**Supporting Information** 

# Nickel-catalyzed C–O Activation of Phenol Derivatives with Potassium Heteroaryltrifluoroborates

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#### **General Considerations**

All commercially obtained reagents were used as received. Both solvents and deionized water were degassed with N<sub>2</sub> each time prior to use. Standard benchtop techniques were employed for handling air-sensitive reagents. Melting points (°C) are uncorrected. NMR spectra were recorded on a 500, 400, or 300 MHz spectrometer. <sup>19</sup>F NMR chemical shifts were referenced to external CFCl<sub>3</sub> (0.0 ppm). <sup>11</sup>B NMR spectra were obtained on a spectrometer equipped with the appropriate decoupling accessories. All <sup>11</sup>B NMR chemical shifts were referenced to external BF<sub>3</sub>·OEt<sub>2</sub> (0.0 ppm) with a negative sign indicating an upfield shift. Data are presented as follows: chemical shift (ppm), multiplicity (*s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet, *br* = broad), coupling constant *J* (Hz) and integration. Analytical thin-layer chromatography (TLC) was performed on TLC silica gel plates (0.25 mm) precoated with a fluorescent indicator. Standard flash chromatography procedures were followed using 32–63 µm silica gel. Visualization was effected with ultraviolet light.

#### Importance of the solvent in the reaction

OPiv	+	Ni(COD) <sub>2</sub> 10 mol % PtBuCy <sub>2</sub> 20 mol % K <sub>3</sub> PO <sub>4</sub> solvent 110 °C, t c		
entry	solvent	с	t	yield <sup>a</sup>
1	$Dioxane/H_2O(1/1)$	0.05	1h	11%
2	$Dioxane/H_2O(6/1)$	0.05	1h	7%
3	$THF/H_{2}O(1/1)$	0.05	1h	/
4	EtOH	0.1	1h	/
5 <sup>b</sup>	$Tol/H_2O(1/1)$	0.05	1h	/
6 <sup>b</sup>	CPME/H <sub>2</sub> O (1/1)	0.05	1h	/
7 <sup>b</sup>	s-BuOH	0.05	1h	/
$8^{\mathrm{b}}$	<i>i</i> -PrOH	0.05	1h	/
9 <sup>b</sup>	MeOH	0.05	1h	/
10 <sup>b</sup>	t-amyl alcohol	0.05	1h	/
11	t-BuOH	0.1	1h	35%
12 <sup>b</sup>	t-BuOH	0.1	1h	29%
13 <sup>b</sup>	t-BuOH	0.05	1h	25%
14 <sup>b</sup>	<i>t</i> -BuOH/H <sub>2</sub> O (1/1)	0.05	1h	56%
15 <sup>b</sup>	t-BuOH/H <sub>2</sub> O (1/1)	0.1	1h	59%
16 <sup>b</sup>	t-BuOH/H <sub>2</sub> O (1/1)	0.2		30%

<sup>a</sup> Relative GC yield using dodecane as an internal standard

<sup>b</sup> PCy<sub>3</sub>HBF<sub>4</sub>

## General Experimental Procedure for Nickel-catalyzed C-O Activation (3-(naphthalen-1-yl)furan (2a) is used as an example)

A Biotage microwave vial was charged with  $K_3PO_4$  (1.80 mmol, 382.0 mg), potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol), **1a** (55.5 mg, 0.25 mmol) and Cy<sub>3</sub>P'HBF<sub>4</sub> (50 µmol, 18.4 mg). In the glove box, Ni(COD)<sub>2</sub> (25 µmol, 6.9 mg) was added and the test tube was sealed with a cap lined with a disposable Teflon septum. Outside of the glove box, a mixture of *t*-BuOH/H<sub>2</sub>O (1.25 mL/1.25 mL) was added under N<sub>2</sub>. The reaction mixture was heated to 110 °C for 4 h before cooling to rt. The reaction mixture was extracted with EtOAc (3 x 2 mL) and then dried (MgSO<sub>4</sub>). The solvent was removed *in vacuo*, and the crude product was purified by silica gel column chromatography (elution with hexanes/EtOAc 90:10) to yield **2a** in 93% yield (43.0 mg) as a yellow oil. <sup>1</sup>H NMR (300 MHz, acetone-*d*<sub>6</sub>)  $\delta$  8.17-8.14 (m, 1H), 7.97-7.85 (m, 3H), 7.75 (t, *J* = 1.7 Hz, 1H), 7.56-7.44 (m, 4H), 6.80 (dd, *J* = 1.7, 0.8 Hz, 1H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>)  $\delta$  144.2, 141.6, 135.0, 132.5, 131.6, 129.3, 128.6, 127.7, 127.1, 126.8, 126.4, 126.2, 125.6, 113.1; FT-IR (neat) 3047, 1510, 1500, 1260 cm<sup>-1</sup>; HRMS (ESI) *m/z* calcd. for C<sub>14</sub>H<sub>11</sub>O (M+H)<sup>+</sup> 195.0810, found 195.0806.

#### 1. Preparation of (naphthalen-1-yl)heteroaryl compounds



**3-(Naphthalen-1-yl)furan (2a).** Following the general procedure, the reaction was also carried out with **1d** (57.0 mg, 0.25 mmol) and potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain **2a** (37.7 mg, 78%) as a yellow oil after silica gel column chromatography (elution with hexanes/EtOAc 90:10).

**3-(Naphthalen-1-yl)thiophene (2b).** Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium thiophen-3-yltrifluoroborate (62.7 mg, 0.33 mmol) to obtain **2b** (47.4 mg, 90%) as a yellow oil after preparative silica gel chromatography (elution with hexanes). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ )  $\delta$  8.04-7.89 (m, 3H), 7.64 (dd, J = 4.9, 3.0 Hz, 1H); 7.56 (dd, J = 3.0, 1.3 Hz, 1H); 7.54-7.46 (m, 4H), 7.34 (dd, J = 4.9, 1.3 Hz, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  142.0, 135.8, 135.0, 132.7, 130.4, 129.3, 128.7, 127.8, 127.1, 126.8, 126.7, 126.5, 126.4, 124.5; FT-IR (neat) 3045, 1591, 1505, 1413; HRMS (ESI) *m/z* calcd. for C<sub>14</sub>H<sub>11</sub>S (M+H)<sup>+</sup> 211.0591, found 211.0581.

Following the general procedure, the reaction was also carried out with 1d (57.0 mg, 0.25 mmol) and potassium thiophen-3-yltrifluoroborate (62.7 mg, 0.33 mmol) using Cy<sub>2</sub>Pt-Bu (12.7 mg, 50  $\mu$ mol) in a mixture of dioxane/H<sub>2</sub>O (2.5 mL/2.5 mL) at 110 °C for 1 h to obtain 2b (39.6 mg, 75%) as a yellow oil after preparative silica gel chromatography (elution with hexanes).

