

# Preparation of Functionalized Alkylmagnesium Derivatives Using an I/Mg-Exchange

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## Supporting Information

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### 1) General considerations

Unless otherwise indicated, all reactions were carried out with magnetic stirring and in flame-dried glassware under argon. Syringes used to transfer reagents and solvents were purged with argon prior to use. Reactions were monitored by gas chromatography (GC and GC-MS) or thin layer chromatography (TLC). TLC was performed with aluminium plates covered with SiO<sub>2</sub> (Merck 60, F-254) and visualized either by UV detection or submerging in KMnO<sub>4</sub> solution (1.5 g KMnO<sub>4</sub>, 10 g K<sub>2</sub>CO<sub>3</sub>, and 1.25 mL 10% NaOH solution in 200 mL H<sub>2</sub>O). Purification via column chromatography was performed using Merck silica gel 60 (40 – 63 µm 230-400 mesh ASTM from Merck). Melting points were measured using a Büchi B-540 apparatus and are uncorrected. NMR spectra were recorded in CDCl<sub>3</sub> or C<sub>6</sub>D<sub>6</sub> and chemical shifts (δ) are reported in parts per million (ppm). Mass spectra and high resolution mass spectra (HRMS) were recorded using electrospray ionization (ESI) except where otherwise noted.

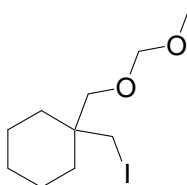
GCs were recorded on machines of the types *Hewlett-Packard* 6890 or 5890 Series II (*Hewlett Packard*, 5% phenylmethylpolysiloxane; length: 10 m, diameter: 0.25 mm; film thickness: 0.25  $\mu\text{m}$ ).

*i*PrMgCl·LiCl and *s*BuMgCl·LiCl solutions were obtained from Chemetall (Frankfurt, Germany) as 14% and 15% solutions (in THF), respectively, and titrated with iodine prior to use. A CuCN·2LiCl (1 M) solution was prepared by heating 1 equiv CuCN and 2 equiv LiCl under vacuum at 130 °C for 6 h. THF was added slowly and the solution was stirred overnight. Acid chlorides, liquid aldehydes were distilled under argon prior to use. Solid aldehydes were used without purification.

## 2) Experimental Procedures and Analytical Data

### Preparation of starting materials

#### 1-(Iodomethyl)-1-[(methoxymethoxy)methyl]cyclohexane (2a)



Ethyl 1-(iodomethyl)cyclohexanecarboxylate (**8a**) (2.96 g, 10.0 mmol) was dissolved in  $\text{CH}_2\text{Cl}_2$  (40 mL) and cooled to  $-78\text{ }^\circ\text{C}$ . *i*Bu<sub>2</sub>AlH (15 mL, 30 mmol, 2M in hexane) was added. After 3 h of stirring, methanol (10 mL) was added and the pH was adjusted to 7 using 1M HCl. The aqueous layer was extracted three times with ether. The organic phase was dried ( $\text{MgSO}_4$ ) and after filtration the solvent was removed under reduced pressure. After flash chromatographic purification (pentane/ $\text{CH}_2\text{Cl}_2$  5:1, silica gel) a colourless liquid (1.21 g, 85%) was obtained. [1-(Iodomethyl)cyclohexyl]methanol (2.59 g, 10.2 mmol) was dissolved in dimethoxymethane (3.04 g, 3.5 mL, 40.0 mmol) and stirred with Amberlyst-15<sup>®</sup> (0.2 g) at 25 °C for 18 h. The resin was filtered off and washed three times with ether (30 mL). The solvent was removed under reduced pressure and after flash chromatographic purification (silica gel, pentane/ ethyl acetate, 50:1,  $R_f$  = 0.27) a colourless liquid (2.09 g, 69%) was obtained.

<sup>1</sup>H-NMR ( $\text{CDCl}_3$ , 300 MHz):  $\delta$  (ppm) = 1.60–1.30 (m, 10 H), 3.34–3.36 (m, 7 H), 4.59 (s, 2 H).

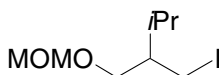
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 19.5 (CH<sub>2</sub>), 27.7 (CH<sub>2</sub>), 26.0 (CH<sub>2</sub>), 32.4 (CH<sub>2</sub>), 36.5, 55.3(CH<sub>3</sub>), 72.5 (CH<sub>2</sub>), 96.7 (CH<sub>2</sub>).

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2924 (s), 2882 (m), 2854 (m), 2822 (w), 1450 (w), 1226 (w), 1212 (w), 1182 (w), 1148 (m), 1126 (w), (m), 1070 (w), 1042 (vs), 996 (w), 976 (w), 960 (w), 918 (m).

**MS (EI, 70 eV):**  $m/z$  (%) = 298 (1), 139 (10), 125 (9), 109 (56), 97 (11), 75 (11), 67 (10), 45 (100).

**HRMS (EI):** calcd. for C<sub>10</sub>H<sub>19</sub><sup>127</sup>I O<sub>2</sub>: 298.0430, found: 298.0452.

#### 1-Iodo-2-[(methoxymethoxy)methyl]-3-methylbutane (2b)



2-(Bromomethyl)-3-methylbutanoic acid (14.6 g, 75.0 mmol) was dissolved in THF (70 mL) and cooled to -20 °C. Then, borane dimethyl sulfide (7.5 g, 9.5 mL, 100 mmol) in THF (70 mL) was added slowly. After addition the reaction mixture was stirred overnight at 25 °C. The reaction mixture was quenched at 0 °C with potassium carbonate (15 g, 108 mmol) in water (225 mL). The organic layer was separated, and the aqueous layer was extracted three times with ether (100 mL). The combined phases were dried (MgSO<sub>4</sub>) and after filtration the solvent was removed under reduced pressure. A colourless oil (11.0 g, 81%) was obtained and used without further purification.

*Rac*-2-(bromomethyl)-3-methylbutan-1-ol (10.9 g, 60.0 mmol) was stirred with Amberlyst15<sup>®</sup> (0.70 g) and dimethoxymethane (62 mL, 0.70 mol) for 48 h. The mixture was filtered and after removing of the solvent a colourless oil (12.2 g, 90%) was obtained and used without further purification. 1-Bromo-2-[(methoxymethoxy)methyl]-3-methylbutane (10.0 g, 44.4 mmol) was dissolved in acetone (150 mL) and heated at reflux for 2 h with sodium iodide (46.1 g, 0.15 mol). The mixture was diluted with water (100 mL) and extracted three times with ether (100 mL). The combined organic layers were dried (MgSO<sub>4</sub>) and after filtration the solvents were removed under reduced pressure. After flash chromatographic purification (pentane/ ethyl acetate, 30:1, silica gel, R<sub>f</sub> = 0.29) a pale yellow liquid (11.8 g, 98%, 71% over three steps) was obtained.

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  (ppm) = 0.93 (d,  $J$  = 6.7 Hz, 6 H), 1.21–1.32 (m, 1 H), 1.62–1.76 (m, 1 H), 3.28–3.49 (m, 3 H), 3.36 (s, 3 H), 3.62 (dd,  $J$  = 9.73 Hz,  $J$  = 4.45 Hz, 1 H), 4.60 (s, 2 H).

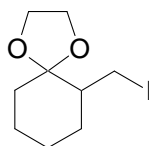
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 10.7 (CH<sub>2</sub>), 19.7 (CH<sub>3</sub>), 20.2 (CH<sub>3</sub>), 29.1 (CH), 46.1 (CH), 55.4 (CH<sub>3</sub>), 68.2 (CH<sub>2</sub>), 96.7 (CH<sub>2</sub>).

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2960 (m), 2928 (m), 2880 (m), 2824 (w), 2767 (w), 1464 (w), 1440 (w), 1424 (w), 1412 (w), 1388 (w), 1256 (w), 1196 (w), 1140 (m), 1108 (s), 1040 (s), 944 (w), 932 (w), 916 (m), 876 (w), 864 (w), 848 (w), 772 (w), 632 (w), 604 (w) 584 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 272 (8), 169 (8), 155 (10), 113 (56), 99 (33), 95 (23), 83 (99), 75 (100), 55 (54), 46 (13), 45 (33).

**HRMS (EI):** calcd. for C<sub>8</sub>H<sub>17</sub><sup>127</sup>IO<sub>3</sub>: 272.0273, found: 272.0256.

#### 6-(Iodomethyl)-1,4-dioxaspiro[4.5]decane (2c)



Triphenylphosphine (16.3 g, 62.0 mmol) was dissolved in toluene (60 mL) and imidazole (5.58 g, 82.0 mmol) was added. Iodine (20.8 g, 82 mmol) was added and the sluggish stirring mixture was heated at 90 °C for 15 min. Then CH<sub>2</sub>Cl<sub>2</sub> (60 mL) was added followed by 1,4-dioxaspiro[4.5]dec-6-ylmethanol<sup>1</sup> (7.05 g, 40.9 mmol) dissolved in a 1:1 mixture of toluene and CH<sub>2</sub>Cl<sub>2</sub> (60 mL). The mixture was heated at reflux using an oil bath heated at 90 °C for 2 h. After cooling to 25 °C, the mixture was extracted with a sat. aq. sodium thiosulfate solution (25 mL), washed with water (25 mL) and dried (MgSO<sub>4</sub>). After filtration, the solvents were removed under reduced pressure. The product was purified by a short filter column (silica gel, pentane/ethyl acetate 25:1, R<sub>f</sub> = 0.30) and a colourless light sensitive liquid (10.1 g, 87%) was obtained.

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  (ppm) = 1.16–1.72 (m, 7 H), 1.86–1.93 (m, 1 H), 2.07–2.13 (m, 1 H), 2.90 (dd,  $J$  = 10.76 Hz,  $J$  = 9.47 Hz, 1 H), 3.52 (dd,  $J$  = 9.54 Hz,  $J$  = 2.59 Hz, 1 H), 3.86–3.99 (m, 4 H).

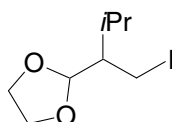
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 7.6 (CH<sub>2</sub>), 23.9 (CH<sub>2</sub>), 24.4 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 34.5 (CH<sub>2</sub>), 47.8 (CH), 64.8 (CH<sub>2</sub>), 110.3.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2932 (s), 2880 (m), 2856 (m), 1476 (w), 1444 (w), 1352 (w), 1320 (w), 1276 (w), 1240 (w), 1176 (m), 1156 (m), 1125 (m), 1084 (s), 1056 (s), 1012 (m), 960 (w), 948 (w), 924 (s), 860(m), 804 (w), 788 (w), 764 (w), 668 (w), 620 (w), 592 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 156 (35), 155 (100), 113 (28), 99 (24), 93 (9), 83 (9), 55 (23).

**HRMS (EI):** calcd. for C<sub>9</sub>H<sub>15</sub>O<sub>2</sub><sup>127</sup>I: 282.0117, found: 282.0131.

## 2-[1-(Iodomethyl)-2-methylpropyl]-1,3-dioxolane (2d)



2-[1-(Bromomethyl)-2-methylpropyl]-1,3-dioxolane<sup>2</sup> (2.58 g, 17.5 mmol) was dissolved in acetone (60 mL) and sodium iodide (8.99 g, 60.0 mmol) was added. The reaction mixture was heated at reflux for 1.5 h and after cooling to room temperature water (150 mL) was added. The water phase was extracted twice with ether (100 mL), and then the combined organic phases were extracted with a sat. aq. sodium thiosulfate solution (50 mL) and with brine (50 mL). The ether phase was dried (MgSO<sub>4</sub>) and after removal of the solids, the solvent was removed under reduced pressure. After flash chromatographic purification (silica gel, pentane/diethyl ether 20:1, R<sub>f</sub> = 0.27) a colorless liquid (3.85 g, 81%) was obtained.

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  (ppm) = 0.97 (d,  $J$  = 2.65 Hz, 3 H), 0.99 (d,  $J$  = 2.43 Hz, 3 H), 1.68–1.75 (m, 1 H), 1.98–2.07 (m, 1 H), 3.22–3.34 (m, 2 H), 3.80–3.97 (m, 4 H), 4.87 (d,  $J$  = 3.53 Hz, 1 H).

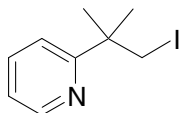
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 4.3 (CH<sub>2</sub>), 19.3 (CH<sub>3</sub>), 20.4 (CH<sub>3</sub>), 28.7 (CH), 48.8 (CH), 64.7 (CH<sub>3</sub>), 65.0 (CH<sub>3</sub>), 104.6 (CH).

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2960 (s), 2876 (s), 2764 (w), 2360 (w), 2340 (w), 1740 (w), 1464 (w), 1424 (w), 1388 (m), 1368 (w), 1296 (w), 1280 (w), 1264 (w), 1200 (w), 1176 (w), 1108 (s), 1032 (m), 1012 (m), 964 (m), 952 (m), 856 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 269 (8), 99 (18), 74 (23), 73 (24), 55 (18), 45 (100).

**HRMS (EI):** calcd. for  $C_8H_{15}O_2^{127}I$ : 270.0117, found: 270.0127.

**2-(2-Iodo-1,1-dimethylethyl)pyridine (2e)**



Triphenylphosphine (16.67 g, 75.0 mmol) was dissolved in toluene (100 mL), imidazole (7.49 g, 110 mmol) was added. Iodine (19.0 g, 75.0 mmol) was added and the sluggish stirring mixture was heated at 90 °C for 15 min. Then  $CH_2Cl_2$  (100 mL) was added, followed by 2-methyl-2-pyridin-2-ylpropan-1-ol<sup>3</sup> (7.40 g, 49.0 mmol) dissolved in a 1:1 mixture of toluene and  $CH_2Cl_2$  (100 mL). The reaction mixture was heated at reflux for 2 h at 90 °C. After cooling to 25 °C, the reaction mixture was extracted with a sat. aq. thiosulfate solution (25 mL), washed with water (25 mL) and dried ( $MgSO_4$ ). After filtration the solvents were removed under reduced pressure. The product was purified by a short filter column (silica gel, pentane/ethyl acetate 20:1,  $R_f$  = 0.29) and a colourless liquid (11.5 g, 90%) was obtained.

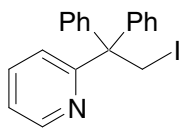
**$^1H$ -NMR ( $CDCl_3$ , 300 MHz):**  $\delta$  (ppm) = 1.50 (s, 6 H), 3.62 (s, 2 H), 7.10–7.15 (m, 1 H), 7.27–7.30 (m, 1 H), 7.59–7.65 (m, 1 H), 8.56–8.58 (m, 1 H).

**$^{13}C$ -NMR ( $CDCl_3$ , 75 MHz):**  $\delta$  (ppm) = 23.1( $CH_2$ ), 27.6 ( $CH_3$ ), 40.9, 119.7( $CH$ ), 121.4 ( $CH$ ), 136.2 ( $CH$ ), 149.0 ( $CH$ ), 164.8.

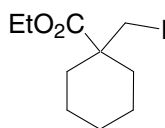
**IR (ATR):**  $\tilde{\nu}$  /  $cm^{-1}$  = 3088 (w), 3052 (w), 3000 (w), 2964 (s), 2928 (m), 2864 (w), 1588 (s), 1572 (m), 1472 (s), 1432 (s), 1380 (m), 1360 (m), 1300 (w), 1212 (m), 1156 (m), 1108 (w), 1092 (w), 1048 (w), 992 (w), 928 (w), 884 (w), 836 (w), 808 (w), 780 (s), 744 (s), 624 (w), 616 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 261 (2), 135 (10), 134 (100), 120 (7), 119 (12), 118 (18), 93 (12), 92 (8).

**HRMS (EI):** calcd. for  $C_9H_{12}N_1^{127}I_1$ : 261.0014, found: 261.0025.

**2-(2-Iodo-1,1-diphenylethyl)pyridine (2f)**

2-(2-Iodo-1,1-diphenylethyl)pyridine was prepared according to the literature.<sup>3</sup>

**Ethyl 1-(iodomethyl)cyclohexane carboxylate (8a)**

Diisopropylamine (6.20 mL, 44.0 mmol) was dissolved in 30 mL THF, cooled to  $-30\text{ }^{\circ}\text{C}$ . *n*BuLi (17.7 mL, 44.0 mmol) was added slowly. After warming up to  $0\text{ }^{\circ}\text{C}$  the reaction mixture was cooled to  $-78\text{ }^{\circ}\text{C}$  and ethyl cyclohexanecarboxylate was added dropwise. After 1 h at  $-78\text{ }^{\circ}\text{C}$   $\text{CH}_2\text{I}_2$  (5.20 mL, 65.0 mmol) was added. The reaction mixture was warmed up to  $25\text{ }^{\circ}\text{C}$  overnight and then poured in 100 mL sat. aq.  $\text{NH}_4\text{Cl}$ -solution and extracted three times with ether. The organic phase was dried ( $\text{MgSO}_4$ ). After filtration, the solvent was removed under reduced pressure and the crude product was purified by fractionated distillation (bp.  $75\text{ }^{\circ}\text{C}$ , 0.5 mbar). A colourless liquid (9.27 g, 68%) was obtained.

**$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  = 1.27 (t,  $J$  = 7.03, 3 H), 1.58–1.33 (m, 8H), 3.31 (s, 2 H), 2.13–2.07 (m, 2 H), 4.17 (q,  $J$  = 7.13 Hz, 2 H).

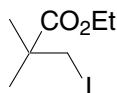
**$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz):**  $\delta$  = 14.3 ( $\text{CH}_3$ ), 15.8 ( $\text{CH}_2$ ), 22.9( $\text{CH}_2$ ), 25.6 ( $\text{CH}_2$ ), 34.2 ( $\text{CH}_2$ ), 47.1, 60.8( $\text{CH}_2$ ), 173.8.

**IR (ATR):**  $\tilde{\nu}$  /  $\text{cm}^{-1}$  = 2980 (w), 2932 (s), 2856 (m), 1724 (s), 1448 (m), 1368 (w), 1316 (w), 1280 (w), 1236 (w), 1212 (s), 1168 (m), 1136 (m), 1116 (w), 1096 (w), 1024 (w), 964 (w), 932 (w), 912 (w), 852 (w), 608 (w).

**MS (EI, 70 eV),  $m/z$  (%):** 296 (8), 223 (14), 169 (85), 141 (9), 123 (46), 96 (16), 95 (100), 81 (27), 67 (19), 55 (16).

**HRMS (EI):** calcd. for  $C_{16}H_{17}O_2^{127}I$ : 296.0273, found: 296.0288.

**Ethyl 3-iodo-2,2-dimethylpropanoate (8b)**



Diisopropylamine (15.4 mL, 0.11 mol) was dissolved in 100 mL THF, cooled to  $-30\text{ }^{\circ}\text{C}$ . *n*-BuLi (44.0 mL, 0.11 mol) was added slowly. After warming up to  $0\text{ }^{\circ}\text{C}$  the reaction mixture was cooled to  $-78\text{ }^{\circ}\text{C}$  and methyl 2-methylpropanoate (13.6 mL, 100 mmol) was added dropwise. After 1 h stirring at  $-78\text{ }^{\circ}\text{C}$   $\text{CH}_2\text{I}_2$  (5.20 mL, 65.0 mmol) was added. The reaction mixture warmed up to  $25\text{ }^{\circ}\text{C}$  overnight and was then poured in 100 mL sat. aq.  $\text{NH}_4\text{Cl}$ -solution and extracted three times with ether. The organic phase was dried ( $\text{MgSO}_4$ ). After filtration the solvent was removed under reduced pressure and the crude product was purified by fractionated distillation (bp.  $75\text{ }^{\circ}\text{C}$ , 3 mbar). A slightly yellow liquid (17.7 g, 66%) was obtained.

**$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  = 1.27 (t,  $J$  = 7.03 Hz, 3 H), 1.32 (s, 6 H), 3.34 (s, 2 H), 4.16 (q,  $J$  = 7.3 Hz, 2 H).

**$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 75 MHz):**  $\delta$  = 14.2 ( $\text{CH}_3$ ), 16.5 ( $\text{CH}_2$ ), 25.4 ( $\text{CH}_3$ ), 43.2, 61.1 ( $\text{CH}_2$ ), 174.4.

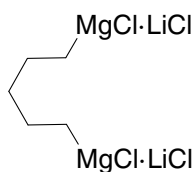
**IR (ATR):**  $\tilde{\nu}$  /  $\text{cm}^{-1}$  = 2980 (m), 2936 (w), 2904 (w), 2872 (w), 1728 (s), 1472 (w), 1444 (w), 1384 (w), 1364 (w), 1296 (m), 1232 (w), 1204 (w), 1176 (s), 1160 (m), 1132 (m), 1084 (w), 1024 (w), 960 (w), 940 (w), 912 (w), 864 (w), 804 (w), 760 (w), 620 (w).

**MS (EI, 70 eV),  $m/z$  (%):** 256 (21), 211 (5), 184 (2), 183 (62), 155 (2), 130 (6), 129 (100), 101 (2), 101 (9), 87 (8), 83 (5), 73 (49), 59 (9), 57 (12), 56 (17), 55 (54), 45 (6), 43 (12).

**HRMS (EI):** calcd. for  $\text{C}_7\text{H}_{13}\text{O}_2^{127}\text{I}$ : 255.9960, found: 255.9972.



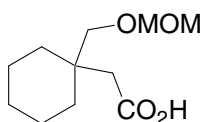
### Pentyl-1,5-dimagnesium chloride (5)



LiCl (0.17 mol, 7.21 g) was dried in high vacuum at 140 °C for 1 h. Then, magnesium (0.225 mol, 5.47 g) and dry THF (45 mL) was added. 1,5-Dichloropentane (75.0 mmol, 10.6 g, 9.8 mL) in THF (30 mL) was added dropwise. After complete addition the reaction mixture was heated at reflux for 2 h. The solution was separated from the solids via cannulation. The volume was determined as 75 mL. Titration with iodine gave a concentration of 0.668 mmol/mL. The GC-analysis showed that 92% of the reactive species was the desired pentyl-1,5-dimagnesium chloride, and 8% were elimination and reduction products.

### Preparation of products

#### {1-[(Methoxymethoxy)methyl]cyclohexyl}acetic acid (4a)



The alkyl iodide **2a** (295 mg, 1.0 mmol) was dissolved in THF (1 mL) and cooled to 0 °C, *i*Pr<sub>2</sub>Mg·LiCl (0.75 mmol, 0.93 mL, 0.81 M in THF) was added and the reaction mixture was warmed to 25 °C. After stirring for 5 h the reaction mixture was cooled to –20 °C and carbon dioxide was bubbled through the solution for 10 min. Ethyl acetate (20 mL) was added and the reaction mixture was extracted twice with a sat. aq. sodium carbonate solution (5mL). The combined aqueous layers were neutralised using 2M HCl and extracted three times with ethyl acetate (15 mL). The solvent was removed under reduced pressure and the product was dried 5 h in high vacuum. A colourless oil (136 mg, 63%) was obtained.

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz):**  $\delta$  (ppm) = 1.39–1.47 (m, 10 H), 2.43 (s, 2 H), 3.35 (s, 3 H), 3.48 (s, 2 H), 4.62 (s, 2 H).

