

# Oxidative *para*-Triflation of Acetanilides

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## SUPPORTING INFORMATION

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## General Considerations

PhI(OAc)<sub>2</sub>, PhI(OCOCF<sub>3</sub>)<sub>2</sub> and AgOTf were purchased from Sigma-Aldrich and Strem Chemicals, respectively, stored in a dessicator cabinet and weighed to air. AgONf was prepared according to a literature procedure,<sup>1</sup> stored in a dessicator cabinet and weighed to air. Anilines, anilides **1a** and **4b** and other reagents were purchased from Sigma-Aldrich, Alfa Aesar, Acros or TCI, and used as received. High-quality grade CHCl<sub>3</sub>, DCE, CH<sub>2</sub>Cl<sub>2</sub> and THF were purified/dried on an MBraun Solvent Purification System and stored in Schlenk flasks under argon over 3 Å molecular sieves. Analytical thin layer chromatographies (TLC) were carried out using Merck silica gel 60 F<sub>254</sub> plates and visualized under UV light (254 nm). Starting materials were purified by manual flash column chromatography with Merck Geduran Si 60 silica gel (40-63 μm). Aryltriflates and arylnonaflates were purified by automatic flash column chromatography (on an Armen Instrument Spot) with 25 g PF-30SiHP Interchim pre-packed silica gel columns.

Triflation and nonaflation reactions were performed on 0.25-0.5 mmol scale in oven-dried 4 mL screw-cap vials under argon and analyzed by GC-MS (on a Shimadzu QP-2010SE) and <sup>19</sup>F NMR in CD<sub>3</sub>OD using 4,4'-difluorobenzophenone as an internal standard (relaxation time set at 10 s).

<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra were recorded at 298K with Bruker AC-400 or DRX-250 spectrometers and referenced from TMS (in the case of <sup>1</sup>H NMR spectra run in CDCl<sub>3</sub>) or from the residual solvent signal (in other cases). Data are reported as follows: chemical shift (in ppm) [multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad), coupling constant (in Hz), integration]. HRMS (Q-TOF) were performed on a JEOL JMS-DX300 spectrometer (3 keV, xenon) in a *m*-nitrobenzylalcohol matrix. Melting points (when applicable) were carried out on a Büchi B-540 melting point apparatus.

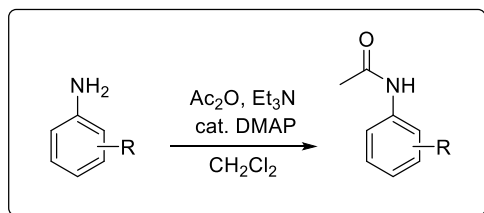
Copies of <sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F NMR spectra for aryltriflates and arylnonaflates can be found in a separate file.

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(1) Hashmi, A. S. K.; Hengst, T.; Lothschütz, C.; Rominger, F. *Adv. Synth. Catal.* **2010**, *352*, 1315-1337.

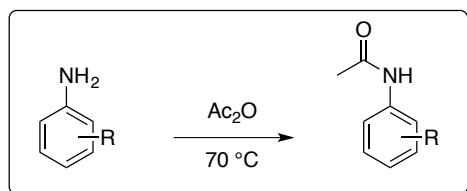
# Synthesis and Characterization of Starting Materials 1b-r and 4a,c,f

## General Procedure A

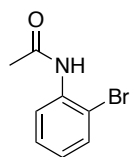


To a solution of the desired aniline (10-15 mmol scale, 1.0 equiv) and triethylamine (2.2 equiv) in CH<sub>2</sub>Cl<sub>2</sub> (0.4 M) at 0 °C under argon was added acetic anhydride (1.2 equiv) dropwise. The resulting mixture was warmed to room temperature and stirred until the reaction was judged to be complete by TLC (2-16 hours). Water was added and the crude product was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic phases were washed with saturated solutions of NaHCO<sub>3</sub> and NH<sub>4</sub>Cl, dried over MgSO<sub>4</sub> and concentrated under reduced pressure. The product was purified by silica gel flash chromatography.

## General Procedure B<sup>2</sup>



To a solution of acetic anhydride (2.0 equiv) at 0 °C under argon was added the desired aniline (10-15 mmol scale, 1.0 equiv). The resulting mixture was stirred at 70 °C until the reaction was judged to be complete by TLC (2-16 hours). The excess of acetic anhydride was evaporated under reduced pressure and the product was purified by silica gel flash chromatography.



### 2'-Bromoacetanilide (1b)

Prepared according to general procedure B, from 2-bromoaniline (36%).

Exhibited spectral data identical to a previous report.<sup>3</sup>

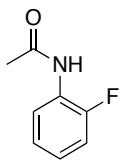
R<sub>f</sub> 0.4 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 8.31 (d, *J* = 8.0 Hz, 1H), 7.62 (br s, NH), 7.52 (dd, *J* = 8.0 and 1.3 Hz, 1H), 7.30 (ddd apparent td, *J* = 7.8 and 0.9 Hz, 1H), 6.96 (ddd apparent td, *J* = 7.7 and 1.0 Hz, 1H), 2.23 (s, 3H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.4, 135.8, 132.3, 128.5, 125.3, 122.1, 113.3, 25.0

(2) Cho, G. Y.; Rémy, P.; Jansson, J.; Moessner, C.; Bolm, C. *Org. Lett.* **2004**, *6*, 3293-3296.

(3) Schröder, N.; Wencel-Delord, J.; Glorius, F. *J. Am. Chem. Soc.* **2012**, *134*, 8298-8301.



### 2'-Fluoroacetanilide (1c)

Prepared according to general procedure A, from 2-fluoroaniline (41% yield).

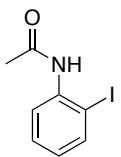
Exhibited spectral data identical to a previous report.<sup>4</sup>

$R_f$  0.4 (petroleum ether/EtOAc 70:30)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  8.29 (ddd apparent td,  $J = 8.1$  and  $1.5$  Hz, 1H), 7.42 (br s, NH), 7.14-7.01 (m, 3H), 2.22 (s, 3H)

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  -131.4

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  168.5, 152.4 (d,  $J_{CF} = 243$  Hz), 126.5 (d,  $J_{CF} = 10$  Hz), 124.7 (d,  $J_{CF} = 4$  Hz), 124.4 (d,  $J_{CF} = 8$  Hz), 121.9, 114.9 (d,  $J_{CF} = 19$  Hz), 24.8



### 2'-Iodoacetanilide (1d)

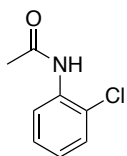
Prepared according to general procedure A, from 2-iodoaniline (88%).

