Catalytic Asymmetric Methallylation of Ketones with an (H_8-BINOLate)Ti-Based Catalyst

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Supporting Information

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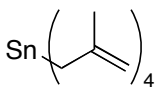
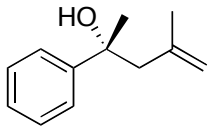
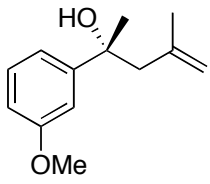
General Methods. All reactions using titanium(IV) isopropoxide were carried out in a Vacuum Atmospheres drybox or under a nitrogen using standard Schlenk techniques. All NMR spectra were obtained on either a Brüker 500 or 300 MHz Fourier transform spectrometer at the University of Pennsylvania NMR facility. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to residual protonated solvent in $CDCl_3$ or C_6D_6. The infrared spectra were obtained using a Perkin-Elmer 1600 series spectrometer. Thin-layer chromatography was performed on Whatman precoated silica gel 60 F-254 plates and visualized by ultraviolet light or by staining with ceric ammonium molybdate stain or phosphomolybdic acid hydrate stain. Silica gel (230-400 mesh, Silicycle) was used for flash chromatography. All reagents were purchased from Aldrich or Acros. Titanium(IV) isopropoxide, isopropanol, and all liquid ketone substrates were distilled prior to use and stored under an inert atmosphere. All glassware was flame- or oven-dried.



Preparation of tetramethallylstannane [Tetrakis-(2-methyl-allyl)-stannane] (1). An oven dried 250 mL round bottom flask with Mg turnings (1.2 g, 50 mmol) was purged with argon. An iodine crystal was added followed by 20 mL of THF (distilled from Na/benzophenone). A solution of 3-chloro-2-methyl-propene (5.9 mL, 60 mmol) in THF (100 mL) was added dropwise over 3 h at rt. The initial brown color vanished when the reaction started. After an additional 3 h stirring, tin(IV) chloride (0.585 mL, 5 mmol) was added to the grey solution over 30 min. The solution was then stirred at room temperature for 3 h. The reaction was quenched with water (200 mL) and extracted three times with 200 mL of hexanes. The combined organic layers were dried over $MgSO_4$, filtered through Celite, and the solvent was removed under reduced pressure. The residue was purified by vacuum distillation to give the product as colorless oil (1.62 g, 95% yield). Spectral data are consistent with previously reported data.[1]

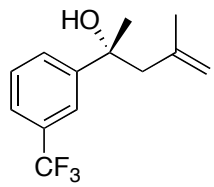


Preparation of 4-Methyl-2-phenyl-pent-4-en-2-ol (2) (General Procedure). (*R*)-H_8-BINOL (8.8 mg, 0.03 mmol, 30 mol%) was weighed into the reaction vessel that was then purged under nitrogen. Under nitrogen, acetonitrile (0.2 mL) and titanium(IV) isopropoxide (8.9 μL, 0.03 mmol, 30 mol%) were added, resulting in formation of a yellow precipitate. Isopropanol (153 μL, 2 mmol, 20 equiv) and tetramethallylstannane (34 mg, 0.1 mmol, 1.0 equiv) were added followed by acetophenone (11.7 μL, 0.1 mmol). The resulting reaction mixture was light yellow and homogeneous. The reaction mixture was then stirred at room temperature until it turned colorless with formation of a white precipitate (18 h). After completion of reaction by tlc, the reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with dichloromethane (3 x 10 mL). The combined organic layer was dried over Na_2SO_4, filtered through Celite, and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 98:2) to give the product (13.7 mg, 75% yield, 75% ee) a colorless oil. $[\alpha]_D^{20}$ = +40.9 (*c* = 0.785, $CHCl_3$); ^{1}H NMR (C_6D_6, 500 MHz): δ 1.38 (t, 3H, *J* = 1.1 Hz), 1.39 (s, 3H), 1.83 (s, 1H), 2.34 (dd, 1H, *J* = 13.4, 0.7 Hz), 2.43 (d, 1H, *J* = 13.4 Hz), 4.65 (m, 1H), 4.77 (m, 1H), 7.0-7.4 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 24.3, 30.8, 52.3, 73.3, 115.5, 125.2, 126.6, 128.3, 142.8, 148.7 ppm; IR (neat): 3465 (br), 3072, 2975, 2978, 2856, 1642, 1493, 1446, 1375, 1092, 700 cm^{-1}; HRMS-CI *m/z* 158.1099 [$(M–H_2O)^+$; calcd for $C_{12}H_{16}O$: 158.1096]; ee determination conditions: Chiralcel OD-H, hexanes : isopropanol = 98:2, flow = 0.3 mL/min, t = 26.9 min, 28.6 min.

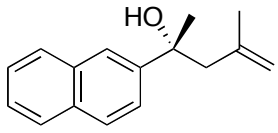


Preparation of 2-(3-Methoxy-phenyl)-4-methyl-pent-4-en-2-ol (3). The General Procedure was applied to 3'-methoxy-acetophenone (13.7 μL, 0.1 mmol). The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 98:2) to give the product (20.6 mg, 99% yield, 72% ee) as an oil. $[\alpha]_D^{20}$ = +23.8 (*c* = 0.98, $CHCl_3$); ^{1}H NMR (C_6D_6, 300 MHz): δ 1.42 (s, 3H), 1.43 (dd, 3H, *J* = 1.2, 1.2 Hz), 1.93 (s, 1H), 2.35 (dd, 1H, *J* = 13.3, 0.7 Hz), 2.47 (d, 1H, *J* = 13.3 Hz), 3.37 (s, 3H), 4.67 (m, 1H), 4.77 (m,

1H), 6.67 (ddd, 1H, *J* = 8.1, 2.6, 0.9 Hz), 6.94 (ddd, 1H, *J* = 7.8, 1.7, 1.0 Hz), 7.11 (t, 1H, *J* = 7.9 Hz), 7.22 (t, 1H, *J* = 1.8 Hz) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 24.5, 31.0, 52.4, 54.9, 73.6, 111.8, 112.0, 115.7, 117.9, 129.4, 143.0, 150.8, 160.4 ppm; IR (neat): 3518 (br), 2972, 2940, 1643, 1600, 1584, 1487, 1433, 1289, 1257, 1048, 892, 783, 702 cm^{-1}; HRMS-CI *m/z* 189.1282 $[(M–OH)^+$; calcd for $C_{13}H_{18}O_2$: 189.1279]; ee determination conditions: Chiralcel OD-H, hexanes : isopropanol = 95:5, flow = 0.5 mL/min, t = 17.7, 24.0 min.

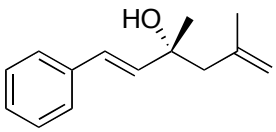


Preparation of 4-Methyl-2-(3-trifluoromethyl-phenyl)-pent-4-en-2-ol (4). The General Procedure was applied to 3'-(trifluoromethyl)-acetophenone (30.6 μL, 0.2 mmol). The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 98:2) to give the product (42.6 mg, 95% yield, 67% ee) as an oil. $[\alpha]_D^{20}$ = +18.5 (*c* = 0.93, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.37 (t, *J* = 1.1 Hz, 3H), 1.53 (s, 3H), 2.33 (s[br], 1H), 2.48 (d, 1H, *J* = 13.7Hz), 2.59 (d, 1H, *J* = 13.7 Hz), 4.70 (m, 1H), 4.87 (m, 1H), 7.39 (t, 1H, *J* = 7.8 Hz), 7.44 (d, 1H, *J* = 7.8 Hz), 7.58 (d, 1H, *J* = 7.8 Hz), 7.68 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 24.4, 31.0, 52.1, 73.3, 116.5, 122.0 (q, *J* = 3.8 Hz), 123.6 (q, *J* = 3.7 Hz), 124.5 (q, *J* = 270 Hz), 128.6, 128.7, 130.7 (q, *J* = 32.0 Hz), 142.1, 149.9 ppm; IR (neat): 3463, 3077, 2979, 2934, 1643, 1437, 1376, 1330, 1164, 1125, 1074 cm^{-1}; HRMS-CI *m/z* 226.0961 $[(M–H_2O)^+$; calcd for $C_{13}H_{15}F_3O$: 226.0969]; ee determination conditions: Chiralcel OD-H, hexanes: isopropanol = 99:1, flow = 0.3 mL/min, t = 24.8, 26.8 min.

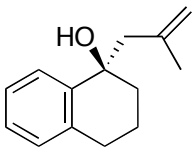


Preparation of 4-Methyl-2-naphthalen-2-yl-pent-4-en-2-ol (5). The General Procedure was applied to 1-naphthalen-2-yl-ethanone (17.0 mg, 0.1 mmol). The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 90:10) to give the product (21.6 mg, 95% yield, 90% ee) as an oil. $[\alpha]_D^{20}$ = +32.3 (*c* = 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.33 (s, 3H), 1.61 (s, 3H), 2.48 (s, 1H), 2.57 (dd, 1H, *J* = 13.4, 0.6 Hz), 2.73 (d, 1H, *J* = 13.4 Hz), 4.75 (m, 1H), 4.86 (m, 1H), 7.3-8.0 (m, 7H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 24.6, 31.1, 52.0, 73.7, 116.1, 123.3, 124.1, 126.0, 126.4, 127.8,

128.0, 128.5, 132.5, 133.5, 142.8, 145.7 ppm; IR (neat): 3465, 3056, 2972, 2928, 1640, 1600, 1506, 1451, 1375, 1125, 940, 869 cm^{-1}; HRMS-CI *m/z* 208.1255 [$(M–H_2O)^+$; calcd for $C_{16}H_{18}O$: 208.1252]; ee determination conditions: Chiralcel OD-H, hexanes:isopropanol = 95:5, flow = 0.5 mL/min, t = 20.7, 28.7 min.

