

Supporting Information
Isomerization of Allyl Ethers Initiated
by Lithium Diisopropylamide (LDA)

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Table of Contents

Materials and Methods	S2
General Procedures for the Synthesis of the Allyl Ethers	S2
General Procedures for the Isomerization of the Allyl Ethers (Table 1 and 2a) to Vinyl Ethers by LDA in THF	S8
General Procedures for the Isomerization of the Allyl Ethers (Table 4) to Vinyl Ethers by tBuOK in DMSO	S13
¹ H and ¹³ C NMR Spectra for the Allyl Ethers	S15
¹ H and ¹³ C NMR Spectra for the Vinyl Ethers	S30
GC spectra of vinyl ethers	S48
References	S56

Materials and Methods. THF and DME were used from a dry solvent dispensing system. DMSO was distilled from calcium hydride under a reduced pressure. Diisopropylamine was distilled from sodium hydride. Solvents for extraction and chromatography were technical grade. Unless otherwise stated, purchased chemicals (Aldrich, Acros, Alfa Aesar) were used as received. The concentration of n-butyllithium in n-pentane was determined according to Kofron double titration method.¹ All reactions under anhydrous conditions were conducted using flame- or oven-dried glassware and standard syringe techniques under an atmosphere of argon.

NMR spectra were recorded at either 300 MHz or 400 MHz using CDCl₃ as the solvent. Chemical shifts are reported in ppm and were referenced to residual protonated solvent for ¹H-NMR (δ 7.27 ppm for CHCl₃) and ¹³C-NMR (δ 77.00 ppm for CDCl₃). Data are represented as follows: chemical shift (multiplicity [br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet], integration, coupling constants in Hz). High-resolution mass spectra were obtained using electron impact or fast atom bombardment ionization methods.

General Procedures for the Synthesis of the Allyl Ethers. Allyl phenyl ether was bought from Aldrich directly. For the synthesis of other allyl ethers, it can be divided into three types.

Type I) (Table 1, entries 2-12 and compound **2a**) The starting alcohol (1 equiv) was dissolved in dry THF under an atmosphere of nitrogen at 0°C. To this solution was added sodium hydride (1.3 equiv; 2.6 equiv for entry 12 and **2a**) and was allowed to stir for 10 minutes at 0°C. After adding allyl bromide (1.3 equiv; 2.6 equiv for entry 12 and **2a**), the solution was then allowed to stir at room temperature for 30 minutes and reflux overnight.

The reaction was quenched by the addition of saturated ammonium chloride solution. The mixture was then extracted with diethyl ether three times and the organic phase was washed with water, brine and dried over NaSO₄. The solvent was removed by rotary evaporation and purification was performed by vacuum distillation except entries 2, 8 and entry 11 which were purified by flash column chromatography and simple distillation respectively.

Type II (Table 1, entries 13, 15) To a solution of tert-butyldimethylsilyl chloride (1 equiv) in dry THF under an atmosphere of nitrogen was added imidazole (2.4 equiv). The solution was stirred for 5 minutes before allyl alcohol or 2-methylprop-2-en-1-ol (1.4 equiv) was added. The resulting mixture was allowed to stir for 2 days before being quenched by saturated ammonium chloride solution. The mixture was then extracted with diethyl ether three times and the organic phase was washed with water, brine and dried over NaSO₄. The solvent was removed by rotary evaporation and purification was performed by flash column chromatography.

Type III (Table 1, entry 14) To a solution of 2-methylprop-2-en-1-ol (1 equiv) in dry THF under an atmosphere of nitrogen at 0°C was added sodium hydride (1 equiv). The mixture was stirred at 0°C for 10 minutes before adding 1-bromohexane (1 equiv). The reaction was stirred at room temperature for 30 minutes and was refluxed overnight. The reaction was quenched by the addition of saturated ammonium chloride solution. The mixture was then extracted with diethyl ether three times and the organic phase was washed with water, brine and dried over NaSO₄. The solvent was removed by rotary evaporation and purification was performed by flash column chromatography.

(Allyloxy)cyclopentane (Table 1, entry 2). (Allyloxy)cyclopentane was prepared as described above from cyclopentanol (0.50g, 5.8mmol). Purification (Hexanes : EtOAc = 25:1) gave a light yellow oil (0.59g, 4.7mmol, 81%). ¹H NMR (CDCl₃, 300 MHz) δ 6.02-5.80

(m, 1H), 5.26 (d, 1H, $J = 16.6$ Hz), 5.14 (d, 1H, $J = 10.0$ Hz), 4.01-3.85 (m, 3H), 1.82-1.40 (m, 8H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 135.5, 116.3, 80.9, 69.8, 32.3, 23.6; HRMS-EI (M^+) calcd for $\text{C}_8\text{H}_{14}\text{O}$ 126.1045, found 126.1042.

(Allyloxy)cyclohexane (Table 1, entry 3). (Allyloxy)cyclohexane was prepared as described above from cyclohexanol (9.62g, 96.0mmol). Purification (bp = 36-37°C, 8 mmHg) gave a colorless oil (10.8g, 77.1mmol, 80%). ^1H NMR (CDCl_3 , 300 MHz) δ 6.00-5.83 (m, 1H), 5.25 (d, 1H, $J = 17.2\text{Hz}$), 5.14 (d, 1H, $J = 10.2\text{Hz}$), 4.06-3.94 (m, 2H), 3.35-3.20 (m, 1H), 2.00-1.06 (m, 10H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 169.3, 155.1, 144.6, 129.7, 128.1, 126.9, 80.0, 67.0, 66.8, 66.7, 49.3, 46.0, 42.6, 35.0, 28.4; MS m/z 140 (M^+), 97, 83, 67, 58, 55.

(Allyloxy)cycloheptane (Table 1, entry 4). (Allyloxy)cycloheptane was prepared as described above from cycloheptanol (1.92g, 16.8mmol). Purification (bp = 54-56°C, 8 mmHg) gave a colorless oil (2.07g, 13.4mmol, 80%). ^1H NMR (CDCl_3 , 400 MHz) δ 5.99-5.85 (m, 1H), 5.26 (dd, 1H, $J = 17.2, 1.2$ Hz), 5.21-5.10 (d, 1H, $J = 9.5$ Hz), 3.99-3.93 (m, 2H), 3.47 (quintet, 1H, $J = 4.0\text{Hz}$), 1.95-1.83 (m, 2H), 1.71-1.49 (m, 8H) , 1.44-1.31 (m, 2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 135.7, 116.2, 79.5, 69.1, 33.9, 28.4, 23.0; HRMS-EI (M^+) calcd for $\text{C}_{10}\text{H}_{18}\text{O}$ 154.1358, found 154.1355.

5-(allyloxy)-1,1,3,3-tetramethylcyclohexane (Table 1, entry 5). 5-(allyloxy)-1,1,3,3-tetramethylcyclohexane was prepared as described above from 3,3,5,5-tetramethylcyclohexanol (4.1g, 26.3mmol). Purification (bp = 78-80°C, 8 mmHg) gave a colorless oil (3.6g, 18.4mmol, 70%). ^1H NMR (CDCl_3 , 400 MHz) δ 6.00-5.87 (m, 1H), 5.27 (d, 1H, $J = 16.2$ Hz), 5.15 (d, 1H, $J = 9.9$ Hz), 4.02 (d, 2H, $J = 4.92$ Hz), 3.65-3.52 (m, 1H), 1.78 (d, 2H, $J = 11.6\text{Hz}$), 1.27-1.17 (m, 1H), 1.12-0.87 (m, 15H); ^{13}C NMR (CDCl_3 , 100

MHz) δ 135.6, 116.3, 77.3, 69.0, 51.8, 45.3, 35.2, 32.3, 27.9; HRMS-EI ($M +$) calcd for $C_{13}H_{24}O$ 196.1827, found 196.1822.

(1S,2R,4R)-2-(allyloxy)-1-isopropyl-4-methylcyclohexane (Table 1, entry 6).

(1S,2R,4R)-2-(allyloxy)-1-isopropyl-4-methylcyclohexane was prepared as described above from (-)-menthol (2.50g, 16.0mmol). Purification (bp = 78-79°C, 8 mmHg) gave a colorless oil (2.56g, 13.1mmol, 82%). 1H NMR ($CDCl_3$, 300 MHz) δ 6.04-5.85 (m, 1H), 5.26 (d, 1H, J = 17.2 Hz), 5.14 (d, 1H, J = 10.2 Hz), 4.21-4.06 (m, 1H), 3.99-3.82 (m, 1H), 3.08 (dt, 1H, J = 10.4, 4.1 Hz), 2.35-2.17 (m, 1H), 2.17-2.04 (m, 1H), 1.74-1.55 (m, 2H), 1.46-1.18 (m, 2H), 1.12-0.71 (m, 14H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 135.8, 116.3, 78.7, 69.5, 48.3, 40.5, 34.6, 31.5, 25.5, 23.4, 22.3, 21.0, 16.2; HRMS-EI ($M +$) calcd for $C_{13}H_{24}O$ 198.1827, found 198.1821.

1-(allyloxy)hexane (Table 1, entry 7). 1-(allyloxy)hexane was prepared as described above from 1-hexanol (3.25g, 31.9mmol). Purification (bp = 36-37°C, 8 mmHg) gave a colorless oil (3.69g, 26.0mmol, 82%). 1H NMR ($CDCl_3$, 400 MHz) δ 5.99-5.85 (m, 1H), 5.27 (dd, 1H, J = 17.2, 1.6 Hz), 5.16 (d, 1H, J = 10.3 Hz), 4.00-3.93 (m, 2H), 3.96 (t, 2H, J = 6.7 Hz), 1.66-1.52 (m, 2H), 1.41-1.24 (m, 6H), 0.89 (t, 3H, J = 6.64Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 135.1, 116.6, 71.8, 70.5, 31.7, 29.7, 25.9, 22.6, 14.0; HRMS-EI ($M +$) calcd for $C_9H_{18}O$ 142.1358, found 142.1360.

(1S,2S,4R)-2-(allyloxy)bicyclo[2.2.1]heptane (Table 1, entry 8). (1S,2S,4R)-2-(allyloxy)bicyclo[2.2.1]heptane was prepared as described above from (1S,2S,4R)-bicyclo[2.2.1]heptan-2-ol (0.50g, 4.5mmol). Purification (Hexanes: EtOAc = 30:1) gave a light yellow oil (0.62g, 4.1mmol, 91%). 1H NMR ($CDCl_3$, 400 MHz) δ 6.02-5.35 (m, 1H), 5.26 (dd, 1H, J = 22.9, 2.2 Hz), 5.14 (dd, 1H, J = 13.2, 1.1 Hz), 4.02-3.86 (m, 2H), 3.45-3.35 (m, 1H), 2.37-2.29 (m, 1H), 2.29-2.20 (m, 1H), 1.65-1.33 (m, 5H), 1.16-0.91 (m,

2H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 135.5, 116.2, 82.1, 69.3, 40.4, 39.6, 35.2, 34.8, 28.5, 24.6; HRMS-EI (M^+) calcd for $\text{C}_{10}\text{H}_{16}\text{O}$ 152.1201, found 152.1206.

(1S,2R,4S)-2-(allyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (Table 1, entry 9).

(1S,2R,4S)-2-(allyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane was prepared as described above from (1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (6.5g, 42.2mmol). Purification (bp = 68-70°C, 8 mmHg) gave a colorless oil (6.8g, 35.1mmol, 83%). ^1H NMR (CDCl_3 , 300 MHz) δ 6.03-5.82 (m, 1H), 5.28 (d, 1H, J = 17.1 Hz), 5.15 (d, 1H, J = 9.1 Hz), 4.11-3.99 (m, 1H), 3.99-3.82 (m, 1H), 3.73-3.55 (m, 1H), 2.21-1.93 (m, 2H), 1.83-1.55 (m, 2H), 1.35-1.13 (m, 2H), 1.12-0.96 (m, 1H), 0.96-0.75 (m, 9H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 135.9, 115.7, 84.3, 70.8, 49.2, 47.8, 45.0, 36.3, 28.2, 26.7, 19.8, 18.8, 14.0; HRMS-EI (M^+) calcd for $\text{C}_{13}\text{H}_{22}\text{O}$ 194.1671, found 194.1668.

(1S,2S,4S)-2-(allyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (Table 1, entry 10).

(1S,2S,4S)-2-(allyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane was prepared as described above from (1S,2S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-ol (3.0g, 19.5mmol). Purification (bp = 65-68°C, 8 mmHg) gave a colorless oil (3.1g, 16.0mmol, 82%). ^1H NMR (CDCl_3 , 400 MHz) δ 5.96-5.82 (m, 1H), 5.26 (dd, 1H, J = 17.2, 1.6 Hz), 5.11 (d, 1H, J = 10.5 Hz), 4.03-3.93 (m, 1H), 3.91-3.81 (m, 1H), 3.29-3.22 (m, 1H), 1.82-1.42 (m, 5H), 1.05-0.95 (m, 5H), 0.91 (s, 3H), 0.81 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 135.9, 115.3, 107.6, 86.5, 83.8, 69.8, 49.2, 46.5, 45.1, 38.7, 34.5, 27.3, 20.24, 20.20, 11.9; HRMS-EI (M^+) calcd for $\text{C}_{13}\text{H}_{22}\text{O}$ 194.1671, found 194.1662.

3-(allyloxy)-2,4-dimethylpentane (Table 1, entry 11).

3-(allyloxy)-2,4-dimethylpentane was prepared as described above from 2,4-dimethylpentan-3-ol (2.0g, 17.2mmol). Purification (bp = 125°C, 760 mmHg) gave a colorless oil (2.2g, 14.1mmol, 82%). ^1H NMR (CDCl_3 , 300 MHz) δ 6.04-5.86 (m, 1H), 5.26 (d, 1H, J = 17.2 Hz), 5.12

(d, 1H, $J = 10.3$ Hz), 4.12-4.04 (m, 2H), 2.70 (t, 1H, $J = 5.6$ Hz), 1.91-1.73 (m, 2H), 0.99-0.85 (m, 12H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 135.6, 115.9, 90.7, 74.8, 30.8, 20.3, 17.7; MS m/z 155 ($\text{M}-\text{H}^+$), 113, 71, 57, 55.

1,6-bis(allyloxy)hexane (Table 1, entry 12). 1,6-bis(allyloxy)hexane was prepared as described above from hexane-1,6-diol (3.5g, 29.7mmol). Purification (bp = 96-98°C, 8 mmHg) gave a colorless oil (4.6g, 23.2mmol, 78%). ^1H NMR (CDCl_3 , 400 MHz) δ 5.99-5.85 (m, 2H), 5.26 (d, 2H, $J = 17.2$ Hz), 5.16 (d, 2H, $J = 10.0$ Hz), 4.00-3.92 (m, 4H), 3.42 (t, 4H, $J = 6.5$ Hz), 1.66-1.54 (m, 4H), 1.44-1.33 (m, 4H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 135.0, 116.7, 71.8, 70.3, 29.7, 26.0; HRMS-FAB ($\text{M} + \text{Na}^+$) calcd for $\text{C}_{12}\text{H}_{22}\text{O}_2$ 221.1518, found 221.1522.

(Allyloxy)(tert-butyl)dimethylsilane (Table 1, entry 13). (Allyloxy)(tert-butyl)dimethylsilane was prepared as described above from tert-butylchlorodimethylsilane (1.2g, 7.96mmol). Purification (Hexanes : EtOAc = 30: 1) gave a colorless oil (1.0g, 5.81mmol, 73%). ^1H NMR (CDCl_3 , 300 MHz) δ 6.01-5.85 (d, 1H), 5.27 (d, 1H, $J = 17.0$ Hz), 5.08 (d, 1H, $J = 9.0$ Hz), 4.26-4.16 (m, 2H), 0.93 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 137.5, 113.9, 64.1, 25.9, 18.4, -5.3; MS m/z 172 (M^+), 115, 99, 85, 75, 73, 59, 57.

1-((2-methylallyl)oxy)hexane (Table 1, entry 14). 1-((2-methylallyl)oxy)hexane was prepared as described above from 2-methylprop-2-en-1-ol (0.77g, 10.7mmol). Purification (Hexanes : EtOAc = 20 : 1) gave a colorless oil (1.31g, 8.40mmol, 78%). ^1H NMR (CDCl_3 , 400 MHz) δ 4.95 (s, 1H), 4.88 (s, 1H), 3.87 (s, 2H), 3.38 (t, 2H, $J = 6.6$ Hz), 1.99-1.21 (m, 11H), 0.89(t, 3H, $J = 5.9$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 142.6, 111.7, 74.7, 70.2, 31.7, 29.7, 25.9, 22.6, 19.4, 14.0; HRMS-EI (M^+) calcd for $\text{C}_{10}\text{H}_{20}\text{O}$

156.1514, found 156.1502.

tert-butyldimethyl((2-methylallyl)oxy)silane (Table 1, entry 15). tert-butyldimethyl((2-methylallyl)oxy)silane was prepared as described above from tert-butylchloro-dimethylsilane (0.6g, 3.98mmol). Purification (Hexanes : EtOAc = 30 : 1) gave a colorless oil (0.5g, 2.69mmol, 68%). ¹H NMR (CDCl₃, 400 MHz) δ 4.99 (s, 1H), 4.81 (s, 1H), 4.05 (s, 2H), 1.71 (s, 3H), 0.94 (s, 9H), 0.09 (s, 6H); ¹³C NMR (CDCl₃, 100 MHz) δ 145.0, 109.5, 67.2, 26.3, 19.3, 18.8, -5.0; HRMS-EI (M + Na) calcd for C₁₀H₂₂OSi 186.1440, found 186.1431.

1,3-bis(allyloxy)-2,2,4-trimethylpentane (2a). 1,3-bis(allyloxy)-2,2,4-trimethylpentane was prepared as described above from 2,2,4-trimethylpentane-1,3-diol (4.0g, 27.4mmol). Purification (bp = 78-80 °C, 8 mmHg) gave a colorless oil (5.80g, 25.7mmol, 93%). ¹H NMR (CDCl₃, 300 MHz) δ 6.02-5.84 (m, 2H), 5.27 (d, 2H, *J* = 17.2 Hz), 5.14 (m, 2H), 4.18-3.92 (m, 4H), 3.31 (d, 1H, *J* = 8.6 Hz), 3.15-3.04 (m, 2H), 2.00-1.86 (m, 1H), 1.07-0.85 (m, 12H); ¹³C NMR (CDCl₃, 75 MHz) δ 135.8, 135.3, 116.2, 115.3, 87.4, 77.9, 74.7, 72.1, 40.5, 28.9, 24.6, 22.3, 21.1, 17.9; MS *m/z* 227 (M + H⁺), 183, 127, 113, 112, 85, 71, 57, 55.

General Procedures for the Isomerization of the Allyl Ethers (Table 1 and 2a)

to Vinyl Ethers by LDA in THF. Under an argon atmosphere, a pentane solution of *n*-butyllithium (2 equiv) was added dropwise to a solution of diisopropylamine (2 equiv) in dry THF (4 mL) at -78°C. After stirring for 5min, the solution was allowed to warm to 0°C for 2 min and was then re-cooled to -78°C. Allyl ether (1 equiv; except Table 1, entries 10-12) was added dropwise to the mixture at -78°C and the mixture was allowed to stir for 5 min at -78°C before warming up to room temperature. The reaction time of the

mixture varied between different kind of allyl ethers (Table 1). After being stirred for the corresponding time, the reaction mixture was quenched by saturated ammonium chloride solution. The mixture was then extracted with diethyl ether three times and the organic phase was washed with water, brine and dried over NaSO₄. The solvent was first removed by rotary evaporation and then by oil pump yielding a yellow liquid which was then characterized by NMR spectroscopy and HRMS.

(Z)-(prop-1-en-1-yloxy)benzene (Table 1, entry 1). (Z)-(prop-1-en-1-yloxy)benzene (187mg, 88%) was obtained from (allyloxy)benzene (165mg) as described above. ¹H NMR (CDCl₃, 400 MHz) δ 7.28-7.30 (m, 2H), 7.10-7.00 (m, 3H), 6.41 (d, 1H, *J* = 4.4 Hz), 4.91 (m, 1H), 1.75 (d, 3H, *J* = 5.9 Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 157.5, 140.8, 129.5, 122.3, 116.1, 107.5, 9.4; HRMS-EI (M +) calcd for C₉H₁₀O 134.0732, found 134.0728.

(Z)-(prop-1-en-1-yloxy)cyclopentane (Table 1, entry 2). (Z)-(prop-1-en-1-yloxy)cyclopentane (151mg, 83%) was obtained from (allyloxy)cyclopentane (182mg) as described above. ¹H NMR (CDCl₃, 400 MHz) δ 5.98-5.94 (dq, 1H, *J* = 6.2 Hz, 1.6 Hz), 4.41 (m, 1H), 4.23 (m, 1H), 1.75 (m, 6H), 1.57 (m, 5H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.3, 101.5, 82.9, 32.6, 23.5, 9.2; HRMS-EI (M +) calcd for C₈H₁₄O 126.1045, found 126.1041.

(Z)-(prop-1-en-1-yloxy)cyclohexane (Table 1, entry 3). (Z)-(prop-1-en-1-yloxy)cyclohexane (182mg, 88%) was obtained from (allyloxy)cyclohexane (207mg) as described above. ¹H NMR (CDCl₃, 300 MHz) δ 6.02-5.90 (d, 1H, *J* = 4.8 Hz), 4.45-4.30 (m, 1H), 3.64-3.45 (m, 1H), 1.90-1.10 (m, 13H), 2.49 (dd, 1H, *J* = 5.6, 12.4 Hz), 2.41 (dd, 1H, *J* = 7.5, 12.4), 1.42 (s, 9H); ¹³C NMR (CDCl₃, 75 MHz) δ 114.2, 101.0, 78.9, 32.3, 25.6, 23.6, 9.3; HRMS-EI (M +) calcd for C₉H₁₆O 140.1201, found 140.1205.

(Z)-(prop-1-en-1-yloxy)cycloheptane (Table 1, entry 4). (Z)-(prop-1-en-1-yloxy)cycloheptane (202mg, 99%) was obtained from (allyloxy)cycloheptane (205mg) as described above. ¹H NMR (CDCl₃, 300 MHz) δ 6.00-5.92 (d, 1H, *J* = 6.2 Hz), 4.44-4.32 (m, 1H), 3.84-3.72 (m, 1H), 1.96-1.32 (m, 15H); ¹³C NMR (CDCl₃, 75 MHz) δ 144.5, 101.1, 81.8, 34.2, 28.3, 22.7, 9.3; HRMS-EI (*M* +) calcd for C₁₀H₁₈O 154.1358, found 154.1356.

(Z)-1,1,3,3-tetramethyl-5-(prop-1-en-1-yloxy)cyclohexane (Table 1, entry 5). (Z)-1,1,3,3-tetramethyl-5-(prop-1-en-1-yloxy)cyclohexane (0.19g, 100%) was obtained from 5-(allyloxy)-1,1,3,3-tetramethylcyclohexane (0.19g) as described above. ¹H NMR (CDCl₃, 400 MHz) δ 6.07-6.00 (d, 1H, *J* = 6.2 Hz), 4.44-4.34 (m, 1H), 3.90-3.78 (m, 1H), 1.83-1.73 (m, 2H), 1.62-1.54 (m, 3H), 1.31-0.89 (m, 16H); ¹³C NMR (CDCl₃, 100 MHz) δ 144.3, 100.9, 75.9, 51.6, 45.4, 34.9, 32.3, 28.0, 9.3; HRMS-EI (*M* +) calcd for C₁₃H₂₄O 196.1827, found 196.1824.

(1S,2R,4R)-1-isopropyl-4-methyl-2-((Z)-prop-1-en-1-yloxy)cyclohexane (Table 1, entry 6). (1S,2R,4R)-1-isopropyl-4-methyl-2-((Z)-prop-1-en-1-yloxy)cyclohexane (0.20g, 100%) was obtained from (1S,2R,4R)-2-(allyloxy)-1-isopropyl-4-methylcyclohexane (0.20g) as described above. ¹H NMR (CDCl₃, 400 MHz) δ 6.04-5.99 (dq, 1H, *J* = 6.2 Hz, 1.6 Hz), 4.38-4.30 (m, 1H), 3.35 (dt, 1H, *J* = 10.7, 4.3 Hz), 2.21-2.10 (m, 1H), 2.05-1.96 (m, 1H), 1.69-1.59 (m, 5H), 1.45-1.32 (m, 2H), 1.06-0.76 (m, 11H); ¹³C NMR (CDCl₃, 100 MHz) δ 114.8, 100.2, 81.3, 47.8, 41.6, 34.4, 31.6, 25.9, 23.6, 22.2, 20.8, 16.4, 9.3; HRMS-EI (*M* +) calcd for C₁₃H₂₄O 196.1827, found 196.1819.

(Z)-1-(prop-1-en-1-yloxy)hexane (Table 1, entry 7). (Z)-1-(prop-1-en-1-yloxy)hexane (180mg, 92%) was obtained from 1-(allyloxy)hexane (195mg) as described above. ¹H NMR (CDCl₃, 400 MHz) δ 5.98-5.91 (d, 1H, *J* = 4.2 Hz), 4.43-4.32 (m, 1H),

3.76-3.68 (t, 2H, $J = 6.6$ Hz), 1.67-1.54 (m, 5H), 1.42-1.24 (m, 6H), 0.94-0.85 (t, 3H, $J = 6.5$ Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 145.6, 100.7, 72.1, 31.6, 29.7, 25.5, 22.6, 14.0, 9.2; HRMS-EI (M^+) calcd for $\text{C}_9\text{H}_{18}\text{O}$ 142.1358, found 142.1360.

(1S,2S,4R)-2-((Z)-prop-1-en-1-yloxy)bicyclo[2.2.1]heptane (Table 1, entry 8). (1S,2S,4R)-2-((Z)-prop-1-en-1-yloxy)bicyclo[2.2.1]heptane (125mg, 89%) was obtained from (1S,2S,4R)-2-(allyloxy)bicyclo[2.2.1]heptane (140mg) as described above. ^1H NMR (CDCl_3 , 400 MHz) δ 5.98-5.93 (dq, 1H, $J = 6.2$ Hz, 1.6 Hz), 4.45-4.37 (m, 1H), 3.70-3.65 (m, 1H), 2.34-2.24 (m, 2H), 1.64-1.40 (m, 8H), 1.15-0.59 (m, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 144.1, 101.5, 83.8, 41.3, 39.3, 35.2, 34.7, 28.5, 24.2, 9.3; HRMS-EI (M^+) calcd for $\text{C}_{10}\text{H}_{16}\text{O}$ 152.1201, found 152.1206.

(1S,2R,4S)-1,7,7-trimethyl-2-((Z)-prop-1-en-1-yloxy)bicyclo[2.2.1]heptane (Table 1, entry 9). (1S,2R,4S)-1,7,7-trimethyl-2-((Z)-prop-1-en-1-yloxy)bicyclo[2.2.1]heptane (185mg, 95%) was obtained from (1S,2R,4S)-2-(allyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (195mg) as described above. ^1H NMR (CDCl_3 , 400 MHz) δ 5.99-5.94 (dq, 1H, $J = 6.1$ Hz, 1.6Hz), 4.39-4.31 (m, 1H), 3.94-3.88 (m, 1H), 2.25-2.14 (m, 1H), 2.10-2.01 (m, 1H), 1.79-1.58 (m, 5H), 1.33-1.21 (m, 2H), 1.15-1.07 (m, 1H), 0.94-0.84 (m, 9H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 145.8, 100.4, 86.6, 49.5, 48.0, 45.0, 36.4, 28.1, 26.7, 19.8, 18.8, 13.8, 9.4; HRMS-EI (M^+) calcd for $\text{C}_{13}\text{H}_{22}\text{O}$ 194.1671, found 194.1668.

(1S,2S,4S)-1,7,7-trimethyl-2-((Z)-prop-1-en-1-yloxy)bicyclo[2.2.1]heptane (Table 1, entry 10). (1S,2S,4S)-1,7,7-trimethyl-2-((Z)-prop-1-en-1-yloxy)bicyclo[2.2.1]heptane (0.20g, 100%) was obtained from (1S,2S,4S)-2-(allyloxy)-1,7,7-trimethylbicyclo[2.2.1]heptane (0.20g) as described above. ^1H NMR (CDCl_3 , 400 MHz) δ 5.95-5.88 (dq, 1H, $J = 6.2\text{Hz}$ Hz, 1.6 Hz), 4.35-4.26 (m, 1H), 3.59-3.52 (m, 1H), 1.90-1.47 (m,

8H), 1.08-0.80 (m, 11H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 145.7, 99.7, 88.9, 49.5, 46.6, 45.0, 38.7, 33.9, 27.2, 20.2, 20.0, 11.8, 9.3; HRMS-EI (M^+) calcd for $\text{C}_{13}\text{H}_{22}\text{O}$ 194.1671, found 194.1665.

(Z)-2,4-dimethyl-3-(prop-1-en-1-yloxy)pentane (Table 1, entry 11). (Z)-2,4-dimethyl-3-(prop-1-en-1-yloxy)pentane (180mg, 87%) was obtained from 3-(allyloxy)-2,4-dimethylpentane (207mg) as described above. ^1H NMR (CDCl_3 , 400 MHz) δ 6.02-5.93 (d, 1H, $J = 6.2$ Hz), 4.22-4.11 (m, 1H), 3.00-2.90 (m, 1H), 1.95-1.80 (m, 2H), 1.64-1.55 (m, 3H), 0.98-0.83 (m, 12H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 149.3, 97.7, 93.5, 30.9, 20.4, 17.9, 9.6; HRMS-EI (M^+) calcd for $\text{C}_{10}\text{H}_{20}\text{O}$ 156.1514, found 156.1510.

1,6-bis((Z)-prop-1-en-1-yloxy)hexane (Table 1, entry 12). 1,6-bis((Z)-prop-1-en-1-yloxy)hexane (192mg, 100%) was obtained from 1,6-bis(allyloxy)hexane (192mg) as described above. ^1H NMR (CDCl_3 , 400 MHz) δ 6.02-5.91 (dq, 2H, $J = 8.2$ Hz, 2.2 Hz), 4.44-4.33 (m, 2H), 3.85-3.68 (m, 4H), 1.82-1.36 (m, 14H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 145.6, 100.8, 71.9, 29.7, 25.6, 9.2; HRMS-EI (M^+) calcd for $\text{C}_{12}\text{H}_{22}\text{O}_2$ 198.1620, found 198.1612.

(Z)-tert-butyldimethyl(prop-1-en-1-yloxy)silane (Table 1, entry 13). (Z)-tert-butyldimethyl(prop-1-en-1-yloxy)silane (160g, 81%) was obtained from (allyloxy)(tert-butyl)dimethylsilane (198mg) as described above. ^1H NMR (CDCl_3 , 400 MHz) δ 6.25-6.17 (dq, 1H, $J = 4.1$ Hz, 1.6 Hz), 4.57-4.46 (m, 1H), 1.63-1.55 (dd, 3H, $J = 6.7$, 1.6 Hz), 0.94 (s, 9H), 0.14 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 139.3, 104.8, 25.7, 18.3, 8.9, -5.4; HRMS-EI (M^+) calcd for $\text{C}_9\text{H}_{20}\text{OSi}$ 172.1283, found 172.1288.

1-((2-methylprop-1-en-1-yl)oxy)hexane (Table 1, entry 14). 1-((2-methylprop-1-en-1-yl)oxy)hexane (140mg, 100%) was obtained from 1-((2-methylallyl)oxy)hexane

(140mg) as described above. ^1H NMR (CDCl_3 , 400 MHz) δ 5.79 (s, 1H), 3.65 (t, 2H, J = 6.6 Hz), 1.68-1.47 (m, 8H), 1.42-1.23 (m, 6H), 0.89 (t, 3H, J = 6.6 Hz); ^{13}C NMR (CDCl_3 , 100 MHz) δ 140.1, 110.1, 71.8, 31.6, 29.7, 25.56, 25.59, 19.5, 14.9, 14.0; HRMS-EI (M^+) calcd for $\text{C}_{10}\text{H}_{20}\text{O}$ 156.1514, found 156.1518.

tert-butyldimethyl((2-methylprop-1-en-1-yl)oxy)silane (Table 1, entry 15). tert-butyldimethyl((2-methylprop-1-en-1-yl)oxy)silane (0.17g, 85%) was obtained from tert-butyldimethyl((2-methylallyl)oxy)silane (0.20g) as described above. ^1H NMR (CDCl_3 , 400 MHz) δ 6.04 (s, 1H), 1.61 (s, 3H), 1.54 (s, 3H), 0.93 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 133.5, 113.3, 25.7, 19.3, 18.2, 14.7, -5.3; HRMS-EI (M^+) calcd for $\text{C}_{10}\text{H}_{22}\text{OSi}$ 186.1440, found 186.1431.

