

**Carbonylative Ring Opening of Terminal Epoxides at Atmospheric Pressure**

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**SUPPORTING INFORMATION**

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**General Experimental**

All carbonylation reactions (except high pressure reactions) were performed in oven (150 °C) and/or flame dried Schlenk flasks. High-pressure reactions (41 bar CO) were performed in a custom built six-cell stainless steel autoclave. THF, CH<sub>2</sub>Cl<sub>2</sub> were dried by percolation through a column packed with neutral alumina and a column packed with Q5 reactant, a supported copper catalyst for scavenging oxygen, under a positive pressure of argon. Methanol was freshly distilled from Mg(OMe)<sub>2</sub> prior used. All terminal epoxides were used as received. Propylene oxide and cyclohexene oxide were heated to reflux over calcium hydride for 12 h, then were distilled, and stored in Schlenk flasks.

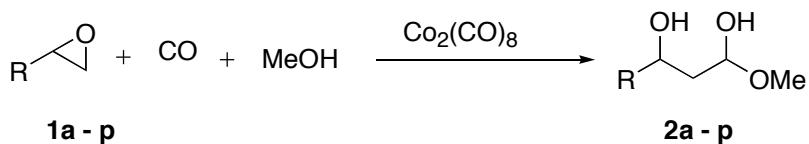
<sup>1</sup>H NMR, and <sup>13</sup>C NMR spectra were recorded at 400 MHz or 500 MHz. Spectra are

referenced to residual chloroform ( $\delta$  7.26 ppm,  $^1\text{H}$ ;  $\delta$  77.0 ppm,  $^{13}\text{C}$ ). Chemical shifts are reported in ppm. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), hept (heptet), and br (broad). Coupling constants  $J$ , are reported in Hertz. Low-resolution electron impact (EI) mass spectra were obtained with a typical ionization voltage of 70 eV. Chemical ionization (CI) spectra were obtained using methane as the carrier gas. Data are reported in the form of ( $m/z$ ). Infrared spectra (IR) are reported in  $\text{cm}^{-1}$  with indicated relative intensities: s (strong, 67-100%); m (medium, 34-66%); w (weak, 0-33%). Melting point (mp) was determined in sealed tubes and are corrected. Analytical thin-layer chromatography was performed on Merck silica gel 60 with F-254 indicator (pre coated plates). Visualization was accomplished with *p*-anisaldehyde stain. Gas chromatography (GC) was performed using a flame ionization detector and a trifluoroacetyl  $\gamma$ -cyclodextrin (G-TA, 30 x 0.25 mm, manufactured by CHIRALDEX<sup>TM</sup>). The separations were performed with a  $\text{H}_2$  head pressure of 12 psi. Injector temperature was 250 °C; the detector temperature was 300 °C. Analytical supercritical fluid chromatography (SFC) was performed on packed-column SFC built-in photometric detector ( $\lambda$  = 220, 258 nm) using Daiciel Chiralpak OD column. Retention times ( $t_{\text{R}}$ ) and peak areas for SFC and GC were obtained from reporting integrators.

Epoxides **1a**, **1b**, **1c**, **1f**, **1g**, **1h**, **1i**, **1l**, **1p** were obtained from commercial vendors and used as received. Epoxides **1d**,<sup>1</sup> **1e**,<sup>2</sup> **1j**,<sup>3</sup> **1k**,<sup>4</sup> **1m**,<sup>5</sup> **1n**,<sup>6</sup> and **1o**,<sup>7</sup> were synthesized according to literature procedures. Carbon monoxide was received from Matheson TRI.GAS, C.P grade (CP = Chemically pure), lot number 4005200303. Dicobalt octacarbonyl was purchased from Strem Chemicals and was sublimed in 100 mL glass sublimation chamber at 0.5 mmHg pressure using acetone/dry ice cold finger at room temperature to 35 °C.

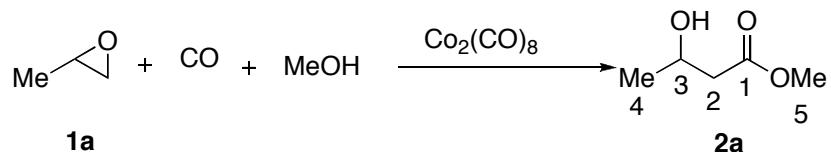
## Experimental Procedures

### General Procedure I. Dicobalt Octacarbonyl Catalyzed Carbonylation of 1a-p.



In a glove box,  $\text{Co}_2(\text{CO})_8$  (84.5 mg, 0.25 mmol. 0.05 equiv.) was placed in a 100-mL Schlenk flask equipped with a magnetic stir bar. The flask was sealed with a rubber septum and was removed from a dry box. The flask was purged three times for 2 sec. with carbon monoxide (filled in 12.7 cm latex balloon). Freshly distilled methanol (5.0 mL) was added and the mixture was stirred for 2 min. before the epoxides (5 mmol) was added in one portion. The mixture was allowed to stir at room temperature for 24 h. After the given reaction time, the carbon monoxide balloon was removed and carefully vented in the hood. The reaction mixture was diluted with ether (50 mL) and was stirred for 30 – 60 minutes to precipitate the cobalt complex. The mixture was passed through silica gel (20 X 100 mm), using diethyl ether as the eluent and upon careful removal of solvent *in vacuo* provided the products, that can be further purified (if necessary) by flash chromatography on silica gel using hexane/ethyl acetate as the eluent.

### Preparation of Methyl 3-Hydroxybutanoate (2a) [Table 2, Entry 1]



Following General Procedure I,  $\text{Co}_2(\text{CO})_8$  (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1a** (350  $\mu\text{L}$ , 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL)

and was stirred for 30 min., then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent under reduced pressure afforded 525 mg (89 %) of **2a** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>8</sup>

Data for **2a**:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

4.19 (m, 1 H), 3.70 (s, 3 H), 2.96 (d, 1 H), 2.49 (dd, *J* = 16.3, 3.4, 1 H), 2.42 (dd, *J* = 16.3, 8.7, 1 H), 1.22 (d, 3 H)

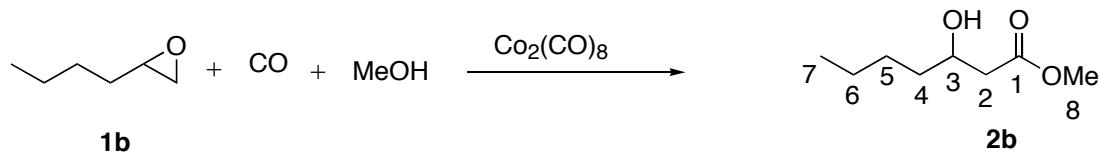
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

173.3, 64.2, 51.7, 42.5, 22.4

IR (neat)

3422 (s), 2975 (s), 2930 (s), 2093 (w), 1724 (s), 1439 (m), 1374 (m), 1299 (m), 1261 (m), 1176 (m), 1124 (m), 1088 (m), 1072 (m), 1006 (m), 946 (m), 851 (w)

**Preparation of Methyl 3-Hydroxyheptanoate (2b) [Table 2, Entry 2]**



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1b** (600  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min., then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 3/1) to afforded 710 mg (89 %) of **2b** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>9</sup>

Data for 2b:<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

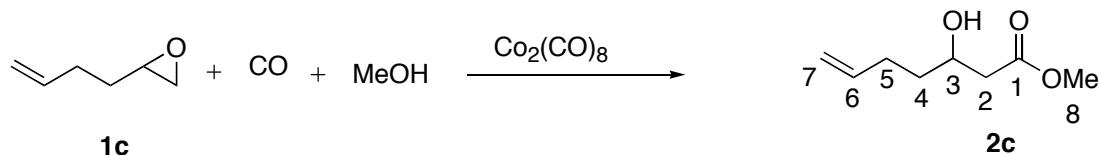
4.00 (m, 1 H), 3.71 (s, 3 H), 2.86 (d, 1 H), 2.51 (dd, *J* = 16.4, 3.0, 1 H), 2.40 (dd, *J* = 16.4, 9.1, 1 H), 1.29-1.53 (br m, 6 H) 0.90 (t, 3 H)

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

173.4, 67.9, 51.7, 41.1, 36.2, 27.6, 22.5, 13.9

IR (neat)

3446 (w), 2956 (m), 2932 (m), 2861 (w), 1738 (s), 1438 (m), 1291 (w), 1169 (m), 1125 (w), 1040 (w)

**Preparation of Methyl 3-Hydroxy-6-heptenoate (2c) [Table 2, Entry 3]**

Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1c** (564  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min., then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 3/1) to afforded 760 mg (96 %) of **2c** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>10</sup>

Data for 2c:<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

5.82 (m, 1 H), 5.05 (dq, 17.2, 1.7, 1 H), 4.98 (dq, 9.7, 1.4, 1 H), 4.03 (m, 1 H),

3.71 (s, 3 H), 2.90 (d, 1 H), 2.52 (dd,  $J = 16.6, 3.1, 1$  H), 2.43 (dd,  $J = 16.3, 9.0, 1$  H), 2.18 (m, 2 H), 1.58 (m, 2 H)

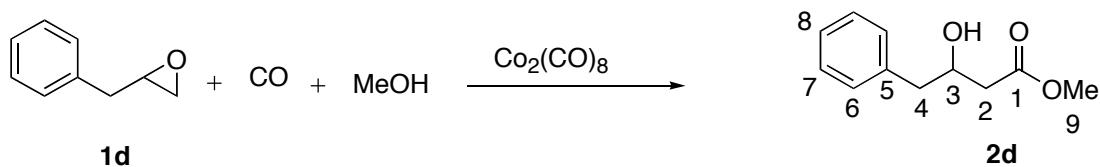
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

173.3, 137.9, 115.0, 67.4, 51.7, 41.1, 35.5, 29.7

IR (neat)

3445 (w), 3077 (w), 2923 (w), 2849 (w), 1737 (m), 1641 (w), 1438 (m), 1359 (w), 1295 (w), 1247 (w), 1200 (w), 1168 (w), 1121 (w), 1082 (w), 1062 (w), 995 (w), 912 (w)

### Preparation of Methyl 3-Hydroxy-4-phenylbutanoate (2d) [Table 2, Entry 4]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1d** (657  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min., then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 3/1) to afforded 529 mg (54 %) of **2d** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>11</sup>

#### Data for 2d:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

7.31 (br t, 2 H), 7.21-7.25 (br m, 3 H), 4.27 (m, 1 H), 3.70 (s, 3 H), 2.86 (m, 2 H), 2.67 (dd,  $J = 13.6, 6.1, 1$  H), 2.53 (dd,  $J = 16.3, 3.4, 1$  H), 2.46 (dd,  $J = 16.3, 8.8,$

1 H), 1.22 (d, 3 H)

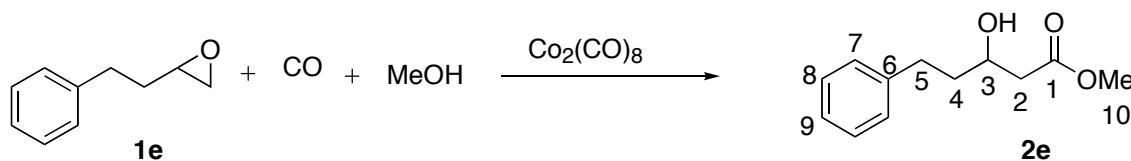
**<sup>13</sup>C NMR** (125 MHz, CDCl<sub>3</sub>)

173.0, 137.5, 129.3, 128.5, 126.6, 69.0, 51.7, 42.9, 40.3

**IR** (neat)

3433 (m), 3087 (w), 3063 (w), 3029 (w), 3004 (w), 2953 (s), 2852 (w), 1731 (s), 1604 (m), 1495 (m), 1455 (m), 1439 (m) 1269 (s), 1200 (s), 1150 (s), 1083 (s), 1054 (s), 1030 (s), 995 (s), 854 (s), 749 (s), 701 (s)

### Preparation of Methyl 3-Hydroxy-5-phenylpentanoate (2e) [Table 2, Entry 5]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1e** (657  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min., then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 3/1) to afforded 625 mg (64 %) of **2e** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>12</sup>

#### Data for 2e:

**<sup>1</sup>H NMR** (500 MHz, CDCl<sub>3</sub>)

7.32 (m, 2 H), 7.25 (br m, 3 H), 4.06 (m, 1 H), 3.75 (s, 3 H), 3.05 (d, 1 H), 2.87 (m, 1 H), 2.75 (m, 1 H), 2.57 (dd, *J* = 16.6, 3.4, 1 H), 2.50 (dd, *J* = 16.6, 8.7, 1 H), 2.46 (dd, *J* = 16.3, 8.8, 1 H), 1.22 (d, 3 H), 1.88 (m, 1 H), 1.79 (m, 1 H)

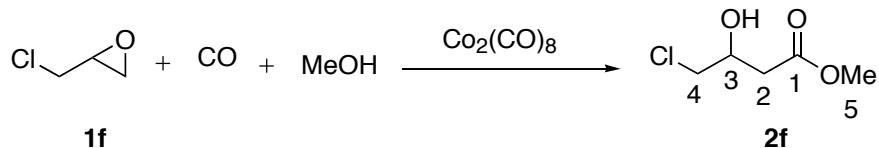
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

173.3, 141.6, 128.3, 128.5, 125.8, 67.1, 51.7, 41.1, 38.0, 31.7

IR (neat)

3447 (w), 3085 (w), 3062 (w), 3027 (w), 3002 (w), 3027 (w), 2951 (w), 2861 (w), 1732 (s), 1603 (m), 1496 (m), 1454 (m), 1438 (s), 1302 (s), 1253 (s), 1175 (s), 1155 (s), 1080 (s), 1025 (s), 1002 (s), 936 (s) 749 (s), 700 (s)

### Preparation of Methyl 4-Chloro-3-Hydroxybutanoate (2f) [Table 2, Entry 6]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1f** (391  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min. in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 3/1) to afforded 556 mg (73 %) of **2f** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>13</sup>

### Data for 2f:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

4.26 (m, 1 H), 3.73 (s, 3 H), 3.61 (m, 2 H), 3.05 (d,  $J$  = 5.1, 1 H), 2.65 (m, 2 H), 1.22 (d, 3 H)

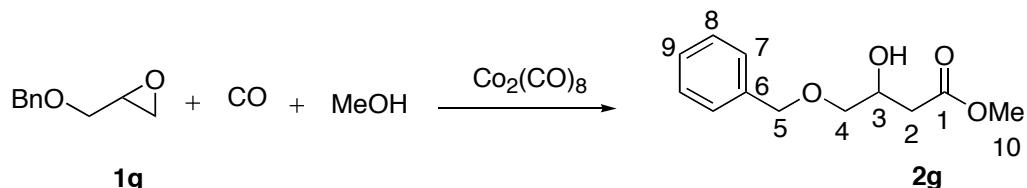
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

172.1, 67.9, 52.0, 48.1, 38.2

IR (neat)

3446 (m), 2956 (w), 2359 (w), 1734 (s), 1437 (m), 1370 (w), 1309 (w), 1266 (w), 1199 (w), 1152 (w), 1090 (w), 1057 (w), 961 (w), 926 (w), 853 (w), 759 (w)

### Preparation of Methyl 4-Benzyl-3-hydroxybutanoate (2g) [Table 2, Entry 7]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1g** (762  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 3/1) to afforded 935 mg (83 %) of **2g** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>14</sup>

### Data for 2g:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

7.29-7.36 (br m, 5 H), 4.56 (s, 2 H), 4.24 (m, 1 H), 3.69 (s, 3 H), 3.52 (dd, *J* = 9.5, 4.3, 1 H), 3.47 (dd, *J* = 9.6, 6.0, 1 H), 2.93 (d, *J* = 5.3, 1 H), 2.55 (d, *J* = 6.6, 2 H)

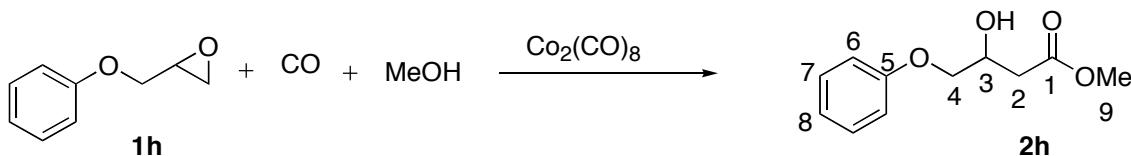
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

172.4, 137.7, 128.3, 127.7, 127.6, 73.3, 73.0, 67.1, 51.7, 38.0

IR (neat)

3453 (m), 3030 (w), 2946 (w), 2931 (w), 2863 (w), 1737 (s), 1496 (w), 1453 (m), 1438 (m), 1361 (m), 1255 (w), 1206 (w), 1170 (m), 1102 (m), 1005 (w), 739 (m), 699 (m)

### Preparation of Methyl 4-Phenoxy-3-Hydroxybutanoate (2h) [Table 2, Entry 8]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1h** (678  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 3/1) to afforded 903 mg (86 %) of **2h** as white solid.

