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### A novel route to the fluorinated diimines: carbon monoxide-promoted reductive homocoupling of fluorinated imidoyl iodides in the presence of a palladium catalyst

Hideki Amii, Mitsuhiro Kohda, Motoharu Seo and Kenji Uneyama\*

#### Synthesis of the fluorinated diimine 2a (0.5 mmol scale).

A two-necked flask attached a CO (1 atm) balloon was charged Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (0.025 g, 0.025 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.138 g, 1 mmol), and toluene (2 mL). Then 0.165 g (0.50 mmol) of trifluoroacetimidoyl iodide **3a** in 2 mL of toluene was added to the catalyst mixture. Subsequently, 0.05 mL of DMF was added. The reaction vessel was wrapped with aluminum foil to minimize exposure to the light. The reaction mixture was stirred at 70 °C for 7 h. The reaction was monitored by TLC. When the imidoyl iodide **3a** was consumed, the resulting suspension was filtered through a short celite column (AcOEt). After evaporation of solvent, the residue was purified by silica gel column chromatography (hexane : ether (9:1) elute) to give yellow solid of **2a** (0.064 g, 0.16 mmol, 64%): Mp 121 °C; IR (KBr) 1598, 1506 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz) δ 6.78 (s, 8 H), 3.80 (s, 6 H); <sup>19</sup>F NMR (CDCl<sub>3</sub>, 188 MHz, C<sub>6</sub>F<sub>6</sub> as an internal standard) δ 93.9 (s, 6 F); MS *m/z* 404 (M<sup>+</sup> 8), 389 (14), 202 (100), 107 (43), 77 (73). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>: C, 53.47; H, 3.49; N, 6.93. Found: C, 53.28; H, 3.34; N, 7.23.

Compound **2b**: yellow solid; Mp 103 °C; IR (KBr) 1604, 1506 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.02 (d, *J* = 8, 4 H), 6.50 (d, *J* = 8, 4 H), 2.33 (s, 6 H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ 93.9 (s, 6 F); MS *m/z* 372 (M<sup>+</sup> 10), 357 (16), 186 (59), 91 (100), 65 (44). Anal. Calcd for C<sub>18</sub>H<sub>14</sub>F<sub>6</sub>N<sub>2</sub>: C, 58.07; H, 3.79; N, 7.52. Found: C, 58.42; H, 3.89; N, 7.45.

Compound **2c**: yellow oil; IR (KBr) 1596, 1488 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.2-7.1 (m, 6 H), 6.5-6.4 (m, 4 H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ 93.9 (s, 6 F); MS *m/z* 344 (M<sup>+</sup> 100), 172 (95), 77 (93). Anal. Calcd for C<sub>16</sub>H<sub>10</sub>F<sub>6</sub>N<sub>2</sub>: C, 55.82; H, 2.93; N, 8.14. Found: C, 55.48; H, 2.76; N, 8.35.

Compound **2d**: yellow solid; Mp 121 °C; IR (KBr) 1486 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.22 (d, *J* = 9, 4 H), 6.44 (d, *J* = 9, 4 H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ 93.8 (s, 6 F); MS *m/z* 412 (M<sup>+</sup> 28), 377 (20), 206 (100), 111 (90), 75 (46). Anal. Calcd for C<sub>16</sub>H<sub>8</sub>Cl<sub>2</sub>F<sub>6</sub>N<sub>2</sub>: C, 46.51; H, 1.95; N, 6.78. Found: C, 46.70; H, 1.90; N, 6.71.

Compound **2e**: red oil; IR (neat) 1680, 1596 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 6.9-7.0 (brs, 6 H), 2.10 (brs, 6H), 1.56 (brs, 6 H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ 95.7 (s, 3 F), 93.5 (s, 3 F); MS *m/z* 400 (M<sup>+</sup> 2), 385 (43), 200 (100), 131 (65), 105 (90), 77 (76). Anal. Calcd for C<sub>20</sub>H<sub>18</sub>F<sub>6</sub>N<sub>2</sub>: C, 60.00; H, 4.53; N, 7.00. Found: C, 60.01; H, 4.87; N, 6.79.

