

## **Supporting Information**

### **Synthesis of Symmetrical Organic Carbonates via Significantly Enhanced Alkylation of Metal Carbonates with Alkyl halides/Sulfonates in Ionic Liquid**

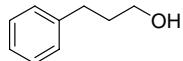
*Yogesh R. Jorapur and Dae Yoon Chi\**

Department of Chemistry, Inha University, 253 Yonghyundong Namgu, Inchon 402-751, Korea

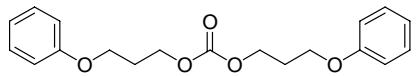
#### **List of Supporting Information:**

Di(3-phenylpropyl)carbonate ( <b>2a</b> ).....	S2
3-Phenyl-propan-1-ol ( <b>3a</b> ).....	S2
Di(3-phenoxypropyl)carbonate ( <b>4</b> ).....	S3
3-Phenoxy-1-propanol ( <b>5</b> ).....	S3
Dipentylcarbonate ( <b>6</b> ).....	S3
Diphenethylcarbonate ( <b>8</b> ).....	S3
2-Phenylethanol ( <b>9</b> ).....	S3
Styrene.....	S3
Di(biphenyl-4-yl-methyl)carbonate ( <b>10</b> ).....	S4
1,1'-Biphenyl-4-yl methanol ( <b>11</b> ).....	S4
Dipentadecanylcarbonate ( <b>12</b> ).....	S4
Pentadecan-1-ol ( <b>13</b> ).....	S4
1- <i>n</i> -Butyl-3-methylimidazolium Hexafluorophosphate.....	S4
Di(3-phenylpropyl)carbonate ( <b>2a</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S5
3-Phenyl-1-propanol ( <b>3a</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S6
Di(3-phenoxypropyl)carbonate ( <b>4</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S7
3-Phenoxy-1-propanol ( <b>5</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S8
Dipentylcarbonate ( <b>6</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S9
Diphenethylcarbonate ( <b>8</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S10
2-Phenylethanol ( <b>9</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S11
Styrene $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S12
Di(biphenyl-4-yl-methyl)carbonate ( <b>10</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S13
1,1'-Biphenyl-4-yl-methanol ( <b>11</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S14

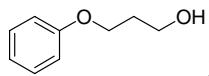
Dipentadecanylcarbonate ( <b>12</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S15
Pentadecan-1-ol ( <b>13</b> ) $^1\text{H}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{CDCl}_3$ ).....	S16
1- <i>n</i> -Butyl-3-methylimidazolium Hexafluorophosphate $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{DMSO}-d_6$ ).....	S17
1- <i>n</i> -Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 1) $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{DMSO}-d_6$ ) .....	S18
1- <i>n</i> -Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 2) $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{DMSO}-d_6$ ) .....	S19
1- <i>n</i> -Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 3) $^1\text{H}$ , $^{19}\text{F}$ and $^{13}\text{C}$ NMR (400, 100 MHz, $\text{DMSO}-d_6$ ) .....	S20
References .....	S21



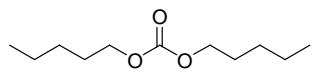
**3-Phenyl-1-propanol (3a).**<sup>2</sup> colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.46 (bs, OH), 1.86-1.93 (m, 2H), 2.70 (t,  $J$  = 8.0 Hz, 2H), 3.67 (t,  $J$  = 6.4 Hz, 2H), 7.17-7.30 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  32.0, 34.2, 62.2, 125.8, 128.3, 128.4, 141.8; MS (EI) 136 ( $M^+$ ), 117 (100); Registry No. 122-97-4.



**Di(3-phenoxypropyl)carbonate (4).**<sup>3</sup> colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.15 (quintet,  $J$  = 6.4 Hz, 4H), 4.05 (t,  $J$  = 6.0 Hz, 4 H), 4.34 (t,  $J$  = 6.4 Hz, 4H), 6.88-6.96 (m, 6H), 7.25-7.29 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  28.6, 63.8, 64.7, 114.4, 120.8, 129.4, 155.1, 158.6; MS FAB 331.0 ( $M+\text{H}^+$ ), 135.5 (100). Anal. Calcd: C, 69.07; H, 6.71. Found: C, 69.06; H, 6.78; Registry No. 109460-00-6.

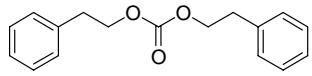


**3-Phenoxy-1-propanol (5).**<sup>4</sup> colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.90 (bs, OH), 2.04 (quintet,  $J$  = 5.6 Hz, 2H), 3.86 (t,  $J$  = 6.0 Hz, 2H), 4.12 (t,  $J$  = 6.0 Hz, 2H), 6.89-6.97 (m, 3H), 7.25-7.30 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  31.9, 60.2, 65.6, 114.5, 120.8, 129.5, 158.7; MS (EI) 152 ( $M^+$ ), 94 (100); Registry No. 6180-61-6.

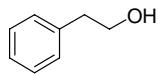


**Dipentylcarbonate (6).**<sup>5</sup> colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87-0.92 (m, 6H), 1.30-1.36 (m, 8H), 1.62-1.69 (m, 4H), 4.10 (t,  $J$  = 6.8 Hz, 4H);  $^{13}\text{C}$  NMR (100 MHz,

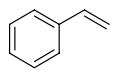
$\text{CDCl}_3$ )  $\delta$  13.9, 22.3, 27.8, 28.3, 67.9, 155.4; MS FAB 203.0 ( $M+\text{H}^+$ ), 154.23 (100). HR FAB Calcd for  $\text{C}_{11}\text{H}_{22}\text{O}_3$  ( $M+\text{H}^+$ ) 203.1647, found 203.1647; Registry No. 2050-94-4.



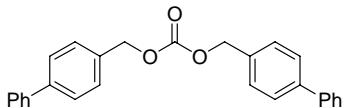
**Diphenethylcarbonate (8).**<sup>1</sup> colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.97 (t,  $J = 7.2$  Hz, 4H), 4.32 (t,  $J = 7.2$  Hz, 4H), 7.20-7.32 (m, 10H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  35.1, 68.2, 126.7, 128.5, 128.9, 137.2, 155.0; MS FAB 271.0 ( $M+\text{H}^+$ ), 105.9 (100). Anal. Calcd: C, 75.53; H, 6.71. Found: C, 75.57; H, 6.99; Registry No. 67879-62-3.



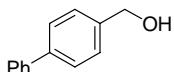
**2-Phenylethanol (9).**<sup>6</sup> colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.49 (bs, OH), 2.87 (t,  $J = 6.8$  Hz, 2H), 3.86 (t,  $J = 6.8$  Hz, 2H), 7.21-7.34 (m, 5H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  39.1, 63.6, 126.4, 128.5, 129.0, 138.4; MS (EI) 122 ( $M^+$ ), 91 (100); Registry No. 60-12-8.



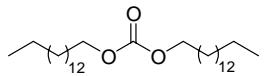
**Styrene.** colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.24 (dd,  $J = 10.4, 0.8$  Hz, 1H), 5.74 (dd,  $J = 17.2, 0.8$  Hz, 1H), 6.71 (dd,  $J = 10.4, 6.8$  Hz, 1H), 7.22-7.26 (m, 2H), 7.30-7.34 (m, 2H), 7.39-7.41 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  113.8, 126.2, 127.8, 128.5, 136.9, 137.5; MS (EI) 104 ( $M^+$ , 100); Registry No. 100-42-5.



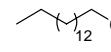
**Di(biphenyl-4-yl-methyl)carbonate (10).**<sup>7</sup> white solid; m.p. 166-168 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.22 (s, 4H), 7.35-7.61 (m, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  69.5, 127.1, 127.3, 127.5, 128.7, 128.8, 134.1, 140.6, 141.5, 155.1; MS (EI) 394 ( $M^+$ ), 167 (100). Anal. Calcd: C, 82.21; H, 5.62. Found: C, 82.12; H, 5.94; Registry No. 30952-04-6.

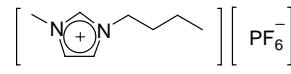


**1,1'-Biphenyl-4yl-methanol (11).**<sup>8</sup> colorless liquid;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.83 (bs, OH), 4.73 (s, 2H), 7.32-7.36 (m, 1H), 7.40-7.45 (m, 4H), 7.56-7.59 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  65.1, 127.1, 127.3, 127.4, 128.7, 139.8, 140.6, 140.8; MS (EI) 184 ( $M^+$ , 100). Anal. Calcd: C, 84.75; H, 6.57. Found: C, 85.0437; H, 6.9451; Registry No. 3597-91-9.

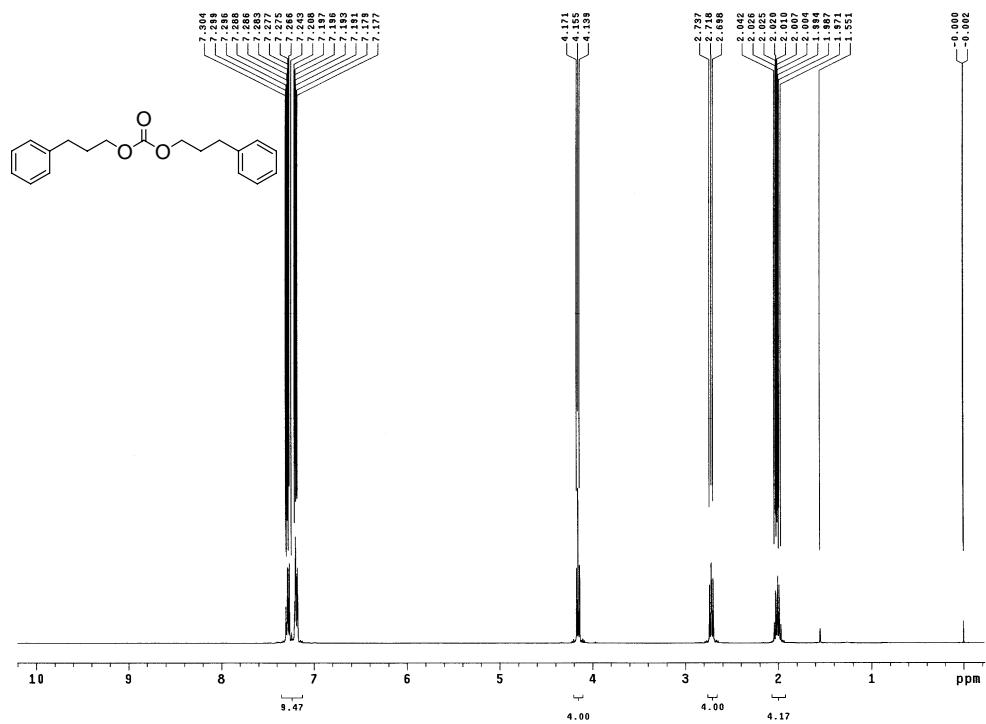


**Dipentadecanylcarbonate (12).**<sup>9</sup> white solid; m.p. 39-41 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.86-0.89 (m, 6H), 1.20-1.38 (m, 48H), 1.66 (t, J = 7.2 Hz, 4H), 4.18 (t, J = 6.8 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.1, 22.7, 25.7, 28.7, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 68.0, 155.4; MS FAB 483.41 (M+H<sup>+</sup>), 154.29 (100). Anal. Calcd: C, 77.12; H, 12.94. Found: C, 77.45; H, 13.06; Registry No. 145197-00-8.