#### Data for 2h:

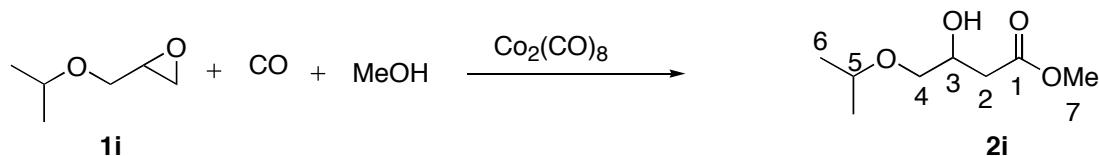
Mp 51-52 °C

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

7.27 (br t,  $J$  = 8.05, 2 H, HC(7)), 6.96 (br t,  $J$  = 7.3, 1 H, HC(8)), 6.90 (d,  $J$  = 7.8, 2 H, HC(6)), 4.42 (m, 1 H, HC(3)), 3.97 (d,  $J$  = 5.1, 2 H, HC(4)), 3.71 (s, 3 H, HC(9)), 3.40 (d,  $J$  = 4.8, 1 H, OH) 2.67 (m, 2 H, HC(2))

<u><sup>13</sup>C NMR</u>	(125 MHz, CDCl <sub>3</sub> )
	172.2 (C(1)), 158.2 (C(5)), 129.3 (C(7)), 120.9 (C(8)), 114.3 (C(6)), 70.5(C(4)), 66.5 (C(3)), 51.7 (C(9)), 37.8 (C(2))
<u>IR</u>	(neat)
	3450 (w), 2952 (w), 2868 (w), 1735 (s), 1599 (m), 1587 (m), 1497 (m), 1454 (w), 1438 (m), 1364 (w), 1292 (m), 1245 (s), 1172 (m), 1078 (w), 1043 (m), 1000 (w), 925 (w), 884 (w), 814 (w), 755 (m), 692 (m)
<u>MS</u>	(CI, 70 eV)
	210 (3), 193 (5), 179 (37), 161 (96), 147 (8), 133 (57), 119 (100), 107 (23), 95 (28), 85 (25), 71 (17), 59 (26)
<u>TLC</u>	Rf0.20 (hexane/EtOAc, 4/1) [silica gel, p-anisaldehyde stain]
<u>Analysis</u>	C <sub>11</sub> H <sub>14</sub> O <sub>4</sub> (210.23)
	Calculated: C, 62.85; H, 6.71 %
	Found: C, 63.19; H, 6.68 %

### Preparation of Methyl 4-(1-Methylethoxy)-3-Hydroxybutanoate (2i) [Table 2, Entry 9]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1i** (632 µL, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography

(SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 3/1) to afforded 703 mg (80 %) of **2i** as clear colorless oil.

Data for **2i**:

bp 95 °C at 0.5 mmHg

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

4.13 (m, 1 H, HC(3)), 3.68 (s, 3 H, HC(7)), 3.57 (hept, *J* = 12.2, 6.1, 1 H, HC(5)), 3.43 (dd, *J* = 9.3, 4.5, 1 H, HC(4)), 3.35 (dd, *J* = 9.5, 6.1, 1 H, HC(4)), 2.97 (d, *J* = 4.6, 1 H, OH), 2.51 (d, *J* = 6.1, 2 H, HC(2)), 1.12 (d, *J* = 6.1, 6 H, HC(6)),

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

172.4 (C(1)), 72.1 (C(5)), 71.0 (C(4)), 67.3 (C(3)), 51.7 (C(7)), 38.1 (C(2)), 22.0 (C(6)), 21.9 (C(6))

IR (neat)

3450 (s), 2973 (s), 2930 (s), 2873 (s), 2630 (w), 1736 (s), 1438 (s), 1369 (s), 1336 (s), 1256 (s), 1163 (s), 1129 (s), 1075 (s), 1007 (m), 938 (m), 1599 (m), 884 (w), 824 (w)

MS (CI, 70 eV)

177 (M<sup>+1</sup>, 100), 159 (55), 145 (62), 135 (74), 117 (75), 103 (80), 85 (69), 71 (37), 61 (42)

TLC *R*f0.22 (hexane/EtOAc, 4/1) [silica gel, p-anisaldehyde stain]

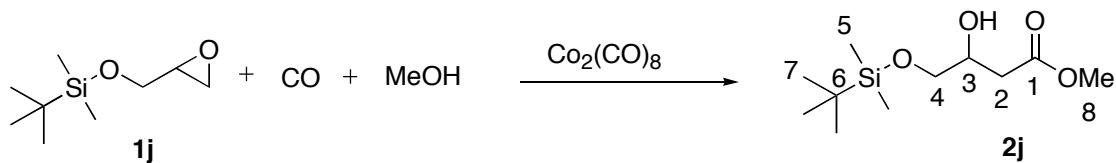
Analysis C<sub>8</sub>H<sub>16</sub>O<sub>4</sub> (176.21)

Calculated: C, 54.53; H, 9.15 %

Found: C, 54.44; H, 9.52 %

**Preparation of Methyl 4-[(1,1-Dimethylethyl)dimethylsilyl]oxy]-3-Hydroxybutanoate (2j)**

**[Table 2, Entry 10]**



Following General Procedure I,  $\text{Co}_2(\text{CO})_8$  (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1j** (1000  $\mu\text{L}$ , 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography ( $\text{SiO}_2$ , 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 4/1) to afforded 272 mg (22 %) of **2j** as clear colorless oil.

Data for 2j:

bp 135 °C at 0.5 mmHg

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )

4.08 (m, 1 H, HC(3)), 3.71 (s, 3 H, HC(8)), 3.63 (dd,  $J = 10.0, 4.8$ , 1 H, HC(4)), 3.56 (dd,  $J = 10.0, 5.8$ , 1 H, HC(4)), 2.83 (d,  $J = 4.8$ , 1 H, OH), 2.52 (m, 2 H, HC(2)), 0.89 (s, 9 H, HC(7)), 0.06 (s, 6 H, HC(5))

$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )

172.5 (C(1)), 68.5 (C(3)), 66.1 (C(4)), 51.8 (C(8)), 37.7 (C(2)), 25.8 (C(7)), 18.3 (C(6)), -5.45(C(5)), -5.47(C(5))

IR (neat)

3475 (s), 2950 (s), 2930 (s), 2858 (s), 2733 (w), 2713 (w), 1736 (s), 1463 (s), 1438 (s), 1362 (s), 1253 (s), 1169 (s), 1119 (s), 1072 (s), 1006 (m), 939 (m), 836

(s), 777 (s), 670 (m)

MS (CI, 70 eV)

249 ( $M^{+1}$ , 84), 233 (82), 217 (100), 191 (90), 173 (88), 159 (90), 131 (75), 117 (91), 85 (67), 75 (66), 59 (75)

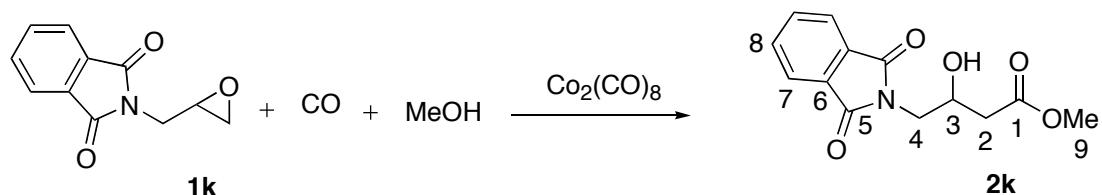
TLC  $R_f$  0.23 (hexane/EtOAc, 4/1) [silica gel, p-anisaldehyde stain]

### Analysis C<sub>11</sub>H<sub>24</sub>O<sub>4</sub>Si (176.21)

Calculated: C, 53.19; H, 9.74 %

Found: C, 52.92; H, 9.99 %

**Preparation of Methyl 4-(N-Pthalimido)-3-Hydroxybutanoate (2k) [Table 2, Entry 11]**



Following General Procedure I,  $\text{Co}_2(\text{CO})_8$  (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1k** (1.01 g, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography ( $\text{SiO}_2$ , 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 1.5/1) to afforded 975 mg (22 %) of **2k** as white solid.

### Data for 2k:

mp 124-126 °C

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

7.86 (dd, *J* = 5.3, 2.9, 2 H, HC(8)), 7.73 (dd, *J* = 5.4, 3.0, 2 H, HC(7)), 4.36 (m, 1 H, HC(3)), 3.89 (dd, *J* = 14.0, 7.2, 1 H, HC(4)), 3.77 (dd, *J* = 13.8, 4.6, 1 H, HC(4)), 3.71 (s, 3 H, HC(9)), 3.2 (d, *J* = 4.8, 1 H, OH), 2.61 (dd, *J* = 16.6, 3.9, 1 H, HC(2)), 2.53 (dd, *J* = 16.6, 8.3, 1 H, HC(2))

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

172.0 (C(1)), 168.4 (C(5)), 134.0(C(6)), 131.7 (C(8)), 123.3 (C(7)), 66.4 (C(3)), 51.8 (C(9)), 42.8 (C(4)), 38.8 (C(2))

IR (neat)

3480 (w), 2952 (w), 1773 (w), 1711 (s), 1467 (w), 1435 (w), 1395 (m), 1301 (w), 1192 (w), 1172 (w), 1058 (w), 1023 (w), 884 (w), 725 (m)

MS (CI, 70 eV)

264 (M<sup>+1</sup>, 93), 260 (1), 247 (3), 246 (19), 245, (4), 232 (15), 214 (58), 186 (43), 162 (16), 161 (100), 160 (52), 133 (32), 132 (19), 117 (25), 105 (21), 104 (27),

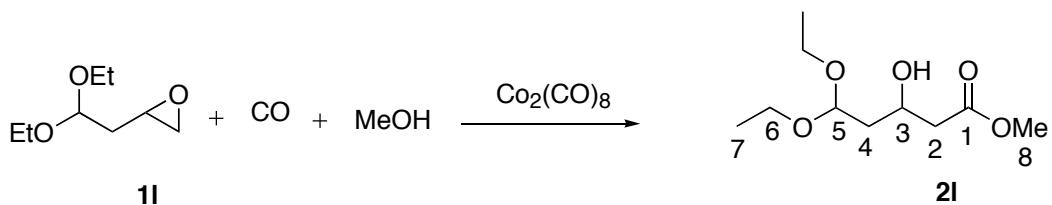
TLC *Rf*0.21 (hexane/EtOAc, 1/1) [silica gel, p-anisaldehyde stain]

Analysis C<sub>13</sub>H<sub>13</sub>NO<sub>5</sub> (263.25)

Calculated: C, 59.31; H, 4.98 N, 5.32 %

Found: C, 59.12; H, 4.92 N, 5.35 %

**Preparation of Methyl 5,5-Diethoxy-3-Hydroxybutanoate (2l) [Table 2, Entry 12]**



Following General Procedure I,  $\text{Co}_2(\text{CO})_8$  (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1l** (800  $\mu\text{L}$ , 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography ( $\text{SiO}_2$ , 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 4/1) to afforded 120 mg (11 %) of **2l** as clear colorless oil.

Data for **2l**:

bp 80 °C at 0.5 mmHg

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )

7.86 (t,  $J = 5.4, 10.9$ , 1 H, HC(5)), 4.23 (m, 1 H, HC(3)), 3.70 (s, 3 H, HC(8)), 3.66 (m, 2 H, HC(6)), 3.52 (m, 2 H, HC(6)), 3.52 (m, 1 H, OH), 2.49 (m, 2 H, HC(2)), 1.21 (t,  $J = 14.1, 7.0$ , 3 H, HC(7)), 1.21 (t,  $J = 13.9, 6.9$ , 3 H, HC(7))

$^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )

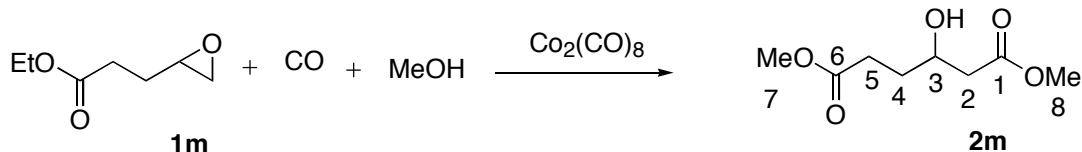
172.6 (C(1)), 101.5 (C(5)), 65.1 (C(3)), 62.2 (C(6)), 61.9 (C(6)), 51.7 (C(8)), 41.4 (C(4)), 39.9 (C(2)), 15.3 (C(7)), 15.3 (C(7))

IR (neat)

3468 (m), 2976 (m), 2925 (m), 1736 (s), 1438 (w), 1374 (w), 1346 (w), 1266 (w), 1168 (m), 1126 (m), 1060 (m), 1008 (w)

<u>MS</u>	(CI, 70 eV)
	243 (M <sup>+</sup> +Na, 3), 229 (4), 219 (M <sup>-1</sup> , 1), 211 (1), 205 (1), 191 (2), 185, (1), 177 (18), 163 (1), 157 (100), 145 (16), 125 (8)
<u>TLC</u>	R <sub>f</sub> 0.22 (hexane/EtOAc, 4/1) [silica gel, p-anisaldehyde stain]
<u>Analysis</u>	C <sub>10</sub> H <sub>20</sub> O <sub>5</sub> (220.26)
	Calculated: C, 54.53; H, 9.15 %
	Found: C, 54.64; H, 9.47 %

### Preparation of Dimethyl 6-Ethyl-3-hydroxyhexanedioate (2m) [Table 2, Entry 13]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1m** (720  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 4/1) to afforded 185 mg (18 %) of **2m** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>15</sup>