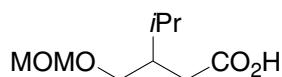
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz):**  $\delta$  (ppm) = 21.4 (CH<sub>2</sub>), 26.6 (CH<sub>2</sub>), 33.0 (CH<sub>2</sub>), 37.0, 40.3 (CH<sub>2</sub>), 55.2 (CH<sub>3</sub>), 73.1 (CH<sub>2</sub>), 96.7 (CH<sub>2</sub>), 177.9.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2926 (vs), 2856 (m), 2826 (w), 1730 (m), 1702 (vs), 1452 (w), 1212 (m), 1148 (m), 1108 (s), 1038 (vs), 918 (m), 900 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 171 (47), 156 (19), 155 (15), 154 (24), 153 (98), 126 (41), 123 (15), 122 (11), 97 (13), 96 (24), 95 (56), 94 (22), 92 (15), 80 (79), 79 (26).

**HRMS (EI):** calcd. for C<sub>11</sub>H<sub>20</sub>O<sub>4</sub> [M-H]<sup>+</sup>: 215.1283, found: 215.1298.

### 3-[(Methoxymethoxy)methyl]-4-methylpentanoic acid (4b)



The alkyl iodide **2b** (272 mg, 1.0 mmol) was dissolved in THF (1 mL) and cooled to 0 °C, *i*Pr<sub>2</sub>Mg·LiCl (1.10 mmol, 1.36 mL, 0.81 M in THF) was added and the reaction mixture was warmed to 25 °C. After 45 min, the reaction mixture was cooled to –20 °C and carbon dioxide was bubbled through the solution for 10 min. Ethyl acetate (20 mL) was added and the reaction mixture was extracted twice with a sat. aq. sodium carbonate solution (10 mL). The combined aqueous layers were neutralised using 2M HCl and extracted three times with ethyl acetate (15mL). The solvent was removed under reduced pressure and the product was dried 5 h in high vacuum. A yellow oil (139 mg, 73%) was obtained.

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  (ppm) = 0.90 (d,  $J$  = 3.09 Hz, 3 H), 0.92 (d,  $J$  = 3.09 Hz, 3 H), 1.75–1.78 (m, 1 H), 1.99–2.10 (m, 1 H), 2.38 (d,  $J$  = 7.06 Hz, 2 H), 3.35 (s, 3 H), 3.45 (dd,  $J$  = 9.70 Hz,  $J$  = 7.06 Hz, 1 H), 3.54–3.59 (m, 1 H), 4.59 (s, 2 H).

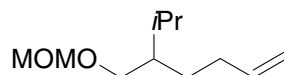
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 19.4 (CH<sub>3</sub>), 19.7 (CH<sub>3</sub>), 28.7 (CH), 34.1 (CH<sub>2</sub>), 41.2 (CH), 55.3 (CH<sub>3</sub>), 68.6 (CH<sub>2</sub>), 96.5 (CH<sub>2</sub>), 179.2.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2960 (s), 2932 (s), 2880 (m), 2828 (w), 2772 (w), 1704 (s), 1468 (w), 1440 (w), 1412 (w), 1388 (w), 1280 (w), 1216 (w), 1148 (m), 1108 (s), 1036 (s), 944 (w), 916 (m).

**MS (EI, 70 eV):**  $m/z$  (%) = 145 (24), 129 (30), 128 (24), 127 (100), 100 (50), 85 (20), 83 (16), 70 (17), 69 (61), 45 (46).

**HRMS (ESI):** calcd. for  $C_9H_{19}O_4[M+H]^+$ : 191.1283, found: 191.1281.

**5-[(Methoxymethoxy)methyl]-6-methylhept-1-ene (4c)**



The alkyl iodide **2b** (0.41 g, 1.50 mmol) was dissolved in THF (1.5 mL) and cooled to 0 °C,  $ClMg(CH_2)_5MgCl \cdot 2LiCl$  (1.65 mmol, 2.68 mL, 0.62 M in THF) was added and the temperature was raised to 25 °C. After 2 h the reaction mixture was cooled to -30 °C and  $CuCN \cdot 2LiCl$  (0.05 mL, 1M in THF) and allyl bromide (0.363 g, 0.26 mL, 3.0 mmol) was added. The reaction mixture was stirred for additional 30 min, then the temperature was raised to 25 °C and the reaction mixture was quenched with a sat. aq.  $NH_4Cl$ -solution (10 mL). The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried ( $MgSO_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/ethyl acetate 40:1,  $R_f$  = 0.28) afforded a colourless liquid (198 mg, 71%).

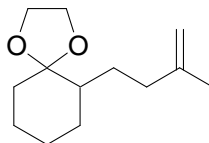
**$^1H$ -NMR ( $CDCl_3$ , 300 MHz):**  $\delta$  (ppm) = 0.88 (d,  $J$  = 7.06 Hz, 6 H), 1.31–1.47 (m, 3 H), 1.76–1.87 (m, 1 H), 1.99–2.16 (m, 2 H), 3.35 (s, 3 H), 3.40–3.50 (m, 2 H), 4.59 (s, 2 H), 4.91–5.03 (m, 2 H), 5.73–5.83 (m, 1 H).

**$^{13}C$ -NMR ( $CDCl_3$ , 75 MHz):**  $\delta$  (ppm) = 19.2 ( $CH_3$ ), 19.6 ( $CH_3$ ), 27.6 ( $CH_2$ ), 28.2 (CH), 32.0 ( $CH_2$ ), 43.6 (CH), 55.2 ( $CH_3$ ), 68.7 ( $CH_2$ ), 96.6 ( $CH_2$ ), 114.3 ( $CH_2$ ), 139.1 (CH).

**IR (ATR):**  $\tilde{\nu}$  /  $cm^{-1}$  = 3076 (w), 2956 (s), 2928 (s), 2876 (s), 2768 (w), 1640 (w), 1463 (w), 1440 (w), 1388 (w), 1368 (w), 1216 (w), 1152 (m), 1108 (m), 1044 (s), 996 (w), 912 (m), 644 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 124 (4), 123 (10), 81 (12), 69 (34), 67 (11), 55 (19), 45 (100).

**HRMS (EI):** calcd. for  $C_{11}H_{22}O_2$ : 186.1620, found: 186.1652

**6-(3-Methylbut-3-en-1-yl)-1,4-dioxaspiro[4.5]decane (4d)**

The alkyl iodide **2c** (564 mg, 2.0 mmol) was dissolved in THF (2 mL) and cooled to  $-15\text{ }^{\circ}\text{C}$ ,  $\text{ClMg}(\text{CH}_2)_5\text{MgCl}\cdot 2\text{LiCl}$  (2.2 mmol, 2.8 mL, 0.79 M in THF) was added. After 3 h, the reaction mixture was cooled to  $-30\text{ }^{\circ}\text{C}$  and  $\text{CuCN}\cdot 2\text{LiCl}$  (0.1 mL, 1M in THF) and 3-bromo-2-methylprop-1-ene (324 mg, 0.25 mL, 2.4 mmol) was added. The reaction mixture was stirred for additional 30 min, then the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution (10 mL). The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ) and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/ethyl acetate 20:1,  $R_f = 0.25$ ) afforded a colourless liquid (302 mg, 72%).

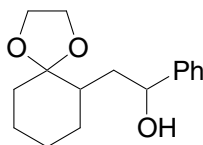
**$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  (ppm) = 1.16–1.36 (m, 4 H), 1.44–1.54 (m, 2 H), 1.58–1.62 (m, 2 H), 1.70 (s, 3 H), 1.72–1.81 (m, 3 H), 1.90–1.95 (m, 1 H), 2.04–2.09 (m, 1 H), 3.89–3.97 (m, 4 H), 4.66–4.67 (m, 2 H).

**$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz):**  $\delta$  (ppm) = 22.4 ( $\text{CH}_3$ ), 23.9 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_2$ ), 26.1 ( $\text{CH}_2$ ), 29.0 ( $\text{CH}_2$ ), 34.7 ( $\text{CH}_2$ ), 35.6 ( $\text{CH}_2$ ), 44.1 (CH), 64.7 ( $\text{CH}_2$ ), 64.8 ( $\text{CH}_2$ ), 109.6 ( $\text{CH}_2$ ), 110.9, 146.4.

**IR (ATR):**  $\tilde{\nu}$  /  $\text{cm}^{-1}$  = 3072 (w), 2932 (s), 2876 (m), 2864 (m), 1648 (w), 1448 (m), 1372 (w), 1352 (w), 1280 (w), 1188 (w), 1156 (m), 1140 (w), 1088 (s), 1060 (m), 1028 (w), 948 (w), 924 (m), 884 (m), 800 (w), 768 (w), 664 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 210 (30), 156 (8), 142 (6), 125 (12), 113 (21), 99 (100), 86 (10), 55 (16), 41 (10).

**HRMS (EI):** calcd. for  $\text{C}_{13}\text{H}_{22}\text{O}_3$ : 210.1620, found: 210.1633.

**2-(1,4-Dioxaspiro[4.5]dec-6-yl)-1-phenylethanol (4e)**

The alkyl iodide **2c** (564 mg, 2.0 mmol) was dissolved in THF (2 mL) and cooled to  $-15\text{ }^{\circ}\text{C}$ ,  $\text{ClMg}(\text{CH}_2)_5\text{MgCl}\cdot 2\text{LiCl}$  (2.2 mmol, 3.3 mL, 0.79 M in THF) was added. After 3 h the reaction mixture was cooled to  $-30\text{ }^{\circ}\text{C}$  and benzaldehyde (318 mg, 0.30 mL, 3.0 mmol) was added. The reaction mixture was stirred for additional 60 min, then the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution. The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/ethyl acetate 3:1,  $R_f = 0.32$ ) afforded a colourless liquid (378 mg, 72%). The diastereomeric ratio was determined by  $^1\text{H-NMR}$  (3:1). NMR-Data is given for the main diastereomer.

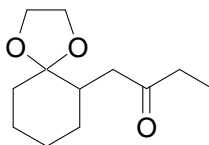
**$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  (ppm) = 1.14–2.14 (m, 11 H), 3.05 (s, 1 H), 3.96–4.05 (m, 4 H), 4.83–4.87 (m, 1 H), 7.24–7.37 (m, 5 H).

**$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz):**  $\delta$  (ppm) = 23.6 ( $\text{CH}_2$ ), 24.6 ( $\text{CH}_2$ ), 31.1 ( $\text{CH}_2$ ), 34.1, 38.5 ( $\text{CH}_2$ ), 40.4 ( $\text{CH}_2$ ), 42.3 (CH), 64.3 ( $\text{CH}_2$ ), 64.6 ( $\text{CH}_2$ ), 72.4 (CH), 110.7, 125.8 (CH), 127.1 (CH), 129.3 (CH), 144.9.

**IR (ATR):**  $\tilde{\nu}$  /  $\text{cm}^{-1}$  = 3420 (w), 3060 (w), 3028 (w), 2932 (s), 2884 (m), 2860 (m), 1492 (w), 1448 (w), 1352 (w), 1336 (w), 1284 (w), 1156 (w), 1088 (s), 1056 (m), 1016 (w), 924 (m), 888 (s), 864 (w), 800 (w), 756 (m), 700 (s).

**MS (EI, 70 eV):**  $m/z$  (%) = 262 (15), 200 (11), 156 (18), 155 (100), 133 (13), 120 (23), 113 (19), 105 (15), 99 (64), 77 (8).

**HRMS (EI):** calcd. for  $\text{C}_{16}\text{H}_{22}\text{O}_3$ : 262.1567, found: 262.1567.

**1-(1,4-Dioxaspiro[4.5]dec-6-yl)butan-2-one (4f)**

The alkyl iodide **2c** (0.564 g, 2.0 mmol) was dissolved in THF (2 mL) and cooled to  $-15\text{ }^{\circ}\text{C}$ ,  $\text{ClMg}(\text{CH}_2)_5\text{MgCl}\cdot 2\text{LiCl}$  (2.2 mmol, 2.8 mL, 0.79 M in THF) was added. After 3 h the reaction mixture was cooled to  $-30\text{ }^{\circ}\text{C}$  and  $\text{CuCN}\cdot 2\text{LiCl}$  (2.5 mL, 2.5 mmol) was added. After stirring for 30 min at  $-30\text{ }^{\circ}\text{C}$  propanoyl chloride (231 mg, 0.22 mL, 2.50 mmol) was added and the reaction mixture was stirred for additional 30 min. The temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution. The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 3:1,  $R_f = 0.29$ ) afforded a colourless liquid (268 mg, 63%).

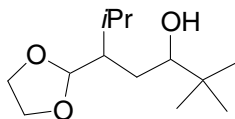
**$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  (ppm) = 1.02 (t,  $J = 7.28\text{ Hz}$ , 3 H), 1.27–1.37 (m, 3 H), 1.4 – 1.50 (m, 1 H), 1.55–1.56 (m, 2 H), 1.68–1.78 (m, 2 H), 2.14 (dd,  $J = 16.10\text{ Hz}$ ,  $J = 7.94\text{ Hz}$ , 1 H), 2.24–2.29 (m, 1 H), 2.37–2.42 (m, 2 H), 2.60 (dd,  $J = 15.88\text{ Hz}$ ,  $J = 5.29\text{ Hz}$ ), 3.63–3.95 (m, 4 H).

**$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz):**  $\delta$  (ppm) = 7.9 ( $\text{CH}_3$ ), 23.8 ( $\text{CH}_2$ ), 24.5 ( $\text{CH}_2$ ), 30.2 ( $\text{CH}_2$ ), 34.2 ( $\text{CH}_2$ ), 36.1 ( $\text{CH}_2$ ), 40.6 (CH), 42.4 ( $\text{CH}_2$ ), 64.4 ( $\text{CH}_2$ ), 64.5 ( $\text{CH}_2$ ), 110.0, 211.1.

**IR (ATR):**  $\tilde{\nu} / \text{cm}^{-1} = 2972$  (m), 2936 (s), 2884 (m), 2860 (m), 1708 (s), 1460 (w), 1448 (w), 1376 (w), 1352 (w), 1276 (w), 1256 (w), 1220 (w), 1156 (m), 1108 (m), 1092 (s), 1064 (w), 1032 (m), 948 (w), 924 (s), 876 (w), 800 (w), 768 (w), 628 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 212 (10), 183 (6), 156 (10), 155 (84), 141 (12), 113 (26), 100 (12), 99 (100), 86 (15), 57 (19), 55 (46).

**HRMS (EI):** calcd. for  $\text{C}_{12}\text{H}_{21}\text{O}_3[\text{M}+\text{H}]^+$ : 213.1491, found: 213.1477.

**4-(1,3-Dioxolan-2-yl)-2,2,5-trimethylhexan-3-ol (4g)**

The alkyl iodide **2d** (540 mg, 2.0 mmol) was dissolved in THF (2 mL) and cooled to  $-20\text{ }^{\circ}\text{C}$ ,  $\text{ClMg}(\text{CH}_2)_5\text{MgCl}\cdot 2\text{LiCl}$  (2.2 mmol, 3.3 mL, 0.67 M in THF) was added. After 3 h *t*BuCHO (215 mg, 0.27 mL, 2.5 mmol) was added. After 30 min of stirring at  $-20\text{ }^{\circ}\text{C}$  the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was stirred for additional 30 min. Then, the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution. The aqueous phase was extracted three times with ethyl acetate (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 20:1,  $R_f = 0.36$ ) afforded a colourless liquid (333 mg, 72%). The diastereomeric ratio was determined by  $^1\text{H}$ -NMR (4:1). NMR data is given for the main diastereomer.

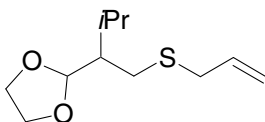
**$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):**  $\delta$  (ppm) = 0.89–1.06 (m, 16 H), 1.45–1.52 (m, 1 H), 1.59–1.64 (m, 1 H), 1.70–1.77 (m, 1 H), 1.9–2.03 (m, 1 H), 3.17–3.43 (m, 5 H), 3.58 (m, 1H), 4.65 (d,  $J = 4.65\text{ Hz}$ , 1 H).

**$^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ , 100 MHz):**  $\delta$  (ppm) = 18.9 ( $\text{CH}_3$ ), 20.7 ( $\text{CH}_3$ ), 26.1 ( $\text{CH}_3$ ), 27.7 ( $\text{CH}_2$ ), 30.0 (CH), 35.5, 46.9 (CH), 64.5 ( $\text{CH}_2$ ), 64.3 ( $\text{CH}_2$ ), 80.4 (CH), 106.2 (CH).

**IR (ATR):**  $\tilde{\nu} / \text{cm}^{-1}$  = 3476 (m), 2956 (s), 2872 (m), 1480 (w), 1468 (w), 1388 (w), 1316 (w), 1244 (w), 1220 (w), 1156 (w), 1116 (m), 1080 (m), 1060 (m), 1008 (m), 948 (m), 812 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 174 (11), 173 (16), 144 (21), 130 (15), 129 (51), 111 (100), 101 (49), 83 (32), 74 (10), 73 (28), 69 (22), 57 (16), 45 (29).

**HRMS (EI):** calcd. for  $\text{C}_{13}\text{H}_{26}\text{O}_3$ : 230.1882, found: 230.1865.

**2-[1-[(Allylthio)methyl]-2-methylpropyl]-1,3-dioxolane (4h)**

The alkyl iodide **2d** (540 mg, 2.0 mmol) was dissolved in THF (2 mL) and cooled to  $-20\text{ }^{\circ}\text{C}$ ,  $\text{ClMg}(\text{CH}_2)_5\text{MgCl}\cdot 2\text{LiCl}$  (2.20 mmol, 3.31 mL, 0.66 M in THF) was added. After 2.5 h *S*-allyl benzenesulfonothioate<sup>4</sup> (563 mg, 2.50 mmol) was added. After 30 min of stirring at  $-20\text{ }^{\circ}\text{C}$  the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was stirred for additional 30 min. Then the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution (10 mL). The aqueous phase was extracted three times with ethyl acetate (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 20:1,  $R_f = 0.24$ ) afforded a yellow liquid (251 mg, 58%).

**$^1\text{H}$ -NMR ( $\text{C}_6\text{D}_6$ , 400 MHz):**  $\delta$  (ppm) = 1.01–1.04 (m, 6 H), 1.93–1.96 (m, 1 H), 2.22–2.27 (m, 1 H), 2.58 (dd,  $J = 12.91\text{ Hz}$ ,  $J = 7.43\text{ Hz}$ , 1 H), 2.82 (dd,  $J = 13.01\text{ Hz}$ ,  $J = 5.38\text{ Hz}$ , 1 H), 2.93–2.98 (m, 2 H), 3.28–3.20 (m, 2 H), 3.45–3.48 (m, 2 H), 4.90–5.02 (m, 3 H), 5.70–5.78 (m, 1 H).

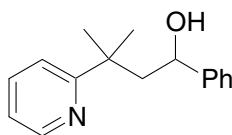
**$^{13}\text{C}$ -NMR ( $\text{C}_6\text{D}_6$ , 100 MHz):**  $\delta$  (ppm) = 20.0 ( $\text{CH}_3$ ), 20.6 ( $\text{CH}_3$ ), 27.8 (CH), 28.5 ( $\text{CH}_2$ ), 35.8 ( $\text{CH}_2$ ), 47.6 (CH), 64.5 ( $\text{CH}_2$ ), 64.9 ( $\text{CH}_2$ ), 104.9 (CH), 116.5 ( $\text{CH}_2$ ), 135.2 (CH).

**IR (ATR):**  $\tilde{\nu} / \text{cm}^{-1} = 3080$  (w), 2956 (s), 2876 (s), 1636 (w), 1468 (w), 1424 (w), 1400 (w), 1368 (w), 1300 (w), 1228 (w), 1176 (w), 1144 (m), 1108 (s), 1048 (m), 1020 (m), 988 (w), 944 (m), 916 (s), 760 (w), 744 (w), 592 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 175 (10), 154 (9), 143 (4), 111 (5), 99 (25), 85 (5), 73 (100), 55 (9).

**HRMS (EI):** calcd. for  $\text{C}_{11}\text{H}_{20}\text{O}_2^{32}\text{S}$ : 216.1184, found: 216.1182.

### 3-Methyl-1-phenyl-3-pyridin-2-ylbutan-1-ol (**4i**)



The alkyl iodide **2e** (0.522 g, 2.0 mmol) was dissolved in THF (1.5 mL) and cooled to  $0\text{ }^{\circ}\text{C}$ ,  $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}$  (1.40 mmol, 2.13 mL, 0.66 M in THF) was added and the reaction mixture was warmed to  $25\text{ }^{\circ}\text{C}$ . After 1.5 h of stirring the reaction mixture was cooled to  $-20\text{ }^{\circ}\text{C}$  and benzaldehyde (0.32 g, 0.31 mL, 3.0 mmol) was added. After 30 min at  $-20\text{ }^{\circ}\text{C}$  the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the



reaction was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution (10 mL). The aqueous phase was extracted three times with ethyl acetate (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ) and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/ethyl acetate 15:2,  $R_f = 0.27$ ) afforded a pale yellow liquid (270 mg, 56%).

**$^1\text{H}$ -NMR ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  (ppm) = 1.46 (s, 3 H), 1.55 (s, 3 H), 1.88 (dd,  $J = 15.00$  Hz,  $J = 2.21$  Hz, 1 H), 2.42 (dd,  $J = 15.00$  Hz,  $J = 2.21$  Hz, 1 H), 4.94 (dd,  $J = 10.14$  Hz,  $J = 2.21$  Hz, 1 H), 6.91 (s, 1 H), 7.18–7.45 (m, 6 H), 7.70–7.76 (m, 1 H), 8.56–8.59 (m, 1 H).

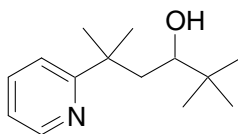
**$^{13}\text{C}$ -NMR ( $\text{CDCl}_3$ , 75 MHz):**  $\delta$  (ppm) = 28.3 ( $\text{CH}_3$ ), 31.5 ( $\text{CH}_3$ ), 41.3, 52.0 ( $\text{CH}_2$ ), 71.2 (CH), 120.6 (CH), 121.3 (CH), 125.8 (CH), 126.7 (CH), 128.2 (CH), 137.3(CH), 146.9, 147.5 (CH), 168.1.

**IR (ATR):**  $\tilde{\nu}$  /  $\text{cm}^{-1}$  = 3360 (m), 3088 (w), 3060 (w), 3028 (w), 2964 (s), 2928 (m), 2908 (m), 2684 (w), 1592 (s), 1572 (m), 1476 (s), 1432 (s), 1388 (w), 1364 (w), 1292 (w), 1200 (w), 1156 (w), 1120 (w), 1064 (m), 1052 (m), 1024 (w), 1004 (w), 912 (w), 788 (m), 748 (m), 727 (m), 700 (s), 636 (w), 564 (w).

**MS (EI, 70 eV):**  $m/z$  (%) = 240 (12), 208 (8), 135 (41), 134 (43), 122 (10), 121 (100), 120 (95), 106 (19), 93 (27), 79 (14), 77 (14).

**HRMS (EI):** calcd. for  $\text{C}_{16}\text{H}_{18}\text{N}_1\text{O}_1$   $[\text{M}-\text{H}]^+$ : 240.1388, found: 240.1392.

#### 2,2,5-Trimethyl-5-pyridin-2-ylhexan-3-ol (4j)



The alkyl iodide **2e** (522 mg, 2.0 mmol) was dissolved in THF (1.5 mL) and cooled to 0 °C,  $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}$  (1.40 mmol, 2.13 mL, 0.66 M in THF) was added and the reaction mixture was warmed to 25 °C. After 1.5 h of stirring the mixture was cooled to –20 °C and pivaldehyde (0.26 g, 0.33 mL, 3.0 mmol) was added. After stirring 30 min at –20 °C the temperature was raised to 25 °C and the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution (10 mL). The aqueous phase was extracted three times with ethyl acetate (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ),

and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/ethyl acetate 15:2,  $R_f$  = 0.33) afforded a slightly yellowish liquid (275 mg, 61%).