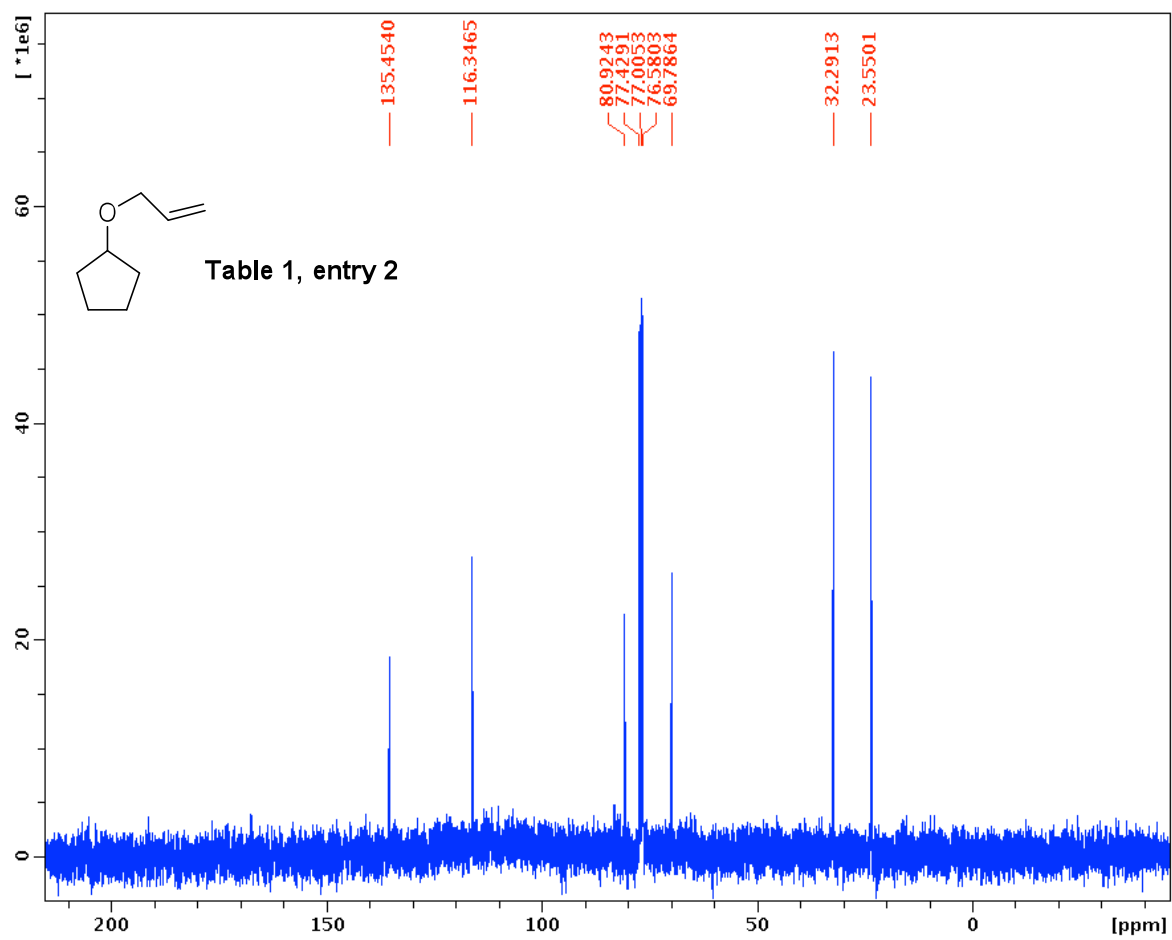
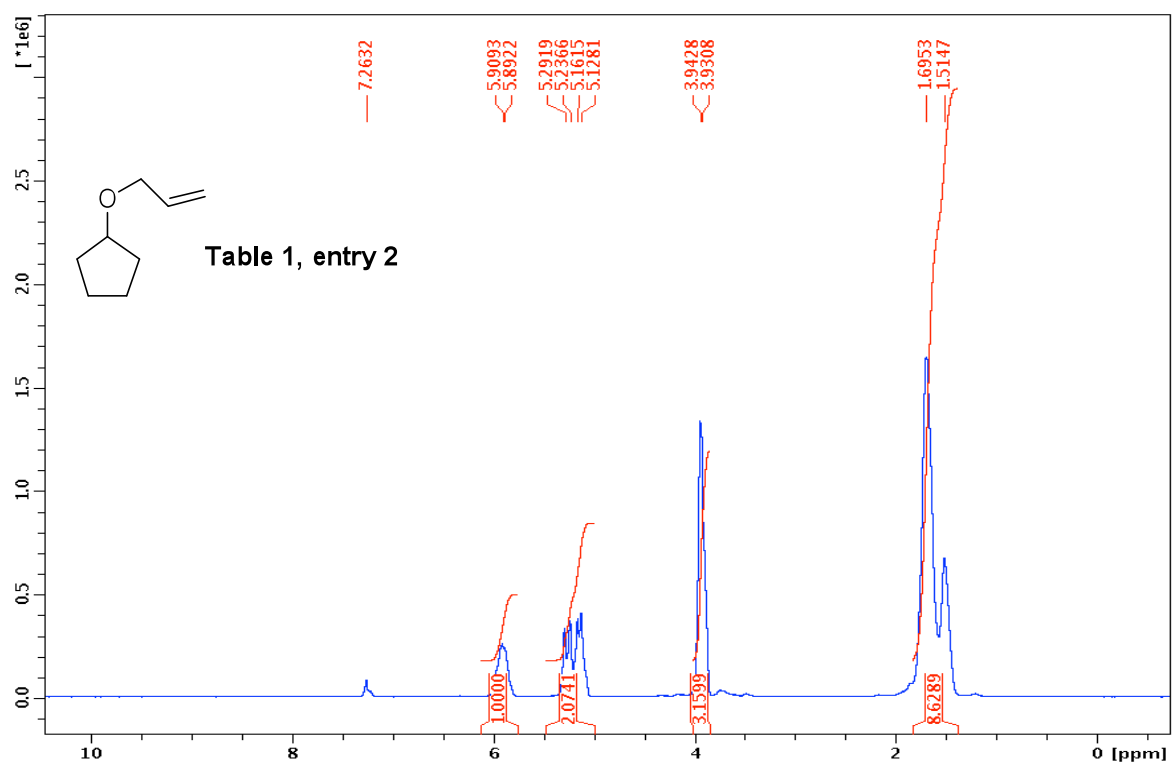
(Z)-3-(allyloxy)-2,2,4-trimethyl-1-(prop-1-en-1-yloxy)pentane (Isomerization of 2a). (Z)-3-(allyloxy)-2,2,4-trimethyl-1-(prop-1-en-1-yloxy)pentane (0.194g, 0.86mmol, 100%) was obtained from 1,3-bis(allyloxy)-2,2,4-trimethyl-pentane (0.194g, 0.86mmol) as described above. ^1H NMR (CDCl_3 , 300 MHz) δ 6.01-5.83 (m, 2H), 5.26 (d, 1H, J = 17.1 Hz), 5.10 (d, 1H, J = 10.4 Hz), 4.40-4.26 (m, 1H), 4.19-3.90 (m, 2H), 3.63 (d, 1H, J = 9.3 Hz), 3.36 (d, 1H, J = 9.4 Hz), 3.12 (s, 1H), 2.03-1.85 (m, 1H), 1.63-1.51 (m, 3H), 1.08-0.82 (m, 12H); ^{13}C NMR (CDCl_3 , 75 MHz) δ 146.4, 135.6, 115.4, 100.0, 87.3, 79.4, 74.7, 40.9, 28.8, 24.7, 22.2, 20.5, 17.9, 9.2; MS m/z 226 (M^+), 183, 157, 127, 125, 113, 111, 85, 71, 69, 57, 55.

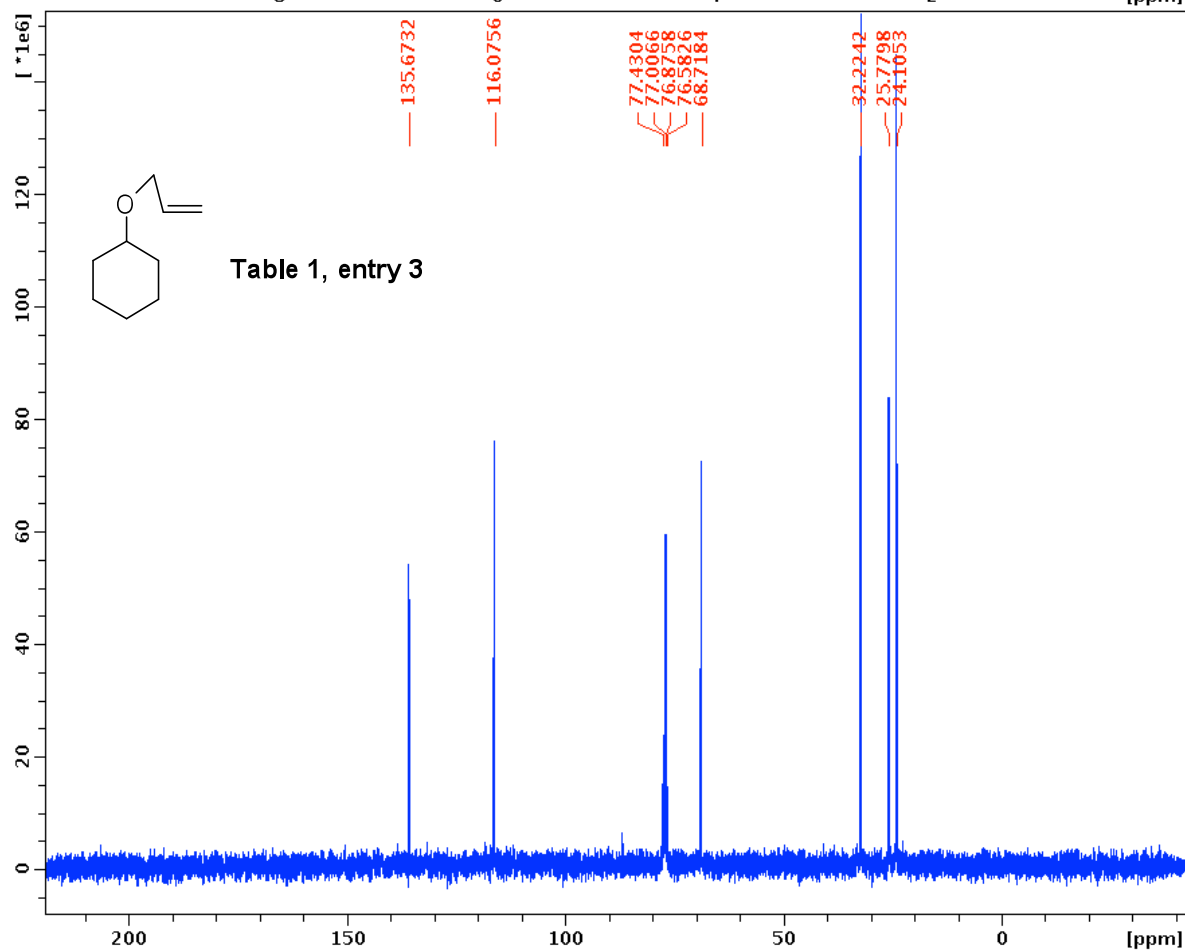
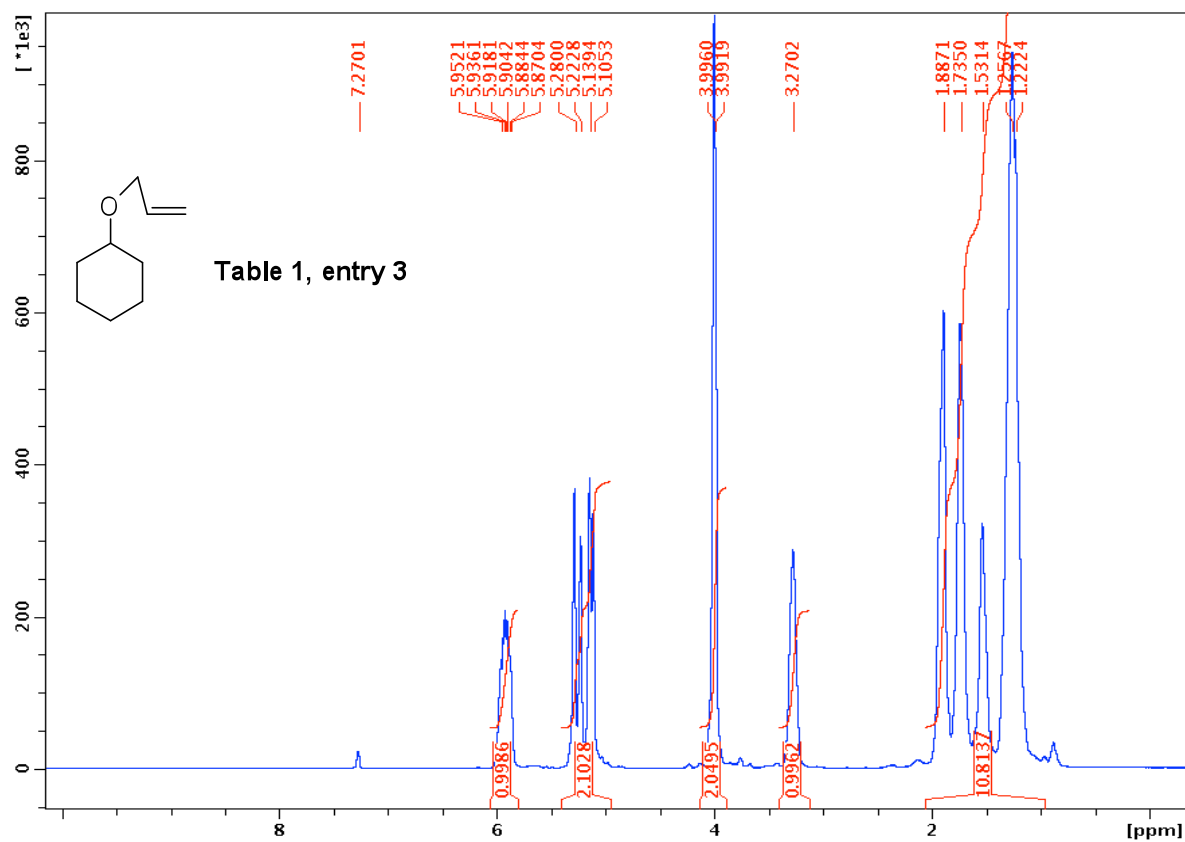
General Procedures for the Isomerization of the Allyl Ethers (Table 4)

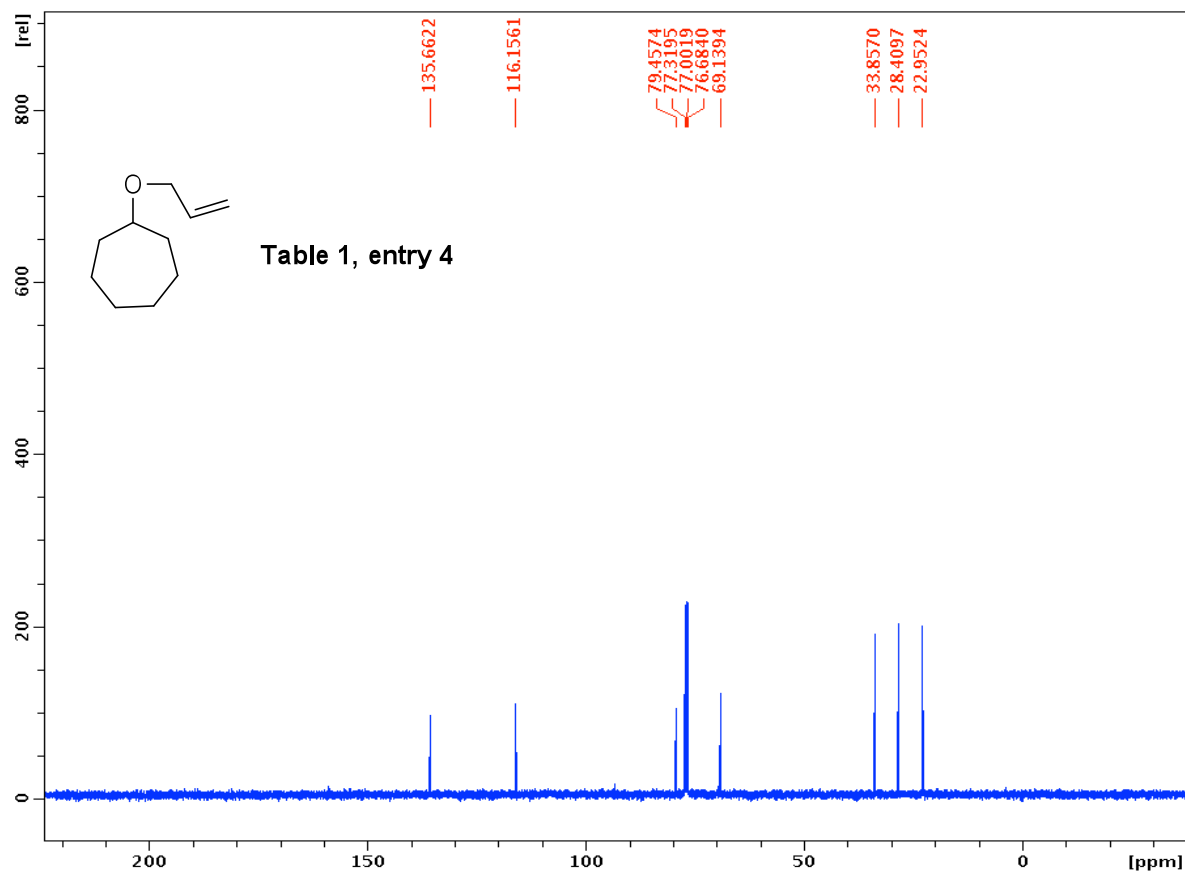
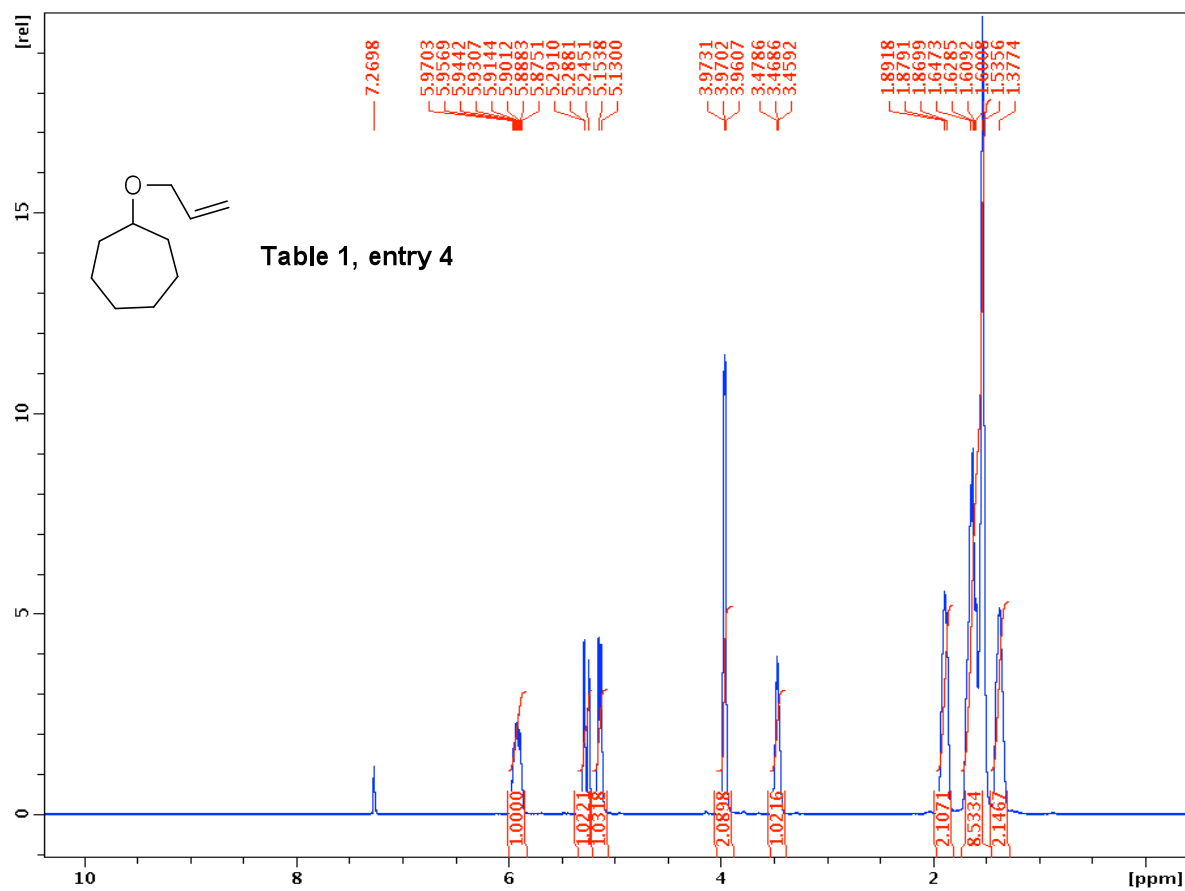
to Vinyl Ethers by tBuOK in DMSO. Under an argon atmosphere, potassium t-butoxide (2 equiv) purchased directly from Aldrich was dissolved in 3mL dry DMSO at room temperature. To this solution was added allyl ether (1 equiv) and the reaction mix

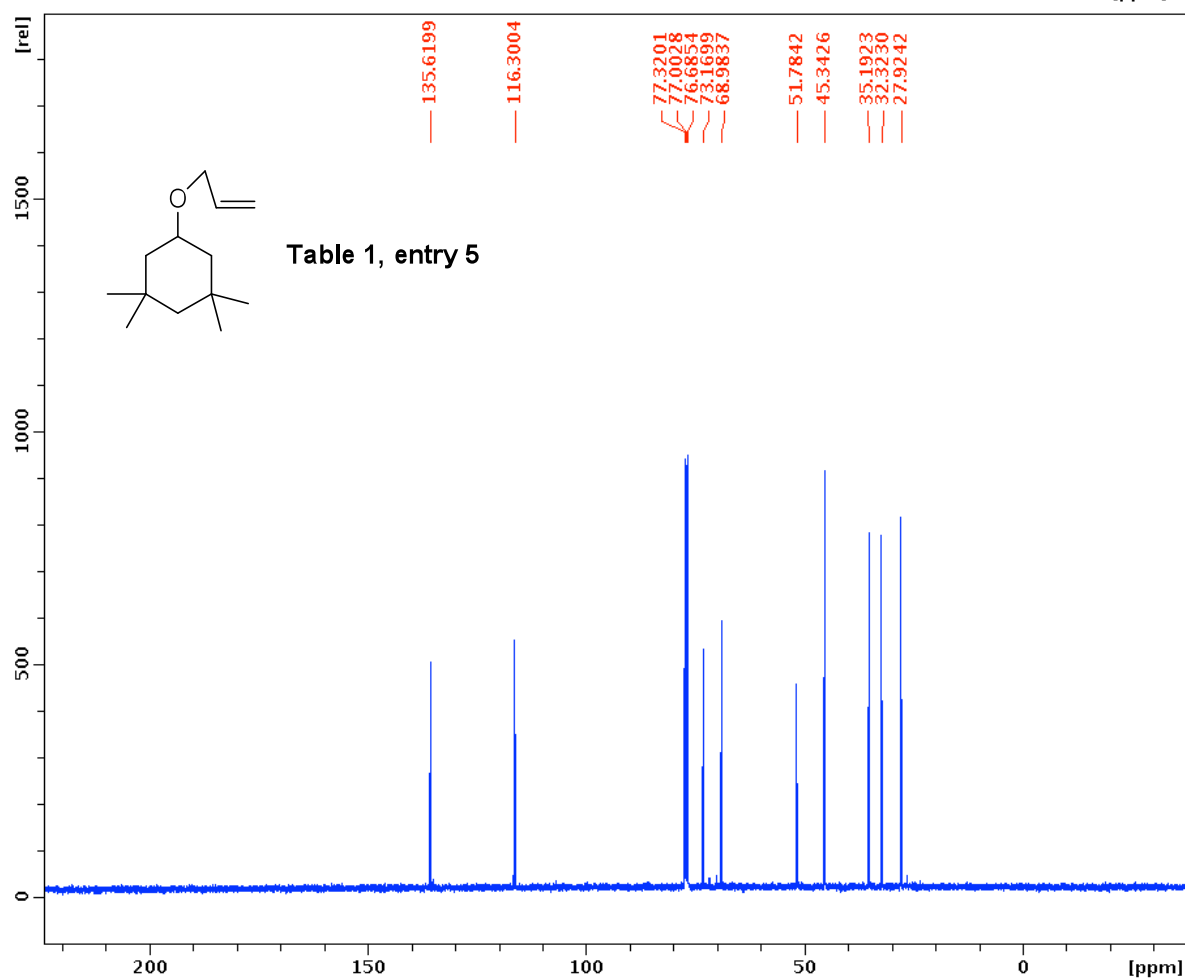
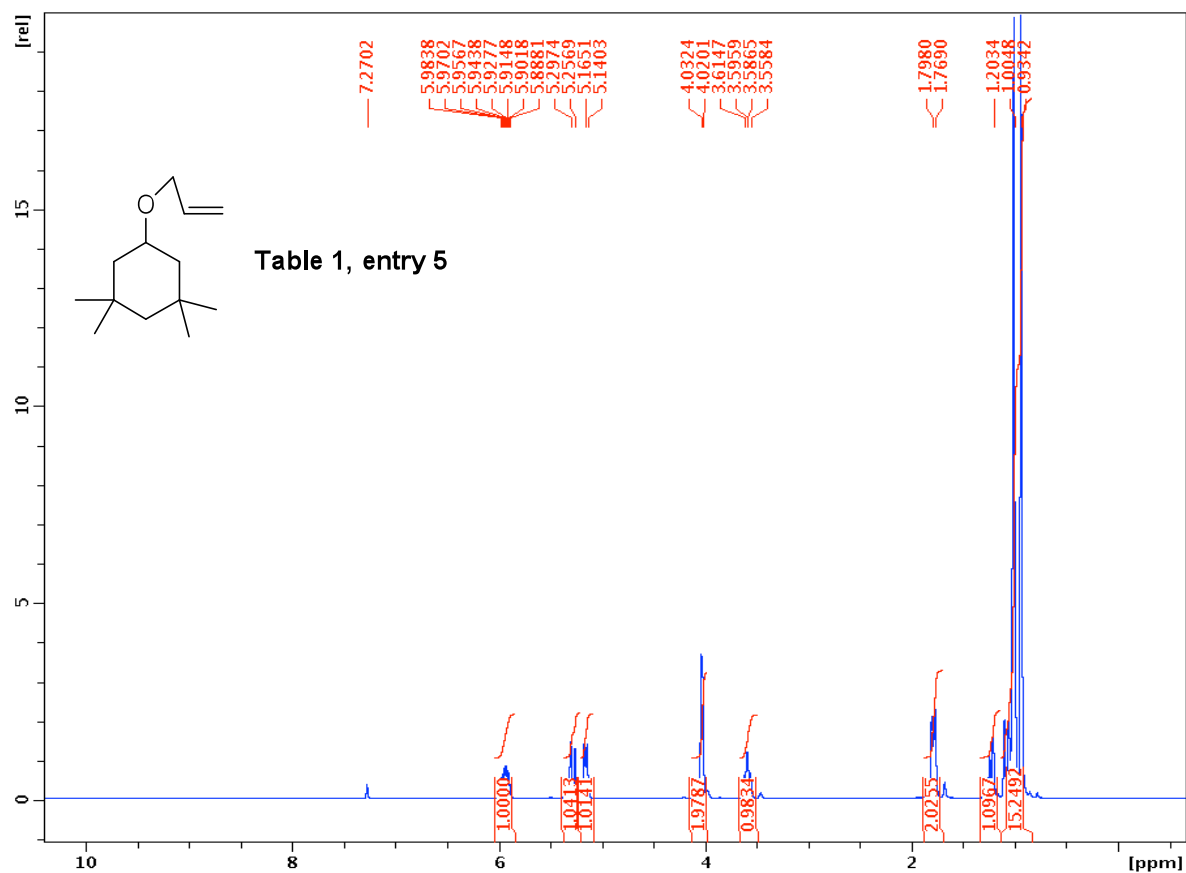
ture was stirred at room temperature, 60°C or 120°C for the amount of time shown in Table 3. The reaction mixture was quenched by saturated ammonium chloride solution. The mixture was then extracted with diethyl ether three times and the organic phase was washed with water, brine and dried over NaSO₄. The solvent was first removed by rotary evaporation and then by oil pump yielding a light yellow liquid which was then characterized by NMR spectroscopy to determine the ratio between the starting allyl ether and vinyl ether product.

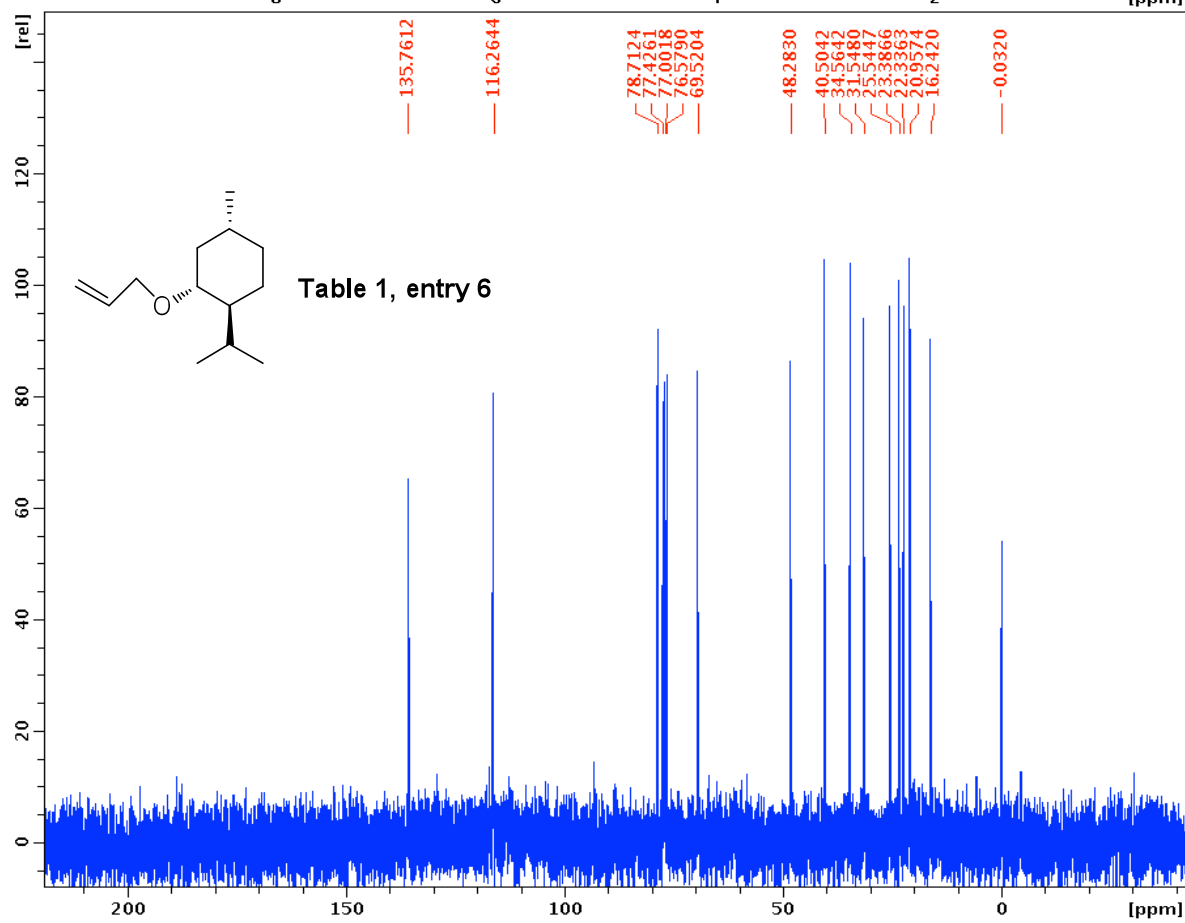
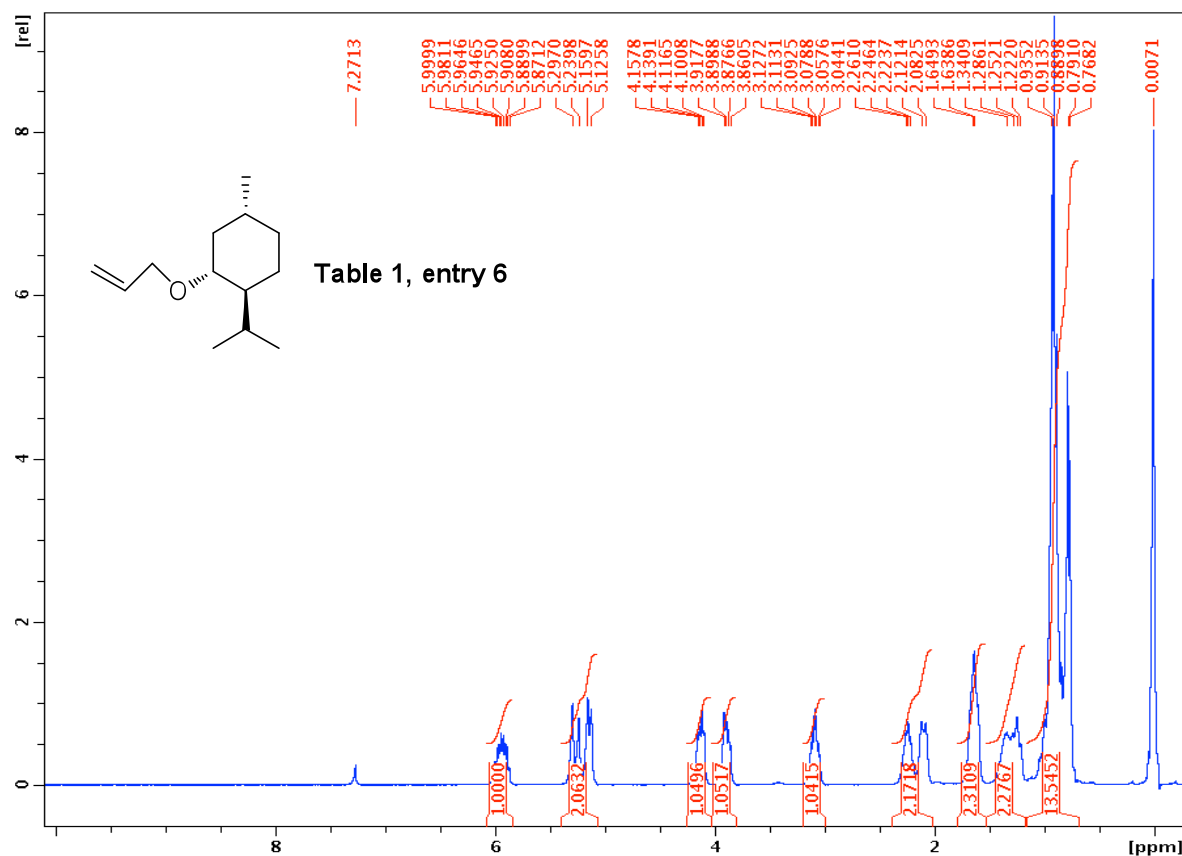
¹H and ¹³C NMR Spectra for Allyl Ethers