**2-(Naphthalen-1-yl)thiophene (2c).** Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium thiophen-2-yltrifluoroborate (62.7 mg, 0.33 mmol) to obtain **2c** (33.8 mg, 64%) as a light yellow oil after silica gel chromatography (elution with hexanes). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.22-8.19 (m, 1H), 8.00-7.94 (m, 2H), 7.61 (dd, J = 5.1, 1.0 Hz, 1H); 7.60-7.52 (m, 4H), 7.30 (dd, J = 3.5, 1.0 Hz, 1H); 7.24 (dd, J = 5.1, 3.5 Hz, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  141.2, 140.0, 132.2, 131.6, 128.4, 128.3, 127.9, 127.4, 127.4, 126.5, 126.0, 125.9, 125.2, 125.2; FT-IR (neat) 3049, 1589, 1505, 1389; HRMS (ESI) *m/z* calcd. for C<sub>14</sub>H<sub>11</sub>S (M+H)<sup>+</sup> 211.0574, found 211.0581.

A Biotage microwave vial was charged with  $K_3PO_4$  (382.0 mg, 1.80 mmol), potassium thiophen-2yltrifluoroborate (62.7 mg, 0.33 mmol) and **1d** (57.0 mg, 0.25 mmol). In the glove box,  $Cy_2Pt$ -Bu (12.7 mg, 50 µmol) and Ni(COD)<sub>2</sub> (6.9 mg, 25 µmol) were added, and the test tube was sealed with a cap lined with a disposable Teflon septum. Outside of the glove box, a mixture of dioxane/H<sub>2</sub>O (2.5 mL/2.5 mL) was added under N<sub>2</sub>. The reaction mixture was heated to 110 °C for 1 h before cooling to rt. Dodecane (42.6 mg, 0.25 mmol) was added, and the mixture was filtered through a thin pad of silica with EtOAc. The filtrate was analyzed by gas chromatography using dodecane as the internal standard to afford **2c** in 26% relative yield. H<sub>2</sub>O

**3-(Naphthalen-1-yl)pyridine (2d).** Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium pyridin-3-yltrifluoroborate (61.0 mg, 0.33 mmol) to obtain **2d** (41.9 mg, 82%) as a yellow oil after silica gel chromatography (elution with hexanes/EtOAc 80:20). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ )  $\delta$  8.70-8.67 (m, 2H), 8.04-7.99 (m, 2H), 7.90 (dt, J = 7.7, 1.9 Hz, 1H); 7.79 (d, J = 8.2 Hz, 1H), 7.64-7.47 (m, 5H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  151.2, 149.6, 137.9, 137.3, 137.0, 134.9, 132.3, 129.4, 129.3, 128.3, 127.5, 127.0, 126.4, 125.9, 124.1; FT-IR (neat) 3034, 1605, 1408, 1394; HRMS (ESI) *m/z* calcd. for C<sub>15</sub>H<sub>12</sub>N (M+H)<sup>+</sup> 206.0963, found 206.0970.

Following the general procedure, the reaction was also carried out with 1d (57.0 mg, 0.25 mmol) and potassium pyridin-3-yltrifluoroborate (61.0 mg, 0.33 mmol) to obtain 2d (30.8 mg, 60%) as a yellow oil after silica gel chromatography (elution with hexanes//EtOAc 80:20).



4-(Naphthalen-1-yl)pyridine (2e). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium pyridin-4-yltrifluoroborate (61.0 mg, 0.33 mmol) to obtain 2e (35.2 mg, 69%) as a white solid after silica gel chromatography (elution with hexanes/EtOAc 80:20). mp: 93-95 °C; <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ )  $\delta$  8.74-8.72 (m, 2H), 8.03-8.00 (m, 2H), 7.84 (d, J = 8.8 Hz, 1H), 7.62-7.47 (m, 6H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  150.8, 149.1, 138.3, 134.8, 131.6, 129.7, 129.4, 127.8, 127.6,

127.0, 126.3, 125.8, 125.7; FT-IR (neat) 3059, 1588, 1410; HRMS (ESI) m/z calcd. for C<sub>15</sub>H<sub>12</sub>N (M+H)<sup>+</sup> 206.0962, found 206.0970.

A Biotage microwave vial was charged with  $K_3PO_4$  (382.0 mg, 1.80 mmol), potassium pyridin-4yltrifluoroborate (61.0 mg, 0.33 mmol), 1d (57.0 mg, 0.25 mmol) and Cy<sub>3</sub>PHBF<sub>4</sub> (18.4 mg, 50 μmol). In the glove box, Ni(COD)<sub>2</sub> (25  $\mu$ mol, 6.9 mg) was added, and the test tube was sealed with a cap lined with a disposable Teflon septum. Outside of the glove box, a mixture of t-BuOH/H<sub>2</sub>O (1.25 mL/1.25 mL) was added under N<sub>2</sub>. The reaction mixture was heated to 110 °C for 4 h before cooling to rt. Dodecane (42.6 mg, 0.25 mmol) was added and the mixture was filtered through a thin pad of silica with EtOAc. The filtrate was analyzed by gas chromatography using dodecane as the internal standard to afford 2e in 32% relative yield.

Potassium Pyrimidin-5-yltrifluoroborate. To a solution of pyrimidin-5-ylboronic acid (5.0 g, 40.0 mmol) in MeOH (11.5 mL, 3.5 M) under N<sub>2</sub> was added KHF<sub>2</sub> (9.5 g, 121.0 mmol) in one portion at 0 °C. To the suspension was added H<sub>2</sub>O dropwise (8.9 mL, 4.5 M) at 0 °C. The ice-₿F₂K water bath was removed, and the reaction was stirred at rt for 1 h. The crude mixture was concentrated and dried overnight in vacuo. The crude solid was purified using continuous Soxhlet extraction (overnight) with acetone (250 mL). The collected solvent was concentrated and then redissolved in a minimal amount of acetone (20 mL). The addition of Et<sub>2</sub>O (125 mL) led to the precipitation of the product. The product was filtered, concentrated, and dried in vacuo to afford the pure compound (3.86 g, 52%) as a white solid. mp > 250 °C. <sup>1</sup>H NMR (500 MHz, DMSO- $d_6$ )  $\delta$  8.88 (s, 1H), 8.54 (s, 2H); <sup>13</sup>C NMR (125 MHz, DMSOd<sub>6</sub>) δ 159.5, 156.5; <sup>19</sup>F NMR (470.8 MHz, DMSO-d<sub>6</sub>) δ -139.3; <sup>11</sup>B NMR (128.4 MHz, DMSO-d<sub>6</sub>) δ

1.317; FT-IR (KBr) 3036, 1582, 1570, 1441 cm<sup>-1</sup>; HRMS (ESI) m/z calcd. for C<sub>4</sub>H<sub>3</sub>BF<sub>3</sub>N<sub>2</sub><sup>-</sup> (M-K)<sup>-</sup> 147.0341, found 147.0343.

5-(Naphthalen-1-yl)pyrimidine (2f). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium pyrimidin-5-yltrifluoroborate (61.4 mg, 0.33 mmol) to obtain 2f (42.9 mg, 83%) as an orange oil after silica gel chromatography (elution with hexanes/EtOAc 80:20). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ )  $\delta$ 9.25 (s, 1H), 8.91 (s, 2H), 8.06-8.02 (m, 2H), 7.80-7.77 (s, 1H), 7.67-7.53 (m, 4H); <sup>13</sup>C NMR (125 MHz, acetone-d<sub>6</sub>) δ 158.5, 158.0, 135.1, 134.9, 133.7, 132.2, 130.1, 129.5, 128.8, 127.9, 127.2, 126.4, 125.5; FT-IR (neat) 3043, 1574, 1548, 1418, 1391; HRMS (ESI) *m/z* calcd. for C<sub>14</sub>H<sub>11</sub>N (M+H)<sup>+</sup> 207.0922, found 207.0918.