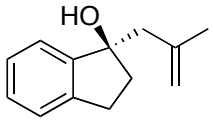


Preparation of 3,5-Dimethyl-1-phenyl-hexa-1,5-dien-3-ol (6). The General Procedure was applied to 4-Phenyl-but-3-en-2-one (14.6 mg, 0.1 mmol). The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 90:10) to give the product (17.6 mg, 87% yield, 72% ee) as an oil. $[\alpha]_D^{20}$ = +1.98 (*c* = 1.01, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.35 (s, 3H), 1.74 (s, 3H), 2.01 (s, 1H), 2.34 (s, 2H), 4.77 (m, 1H), 4.90 (m, 1H), 6.26 (d, *J* = 16 Hz, 1H), 6.56 (d, *J* = 16 Hz, 1H), 7.16-7.34 (m, 5H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 25.0, 29.0, 51.2, 72.4, 115.8, 126.7, 126.9, 127.6, 128.9, 137.2, 137.3, 142.6 ppm; IR (neat): 3441, 3073, 3026, 2971, 2931, 1702, 1642, 1600, 1494, 1448, 1373, 971, 894, 693 cm^{-1}; HRMS-CI *m/z* 185.1338 [$(M–OH)^+$; calcd for $C_{14}H_{18}O$: 185.1330]; ee determination conditions: Chiralcel OD-H, hexanes:isopropanol = 95:5, flow = 0.5 mL/min, t = 20.1, 30.3 min.



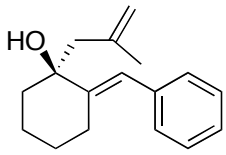
Preparation of 1-(2-Methyl-allyl)-1,2,3,4-tetrahydro-naphthalen-1-ol (7). The General Procedure was applied to α-tetralone (13.3 μL, 0.1 mmol). The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 99:1) to give the product (17.1 mg, 84% yield, 84% ee) as an oil. $[\alpha]_D^{20}$ = +20.0 (*c* = 0.35, $CHCl_3$); ^1H NMR (C_6D_6, 500 MHz): δ 1.36 (s, 1H), 1.47-1.60 (m, 3H), 1.77 (dd, *J* = 1.1, 1.1 Hz, 3H), 1.92-1.98 (m, 1H), 2.39 (d, *J* = 13.8 Hz, 1H), 2.43-2.52 (m, 2H), 2.55 (d, *J* = 13.8 Hz, 1H), 4.70-4.72 (m, 1H), 4.87-4.90 (m, 1H), 6.88-7.54 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 20.4, 24.6, 30.0, 36.1, 50.6, 72.3, 115.0, 126.4, 127.0, 127.1, 128.9, 136.3, 143.4, 143.7 ppm; IR (neat): 3447 (br), 3070, 2940, 1654, 1639, 1488, 1449, 1375, 1159, 1086 cm^{-1}; HRMS-CI *m/z* 185.1326 [$(M–OH)^+$; calcd for $C_{14}H_{18}O$: 185.1330]; ee determination conditions: Chiralcel OD-H, hexanes:isopropanol = 97:3, flow = 0.5 mL/min, t = 15.3, 16.9 min.

Preparation of 2,3-dihydro-1-(2-methylallyl)-1*H*-inden-1-ol (8).

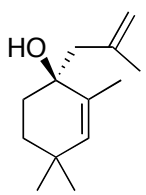


The title compound was prepared using the general procedure from 2,3-dihydroinden-1-one (0.1 mmol, 13.2 mg), purified via silica gel chromatography (2-11% EtOAc/hexanes) and obtained in 81% yield as an oil (15.3mg, 44% ee). $[\alpha]_d^{20}$ = -4.9 (*c* = 0.306, $CHCl_3$); ^1H NMR (C_6D_6, 500 MHz): δ 7.03-7.24 (4H, m), 4.86-4.87 (m ,1H), 4.72 (s, 1H), 2.71 (ddd,1H, *J* = 15.8, 4.36, 4.36 Hz), 2.51-2.58 (m, 2H), 2.30 (d, 2H, *J* = 13.51 Hz), 2.17-2.22 (m, 1H), 1.78-1.84 (m, 1H), 1.71 (s, 3H), 1.48 (s, 1H) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 148.8, 143.3, 128.4, 126.9, 125.1, 123.5, 114.9, 83.2, 48.7, 40.2, 29.8, 24.7 ppm; IR (neat): 3390 (br), 3033, 2934, 1641, 1475, 1457, 1155, 1065 cm^{-1} HRMS-CI *m/z* 170.1088 $[(M-H_2O)^+$; calcd for $C_{13}H_{14}$: 170.1096]; ee determination conditions: Chiralcel OD-H column: hexanes:isopropanol = 95:5, flow 0.5 mL/min, t = 11.3, 13.4 min.

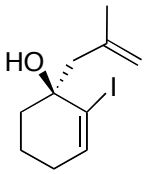
Preparation of 2-Benzylidene-1-(2-methyl-allyl)-cyclohexanol (9).



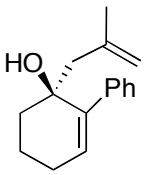
The General Procedure was applied to 2-benzylidene-cyclohexanone (18.6 mg, 0.1 mmol). The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 97.5:2.5) to give the product (21.7 mg, 90% yield, 80% ee) as an oil. $[\alpha]_D^{20}$ = 36.4 (*c* = 0.77, $CHCl_3$); ^1H NMR (C_6D_6, 500 MHz): δ 1.13 (m, 1H), 1.33 (m, 1H), 1.46 (m, 2H), 1.53 (td, 1H, *J* = 13.0, 4.1 Hz), 1.74 (s, 1H), 1.77 (dd, 3H, *J* = 1.5, 0.8 Hz), 1.71-1.83 (m, 2H), 2.18 (dd, 1H, *J* = 13.1, 0.7 Hz), 2.54 (d, 1H, *J* = 13.1 Hz), 2.88 (m, 1H), 4.75 (m, 1H), 4.88 (m, 1H), 6.81 (d, 1H, *J* = 1.0 Hz), 7.06 (m, 1H), 7.16-7.22 (m, 4H) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz): δ 23.8, 24.4, 27.5, 27.9, 41.9, 46.3, 74.2, 115.2, 121.9, 126.4, 128.4, 129.4, 139.0, 143.1, 146.5 ppm; IR (neat): 3464, 3075, 3021, 2930, 2857, 1645, 1598, 1494, 1446, 1094, 1073, 882, 767, 741 cm^{-1}; HRMS-CI *m/z* 224.1568 $[(M–H_2O)^+$; calcd for $C_{17}H_{22}O$: 224.1565]; ee determination conditions: Chiralcel OD-H, hexanes:isopropanol = 95:5, flow = 0.5 mL/min, t = 10.3, 12.2 min.



Preparation of 2,4,4-Trimethyl-1-(2-methyl-allyl)-cyclohex-2-enol (10). The General Procedure was applied to 2,4,4-trimethyl-cyclohex-2-enone (30 μL, 0.2 mmol). The crude product was purified by column chromatography on silica gel (hexanes:EtOAc, 95:5) to give the product (38.5 mg, 99% yield, 77% ee) as an oil. $[\alpha]_D^{20}$ = -5.37 (*c* = 0.41, $CHCl_3$); ^1H NMR (C_6D_6, 300 MHz): δ 1.00 (s, 3H), 1.19 (s, 3H), 1.19 (s, 1H), 1.51 (dt, 2H, *J* = 8.6, 3.6 Hz), 1.66 (m, 1H), 1.82 (d, 3H, *J* = 1.4 Hz), 1.94 (s, 3H), 2.00 (m, 1H), 2.31 (d, 1H, *J* = 13.7), 2.52 (d, 1H, *J* = 13.7 Hz), 4.89 (m,1H), 5.01 (m, 1H), 5.18 (d, 1H, *J* = 0.6 Hz) ppm; $^{13}C\{^1H\}$ NMR (C_6D_6, 75 MHz): δ 18.3, 24.8, 29.2, 30.2, 32.4, 33.1, 34.4, 46.8, 72.1, 114.7, 128.7, 135.5, 143.6 ppm; IR (neat): 3477, 2953, 2862, 1682, 1668, 1644, 1615, 1558, 1455, 1374, 1360, 1260 cm^{-1}; HRMS-CI *m/z* 176.1560 $[(M–H_2O)^+$; calcd for $C_{13}H_{22}O$: 176.1565]; ee determination conditions: β–dex™ 120 on HP6890 GC, 110 °C, flow = 1.6 mL/min, t = 27.3, 29.9 min.



