Supporting Information

Dehydrative Allylation of α C(sp^3)–H Bonds of Alkylamines with Allylic Alcohols

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General.

All reactions were carried out under a nitrogen atmosphere. Irradiation of photoreactions was carried out using a CCS LED lamp (Controller: PD3-5024-4-PI, Head: LDL2-14630BL2, λ_{max} = 470 nm, light intensity: 37 mW/cm^2). IR measurements were performed on a FTIR SHIMADZU DR-8000 spectrometer fitted with a Pike Technologies MIRacle Single Reflection ATR adapter. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECZ400S/L1 (^{1}H at 399.78 MHz and ^{13}C at 100.52 MHz). NMR data were obtained in $CDCl_3$. Proton chemical shifts were referenced to the residual proton signal of the solvent at 7.26 ppm ($CHCl_3$). Carbon chemical shifts were referenced to the carbon signal of the solvent at 77.0 ppm ($CDCl_3$). High-resolution mass spectra were recorded on a Thermo Scientific Exactive spectrometer. Flash column chromatography was performed with silica gel 60N (Kanto). Preparative thin-layer chromatography (PTLC) was performed on silica gel plates with silica gel 60 PF_{254} (Merck). Gel permeation chromatography was performed by LaboAce LC5060 with JAIGEL 2HR (Japan Analytical Industry Co., Ltd.).

Materials.

Anhydrous toluene was purchased from FUJIFILM Wako Pure Chemical Corporation. $Pd(OAc)_2$ (FUJIFILM Wako), BrettPhos (Sigma-Aldrich), BIPHEP (TCI), *N,N*-dimethylaniline (Nacalai tesque), β-methallyl alcohol (TCI), allyl alcohol (Nacalai tesque), 2-buten-1-ol (TCI), 1-buten-3-ol (TCI), and 2-penten-1-ol (TCI) were obtained from commercial suppliers and used without further purification. $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ was synthesized according to the reported method.[1] Other aniline derivatives[2] and allylic alcohols[3] were prepared according to the literature procedures.

Photoreaction setup

Reactions were irradiated using a photo-reactor (CCS, Controller: PD3-5024-4-PI, Head: LDL2-14630BL2, λ_{max} = 470 nm, light intensity: 37 mW/cm^2) shown in Figure S1. Ordinary Pyrex® reaction vial was used for the reaction. In order to keep the reaction temperature at room temperature, a simple cooling fan was installed at the front of the reaction vial. This setup secured a reliable irradiation while keeping a constant distance of 3 cm between the reaction vessel and the light source. Emission spectrum of the light source is shown in Figure S2.

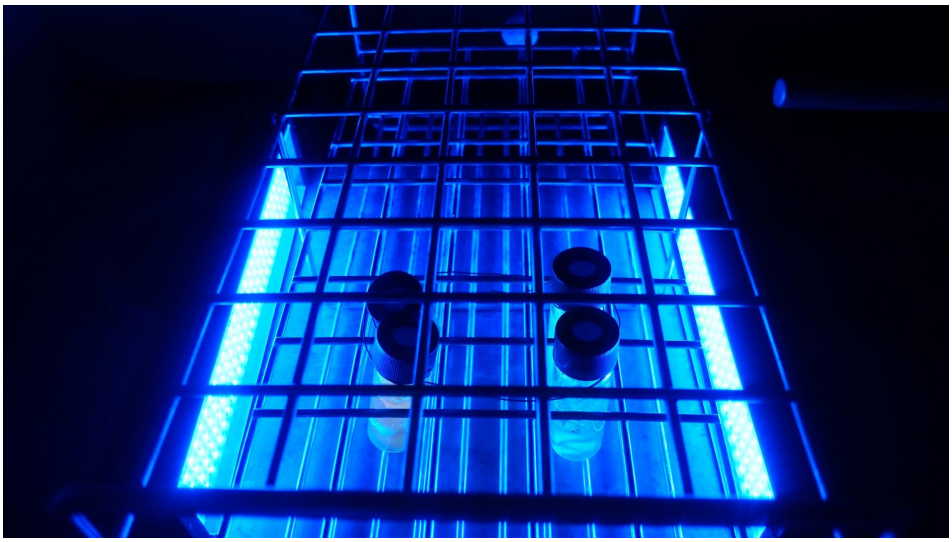


Figure S1. Photoreaction setup

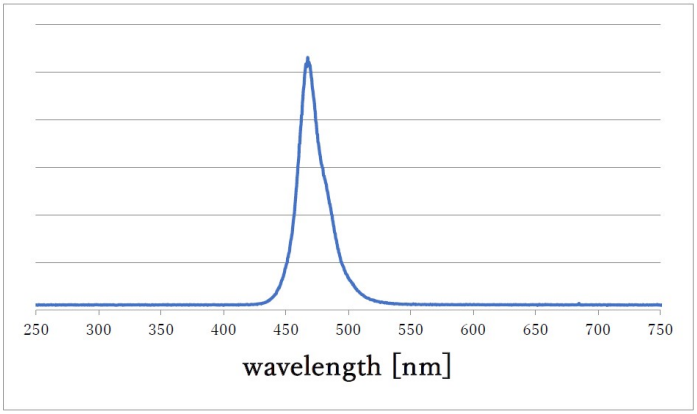
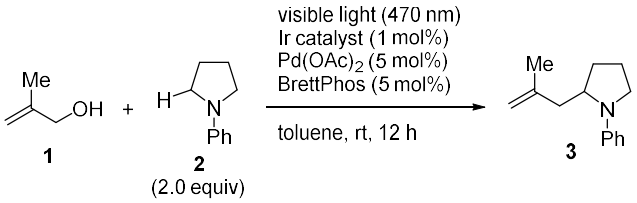
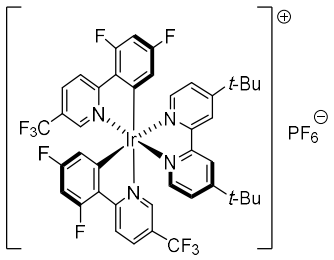


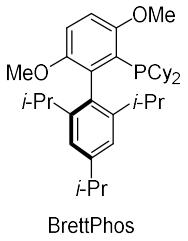
Figure S2. Emission spectrum of blue LEDs

・**Control experiments**





Ir[(dFCF$_3$ppy)$_2$dtbbpy]PF$_6$
(Ir catalyst)



BrettPhos

entry	Changes from above conditions	NMR yield of **3**
1	none	83%
2	PPh_3 instead of BrettPhos	not detected
3	P*n*-Bu_3 instead of BrettPhos	not detected
4	DPPF instead of BrettPhos	< 5%
5	BINAP instead of BrettPhos	55%
6	MeCN instead of toluene	not detected
7	THF instead of toluene	not detected
8	in the dark	not detected
9	without $Pd(OAc)_2$	not detected
10	without Ir catalyst	not detected

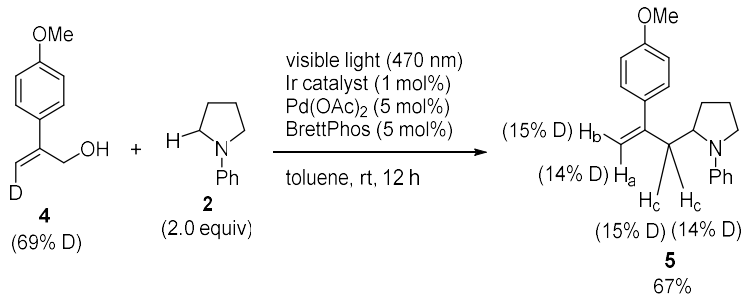
11	PdCp(π-allyl) instead of $Pd(OAc)_2$	13%
12	PdCp(π-allyl) + AcOH (10 mol%) instead of $Pd(OAc)_2$	75%

To an oven-dried 4 mL vial equipped with a stirrer bar, Pd precursor (0.01 mmol, 5 mol%), a phosphine ligand (0.01 mmol, 5 mol%) and Ir catalyst (2.1 mg, 0.002 mmol, 1 mol%) were added. The vial was capped with a silicon-sealed open-top screw cap. Then, the vial was placed in a nitrogen-filled glovebox. Toluene (2.0 mL) was added into the vial and the resulting mixture was pre-stirred for 30 s in the glovebox. The vial was removed from the glovebox. Allylic alcohol **1** (14.4 mg, 0.20 mmol, 1.0 equiv) and pyrrolidine **2** (58.9 mg, 0.40 mmol, 2.0 equiv) were added via syringe through the silicon-sealed cap. The reaction mixture was stirred under photoirradiation (470 nm) at room temperature. After irradiating for 12 h, the resulting mixture was passed through a pad of Florisil® and eluted with diethyl ether. The solvent was removed by rotary evaporator. Yield of **3** was determined by ^1H NMR analysis using 1,1,2,2,-tetrachloroethane as an internal standard.

・**Mechanistic study**

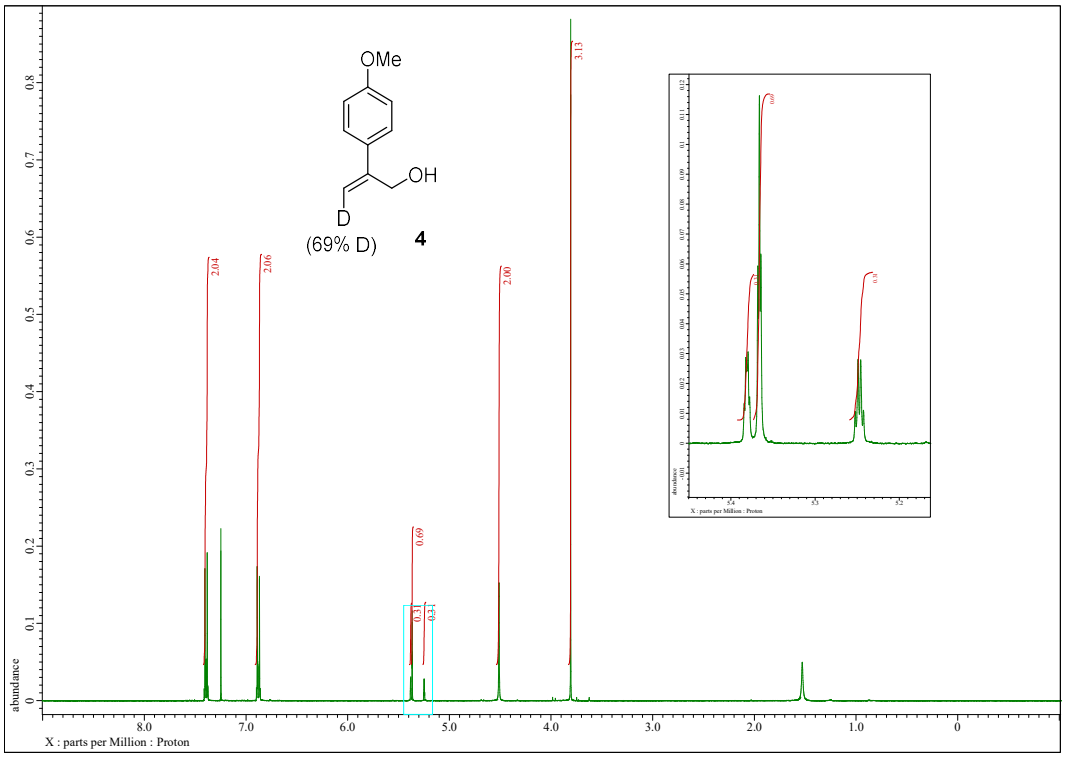
Deuterium labeling experiment

Allylic alcohol **4** was synthesized according to the literature method.[4]

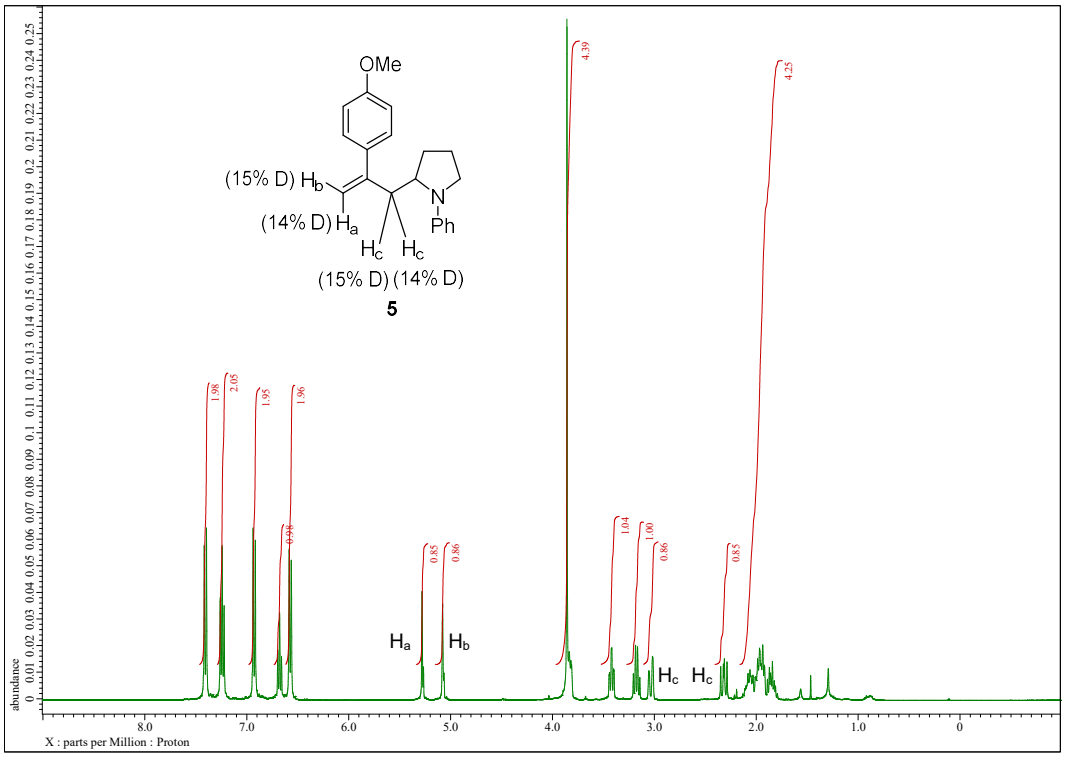


To an oven-dried 4 mL vial equipped with a stirrer bar, $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5 mol%), BrettPhos (5.3 mg, 0.01 mmol, 5 mol%) and Ir catalyst (2.1 mg, 0.002 mmol, 1 mol%) were added. The vial was capped with a silicon-sealed open-top screw cap. Then, the vial was placed in a nitrogen-filled glovebox. Toluene (2.0 mL) was added into the vial and the resulting mixture was pre-stirred for 30 s in the glovebox. The vial was removed from the glovebox. Deuterated allylic alcohol **4** (32.8 mg, 0.20 mmol, 1.0 equiv) and pyrrolidine **2** (58.9 mg, 0.40 mmol, 2.0 equiv) were added via syringe through the silicon-sealed cap. The reaction mixture was stirred under photoirradiation (470 nm) at room temperature. After irradiating for 12 h, the resulting mixture was passed through a pad of Florisil® and eluted with diethyl ether. The solvent was removed by rotary evaporator. The residue was purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to afford the product **5** as a white solid (39.3 mg, 0.14 mmol, 67% yield).

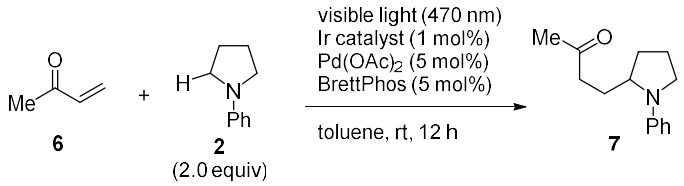
^{1}H NMR of **4** (400 MHz, $CDCl_3$)



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



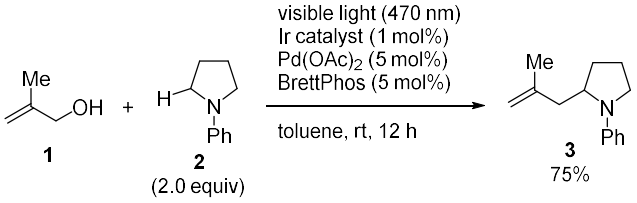
Radical trapping experiment



To an oven-dried 4 mL vial equipped with a stirrer bar, $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5 mol%), BrettPhos (5.3 mg, 0.01 mmol, 5 mol%) and Ir catalyst (2.1 mg, 0.002 mmol, 1 mol%) were added. The vial was capped with a silicon-sealed open-top screw cap. Then, the vial was placed in a nitrogen-filled glovebox. Toluene (2.0 mL) was added into the vial and the resulting mixture was pre-stirred for 30 s in the glovebox. The vial was removed from the glovebox. Ketone **6** (14.0 mg, 0.20 mmol, 1.0 equiv) and pyrrolidine **2** (58.9 mg, 0.40 mmol, 2.0 equiv) were added via syringe through the silicon-sealed cap. The reaction mixture was stirred under photoirradiation (470 nm) at room temperature. After irradiating for 12 h, the resulting mixture was passed through a pad of Florisil® and eluted with diethyl ether. The solvent was removed by rotary evaporator. The residue was purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 94/5/1) to afford the product **7** as a white solid (16.5 mg, 0.08 mmol, 38% yield).

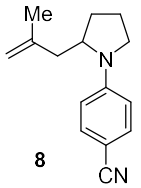
Mp: 56-58 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.55-1.65 (m, 1H), 1.74-1.78 (m, 1H), 1.91-2.07 (m, 4H), 2.14 (s, 3H), 2.49 (t, *J* = 7.0 Hz, 2H), 3.12-3.19 (m, 1H), 3.42-3.46 (m, 1H), 3.71-3.75 (m, 1H), 6.63-6.69 (m, 3H), 7.21-7.26 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.4, 27.1, 29.9, 30.1, 40.4, 48.5, 57.4, 111.9, 115.5, 129.2, 147.3, 208.4; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{20}NO$ 218.1539, Found 218.1541; **IR** (ATR): 2945, 1712, 1593, 1506, 1362, 1163, 746, 694 cm^{-1}.

A typical procedure for dehydrative allylation of 1 with 2.



To an oven-dried 4 mL vial equipped with a stirrer bar, $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5 mol%), BrettPhos (5.3 mg, 0.01 mmol, 5 mol%) and Ir catalyst (2.1 mg, 0.002 mmol, 1 mol%) were added. The vial was capped with a silicon-sealed open-top screw cap. Then, the vial was placed in a nitrogen-filled glovebox. Toluene (2.0 mL) was added into the vial and the resulting mixture was pre-stirred for 30 s in the glovebox. The vial was removed from the glovebox. Allylic alcohol **1** (14.4 mg, 0.20 mmol, 1.0 equiv) and pyrrolidine **2** (58.9 mg, 0.40 mmol, 2.0 equiv) were added via syringe through the silicon-sealed cap. The reaction mixture was stirred under photoirradiation (470 nm) at room temperature. After irradiating for 12 h, the resulting mixture was passed through a pad of Florisil® and eluted with diethyl ether. The solvent was removed by rotary evaporator. The residue was purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 97/2/1) to afford the product **3** as colorless oil (30.0 mg, 0.15 mmol, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86 (s, 3H), 1.91-2.11 (m, 5H), 2.51 (d, J = 14.4 Hz, 1H), 3.16-3.22 (m, 1H), 3.42-3.47 (m, 1H), 3.90-3.95 (m, 1H), 4.79 (s, 1H), 4.86 (s, 1H), 6.62 (d, J = 8.2 Hz, 2H), 6.68 (t, J = 7.2 Hz, 1H), 7.23-7.27 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.0, 23.1, 29.7, 40.6, 48.1, 56.7, 111.7, 112.2, 115.3, 129.2, 143.6, 147.0; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{20}N$ 202.1590, Found 202.1589; **IR** (ATR): 2967, 1645, 1595, 1504, 1362, 887, 743 cm^{-1}.

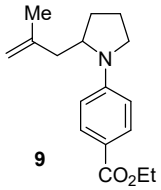


8

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 94/5/1) to give the title compound as a white solid (34.1 mg, 0.15 mmol, 75% yield)

from **1** (14.4 mg, 0.20 mmol) and 1-(4-cyanophenyl)-pyrrolidine (68.9 mg, 0.40 mmol).

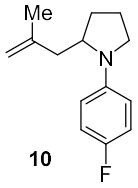
Mp: 61-63 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.82 (s, 3H), 1.90-1.99 (m, 3H), 2.02-2.13 (m, 2H), 2.39 (d, *J* = 14.4 Hz, 1H), 3.18-3.25 (m, 1H), 3.41-3.46 (m, 1H), 3.92-3.98 (m, 1H), 4.76 (s, 1H), 4.86 (s, 1H), 6.51-6.54 (m, 2H), 7.43-7.46 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 22.77, 22.83, 29.4, 39.8, 47.8, 56.8, 96.6, 111.6, 112.9, 120.9, 133.5, 142.6, 149.2; **HRMS** (APCI$^+$) m/z: $[M+H]^+$ Calcd for $C_{15}H_{19}N_2$ 227.1543, Found 227.1542; **IR** (ATR): 2973, 2210, 1645, 1603, 1518, 1381, 1175, 812, 731 cm^{-1}.



9

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 94/5/1) to give the title compound as colorless oil (38.0 mg, 0.14 mmol, 70% yield) from **1** (14.4 mg, 0.20 mmol) and 1-(4-ethoxycarbonyl)-pyrrolidine (87.7 mg, 0.40 mmol).

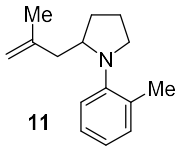
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.36 (t, *J* = 7.1 Hz, 3H), 1.83 (s, 3H), 1.91-2.11 (m, 5H), 2.45 (d, *J* = 14.3 Hz, 1H), 3.20-3.27 (m, 1H), 3.44-3.49 (m, 1H), 3.95-4.01 (m, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 4.76 (s, 1H), 4.85 (s, 1H), 6.51-6.55 (m, 2H), 7.89-7.93 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 14.5, 22.8 (2C), 29.4, 40.0, 47.8, 56.7, 60.0, 110.8, 112.7, 116.7, 131.4, 143.0, 149.9, 167.1; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{24}NO_2$ 274.1802, Found 274.1803; **IR** (ATR): 2974, 1697, 1647, 1603, 1375, 1269, 1179, 768 cm^{-1}.