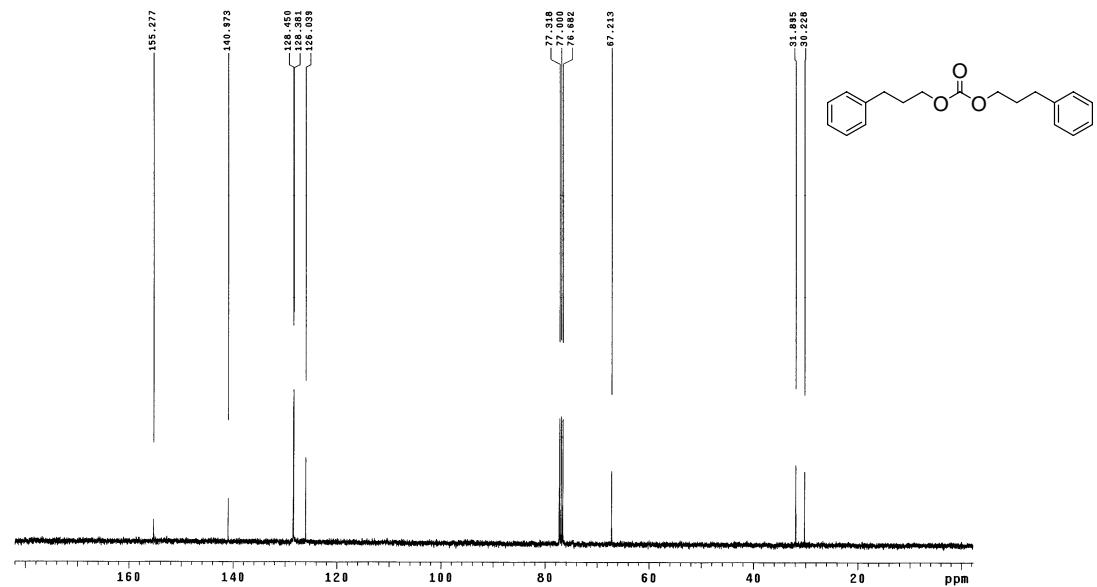
 **Pentadecan-1-ol (13).**<sup>10</sup> white solid; m.p. 45-47 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 0.86 (t, J = 7.2 Hz, 3H), 1.23-1.31 (m, 24H), 1.45 (bs, OH), 1.50-1.56 (m, 2H), 3.62 (t, J = 6.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 14.1, 22.7, 25.7, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 32.8, 63.1; MS (EI) 210 (M-H<sub>2</sub>O), 58 (100). MS FAB 211.1 (M+H-H<sub>2</sub>O), 154.23 (100); Registry No. 629-76-5.

 **1-n-Butyl-3-methylimidazolium Hexafluorophosphate.** colorless liquid; <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ 0.94 (t, J = 7.2 Hz, 3H), 1.30 (tq, J = 7.6, 7.2 Hz, 2H), 1.80 (quintet, J = 7.6 Hz, 2H), 3.88 (s, 3H), 4.19 (t, J = 7.2 Hz, 2H), 7.74 (d, J = 1.6 Hz, 2H), 9.11 (s, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>) δ 13.2, 18.8, 31.3, 35.7, 48.5, 122.2, 123.6, 136.5; <sup>19</sup>F NMR (400 MHz, DMSO-d<sub>6</sub>) δ -66.83, -64.95; Registry No. 174501-64-5.

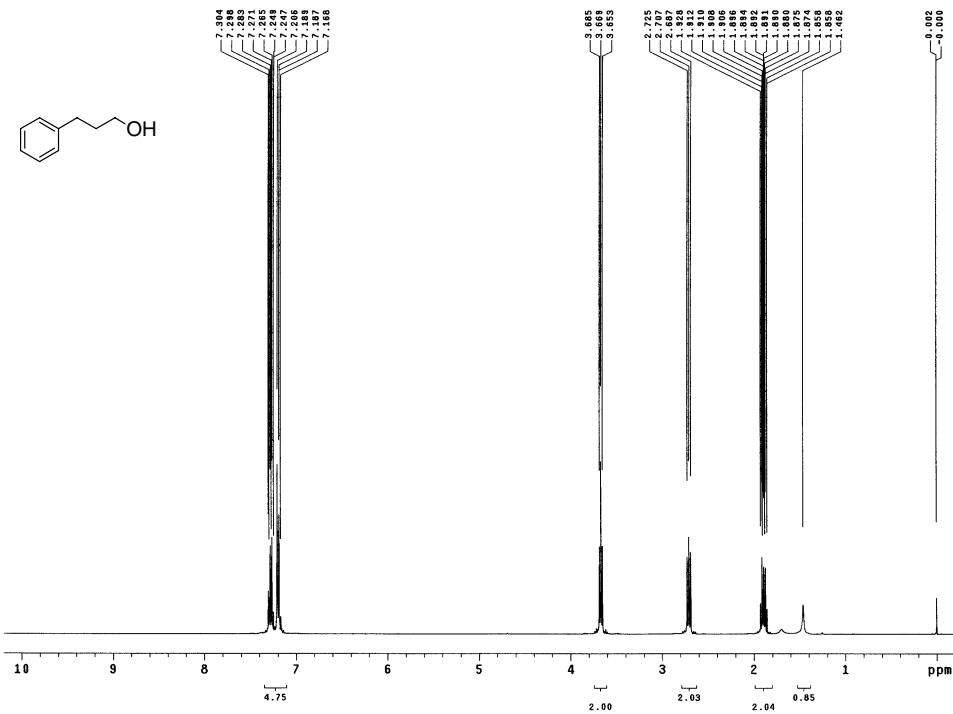
**Di(3-phenylpropyl)carbonate (2a).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



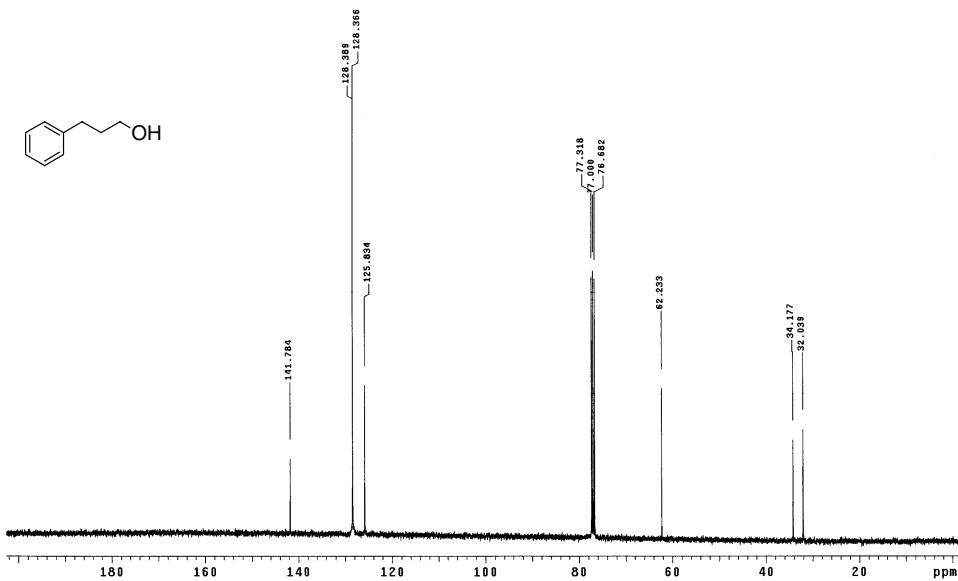
**Di(3-phenylpropyl)carbonate (2a).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



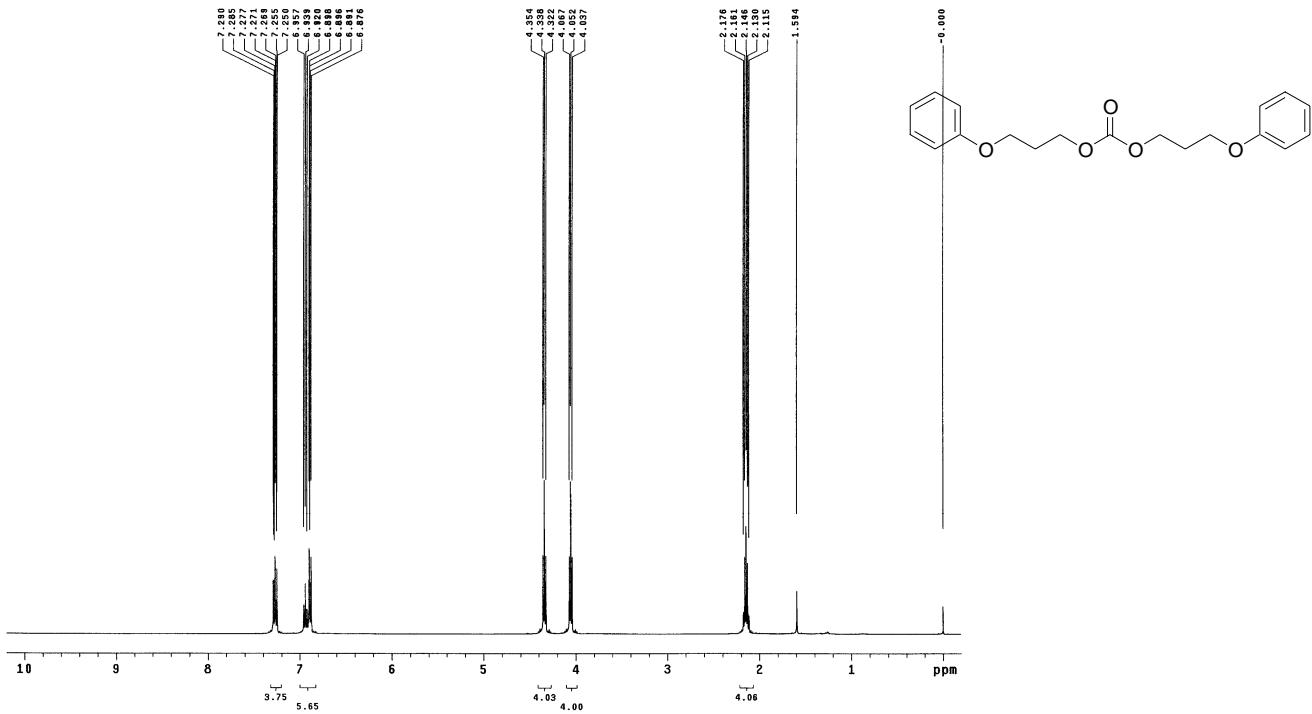
**3-Phenyl-1-propanol (3a).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