Preparation of 2-iodo-1-(2-methyallyl)cyclohex-2-enol (11). The title compound was prepared using the general procedure from 2-iodocyclohex-2-enone (0.1 mmol, 22.2 mg). [2] The product was purified via silica gel chromatography (0-12% EtOAc/hexanes) and obtained in 55% yield (15.3mg, 49% ee) as a colorless oil. $[\alpha]_d^{20}$ = -8.3 (*c* = 0.248, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 6.51 (t, 1H, *J* = 4.2 Hz), 4.91-4.93 (m, 1H), 4.78-4.80 (m, 1H), 2.33-2.50 (m, 2H), 2.03-2.15 (m, 3H), 1.92 (s, 1H), 1.71-1.81 (m, 6H) ppm; $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz): δ 142.2, 141.2, 115.7, 113.9, 73.6, 50.19, 34.4, 30.0, 24.7, 19.65 ppm; IR (neat): 3439 (br), 3071, 2940,1641, 1443, 1202, 1166, 1083 cm^{-1}; HRMS-CI *m/z* 261.0141 $[(M\text{-}OH)^+$; calcd for $C_{10}H_{14}I$: 261.0141]; ee determination conditions: Chiralcel AD-H, hexanes:isopropanol = 99.5:0.5, flow 0.3 mL/min, t = 22.5, 26.1 min.

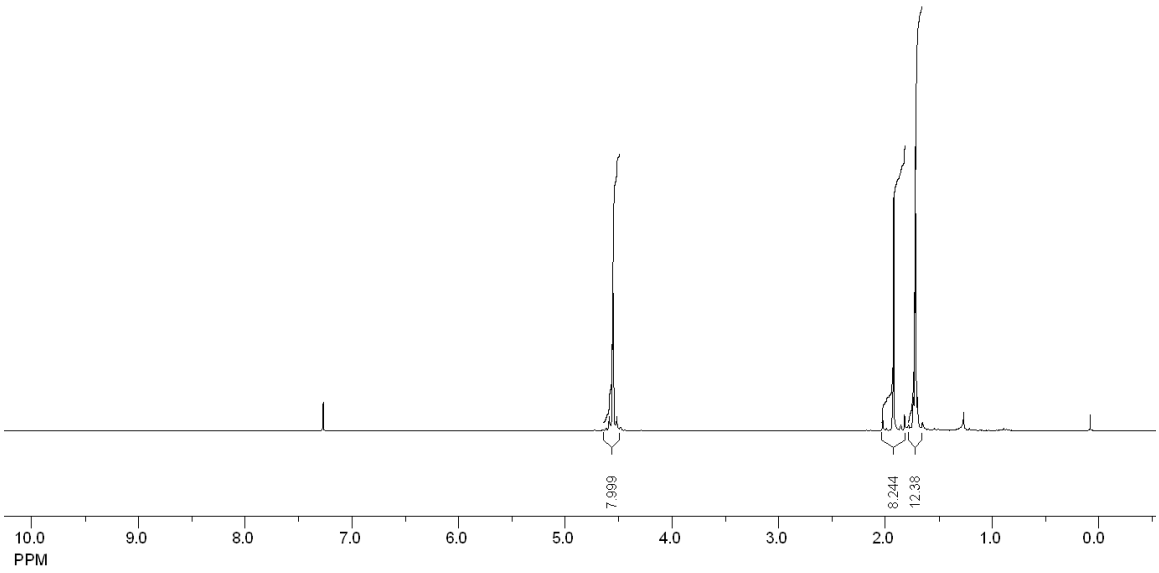


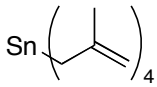
Preparation of 1-(2-methylallyl)-2-phenylcyclohex-2-enol (12). The title compound was prepared using the General Procedure from 2-phenylcyclohex-2-enone (0.1 mmol, 17.3 mg), purified via silica gel chromatography (0-15% EtOAc/hexanes) and obtained in 91% yield as a solid (20.7mg, 46% ee). $[\alpha]_d^{20}$ = +11.1 (*c* = 0.414, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz):

δ 7.45-7.48 (m, 2H), 7.26-7.35 (3H, m), 5.84 (1H, dd, *J* = 4.9, 2.9 Hz), 4.85-4.87 (1H, m), 4.69-4.71 (1H, m), 2.09-2.38 (4H, m), 1.91 (1H, s), 1.75-1.86 (7H, m) ppm; $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz): δ 144.1, 143.2, 142.0, 130.6, 129.2, 128.2, 127.0, 115.0, 72.1, 48.2, 36.5, 26.4, 25.05, 19.1 ppm; mp: 88.5-90°C; IR (neat): 3319 (br), 3011, 2907,1638,1487,1161, 1073 cm^{-1}; HRMS-CI *m/z* 210.1404 [$(M-H_2O)^+$; calcd for $C_{16}H_{18}$: 210.1409]; ee determination conditions: Chiralcel OD-H column: hexanes:isopropanol = 98:2, flow 0.5 mL/min, t = 12.9, 15.9 min.

(1) Fraenkel, G.; Winchester, W. R. *Journal of the American Chemical Society* **1989**, *111*, 3794-3797.

(2) Ruel, F. S.; Braun, M. P.; Johnson, C. R. *Organic Syntheses* **1998**, *75*, 69-74.

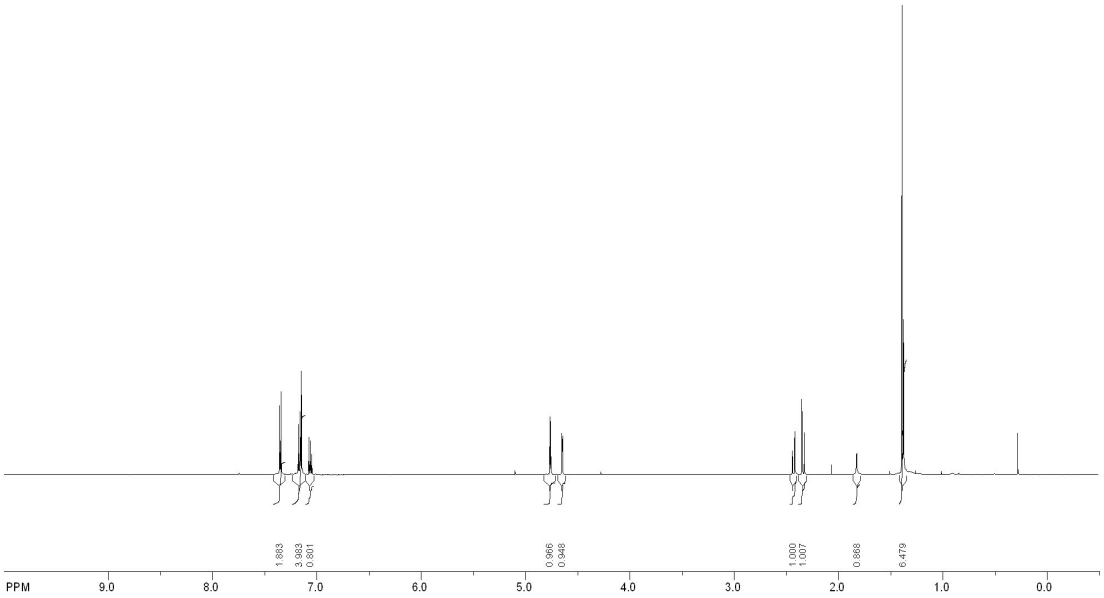


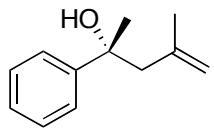


(1)

300 MHz NMR in $CDCl_3$ of tetramethallylstannane [Tetrakis-(2-methyl-allyl)-stannane]

(1)