10

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 97/2/1) to give the title compound as colorless oil (16.0 mg, 0.07 mmol, 36% yield) from **1** (14.4 mg, 0.20 mmol) and 1-(4-fluoro)-pyrrolidine (66.1 mg, 0.40 mmol).

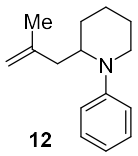
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.83 (s, 3H), 1.89-2.11 (m, 5H), 2.43 (d, *J* = 14.9 Hz, 1H), 3.09-3.15 (m, 1H), 3.37-3.41 (m, 1H), 3.80-3.86 (m, 1H), 4.75 (s, 1H), 4.84 (s, 1H), 6.47-6.52 (m, 2H), 6.91-6.97 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.0, 23.2, 29.8, 40.7, 48.6, 57.2, 112.1 (d, *J* = 7 Hz), 112.3, 115.6 (d, *J* = 22 Hz), 143.5, 143.8, 154.7 (d, *J* = 233 Hz); **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{19}FN$ 220.1496, Found 220.1497; **IR** (ATR): 2968, 1647, 1610, 1514, 1364, 1225, 887, 806 cm^{-1}.



11

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to give the title compound as colorless oil (30.4 mg, 0.14 mmol, 71% yield) from **1** (14.4 mg, 0.20 mmol) and 1-(2-methyl)-pyrrolidine (64.5 mg, 0.40 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59-1.70 (m, 1H), 1.74 (s, 3H), 1.78-1.85 (m, 2H), 1.87-1.97 (m, 1H), 2.10-2.18 (m, 1H), 2.28 (d, *J* = 14.4 Hz, 1H), 2.30 (s, 3H), 2.82 (td, *J* = 8.5, 4.5 Hz, 1H), 3.55 (q, *J* = 7.8 Hz, 1H), 3.75-3.82 (m, 1H), 4.70 (s, 1H), 4.75 (s, 1H), 6.91 (t, *J* = 7.3 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 7.13-7.17 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 19.6, 23.0, 23.7, 31.1, 41.9, 53.0, 58.0, 111.5, 118.3, 121.3, 126.1, 131.3, 131.9, 143.9, 148.3; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}N$ 216.1747, Found 216.1747; **IR** (ATR): 2967, 1647, 1597, 1491, 1294, 887, 756 cm^{-1}.

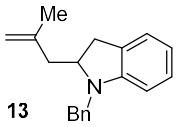


12

Purified by gel permeation chromatography to give the title compound as colorless oil (21.4 mg, 0.10 mmol, 50% yield) from **1** (14.4 mg, 0.20 mmol) and 1-phenylpiperidine (64.5 mg, 0.40 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.55-1.80 (m, 9H), 2.05 (dd, *J* = 13.5, 3.7 Hz, 1H), 2.36 (dd, *J* = 13.5, 10.8 Hz, 1H), 2.93-3.00 (m, 1H), 3.34 (d, *J* = 12.0 Hz, 1H), 3.97-4.03 (m, 1H), 4.70 (s, 1H), 4.76 (s, 1H), 6.79 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 2H),

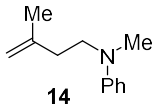
7.22-7.27 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 18.9, 22.3, 25.7, 26.9, 35.0, 43.7, 53.7, 112.2, 116.4, 118.5, 129.1, 143.5, 150.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{22}N$ 216.1747, Found 216.1746; **IR** (ATR): 2932, 1645, 1597, 1497, 1248, 885, 750 cm^{-1}.



13

Purified by gel permeation chromatography to give the title compound as colorless oil (33.0 mg, 0.13 mmol, 63% yield) from **1** (14.4 mg, 0.20 mmol) and 1-benzylindoline (83.7 mg, 0.40 mmol).

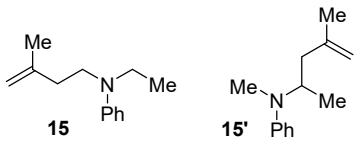
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.73 (s. 3H), 2.23 (dd, *J* = 13.8, 10.0 Hz, 1H), 2.58 (dd, *J* = 13.8, 3.7 Hz, 1H), 2.80 (dd, *J* = 15.8, 8.8 Hz, 1H), 3.16 (dd, *J* = 15.9, 8.8 Hz, 1H), 3.84 (dtd, *J* = 9.9, 8.9, 3.8 Hz, 1H), 4.27 (d, *J* = 16.1 Hz, 1H), 4.44 (d, *J* = 16.2 Hz, 1H), 4.77 (s, 1H), 4.83 (s, 1H), 6.35 (d, *J* = 7.8 Hz, 1H), 6.64-6.68 (m, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.25-7.29 (m, 1H), 7.32-7.39 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 22.7, 35.0, 42.6, 51.5, 63.2, 106.8, 112.6, 117.4, 124.2, 126.9, 127.2, 127.3, 128.4, 128.6, 139.1, 142.5, 152.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}N$ 264.1747, Found 264.1747; **IR** (ATR): 3026, 1647, 1604, 1483, 1652, 889, 743 cm^{-1}.



14

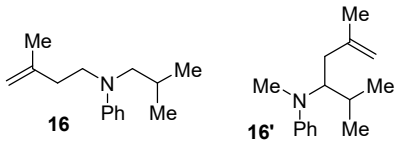
Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 97/2/1) to give the title compound as colorless oil (27.3 mg, 0.16 mmol, 78% yield) from **1** (14.4 mg, 0.20 mmol) and *N,N*-dimethylaniline (72.7 mg, 0.60 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.81 (s, 3H), 2.27-2.30 (m, 2H), 2.96 (s, 3H), 3.45-3.49 (m, 2H), 4.75 (s, 1H), 4.81 (s, 1H), 6.69-6.74 (m, 3H), 7.23-7.27 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 22.8, 34.2, 38.1, 51.5, 111.3, 112.1, 116.0, 129.2, 143.6, 149.0; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}N$ 176.1434, Found 176.1432; **IR** (ATR): 2967, 1647, 1597, 1504, 1369, 887, 745 cm^{-1}.



Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 97/2/1) to give a mixture of the title compounds (**15**:**15'** = 91:9) as colorless oil (33.4 mg, 0.18 mmol, 88% yield) from **1** (14.4 mg, 0.20 mmol) and *N*-ethyl-*N*-methylaniline (81.1 mg, 0.60 mmol).

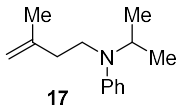
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.15 (d, *J* = 6.6 Hz, 0.3H), 1.18 (t, *J* = 7.0 Hz, 3H), 1.76 (s, 0.3H), 1.82 (s, 3H), 2.18 (dd, *J* = 14.0, 7.6 Hz, 0.1H), 2.29-2.33 (m, 2H), 2.37 (dd, *J* = 14.0, 7.3 Hz, 0.1H), 2.74 (s, 0.3H), 3.36-3.43 (m, 4H), 4.10-4.19 (m, 0.1H), 4.76-4.77 (m, 1.2H), 4.82 (s, 1H), 6.65-6.71 (m, 3.1H), 6.80-6.82 (m, 0.2H), 7.21-7.27 (m, 2.2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 12.4 (**15**), 16.7 (**15'**), 22.3 (**15'**), 22.8 (**15**), 30.0 (**15'**), 35.2 (**15**), 42.7 (**15'**), 44.8 (**15**), 49.2 (**15**), 51.6 (**15'**), 111.2 (**15**), 111.7 (**15**), 112.3 (**15'**), 113.0 (**15'**), 115.4 (**15**), 116.3 (**15'**), 129.1 (**15'**), 129.3 (**15**), 143.3 (**15'**), 143.7 (**15**), 147.7 (**15**), 150.2 (**15'**); **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}N$ 190.1590, Found 190.1588; **IR** (ATR): 2968, 1647, 1597, 1504, 1352, 885, 743 cm^{-1}.



Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 97/2/1) to give a mixture of the title compounds (**16**:**16'** = 94:6) as colorless oil (31.0 mg, 0.14 mmol, 71% yield) from **1** (14.4 mg, 0.20 mmol) and *N*-*i*-butyl-*N*-methylaniline (65.3 mg, 0.40 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 0.85 (d, *J* = 6.8 Hz, 0.18H), 0.96 (d, *J* = 6.6 Hz, 6H), 1.02 (d, *J* = 6.6 Hz, 0.18H), 1.65 (s, 0.18H), 1.81 (s, 3H), 1.86-1.93 (m, 0.06H), 2.02-2.12 (m, 1H), 2.26-2.37 (m, 2.12H), 2.75 (s, 0.18H), 3.08 (d, *J* = 7.3 Hz, 2H), 3.44-3.48 (m, 2H), 3.69-3.75 (m, 0.06H), 4.67 (s, 0.06H), 4.70 (s, 0.06H), 4.75 (s, 1H), 4.82 (s, 1H), 6.61-6.74 (m, 3.18H), 7.18-7.25 (m, 2.12H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 20.4 (**16**), 20.7 (**16'**), 22.3 (**16'**), 22.9 (**16**), 27.1 (**16**), 30.6 (**16'**), 32.3 (**16'**),

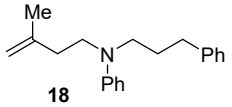
34.1 (**16**), 39.1 (**16'**), 50.7 (**16**), 59.0 (**16**), 62.1 (**16'**), 111.1 (**16**), 111.7 (**16'**), 112.0 (**16**), 112.3 (**16'**), 115.1 (**16'**), 115.3 (**16**), 128.9 (**16'**), 129.2 (**16**), 142.5 (**16'**), 143.7 (**16**), 143.8 (**16'**), 148.1 (**16**); **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{15}H_{24}N$ 218.1903, Found 218.1904; **IR** (ATR): 2955, 1647, 1597, 1504, 1356, 885, 745 cm^{-1}.



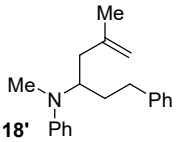
17

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to give the title compound as colorless oil (30.0 mg, 0.15 mmol, 74% yield) from **1** (14.4 mg, 0.20 mmol) and *N*-methyl-*N*-*i*-propylaniline (59.7 mg, 0.40 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.22 (d, *J* = 6.6 Hz, 6H), 1.83 (s, 3H), 2.27-2.32 (m, 2H), 3.27-3.31 (m, 2H), 4.08 (sep, *J* = 6.6 Hz, 1H), 4.78 (s, 1H), 4.83 (s, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.78 (d, *J* = 8.1 Hz, 2H), 7.23-7.27 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 20.1, 22.9, 37.3, 42.9, 48.3, 110.9, 113.0, 116.0, 129.2, 144.0, 148.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{14}H_{22}N$ 204.1747, Found 204.1746; **IR** (ATR): 2968, 1647, 1597, 1502, 1350, 1171, 887, 746 cm^{-1}.



18

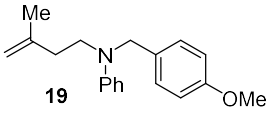


18'

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 97/2/1) to give a mixture of the title compounds (**18**:**18'** = 89:11) as colorless oil (46.6 mg, 0.17 mmol, 83% yield) from **1** (14.4 mg, 0.20 mmol) and *N*-methyl-*N*-(3-phenylpropyl)aniline (90.1 mg, 0.40 mmol).

^{1}H NMR (400 MHz, $CDCl_3$): δ 1.70 (s, 0.3H), 1.81 (s, 3H), 1.88-2.02 (m, 2.2H), 2.21-2.36 (m, 2.2H), 2.55-2.66 (m, 0.2H), 2.69-2.73 (m, 2H), 2.81 (s, 0.3H), 3.33-3.36 (m, 2H), 3.42-3.46 (m, 2H), 4.00-4.07 (m, 0.1H), 4.75 (s, 0.1H), 4.77 (s, 1.1H), 4.83 (s, 1H), 6.66-6.79 (m, 3.3H), 7.15-7.35 (m, 7.7H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 22.3 (**18'**), 22.8 (**18**), 28.8 (**18**), 29.9 (**18'**), 32.9 (**18'**), 33.3 (**18**), 34.1 (**18'**), 34.9 (**18**), 40.9 (**18'**), 49.8 (**18**), 50.3 (**18**), 55.6 (**18'**), 111.2 (**18**), 111.8 (**18**), 112.5 (**18'**), 112.7 (**18'**),

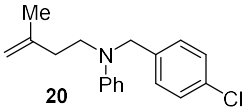
115.6 (**18**), 116.1 (**18'**), 125.7 (**18'**), 125.9 (**18**), 128.28 (**18'**), 128.3 (**18**), 128.4 (**18**), 128.4 (**18'**), 129.1 (**18'**), 129.2 (**18**), 141.7 (**18**), 142.0 (**18'**), 143.1 (**18'**), 143.6 (**18**), 147.8 (**18**), 150.6 (**18'**); **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{26}N$ 280.2060, Found 280.2060; **IR** (ATR): 2938, 1647, 1597, 1504, 1368, 745, 692 cm^{-1}.



19

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to give the title compound as a white solid (25.0 mg, 0.09 mmol, 44% yield) from **1** (14.4 mg, 0.20 mmol) and *N*-methyl-*N*-(4-methoxybenzyl)aniline (90.9 mg, 0.40 mmol).

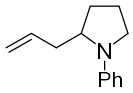
Mp: 69-71 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.79 (s, 3H), 2.34-2.38 (m, 2H), 3.50-3.54 (m, 2H), 3.80 (s, 3H), 4.50 (s, 2H), 4.75 (s, 1H), 4.81 (s, 1H), 6.67-6.73 (m, 3H), 6.84-6.88 (m, 2H), 7.16-7.24 (m, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 22.8, 34.8, 49.8, 53.7, 55.2, 111.4, 112.1, 114.0, 116.1, 127.7, 129.2, 130.8, 143.5, 148.4, 158.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{24}NO$ 282.1852, Found 282.1853; **IR** (ATR): 2997, 1647, 1597, 1506, 1242, 1171, 810, 748 cm^{-1}.



20

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to give the title compound as a white solid (7.6 mg, 0.03 mmol, 13% yield) from **1** (14.4 mg, 0.20 mmol) and *N*-methyl-*N*-(4-chlorobenzyl)aniline (92.7 mg, 0.40 mmol).

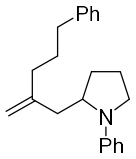
Mp: 60-61 °C; **^{1}H NMR** (400 MHz, $CDCl_3$): δ 1.78 (s, 3H), 2.33-2.37 (m, 2H), 3.49-3.53 (m, 2H), 4.50 (s, 2H), 4.74 (s, 1H), 4.80 (s, 1H), 6.66-6.71 (m, 3H), 7.16-7.22 (m, 4H), 7.26-7.29 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 22.8, 34.8, 50.1, 53.9, 111.6, 112.2, 116.5, 127.9, 128.7, 129.3, 132.4, 137.5, 143.3, 148.0; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{21}ClN$ 286.1357, Found 286.1359; **IR** (ATR): 2924, 1647, 1597, 1506, 1171, 804, 747 cm^{-1}



21

Purified by gel permeation chromatography to give the title compound as colorless oil (22.3 mg, 0.12 mmol, 60% yield) from allyl alcohol (11.6 mg, 0.20 mmol) and **2** (58.9 mg, 0.40 mmol).

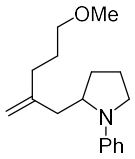
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.88-2.12 (m, 5H), 2.49-2.55 (m, 1H), 3.15-3.21 (m, 1H), 3.42-3.47 (m, 1H), 3.75-3.80 (m, 1H), 5.08-5.16 (m, 2H), 5.79-5.90 (m, 1H), 6.56-6.62 (m, 2H), 6.66-6.70 (m, 1H), 7.22-7.27 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.2, 29.7, 37.3, 48.3, 58.0, 111.8, 115.4, 116.9, 129.2, 135.6, 147.1; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{18}N$ 188.1434, Found 188.1433; **IR** (ATR): 2970, 1638, 1595, 1504, 1362, 908, 745, 691 cm^{-1}.



22

Purified by gel permeation chromatography to give the title compound as colorless oil (31.5 mg, 0.10 mmol, 52% yield) from 2-hydroxymethyl-5-phenyl-1-pentene (35.3 mg, 0.20 mmol) and **2** (58.9 mg, 0.40 mmol).

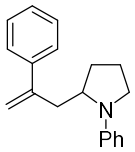
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76-2.10 (m, 7H), 2.17 (d, J = 8.1 Hz, 2H), 2.54 (d, J = 14.9 Hz, 1H), 2.62-2.73 (m, 2H), 3.15-3.22 (m, 1H), 3.42-3.46 (m, 1H), 3.89-3.94 (m, 1H), 4.86 (s, 1H), 4.90 (s, 1H), 6.60 (d, J = 7.8 Hz, 2H), 6.69 (t, J = 7.3 Hz, 1H), 7.20-7.34 (m, 7H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.1, 29.7 (2C), 35.6, 36.1, 38.7, 48.0, 56.8, 111.4, 111.7, 115.3, 125.7, 128.3, 128.4, 129.2, 142.3, 146.9, 147.2; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{28}N$ 306.2216, Found 306.2220; **IR** (ATR): 2936, 1641, 1597, 1504, 1364, 907, 729 cm^{-1}.



23

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to give the title compound as colorless oil (33.5 mg, 0.13 mmol, 65% yield) from 2-hydroxymethyl-5-methoxy-1-pentene (26.0 mg, 0.20 mmol) and **2** (58.9 mg, 0.40 mmol).

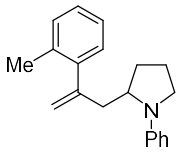
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71-1.84 (m, 2H), 1.88-2.08 (m, 5H), 2.17 (t, *J* = 7.7 Hz, 2H), 2.53 (d, *J* = 14.8 Hz, 1H), 3.14-3.21 (m, 1H), 3.36 (s, 3H), 3.40-3.46 (m, 3H), 3.89-3.95 (m, 1H), 4.84 (s, 1H), 4.88 (s, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 7.22-7.27 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.1, 27.8, 29.7, 32.8, 38.8, 48.0, 56.8, 58.6, 72.2, 111.3, 111.7, 115.3, 129.2, 146.95, 147.01; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{26}NO$ 260.2009, Found 260.2010; **IR** (ATR): 2924, 1641, 1597, 1504, 1362, 1117, 745, 691 cm^{-1}.



24

Purified by gel permeation chromatography to give the title compound as colorless oil (32.1 mg, 0.12 mmol, 61% yield) from 2-phenyl-1-pentene-3-ol (26.8 mg, 0.20 mmol) and **2** (58.9 mg, 0.40 mmol).

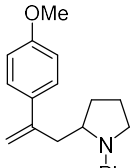
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.77-2.11 (m, 4H), 2.32 (dd, *J* = 14.5, 10.5 Hz, 1H), 3.05 (d, *J* = 14.4 Hz, 1H), 3.12-3.18 (m, 1H), 3.38-3.42 (m, 1H), 3.77-3.82 (m, 1H), 5.14 (s, 1H), 5.31 (s, 1H), 6.54 (d, *J* = 8.1 Hz, 2H), 6.65 (t, *J* = 7.3 Hz, 1H), 7.19-7.23 (m, 2H), 7.29-7.33 (m, 1H), 7.35-7.39 (m, 2H), 7.44 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.0, 29.3, 38.0, 48.0, 57.0, 111.8, 114.6, 115.3, 126.3, 127.6, 128.3, 129.2, 141.6, 146.9, 147.0; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{22}N$ 264.1747, Found 264.1750; **IR** (ATR): 3057, 1624, 1597, 1504, 1364, 907, 729, 691 cm^{-1}.



25

Purified by gel permeation chromatography to give the title compound as colorless oil (38.6 mg, 0.14 mmol, 70% yield) from 2-(2-methylphenyl)-1-pentene-3-ol (29.6 mg, 0.20 mmol) and **2** (58.9 mg, 0.40 mmol).

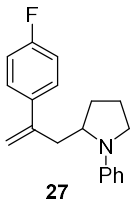
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.86-2.15 (m, 4H), 2.20 (dd, *J* = 14.2, 10.9 Hz, 1H), 2.37 (s, 3H), 2.90 (d, *J* = 14.2 Hz, 1H), 3.12-3.18 (m, 1H), 3.41-3.45 (m, 1H), 3.67-3.72 (m, 1H), 5.02 (s, 1H), 5.31 (s, 1H), 6.37 (d, *J* = 8.8 Hz, 2H), 6.61-6.65 (m, 1H), 7.13-7.19 (m, 3H), 7.20-7.27 (m, 3H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 19.8, 23.1, 29.6, 40.9, 47.9, 56.6, 111.6, 115.2, 115.9, 125.5, 127.1, 128.5, 129.1, 130.3, 134.8, 142.2, 146.7, 147.8; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}N$ 278.1903, Found 278.1907; **IR** (ATR): 2965, 1636, 1595, 1504, 1364, 745, 691 cm^{-1}.



26

Purified by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to give the title compound as colorless oil (39.3 mg, 0.13 mmol, 67% yield) from 2-(4-methoxyphenyl)-1-pentene-3-ol (32.8 mg, 0.20 mmol) and **2** (58.9 mg, 0.40 mmol).

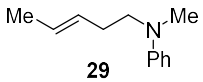
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.79-1.89 (m, 1H), 1.92-2.11 (m, 3H), 2.31 (dd, *J* = 14.5, 10.4 Hz, 1H), 3.04 (d, *J* = 14.5 Hz, 1H), 3.14-3.20 (m, 1H), 3.42 (dd, *J* = 8.7, 2.5 Hz, 1H), 3.81-3.85 (m, 1H), 3.86 (s, 3H), 5.08 (s, 1H), 5.28 (s, 1H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.91-6.94 (m, 2H), 7.21-7.27 (m, 2H), 7.39-7.42 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.0, 29.3, 38.0, 47.9, 55.3, 57.0, 111.8, 113.2, 113.7, 115.3, 127.4, 129.2, 134.0, 146.2, 146.9, 159.2; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{24}NO$ 294.1852, Found 294.1855; **IR** (ATR): 2959, 1595, 1504, 1364, 1246, 835, 745 cm^{-1}.



