Supporting information

Gold(I)-Catalysed Alcohol Addition to Cyclopropenes

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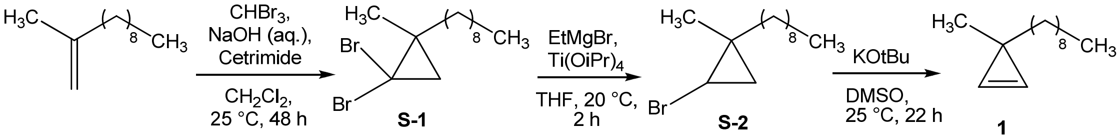
1. General Experimental Section

^{1}H NMR spectra were recorded on Bruker AC 200, DPX 400 and AV 400 spectrometers at 200 and 400 MHz respectively and referenced to residual solvent. ^{13}C NMR spectra were recorded at 50 and 100 MHz on the same spectrometers. Chemical shift data are quoted in parts per million (δ in ppm), J values are given in Hz and s, d, dd, t, q and m represent singlet, doublet, doublet of doublet, triplet, quartet and multiplet. Mass spectra were obtained at the EPSRC National Mass Spectrometry Service Centre in Swansea. Infrared spectra were obtained on Perkin-Elmer Spectrum 100 FT-IR Universal ATR Sampling Accessory, deposited neat or as a chloroform solution to a diamond/ZnSe plate. Br, s, m, w and vw represent broad, strong, medium, weak and very weak respectively. Flash column chromatography was carried out using Matrix silica gel 60 from Fisher Chemicals and TLC was performed using Merck silica gel 60 F254 pre-coated sheets and visualised by UV (254 nm) or stained by the use of aqueous acidic $KMnO_4$ or aqueous acidic ammonium molybdate as appropriate. Chemicals were purchased from Aldrich and Fisher chemical companies and used without further purification unless otherwise stated. Tetrahydrofuran was dried by distillation from sodium – benzophenone under nitrogen. Dichloromethane stored over 4 Å molecular sieves and all alcohol nucleophiles were used as purchased. Petrol ether refers to petroleum ether (40 – 60 %).

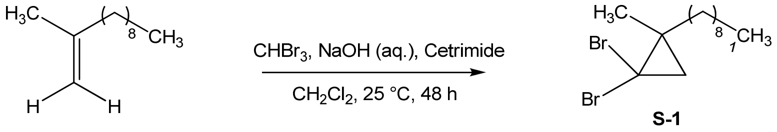
2. Experimental Procedures

Cyclopropenes **1, 6, 4, 9, 11 and 14** were synthesized following a general procedure by Gevorgyan (Scheme 1).[1-2]



Scheme 1

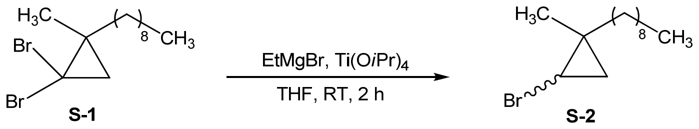
1,1-Dibromo-2-methyl-2-nonylcyclopropane S-1[3]



Bromoform (30.9 g, 122 mmol) and dichloromethane (5 mL) were added dropwise to a stirring mixture of aqueous sodium hydroxide (30 mL, 11.2 g, 280 mmol), cetrimide (2.52 g), 2-methylundec-1-ene (10.3 g, 61.2 mmol) and dichloromethane (10 mL). The mixture was allowed to stir at 25 °C. After 48 h, the reaction mixture was diluted with water (75 mL). Dichloromethane (30 ml) was added and the layers partitioned. The aqueous layer was washed twice with dichloromethane (30 ml). The combined organic layers were washed with brine (50 mL), dried over magnesium sulphate and concentrated under reduced pressure. The resulting material was purified by flash column chromatography (hexanes) and the remaining bromoform was evaporated under high vacuum (10 h, 30 °C) to yield 1,1-dibromo-2-methyl-2-nonylcyclopropane **S-1** (16.8 g, 49.5 mmol, 81%) as a colourless oil.

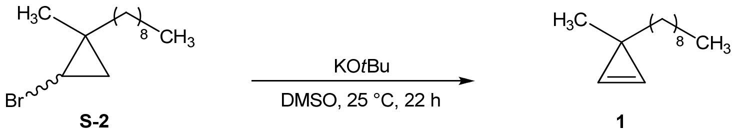
ν_{max}/cm^{-1} 689 s (Br-C); δ_H (200 MHz, $CDCl_3$) 1.67 – 1.18 (21H, m, alkyl-H), 0.88 (3H, t, *J* = 6.6, H-1); δ_C (50 MHz, $CDCl_3$) 39.9 (C), 38.8 (CH_2), 34.8 (CH_2), 31.8 (CH_2), 29.7 (C), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 26.4 (CH_2), 22.7 (CH_2), 22.5 (CH_3), 14.1 (CH_3); M^+(EI) = 338.0245 required *M* = 338.0245.

2-Bromo-1-methyl-1-nonylcyclopropane S-2[3]



A solution of ethylmagnesium bromide (1.38 M in Et_2O, 38.6 mL, 53.3 mmol) was added over 1 hour to a strirring solution of 1,1-dibromo-2-methyl-2-nonylcyclopropane **S-1** (14.1 g, 41.5 mmol), $Ti(OiPr)_4$ (0.235 g, 0.827 mmol) and tetrahydrofuran (100 mL). The solution was allowed to stir for an additional hour at 20 °C. The reaction was quenched by slow addition of water (20 mL), then 20% aqueous sulphuric acid (50 mL) was added and the mixture stirred for 30 minutes. Diethyl ether (50 mL) was added and the layers were partitioned. The aqueous layer was washed further three times with diethyl ether (50 mL). The combined organic layers were washed twice with saturated sodium bicarbonate (50 mL), washed with brine (50 mL), dried over magnesium sulphate and concentrated under reduced pressure. The crude material was purified by flash column chromatography (eluent: petrol ether) to yield a mixture of the two diastereomers of 2-bromo-1-methyl-1-nonylcyclopropane **S-2** (8.25 g, 31.6 mmol, 77%) as a colourless oil.
δ_H (200 MHz, $CDCl_3$) 2.82 (1H x 2, m, C*H*Br), 1.55 – 0.82 (22H x 2, m, alkyl-H), 0.62 (2H x 2, m, CHBrCH_2); δ_C (50 MHz, $CDCl_3$) 38.9 (CH_2), 36.4 (CH_2), 31.9 (CH_2), 30.7 (CH_2), 30.1 (CH), 29.8 (CH), 29.7 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_2), 26.5 (CH_2), 26.3 (CH_2), 22.8 (CH_2), 22.7 (CH_2), 22.5 (CH_2), 22.1 (CH_3), 21.3 (C), 21.0 (C), 20.2 (CH_3), 14.1 (CH_3); M^+(EI) = 260.1121 required $M = 260.1140$.

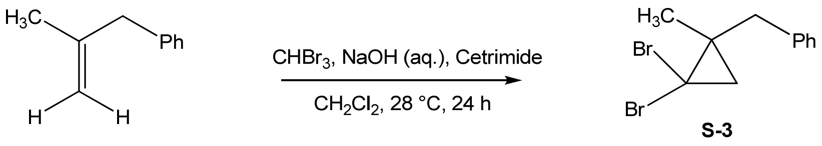
3-Methyl-3-nonylcycloprop-1-ene 1[3]



Potassium *tert*-butoxide (12.21 g, 109.0 mmol) and dimethyl sulfoxide (168 mL) were heated to 50 °C and allowed to stir for 30 minutes at this temperature. The solution was cooled to room temperature and 2-bromo-1-methyl-1-nonylcyclopropane **S-2** (14.36 g, 55.0 mmol) was added dropwise over 3 hours. The reaction mixture was allowed to stir for 22 h at 25 °C, then quenched by addition of water (200 mL). Pentane (200 mL) was added and the layers partitioned. The aqueous layer was washed three times with pentane (200 mL). The combined organic layers were washed twice with brine (300 mL), dried over magnesium sulphate and concentrated under reduced pressure. The resulting material was purified by flash column chromatography (pentane) to yield 3-methyl-3-nonylcycloprop-1-ene **1** (9.20 g, 51.1 mmol, 93%) as a colourless oil.

ν_{max}/cm^{-1} 1628 vw (C=C); δ_H (200 MHz, $CDCl_3$) 7.34 (2H, s, C=C*H*), 1.54 – 1.03 (19H, m, alkyl-H), 0.88 (3H, t, *J* = 6.4, CH_2CH_3); δ_C (50 MHz, $CDCl_3$) 122.1 (CH), 40.2 (CH_2), 31.9 (CH_2), 29.8 (CH_2), 29.6 (CH_2), 29.6 (C), 29.4 (CH_2), 27.3 (CH_3), 27.1 (CH_2), 22.7 (CH_2), 14.1 (CH_3); M$^+$(EI) = 180.1897 required *M* = 180.1878.

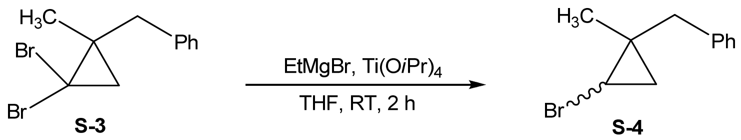
((2,2-Dibromo-1-methylcyclopropyl)methyl)benzene S-3



A solution of 10 M aqueous sodium hydroxide (29 mL) was added to a flask charged with cetrimide (2.80 g). A solution of 2-(2-methylallyl)benzene (10.0 g, 75.6 mmol) in dichloromethane (10 mL) was added to the stirring mixture. Bromoform (38.2 g, 151 mmol) in dichloromethane (7 mL) was added dropwise over a period of 3 hours. The mixture was allowed to stir vigorously at 28 °C. After 24 h, the reaction mixture was diluted with water (100 mL). Dichloromethane (30 ml) was added and the layers partitioned. The aqueous layer was washed twice with dichloromethane (30 ml). The combined organic layers were washed with brine (50 mL), dried over magnesium sulphate and concentrated under reduced pressure. The resulting brown oil was purified by flash column chromatography (hexane) and the remaining bromoform was evaporated under high vacuum (10 h, 30 °C) to yield ((2,2-dibromo-1-methylcyclopropyl)methyl)benzene **S-3** (20.7 g, 68.1 mmol, 90%) as a yellow oil.

ν_{max}/cm^{-1} 1602 w, 1582 w, 1493 m, (Ar C=C), 710 s (Br-C); δ_H (200 MHz, $CDCl_3$) 7.38-7.25 (5H, m, Ar-H), 3.09 (1H, d, *J* = 14.8, C*H*HPh), 3.01 (1H, d, *J* = 14.8, CH*H*Ph), 1.73 (1H, d, *J* = 7.4, CH*H*CBr_2), 1.54 (1H, d, *J* = 7.4, CH*H*CBr_2), 1.31 (3H, s, CH_3); δ_C (50 MHz, $CDCl_3$) 138.6 (C), 129.2 (CH), 128.5 (CH), 126.5 (CH), 43.9 (CH_2), 39.2 (C), 34.3 (CH_2), 30.5 (C), 22.9 (CH_3); M^+(EI) = 301.9297 required *M* = 301.9300

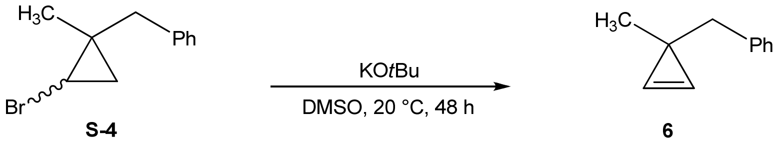
((2-Bromo-1-methylcyclopropyl)methyl)benzene S-4



A solution of ethylmagnesium bromide (3 M in Et_2O, 17.0 mL, 51.0 mmol) was added over 1 hour to a strirring solution of ((2,2-dibromo-1-methylcyclopropyl)methyl)benzene **S-3** (11.9 g, 39.2 mmol), $Ti(OiPr)_4$ (0.223 g, 0.785 mmol) and tetrahydrofuran (80 mL). The solution was allowed to stir for an additional hour at 20 °C. The reaction was quenched by slow addition of water (20 mL), then 20% aqueous sulphuric acid (50 mL) was added and the mixture stirred for 30 minutes. Diethyl ether (50 mL) was added and the layers were partitioned. The aqueous layer was washed further three times with diethyl ether (50 mL). The combined organic layers were washed twice with saturated sodium bicarbonate (50 mL), washed with brine (50 mL), dried over magnesium sulphate and concentrated under reduced pressure. The crude material was purified by flash column chromatography (eluent: petrol ether) to yield a mixture of the two diastereomers of ((2-bromo-1-methylcyclopropyl)methyl)benzene **S-4** (7.96 g, 35.4 mmol, 90%) as a colourless oil.

ν_{max}/cm^{-1} 1603 w, 1496 m, 1453 m, (Ar C=C), 704 s (Br-C); δ_H (200 MHz, $CDCl_3$) 7.28-7.09 (5H, m, ArH), 2.99-2.61 (3H, m, C*H*Br and CH_2Ph), 1.18-0.63 (5H, m, CH_2CHBr and CH_3); δ_C (50 MHz, $CDCl_3$) 139.6 (C), 138.6 (C), 129.3 (CH), 129.2 (CH), 128.3 (CH), 128.2 (CH), 126.3 (CH), 126.1 (CH), 44.0 (CH_2), 41.9 (CH_2), 29.9 (CH), 29.3 (CH), 22.6 (CH_3), 22.3 (CH_2), 22.0 (C), 21.8 (C), 21.5 (CH_2), 20.8 (CH_3).

((1-Methylcycloallyl)methyl)benzene 6



Potassium *tert*-butoxide (5.40 g, 48.0 mmol) and dimethyl sulfoxide (35 mL) were heated to 60 °C and allowed to stir for 30 minutes at this temperature until the solution became homogenous. The solution was cooled to room temperature and ((2-bromo-1-methylcyclopropyl)methyl)benzene **S-4** (7.78 g, 34.6 mmol) was added dropwise over a period of 1 hour. The reaction mixture was allowed to stir for 48 h at 20 °C, then quenched by addition of ice cold water (100 mL). Pentane (500 mL) was added and the layers partitioned. The aqueous layer was washed three times with pentane (50 mL). The combined organic layers were washed with water (50 mL x 3), brine (100 mL), dried over magnesium sulphate and concentrated under reduced pressure. The resulting yellow-orange oil was purified by flash column chromatography (pentane) to yield ((1-methylcycloallyl)methyl)benzene **6** (2.98 g, 20.7 mmol, 60%) as a colourless oil.

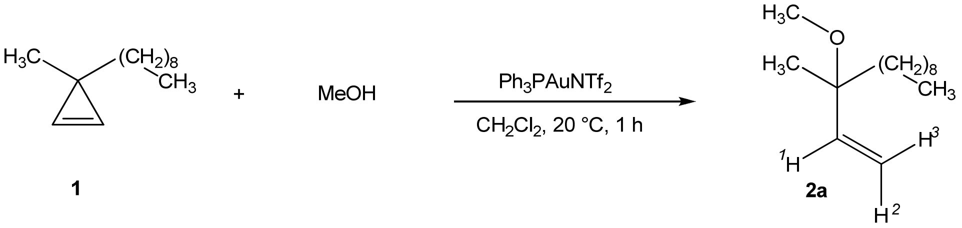
ν_{max}/cm^{-1} 1629 w (C=C), 1604 w, 1495 m, 1452 m, (Ar C=C); δ_H (200 MHz, $CDCl_3$) 7.28 (2H, s, C=C*H*), 7.25-7.00 (5H, m, ArH), 2.70 (2H, s, CH_2Ph), 1.12 (3H, s, CH_3); δ_C (50 MHz, $CDCl_3$) 141.1 (C), 129.2 (CH), 128.0 (CH), 125.5 (CH), 122.0 (CH), 47.7 (CH_2), 26.8 (CH_3), 21.6 (C); M^+(EI) = 143.0853 required *M* = 143.0855.

General Procedure: Gold(I) catalysed addition of alcohols to cyclopropene 1

Method A: Ph_3PAuCl (5 mol%) and AgOTf (5 mol%) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (1 eq.) and ROH (6 eq.) in dichloromethane (0.55 M). The reaction mixture was allowed to stir for 1-2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography to yield the corresponding *tert*-allylic ether product.

Method B: $Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (5 mol%) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (1 eq.) and ROH (6 eq.) in dichloromethane (0.55 M). The reaction mixture was allowed to stir for 1-2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography to yield the corresponding *tert*-allylic ether product.

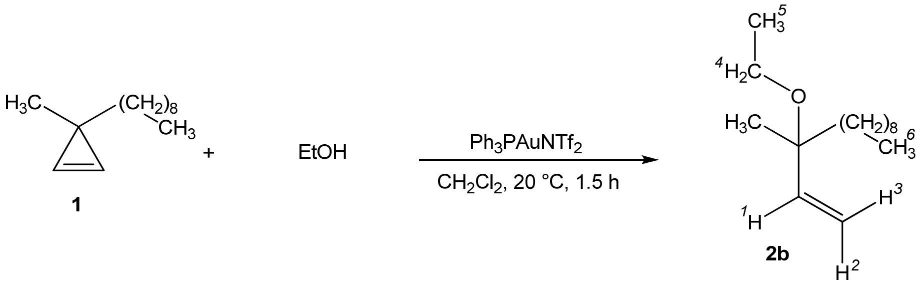
3-Methoxy-3-methyldodec-1-ene 2a



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (9.1 mg, 1.15 x 10^{-5} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (48.2 mg, 0.267 mmol) and methanol (48.5 mg, 1.51 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (95% petrol ether, 5% diethyl ether) to yield 3-methoxy-3-methyldodec-1-ene **2a** (49.0 mg, 0.231 mmol, 86%) as a colourless oil.

ν_{max}/cm^{-1} 1639 vw (C=C), 1079 s (C-O); δ_H (200 MHz, $CDCl_3$) 5.74 (1H, dd, *J* = 17.4, 10.8, H-1), 5.15 (1H, dd, *J* = 10.8, 1.7, H-2), 5.10 (1H, dd, *J* = 17.4, 1.7, H-3), 3.14 (3H, s, OCH_3), 1.33 - 0.81 (22H, m, alkyl-H); δ_C (50 MHz, $CDCl_3$) 143.0 (CH), 114.5 (CH_2), 77.4 (C), 50.0 (CH_3), 39.7 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.2 (CH_3), 14.1 (CH_3); M^+(EI) = 212.2153 required *M* = 212.2140.

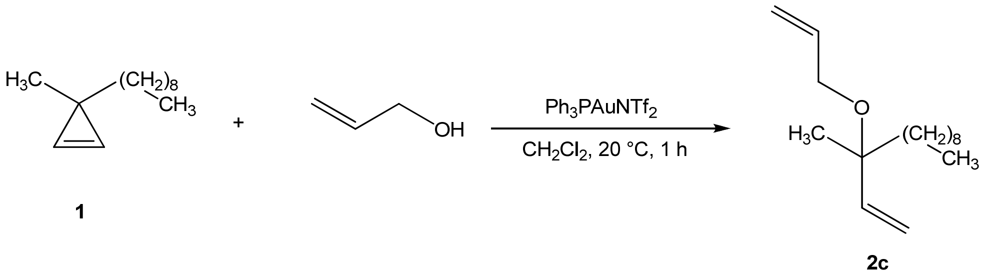
3-Ethoxy-3-methyldodec-1-ene 2b



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.7 mg, 1.49 x 10^{-5} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (53.6 mg, 0.297 mmol) and ethanol (85.9 mg, 1.86 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-ethoxy-3-methyldodec-1-ene **2b** (55.7 mg, 0.246 mmol, 83%) as a colourless oil.

ν_{max}/cm^{-1} 1660 vw (C=C), 1070 s (C-O); δ_H (200 MHz, $CDCl_3$) 5.76 (1H, dd, *J* = 17.0, 11.2, H-1), 5.12 (1H, dd, *J* = 11.2, 1.2, H-2), 5.08 (1H, dd, *J* = 17.0, 1.2, H-3), 3.32 (2H, q, *J* = 7.1, H-4), 1.62 – 1.19 (19H, m, alkyl-H), 1.14 (3H, t, *J* = 7.1, H-5), 0.87 (3H, t, *J* = 6.4, H-6); δ_C (50 MHz, $CDCl_3$) 143.7 (CH), 113.9 (CH_2), 77.2 (C), 57.3 (CH_2), 39.9 (CH_2), 31.9 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 27.6 (CH_2), 23.6 (CH_2), 22.6 (CH_2), 22.1 (CH_3), 16.0 (CH_3), 14.1 (CH_3); M^+(EI) = 226.2291 required *M* = 226.2292.

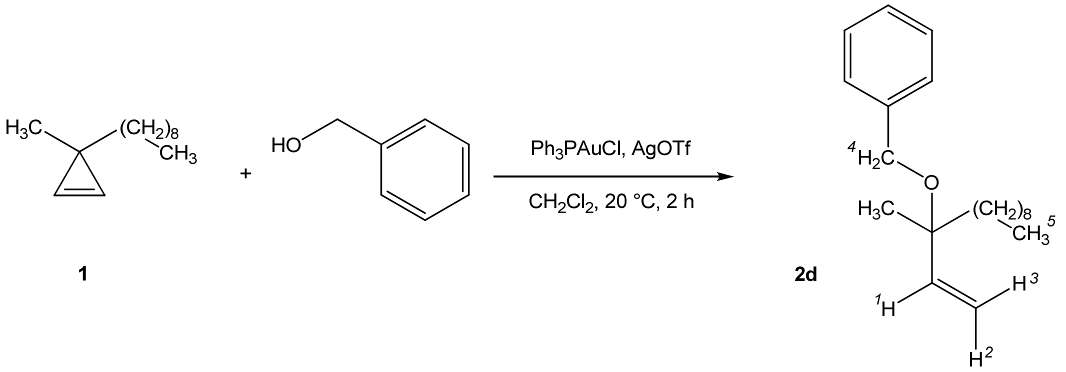
3-(Allyloxy)-3-methyldodec-1-ene 2c



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.0 mg, 1.40 x 10^{-5} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (50.0 mg, 0.277 mmol) and 2-propen-1-ol (97 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-(allyloxy)-3-methyldodec-1-ene **2c** (58.1 mg, 0.244 mmol, 88%) as a colourless oil.

ν_{max}/cm^{-1} 1712 vw (C=C), 1646 w (C=C), 1060 s (C-O); δ_H (200 MHz, $CDCl_3$) 6.00 - 5.70 (2H, m, C*H*=CH_2 x 2), 5.32 – 5.07 (4H, m, CH=CH_2 x 2), 3.82 (2H, dt, *J* = 5.4, 1.7, OCH_2), 1.50 – 1.16 (19H, m, alkyl-H), 0.87 (3H, t, *J* = 6.2, CH_2CH_3) ; δ_C (50 MHz, $CDCl_3$) 143.2 (CH), 136.0 (CH), 115.5 (CH_2), 114.4 (CH_2), 77.6 (C), 63.5 (CH_2), 40.1 (CH_2), 31.8 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.9 (CH_3), 14.1 (CH_3); $[M+NH_4]^+$(ESI) = 256.2636 required *M* = 256.2635.

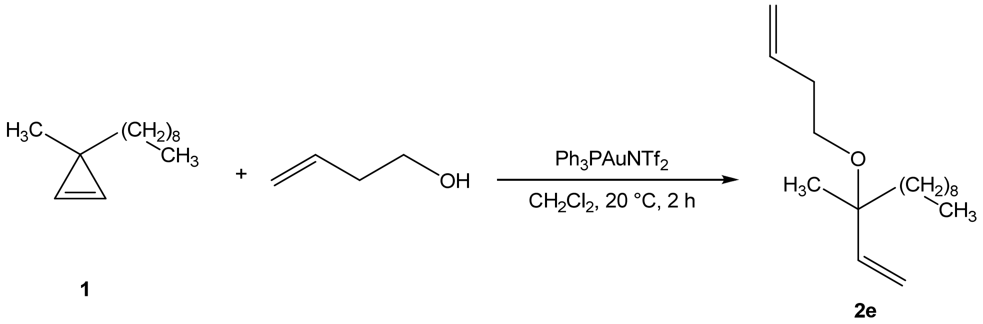
1-((3-Methyldodec-1-en-3-yloxy)methyl)benzene 2d



Ph_3PAuCl (7.2 mg, 14.6 μmol) and AgOTf (3.5 mg, 13.6 μmol) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (50.9 mg, 0.282 mmol) and phenylmethanol (180 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 2 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 1-((3-methyldodec-1-en-3-yloxy)methyl)benzene **2d** (63.5 mg, 0.220 mmol, 78%) as a colourless oil.

