SUPPORTING INFORMATION

Palladium-Catalyzed Hydroxycarbonylation of Aryl and Vinyl Halides or Triflates by Acetic Anhydride and Formate Anions

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Melting points were determined with a Büchi apparatus and are uncorrected. All of the reagents, catalysts, ligands, and solvents are commercially available and were used as purchased, without further purification. Reaction products were purified on axially compressed columns, packed with SiO_2 25-40 μm (Macherey Nagel), connected to a Gilson solvent delivery system and to a Gilson refractive index detector, and eluting with *n*-hexane/ethyl acetate mixtures. ^{1}H NMR spectra (400 MHz) and ^{13}C NMR spectra (100.6 MHz) were recorded with a Bruker Avance 400 spectrometer. IR spectra were recorded with a Jasco FT/IR 430 spectrometer.

Typical Procedure for the Preparation of Carboxylic Acids: a solution of HCOOLi (133.1 mg, 2.56 mmol), $EtN(Pr^i)_2$ (298 μL, 1.71 mmol), acetic anhydride (161.5 μL, 1.71 mmol) in anhydrous DMF (1 mL) was stirred at room temperature for 1 hour. Then, ethyl *p*-iodobenzoate (236.0 mg, 0.85 mmol), $Pd_2(dba)_3$ (19.6 mg, 0.021 mmol), LiCl (108.7 mg, 2.56 mmol) in anhydrous DMF (2 mL) were added. The reaction mixture was stirred at 80 °C for 3 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with 2 N HCl, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography (silica gel, 35 g; *n*-hexane/ethylacetate 70/30 v/v) to give 150.9 mg (91% yield) of **2n**: mp: 168-170 °C; IR (KBr): 2980, 1710 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 13.37 (bs, 1 H), 8.07 (s, 4 H), 4.35 (q, J = 7.1 Hz, 2 H), 1.35 (t, J = 7.1 Hz, 3 H); ^{13}C NMR (DMSO-d_6) δ 167.1, 165.6, 135.3, 134.0, 130.1, 129.8, 61.7, 14.6; Anal calcd for $C_{10}H_{10}O_4$, C, 61.85; H, 5.19; found C, 61.75; H, 5.18.

Preparation of *p*-Anisic Acid (2a): a solution of HCOOK (215.5 mg, 2.56 mmol), Et_3N (238 μL, 1.71 mmol), acetic anhydride (161.5 μL, 1.71 mmol) in anhydrous DMF (1 mL) was stirred at room temperature for an hour; then, *p*-iodoanisole (200.0 mg, 0.85 mmol), Pd_2dba_3 (19.6 mg, 0.021 mmol), LiCl (108.7 mg, 2.56 mmol) in anhydrous DMF (2 mL) were added. The reaction mixture was refluxed at 80 °C for 3 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with HCl 2 N, dried over Na_2SO_4 and concentrated under reduced pressure. The reaction mixture was purified by chromatography (silica gel, 35 g; *n*-hexane/ethylacetate 75/25 v/v) to give 101.5 mg (78 % of yield) of **2a**; mp: 178-180 °C; lit. mp (Merck Index) 184 °C.

Typical Procedure for the Preparation of Carboxylic Acids from Aryl Bromides and Triflates: a solution of HCOOLi (133.1 mg, 2.56 mmol), $EtN(Pr^i)_2$ (298 μL, 1.71 mmol), acetic anhydride (161.5 μL, 1.71 mmol) in anhydrous DMF (1 mL) was stirred at room temperature for an hour; then, *p*-bromobiphenyl (199.3 mg, 0.855 mmol), $PdCl_2$(dppp) (25.2 mg, 0.043 mmol), LiCl (108.7 mg, 2.56 mmol) in anhydrous DMF (2 mL) were added. The reaction mixture was refluxed at 80 °C for 3 h. After cooling, the reaction mixture was diluted with ethyl acetate, washed with HCl 2 N, dried over Na_2SO_4 and concentrated under reduced pressure. The reaction mixture was

purified by chromatography (silica gel, 35 g; *n*-hexane/ethylacetate 85/15 v/v) to give 130.4 mg (77% of yield) of **2i**; mp 223-224 °C**;** lit. mp (Aldrich Catalogue) 225-226°C.