27

Purified by gel permeation chromatography to give the title compound as colorless oil (39.1 mg, 0.14 mmol, 70% yield) from 2-(4-fluorophenyl)-1-pentene-3-ol (30.4 mg, 0.20 mmol) and **2** (58.9 mg, 0.40 mmol)..

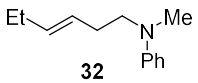
^{1}H NMR (400 MHz, $CDCl_3$): δ 1.80-2.12 (m, 4H), 2.34 (dd, *J* = 14.6, 10.2 Hz, 1H), 3.00 (d, *J* = 13.8 Hz, 1H), 3.13-3.20 (m, 1H), 3.38-3.42 (m, 1H), 3.78-3.84 (m, 1H), 5.14 (s, 1H), 5.29 (s, 1H), 6.53 (d, *J* = 7.8 Hz, 2H), 6.68 (t, *J* = 7.3 Hz, 1H), 7.03-7.09 (m, 2H), 7.21-7.25 (m, 2H), 7.38-7.43 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$): δ 23.0, 29.3, 38.2, 48.0, 56.9, 111.8, 114.6, 115.2 (d, *J* = 21 Hz), 115.4, 127.9 (d, *J* = 8 Hz), 129.2, 137.7 (d, *J* = 3 Hz), 145.9, 146.8, 162.4 (d, *J* = 246 Hz); **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{21}FN$ 282.1653, Found 282.1654; **IR** (ATR): 2968, 1624, 1597, 1504, 1364, 839, 745 cm^{-1}.



29

BIPHEP was used as the ligand. The product was isolated by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to give the title compound as colorless oil (22.1 mg, 0.12 mmol, 63% yield) from 2-buten-1-ol (14.4 mg, 0.20 mmol) and *N,N*-dimethylaniline (72.7 mg, 0.60 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 1.65-1.67 (m, 3H), 2.22-2.27 (m, 2H), 2.92 (s, 3H), 3.32-3.36 (m, 2H), 5.39-5.56 (m, 2H), 6.66-6.72 (m, 3H), 7.19-7.27 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 12.3, 24.0, 32.5, 47.1, 106.3, 110.1, 121.2, 122.5, 123.4, 143.3 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{12}H_{18}N$ 176.1434. Found 176.1433; **IR** (ATR): 2960, 1648, 1597, 1504, 1350, 886, 745 cm^{-1}.



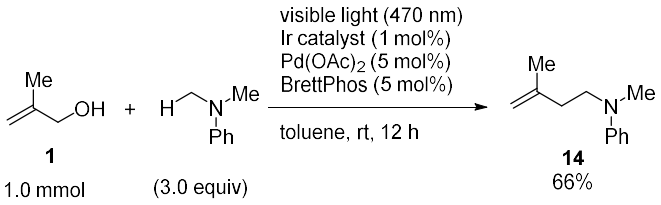
32

BIPHEP was used as the ligand. The product was isolated by preparative thin-layer chromatography (hexane/acetone/triethylamine = 96/3/1) to give the title compound as

colorless oil (16.8 mg, 0.09 mmol, 44% yield) from 2-penten-1-ol (17.2 mg, 0.20 mmol) and *N,N*-dimethylaniline (72.7 mg, 0.60 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.5 Hz, 3H), 2.00 (dq, *J* = 7.1, 7.1 Hz, 2H), 2.25 (dt, *J* = 7.3, 7.3 Hz, 2H), 2.93 (s, 3H), 3.33-3.36 (m, 2H), 5.37-5.44 (m, 1H), 5.50-5.57 (m, 1H), 6.66-6.71 (m, 3H), 7.20-7.25 (m, 2H) ppm; **^{13}C NMR** (101 MHz, $CDCl_3$) δ 13.9, 25.8, 29.9, 38.4, 53.0, 112.2, 116.0, 126.1, 129.2, 134.2, 149.2 ppm; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{13}H_{20}N$ 190.1590. Found 190.1589; **IR** (ATR): 2966, 1647, 1597, 1504, 1369, 877, 745 cm^{-1}.

A 1 mmol scale reaction of 1 with *N,N*-dimethylaniline.



To an oven-dried 10 mL vial equipped with a stirrer bar, $Pd(OAc)_2$ (11.0 mg, 0.05 mmol, 5 mol%), BrettPhos (26.5 mg, 0.05 mmol, 5 mol%) and Ir catalyst (10.5 mg, 0.01 mmol, 1 mol%) were added. The vial was capped with a silicon-sealed open-top cap. Then, the vial was placed in a nitrogen-filled glovebox. Toluene (8.0 mL) was added into the vial and the resulting mixture was pre-stirred for 30 s in the glovebox. The vial was removed from the glovebox. Allylic alcohol **1** (72.0 mg, 1.0 mmol, 1.0 equiv) and *N,N*-dimethylaniline (364 mg, 3.0 mmol, 3.0 equiv) were added via syringe through the silicon-sealed cap. The reaction mixture was stirred under photoirradiation (470 nm) at room temperature. After irradiating for 12 h, the resulting mixture was passed through a pad of Florisil® and eluted with diethyl ether. The solvent was removed by rotary evaporator. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 100/0 to 95/5) to afford the product **14** as colorless oil (115 mg, 0.66 mmol, 66% yield).

References

(1) Rossolini, T.; Leitch, J. A.; Grainger, R.; Dixon, D. J. *Org. Lett.* **2018**, *20*, 6794.

(2) (a) Tayama, E.; Yanaki, T.; Iwamoto, H.; Hasegawa, E. *Eur. J. Org. Chem.* **2010**, 6719. (b) McNally, A.; Prier, C. K.; MacMillan, D. W. C. *Science* **2011**, *334*, 1114. (c) Uraguchi, D.; Kinoshita, N.; Kizu, T.; Ooi, T. *J. Am. Chem. Soc.* **2015**, *137*, 13768. (d) Joeand, C. L.; Doyle, A. G. *Angew. Chem. Int. Ed.* **2016**, *55*, 4040. (e) Matsumoto, K.; Takeda, S.; Hirokane, T.; Yoshida, M. *Org. Lett.* **2019**, *21*, 7279.

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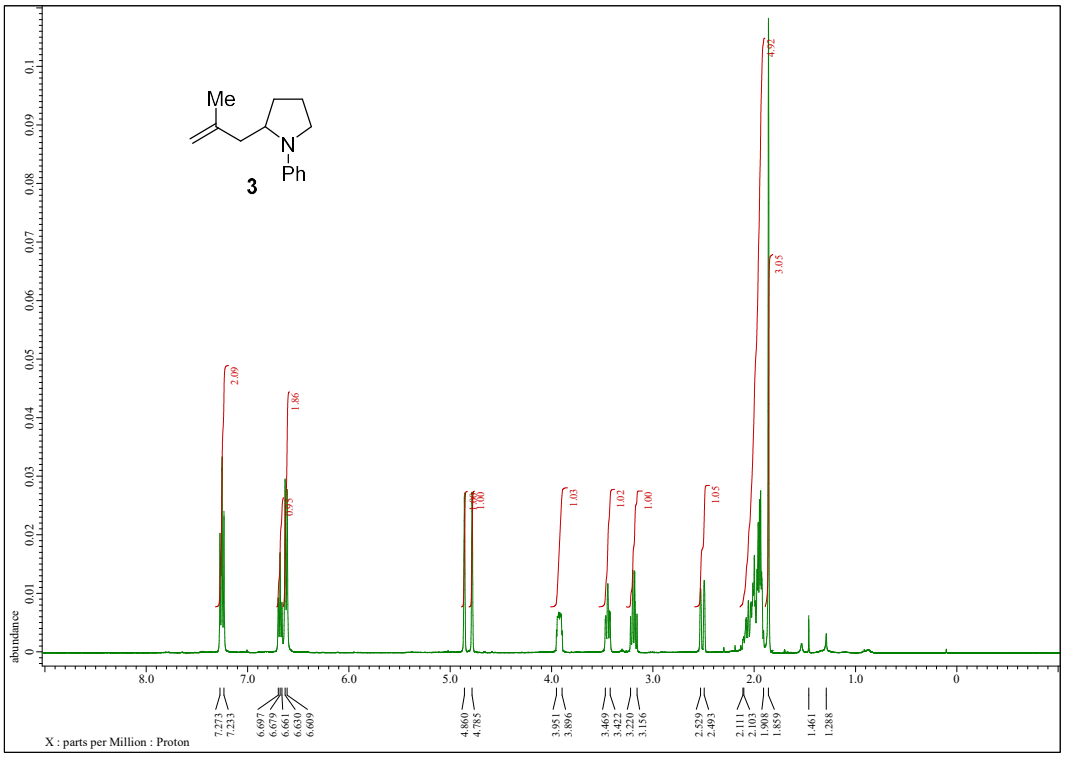
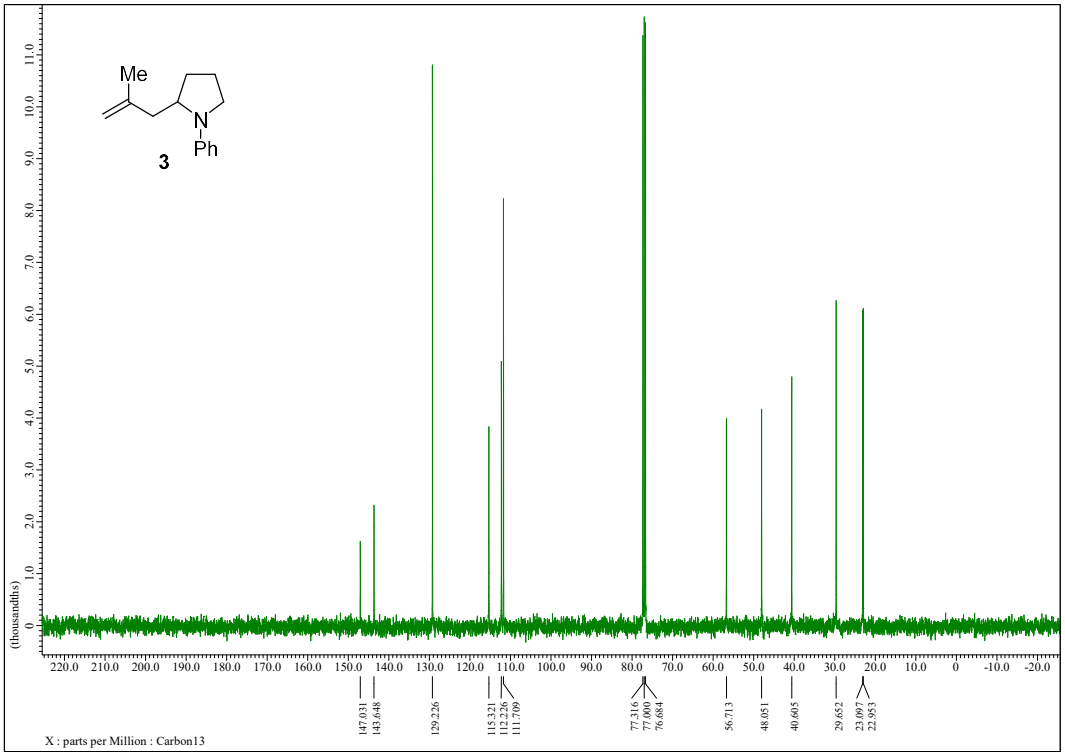
^{1}H and ^{13}C NMR spectra

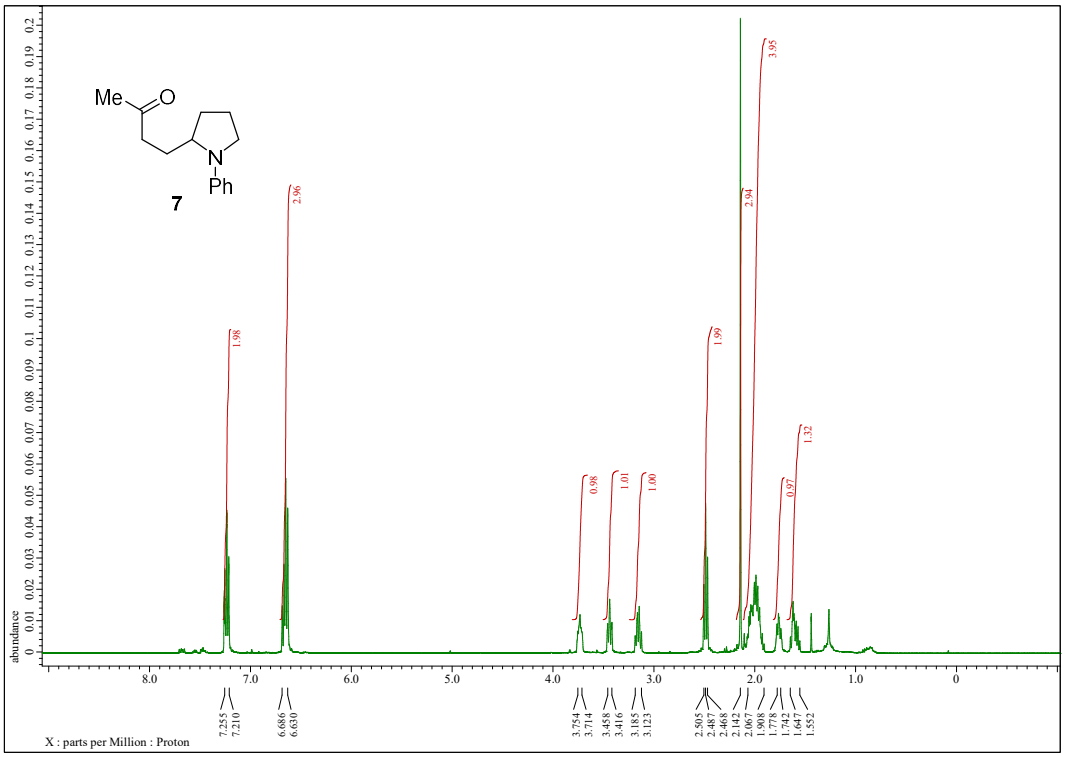
^{1}H NMR of **3** (400 MHz, $CDCl_3$)



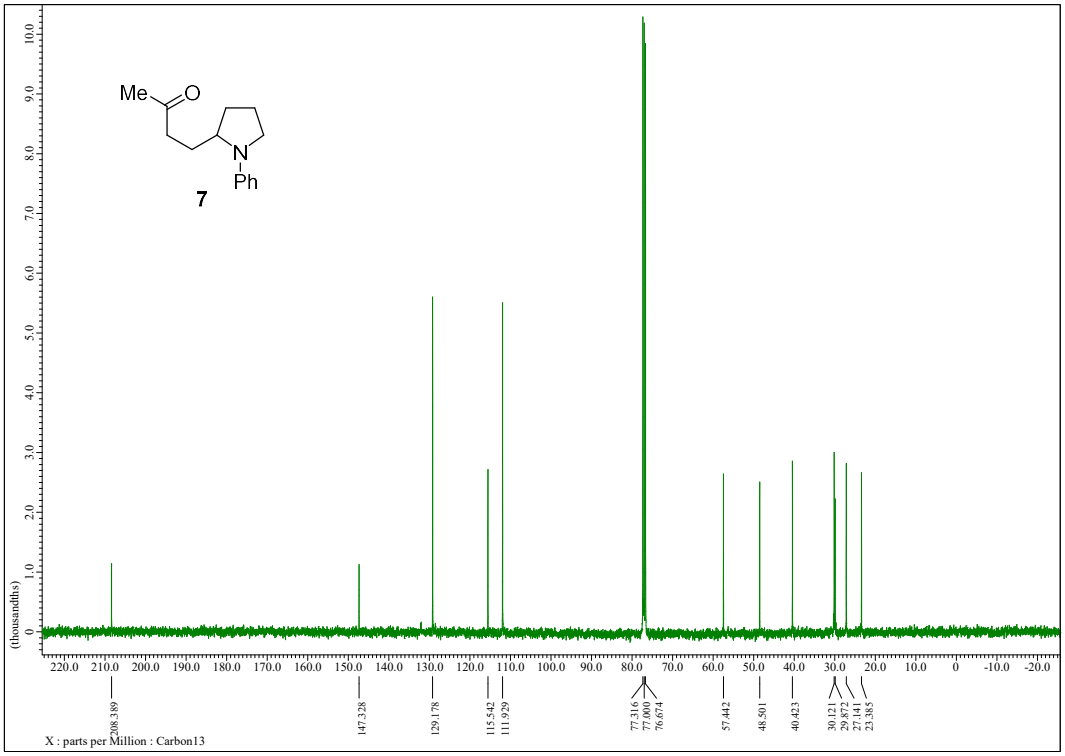
^{13}C NMR of **3** (101 MHz, $CDCl_3$)



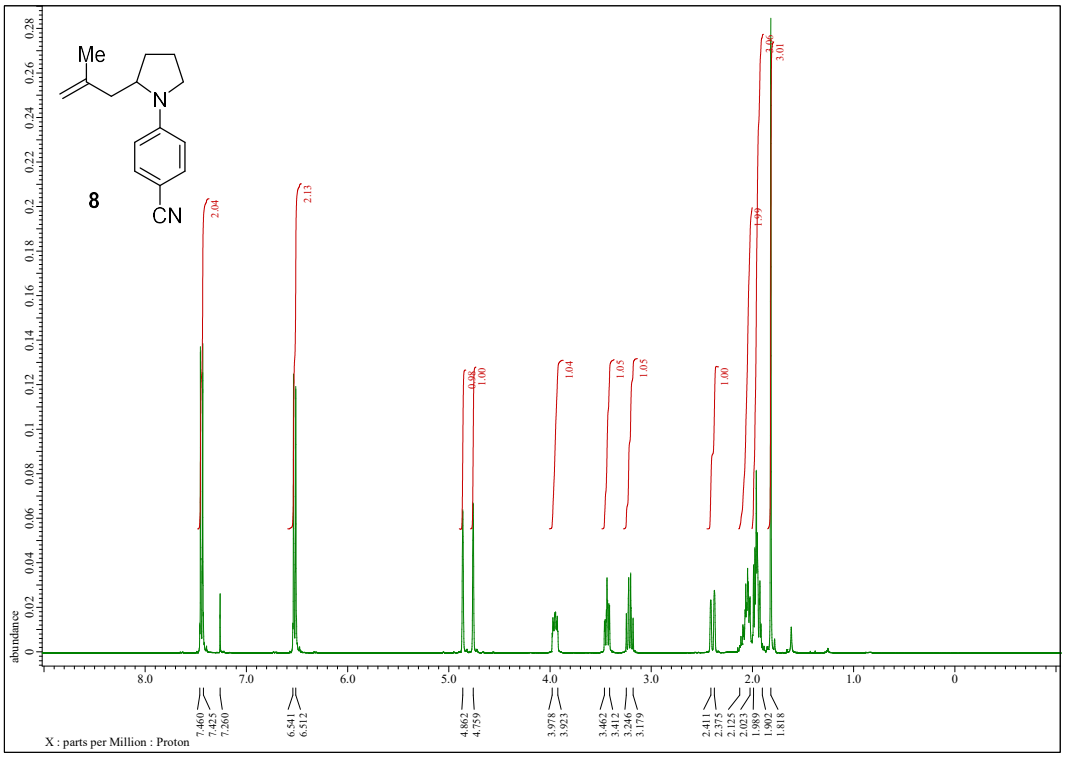
^{1}H NMR of **7** (400 MHz, $CDCl_3$)



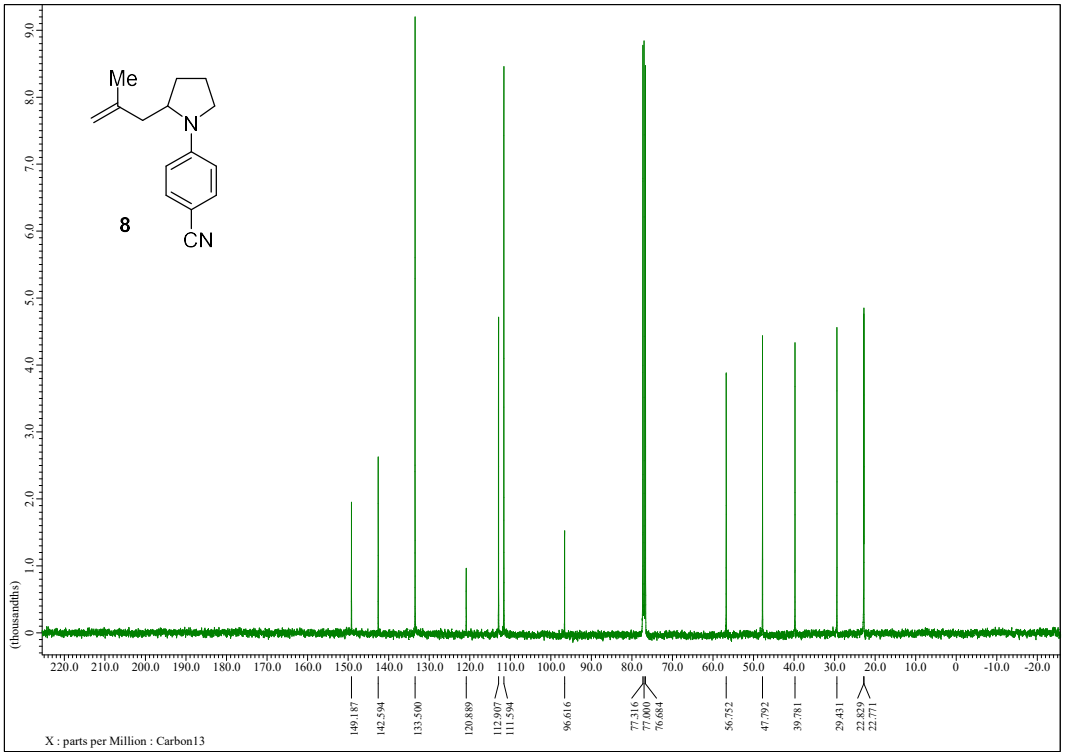
^{13}C NMR of **7** (101 MHz, $CDCl_3$)