ν_{max}/cm^{-1} 1639 vw (C=C), 1607 vw, 1497 w, 1454 m, (Ar C=C), 1060 s (C-O); δ_H (400 MHz, $CDCl_3$) 7.38 – 7.24 (5H, m, aryl-H), 5.89 (1H, dd, *J* = 18.2, 10.3, H-1), 5.22 (1H, dd, *J* = 10.3, 1.2, H-2), 5.21 (1H, dd, *J* = 18.2, 1.2, H-3), 4.40 (2H, s, H-4), 1.67 – 1.25 (19H, m, alkyl-H), 0.91 (3H, t, *J* = 6.9, H-5) ; δ_C (100 MHz, $CDCl_3$) 143.4 (CH), 139.9 (C), 128.2 (CH), 127.2 (CH), 127.0 (CH), 114.6 (CH_2), 77.9 (C), 64.4 (CH_2), 40.2 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.7 (CH_2), 22.7 (CH_2), 22,1 (CH_3), 14.1 (CH_3); M^+(EI) = 288.2449 required *M* = 288.2453.

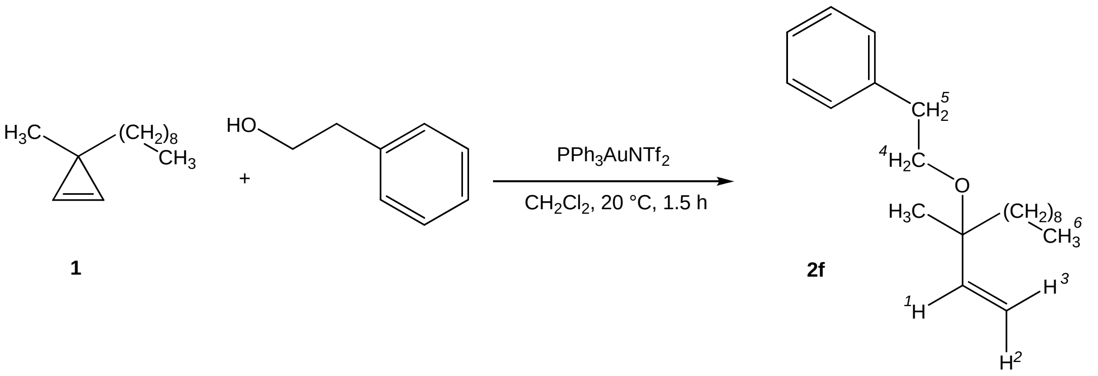
3-(But-3-enyloxy)-3-methyldodec-1-ene 2e



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.2 mg, 1.42 x 10^{-5} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (58.4 mg, 0.268 mmol) and 3-buten-1-ol (119 mg, 1.65 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-(but-3-enyloxy)-3-methyldodec-1-ene **2e** (59.6 mg, 0.236 mmol, 88%) as a colourless oil.

ν_{max}/cm^{-1} 1722 vw (C=C), 1641 w (C=C), 1083 s (C-O); δ_H (200 MHz, $CDCl_3$) 5.92 - 5.69 (2H, m, C*H*=CH_2 x), 5.15 – 4.96 (4H, m, CH=CH_2 x 2), 3.03 (2H, dt, *J* = 1.2, 7.1, OCH_2), 2.27 (2H, m, CH_2CH=CH_2), 1.50 – 1.18 (19H, m, alkyl-H), 0.87 (3H, t, *J* = 5.8, CH_2CH_3) ; δ_C (50 MHz, $CDCl_3$) 143.5 (CH), 135.7 (CH), 115.9 (CH_2), 114.1 (CH_2), 77.2 (C), 61.5 (CH_2), 39.9 (CH_2), 35.0 (CH_2), 31.8 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.9 (CH_3), 14.1 (CH_3); $[M+NH_4]^+$(ESI) = 270.2793 required *M* = 270.2791.

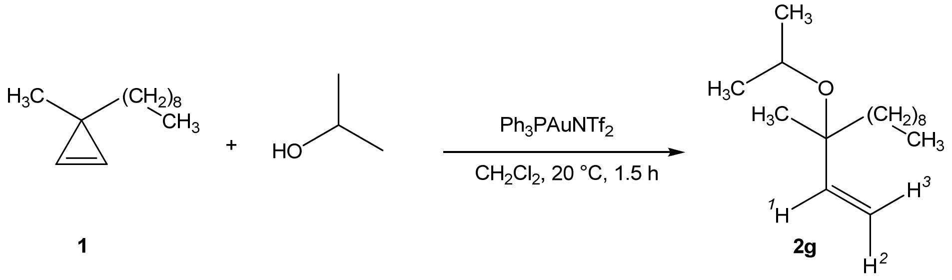
1-(2-(3-Methyldodec-1-en-3-yloxy)ethyl)benzene 2f



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.4 mg, 1.45 x 10^{-5} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (50.0 mg, 0.277 mmol) and 2-phenylethanol (203 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 1-(2-(3-methyldodec-1-en-3-yloxy)ethyl)benzene **2f** (64.5 mg, 0.213 mmol, 77%) as a colourless oil.

ν_{max}/cm^{-1} 1642 vw (C=C), 1605 vw, 1496 w, 1456 m, (Ar C=C), 1077 s (C-O); δ_H (200 MHz, $CDCl_3$) 7.25 – 7.07 (5H, m, aryl-H), 5.63 (1H, dd, *J* = 17.4, 10.8, H-1), 5.02 (1H, dd, *J* = 10.8, 1.2, H-2), 4.98 (1H, dd, *J* = 17.4, 1.2, H-3), 3.35 (2H, t, *J* = 7.5, H-4), 2.75 (2H, t, *J* = 7.5, H-5), 1.51 – 1.08 (19H, m, alkyl-H), 0.81 (3H, t, *J* = 6.5, H6) ; δ_C (50 MHz, $CDCl_3$) 143.4 (CH), 139.4 (C), 129.0 (CH), 128.1 (CH), 126.0 (CH), 114.2 (CH_2), 77.4 (C), 63.4 (CH_2), 40.0 (CH_2), 37.2 (CH_2), 31.9 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.9 (CH_3), 14.1 (CH_3); M^+(EI) = 302.2604 required *M* = 302.2603.

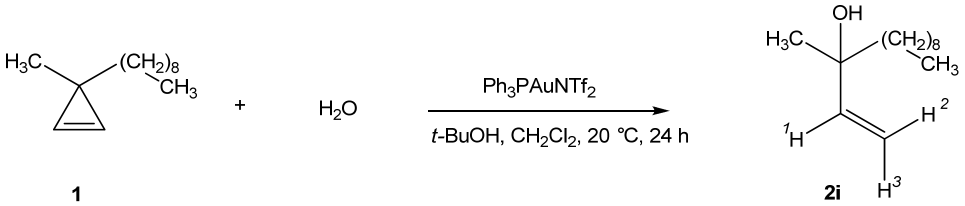
3-Isopropoxy-3-methyldodec-1-ene 2g



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.4 mg, 1.45 x 10^{-5} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (51.0 mg, 0.283 mmol) and propan-2-ol (107 mg, 1.78 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. ^{1}H-NMR analysis of the crude product showed 97:3 ratio of **2g** and **3g**. The solvent was evaporated and the residue was purified by flash column chromatography (90% petrol ether, 10% diethyl ether) to yield 3-isopropoxy-3-methyldodec-1-ene **2g** (47.7 mg, 0.198 mmol, 70%) as a colourless oil.

ν_{max}/cm^{-1} 1639 vw (C=C), 1102 s (C-O); δ_H (200 MHz, $CDCl_3$) 5.82 (1H, dd, J = 17.4, 11.2, H-1), 5.12 (1H, dd, J = 11.2, 1.2, H-2), 5.07 (1H, dd, J = 17.4, 1.2, H-3), 3.66 (1H, *septet*, J = 6.2, C*H*Me_2), 1.62 – 1.19 (19H, m, alkyl-H), 1.09 (3H, d, J = 6.2, CH_3), 1.07 (3H, d, J = 6.2, CH_3), 0.87 (3H, t, J = 6.0, CH_2CH_3); δ_C (50 MHz, $CDCl_3$) 144.2 (CH), 114.0 (CH_2), 77.9 (C), 64.2 (CH), 41.2 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 25.0 (CH_3), 24.9 (CH_3), 23.9 (CH_2), 22.7 (CH_2), 22.0 (CH_3), 14.1 (CH_3); M^+(EI) = 240.2448 required M = 240.2447.

3-Methyldodec-1-en-3-ol 2i

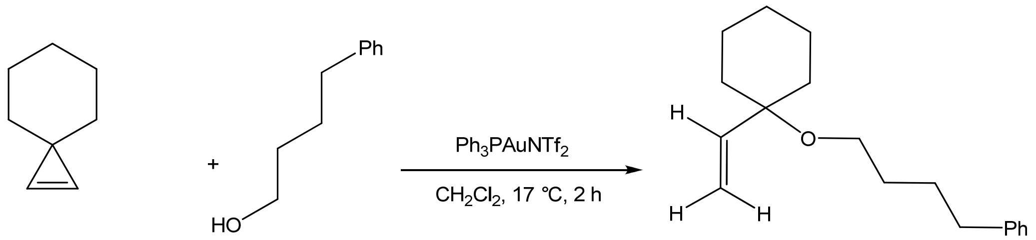


$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (5.8 mg, 7.37 x 10^{-6} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (25.2 mg, 0.140 mmol), water (16.1 mg, 0.893 mmol), *tert*-butanol[§] (154 mg, 2.07 mmol) and dichloromethane (0.2 mL). The reaction mixture was allowed to stir for 24 h at 20 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (50% petrol ether, 50% diethyl ether) to yield 3-methyldodec-1-en-3-ol **2i** (9.4 mg, 0.0474 mmol, 34%) as a colourless oil.

ν_{max}/cm^{-1} 3391 br (OH), 1641 vw (C=C); δ_H (200 MHz, CDCl$_3$) 5.91 (1H, dd, *J* = 17.4, 10.8, H-1), 5.19 (1H, dd, *J* = 17.4, 1.2, H-2), 5.04 (1H, dd, *J* = 10.8, 1.2, H-3), 1.59 – 1.16 (19H, m, alkyl-H), 0.87 (3H, t, *J* = 6.2, CH$_2$C*H*$_3$); δ_C (50 MHz, CDCl$_3$) 145.2 (CH), 111.4 (CH$_2$), 73.3 (C), 42.3 (CH$_2$), 31.8 (CH$_2$), 30.0 (CH$_2$), 29.6 (CH$_2$), 29.3 (CH$_2$), 27.6 (CH$_3$), 23.9 (CH$_2$), 22.6 (CH$_2$), 14.1 (CH$_3$); M$^+$(EI) = 198.1970 required *M* = 198.1984.

[§] *t*-BuOH was added as a co-solvent to homogenize the layers. In the absence of *t*-BuOH co-solvent, a lower yield of 17% was observed. This lower yield is probably due to the biphasic nature (H_2O/CH_2Cl_2) of the resulting reaction mixture.

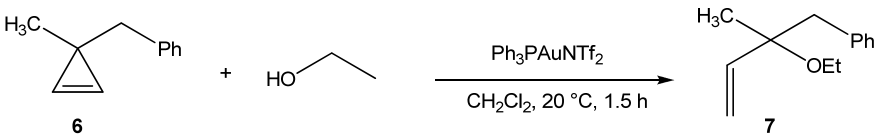
(4-(1-Vinylcyclohexyloxy)butyl)benzene 5



4 **5**

$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (7.7 mg, 9.74 x 10^{-6} mol) was added to a solution of spiro[2.5]oct-1-ene **4**[5] (20.0 mg, 0.185 mmol), 4-phenylbutan-1-ol (0.17 mL, 1.11 mmol) and dichloromethane (0.4 mL). The reaction mixture was allowed to stir for 2 h at ambient temperature (17 °C). Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% n-pentane, 2% diethyl ether) to yield (4-(1-vinylcyclohexyloxy)butyl)benzene **5** (41.5 mg, 0.161 mmol, 87%) as a colourless oil. ν_{max}/cm^{-1} 1638 vw (C=C), 1604 vw, 1495 w, 1451 m, (Ar C=C), 1073 s (C-O); δ_H (400 MHz, $CDCl_3$) 7.21-7.07 (5H, m, ArH), 5.64 (1H, dd, J = 17.7, 11.0, C*H*=CH_2), 5.04 (2H, m, CH=C*H*$_2$), 3.16 (2H, t, J = 6.5, OCH_2), 2.56 (2H, t, J = 7.6, $PhCH_2$), 1.69 – 1.11 (14H, m, CH_2); δ_C (100 MHz, $CDCl_3$) 143.8 (CH), 142.7 (C), 128.4 (CH), 128.2 (CH), 125.6 (CH), 114.2 (CH_2), 75.2 (C), 61.0 (CH_2), 35.9 (CH_2), 34.3 (CH_2), 30.1 (CH_2), 28.3 (CH_2), 25.8 (CH_2), 21.9 (CH_2); $[M+ NH_4]^+$ (ESI) = 276.2326 required $[M+ NH_4]^+$ = 276.2322.

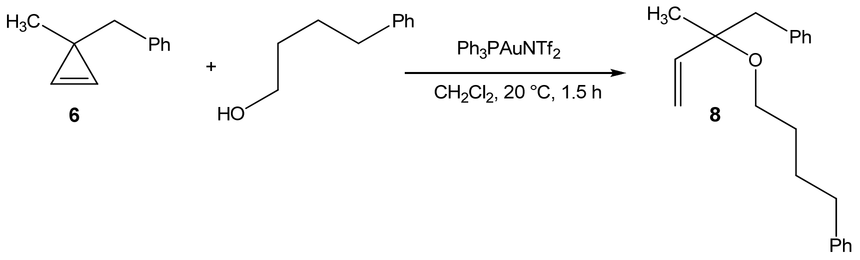
2-Ethoxy-2-methylbut-3-enyl)benzene 7



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.0 mg, 1.4 x 10^{-5} mol) was added to a solution of ((1-methylcycloallyl)methyl)benzene **6** (39.0 mg, 0.270 mmol) and ethanol (77 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The crude product was filtered through a plug of silica (eluent: diethyl ether) and a crude ^{1}H-NMR spectra was obtained. The solvent was evaporated and the residue was purified by flash column chromatography (98% pentane, 2% diethyl ether) to yield 2-ethoxy-2-methylbut-3-enyl)benzene **7** (40.9 mg, 0.215 mmol, 80%) as a colourless oil.

ν_{max}/cm^{-1} 1646 vw (C=C), 1602 vw, 1495 w, 1454 w, (Ar C=C), 1063 s (C-O); δ_H (200 MHz, $CDCl_3$) 7.22-7.02 (5H, m, ArH), 5.71 (1H, dd, J = 17.4, 10.8, CH=CH_2), 5.07 (1H, dd, J = 10.8, 1.2, CH=CHH_{cis}), 4.96 (1H, dd, J = 17.4, 1.2, CH=CHH_{trans}), 3.31 (2H, q, J = 6.6, OCH_2), 2.80 (1H, d, J = 13.3, CHHPh), 2.71 (1H, d, J = 13.3, CHHPh), 1.11 (3H, s, CH_3), 1.10 (3H, t, J = 6.6, OCH_2CH_3); δ_C (50 MHz, $CDCl_3$) 142.9 (CH), 137.6 (C), 130.8 (CH), 127.6 (CH), 126.0 (CH), 114.7 (CH_2), 57.6 (CH_2), 47.2 (CH_2), 21.1 (CH_3), 15.9 (CH_3). $[M-H]^+$ = 189.1274 required $[M-H]^+$ = 189.1274.

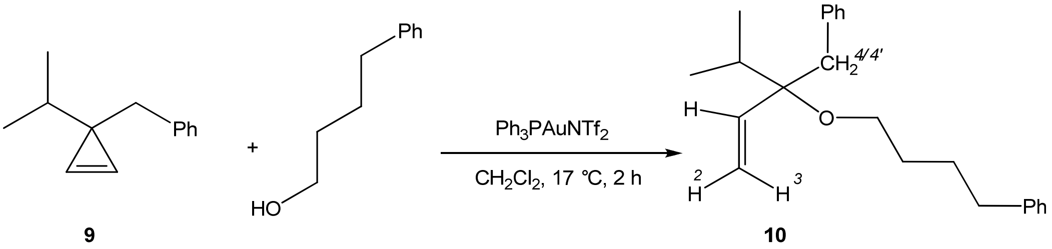
(4-(2-Methyl-1-phenylbut-3-en-2-yloxy)butyl)benzene 8



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (13.4 mg, 1.7 x 10^{-5} mol) was added to a solution of ((1-methylcycloallyl)methyl)benzene **6** (46.8 mg, 0.325 mmol) and 4-phenyl-1-butanol (0.3 mL, 1.95 mmol) in dichloromethane (0.7 mL). The reaction mixture was allowed to stir for 1.5 h at 20 °C. The crude product was filtered through a plug of silica (eluent: diethyl ether) and a crude ^{1}H-NMR spectra was obtained. The solvent was evaporated and the residue was purified by flash column chromatography (98% pentane, 2% diethyl ether) to yield (4-(2-methyl-1-phenylbut-3-en-2-yloxy)butyl)benzene **8** (82.4 mg, 0.284 mmol, 86%) as a colourless oil.

ν_{max}/cm^{-1} 1630 vw (C=C), 1603 w, 1495 m, 1453 m, (Ar C=C), 1077 s (C-O); δ_H ($CDCl_3$, 200 MHz) δ 7.34 - 7.14 (10H, m, Ar-H), 5.78 (1H, dd, *J* = 17.6, 10.9, $\underline{H}C=CH_2$), 5.15 (1H, dd, *J* = 10.9, 1.3, $HC=C\underline{H}_2$), 5.05 (1H, dd, *J* = 17.6, 1.3, $HC=C\underline{H}_2$), 3.34 (2H, t, *J* = 6.3, $O-C\underline{H}_2$), 2.82 (2H, dd, *J* = 15.5, 2.2 $Ar-C\underline{H}_2-C$), 2.63 (2H, t, *J* = 7.2, $Ar-C\underline{H}_2-CH_2$), 1.64 (4H, m, $C\underline{H}_2$), 1.19, (3H, s, $C\underline{H}_3$); δ_C ($CDCl_3$, 50 MHz) δ 143.2 (CH), 142.9 (C), 137.9 (C), 131.1 (CH), 128.6 (CH), 128.4 (CH), 127.8 (CH), 126.3 (CH), 125.8 (CH), 115.0 (CH_2), 77.6 (C), 62.2 (CH_2), 47.8 (CH_2), 36.0 (CH_2), 30.3 (CH_2), 28.4 (CH_2), 21.1 (CH_3); $[M + NH_4]^+$ = 312.2326 required $[M + NH_4]^+$ = 312.2322.

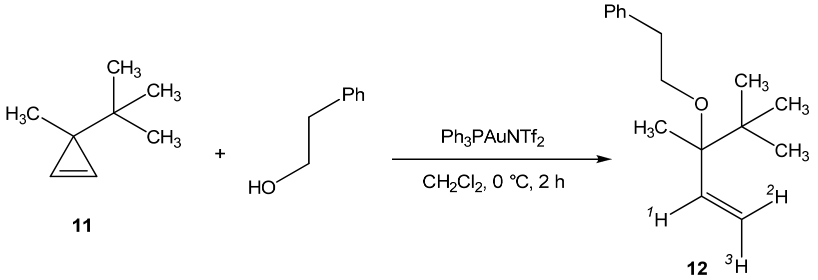
(4-(3-Benzyl-4-methylpent-1-en-3-yloxy)butyl)benzene 10



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (7.2 mg, 9.16 x 10^{-6} mol) was added to a solution of ((1-isopropylcycloallyl)methyl)benzene **9** (30.0 mg, 0.174 mmol), 4-phenylbutan-1-ol (0.16 mL, 1.02 mmol) and dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 2 h at 17 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (99% n-pentane, 1% diethyl ether) to yield (4-(3-benzyl-4-methylpent-1-en-3-yloxy)butyl)benzene **10** (40.8 mg, 0.127 mmol, 73%) as a colourless oil.

ν_{max}/cm^{-1} 1639 vw (C=C), 1603 w, 1496 m, 1453 m, (Ar C=C), 1080 s (C-O); δ_H (200 MHz, $CDCl_3$) 7.36-7.11 (10H, m, Ar-$\underline{H}$), 5.77 (1H, dd, *J* = 17.7, 11.3, $\underline{H}C=CH_2$), 5.27 (1H, dd, *J* = 11.3, 1.6, H-2), 5.13 (1H, dd, *J* = 17.7, 1.6, H-3), 3.42 (2H, m, O-CH_2), 3.03 (1H, d, *J* = 14.8, H-4), 2.84 (1H, d, *J* =14.8, H-4'), 2.63 (2H, t, *J* = 7.1, Ph-$C\underline{H}_2$), 1.95-1.50 (5H, m, 2x$C\underline{H}_2$ + $\underline{H}C(CH_3)_2$), 0.88 (3H, d, *J* = 6.8, HC-$(C\underline{H}_3)_2$), 0.82 (3H, d, *J* = 6.8, HC-$(C\underline{H}_3)_2$); δ_C (100 MHz, $CDCl_3$) 142.7 (C), 139.0 (CH), 137.9 (C), 130.5 (CH), 128.4 (CH), 128.2 (CH), 127.8 (CH), 125.9 (CH), 125.6 (CH), 116.5 (CH_2), 81.8 (C), 61.4 (CH_2), 36.6 (CH_2), 35.8 (CH_2), 32.7 (CH), 29.9 (CH_2), 28.2 (CH_2), 17.6 (CH_3), 16.8 (CH_3); $[M+NH_4]^+$ (ESI) = 340.2639 required $[M+NH_4]^+$ = 340.2635.

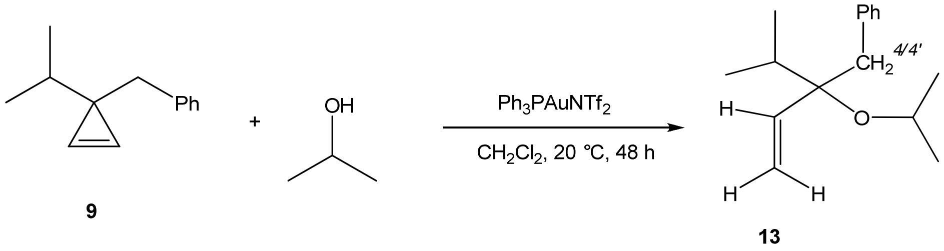
(4-(3,4,4-Trimethylpent-1-en-3-yloxy)butyl)benzene 12



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (11.6 mg, 1.47 x 10^{-5} mol) was added to a solution of 3-tert-butyl-3-methylcycloprop-1-ene **11**[4] (30.8 mg, 0.280 mmol), phenethyl alcohol (0.20 mL, 1.680 mmol) and dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 2 h at 0 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% n-pentane, 2% diethyl ether) to yield (4-(3,4,4-trimethylpent-1-en-3-yloxy)butyl)benzene **12** (41.5 mg, 0.179 mmol, 64%) as a colourless oil.

