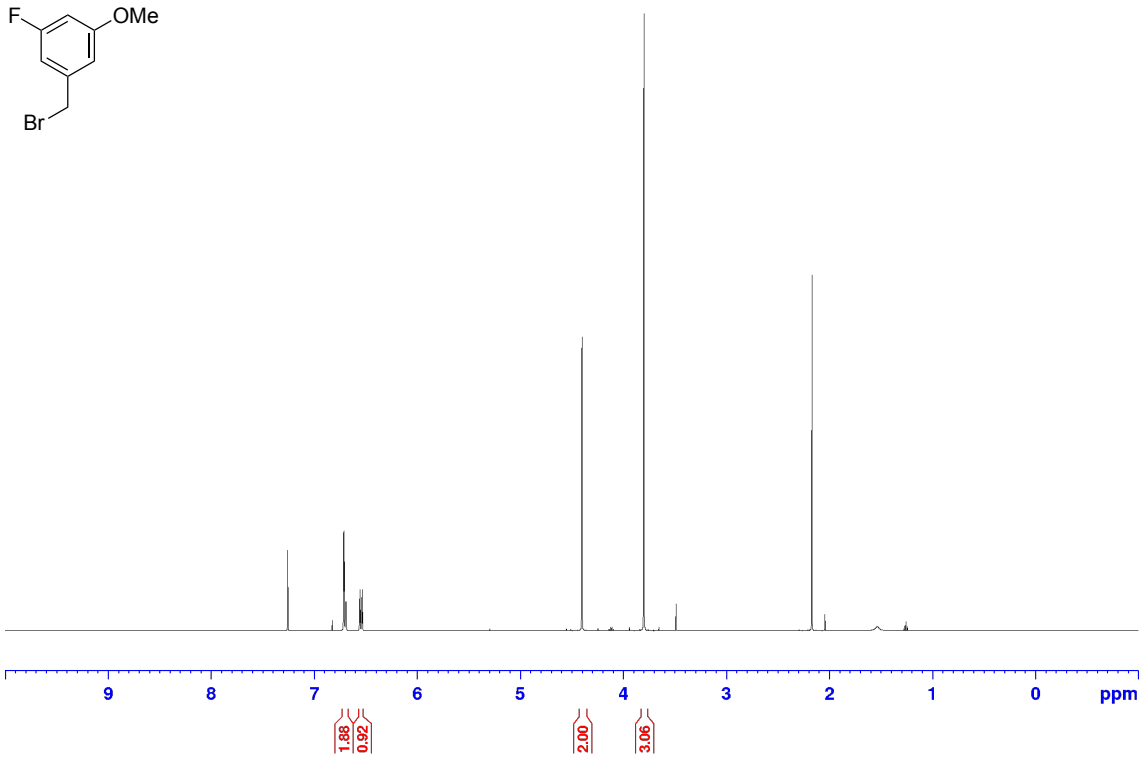
^{1}H NMR spectrum of **32c** ($CDCl_3$, 500 MHz)



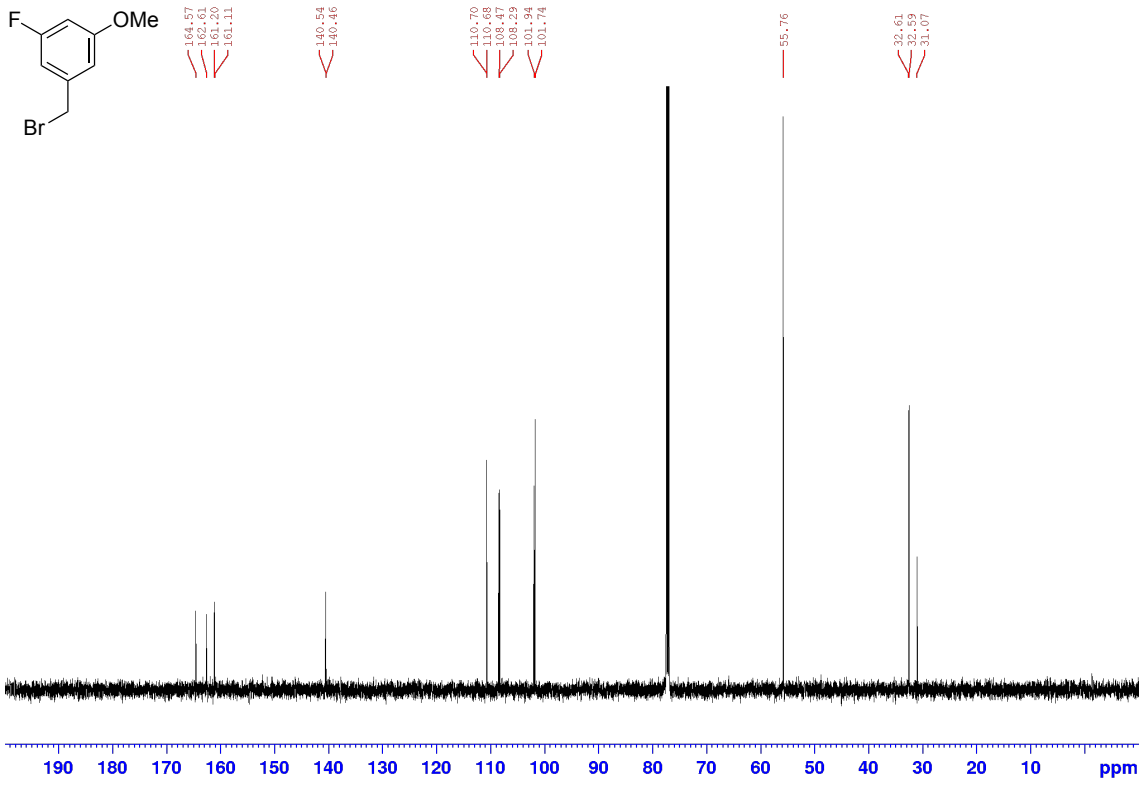
^{13}C NMR spectrum of **32c** ($CDCl_3$, 125 MHz)



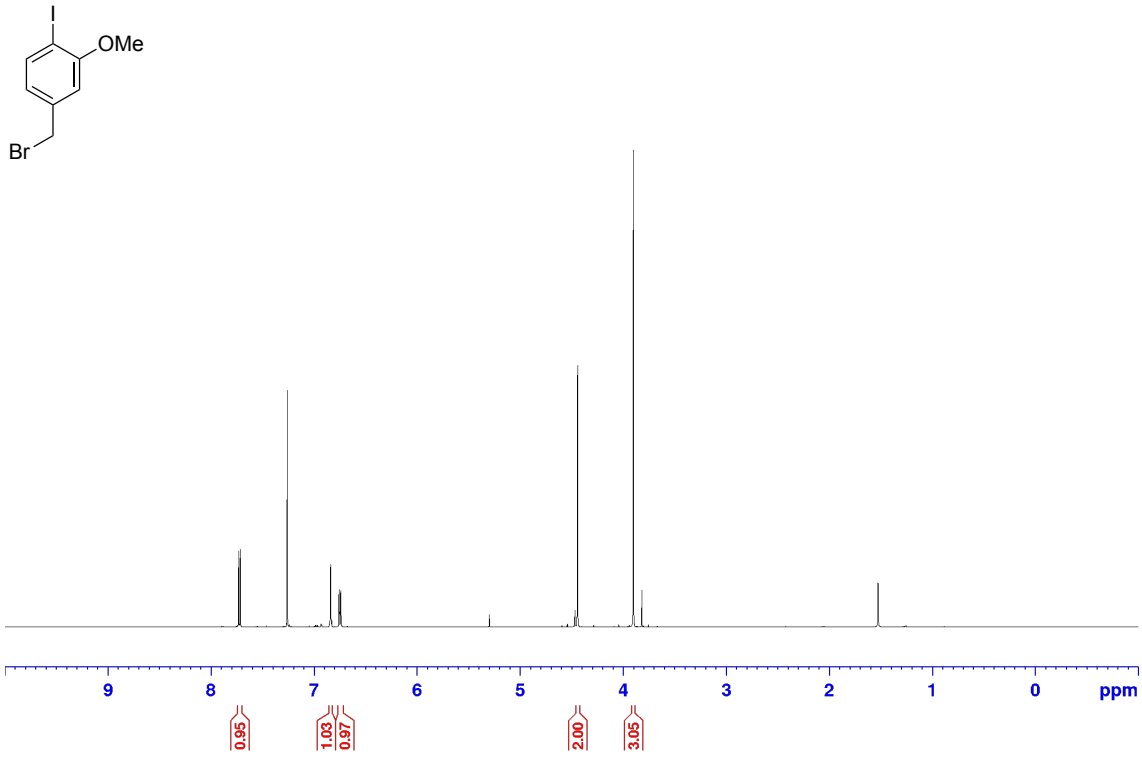
^{1}H NMR spectrum of **32d** ($CDCl_3$, 500 MHz)



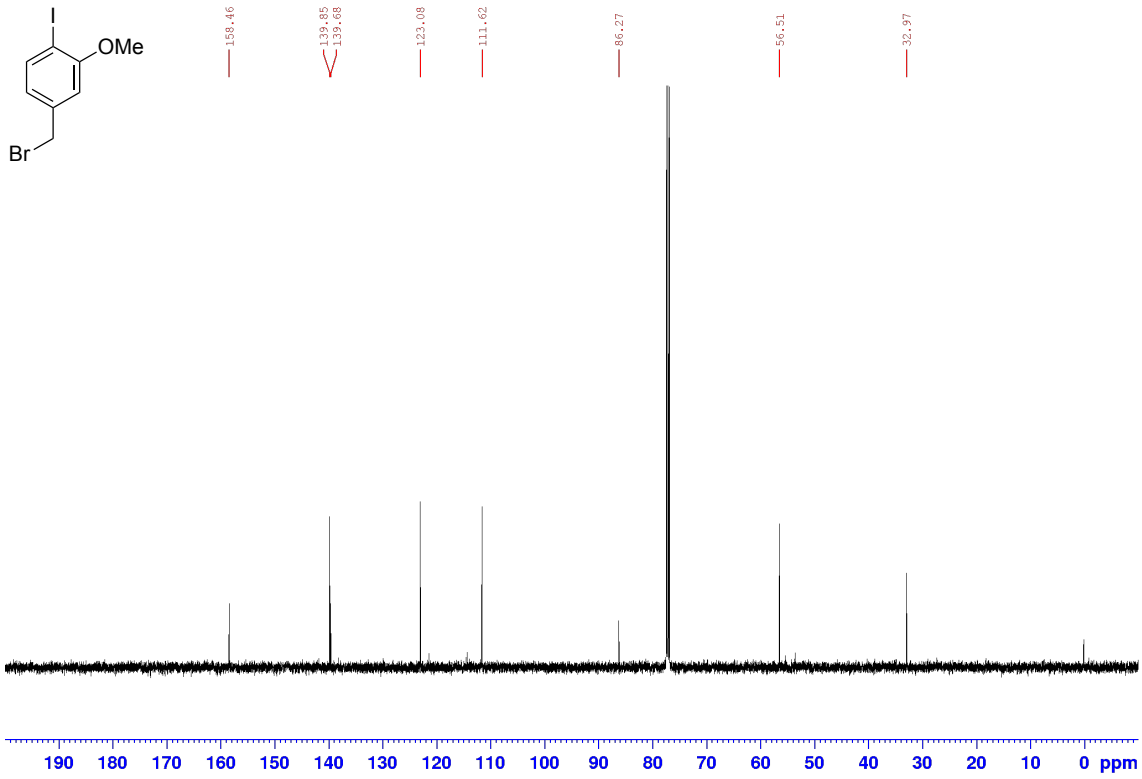
^{13}C NMR spectrum of **32d** ($CDCl_3$, 125 MHz)



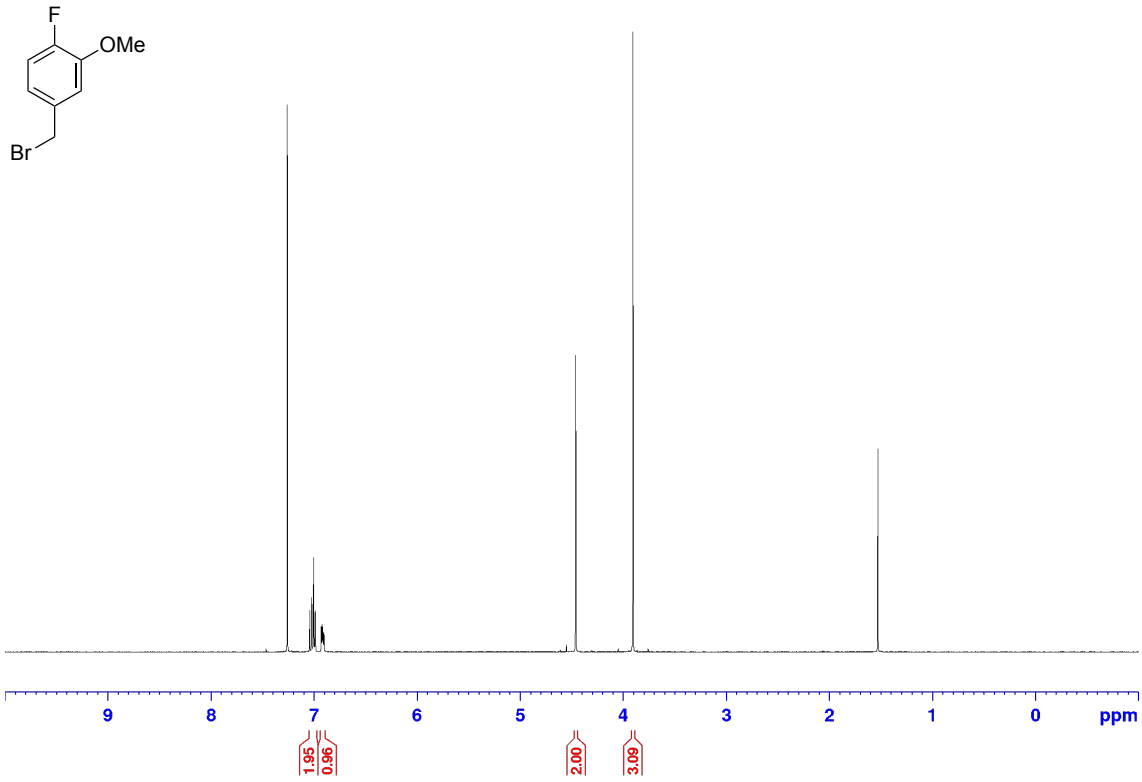
^{1}H NMR spectrum of **32h** ($CDCl_3$, 500 MHz)



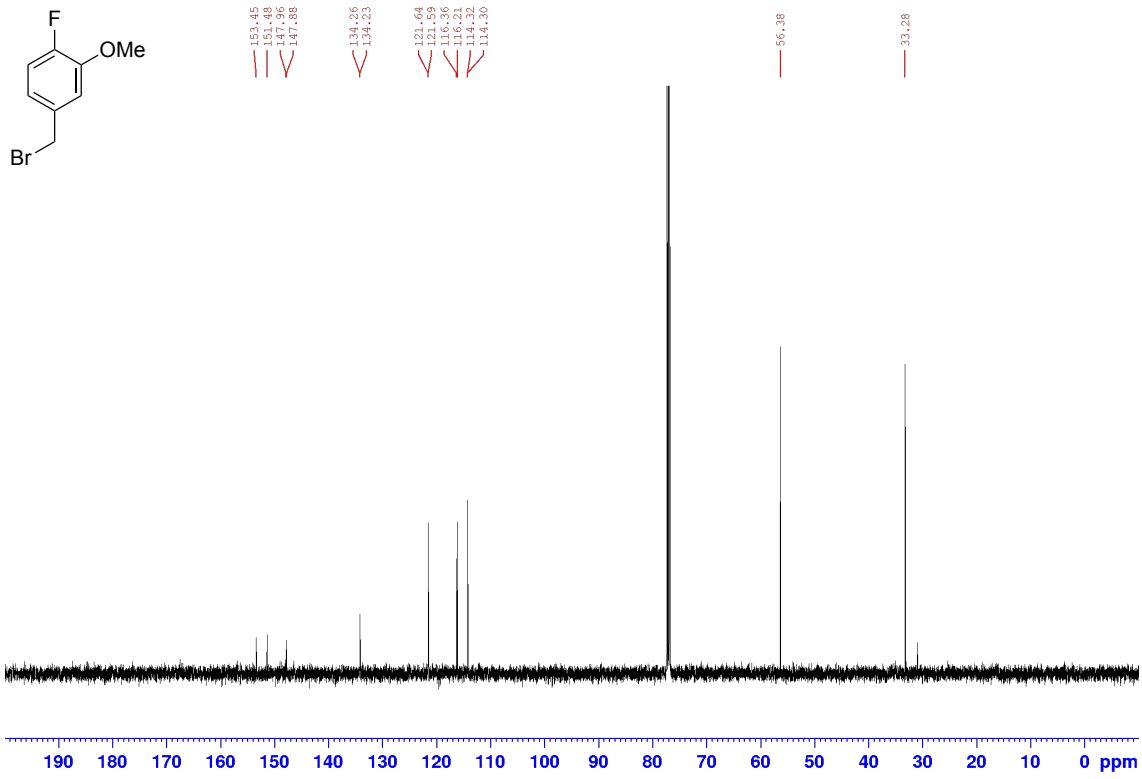
^{13}C NMR spectrum of **32h** ($CDCl_3$, 125 MHz)



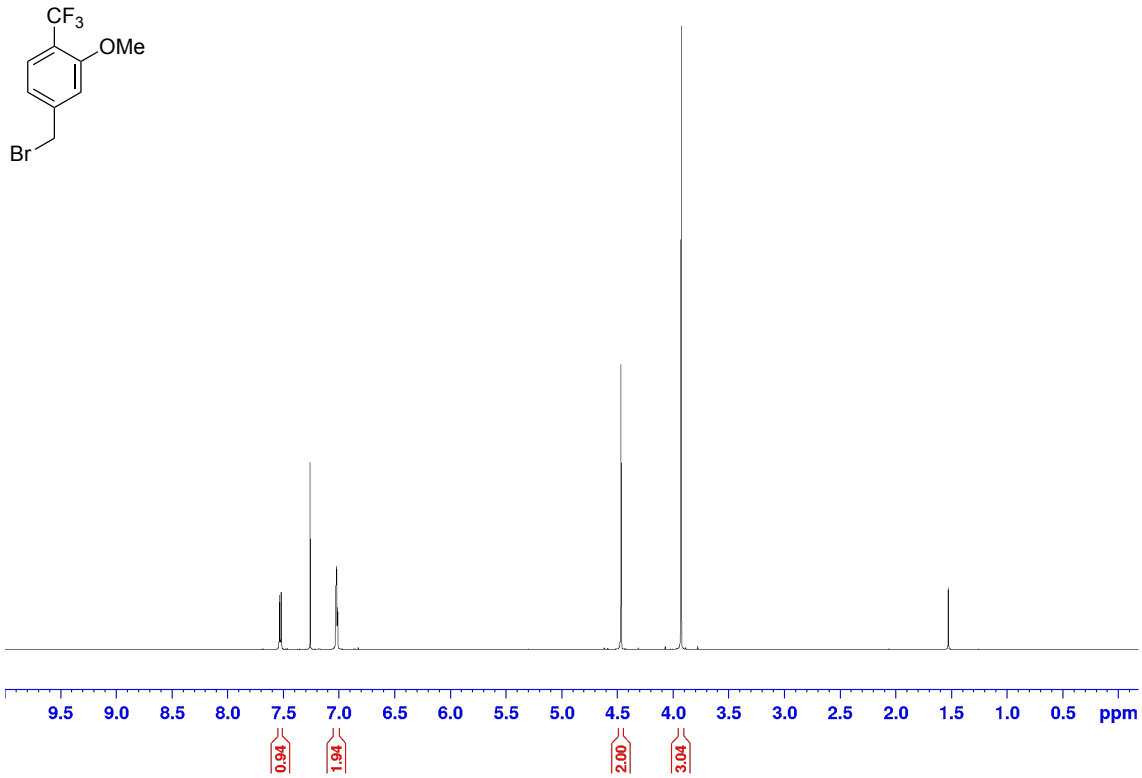
^{1}H NMR spectrum of **32k** ($CDCl_3$, 500 MHz)



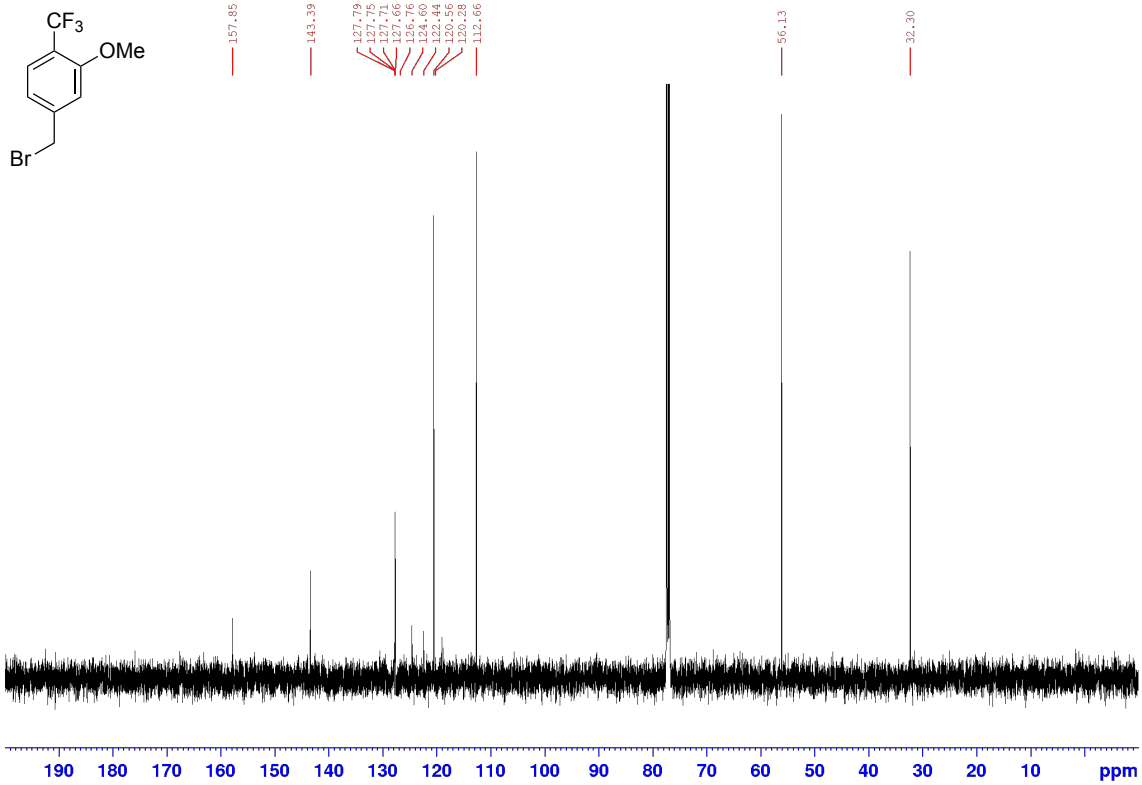
^{13}C NMR spectrum of **32k** ($CDCl_3$, 125 MHz)



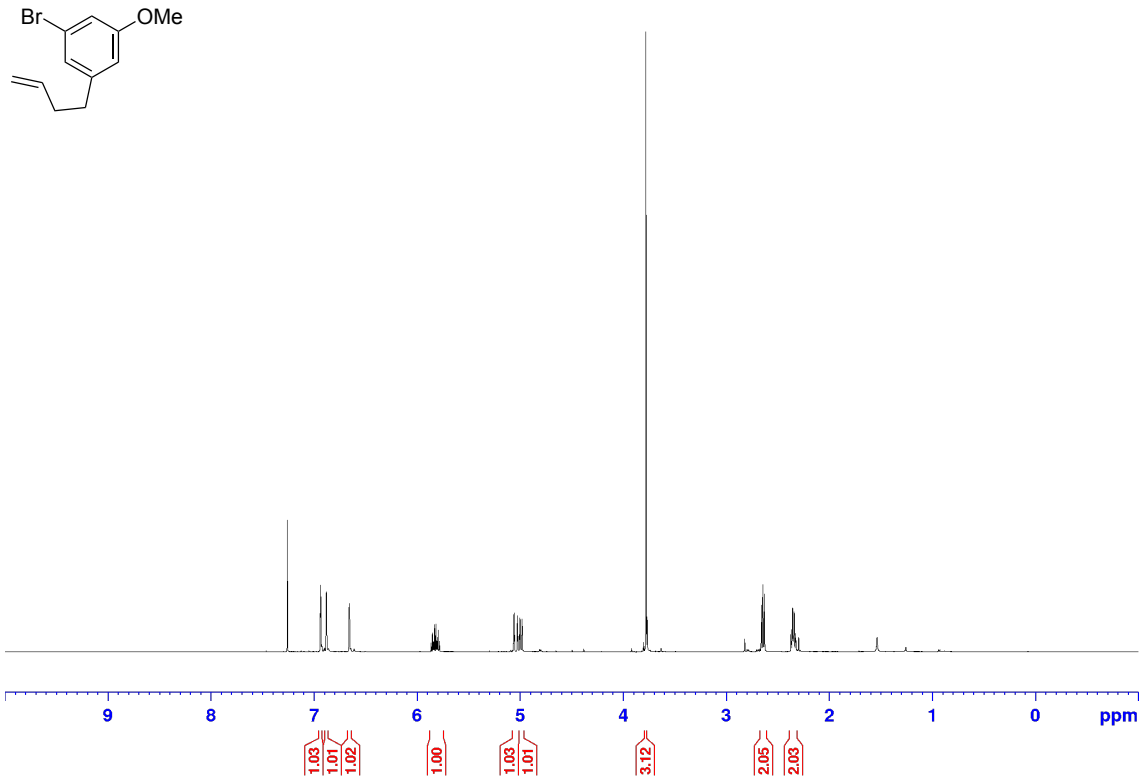
^{1}H NMR spectrum of **32l** ($CDCl_3$, 500 MHz)



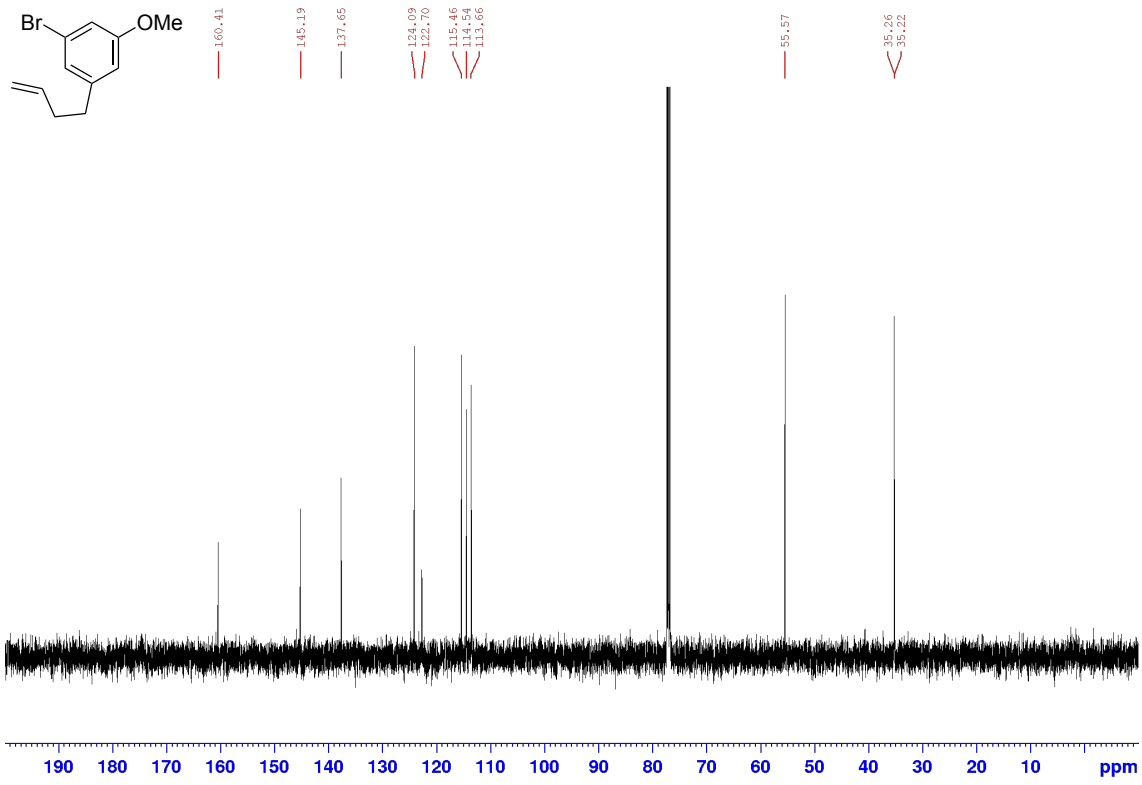
^{13}C NMR spectrum of **32l** ($CDCl_3$, 125 MHz)



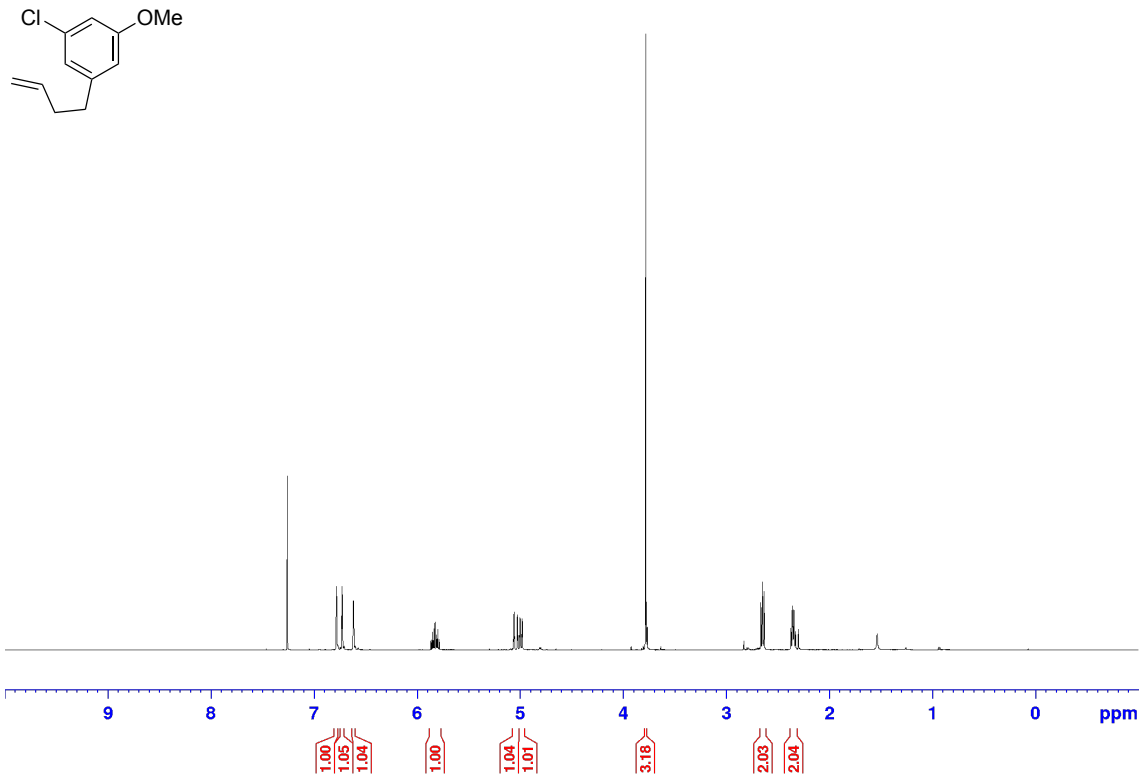
^{1}H NMR spectrum of **33b** ($CDCl_3$, 500 MHz)



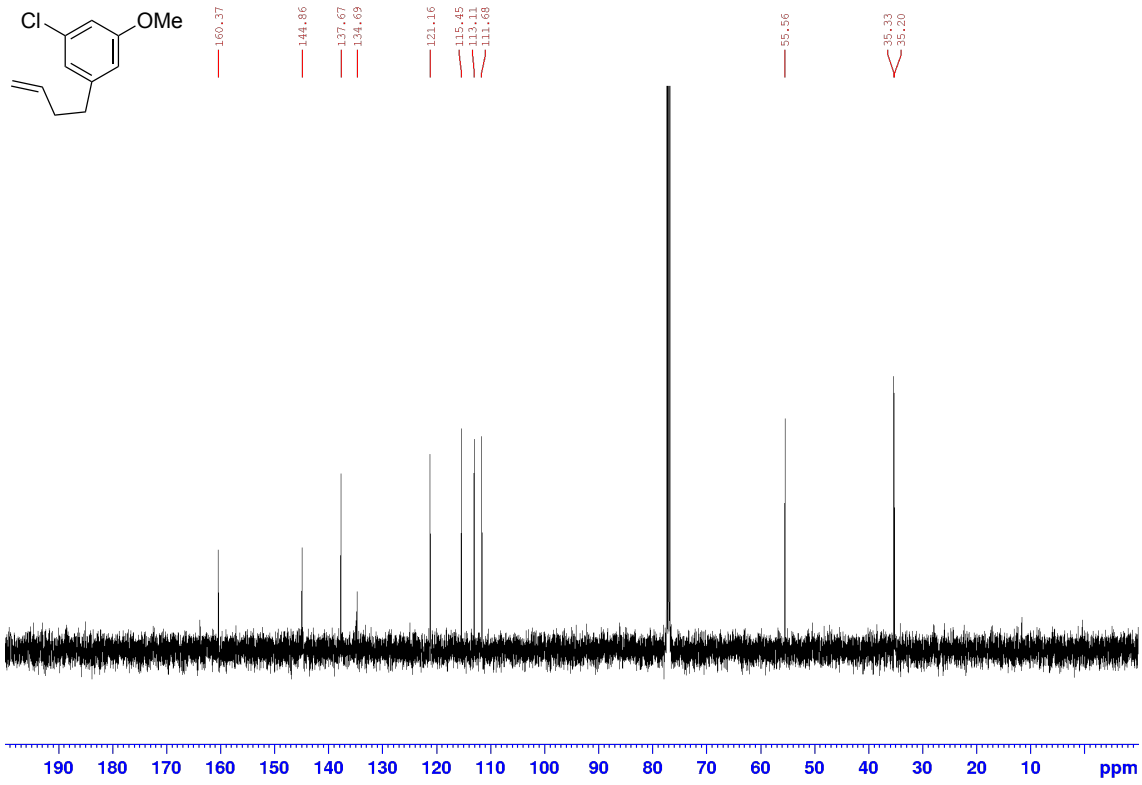
^{13}C NMR spectrum of **33b** ($CDCl_3$, 125 MHz)



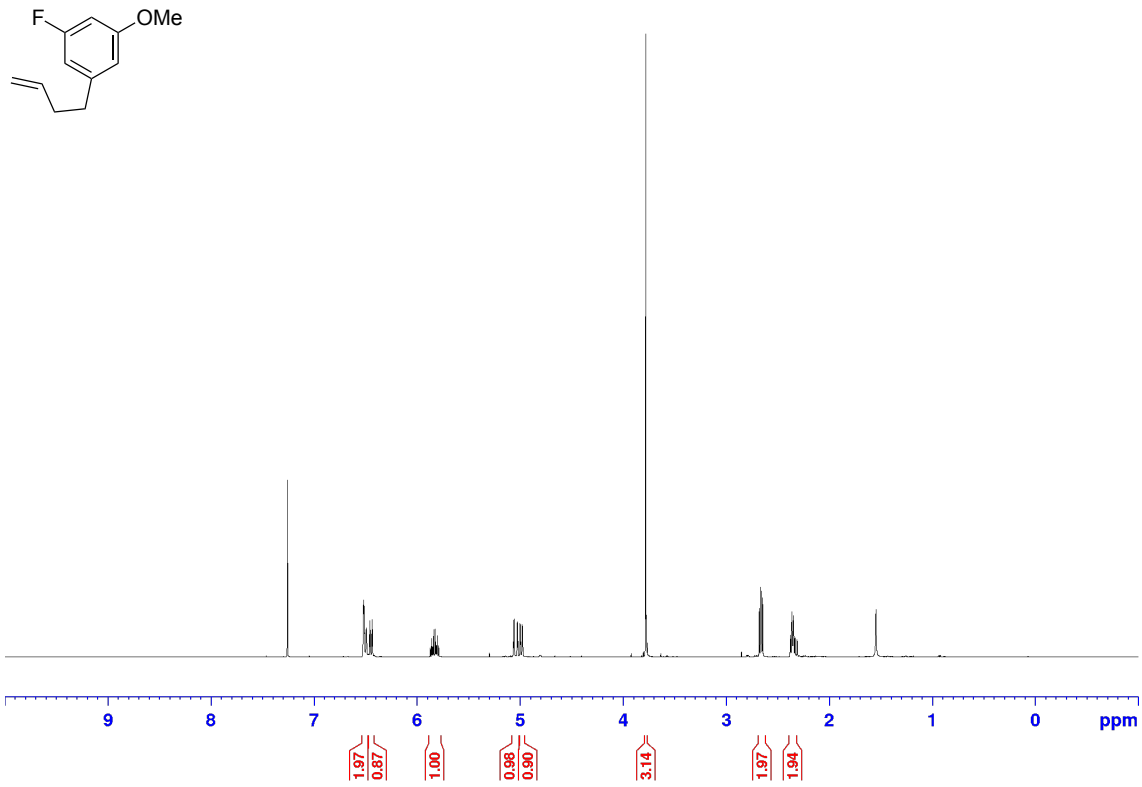
^{1}H NMR spectrum of **33c** ($CDCl_3$, 500 MHz)



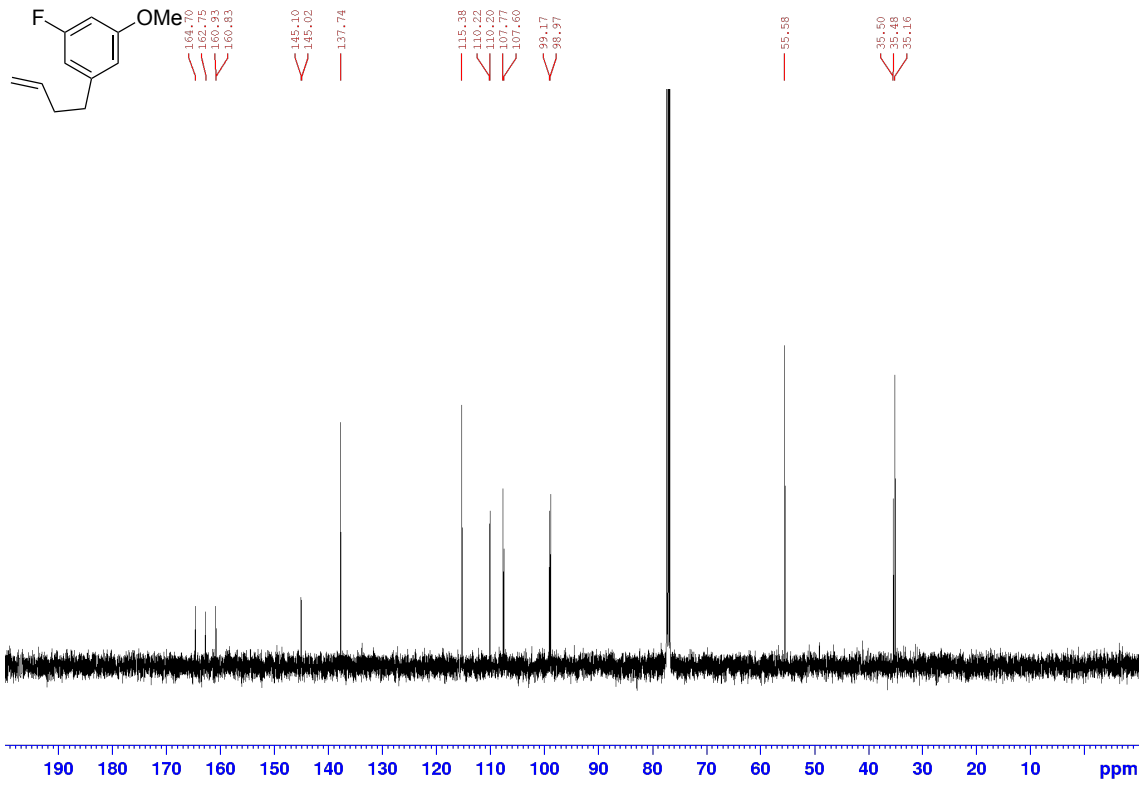
^{13}C NMR spectrum of **33c** ($CDCl_3$, 125 MHz)



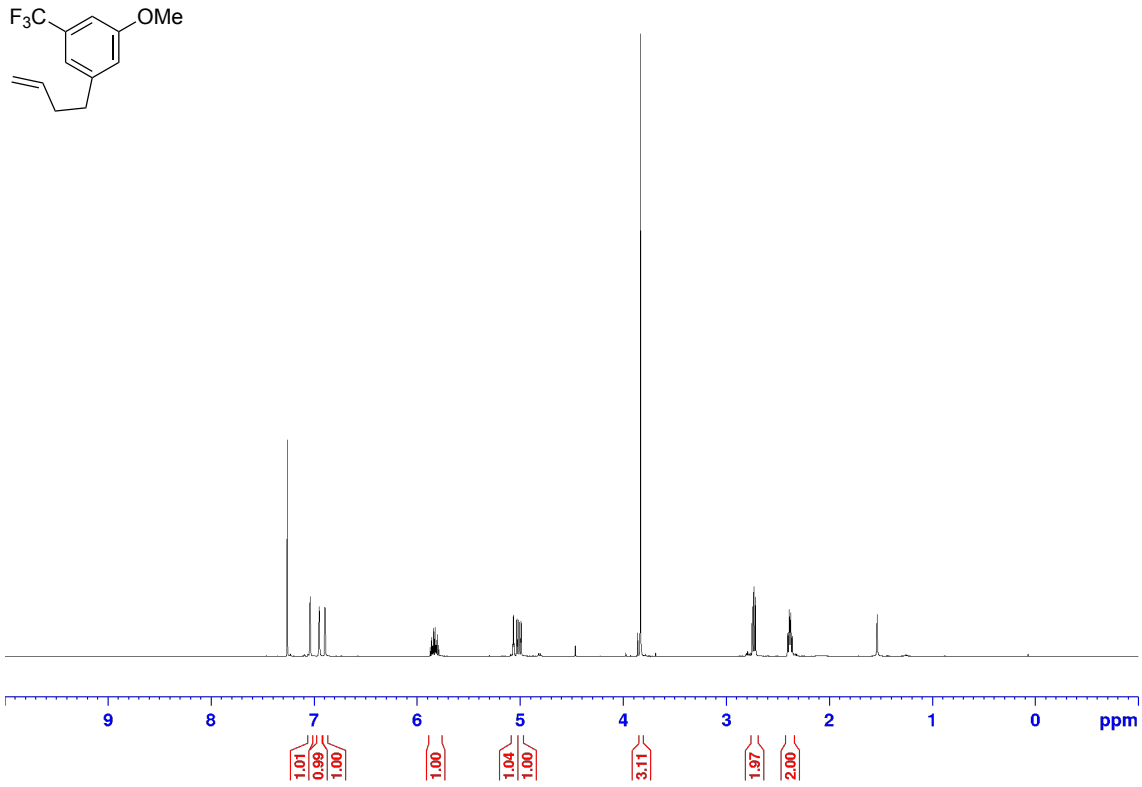
^{1}H NMR spectrum of **33d** ($CDCl_3$, 500 MHz)



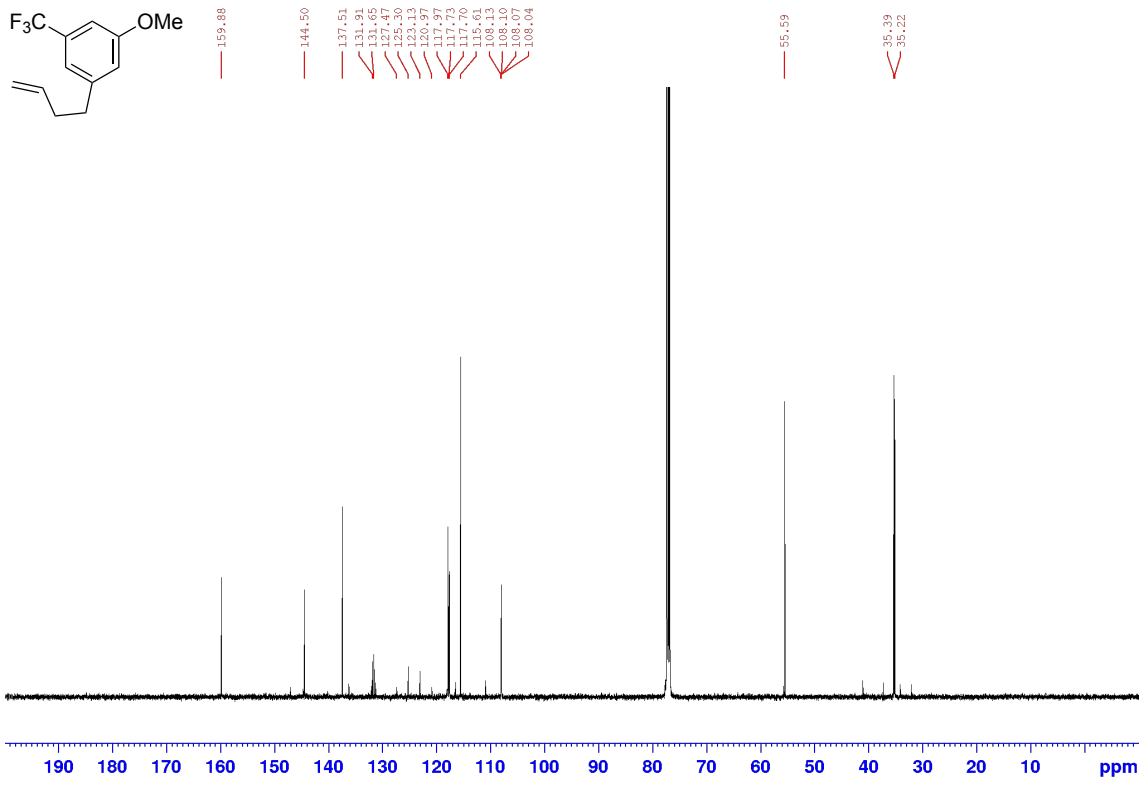
^{13}C NMR spectrum of **33d** ($CDCl_3$, 125 MHz)



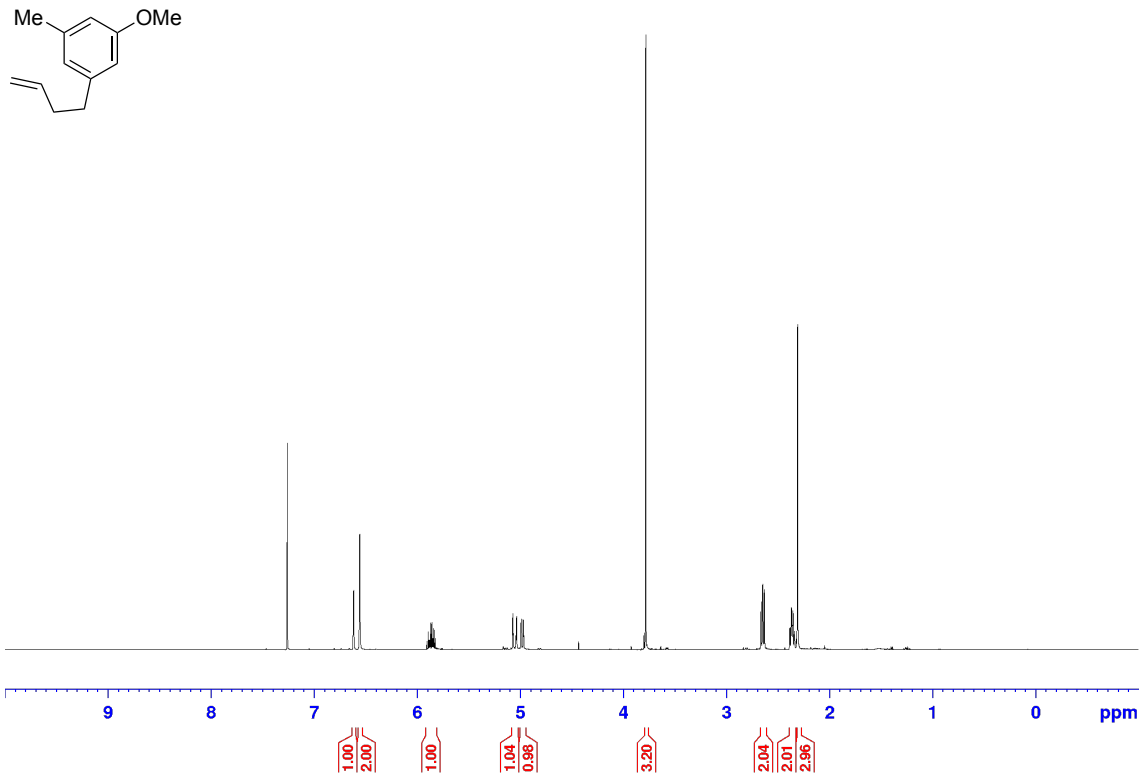
^{1}H NMR spectrum of **33e** ($CDCl_3$, 500 MHz)



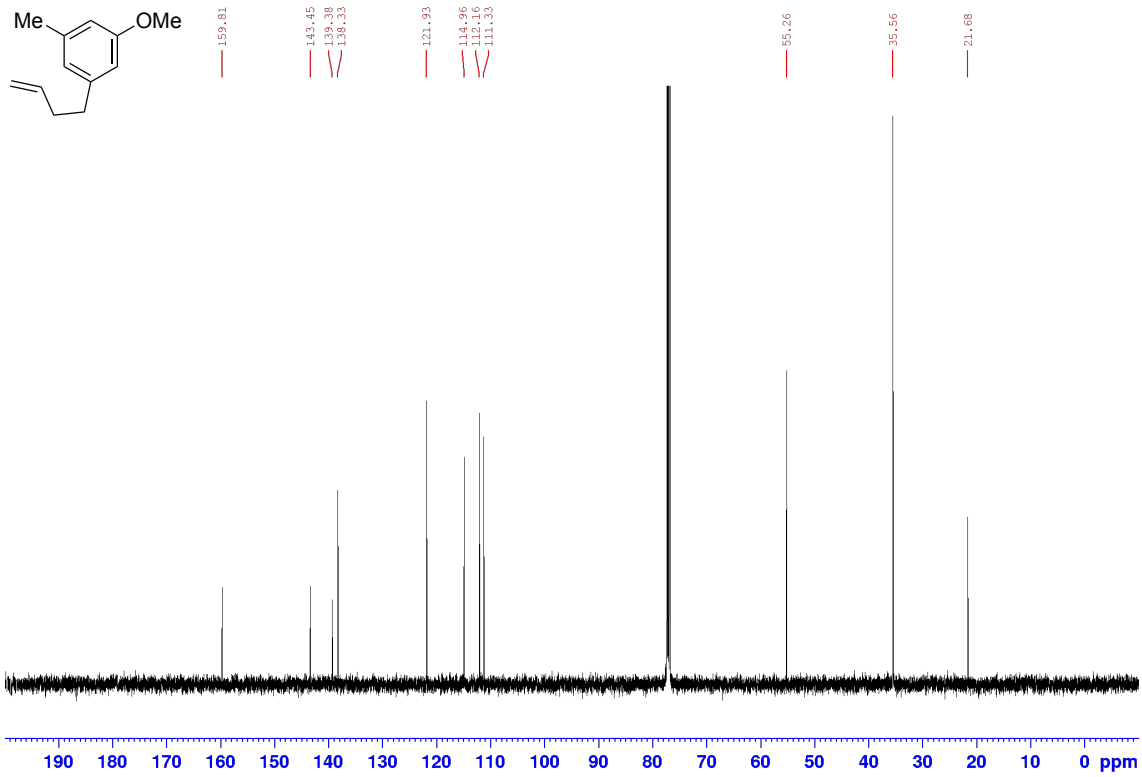
^{13}C NMR spectrum of **33e** ($CDCl_3$, 125 MHz)



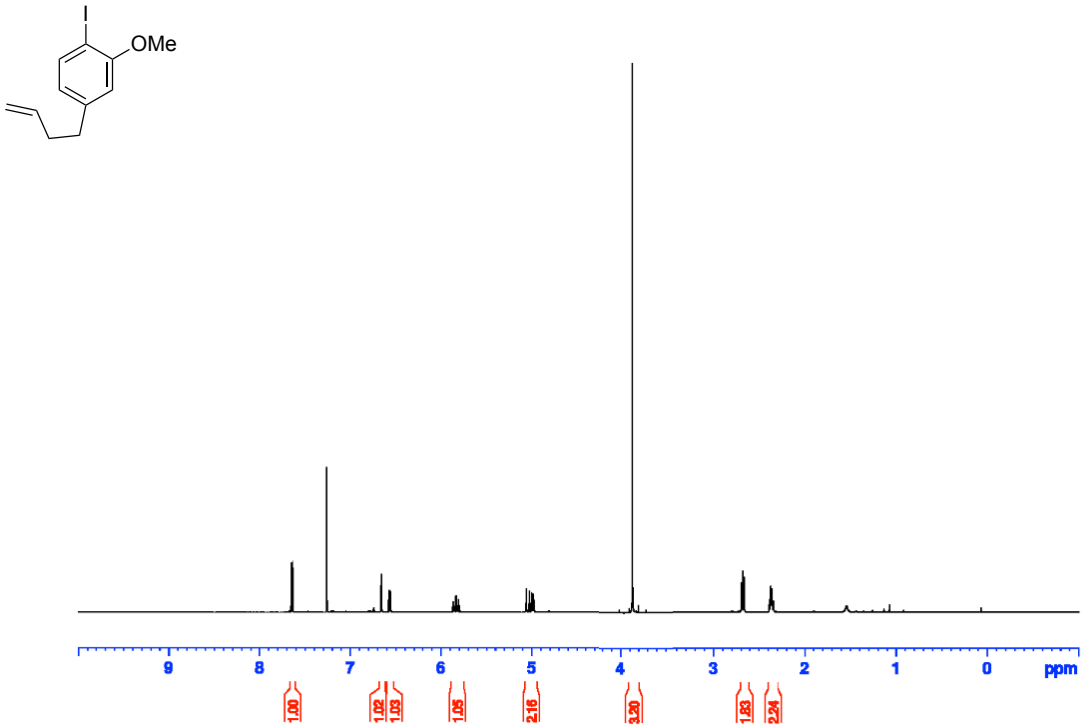
^{1}H NMR spectrum of **33f** ($CDCl_3$, 500 MHz)



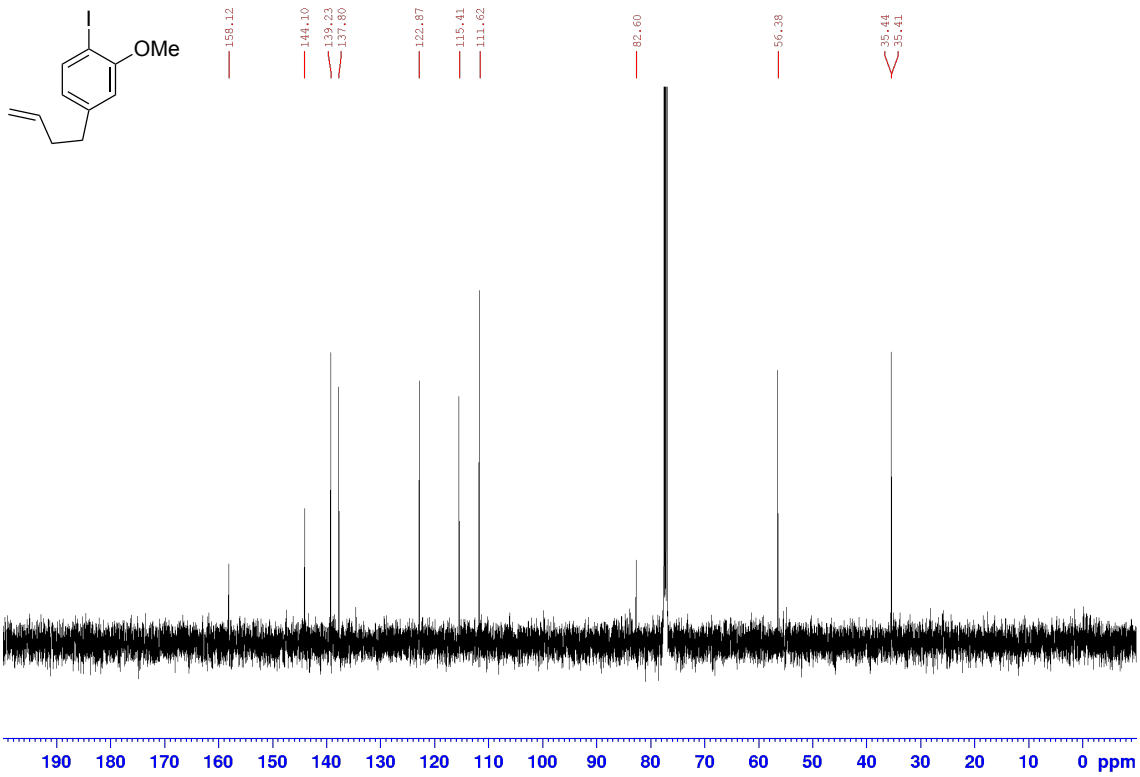
^{13}C NMR spectrum of **33f** ($CDCl_3$, 125 MHz)



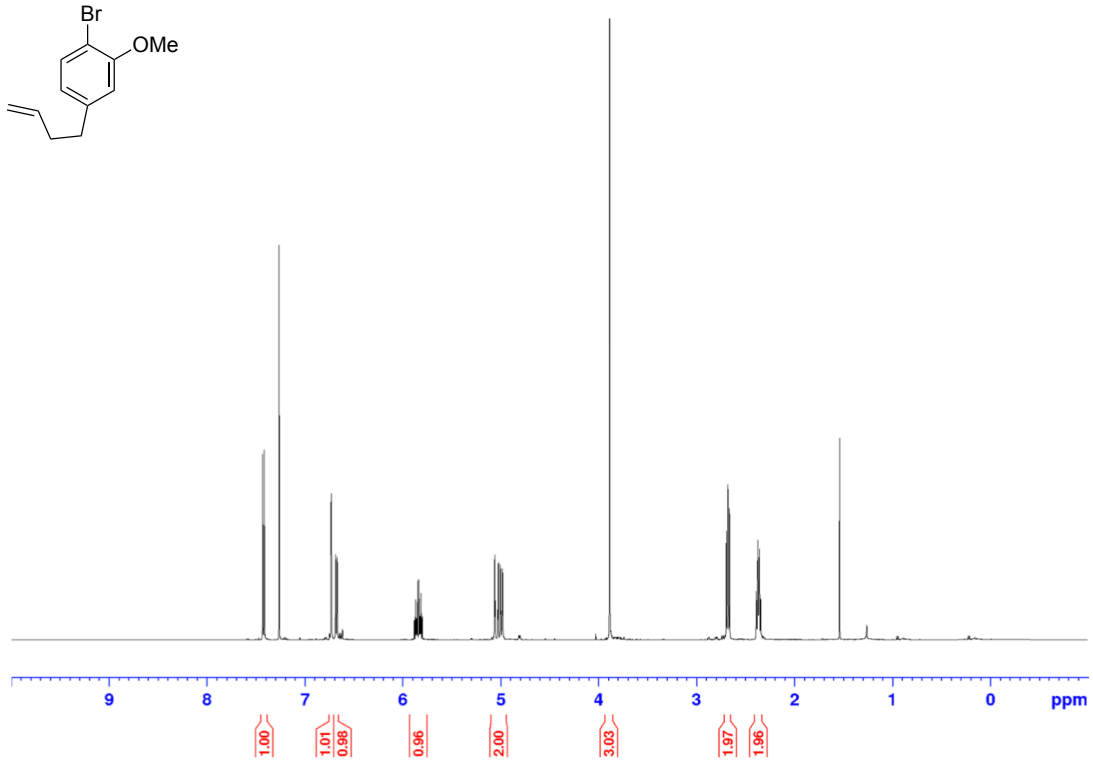
^{1}H NMR spectrum of **33h** ($CDCl_3$, 500 MHz)



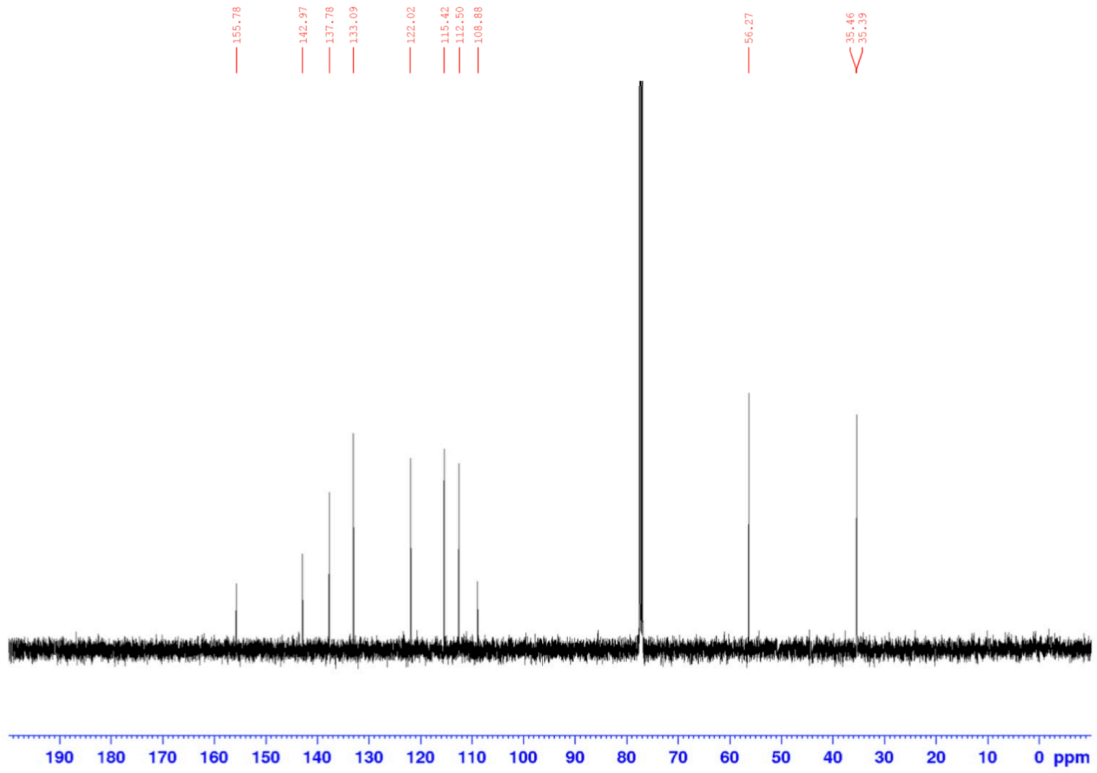
^{13}C NMR spectrum of **33h** ($CDCl_3$, 125 MHz)



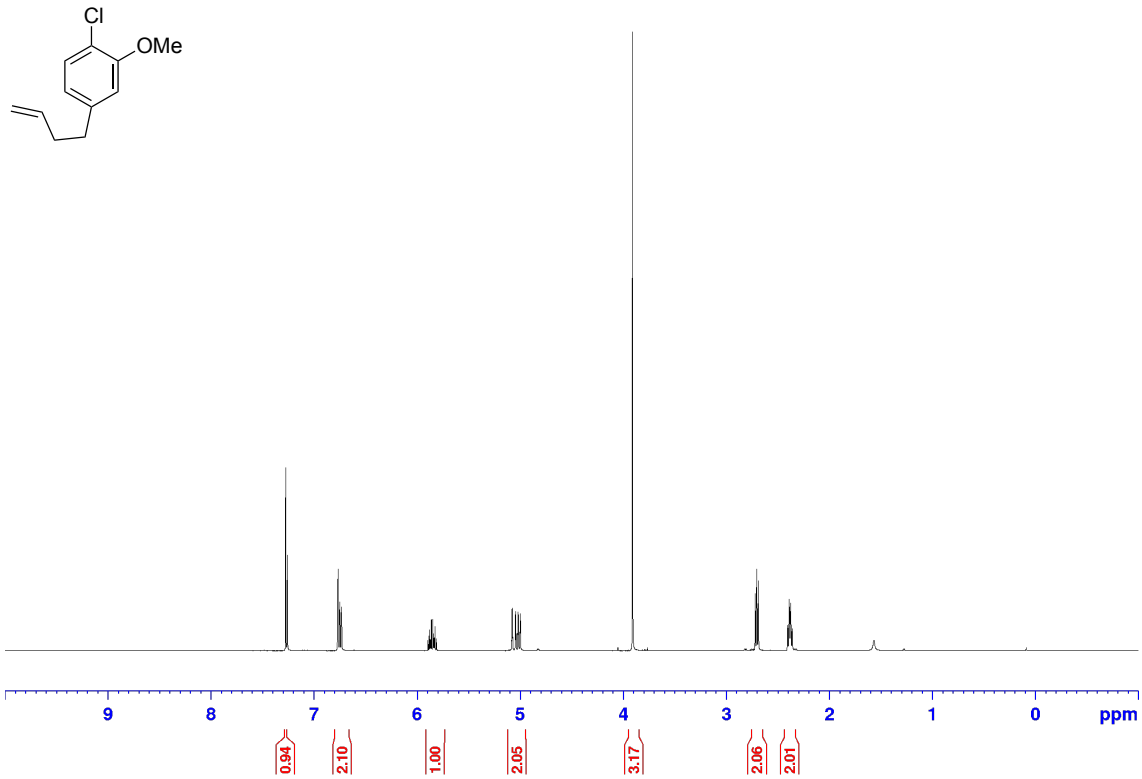
^{1}H NMR spectrum of **33i** ($CDCl_3$, 500 MHz)



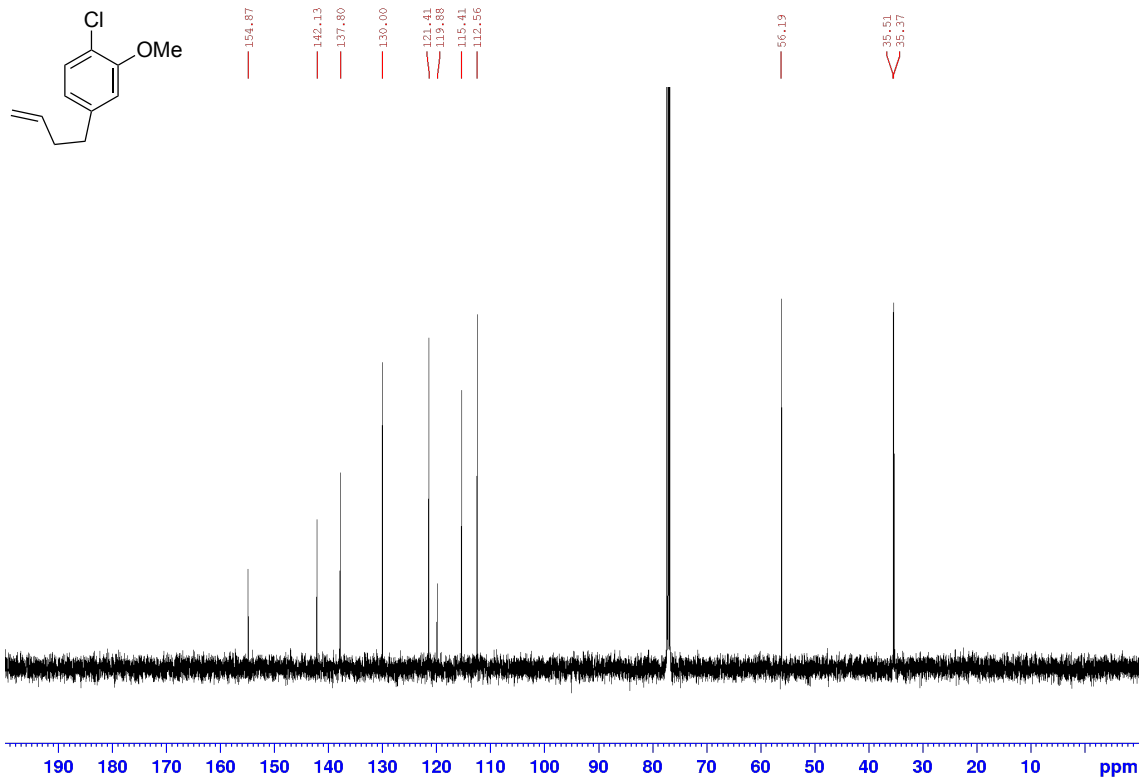
^{13}C NMR spectrum of **33i** ($CDCl_3$, 125 MHz)



