

Electronic Supplementary Information

for

Oxidative Carboxylation of Arylaldehydes with Water by A Sulfoxylalkyl-Substituted *N*-Heterocyclic Carbene Catalyst

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General. Materials were obtained from commercial suppliers and used without further purification except when otherwise noted. Solvents were dried and distilled according to standard protocol. Imidazolium salts **1a**, **1d**, **1h**, *N*-(2,6-diisopropylphenyl)imidazole and *N*-phenylimidazoles were prepared according to the procedures described in the literature.^[1-3]

Preparation and Spectral Data of Imidazolium Salts

3-(1-Methyl-1H-imidazol-3-ium-3-yl)propane-1-sulfonate (**1b**)

To a stirred solution of *N*-methylimidazole (1.03 g, 12.5 mmol) in acetone (20 mL) was added 1,3-propanesultone (1.53 g, 12.5 mmol) in acetone (20 mL) at 0 °C, and the reaction mixture was stirred at rt for 5 days. After filtration of the reaction mixture through a glass filter, the resulting solid were washed by acetone twice and dried in vacuo at 60 °C to afford the imidazolium salt **1b** (1.65 g, 65%) as white solid: mp 182–183 °C; IR (KBr) 3111, 2104, 1566, 667 cm⁻¹; ¹H-NMR (400 MHz, *d*₆-DMSO) δ 9.10 (1H, s), 7.77 (1H, s), 7.68 (1H, s), 4.29 (2H, t, *J* = 6.8 Hz), 3.84 (3H, s), 2.40 (2H, t, *J* = 6.8 Hz), 2.07 (2H, quint, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, *d*₆-DMSO) δ 136.7 (Cq), 123.5 (CH), 122.3 (CH), 47.7 (CH₂), 47.2 (CH₂), 35.7 (CH), 26.2 (CH₂); HRMS (ESI) *m/z* calcd for C₇H₁₂N₂O₃SNa [M+Na]⁺ 227.0466, found 227.0469.

3-(1-Phenyl-1H-imidazol-3-ium-3-yl)propane-1-sulfonate (**1c**)

By following the same procedure described for **1b**, the imidazolium salt **1c** was obtained from *N*-phenylimidazole and 1,3-propanesultone in 36% yield as white solid: mp 263–264 °C; IR (KBr) 3451, 3093, 1556, 1203 cm⁻¹; ¹H-NMR (400 MHz, *d*₆-DMSO) δ 9.81 (1H, s), 8.31 (1H, s), 8.06 (1H, s), 7.81 (2H, d, *J* = 7.2 Hz), 7.66 (2H, t, *J* = 7.2 Hz), 7.58 (1H, t, *J* = 7.2 Hz), 4.40 (2H, t, *J* = 7.2 Hz), 2.52 (2H, t, *J* = 7.2 Hz), 2.21 (2H, quint, *J* = 7.2 Hz); ¹³C-NMR (100 MHz, *d*₆-DMSO) δ 135.5 (Cq), 134.8 (CH), 130.1 (CH), 129.6 (CH), 123.4 (CH), 121.9 (CH), 121.1 (CH), 48.5 (CH₂), 47.5 (CH₂), 25.9 (CH₂); HRMS (ESI) *m/z* calcd for C₁₂H₁₅N₂O₃S [M+H]⁺ 267.0803, found 267.0802.

3-Butyl-1-(2,6-diisopropylphenyl)-1H-imidazol-3-ium bromide (1e)

To a stirred solution of *N*-(2,6-diisopropylphenyl)imidazole (300 mg, 1.31 mmol) in toluene (3.5 mL) was added 1-bromobutane (0.70 mL, 6.55 mmol) at rt, and the reaction mixture was stirred at 80 °C for 3 days. During the reaction, 1-bromobutane (0.70 mL, 6.55 mmol) was further added for four times. The reaction mixture was filtered through a glass filter, and the resulting solid was extracted with water and ether at 0 °C. The product was dried in vacuo for 2 h to afford the catalyst as white solid (395 mg, 82%): mp 81–82 °C; IR (KBr) 3600, 3517, 3070, 2965, 1542, 1213 cm⁻¹; ¹H-NMR (400 MHz, *d*₆-DMSO) δ 9.76 (1H, s), 8.24 (1H, s), 8.14 (1H, s), 7.64 (1H, t, *J* = 8.0 Hz), 7.46 (2H, d, *J* = 8.4 Hz), 4.36 (2H, t, *J* = 6.8 Hz), 2.25 (2H, septet, *J* = 6.4 Hz), 1.90 (2H, quint, *J* = 6.8 Hz), 1.26 (2H, quint, *J* = 6.8 Hz), 1.15 (12H, d, *J* = 6.4 Hz) 0.93 (3H, t, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, *d*₆-DMSO) δ 145.0 (Cq), 137.6 (CH), 131.4 (CH), 130.4 (Cq), 125.1 (CH), 124.3 (CH), 123.4 (CH), 49.0 (CH₂), 30.9 (CH₂), 28.0 (CH), 23.7 (CH₃), 18.5 (CH₂), 13.1 (CH₃); HRMS (ESI) *m/z* calcd for C₁₉H₂₈BrN₂ [M–H]⁺ 363.1436, found 363.1429.