A Biotage microwave vial was charged with K<sub>3</sub>PO<sub>4</sub> (382.0 mg, 1.80 mmol), potassium pyrimidin-5yltrifluoroborate (61.4 mg, 0.33 mmol), 1d (57.0 mg, 0.25 mmol) and  $Cy_3PHBF_4$  (18.4 mg, 50  $\mu$ mol). In the glove box, Ni(COD)<sub>2</sub> (25  $\mu$ mol, 6.9 mg) was added, and the test tube was sealed with a cap lined with a disposable Teflon septum. Outside of the glove box, a mixture of t-BuOH/H<sub>2</sub>O (1.25 mL/1.25 mL) was added under N2. The reaction mixture was heated to 110 °C for 4 h before cooling to rt. Dodecane (42.6 mg, 0.25 mmol) was added and the mixture was filtered through a thin pad of silica with EtOAc. The filtrate was analyzed by gas chromatography using dodecane as the internal standard to afford 2f in 26% relative yield.

2-(Naphthalen-1-yl)furan (2g). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium furan-2-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain 2g (38.2 mg, 79%) as a brown oil after silica gel chromatography (elution with hexanes). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.42 (d, J = 8.3 Hz, 1H), 7.96 (d, J = 7.6Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.79-7.75 (m, 2H), 7.60-7.53 (m, 3H), 6.85 (d, J = 3.2 Hz, 1H), 6.67 (dd, J = 3.2, 1.7 Hz, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  154.2, 143.7, 135.0, 131.1, 129.4, 129.4, 129.4, 127.5, 126.9, 126.9, 126.3, 126.2, 112.4, 110.2; FT-IR (neat) 3043, 1509, 1238; HRMS (ESI) m/z calcd. for  $C_{14}H_{10}O(M)^+$  194.0732, found 194.0738.



3-(Naphthalen-1-yl)quinoline (2h). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium quinolin-3-yltrifluoroborate (77.6 mg, 0.33 mmol) to obtain 2h (60.6 mg, 95%) as a colorless oil after silica gel chromatography (elution with hexanes/EtOAc 80:20). <sup>1</sup>H NMR (300 MHz, acetone- $d_6$ )  $\delta$ 9.02 (d, J = 2.1 Hz, 1H), 8.39 (d, J = 2.1 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 8.04-8.01 (m, 3H), 7.86 (d, J = 8.4 Hz, 1H), 7.83-7.80 (m, 1H), 7.68-7.62 (m, 2H), 7.59 (d, J = 6.7 Hz,

1H), 7.54 (d, J = 7.8 Hz, 1H), 7.52-7.49 (m, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  152.5, 148.4, 137.3, 137.3, 136.8, 134.9, 134.5, 132.5, 130.3, 130.1, 129.4, 129.4, 129.1, 128.7, 127.8, 127.5, 127.0, 126.4, 126.0; FT-IR (neat) 3057, 1567, 1508, 1490; HRMS (ESI) m/z calcd. for  $C_{19}H_{14}N$  (M+H)<sup>+</sup> 256.1126, found 256.1115.

2-(Naphthalen-1-yl)benzothiophene (2i). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium benzothiophen-2yltrifluoroborate (79.2 mg, 0.33 mmol) to obtain 2i (27.4 mg, 42%) as a white solid after silica gel chromatography (elution with hexanes). mp: 104-106 °C; <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.31-8.27 (m, 1H), 8.03-7.90 (m, 3H), 7.94 (dd, J = 7.3, 1.7 Hz, 1H), 7.70 (dd, J = 7.1, 1.2 Hz, 1H), 7.61-7.54 (m, 4H), 7.45 (td, J = 7.1, 1.2 Hz, 1H), 7.41 (td, J = 7.1, 1.5 Hz, 1H);<sup>13</sup>C NMR (125 MHz, acetone- $d_6$ ) δ 142.6, 141.3, 141.0, 135.0, 133.1, 132.5, 129.9, 129.4, 129.3, 127.7, 127.2, 126.2, 126.2, 125.5, 125.4, 125.2, 124.7, 122.9; FT-IR (neat) 3052, 1504, 1455, 1435, 1390; HRMS (ESI) m/z calcd. for C<sub>18</sub>H<sub>12</sub>S (M)<sup>+</sup> 260.0660, found 260.0658.



2-(Naphthalen-1-yl)benzofuran (2j). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium benzofuran-2-yltrifluoroborate (74.0 mg, 0.33 mmol) to obtain 2j (49.7 mg, 81%) as a light yellow oil after silica gel chromatography (elution with hexanes/EtOAc 80:20). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$ 8.51 (d, J = 8.3 Hz, 1H), 8.03-8.00 (m, 2H), 7.95 (dd, J = 7.2, 0.9 Hz, 1H), 7.74 (d, J = 7.7 Hz, 1H), 7.65-7.58 (m, 4H), 7.38 (t, J = 8.3 Hz, 1H), 7.31 (t, J = 7.7 Hz, 1H), 7.28 (s, 1H); <sup>13</sup>C NMR (125)

MHz, acetone-d<sub>6</sub>) δ 156.4, 155.9, 135.0, 131.4, 130.5, 130.0, 129.6, 128.9, 128.2, 127.9, 127.1, 126.3, 126.2, 125.4, 124.0, 122.1, 111.9, 106.9; FT-IR (neat) 3044, 1452, 1258; HRMS (ESI) m/z calcd. for  $C_{18}H_{12}O(M)^+$  244.0888, found 244.0889.



**Potassium Isoquinolin-5-yltrifluoroborate**. To a solution of isoquinolin-5-ylboronic acid (5.0 g, 28.91 mmol) in MeOH (8.5 mL, 3.5 M) under N<sub>2</sub> was added KHF<sub>2</sub> (6.8 g, 86.7 mmol) in one portion at 0 °C. To the suspension was added H<sub>2</sub>O dropwise (6.4 mL,

4.5M) at 0 °C. The ice-water bath was removed, and the reaction was stirred at rt for 1 h. The crude mixture was concentrated and dried overnight *in vacuo*. The crude solid was purified using continuous Soxhlet extraction (overnight) with acetone (200 mL). The collected solvent was concentrated and then redissolved in a minimal amount of acetone (15 mL). The addition of Et<sub>2</sub>O (100 mL) led to the precipitation of the product. The product was filtered, concentrated, and dried *in vacuo* to afford the pure compound (2.89 g, 43%) as a white solid. mp > 250 °C. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  9.13 (s, 1H), 8.32 (d, *J* = 5.9 Hz, 1H), 8.18 (d, *J* = 5.9 Hz, 1H), 7.80-7.76 (m, 2H), 7.48-7.44 (m, 1H); <sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  152.0, 140.8, 138.7, 132.7, 132.7, 128.5, 126.4, 124.8, 122.8; <sup>19</sup>F NMR (470.8 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  -135.8. <sup>11</sup>B NMR (128.4 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  2.435. FT-IR (KBr) 3032, 1613, 1572 cm<sup>-1</sup>. HRMS (ESI) *m/z* calcd. for C<sub>9</sub>H<sub>6</sub>OBF<sub>3</sub>N<sup>-</sup> (M-K)<sup>-</sup> 196.0545, found 196.0536.