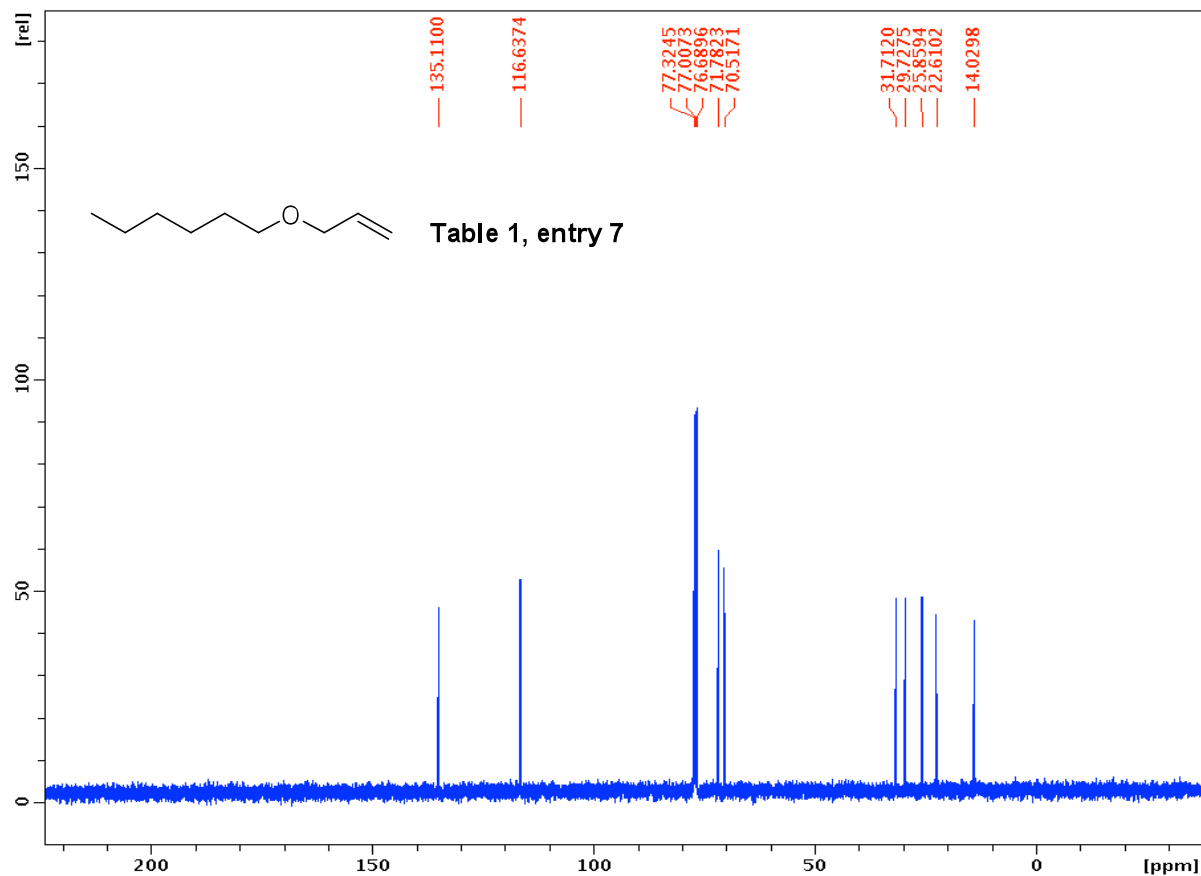
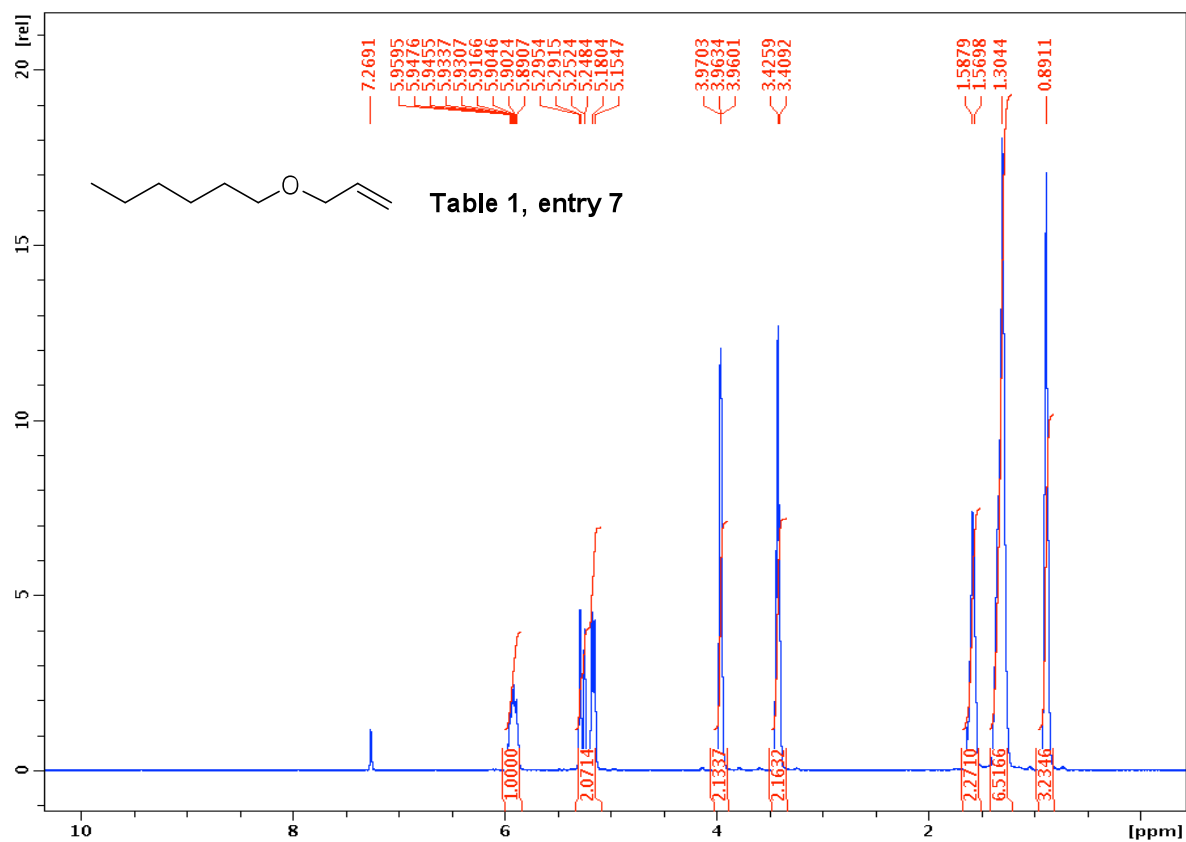


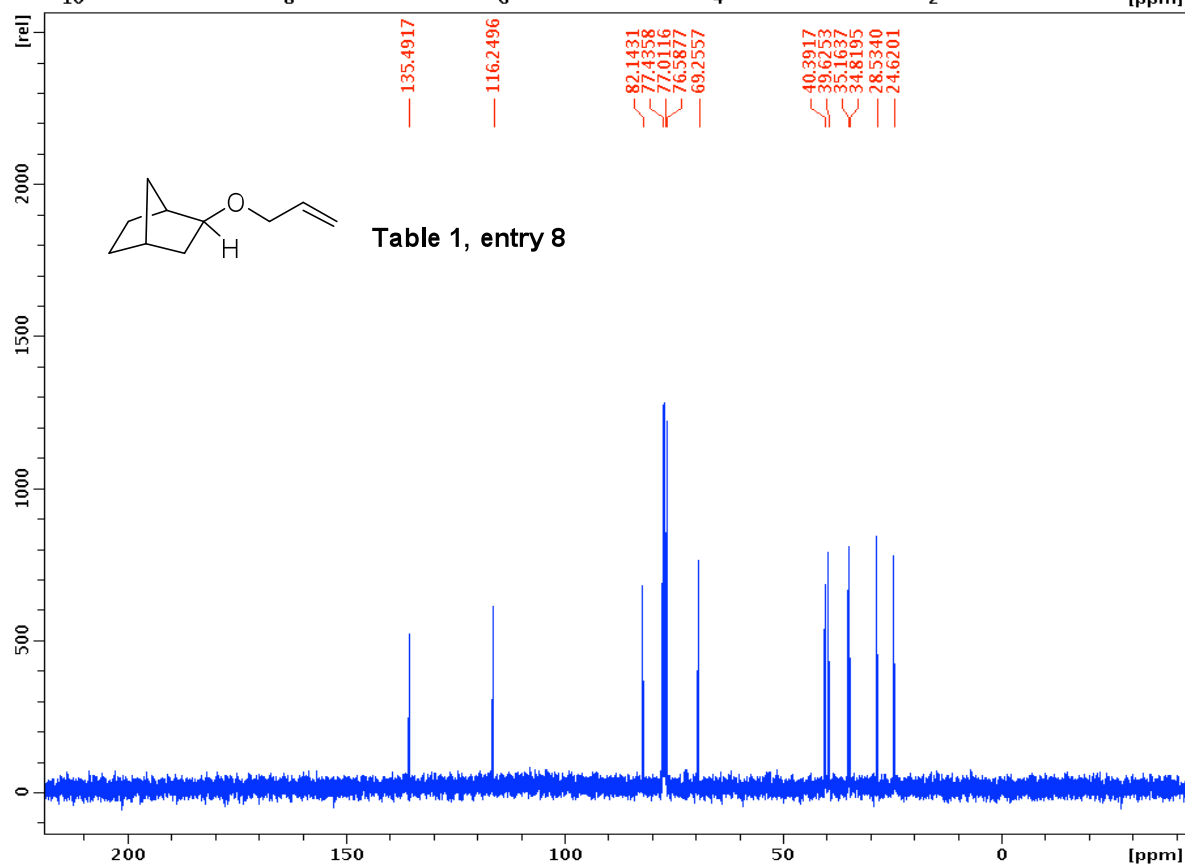
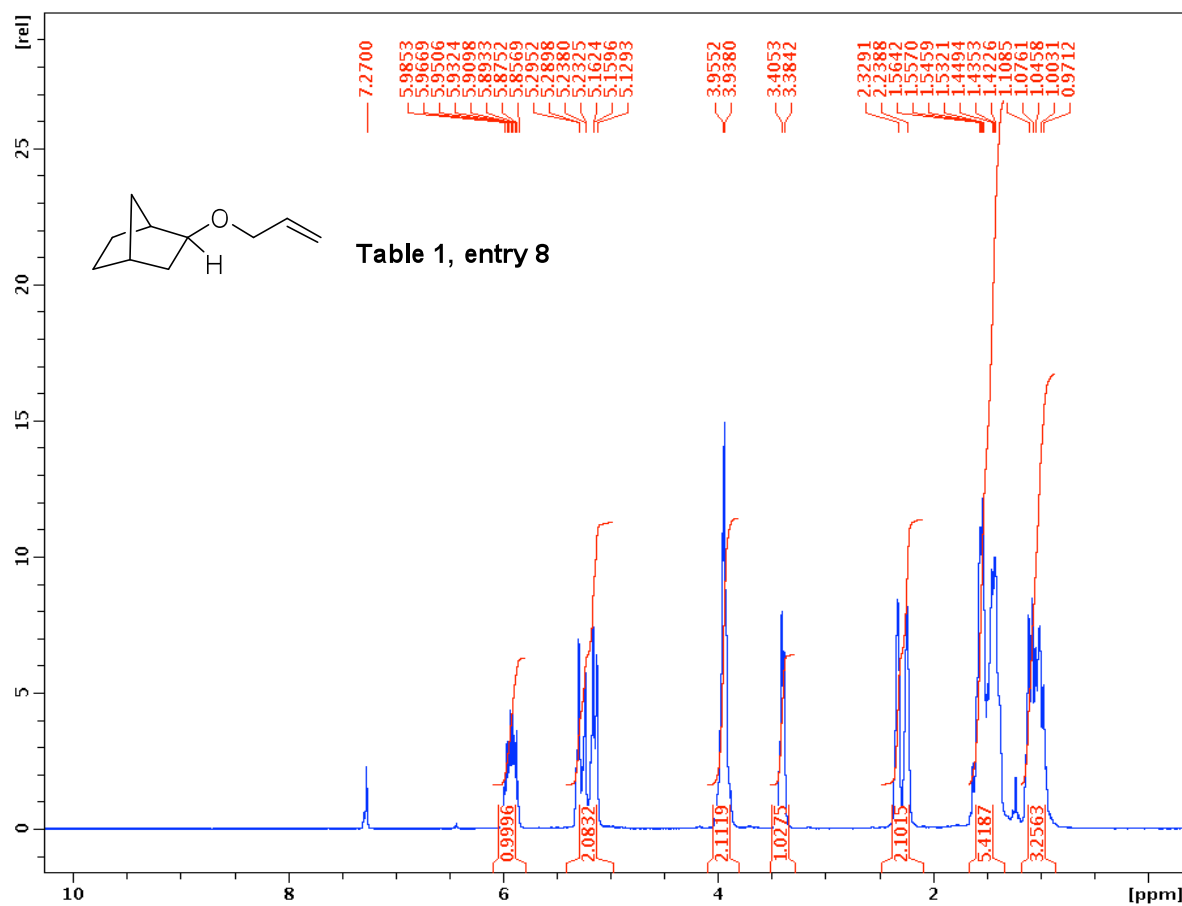


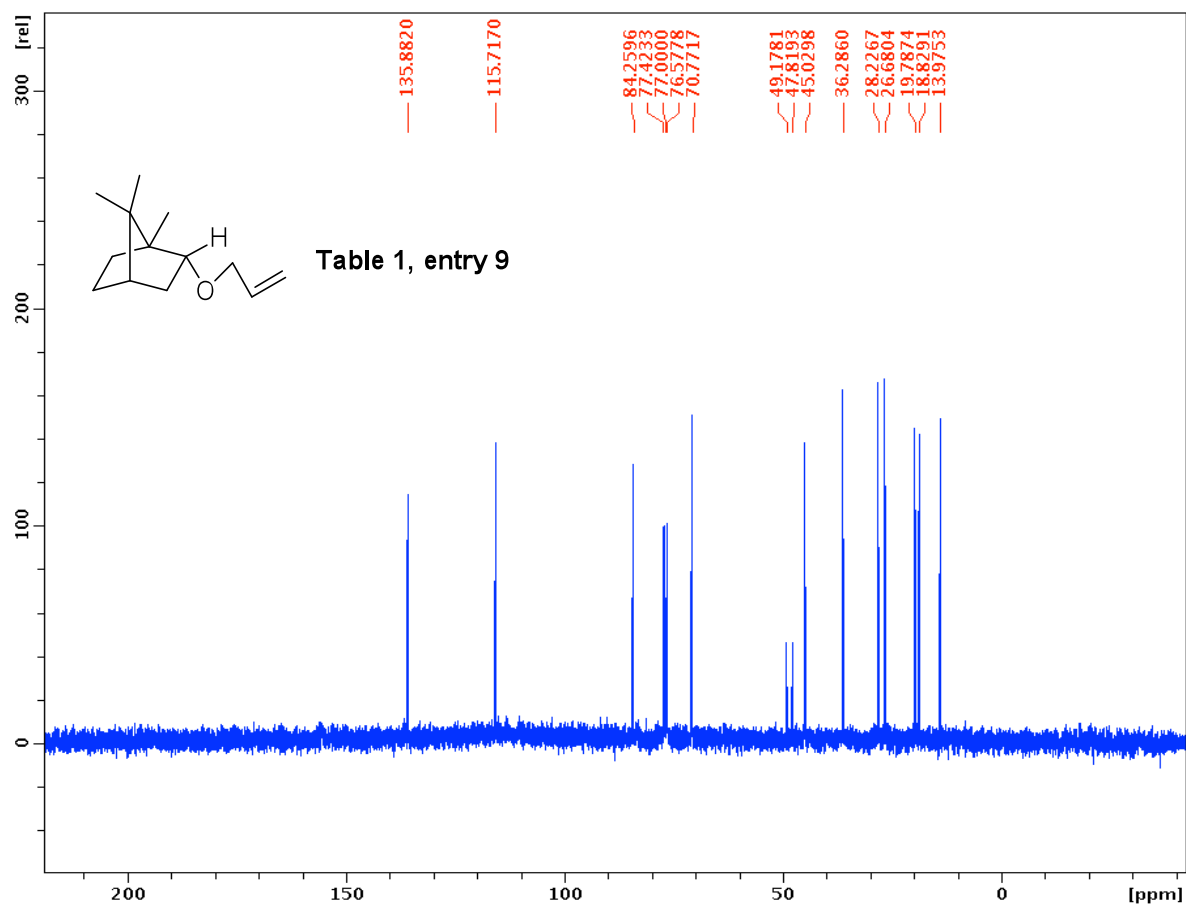
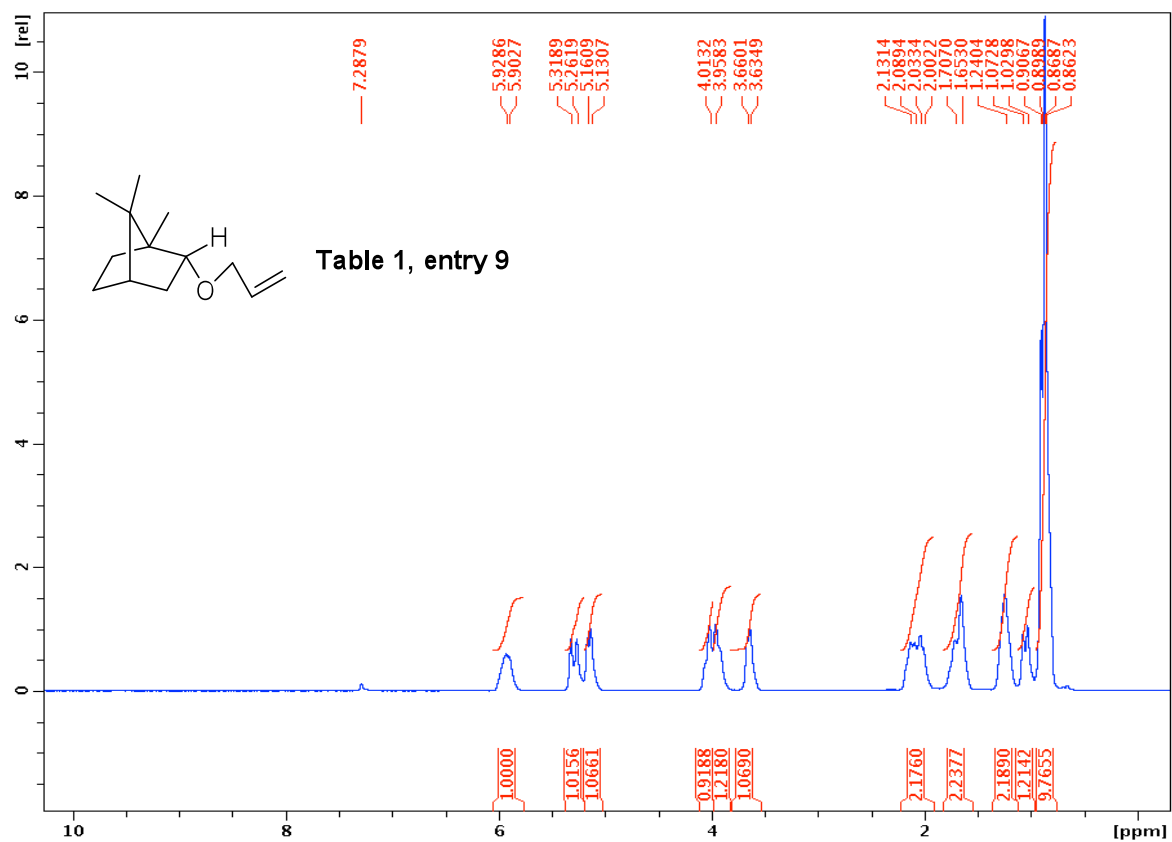


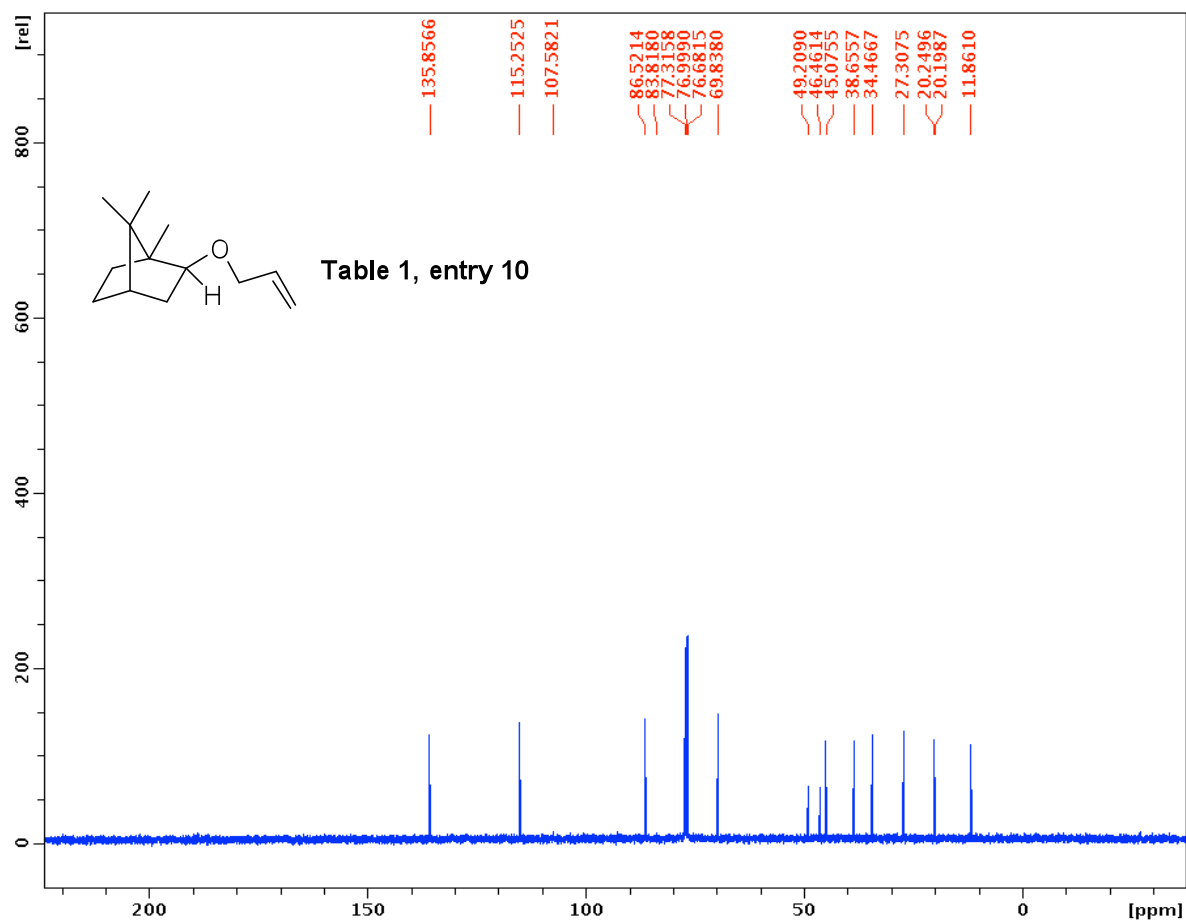
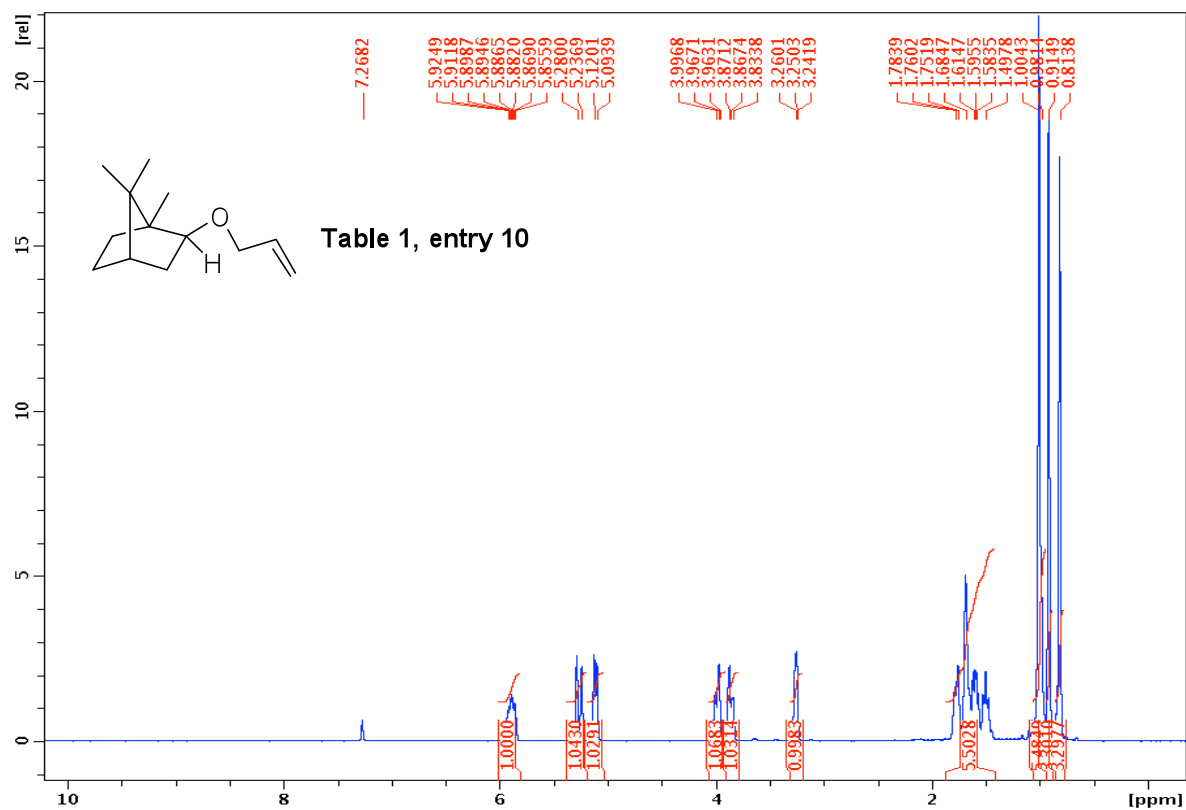


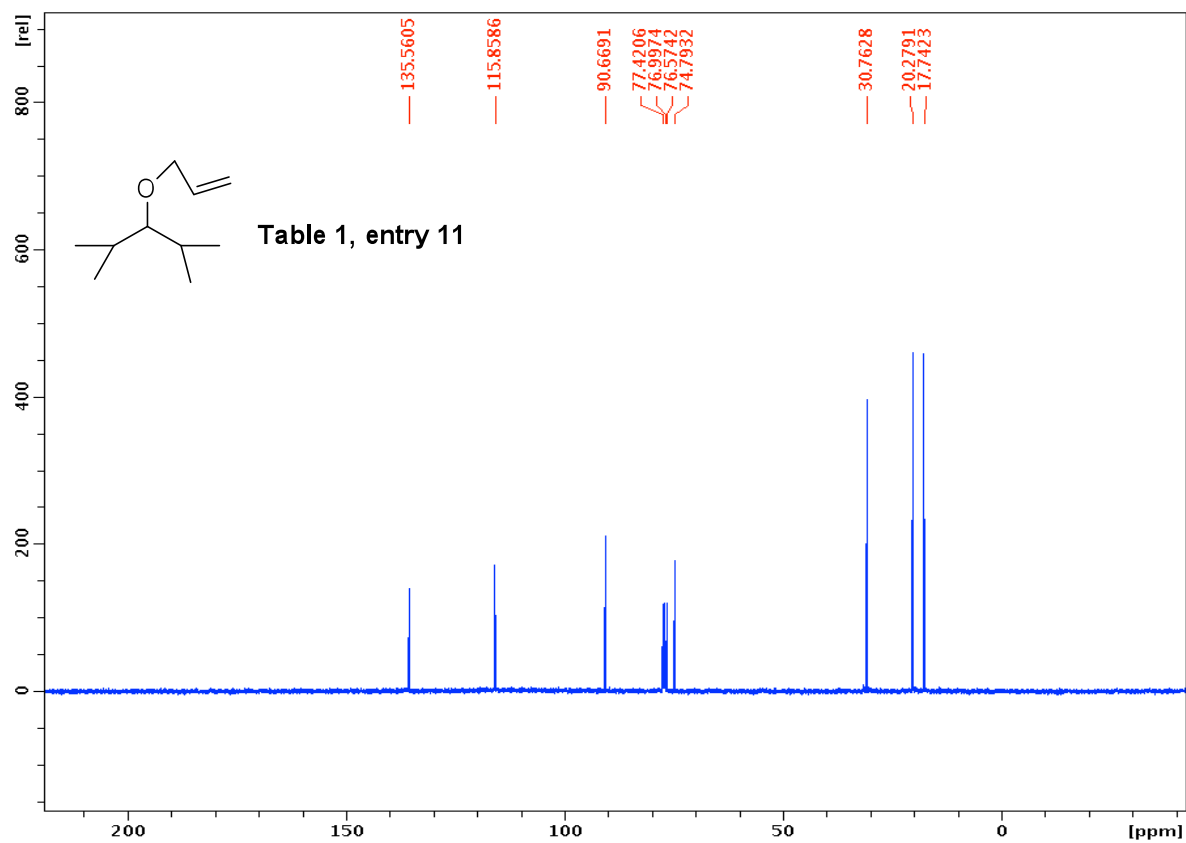
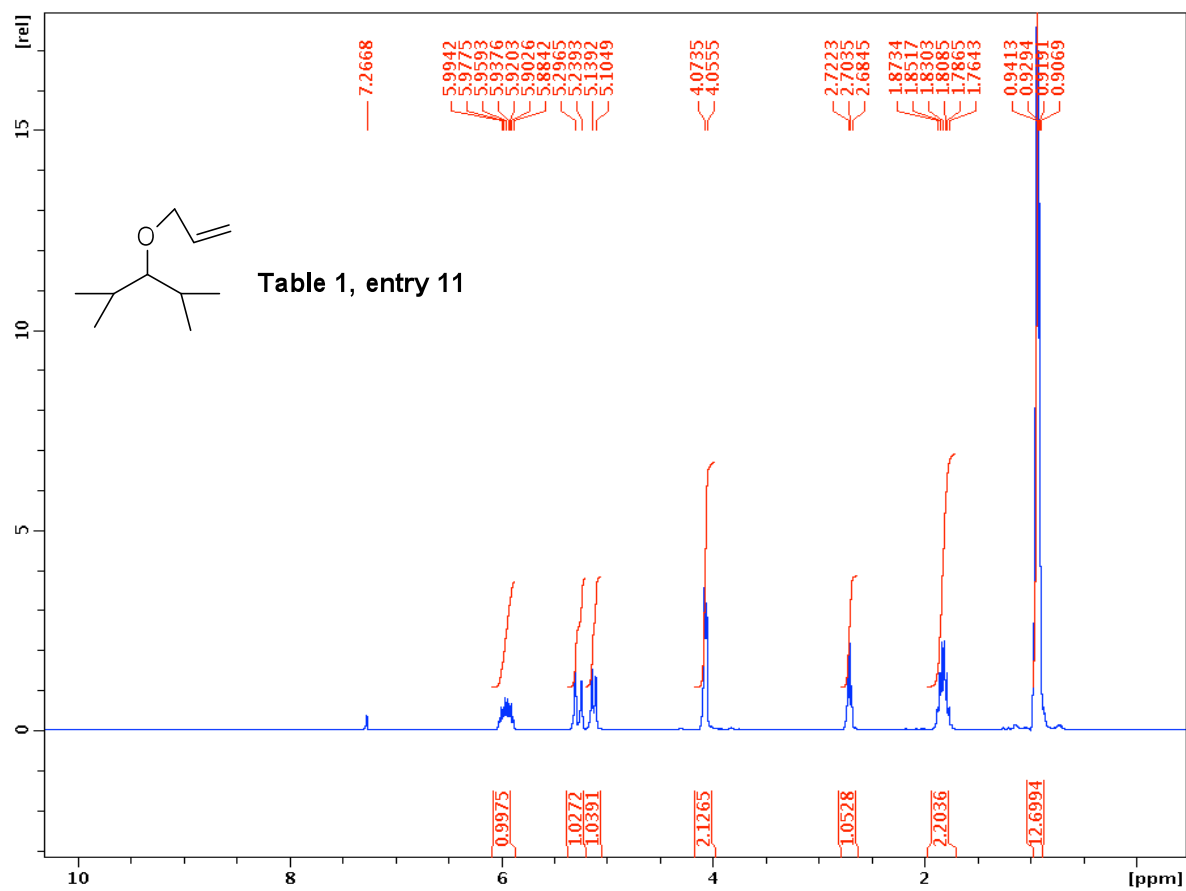


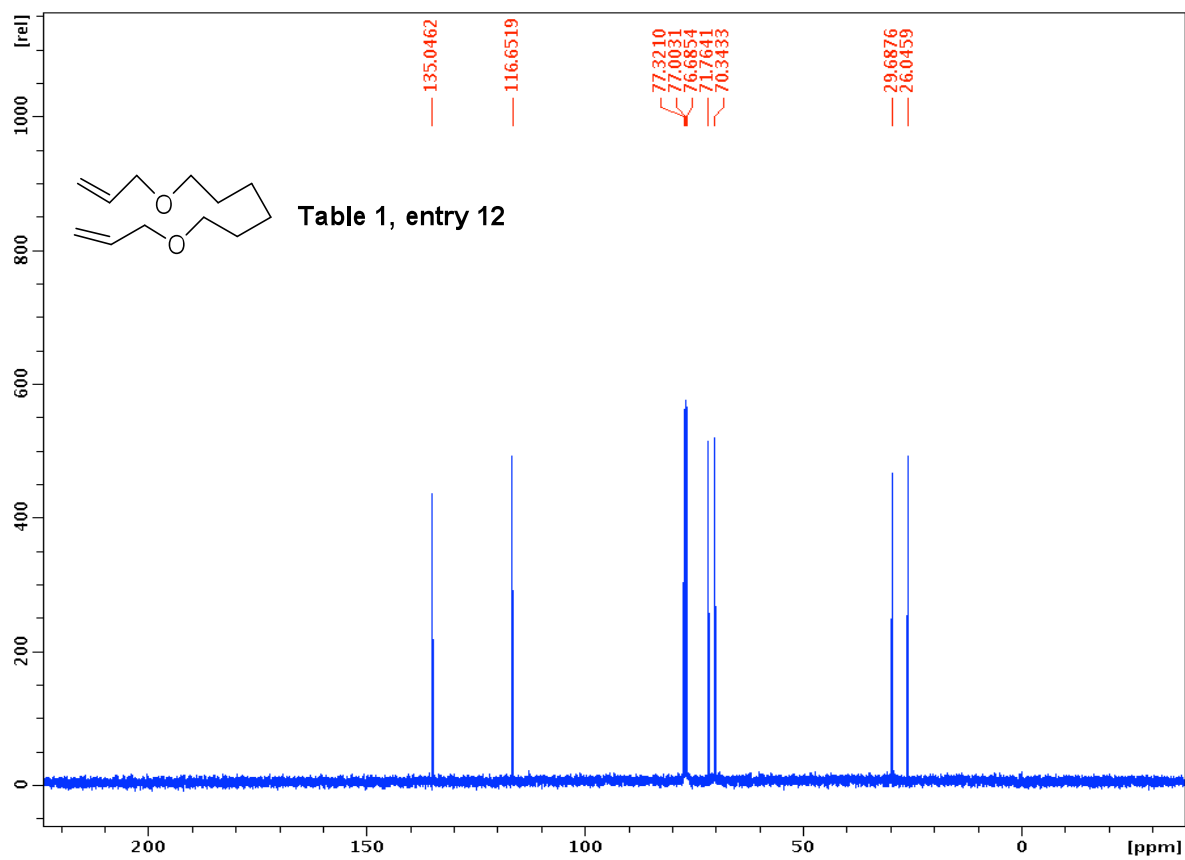
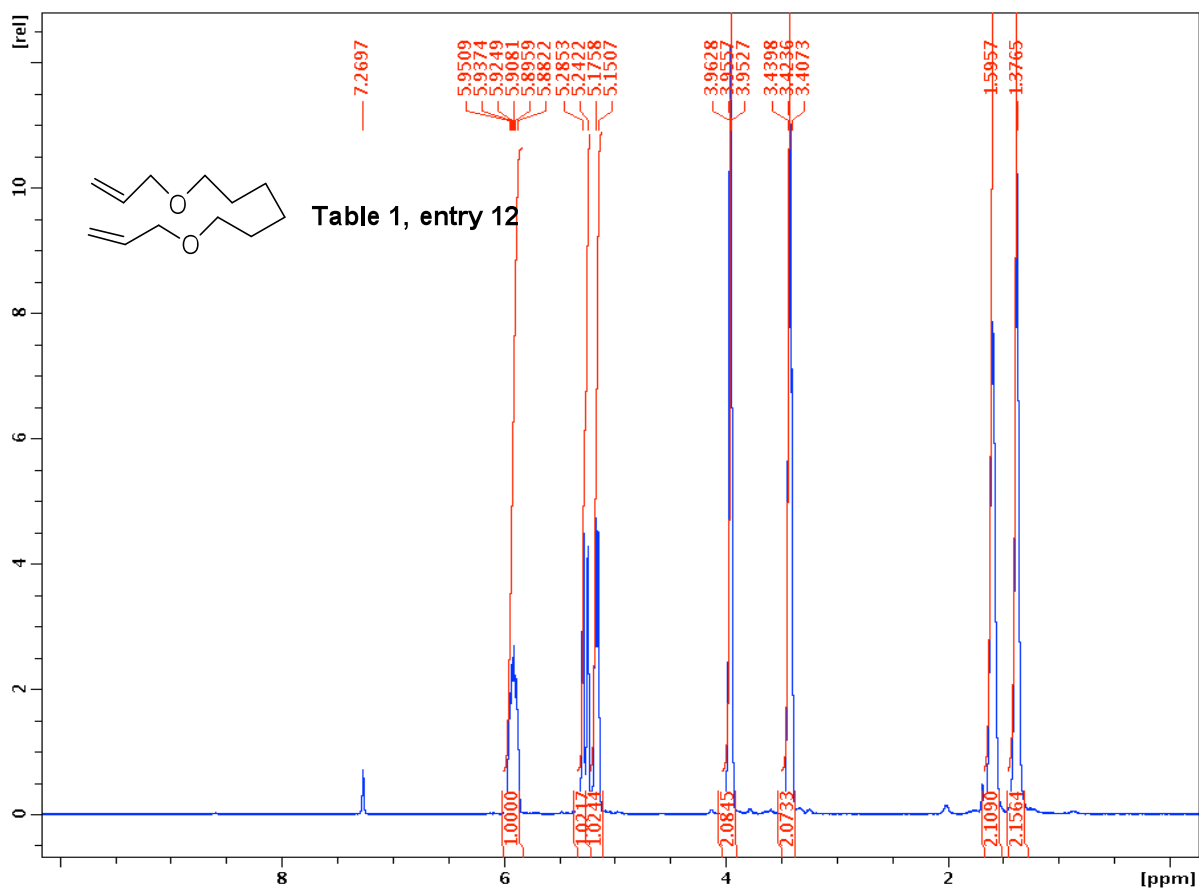


