Using Geminal Dicationic Ionic Liquids as Solvents for High Temperature Organic Reactions

Supporting Information

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Genaral Methods

NMR spectra were recorded using a Varian 300 MHz NMR and samples were prepared in deuterated solvents. The HPLC system included two Shimadzu LC-10AD pumps, one Shimadzu SPD-6A UV VWD detector, and one Shimadzu CR 601 integrator. The C18 column is obtained from Advanced Separation Technologies (Whippany, NJ, USA). The UV detection wavelength for all the compounds is 254 nm and the flow rate of mobile phase is 1.0 mL/min. The mobile phase is the mixture of acetonitrile and water. All chemicals were purchased form Aldrich and used directly unless otherwise noted. All the three dicationic ionic liquids were prepared following the previous procedure.[1] The synthesis of *m*-substituted allyl phenyl ether is also illustrated elsewhere[2].

Isomerization of carvone to carvacrol (1). 300 mg carvone was dissolved in 5 mL dicationic ionic liquid and the mixture was heated to 250 °C or 300 °C under argon. The reaction was monitored by TLC. After the reaction was completed, ethyl ether (5 x 5 mL) was used to extract the product from the cooled down ionic liquid solution. Ethyl ether was removed under vacume and the residue was purified by flash chromatography (hexanes/EtOAc). Yield was different according to different reaction condition. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (d, J = 7.8 Hz, 1H), 6.73 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H), 6.66 (d, J = 1.6 Hz, 1H), 4.58 (br, 1H), 2.83 (m, J = 6.9 Hz, 1H), 2.22 (s, 3H), 1.22 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.8, 148.7, 131.1, 121.1, 119.0, 113.3, 33.9, 24.2, 15.6. The NMR results are matched with literature[3].

Claisen Rearrangement (2-5). 200 mg allyl phenyl ether was dissolved in 5 mL dicationic ionic liquid and the mixture was heated to 250 °C or 300 °C under argon for 10 minutes (by TLC). After the reaction was completed, ethyl ether (5 x 5mL) was used to extract the product from the cooled down ionic liquid solution. Ethyl ether was removed under vacume and the residue was purified by flash chromatography (hexanes/EtOAc). Yield was different according to different reaction condition. Similar procedure was used for the rearrangement of *m*-substituted allyl phenyl ether.

2-allylphenol: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18-7.13 (m, 2H), 6.94-6.89 (m, 1H), 6.83 (d, J = 8.1 Hz, 1H), 6.09-5.98 (m, 1H), 5.22-5.19 (m, 1H), 5.16-5.15 (m, 1H), 5.08 (s, 1H), 3.44 (d, J = 6.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3, 136.7, 130.7, 128.1, 125.6, 121.2, 116.7, 116.0, 35.3. The NMR results are matched with literature[4].

2-Allyl-5-methoxyphenol. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, J = 8.1 Hz, 1H), 6.46 (dd, J_1 = 8.1 Hz, J_2 = 2.4 Hz, 1H), 6.42 (d, J = 2.4 Hz, 1H), 6.07-5.94 (m, 1H), 5.20-5.16 (m, 1H), 5.16-5.12 (m, 1H), 5.10 (s, 1H), 3.77 (s, 3H), 3.35 (d, J = 6.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.8, 155.3, 137.0, 131.1, 117.5, 116.5, 106.6, 102.3, 55.6, 34.8. The NMR results are matched with literature[5].

2-Allyl-3-methoxyphenol. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (t, J = 8.1 Hz, 1H), 6.50 (d, J = 8.1 Hz,

1H), 6.49 (d, J = 8.1 Hz, 1H), 6.05-5.92 (m, 1H), 5.15-5.13 (m, 1H), 5.11-5.06 (m, 1H), 5.01 (s, 1H), 3.81 (s, 3H), 3.47 (dt, J_1 = 6.0 Hz, J_2 = 1.8 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 155.4, 136.5, 127.8, 115.7, 113.8, 109.0, 103.6, 56.0, 27.6. The NMR results are matched with literature[5].

2-Allyl-5-trifluoromethylphenol. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22 (d, J = 8.1 Hz, 1H), 7.15 (d, J = 8.1 Hz, 1H), 7.07 (s, 1H), 6.07-5.94 (m, 1H), 5.23-5.21 (m, 1H), 5.19 (s, 1H), 5.16-5.15 (m, 1H), 3.46 (d, J = 6.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.4, 135.5, 131.1, 130.5 (q, J = 32.4 Hz), 129.6 (q , J = 1.2 Hz), 124.1 (q , J = 270.3 Hz), 117.9 (q , J = 3.9 Hz), 117.6, 113.0 (q , J = 3.9 Hz), 35.1.

