One-Pot Catalytic Enantio- and Diastereoselective Syntheses of *Anti-*, *cis*-Disubstituted and Vinyl Cyclopropyl Alcohols

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Supporting Information

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General Methods. All reactions were carried out under a nitrogen atmosphere with oven-dried glassware. The progress of all reactions was monitored by thin-layer chromatography to ensure the reactions had reached completion. All manipulations involving dialkylzinc reagents were carried out an inert atmosphere in a Vacuum Atmosphere drybox with an attached MO-40 Dritrain or by using standard Schlenk or vacuum line techniques. Dialkylzinc compounds, except dimethyl- and diethylzinc, which are commercially available, were prepared by literature methods.[1-2] Dichloromethane and hexanes were dried through alumina columns. All aldehydes were distilled prior to use and stored under N_2. Unless otherwise specified, all chemicals were obtained from Aldrich, Acros, or GFS chemicals, and all solvents were purchased from Fischer Scientific. The ^{1}H NMR and ^{13}C{^{1}H} NMR spectra were obtained on a Brüker Fourier transform NMR spectrometer at either 300 or 500 and 75 or 125 MHz, respectively. ^{1}H NMR spectra were referenced to tetramethylsilane in $CDCl_3$ or residual protonated solvent; ^{13}C{^{1}H} NMR spectra were referenced to residual solvent. Chemical Shifts are reported in units of parts per million downfield from tetramethylsilane, and all coupling constants are reported in Hertz. Analysis of enantiomeric excess was performed using a Hewlett-Packard 1100 Series HPLC and a chiral column. The optical rotations were recorded using a JASCO DIP-370. Infrared spectra were obtained using a Perkin-Elmer Spectrum 100 Series spectrometer. Thin-layer chromatography was performed on Whatman precoated silica gel 60 F-254 plates and visualized by ultra-violet light or by staining with ceric ammonium molybdate stain. Silica gel (230-400 mesh, Silicycle) was used for air-flashed chromatography.

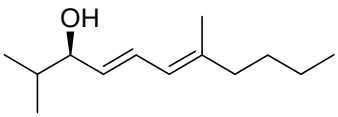
Deactivated silica gel was prepared by combining silica gel with 2.5 wt% NEt_3.

We thank the NIH (1S10RR23444) for funds to purchase a Waters LCTOF-Xe Premier MS used to collect the mass specs data herein reported.

Cautionary Note: Dialkylzinc reagents and *t*-BuLi are highly reactive compounds and require extreme caution.

Substrates and Products from Table 2.

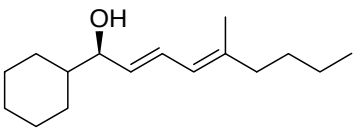
General Procedure A.



(*4E,6E*)-2,7-Dimethylundeca-4,6-dien-3-ol (1a).

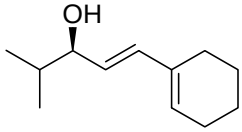
(*E*)-4-methyloct-3-en-1-yne (80 mg, 0.65 mmol) and diethylborane (0.65 mL, 0.65 mmol, 1.0 M in toluene) were added to a dry flask under nitrogen and stirred at room temperature for 30 min. The reaction flask was then cooled to –78 ºC, (–)-MIB (11.75 mg, 0.05 mmol, 10 mol %) was added followed by Et_2Zn (0.75 mL, 1.0 M in hexanes, 0.75 mmol). The reaction mixture was then warmed to –10 ºC and a solution of isobutyraldehyde (45 μL, 0.5 mmol in 3 mL hexanes) was added dropwise for 20 min. The reaction was stirred at –10 ºC for 10 h until vinyl addition was complete by TLC and quenched with a saturated solution of NH_4Cl (10 mL). The organic and aqueous layers were separated, and the aqueous layer was extracted with 3×15 mL dichloromethane. The combined organic layers were then washed with brine, dried over $MgSO_4$, and filtered.

The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 88% yield. $[\alpha]_D^{20}$ = –5.3 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.44 (dd, 1H, *J* = 15.3, 11.0 Hz), 5.85 (d, 1H, *J* = 11.0 Hz), 5.59 (dd, 1H, *J* = 15.3, 7.5 Hz), 3.90 (dd, 1H, *J* = 7.5, 6.6 Hz), 2.07 (m, 2H), 1.90 (br s, 1H), 1.77 (m, 3H), 1.72 (m, 1H), 1.37 (m, 4H), 0.96 (d, 3H, *J* = 6.6 Hz), 0.92 (t, 3H, *J* = 7.1 Hz), 0.91 (d, 3H, *J* = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 140.3, 132.1, 128.7, 124.2, 78.7, 40.0, 34.4, 30.4, 22.8, 18.7, 18.5, 17.0, 14.4; IR (neat): 3383 (OH), 2954, 2850, 1452, 1399, 1288, 1118, 1068, 1020, 987 cm^{-1}; HRMS-CI m/z 178.1720 [$(M-H_2O)^+$; calcd for $C_{13}H_{22}$: 178.1722].



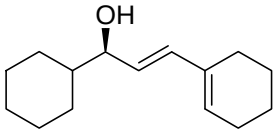
(*2E,4E*)-1-Cyclohexyl-5-methylnona-2,4-dien-1-ol (2a).

The product was prepared by General Procedure A using cyclohexane carboxaldehyde (61 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 90% yield. $[\alpha]_D^{20}$ = –17.3 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.48 (dd, 1H, *J* = 15.7, 10.8 Hz), 5.80 (d, 1H, *J* = 10.8 Hz), 5.67 (dd, 1H, *J* = 15.7, 10.8 Hz), 3.96 (m, 1H), 1.98 (m, 2H), 1.90 (br s, 1H), 1.75 (m, 2H), 1.71 (s, 3H), 1.47 (m, 2H), 1.30 (m, 9H), 1.15 (m, 2H), 0.89 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 141.4, 135.1, 128.8, 125.4, 80.1, 44.2, 39.2, 29.8, 28.9, 28.4, 26.9, 26.5, 26.3, 22.3, 18.8, 14.9; IR (neat): 3298 (OH), 2864, 2848, 1386, 1188, 1068, 897, 763 cm^{-1}; HRMS-CI m/z 218.2070 [$(M-H_2O)^+$; calcd for $C_{16}H_{26}$: 218.2077].



(*1E*)-1-Cyclohexenyl-4-methylpent-1-en-3-ol (3a).

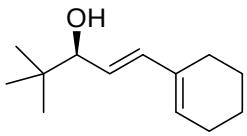
The product was prepared by General Procedure A using 1-ethynylcyclohexene (74 μL, 0.65 mmol) and isobutyraldehyde (45 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 85% yield. $[\alpha]_D^{20}$ = +12.5 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.17 (d, 1H, *J* = 15.7 Hz), 5.73 (m, 1H), 5.52 (dd, 1H, *J* = 7.5, 15.7 Hz), 3.84 (dd, 1H, *J* = 6.8, 7.5 Hz), 2.10 (m, 3H), 2.05 (br s, 1H), 1.65 (m, 6H), 0.92 (d, 3H, *J* = 6.7 Hz), 0.86 (d, 3H, *J* = 6.7 Hz); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 135.6, 135.5, 130.2, 127.0, 78.9, 34.5, 26.2, 24.9, 22.9, 22.8, 18.7, 18.6; IR (neat): 3400 (OH), 2933, 1260, 1152, 1035, 987, 795cm^{-1}; HRMS-CI m/z 163.1485 [$(M-OH)^+$; calcd for $C_{12}H_{19}$: 163.1492].



(*2E*)-3-Cyclohexenyl-1-cyclohexylprop-2-en-1-ol (4a).

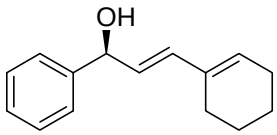
The product was prepared by General Procedure A using 1-ethynylcyclohexene (74 μL, 0.65 mmol) and cyclohexane carboxaldehyde (61 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 80% yield. $[\alpha]_D^{20}$ = +8.3 (c = 1.0, $CHCl_3$);^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.15 (d, 1H, *J* = 15.7 Hz), 5.73 (m, 1H), 5.52 (dd, 1H, *J* = 7.5, 15.7 Hz), 3.84 (dd, 1H, *J* = 7.1, 7.5 Hz), 2.11 (m, 4H), 1.87 (br s, 1H), 1.64 (m, 8H), 1.39 (m, 1H), 1.18 (m, 4H), 0.96 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 135.5, 135.3, 130.2, 127.4, 78.4, 44.3,

29.3, 29.2, 26.9, 26.5, 26.5, 26.3, 24.9, 22.9, 22.8; IR (neat): 3400 (OH), 2948, 1368, 1260, 1100, 1035, 800 cm^{-1}; HRMS-CI m/z 203.1795 [$(M\text{-}OH)^+$; calcd for $C_{15}H_{23}$: 203.1804].



(*1E*)-1-Cyclohexenyl-4,4-dimethylpent-1-en-3-ol (5a).

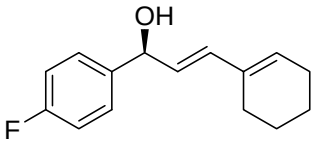
The product was prepared by General Procedure A using ethynylcyclohexene (74 μL, 0.65 mmol) and pivaladehyde (56 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 85% yield. $[\alpha]_D^{20} = -12.6$ (c = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 6.20 (d, 1H, *J* = 15.6 Hz), 5.76 (m, 1H), 5.60 (dd, 1H, *J* = 7.8, 15.6 Hz), 3.79 (d, 1H, *J* = 7.8 Hz), 2.14 (m, 4H), 1.64 (m, 4H), 1.49 (br s, 1H), 0.92 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 136.2, 135.6, 130.1, 125.6, 81.7, 30.1, 26.2, 26.2 (3C), 25.0, 22.9, 22.8; IR (neat): 3421 (OH), 2950, 1363, 1260, 1035, 985, 823, 789 cm^{-1}; HRMS-CI m/z 177.1642 [$(M\text{-}OH)^+$; calcd for $C_{13}H_{21}$: 177.1648].



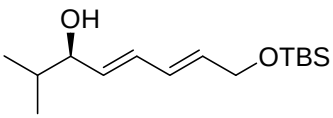
(*2E*)-3-Cyclohexenyl-1-phenylprop-2-en-1-ol (6a).

The product was prepared by General Procedure A using ethynylcyclohexene (74 μL, 0.65 mmol) and benzaldehyde (50 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 93% yield. $[\alpha]_D^{20}$ = +27.5 (c = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.32 (m, 4H), 7.22 (m, 1H), 6.23 (d, 1H, *J* = 15.5 Hz), 5.74 (m, 1H), 5.67 (dd, 1H, *J* = 6.8, 15.5 Hz), 5.18 (d, 1H, J = 6.8 Hz)

2.08 (m, 4H), 2.03 (br s, 1H), 1.60 (m, 2H), 1.54 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz,): δ 143.7, 135.3, 134.9, 130.8, 128.7 (2C), 127.9, 127.7, 126.5 (2C), 75.7, 26.2, 24.8, 22.7, 22.6; IR (neat): 3408 (OH), 2929, 2857, 1601, 1507, 1226, 1156, 966, 836 cm^{-1}; HRMS-CI m/z 197.1334 [(M-OH)$^+$; calcd for $C_{15}H_{17}$: 197.1335].



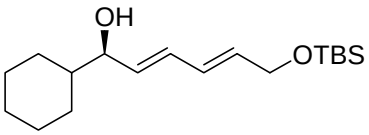
(*2E*)-3-Cyclohexenyl-1-(4-fluorophenyl)prop-2-en-1-ol (7a). The product was prepared by General Procedure A using ethynylcyclohexene (74 μL, 0.65 mmol) and 4-fluorobenzaldehyde (54 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 94% yield. $[\alpha]_D^{20}$ = +17.3 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.35 (m, 2H), 7.03 (m, 2H), 6.27 (d, 1H, *J* = 15.7 Hz), 5.80 (m, 1H), 5.68 (dd, 1H, *J* = 7.0, 15.7 Hz), 5.23 (d, 1H, *J* = 7.0 Hz), 2.128 (m, 4H), 1.96 (br s, 1H), 1.65 (m, 2H), 1.59 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz,): δ 163.4, 161.5, 139.3, 135.1, 131.1, 128.1, 128.1, 127.6, 115.6, 115.4, 75.0, 26.1, 24.8, 22.7, 22.6; IR (neat): 3407 (OH), 2932, 2858, 1448, 1141, 1090, 965, 749, 699 cm^{-1}; HRMS-CI m/z 213.1259 [(M-F)$^+$; calcd for $C_{15}H_{17}O$: 213.1279].



(*4E,6E*)-8-(*tert*-Butyldimethylsilyloxy)-2-methylocta-4,6-dien-3-ol (8a).

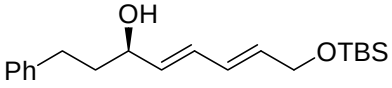
The product was prepared by General Procedure A using (*E*)-*tert*-butyldimethyl(pent-2-en-4-ynyloxy)silane (128 mg, 0.65 mmol) and isobutyraldehyde (45 μL, 0.5 mmol in 3 mL

hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 90% yield. $[\alpha]_D^{20}$ = + 15.2 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.23 (m, 2H), 5.73 (m, 2H), 4.21 (m, 2H), 3.88 (dd, 1H, *J* = 6.8, 7.4 Hz), 1.74 (m, 1H), 1.25 (br s, 1H), 0.93 (d, 3H, J = 6.8 Hz) 0.91 (s, 9H), 0.89 (d, 3H, *J* = 6.8 Hz), 0.076 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 134.3, 133.3, 131.4, 129.5, 78.2, 63.8, 34.4, 26.3 (3C), 18.8, 18.6, 18.4, -4.8 (2C); IR (neat): 3395 (OH), 2959, 2853, 1260, 1150, 1100, 1035, 983 cm^{-1}; HRMS-CI m/z 253.1982 $[(M\text{-}OH)^+$; calcd for $C_{15}H_{29}OSi$: 253.1987].



(*2E,4E*)-6-(*tert*-Butyldimethylsilyloxy)-1-cyclohexylhexa-2,4-dien-1-ol (9a).

The product was prepared by General Procedure A using (*E*)-*tert*-butyldimethyl(pent-2-en-4-ynyloxy)silane (128 mg, 0.65 mmol) and cyclohexane carboxaldehyde (61 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 93% yield. $[\alpha]_D^{20}$ = +12.6 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.19 (m, 2H), 5.20 (m, 2H), 4.21 (m, 2H), 3.86 (dd, 1H, *J* = 6.6, 7.9 Hz), 1.84 (br s, 1H), 1.68 (m, 5H), 1.44 (m, 2H), 1.19 (m, 4H), 0.91 (s, 9H), 0.072 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 134.7, 133.3, 131.2, 129.5, 76.9, 63.8, 44.2, 29.2, 28.9, 26.9, 26.5, 26.4, 26.3 (3C), 18.8, -4.8 (2C); IR (neat): 3387 (OH), 2954, 2850, 1260, 1152, 1118, 1093, 1068, 1020, 871 cm^{-1}; HRMS-CI m/z 293.2311 $[(M\text{-}OH)^+$; calcd for $C_{18}H_{33}OSi$: 293.2300].

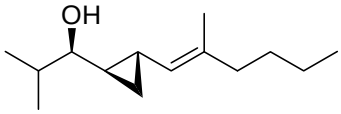


(*4E,6E*)-8-(*tert*-Butyldimethylsilyloxy)-1-phenylocta-4,6-dien-3-ol (10a).

The product was prepared by General Procedure A using (*E*)-*tert*-butyldimethyl(pent-2-en-4-ynyloxy)silane (128 mg, 0.65 mmol) and hydrocinnamaldehyde (66 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 79% yield. $[\alpha]_D^{20}$ = +12.1 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.31 (m, 2H), 7.22 (m, 3H), 6.26 (m, 2H), 5.83 (m, 2H), 4.25 (m, 2H), 4.18 (m, 1H), 2.74 (m, 2H), 1.92 (m, 2H), 1.71 (br s, 1H), 0.96 (s, 9H), 0.11 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz,) : δ 142.3, 135.6, 133.7, 130.7, 129.3, 128.9 (2C), 128.8 (2C), 126.2, 72.3, 63.8, 39.1, 32.1, 26.4 (3C), 18.9, –4.8 (2C); IR (neat): 3390 (OH), 3075, 2959, 2853, 1471, 1424, 1072, 920, 793 cm^{-1}; HRMS-CI m/z 315.2150 [$(M\text{-}OH)^+$; calcd for $C_{20}H_{31}OSi$: 315.2144].

Substrates and Products from Table 3.

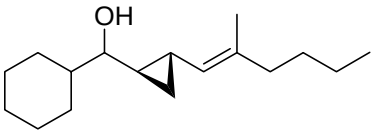
General Procedure B



2-Methyl-1-(2-((*E*)-2-methylhex-1-enyl)cyclopropyl) propan-1-ol (1b).

An oven-dried 10 mL Schlenk flask that had been thoroughly purged with N_2 was charged with (*E*)-4-methyloct-3-en-1-yne (80 mg, 0.65 mmol) and diethylborane (0.65 mL, 0.65 mmol, 1.0 M in toluene) and stirred at room temperature for 30 min. After the reaction flask was cooled to –78 ºC, (–)-MIB (11.75 mg, 0.05 mmol, 10 mol %) was added, followed by Et_2Zn (0.75 mL, 1.0 M in hexanes, 0.75 mmol) and resulting solution stirred at this temperature for 10 min. The reaction mixture was then warmed to –10 ºC and a solution of isobutyraldehyde (45 μL, 0.5 mmol in 3 mL hexanes) was added dropwise for 20 min. The reaction mixture was stirred at –10 ºC for 10 h until vinyl addition was complete by TLC. The solvent and byproduct Et_3B were removed *in vacuo* at 0 ºC and 2 mL of hexanes was added. This step was done three times to remove byproduct Et_3B completely. A solution of Et_2Zn (1.0 mL, 1.0 M in hexanes, 1.0 mmol) and diiodomethane (81 μL, 1.0 mmol) were added at 0 ºC. The reaction was stirred with light exclusion at room temperature for 10 h. A solution of Et_2Zn (1.0 mL, 1.0 M in hexanes, 1.0 mmol) and diiodomethane (81 μL, 1.0 mmol) were added at 0 ºC and then the reaction mixture was warmed to room temperature. The flask was covered with aluminum foil to exclude light and stirred at room temperature for 20 h. It was then quenched with saturated solution of NH_4Cl (15 mL). The organic and

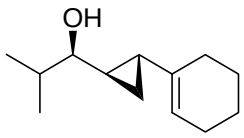
aqueous layers were separated and the aqueous layer was extracted with 3×20 mL dichloromethane. The combined organic layers were then washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 75% yield. $[\alpha]_D^{20} = -18.3$ (c = 0.4, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.56 (d, 1H, *J* = 9.2 Hz), 2.70 (dd, 1H, *J* = 9.1, 6.2 Hz), 1.95 (m, 2H), 1.78 (m, 1H), 1.68 (s, 2H), 1.48 (br s, 1H), 1.32 (m, 5H), 1.02 (m, 1H), 0.98 (d, 3H, *J* = 7.0 Hz), 0.95 (d, 3H, *J* = 7.0 Hz), 0.88 (t, 3H, *J* = 7.2 Hz), 0.81 (m, 1H), 0.68 (m, 1H), 0.49 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz):δ 135.3, 126.7, 81.6, 39.6, 35.0, 30.5, 25.5, 22.7, 19.0, 18.9, 17.5, 16.7, 14.4, 11.4; IR (neat): 3400 (OH), 2875, 2778, 1054, 976, 897 cm^{-1}; HRMS-CI m/z 193.1963 [$(M-H_2O)^+$; calcd for $C_{14}H_{24}$: 193.1962].



Cyclohexyl(2-((E)-2-methylhex-1-enyl)cyclopropyl) Methanol (2b).

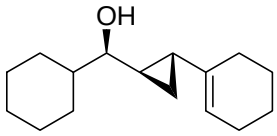
The product was prepared by General Procedure B using (*E*)-4-methyloct-3-en-1-yne (80 mg, 0.65 mmol) and cyclohexane carboxaldehyde (61 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 80% yield. $[\alpha]_D^{20} = -12.3$ (c = 0.6, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.57 (d, 1H, *J* = 9.4 Hz), 2.72 (dd, 1H, *J* = 6.8, 8.8 Hz), 1.97 (m, 2H), 1.92 (br s, 1H), 1.78 (m, 2H), 1.70 (s, 3H), 1.50 (m, 2H), 1.26 (m, 10H), 1.06 (m, 2H), 0.90 (t, 3H, *J* = 7.0 Hz), 0.83 (m, 1H), 0.69 (m, 1H), 0.52 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 133.3, 128.1, 80.5, 45.3, 39.8, 30.6, 29.5, 29.3, 26.9, 26.5, 26.4,

25.5, 22.4, 18.7, 17.5, 15.6, 11.8; IR (neat): 3390 (OH), 2874, 2835, 1366, 1087, 996, 936cm^{-1}; HRMS-CI m/z 233.2272 [(M-OH)$^{+}$; calcd for $C_{17}H_{29}$: 233.2274].



