Supporting Information

A Novel and Efficient Synthesis of -Sultones

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Typical procedure for synthesis of the ionic liquid [MSIm]OTfHCl
To a flask, kept in an ice-cooled bath and equipped with a magnetic stirring bar, was added a solution of 1-methylimidazole, 0.8 mL (10 mmol), in dry 15 mL dichloromethane. To this continually stirring solution was added dropwise chlorosulfonic acid, 0.66 mL (10 mmol), thereby white suspended solids were produced. After an hour additional stirring at room temperature, trifluoromethanesulfonic acid, 0.88 mL (10 mmol) was added slowly over a period of 15 min to the flask. Within this time, the suspended white salt inside the flask was completely dissolved. Stirring of this solution was continued for about 30 minutes at room temperature, and then the solvent was removed under reduced pressure. According to this procedure, the ionic liquid [MSIm]OTfHCl was obtained as a viscous yellow oil. Treatment of aqueous solution of the ionic liquid with AgNO₃(aq) results in formation and precipitation of AgCl solids. Anal Calcd for [MSIm]OTfHCl: C, 17.22; H, 2.31; N, 8.03%. Found: C, 17.33; H, 2.43; N, 7.87%.

NMR data for [MSIm]OTfHCl
1H NMR (CDCl₃, 400.13 MHz); for the minor component, δH 12.62 (1H, s), 12.52 (1H, s), 8.75 (1H, s, CH), 7.60 (1H, s, CH), 7.31 (1H, s, CH), 4.0 (3H, s, CH₃); for the major component, δH 12.62 (1H, s), 11.49 (1H, s, NH), 8.44 (1H, s, CH), 7.36 (1H, s, CH), 7.31 (1H, s, CH), 3.90 (3H, s, CH₃). 13C NMR (CDCl₃, 100.6 MHz); for the minor component, δC 135.15 (CH), 123.90 (CH), 12.30 (CH), 118.93 (q, J_C-F =317 Hz, CF₃), 36.29 (CH₃); for the major component, δC 134.77 (CH), 123.19 (CH), 119.90 (CH), 119.93 (q, J_C-F =317 Hz, CF₃), 35.84 (CH₃).

General method for the synthesis of 1,2-oxathiine-2,2-dioxides 2a-f
An acetoephone derivative (1 mmol in each case) was mixed with the ionic liquid 1-methyl-3-sulfonylimidazolium triflate hydrochloride (0.2 mL) in a glass vial containing a stirring bar. The mixture was stirred for appropriate time until disappearance of acetoephone at room temperature (see Table 2). Progress of the reaction was monitored by TLC using silica gel coated sheets and 1:4 ratio of ethyl acetate : petroleum ether as eluents. After completion of the reaction (usually less than 5 min), cold distilled water (10 °C, 10 mL) was added to the reaction mixture and the precipitated solids were filtered, dried in air and recrystallized from ethanol (95%).
4,6-Di(4-chlorophenyl)-[1,2]-oxathiine-2,2-dioxide (2a): Mp 222 °C, Lit. mp 200 °C. IR (KBr) cm⁻¹; 3100, 1620, 1350, 1160, 770, 820, 860, 930. ¹H NMR (CDCl₃, 400.2 MHz); δH 7.77 (d, J = 8.8 Hz, 2H), 7.52 (s, 4H), 7.50 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 0.8 Hz, 1H), 6.69 (d, J = 0.8 Hz, 1H). ¹³C NMR (CDCl₃, 100.63 MHz); δC 155.8, 146.5, 137.3, 133.8, 129.2, 129.3, 129.4, 128.2, 113.6, 102.1. MS (70 eV) m/z (%); 356 (M⁺, 37Cl 37Cl, 11), 354 (M⁺, 35Cl 37Cl, 49), 353 (22), 292 (M⁺ -SO₂, 37Cl 37Cl, 13), 290 (M⁺ -SO₂, 35Cl 37Cl, 73), 289 (31), 288 (M⁺ -SO₂, 35Cl 35Cl, 100), 261 (M⁺ -CHSO₃, 37Cl 35Cl, 19), 259 (M⁺ -CHSO₃, 35Cl 35Cl, 30), 227 (M⁺ -ClC₆H₄O, 37Cl, 32), 225 (M⁺ -ClC₆H₄O, 35Cl, 90), 189 (50), 139 (35), 111 (50). Anal Calcd for C₁₆H₁₀Cl₂O₃S (353.22): C, 54.41; H, 2.85%. Found: C, 54.36; H, 2.88%.