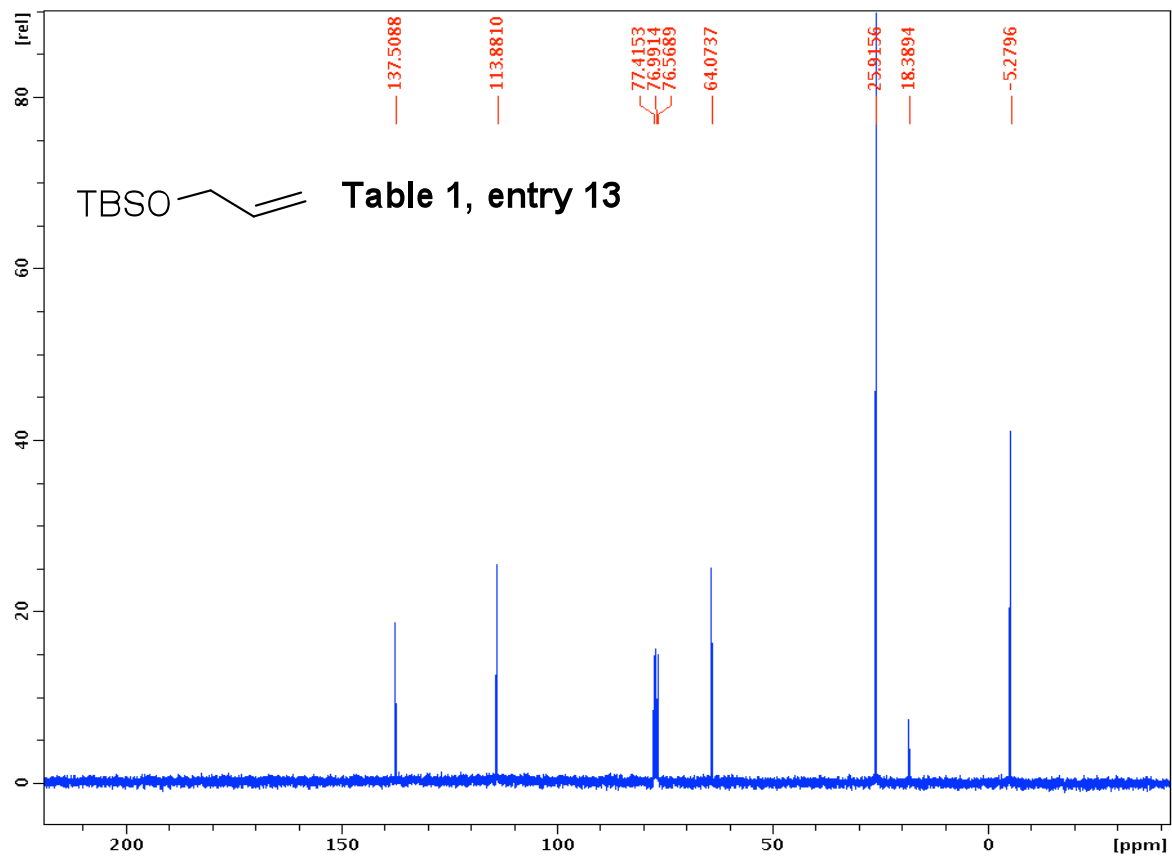
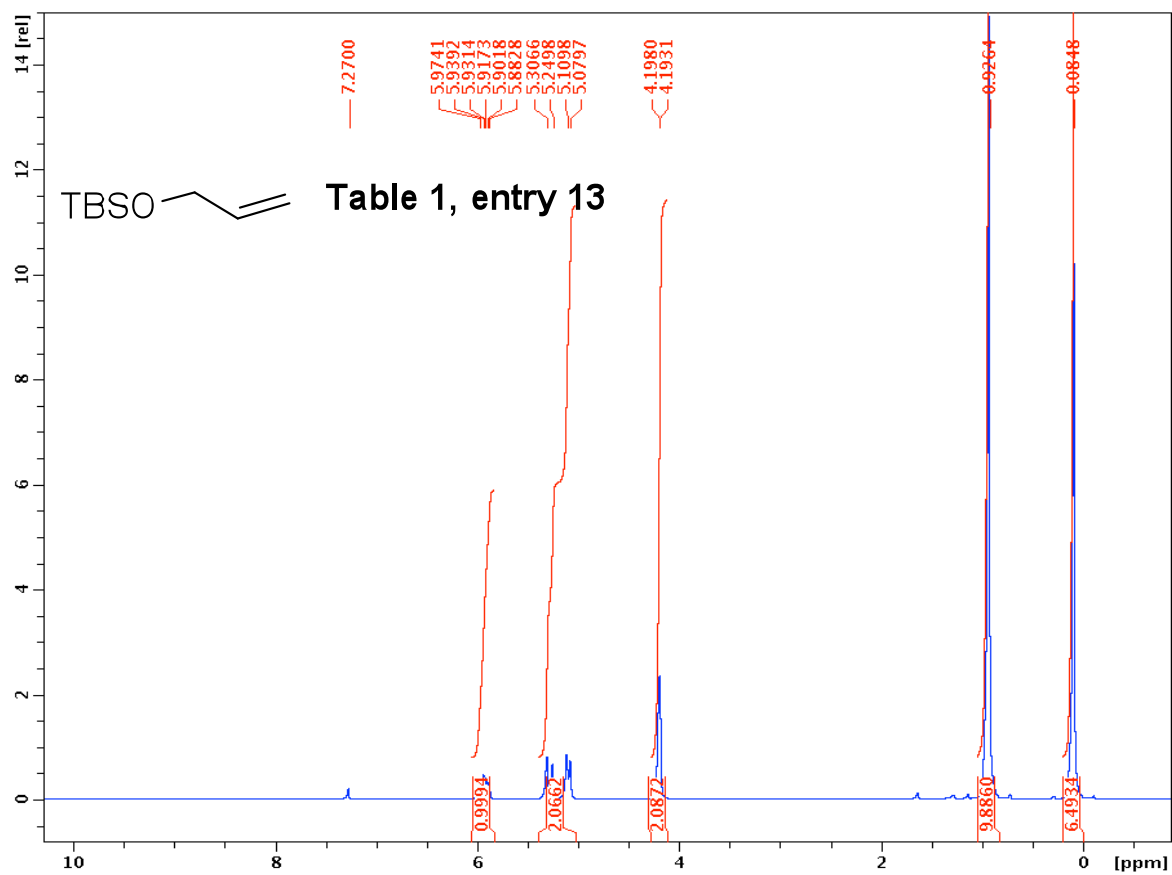


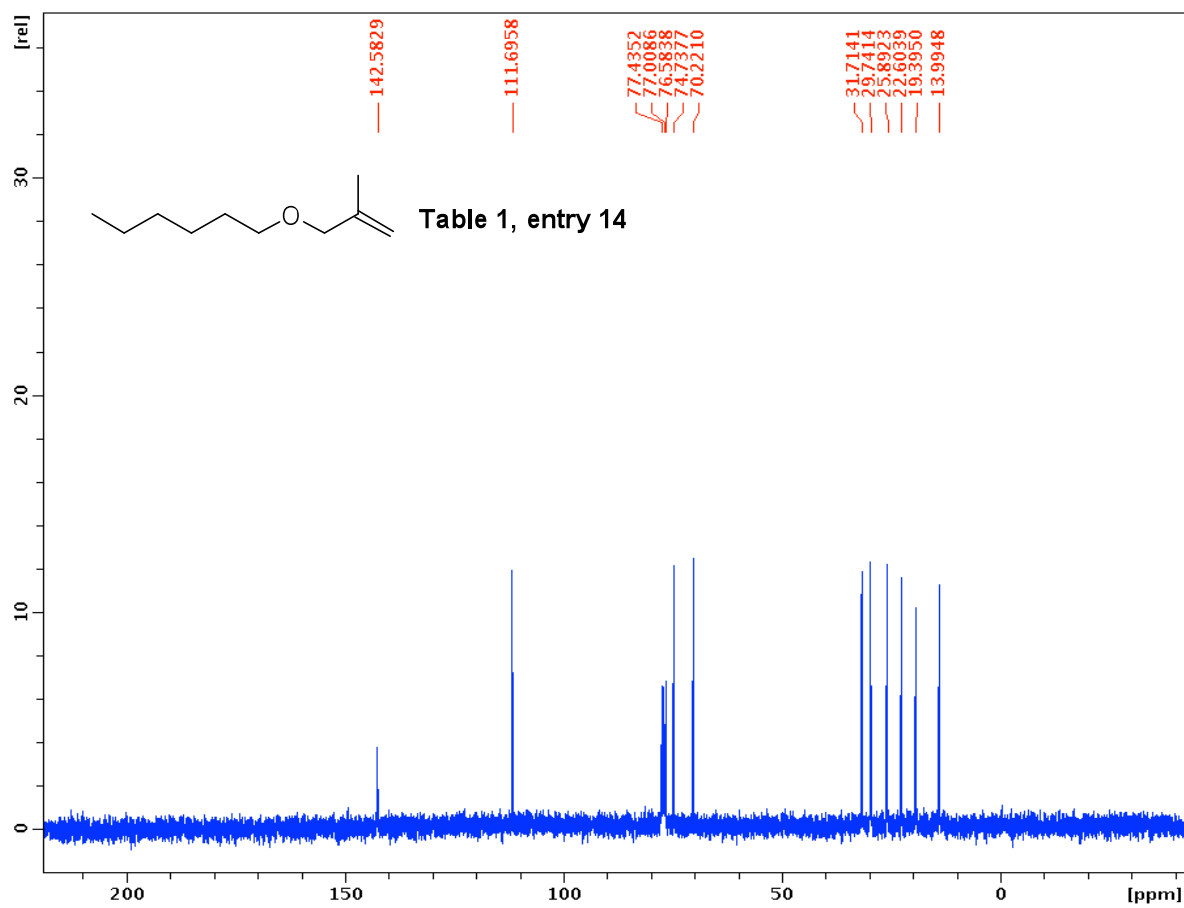
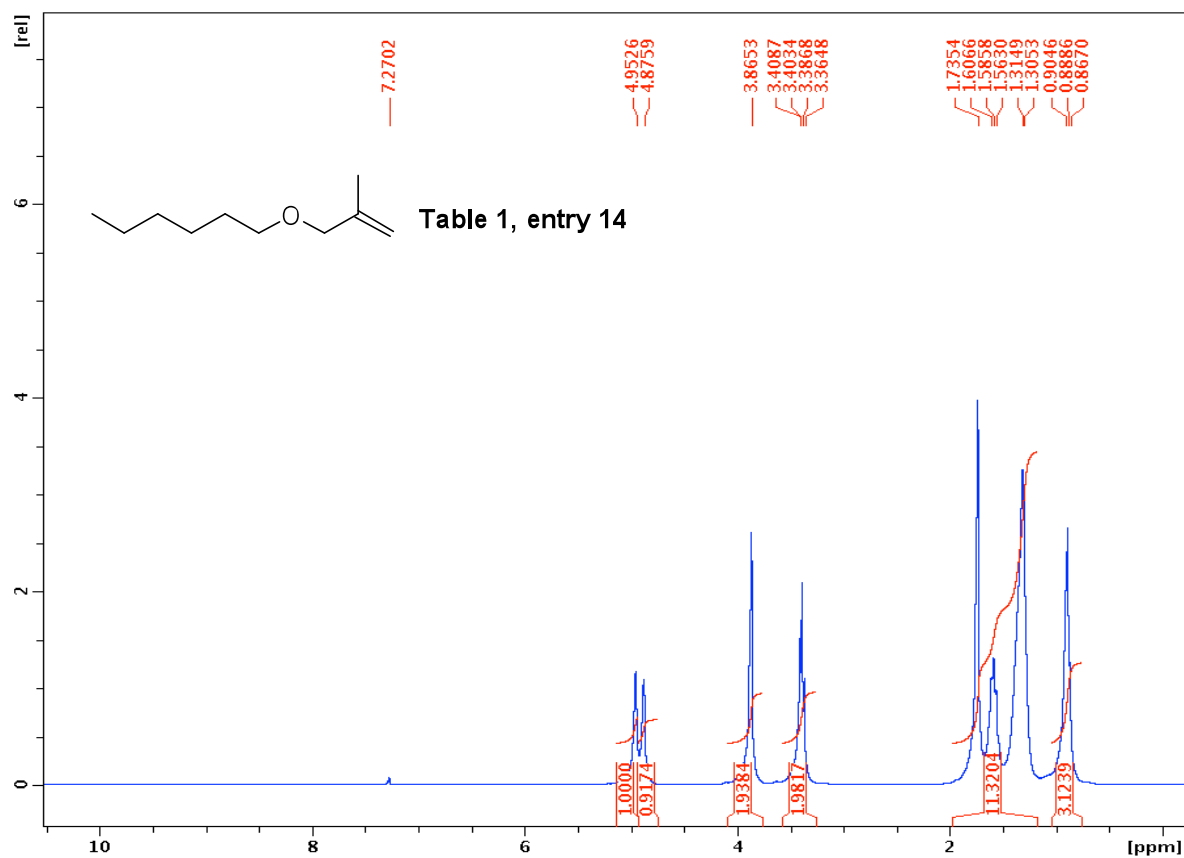


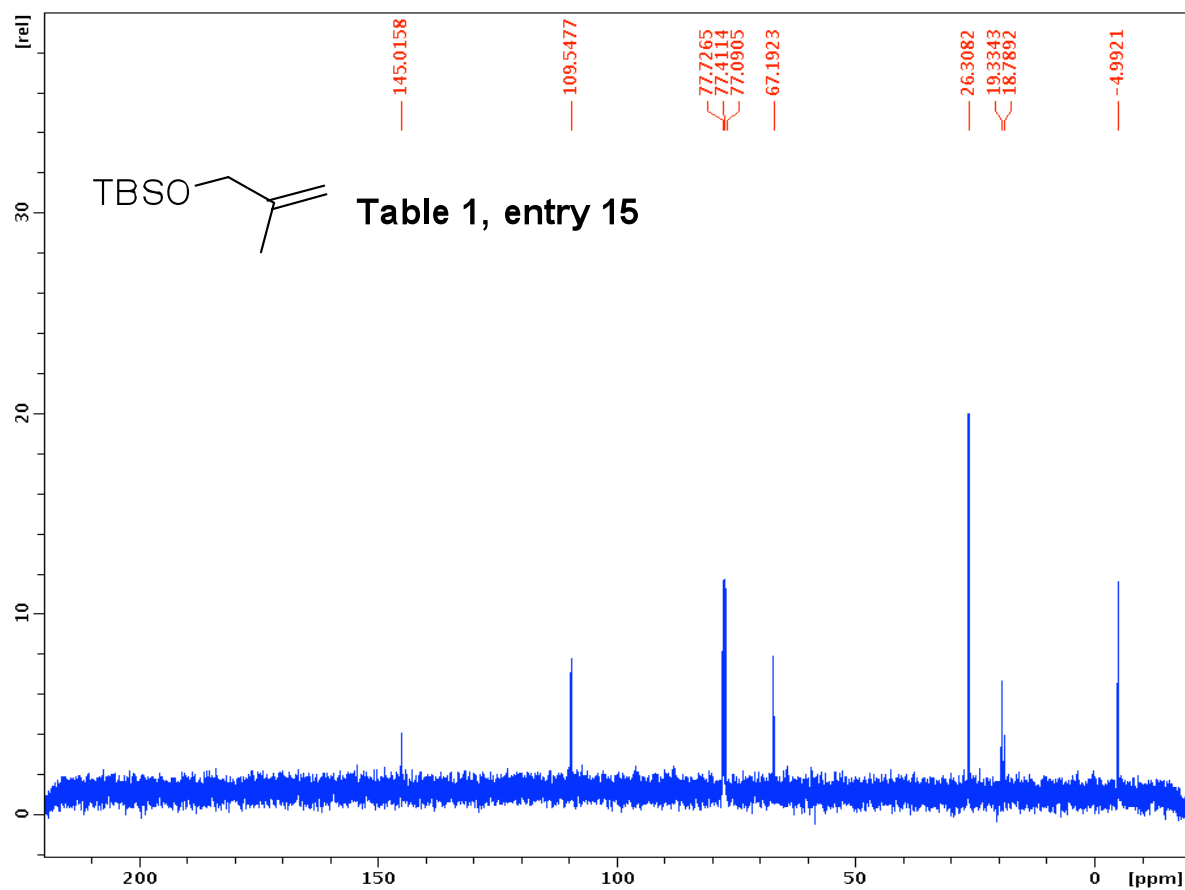
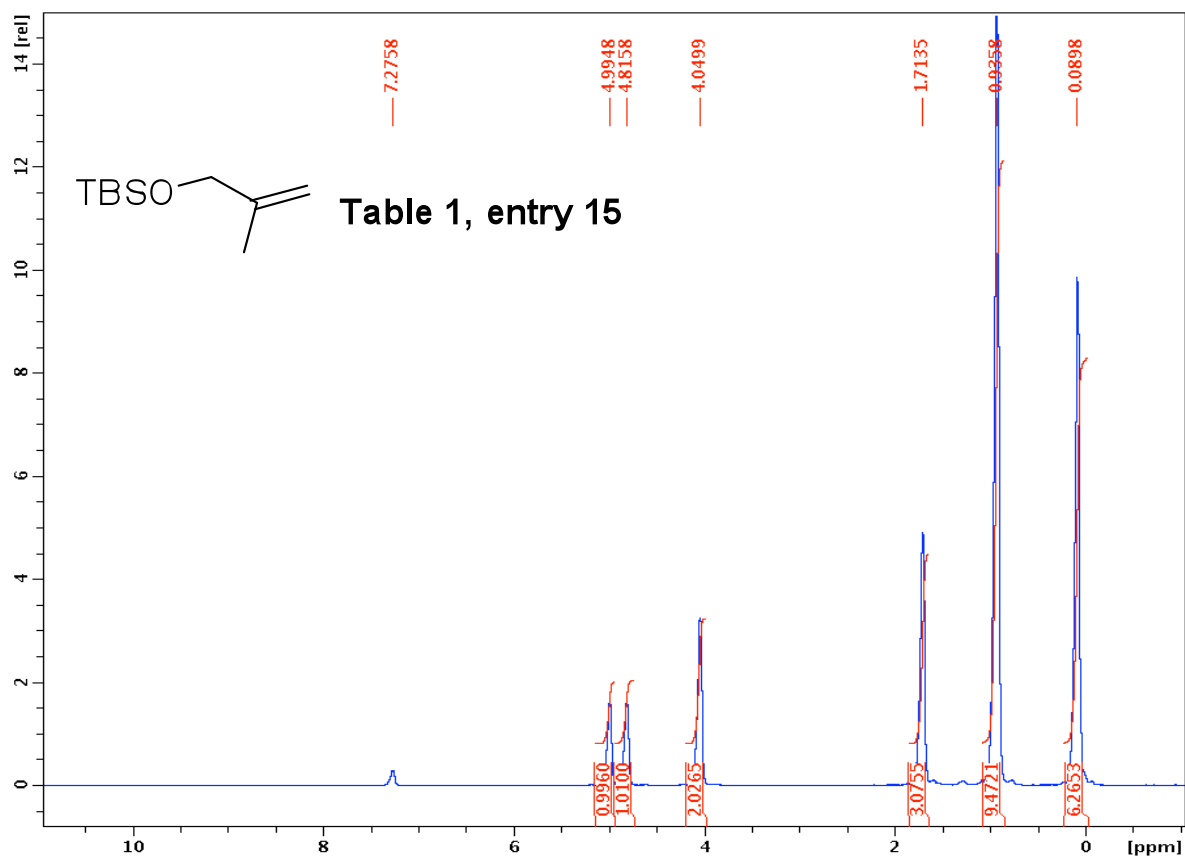


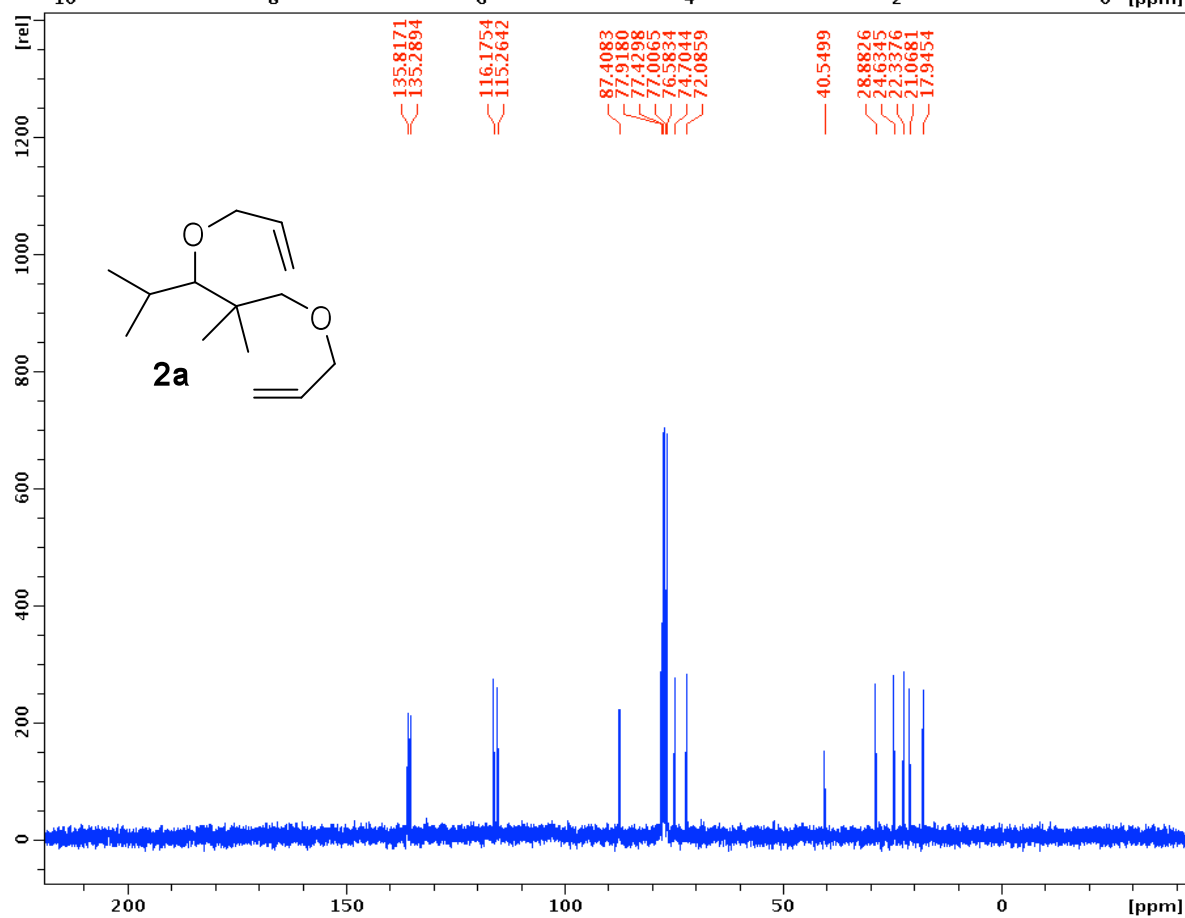
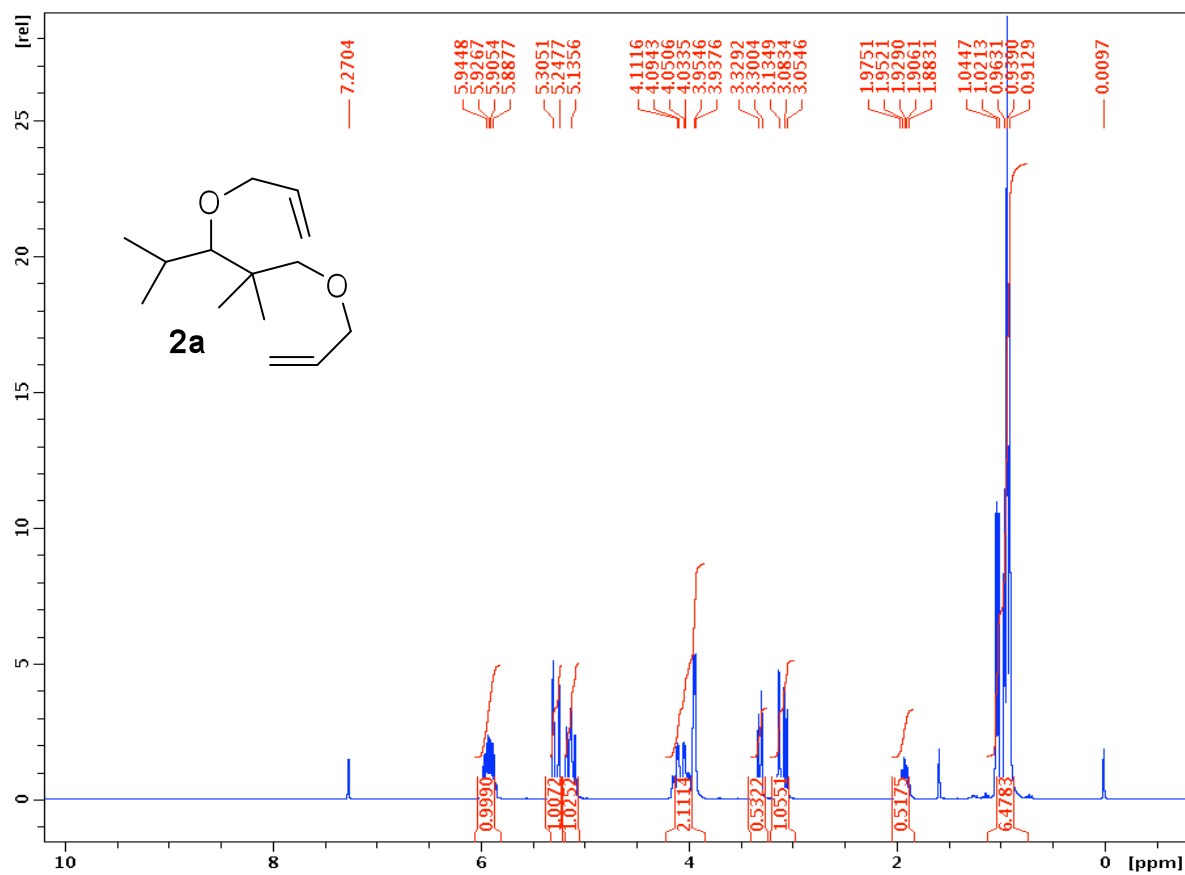




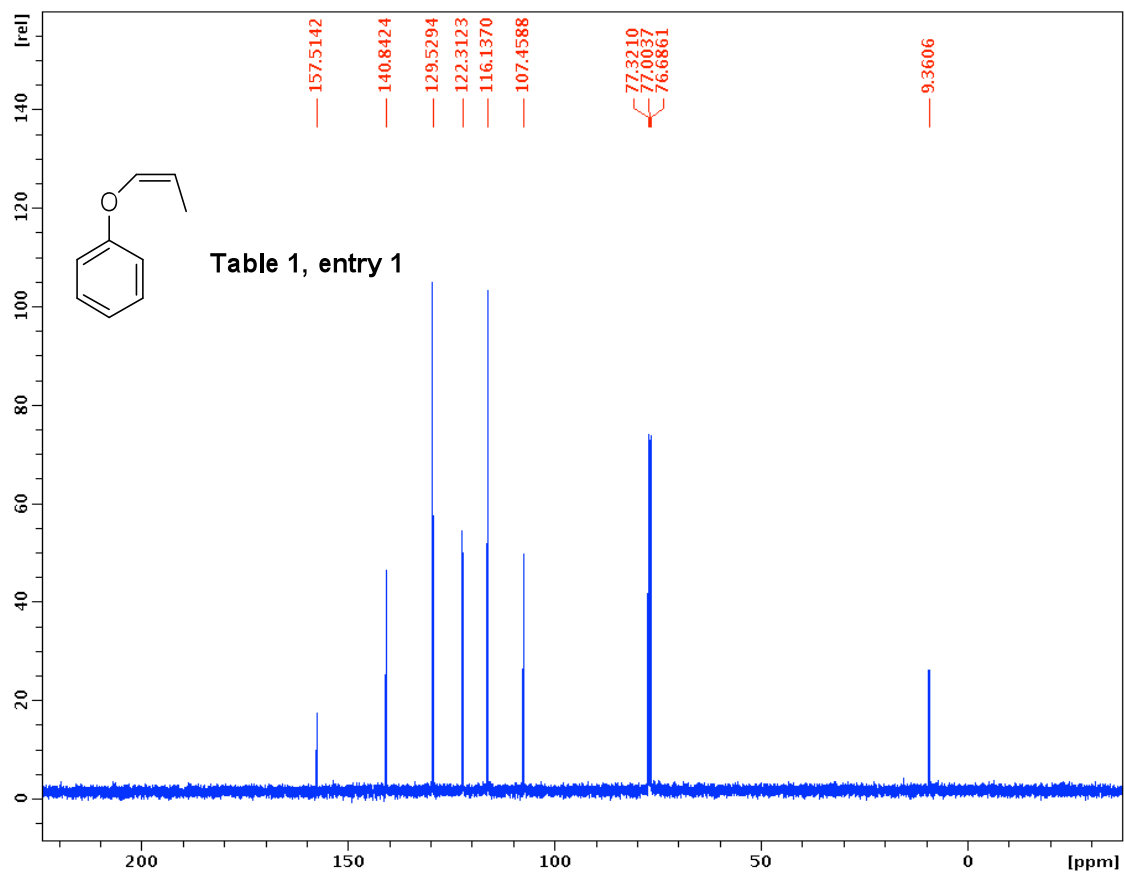
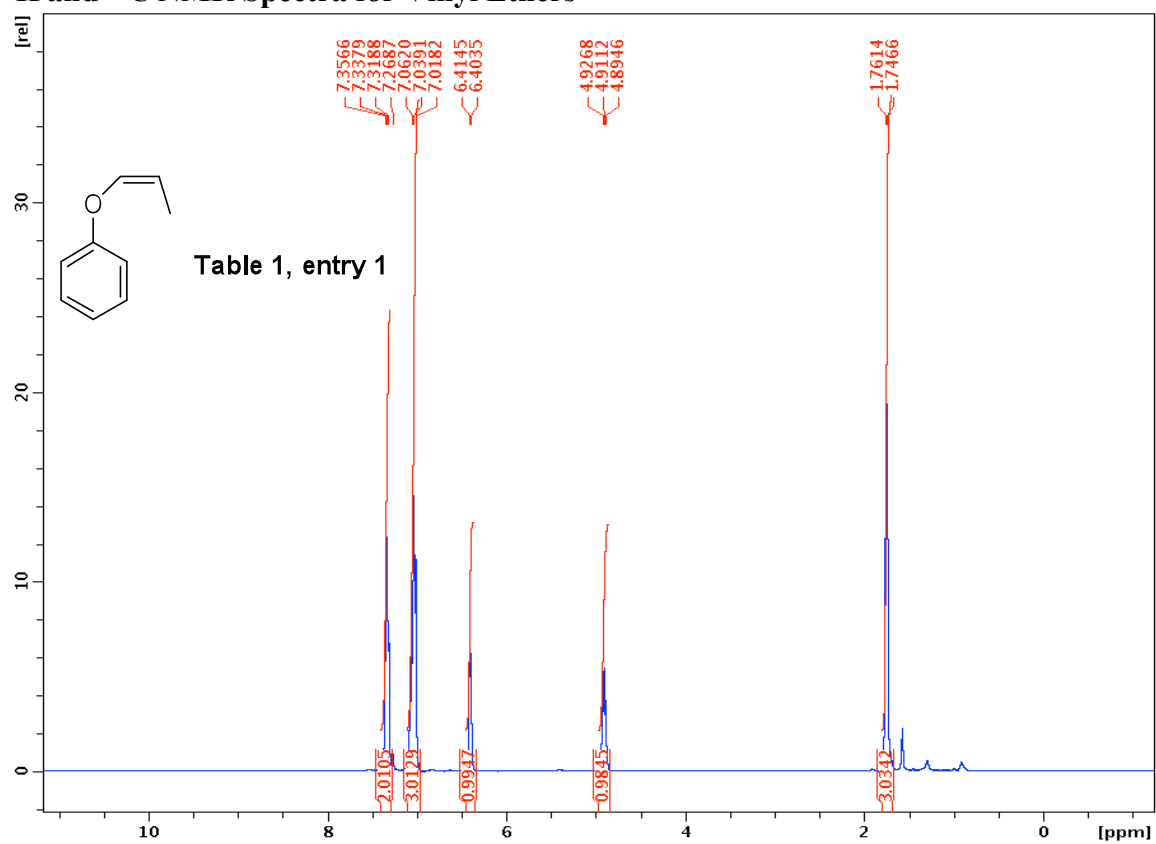