1-(2-Cyclohexenylcyclopropyl)-2-methylpropan-1-ol (3b).

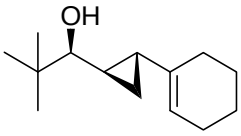
The product was prepared by General Procedure B using 1-ethynylcyclohexene (76 μL, 0.65 mmol) and isobutyraldehyde (45 μL, 0.5 mmol). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 80% yield. $[\alpha]_D^{20}$ = –52.5 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.54 (m, 1H), 0.64 (m, 1H), 0.96 (d, 3H, *J* = 6.8 Hz), 0.98 (d, 3H, *J* = 6.8 Hz), 1.03 (m, 1H), 1.21 (m, 1H), 1.50 (br s, 1H), 1.56 (m, 4H), 1.79 (m, 3H), 1.97 (m, 2H), 2.69 (dd, 1H, *J* = 5.8, 8.6 Hz), 5.43 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 8.9, 18.7, 19.1, 22.9, 23.0, 23.2, 24.7, 25.6, 27.0, 34.7, 81.7, 120.8, 136.9; IR (neat): 3394 (OH), 2929, 2835, 1467, 1024, 996 cm^{-1}; HRMS-CI m/z 194.1664 [(M)$^{+}$; calcd for $C_{13}H_{22}O_1$: 194.1670].



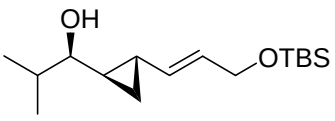
(2-Cyclohexenylcyclopropyl)(cyclohexyl)methanol (4b).

The product was prepared by General Procedure B using 1-ethynylcyclohexene (76 μL, 0.65 mmol) and cyclohexane carboxaldehyde (61 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 85% yield. $[\alpha]_D^{20}$ = –20.4 (c = 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.50 (m, 1H), 0.64 (m, 1H), 0.87 (m, 1H), 1.04 (m, 3H), 1.23 (m, 6H), 1.58 (m, 4H), 1.79 (m, 6H), 1.97 (m,

2H), 2.70 (dd, 1H, *J* = 6.1, 8.5 Hz), 5.40 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 8.9, 23.0, 23.1, 23.3, 24.5, 25.6, 26.6, 26.8, 27.0, 27.2, 29.2, 29.5, 44.8, 81.0, 120.7, 137.1; IR (neat): 3390 (OH), 2924, 2853, 1449, 1134, 1102 cm^{-1}; HRMS-CI m/z 217.1967 [(M-OH)$^+$; calcd for $C_{16}H_{25}$: 217.1956].



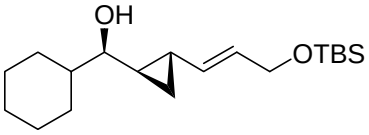
1-(2-Cyclohexenylcyclopropyl)-2,2-dimethylpropan-1-ol (5b). The product was prepared by General Procedure B using 1-ethynylcyclohexene (76 μL, 0.65 mmol) and pivaladehyde (56 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 65% yield. $[\alpha]_D^{20}$ = –36.8 (c = 1.0, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.51 (m, 1H), 0.62 (m, 1H), 0.88 (m, 1H), 0.96 (s, 9H), 1.05 (m, 1H), 1.43 (br s, 1H), 1.56 (m, 4H), 1.79 (m, 2H), 1.98 (m, 2H), 2.61 (d, 1H, *J* = 8.9 Hz), 5.43 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 8.8, 21.1, 23.0, 23.3, 25.6, 25,9, 26.4 (3C), 26.9, 36.0, 84.4, 120.9, 136.8; IR (neat): 3402 (OH), 2950, 2868, 1153, 1004 cm^{-1}; HRMS-CI m/z 190.1710 [(M-H_2O)$^+$; calcd for $C_{14}H_{22}O$: 190.1722].



(*E*)-1-(2-(3-(*tert*-Butyldimethylsilyloxy)prop-1-enyl) cyclopropyl) -2-methylpropan-1-ol (8b).

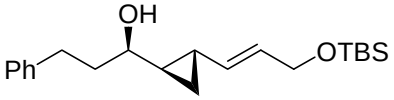
The product was prepared by General Procedure B using (*E*)-*tert*-butyldimethyl(pent-2-en-4-ynyloxy)silane (128 mg, 0.65 mmol) and isobutyraldehyde (45 μL, 0.5 mmol). The crude product was purified by column chromatography on silica (5% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 71% yield. $[\alpha]_D^{20}$ = –23.7 (c = 1.0, $CHCl_3$);

^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.59 (m, 1H), 5.22 (m, 1H), 4.11 (dd, 2H, *J* = 5.5, 1.2 Hz), 2.72 (m, 1H), 1.78 (m, 1H), 1.45 (br s, 1H), 1.30 (m. 1H), 0.98 (d, 3H, *J* = 5.7 Hz), 0.96 (d, 3H, *J* = 5.7 Hz), 0.96 (m, 1H), 0.89 (s, 9H), 0.70 (m, 1H), 0.61(m, 1H), 0.065 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 133.2, 128.1, 81.1, 64.2, 34.9, 30.2, 26.4 (3C), 25.4, 20.5, 18.9, 18.8, 11.2, -4.7 (2C); IR (neat): 3400 (OH), 2957, 2929, 1255, 1111, 1053, 836, 775 cm^{-1}; HRMS-CI m/z 285.2238 [$(MH)^+$; calcd for $C_{16}H_{33}O_2Si$: 285.2249].



(*E*)-(2-(3-(*tert*-Butyldimethylsilyloxy)prop-1-enyl) cyclopropyl)(cyclohexyl)methanol (9b).

The product was prepared by General Procedure B using (*E*)-*tert*-butyldimethyl(pent-2-en-4-ynyloxy)silane (128 mg, 0.65 mmol) and cyclohexane carboxaldehyde (61 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5.0% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 79% yield. $[\alpha]_D^{20}$ = –9.1 (c = 1.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 5.58 (dt, 1H, *J* = 5.4, 15.4 Hz), 5.21 (m, 1H), 4.12 (dd, 2H, *J* = 5.4, 1.41 Hz), 2.70 (dd, 1H, *J* = 6.6, 9.0 Hz), 1.90 (br s, 1H), 1.76 (m, 4H), 1.43 (m, 2H), 1.23 (m, 4H), 1.02 (m, 2H), 0.97 (m, 1H), 0.89 (s, 9H), 0.68 (m, 1H), 0.58 (m, 1H), 0.063 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 133.3, 128.1, 80.5, 64.3, 44.9, 29.5, 29.4, 26.9, 26.8, 26.6, 26.4 (3C), 25.5, 20.4, 18.7, 11.2, -4.7 (2C); IR (neat): 3374 (OH), 2927, 2854, 1103, 989 cm^{-1}; HRMS-CI m/z 307.2434 [$(M-OH)^+$; calcd for $C_{19}H_{35}O_1Si$: 307.2457].

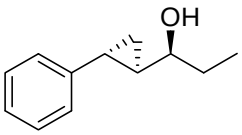


(*E*)-1-(2-(3-(*tert*-Butyldimethylsilyloxy)prop-1-enyl) cyclopropyl)-3-phenylpropan-1-ol (10b).

The product was prepared by General Procedure B using (*E*)-*tert*-butyldimethyl(pent-2-en-4-ynyloxy)silane (128 mg, 0.65 mmol) and hydrocinnamaldehyde (66 μL, 0.5 mmol in 3 mL hexanes). The crude product was purified by column chromatography on silica (5.0% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 85% yield. $[\alpha]_D^{20}$ = –25.2 (c = 0.5, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.26 (m, 5H), 5.62 (dt, 1H, *J* = 5.5, 15.6 Hz), 5.26 (m, 1H), 4.13 (dd, 2H, *J* = 5.5, 1.5 Hz), 3.07 (m, 1H), 2.77 (m, 2H), 1.94 (m, 2H), 1.54 (br s, 1H), 1.31 (m, 1H), 1.00 (m, 1H), 0.92 (s, 9H), 0.74 (m, 1H), 0.64 (m, 1H), 0.083 (s, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz,): δ 142.6, 133.2, 128.8 (4C), 128.3, 128.1, 75.2, 64.2, 39.1, 32.3, 27.6, 26.4 (3C), 19.5, 18.2, 11.7, -4.7 (2C); IR (neat): 3550 (OH), 2928, 1454, 1153, 1054, 838 cm^{-1}; HRMS-CI m/z 369.2224 [$(M+Na)^+$; calcd for $C_{21}H_{34}O_2NaSi$: 369.2225].

Substrates and Products from Table 5.

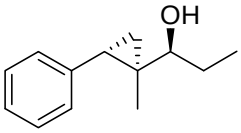
General Procedure C



1-(2-Phenylcyclopropyl)propan-1-ol (11).

A 10 mL Schlenk flask was charged with (–)-MIB (2.9 mg, 0.012 mmol) and cooled to 0 ºC. A solution of Et_2Zn (0.45 mL, 1.0 M in hexanes) was added, followed by dropwise addition of *trans*-cinnamaldehyde (38 μL, 0.3 mmol). The reaction

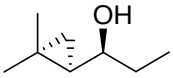
mixture was stirred at 0 ºC for 8 h until alkyl addition was complete by TLC. 1.5 Equiv. trimethylsilane chloride (0.45 mmol) and 1.5 equiv. triethyl amine (0.45 mmol) were added with 2 mL dichloromethane at 0 ºC. The reaction flask was slowly warmed to room temperature and stirred for 14 h. Next, 5 equiv of Et_2Zn (0.75 mL, 2.0 M in dichloromethane) and 5 equiv CF_3CH_2OH (108 μL, 1.5 mmol) were added slowly at 0 ºC. After stirring at 0 ºC for 10 min, 5 equiv CH_2I_2 (120 μL, 1.5 mmol) was added. The reaction mixture was stirred with light exclusion at room temperature for 24 h. It was then quenched with 3-4 drops of water and 2 equiv TBAF (1M solution in THF) at 0 ºC. After stirring for 1 h, 5 mL of saturated NH_4Cl solution was added. The organic and aqueous layers were separated and the aqueous layer was extracted three times with 10 mL dichloromethane. The combined organic layers were then washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by column chromatography on deactivated silica (10% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 75% yield. $[\alpha]_D^{20}$ = +12.6 (c = 0.50, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.36 (m, 2H), 7.26 (m, 1H), 7.16 (m, 2H), 3.24 (m, 1H), 1.93 (m, 1H), 1.86 (br s, 1H), 1.78 (m, 2H), 1.34 (m, 1H), 1.10 (t, 3H, *J* = 7.5 Hz), 1.06 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz,): δ 142.7, 128.6, 126.1, 125.9, 77.2, 30.5, 29.5, 21.4, 13.3, 10.3; IR (neat); 3385 (OH), 3057, 2950, 1459, 1299, 1071, 924, 720 cm^{-1}.



1-(1-Methyl-2-phenylcyclopropyl)propan-1-ol (12).

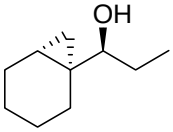
The product was prepared by General Procedure C using 2-methylcinnamaldehyde (42 μL, 0.3 mmol). The crude product was purified by column

chromatography on deactivated silica (10% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 82% yield. $[\alpha]_D^{20}$ = +3.9 (c = 0.50, $CHCl_3$); ^1H NMR (C_6D_6, 500 MHz): δ 7.25 (m, 3H), 7.15 (m, 2H), 2.73 (t, 1H, *J* = 6.3 Hz), 1.85 (t, 1H, *J* = 7.5 Hz), 1.58 (m, 2H), 1.13 (br, s, 1H), 1.08 (t, 3H, *J* = 7.4 Hz), 0. 77 (s, 3H), 0.73 (d, 2H, *J* = 7.5 Hz); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz,): δ 139.7, 129.5, 127.4, 125.4, 83.3, 27.8, 27.6, 26.6, 17.8, 14.6, 12.2; IR (neat); 3380 (OH), 3060, 3011, 2962, 2870, 1458, 1198, 1016, 970, 782 cm^{-1}.



1-(2,2-Dimethylcyclopropyl)propan-1-ol (13).

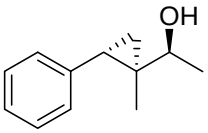
The product was prepared by General Procedure C using 3-methyl-2-butenal (29 μL, 0.3 mmol). The crude product was purified by column chromatography on deactivated silica (10% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 67% yield. $[\alpha]_D^{20}$ = +12.2 (c = 0.50, $CHCl_3$); ^1H NMR (C_6D_6, 500 MHz): δ 2.98 (m, 1H), 1.59 (m, 1H), 1.53 (m, 1H), 1.30 (br s, 1H), 0.96 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H), 0.55 (m, 1H), 0. 37 (dd, 1H, *J* = 4.2, 7.8 Hz), 0.08 (m, 1H); $^{13}C\{^1H\}$ NMR (C_6D_6, 125 MHz,): δ 75.2, 33.5, 32.2, 28.3, 20.3, 19.2, 18.4, 9.8; IR (neat); 3385 (OH), 2950, 2921, 1460, 1260, 1004, 820 cm^{-1}.



1-(Bicyclo[4.1.0]heptan-1-yl)propan-1-ol (14).

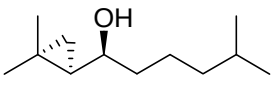
The product was prepared by General Procedure C using 1-cyclohexene carboxaldehye (34 μL 0.3 mmol). The crude product was purified by column chromatography on deactivated silica (10% ethyl acetate in hexanes) to afford the title

compound as a colorless oil in 67% yield. $[\alpha]_D^{20}$ = +12.6 (c = 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): δ 2.65 (t, 1H, *J* = 6.9 Hz), 1.82 (m, 2H), 1.74 (m. 1H), 1.55 (m, 3H), 1.25 (m, 3H), 1.15 (m, 2H), 0.85 (t, 3H, *J* = 7.2 Hz), 0.70 (m, 1H), 0.41 (m, 1H), 0.18 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75 MHz,): δ 83.3, 27.8, 25.1, 24.7, 24.5, 22.2, 22.0, 21.5, 18.7, 10.7; IR (neat); 3386 (OH), 3024, 2875, 1453, 1016, 940, 796 cm^{-1}.



1-(1-Mmethyl-2-phenylcyclopropyl)ethanol (15).

The product was prepared by General Procedure C using 7.2 mg (–)-MIB (0.03 mmol, 10 mol%), 1.0 mL Me_2Zn (1.2 mmol, 1.2 M in toluene) and 2-methylcinnamaldehyde (42 μL, 0.3 mmol). The crude product was purified by column chromatography on deactivated silica (10% ethyl acetate in hexanes) to afford the title compound as a colorless oil in 80% yield. $[\alpha]_D^{20}$ = +2.1 (c = 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 7.24 (m, 3H), 7.15 (m, 2H), 3.36 (m, 1H), 2.08 (1H, dd, *J* = 8.6, 5.9 Hz), 1.56 (br s, 1H), 1.29 (3H, d, *J* = 6.4 Hz), 0.98 (m, 1H), 0.82 (m, 1H), 0.77 (s, 3H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz,): δ 140.0, 129.3, 128.1, 125.9, 75,0, 28.0, 21.1, 19.8, 15.2, 12.9; IR (neat); 3380 (OH), 3024, 2962, 2929, 2874, 1460, 1108, 1010, 940, 800 cm^{-1}.



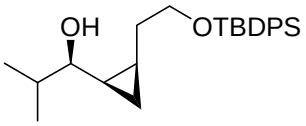
5-Methyl-1-(2,2-dimethylcyclopropyl)hexan-1-ol (16).

The product was prepared by General Procedure C using 3-methyl-2-butenal (29 μL, 0.3 mmol) and 0.6 mL dialkylzinc (0.6 mmol, 1.0 M in hexanes). The crude product was purified by column chromatography on deactivated silica (5% ethyl acetate in

hexanes) to afford the title compound as a colorless oil in 60% yield. $[\alpha]_D^{20}$ = +12.1 (c = 0.50, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz); δ 3.15 (m, 1H), 1.53 (m, 4H), 1.22 (m, 3H), 0.96 (s, 3H), 0.94 (s, 3H), 0.91 (d, 3H, *J* = 1.5 Hz), 0.58 (m, 1H), 0. 37 (dd, 1H, *J* = 8.6, 5.3 Hz), 0.06 (m, 1H) 0.04 (dd, 1H, *J* = 4.5, 5.0 Hz), 0.31 (dd, 1H, *J* = 8.6, 4.5 Hz), 0.56 (m, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz,): δ 71.9, 39.3, 39.0, 32.7, 32.0, 26.8, 25.2, 22.9, 22.9, 21.5, 18.5, 17.7; IR (neat); 3390 (OH), 3057, 2960, 1453, 1378, 1046, 1020, 740 cm^{-1}.

Substrates and Products from Table 6.

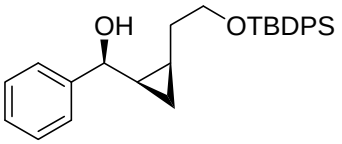
General procedure D.



(*Z*)-1-(2-(2-(*tert*-Butyldiphenylsilyloxy)ethyl)cyclopropyl)-2-methylpropan-1-ol (17).

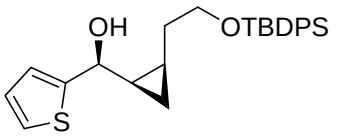
Dicyclohexylborane (88 mg, 0.5 mmol) was weighed into a Schlenk flask under nitrogen and dry *t*-BuOMe (1 mL) was added. *tert*-Butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (160 μL, 0.5 mmol) was then added slowly to the reaction mixture at 0 °C. After 15 min the reaction mixture was warmed to room temperature and stirred for 45 min resulting in a clear solution. *t*-BuLi (0.365 mL, 0.55 mmol, 1.5 M solution in pentane) was added dropwise at –78 °C and stirred for 60 min. The solution was warmed to room temperature and stirred for an additional 60 min during which time a precipitate formed. Diethylzinc (0.275 mL, 0.55 mmol, 2 M solution in hexanes) was slowly added to the reaction mixture at –78 °C and stirred for 20 min. Addition of TEEDA (14 μL, 0.066 mmol) and hexanes (4

mL) was performed at –78 °C. The solution was warmed to 0 °C and (–)-MIB (166 μL, 0.017 mmol) and isobutyraldehyde (30 μL, 0.332 mmol) were added. The reaction mixture was then slowly warmed to room temperature and stirred 12–16 h. After the reaction was complete by TLC analysis, the temperature was lowered to 0 °C and $ZnEt_2$ (0.83 mL, 1.66 mmol, 2 M solution in hexanes) was added. Next, CF_3CH_2OH (120 μL, 1.65 mmol) was added dropwise. After stirring at 0 ºC for 10 min, CH_2I_2 (135 μL, 1.67 mmol) was added. The reaction mixture was stirred with light exclusion at room temperature for 24 h. It was then quenched with saturated solution of NH_4Cl. The organic and aqueous layers were separated and the aqueous layer was extracted with dichloromethane (3×5 mL). The combined organic layers were then washed with brine, dried over $MgSO_4$, and filtered. The filtrate was concentrated *in vacuo* and the crude product was purified by column chromatography on deactivated silica gel (5% ethyl acetate in hexanes) to afford the title compound (92.1 mg, 70% yield) as an oil. $[\alpha]_D^{20}$ = +4.4 (*c* = 0.026, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.05 (m, 1H), 0.67 (m, 1H), 0.93 (m, 2H), 0.98 (t, *J* = 7.9 Hz, 6H), 1.1 (m, 9H), 1.23 (m, 1H), 1.3 (d, *J* = 3.6 Hz, 1H), 1.74 (m, 1H), 1.91 (m, 1H), 2.96 (m, 1H), 3.76 (m, 2H), 7.42 (m, 6H), 7.7 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 8.9, 14.8, 17.6, 19.2, 19.4, 21.1, 27.1, 32.8, 34.7, 64.5, 76.7, 127.8, 129.8, 134.2, 135.8; IR (neat): 3599, 3411, 3134, 3070, 3050, 3013, 2952, 2912, 2895, 2858, 2739, 2319, 1958, 1888, 1823, 1589, 1486, 1471, 1428, 1362, 1331, 1306, 1260, 1235, 1187, 1157, 1110 1029, 1007 cm^{-1}; HRMS calcd for $C_{25}H_{36}O_2NaSi$ $(M+Na)^+$: 419.2382, found 419.2377.