**5-(Naphthalen-1-yl)isoquinoline (2k).** Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium isoquinolin-5-yltrifluoroborate (77.6 mg, 0.33 mmol) to obtain **2k** (58.1 mg, 91%) as a white powder after silica gel chromatography (elution with petroleum ether/EtOAc 80:20). mp: 121-123 °C. <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  9.41 (s, 1H), 8.35 (d, J = 5.9 Hz, 1H), 8.23 (d, J = 8.1 Hz, 1H),

8.06 (d, J = 8.3 Hz, 1H), 8.04 (d, J = 8.3 Hz, 1H), 7.83 (dd, J = 8.1, 7.1 Hz, 1H), 7.77 (dd, J = 7.1, 1.2 Hz, 1H), 7.66 (dd, J = 8.3, 7.1 Hz, 1H), 7.54-7.49 (m, 2H), 7.36-7.33 (m, 1H), 7.27 (d, J = 8.3 Hz, 1H), 7.11 (d, J = 5.9 Hz, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ ) δ 153.8, 144.3, 138.3, 137.5, 135.9, 134.7, 133.4, 132.7, 129.7, 129.3, 129.3, 128.8, 128.4, 127.9, 127.2, 126.9, 126.6, 126.4, 119.3; FT-IR (neat) 3046, 1732, 1616, 1586; HRMS (ESI) *m/z* calcd. for C<sub>19</sub>H<sub>14</sub>N (M+H)<sup>+</sup> 256.1126, found 256.1120.



*N*-Methyl-5-(naphthalen-1-yl)indole (21). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium *N*-methyl-indol-5-yltrifluoroborate (78.2 mg, 0.33 mmol) to obtain 2l (47.5 mg, 74%) as a colorless oil after silica gel chromatography (elution with hexanes/EtOAc 90:10). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.99-7.96 (m, 2H), 7.91 (d, J = 8.2 Hz, 1H), 7.68-7.67 (m, 1H), 7.58-7.43 (m, 5H), 7.33-7.30 (m, 2H), 6.53 (dd, J = 3.1, 0.7 Hz, 1H), 3.02 (s, 3H); <sup>13</sup>C NMR (125 MHz,

acetone-d<sub>6</sub>) § 142.5, 137.2, 135.0, 133.1, 132.4, 130.7, 129.7, 129.1, 128.0, 127.8, 127.1, 126.6, 126.5,

126.3, 124.4, 122.6, 110.0, 101.7, 33.0; FT-IR (neat) 3042, 1513, 1490, 1394, 1243; HRMS (ESI) m/z calcd. for C<sub>19</sub>H<sub>15</sub>N (M)<sup>+</sup> 257.1204, found 257.1200.

**NH 5-(Naphthalen-1-yl)-1***H***-indole (2m). Following the general procedure, the reaction was carried out with <b>1a** (55.5 mg, 0.25 mmol) and potassium 1*H*-indol-5-yltrifluoroborate (73.6 mg, 0.33 mmol) to obtain **2m** (54.5 mg, 90%) as a yellow oil contaminated with 10% of impurities that cannot be separated after silica gel chromatography (elution with hexanes/CH<sub>2</sub>Cl<sub>2</sub> 70:30). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  10.38 (br s, 1H, NH), 7.98 (d, *J* = 8.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.70-7.69 (m, 1H), 7.59-7.62 (m, 2H), 7.50-7.46 (m, 2H), 7.44-7.40 (m, 2H), 7.25 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.58-6.56 (m, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  142.6, 136.6, 135.0, 133.1, 132.5, 129.2, 129.1, 128.0, 127.7, 127.1, 126.6, 126.4, 126.4, 126.3, 124.5, 122.3, 111.9, 102.7; FT-IR (neat) 3419, 3045, 1574, 1506, 1262; HRMS (ESI) *m*/z calcd. for C<sub>18</sub>H<sub>13</sub>N (M)<sup>+</sup> 243.1048, found 243.1048.

#### 2. Preparation of (naphthalen-1-yl)aryl compounds



**1-PhenyInaphthalene (3a).** Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium phenyltrifluoroborate (60.7 mg, 0.33 mmol) to obtain **3a** (36.1 mg, 71%) as a white solid after silica gel chromatography (elution with hexanes). mp: 40-41 °C (lit. 41-43 °C). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.97 (d, J = 8.3 Hz, 1H), 7.93 (d, J = 8.3 Hz, 1H), 7.86 (d, J = 8.6 Hz, 1H), 7.58-7.42 (m, 9H).

<sup>1</sup>H NMR is comparable to the literature.<sup>1</sup>



**1-(***p***-Tolyl)naphthalene (3b).** Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium *p*-tolyltrifluoroborate (65.3 mg, 0.33 mmol) to obtain **3b** (41.4 mg, 76%) as a white solid after silica gel chromatography (elution with hexanes). mp: 51-52 °C (lit. 52-54 °C). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.96 (d, J = 8.1 Hz, 1H), 7.91-7.88 (m, 2H), 7.56-7.49 (m, 2H), 7.47-7.44 (m, 1H), 7.40 (dd, J = 7.1, 1.2 Hz,

<sup>&</sup>lt;sup>1</sup> Quasdorf, K. W.; Tian, X.; Garg, N. K. J. Am. Chem. Soc. 2008, 130, 14422-14423.

1H), 7.37 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 2.43 (s, 3H). <sup>1</sup>H NMR is comparable to the literature.<sup>1</sup>

OMe 1-(4-Methoxyphenyl)naphthalene (3c). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium *p*methoxyphenyltrifluoroborate (70.6 mg, 0.33 mmol) to obtain 3c (53.1 mg, 91%) as a white solid after silica gel chromatography (elution with hexanes/EtOAc 80/20). mp: 112-113 °C (lit. 113-115 °C). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.96 (dd, J = 8.1, 1.5 Hz, 1H), 7.89 (d, J = 8.3 Hz, 2H), 7.56-7.44 (m, 3H), 7.43-7.39 (m, 3H), 7.11-7.07 (m, 2H), 3.89 (s, 3H). <sup>1</sup>H NMR is comparable to the literature.<sup>2</sup>



**1-(3-Methoxyphenyl)naphthalene (3d).** Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium *m*-methoxyphenyltrifluoroborate (70.6 mg, 0.33 mmol) to obtain **3d** (57.5 mg, 98%) as a colorless oil after silica gel chromatography (elution with hexanes/EtOAc 80/20). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.96 (d, J = 8.8 Hz, 1H), 7.91 (dd, J = 8.3, 3.2 Hz,

2H), 7.56-7.50 (m, 2H), 7.48-7.40 (m, 3H), 7.06-7.01 (m, 3H), 3.85 (s, 3H).

