

## **SUPPORTING INFORMATION**

# ***ortho*-Arylation of Benzamides**

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## Experimental Section

**General considerations.** The coupling reactions were performed without special precautions in 2-dram screw-cap vials. Flash chromatography was performed on 60 Å silica gel (Sorbent Technologies). GC analyses were performed on a Shimadzu GC-2010 chromatograph equipped with a Restek column (Rtx®-5, 15 m, 0.25 mm ID). The <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a GE QE-300 spectrometer using TMS or solvent peak as a standard. Melting points were measured on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab Inc. of Norcross, GA. IR-spectra were obtained using a ThermoNicolet Avatar 370 FT-IR instrument. Chemicals were used as received. 4-Iodoacetophenone and 4-ethyl iodobenzoate were purchased from Acros. 3-Iodobenzotrifluoride, 4-*t*-butyliodobenzene, 3,5-bis(trifluoromethyl)-iodobenzene, 4-chloroiodobenzene, 3-trifluoromethoxyiodobenzene and 4-bromoiodobenzene were purchased from Oakwood. Starting amides are known: 3,4-dimethylbenzoic acid isopropylamide,<sup>1</sup> 3-bromobenzoic acid isopropylamide,<sup>2</sup> 2-chlorobenzoic acid isopropylamide,<sup>3</sup> 2-naphthoic acid isopropylamide,<sup>4</sup> benzoic acid isopropylamide,<sup>5</sup> *p*-toluic acid isopropylamide.<sup>5</sup>

### *Silver Acetate Preparation.*

An aqueous solution of silver nitrate (6M) was added to an aqueous solution of sodium acetate (1M; 10% excess). Resulting mixture was stirred at room temperature for 40 minutes. Precipitate was filtered and washed with water, methanol and ether to give a

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<sup>1</sup> O'Connor, C. J.; Martin, R. W.; Calvert, D. J. *Austr. J. Chem.* **1981**, *34*, 2297.

<sup>2</sup> Ohmori, H.; Maeda, H.; Kikuoka; Maki, T.; Masui, M. *Tetrahedron* **1991**, *47*, 767.

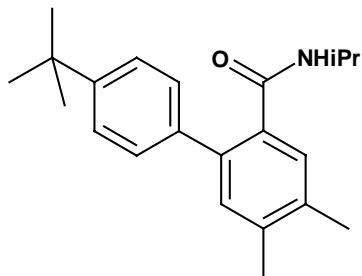
<sup>3</sup> Dong, C.-Z.; Julia, M.; Tang, J. *Eur. J. Org. Chem.* **1998**, 1689.

<sup>4</sup> Rahman, O.; Kihlberg, T.; Långström, B. *J. Org. Chem.* **2003**, *68*, 3558.

<sup>5</sup> van den Hoven, B. G.; Alper, H. *J. Am. Chem. Soc.* **2001**, *123*, 10214.

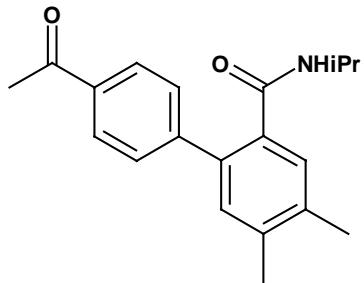
product as a white solid. Product was dried under vacuum for 5 hours. Typically, about 85% yields were obtained.

**General procedure:** A 2-dram screw-cap vial was charged with Pd(OAc)<sub>2</sub> (5 mol%), AgOAc (1.5-3 equiv), iodide (2.3-4 equiv), substrate, and TFA (0.5 mL). The resulting solution was stirred and heated at 130°C. The conversion was monitored by GC. After completion of reaction, ether was added to reaction mixture followed by filtration through a pad of Celite®. The filtrate was evaporated under reduced pressure and residue was dried under vacuum to remove solvent. The residue was purified by flash chromatography.