(*Z*)-(2-(2-(*tert*-Butyldiphenylsilyloxy)ethyl)cyclopropyl) (phenyl)methanol (18).

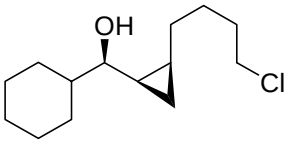
General Procedure D was applied to benzaldehyde (34 μL, 0.332 mmol) and *tert*-butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (160 μL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (5% ethyl acetate in hexanes) to afford the title compound (88.1 mg, 62% yield) as an oil. $[\alpha]_D^{20}$ = +35.4 (*c* = 0.023, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 0.27 (dd, *J* = 5.4, 10.5 Hz, 1H), 0.83 (dt, *J* = 5.4, 8.3 Hz, 1H), 1.05 (s, br, 10H), 1.26 (m, 1H), 1.40 (m, 1H), 1.83 (d, *J* = 3.4 Hz, 1H), 1.86 (m, 1H), 3.66 (t, *J* = 6.6 Hz, 2H), 4.20 (dd, *J* = 3.4, 10.5 Hz, 1H), 7.34 (m, 11H), 7.63 (m, 4H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 9.9, 13.6, 19.1, 23.6, 26.8 32.3, 64.1, 74.7, 126.1, 127.5, 128.4, 129.5, 133.9, 135.5, 144.2; IR (neat): 3564, 3365, 3069, 3029, 2997, 2955, 2892, 2857, 2318, 1958, 1888, 1823, 1774, 1660, 1602, 1589, 1567, 1557, 1487, 1471, 1461, 1427, 1361, 1322, 1302, 1287, 1232, 1190, 1157, 1110, 1030, 992 cm^{-1}; HRMS calcd for $C_{28}H_{34}O_2NaSi$ $(M+Na)^+$: 453.2226, found 453.2229.



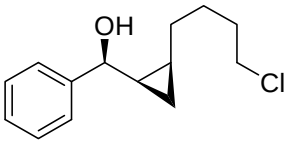
(*Z*)-(2-(2-(*tert*-Butyldiphenylsilyloxy)ethyl)cyclopropyl) (thiophen-2-yl)methanol (19).

General Procedure D was applied to 2-thiopenecarboxaldehyde (31 μL, 0.332 mmol) and *tert*-butyl-(4-chloro-but-3-ynyloxy)-diphenyl-silane (160 μL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (5% ethyl acetate in hexanes) to afford the title compound (69.0 mg, 48% yield) as an oil. $[\alpha]_D^{20}$ = +26.6 (*c* = 0.022, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 0.27 (dd, *J* = 6.9, 11.4 Hz, 1H), 0.87 (m,

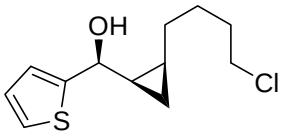
1H), 0.98 (m, 1H), 1.05 (s, 9H), 1.35 (m, 2H), 1.89 (m, 1H), 1.99 (d, J = 4.4 Hz, 1H), 3.7 (t, J = 6.9 Hz, 2H), 4.45 (dd, J = 4.4, 9.7 Hz, 1H), 6.98 (m, 2H), 7.25 (m, 1H), 7.40 (m, 6H), 7.66 (m, 4H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 10.4, 13.9, 19.4, 24.1, 27.1, 32.3, 64.3, 71.1, 124.0, 124.9, 127.8, 129.8, 134.2, 135.8, 148.4; IR (neat): 3374, 3070, 3049, 3012, 2929, 2857, 2739, 1959, 1889, 1825, 1778, 1729, 1656, 1589, 1471, 1462, 1446, 1389, 1306, 1264, 1230, 1188, 1157, 1107, 1030, 1008, 997 cm^{-1}; HRMS calcd for $C_{26}H_{31}O_2SSi$ $(M-H)^+$: 435.1811, found 435.1814.



(*Z*)-(2-(4-Chlorobutyl)cyclopropyl)(cyclohexyl)methanol (20). General Procedure D with 30 mol% TEEDA (0.099 mmol, 21 μL) was applied to cyclohexane carboxaldehyde (40 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (5% ethyl acetate in hexanes) to afford the title compound (57.1 mg, 70% yield) as an oil. $[\alpha]_D^{20}$ = +17.1 (c = 0.086, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.20 (dd, J = 5.4, 10.7 Hz, 1H), 0.69 (m, 1H), 0.86 (m, 1H), 0.99 (m, 2H), 1.05 (m, 3H), 1.23 (m, 2H), 1.30 (d, J = 3.8 Hz, 1H), 1.39 (m, 1H), 1.53 (m, 2H), 1.64 (m, 2H), 1.77 (m, 5H), 1.91 (d, J = 12.7 Hz, 1H), 2.94 (m, 1H), 3.52 (t, J = 6.4 Hz, 2H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 8.8, 17.4, 21.4, 26.2, 26.4, 26.5, 27.2, 28.1, 28.8, 29.2, 32.3, 44.7, 45.0, 76.0; IR (neat): 3390, 3062, 2991, 2922, 2852, 2667, 2044, 1634, 1448, 1416, 1309, 1262, 1220, 1188, 1150, 1099, 1084, 1069, 1025, 982 cm^{-1}; HRMS calcd for $C_{14}H_{24}Cl$ $(M-OH)^+$: 227.1567, found 227.1574.

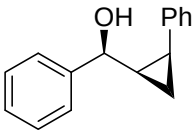


(*Z*)- (2-(4-Chlorobutyl)cyclopropyl)(phenyl)methanol (21). General Procedure D with 30 mol% TEEDA (0.099 mmol, 21 μL) was applied to benzaldehyde (34 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (5% ethyl acetate in hexanes) to afford the title compound (55.8 mg, 70% yield) as an oil. $[\alpha]_D^{20}$ = +53.8 (*c* = 0.037, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.29 (d, *J* = 5.3 Hz, 1H), 0.89 (m, 2H), 1.19 (m, 1H), 1.28 (m, 1H), 1.40 (m, 1H), 1.48 (m, 1H), 1.56 (m, 1H), 1.74 (m, 2H), 1.87 (br, 1H), 3.47 (t, *J* = 6.7 Hz, 2H), 4.24 (d, *J* = 9.6 Hz, 1H), 7.28 (m, 1H), 7.35 (m, 2H), 7.43 (m, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 10.5, 17.0, 24.2, 27.6, 28.8, 32.6, 45.2, 75.0, 126.5, 127.9, 128.7, 144.5; IR (neat): 3367, 3062, 3029, 2993, 2932, 2858, 2048, 1950, 1882, 1809, 1758, 1603, 1492, 1454, 1408, 1307, 1195, 1140, 1031, 915 cm^{-1}; HRMS calcd for $C_{14}H_{18}Cl$ $(M\text{-}OH)^+$: 221.1097, found 221.1097.



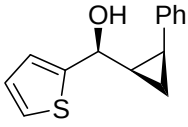
(*Z*)-(2-(4-Chlorobutyl)cyclopropyl)(thiophen-2-yl)methanol (22). General Procedure D with 30 mol% TEEDA (0.099 mmol, 21 μL) was applied to 2-thiophenecarboxaldehyde (31 μL, 0.332 mmol) and 1,6-dichloro-hex-1-yne (66 μL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (5% ethyl acetate in hexanes) to afford the title compound (50.3 mg, 62% yield) as an oil. $[\alpha]_D^{20}$ = +78.4 (*c* = 0.063, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.30 (dd, *J* = 5.4, 10.4 Hz, 1H), 0.90 (m, 1H), 0.97 (m, 1H), 1.15 (m, 1H), 1.35 (m, 1H), 1.52 (m, 3H), 1.76 (m, 2H), 1.98 (d, *J* = 3.9 Hz, 1H), 3.48 (t, *J* = 6.6 Hz, 2H), 4.47 (dd, *J* = 3.9, 9.6 Hz, 1H),

6.96 (m, 1H), 7.04 (dd, J = 3.4, 5.1 Hz, 1H), 7.26 (dd, J = 1.1, 5.1 Hz, 1H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 10.5, 16.7, 24.2, 27.2, 28.2, 32.3, 44.9, 70.8, 123.8, 124.7, 126.5, 148.2; IR (neat): 3364, 3105, 3068, 2993, 2934, 2857, 2051, 1794, 1729, 1645, 1543, 1455, 1393, 1359, 1300, 1267, 1229, 1167, 1136, 1106, 1073 1031 cm^{-1}; HRMS calcd for $C_{12}H_{16}SCl$ $(M\text{-}OH)^+$: 227.0661, found 227.0668.



(*Z*)-Phenyl(2-phenylcyclopropyl)methanol (23).

General Procedure D was applied to benzaldehyde (34 μL, 0.332 mmol) and chloroethynyl-benzene (60 μL, 0.5 mmol). The crude product was purified by column chromatography on deactivated silica gel (5% ethyl acetate in hexanes) to afford the title compound (31.6 mg, 43% yield) as an oil. $[\alpha]_D^{20}$ = +47.2 (c = 0.045, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.18 (dt, J = 5.7, 8.3 Hz, 1H), 1.28 (dd, J = 5.7, 11.5 Hz, 1H), 1.60 (m, 1H), 1.71 (d, J = 3.3 Hz, 1H), 2.29 (m, 1H), 3.91 (dd, J = 2.5, 9.4 Hz, 1H), 6.97 (m, 2H), 7.12 (m, 2H), 7.22 (m, 6H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 125 MHz): δ 8.0, 21.5, 26.8, 73.9, 126.0, 126.1, 127.4, 127.9, 128.1, 128.9, 137.8, 143.6; IR (neat): 3360, 3061, 3028, 3005, 2923, 2851, 2245, 1948, 1882, 1807, 1754, 1602, 1582, 1541, 1495, 1454, 1411, 1384, 1335, 1285, 1256, 1224, 1197, 1137, 1108, 1083, 1015, 971, 920 cm^{-1}; HRMS calcd for $C_{16}H_{15}$ $(M\text{-}OH)^+$: 207.1174, found 207.1168.



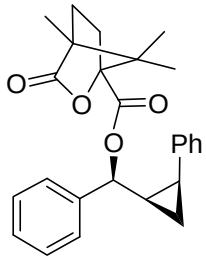
(*Z*)-(2-Phenylcyclopropyl)(thiophen-2-yl)methanol (24).

General Procedure D was applied to 2-thiophenecarboxaldehyde (31 μL, 0.332 mmol) and chloroethynyl-benzene (60 μL, 0.5 mmol). The crude product was

purified by column chromatography on deactivated silica gel (5% ethyl acetate in hexanes) to afford the title compound (31.6 mg, 42% yield) as an oil. 24.4 mg of the allylic alcohol were recovered accounting for the relatively low yield. $[\alpha]_D^{20}$ = +28.7 (*c* = 0.061, $CHCl_3$); ^1H NMR ($CDCl_3$, 500 MHz): δ 1.20 (dt, *J* = 5.5, 8.3 Hz, 1H), 1.26 (dd, *J* = 5.5, 11.8 Hz, 1H), 1.66 (m, 1H), 1.85 (d, *J* = 4.0 Hz, 1H), 2.35 (m, 1H), 4.12 (dd, *J* = 4.0, 9.3 Hz, 1H), 6.55 (m, 1H), 6.85 (dd, *J* = 3.5, 5.0 Hz, 1H), 7.13 (m, 2H), 7.18 (m, 2H), 7.21 (m, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125 MHz): δ 8.2, 21.5, 26.8, 70.2, 123.7, 124.4, 126.2, 126.3, 128.0, 128.9, 137.4, 147.4; IR (neat): 3928, 3824, 3363, 3106, 3064, 3026, 3006, 2922, 2850, 2340, 2067, 1947, 1885, 1799, 1728, 1652, 1602, 1580, 1535, 1497, 1446, 1372, 1301, 1259, 1230, 1165, 1134, 1083, 1011 cm^{-1}; HRMS calcd for $C_{14}H_{14}ONaS$ $(M+Na)^+$: 253.0663, found 263.0656.

Crystallization

General Procedure E



Phenyl(2-phenylcyclopropyl)methyl4,7,7-trimethyl-3-oxo-2-oxa-bicyclo[2.2.1]heptane-1-carboxylate.

A solution of the compound **23** (106.7 mg, 0.476 mmol) and (dimethylamino)pyridine (DMAP) (103 mg, 0.84 mmol) in 2 mL dichloromethane was treated with (–)-camphanic acid chloride (136 mg, 0.63 mmol), and the mixture was stirred at room temperature for 24 h. The crude product was purified by

column chromatography on silica gel to give the title compound. Clear crystals suitable for an X-ray diffraction study were formed by a slow evaporation of a CH_2Cl_2/hexanes solution of the title compound. $[\alpha]_D^{20}$ = –32.9 (*c* = 0.031, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.94 (s, 3H), 1.05 (s, 3H), 1.09 (s, 3H), 1.16 (dd, *J* = 5.6, 8.2 Hz, 1H), 1.34 (q, *J* = 5.9 Hz, 1H), 1.65 (m, 1H), 1.75 (m, 1H), 1.88 (m, 1H), 1.97 (m, 1H), 2.36 (m, 2H), 5.31 (d, *J* = 5.4 Hz, 1H), 6.89 (m, 2H), 7.12 (m, 2H), 7.19 (m, 4H), 7.25 (m, 2H) ppm; ^{13}C{^{1}H} NMR ($CDCl_3$, 125 MHz): δ 9.0, 9.6, 16.6, 16.7, 21.9, 24.7, 28.9, 30.4, 54.0, 54.7, 78.1, 91.0, 126.3, 126.6, 127.9, 128.0 128.1, 128.2, 128.5, 128.7, 136.9, 139.1,166.8, 178.1; IR (in CH_2Cl_2): 3944, 3756, 3689, 3554, 3055, 2975, 2935, 2877, 2685, 2522, 2410, 2305, 2126, 1952, 1884, 1788, 1744, 1603, 1497, 1450, 1422, 1397, 1383, 1359, 1319, 1265, 1217, 1169, 1125, 1103, 1062 cm^{-1}: HRMS calcd for $C_{26}H_{28}O_4Na$ $(M+Na)^+$: 427.1885, found 427.1874.

Conditions for the Determination of Enantiometric Excess.

The enantiomeric excess values for the following dienyl alcohols were determined by chiral HPLC analysis using a Chiralcel OD-H or AD-H column. The conditions for the resolution of the racemates are described below. The conditions for other allylic alcohols were previously published.[3-5]

(1) **(*2E*)-3-cyclohexenyl-1-cyclohexylprop-2-en-1-ol:** t_1 = 26.35 min, t_2 = 27.58 min (AD-H column, hexanes / 2-propanol: 97/3, 0.5 mL/min)

(2) **(*1E*)-1-cyclohexenyl-4-methylpent-1-en-3-ol:** t_1 = 20.87 min, t_2 = 23.85 min (AD-H column, hexanes / 2-propanol: 97/3, 0.5 mL/min)

(3) ***(1E)*-1-cyclohexenyl-4,4-dimethylpent-1-en-3-ol:** t_1 = 17.71 min, t_2 = 20.51 min (AD-H column, hexanes / 2-propanol: 97/3, 0.5 mL/min)

(4) **((*4E,6E*)-8-(tert-butyldimethylsilyloxy)-2-methylocta-4,6-dien-3-ol:** t_1 = 11.29 min, t_2 = 12.09 min (AD-H column, hexanes / 2-propanol: 97/3, 0.5 mL/min)

(5) **(*2E,4E*)-6-(tert-butyldimethylsilyloxy)-1-cyclohexylhexa-2,4-dien-1-ol:** t_1 = 12.50 min, t_2 = 13.15 min (AD-H column, hexanes / 2-propanol: 97/3, 0.5 mL/min).

(6) **(*4E,6E*)-8-(tert-butyldimethylsilyloxy)-1-phenylocta-4,6-dien-3-ol:** t_1 = 15.50 min, t_2 = 16.72 min (AD-H column, hexanes / 2-propanol: 97/3, 0.5 mL/min).

(7) **(*4E,6E*)-2,7-dimethylundeca-4,6-dien-3-ol:** t_1 = 33.35 min, t_2 = 34.05 min (AD-H column, hexanes / 2-propanol: 98/2, 0.3 mL/min)

(8) **(*2E,4E*)-1-cyclohexyl-5-methylnona-2,4-dien-1-ol:** t_1 = 47.63 min, t_2 = 49.80 min (AD-H column, hexanes / 2-propanol: 98/2, 0.3 mL/min)

(9) **(*2E*)-3-cyclohexenyl-1-phenylprop-2-en-1-ol:** t_1 = 25.24 min, t_2 = 32.50 min (OD-H column, hexanes / 2-propanol: 97/3, 0.5 mL/min)

(10) **(*2E*)-3-cyclohexenyl-1-(4-fluorophenyl)prop-2-en-1-ol:** t_1 = 21.12 min, t_2 = 22.54 min (OD-H column, hexanes / 2-propanol: 97/3, 0.5 mL/min)

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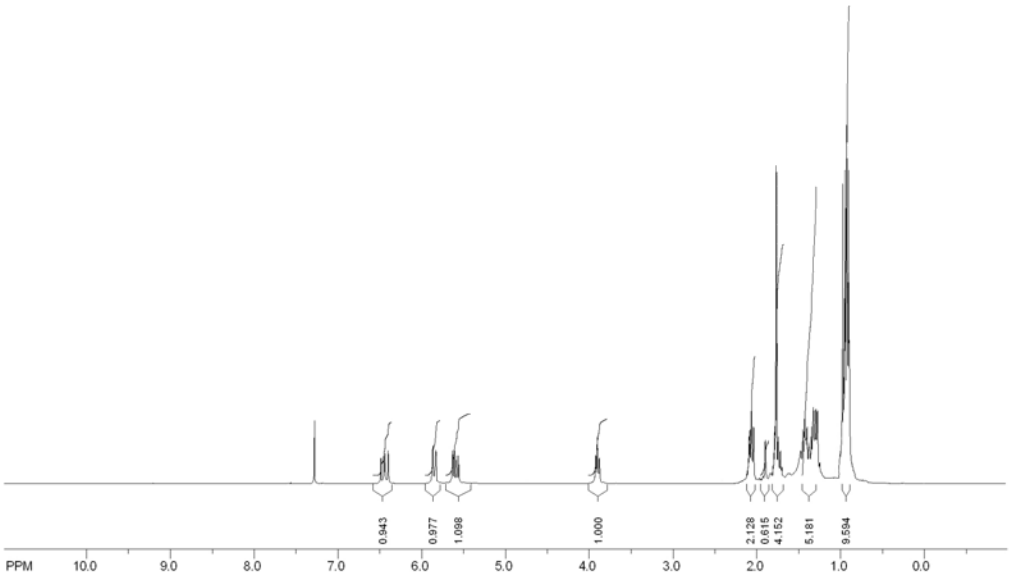
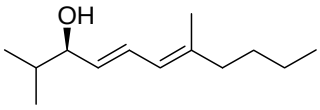
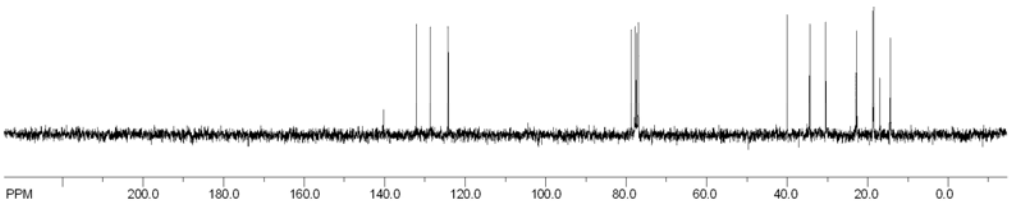
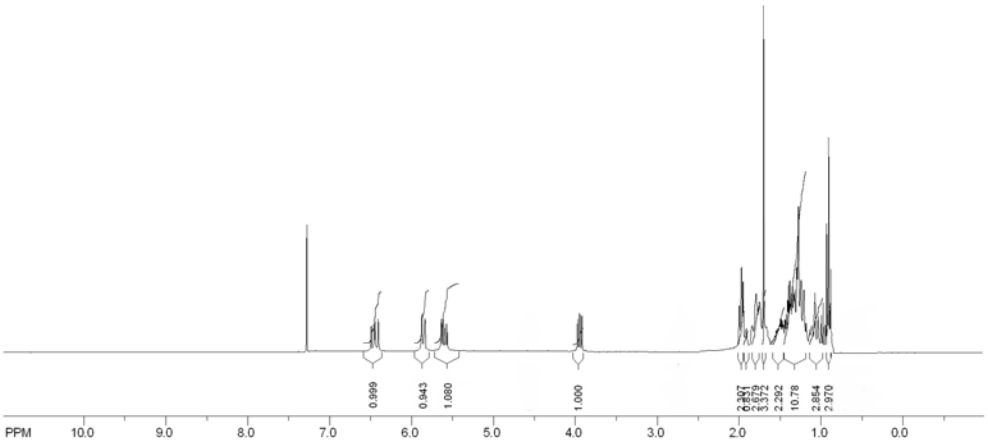