**$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):**  $\delta$  (ppm) = 0.89 (s, 9 H), 1.37 (d,  $J$  = 7.5 Hz, 6 H) 1.71–1.73 (m, 1 H) 1.99–2.07 (m, 1 H) 3.32–3.35 (m, 1 H), 5.36 (s, 1 H), 7.08–7.12 (m, 1 H), 7.35–7.39 (m, 1 H), 7.61–7.67 (m, 1 H), 8.45–8.49 (m, 1 H).

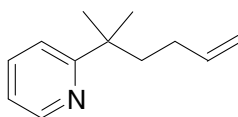
**$^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , 75 MHz):** 25.8 (3  $\text{CH}_3$ ), 27.8 (CH), 32.3 (CH), 35.0, 40.8 (2  $\text{CH}_2$ ), 44.0, 75.8 (CH), 120.8 (CH), 121.1 (CH), 137.0 (CH), 147.5 (CH), 168.5.

**IR (ATR):**  $\tilde{\nu}$  /  $\text{cm}^{-1}$  = 3224 (m), 3088 (w), 3060 (w), 3032 (w), 2952 (s), 2864 (m), 1592 (m), 1568 (w), 1492 (w), 1476 (w), 1428 (w), 1360 (w), 1244 (w), 1156 (w), 1096 (w), 1076 (w), 1036 (w), 1016 (w), 944 (w), 756 (w), 700 (m).

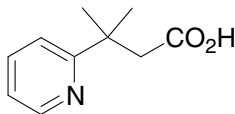
**MS (EI, 70 eV):**  $m/z$  (%) = 206 (5), 165 (10), 164 (100), 134 (22), 121 (66), 119 (96), 118 (6), 106 (8), 93 (7), 92 (7).

**HRMS (EI):** calcd. for  $\text{C}_{14}\text{H}_{22}\text{O}_1\text{N}_1$   $[\text{M-H}]^+$ : 220.1780, found: 220.1771.

#### 2-(1,1-dimethylpent-4-en-1-yl)pyridine (4k)



The alkyl iodide **2e** (522 mg, 2.0 mmol) was dissolved in THF and cooled to 0 °C,  $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}$  (1.4 mmol, 2.12 ml, 0.66 M in THF) was added. Then solution was warmed to 25 °C and stirred for 1 h. After cooling to –20 °C  $\text{CuCN}\cdot 2\text{LiCl}$  (0.1 mL, 1M in THF) was added followed by allyl bromide (363 mg, 3.00 mmol, 0.26 mL). After stirring for 30 min at –20 °C the temperature was raised to 25 °C and after additional 30 min of stirring the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution. The aqueous phase was extracted twice with ethyl acetate (30 mL), and two times with ether (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvents were removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 22:1,  $R_f$  = 0.30) afforded a colourless liquid (226 mg, 64%).<sup>5</sup>

**3-Methyl-3-pyridin-2-ylbutanoic acid (4l)**

The alkyl iodide **2e** (522 mg, 2.0 mmol) was dissolved in THF (1.5 mL) and cooled to 0 °C,  $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}$  (1.40 mmol, 2.13 mL, 0.66 M in THF) was added and the reaction mixture was warmed to 25 °C. After 1.5 h of stirring the reaction mixture was cooled to –20 °C and carbon dioxide was bubbled through the solution for 10 min. Ethyl acetate (20 mL) was added and the reaction mixture was extracted twice with 2 M NaOH (10 mL). The combined aqueous layers were neutralised using 2M aq. HCl and extracted three times with ethyl acetate (20 mL). The solvent was removed under reduced pressure and the product was dried 5 h in high vacuum. A yellow solid (268 mg, 75%) was obtained.

**mp** (°C): 68–69.

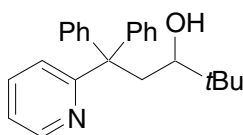
**$^1\text{H}$ -NMR (DMSO- $d_6$ , 400 MHz):**  $\delta$  (ppm) = 1.36 (s, 6 H), 2.69 (s, 2 H), 7.16 (dd,  $J$  = 7.41 Hz,  $J$  = 4.79 Hz, 1 H), 7.40 (d,  $J$  = 8.61 Hz, 1 H), 7.64–7.71 (m, 1 H), 8.47–8.48 (m, 1 H), 11.90 (s, 1 H).

**$^{13}\text{C}$ -NMR (DMSO- $d_6$ , 75 MHz):**  $\delta$  (ppm) = 28.0 ( $\text{CH}_3$ ), 39.1, 45.8 ( $\text{CH}_2$ ), 119.5 (CH), 120.9 (CH), 136.4 (CH), 148.0 (CH), 166.7, 172.6.

**IR (ATR):**  $\tilde{\nu}$  /  $\text{cm}^{-1}$  = 3084 (w), 2972 (m), 2935 (w), 2880 (w), 2472 (m), 1956 (m), 1708 (s), 1600 (s), 1572 (m), 1480 (m), 1436 (m), 1368 (m), 1344 (m), 1304 (m), 1228 (s), 1212 (m), 1168 (s), 1144 (s), 1096 (w), 1048 (w), 1008 (s), 936 (w), 892 (w), 168 (w), 792 (s), 760 (s), 696 (w), 636 (m).

**MS (EI, 70 eV):**  $m/z$  (%) = 179 (4), 146 (19), 135 (12), 134 (100), 129 (11), 120 (33), 41 (4).

**HRMS (EI):** calcd. for  $\text{C}_{10}\text{H}_{13}\text{NO}_2$ : 179.0946, found: 179.0936.

**4,4-Dimethyl-1,1-diphenyl-1-pyridin-2-ylpentan-3-ol (4m)**

The alkyl iodide **2f** (578 mg, 1.5 mmol) was dissolved in THF (1.5 mL) and cooled to 0 °C, *i*Pr<sub>2</sub>Mg·LiCl (0.9 mmol, 2.01 mL, 0.45 M in THF) was added and the reaction mixture was warmed to 25 °C. After 2.5 h of stirring the reaction mixture was cooled to –20 °C and pivaldehyde (194 mg, 0.24 mL, 2.25 mmol) was added. After additional 30 min of stirring at –20 °C the temperature was raised to 25 °C and the reaction mixture was quenched with a sat. aq. NH<sub>4</sub>Cl-solution (10 mL). The aqueous phase was extracted three times with ethyl acetate (30 mL). The combined organic layers were dried (MgSO<sub>4</sub>), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/ethyl acetate gradient from 15:1 to 1:1, R<sub>f</sub> = 0.40) afforded pale yellow crystals (304 mg, 59%).

**mp** (°C): 158–160.

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 600 MHz):** δ (ppm) = 0.83 (s, 9H), 2.53 (dd, *J* = 14.77 Hz, *J* = 1.10 Hz, 1 H), 2.68 (dd, *J* = 8.60 Hz, *J* = 0.88 Hz, 1 H), 3.10 (dd, *J* = 14.77 Hz, *J* = 8.60 Hz, 1 H), 6.83 (d, *J* = 9.70 Hz, 2 H), 6.88 (d, *J* = 10.14 Hz, 1 H), 7.17–7.19 (m, 1 H), 7.21–7.30 (m, 8 H), 7.51–7.54 (m, 1 H), 7.93 (s, 1 H), 8.56–8.58 (m, 1 H).

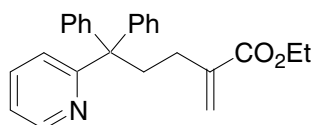
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 150 MHz):** δ (ppm) = 25.9 (CH<sub>3</sub>), 35.3, 44.6 (CH<sub>2</sub>), 60.8, 74.6 (CH), 121.5 (CH), 126.4 (CH), 126.5 (CH), 127.2 (CH), 127.8 (CH), 128.2 (CH), 128.6 (CH), 130.0 (CH), 136.6 (CH), 144.6 (CH), 146.6 (CH), 150.3, 165.4.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>–1</sup> = 3196 (s), 3056 (m), 2960 (s), 2946 (s), 2868 (s), 1591 (s), 1564 (m), 1481 (m), 1469 (s), 1423 (m), 1389 (w), 1358 (w), 1289 (w), 1244 (w), 1159 (w), 10897 (m), 1082 (m), 1063 (m), 1049 (w), 788 (w), 756 (s), 701 (s), 635 (m).

**MS (EI, 70 eV):** *m/z* (%) = 345 (3), 289 (19), 288 (100), 259 (12), 258 (54), 245 (30), 244 (40), 243 (17), 167 (18).

**HRMS (EI):** calcd. for C<sub>24</sub>H<sub>27</sub>N<sub>1</sub>O<sub>1</sub>: 345.2093, found: 345.2106.

#### Ethyl 2-(3,3-diphenyl-3-pyridin-2-ylpropyl)acrylate (**4n**)



The alkyl iodide **2f** (578 mg, 2.0 mmol) was dissolved in THF (1.5 mL) and cooled to 0 °C, *i*Pr<sub>2</sub>Mg·LiCl (0.9 mmol, 2.01 mL, 0.45 M in THF) was added and the reaction mixture was warmed to 25 °C. After 2.5 h the reaction mixture was cooled to –20 °C and ethyl 2-(bromomethyl)acrylate (386 mg, 2.9 mmol) and CuCN·2LiCl (0.1 mL, 1M in THF) was added. After 5 min of stirring at –20 °C the temperature was raised to 25 °C and the reaction mixture was quenched with a sat. aq. NH<sub>4</sub>Cl-solution (10 mL). The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried (MgSO<sub>4</sub>), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/ethyl acetate 20:1, R<sub>f</sub> = 0.30) afforded a colourless liquid (328 mg, 59%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  (ppm) = 1.30 (t, *J* = 7.06, 3 H), 2.09–2.15 (m, 2 H), 2.86–2.92 (m, 2 H), 4.20 (q, *J* = 7.06, 2 H), 5.53 (s, 1 H), 6.13 (s, 1 H), 7.08–7.12 (m, 1 H), 7.19–7.21 (m, 11 H), 7.54–7.59 (m, 1 H), 8.60–8.62 (m, 1 H).

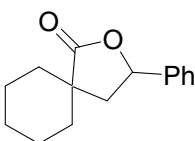
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 14.2 (CH<sub>3</sub>), 28.4 (CH<sub>2</sub>), 39.0 (CH<sub>2</sub>), 59.0, 60.5 (CH<sub>2</sub>), 120.9 (CH), 124.2 (CH<sub>2</sub>), 124.2 (CH<sub>2</sub>), 124.8 (CH), 126.1 (CH), 127.8 (CH), 129.4 (CH), 141.3, 146.2, 148.5 (CH), 166.0, 167.3.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>–1</sup> = 3085 (w), 3055 (w), 3030 (w), 2979 (w), 2936 (w), 1710 (s), 1628 (w), 1585 (m), 1567 (w), 1368 (w), 1326 (m), 1304 (w), 1257 (m), 1231 (m), 1180 (s), 1133 (s), 1029 (m), 941 (m), 787 (w), 747 (s), 698 (s), 614 (m), 589 (m).

**MS (EI, 70 eV):** *m/z* (%) = 371 (5), 259 (18), 258 (100), 245 (25), 244 (20), 243 (14), 167 (13).

**HRMS (EI):** calcd. for C<sub>25</sub>H<sub>25</sub>O<sub>2</sub>N<sub>1</sub>: 371.1885, found: 371.1875.

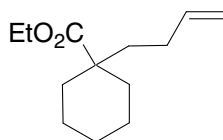
### 3-Phenyl-2-oxaspiro[4.5]decan-1-one (9a)



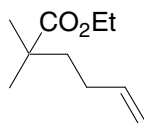
The alkyl iodide **8a** (296 mg, 1.0 mmol) was dissolved in THF (1 mL) and DMPU (1 mL) and cooled to  $-10\text{ }^{\circ}\text{C}$ , then  $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}$  (0.8 mmol, 0.95 mL, 0.84 M in THF) was added and the reaction mixture was stirred overnight. The reaction mixture was cooled to  $-20\text{ }^{\circ}\text{C}$  and benzaldehyde (0.18 g, 0.17 mL, 1.7 mmol) was added. After 30 min of stirring at  $-20\text{ }^{\circ}\text{C}$  the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution. The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 6:1,  $R_f = 0.31$ ) afforded colourless crystals (157 mg, 68%).<sup>6</sup>

**mp** ( $^{\circ}\text{C}$ ): 59–60.

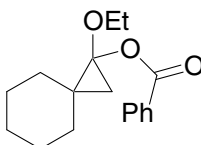
#### **Ethyl 1-but-3-en-1-ylcyclohexanecarboxylate (9b)**



The alkyl iodide **8a** (296 mg, 1.0 mmol) was dissolved in THF (1 mL) and DMPU (1 mL) and cooled to  $-10\text{ }^{\circ}\text{C}$ , then  $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}$  (0.7 mmol, 0.95 mL, 0.74 M in THF) was added and the reaction mixture was stirred overnight. Then, the reaction mixture was cooled to  $-20\text{ }^{\circ}\text{C}$  and  $\text{CuCN}\cdot 2\text{LiCl}$  (0.1 mL, 1M in THF) was added followed by allyl bromide (240 mg, 2.0 mmol, 0.17 mL). After 30 min at  $-20\text{ }^{\circ}\text{C}$  the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution. The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 10:1,  $R_f = 0.30$ ) afforded a colourless liquid (164 mg, 78%).<sup>7</sup>

**Ethyl 2,2-dimethylhex-5-enoate (9c)**

The alkyl iodide **8b** (256 mg, 1.0 mmol) was dissolved in THF (1 mL) and DMPU (1 mL) and cooled to  $-10\text{ }^{\circ}\text{C}$ , then  $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}$  (0.65 mmol, 1.02 mL, 0.64 M in THF) was added and the reaction mixture stirred overnight. Then, the mixture was cooled to  $-20\text{ }^{\circ}\text{C}$  and  $\text{CuCN}\cdot 2\text{LiCl}$  (0.1 mL, 1M in THF) was added followed by allyl bromide (302 mg, 2.50 mmol, 0.22 mL). After 30 min of stirring at  $-20\text{ }^{\circ}\text{C}$  the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution. The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 20:1,  $R_f = 0.29$ ) afforded a colourless liquid (116 mg, 68%).<sup>8</sup>

**1-Ethoxyspiro[2.5]oct-1-yl benzoate (9d)**

The alkyl iodide **8a** (296 mg, 1.0 mmol) was dissolved in THF (1 mL) and DMPU (1 mL) and cooled to  $-10\text{ }^{\circ}\text{C}$ ,  $i\text{Pr}_2\text{Mg}\cdot\text{LiCl}$  (0.7 mmol, 0.95 mL, 0.74 M in THF) was added. After 7 h of stirring the mixture was cooled to  $-20\text{ }^{\circ}\text{C}$  and  $\text{CuCN}\cdot 2\text{LiCl}$  (1.40 mmol, 1.40 mL) was added. After 30 min of stirring,  $\text{PhCOCl}$  (211 mg, 1.50 mmol, 0.17 mL) was added. After additional 30 min of stirring at  $-20\text{ }^{\circ}\text{C}$  the temperature was raised to  $25\text{ }^{\circ}\text{C}$  and the reaction mixture was quenched with a sat. aq.  $\text{NH}_4\text{Cl}$ -solution (10 mL). The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried ( $\text{MgSO}_4$ ), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 30:1,  $R_f = 0.31$ ) afforded a colourless liquid (194 mg, 71%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  (ppm) = 0.82 (d,  $J$  = 6.08 Hz, 1 H), 0.90 (d,  $J$  = 6.08 Hz, 1 H), 1.18 (t,  $J$  = 7.17 Hz, 3 H), 1.26–1.77 (m, 10 H), 3.68–3.89 (m, 2 H), 7.40–7.46 (m, 2 H), 7.53–7.58 (m, 1 H), 8.03–8.06 (m, 2 H).

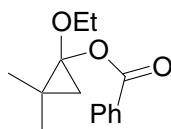
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 15.4 (CH<sub>2</sub>), 22.6 (CH<sub>2</sub>), 24.9 (CH<sub>2</sub>), 25.0 (CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 30.9 (CH<sub>2</sub>), 31.1, 64.3 (CH<sub>2</sub>), 93.5, 128.4 (CH), 129.7 (CH), 130.3, 133.0 (CH), 165.5.

**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2976 (w), 2928 (s), 2852 (m), 1732 (s), 1600 (w), 1448 (m), 1380 (w), 1336 (w), 1312 (w), 1272 (s), 1240 (m), 1168 (m), 1120 (m), 1084 (s), 1064 (s), 1024 (s), 992 (w), 912 (w), 708 (s).

**MS (EI, 70 eV):**  $m/z$  (%) = 169 (7), 168 (6), 123 (9), 106 (9), 105 (100), 95 (19), 81 (18), 77 (21).

**HRMS (EI):** calcd. for C<sub>17</sub>H<sub>22</sub>O<sub>3</sub>: 274.1569, found: 274.1590.

#### 1-Ethoxy-2,2-dimethylcyclopropyl benzoate (9e)



The alkyl iodide **8b** (768 mg, 3.0 mmol) was dissolved in THF (1 mL) and DMPU (1 mL) and cooled to –10 °C, *i*Pr<sub>2</sub>Mg·LiCl (1.95 mmol, 4.40 ml, 0.44 M in THF) was added and the reaction mixture was stirred overnight. The reaction mixture was cooled to –20 °C and CuCN·2LiCl (4.50 mmol, 4.50 mL) was added. After 30 min of stirring PhCOCl (633 mg, 4.50 mmol, 0.52 mL) was added. After additional 30 min of stirring at –20 °C the temperature was raised to 25 °C and the reaction mixture was quenched with a sat. aq. NH<sub>4</sub>Cl-solution. The aqueous phase was extracted three times with ether (30 mL). The combined organic layers were dried (MgSO<sub>4</sub>), and after filtration the solvent was removed under reduced pressure. Flash chromatographic purification (silica gel, pentane/diethyl ether 30:1,  $R_f$  = 0.30) afforded a colourless liquid (526 mg, 75%).

**<sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):**  $\delta$  (ppm) = 0.84 (d,  $J$  = 6.17 Hz, 1 H), 0.90 (d,  $J$  = 6.17 Hz, 1 H), 1.14 (s, 3 H), 1.19 (t,  $J$  = 7.28 Hz, 3 H), 1.28 (s, 3 H), 3.68–3.85 (m, 2 H), 7.41–7.46 (m, 2 H), 7.54–7.58 (m, 1 H), 8.04–8.08 (m, 2 H).



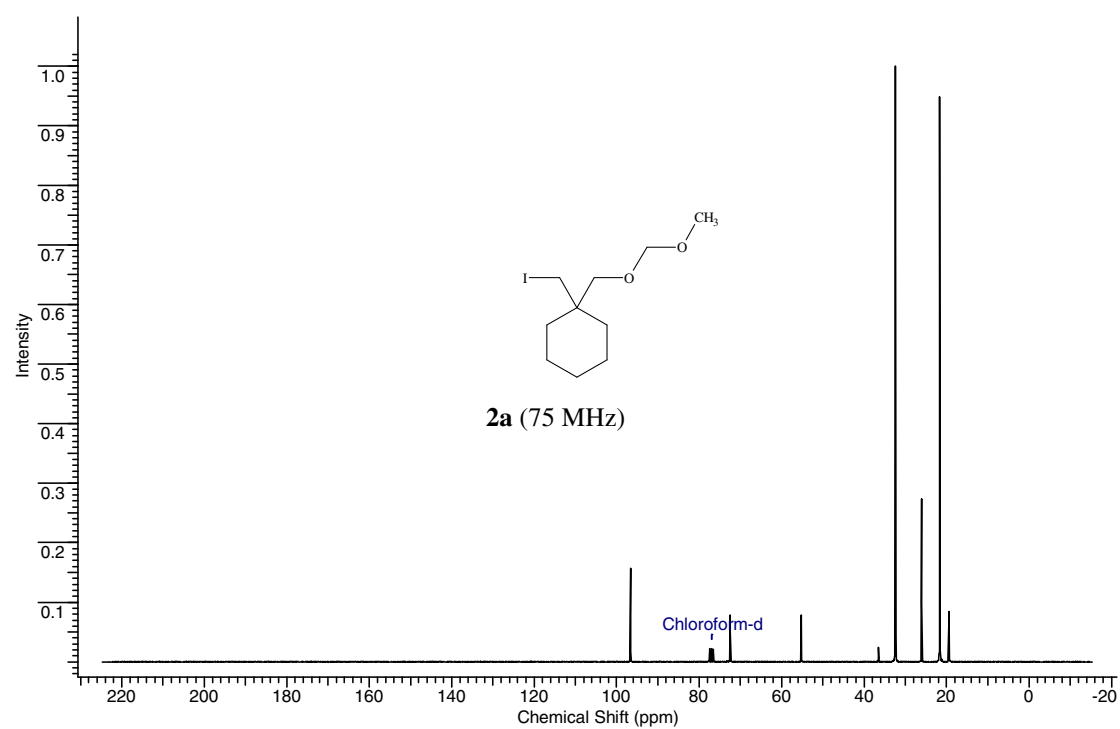
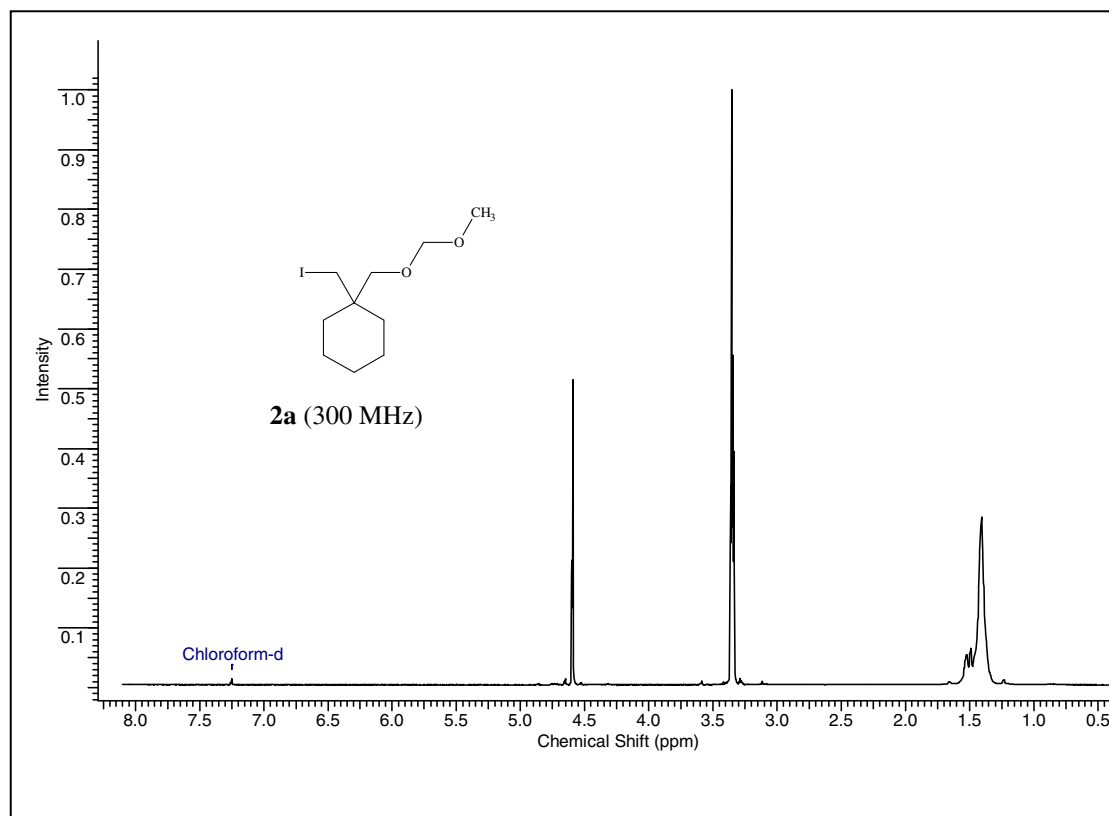
**<sup>13</sup>C-NMR (CDCl<sub>3</sub>, 75 MHz):**  $\delta$  (ppm) = 15.3 (CH<sub>3</sub>), 20.3 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 23.6 (CH<sub>2</sub>), 24.1, 64.2 (CH<sub>2</sub>), 93.2, 128.4 (CH), 129.7 (CH), 130.2, 133.0 (CH), 165.4.