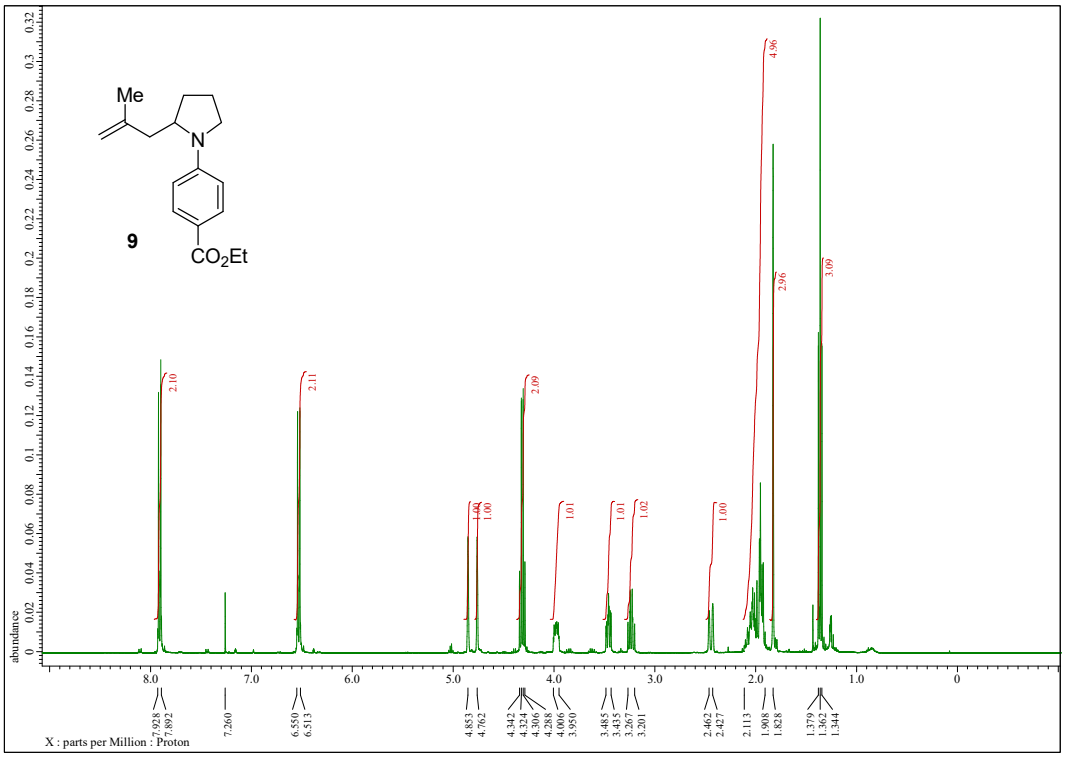
^{1}H NMR of **8** (400 MHz, $CDCl_3$)



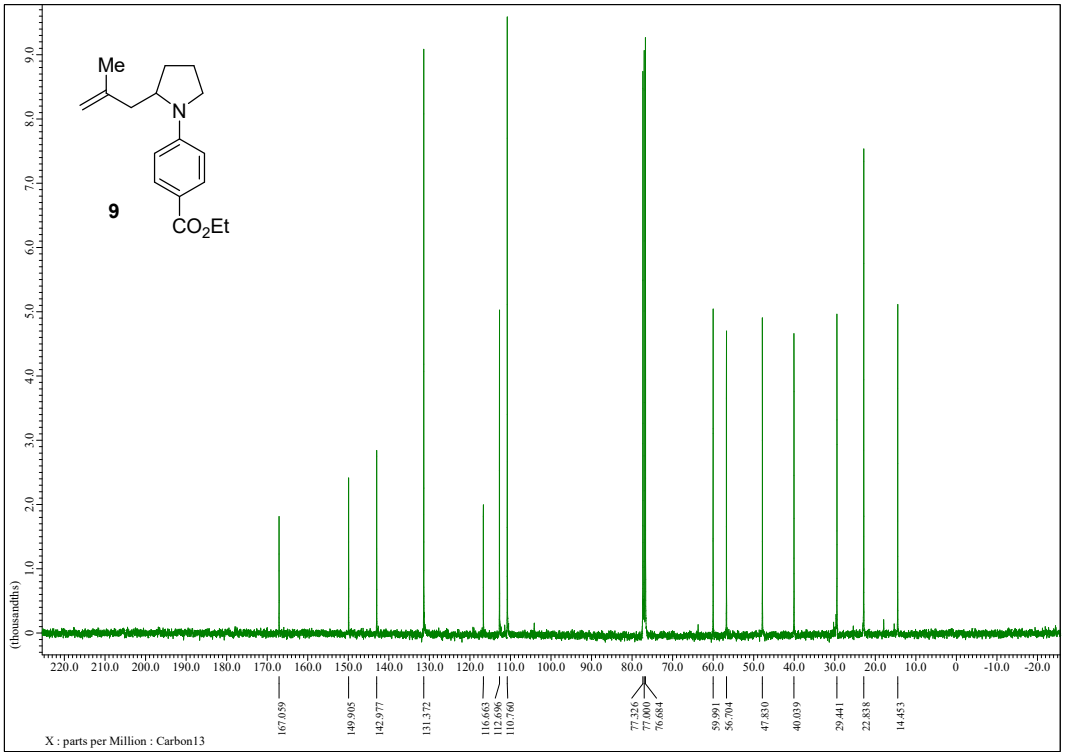
^{13}C NMR of **8** (101 MHz, $CDCl_3$)



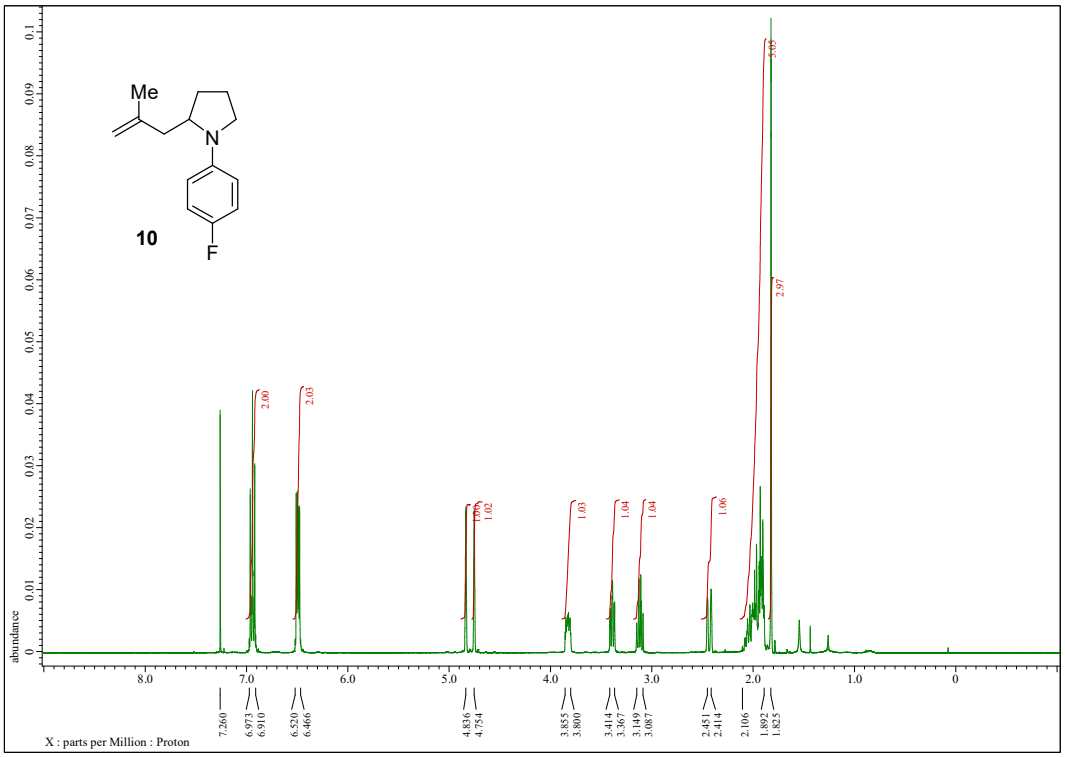
^{1}H NMR of **9** (400 MHz, $CDCl_3$)



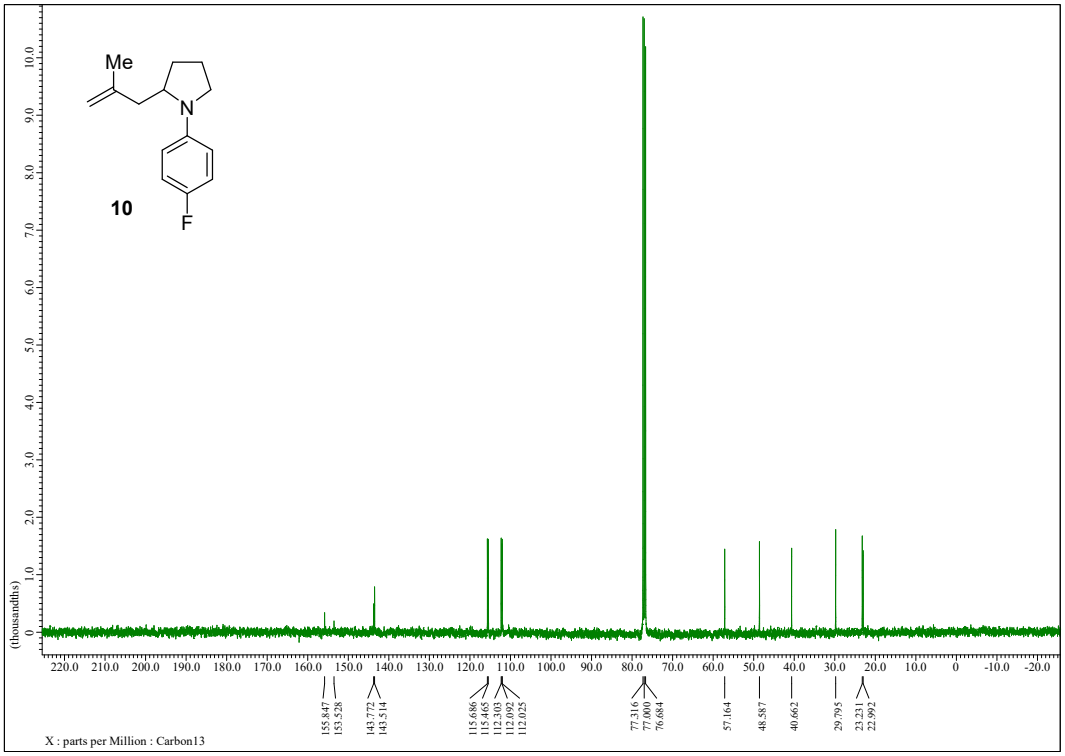
^{13}C NMR of **9** (101 MHz, $CDCl_3$)



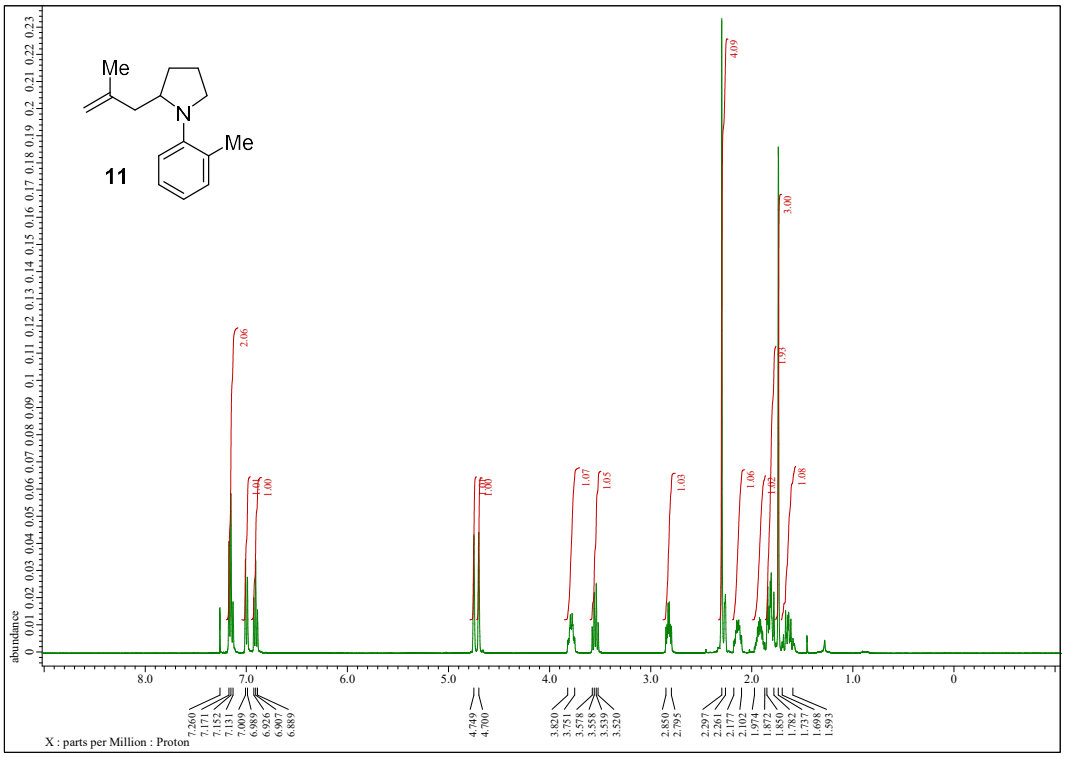
^{1}H NMR of **10** (400 MHz, $CDCl_3$)



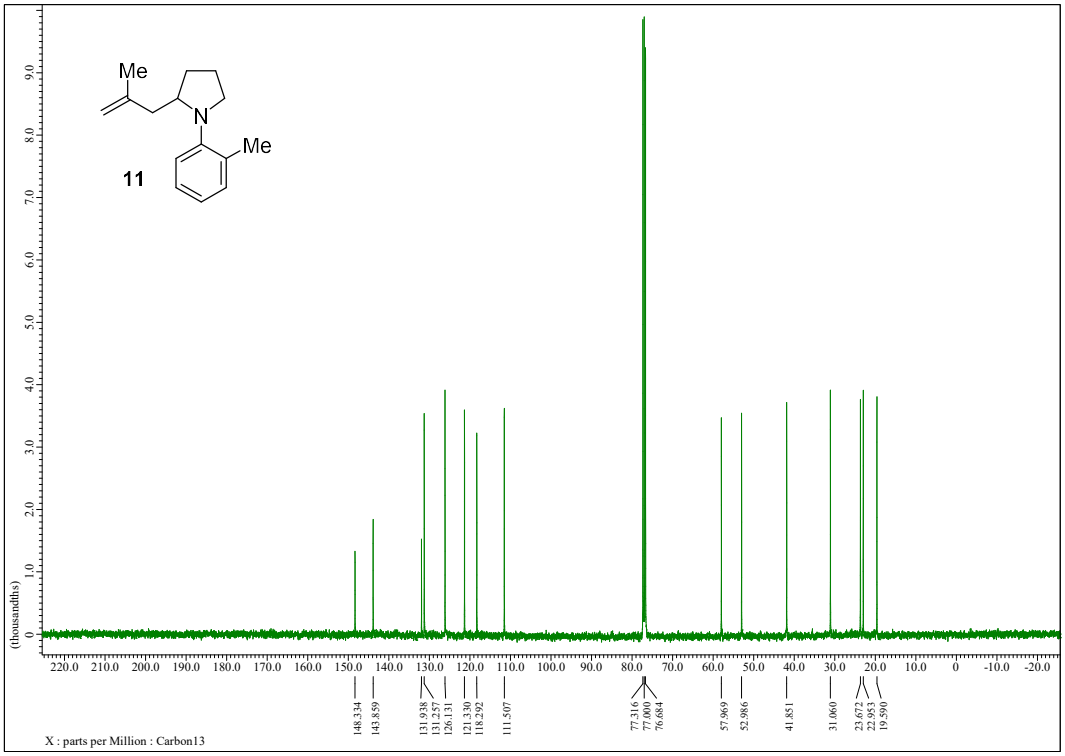
^{13}C NMR of **10** (101 MHz, $CDCl_3$)



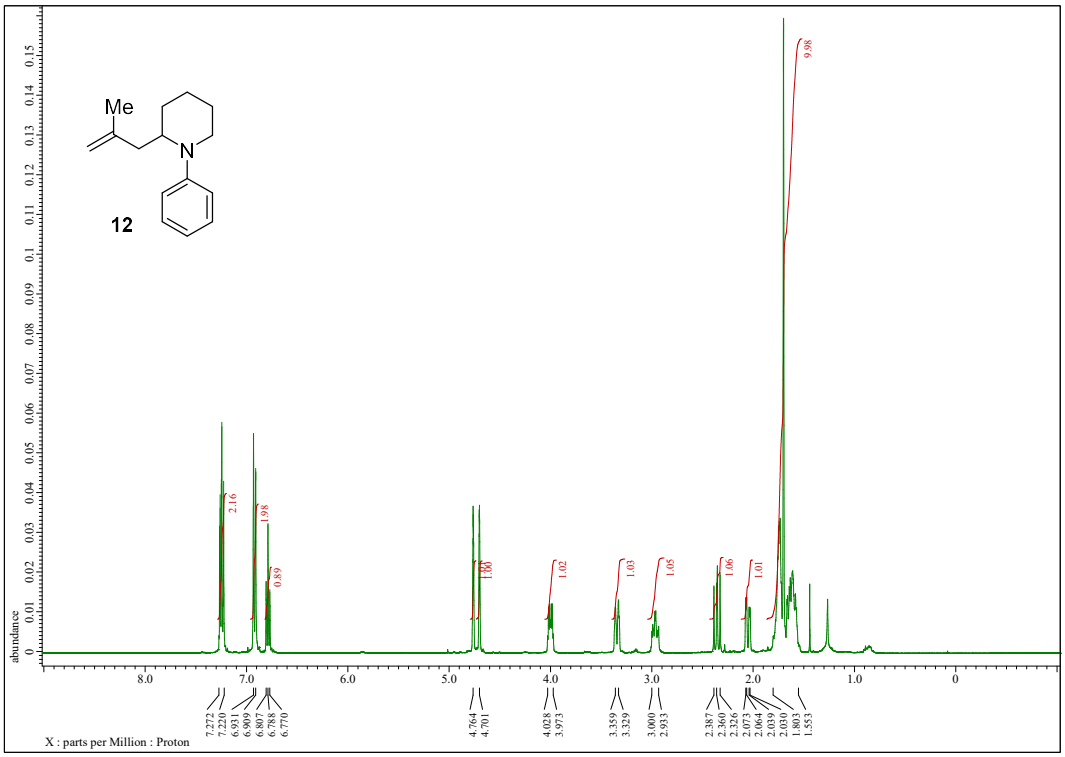
^{1}H NMR of **11** (400 MHz, $CDCl_3$)



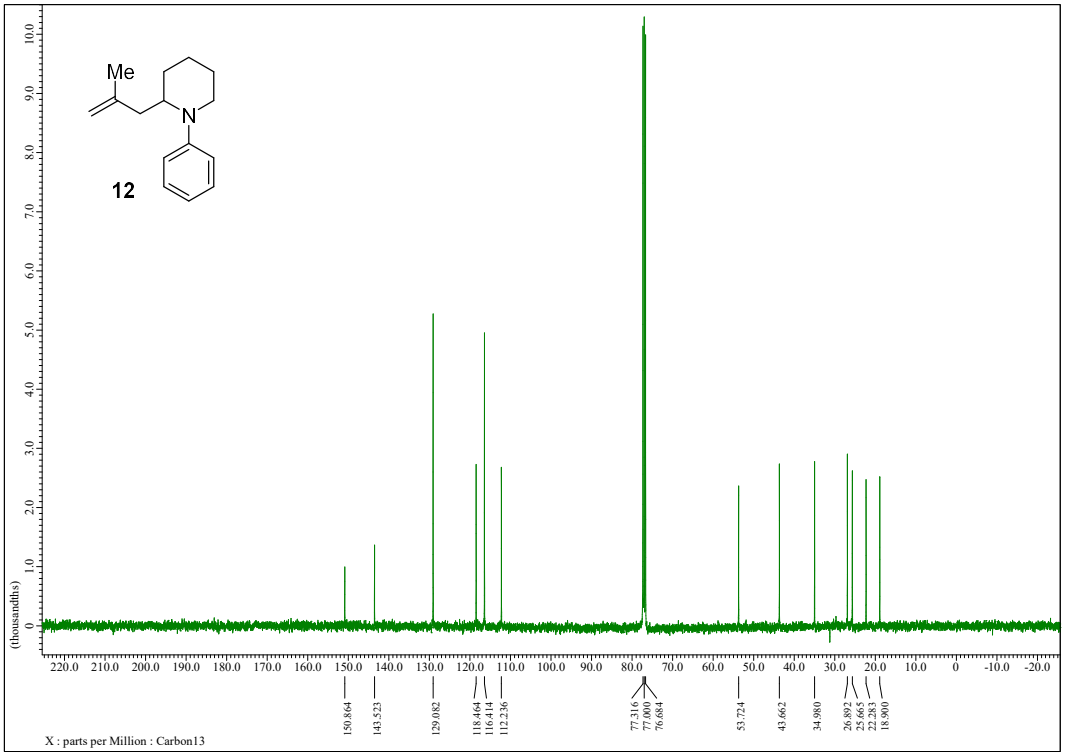
^{13}C NMR of **11** (101 MHz, $CDCl_3$)