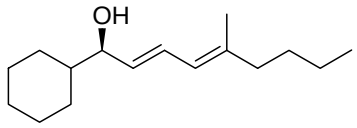


(4*E*,6*E*)-2,7-Dimethylundeca-4,6-dien-3-ol

(1a)

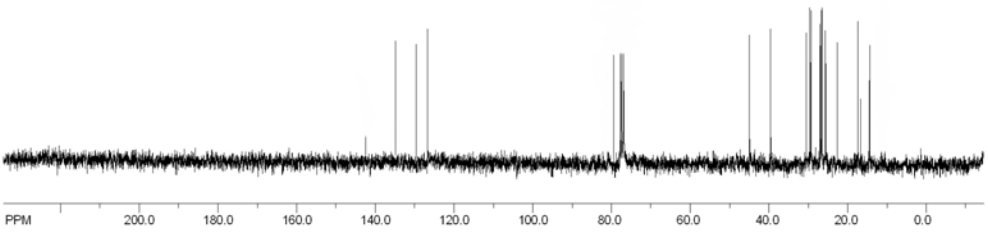


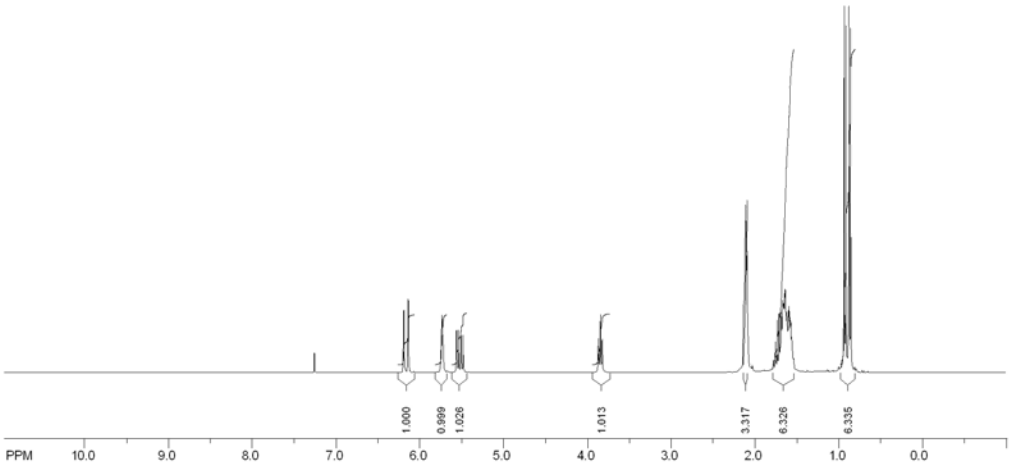


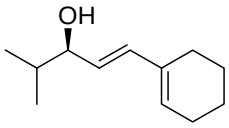


(2*E*,4*E*)-1-Cyclohexyl-5-methylnona-2,4-dien-1-ol

(2a)

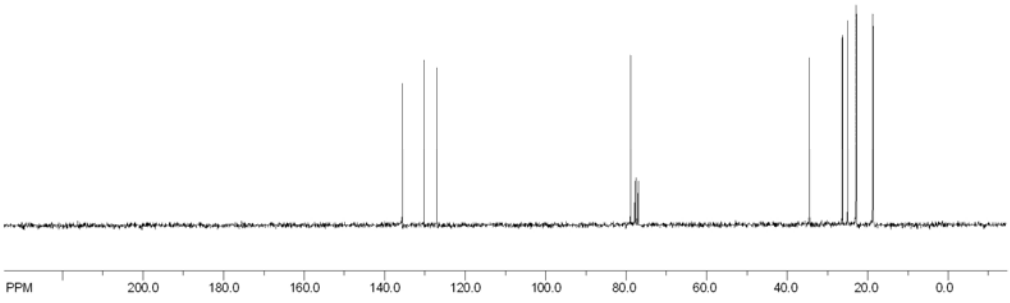


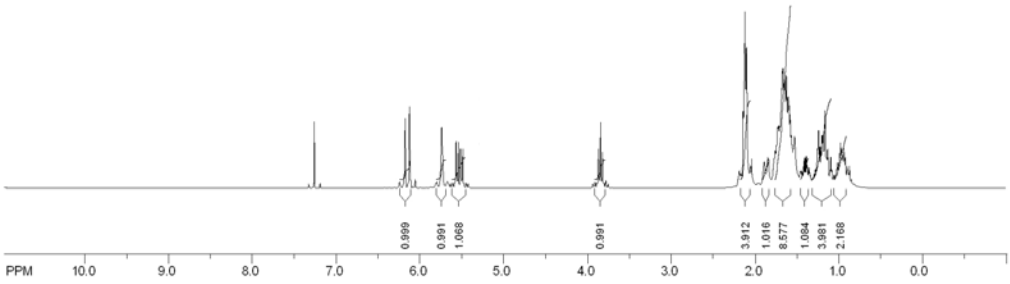


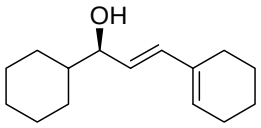


(1*E*)-1-Cyclohexenyl-4-methylpent-1-en-3-ol

(3a)

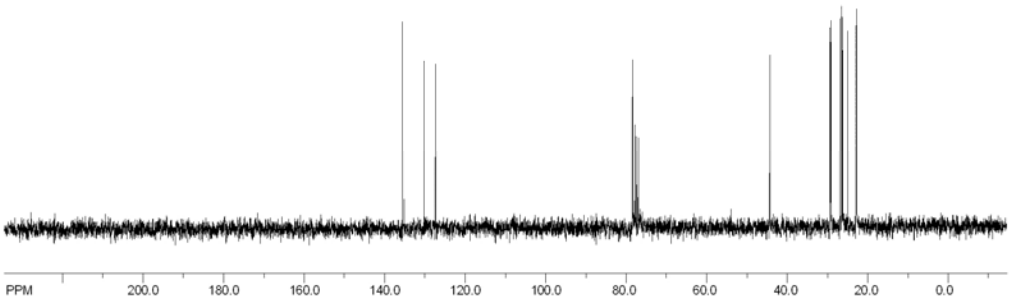


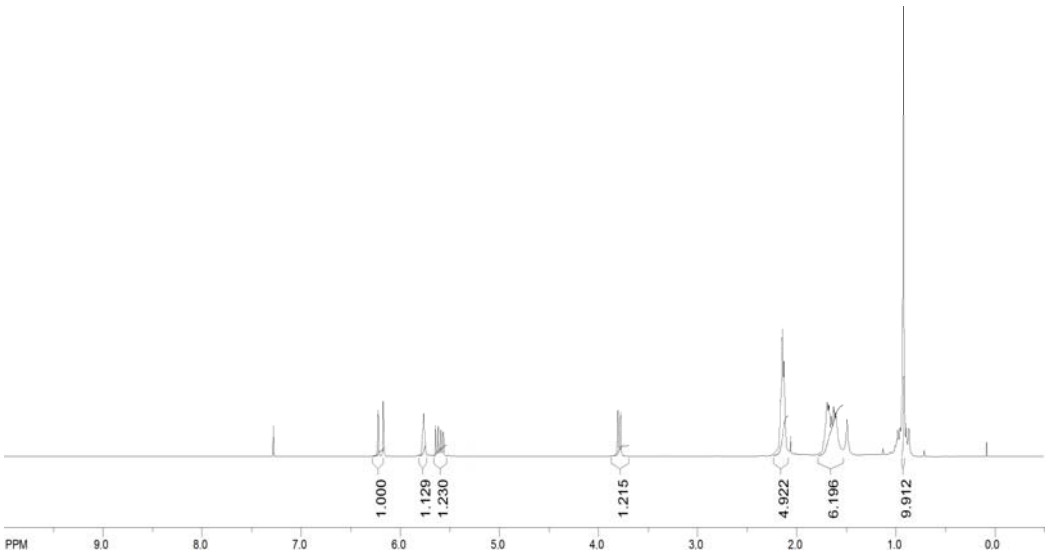


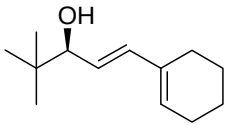


(2*E*)-3-Cyclohexenyl-1-cyclohexylprop-2-en-1-ol

(4a)

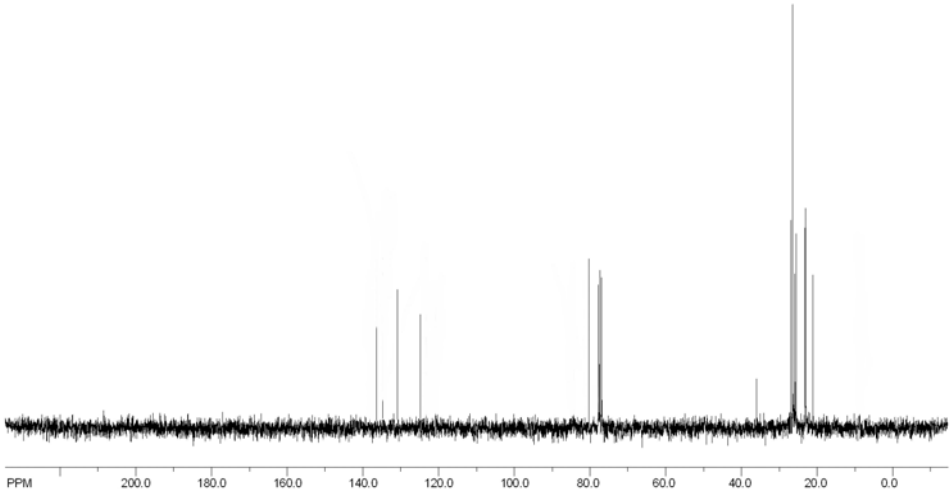


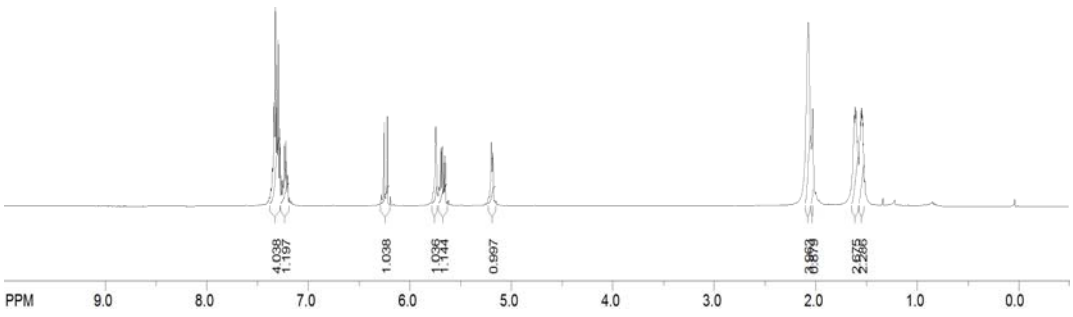


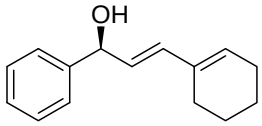


(1*E*)-1-Cyclohexenyl-4,4-dimethylpent-1-en-3-ol

(5a)

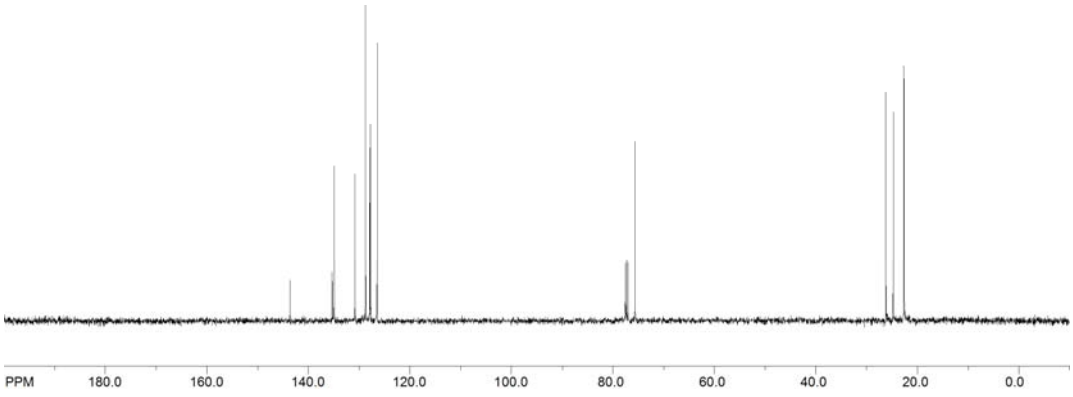


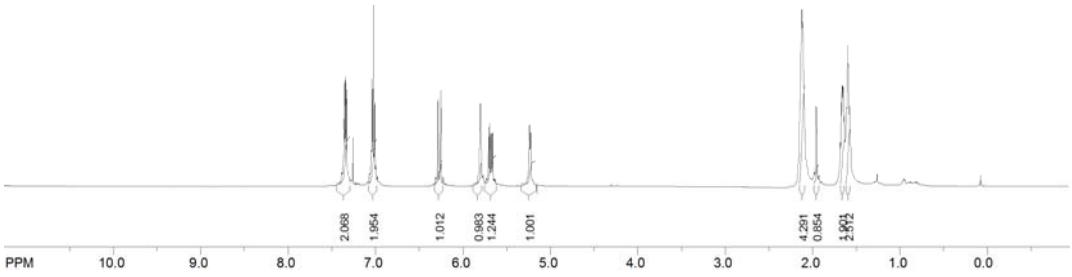


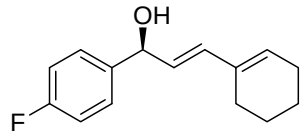


(*2E*)-3-Cyclohexenyl-1-phenylprop-2-en-1-ol

(6a)

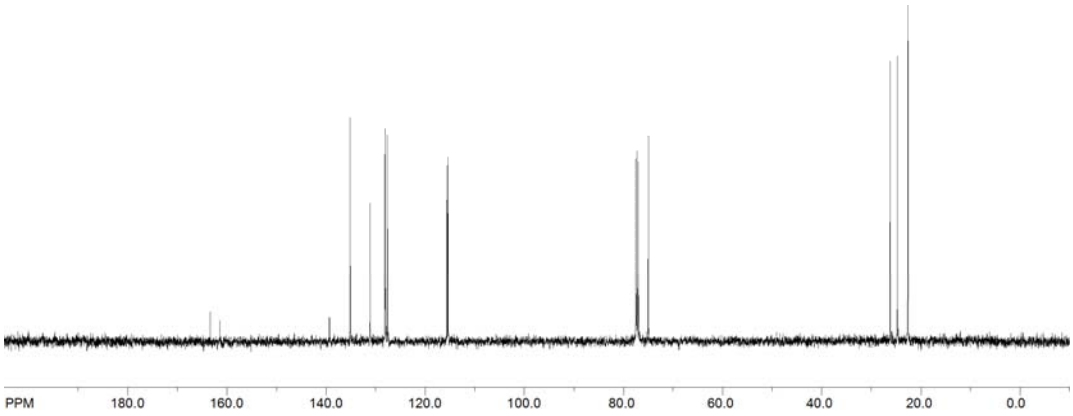


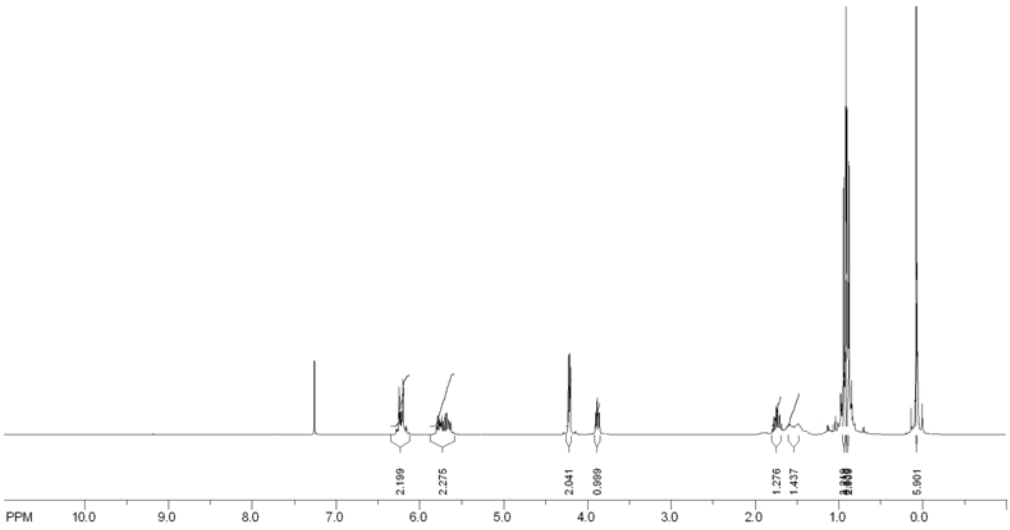


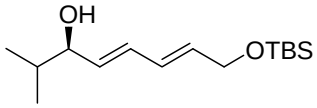


(2*E*)-3-Cyclohexenyl-1-(4-fluorophenyl)prop-2-en-1-ol

(7a)

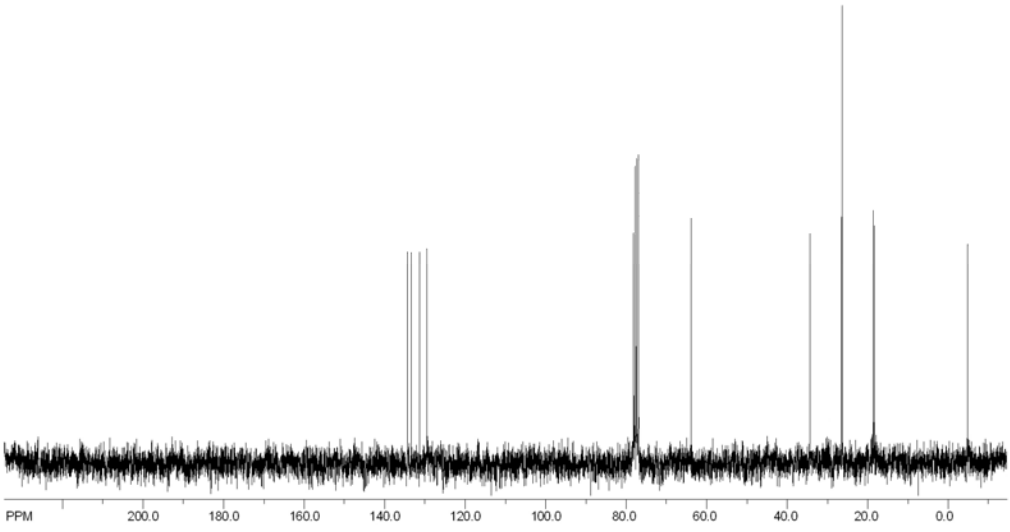


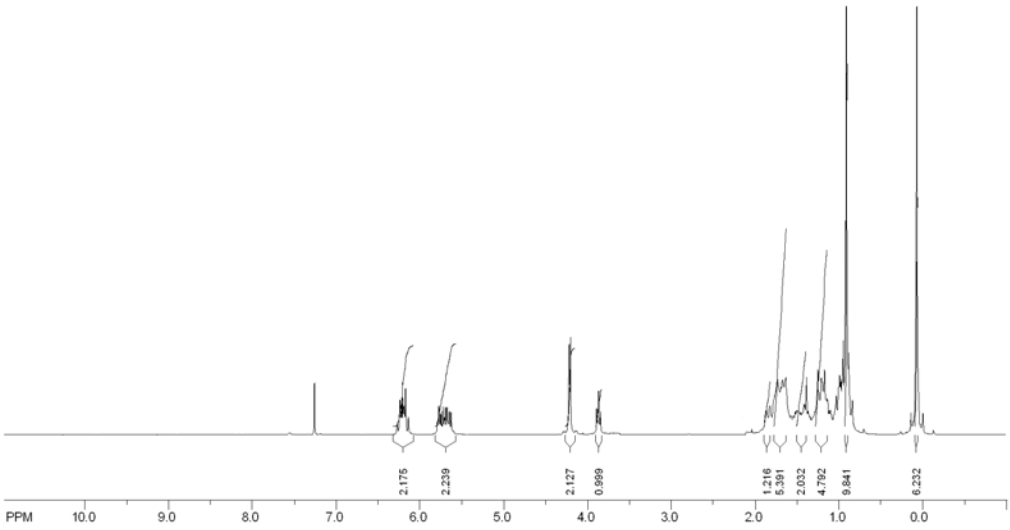


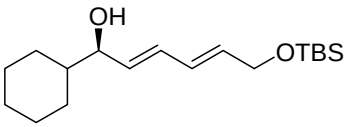


(*4E*,*6E*)-8-(tert-Butyldimethylsilyloxy)-2-methylocta-4,6-dien-3-ol

(8a)