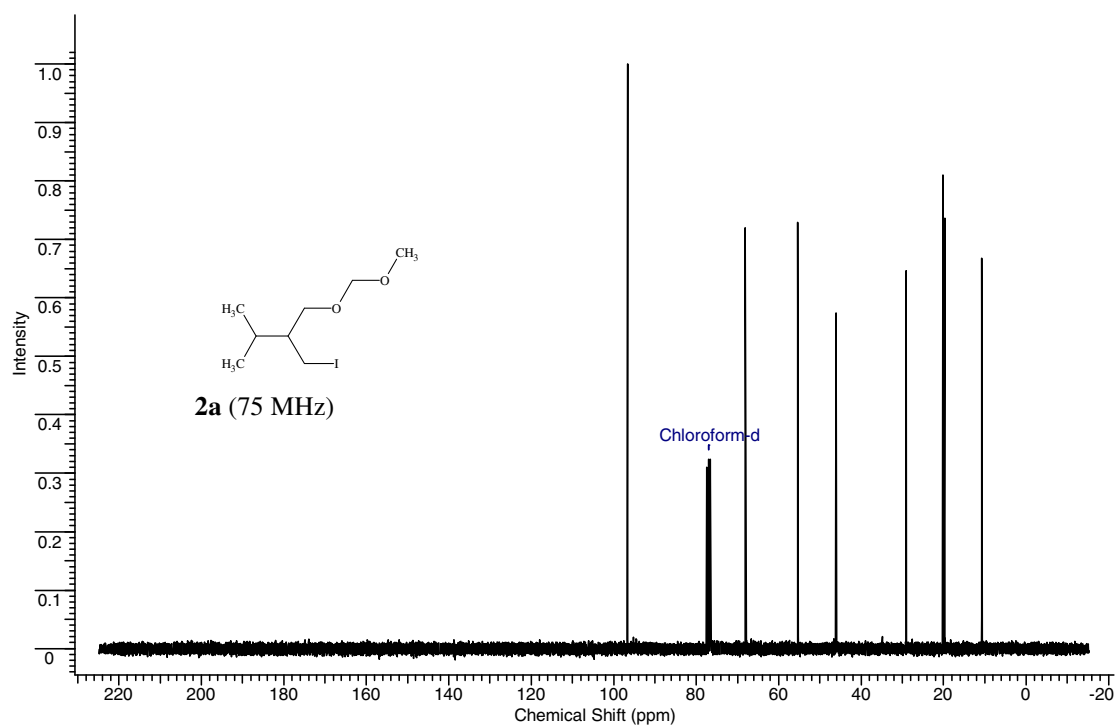
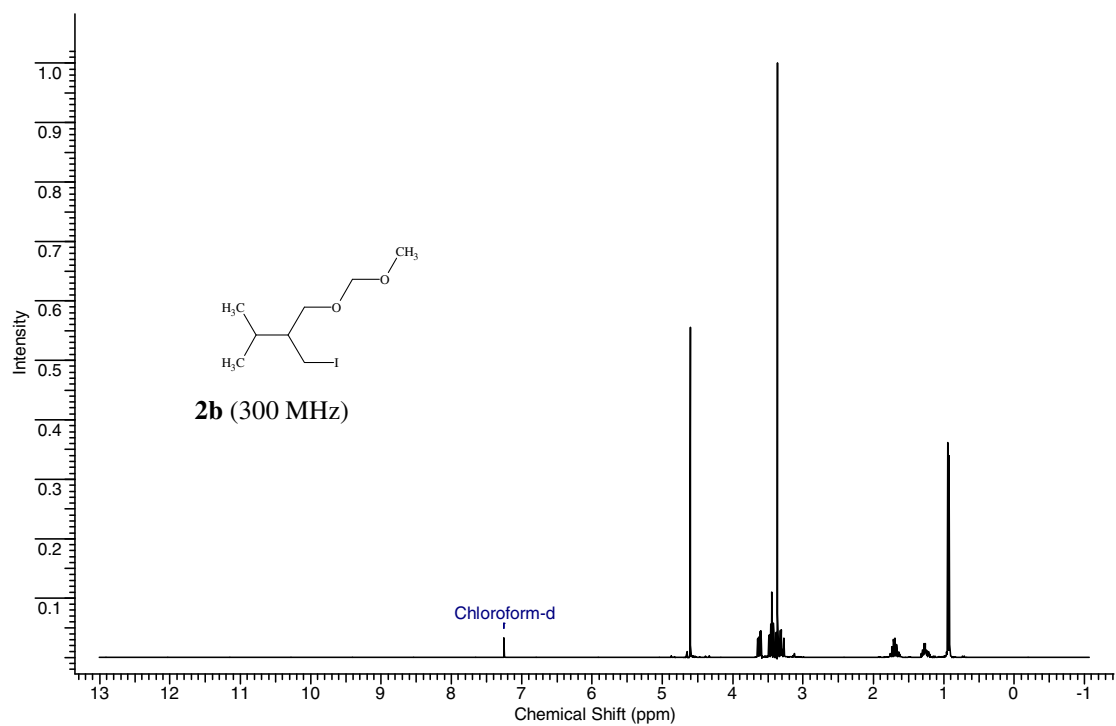
**IR (ATR):**  $\tilde{\nu}$  / cm<sup>-1</sup> = 2980 (m), 2956 (m), 2928 (m), 2888 (m), 2872 (m), 1732 (s), 1476 (w), 1452 (w), 1372 (w), 1316 (w), 1284 (w), 1260 (m), 1200 (m), 1124 (m), 1084 (s), 1048 (s), 1024 (m), 912 (w), 708 (s).

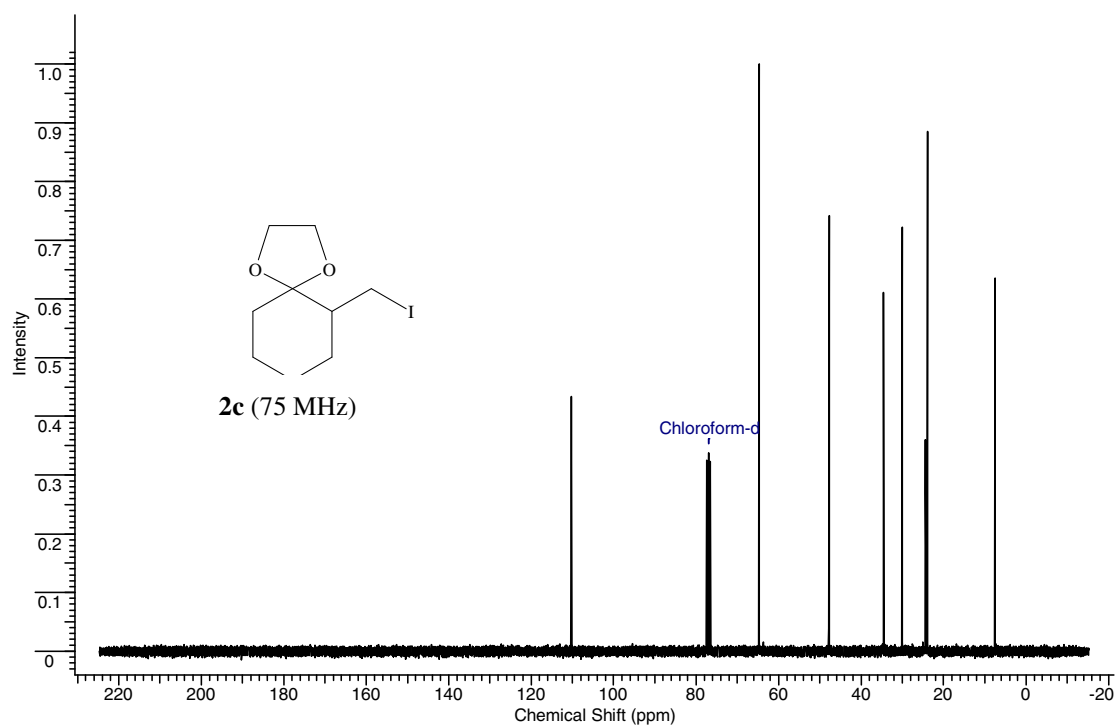
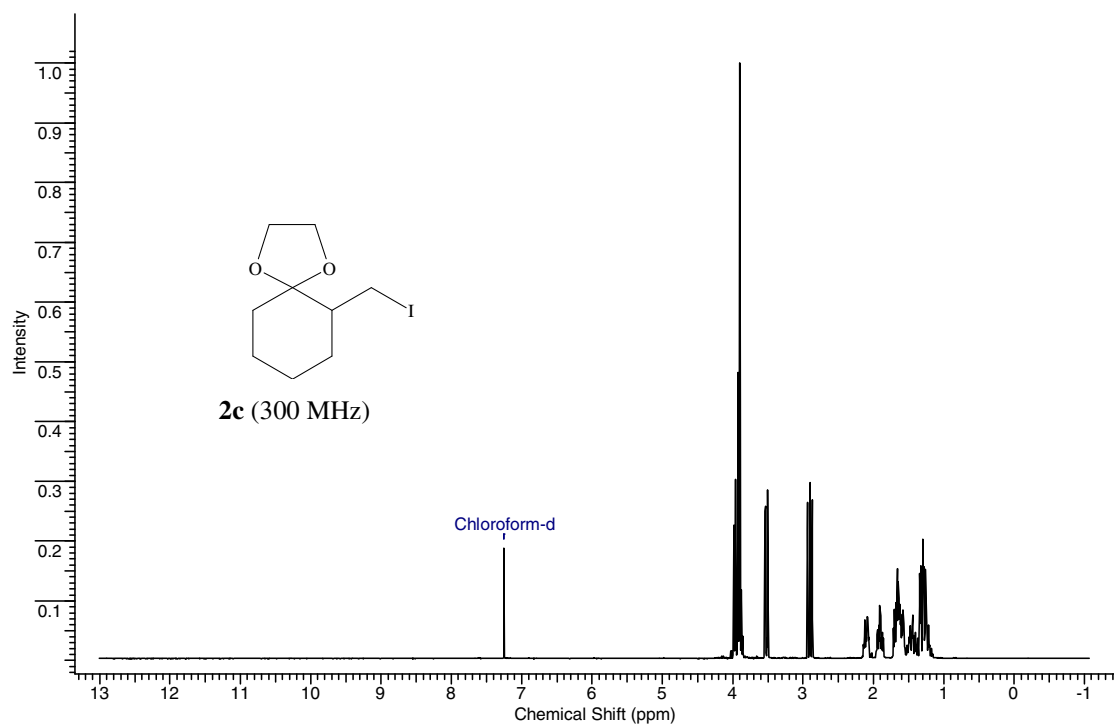
**MS (EI, 70 eV):** m/z (%) = 235 (0.01), 113 (2), 106 (6), 105 (100), 77 (10).

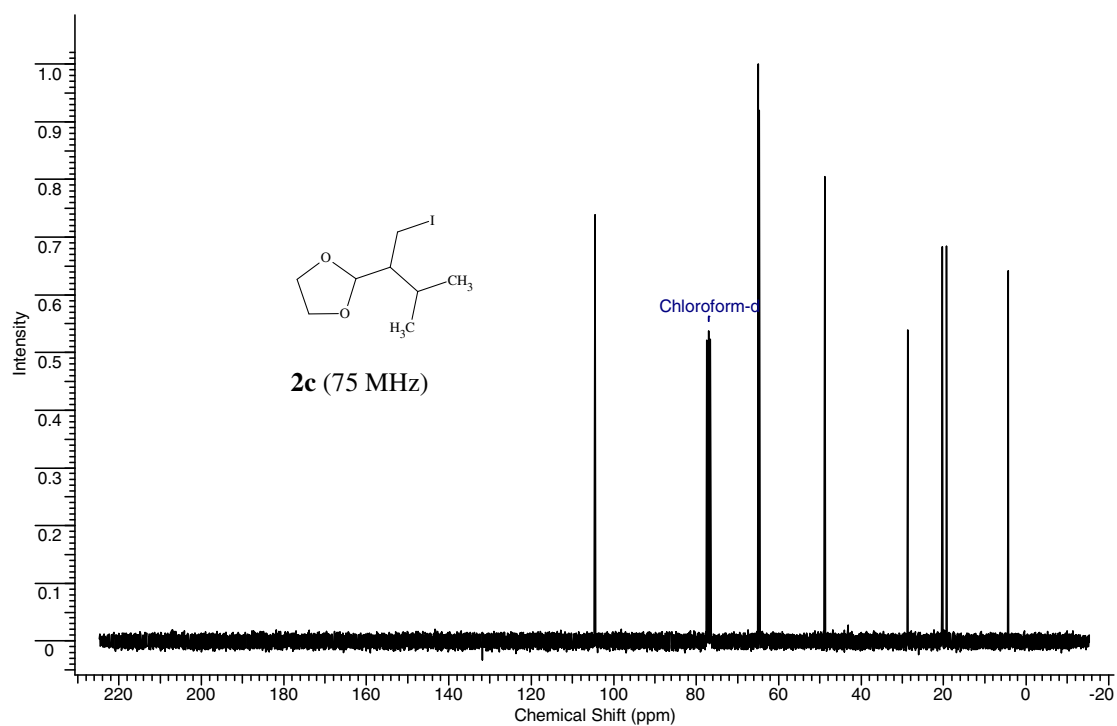
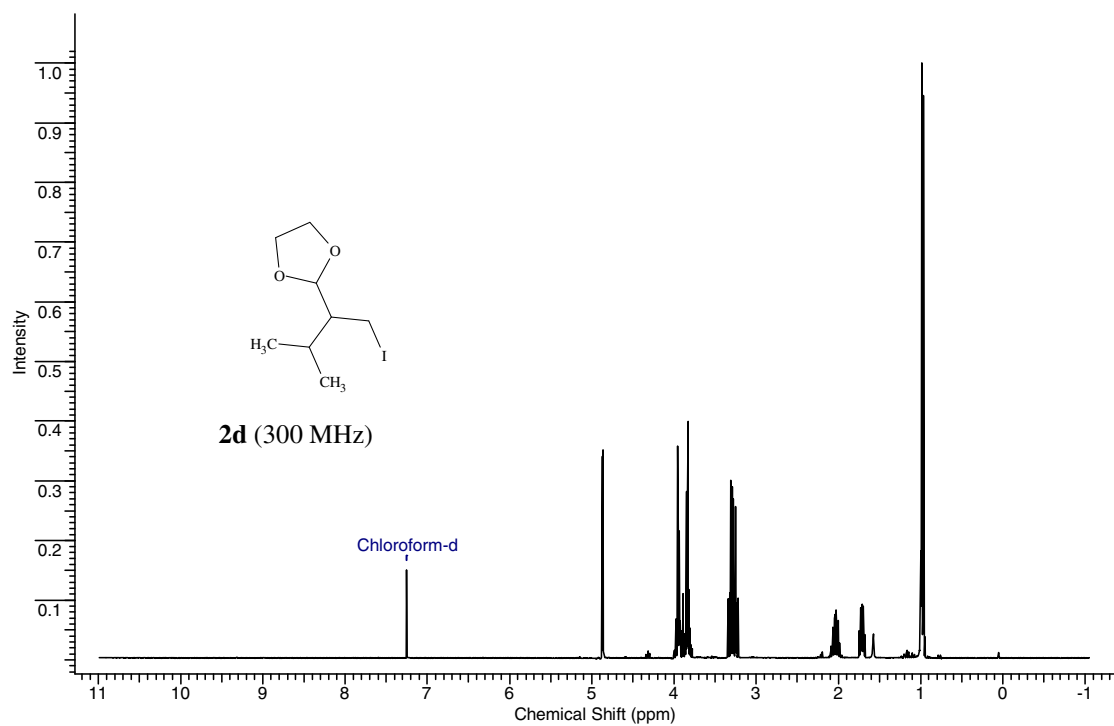
**HRMS (EI):** calcd. for C<sub>14</sub>H<sub>19</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 235.1286, found: 235.1286.

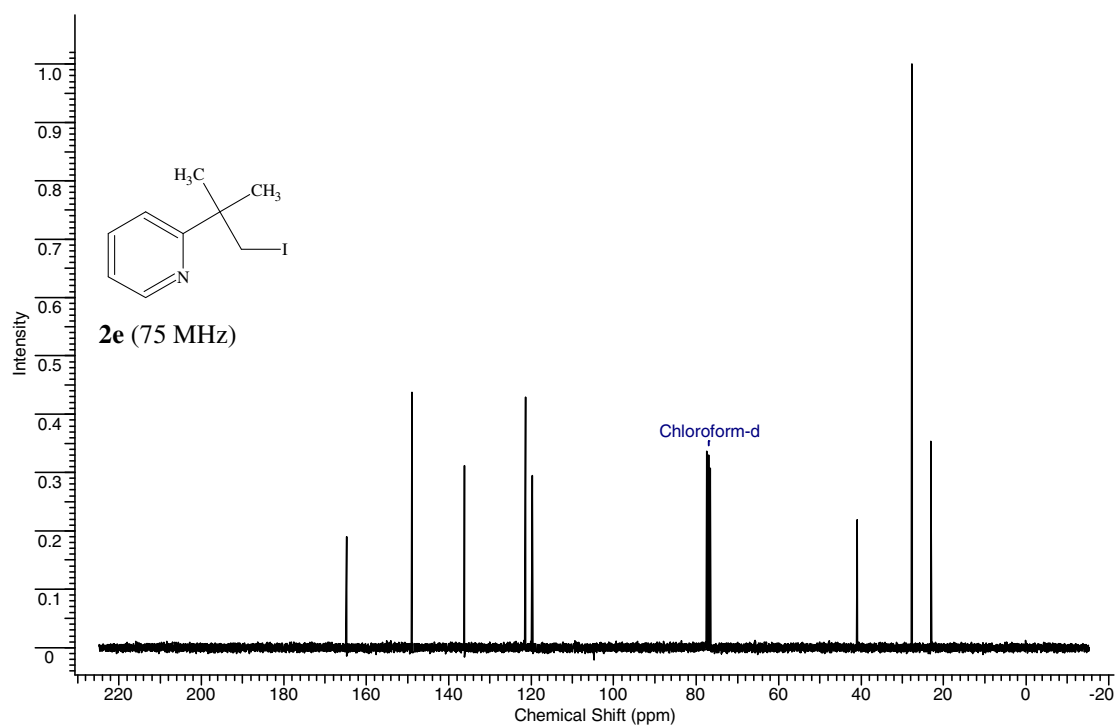
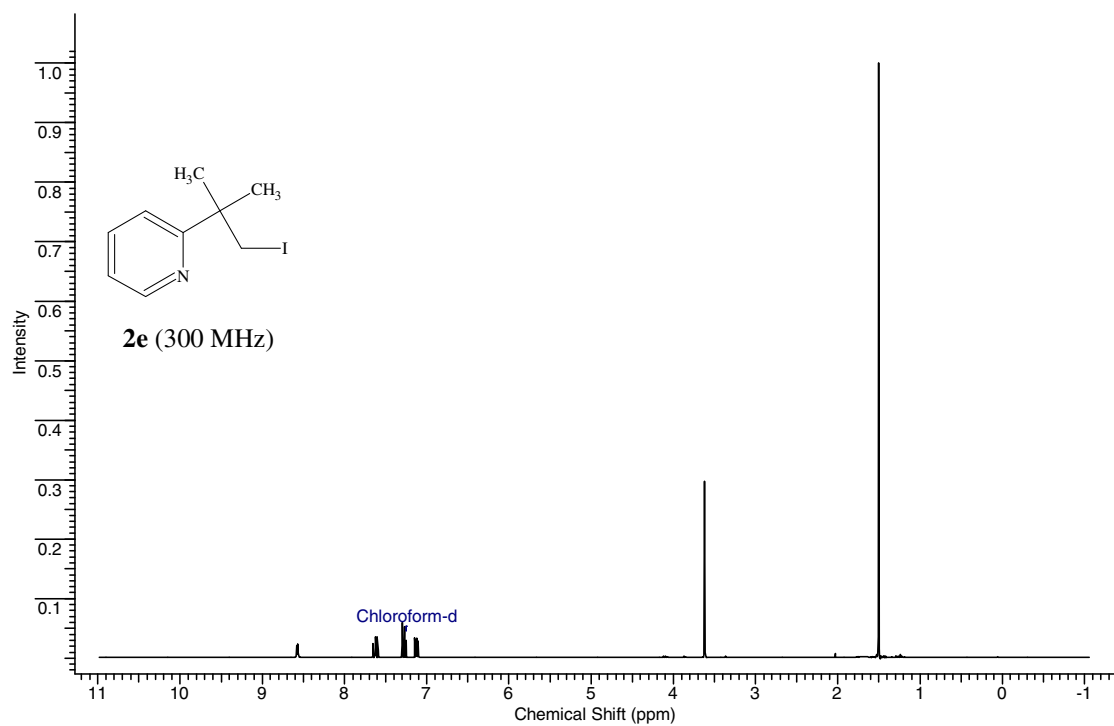
## III. NMR Spectra