Exhibited spectral data identical to a previous report.<sup>5</sup>

$R_f$  0.3 (petroleum ether/EtOAc 80:20)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  8.21 (d,  $J = 7.9$  Hz, 1H), 7.78 (dd,  $J = 7.9$  and  $1.0$  Hz, 1H), 7.42 (br s, NH), 7.35 (ddd, apparent td,  $J = 7.9$  and  $1.0$  Hz, 1H), 6.85 (dd apparent t,  $J = 7.3$  Hz, 1H), 2.25 (s, 3H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  168.4, 138.9, 138.3, 129.4, 126.1, 122.2, 90.1, 25.0



### 2'-Chloroacetanilide (1e)

Prepared according to general procedure A, from 2-chloroaniline (24% yield).

Exhibited spectral data identical to a previous report.<sup>6</sup>

$R_f$  0.4 (petroleum ether/EtOAc 70:30)

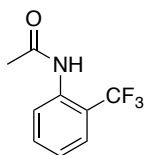
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  8.35 (dd apparent br d,  $J = 8.1$  Hz, 1H), 7.65 (br s, NH), 7.36 (dd,  $J = 8.0$  and  $1.4$  Hz, 1H), 7.26 (ddd apparent td,  $J = 7.9$  and  $1.6$  Hz, 1H), 7.03 (ddd apparent td,  $J = 7.7$  and  $1.0$  Hz, 1H), 2.24 (s, 3H)

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  168.4, 134.7, 129.1, 127.8, 124.7, 122.7, 121.8, 25.0

(4) Naik, S.; Bhattacharjya, G.; Talukdar, B.; Patel, B. K. *Eur. J. Org. Chem.* **2004**, 1254-1260.

(5) Kee, C. H.; Ariffin, A.; Awang, K.; Takeya, K.; Morita, H.; Hussain, S. I.; Chan, K. M.; Wood, P. J.; Threadgill, M. D.; Lim, C. G.; Ng, S. W.; Weber, J. F. F.; Thomas, N. F. *Org. Biomol. Chem.* **2010**, *8*, 5646-5660.

(6) Bedford, R. B.; Haddow, M. F.; Mitchell, C. J.; Webster, R. L. *Angew. Chem. Int. Ed.* **2011**, *50*, 5524-5527.



### 2'-Trifluoromethylacetanilide (1f)

Prepared according to a literature procedure,<sup>7</sup> from 2-trifluoromethylaniline (86% yield).

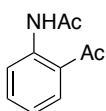
Exhibited spectral data identical to a previous report.<sup>8</sup>

**R<sub>f</sub>** 0.3 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 8.14 (d, *J* = 8.1 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.55 (dd apparent t, *J* = 7.9 Hz, 1H), 7.44 (br s, NH), 7.23 (dd apparent t, *J* = 7.6 Hz, 1H), 2.21 (s, 3H)

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)** δ -60.6

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 168.6, 135.3 (q apparent d, *J*<sub>CF</sub> = 1 Hz), 133.0, 126.1 (q, *J*<sub>CF</sub> = 5 Hz), 124.9, 124.7, 124.2 (q apparent d, *J*<sub>CF</sub> = 273 Hz), 120.4 (d, *J*<sub>CF</sub> = 30 Hz), 24.8



### 2'-Acetylacetanilide (1g)

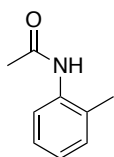
Prepared according to general procedure A, from 2-acetylaniline (66%).

Exhibited spectral data identical to a previous report.<sup>9</sup>

**R<sub>f</sub>** 0.5 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 11.70 (br s, NH), 8.74 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.55 (dd apparent t, *J* = 7.9 Hz, 1H), 7.12 (dd, apparent t, *J* = 7.6 Hz, 1H), 2.67 (s, 3H), 2.23 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 202.9, 169.5, 141.0, 135.2, 131.6, 122.3, 121.7, 120.7, 28.7, 25.6



### 2'-Methylacetanilide (1h)

Prepared according to general procedure B, from 2-methylaniline (26% yield).

Exhibited spectral data identical to a previous report.<sup>10</sup>

**R<sub>f</sub>** 0.2 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.21-7.06 (m, 4H), 2.25 (s, 3H), 2.18 (s, 3H)

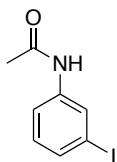
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 168.5, 135.8, 130.6, 129.6, 126.8, 125.5, 123.7, 24.4, 17.9

(7) Fifolt, M. J.; Olczak, R. T.; Mundhenke, R. F.; Bieron, J. F. *J. Org. Chem.* **1985**, *50*, 4576-4582.

(8) Strekowski, L.; Patterson, S. E.; Janda, L.; Wydra, R. L.; Harden, D. B.; Lipowska, M.; Cegla, M. T. *J. Org. Chem.* **1992**, *57*, 196-201.

(9) Tobisu, M.; Ano, Y.; Chatani, N. *Org. Lett.* **2009**, *11*, 3250-3252.

(10) Brasche, G.; García-Fortanet, J.; Buchwald, S. L. *Org. Lett.* **2008**, *10*, 2207-2210.



### 3'-Iodoacetanilide (1i)

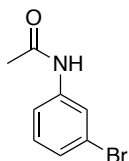
Prepared according to general procedure B, from 3-iodoaniline (55% yield).

Exhibited spectral data identical to a previous report.<sup>11</sup>

**R<sub>f</sub>** 0.2 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  7.91 (dd apparent t,  $J$  = 1.8 Hz, 1H), 7.88 (br s, NH), 7.46 (ddd,  $J$  = 8.2, 2.0 and 0.8 Hz, 1H), 7.41 (ddd apparent dt,  $J$  = 7.9 and 1.2 Hz, 1H), 7.01 (dd apparent t,  $J$  = 8.0 Hz, 1H), 2.16 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  168.9, 139.2, 133.4, 130.5, 128.8, 119.3, 94.2, 24.7



### 3'-Bromoacetanilide (1j)

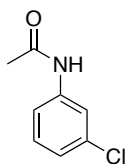
Prepared according to general procedure B, from 3-bromoaniline (59% yield)

Exhibited spectral data identical to a previous report.<sup>12</sup>

**R<sub>f</sub>** 0.25 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  7.81 (br s, NH), 7.76 (dd apparent t,  $J$  = 1.9 Hz, 1H), 7.40 (dd,  $J$  = 8.0 and 0.7 Hz, 1H), 7.22 (ddd apparent dt,  $J$  = 8.2 and 1.4 Hz, 1H), 7.15 (dd apparent t,  $J$  = 8.0 Hz, 1H), 2.17 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  168.9, 139.3, 130.4, 127.38, 123.0, 122.7, 118.5, 24.7



### 3'-Chloroacetanilide (1k)

Prepared according to general procedure B, from 3-chloroaniline (61% yield).

