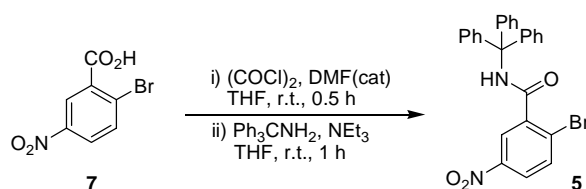


# **Intramolecular six-membered N–H...Br and N–H...I hydrogen bonding in aromatic amides in the absence of competing interactions**

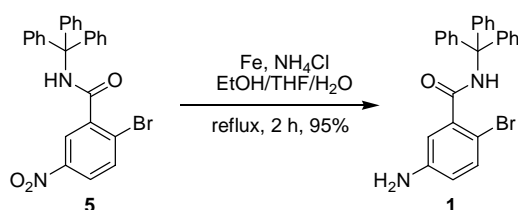
**Yuan-Yuan Zhu, Long Jiang, Tong-Bu Lu and Zhan-Ting Li**

**Supporting Information**

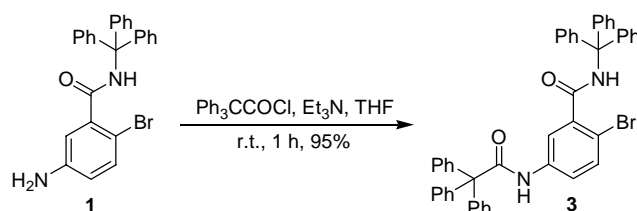
**Synthesis and Characterization**



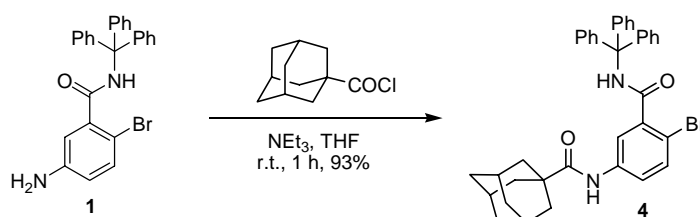
**Compound 5.** To a stirred solution of 2-bromo-5-nitrobenzoic acid **7**<sup>1</sup> (0.49 g, 2.00 mmol) in THF (15 mL), cooled in an ice-bath, were added oxalyl dichloride (1.60 mL, 20.0 mmol) and DMF (50  $\mu$ L). The solution was stirred for 30 min and then concentrated with a rotavapor to give 2-bromo-5-nitrobenzoyl chloride as white solid, which was then dissolved in THF (10 mL). The solution was added slowly to a stirred solution of (triphenylmethyl)amine (0.52 g, 2.00 mmol) and triethylamine (0.30 mL, 2.20 mL) in THF (10 mL). After stirring for 1 hour, the solution was concentrated with a rotavapor. The resulting residue was dissolved in chloroform (20 mL) and the solution washed successively with hydrochloric acid (0.5 N, 10 mL), water (20 mL  $\times$  2) and brine (10 mL) and dried over sodium sulfate. After the solvent was removed, the crude product was subjected to column chromatography (petroleum ether/EtOAc, 6:1) to give **5** as white solid (0.88 g, 90%). Mp: 242-243  $^{\circ}$ C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.36 (d,  $J$  = 3.0 Hz, 1 H), 8.10 (dd,  $J_1$  = 8.7 Hz,  $J_2$  = 1.0 Hz, 1 H), 7.80 (d,  $J$  = 8.7 Hz, 1 H), 7.39–7.27 (m, 15 H), 7.25 (s, 1 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 163.9, 147.2, 143.9, 139.6, 134.8, 128.7, 128.2, 127.4, 126.5, 125.5, 124.9, 71.9. MS (ESI):  $m/z$  509.1 [M + Na]<sup>+</sup>. Anal. Calcd. For C<sub>26</sub>H<sub>19</sub>BrN<sub>2</sub>O<sub>3</sub>: C, 64.08; H, 3.93; N, 5.75. Found: C, 63.99; H, 4.34; N, 5.50.



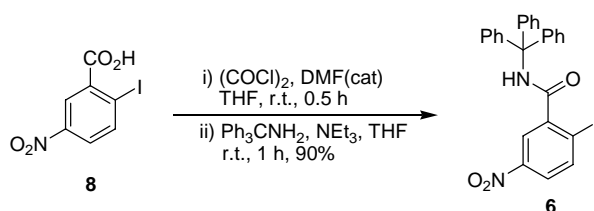
**Compound 1.** To a solution of compound **5** (0.49 g, 1.00 mmol) in EtOH (10 mL), THF (5 mL) and water (5 mL) were added ammonium chloride (55 mg, 1.00 mmol) and iron powder (0.28 g, 5.00 mmol). The suspension was stirred under reflux for 2 hours and then cooled to room temperature. The solid was filtrated off and washed with chloroform (10 mL) and the filtrate concentrated with a rotavapor. The resulting residue was dissolved in chloroform (30 mL) and the solution washed successively with water (15 mL  $\times$  2) and brine (15 mL) and dried over magnesium sulfate. Upon removal of the solvent under reduced pressure, the resulting residue was purified by column chromatography (chloroform/EtOAc 10:1) to give compound **1** as white solid (0.43 g, 95%). Mp: 184-185  $^{\circ}$ C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.33–7.25 (m, 17 H), 6.82 (d,  $J$  = 2.7 Hz, 1 H), 6.51 (dd,  $J_1$  = 9.0 Hz,  $J_2$  = 3.0 Hz, 1 H), 3.75 (br, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 166.1, 146.1, 144.4, 138.3, 134.0, 128.8, 128.0, 127.1, 118.0, 116.5, 106.2, 71.3. MS (ESI):  $m/z$  479.1 [M + Na]<sup>+</sup>. HRMS (MALDI-FT): Calcd. For C<sub>26</sub>H<sub>21</sub>BrN<sub>2</sub>ONa [M + Na]<sup>+</sup>: 479.0730. Found: 479.0743.