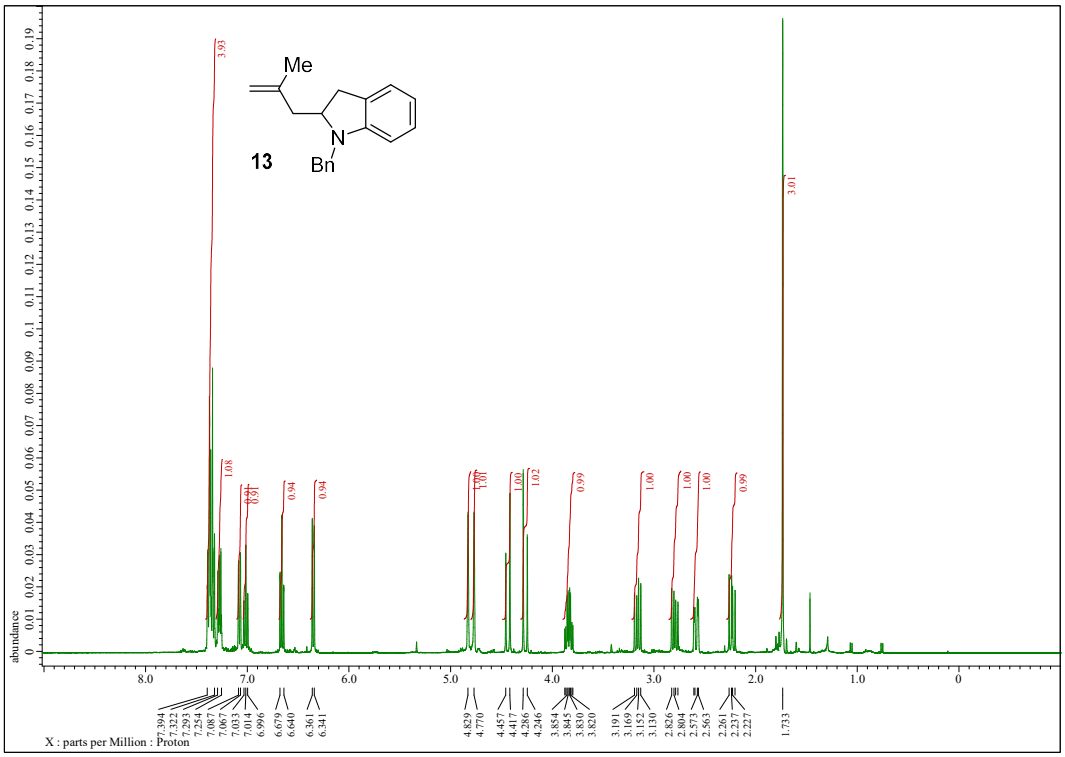
^{1}H NMR of **12** (400 MHz, $CDCl_3$)



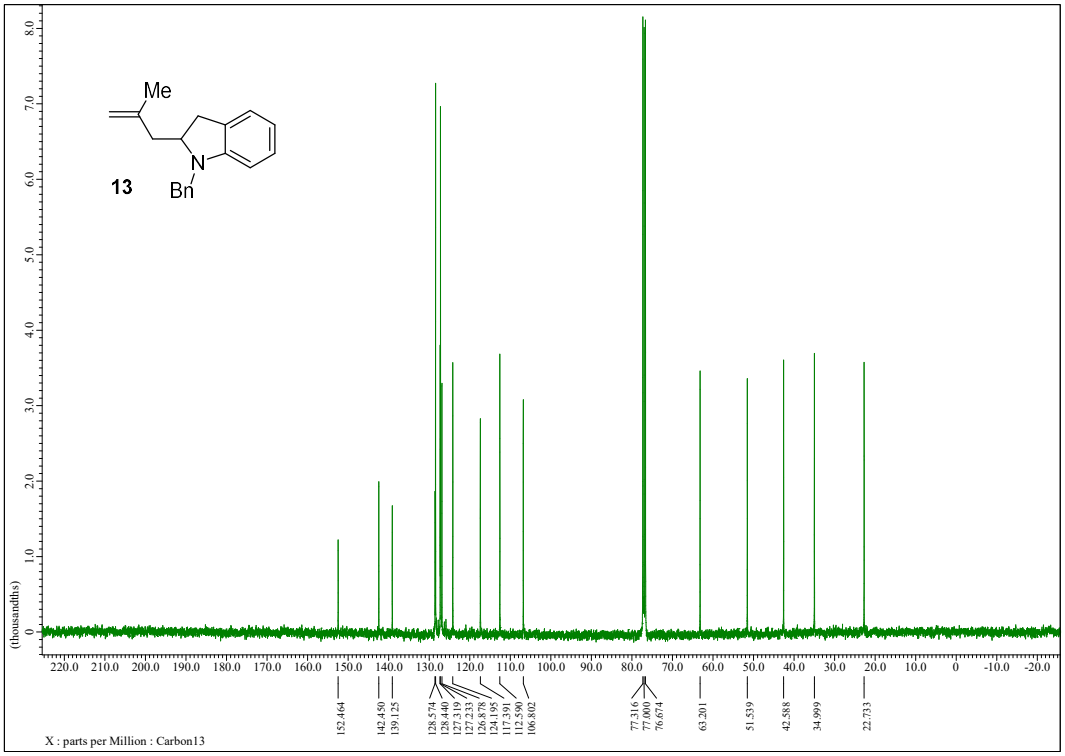
^{13}C NMR of **12** (101 MHz, $CDCl_3$)



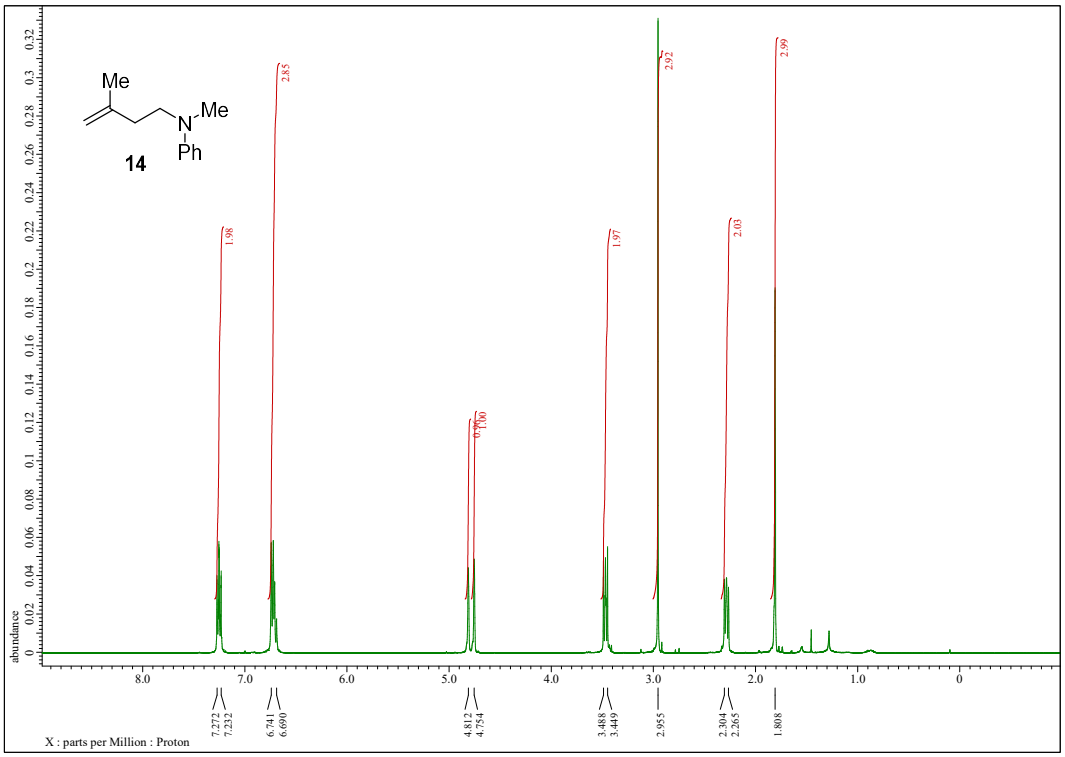
^{1}H NMR of **13** (400 MHz, $CDCl_3$)



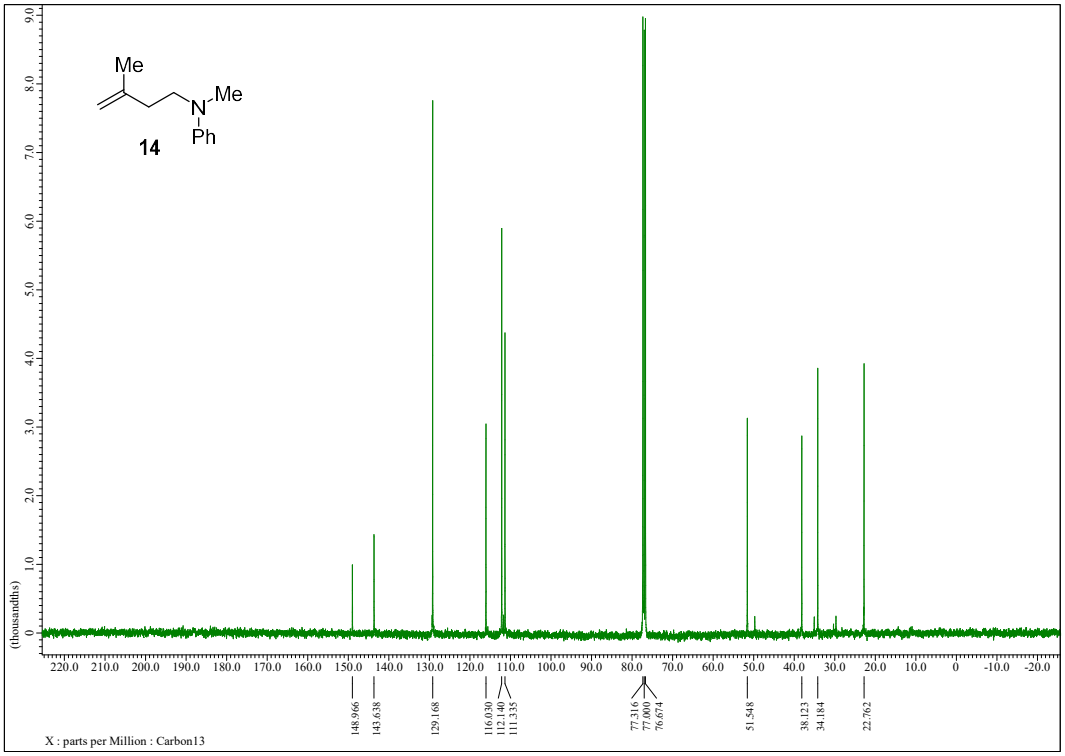
^{13}C NMR of **13** (101 MHz, $CDCl_3$)



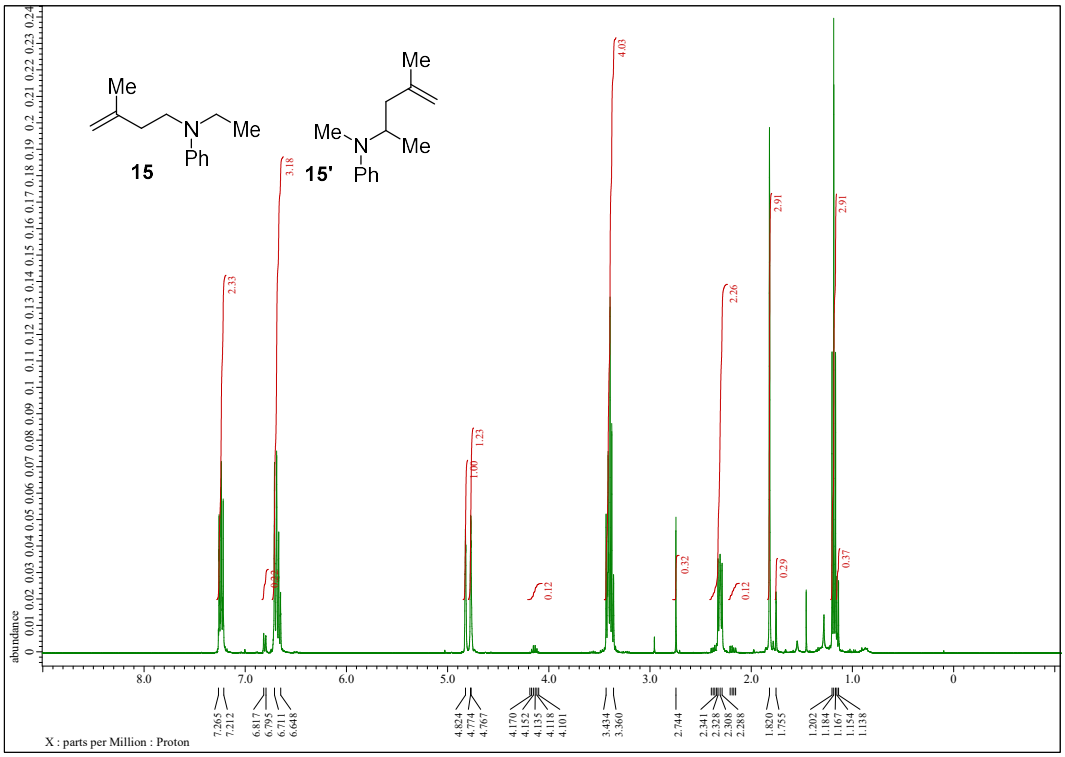
^{1}H NMR of **14** (400 MHz, $CDCl_3$)



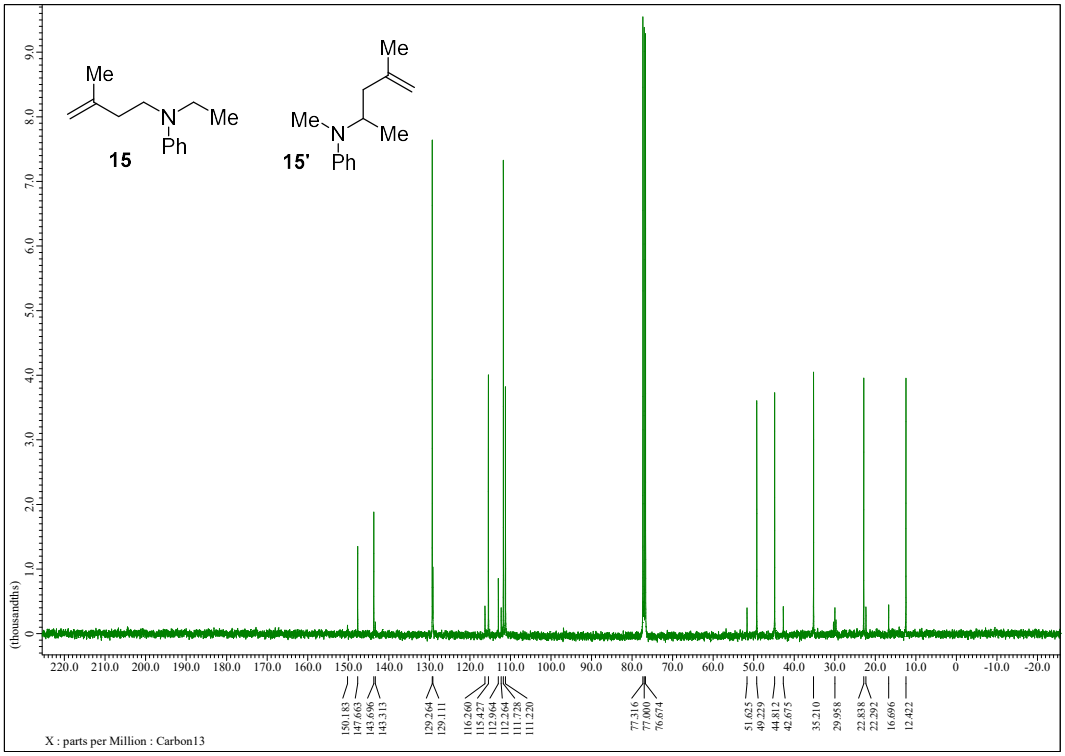
^{13}C NMR of **14** (101 MHz, $CDCl_3$)



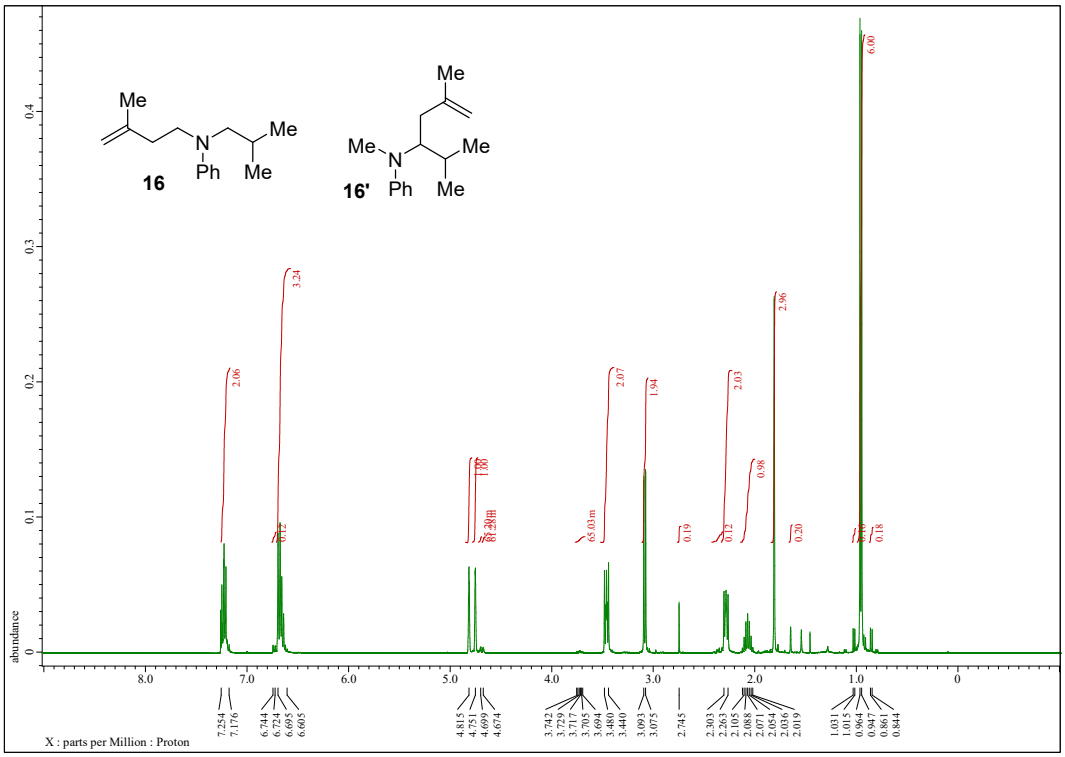
^{1}H NMR of **15** and **15'** (91:9) (400 MHz, $CDCl_3$)



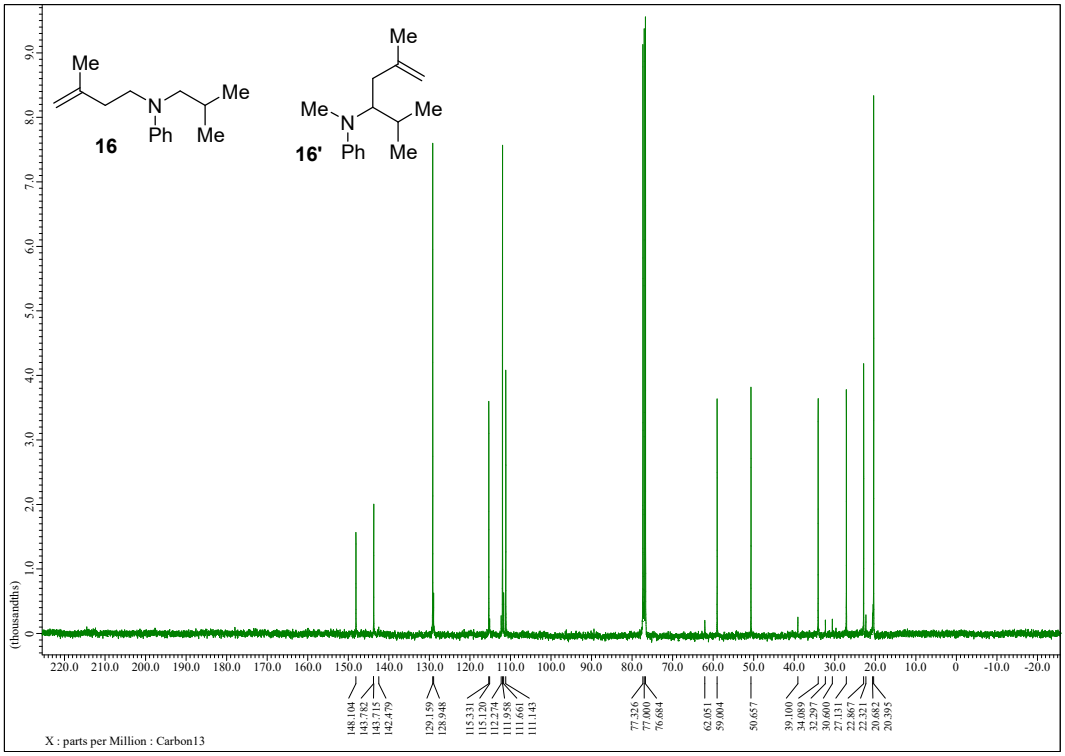
^{13}C NMR of **15** and **15'** (91:9) (101 MHz, $CDCl_3$)