#### Data for 2m:

<u><sup>1</sup>H NMR</u>	(500 MHz, CDCl <sub>3</sub> )
	4.04 (m, 1 H), 3.72 (s, 3 H), 3.68 (s, 3 H), 3.08 (d, 1 H), 1.75-1.88 (m, 2 H), 2.40-2.55 (m, 4 H), 2.42 (dd, <i>J</i> = 16.2, 8.7, 1 H), 1.22 (d, 3 H)

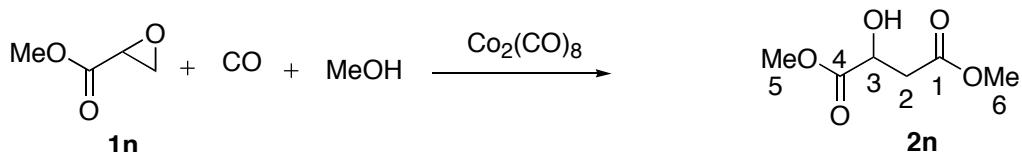
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

174.1, 173.0, 67.1, 51.8, 51.7, 41.1, 31.2, 30.2

IR (neat)

3530, 2950, 1740, 1674 (w), 1458 (m), 1375 (w), 1283 (m), 1243 (m), 1169 (m), 1119 (m), 1041 (w), 983 (w), 855 (w), 788 (w)

### Preparation of Dimethyl 2-Hydroxybutanedioate (2n) [Table 2, Entry 14]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1n** (440  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 4/1) to afforded 283 mg (35 %) of **2n** as clear colorless oil. NMR spectral data matched that previously reported in the literature.<sup>16</sup>

#### Data for 2n:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

4.49 (m, 1 H), 3.80 (s, 3 H), 3.70 (s, 3 H), 3.27 (d, 1 H), 2.86 (dd, *J* = 16.4, 4.2, 1 H), 2.78 (dd, *J* = 16.6, 6.1, 1 H)

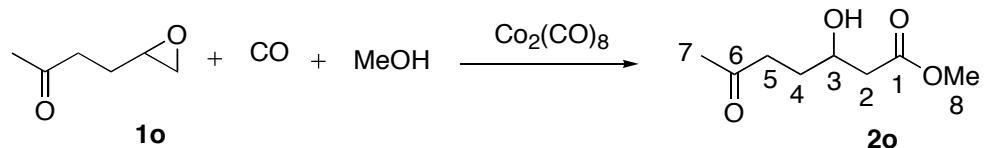
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

173.7, 170.9, 67.2, 52.8, 52.0, 38.3

IR (neat)

3458 (m), 3008 (w), 2958 (w), 1731 (s), 1640 (w), 1440 (m), 1370 (w), 1278 (m),  
1223 (m), 1173 (m), 1110 (m), 1045 (w), 992 (w), 849 (w), 786 (w)

**Preparation of Methyl 3-Hydroxy-6-oxo-heptanoate (2o) [Table 2, Entry 15]**



Following General Procedure I,  $\text{Co}_2(\text{CO})_8$  (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and **1o** (570  $\mu\text{L}$ , 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min in air, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography ( $\text{SiO}_2$ , 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 4/1) to afforded 148 mg (17 %) of **2o** as clear colorless oil.

Data for **2o**:

bp 170 °C at 0.5 mmHg

<sup>1</sup>H NMR (400 MHz,  $\text{CDCl}_3$ )

3.98 (m, 1 H, HC(3)), 3.71 (s, 3 H, HC(8)), 3.12 (d,  $J = 3.41$ , 1 H, OH), 2.64 (m, 2 H, HC(5)), 2.52 (d,  $J = 16.6$ , 3.4, 1 H, HC(2)), 2.44 (d,  $J = 16.6$ , 8.5, 1 H, HC(2)), 2.17 (s, 3 H, HC(7)), 1.76 (m, 1 H, HC(4)), 1.70 (m, 1 H, HC(4))

<sup>13</sup>C NMR (125 MHz,  $\text{CDCl}_3$ )

208.9 (C(6)), 173.2 (C(1)), 67.2 (C(3)), 51.8 (C(8)), 41.2 (C(2)), 39.6 (C(5)), 30.0 (C(4)), 29.9 (C(7))

IR (neat)

3461 (m), 2953 (m), 1736 (s), 1711 (s), 1437 (s), 1363 (s), 1283 (s), 1259 (s), 1197 (s), 1170 (s), 1095 (m), 1012 (m), 934 (w), 885 (w)

MS (ES, 70 eV)

197 ( $M^+ + \text{Na}$ , 42), 174 (5), 158 (13), 157 (100), 126 (1), 125 (10), 115 (13)

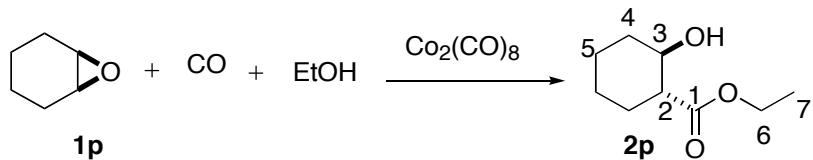
TLC  $R_f$  0.25 (hexane/EtOAc, 1/1) [silica gel, p-anisaldehyde stain]

Analysis  $C_8H_{14}O_4$  (174.19)

Calculated: C, 55.16; H, 8.10 %

Found: C, 54.93; H, 8.00 %

### Preparation of *trans* Ethyl 2-Hydroxycyclohexanoate (2p) [Table 2, Entry 16]



Following General Procedure I,  $\text{Co}_2(\text{CO})_8$  (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled ethanol (5.0 mL) and **1p** (506  $\mu\text{L}$ , 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min., then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent *in vacuo* followed by column chromatography ( $\text{SiO}_2$ , 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 4/1) to 175 mg (20 %) of **2p** as clear colorless oil. NMR spectral data matched those previously reported in the literature.<sup>17</sup>

#### Data for 2p:

$^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )

4.16 (q,  $J = 7.1$ , 2 H), 3.75 (m, 1 H), 2.82 (d,  $J = 3.4$ , 1 OH), 2.23 (ddd,  $J = 9.2$ ,

9.1, 3.2, 1 H), 2.01-2.06 (br m, 2 H), 1.75-1.78 (br m, 1 H), 1.69-1.73 (br m, 1 H), 1.27 (t,  $J$  = 7.0, 3 H), 1.09-1.38 (br m, 4 H)

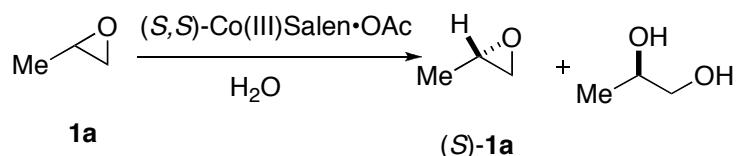
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

175.2, 70.9, 60.6, 51.3, 33.6, 28.0, 25.1, 24.3, 14.2

IR (neat)

3431 (s), 2980 (w), 2936 (s), 2860 (m), 1718 (s), 1450 (m), 1376 (m), 1323 (m), 1251 (m), 1229 (m), 1180 (s), 1067 (s), 1034 (s), 987 (s), 952 (s), 860 (s)

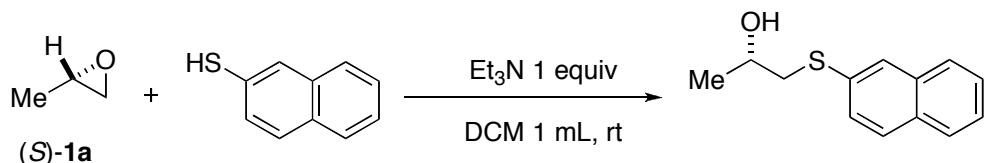
### Preparation of (S)-Propylene Oxide ((S)-1a) [Scheme 2]



Following Jacobsen Procedure,<sup>18</sup> (S)-Cobalt salen complex (242 mg, 400  $\mu$ mol, 0.002 equiv.), in 5.0 mL toluene (from SDS) was treated with 240  $\mu$ L AcOH. The crude catalyst obtained after concentration was dissolved in propylene oxide (14.0 mL, 11.6 g, 200 mmol), and H<sub>2</sub>O (1.98 mL, 110 mmol, 0.55 equiv) at 0 °C was added drop wise. After 14 h at rt, propylene oxide (5.14 g, 44 %) was isolated by direct distillation at 34 °C. The <sup>1</sup>H NMR spectrum matched that of the racemic epoxide.

Opt. Rot.:  $[\alpha]_D^{23} -11.58$  (neat); lit<sup>19</sup>  $[\alpha]_D^{23} -11.6$  (neat)

**Determination of Enantiopurity of Propylene Oxide ((S)-1a) [Scheme 2]**



Oven-dried, 10-mL, round-bottomed flask was charged with 2-naphthalenthiol (160 mg, 1.0 mmol) followed by 1 mL of dichloromethane and triethylamine (134  $\mu$ L, 1.0 mmol, 1.0 equiv) and was stirred for 30 s whereupon the colorless mixture turned pale yellow. At this point (S)-propylene oxide (70  $\mu$ L, 1.0 mmol) was added drop wise and the mixture was stirred for 6 h (monitored by TLC (silica gel plate, hexane/EtOAc 4/1). The reaction mixture was subjected to column chromatography (SiO<sub>2</sub>, 20 mm X 20 cm, hexane/EtOAc, hexane, 20/1, 4/1) to afford 110 mg (51 %) of 1-(2-naphthalenthio)-2-propanol.<sup>20</sup>

Data for 1-(2-naphthalenthio)-2-propanol:

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)

7.83 (s, 1 H), 7.78 (m, 3 H), 7.47 (m, 3 H), 3.91 (m, 1 H), 3.20 (dd, *J* = 13.6, 3.9, 1 H), 2.95 (dd, *J* = 13.7, 8.4, 1 H), 2.60 (s, 1 H), 6.34 (d, *J* = 6.3, 3 H)

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)

133.1, 132.5, 131.9, 128.5, 128.1, 127.7, 127.6, 127.0, 126.6, 125.9, 65.6, 43.4, 21.9

IR (neat)

3346 (s), 3043 (m), 2968 (s), 2909 (s), 1586 (m), 1371 (m), 1129 (m), 1074 (w), 1033 (w), 940 (w), 844 (w), 814 (m), 737 (m)

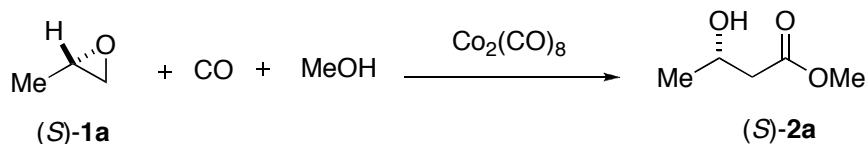
SFC: *t*<sub>R</sub> 6.30 min (98.4%); *t*<sub>R</sub> 6.95 min (1.6%) (Chiraldak OD, 125 psi, 40 °C, 10% MeOH in CO<sub>2</sub>, 3.0 mL/min, 220 nm)

Analysis C<sub>13</sub>H<sub>14</sub>OS (218.31)

Calculated: C, 71.52; H, 6.46 %

Found: C, 71.50; H, 6.50 %

### Preparation of (S) Methyl 3-Hydroxybutanoate (2a) [Scheme 2]



Following General Procedure I, Co<sub>2</sub>(CO)<sub>8</sub> (84.5 mg, 0.25 mmol, 0.05 equiv.), freshly distilled methanol (5.0 mL) and (S)-1a (350  $\mu$ L, 5.0 mmol) were stirred under a CO atmosphere (1 atm) at room temperature for 24 h. The reaction mixture was diluted with diethyl ether (50 mL) and was stirred for 30 min, then passed through silica gel (20 X 100 mm), with diethyl ether (10 mL) as the eluent. Careful removal of solvent under reduced pressure afforded 520 mg (88%) of (S)-2a as clear, colorless oil. The <sup>1</sup>H NMR spectrum of this product matched that of the racemic material.

Opt. Rot.:  $[\alpha]_D^{23} +25.74$  (c = 0.3, CHCl<sub>3</sub>); lit<sup>21</sup>  $[\alpha]_D^{23} +24.2$  (c = 0.82, CHCl<sub>3</sub>)

GC:  $t_R$  4.99 min (>99.9%);  $t_R$  5.37 min (<0.1%) (G-TA, 80 °C, isothermal, H<sub>2</sub> head pressure of 15 psi)