<sup>1</sup>H NMR is comparable to the literature.<sup>2</sup>



**1-(2-Methoxyphenyl)naphthalene (3e).** Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium *o*-methoxyphenyltrifluoroborate (70.6 mg, 0.33 mmol) to obtain **3e** (49.8 mg, 85%) as a yellow powder after silica gel chromatography (elution with hexanes/EtOAc 80/20). mp: 96-98 °C (lit. 98-99 °C). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.93 (d, J = 8.3 Hz,

1H), 7.90 (d, J = 8.3 Hz, 1H), 7.55-7.25 (m, 2H), 7.49-7.43 (m, 2H), 7.41-7.36 (m, 2H), 7.25 (dd, J = 7.3, 1.7 Hz, 1H), 7.16 (d, J = 8.3 Hz, 1H), 7.09 (td, J = 7.3, 1.0 Hz, 1H), 3.66 (s, 3H). <sup>1</sup>H NMR is comparable to the literature.<sup>3</sup>

<sup>&</sup>lt;sup>2</sup> Cella, R.; Cunha, R.; Reis, A. E. S.; Pimenta, D. C.; Klitzke, C. F.; Stefani, H. A. J. Org. Chem. 2006, 71, 244-250.

<sup>&</sup>lt;sup>3</sup> Hatakeyama, T.; Nakamura, M. J. Am. Chem. Soc. 2007, 129, 9844-9845.

1-(4-Fluorophenyl)naphthalene (3f). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium p-fluorophenyltrifluoroborate (66.7 mg, 0.33 mmol) to obtain **3f** (49.9 mg, 90%) as a white powder after preparative silica gel chromatography (elution with hexanes). mp: 71-72 °C (lit. 71-72 °C). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  7.97 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.82 (d, J = 8.3 Hz, 1H), 7.57-7.45 (m, 5H), 7.41 (dd, J = 7.1 Hz J = 1.2 Hz, 1H), 7.31-7.26 (m, 2H).

<sup>1</sup>H NMR is comparable to the literature.<sup>4</sup>



1-(4-(Trifluoromethyl)phenyl)naphthalene (3g). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium ptrifluorophenyltrifluoroborate (83.2 mg, 0.33 mmol) to obtain **3g** (48.6 mg, 71%) as a white powder after preparative silica gel chromatography (elution with hexanes/EtOAc 95/5). mp: 45-46 °C (lit. 47-49 °C). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.01-7.97 (m, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.80 (d, J = 8.6 Hz, 1H), 7.70 (d, J = 8.3 Hz, 2H), 7.60-7.53 (m, 2H), 7.51-7.46 (m, 2H).

<sup>1</sup>H NMR is comparable to the literature.<sup>1</sup>

CHO 4-(Naphthalen-1-yl)benzaldehyde (3h). Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium *p*formylphenyltrifluoroborate (70.0 mg, 0.33 mmol) to obtain **3h** (12.3 mg, 21%) as a yellow powder after preparative silica gel chromatography (elution with hexanes/EtOAc 80/20). mp: 79-81 °C (lit. 84 °C). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  10.16 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 8.02-7.98 (m, 2H), 7.83 (d, *J* = 8.6 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.62-7.54 (m, 2H), 7.52-7.49 (m, 2H).

<sup>1</sup>H NMR is comparable to the literature.<sup>5</sup>



1-(4-(Naphthalen-1-yl)phenyl)ethanone (3i). Following the general procedure, the reaction was carried out with **1a** (55.5 mg, 0.25 mmol) and potassium pacetylphenyltrifluoroborate (74.6 mg, 0.33 mmol) to obtain 3i (57.6 mg, 94%) as a white powder after preparative silica gel chromatography (elution with hexanes/EtOAc 80/20). mp: 103-104 °C (lit. 102-103 °C). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.13 (d, J = 8.3 Hz,

<sup>&</sup>lt;sup>4</sup> Glass, A. C.; Morris, B. B.; Zakharov, L. N.; Liu, S. Y. Org. Lett. 2008, 10, 4855-4857.

<sup>&</sup>lt;sup>5</sup> Saha, D.; Chattopadhyay, K.; Ranu, B. C. *Tetrahedron Lett.* 2009, 50, 1003-1006.

2H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 8.3 Hz, 1H), 7.61 (d, *J* = 8.3 Hz, 2H), 7.60-7.52 (m, 2H), 7.50-7.44 (m, 2H), 2.66 (s, 3H). <sup>1</sup>H NMR is comparable to the literature.<sup>6</sup>

CN 4-(Naphthalen-1-yl)benzonitrile (3j). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium *p*-cyanophenyltrifluoroborate (69.0 mg, 0.33 mmol) to obtain 3j (40.5 mg, 71%) as a colorless oil after preparative silica gel chromatography (elution with hexanes/EtOAc 95/5). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.03-8.00 (m, 2H), 7.95 (d, J = 8.6 Hz, 2H), 7.80 (d, J = 8.6 Hz, 1H), 7.72 (d, J = 8.6 Hz, 2H), 7.63-7.55 (m, 2H), 7.54-7.48 (m, 2H).

<sup>1</sup>H NMR is comparable to the literature.<sup>7</sup>



Methyl 3-(Naphthalen-1-yl)benzoate (3k). Following the general procedure, the reaction was carried out with 1a (55.5 mg, 0.25 mmol) and potassium *m*-methoxycarbonylphenyltrifluoroborate (79.9 mg, 0.33 mmol) to obtain 3k (30.2 mg, 46%) as a yellow powder after preparative silica gel chromatography (elution with hexanes/EtOAc 80/20). mp: 69-71 °C (lit. 70-70.5 °C). <sup>1</sup>H NMR (500 MHz,

acetone- $d_6$ )  $\delta$  8.12-8.10 (m, 2H), 8.00 (d, J = 7.6 Hz, 1H), 7.98 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.3 Hz, 1H), 7.75 (dt, J = 7.6, 1.5 Hz, 1H), 7.70-7.66 (m, 1H), 7.61-7.53 (m, 2H), 7.51-7.46 (m, 2H), 3.91 (s, 3H). <sup>1</sup>H NMR is comparable to the literature.<sup>8</sup>

#### 3. Preparation of heteroarylmethanesulfonate compounds



**2-Methylpyridin-3-yl Methanesulfonate (4b).** To a stirred solution of 2-methylpyridin-3ol (360.0 mg, 3.3 mmol) in 0.5 mL of 2,6-lutidine and 4.5 mL of CHCl<sub>3</sub> at 0 °C was slowly added CH<sub>3</sub>SO<sub>2</sub>Cl (378.0 mg, 3.3 mmol). The reaction mixture was allowed to warm to rt and then refluxed overnight before cooling down. The reaction mixture was washed with

<sup>&</sup>lt;sup>6</sup> So, C. M.; Lau, C. P.; Kwong, F. Y. Org. Lett. 2007, 9, 2795-2798.

<sup>&</sup>lt;sup>7</sup> Kuroda, J. I.; Inamoto, K.; Hiroya, K.; Doi, T. Eur. J. Org. Chem. 2009, 2251-2261.