Exhibited spectral data identical to a previous report.<sup>13</sup>

**R<sub>f</sub>** 0.2 (petroleum ether/EtOAc 70:30)

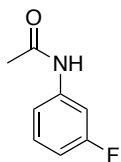
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  8.09 (br s, NH), 7.64 (dd apparent t,  $J$  = 2.0 Hz, 1H), 7.33 (ddd,  $J$  = 8.1, 2.0 and 0.9 Hz, 1H), 7.20 (dd apparent t,  $J$  = 8.1 Hz, 1H), 7.06 (ddd,  $J$  = 8.0, 2.0 and 1.0 Hz, 1H), 2.17 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  169.0, 139.2, 134.6, 130.0, 124.4, 120.2, 118.0, 24.6

(11) Heys, J. R.; Elmore C. S. *J. Label Compd. Radiopharm* **2009**, 52 189-200.

(12) Choi, H. Y.; Chi, D. Y. *J. Am. Chem. Soc.* **2001**, 123, 9202-9203.

(13) Kim, B. S.; Jang, C.; Lee, D. J.; Youn, S. W. *Chemistry - An Asian Journal* **2010**, 5, 2336-2340.



### 3'-Fluoroacetanilide (1l)

Prepared according to general procedure B, from 3-fluoroaniline (71% yield).

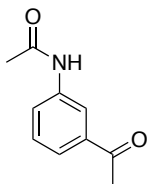
Exhibited spectral data identical to a previous report.<sup>11</sup>

**R<sub>f</sub>** 0.25 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 8.00 (br s, NH), 7.48 (ddd apparent dt, *J* = 11.0 and 2.2 Hz, 1H), 7.23 (ddd apparent td, *J* = 8.1 and 6.4 Hz, 1H), 7.14 (ddd, *J* = 8.1, 1.8 and 0.9 Hz, 1H), 6.79 (dddd apparent tdd, *J* = 8.3, 2.5 and 0.9 Hz, 1H), 2.17 (s, 3H)

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)** δ -111.5

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 169.0, 163.1 (d, *J*<sub>CF</sub> = 245 Hz), 139.6 (d, *J*<sub>CF</sub> = 11 Hz), 130.1 (d, *J*<sub>CF</sub> = 9 Hz), 115.3 (d, *J*<sub>CF</sub> = 3 Hz), 111.1 (d, *J*<sub>CF</sub> = 21 Hz), 107.5 (d, *J*<sub>CF</sub> = 26 Hz), 24.6



### 3'-Acetylacetanilide (1m)

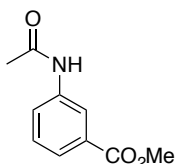
Prepared according to general procedure B, from 3-acetylaniline (72% yield).

Exhibited spectral data identical to a previous report.<sup>14</sup>

**R<sub>f</sub>** 0.1 (petroleum ether/ EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 8.17 (br s, NH), 8.03 (dd apparent t, *J* = 1.9 Hz, 1H), 7.97 (ddd, *J* = 8.1, 2.2 and 0.9 Hz, 1H), 7.67 (ddd, *J* = 7.8, 1.5 and 1.1 Hz, 1H), 7.41 (dd apparent t, *J* = 7.9 Hz, 1H), 2.59 (s, 3H), 2.21 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 198.4, 169.1, 138.8, 137.7, 129.5, 124.8, 124.3, 119.3, 26.9, 24.7



### Methyl 3-acetamidobenzoate (1n)

Prepared according to general procedure B, from methyl 3-aminobenzoate (76%).

Exhibited spectral data identical to a previous report.<sup>15</sup>

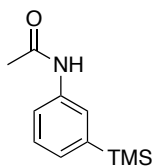
**R<sub>f</sub>** 0.15 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 8.05 (br s, NH), 8.05 (dd apparent t, *J* = 1.8 Hz, 1H), 7.89 (ddd, *J* = 8.1, 2.1 and 0.9 Hz, 1H), 7.75 (ddd apparent dt, *J* = 7.8 and 1.2 Hz, 1H), 7.36 (dd apparent t, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 2.19 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 169.0, 166.9, 138.4, 130.8, 129.2, 125.3, 124.6, 120.9, 52.4, 24.6

(14) Shaikh, A. C.; Chen, C. *J. Label Compd. Radiopharm* **2008**, *51*, 72–76.

(15) Stuart, D. R.; Alsabeh, P.; Kuhn, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 18326-18339.



### 3'-(Trimethylsilyl)acetanilide (1o)

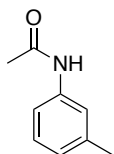
Prepared according to literature procedures,<sup>16,17</sup> from 3-chloroaniline (30%, 2 steps).

Exhibited spectral data identical to a previous report.<sup>17</sup>

**R<sub>f</sub>** 0.2 (petroleum ether/EtOAc 80:20)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  7.63 (ddd,  $J$  = 7.9, 2.2 and 1.3 Hz, 1H), 7.49 (dd apparent br d,  $J$  = 1.9 Hz, 1H), 7.40 (br s, NH), 7.31 (dd apparent t,  $J$  = 7.6 Hz, 1H), 7.25 (d,  $J$  = 7.2 Hz, 1H), 2.17 (s, 3H), 0.25 (s, 9H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  168.5, 141.7, 137.4, 129.4, 128.6, 124.6, 120.8, 24.7, -1.1



### 3'-Methylacetanilide (1p)

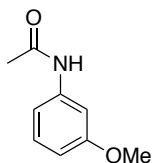
Prepared according to general procedure A, from 3-methylaniline (95%).

Exhibited spectral data identical to a previous report.<sup>18</sup>

**R<sub>f</sub>** 0.2 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  7.61 (br s, NH), 7.36 (s, 1H), 7.28 (d,  $J$  = 8.5 Hz, 1H), 7.18 (dd apparent t,  $J$  = 7.8 Hz, 1H), 6.91 (dd,  $J$  = 7.5 and 0.3 Hz, 1H), 2.31 (s, 3H), 2.15 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  168.7, 138.9, 137.9, 128.9, 125.2, 120.7, 117.1, 24.7, 21.6



### 3'-Methoxyacetanilide (1q)

Prepared according to general procedure A, from 3-methoxyaniline (76%).

Exhibited spectral data identical to a previous report.<sup>19</sup>

**R<sub>f</sub>** 0.25 (petroleum ether/EtOAc 60:40)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  7.85 (br s, NH), 7.27 (dd apparent t,  $J$  = 2.2 Hz, 1H), 7.18 (dd apparent t,  $J$  = 8.1 Hz, 1H), 6.99 (dd,  $J$  = 8.0 and 1.1 Hz, 1H), 6.64 (ddd,  $J$  = 8.3, 2.5 and 0.7 Hz, 1H), 3.76 (s, 3H), 2.14 (s, 3H)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  168.9, 160.1, 139.3, 129.7, 112.2, 110.0, 105.8, 55.3, 24.7

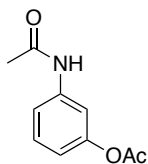
(16) McNeill, E.; Barder, T. E.; Buchwald, S. L. *Org. Lett.* **2007**, *9*, 3785-3788.