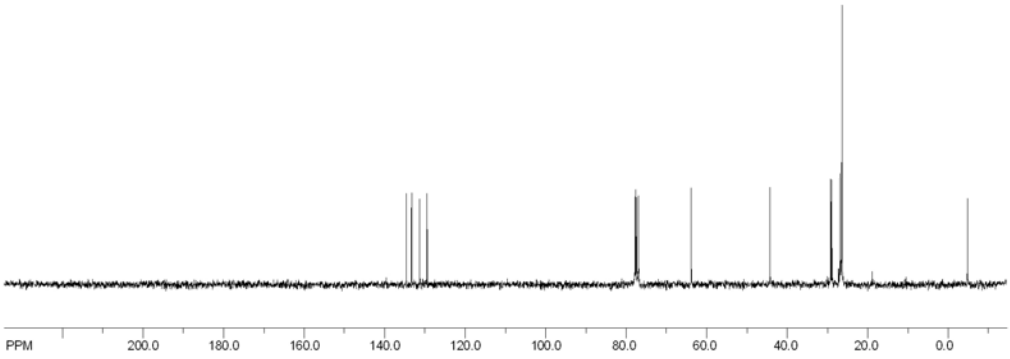


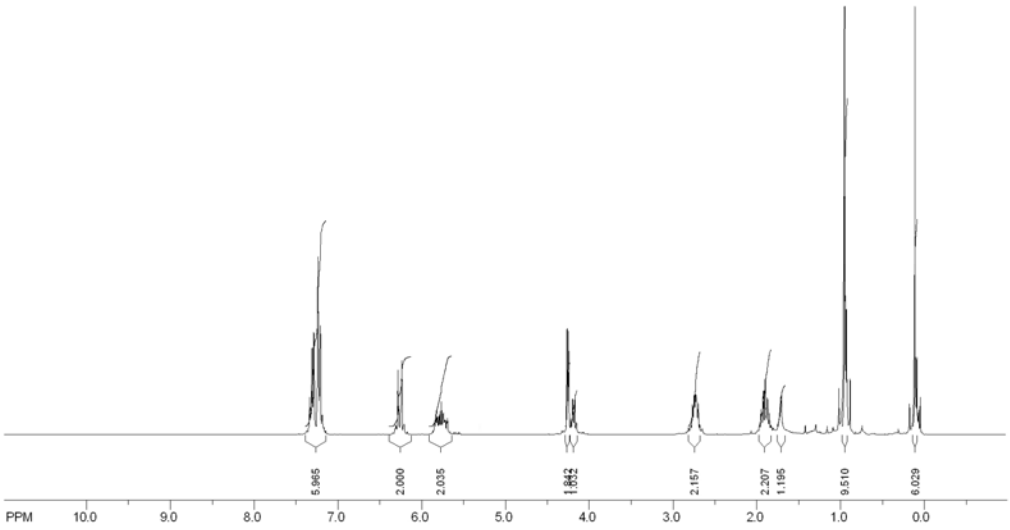


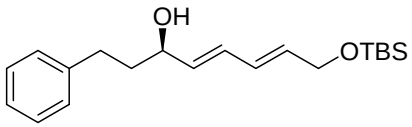


(*2E,4E*)-6-(*tert*-Butyldimethylsilyloxy)-1-cyclohexylhexa-2,4-dien-1-ol

(9a)

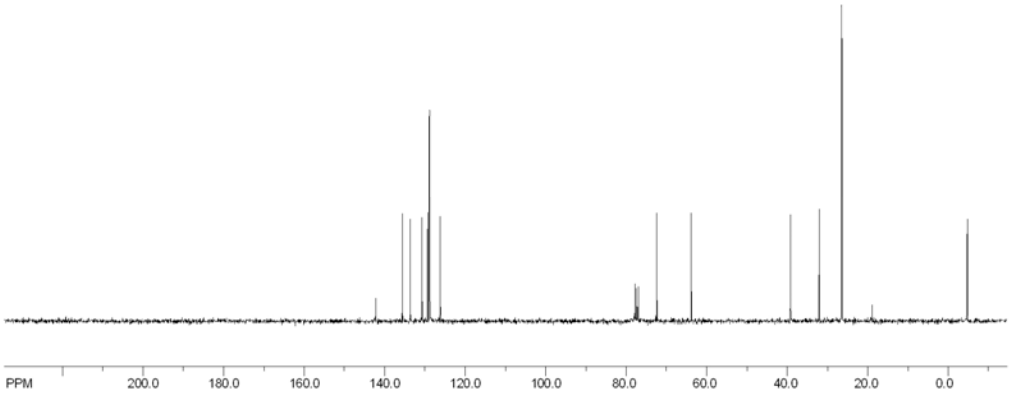


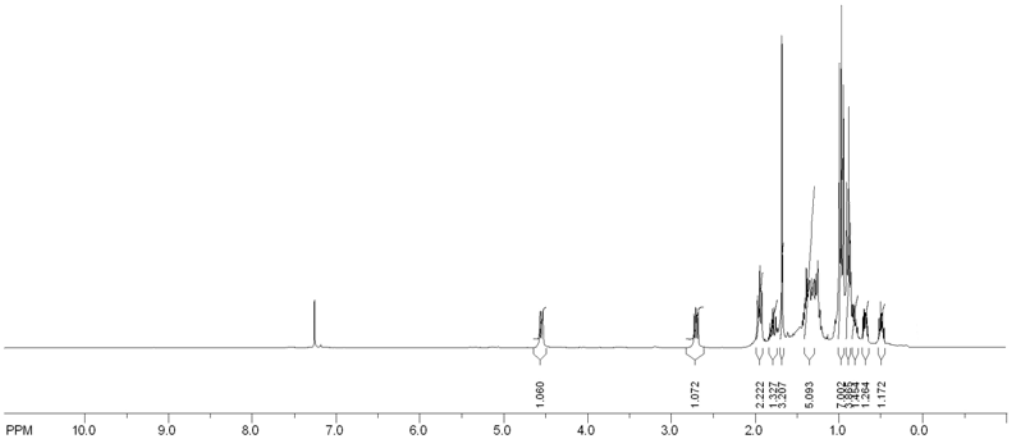


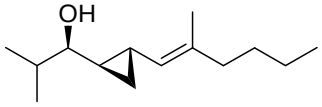


(*4E*,*6E*)-8-(*tert*-Butyldimethylsilyloxy)-1-phenylocta-4,6-dien-3-ol

(10a)

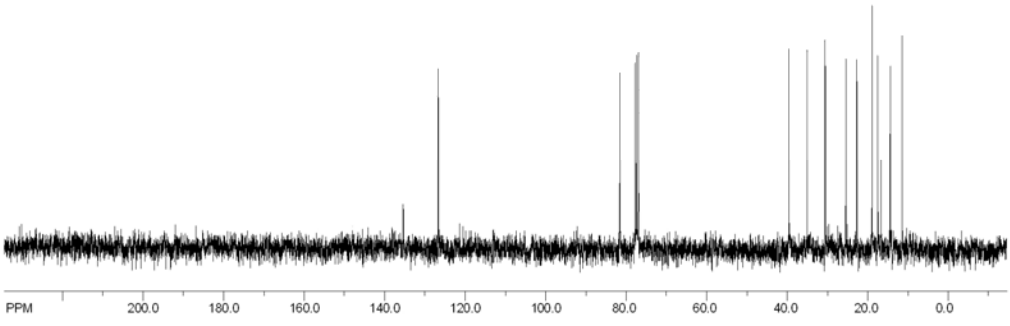


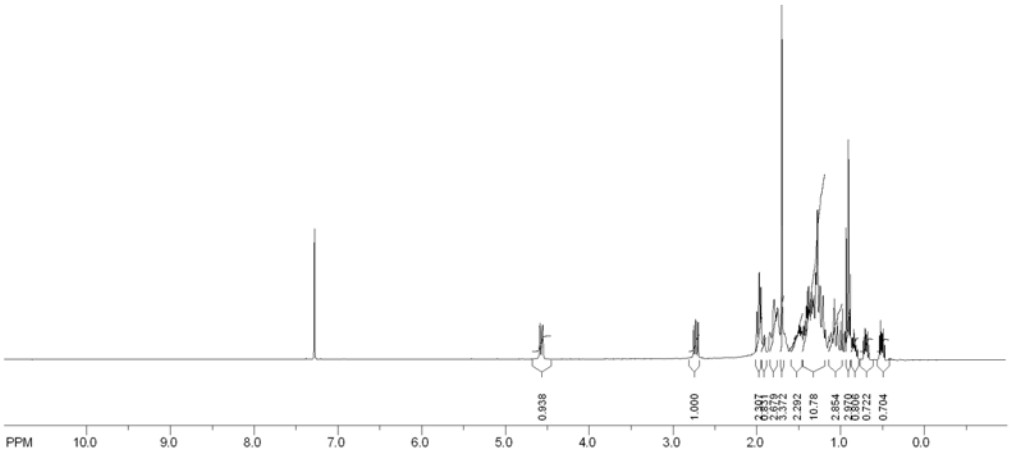


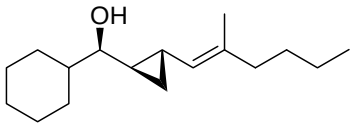


2-Methyl-1-(2-((*E*)-2-methylhex-1-enyl)cyclopropyl)propan-1-ol

(1b)

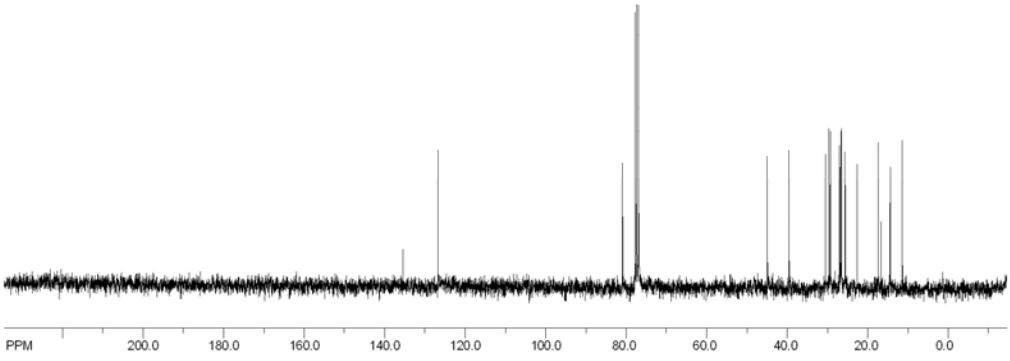


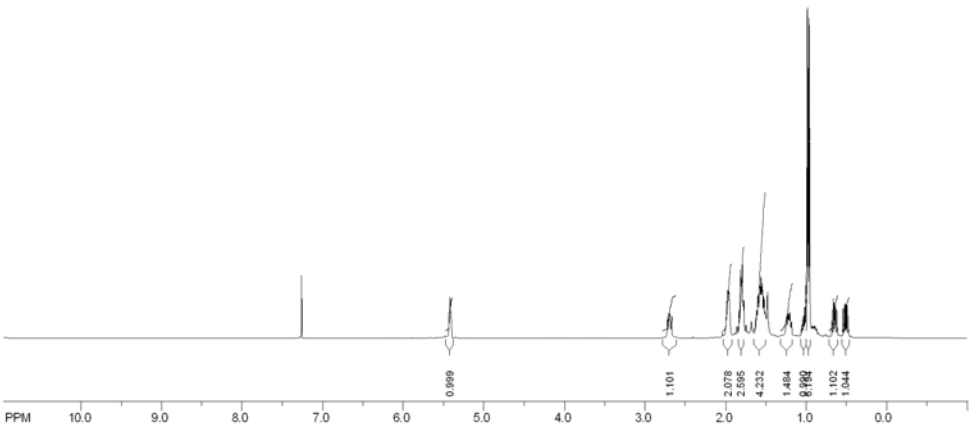


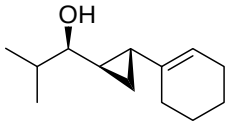


Cyclohexyl(2-((*E*)-2-methylhex-1-enyl)cyclopropyl)methanol

(2b)

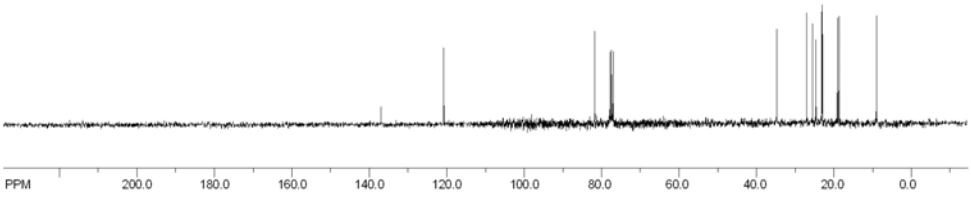


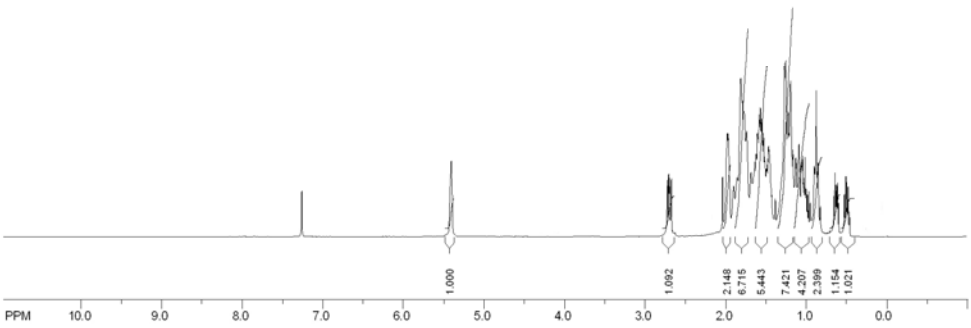


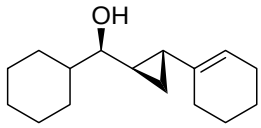


1-(2-Cyclohexenylcyclopropyl)-2-methylpropan-1-ol

(3b)

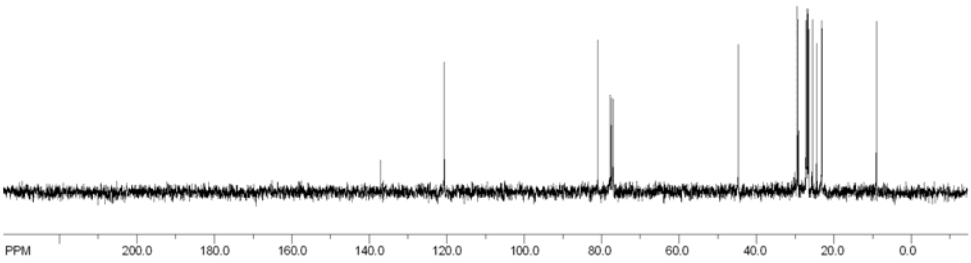


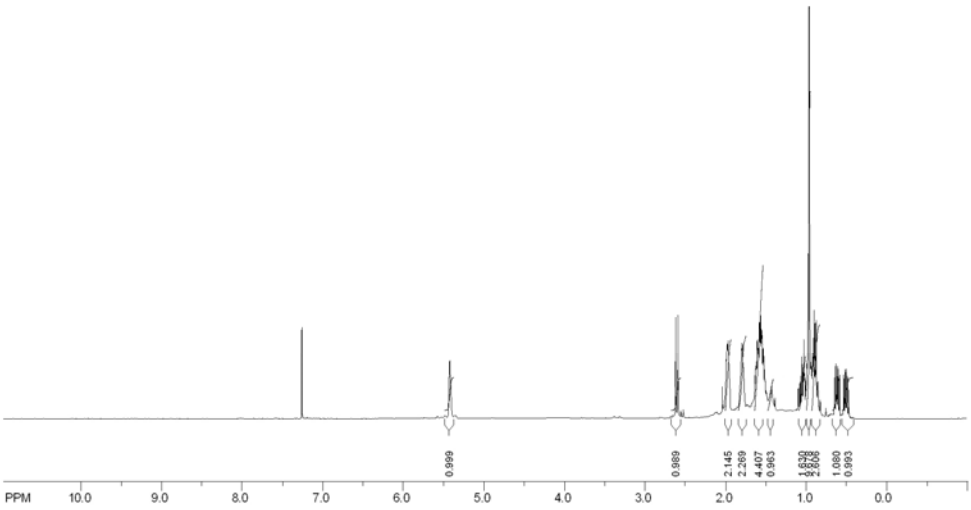


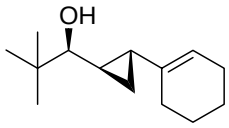


(2-Cyclohexenylcyclopropyl)(cyclohexyl)methanol

(4b)

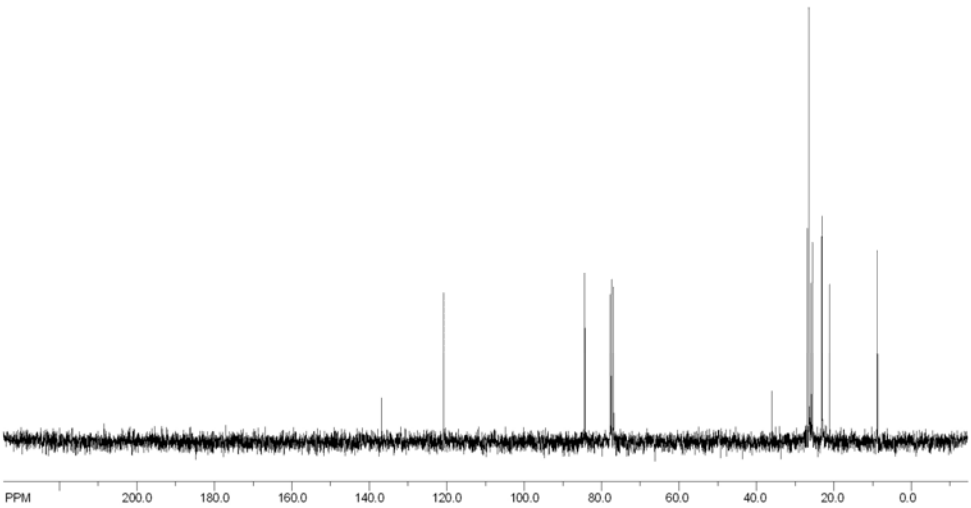


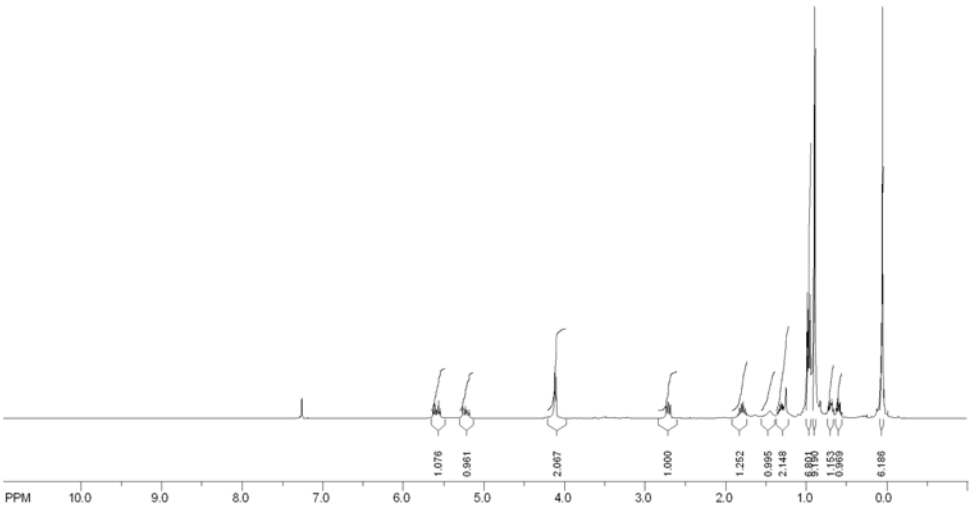


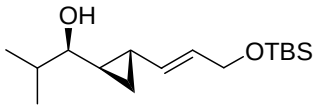


1-(2-Cyclohexenylcyclopropyl)-2,2-dimethylpropan-1-ol

(5b)

