

## Supporting Information

### Nickel-Catalyzed Amination of Aryl Tosylates

Cai-Yan Gao<sup>†,‡</sup> and Lian-Ming Yang<sup>\*,†</sup>

<sup>†</sup>Beijing National Laboratory For Molecular Sciences (BNLMS), Laboratory of New Materials, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

<sup>‡</sup>Graduate School of Chinese Academy of Sciences, Beijing 100049, China

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**General Method.** All reactions were carried out under nitrogen atmosphere with oven-dried glassware and heated in an oil bath. THF and dioxane were distilled from sodium/benzophenone before use. Secondary cyclic amines, anilines and anhydrous sodium *tert*-butoxide were commercially available and used without further purification. Column chromatography was performed on silica gel (200–300 mesh). Aryl tosylates were synthesized according to the previously published procedure.<sup>1</sup> The Ni(II)–( $\sigma$ -aryl) complexes were prepared according to the literature procedures.<sup>2</sup> All yields refer to isolated yields (average of two run) of compounds estimated to be >95% pure as determined by <sup>1</sup>H NMR. The known compounds were partly characterized by melting points (for solid samples), MS and <sup>1</sup>H NMR, and compared to authentic samples or the literature data. Four new compounds were fully characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, MS and EA.

**General Procedure A for the Amination of Aryl Tosylates with Secondary Cyclic Amines.** An oven-dried 100-mL three-necked flask was charged with NaO<sup>t</sup>Bu (1.6 mmol, 154 mg), Ni(PPh<sub>3</sub>)<sub>2</sub>(1-naphthyl)Cl (5 mol % relative to aryl tosylate, 37 mg), and IPr-HCl (5 mol% relative to aryl tosylate, 21 mg). The aryl tosylate (1.0 mmol) was added at this time. The flask was evacuated and backfilled with nitrogen, with the operation being repeated twice. The amine (1.5 mmol) was added via syringe, followed by dried dioxane (5 mL). The reaction mixture was heated at an oil bath of 110 °C for 15 min. The reaction mixture was allowed to cool to room temperature and filtered through a pad of silica gel that was washed with ethyl acetate (20 mL  $\times$  3). Then the combined organic phases were evaporated under reduced pressure and the residue purified by column chromatography on silica gel with petroleum/ethyl acetate to give the desired product.

**General Procedure B for the Amination of Aryl Tosylates with Anilines.** An oven-dried 100-mL three-necked flask was charged with NaO<sup>t</sup>Bu (1.6 mmol, 154 mg), Ni(PPh<sub>3</sub>)<sub>2</sub>(1-naphthyl)Cl (5 mol% relative to aryl tosylate, 37 mg), and IPr-HCl (10 mol% relative to aryl tosylate, 42 mg). The aryl tosylate (1.0 mmol) and the aniline (1.5 mmol) were added at this time if solid. The flask was evacuated and

backfilled with nitrogen, with the operation being repeated twice. The aniline (1.5 mmol) was added at this time via syringe if liquid. Then dried dioxane (5 mL) was added via syringe. The reaction mixture was heated at an oil bath of 110 °C for 30 min. The reaction mixture is allowed to cool to room temperature and filtered through a pad of silica gel that was washed with ethyl acetate (20 mL × 3). Then the combined organic phases were evaporated under reduced pressure and the residue purified by column chromatography on silica gel with petroleum /ethyl acetate to give the desired product.

***N*-Phenylmorpholine**<sup>3</sup> (Table 2, entry 1). According to General Procedure A, phenyl tosylate (248 mg, 1.0 mmol) and morpholine (131 mg, 1.5 mmol) were transformed into the product as a colorless solid (138 mg, 85%): mp 49–51 °C, (lit.<sup>3</sup> mp 52–53 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.13–3.25 (m, overlapped, 4H), 3.80–4.00 (m, overlapped, 4H), 6.86–7.05 (m, overlapped, 3H), 7.28–7.37 (m, overlapped, 2H); MS (EI): *m/z* 163 (M<sup>+</sup>). CAS Number: 92-53-5.

