Supporting Information to:

Dimethylformamide as a Carbon Monoxide Source in Fast Palladium-Catalyzed
Aminocarbonylations of Aryl Bromides

By

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S1-S2 Purification details and NMR-data

4,*N,N*-Trimethyl-benzamide (1): With hexane/acetone (3:1) as eluent gave 71.7 mg of the title compound as a colorless liquid. IR (neat) ν 1635 cm^{-1} ; MS m/z 162(M^+); ^1H NMR (CDCl_3) δ 7.32 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 7.9 Hz, 2H), 3.08 (s, 3H), 2.98 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (CDCl_3) δ 171.7, 139.5, 133.3, 128.8, 127.1, 39.6, 35.4, 21.4.

***N*-Benzyl-4-methyl-benzamide (2):** With hexane/acetone (4:1) as eluent gave 128.6 mg of the title compound as a white solid. IR (neat) ν 1638 cm^{-1} ; MS m/z 225(M^+); ^1H NMR (CDCl_3) δ 7.63 (d, J = 8.1 Hz, 2H), 7.27-7.12 (m, 7H), 6.52 (brs, 1H), 4.55 (d, J = 5.8 Hz, 2H), 2.31 (s, 3H); ^{13}C NMR (CDCl_3) δ 167.3, 141.9, 138.2, 131.4, 129.2, 128.7, 127.8, 127.5, 126.9, 43.9, 21.4.

4-Methyl-*N*-phenyl-benzamide (3): With hexane/acetone (3:1) as eluent gave 122.7 mg of the title compound as a white solid. IR (neat) ν 1652 cm^{-1} ; MS m/z 211(M^+); ^1H NMR (CDCl_3) δ 7.92 (brs, 1H), 7.78 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 7.7 Hz, 2H), 7.39-7.11 (m, 5H), 2.41 (s, 3H); ^{13}C NMR (CDCl_3) δ 165.7, 142.3, 138.0, 132.0, 129.3, 129.0, 127.0, 124.4, 120.1, 21.5.

4-Methyl-*N*-morpholine-benzamide (4): With $\text{CHCl}_3/\text{MeOH}$ (35:1) as eluent gave 119.6 mg of the title compound as a colorless liquid. IR (neat) ν 1649 cm^{-1} ; MS m/z 204(M^+); ^1H NMR (CDCl_3) δ 7.31 (m, 2H), 7.21 (m, 2H), 3.70-3.08 (m, 8H), 2.37 (s, 3H); ^{13}C NMR (CDCl_3) δ 170.8, 140.3, 132.5, 129.4, 127.4, 67.1, 48.2, 42.8, 21.6.

***N*-benzyl-2-methyl-benzamide (5):** With hexane/acetone (3:1) as eluent gave 158.3 mg of the title compound as a white solid. IR (neat) ν 1627 cm^{-1} ; MS m/z 225(M^+); ^1H NMR (CDCl_3) δ 7.36-7.11 (m, 9H), 6.24 (brs, 1H), 4.59 (d, J = 5.9 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (CDCl_3) δ 169.9, 130.9, 129.8, 128.7, 127.7, 127.5, 126.6, 125.6, 43.8, 19.8.

***N*-benzyl-benzamide (6):** With hexane/acetone (3:1) as eluent gave 128.9 mg of the title compound as a white solid. IR (neat) ν 1636 cm^{-1} ; MS m/z 211(M^+); ^1H NMR (CDCl_3) δ 7.81-7.75 (m, 2H), 7.50-7.30 (m, 8H), 6.80 (brs, 1H), 4.59 (d, $J = 5.9$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 167.4, 138.1, 131.4, 128.6, 128.4, 127.7, 127.4, 126.9, 43.9.

***N*-Benzyl-4-methoxy-benzamide (7):** With hexane/acetone (3:1) as eluent gave 125.7 mg of the title compound as a white solid. IR (neat) ν 1632 cm^{-1} ; MS m/z 241(M^+); ^1H NMR (CDCl_3) δ 7.78-7.75 (m, 2H), 7.34-7.28 (m, 5H), 6.90-6.86 (m, 2H), 6.68 (brs, 1H), 4.59 (d, $J = 5.8$ Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (CDCl_3) δ 166.8, 162.1, 138.4, 128.7, 128.6, 127.8, 127.4, 126.5, 113.6, 55.3, 43.9.

***N*-Formylbenzylamin:** With $\text{CHCl}_3/\text{MeOH}$ (50:1) as eluent gave 67.9 mg of the title compound as a white solid. IR (neat) ν 1663 cm^{-1} ; MS m/z 135(M^+); ^1H NMR (CDCl_3) δ 8.19 (s, 0.9H), 8.10 (d, $J = 11.8$ Hz, 0.1H), 7.40-7.15 (m, 5H), 6.17 (brs, H), 4.44 (d, $J = 5.9$ Hz, 1.8H), 4.37 (d, $J = 6.4$ Hz, 0.2H); ^{13}C NMR (CDCl_3) δ 164.6, 161.0, 137.5, 128.8, 128.6, 127.9, 127.7, 127.6, 126.9, 45.6, 42.1.