

# **A Nickel/Organoboron Catalyzed Coupling of Aryl Bromides with Sodium Sulfinates: Synthesis of Sulfones under Visible Light**

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# 1. General considerations

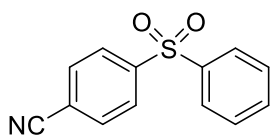
**General.** Unless otherwise noted, all reactions were carried out under an air atmosphere. Analytical thin-layer chromatography (TLC) was performed on glass plates coated with 0.25 mm 230–400 mesh silica gel containing a fluorescent indicator. Visualization was accomplished by exposure to a UV lamp. All the products in this article are compatible with standard silica gel chromatography. Column chromatography was performed on silica gel (200–300 mesh) using standard methods.

**Structural analysis.** NMR spectra were measured on a Bruker Ascend 400 spectrometer and chemical shifts ( $\delta$ ) are reported in parts per million (ppm).  $^1\text{H}$  NMR spectra were recorded at 400 MHz in NMR solvents and referenced internally to corresponding solvent resonance, and  $^{13}\text{C}$  NMR spectra were recorded at 101 MHz and referenced to corresponding solvent resonance. Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Infrared spectra were collected on a Thermo Fisher Nicolet 6700 FT-IR spectrometer using ATR (Attenuated Total Reflectance) method. Absorption maxima ( $\nu_{\text{max}}$ ) are reported in wavenumbers ( $\text{cm}^{-1}$ ). High resolution mass spectra (HRMS) were acquired on Thermo Scientific LTQ Orbitrap XL with an ESI source.

**Materials.** Commercial reagents and solvent were purchased from Adamas, J&K, Energy, Sigma-Aldrich, Alfa Aesar, Acros Organics, TCI and used as received unless otherwise stated.

## 2. Characterization data

### (3a) 4-(phenylsulfonyl)benzonitrile (CAS: 28525-13-5)<sup>1</sup>



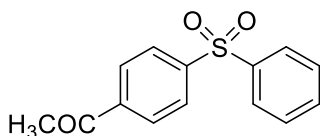
4-(phenylsulfonyl)benzonitrile  
Chemical Formula: C<sub>13</sub>H<sub>9</sub>NO<sub>2</sub>S  
Exact Mass: 243.0354  
Molecular Weight: 243.2800

Following the General Procedure with 4-Bromobenzonitrile (36.4 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3a** was obtained as white solid (41.3 mg, 85%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.9, 140.2, 134.1, 133.1, 129.7, 128.3, 128.0, 117.2, 116.9.

### (3b) (4-(phenylsulfonyl)phenyl)ethan-1-one (CAS: 65085-83-8)<sup>1</sup>



1-(4-(phenylsulfonyl)phenyl)ethan-1-one  
Chemical Formula: C<sub>14</sub>H<sub>12</sub>O<sub>3</sub>S  
Exact Mass: 260.0507  
Molecular Weight: 260.3070

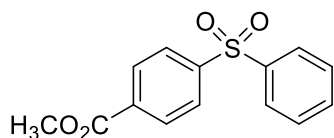
Following the General Procedure with 1-(4-bromophenyl)ethan-1-one (39.8 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3b** was obtained as white solid (41.6 mg, 80%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (s, 4H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 6.0 Hz, 1H), 7.54 (d, *J* = 6.8

Hz, 2H), 2.62 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.7, 145.4, 140.8, 140.4, 133.7, 129.5, 129.1, 128.0, 127.9, 26.9.

### (3c) methyl 4-(phenylsulfonyl)benzoate (CAS: 38337-00-7)<sup>1</sup>



methyl 4-(phenylsulfonyl)benzoate  
Chemical Formula: C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>S  
Exact Mass: 276.0456  
Molecular Weight: 276.3060

Following the General Procedure with methyl 4-bromobenzoate (42.8 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3c** was obtained as white solid (22.1 mg, 40%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 8.5 Hz, 2H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.58 (d, *J*

= 7.2 Hz, 1H), 7.52 (t, *J* = 6.8 Hz, 2H), 3.92 (s, 3H).

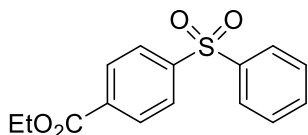
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.5, 145.5, 140.8, 134.3, 133.6, 130.5, 129.5, 127.8, 127.7, 52.7.

**(3d) (4-(phenylsulfonyl)phenyl)propan-1-one (CAS: 69567-00-6)**

Following the General Procedure with methyl 1-(4-bromophenyl)propan-1-one (45.6 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3d** was obtained as white solid (42.7 mg, 78%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 5.2 Hz, 4H), 7.94 (d, *J* = 8.4 Hz, 2H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 2.97 (d, *J* = 7.2 Hz, 2H), 1.18 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 199.5, 145.2, 140.8, 140.3, 133.7, 129.5, 128.8, 128.0, 127.8, 32.3, 8.0.



ethyl 4-(phenylsulfonyl)benzoate

Chemical Formula: C<sub>15</sub>H<sub>14</sub>O<sub>4</sub>S

Exact Mass: 290.0613

Molecular Weight: 290.3330

HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>15</sub>O<sub>3</sub>S<sup>+</sup> M+H<sup>+</sup> 275.3415, found 275.3415.

IR: 3070, 2978, 2935, 1697, 1582, 1448, 1155, 730, 600.