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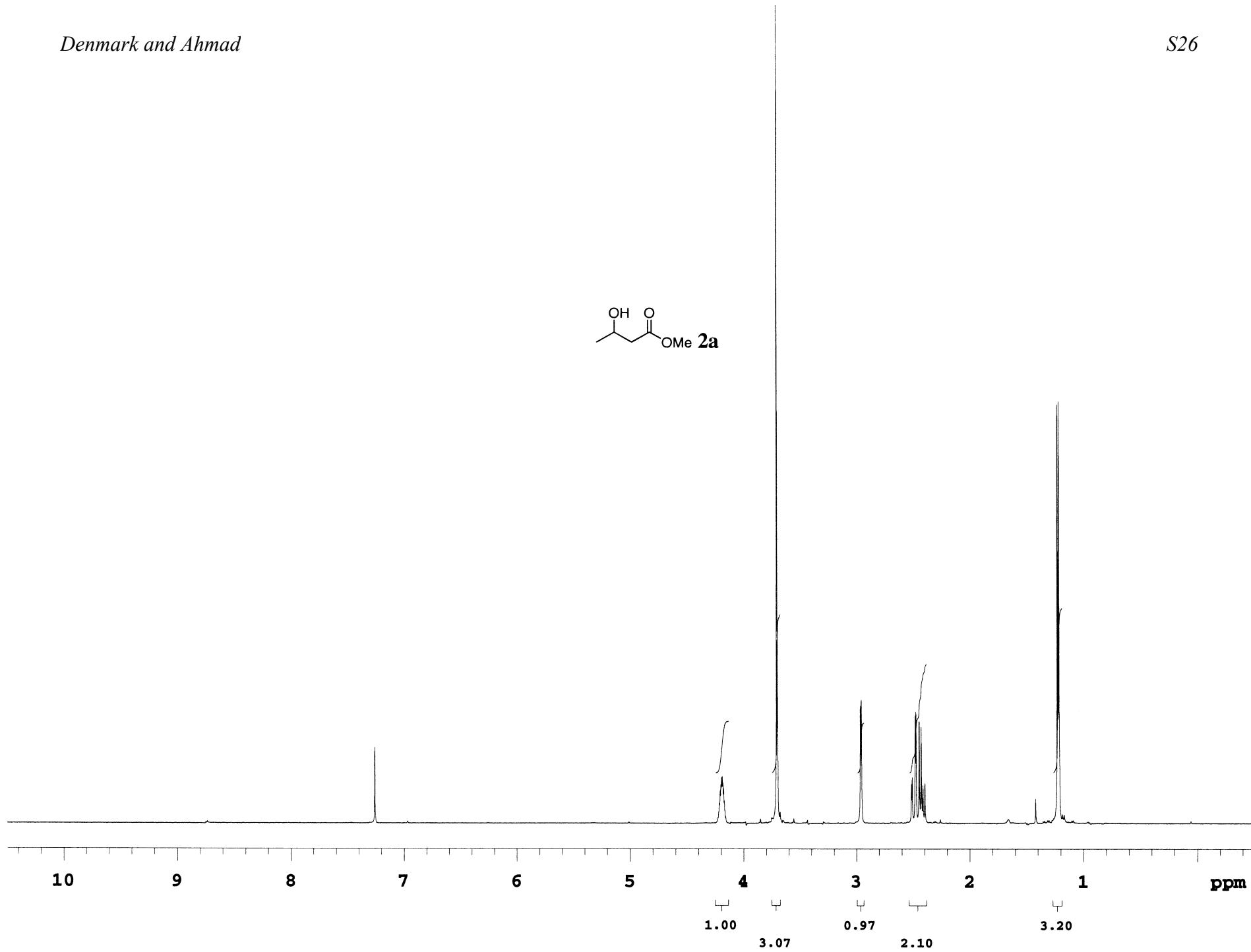
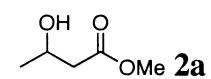
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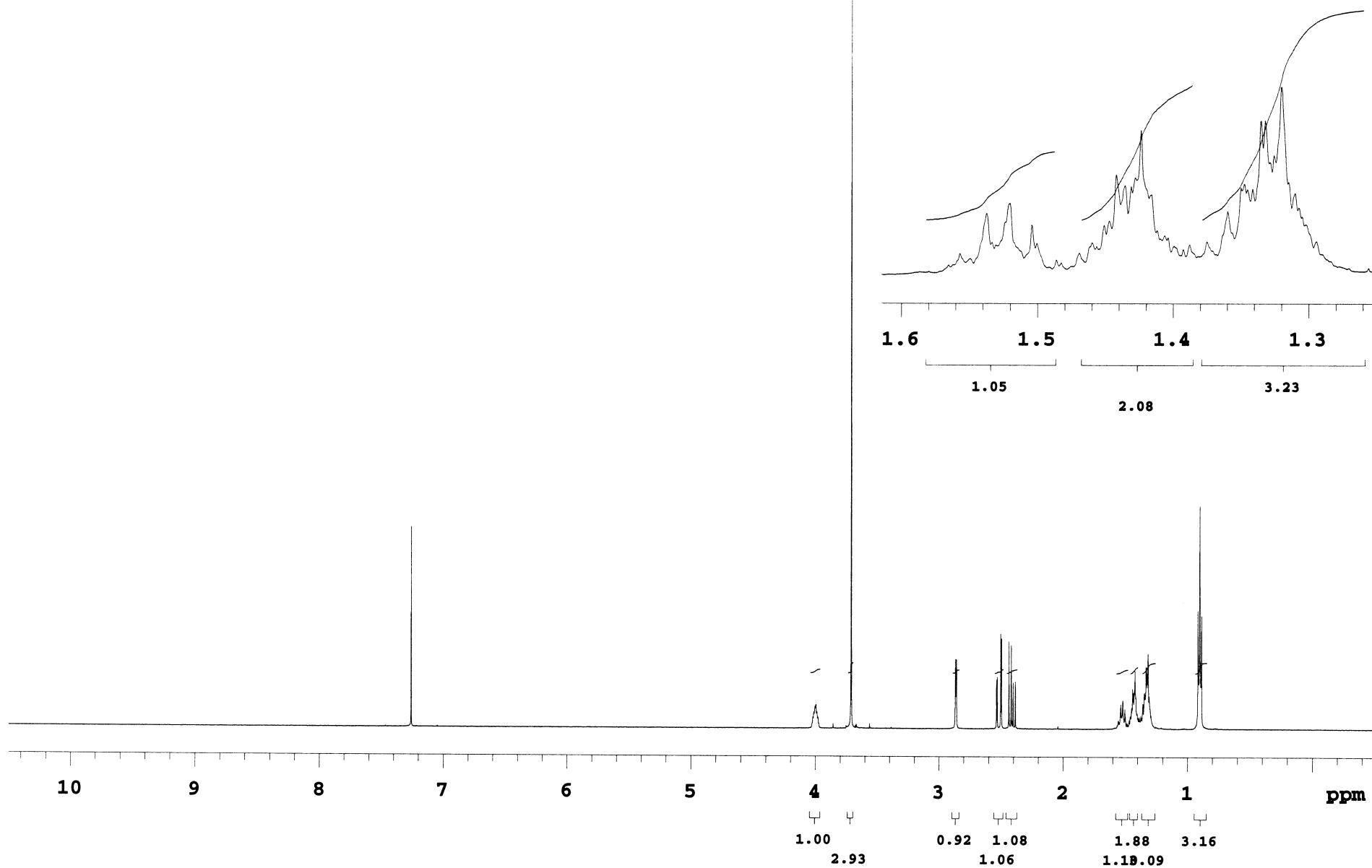
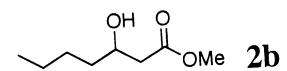
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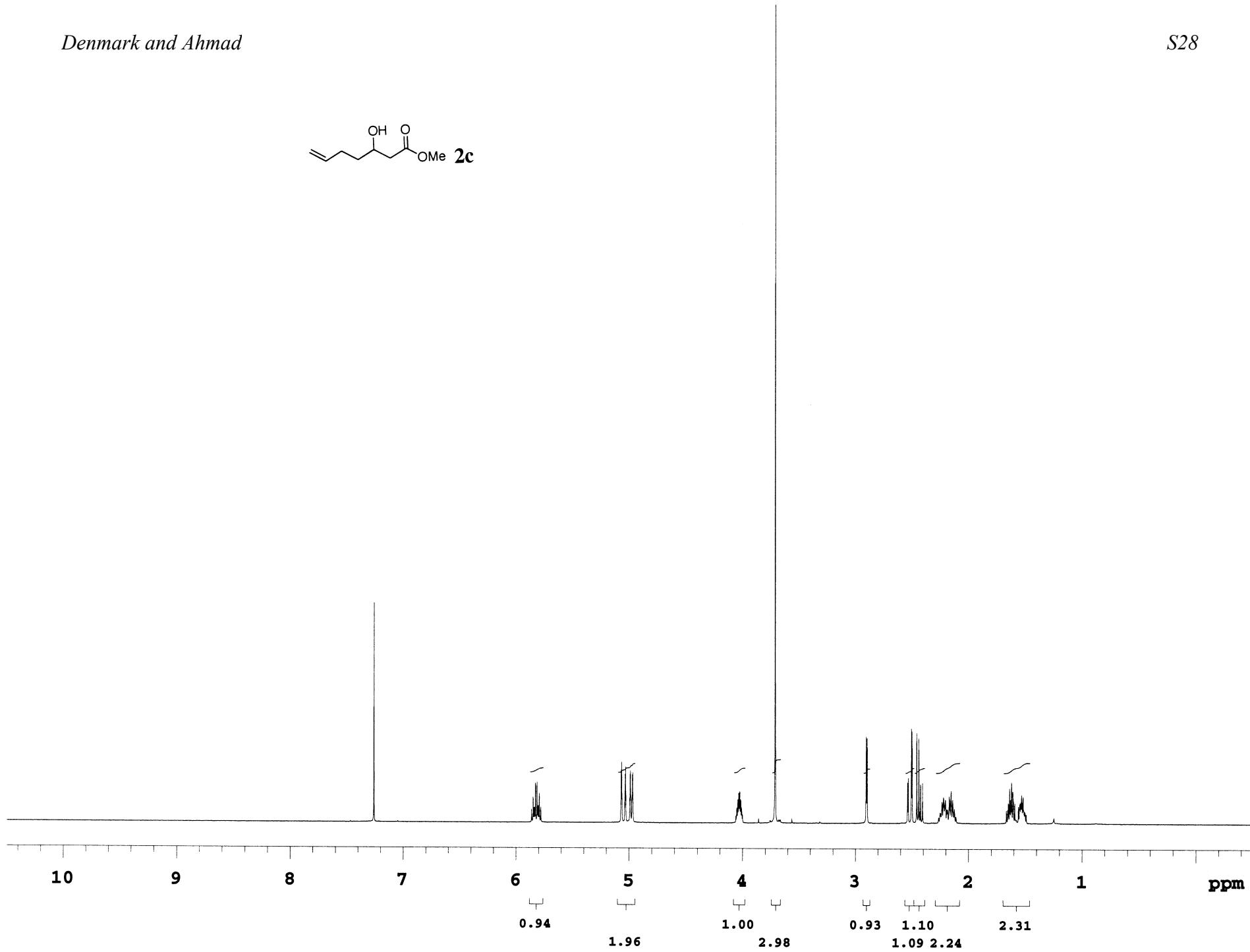
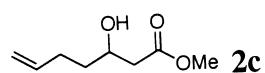
(19) (a) Ellis, M. K.; Golding, B. T. *Org. Synth., Coll. Vol. VII* **1990**, 356-359. (b) Schaus, S. E. Brandes, B. D.; Larrow, J. F.; Tokunga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307-1315.

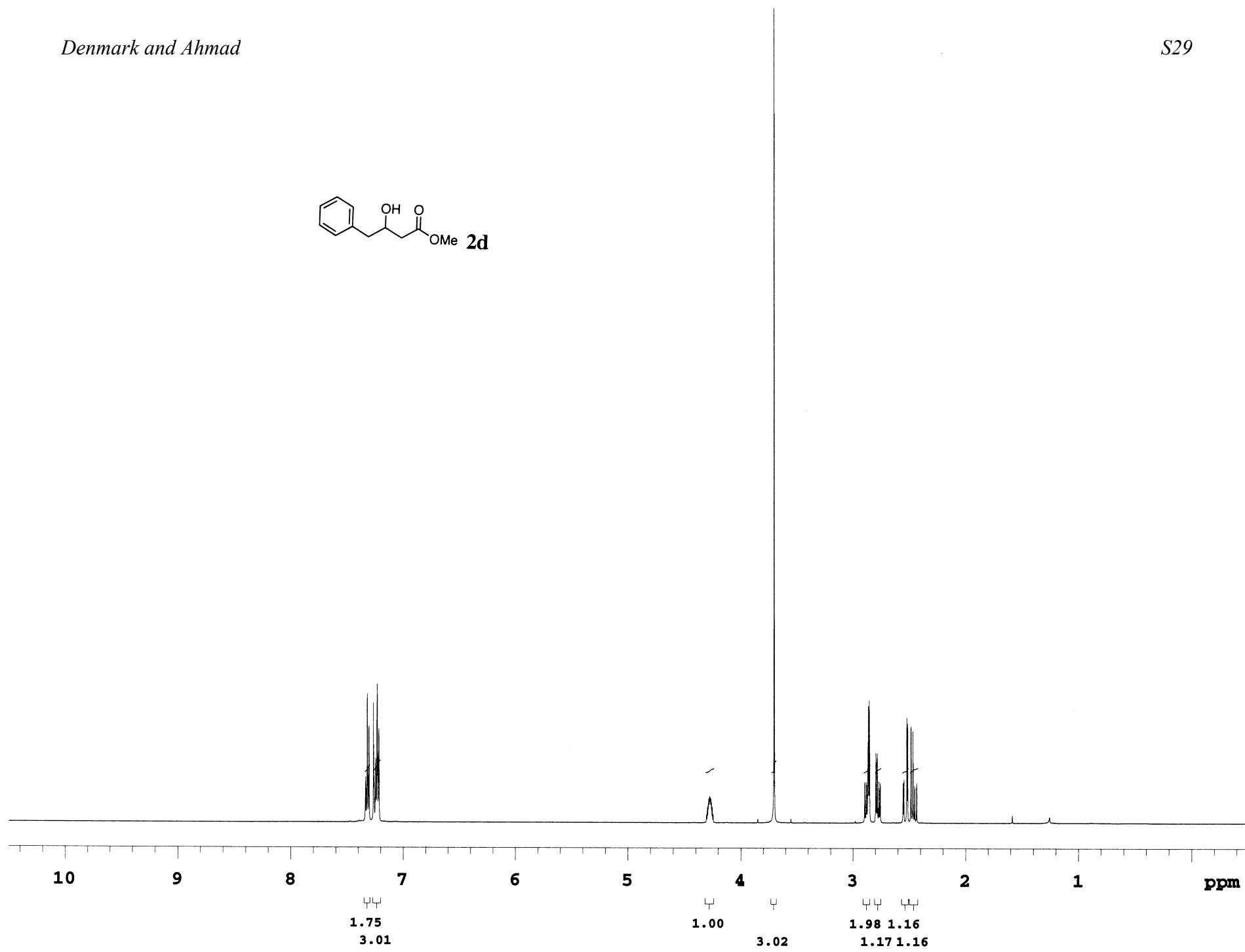
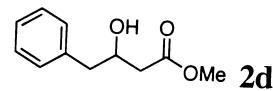
(20) Singh, S.; Kumar, S.; Chimni, S. S. *Tetrahedron: Asymmetry* **2001**, *12*, 2457-2462.

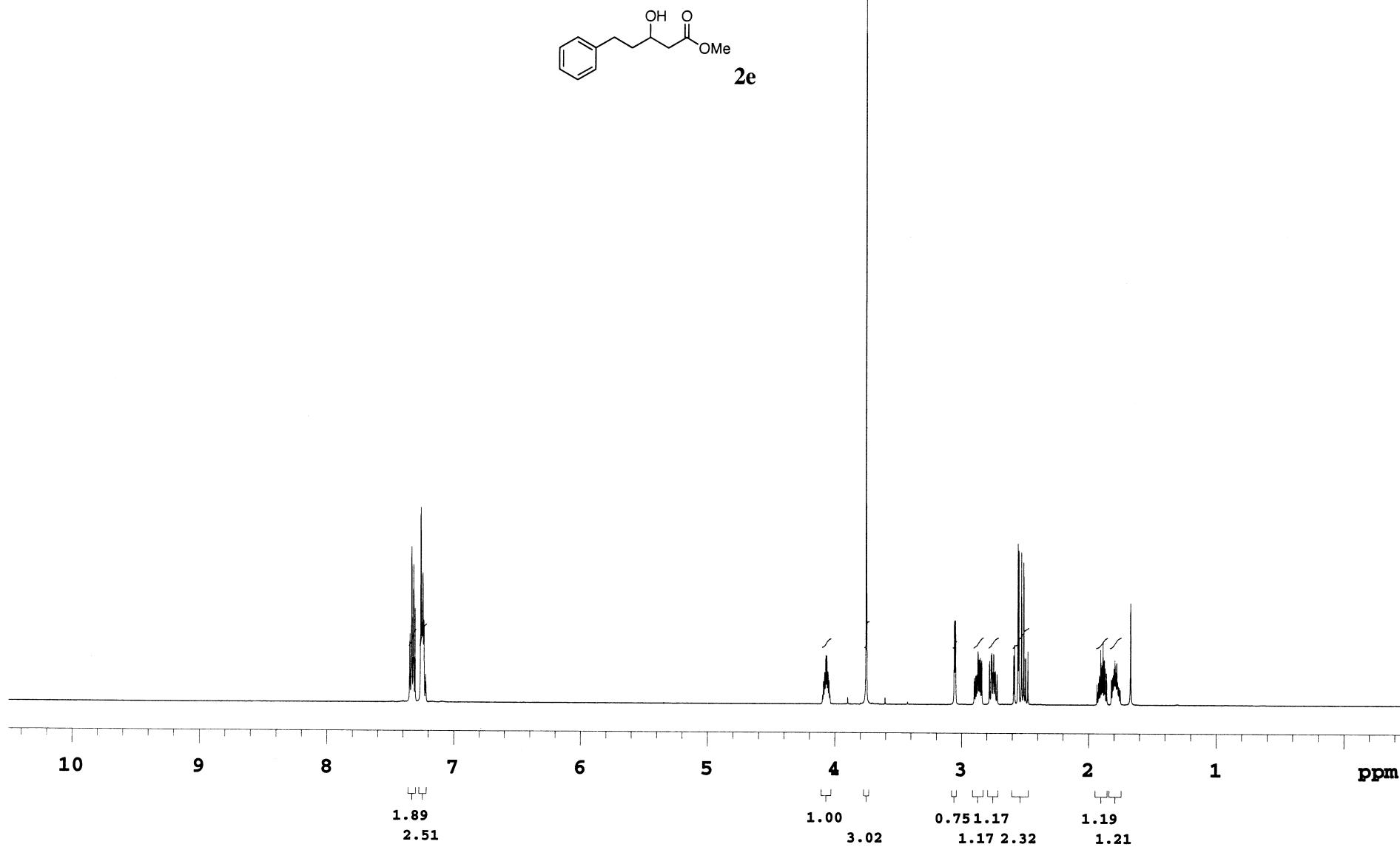
(21) Salvi, N. A.; Chattopadhyay, S. *Tetrahedron: Asymmetry* **2004**, *15*, 3397-3400.