4-[1-(2,6-Diisopropylphenyl)-1H-imidazol-3-ium-3-yl]butane-1-sulfonate (1f)

To a stirred solution of *N*-(2,6-diisopropylphenyl)imidazole (200 mg, 0.875 mmol) in toluene (2.0 mL) was added 1,4-butanedisulfone (0.179 mL, 1.75 mmol) at 0 °C, and the reaction mixture was stirred at 100 °C for 3 days. After filtration of the reaction mixture through a glass filter, the resulting solid were washed by acetone twice and dried in vacuo at 65 °C for 1 h to afford the imidazolium salt **1f** (229 mg, 75%) as white solid: mp 310–311 °C; IR (KBr) 3519, 2962, 1560, 1190 cm⁻¹; ¹H-NMR (400 MHz, *d*₆-DMSO) δ 9.61 (1H, s), 8.17 (1H, s), 8.11 (1H, s), 7.62 (1H, t, *J* = 7.6 Hz), 7.44 (2H, d, *J* = 7.6 Hz), 4.35 (2H, t, *J* = 6.8 Hz), 2.45–2.53 (2H, m), 2.25 (2H, septet, *J* = 6.8 Hz), 1.99 (2H, quint, *J* = 6.8 Hz), 1.56 (2H, quint, *J* = 6.8 Hz), 1.14 (12H, d, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, *d*₆-DMSO) δ 145.1 (Cq), 137.7 (CH), 131.4 (CH), 130.5 (Cq), 125.1 (CH), 124.3

(CH), 123.4 (CH), 50.3 (CH₂), 49.1 (CH₂) 28.4 (CH₂) 28.1 (CH) 23.8 (CH₃) 21.6 (CH₂); HRMS (ESI) *m/z* calcd for C₁₉H₂₉N₂O₃S [M+H]⁺ 365.1899, found 365.1902.

2-[1-(2,6-Diisopropylphenyl)-1H-imidazol-3-ium-3-yl]ethane-1-sulfonate hydrogen bromide (1g)

To a solution of 2,6-diisopropylphenyl-imidazole (237 mg, 1.04 mmol) in toluene (3.0 mL), the 2-bromoethanesulfonic acid (190 mg, 1.04 mmol) was added at rt. Then the mixture was stirred at 100 °C for 3 days. The reaction mixture was filtered through a glass filter, and the resulting solid was washed by ether at 0 °C. The product was dried in vacuo at 70 °C for 2 h to afford the imidazolium salt **1g** as white solid (308 mg, 71%): mp 168–170 °C IR (KBr) 3525, 3102, 2964, 1540, 1236 cm⁻¹; ¹H-NMR (400 MHz, *d*₆-DMSO) δ 9.48 (1H, s), 8.06 (1H, s), 8.00 (1H, s), 7.62 (1H, t, *J* = 7.6 Hz), 7.44 (2H, d, *J* = 7.6 Hz), 3.55 (2H, t, *J* = 8.0 Hz), 2.93 (2H, t, *J* = 8.0 Hz), 2.20 (2H, septet, *J* = 6.8 Hz), 1.14 (12H, d, *J* = 6.8 Hz); ¹³C-NMR (100 MHz, *d*₆-DMSO) δ 145.1 (Cq), 137.0 (CH), 131.2 (CH), 130.6 (Cq), 124.7 (CH), 124.2 (CH), 121.0 (CH), 54.5 (CH₂), 28.0 (CH), 23.7 (CH₃); HRMS (ESI) *m/z* calcd for C₁₇H₂₄BrN₂O₃S [M-H]⁺ 415.0691, found 415.0695.

General Procedure for the Oxidative Carboxylation of Arylaldehydes with Water (Table 1, entry 10)

To a stirred solution of 4-nitrobenzaldehyde (**2a**) (57.0 mg, 0.377 mmol) and the imidazolium catalyst **1a** (6.6 mg, 0.0189 mmol) in DMF (1.0 mL) and H₂O (0.1 mL) was added DBU (0.112 mL, 0.756 mmol) at rt. After stirring at rt for 10 h, the reaction mixture was added to 10% aq. NaOH and extracted with AcOEt. 10% Aq. HCl was added to the water phase and it was carefully extracted with AcOEt again. The separated organic layer was dried over anhydrous MgSO₄ and the solvent was evaporated under reduced pressure to provide 4-nitrobenzoic acid (**3a**) (58.6 mg, 0.351 mmol) in 93% yield.