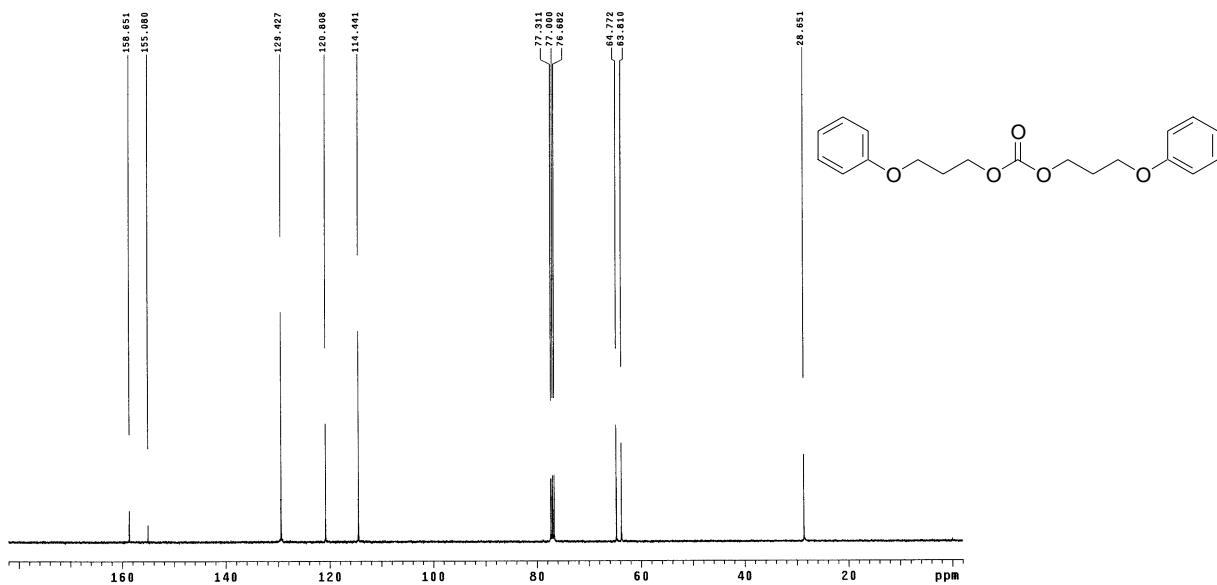
**3-Phenyl-1-propanol (3a).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



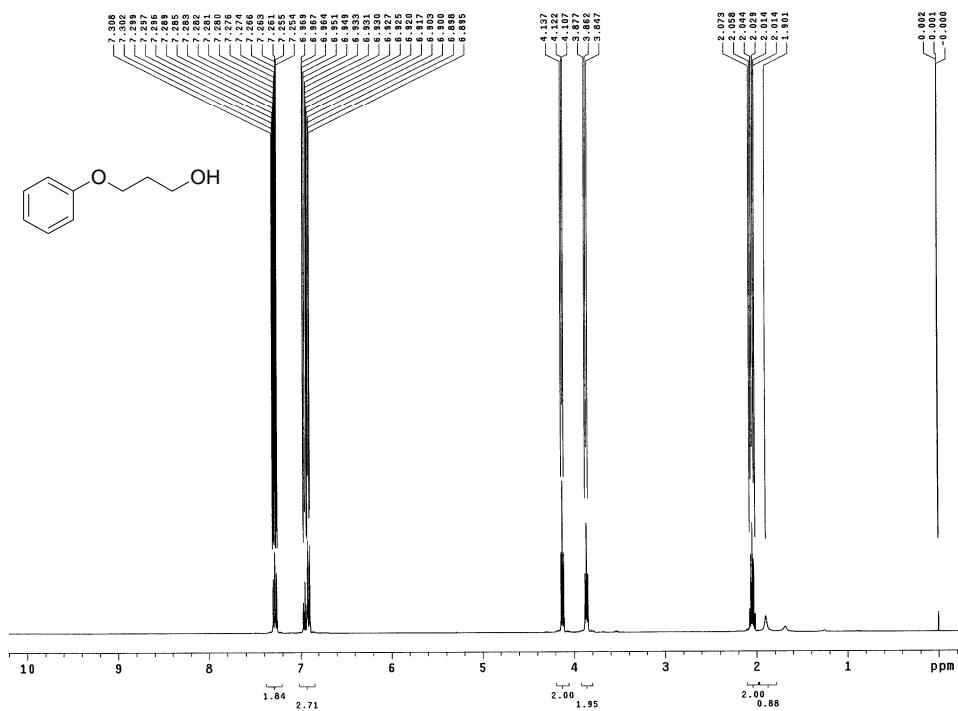
**Di(3-phenoxypropyl)carbonate (4).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



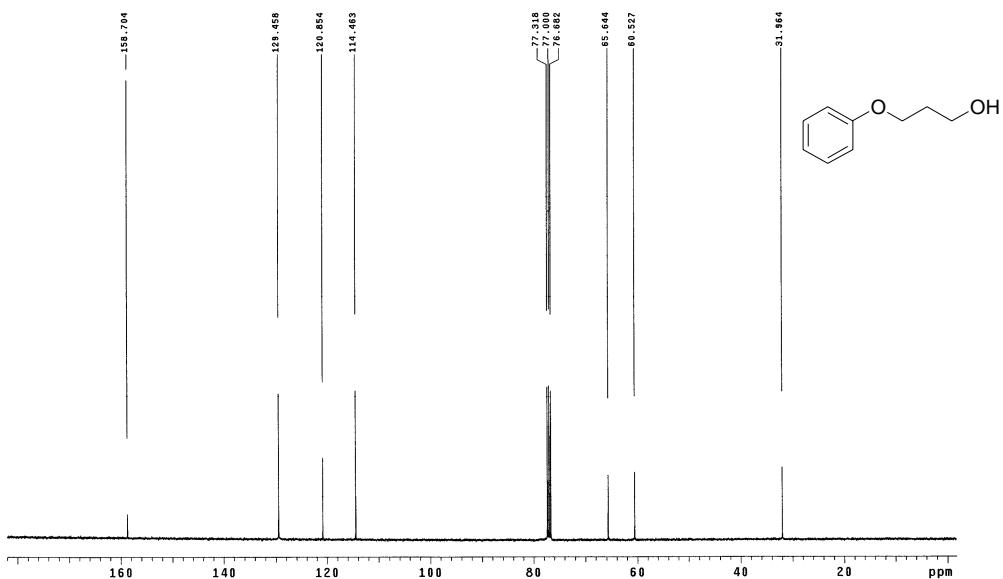
**Di(3-phenoxypropyl)carbonate (4).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



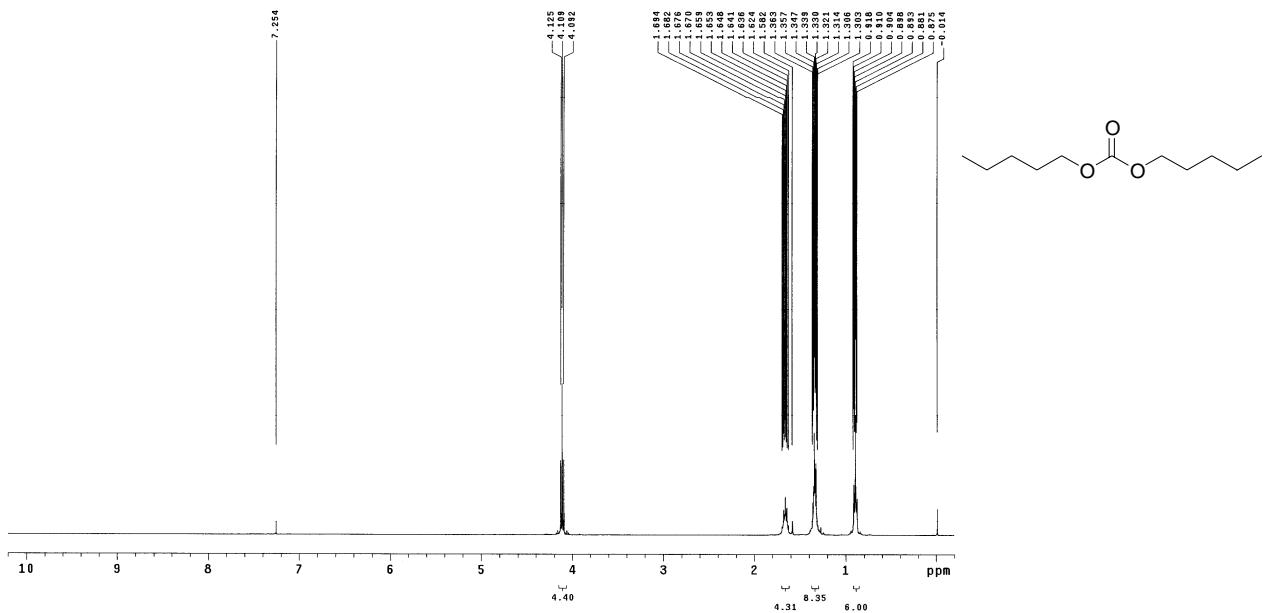
**3-Phenoxy-1-propanol (5).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