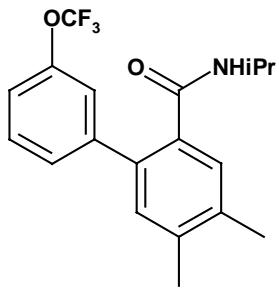


**2-(4-*t*-Butylphenyl)-4,5-dimethylbenzoic acid isopropylamide:** 3,4-Dimethylbenzoic acid isopropylamide (**1a**, 134 mg, 0.7 mmol), Pd(OAc)<sub>2</sub> (7.8 mg, 0.035 mmol), AgOAc (210 mg, 1.26 mmol), and 4-*t*-butyliodobenzene (455 mg, 1.75 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 45 min. Purification by flash chromatography (acetone/hexanes 1/8) gave 178 mg (79%) of colorless crystals, mp 138-140°C (acetone/hexanes),  $R_f$ =0.34 (EtOAc/hexanes 1/4). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.56 (s, 1H) 7.46-7.40 (m, 2H) 7.33-7.28 (m, 2H) 7.12 (s, 1H) 4.85 (br d, 1H,  $J$ =7.9 Hz) 3.98 (doublet of septets, 1H,  $J$ =7.9, 6.6 Hz) 2.32 (s, 3H) 2.31 (s, 3H) 1.35 (s, 9H)

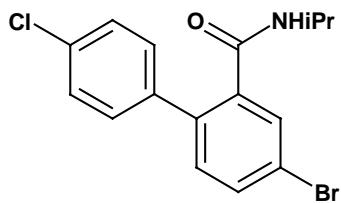
0.78 (d, 6H,  $J= 6.6$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  168.5, 151.1, 138.8, 138.1, 137.4, 136.1, 133.8, 131.5, 130.7, 128.9, 125.7, 41.7, 34.8, 31.6, 22.4, 19.6, 19.3. FT-IR (neat,  $\text{cm}^{-1}$ )  $\nu$  3252, 1629. Anal. calcd. for  $\text{C}_{22}\text{H}_{29}\text{NO}$ : C 81.69, H 9.04, N 4.33. Found: C 81.64, H 9.05, N 4.20.



**2-(4-Acetylphenyl)-4,5-dimethylbenzoic acid isopropylamide:** 3,4-Dimethylbenzoic acid isopropylamide (**1a**, 134 mg, 0.7 mmol),  $\text{Pd}(\text{OAc})_2$  (7.8 mg, 0.035 mmol),  $\text{AgOAc}$  (175 mg, 1.05 mmol), and 4-acetyliodobenzene (430 mg, 1.75 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 1 h. Purification by flash chromatography (acetone/hexanes 1/4) followed by recrystallization from  $\text{EtOAc/hexanes}$  gave 124 mg (57%) of yellow crystals, mp 171-173°C ( $\text{EtOAc/hexanes}$ ),  $R_f=0.11$  ( $\text{EtOAc/hexanes}$  1/4).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.02-7.96 (m, 2H) 7.53-7.48 (m, 2H) 7.46 (s, 1H) 7.14 (s, 1H) 4.98 (br d, 1H,  $J= 7.9$  Hz) 4.03 (doublet of septets, 1H,  $J= 7.9, 6.6$  Hz) 2.64 (s, 3H) 2.33 (s, 6H) 0.88 (d, 6H,  $J= 6.6$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  197.4, 168.5, 145.7, 139.0, 137.1, 136.6, 136.3, 134.2, 131.3, 130.2, 129.3, 128.6, 42.0, 26.6, 22.4, 19.6, 19.3. FT-IR (neat,  $\text{cm}^{-1}$ )  $\nu$  3252, 1673, 1634. Anal. calcd. for  $\text{C}_{20}\text{H}_{23}\text{NO}_2$ : C 77.64, H 7.49, N 4.53. Found: C 77.22, H 7.49, N 4.40.

