Supplementary Information

**HIGHLY EFFICIENT SYNTHESIS OF 1,3-DIOXANES VIA PRINS REACTION IN
BRØNSTED-ACIDIC IMIDAZOLIUM IONIC LIQUID**

Rajesh G. Kalkhambkar,¹ and Yeon T. Jeong,²

¹ *Department of Chemistry, Karnatak University's Karnatak Science College, Dharwad
Karnatak 580001, India*

² *Department of Image Science and Engineering, Pukyong National University, Busan
608-739, Republic of Korea.*

Synthesis of Brønsted-Acidic IL [bmim(SO₃H)][OTf]

To butanesultone (31.97 mmol) in a two-necked flask under nitrogen was slowly added 1-methylimidazole (32.25 mmol), and the mixture was stirred for 48 h at room temperature. The solid so obtained was repeatedly washed with toluene and diethyl ether and dried under vacuum at room temperature to give the corresponding zwitterion 3-(1-methyl-1*H*-imidazol-3-ium-3-yl)butane-1-sulfonate in 96% yield. Further, the resulting mixture of 3-(1-methyl-1*H*-imidazol-3-ium-3-yl)butane-1-sulfonate (10.0 mmol) and trifluoromethanesulfonic acid (10.85 mmol) was heated to 40 °C and stirred at the same temperature for 48 h. After being allowed to cool to room temperature, the obtained ionic liquid was washed repeatedly with toluene and diethyl ether to remove non-ionic residues, and dried under vacuum at room temperature to give [bmim(SO₃H)][OTf] (**1**) (98%). The intermediate 3-(1-methyl-1*H*-imidazol-3-ium-3-yl)butane-1-sulfonate and the product [bmim(SO₃H)][OTf] were thoroughly characterized by IR, ¹H NMR and ¹³C NMR and the data obtained were in agreement with the reported values.

Experimental and characterization data of ionic liquid and various substituted 1,3-dioxanes

4-(1-methyl-1*H*-imidazol-3-ium-4-yl)butane-1-sulfonate¹: Colorless hygroscopic solid, Yield: 96%, mp: 186-188 °C; IR (KBr, cm⁻¹): 1573, 1180, 1022; ¹HNMR (300MHz, D₂O): δ_H 3.45 (s, 3H), 2.98 (t, 2H, *J* = 7.5 Hz), 3.72 (t, 2H, *J* = 7.5 Hz), 2.12 (quint, 2H, *J* = 7.5 Hz), 1.96 (quint, 2H, *J* = 7.5 Hz), 7.48 (d, 1H, *J* = 15.5 Hz), 7.60 (d, 1H, *J* = 15.5 Hz), 8.75 (s, 1H); ¹³CNMR (75MHz, D₂O): δ_C 24.6, 30.4, 38.8, 52.4, 56.2, 121.9, 124.4, 145.4.

1-methyl-3-(4-sulfonylbutyl)-1H-imidazol-3-ium trifluoromethanesulfonate [bmim(SO₃H)][OTf] (1)¹

: Colorless viscous liquid, Yield: 98%; IR (KBr, cm⁻¹): 1580, 1240, 1090; ¹HNMR (300MHz, D₂O): δ_H 3.48 (s, 3H), 3.10 (t, 2H, *J* = 7.5 Hz), 3.70 (t, 2H, *J* = 7.5 Hz), 2.17 (quint, 2H, *J* = 7.5 Hz), 2.10 (quint, 2H, *J* = 7.5 Hz), 7.50 (d, 1H, *J* = 15.5 Hz), 7.64 (d, 1H, *J* = 15.5 Hz), 8.76 (s, 1H); ¹³CNMR (75MHz, D₂O): δ_C 23.8, 29.6, 38.6, 54.2, 56.6, 122.0, 124.2, 125.2 (q, *J*_{C-F} = 318 Hz), 146.0.

