Complex Allylation by the Direct Cross-Coupling of Imines with Unactivated Allylic Alcohols

Masayuki Takahashi, Martin McLaughlin and Glenn C. Micalizio*

Department of Chemistry, Scripps Florida, Jupiter, FL 33458, USA

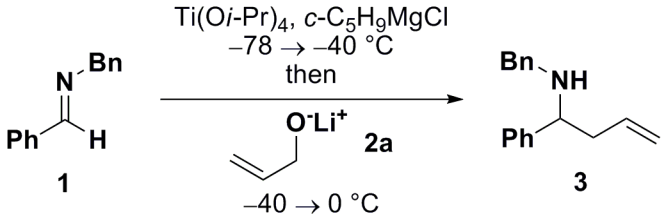
E-mail: micalizio@scripps.edu

SUPPORTING INFORMATION

Experimental Procedures and Spectral Data

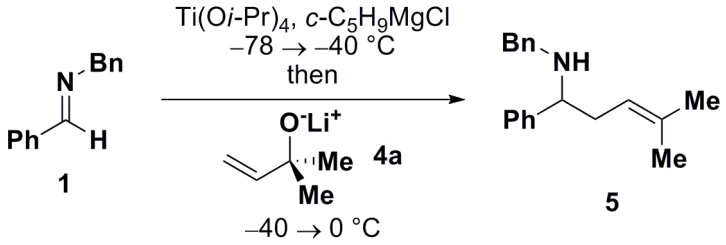
General. All reactions were conducted in flame-dried glassware under a nitrogen atmosphere with dry solvents, unless otherwise noted. Dry diethyl ether, tetrahydrofuran, toluene and dichloromethane were obtained by passing inhibitor-free, HPLC grade solvents through activated alumina columns. *N*,*N*-Dimethylformamide and *N*,*N*-diisopropylethylamine were purchased in anhydrous forms and used without further purification. Titanium(IV) tetraisopropoxide was purified by distillation at 150 millitorr prior to use. Chlorotriisopropoxytitanium(IV) was purchased from Sigma-Aldrich Co. as a solution in hexanes and used as received within one month of opening. Cyclopentylmagnesium chloride and *n*-butyllithium were purchased as solutions in Et_2O and hexanes, respectively, and titrated on a monthly basis.[1] *N*-Bromosuccinimide was recrystallized from boiling water and dried under high vacuum for 24 h, powdered cesium fluoride was dried under high vacuum at 140 °C for 4 h, and chlorotrimethylsilane was distilled from calcium hydride prior to use. Dess-Martin periodinane was prepared according to literature procedures.[2,3] Commercially available alcohols **2**, **4** and **19** were distilled under nitrogen atmosphere prior to use. Imines **1**,[4] **45**[5] and alcohols **20**,[6] **21**,[7] **30**,[8] were prepared according to literature procedures. Intermediates were prepared according to literature procedures (S-**7**,[9] S-**15**,[10] S-**18**,[11] S-**21**[12] and S-**23**[13]) or by adaptation of literature procedures for similar compounds (S-**9**,[14] S-**10**,[15] S-**12**,[16] S-**13**,[15] S-**17**[16] and S-**19**[17]). All other commercially available reagents were used as received. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography carried out on 250 μm E. Merck silica gel plates (60F-254) and visualized using UV light or appropriate stains, including ninhydrin, *p*-anisaldehyde, ceric ammonium nitrate, and potassium permanganate. Silica gel for flash column chromatography was purchased from Silicycle (P60, particle size 40-63 μm). ^{1}H NMR data were recorded at 400 or 500 MHz using a Bruker AM-400 or AM-500 instrument. ^{1}H NMR chemical shifts are reported relative to residual $CHCl_3$ (7.26 ppm) or TMS (0.00 ppm). ^{13}C NMR data were recorded at 100 or 126 MHz using a Bruker AM-400 or AM-500 instrument. ^{13}C NMR chemical shifts were reported relative to the central line of $CDCl_3$ (77.23 ppm). Infrared spectra were recorded using a Thermo Electron Nicolet 6700 FT-IR spectrometer. Low resolution mass spectrometry was performed on a Waters Micromass® ZQ_{TM} instrument using electrospray ionization. High resolution mass spectrometry was performed at the W. M. Keck Foundation Biotechnology and Resource Laboratory at Yale University using a Bruker 9.4T Apex-Qe Hybrid Fourier Transform Ion Cyclotron Resonance mass spectrometer consisting of an Apollo II electrospray ionization source. Optical rotations were measured on a Perkin Elmer Model 341 polarimeter using a 1 mL capacity micro cell with a 10 cm path length. All compounds purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise. Relative stereochemistry was defined using the *R**/*S** convention proposed by IUPAC.

Preparation of Homoallylic Amines via Cross-Coupling of Allylic Alcohols with Imines



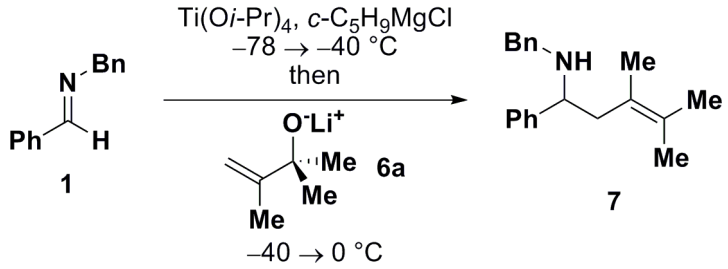
Synthesis of (±)-*N*-benzyl-1-phenylbut-3-en-1-amine (3). To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at –78 °C was added *c*-C_5H_9MgCl (2.25 M in Et_2O, 2.03 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 1 h at this temperature. A solution of lithium alkoxide **2a**, prepared by the deprotonation of alcohol **2** (69 μL, 58.9 mg, 1.01 mmol) in THF (1.0 mL) at –78 °C with *n*-BuLi (2.56 M in hexanes, 1.08 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to 0 °C over 30 min then stirred at this temperature for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford homoallylic amine **3** as a colorless oil (112 mg, 70%).

Data for (±)-*N*-benzyl-1-phenylbut-3-en-1-amine (3): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37–7.21 (m, 10H), 5.75–5.66 (m, 1H), 5.09–5.02 (m, 2H), 3.71–3.66 (m, 2H), 3.52 (d, J = 13.3 Hz, 1H), 2.46–2.36 (m, 2H), 1.75 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.08, 140.89, 135.70, 128.60, 128.55, 128.33, 127.53, 127.26, 127.03, 117.71, 61.88, 51.68, 43.33; IR (thin film, NaCl) 3063, 3026, 2835, 1639, 1603, 1585, 1493, 1453, 1356, 1326, 1307, 1198, 1117, 1070, 1028, 995, 916, 824, 759, 700 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{17}H_{19}N+H^+$ 238.1590, found 238.1590; R_f 0.66 (silica gel, 1:3 EtOAc/hexanes).



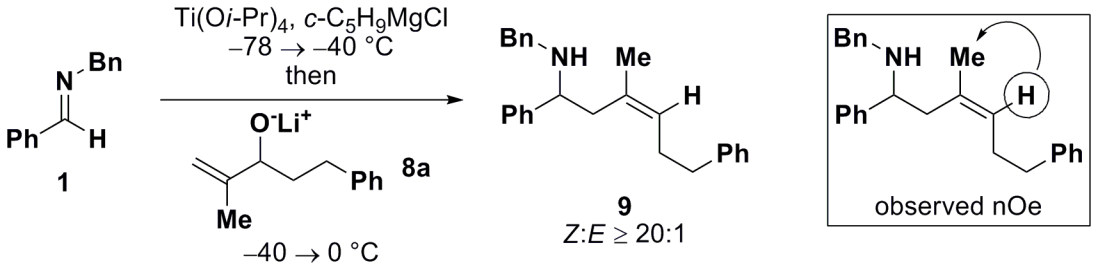
Synthesis of (±)-*N*-benzyl-4-methyl-1-phenylpent-3-en-1-amine (5). To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at –78 °C was added *c*-C_5H_9MgCl (2.25 M in Et_2O, 2.03 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 1 h at this temperature. A solution of lithium alkoxide **4a**, prepared by the deprotonation of alcohol **4** (106 μL, 87.3 mg, 1.01 mmol) in THF (1.0 mL) at –78 °C with *n*-BuLi (2.56 M in hexanes, 1.08 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to 0 °C over 30 min then stirred at this temperature for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford homoallylic amine **5** as a colorless oil (148 mg, 83%).

Data for (±)-*N*-benzyl-4-methyl-1-phenylpent-3-en-1-amine (5): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.21 (m, 10H), 5.09–5.05 (m, 1H), 3.67 (d, *J* = 13.4 Hz, 1H), 3.63 (dd, *J* = 8.0, 5.8 Hz, 1H), 3.52 (d, *J* = 13.4 Hz, 1H), 2.43–2.36 (m, 1H), 2.30–2.24 (m, 1H), 1.73 (br, 1H), 1.67 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.57, 141.10, 134.66, 128.51, 128.50, 128.25, 127.54, 127.08, 126.95, 121.24, 62.81, 51.79, 37.72, 26.02, 18.15; IR (thin film, NaCl) 3027, 2912, 1602, 1494, 1453, 1376, 1358, 1306, 1199, 1108, 1072, 1028, 983, 911, 804, 754, 700 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{19}H_{23}N+H^+$ 266.1903, found 266.1904; R_f 0.69 (silica gel, 1:3 EtOAc/hexanes).



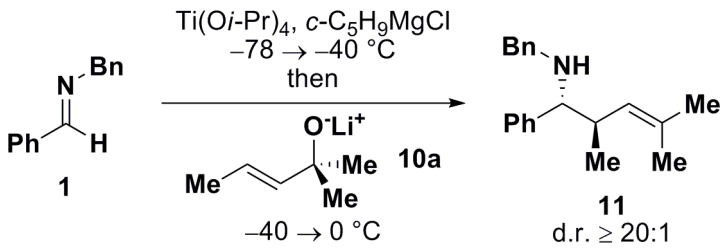
Synthesis of (±)-*N*-benzyl-3,4-dimethyl-1-phenylpent-3-en-1-amine (7). To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at −78 °C was added *c*-C_5H_9MgCl (2.25 M in Et_2O, 2.03 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 1 h at this temperature. A solution of lithium alkoxide **6a**, prepared by the deprotonation of alcohol **6** (101 mg, 1.01 mmol) in THF (1.0 mL) at −78 °C with *n*-BuLi (2.56 M in hexanes, 1.08 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to 0 °C over 30 min then stirred at this temperature for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford homoallylic amine **7** as a colorless oil (151 mg, 80%).

Data for (±)-*N*-benzyl-3,4-dimethyl-1-phenylpent-3-en-1-amine (7): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.20 (m, 10H), 3.73 (dd, *J* = 8.9, 5.5 Hz, 1H), 3.69 (d, *J* = 13.7 Hz, 1H), 3.48 (d, *J* = 13.7 Hz, 1H), 2.57 (dd, *J* = 13.4, 8.9 Hz, 1H), 2.13 (dd, *J* = 13.4, 5.4 Hz, 1H), 1.70 (s, 1H), 1.63 (s, 3H), 1.59 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.93, 141.19, 128.49, 128.44, 128.08, 127.97, 127.48, 127.01, 126.87, 124.68, 60.79, 51.70, 44.36, 20.97, 20.74, 18.67; IR (thin film, NaCl) 3026, 2913, 2858, 1603, 1493, 1453, 1373, 1356, 1328, 1308, 1199, 1155, 1116, 1071, 1028, 911, 759, 734, 717, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{20}H_{25}N+H^+$ 280.2060, found 280.2060; R_f 0.68 (silica gel, 1:3 EtOAc/hexanes).



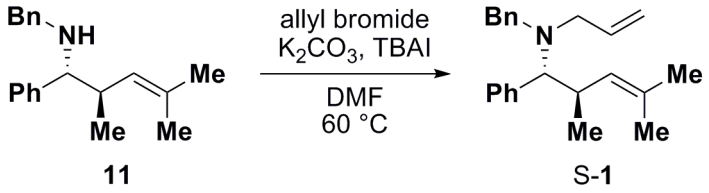
Synthesis of (±)-(*Z*)-*N*-benzyl-3-methyl-1,6-diphenylhex-3-en-1-amine (9). To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at −78 °C was added *c*-C_5H_9MgCl (2.03 M in Et_2O, 2.03 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 1 h at this temperature. A solution of lithium alkoxide **8a**, prepared by the deprotonation of alcohol **8** (178 mg, 1.01 mmol) in THF (1.0 mL) at −78 °C with *n*-BuLi (2.63 M in hexanes, 1.08 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to 0 °C over 30 min then stirred at this temperature for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5% EtOAc/hexanes) to afford homoallylic amine **9** as a colorless oil (*Z*:*E* ≥ 20:1, 208 mg, 87%). No evidence for minor isomer was observed by ^{1}H NMR.

Data for (±)-(*Z*)-*N*-benzyl-3-methyl-1,6-diphenylhex-3-en-1-amine (9): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.10 (m, 15H), 5.26 (app t, *J* = 7.0 Hz, 1H), 3.74 (dd, *J* = 8.6, 5.9 Hz, 1H), 3.66 (d, *J* = 13.5 Hz, 1H), 3.47 (d, *J* = 13.5 Hz, 1H), 2.56–2.43 (m, 3H), 2.32–2.19 (m, 2H), 2.16 (dd, *J* = 13.4, 5.9 Hz, 1H), 1.66 (br, 1H), 1.59 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.58, 142.36, 141.02, 132.70, 128.65, 128.55, 128.50, 128.45, 128.23, 128.02, 127.52, 127.20, 126.96, 125.92, 60.32, 51.73, 41.81, 36.30, 29.99, 23.74; IR (thin film, NaCl) 3026, 2920, 2853, 1603, 1585, 1494, 1453, 1377, 1362, 1329, 1307, 1199, 1116, 1070, 1028, 912, 749, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{26}H_{29}N+H^+$ 356.2373, found 356.2363; R_f 0.31 (silica gel, 1:9 EtOAc/hexanes).



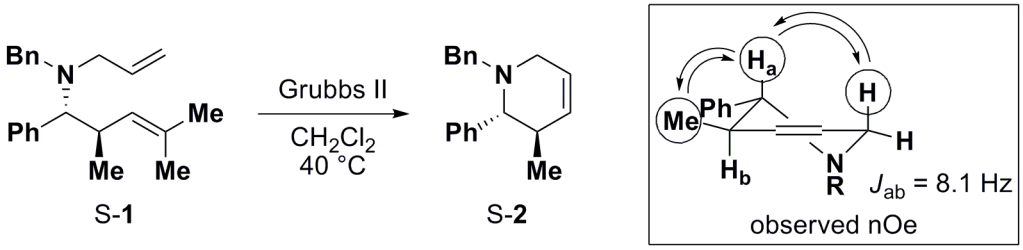
Synthesis of (1*R,2*R**)-*N*-benzyl-2,4-dimethyl-1-phenylpent-3-en-1-amine (11).** To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at −78 °C was added *c*-C_5H_9MgCl (2.03 M in Et_2O, 2.03 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 1 h at this temperature. A solution of lithium alkoxide **10a**, prepared by the deprotonation of alcohol **10** (101 mg, 1.01 mmol) in THF (1.0 mL) at −78 °C with *n*-BuLi (2.63 M in hexanes, 1.08 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to 0 °C over 30 min then stirred at this temperature for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5% EtOAc/hexanes) to afford homoallylic amine **11** as a white solid (d.r. ≥ 20:1, 153 mg, 81%). No evidence for minor isomer was observed by ^{1}H NMR. See **11**→S-**1**→S-**2** for the stereochemical assignment.

Data for (1*R,2*R**)-*N*-benzyl-2,4-dimethyl-1-phenylpent-3-en-1-amine (11):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.19 (m, 10H), 4.94–4.90 (m, 1H), 3.60 (d, *J* = 13.8 Hz, 1H), 3.40 (d, *J* = 13.8 Hz, 1H), 3.20 (d, *J* = 9.0 Hz, 1H), 2.56 (app tq, *J* = 9.2, 6.7 Hz, 1H), 2.00 (br, 1H), 1.74 (d, *J* = 1.1 Hz, 3H), 1.66 (d, *J* = 1.2 Hz, 3H), 0.65 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.32, 141.31, 133.68, 128.87, 128.70, 128.44, 128.27, 128.13, 127.15, 126.79, 68.22, 51.58, 40.09, 26.19, 18.55, 18.41; IR (thin film, NaCl) 3026, 2967, 2927, 1602, 1494, 1453, 1376, 1305, 1200, 1107, 1070, 1028, 980, 913, 837, 764, 735, 700 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{20}H_{25}N+H^+$ 280.2060, found 280.2060; R_f 0.37 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (1*R,2*R**)-*N*-allyl-*N*-benzyl-2,4-dimethyl-1-phenylpent-3-en-1-amine (S-1) (from 10).** Allyl bromide (93 μL, 130 mg, 1.07 mmol) was added to a mixture of amine **11** (100 mg, 0.358 mmol), K_2CO_3 (247 mg, 1.79 mmol) and tetrabutylammonium iodide (13 mg, 0.035 mmol) in DMF (0.90 mL). The reaction was stirred at 60 °C for 18 h, poured into H_2O (25 mL), and the aqueous phase extracted with Et_2O (3 × 50 mL). The organic extracts were combined, washed with brine (1 × 25 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/hexanes) to afford amine S-**1** as a colorless liquid (108 mg, 94%).

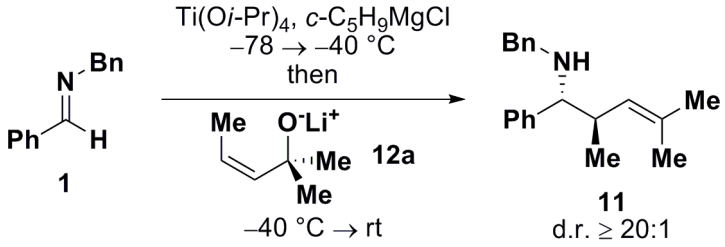
Data for (1*R,2*R**)-*N*-allyl-*N*-benzyl-2,4-dimethyl-1-phenylpent-3-en-1-amine (S-1):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.16 (m, 10H), 5.77 (dddd, *J* = 17.3, 10.2, 8.6, 3.8 Hz, 1H), 5.18–5.07 (m, 3H), 3.86 (d, *J* = 13.8 Hz, 1H), 3.43 (d, *J* = 10.6 Hz, 1H), 3.19 (app ddt, *J* = 14.2, 3.8, 2.0 Hz, 1H), 3.09 (ddq, *J* = 13.2, 10.3, 6.6 Hz, 1H), 2.94 (d, *J* = 13.8 Hz, 1H), 2.56 (dd, *J* = 14.2, 8.6 Hz, 1H), 1.80 (d, *J* = 1.1 Hz, 3H), 1.65 (d, *J* = 1.2 Hz, 3H), 0.66 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.03, 138.01, 137.82, 130.84, 129.46, 128.93, 128.81, 128.21, 128.05, 127.02, 126.72, 116.72, 68.66, 53.47, 52.73, 34.08, 26.11, 19.25, 18.00; IR (thin film, NaCl) 3062, 3026, 2965, 2925, 2810, 1641, 1601, 1494, 1453, 1419, 1373, 1313, 1289, 1259, 1201, 1154, 1125, 1090, 1072, 1056, 1029, 987, 945, 915, 870, 836, 760, 738, 703 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{23}H_{29}N+H^+$ 320.2373, found 320.2375; R_f 0.59 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2) (from 10).** To a solution of amine S-**1** (81 mg, 0.254 mmol) in CH_2Cl_2 (9.0 mL) was added Grubbs II catalyst (2.1 mg, 0.0025 mmol). The reaction was refluxed for 1 h, treated with DMSO (20 μL), then stirred for 24 h at ambient temperature. The mixture was concentrated *in vacuo*, and the

crude product was purified by flash column chromatography on silica gel (2% EtOAc/hexanes) to afford tetrahydropyridine S-**2** as a white solid (65 mg, 97%).

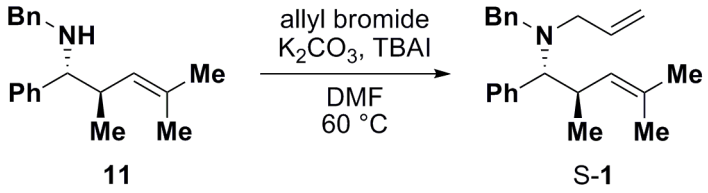
Data for (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.37–7.33 (m, 2H), 7.28–7.23 (m, 5H), 7.21–7.17 (m, 1H), 5.69–5.64 (m, 2H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.19 (dd, *J* = 17.2, 2.6 Hz, 1H), 3.04 (d, *J* = 8.1 Hz, 1H), 2.86 (d, *J* = 13.1 Hz, 1H), 2.74 (dd, *J* = 17.0, 3.8 Hz, 1H), 2.57–2.50 (m, 1H), 0.84 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.82, 139.74, 131.38, 128.96, 128.85, 128.62, 128.32, 127.44, 126.92, 124.07, 72.27, 60.03, 52.29, 38.96, 19.02; IR (thin film, NaCl) 3027, 2956, 2925, 2872, 2786, 1601, 1493, 1454, 1372, 1361, 1329, 1309, 1282, 1254, 1236, 1197, 1162, 1125, 1102, 1072, 1029, 993, 971, 913, 832, 759, 731, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{19}H_{21}N+H^+$ 264.1747, found 264.1742; R_f 0.54 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (1*R,2*R**)-*N*-benzyl-2,4-dimethyl-1-phenylpent-3-en-1-amine (11).** To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at –78 °C was added *c*-C_5H_9MgCl (2.23 M in Et_2O, 2.01 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 1 h at this temperature. A solution of lithium alkoxide **12a**, prepared by the deprotonation of alcohol **12** (101 mg, 1.01 mmol) in THF (1.0 mL) at –78 °C with *n*-BuLi (2.66 M in hexanes, 1.06 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to room temperature over 30 min then stirred for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5% EtOAc/hexanes) to afford homoallylic amine **11** as a white solid (d.r. ≥ 20:1, 128 mg, 68%). No evidence for minor isomer was observed by ^{1}H NMR. See **11**→S-**1**→S-**2** for the stereochemical assignment.

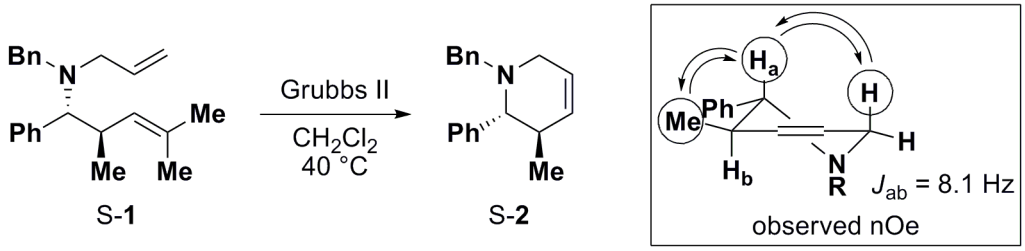
Data for (1*R,2*R**)-*N*-benzyl-2,4-dimethyl-1-phenylpent-3-en-1-amine (11):** ^{1}H NMR (500

MHz, $CDCl_3$) δ 7.36–7.19 (m, 10H), 4.94–4.90 (m, 1H), 3.60 (d, *J* = 13.8 Hz, 1H), 3.40 (d, *J* = 13.8 Hz, 1H), 3.20 (d, *J* = 9.0 Hz, 1H), 2.56 (app tq, *J* = 9.2, 6.7 Hz, 1H), 1.99 (br, 1H), 1.74 (d, *J* = 1.0 Hz, 3H), 1.66 (d, *J* = 1.1 Hz, 3H), 0.65 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.33, 141.32, 133.68, 128.88, 128.71, 128.44, 128.27, 128.14, 127.15, 126.80, 68.24, 51.59, 40.09, 26.19, 18.55, 18.40; IR (thin film, NaCl) 3026, 2967, 2927, 1602, 1494, 1453, 1376, 1305, 1200, 1107, 1070, 1028, 980, 913, 837, 764, 735, 700 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{20}H_{25}N+H^+$ 280.2060, found 280.2060; R_f 0.38 (silica gel, 1:9 EtOAc/hexanes).



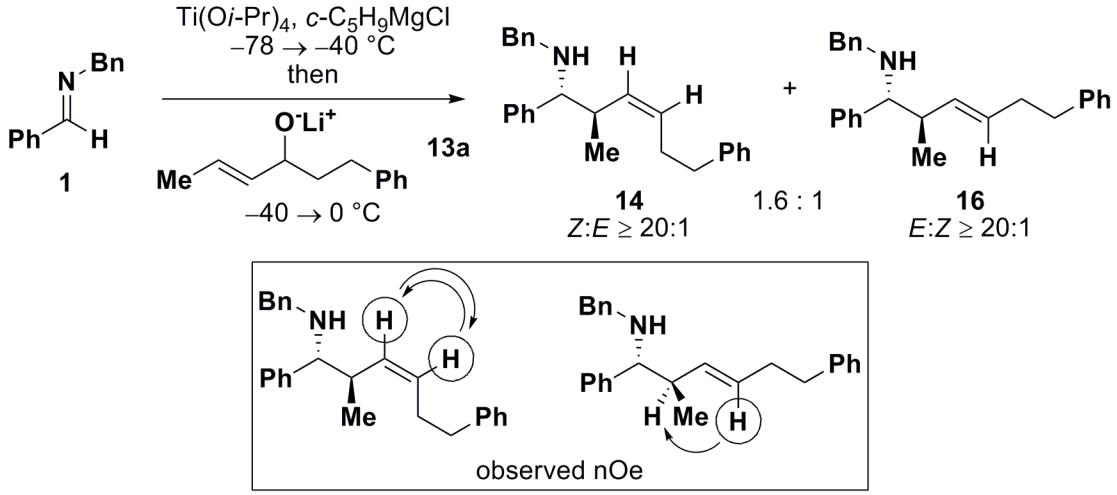
Synthesis of (1*R,2*R**)-*N*-allyl-*N*-benzyl-2,4-dimethyl-1-phenylpent-3-en-1-amine (S-1) (from 12).** Allyl bromide (93 μL, 130 mg, 1.07 mmol) was added to a mixture of amine **11** (100 mg, 0.358 mmol), K_2CO_3 (247 mg, 1.79 mmol) and tetrabutylammonium iodide (13 mg, 0.035 mmol) in DMF (0.90 mL). The reaction was stirred at 60 °C for 18 h, poured into H_2O (25 mL), and the aqueous phase extracted with Et_2O (3 × 50 mL). The organic extracts were combined, washed with brine (1 × 25 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/hexanes) to afford amine S-**1** as a colorless liquid (105 mg, 92%).

Data for (1*R,2*R**)-*N*-allyl-*N*-benzyl-2,4-dimethyl-1-phenylpent-3-en-1-amine (S-1):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.16 (m, 10H), 5.77 (dddd, *J* = 17.3, 10.2, 8.6, 3.8 Hz, 1H), 5.18–5.07 (m, 3H), 3.86 (d, *J* = 13.8 Hz, 1H), 3.43 (d, *J* = 10.6 Hz, 1H), 3.19 (app ddt, *J* = 14.1, 3.8, 2.0 Hz, 1H), 3.13–3.04 (m, 1H), 2.94 (d, *J* = 13.8 Hz, 1H), 2.56 (dd, *J* = 14.2, 8.6 Hz, 1H), 1.80 (d, *J* = 1.1 Hz, 3H), 1.65 (d, *J* = 1.1 Hz, 3H), 0.66 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.03, 138.01, 137.82, 130.84, 129.46, 128.93, 128.81, 128.21, 128.05, 127.03, 126.73, 116.72, 68.66, 53.47, 52.73, 34.08, 26.11, 19.25, 18.00; IR (thin film, NaCl) 3062, 3026, 2965, 2924, 2811, 1641, 1601, 1583, 1494, 1453, 1419, 1373, 1314, 1259, 1200, 1154, 1126, 1090, 1071, 1050, 1029, 987, 965, 915, 870, 839, 760, 738, 703 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{23}H_{29}N+H^+$ 320.2373, found 320.2374; R_f 0.59 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2) (from 12).** To a solution of amine S-**1** (79 mg, 0.247 mmol) in CH_2Cl_2 (9.0 mL) was added Grubbs II catalyst (2.1 mg, 0.0025 mmol). The reaction was refluxed for 1 h, treated with DMSO (20 μL), then stirred for 24 h at ambient temperature. The mixture was concentrated *in vacuo*, and the crude product was purified by flash column chromatography on silica gel (2% EtOAc/hexanes) to afford tetrahydropyridine S-**2** as a white solid (61 mg, 94%).

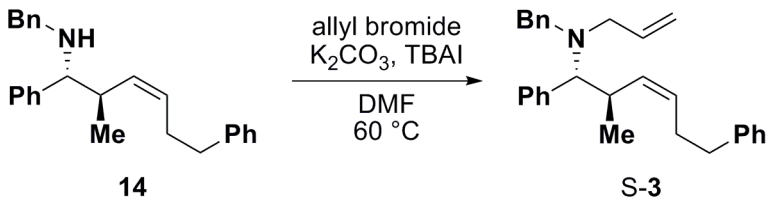
Data for (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.37–7.33 (m, 2H), 7.28–7.23 (m, 5H), 7.21–7.17 (m, 1H), 5.69–5.64 (m, 2H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.19 (dd, *J* = 17.2, 2.6 Hz, 1H), 3.04 (d, *J* = 8.1 Hz, 1H), 2.86 (d, *J* = 13.1 Hz, 1H), 2.74 (dd, *J* = 16.9, 3.8 Hz, 1H), 2.57–2.50 (m, 1H), 0.84 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.82, 139.75, 131.38, 128.96, 128.85, 128.62, 128.32, 127.44, 126.91, 124.07, 72.27, 60.03, 52.29, 38.96, 19.02; IR (thin film, NaCl) 3027, 2956, 2925, 2872, 2786, 1601, 1493, 1454, 1372, 1361, 1329, 1309, 1282, 1254, 1236, 1197, 1162, 1125, 1102, 1072, 1029, 993, 971, 913, 832, 759, 731, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{19}H_{21}N+H^+$ 264.1747, found 264.1744; R_f 0.54 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (1*R,2*R**,*Z*)-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (14) and (1*R**,2*R**,*E*)- *N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (16).** To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at −78 °C was added *c*-C_5H_9MgCl (2.23 M in Et_2O, 2.01 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 2 h at this temperature. A solution of lithium alkoxide **13a**, prepared by the deprotonation of alcohol **13** (178 mg, 1.01 mmol) in THF (1.0 mL) at −78 °C with *n*-BuLi (2.66 M in hexanes, 1.06 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to 0 °C over 30 min then stirred at this temperature for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (2→5% EtOAc/hexanes) to afford homoallylic amines **14** (d.r. ≥ 20:1, *Z*:*E* ≥ 20:1, 136 mg, 57%) and **16** (d.r. ≥ 20:1, *E*:*Z* ≥ 20:1, 84 mg, 35%) as colorless oils. No evidence for minor isomer was observed by ^{1}H NMR of each product. See **14**→S-**3**→S-**2** and **16**→S-**4**→S-**2** for the stereochemical assignment.

Data for (1*R,2*R**,*Z*)-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (14):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.14 (m, 15H), 5.52 (app dt, *J* = 10.7, 7.3 Hz, 1H), 5.22–5.16 (m, 1H), 3.58 (d, *J* = 13.7 Hz, 1H), 3.37 (d, *J* = 13.7 Hz, 1H), 3.20 (d, *J* = 8.9 Hz, 1H), 2.71–2.58 (m, 3H), 2.45–2.40 (m, 2H), 1.89 (br, 1H), 0.61 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.96, 142.08, 141.19, 134.40, 130.73, 128.71, 128.67, 128.49, 128.44, 128.32, 128.23, 127.26, 126.85, 126.03, 67.72, 51.60, 39.40, 36.16, 29.71, 18.26; IR (thin film, NaCl) 3062, 3026, 3001, 2958, 2926, 2872, 1603, 1585, 1494, 1454, 1419, 1404, 1371, 1352, 1329, 1306, 1279, 1199, 1118, 1074, 1028, 971, 912, 842, 763, 737, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{26}H_{29}N+H^+$ 356.2373, found 356.2373; R_f 0.45 (silica gel, 1:9 EtOAc/hexanes).

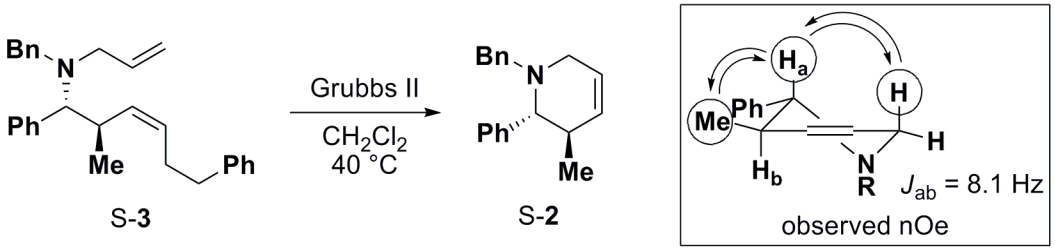
Data for (1*R,2*R**,*E*)-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (16):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.11 (m, 15H), 5.59 (app dt, *J* = 15.0, 6.7 Hz, 1H), 5.22 (app ddt, *J* = 15.2, 9.0, 1.2 Hz, 1H), 3.59 (d, *J* = 13.7 Hz, 1H), 3.36 (d, *J* = 13.7 Hz, 1H), 3.18 (d, *J* = 8.9 Hz, 1H), 2.74–2.64 (m, 2H), 2.39–2.25 (m, 3H), 1.92 (br, 1H), 0.68 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.89, 142.09, 141.11, 134.78, 131.46, 128.72, 128.67, 128.51, 128.45, 128.30, 128.27, 127.21, 126.86, 126.06, 66.97, 51.48, 44.66, 36.18, 34.68, 18.50; IR (thin film, NaCl) 3062, 3025, 2966, 2926, 2854, 1603, 1585, 1494, 1453, 1420, 1372, 1351, 1306, 1279, 1199, 1113, 1072, 1028, 974, 913, 840, 748, 700 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{26}H_{29}N+H^+$ 356.2373, found 356.2374; R_f 0.39 (silica gel, 1:9 EtOAc/hexanes).



14 S-**3**

Synthesis of (1*R,2*R**,*Z*)-*N*-allyl-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (S-3).** Allyl bromide (85 μL, 119 mg, 0.982 mmol) was added to a mixture of amine **14** (117 mg, 0.329 mmol), K_2CO_3 (227 mg, 1.64 mmol) and tetrabutylammonium iodide (12 mg, 0.032 mmol) in DMF (0.80 mL). The reaction was stirred at 60 °C for 20 h, poured into H_2O (25 mL), and the aqueous phase extracted with Et_2O (3 × 50 mL). The organic extracts were combined, washed with brine (1 × 25 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/hexanes) to afford amine S-**3** as a colorless liquid (110 mg, 85%).

Data for (1*R,2*R**,*Z*)-*N*-allyl-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (S-3):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.34 (m, 4H), 7.31–7.14 (m, 11H), 5.79 (dddd, *J* = 17.4, 10.2, 8.7, 3.8 Hz, 1H), 5.51–5.42 (m, 2H), 5.17–5.06 (m, 2H), 3.85 (d, *J* = 13.8 Hz, 1H), 3.43 (d, *J* = 10.6 Hz, 1H), 3.26–3.14 (m, 2H), 2.92 (d, *J* = 13.8 Hz, 1H), 2.73–2.61 (m, 2H), 2.56 (dd, *J* = 14.1, 8.7 Hz, 1H), 2.51–2.36 (m, 2H), 0.61 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.39, 140.75, 137.89, 137.33, 136.07, 129.50, 129.03, 128.65, 128.50, 128.28, 128.09, 127.14, 126.85, 126.82, 126.01, 116.96, 68.37, 53.57, 52.62, 36.35, 33.32, 29.81, 19.33; IR (thin film, NaCl) 3062, 3026, 3004, 2965, 2926, 2810, 1641, 1602, 1494, 1453, 1418, 1370, 1257, 1155, 1122, 1092, 1074, 1057, 1029, 986, 916, 962, 737, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{29}H_{33}N+H^+$ 396.2686, found 396.2687; R_f 0.55 (silica gel, 1:9 EtOAc/hexanes).

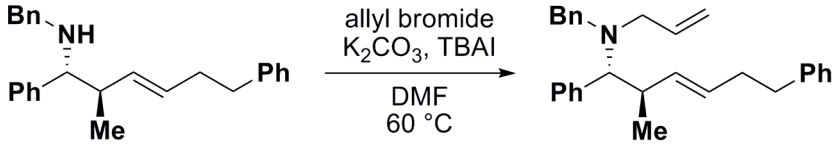


S-**3** S-**2**

Synthesis of (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2) (from 13, via 14).** To a solution of amine S-**3** (94 mg, 0.238 mmol) in CH_2Cl_2 (8.0 mL) was added Grubbs II catalyst (2.0 mg, 0.0024 mmol). The reaction was refluxed for 5 h, treated with DMSO (20 μL), then stirred for 24 h at ambient temperature. The mixture was concentrated *in vacuo*, and

the crude product was purified by flash column chromatography on silica gel (2% EtOAc/hexanes) to isolate S-**2** containing minor impurity by TLC (presumably 4-phenyl-1-butene). The mixture was diluted with Et_2O (100 mL), washed with 1 N HCl (25 mL), then the aqueous phase was basified with 3 N NaOH (25 mL) and extracted with Et_2O (100 mL). The organic extract was dried over $MgSO_4$ then concentrated *in vacuo* to afford tetrahydropyridine S-**2** as a white solid (52 mg, 83%).

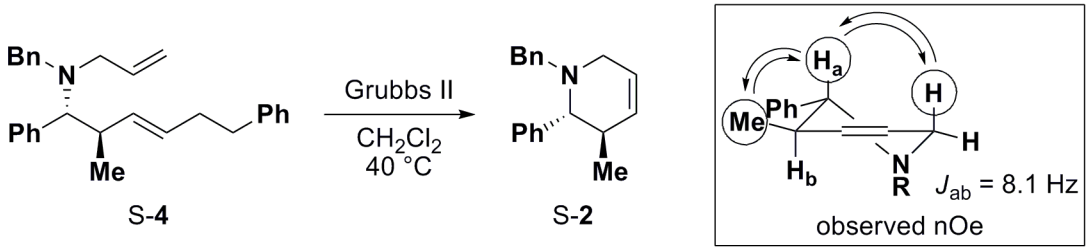
Data for (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.36–7.32 (m, 2H), 7.28–7.23 (m, 5H), 7.21–7.16 (m, 1H), 5.69–5.63 (m, 2H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.21–3.15 (m, 1H), 3.04 (d, *J* = 8.1 Hz, 1H), 2.86 (d, *J* = 13.1 Hz, 1H), 2.76–2.71 (m, 1H), 2.58–2.49 (m, 1H), 0.84 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.82, 139.75, 131.37, 128.95, 128.84, 128.61, 128.31, 127.44, 126.91, 124.08, 72.26, 60.02, 52.28, 38.95, 19.02; IR (thin film, NaCl) 3027, 2956, 2925, 2872, 2786, 1601, 1493, 1454, 1372, 1361, 1329, 1309, 1282, 1254, 1236, 1197, 1162, 1125, 1102, 1072, 1029, 993, 971, 913, 832, 759, 731, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{19}H_{21}N+H^+$ 264.1747, found 264.1747; R_f 0.53 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (1*R,2*R**,*E*)-*N*-allyl-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (S-4) (from 13).** Allyl bromide (53 μL, 74.1 mg, 0.612 mmol) was added to a mixture of amine **16** (72 mg, 0.203 mmol), K_2CO_3 (140 mg, 1.01 mmol) and tetrabutylammonium iodide (7.5 mg, 0.020 mmol) in DMF (0.50 mL). The reaction was stirred at 60 °C for 20 h, poured into H_2O (25 mL), and the aqueous phase extracted with Et_2O (3 × 50 mL). The organic extracts were combined, washed with brine (1 × 25 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/hexanes) to afford amine S-**4** as a colorless liquid (74 mg, 92%).

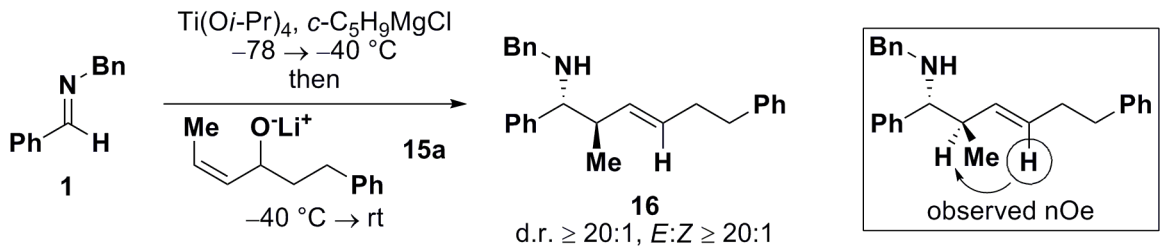
Data for (1*R,2*R**,*E*)-*N*-allyl-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (S-4):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.12 (m, 15H), 5.79 (dddd, *J* = 17.4, 10.2, 8.6, 3.8 Hz, 1H), 5.62–5.56 (m, 1H), 5.52–5.45 (m, 1H), 5.17–5.07 (m, 2H), 3.90 (d, *J* = 14.0 Hz, 1H), 3.41 (d, *J* = 10.7 Hz, 1H), 3.34–3.23 (m, 1H), 2.96 (d, *J* = 14.0 Hz, 1H), 2.92–2.82 (m, 1H), 2.80–2.69 (m, 2H), 2.56 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.49–2.36 (m, 2H), 0.70 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.57, 140.82, 137.81, 137.33, 136.11, 129.46, 128.94, 128.69, 128.50, 128.27,

128.06, 127.97, 127.08, 126.80, 125.94, 116.89, 68.29, 53.34, 52.41, 38.43, 36.36, 34.87, 19.55; IR (thin film, NaCl) 3026, 2972, 2927, 2810, 1641, 1602, 1584, 1494, 1453, 1417, 1371, 1311, 1256, 1155, 1124, 1072, 1029, 989, 962, 916, 867, 762, 739, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{29}H_{33}N+H^+$ 396.2686, found 396.2689; R_f 0.55 (silica gel, 1:9 EtOAc/hexanes).



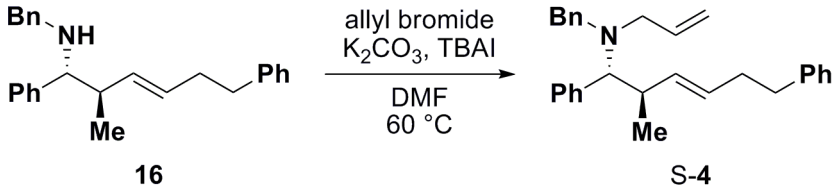
Synthesis of (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2) (from 13, via 16).** To a solution of amine S-**4** (62 mg, 0.157 mmol) in CH_2Cl_2 (5.3 mL) was added Grubbs II catalyst (1.4 mg, 0.0016 mmol). The reaction was refluxed for 5 h, treated with DMSO (20 μL), then stirred for 24 h at ambient temperature. The mixture was concentrated *in vacuo*, and the crude product was purified by flash column chromatography on silica gel (2% EtOAc/hexanes) to isolate S-**2** containing minor impurity by TLC (presumably 4-phenyl-1-butene). The mixture was diluted with Et_2O (100 mL), washed with 1 N HCl (25 mL), then the aqueous phase was basified with 3 N NaOH (25 mL) and extracted with Et_2O (100 mL). The organic extract was dried over $MgSO_4$ then concentrated *in vacuo* to afford tetrahydropyridine S-**2** as a white solid (33 mg, 80%).

Data for (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.36–7.32 (m, 2H), 7.28–7.23 (m, 5H), 7.21–7.16 (m, 1H), 5.69–5.63 (m, 2H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.21–3.15 (m, 1H), 3.04 (d, *J* = 8.1 Hz, 1H), 2.86 (d, *J* = 13.1 Hz, 1H), 2.76–2.71 (m, 1H), 2.58–2.49 (m, 1H), 0.84 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.82, 139.75, 131.37, 128.95, 128.84, 128.62, 128.31, 127.44, 126.91, 124.08, 72.26, 60.02, 52.28, 38.95, 19.02; IR (thin film, NaCl) 3027, 2956, 2925, 2872, 2786, 1601, 1493, 1454, 1372, 1361, 1329, 1309, 1282, 1254, 1236, 1197, 1162, 1125, 1102, 1072, 1029, 993, 971, 913, 832, 759, 731, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{19}H_{21}N+H^+$ 264.1747, found 264.1748; R_f 0.53 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (1*R,2*R**,*E*)-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (16).** To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at −78 °C was added *c*-C_5H_9MgCl (2.23 M in Et_2O, 2.01 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 2 h at this temperature. A solution of lithium alkoxide **15a**, prepared by the deprotonation of alcohol **15** (178 mg, 1.01 mmol) in THF (1.0 mL) at −78 °C with *n*-BuLi (2.66 M in hexanes, 1.06 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to room temperature over 30 min then stirred for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (2→5% EtOAc/hexanes) to afford homoallylic amine **16** (d.r. ≥ 20:1, *E*:*Z* ≥ 20:1, 131 mg, 55%) as a colorless oil. No evidence for minor isomer was observed by ^{1}H NMR. A small amount of amine **14** (d.r. ≥ 20:1, *Z*:*E* ≥ 20:1, 5 mg, 2%) containing trace impurities was also isolated. See **16**→S-**4**→S-**2** for the stereochemical assignment.

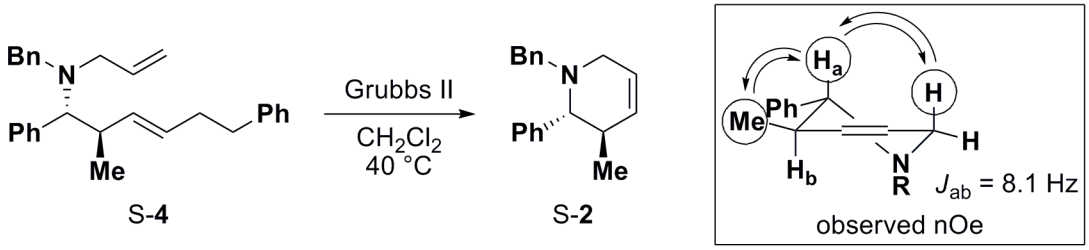
Data for (1*R,2*R**,*E*)-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (16):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.11 (m, 15H), 5.59 (app dt, *J* = 15.0, 6.7 Hz, 1H), 5.22 (app ddt, *J* = 15.2, 9.0, 1.2 Hz, 1H), 3.59 (d, *J* = 13.7 Hz, 1H), 3.36 (d, *J* = 13.7 Hz, 1H), 3.18 (d, *J* = 8.9 Hz, 1H), 2.74–2.64 (m, 2H), 2.39–2.24 (m, 3H), 1.91 (br, 1H), 0.68 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.89, 142.09, 141.11, 134.78, 131.46, 128.72, 128.66, 128.51, 128.45, 128.30, 128.27, 127.21, 126.86, 126.05, 66.97, 51.48, 44.66, 36.17, 34.68, 18.50; IR (thin film, NaCl) 3062, 3025, 2966, 2926, 2854, 1603, 1585, 1494, 1453, 1420, 1372, 1351, 1306, 1279, 1199, 1113, 1072, 1028, 974, 913, 840, 748, 700 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{26}H_{29}N+H^+$ 356.2373, found 356.2373; R_f 0.37 (silica gel, 1:9 EtOAc/hexanes).



16 S-**4**

Synthesis of (1*R,2*R**,*E*)-*N*-allyl-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (S-4) (from 15).** Allyl bromide (83 μL, 116 mg, 0.959 mmol) was added to a mixture of amine **16** (114 mg, 0.321 mmol), K_2CO_3 (222 mg, 1.61 mmol) and tetrabutylammonium iodide (12 mg, 0.032 mmol) in DMF (0.80 mL). The reaction was stirred at 60 °C for 20 h, poured into H_2O (25 mL), and the aqueous phase extracted with Et_2O (3 × 50 mL). The organic extracts were combined, washed with brine (1 × 25 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/hexanes) to afford amine S-**4** as a colorless liquid (116 mg, 91%).

Data for (1*R,2*R**,*E*)-*N*-allyl-*N*-benzyl-2-methyl-1,6-diphenylhex-3-en-1-amine (S-4):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.12 (m, 15H), 5.79 (dddd, *J* = 17.4, 10.2, 8.6, 3.8 Hz, 1H), 5.62–5.56 (m, 1H), 5.52–5.45 (m, 1H), 5.17–5.07 (m, 2H), 3.90 (d, *J* = 14.0 Hz, 1H), 3.41 (d, *J* = 10.7 Hz, 1H), 3.32–3.26 (m, 1H), 2.96 (d, *J* = 14.0 Hz, 1H), 2.91–2.82 (m, 1H), 2.80–2.69 (m, 2H), 2.56 (dd, *J* = 14.2, 8.6 Hz, 1H), 2.48–2.36 (m, 2H), 0.70 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.56, 140.81, 137.81, 137.33, 136.11, 129.45, 128.94, 128.68, 128.50, 128.26, 128.06, 127.97, 127.08, 126.80, 125.94, 116.89, 68.29, 53.34, 52.41, 38.43, 36.35, 34.86, 19.55; IR (thin film, NaCl) 3026, 2972, 2927, 2810, 1641, 1602, 1584, 1494, 1453, 1417, 1371, 1311, 1256, 1155, 1124, 1072, 1029, 989, 962, 916, 867, 762, 739, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{29}H_{33}N+H^+$ 396.2686, found 396.2688; R_f 0.55 (silica gel, 1:9 EtOAc/hexanes).

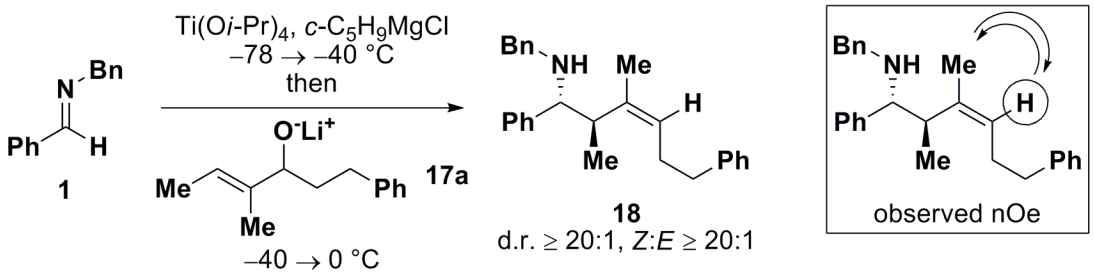


S-**4** S-**2**

Synthesis of (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2) (from 15).** To a solution of amine S-**4** (102 mg, 0.258 mmol) in CH_2Cl_2 (8.7 mL) was added Grubbs II catalyst (2.2 mg, 0.0026 mmol). The reaction was refluxed for 5 h, treated with DMSO (20 μL), then stirred for 24 h at ambient temperature. The mixture was concentrated *in vacuo*, and the crude product was purified by flash column chromatography on silica gel (2% EtOAc/hexanes) to

isolate S-**2** containing minor impurity by TLC (presumably 4-phenyl-1-butene). The mixture was diluted with Et_2O (100 mL), washed with 1 N HCl (25 mL), then the aqueous phase was basified with 3 N NaOH (25 mL) and extracted with Et_2O (100 mL). The organic extract was dried over $MgSO_4$ then concentrated *in vacuo* to afford tetrahydropyridine S-**2** as a white solid (56 mg, 82%).

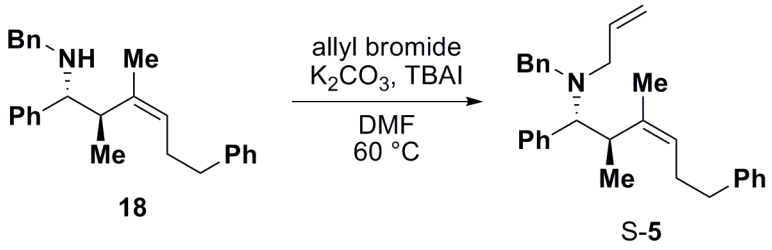
Data for (2*R,3*R**)-1-benzyl-3-methyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-2):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43–7.40 (m, 2H), 7.36–7.32 (m, 2H), 7.28–7.22 (m, 5H), 7.20–7.16 (m, 1H), 5.69–5.63 (m, 2H), 3.71 (d, *J* = 13.1 Hz, 1H), 3.21–3.15 (m, 1H), 3.04 (d, *J* = 8.1 Hz, 1H), 2.86 (d, *J* = 13.1 Hz, 1H), 2.76–2.71 (m, 1H), 2.57–2.49 (m, 1H), 0.84 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.82, 139.75, 131.37, 128.95, 128.84, 128.61, 128.31, 127.44, 126.91, 124.08, 72.25, 60.02, 52.28, 38.95, 19.02; IR (thin film, NaCl) 3027, 2956, 2925, 2872, 2786, 1601, 1493, 1454, 1372, 1361, 1329, 1309, 1282, 1254, 1236, 1197, 1162, 1125, 1102, 1072, 1029, 993, 971, 913, 832, 759, 731, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{19}H_{21}N+H^+$ 264.1747, found 264.1748; R_f 0.53 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (1*R,2*R**,*Z*)-*N*-benzyl-2,3-dimethyl-1,6-diphenylhex-3-en-1-amine (18).** To a solution of imine **1** (125 μL, 131.3 mg, 0.672 mmol) and Ti(O*i*-Pr)$_4$ (300 μL, 288 mg, 1.01 mmol) in Et_2O (2.5 mL) at −78 °C was added *c*-C_5H_9MgCl (2.23 M in Et_2O, 2.01 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 2 h at this temperature. A solution of lithium alkoxide **17a**, prepared by the deprotonation of alcohol **17** (192 mg, 1.01 mmol) in THF (1.0 mL) at −78 °C with *n*-BuLi (2.66 M in hexanes, 1.06 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was warmed to 0 °C over 30 min then stirred at this temperature for 3 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (2→4% EtOAc/hexanes) to afford homoallylic amine **18** as a colorless oil (d.r. ≥ 20:1, *Z*:*E* ≥ 20:1, 133 mg, 54%). No

evidence for minor isomer was observed by ^{1}H NMR. See **18**→S-**5**→S-**6** for the stereochemical assignment.