4,6-Di(4-fluorophenyl)-[1,2]-oxathiine-2,2-dioxide (2b): Mp 220 °C. IR (KBr) cm⁻¹; 3100, 1622, 1350, 1160, 780, 840. ¹H NMR (CDCl₃, 400.2 MHz); δH 7.84 (dd, JHH = 8.6 Hz, JFH = 4.8 Hz, 2H), 7.60 (dd, JHH = 8.6 Hz, JFH = 5.2 Hz, 2H), 7.23 (t, J = 8.6 Hz, 2H), 7.22 (t, J = 8.6 Hz, 2H), 6.72 (s, 1H), 6.66 (s, 1H). ¹³C NMR (CDCl₃, 100.63 MHz); δC 164.7 (d, J = 254 Hz), 164.3 (d, J = 253 Hz), 155.8, 146.7, 131.6 (d, J = 4 Hz), 128.9 (d, J = 9 Hz), 128.3 (d, J = 9 Hz), 127.1 (d, J = 3 Hz), 116.6 (d, J = 22 Hz), 116.4 (d, J = 22 Hz), 113.0, 101.9. MS (70 eV) m/z (%); 320 (M⁺, 52), 256 (M⁺ -SO₂, 83), 227 (M⁺ -CHSO₃, 100), 207 (19), 149 (22), 133 (40), 123 (45), 95 (62). Anal Calcd for C₁₆H₁₀F₂O₃S (320.31): C, 60.00; H, 3.15%. Found: C, 60.13; H, 3.21%.
4,6-Di(4-bromophenyl)-[1,2]-oxathiine-2,2-dioxide (2c): Mp 216 °C. IR (KBr) cm⁻¹; 3095, 1620, 1355, 1165, 770, 820. ¹H NMR (CDCl₃, 400.2 MHz); δH 7.70 (d, J = 9.2 Hz, 2H), 7.68 (d, J = 9.2 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 1 Hz, 1H), 6.70 (d, J = 1 Hz, 1H). ¹³C NMR (CDCl₃, 100.63 MHz); δC 155.9, 146.5, 134.3, 129.7, 126.4, 125.6, 132.7, 132.4, 128.4, 127.3, 113.7, 102.1. MS (70 eV) m/z (%); 444 (M⁺, ⁸¹Br ⁸¹Br, 12), 442 (M⁺, ⁸¹Br ⁷⁹Br, 22), 440 (M⁺, ⁷⁹Br ⁷⁹Br, 12), 380 (M⁺ -SO₂, ⁸¹Br ⁸¹Br, 42), 378 (M⁺ -SO₂, ⁸¹Br ⁷⁹Br, 53), 376 (M⁺ -SO₂, ⁷⁹Br ⁷⁹Br, 22), 359 (37), 351 (M⁺ -CHSO₃, ⁸¹Br ⁸¹Br, 5), 349 (M⁺ -CHSO₃, ⁸¹Br ⁷⁹Br, 10), 347 (M⁺ -CHSO₃, ⁷⁹Br ⁷⁹Br, 6), 301 (60), 299 (62), 271 (M⁺ -BrC₆H₄O, ⁸¹Br, 32), 269 (M⁺ -BrC₆H₄O, ⁷⁹Br, 33), 220 (66), 189 (81), 157 (50), 155 (52), 115 (100). Anal Calcd for C₁₆H₁₀Br₂O₃S (442.12): C, 43.47; H, 2.28%. Found: C, 43.41; H, 2.33%.