4-Phenyl-1,3-dioxane (1)^{2, 3, 4, 5, 6}

Colorless liquid; GC-MS: *m/z* 164; ¹H NMR (300 MHz, CDCl₃): δ 1.67-1.70 (m, 1H), 2.02-2.09 (m, 1H), 3.80-3.85 (m, 2H), 4.15-4.19 (m, 1H), 4.86 (d, 1H, *J* = 6.4 Hz), 5.17 (d, 1H, *J* = 6.4 Hz), 7.24-7.29 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ 27.8, 34.1, 41.9, 76.3, 133.2, 135.4, 136.9, 137.5, 141.7, 142.4; Anal. Calcd for C₁₀H₁₂O₂: C, 73.15; H, 7.37. Found: C, 73.12; H, 7.38.

2,4-Dimethyl-6-phenyl-1,3-dioxane (2)^{2, 4, 5}

Colorless Liquid; GC-MS: *m/z* 192; ¹H NMR (300 MHz, CDCl₃): δ 1.24 (d, 3H, *J* = 6.0 Hz), 1.41 (d, 3H, *J* = 5.2 Hz), 3.12 (dd, 1H, *J* = 4.5, 11.3 Hz), 3.89 (t, 1H, *J* = 11.3 Hz), 4.19 (dd, 1H, *J* = 4.5, 11.3 Hz), 4.61 (q, 1H, *J* = 9.8 Hz), 4.92 (q, 1H, *J* = 6.0 Hz), 6.91-

7.10 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.0, 21.6, 49.1, 71.8, 84.1, 94.0, 126.9, 127.1, 127.7, 137.1, 139.0, 141.20; Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_2$: C, 74.97; H, 8.39. Found: C, 74.95; H, 8.38.

2,4-Dicyclohexyl-6-phenyl-1,3-dioxane (3)^{2, 4, 5}

Crystalline solid; mp 94-96 °C; GC-MS: m/z 328; ^1H NMR (300 MHz, CDCl_3): δ 0.82–2.02 (m, 24H), 3.36 (m, 1H), 4.35 (d, 1H, J = 5.3 Hz), 4.53 (dd, 1H, J = 3.0, 11.3 Hz), 7.15–7.24 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 25.8, 26.6, 27.5, 27.8, 28.2, 28.8, 35.3, 36.7, 42.5, 42.7, 45.8, 47.3, 48.9, 75.4, 76.8, 78.1, 80.7, 104.8, 125.7, 127.3, 128.3, 142.6; Anal. Calcd for $\text{C}_{22}\text{H}_{32}\text{O}_2$: C, 80.44; H, 9.82. Found: C, 80.41; H, 9.82.

4-(4-Fluorophenyl)-1,3-dioxane (4)^{2, 4, 5}

Colorless crystalline solid; mp 77-79 °C; GC-MS: m/z 182; ^1H NMR (300 MHz, CDCl_3): δ 1.41–1.46 (m, 1H), 1.70 (td, 2H, J = 2.2, 13.6 Hz), 3.84 (m, 1H), 4.58 (dd, 2H, J = 3.0, 11.3 Hz), **4.80 (m, 1H)**, 7.21–7.34 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 41.3, 71.3, 77.5, 98.7, 127.1, 127.4, 131.2, 161.3 (C-F, J = 246.30 Hz); Anal. Calcd for $\text{C}_{10}\text{H}_{11}\text{FO}_2$: C, 65.92; H, 6.09. Found: C, 65.90; H, 6.10.

2,4-Dimethyl-6-(4-fluorophenyl)-1,3-dioxane (5)^{4, 5}

Yellow solid; mp 81-83 °C; GC-MS: *m/z* 210; ¹H NMR (300 MHz, CDCl₃): δ 1.24 (d, 3H, *J* = 6.0 Hz), 1.38 (d, 3H, *J* = 5.2 Hz), 1.43–1.48 (m, 1H), 1.69 (td, 1H, *J* = 2.2, 13.6 Hz), 3.82 (m, 1H), 4.57 (dd, 1H, *J* = 3.0, 11.3 Hz), 4.83 (q, 1H, *J* = 5.3 Hz), 7.22–7.32 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 21.1, 21.4, 40.3, 72.3, 77.5, 98.7, 127.1, 128.4, 133.2, 160.2 (C-F, *J* = 246.10 Hz); Anal. Calcd for C₁₂H₁₅FO₂: C, 68.55; H, 7.19. Found: C, 68.56; H, 7.18.