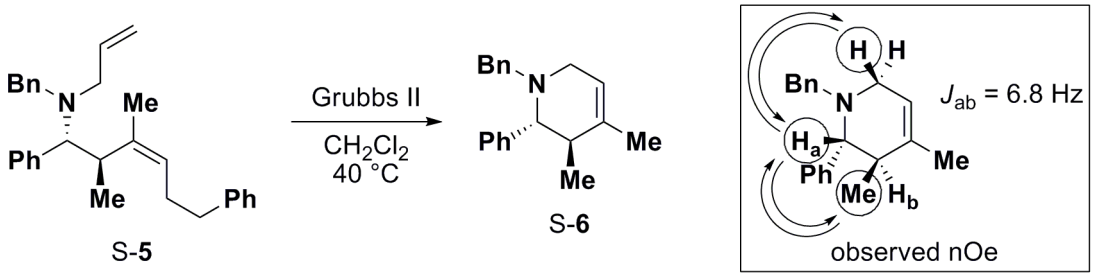
Data for (1*R,2*R**,*Z*)-*N*-benzyl-2,3-dimethyl-1,6-diphenylhex-3-en-1-amine (18):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.14 (m, 15H), 5.35 (app td, *J* = 7.1, 1.3 Hz, 1H), 3.58 (d, *J* = 13.7 Hz, 1H), 3.32 (d, *J* = 13.7 Hz, 1H), 3.31 (d, *J* = 10.0 Hz, 1H), 2.79 (dq, *J* = 10.0, 6.9 Hz, 1H), 2.75–2.60 (m, 2H), 2.51–2.43 (m, 2H), 1.75 (br, 1H), 1.50 (d, *J* = 1.2 Hz, 3H), 0.58 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.52, 142.37, 141.20, 137.71, 128.80, 128.72, 128.48, 128.40, 128.37, 128.34, 128.06, 127.27, 126.85, 125.96, 64.83, 51.55, 41.69, 36.52, 29.52, 18.13, 16.31; IR (thin film, NaCl) 3062, 3026, 2965, 2933, 2855, 1602, 1585, 1494, 1454, 1380, 1373, 1352, 1331, 1304, 1281, 1199, 1096, 1069, 1029, 839, 784, 749, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{27}H_{31}N+H^+$ 370.2529, found 370.2531; R_f 0.53 (silica gel, 1:9 EtOAc/hexanes).



Synthesis of (1*R,2*R**,*Z*)-*N*-allyl-*N*-benzyl-2,3-dimethyl-1,6-diphenylhex-3-en-1-amine (S-5).** Allyl bromide (80 μL, 112 mg, 0.924 mmol) was added to a mixture of amine **18** (114 mg, 0.308 mmol), K_2CO_3 (213 mg, 1.54 mmol) and tetrabutylammonium iodide (11 mg, 0.030 mmol) in DMF (0.75 mL). The reaction was stirred at 60 °C for 20 h, poured into H_2O (25 mL), and the aqueous phase extracted with Et_2O (3 × 50 mL). The organic extracts were combined, washed with brine (1 × 25 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3% EtOAc/hexanes) to afford amine S-**5** as a white solid (109 mg, 86%).

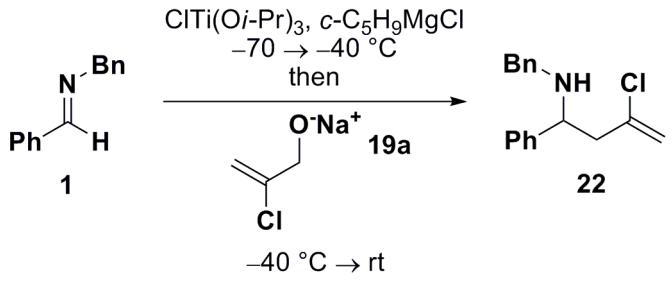
Data for (1*R,2*R**,*Z*)-*N*-allyl-*N*-benzyl-2,3-dimethyl-1,6-diphenylhex-3-en-1-amine (S-5):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.36 (m, 2H), 7.33–7.13 (m, 11H), 7.10–7.08 (m, 2H), 5.82–5.74 (m, 1H), 5.24 (app t, *J* = 6.8 Hz, 1H), 5.12–5.07 (m, 2H), 3.94 (d, *J* = 13.4 Hz, 1H), 3.65 (d, *J* = 11.2 Hz, 1H), 3.37 (dq, *J* = 13.4, 6.7 Hz, 1H), 3.11–3.06 (m, 1H), 2.91 (d, *J* = 13.4 Hz, 1H), 2.60–2.41 (m, 4H), 2.30 (app td, *J* = 14.3, 7.1 Hz, 1H), 1.75 (s, 3H), 0.63 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.57, 140.75, 139.06, 137.85, 137.64, 129.61, 129.16, 128.62, 128.44, 128.16, 128.15, 127.16, 126.82, 125.90, 124.88, 117.18, 66.23, 53.74, 53.58, 36.46, 35.89, 29.89, 18.60, 17.72; IR (thin film, NaCl) 3026, 2964, 2931, 2813, 1641, 1602, 1494, 1453, 1418, 1374, 1331, 1259, 1156, 1120, 1098, 1074, 1029, 998, 986, 919, 868, 844, 761, 740,

700 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{30}H_{35}N+H^+$ 410.2842, found 410.2844; R_f 0.59 (silica gel, 1:9 EtOAc/hexanes).



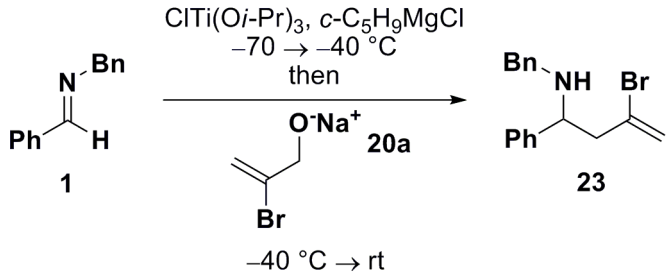
Synthesis of (2*R,3*R**)-1-benzyl-3,4-dimethyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-6).** To a solution of amine S-**5** (93 mg, 0.227 mmol) in CH_2Cl_2 (7.7 mL) was added Grubbs II catalyst (2.0 mg, 0.0024 mmol). The reaction was refluxed for 20 h, treated with DMSO (20 μL), then stirred for 24 h at ambient temperature. The mixture was concentrated *in vacuo*, and the crude product was purified by flash column chromatography on silica gel (1→2% EtOAc/hexanes) to isolate S-**6** containing minor impurity by TLC (presumably 4-phenyl-1-butene). The mixture was diluted with Et_2O (100 mL), washed with 1 N HCl (25 mL), then the aqueous phase was basified with 3 N NaOH (25 mL) and extracted with Et_2O (100 mL). The organic extract was dried over $MgSO_4$ then concentrated *in vacuo* to afford tetrahydropyridine S-**6** as a white solid (51 mg, 81%).

Data for (2*R,3*R**)-1-benzyl-3,4-dimethyl-2-phenyl-1,2,3,6-tetrahydropyridine (S-6):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.32 (m, 4H), 7.29–7.24 (m, 5H), 7.21–7.17 (m, 1H), 5.43–5.40 (m, 1H), 3.59 (d, *J* = 13.1 Hz, 1H), 3.15 (d, *J* = 6.8 Hz, 1H), 3.08–3.01 (m, 1H), 2.95 (d, *J* = 13.1 Hz, 1H), 2.80–2.73 (m, 1H), 2.40–2.32 (m, 1H), 1.72 (s, 3H), 0.97 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.55, 139.73, 136.55, 129.03, 128.98, 128.53, 128.32, 127.38, 126.92, 119.83, 71.66, 60.04, 51.45, 42.00, 21.27, 17.32; IR (thin film, NaCl) 3026, 2966, 2933, 2876, 2788, 1601, 1585, 1493, 1451, 1419, 1374, 1329, 1312, 1237, 1137, 1098, 1068, 1048, 1029, 1000, 977, 928, 909, 876, 836, 801, 781, 754, 702 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{20}H_{23}N+H^+$ 278.1903, found 278.1904; R_f 0.55 (silica gel, 1:9 EtOAc/hexanes).



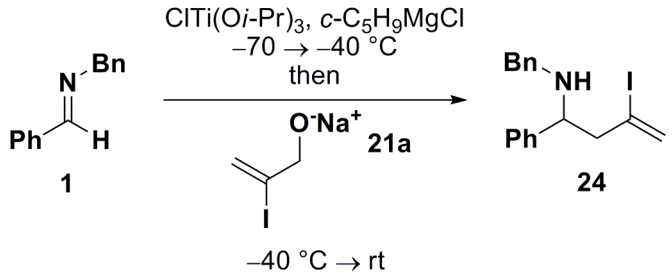
Synthesis of (±)-*N*-benzyl-3-chloro-1-phenylbut-3-en-1-amine (22). To a solution of imine **1** (92 μL, 96 mg, 0.493 mmol) in Et_2O (2.0 mL) at room temperature was added $ClTi(O\textit{i}\text{-}Pr)_3$ (1.0 M in hexanes, 0.616 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 1.23 mmol) was added in a drop-wise manner. The mixture was warmed to –40 °C over 20 min and stirred for 1.5 h at this temperature. A solution of sodium alkoxide **19a**, prepared by the deprotonation of alcohol **19** (59 μL, 68 mg, 0.740 mmol) in THF (2.0 mL) at 0 °C with NaH (60% dispersion in mineral oil, 32 mg, 0.925 mmol) for 30 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (2.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5→7% EtOAc/hexanes) to afford homoallylic amine **22** as a colorless oil (79 mg, 59%).

Data for (±)-*N*-benzyl-3-chloro-1-phenylbut-3-en-1-amine (22): ^1H NMR (500 MHz, $CDCl_3$) δ 7.40–7.21 (m, 10H), 5.18 (d, J = 1.1 Hz, 1H), 5.11 (s, 1H), 4.01 (dd, J = 8.7, 5.2 Hz, 1H), 3.67 (d, J = 13.2 Hz, 1H), 3.53 (d, J = 13.2 Hz, 1H), 2.67 (dd, J = 14.2, 8.7 Hz, 1H), 2.57 (dd, J = 14.2, 5.1 Hz), 1.70 (s (broad), 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 140.5, 139.8, 128.7, 128.6, 128.3, 127.6, 127.5, 127.1, 115.3, 59.5, 51.8, 48.7; IR (thin film, NaCl) 3329, 3062, 3027, 2915, 2837, 1622, 1453, 1139, 734, 699 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{17}H_{18}ClN+H^+$ 272.1, found 272.1.



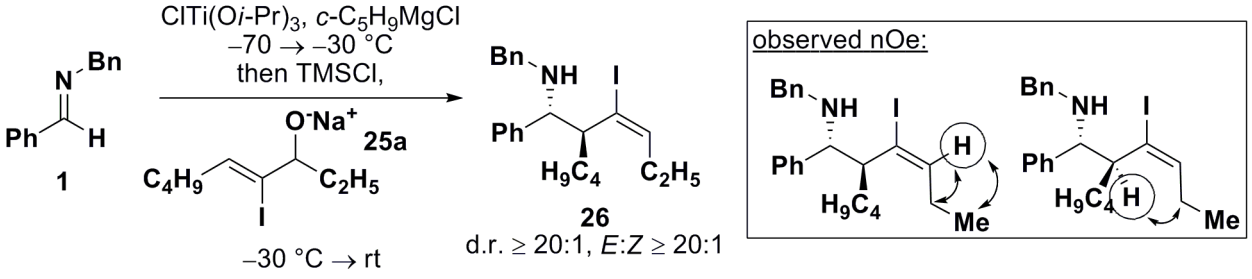
Synthesis of (±)-*N*-benzyl-3-bromo-1-phenylbut-3-en-1-amine (23). To a solution of imine **1** (92 μL, 96 mg, 0.493 mmol) in Et_2O (2.0 mL) at room temperature was added $ClTi(O\textit{i}\text{-}Pr)_3$ (1.0 M in hexanes, 0.616 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 1.23 mmol) was added in a drop-wise manner. The mixture was warmed to –40 °C over 20 min and stirred for 1.5 h at this temperature. A solution of sodium alkoxide **20a**, prepared by the deprotonation of alcohol **20** (100 mg, 0.740 mmol) in THF (2.0 mL) at 0 °C with NaH (60% dispersion in mineral oil, 32 mg, 0.925 mmol) for 30 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (2.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5→7% EtOAc/hexanes) to afford homoallylic amine **23** as a colorless oil (94 mg, 61%).

Data for (±)-*N*-benzyl-3-bromo-1-phenylbut-3-en-1-amine (23): ^1H NMR (500 MHz, $CDCl_3$) δ 7.44–7.16 (m, 10H), 5.55 (s, 1H), 5.43 (d, J = 1.6 Hz, 1H), 4.01 (dd, J = 8.6, 5.1 Hz, 1H), 3.67 (d, J = 13.2 Hz, 1H), 3.54 (d, J = 13.2 Hz, 1H), 2.73 (dd, J = 14.3, 8.6 Hz, 1H), 2.66 (dd, J = 14.3, 5.1 Hz, 1H), 1.68 (s (broad), 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.9, 140.5, 131.2, 128.7, 128.6, 128.4, 127.6, 127.6, 127.1, 119.9, 60.1, 51.8, 50.7; IR (thin film, NaCl) 3026, 2907, 2836, 1629, 1453, 1129, 892, 700 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{17}H_{18}BrN+H^+$ 316.1, 318.1, found 316.1, 318.1.



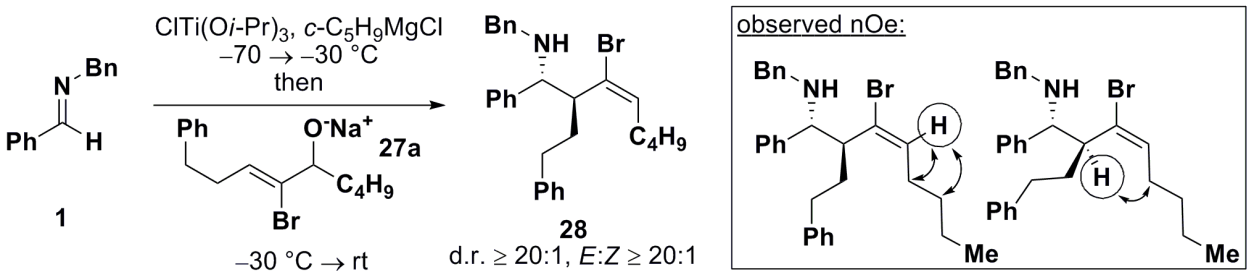
Synthesis of (±)-*N*-benzyl-3-iodo-1-phenylbut-3-en-1-amine (24). To a solution of imine **1** (92 μL, 96 mg, 0.493 mmol) in Et_2O (2.0 mL) at room temperature was added $ClTi(O\textit{i}\text{-}Pr)_3$ (1.0 M in hexanes, 0.616 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 1.23 mmol) was added in a drop-wise manner. The mixture was warmed to –40 °C over 20 min and stirred for 1.5 h at this temperature. A solution of sodium alkoxide **21a**, prepared by the deprotonation of alcohol **21** (135 mg, 0.740 mmol) in THF (2.0 mL) at 0 °C with NaH (60% dispersion in mineral oil, 32 mg, 0.925 mmol) for 30 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (2.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5→7% EtOAc/hexanes) to afford homoallylic amine **24** as a colorless oil (108 mg, 60%).

Data for (±)-*N*-benzyl-3-iodo-1-phenylbut-3-en-1-amine (24): ^1H NMR (500 MHz, $CDCl_3$) δ 7.45–7.15 (m, 10H), 6.03 (d, J = 1.2 Hz, 1H), 5.74 (d, J = 1.2 Hz, 1H), 3.93 (dd, J = 7.7, 6.0 Hz, 1H), 3.66 (d, J = 13.2 Hz, 1H), 3.53 (d, J = 13.2 Hz, 1H), 2.67–2.55 (m, 2H), 1.64 (s (broad), 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 140.5, 128.8, 128.7, 128.6, 128.4, 127.7, 127.6, 127.1, 108.5, 61.0, 54.2, 51.8; IR (thin film, NaCl) 3026, 2900, 2833, 1613, 1493, 1125, 759, 669 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{17}H_{18}IN+H^+$ 364.1, found 364.1.



Synthesis of (1*R,2*S**,*E*)-*N*-benzyl-2-butyl-3-iodo-1-phenylhex-3-en-1-amine (26).** To a solution of imine **1** (250 μL, 260 mg, 1.34 mmol) in toluene (2.8 mL) at room temperature was added $ClTi(O\textit{i}\text{-}Pr)_3$ (1.0 M in hexanes, 1.40 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 2.80 mmol) was added in a drop-wise manner. The mixture was warmed to –30 °C over 30 min and stirred for 2 h at this temperature. Then freshly distilled TMSCl (160 μL, 137 mg, 1.27 mmol) was added and the reaction stirred at –30 °C for an additional 1 h. A solution of sodium alkoxide **25a**, prepared by the deprotonation of alcohol **25** (90 mg, 0.335 mmol) in THF (2.0 mL) at 0 °C with NaH (60% dispersion in mineral oil, 20 mg, 0.502 mmol) for 30 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –30 °C via Teflon cannula. An additional 3 mL of toluene was added to facilitate stirring. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (5.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3→4% EtOAc/hexanes) to afford homoallylic amine **26** as a yellow oil (d.r. ≥ 20:1, *E*:*Z* ≥ 20:1, 79 mg, 53%). A portion of the product was purified a second time by flash column chromatography on silica gel (3% EtOAc/hexanes) to yield analytically pure **26**. No evidence for minor isomer was observed by ^1H NMR.

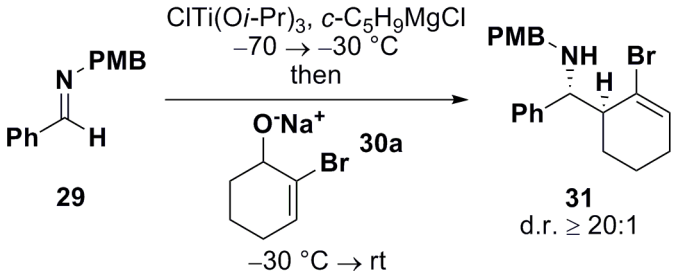
Data for (1*R,2*S**,*E*)-*N*-benzyl-2-butyl-3-iodo-1-phenylhex-3-en-1-amine (26):** ^1H NMR (500 MHz, $CDCl_3$) δ 7.42–7.02 (m, 10H), 6.44 (t, *J* = 7.5 Hz, 1H), 3.46 (d, *J* = 13.4 Hz, 1H), 3.34 (d, *J* = 13.4 Hz, 1H), 3.27 (d, *J* = 9.3 Hz, 1H), 2.28–2.09 (m, 2H), 1.94–1.87 (m 1H), 1.77 (s (broad), 1H), 1.14–0.90 (m, 7H), 0.83–0.59 (m, 5H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.6, 142.0, 140.9, 129.3, 128.5, 128.4, 128.4, 127.6, 126.9, 110.6, 66.4, 51.8, 50.2, 31.1, 29.2, 25.6, 22.6, 14.1, 14.0; IR (thin film, NaCl) 3026, 2958, 2932, 2871, 2858, 1455, 1132, 756, 700 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{23}H_{30}IN+H^+$ 448.1, found 448.2.



Synthesis of (1*R,2*S**,*E*)-*N*-benzyl-3-bromo-2-phenethyl-1-phenyloct-3-en-1-amine (28).** To

a solution of imine **1** (1.17 mL, 1.23 g, 6.32 mmol) in toluene (25 mL) at room temperature was added ClTi(O*i*-Pr)$_3$ (1.0 M in hexanes, 6.63 mmol). The reaction was then cooled to −70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 13.27 mmol) was added in a drop-wise manner. The mixture was warmed to −30 °C over 30 min and stirred for 2 h at this temperature. A solution of sodium alkoxide **27a**, prepared by the deprotonation of alcohol **27** (424 mg, 1.58 mmol) in THF (5.0 mL) at 0 °C with NaH (60% dispersion in mineral oil, 79 mg, 1.97 mmol) for 30 min, was added in a drop-wise manner to the brown solution of imine−Ti complex at −30 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (10 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (100 mL) and extracted with Et_2O (3 × 70 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (3→5% EtOAc/hexanes) to afford homoallylic amine **28** as a yellow oil (d.r. ≥ 20:1, *E*:*Z* ≥ 20:1, 420 mg, 56%). A portion of the product was purified a second time by flash column chromatography on silica gel (3% EtOAc/hexanes) to yield analytically pure **28**. No evidence for minor isomer was observed by ^{1}H NMR.

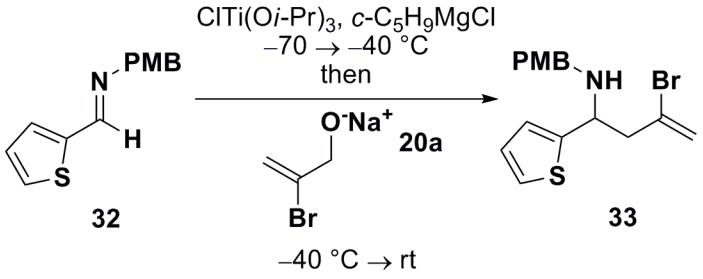
Data for (1*R,2*S**,*E*)-*N*-benzyl-3-bromo-2-phenethyl-1-phenyloct-3-en-1-amine (28):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–6.99 (m, 13H), 6.89 (d, *J* = 7.5 Hz, 2H), 6.13 (t, *J* = 7.5 Hz, 1H), 3.56–3.43 (m, 2H), 3.33 (d, *J* = 13.5 Hz, 1H), 2.69 (td, *J* = 10.7, 3.5 Hz, 1H), 2.54–2.36 (m, 1H), 2.18–1.89 (m, 3H), 1.81 (s (broad), 1H), 1.65–1.55 (m, 1H), 1.37–1.12 (m, 5H), 0.80 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.0, 141.9, 140.9, 138.3, 129.0, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 127.7, 126.9, 125.9, 65.0, 51.6, 49.4, 33.2, 32.0, 31.5, 30.0, 22.6, 14.1; IR (thin film, NaCl) 3026, 2926, 1642, 1494, 1453, 734, 698 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{29}H_{34}BrN+H^+$ 476.2, 478.2, found 476.3, 478.3.



Synthesis of (*R)-1-((*S**)-2-bromocyclohex-2-enyl)-*N*-(4-methoxybenzyl)-1-phenylmethanamine (31).** To a solution of imine **29** (320 μL, 360 mg, 1.60 mmol) in toluene (6.4 mL) at room temperature was added ClTi(O*i*-Pr)$_3$ (1.0 M in hexanes, 1.68 mmol). The reaction was then

cooled to −70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 3.36 mmol) was added in a drop-wise manner. The mixture was warmed to −30 °C over 30 min and stirred for 2 h at this temperature. A solution of sodium alkoxide **30a**, prepared by the deprotonation of alcohol **30** (70 mg, 0.400 mmol) in THF (1.5 mL) at 0 °C with NaH (60% dispersion in mineral oil, 20 mg, 0.500 mmol) for 30 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at −30 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (4.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford homoallylic amine **31** as a colorless oil (d.r. ≥ 20:1, 82 mg, 53%). A portion of the product was purified a second time by flash column chromatography on silica gel (3% EtOAc/hexanes) to yield analytically pure **31**. No evidence for minor isomer was observed by ^{1}H NMR.

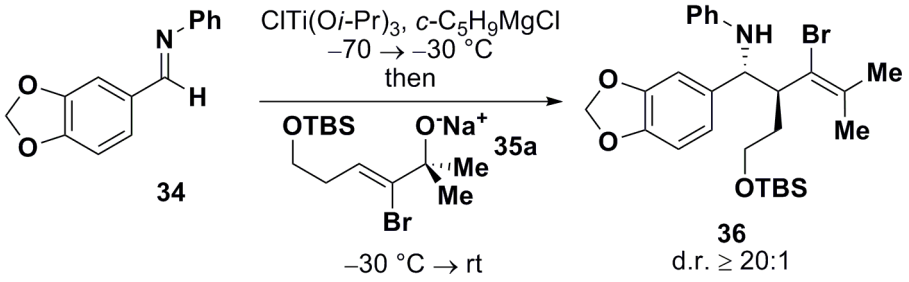
Data for (*R)-1-((*S**)-2-bromocyclohex-2-enyl)-*N*-(4-methoxybenzyl)-1-phenylmethanamine (31):** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (app d, *J* = 7.2 Hz, 2H), 7.32 (app t, *J* = 7.3 Hz, 2H), 7.28–7.21 (m, 3H), 6.90–6.81 (m, 2H), 6.14 (dd, *J* = 4.1, 2.9 Hz, 1H), 4.35 (d, *J* = 4.2 Hz, 1H), 3.80 (s, 3H), 3.67 (d, *J* = 12.9 Hz, 1H), 3.59 (d, *J* = 12.9 Hz, 1H), 2.75–2.68 (m 1H), 1.96–1.24 (m, 5H), 1.28–1.19 (m, 1H), 0.82–0.67 (m, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 140.9, 133.1, 132.9, 129.5, 128.2, 128.2, 127.2, 125.5, 114.0, 63.5, 55.5, 51.6, 48.4, 27.7, 25.2, 18.5; IR (thin film, NaCl) 2935, 2833, 1512, 1452, 1246, 1036, 807, 704 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{21}H_{24}BrNO+H^+$ 386.1114, 388.1094, found 386.1097, 388.1078.



Synthesis of (±)-*N*-(4-methoxybenzyl)-3-bromo-1-(thiophen-2-yl)but-3-en-1-amine (33). To a solution of imine **33** (113 mg, 0.493 mmol) in Et_2O (2.0 mL) at room temperature was added $ClTi(O$*i*-$Pr)_3$ (1.0 M in hexanes, 0.616 mmol). The reaction was then cooled to −70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 1.23 mmol) was added in a drop-wise manner. The mixture was warmed to −40 °C over 20 min and stirred for 1.5 h at this temperature. A solution of sodium

alkoxide **20a**, prepared by the deprotonation of alcohol **20** (100 mg, 0.740 mmol) in THF (2.0 mL) at 0 °C with NaH (60% dispersion in mineral oil, 32 mg, 0.925 mmol) for 30 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (4.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (7→9% EtOAc/hexanes) to afford homoallylic amine **33** as a yellow oil (86 mg, 53%). A portion of the product was purified a second time by flash column chromatography on silica gel (3% EtOAc/hexanes) to yield analytically pure **33**.

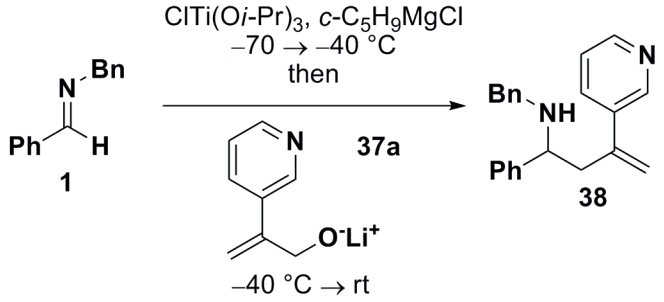
Data for (±)-*N*-(4-methoxybenzyl)-3-bromo-1-(thiophen-2-yl)but-3-en-1-amine (33): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30–7.24 (m, 1H), 7.24–7.15 (m, 2H), 7.00–6.95 (m, 2H), 6.90–6.83 (m, 2H), 5.60 (s, 1H), 5.47 (d, *J* = 1.6 Hz, 1H), 4.34 (dd, *J* = 8.4, 5.4 Hz, 1H), 3.80 (s, 3H), 3.75 (d, *J* = 13.0 Hz, 1H), 3.57 (d, *J* = 13.0 Hz, 1H), 2.84 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.75 (dd, *J* = 14.3, 4.6 Hz, 1H), 1.71 (s (broad), 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 148.0, 132.3, 130.5, 129.6, 126.7, 125.0, 124.6, 120.2, 114.0, 55.7, 55.5, 51.2, 51.0; IR (thin film, NaCl) 2833, 1611, 1512, 1247, 1036, 825, 701 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{16}H_{18}BrNOS+H^+$ 352.0365, 354.0345, found 352.0363, 354.0341.



Synthesis of *N*-((1*R,2*S**)-1-(benzo[*d*][1,3]dioxol-5-yl)-3-bromo-2-(2-(*tert*-butyldimethylsilyloxy)ethyl)-4-methylpent-3-enyl)aniline (36).** To a solution of imine **34** (279 mg, 1.24 mmol) in toluene (5.0 mL) at room temperature was added ClTi(O*i*-Pr)$_3$ (1.0 M in hexanes, 1.30 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 2.60 mmol) was added in a drop-wise manner. The mixture was warmed to –30 °C over 30 min and stirred for 2 h at this temperature. A solution of sodium alkoxide **35a**, prepared by the deprotonation of alcohol **35** (100 mg, 0.310 mmol) in THF (1.5 mL) at 0 °C with NaH (60% dispersion in mineral oil, 39 mg, 0.387 mmol) for 30 min, was added in a drop-wise manner to the brown solution of

imine–Ti complex at –30 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by the addition of a saturated aqueous solution of NH_4Cl (4.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford homoallylic amine **36** as a white solid (d.r. ≥ 20:1, 85 mg, 52%). No evidence for minor isomer was observed by ^{1}H NMR.

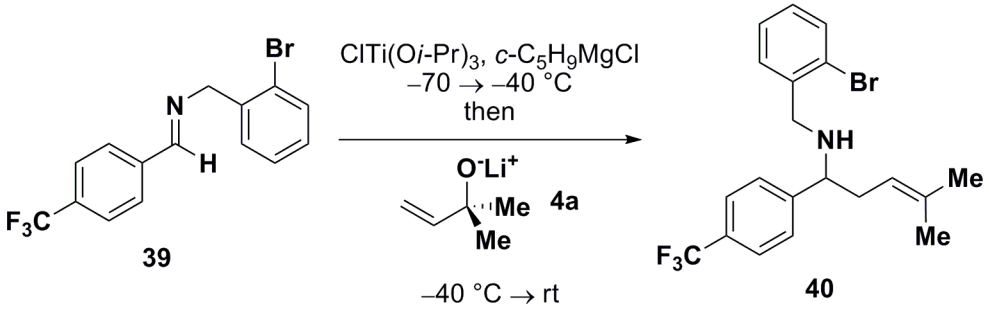
Data for *N*-((1*R,2*S**)-1-(benzo[*d*][1,3]dioxol-5-yl)-3-bromo-2-(2-(*tert*-butyldimethylsilyl-oxy)ethyl)-4-methylpent-3-enyl)aniline (36):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (dd, *J* = 8.4, 7.6 Hz, 2H), 6.92 (d, *J* = 1.6 Hz, 1H), 6.89 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.77 (d, *J* = 7.9 Hz, 2H), 6.64 (t, *J* = 7.3 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 2H), 5.92 (s, 1H), 4.26 (s, 1H), 4.16 (d, *J* = 9.1 Hz, 1H), 3.49 (ddd, *J* = 9.9, 5.9, 3.7 Hz, 1H), 3.36 (ddd, *J* = 10.1, 4.5, 4.5 Hz, 1H), 3.14 (td, *J* = 10.4, 3.4 Hz, 1H), 1.99 (s, 3H), 1.91 (s, 3H), 1.76–1.67 (m, 1H), 1.48–1.39 (m, 1H), 0.83 (s, 9H), –0.04 (s, 3H), –0.09 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.2, 148.0, 146.9, 137.0, 135.8, 129.1, 124.0, 121.7, 117.8, 114.2, 108.2, 108.0, 101.1, 61.7, 60.2, 47.2, 33.6, 26.1, 26.0, 21.8, 18.3, –5.2; IR (thin film, NaCl) 3395, 2954, 1602, 1502, 1246, 1040, 940, 836, 775, 748, 691 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{27}H_{38}BrNO_3Si+H^+$ 532.2, 534.2, found 532.4, 534.3.



Synthesis of (±)-*N*-benzyl-1-phenyl-3-(pyridin-3-yl)but-3-en-1-amine (38). To a solution of imine **1** (92 μL, 96 mg, 0.493 mmol) in Et_2O (2.0 mL) at room temperature was added $ClTi(O$*i*$-Pr)_3$ (1.0 M in hexanes, 0.740 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.42 M in Et_2O, 1.48 mmol) was added in a drop-wise manner. The mixture was warmed to –40 °C over 20 min and stirred for 1.5 h at this temperature. This solution of the brown imine–Ti complex at –40 °C was rapidly added via Teflon cannula (< 30 s) to a solution of lithium alkoxide **37a**, prepared by the deprotonation of alcohol **37** (100 mg, 0.740 mmol) in THF (1.5 mL) at –78 °C with *n*-BuLi (2.50 M in hexanes, 0.925 mmol) for 15 min; the solution of the lithium alkoxide was neon orange in color and contained a precipitate. The mixture was then

warmed to –40 °C over 1 min and allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl (2.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (50→60% EtOAc/hexanes) to afford homoallylic amine **38** as a yellow oil (85 mg, 55%).

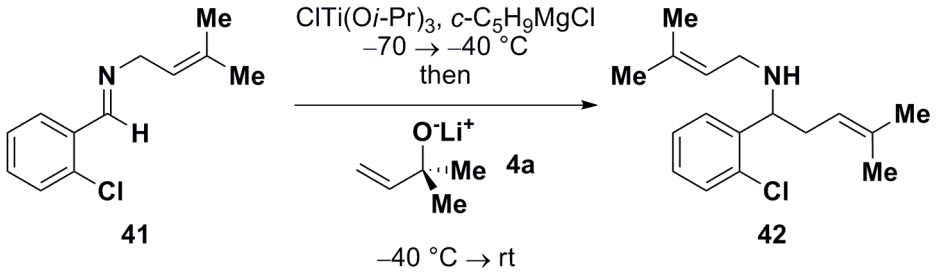
Data for (±)-*N*-benzyl-1-phenyl-3-(pyridin-3-yl)but-3-en-1-amine (38): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 1.7 Hz, 1H), 8.45 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.58–7.48 (m, 1H), 7.33–7.01 (m, 11H), 5.27 (s, 1H), 5.09 (s, 1H), 3.66–3.50 (m, 2H), 3.32 (d, *J* = 13.3 Hz, 1H), 2.85–2.70 (m, 2H), 1.68 (s (broad), 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.9, 148.0, 143.7, 143.0, 140.5, 136.3, 133.7, 128.7, 128.5, 128.2, 127.5, 127.4, 127.0, 123.3, 117.3, 60.2, 51.6, 44.9; IR (thin film, NaCl) 3026, 2927, 2838, 1626, 1453, 1119, 908, 700 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{22}H_{22}N_2$+H$^+$ 315.2, found 315.2.



Synthesis of (±)-*N*-(2-bromobenzyl)-1-(4-(trifluoromethyl)phenyl)-4-methylpent-3-en-1-amine (40). To a solution of imine **39** (170 mg, 0.500 mmol) in Et_2O (3.3 mL) at room temperature was added $ClTi(O$*i*$-Pr)_3$ (1.0 M in hexanes, 0.750 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 1.50 mmol) was added in a drop-wise manner. The mixture was warmed to –40 °C over 20 min and stirred for 1.5 h at this temperature. A solution of lithium alkoxide **4a**, prepared by the deprotonation of alcohol **4** (65 mg, 0.750 mmol) in THF (1.5 mL) with *n*-BuLi (2.50 M in hexanes, 0.925 mmol) at –78 °C and warming to room temperature over 30 min; was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl (4.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over

$MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5→7.5% EtOAc/hexanes) to afford homoallylic amine **40** as a colorless oil (137 mg, 67%).

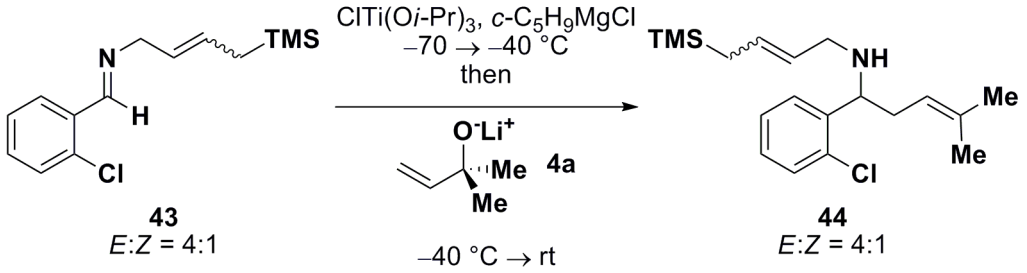
Data for (±)-*N*-(2-bromobenzyl)-1-(4-(trifluoromethyl)phenyl)-4-methylpent-3-en-1-amine (40): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 2H), 7.56–7.47 (m, 3H), 7.28–7.22 (m, 1H), 7.20 (dd, *J* = 7.5, 7.1 Hz, 1H), 7.12 (td, *J* = 7.7, 1.8 Hz, 1H), 5.06–5.00 (m, 1H), 3.72 (d, *J* = 13.9 Hz, 1H), 3.66–3.53 (m, 2H), 2.42–2.31 (m, 1H), 2.27–2.18 (m, 1H), 2.14 (s (broad), 1H), 1.69 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.7, 139.9, 135.6, 133.1, 130.8, [129.8, 129.6, 129.3, 129.0, F_3C-C], 128.9, 127.9, 127.5, [127.8, 125.6, 123.5, 121.3, F_3C-], [125.51, 125.48, 125.45, 125.42, F_3C-C-CH], 124.2, 120.6, 60.0, 51.9, 37.8, 26.0, 18.2; IR (thin film, NaCl) 2972, 2915, 1440, 1325, 1164, 1125, 1067 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{20}H_{21}BrF_3N+H^+$ 412.1, 414.1, found 412.4, 414.4.



Synthesis of (±)-1-(2-chlorophenyl)-4-methyl-*N*-(3-methylbut-2-enyl)pent-3-en-1-amine (42). To a solution of imine **41** (103 mg, 0.500 mmol) in Et_2O (3.3 mL) at room temperature was added $ClTi(O$*i*$-Pr)_3$ (1.0 M in hexanes, 0.750 mmol). The reaction was then cooled to −70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 1.50 mmol) was added in a drop-wise manner. The mixture was warmed to –40 °C over 20 min and stirred for 1.5 h at this temperature. A solution of lithium alkoxide **4a**, prepared by the deprotonation of alcohol **4** (65 mg, 0.750 mmol) in THF (1.5 mL) with *n*-BuLi (2.50 M in hexanes, 0.925 mmol) at −78 °C and warming to room temperature over 30 min; was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl (4.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5→10% EtOAc/hexanes) to afford homoallylic amine **42** as a yellow oil (110 mg, 79%).

Data for (±)-1-(2-chlorophenyl)-4-methyl-*N*-(3-methylbut-2-enyl)pent-3-en-1-amine (42): ^{1}H

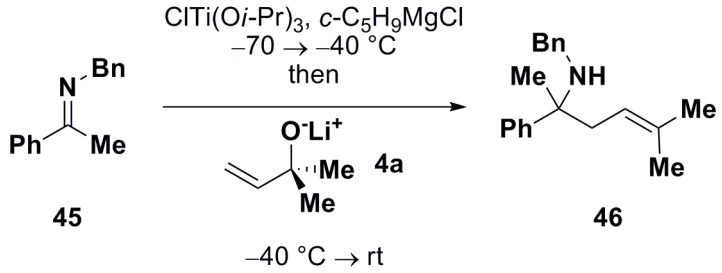
NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 7.7 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.28–7.21 (m, 1H), 7.18–7.08 (m, 1H), 5.22 (dd, *J* = 6.9, 5.6 Hz, 1H), 5.15–5.05 (m, 1H), 4.21–4.16 (m, 1H), 3.00 (d, *J* = 6.9 Hz, 2H), 2.42–2.20 (m, 2H), 1.69 (s, 6H), 1.55 (s, 3H), 1.50–1.36 (m, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.6, 135.0, 134.6, 133.9, 129.6, 128.3, 127.8, 127.0, 123.2, 120.8, 58.8, 45.4, 35.7, 26.1, 25.9, 18.1, 18.0; IR (thin film, NaCl) 2968, 2914, 2855, 1442, 1376, 1104, 1046, 1033, 754 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{17}H_{24}ClN+H^+$ 278.2, found 278.4.



Synthesis of (±)-1-(2-chlorophenyl)-4-methyl-*N*-(4-(trimethylsilyl)but-2-enyl)pent-3-en-1-amine (44). To a solution of imine **43** (*E*:*Z* = 4:1, 132 mg, 0.500 mmol) in Et_2O (3.3 mL) at room temperature was added $ClTi(O$*i*$-Pr)_3$ (1.0 M in hexanes, 0.750 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 1.50 mmol) was added in a drop-wise manner. The mixture was warmed to –40 °C over 20 min and stirred for 1.5 h at this temperature. A solution of lithium alkoxide **4a**, prepared by the deprotonation of alcohol **4** (65 mg, 0.750 mmol) in THF (1.5 mL) with *n*-*B*uLi (2.50 M in hexanes, 0.925 mmol) at –78 °C and warming to room temperature over 30 min; was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl (3.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (8→15% EtOAc/hexanes) to afford homoallylic amine **44** as a yellow oil (*E*:*Z* = 4:1, 116 mg, 69%).

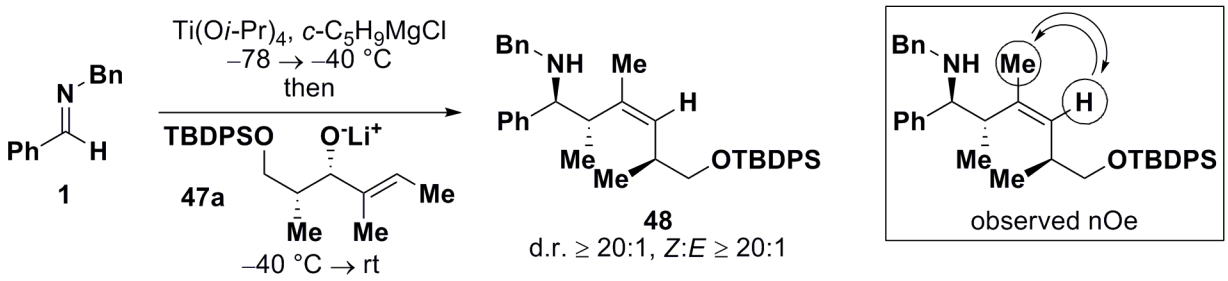
Data for (±)-1-(2-chlorophenyl)-4-methyl-*N*-(4-(trimethylsilyl)but-2-enyl)pent-3-en-1-amine (44): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55–7.53 (m, 1H), 7.32–7.30 (m, 1H), 7.27–7.24 (m, 1H), 7.16–7.13 (m, 1H), 5.52–5.46 (m, 1H), 5.36–5.31 (m, 1H), 5.15–5.11 (m, 1H), 4.22–4.19 (m, 1H), 3.05–3.01 (m, 1H), 2.93–2.89 (m, 1H), 2.38–2.33 (m, 1H), 2.29–2.23 (m, 1H), 1.69 (s, 3H), 1.56 (s, 3H), 1.44–1.38 (m, 3H), –0.01 to –0.05 (m, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.7, 141.6, 135.0, 134.9, 133.9, 133.8, 129.6, 129.2, 128.4, 128.3, 128.2, 127.8, 127.8, 127.0, 127.0,

127.0, 125.8, 120.8, 59.0, 58.4, 50.0, 44.4, 35.7, 26.0, 22.9, 19.0, 18.1, 18.1, –1.1, –1.7; IR (thin film, NaCl) 2954, 2914, 1442, 1248, 1033, 857, 754, 693 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{19}H_{30}ClNSi+H^+$ 336.2, found 336.5.



Synthesis of (±)-*N*-benzyl-5-methyl-2-phenylhex-4-en-2-amine (46). To a solution of ketimine **45** (104 mg, 0.500 mmol) in Et_2O (3.3 mL) at room temperature was added $ClTi(Oi\text{-}Pr)_3$ (1.0 M in hexanes, 0.750 mmol). The reaction was then cooled to –70 °C and *c*-C_5H_9MgCl (2.28 M in Et_2O, 1.50 mmol) was added in a drop-wise manner. The mixture was warmed to –40 °C over 20 min and stirred for 1.5 h at this temperature. A solution of lithium alkoxide **4a**, prepared by the deprotonation of alcohol **4** (65 mg, 0.750 mmol) in THF (1.5 mL) with *n*-BuLi (2.50 M in hexanes, 0.925 mmol) at –78 °C and warming to room temperature over 30 min; was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via Teflon cannula. The mixture was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl (3.0 mL) followed by rapid stirring at room temperature for 15 min. The mixture was then diluted with saturated aqueous $NaHCO_3$ (50 mL) and extracted with Et_2O (3 × 40 mL). The combined organic extracts were washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5→7% EtOAc/hexanes) to afford tertiary carbinolamine amine **46** as a colorless oil (115 mg, 83%).

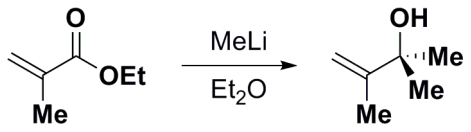
Data for (±)-*N*-benzyl-5-methyl-2-phenylhex-4-en-2-amine (46): ^1H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.35–7.09 (m, 8H), 5.01 (t, *J* = 7.4 Hz, 1H), 3.51 (d, *J* = 12.6 Hz, 1H), 3.38 (d, *J* = 12.6 Hz, 1H), 2.49–2.32 (m, 2H), 1.63 (s, 3H), 1.52 (s (broad), 4H), 1.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.2, 141.7, 134.8, 128.5, 128.3, 128.3, 126.9, 126.6, 126.4, 119.9, 59.4, 47.2, 41.9, 26.3, 25.5, 18.2; IR (thin film, NaCl) 3026, 2970, 2912, 2853, 1601, 1494, 1451, 1337, 1028, 763, 700 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{20}H_{25}N+H^+$ 280.2, found 280.2.



Synthesis of (1*S*,2*S*,5*S*,*Z*)-*N*-benzyl-6-(*tert*-butyldiphenylsilyloxy)-2,3,5-trimethyl-1-phenylhex-3-en-1-amine (48). To a solution of imine **1** (100 μL, 105 mg, 0.538 mmol) and Ti(O*i*-Pr)$_4$ (240 μL, 230.4 mg, 0.811 mmol) in Et_2O (2.0 mL) at −78 °C was added *c*-C_5H_9MgCl (2.26 M in Et_2O, 1.63 mmol) in a drop-wise manner. The mixture was warmed to –40 °C over 30 min and stirred for 1 h at this temperature. A solution of lithium alkoxide **47a**, prepared by the deprotonation of alcohol **47** (100 mg, 0.261 mmol) in THF (1.0 mL) at −78 °C with *n*-BuLi (2.47 M in hexanes, 0.272 mmol) followed by warming to 0 °C over 15 min, was added in a drop-wise manner to the brown solution of imine–Ti complex at –40 °C via cannula. The mixture was gradually warmed to room temperature over 2 h then stirred for 6 h. The reaction was quenched by addition of water (1.0 mL) followed by rapid stirring until the precipitate became white in color. The mixture was diluted with saturated aqueous $NaHCO_3$ (20 mL) and extracted with EtOAc (3 × 20 mL). The organic extracts were combined, dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (1→3% EtOAc/hexanes) to afford homoallylic amine **48** as a colorless oil (d.r. ≥ 20:1, *Z*:*E* ≥ 20:1, 105 mg, 72%). No evidence for minor isomer was observed by ^{1}H NMR.

Data for (1*S*,2*S*,5*S*,*Z*)-*N*-benzyl-6-(*tert*-butyldiphenylsilyloxy)-2,3,5-trimethyl-1-phenylhex-3-en-1-amine (48): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66–7.62 (m, 4H), 7.41–7.17 (m, 16H), 5.08 (d, *J* = 9.6 Hz, 1H), 3.60 (d, *J* = 13.8 Hz, 1H), 3.47–3.37 (m, 2H), 3.34 (d, *J* = 13.8 Hz, 1H), 3.29 (d, *J* = 10.0 Hz, 1H), 2.90–2.80 (m, 1H), 2.77–2.70 (m, 1H), 1.77 (br, 1H), 1.47 (s, 3H), 1.07 (d, *J* = 6.5 Hz, 3H), 1.03 (s, 9H), 0.54 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.44, 141.18, 137.21, 135.82, 135.78, 134.26, 134.22, 132.33, 129.71, 129.68, 128.85, 128.40, 128.35, 128.22, 127.77, 127.29, 126.83, 69.09, 64.73, 51.61, 41.95, 35.00, 27.11, 19.51, 18.23, 18.13, 16.59; IR (thin film, NaCl) 3027, 2961, 2931, 2858, 1602, 1590, 1492, 1472, 1454, 1428, 1382, 1361, 1306, 1263, 1192, 1113, 1074, 1028, 1008, 999, 938, 824, 739, 701 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{38}H_{47}NOSi+H^+$ 562.3500, found 562.3475; $[\alpha]_D^{20}$ –6.0 (*c* 1.00, $CHCl_3$); R_f 0.50 (silica gel, 1:9 EtOAc/hexanes).

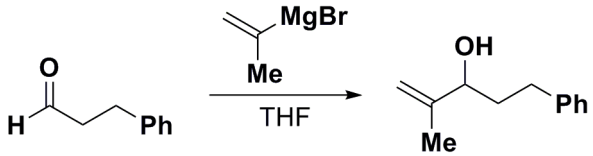
Preparation of Allylic Alcohols and Imines



6

Synthesis of 2,3-dimethylbut-3-en-2-ol (6). A solution of ethyl methacrylate (5.00 mL, 4.58 g, 40.1 mmol) in Et_2O (25 mL) was added drop-wise to MeLi (1.6 M in Et_2O, 88.0 mmol) at –78 °C over a 15 min period. The mixture was warmed to room temperature over 1 h then stirred for additional 16 h. The reaction was cooled to 0 °C and carefully quenched with saturated aqueous NH_4Cl (40 mL). The mixture was diluted with Et_2O (120 mL) and the organic phase was washed with brine (1 × 40 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by fractional distillation (110–111 °C, 760 mm) to afford allylic alcohol **6** as a colorless oil (2.26 g, 56%).

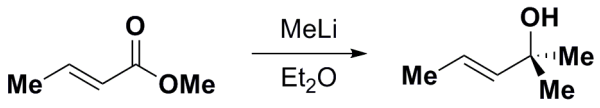
Data for 2,3-dimethylbut-3-en-2-ol (6): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.00–4.98 (m, 1H), 4.77-4.75 (m, 1H), 1.81–1.79 (m, 3H), 1.48 (s, 1H), 1.34 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.15, 108.62, 73.34, 29.06, 19.36; IR (thin film, NaCl) 3355 (br), 3092, 2977, 1644, 1450, 1375, 1281, 1172, 1041, 1010, 961, 934, 901, 870, 859 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_6H_{12}O+H^+$ 101.1, found 101.1.



8

Synthesis of (±)-2-methyl-5-phenylpent-1-en-3-ol (8). A solution of hydrocinnamaldehyde (1.00 mL, 1.02 g, 7.59 mmol) in THF (10 mL) was added drop-wise to isopropenylmagnesium bromide (0.5 M in THF, 9.15 mmol) at 0 °C. The mixture was warmed to room temperature over 30 min then stirred for additional 1 h. The reaction was cooled to 0 °C and carefully quenched with saturated aqueous NH_4Cl (10 mL). The mixture was poured into H_2O (5 mL), layers separated, and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic extract was washed with brine (1 × 30 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10→20% EtOAc/hexanes) to afford allylic alcohol **8** as a colorless oil (1.08 g, 81%).

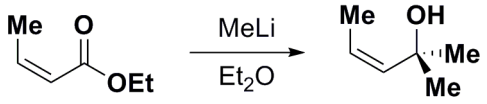
Data for (±)-2-methyl-5-phenylpent-1-en-3-ol (8): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.14 (m, 5H), 4.95–4.94 (m, 1H), 4.86–4.84 (m, 1H), 4.09–4.05 (m, 1H), 2.74–2.67 (m, 1H), 2.65–2.58 (m, 1H), 1.90–1.79 (m, 2H), 1.72 (s, 3H), 1.52 (d, J = 3.3 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.61, 142.20, 128.66, 128.59, 126.04, 111.46, 75.49, 36.78, 32.10, 17.83; IR (thin film, NaCl) 3341 (br), 3027, 2944, 2862, 1650, 1604, 1496, 1454, 1373, 1301, 1154, 1030, 900, 803, 749, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{12}H_{16}O$+Na^+ 199.1093, found 199.1094; R_f 0.22 (silica gel, 1:9 EtOAc/hexanes).



10

Synthesis of (*E*)-2-methylpent-3-en-2-ol (10). A solution of methyl crotonate (7.70 mL, 7.27 g, 72.6 mmol) in Et_2O (45 mL) was added drop-wise to MeLi (1.6 M in Et_2O, 160 mmol) at –78 °C over a 10 min period. The mixture was warmed to room temperature over 1 h and stirred for additional 16 h. The reaction was cooled to 0 °C and carefully quenched with saturated aqueous NH_4Cl (80 mL). The mixture was diluted with Et_2O (240 mL) and the organic phase was washed with brine (1 × 80 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by fractional distillation (118–119 °C, 760 mm) to afford allylic alcohol **10** as a colorless oil (5.14 g, 71%).

Data for (*E*)-2-methylpent-3-en-2-ol (10): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.68–5.59 (m, 2H), 1.69–1.67 (m, 3H), 1.43 (s, 1H), 1.29 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.30, 122.16, 70.81, 29.94, 17.83; IR (thin film, NaCl) 3340 (br), 3029, 2975, 1675, 1452, 1377, 1293, 1233, 1152, 1083, 992, 968, 896, 791, 770 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_6H_{12}O$+H^+ 101.1, found 101.1.

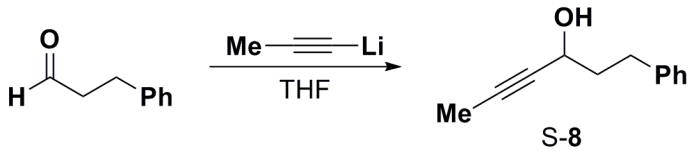


S-**7** **12**

Synthesis of (*Z*)-2-methylpent-3-en-2-ol (12). A solution of ester S-**7** (3.83 g, 33.6 mmol) in Et_2O (20 mL) was added drop-wise to MeLi (1.6 M in Et_2O, 73.6 mmol) at –78 °C over a 30 min period. The mixture was warmed to room temperature over 1 h then stirred for additional 16 h. The reaction was cooled to 0 °C and carefully quenched with saturated aqueous NH_4Cl (40 mL).

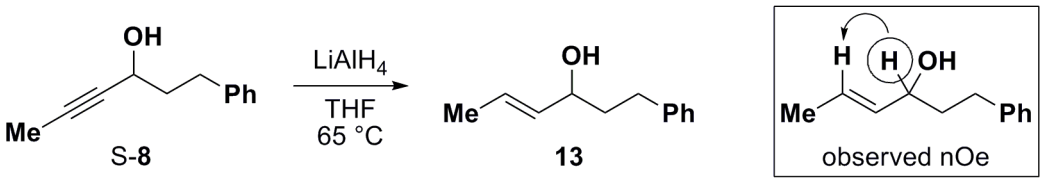
The mixture was diluted with Et_2O (120 mL) and the organic phase was washed with brine (1 × 40 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by fractional distillation (114–115 °C, 760 mm) to afford allylic alcohol **12** as a colorless oil (1.76 g, 52%).

Data for (*Z*)-2-methylpent-3-en-2-ol (12): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.52–5.47 (m, 1H), 5.42 (dq, *J* = 11.8, 7.0 Hz, 1H), 1.83 (dd, *J* = 7.0, 1.5 Hz, 3H), 1.51 (d, *J* = 1.1 Hz, 1H), 1.37 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.95, 125.27, 71.88, 31.13, 14.18; IR (thin film, NaCl) 3356 (br), 3014, 2974, 2931, 1658, 1464, 1447, 1364, 1276, 1210, 1182, 1148, 967, 941, 881, 769, 710 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_6H_{12}O$+H^+ 101.1, found 101.1.