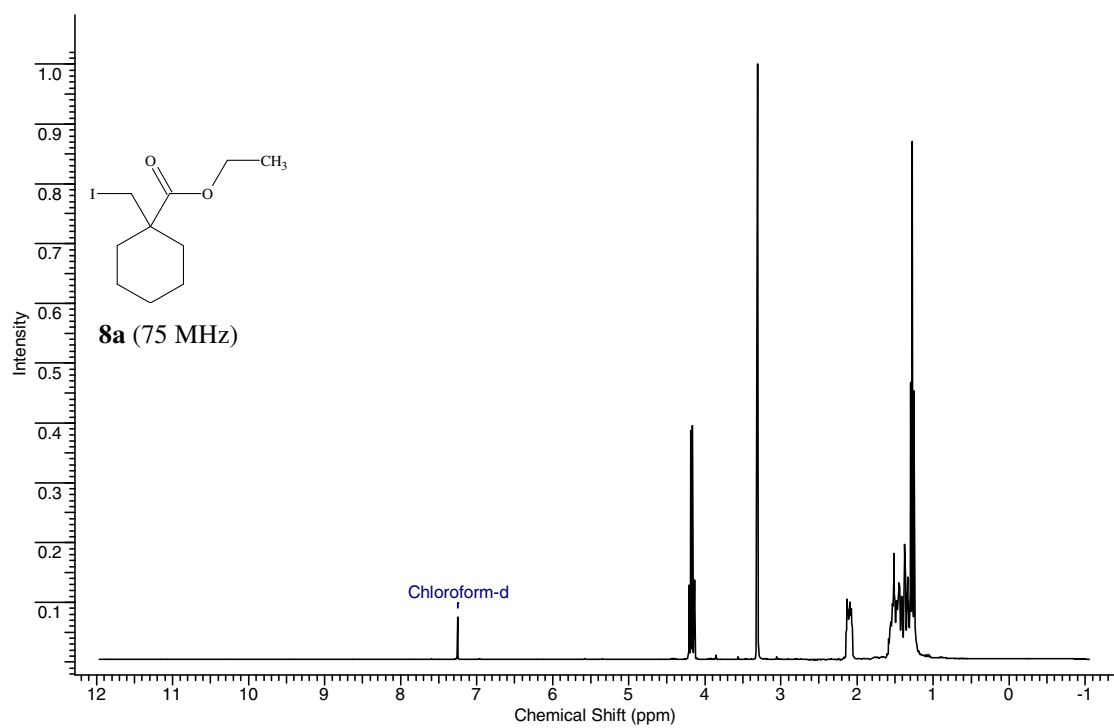
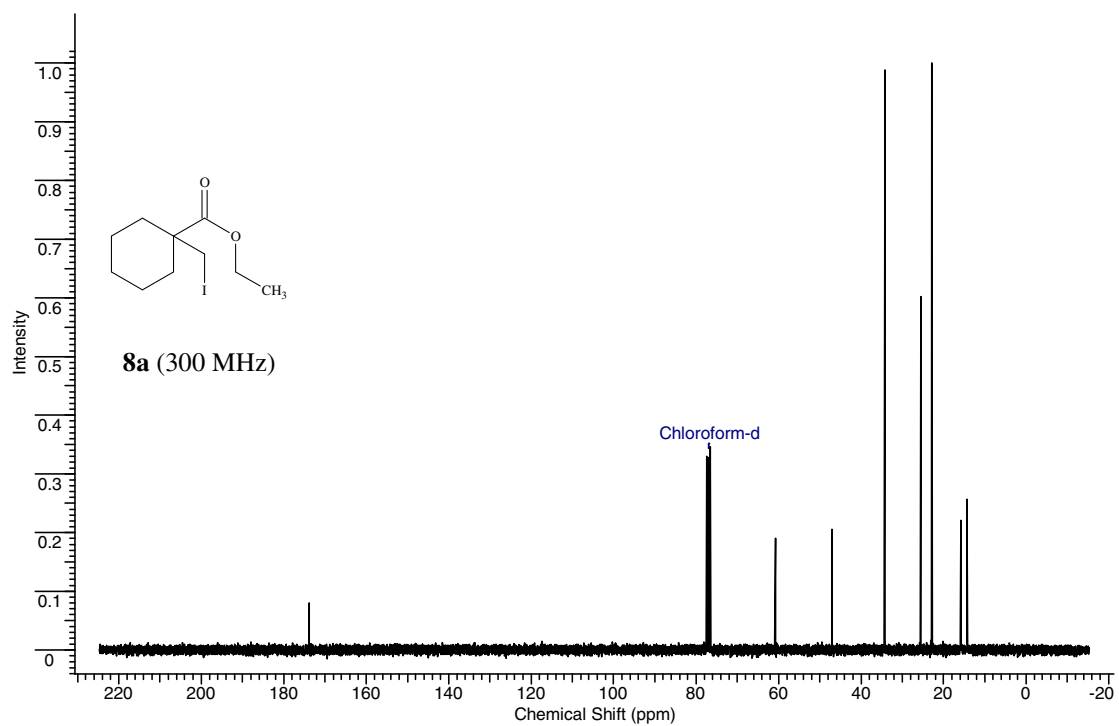


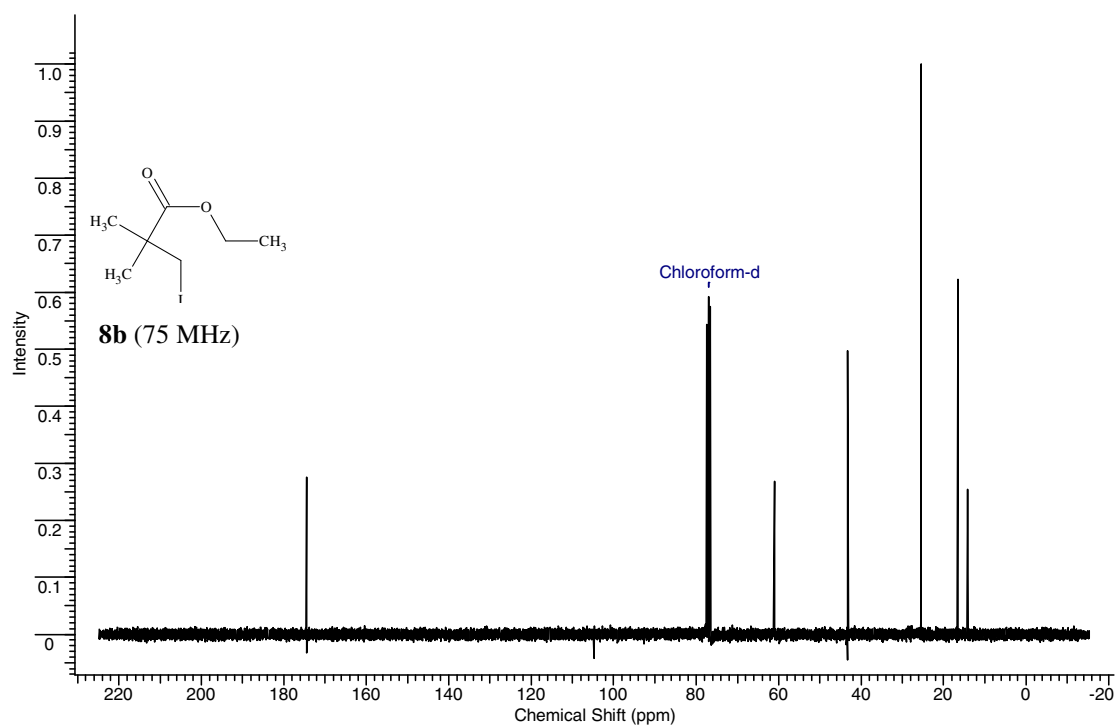
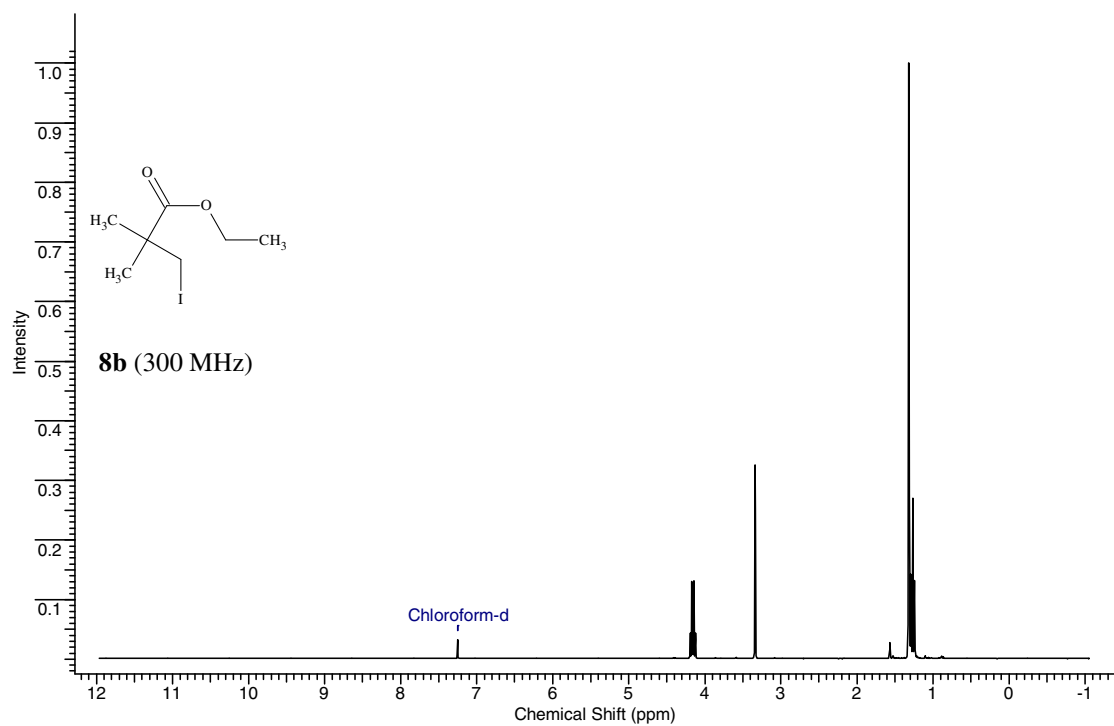




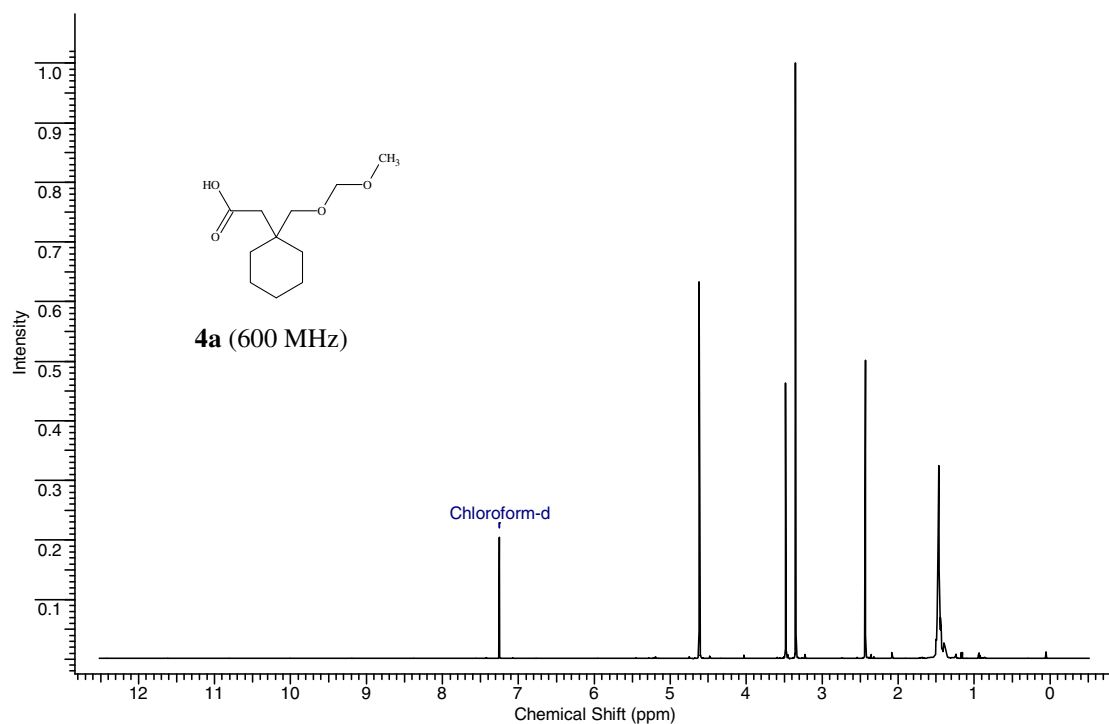








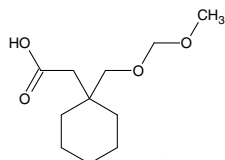




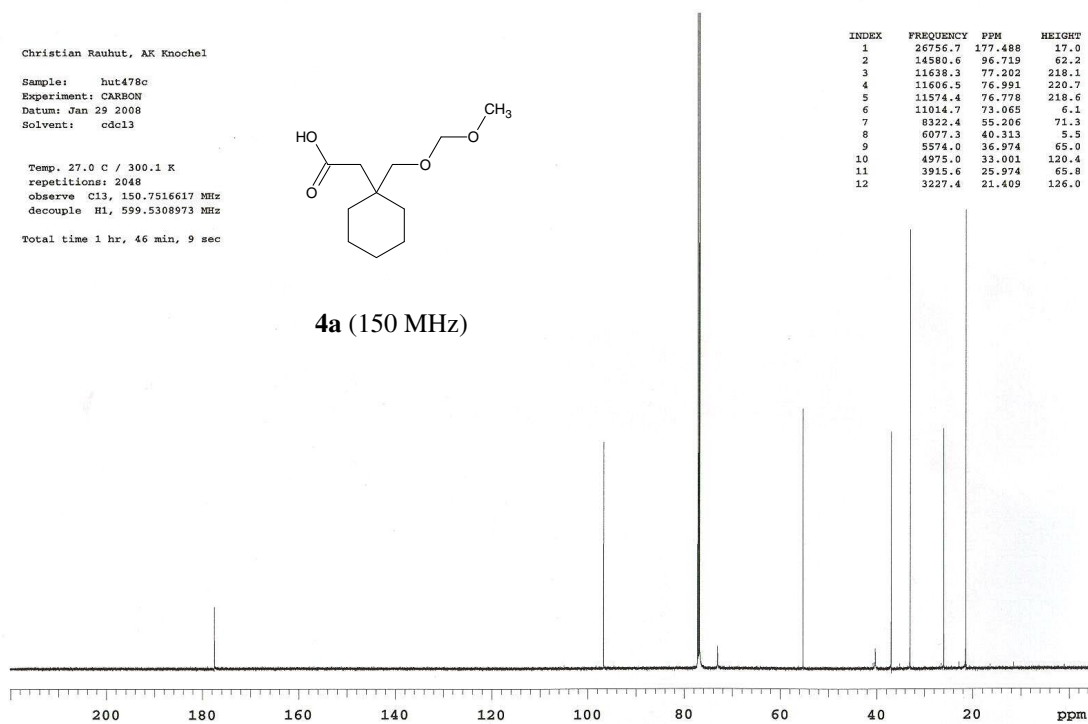
Christian Rauhut, AK Knochel

Sample: hut478c  
Experiment: CARBON  
Datum: Jan 29 2008  
Solvent: cdcl3

Temp. 27.0 C / 300.1 K  
repetitions: 2048  
observe C13, 150.7516617 MHz  
decouple H1, 599.5308973 MHz  
Total time 1 hr, 46 min, 9 sec



**4a** (150 MHz)



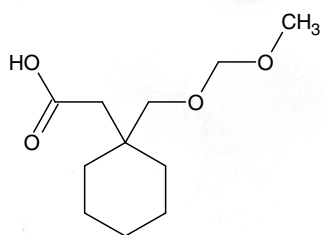
/home/var600/Knochel/Rauhut/hut478c/hut478c\_CARBON\_601

Christian Rauhut, AK Knochel

Sample: hut478c  
Experiment: HSQCAD  
Datum: Jan 30 2008  
Solvent: cdcl3

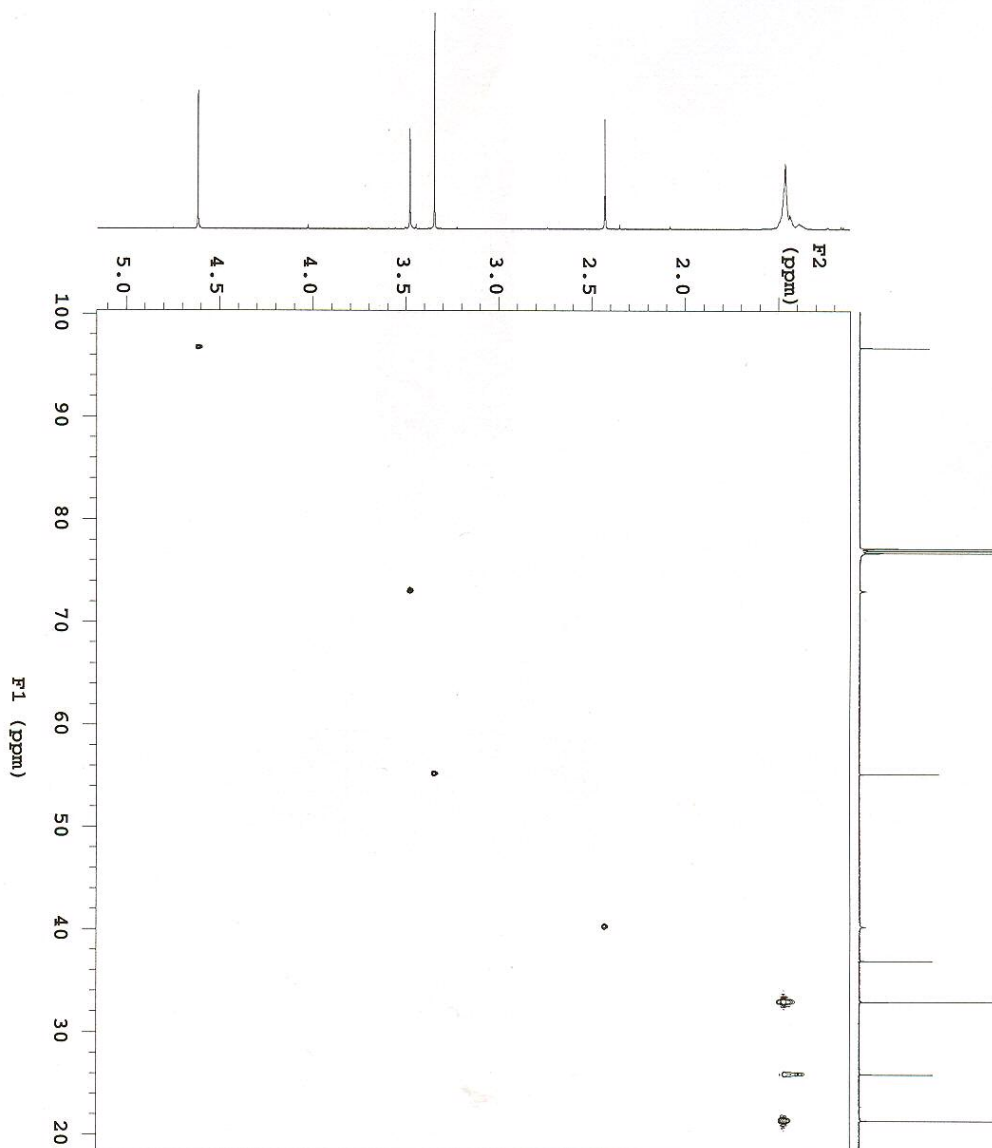
Temp: 27.0 C / 300.1 K  
repetitions: 4  
increments: 2 x 256  
observe H1, 599.528897 MHz  
decouple C13, 150.7633448 MHz

Total time 45 min, 41 sec



**4a** (600, 150 MHz)

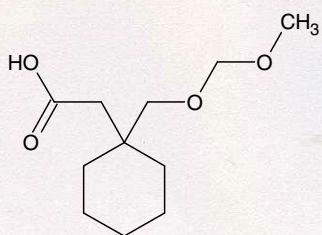
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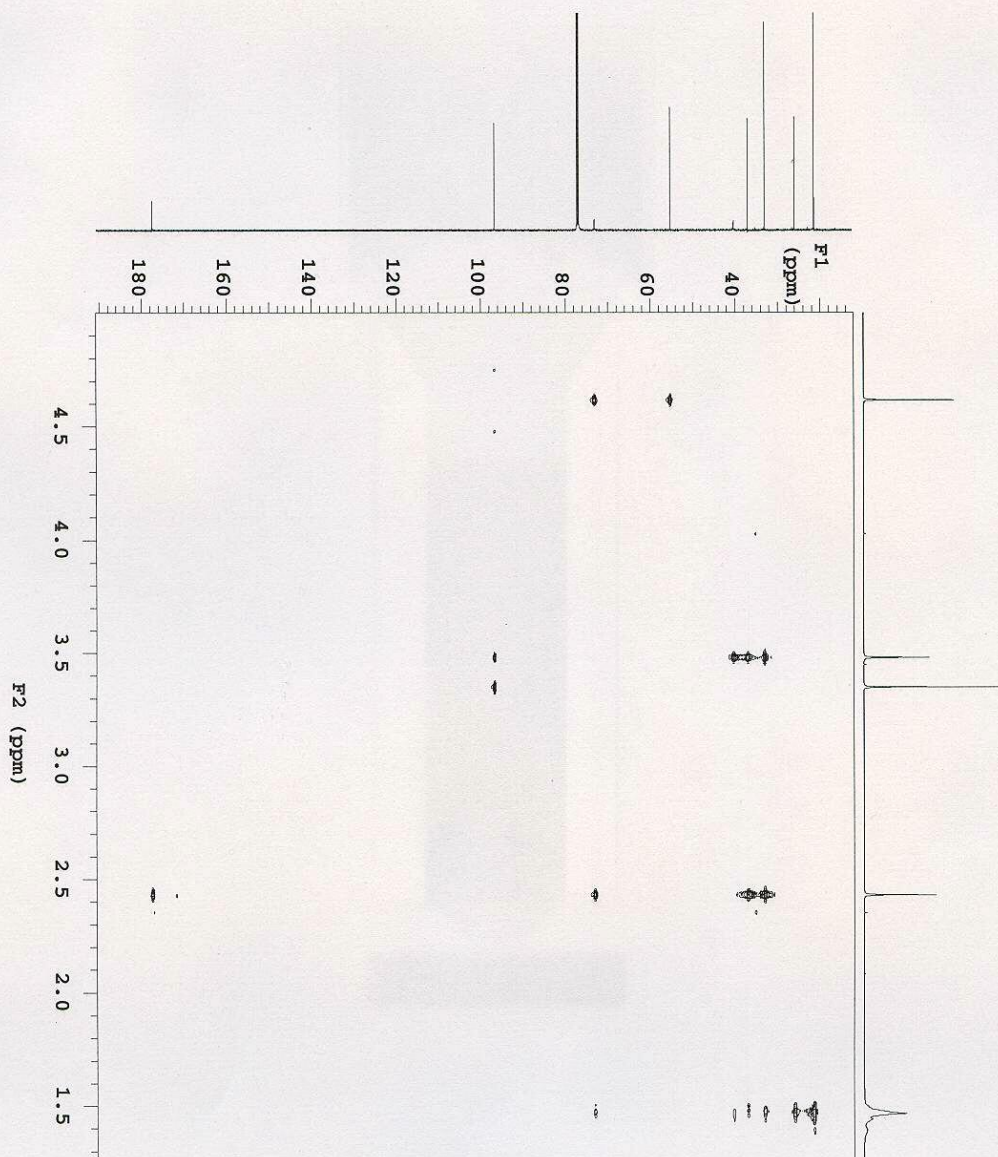
Christian Rauhut, AK Knochel