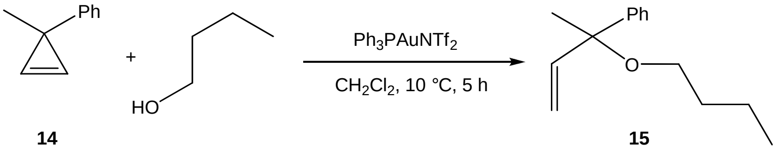
ν_{max}/cm^{-1} 1642 vw (C=C), 1605 vw, 1496 w, 1454 m (Ar C=C), 1064 s (C-O); δ_H (200 MHz, $CDCl_3$) 7.14-7.30 (5H, m, ArH), 5.72 (1H, dd, *J* = 17.7, 11.1, H-1), 5.14 (1H, dd, *J* = 17.7, 1.7, H-2), 4.95 (1H, dd, *J* = 11.1, 1.7, H-3), 3.44 (2H, m, OCH_2), 2.79 (2H, t, *J* = 6.9, $C\mathit{H}_2Ph$), 1.13 (3H, s, $C\mathit{H}_3$), 0.87 (9H, s, $C(C\mathit{H}_3)_3$); δ_C (100 MHz, $CDCl_3$) 141.4 (CH), 140.1 (C), 129.0 (CH), 128.0 (CH), 125.8 (CH), 115.7 (CH_2), 81.2 (C), 63.4 (CH_2), 37.8 (C), 37.3 (CH_2), 25.5 (CH_3), 15.8 (CH_3); $[M+ NH_4]^+$ (ESI) = 250.2165 required $[M+ NH_4]^+$ = 250.2168.

(2-Isopropoxy-2-isopropylbut-3-enyl)benzene 13



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (6.2 mg, 7.93 x 10^{-6} mol) was added to a solution of ((1-isopropylcycloallyl)methyl)benzene **9** (26 mg, 0.151 mmol), propan-2-ol (69 μL, 0.906 mmol) and dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 48 h at 20 °C. Then, the solvent was evaporated and the residue was purified twice by flash column chromatography (99% n-pentane, 1% diethyl ether) to yield (2-isopropoxy-2-isopropylbut-3-enyl)benzene **13a** (15.6 mg, 0.0672 mmol, 45%) as a pale green oil. ν_{max}/cm^{-1} 1637 vw (C=C), 1602 w, 1495 m, 1454 m, (Ar C=C), 1076 s (C-O); δ_H (400 MHz, $CDCl_3$) 7.47-7.11 (5H, m, Ar-H), 5.93 (1H, dd, *J* = 17.9, 11.4, $\underline{H}C{=}CH_2$), 5.35 (1H, dd, *J* = 11.4, 1.3, $HC{=}CH\underline{H}$), 5.26 (1H, dd, *J* = 17.9, 1.3, $HC{=}C\underline{H}H$), 3.93 (1H, septet, *J* = 6.2, $O\text{-}C\underline{H}(CH_3)_2$), 3.05 (1H, d, *J* = 14.9, H-4), 2.94 (1H, d, *J* =14.9, H-4’), 1.89 (1H, septet, *J* = 6.8, $C\underline{H}(CH_3)_2$), 1.21 (3H, d, *J* = 6.2, $CH(C\underline{H}_3)_2$), 1.18(3H, d, *J* = 6.2, $CH(C\underline{H}_3)_2$), 0.96 (3H, d, *J* = 6.8, $CH(C\underline{H}_3)_2$), 0.76 (3H, d, *J* = 6.8, $CH(C\underline{H}_3)_2$); δ_C (100 MHz, $CDCl_3$) 139.5 (CH), 130.8 (C), 128.4 (CH), 127.7 (CH), 125.9 (CH), 116.3 (CH_2), 82.8 (C), 77.2 (CH), 38.2 (CH_2), 32.8 (CH), 25.2 (CH_3), 21.9 (CH_3), 17.3 (CH_3), 17.2 (CH_3); $[M+H]^+$ = 233.1902 required $[M+H]^+$ = 233.1900.

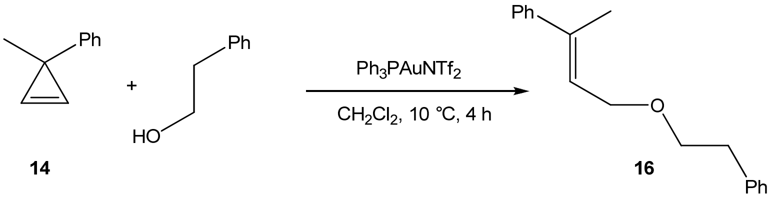
((2-Butoxybut-3-en-2-yl)benzene 15



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (6.4 mg, 8.09 x 10^{-6} mol) was added to a solution of (1-methylcycloallyl)benzene **14** (20.0 mg, 0.154 mmol), butan-1-ol (0.21 mL, 2.310 mmol) and dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 5 h at 10 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (99.2% n-pentane, 0.8% diethyl ether) to yield ((2-Butoxybut-3-en-2-yl)benzene **15** (20.4 mg, 0.100 mmol, 65%) as a colourless oil.

δ_H (400 MHz, $CDCl_3$) 7.45 (2H, m, Ar-H), 7.35-7.25 (3H, m, Ar-H), 6.04 (1H, dd, *J* = 17.5, 10.7, HC=CH_2), 5.27 (1H, dd, *J* = 17.5, 1.4, HC=CHH), 5.23 (1H, dd, *J* = 10.7, 1.4, HC=CHH), 3.32 (2H, m, O-CH_2), 1.62 (3H, s, O-C-CH_3), 1.40 (2H, m, CH_2), 0.93 (5H, m, CH_2CH_3); δ_C (100 MHz, $CDCl_3$) 145.3 (C), 143.4 (CH), 128.0 (CH), 126.8 (CH), 126.2 (CH), 114.0 (CH_2), 78.7 (C), 62.4 (CH_2), 32.6 (CH_2), 24.3 (CH_3), 19.5 (CH_2), 14.0 (CH_3); $[M+H]^+$(EI) = 205.1587 required $[M+H]^+$ = 205.1587.

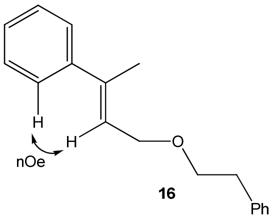
(*E*)-(4-Phenethoxybut-2-en-2-yl)benzene 16



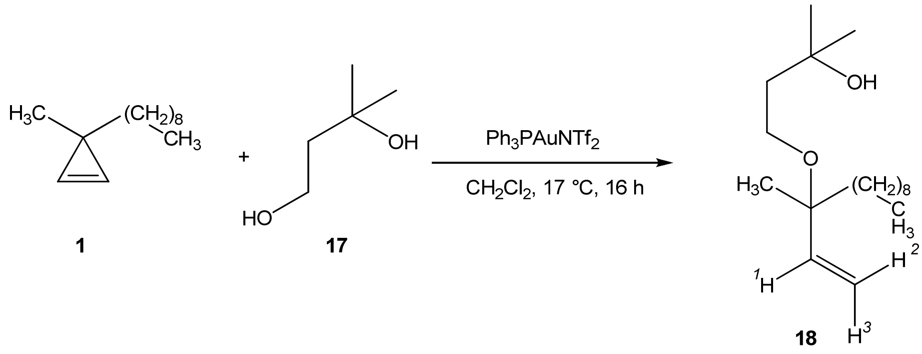
$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (6.4 mg, 8.09 x 10^{-6} mol) was added to a solution of (1-methylcycloallyl)benzene **14** (20.0 mg, 0.154 mmol), 2-phenylethanol (0.28 mL, 2.310 mmol) and dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 4 h at 10 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% n-pentane, 2% diethyl ether) to yield (*E*)-(4-phenethoxybut-2-en-2-yl)benzene **16** (25.3 mg, 0.100 mmol, 65%) as a colourless oil.

ν_{max}/cm^{-1} 1648 vw (C=C), 1602 w, 1495 m, 1453 m, (Ar C=C), 1097 s (C-O); δ_H (400 MHz, $CDCl_3$) 7.45 – 7.17 (10H, m, Ar-$\underline{H}$), 5.95 (1H, tq, *J* = 6.5, 1.4, C=C$\underline{H}$), 4.25 (2H, d, *J* = 6.6, HC-C$\underline{H_2}$-O), 3.74 (2H, t, *J* = 7.3, O-C$\underline{H_2}$CH$_2$), 2.97 (2H, t, *J* = 7.3, O-CH$_2$C$\underline{H_2}$), 2.09 (3H, d, *J* = 1.4, C$\underline{H_3}$); δ_C (100 MHz, $CDCl_3$) 143.0 (C), 139.0 (C), 138.1 (C), 128.9 (CH), 128.4 (CH), 128.2 (CH), 127.2 (CH), 126.2 (CH), 125.8 (CH), 124.5 (CH), 71.4 (CH$_2$), 68.0 (CH$_2$), 36.5 (CH$_2$), 16.2 (CH$_3$); $[M+ NH_4]^+$ = 270.1853 required *M* = 270.1852.

E Stereochemistry confirmed by 400 MHz NOESY:

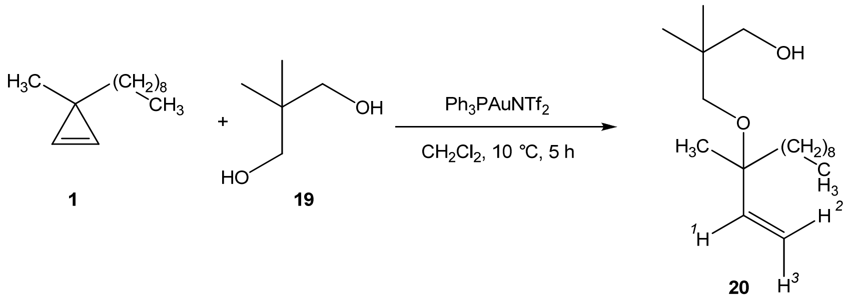


2-Methyl-4-(3-methyldodec-1-en-3-yloxy)butan-2-ol 18



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (5.8 mg, 7.8 x 10^{-6} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (50.4 mg, 0.28 mmol), 3-methyl-1,3-butandiol (90 µL, 0.84 mmol), and dichloromethane (0.5 mL). The reaction mixture was allowed to stir for 16 h at 17 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (6:1 n-pentane / diethyl ether) to yield 2-methyl-4-(3-methyldodec-1-en-3-yloxy)butan-2-ol **18** (45.6 mg, 0.16 mmol, 58%) as a colourless oil. ν_{max}/cm^{-1} 3452 br (OH), 1632 vw (C=C), 1076 s (C-O); δ_H (200 MHz, $CDCl_3$) 5.75 (1H, dd, J = 17.5, 11.0, H-1), 5.16 (1H, dd, J = 11.0, 1.3, H-3), 5.08 (1H, dd, J = 17.5, 1.3, H-2), 3.92 (1H, s, OH), 3.52 (2H, m, $\underline{H}_2C$-O) , 1.68 (2H, t, J = 5.8, H_2C-($C\underline{H}_2$)-C) 1.59 – 1.10 (25H, m, alkyl-H), 0.84 (3H, t, J = 6.1, $CH_2C\underline{H}_3$); δ_C (100 MHz, $CDCl_3$) 142.6 (CH), 114.8 (CH_2), 77.9 (C), 70.6 (C), 59.6 (CH_2), 41.5 (CH_2), 40.2 (CH_2), 31.9 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.5 (CH_2), 29.3 (CH_3), 29. 2 (CH_3), 23.6 (CH_2), 22.7 (CH_2), 21.4 (CH_3), 14.1 (CH_3); $[M+Na]^+$ (ESI) = 307.2604 required $[M+Na]^+$ = 307.2608.

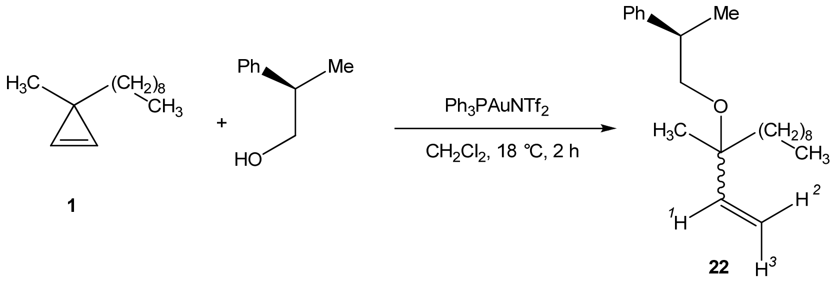
2,2-Dimethyl-3-(3-methyldodec-1-en-3-yloxy)propan-1-ol 20



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (5.8 mg, 7.35 x 10^{-6} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (25.2 mg, 0.14 mmol), neopentyl glycol (87.4 mg, 0.84 mmol), and dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 5 h at 10 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (7:1 n-pentane / diethyl ether) to yield 2,2-Dimethyl-3-(3-methyldodec-1-en-3-yloxy)propan-1-ol **20** (13.0 mg, 0.046 mmol, 33%) as a colourless oil.

ν_{max}/cm^{-1} 3383 br (OH), 1639 vw (C=C), 1070 s (C-O); δ_H (400 MHz, $CDCl_3$) 5.74 (1H, dd, *J* = 17.6, 10.9, H-1), 5.16 (1H, dd, *J* = 11.0, 1.3, H-3), 5.10 (1H, dd, *J* = 17.6, 1.3, H-2), 3.44 (2H, d, *J* = 5.2, OCH_2), 3.20 – 3.12 (3H, m, OCH_2 and OH), 1.56 – 1.47 (2H, m, CH_2), 1.37 – 1.23 (14H, m, alkyl-H), 1.22 (3H, s, CH_3), 0.91 (3H, s, CH_3), 0.90 (3H, s, CH_3), 0.88 (3H, t, *J* = 6.9 Hz, CH_2CH_3); δ_C (101 MHz, $CDCl_3$) 142.9 (CH), 114.7 (CH_2), 77.5 (C), 72.9 (CH_2), 72.2 (CH_2), 40.1 (CH_2), 35.6 (C), 31.9 (CH_2), 30.3 (CH_2), 30.1 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 22.1 (CH_3), 22.0 (CH_3), 21.6 (CH_3), 14.1 (CH_3); $[M+Na]^+$ (ESI) = 307.2611 required $[M+Na]^+$ = 307.2608.

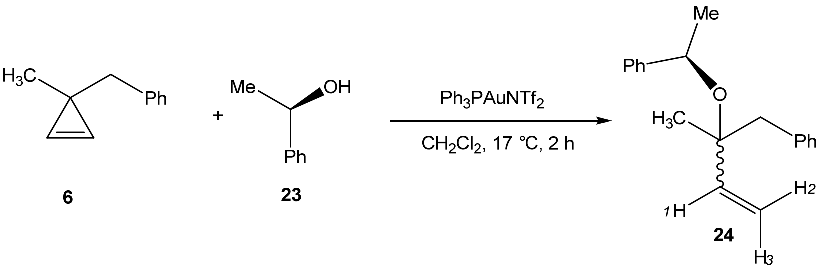
((2*R*)-1-(3-Methyldodec-1-en-3-yloxy)propan-2-yl)benzene 22



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (5.8 mg, 7.37 x 10^{-6} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (25.2 mg, 0.140 mmol) and (*R*)-2-phenyl-1-propanol (0.12 mL, 0.84 mmol) in dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 2 h at 18 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% *n*-pentane, 2% diethyl ether) to yield a 1:1 inseparable mixture of the diastereomers **22** (28.7 mg, 0.0908 mmol, 65%) as a colourless oil.

ν_{max}/cm^{-1} 1635 vw (C=C), 1604 vw, 1495 w, 1453 m, (Ar C=C), 1080 s (C-O); δ_H (400 MHz, $CDCl_3$) 7.09-7.23 (5H x 2, m, Ar-H), 5.64 (1H, dd, *J* = 17.6, 10.8, H-1), 5.58 (1H, dd, *J* = 17.6, 10.8, H-1’), 5.04-4.93 (2H x 2, m, H-2, H-3), 3.34-3.27 (1H x 2, m, C*H*HO), 3.22-3.15 (1H x 2, m, CH*H*O), 2.88-2.79 (1H x 2, m, C*H*Ph), 1.35-1.45 (2H x 2, m, CH_2), 1.23-1.14 (17H x 2, m, CH_2, CH_3), 1.10 (3H x 2, *J* = 11.2, CH_3CHPh), 0.81 (3H, t, *J* = 6.4, CH_2CH_3); δ_C (100 MHz, $CDCl_3$) 145.0 (C), 144.95 (C), 143.69 (CH), 143.66 (CH), 128.14 (CH), 128.12 (CH), 127.49 (CH), 127.47 (CH), 126.1 (CH x 2), 114.1 (CH_2), 114.0 (CH_2), 77.2 (C), 77.1 (C), 69.2 (CH_2 x 2), 40.6 (CH x 2), 40 2 (CH_2), 40.0 (CH_2), 31.9 (CH_2 x 2), 30.1 (CH_2 x 2), 29.62 (CH_2), 29.59 (CH_2), 29.3 (CH_2 x 2), 23.54 (CH_2), 23.52 (CH_2), 22.7 (CH_2 x 2), 22.0 (CH_3), 21.9 (CH_3), 18.28 (CH_3), 18.25 (CH_3), 14.11 (CH_3 x 2); $[M+NH_4]^+$ (ESI) = 334.3106 required $[M+NH_4]^+$ = 334.3104.

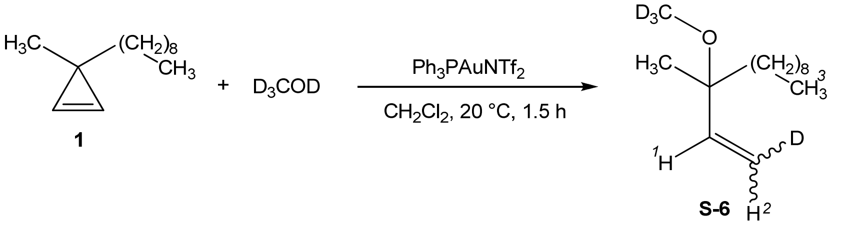
(*R*)-(1-(2-Methyl-1-phenylbut-3-en-2-yloxy)ethyl)benzene 24



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (6.2 mg, 7.88 x 10^{-6} mol) was added to a solution of ((1-methylcycloallyl)methyl)benzene **6** (21.6 mg, 0.150 mmol) and (*R*)-sec-phenethyl alcohol (0.11 mL, 0.90 mmol) in dichloromethane (0.3 mL). The reaction mixture was allowed to stir for 2 h at 17 °C. Then, the solvent was evaporated and the residue was purified by flash column chromatography (98% *n*-pentane, 2% diethyl ether) to yield a 1:1 inseparable mixture of the diastereomers **24** (18.2 mg, 0.0684 mmol, 46%, dr 1:1) as a yellow oil.

ν_{max}/cm^{-1} 1668 vw (C=C), 1605 vw, 1493 w, 1452 m, (Ar C=C), 1091 s (C-O); δ_H (400 MHz, $CDCl_3$) 7.40 – 7.16 (5H x 2, m, Ar-H), 5.90 (1H, dd, *J* = 17.9, 10.9, H-1), 5.58 (1H, dd, *J* = 17.9, 10.6, H-1'), 5.23 (1H, dd, *J* = 10.9, 1.5, H-3), 5.10 (1H, dd, *J* = 17.9, 1.3, H-2), 5.00 (1H, dd, *J* = 17.9, 1.5, H-2'), 4.99 (1H, dd, *J* = 10.6, 1.5, H-3'), 4.60 (1H, m, HCO), 2.90 (2H x 2, m, CH_2Ph), 1.39 (3H, d, *J* = 6.5, H_3C-CH), 1.37 (3H, d, *J* = 6.5, H_3C-CH), 1.32 (3H, s, CH_3), 0.96 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 147.6 (C), 147.0 (C), 143.2 (CH), 143.1 (CH), 137.7 (2 x C), 131.1 (CH), 131.1 (CH), 128.0 (CH), 128.0 (CH), 127.5 (CH), 127.5 (CH), 126.4 (CH), 126 .1 (CH), 125.8 (2 x CH), 125.5 (2 x CH), 115.1 (CH_2), 114.6, (CH_2), 79.2 (C), 77.2 (C), 71.0 (CH), 70.7 (CH), 49.1 (CH_2), 48.7 (CH_2), 26.6 (CH_3), 26.5 (CH_3), 21.8 (CH_3), 21.7 (CH_3); $[M+ NH_4]^+$ (ESI) = 284.2012 required $[M+ NH_4]^+$ = 284.2009.

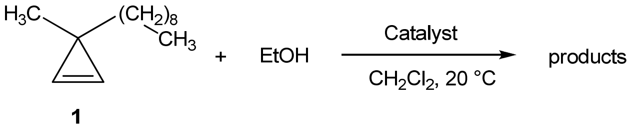
Reaction with CD_3OD



$Ph_3PAuNTf_2$ (as the 2:1 toluene adduct) (4.4 mg, 5.6 x 10^{-6} mol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (100 mg, 0.555 mmol) and d_4-methanol (0.14 mL, 3.33 mmol) in dichloromethane (1 mL) with 3 Å molecular sieves. The reaction mixture was allowed to stir for 1.5 h at 20 °C. The solvent was evaporated and the product purified by column chromatography (diethyl ether) to yield **S-3** (47 mg, 0.22 mmol, 40%) as a mixture of the *E* and *Z* isomers (ratio 1:1, 90% D incorporation) as a colourless oil.

ν_{max}/cm^{-1} 2198 w (C-D), 2063 m (C-D), 1639 vw (C=C), 1117 s (C-O); δ_H (400 MHz, $CDCl_3$) 5.77 – 5.70 (1H, m, H-1), 5.15 (1H, d, *J* = 10.9, H-2_{cis}), 5.09 (1H, d, *J* = 17.7, H-2_{trans}), 1.55 – 1.20 (19H, m, alkyl-H), 0.87 (3H, t, *J* = 6.7, H-3); δ_C (50 MHz, $CDCl_3$) 142.9 (*C*H=CHD), 114.2 (t, *J* = 24.0, CH=*C*HD), 77.3 (*C*OCD_3), 49.1 (septet, *J* = 21.4, *C*D_3), 39.7 (CH_2), 31.9 (CH_2), 30.2 (CH_2), 29.6 (CH_2), 29.3 (CH_2), 23.6 (CH_2), 22.7 (CH_2), 21.3 (CH_3), 14.1 (CH_3); M^+(EI) = 216.2.

Control Reactions



Catalyst: Trifluoromethanesulfonic acid

Trifluoromethanesulfonic acid (21 μL of a 0.666 M solution in dichloromethane, 14.0 μmol) were added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (48.9 mg, 0.271 mmol) and ethanol (77.2 mg, 1.68 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and there was no sign of any product formed. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether). Analysis of the crude mixture by ^{1}H-NMR (200 MHz, $CDCl_3$) showed that no reaction took place (>95% of starting material).

Catalyst: AgOTf

AgOTf (3.7 mg, 14.4 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (48.3 mg, 0.268 mmol) and ethanol (70.1 mg, 1.72 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of product were detected. After a further 22.5 h at room temperature the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 48.4 mg of a mixture of unreacted **1**:**2b** (7:4 ratio) along with traces of **3b**, **25** and other unidentified by-products. The products were identified and ratios determined by ^{1}H-NMR (200 MHz, $CDCl_3$).