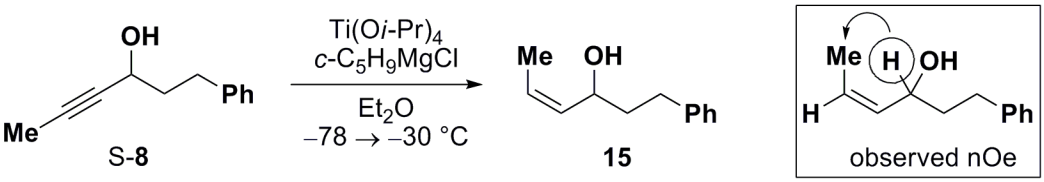
Synthesis of (±)-1-phenylhex-4-yn-3-ol (S-8). To a solution of 1-bromopropene (8.80 mL, 12.4 g, 103 mmol) in THF (70 mL) at −78 °C was added *n*-BuLi (2.56 M in Et_2O, 151 mmol) drop-wise over a 30 min period. The resulting white suspension was stirred for 2 h at −78 °C. A solution of hydrocinnamaldehyde (9.00 mL, 9.17 g, 68.3 mmol) in THF (35 mL) was added to the *in situ* generated 1-propynyllithium[18] drop-wise over 10 min, and the mixture was stirred for additional 30 min at −78 °C. The reaction was quenched with saturated aqueous NH_4Cl (35 mL), warmed to room temperature, then poured into a mixture of Et_2O and H_2O (70 mL each). The layers were separated, and the aqueous phase was extracted with Et_2O (3 × 70 mL). The combined organic extract was washed with brine (2 × 70 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10→20% EtOAc/hexanes) to afford propargylic alcohol S-**8** as a colorless oil (10.7 g, 90%).

Data for (±)-1-phenylhex-4-yn-3-ol (S-8): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.22 (m, 5H), 4.40–4.38 (m, 1H), 2.84 (app t, *J* = 7.9 Hz, 2H), 2.10–1.98 (m, 2H), 1.92 (d, *J* = 2.1 Hz, 3H), 1.82 (br, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.66, 128.69, 128.61, 126.13, 81.65, 80.35, 62.27, 39.75, 31.64, 3.78; IR (thin film, NaCl) 3322 (br), 3027, 2920, 2859, 2229, 1717, 1670, 1603, 1584, 1496, 1454, 1336, 1176, 1136, 1055, 1030, 916, 847, 801, 781, 751, 700 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{12}H_{14}O$+Na^+ 197.0937, found 197.0937; R_f 0.48 (silica gel, 1:3 EtOAc/hexanes).



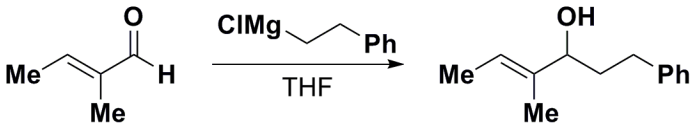
Synthesis of (±)-(*E*)-1-phenylhex-4-en-3-ol (13). A solution of propargylic alcohol S-**8** (1.60 g, 9.18 mmol) in THF (10 mL) was added drop-wise to a suspension of $LiAlH_4$ (700 mg, 18.4 mmol) in THF (25 mL) at 0 °C over a 5 min period. The mixture was warmed to room temperature over 30 min, then refluxed for 24 h. The reaction was cooled to 0 °C, carefully quenched with H_2O (25 mL) and saturated aqueous Na,K-tartrate (25 mL), then stirred at room temperature for 1 h. The mixture was diluted with Et_2O (150 mL) and the organic phase was washed with brine (1 × 50 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10→20% EtOAc/hexanes) to afford a single isomer of allylic alcohol **13** as a colorless oil (1.52 g, 94%).

Data for (±)-(*E*)-1-phenylhex-4-en-3-ol (13): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.14 (m, 5H), 5.66 (dqd, *J* = 15.2, 6.4, 0.8 Hz, 1H), 5.50 (ddq, *J* = 15.3, 7.2, 1.5 Hz, 1H), 4.07–4.02 (m, 1H), 2.73–2.61 (m, 2H), 1.89–1.74 (m, 2H), 1.70–1.68 (m, 3H), 1.45 (d, *J* = 3.5 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.23, 134.26, 128.65, 128.56, 127.40, 125.98, 72.64, 38.96, 31.99, 17.90; IR (thin film, NaCl) 3325 (br), 3027, 2918, 2858, 1673, 1603, 1496, 1454, 1378, 1306, 1178, 1119, 1053, 1030, 1006, 966, 923, 747, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{12}H_{16}O+Na^+$ 199.1093, found 199.1093; R_f 0.52 (silica gel, 1:3 EtOAc/hexanes).



Synthesis of (±)-(*Z*)-1-phenylhex-4-en-3-ol (15). To a solution of propargylic alcohol S-**8** (2.32 g, 13.3 mmol) and Ti(O*i*-Pr)$_4$ (7.90 mL, 7.58 g, 26.7 mmol) in Et_2O (65 mL) at –78 °C was added *c*-C_5H_9MgCl (2.03 M in Et_2O, 67.0 mmol) drop-wise over a 20 min period. The mixture was warmed to –30 °C over 1 h and stirred for additional 1 h at this temperature. The reaction was quenched by addition of saturated aqueous $NaHCO_3$ (5.5 mL) and warmed to room temperature. To the mixture were added celite and NaF (25 g each), and the resulting slurry was stirred rapidly for 2 h. The suspension was filtered through celite and the filtrate concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10→20% EtOAc/hexanes) to afford a single isomer of allylic alcohol **15** as a colorless oil (1.78 g, 76%).

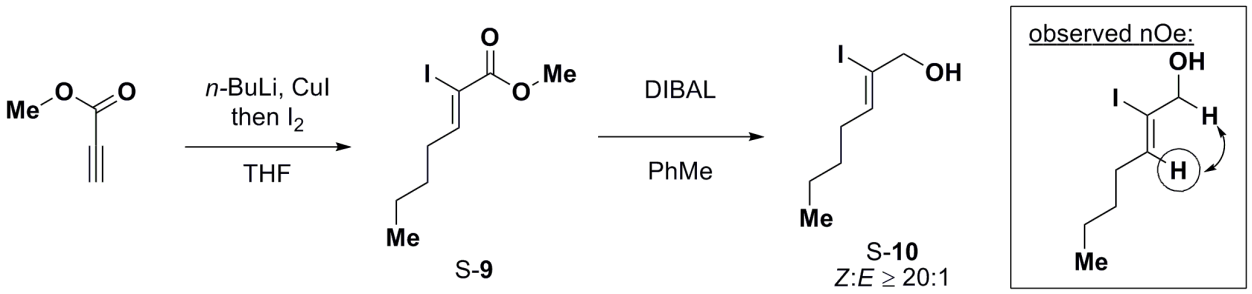
Data for (±)-(*Z*)-1-phenylhex-4-en-3-ol (15): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.14 (m, 5H), 5.58 (dqd, *J* = 10.9, 6.9, 1.0 Hz, 1H), 5.46–5.40 (m, 1H), 4.50–4.44 (m, 1H), 2.72–2.61 (m, 2H), 1.96–1.88 (m, 1H), 1.79–1.71 (m, 1H), 1.63 (dd, *J* = 6.9, 1.7 Hz, 3H), 1.42 (d, *J* = 3.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.15, 133.45, 128.61, 128.57, 126.95, 126.01, 67.04, 39.11, 31.87, 13.57; IR (thin film, NaCl) 3325 (br), 3026, 2921, 2859, 1659, 1603, 1496, 1454, 1317, 1168, 1044, 998, 922, 817, 749, 730, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{12}H_{16}O+Na^+$ 199.1093, found 199.1093; R_f 0.50 (silica gel, 1:3 EtOAc/hexanes).



17

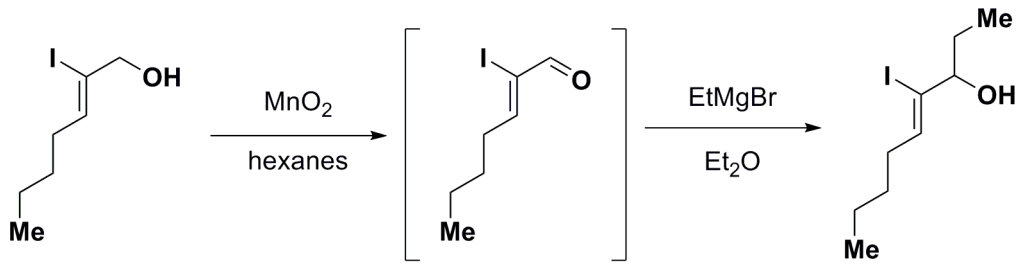
Synthesis of (±)-(*E*)-4-methyl-1-phenylhex-4-en-3-ol (17). A solution of tiglic aldehyde (1.00 mL, 871 mg, 10.4 mmol) in THF (20 mL) was added drop-wise to phenethylmagnesium chloride (1.0 M in THF, 12.5 mmol) at 0 °C, and the mixture was warmed to room temperature over 1 h. The reaction was stirred for additional 1 h, then cooled to 0 °C and carefully quenched with 20% aqueous NH_4Cl (20 mL). The layers were separated, and the aqueous phase was extracted with Et_2O (3 × 40 mL). The combined organic extract was washed with brine (1 × 40 mL), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford allylic alcohol **17** as a colorless oil (1.87 g, 94%).

Data for (±)-(*E*)-4-methyl-1-phenylhex-4-en-3-ol (17): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.15 (m, 5H), 5.51–5.46 (m, 1H), 4.02 (app td, *J* = 7.0, 3.0 Hz, 1H), 2.67 (ddd, *J* = 14.1, 9.8, 6.1 Hz, 1H), 2.57 (ddd, *J* = 13.9, 9.6, 6.5 Hz, 1H), 1.92–1.79 (m, 2H), 1.63–1.61 (m, 6H), 1.42 (d, *J* = 3.2 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.35, 137.99, 128.64, 128.54, 125.96, 121.31, 77.58, 36.69, 32.39, 13.25, 11.16; IR (thin film, NaCl) 3324 (br), 3063, 3026, 2920, 2861, 1670, 1604, 1584, 1496, 1454, 1380, 1320, 1211, 1153, 1030, 1006, 916, 828, 781, 749, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{13}H_{18}O+Na^+$ 213.1250, found 213.1250; R_f 0.57 (silica gel, 1:3 EtOAc/hexanes).



Synthesis of (*Z*)-2-iodohept-2-en-1-ol (S-10). To a suspension of CuI (1.24 g, 6.54 mmol) in THF (20 mL) at 0 °C, was added *n*-BuLi (2.5 M in hexanes, 13.1 mmol) in a drop-wise manner. After stirring at 0 °C for 30 min the reaction was cooled to −78 °C. Then a solution of methyl propiolate (0.500 g, 5.95 mmol) in THF (3 mL) was added drop-wise via Teflon cannula. The reaction stirred at −78 °C for 4 h, then I_2 (3.32 g, 13.09 mmol) was added as a solid. The reaction was then allowed to warm to room temperature in the cooling bath overnight, and stir for 24 h. The reaction was then quenched with 20 mL saturated aqueous NH_4Cl then diluted with saturated aqueous $Na_2S_2O_3$ and extracted to with Et_2O (3 × 50 mL) the combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5% EtOAc/hexanes) to afford a brown viscous oil (1.045g) whose ^{1}H NMR had signals consistent with ester S-**9**, but was contaminated with numerous unidentified side products. This brown oil was carried directly onto the next reaction without further purification. The brown oil (1.045 g, 3.89 mmol), was dissolved in toluene (12 mL) and cooled to −78 °C. DIBAL (1.0 M in hexanes, 8.96 mmol) was then added in a drop-wise manner. The reaction stirred at −78 °C for 30 min. The cooling bath was then removed for 10 min, and then replaced with a 0 °C bath for 1 h. The reaction was quenched with H_2O (15 mL) and then 1.7 g of L-tartaric acid was added. The reaction stirred vigorously for 20 min until two clear layers formed. The layers were then separated, the aqueous layer extracted with Et_2O (2 × 50 mL), the combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (15% EtOAc/hexanes) to afford alcohol S-**10** as a yellow oil (*Z*:*E* ≥ 20:1, 634 mg, 44% over two steps). No evidence for minor isomer was observed by ^{1}H NMR.

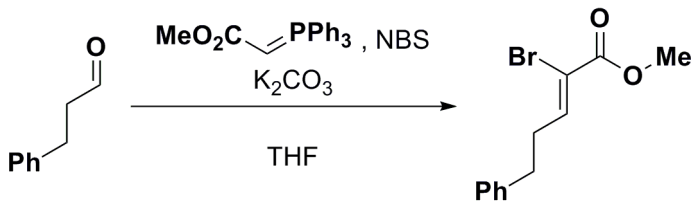
Data for (*Z*)-2-iodohept-2-en-1-ol (S-10): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (t, *J* = 6.8 Hz, 1H), 4.24 (d, *J* = 6.6 Hz, 2H), 2.20–2.12 (m, 2H), 2.05–1.97 (m, 1H), 1.46–1.28 (m, 4H), 0.91 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.8, 108.3, 71.9, 35.6, 30.5, 22.5, 14.1; IR (thin film, NaCl) 3311, 2955, 2927, 2857, 1464, 1084, 1012, 833 cm^{-1}.



S-**10** S-**11** **25**

Synthesis of (±)-(*Z*)-4-iodonon-4-en-3-ol (25). To a solution of S-**10** (1.0 g, 4.16 mmol) in hexanes (85 mL) at room temperature was added MnO_2 (10.87 g, 125.0 mmol). The reaction stirred vigorously at room temperature for 2 h, then another portion of MnO_2 (5.0 g, 5.74 mmol) is added. The reaction was then stirred for three more hours at room temperature. The reaction was then filtered through Celite with the aid of Et_2O, and concentrated *in vacuo*. The crude ^1H NMR was consistent with clean conversion to aldehyde S-**14**. The aldehyde was used in the next reaction without any further purification. The crude oil was taken up in Et_2O (40 mL) and cooled to 0 °C in an ice bath, then ethylmagnesium bromide (3.0 M in Et_2O, 4.99 mmol) was then added in a drop-wise manner. The reaction stirred for 30 min at 0 °C, before being quenched with H_2O (1 mL). Sufficient $MgSO_4$ was then added to absorb all of the water, and the reaction was filtered, washed with Et_2O (200 mL) and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford alcohol **25** as a colorless oil (310 mg, 28% over two steps).

Data for (±)-(*Z*)-4-iodonon-4-en-3-ol (25): ^1H NMR (500 MHz, $CDCl_3$) δ 5.89 (t, J = 6.8, 1H), 3.54–3.50 (m, 1H), 2.19 (dd, J = 14.3, 7.0 Hz, 2H), 1.81 (d, J = 5.8 Hz, 1H), 1.63–1.58 (m, 2H), 1.44–1.30 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 116.2, 80.0, 35.5, 30.6, 30.1, 22.5, 14.2, 9.8; IR (thin film, NaCl) 3358, 2960, 2930, 2872, 2858, 1460, 1013 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_9H_{17}IO+Na^+$ 291.0216, found 291.0220.

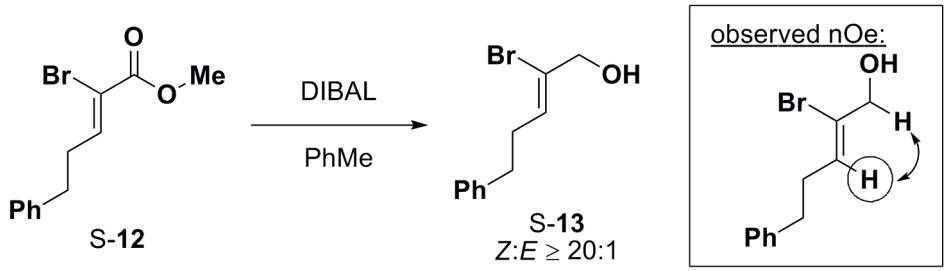


S-**12**

Synthesis of (*Z*)-methyl 2-bromo-5-phenylpent-2-enoate (S-12). To a solution of the

methyl(triphenylphosphoranylidene)acetate (7.47 g, 22.38 mmol) in THF (60 mL) at –20 °C was added *N*-bromosuccinimide (4.35 g, 24.61 mmol) as a solid. The reaction was allowed to stir for 20 min at –20 °C and turned pale yellow in color. Then K_2CO_3 (5.14 g, 37.30 mmol) was added as a solid, followed by hydrocinnamaldehyde (2.0 mL, 2.0 g, 14.9 mmol) neat, in a drop-wise manner. The reaction was allowed to warm to room temperature and stir 8 h. At this point hexanes (60 mL) was added, the reaction stirred 5 min at room temperature, and the resulting slurry was filtered through a one-inch plug of silica gel with the aid of Et_2O and concentrated *in vacuo*. Crude ^{1}H NMR showed the product was formed in 5:1 (*Z*:*E*) selectivity. The crude product was purified by flash column chromatography on silica gel (1.5→3% EtOAc/hexanes) to afford pure (*Z*) alcohol S-**12** as a colorless oil (2.6 g, 65%).

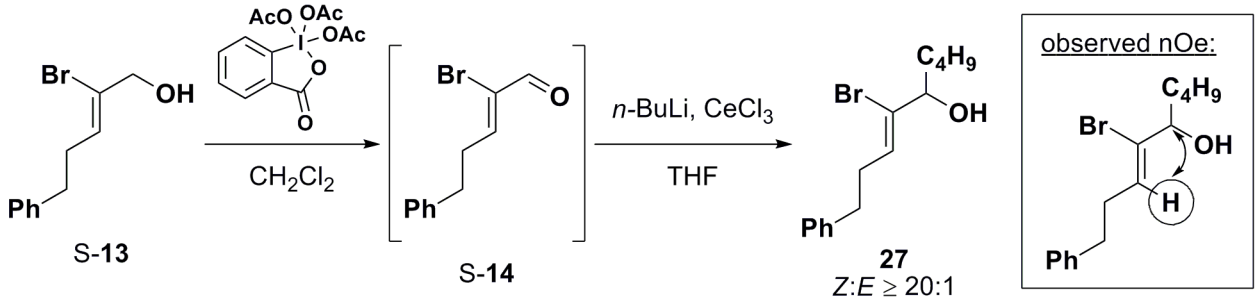
Data for (*Z*)-methyl 2-bromo-5-phenylpent-2-enoate (S-12): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.30 (m, 3H), 7.25–7.20 (m, 3H), 3.82 (s, 3H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.72–2.59 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 145.45, 140.6, 128.8, 128.5, 126.6, 116.7, 53.5, 33.9, 33.7; IR (thin film, NaCl) 3438, 3027, 2951, 2859, 1726, 1624, 1435, 1268, 1045, 742 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{12}H_{13}BrO_2$+Na^+ 290.9991, found 290.9979.



Synthesis of (*Z*)-2-bromo-5-phenylpent-2-en-1-ol (S-13). To a solution of S-**12** (2.90 g, 10.82 mmol) in toluene (30 mL) at –78 °C was added DIBAL (1.0 M in hexanes, 24.9 mmol) via Teflon cannula over 30 min. The reaction was stirred at –78 °C for 30 min, the cooling bath was then removed for 10 min, and then replaced with a 0 °C bath for 1 h. The reaction was then quenched with H_2O (15 mL), diluted with H_2O (100 mL) and 15 g of L-tartaric acid was added. The reaction stirred vigorously for 1 h until two clear layers formed. The layers were then separated, the aqueous layer extracted with Et_2O (2 × 150 mL), the combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (15% EtOAc/hexanes) to afford alcohol S-**13** as a colorless oil (*Z*:*E* ≥ 20:1, 2.30 g, 88%). No evidence for minor isomer was observed by ^{1}H NMR.

Data for (*Z*)-2-bromo-5-phenylpent-2-en-1-ol (S-13): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34–7.27 (m, 2H), 7.25–7.18 (m, 3H), 6.04 (t, *J* = 6.9 Hz, 1H), 4.24 (d, *J* = 5.0 Hz, 2H), 2.75 (t, *J* = 7.8 Hz,

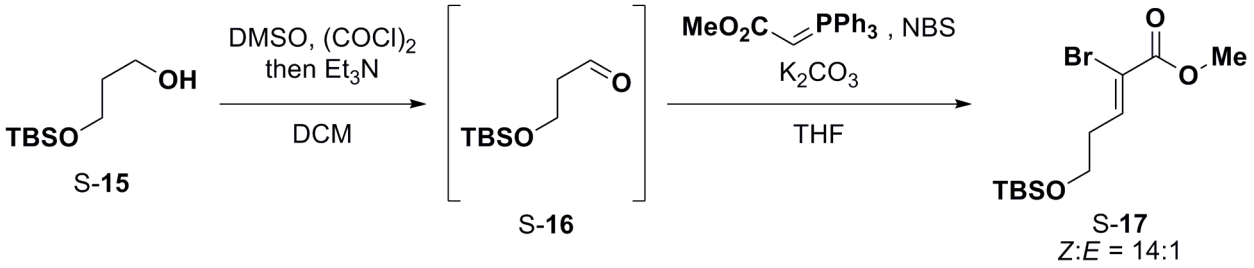
2H), 2.54 (dd, J = 15.2, 7.3 Hz, 2H), 1.94 (td, J = 6.7, 1.4 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 129.5, 128.7, 128.6, 127.6, 126.3, 68.6, 34.5, 32.6; IR (thin film, NaCl) 3331, 2925, 2858, 1495, 1453, 1096, 1022, 698 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{11}H_{13}BrO+Na^+$ 263.0042, found 263.0042.



Synthesis of (±)-(*Z*)-4-bromo-1-phenylnon-3-en-5-ol (27). To a solution of S-**13** (1.4 g, 5.80 mmol) in CH_2Cl_2 (25 mL) at 0 °C was added Dess-Martin periodinane (4.93 g, 11.66 mmol) in one portion as a solid. The reaction was stirred vigorously at 0 °C for 6 h. The reaction was then diluted with 200 mL of 20% EtOAc/hexanes and washed with a 1:1 mixture of saturated aqueous $NaHCO_3$ and NaS_2O_3 solutions (3 × 60 mL). The organic layer was dried with $MgSO_4$ and concentrated *in vacuo*. The crude ^{1}H NMR was consistent with clean conversion to aldehyde S-**14**. The aldehyde was used in the next reaction without any further purification. A suspension of anhydrous $CeCl_3$ (2.13 g, 8.70 mmol) in THF (19 mL) at –78 °C was stirred for 45 min. Then, to the suspension was added *n*-BuLi (2.73 M in hexanes, 8.70 mmol), in a drop-wise manner. The reaction stirred 45 min at –78 °C and turned dark brown/black in color. Then a solution of aldehyde S-**14** (5.80 mmol) in THF (5 mL) was added via Teflon cannula. The cannula and flask were rinsed with THF (3 mL). The reaction was allowed to warm to room temperature in the cooling bath overnight. The reaction was then quenched with saturated aqueous $NaHCO_3$ (1 mL) and diluted with Et_2O (200 mL) and brine (200 mL). Layers separated, and the aqueous layer extracted to Et_2O (2 × 200 mL), the combined organics were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (5→7% EtOAc in 1:1 hexanes/benzene) to afford alcohol **27** as a colorless oil (*Z*:*E* ≥ 20:1, 424 mg, 25% over two steps). No evidence for minor isomer was observed by ^{1}H NMR.

Data for (±)-(*Z*)-4-bromo-1-phenylnon-3-en-5-ol (27): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.27 (m, 2H), 7.23–7.17 (m, 3H), 5.98 (t, J = 6.8 Hz, 1H), 4.07–4.00 (m, 1H), 2.81–2.66 (m, 2H), 2.59–2.44 (m, 2H), 1.79 (d, J = 6.3 Hz, 1H), 1.70–1.56 (m, 2H), 1.38–1.13 (m, 4H), 0.90 (t, J = 7.2 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.3, 132.6, 129.4, 128.6, 126.3, 76.9, 33.6, 34.6, 32.6, 27.7, 22.6, 14.2; IR (thin film, NaCl) 3362, 3026, 2924, 2858, 1656, 1495, 1453, 1097,

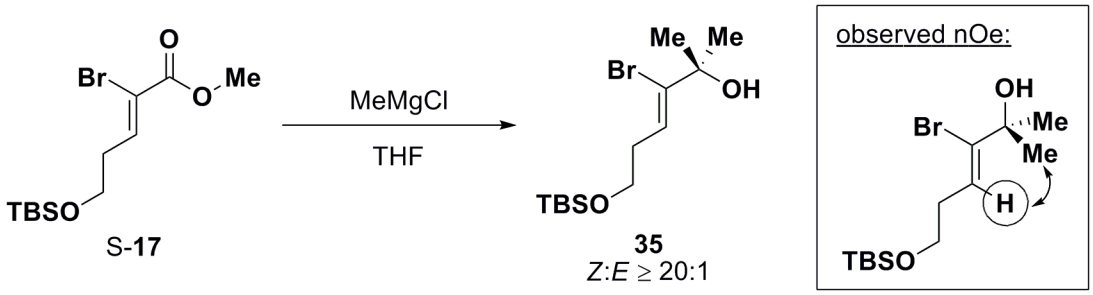
1021, 748, 699 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{15}H_{21}BrO+Na^+$ 319.0668, 321.0648, found 319.0659, 321.0638.



Synthesis of (*Z*)-methyl 2-bromo-5-(*tert*-butyl-dimethyl-silanyloxy)-pent-2-enoate (S-17). To a solution of DMSO (560 μL, 0.615 g, 7.89 mmol) in CH_2Cl_2 (13 mL) at −78 °C was added oxalyl chloride (460 μL, 0.668 g, 5.26 mmol), in a drop-wise manner. The reaction was then allowed to stir 10 min at −78 °C. To the reaction was then added alcohol S-**15** (0.500 g, 2.63 mmol). The reaction stirred 15 min at −78 °C. Then freshly distilled Et_3N (1.82 mL, 1.32 g, 13.15 mmol) was added in a drop-wise manner. The reaction stirred 10 min at −78 °C, the cooling bath was then removed, and the reaction allowed to warm to room temperature. The reaction was then diluted with 1.0 M $KHSO_4$ (20 mL) and extracted with CH_2Cl_2 (2 × 30 mL). The combined organics were then washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude ^{1}H NMR was consistent with clean conversion to aldehyde S-**16**. The aldehyde was used in the next reaction without any further purification. To a solution of the methyl(triphenylphosphoranylidene)acetate (1.31 g, 3.94 mmol) in THF (11 mL) at –20 °C was added *N*-bromosuccinimide (0.768 g, 4.33 mmol) as a solid. The reaction was allowed to stir for 20 min at –20 °C and turned pale yellow in color. Then K_2CO_3 (0.362 g, 6.57 mmol) was added as a solid, followed by aldehyde S-**16** (2.63 mmol) as a solution in THF (3 mL), in a drop-wise manner via cannula. The reaction was allowed to warm to room temperature and stir 8 h. At this point hexanes (25 mL) was added, the reaction stirred 5 min at room temperature, and the resulting slurry was filtered through a 1-inch plug of silica gel with the aid of Et_2O and concentrated *in vacuo*. Crude ^{1}H NMR showed the product was formed in 11:1 *Z*/*E* selectivity. The crude product was purified by flash column chromatography on silica gel (5% EtOAc/hexanes) to afford alcohol S-**17** as a colorless oil (370 g, 44% over two steps). Analysis of the purified product by ^{1}H NMR indicated *Z*/*E* ratio of 14:1.

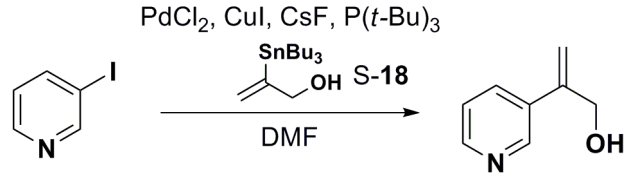
Data for (*Z*)-methyl 2-bromo-5-(*tert*-butyl-dimethyl-silanyloxy)-pent-2-enoate (S-17): major isomer (*Z*): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 6.9 Hz, 1H), 3.82 (s, 3H), 3.75 (t, *J* = 6.4 Hz, 2H), 2.57–2.53 (m, 2H), 0.88 (s, 9H), 0.07 to –0.04 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.1, 143.9, 117.1, 60.8, 53.4, 36.0, 26.0, 18.5, –5.2; **minor isomer (*E*):** ^{1}H NMR (400 MHz,

$CDCl_3$) δ 6.79 (t, *J* = 7.5 Hz, 1H), 3.81 (s, 3H), 3.70 (t, *J* = 6.2 Hz, 2H), 2.75–2.70 (m, 2H), 0.88 (s, 9H), 0.07 to –0.04 (m, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.5, 146.5, 111.9, 61.6, 53.0, 35.1, 26.0, 18.5, –5.2; **mixture of olefin isomers:** IR (thin film, NaCl) 2954, 2929, 2857, 1753, 1627, 1472, 1260, 1097, 837, 777 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{12}H_{23}BrO_3Si+H^+$ 325.0653 found 325.0645.



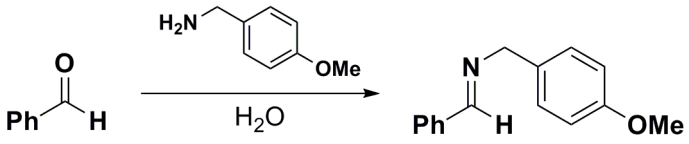
Synthesis of (*Z*)-3-Bromo-6-(*tert*-butyl-dimethyl-silanyloxy)-2-methyl-hex-3-en-2-ol (35). To a solution of methylmagnesium chloride (2.76 M in THF, 3.72 mmol) in THF (10 mL) at –78 °C was added ester S-**17** (0.545 g, 1.69 mmol) in a drop-wise manner as a solution in THF (2 mL) via Teflon cannula. The reaction was allowed to warm to room temperature in the cooling bath and stir overnight. The reaction was then quenched with saturated aqueous $NaHCO_3$ (2 mL), diluted with saturated aqueous $NaHCO_3$ (40 mL), extracted with Et_2O (2 × 40 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (10→15% EtOAc/hexanes) to afford alcohol **35** as a pale yellow oil as the only product isolated (*Z*:*E* ≥ 20:1, 290 mg, 53%). No evidence for minor isomer was observed by ^{1}H NMR.

Data for (*Z*)-3-Bromo-6-(*tert*-butyl-dimethyl-silanyloxy)-2-methyl-hex-3-en-2-ol (35): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.09 (t, *J* = 6.7 Hz, 1H), 3.68 (t, *J* = 6.6 Hz, 2H), 2.39–2.32 (m, 2H), 1.99 (s, 1H), 1.48 (s, 6H), 0.89 (s, 9H), 0.06 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.1, 123.9, 74.2, 61.7, 35.4, 29.3, 26.1, 18.5, –5.0; IR (thin film, NaCl) 3412, 2955, 2929, 2858, 1472, 1256, 1103, 836 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{13}H_{27}BrO_2Si+Na^+$ 345.0856, 347.0836 found 345.0851, 347.0830.



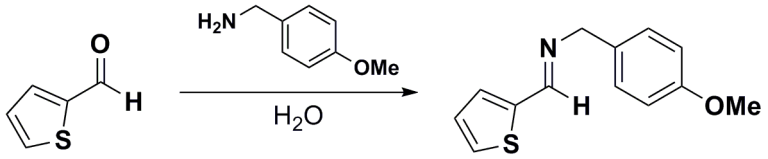
37

Synthesis of 2-(pyridin-3-yl)prop-2-en-1-ol (37). To a solution of 3-iodopyridine (1.46 g, 7.15 mmol) and stannane S-**18** (3.0 g, 8.58 mmol) in DMF (15 mL) at room temperature was sequentially added $PdCl_2$ (0.126 g, 0.715 mmol), CsF (2.16 g, 14.30 mmol), CuI (0.270 g, 1.43 mmol) and P(*t*-Bu)$_3$ (1.0 M in toluene, 1.43 mmol). The reaction flask was then evacuated and backfilled with argon five times, and then heated to 45 °C for 3 h. The reaction turned jet black within 5 min at 45 °C. After 3 h a distillation head was put on the reaction flask and the DMF was removed by vacuum distillation. The residue was purified by flash column chromatography on silica gel (90% EtOAc/hexanes, then EtOAc) to afford alcohol **37** as a yellow oil (420 mg, 44%).
Data for 2-(pyridin-3-yl)prop-2-en-1-ol (37): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (s, 1H), 8.39 (d, *J* = 4.5 Hz, 1H), 7.75–7.71 (m, 1H), 7.22 (dd, *J* = 7.9, 4.9 Hz, 1H), 5.45 (s, 1H), 5.43 (s, 1H), 4.72 (s, 1H), 4.48 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 147.2, 144.8, 134.9, 134.0, 123.5, 114.4, 64.2; IR (thin film, NaCl) 3216, 2860, 1931, 1589, 1569, 1477, 1414, 1061, 1035, 911, 816, 723 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_8H_9NO+H^+$ 136.1, found 136.3.



29

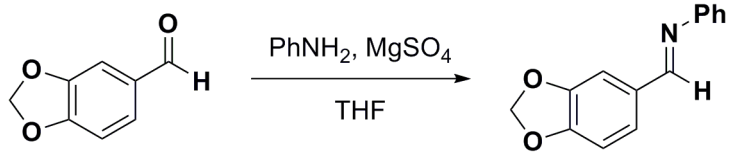
Synthesis of *N*-(4-methoxybenyl)benzylideneamine (29). To a flask with 150 mL of water at room temperature was sequentially added *p*-methoxybenzylamine (10.5 g, 76.64 mmol), and freshly distilled benzaldehyde (8.12 g, 76.64 mmol). The resulting heterogeneous mixture was stirred vigorously for 60 minutes. The reaction was then extracted with CH_2Cl_2 (3 × 200 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The resulting residue was distilled under reduced pressure (158–165 °C, 0.5 torr) to yield imine **5** as a colorless oil (11.3 g, 65%).
Data for *N*-(4-methoxybenyl)benzylideneamine (29): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.78–7.76 (m, 2H), 7.43–7.38 (m, 3H), 7.27–7.24 (m, 2H), 6.90–6.87 (m, 2H), 4.77 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 158.8, 136.3, 131.5, 130.9, 129.4, 128.7, 128.4, 114.1, 64.7, 55.4; IR (thin film, NaCl) 3027, 2834, 1643, 1611, 1512, 1480, 1247, 1174, 1035 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{15}H_{15}NO+H^+$ 226.1; found 226.0.



32

Synthesis of *N*-(4-methoxybenyl)-2-thiophenylideneamine (32). To a flask with 70 mL of water at room temperature was sequentially added *p*-methoxybenzylamine (8.73 mL, 9.35 g, 45.04 mmol), and 2-thiophene carbaldehyde (4.09 mL, 5.0 g, 45.04 mmol). The resulting heterogeneous mixture was stirred vigorously overnight. The reaction was then extracted with CH_2Cl_2 (3 × 200 mL), dried over Na_2SO_4, and concentrated *in vacuo*. The resulting residue was distilled under reduced pressure (160–163 °C, 0.5 torr) to yield imine **32** as a yellow oil which solidified upon standing (3.22 g, 31%).

Data for *N*-(4-methoxybenyl)-2-thiophenylideneamine (32): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* = 1.1 Hz, 1H), 7.40 (d, *J* = 5.0 Hz, 1H), 7.32 (dd, *J* = 9.0, 3.6 Hz, 1H), 7.24 (d, *J* = 8.7 Hz, 2H), 7.07 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.91–6.86 (m, 2H), 4.74 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 155.0, 142.7, 131.3, 130.7, 129.5, 129.1, 127.5, 114.1, 60.0, 55.5; IR (thin film, NaCl) 3002, 2834, 1632, 1611, 1513, 1431, 1248, 1035, 819, 715 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{13}H_{13}NOS+H^+$ 232.0791, found 232.0789.

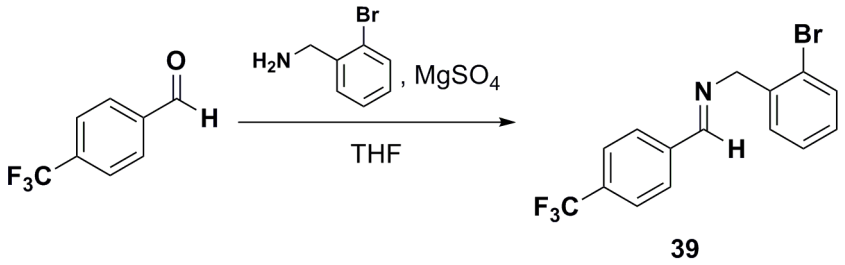


34

Synthesis of *N*-phenyl(benzo[*d*][1,3]dioxol-6-yl)methylideneamine (34). To a suspension of piperonal (6.0 g, 39.97 mmol) in THF (160 mL), and $MgSO_4$ (25 g) at room temperature was added aniline (3.65 mL, 3.72 g, 39.97 mmol). The reaction was stirred vigorously overnight. The following morning the reaction was filtered and concentrated *in vacuo*. The crude product was crystallized from 100 mL of boiling heptane to yield imine **34** as white needles (4.97 g, 55%).

Data for *N*-phenyl(benzo[*d*][1,3]dioxol-6-yl)methylideneamine (34): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.54 (d, *J* = 1.5 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H), 7.30–7.25 (m, 1H), 7.24–7.15 (m, 3H), 6.89 (d, *J* = 8.0 Hz, 1H), 6.04 (d, *J* = 1.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 152.3, 150.7, 148.7, 131.5, 129.3, 125.9, 121.1, 108.4, 107.1, 101.8; IR (KBr) 2894, 1625, 1602, 1584, 1493, 1454, 1266, 1042, 936, 814, 767, 699 cm^{-1}; HRMS (ESI, FT-ICR)

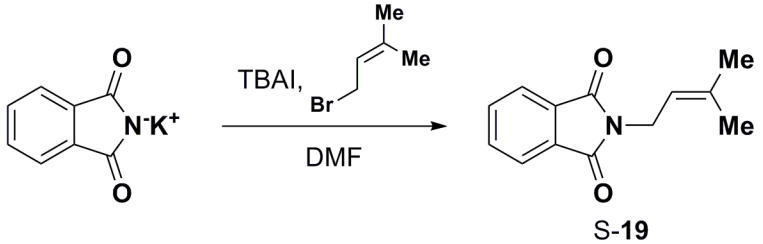
m/z calc'd for $C_{14}H_{11}NO_2$+H^+ 226.0863, found 226.0860.



39

Synthesis of *N*-(2-Bromo-benzyl)-(4-trifluoromethyl)benzylideneamine (39). To a suspension of 4-trifluoromethylbenzaldehyde (1.53 mL, 2.0 g, 11.49 mmol) and $MgSO_4$ (20 g) in THF (25 mL) at room temperature was added 2-bromobenzylamine (2.02 g, 10.94 mmol). After vigorous stirring overnight, the reaction was treated with additional 4-trifluoromethylbenzaldehyde (400 μL, 0.520 g, 2.98 mmol) and stirred for 4 h at room temperature. The reaction was then filtered and concentrated *in vacuo*. The crude product was purified by bulb-to-bulb distillation (250–270 °C, 1 torr) to yield imine **39** as a yellow oil (1.0 g, 27%) containing unidentified minor impurity.

Data for *N*-(2-Bromo-benzyl)-(4-trifluoromethyl)benzylideneamine (39): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (s, 1H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.32 (app t, *J* = 7.5 Hz, 1H), 7.17 (app t, *J* = 7.6 Hz, 1H), 4.93 (s, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.3, 139.3, 138.4, 132.7, [132.8, 132.5, 132.3, 132.1, F_3C-C], 129.9, 128.8, 128.6, 127.7, [127.3, 125.2, 123.0, 120.8, F_3C-], [125.7, 125.6, 125.6, 125.66, F_3C-C-CH], 123.7, 64.3; IR (thin film, NaCl) 1649, 1568, 1466, 1440, 1336, 1146, 1065, 1043, 838, 752 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{15}H_{11}BrF_3N$+H^+ 342.0, 344.0, found 342.1, 344.2.

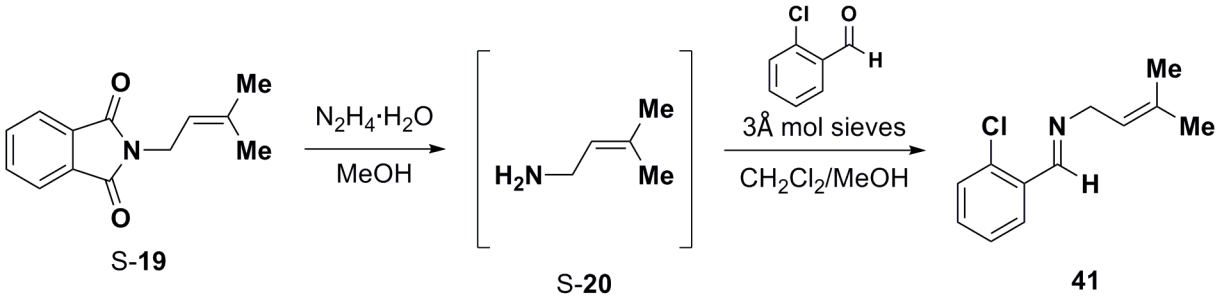


S-**19**

Synthesis of 2-(3-methylbut-2-enyl)isoindoline-1,3-dione (S-19). To a suspension of potassium phthalimide (9.54 g, 51.62 mmol) and TBAI (1.84 g, 5.16 mmol) in DMF (25 mL) in a room temperature bath was added prenyl bromide (7.80 mL, 10.0 g, 67.70 mmol) neat via Teflon cannula. The reaction then stirred 18 h at room temperature. The reaction was then poured into

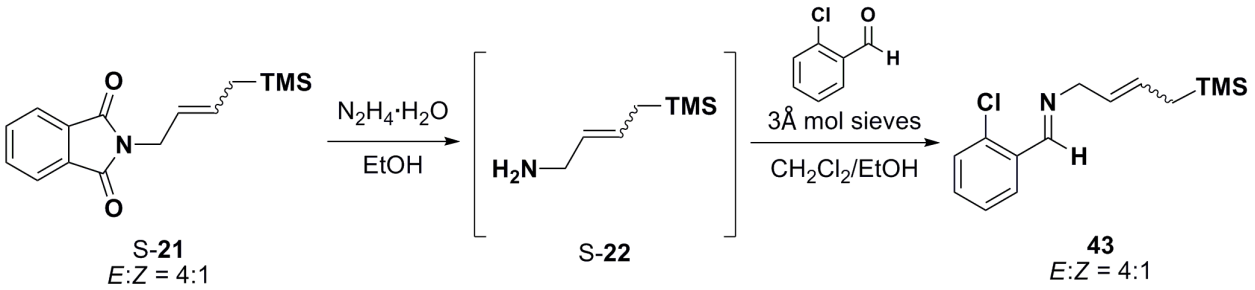
200 mL of H_2O and filtered. The crude product was crystallized from 100 mL of boiling hexanes to yield compound S-**19** as yellow plates (7.77 g, 53%).

Data for 2-(3-methylbut-2-enyl)isoindoline-1,3-dione (S-19): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.79 (m, 2H), 7.73–7.66 (m, 2H), 5.35–5.18 (m, 1H), 4.26 (d, J = 7.2 Hz, 2H), 1.83 (s, 3H), 1.71 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 137.4, 133.9, 132.5, 123.3, 118.5, 36.0, 25.8, 18.1; IR (KBr) 3455, 2972, 2937, 2917, 1708, 1426, 1392, 1323, 1096, 944, 722, 530 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{13}H_{13}NO_2$+Na^+ 238.0839, found 238.0837.



Synthesis of *N*-(3-methylbut-2-ene)-2-chlorobenzylideneamine (41). To a solution of protected amine S-**19** (3.0 g, 13.95 mmol) in MeOH (50 mL) at room temperature was added hydrazine hydrate (767 μL, 0.767 g, 15.34 mmol). The reaction was stirred at room temperature for 3 h, then additional hydrazine hydrate (767 μL, 0.767 g, 15.34 mmol) was added, and the reaction was heated to 45 °C for 2 h. At this point compound S-**19** had been consumed according to TLC (20% EtOAc/hexanes). The reaction was cooled to room temperature and CH_2Cl_2 (50 mL), activated 3Å molecular sieves (20 g), and *o*-chlorobenzaldehyde (4.68 mL, 5.89 g, 41.85 mmol) were sequentially added. The reaction was then stirred vigorously at room temperature for 72 h. The reaction was then filtered through Celite, diluted with H_2O (200 mL), layers separated, the aqueous layer extracted to CH_2Cl_2 (1 × 200 mL), the combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by vacuum distillation (108–110 °C, 1 torr) with trace residual aldehyde being removed under high vacuum (100 °C, 0.5 torr) for 10 min. This yielded imine **41** as a colorless oil (1.05 g, 37%).

Data for *N*-(3-methylbut-2-ene)-2-chlorobenzylideneamine (41): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.94 (dd, J = 7.6, 1.8 Hz, 1H), 7.31–7.11 (m, 3H), 5.28 (dd, J = 7.6, 6.3 Hz, 1H), 4.19 (d, J = 6.9 Hz, 2H), 1.69 (s, 3H), 1.65 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.1, 135.4, 135.2, 133.6, 131.5, 129.9, 128.5, 127.1, 121.6, 59.3, 26.0, 18.3; IR (thin film, NaCl) 2969, 2912, 1633, 1593, 1443, 1376, 1273, 1052, 755 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{12}H_{14}ClN$+H^+ 208.1, found 208.3.



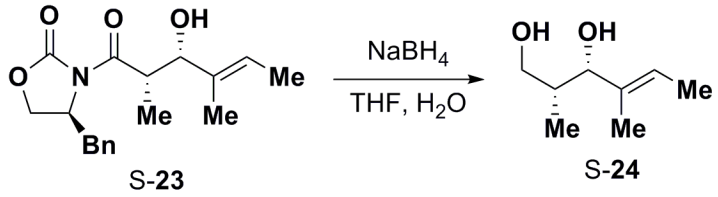
S-**21**
E:*Z* = 4:1

S-**22**

43
E:*Z* = 4:1

Synthesis of *N*-(2-chlorobenzylidene)-4-(trimethylsilyl)but-2-en-1-amine (43). To a solution of protected amine S-**21** (3.0 g, 10.98 mmol) in EtOH (32 mL) at room temperature was added hydrazine hydrate (686 μL, 0.686 g, 13.74 mmol). The reaction was stirred at room temperature for 15 h, then additional hydrazine hydrate (400 μL, 0.400 g, 8.00 mmol) was added, and the reaction stirred 6 h at room temperature. At this point compound S-**21** had been consumed according to TLC (20% EtOAc/hexanes) and a precipitate had formed. The reaction was filtered through Celite with the aid of CH_2Cl_2 (70 mL). To the filtrate was then sequentially added activated 3Å molecular sieves (25 g), and *o*-chlorobenzaldehyde (3.68 mL, 4.61 g, 32.94 mmol). The reaction was then stirred vigorously at room temperature for 18 h. The reaction was then filtered through Celite, diluted with H_2O (200 mL), layers separated, the aqueous layer extracted to CH_2Cl_2 (1 × 200 mL), the combined organic extracts were washed with saturated aqueous $NaHCO_3$ and brine, dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by vacuum distillation (108–113 °C, 1 torr) to yield imine **43** as a yellow oil that was contaminated with trace amounts of unidentified impurities (*E*:*Z* = 4:1, 1.05 g, 36%).

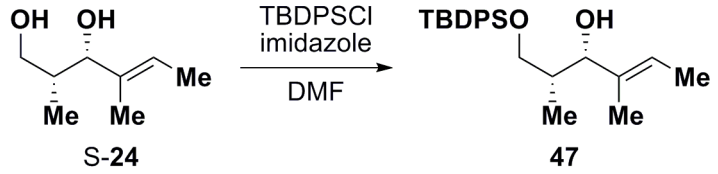
Data for *N*-(2-chlorobenzylidene)-4-(trimethylsilyl)but-2-en-1-amine (43): major isomer (*E*): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (s, 1H), 7.97–7.92 (m, 1H), 7.29–7.16 (m, 3H), 5.62–5.53 (m, 1H), 5.47–5.28 (m, 1H), 4.16 (d, *J* = 6.3 Hz, 2H), 1.42 (d, *J* = 8.1 Hz, 2H), –0.02 to –0.14 (m, 9H); **minor isomer (*Z*):** ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.97–7.92 (m, 1H), 7.29–7.16 (m, 3H), 5.62–5.53 (m, 1H), 5.47–5.28 (m, 1H), 4.22 (d, *J* = 6.7 Hz, 2H), 1.52 (d, *J* = 9.3 Hz, 2H), –0.02 to –0.14 (m, 9H); **mixture of olefin isomers:** ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 159.2, 158.9, 158.2, 158.0, 143.2, 135.2, 134.0, 133.6, 133.6, 132.6, 132.4, 132.4, 131.8, 131.7, 130.2, 130.1, 130.0, 129.9, 128.9, 128.6, 128.5, 127.1, 125.6, 124.1, 123.3, 121.5, 66.3, 63.5, 58.2, 40.1, 23.1, 19.3, –1.5, –1.8; IR (thin film, NaCl) 2954, 2889, 1718, 1653, 1469, 1248, 855, 755 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_{14}H_{20}ClNSi+H^+$ 266.1, found 266.4.



S-**23** S-**24**

Synthesis of (2*R*,3*S*,*E*)-2,4-dimethylhex-4-ene-1,3-diol (S-24). To a solution of alcohol S-**23** (d.r. ≥ 99:1, 1.07 g, 3.37 mmol) in THF (90 mL) at 0 °C was added a solution of $NaBH_4$ (0.64 g, 17.0 mmol) in H_2O (20 mL). The mixture was stirred at 0 °C for 10 min, warmed to room temperature over 30 min, then stirred for 5 h. The reaction was quenched with saturated aqueous NH_4Cl (20 mL) and stirred for additional 1 h. The layers were separated, and the aqueous phase was extracted with EtOAc (3 × 50 mL). The organic extracts were combined, washed with saturated aqueous $NaHCO_3$ and brine (1 × 50 mL each), dried over $MgSO_4$ then concentrated *in vacuo*. The crude product was purified by flash column chromatography on silica gel (25→50% EtOAc/CH_2Cl_2) to afford diol S-**24** as a colorless oil (d.r. ≥ 99:1, 455 mg, 94%). No evidence for minor isomer was observed by ^{1}H NMR.

Data for (2*R*,3*S*,*E*)-2,4-dimethylhex-4-ene-1,3-diol (S-24): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.54–5.48 (m, 1H), 4.09 (d, *J* = 4.9 Hz, 1H), 3.62 (app d, *J* = 5.2 Hz, 2H), 2.41 (br, 1H), 2.30 (br, 1H), 1.92–1.84 (m, 1H), 1.64 (d, *J* = 6.7 Hz, 3H), 1.60 (s, 3H), 0.90 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.92, 120.05, 79.24, 66.89, 37.94, 13.18, 12.94, 11.07; IR (thin film, NaCl) 3336 (br), 2918, 1748, 1671, 1456, 1419, 1381, 1339, 1316, 1032, 993, 858, 826, 772 cm^{-1}; LRMS (ESI) *m/z* calc'd for $C_8H_{16}O_2$+Na^+ 167.1, found 167.1; $[\alpha]_D^{20}$ –21.6 (*c* 0.50, $CHCl_3$); R_f 0.32 (silica gel, 1:1 EtOAc/$CHCl_3$).



S-**24** **47**

Synthesis of (2*R*,3*S*,*E*)-1-(*tert*-butyldiphenylsilyloxy)-2,4-dimethylhex-4-en-3-ol (47). To a solution of diol S-**24** (d.r. ≥ 99:1, 429 mg, 2.97 mmol) in DMF (12 mL) were added imidazole (505 mg, 7.42 mmol) and *tert*-butyldiphenylsilyl chloride (800 μL, 859 mg, 3.13 mmol). The mixture was stirred at room temperature for 12 h, poured into H_2O (100 mL) and extracted with Et_2O (4 × 50 mL). The organic extracts were combined, washed successively with 1 N HCl, saturated aqueous $NaHCO_3$ and brine (1 × 50 mL each), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was subjected to flash column chromatography on silica gel (5%

EtOAc/hexanes) to isolate **47** containing minor impurity (presumably *tert*-butyldiphenylsilanol). Further purification by flash chromatography on silica gel (50% CH_2Cl_2/hexanes) afforded alcohol **47** as a colorless oil (d.r. ≥ 99:1, 879 mg, 77%). No evidence for minor isomer was observed by ^{1}H NMR.

Data for (2*R*,3*S*,*E*)-1-(*tert*-butyldiphenylsilyloxy)-2,4-dimethylhex-4-en-3-ol (47): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69–7.65 (m, 4H), 7.45–7.36 (m, 6H), 5.56–5.50 (m, 1H), 4.18 (d, *J* = 4.5 Hz, 1H), 3.66–3.59 (m, 2H), 2.31 (s, 1H), 1.89–1.80 (m, 1H), 1.61 (d, *J* = 6.8 Hz, 3H), 1.53 (s, 3H), 1.06 (s, 9H), 0.93 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.34, 135.88, 135.81, 133.68, 133,52, 129.92, 129.88, 127.90, 120.09, 78.54, 67.85, 38.20, 27.07, 19.44, 13.18, 12.83, 11.20; IR (thin film, NaCl) 3448 (br), 3071, 2931, 2858, 1889, 1825, 1720, 1668, 1590, 1473, 1428, 1390, 1362, 1306, 1261, 1188, 1113, 1007, 940, 824, 740, 702 cm^{-1}; HRMS (ESI, FT-ICR) *m/z* calc'd for $C_{24}H_{34}O_2Si$+Na^+ 405.2220, found 405.2222; $[\alpha]_D^{20}$ –11.5 (*c* 1.00, $CHCl_3$); R_f 0.41 (silica gel, $CHCl_3$).