***N*-Phenylpiperidine**<sup>4</sup> (Table 2, entry 2). According to General Procedure A, phenyl tosylate (248 mg, 1.0 mmol) and piperidine (128 mg, 1.5 mmol) were transformed into the product as a colorless liquid (118 mg, 73%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.56–1.63 (m, 2H), 1.70–1.75 (m, 4H), 3.16 (t, *J* = 5.6 Hz 4H), 6.81 (dd, *J*<sub>1</sub> = *J*<sub>2</sub> = 7.26 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.4 Hz, 2H); MS (EI): *m/z* 161 (M<sup>+</sup>). CAS Number: 4096-20-2.

***N*-Phenylpyrrolidine**<sup>5</sup> (Table 2, entry 3). According to General Procedure A, phenyl tosylate (248 mg, 1.0 mmol) and pyrrolidine (106 mg, 1.5 mmol) were transformed into the product as a colorless liquid (88 mg, 60%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.99 (t, *J* = 6.2 Hz, 4H), 3.23–3.38 (m, 4H), 6.57 (d, *J* = 7.8 Hz, 2H), 6.66 (t, *J* = 7.1 Hz, 1H), 7.22 (t, *J* = 8.4 Hz, 2H); MS (EI): *m/z* 147 (M<sup>+</sup>). CAS Number: 4096-21-3.

***N*-(*m*-Anisyl)morpholine**<sup>6</sup> (Table 2, entry 6). According to General Procedure A, *m*-anisyl tosylate (278 mg, 1.0 mmol) and morpholine (131 mg, 1.5 mmol) were transformed into the product as a colorless liquid (183 mg, 95%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.16 (t, *J* = 4.8 Hz, 4H), 3.79 (s, 3H), 3.82–4.00 (m, 4H), 6.40–6.65 (m, 3H), 7.19 (t, *J* = 8.2 Hz, 1H); MS (EI): *m/z* 193 (M<sup>+</sup>). CAS Number: 32040-09-8.

***N*-(*m*-Anisyl)piperidine**<sup>7</sup> (Table 2, entry 7). According to General Procedure A, *m*-anisyl tosylate (278 mg, 1.0 mmol) and piperidine (128 mg, 1.5 mmol) were transformed into the product as a colorless liquid (140 mg, 74%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.48–1.55 (m, 2H), 1.56–1.78 (m, 4H), 3.18 (t, *J* = 5.1 Hz, 4H), 3.81 (s, 3H), 6.41 (d, *J* = 8.0 Hz, 1H), 6.51 (s, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 8.2 Hz, 1H); MS (EI): *m/z* 191 (M<sup>+</sup>). CAS Number: 32040-06-5.

***N*-(*m*-Anisyl) pyrrolidine**<sup>8</sup> (Table 2, entry 8). According to General Procedure A, *m*-anisyl tosylate (278 mg, 1.0 mmol) and pyrrolidine (106 mg, 1.5 mmol) were transformed into the product as a colorless liquid (92 mg, 52%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 1.92–2.08 (m, 4H), 3.25–3.35 (m, 4H), 3.81 (s, 4H), 3.78 (s, 3H), 6.04–6.30 (m, 3H), 7.08–7.20 (m, 1H); MS (EI): *m/z* 177 (M<sup>+</sup>). CAS Number: 32040-07-6.

**4-morpholinobenzophenone**<sup>9</sup> (Table 2, entry 9). According to General Procedure A except with Ni(PPh<sub>3</sub>)<sub>2</sub>(naph)Cl (15 mol%)–IPr·HCl (15 mol%) in place of Ni(PPh<sub>3</sub>)<sub>2</sub>(naph)Cl (5 mol%)–IPr·HCl (5 mol%), 4-benzoylphenyl tosylate (352 mg) and morpholine (131 mg, 1.5 mmol) were transformed into the product as a pale yellow solid (179 mg, 67%): mp 135–136 °C, (lit.<sup>9</sup> mp 140–142 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 3.32 (t, *J* = 5.2 Hz, 4H), 3.75 (t, *J* = 4.6 Hz, 4H), 7.04 (d, *J* = 8.9 Hz, 2H), 7.53 (t, *J* = 7.5 Hz, 2H), 7.59–7.69 (m, 5H); MS (EI): *m/z* 267 (M<sup>+</sup>). CAS Number: 13672-14-5.