Sample: hut478c  
Experiment: ghmrcad  
Datum: Jan 30 2008  
Solvent: cdcl3

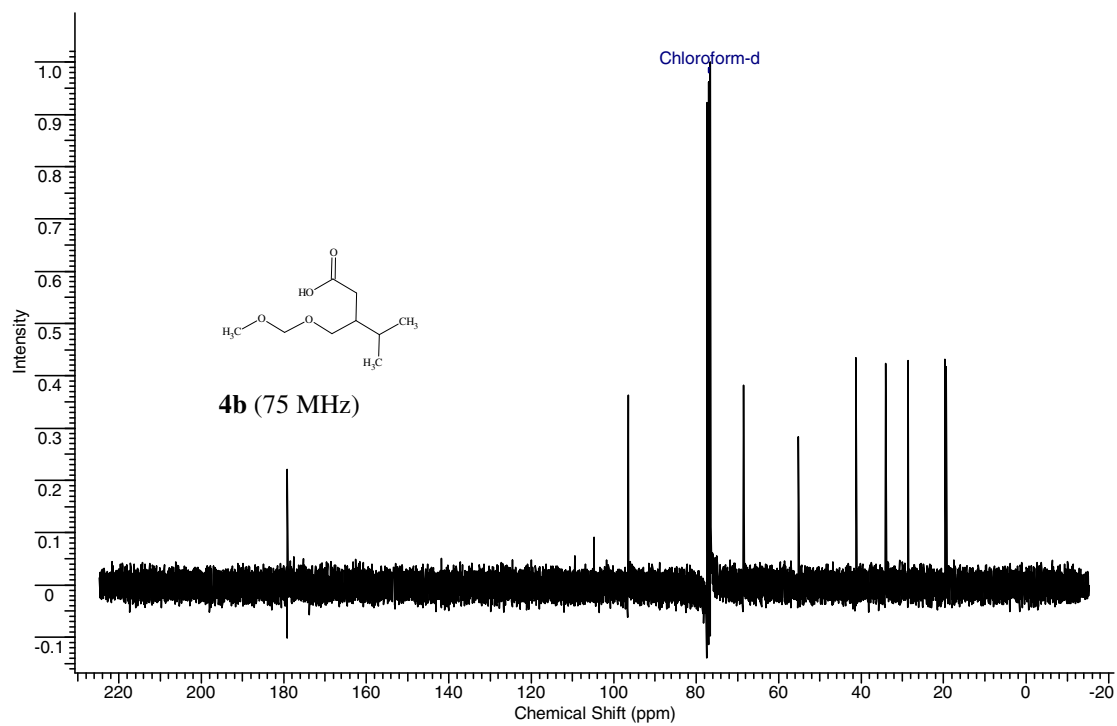
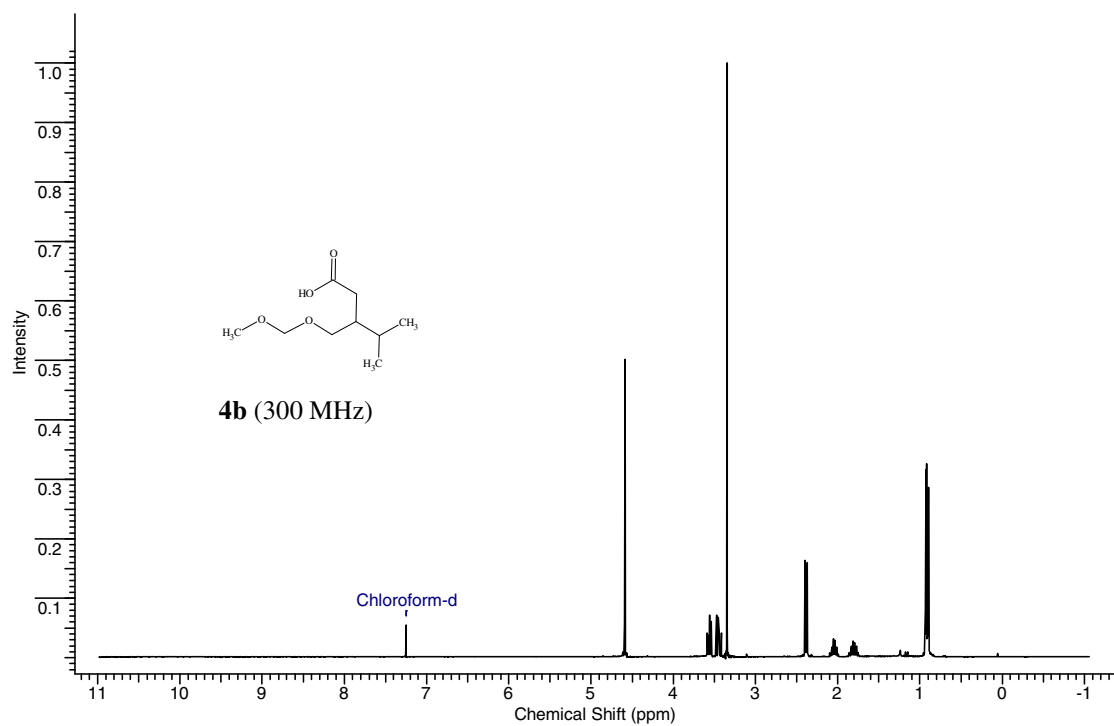
Temp: 27.0 C / 300.1 K  
Repetitions: 4  
increments: 2 x 256  
observe H1, 599.528997 MHz  
Total time 47 min, 7 sec

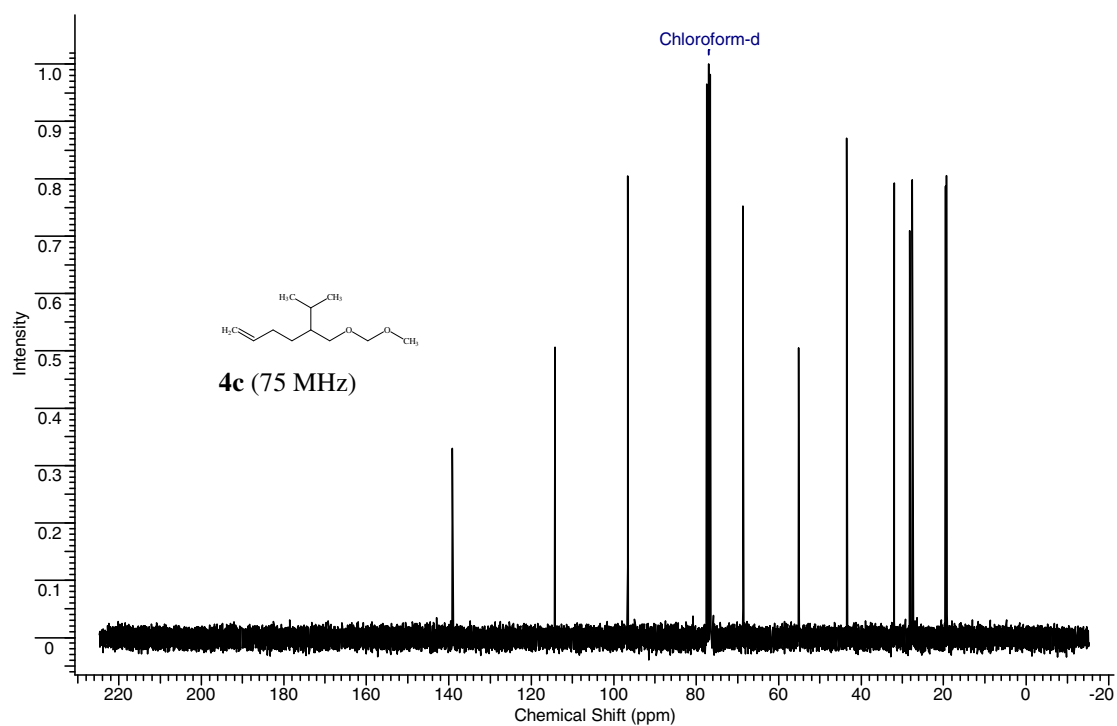
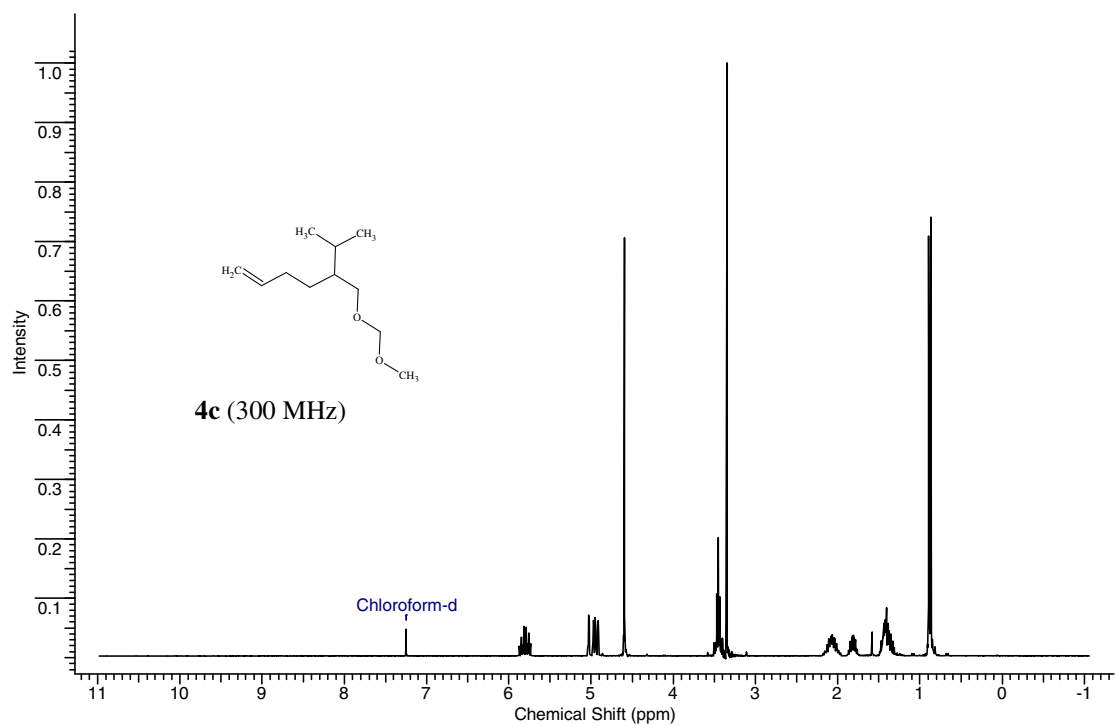


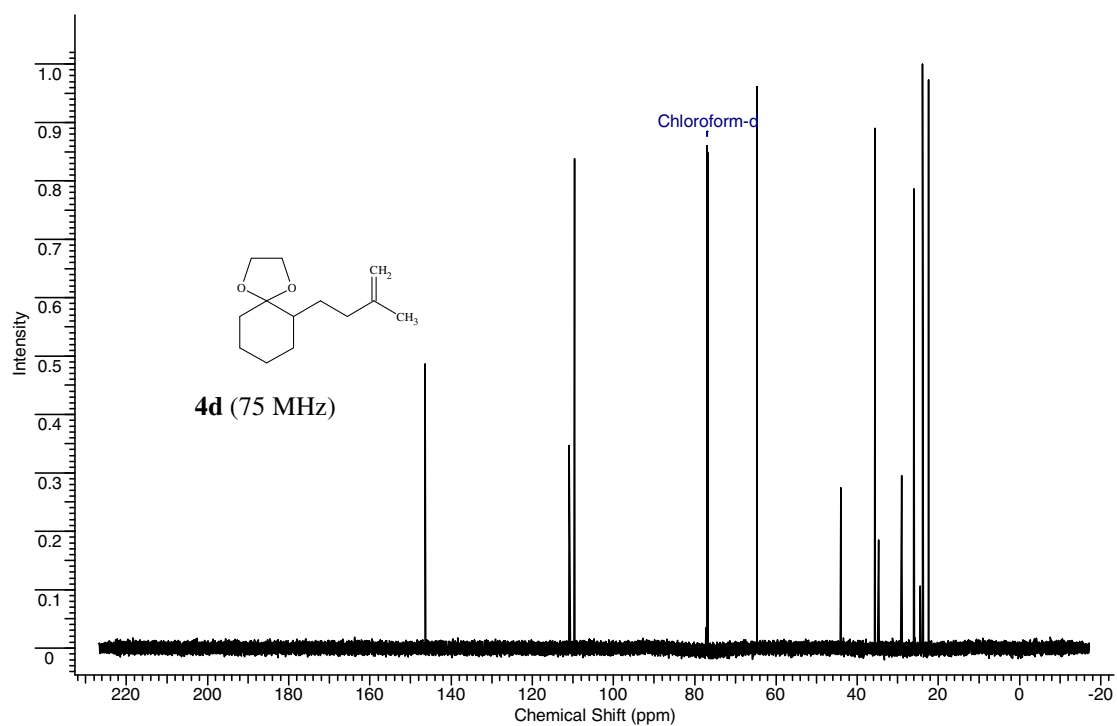
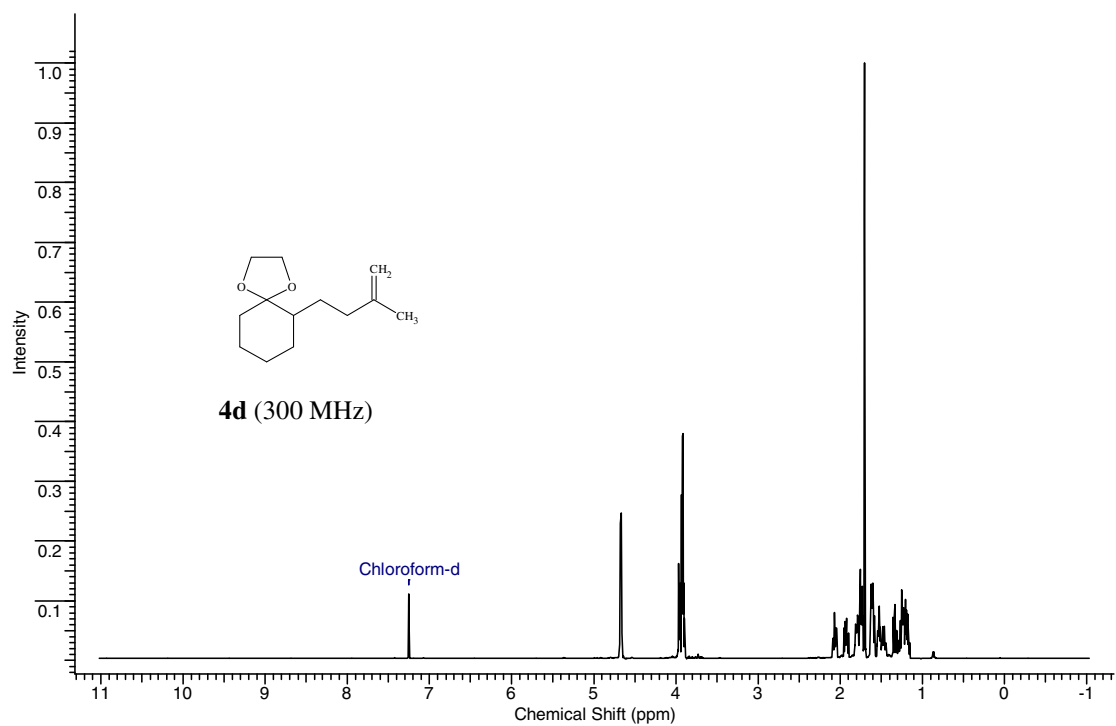
**4a** (600,MHz)

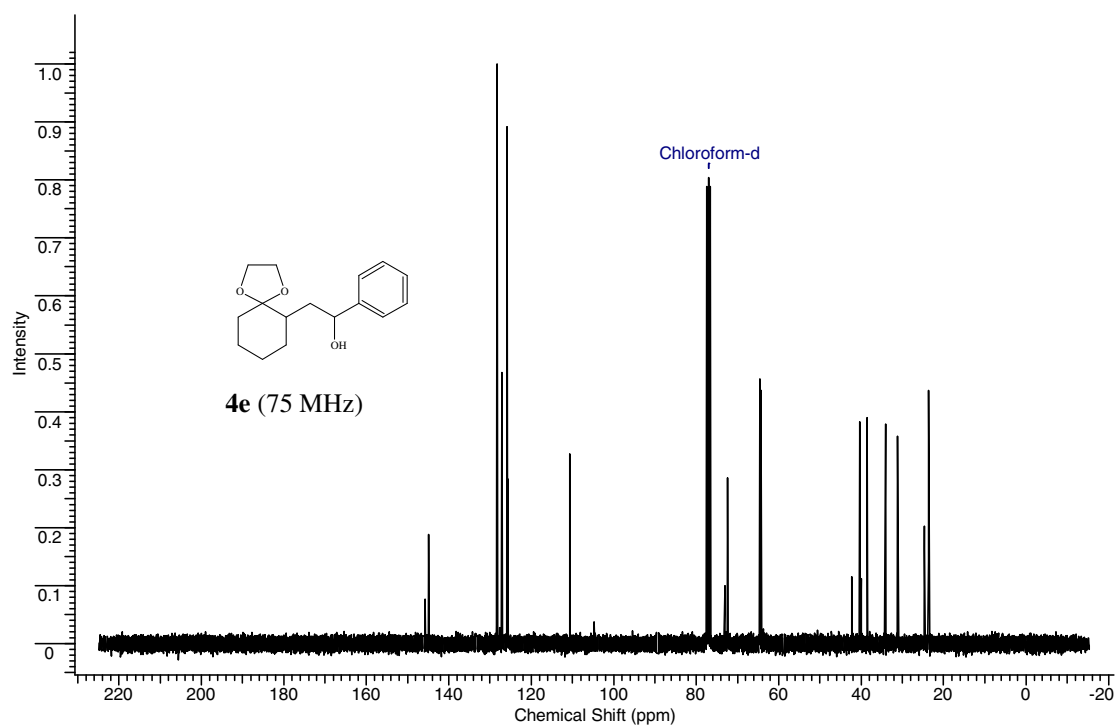
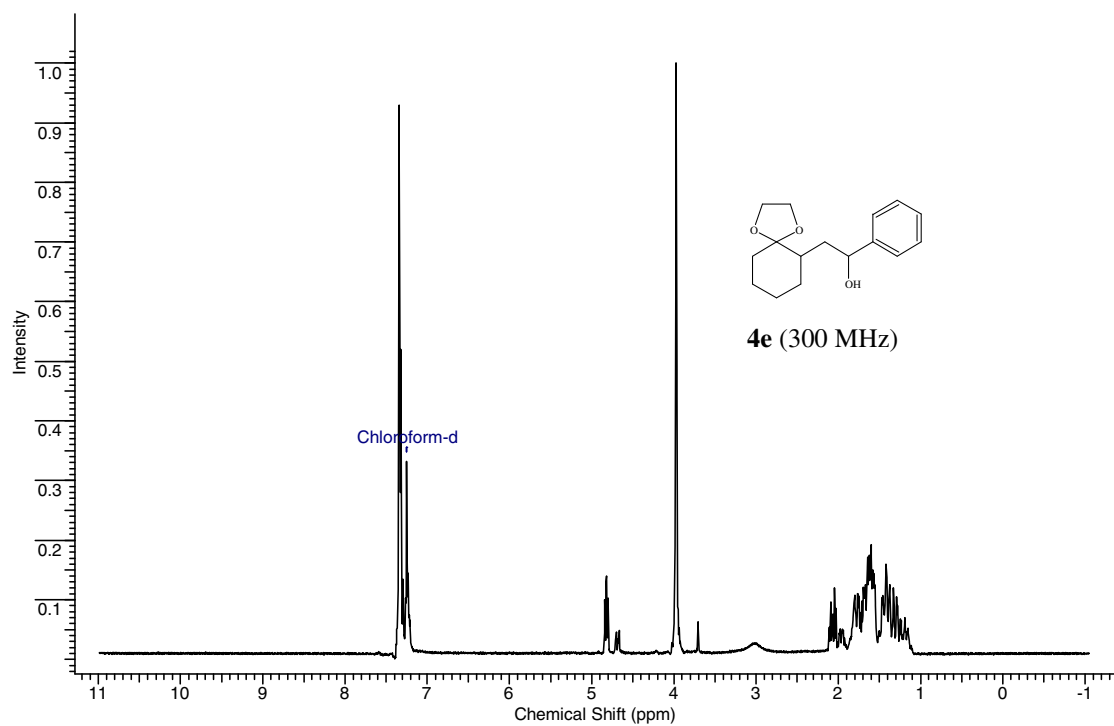