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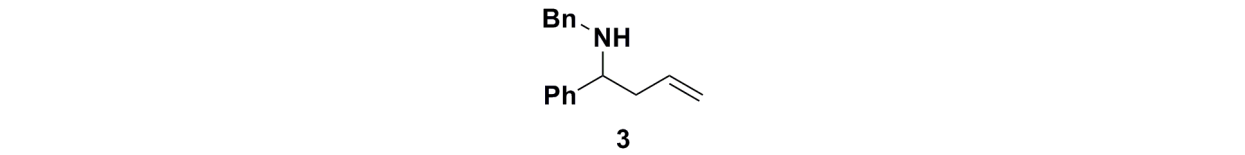

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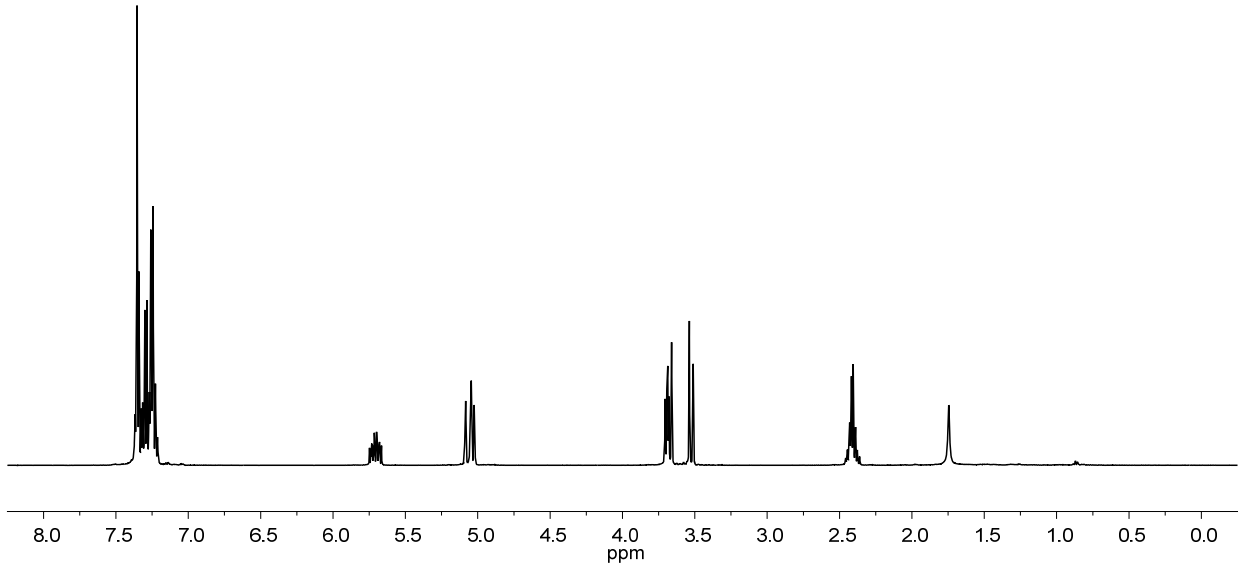
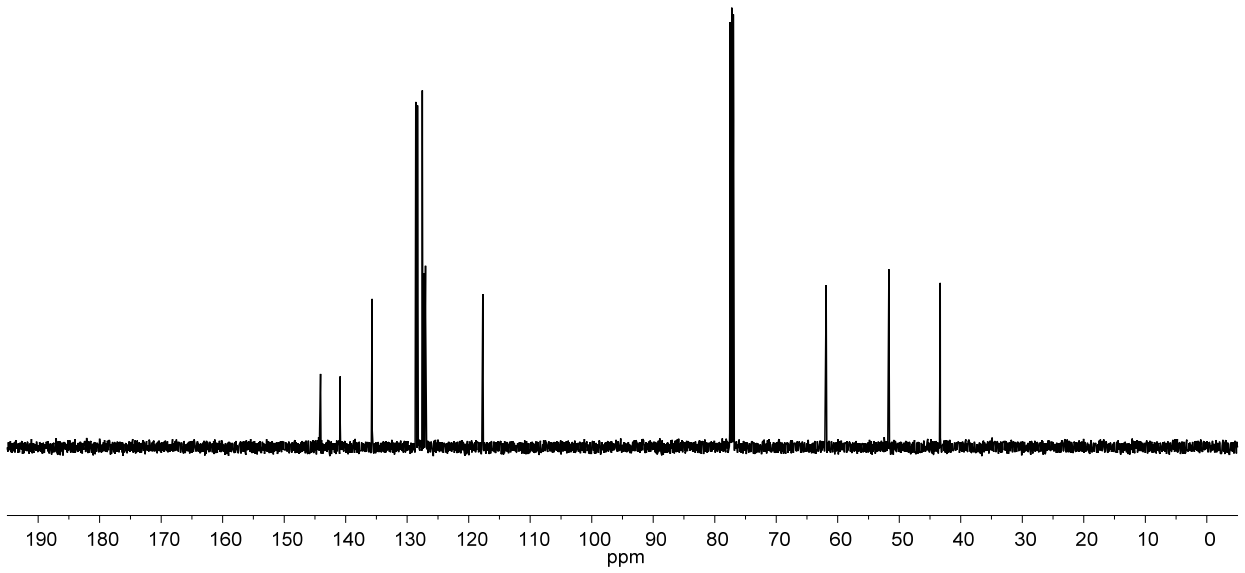
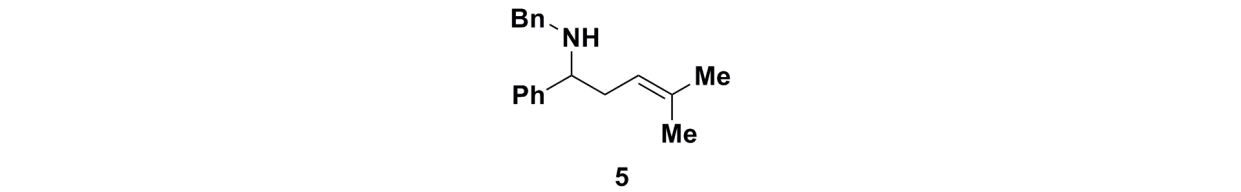




^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **3**



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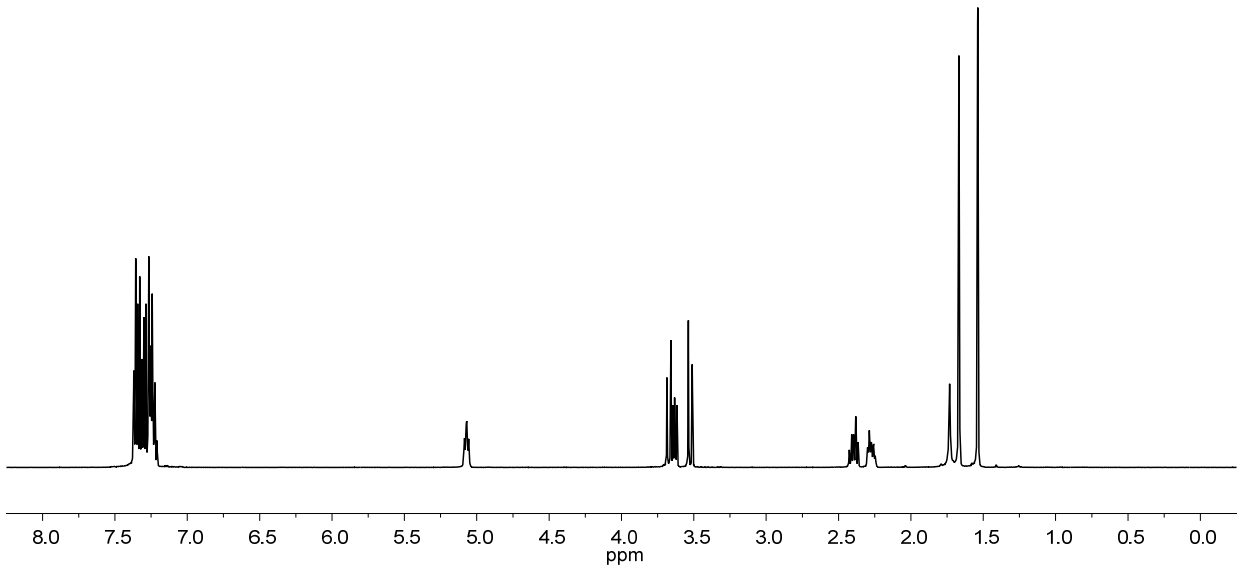
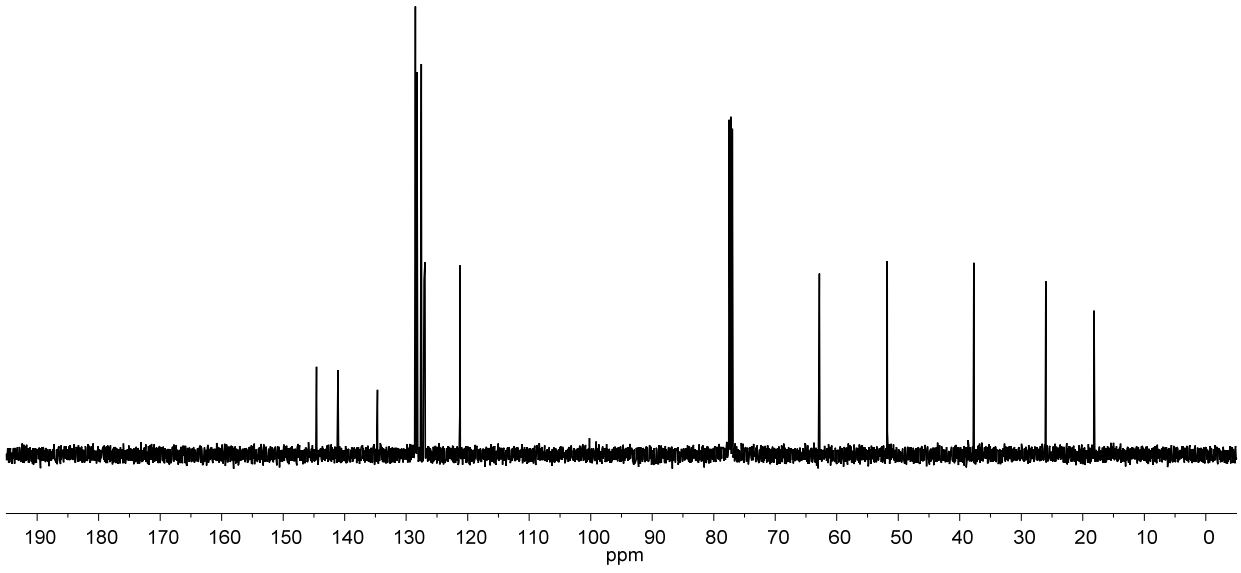
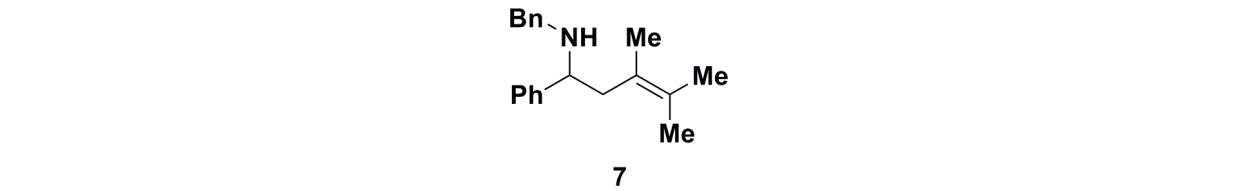




^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **5**



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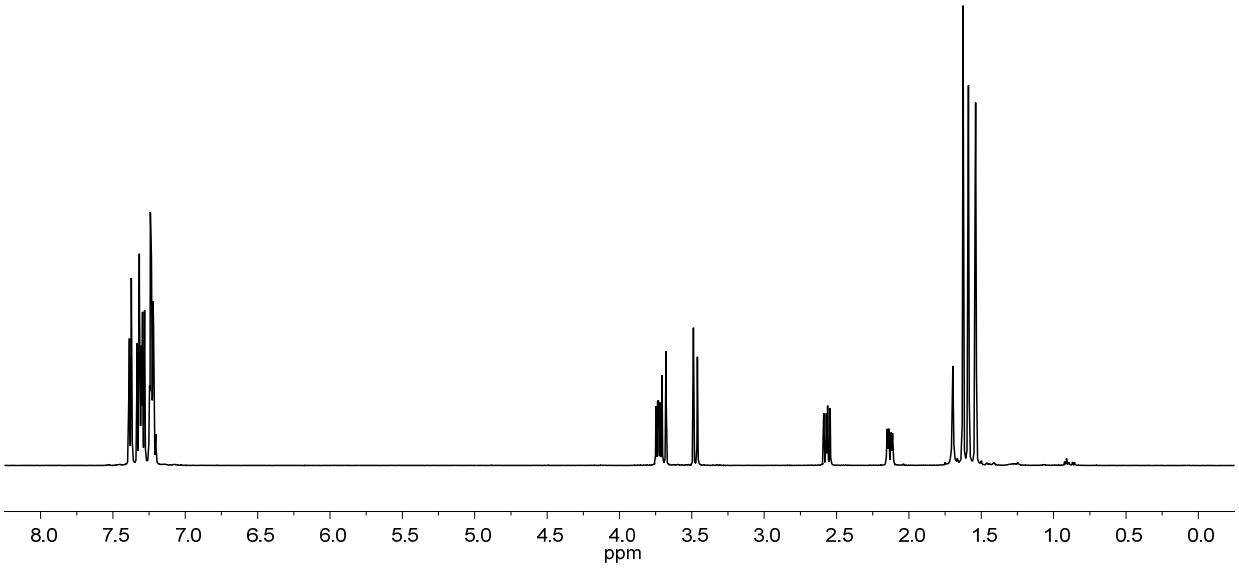
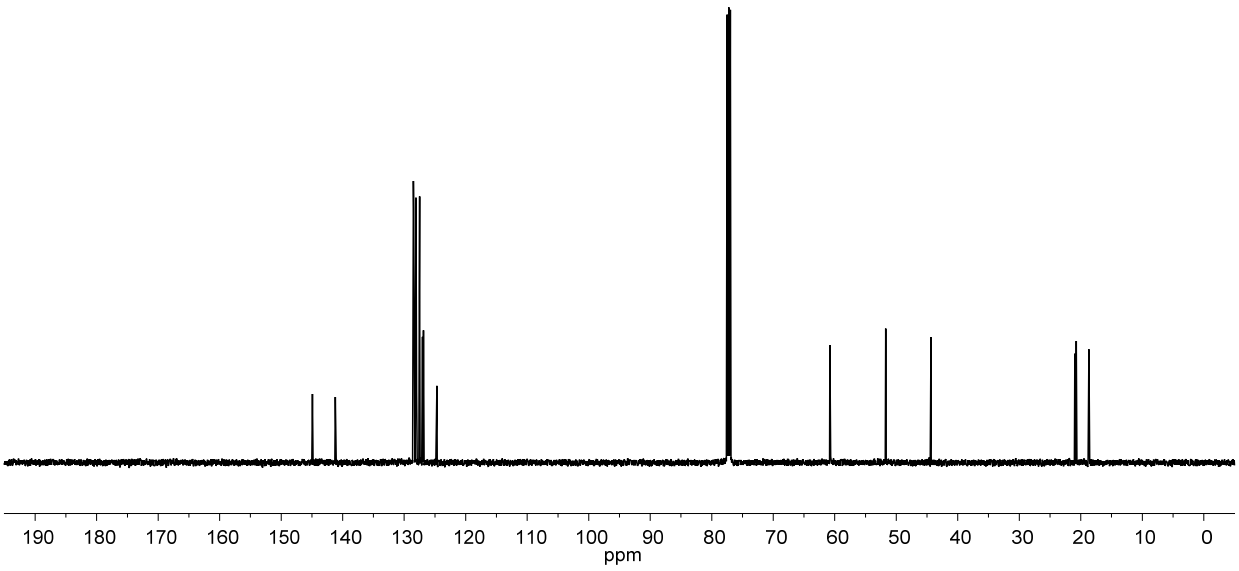
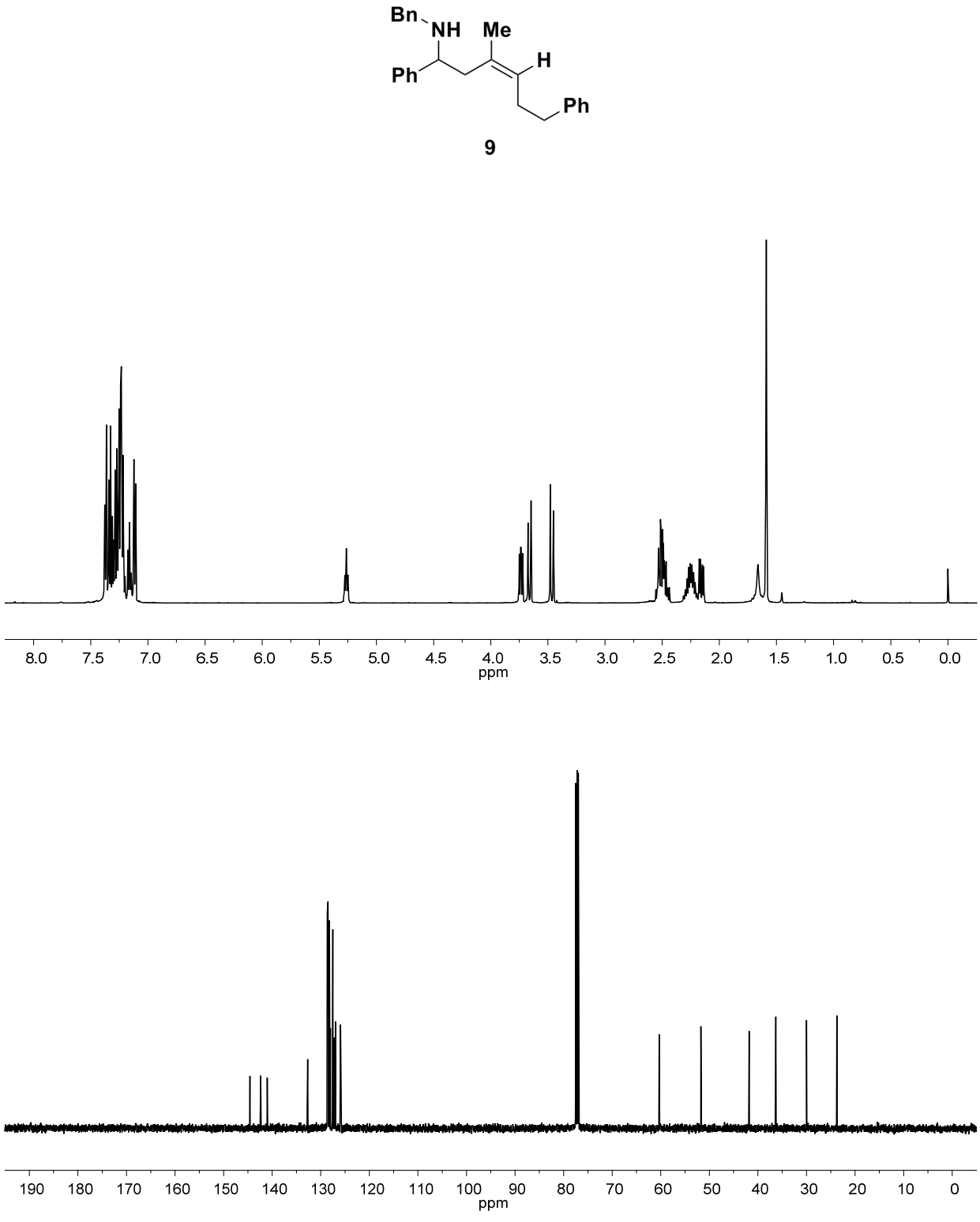
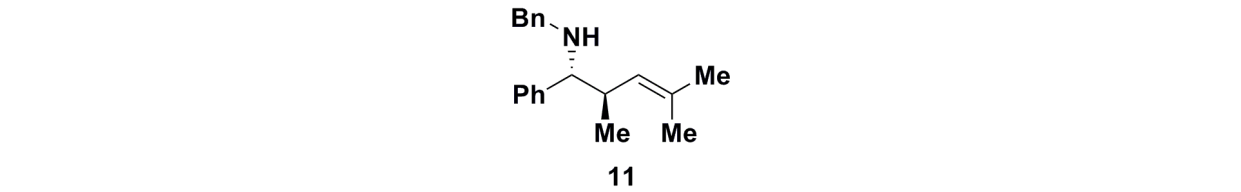




^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **7**



^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **9**



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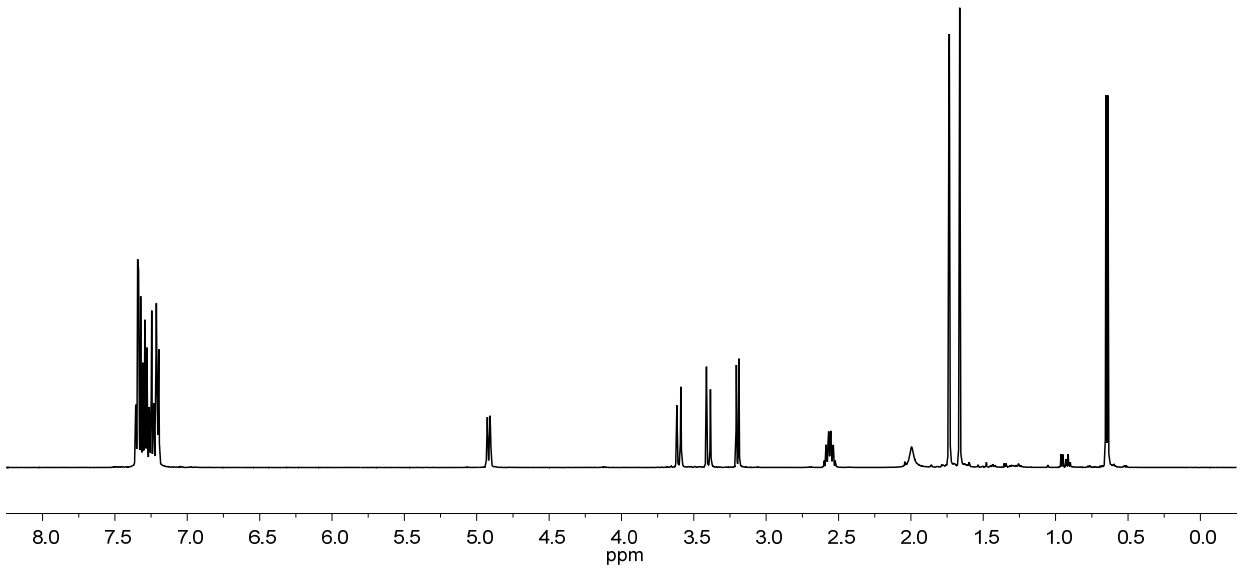
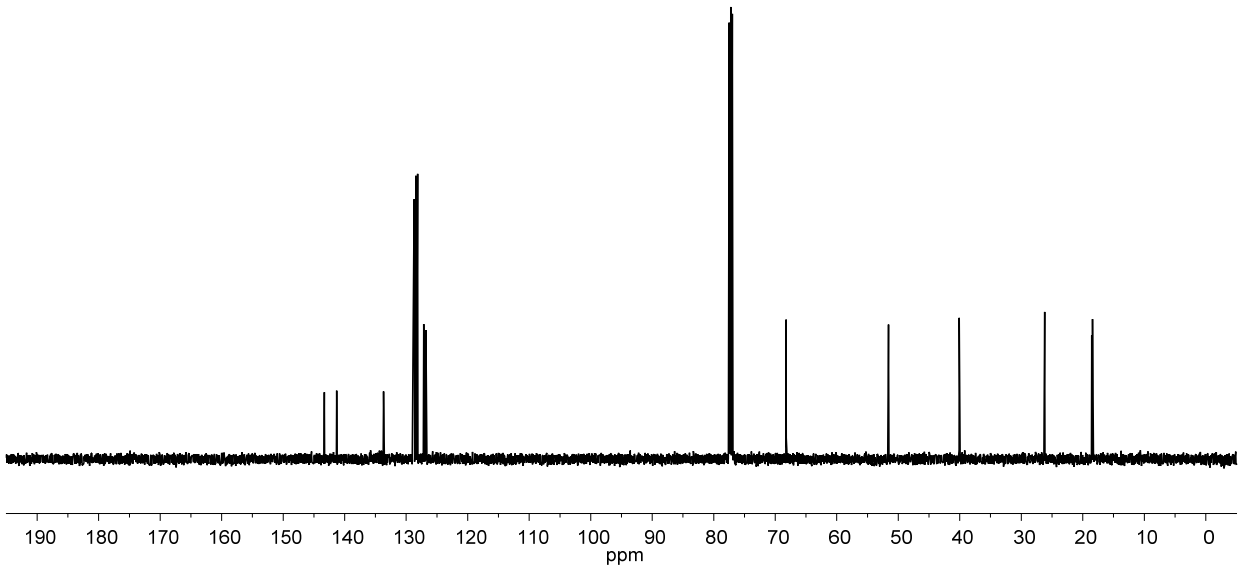
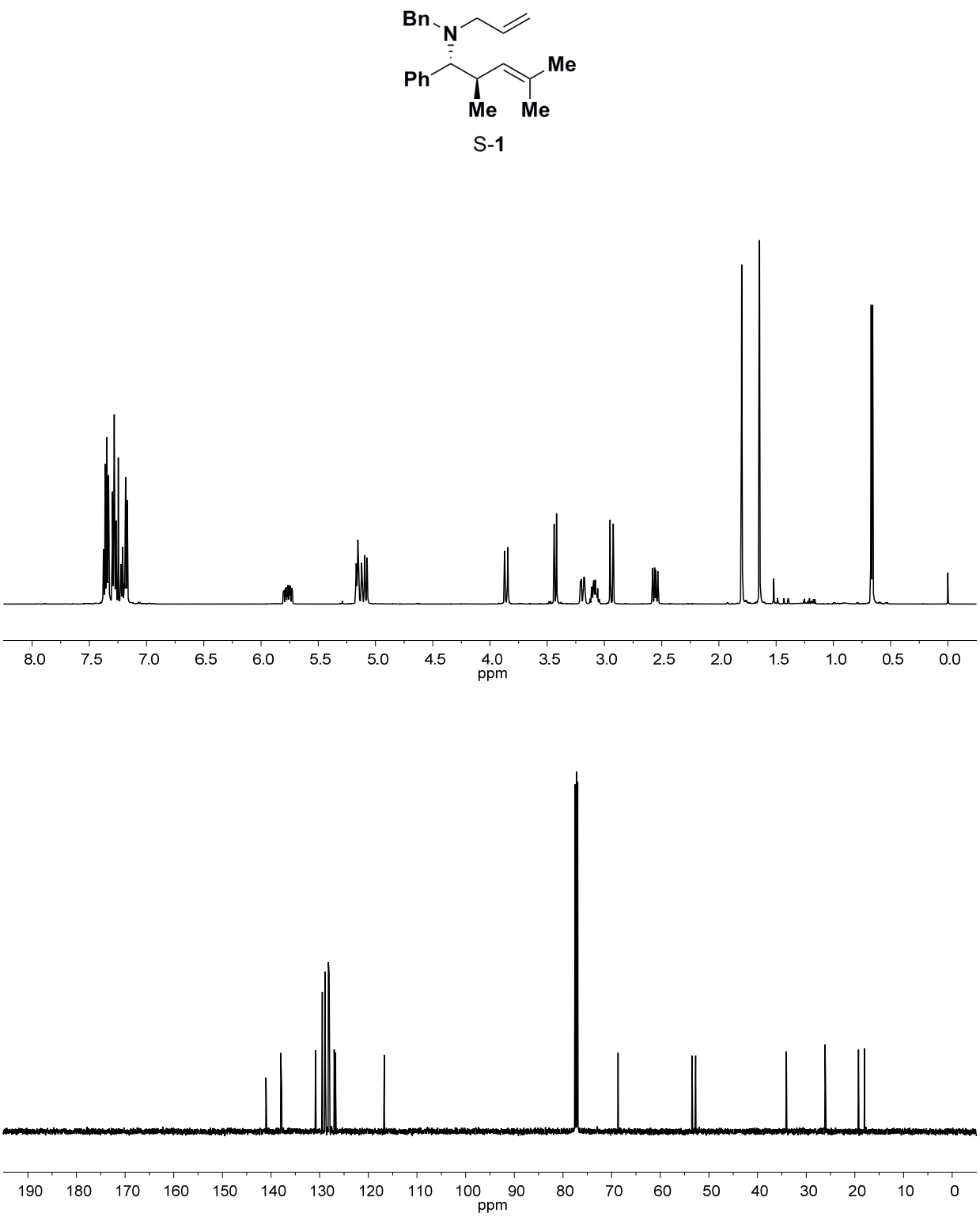


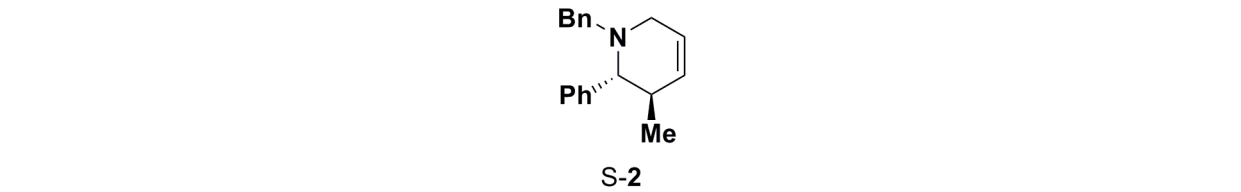


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **11** (from **10**)

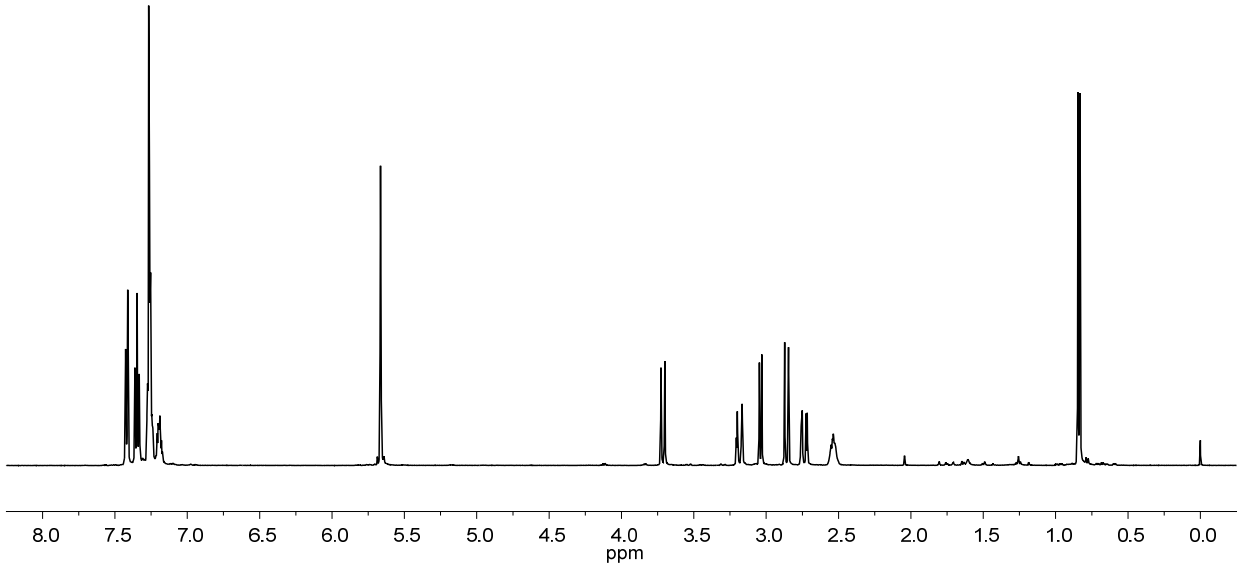


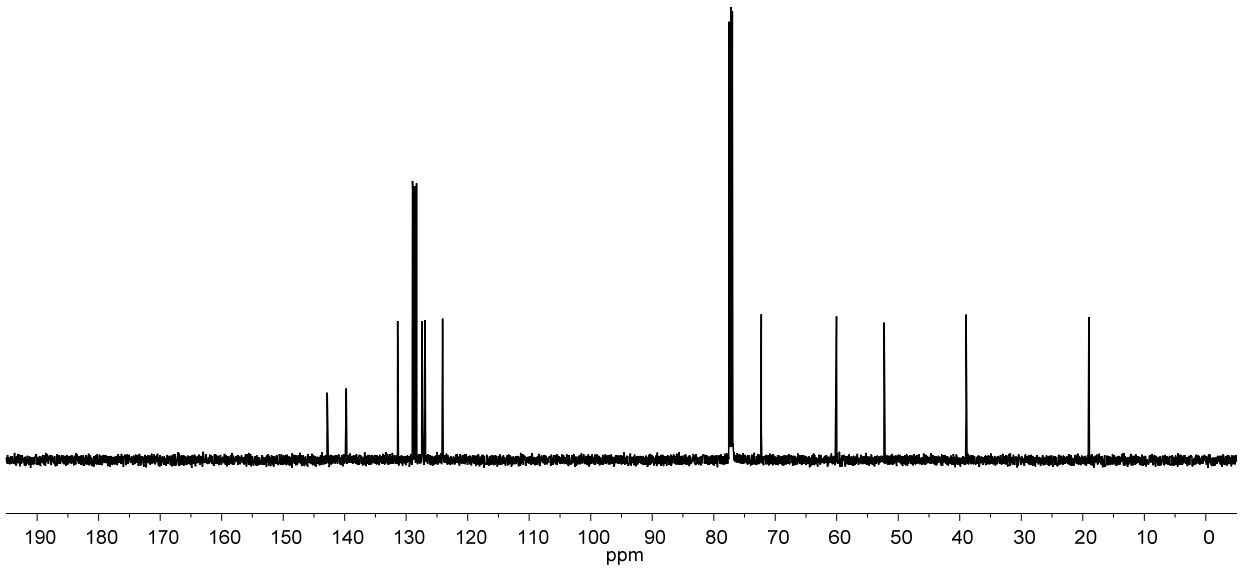
S-**1**

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**1** (from **10**)



S-**2**





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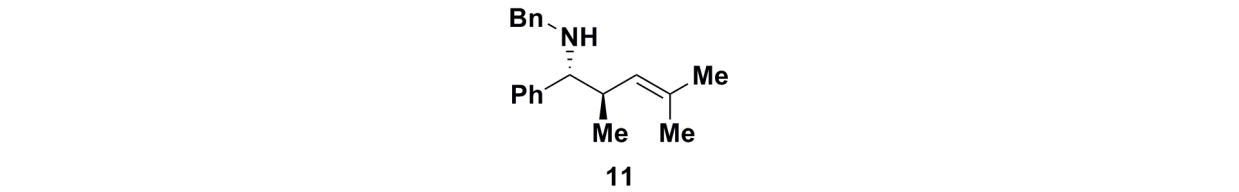

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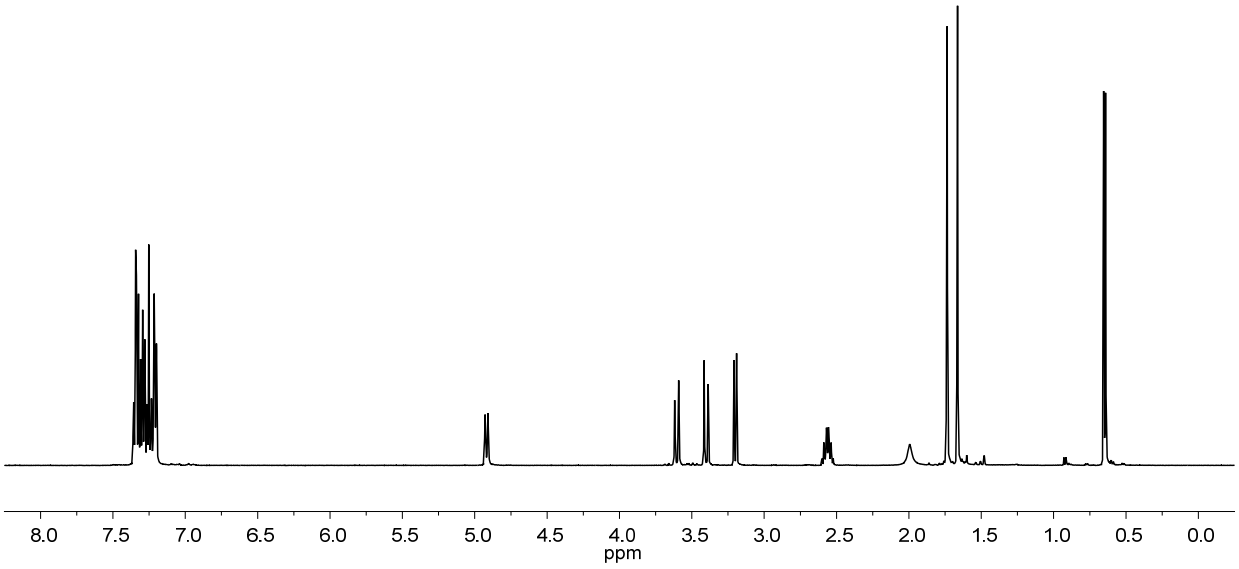
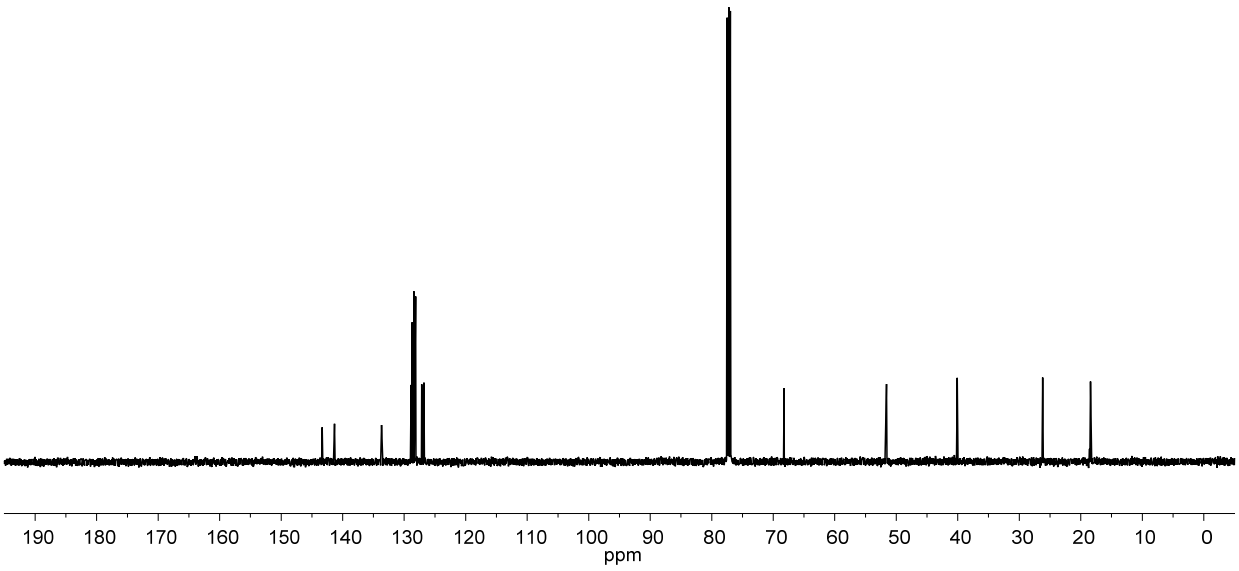
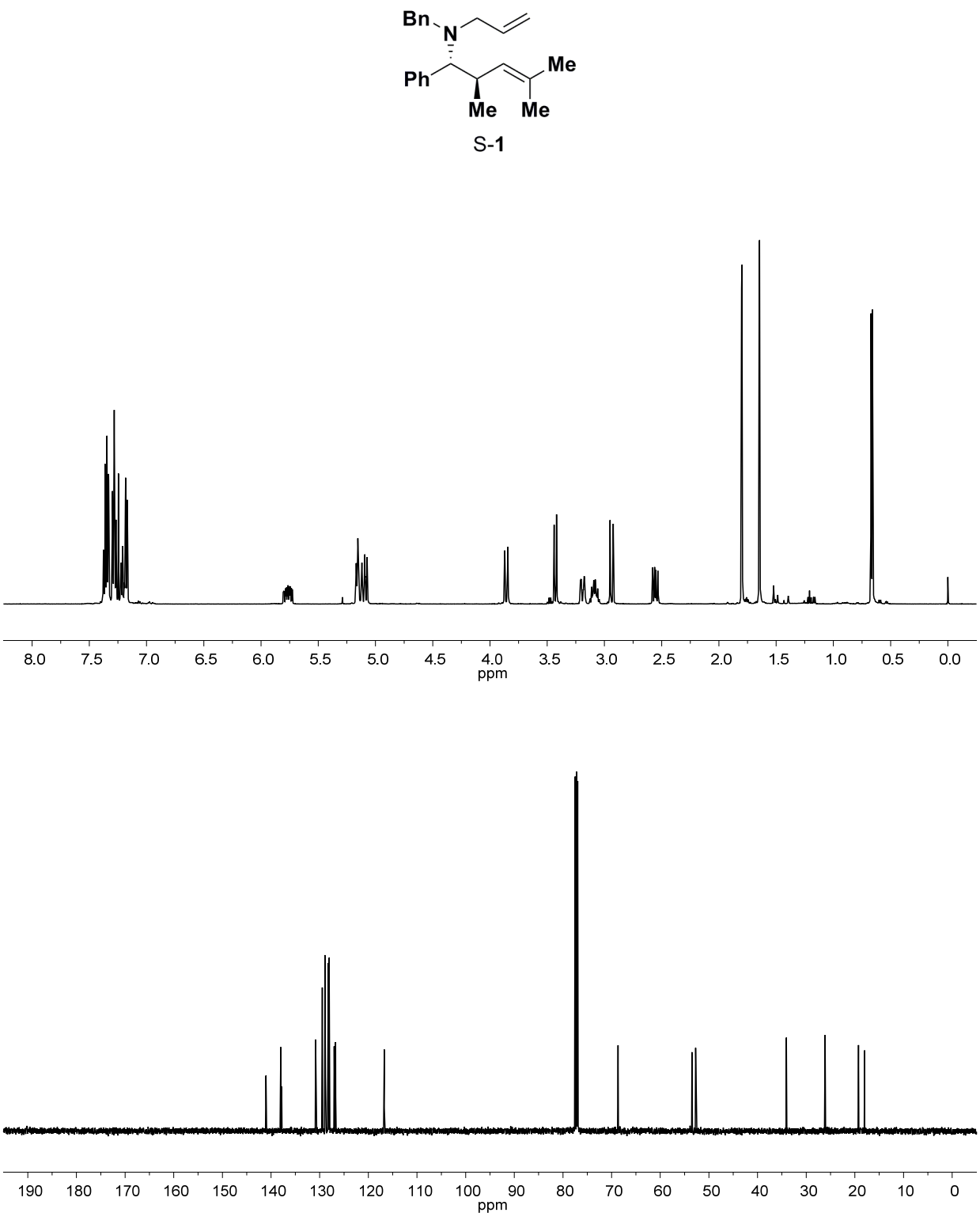


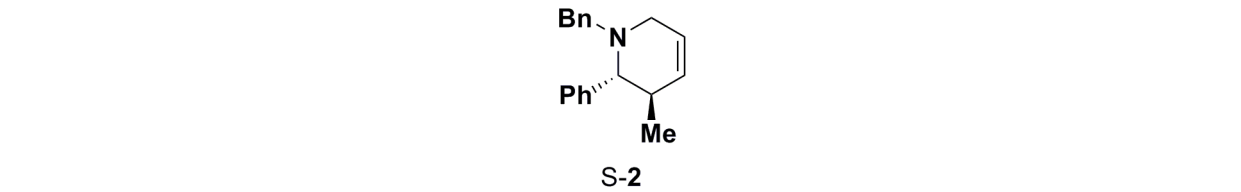


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **11** (from **12**)

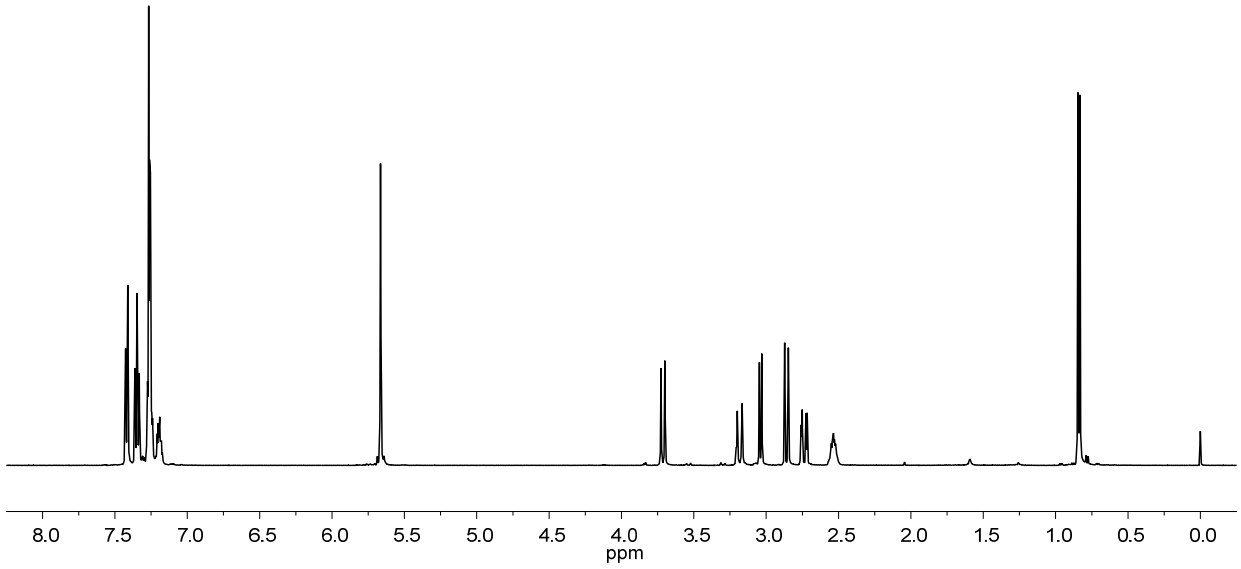


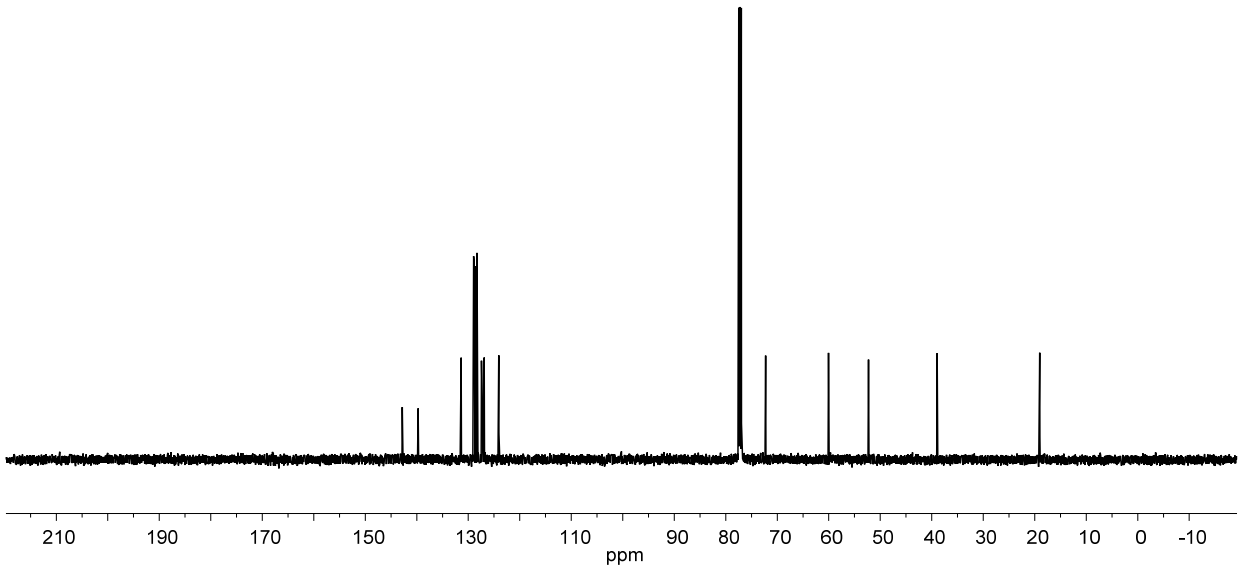
S-**1**

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**1** (from **12**)

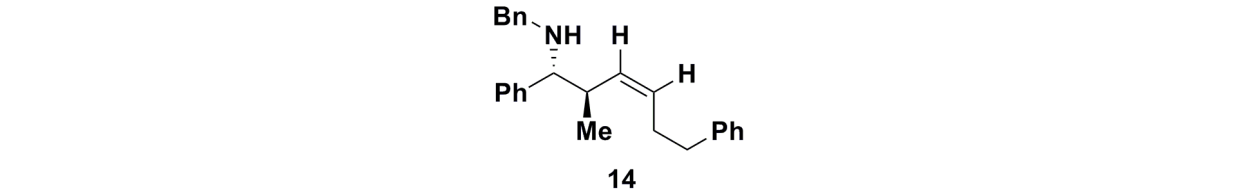


S-**2**





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**2** (from **12**)



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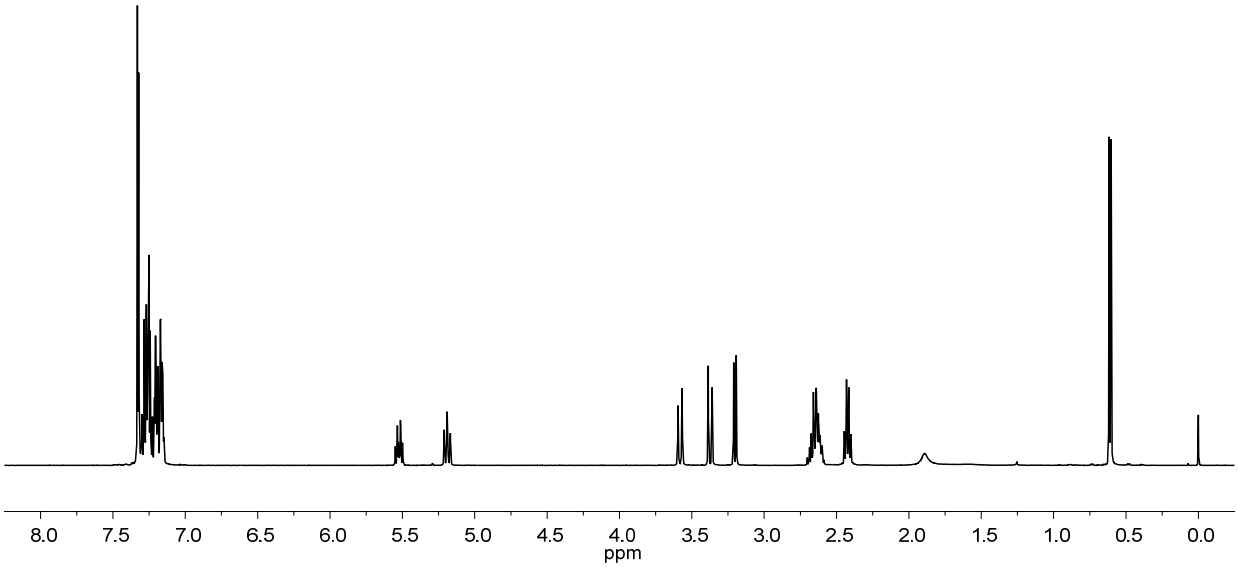
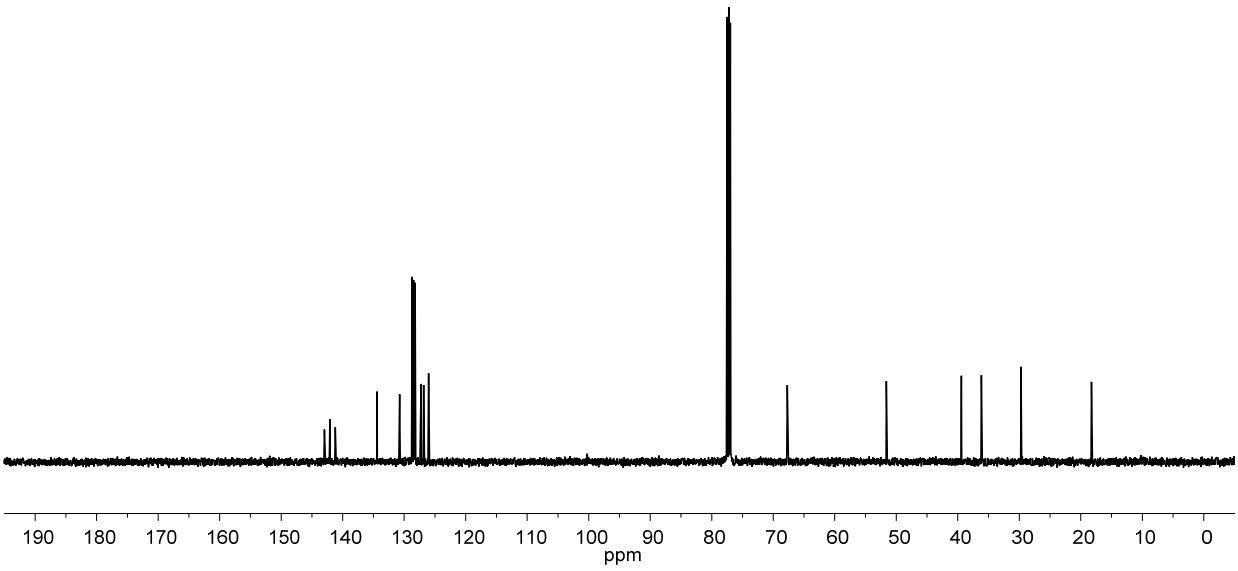
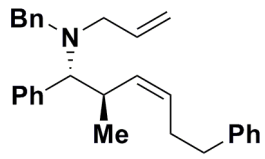
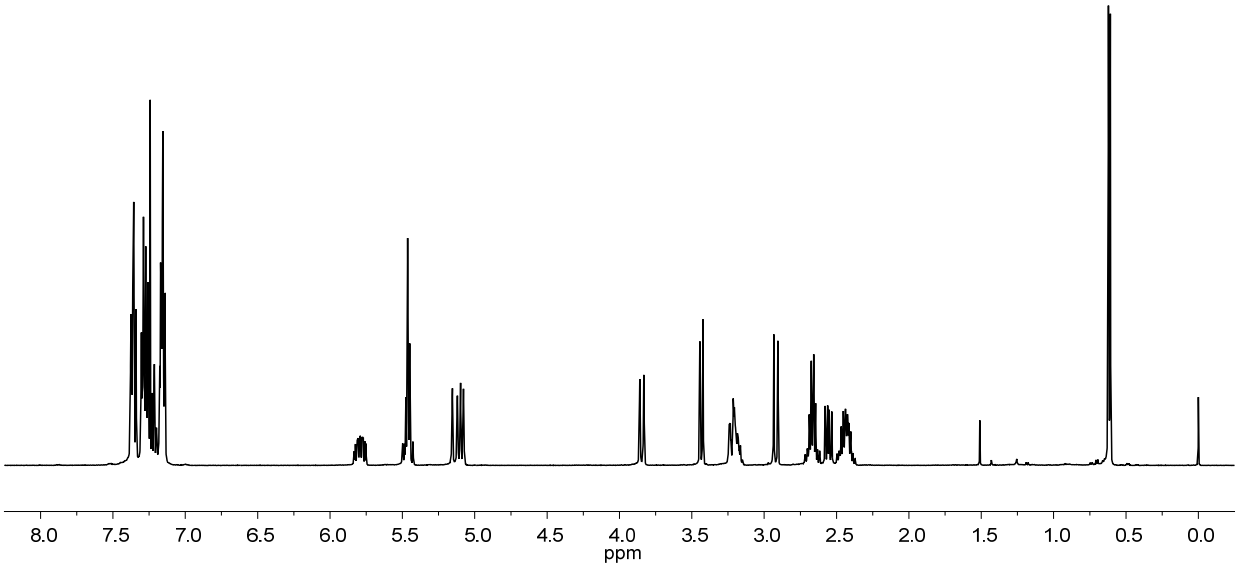