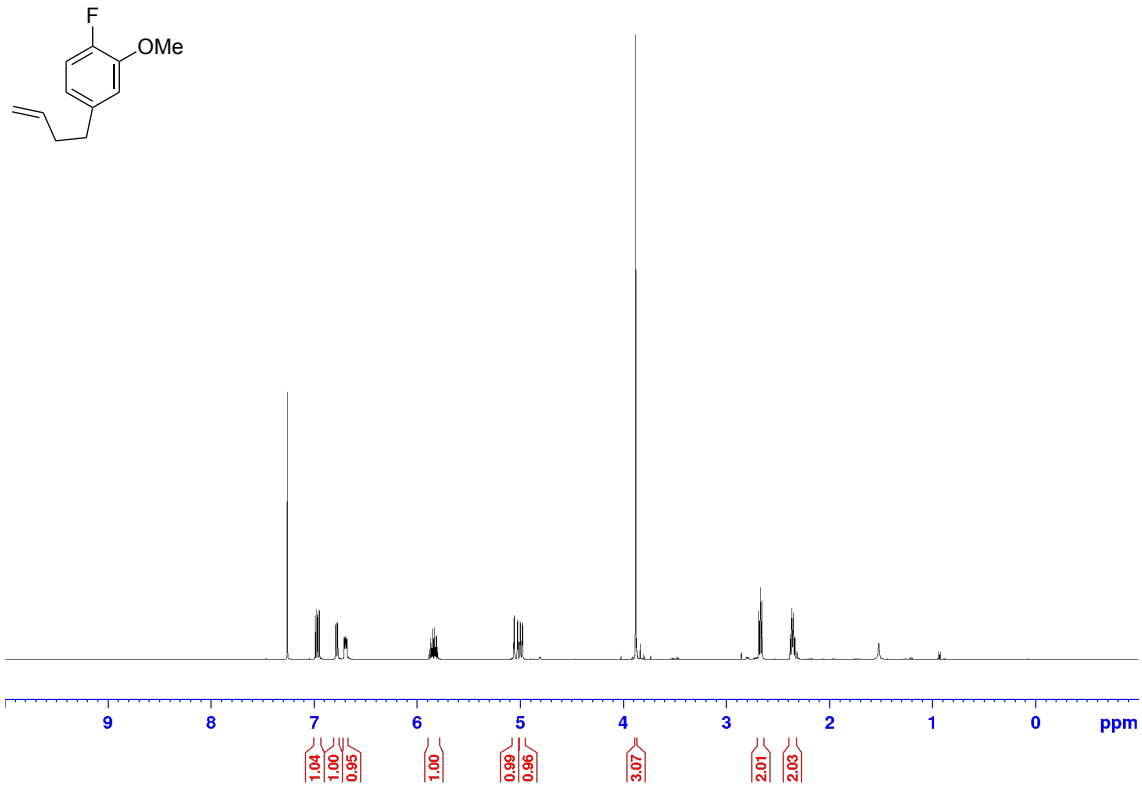
^{1}H NMR spectrum of **33j** ($CDCl_3$, 500 MHz)



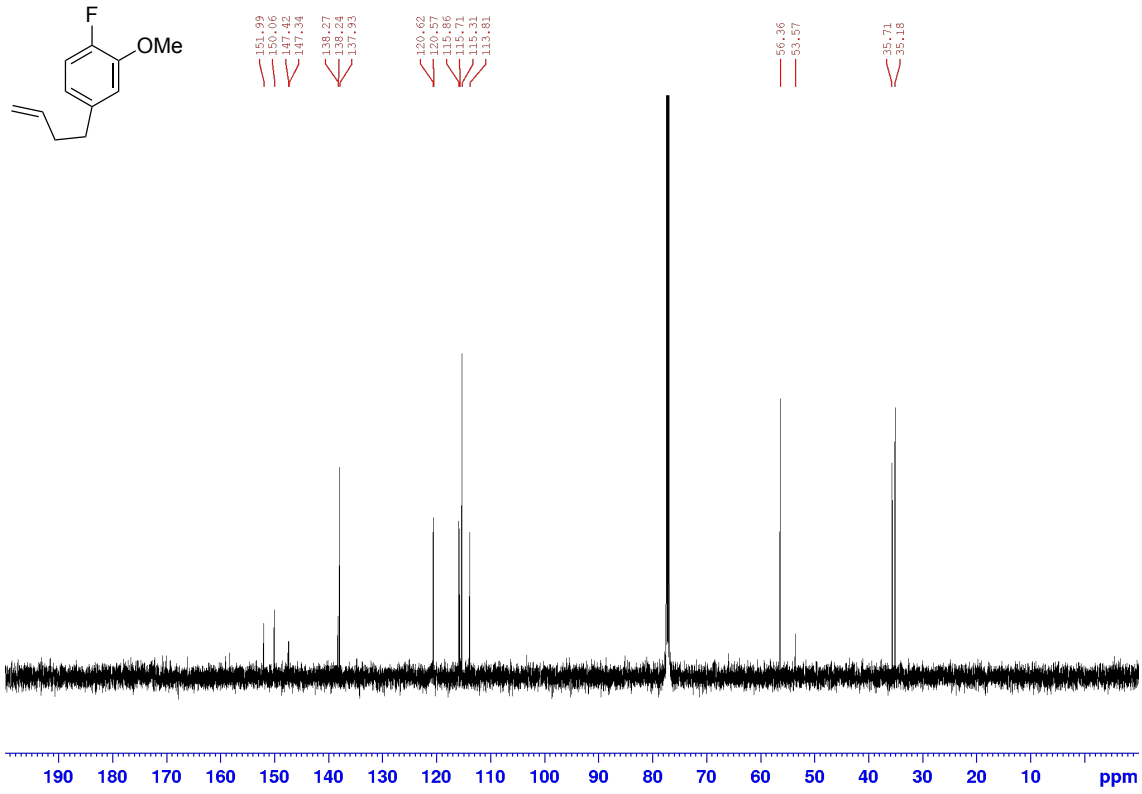
^{13}C NMR spectrum of **33j** ($CDCl_3$, 125 MHz)



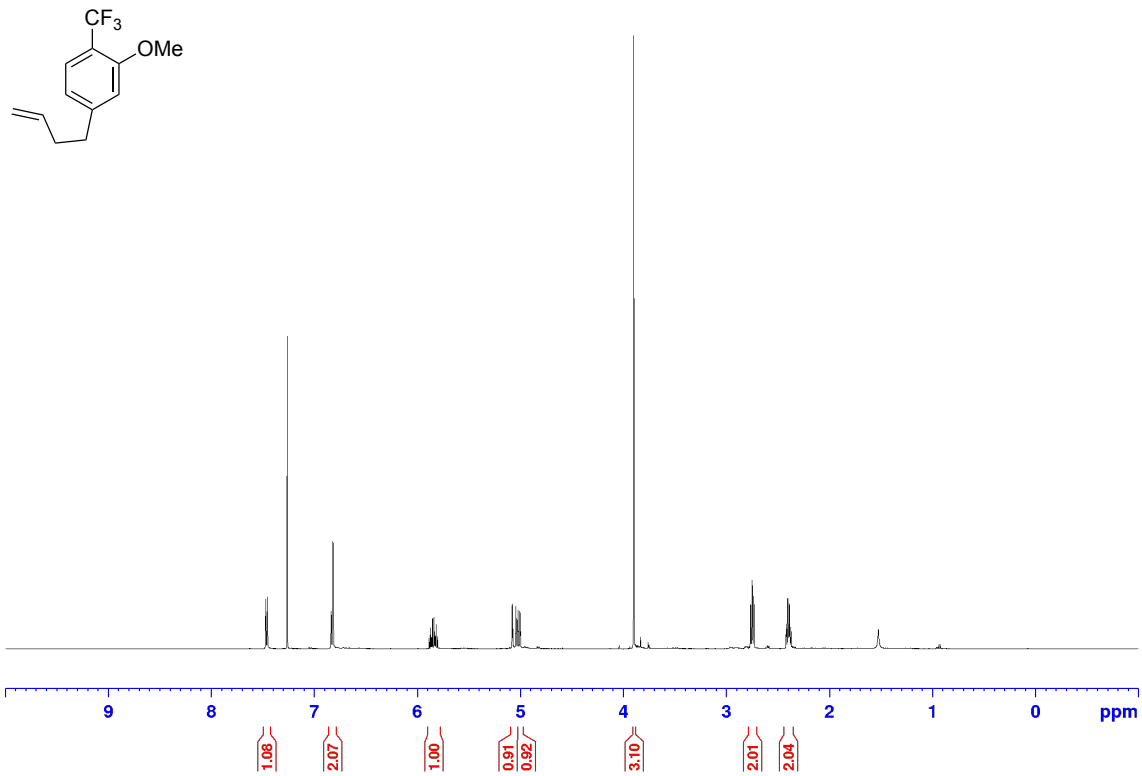
^{1}H NMR spectrum of **33k** ($CDCl_3$, 500 MHz)



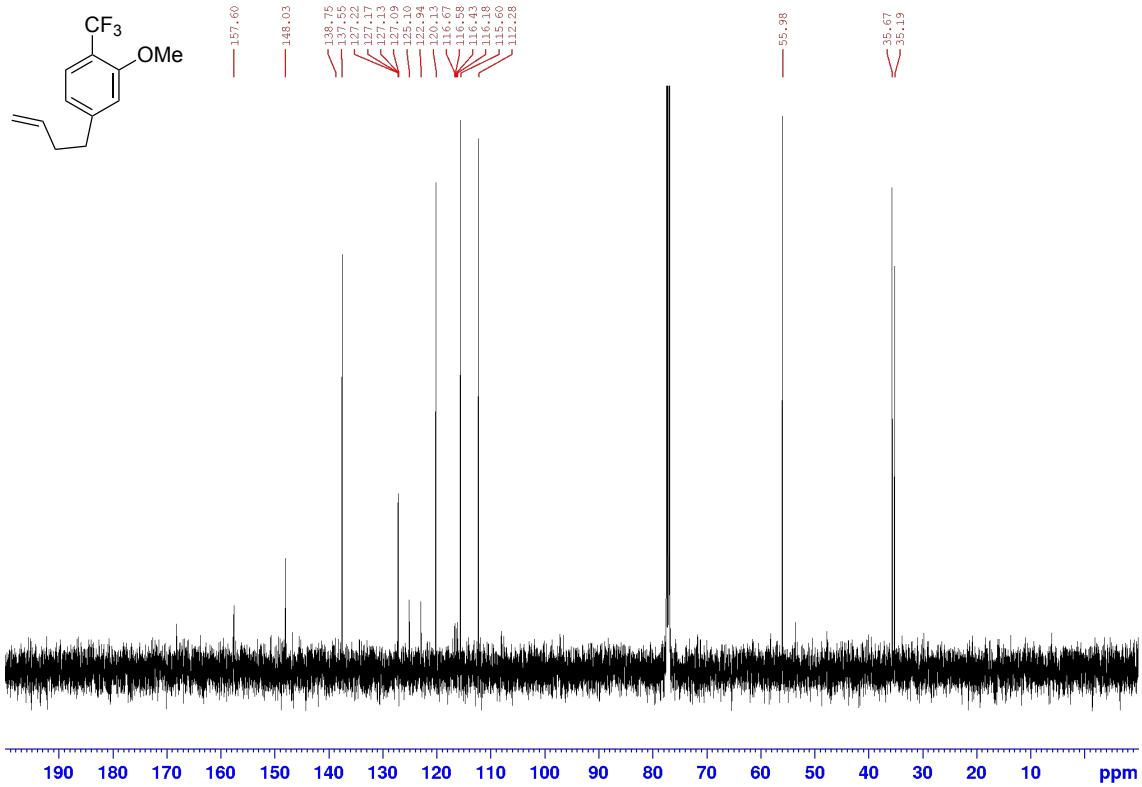
^{13}C NMR spectrum of **33k** ($CDCl_3$, 125 MHz)



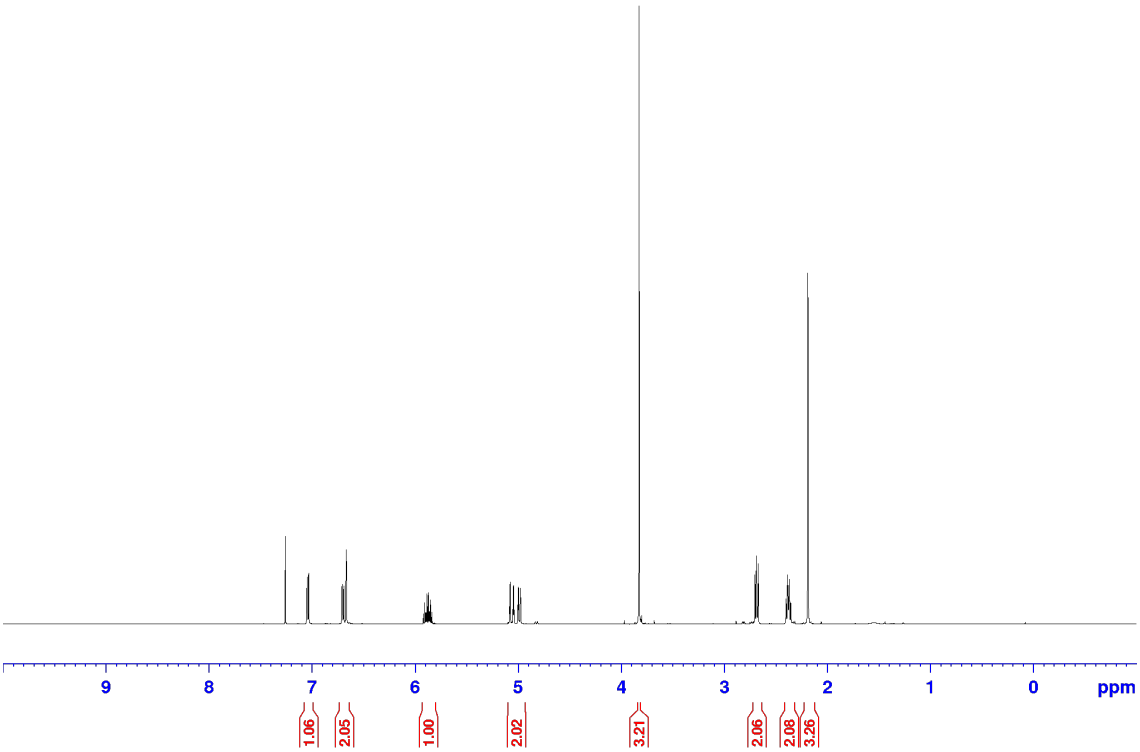
^{1}H NMR spectrum of **33l** ($CDCl_3$, 500 MHz)



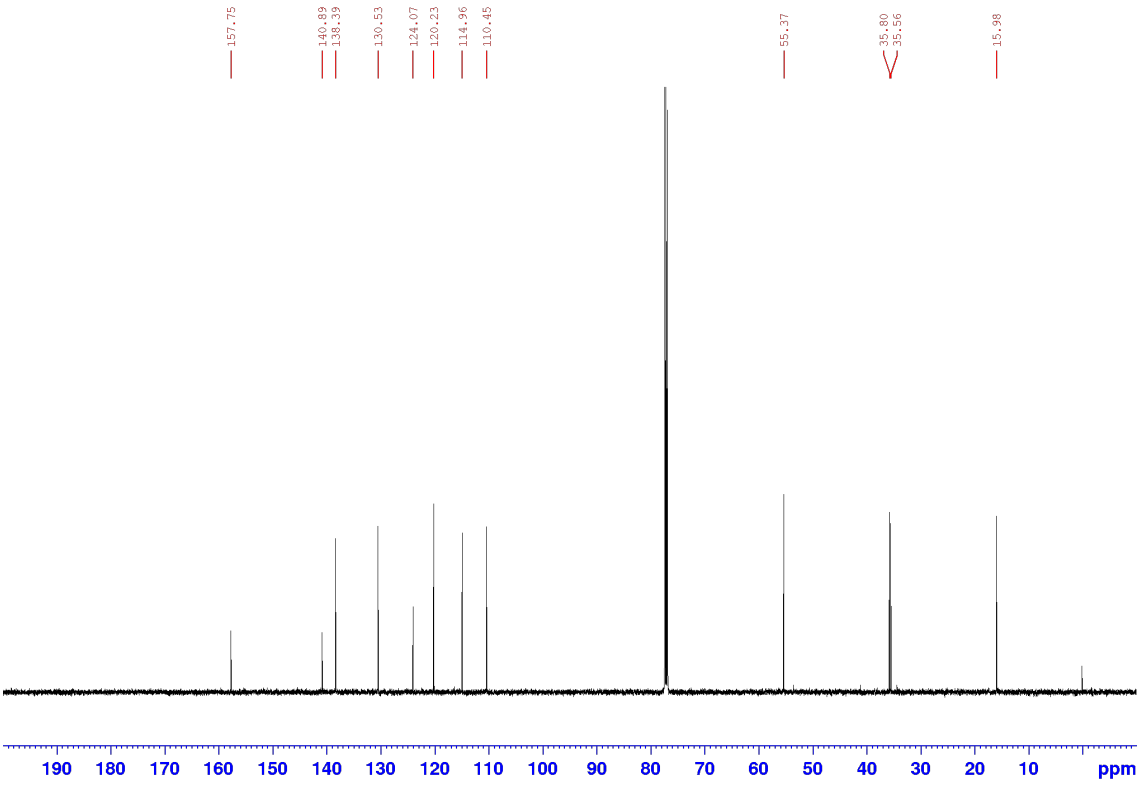
^{13}C NMR spectrum of **33l** ($CDCl_3$, 125 MHz)



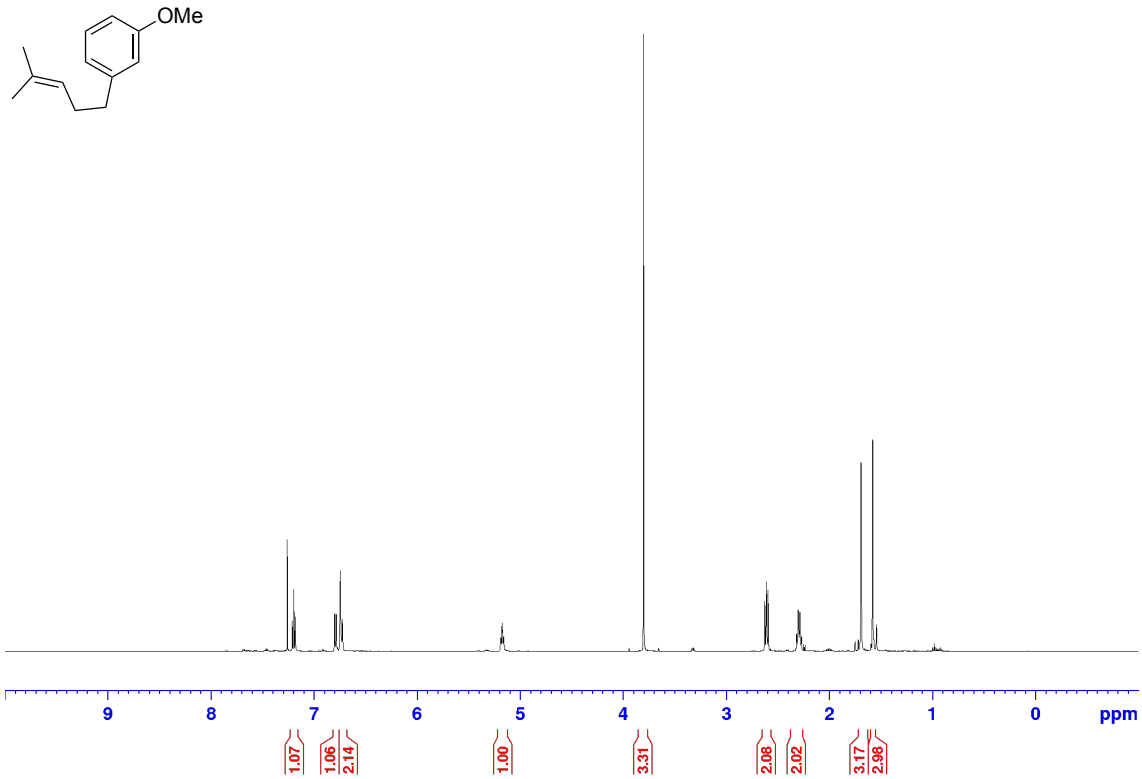
^{1}H NMR spectrum of **33m** ($CDCl_3$, 500 MHz)



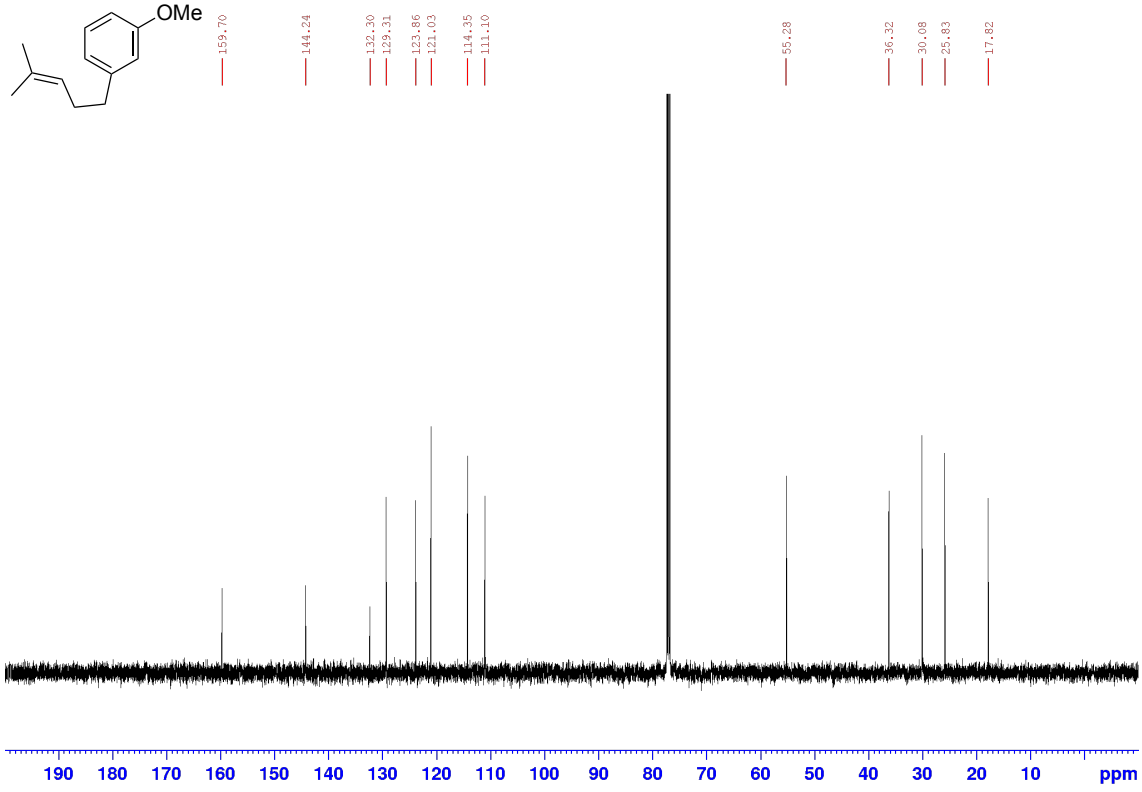
^{13}C NMR spectrum of **33m** ($CDCl_3$, 125 MHz)



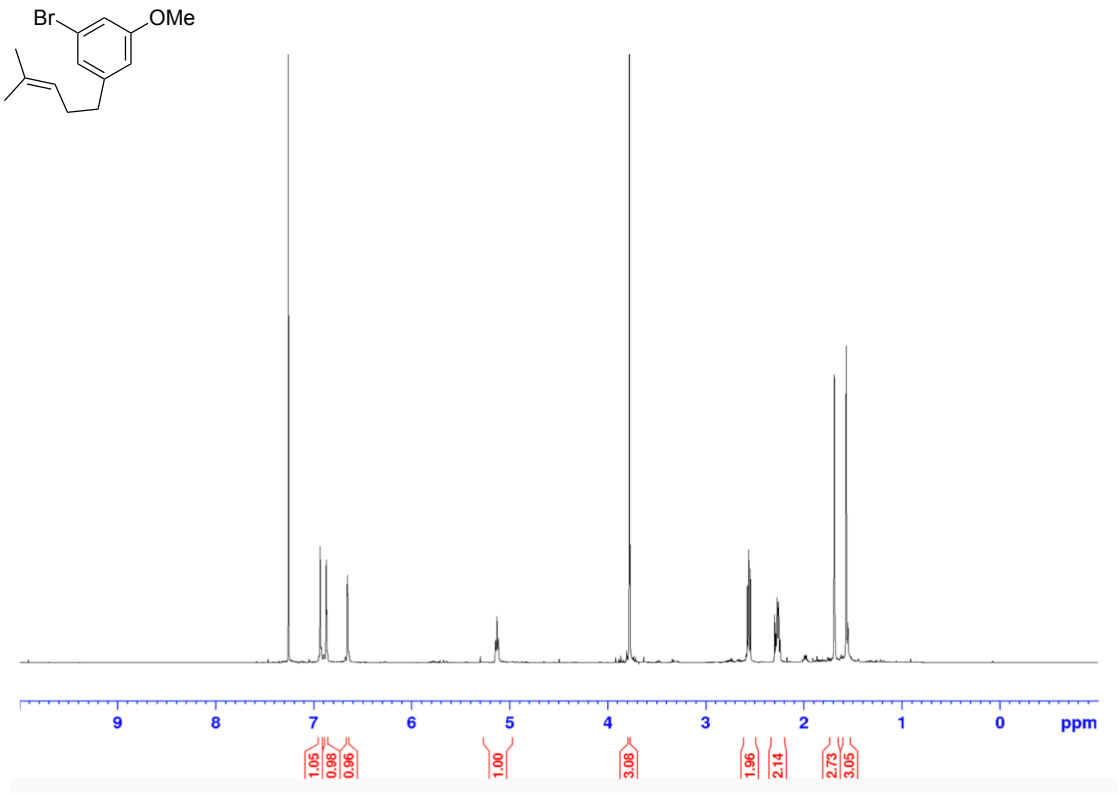
^{1}H NMR spectrum of **34a** ($CDCl_3$, 500 MHz)



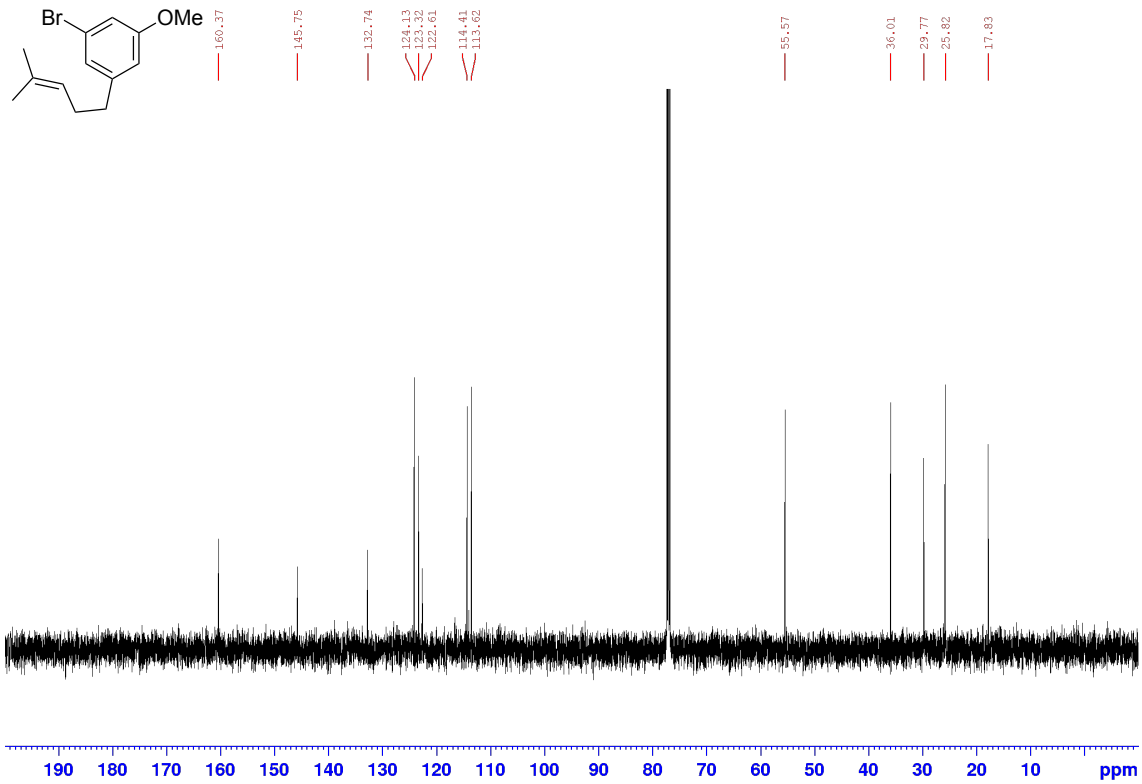
^{13}C NMR spectrum of **34a** ($CDCl_3$, 125 MHz)



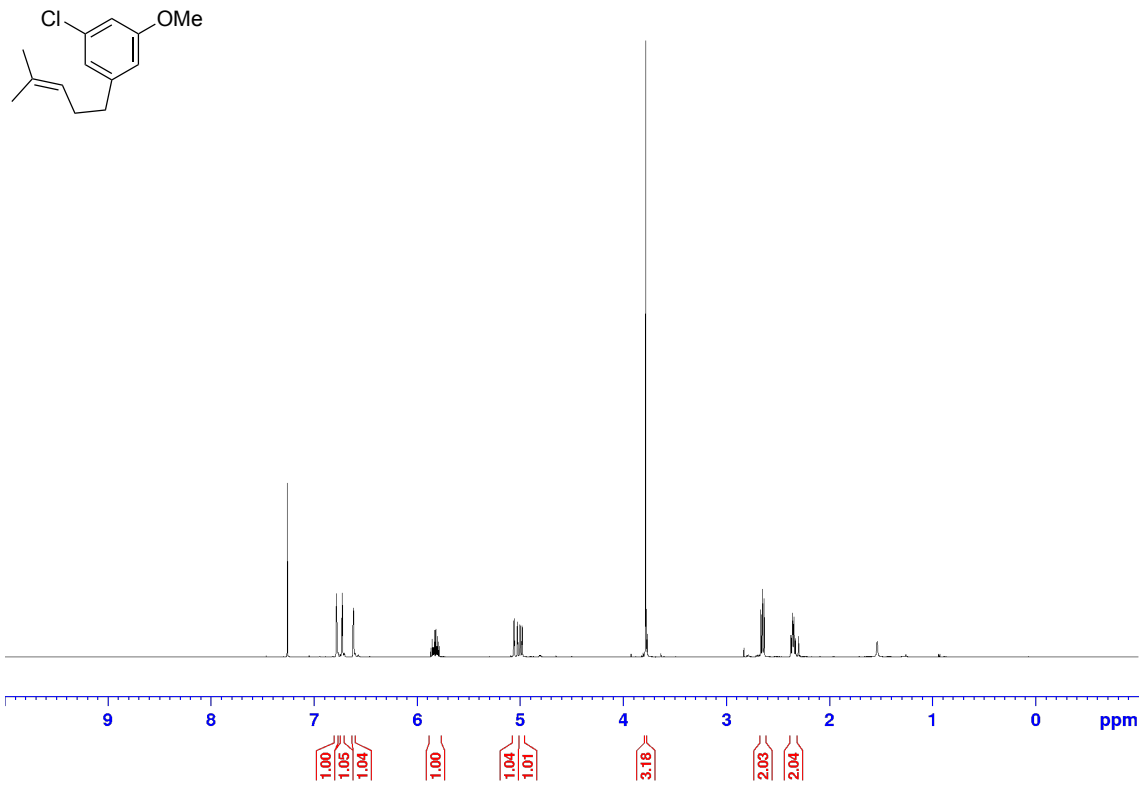
^{1}H NMR spectrum of **34b** ($CDCl_3$, 500 MHz)



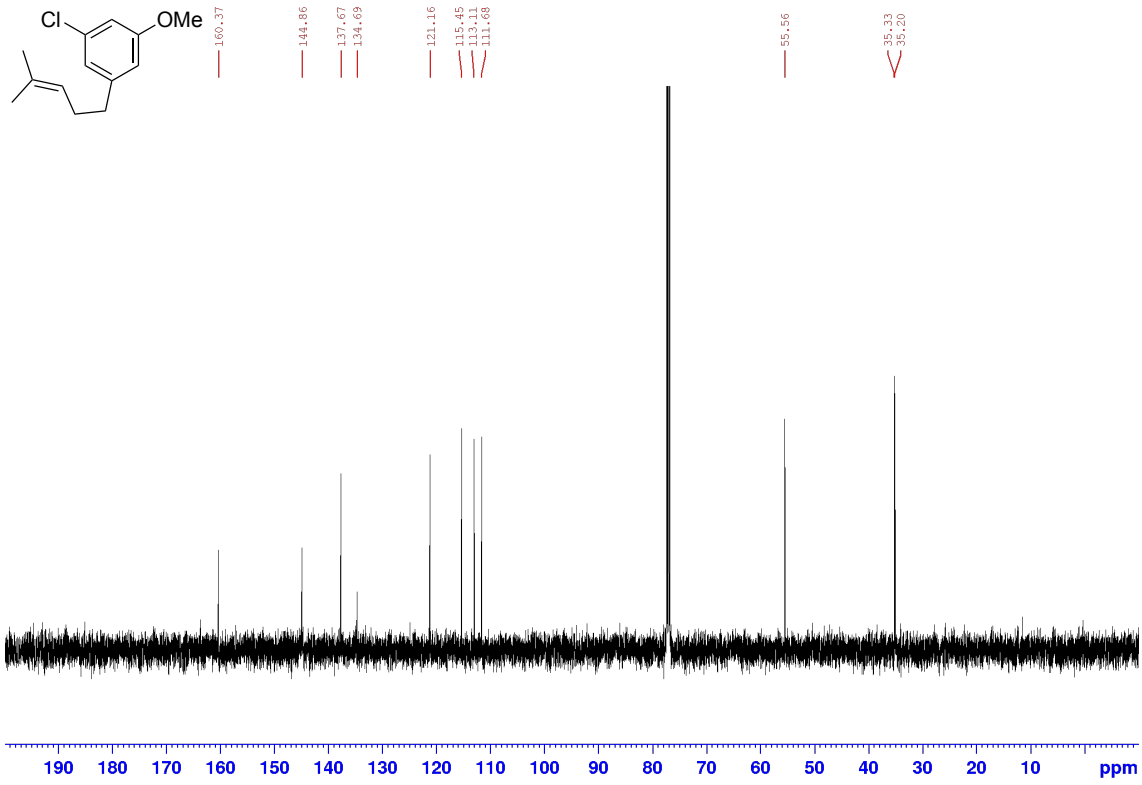
^{13}C NMR spectrum of **34b** ($CDCl_3$, 125 MHz)



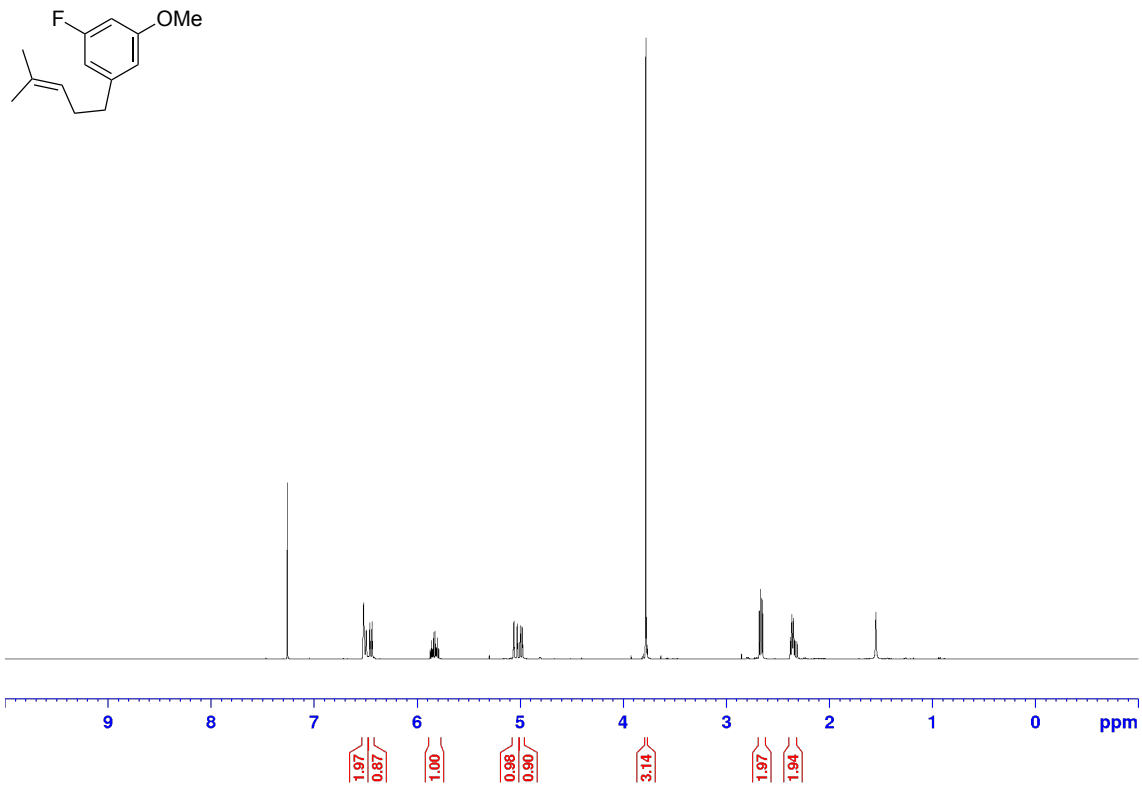
^{1}H NMR spectrum of **34c** ($CDCl_3$, 500 MHz)



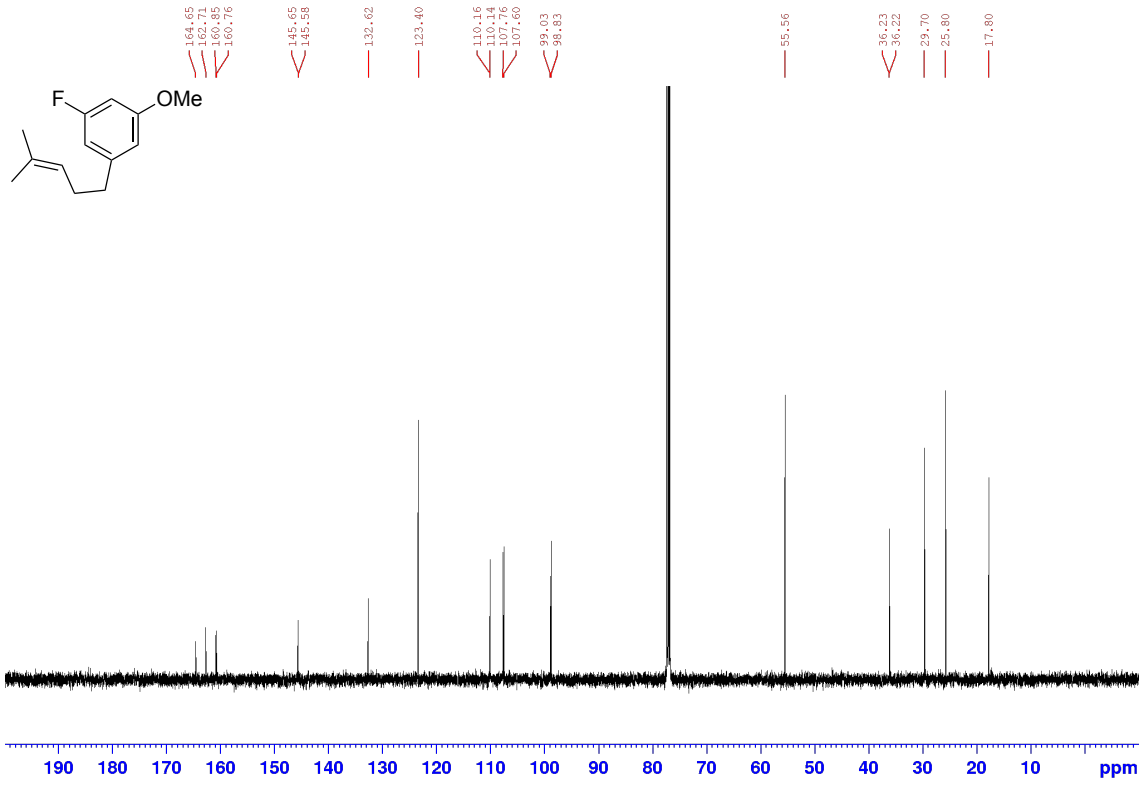
^{13}C NMR spectrum of **34c** ($CDCl_3$, 125 MHz)



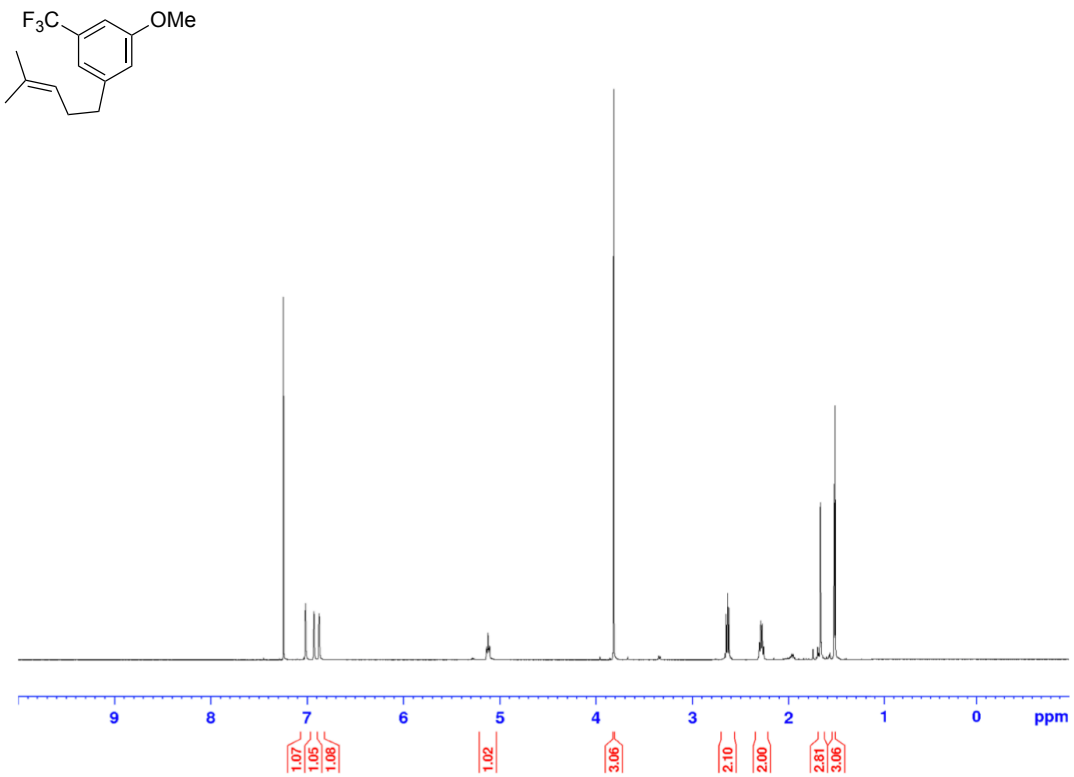
^{1}H NMR spectrum of **34d** ($CDCl_3$, 500 MHz)



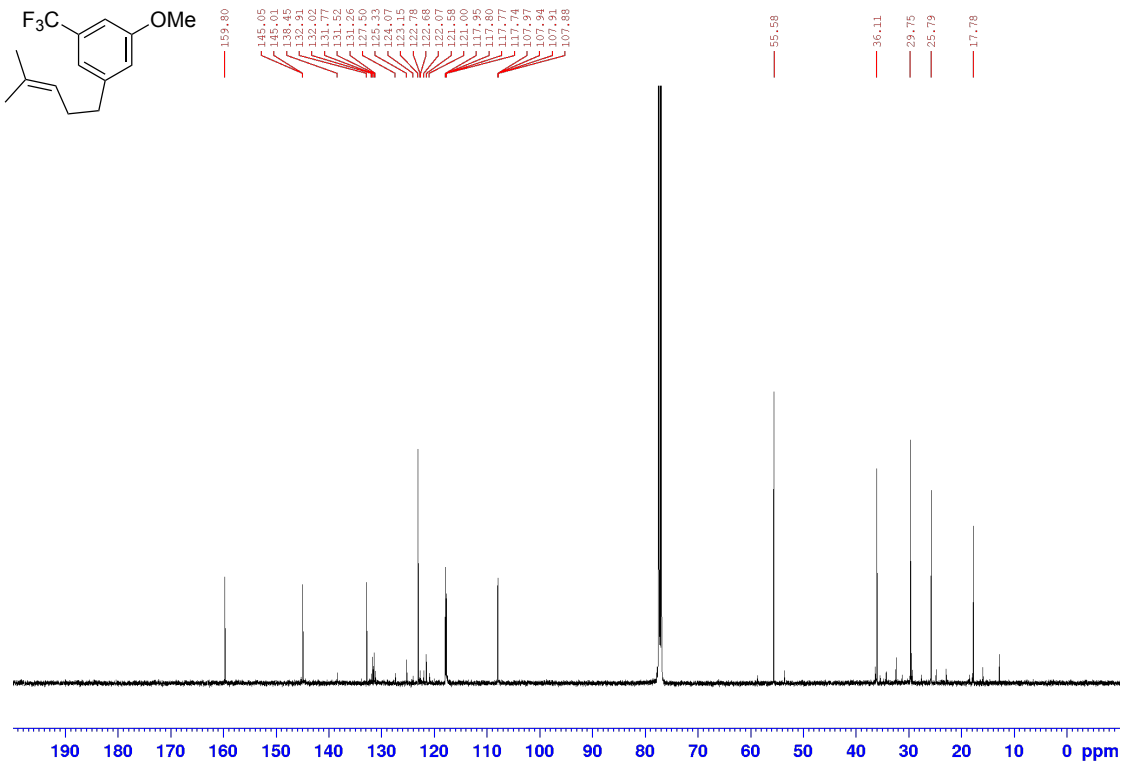
^{13}C NMR spectrum of **34d** ($CDCl_3$, 125 MHz)



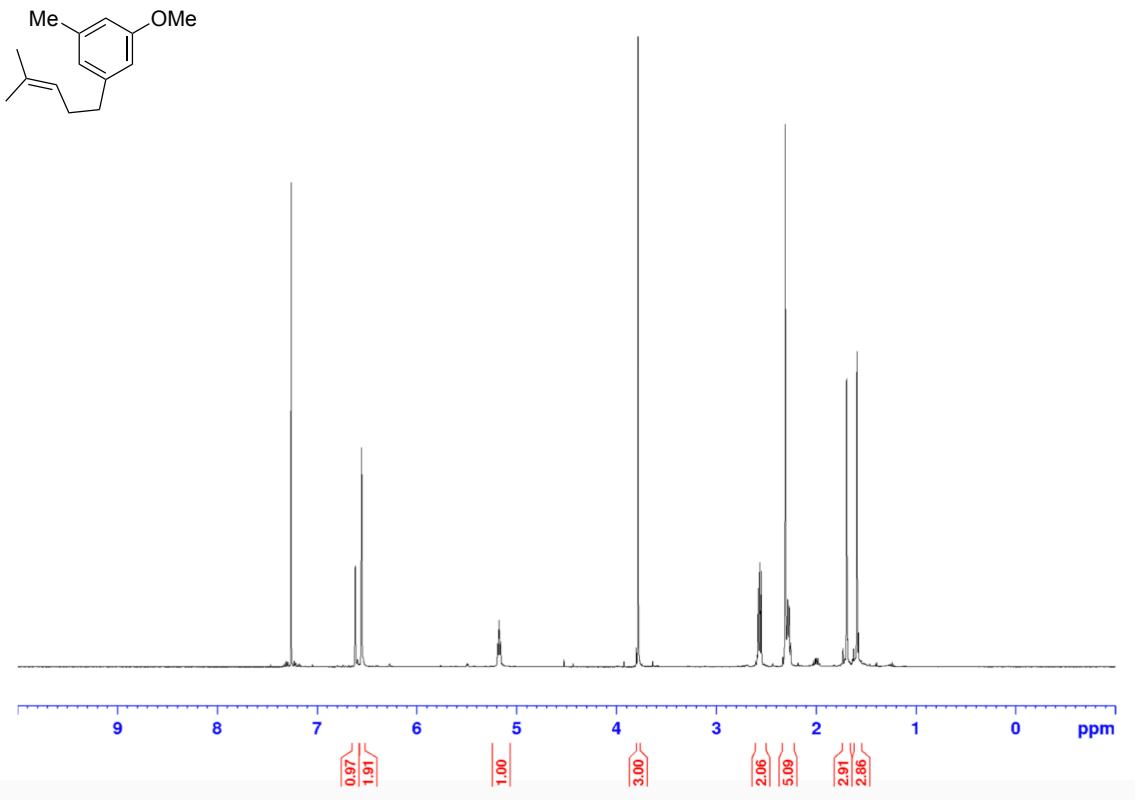
^{1}H NMR spectrum of **34e** ($CDCl_3$, 500 MHz)



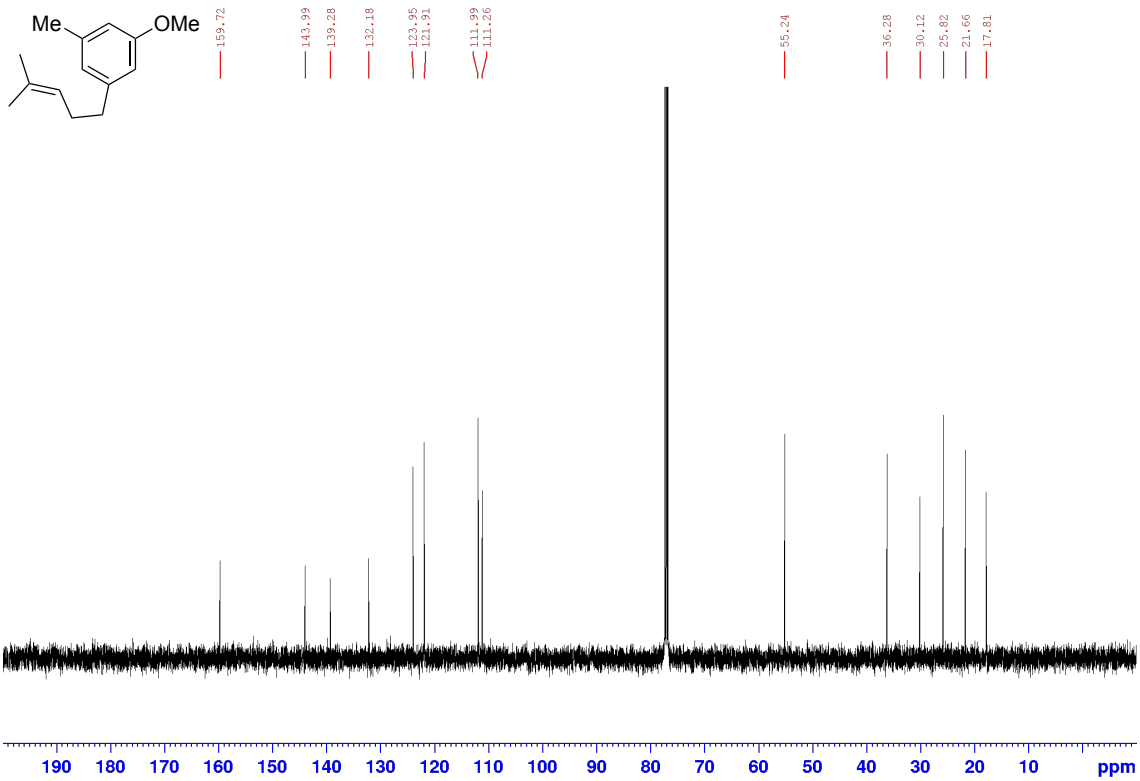
^{13}C NMR spectrum of **34e** ($CDCl_3$, 125 MHz)



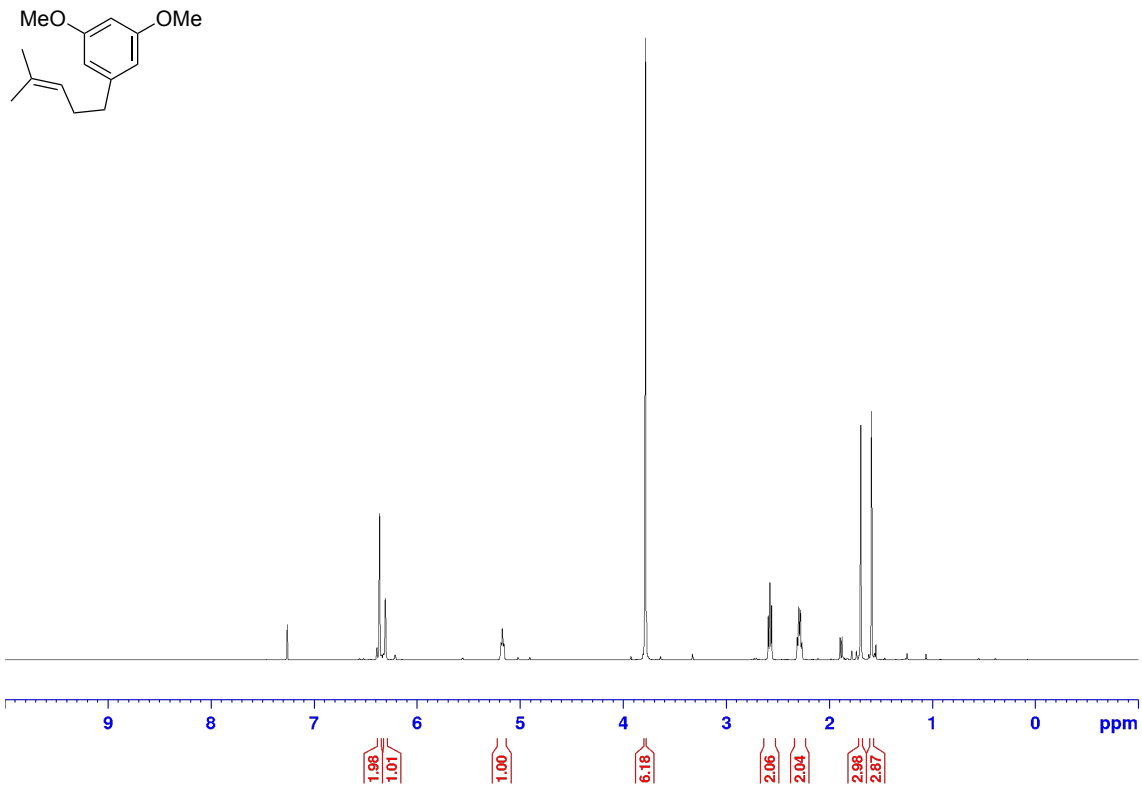
^{1}H NMR spectrum of **34f** ($CDCl_3$, 500 MHz)



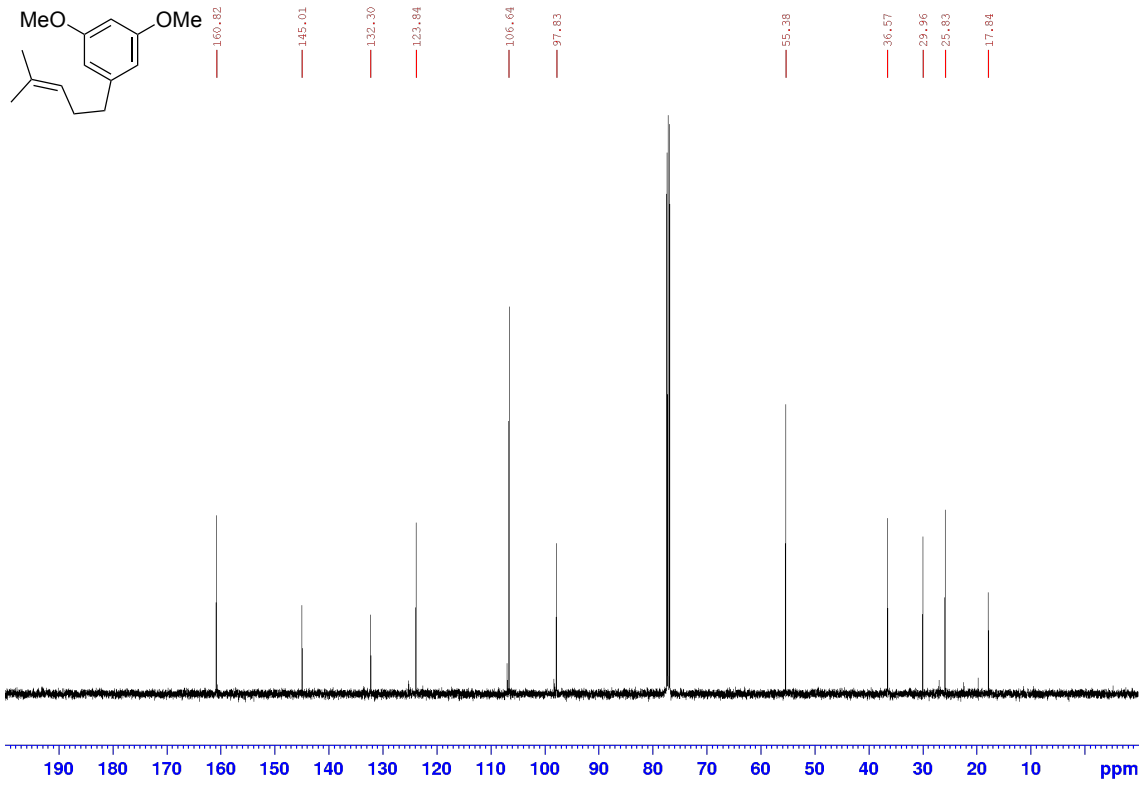
^{13}C NMR spectrum of **34f** ($CDCl_3$, 125 MHz)



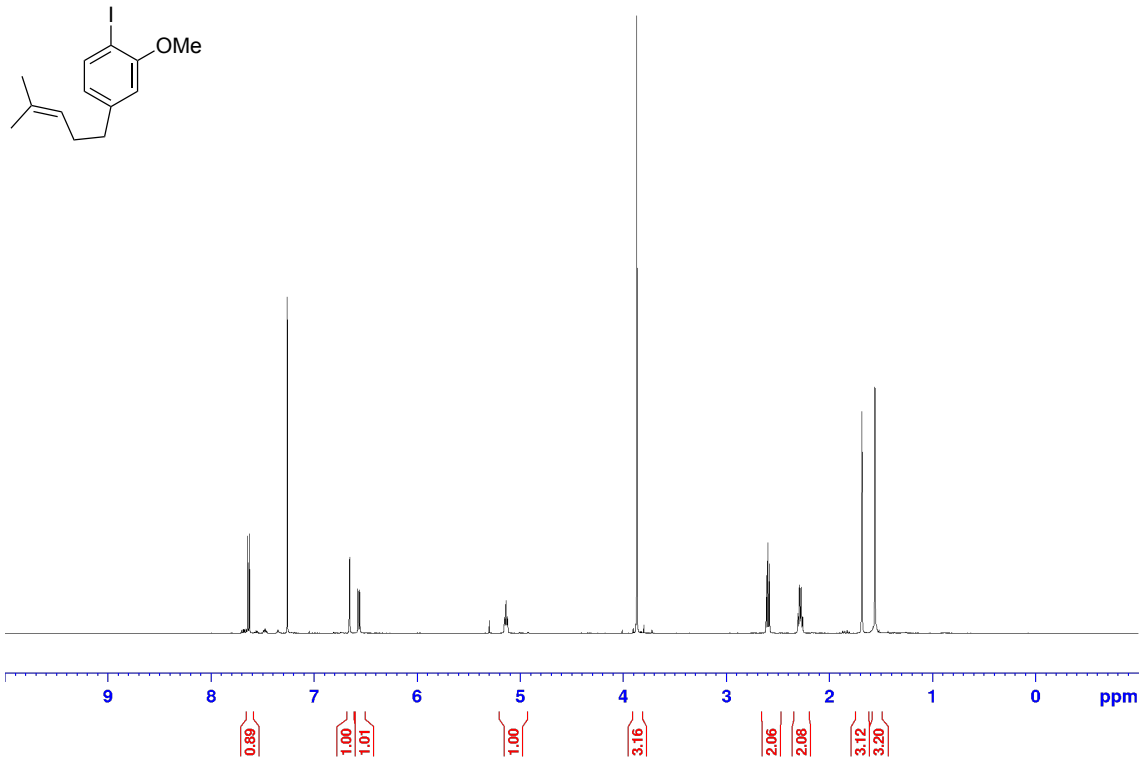
^{1}H NMR spectrum of **34g** ($CDCl_3$, 500 MHz)



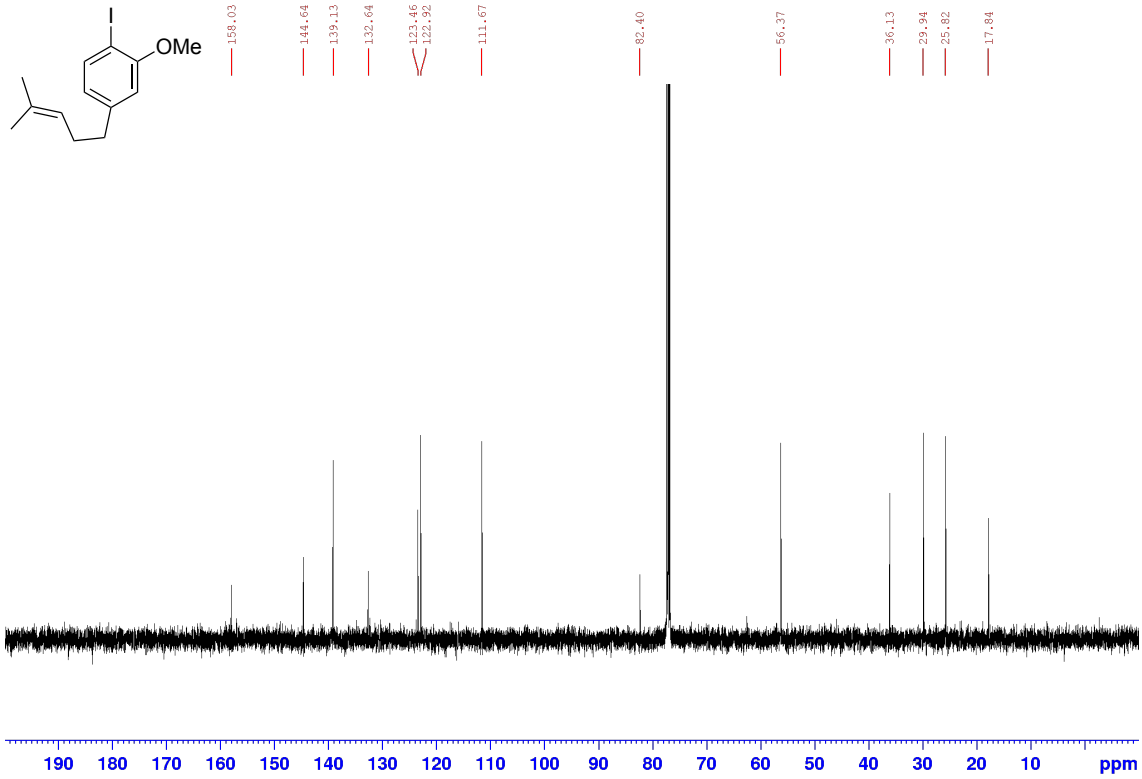
^{13}C NMR spectrum of **34g** ($CDCl_3$, 125 MHz)



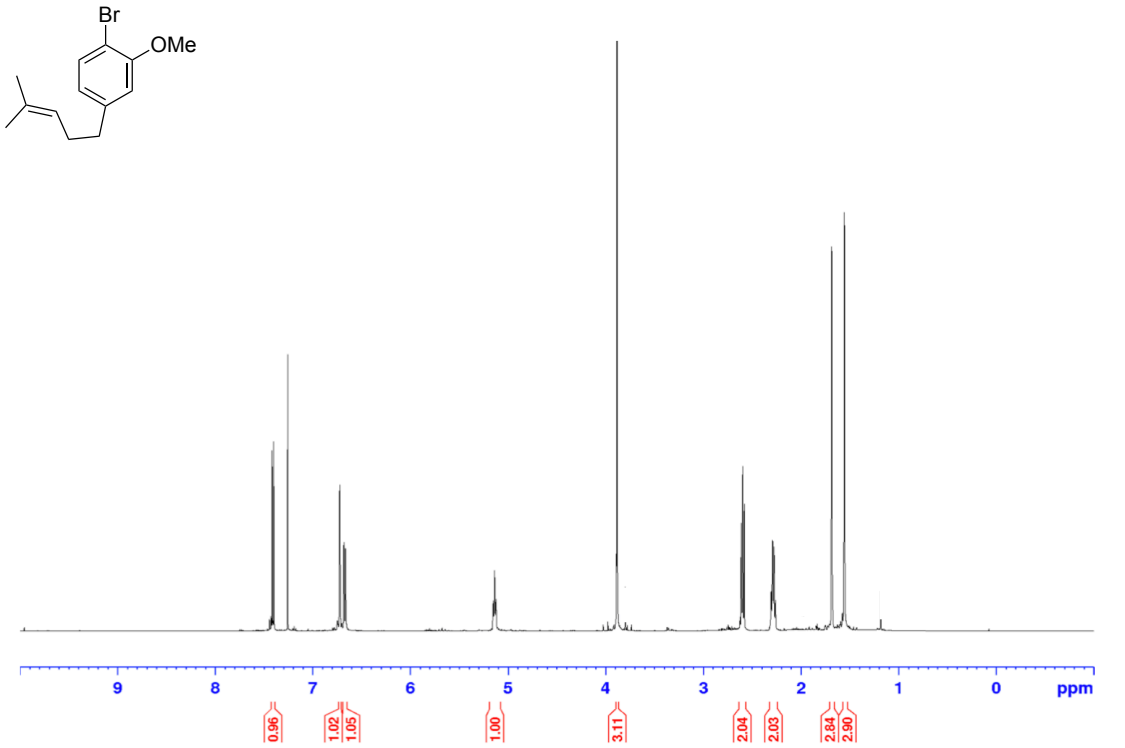
^{1}H NMR spectrum of **34h** ($CDCl_3$, 500 MHz)



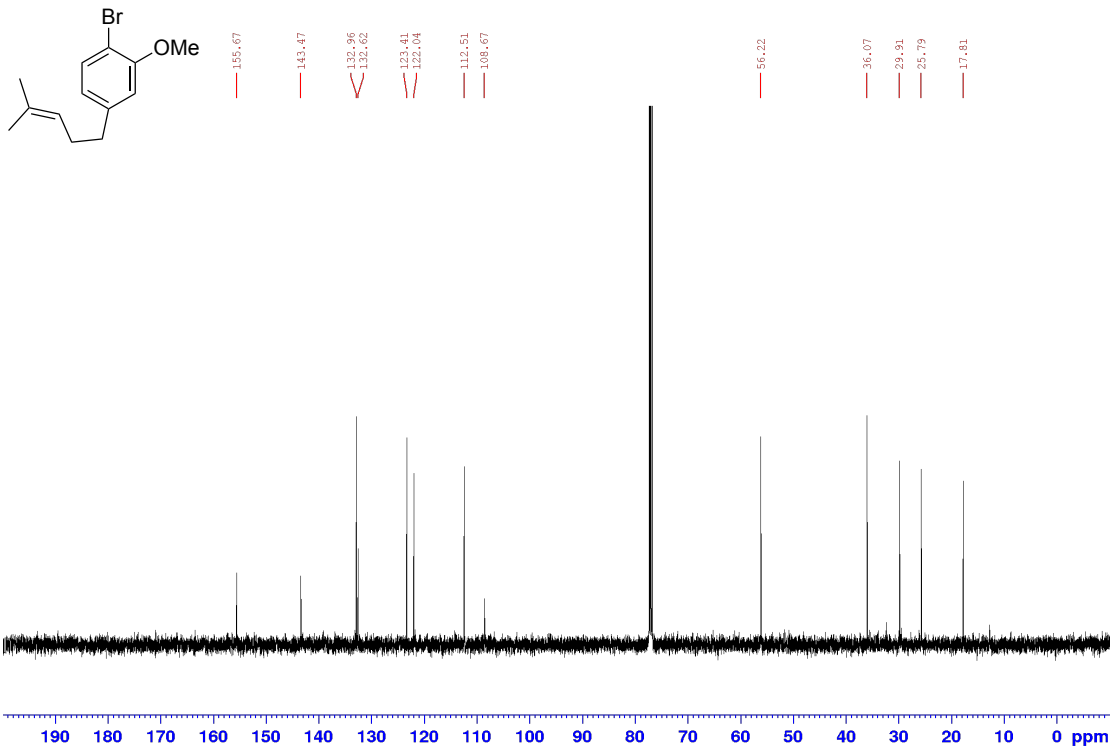
^{13}C NMR spectrum of **34h** ($CDCl_3$, 125 MHz)