2-Allyl-3-trifluoromethylphenol. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29-7.20 (m, 2H), 7.04-7.01 (m, 1H), 6.05-5.92 (m, 1H), 5.24 (s, 1H), 5.20-5.15 (m, 1H), 5.12-5.10 (m, 1H), 3.58 (d, J = 5.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.6, 135.4, 130.3 (q, J = 29.4 Hz), 127.9, 124.5 (q , J = 272.3 Hz), 124.1 (q , J = 1.6 Hz), 120.3 (q , J = 1.0 Hz), 118.8 (q , J = 5.8 Hz), 116.96, 31.2 (q , J = 2.1 Hz).

2-Allyl-5-methylphenol and 2-Allyl-3-methylphenol. These two compounds cannot be separated by flash chromatography. ^{1}H NMR (300 MHz, $CDCl_3$) 7.05-6.98 (m, 2H), 6.79-6.65 (m, 4H), 6.08-5.91 (m, 2H), 5.18-4.99 (m, 4H), 4.86 (s, 1H), 4.79 (s, 1H), 3.43 (dt, J_1 = 5.7 Hz, J_2 = 1.8 Hz, 2H), 3.38 (d, J = 6.3 Hz, 2H), 2.29 (s, 6H). The ^{1}H NMR result is matched with literature[5].

Diels-Alder reaction (6). 178 mg anthracene and 172 mg diethyl fumarate were dissolved in 5 mL dicationic ionic liquid and the mixture was heated to 220 °C under argon for 10 minutes. After the reaction was completed, ethyl ether (5 x 5mL) was used to extract the product from the cooled down ionic liquid solution. Ethyl ether was removed under vacume and the residue was purified by flash chromatography (hexanes/EtOAc). Yield was different according to different reaction condition.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.32 (m, 2H), 7.24-7.21 (m, 2H), 7.14-7.08 (m, 4H), 4.73 (s, 2H), 4.13-4.00 (m, 4H), 3.42 (s, 2H), 1.22 (t, J = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 142.3, 140.6, 126.6, 126.4, 124.8, 124.0, 61.2, 48.0, 47.0, 14.5. The NMR results are matched with literature[6].

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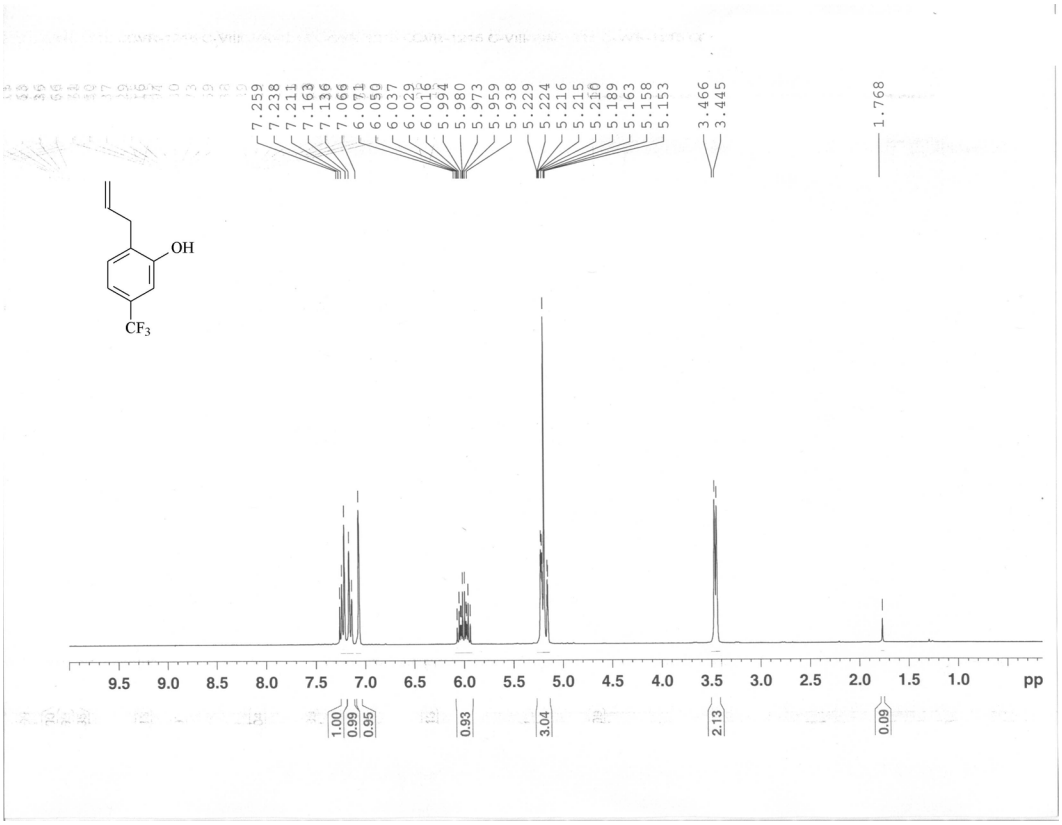
(2) White, W. N.; Slater, C. D. *J. Org. Chem.* **1961**, *26*, 3631-3638.