(17) Félix, G.; Dunoguès, J.; Calas, R. *Angew. Chem.* **1979**, *91*, 430-432.

(18) Taylor, J. E.; Jones, M. D.; Williams, J. M. J.; Bull, S. D. *J. Org. Chem.* **2012**, *77*, 2808-2018.

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### 3-Acetamidophenyl acetate (1r)

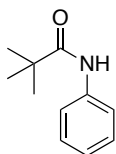
Prepared according to a literature procedure,<sup>20</sup> from 3-aminophenol (98%).

Exhibited spectral data identical to a previous report.<sup>21</sup>

$R_f$  0.3 (CH<sub>2</sub>Cl<sub>2</sub>/MeOH 97:3)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  7.77 (br s, NH), 7.47 (dd, apparent t,  $J$  = 2.1 Hz, 1H), 7.25 (dd apparent t,  $J$  = 8.1 Hz, 1H), 7.13 (ddd,  $J$  = 8.1, 2.0 and 0.9 Hz, 1H), 6.79 (ddd,  $J$  = 8.1, 2.2 and 0.9 Hz, 1H), 2.30 (s, 3H), 2.07 (s, 3H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  170.1, 168.8, 151.0, 139.4, 129.6, 117.1, 113.4, 24.6, 21.3



### N-Pivaloylaniline (4a)

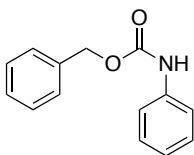
Prepared according to general procedure A (using pivaloyl chloride instead of acetic anhydride), from aniline (83%).

Exhibited spectral data identical to a previous report.<sup>22</sup>

$R_f$  0.4 (petroleum ether/EtOAc 90:10)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  7.53 (dd,  $J$  = 8.6 and 1.1 Hz, 2H), 7.32 (br s, NH), 7.32 (dd,  $J$  = 8.5 and 7.5 Hz, 2H), 7.10 (tt,  $J$  = 7.4 and 1.0 Hz, 1H), 1.32 (s, 9H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)  $\delta$  176.7, 138.1, 129.1, 124.3, 120.0, 39.7, 27.8



### Benzyl phenylcarbamate (4c)

Prepared according to a literature procedure,<sup>23</sup> from aniline (82%).

Exhibited spectral data identical to a previous report.<sup>24</sup>

$R_f$  0.6 (petroleum ether/EtOAc 90:10)

<sup>1</sup>H NMR (400 MHz; CDCl<sub>3</sub>)  $\delta$  7.42-7.33 (m, 7H), 7.32-7.27 (m, 2H), 7.06 (ddt,  $J$  = 7.5, 7.2 and 1.2 Hz, 1H), 6.67 (br s, NH), 5.20 (s, 2H)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  153.4, 137.9, 136.1, 129.2, 128.7, 128.48, 128.44, 123.6, 118.8, 67.1

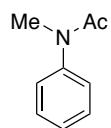
(20) Guckian, K. M.; Caldwell, R. D.; Kumaravel, G.; Lee, W.-C.; Lin, E. Y.-S.; Liu, X.; Ma, B.; Scott, D. M.; Shi, Z.; Zheng, G. Z.; Taveras, A. G.; Thomas, J. WO 2010/051031 Patent, 2010.

(21) Ishikawa, T.; Arai, M.; Nishiuchi, H.; Ishiguro, H.; Saito, S.; *Chem. Lett.* **2008**, *37*, 1066-1067.

(22) Ma, F.; Xie, X.; Zhang, L.; Peng, Z.; Ding, L.; Fu, L.; Zhang, Z. *J. Org. Chem.* **2012**, *77*, 5279-5285.

(23) Wipf, P.; Maciejewski, J. P. *Org. Lett.* **2008**, *10*, 4383-4386.

(24) Lebel, H.; Leogane, O.; *Org. Lett.* **2006**, *8*, 5717-5720.



**N-Methylacetanilide (4f)**

Prepared according to a literature procedure,<sup>25</sup> from acetanilide (25%).

Exhibited spectral data identical to a previous report.<sup>25</sup>

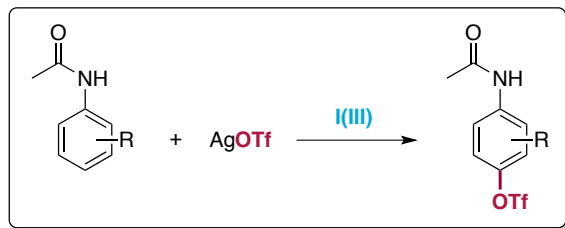
**R<sub>f</sub>** 0.3 (petroleum ether/EtOAc 60:40)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  7.42 (t,  $J$  = 7.5 Hz, 2H), 7.34 (t,  $J$  = 7.4 Hz, 1H), 7.19 (d,  $J$  = 7.1 Hz, 2H), 3.27 (s, 3H), 1.87 (s, 3H)

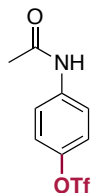
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  170.7, 144.7, 129.8, 127.8, 127.2, 37.3, 22.6

# Synthesis and Characterization of Aryltriflates 2a-r

## General Procedure C



To a solution of acetanilide **1** (0.5 mmol, 1.0 equiv) and AgOTf (or AgONf) (0.6 mmol, 1.2 equiv) in DCE (4 mL, 0.125 M) in a 4 mL screw-cap vial under argon is added [bis(trifluoroacetoxy)iodo]benzene (BTI) (0.75 mmol, 1.5 equiv). The resulting mixture is stirred for 1 hour at 20 °C or 50 °C then filtered over a short plug of Celite<sup>®</sup> and concentrated under reduced pressure. The crude product is purified by silica gel flash chromatography.



### 4-acetamidophenyl trifluoromethanesulfonate (**2a**)

Prepared according to general procedure C (20 °C), from acetanilide **1a** (66%, white powder). Exhibited spectral data identical to a previous report.<sup>26</sup>

#### Large-scale procedure

To a solution of acetanilide **1a** (676 mg, 5.00 mmol, 1.00 equiv) and AgOTf (1.54 g, 6.00 mmol, 1.20 equiv) in DCE (40 mL, 0.125 M) in a Schlenk flask under argon is added [bis(trifluoroacetoxy)iodo]benzene (BTI) (3.22 g, 7.20 mmol, 1.50 equiv). The resulting mixture is stirred for 1 hour at 20 °C. Water is then added and the crude product is extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with a saturated solution of NaCl, dried with MgSO<sub>4</sub> and concentrated under reduced pressure. The crude product is purified by silica gel flash chromatography to afford 793 mg of aryltriflate **2a** (56%) as a white powder.

mp 138-140 °C

R<sub>f</sub> 0.25 (petroleum ether/EtOAc 75:25)

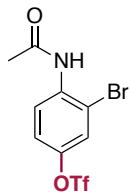
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.60 (d, *J* = 9.1 Hz, 2H), 7.35 (br s, NH), 7.23 (d, *J* = 9.1 Hz, 2H), 2.20 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -72.7

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.6, 145.4, 138.1, 122.1, 121.2, 118.9 (q, *J*<sub>CF</sub> = 321 Hz), 24.7

HRMS Calculated for C<sub>9</sub>H<sub>8</sub>F<sub>3</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 284.0199, found 284.0190

(26) Kale, A. P.; Pawar, G. G.; Kapur, M. *Org. Lett.* **2012**, *14*, 1808–1811.