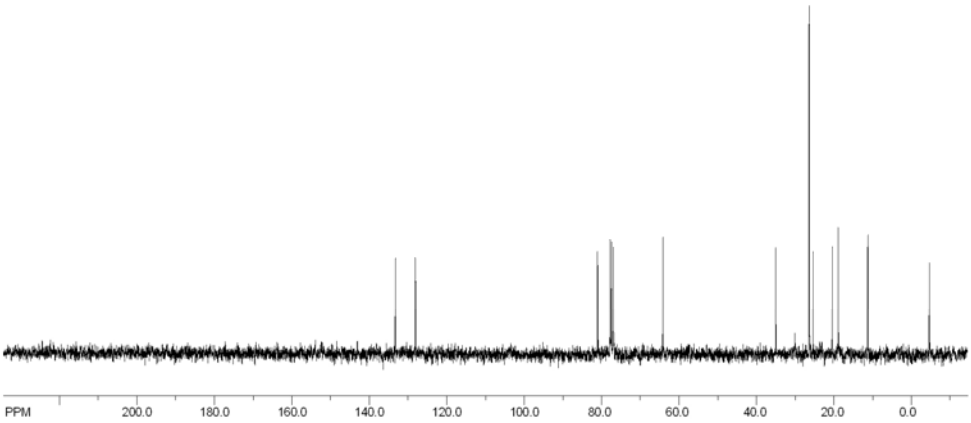


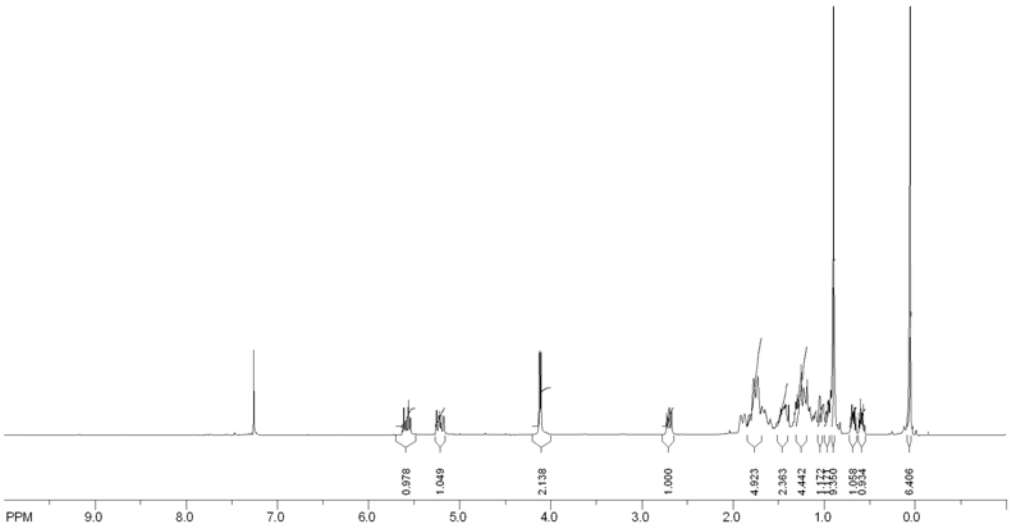


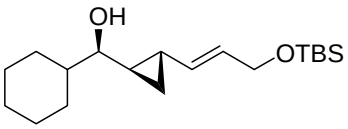


(*E*)-1-(2-(3-(tert-Butyldimethylsilyloxy)prop-1-enyl)cyclopropyl)-2-methylpropan-1-ol

(8b)

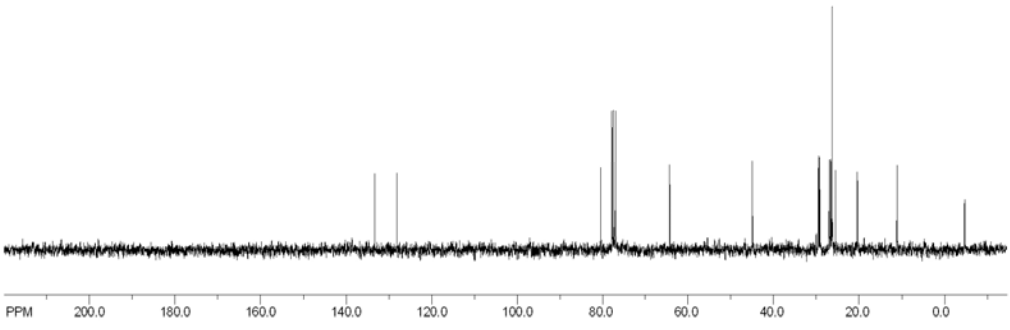


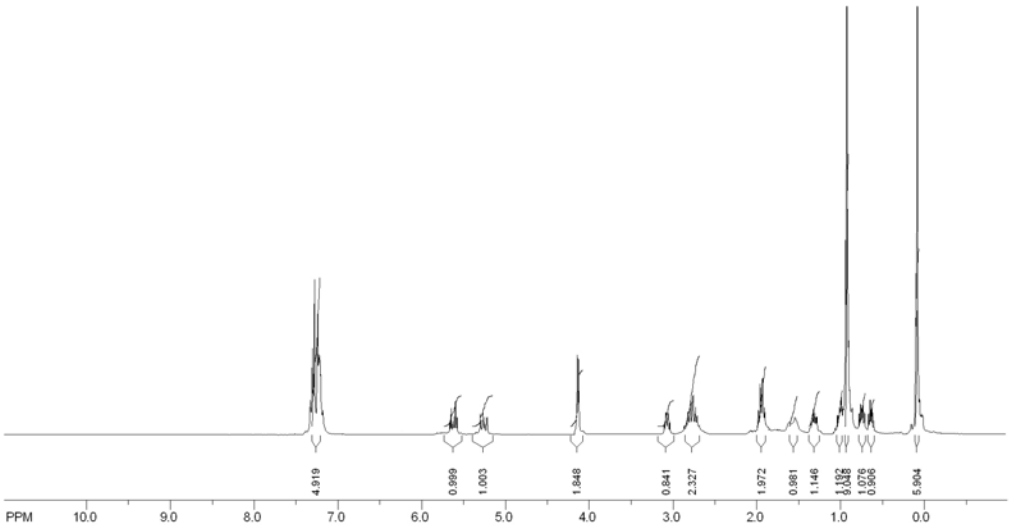


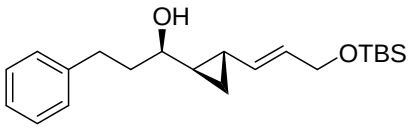


(*E*)-(2-(3-(*tert*-Butyldimethylsilyloxy)prop-1-enyl)cyclopropyl)(cyclohexyl)methanol

(9b)

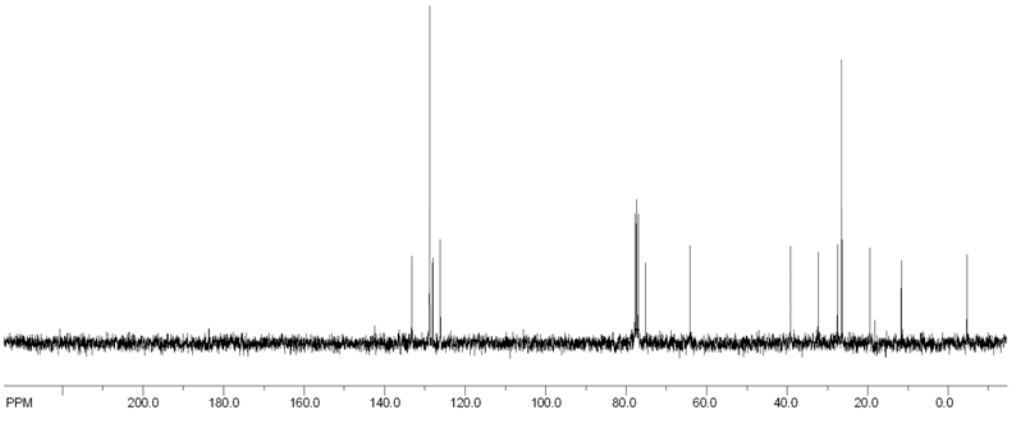


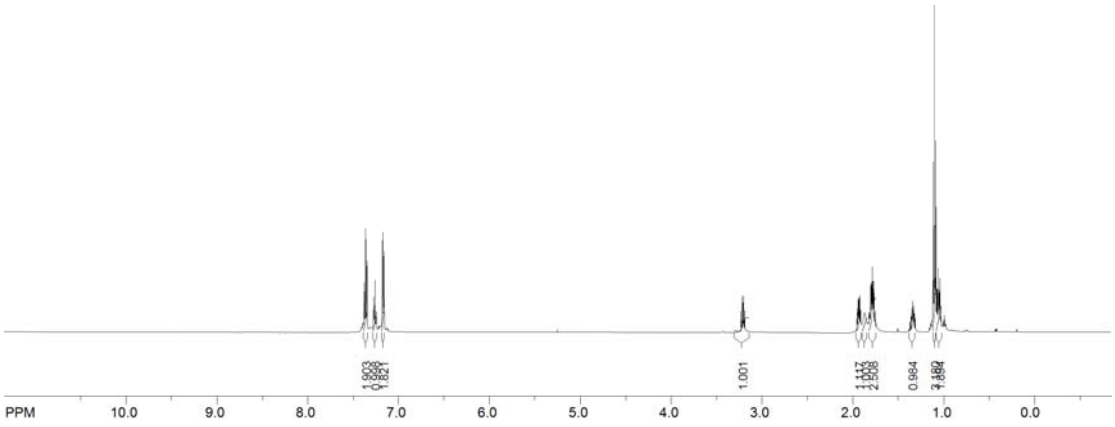


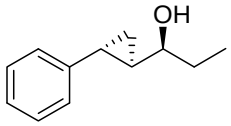


(*E*)-1-(2-(3-(*tert*-Butyldimethylsilyloxy)prop-1-enyl)cyclopropyl)-3-phenylpropan-1-ol

(10b)

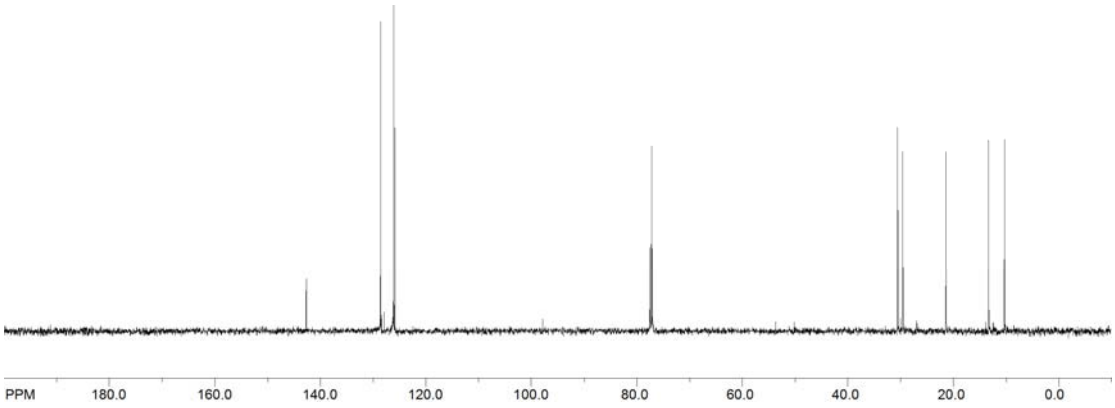


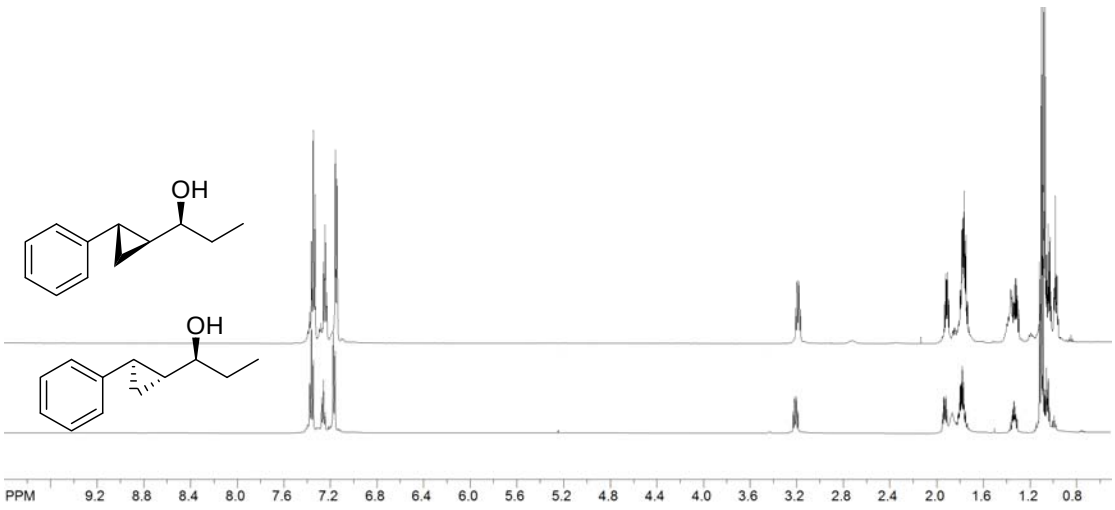


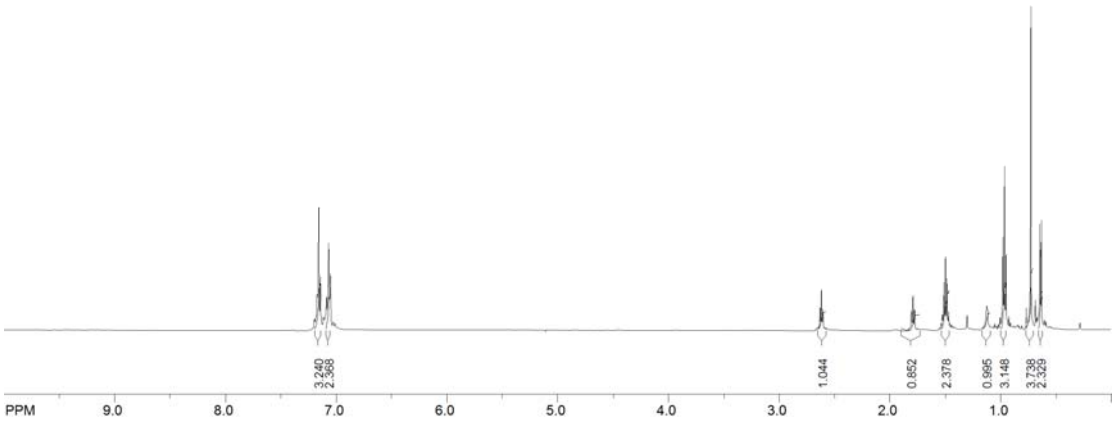


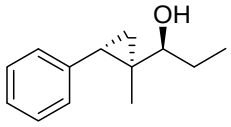
1-(2-Phenylcyclopropyl)propan-1-ol

(11)



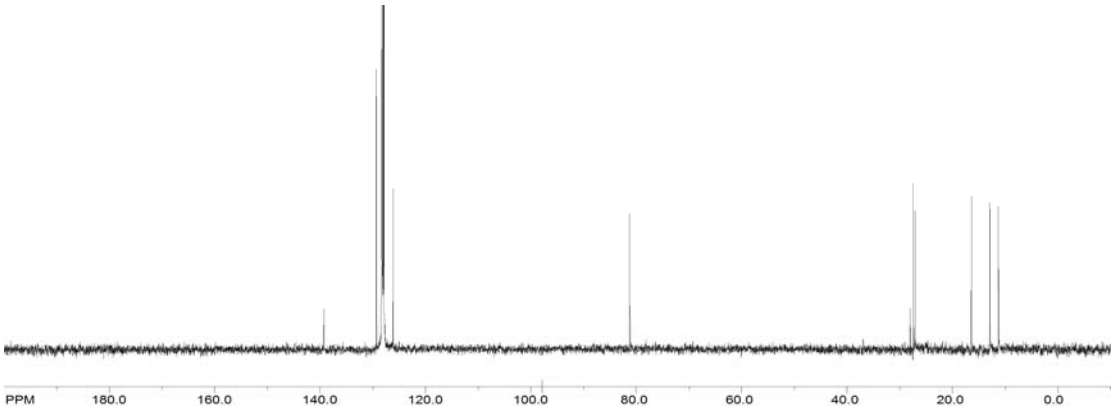


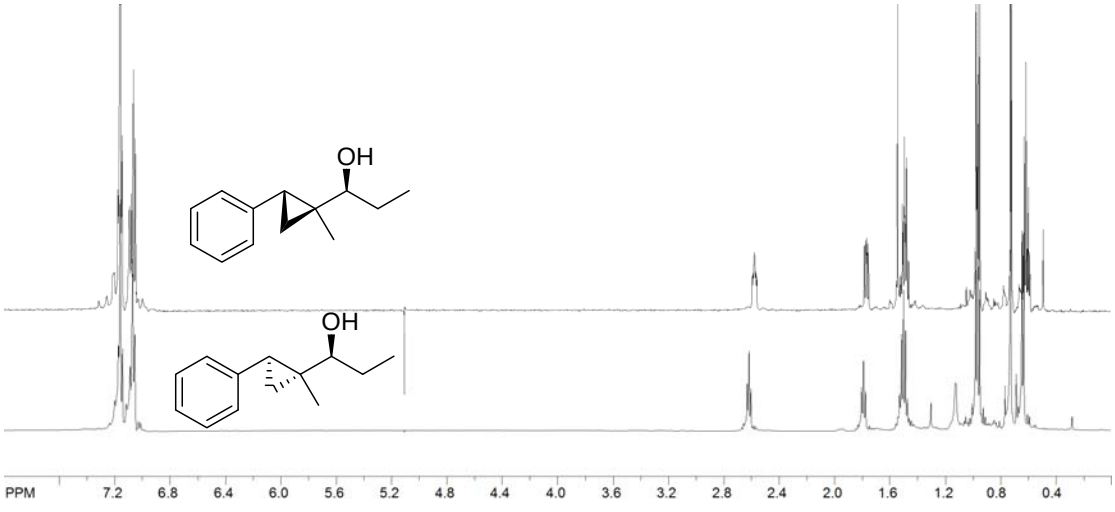


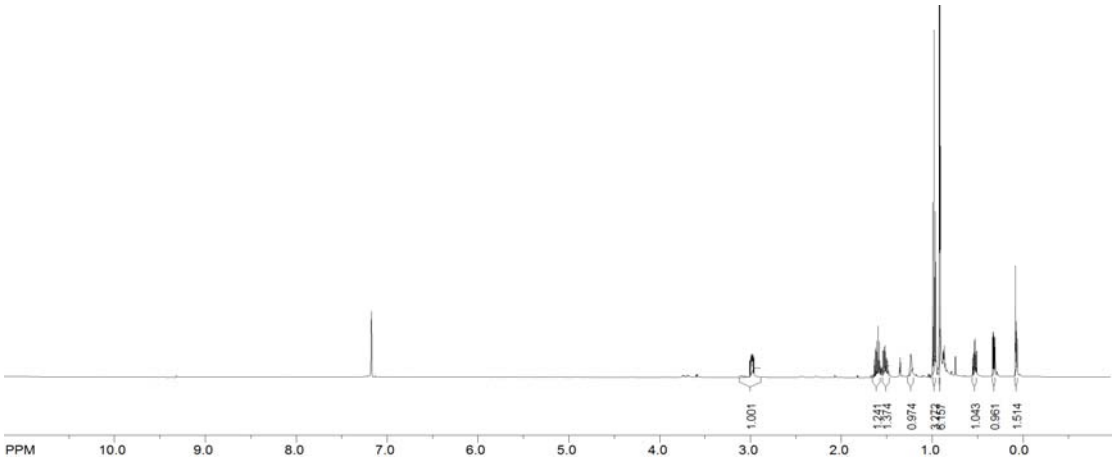


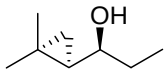
1-(1-Methyl-2-phenylcyclopropyl)propan-1-ol

(12)