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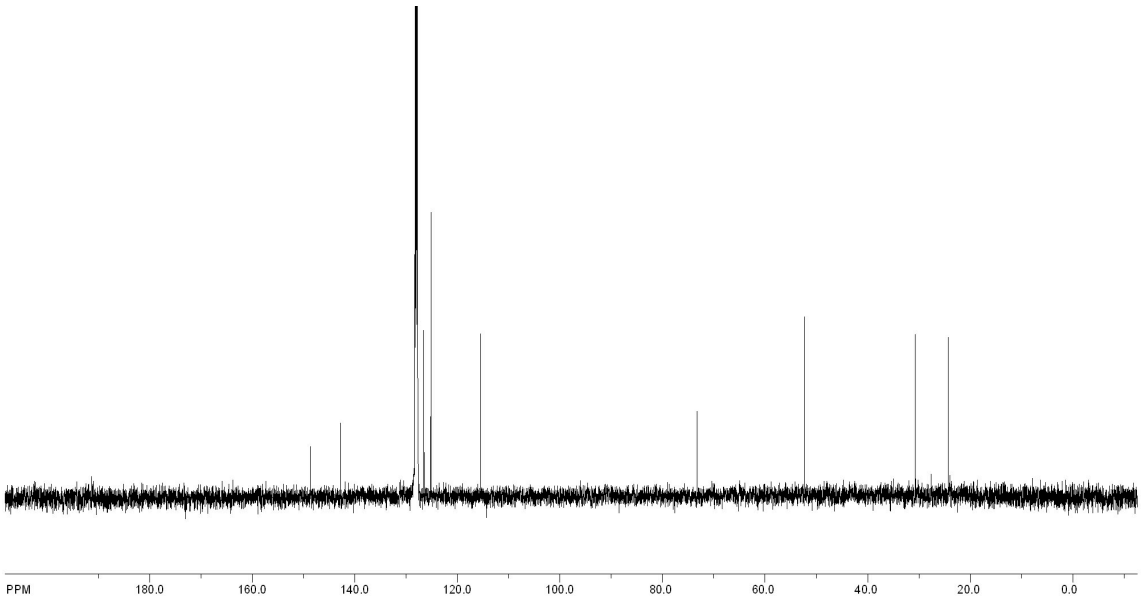
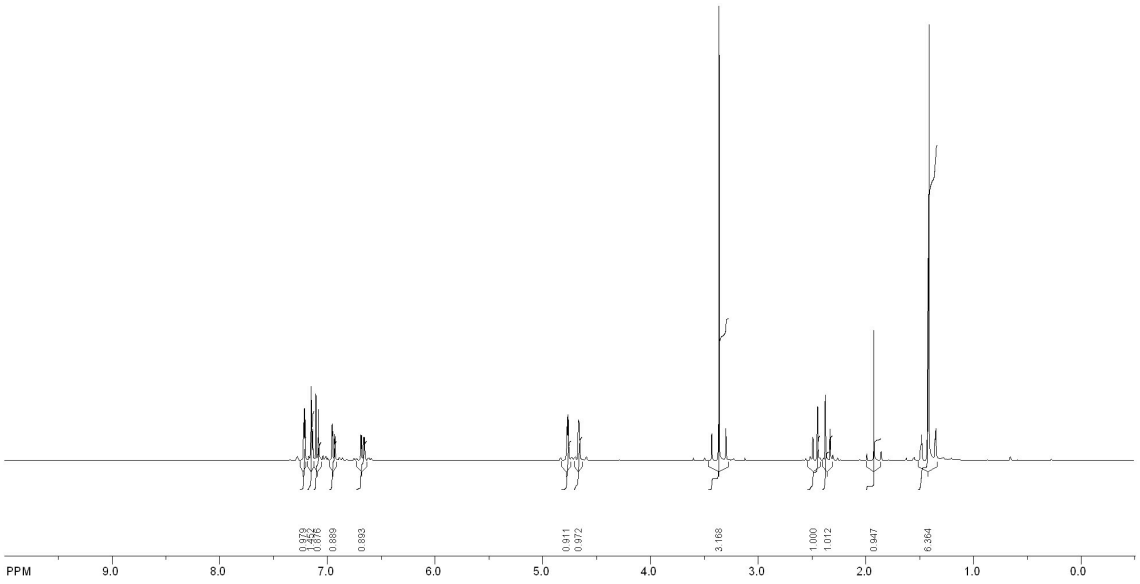
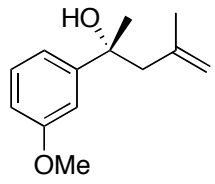


500 MHz ^{1}H & 125 MHz $^{13}C\{^{1}H\}$ NMR in C_6D_6 of 4-Methyl-2-phenyl-pent-4-en-2-ol **(2)**





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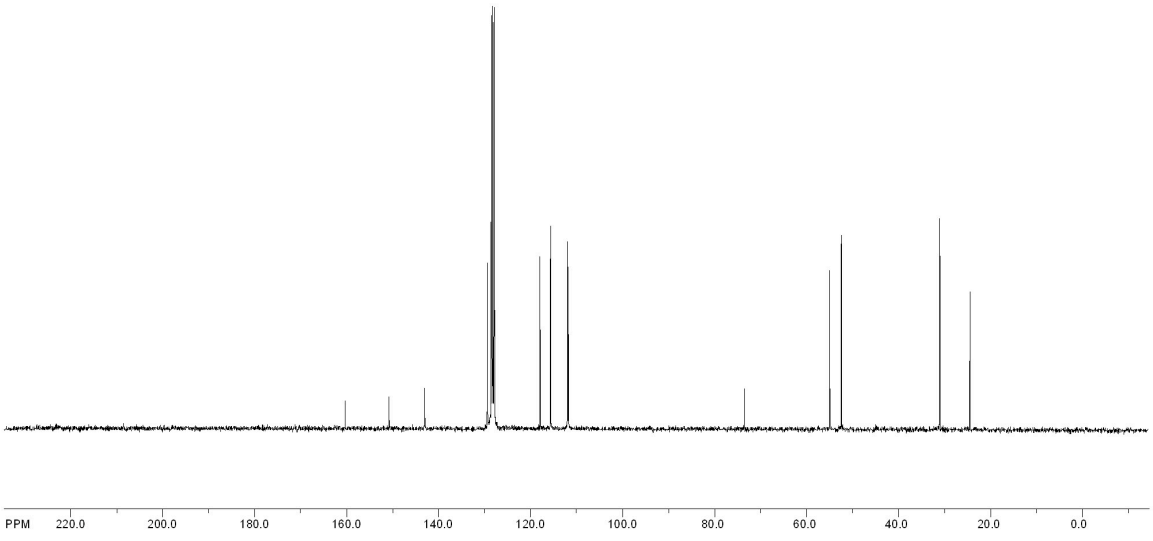
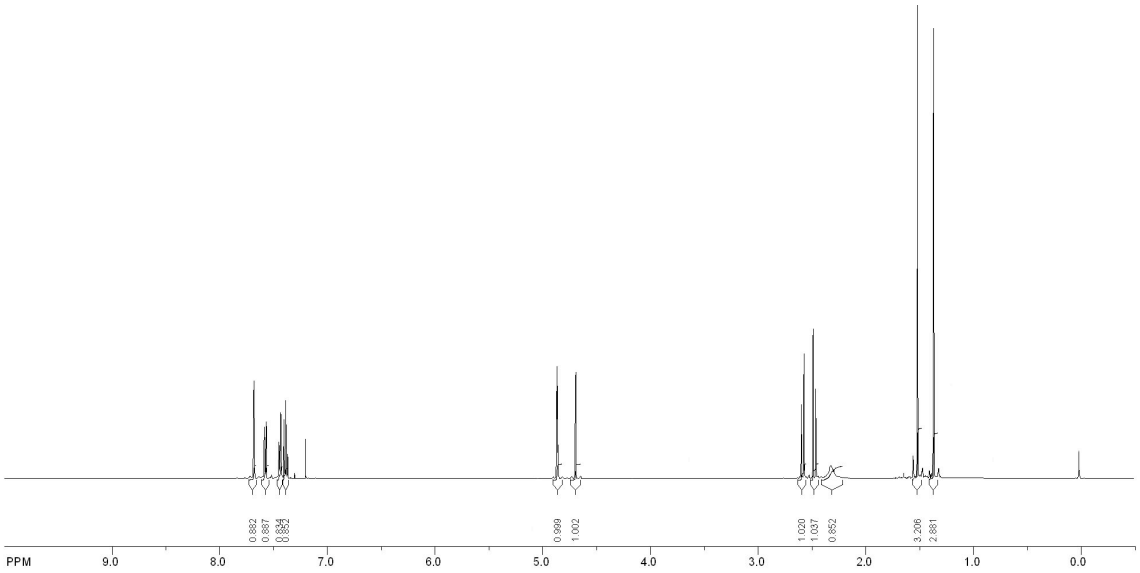
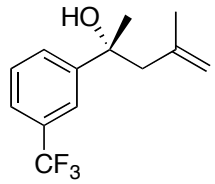