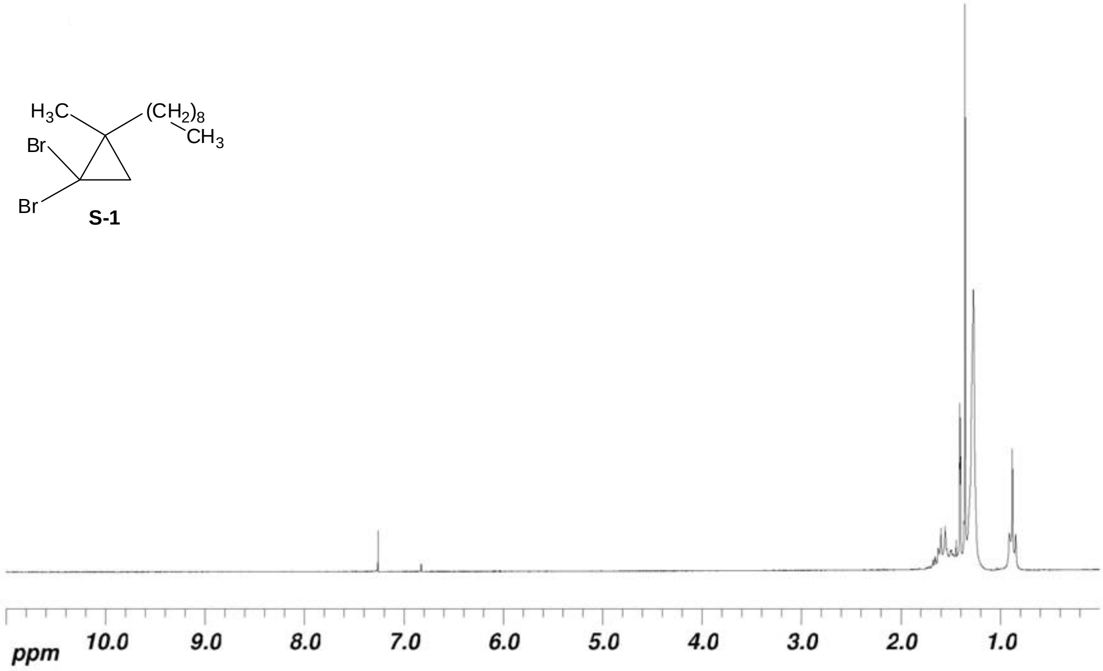
Catalyst: $Rh(OAc)_2$

$[Rh(OAc)_2]_2$ (3.1 mg, 7.01 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (47.3 mg, 0.262 mmol) and ethanol (76.3 mg, 1.66 mmol) in dichloromethane (0.5 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of products were detected. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 18.4 mg of a mixture of **25** along with traces of **3b** and **2b**. The products were identified by ^{1}H-NMR (200 MHz, $CDCl_3$) analysis of the crude mixture.

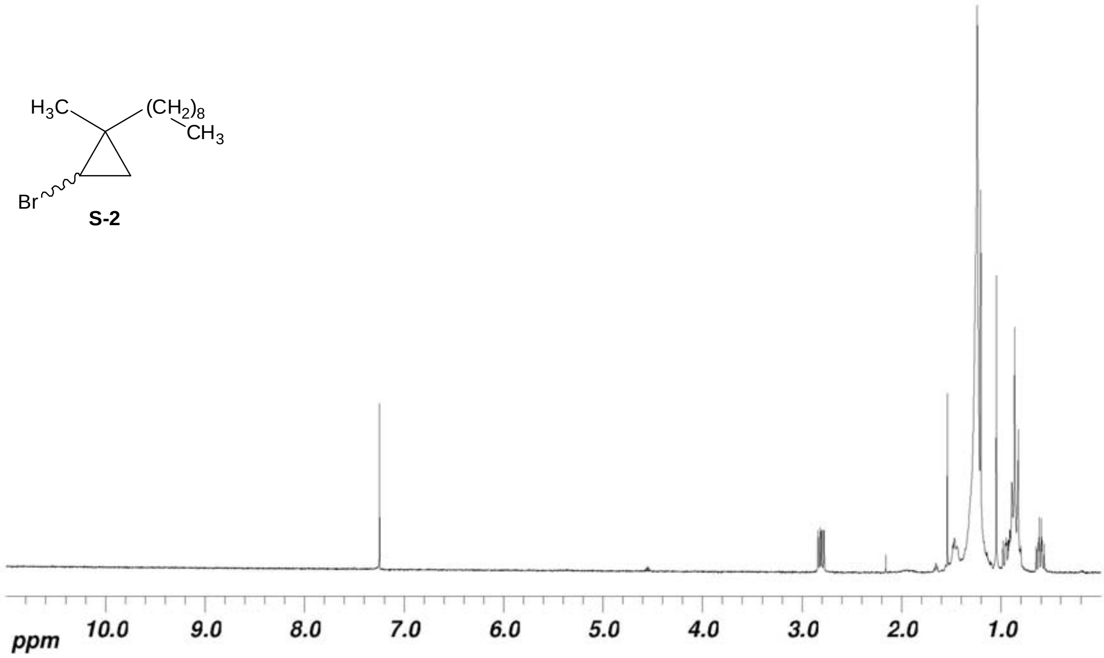
Catalyst: $AuCl_3$

$AuCl_3$ (1.7 mg, 5.60 μmol) was added to a solution of 3-methyl-3-nonylcycloprop-1-ene **1** (21.7 mg, 0.120 mmol) and ethanol (34.7 mg, 0.753 mmol) in dichloromethane (0.2 mL). The reaction mixture was allowed to stir at 20 °C. After 1.5 h the reaction was monitored by TLC (eluent: 90% petrol ether, 10% diethyl ether) and only traces of product were detected. After a further 22.5 h at 20 °C the solvent was evaporated and the residue was filtered through a silica short plug (diethyl ether) to give 25.3 mg of a mixture mainly **25** along with traces of **2b**, **3b** and other unidentified by-products. The products were identified by ^{1}H-NMR (200 MHz, $CDCl_3$) analysis of the crude mixture. Purification by column chromatography (9:1 hexane:ether) produced a mixture of **25** as a colourless oil (12 mg, 61 μmol, 50%).

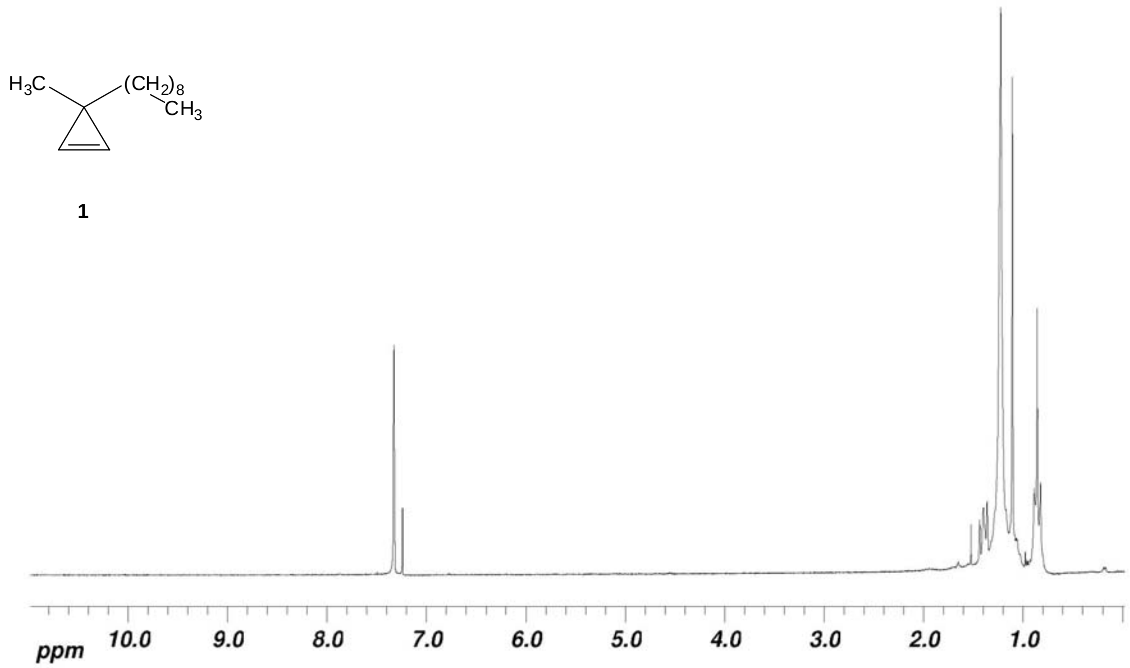
3. ^{1}H-NMR Spectra of Synthesised Compounds



S-1



S-2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CH_3
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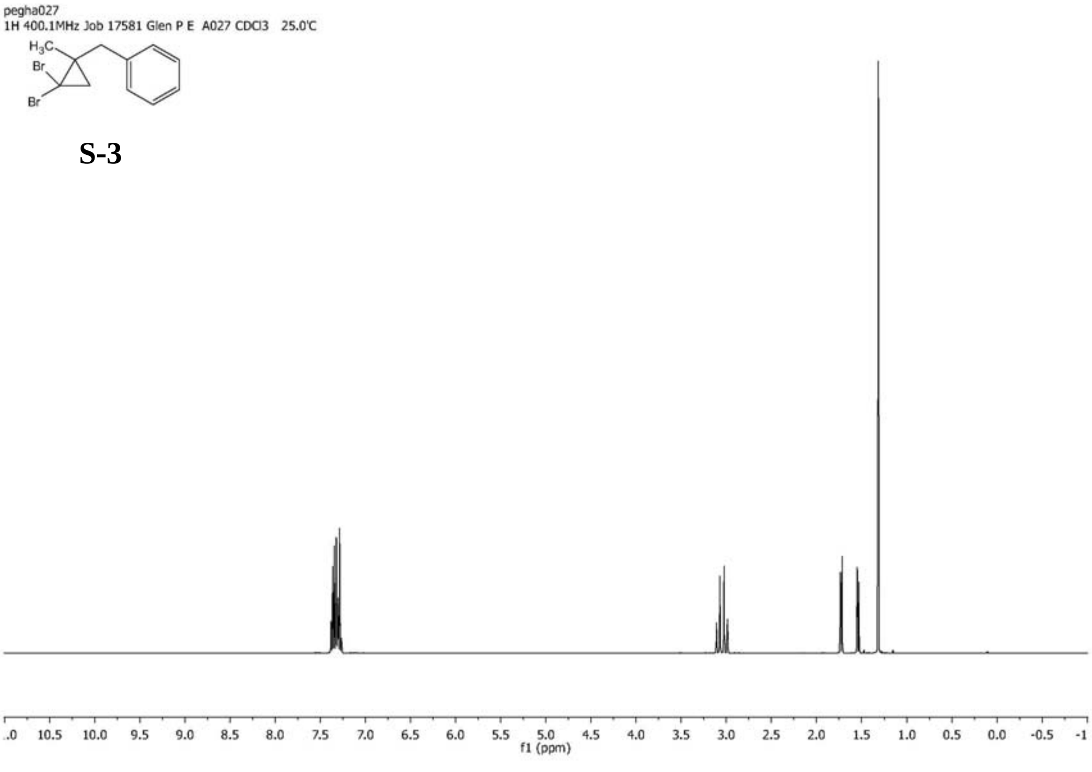
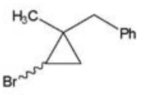
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

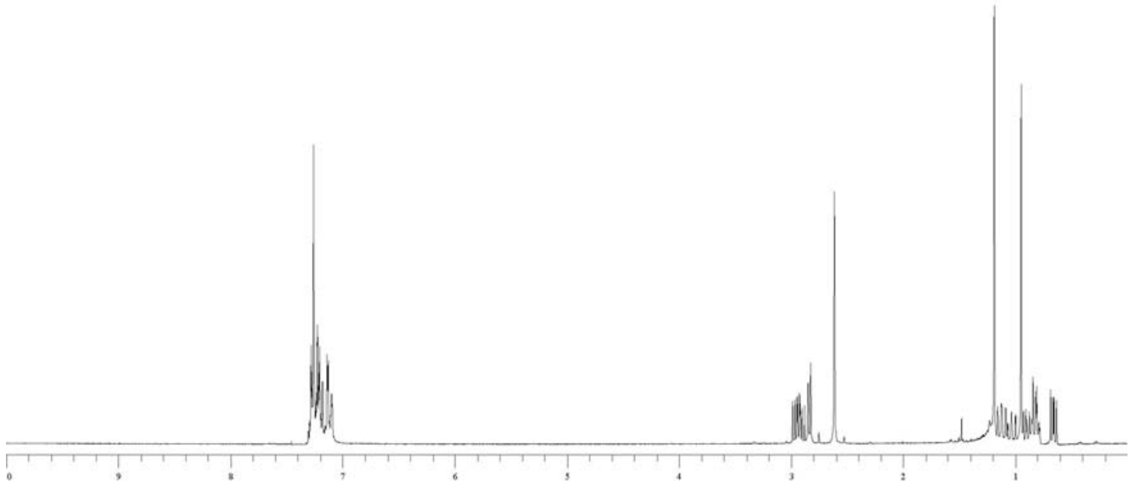
1


pegha027
1H 400.1MHz Job 17581 Glen P E A027 CDCl3 25.0'C
H_3C
Br
Br
.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

S-3

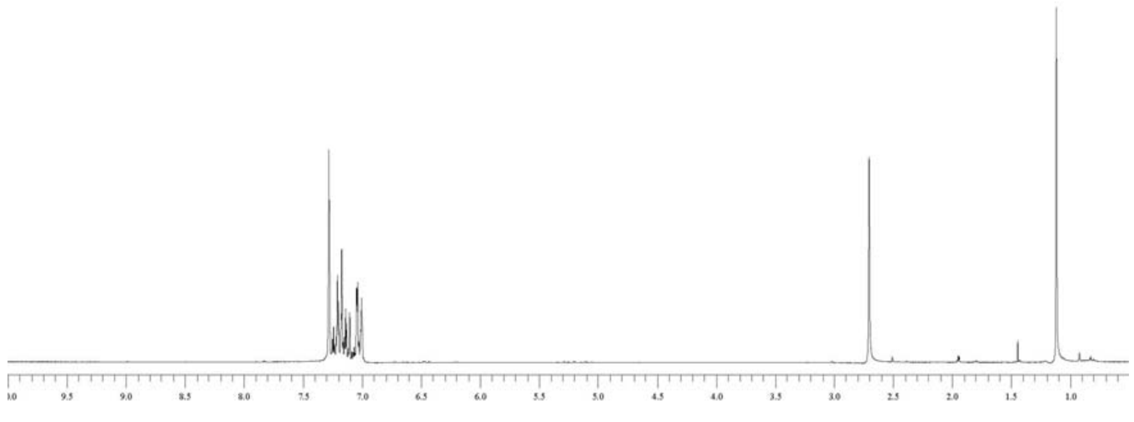
S-4


H3C
Ph
Br


10
9
8
7
6
5
4
3
2
1


H3C
Ph

6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8.5
8.0
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7.0
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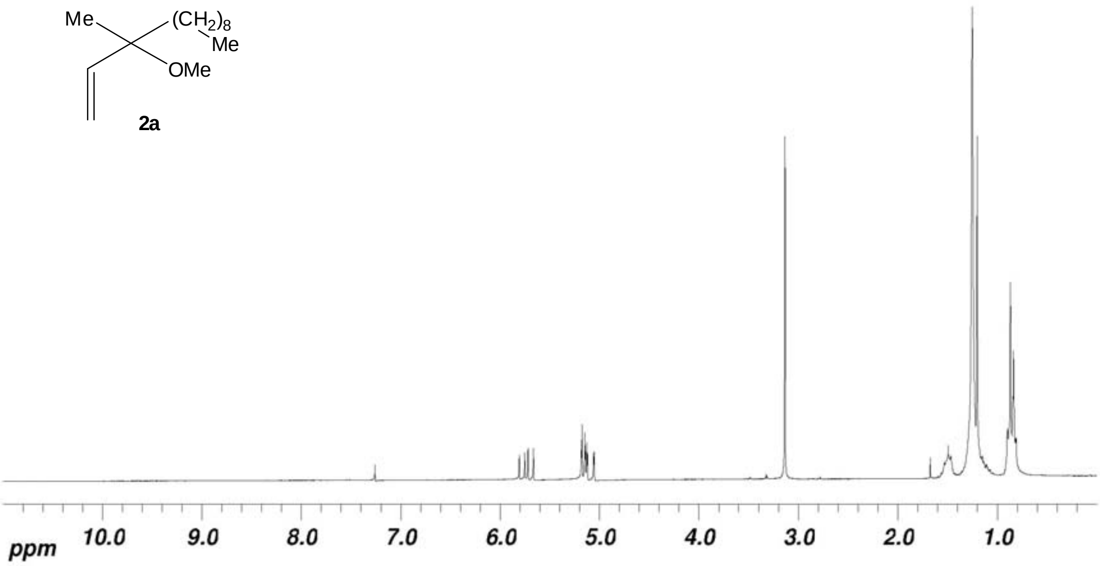
2.5
2.0
1.5
1.0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Me
OMe
ppm
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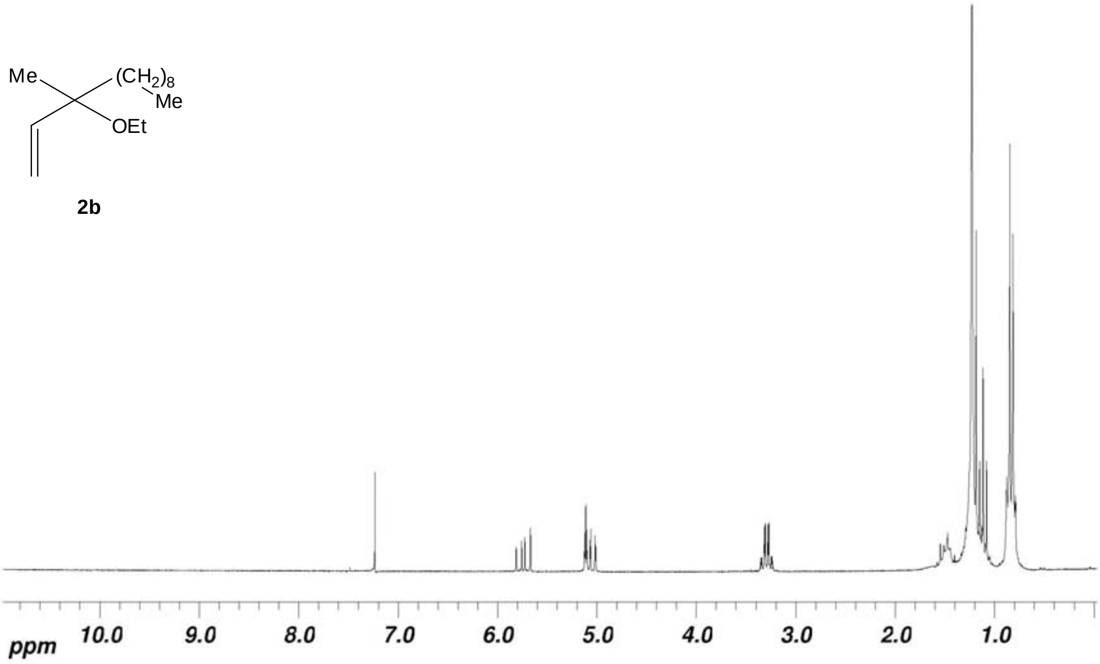
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

2a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Me
OEt
ppm
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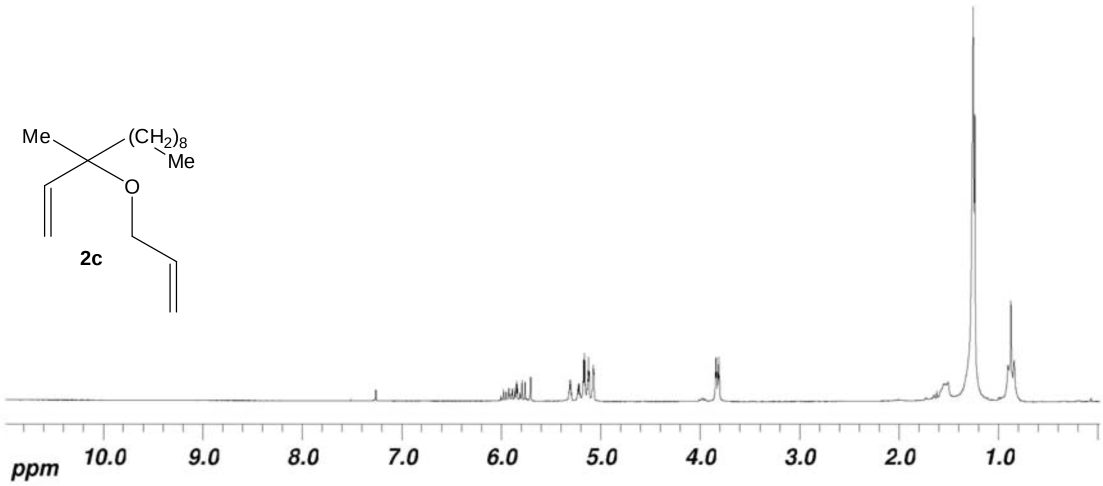
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0