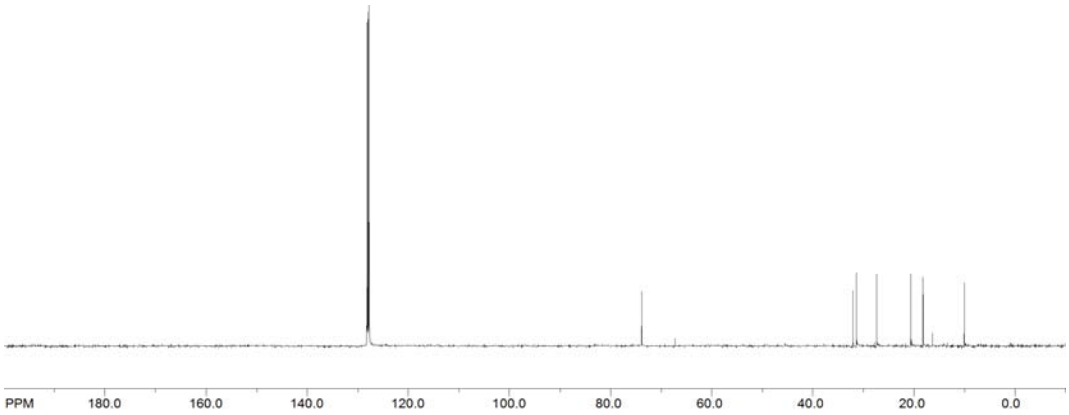


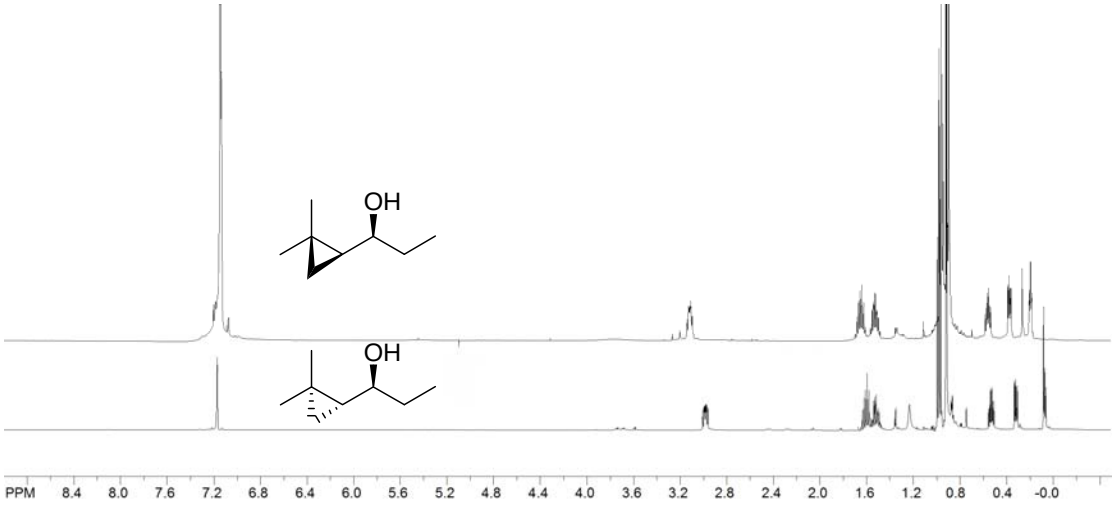


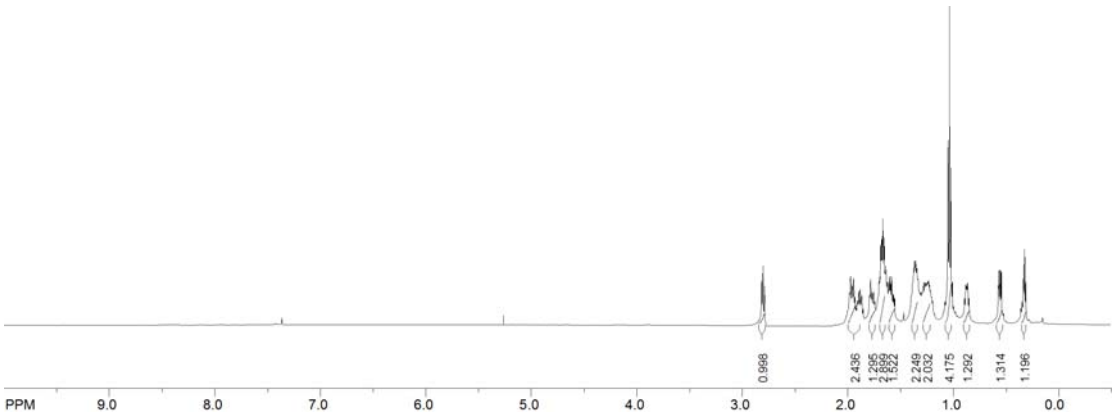


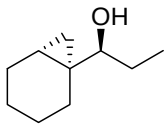
1-(2,2-Dimethylcyclopropyl)propan-1-ol

(13)



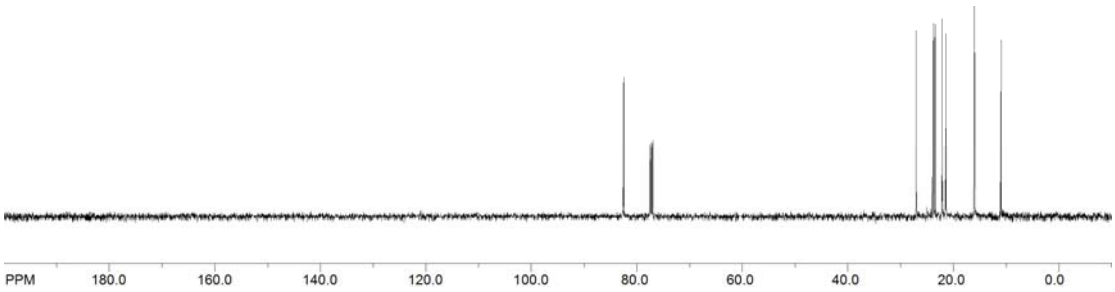


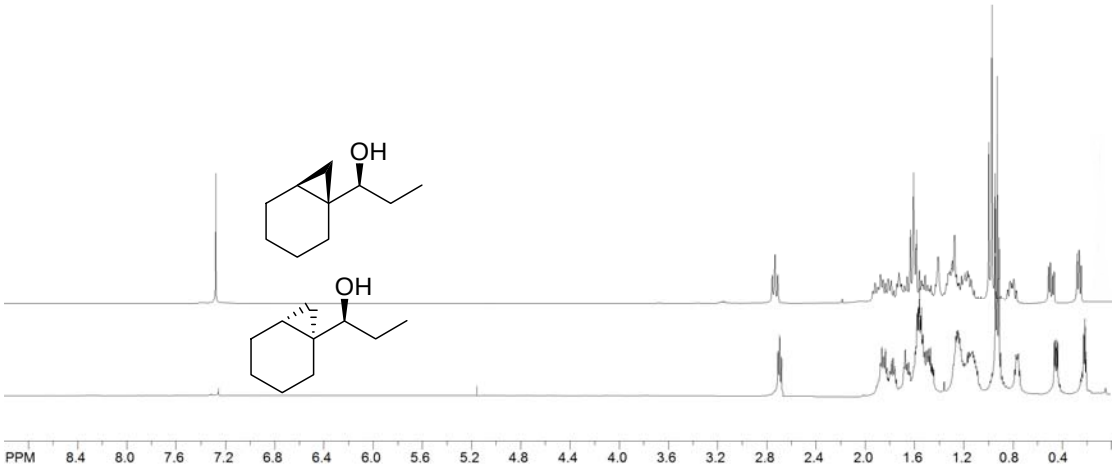


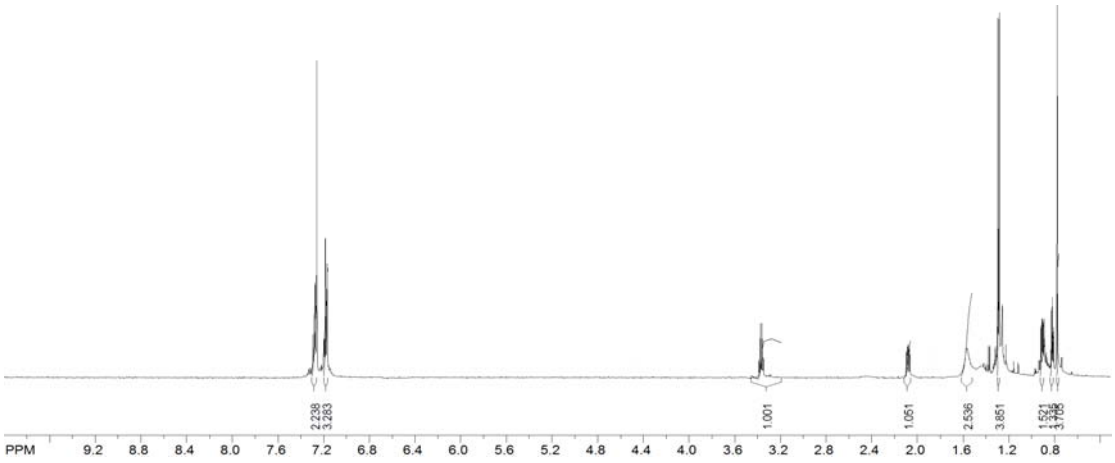


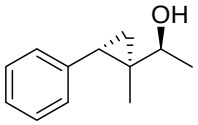
1-(Bicyclo[4.1.0]heptan-1-yl)propan-1-ol

(14)



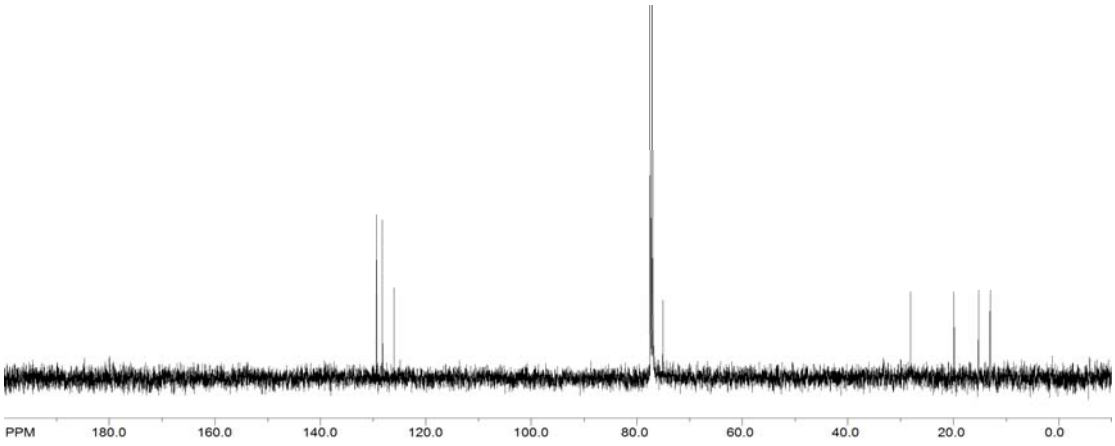


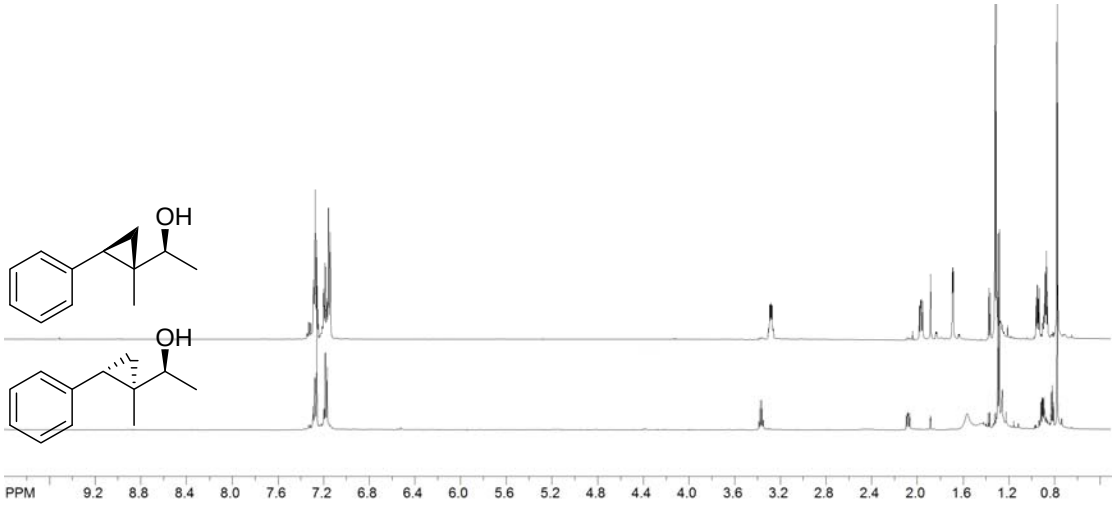


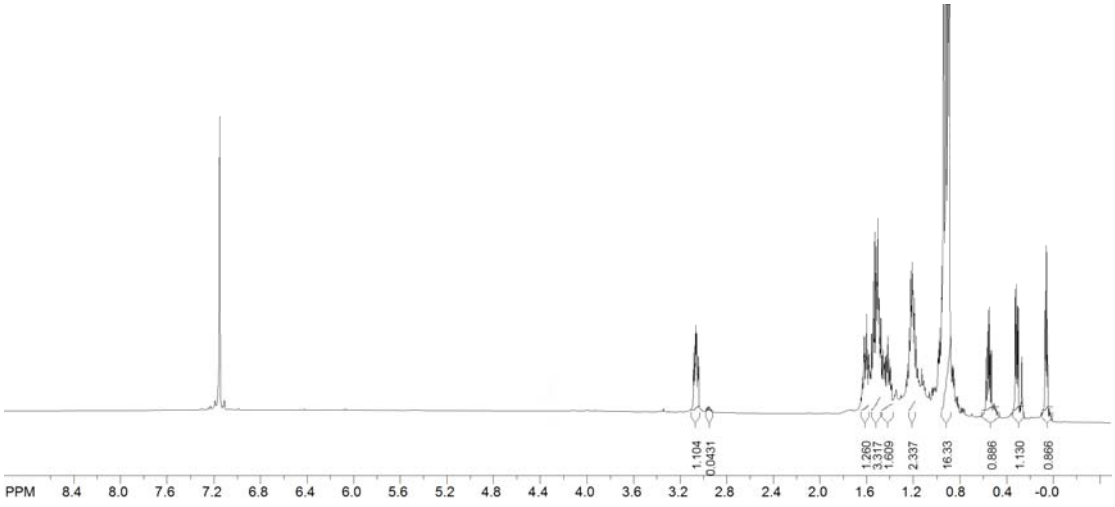


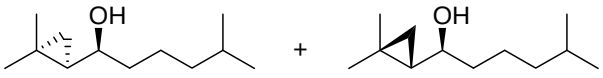
1-(1-Methyl-2-phenylcyclopropyl)ethanol

(15)





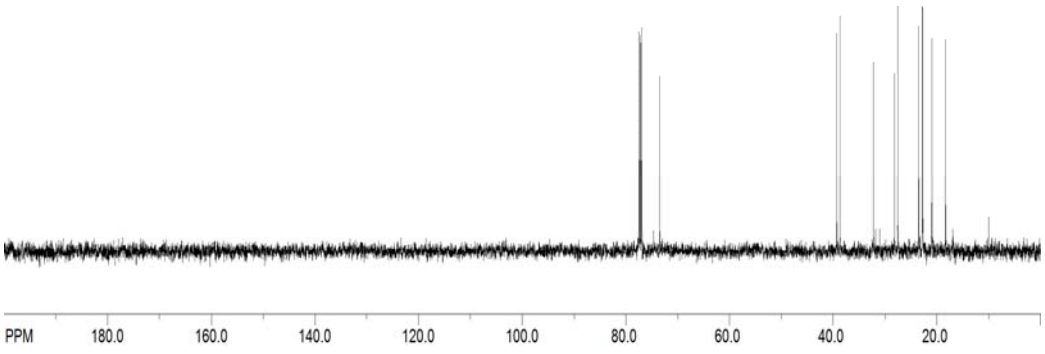


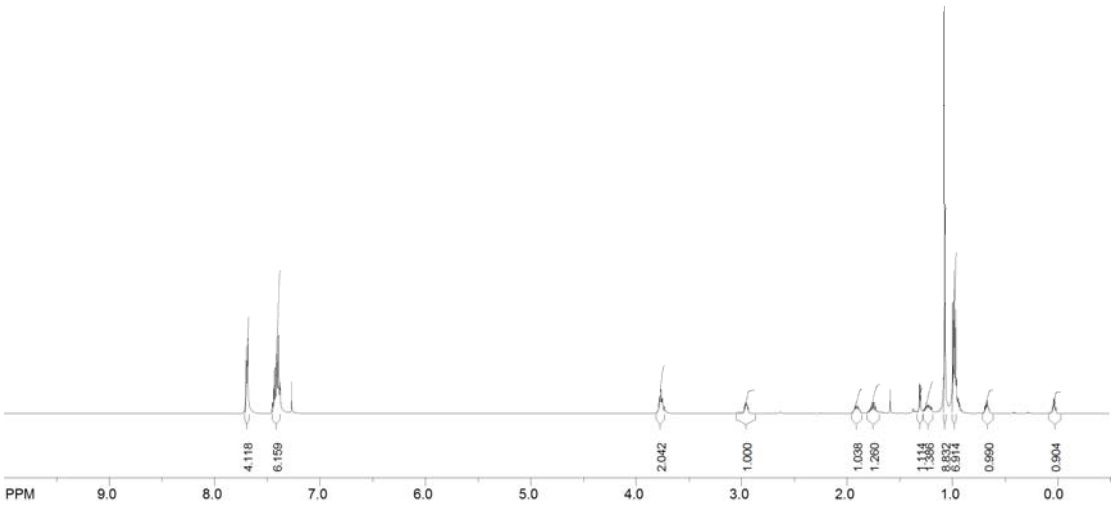


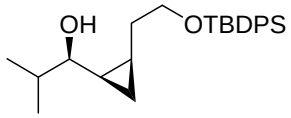
(major) (minor)

5-Methyl-1-(2,2-dimethylcyclopropyl)hexan-1-ol

(16)

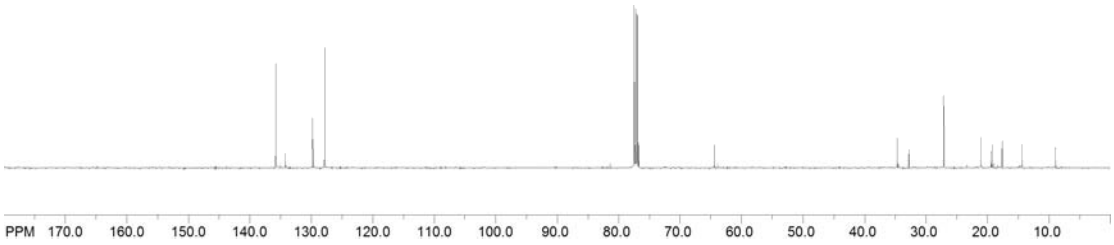


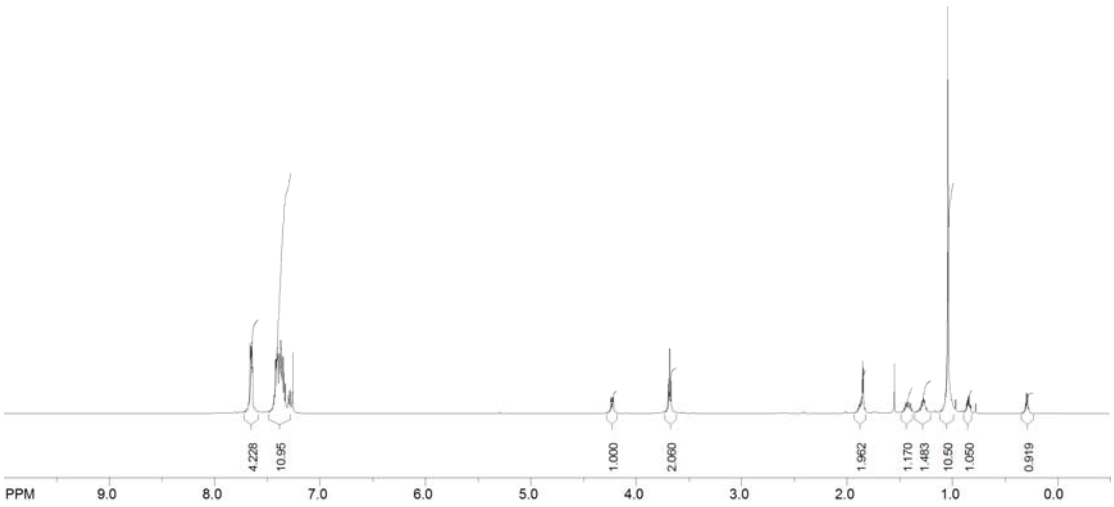


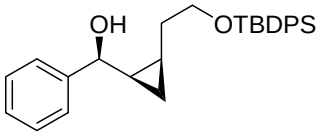


1-(2-((*tert*-Butyldiphenylsilyloxy)methyl)cyclopropyl)-2-methylpropan-1-ol

(17)