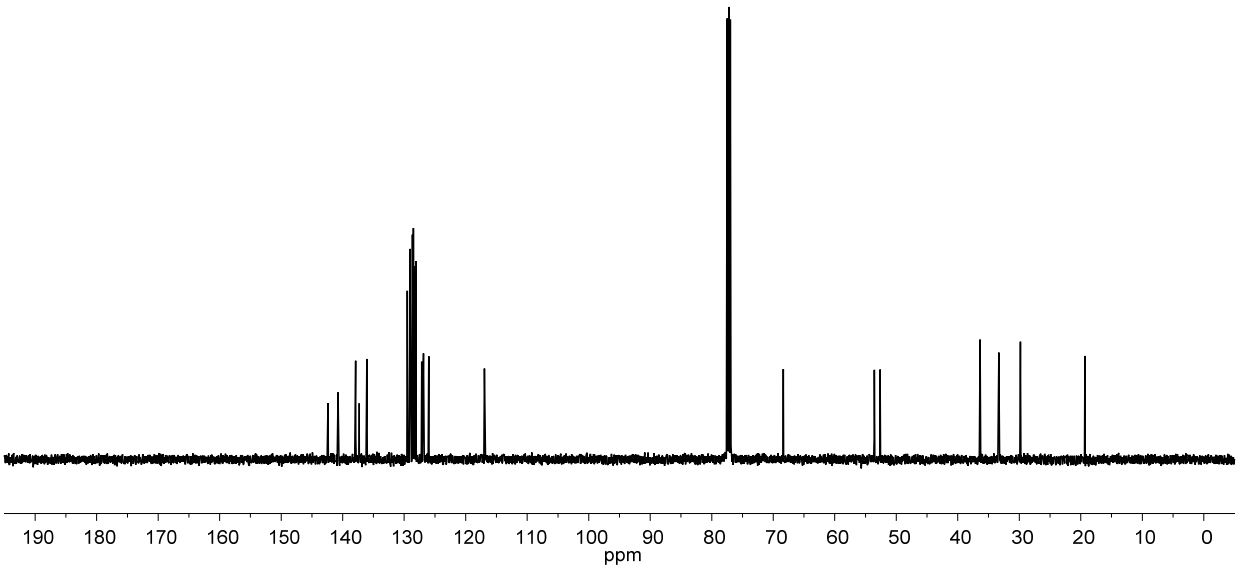


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **14**

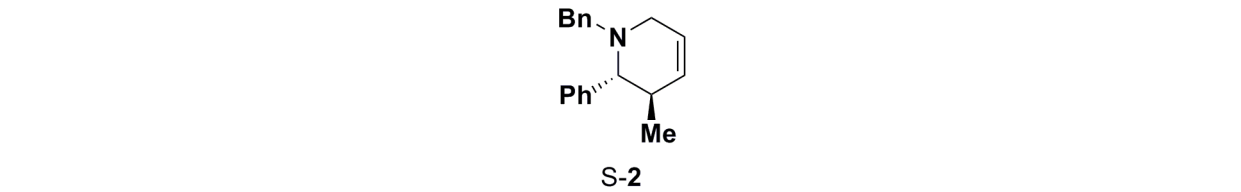


S-**3**

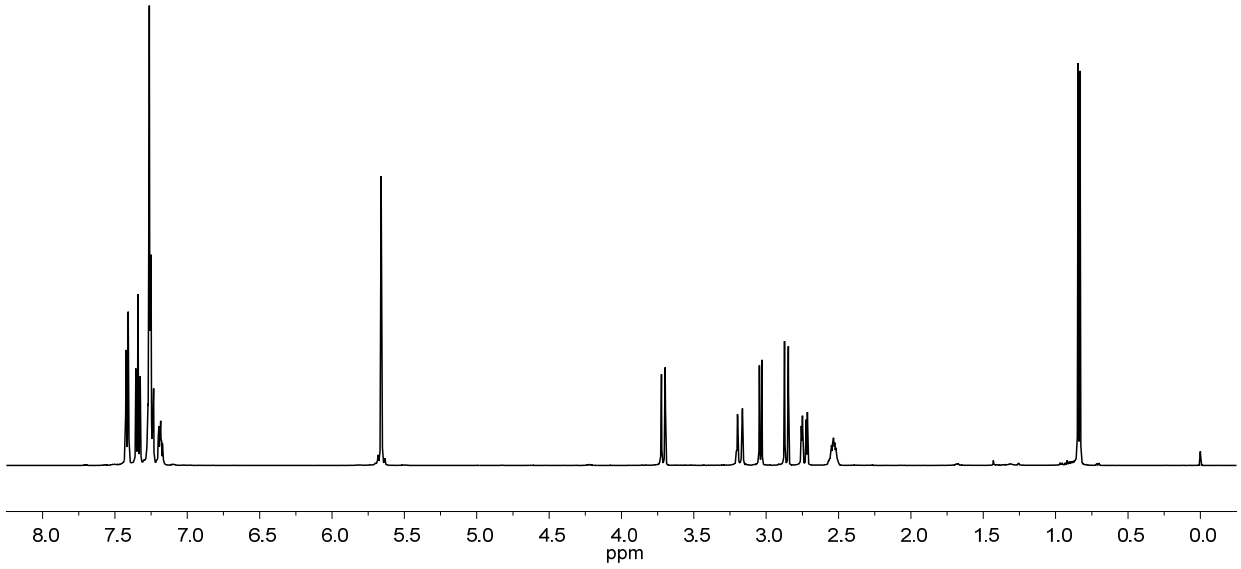


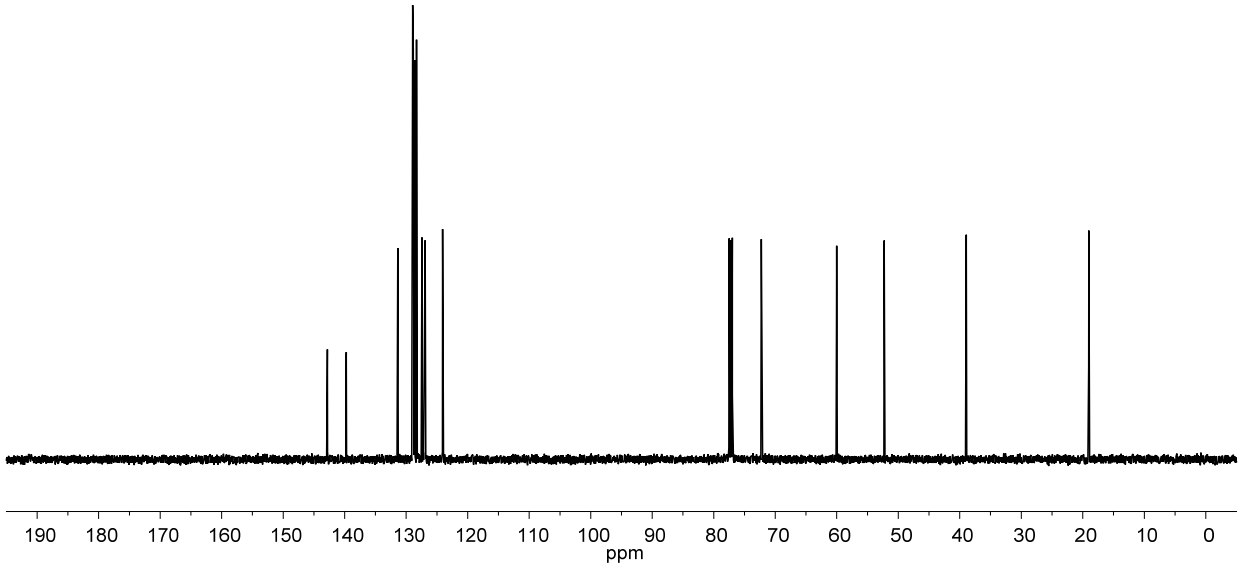


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**3**

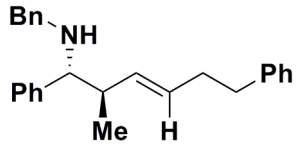


S-**2**





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**2** (from **13**, via **14**)



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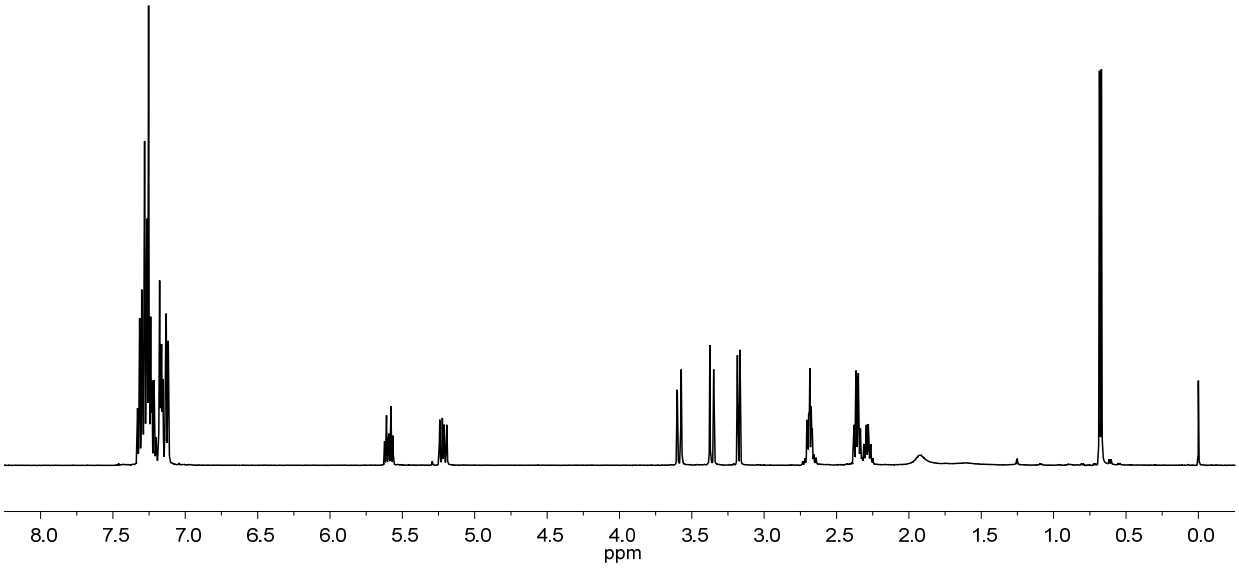
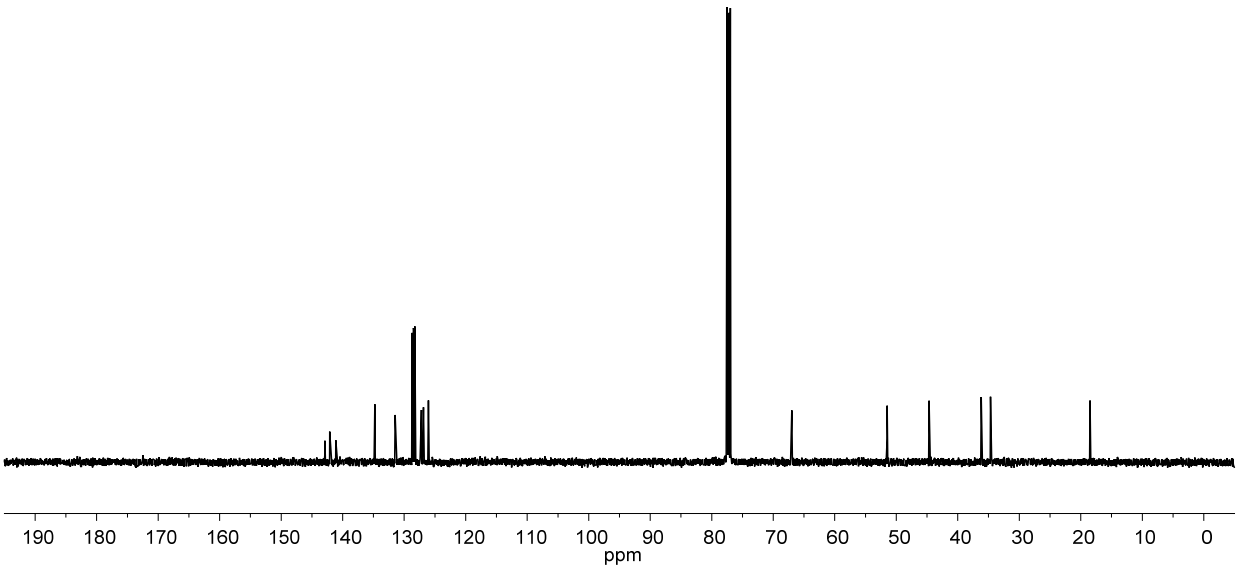
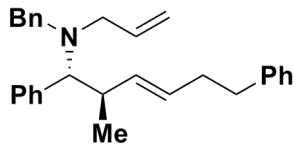
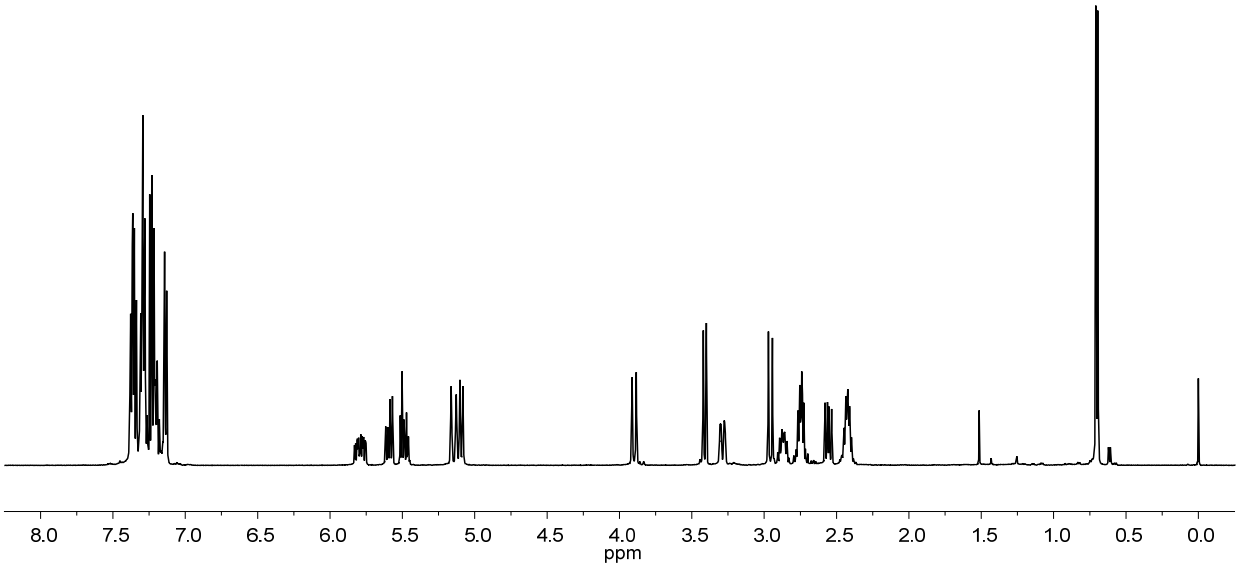


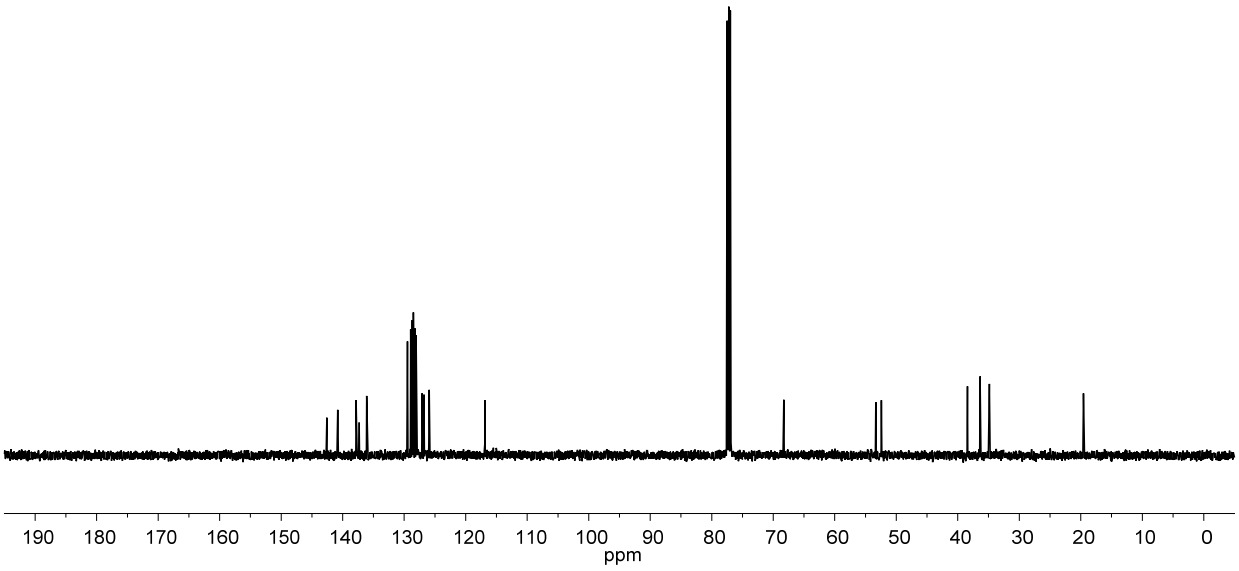


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **16** (from **13**)

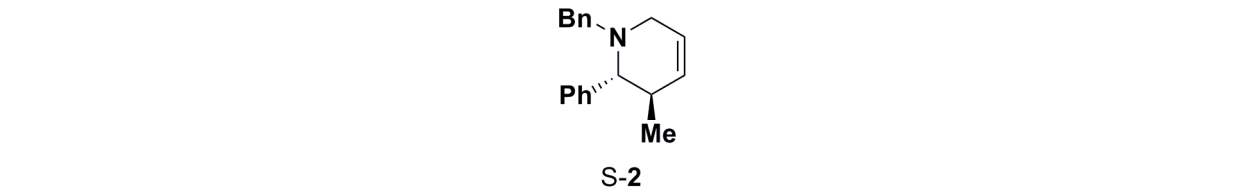


S-**4**

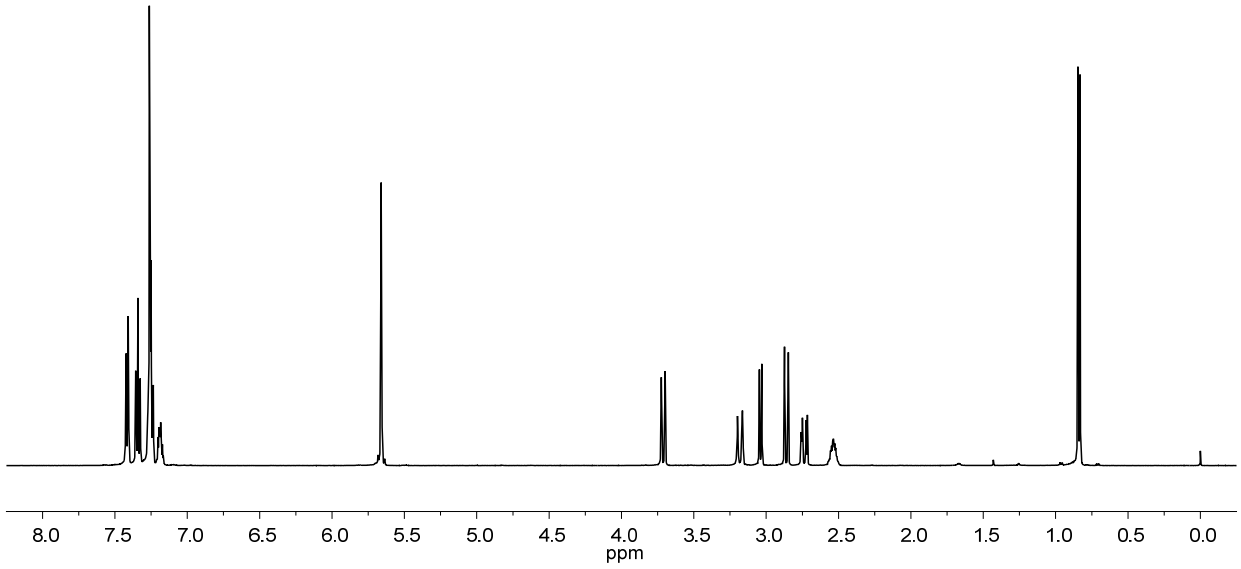


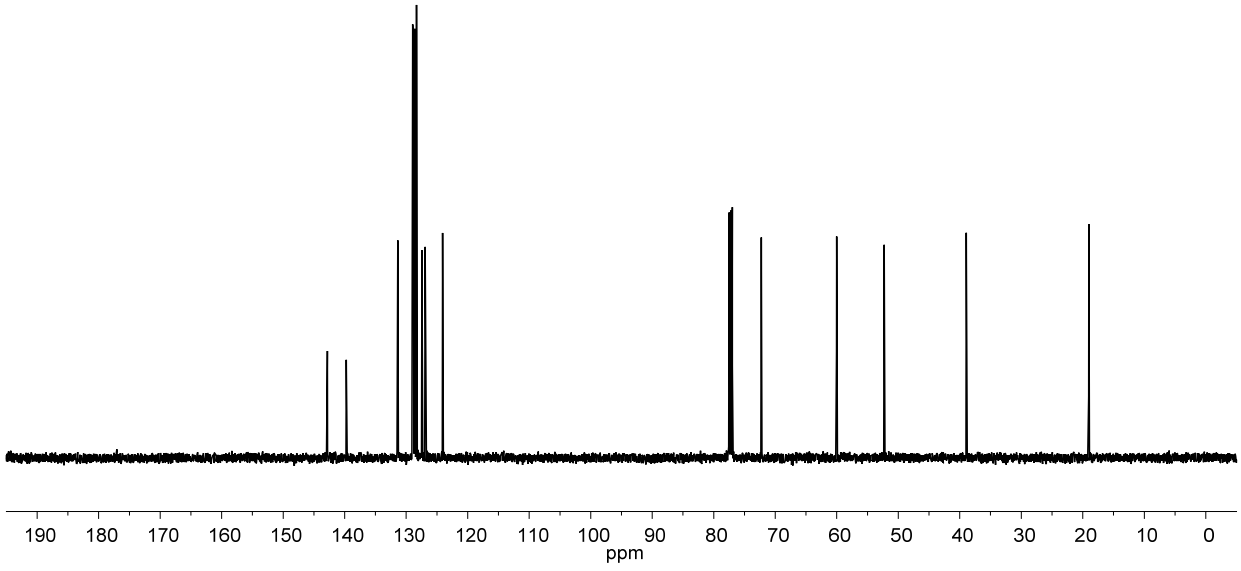


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**4** (from **13**)

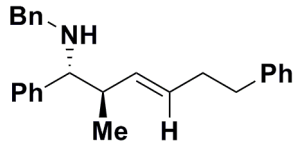


S-**2**

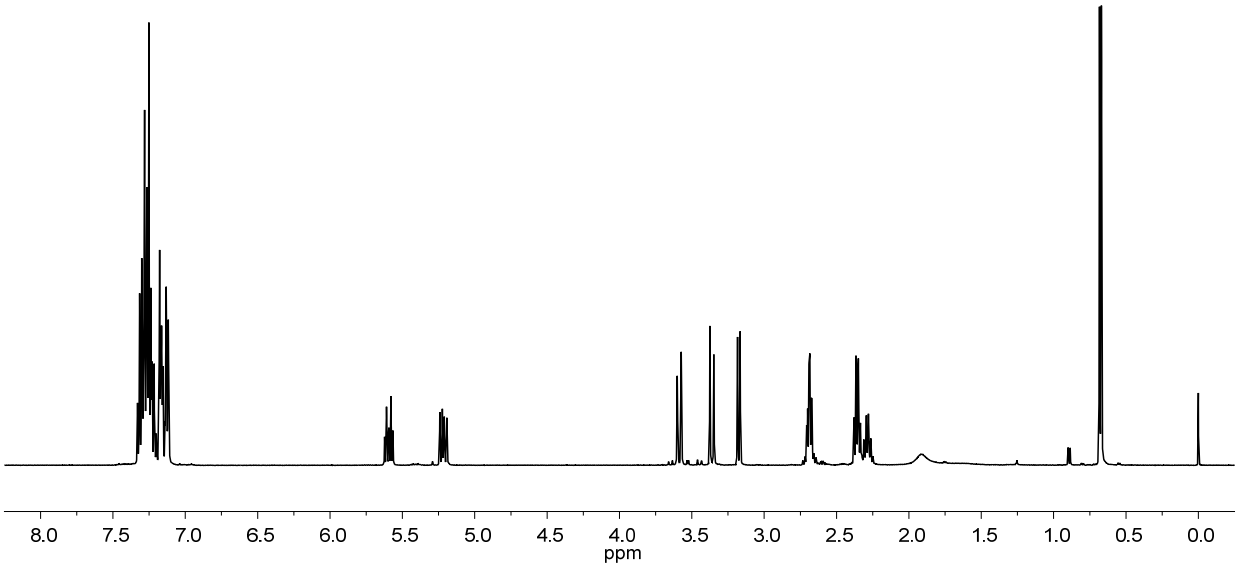


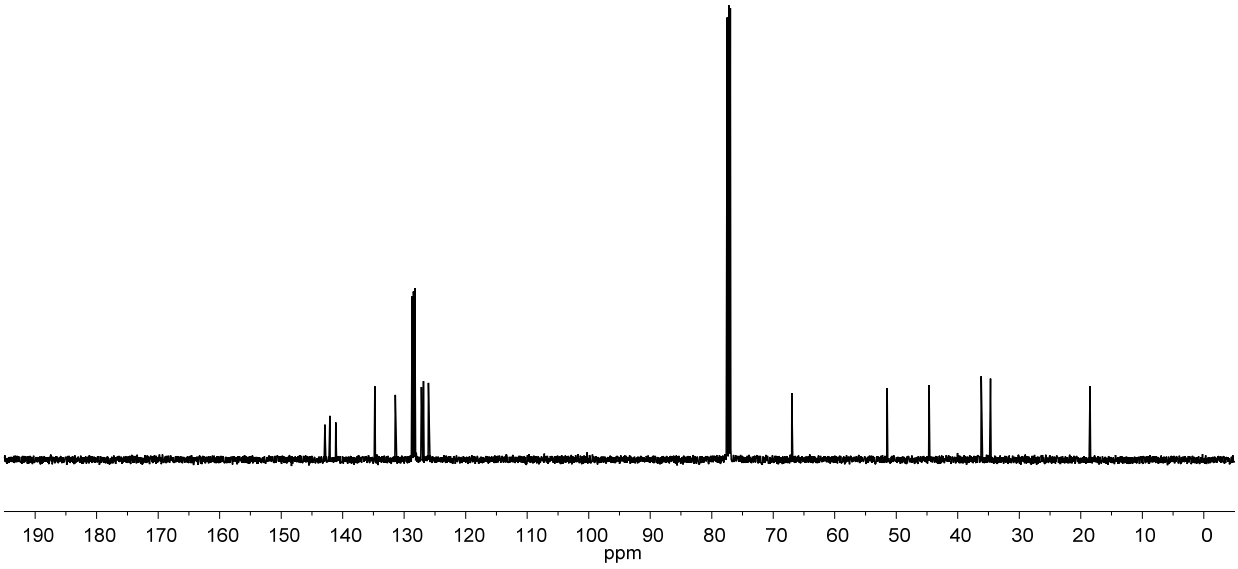


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**2** (from **13**, via **16**)

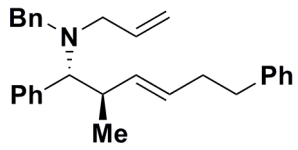


16

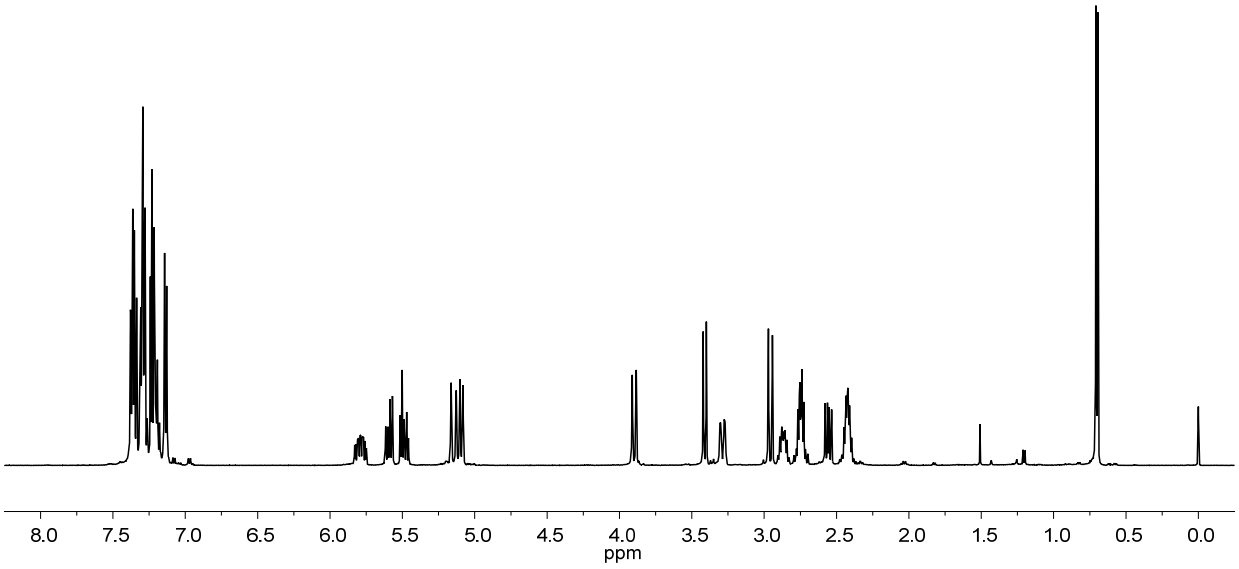


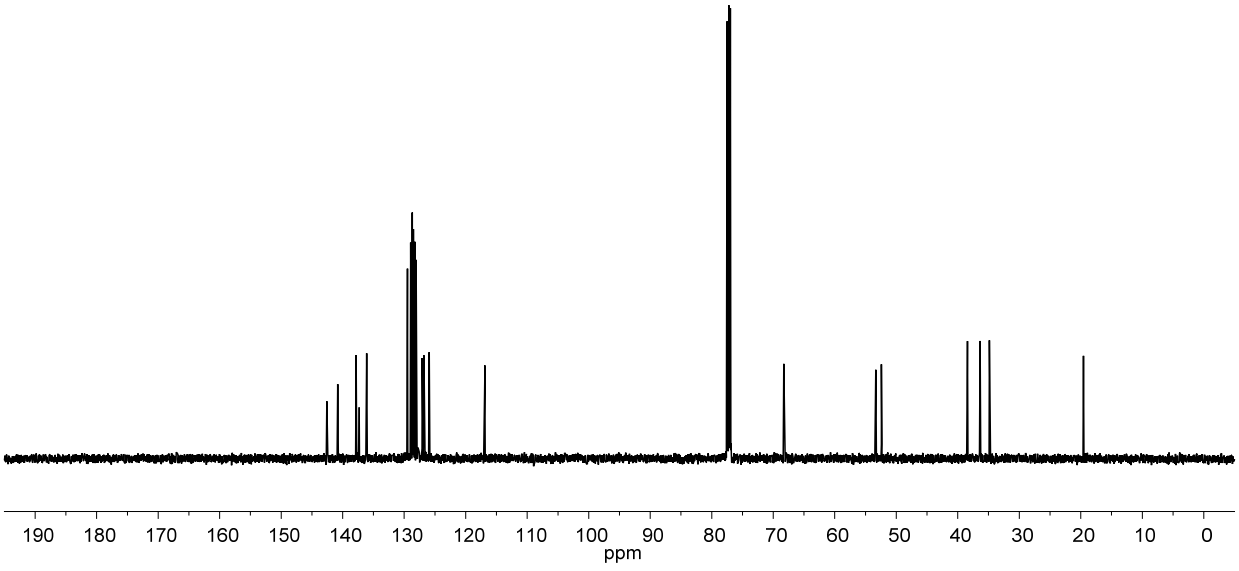


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **16** (from **15**)

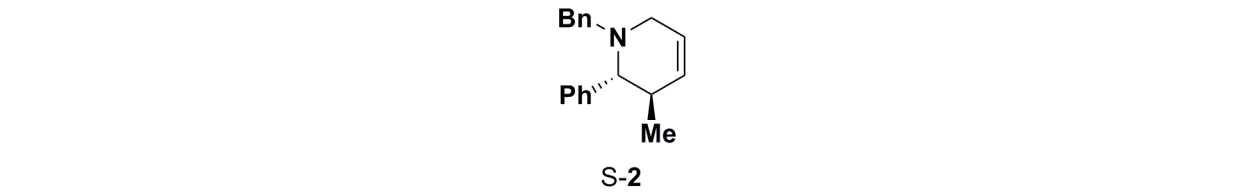


S-**4**

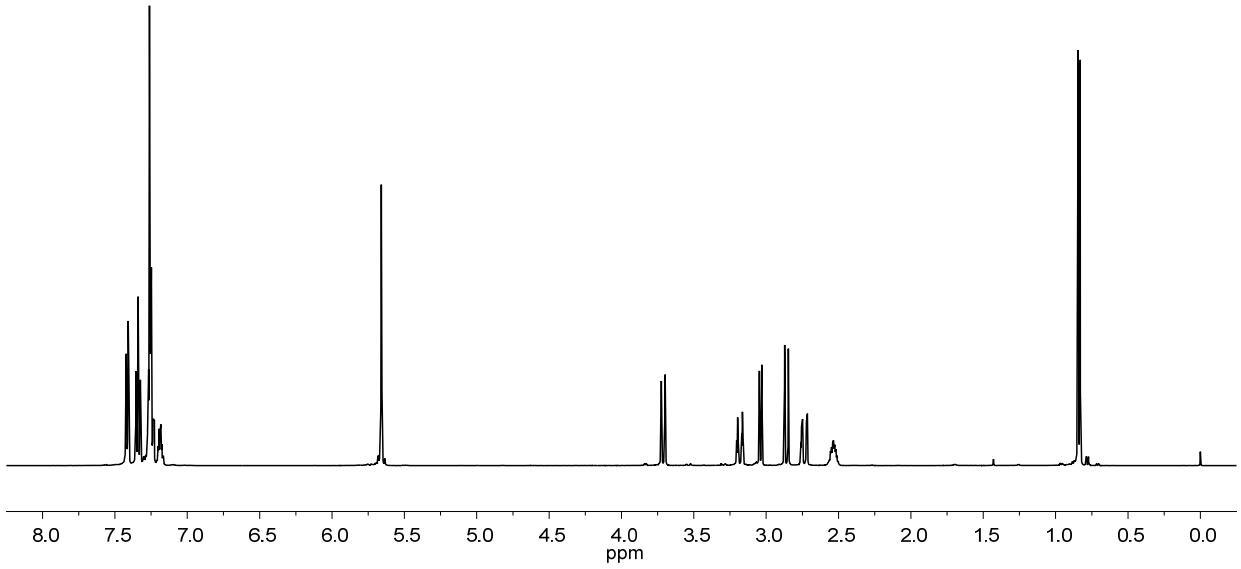


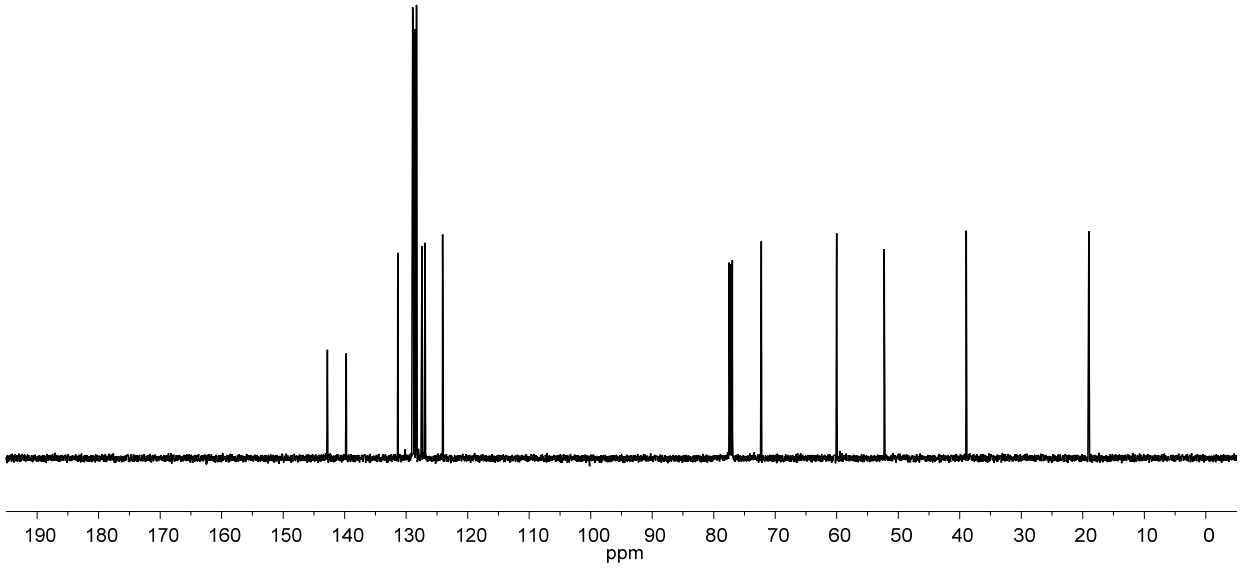


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**4** (from **15**)

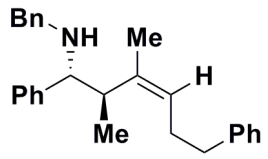


S-**2**

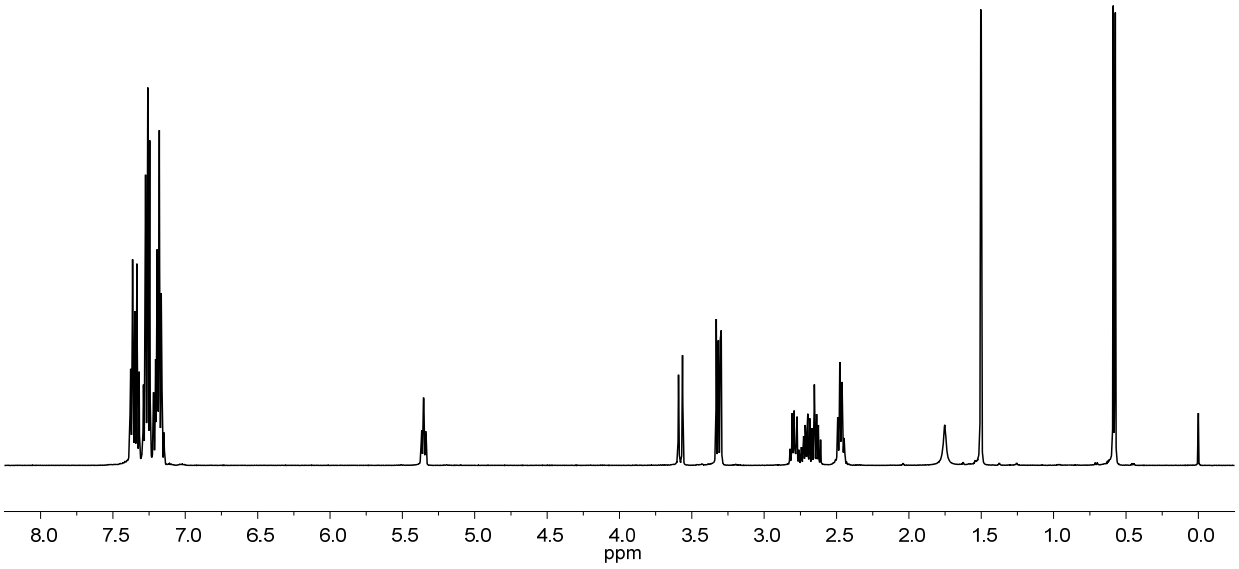


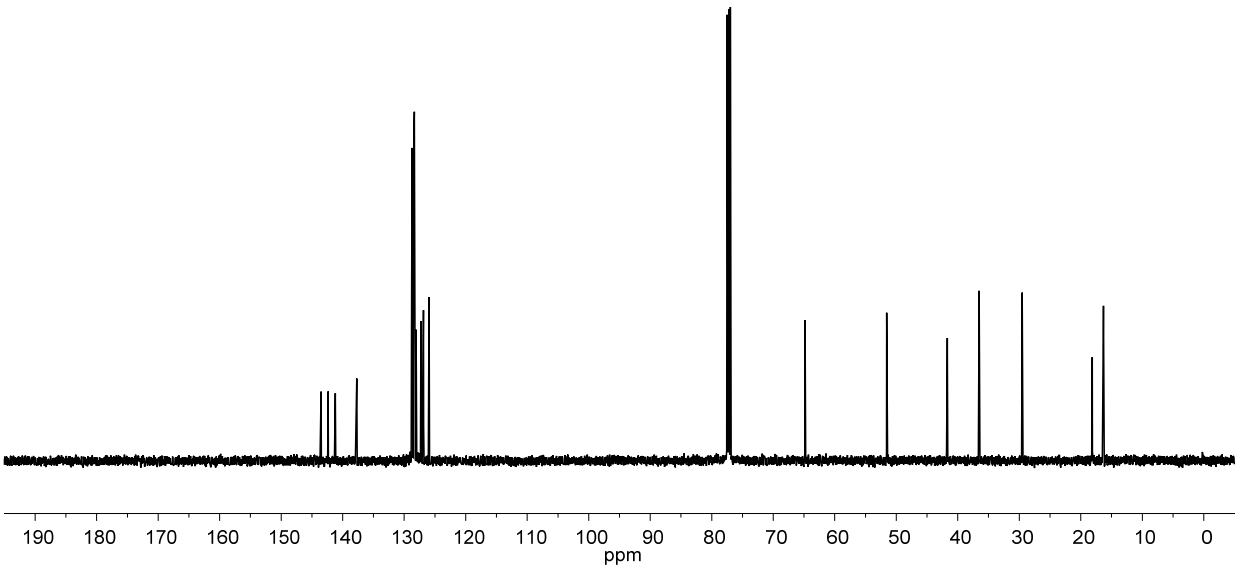


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**2** (from **15**)

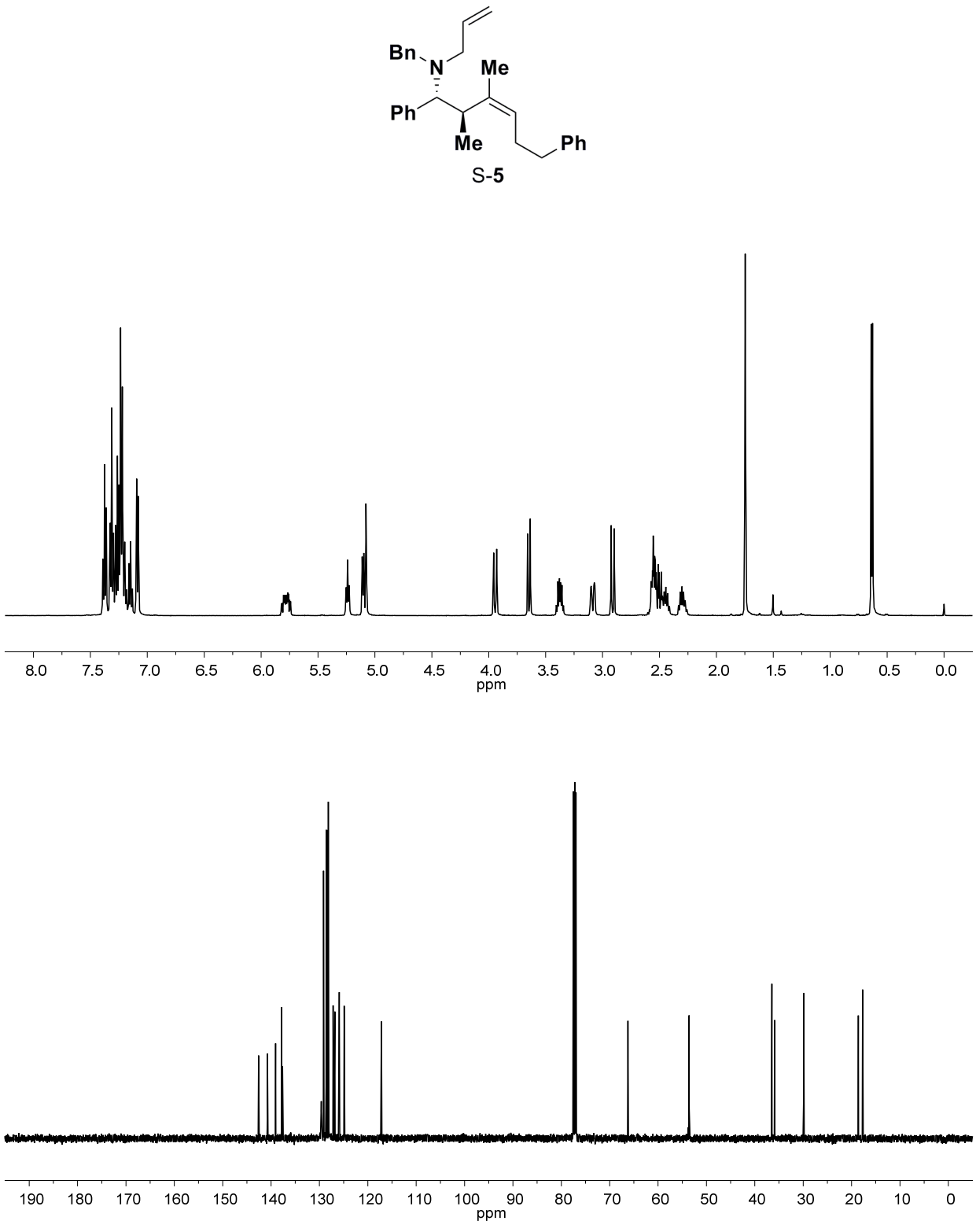


18

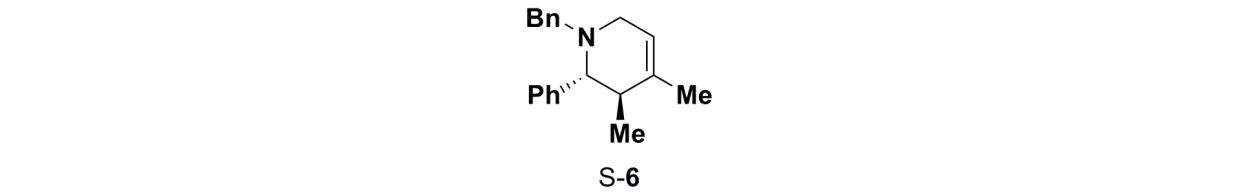




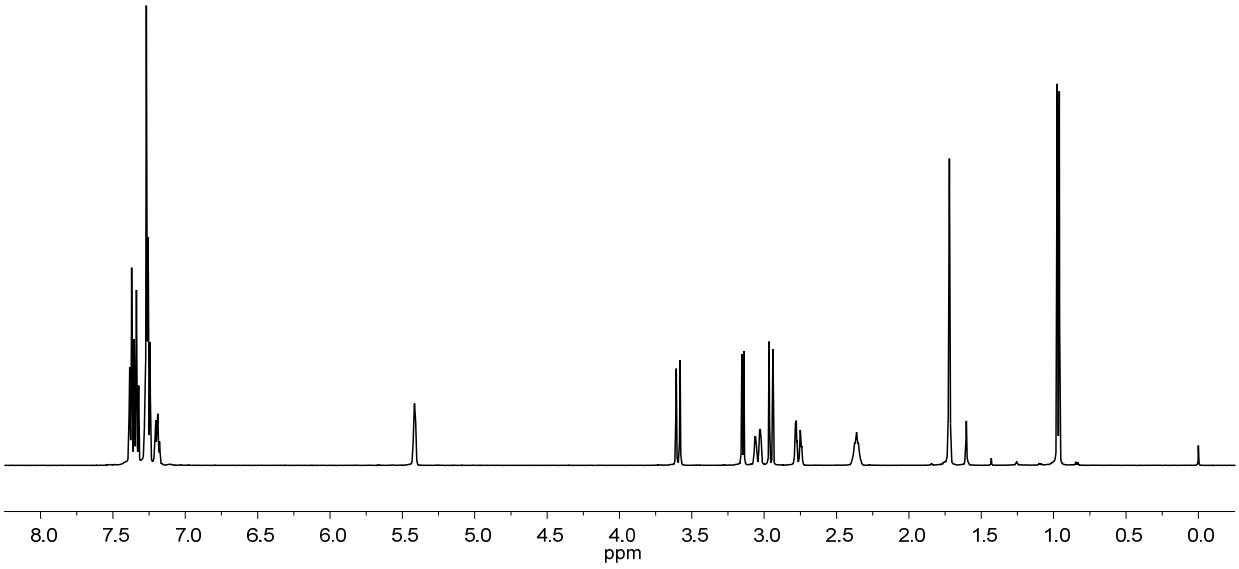
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **18**

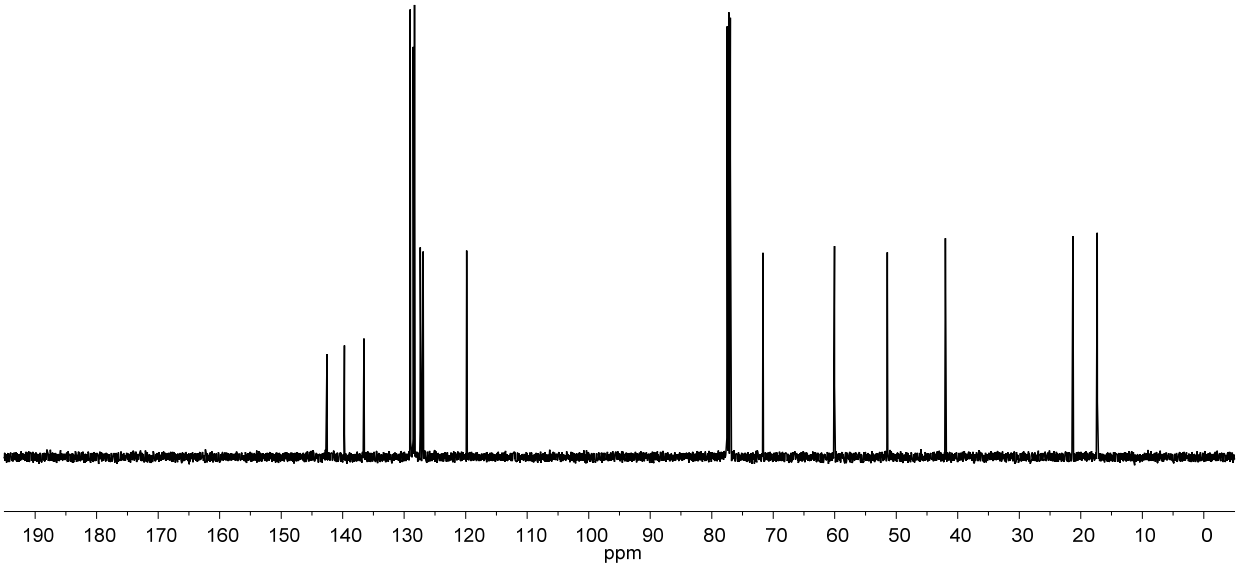


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**5**

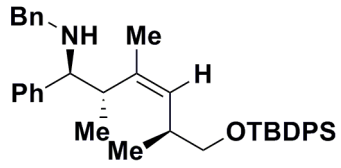


S-**6**





^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**6**



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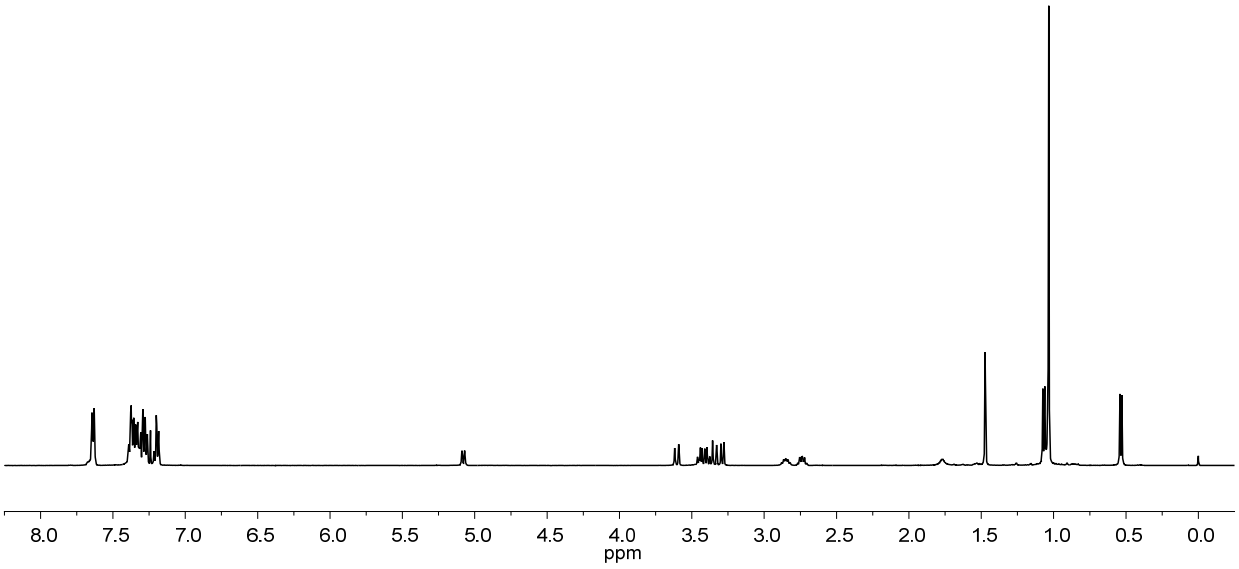
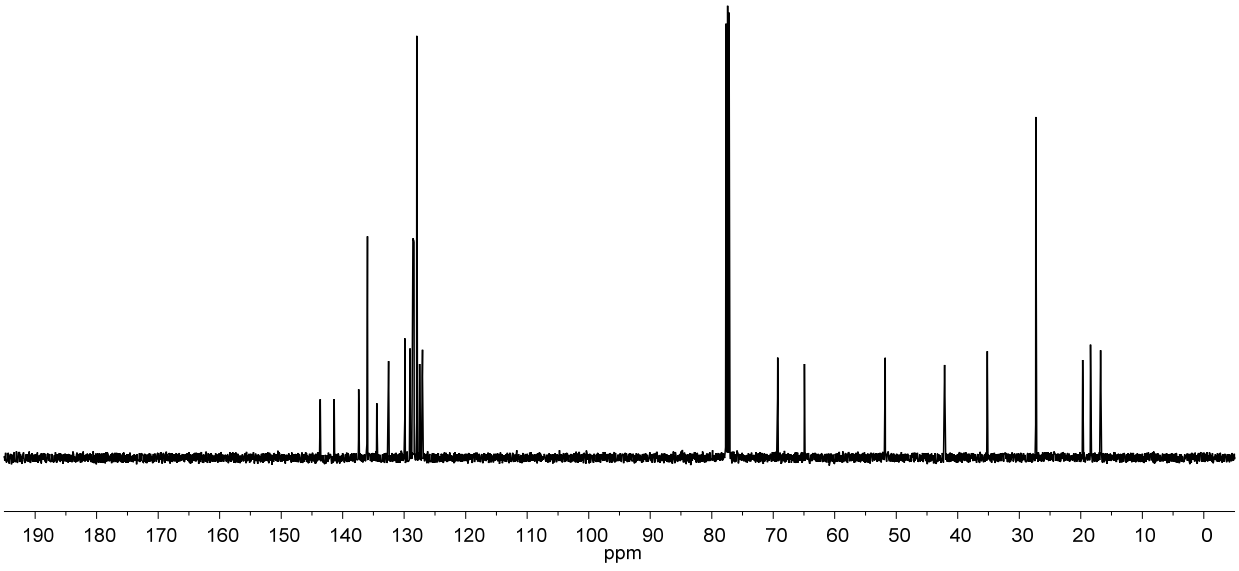
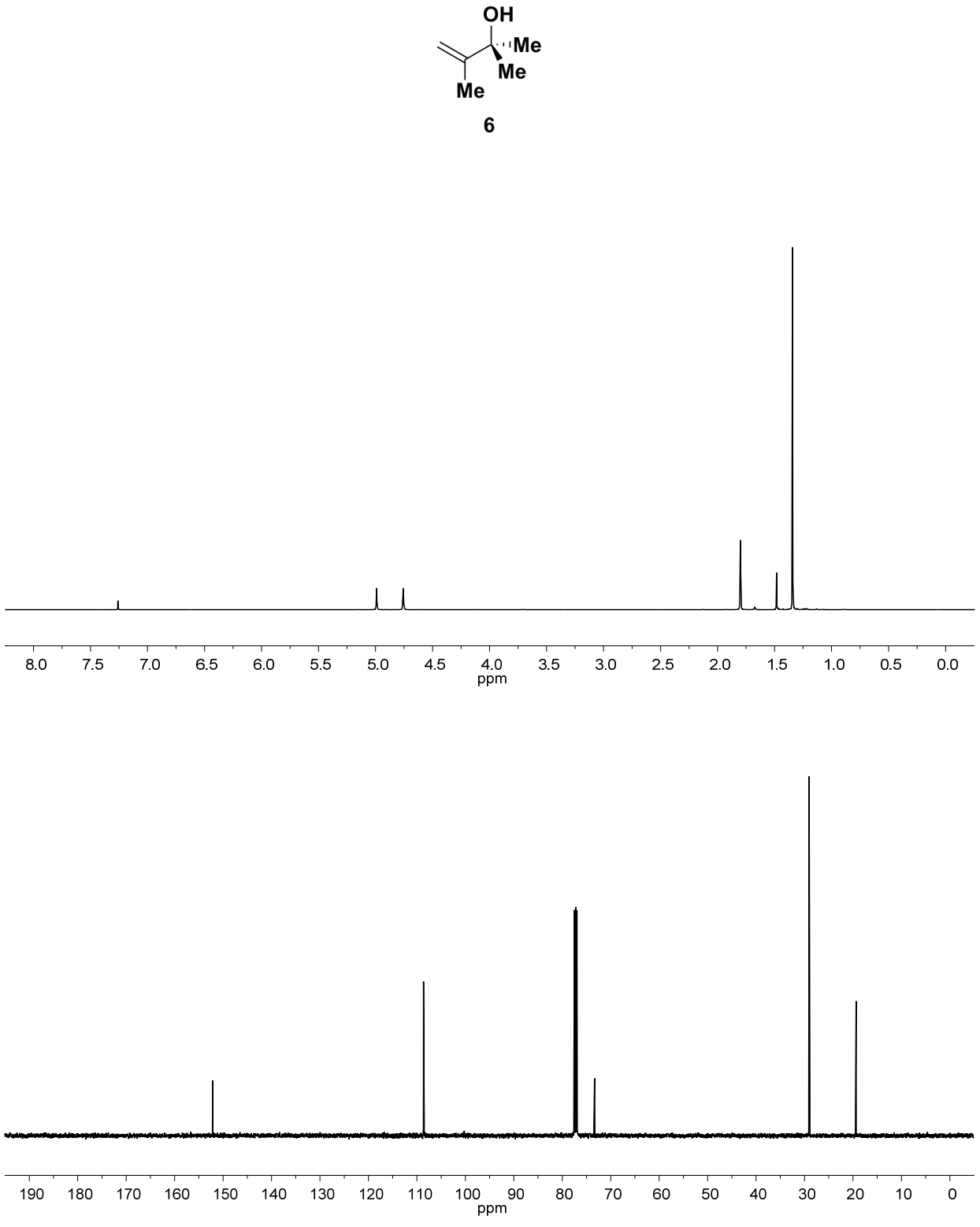
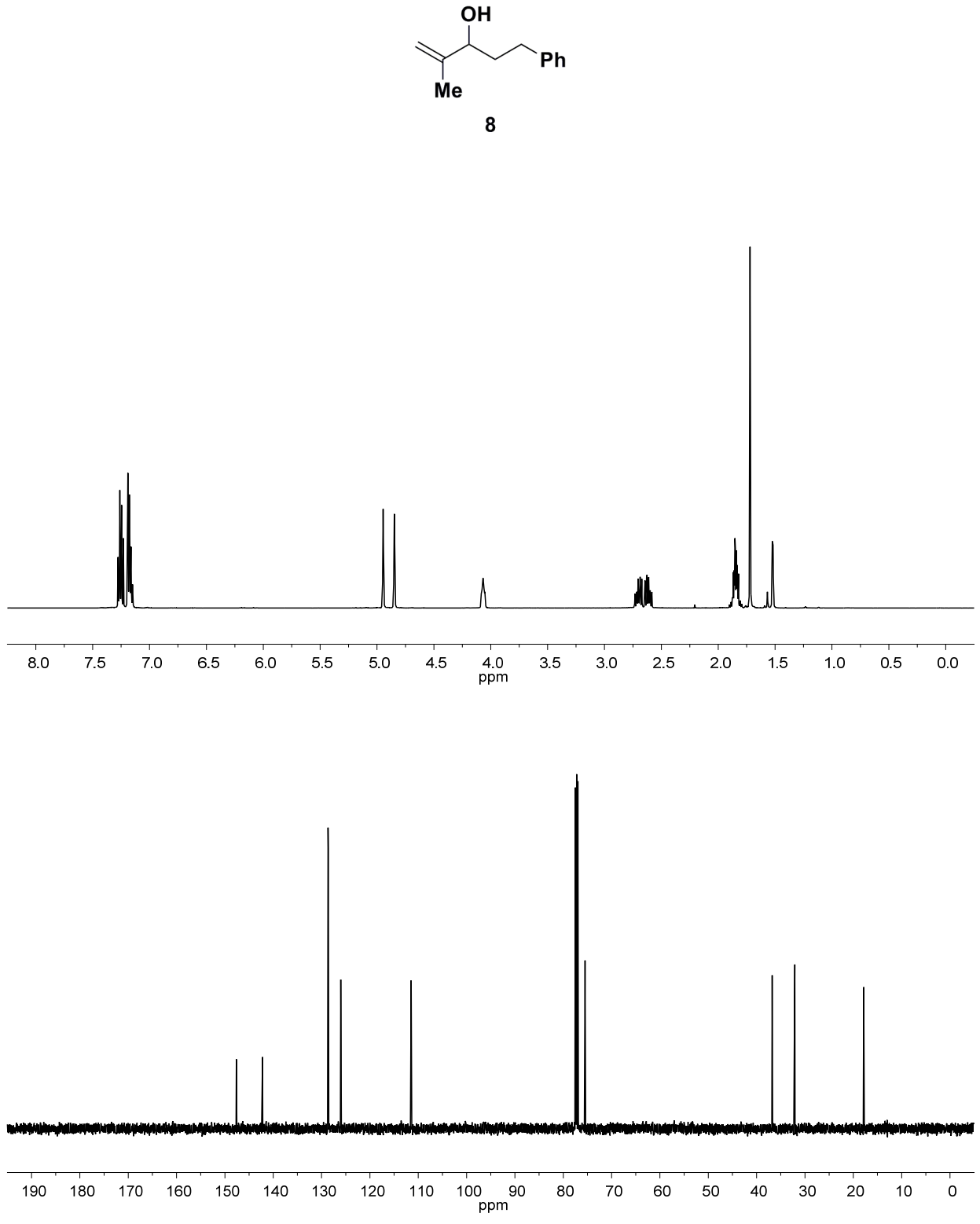




