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Supporting Information

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Clean and Highly Selective Oxidation of Alcohols in Ionic Liquid Employing Ion-Supported Hypervalent Iodine^{III} Reagent.

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Experimental Section

^{1}H NMR and ^{13}C NMR spectra were determined in $CDCl_3$ or DMSO-d_6 on a Bruker 400 MHz spectrometer with TMS as the internal standard. IR spectra were recorded on a Bruker Vector-22 infrared spectrometer. C, H, N were analyzed on a Carlo Erba 1110 elemental analyzer. All melting points were uncorrected. The columns were handpacked with silica gel H60 (~400). Reactions were carried out under atmosphere.

Synthesis of oxidant [dibmim]$^{+}$[BF$_4$]$^{-}$. The bromide and tetrafluoroborate salts of the oxidant were prepared by modification of published literature procedures.[17] The oxidant was made by modification of the method described by Pausacker.[16]

1-(4-iodobenzyl)-3-methylimidazolium bromide. Under stirring, 29.69g (0.1 mol) of 1-(bromomethyl)-4-iodobenzene was slowly added to a solution of 8.61g (0.105 mol) of 1-methylimidazole in 25 mL of acetonitrile. The mixture was stirred for 6 h at 60°C. After cooling to room temperature, 25 mL ether was added to the mixture causing precipitation of 1-(4-iodobenzyl)-3-methylimidazolium bromide as a white solid. This solid was recovered by filtration and washed with ether twice. The yield was 36.4g (96%). m.p. 150~152 °C ^{1}H NMR (DMSO-d_6, ppm): δ=3.86(s, 3H; CH_3), 5.42(s, 2H; CH_2), 7.25(d, ^{3}J(H,H)= 8.4 Hz, 2H;

Ar-H), 7.74-7.75(m, 1H; imidazolium-H), 7.79-7.82(m, 3H), 9.27(s, 1H; imidazolium-H); ^{13}C NMR (DMSO-d_6, ppm): δ=36.03, 51.37, 95.49, 122.43, 124.14, 130.75, 134.65, 136.87, 137.84; IR(KBr): ν=3150, 3084, 2936, 2872, 1601, 1571, 1485, 1455, 1400, 1165 cm^{-1}; MS(ESI): *m/z*(%): 298.9 (100) [M^+-Br^-]; Anal. calcd. for $C_{11}H_{12}BrIN_2$: C34.86, H3.19, N7.39. Found: C34.93, H3.20, N7.51.

1-(4-iodobenzyl)-3-methylimidazolium tetrafluoroborate. The 1-(4-iodobenzyl)-3-methylimidazolium bromide obtained above 18.95g (0.05 mol) was added to a suspension of $NaBF_4$ (6.04g, 0.055 mol) in acetone (100 ml). After the mixture was stirred for 12h at room temperature and then refluxed for 60h, the sodium bromide precipitate was removed by filtration and the filtrate concentrated by rotary evaporation. The yield was 18.3g (95%). m.p. 93~95 °C ^{1}H NMR (DMSO-d_6, ppm): δ=3.85(s, 3H; CH_3), 5.37(s, 2H; CH_2), 7.22(d, ^3J(H,H) = 8.0 Hz, 2H; Ar-H), 7.70-7.76(m, 2H; imidazolium-H), 7.80(d, ^3J(H,H) = 8.0Hz, 2H; Ar-H), 9.15(s, 1H; imidazolium-H); ^{13}C NMR (DMSO-d_6, ppm): δ=36.10, 51.60, 95.41, 122.52, 124.26, 130.83, 134.65, 136.93, 138.01; IR(KBr) ν=3151, 3084, 2937, 1602, 1571, 1486, 1401, 1166, 1083 cm^{-1}; MS(ESI): *m/z*(%): 298.8 (100) [M^+-BF_4^-]; Anal. calcd. for $C_{11}H_{12}BF_4IN_2$: C34.23, H3.13, N7.26. Found: C34.12, H3.25, N7.21.