300 MHz ^{1}H & 75 MHz $^{13}C\{^{1}H\}$ NMR in C_6D_6 of 2-(3-Methoxy-phenyl)-4-methyl-pent-4-en-2-ol **(3)**





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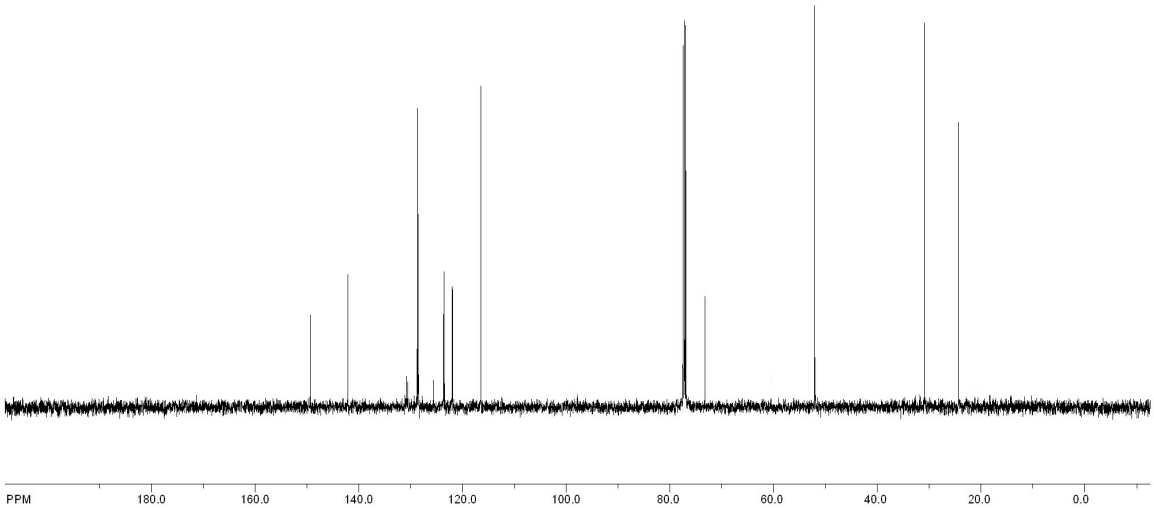
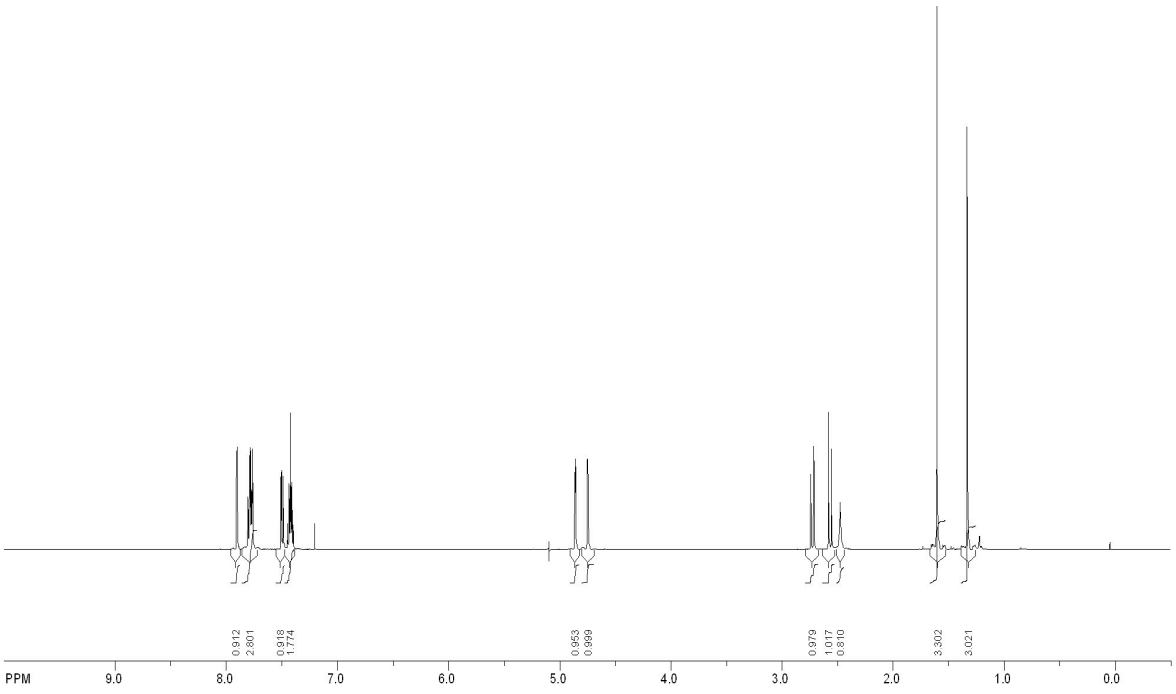
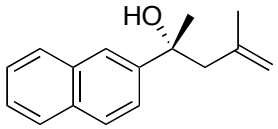


500 MHz ^{1}H & 125 MHz $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ of 4-Methyl-2-(3-trifluoromethyl-phenyl)-pent-4-en-2-ol **(4)**





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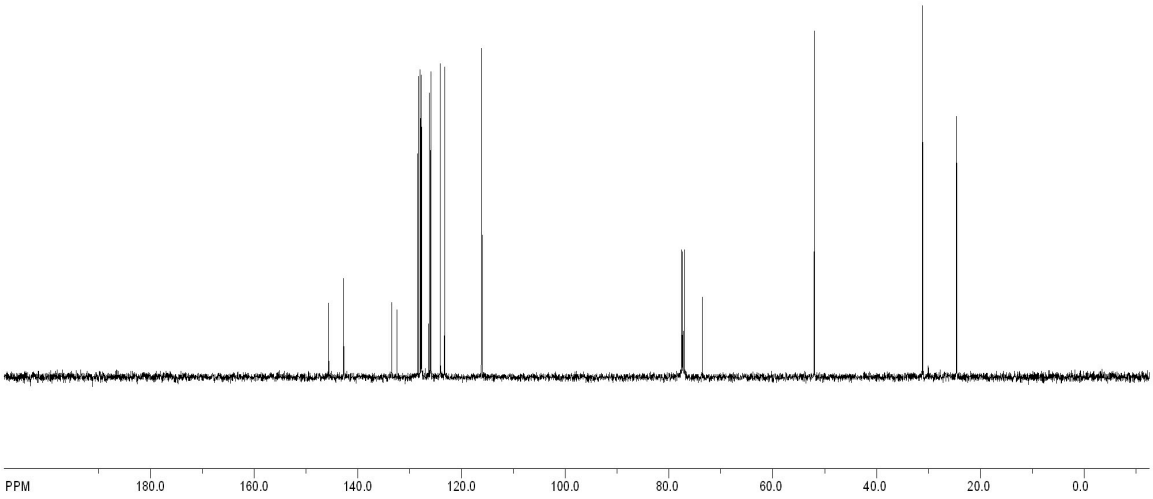
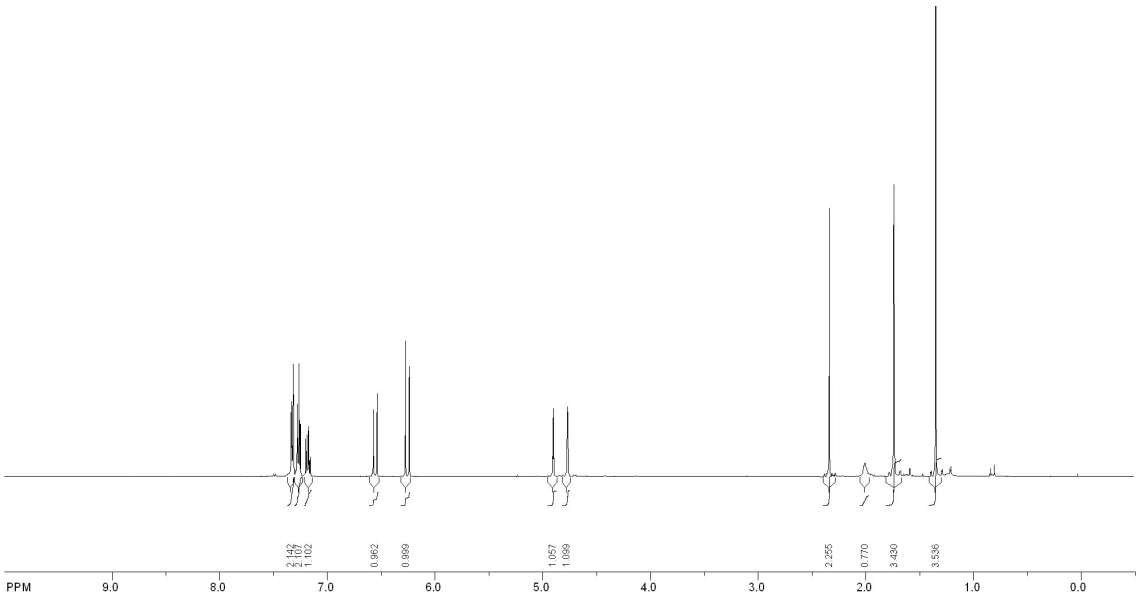
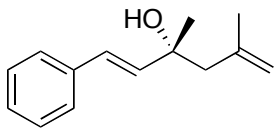


500 MHz ^{1}H & 125 MHz $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ of 4-Methyl-2-naphthalen-2-yl-pent-4-en-2-ol **(5)**





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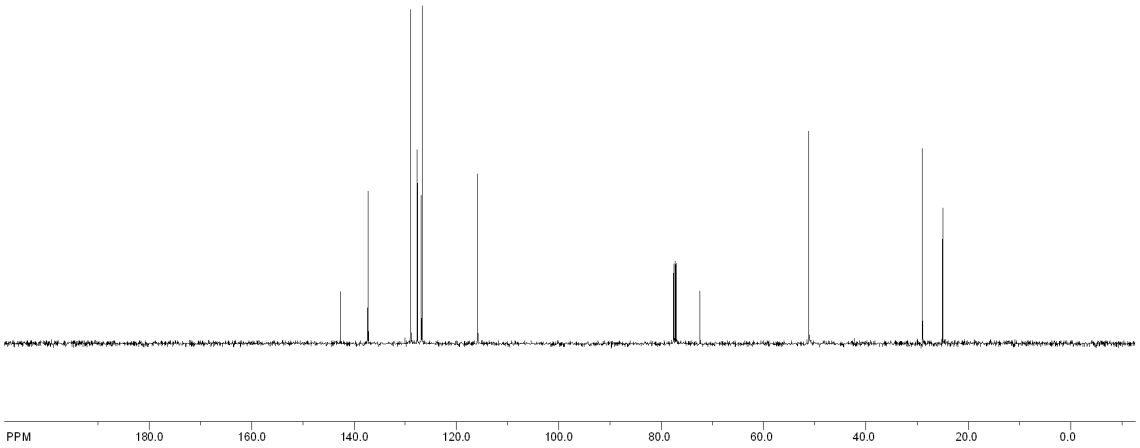
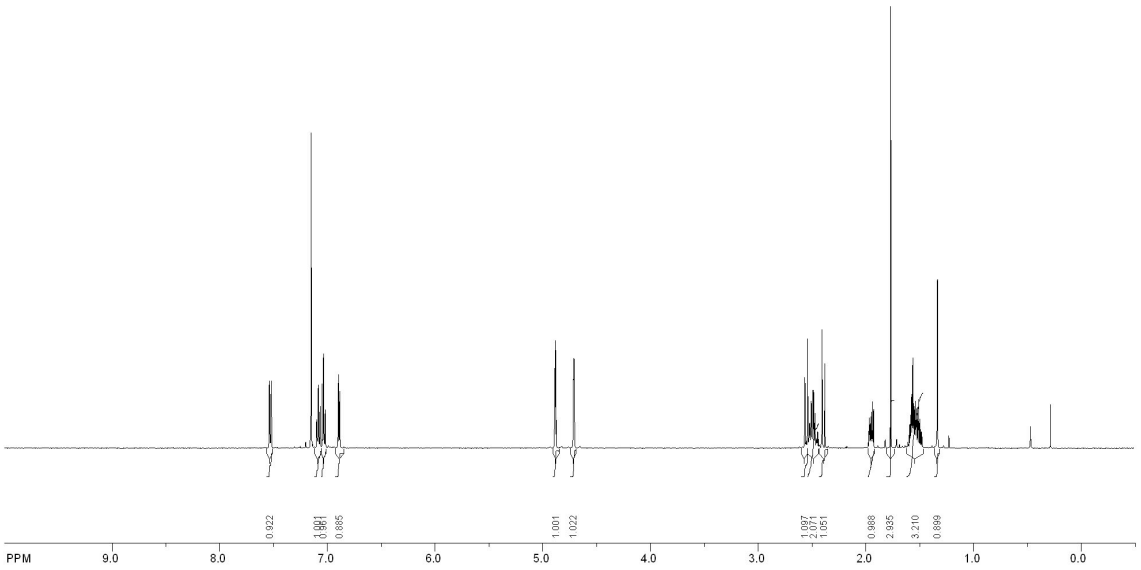
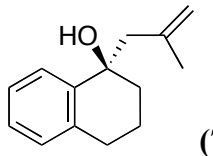