^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **48**

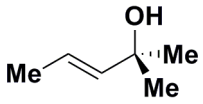


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **6**



8

^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **8**



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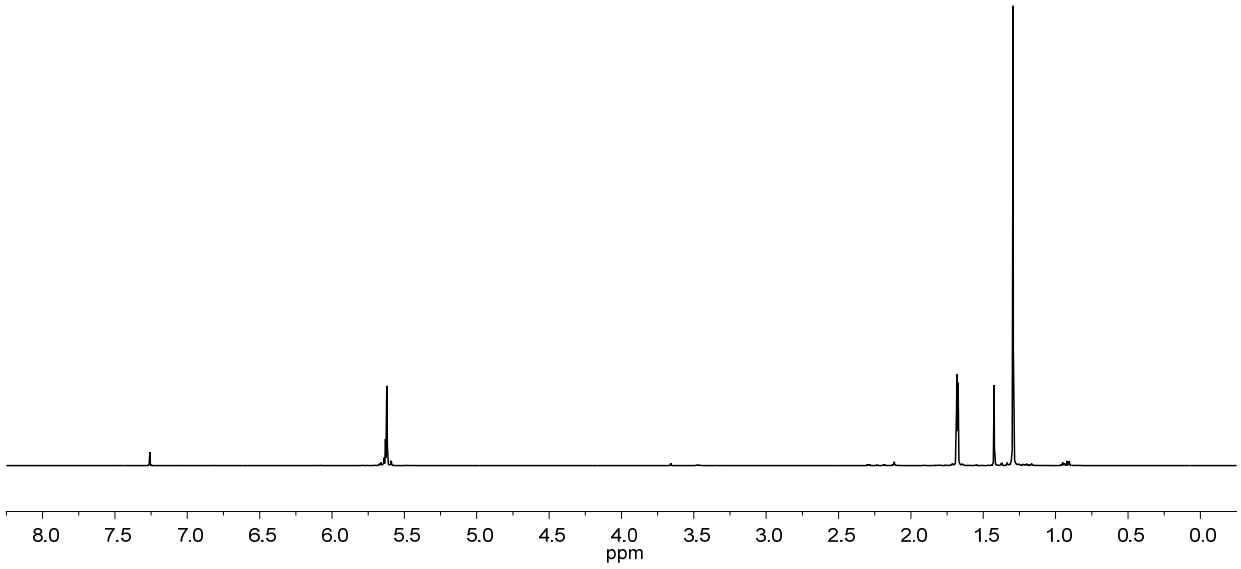
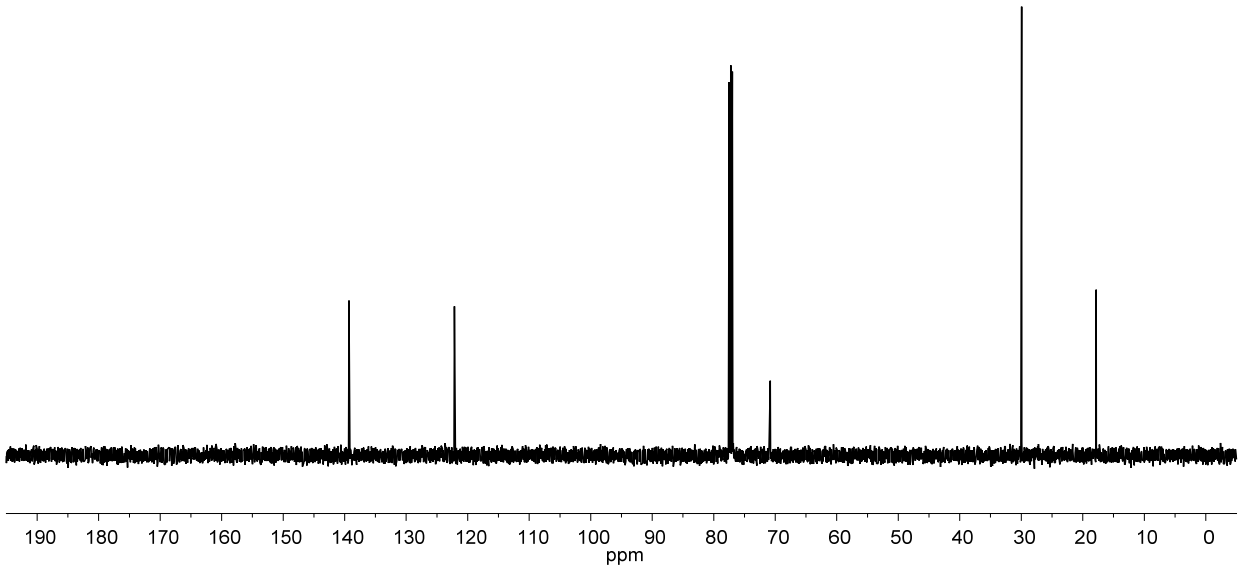
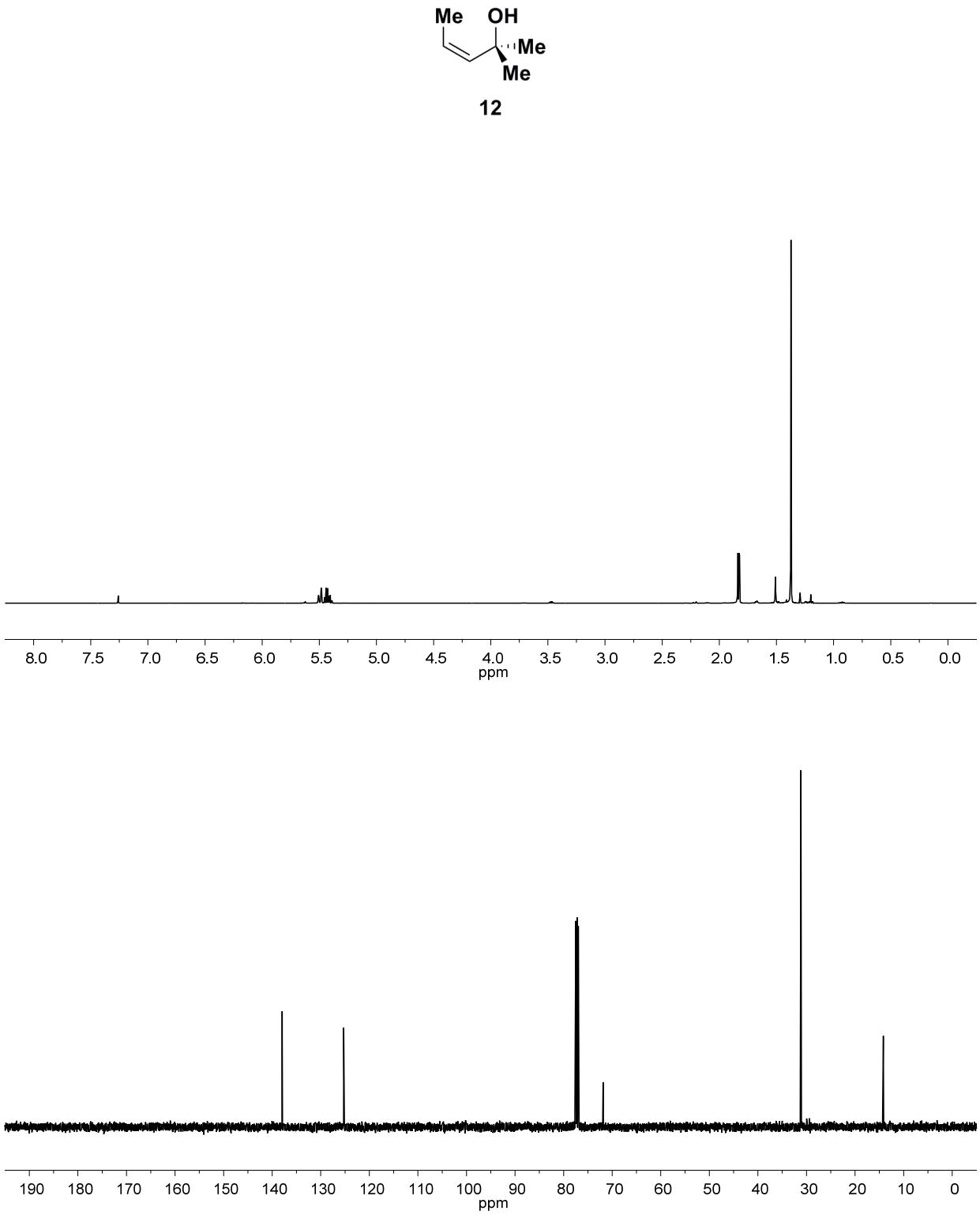
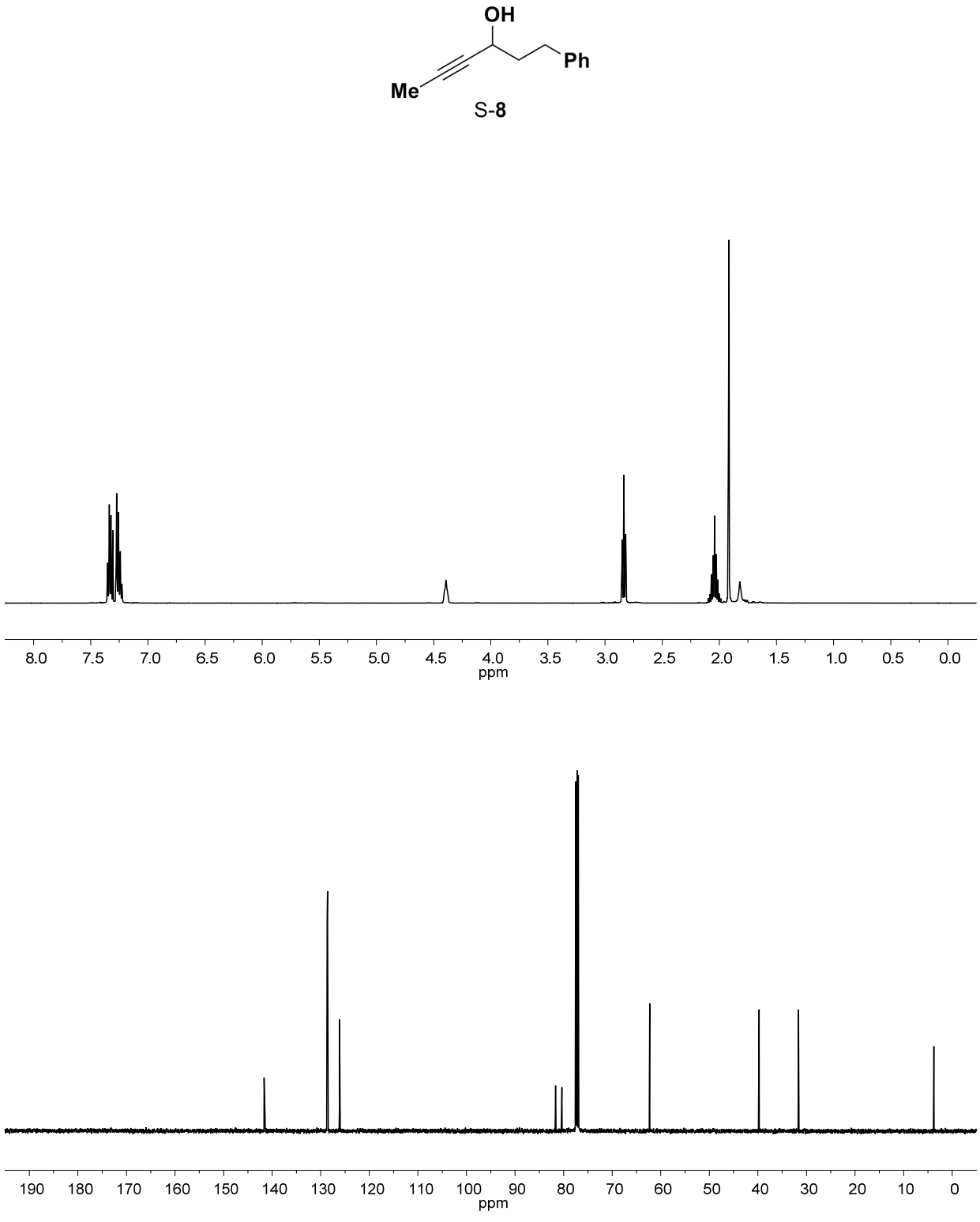




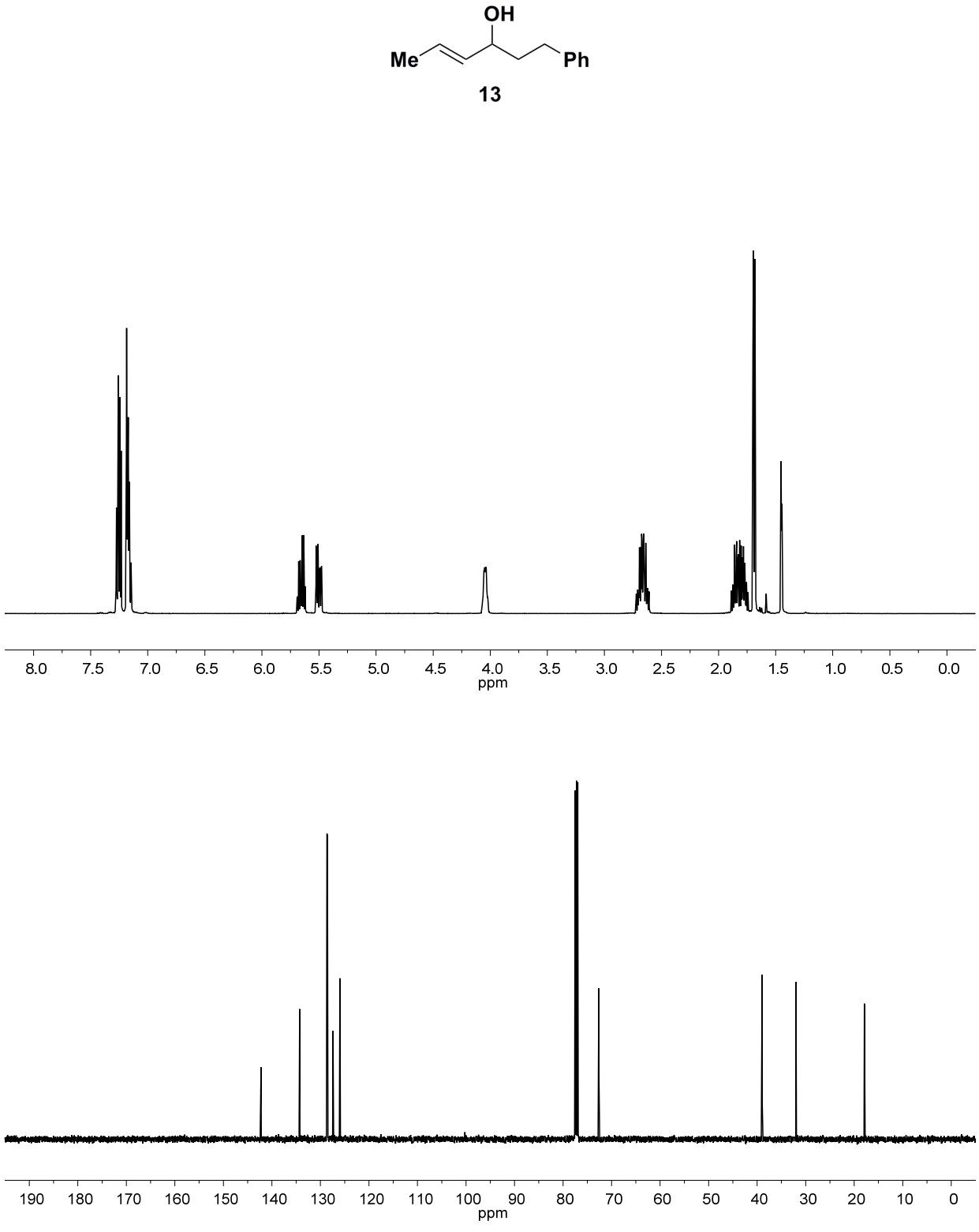
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **10**



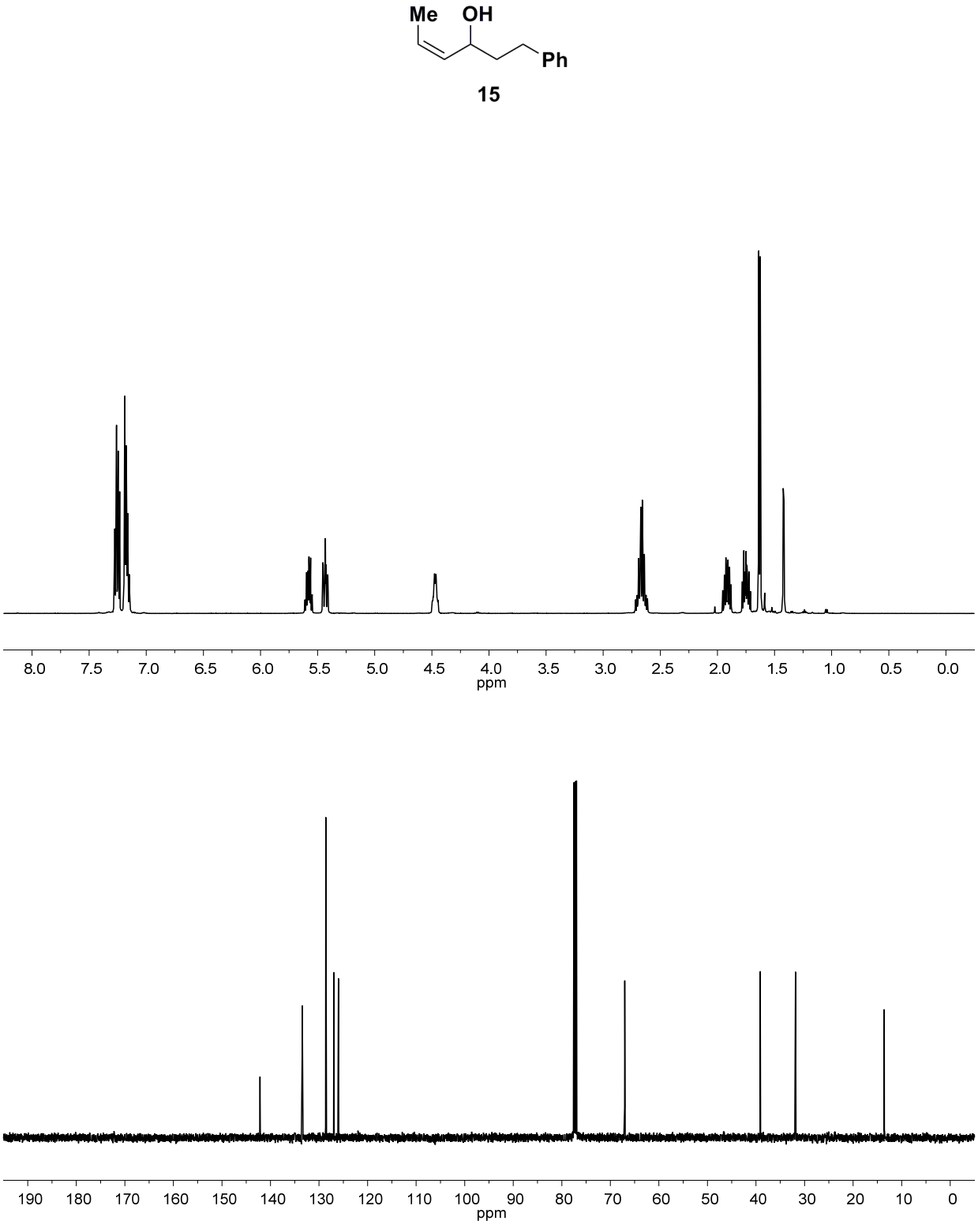
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **12**



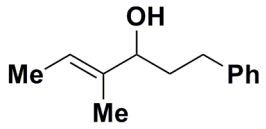
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**8**



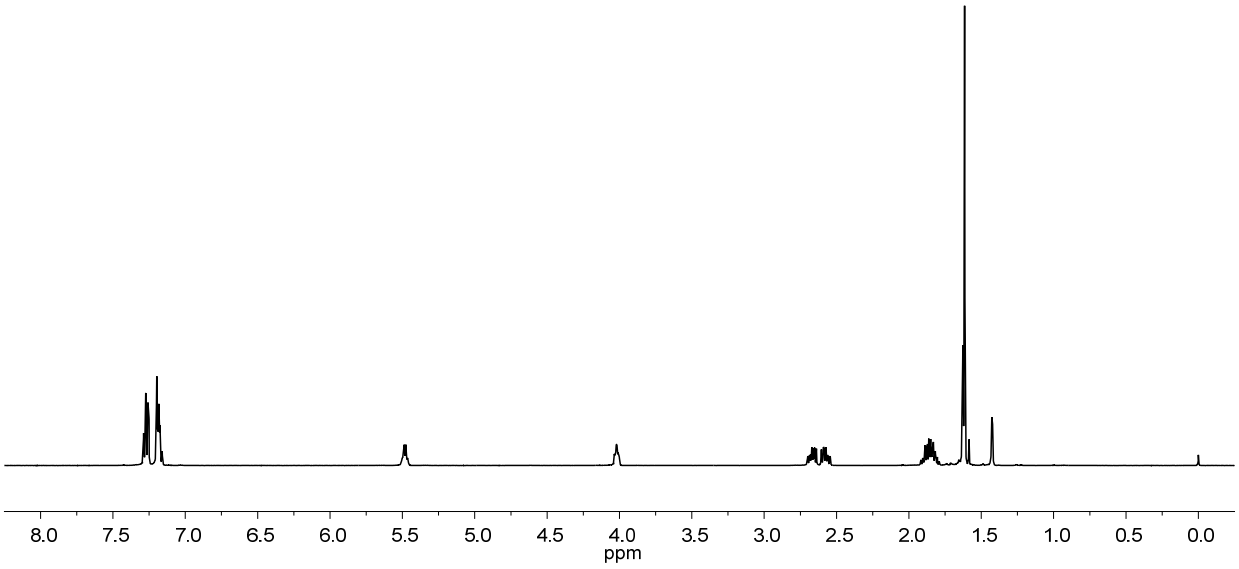
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **13**

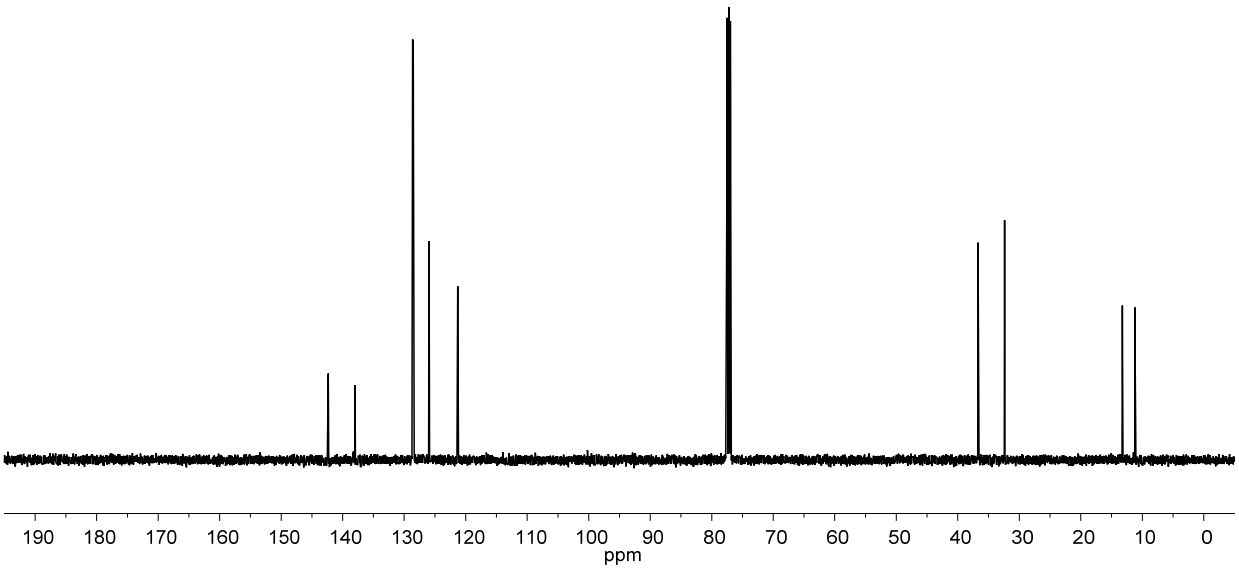


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **15**

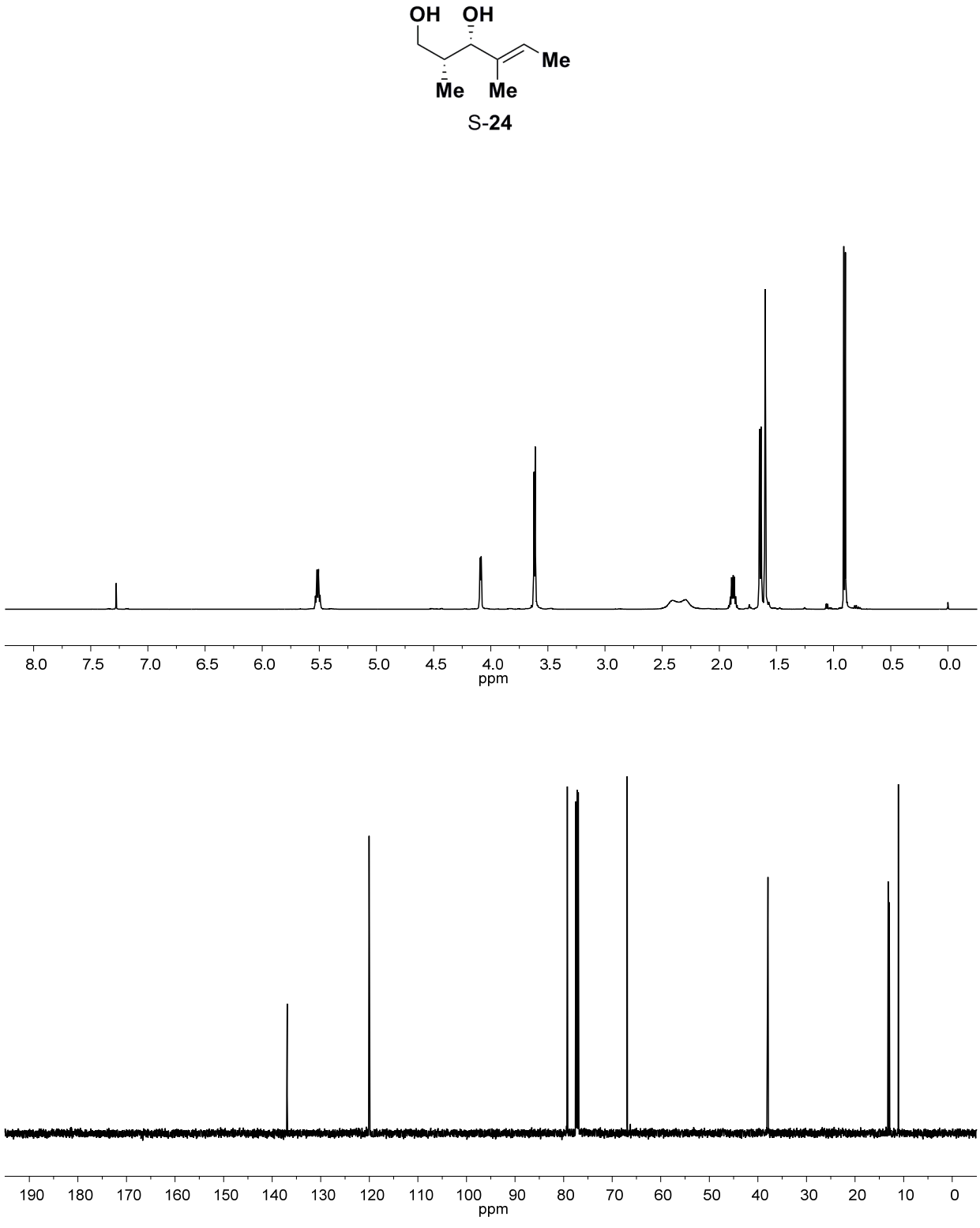


17



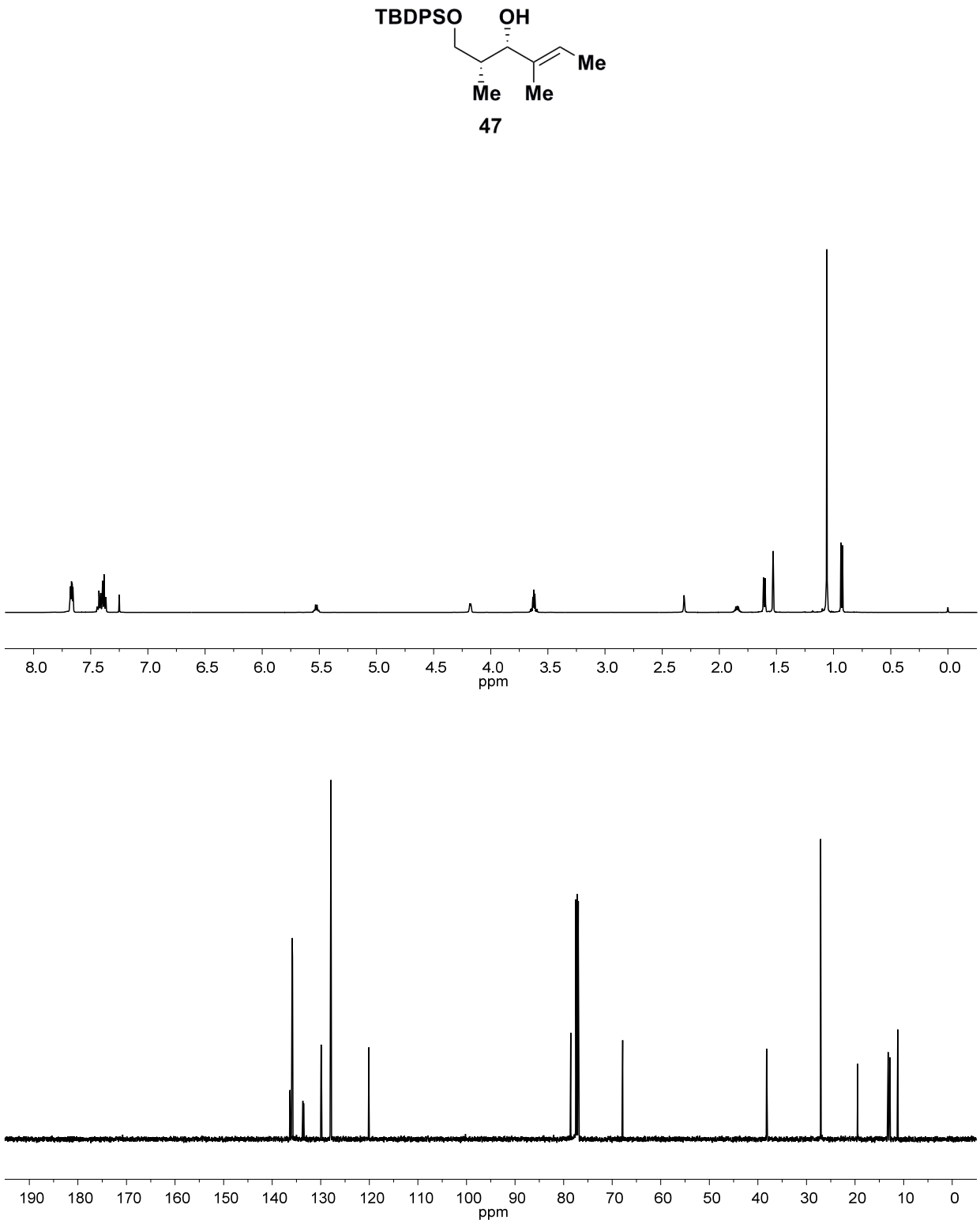


^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **17**

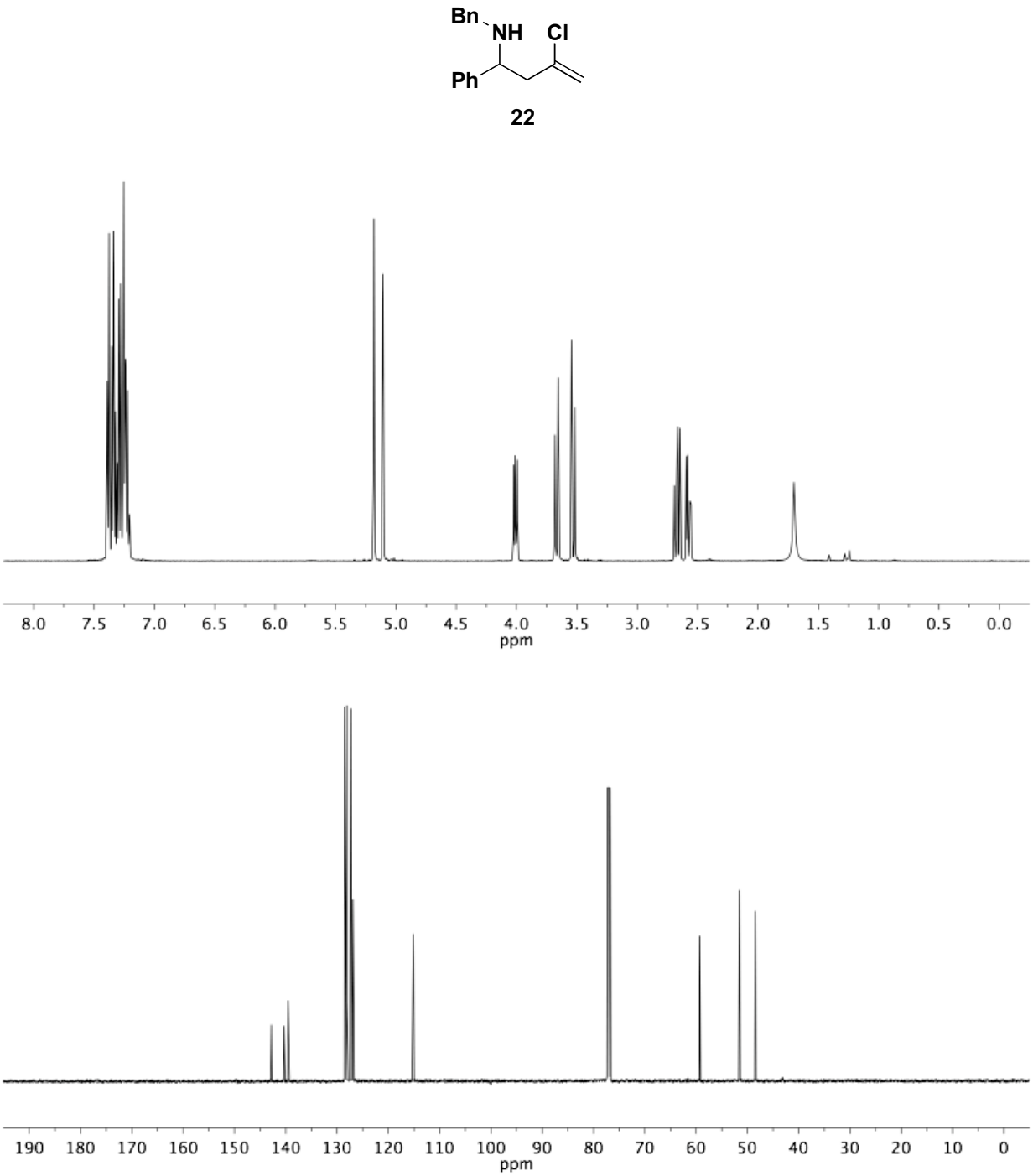


S-**24**

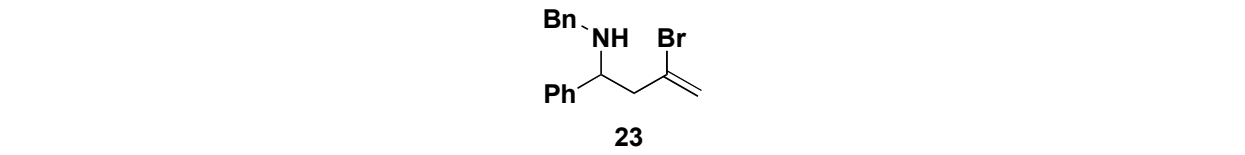
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound S-**24**



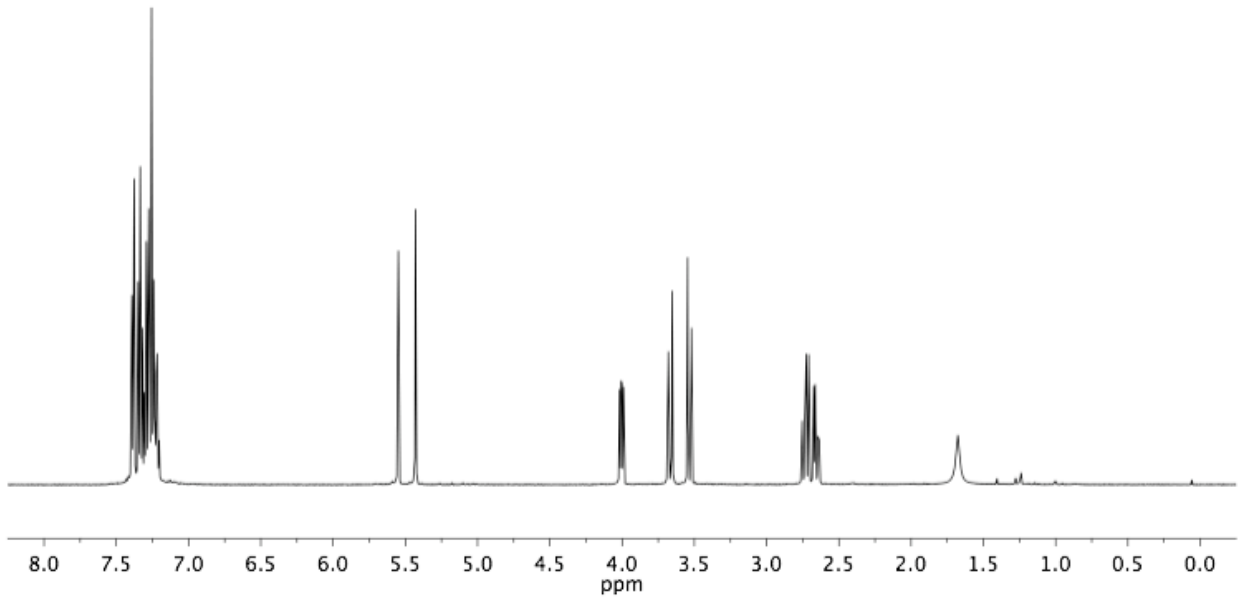
^{1}H NMR (500 MHz) and ^{13}C NMR (126 MHz) of compound **47**

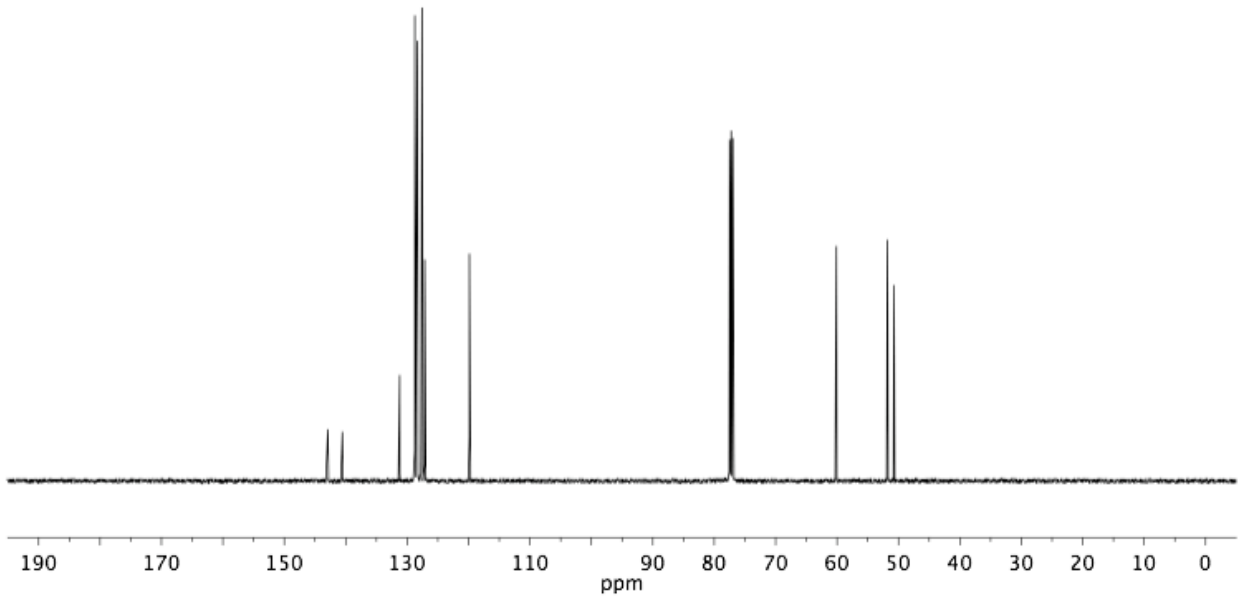


^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **22**

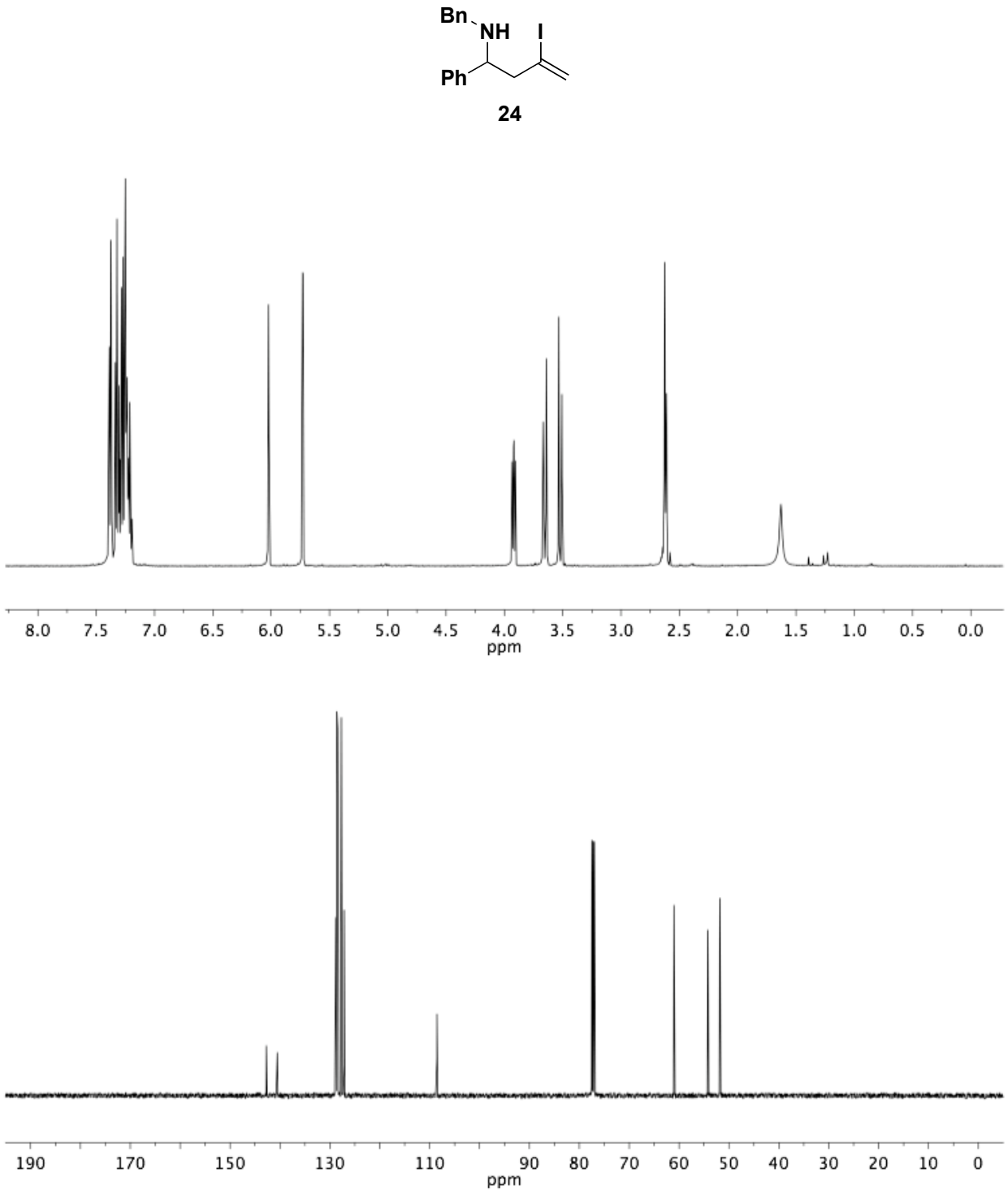


23



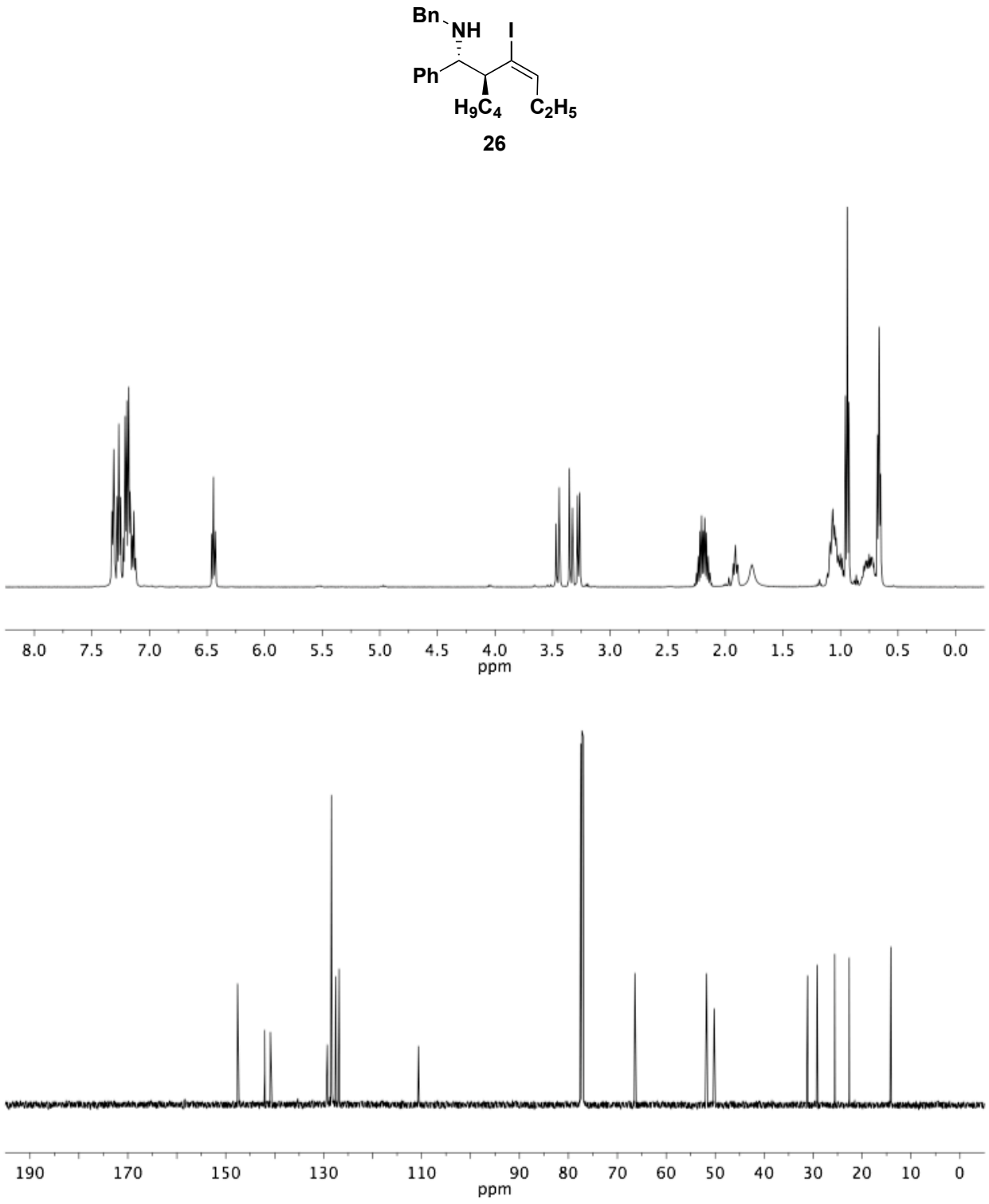


^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **23**

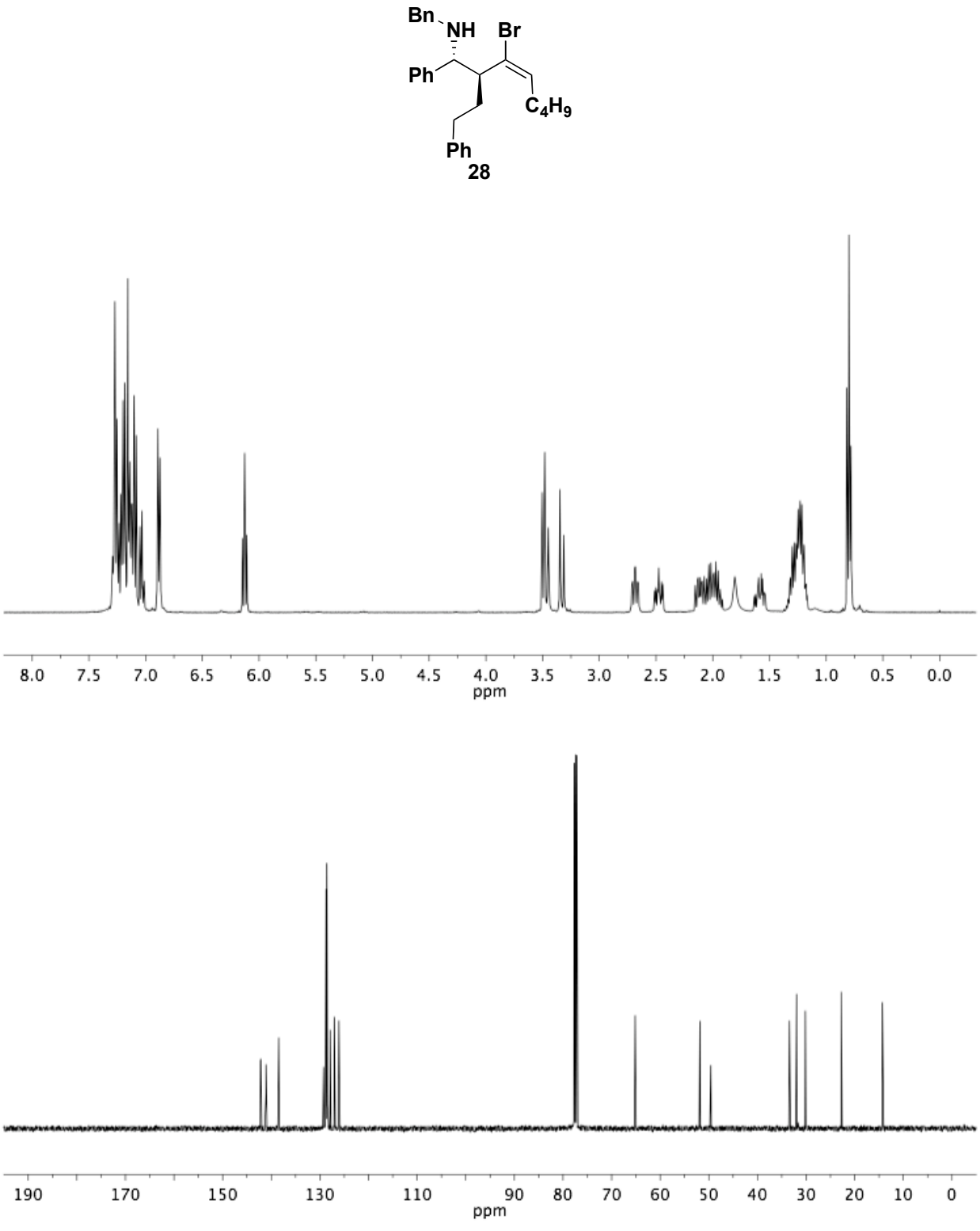


24

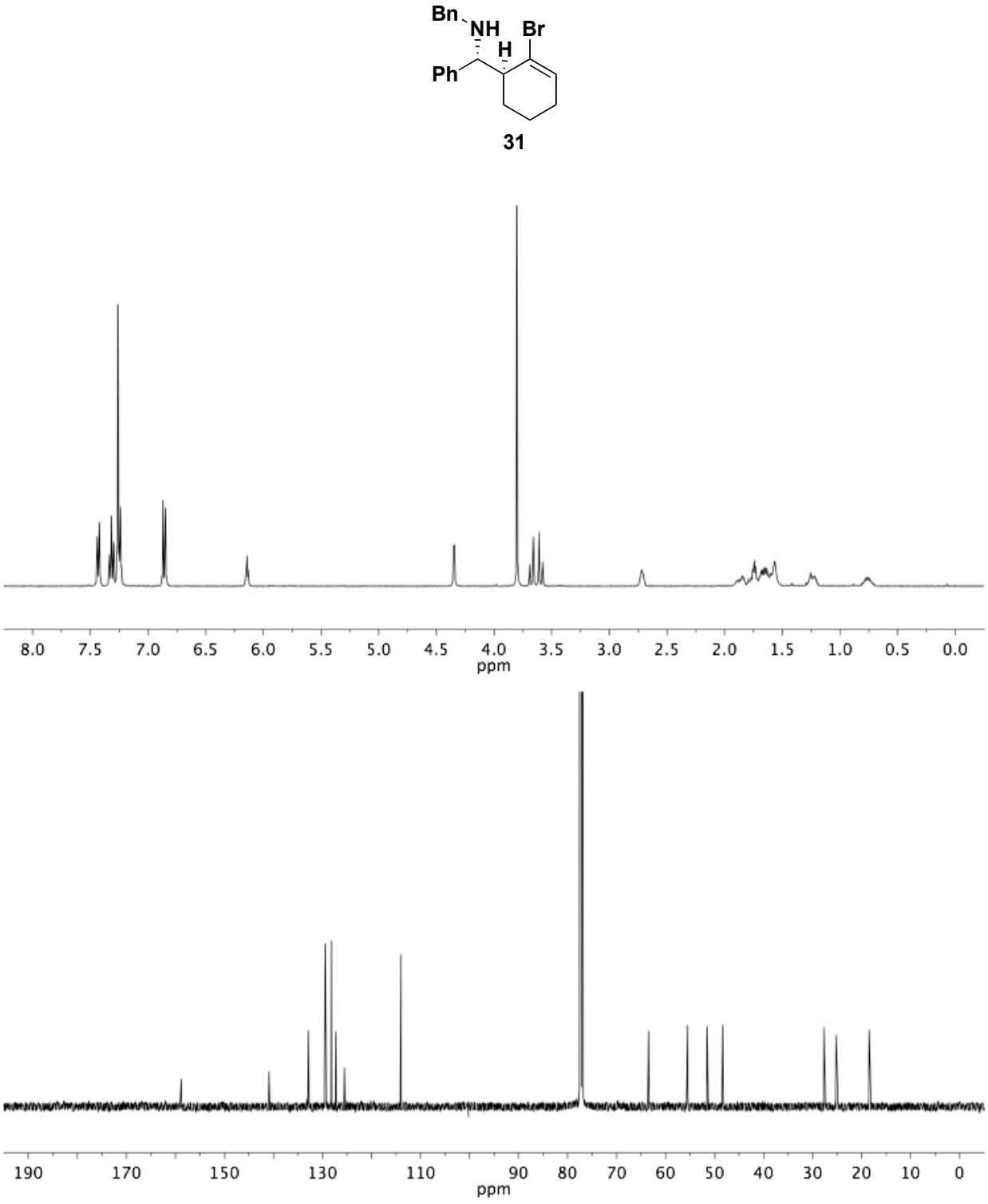
^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **24**