(3) From website: http://www.sigmaaldrich.com/spectra/fnmr/FNMR011649.PDF

(4) From website: http://www.sigmaaldrich.com/spectra/fnmr/FNMR009224.PDF

(5) Gozzo, F. C.; Fernandes, S. A.; Rodrigues, D. C.; Eberlin, M. N.; Marsaioli, A. J. *J. Org. Chem.* **2003**, *68*, 5493-5499.

(6) Garrigues, B.; Laporte, C.; Laurent, R.; Laporterie, A.; Dubac, J. *Liebigs Ann.* **1996**, 739-741.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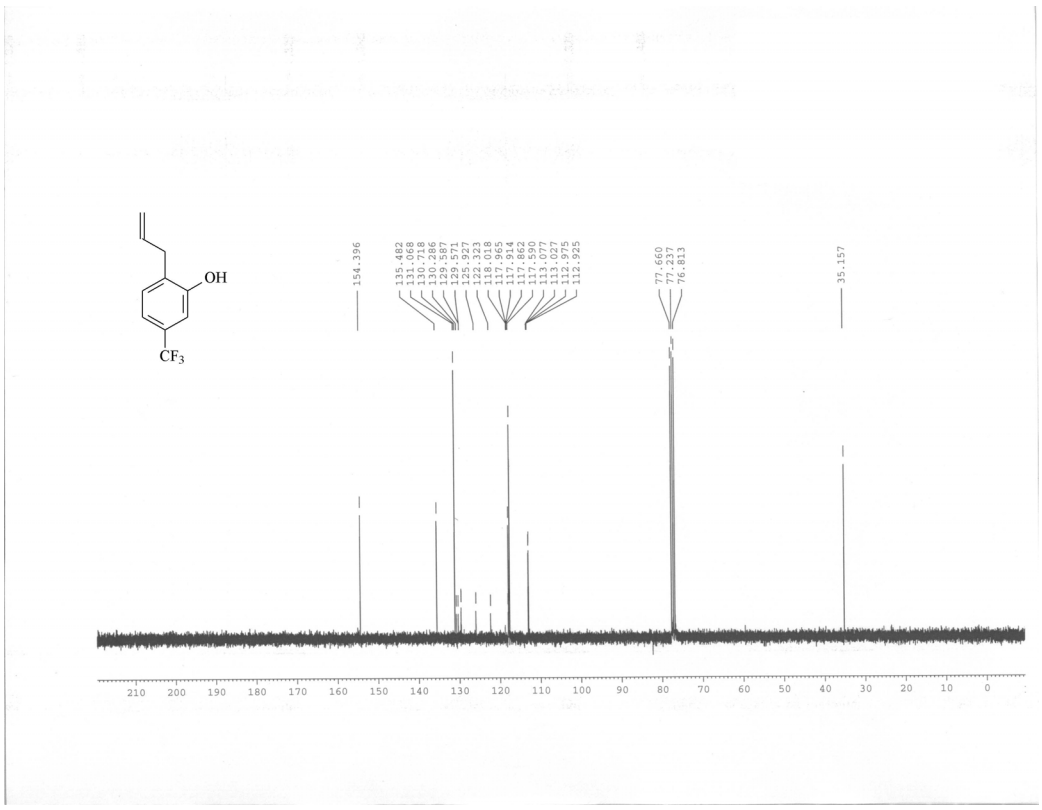
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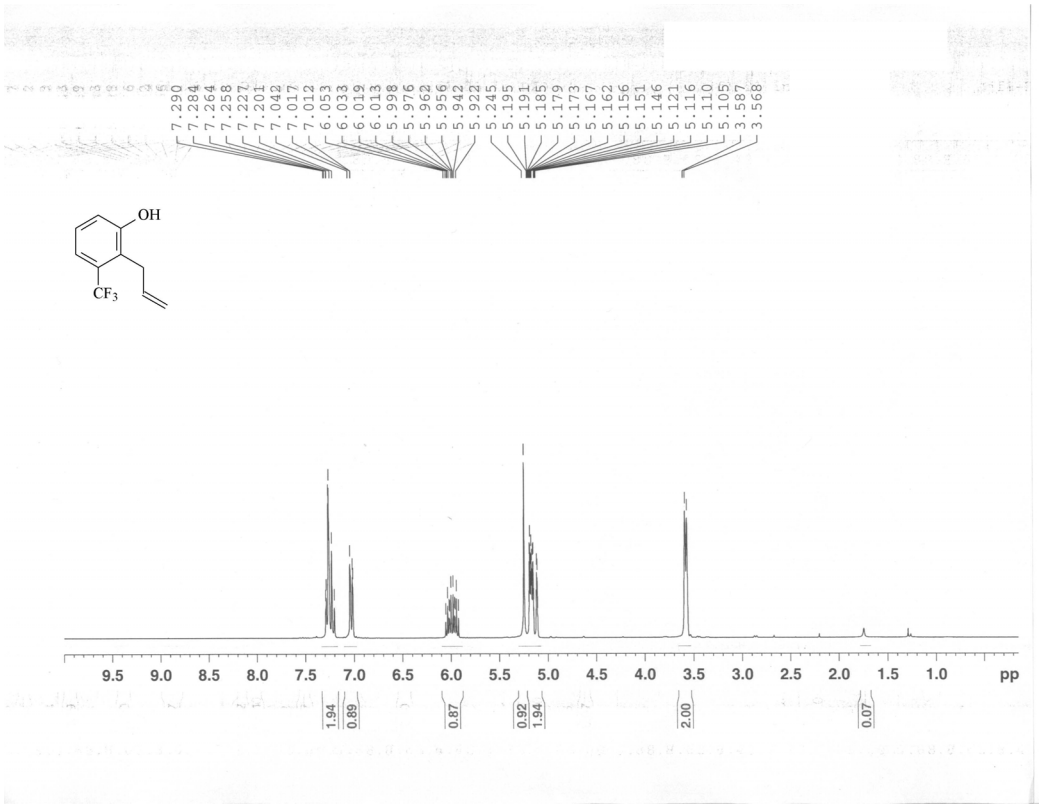
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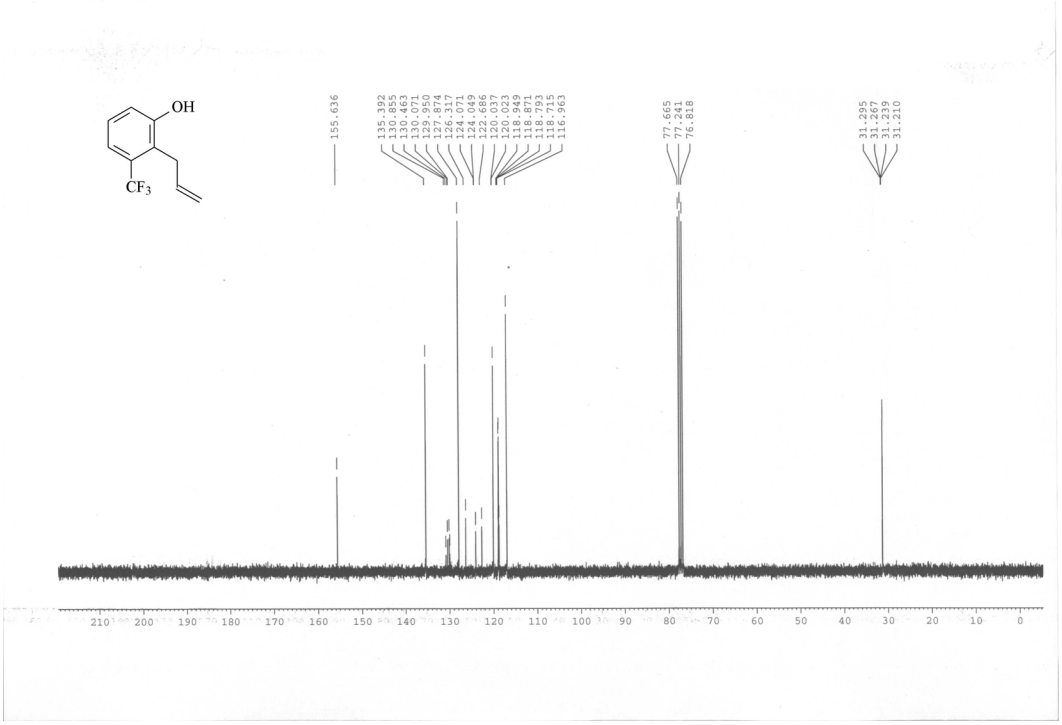
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