500 MHz ^{1}H & 125 MHz $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ of 3,5-Dimethyl-1-phenyl-hexa-1,5-dien-3-ol **(6)**





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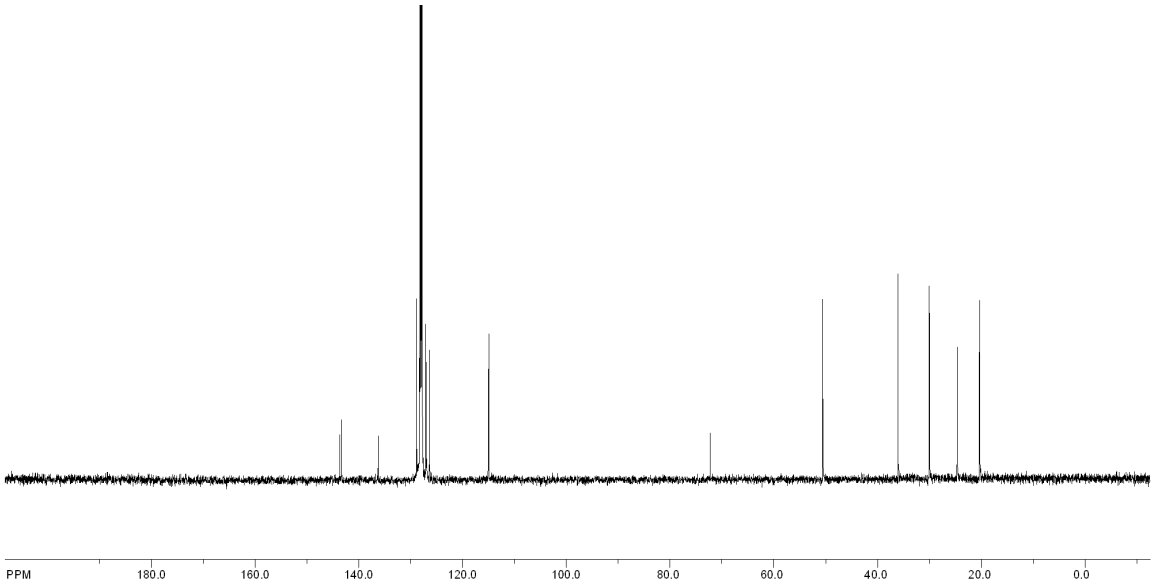
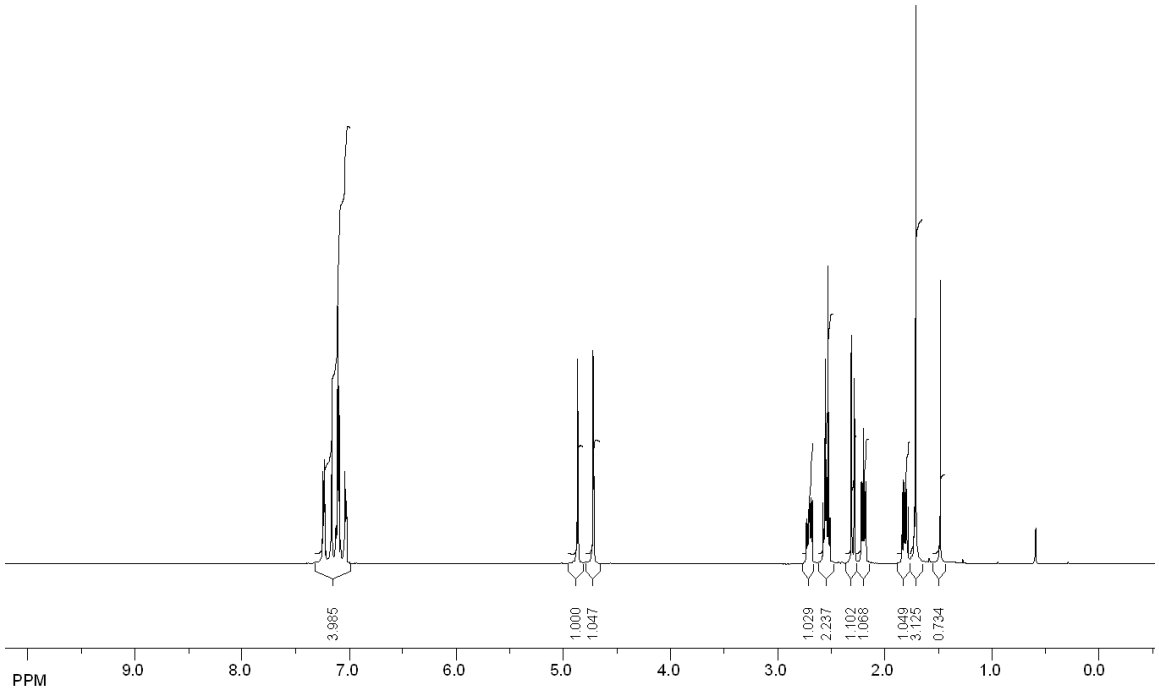
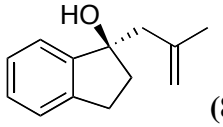


500 MHz ^{1}H & 125 MHz $^{13}C\{^{1}H\}$ NMR in C_6D_6 of 1-(2-Methyl-allyl)-1,2,3,4-tetrahydro-naphthalen-1-ol **(7)**





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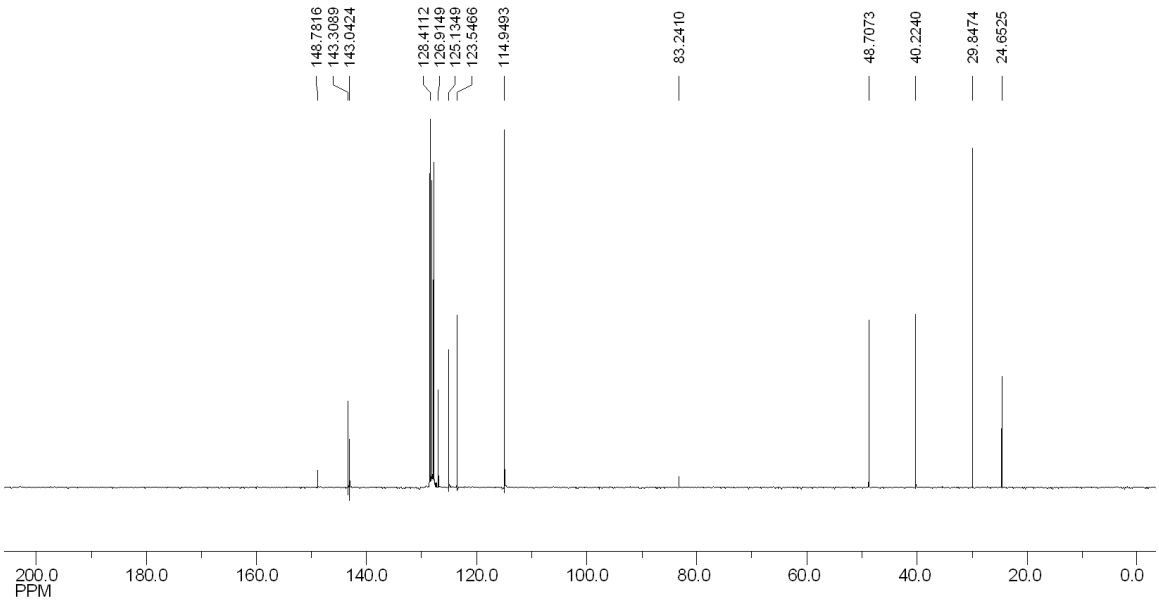
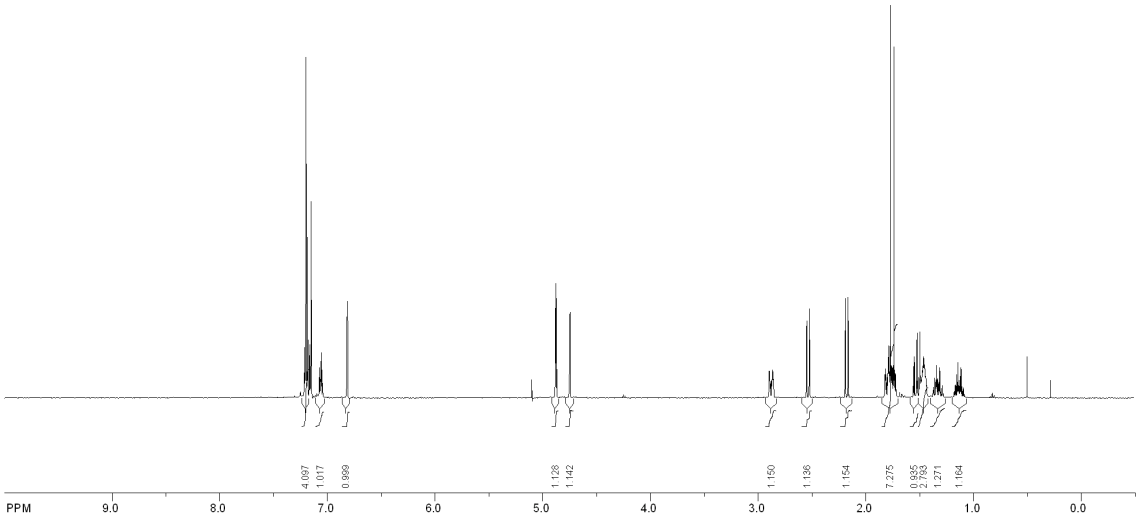
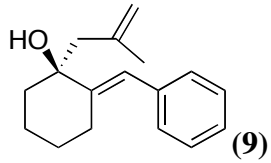