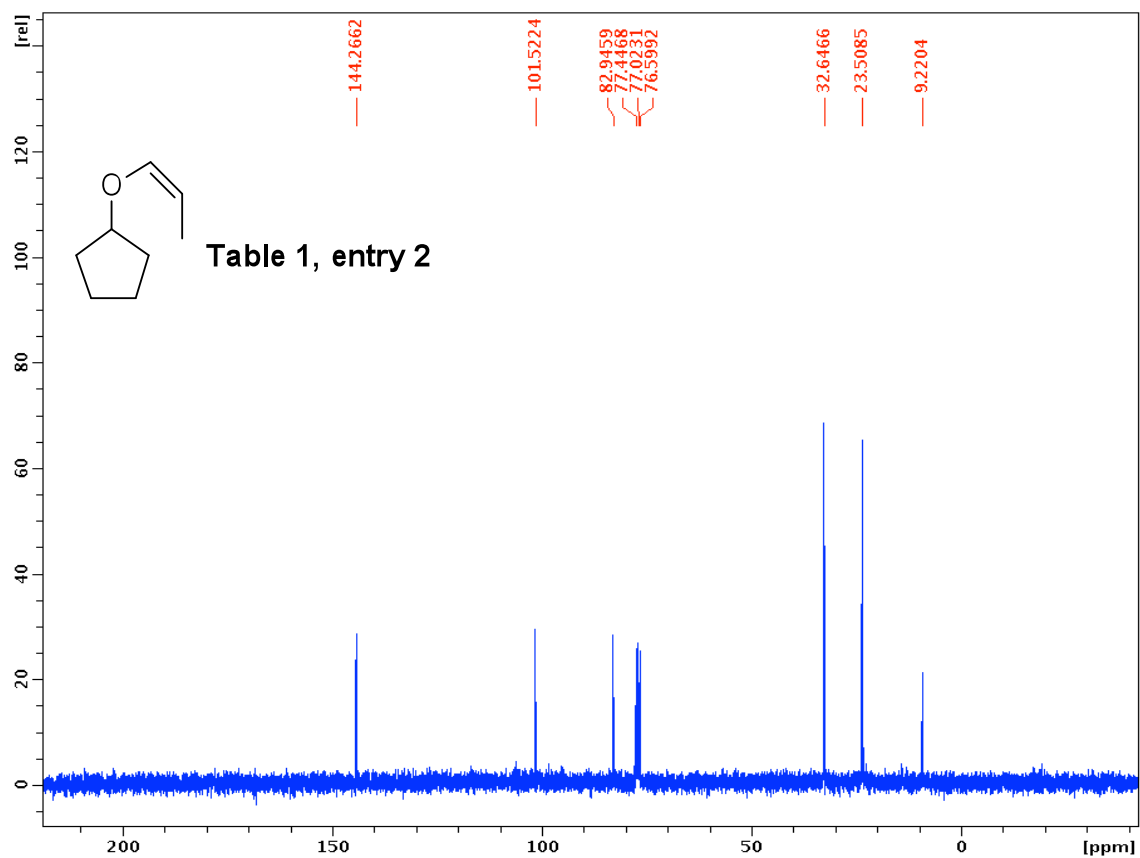
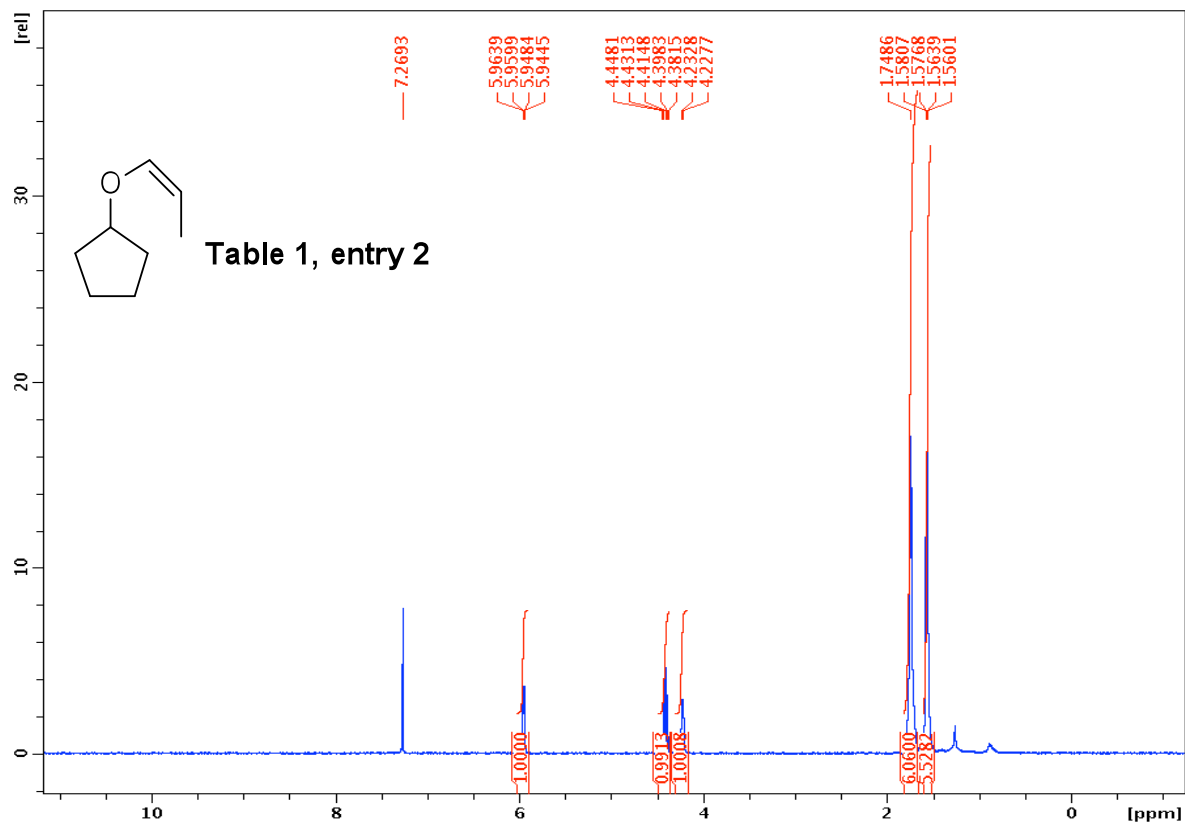


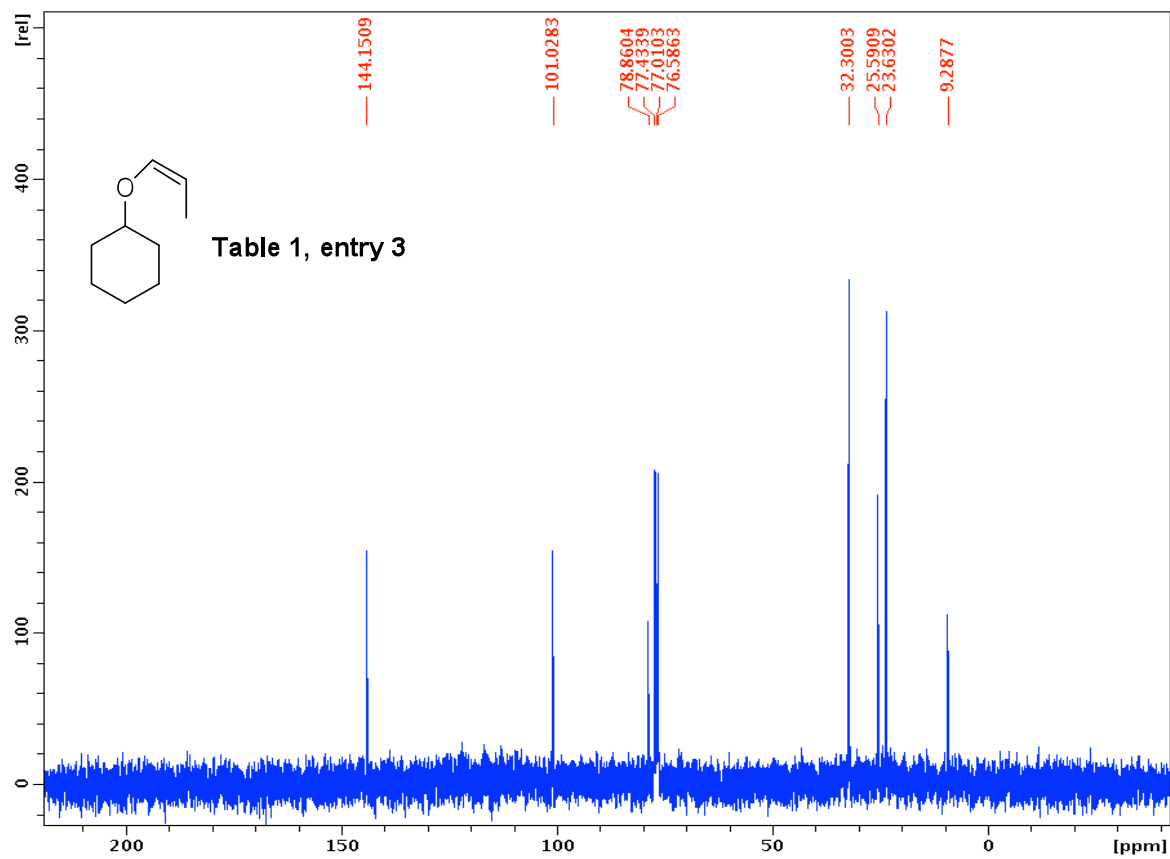
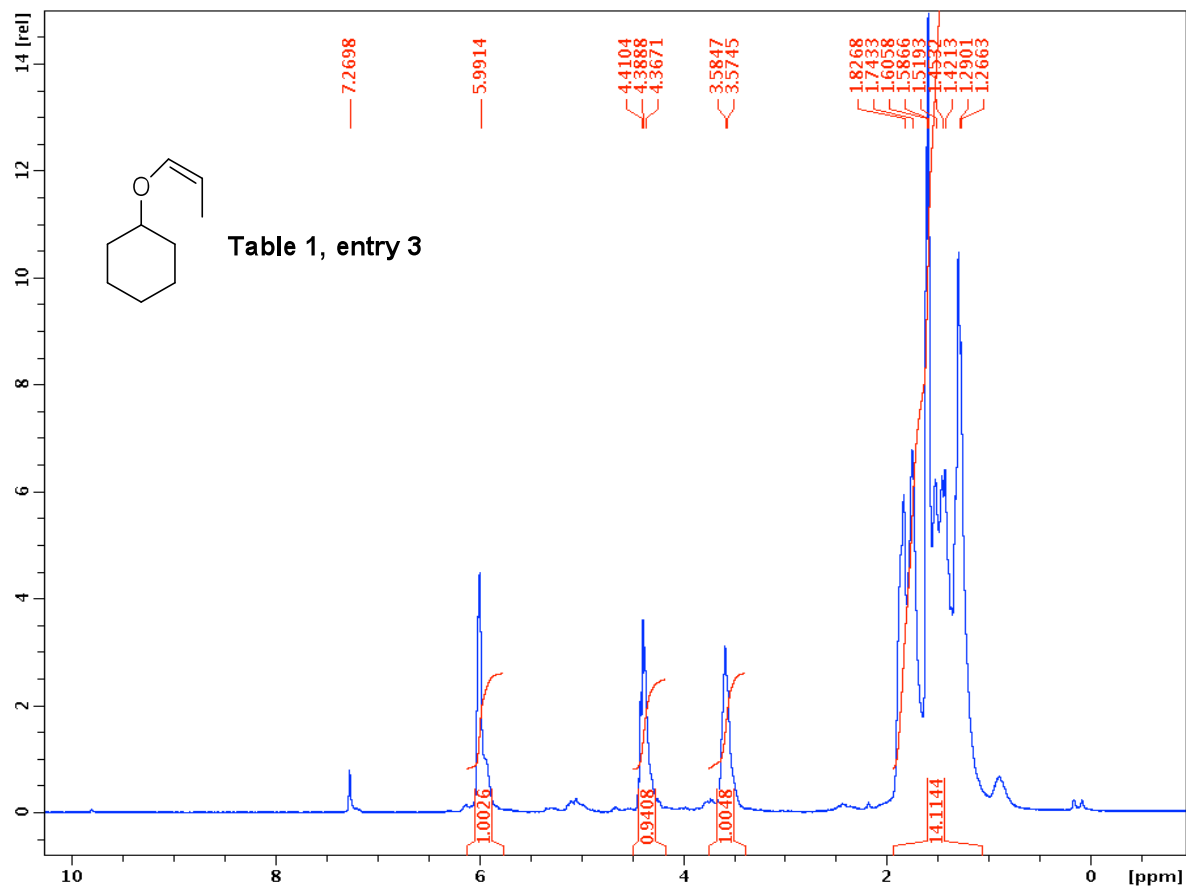


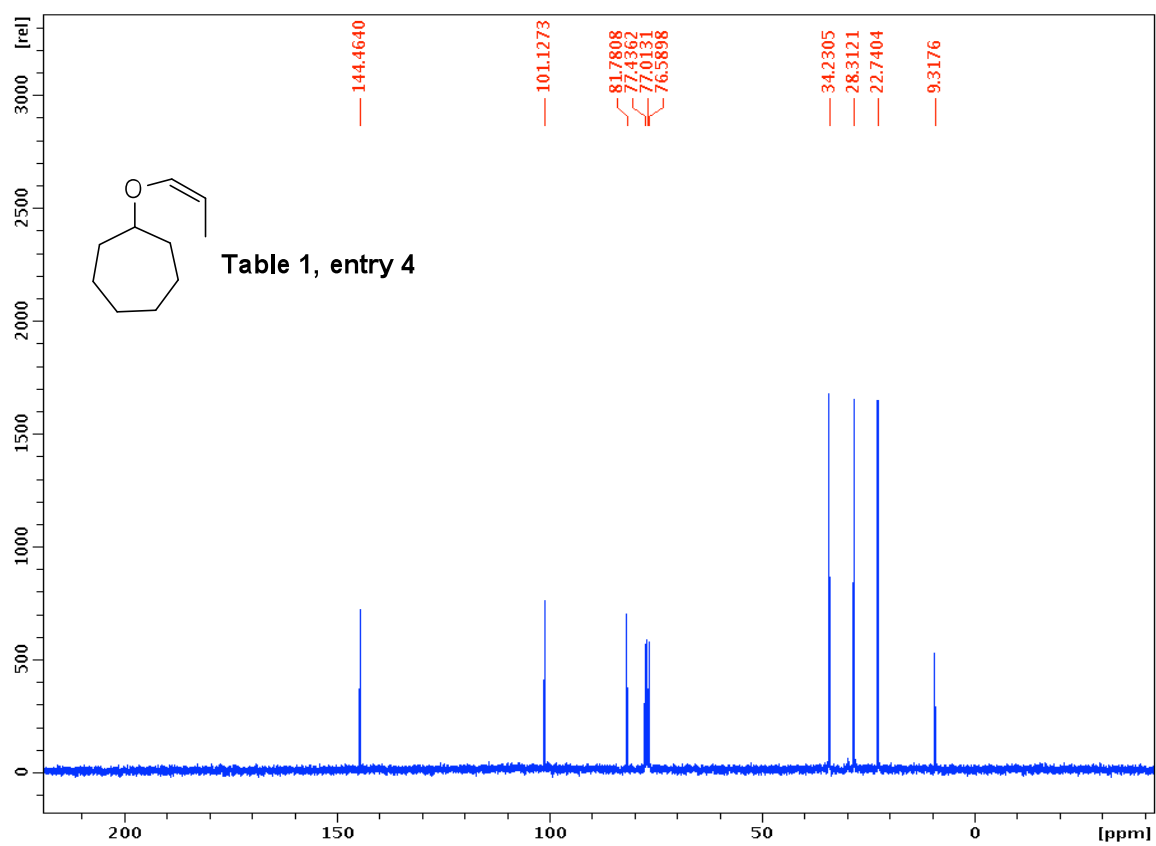
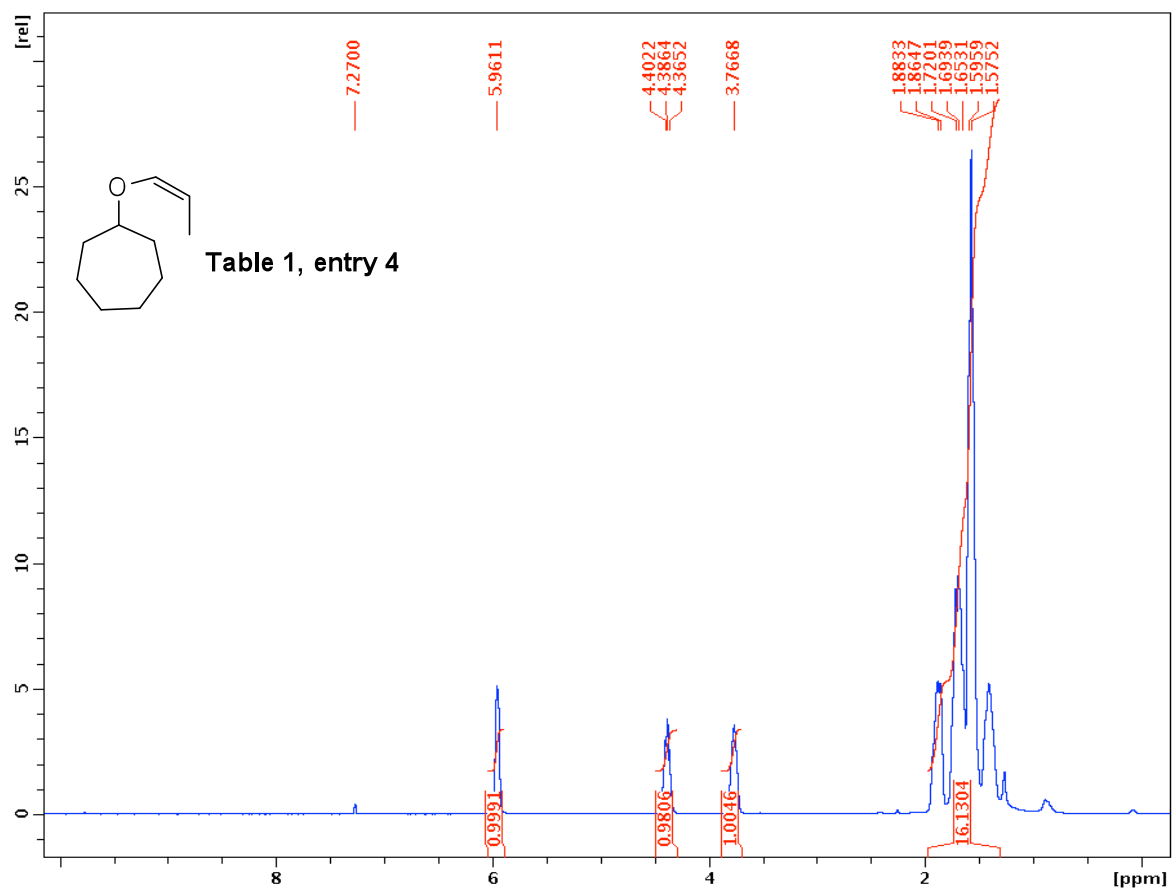


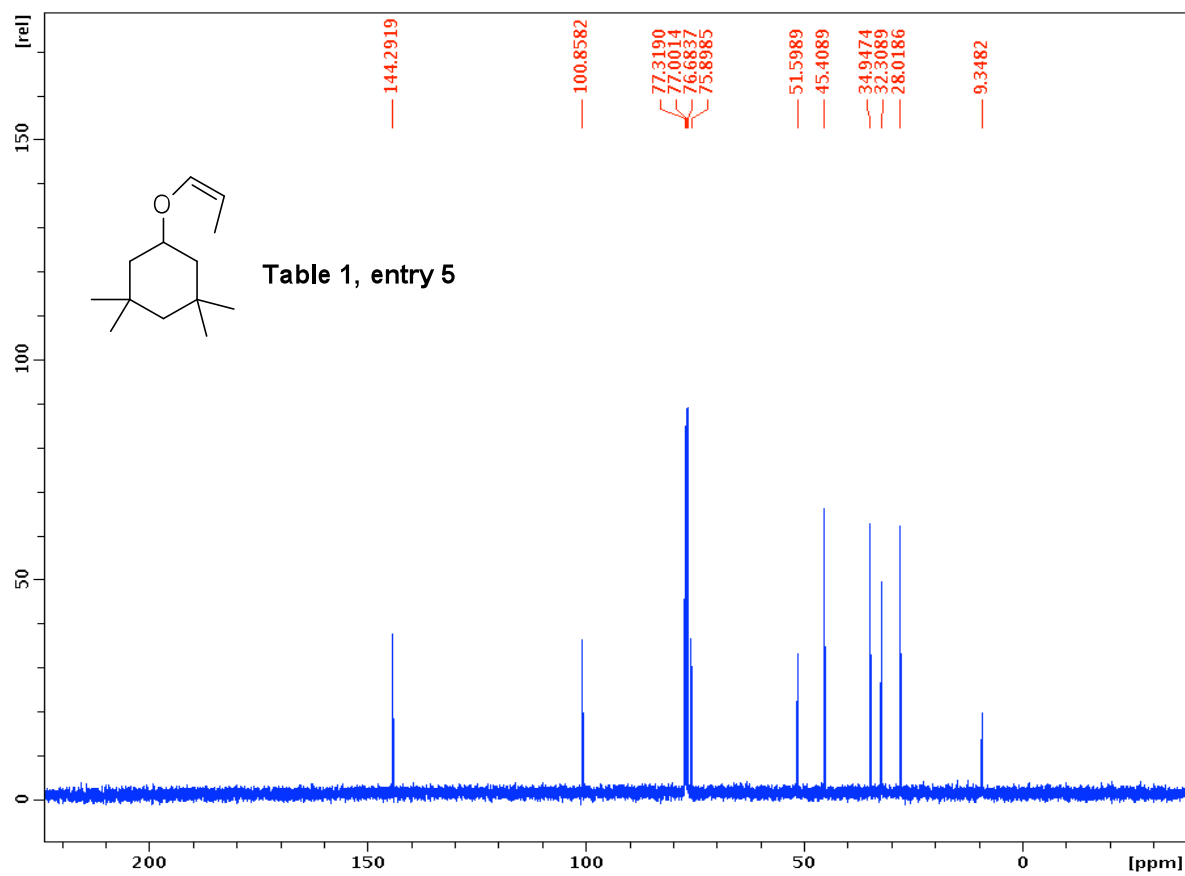
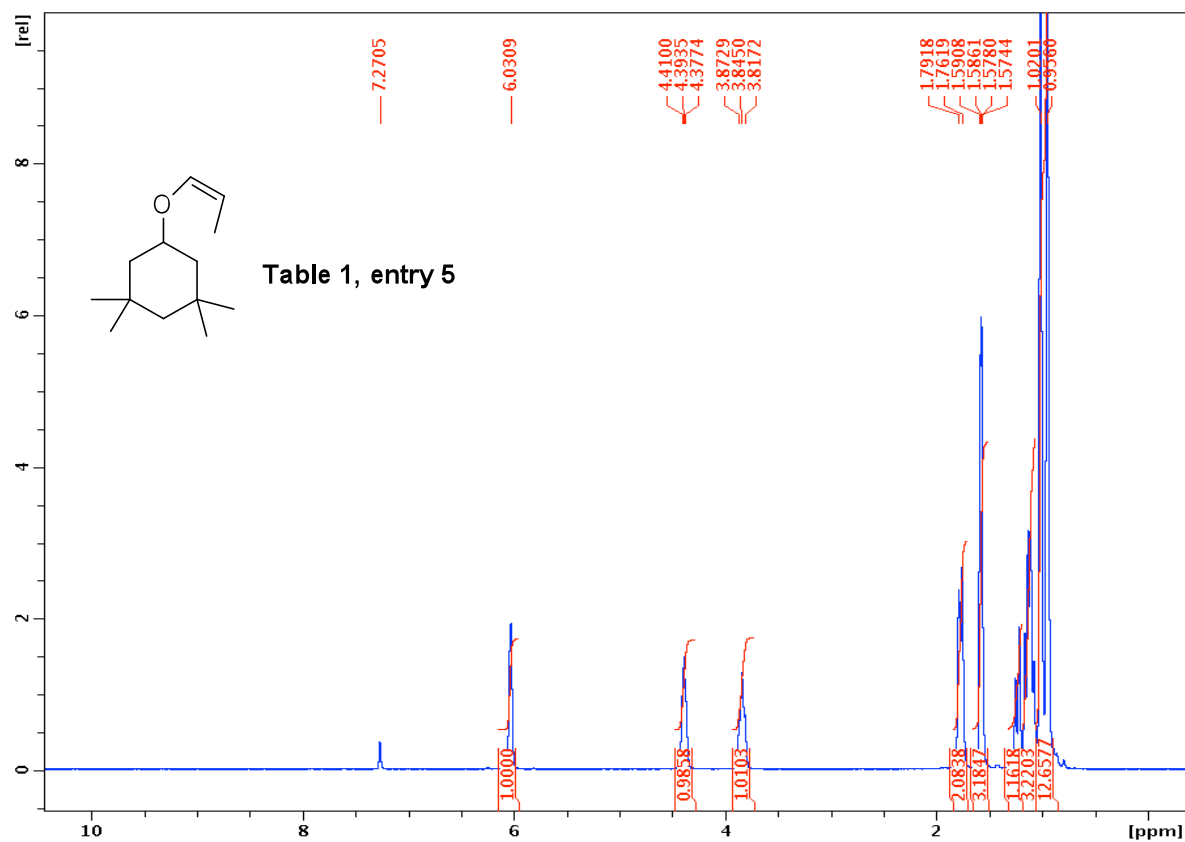
¹H and ¹³C NMR Spectra for Vinyl Ethers

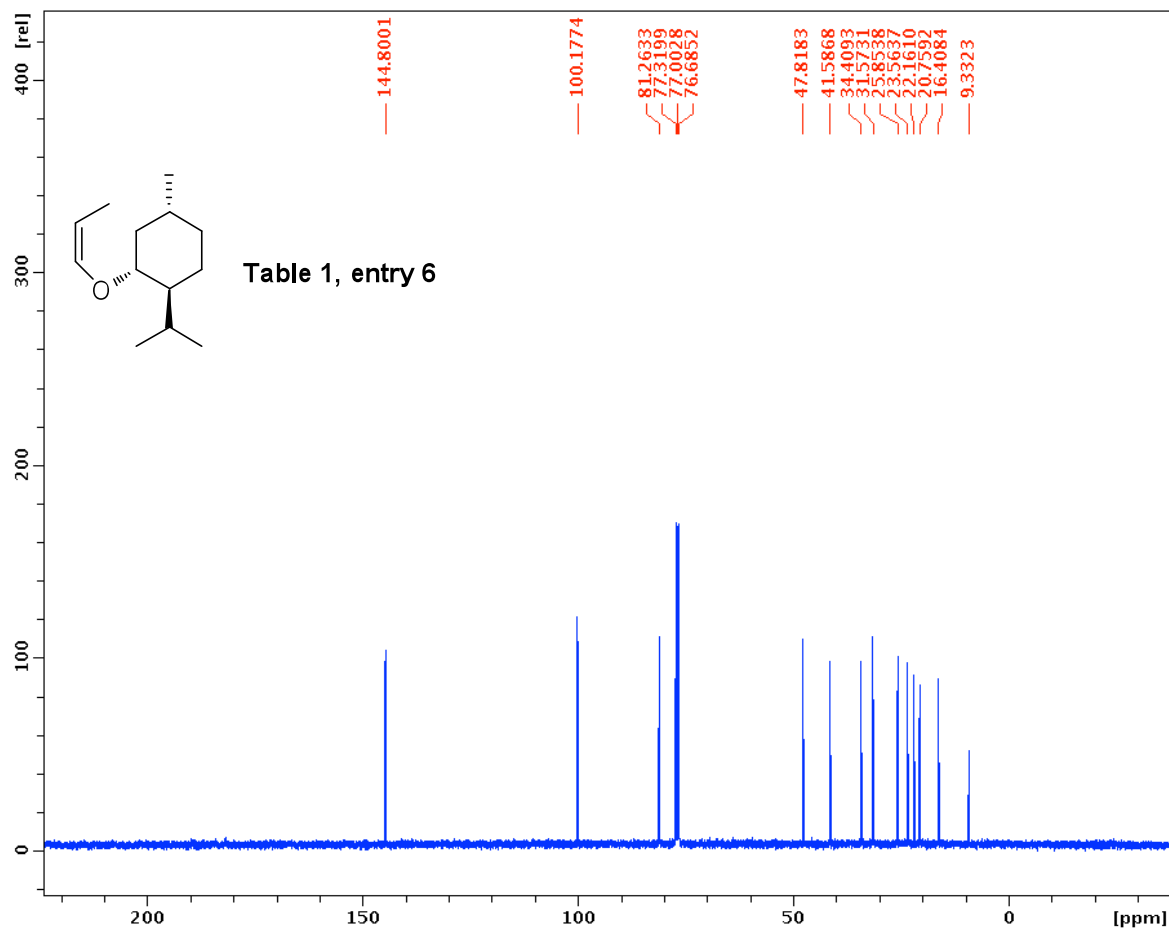
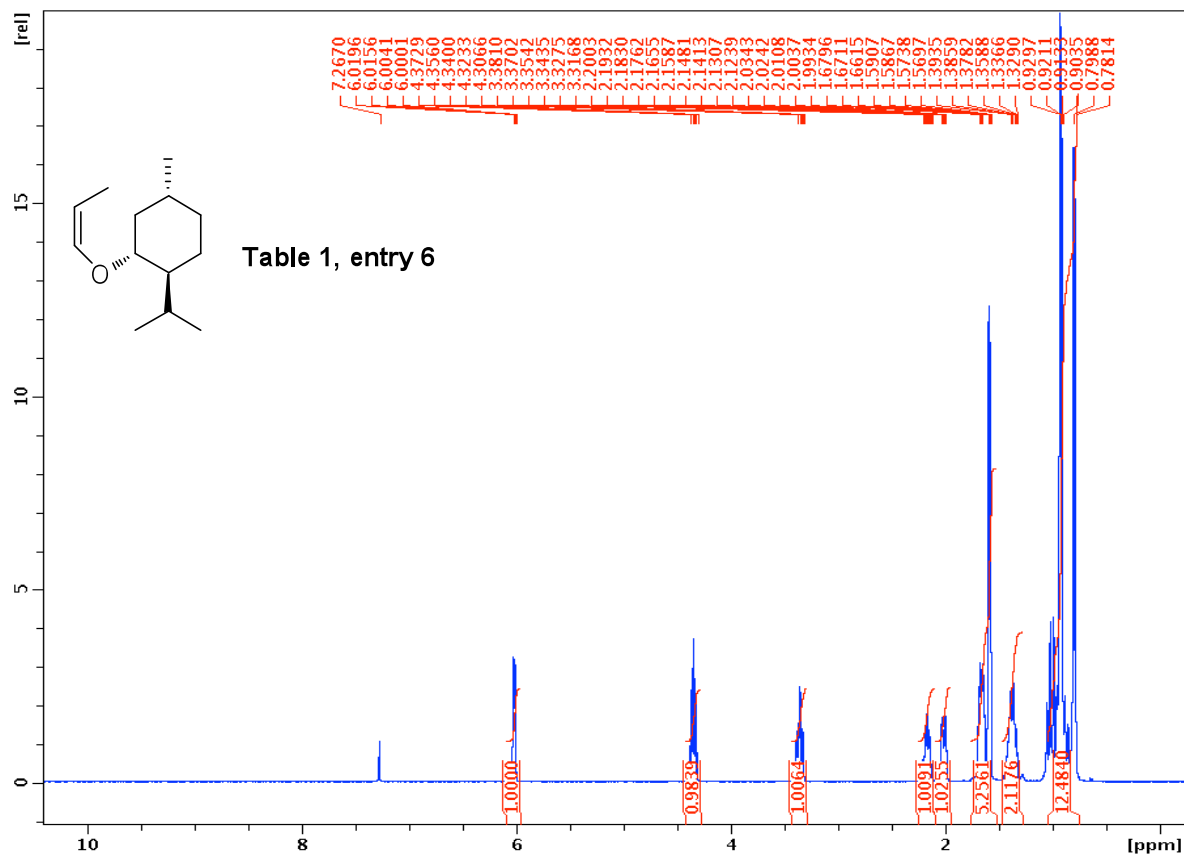