4-Nitrobenzoic acid (3a)

White solid; mp 241–242 °C; IR (KBr) 3116, 1695, 1540, 1351 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ 8.30 (2H, d, $J = 8.8$ Hz), 8.15 (2H, d, $J = 8.8$ Hz); $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ 165.8 (Cq), 150.0 (Cq), 136.4 (Cq), 130.7 (CH), 123.7 (CH); HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_4\text{NO}_4$ $[\text{M-H}]^+$ 166.0140, found 166.0140.

2-Nitrobenzoic acid (3b)

White solid; mp 145–146 °C; IR (KBr) 2888, 1683, 1490, 1365 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ 7.97 (1H, d, $J = 8.0$ Hz), 7.85 (1H, d, $J = 6.8$ Hz), 7.74–7.81 (2H, m); $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ 165.9 (Cq), 148.4 (Cq), 133.1 (CH), 132.4 (CH), 129.9 (CH), 127.3 (Cq), 123.7 (CH); HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_4\text{NO}_4$ $[\text{M-H}]^+$ 166.0140, found 166.0138.

3-Nitro-benzoic acid (3c)

White solid; mp 139–140 °C; IR (KBr) 2925, 1710, 1482, 1351 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ 8.61 (1H, s), 8.46 (1H, d, $J = 8.0$ Hz), 8.34 (1H, d, $J = 8.0$ Hz), 7.80 (1H, t, $J = 8.0$ Hz); $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ 165.9 (Cq), 148.4 (Cq), 133.1 (CH), 132.4 (CH), 129.9 (CH), 127.3 (Cq), 123.7 (CH); HRMS (ESI) m/z calcd for $\text{C}_7\text{H}_4\text{NO}_4$ $[\text{M-H}]^+$ 166.0140, found 166.0138.

4-Acetylbenzoic acid (3d)

White solid; mp 208–210 °C; IR (KBr): 2925, 1681 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ 8.04 (4H, s), 2.61 (3H, s); $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ 197.8 (Cq), 166.7 (Cq), 139.8 (Cq), 134.7 (Cq), 129.5 (CH), 128.3 (CH), 27.0 (CH_3); HRMS (ESI) m/z calcd for $\text{C}_9\text{H}_7\text{O}_3$ $[\text{M-H}]^+$ 163.0395, found 163.0392.

4-Fluorobenzoic acid (3e)

White solid; mp 184–186 °C; IR (neat) 2923, 1678, 1234 cm^{-1} ; $^1\text{H-NMR}$ (400 MHz, d_6 -DMSO) δ 7.97–8.01 (2H, m), 7.29–7.33 (2H, m); $^{13}\text{C-NMR}$ (100 MHz, d_6 -DMSO) δ 166.3 (Cq), 132.1 (CH),

132.0 (Cq), 115.7 (CH), 115.5 (Cq); HRMS (EI) m/z calcd for $C_7H_4O_2F$ $[M-H]^+$ 139.0195, found 139.0193.

4-Chlorobenzoic acid (3f)

White solid; mp 242–243 °C; IR(KBr): 2981, 1685, 1016 cm^{-1} ; 1H -NMR (400 MHz, d_6 -DMSO) δ 7.93 (2H, d, $J = 8.8$ Hz), 7.56 (2H, d, $J = 8.8$ Hz); ^{13}C -NMR (100 MHz, d_6 -DMSO) δ 166.4 (Cq), 137.8 (Cq), 131.1 (CH), 129.6 (Cq), 128.7 (CH); HRMS (ESI) m/z calcd for $C_7H_4O_2Cl$ $[M-H]^+$ 154.9900, found 154.9900.

4-Nitrocinnamic acid (3g)

White solid; mp 246–248 °C (decomp); IR (KBr) 3000, 1687, 1629, 1529, 1348 cm^{-1} ; 1H -NMR (400 MHz, d_6 -DMSO) δ 8.23 (2H, d, $J = 8.6$ Hz), 7.97 (2H, d, $J = 8.6$ Hz), 7.68 (1H, d, $J = 16.0$ Hz), 6.74 (1H, d, $J = 16.0$ Hz); ^{13}C -NMR (100 MHz, d_6 -DMSO) δ 167.0 (Cq), 148.0 (Cq), 141.3 (CH), 140.7 (Cq), 129.3 (CH), 123.9 (CH), 123.6 (CH); HRMS (ESI) m/z calcd for $C_9H_6NO_4$ $[M-H]^+$ 192.0297, found 192.0291.