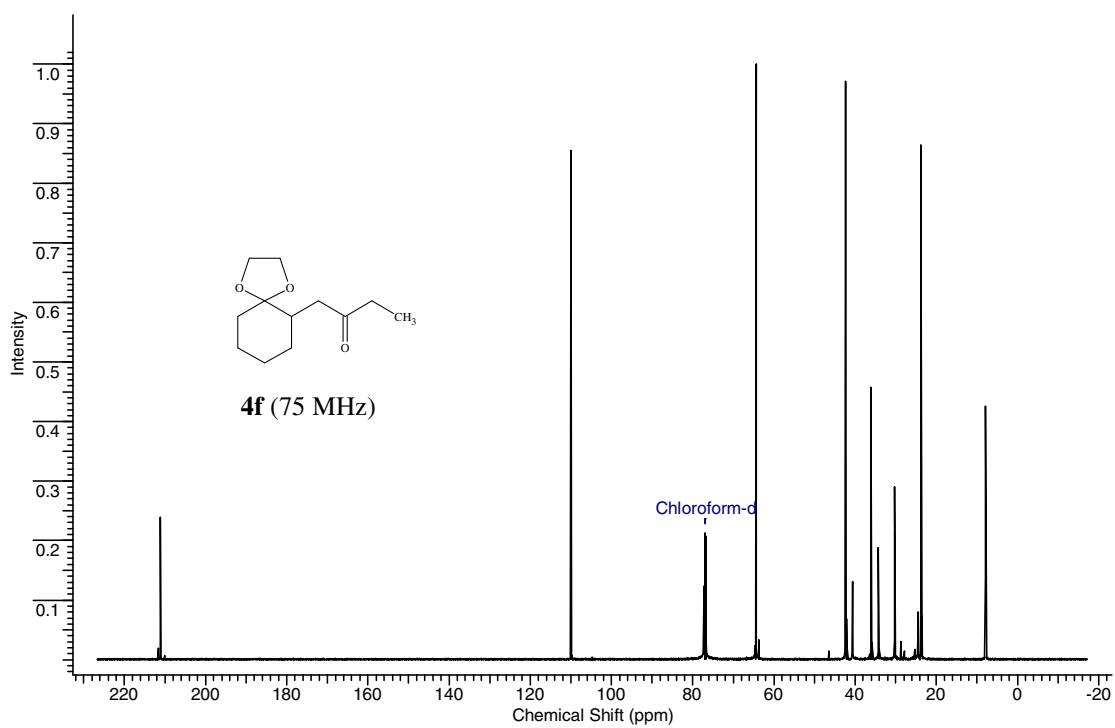
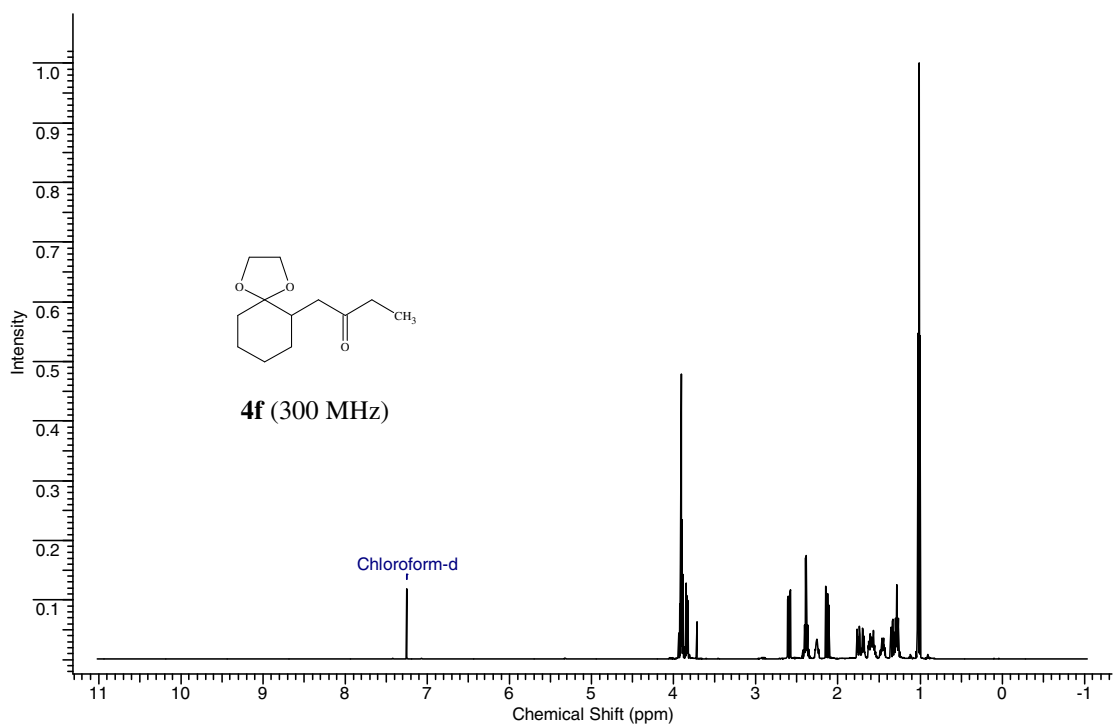
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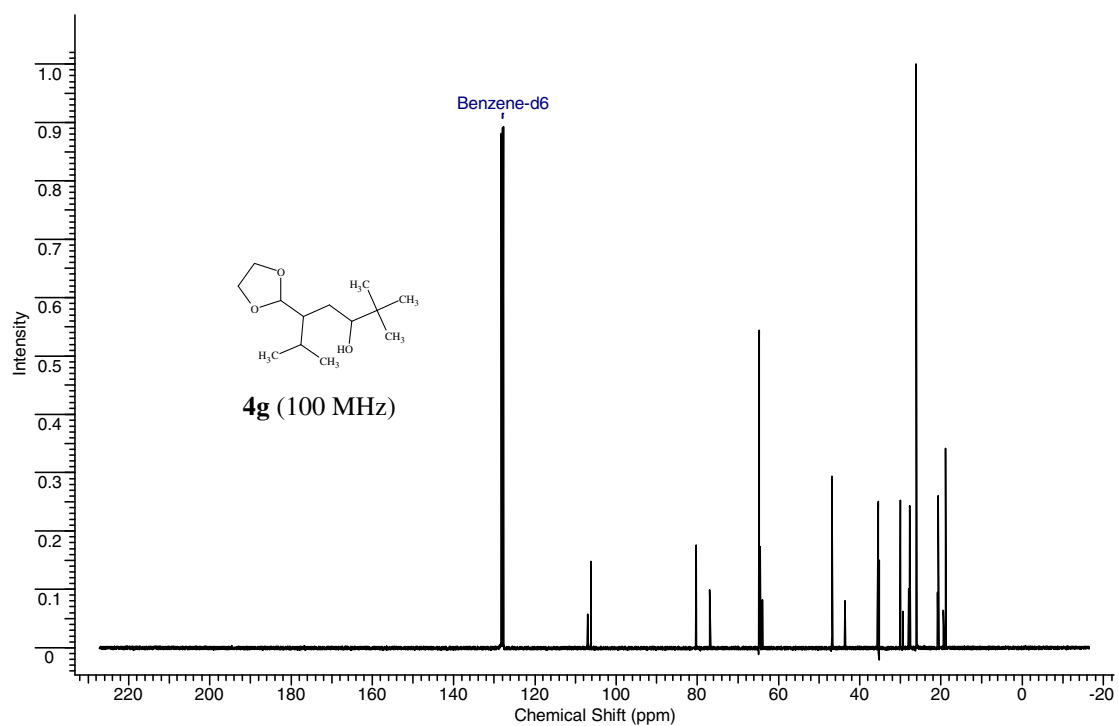
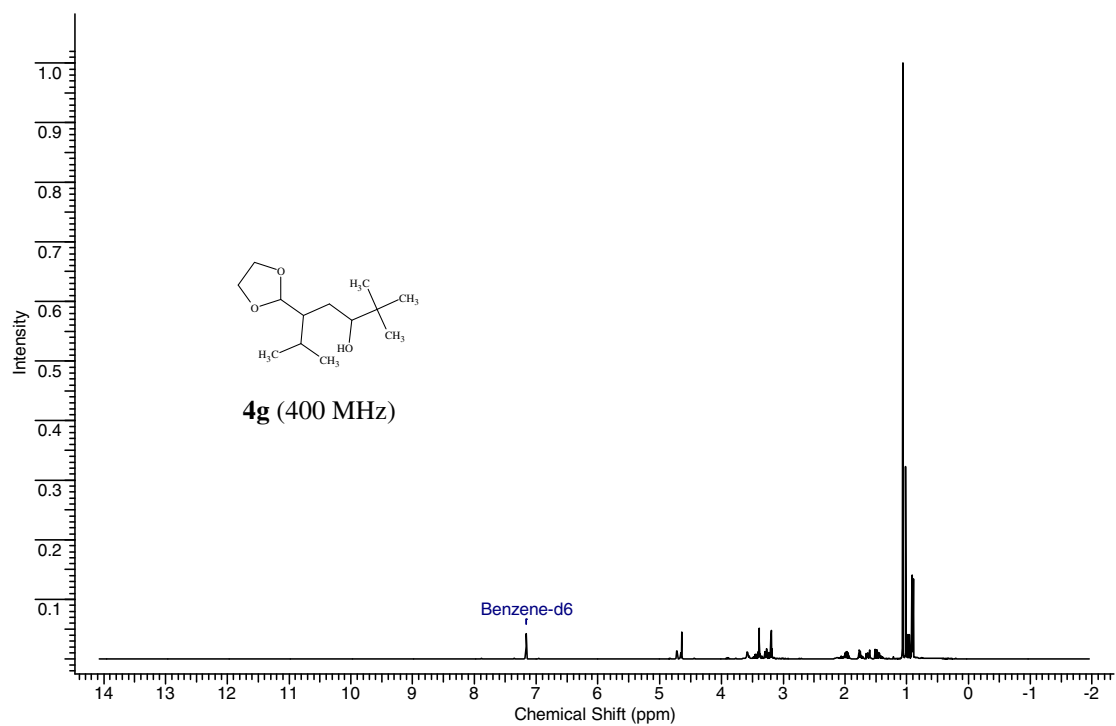


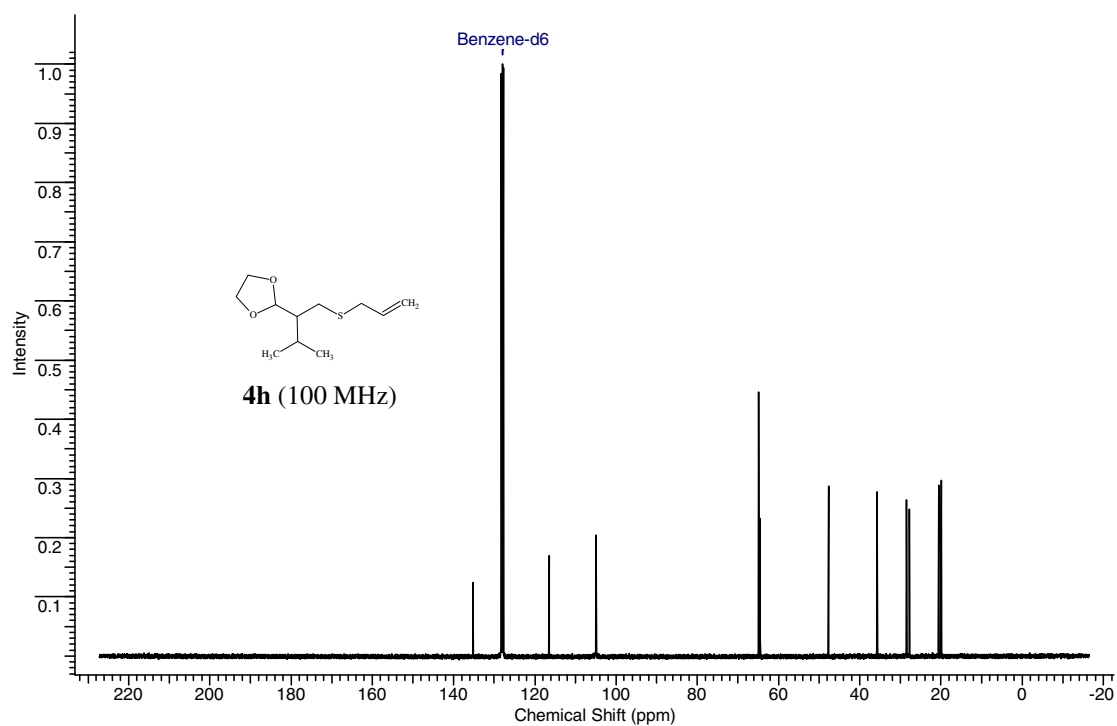
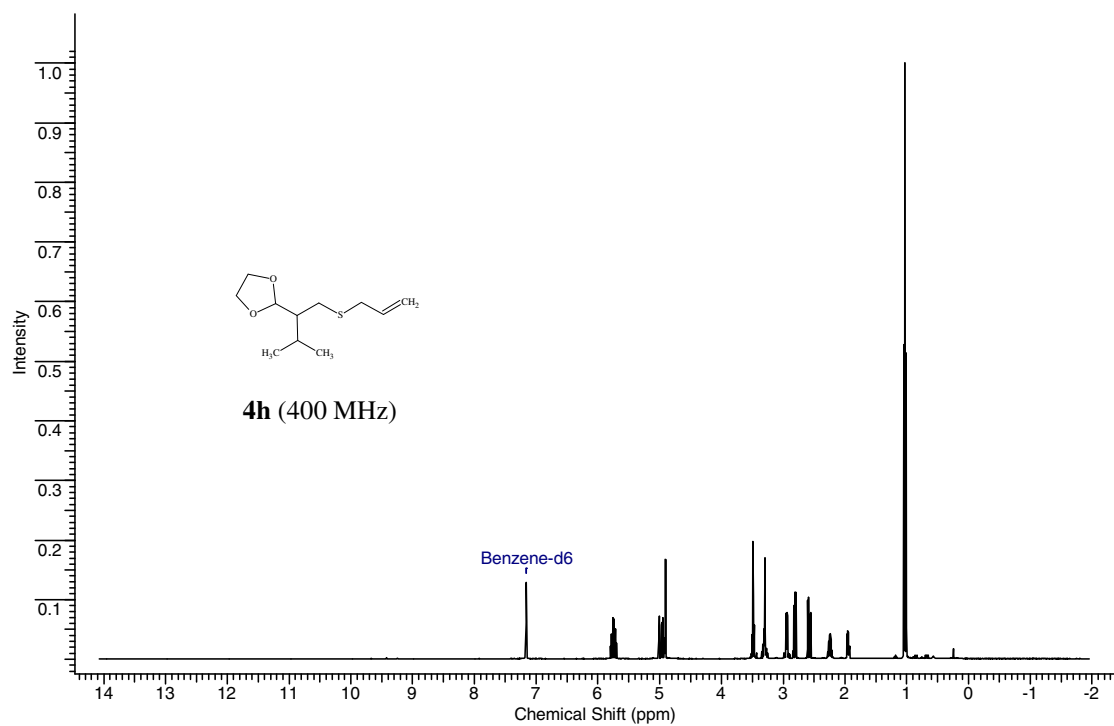


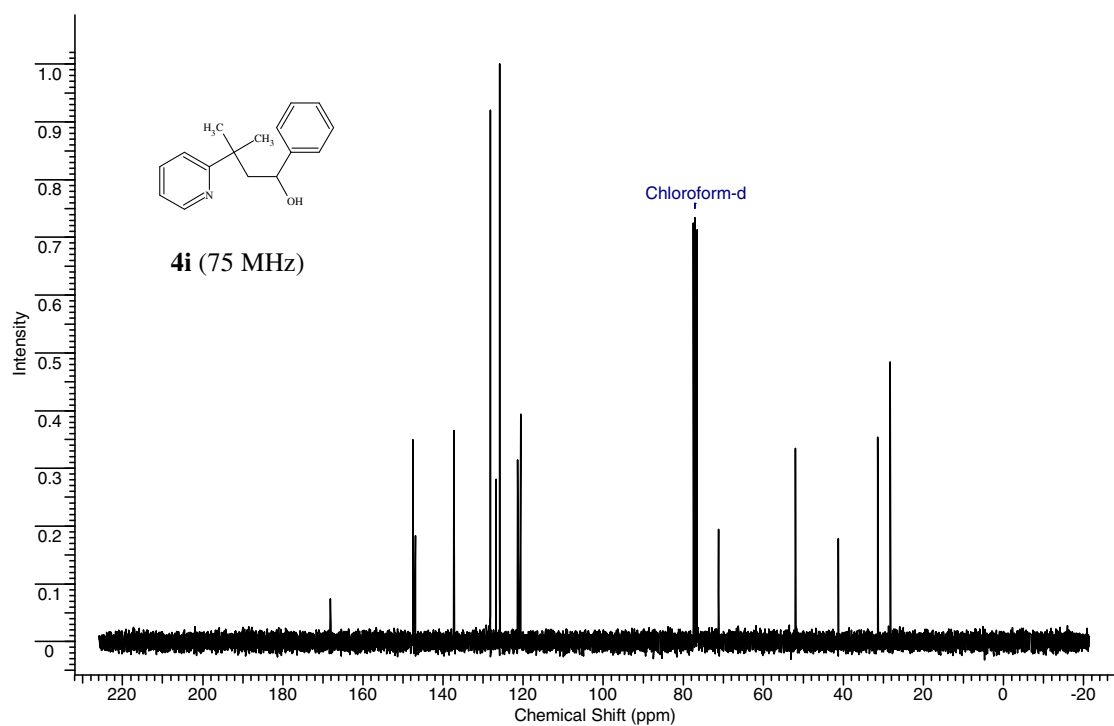
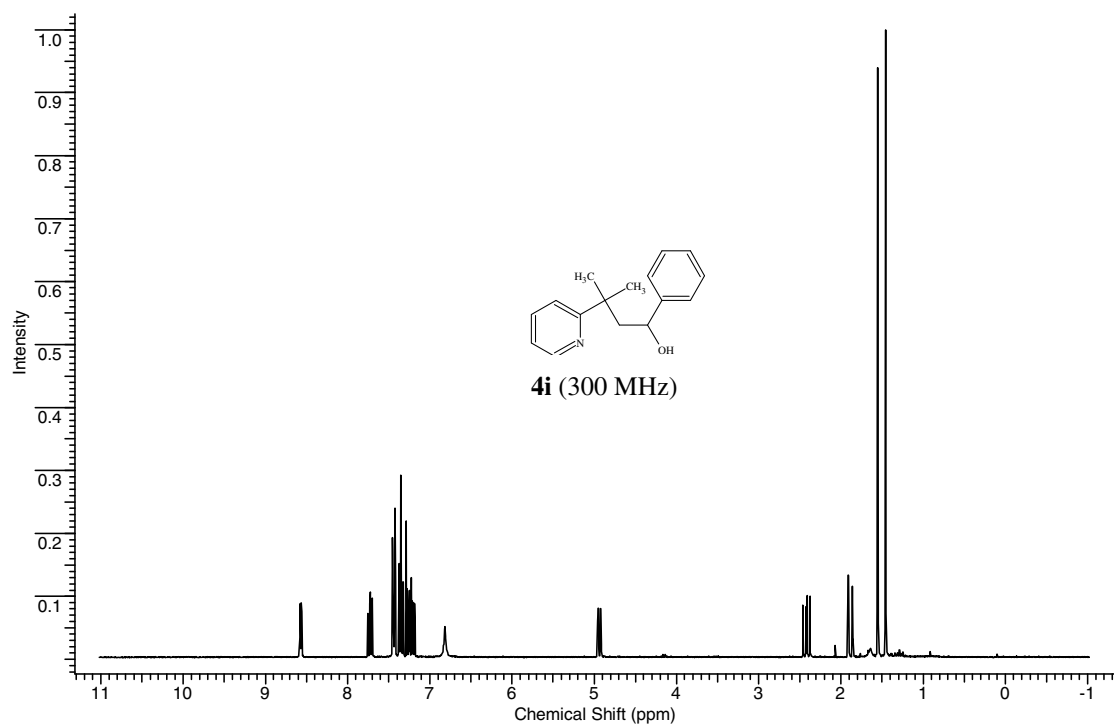


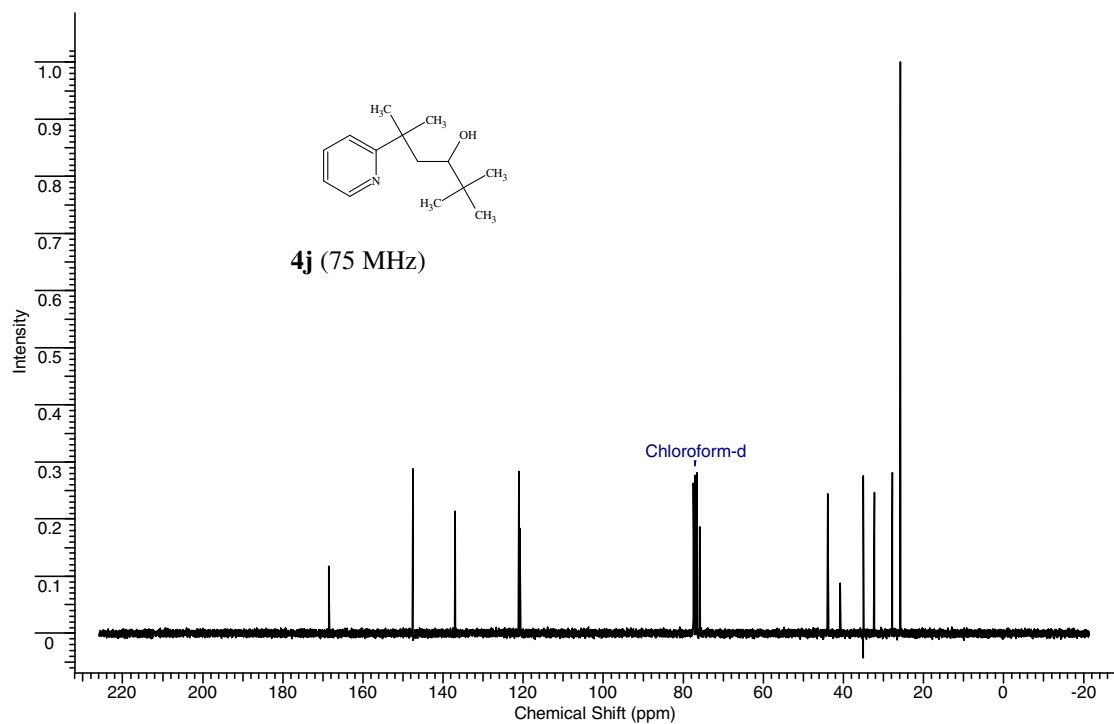
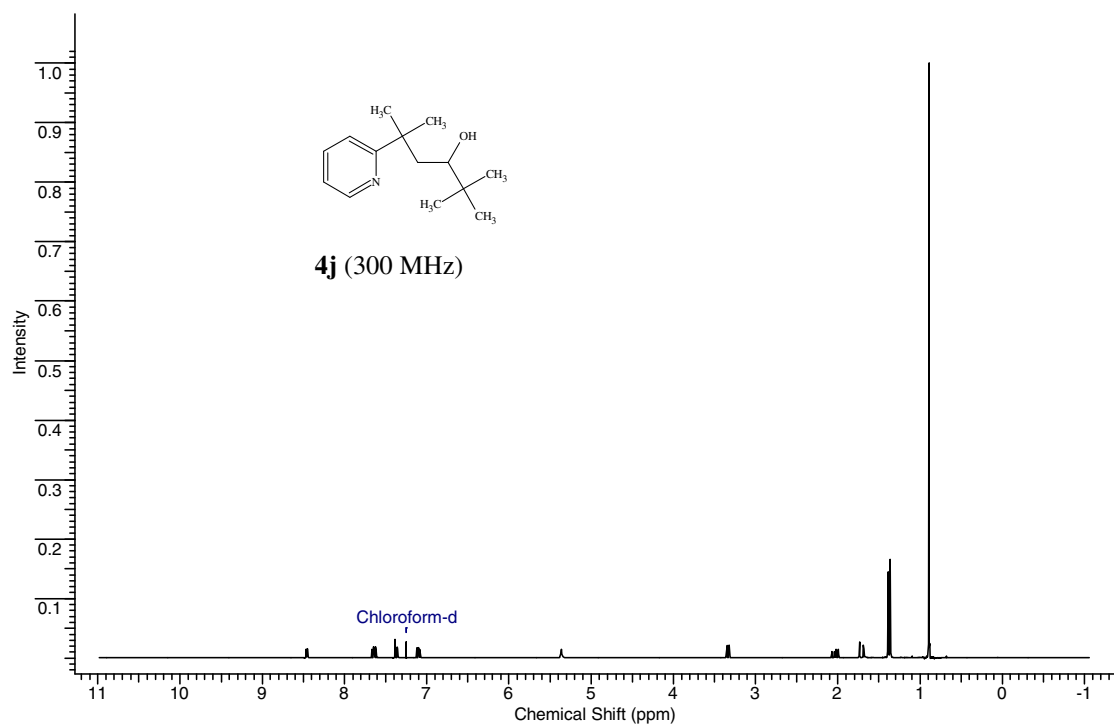