2b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Me
O
ppm
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9.0
8.0
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6.0
5.0
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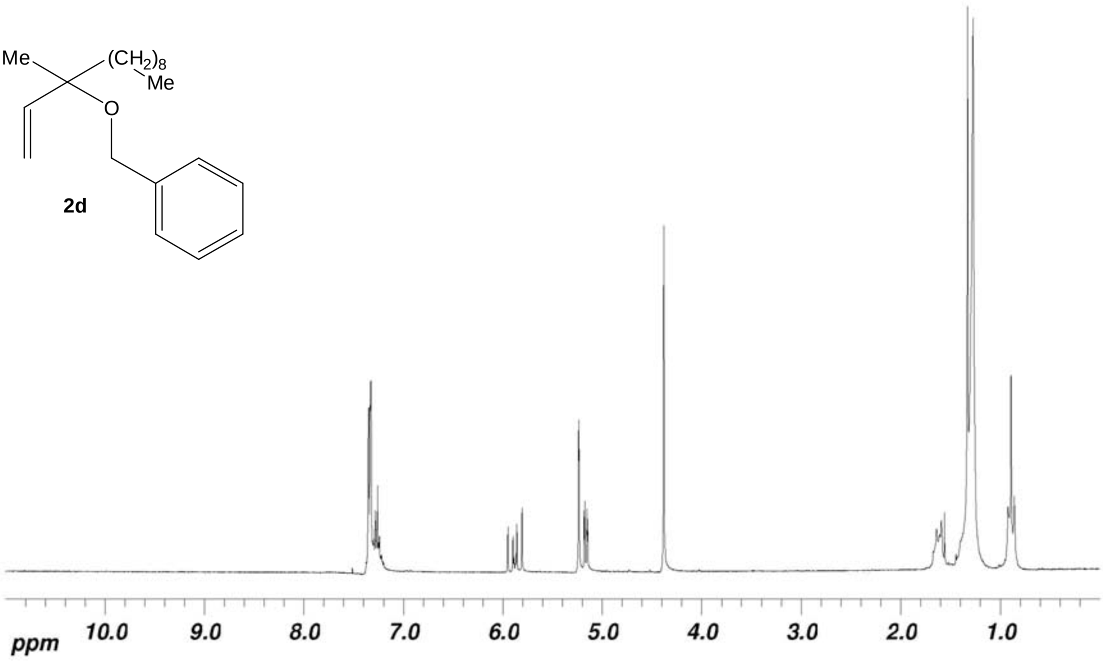
3.0
2.0
1.0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O
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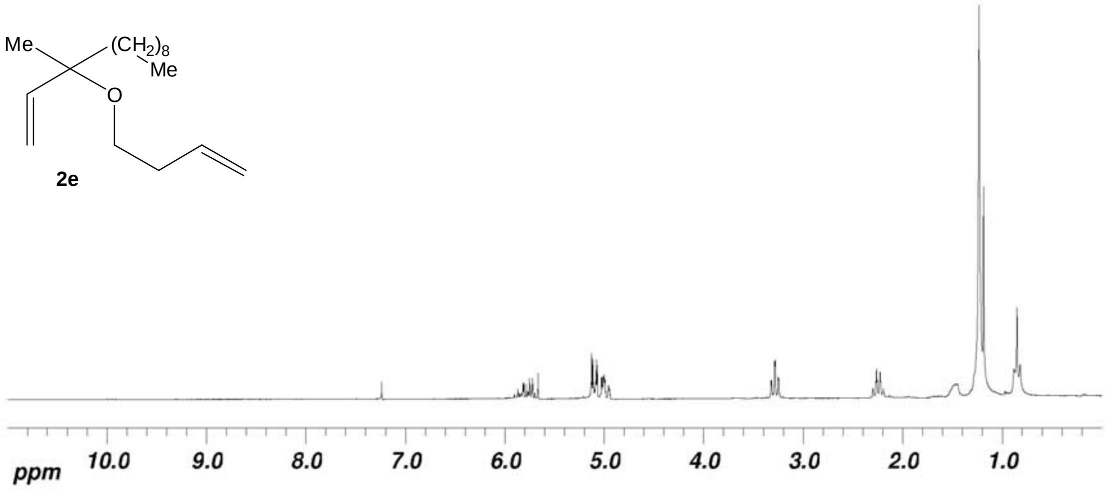
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Me
O
ppm
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7.0
6.0
5.0
4.0
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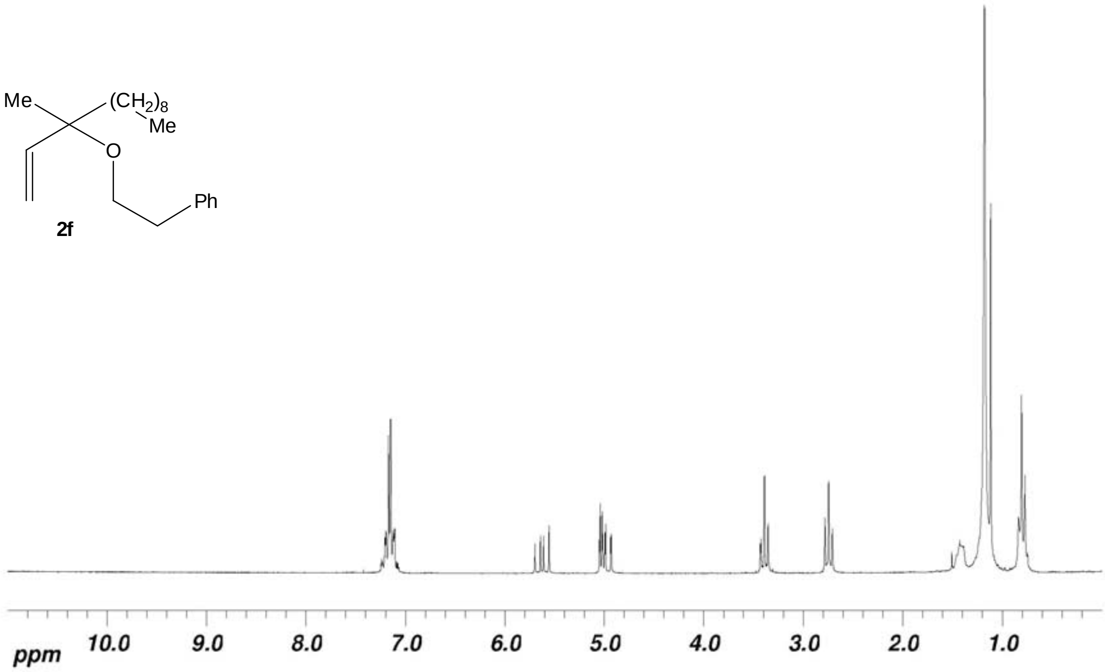
2.0
1.0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Me
(CH2)8
Me
O
Ph
ppm
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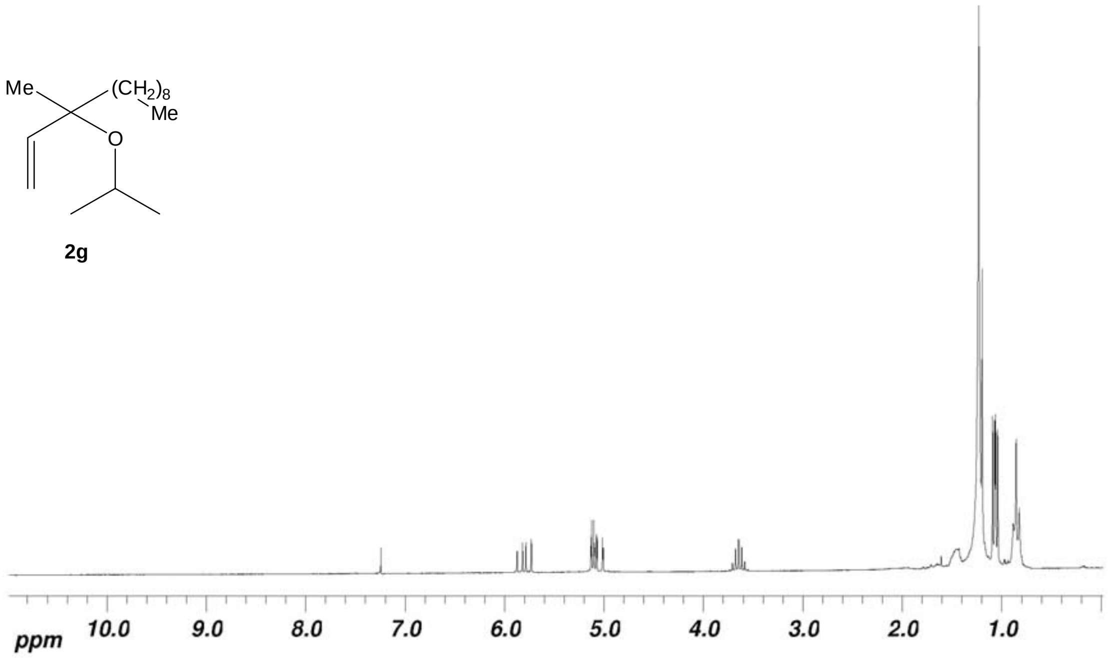
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0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Me
O
ppm
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9.0
8.0
7.0
6.0
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4.0
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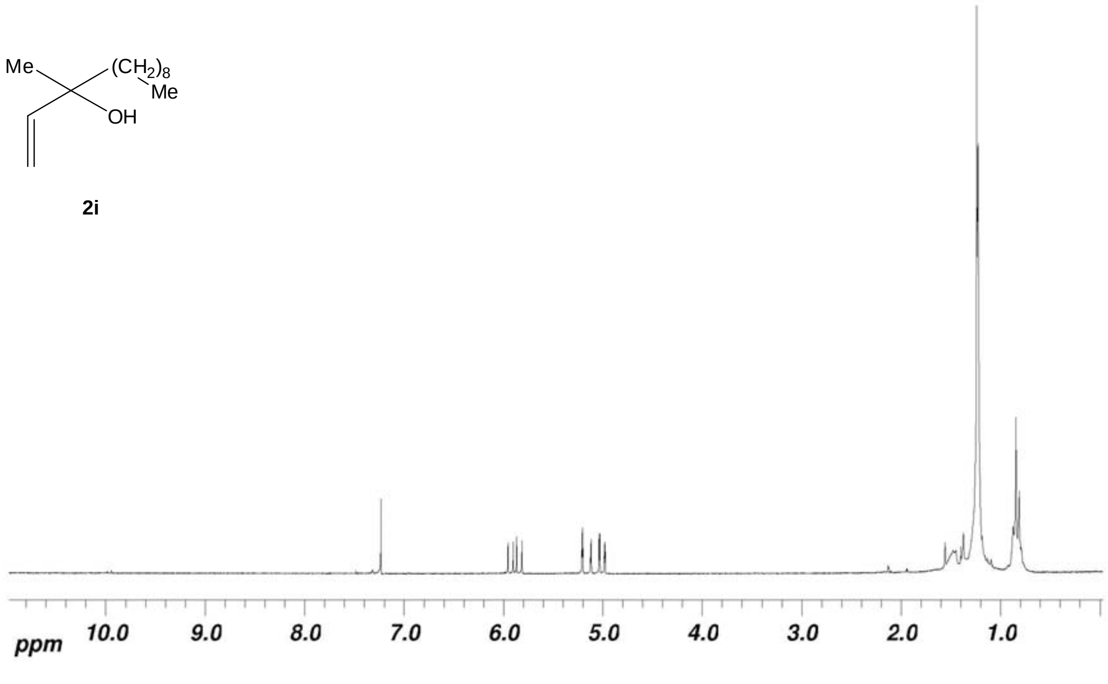
2.0
1.0

2g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OH
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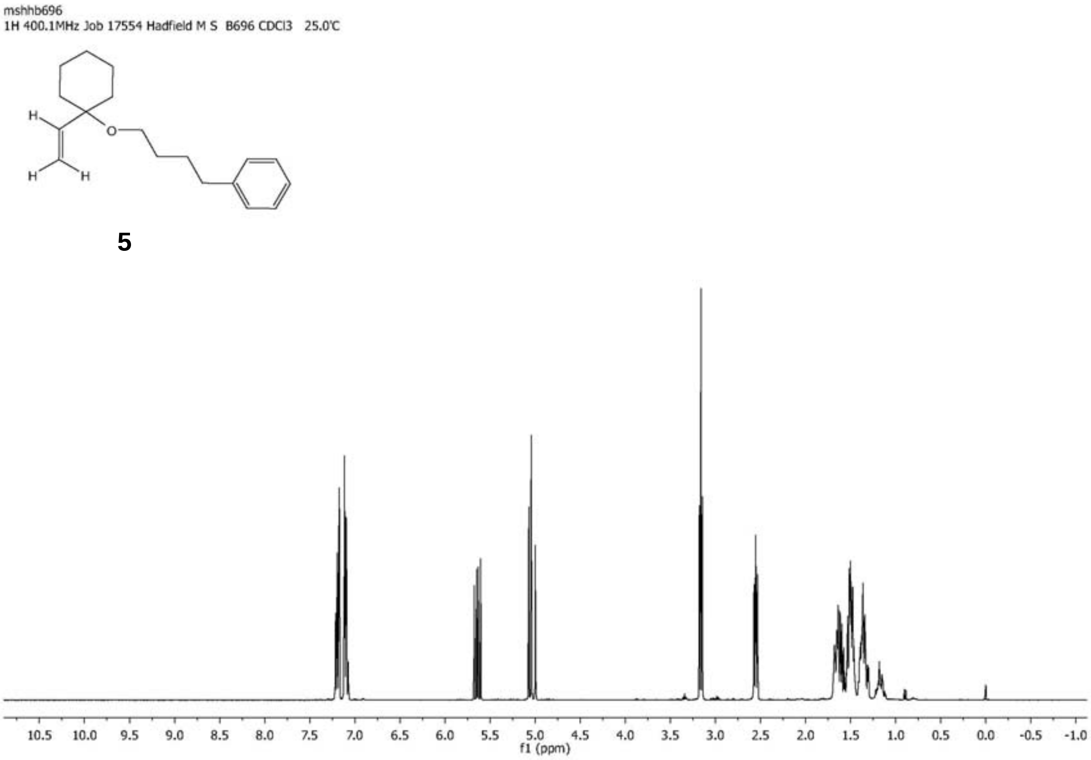
1.0

2i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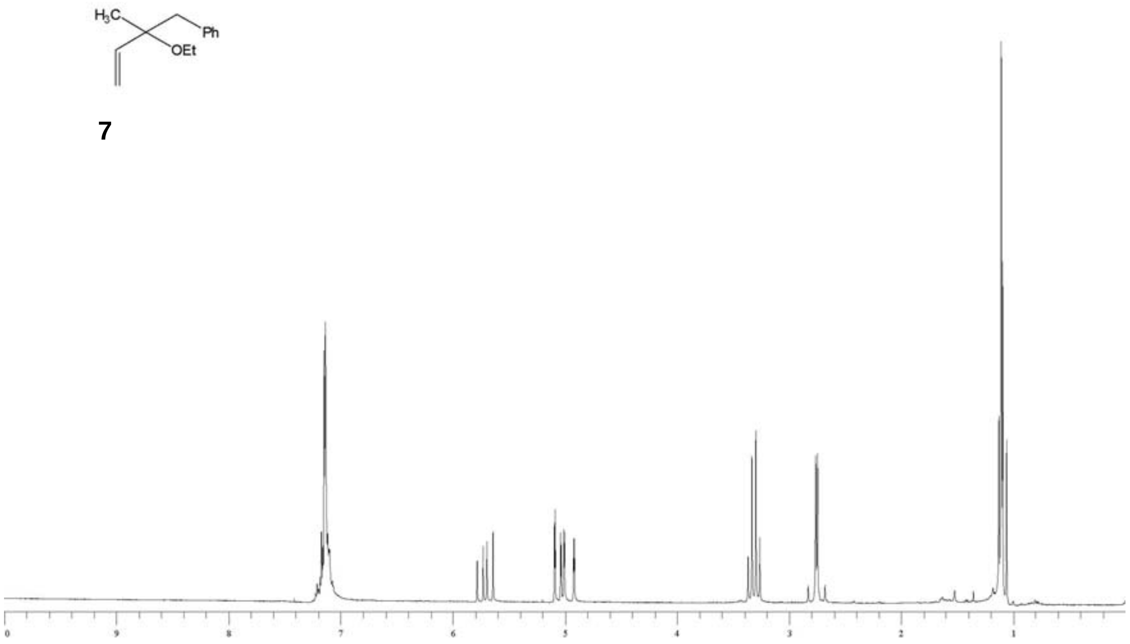
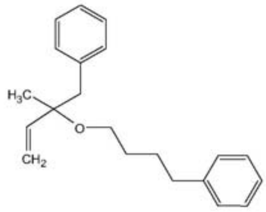
1H 400.1MHz Job 17554 Hadfield M S B696 CDCl3 25.0'C
H
O
H
H
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

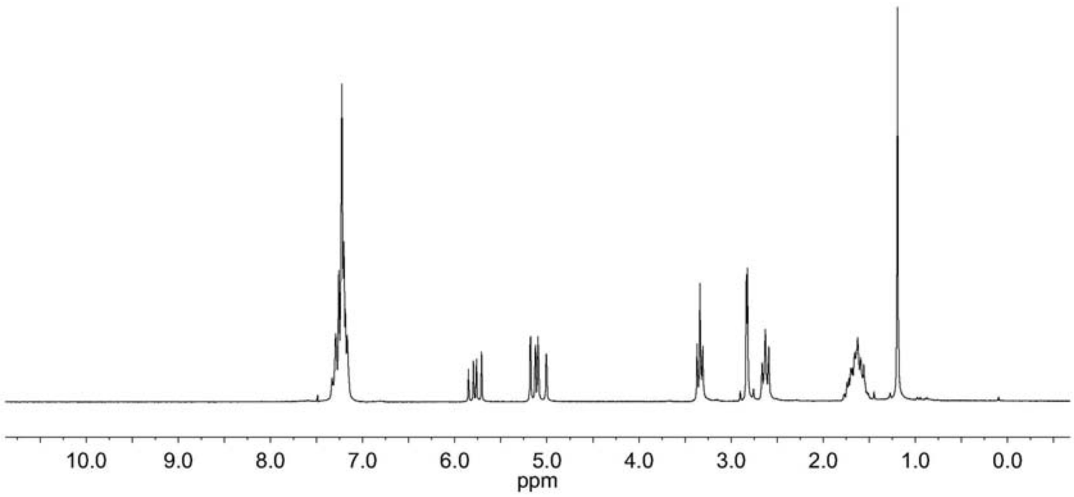
5


H_3C
Ph
OEt
0
9
8
7
6
5
4
3
2
1

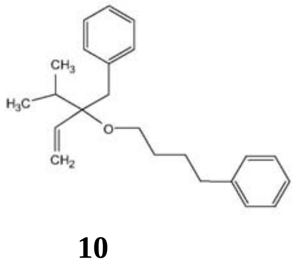
7

8

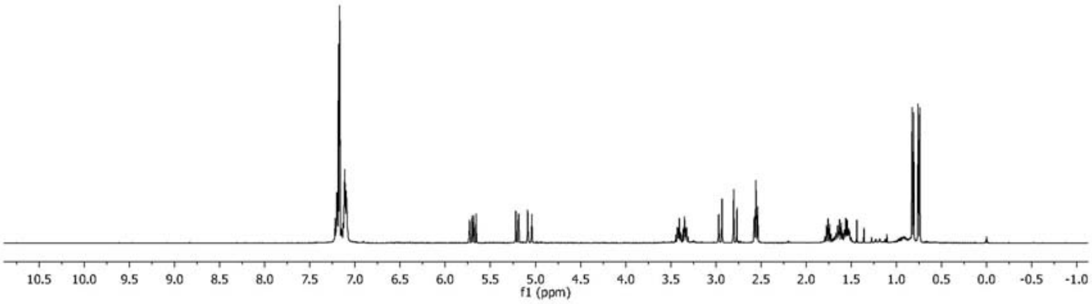




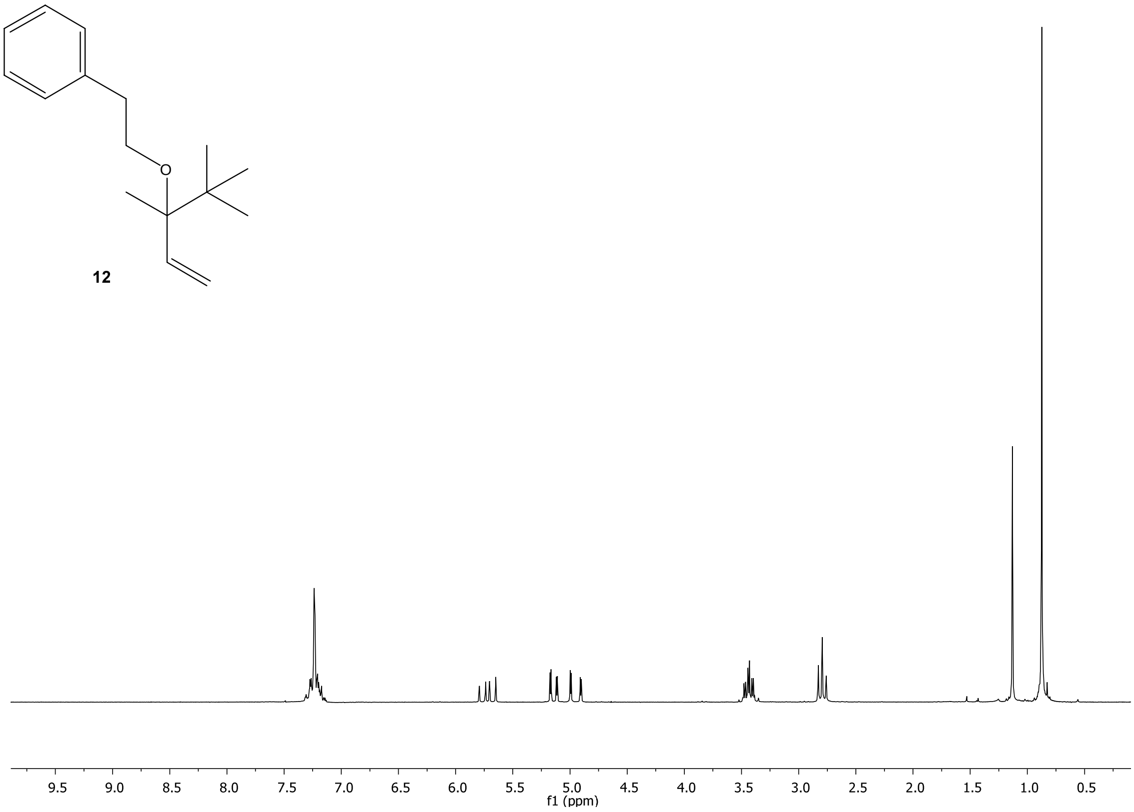
mshha687
1H 400.1MHz Job 17546 Hadfield M S A687 CDCl3 25.0˚C



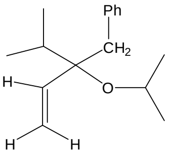
10



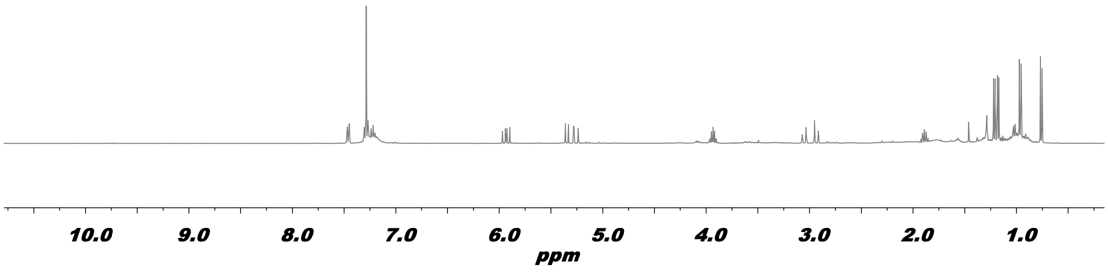
(200 MHz)


O
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

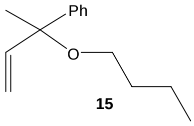
12


Ph
CH2
H
O
H
H

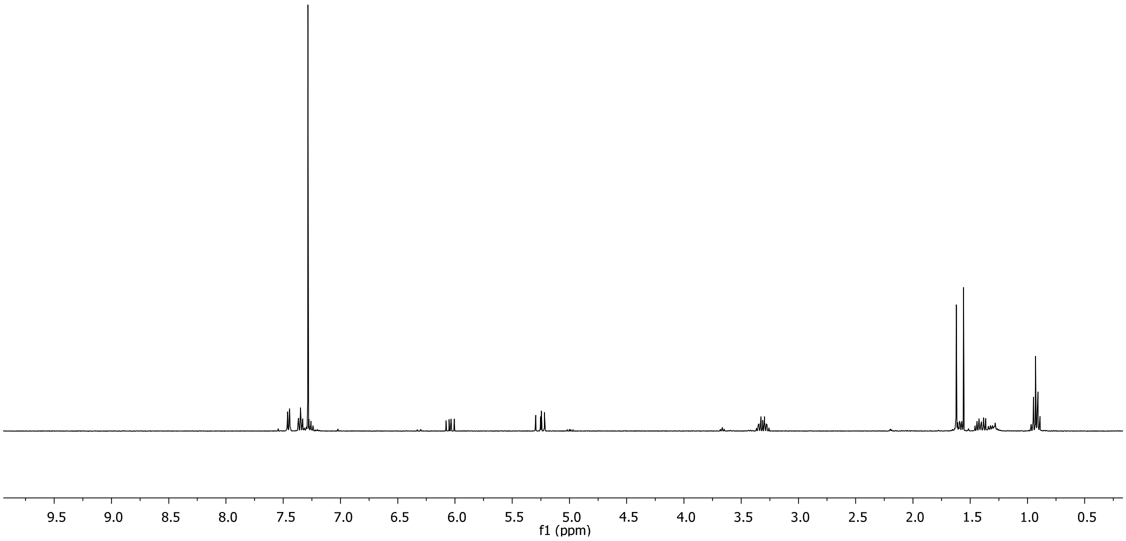
13


10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm

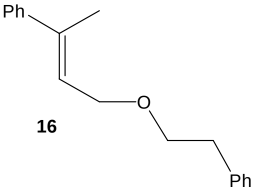
mshhc705
1H 400.1MHz Job 17716 Hadfield M S C705 CDCl3 25.0'C