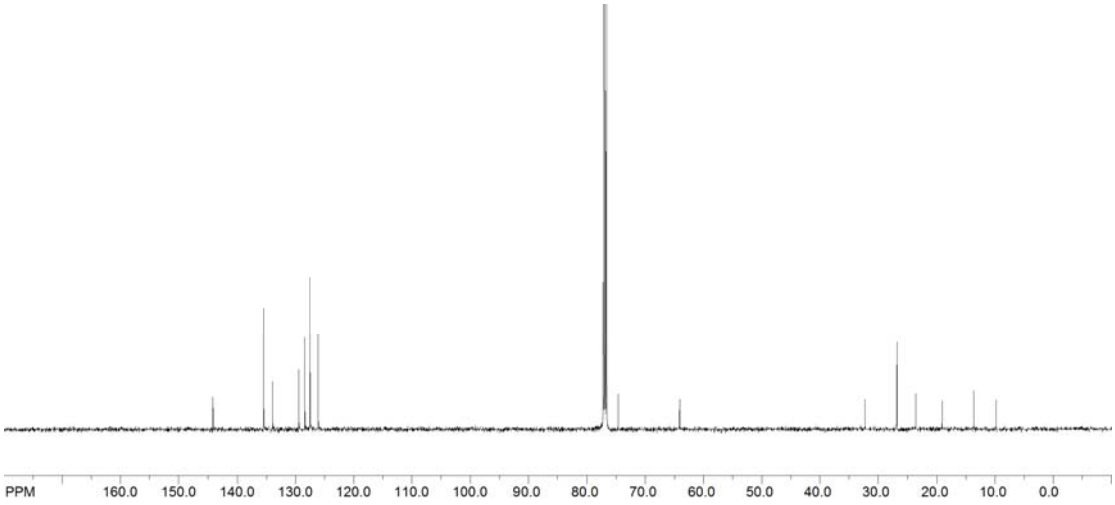


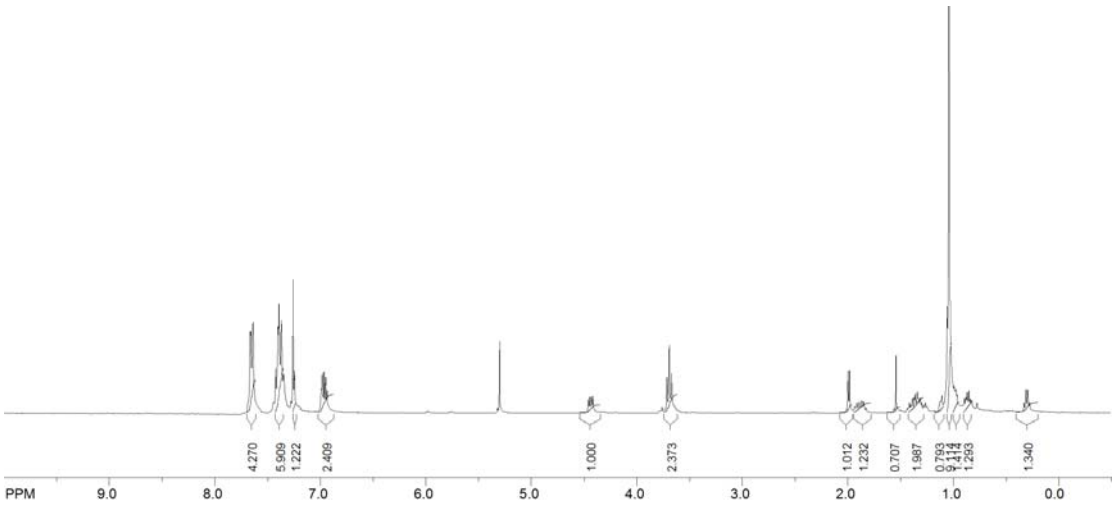


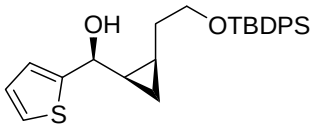


(2-((*tert*-Butyldiphenylsilyloxy)methyl)cyclopropyl)(phenyl)methanol

(18)

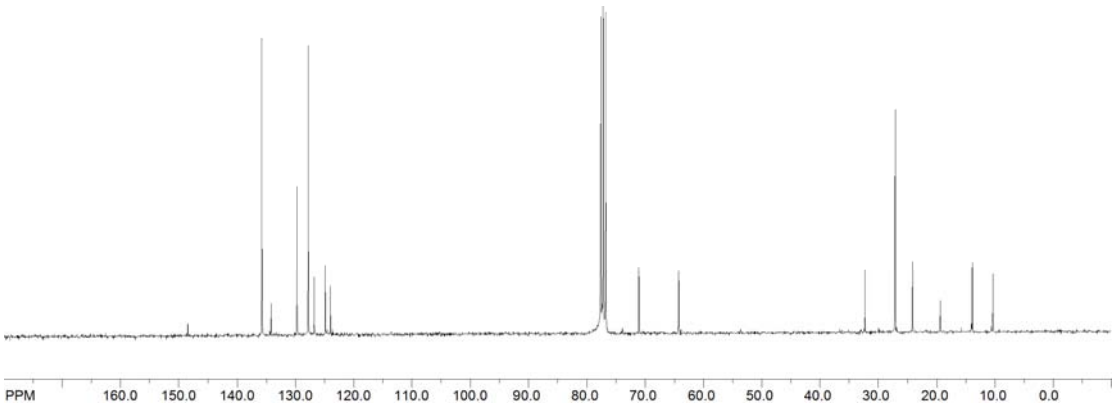


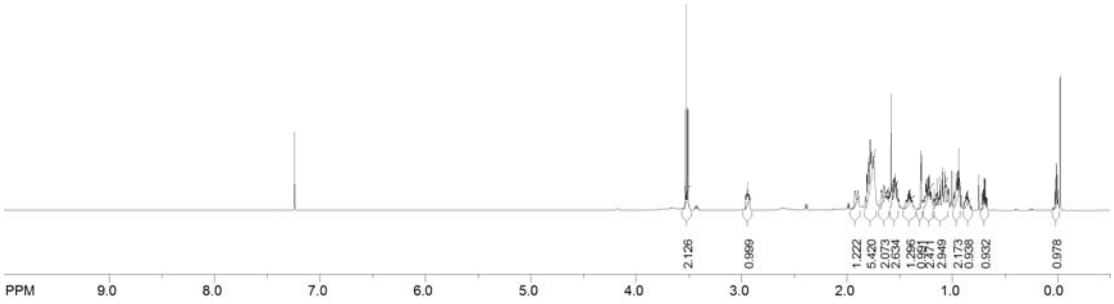


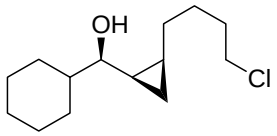


(2-((*tert*-Butyldiphenylsilyloxy)methyl)cyclopropyl)(thiophen-2-yl)methanol

(19)

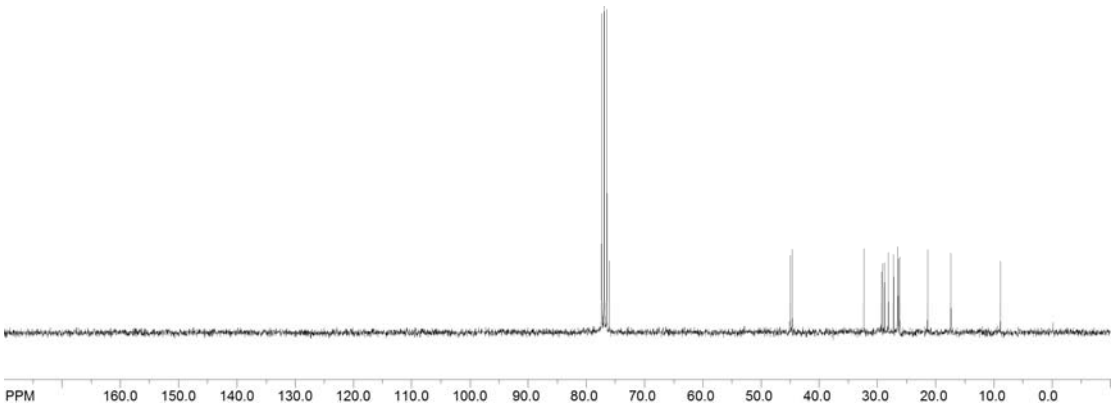


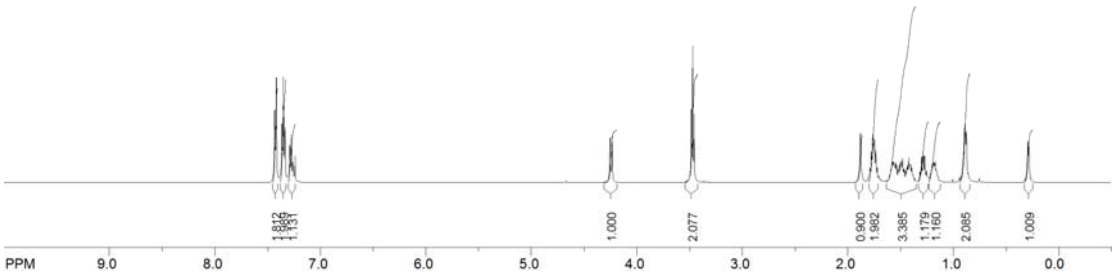


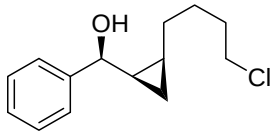


(2-(4-Chlorobutyl)cyclopropyl)(cyclohexyl)methanol

(20)

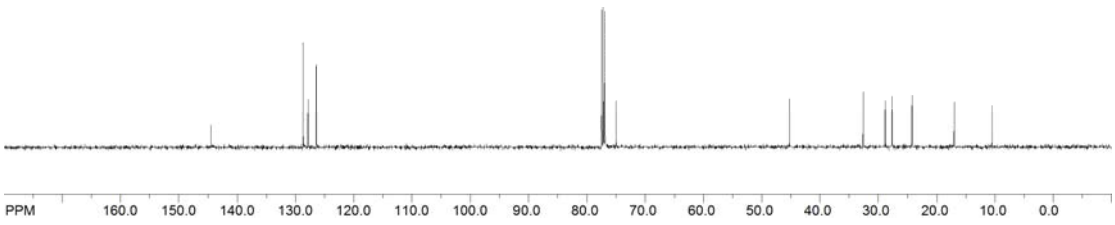


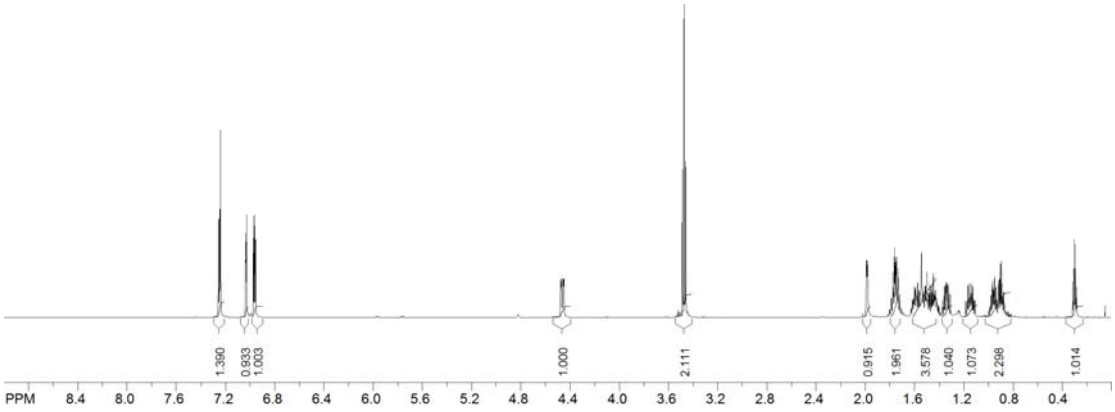


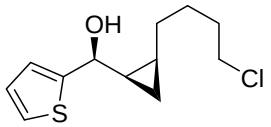


(2-(4-Chlorobutyl)cyclopropyl)(phenyl)methanol

(21)

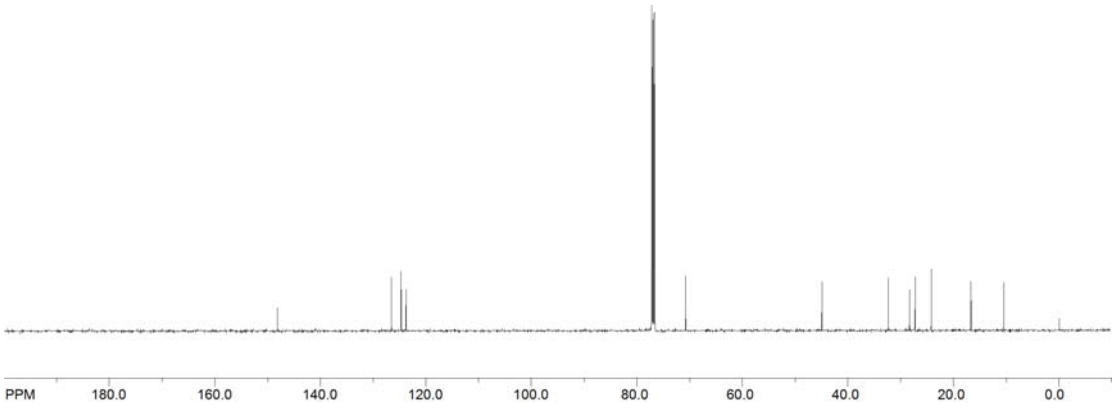


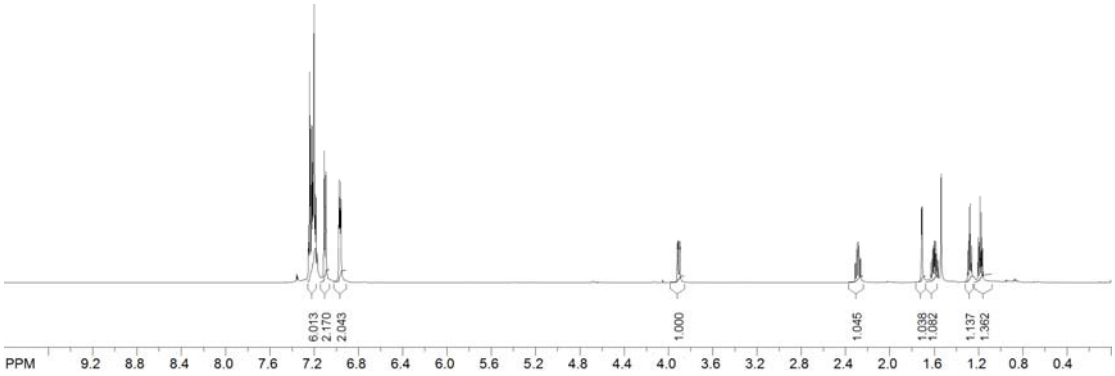


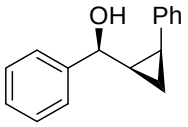


(2-(4-Chlorobutyl)cyclopropyl)(thiophen-2-yl)methanol

(22)

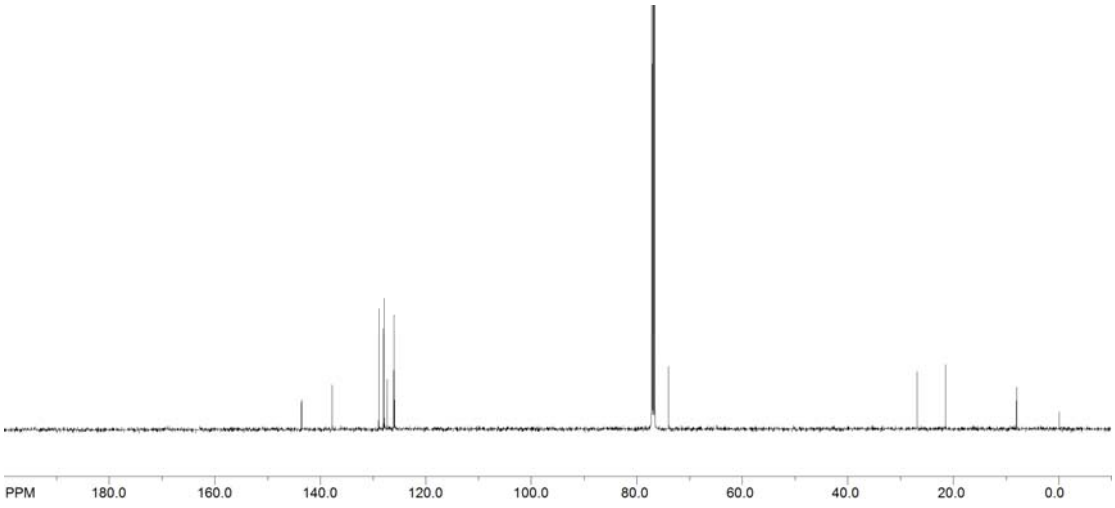


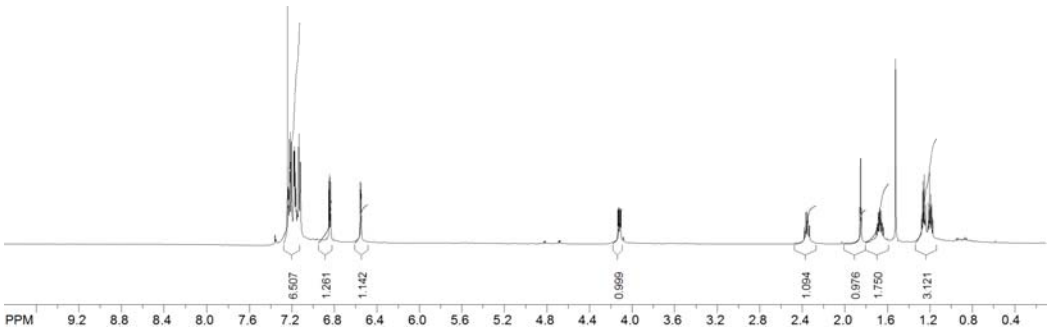


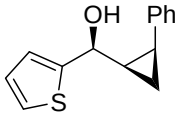


Phenyl(2-phenylcyclopropyl)methanol

(23)

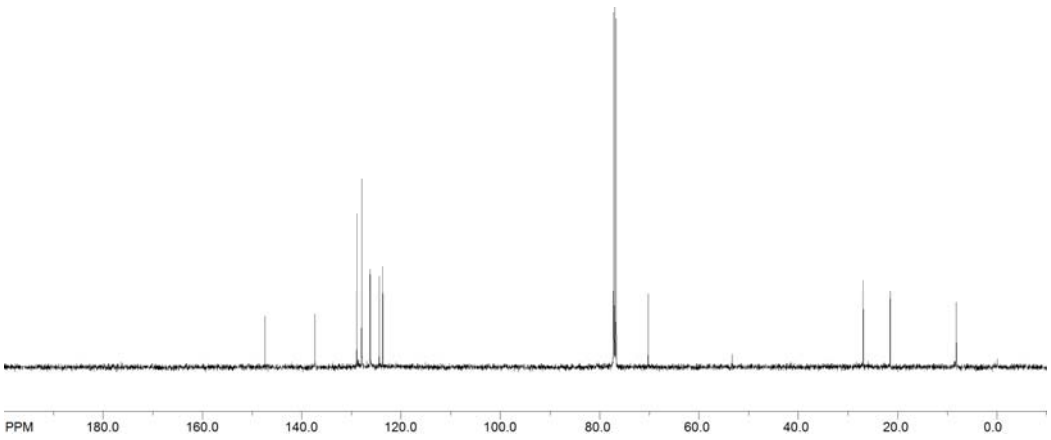


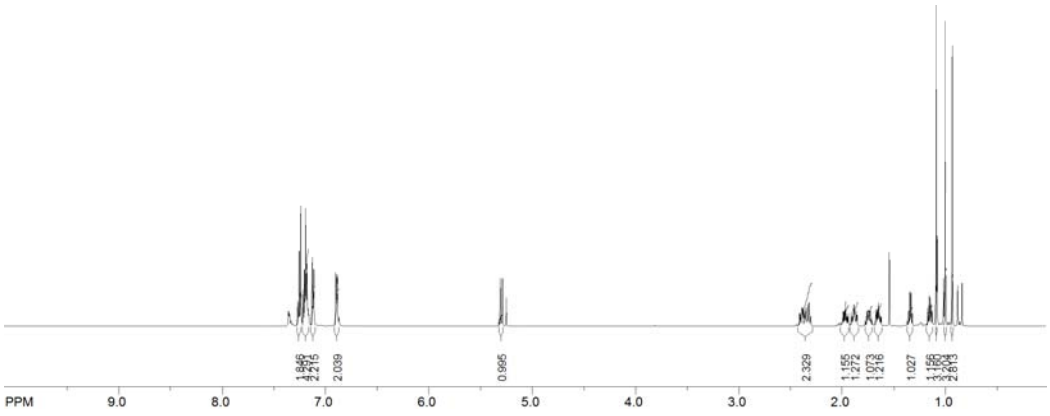


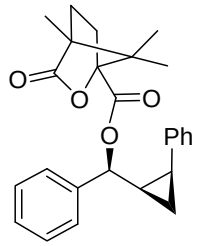


(2-Phenylcyclopropyl)(thiophen-2-yl)methanol

(24)







Phenyl(2-phenylcyclopropyl)methyl 4,7,7-trimethyl-3-oxo-2-oxa-bicyclo[2.2.1]heptane-1-carboxylate