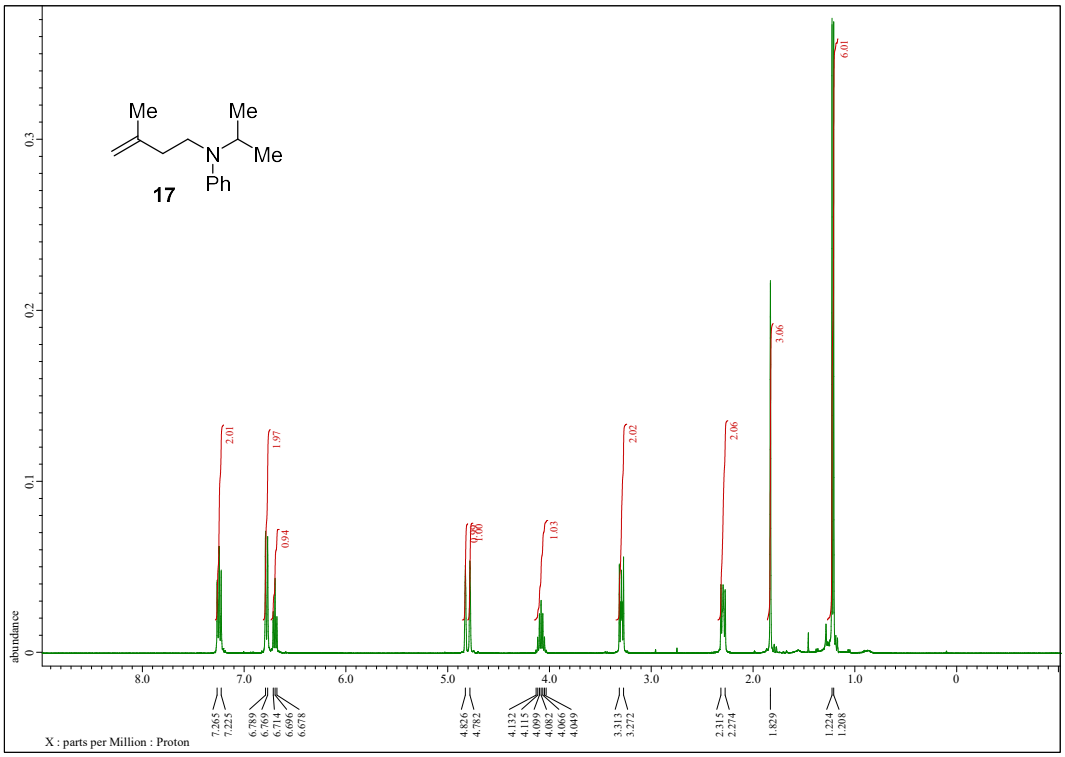
^{1}H NMR of **16** and **16'** (94:6) (400 MHz, $CDCl_3$)



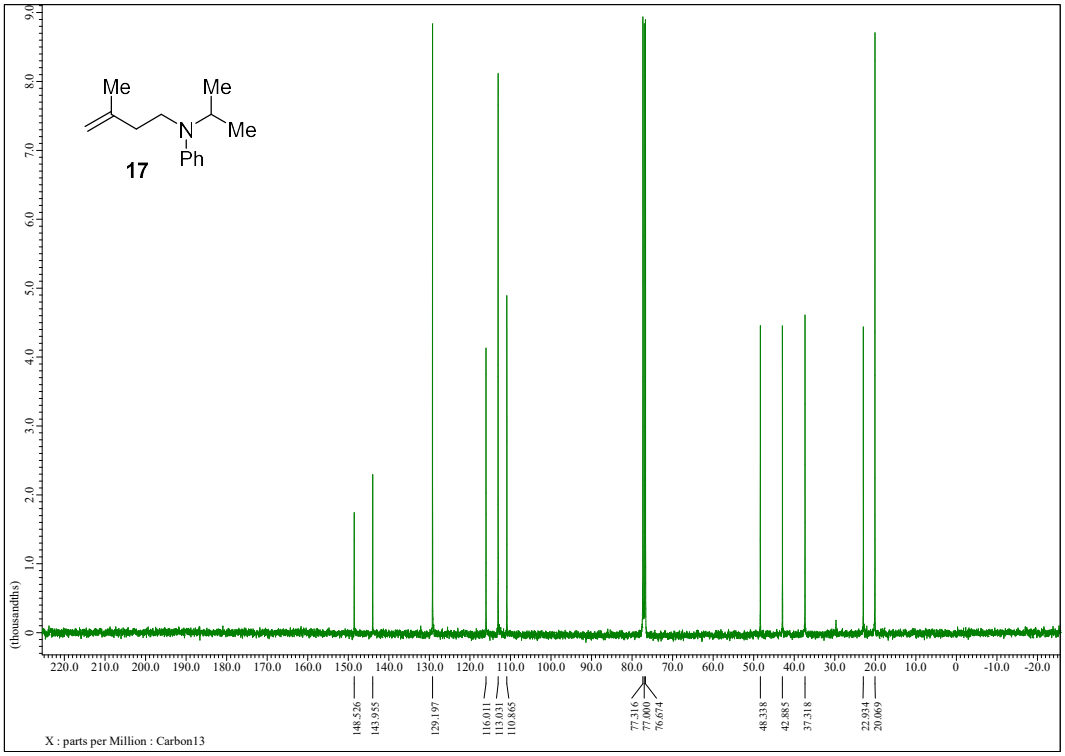
^{13}C NMR of **16** and **16'** (94:6) (101 MHz, $CDCl_3$)



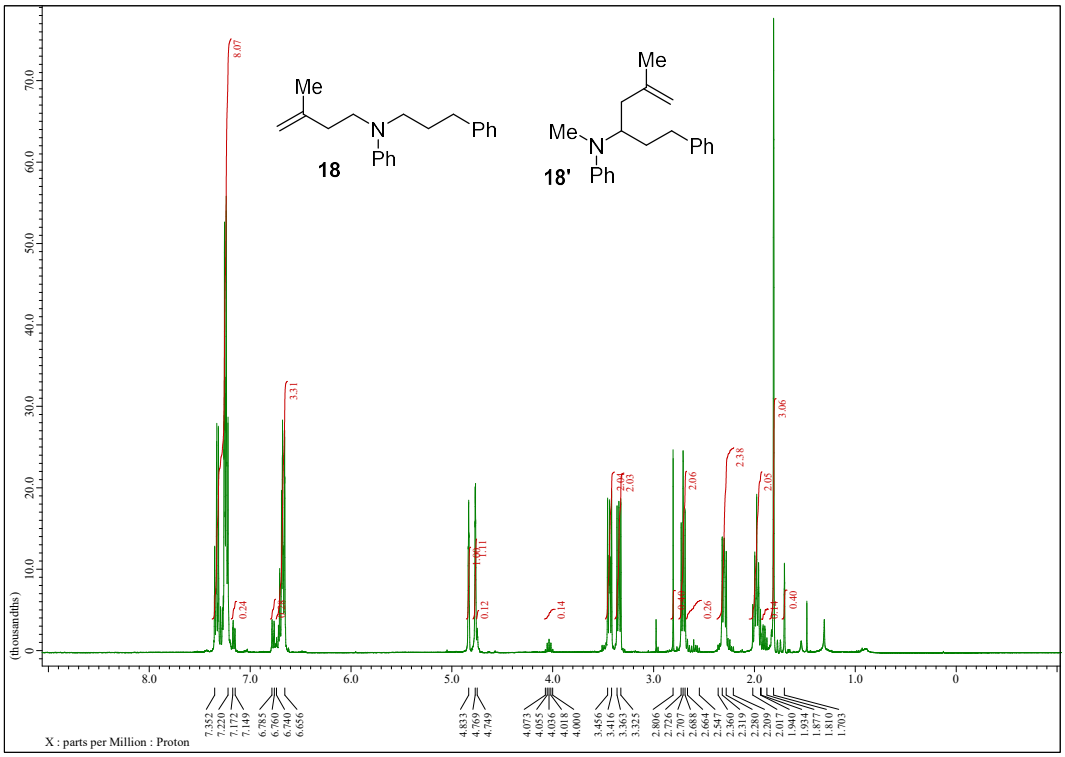
^{1}H NMR of **17** (400 MHz, $CDCl_3$)



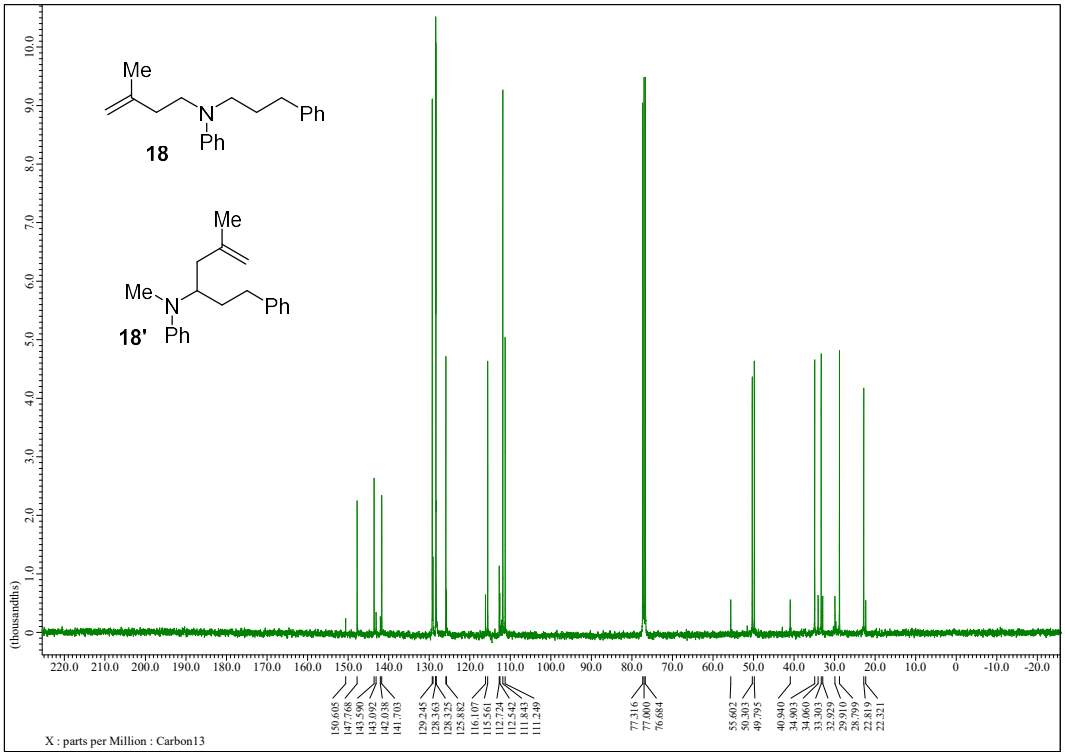
^{13}C NMR of **17** (101 MHz, $CDCl_3$)



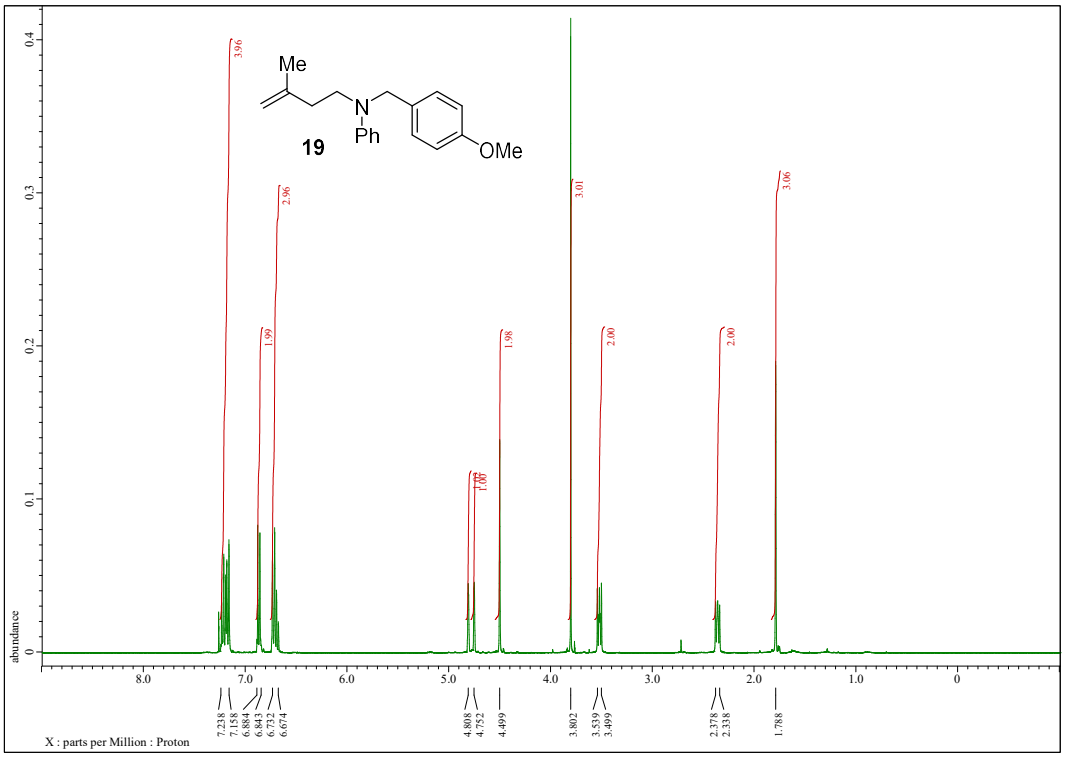
^{1}H NMR of **18** and **18'** (89:11) (400 MHz, $CDCl_3$)



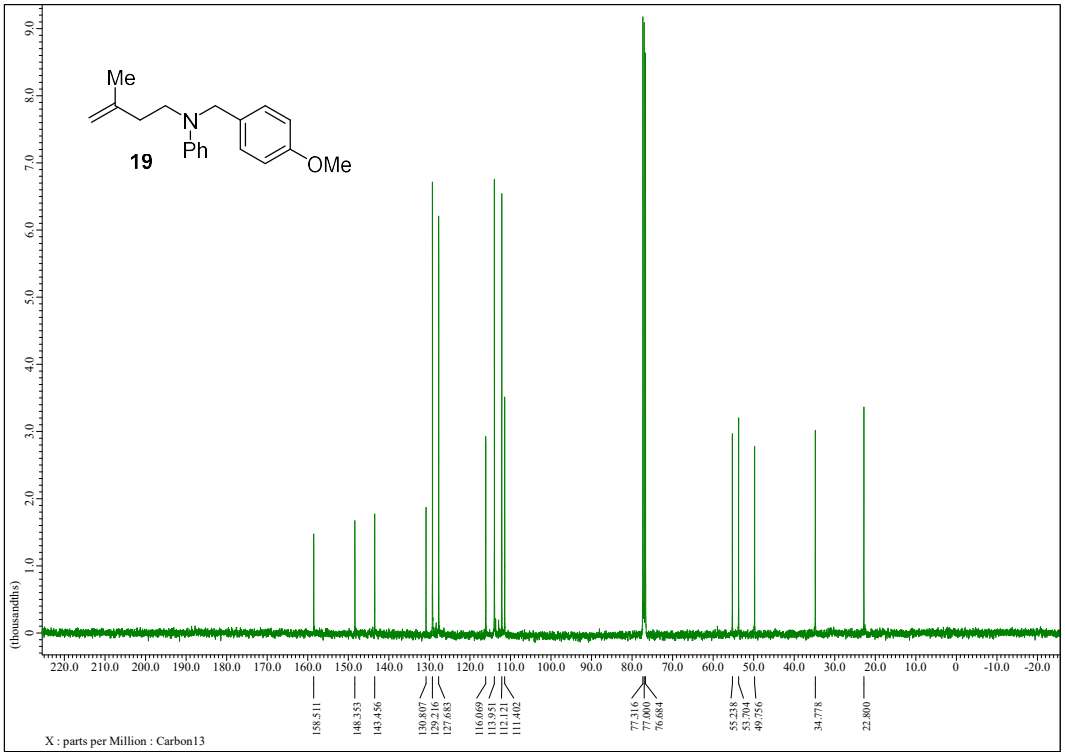
^{13}C NMR of **18** and **18'** (89:11) (101 MHz, $CDCl_3$)



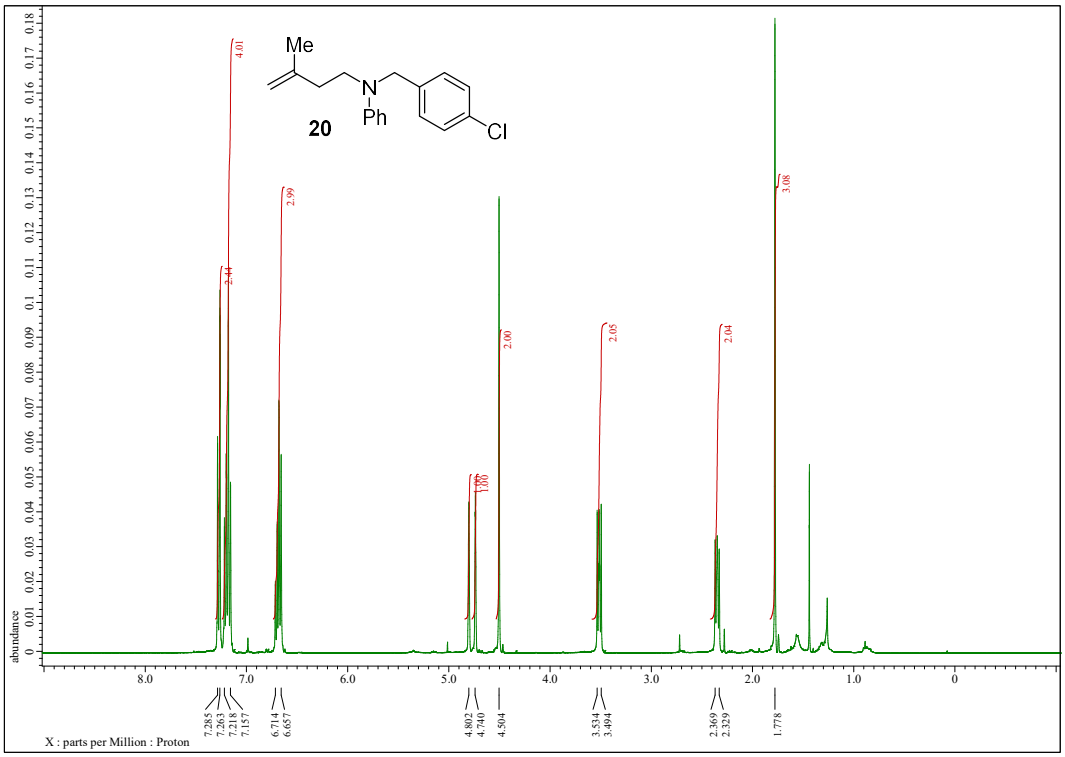
^{1}H NMR of **19** (400 MHz, $CDCl_3$)



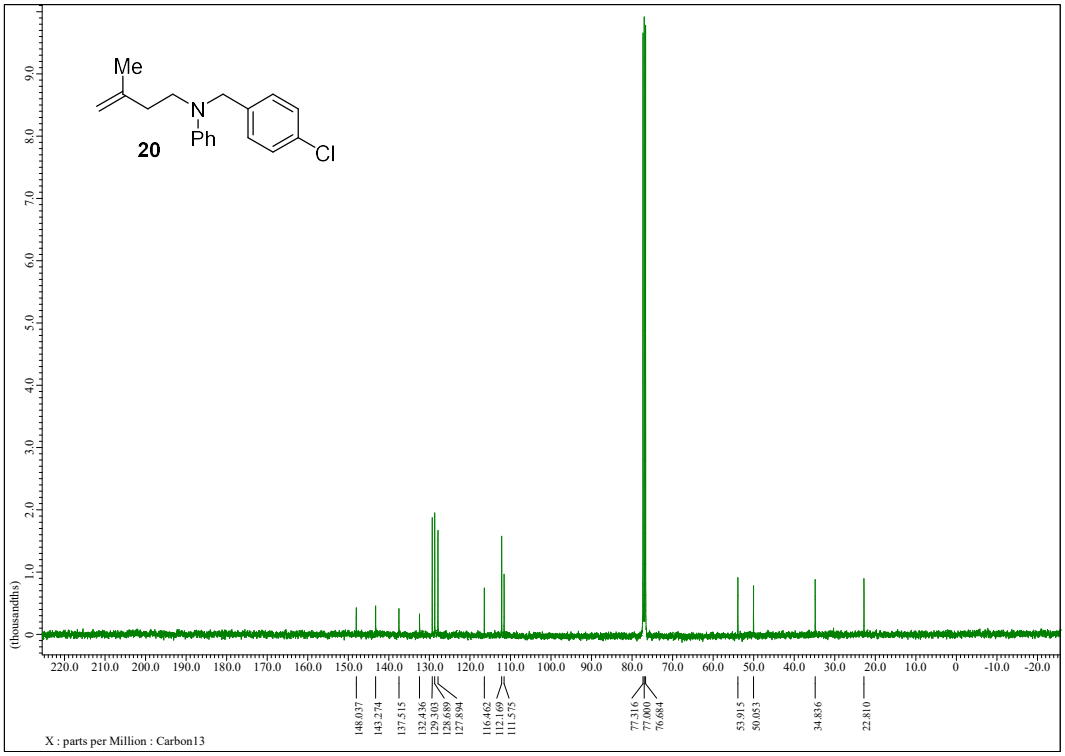
^{13}C NMR of **19** (101 MHz, $CDCl_3$)



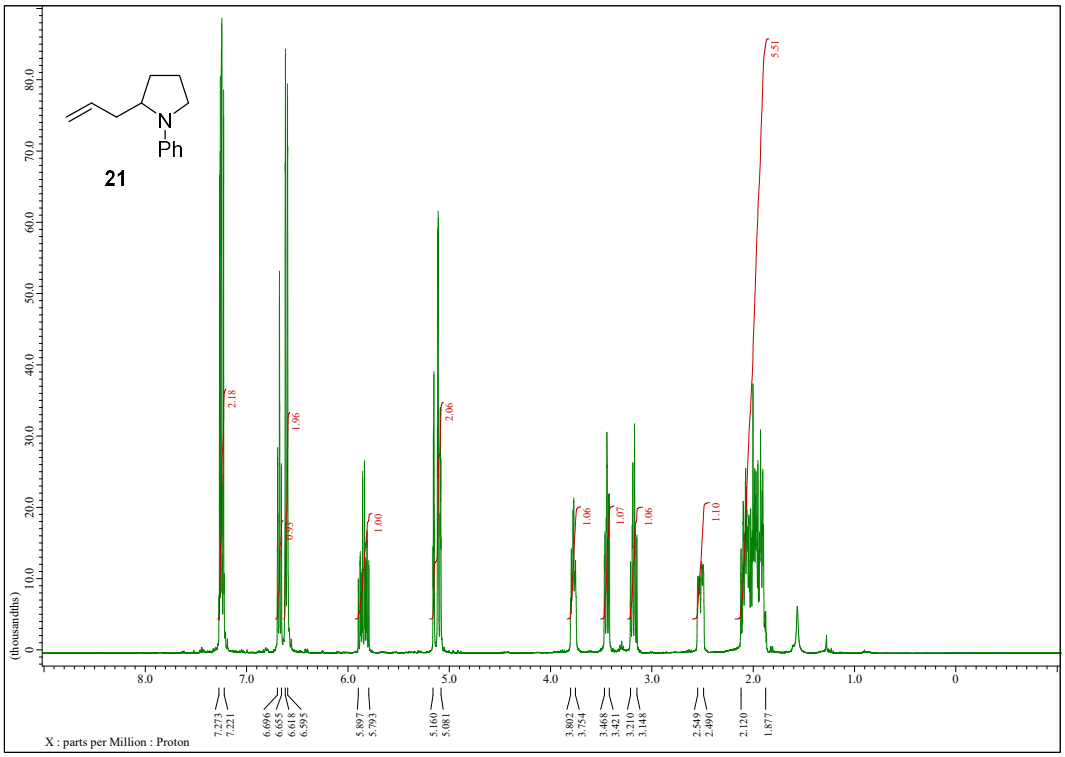
^{1}H NMR of **20** (400 MHz, $CDCl_3$)