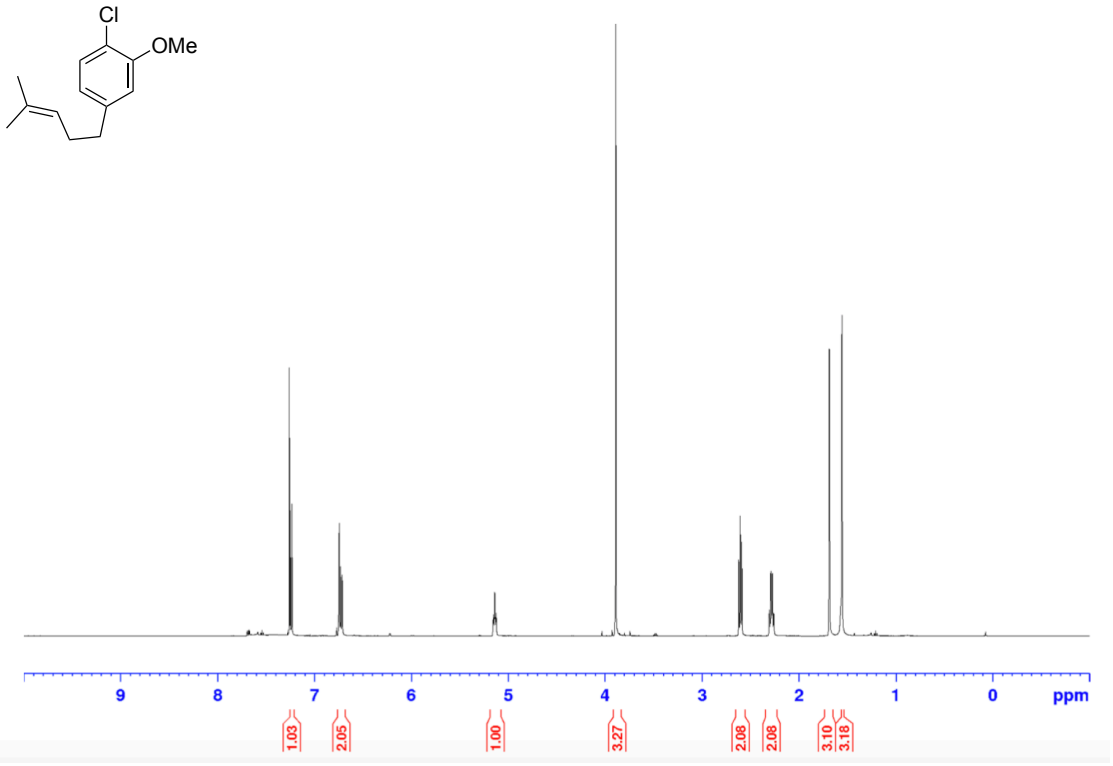
^{1}H NMR spectrum of **34i** ($CDCl_3$, 500 MHz)



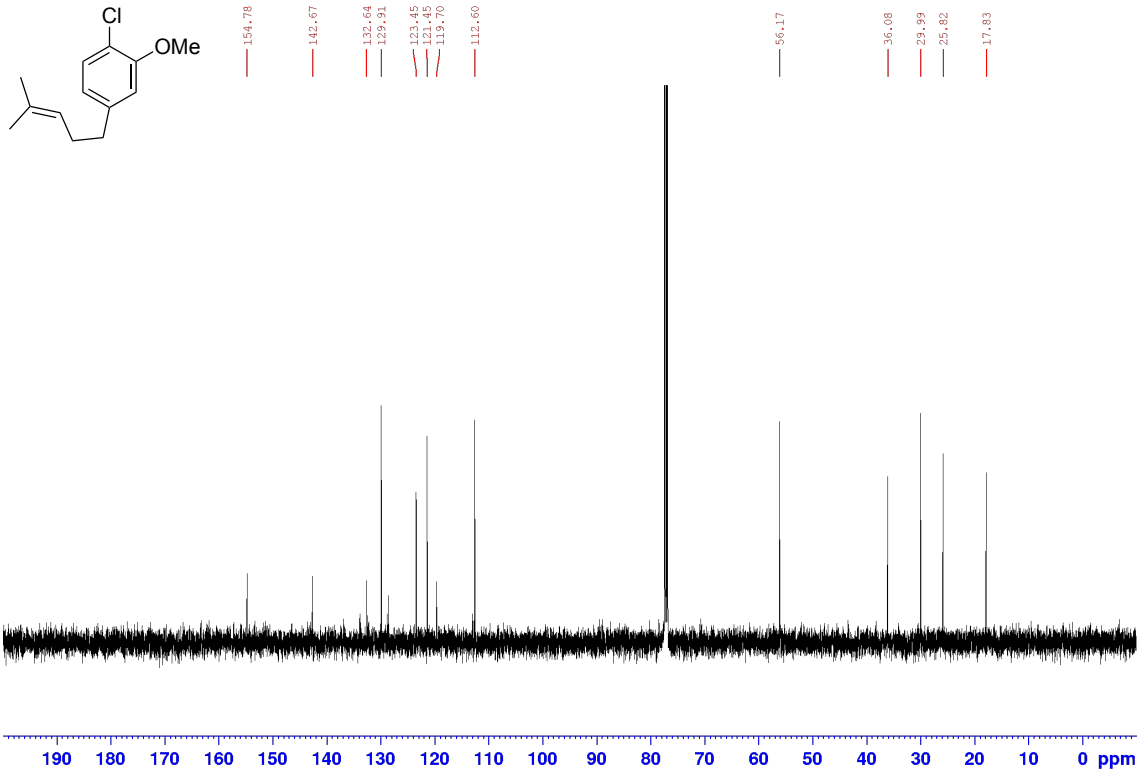
^{13}C NMR spectrum of **34i** ($CDCl_3$, 125 MHz)



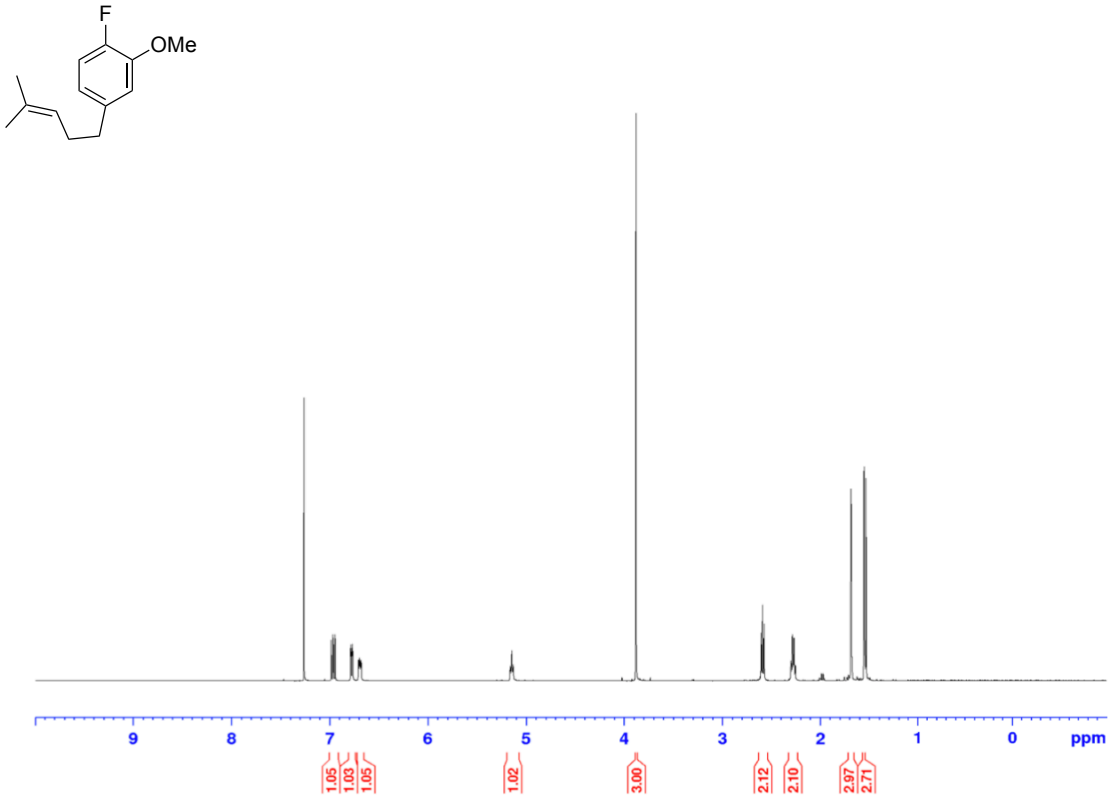
^{1}H NMR spectrum of **34j** ($CDCl_3$, 500 MHz)



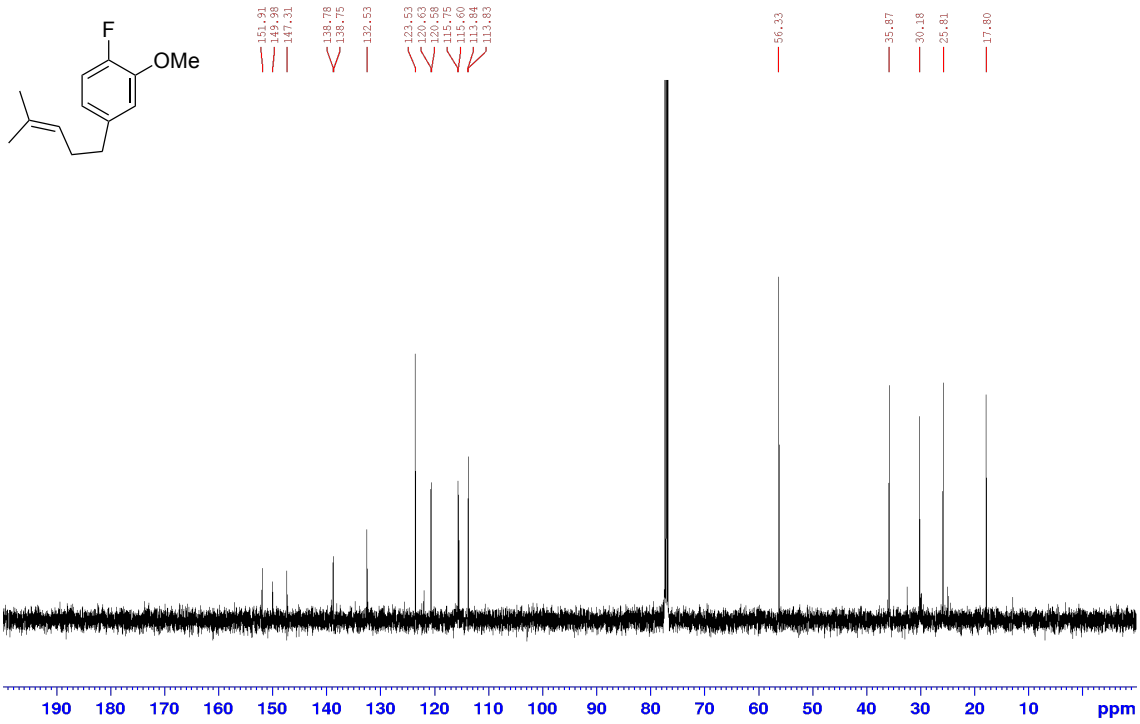
^{13}C NMR spectrum of **34j** ($CDCl_3$, 125 MHz)



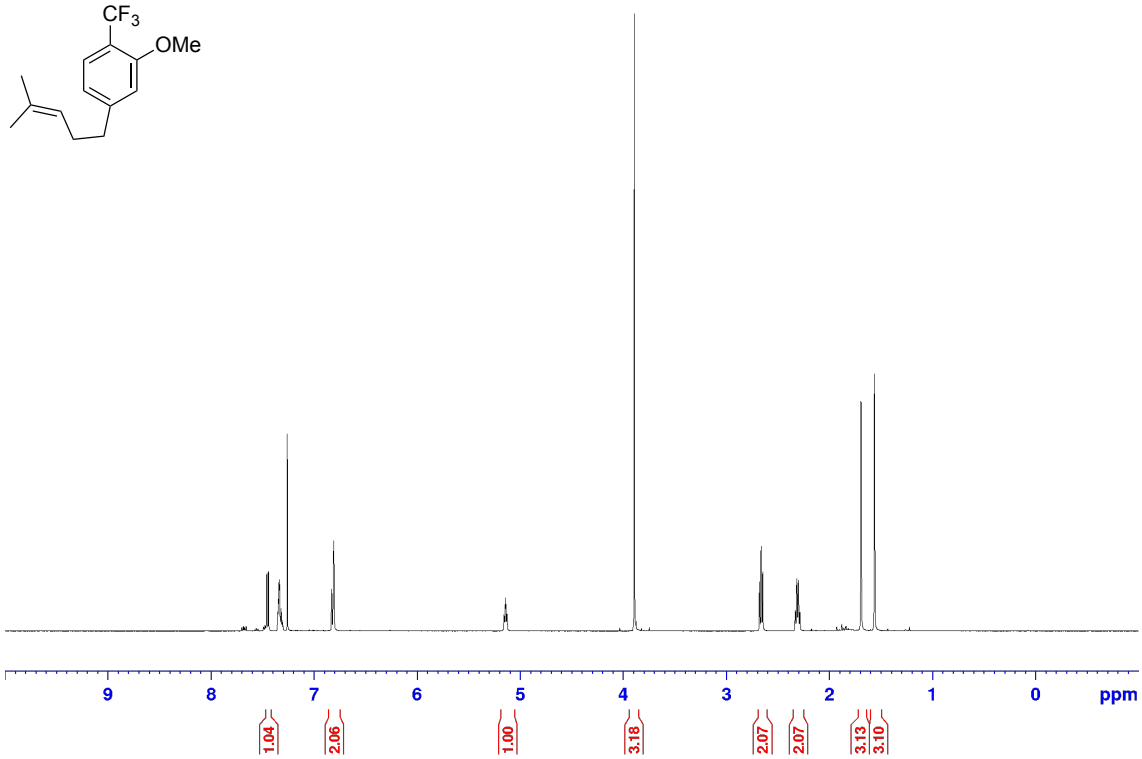
^{1}H NMR spectrum of **34k** ($CDCl_3$, 500 MHz)



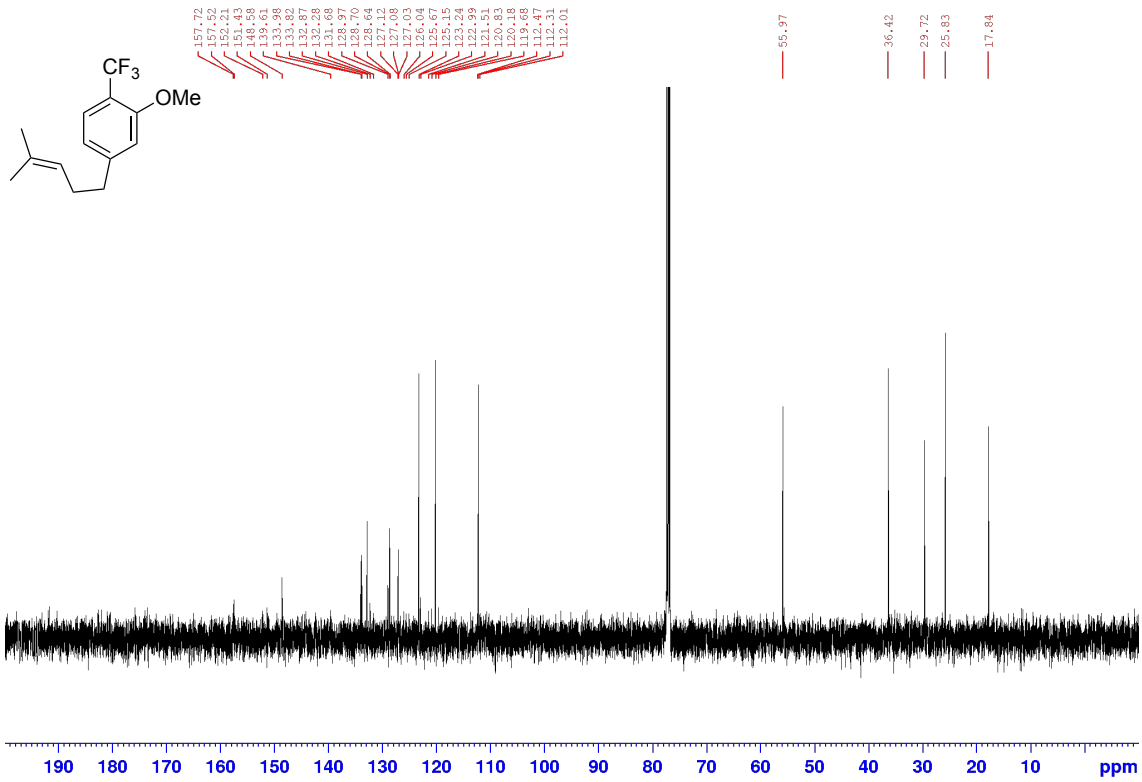
^{13}C NMR spectrum of **34k** ($CDCl_3$, 125 MHz)



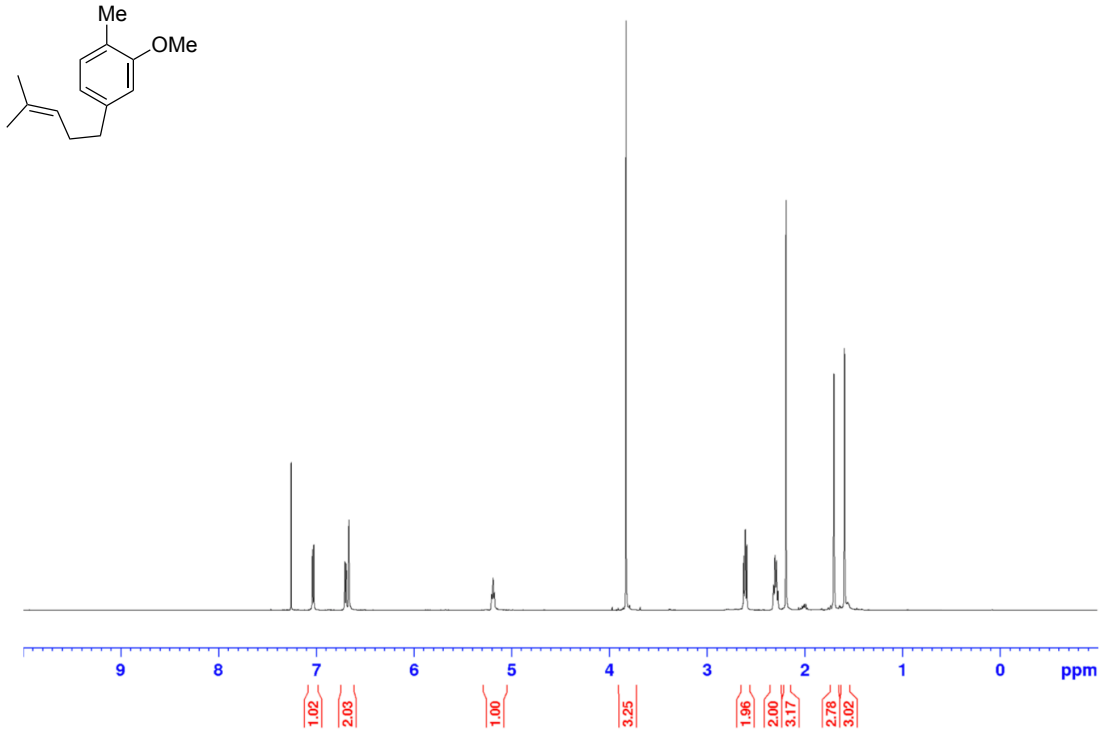
^{1}H NMR spectrum of **34l** ($CDCl_3$, 500 MHz)



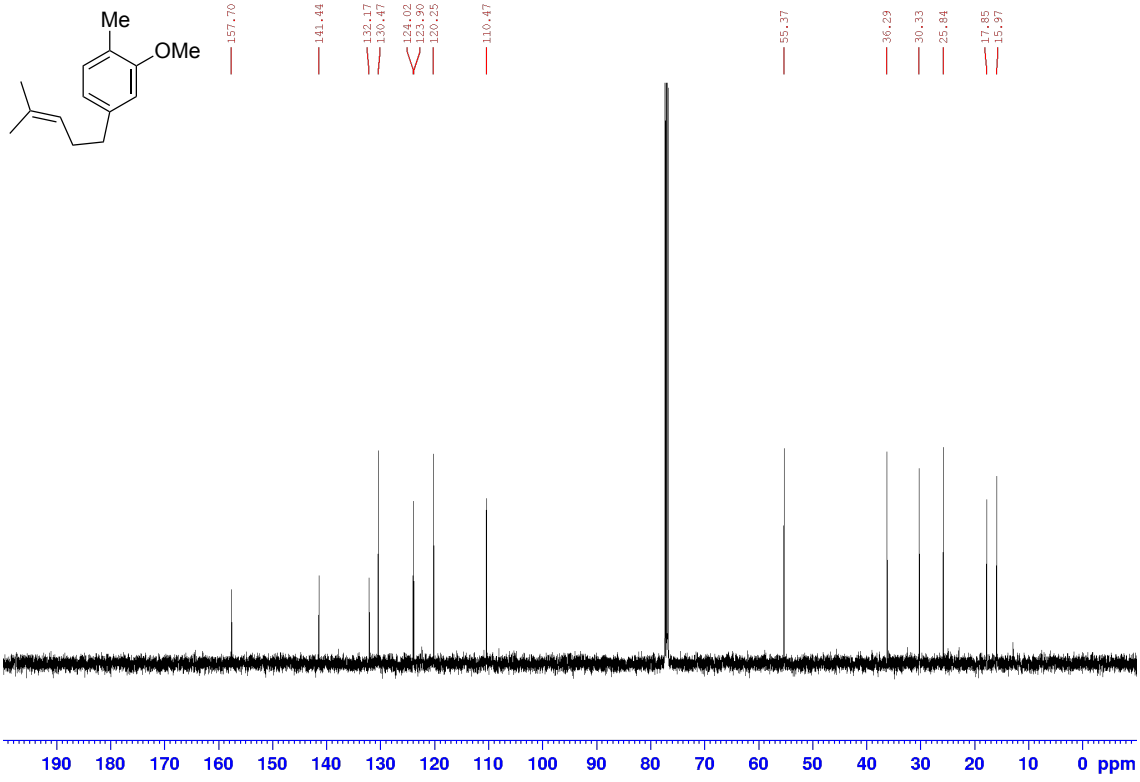
^{13}C NMR spectrum of **34l** ($CDCl_3$, 125 MHz)



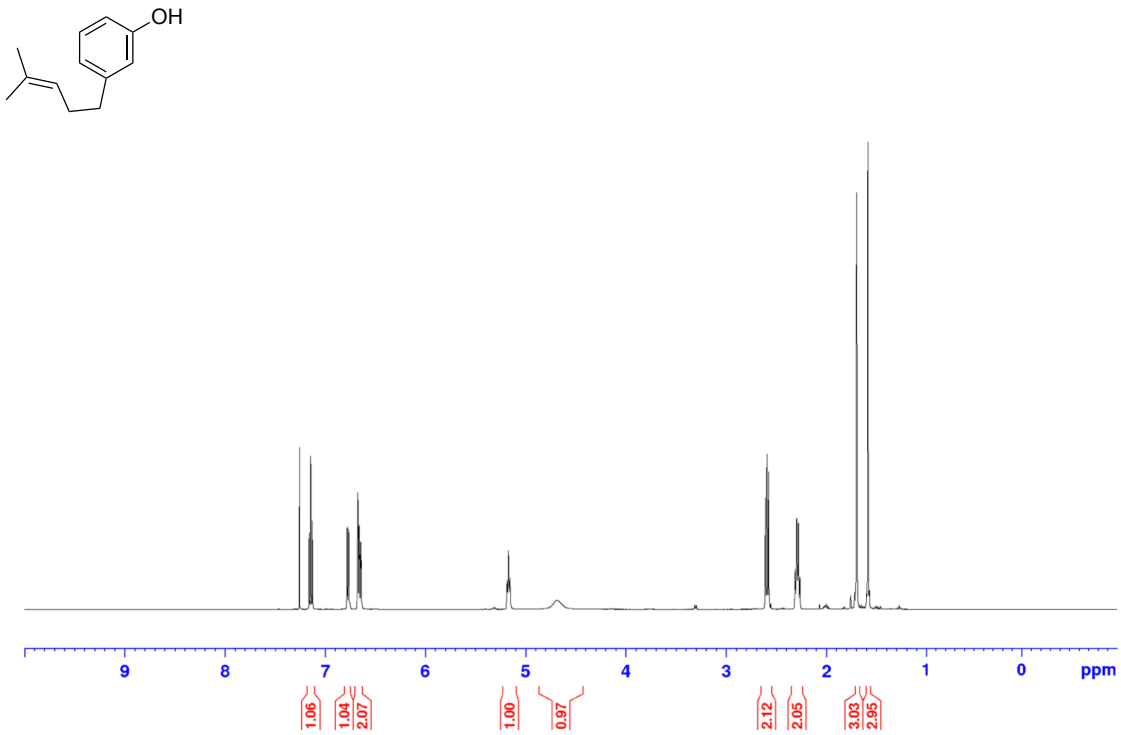
^{1}H NMR spectrum of **34m** ($CDCl_3$, 500 MHz)



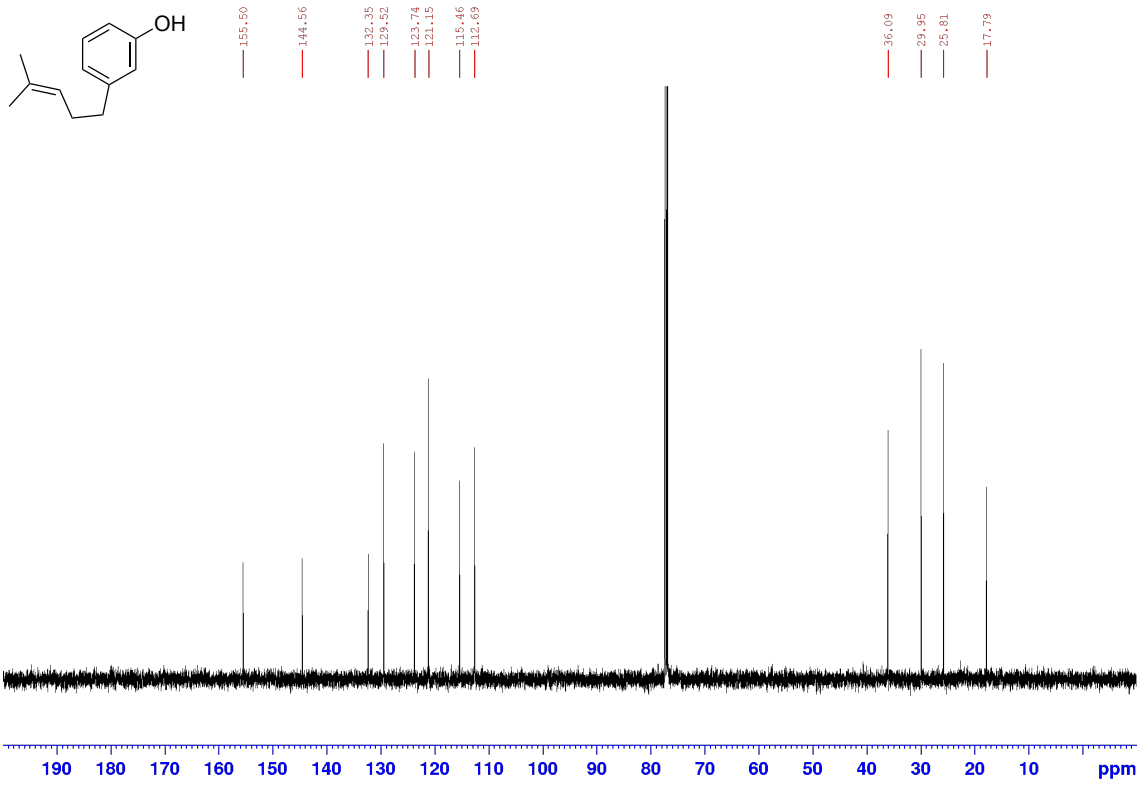
^{13}C NMR spectrum of **34m** ($CDCl_3$, 125 MHz)



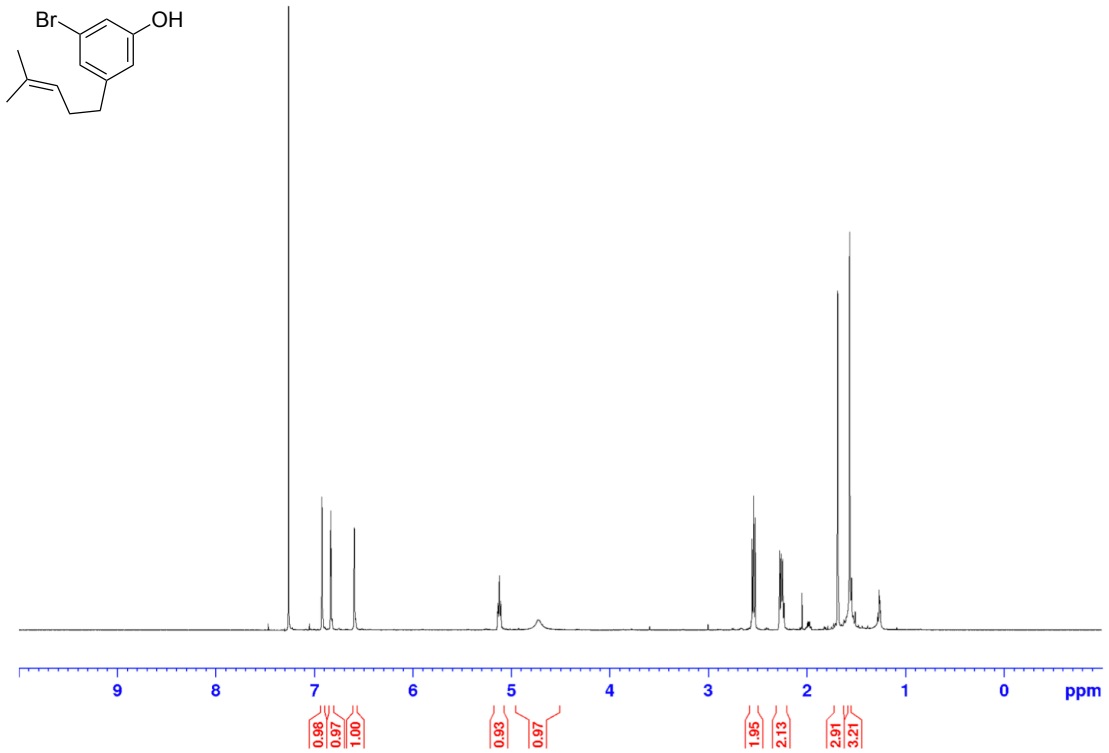
^{1}H NMR spectrum of **7a** ($CDCl_3$, 500 MHz)



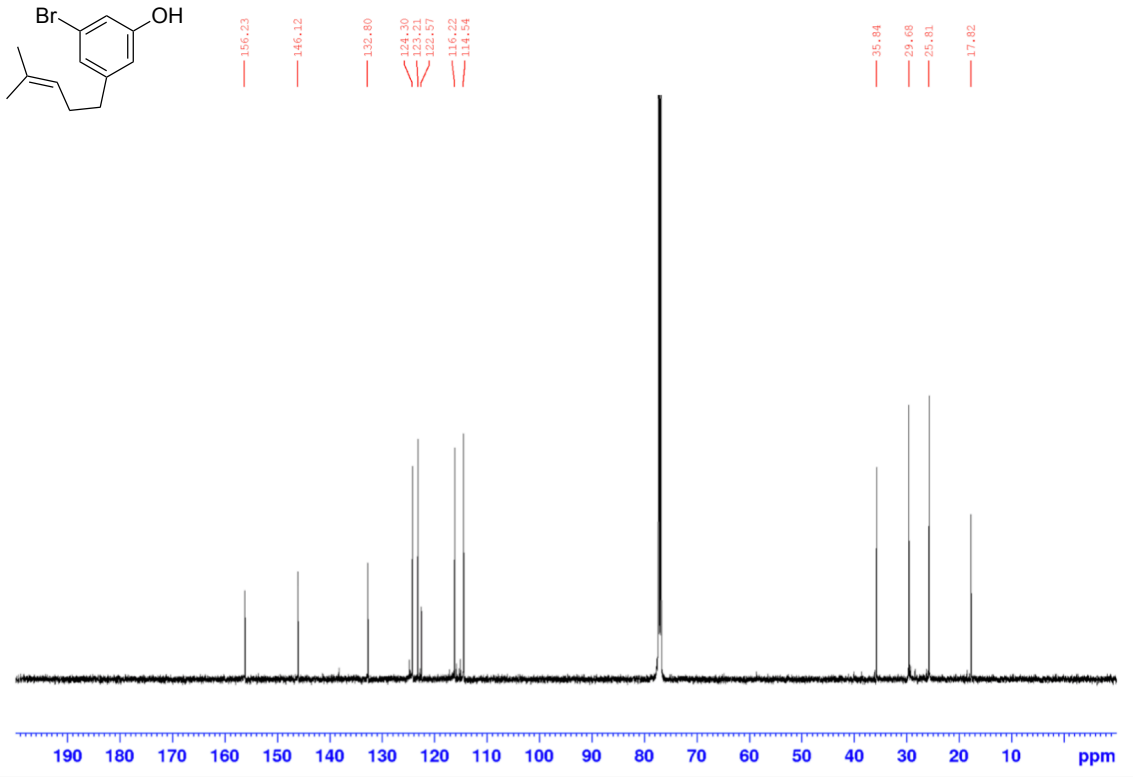
^{13}C NMR spectrum of **7a** ($CDCl_3$, 125 MHz)



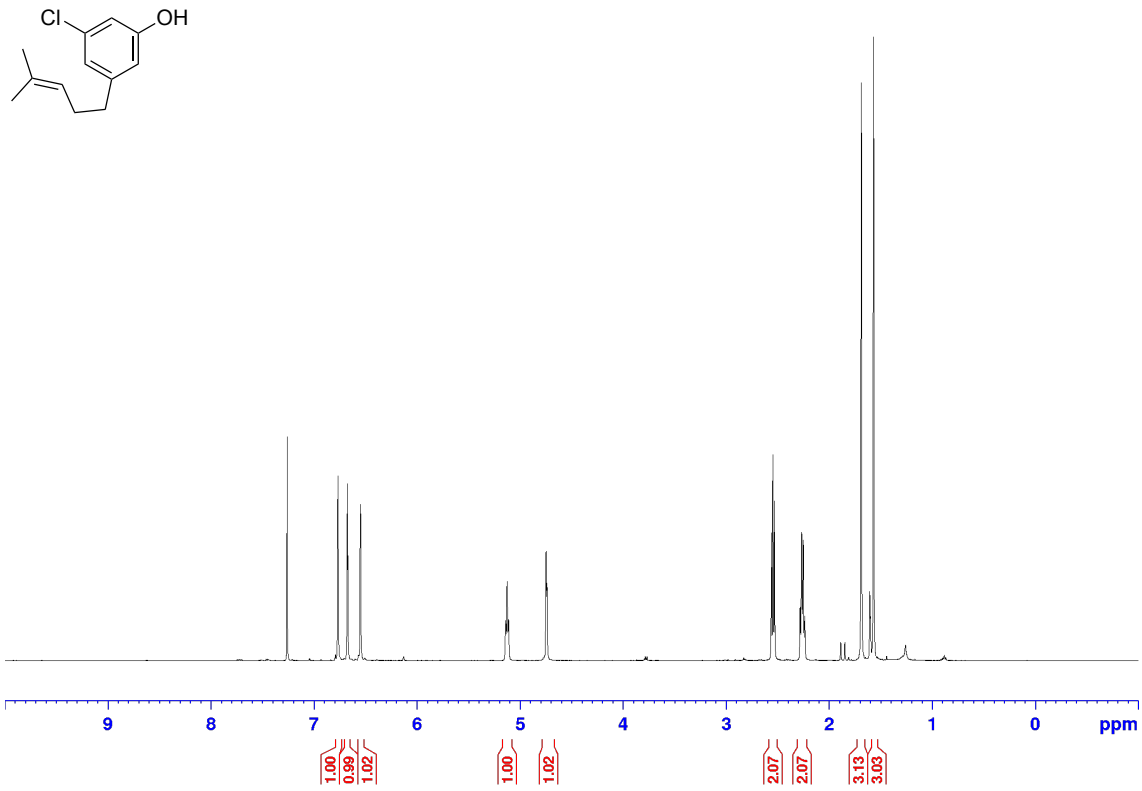
^{1}H NMR spectrum of **7b** ($CDCl_3$, 500 MHz)



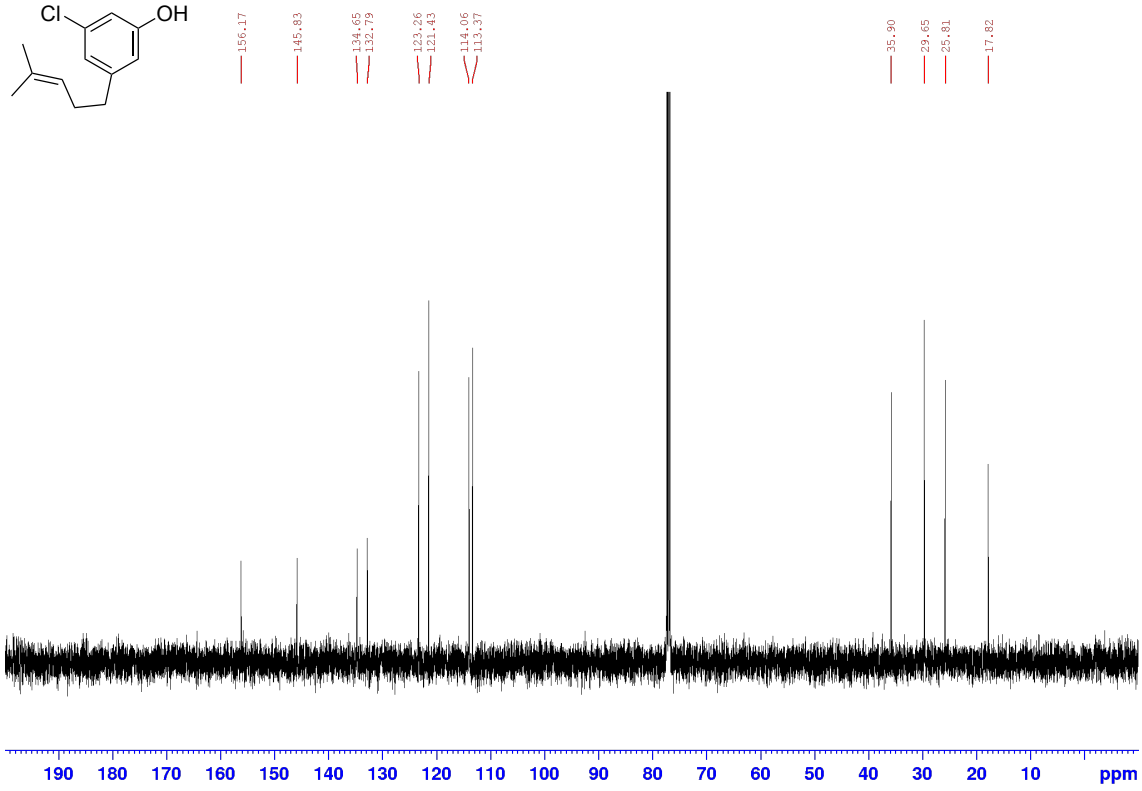
^{13}C NMR spectrum of **7b** ($CDCl_3$, 125 MHz)



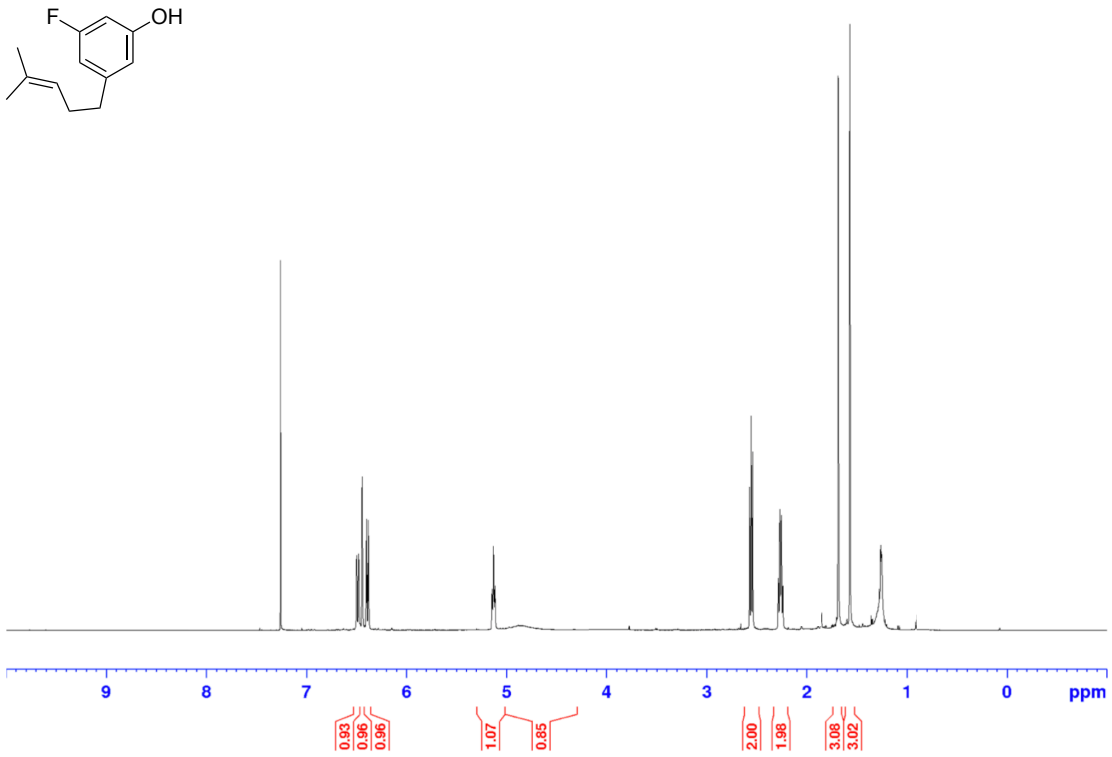
^{1}H NMR spectrum of **7c** ($CDCl_3$, 500 MHz)



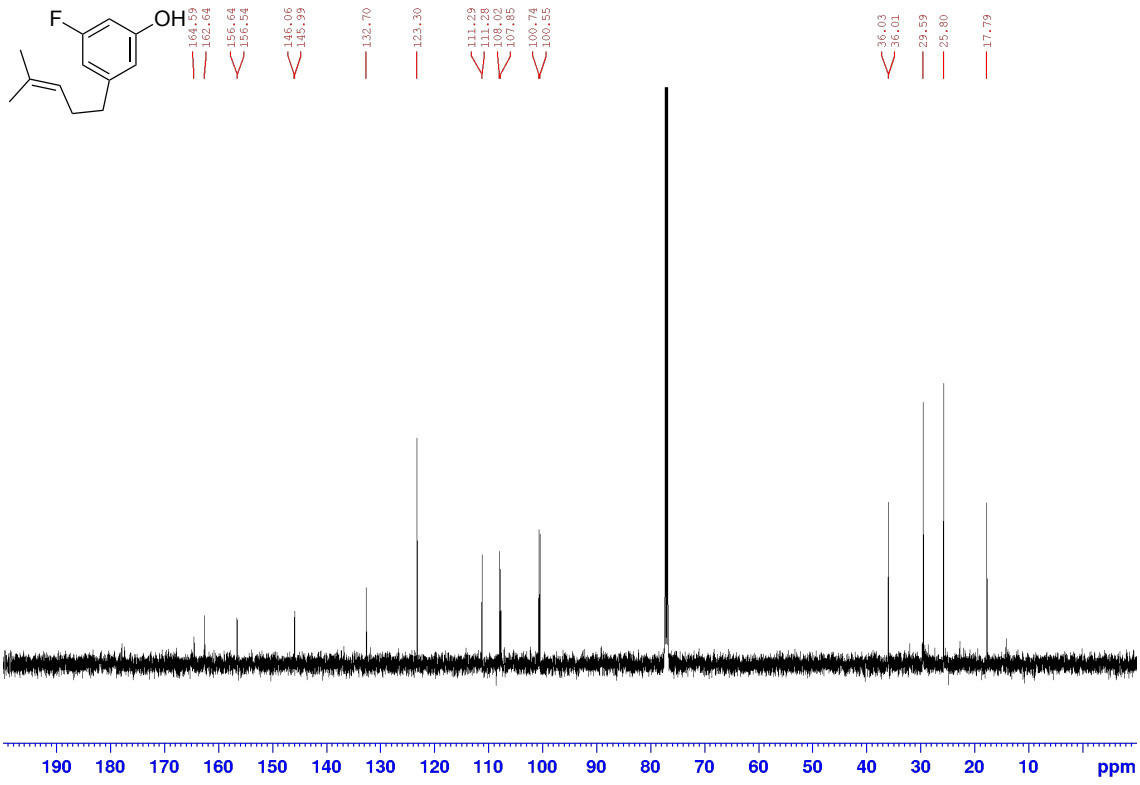
^{13}C NMR spectrum of **7c** ($CDCl_3$, 125 MHz)



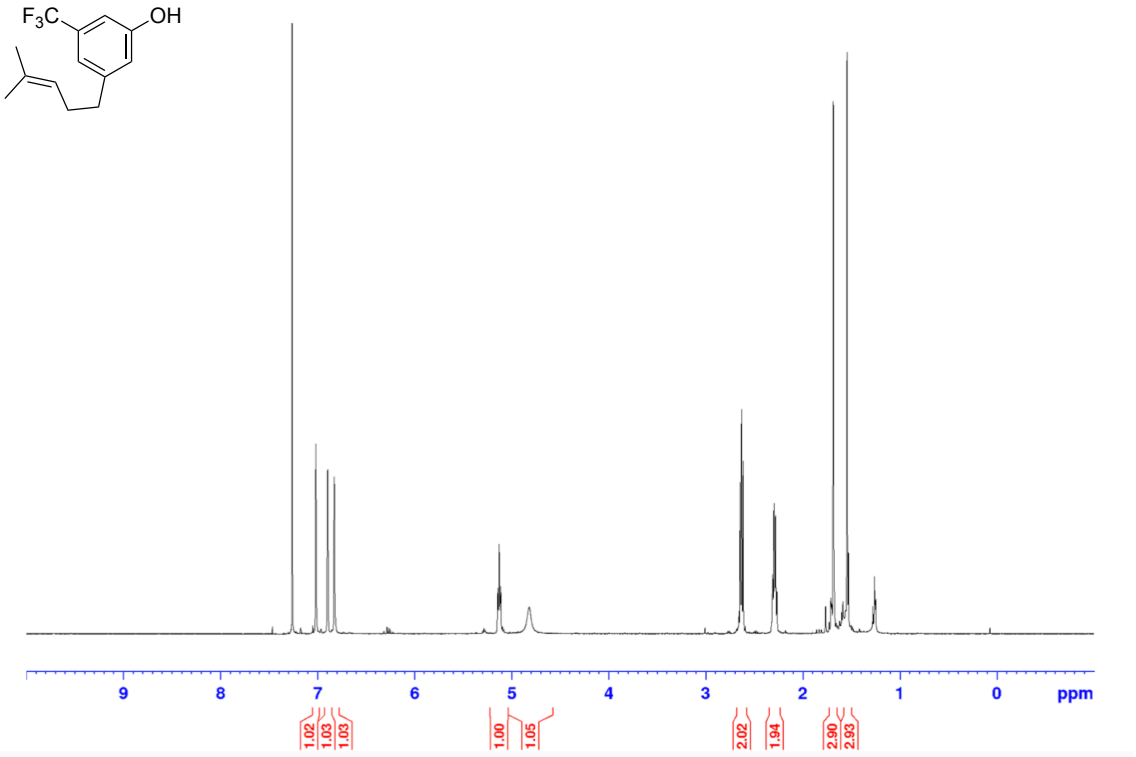
^{1}H NMR spectrum of **7d** ($CDCl_3$, 500 MHz)



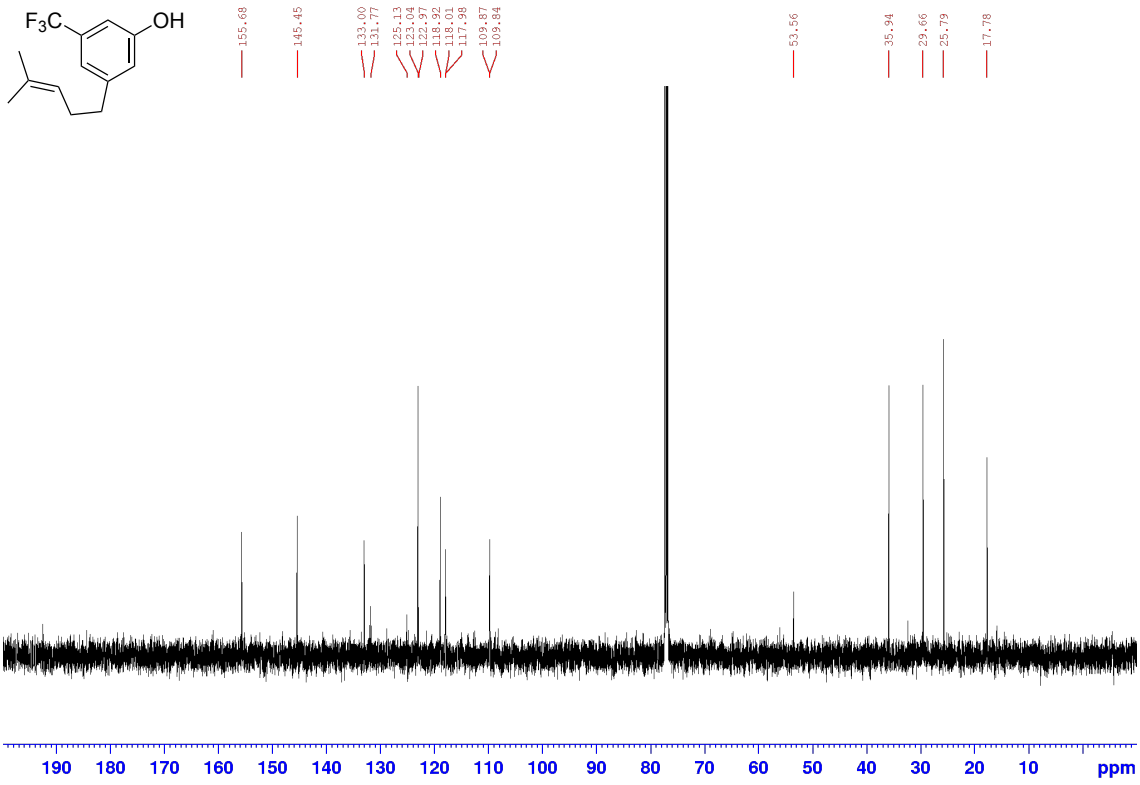
^{13}C NMR spectrum of **7d** ($CDCl_3$, 125 MHz)



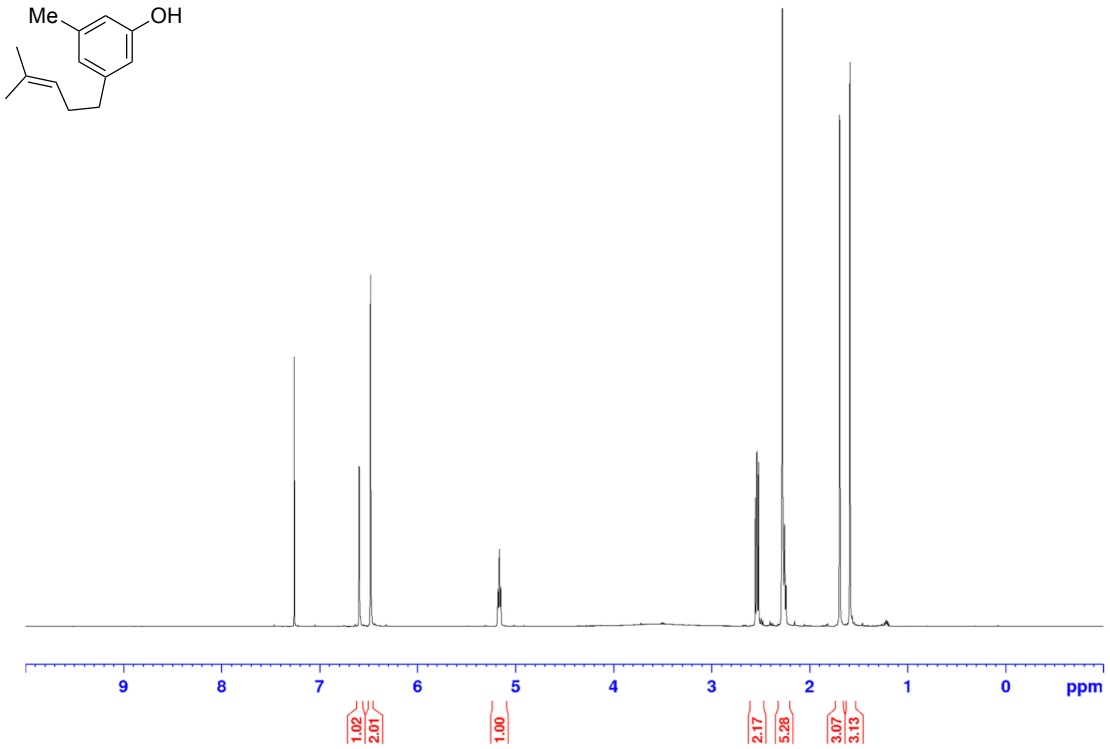
^{1}H NMR spectrum of **7e** ($CDCl_3$, 500 MHz)



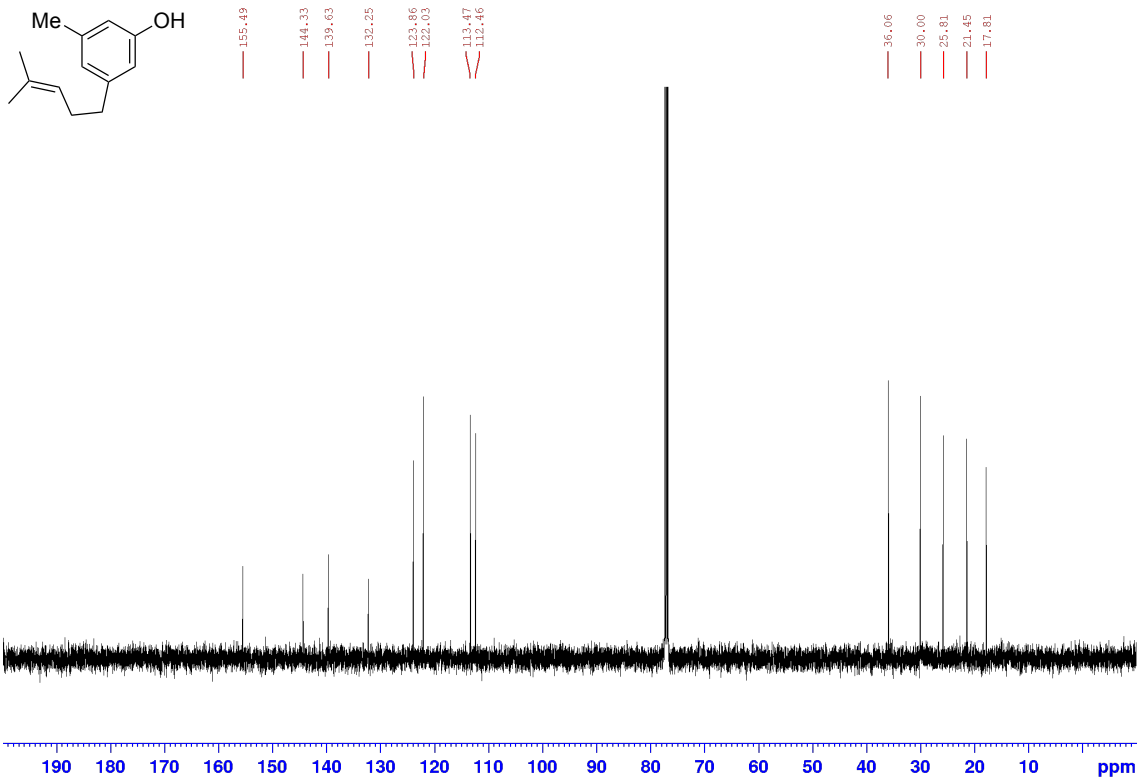
^{13}C NMR spectrum of **7e** ($CDCl_3$, 125 MHz)



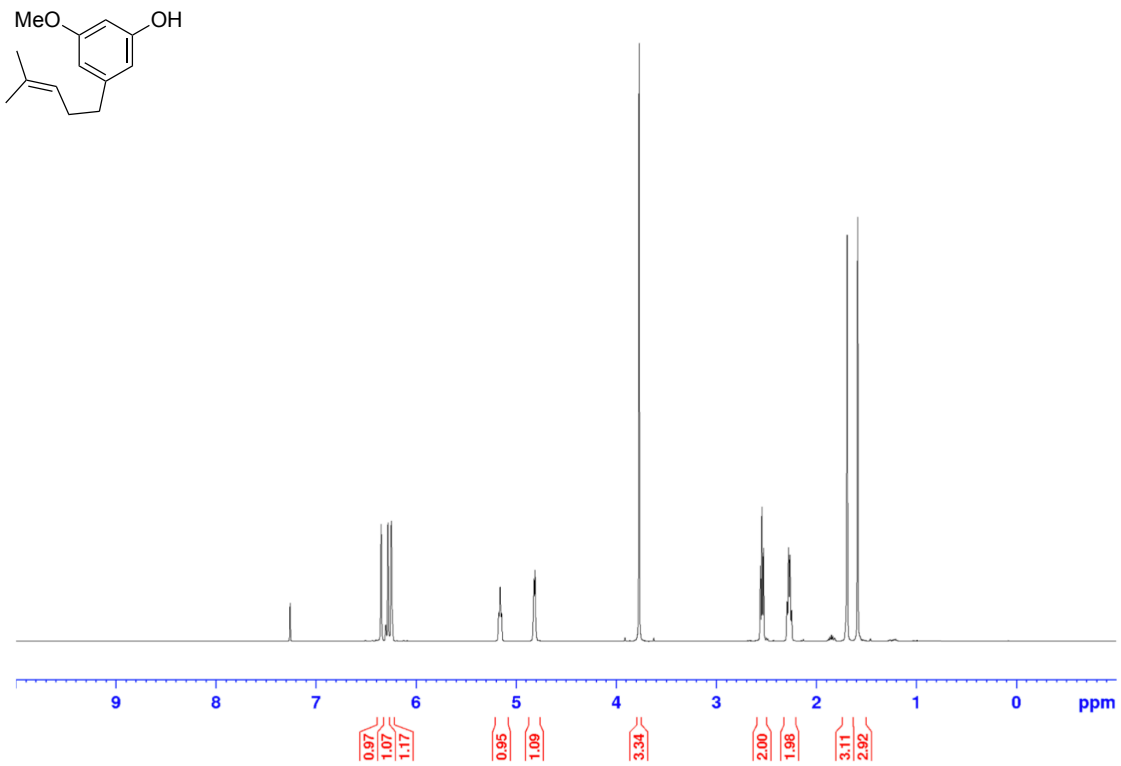
^{1}H NMR spectrum of **7f** ($CDCl_3$, 500 MHz)



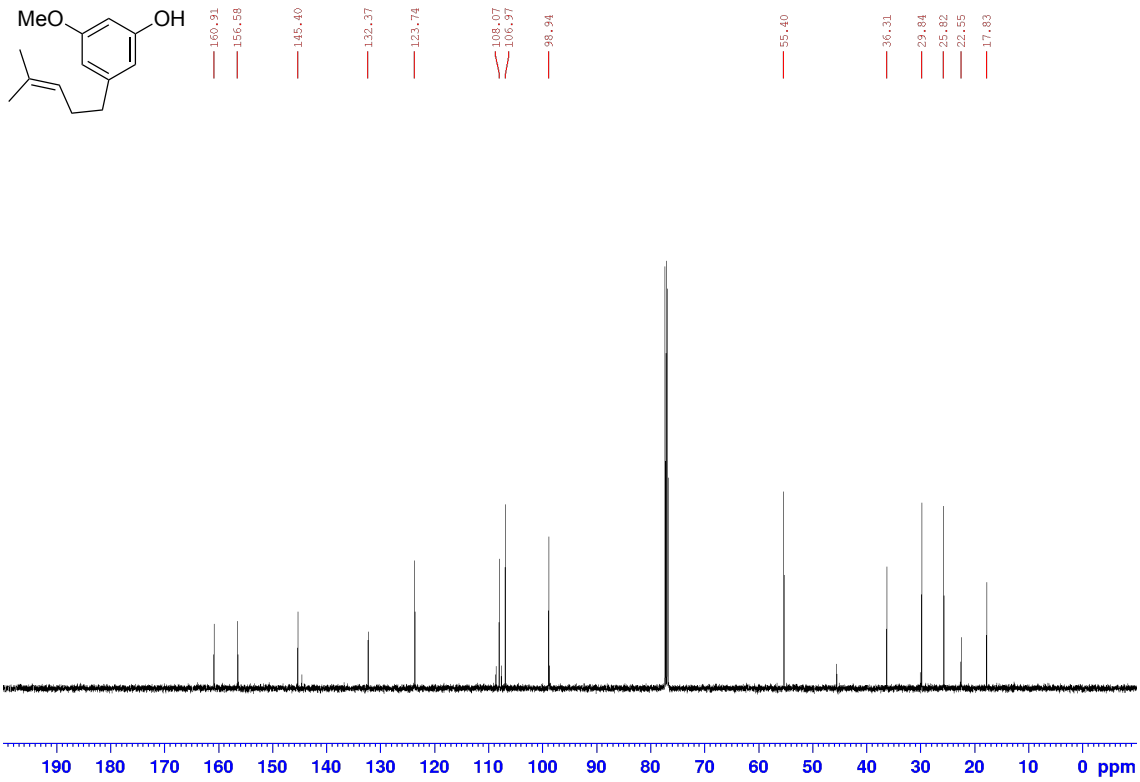
^{13}C NMR spectrum of **7f** ($CDCl_3$, 125 MHz)



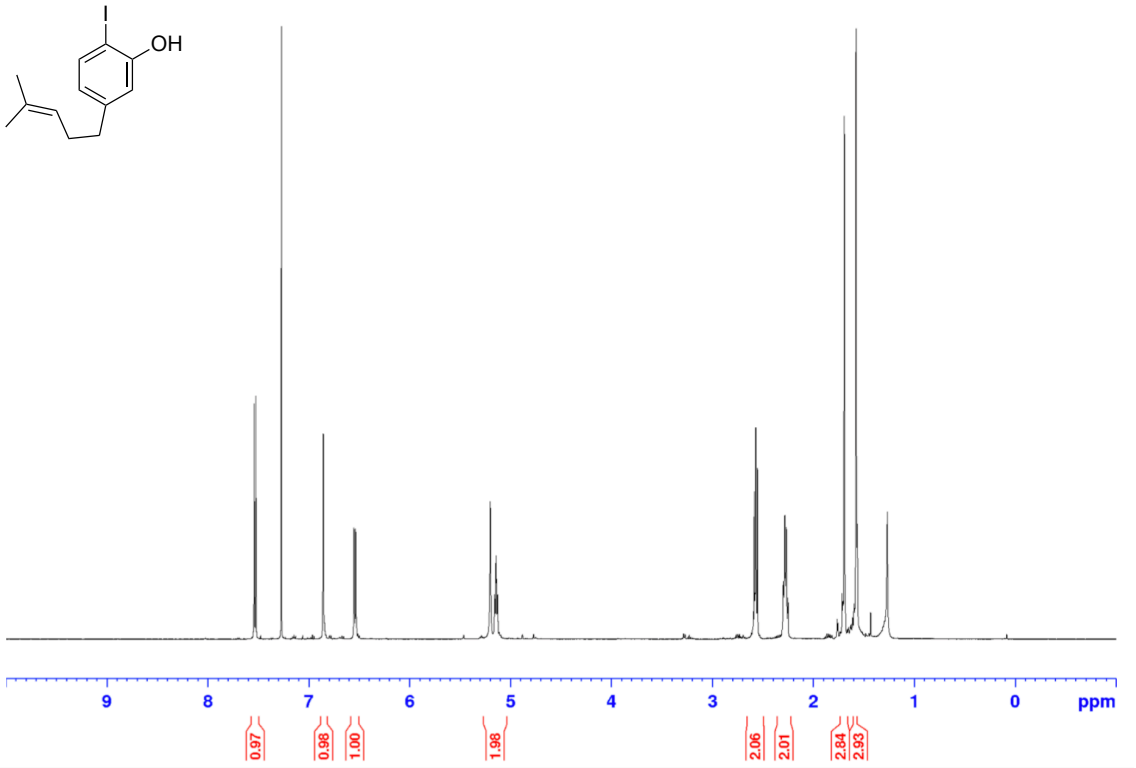
^{1}H NMR spectrum of **7g** ($CDCl_3$, 500 MHz)



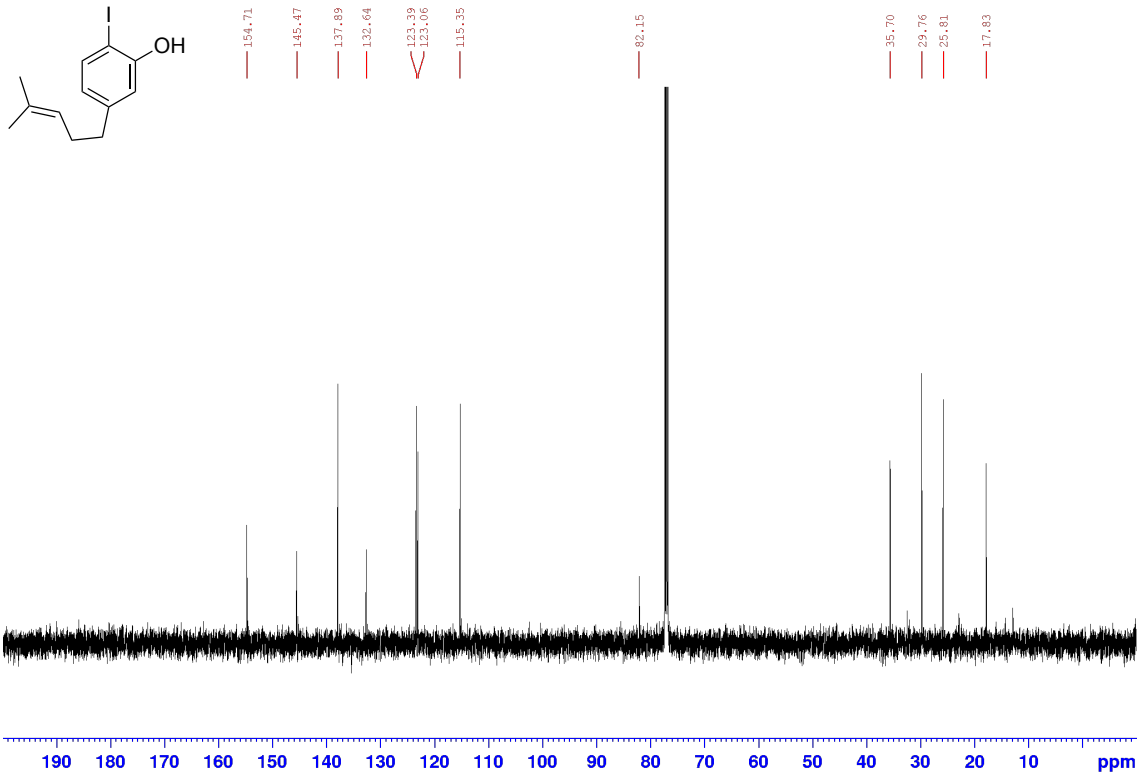
^{13}C NMR spectrum of **7g** ($CDCl_3$, 125 MHz)



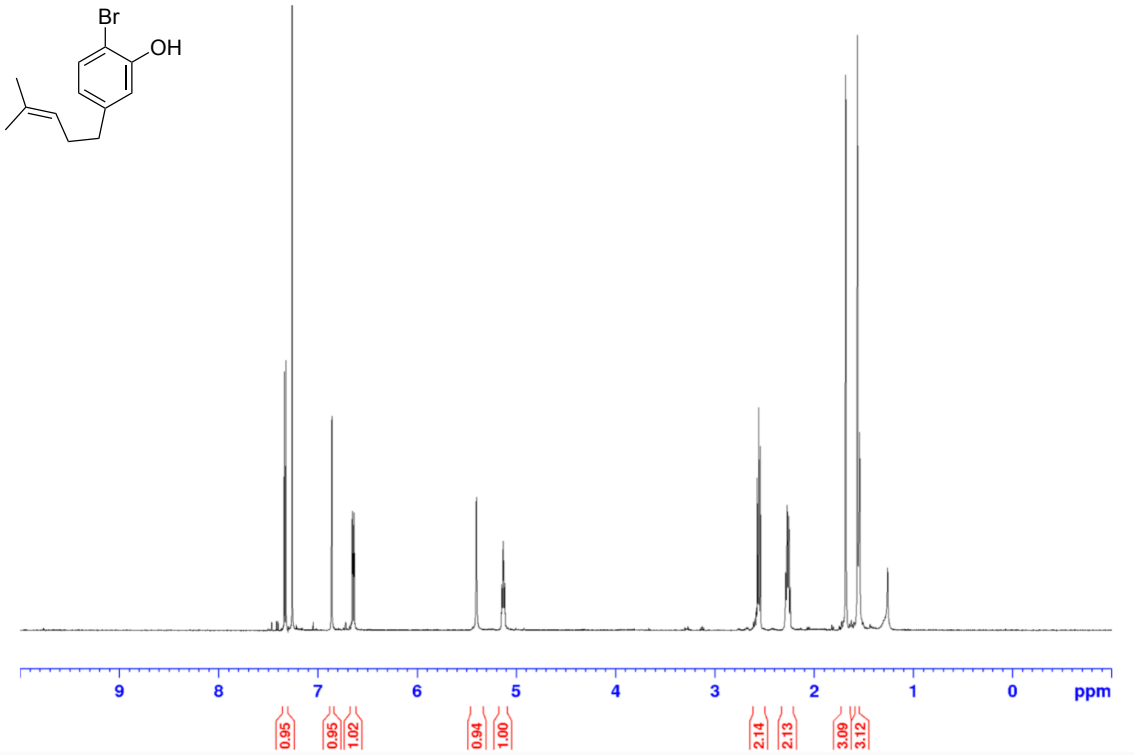
^{1}H NMR spectrum of **7h** ($CDCl_3$, 500 MHz)