2-Picolinic acid (3h)

Yellow solid; mp 137–138 °C; IR (KBr) 2709, 1774 cm^{-1} ; 1H -NMR (400 MHz, $CDCl_3$) δ 8.46–8.48 (1H, m), 7.82–7.91 (3H, m), 7.17–7.26 (1H, m); ^{13}C -NMR (100 MHz, d_6 -DMSO) δ 156.6 (Cq), 145.6 (CH), 137.5 (CH), 135.9 (Cq), 121.1 (CH), 119.5 (CH); HRMS (ESI) m/z calcd for $C_6H_4NO_2$ $[M-H]^+$ 122.0242, found 122.0238.

Quinoline-2-carboxylic acid (3i)

Brown solid; mp 157–159 °C; IR (KBr) 2925, 1710 cm^{-1} ; 1H -NMR (400 MHz, d_6 -DMSO) δ 8.53 (1H, d, $J = 8.4$ Hz), 8.06–8.16 (3H, m), 7.86 (1H, t, $J = 7.6$ Hz), 7.73 (1H, t, $J = 7.6$ Hz); ^{13}C -NMR (100 MHz, d_6 -DMSO) δ 166.4 (Cq), 148.7 (Cq), 146.7 (Cq), 137.6 (CH), 130.5 (CH), 129.7 (CH),

128.8 (CH), 128.5 (Cq), 128.0 (CH); HRMS (ESI) m/z calcd for C₁₀H₆NO₂ [M-H]⁺ 172.1602, found 172.1604.

Procedure for the Oxidative Esterification of An Arylaldehyde with An Alcohol (Scheme 4)

To a stirred solution of 4-nitrobenzaldehyde (**2a**) (50.0 mg, 0.333 mmol) and the imidazolium salt **1a** (5.8 mg, 0.0165 mmol) in THF (0.5 mL) and methanol (0.05 mL) was added DBU (0.112 mL, 0.756 mmol) at rt. After stirring for 12 h, the reaction mixture was added to 10% aq. NaOH and extracted with AcOEt. The organic layer was washed with brine and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure, and the crude material was chromatographed on silica gel with hexane–AcOEt (70:30 v/v) as eluent to give the methyl ester **3k** (41.1 mg, 0.227 mmol) in 68% yield.

Methyl 4-nitrobenzoate (**3k**)

Colourless crystals; mp: 94–96 °C IR (KBr) 3113, 3079, 1718, 1608, 1597, 1524, 1347 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 8.29 (2H, d, J = 9.2 Hz), 8.21 (2H, d, J = 9.2 Hz), 3.98 (3H, s); ¹³C-NMR (100 MHz, CDCl₃) δ 165.1 (Cq), 150.6 (Cq), 135.5 (Cq), 130.7 (CH), 123.5 (CH), 52.8 (CH₃); HRMS (ESI) m/z calcd for C₈H₆NO₄ [M-H]⁺ 180.0297, found 180.0300.

Procedure for the Oxidative Amidation of An Arylaldehyde with An Amine (Scheme 4)

To a stirred solution of 4-nitrobenzaldehyde (**2a**) (57.0 mg, 0.377 mmol) and the imidazolium salt **1a** (6.6 mg, 0.0189 mmol) and dimethylamine (102 μL of 50% MeOH solution, 1.13 mmol) in DMSO (1.0 mL) was added DBU (0.112 mL, 0.756 mmol) at rt. After stirring for 5 h, the reaction mixture was added to water and extracted with AcOEt. The organic layer was washed with brine and dried over anhydrous MgSO₄. After removal of the solvent under reduced pressure, the crude material was chromatographed on silica gel with hexane–AcOEt (70:30 v/v) as eluent to give the dimethyl amide **3l** (44.0 mg, 0.227 mmol) in 60% yield.

***N,N*-Dimethyl-4-nitrobenzamide (3l)**

Yellow solid; mp: 96–97 °C; IR (KBr) 1635 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 8.28 (2H, d, *J* = 8.2 Hz), 7.59 (2H, d, *J* = 8.2 Hz), 3.15 (3H, s), 2.97 (3H, s); ¹³C-NMR (100 MHz, CDCl₃) δ 136.2 (Cq), 115.2 (Cq), 109.4 (Cq), 95.0 (CH), 90.7 (CH), 6.22 (CH₃), 2.3 (CH₃); HRMS (ESI) *m/z* calcd for C₉H₁₁N₂O₃ [M+H]⁺ 195.1953, found 195.1953.

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