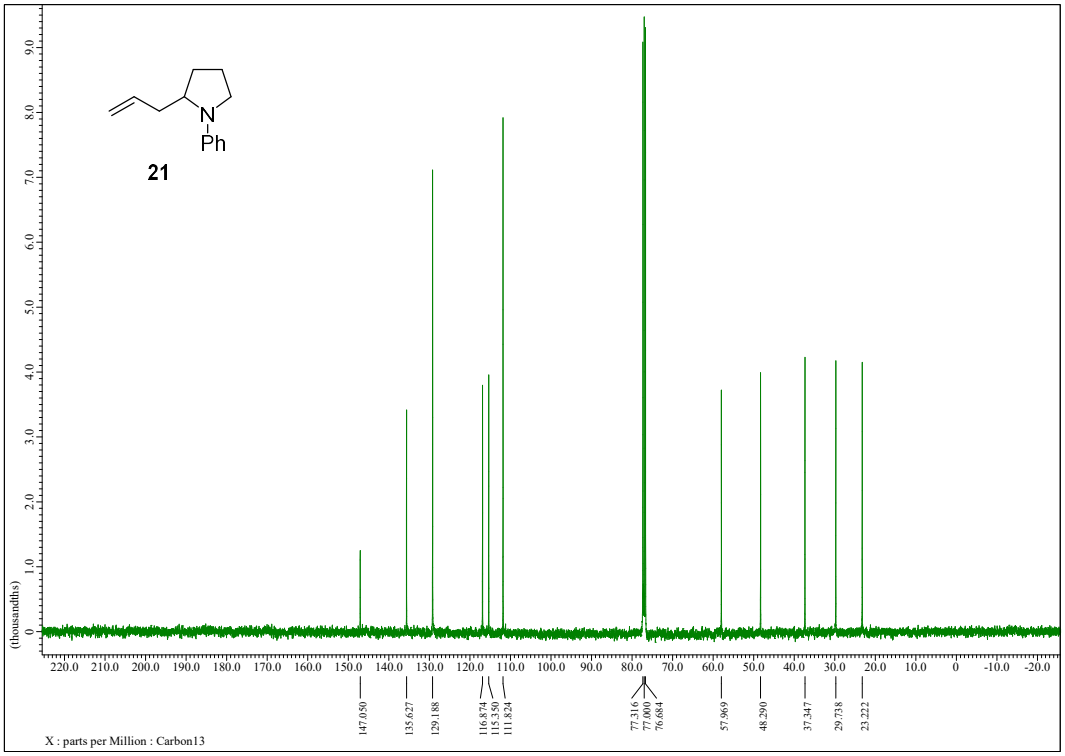
^{13}C NMR of **20** (101 MHz, $CDCl_3$)



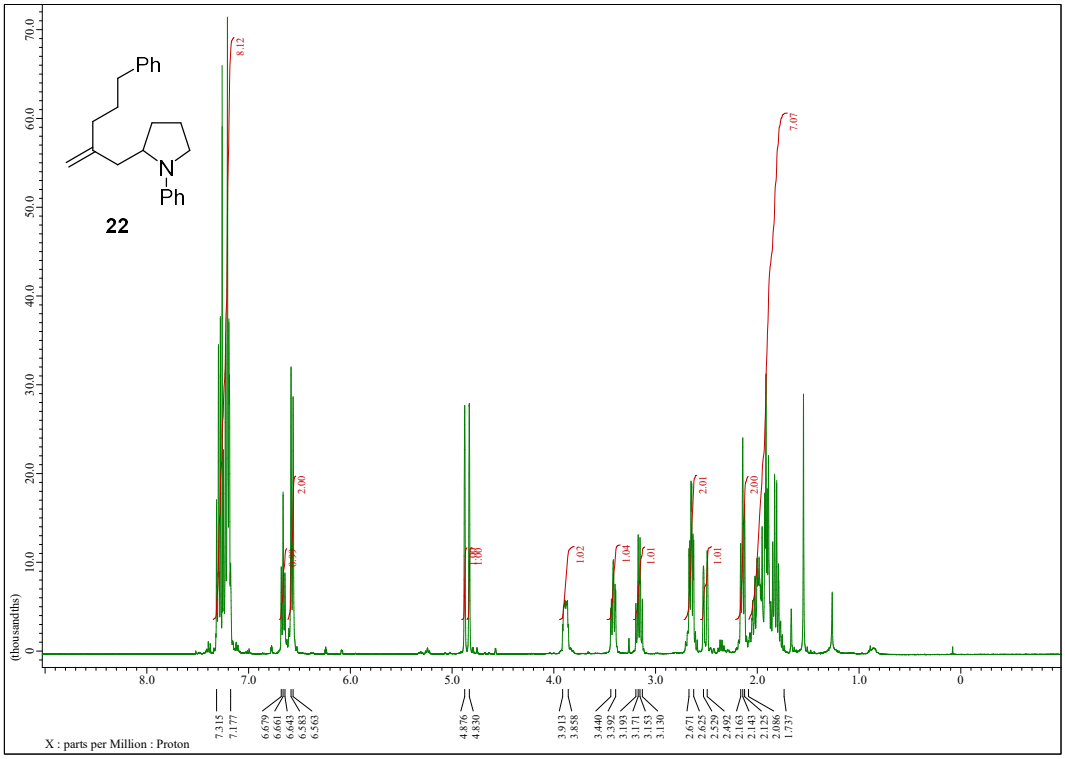
^{1}H NMR of **21** (400 MHz, $CDCl_3$)



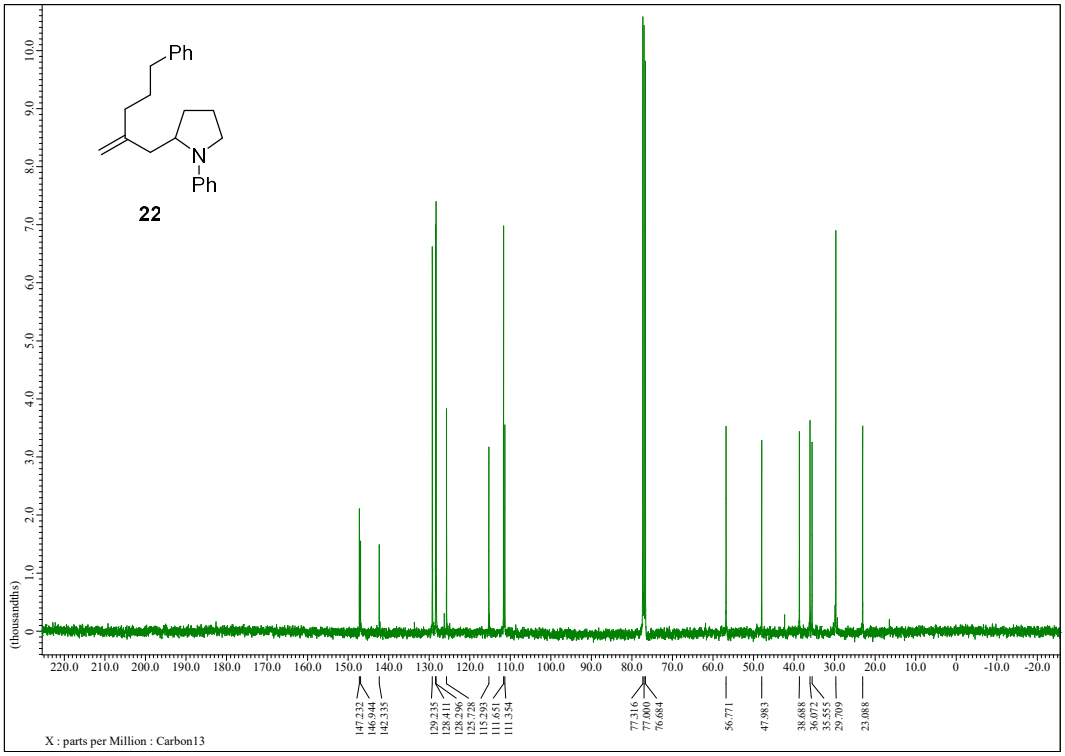
^{13}C NMR of **21** (101 MHz, $CDCl_3$)



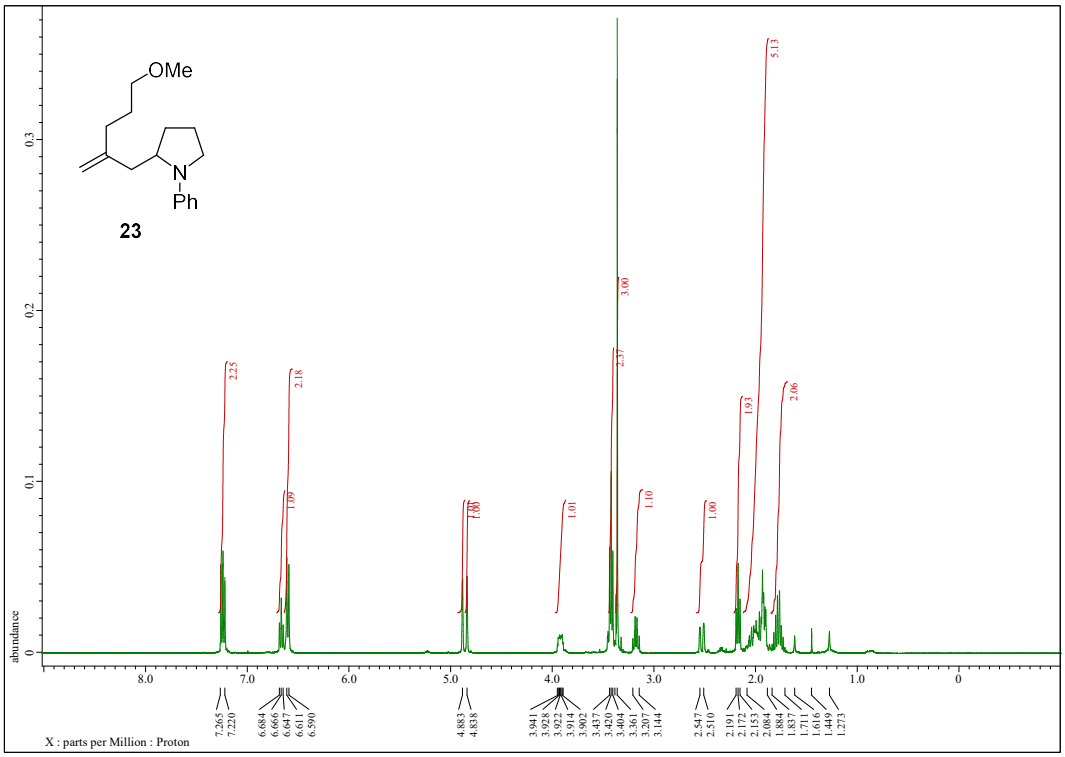
^{1}H NMR of **22** (400 MHz, $CDCl_3$)



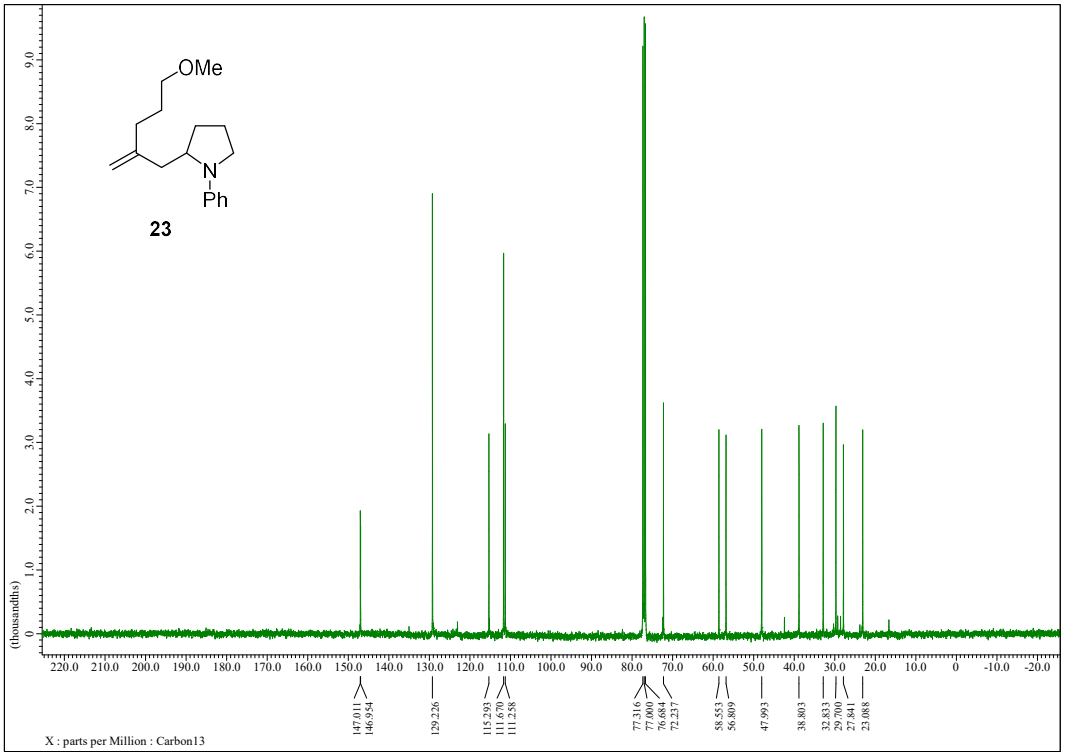
^{13}C NMR of **22** (101 MHz, $CDCl_3$)



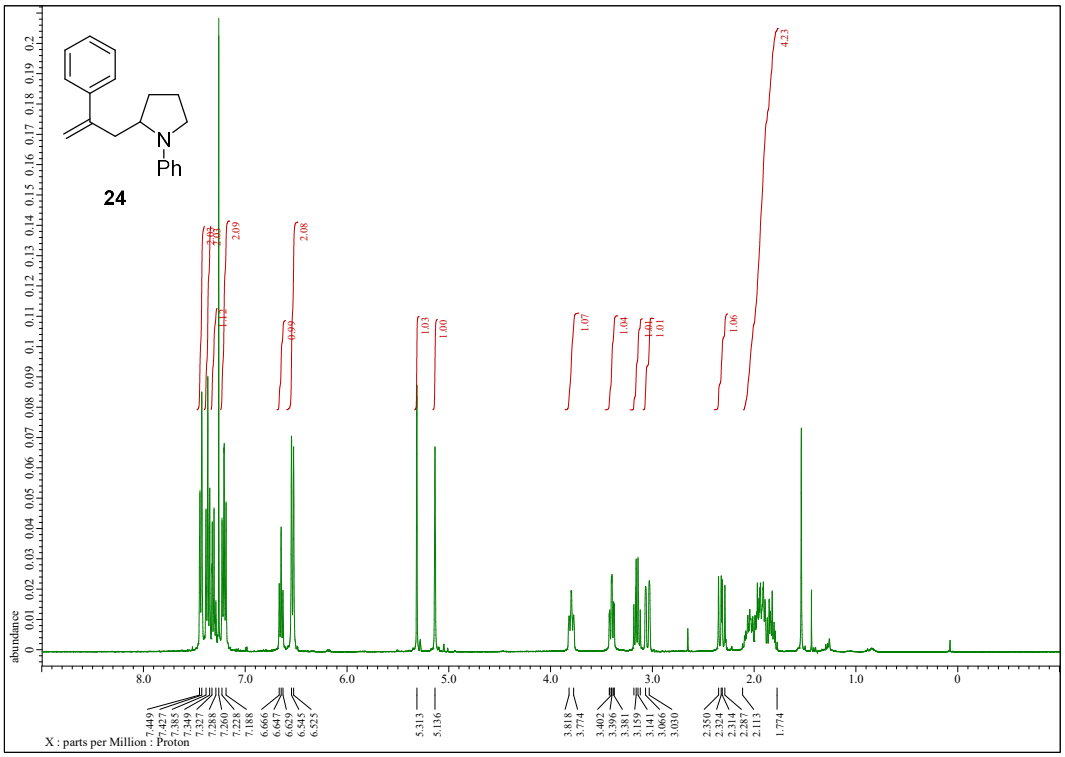
^{1}H NMR of **23** (400 MHz, $CDCl_3$)



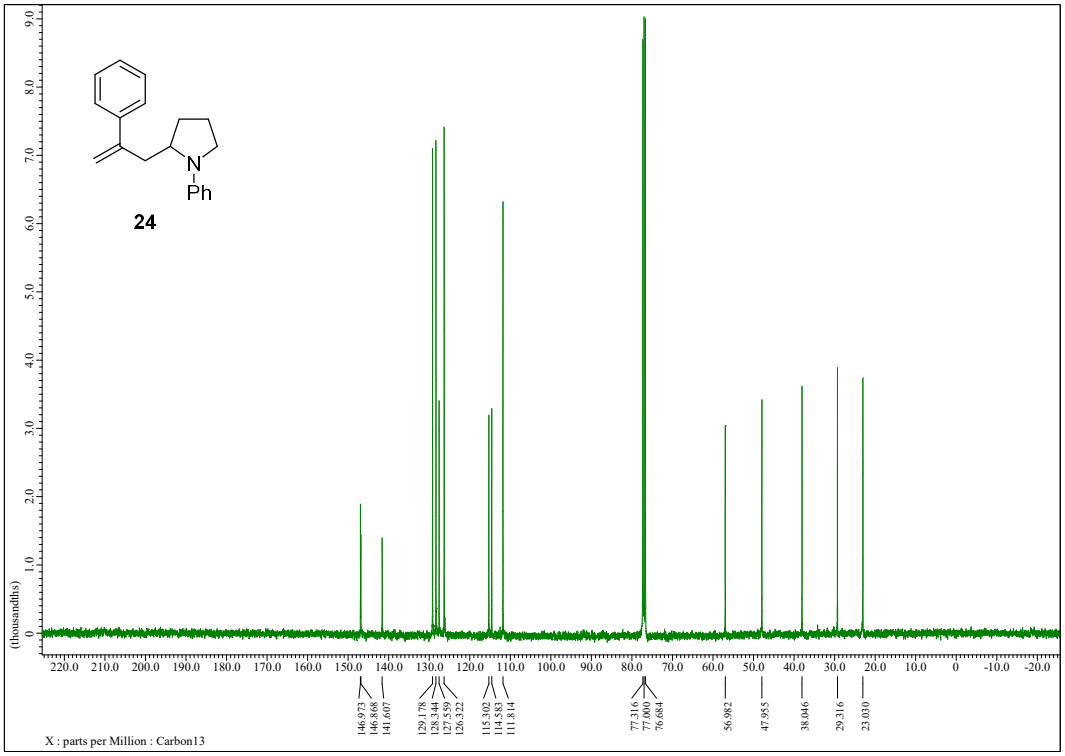
^{13}C NMR of **23** (101 MHz, $CDCl_3$)



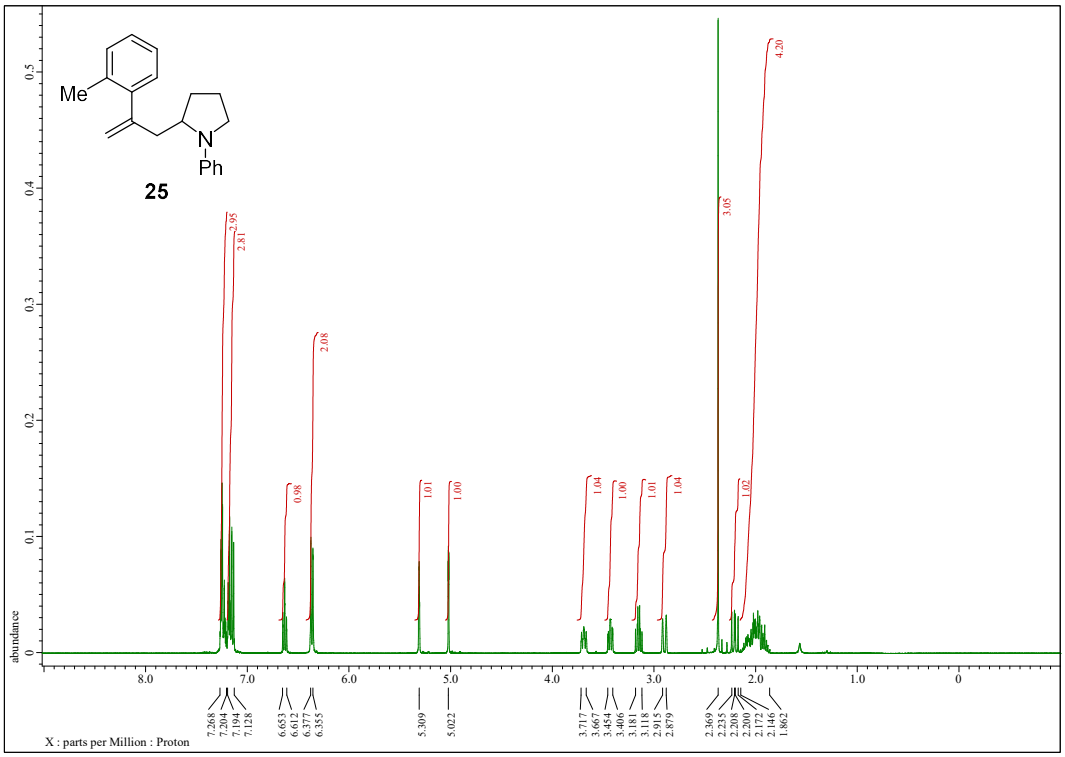
^{1}H NMR of **24** (400 MHz, $CDCl_3$)