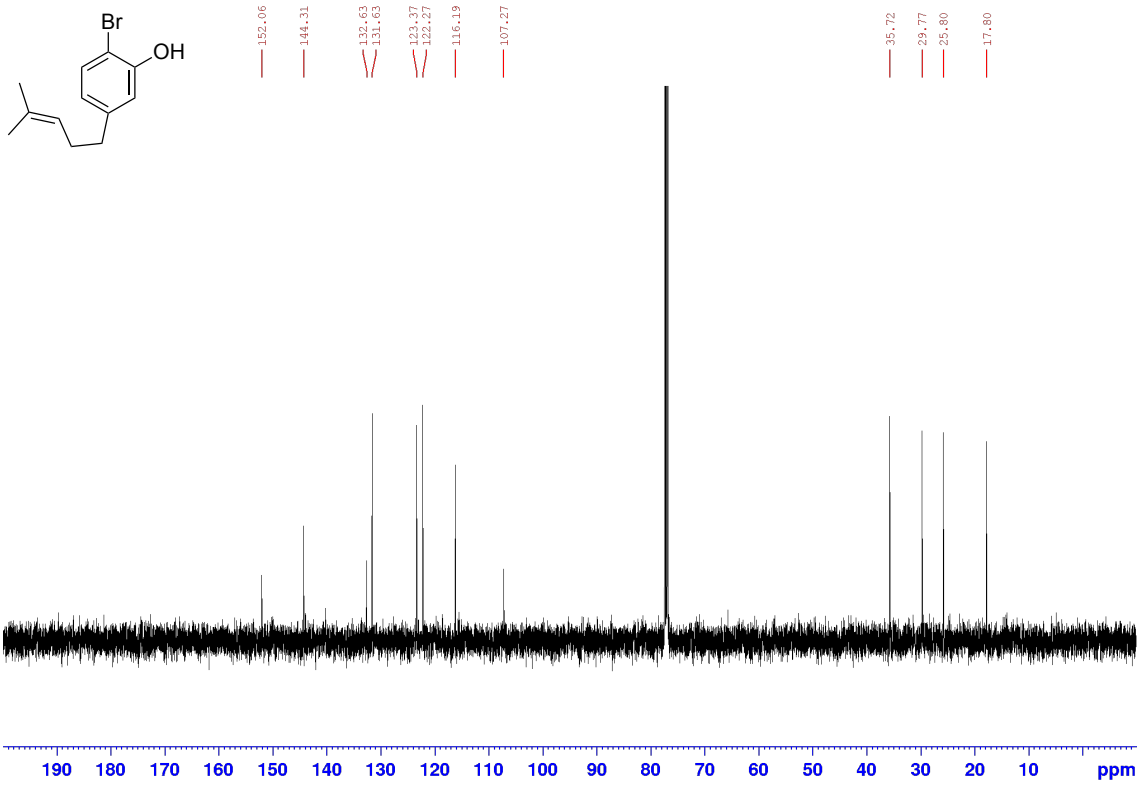
^{13}C NMR spectrum of **7h** ($CDCl_3$, 125 MHz)



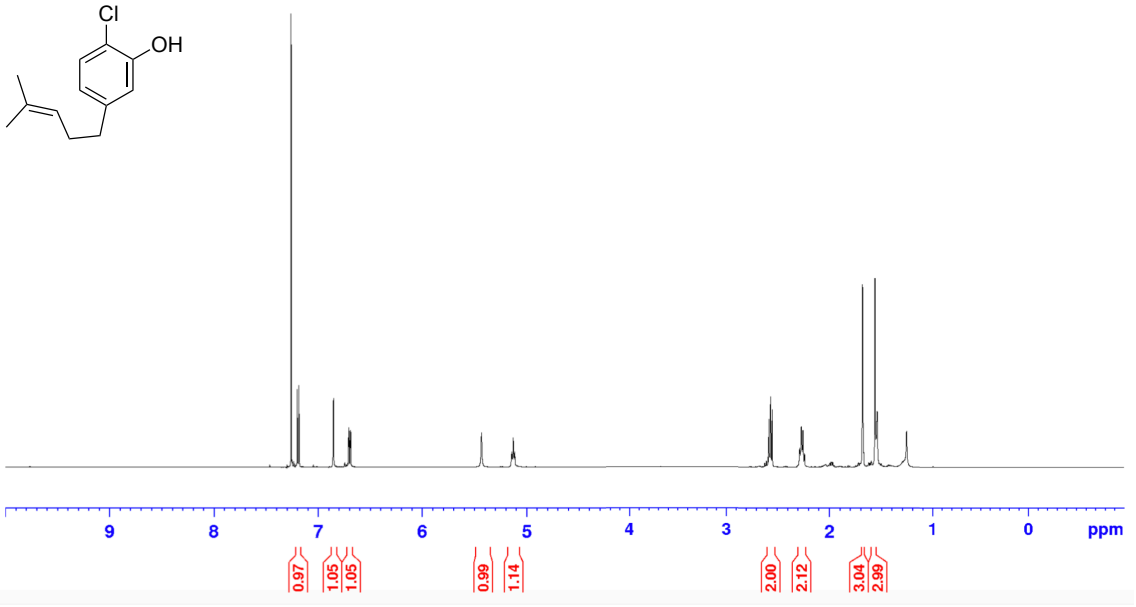
^{1}H NMR spectrum of **7i** ($CDCl_3$, 500 MHz)



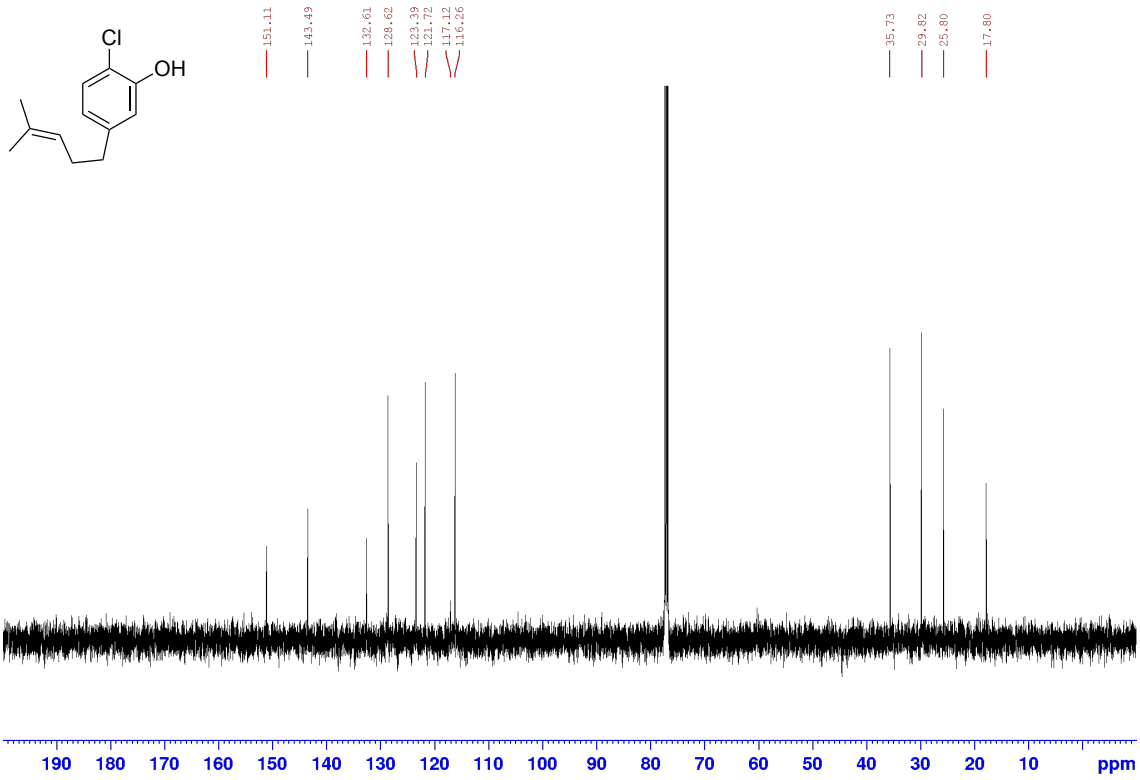
^{13}C NMR spectrum of **7i** ($CDCl_3$, 125 MHz)



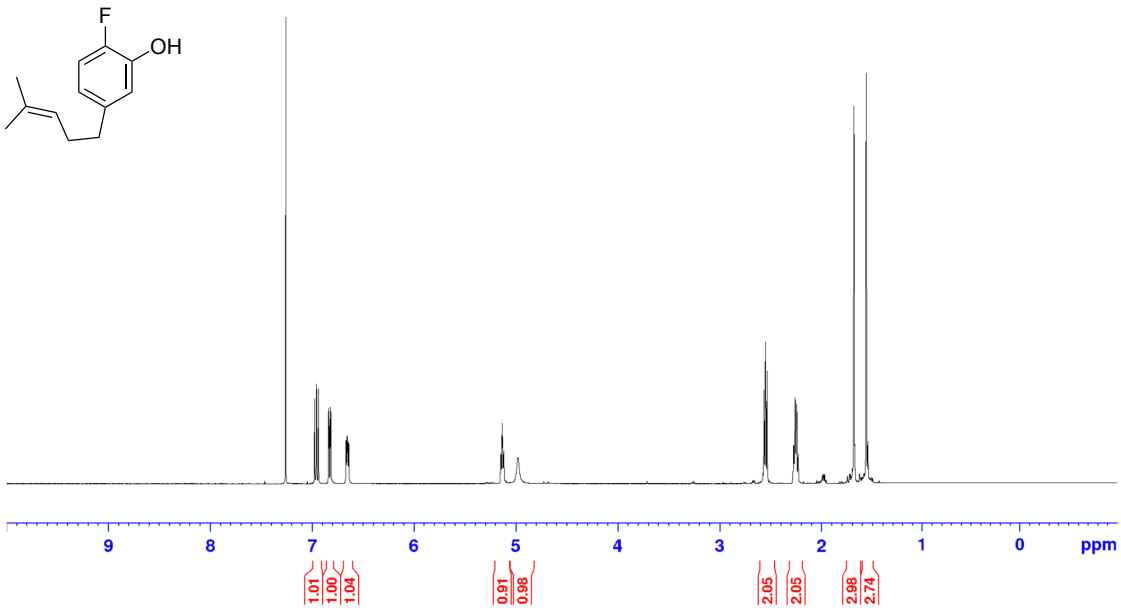
^{1}H NMR spectrum of **7j** ($CDCl_3$, 500 MHz)



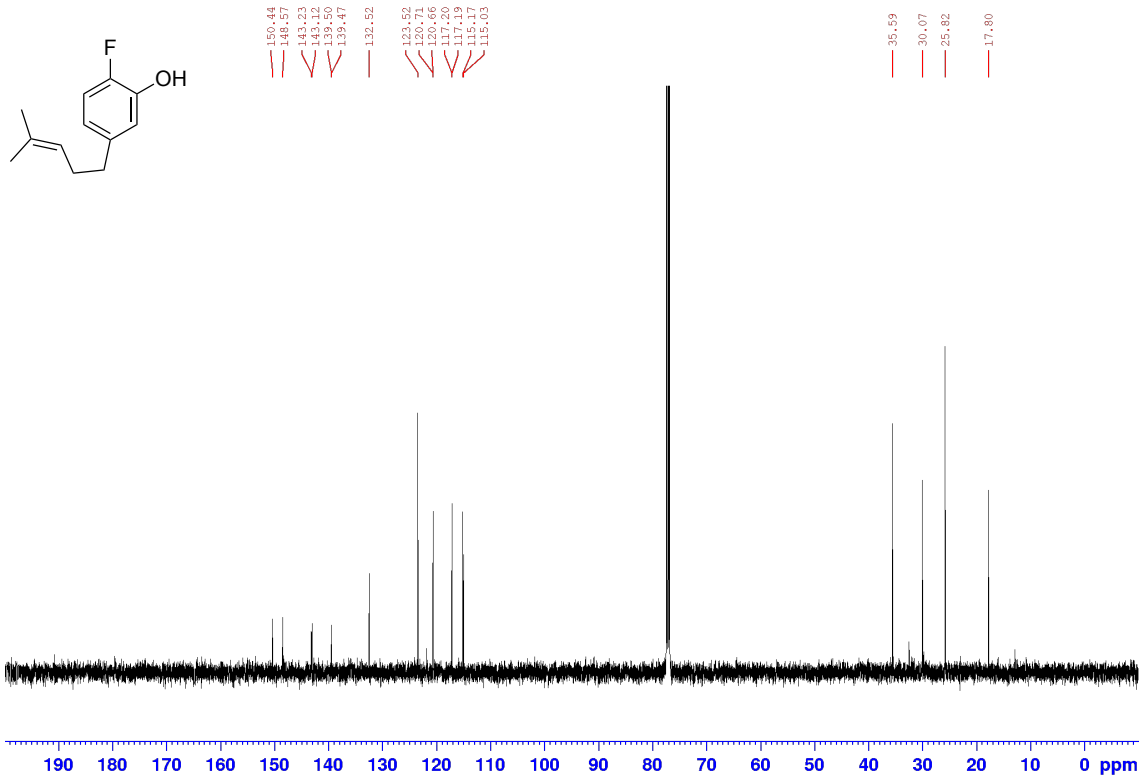
^{13}C NMR spectrum of **7j** ($CDCl_3$, 125 MHz)



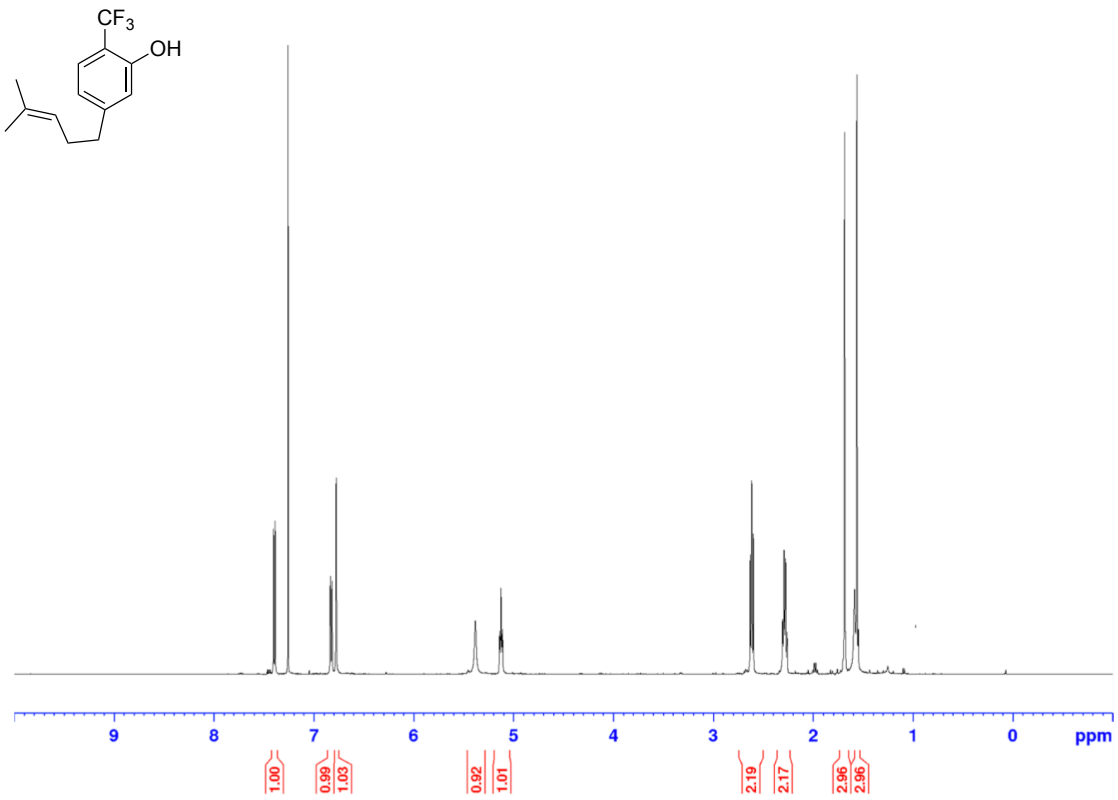
^{1}H NMR spectrum of **7k** ($CDCl_3$, 500 MHz)



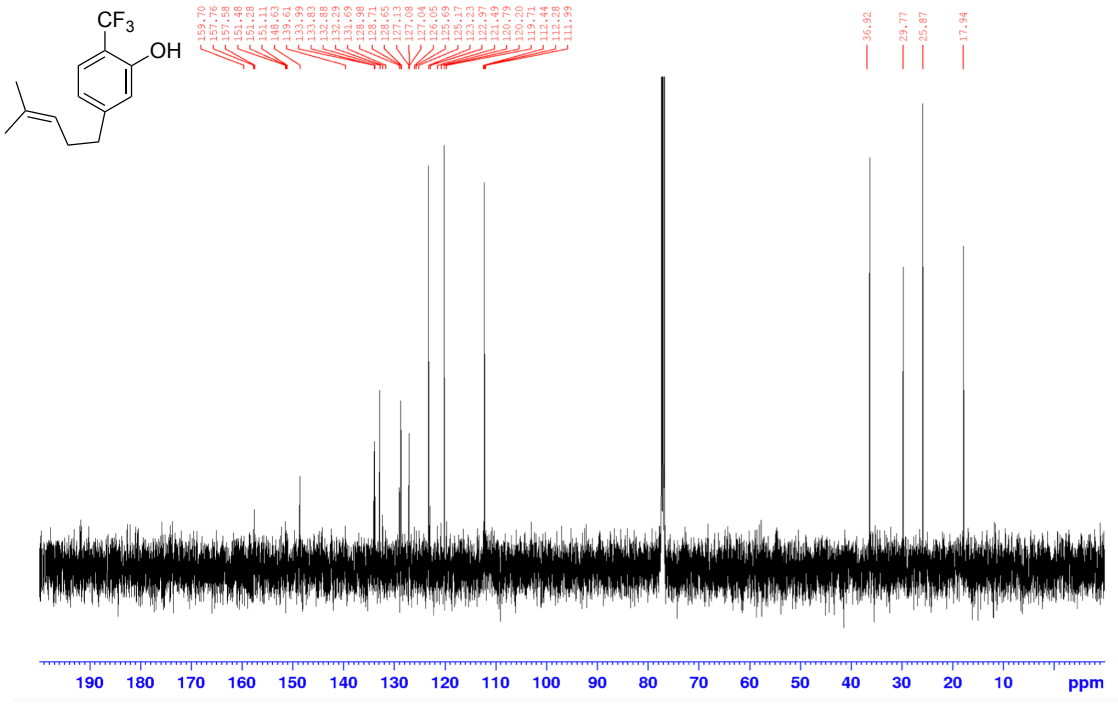
^{13}C NMR spectrum of **7k** ($CDCl_3$, 125 MHz)



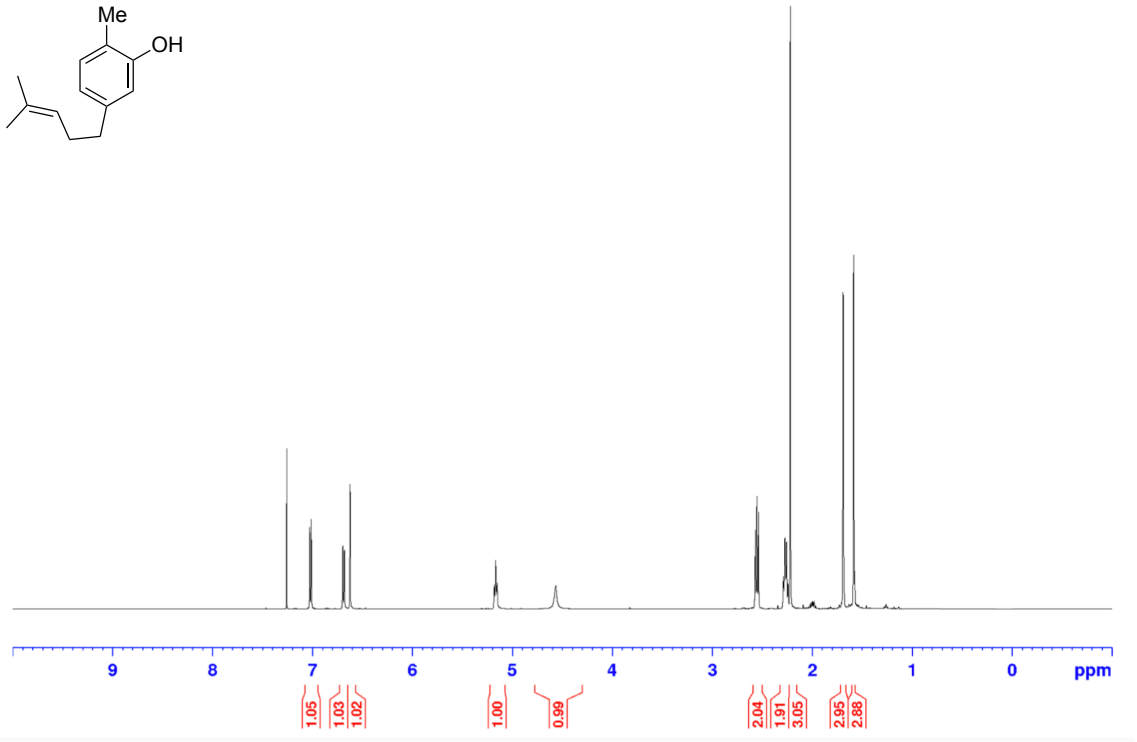
^{1}H NMR spectrum of **7l** ($CDCl_3$, 500 MHz)



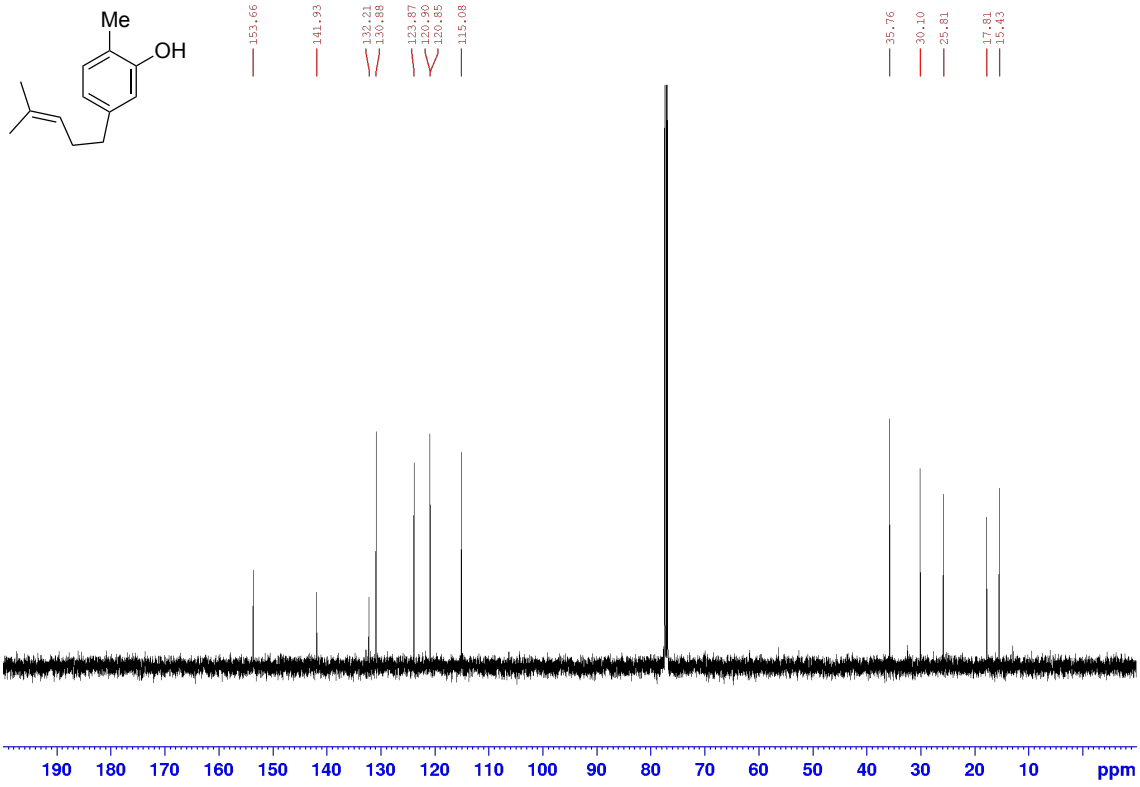
^{13}C NMR spectrum of **7l** ($CDCl_3$, 125 MHz)



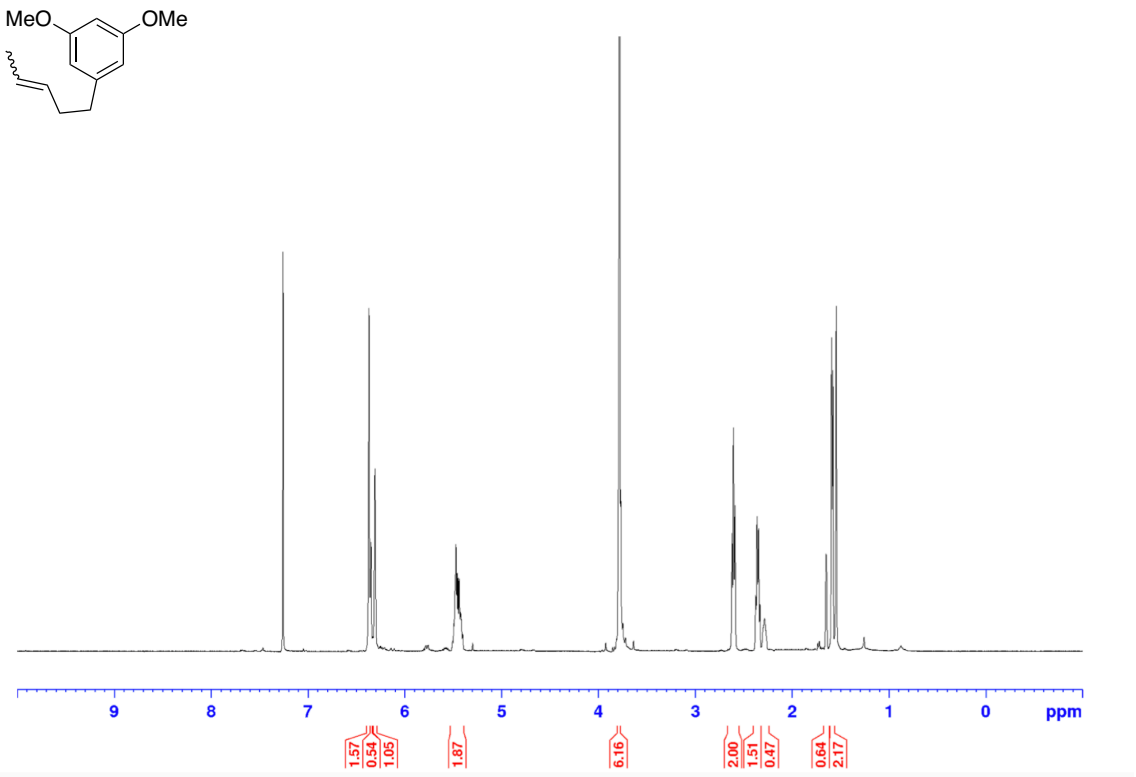
^{1}H NMR spectrum of **7m** ($CDCl_3$, 500 MHz)



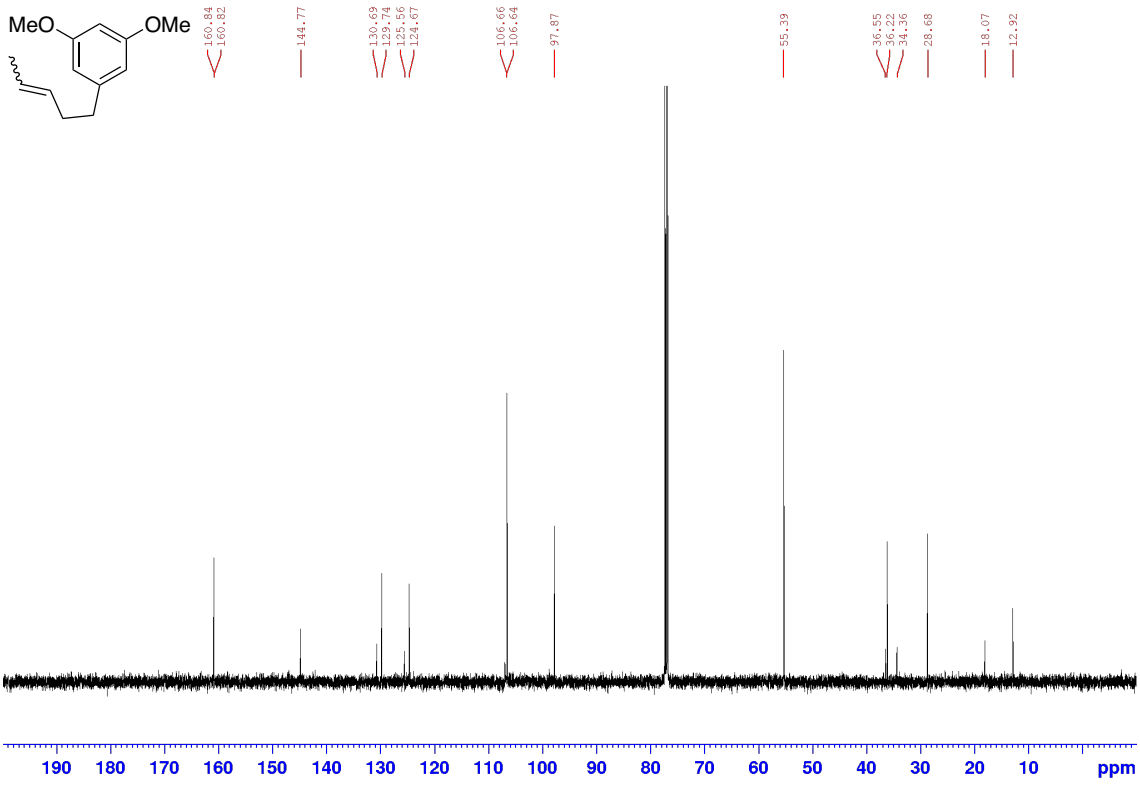
^{13}C NMR spectrum of **7m** ($CDCl_3$, 125 MHz)



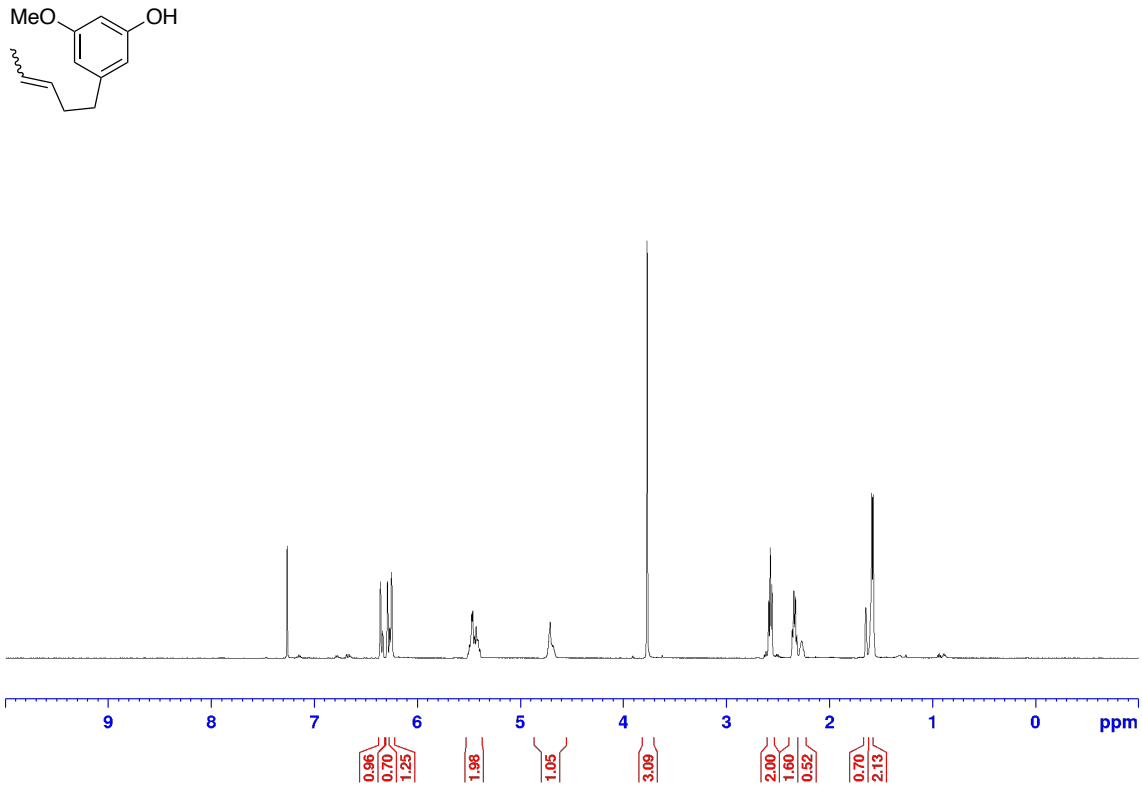
^{1}H NMR spectrum of **35b** ($CDCl_3$, 500 MHz)



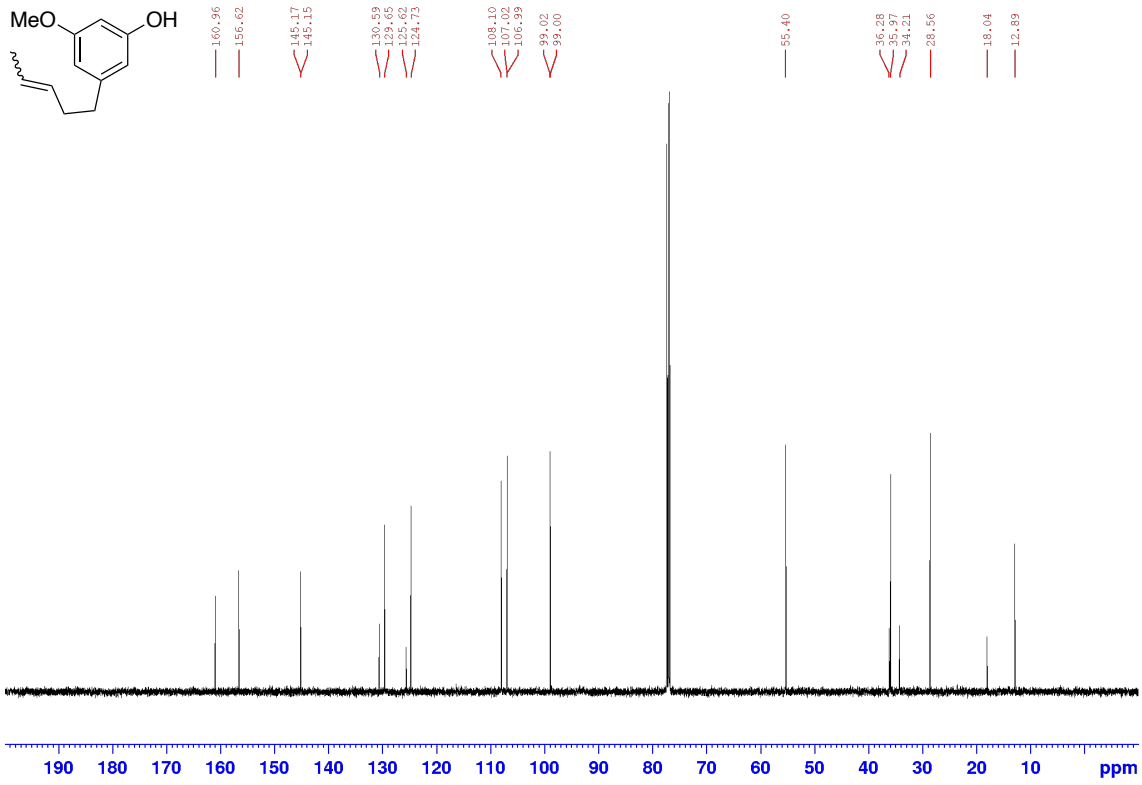
^{13}C NMR spectrum of **35b** ($CDCl_3$, 125 MHz)



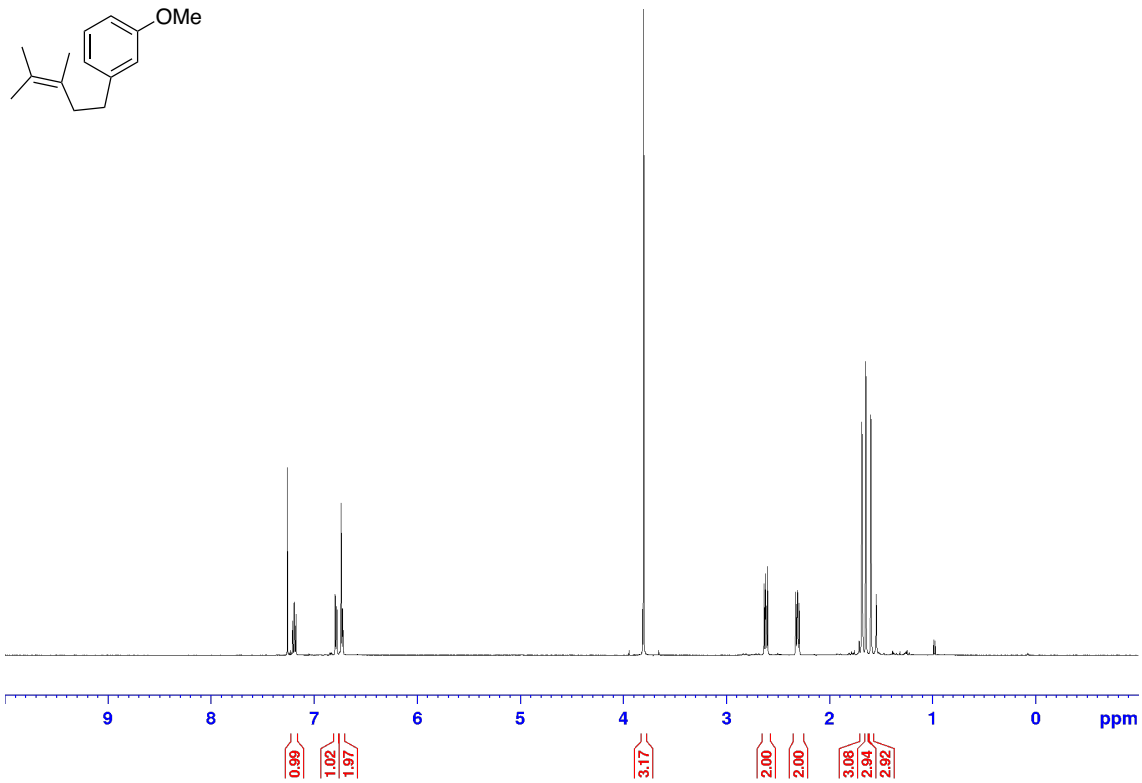
^{1}H NMR spectrum of **23** ($CDCl_3$, 500 MHz)



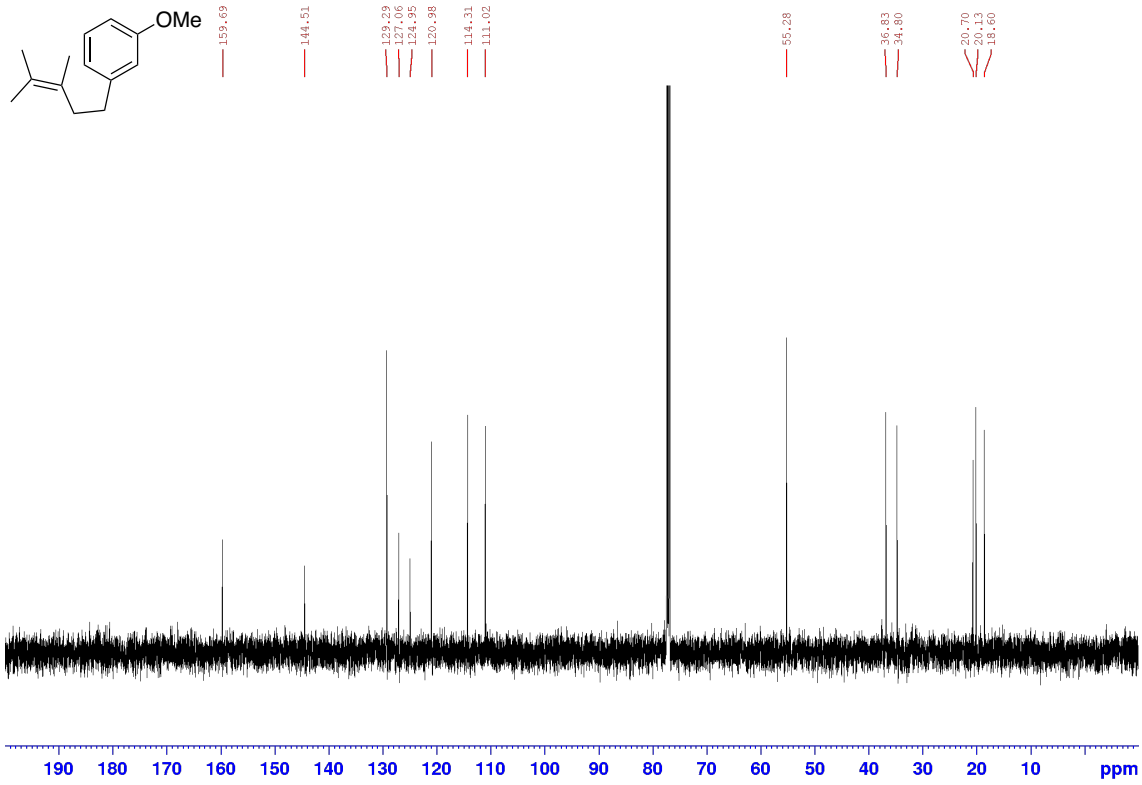
^{13}C NMR spectrum of **23** ($CDCl_3$, 125 MHz)



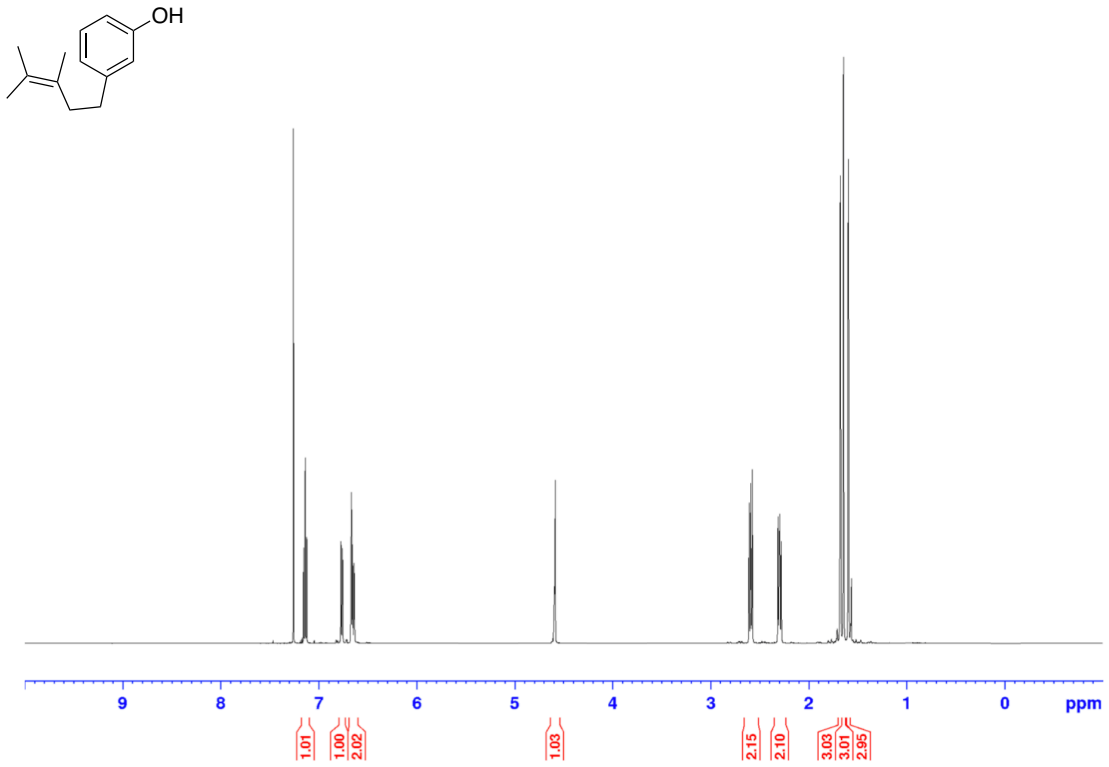
^{1}H NMR spectrum of **36c** ($CDCl_3$, 500 MHz)



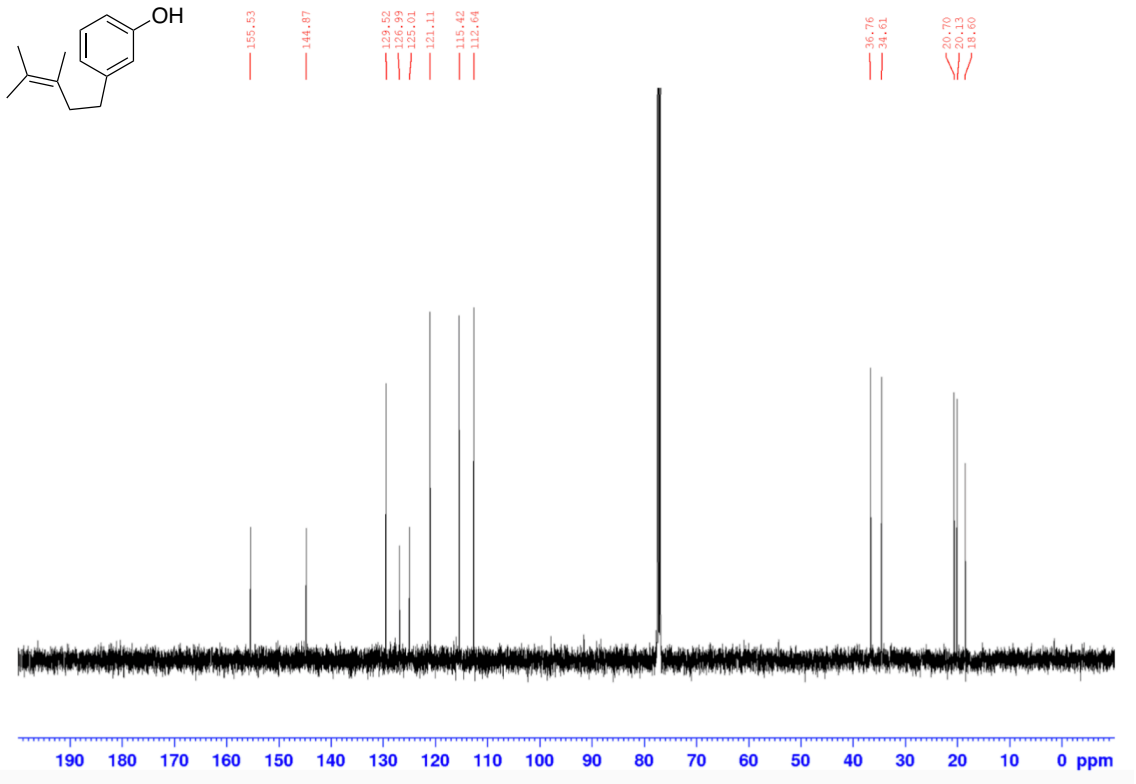
^{13}C NMR spectrum of **36c** ($CDCl_3$, 125 MHz)



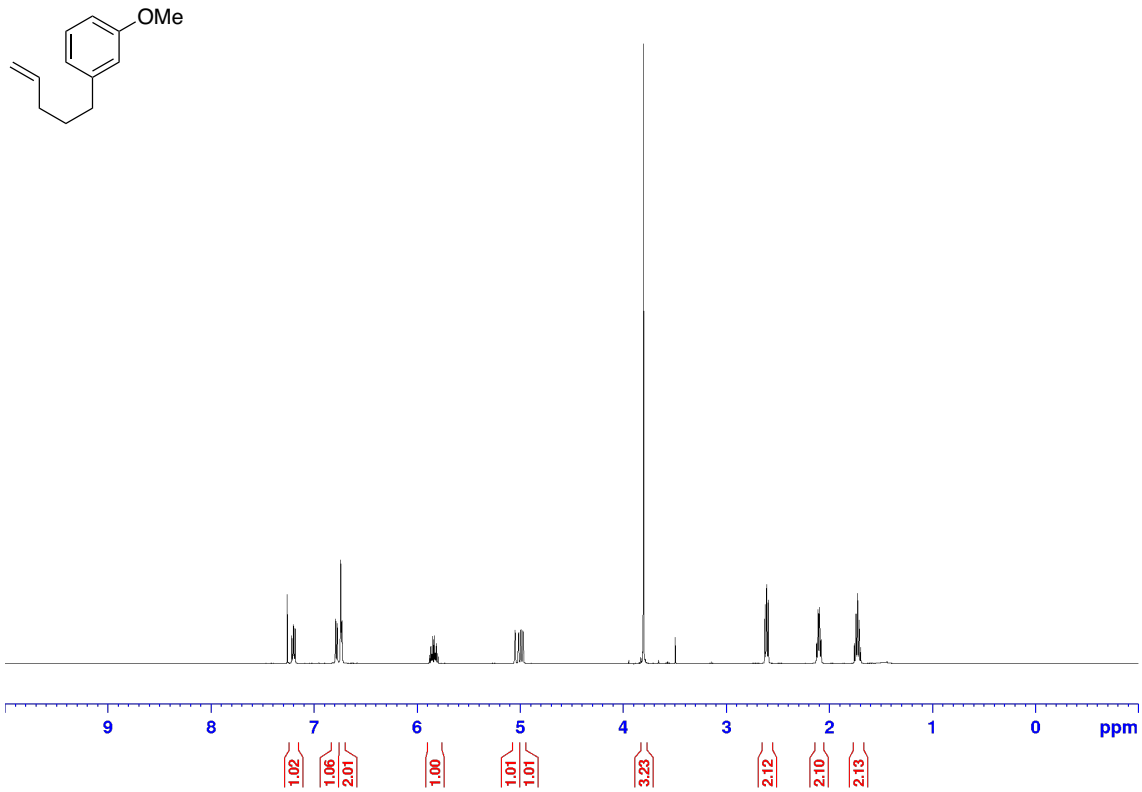
^{1}H NMR spectrum of **24** ($CDCl_3$, 500 MHz)



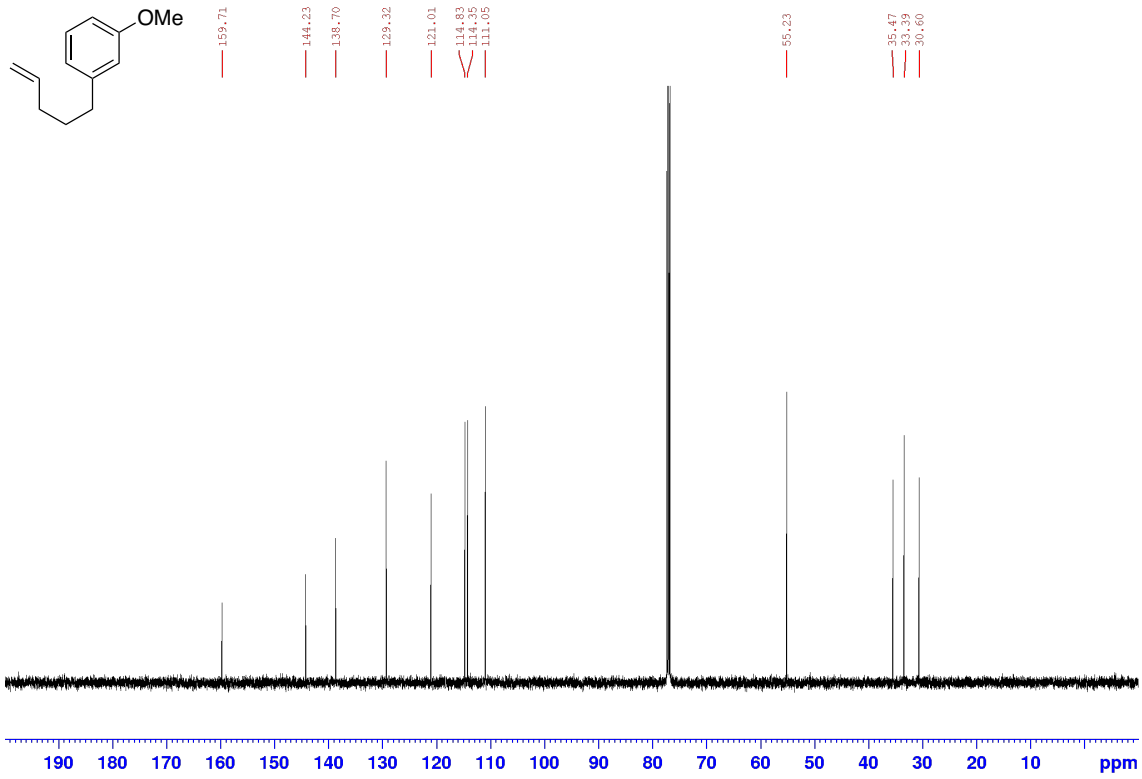
^{13}C NMR spectrum of **24** ($CDCl_3$, 125 MHz)



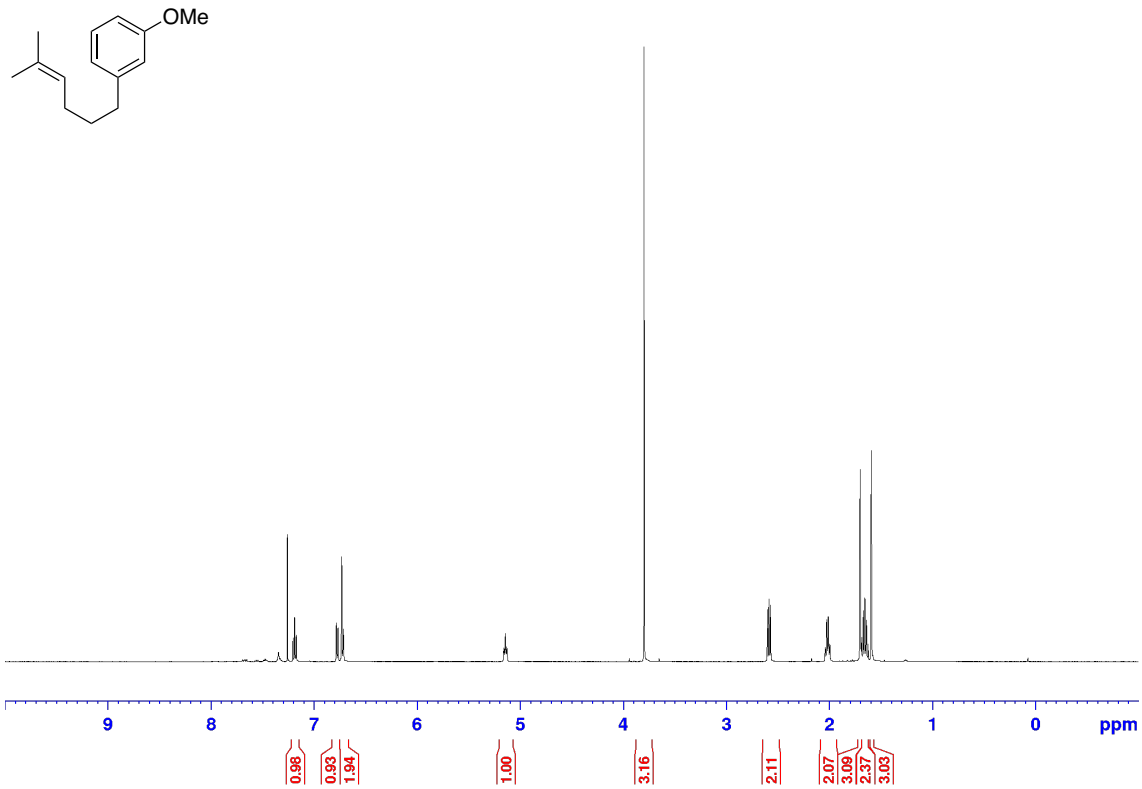
^{1}H NMR spectrum of **37b** ($CDCl_3$, 500 MHz)



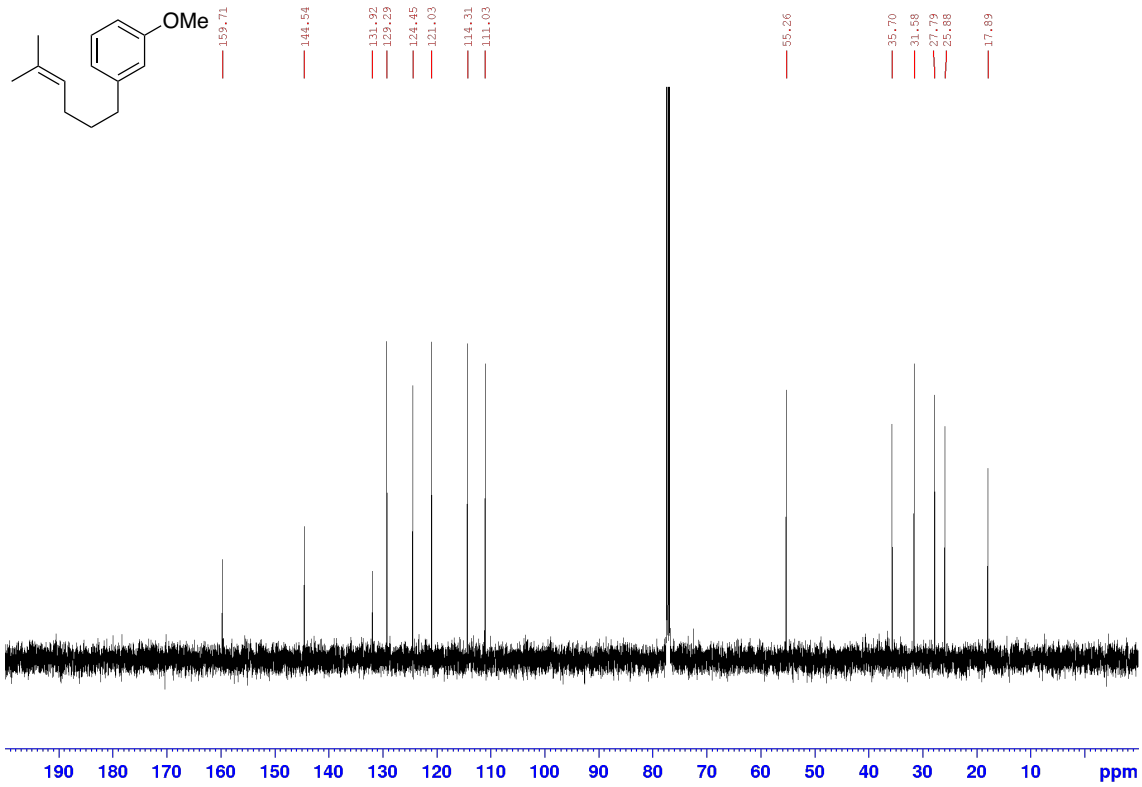
^{13}C NMR spectrum of **37b** ($CDCl_3$, 125 MHz)



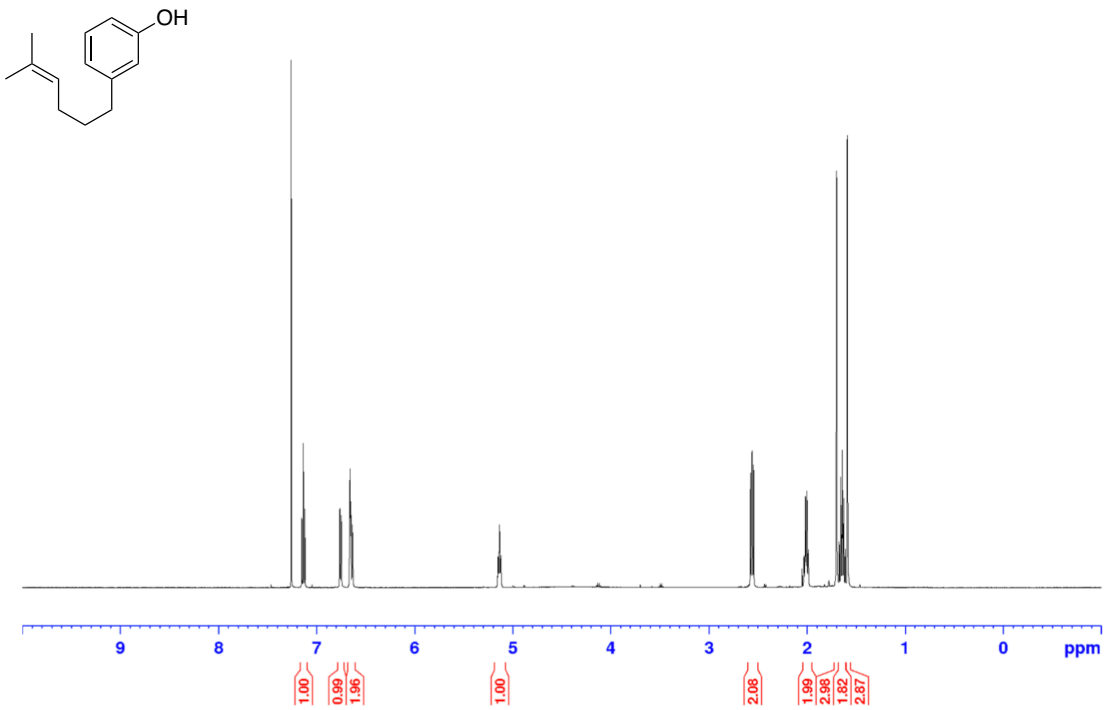
^{1}H NMR spectrum of **37c** ($CDCl_3$, 500 MHz)



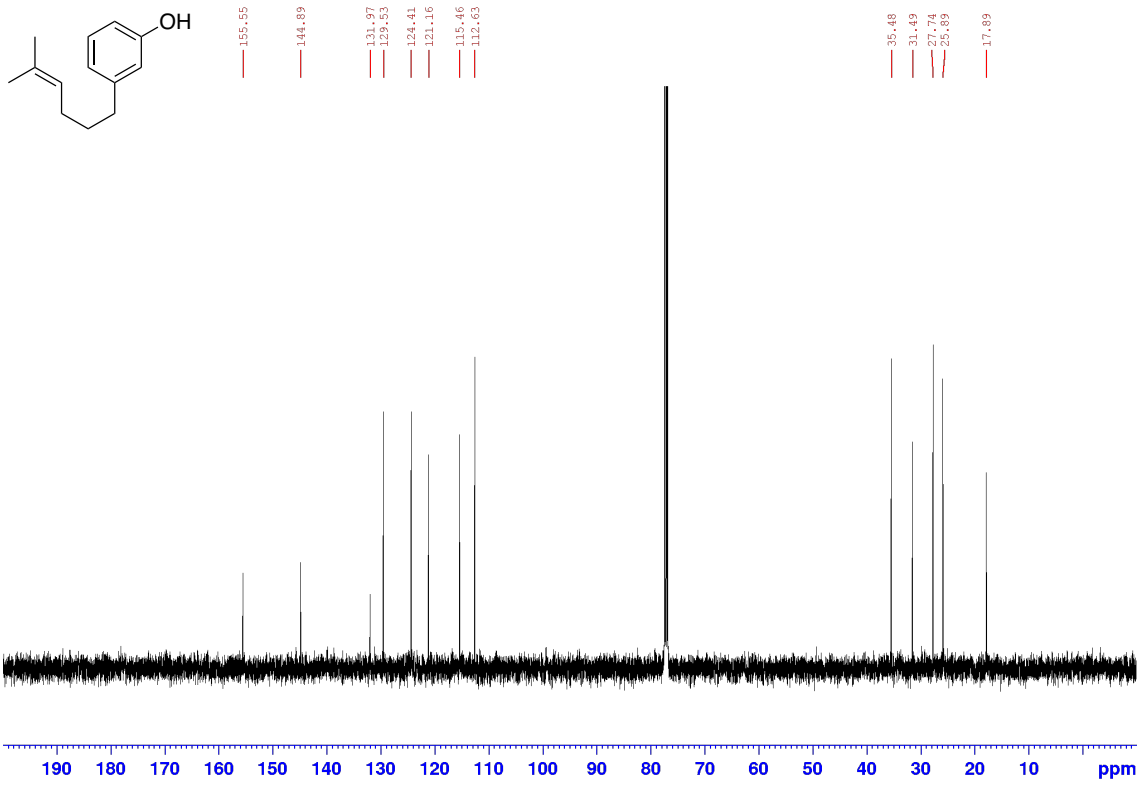
^{13}C NMR spectrum of **37c** ($CDCl_3$, 125 MHz)



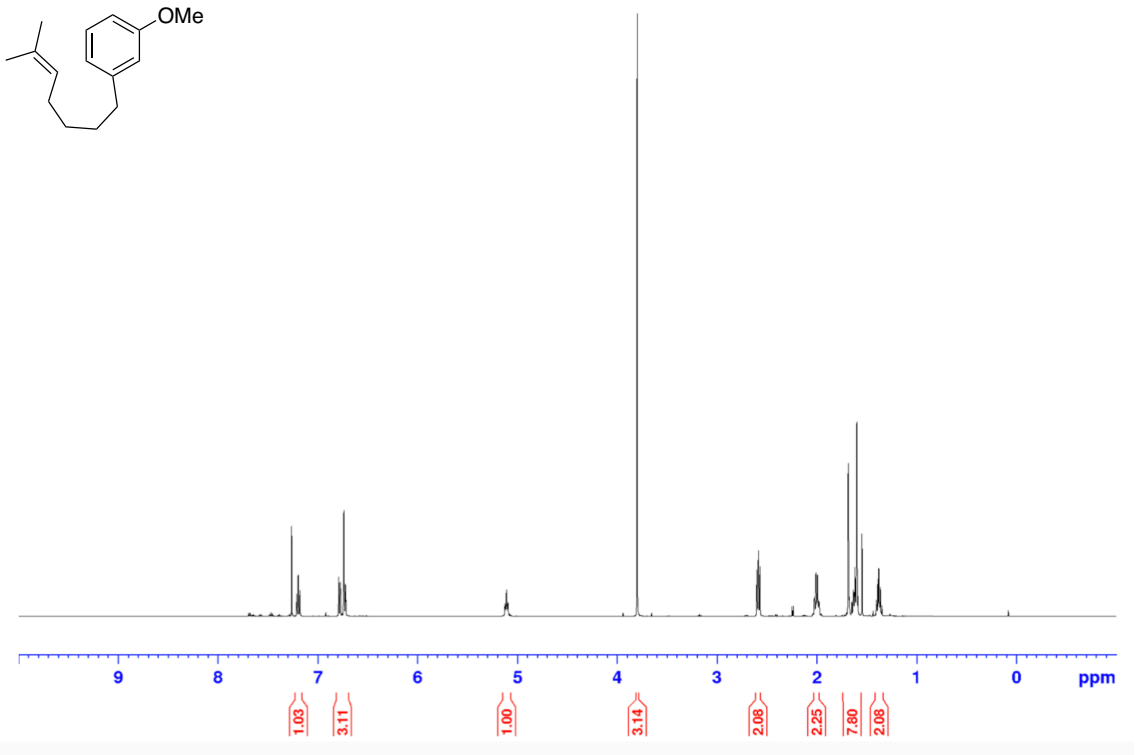
^{1}H NMR spectrum of **11** ($CDCl_3$, 500 MHz)