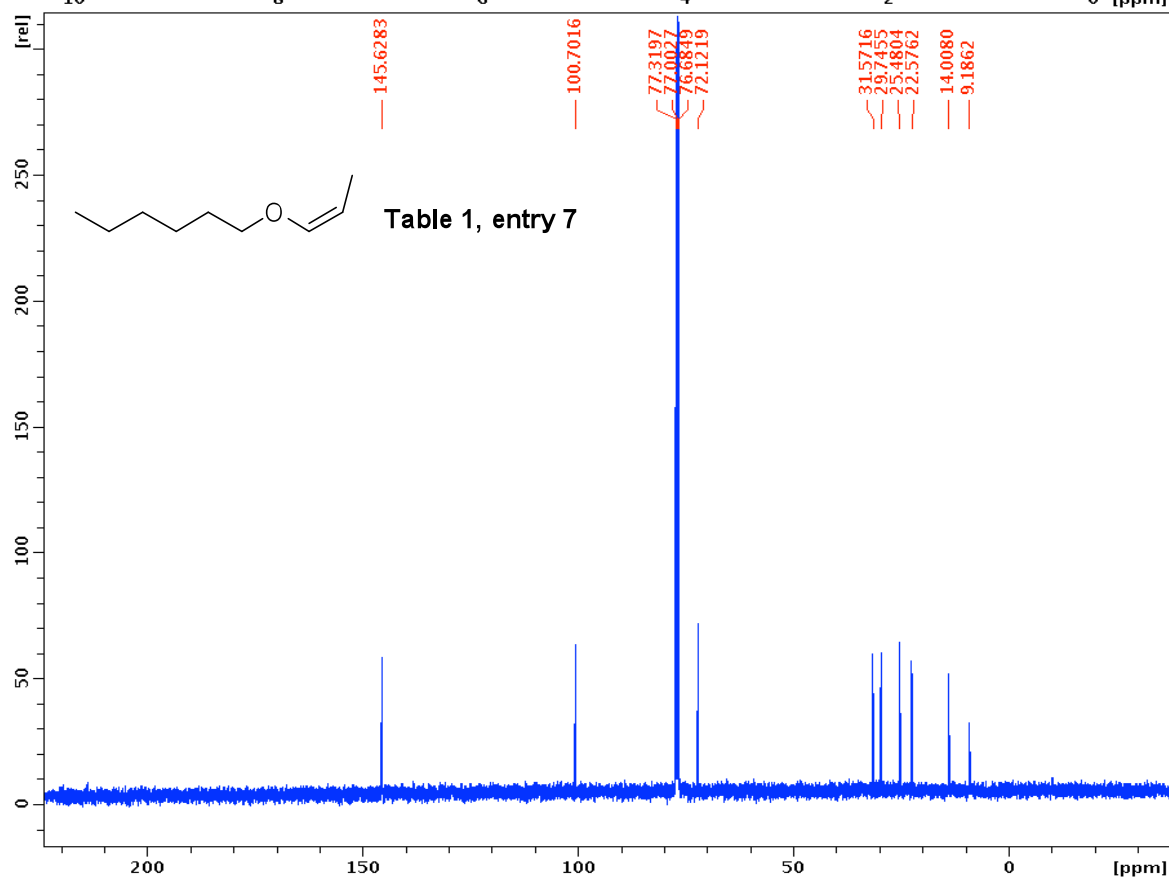
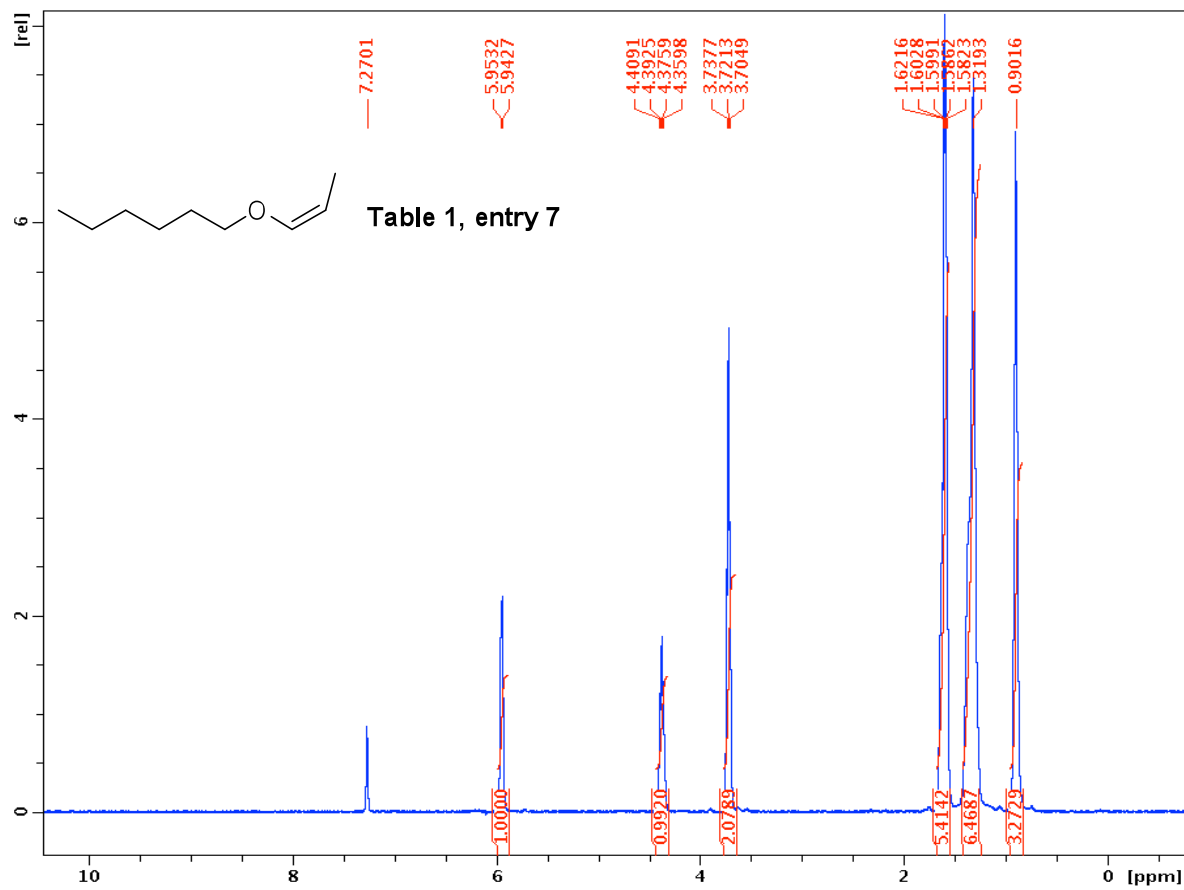


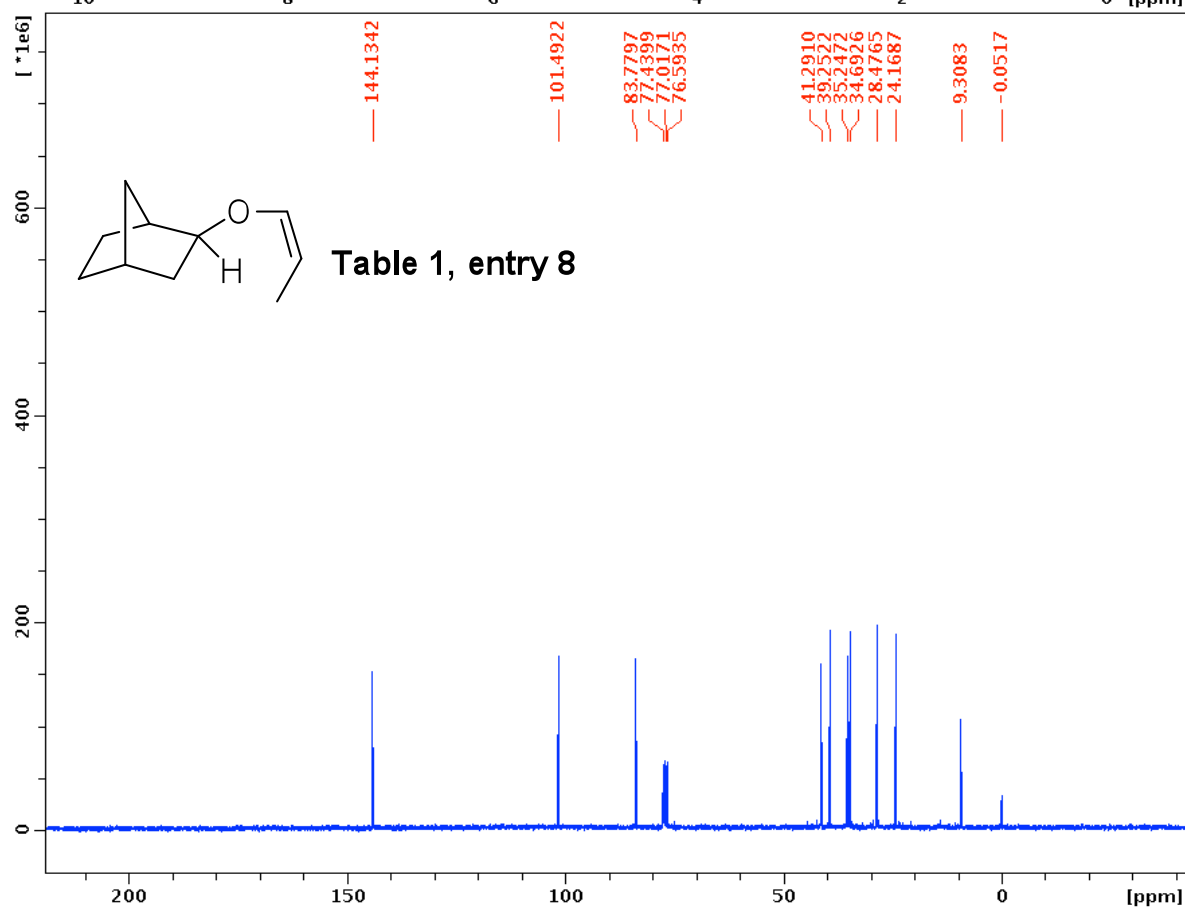
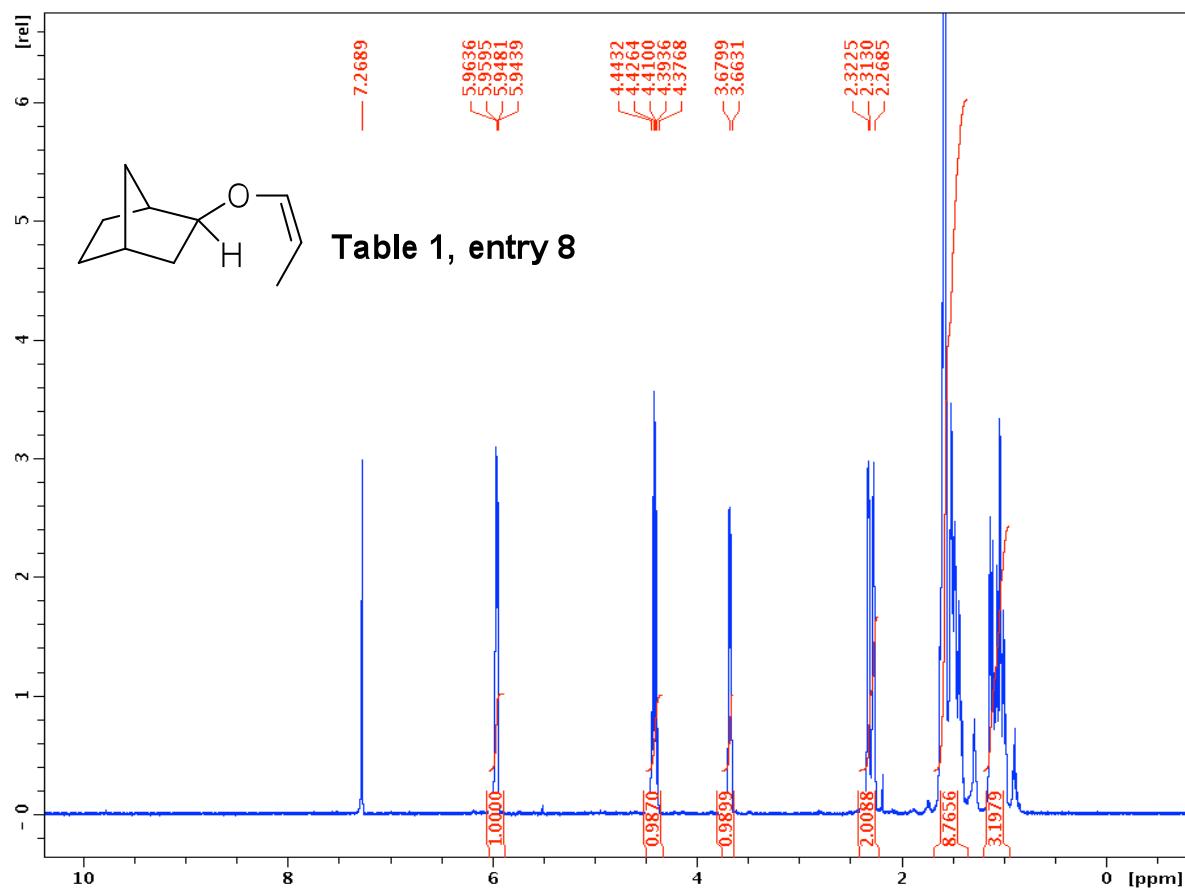


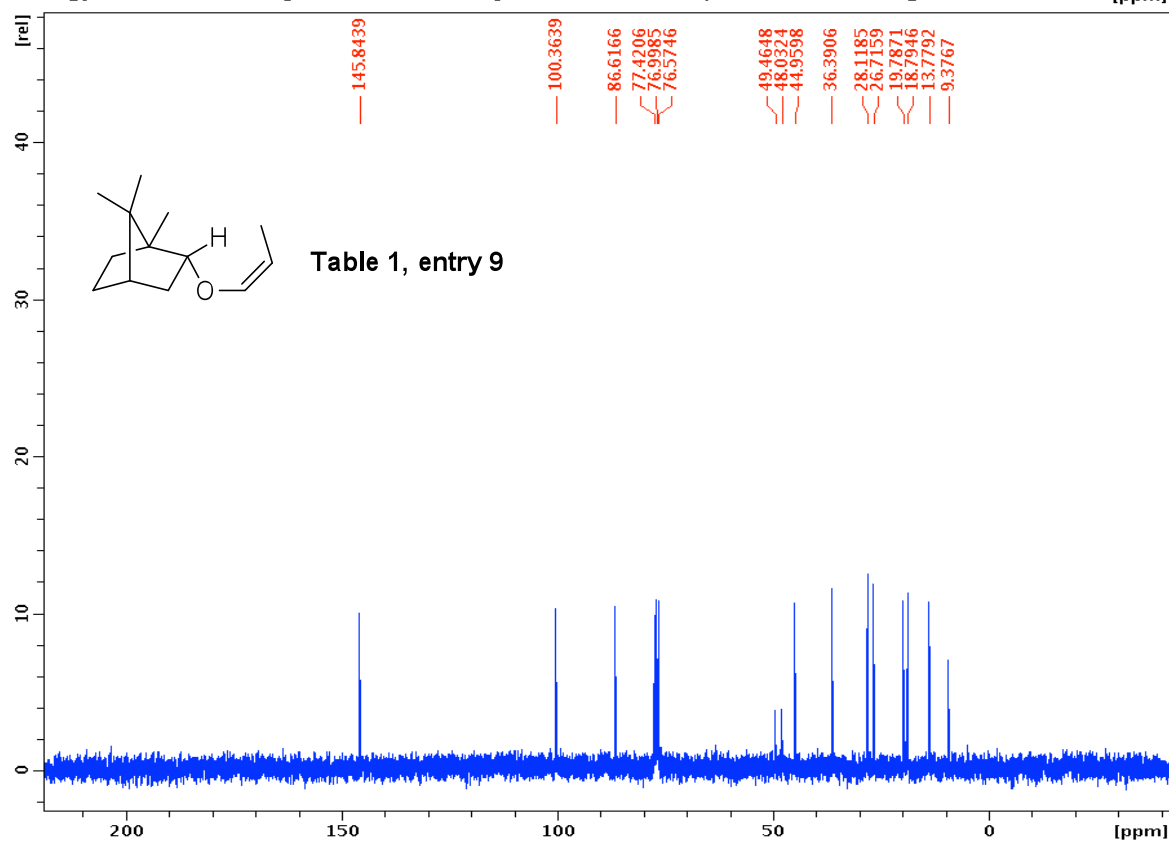
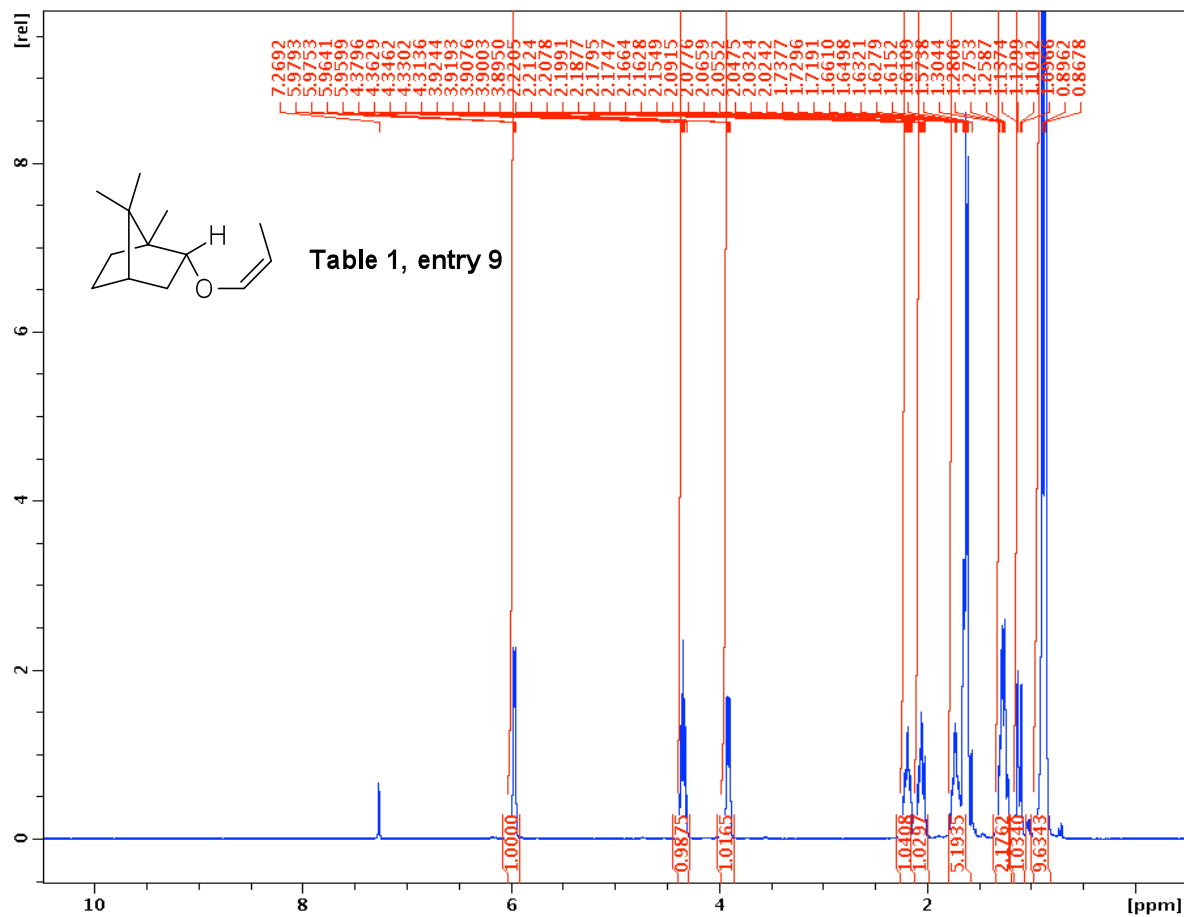


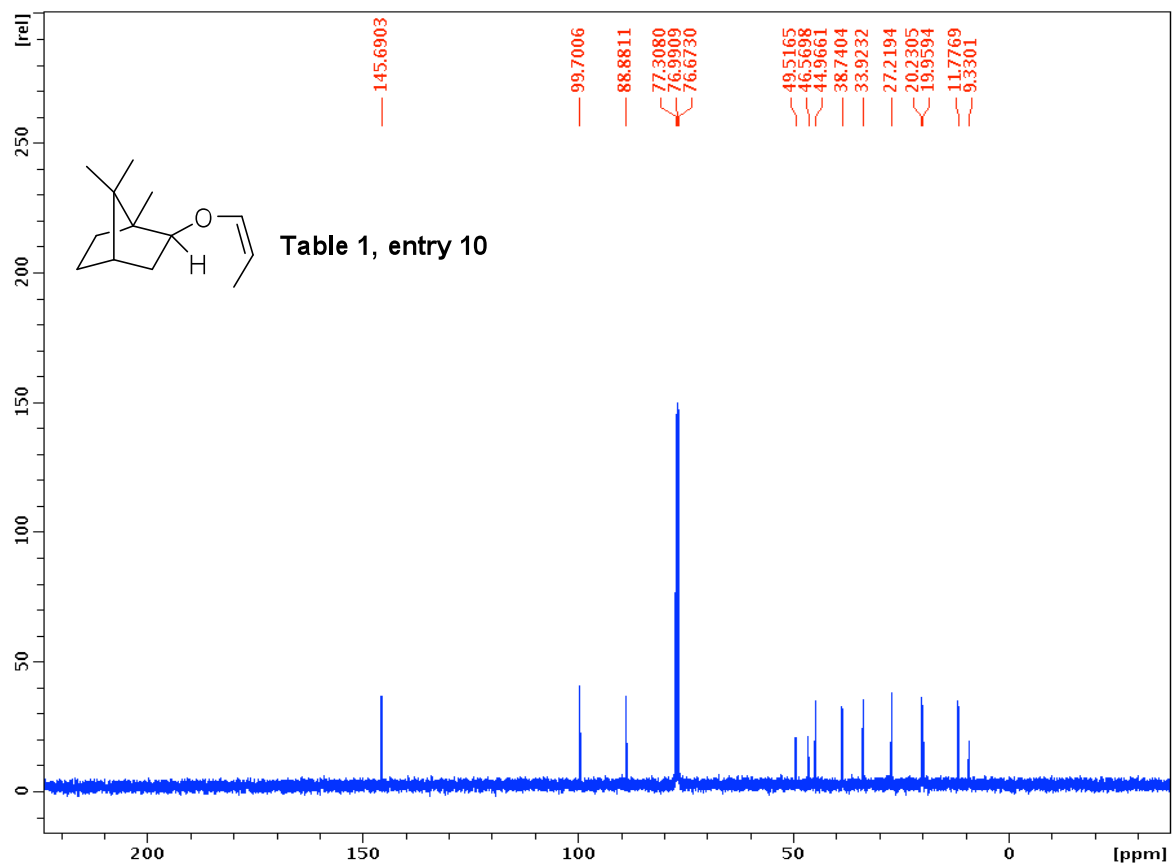
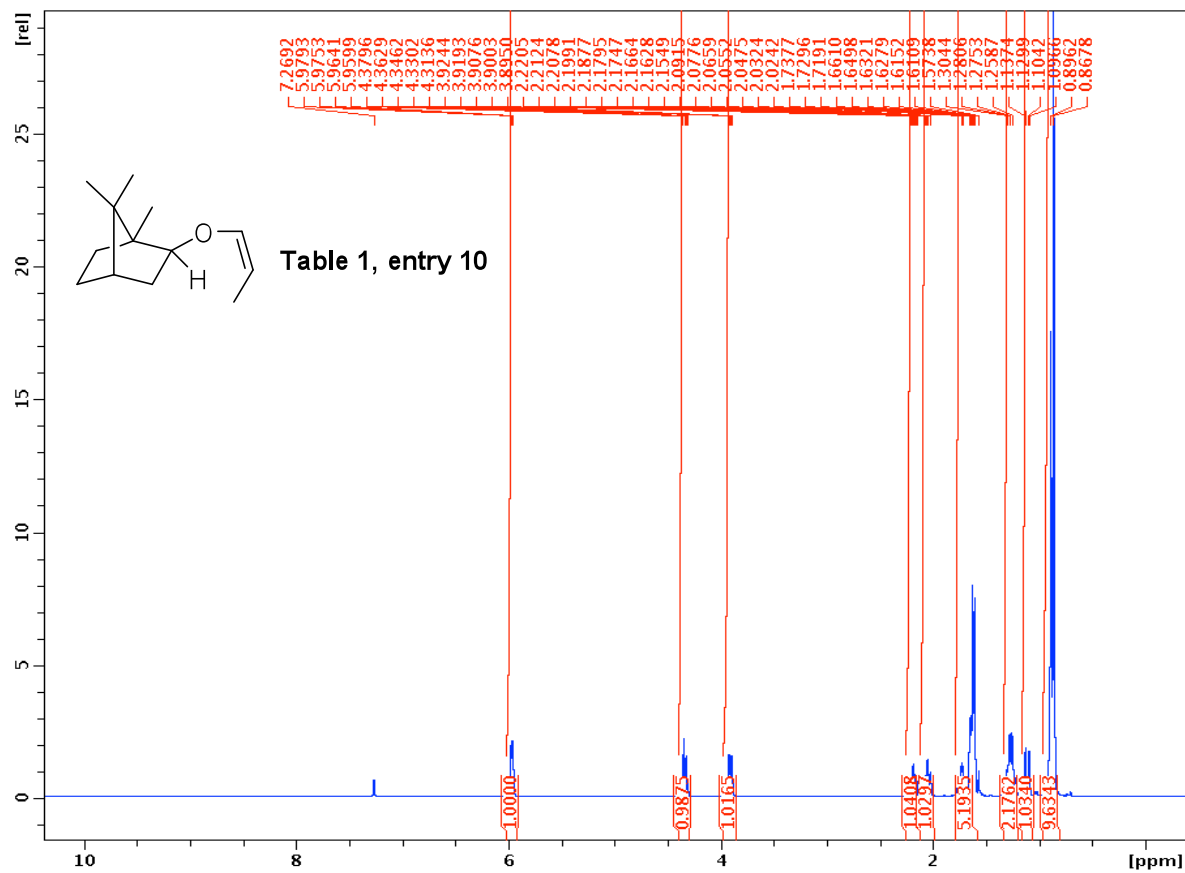


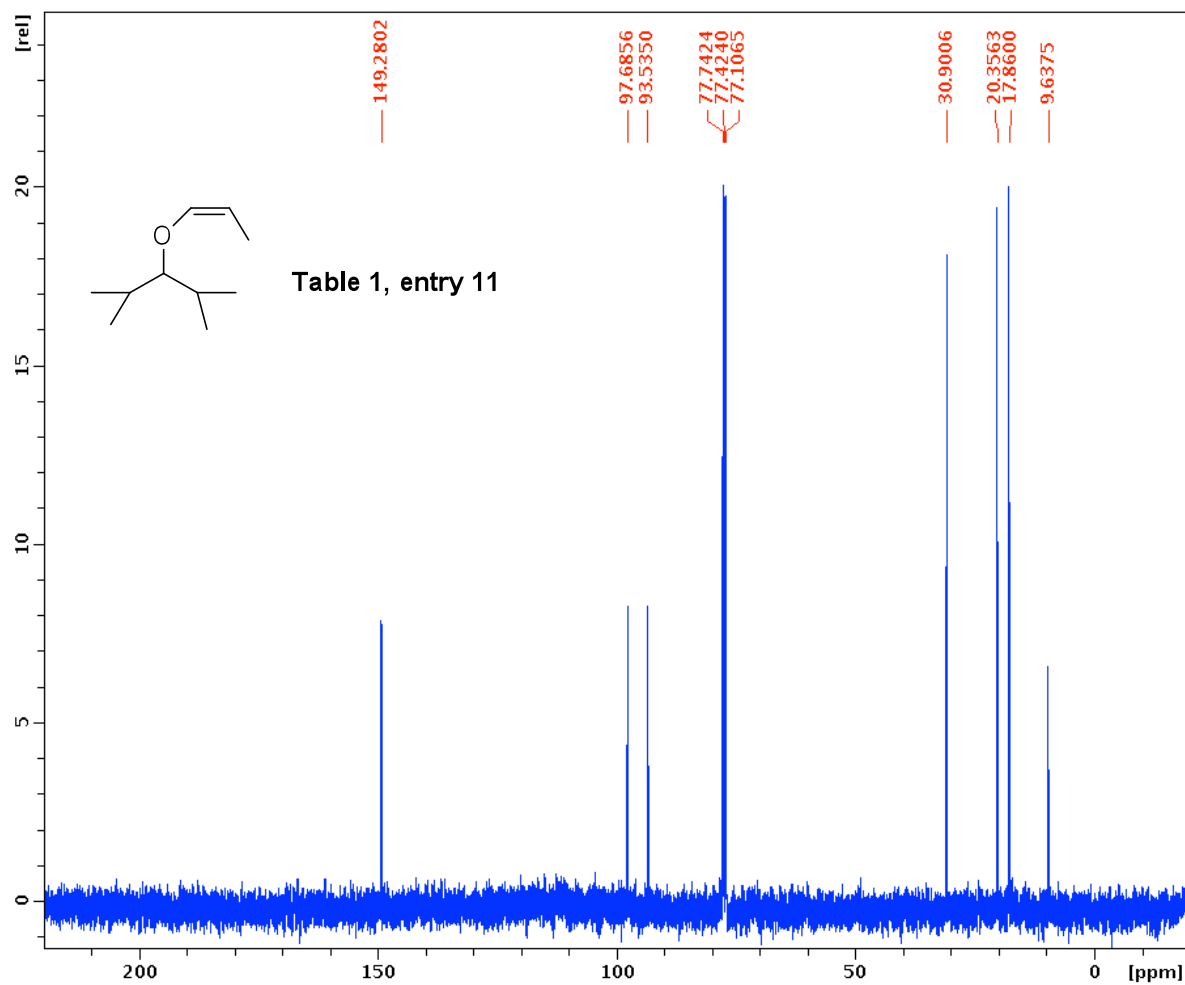
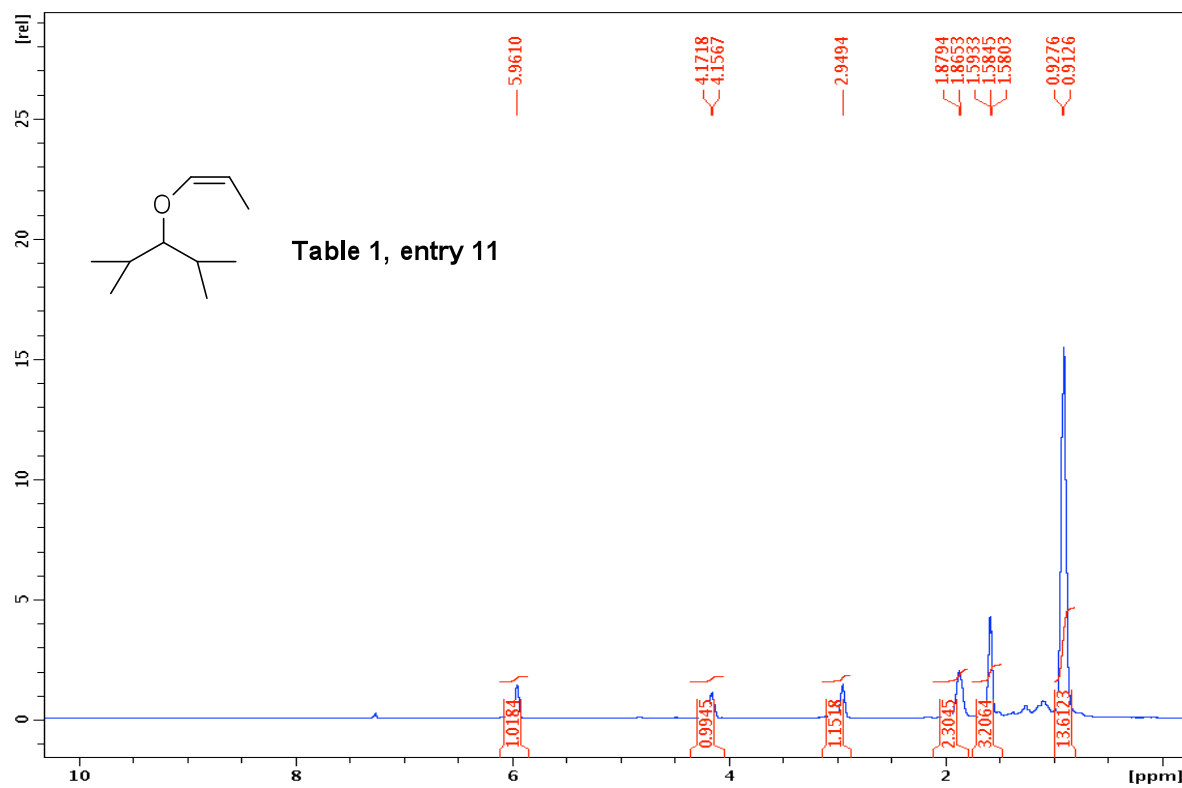


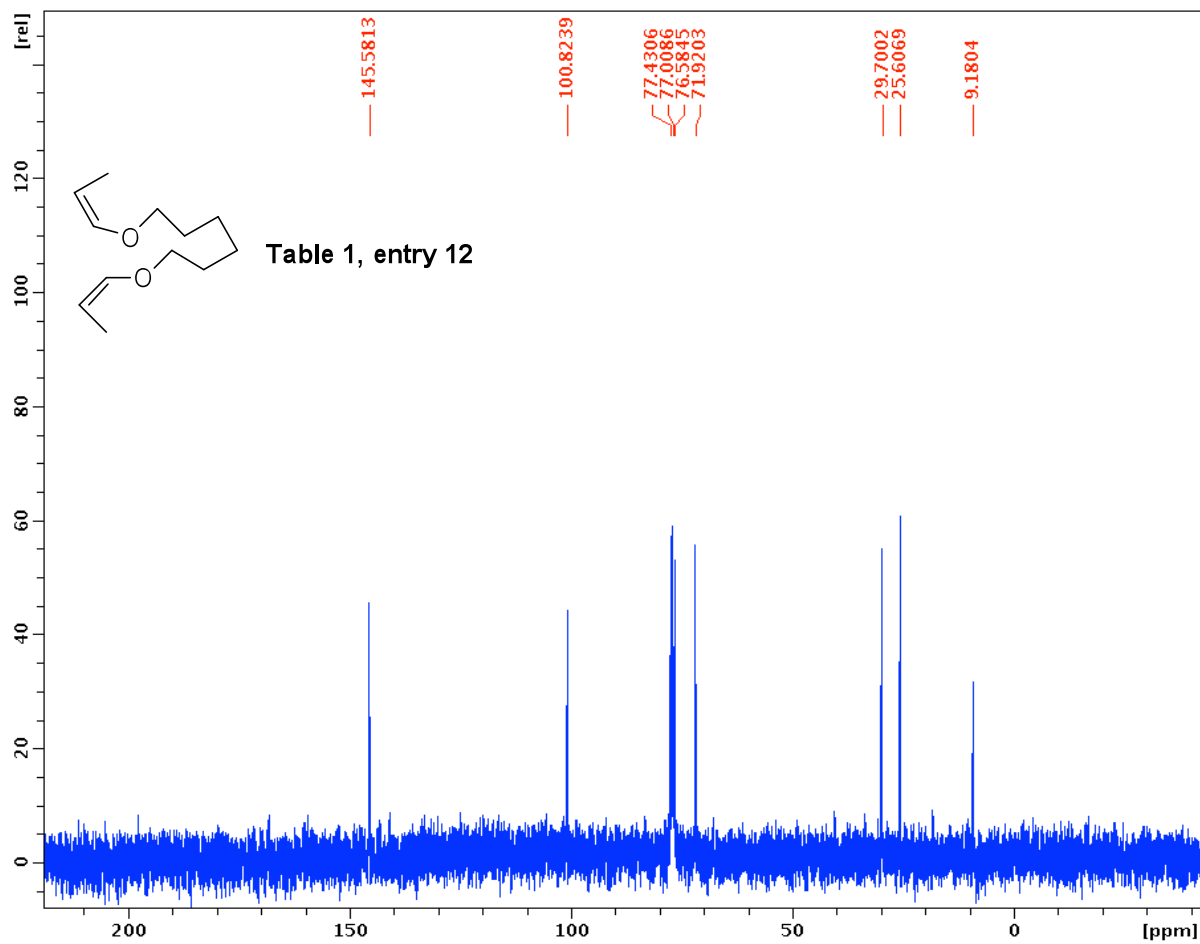
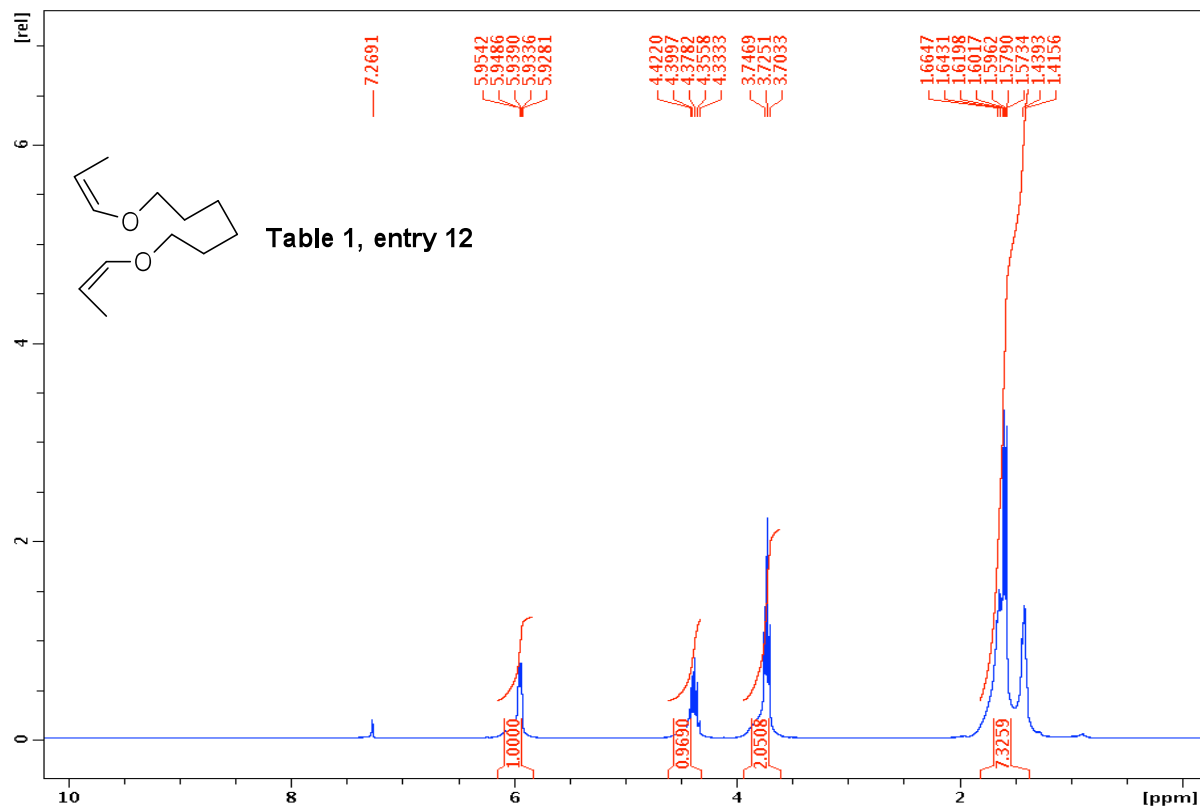


