Supporting Information for

Rapid and Efficient Microwave-Assisted Amination of Electron-Rich Aryl Halides without Transition-Metal Catalyst

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Experimental

General Information: The materials were used as purchased and DMSO was used without any additional purification. All reactions under microwave irradiation were monitored by thin-layer chromatography (TLC) on gel F₂₅₄ plates. The silica gel (200–300 meshes) for column chromatography was from the Qingdao Marine Chemical Factory in China.

¹H and ¹³C NMR spectra were recorded in CDCl₃ solution on the Varian Mercury-plus 300BB instruments, and spectral data are reported in *ppm* relative to tetramethylsilane (TMS) as internal standard. The amination syntheses under microwave conditions were performed on a 700 W LG microwave oven (model WD 700) set at a power setting of 20%.

Details of compound characterization are provided hereinafter.

General Procedure for Aryl Aminations: the aryl halide (ArX, 1 mmol), the amine (1.5~4 mmol) and KO^tBu (1.5~2 mmol) were added to 5 mL DMSO. The reaction was found not to be sensitive to air and moisture, hence there was no need for inert atmosphere. The vessel was placed in a beaker inside the center of the microwave oven and heated to reflux (which took 22 sec at the power setting of 20%), and then held at that temperature for 5~20 min. After completion of the reaction, it was cooled to room temperature, poured into ice water and stirred for 5 min to precipitate the product. Diethylether and saturated aqueous NH₄Cl solution were added to the resulting mixture, and the organic layer was separated followed by the extraction of the aqueous layer with Et₂O. The combined organic extracts were washed with a saturated NH₄Cl solution and brine, and dried over anhydrous Na₂SO₄. After removal of the solvent the residue was purified by the column chromatography on silica gel to furnish the expected product.

Spectroscopic data for following adducts:

¹H NMR (300 MHz, CDCl₃): δ 7.38–7.31 (m, 2H), 6.98–6.93 (m, 3H), 3.92–3.88 (m, 4H), 3.21–3.17 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 151.1, 129.0 (2C), 119.8, 115.5 (2C), 66.7 (2C), 49.1(2C).

¹H NMR (300 MHz, CDCl₃): δ 7.20–7.13 (m, 1H), 6.72–6.69 (m, 3H), 3.86–3.82 (m, 4H), 3.14–3.10 (m, 4H), 2.31 (s, 3H); ¹³C NMR (75 MHz, CDCl₃): δ 151.6, 139.1,

129.3, 121.2, 116.8, 113.1, 67.2 (2C), 49.7(2C), 22.0.

^1H NMR (300 MHz, CDCl_3): δ 7.13–7.10 (d, J = 8.7 Hz, 2H), 6.87–6.84 (d, J = 9 Hz, 2H), 3.90–3.86 (m, 4H), 3.14–3.10 (m, 4H), 2.29 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 149.5, 146.8, 130.0 (2C), 116.3 (2C), 67.2 (2C), 50.2 (2C), 20.7.

^1H NMR (300 MHz, CDCl_3): δ 6.87–6.84 (m, 4H), 3.88–3.82 (m, 4H), 3.77 (s, 3H), 3.08–3.04 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 154.2, 145.9, 118.0 (2C), 114.7 (2C), 67.3 (2C), 55.8, 51.0 (2C).

^1H NMR (300 MHz, CDCl_3): δ 7.15–7.09 (m, 1H), 6.52–6.47 (m, 1H), 6.39–6.33 (m, 2H), 6.02 (brs, 1H), 3.91–3.84 (m, 4H), 3.13–3.10 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 157.0, 153.0, 130.4, 108.4, 107.4, 103.2, 67.0 (2C), 49.4 (2C).

^1H NMR (300 MHz, CDCl_3): δ 7.09–6.99 (m, 1H), 6.42–6.33 (m, 1H), 6.25–6.21 (m, 2H), 3.85–3.72 (m, 4H), 3.63 (brs, 2H), 3.14–3.10 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 152.8, 147.6, 130.2, 107.6, 106.7, 102.8, 67.2 (2C), 49.5 (2C).

^1H NMR (300 MHz, CDCl_3): δ 7.19–7.13 (m, 1H), 6.36–6.28 (m, 3H), 3.89–3.85 (m, 4H), 3.19–3.15 (m, 4H), 2.95 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 152.5, 151.7, 129.6, 105.5, 105.0, 100.8, 67.0 (2C), 49.8 (2C), 40.7 (2C).