1-(4-diacetoxyiodobenzyl)-3-methylimidazolium tetrafluoroborate. Hydrogen peroxide (30%, 7.4 ml) and acetic anhydride(14 ml) were stirred for 5h at 40°C. The 1-(4-iodobenzyl)-3-methylimidazolium tetrafluoroborate 10.0g (25.9 mmol) was slowly added to the solution keeping temperature below 10°C. After adding the mixture was stirred 12h at room temperature and then 2h at 40°C. The solution was concentrated to a small volume by rotary evaporation keeping the temperature of water bath below 50°C. The oil stood over night to solidified. The solid was collected by filtration, washed with acetone twice, dried (NaOH) in a

vacuum desiccator and stored away from direct sunlight(yield 10.2g, 78%). m.p. 126~128°C ^{1}H NMR (DMSO-d_6, ppm): δ=1.90(s, 6H; 2CH_3), 3.87(s, 3H; CH_3), 5.53(s, 2H; CH_2), 7.54 (d, ^3J(H,H) = 8.4Hz, 2H; Ar-H), 7.75(s, 1H; imidazolium-H), 7.84(s, 1H; imidazolium-H), 8.28(d, ^3J(H,H) = 8.4Hz, 2H; Ar-H), 9.24(s, 1H; imidazolium-H); ^{13}C NMR (DMSO-d_6, ppm): δ=20.3, 36.0, 51.4, 95.4, 122.5, 124.4, 130.8, 135.8, 137.9, 139.0, 172.2; IR(Nujol): ν =3172, 1644, 1575, 1566, 1297, 1274, 1165, 1059 cm^{-1}; MS(70eV): *m/z*(%): 297 (100) [M^+-BF_4^- -2CH_3CO_2H]; Anal. calcd. for $C_{15}H_{18}BF_4IN_2O_4$: C35.74, H3.60, N5.56. Found: C35.38, H3.74, N5.24.

General Procedure for Alcohol Oxidations. [dibmim]$^+$[BF_4]$^-$ (353mg, 0.7mmol) was added to a solution of alcohol (0.5 mmol) in 1.5g of [emim]$^+$[BF_4]$^-$. The reaction mixture was stirred at 30°C for a given time. The mixture was extracted with ether (3 X 8ml) and concentrated under reduced pressure. The product was purified by flash column chromatography using petroleum ether and Et_2O as eluent.

All products were commercially available and identified by comparison of the isolated products with authentic samples.

Benzaldehyde(2a) ^{1}H NMR ($CDCl_3$, ppm): δ=7.52~7.56(m, 2H; Ar-H), 7.62~7.65(m, 1H; Ar-H), 7.88~7.90(m, 2H; Ar-H), 10.03(s, 1H; CHO); IR (neat): ν =1703 cm^{-1} (C=O); MS(70eV): *m/z*(%): 106 (100) [M^+], 105 (94) [M^+-H], 77 (92) [$C_6H_5^+$].

4-Methoxybenzaldehyde(2b) ^{1}H NMR ($CDCl_3$, ppm): δ=3.90(s, 3H; CH_3), 7.01(d, ^3J(H,H) = 7.6Hz, 2H; Ar-H), 7.85(d, ^3J(H,H) = 7.6Hz, 2H; Ar-H), 9.89(s, 1H; CHO); IR (neat): ν =1685 cm^{-1} (C=O); MS(70eV): *m/z*(%): 136 (76) [M^+], 135 (100) [M^+-H].

4-Chlorobenzaldehyde(2c) m.p. 46~47°C ^{1}H NMR ($CDCl_3$, ppm): δ=7.53(d, ^3J(H,H) =

8.4Hz, 2H; Ar-H), 7.83(d, ^3J(H,H) = 8.4Hz, 2H; Ar-H), 9.99(s, 1H; CHO); IR (KBr): ν =1702 cm^{-1} (C=O); MS(70eV): *m/z*(%): 139 (100) [M^+], 141 (33) [M^++2].