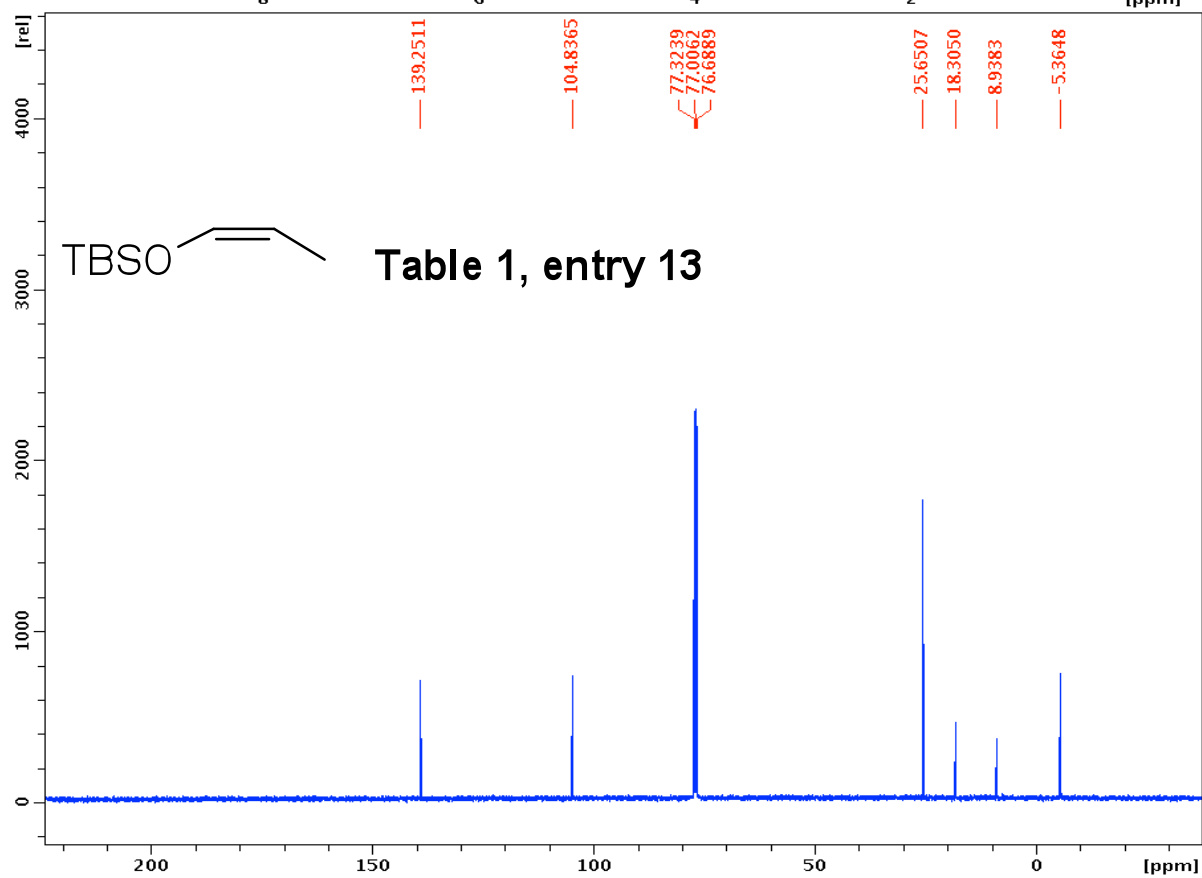
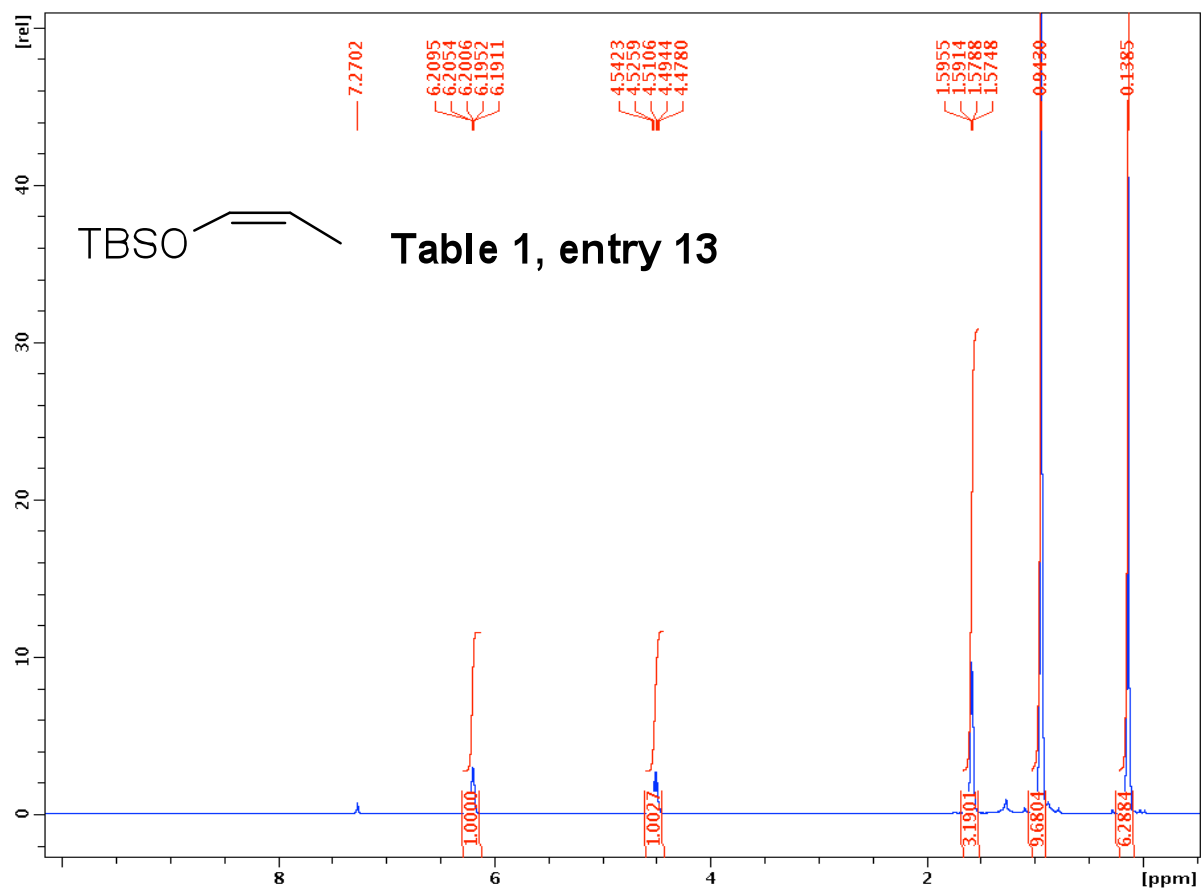


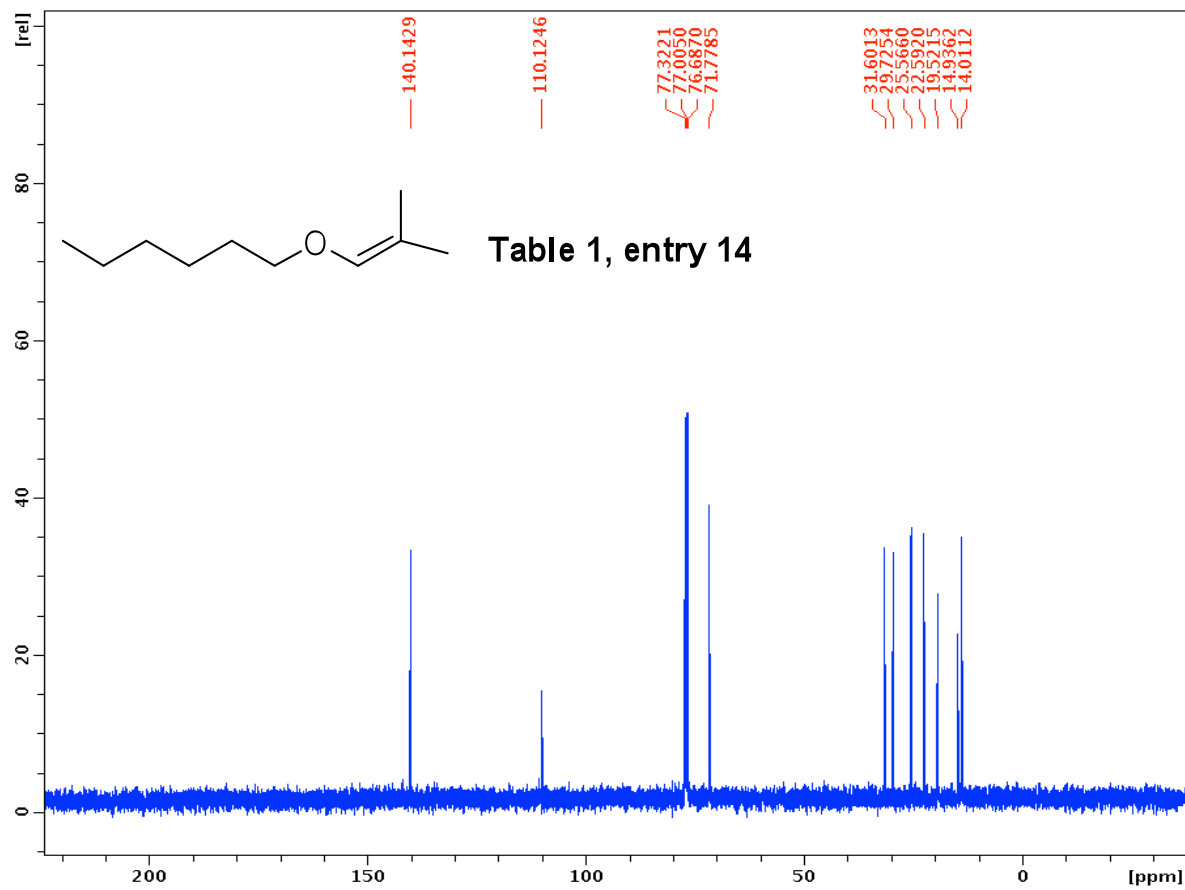
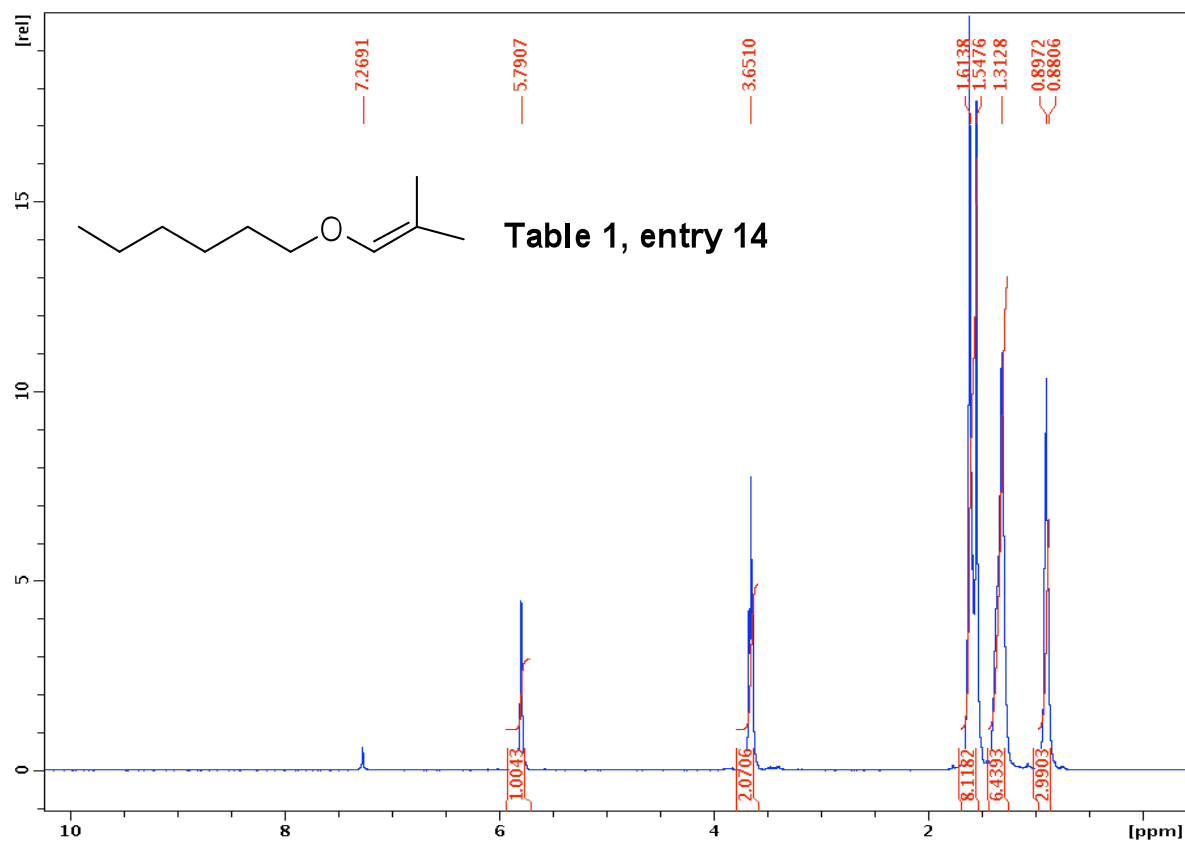


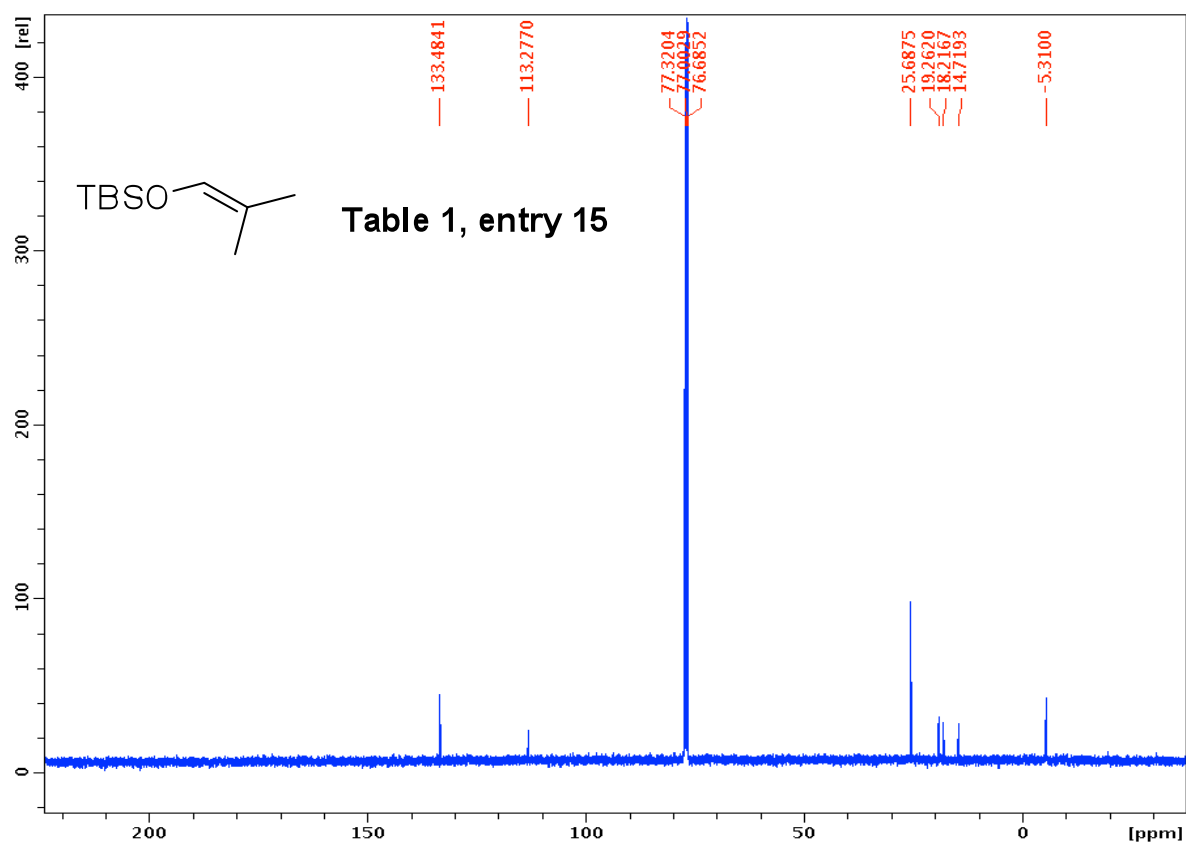
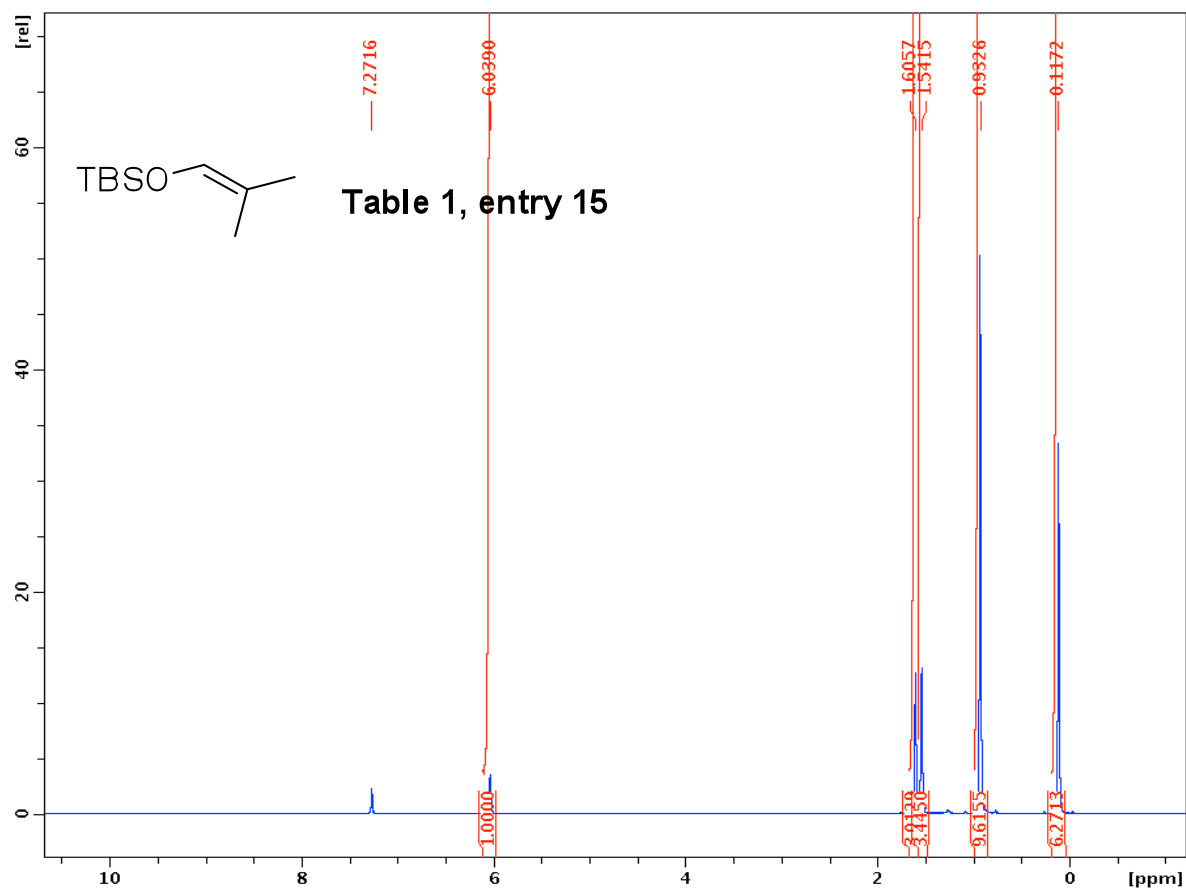


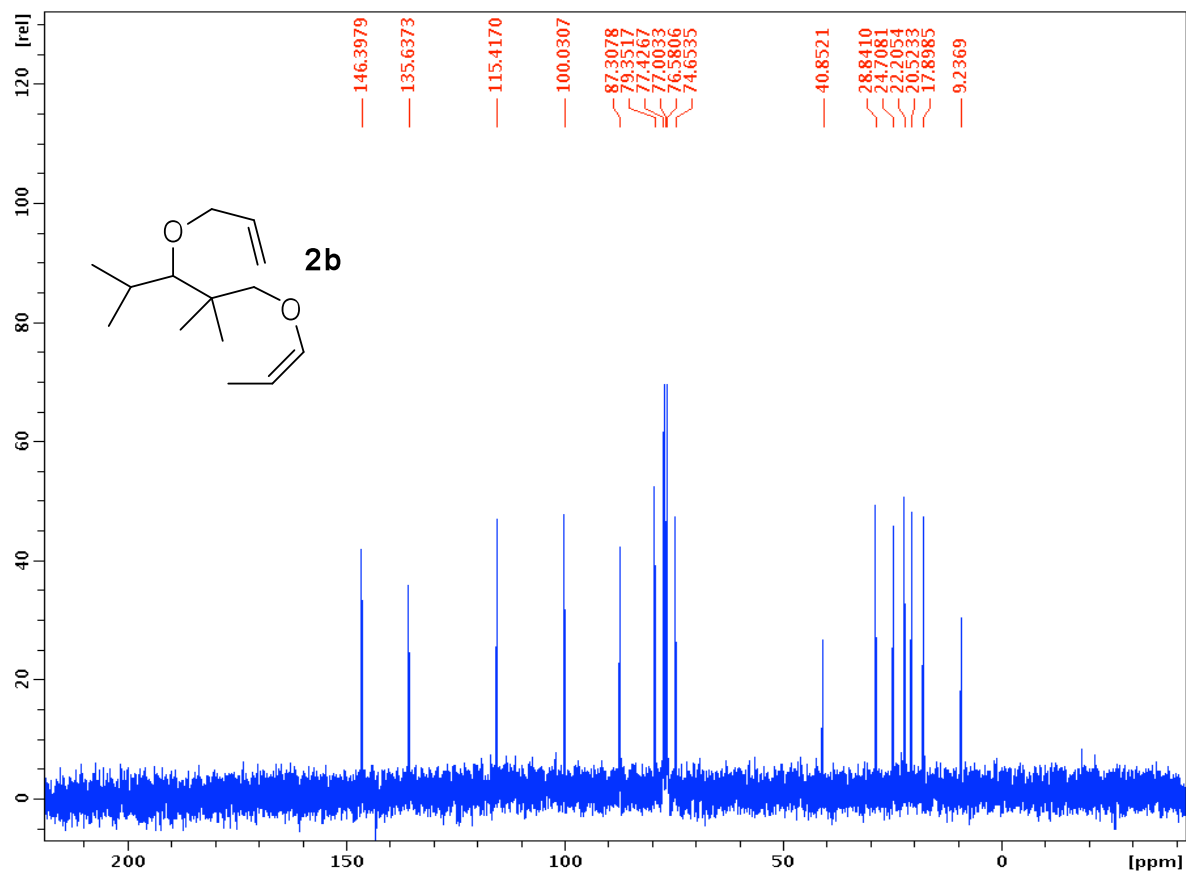
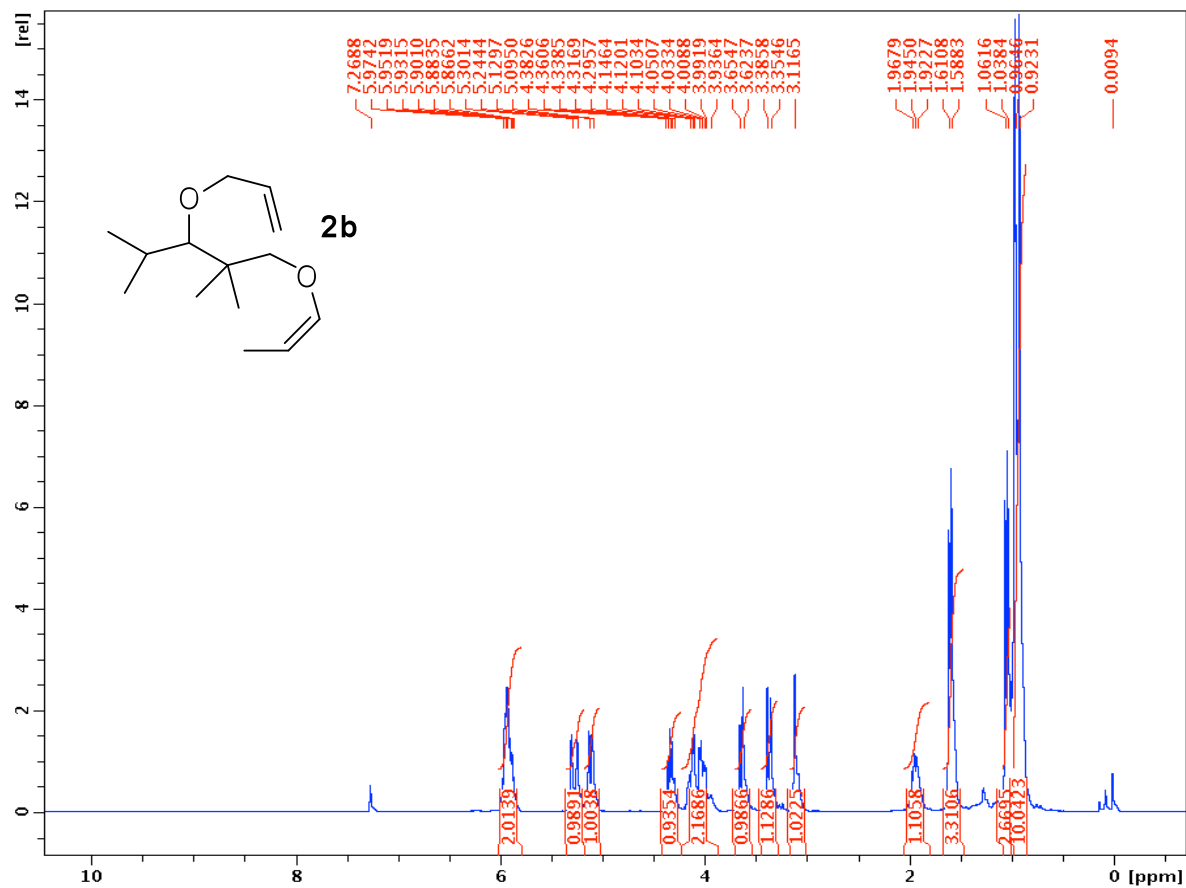


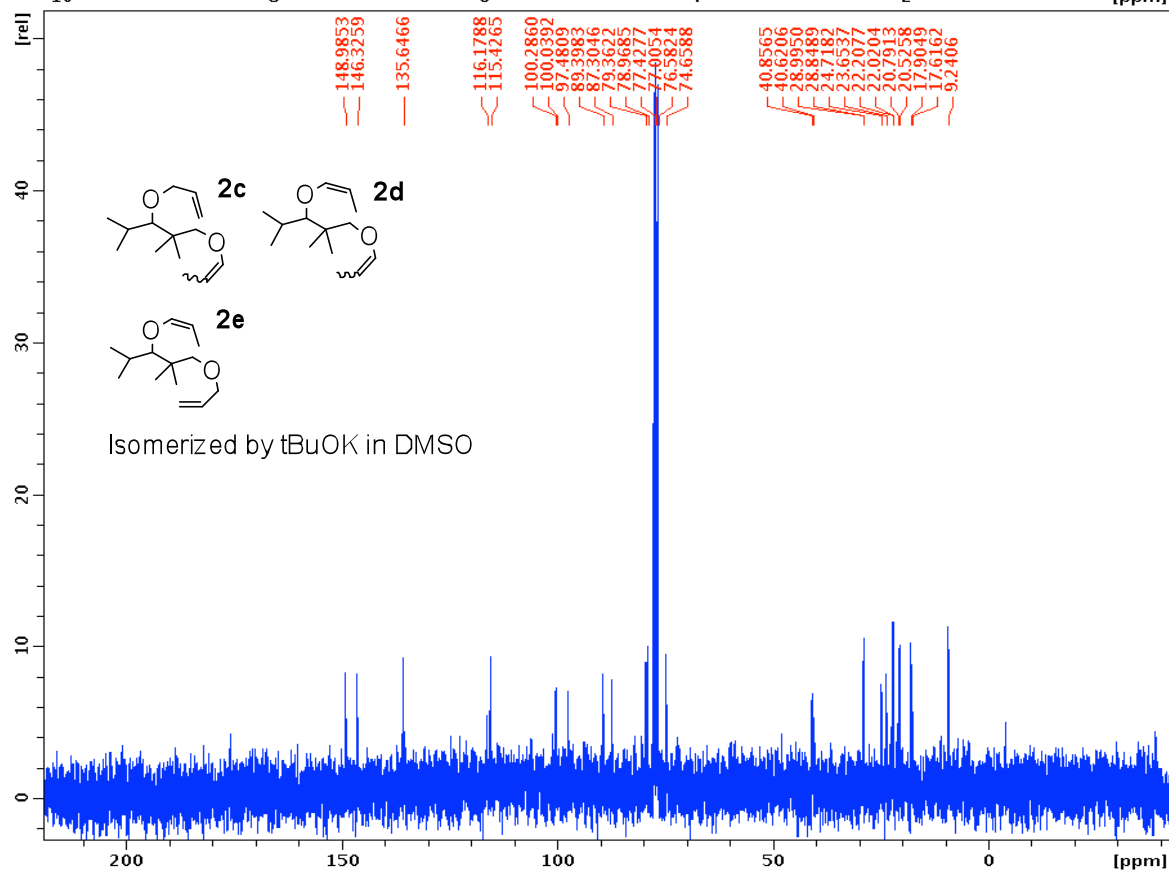
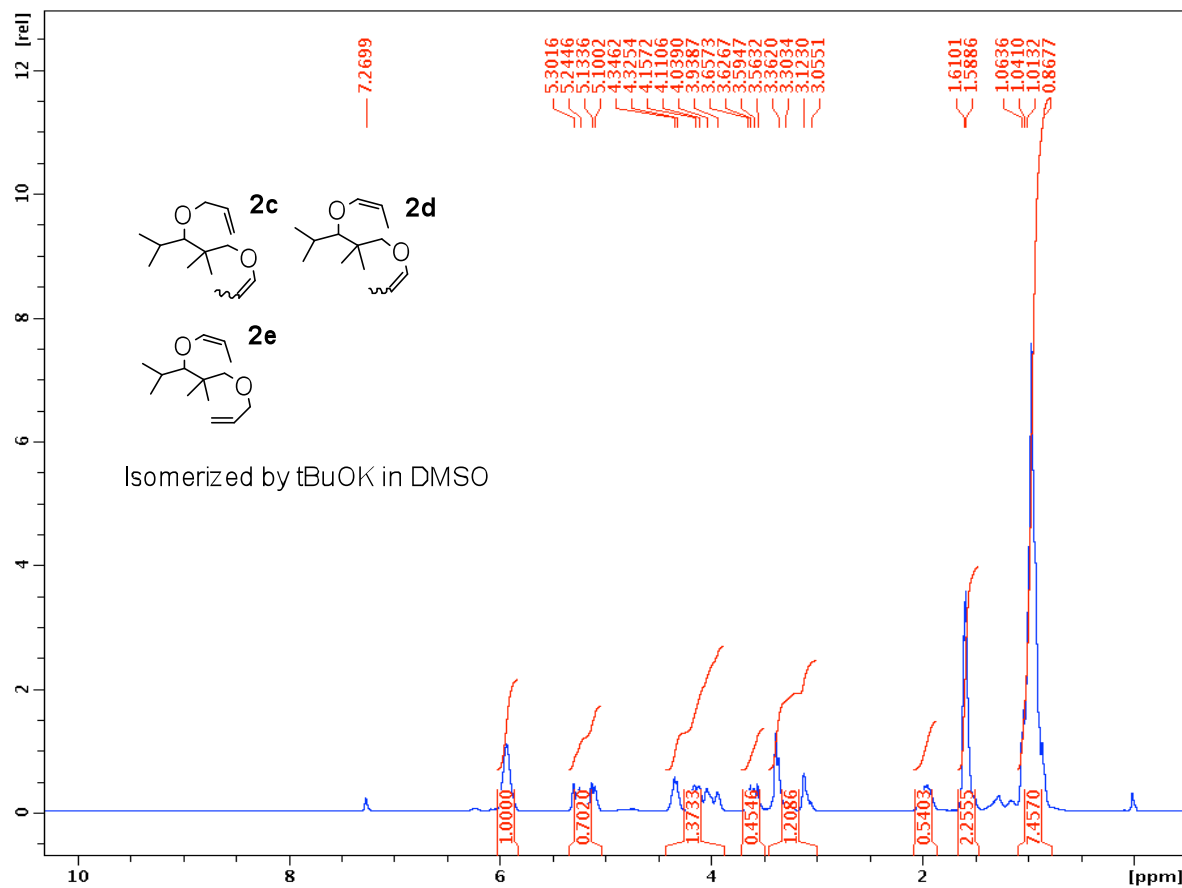