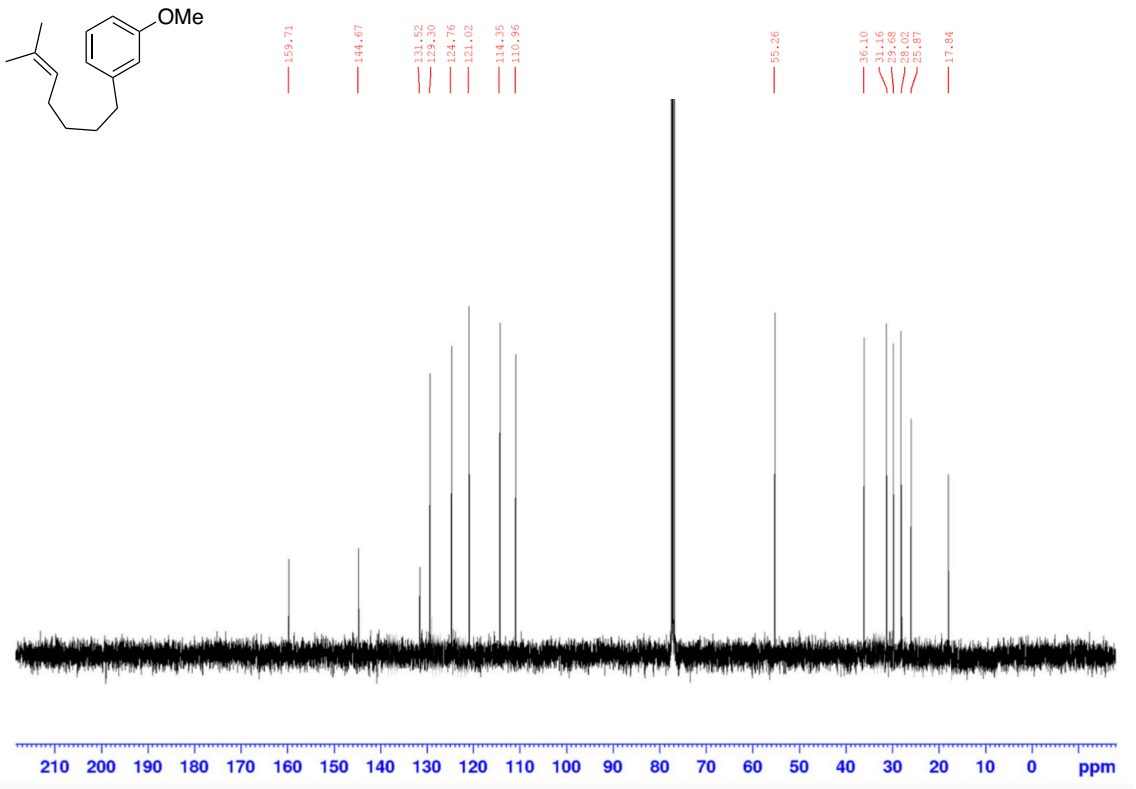
^{13}C NMR spectrum of **11** ($CDCl_3$, 125 MHz)



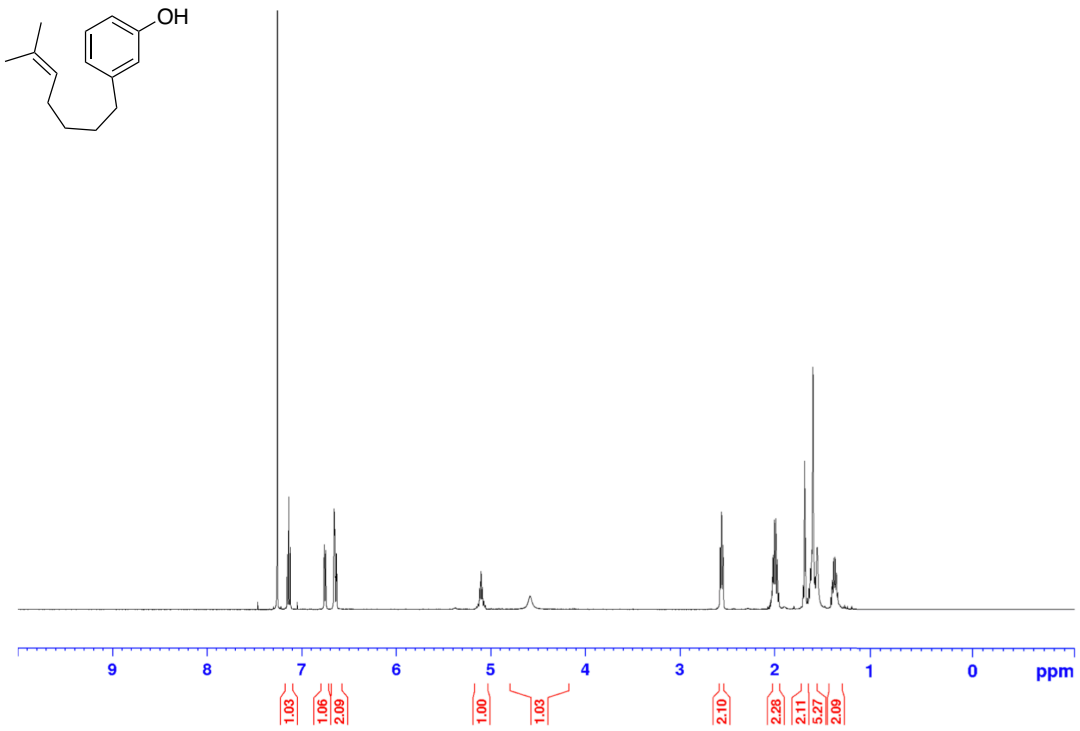
^{1}H NMR spectrum of **38e** ($CDCl_3$, 500 MHz)



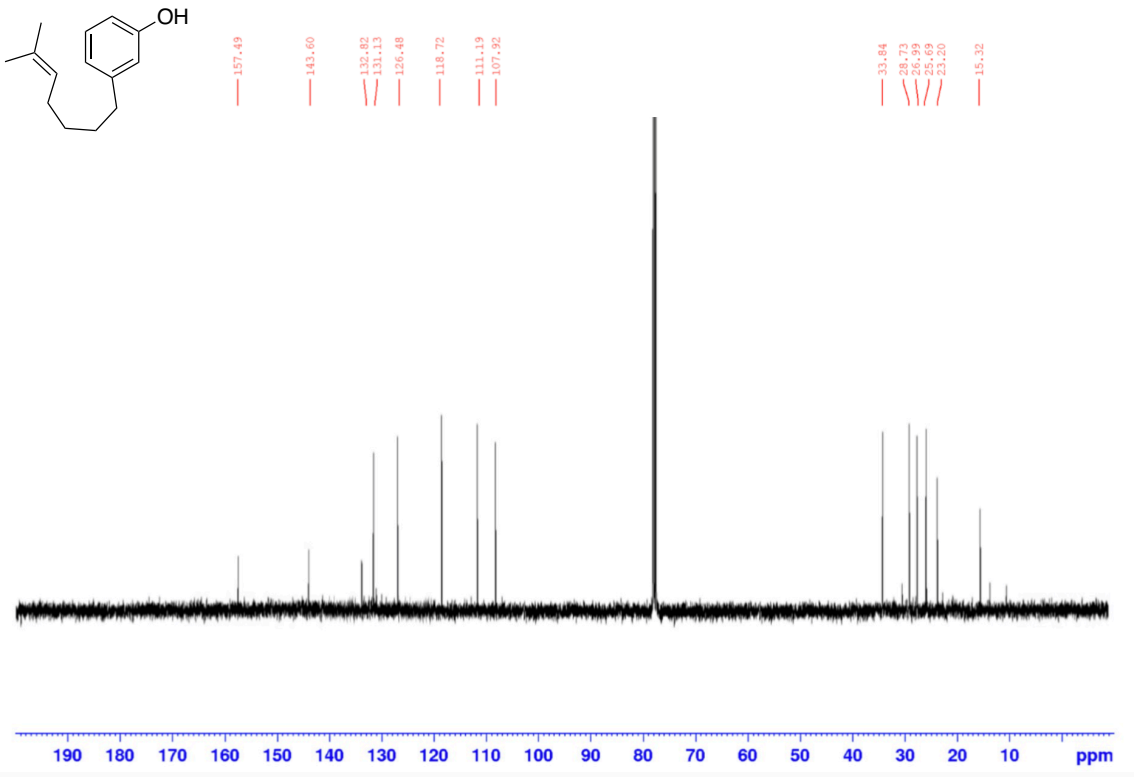
^{13}C NMR spectrum of **38e** ($CDCl_3$, 125 MHz)



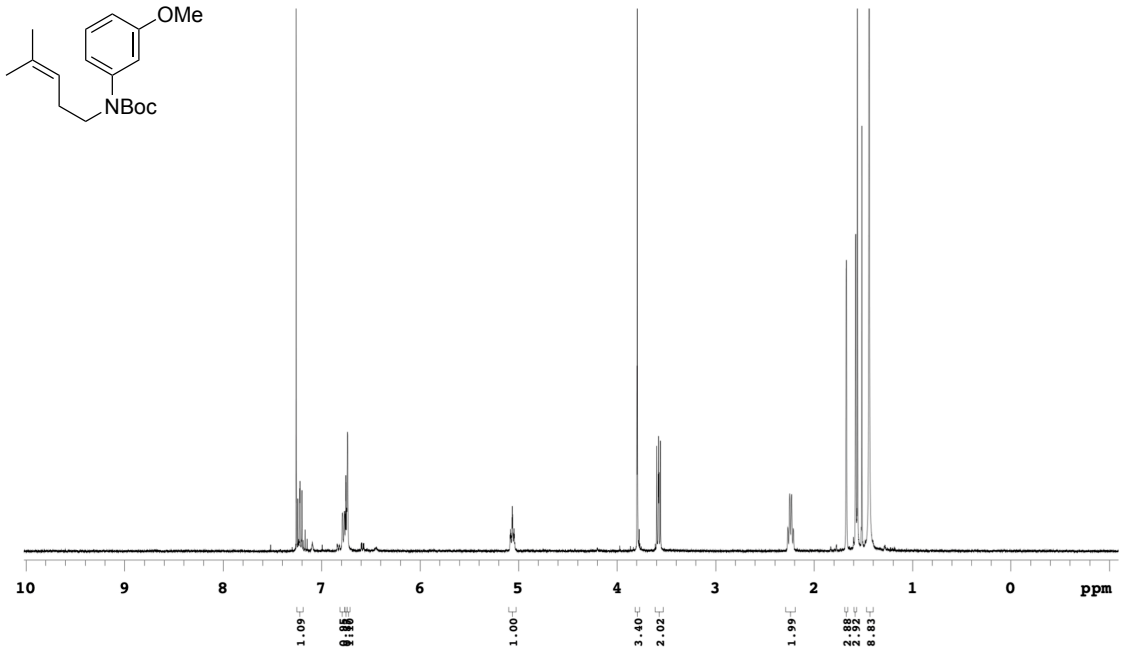
^{1}H NMR spectrum of **12** ($CDCl_3$, 500 MHz)



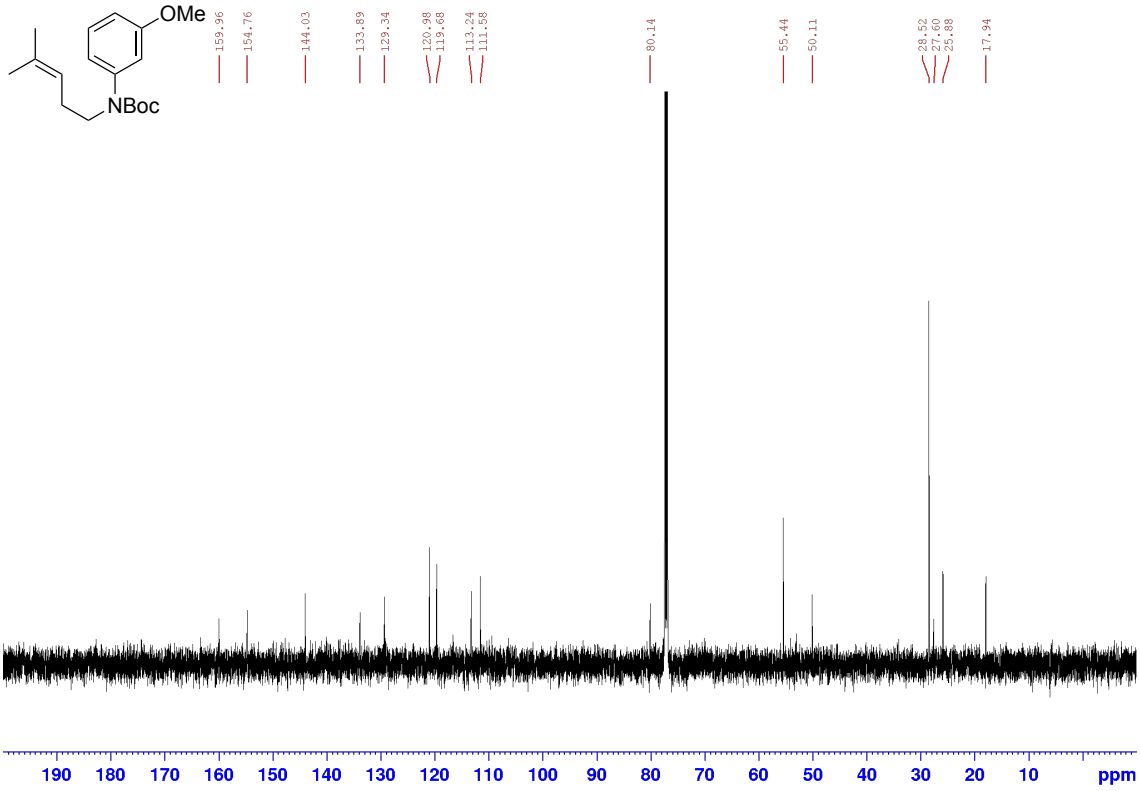
^{13}C NMR spectrum of **12** ($CDCl_3$, 125 MHz)



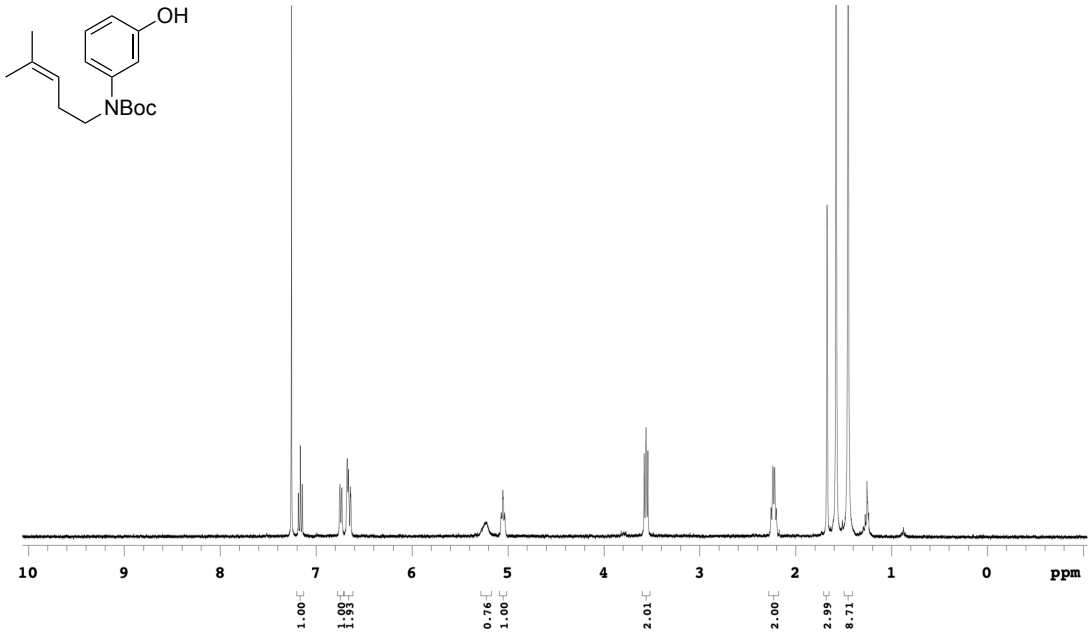
^{1}H NMR spectrum of **39b** ($CDCl_3$, 500 MHz)



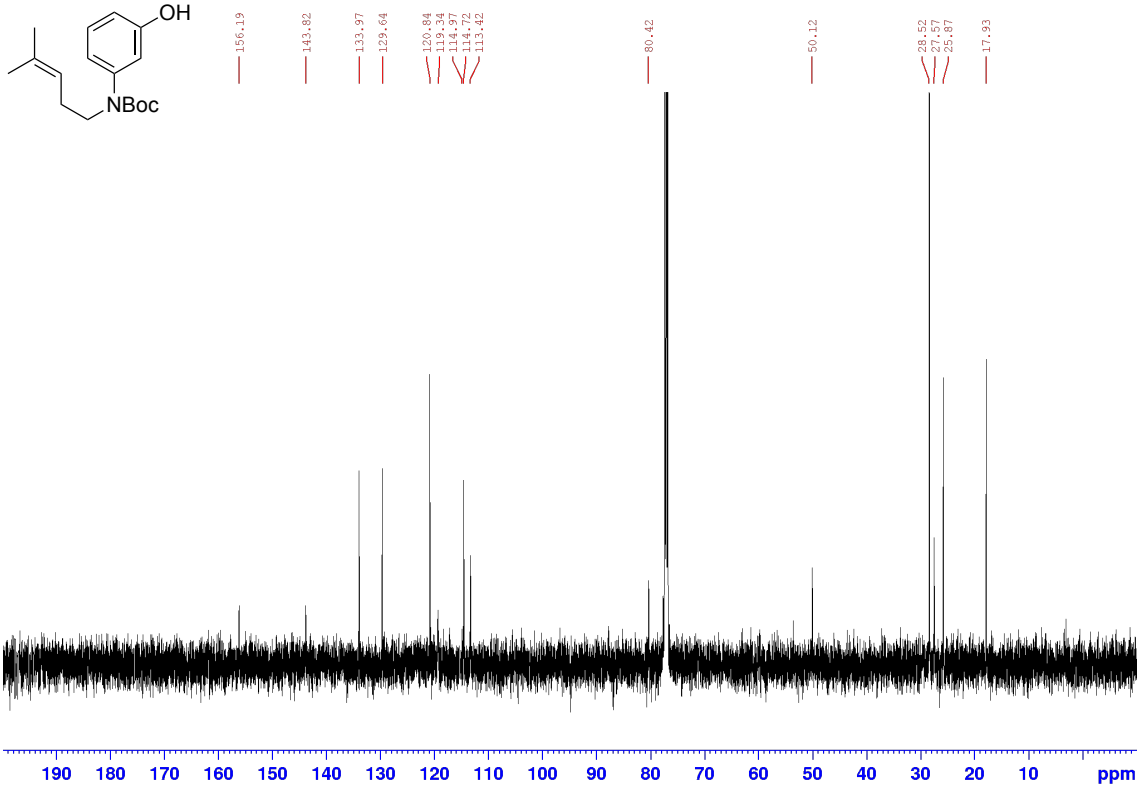
^{13}C NMR spectrum of **39b** ($CDCl_3$, 125 MHz)



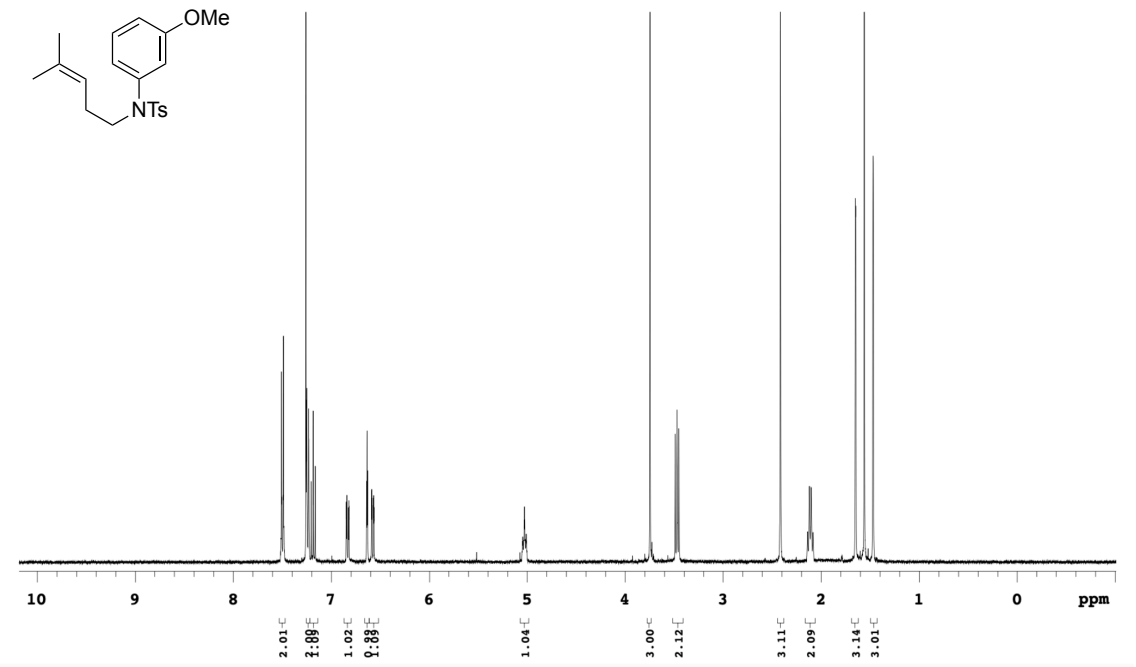
^{1}H NMR spectrum of **15a** ($CDCl_3$, 500 MHz)



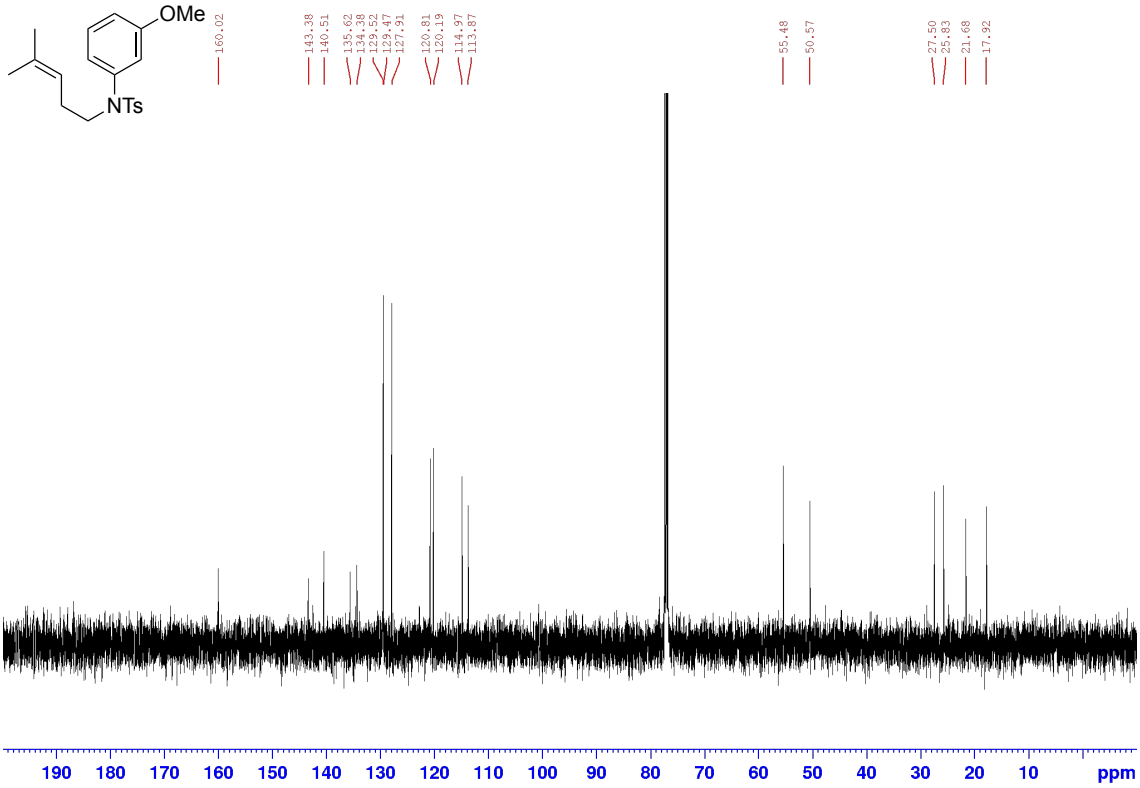
^{13}C NMR spectrum of **15a** ($CDCl_3$, 125 MHz)



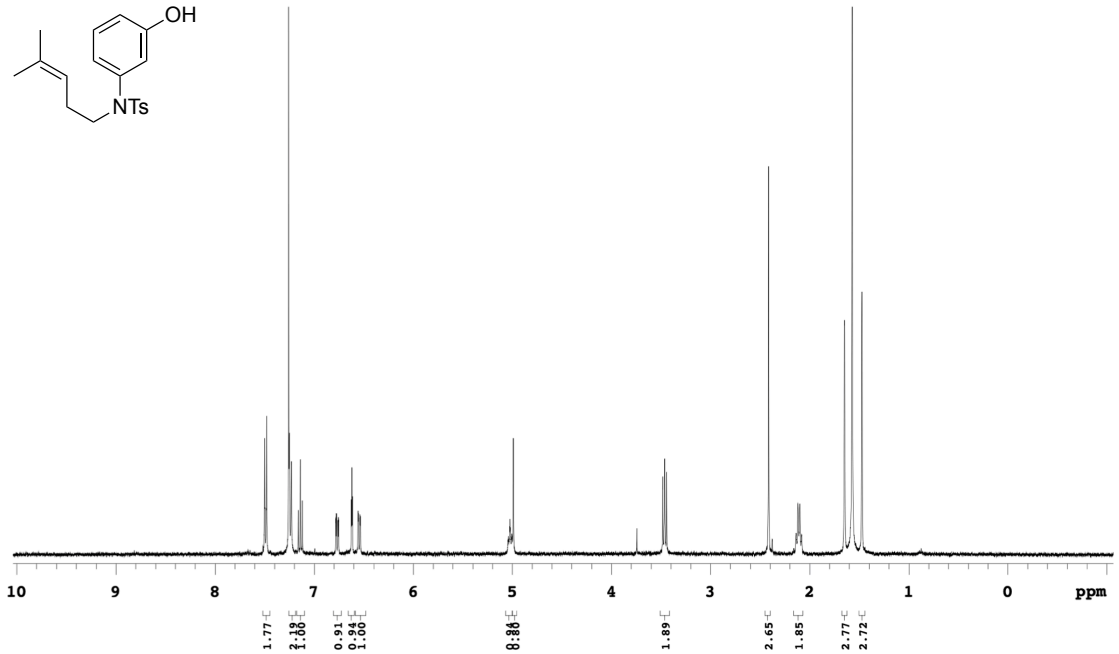
^{1}H NMR spectrum of **39c** ($CDCl_3$, 500 MHz)



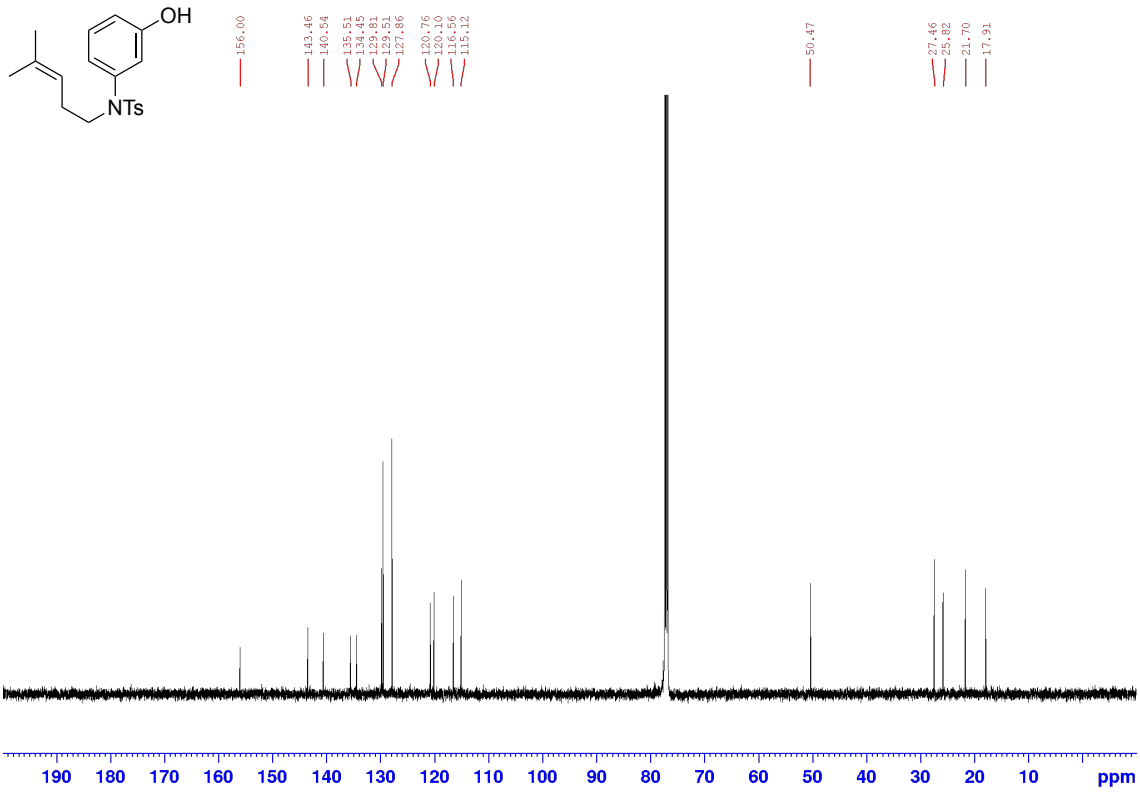
^{13}C NMR spectrum of **39c** ($CDCl_3$, 125 MHz)



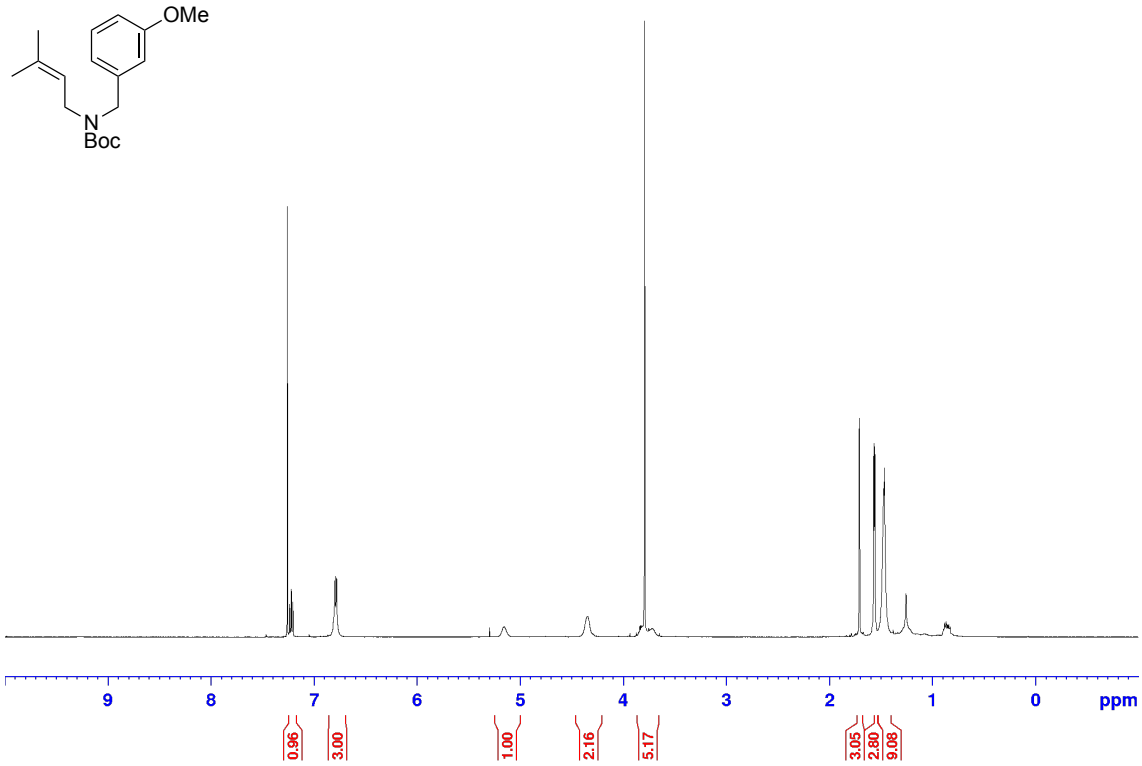
^{1}H NMR spectrum of **15b** ($CDCl_3$, 500 MHz)



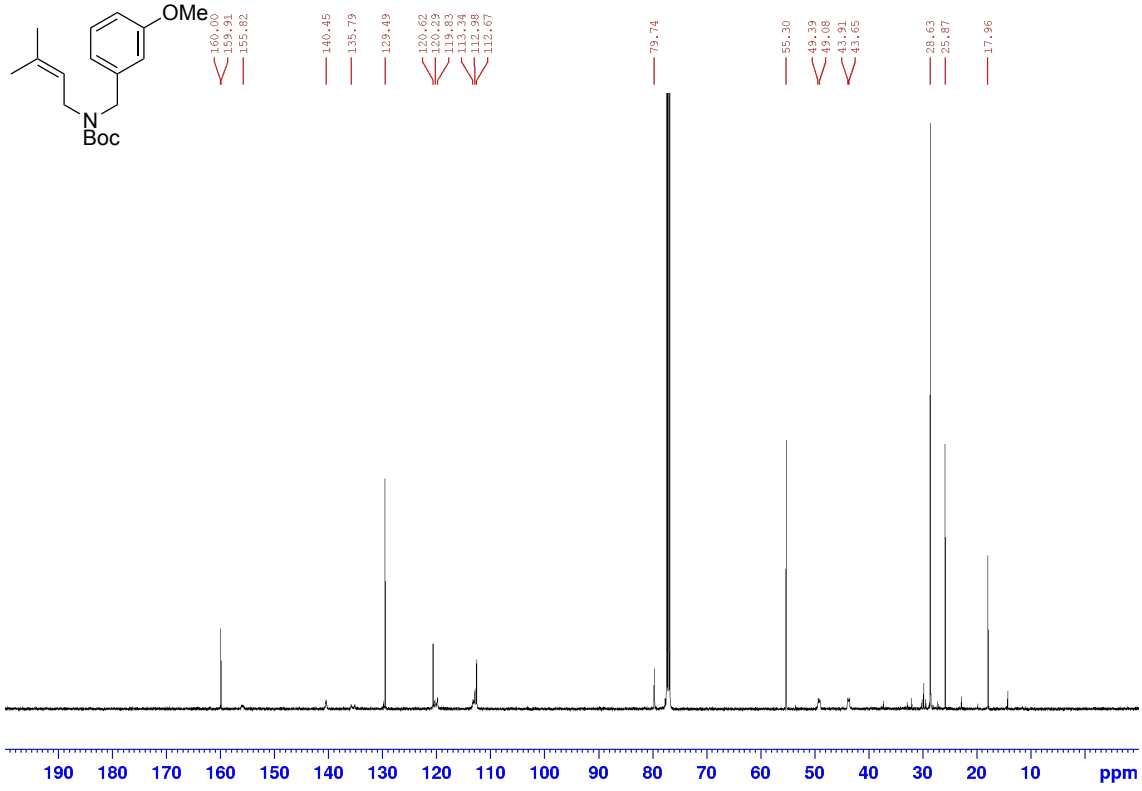
^{13}C NMR spectrum of **15b** ($CDCl_3$, 125 MHz)



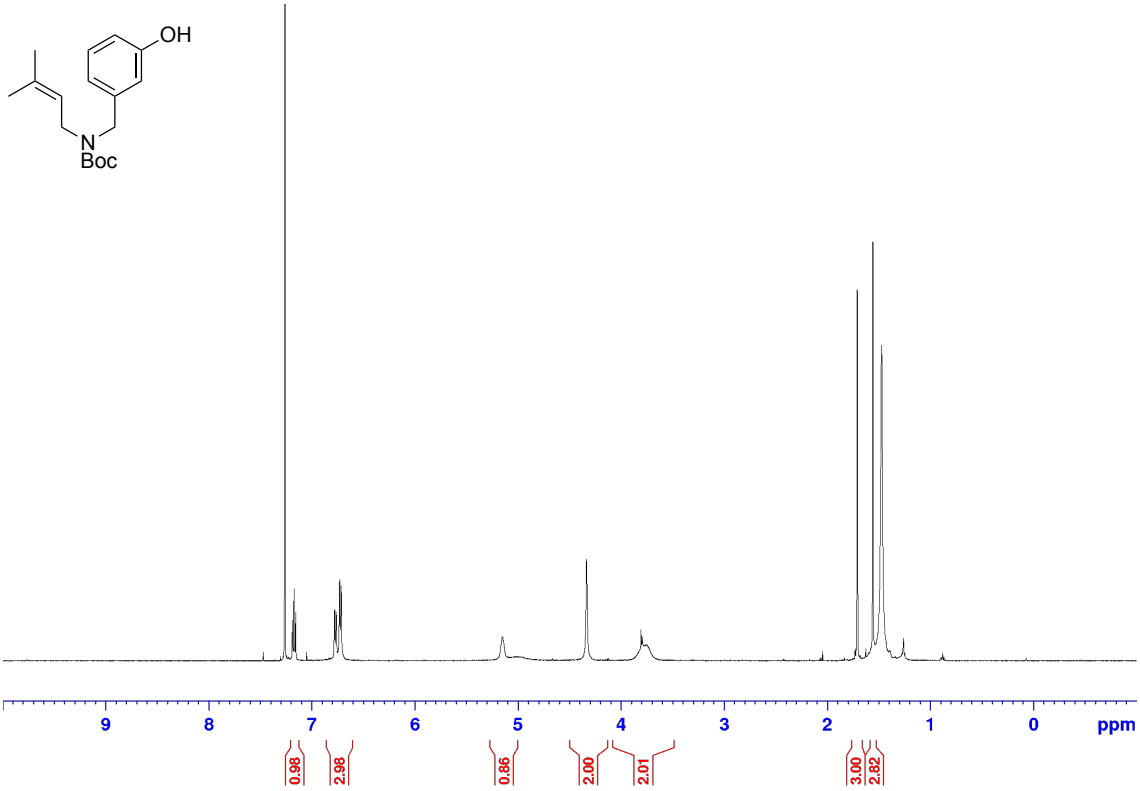
^{1}H NMR spectrum of **40b** ($CDCl_3$, 500 MHz)



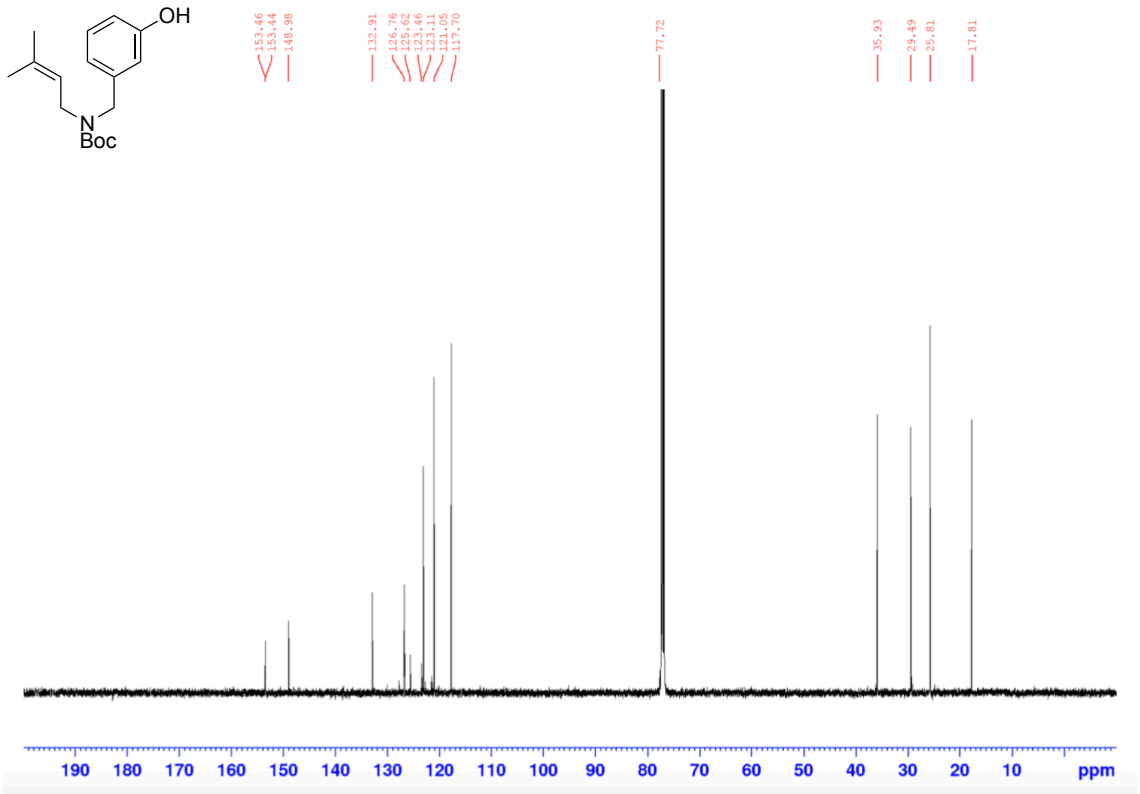
^{13}C NMR spectrum of **40b** ($CDCl_3$, 125 MHz)



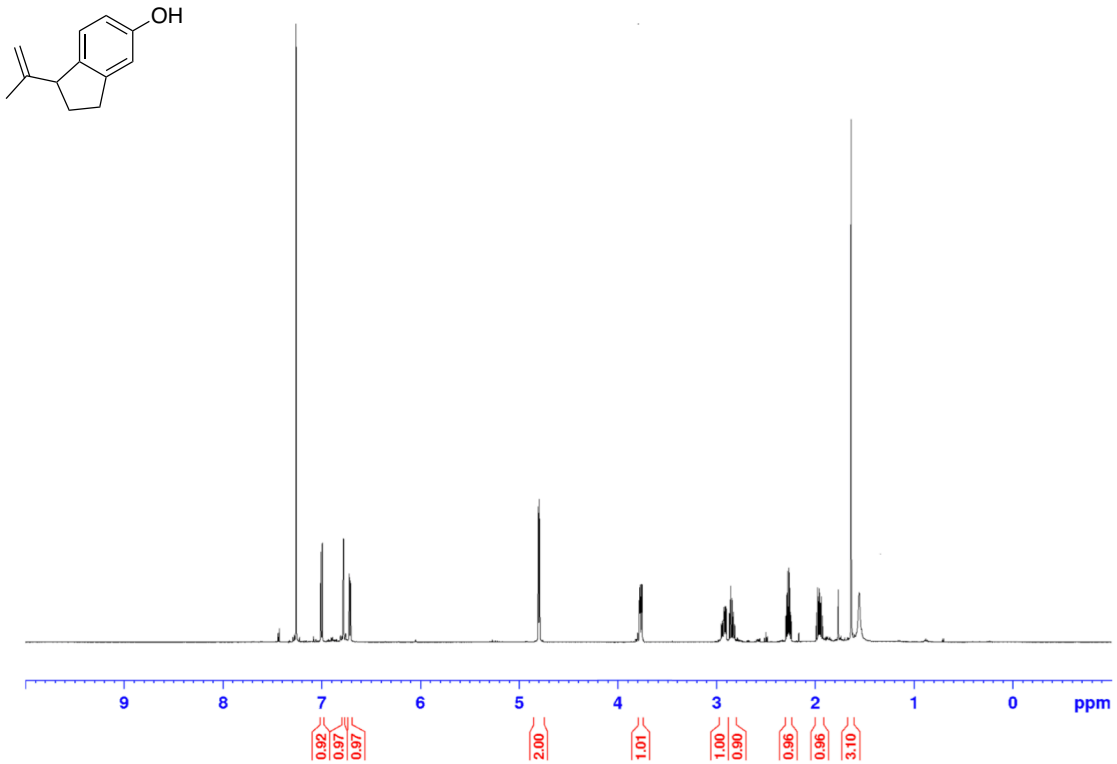
^{1}H NMR spectrum of **16** ($CDCl_3$, 500 MHz)



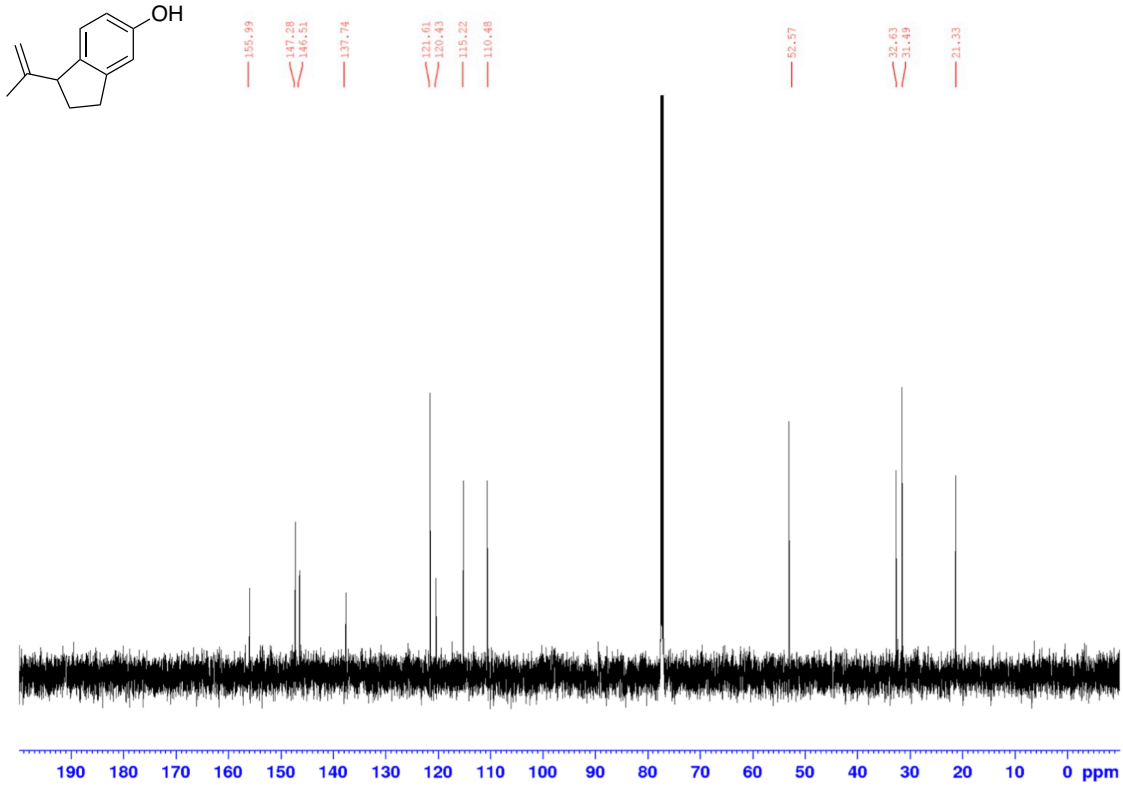
^{13}C NMR spectrum of **16** ($CDCl_3$, 125 MHz)



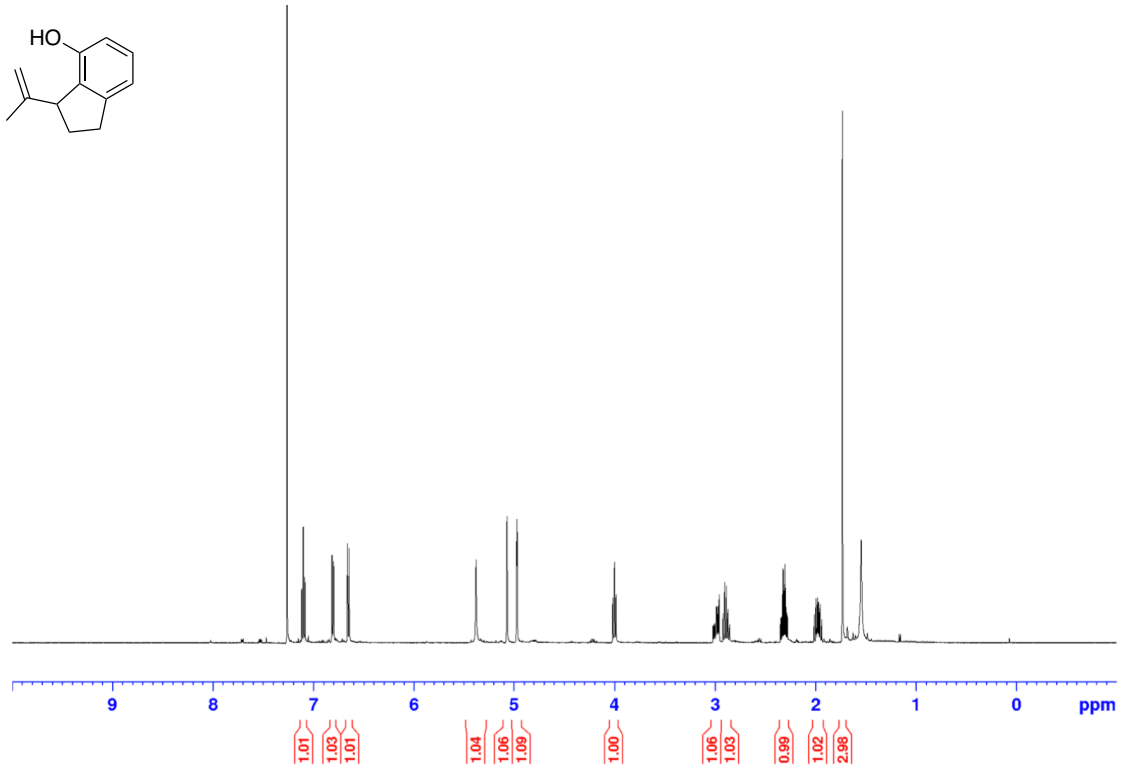
^{1}H NMR spectrum of **8ax** ($CDCl_3$, 500 MHz)



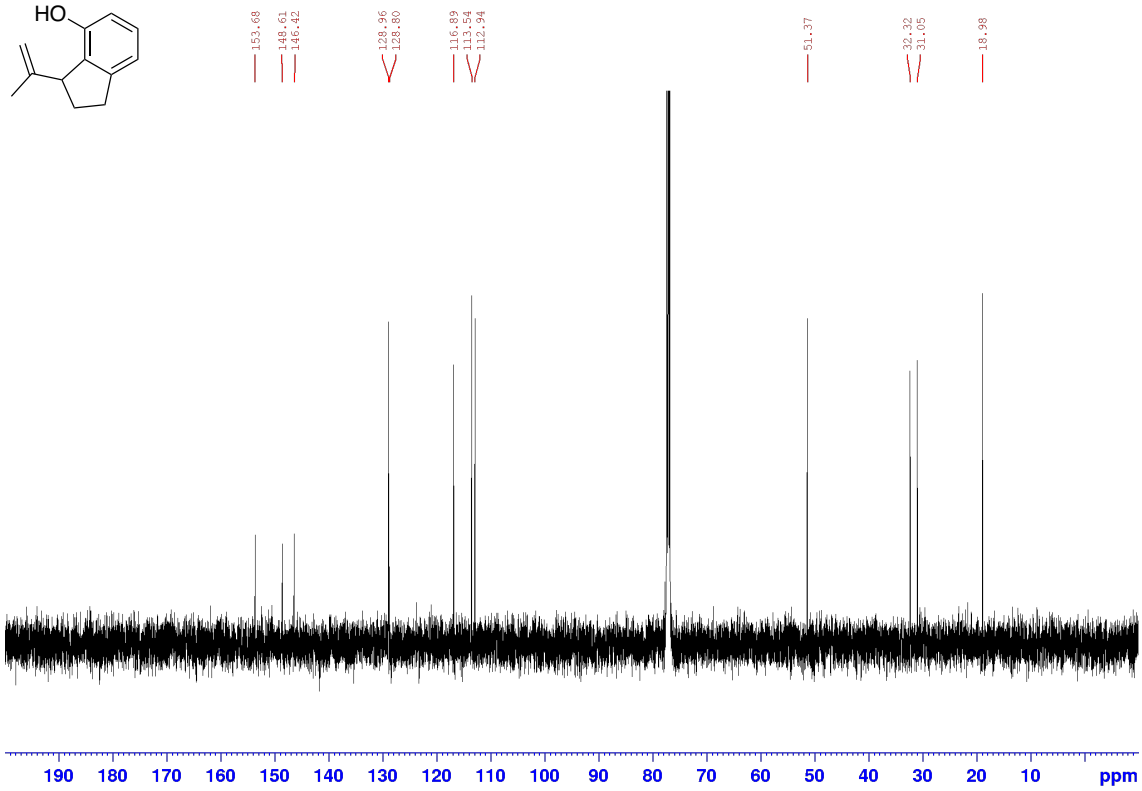
^{13}C NMR spectrum of **8ax** ($CDCl_3$, 125 MHz)



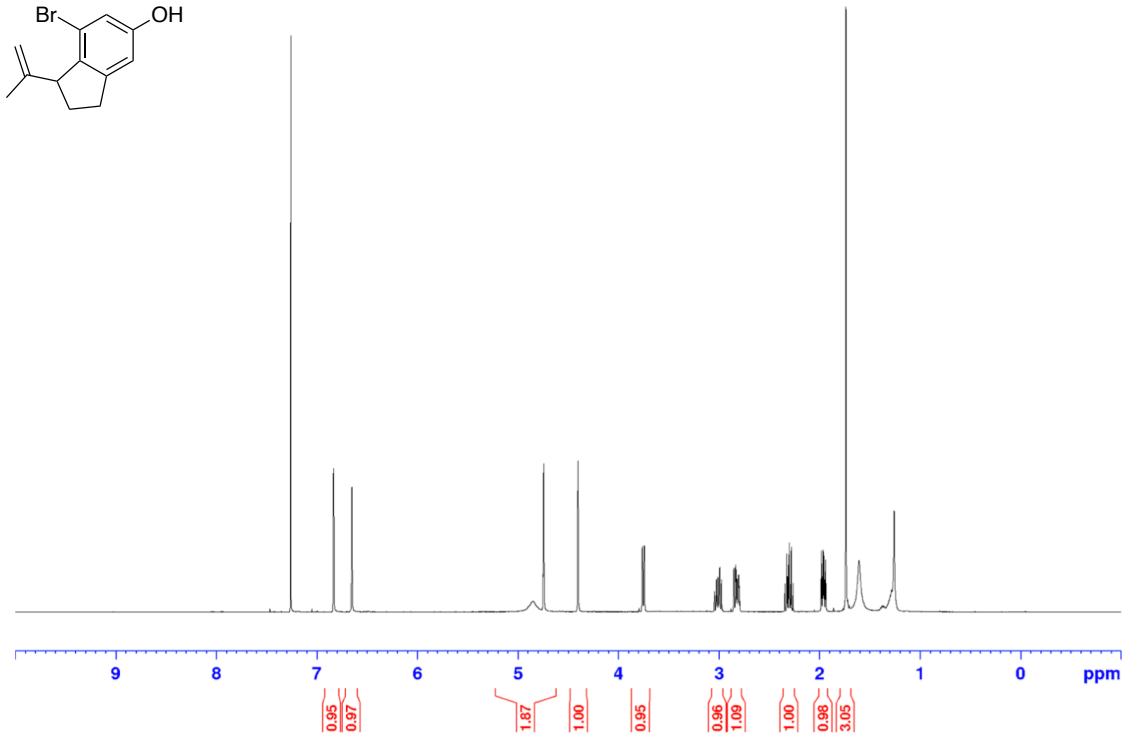
^{1}H NMR spectrum of **8ay** ($CDCl_3$, 500 MHz)



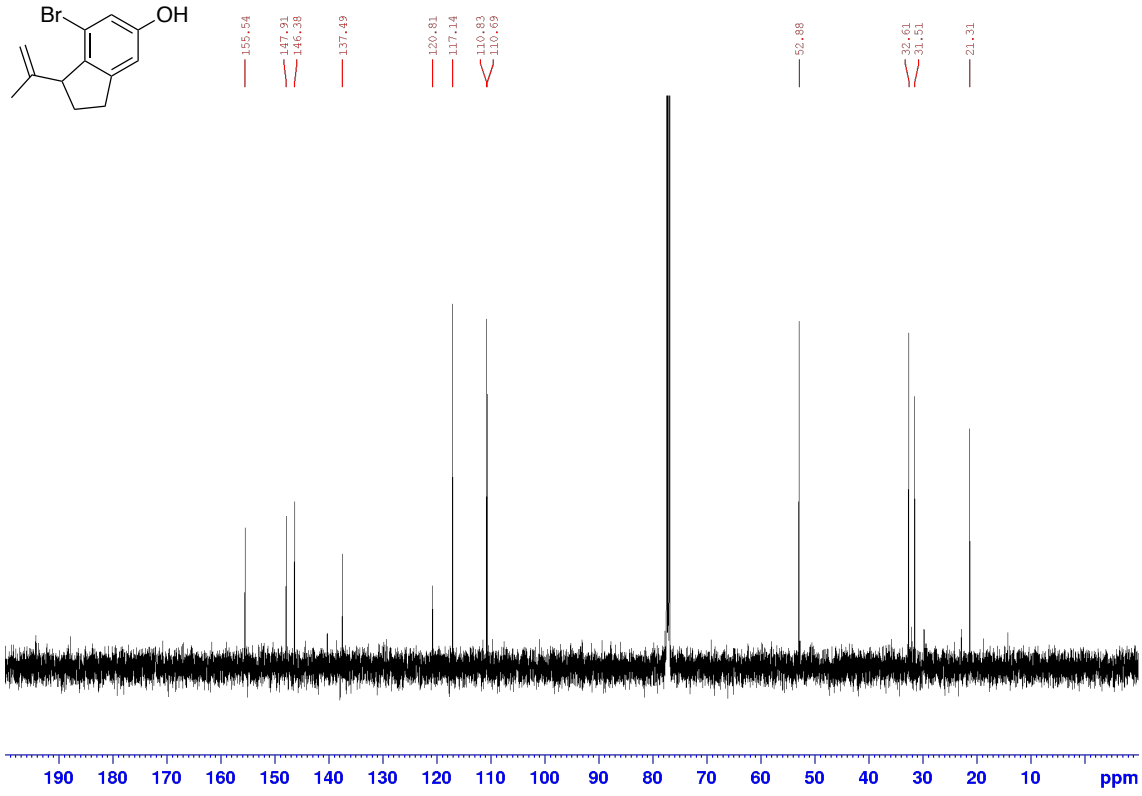
^{13}C NMR spectrum of **8ay** ($CDCl_3$, 125 MHz)



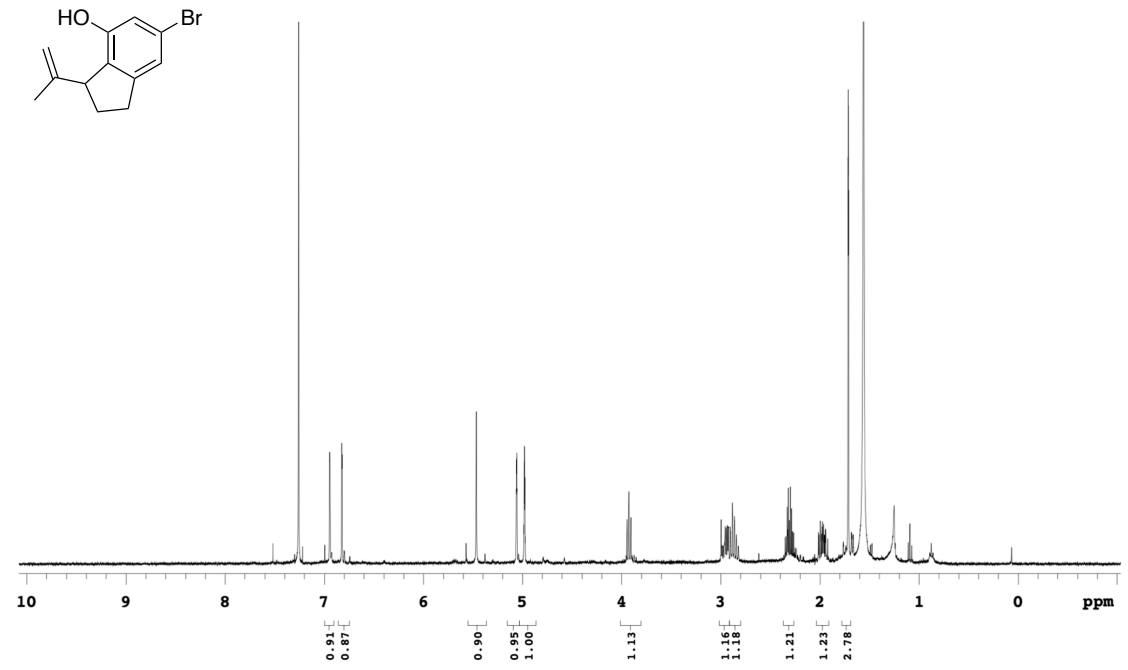
^{1}H NMR spectrum of **8bx** ($CDCl_3$, 500 MHz)



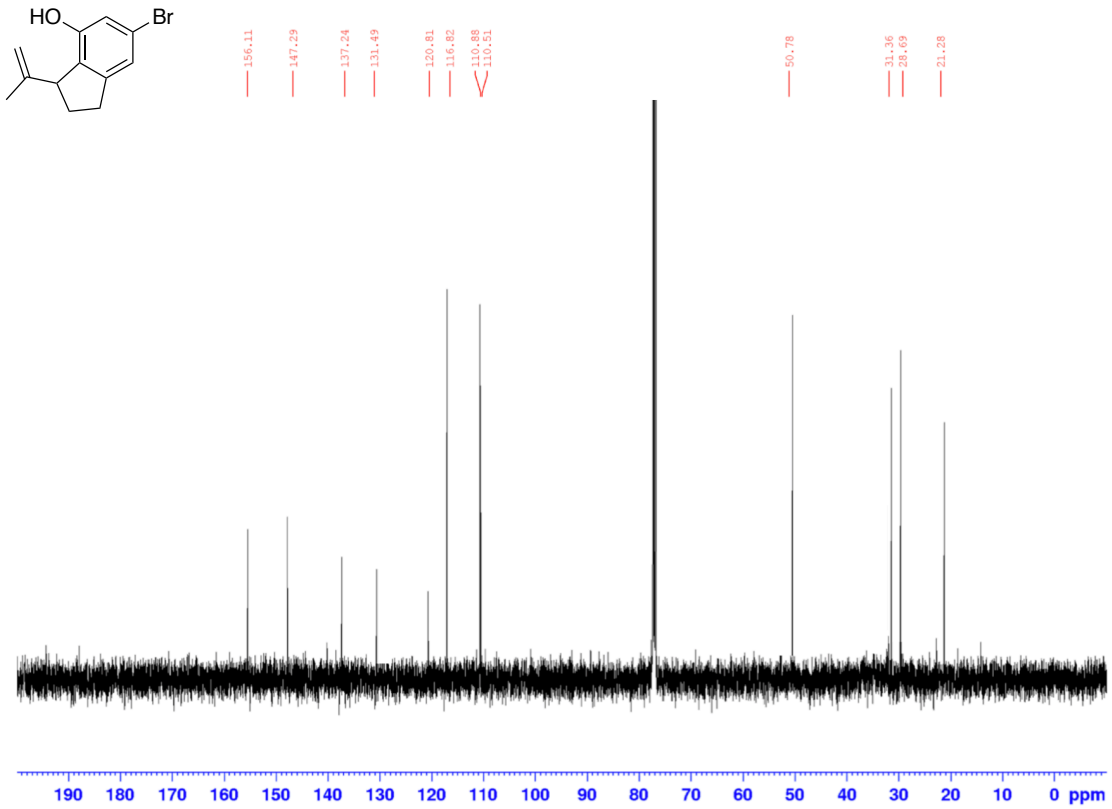
^{13}C NMR spectrum of **8bx** ($CDCl_3$, 125 MHz)



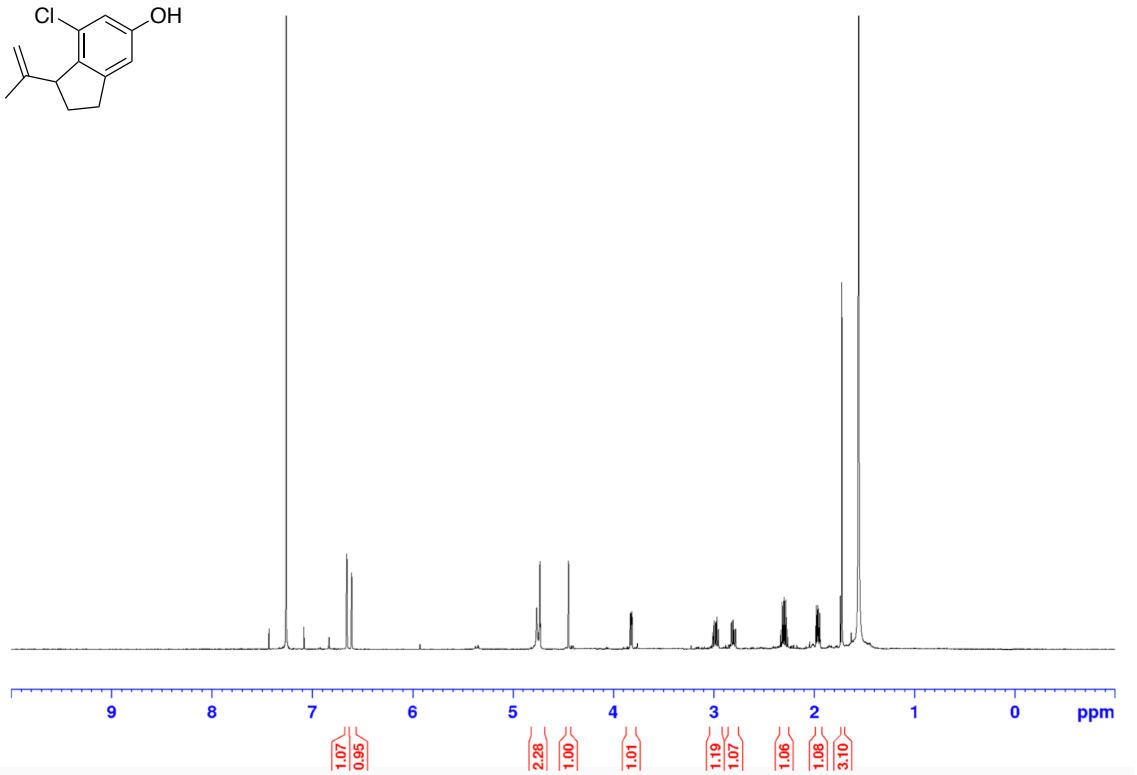
^{1}H NMR spectrum of **8by** ($CDCl_3$, 400 MHz)



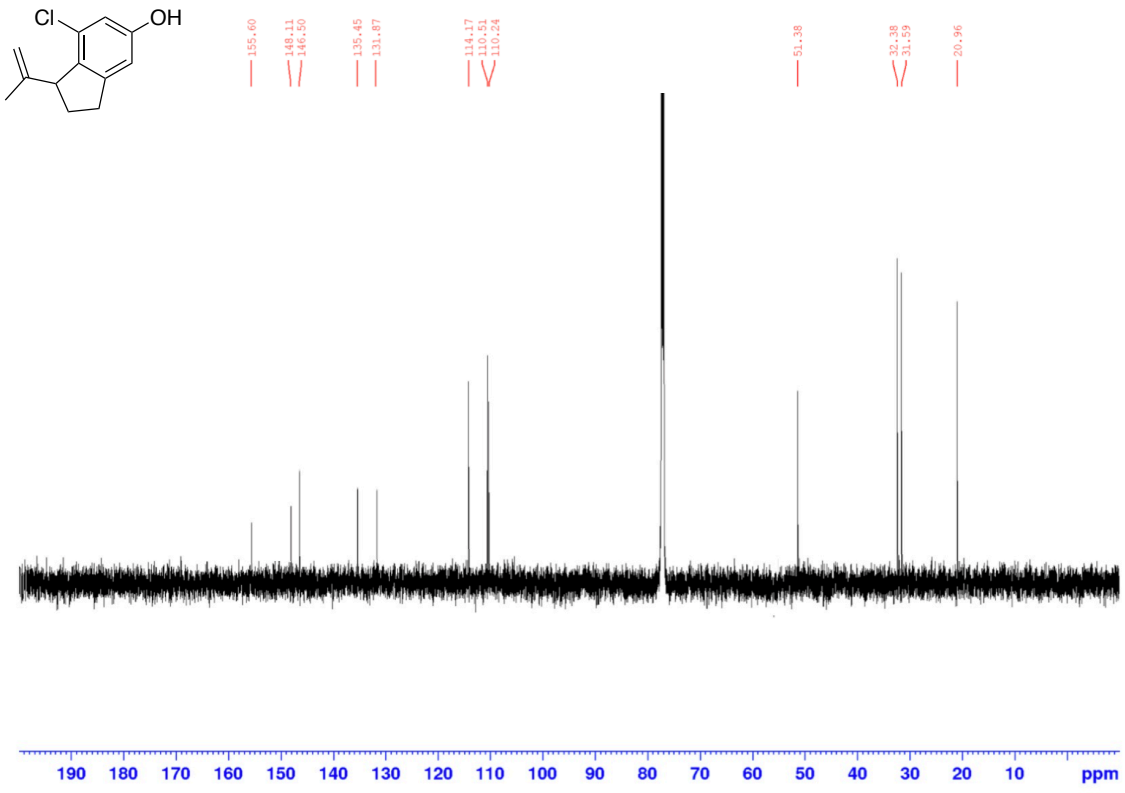
^{13}C NMR spectrum of **8by** ($CDCl_3$, 125 MHz)