**1,4-Dimorpholinobenzene**<sup>10</sup> (Table 2, entry 11). According to General Procedure A, 1,4-phenylene bistosylate (418 mg, 1 mmol) and morpholine (262 mg, 3.0 mmol) were transformed into the product as a colorless solid (60 mg, 24%): mp 191–192 °C, (lit.<sup>10</sup> mp 198–200 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.00–3.20 (m, 8H), 3.80–3.86 (m, 8H), 6.83–7.00 (m, 4H); MS (EI): *m/z* 248 (M<sup>+</sup>). CAS Number: 4096-22-4.

***N*-(2-Naphthyl)morpholine**<sup>11</sup> (Table 2, entry 12). According to General Procedure A, 2-naphthyl tosylate (298 mg, 1 mmol) and morpholine (131 mg, 1.5 mmol) were transformed into the product as a colorless solid (204 mg, 96%): mp 87–88 °C, (lit.<sup>11</sup> mp 87–88 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.20–3.40 (m, overlapped, 4H), 3.85–4.10 (m, overlapped, 4H), 7.02–7.15 (m, 1H), 7.18–7.31 (m, 2H), 7.38 (t, *J* = 7.2 Hz, 1H), 7.65–7.75 (m, 3H); MS (EI): *m/z* 213 (M<sup>+</sup>). CAS Number: 7508-21-6.

***N*-(2-Naphthyl)piperidine**<sup>11</sup> (Table 2, entry 13). According to General Procedure A, 2-naphthyl tosylate (298 mg, 1mmol) and piperidine (128 mg, 1.5 mmol) were transformed into the product as a colorless solid (167 mg, 79%): mp 56–58 °C, (lit.<sup>11</sup> 58–59 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 1.52–1.62 (m, 2H), 1.63–1.70 (m, 4H), 3.20–3.30 (m, 4H), 7.12 (s, 1H), 7.21 (t, *J* = 7.4 Hz, 1H), 7.33 (dd, *J*<sub>1</sub> = 12.8 Hz, *J*<sub>2</sub> = 7.9 Hz, 2H), 7.67 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 9.1 Hz, 2H); MS (EI): *m/z* 211 (M<sup>+</sup>). CAS Number: 5465-85-0.

***N*-(2-Naphthyl)pyrrolidine**<sup>12</sup> (Table 2, entry 14). According to General Procedure A, 2-naphthyl tosylate (298 mg, 1mmol) and pyrrolidine (107 mg, 1.5 mmol) were transformed into the product as a colorless solid (114 mg, 58%): mp 90–92 °C, (lit.<sup>12</sup> 91–91.5 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 1.92–2.06 (m, 4H), 3.25–3.45 (m, 4H), 6.74 (s, 1H), 7.03 (d, *J* = 5.7 Hz, 1H), 7.11 (t, *J* = 6.9 Hz, 1H), 7.31 (t, *J* = 6.9 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H); MS (EI): *m/z* 197 (M<sup>+</sup>). CAS Number: 13672-14-5.

***N*-(1-Naphthyl)morpholine**<sup>13</sup> (Table 2, entry 15). According to General Procedure A, 1-naphthyl tosylate (298 mg, 1mmol) and morpholine (131 mg, 1.5 mmol) were transformed into the product as a colorless solid (162 mg, 76%): mp 83–84 °C, (lit.<sup>13</sup> 82 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.05–3.25 (m, overlapped, 4H), 4.04 (t, *J* = 4.2 Hz, 4H), 7.08–7.21 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.47–7.57 (m, 2H), 7.62 (d, *J* = 8.2 Hz, 1H), 7.83–7.88 (m, 1H), 8.27 (d, *J* = 8.1 Hz, 1H); MS (EI): *m/z* 213 (M<sup>+</sup>). CAS Number: 98223-72-4.

***N*-(1-Naphthyl)piperidine**<sup>14</sup> (Table 2, entry 16). According to General Procedure A, 1-naphthyl tosylate (298 mg, 1mmol) and piperidine (128 mg, 1.5 mmol) were transformed into the product as a colorless liquid (120 mg, 57%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.48–1.78 (m, 2H), 1.79–1.93 (m, 4H), 2.80–3.30 (m, 4H), 7.04 (d, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.40–7.53 (m, 3H), 7.80 (d, *J* = 7.7 Hz, 1H), 8.20 (d, *J* = 7.8 Hz, 1H); MS (EI): *m/z* 211 (M<sup>+</sup>). CAS Number: 62062-39-9.