2-Chlorobenzaldehyde(2d) ^{1}H NMR ($CDCl_3$, ppm): δ=7.38-7.41(m, 1H; Ar-H), 7.46(d, ^3J(H,H) = 8.0Hz, 1H; Ar-H), 7.52-7.56(m, 1H; Ar-H), 7.93(dd, ^4J(H,H) = 1.6Hz, ^3J(H,H) = 8.0Hz, 1H; Ar-H), 10.49(s, 1H; CHO); IR (neat): ν =1699 cm^{-1} (C=O); MS(70eV): *m/z*(%): 139 (100) [M^+], 141 (33) [M^++2].

3,4-Methylenedioxybenzaldehyde(2e) m.p. 35~37°C ^{1}H NMR ($CDCl_3$, ppm): δ=6.09(s, 2H; CH_2), 6.94(d, ^3J(H,H) = 8.0Hz, 1H; Ar-H), 7.34(s, 1H; Ar-H), 7.42(d, ^3J(H,H) = 8.0Hz, 1H; Ar-H), 9.82(s, 1H; CHO); IR (KBr): ν =1687 cm^{-1} (C=O); MS(70eV): *m/z*(%): 150 (95) [M^+], 149 (100) [M^+-H].

Furaldehyde(2f) ^{1}H NMR ($CDCl_3$, ppm): δ =6.61-6.63(m, 1H), 7.27-7.30 (m, 1H), 7.70-7.71 (m, 1H), 9.67(s, 1H; CHO); IR (neat): ν =1675 cm^{-1} (C=O); MS(70eV): *m/z*(%): 96(100) [M^+], 95 (94) [M^+-H], 39(58) [$C_3H_3^+$].

Cinnamaldehyde(2g) ^{1}H NMR ($CDCl_3$, ppm): δ=6.73(dd, ^3J(H,H) = 8.0Hz, ^3J(H,H) = 15.6Hz, 1H; CH), 7.44~7.45(m, 3H; Ar-H), 7.49(d, ^3J(H,H) = 15.6Hz, 1H; CH), 7.56~7.58(m, 2H; Ar-H), 9.71(d, ^3J(H,H) = 8.0Hz, 1H; CH); IR (neat): ν =1679 cm^{-1} (C=O); MS(70eV): *m/z*(%): 132 (73) [M^+], 131 (100) [M^+-H], 103(56) [$C_8H_7^+$].

2,3-Dibromo-3-phenylpropanol(2g') m.p. 70~71°C ^{1}H NMR ($CDCl_3$, ppm): δ=2.28 (br, 1H; OH), 4.23~4.37(m, 2H; CH_2), 4.69~4.72 (m, 1H; CH), 5.28(d, ^3J(H,H) = 11.2Hz, 1H; CH), 7.36~7.39(m, 5H; Ar-H); IR (KBr, cm^{-1}) ν =3375.1, 3031.9, 2926.7, 1454.4, 1055.2, 694.0, 583.3; MS(70eV): *m/z*(%): 294(0.53) [M^++2], 213(31) [M^+-Br], 215(30) [M^++2-Br], 185(62) [$C_8H_8Br^+$], 183(63) [$C_8H_8Br^+$], 105(92) [$C_8H_9^+$],104(93) [$C_8H_8^+$], 91(100) [$C_7H_7^+$], 77(70) [$C_6H_5^+$].

4-Methylcyclohexanone(2h) ^{1}H NMR ($CDCl_3$, ppm): δ=1.02(d, ^3J(H,H) = 6.8Hz, 3H; CH_3), 1.37~1.48(m, 2H), 1.86~1.94(m, 1H; CH), 1.98~2.02(m, 2H), 2.34~2.38(m, 4H); IR (neat): ν =1714 cm^{-1} (C=O); MS(70eV): *m/z*(%): 112(43) [M^+], 55(100) [$C_3H_3O^+$].

2-Isopropyl-5-methylcyclohexanone(2i) ^{1}H NMR ($CDCl_3$, ppm): δ=0.85(d, ^3J(H,H) = 6.8Hz, 3H; CH_3), 0.91(d, ^3J(H,H) = 6.8Hz, 3H; CH_3), 1.01(d, ^3J(H,H) = 6.8Hz, 3H; CH_3), 1.33~1.39(m, 2H), 1.84~2.01(m, 5H), 2.11~2.24(m, 1H), 2.35~2.38(m, 1H); IR (neat): ν =1711 cm^{-1} (C=O); MS(70eV): *m/z*(%): 154 (26) [M^+], 112(100) [$C_7H_{12}O^+$].