500 MHz ^{1}H & 75 MHz $^{13}C\{^{1}H\}$ NMR in C_6D_6 of 2,3-dihydro-1-(2-methylallyl)-1H-inden-1-ol **(8)**





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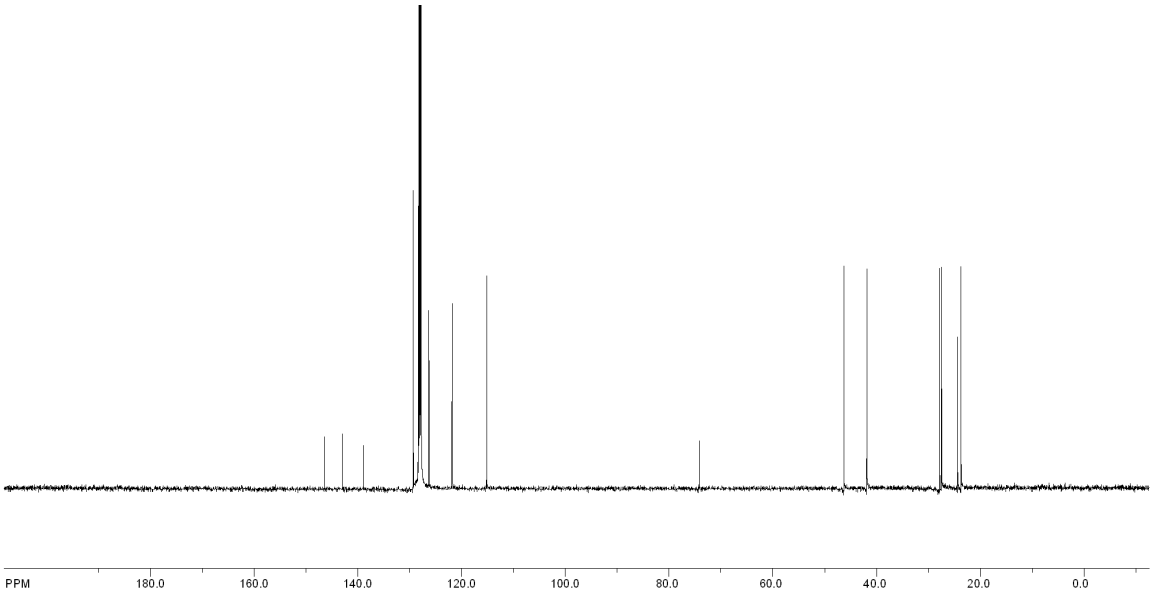
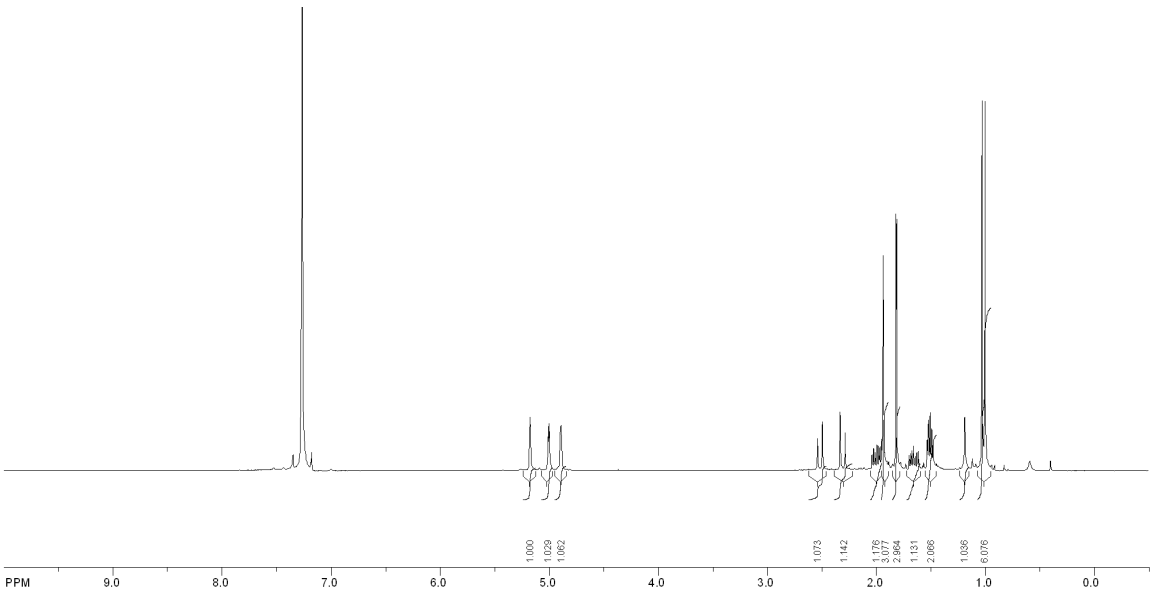
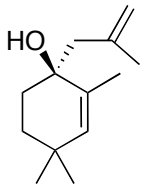


500 MHz ^{1}H & 125 MHz $^{13}C\{^{1}H\}$ NMR in C_6D_6 of 2-Benzylidene-1-(2-methyl-allyl)-cyclohexanol (**9**)





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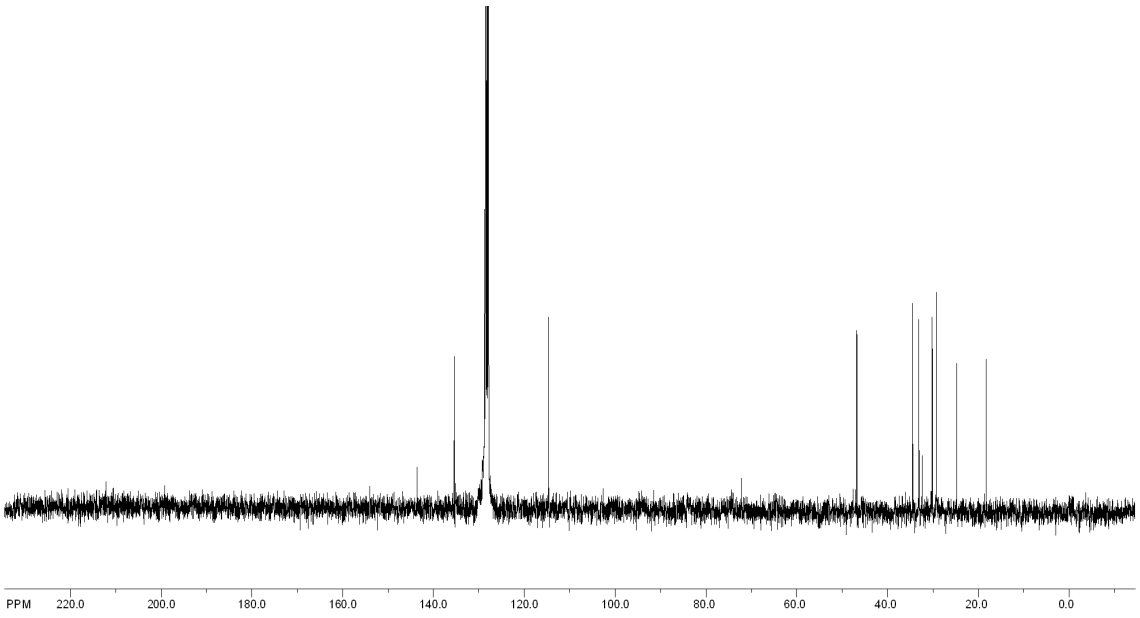
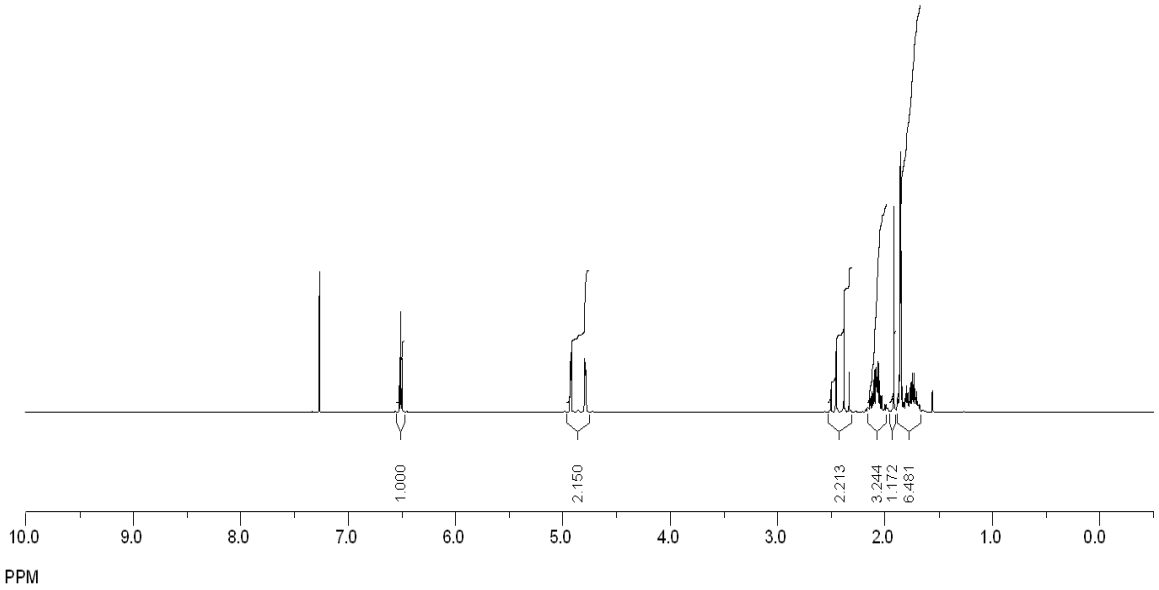
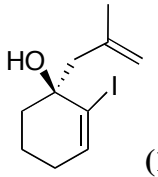