#### 4-acetamido-3-bromophenyl trifluoromethanesulfonate (2b)

Prepared according to general procedure C (20 °C), from acetanilide **1b** (71%, white powder).

Exhibited spectral data identical to a previous report.<sup>27</sup>

**mp** 91-92 °C

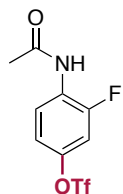
**R<sub>f</sub>** 0.15 (petroleum ether/EtOAc 90:10)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 8.51 (d, *J* = 9.2 Hz, 1H), 7.63 (br s, NH), 7.50 (d, *J* = 2.8 Hz, 1H), 7.26 (dd, *J* = 9.2 and 2.8 Hz, 1H), 2.26 (s, 3H)

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)** δ -72.6

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 168.5, 144.5, 136.2, 125.3, 122.4, 121.5, 118.7 (q, *J*<sub>CF</sub> = 321 Hz), 113.0, 25.0

**HRMS** Calculated for C<sub>9</sub>H<sub>7</sub>BrF<sub>3</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 361.9304, found 361.9295



#### 4-acetamido-3-fluorophenyl trifluoromethanesulfonate (2c)

Prepared according to general procedure C (20 °C), from acetanilide **1c** (60%, brown powder).

**mp** 127-129 °C

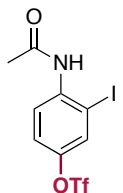
**R<sub>f</sub>** 0.3 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 8.48 (dd apparent t, *J* = 9.1 Hz, 1H), 7.39 (br s, NH), 7.11-7.07 (m, 2H), 2.25 (s, 3H)

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)** δ -72.6 (3F), -126.4 (1F)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 168.5 (d, *J*<sub>CF</sub> = 4 Hz), 151.7 (d, *J*<sub>CF</sub> = 248 Hz), 144.2 (d, *J*<sub>CF</sub> = 11 Hz), 127.0 (d, *J*<sub>CF</sub> = 10 Hz), 122.4 (d, *J*<sub>CF</sub> = 2 Hz), 118.9 (q, *J*<sub>CF</sub> = 321 Hz), 117.8 (d, *J*<sub>CF</sub> = 4 Hz), 109.5 (d, *J*<sub>CF</sub> = 24 Hz), 24.7

**HRMS** Calculated for C<sub>9</sub>H<sub>7</sub>F<sub>4</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 302.0105, found 302.0091



#### 4-acetamido-3-iodophenyl trifluoromethanesulfonate (2d)

Prepared according to general procedure C (20 °C), from acetanilide **1d** (46%, yellow powder).

**mp** 123-125 °C

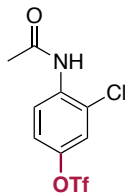
**R<sub>f</sub>** 0.3 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 8.36 (d, *J* = 9.2 Hz, 1H), 7.69 (d, *J* = 2.8 Hz, 1H), 7.48 (br s, NH), 7.29 (dd, *J* = 9.2 and 2.8 Hz, 1H), 2.26 (s, 3H)

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)** δ -72.6

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 168.5, 144.8, 138.7, 131.5, 122.3, 122.1, 118.8 (q, *J*<sub>CF</sub> = 321 Hz), 88.8, 25.0

**HRMS** Calculated for C<sub>9</sub>H<sub>7</sub>F<sub>3</sub>INO<sub>4</sub>S [M+H]<sup>+</sup> 409.9165, found 409.9157



#### 4-Acetamido-3-chlorophenyl trifluoromethanesulfonate (2e)

Prepared according to general procedure C (20 °C), from acetanilide **1e** (84%, light grey powder).

mp 77-79 °C

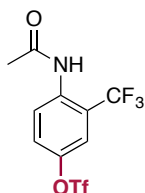
R<sub>f</sub> 0.3 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 8.54 (d, *J* = 9.3 Hz, 1H), 7.63 (br s, NH), 7.35 (d, *J* = 2.8 Hz, 1H), 7.21 (dd, *J* = 9.2 and 2.8 Hz, 1H), 2.27 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -72.6

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.5, 144.4, 135.1, 123.0, 122.36, 122.23, 121.0, 118.8 (q apparent d, *J*<sub>CF</sub> = 321 Hz), 25.1

HRMS Calculated for C<sub>9</sub>H<sub>7</sub>ClF<sub>3</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 317.9809, found 317.9815



#### 4-Acetamido-3-(trifluoromethyl)phenyl trifluoromethanesulfonate (2f)

Prepared according to general procedure C (50 °C), from acetanilide **1f** (45%, white powder).

mp 98-100 °C

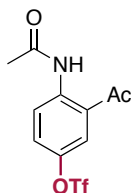
R<sub>f</sub> 0.3 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 8.42 (d, *J* = 9.1 Hz, 1H), 7.51 (d, *J* = 2.9 Hz, 1H), 7.47 (dd, *J* = 9.1 and 2.9 Hz, 1H), 7.45 (br s, NH), 2.25 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -61.2 (ArCF<sub>3</sub>), -72.5 (ArOSO<sub>2</sub>CF<sub>3</sub>)

<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>, 298 K) δ 168.5, 144.9, 135.6 (q apparent d, *J*<sub>CF</sub> = 1 Hz), 126.2, 126.0, 122.9 (q, *J*<sub>CF</sub> = 274 Hz), 121.4 (q apparent d, *J*<sub>CF</sub> = 30 Hz), 119.7 (q, *J*<sub>CF</sub> = 6 Hz), 118.8 (q, *J*<sub>CF</sub> = 321 Hz), 24.8

HRMS Calculated for C<sub>10</sub>H<sub>7</sub>F<sub>6</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 352.0073, found 352.0067



#### 4-Acetamido-3-acetylphenyl trifluoromethanesulfonate (2g)

Prepared according to general procedure C (20 °C), from acetanilide **1g** (55%, white powder).

mp 83-84 °C

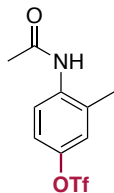
R<sub>f</sub> 0.6 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 11.66 (br s, NH), 8.90 (d, *J* = 9.4 Hz, 1H), 7.76 (d, *J* = 2.9 Hz, 1H), 7.44 (dd, *J* = 9.4 and 2.9 Hz, 1H), 2.69 (s, 3H), 2.25 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -72.5