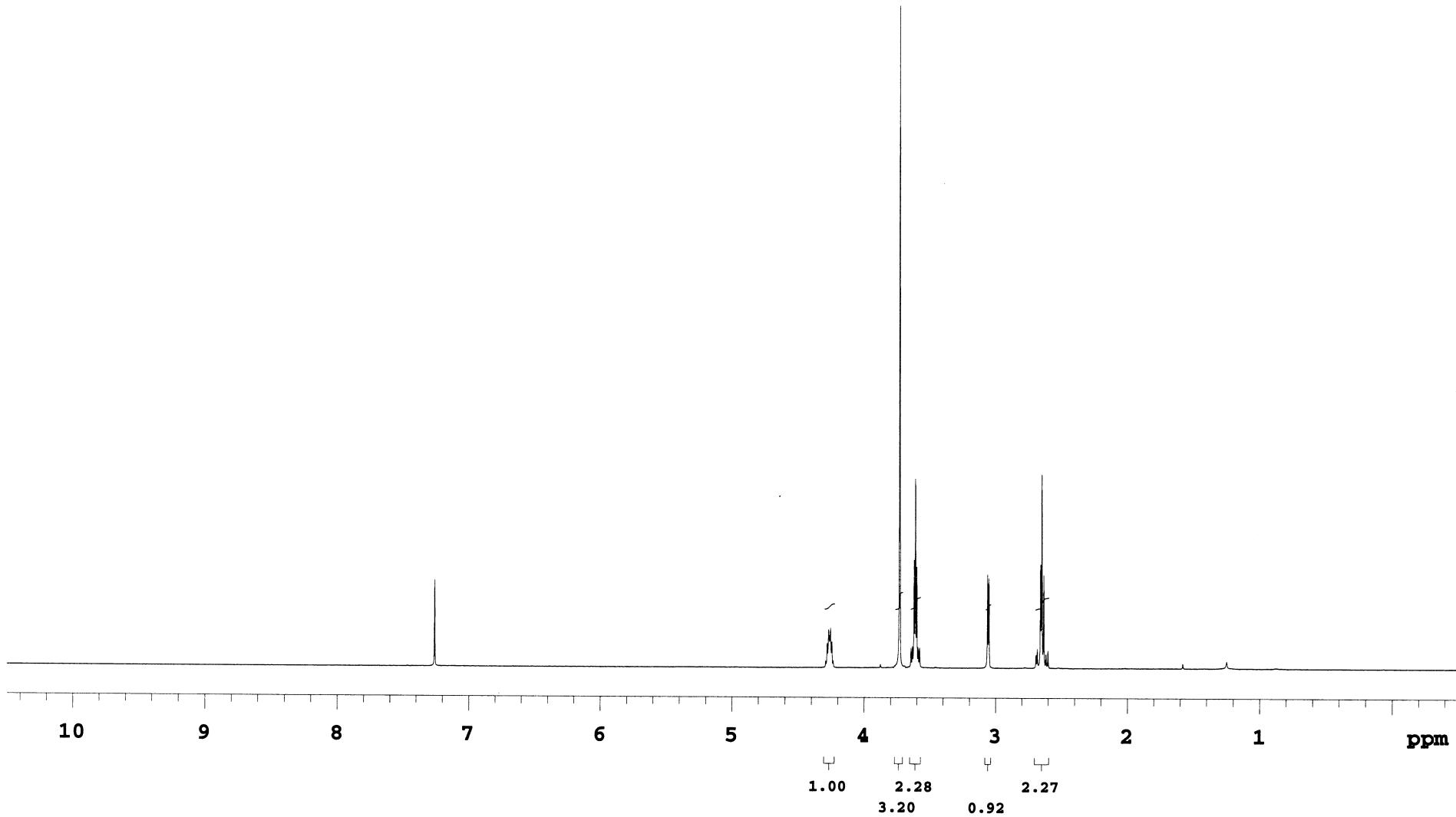
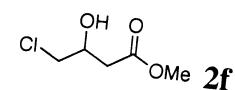


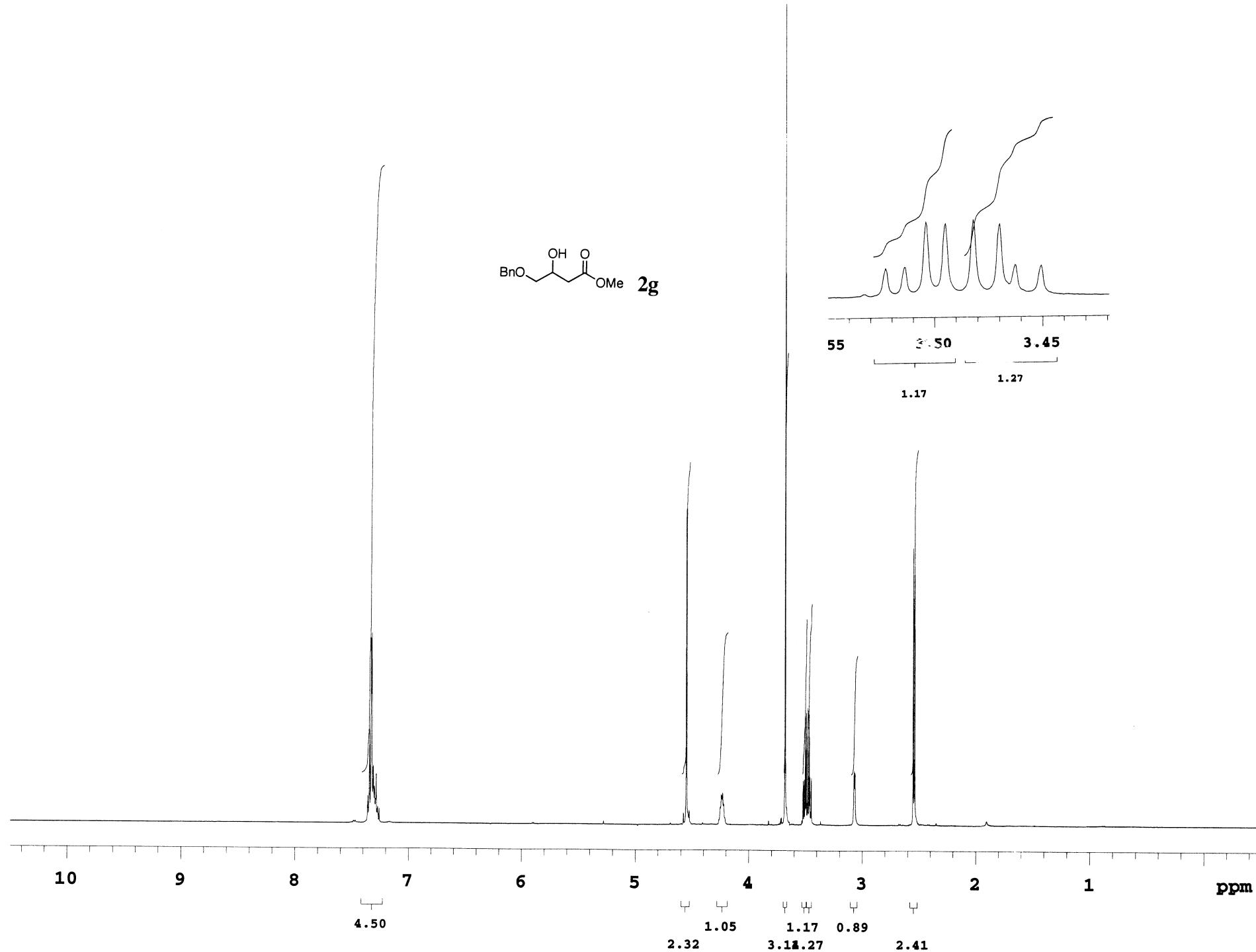


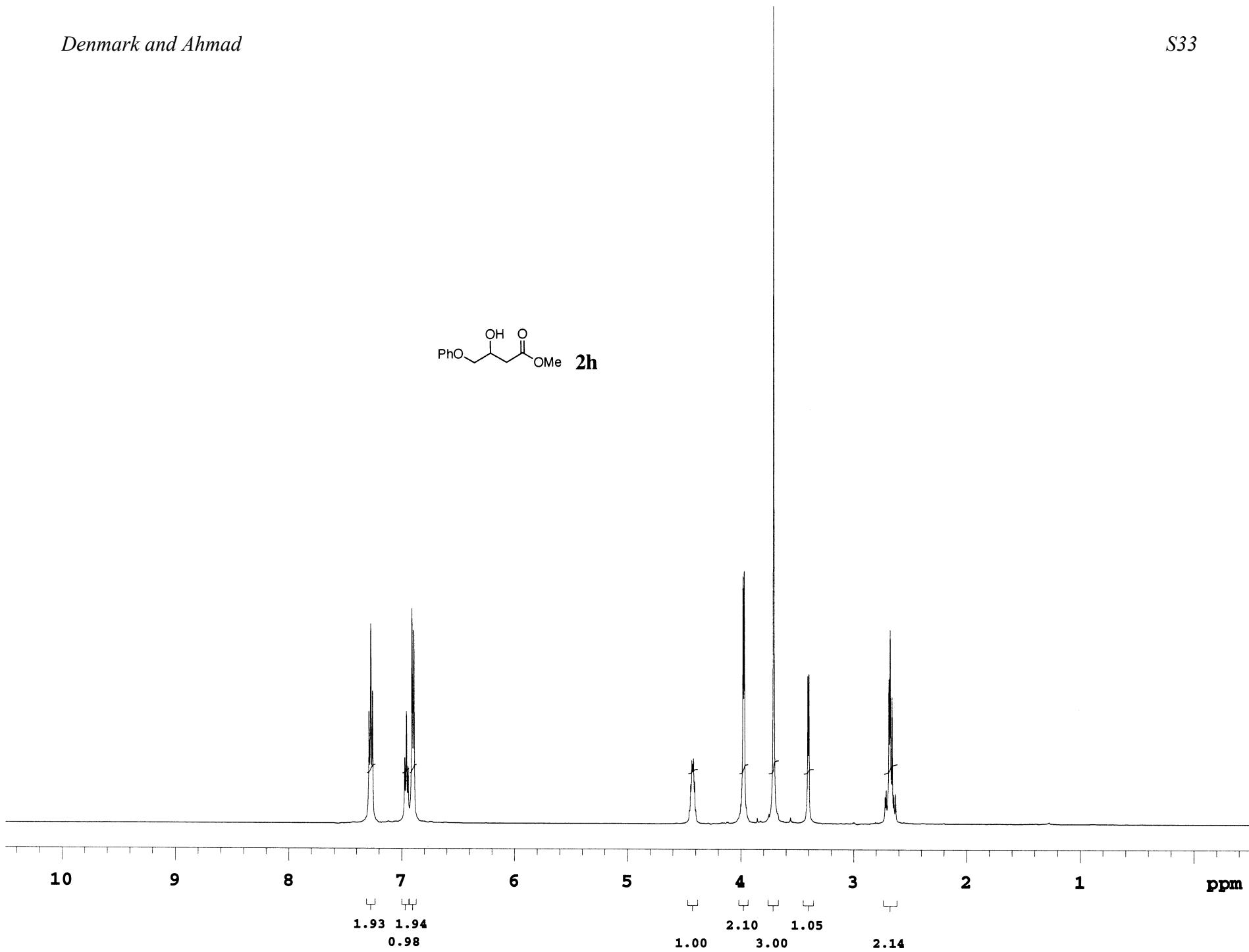
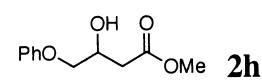


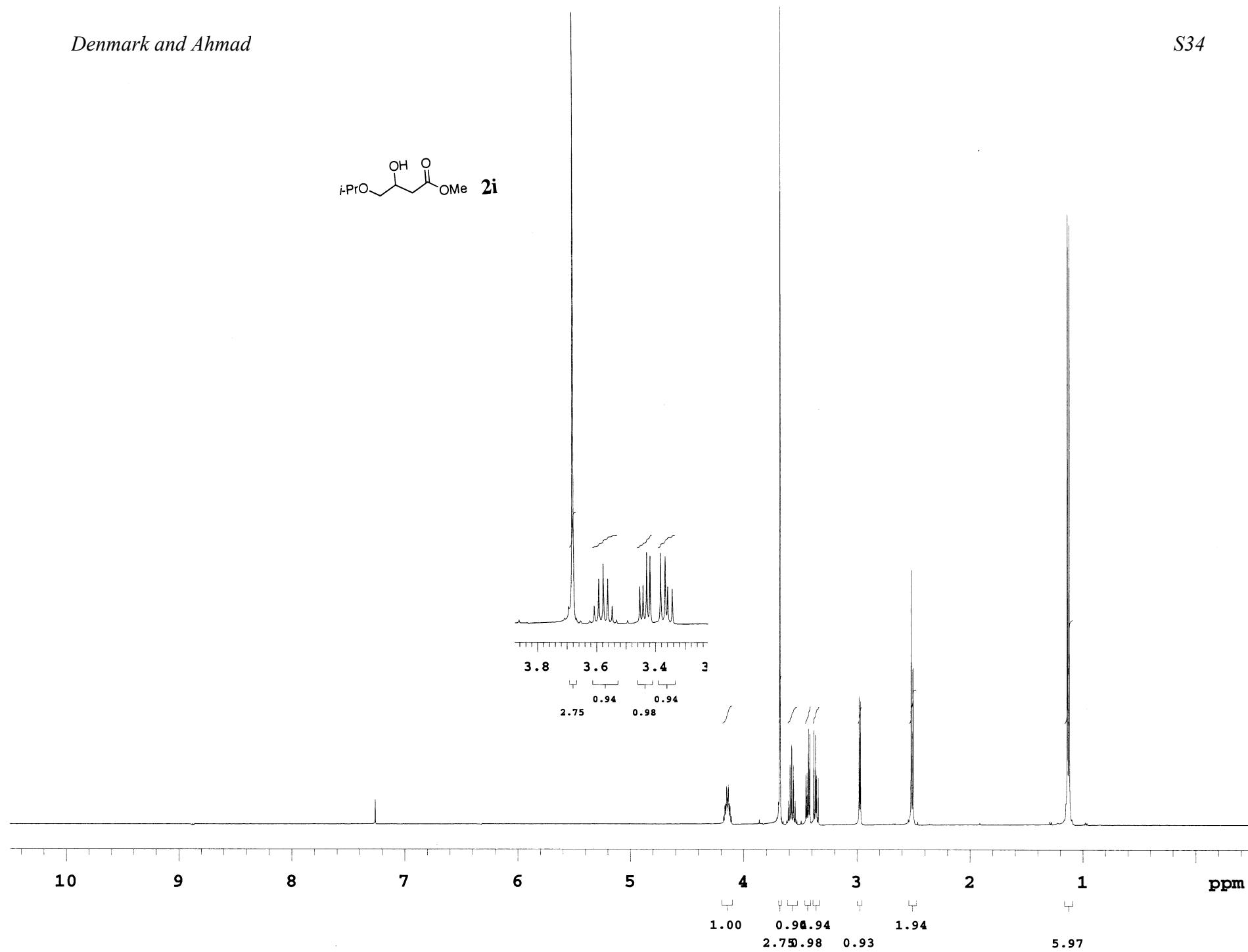
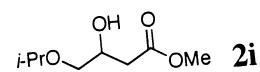