4,6-Di(3-chlorophenyl)-[1,2]-oxathiine-2,2-dioxide (2d): Mp 153 °C, Lit. mp 137-138 °C. IR (KBr) cm⁻¹; 3100, 1620, 1350, 1160, 850, 770. ¹H NMR (CDCl₃, 400.2 MHz); δH 7.82 (t, J = 1.8 Hz, 1H), 7.73 (dt, J = 7.6 Hz and J 1.6 Hz, 1H), 7.57-7.45 (m, 6H), 6.80 (d, J = 0.8 Hz, 1H), 6.72 (d, J = 0.8 Hz, 1H). ¹³C NMR (CDCl₃, 100.63 MHz); δC 155.4, 146.2, 137.1, 135.5, 135.3, 132.4, 131.6, 131.0, 130.7, 130.4, 127.0, 126.0, 125.0, 124.1, 114.6, 102.7. MS (70 eV) m/z (%); 356 (M⁺, ³⁷Cl ³⁷Cl, 11), 354 (M⁺, ³⁷Cl ³⁵Cl, 49), 353 (13), 352 (M⁺, ³⁵Cl ³⁵Cl, 60), 292 (M⁺ -SO₂, ³⁷Cl ³⁷Cl, 37), 290 (M⁺ -SO₂, ³⁷Cl ³⁵Cl, 100), 289 (45), 288 (M⁺ -SO₂, ³⁵Cl ³⁵Cl, 98), 263 (M⁺ -CHSO₃, ³⁷Cl ³⁷Cl, 4), 261 (M⁺ -CHSO₃, ³⁷Cl ³⁵Cl, 22), 259 (M⁺ -CHSO₃, ³⁵Cl ³⁵Cl, 31), 227 (M⁺ -
4,6-Di(4-methylphenyl)-[1,2]-oxathiine-2,2-dioxide (2e): Mp 195 °C, Lit.16 mp 189 °C. IR (KBr) cm\(^{-1}\): 3095, 1620, 1345, 1160, 920, 870. \(^1\)H NMR (CDCl\(_3\), 400.2 MHz); \(\delta\) \(\text{H} 7.73\) (d, \(J = 8\) Hz, 2H), 7.49 (d, \(J = 8\) Hz, 2H), 7.33 (d, \(J = 8\) Hz, 2H), 7.32 (d, \(J = 8\) Hz, 2H), 6.72 (s, 1H), 6.71 (s, 1H), 2.46 (s, 3H), 2.45 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 100.63 MHz); \(\delta\) \(\text{C} 156.6, 147.7, 142.1, 141.3, 132.8, 128.2, 130.0, 129.7, 126.8, 125.9, 111.9, 101.5, 21.6, 21.4. MS (70 eV) m/z (%); 312 (M\(^+\), 68), 248 (M\(^+\)-SO\(_2\), 100), 219 (M\(^+\)-CHSO\(_3\), 42), 205 (M\(^+\)-MeC\(_6\)H\(_4\)O, 53), 189 (9), 119 (27), 91 (45). Anal Calcd for C\(_{18}\)H\(_{16}\)O\(_3\)S (312.38): C, 69.21; H, 5.16%. Found: C, 69.25; H, 5.11%.

4,6-Diphenyl-[1,2]-oxathiine-2,2-dioxide (2f): Mp 156 °C, Lit.16 mp 158 °C. IR (KBr) cm\(^{-1}\): 3090, 1620, 1345, 1160, 750, 850, 680, 725. \(^1\)H NMR (CDCl\(_3\), 400.2 MHz); \(\delta\) \(\text{H} 7.86-7.83\) (m, 2H), 7.61-7.59 (m, 2H), 7.57-7.49 (m, 6H), 6.78 (s, 1H), 6.76 (s, 1H).