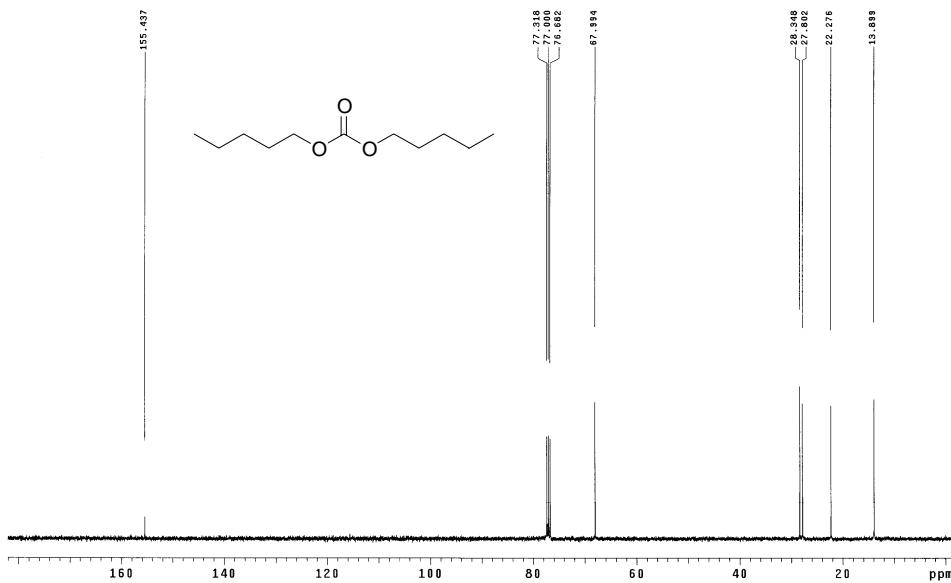
**3-Phenoxy-1-propanol (5).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



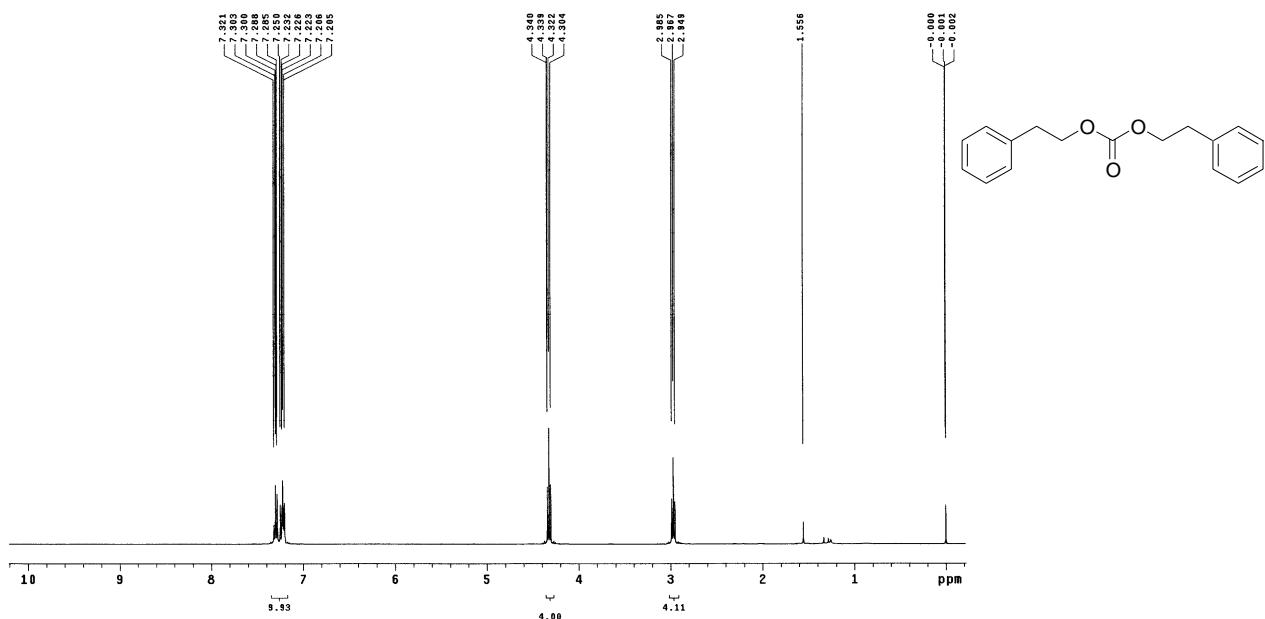
**Dipentylcarbonate (6).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



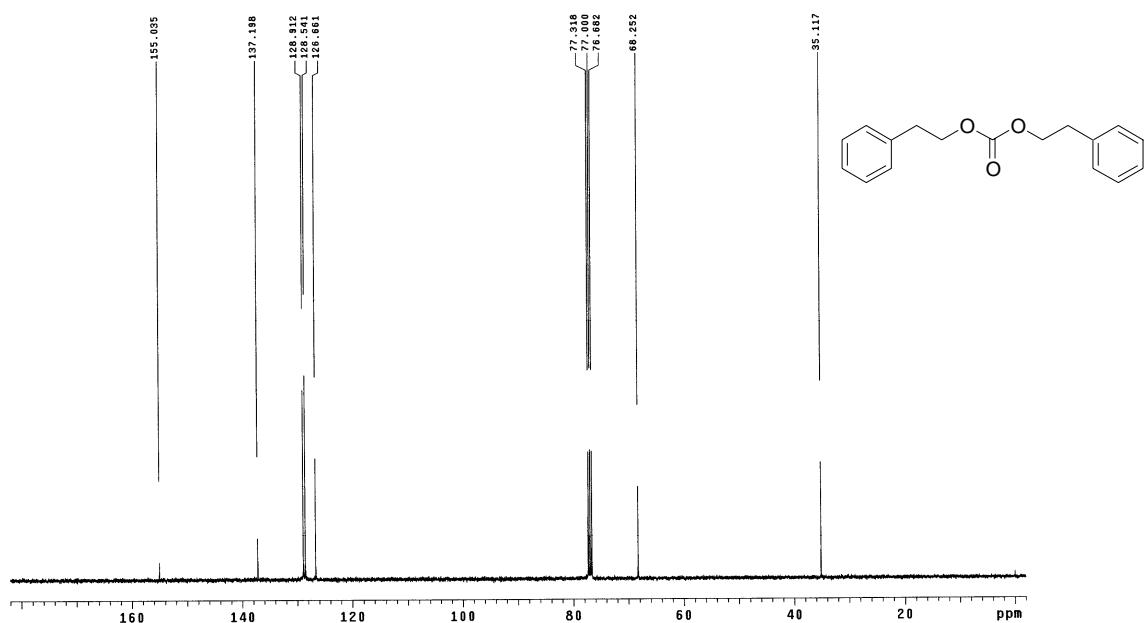
**Dipentylcarbonate (6).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



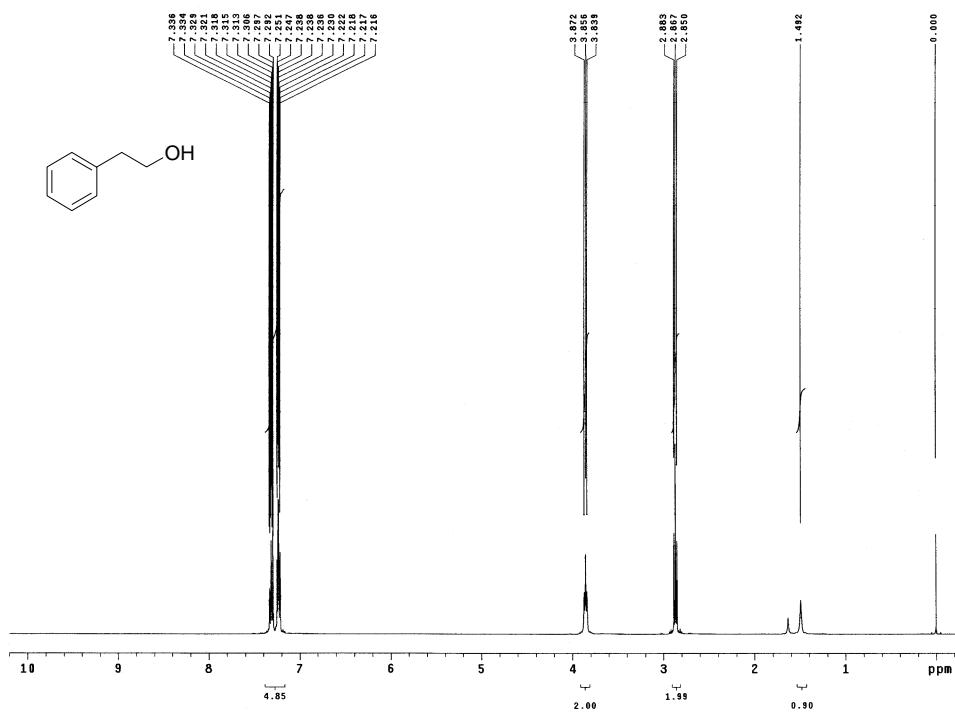
**Diphenethylcarbonate (8).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



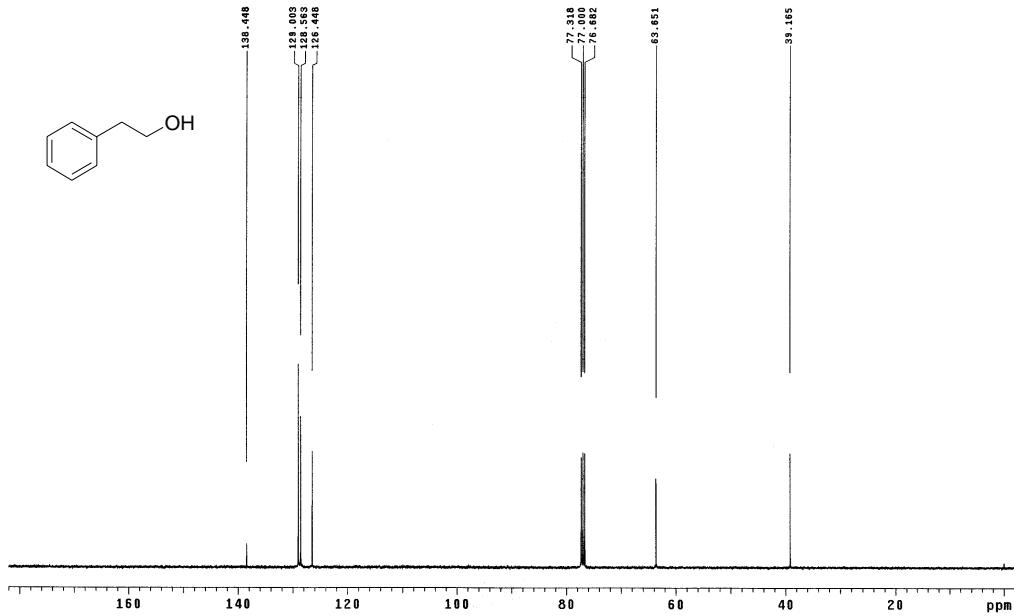
**Diphenethylcarbonate (8).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