(2b): mp: 105-107 °C; lit. mp (Aldrich Catalogue) 106-108 °C
(2c): mp: 101-102 °C; lit. mp (Aldrich Catalogue) 98-100 °C
(2d): mp: 179-180 °C; lit. mp (Merck Index) 180-181 °C
(2d'): mp: 179-180 °C; IR (KBr): 2980, 1710 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 12.78 (bs, 1 H), 7.84 (dd, $J_{3H\text{-}H}$ = 8.1 Hz, $J_{3H\text{-}C}$ = 4.0 Hz, 2 H),), 7.30 (d, *J*= 8.1 Hz, 2 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 2.37 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 167.8, (t, $J_{3H\text{-}C}$ = 4.0 Hz), 129.9 (d, *J*=2.6 Hz); 129.7 (d, *J*=4.5 Hz), 128.6 (d, *J*=72.2 Hz), 21.7. MS: *m/z* (relative intensity) 137 (56) [M^{+}], 120 (52), 91 (100), 65 (25).
(2e): mp: 108-109 °C; lit. mp (Merck Index) 111-113 °C
(2f): mp: 103-104 °C; lit. mp (Merck Index) 107-108 °C
(2g): mp: 161-162 °C; lit. mp (Merck Index) 160.5-162°C
(2h): mp: 120-121 °C; lit. mp (Merck Index) 122.4°C
(2j): mp: 183-184 °C; lit. mp (Merck Index) 182.6 °C
(2k): mp: 120-123 °C; lit. mp (Aldrich Catalogue) 123-125 °C
(2l): mp: 239-240 °C; lit. mp (Merck Index) 243 °C
(2m): mp: 208-209 °C; lit. mp (Aldrich Catalogue) 208-210 °C
(2o): mp: 187-188 °C; IR (KBr): 1694, 1616cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 13.81 (bs, 1H), 8.39 (d, *J* = 1.7 Hz, 1 H), 8.10 (dd, J_1 = 7.9 Hz, J_2 = 1.7 Hz, 1 H), 7.61 (d, *J* = 7.9 Hz, 1 H), 2.57 (s, 3 H); ^{13}C NMR (DMSO-d_6) δ 165.9, 156.5, 149.2, 138.1, 133.8, 130.5, 125.4, 20.1; Anal calcd for $C_8H_7NO_4$, C, 53.04; H, 3.89; N, 7.73; found C, 53.13; H, 3.90; N, 7.74.
(2p): mp: 237-238 °C; lit. mp (Merck Index) 242.4 °C.
(2q): mp: 130-131 °C; lit. mp (Merck Index) 133 °C.
(2r): 108-109 °C; IR (KBr) 1681, 1606, 1041 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 12.51 (bs,1 H), 7.72 (d, *J* = 8.4 Hz, 1 H), 6.98 (t, *J* = 4.8 Hz, 1 H), 6.80-6.74 (m, 2 H), 3.74 (s, 3 H), 2.70-2.65 (m, 2 H), 2.34-2.27 (m, 2H); ^{13}C NMR (DMSO-d_6) δ 168.1, 158.9, 138.5, 137.5, 130.63, 127.7, 124.3, 113.8, 111.7, 55.6, 27.9, 23.4; Anal calcd for $C_{12}H_{12}O_3$ C, 70.57; H, 5.92; found C, 70.60, H 5.94.
(2s): mp: 177-178 °C; IR (KBr): 3431, 1733, 1661, 1373 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 12.13 (s, 1 H), 6.93 (s, 1 H), 5.83 (s, 1 H), 4.54 (t, *J* = 8.12 Hz, 1 H), 2.49-2.10 (m, 4 H), 2.00 (s, 3 H), 1.99-0.88 (m, 13 H), 0.86 (s, 3H), 0.79 (3 H); ^{13}C NMR (DMSO-d_6) δ 170.9, 168.9, 141.3, 137.9, 131.5, 126.6, 82.4, 50.9, 48.0, 42.7, 36.7, 34.8, 33.6, 31.8, 31.6, 27.7, 23.5, 22.1, 21.4, 20.7, 19.3, 12.5. Anal calcd for $C_{22}H_{30}O_4$, C, 73.71; H, 8.44; found C, 73.66; H, 8.43.