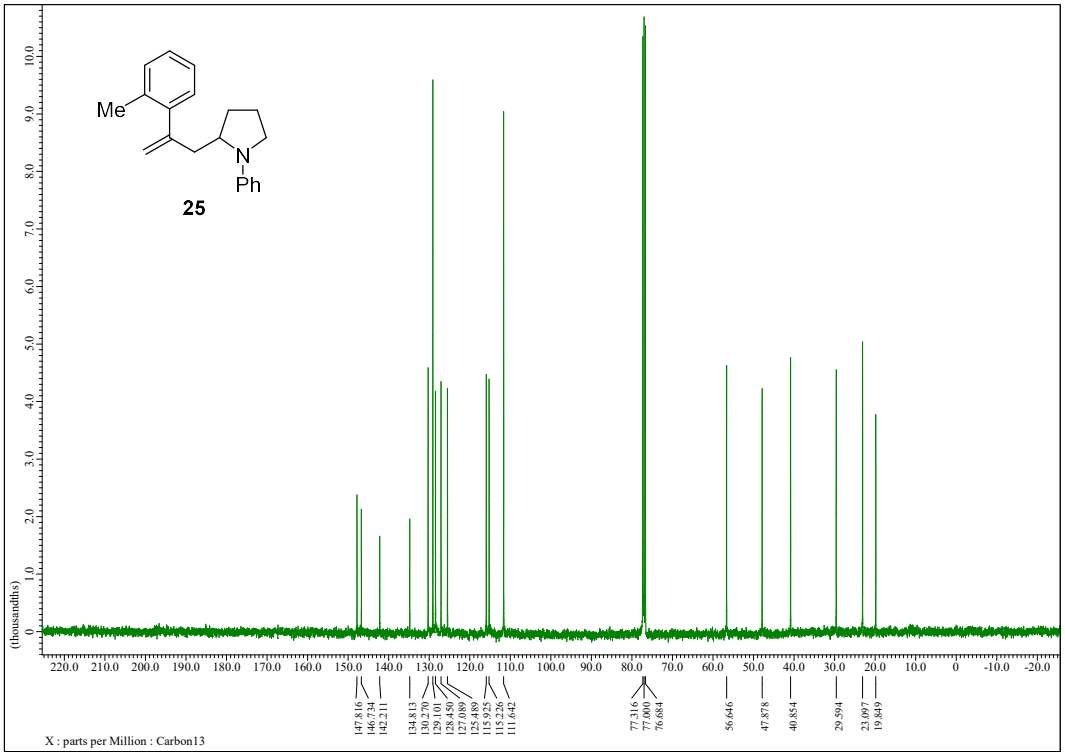
^{13}C NMR of **24** (101 MHz, $CDCl_3$)



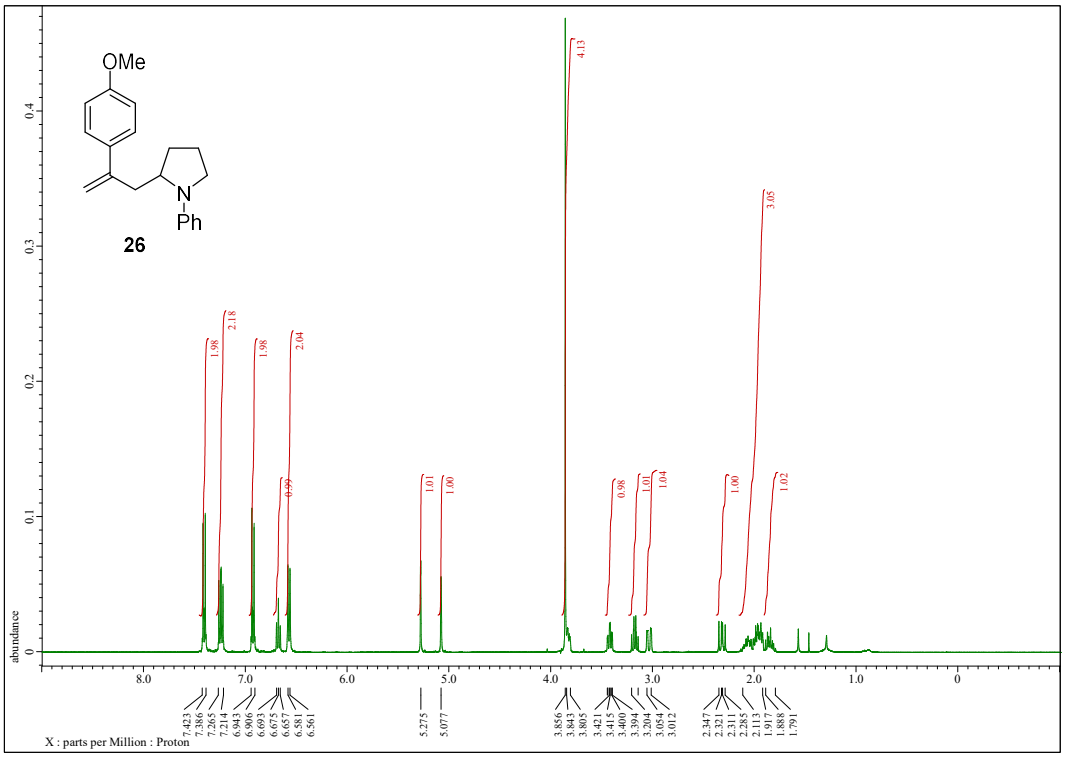
^{1}H NMR of **25** (400 MHz, $CDCl_3$)



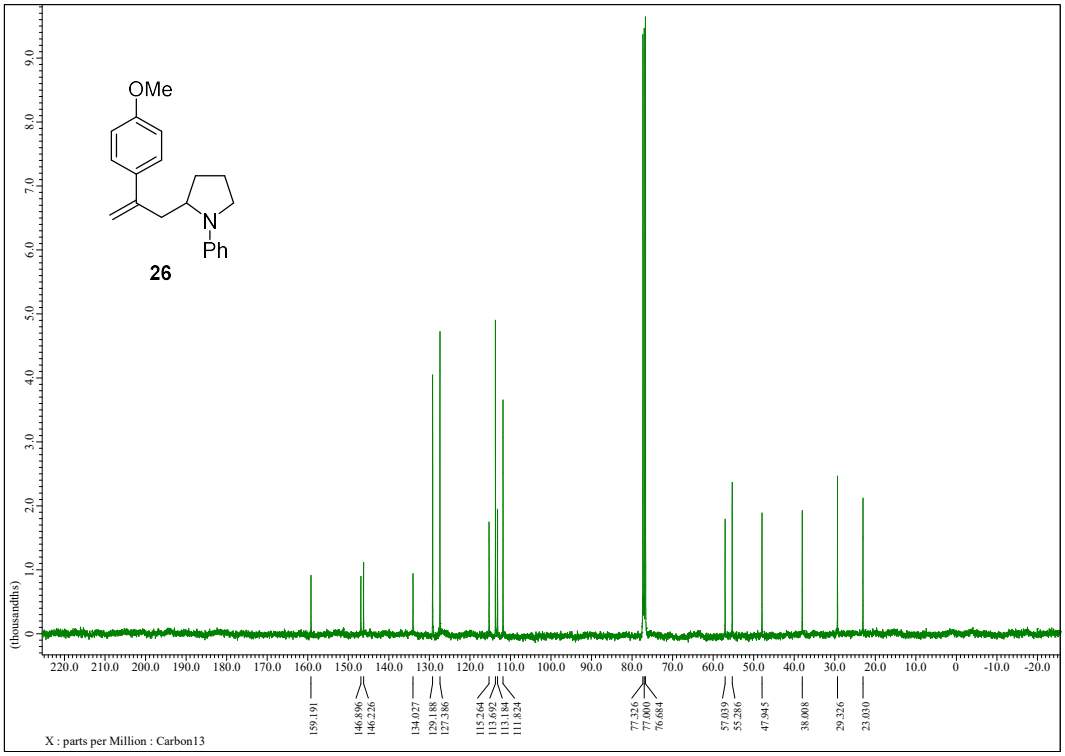
^{13}C NMR of **25** (101 MHz, $CDCl_3$)



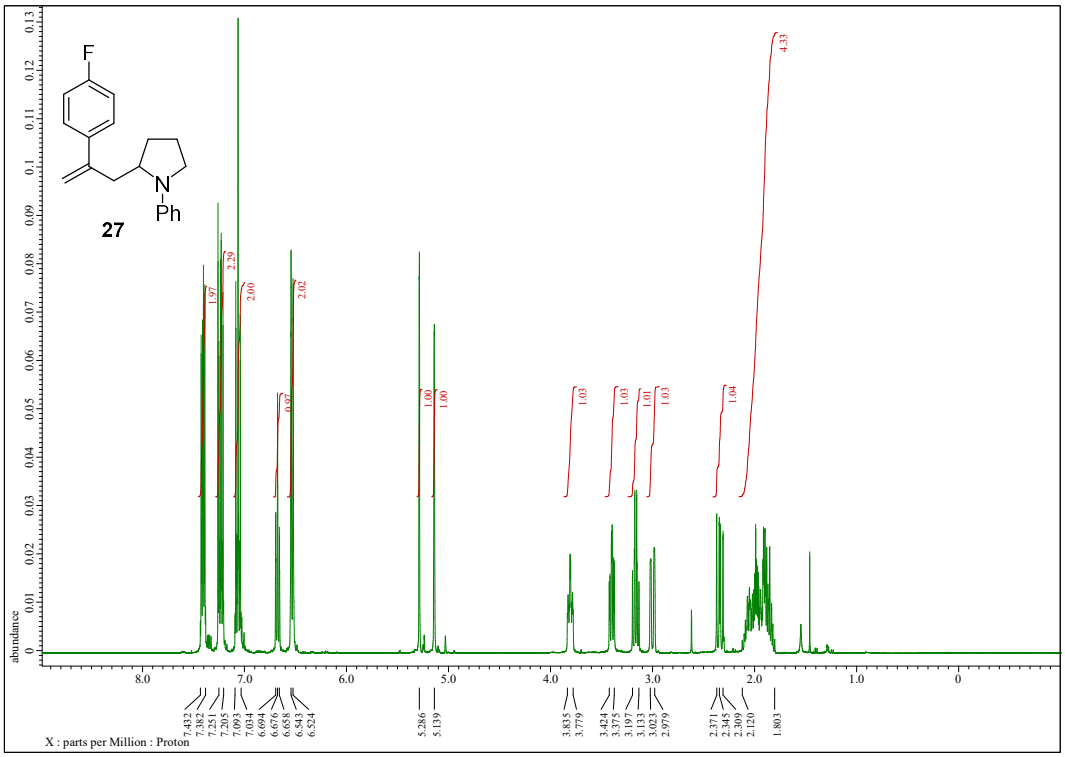
^{1}H NMR of **26** (400 MHz, $CDCl_3$)



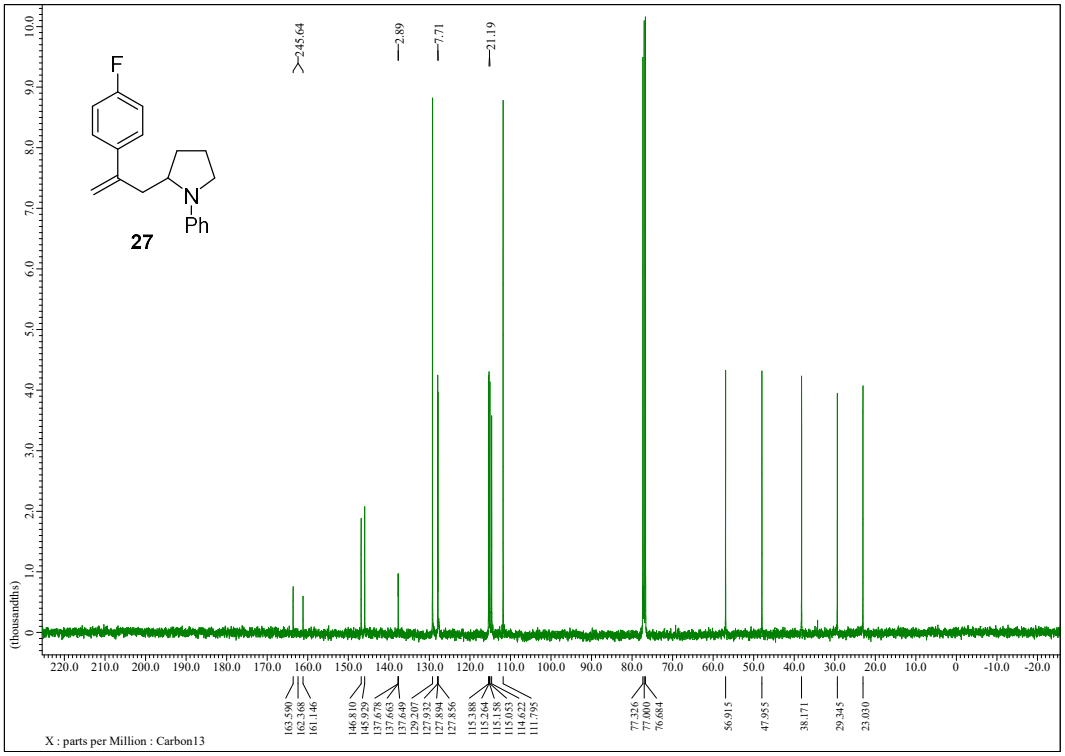
^{13}C NMR of **26** (101 MHz, $CDCl_3$)



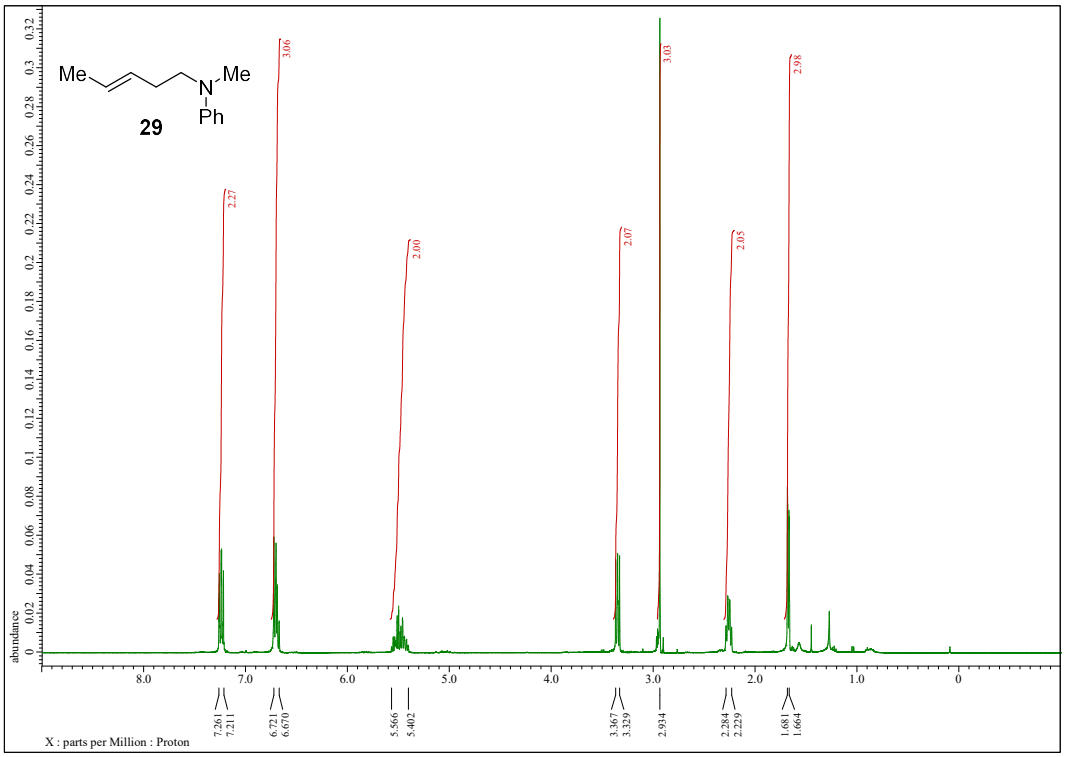
^{1}H NMR of **27** (400 MHz, $CDCl_3$)



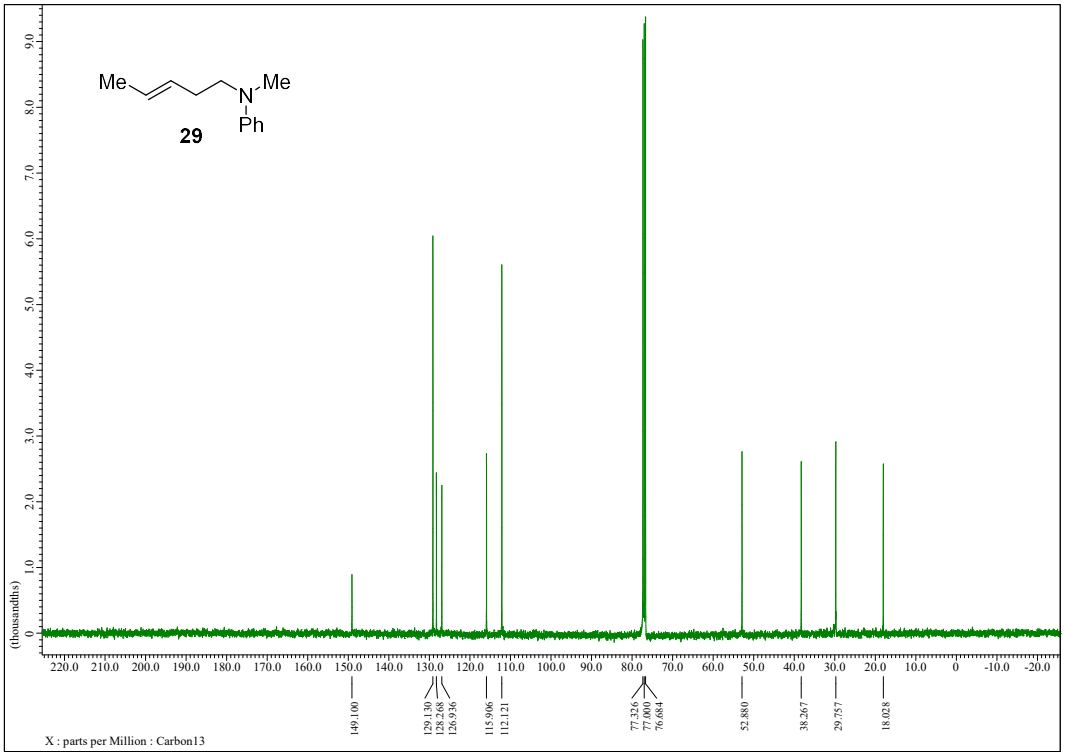
^{13}C NMR of **27** (101 MHz, $CDCl_3$)



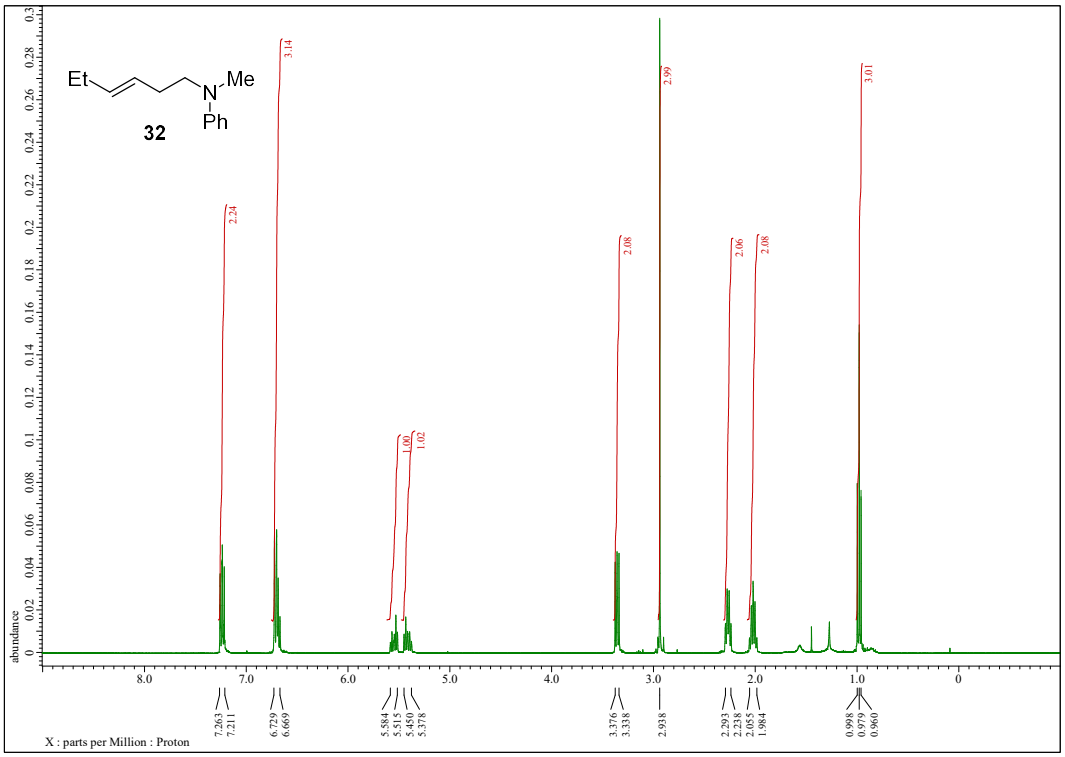
^{1}H NMR of **29** (400 MHz, $CDCl_3$)



^{13}C NMR of **29** (101 MHz, $CDCl_3$)



^{1}H NMR of **32** (400 MHz, $CDCl_3$)



^{13}C NMR of **32** (101 MHz, $CDCl_3$)