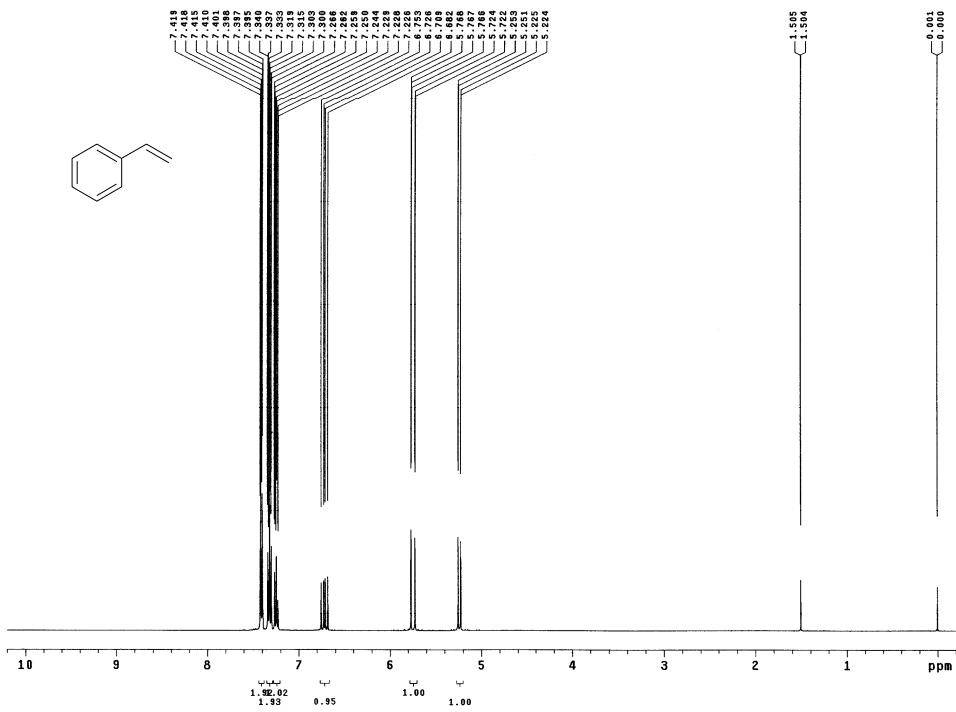
**2-Phenylethanol (9).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



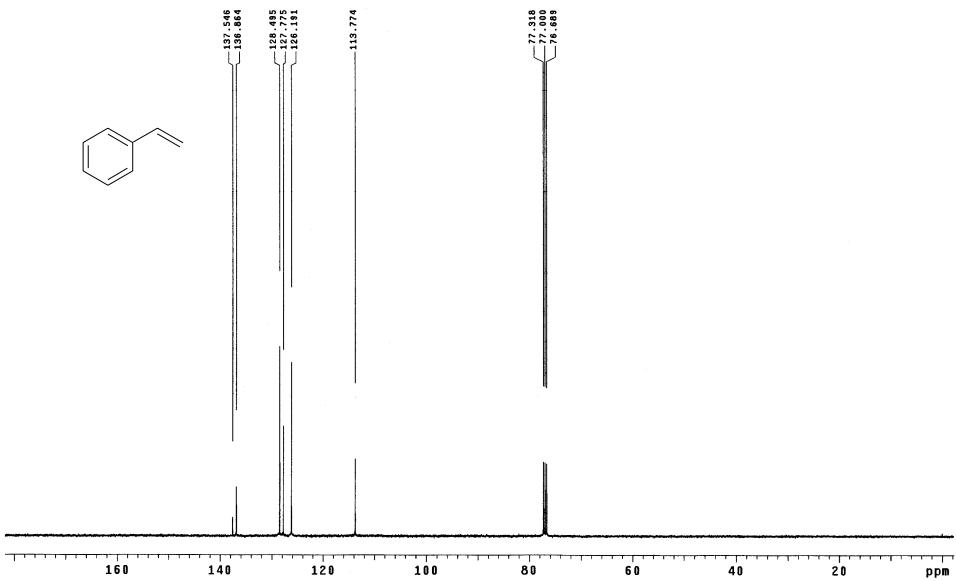
**2-Phenylethanol (9).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



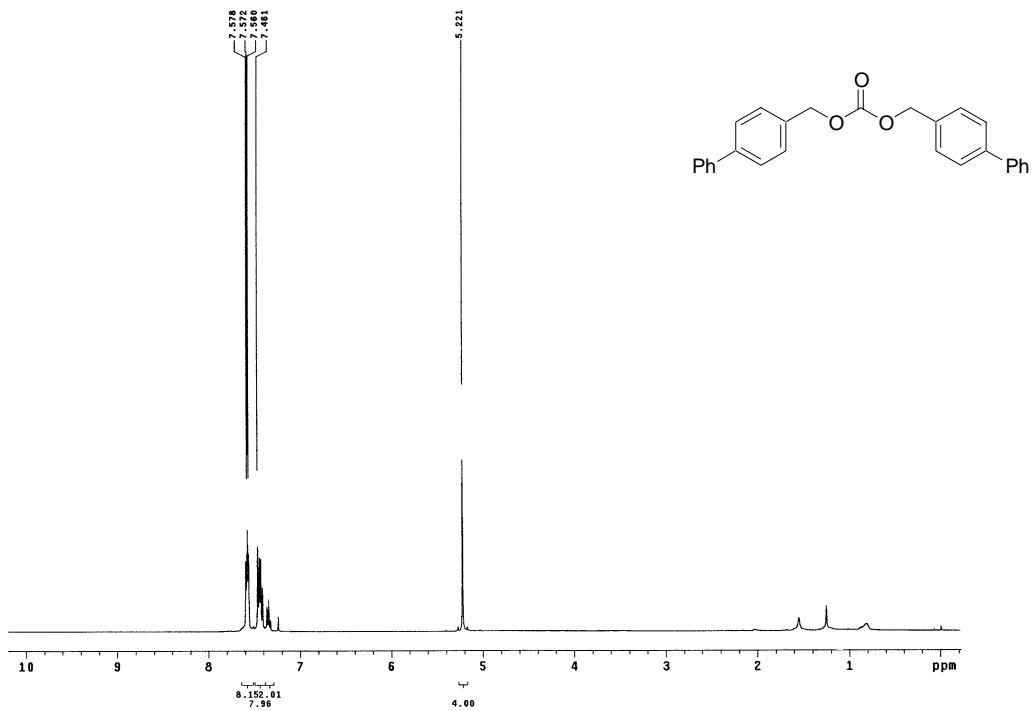
**Styrene.**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



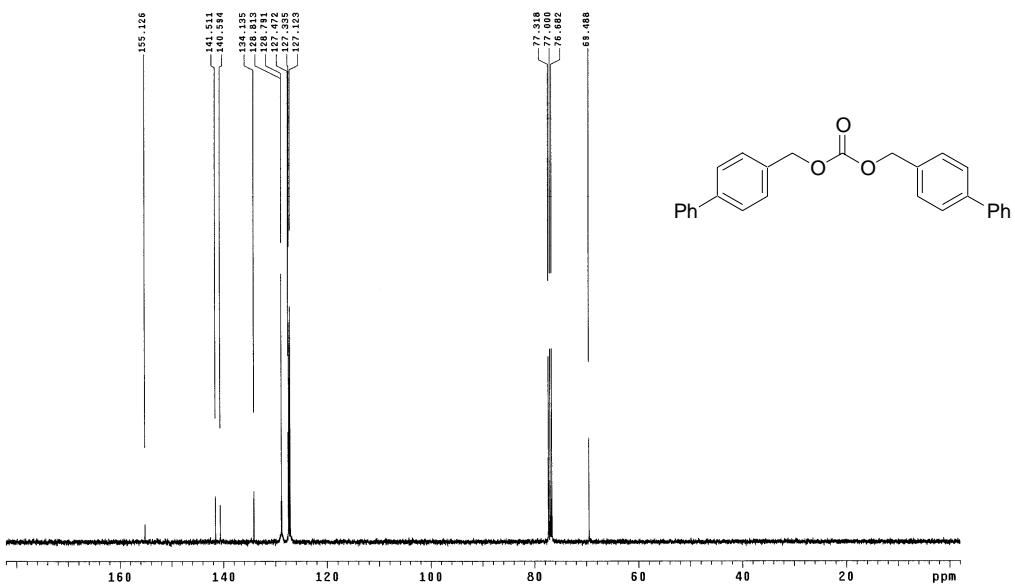
**Styrene.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



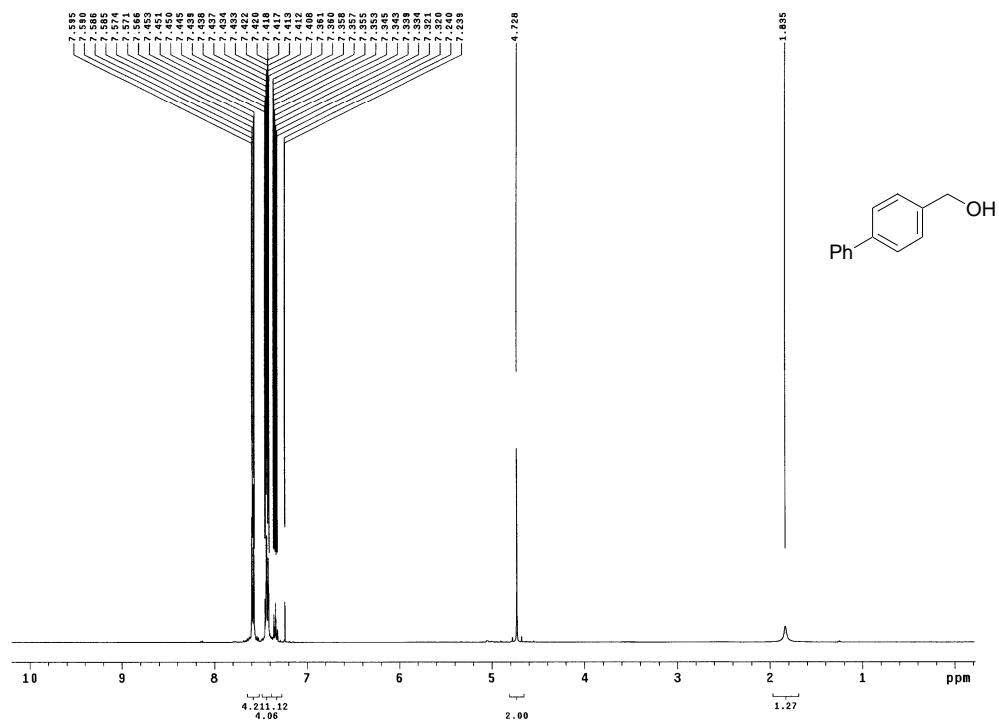
**Di(biphenyl-4-ylmethyl)carbonate (10).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