2,4-Diethyl-6-(4-fluorophenyl)-1,3-dioxane (6)⁴

Colorless solid; mp 81-83 °C; GC-MS: *m/z* 238; ¹H NMR (300 MHz, CDCl₃): δ 0.64 (d, 1H, *J* = 6.9 Hz), 0.96 (t, 1H, *J* = 7.5 Hz), 1.02 (t, 1H, *J* = 7.5 Hz), 1.46 (ddq, 2H, *J* = 14.0, 6.0, 7.5 Hz), 1.67 (ddq, 2H, *J* = 14.0, 8.0, 7.5 Hz), 1.75-1.77 (m, 4H), 3.73 (ddd, 1H, *J* = 8.0, 6.0, 2.3 Hz), 4.69 (t, 1H, *J* = 5.0 Hz), 4.82 (d, 1H, *J* = 2.3 Hz), 7.22 (tt, 1H, *J* = 7.1, 1.9 Hz), 7.37–7.44 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 4.8, 8.9, 28.3, 29.8, 47.2, 74.2, 76.6, 104.4, 113.2, 129.9, 134.6, 160.6 (C-F, *J* = 245.40 Hz); Anal. Calcd for C₁₄H₁₉FO₂: C, 70.56; H, 8.04. Found: C, 70.58; H, 8.03.

4-(4-Methylphenyl)-1,3-dioxane (7)^{4, 5}

Colorless solid; mp 74-76 °C; GC-MS: m/z 178; ¹H NMR (300 MHz, CDCl₃): δ 2.34 (s, 3H), 1.44–1.47 (m, 2H), 1.78 (td, 1H, *J* = 2.2, 13.6 Hz), 3.80 (m, 2H), 4.60 (dd, 1H, *J* = 3.0, 11.3 Hz), 4.85 (q, 1H, *J* = 5.3 Hz), 7.22–7.32 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): 20.6, 32.5, 48.3, 81.4, 98.7, 128.1, 130.4, 134.6, 136.2; Anal. Calcd for C₁₁H₁₄O₂: C, 74.13; H, 7.92. Found: C, 74.10; H, 7.92.

2,4-Dimethyl-6-(4-methylphenyl)-1,3-dioxane (8)^{4, 5}

Colorless solid; mp 84-86 °C; GC-MS: m/z 206; ¹H NMR (300 MHz, CDCl₃): δ 2.28 (s, 3H), 1.22 (d, 3H, *J* = 6.0 Hz), 1.40 (d, 3H, *J* = 5.2 Hz), 1.45–1.48 (m, 1H), 1.70 (td, 1H, *J* = 2.2, 13.6 Hz), 3.84 (m, 1H), 4.55 (dd, 1H, *J* = 3.0, 11.3 Hz), 4.80 (q, 1H, *J* = 5.3 Hz), 7.28–7.36 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 18.90, 21.1, 21.4, 40.3, 72.3, 77.5, 98.7, 127.1, 128.4, 133.2, 135.8; Anal. Calcd for C₁₃H₁₈O₂: C, 75.69; H, 8.80. Found: C, 75.71; H, 8.80.

2,4-Diethyl-6-(4-methylphenyl)-1,3-dioxane (9)⁴

Colorless solid; mp 80-82 °C; GC-MS: m/z 234; ¹H NMR (300 MHz, CDCl₃): δ 0.66 (d, 1H, *J* = 6.9 Hz), 0.98 (t, 1H, *J* = 7.5 Hz), 1.03 (t, 1H, *J* = 7.5 Hz), 1.50 (ddq, 2H, *J* =

14.0, 6.0, 7.5 Hz), 1.65 (ddq, 2H, $J = 14.0, 8.0, 7.5$ Hz), 1.70 (m, 2H), 1.76 (m, 2H), 3.80 (ddd, 1H, $J = 8.0, 6.0, 2.3$ Hz), 2.38 (s, 3H), 4.50 (t, 1H, $J = 5.0$ Hz), 4.86 (d, 1H, $J = 2.3$ Hz), 7.25 (tt, 1H, $J = 7.1, 1.9$ Hz), 7.30–7.42 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 8.5, 12.3, 25.3, 28.6, 29.3, 44.6, 74.5, 78.7, 103.1, 127.4, 128.9, 135.7, 136.2; Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2$: C, 76.88; H, 9.46. Found: C, 76.90; H, 9.45.