500 MHz ^{1}H & 125 MHz $^{13}C\{^{1}H\}$ NMR in C_6D_6 of 2,4,4-Trimethyl-1-(2-methyl-allyl)-cyclohex-2-enol **(10)**





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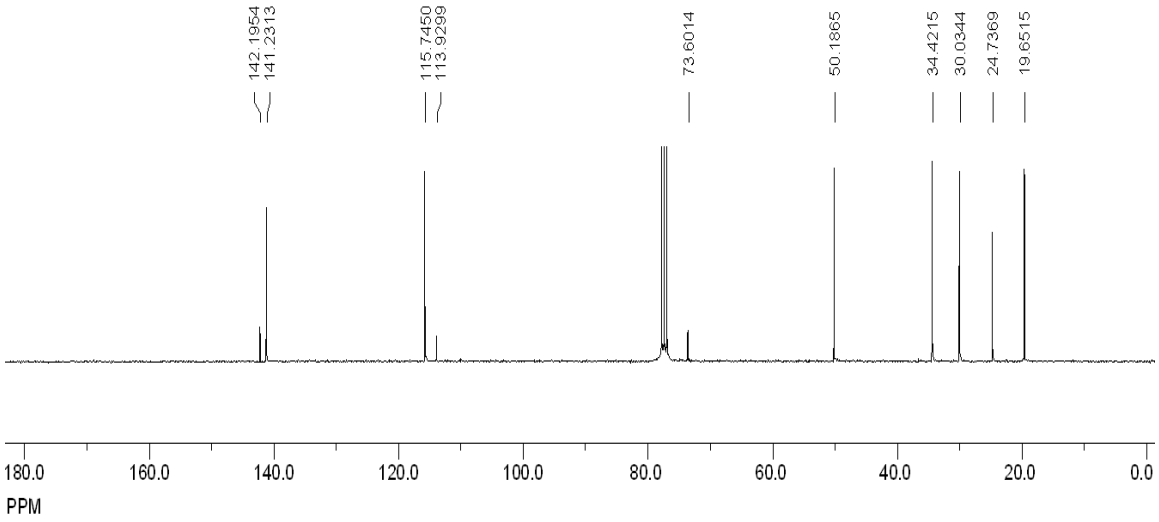
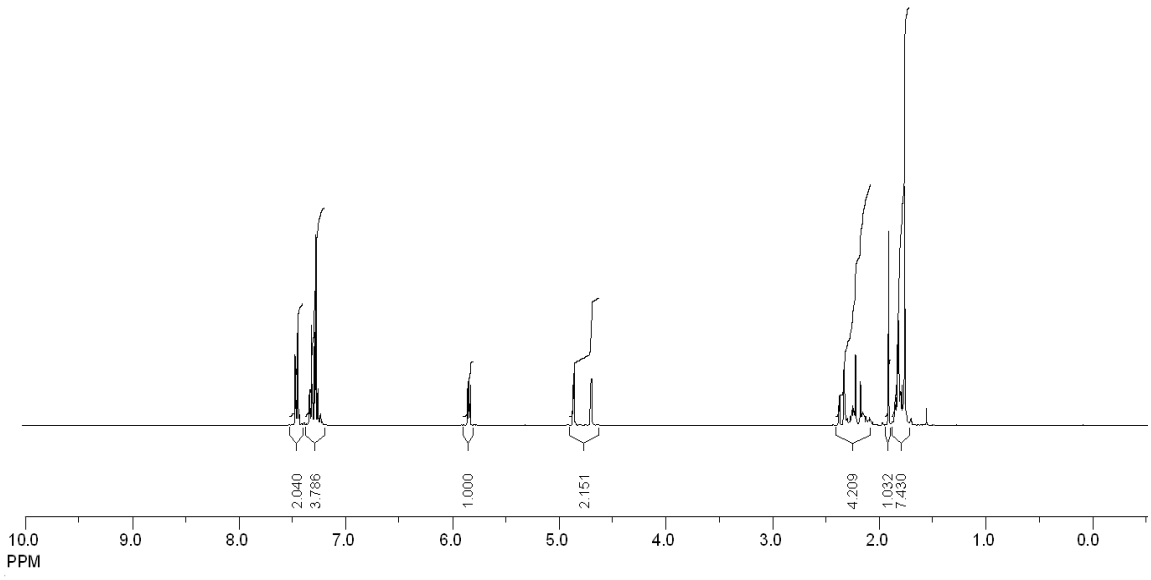
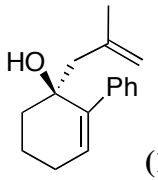


300 MHz ^{1}H & 75 MHz $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ of 2-iodo-1-(2-methyallyl)cyclohex-2-enol **(11)**





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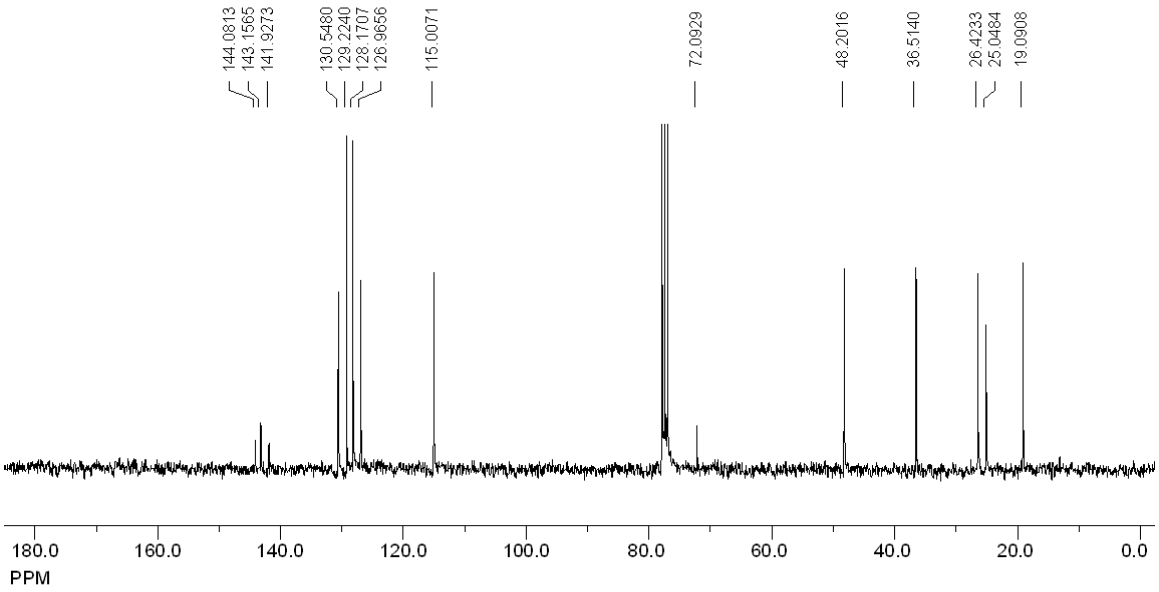

300 MHz ^{1}H & 75 MHz $^{13}C\{^{1}H\}$ NMR in $CDCl_3$ of 1-(2-methylallyl)-2-phenylcyclohex-2-enol **(12)**