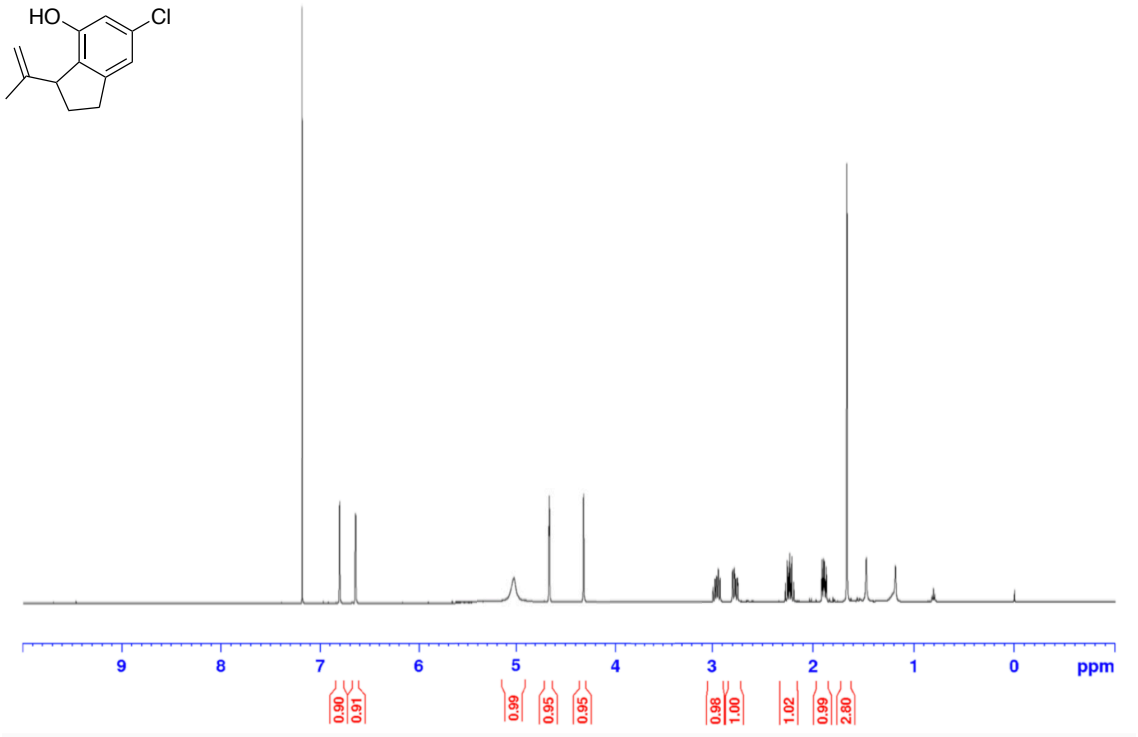
^{1}H NMR spectrum of **8cx** ($CDCl_3$, 500 MHz)



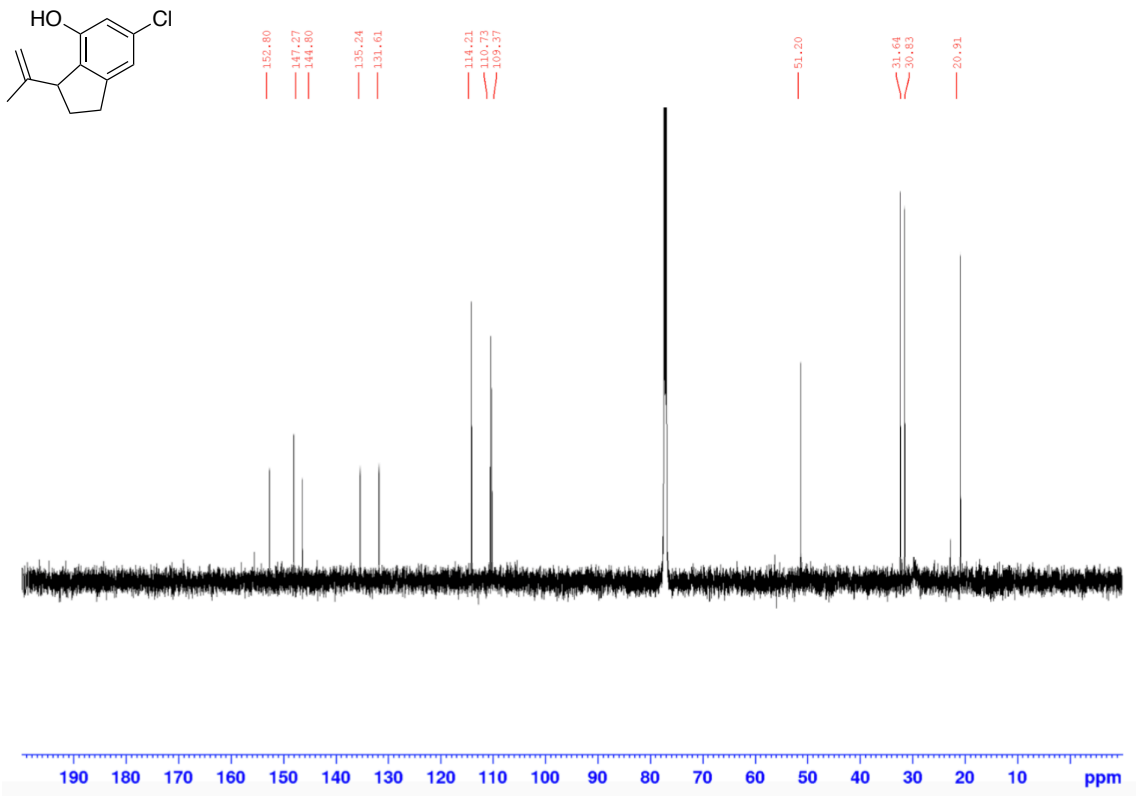
^{13}C NMR spectrum of **8cx** ($CDCl_3$, 125 MHz)



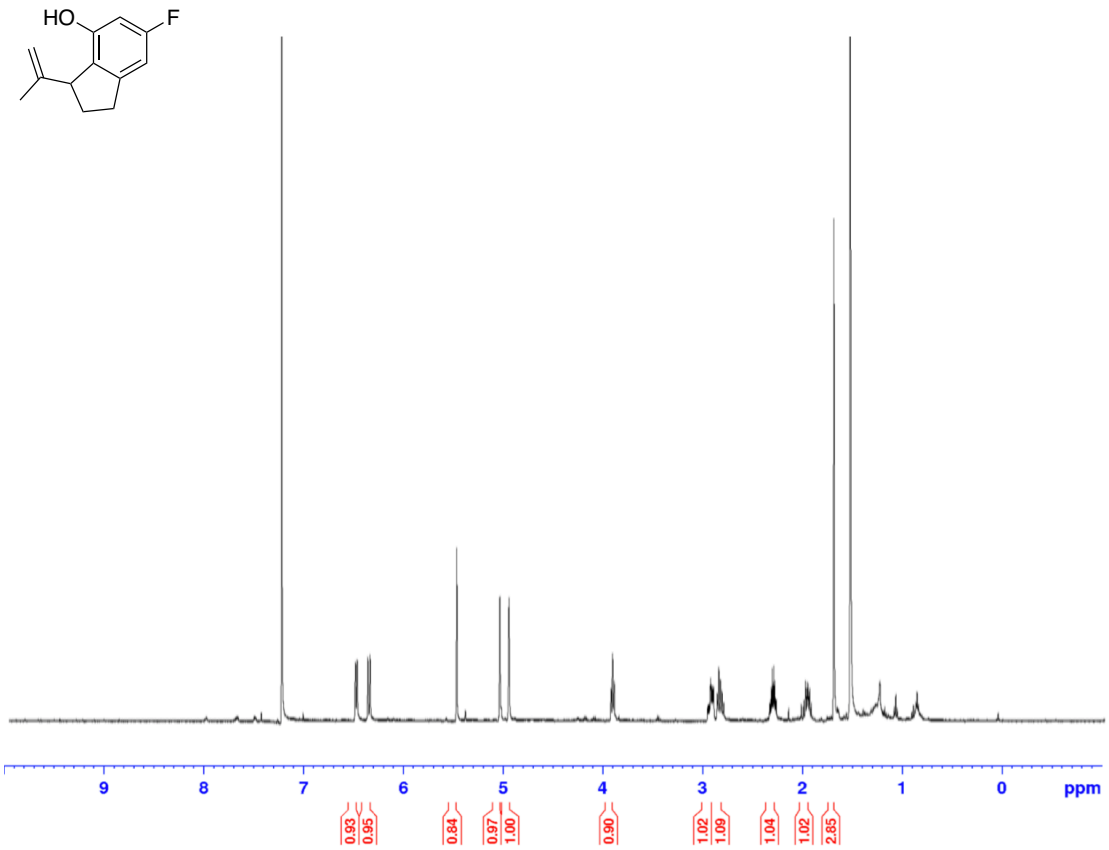
^{1}H NMR spectrum of **8cy** ($CDCl_3$, 500 MHz)



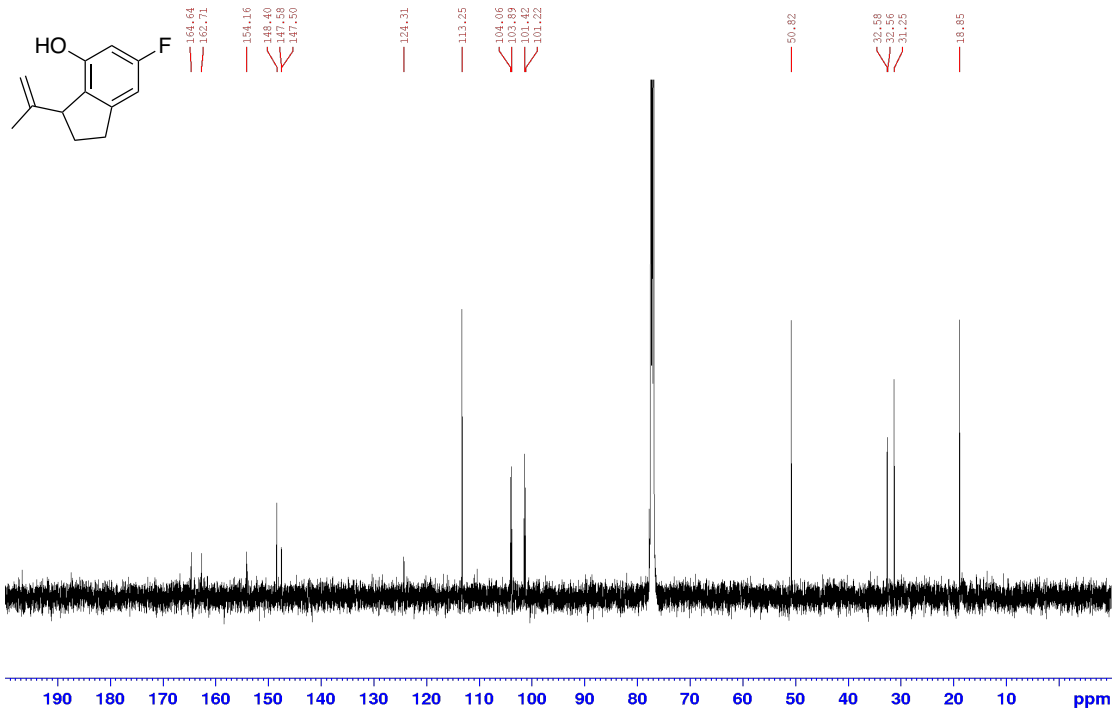
^{13}C NMR spectrum of **8cy** ($CDCl_3$, 125 MHz)



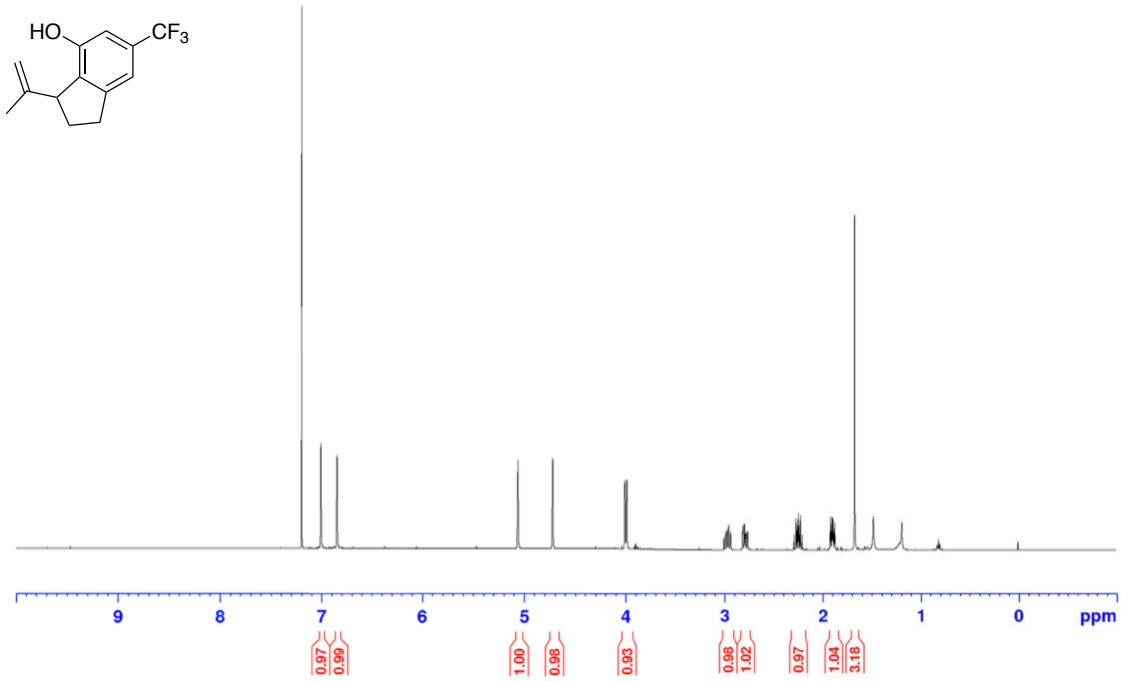
^{1}H NMR spectrum of **8dy** ($CDCl_3$, 500 MHz)



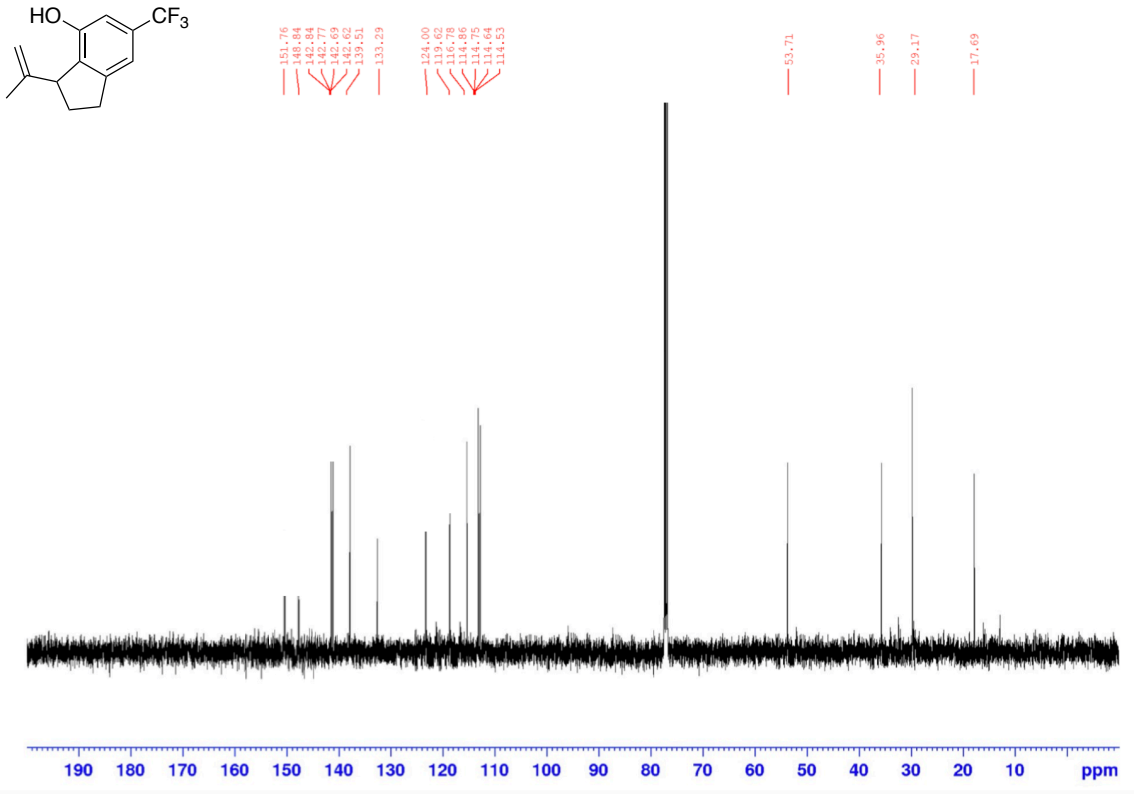
^{13}C NMR spectrum of **8dy** ($CDCl_3$, 125 MHz)



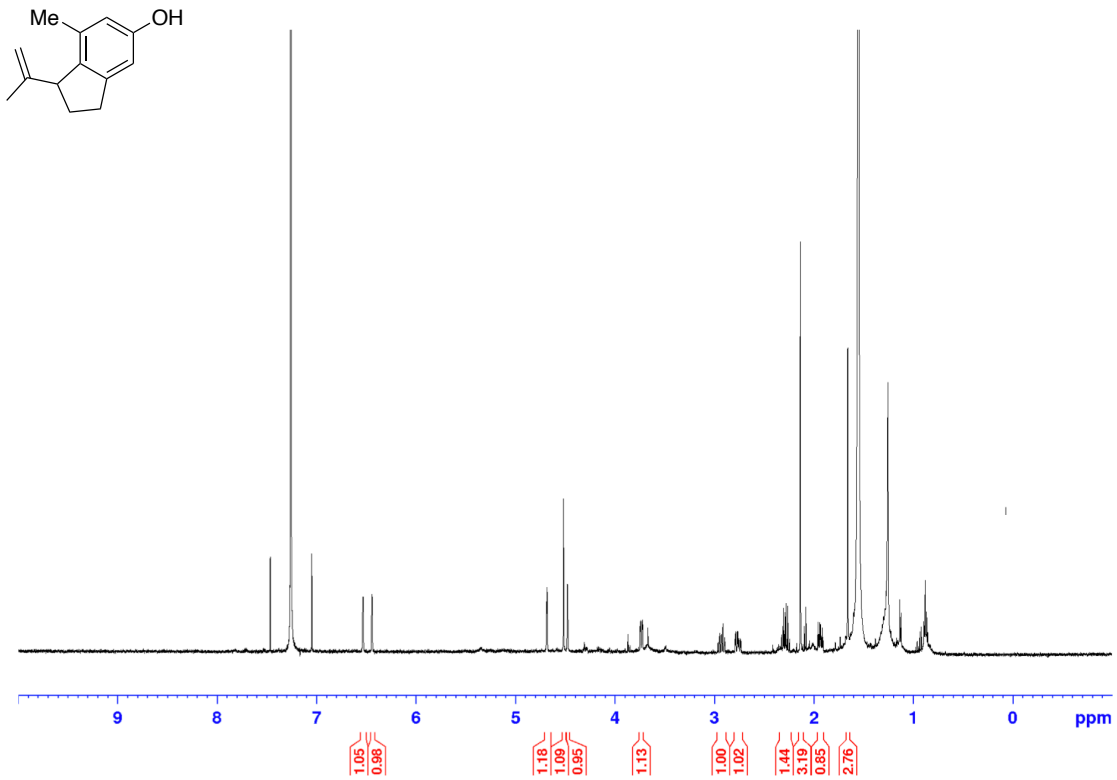
^{1}H NMR spectrum of **8ey** ($CDCl_3$, 500 MHz)



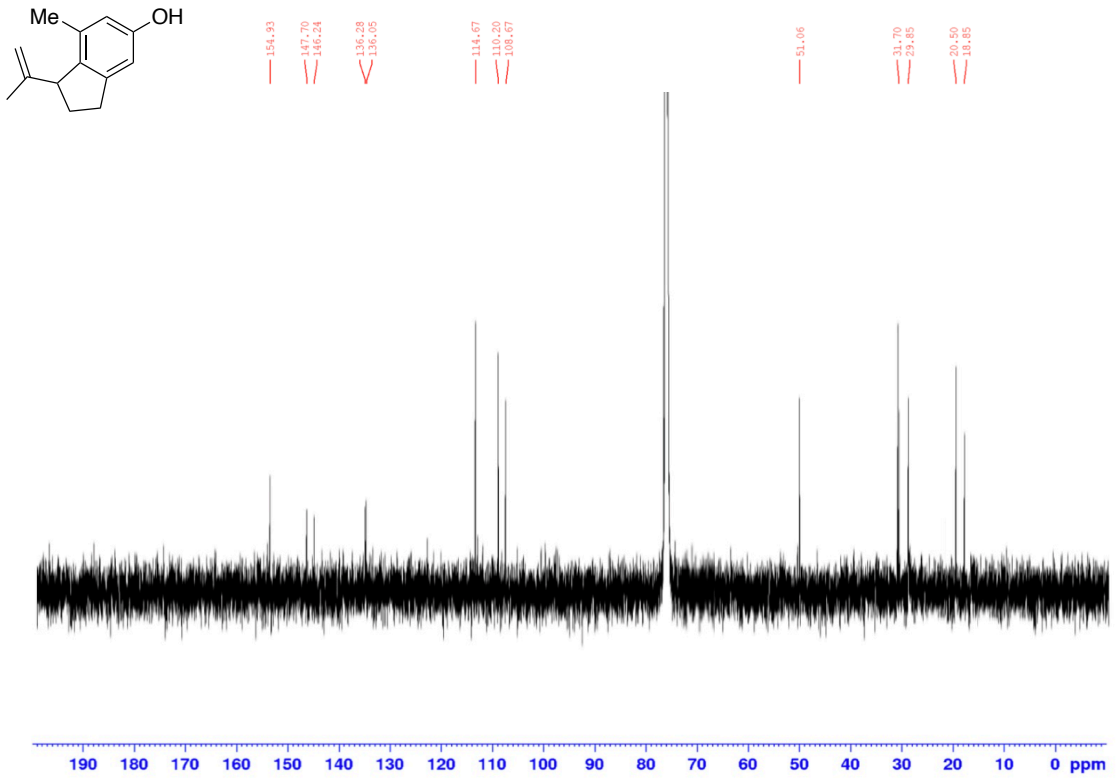
^{13}C NMR spectrum of **8ey** ($CDCl_3$, 125 MHz)



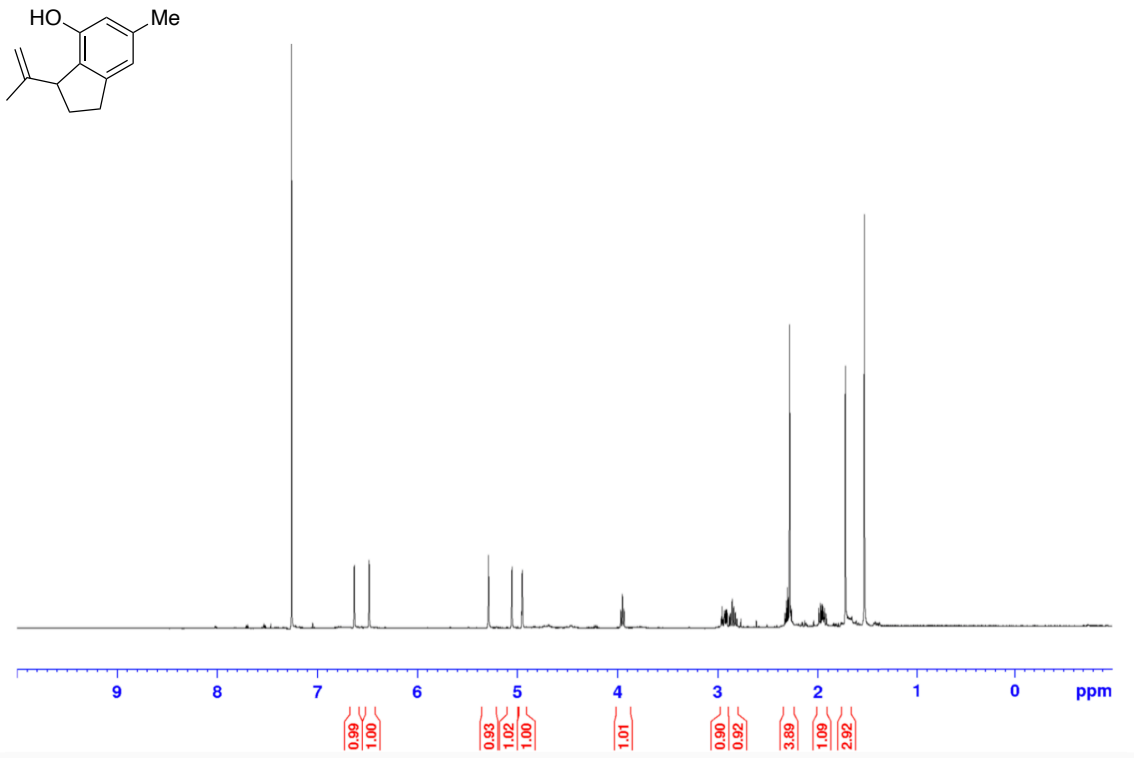
^{1}H NMR spectrum of **8fx** ($CDCl_3$, 500 MHz)



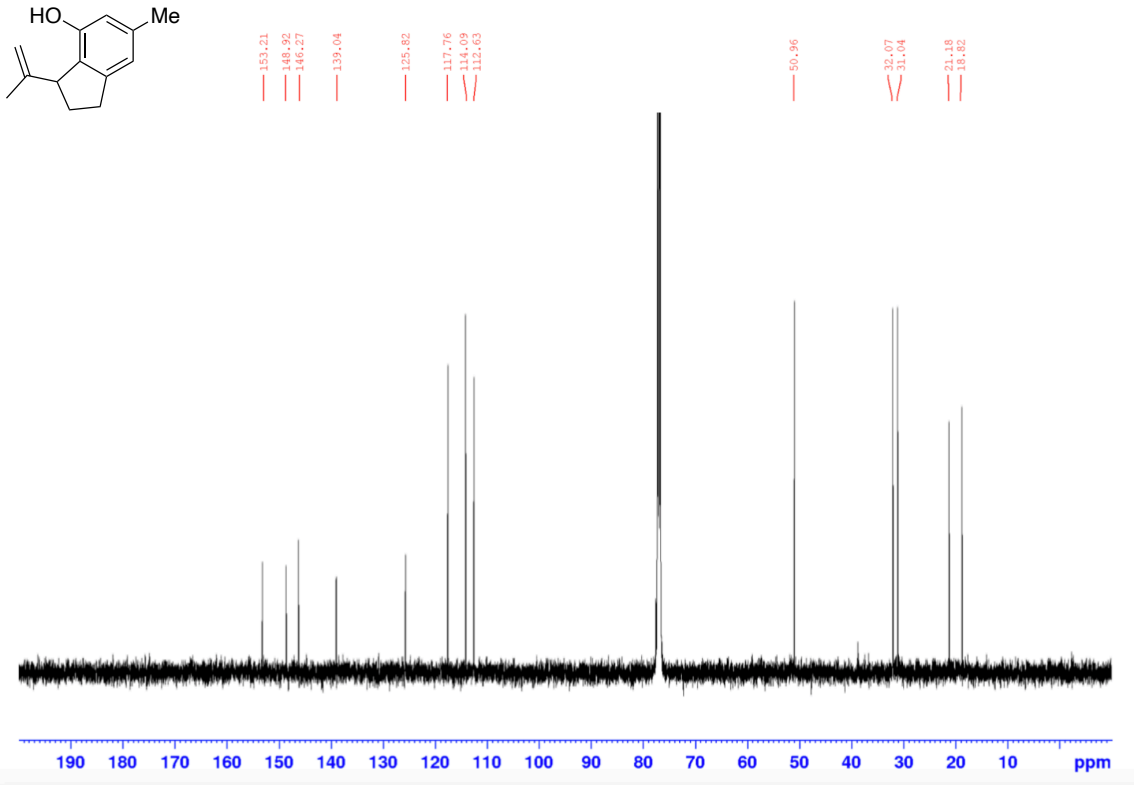
^{13}C NMR spectrum of **8fx** ($CDCl_3$, 125 MHz)



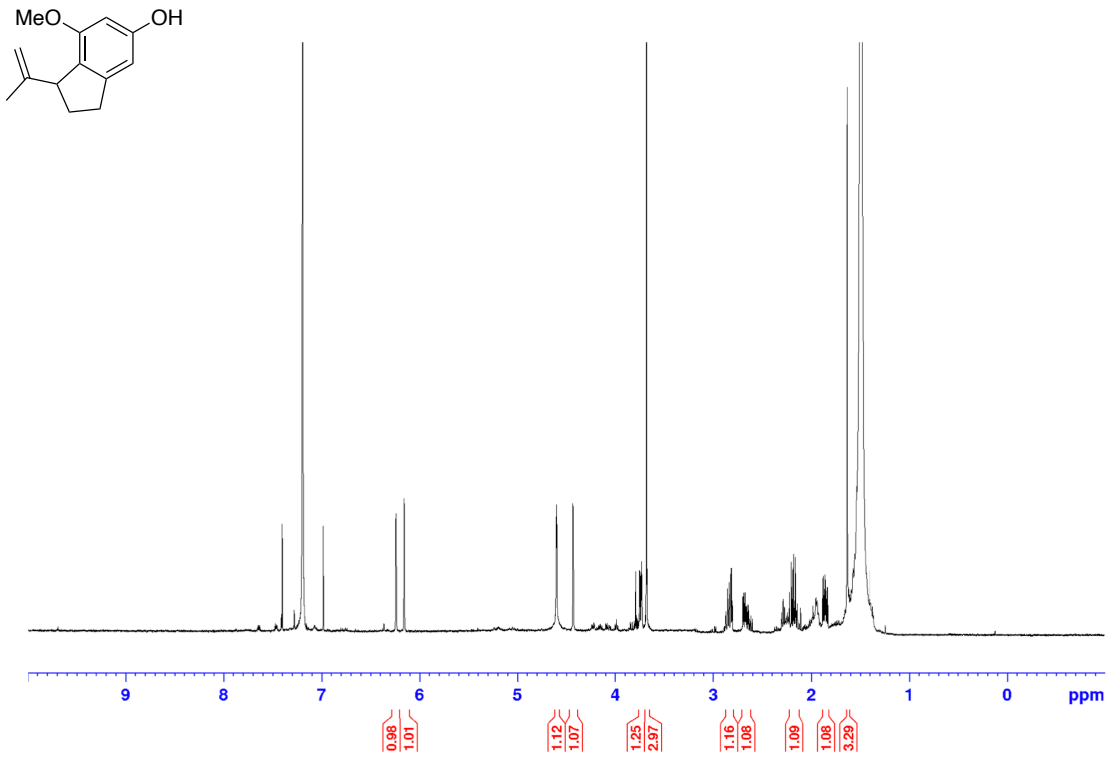
^{1}H NMR spectrum of **8fy** ($CDCl_3$, 500 MHz)



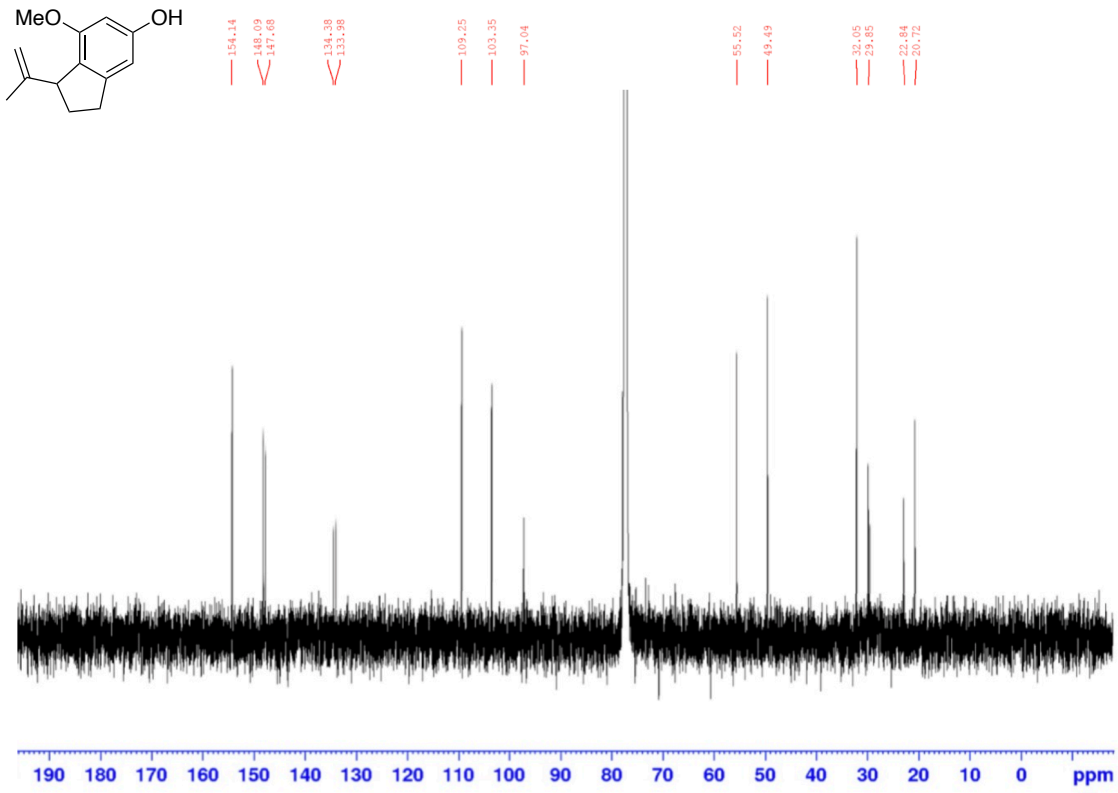
^{13}C NMR spectrum of **8fy** ($CDCl_3$, 125 MHz)



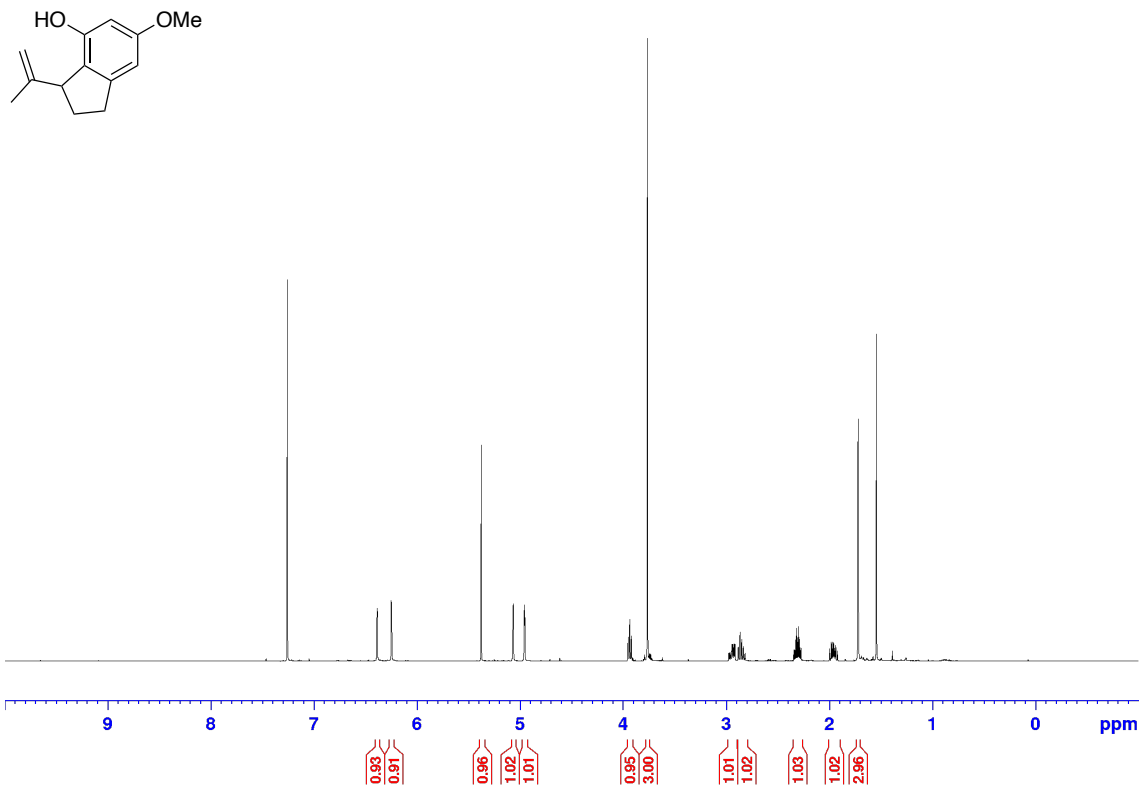
^{1}H NMR spectrum of **8gx** ($CDCl_3$, 500 MHz)



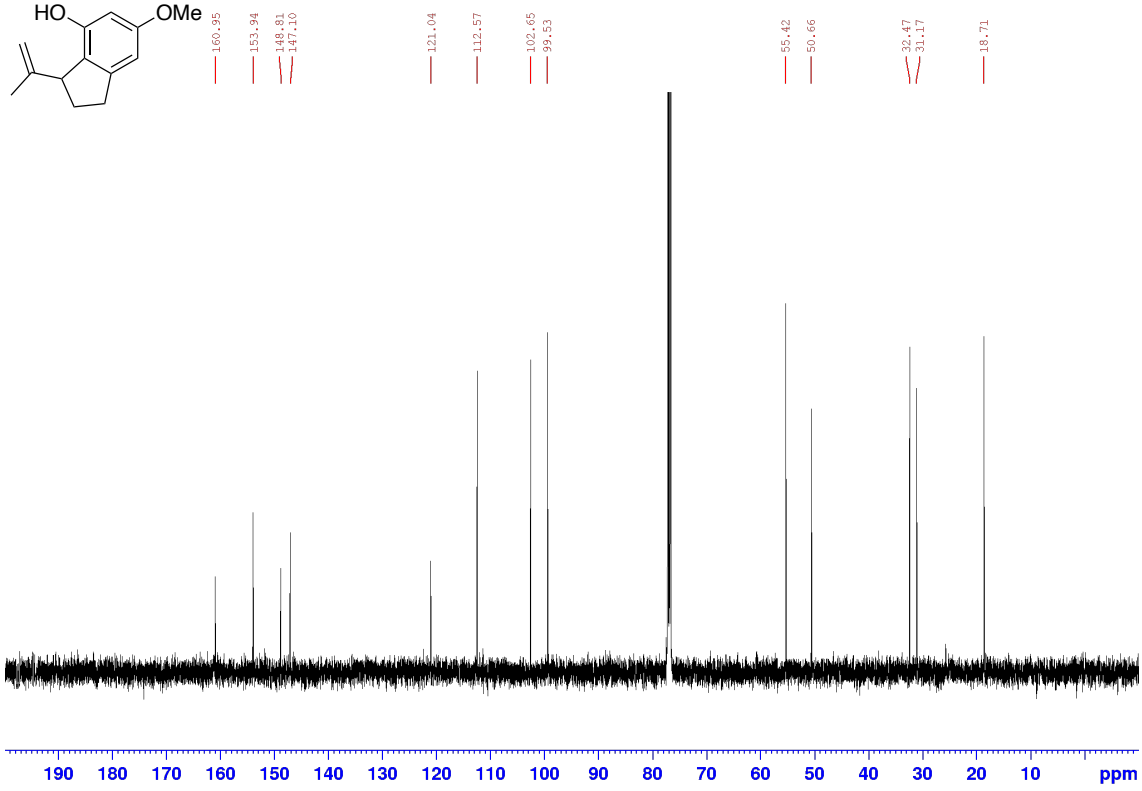
^{13}C NMR spectrum of **8gx** ($CDCl_3$, 125 MHz)



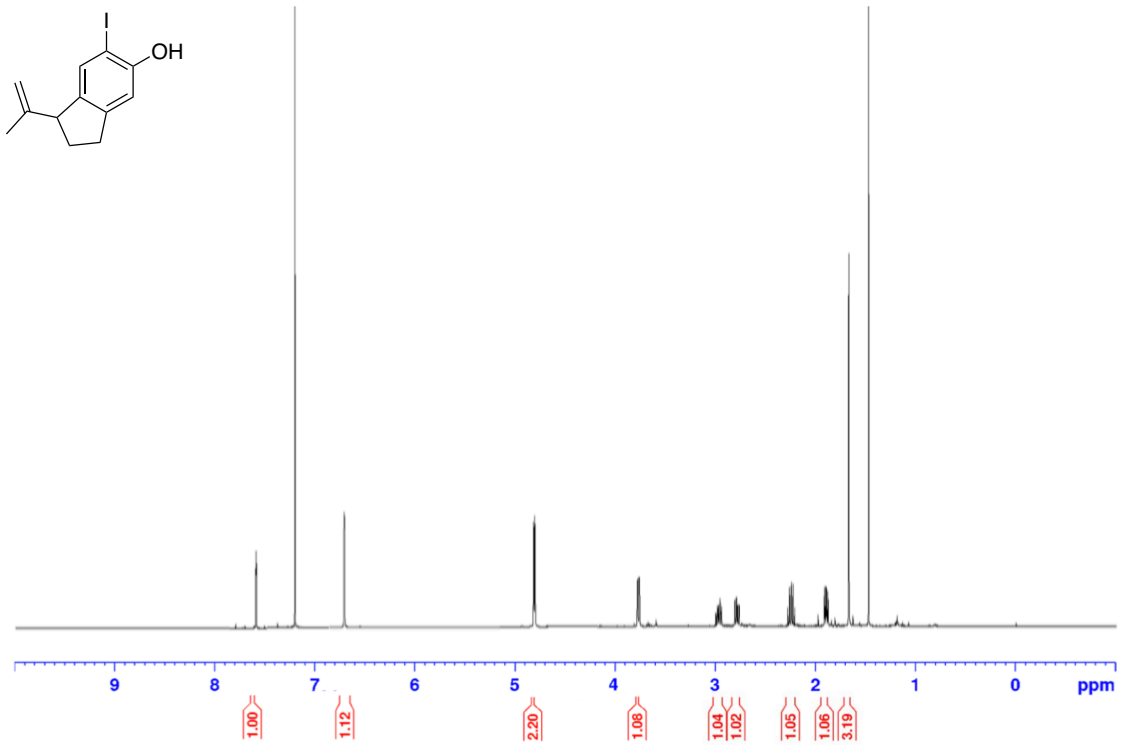
^{1}H NMR spectrum of **8gy** ($CDCl_3$, 500 MHz)



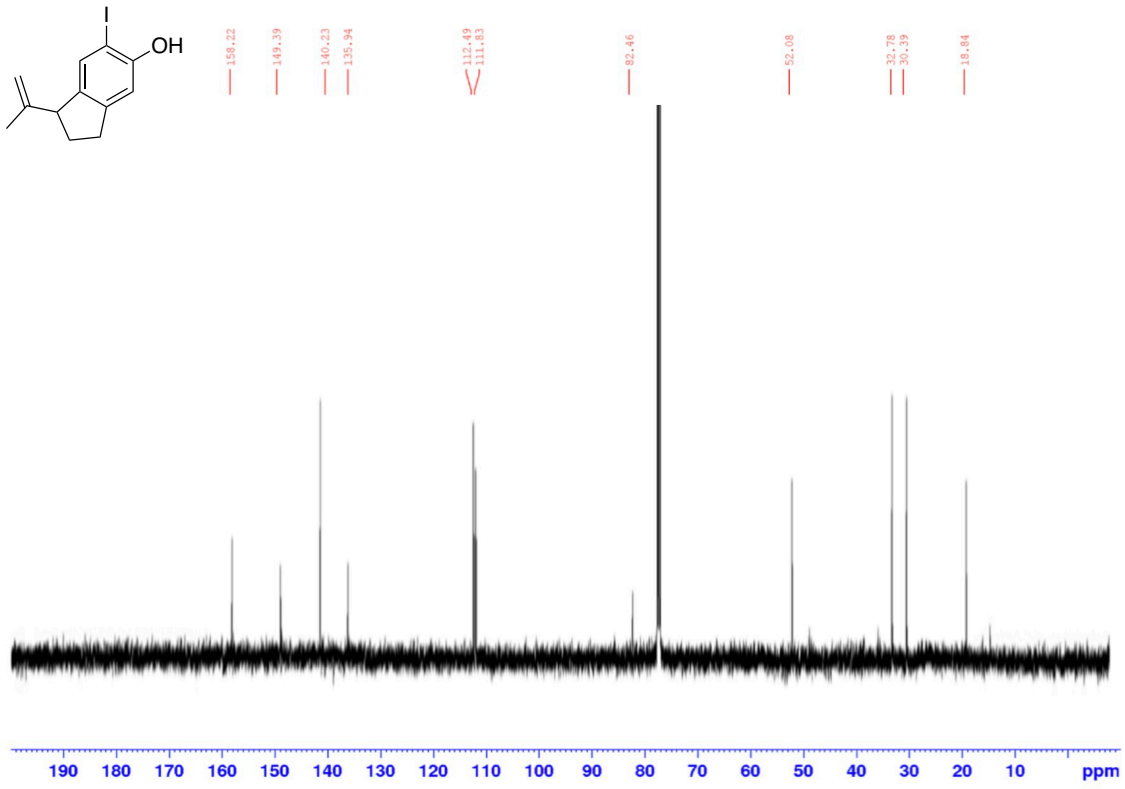
^{13}C NMR spectrum of **8gy** ($CDCl_3$, 125 MHz)



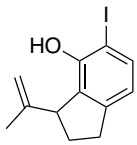
^{1}H NMR spectrum of **8hx** ($CDCl_3$, 500 MHz)



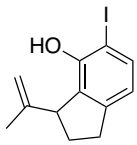
^{13}C NMR spectrum of **8hx** ($CDCl_3$, 125 MHz)



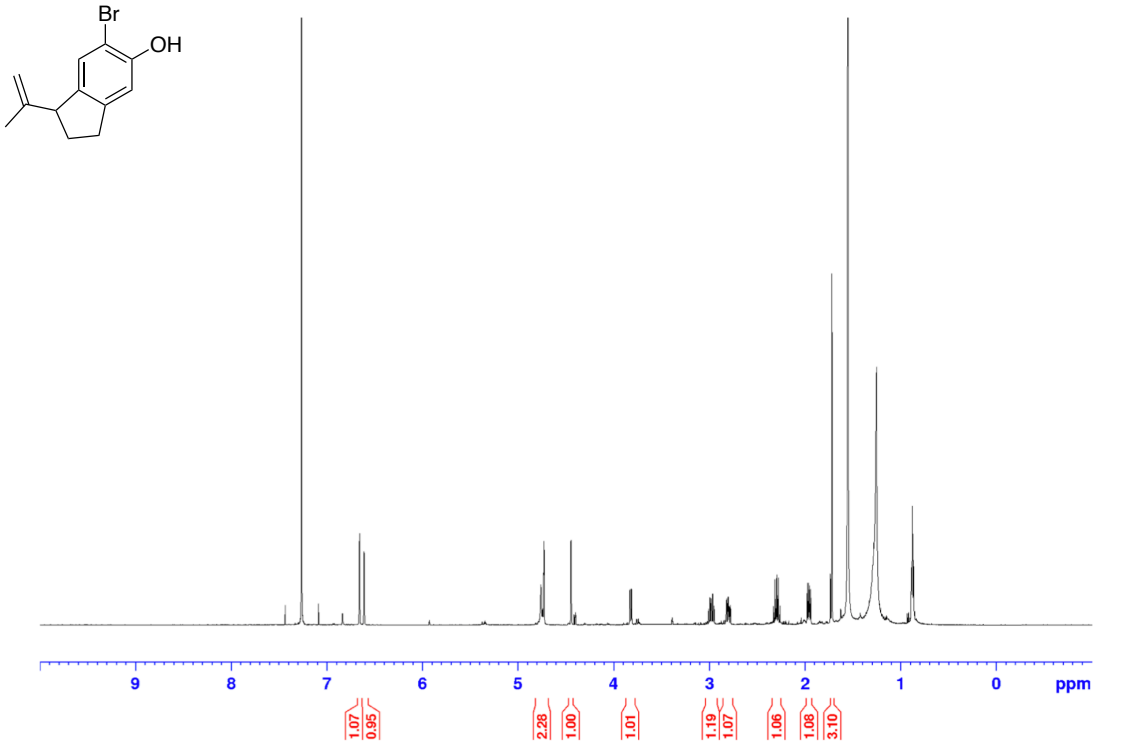
^{1}H NMR spectrum of **8hy** ($CDCl_3$, 500 MHz)



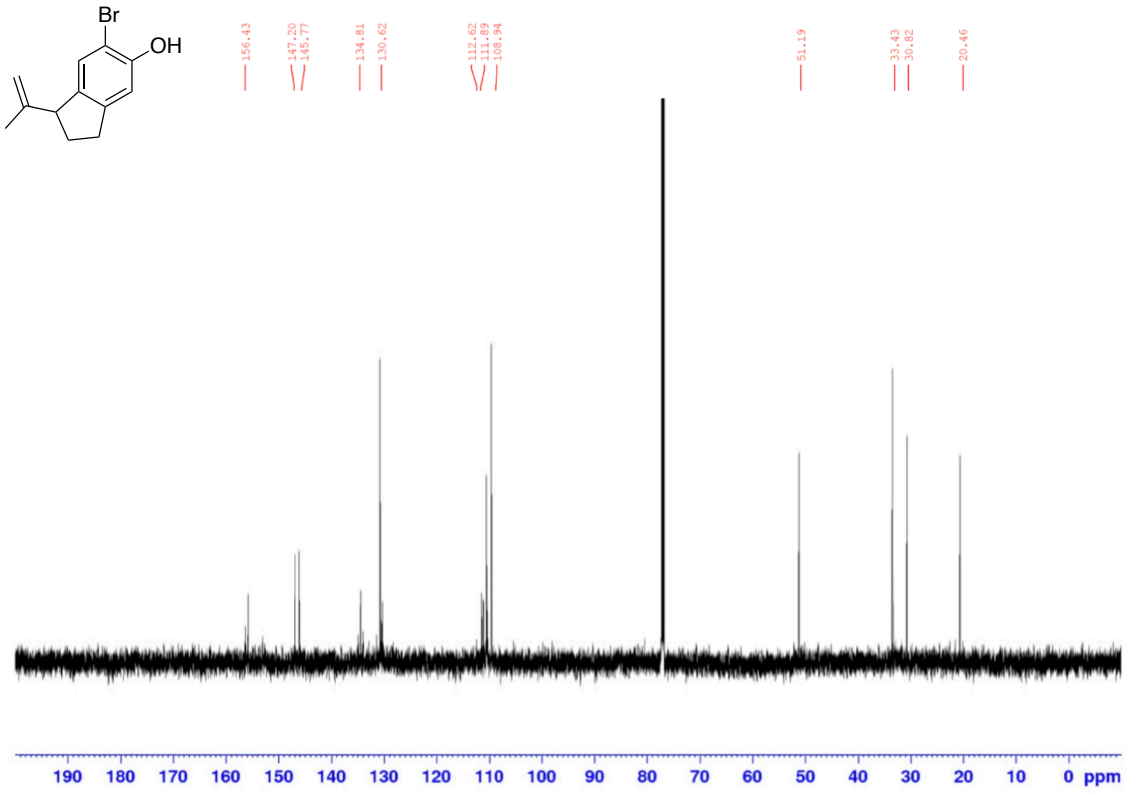
^{13}C NMR spectrum of **8hy** ($CDCl_3$, 125 MHz)



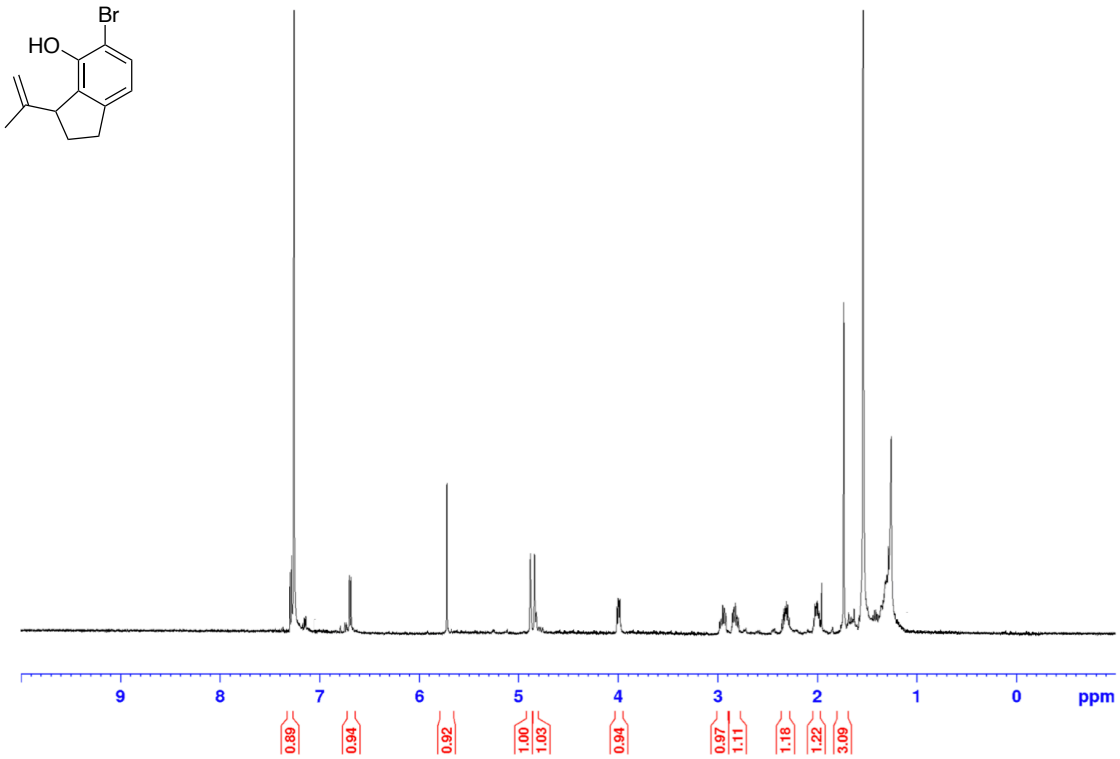
^{1}H NMR spectrum of **8ix** ($CDCl_3$, 500 MHz)



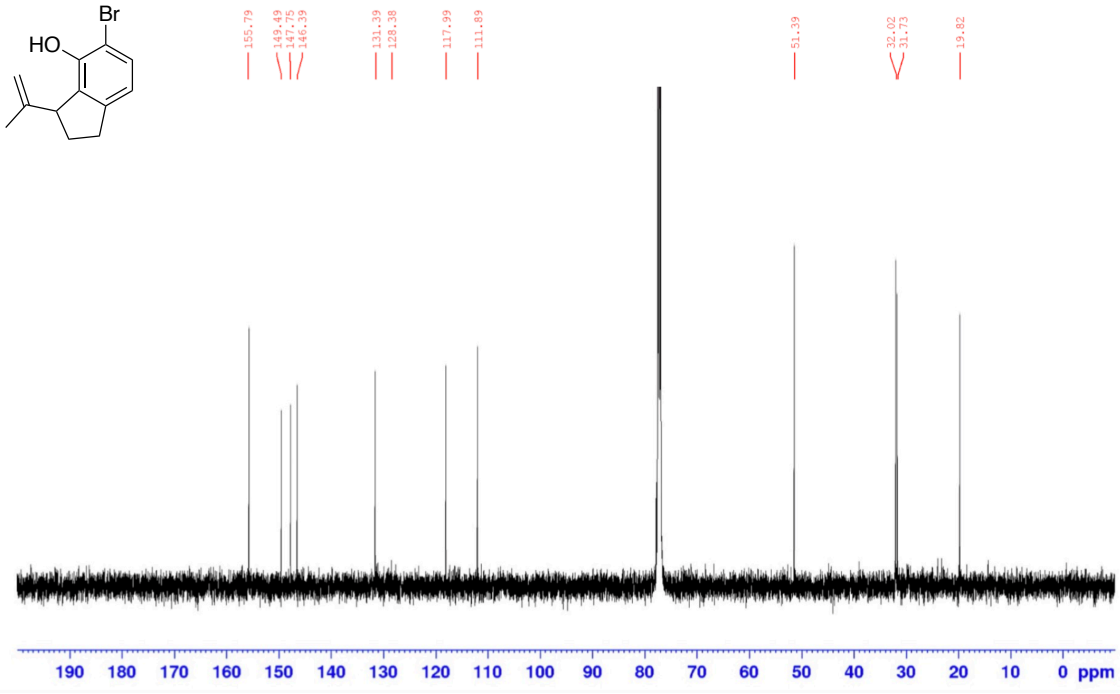
^{13}C NMR spectrum of **8ix** ($CDCl_3$, 125 MHz)



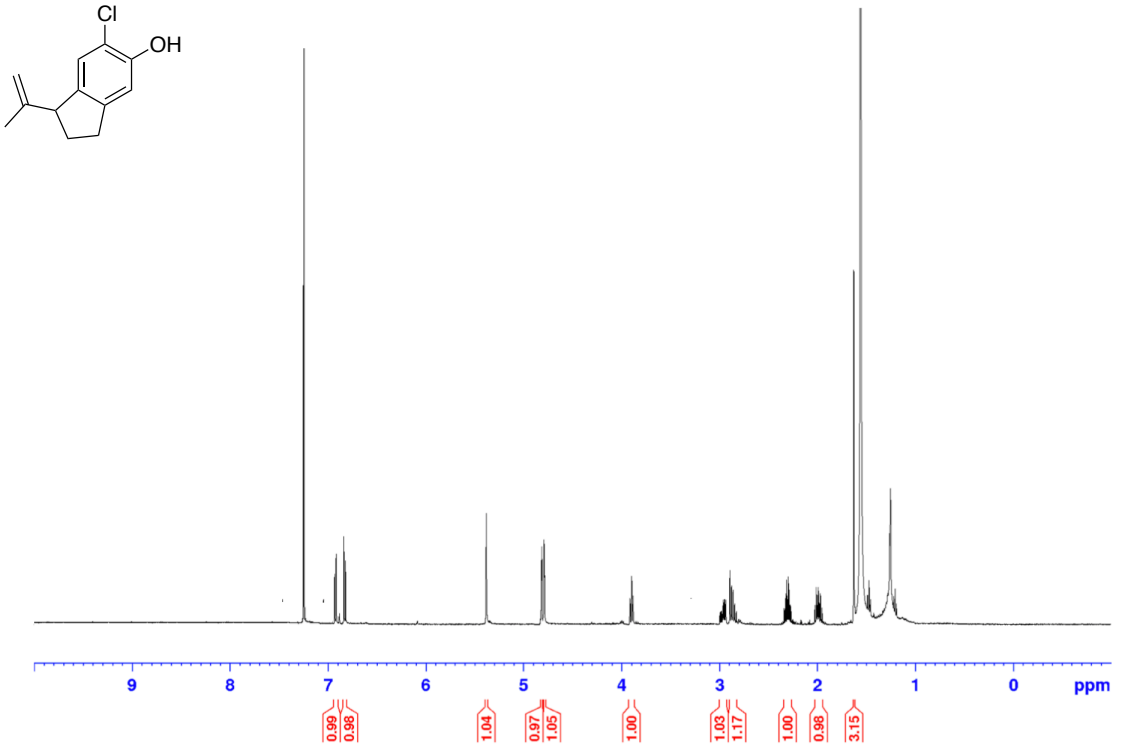
^{1}H NMR spectrum of **8iy** ($CDCl_3$, 500 MHz)



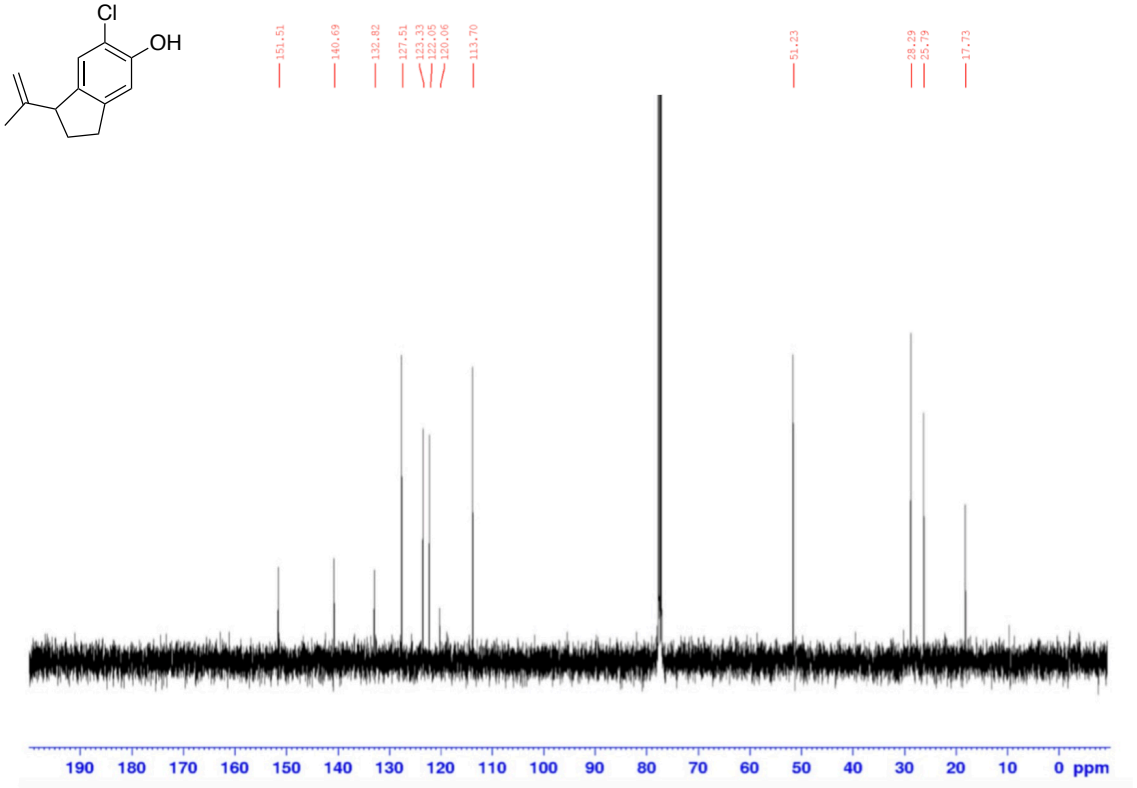
^{13}C NMR spectrum of **8iy** ($CDCl_3$, 125 MHz)



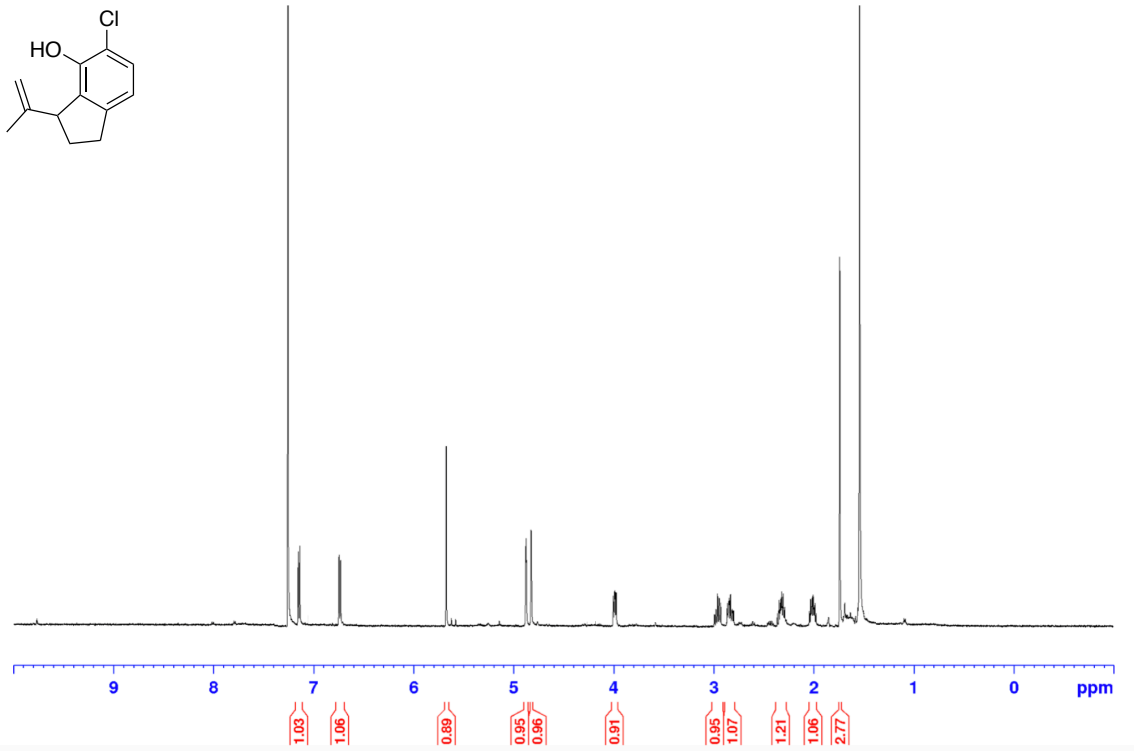
^{1}H NMR spectrum of **8jx** ($CDCl_3$, 500 MHz)



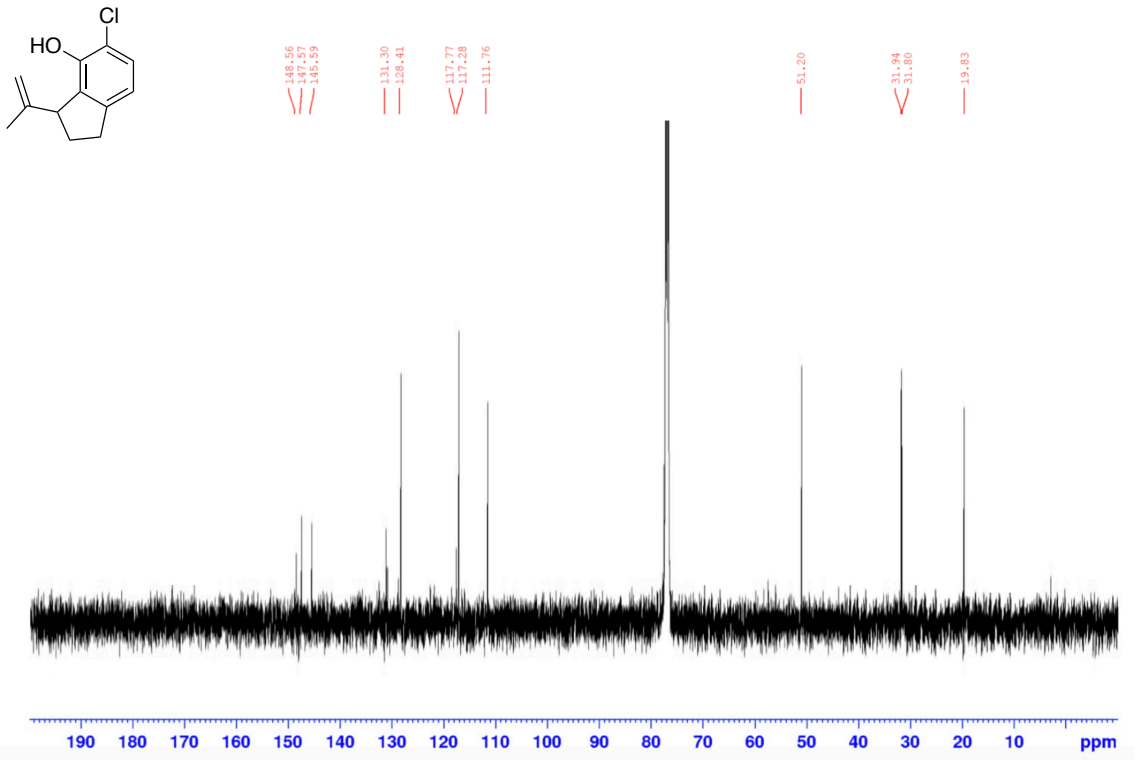
^{13}C NMR spectrum of **8jx** ($CDCl_3$, 125 MHz)