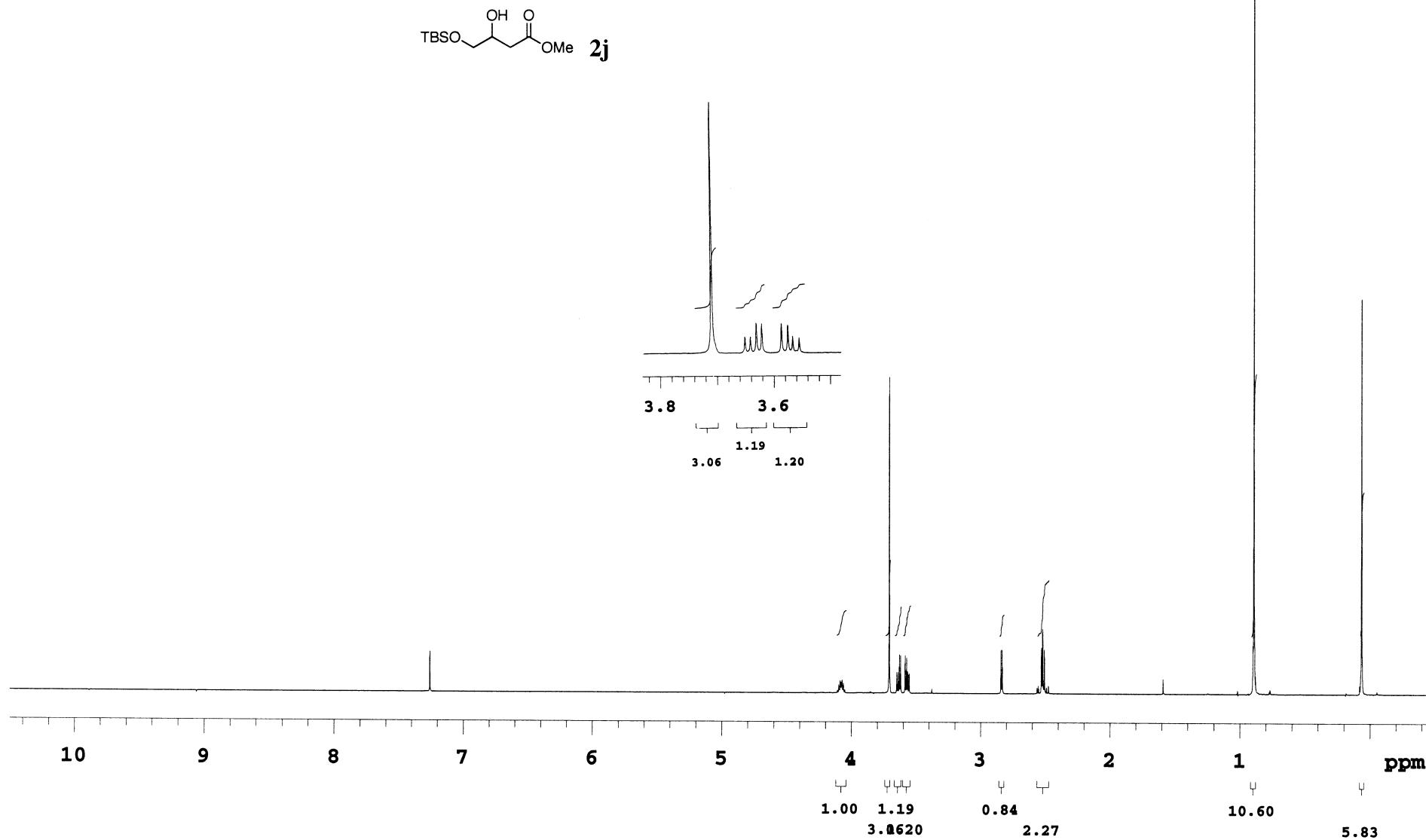


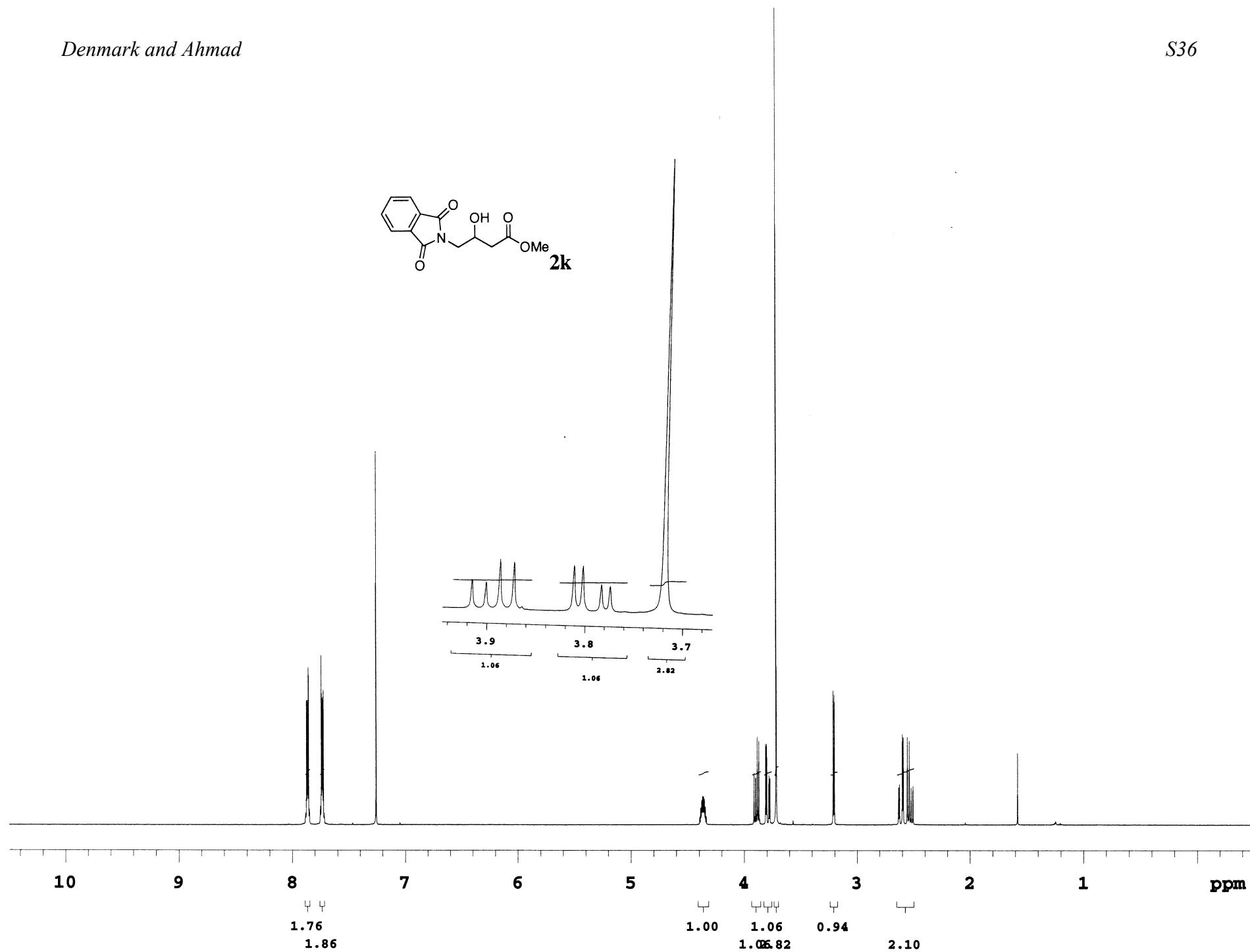
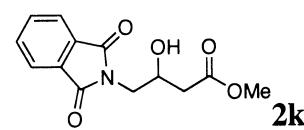


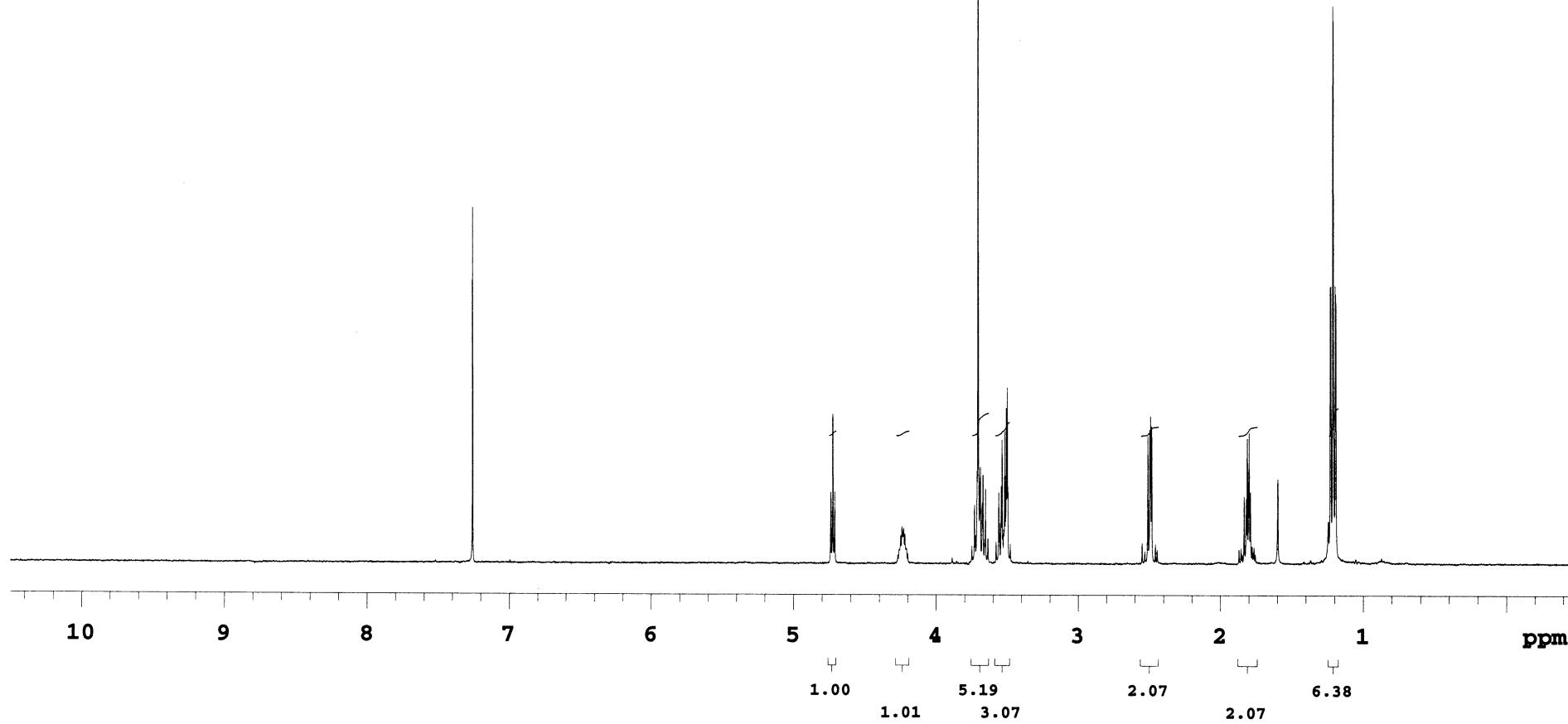
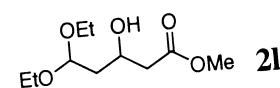


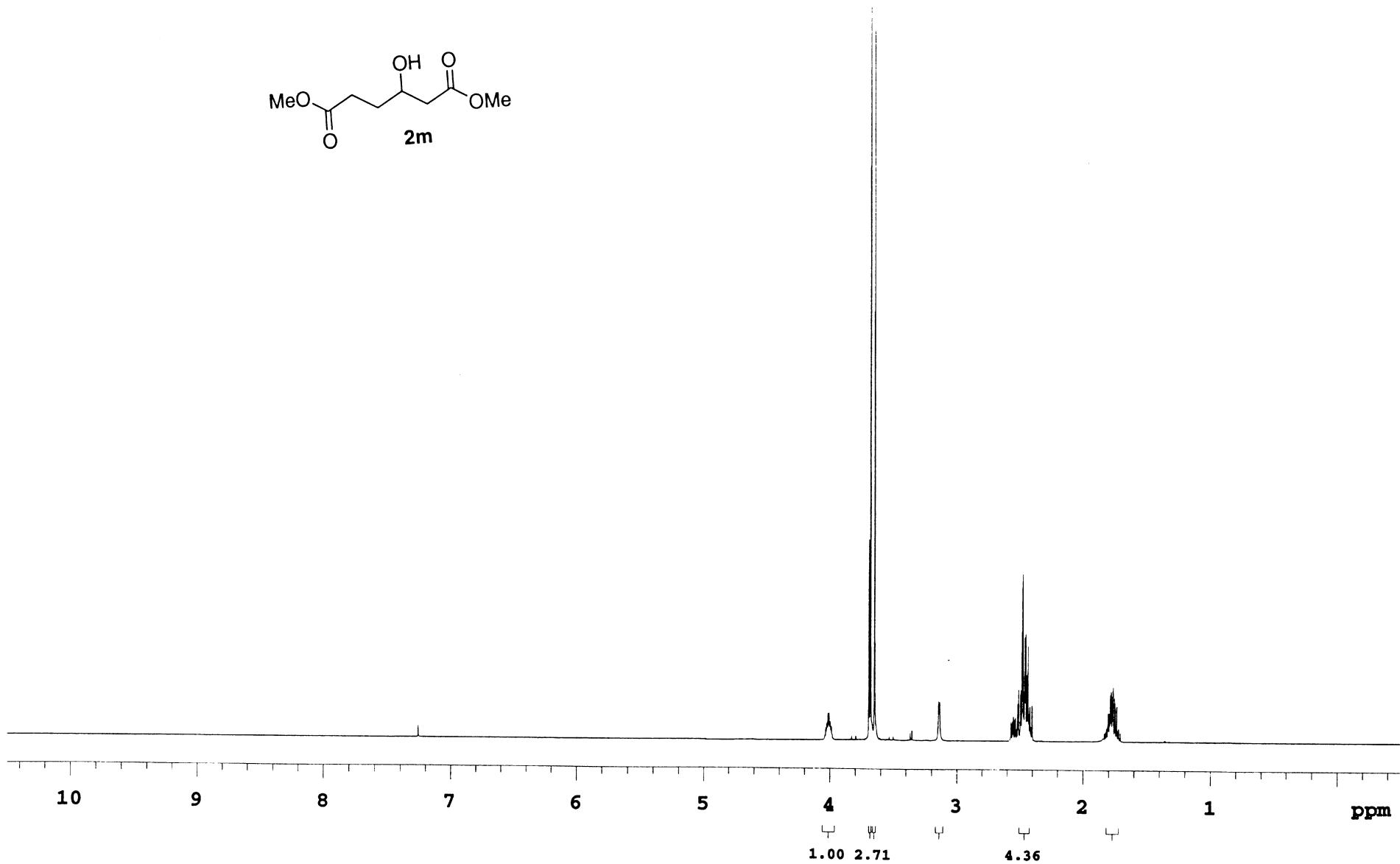
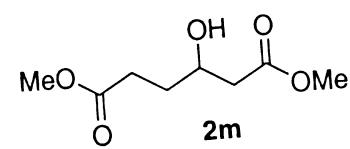