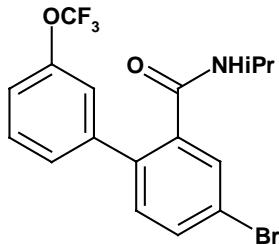


**2-(3-Trifluoromethoxyphenyl)-4,5-dimethylbenzoic acid isopropylamide:** 3,4-Dimethylbenzoic acid isopropylamide (**1a**, 134 mg, 0.7 mmol), Pd(OAc)<sub>2</sub> (7.8 mg, 0.035 mmol), AgOAc (175 mg, 1.05 mmol), and 3-trifluoromethoxyiodobenzene (463 mg, 1.61 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 1 h. Purification by flash chromatography (acetone/hexanes from 1/10 to 1/8) gave 237 mg (96%) of colorless crystals, mp 102-103°C (acetone/hexanes),  $R_f$ =0.25 (acetone/hexanes 1/4). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.47 (s, 1H) 7.46-7.39 (m, 1H) 7.35-7.30 (m, 1H) 7.28-7.19 (m, 2H) 7.11 (s, 1H) 4.92 (br d, 1H,  $J$ = 7.9 Hz) 4.01 (doublet of septets, 1H,  $J$ = 7.9, 6.5 Hz) 2.32 (s, 6H) 0.87 (d, 6H,  $J$ = 6.5 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  168.4, 149.5, 142.7, 139.1, 137.1, 135.5, 133.8, 131.2, 130.1, 130.0, 127.5, 121.4, 120.6 (q,  $J_{C-F}$ = 259.4 Hz), 119.9, 41.8, 22.3, 19.8, 19.5. FT-IR (neat, cm<sup>-1</sup>)  $\nu$  3301, 1637. Anal. calcd. for C<sub>19</sub>H<sub>20</sub>F<sub>3</sub>NO<sub>2</sub>: C 64.95, H 5.74, N 3.99. Found: C 64.85, H 5.67, N 3.97.



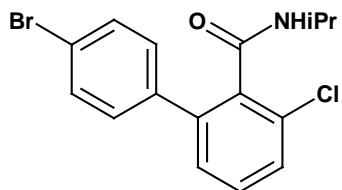
**5-Bromo-2-(4-chlorophenyl)-benzoic acid isopropylamide:** 3-Bromobenzoic acid isopropylamide (**1b**, 169 mg, 0.7 mmol), Pd(OAc)<sub>2</sub> (7.8 mg, 0.035 mmol), AgOAc (175 mg, 1.05 mmol), and 4-chloroiodobenzene (417 mg, 1.75 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 2.5 h. Purification by flash chromatography

(acetone/hexanes 1/6) following by recrystallization from EtOAc/hexanes gave 194 mg (79%) of white crystals, mp 173-174°C (EtOAc/hexanes),  $R_f$ =0.35 (EtOAc/hexanes 1/4).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.78 (d, 1H,  $J$ = 2.0 Hz) 7.59 (dd, 1H,  $J$ = 8.3, 2.0 Hz) 7.42-7.38 (m, 2H) 7.36-7.30 (m, 2H) 7.20 (d, 1H,  $J$ = 8.3 Hz) 5.03 (br d, 1H,  $J$ = 7.9 Hz) 4.03 (doublet of septets, 1H,  $J$ = 7.9, 6.7 Hz) 0.93 (d, 6H,  $J$ = 6.7 Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  166.8, 138.4, 138.1, 137.4, 134.7, 133.2, 131.9, 131.7, 130.2, 129.1, 122.3, 42.2, 22.4. FT-IR (neat,  $\text{cm}^{-1}$ )  $\nu$  3273, 1628. Anal. calcd. for  $\text{C}_{16}\text{H}_{15}\text{BrClNO}$ : C 54.49, H 4.29, N 3.97. Found: C 54.75, H 4.31, N 3.99.

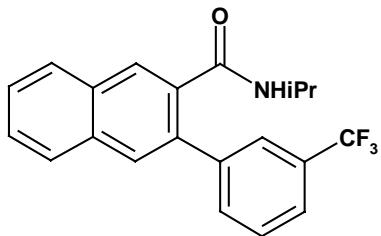


**3-Bromo-6-(3-trifluoromethoxyphenyl)-benzoic acid isopropylamide:** 3-Bromo-benzoic acid isopropylamide (**1b**, 169 mg, 0.7 mmol),  $\text{Pd}(\text{OAc})_2$  (7.8 mg, 0.035 mmol),  $\text{AgOAc}$  (210 mg, 1.26 mmol), and 3-trifluoromethoxyiodobenzene (504 mg, 1.75 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 4 h. Purification by flash chromatography (acetone/hexanes from 1/10 to 1/8) gave 236 mg (84%) of white crystalline material, mp 104-105°C (acetone/hexanes),  $R_f$ =0.26 (acetone/hexanes 1/4).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.80 (d, 1H,  $J$ = 2.2 Hz) 7.61 (dd, 1H,  $J$ = 8.3, 2.2 Hz) 7.49-7.43 (m, 1H) 7.36-7.31 (m, 1H) 7.29-7.21 (m, 3H) 5.01 (br d, 1H,  $J$ = 7.7 Hz) 4.01 (doublet of septets, 1H,  $J$ = 7.7, 6.5 Hz) 0.90 (d, 6H,  $J$ = 6.5 Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  166.8, 149.6, 141.4, 138.2, 136.9, 133.3, 131.8, 131.7, 130.4, 127.3, 122.6, 121.3, 120.6 (q,  $J_{\text{C-F}}$ = 258.7 Hz), 120.5, 42.1, 22.3. FT-IR (neat,  $\text{cm}^{-1}$ )  $\nu$  3280,