<sup>13</sup>C NMR (63 MHz, CDCl<sub>3</sub>, 298 K) δ 201.3, 169.7, 143.2, 141.0, 127.7, 124.2, 122.6, 122.4, 118.8 (q, *J*<sub>CF</sub> = 321 Hz), 28.7, 25.6

HRMS Calculated for C<sub>11</sub>H<sub>10</sub>F<sub>3</sub>NO<sub>5</sub>S [M+H]<sup>+</sup> 326.0305, found 326.0304



#### 4-Acetamido-3-methylphenyl trifluoromethanesulfonate (2h)

Prepared according to general procedure C (20 °C), from acetanilide **1h** (28%, white powder).

mp 98-99 °C

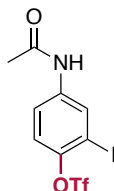
R<sub>f</sub> 0.1 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.94 (d, *J* = 9.7 Hz, 1H), 7.12-7.09 (m, 2H), 7.07 (br s, NH), 2.28 (s, 3H), 2.22 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -72.8

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.4, 145.8, 135.8, 131.1, 124.3, 123.1, 119.5, 118.7 (q, *J*<sub>CF</sub> = 321 Hz), 24.4, 17.9

HRMS Calculated for C<sub>10</sub>H<sub>10</sub>F<sub>3</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 298.0355, found 298.0348



#### 4-Acetamido-2-iodophenyl trifluoromethanesulfonate (2i)

Prepared according to general procedure C (50 °C), from acetanilide **1i** (42%, colorless oil).

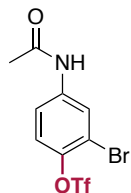
R<sub>f</sub> 0.3 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 8.11 (d, *J* = 2.6 Hz, 1H), 7.58 (dd, *J* = 9.0 and 2.6 Hz, 1H), 7.29 (br s, NH), 7.24 (d, *J* = 9.0 Hz, 1H), 2.19 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -73.1

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.7, 146.3, 138.6, 131.0, 122.2, 120.8, 118.8 (q, *J*<sub>CF</sub> = 321 Hz), 89.5, 24.7

HRMS Calculated for C<sub>9</sub>H<sub>7</sub>F<sub>3</sub>INO<sub>4</sub>S [M+H]<sup>+</sup> 409.9165, found 409.9157



#### 4-Acetamido-2-bromophenyl trifluoromethanesulfonate (2j)

Prepared according to general procedure C (50 °C), from acetanilide **1j** (50%, brown oil).

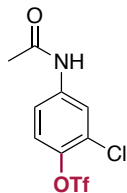
R<sub>f</sub> 0.2 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.98 (d, *J* = 2.6 Hz, 1H), 7.50 (dd, *J* = 9.0 and 2.6 Hz, 1H), 7.31 (br s, NH), 7.28 (d, *J* = 9.1 Hz, 1H), 2.20 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -73.3

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.5, 138.6, 124.8, 123.2, 119.6, 118.8 (q apparent d, *J*<sub>CF</sub> = 321 Hz), 116.5, 108.5, 24.8

HRMS Calculated for C<sub>9</sub>H<sub>7</sub>BrF<sub>3</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 361.9304, found 361.9305



#### 4-Acetamido-2-chlorophenyl trifluoromethanesulfonate (2k)

Prepared according to general procedure C (50 °C), from acetanilide **1k** (62%, yellow oil).

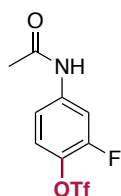
$R_f$  0.2 (petroleum ether/EtOAc 70:30)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  8.00 (br s, NH), 7.85 (d,  $J = 2.6$  Hz, 1H), 7.41 (dd,  $J = 9.0$  and 2.6 Hz, 1H), 7.25 (d,  $J = 9.3$  Hz, 1H), 2.19 (s, 3H)

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  -73.4

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  169.1, 141.5, 138.7, 127.8, 123.3, 121.9, 119.1, 118.7 (q,  $J_{CF} = 321$  Hz), 24.6

HRMS Calculated for  $\text{C}_9\text{H}_7\text{ClF}_3\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$  317.9809, found 317.9815



#### 4-Acetamido-2-fluorophenyl trifluoromethanesulfonate (2l)

Prepared according to general procedure C (50 °C), from acetanilide **1l** (58%, white powder).

mp 83-84 °C

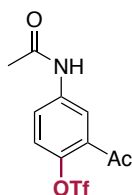
$R_f$  0.15 (petroleum ether/EtOAc 70:30)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  7.81 (br s, NH), 7.76 (dd,  $J = 11.9$  and 2.4 Hz, 1H), 7.24 (dd,  $J = 7.9$  and 7.9 Hz, 1H), 7.17 (ddd,  $J = 9.0$ , 2.4 and 1.3 Hz, 1H), 2.19 (s, 3H)

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  -73.15 (3F), -125.0 (1F)

$^{13}\text{C NMR}$  (63 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  168.9, 153.8 (d,  $J_{CF} = 252$  Hz), 139.2 (d,  $J_{CF} = 10$  Hz), 132.5 (d,  $J_{CF} = 14$  Hz), 123.7, 118.8 (q,  $J = 321$  Hz), 115.3 (d,  $J_{CF} = 3$  Hz), 109.1 (d,  $J_{CF} = 23$  Hz), 24.7

HRMS Calculated for  $\text{C}_9\text{H}_7\text{F}_4\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$  302.0105, found 302.0113



#### 4-Acetamido-2-acetylphenyl trifluoromethanesulfonate (2m)

Prepared according to general procedure C (50 °C), from acetanilide **1m** (62%, white powder).

mp 111-113 °C

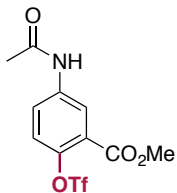
$R_f$  0.1 (petroleum ether/EtOAc 70:30)

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  8.01 (d,  $J = 2.7$  Hz, 1H), 7.77 (dd,  $J = 8.9$  and 2.8 Hz, 1H), 7.54 (br s, NH), 7.27 (d,  $J = 9.1$  Hz, 2H), 2.63 (s, 3H), 2.22 (s, 3H)

$^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  -73.2

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ , 298 K)  $\delta$  196.5, 168.6, 142.2, 138.1, 132.5, 123.9, 123.4, 121.2, 118.6 (q,  $J_{CF} = 321$  Hz), 29.5, 24.6

HRMS Calculated for  $\text{C}_{11}\text{H}_{10}\text{F}_3\text{NO}_5\text{S}$   $[\text{M}+\text{H}]^+$  326.0305, found 326.0319



#### Methyl 5-acetamido-2-((trifluoromethyl)sulfonyl)oxybenzoate (2n)

Prepared according to general procedure C (50 °C), from acetanilide **1n** (71%, grey powder).