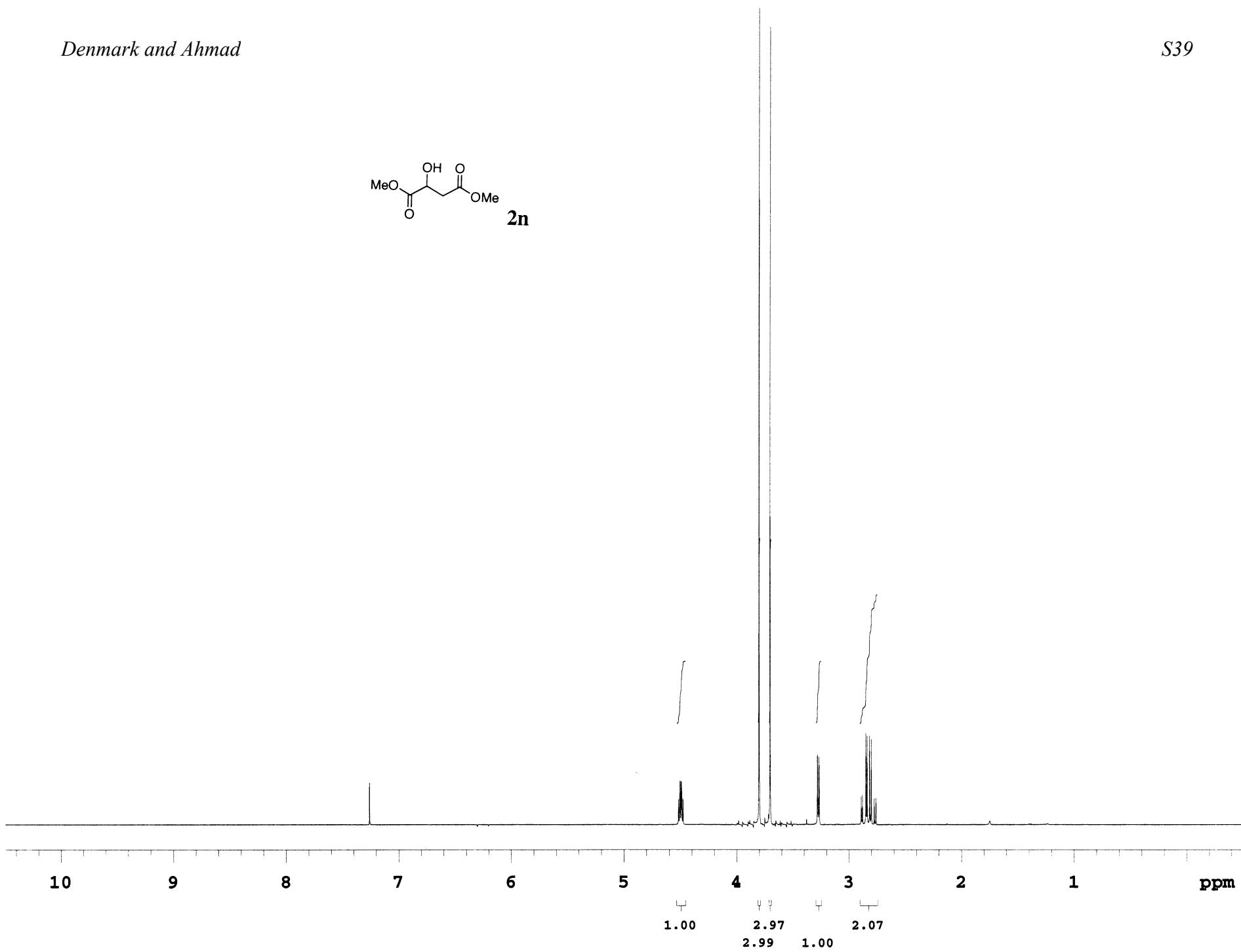
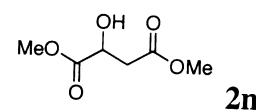


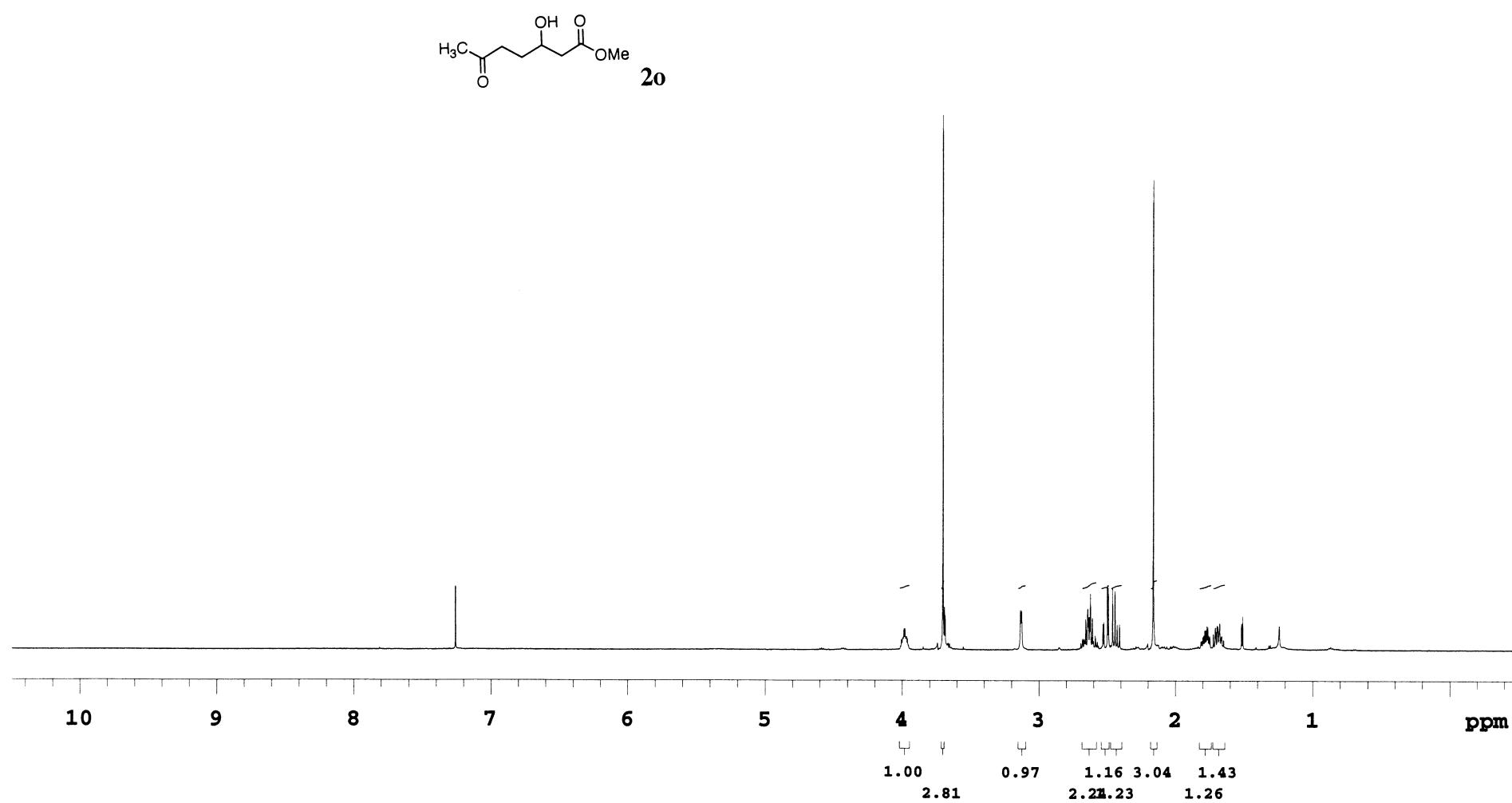


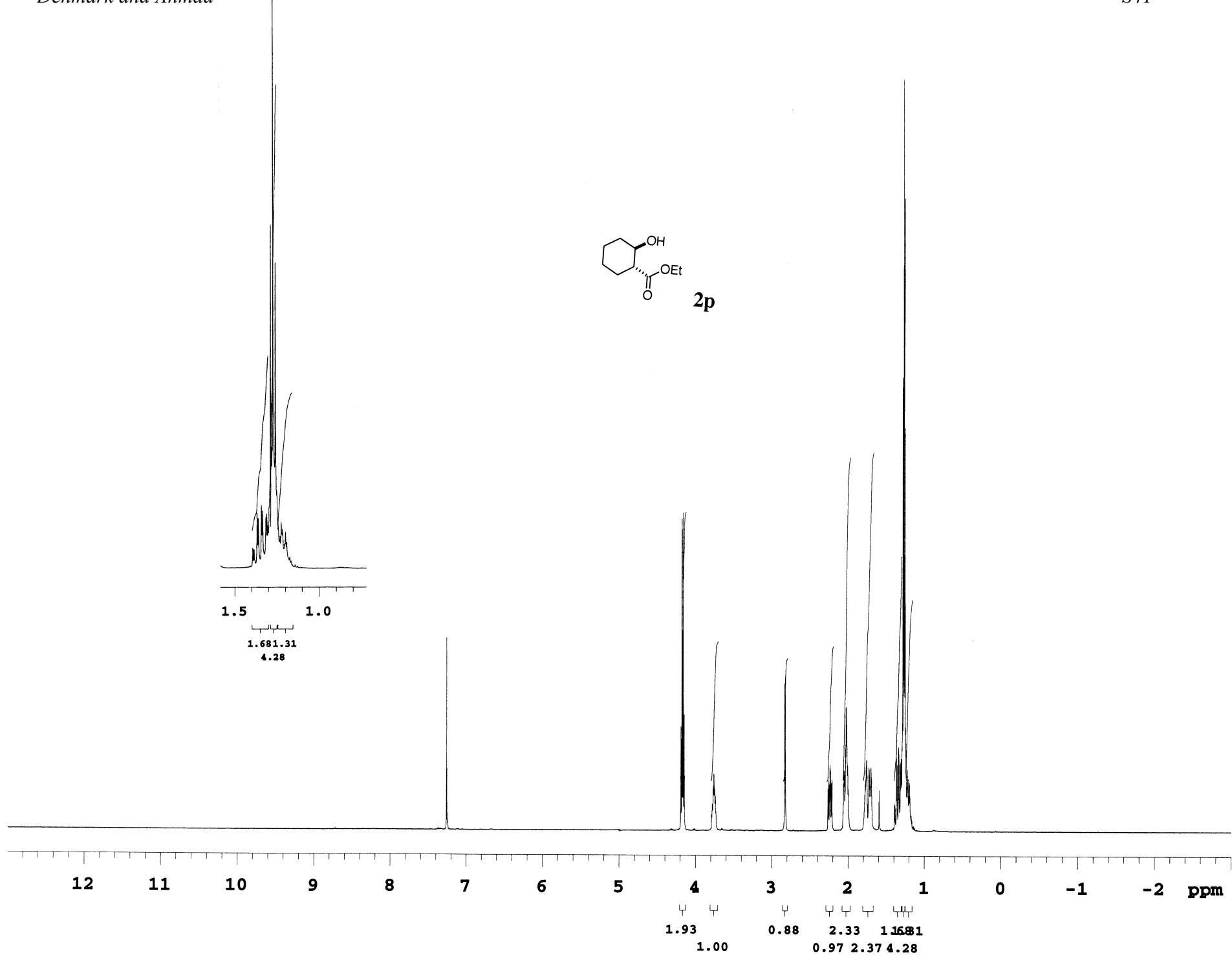


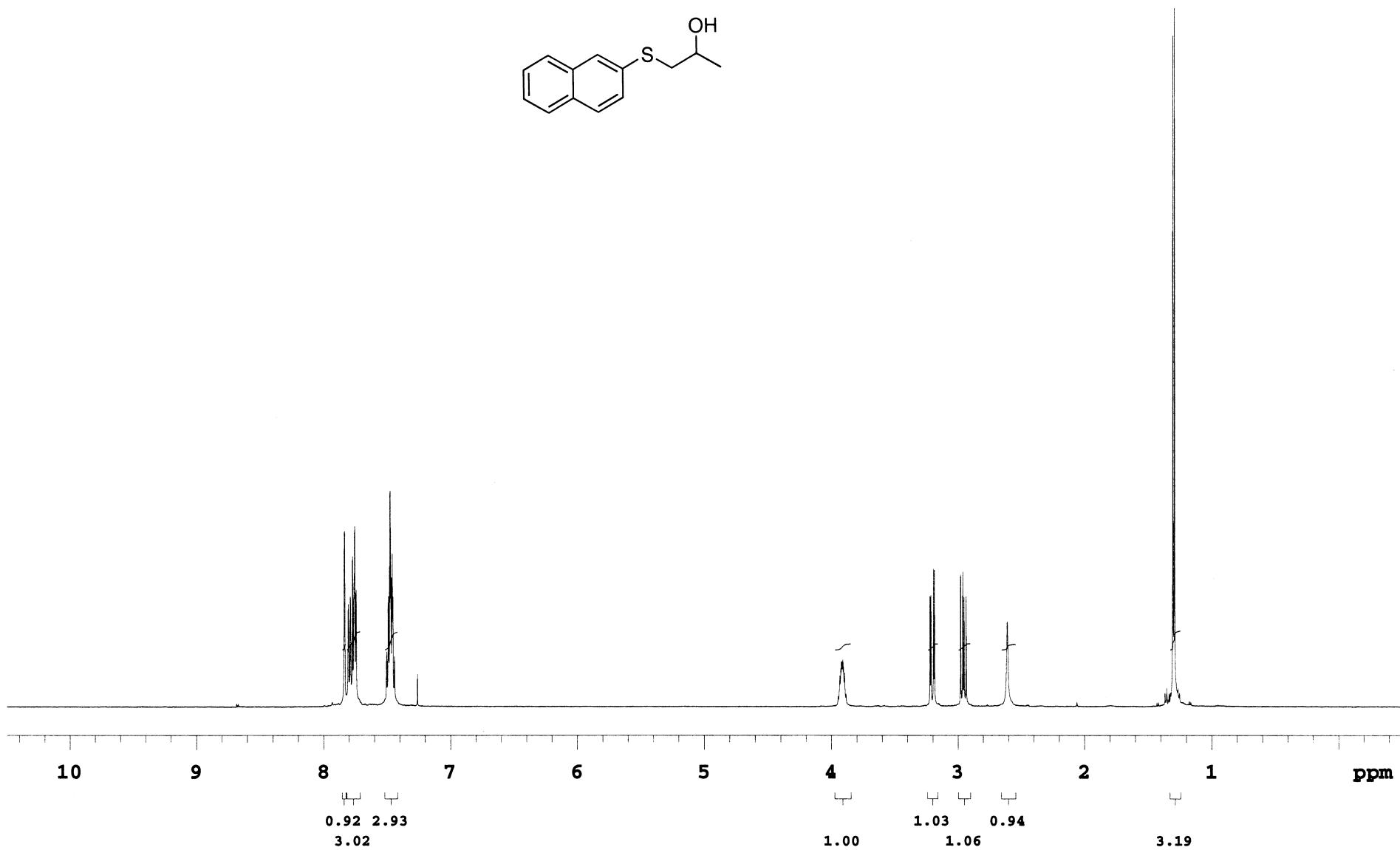
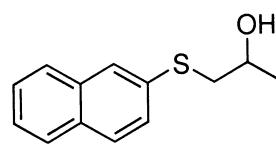