Compound **2f**: red oil; IR (neat) 1684 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.2-6.9 (brs, 6 H), 2.9-2.6 (brs, 4 H), 1.3-0.8 (brs, 24 H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ 98-97 (brs, 3 F), 95-94 (brs, 3 F); MS *m/z* 512 (M<sup>+</sup> 1), 469 (15), 256 (100), 214 (33). Anal. Calcd for C<sub>28</sub>H<sub>34</sub>F<sub>6</sub>N<sub>2</sub>: C, 65.61; H, 6.69; N, 5.47. Found: C, 65.70; H, 7.08; N, 5.73.

Compound **2g**: yellow solid; Mp 115 °C; IR (KBr) 1592, 1508 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.4-7.1 (m, 8 H), 7.0-6.9 (m, 2 H), 6.8-6.6 (m, 4 H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ 94.1 (s, 6 F); MS *m/z* 444 (M<sup>+</sup> 75), 375 (66), 222 (57), 202 (94), 127 (100). Anal. Calcd for C<sub>24</sub>H<sub>14</sub>F<sub>6</sub>N<sub>2</sub>: C, 64.87; H, 3.18; N, 6.30. Found: C, 64.61; H, 3.11; N, 6.27.

Compound **2h**: yellow solid; Mp 70 °C; IR (KBr) 1596, 1506 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 7.05 (d, *J* = 9, 4 H), 6.85 (d, *J* = 9, 4 H), 3.83 (s, 6 H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ 81.7 (t, *J* = 21, 6 F), 60-58 (m, 2 F), 49-46 (m, 2 F), 37.7 (t, *J* = 6, 4 F); MS *m/z* 604 (M<sup>+</sup> 2), 302 (100), 92 (38), 77 (67). Anal. Calcd for C<sub>22</sub>H<sub>14</sub>F<sub>14</sub>N<sub>2</sub>O<sub>2</sub>: C, 43.72; H, 2.33; N, 4.64. Found: C, 43.55; H, 2.48; N, 4.27.

Compound **2i**: as a mixture of *E/E*, *Z/Z* or *E/Z* diastereomers. A diastereomer ratio of 9:2 was determined by comparing the intensities of the indicated <sup>19</sup>H NMR peaks (\* = major isomer; \*\* = minor isomer); [α]<sub>D</sub><sup>23</sup> -4.37 (*c* 0.79, CHCl<sub>3</sub>); IR (neat) 1660 cm<sup>-1</sup>; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>) δ 6.8-7.4 (m, 10 H), \*\*4.57 (q, *J* = 6, 2 H), \*4.19 (q, *J* = 6, 2 H), \*\*1.63 (d, *J* = 6, 6 H), \*1.39 (d, *J* = 6, 6 H); <sup>19</sup>F NMR (188 MHz, CDCl<sub>3</sub>) δ \*\*92.0 (s, 6 F), \*91.9 (s, 6 F); MS *m/z* 400 (M<sup>+</sup> 1), 295 (15), 281 (12), 105 (100). Anal. Calcd for C<sub>20</sub>H<sub>18</sub>F<sub>6</sub>N<sub>2</sub>: C, 60.00; H, 4.53; N, 7.00. Found: C, 60.28; H, 4.32; N, 6.85.

#### Synthesis of the fluorinated diimine **2a** (10 mmol scale).

A two-necked flask attached a CO (1 atm) balloon was charged Pd<sub>2</sub>(dba)<sub>3</sub>•CHCl<sub>3</sub> (0.522 g, 0.506 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.81 g, 20.3 mmol), and toluene (10 mL). Then 3.31 g (10.1 mmol) of trifluoroacetimidoyl iodide **3a** in 10 mL of toluene was added to the catalyst mixture. Subsequently, 1.0 mL of DMF was added. The reaction vessel was wrapped with aluminum foil to minimize exposure to the light. The reaction mixture was stirred at 70 °C overnight. When the imidoyl iodide **3a** was consumed, the resulting suspension was filtered through a short celite column (AcOEt). After evaporation of solvent, the residue was purified by silica gel column chromatography (hexane : ether (9:1) elute) to give yellow solid of **2a** (1.29 g, 3.19 mmol, 63%).