***N*-(1-Naphthyl)pyrrolidine**<sup>12</sup> (Table 2, entry 17). According to General Procedure A, 1-naphthyl tosylate (298 mg, 1mmol) and pyrrolidine (107 mg, 1.5 mmol) were transformed into the product as a colorless

liquid (89 mg, 45%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz): δ 1.98–2.12 (m, 4H), 3.32–3.50 (m, 4H), 7.02 (d, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.44–7.55 (m, 3H), 7.83–7.92 (m, 1H), 8.24–8.32 (m, 1H); MS (EI): *m/z* 197 (M<sup>+</sup>). CAS Number: 82238-92-4.

**Diphenylamine**<sup>15</sup> (Table 3, entry 1). According to General Procedure B, phenyl tosylate (248 mg, 1.0 mmol) and aniline (140 mg, 1.5 mmol) were transformed into the product as a pale yellow solid (115 mg, 68%): mp 48–50 °C, (lit.<sup>15</sup> mp 50–52 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 5.69 (br, 1H), 6.97 (t, *J* = 7.2 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 4H), 7.27 (t, *J* = 7.9 Hz, 4H); MS (EI): *m/z* 169 (M<sup>+</sup>). CAS Number: 122-39-4.

**(*p*-Anisyl)phenylamine**<sup>16</sup> (Table 3, entry 2). According to General Procedure B, phenyl tosylate (248 mg, 1.0 mmol) and *p*-anisidine (161 mg, 1.5 mmol) were transformed into the product as a colorless solid (126 mg, 69%): mp 101–103 °C, (lit.<sup>16</sup> mp 106 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 3.70 (s, 3H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 2H), 6.89 (d, *J* = 7.8 Hz, 2H), 7.02 (t, *J* = 7.9 Hz, 2H), 7.14 (t, *J* = 7.2 Hz, 2H), 7.79 (s, 1H); MS (EI): *m/z* 199 (M<sup>+</sup>). CAS Number: 1208-86-2.

**Phenyl(*p*-tolyl)amine**<sup>17</sup> (Table 3, entry 3). According to General Procedure B, phenyl tosylate (248 mg, 1.0 mmol) and *p*-toluidine (161 mg, 1.5 mmol) were transformed into the product as a colorless solid (84 mg, 46%): mp 85–86 °C, (lit.<sup>17</sup> mp 89 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 2.22 (s, 3H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.96 (t, *J* = 6.9 Hz, 4H), 7.04 (d, *J* = 8.3 Hz, 2H), 7.18 (t, *J* = 7.4 Hz, 2H), 7.96 (s, 1H); MS (EI): *m/z* 183 (M<sup>+</sup>). CAS Number: 620-84-8.

**Phenyl(*m*-tolyl)amine**<sup>18</sup> (Table 3, entry 4). According to General Procedure B, phenyl tosylate (248 mg, 1.0 mmol) and *m*-toluidine (161 mg, 1.5 mmol) were transformed into the product as a colorless liquid (92 mg, 50 %), (lit.<sup>18</sup> mp 30–31 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.34 (s, 3H), 5.71 (br, 1H), 6.80 (d, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.0 Hz, 1H), 6.97 (t, *J* = 7.3 Hz, 2H), 7.12 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.38 Hz, 1H), 7.27–7.33 (m, 2H); MS (EI): *m/z* 183 (M<sup>+</sup>). CAS Number: 1205-64-7.

**(2,6-Dimethylphenyl)phenylamine**<sup>19</sup> (Table 3, entry 5). According to General Procedure B, phenyl tosylate (248 mg, 1.0 mmol) and 2,6-dimethylphenylamine (182 mg, 1.5 mmol) were transformed into the product as a colorless solid (73 mg, 37%): mp 48–50 °C, (lit.<sup>19</sup> mp 53–56 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):

$\delta$  2.21 (s, 6H), 6.52 (d,  $J$  = 7.8 Hz, 2H), 6.76 (t,  $J$  = 7.6 Hz, 1H), 7.06–7.20 (m, 5H); MS (EI):  $m/z$  197 ( $M^+$ ).  
CAS Number: 4058-04-2.