Acetophenone(2j) ^{1}H NMR ($CDCl_3$, ppm): δ=2.59(s, 3H; CH_3), 7.43~7.47(m, 2H; Ar-H), 7.54~7.57(m, 1H; Ar-H), 7.95(d, ^3J(H,H) = 8.8Hz, 2H; Ar-H); IR (neat): ν =1686 cm^{-1} (C=O); MS *m/z* 120 (M^+). MS(70eV): *m/z*(%): 120 (25) [M^+], 105 (100) [$C_7H_5O^+$], 77 (73) [$C_6H_5^+$].

4-Methoxyacetophenone(2k) m.p. 37~39°C ^{1}H NMR ($CDCl_3$, ppm): δ=2.56(s, 3H; CH_3), 3.87(s, 3H; CH_3), 6.94(d, ^3J(H,H) = 8.4Hz, 2H; Ar-H), 7.94(d, ^3J(H,H) = 8.4Hz, 2H; Ar-H); IR (KBr): ν =1677 cm^{-1} (C=O); MS *m/z* 150(M^+). MS(70eV): *m/z*(%): 150 (29) [M^+], 135 (100) [$C_8H_7O_2^+$],

4-Bromoacetophone(2l) m.p. 50~51°C ^{1}H NMR ($CDCl_3$, ppm): δ=2.59(s, 3H), 7.61(d, ^3J(H,H) = 8.4Hz, 2H; Ar-H), 7.82 (d, ^3J(H,H) = 8.4Hz, 2H; Ar-H); IR (KBr): ν =1676 cm^{-1} (C=O); MS *m/z* 198(M^+), 200(M+2). MS(70eV): *m/z*(%): 198 (29) [M^+], 200 (27) [M^++2], 183 (99) [$C_7H_4OBr^+$], 185(100) [$C_7H_4OBr^+$].

2-Hydroxy-1,2-diphenylethanone(2m) m.p. 132~134 °C ^{1}H NMR ($CDCl_3$, ppm): δ =4.56(d, ^3J(H,H) = 6.0Hz,1H;OH), 5.96(d, ^3J(H,H) = 6.0Hz,1H;CH), 7.27~7.34(m, 5H; Ar-H), 7.38~7.42(m, 2H; Ar-H), 7.50~7.54(m, 1H; Ar-H), 7.91~7.93(m, 2H; Ar-H); IR (KBr): ν =3417 (OH), 1680 cm^{-1} (C=O); MS(70eV): *m/z*(%):212(3) [M^+], 105(100) [$C_7H_5O^+$].

Benzophenone(2n) m.p. 48~49°C ^{1}H NMR ($CDCl_3$, ppm): δ=7.45~7.49(m, 4H; Ar-H), 7.56~7.60(m, 2H; Ar-H), 7.80(d, ^{3}J(H,H) = 8.4Hz, 4H; Ar-H); IR (KBr): ν =1655 cm^{-1} (C=O); MS(70eV): *m/z*(%):182 (50) [M^+], 105(100) [$C_7H_5O^+$].

9*H*-floren-9-one(2o) m.p. 82~82°C ^{1}H NMR ($CDCl_3$, ppm): δ=7.27~7.31(m, 2H; Ar-H), 7.46~7.53(m, 4H; Ar-H), 7.65~7.67(m, 2H; Ar-H); IR (KBr): ν =1715 cm^{-1} (C=O); MS(70eV): *m/z*(%):180 (100) [M^+].

Additional References:

[17] a) J.S. Wilkes, M.J. Zaworotko, *Chem. Commun*. **1992**, 965-967; b) J.D. Holbrey, K.R. Seddon, *J. Chem. Soc. Dolton Trans.* **1999**, 2133-2139.