<sup>&</sup>lt;sup>8</sup> House, H. O.; Bashe, R. W. J. Org. Chem. 1967, 32, 784-791.

H<sub>2</sub>O (3 x 3 mL) and then dried (MgSO<sub>4</sub>). The solvent was concentrated and the residue fractionated under vacuum, yielding **4b** as a brown oil (400 mg, 65%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.46 (dd, J = 4.9, 1.5 Hz, 1H), 7.65 (dd, J = 8.1, 1.5 Hz, 1H), 7.21 dd, J = 8.1, 4.9 Hz, 1H), 3.24 (s, 3H), 2.61 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 152.4, 147.7, 144.5, 130.2, 122.4, 38.7, 19.9; FT-IR (neat) 3636, 3034, 1598, 1499, 1470, 1361, 1179; HRMS (ESI) *m/z* calcd. for C<sub>7</sub>H<sub>10</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 188.0381, found 188.0380.

H<sub>3</sub>C S Quinolin-8-yl Methanesulfonate (4d). To a stirred solution of quinolin-8-ol (363.0 mg, 2.50 mmol) in 2.5 mL of CH<sub>2</sub>Cl<sub>2</sub> was added Et<sub>3</sub>N (507 μL, 3.75 mmol). The reaction mixture was cooled to 0 °C and CH<sub>3</sub>SO<sub>2</sub>Cl (378.0 mg, 3.3 mmol) was slowly added. The reaction mixture was allowed to warm to rt for 1 h and then quenched with H<sub>2</sub>O (3 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 3 mL) and then dried (MgSO<sub>4</sub>). The solvent was concentrated and the product was purified by silica gel column chromatography (elution with hexanes/EtOAc 70:30) to yield 4d in 94% yield (524.3 mg) as a yellow powder. mp: 46-48 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.99 (dd, J = 4.2, 1.7 Hz, 1H), 8.22 (dd, J = 8.3, 1.5 Hz, 1H), 7.81 (dd, J = 8.3, 1.2 Hz, 1H), 7.73 (dd, J = 7.6, 1.5 Hz, 1H), 7.57 (t, J = 7.6 Hz, 1H), 7.50 (dd, J = 8.3, 4.2 Hz, 1H), 3.46 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 150.9, 145.5, 141.3, 136.1, 129.7, 127.1, 126.3, 123.7, 122.0, 39.1; FT-IR (neat) 3635, 3034, 1744, 1598, 1499, 1471, 1362, 1180; HRMS (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>10</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 224.0381, found 224.0386.

H<sub>3</sub>C, O H<sub>3</sub>C, C H<sub>4</sub>C, C H<sub>4</sub>



**1***H***-Indol-5-yl Methanesulfonate (4g).** To a stirred solution of 1*H*-indol-5-ol (166.0 mg, 1.25 mmol) in 1.25 mL of  $CH_2Cl_2$  was added  $Et_3N$  (186  $\mu$ L, 1.37 mmol). The reaction mixture was cooled to 0 °C and  $CH_3SO_2Cl$  (178.0 mg, 1.56

mmol) was slowly added. The reaction mixture was allowed to warm to rt for 1 h and then quenched with H<sub>2</sub>O (1.5 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 3 mL) and then dried (MgSO<sub>4</sub>). The solvent was concentrated and the product was purified by silica gel column chromatography (elution with hexanes/EtOAc 70:30) to yield **4g** in 83% yield (219.3 mg) as an off-white powder. mp: 96-98 °C. <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  10.47 (br s, 1H), 7.56 (d, J = 2.2 Hz, 1H), 7.49 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 2.7 Hz, 1H), (dd, J = 8.8, 2.2 Hz, 1H), 6.55-6.54 (m, 1H), 3.21 (s, 3H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  144.3, 135.7, 129.2, 127.9, 116.6, 114.1, 112.9, 103.0, 37.0; FT-IR (neat) 3397, 3038, 1622, 1576, 1374, 1171; HRMS (ESI) *m/z* calcd. for C<sub>9</sub>H<sub>10</sub>NO<sub>3</sub>S (M+H)<sup>+</sup> 212.0381, found 212.0387.

#### 4. Preparation of (furan-3-yl)heteroaryl compounds

**3-(Furan-3-yl)pyridine (5a).** Following the general procedure, the reaction was carried out with **4a** (43.3 mg, 0.25 mmol) and potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain **5a** (28.9 mg, 80%) as a yellow oil after silica gel chromatography (elution with hexanes/EtOAc 50:50). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.75 (d, *J* = 2.2 Hz, 1H), 8.49 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.77 (s, 1H), 7.74 (dt, *J* = 7.8, 2.2 Hz, 1H), 7.51 (s, 1H), 7.30-7.26 (m, 1H), 6.71-6.70 (m, 1H).

<sup>1</sup>H NMR is comparable to the literature.<sup>9</sup>

**3-(Furan-3-yl)-2-methylpyridine (5b).** Following the general procedure, the reaction was carried out with **4b** (46.8 mg, 0.25 mmol) and potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain **5b** (27.7 mg, 70%) as a brown oil after silica gel chromatography (elution with hexanes/EtOAc 65:35). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.44-8.43 (m, 1H), 7.59 (dd, *J* = 4.9, 1.2 Hz, 1H), 7.55 (s, 1H), 7.51-7.50 (m, 1H), 7.14 (dd, *J* = 7.6, 4.9 Hz, 1H), 6.58 (s 1H), 2.62 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  156.1, 147.8, 143.2, 140.4, 136.7, 127.9, 124.0, 121.3, 111.2, 24.1; FT-IR (neat) 3401, 3050, 1578, 1505, 1434; HRMS (ESI) *m/z* calcd. for C<sub>10</sub>H<sub>9</sub>NO (M)<sup>+</sup> 159.0684, found 159.0685.

<sup>&</sup>lt;sup>9</sup> Bhayana, B.; Fors, B. P.; Buchwald, S. L. Org. Lett. 2009, 11, 3954-3957.



**6-(Furan-3-yl)quinoline (5c).** Following the general procedure, the reaction was carried out with **4c** (55.8 mg, 0.25 mmol) and potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain **5c** (48.1 mg, 99%) as a yellow powder after silica

gel chromatography (elution with hexanes/EtOAc 60:40). mp: 88-90 °C. <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.86 (dd, J = 4.2, 1.5 Hz, 1H), 8.27 (dd, J = 8.3, 1.5 Hz, 1H), 8.20-8.19 (m, 1H), 8.13 (d, J = 2.0 Hz, 1H), 8.06-8.00 (m, 2H), 7.70 (t, J = 1.7 Hz, 1H), 7.47 (dd, J = 8.3, 4.2 Hz, 1H), 7.04 (dd, J = 2.0, 1.0 Hz, 1H).