**(2-Naphthyl)phenylamine**<sup>20</sup> (Table 3, entry 6). According to General Procedure B, 2-naphthyl tosylate (298 mg, 1.0 mmol) and aniline (140 mg, 1.5 mmol) were transformed into the product as a colorless solid (201 mg, 92%): mp 108–110 °C, (lit.<sup>20</sup> mp 107–108 °C). <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  7.01 (t,  $J$  = 7.3 Hz, 1H), 7.21 (d,  $J$  = 7.5 Hz, 2H), 7.25–7.32 (m, 4H), 7.38 (t,  $J$  = 7.5 Hz, 1H), 7.47 (d,  $J$  = 2.0 Hz, 1H), 7.68 (d,  $J$  = 8.1 Hz, 1H), 7.75 (d,  $J$  = 8.2 Hz, 1H), 7.78 (d,  $J$  = 8.8 Hz, 1H), 8.40 (s, 1H); MS (EI):  $m/z$  219 ( $M^+$ ). CAS Number: 73405-62-6.

**(*p*-Anisyl)(2-naphthyl)amine**<sup>21</sup> (Table 3, entry 7). According to General Procedure B, 2-naphthyl tosylate (298 mg, 1.0 mmol) and *p*-anisidine (161 mg, 1.5 mmol) were transformed into the product as a colorless solid (237 mg, 95%): mp 104–105 °C, (lit.<sup>21</sup> mp 101 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  3.79 (s, 3H), 5.75–6.20 (br, 1H), 6.88 (d,  $J$  = 8.8 Hz, 2H), 7.09 (d,  $J$  = 8.8 Hz, 1H), 7.14 (d,  $J$  = 8.8 Hz, 2H), 7.21 (d,  $J$  = 7.1 Hz, 2H), 7.34 (t,  $J$  = 7.0 Hz, 1H), 7.56 (d,  $J$  = 8.2 Hz, 1H), 7.67 (d,  $J$  = 7.9 Hz, 2H); MS (EI):  $m/z$  249 ( $M^+$ ). CAS Number: 6949-67-3.

**(2-Naphthyl)(*p*-tolyl)amine** (Table 3, entry 8). According to General Procedure B, 2-naphthyl tosylate (298 mg, 1.0 mmol) and *p*-toluidine (161 mg, 1.5 mmol) were transformed into the product as a colorless solid (193 mg, 83%): mp 101–103 °C, (lit.<sup>22</sup> mp 102–103 °C). <sup>1</sup>H NMR (DMSO- $d_6$ , 400 MHz):  $\delta$  2.26 (s, 3H), 7.08–7.13 (m, 4H), 7.18–7.24 (m, 2H), 7.33–7.37 (m, 2H), 7.63 (d,  $J$  = 8.2 Hz, 1H), 7.73 (t,  $J$  = 8.7 Hz, 2H), 8.24 (s, 1H); MS (EI):  $m/z$  233 ( $M^+$ ). CAS Number: 644-16-6.

**(2,6-Dimethylphenyl)(2-naphthyl)amine** (Table 3, entry 9). According to General Procedure B, 2-naphthyl tosylate (298 mg, 1.0 mmol) and 2,6-dimethylphenylamine (182 mg, 1.5 mmol) were transformed into the product as a colorless solid (217 mg, 88%): mp 63–65 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):  $\delta$  2.24 (s, 6H), 6.58 (s, 1H), 6.97 (d,  $J$  = 6.7 Hz, 1H), 7.10–7.20 (m, 4H), 7.32 (t,  $J$  = 7.1 Hz, 1H), 7.49 (d,  $J$  = 8.2 Hz, 1H), 7.65–7.70 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):  $\delta$  18.5, 106.4, 117.7, 122.4, 126.2, 126.5, 127.8, 128.1, 128.8, 129.3, 135.1, 136.2, 138.1, 144.0; MS (EI):  $m/z$  247 ( $M^+$ ). Anal. calcd.

for C<sub>18</sub>H<sub>17</sub>N: C, 87.41; H, 6.93; N, 5.66%; found: C, 87.25; H, 6.86; N, 5.72%.