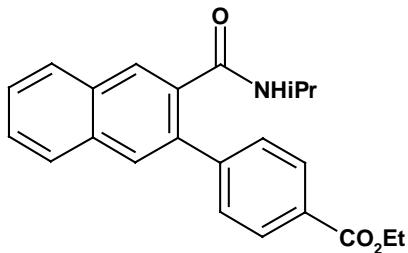
1639. Anal. calcd. for  $C_{17}H_{15}BrF_3NO_2$ : C 50.77, H 3.76, N 3.48. Found: C 50.89, H 3.69, N 3.51.



**2-Chloro-6-(4-bromophenyl)-benzoic acid isopropylamide:** 2-Chlorobenzoic acid isopropylamide (**1c**, 138 mg, 0.7 mmol),  $Pd(OAc)_2$  (7.8 mg, 0.035 mmol),  $AgOAc$  (175 mg, 1.05 mmol), and 4-bromoiodobenzene (594 mg, 2.1 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 4 h. Purification by flash chromatography (acetone/hexanes from 1/8 to 1/5) following by recrystallization from  $EtOAc/hexanes$  gave 146 mg (59%) of white crystalline material, mp 206-207°C ( $EtOAc/hexanes$ ),  $R_f=0.23$  ( $EtOAc/hexanes$  1/4).  $^1H$  NMR (300 MHz,  $CDCl_3$ , ppm)  $\delta$  7.56-7.50 (m, 2H) 7.43-7.31 (m, 4H) 7.24 (dd, 1H,  $J=7.5, 1.4$  Hz) 5.24 (br d, 1H,  $J=8.3$  Hz) 4.09 (doublet of septets, 1H,  $J=8.3, 6.6$  Hz) 0.97 (d, 6H,  $J=6.6$  Hz).  $^{13}C$  NMR (75 MHz,  $CDCl_3$ , ppm)  $\delta$  165.6, 140.6, 138.6, 136.7, 132.1, 131.7, 130.6, 130.0, 129.1, 128.3, 122.7, 42.1, 22.4. FT-IR (neat,  $cm^{-1}$ )  $\nu$  3249, 1636. Anal. calcd. for  $C_{16}H_{15}BrClNO$ : C 54.49, H 4.29, N 3.97. Found: C 54.57, H 4.29, N 4.02.