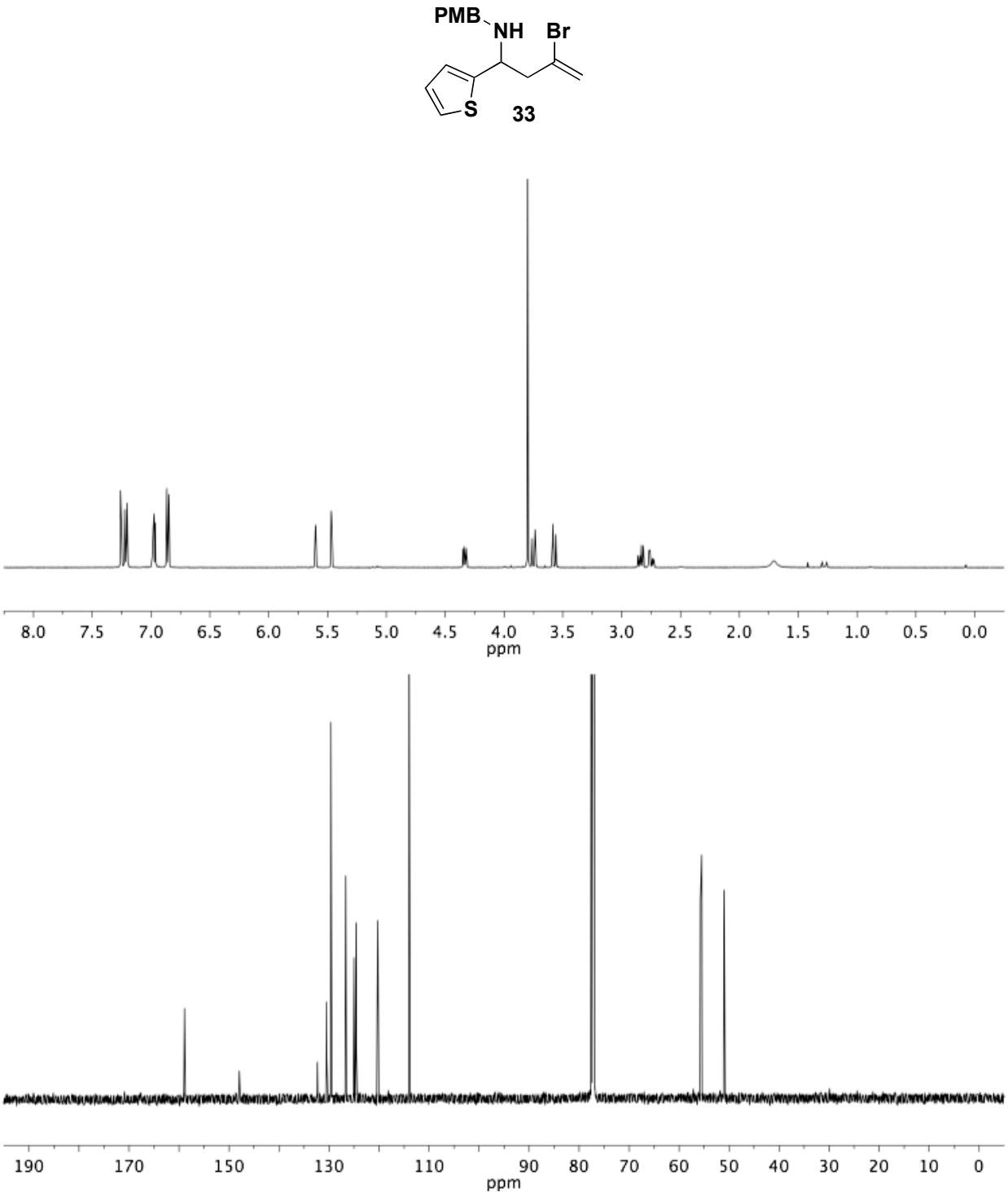
^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **26**



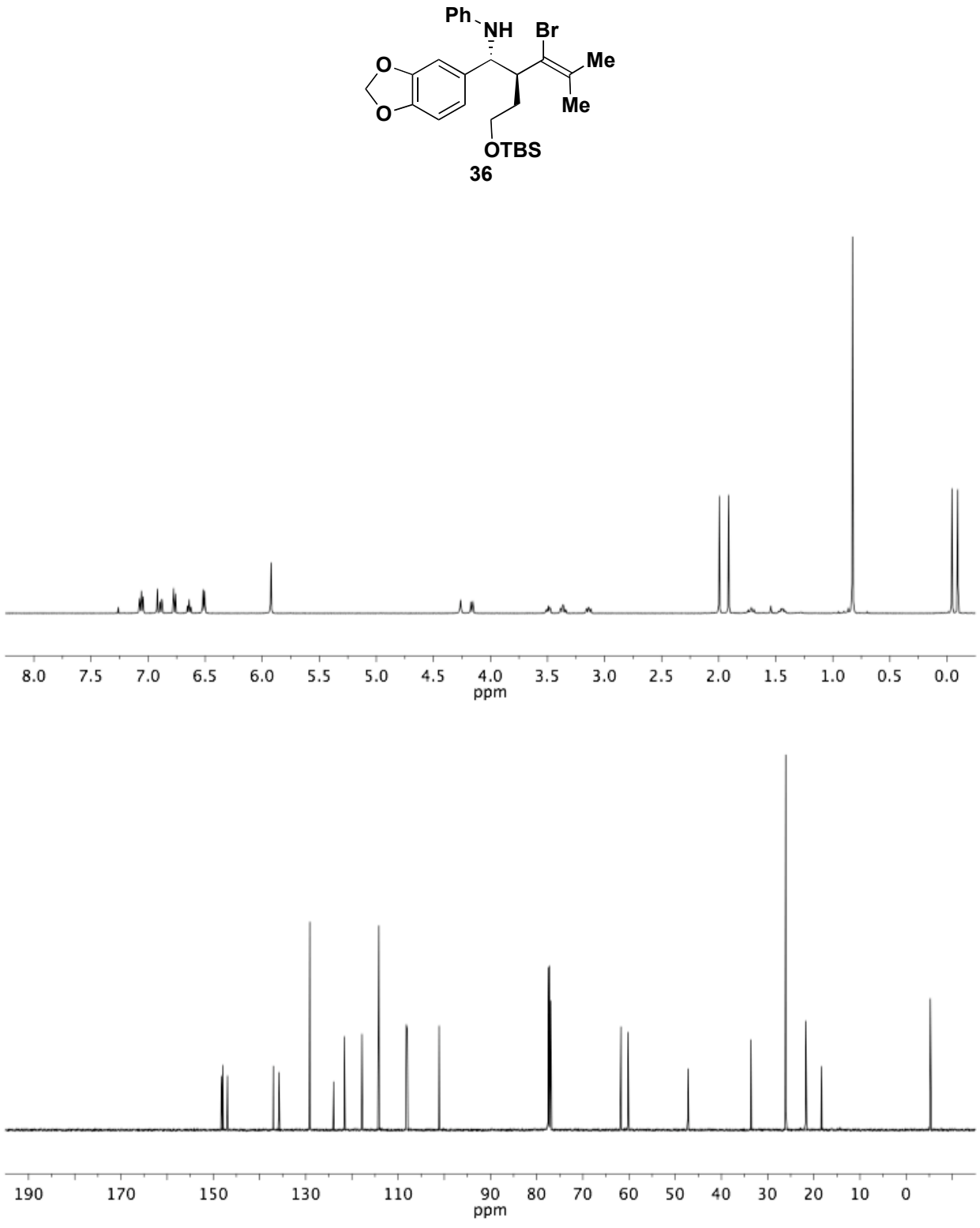
^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound **28**



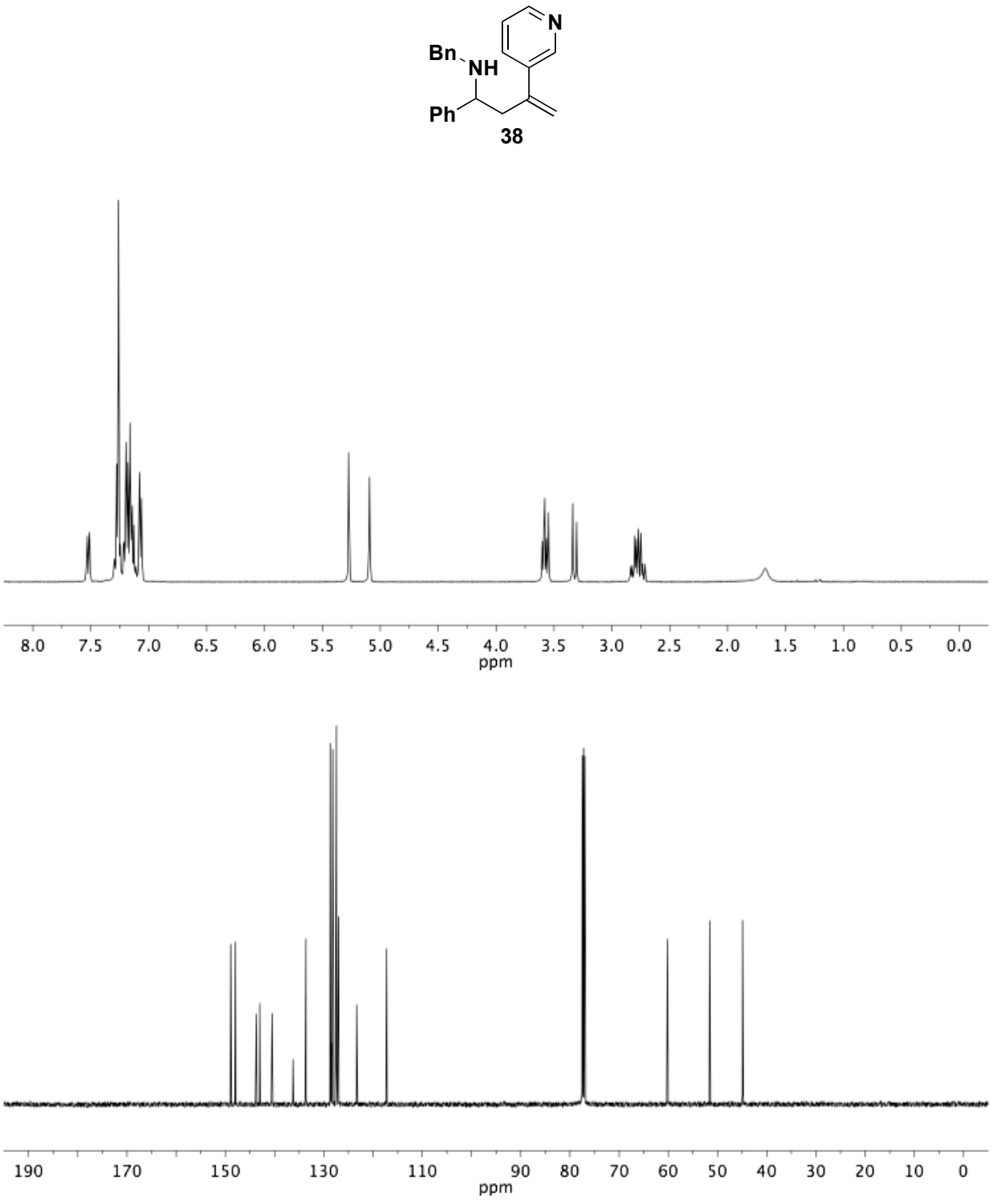
^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound **31**



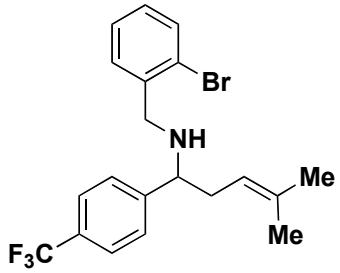
^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **33**



^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **36**



^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound **38**



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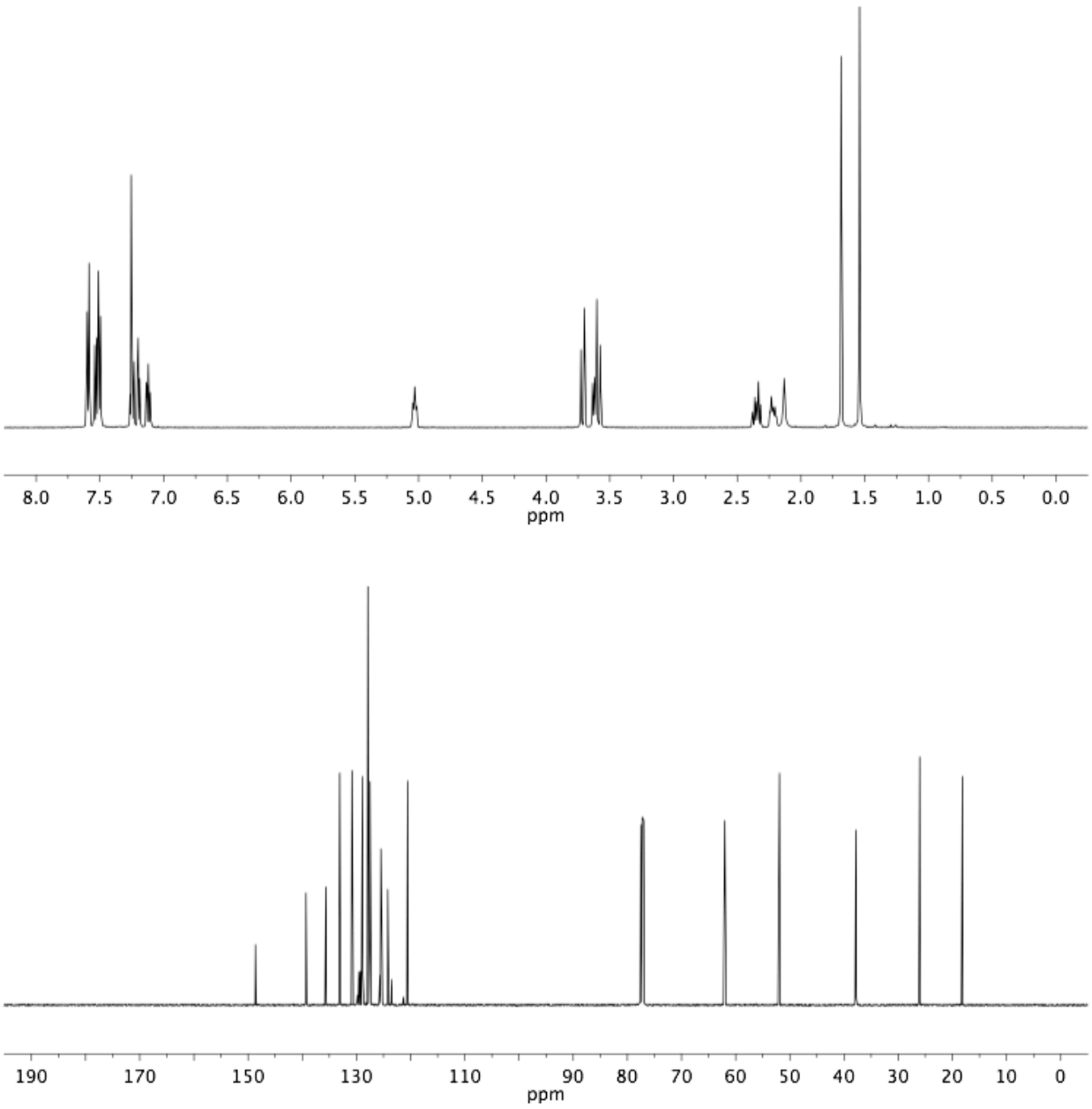
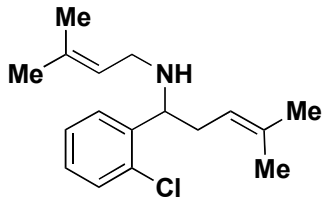
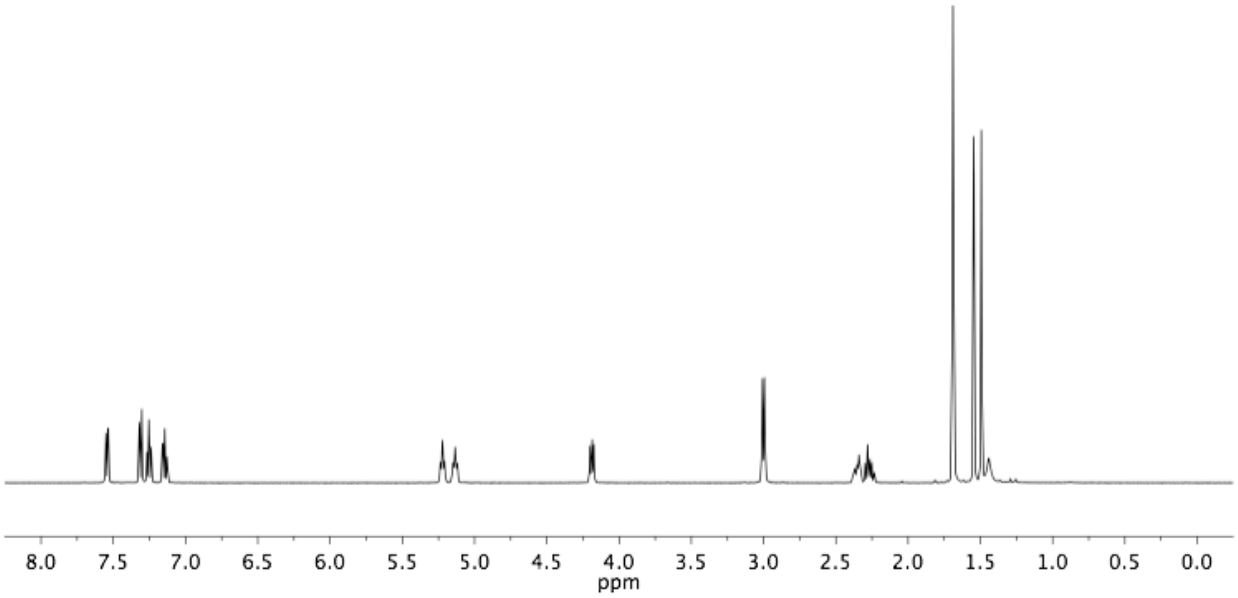
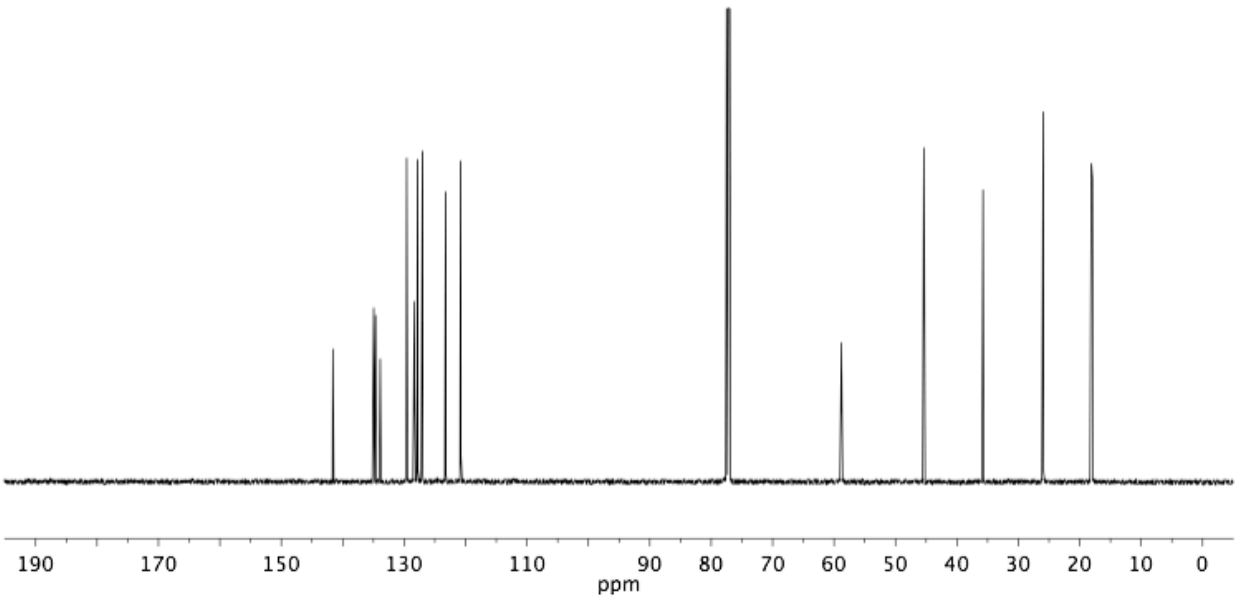


^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound **40**

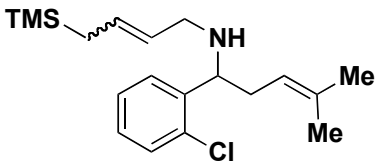


42





^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **42**



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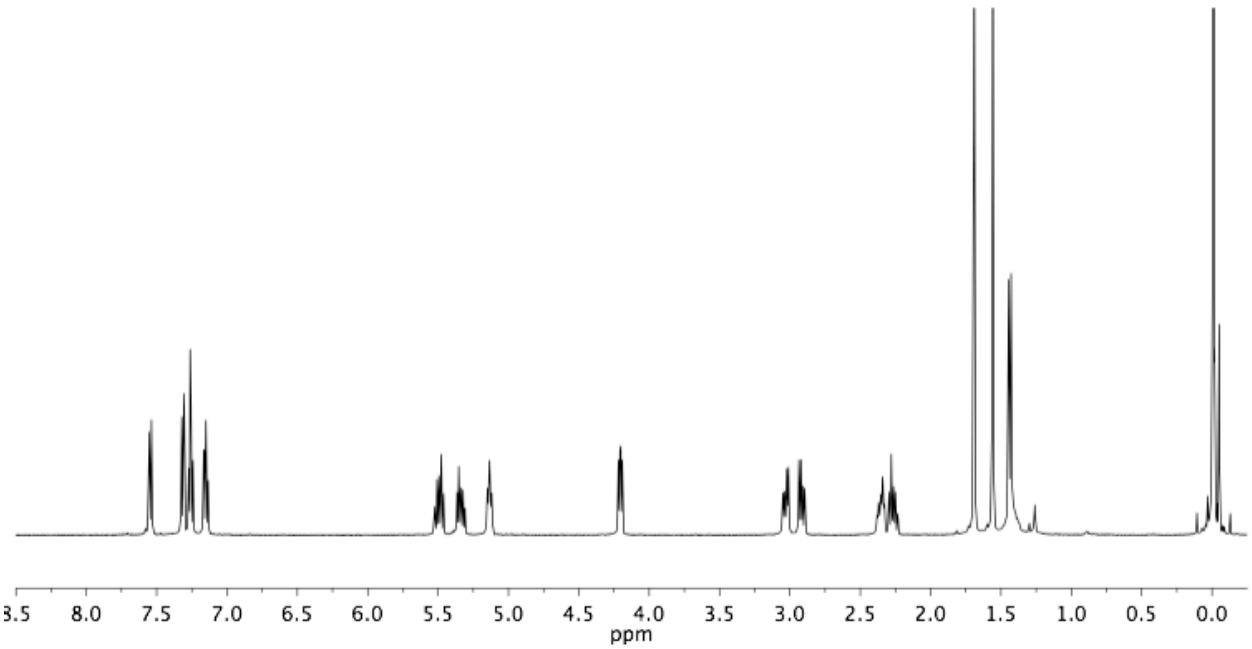
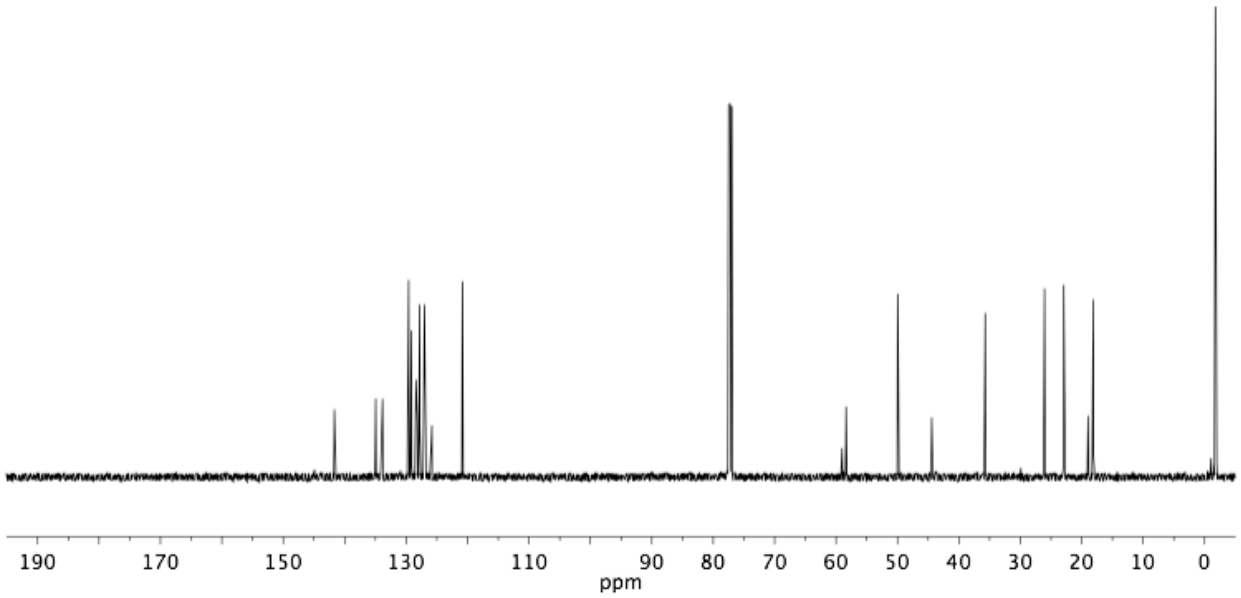
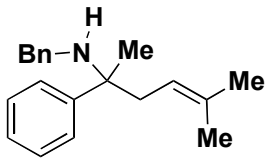
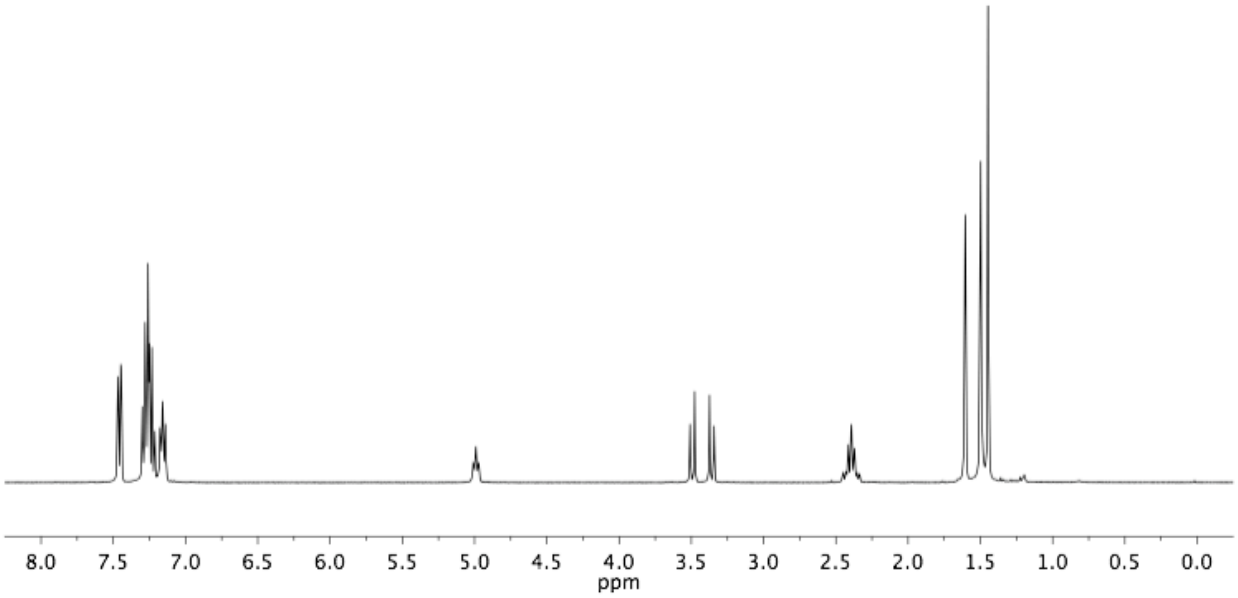


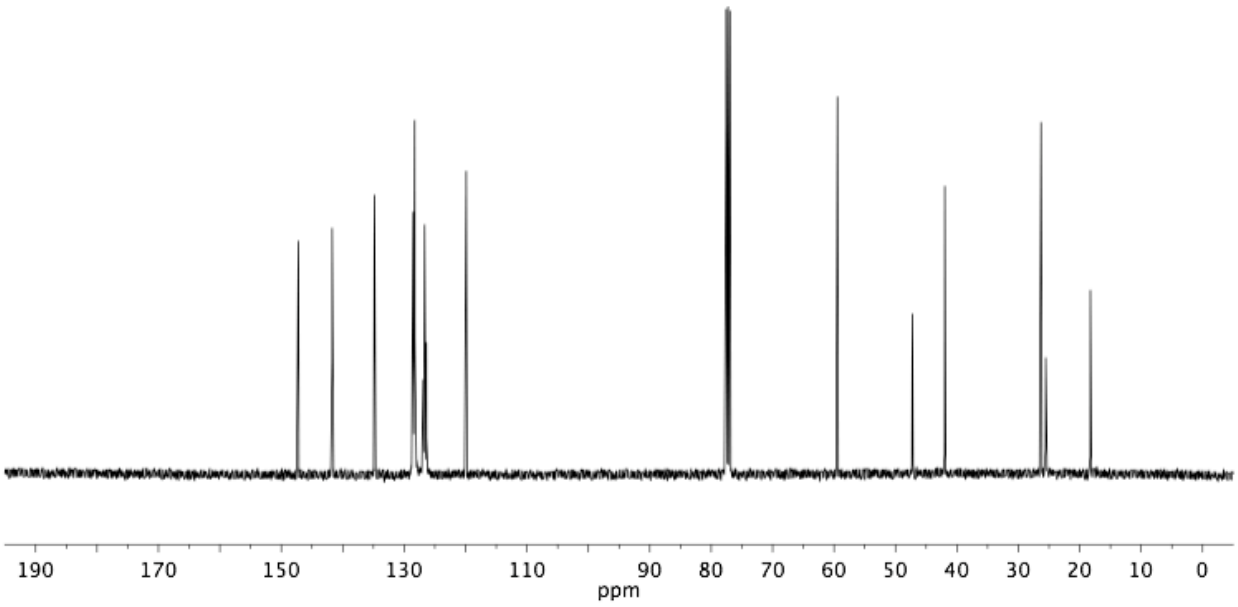


^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **44**

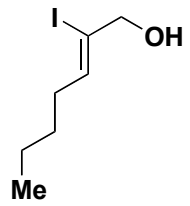


46

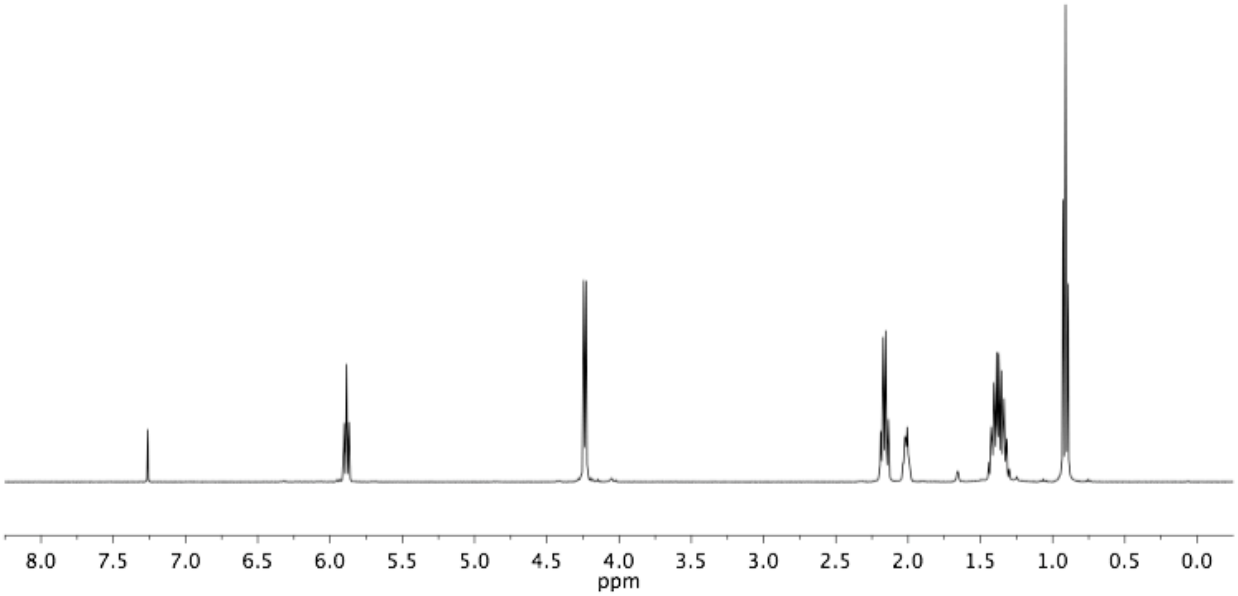


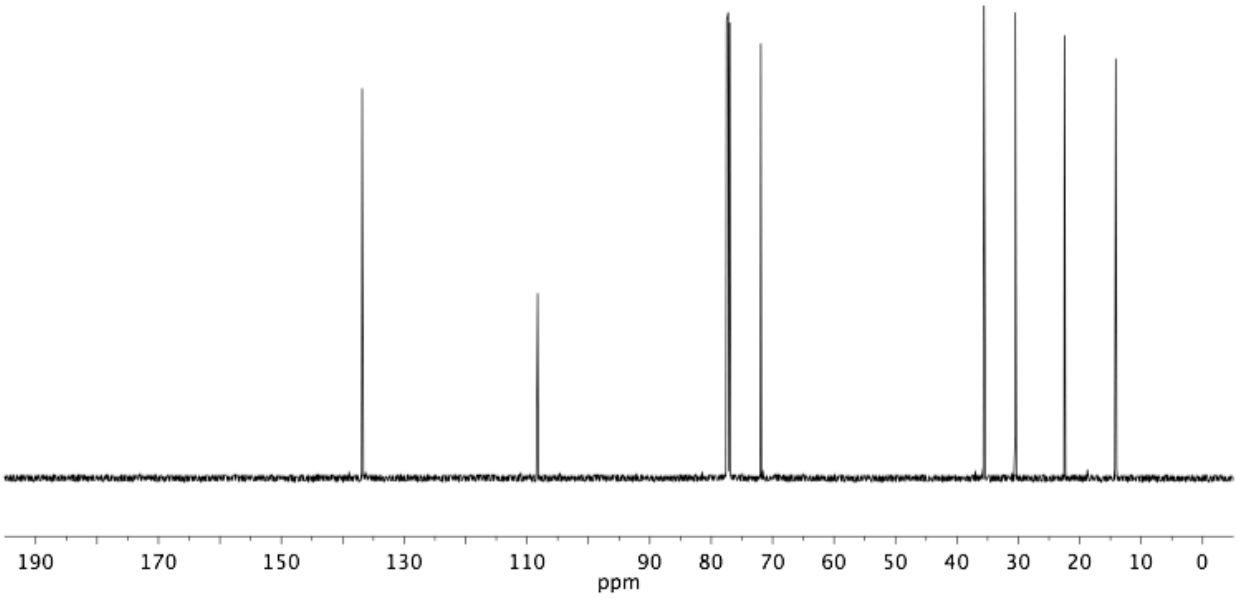


^{1}H NMR (400 Mhz) and ^{13}C NMR (100 Mhz) of compound **46**

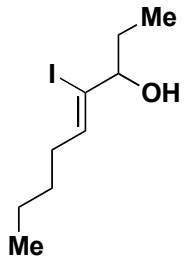


S-**10**





^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound S-**10**



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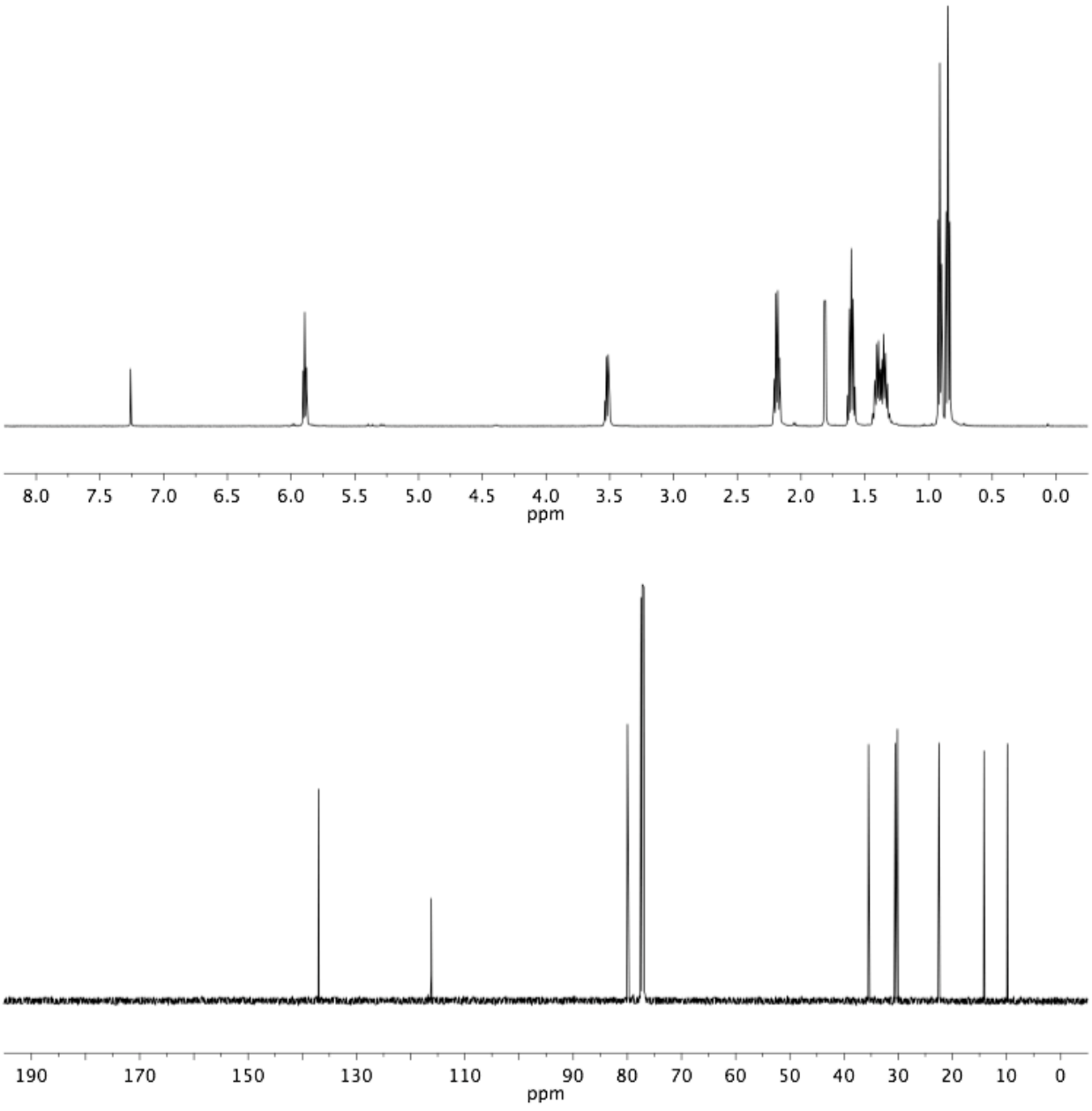
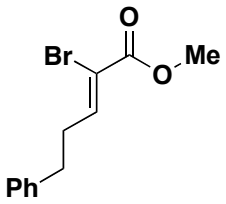
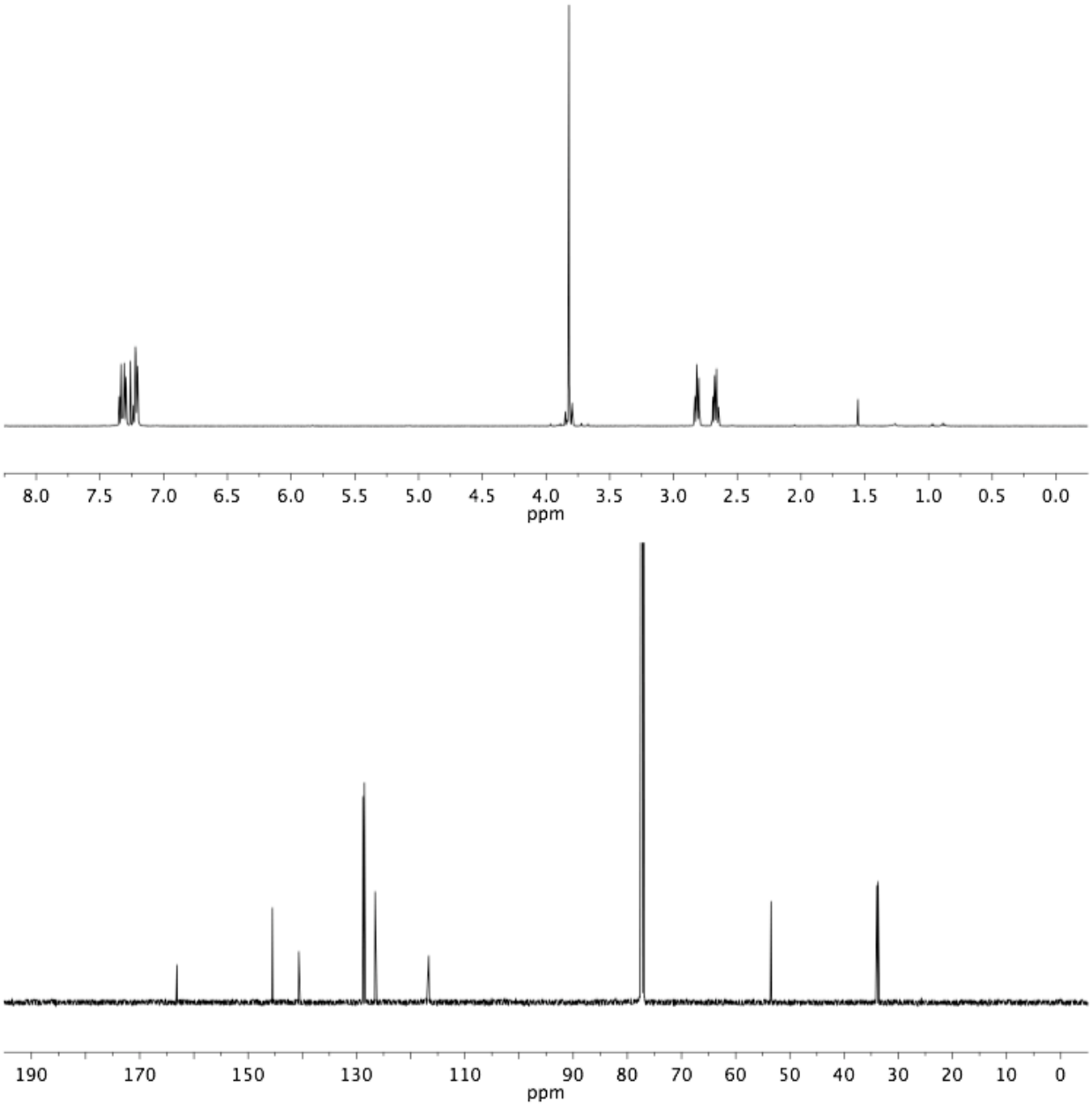


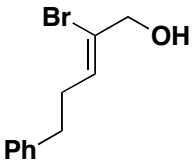
^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **25**