**(2,3-Dimethylphenyl)(2-naphthyl)amine** (Table 3, entry 10). According to General Procedure B, 2-naphthyl tosylate (298 mg, 1.0 mmol) and 2,3-dimethylphenylamine (182 mg, 1.5 mmol) were transformed into the product as a colorless solid (227 mg, 92%): mp 111–113 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.22 (s, 3H), 2.35 (s, 3H), 6.90–7.00 (m, 3H), 7.03 (t, *J* = 7.7 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.43–7.55 (m, 3H), 7.85 (d, *J* = 7.4 Hz, 1H), 8.06 (br. s, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 13.9, 20.9, 110.1, 119.5, 119.6, 123.1, 125.3, 126.2, 126.4, 126.5, 127.8, 128.8, 129.2, 129.4, 134.9, 138.2, 140.7, 142.9; MS (EI): *m/z* 247 (M<sup>+</sup>). Anal. calcd. for C<sub>18</sub>H<sub>17</sub>N: C, 87.41; H, 6.93; N, 5.66%; found: C, 87.24; H, 6.93; N, 5.67%.

***N*-Methyl-*N*-(2-naphthyl)aniline**<sup>23</sup> (Table 3, entry 11). According to General Procedure B, 2-naphthyl tosylate (298 mg, 1.0 mmol) and *N*-methylaniline (161 mg, 1.5 mmol) were transformed into the product as a pale yellow liquid (121 mg, 52%), (lit.<sup>23</sup> mp 88–90 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.43 (s, 3H), 7.03 (t, *J* = 7.3 Hz, 1H), 7.12 (d, *J* = 7.9 Hz, 2H), 7.22–7.27 (m, 1H), 7.27–7.36 (m, 3H), 7.40 (m, 1H), 7.42 (t, *J* = 7.0 Hz, 1H), 7.67–7.75 (m, 3H); MS (EI): *m/z* 233 (M<sup>+</sup>). CAS Number: 6364-05-2.

**(1-Naphthyl)phenylamine**<sup>24</sup> (Table 3, entry 12). According to General Procedure B, 1-naphthyl tosylate (298 mg, 1.0 mmol) and aniline (140 mg, 1.5 mmol) were transformed into the product as a colorless solid (180 mg, 82%): mp 55–56 °C, (lit.<sup>24</sup> mp 56–57 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 6.92 (t, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 7.7 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 2H), 7.39 (d, *J* = 5.1 Hz, 2H), 7.48–7.52 (m, 2H), 7.58 (t, *J* = 4.9 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.6 Hz, 1H); MS (EI): *m/z* 219 (M<sup>+</sup>). CAS Number: 90-30-2.

**(*p*-Anisyl)(1-naphthyl)amine**<sup>25</sup> (Table 3, entry 13). According to General Procedure B, 1-naphthyl tosylate (298 mg, 1.0 mmol) and *p*-anisidine (161 mg, 1.5 mmol) were transformed into the product as a colorless solid (222 mg, 89%): mp 114–115 °C, (lit.<sup>25</sup> mp 110 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.80 (s, 3H), 6.86 (d, *J* = 8.6 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 6.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.42–7.52 (m, 3H), 7.80–7.88 (m, 1H), 8.00 (d, *J* = 8.1 Hz, 1H); MS (EI): *m/z* 249 (M<sup>+</sup>). CAS Number:

6314-38-1.

**(1-Naphthyl)(*p*-tolyl)amine** (Table 3, entry 14). According to General Procedure B, 1-naphthyl tosylate (298 mg, 1.0 mmol) and *p*-toluidine (161 mg, 1.5 mmol) were transformed into the product as a colorless solid (205 mg, 88%): mp 78–79 °C, (lit.<sup>26</sup> mp 78.5–79 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 2.07 (s, 3H), 7.10 (s, 4H), 7.19–7.25 (m, 2H), 7.28–7.37 (m, 2H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.73 (t, *J* = 8.9 Hz, 2H), 8.24 (s, 1H); MS (EI): *m/z* 233 (M<sup>+</sup>). CAS Number: 6314-38-1.

**(2,6-Dimethylphenyl)(1-naphthyl)amine**<sup>27</sup> (Table 3, entry 15). According to General Procedure B, 1-naphthyl tosylate (298 mg, 1.0 mmol) and 2,6-dimethylphenylamine (182 mg, 1.5 mmol) were transformed into the product as a colorless solid (222 mg, 90%): mp 124–125 °C, (lit.<sup>27</sup> mp 124 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.21 (s, 6H), 6.23 (d, *J* = 7.5 Hz, 1H), 7.11–7.23 (m, 4H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.48–7.55 (m, 2H), 7.84–7.87 (m, 1H), 8.05–8.10 (m, 1H); MS (EI): *m/z* 247 (M<sup>+</sup>). CAS Number: 4558-20.