2,4-Dicyclohexyl-6-(4-methylphenyl)-1,3-dioxane (10)^{4, 5, 6}

Colorless solid; mp 90–92 °C; GC-MS: m/z 342; ^1H NMR (300 MHz, CDCl_3): δ 0.80–2.06 (m, 24H), 2.28 (s, 3H), 3.38 (m, 1H), 4.30 (d, 1H, $J = 5.3$ Hz), 4.58 (dd, 1H, $J = 3.0, 11.3$ Hz), 7.10–7.20 (m, 4H). ^{13}C NMR (75 MHz, CDCl_3): δ 20.2, 24.9, 26.4, 27.6, 27.9, 28.4, 28.6, 35.8, 36.2, 42.75, 42.5, 76.3, 78.8, 80.8, 82.4, 104.2, 125.4, 127.3, 128.3, 129.6, 144.5; Anal. Calcd for $\text{C}_{23}\text{H}_{34}\text{O}_2$: C, 80.65; H, 10.01. Found: C, 80.68; H, 10.00.

5-Methyl-6-phenyl-1,3-dioxane (11)^{4, 5}

Colorless liquid; GC-MS: m/z 178; ^1H NMR (300 MHz, CDCl_3): δ 1.25 (d, 3H, $J = 6.0$ Hz), 1.68–1.70 (m, 1H), 2.02–2.10 (m, 1H), 3.80–3.87 (m, 1H), 4.15–4.20 (m, 1H), 4.86–4.91 (m, 1H), 5.17 (d, 1H, $J = 6.4$ Hz), 7.24–7.29 (m, 5H); ^{13}C NMR (75 MHz, CDCl_3): δ 21.3, 27.8, 34.1, 41.9, 76.3, 133.2, 135.4, 136.9, 137.5, 141.7, 142.4; Anal. Calcd for $\text{C}_{11}\text{H}_{14}\text{O}_2$: C, 74.13; H, 7.92. Found: C, 74.10; H, 7.92.

2,4-Dimethyl-6-naphthyl-1,3-dioxane (13)^{3, 4, 5}

Colorless solid; mp 78-80 °C; GC-MS: m/z 242; ¹H NMR (300 MHz, CDCl₃): δ 1.26 (d, 3H, *J* = 6.0 Hz), 1.40 (d, 3H, *J* = 5.2 Hz), 3.11 (dt, 1H, *J* = 4.5, 11.3 Hz), 3.90 (t, 1H, *J* = 11.3 Hz), 4.18 (dd, 1H, *J* = 4.5, 11.3 Hz), 4.64 (d, 1H, *J* = 9.8 Hz), 4.95 (d, 1H, *J* = 6.0 Hz), 6.92–6.98–7.10 (m, 2H), 7.12–7.18 (m, 2H), 7.19–7.21 (m, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 21.0, 21.6, 49.1, 71.8, 84.1, 94.0, 126.9, 127.1, 127.7, 127.9, 128.3, 128.4, 137.1, 139.0, 141.20, 145.30; Anal. Calcd for C₁₆H₁₈O₂: C, 79.31; H, 7.49. Found: C, 79.30; H, 7.50.