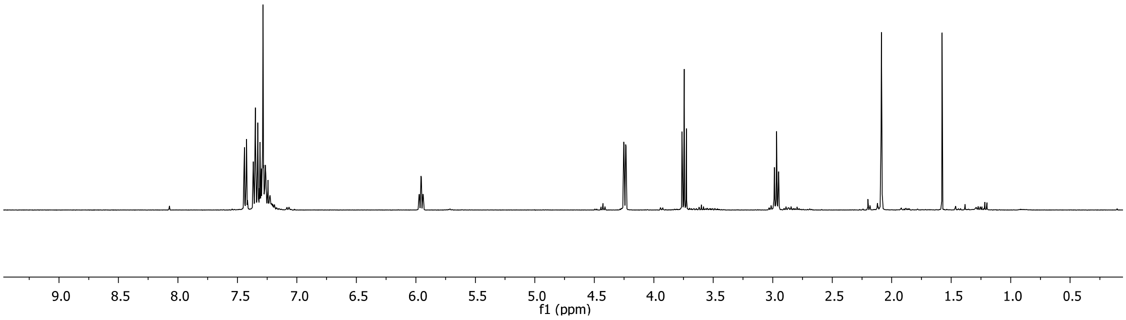
15



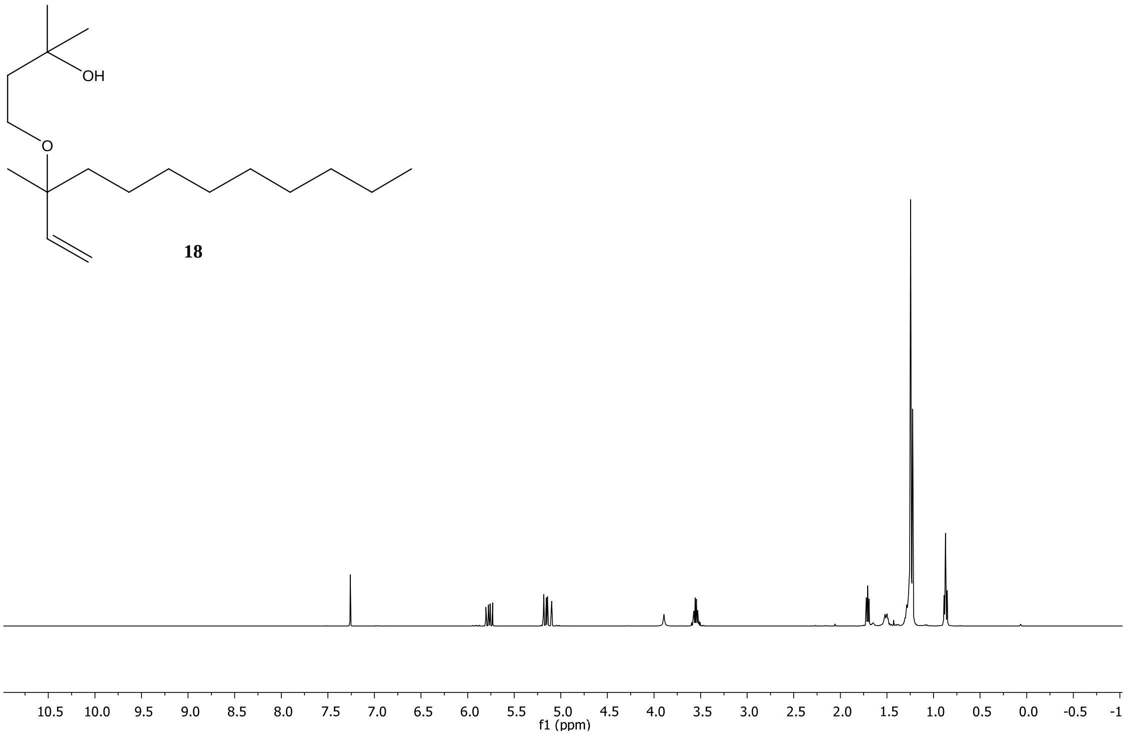
mshhc703
1H 400.1MHz Job 17680 Hadfield M S C703 CDCl3 25.0'C



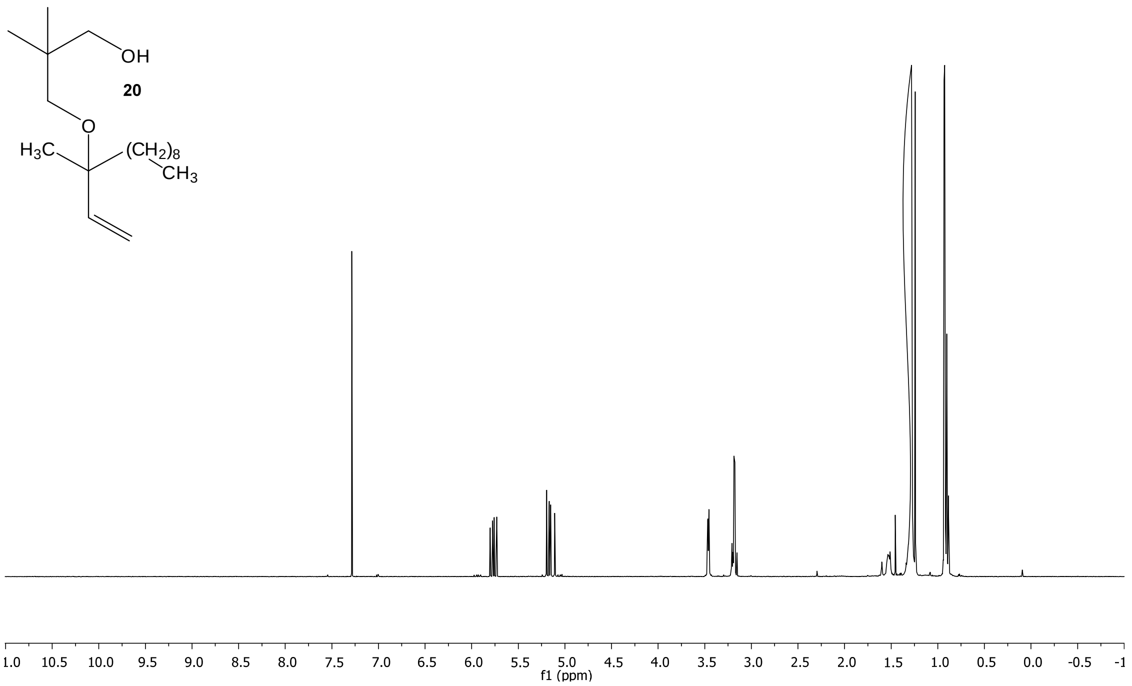
16



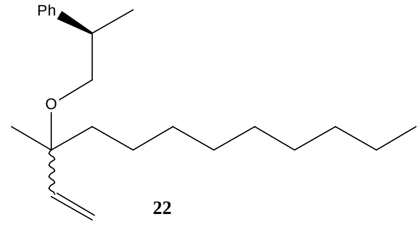
mshhb693
1H 400.1MHz Job 17595 Hadfield M S B693 CDCl3 25.0'C



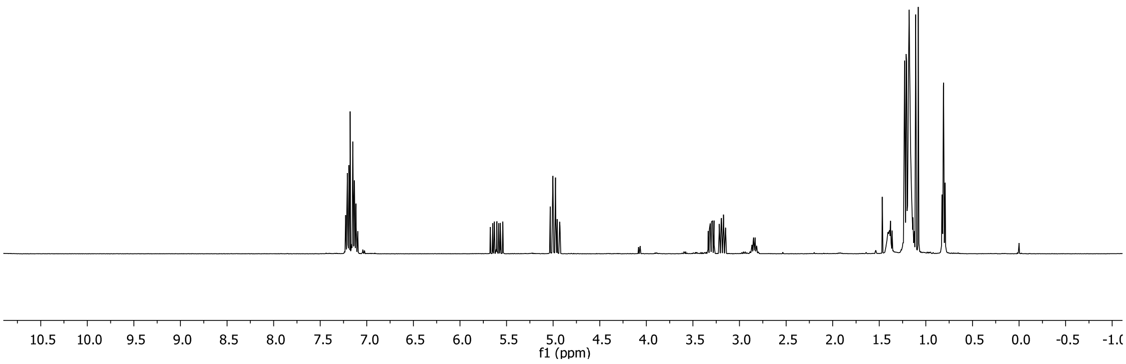
mshhb704
1H 400.1MHz Job 17665 Hadfield M S B704 CDCl3 25.0'C



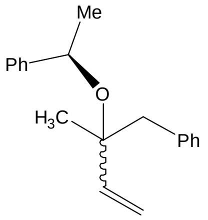
mshhb688
1H 400.1MHz Job 17459 Hadfield M S B688 CDCl3   25.0'C



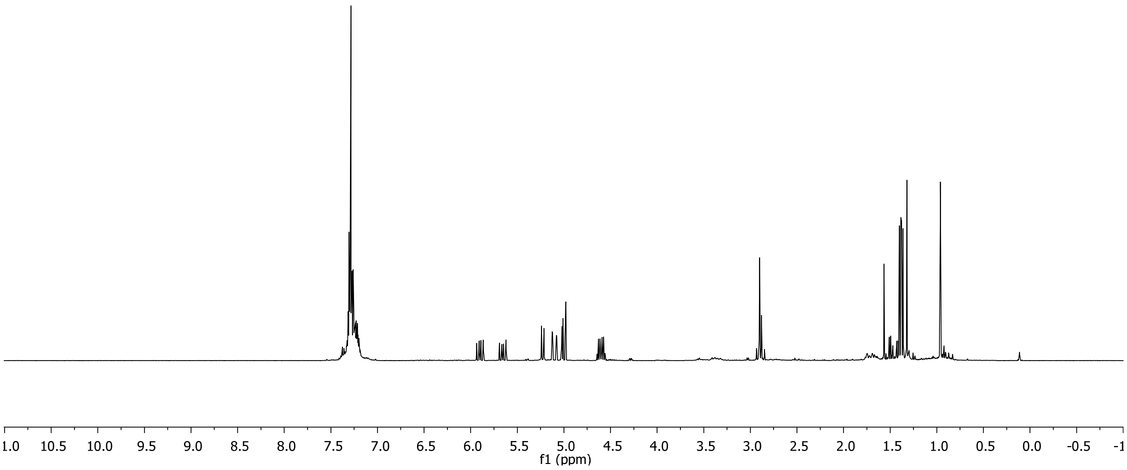
22



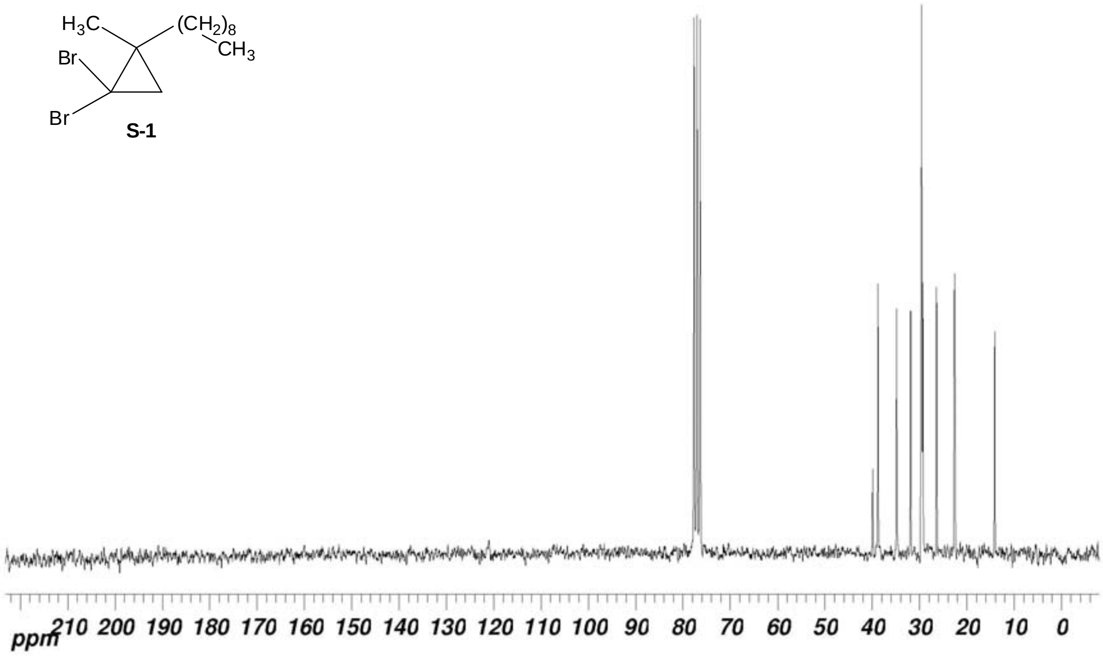
mshha708
1H 400.1MHz Job 17686 Hadfield M S A708 CDCl3   25.0'C



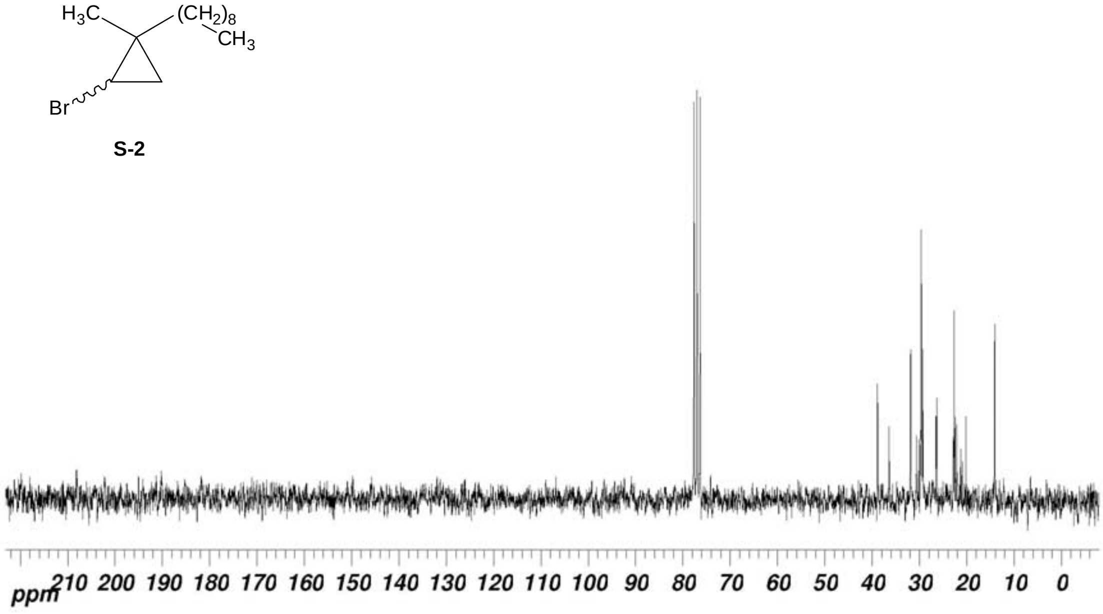
24



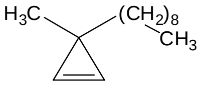
4. ^{13}C-NMR Spectra of Synthesised Compounds



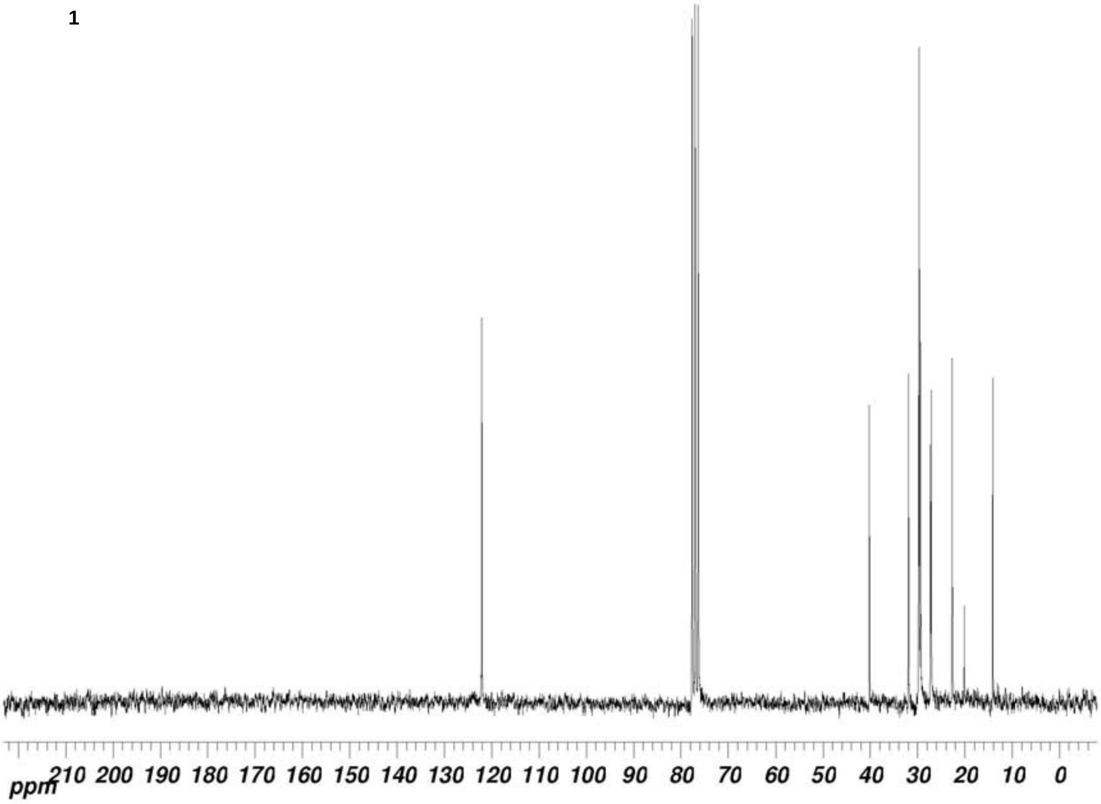
S-1



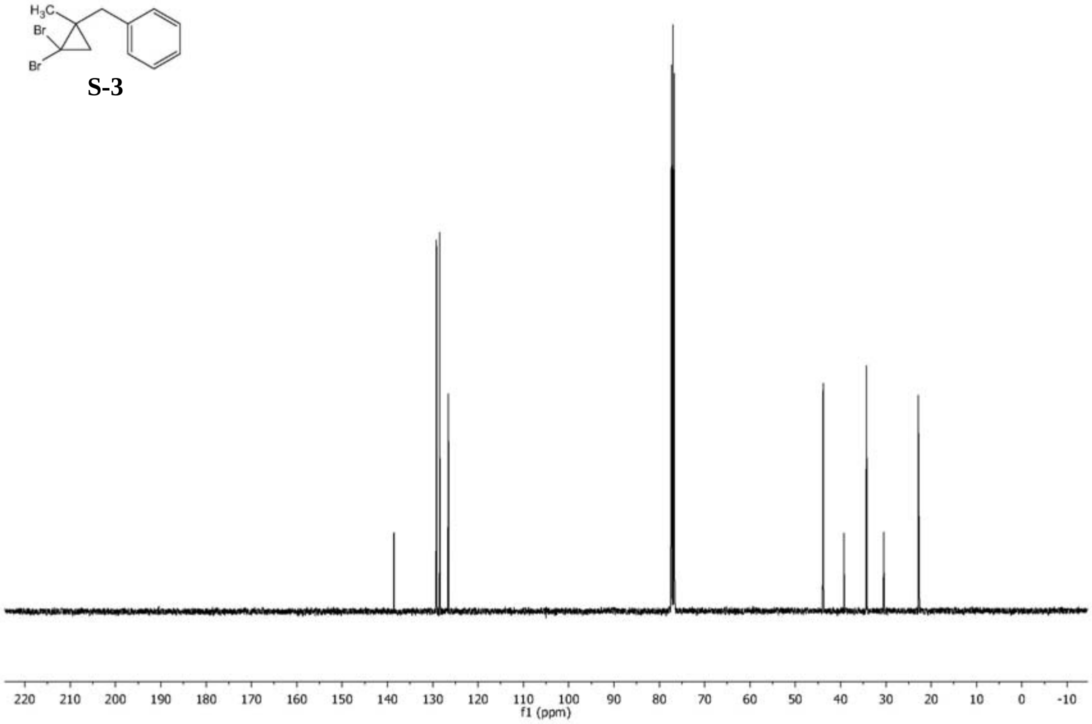
S-2



1

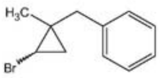


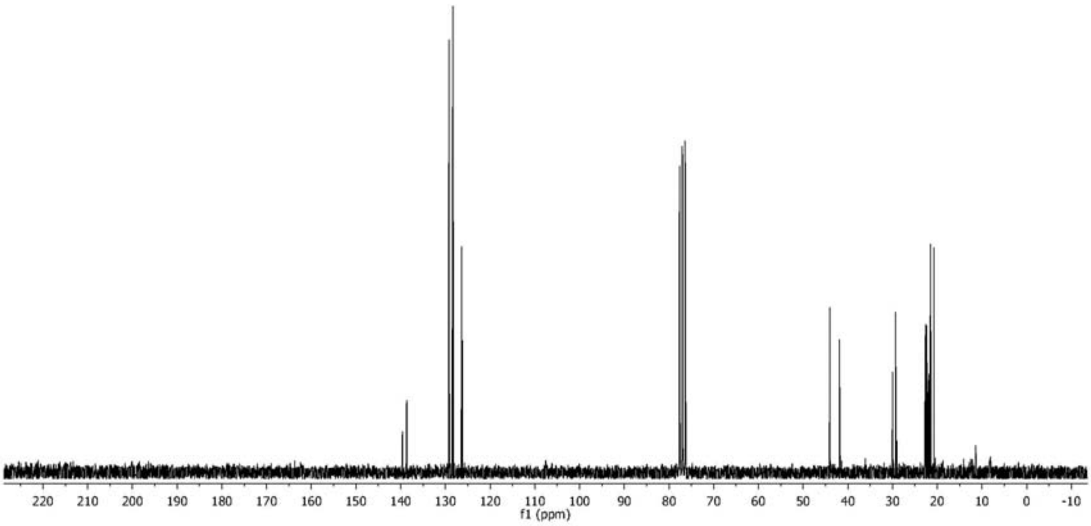
pegca027
13C 100.6MHz Job 17583 Glen P E A027 CDCl3 25.0'C 1 hour 27 min