**(2,3-Dimethylphenyl)(1-naphthyl)amine**<sup>27</sup> (Table 3, entry 16). According to General Procedure B, 2-naphthyl tosylate (298 mg, 1.0 mmol) and 2,3-dimethylphenylamine (182 mg, 1.5 mmol) were transformed into the product as a colorless solid (178 mg, 72%): mp 68–69 °C, (lit.<sup>27</sup> mp 58 °C). <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz): δ 2.05 (s, 3H), 2.27 (s, 3H), 6.43 (d, *J* = 7.3 Hz, 1H), 6.81 (d, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.42–7.51 (m, 2H), 7.65 (s, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 8.22 (d, *J* = 7.8 Hz, 1H); MS (EI): *m/z* 247 (M<sup>+</sup>). CAS Number: 3302724.

**4-(4-methoxyphenylamino)benzophenone** (Table 3, entry 17). According to General Procedure B except with Ni(PPh<sub>3</sub>)<sub>2</sub>(naphthyl)Cl (15 mol%)–IPr–HCl (30 mol%) in place of Ni(PPh<sub>3</sub>)<sub>2</sub>(naphthyl)Cl (5 mol%)–IPr–HCl (10 mol%), 4-benzoylphenyl tosylate (352 mg) and *p*-anisidine (161 mg, 1.5 mmol) were transformed into the product as a yellow solid (0.20 mg, 66%): mp 128–130 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 3.85 (s, 3H), 6.75–7.04 (m, 4H), 7.07–7.25 (m, 2H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.67–7.88 (m, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ 55.7, 113.2, 114.9, 124.7, 127.9, 128.2, 129.7, 131.5, 133.0, 133.3, 139.0, 150.0, 156.9, 195.2; MS (EI): *m/z* 303 (M<sup>+</sup>). Anal. calcd. for C<sub>20</sub>H<sub>17</sub>NO<sub>2</sub>: C,

79.19; H, 5.65; N, 4.62%; found: C, 78.89; H, 5.66; N, 4.70%.

**4-anilinobenzophenone**<sup>28</sup> (Table 3, entry 18). According to General Procedure B except with Ni(PPh<sub>3</sub>)<sub>2</sub>(naphthyl)Cl (15 mol%)-IPr·HCl (30 mol%) in place of Ni(PPh<sub>3</sub>)<sub>2</sub>(naphthyl)Cl (5 mol%)-IPr·HCl (10 mol%), 4-benzoylphenyl tosylate (352 mg) and aniline (140 mg, 1.5 mmol) were transformed into the product as a yellow solid (199 mg, 73%): mp 151–152 °C, (lit.<sup>28</sup> mp 152–155 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 7.04 (d, *J* = 8.7 Hz, 2H), 7.11 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 8.1 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.77 (d, *J* = 7.2 Hz, 2H), 7.80 (d, *J* = 8.7 Hz, 2H); MS (EI): *m/z* 273 (M<sup>+</sup>). CAS Number: 4058-17-7.

**4-(2,6-dimethylphenylamino)benzophenone** (Table 3, entry 19). According to General Procedure B except with Ni(PPh<sub>3</sub>)<sub>2</sub>(naphthyl)Cl (15 mol%)-IPr·HCl (30 mol%) in place of Ni(PPh<sub>3</sub>)<sub>2</sub>(naphthyl)Cl (5 mol%)-IPr·HCl (10 mol%), 4-benzoylphenyl tosylate (352 mg) and 2,6-dimethylphenylamine (182 mg, 1.5 mmol) were transformed into the product as a yellow solid (196 mg, 65%): mp 152–154 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ 2.21 (s, 6H), 6.48 (d, *J* = 8.6 Hz, 2H), 7.12–7.17 (m, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 4H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ 18.4, 77.0, 77.2, 77.4, 112.1, 127.1, 128.1, 128.8, 129.6, 131.4, 133.1, 136.6, 136.7, 139.1, 150.9, 195.3; MS (EI): *m/z* 301 (M<sup>+</sup>). Anal. calcd. for C<sub>21</sub>H<sub>19</sub>NO: C, 83.69; H, 6.35; N, 4.65%; found: C, 84.07; H, 6.23; N, 4.58%.

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