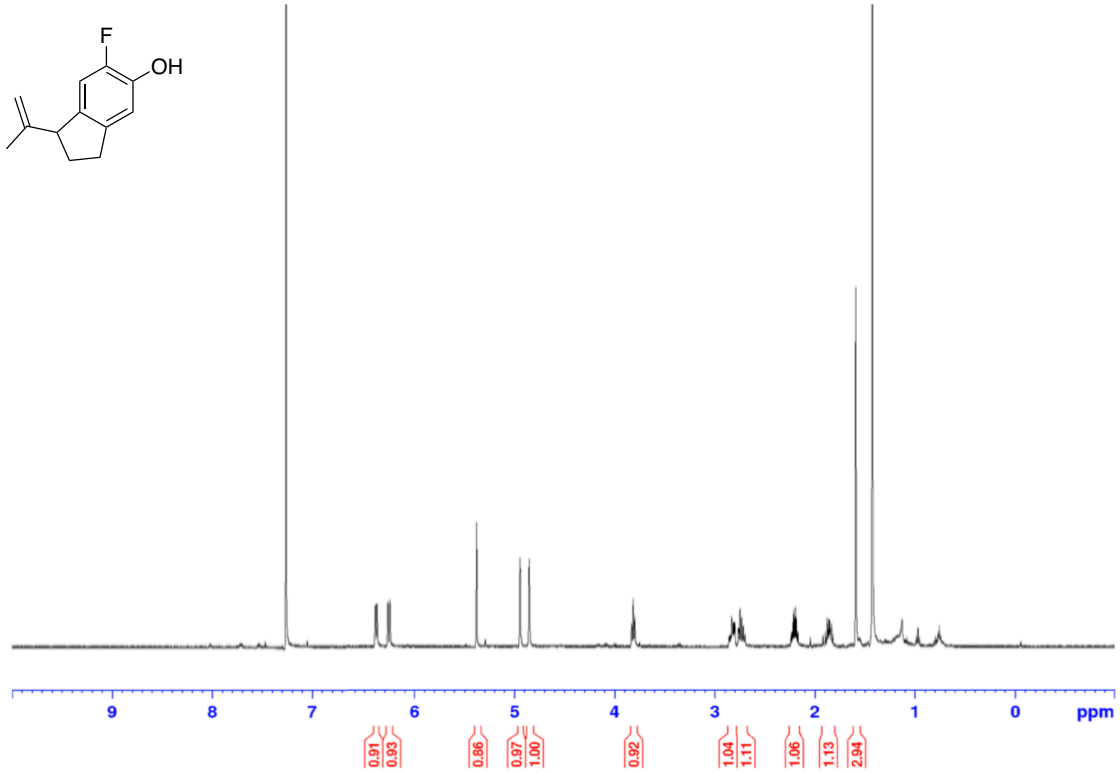
^{1}H NMR spectrum of **8jy** ($CDCl_3$, 500 MHz)



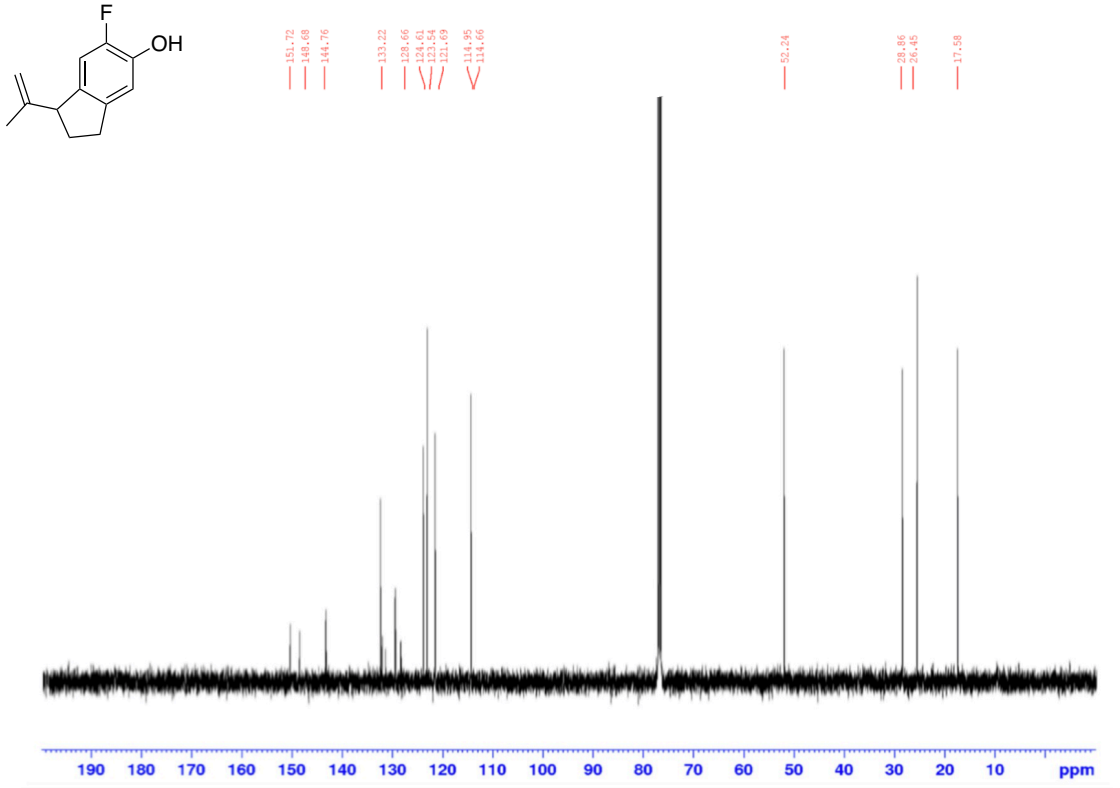
^{13}C NMR spectrum of **8jy** ($CDCl_3$, 125 MHz)



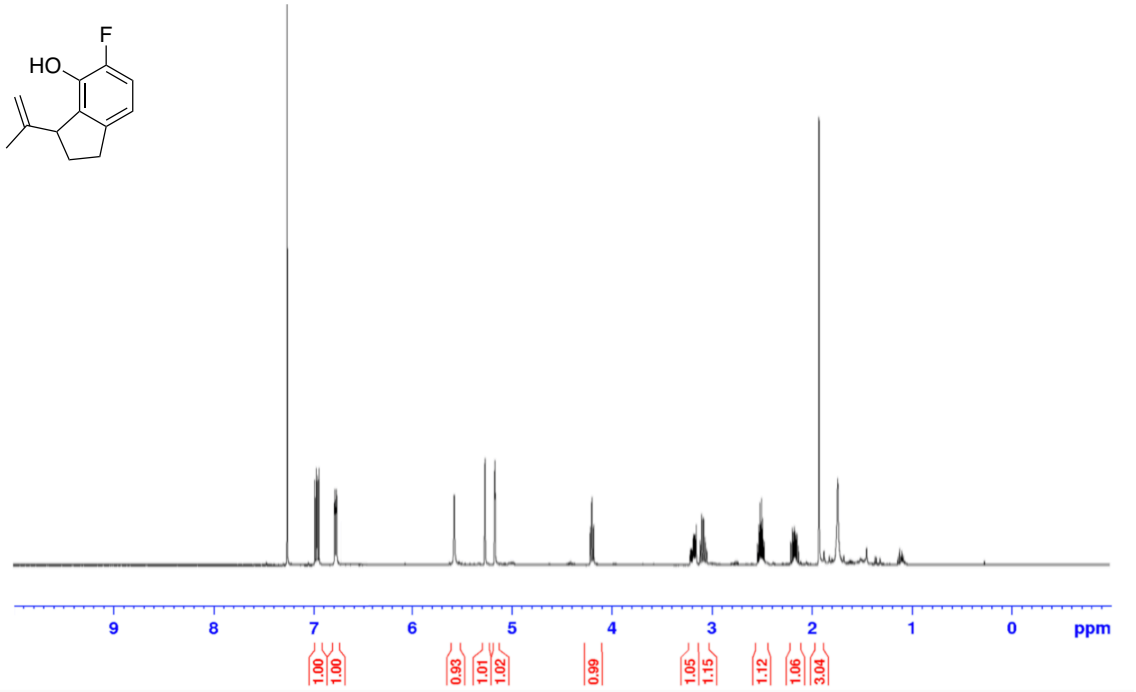
^{1}H NMR spectrum of **8kx** ($CDCl_3$, 500 MHz)



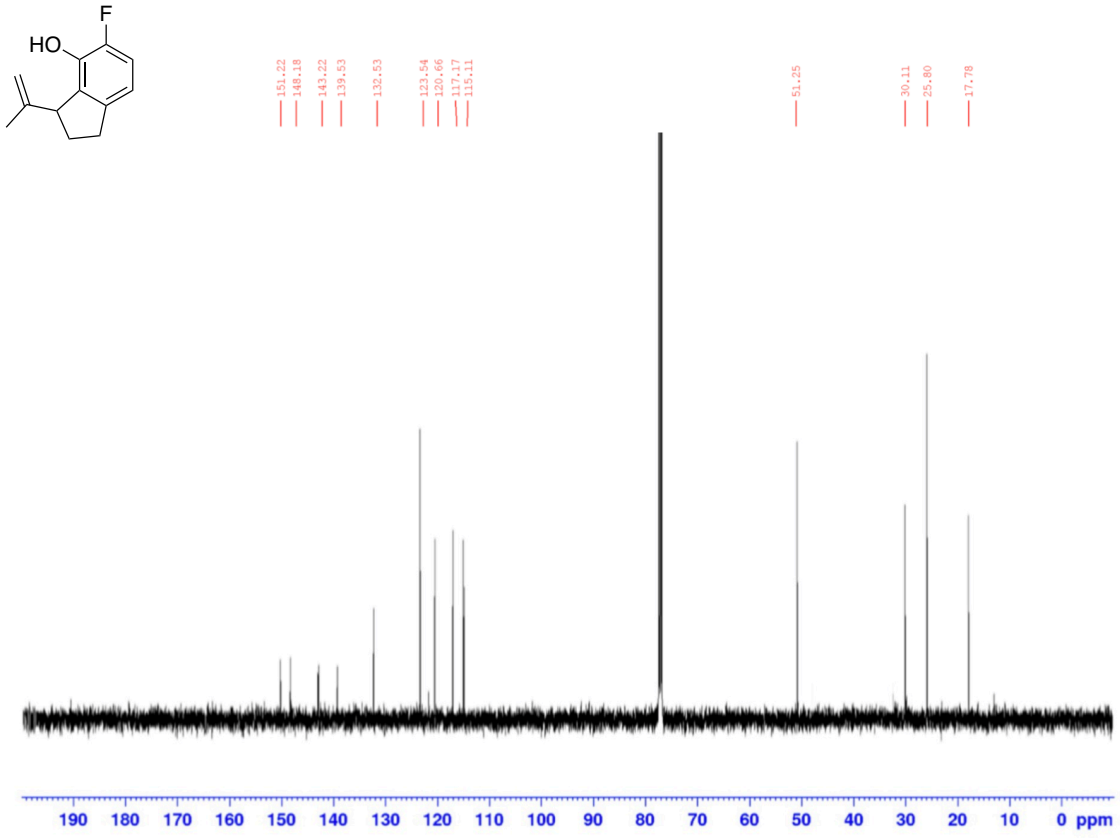
^{13}C NMR spectrum of **8kx** ($CDCl_3$, 125 MHz)



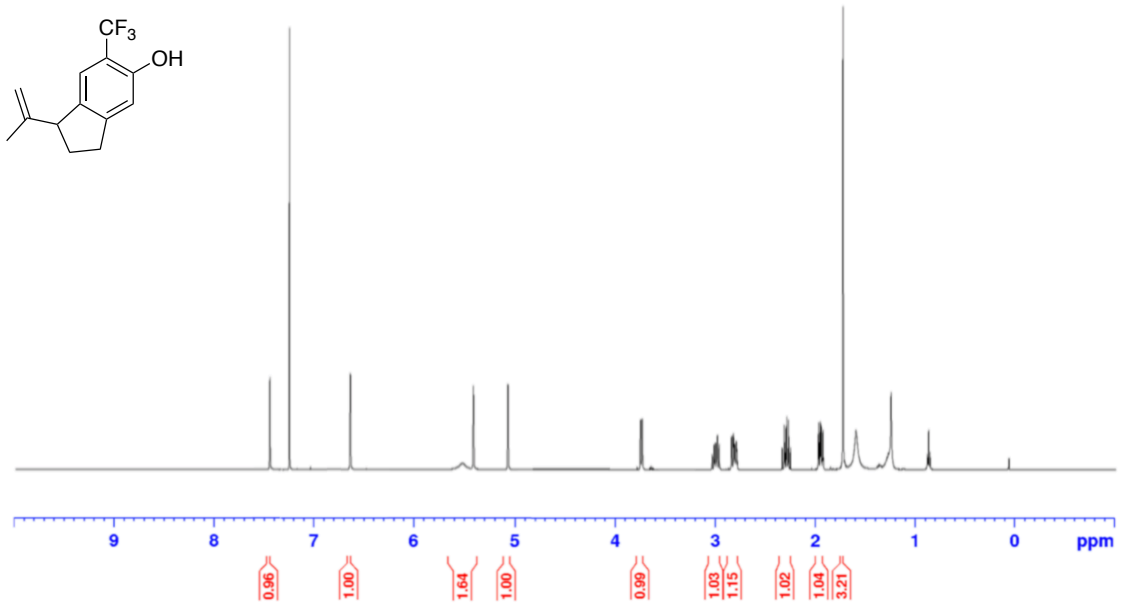
^{1}H NMR spectrum of **8ky** ($CDCl_3$, 500 MHz)



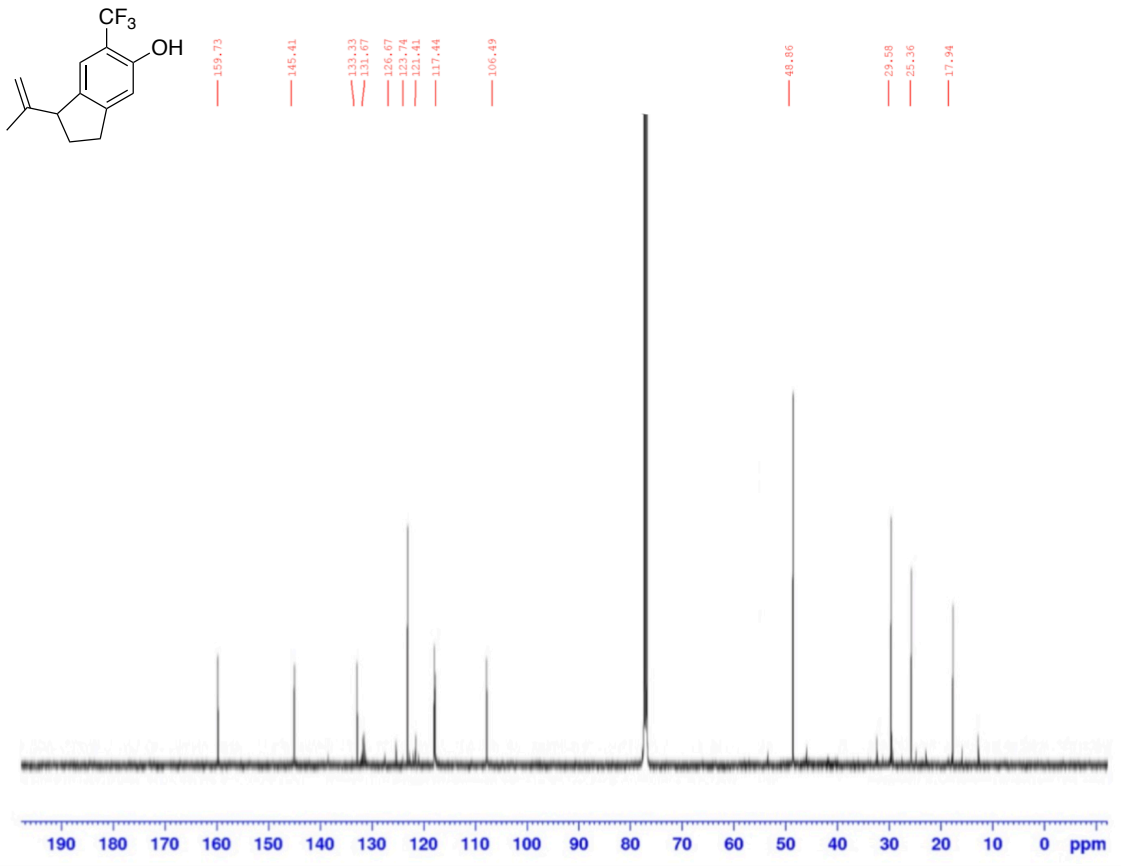
^{13}C NMR spectrum of **8ky** ($CDCl_3$, 125 MHz)



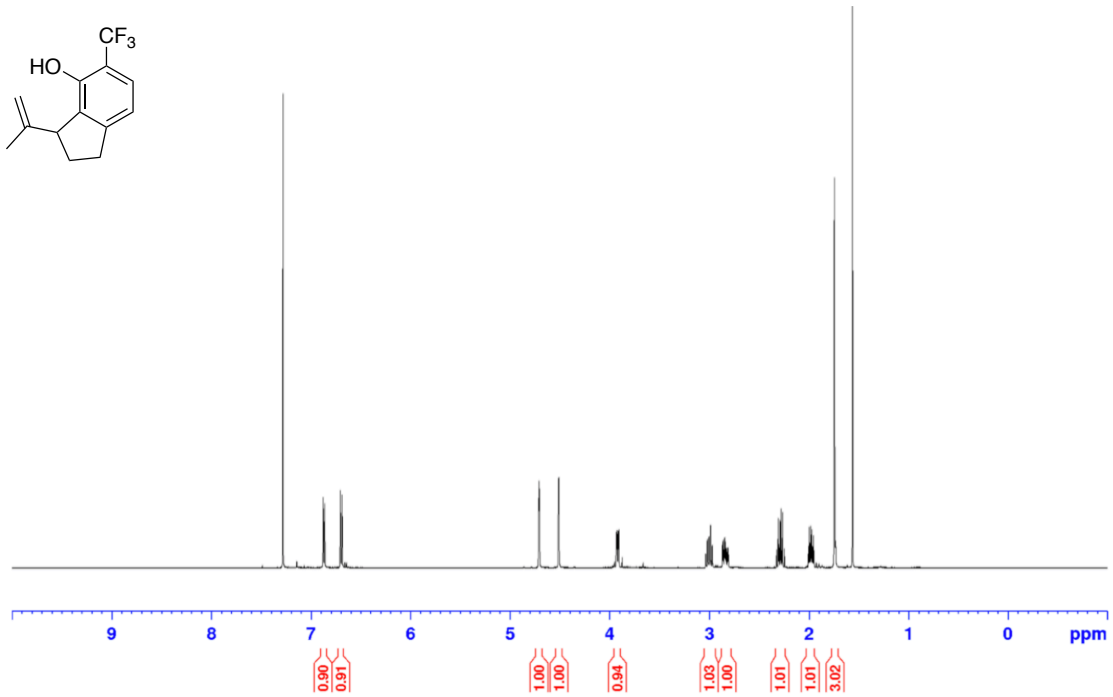
^{1}H NMR spectrum of **8lx** ($CDCl_3$, 500 MHz)



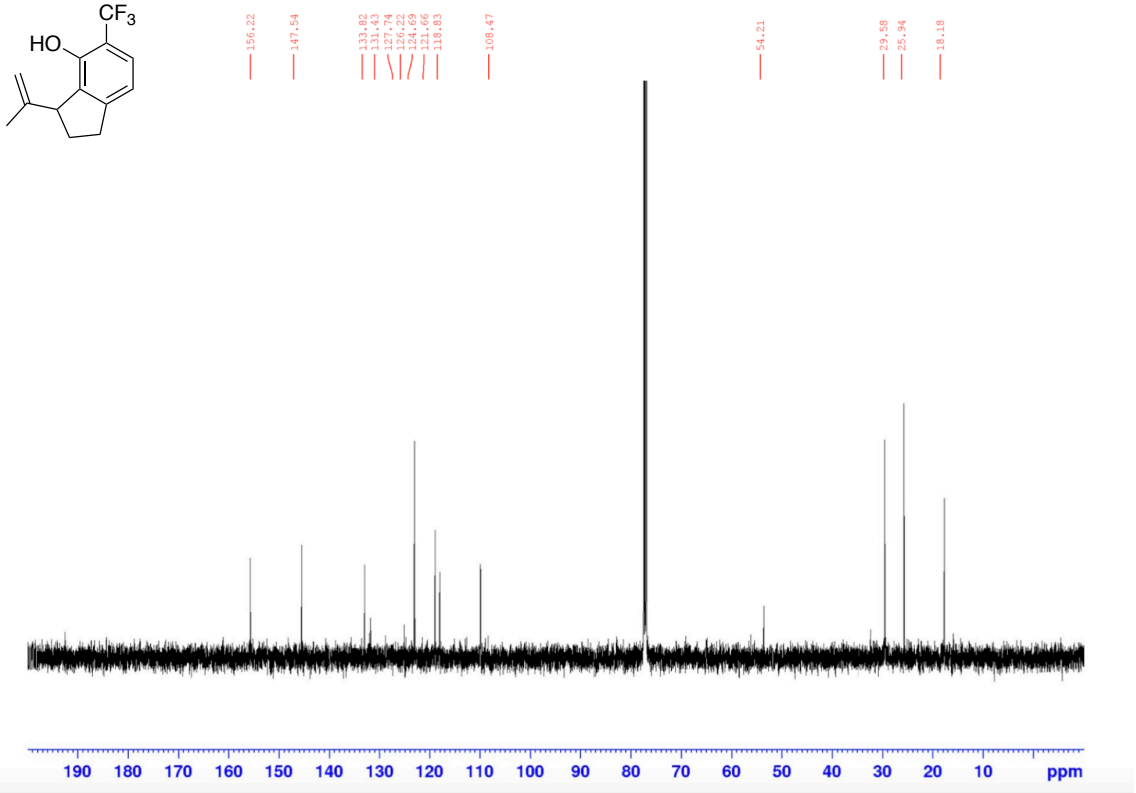
^{13}C NMR spectrum of **8lx** ($CDCl_3$, 125 MHz)



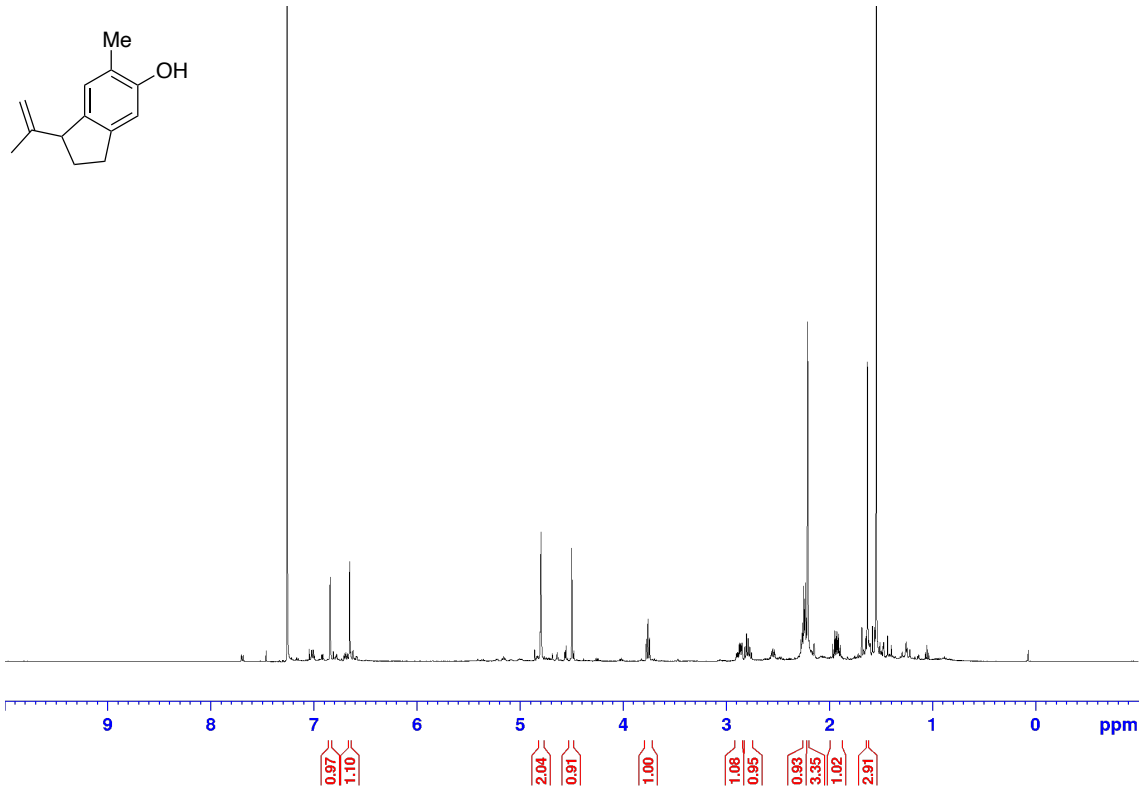
^{1}H NMR spectrum of **8ly** ($CDCl_3$, 500 MHz)



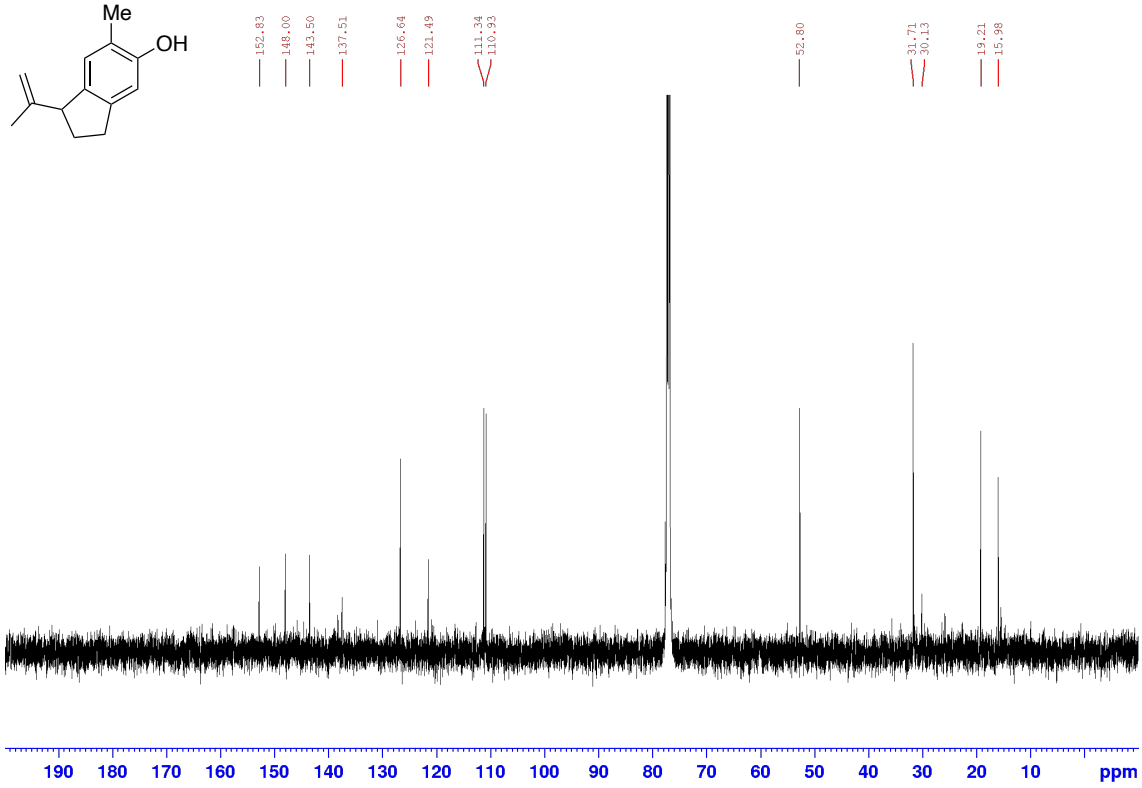
^{13}C NMR spectrum of **8ly** ($CDCl_3$, 125 MHz)



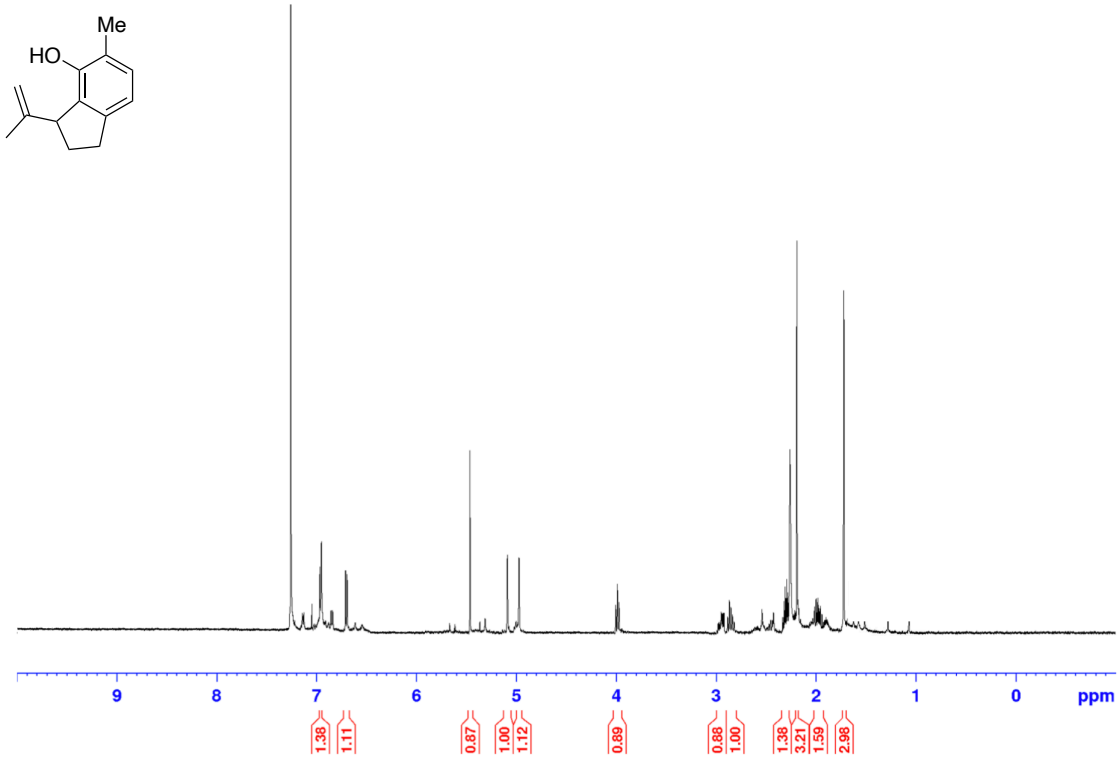
^{1}H NMR spectrum of **8mx** ($CDCl_3$, 500 MHz)



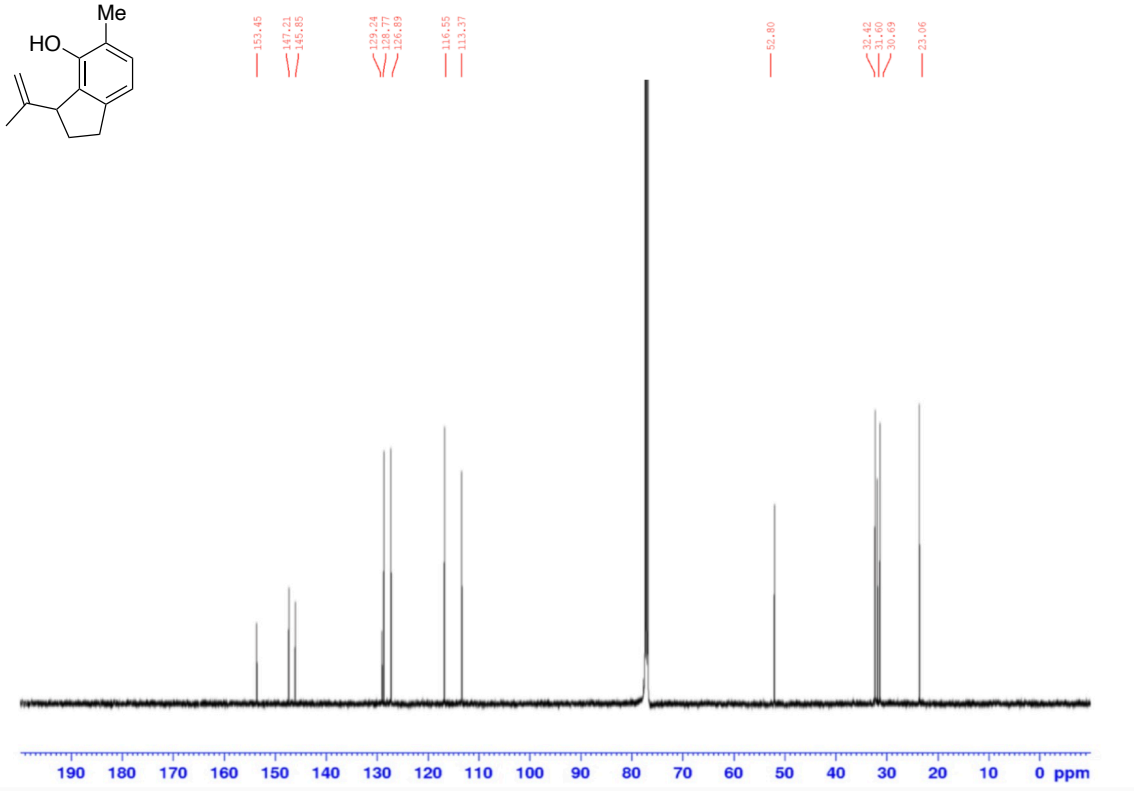
^{13}C NMR spectrum of **8mx** ($CDCl_3$, 125 MHz)



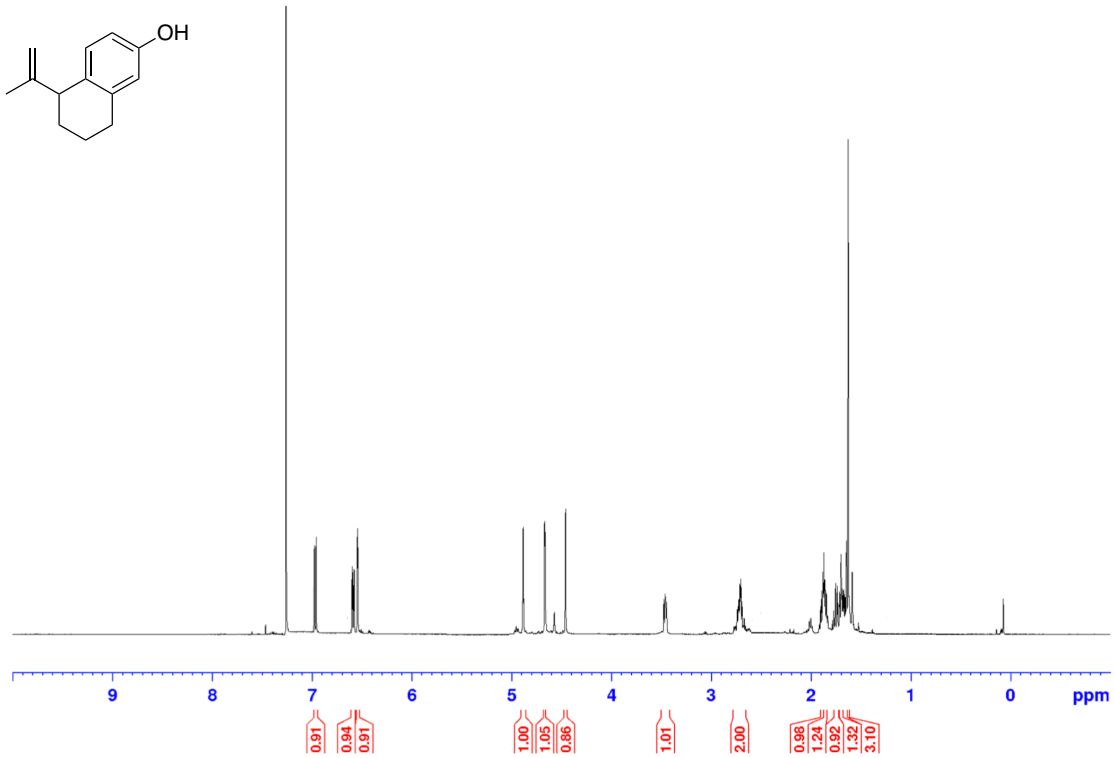
^{1}H NMR spectrum of **8my** ($CDCl_3$, 500 MHz)



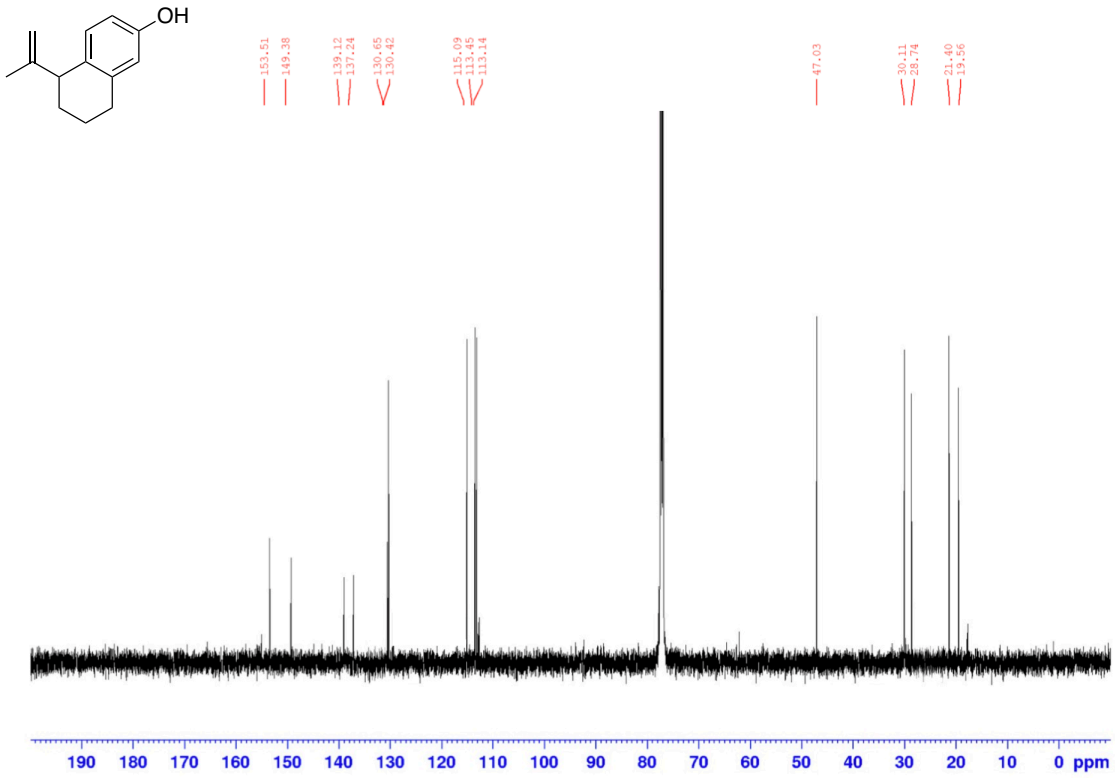
^{13}C NMR spectrum of **8my** ($CDCl_3$, 125 MHz)



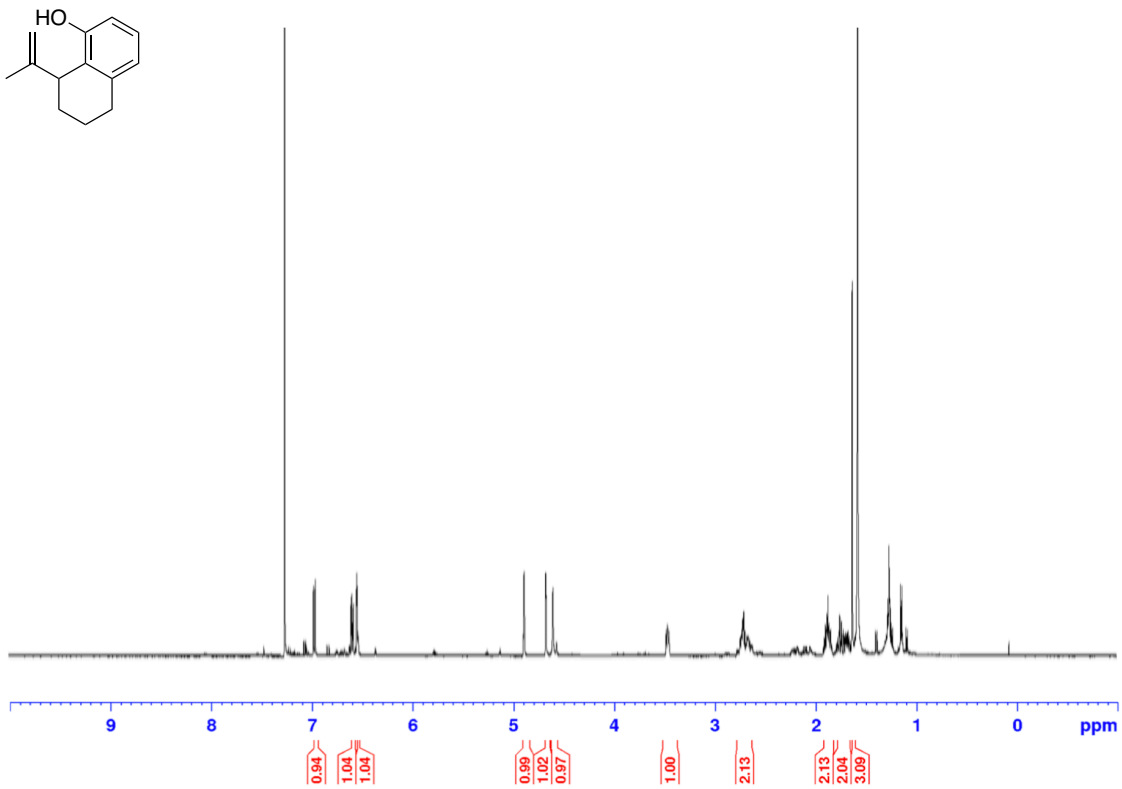
^{1}H NMR spectrum of **13x** ($CDCl_3$, 500 MHz)



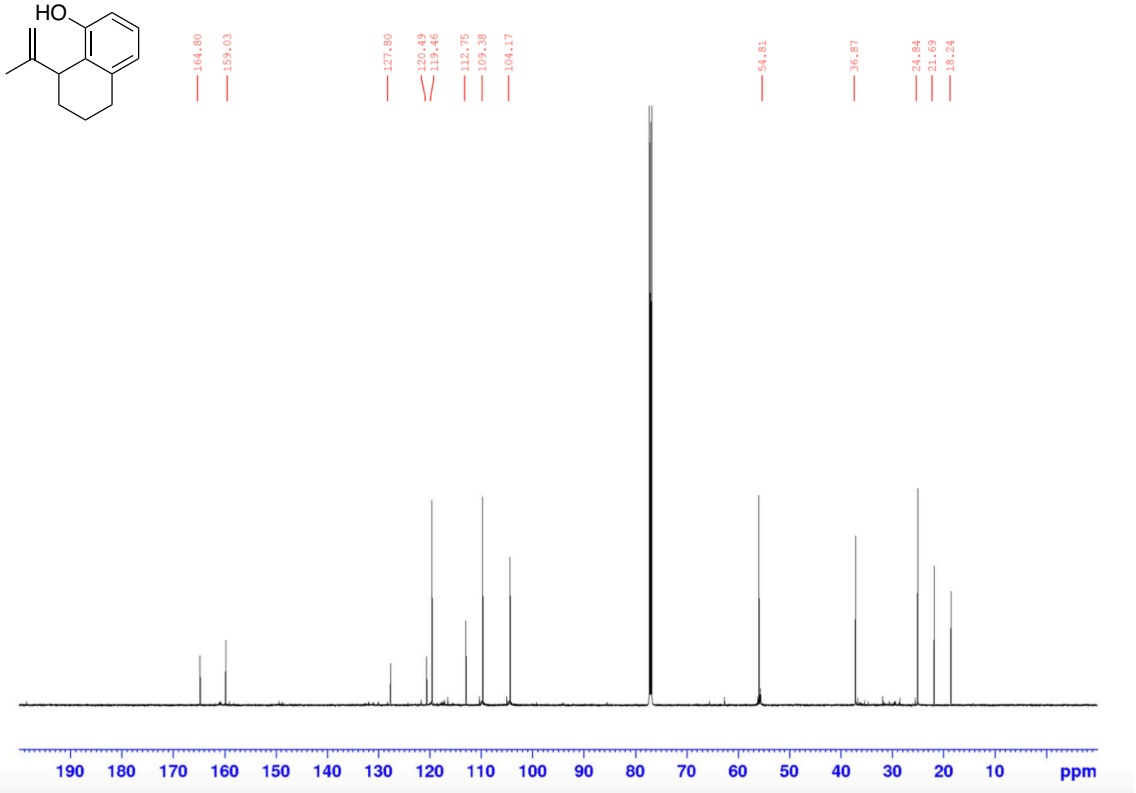
^{13}C NMR spectrum of **13x** ($CDCl_3$, 125 MHz)



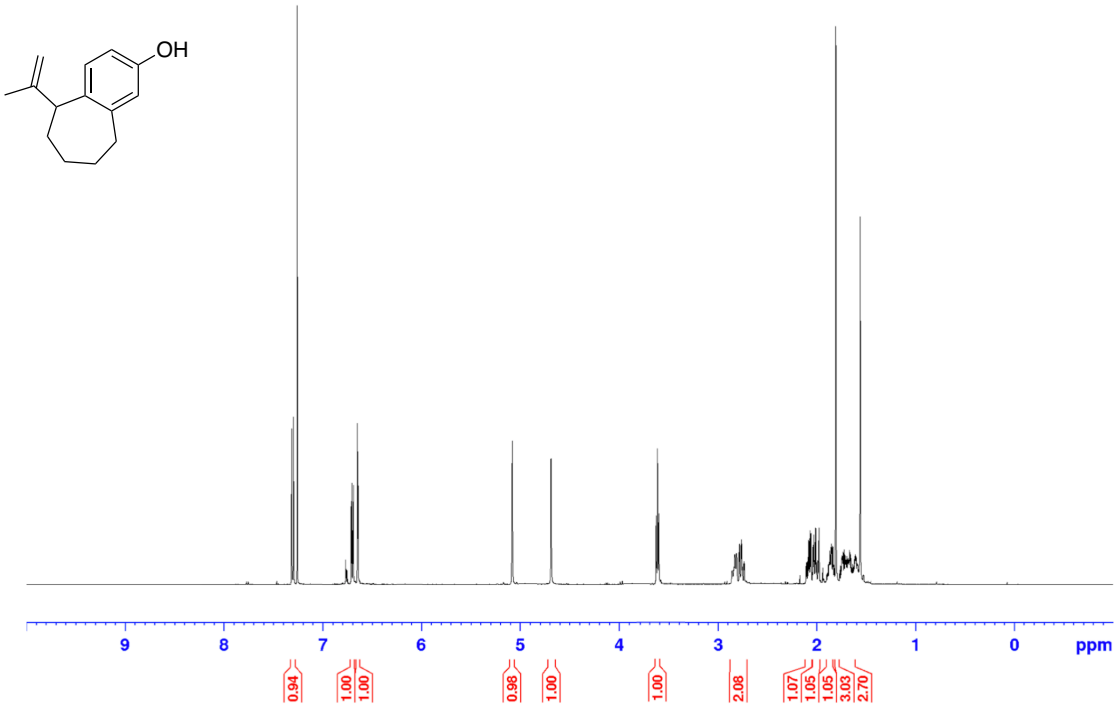
^{1}H NMR spectrum of **13y** ($CDCl_3$, 500 MHz)



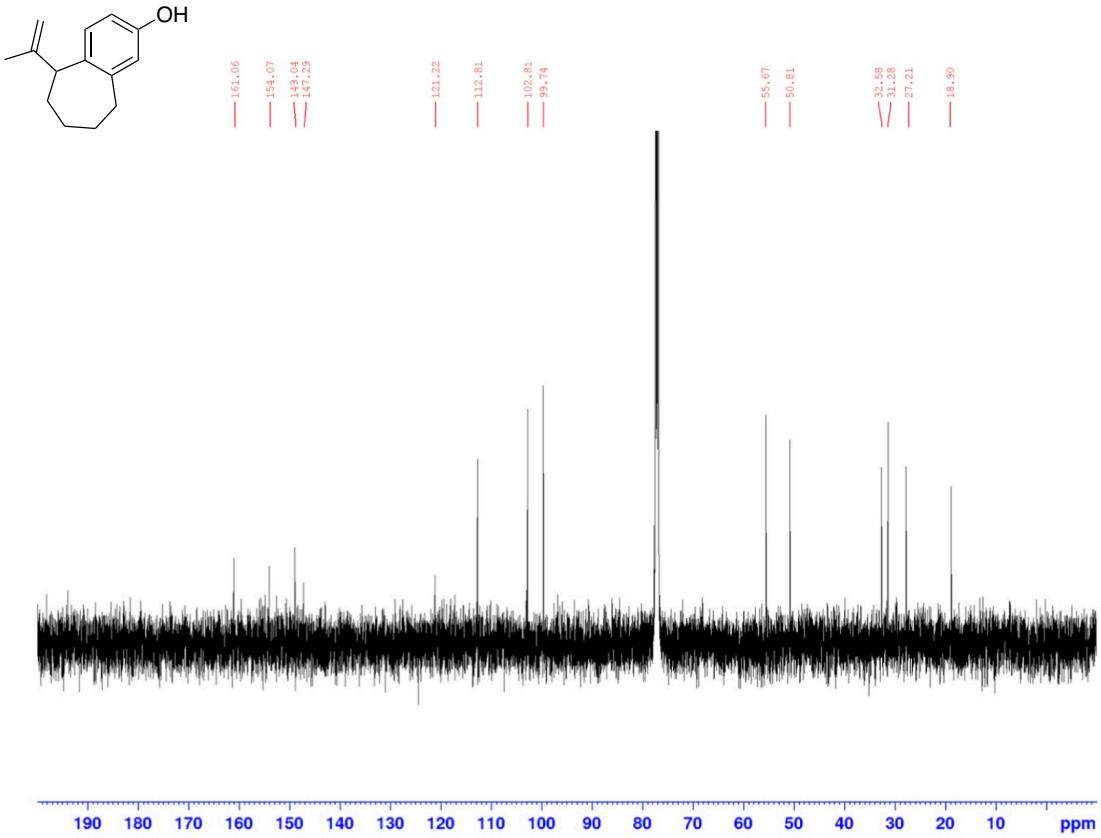
^{13}C NMR spectrum of **13y** ($CDCl_3$, 125 MHz)



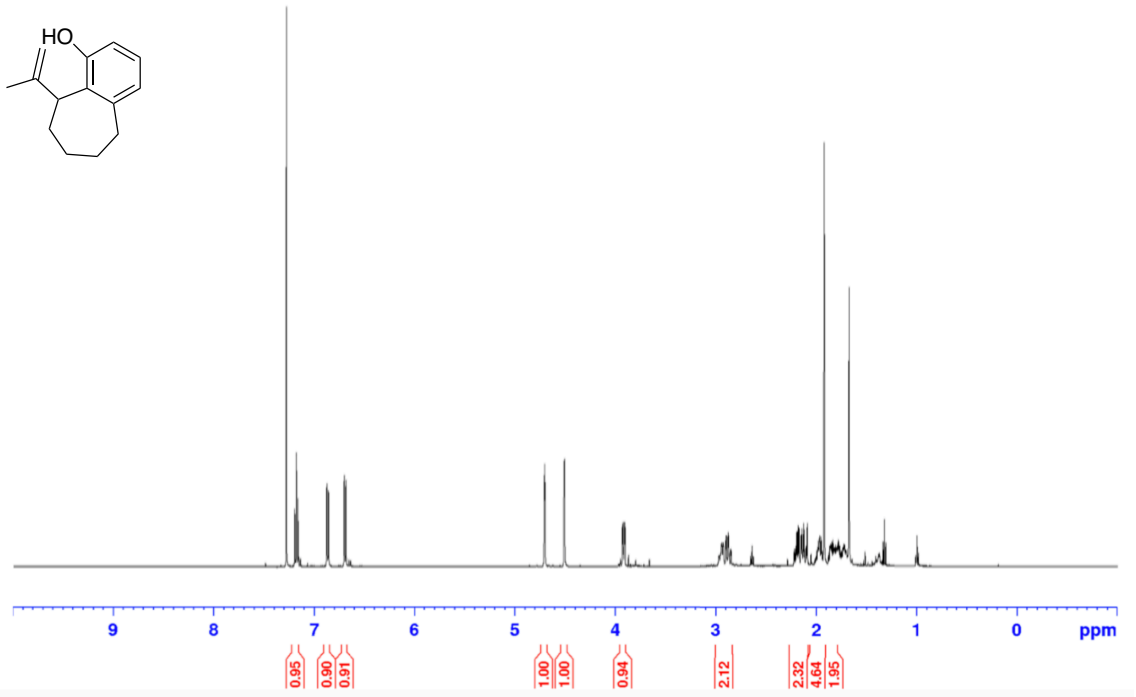
^{1}H NMR spectrum of **14x** ($CDCl_3$, 500 MHz)



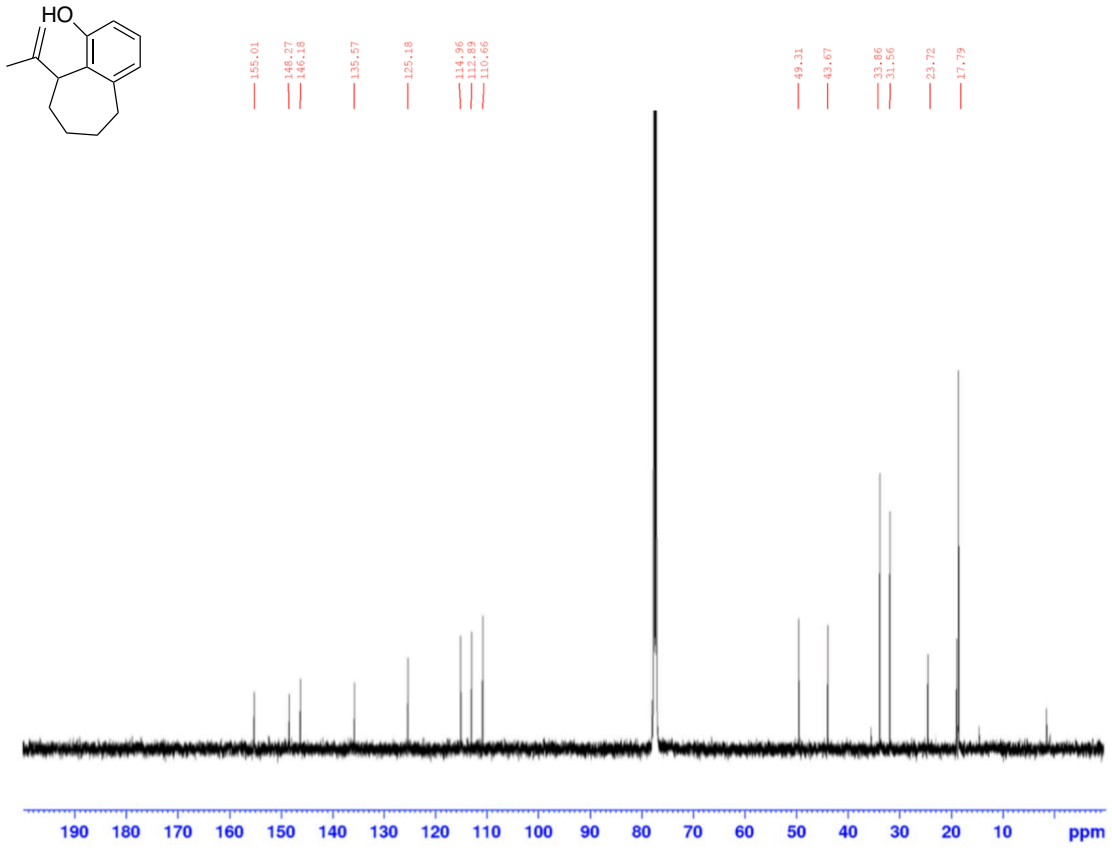
^{13}C NMR spectrum of **14x** ($CDCl_3$, 125 MHz)



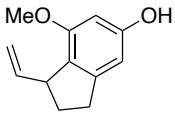
^{1}H NMR spectrum of **14y** ($CDCl_3$, 500 MHz)



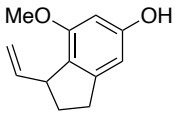
^{13}C NMR spectrum of **14y** ($CDCl_3$, 125 MHz)



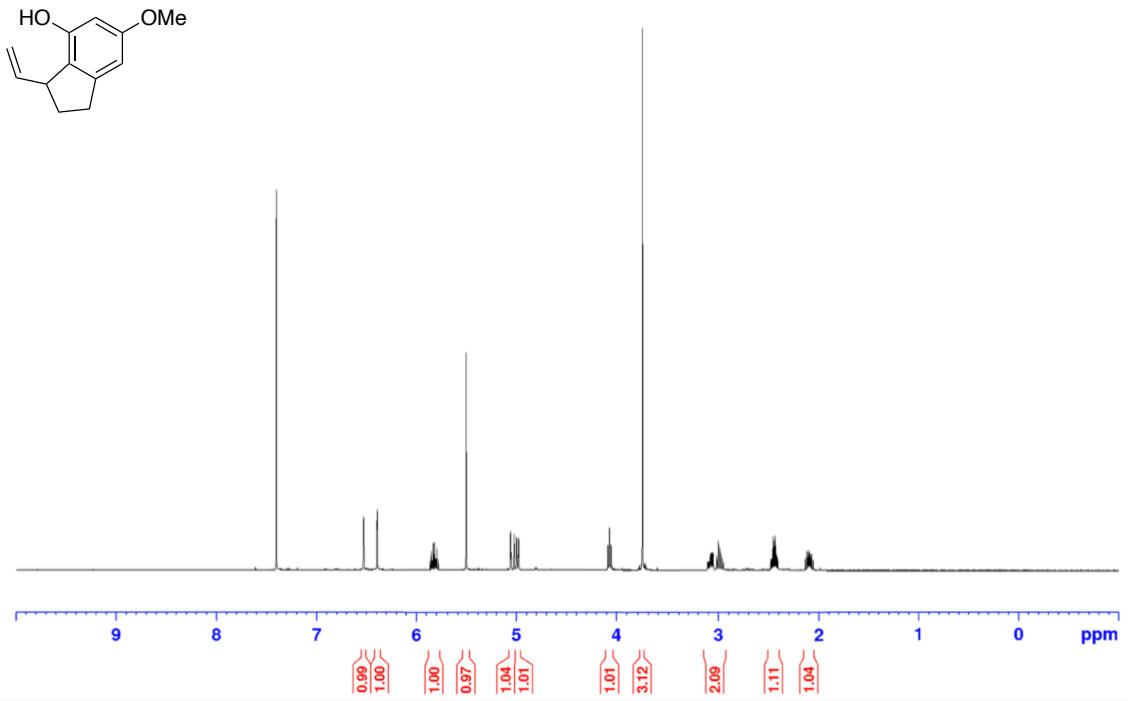
^{1}H NMR spectrum of **25x** ($CDCl_3$, 500 MHz)



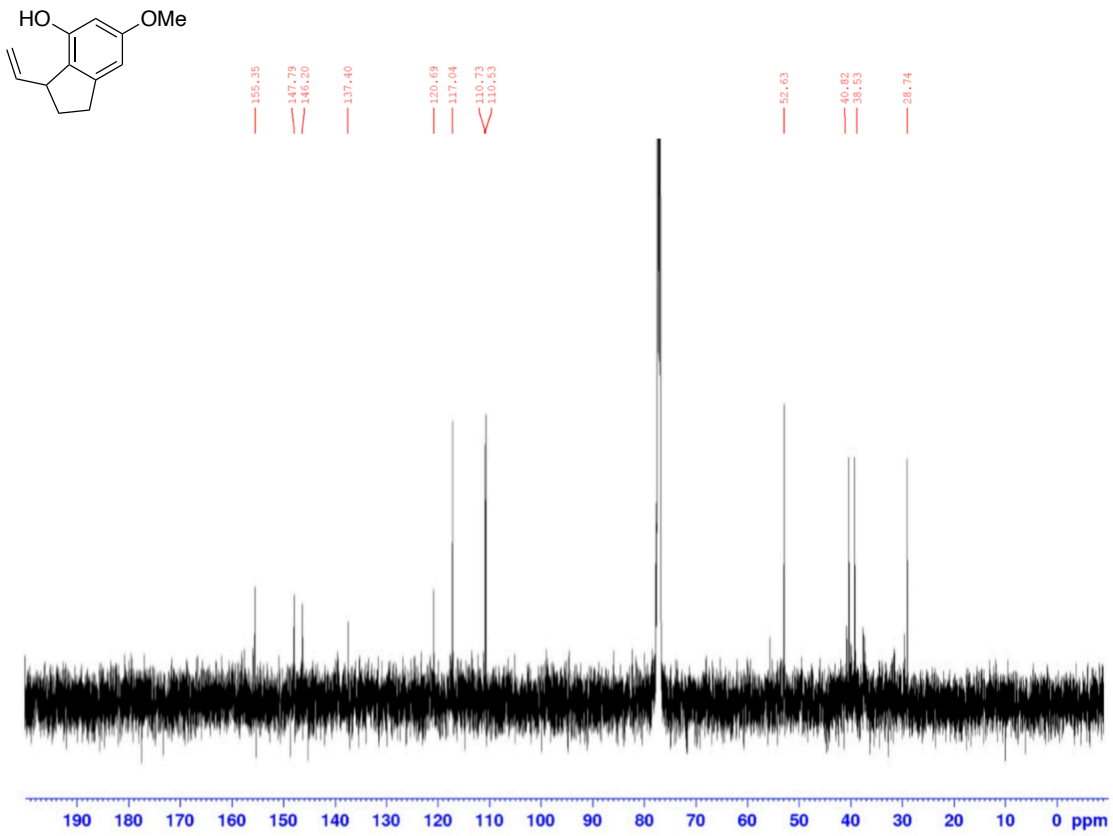
^{13}C NMR spectrum of **25x** ($CDCl_3$, 125 MHz)



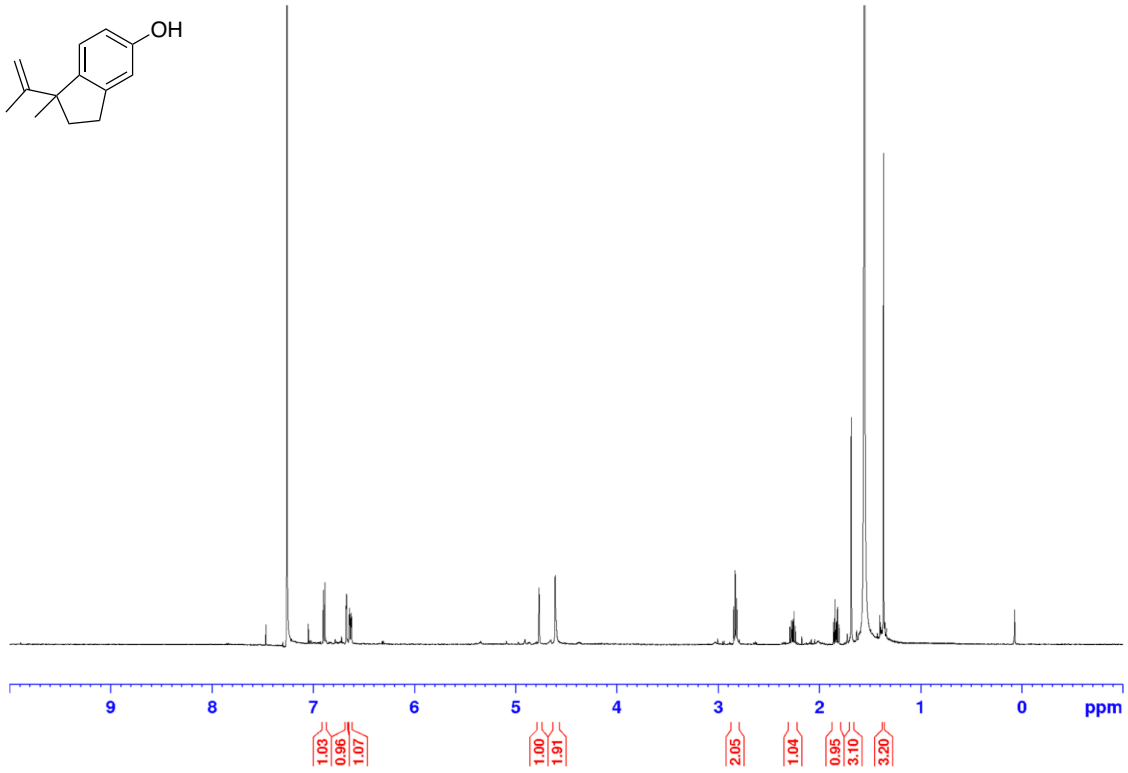
^{1}H NMR spectrum of **25y** ($CDCl_3$, 500 MHz)



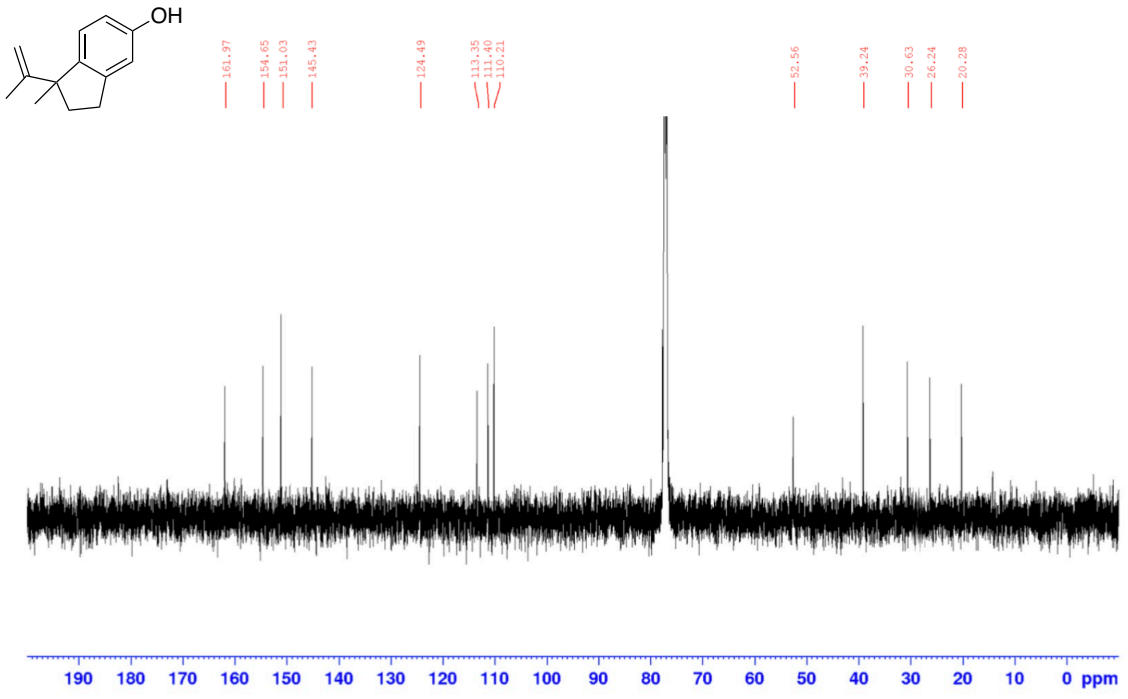
^{13}C NMR spectrum of **25y** ($CDCl_3$, 125 MHz)



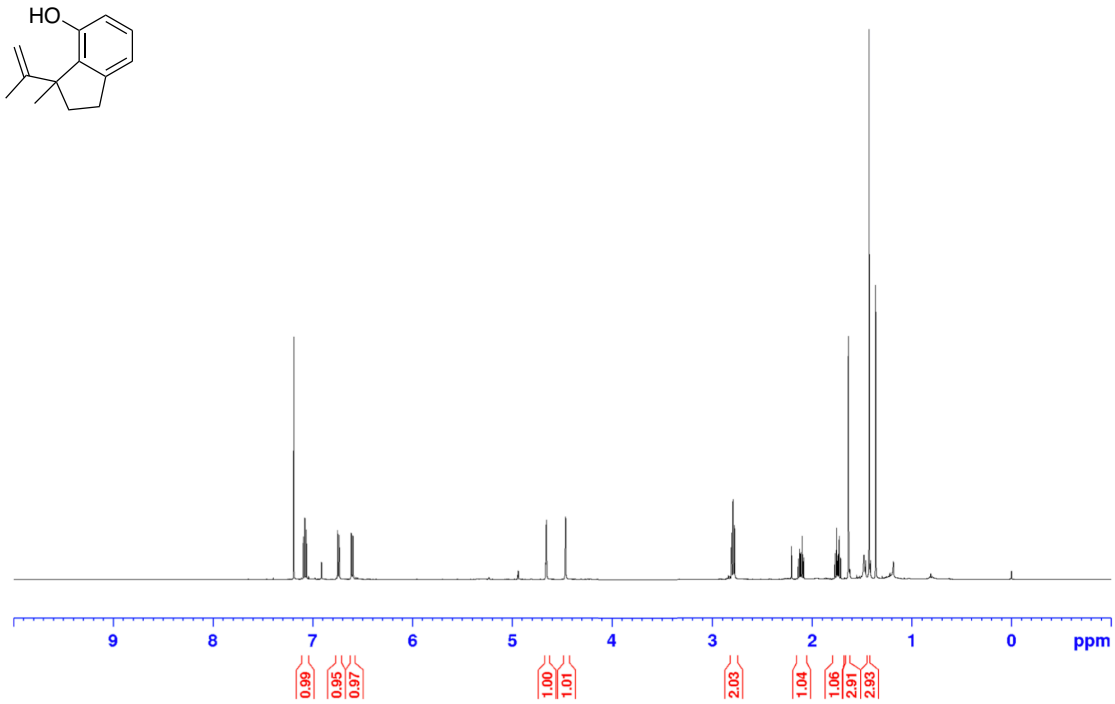
^{1}H NMR spectrum of **26x** ($CDCl_3$, 500 MHz)