mp 150-152 °C

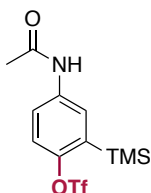
R<sub>f</sub> 0.1 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 8.05 (dd, *J* = 8.9 and 2.8 Hz, 1H), 8.00 (d, *J* = 2.8 Hz, 1H), 7.51 (s, 1H), 7.25 (d, *J* = 8.9 Hz, 1H), 3.96 (s, 3H), 2.22 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -73.4

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.7, 164.0, 143.9, 138.1, 124.99, 124.88, 123.7, 123.0, 118.8 (q apparent d, *J*<sub>CF</sub> = 321 Hz), 53.0, 24.7

HRMS Calculated for C<sub>11</sub>H<sub>10</sub>F<sub>3</sub>NO<sub>6</sub>S [M+H]<sup>+</sup> 342.0254, found 342.0261



#### 4-Acetamido-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (2o)

Prepared according to general procedure C (20 °C), from acetanilide **1o** (41%, grey powder).

mp 128-130 °C

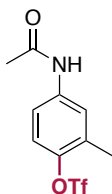
R<sub>f</sub> 0.2 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.72 (dd, *J* = 9.0 and 2.8 Hz, 1H), 7.50 (d, *J* = 2.7 Hz, 1H), 7.28 (d, *J* = 9.0 Hz, 1H), 2.20 (s, 3H), 0.36 (s, 9H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -73.9

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.3, 150.6, 136.9, 133.7, 126.7, 122.3, 120.3, 118.6 (q, *J*<sub>CF</sub> = 320 Hz), 24.6, -0.9

HRMS Calculated for C<sub>12</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>4</sub>SSi [M+H]<sup>+</sup> 356.0594, found 356.0600



#### 4-Acetamido-2-methylphenyl trifluoromethanesulfonate (2p)

Prepared according to general procedure C (20 °C), from acetanilide **1p** (26%, white powder).

mp 72-73 °C

R<sub>f</sub> 0.2 (petroleum ether/EtOAc 50:50)

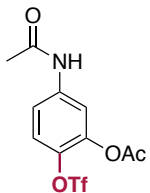
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.53 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.9 and 2.5 Hz, 1H), 7.32 (br s, NH), 7.17 (d, *J* = 8.9 Hz, 1H), 2.35 (s, 3H), 2.18 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -73.7

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.7, 144.5, 137.6, 132.0, 123.0, 122.0, 118.7, 118.7 (q apparent d, *J*<sub>CF</sub> = 321 Hz), 24.7, 16.7

HRMS Calculated for C<sub>10</sub>H<sub>10</sub>F<sub>3</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 298.0355, found 298.0362





**5-Acetamido-2-(((trifluoromethyl)sulfonyl)oxy)phenyl acetate (2r)**

Prepared according to general procedure C (20 °C), from acetanilide **1r** (64%, white powder).

**mp** 109-111 °C

**R<sub>f</sub>** 0.1 (petroleum ether/EtOAc 70:30)

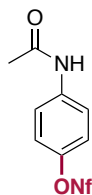
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  7.77 (d,  $J$  = 2.5 Hz, 1H), 7.61 (br s, NH), 7.16 (d,  $J$  = 9.0 Hz, 1H), 7.11 (dd,  $J$  = 9.0 and 2.5 Hz, 1H), 2.37 (s, 3H), 2.15 (s, 3H)

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  -73.7

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)**  $\delta$  168.8, 168.5, 142.5, 138.6, 136.5, 122.8, 118.7 (q apparent d,  $J_{CF}$  = 321 Hz), 117.5, 115.5, 24.7, 20.8

**HRMS** Calculated for C<sub>11</sub>H<sub>10</sub>F<sub>3</sub>NO<sub>6</sub>S [M+H]<sup>+</sup> 342.0254, found 342.0266

## Synthesis and Characterization of Arylnonaflates 3a, 3e, 3l and 3r



### 4-Acetamidophenyl nonafluorobutanesulfonate (3a)

Prepared according to general procedure C (20 °C), from acetanilide **1a** (58%, brown powder).

mp 110-112 °C

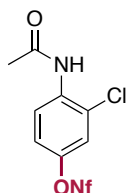
R<sub>f</sub> 0.25 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.60 (d, *J* = 9.1 Hz, 2H), 7.30 (br s, NH), 7.24 (d, *J* = 9.1 Hz, 2H), 2.20 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -80.6 (t, *J* = 10 Hz, 3F), -108.9 (t, *J* = 14 Hz, 2F), -120.9 (m, 2F), -125.8 (m, 2F)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.3, 145.5, 137.8, 122.0, 120.9, 24.6

HRMS Calculated for C<sub>12</sub>H<sub>8</sub>F<sub>9</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 434.0103, found 434.0124



### 4-Acetamido-3-chlorophenyl nonafluorobutanesulfonate (3e)

Prepared according to general procedure C (20 °C), from acetanilide **1e** (65%, light brown powder).

mp 85-87 °C

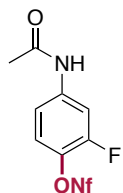
R<sub>f</sub> 0.4 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 8.55 (d, *J* = 9.2 Hz, 1H), 7.66 (br s, NH), 7.37 (d, *J* = 2.8 Hz, 1H), 7.23 (dd, *J* = 9.2 and 2.8 Hz, 1H), 2.29 (s, 3H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -80.6 (t, *J* = 10 Hz, 3F), -108.7 (t, *J* = 14 Hz, 2F), -120.9 (m, 2F), -125.8 (m, 2F)

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 168.3, 144.5, 134.9, 122.9, 122.2, 122.1, 120.8, 24.9

HRMS Calculated for C<sub>12</sub>H<sub>7</sub>ClF<sub>9</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 467.9713, found 467.9702



### N-(3-Fluoro-4-(perfluorobutoxy)phenyl)acetamide (3l)

Prepared according to general procedure C (20 °C), from acetanilide **1l** (65%, yellow powder).

mp 79-80 °C

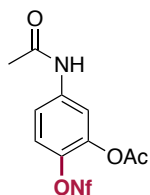
R<sub>f</sub> 0.15 (petroleum ether/EtOAc 70:30)

<sup>1</sup>H NMR (400 MHz, MeOD, 298 K) δ 7.86 (dd, *J* = 12.7, 2.3 Hz, 1H), 7.41-7.32 (m, 2H), 2.14 (s, 3H)

<sup>19</sup>F NMR (376 MHz, MeOD, 298 K) δ -82.3 (t, *J* = 10 Hz, 3F), -110.8 (t, *J* = 14 Hz, 2F), -122.0 (m, 2F), -127.1 (m, 2F), -128.0 (s, 1F)

<sup>13</sup>C NMR (100 MHz, MeOD, 298 K) δ 171.9, 154.8 (d, *J*<sub>CF</sub> = 249 Hz, 1C), 141.8 (d, *J*<sub>CF</sub> = 10 Hz, 1C), 133.4 (d, *J*<sub>CF</sub> = 14 Hz, 1C), 124.7, 116.7 (d, *J*<sub>CF</sub> = 3 Hz, 1C), 109.3 (d, *J*<sub>CF</sub> = 24 Hz, 1C), 23.9

HRMS Calculated for C<sub>12</sub>H<sub>7</sub>F<sub>10</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 452.0009, found 452.0020



**5-Acetamido-2-(perfluorobutoxy)phenyl acetate (3r)**

Prepared according to general procedure C (20 °C), from acetanilide **1r** (42%, yellow powder).