2,4-Dicyclohexyl-6-naphthyl-1,3-dioxane (14)^{4, 5}

Colorless solid; mp 104-106 °C; GC-MS: m/z 378; ¹H NMR (300 MHz, CDCl₃): δ 0.88–2.12 (m, 24H), 3.40 (m, 1H), 4.30 (d, 1H, *J* = 5.3 Hz), 4.43 (dd, 1H, *J* = 3.0, 11.3 Hz), 7.15–7.24 (m, 7H); ¹³C NMR (75 MHz, CDCl₃): δ 25.2, 26.4, 27.8, 28.0, 28.4, 28.6, 36.8, 42.8, 42.9, 78.8, 80.4, 82.6, 105.4, 125.8, 127.3, 128.3, 128.4, 129.5, 130.8, 133.4, 137.1, 139.0, 141.20, 140.19, 145.30, 146.1; Anal. Calcd for C₂₆H₃₄O₂: C, 82.49; H, 9.05. Found: C, 82.48; H, 9.04.

4a,5,6,10b-Tetrahydro-4*H*-naphtho(1,2-*d*)(1,3)-dioxane (15)^{4, 5}

Brownish liquid; GC-MS: *m/z* 190; ¹H NMR (300 MHz, CDCl₃): δ 1.66–1.78 (m, 2H), 2.43–2.50 (m, 1H), 2.94 (ddd, 1H, *J* = 3.0, 6.0, 16.6 Hz), 3.90–4.04 (m, 2H), 4.61 (d, 2H, *J* = 3.0 Hz), 4.86 (d, 1H, *J* = 6.0 Hz), 4.99 (d, 1H, *J* = 6.0 Hz), 7.06–7.26 (m, 5H); ¹³C NMR (75 MHz, CDCl₃): δ_C 28.1, 35.1, 40.9, 77.2, 80.7, 99.7, 132.2, 134.4, 134.9, 136.5, 140.7, 143.4; Anal. Calcd for C₁₂H₁₄O₂: C, 75.76; H, 7.42. Found: C, 75.72; H, 7.40.

4a,5,6,10b-Tetrahydro-2,4-dimethyl-4*H*-naphtho(1,2-*d*)(1,3)-dioxane (16)^{4, 5}

Yellowish liquid; GC-MS: *m/z* 218; ¹H NMR (300 MHz, CDCl₃): δ 1.28–1.30 (m, 3H), 1.34–1.36 (m, 3H), 1.54–1.68 (m, 2H), 2.40–2.48 (m, 1H), 2.94–2.98 (m, 2H), 3.88–3.96 (m, 1H), 4.64–4.71 (m, 1H), 4.90–94 (m, 1H), 7.10–7.23 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 18.8, 20.2, 26.5, 32.4, 40.5, 77.4, 78.8, 100.2, 132.2, 134.8, 135.6, 136.8, 141.4, 142.8; Anal. Calcd for C₁₄H₁₈O₂: C, 77.03; H, 8.32. Found: C, 77.05; H, 8.30.

REFERENCES

1. (a) Hubbard, A.; Okazaki, Z. T.; Laali. K. K. *Aust. J. Chem.* **2007**, 60, 923; (b) Fehér, C.; Kriván, E.; Hancsók, J.; Skoda-Földes. R. *Green Chemistry.* **2012**, 14, 403; (c) Funabiki, K.; Komeda, T.; Kubota, Y.; Matsui, M. *Tetrahedron.* **2009**, 65, 7457
2. Wang, W.; Shao, L.; Cheng, W.; Yang, J.; He, M. *Catal Comm.* **2008**, 9, 337.
3. (a) Fang, D.; Zhou, X. L.; Ye, Z. W.; Liu, Z. L. *Ind. Eng. Chem. Res.* **2006**, 45, 7982. (b) Fang, D.; Jiao, C. M.; Zhang, H. B.; Bao-hua, Ji. *Ind. Eng. Chem. Res.* **2010**, 16, 233.
4. Yadav, J. S.; Subba Reddy, B. V.; Hara Gopal, A. V.; Narayana Kumar, G. G. K. S.; Madavi, C.; Kunwar, A.C. *Tetrahedron Lett.* **2008**, 49, 4420.
5. He-yuan, S.; Zhong-hua, T. *Chen, Jing Fenzi Cuihua.* **2008**, 22, 5.
6. Yanlong, G.; Chikako, O.; Kobayashi, S. *Chemistry Letters.* **2006**, 35, 10, 1176.