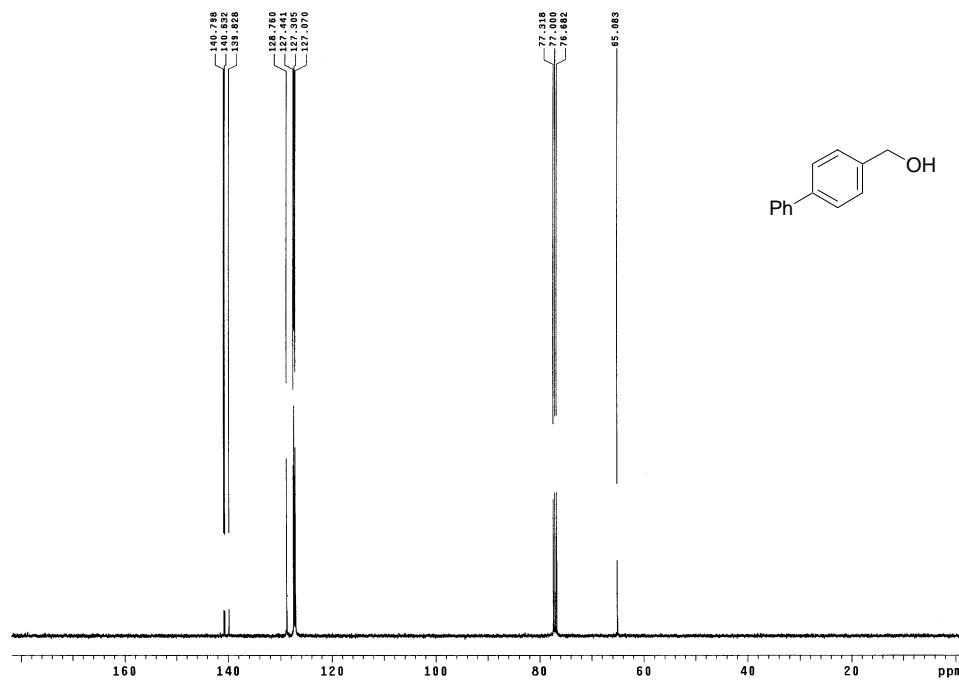
**Di(biphenyl-4-ylmethyl)carbonate (10).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



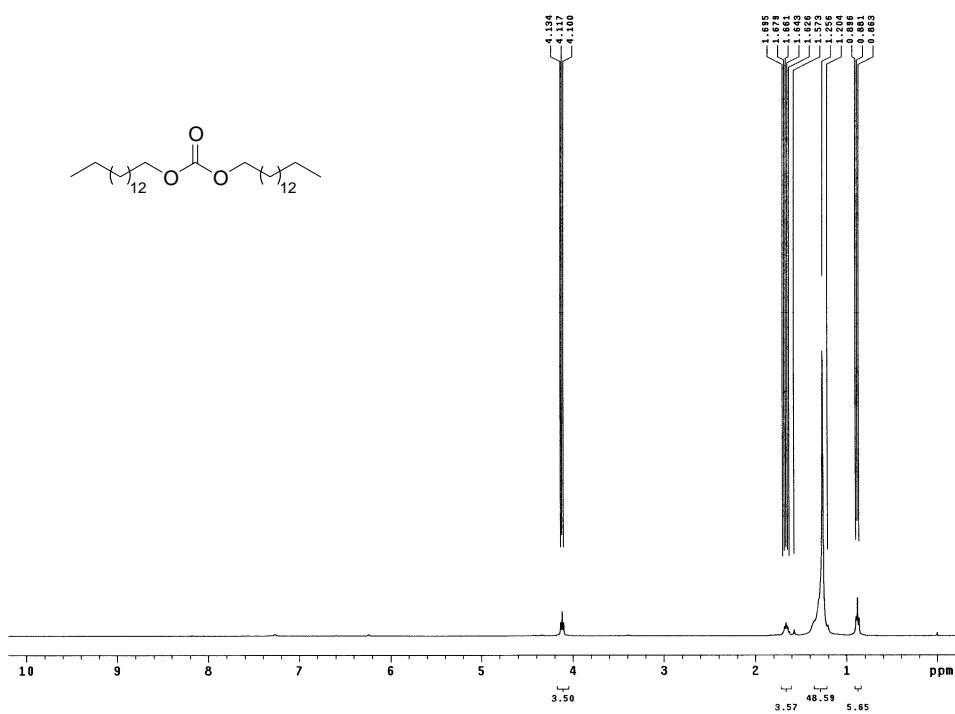
**1,1'-Biphenyl-4-yl-methanol (11).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



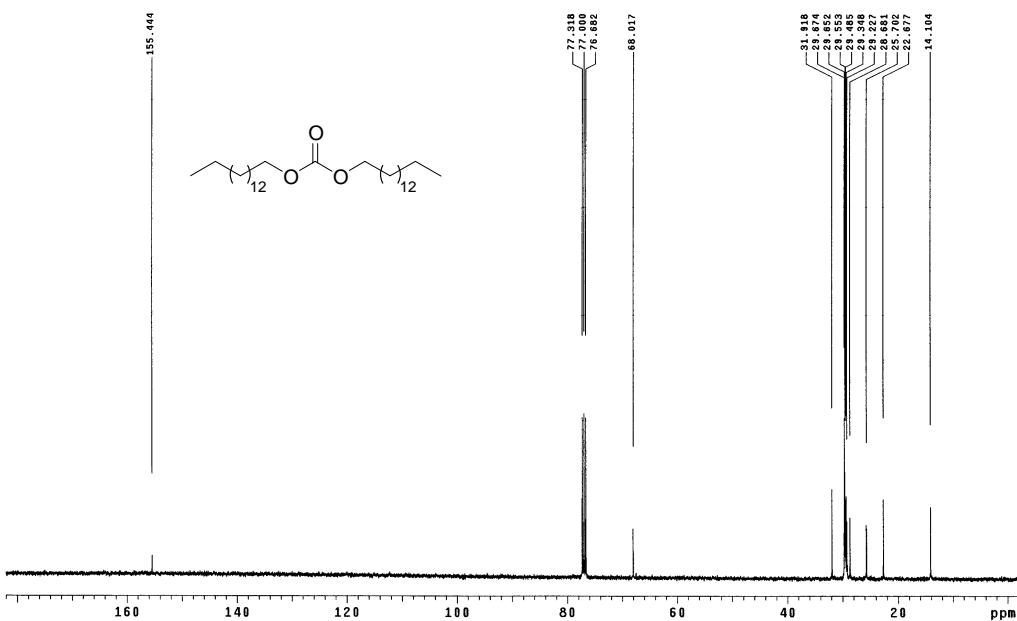
**1,1'-Biphenyl-4-yl-methanol (11).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



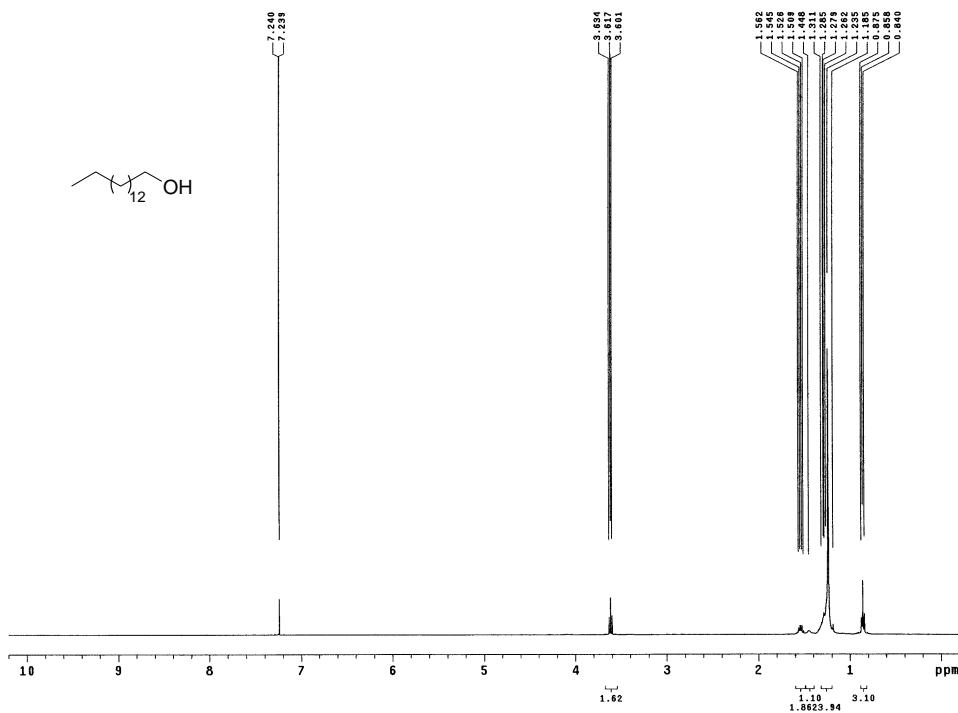
**Dipentadecanylcarbonate (12).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



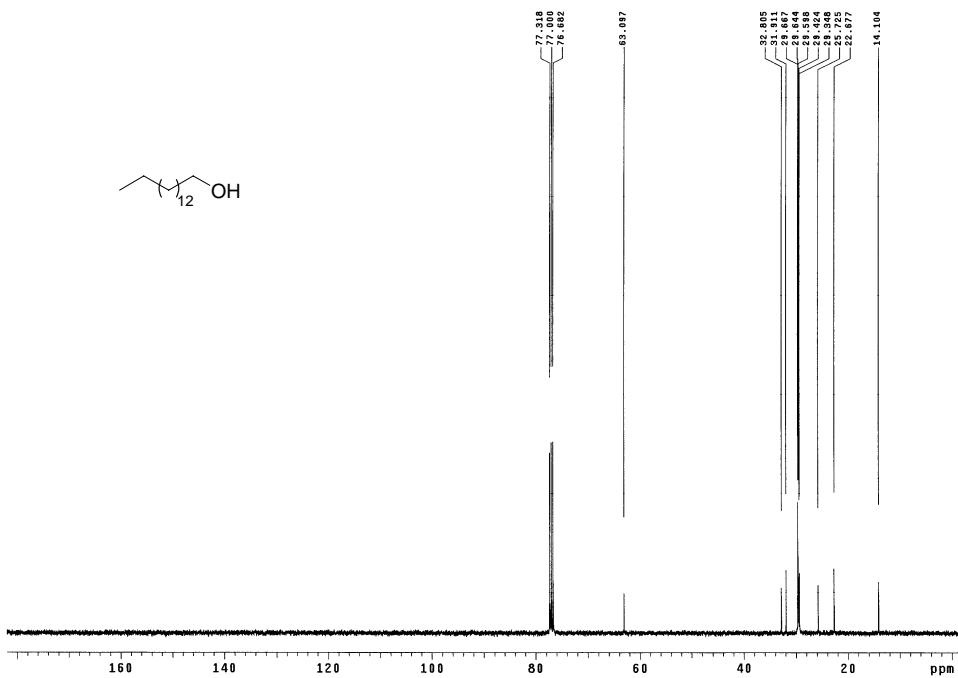
**Dipentadecanylcarbonate (12).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