^1H NMR (300 MHz, CDCl_3): δ 7.38–7.20 (m, 2H), 7.12–6.99 (m, 2H), 6.95–6.90 (m, 1H), 3.27–3.23 (m, 4H), 1.85–1.78 (m, 4H), 1.74–1.63 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 152.6, 129.3 (2C), 119.5, 116.9 (2C), 51.0 (2C), 26.2 (2C), 24.7.

^1H NMR (300 MHz, CDCl_3): δ 7.41–7.31 (m, 2H), 6.82–6.77 (m, 1H), 6.70–6.66 (m, 2H), 3.48–3.33 (m, 4H), 2.19–2.04 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 148.3, 129.5 (2C), 115.7, 112.0 (2C), 47.9 (2C), 25.8 (2C).

^1H NMR (300 MHz, CDCl_3): δ 7.54–6.86 (m, 9H), 3.81–3.77 (m, 2H), 3.05–3.00 (m, 2H), 2.24–2.16 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 148.8, 144.8, 129.8 (3C), 129.3, 126.8, 125.0 (2C), 124.0, 118.8, 116.3, 51.2, 28.2, 23.2.

^1H NMR (300 MHz, CDCl_3): δ 7.75–7.73 (d, $J = 6.9$ Hz, 1H), 7.63–7.60 (d, $J = 8.1$ Hz, 1H), 7.75–7.54 (d, $J = 4.2$ Hz, 4H), 7.43–7.36 (m, 2H), 7.29–7.19 (m, 2H), 6.73–6.72 (d, $J = 3.0$ Hz, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 139.8, 135.8, 129.6 (2C), 129.3, 127.9, 126.4, 124.3 (2C), 122.3, 121.1, 120.3, 110.5, 103.5.

^1H NMR (300 MHz, CDCl_3): δ 7.47–7.37 (m, 4H), 7.23–7.21 (m, 4H), 7.14–7.04 (m,

2H), 5.75 (brs, 1H); ^{13}C NMR (75 MHz, CDCl_3): δ 143.6(2C), 129.8 (4C), 121.4 (2C), 118.3 (4C).

^1H NMR (300 MHz, CDCl_3): δ 7.43–7.29 (m, 6H), 7.18–7.15 (m, 6H), 7.11–7.04 (m, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 148.2 (3C), 129.5 (6C), 124.5 (6C), 123.0 (3C).

^1H NMR (300 MHz, CDCl_3): δ 7.23–7.17 (m, 2H), 7.09–6.93 (m, 3H), 3.34–3.24 (m, 2H), 1.67–1.66 (m, 8H), 1.63–1.47 (m, 8H), 1.39–1.23 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 149.0, 128.5 (2C), 121.5 (2C), 119.5, 57.8 (2C), 32.3 (4C), 26.6 (4C), 26.3 (2C).

^1H NMR (300 MHz, CDCl_3): δ 7.45–7.26 (m, 2H), 7.22–7.00 (m, 3H), 3.91–3.82 (m, 2H), 1.33–1.30 (d, J = 6.6 Hz, 12H); ^{13}C NMR (75 MHz, CDCl_3): δ 148.4, 128.7 (2C), 120.0 (2C), 118.7, 47.9 (2C), 21.7 (4C).

^1H NMR (300 MHz, CDCl_3): δ 7.50–7.39 (m, 2H), 6.92–6.84 (m, 3H), 3.58–3.51 (m, 4H), 1.40–1.33 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 148.2, 129.7(2C), 115.9, 112.3 (2C), 44.7 (2C), 13.0 (2C).

Further direct evidence for the identification of benzyne intermediate was provided.

^1H NMR (300 MHz, CDCl_3): δ 7.26–7.22 (m, 2H), 7.02 (s, 2H), 6.99–6.94 (m, 2H), 5.71 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 149.0 (2C), 143.0 (2C), 125.0 (2C), 120.2 (2C), 82.3 (2C).

Supplement:

The direct amination of aryl halides bearing an electron-poor substituent was known to be more favored toward the $\text{S}_{\text{N}}\text{Ar}$ reaction, to clarify this discrepancy with those bearing an electron-rich substituent, 2-nitrophenylbromide was examined to afford only *ortho*-substituted product, and no cine substitution effect was observed.

^1H NMR (300 MHz, CDCl_3): δ 7.78–7.76 (d, J = 8.1 Hz, 1H), 7.52–7.47 (t, J = 8.1 Hz, J = 8.4 Hz, 1H), 7.16–7.14 (d, J = 8.4 Hz, 1H), 7.10–7.05 (t, J = 8.1 Hz, J = 8.4 Hz, 1H), 3.86–3.80 (m, 4H), 3.07–3.03 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3): δ 145.8, 143.8, 133.5, 125.8, 122.3, 120.9, 66.8 (2C), 52.1 (2C).