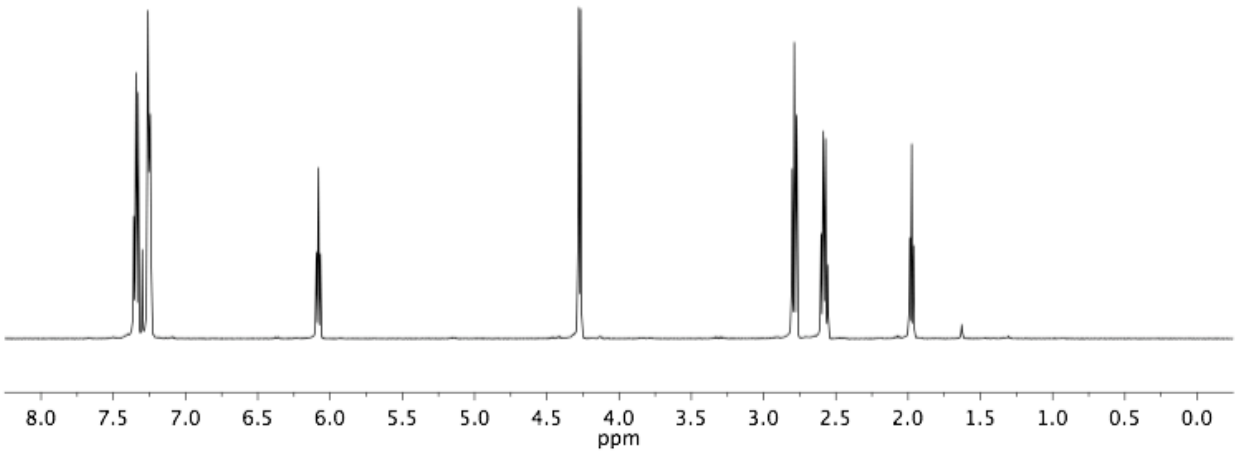
S-**12**

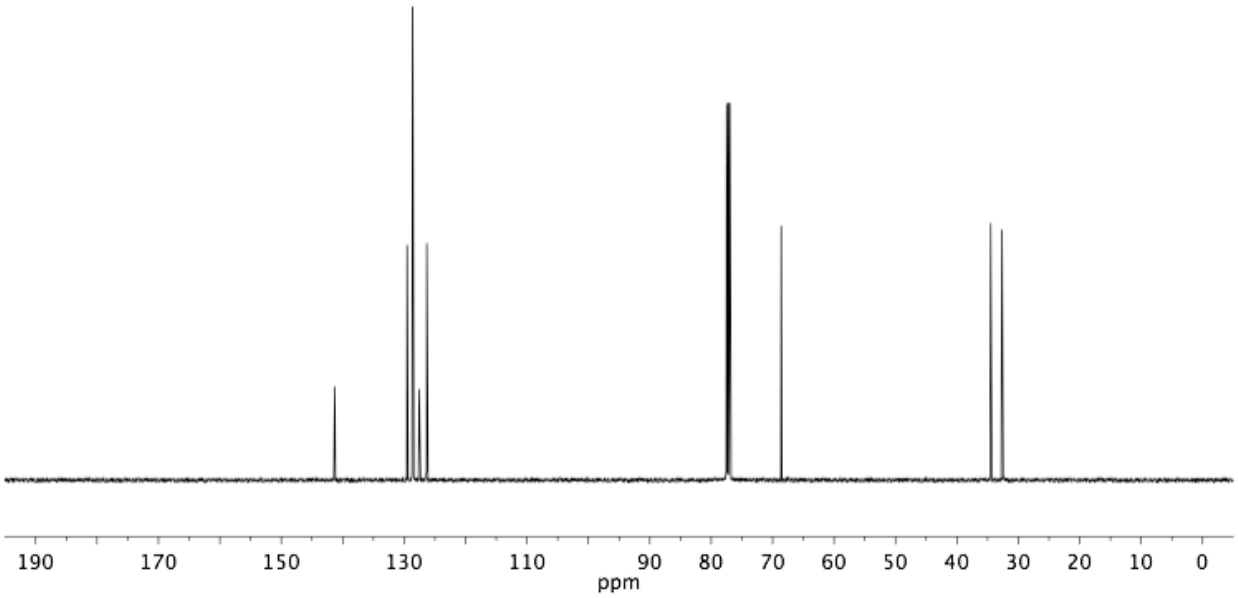


^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound S-**12**

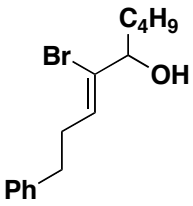


S-**13**





^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound S-**13**



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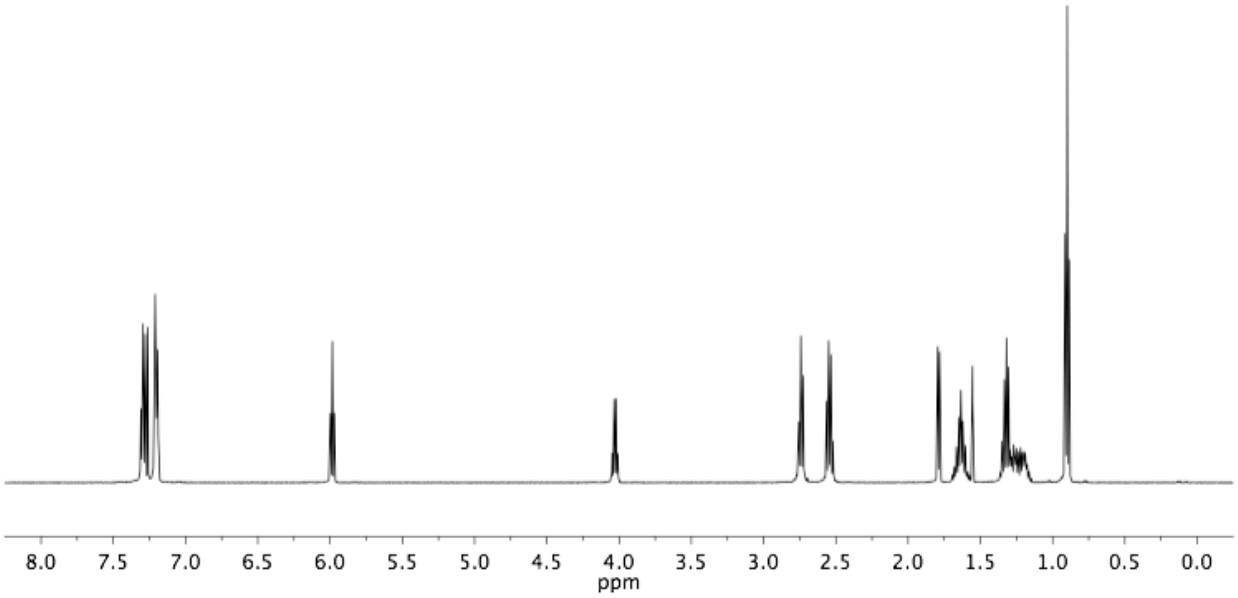
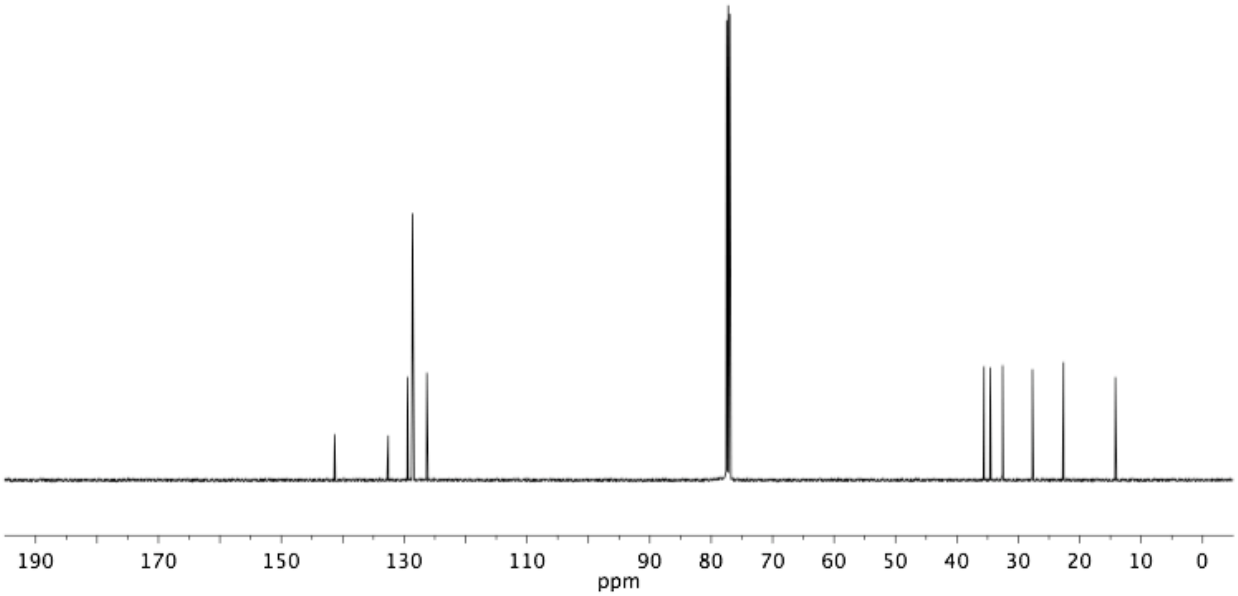
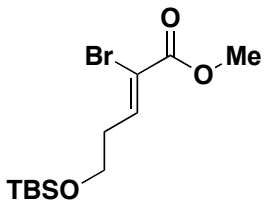
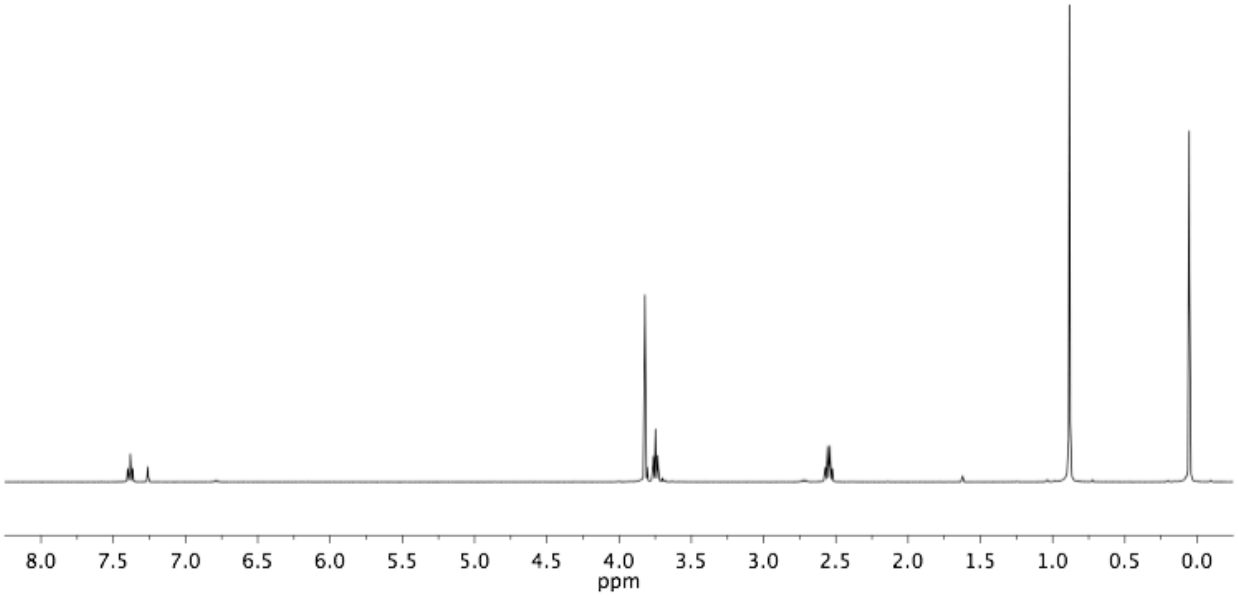


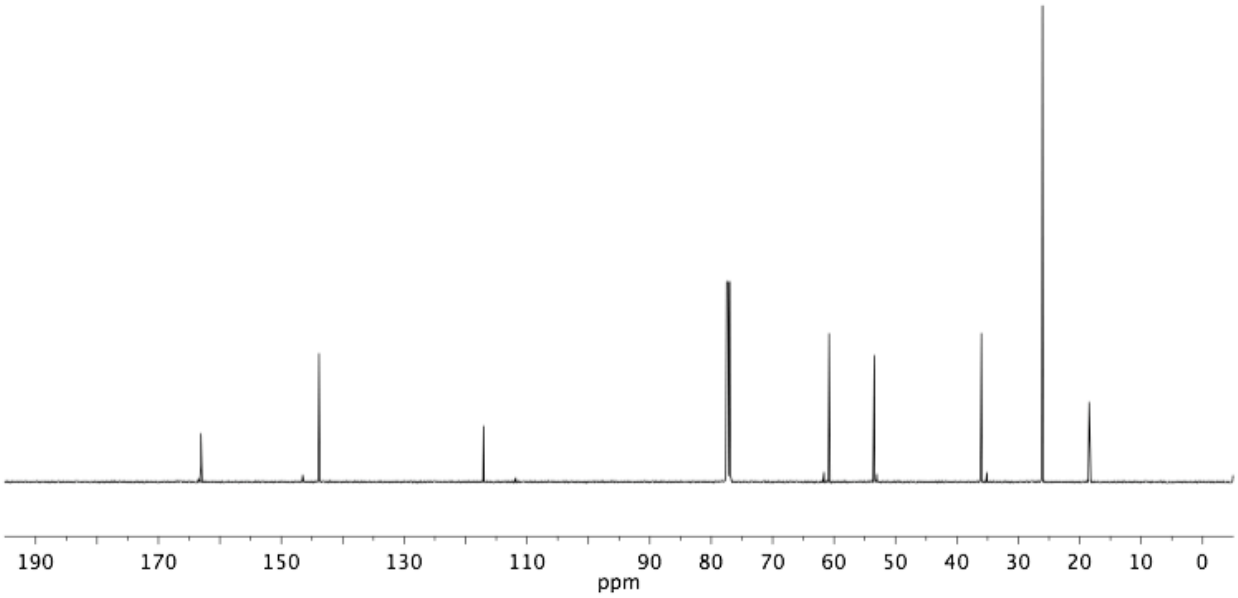


^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **27**

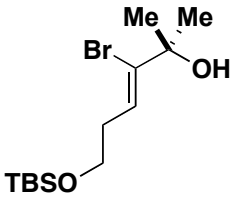


S-**17**





^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound S-**17**



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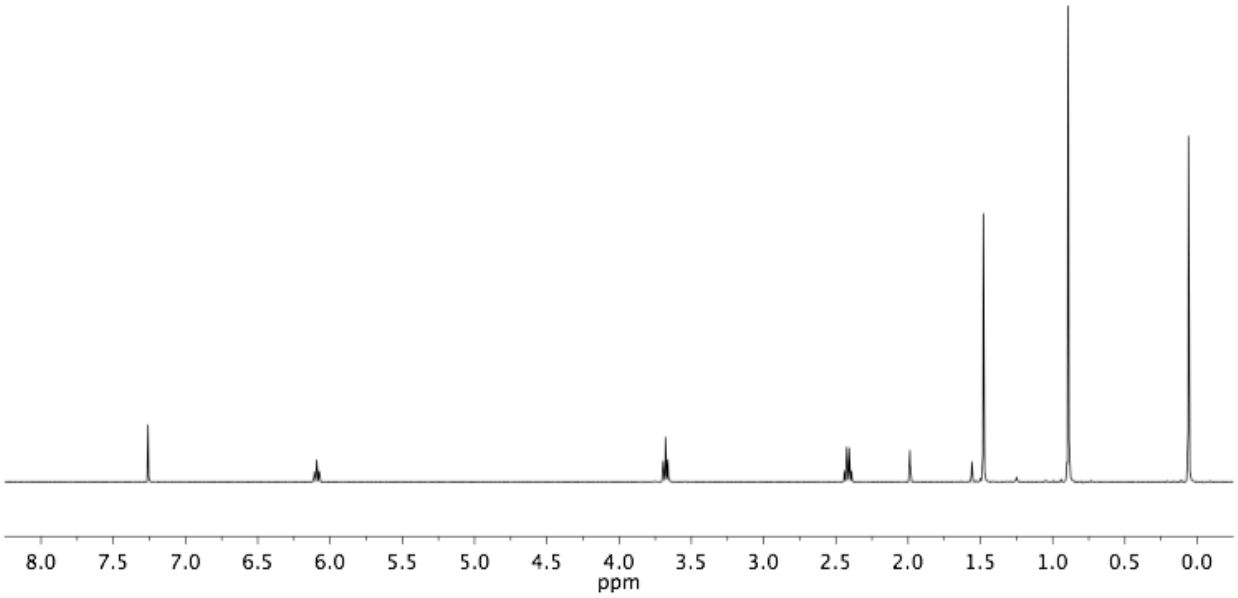
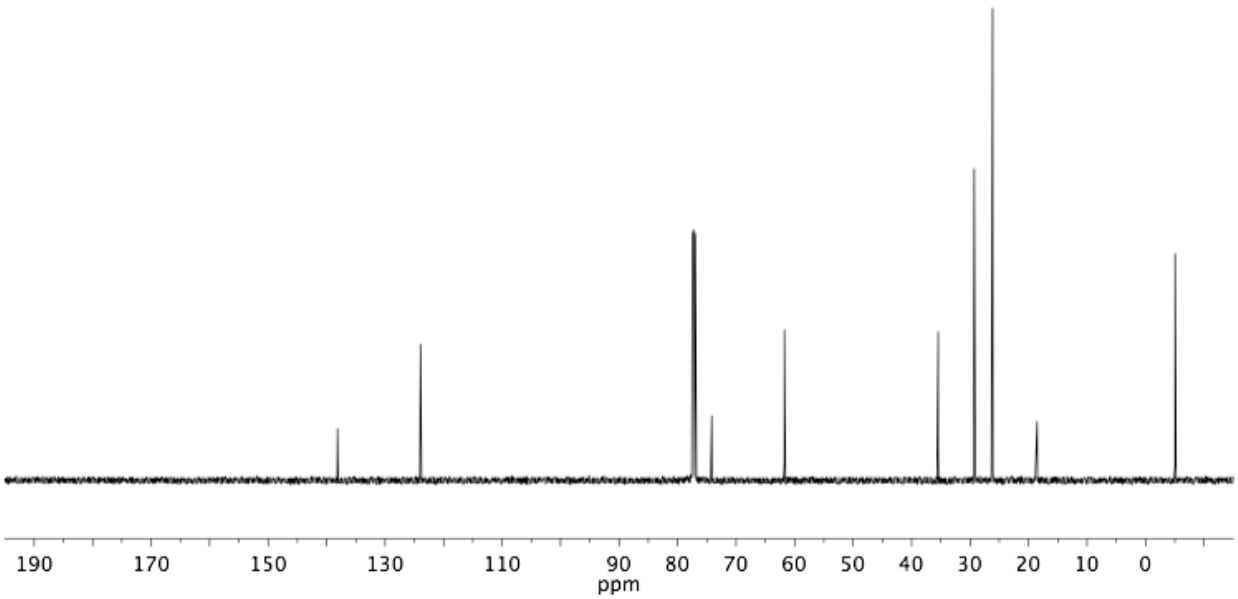
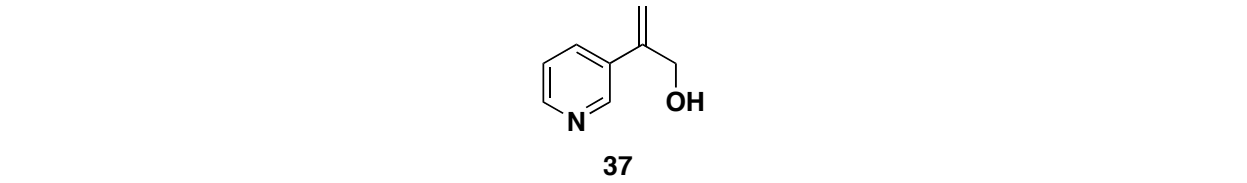




^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound **35**



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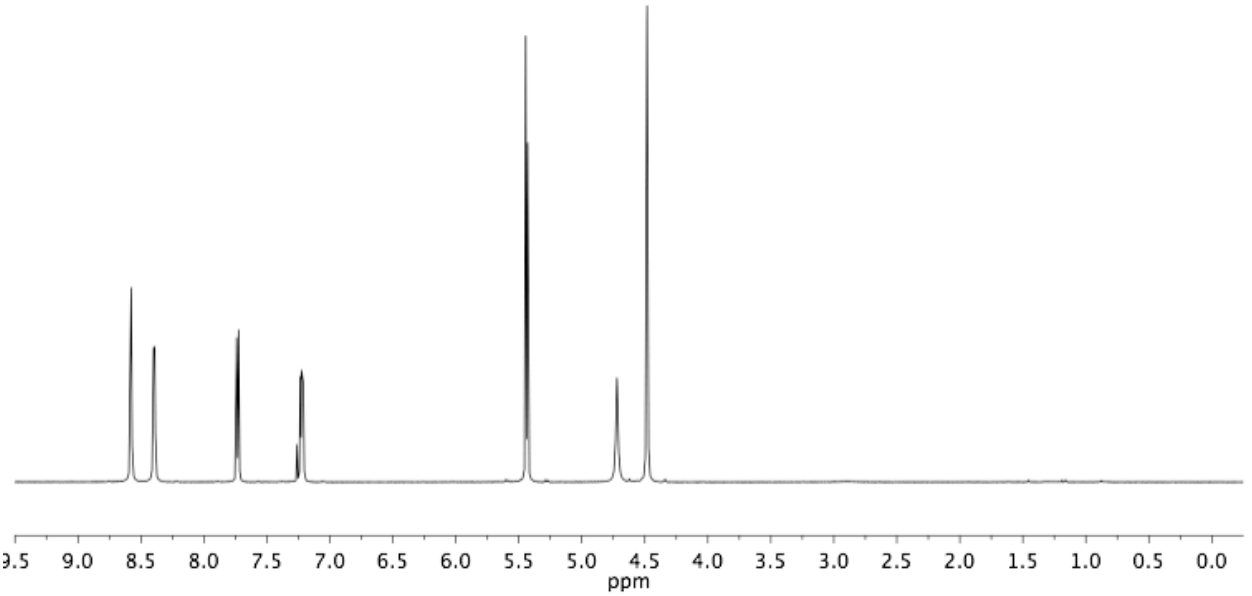
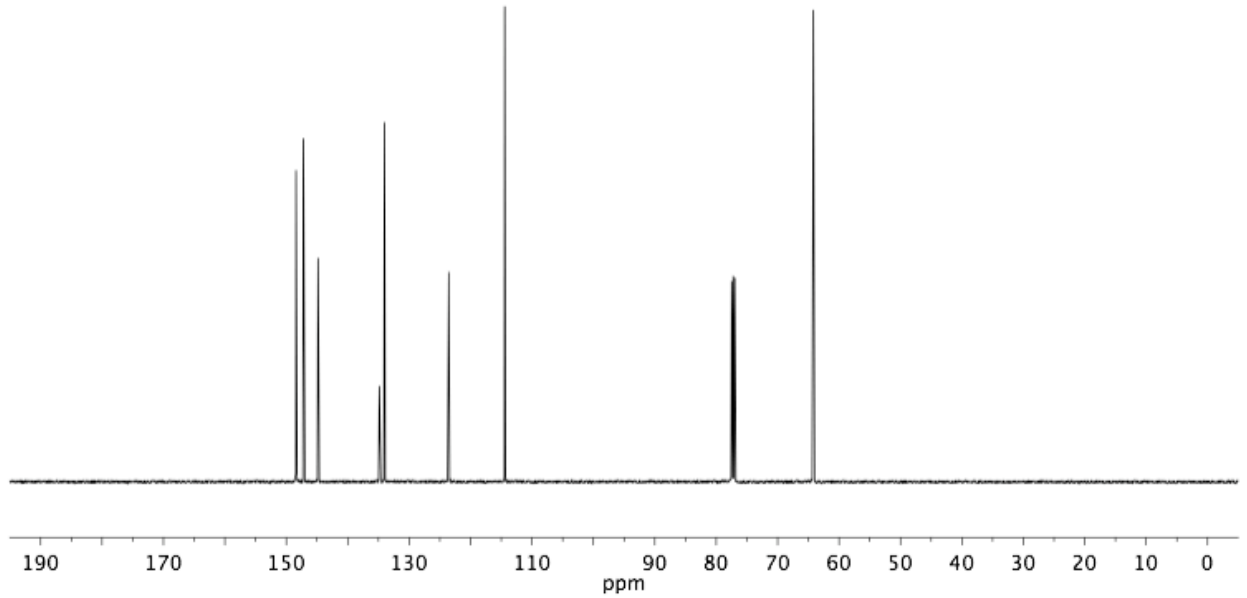
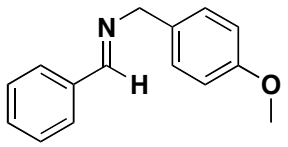




^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **37**



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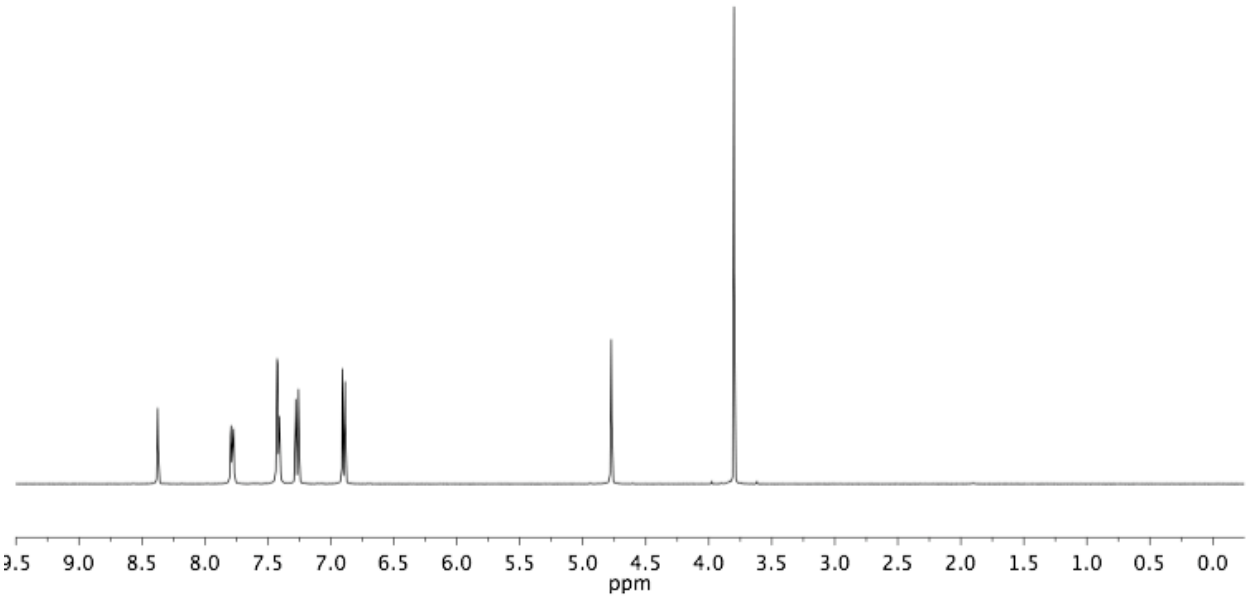
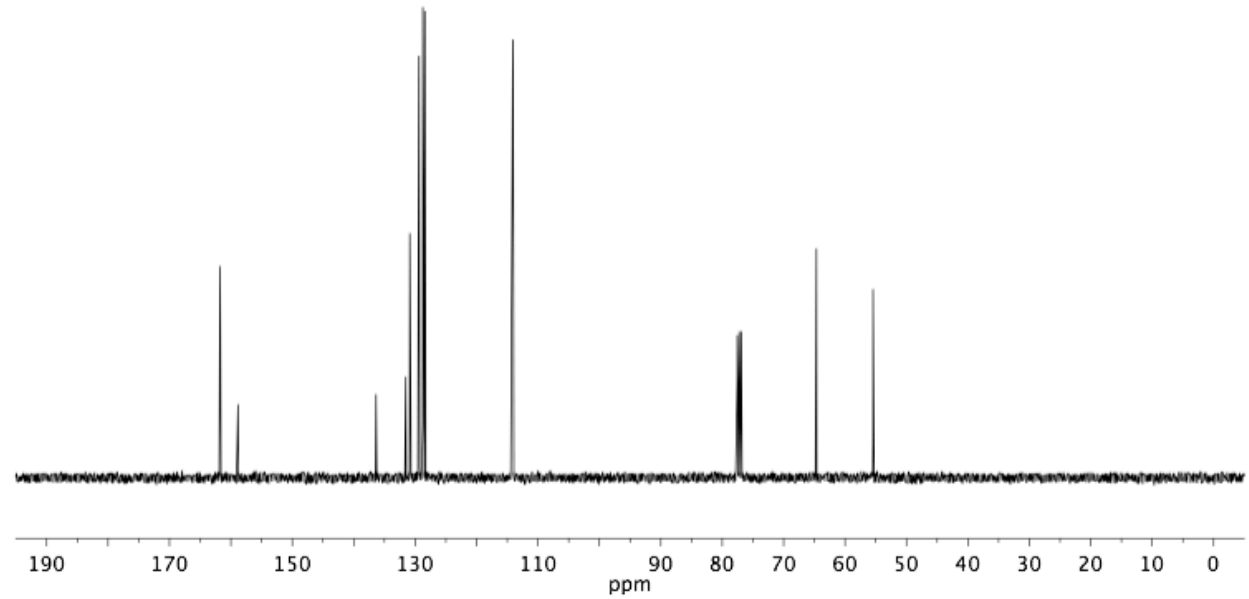
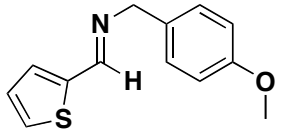
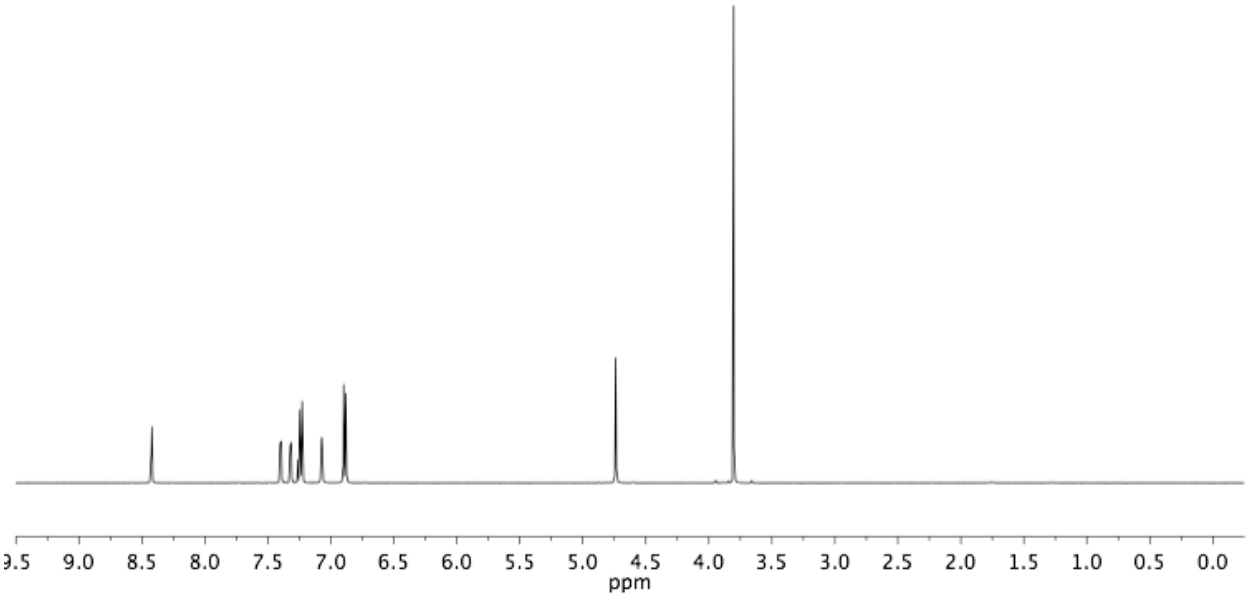


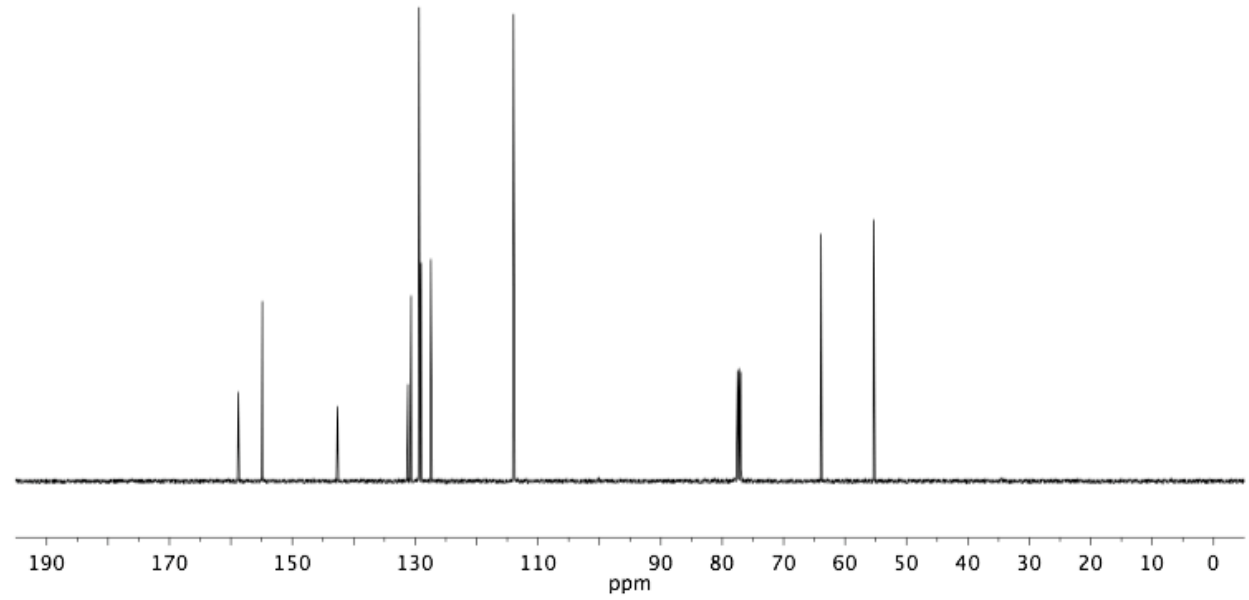


^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **29**

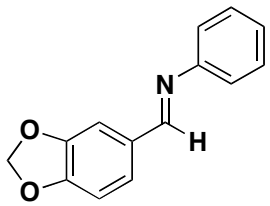


32





^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **32**



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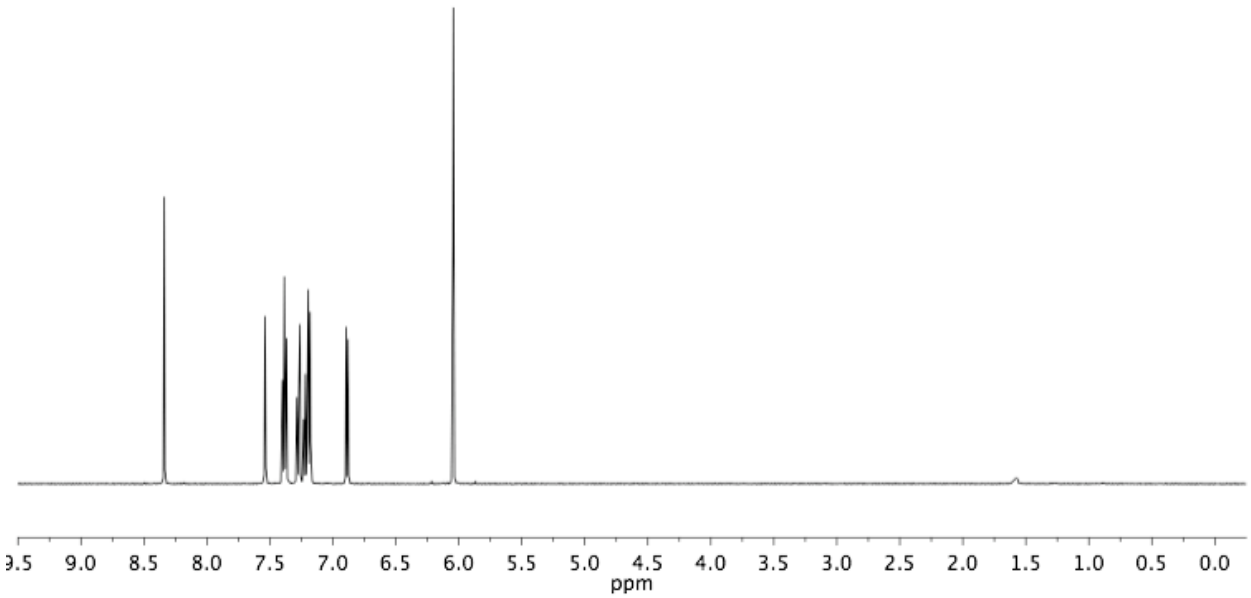
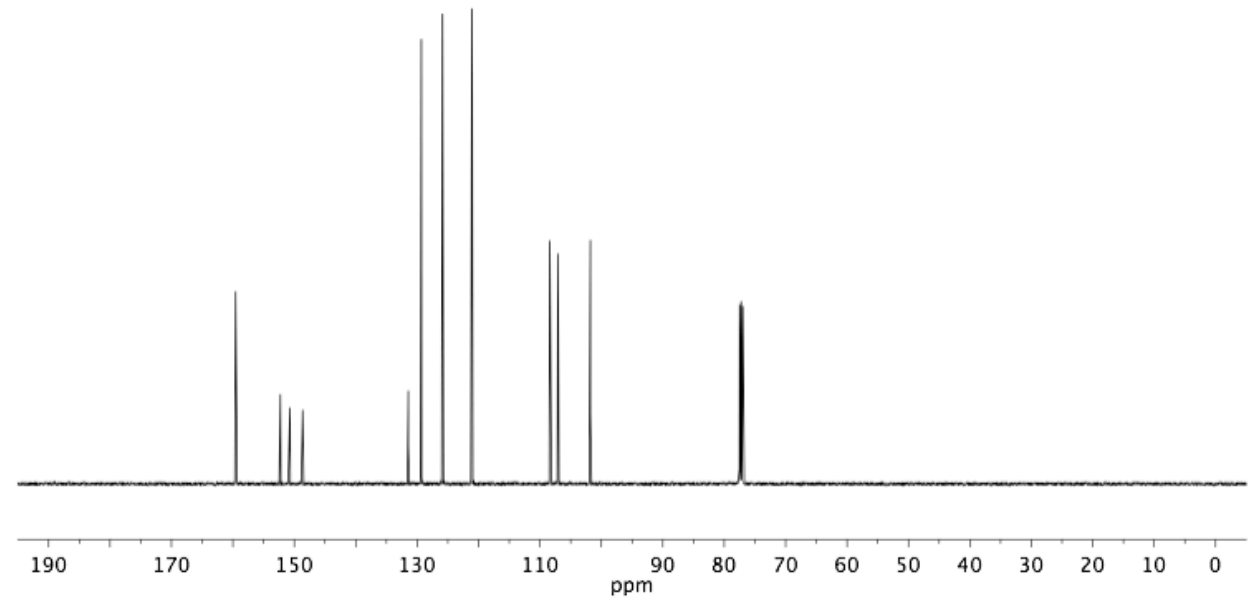
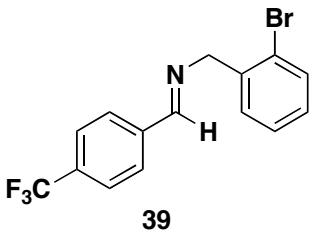




^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **34**



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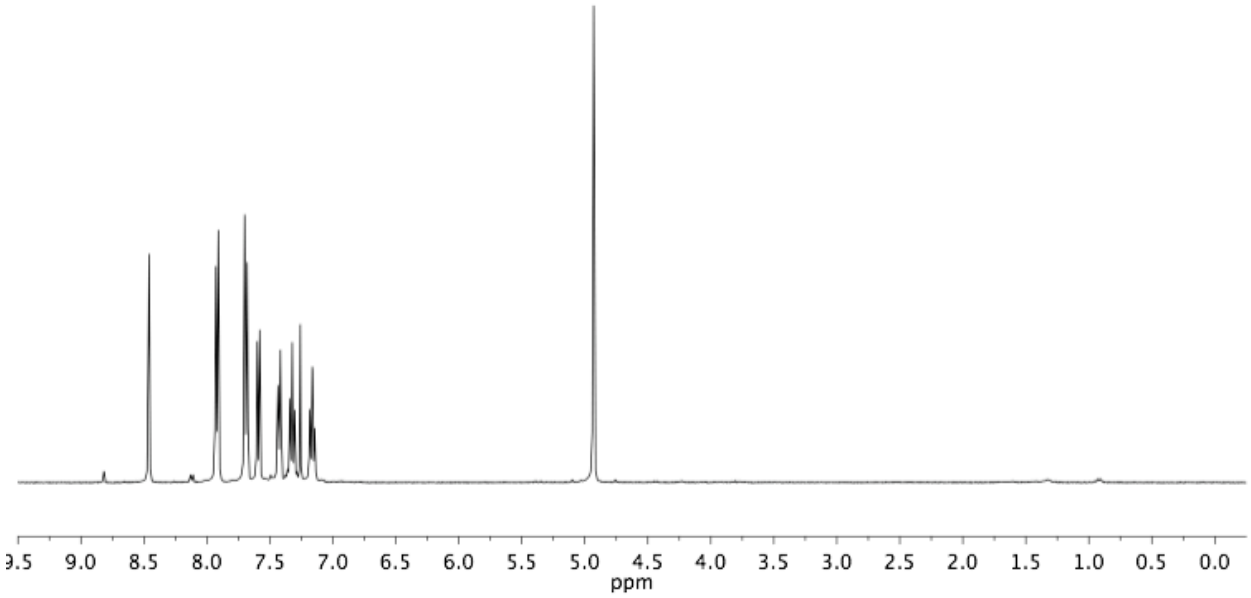
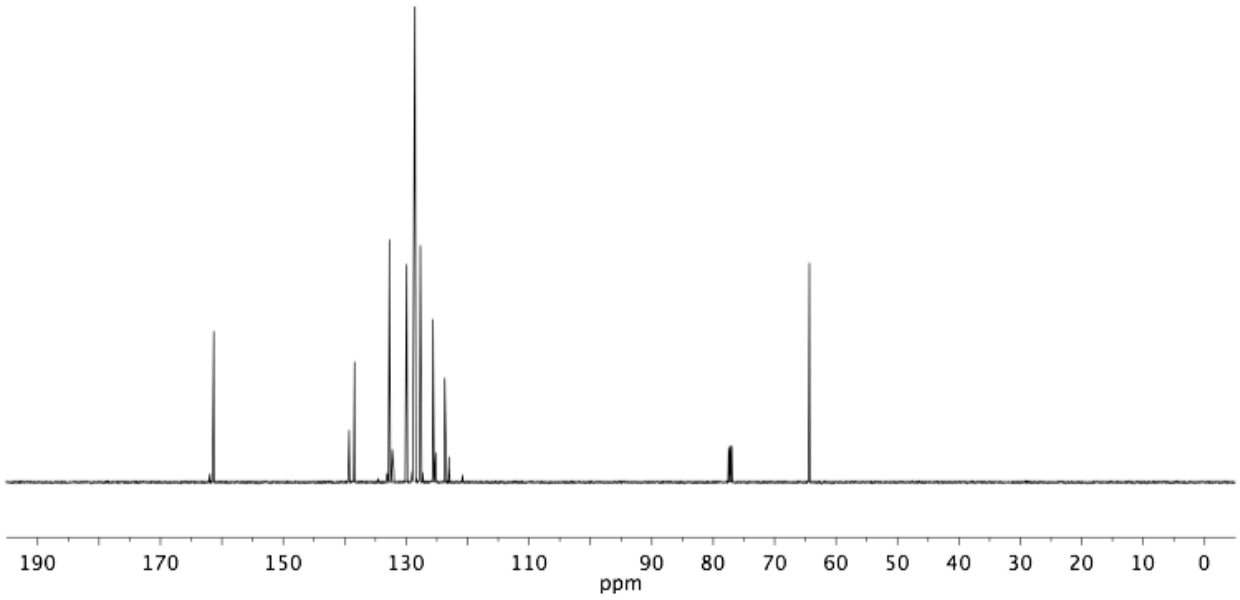
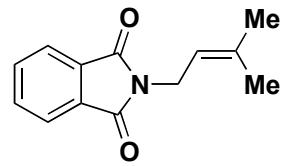
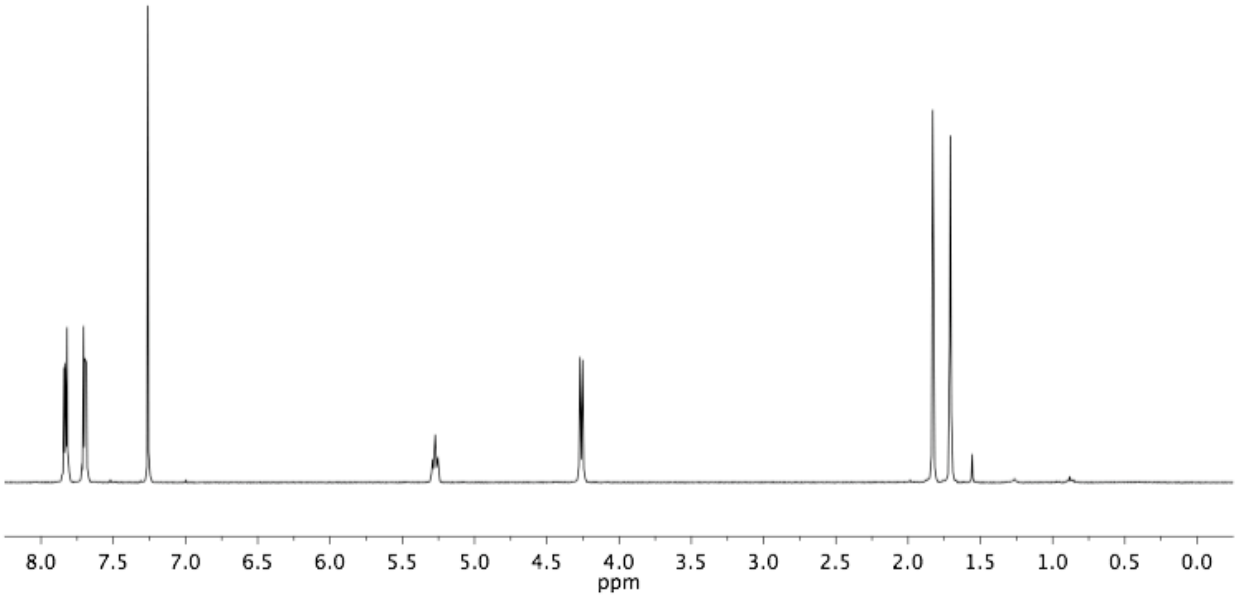


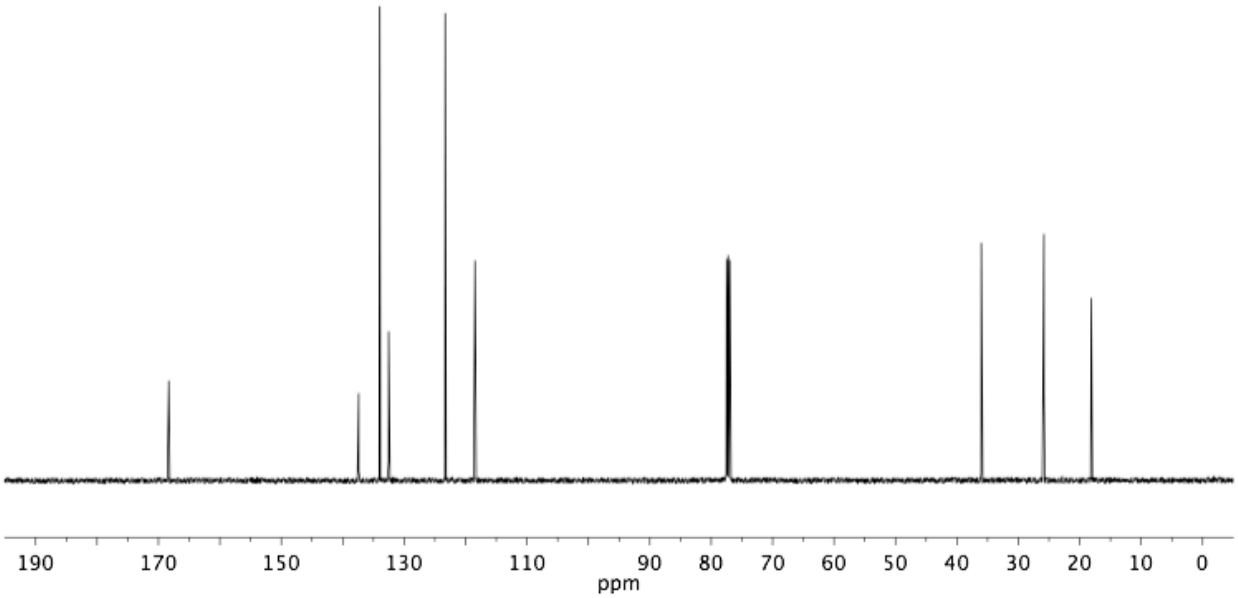


^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound **39**

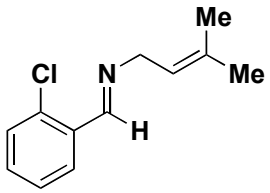


S-**19**

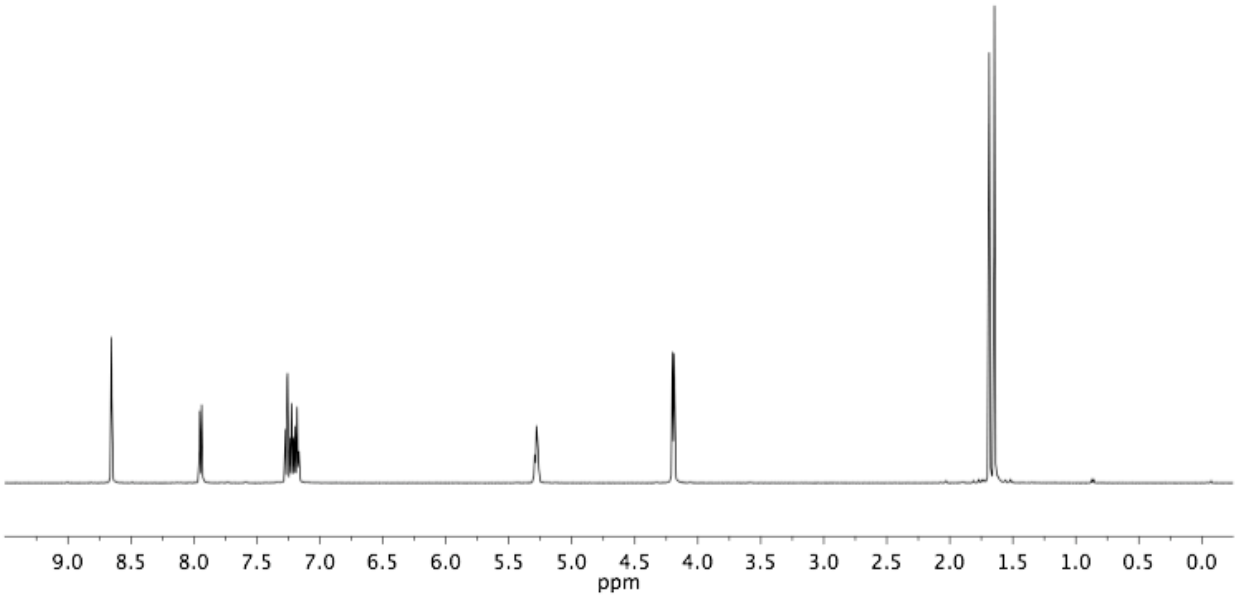


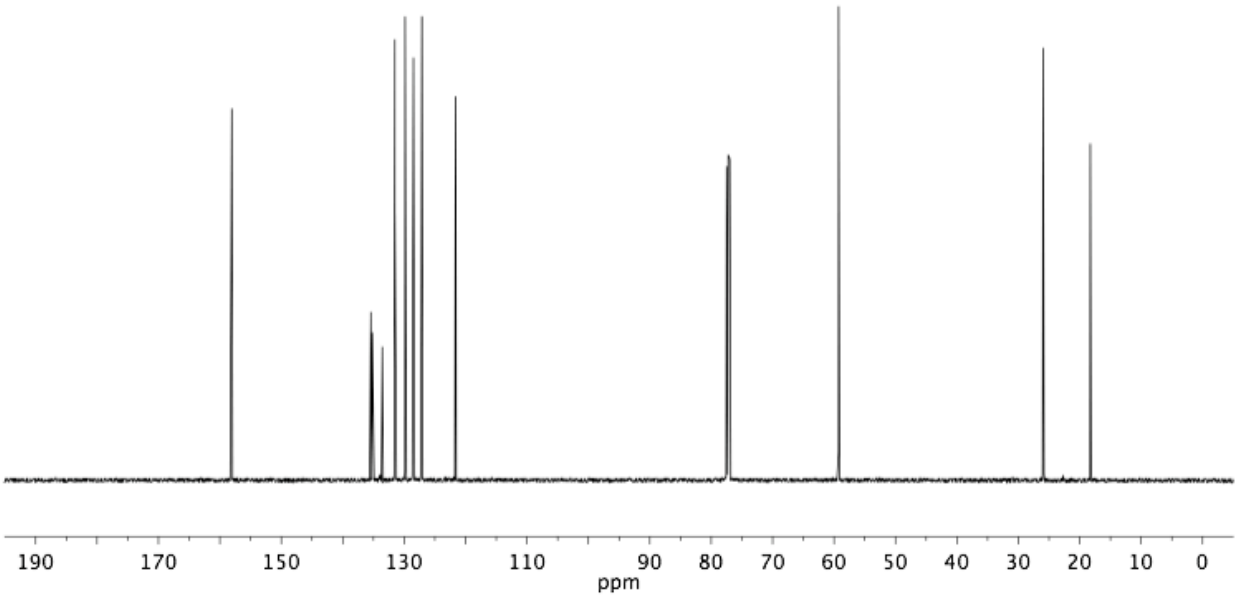


^{1}H NMR (400 Mhz) and ^{13}C NMR (126 Mhz) of compound S-**19**

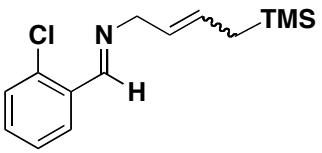


41





^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **41**



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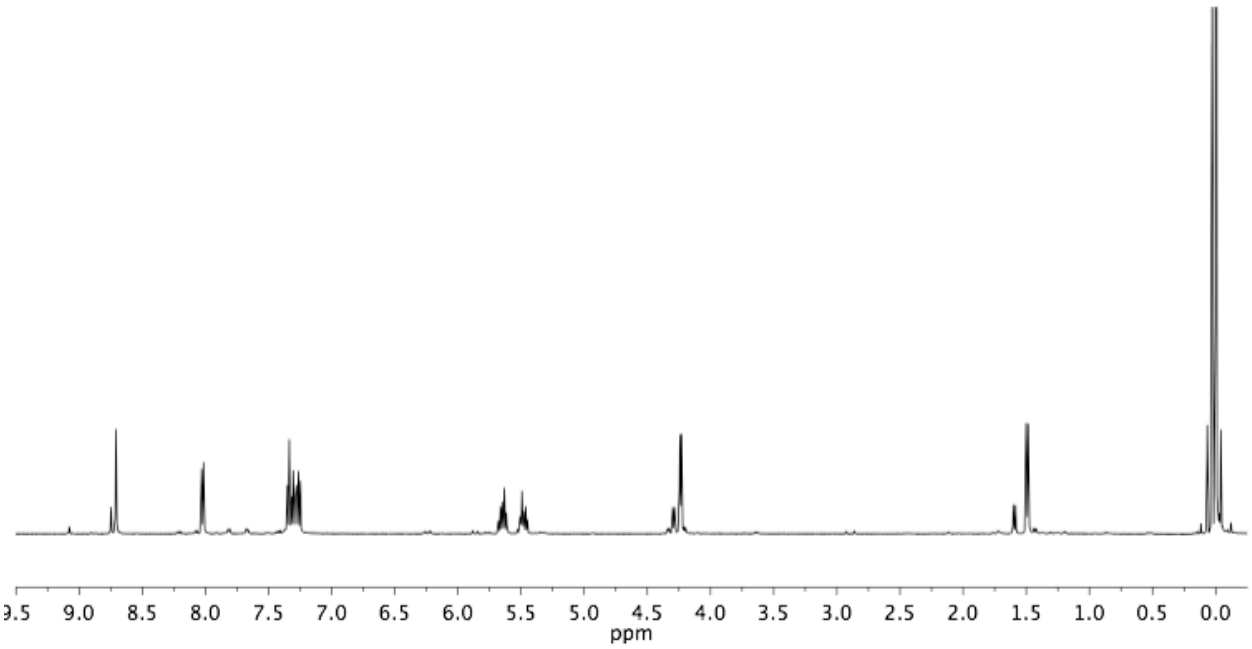

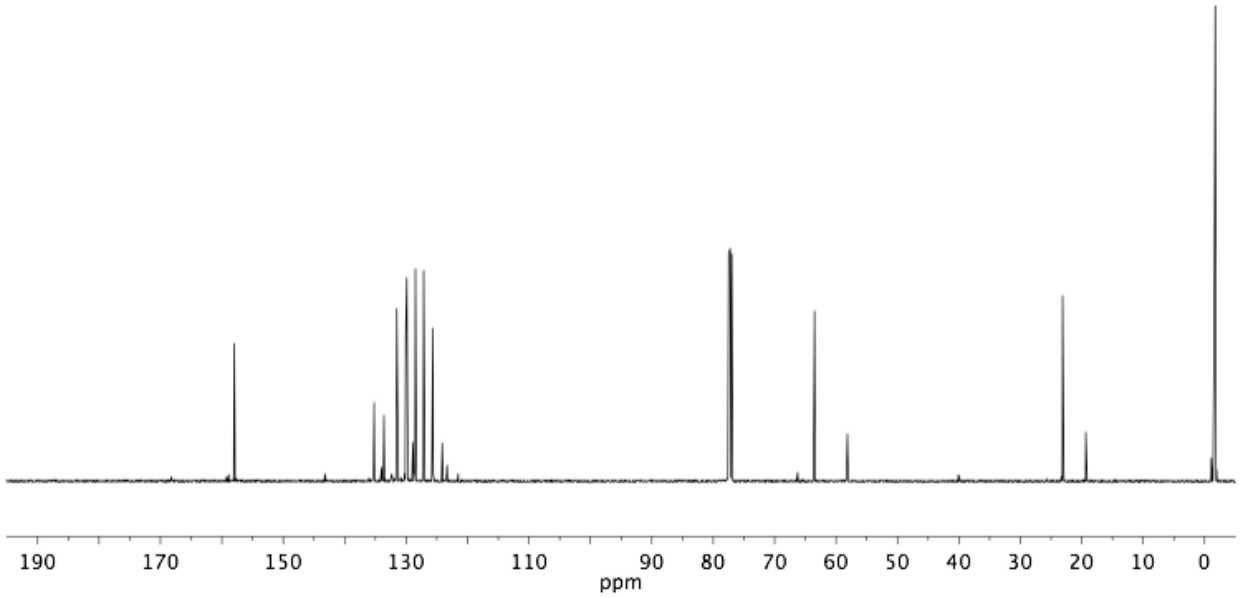

^{1}H NMR (500 Mhz) and ^{13}C NMR (126 Mhz) of compound **43**