**mp** 107-108 °C

**R<sub>f</sub>** 0.1 (petroleum ether/EtOAc 70:30)

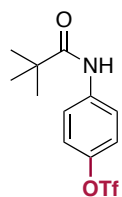
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 7.79 (d, *J* = 2.5 Hz, 1H), 7.64 (s, 1H), 7.13 (d, *J* = 9.0 Hz, 1H), 7.06 (dd, *J* = 9.0 and 2.6 Hz, 1H), 2.37 (s, 3H), 2.15 (s, 3H)

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K)** δ -80.6 (t, *J* = 10 Hz, 3F), -109.6 (t, *J* = 14 Hz, 2F), -120.8 (m, 2F), -125.9 (m, 2F)

**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K)** δ 168.8, 168.7, 142.5, 138.7, 136.5, 122.6, 117.4, 115.4, 24.7, 20.8

**HRMS** Calculated for C<sub>14</sub>H<sub>10</sub>F<sub>9</sub>NO<sub>6</sub>S [M+H]<sup>+</sup> 492.0158, found 492.0151

## Synthesis and Characterization of Aryltriflates 5a-c



### 4-Pivalamidophenyl trifluoromethanesulfonate (5a)

Prepared according to general procedure C (20 °C), from *N*-pivaloylaniline **4a** (50%, white powder).

mp 130-132 °C

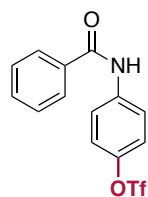
R<sub>f</sub> 0.3 (petroleum ether/EtOAc 90:10)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.63 (d, *J* = 9.1 Hz, 2H), 7.43 (br s, NH), 7.23 (d, *J* = 8.8 Hz, 2H), 1.32 (s, 9H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -72.7

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 177.0, 145.3, 138.2, 122.0, 121.4, 118.8 (q apparent d, *J*<sub>CF</sub> = 321 Hz), 39.8, 27.6

HRMS Calculated for C<sub>12</sub>H<sub>14</sub>F<sub>3</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 326.0668, found 326.0664



### 4-Benzamidophenyl trifluoromethanesulfonate (5b)

Prepared according to general procedure C (20 °C), from *N*-benzoylaniline **4b** (30%, light pink powder).

mp 180-182 °C

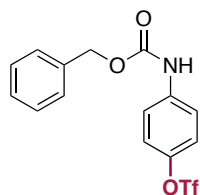
R<sub>f</sub> 0.2 (petroleum ether/EtOAc 90:10)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.92 (br s, NH), 7.87 (dd, *J* = 8.3 and 1.3 Hz, 2H), 7.77-7.74 (m, 2H), 7.59 (m, 1H), 7.51 (tt, *J* = 7.4 and 1.5 Hz, 2H), 7.30-7.28 (m, 2H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -72.7

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 165.9, 145.6, 138.1, 134.4, 132.4, 129.1, 127.2, 122.2, 121.6

HRMS Calculated for C<sub>14</sub>H<sub>10</sub>F<sub>3</sub>NO<sub>4</sub>S [M+H]<sup>+</sup> 346.0355, found 346.0356



### 4-(((Benzyloxy)carbonyl)amino)phenyl trifluoromethanesulfonate (5c)

Prepared according to modified general procedure C (using 1.5 equiv of PhI(OAc)<sub>2</sub> and 2.0 equiv of AgOTf in CHCl<sub>3</sub> at 20 °C), from benzyl phenylcarbamate **4c** (60%, light brown powder).

mp 95-97 °C

R<sub>f</sub> 0.4 (petroleum ether/EtOAc 90:10)

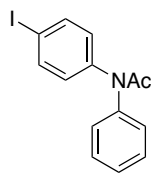
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.49 (d, *J* = 8.9 Hz, 2H), 7.43-7.36 (m, 5H), 7.24-7.22 (m, 2H), 6.83 (br s, NH), 5.23 (s, 2H)

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>, 298 K) δ -72.7

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 153.2, 145.0, 138.0, 135.8, 128.84, 128.72, 128.55, 122.2, 119.9, 118.8 (q apparent d, *J*<sub>CF</sub> = 321 Hz), 67.6

HRMS Calculated for C<sub>15</sub>H<sub>12</sub>F<sub>3</sub>NO<sub>5</sub>S [M+H]<sup>+</sup> 376.0461, found 376.0449

## Synthesis and Characterization of Diarylamide 6



### ***N*-(4-iodophenyl)-*N*-phenylacetamide (6)**

Prepared according to modified general procedure C (using HFIP instead of DCE, 20 °C), from acetanilide **1a** (21%, light brown powder).

Exhibited spectral data identical to a previous report.<sup>28</sup>

**R<sub>f</sub>** 0.4 (petroleum ether/EtOAc 70:30)

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K)** δ 7.65 (d apparent br s, 2H), 7.50-7.28 (br m, 3H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 2.05 (s, 3H)

**HRMS** Calculated for C<sub>14</sub>H<sub>12</sub>I<sup>127</sup>NO [M+H]<sup>+</sup> 338.0036, found 338.0013

<sup>28</sup> He, C.; Chen, C.; Cheng, J.; Liu, C.; Liu, W.; Li, Q.; Lei, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 6414-6417.

## Triflate Salt Solubilities (at 20 °C)

### *Procedure for the determination of the solubilities*

1 mL of a saturated solution of the triflate salt was filtered through a small piece of cotton in a pipette then evaporated and dried under reduced pressure.

Triflate Salt	Solvent	Solubility (mg.mL <sup>-1</sup> )
Cu(OTf) <sub>2</sub>	CHCl <sub>3</sub>	1.1
Zn(OTf) <sub>2</sub>	CHCl <sub>3</sub>	3.2
Fe(OTf) <sub>2</sub>	CHCl <sub>3</sub>	1.8
Ce(OTf) <sub>3</sub>	DCE	2.4
(CuOTf) <sub>2</sub> ·Tol	CHCl <sub>3</sub>	2.1
NaOTf	DCE	0.9
KOTf	DCE	6.1
AgOTf	CHCl <sub>3</sub>	4.4
AgOTf	DCE	3.1