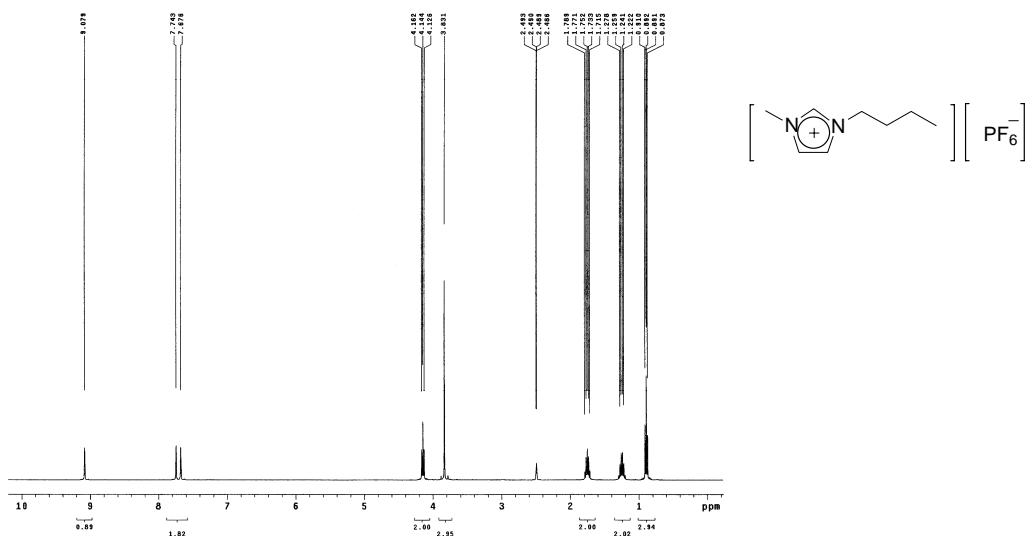
**Pentadecan-1-ol (13).**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



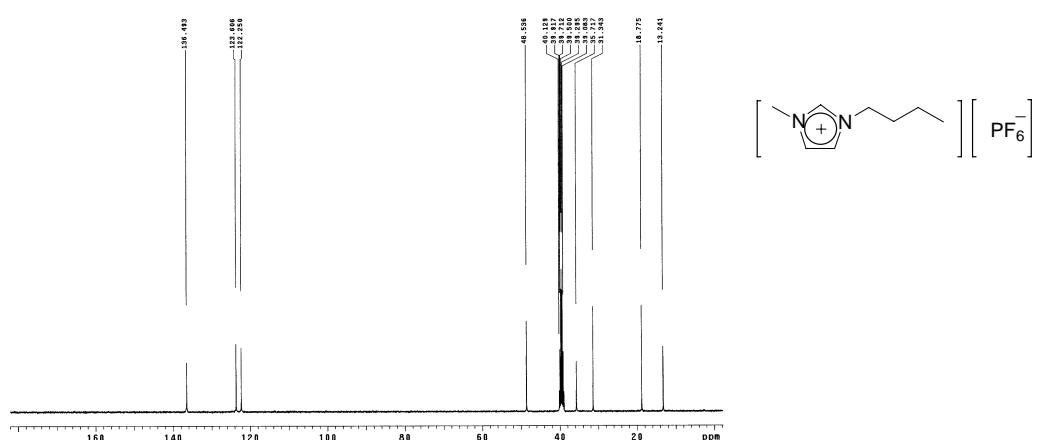
**Pentadecan-1-ol (13).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



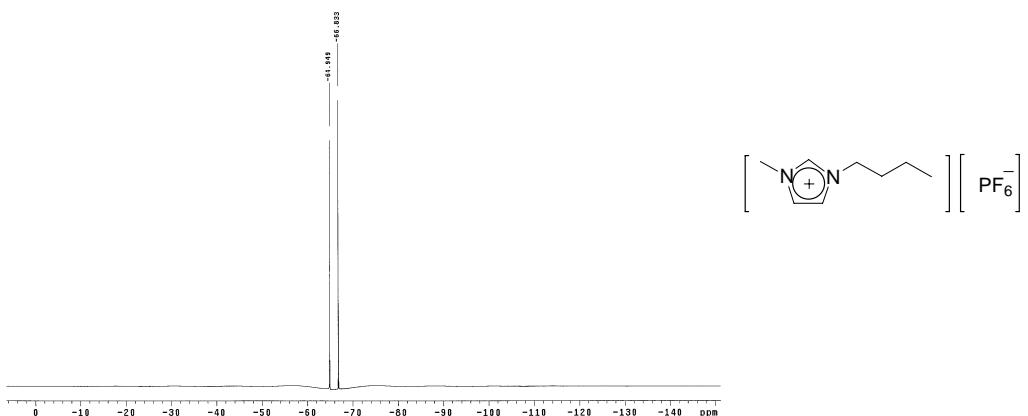
**1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate.**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )



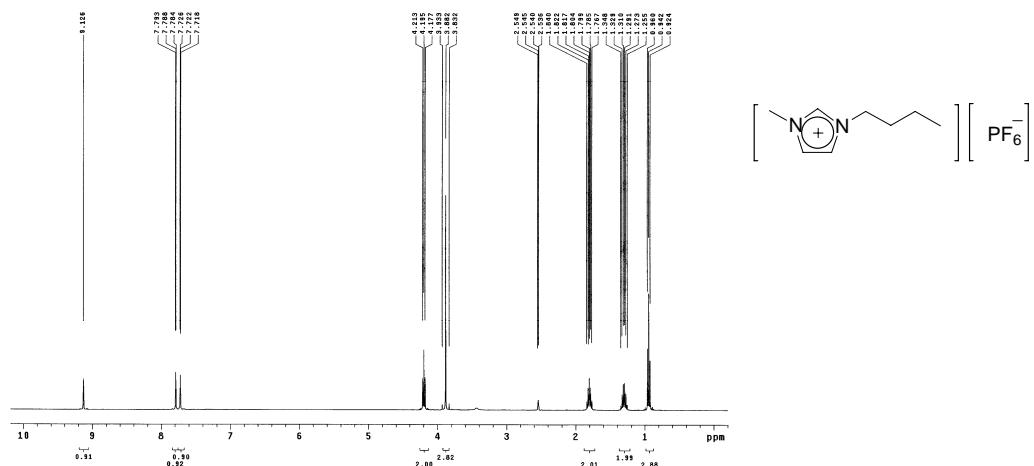
**1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate.**  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )



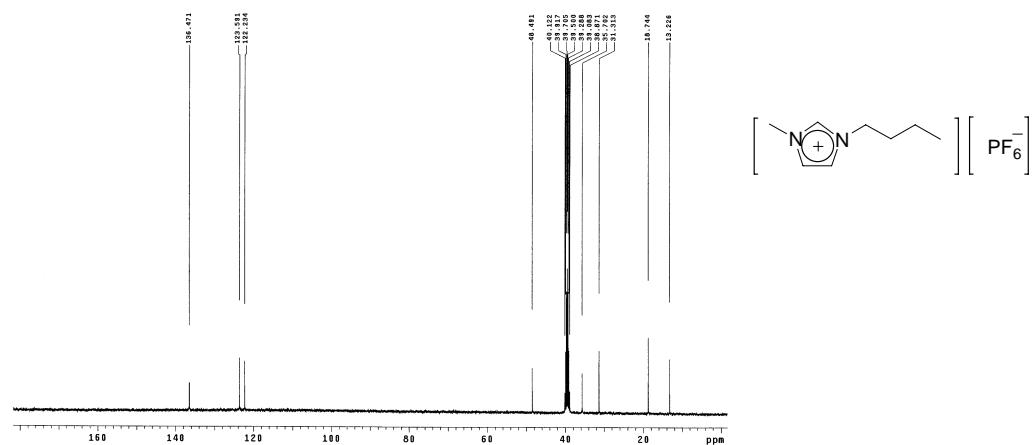
**1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate.**  $^{19}\text{F}$  NMR (400 MHz, DMSO- $d_6$ )



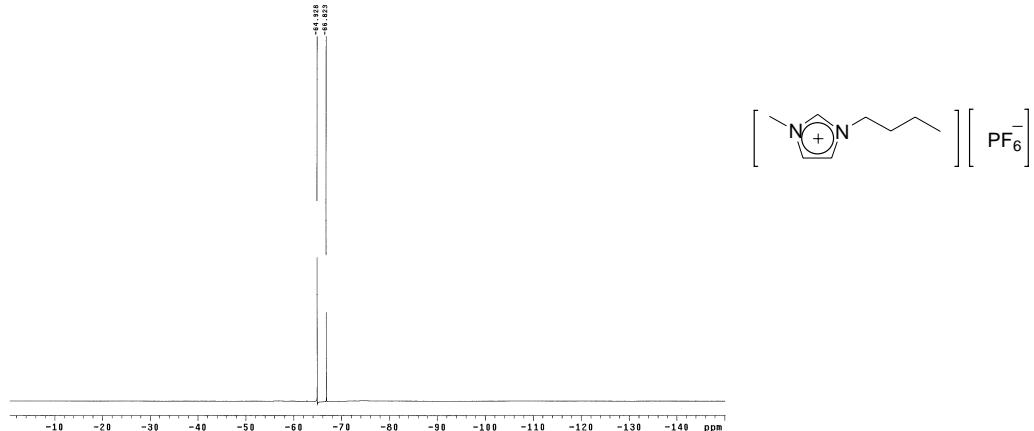
**1-n-Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 1).**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )