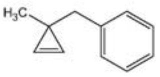
S-3

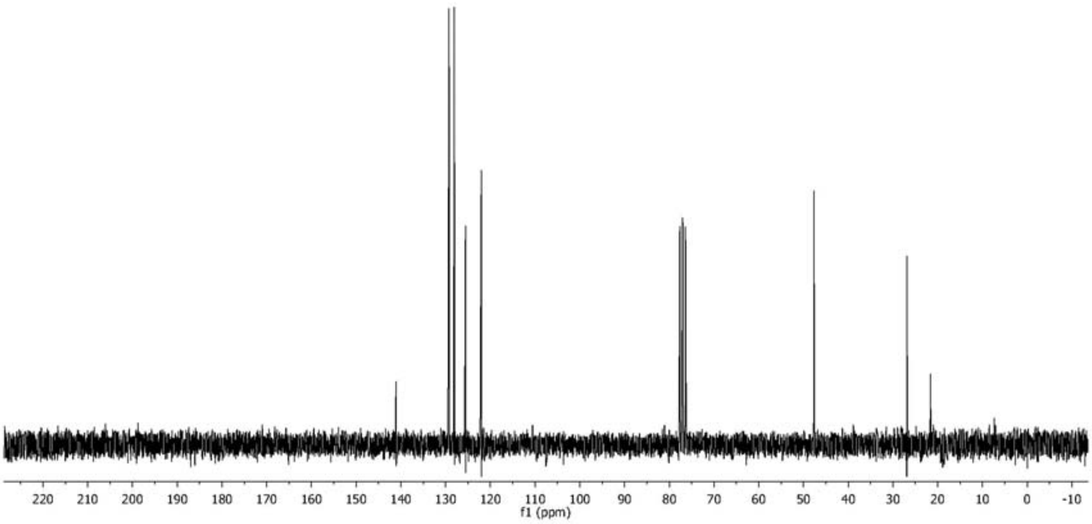
S4

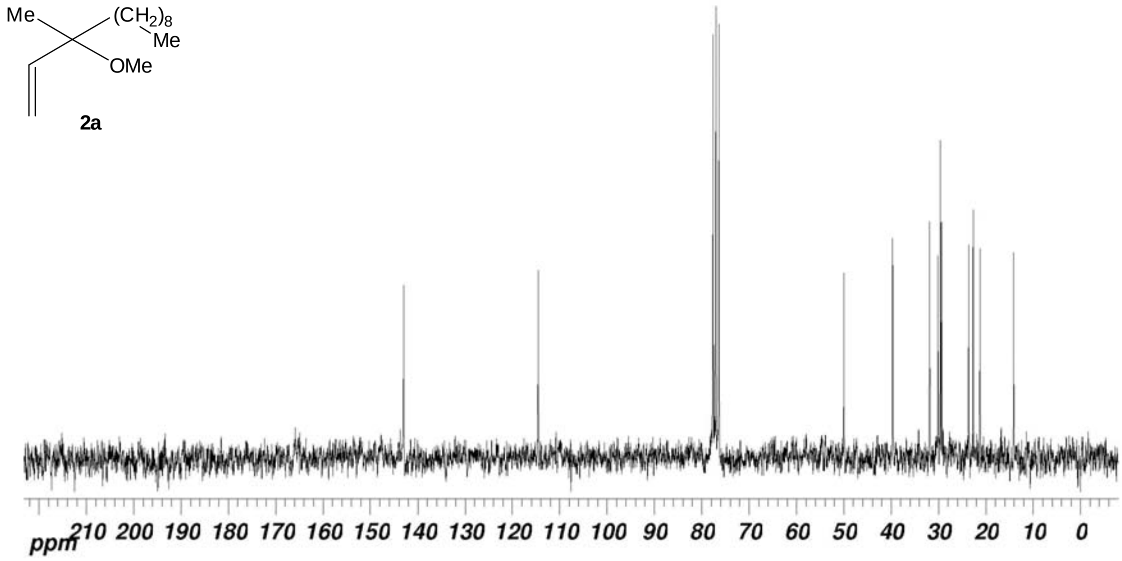

H3C
Br


220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

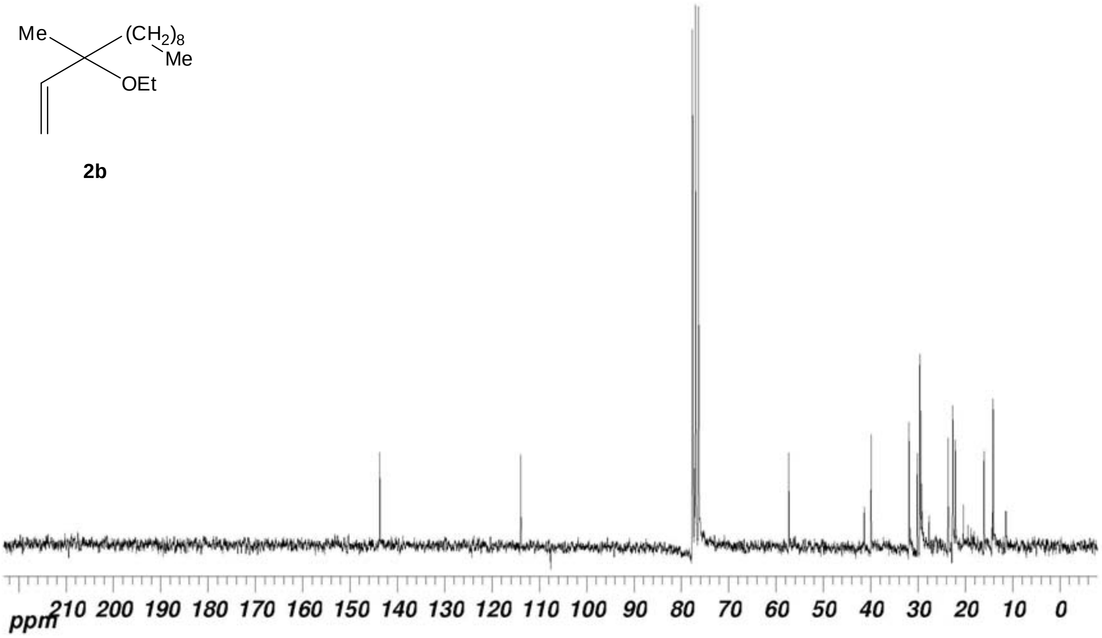
6


H3C

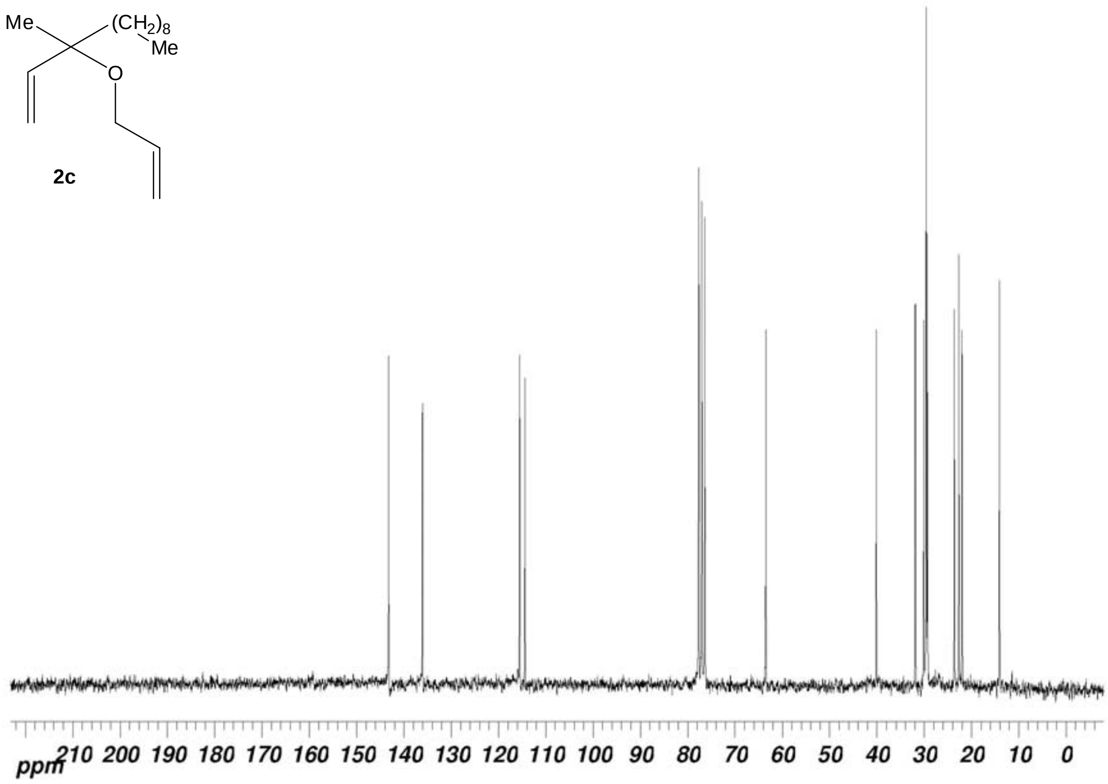

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
(CH2)8
Me
OMe
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

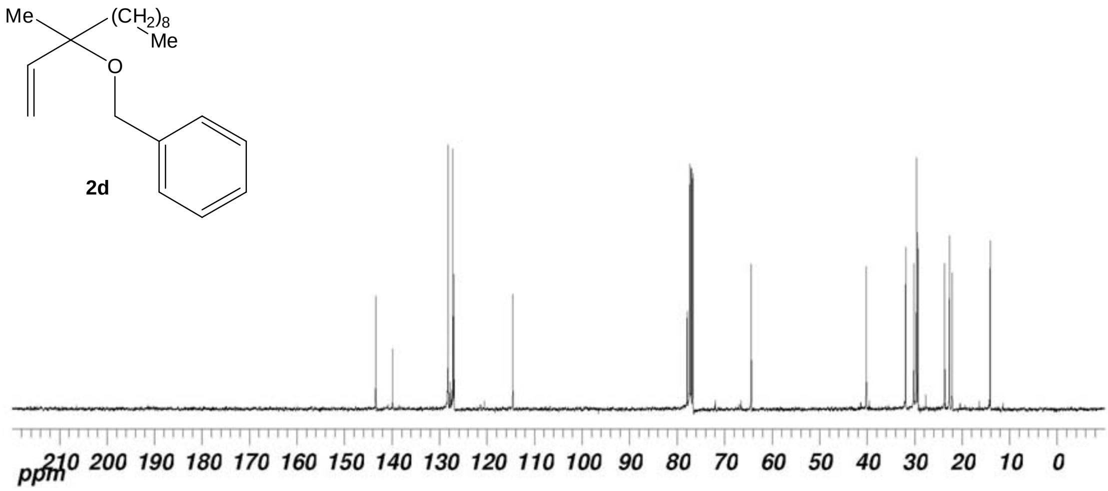
2a


Me
(CH2)8
Me
OEt
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

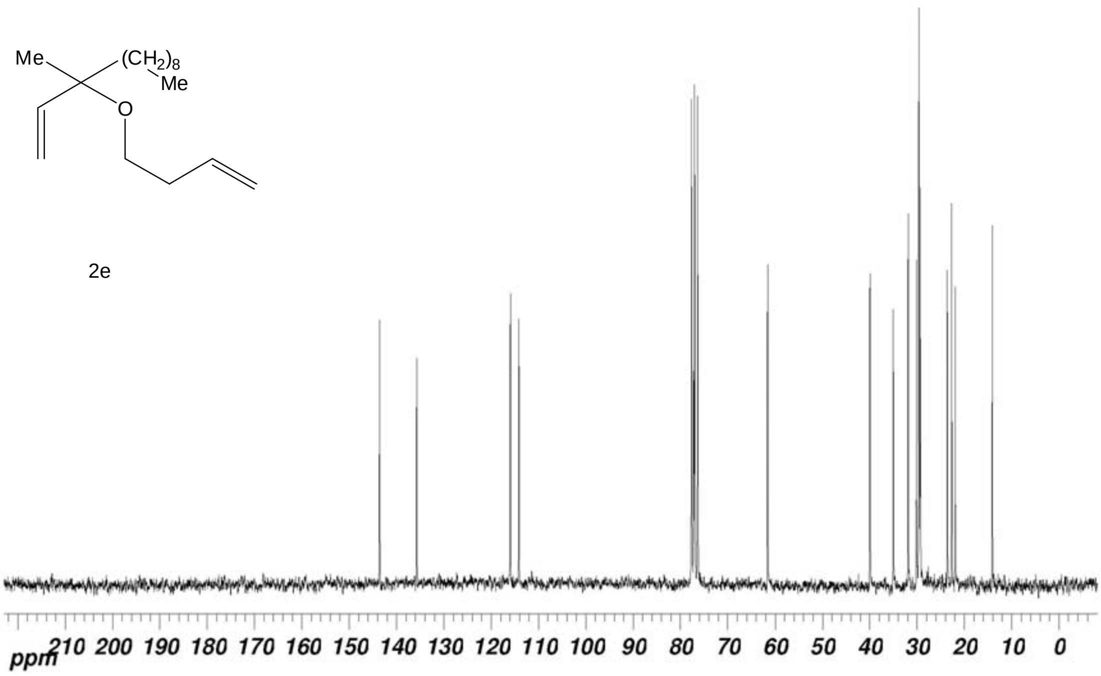
2b


Me
(CH2)8
Me
O
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

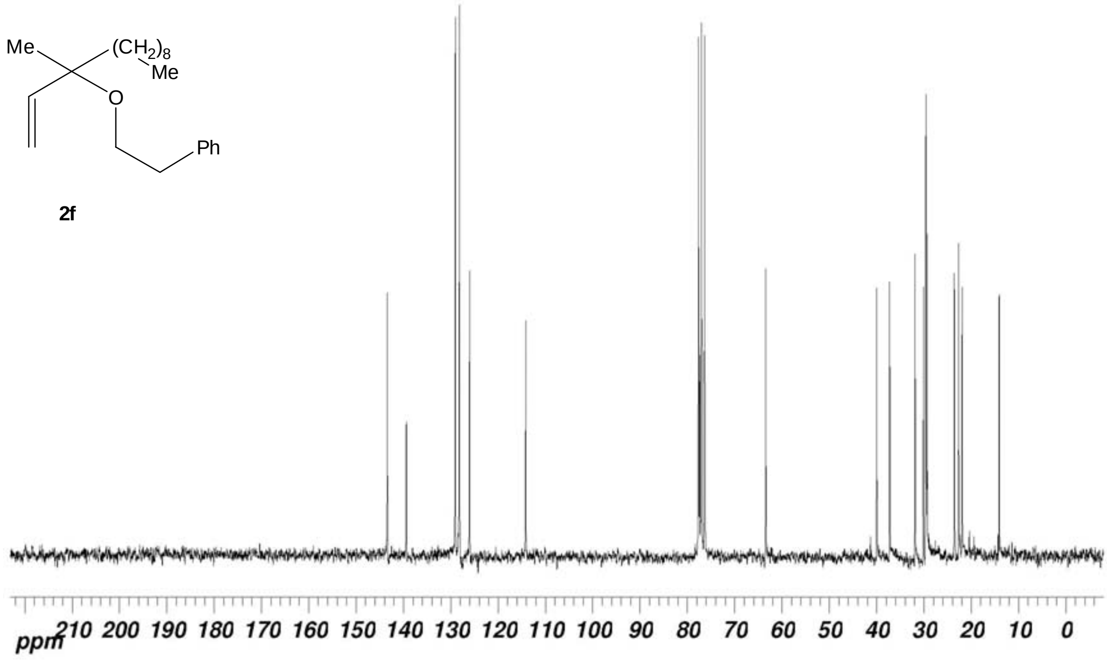
2c


Me
(CH2)8
Me
O
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

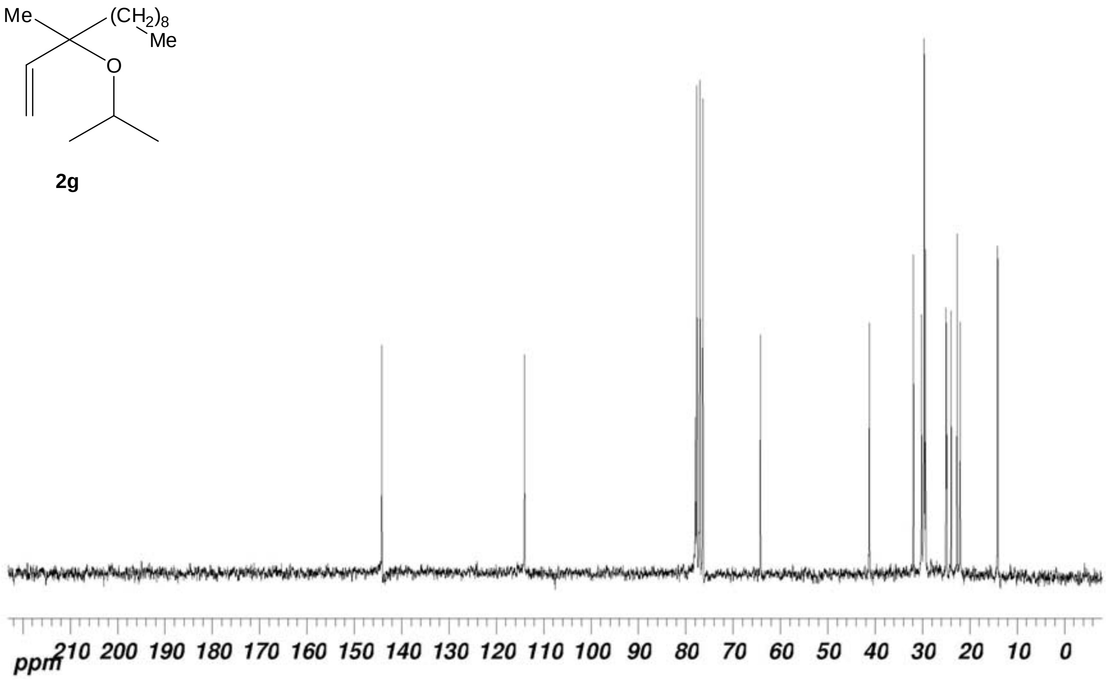
2d


Me
(CH2)8
Me
O
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

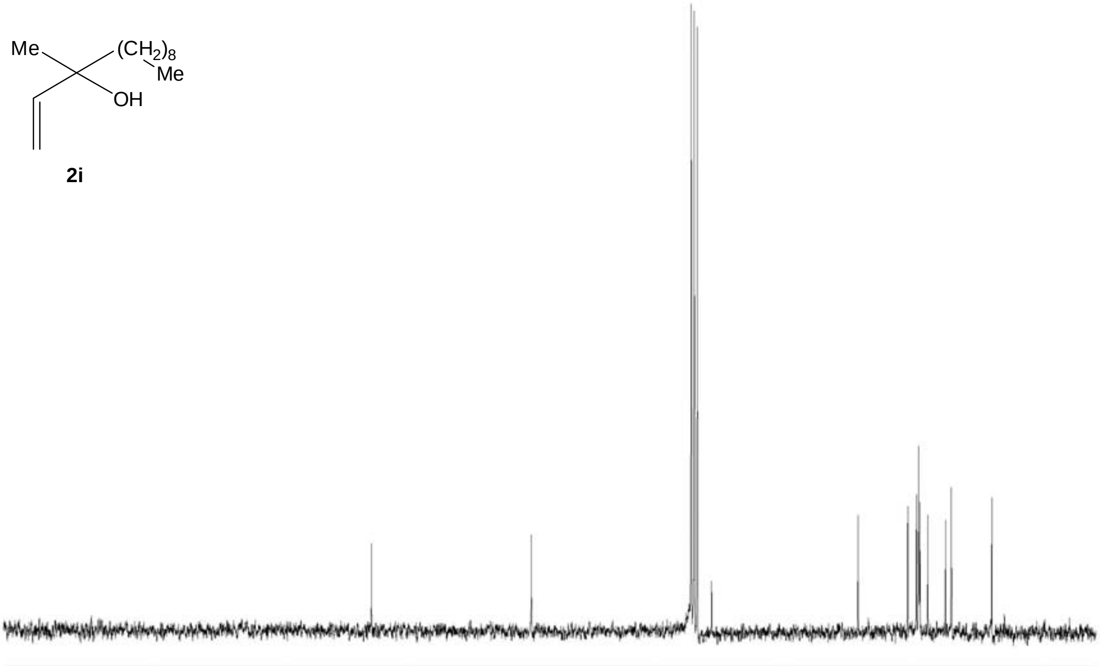
2e


Me
(CH2)8
Me
O
Ph
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

2f

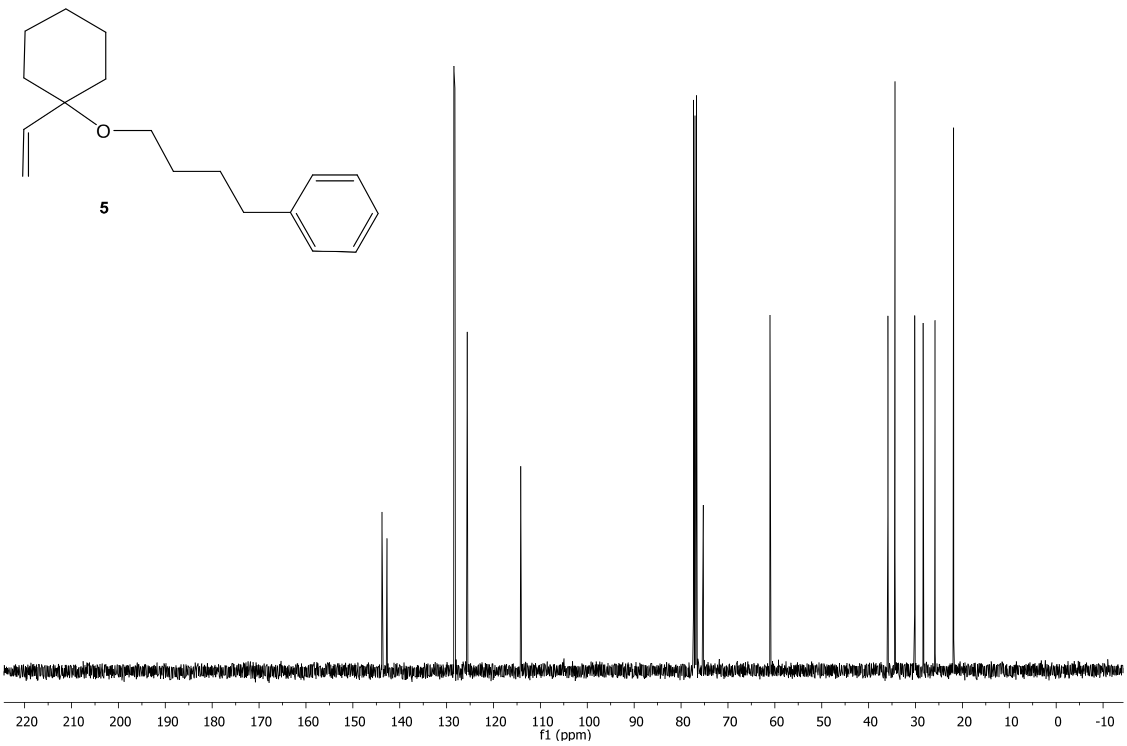

Me
(CH2)8
Me
O
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

2g

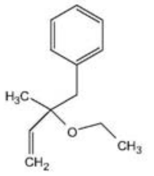

Me
(CH2)8
Me
OH
ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

2i

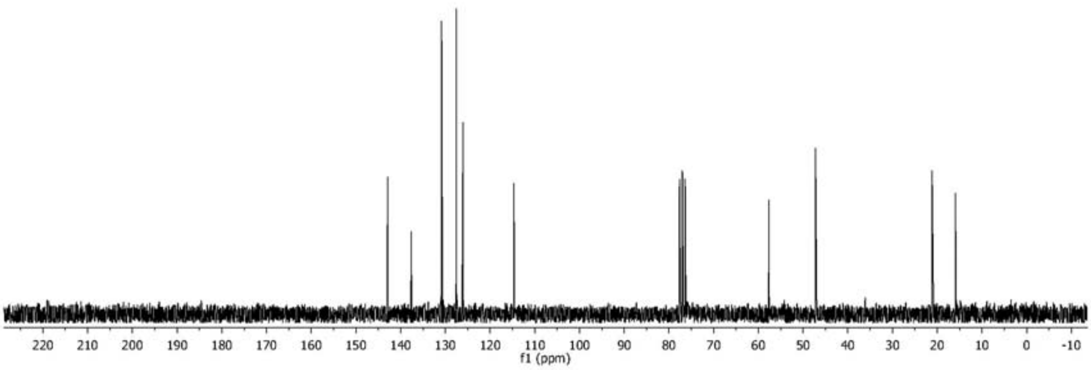
mshcb696
13C 100.6MHz Job 17555 Hadfield M S B696 CDCl3 25.0'C 0 hour 14 min