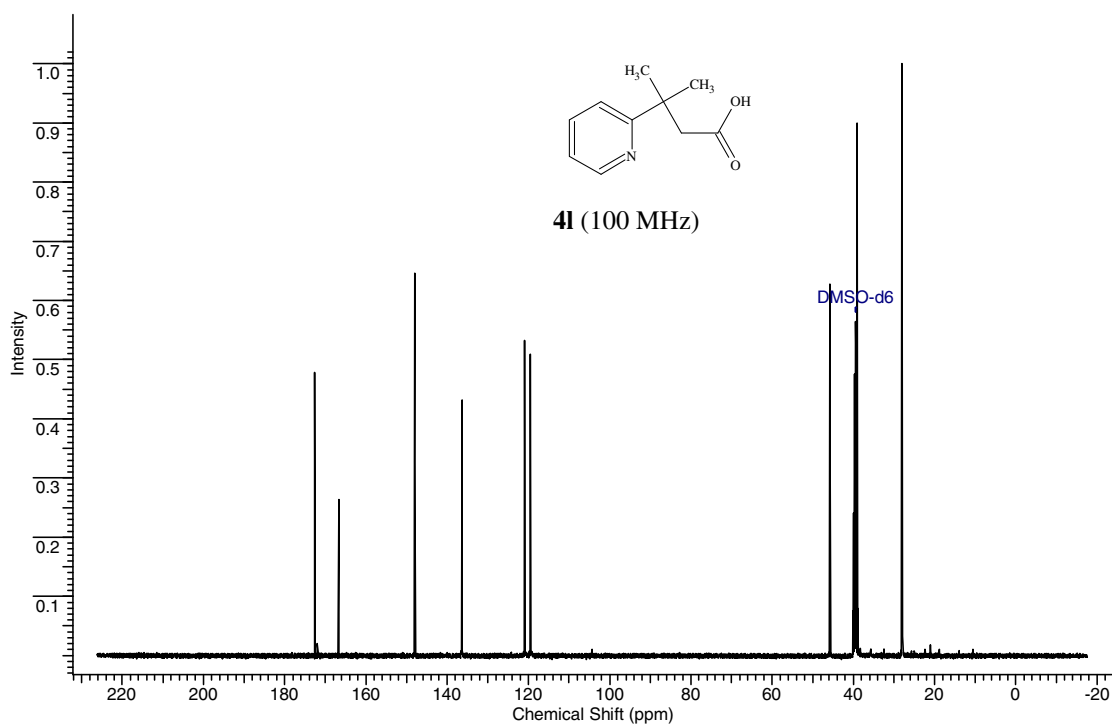
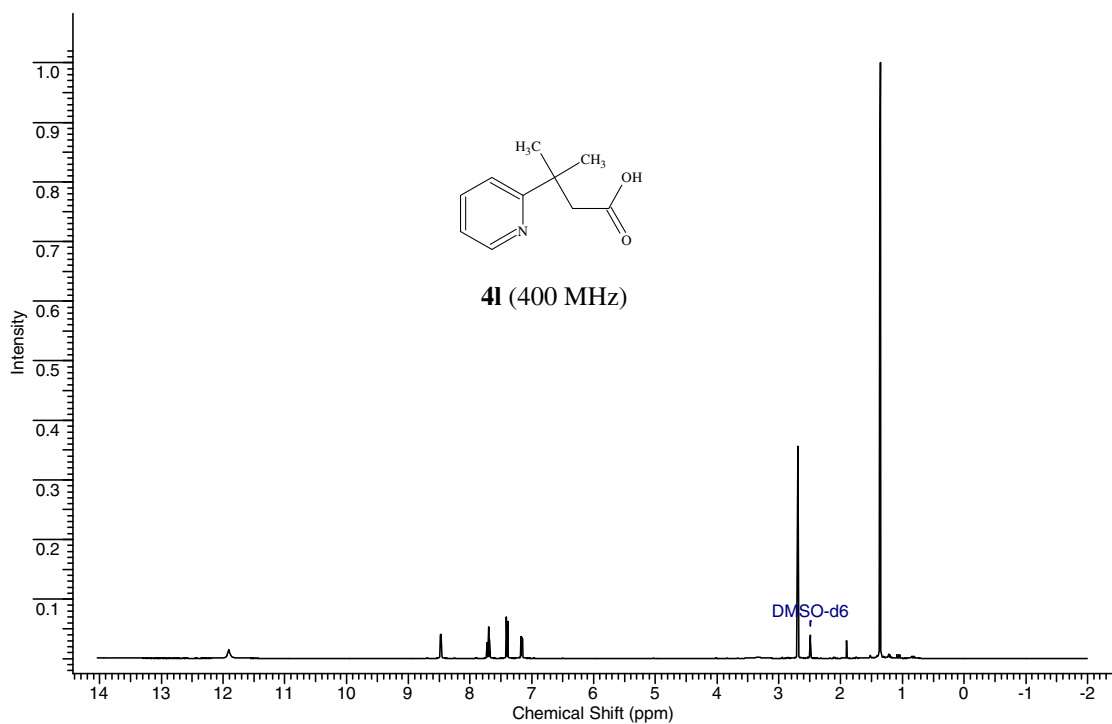


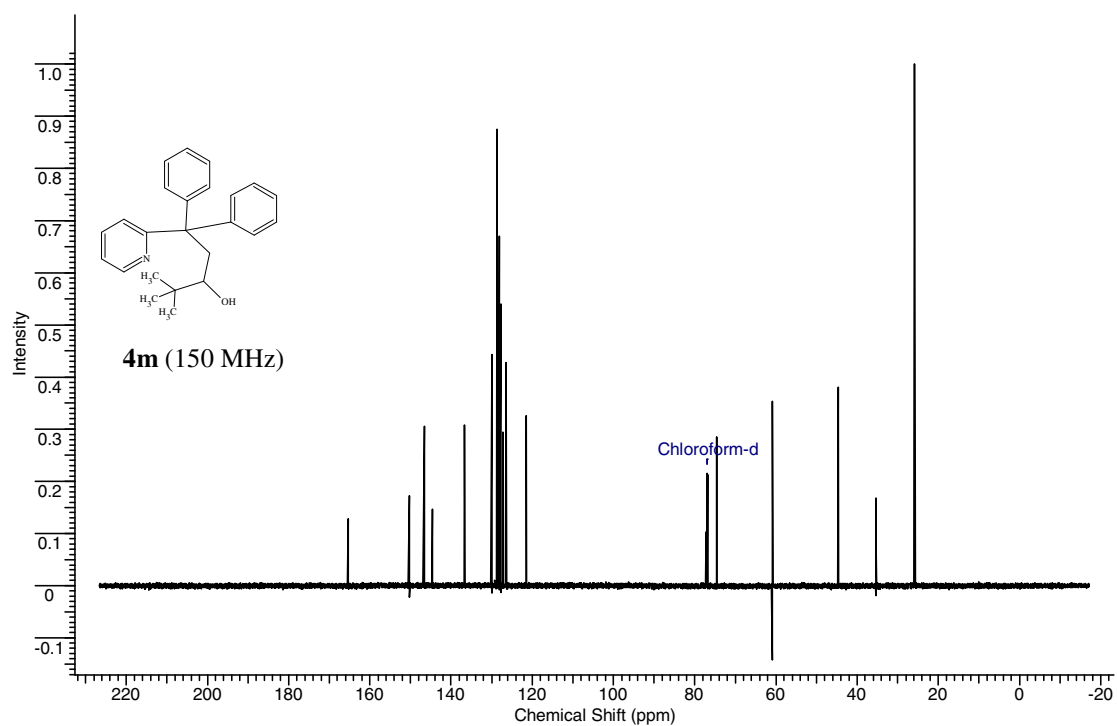
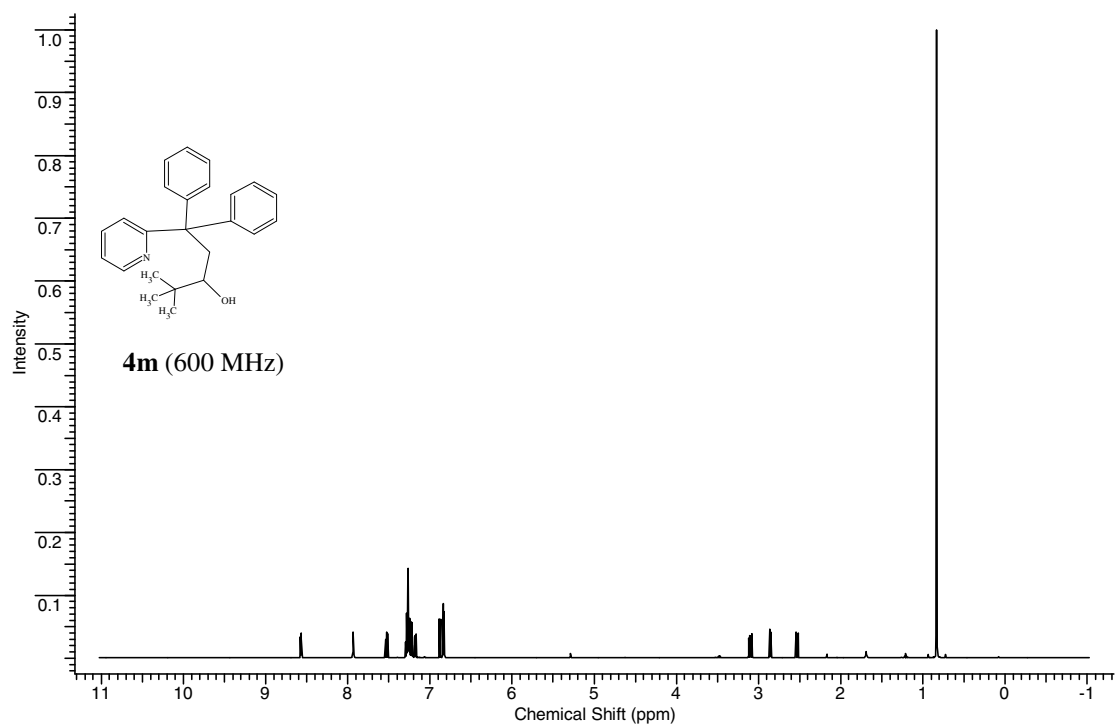


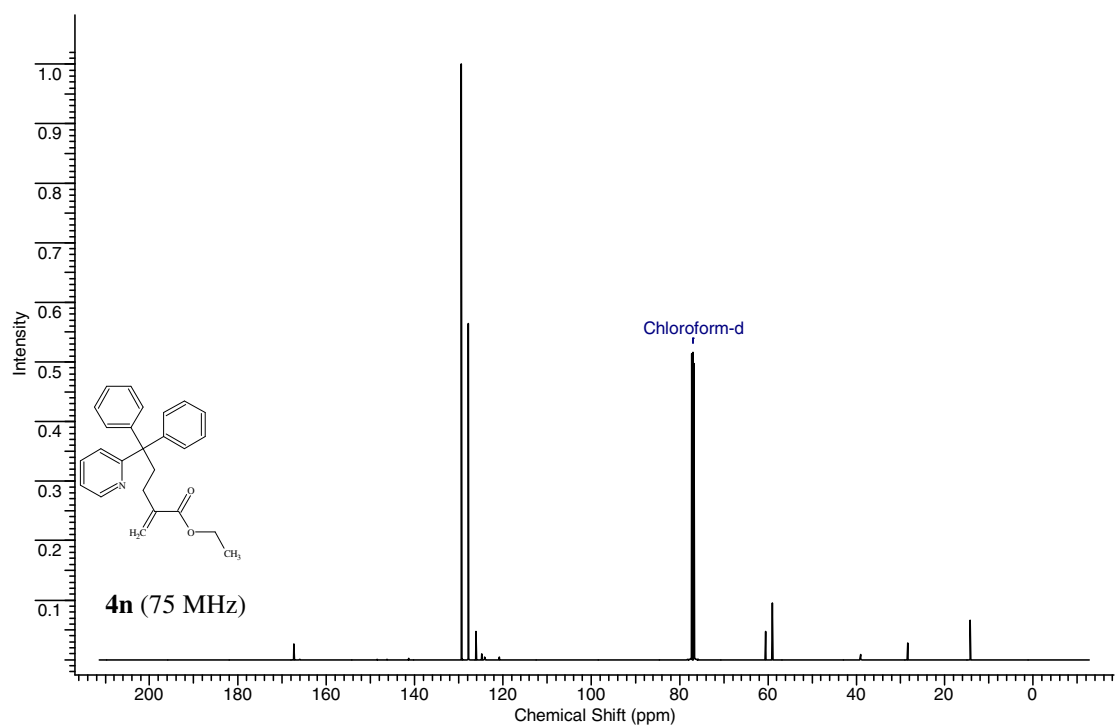
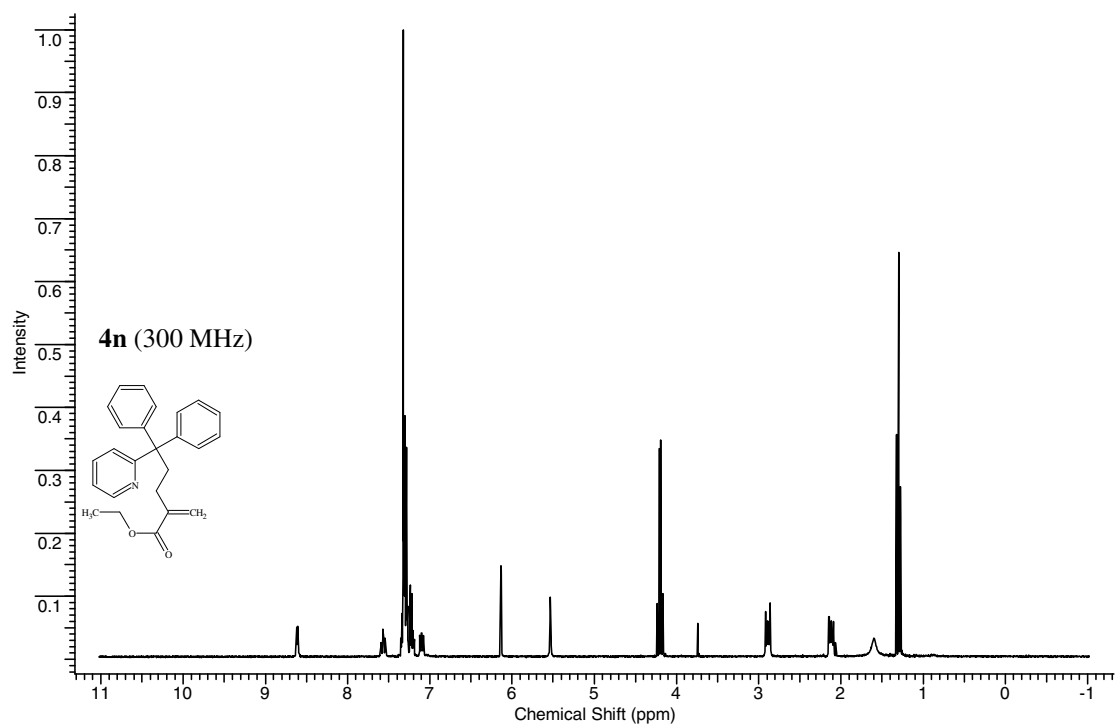


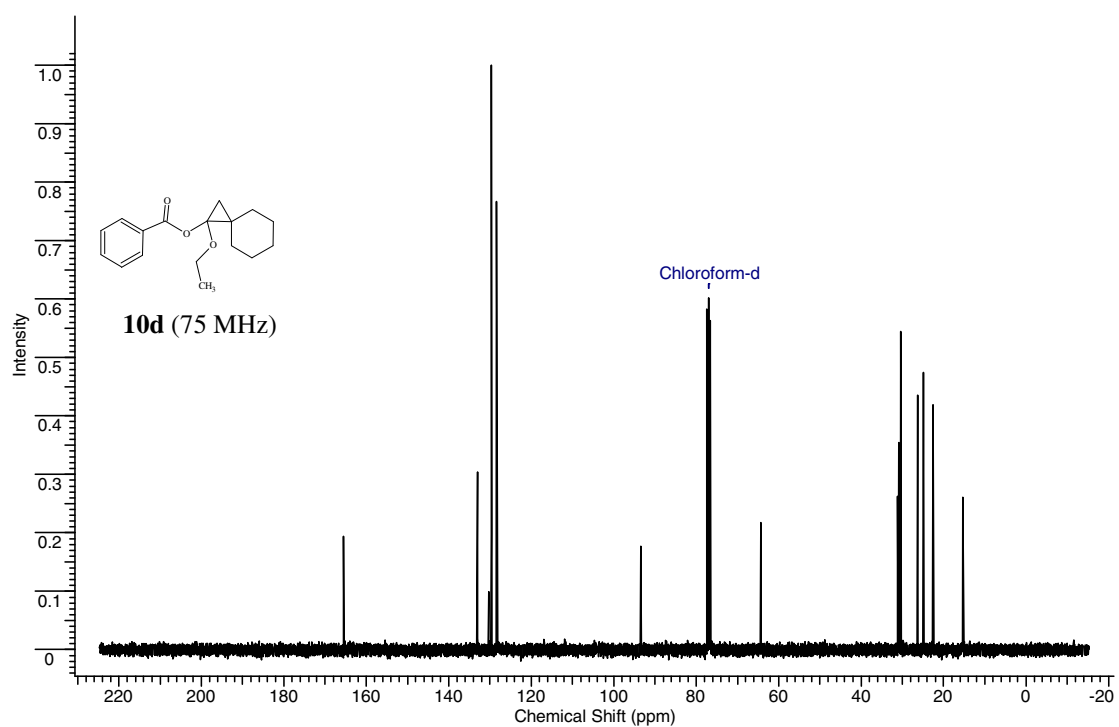
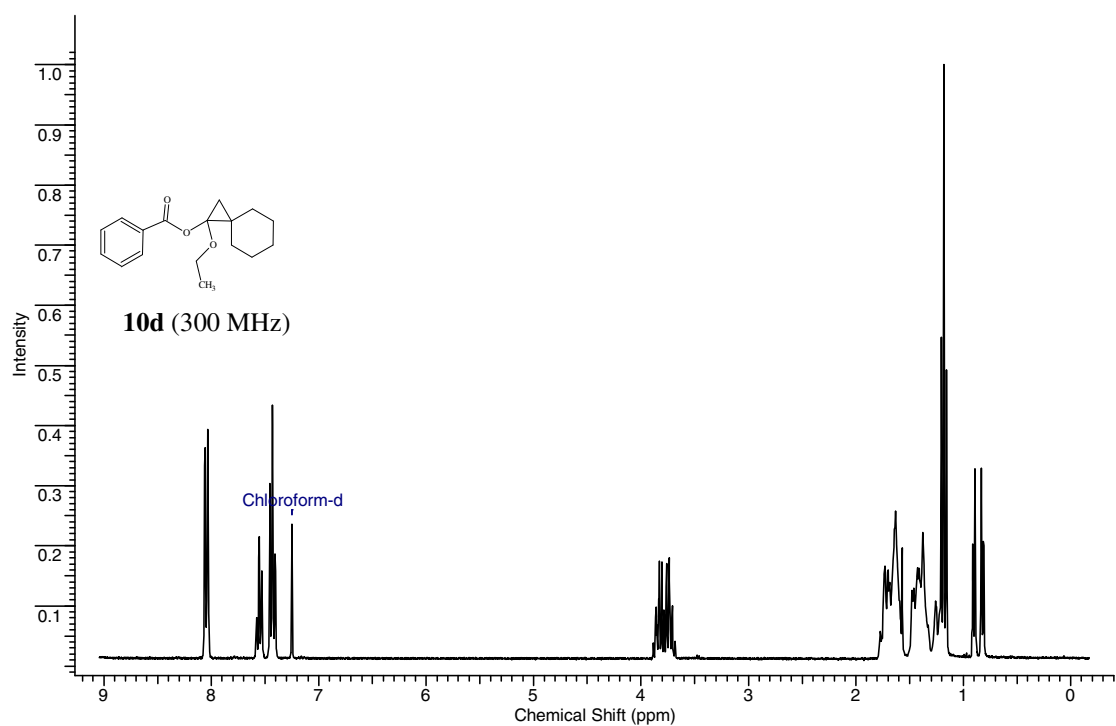




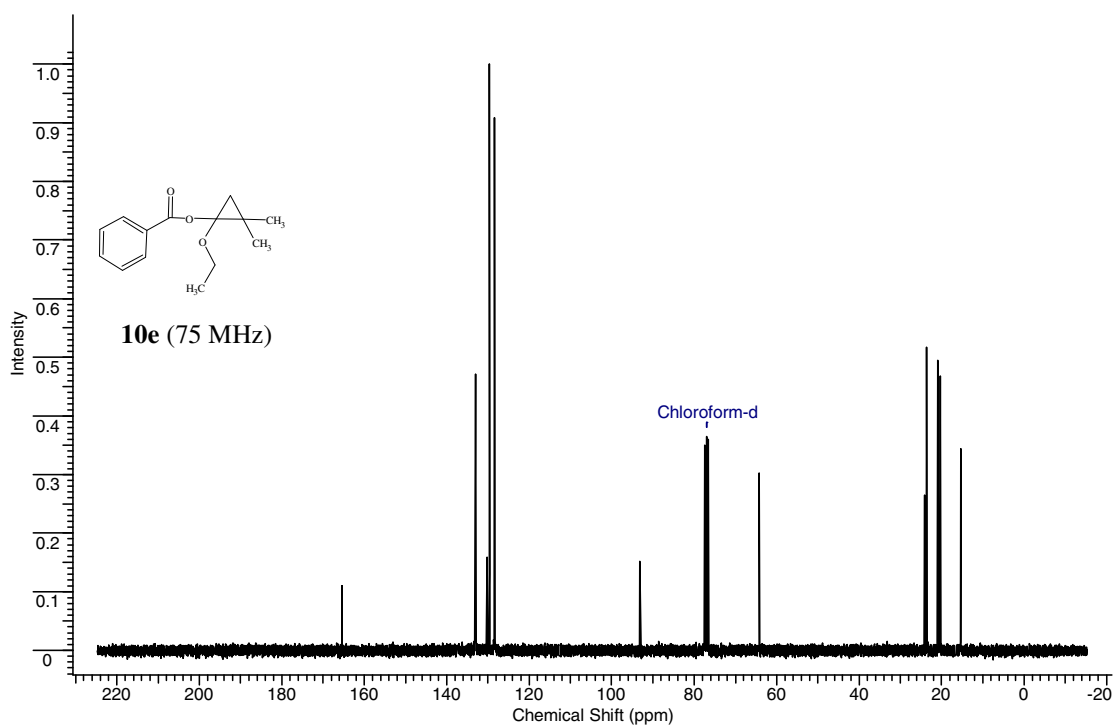
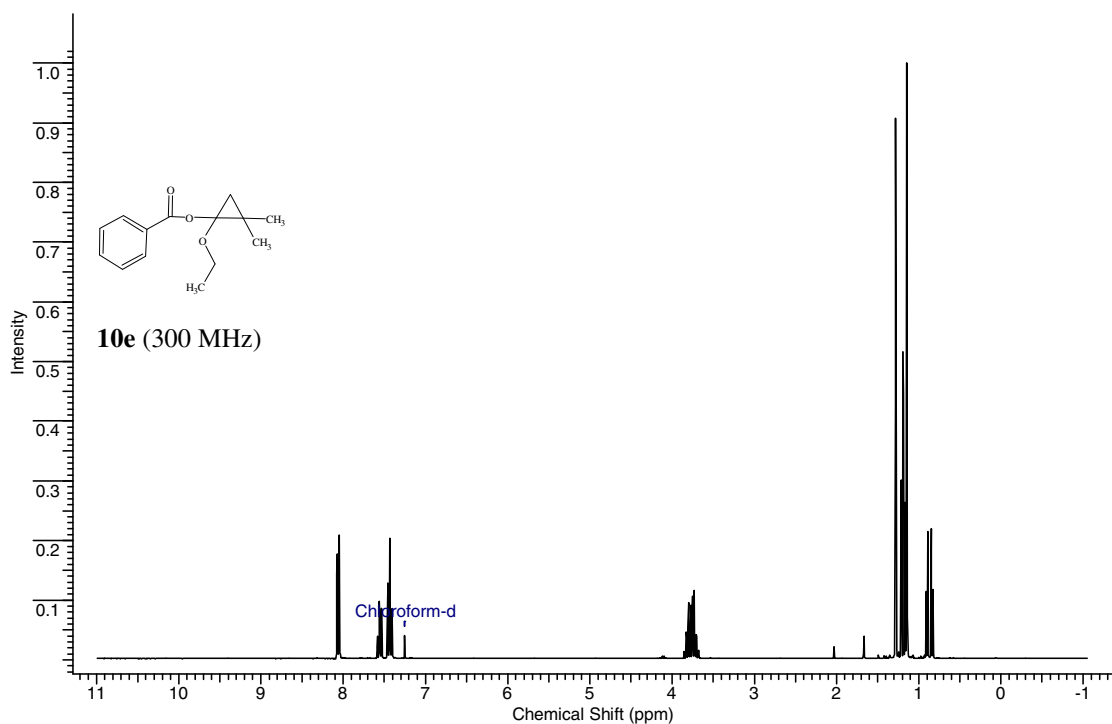












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