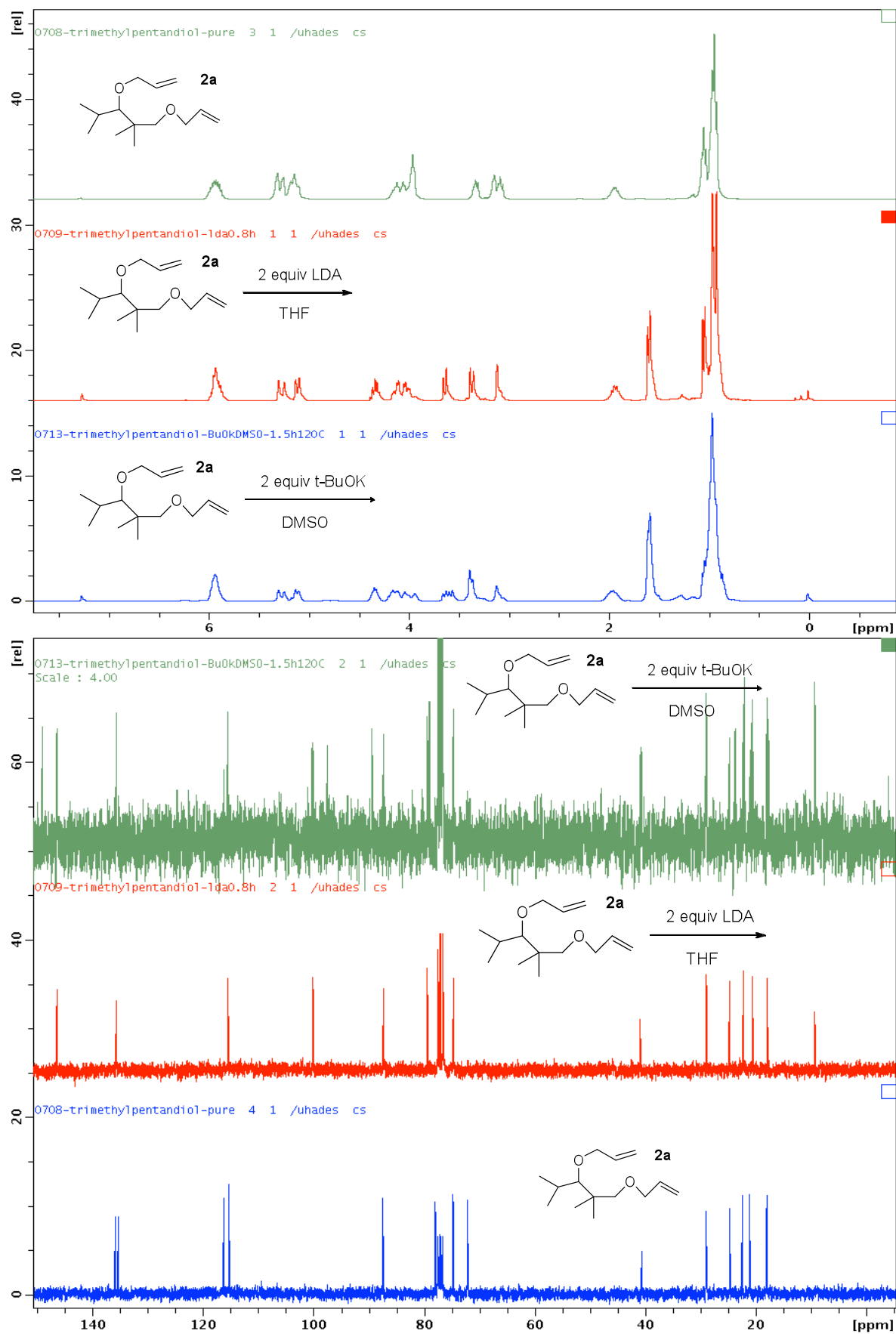












GC Spectra for Vinyl Ethers

Brown University

6/29/10

File: RQ6812

Date Run: 06-29-2010

Sample: chichenug su/pgw, mw 134.1

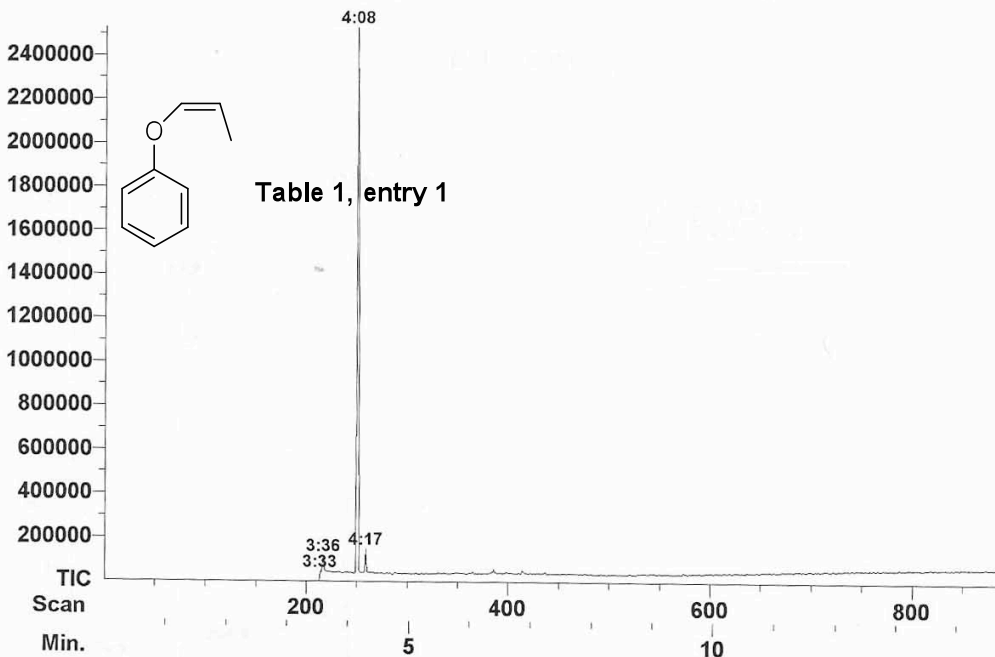
Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

Printed by: MS-600



Brown University

7/6/10

File: RQ6831

Date Run: 07-06-2010

Sample: chicheung su/pgw, mw 126.1

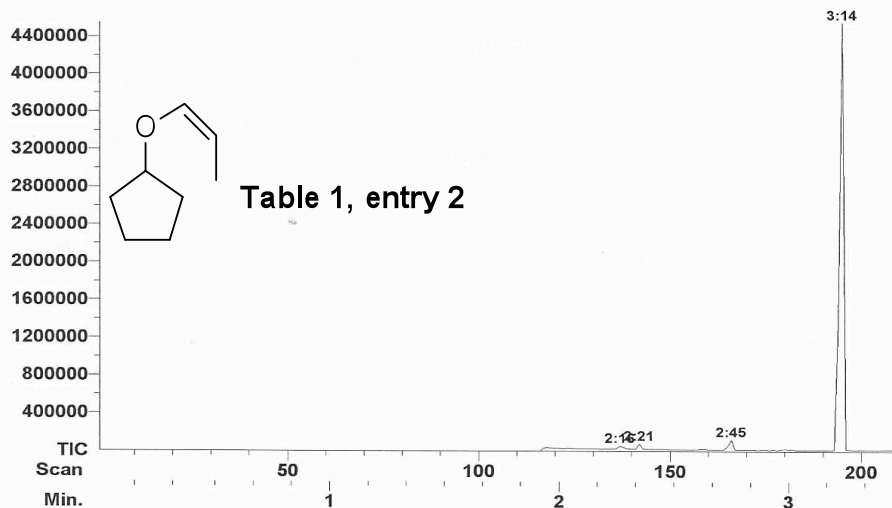
Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

Printed by: MS-600



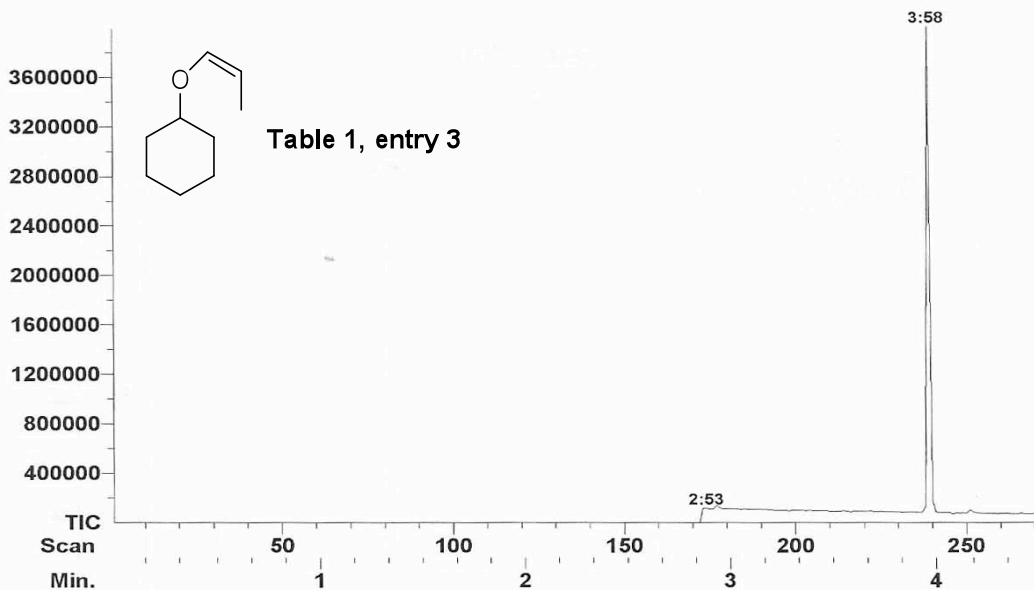
Brown University
6/29/10

File: RQ6780
Sample: 140.1
Instrument: JEOL JMS600
Inlet: GC

Date Run: 06-29-2010

Ionization mode: EI+

Run By: MS-600
Printed by: MS-600



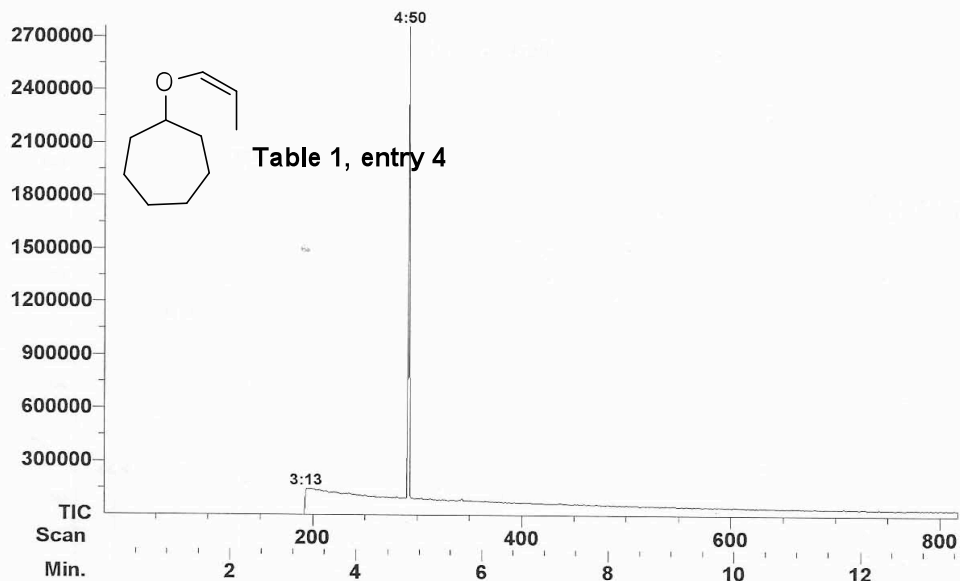
Brown University
6/30/10

File: RQ6815
Sample: chicheung su/pgw, mw 154.1
Instrument: JEOL JMS600
Inlet: GC

Date Run: 06-30-2010

Ionization mode: EI+

Run By: MS-600
Printed by: MS-600



Brown University

6/29/10

File: RQ6813

Date Run: 06-29-2010

Sample: chicheung su/pgw, mw 196.2

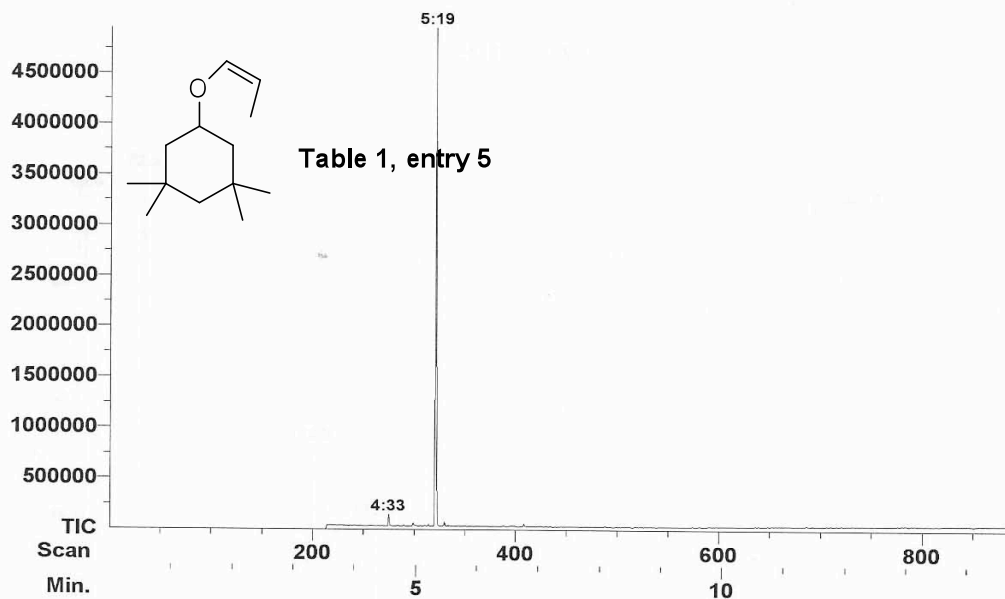
Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

Printed by: MS-600



Brown University

8/19/10

File: RQ6985

Date Run: 08-19-2010

Sample: cs/pgw, mw 196.2

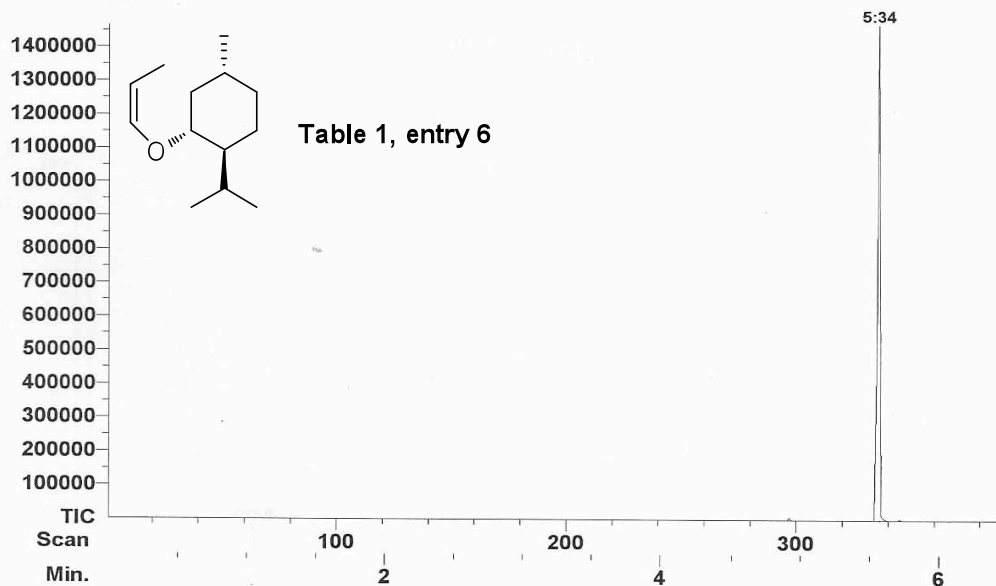
Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

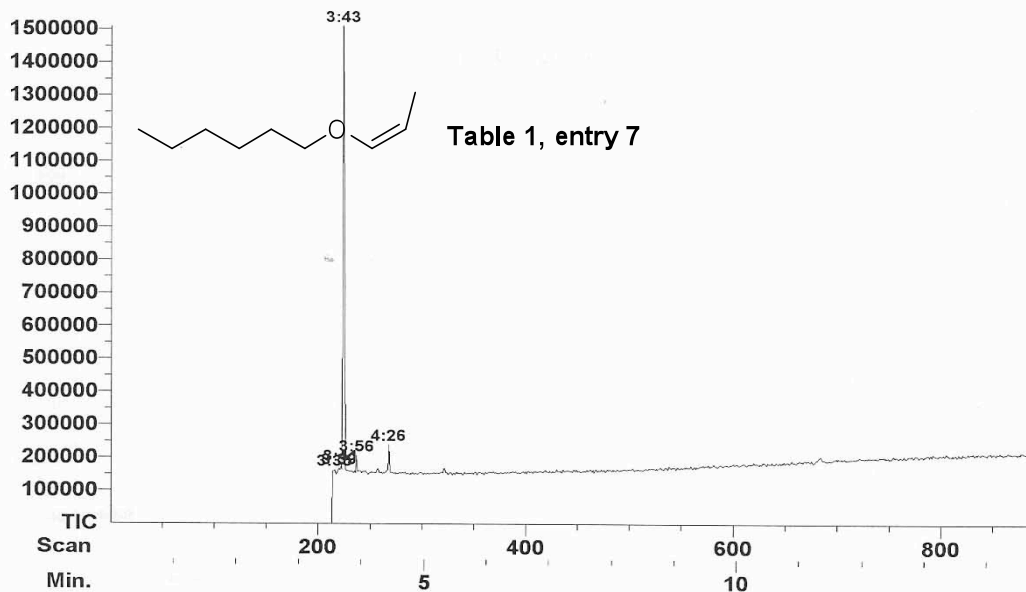
Printed by: MS-600



Brown University
6/24/10

File: RQ6778 Date Run: 06-24-2010
Sample: chicheung su/pgw, mw 142
Instrument: JEOL JMS600
Inlet: GC Ionization mode: EI+

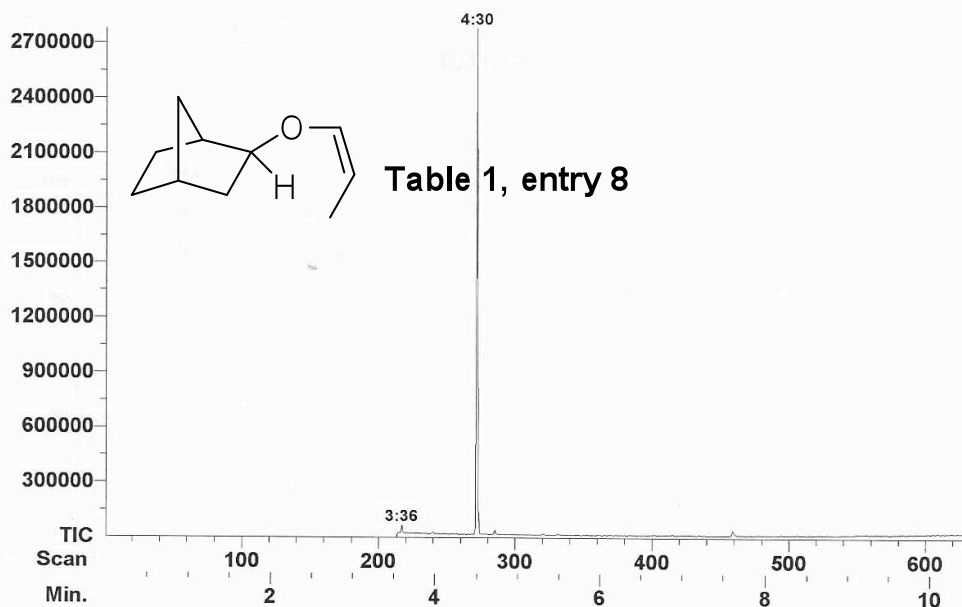
Run By: MS-600
Printed by: MS-600



Brown University
8/18/10

File: RQ6979 Date Run: 08-18-2010
Sample: cs/pgw, mw 152.1
Instrument: JEOL JMS600
Inlet: GC Ionization mode: EI+

Run By: MS-600
Printed by: MS-600



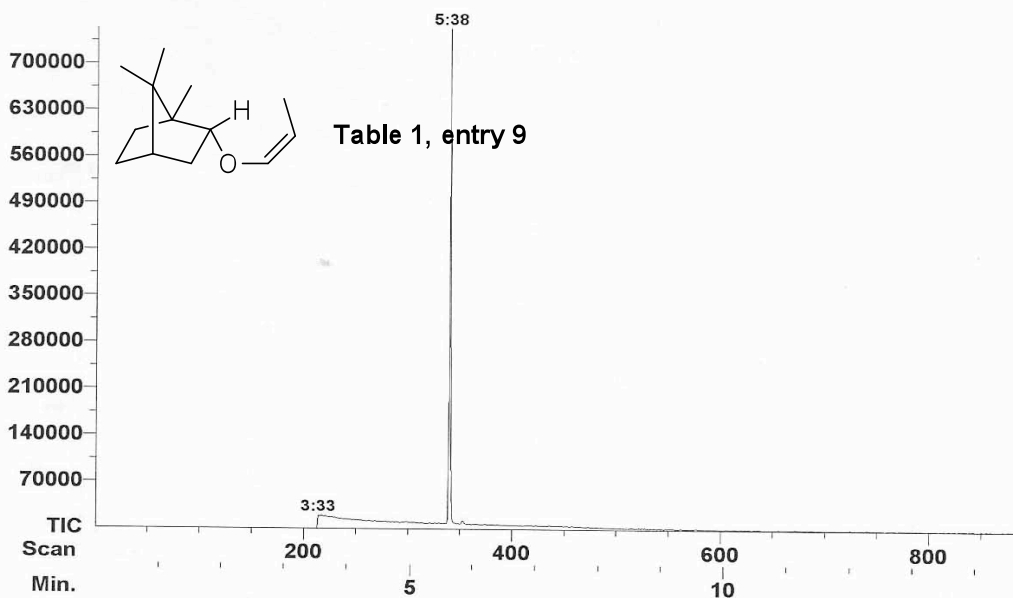
Brown University
8/19/10

File: RQ6984
Sample: cs/pgw, mw 194.2
Instrument: JEOL JMS600
Inlet: GC

Date Run: 08-19-2010

Ionization mode: EI+

Run By: MS-600
Printed by: MS-600



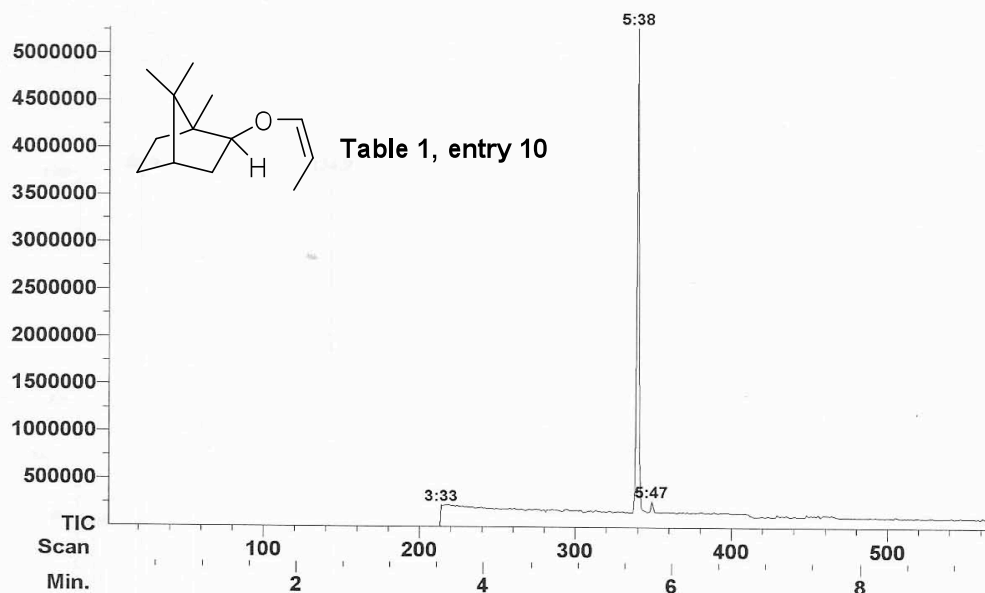
Brown University
8/18/10

File: RQ6977
Sample: cs/pgw, mw 194.2
Instrument: JEOL JMS600
Inlet: GC

Date Run: 08-18-2010

Ionization mode: EI+

Run By: MS-600
Printed by: MS-600



Brown University

6/24/10

File: RQ6777B

Date Run: 06-24-2010

Sample: chicheung su/pgw, mw 156

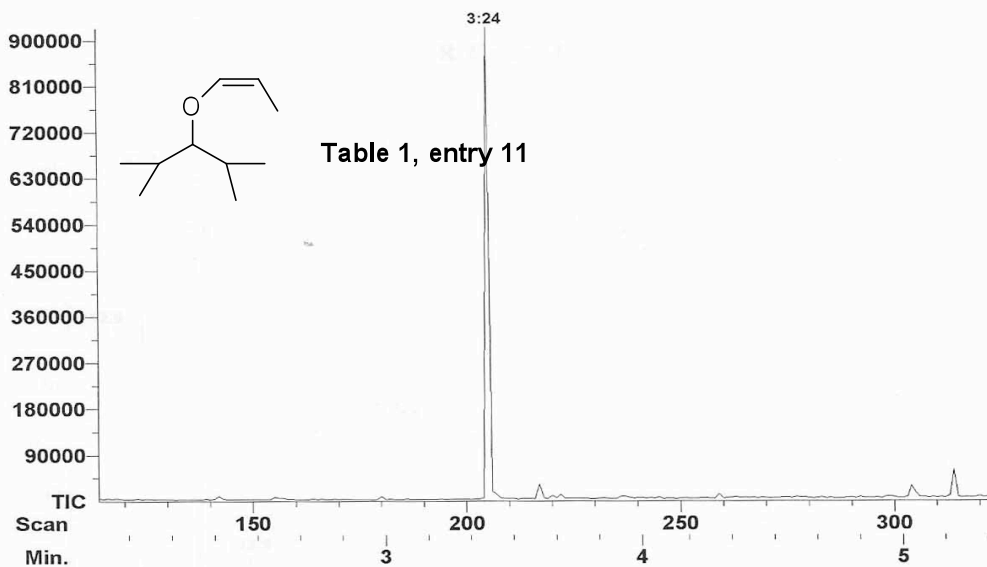
Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

Printed by: MS-600



Brown University

6/29/10

File: RQ6779B

Date Run: 06-29-2010

Sample: chicheung su/pgw, mw 198.2

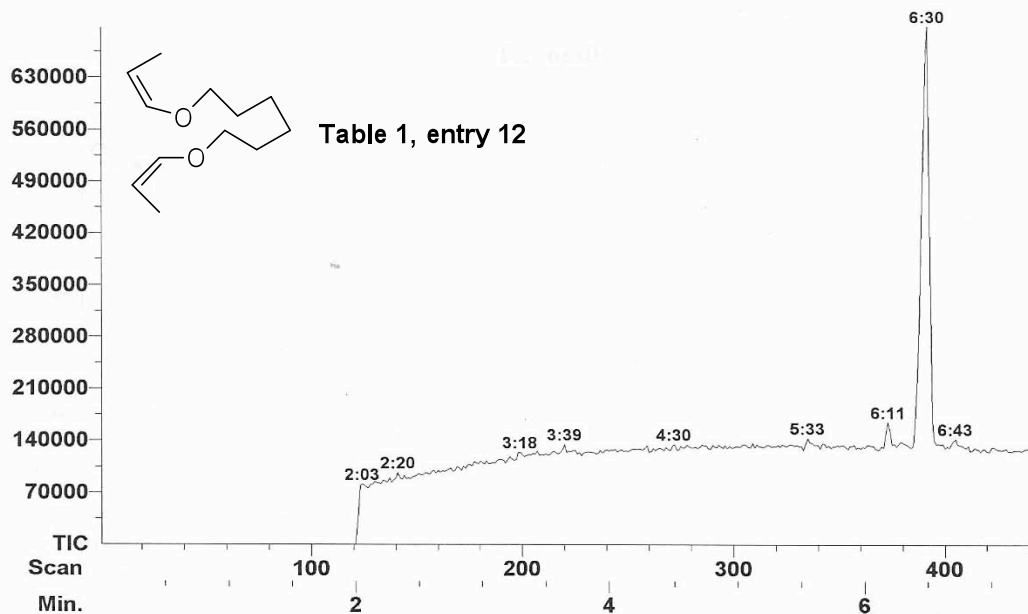
Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

Printed by: MS-600



Brown University
8/19/10

File: RQ6986

Date Run: 08-19-2010

Sample: cs/pgw, mw 172.1

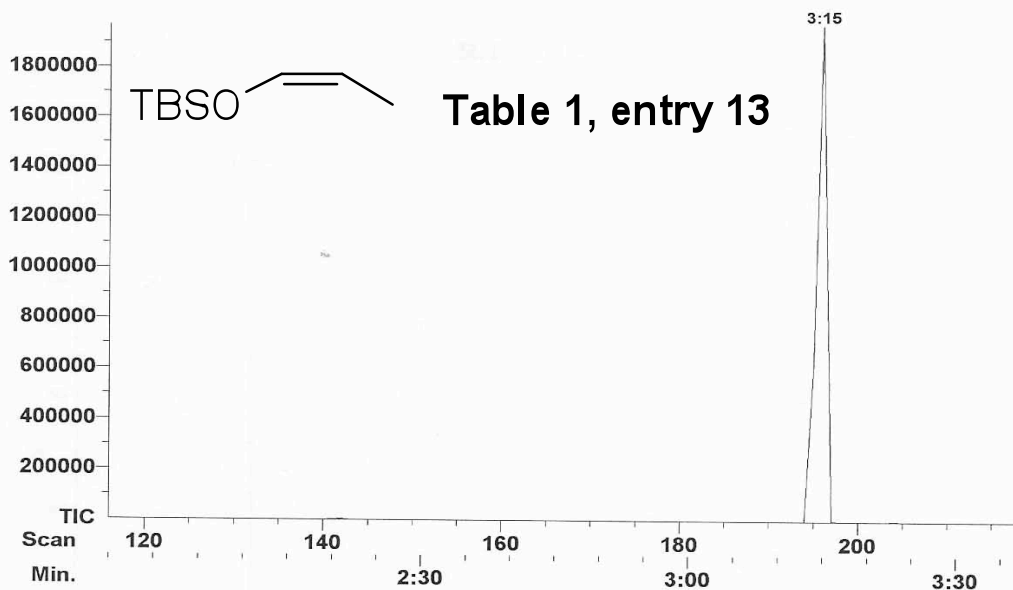
Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

Printed by: MS-600



Brown University
6/24/10

File: RQ6779

Date Run: 06-24-2010

Sample: chicheung su/pgw, mw 156

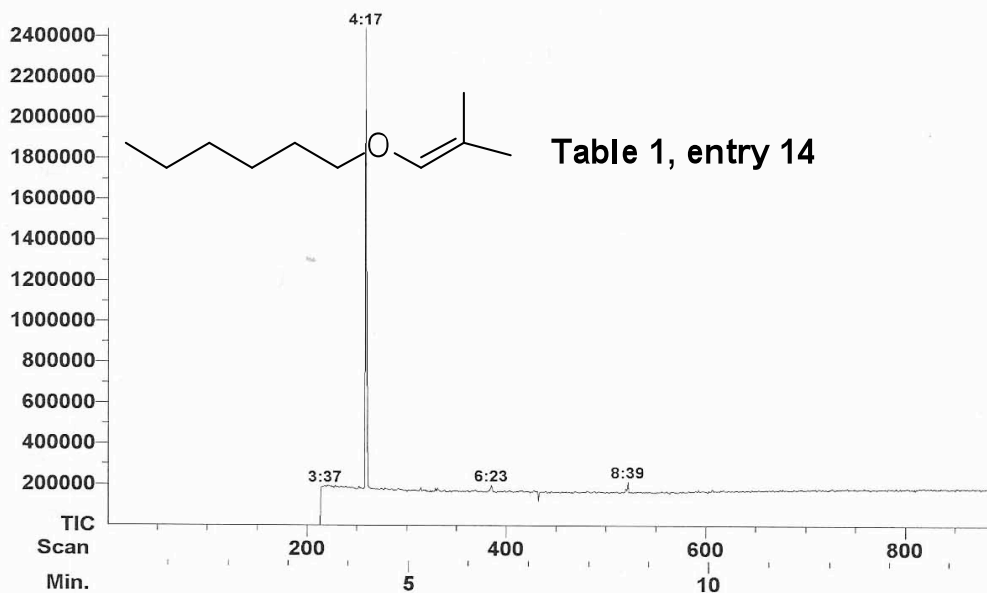
Instrument: JEOL JMS600

Inlet: GC

Ionization mode: EI+

Run By: MS-600

Printed by: MS-600



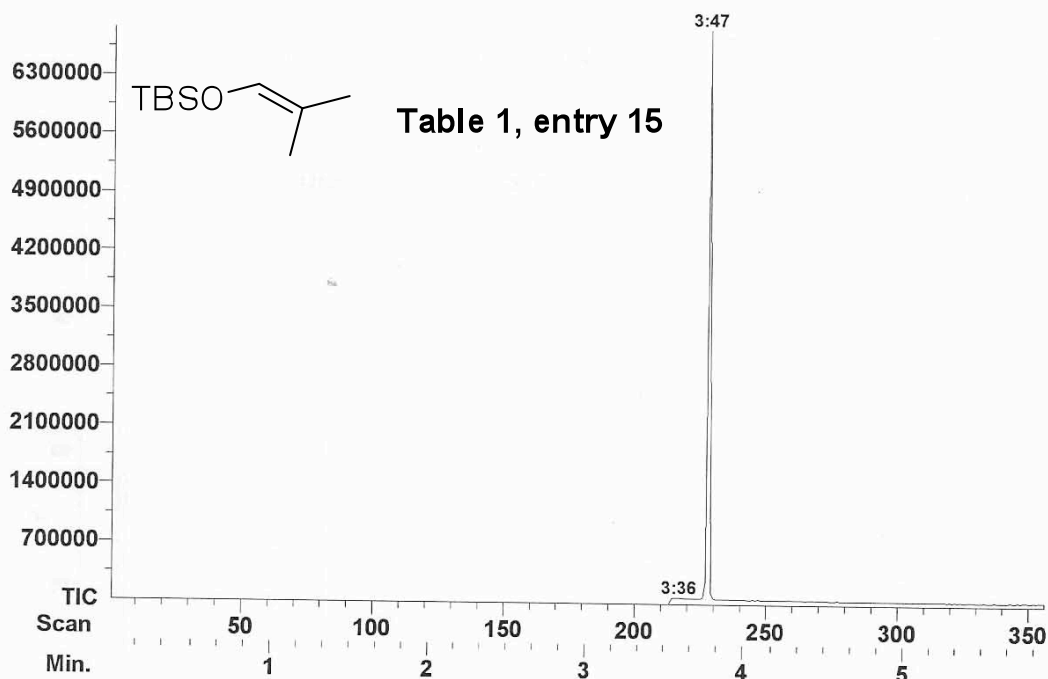
Brown University
8/18/10

File: RQ6978
Sample: cs/pgw, mw186.1
Instrument: JEOL JMS600
Inlet: GC

Date Run: 08-18-2010

Ionization mode: EI+

Run By: MS-600
Printed by: MS-600



References

1. Kofron, W. G.; Baclawski, L. M. *J. Org. Chem.* **1975**, *41*, 1879-1880.