<sup>1</sup>H NMR is comparable to the literature.<sup>9</sup>

8-(Furan-3-yl)quinoline (5d). Following the general procedure, the reaction was carried out with 4d (55.8 mg, 0.25 mmol) and potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain 5d (44.9 mg, 92%) as a brown oil after silica gel chromatography (elution with hexanes/EtOAc 85:15). <sup>1</sup>H NMR (500 MHz, acetone-*d*<sub>6</sub>) δ 9.00 (dd, *J* = 4.2, 2.0 Hz, 1H), 8.83-8.82 (m, 1H), 8.34 (dd, *J* = 8.3, 2.0 Hz, 1H), 8.05 (dd, *J* = 7.3, 1.2 Hz, 1H), 7.84 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.67 (t, *J* = 1.7 Hz, 1H), 7.60 (dd, *J* = 8.3, 7.3 Hz, 1H), 7.54 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.18 (dd, *J* = 2.0, 0.7 Hz, 1H); <sup>13</sup>C NMR (125 MHz, acetone-*d*<sub>6</sub>) δ 150.6, 146.4, 144.6, 143.2, 137.4, 132.1, 129.8, 128.3, 127.8, 127.3, 123.7, 122.2, 111.0; FT-IR (neat) 3047, 1732, 1614, 1597, 1514; HRMS (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>9</sub>NO (M)<sup>+</sup> 195.0684, found 195.0689.

**5-(Furan-3-yl)isoquinoline (5e).** Following the general procedure, the reaction was carried out with **4e** (55.8 mg, 0.25 mmol) and potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain **5e** (42.4 mg, 87%) as a yellow oil after silica gel chromatography (elution with hexanes/EtOAc 85:15). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  9.33 (s, 1H), 8.53 (d, J = 5.9 Hz, 1H), 8.07 (d, J = 8.3 Hz, 1H), 7.97 (d, J = 5.9 Hz, 1H), 7.95-7.94 (m, 1H), 7.79-7.77 (m, 2H), 7.69 (dd, J = 8.1, 7.1 Hz, 1H), 6.85 (dd, J = 1.7, 0.7 Hz, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  153.8, 144.6, 144.5, 141.8, 134.7, 131.4, 130.6, 130.0, 128.0, 127.9, 124.3, 118.7, 112.6; FT-IR (neat) 3418, 3031, 1732, 1615, 1602, 1505; HRMS (ESI) *m/z* calcd. for C<sub>13</sub>H<sub>10</sub>NO (M+H)<sup>+</sup> 196.0762, found 196.0765.



**5-(Furan-3-yl)-2-methylbenzo[d]thiazole (5f).** Following the general procedure, the reaction was carried out with **4f** (60.8 mg, 0.25 mmol) and potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain **5f** (41.2 mg,

77%) as a white powder after silica gel chromatography (elution with hexanes/EtOAc 70:30). mp: 105-106 °C; <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  8.12-8.11 (m, 2H), 7.93 (d, J = 8.3 Hz, 1H), 7.67 (t, J = 1.7 Hz, 1H), 7.63 (dd, J = 8.3, 1.7 Hz, 1H), 6.99 (dd, J = 2.0, 1.0 Hz, 1H), 2.79 (s, 3H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  168.2, 155.3, 145.0, 140.1, 135.1, 131.5, 127.1, 123.6, 122.7, 119.9, 109.7, 20.0; FT-IR (neat) 3049, 1749, 1590, 1543, 1530; HRMS (ESI) *m*/*z* calcd. for C<sub>12</sub>H<sub>9</sub>NO (M)<sup>+</sup> 215.0405, found 215.0400.



**5-(Furan-3-yl)-1***H***-indole (5g).** Following the general procedure, the reaction was carried out with **4g** (52.8 mg, 0.25 mmol) and potassium furan-3-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain **5g** (20.1 mg, 44%) as an off-white powder after silica gel chromatography (elution with hexanes/EtOAc 70:30). mp: 89-91 °C; <sup>1</sup>H

NMR (500 MHz, acetone- $d_6$ )  $\delta$  10.24 (br s, 1H), 7.91-7.90 (m, 1H), 7.79-7.78 (m, 1H), 7.59 (t, J = 1.7 Hz, 1H), 7.43 (td, J = 8.3, 0.7 Hz, 1H), 7.36 (dd, J = 8.3, 1.7 Hz, 1H), 7.33 (t, J = 2.7 Hz, 1H), 6.88 (dd, J = 1.7, 0.7 Hz, 1H), 6.48-6.46 (m, 1H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  144.4, 138.5, 136.6, 129.5, 128.7, 126.2, 124.5, 120.8, 118.2, 112.5, 109.9, 102.5; FT-IR (neat) 3426, 3023, 1728, 1469; HRMS (ESI) m/z calcd. for C<sub>12</sub>H<sub>10</sub>NO (M+H)<sup>+</sup> 184.0762, found 184.0761.

### 5. Preparation of (substituted phenyl)heteroaryl compounds



**3-Phenylquinoline (6a).** Following the general procedure, the reaction was carried out with phenyl methanesulfonate (43.0 mg, 0.25 mmol) and potassium quinolin-3-yltrifluoroborate (77.6 mg, 0.33 mmol) to obtain **6a** (38.4 mg, 75%) as a brown oil after silica gel chromatography (elution with hexanes/EtOAc 80:20). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  9.22 (d, J = 2.4 Hz, 1H), 8.51 (d, J = 2.4 Hz, 1H), 8.09 (d, J = 8.6 Hz, 1H), 8.01 (d, J = 8.1 Hz, 1H), 7.85-7.83 (m, 2H), 7.77-7.73 (m, 1H), 7.64-7.60 (m, 1H), 7.57-7.53 (m, 2H), 7.47-7.43

(m, 1H).

<sup>1</sup>H NMR is comparable to the literature.<sup>10</sup>

<sup>&</sup>lt;sup>10</sup> Wang, Y.; Xin, X.; Liang, Y. J.; Lin, Y. J.; Zhang, R.; Dong, D. W. Eur. J. Org. Chem. 2009, 4165-4169.

**4-(Thiophen-3-yl)benzonitrile (6b).** Following the general procedure, the reaction was carried out with 4-cyanophenyl methanesulfonate (49.3 mg, 0.25 mmol) and potassium thiophen-3-yltrifluoroborate (62.0 mg, 0.33 mmol) to obtain **6b** (31.2 mg, 68%) as a white solid after silica gel chromatography (elution with hexanes/EtOAc 80:20). mp: 106-108 °C (lit. 100-101 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  7.68 (s, 4H), 7.57 (dd, *J* = 2.9, 1.5 Hz, 1H), 7.44 (dd, *J* = 5.1, 2.9 Hz, 1H), 7.40 (dd, *J* = 5.1, 1.5 Hz, 1H).

<sup>1</sup>H NMR is comparable to the literature.<sup>11</sup>



**2-(4-Methoxyphenyl)benzofuran (6c).** Following the general procedure, the reaction was carried out with 4-methoxyphenyl methanesulfonate (50.5 mg, 0.25 mmol) and potassium benzofuran-2-yltrifluoroborate (74.0 mg, 0.33 mmol) to obtain **6c** (39.0 mg, 70%) as a white solid after silica gel chromatography (elution with hexanes/EtOAc 80:20). mp: 149-151 °C (lit. 148-150 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (d, *J* = 8.8 Hz, 2H), 7.93 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.65-7.57 (m, 2H), 7.35 (d, *J* = 8.8 Hz, 2H), 7.26 (s, 1H), 4.23 (s,

<sup>1</sup>H NMR is comparable to the literature.<sup>12</sup>



4.9 Hz, 1H), 2.65 (s, 3H).

<sup>1</sup>H NMR is comparable to the literature.<sup>13</sup>

<sup>&</sup>lt;sup>11</sup> Molander, G. A.; Canturk, B.; Kennedy, L. E. J. Org. Chem. 2009, 74, 973-980.