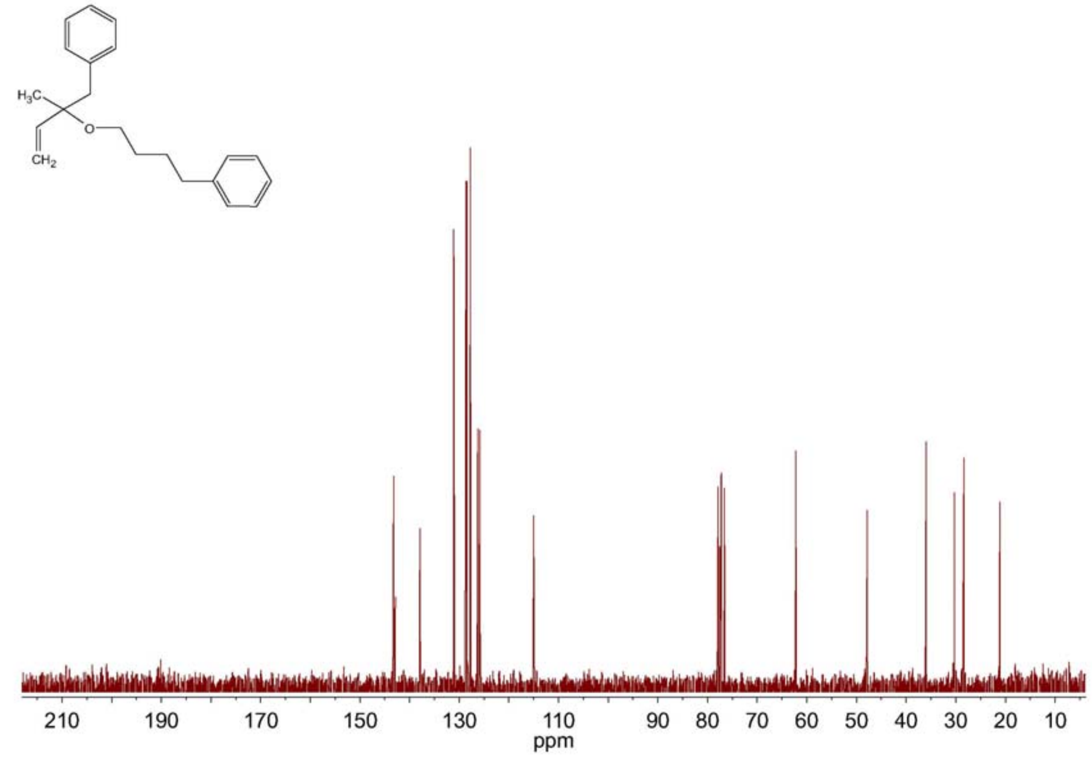
5



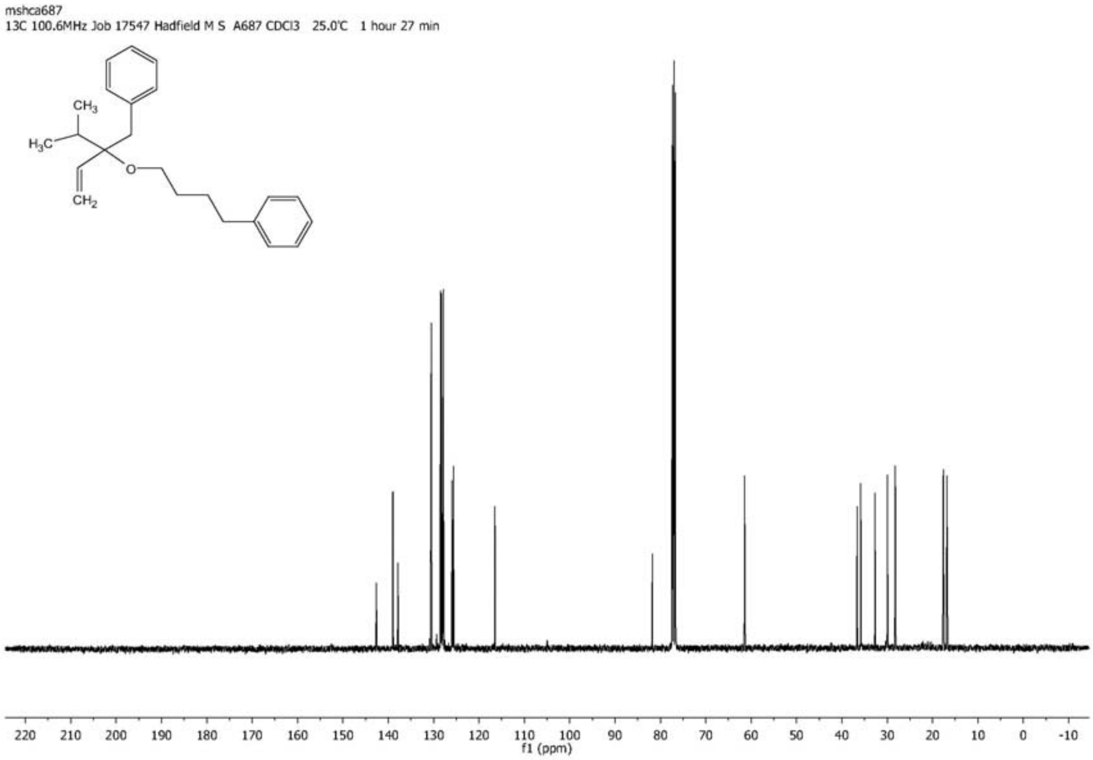
7



8

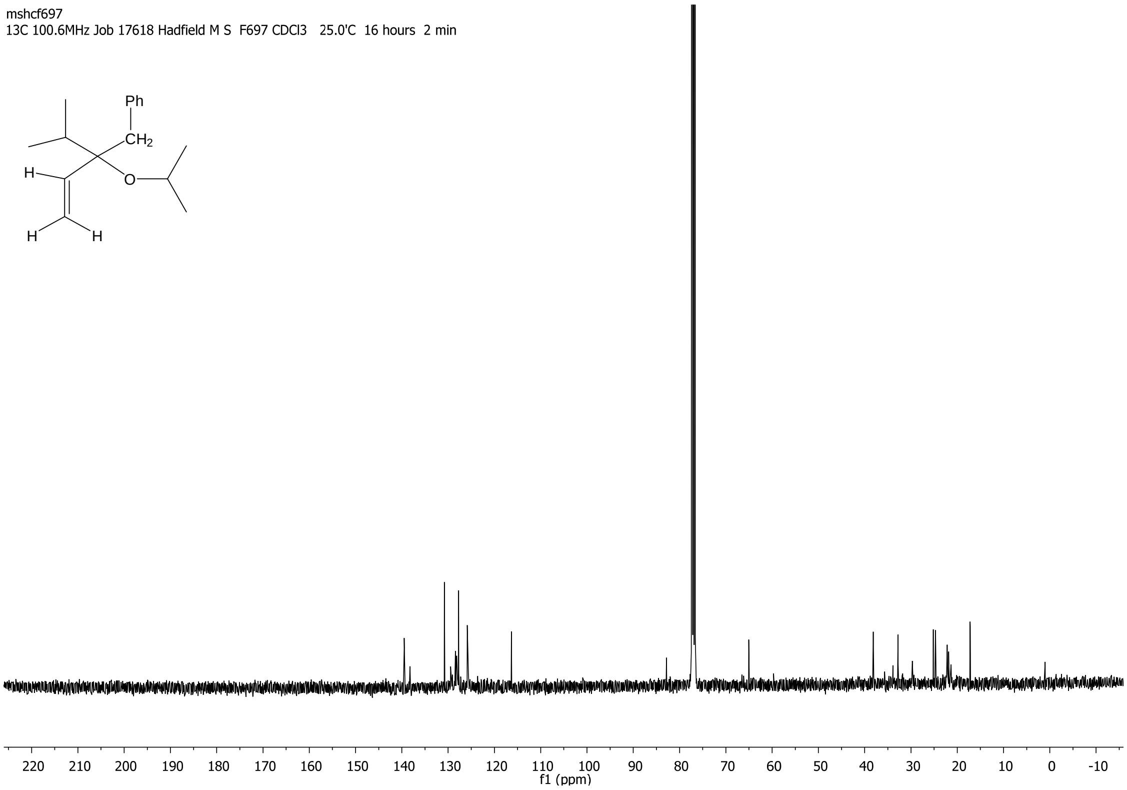

H$_3$C
O
CH$_2$
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
ppm

10


mshca687
13C 100.6MHz Job 17547 Hadfield M S A687 CDCl3 25.0℃ 1 hour 27 min
CH$_3$
H$_3$C
O
CH$_2$
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

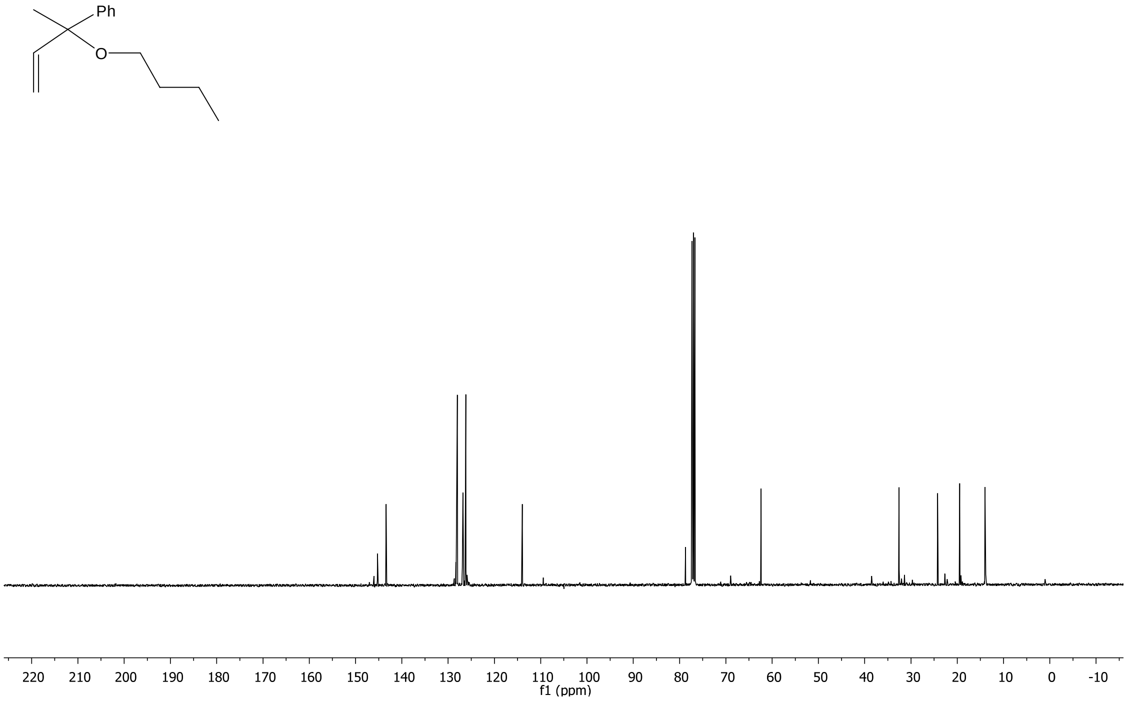
13

mshcf697
13C 100.6MHz Job 17618 Hadfield M S F697 CDCl3 25.0'C 16 hours 2 min



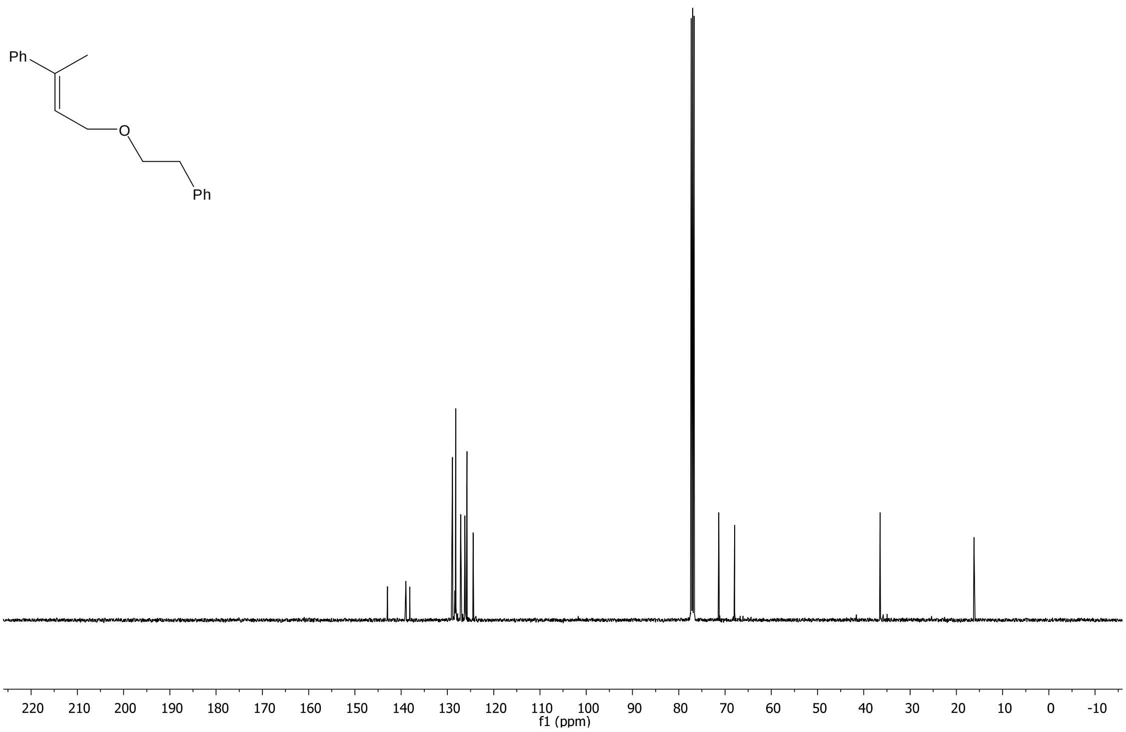
15

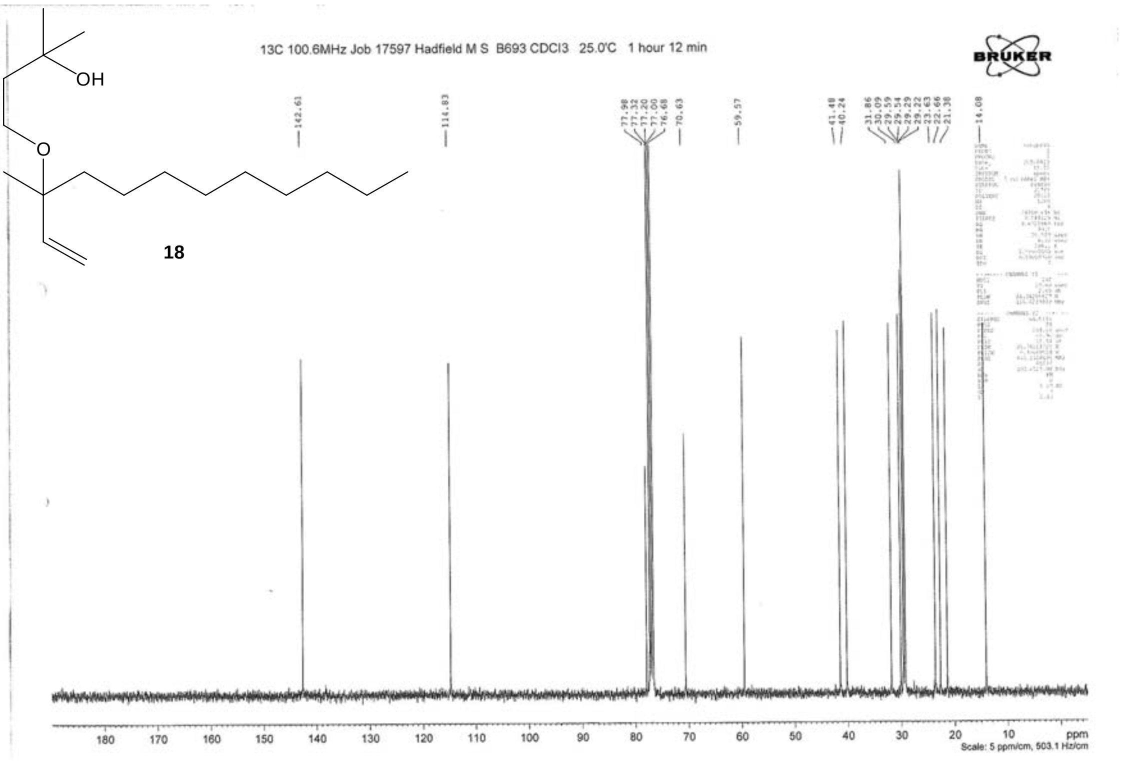
mshcd705
13C 100.6MHz Job 17724 Hadfield M S D705 CDCl3 25.0'C 8 hours 15 min



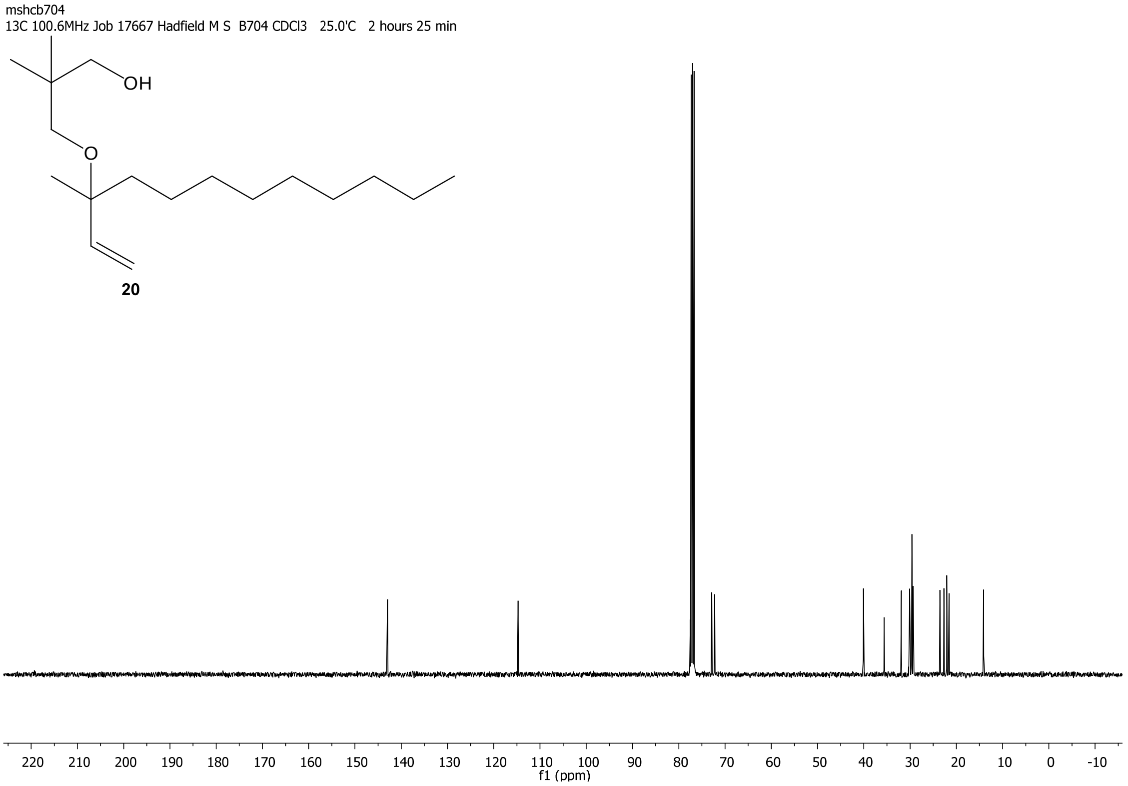
16

mshcc703
13C 100.6MHz Job 17682 Hadfield M S C703 CDCl3 25.0'C 5 hours 6 min



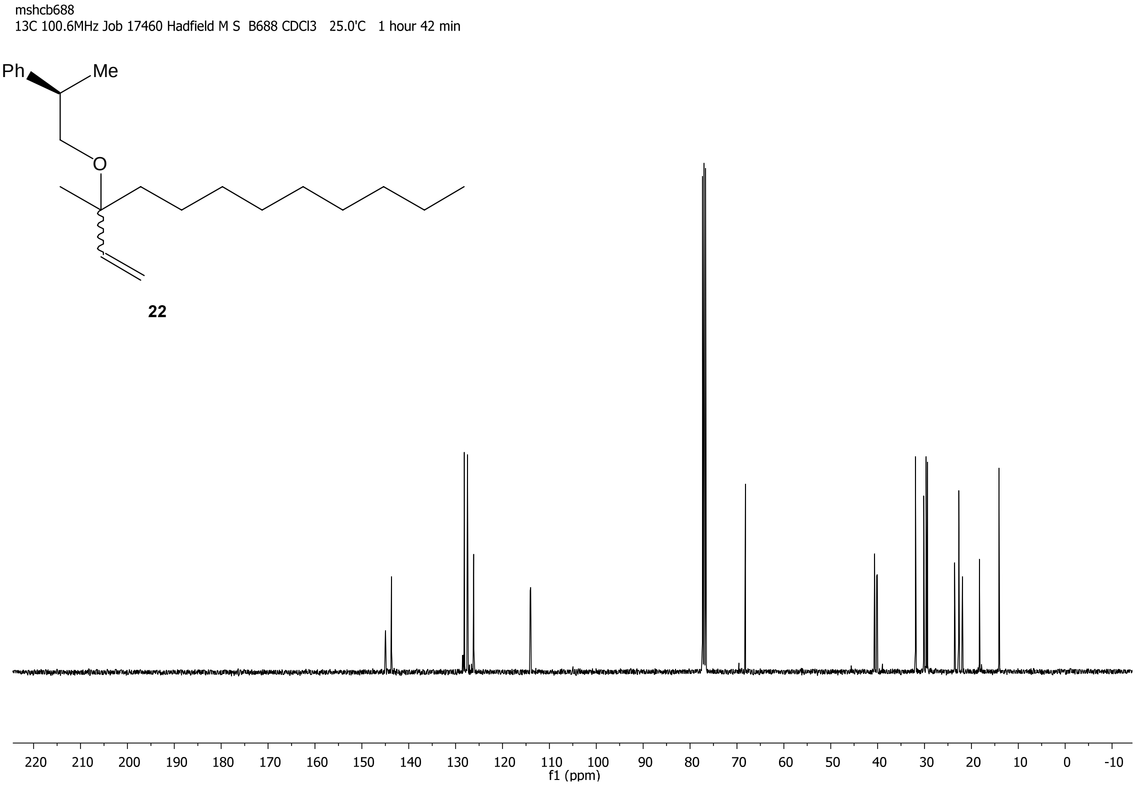


18



20

mshcb704
13C 100.6MHz Job 17667 Hadfield M S B704 CDCl3 25.0'C 2 hours 25 min
OH
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

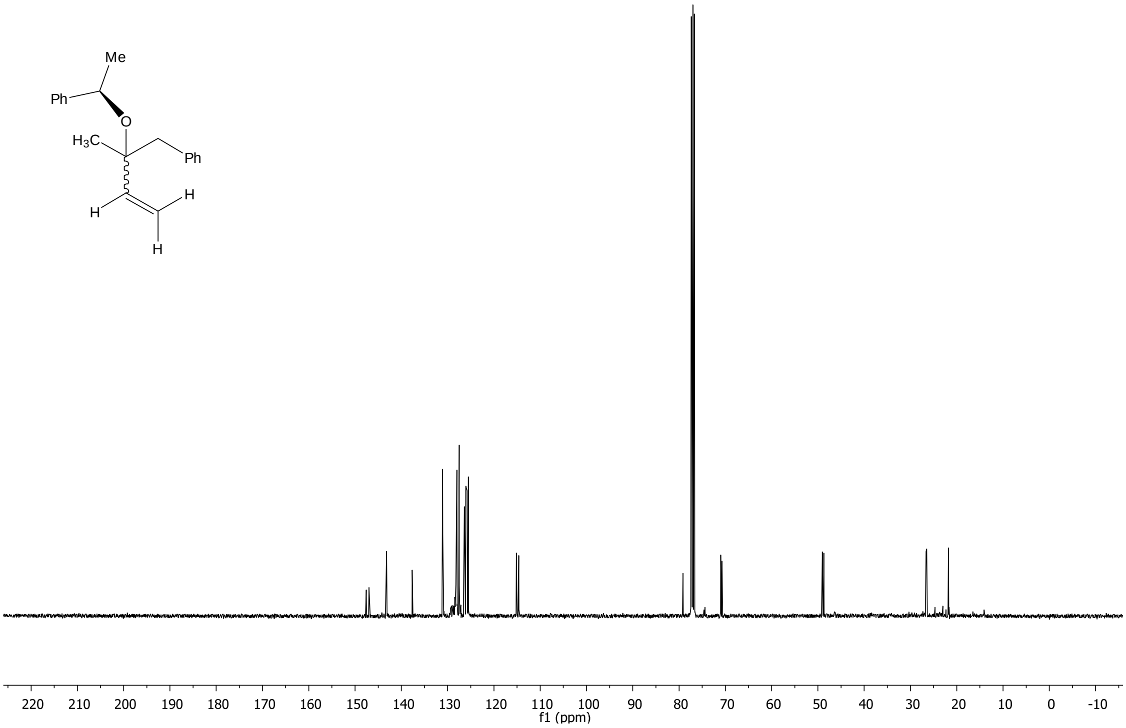


22

mshcb688
13C 100.6MHz Job 17460 Hadfield M S B688 CDCl3 25.0'C 1 hour 42 min
Ph
Me
O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

24

mshca708
13C 100.6MHz Job 17687 Hadfield M S A708 CDCl3 25.0'C 4 hours 37 min



5. References

1) M. Rubin, V. Gevorgyan, *Synthesis,* 2004, **5**, 796.
2) M. Rubin, M. Rubina, V. Gevorgyan, *Synthesis,* 2006, **8**, 1221.
3) J. T. Bauer, M. S. Hadfield and A.-L. Lee, *Chem. Commun.,* 2008, 6405.
4) R. E. Giudici, A.H. Hoveyda, *Am. Chem. Soc.*, 2007, **129**, 3824
5) M. A. Smith, H. G. Richey, *Organometallics*, 2007, **26**, 609