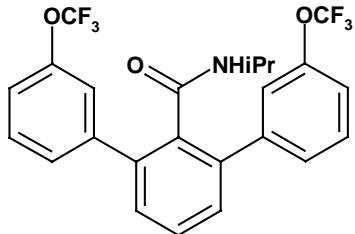


**3-(3-Trifluoromethylphenyl)-2-naphthoic acid isopropylamide:** 2-Naphthoic acid isopropylamide (**1d**, 149 mg, 0.7 mmol), Pd(OAc)<sub>2</sub> (7.8 mg, 0.035 mmol), AgOAc (175 mg, 1.05 mmol), and 3-trifluoromethyliodobenzene (476 mg, 1.75 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 0.5 h. Purification by flash chromatography (acetone/hexanes from 1/10 to 1/8) following by recrystallization from EtOAc/hexanes gave 152 mg (61%) of colorless crystals, mp 146-148°C (EtOAc/hexanes),  $R_f$ =0.21 (EtOAc/hexanes 1/4). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.17 (s, 1H) 7.95-7.85 (m, 2H) 7.83 (s, 1H) 7.79-7.64 (m, 3H) 7.62-7.53 (m, 3H) 5.23 (br d, 1H,  $J$ = 7.8 Hz) 4.10 (doublet of septets, 1H,  $J$ = 7.8, 6.7 Hz) 0.97 (d, 6H,  $J$ = 6.7 Hz). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  168.3, 141.5, 135.6, 134.4, 133.7, 132.5, 132.3, 131.1 (q,  $J_{C-F}$ = 32.4 Hz), 129.7, 129.2, 128.8, 128.4, 128.0, 127.9, 127.3, 125.7, 124.4 (q,  $J_{C-F}$ = 5.0 Hz), 124.2 (q,  $J_{C-F}$ = 272.9 Hz), 42.1, 22.4. FT-IR (neat, cm<sup>-1</sup>)  $\nu$  3301, 1637. Anal. calcd. for C<sub>21</sub>H<sub>18</sub>F<sub>3</sub>NO: C 70.58, H 5.08, N 3.92. Found: C 70.20, H 5.20, N 3.88.



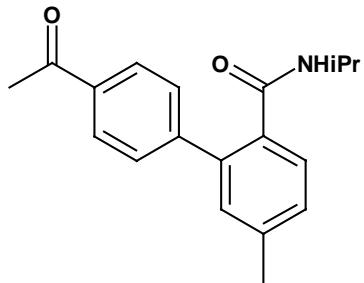
**3-(4-Ethoxycarbonylphenyl)-2-naphthoic acid isopropylamide:** 2-Naphthoic acid isopropylamide (**1d**, 149 mg, 0.7 mmol), Pd(OAc)<sub>2</sub> (7.8 mg, 0.035 mmol), AgOAc (175

mg, 1.05 mmol), and ethyl 4-iodobenzoate (444 mg, 1.61 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 0.5 h. Purification by flash chromatography (acetone/hexanes from 1/8 to 1/6) following by recrystallization from EtOAc/hexanes gave 146 mg (58%) of white crystalline material, mp 144-146°C (EtOAc/hexanes),  $R_f$ =0.14 (EtOAc/hexanes 1/4).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.20 (s, 1H) 8.15-8.11 (m, 2H) 7.95-7.86 (m, 2H) 7.85 (s, 1H) 7.62-7.53 (m, 4H) 5.16 (br d, 1H,  $J$ = 7.9 Hz) 4.42 (q, 2H,  $J$ = 7.1Hz) 4.10 (doublet of septets, 1H,  $J$ = 7.9, 6.6 Hz) 1.43 (t, 3H,  $J$ = 7.1Hz) 0.95 (d, 6H,  $J$ = 6.6 Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  168.4, 166.6, 145.2, 136.1, 134.3, 133.8, 132.3, 129.9, 129.8, 129.6, 129.1, 128.5, 128.1, 127.9, 127.3, 61.3, 42.1, 22.4, 14.5 (one carbon signal could not be detected). FT-IR (neat,  $\text{cm}^{-1}$ )  $\nu$  3302, 1716, 1638. Anal. calcd. for  $\text{C}_{23}\text{H}_{23}\text{NO}_3$ : C 76.43, H 6.41, N 3.88. Found: C 76.15, H 6.35, N 3.79.

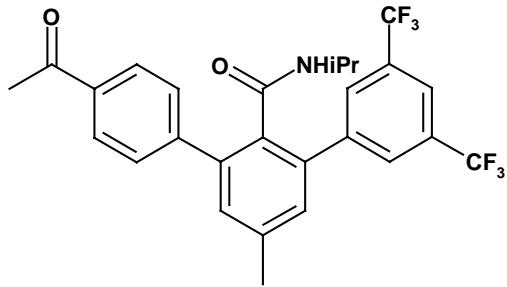


**2,6-bis-(3-Trifluoromethoxyphenyl)-benzoic acid isopropylamide:** Benzoic acid isopropylamide (**1e**, 114 mg, 0.7 mmol),  $\text{Pd}(\text{OAc})_2$  (7.8 mg, 0.035 mmol),  $\text{AgOAc}$  (350 mg, 2.1 mmol), and 3-trifluoromethoxyiodobenzene (806 mg, 2.8 mmol) were dissolved in TFA (0.5 mL). Resulting solution was heated for 5 h. Purification by flash chromatography (acetone/hexanes from 1/13 to 1/10) gave 246 mg (73%) of white crystalline material, mp 152-153°C (acetone/hexanes),  $R_f$ =0.27 (acetone/hexanes 1/4).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.54-7.48 (m, 1H) 7.45-7.39 (m, 5H) 7.37-7.33 (m, 3H) 7.26-7.20 (m, 2H) 5.08 (br d, 1H,  $J$ = 8.1 Hz) 3.81 (doublet of septets, 1H,  $J$ = 8.1, 6.6 Hz)