<sup>&</sup>lt;sup>12</sup> Geary, L. M.; Hultin, P. G. Org. Lett. **2009**, *11*, 5478-5481.

<sup>&</sup>lt;sup>13</sup> Cioffi, C. L.; Spencer, W. T.; Richards, J. J.; Herr, R. J. J. Org. Chem. 2004, 69, 2210-2212.

**Methyl 4-(Furan-2-yl)benzoate (6e).** Following the general procedure, the reaction was carried out with methyl 4-((methylsulfonyl)oxy)benzoate (57.5 mg, 0.25 mmol) and potassium furan-2-yltrifluoroborate (57.4 mg, 0.33 mmol) to obtain **6e** (41.1 mg, 81%) as an orange powder after silica gel chromatography (elution with hexanes/EtOAc 85:15). mp:

 $\dot{CO}_2$ Me 117-118 °C (lit. 116-117 °C). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (d, J = 8.6 Hz, 2H), 7.72 (d, J = 8.6 Hz, 2H), 7.51 (dd, J = 1.7, 0.5 Hz, 1H), 6.78 (d, J = 3.4 Hz, 1H), 6.50 (dd, J = 3.4, 1.7 Hz, 1H), 3.92 (s, 3H).

<sup>1</sup>H NMR is comparable to the literature.<sup>11</sup>



**5-(2,4-Dimethylphenyl)isoquinoline (6f).** Following the general procedure, the reaction was carried out with 2,4-dimethylphenyl methanesulfonate (50.0 mg, 0.25 mmol) and potassium isoquinolin-5-yltrifluoroborate (77.6 mg, 0.33 mmol) to obtain **6f** (22.9 mg, 39%) as a colorless oil after silica gel chromatography (elution with hexanes/EtOAc 85:15). <sup>1</sup>H NMR (500 MHz, acetone- $d_6$ )  $\delta$  9.34 (s, 1H), 8.43 (d, J = 5.9 Hz, 1H), 8.12

(dd, J = 8.3, 1.0 Hz, 1H), 7.74 (dd, J = 8.3, 7.1 Hz, 1H), 7.59 (dd, J = 7.1, 1.2 Hz, 1H), 7.23 (dd, J = 5.9, 1.0 Hz, 1H), 7.21-7.20 (m, 1H), 7.15 (d, J = 7.6 Hz, 1H), 7.10 (d, J = 7.6 Hz, 1H), 2.40 (s, 3H), 1.96 (s, 3H); <sup>13</sup>C NMR (125 MHz, acetone- $d_6$ )  $\delta$  152.7, 143.3, 138.7, 137.5, 136.0, 135.5, 134.3, 130.7, 130.7, 129.9, 128.7, 126.8, 126.4, 118.1, 20.2, 19.0; FT-IR (neat) 3008, 1615, 1587; HRMS (ESI) m/z calcd. for C<sub>17</sub>H<sub>15</sub>N (M)<sup>+</sup> 233.1204, found 233.1200.

#### NMR Spectra









<sup>13</sup>C NMR (125 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 3-(naphthalen-1-yl)thiophene **2b** (Table 2, entry 2)











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S29





<sup>19</sup>F NMR (471 MHz, DMSO-*d*<sub>6</sub>) Spectrum of potassium pyrimidin-5-yltrifluoroborate



<sup>11</sup>B NMR (128 MHz, DMSO-*d*<sub>6</sub>) Spectrum of potassium pyrimidin-5-yltrifluoroborate



<sup>1</sup>H NMR (300 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 5-(naphthalen-1-yl)pyrimidine **2f** (Table 2, entry 6)



<sup>13</sup>C NMR (125 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 5-(naphthalen-1-yl)pyrimidine **2f** (Table 2, entry 6)






S37





S39



<sup>13</sup>C NMR (125 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 2-(naphthalen-1-yl)benzothiophene **2i** (Table 2, entry 9)





S42



<sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) Spectrum of potassium isoquinolin-5-yltrifluoroborate



<sup>13</sup>C NMR (125 MHz, DMSO-*d*<sub>6</sub>) Spectrum of potassium isoquinolin-5-yltrifluoroborate



S45





<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 5-(naphthalen-1-yl)isoquinoline **2k** (Table 2, entry 11)



<sup>13</sup>C NMR (125 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 5-(naphthalen-1-yl)isoquinoline **2k** (Table 2, entry 11)



<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of *N*-methyl-5-(naphthalen-1-yl)indole **2l** (Table 2, entry 12)



S50







<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 1-phenylnaphthalene **3a** (Table 3, entry 1)







<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 1-(3-methoxyphenyl)naphthalene **3d** (Table 3, entry 4)



<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 1-(2-methoxyphenyl)naphthalene **3e** (Table 3, entry 5)



<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 1-(4-fluorophenyl)naphthalene **3f** (Table 3, entry 6)



<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 1-(4-(trifluoromethyl)phenyl)naphthalene **3g** (Table 3, entry 7)





<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 1-(4-(naphthalen-1-yl)phenyl)ethanone **3i** (Table 3, entry 9)



<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 4-(naphthalen-1-yl)benzonitrile **3j** (Table 3, entry 10)



<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of methyl 3-(naphthalen-1-yl)benzoate **3k** (Table 3, entry 11)



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of 2-methylpyridin-3-yl methanesulfonate **4b** (Table 4, entry 2)



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum of 2-methylpyridin-3-yl methanesulfonate **4b** (Table 4, entry 2)



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of quinolin-8-yl methanesulfonate **4d** (Table 4, entry 4)



<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) Spectrum of quinolin-8-yl methanesulfonate **4d** (Table 4, entry 4)



<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of isoquinolin-5-yl methanesulfonate **4e** (Table 4, entry 5)





<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 1*H*-indol-5-yl methanesulfonate **4g** (Table 4, entry 7)












<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 8-(furan-3-yl)quinoline **5d** (Table 4, entry 4)



<sup>13</sup>C NMR (125 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 8-(furan-3-yl)quinoline **5d** (Table 4, entry 4)





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<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 5-(furan-3-yl)-2-methylbenzo[d]thiazole **5f** (Table 4, entry 6)



<sup>13</sup>C NMR (125 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 5-(furan-3-yl)-2-methylbenzo[d]thiazole **5f** (Table 4, entry 6)













<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) Spectrum of 1-(4-(pyridin-3-yl)phenyl)ethanone **6d** (Table 5, entry 4)



S88



<sup>1</sup>H NMR (500 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 5-(2,4-dimethylphenyl)isoquinoline **6f** (Table 5, entry 6)



<sup>13</sup>C NMR (125 MHz, C<sub>3</sub>D<sub>6</sub>O) Spectrum of 5-(2,4-dimethylphenyl)isoquinoline **6f** (Table 5, entry 6)