**Compound 3.** To a solution of triphenylacetic acid (0.14 g, 0.50 mmol) in THF (10 mL) were added oxalyl dichloride (0.40 mL, 5.00 mmol) and DMF (50  $\mu\text{L}$ ). The mixture was stirred for 0.5 hour and then concentrated with a rotavapor to give triphenylacetic chloride as white solid. This residue was dissolved in THF (10 mL) and the solution added to a solution of compound **1** (0.23 g, 0.50 mmol) and triethylamine (0.10 mL, 0.70 mmol) in THF (10 mL). The solution was stirred for 1 hour and then concentrated with a rotavapor. The resulting residue was dissolved in chloroform (20 mL) and then washed successively with hydrochloric acid (0.5 N, 10 mL), water (10 mL  $\times$  2) and brine (10 mL) and dried over sodium sulfate. After the solvent was removed under reduced pressure, the crude product was subjected to column chromatography (chloroform/AcOEt 20:1) to give compound **3** as white solid (0.69 g, 95%). Mp: 124-125  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.87 (dd,  $J_1 = 8.7$  Hz,  $J_2 = 2.7$  Hz, 1 H), 7.54 (s, 1 H), 7.53 (d,  $J = 8.4$  Hz, 1 H), 7.46 (s, 1 H), 7.36–7.27 (m, 31 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 171.8, 165.1, 144.2, 142.6, 137.7, 137.5, 134.3, 130.4, 128.8, 128.2, 128.0, 127.4, 127.2, 123.0, 121.6, 71.6, 68.7. MS (ESI):  $m/z$  749.3  $[\text{M} + \text{Na}]^+$ . HRMS (MALDI-FT): Calcd. For  $\text{C}_{46}\text{H}_{35}\text{BrN}_2\text{O}_2\text{Na}$   $[\text{M} + \text{Na}]^+$ : 749.1774. Found: 749.1775.

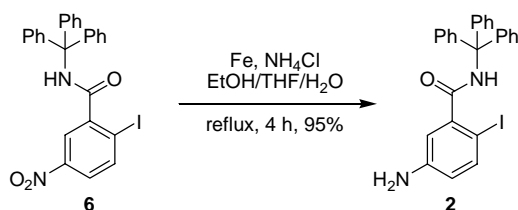


**Compound 4** was prepared from the reaction of **1** and chloroformyl adamantane as white solid in 93% yield. Mp: 300-302  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 7.81 (dd,  $J_1 = 8.7$  Hz,  $J_2 = 2.7$  Hz, 1 H), 7.50 (d,  $J = 8.7$  Hz, 1 H), 7.44 (s, 1 H), 7.42 (s, 1 H), 7.41 (s, 1 H), 7.35–7.25 (m, 15 H), 2.08 (bs, 3 H), 1.91 (br, 6 H), 1.78–1.68 (m, 6 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 176.3, 165.4, 144.2, 137.9, 137.9, 134.1, 129.1, 128.8, 128.0, 127.1, 123.3, 121.4, 112.8, 71.5, 41.6, 39.1, 36.3, 28.0. MS (ESI):  $m/z$  641.1  $[\text{M} + \text{Na}]^+$ . HRMS (MALDI-FT): Calcd. For  $\text{C}_{37}\text{H}_{35}\text{BrN}_2\text{O}_2\text{Na}$   $[\text{M} + \text{Na}]^+$ : 641.1774. Found: 641.1773.



**Compound 6** was prepared as white solid starting from **8**<sup>2</sup> and triphenylmethylamine. Yield: 90%. Mp: 256-258  $^\circ\text{C}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.19 (d,  $J = 2.7$  Hz, 1 H), 8.09 (d,  $J = 8.7$  Hz, 1 H), 7.92 (d d,  $J_1 = 8.7$  Hz,  $J_2 = 2.7$  Hz, 1 H), 7.39–7.28 (m, 15 H), 7.02 (s, 1 H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 165.7, 147.9, 143.9, 143.7, 141.6, 128.8, 128.2, 127.5, 125.2, 123.1, 100.7, 71.8. MS

(ESI):  $m/z$  557.0  $[M + Na]^+$ . Anal. Calcd. For  $C_{26}H_{19}IN_2O_3 \cdot 1/6CH_2Cl_2$ : C, 57.30; H, 3.55; N, 5.11. Found: C, 57.59; H, 3.40; N, 4.98.



**Compound 2** was prepared from **6** as pale yellow solid in 95% yield. Mp: 150-153 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.53 (d,  $J$  = 8.7 Hz, 1 H), 7.37–7.24 (m, 15 H), 7.00 (s, 1 H), 6.70 (d,  $J$  = 2.7 Hz, 1 H), 6.39 (dd,  $J_1$  = 8.7 Hz,  $J_2$  = 2.7 Hz, 1 H), 3.76 (br, 2 H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ : 167.6, 146.7, 144.4, 142.8, 140.6, 128.9, 128.0, 127.1, 118.3, 115.7, 71.3. MS (ESI):  $m/z$  527.1  $[M + Na]^+$ . Anal. Calcd. For  $C_{26}H_{21}IN_2O \cdot 1/4 CH_2Cl_2$ : C, 59.99; H, 4.12; N, 5.33. Found: C, 59.86; H, 4.24; N, 4.91.

## References

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- 2) V. Subramanian, V. R. Batchu, D. Barange, M. Pal, *J. Org. Chem.*, 2005, **70**, 4778.