0.72 (d, 6H,  $J= 6.6$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  167.2, 149.3, 142.3, 138.8, 136.4, 129.9, 129.7, 129.4, 127.6, 121.5, 120.7 (q,  $J_{\text{C-F}}= 256.8$  Hz), 120.3, 41.6, 22.0. FT-IR (neat,  $\text{cm}^{-1}$ )  $\nu$  3261, 1625. Anal. calcd. for  $\text{C}_{24}\text{H}_{19}\text{F}_6\text{NO}_3$ : C 59.63, H 3.96, N 2.90. Found: C 59.33, H 3.83, N 2.89.

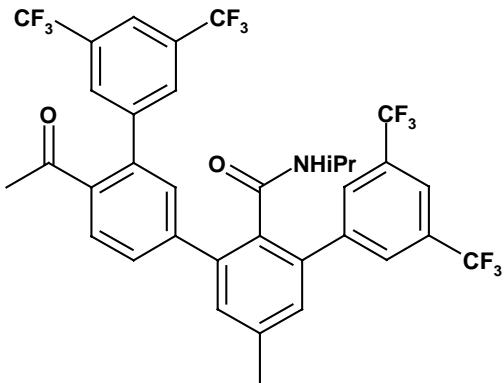


**2-(4-Acetylphenyl)-p-toluic acid isopropylamide:** p-Toluic acid isopropylamide (**1f**, 124 mg, 0.7 mmol),  $\text{Pd}(\text{OAc})_2$  (7.8 mg, 0.035 mmol),  $\text{AgOAc}$  (210 mg, 1.26 mmol), and 4-iodoacetophenone (396 mg, 1.61 mmol) were dissolved in a 4/1 mixture of  $\text{AcOH}/\text{TFA}$  (0.5 mL). Resulting solution was heated for 3.5 h. Purification by flash chromatography (acetone/hexanes from 1/8 to 1/2) gave 110 mg (53%) of colorless crystals, mp 153-154°C (acetone/hexanes),  $R_f=0.34$  (acetone/hexanes 1/2).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  8.03-7.98 (m, 2H) 7.58 (d, 1H,  $J= 7.8$  Hz) 7.54-7.50 (m, 2H) 7.28-7.23 (m, 1H) 7.17 (s, 1H) 5.00 (br d, 1H,  $J= 7.9$  Hz) 4.03 (doublet of septets, 1H,  $J= 7.9, 6.7$  Hz) 2.64 (s, 3H) 2.42 (s, 3H) 0.89 (d, 6H,  $J= 6.7$  Hz).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  197.9, 168.5, 145.6, 140.4, 138.5, 136.3, 133.7, 130.8, 129.2, 129.1, 128.9, 128.7, 41.9, 26.9, 22.4, 21.5. FT-IR (neat,  $\text{cm}^{-1}$ )  $\nu$  3243, 1683, 1629. Anal. calcd. for  $\text{C}_{19}\text{H}_{21}\text{NO}_2$ : C 77.26, H 7.17, N 4.74. Found: C 77.04, H 7.13, N 4.68.