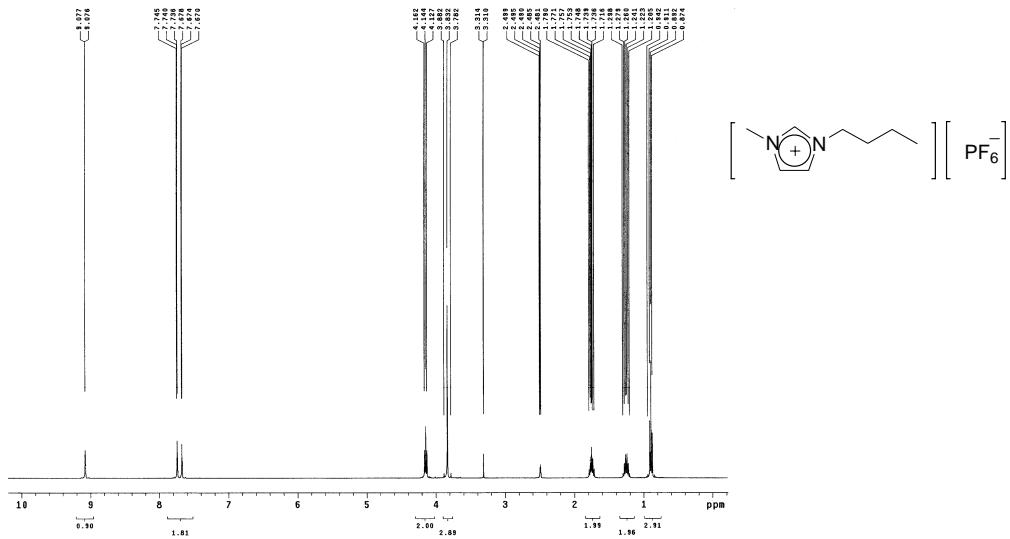
**1-n-Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 1).**  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ )



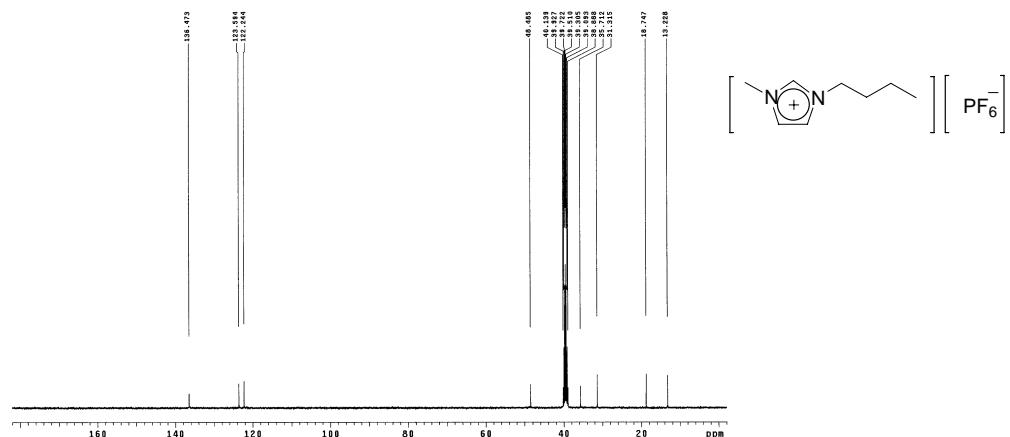
**1-n-Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 1).**  $^{19}\text{F}$  NMR (400 MHz, DMSO- $d_6$ )



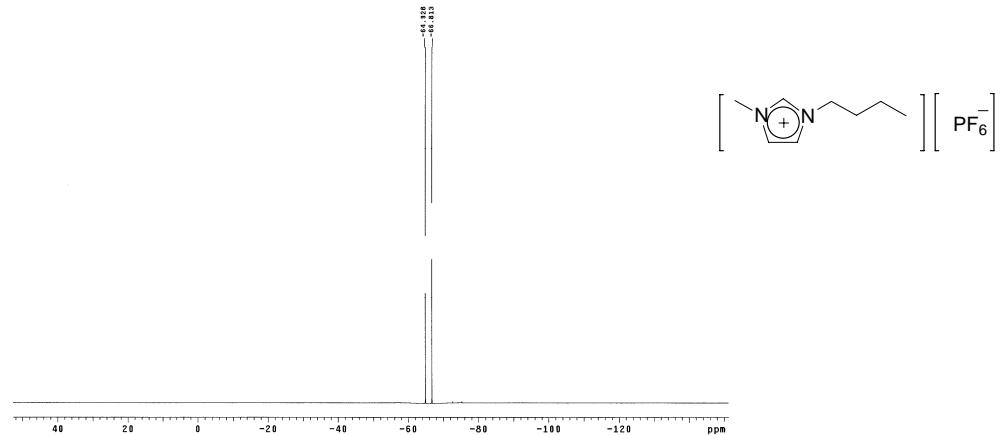
**1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 2).**  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )



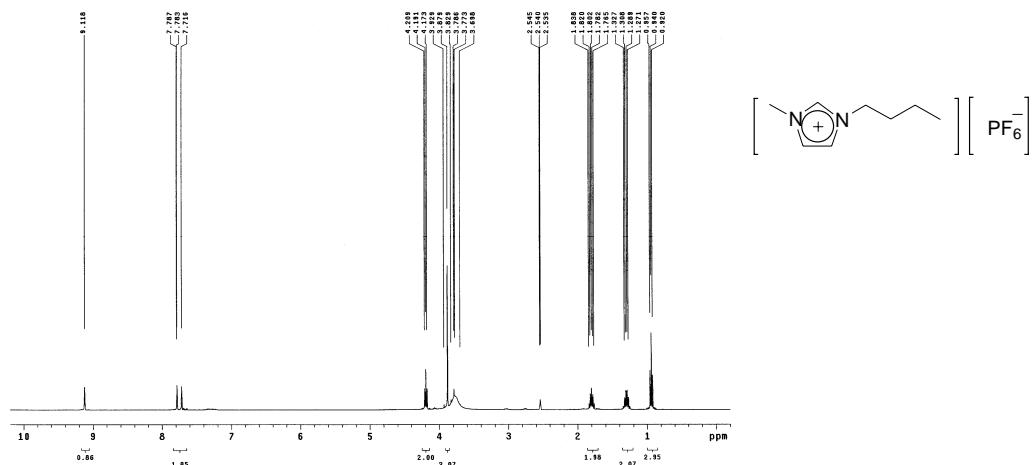
**1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 2).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )



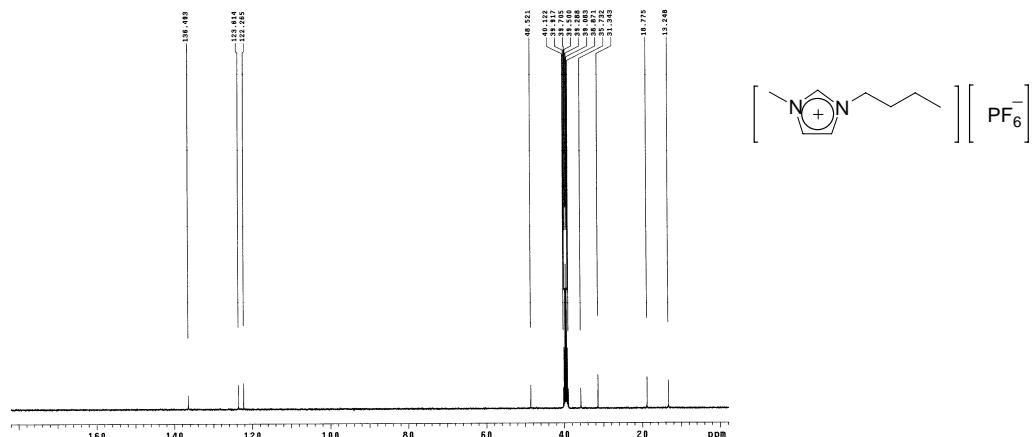
**1-*n*-Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 2).**  $^{19}\text{F}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )



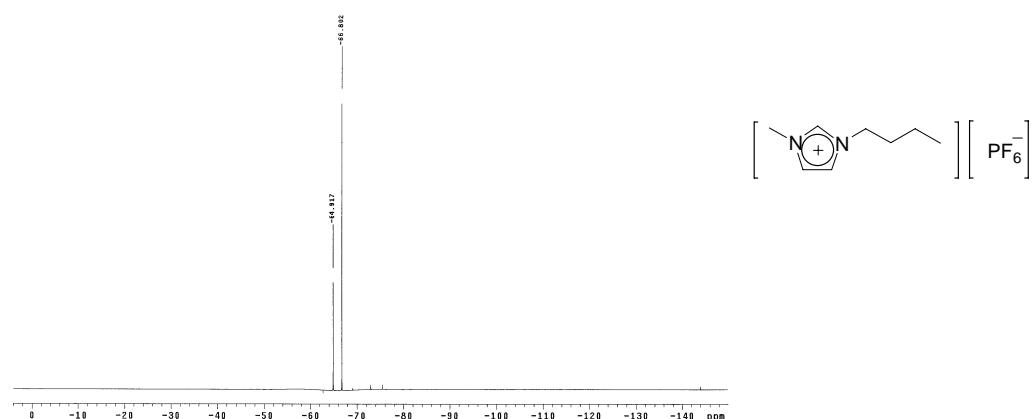
**1-n-Butyl-3-methylimidazolium Hexafluorophosphate (recycle 3).**  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )



**1-n-Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 3).**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ )



**1-n-Butyl-3-methylimidazolium Hexafluorophosphate (Recycle 3).**  $^{19}\text{F}$  NMR (400 MHz,  $\text{DMSO}-d_6$ )



## References

- (1) Muccianti, V.; Rossi, L.; Feroci, M.; Sotgiu, G. *Syn. Commun.* **2002**, *32*, 1205-1210.
- (2) Nakao, R.; Rhee, H.; Uozumi, Y. *Org. Lett.* **2005**, *7*, 163-165.
- (3) Satomura, M.; Iwakura, K.; Igarashi, A. *Jpn. Kokai Tokkyo Koho* **1986**, 501-507.
- (4) Tei, T.; Sato, Y.; Hagiya, K.; Tai, A.; Okuyama, T.; Sugimura, T. *J. Org. Chem.* **2002**, *67*, 6593-6598.
- (5) Ataka, K.; Yamamoto, S. *Jpn. Kokai Tokkyo Koho* **2003**, *3*.
- (6) Karimi, B.; Zamani, A.; Zareyee, D. *Tetrahedron Lett.* **2004**, *45*, 9139-9141.
- (7) Choi, J. K.; Joncich, M. J. *J. Chem. Eng. Data* **1971**, *16*, 87-90.
- (8) Na, Y.; Park, S.; Han, S. B.; Han, H.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2004**, *126*, 250-258.
- (9) Sano, H. *Jpn. Kokai Tokkyo Koho* **2003**, *5*.
- (10) Chandrasekhar, S.; Shyamsunder, T.; Chandrashekar, G.; Narsihmulu, C. *Synlett* **2004**, *3*, 522-524.