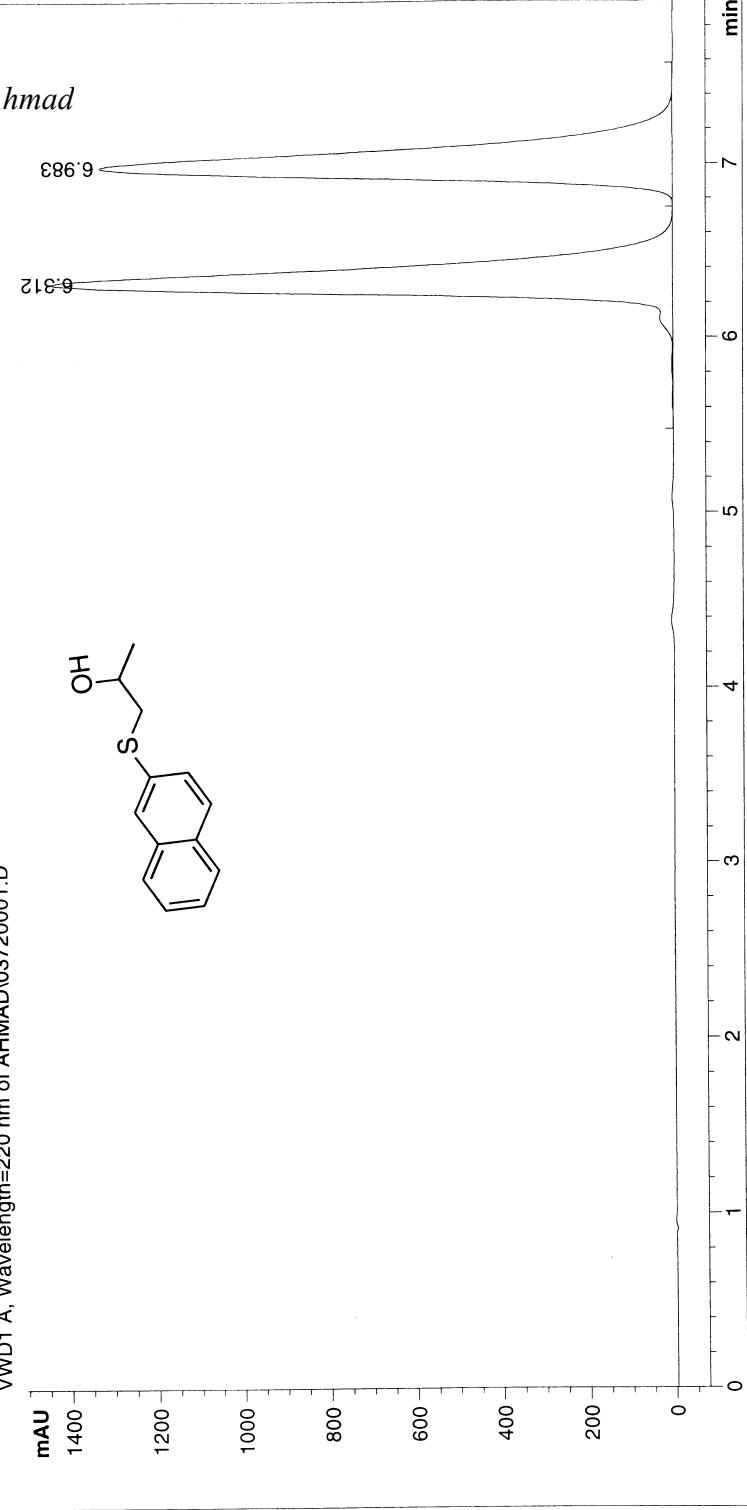








OD, 3ml/min, 125 bar, 10% MeOH

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Acq. Operator : Ahmad  
Injection Date : 6/28/2007 8:42:22 PM  
Sample Name : MA-238Analysis Method : D:\BERGER\1\METHODS\DTTEST.M  
(modified after loading)

Denmark and Ahmad

S43

Sorted by Signal  
Multiplier : 1.000000

Signal 1: VWD1 A, Wavelength=220 nm

Peak #	RT [min]	Type	Width [min]	Area [mAU*sec]	Height [mAU]	Area %
1	6.312	BV	0.155	14694.30957	1433.85730	50.0196
2	6.983	VB	0.169	14682.82031	1323.45386	49.9804

Totals : 29377.12891 2757.31104

\*\*\* End of Report \*\*\*

OD, 3.0 ml/min, 10 % MeOH, 125 bar

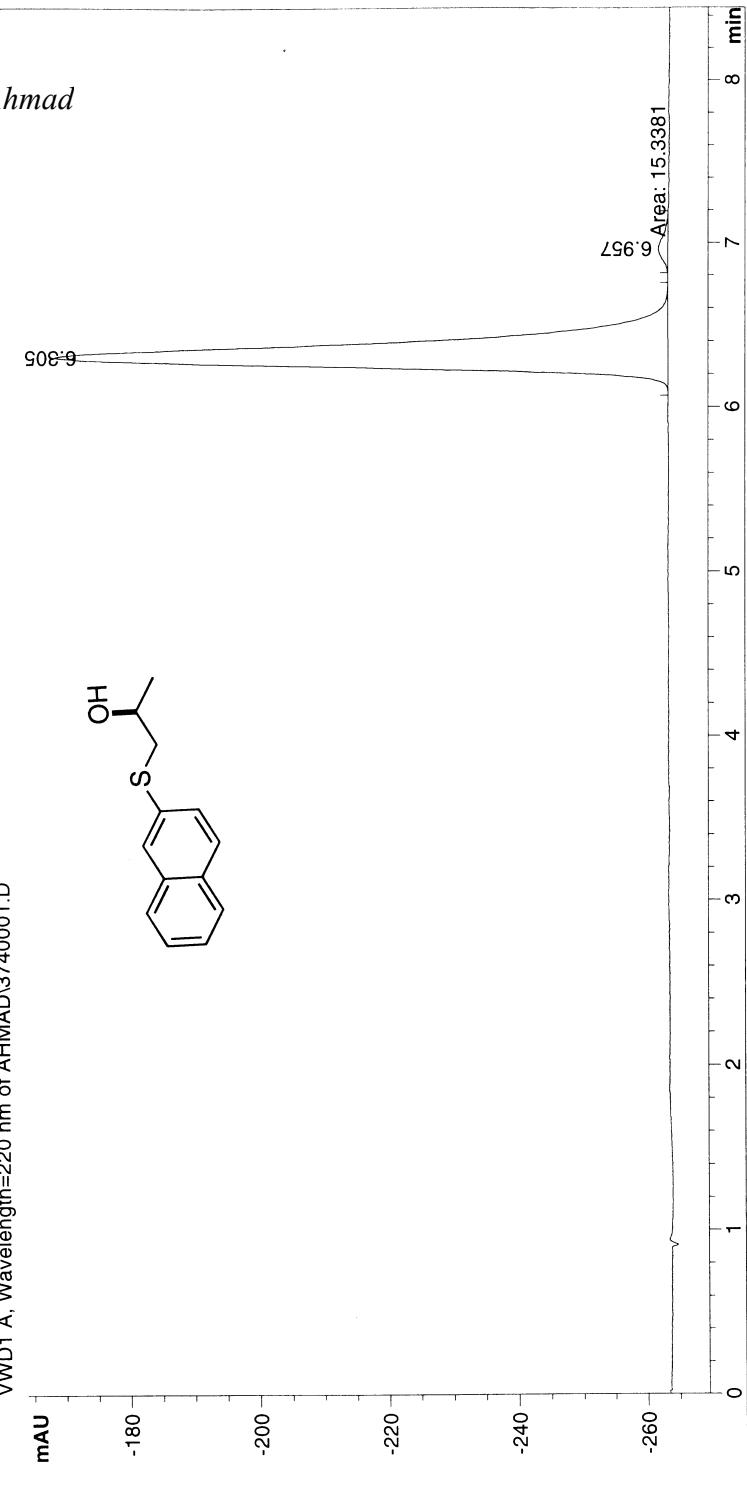
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(modified after loading)

Wavelength = 220 nm

mAU

-180

Denmark and Ahmad



Sorted by Signal Multiplier : 1.000000

Signal 1: VWD1 Å, Wavelength=220 nm

Peak RT Time Width

Year	#	Run	Run	Run	Run	Run	Run
1	1	6.305	BB	0.148	926.21722	94.68026	98.3710
2	2	6.957	MM	0.166	15.33806	1.53912	1.6290

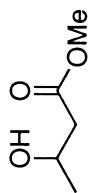
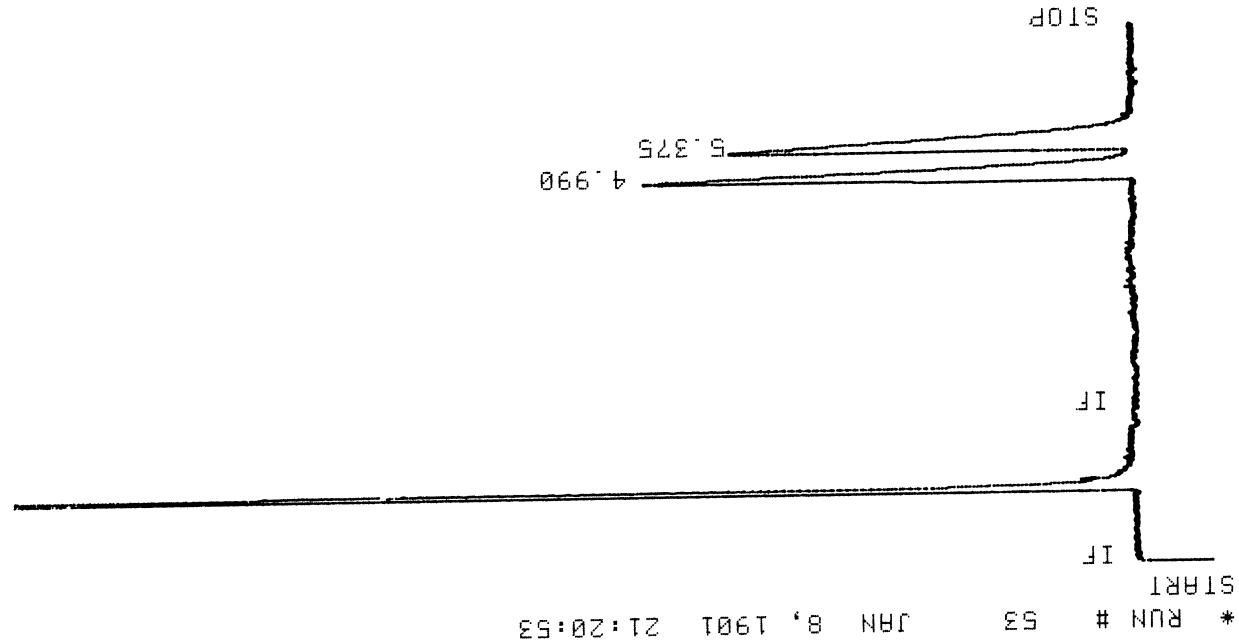
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\*\*\* End of Report \*\*\*

Agilent Technologies

PART NUMBER 5181-1219

PRINT

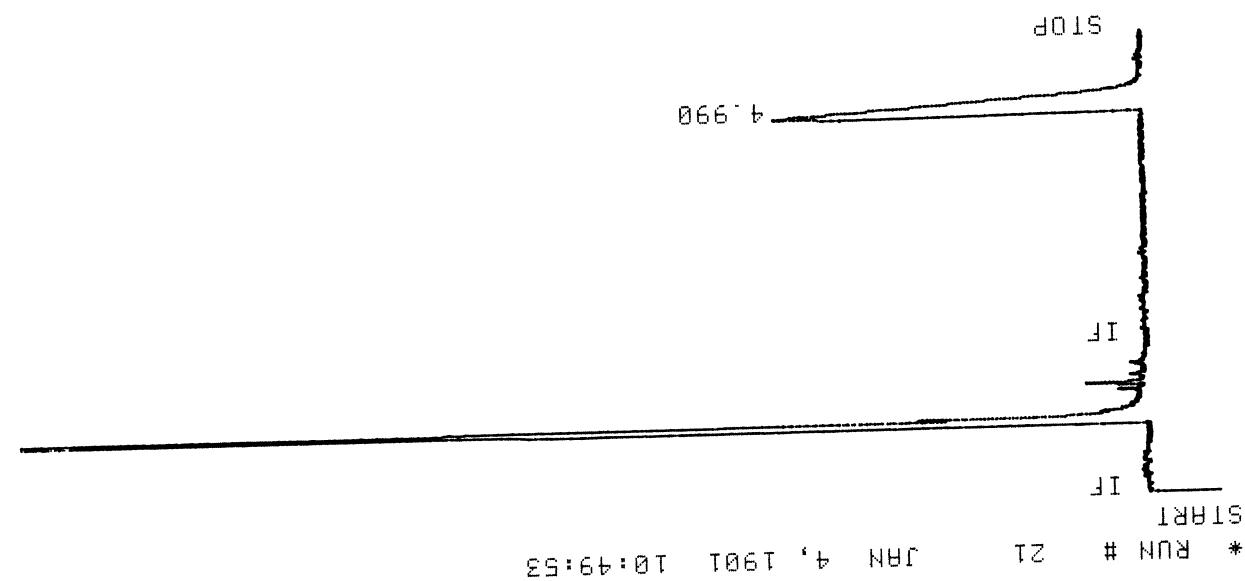
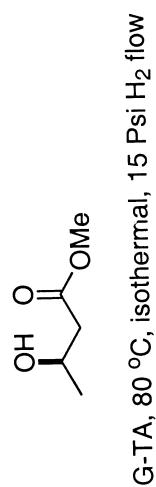
G-TA, 80 °C, isothermal, 15 Psi H<sub>2</sub> flow

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5.375 3762 UP .175 50.08654

RUN# 53 JAN 8, 1901 21:20:53

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