**2-(4-Acetylphenyl)-6-(3,5-bis-trifluoromethylphenyl)-p-toluic acid isopropylamide:**

p-Toluic acid isopropylamide (**1g**, 148 mg, 0.5 mmol), Pd(OAc)<sub>2</sub> (5.6 mg, 0.025 mmol), AgOAc (125 mg, 0.75 mmol) and 3,5-bis-trifluoromethyliodobenzene (391 mg, 1.15 mmol) were dissolved in TFA (0.35 mL). Resulting solution was heated for 3 h. Purification by flash chromatography (acetone/hexanes from 1/8 to 1/4) gave 163 mg (64%) of colorless crystals, mp 261-262°C (acetone/hexanes),  $R_f$ =0.47 (acetone/hexanes 1/2). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  8.03-7.99 (m, 2H) 7.94 (br s, 2H) 7.88 (br s, 1H) 7.59-7.54 (m, 2H) 7.26 (s, 1H, partial overlap with solvent peak) 7.21 (s, 1H) 5.12 (br d, 1H,  $J$ = 7.9 Hz) 3.77 (doublet of septets, 1H,  $J$ = 7.9, 6.7 Hz) 2.64 (s, 3H) 2.47 (s, 3H) 0.71 (d, 6H,  $J$ = 6.7 Hz). <sup>13</sup>C NMR (75 MHz, acetic acid-d<sub>4</sub>, ppm)  $\delta$  200.9, 169.8, 146.1, 143.7, 141.3, 140.6, 138.7, 137.1, 133.5, 132.4 (q,  $J_{C-F}$ = 32.9 Hz), 131.5, 131.1, 130.1, 129.6, 124.5 (q,  $J_{C-F}$ = 272.9 Hz), 122.3, 42.9, 26.7, 21.6, 21.3. Signal for one carbon could not be located. FT-IR (neat, cm<sup>-1</sup>)  $\nu$  3258, 1686, 1626. Anal. calcd. for C<sub>27</sub>H<sub>23</sub>F<sub>6</sub>NO<sub>2</sub>: C 63.90, H 4.57, N 2.76. Found: C 63.78, H 4.45, N 2.74.



The diarylated product **f1** was isolated as a byproduct in the above reaction,  $R_f=0.52$  (acetone/hexanes 1/2). Yield 24 mg (7%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.93 (br s, 2H), 7.89 (br s, 2H), 7.82 (d, 1H,  $J= 8.2$  Hz), 7.74 (br s, 2H), 7.64 (dd, 1H,  $J= 8.2, 1.8$  Hz), 7.44 (d, 1H,  $J= 1.8$  Hz), 7.29 (d, 1H,  $J= 1.4$  Hz), 7.24 (d, 1H,  $J= 1.4$  Hz), 5.20 (d, 1H,  $J= 8.0$  Hz), 3.78 (doublet of septets, 1H,  $J= 8.0, 6.6$  Hz), 2.48 (s, 3H), 2.36 (s, 3H), 0.71 (d, 6H,  $J= 6.6$  Hz).

### Competition experiments:

**Experiment A:** Isopropylamide **1a** (287 mg, 1.5 mmol), **1b** (363 mg, 1.5 mmol),  $\text{Pd}(\text{OAc})_2$  (5.6 mg, 0.025 mmol),  $\text{AgOAc}$  (83 mg, 0.5 mmol) and 3-trifluoromethoxyiodobenzene (144 mg, 0.5 mmol) were dissolved in TFA (0.5 mL). Resulting mixture was heated for 2 h. After that reaction mixture was diluted to 10 mL with EtOAc and internal standard (bromobenzene) was added. Aliquot of this solution (0.1 mL) was then diluted with EtOAc to 4 mL. This solution was used to obtain ratio of products by GC. A 8.8/1 ratio of arylated **1a**/arylated **1b** was observed. Complete consumption of aryl iodide was observed. Response factors were obtained by a separate injection of a known mixture of internal standard, starting amides and products.

**Experiment B:** Isopropylamide **1a** (134 mg, 0.7 mmol), Pd(OAc)<sub>2</sub> (7.8 mg, 0.035 mmol), AgOAc (117 mg, 0.7 mmol), 4-acetyl iodobenzene (689 mg, 2.8 mmol) and 4-*t*-butyliodobenzene (728 mg, 2.8 mmol) were dissolved in TFA (0.5 mL). Resulting mixture was heated for 20 min. After that reaction mixture was diluted to 10 mL with EtOAc and internal standard (bromobenzene) was added. Aliquot of this solution (0.1 mL) was then diluted with EtOAc to 4 mL volume. This solution was used to obtain ratio of products by GC. A 2/1 ratio of 4-*t*-butylphenylated **1a**/4-acetylphenylated **1a** was observed. About 66% conversion (based on **1a**) was observed. Response factors were obtained by a separate injection of a known mixture of internal standard, starting amides and products.