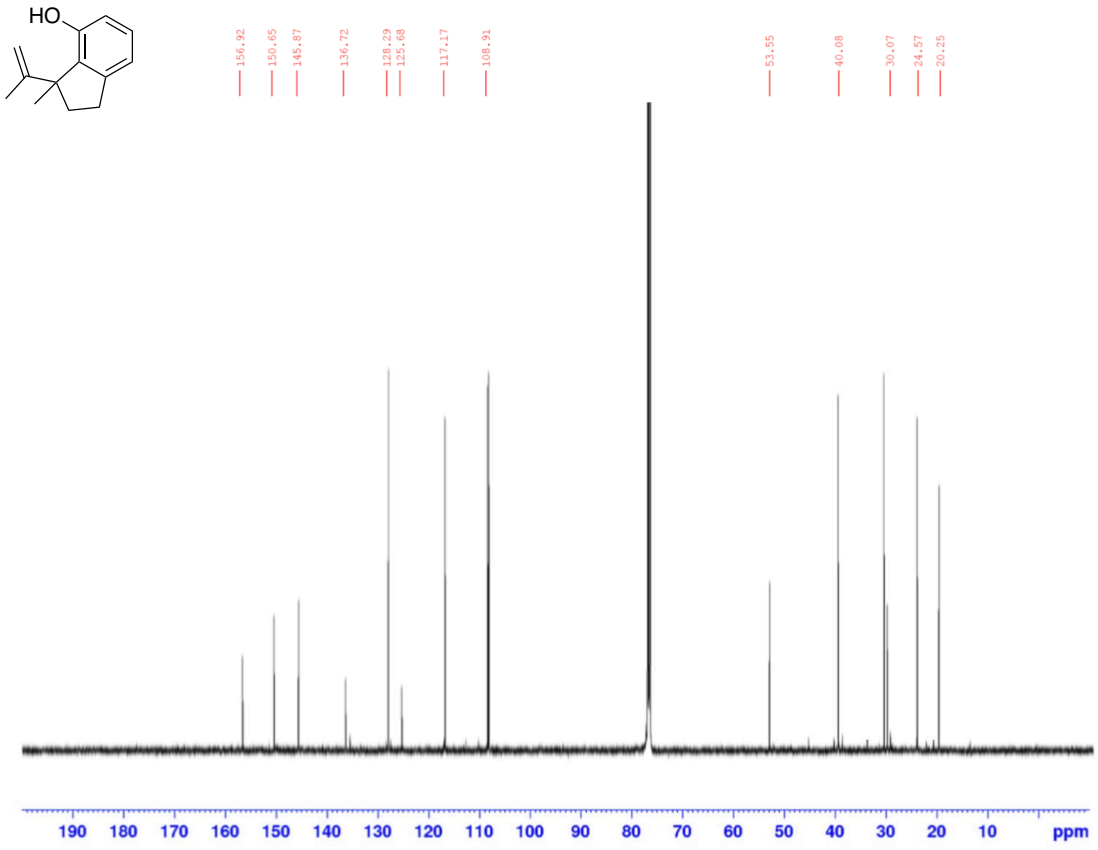
^{13}C NMR spectrum of **26x** ($CDCl_3$, 125 MHz)



^{1}H NMR spectrum of 2**6y** ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum of **26y** ($CDCl_3$, 125 MHz)



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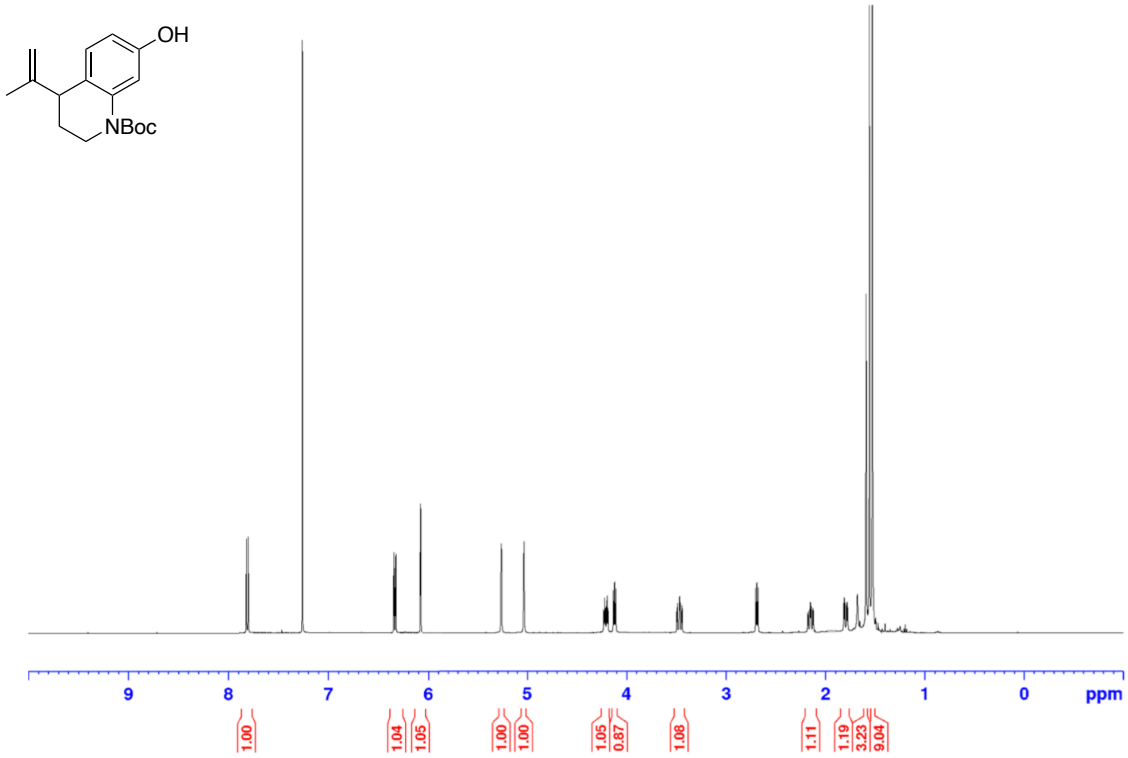
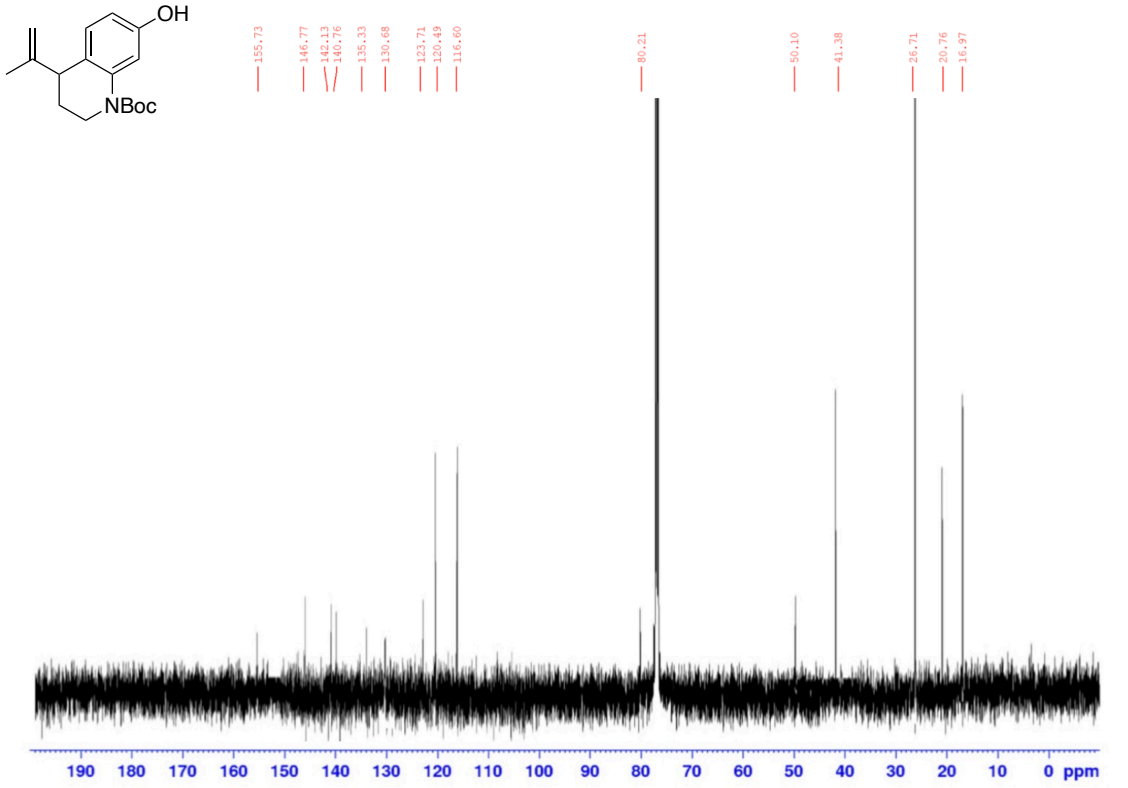
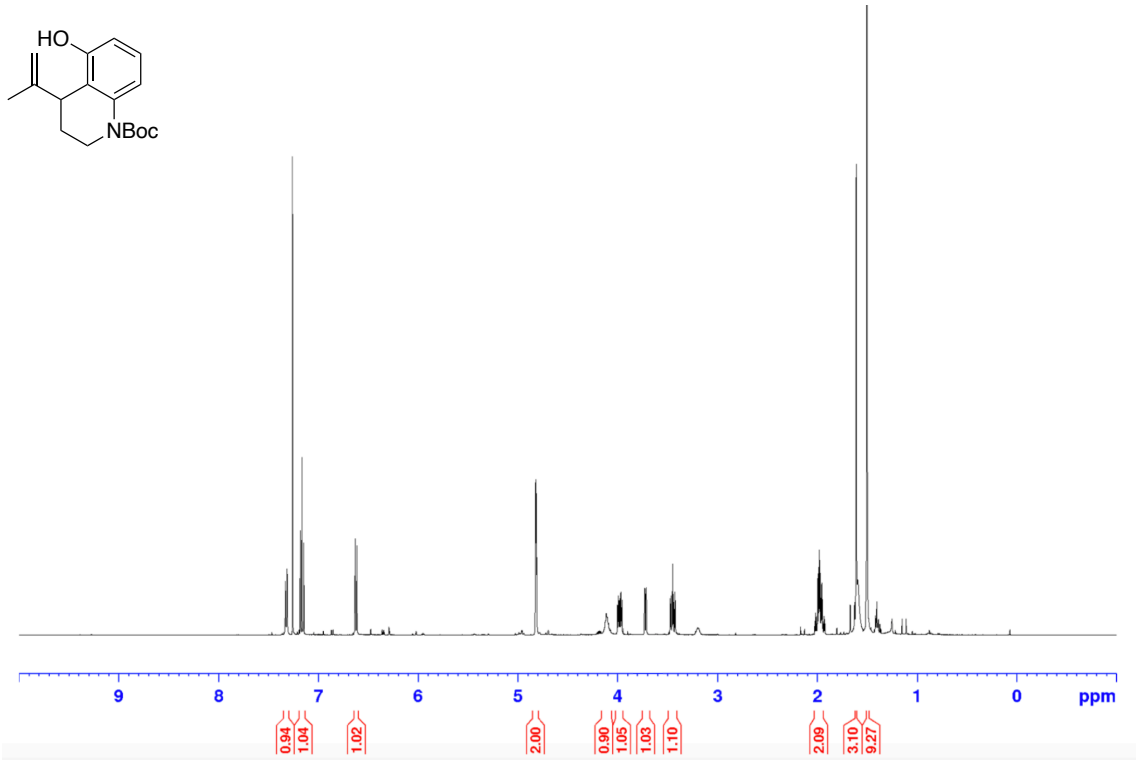


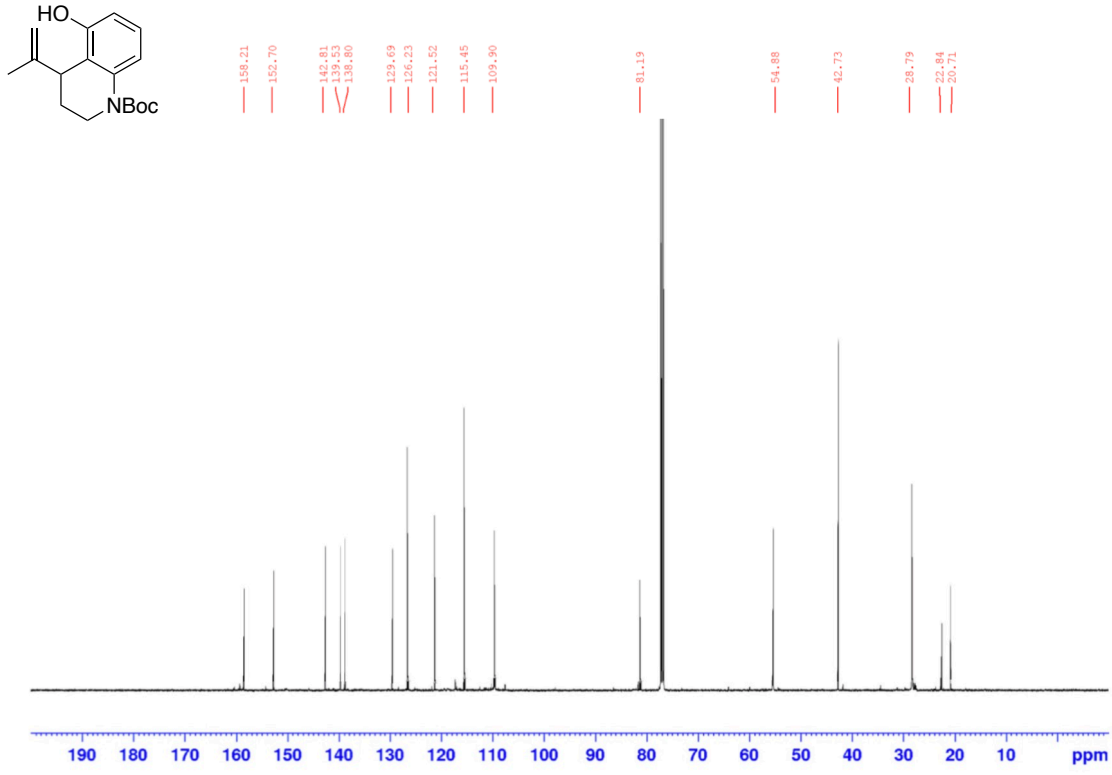
^{13}C NMR spectrum of **19ax** ($CDCl_3$, 125 MHz)



^{1}H NMR spectrum of **19ay** ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum of **19ay** ($CDCl_3$, 125 MHz)



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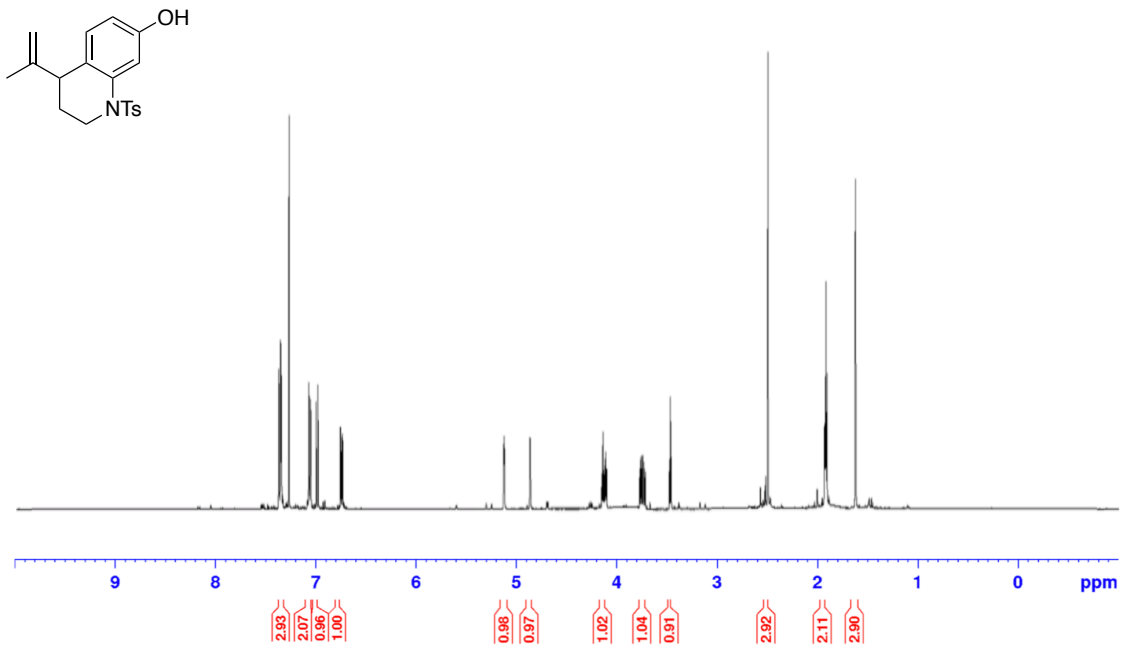
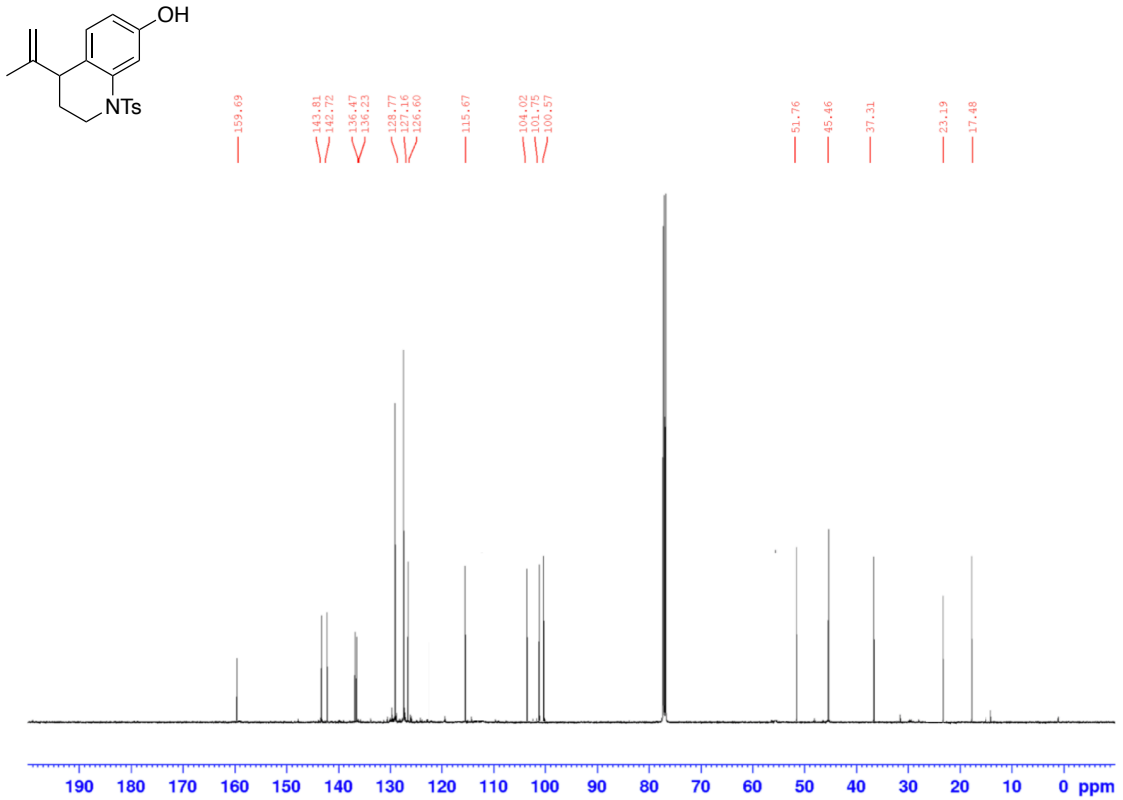
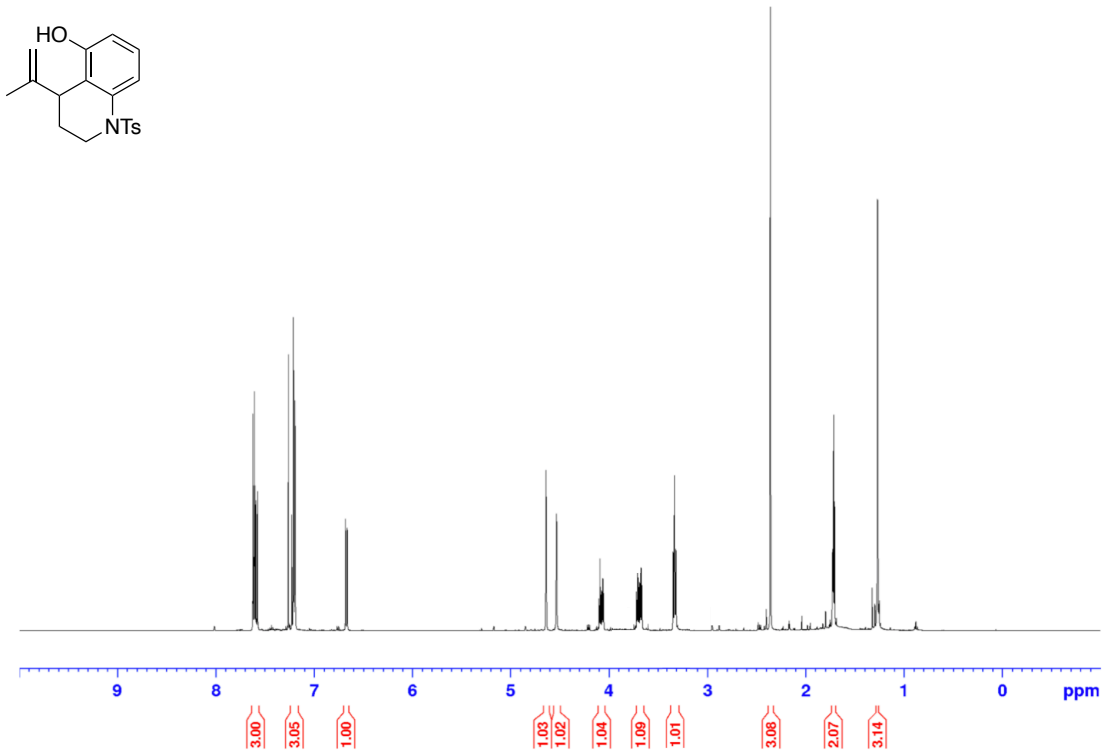


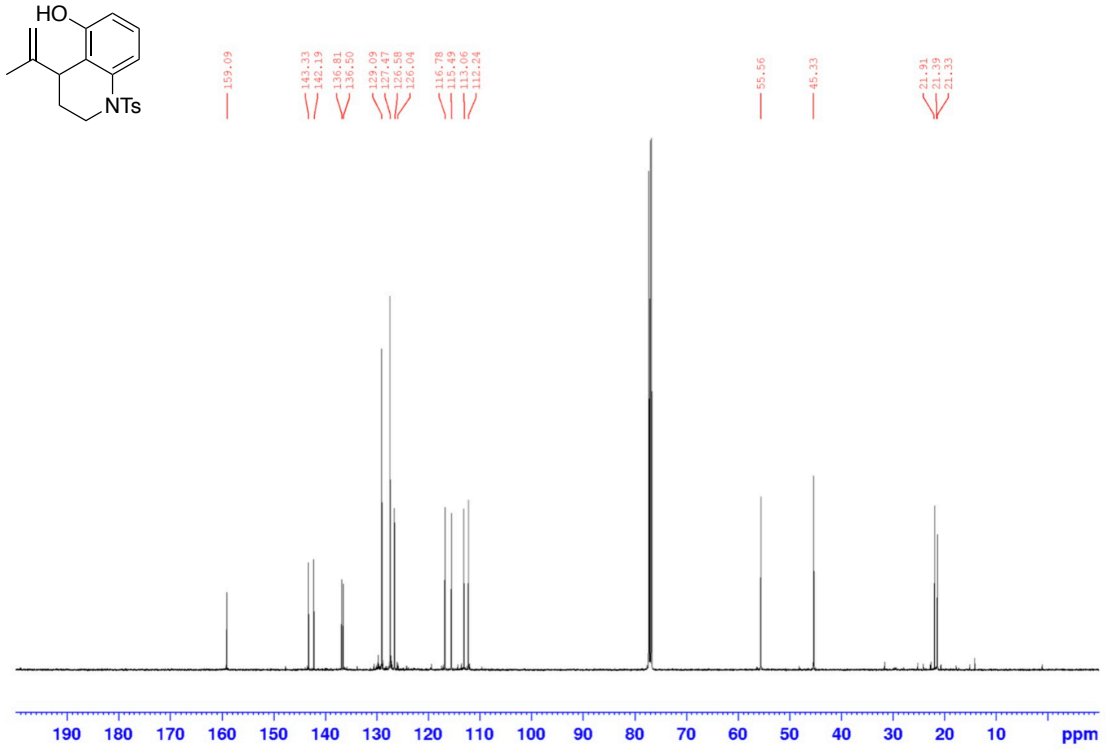
^{13}C NMR spectrum of **19bx** ($CDCl_3$, 125 MHz)



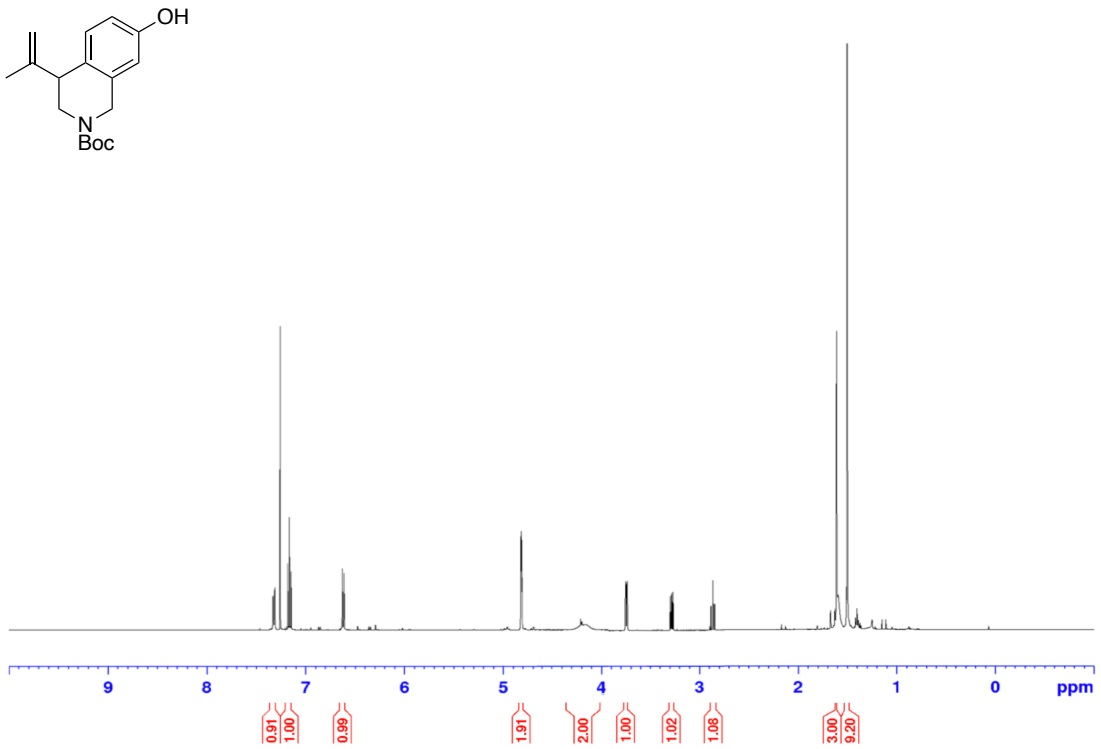
^{1}H NMR spectrum of **19by** ($CDCl_3$, 500 MHz)



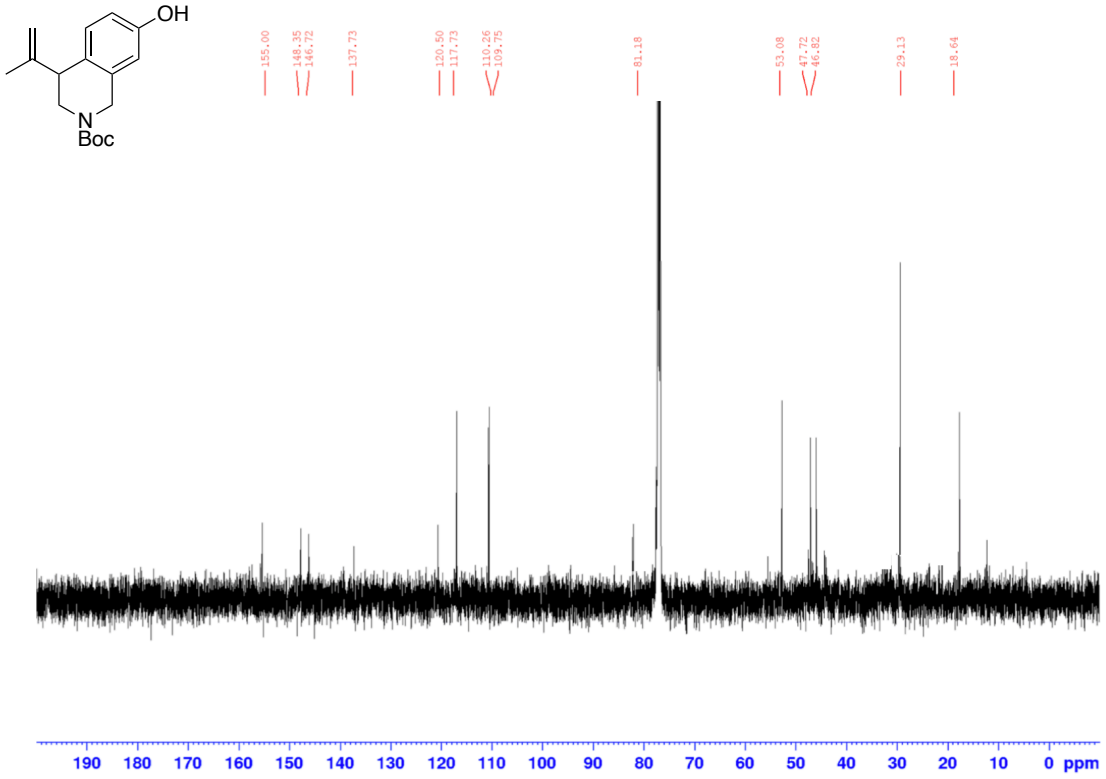
^{13}C NMR spectrum of **19by** ($CDCl_3$, 125 MHz)



^{1}H NMR spectrum of **20x** ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum of **20x** ($CDCl_3$, 125 MHz)



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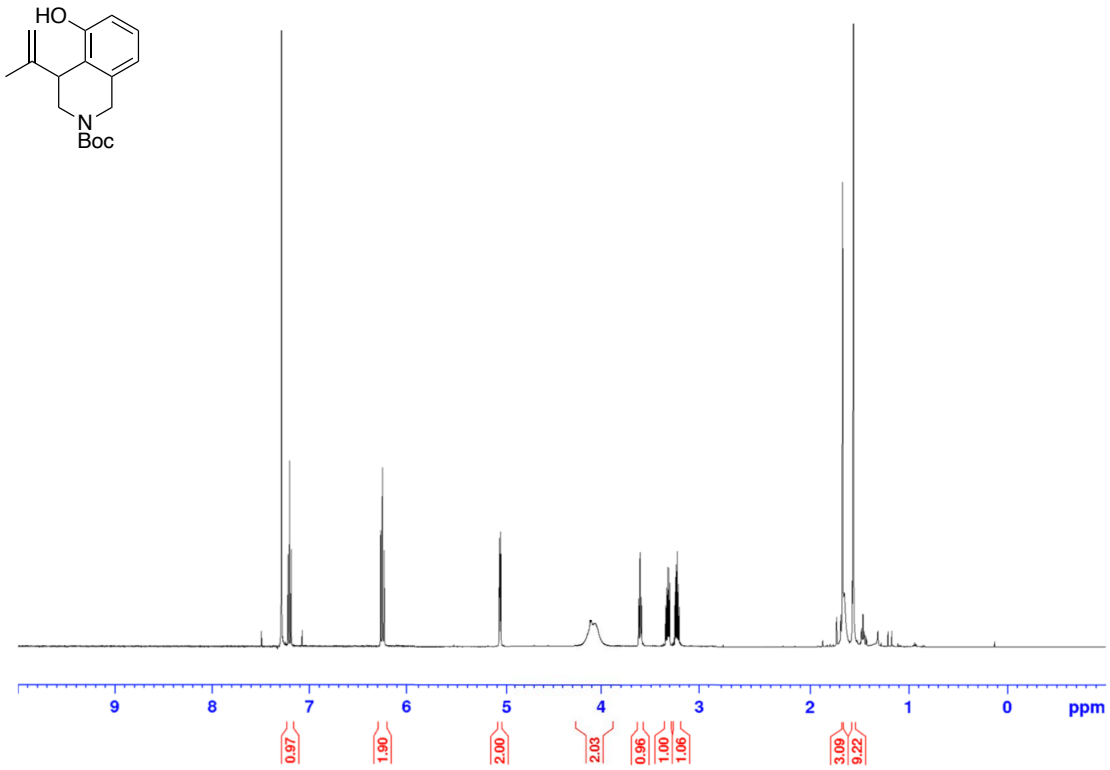
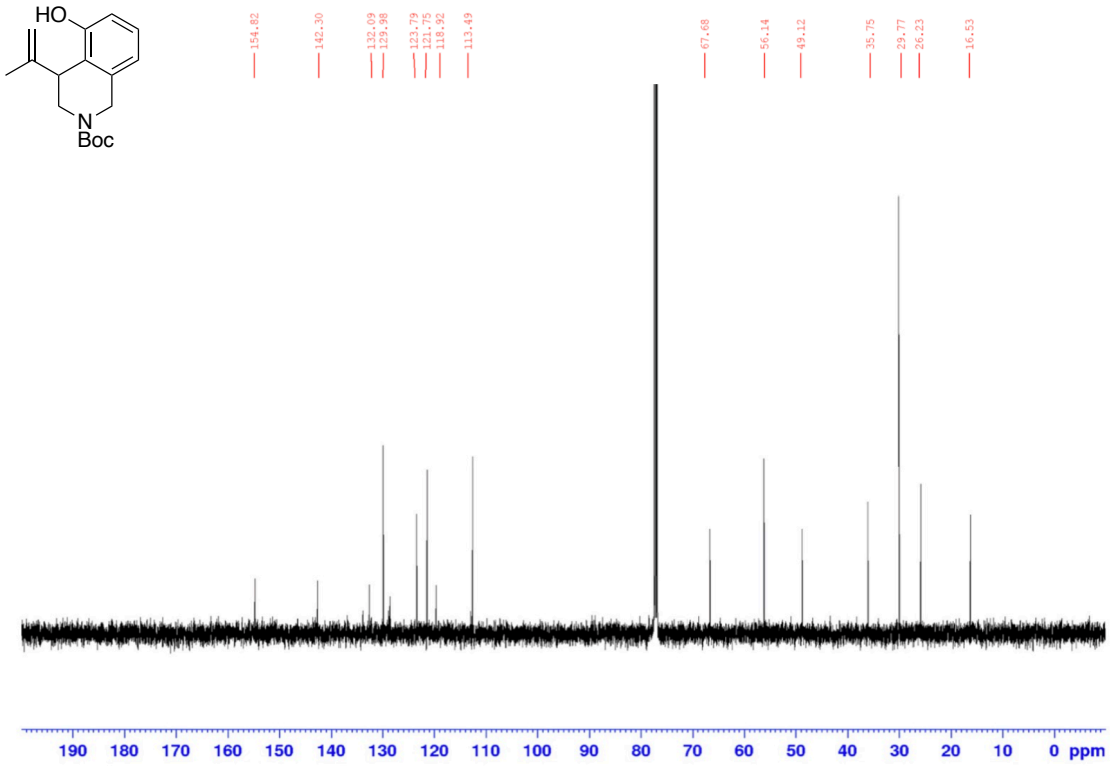
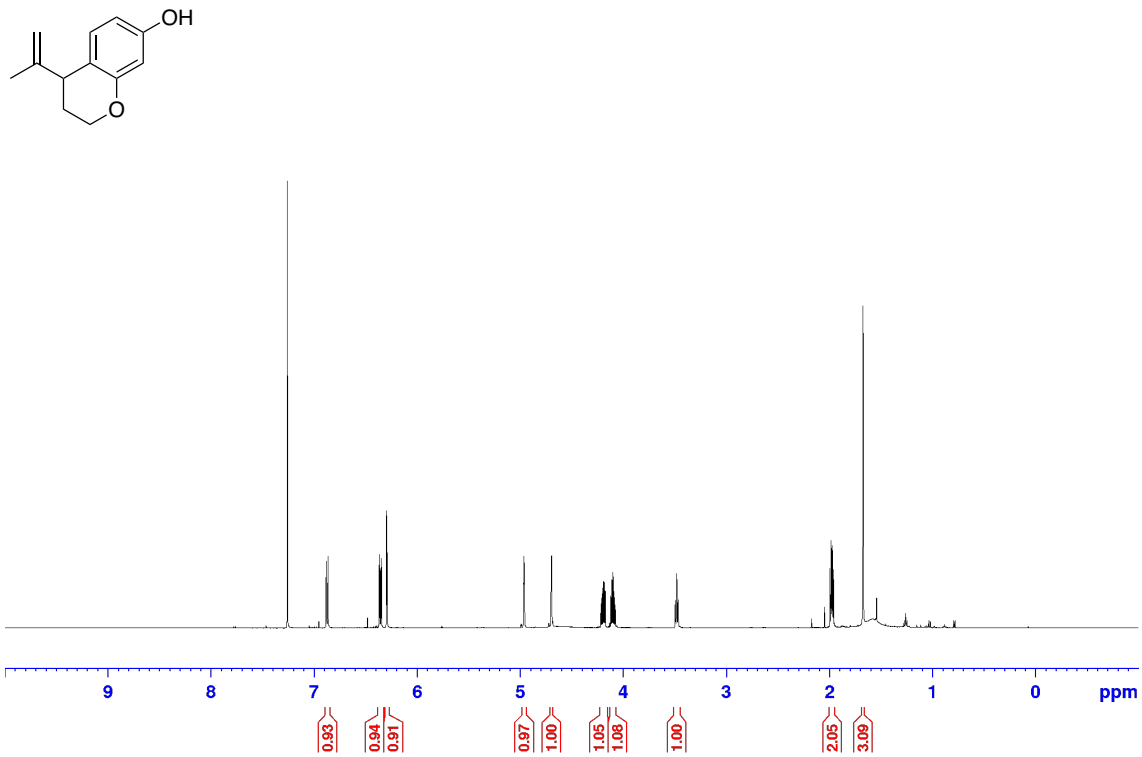


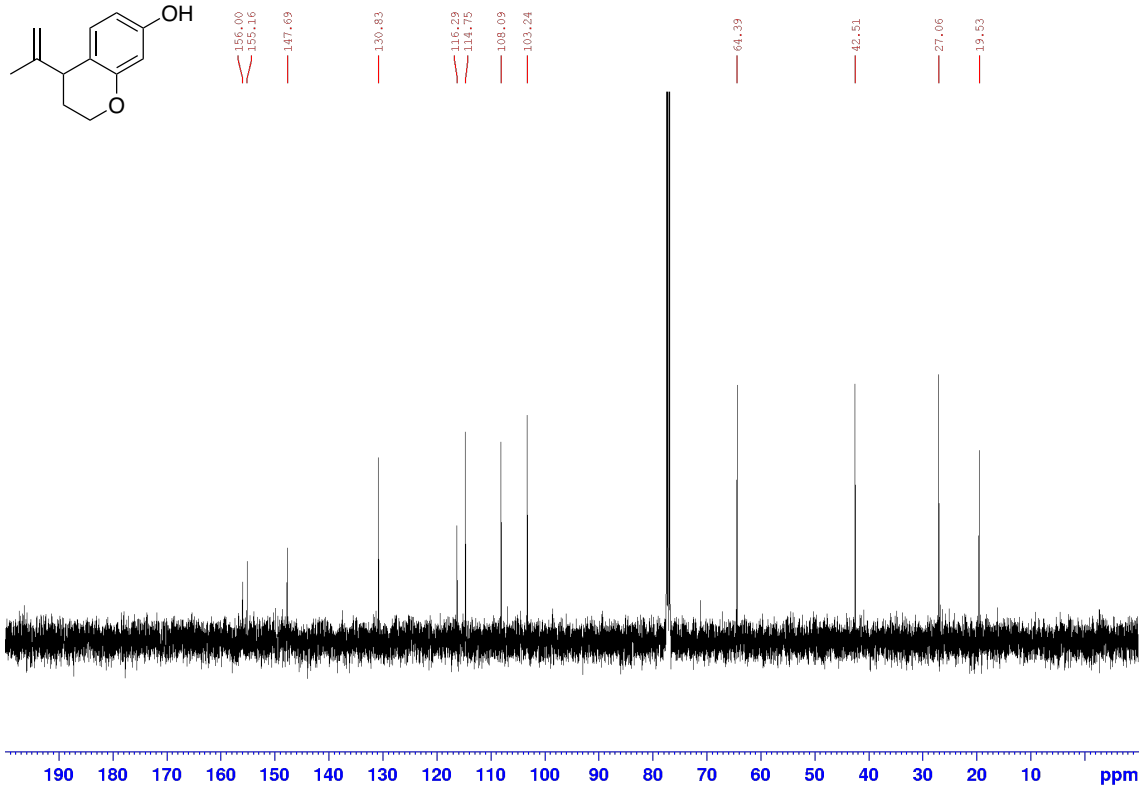
^{13}C NMR spectrum of **20y** ($CDCl_3$, 125 MHz)



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



^{13}C NMR spectrum of **21x** ($CDCl_3$, 125 MHz)



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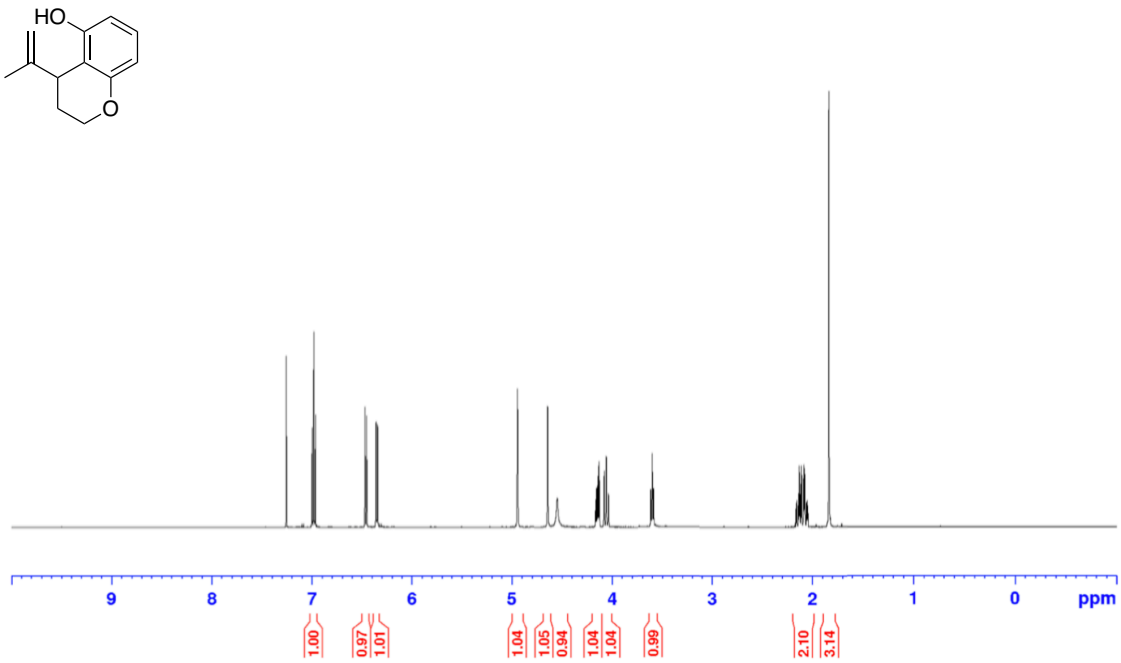

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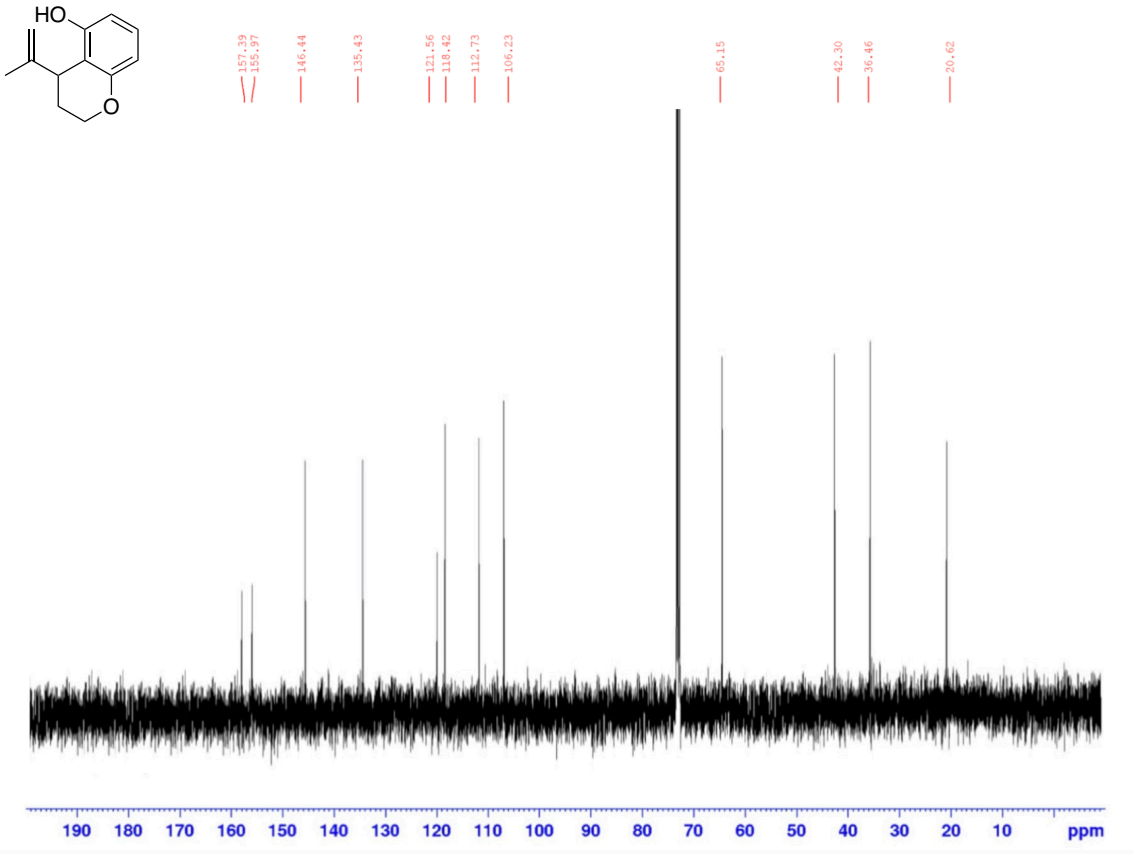
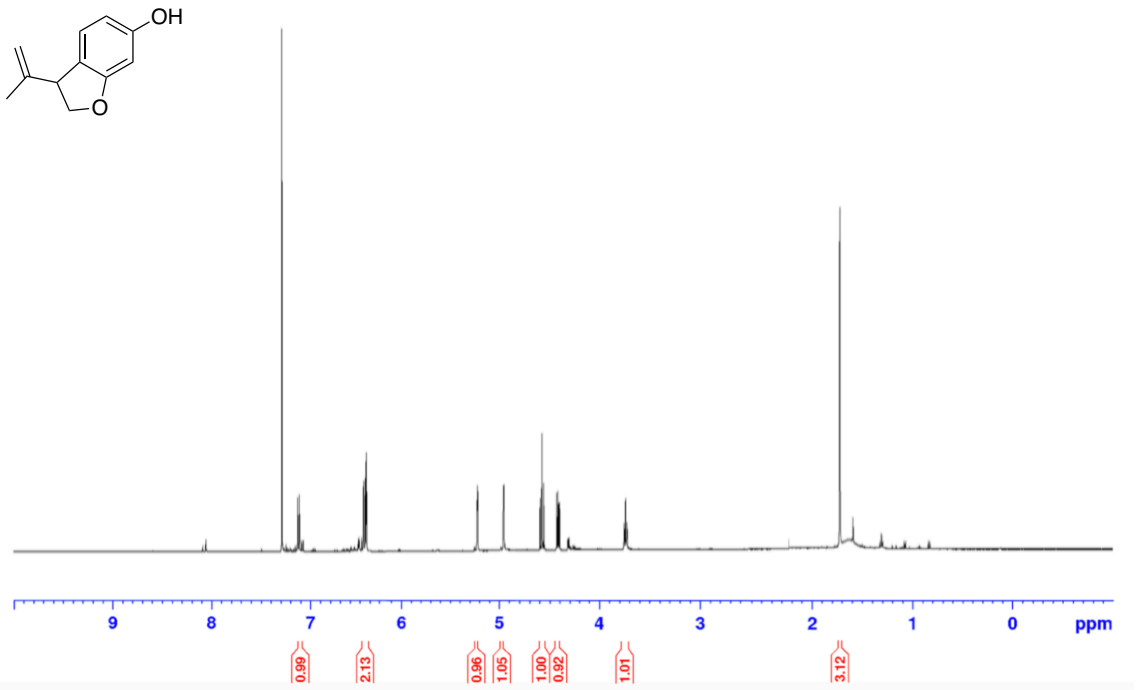
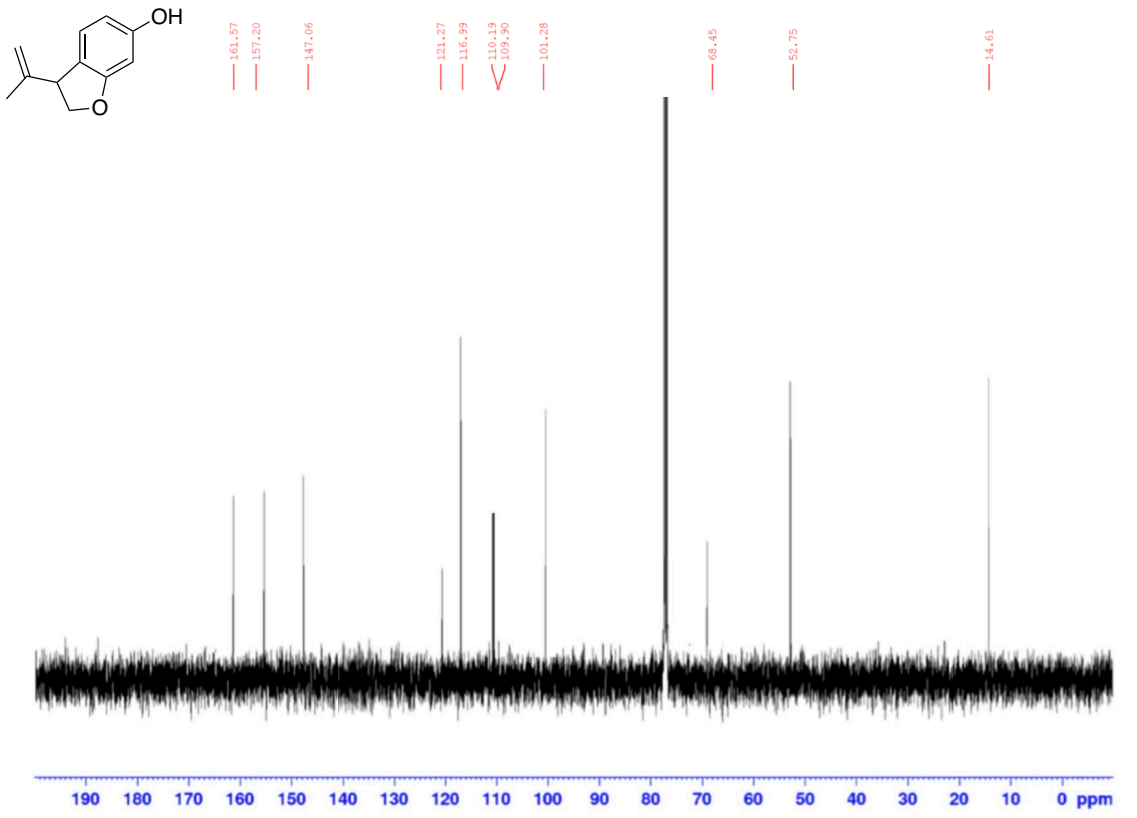


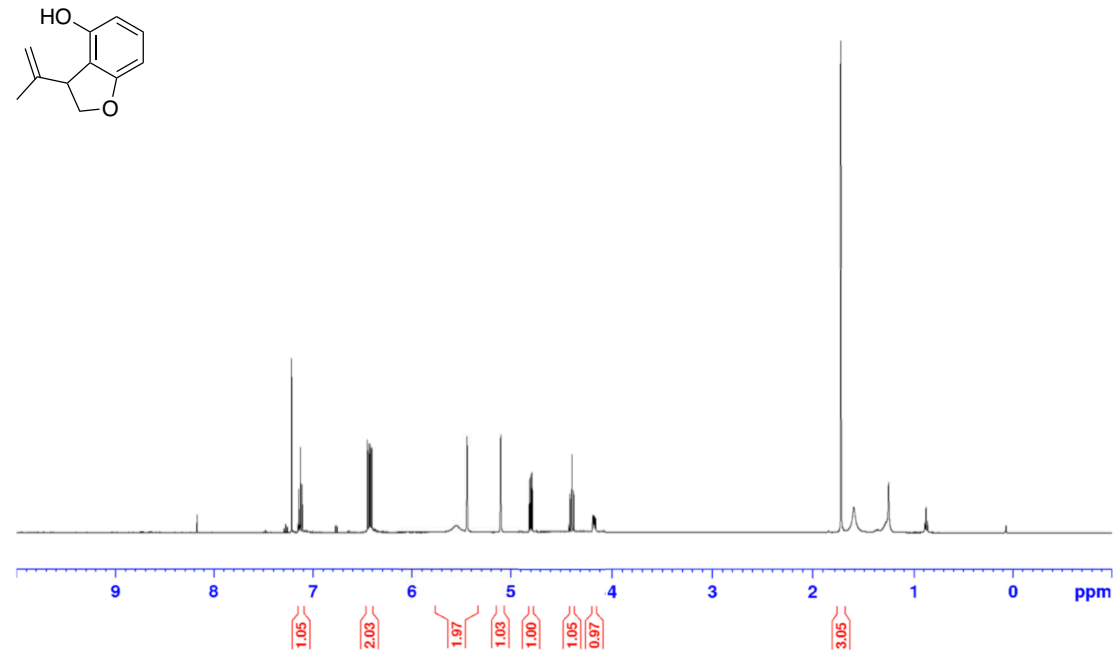
^{1}H NMR spectrum of **22x** ($CDCl_3$, 500 MHz)



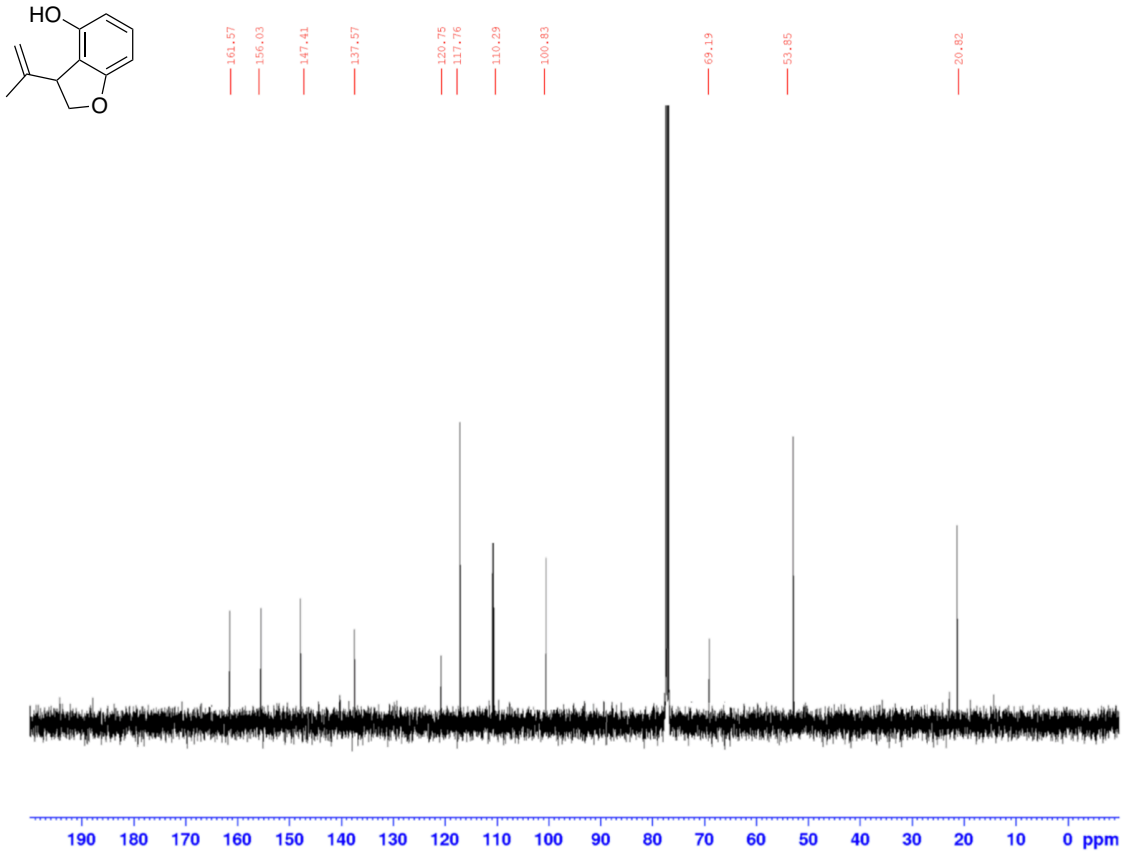
^{13}C NMR spectrum of **22x** ($CDCl_3$, 125 MHz)



^{1}H NMR spectrum of **22y** ($CDCl_3$, 500 MHz)



^{13}C NMR spectrum of **22y** ($CDCl_3$, 125 MHz)



5. Theoretical Calculation

DFT calculation were performed at PBE0/6-31+G(d) level of theory by using the Gaussian 16 program package.[34] The structures were optimized, and the vibrational frequency analyses were conducted on the optimized structures. The given energies are zero-point corrected.

1

E = -196.295210 a.u.
HOMO: - 6.555818672 eV
C -0.73530000 -0.67179400 0.00004700
H -0.71354200 -1.76358900 -0.00003000
C 0.44909300 -0.04092400 0.00007900
C 0.62881500 1.45070300 -0.00000200
H 1.20421100 1.76964000 -0.88003500
H -0.31407100 2.00257900 0.00011700
H 1.20453600 1.76971600 0.87978900
C -2.10806400 -0.07508000 -0.00002300
H -2.67660300 -0.40448300 -0.88010500
H -2.67678100 -0.40472400 0.87984400
H -2.10321200 1.01829300 0.00013900
C 1.73598000 -0.81950400 -0.00002400
H 2.34606800 -0.57374400 -0.88044700
H 2.34609400 -0.57398900 0.88044900
H 1.56015200 -1.90011100 -0.00018500

2

E = -157.026651 a.u.
HOMO: -6.839363544 eV
C 0.53838700 0.39537100 0.00015000
C -0.53837100 -0.39534100 0.00018900
H -0.39055400 -1.47802800 -0.00005900
C 1.95728200 -0.07937800 -0.00007900
H 2.50067800 0.28802800 0.88053100
H 2.01385800 -1.17342600 -0.00022000
H 2.50038600 0.28818300 -0.88080900
C -1.95728200 0.07936600 -0.00008500
H -2.50039400 -0.28834200 -0.88075400
H -2.50060500 -0.28797400 0.88059900
H -2.01393700 1.17340500 -0.00035100
H 0.39047200 1.47804500 0.00000700

3

E = -235.560346 a.u.
HOMO: - 6.3139075479999995 eV
C 0.67472800 0.00000000 0.00009100
C -0.67472800 0.00000000 -0.00003200
C 1.52444500 -1.24370200 0.00009300
H 0.95949900 -2.17704500 0.00009200
H 2.18396700 -1.25609700 -0.87905500
H 2.18396700 -1.25608500 0.87923800
C -1.52444500 1.24370200 -0.00012900
H -2.18408300 1.25608000 0.87893000
H -0.95949900 2.17704500 -0.00004900
H -2.18385300 1.25610200 -0.87936300
C 1.52444400 1.24370300 0.00016800
H 2.18392200 1.25605500 0.87934800
H 2.18401000 1.25613100 -0.87894500
H 0.95949600 2.17704500 0.00017900
C -1.52444300 -1.24370300 -0.00015800
H -2.18405800 -1.25611100 0.87892000
H -2.18387400 -1.25607600 -0.87937300
H -0.95949500 -2.17704400 -0.00011800

4

E = -307.121034 a.u.
HOMO: - 6.519083012 eV
C 1.16809289 -1.18830018 0.00000009
C -0.22251277 -1.22124298 -0.00000007
C -0.93966759 -0.02407564 -0.00000010
C -0.26387842 1.19753058 0.00000005
C 1.12953033 1.21672550 0.00000017
C 1.85383407 0.02692783 0.00000018
H 1.72122443 -2.12446737 0.00000014
H -0.76706589 -2.16098722 -0.00000021
H -0.82462837 2.13146175 0.00000000
H 1.64840709 2.17226264 0.00000030
H 2.94007329 0.04556592 0.00000026
O -2.29877785 -0.11082570 -0.00000026
H -2.68017892 0.77737922 -0.00000029

5

E = -422.741945 a.u.

HOMO: - 6.7035776600000005 eV
C 1.52230600 -1.12140500 -0.23998200
C 0.44538200 -1.98918100 0.39437600
C -0.93056700 -1.58248700 -0.11893500
H 1.56938200 -1.31125500 -1.32354900
H 2.51696200 -1.33671600 0.16211600
H 0.62584100 -3.05007200 0.18629700
H 0.47150000 -1.86572500 1.48487400
H -1.06092300 -1.90792700 -1.16369700
H -1.71632500 -2.08799600 0.46283500
C 1.25665800 0.36152300 -0.05312900
C -0.13835700 0.81427700 0.02644700
C -1.13668100 -0.09895000 -0.04324100
O 2.18524300 1.15885200 -0.01323900
C -0.38426600 2.28857400 0.12607400
H 0.24960700 2.72423200 0.90499900
H -0.11607800 2.79337700 -0.81020400
H -1.43157400 2.50460700 0.34812100
O -2.42177300 0.33211100 -0.08072300
H -3.02300100 -0.42433000 -0.04976100

6
E = -192.906129 a.u.
HOMO: - 6.470646364 eV
C -0.46266100 1.35085700 0.00000000
H -1.53012800 1.54152800 0.00000000
H 0.19981000 2.21352000 0.00000000
C 0.00000000 0.09475200 0.00000000
O 1.32570800 -0.22554300 0.00000000
H 1.85057200 0.58811700 0.00000000
C -0.85499500 -1.13946800 0.00000000
H -1.49824200 -1.17216500 0.88521700
H -1.49824200 -1.17216500 -0.88521700
H -0.22349600 -2.03133300 0.00000000

6. References

(1) C. A. Bewley and P. Wipf, *WO* **2012**/116254 A3, 2012.

(2) O. Ablialimov, M. Kedziorek, M. Malinska, K. Wozniak and K. Grela, *Organimetallics*, **2014**, *33*, 2160-2171.

(3) K. Yashiro, K. Hanaya, M. Shoji and T. Sugai, T. *Biosci. Biotech. Biochem*., **2015**, *79*, 1926-1930.

(4) T. Shindo, Y. Fukuyama and T. Sugai, *Synthesis*, **2004**, 692-700.

(5) C. Francesco, D. S. Antonio, N. Fabrizio, M. C. Gian, G. Gianfabio, A. F. Jose`, Y. M. Gisela, E. R. Maria and R. Elizabeth, *J. Med. Chem*., **2000**, *43*, 599-608.

(6) R. V. Bonnert, T. J. Luker, R. T. Mohammed, S. Thom and A. Cook, A. *WO* **2007**/068894 A2, 2007.

(7) M. Kahraman, S. P. Govek, J. Y. Nagasawa and N. D. Smith, *WO* **2011**/156518 A2, 2011.

(8) L. Wei, B. Matthew, C. Nan, S. Muhong, J. T. Nicholas, A. Jalil, W. Xing, B. H. Brian and I. D. Gary *Org. Lett*., **2007**, *9*, 2915-2918.

(9) A. A. Faisal, S. Wei, E. L. Mark and C. H. David, *Tetrahedron*, **2020**, *76*, 131521.

(10) P. H. Gilmartin and M. C. Kozlowski, *Org. Lett*., **2020**, *22*, 2914-2919.

(11) D. G. Batt, *WO* **2010**/009069 A1, 2010.

(12) T. Aotsuka, H. Kanazawa and K. Kumazawa, *WO* **2009**/072581 A1, 2009.

(13) S. Sengupta, M. G. B. Drew, R. Mukhopadhyay, B. Achari, A. Kr. Banerjee, *J. Org. Chem*., **2005**, *70*, 7694-7700.

(14) J. Mao, S. Q. Zhang, B. F. Shi and W. Bao W, *Chem. Commun*., **2014**, *50*, 3692-3694.

(15) T. Barf, K. Hammer, M. Luthman, F. Lehmann and R. Ringom, *WO* **2004**/063156 A1, 2004.

(16) A. Srikrishna and P. C. Ravikumar, *Synthesis*, **2007**, 65-74.

(17) S. A. Snyder, S. P. Breazzano, A. G. Ross, Y. Lin and A. L. Zografos, *J. Am. Chem. Soc*., **2009**, *131*, 1753-1765.

(18) J. A. Christopher, P. Bamborough, C. Alder, A. Campbell, G. J. Cutler, K. Down, A. M. Hamadi, A. M. Jolly, J. K. Kerns, F. S. Lucas, G. W. Mellor, D. Miller, M. A. Morse, K. D. Pancholi, W. Rumsey, Y. E. Solanke and R. Williamson R. *J. Med. Chem*., **2009**, *52*, 3098-3102.

(19) V. Bollu, B. C. Boren, J. Dalgard, B. T. Flatt, N. Haq, S. Hudson, R. Mohan, M. Morrissey and B. Pratt, *WO* **2011**/071565 A1, 2011.

(20) G. Majetich, R. Hicks, Y. Zhang, X. Tian, T. L. Feltman, J. Fang and S. Jr. Duncan, *J. Org. Chem*., **1996**, *61*, 8169-8165.

(21) Y. F. Wang, Y. R. Gao, S. Mao, Y. L. Zhang, D. D. Guo, Z. L. Yan, S. H. Guo and Y. Q. Wang, *Org. Lett*., **2014**, *16*, 1610-1613.

(22) Y. Li, Y. Y. Hu and S. L. Zhang, *Chem. Commun*., **2013**, *49*, 10635-10637.

(23) K. A. Bahou, D. Braddock, M. Christopher, G. Adam, G. P. Savage, Z. Shi and T. He, *J. Org. Chem*., **2020**, *85*, 4906-4917.

(24) W. W. Qiu, K. Surendra, L. Yin and E. J. Corey, E. J. *Org. Lett*., **2011**, *13*, 5893-5895.

(25) J. C. Conrad, J. Kong, B. N. Laforteza and D. W. C. MacMillan, *J. Am. Chem. Soc*., **2009**, *131*, 11640-11641

(26) P. Zhao and C. M. Beaudry, *Org. Lett*., **2013**, *15*, 402-405.

(27) M. Kiuchi, K. Marukawa, M. Hamada and K. Sugahara, *WO* **2008**/153159 A1, 2008.

(28) A. R. B. Manas and R. A. J. Smith, *Tetrahedron*, **1987**, *43*, 1847-1856.

(29) I. Sokolovs, D. Lubriks and E. Suna, *J. Am. Chem. Soc*., **2014**, *136*, 6920-6938.

(30) S. Y. Moon, J. Nam, K. Rathwell and W. S. Kim, *Org. Lett*., **2014**, *16*, 338-341.

(31) S. D. Nielsen, G. Smith, M. Begtrup and J. L. Kristensen, *Org. Lett.*, **2010**, *16*, 4557-4566.
(32) N. Hoffmann and J. P. Pete, *J. Org. Chem.*, **1997**, *62*, 6952-6960.
(33) P. F. Schuda and W. A. Price, *J. Org. Chem.*, **1987**, *52*, 1972-1979.
(34) Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Y. D. Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A., Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.