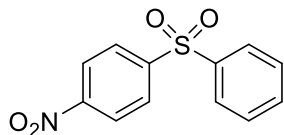
Melting point (°C): 57.9-59.1

**(3e) ethyl 4-(phenylsulfonyl)benzoate (CAS: 101094-06-8)<sup>1</sup>**

Following the General Procedure with ethyl 4-bromobenzoate (45.8 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3e** was obtained as white solid (24.4 mg, 42%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 8.0 Hz, 2H), 8.00 (d, *J* = 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.2 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 4.38 (d, *J* = 7.2 Hz, 2H), 1.38 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.0, 145.4, 140.9, 134.7, 133.6, 130.4, 129.5, 129.3, 127.8, 127.7, 61.7, 14.2.



1-nitro-4-(phenylsulfonyl)benzene

Chemical Formula: C<sub>12</sub>H<sub>9</sub>NO<sub>4</sub>S

Exact Mass: 263.0252

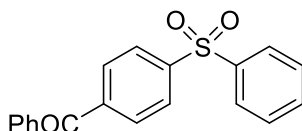
Molecular Weight: 263.2670

**(3f) nitro-4-(phenylsulfonyl)benzene (CAS: 1146-39-0)<sup>1</sup>**

Following the General Procedure with methyl 1-bromo-4-nitrobenzene (40.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3f** was obtained as white solid (38.3 mg, 73%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 (d, *J* = 8.8 Hz, 2H), 8.13 (d, *J* = 6.7 Hz, 2H), 7.97 (d, *J* = 7.9 Hz, 2H), 7.62 (d, *J* = 6.4 Hz, 1H), 7.56 (d, *J* = 6.9 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 150.4, 147.4, 140.0, 134.2, 129.7, 129.0, 128.1, 124.6.



phenyl(4-(phenylsulfonyl)phenyl)methanone

Chemical Formula: C<sub>19</sub>H<sub>14</sub>O<sub>3</sub>S

Exact Mass: 322.0664

Molecular Weight: 322.3780

C<sub>2</sub>H<sub>5</sub>OC

1-(4-(phenylsulfonyl)phenyl)propan-1-one

Chemical Formula: C<sub>15</sub>H<sub>14</sub>O<sub>3</sub>S

Exact Mass: 274.0664

Molecular Weight: 274.3340

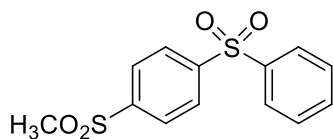
**(3g) phenyl(4-(phenylsulfonyl)phenyl)methanone (CAS: 54687-39-7)<sup>2</sup>**

Following the General Procedure with (4-bromophenyl)(phenyl)methanone (52.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3g** was obtained as white solid (32.8 mg, 51%). This product of interest

is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.06 (d, *J* = 6.4 Hz, 2H), 7.99 (d, *J* = 7.6 Hz, 2H), 7.88 (d, *J* = 6.8 Hz, 2H), 7.77 (d, *J* = 7.6 Hz, 2H), 7.66 – 7.59 (m, 2H), 7.56 (d, *J* = 6.8 Hz, 2H), 7.49 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 195.2, 144.7, 141.7, 140.9, 136.4, 133.7, 133.3, 130.5, 130.1, 129.5, 128.6, 127.9, 127.7.



1-(methylsulfonyl)-4-(phenylsulfonyl)benzene

Chemical Formula: C<sub>13</sub>H<sub>12</sub>O<sub>4</sub>S<sub>2</sub>

Exact Mass: 296.0177

Molecular Weight: 296.3550

**(3h) (methylsulfonyl)-4-**

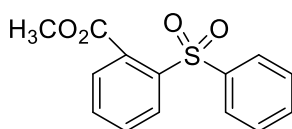
**(phenylsulfonyl)benzene (CAS: 3112-84-3) <sup>3</sup>**

Following the General Procedure with 1-bromo-4-(methylsulfonyl)benzene (46.4 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3h** was

obtained as white solid (26.6 mg, 45%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 8.4 Hz, 2H), 8.08 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.63 (d, *J* = 6.8 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 2H), 3.07 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.8, 144.8, 140.2, 134.1, 129.7, 128.7, 128.5, 128.0, 44.3.



methyl 2-(phenylsulfonyl)benzoate

Chemical Formula: C<sub>14</sub>H<sub>12</sub>O<sub>4</sub>S

Exact Mass: 276.0456

Molecular Weight: 276.3060

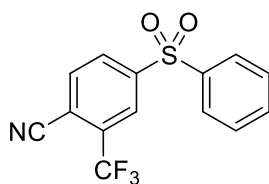
**(3i) methyl 2-(phenylsulfonyl)benzoate (CAS: 67373-14-2) <sup>1</sup>**

Following the General Procedure with methyl 2-iodobenzoate (52.4 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3i** was obtained as white solid (35.3 mg, 64%). This product of interest is purified by silica gel flash chromatography (PE:

EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (m, 1H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.62 (m, 2H), 7.57 (m, 2H), 7.51 (t, *J* = 7.4 Hz, 2H), 3.92 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.7, 141.5, 139.0, 133.3, 130.9, 130.2, 129.2, 129.0, 127.8, 53.0.



4-(phenylsulfonyl)-2-(trifluoromethyl)benzonitrile

Chemical Formula: C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NO<sub>2</sub>S

Exact Mass: 311.0228

Molecular Weight: 311.2782

**(3j) 4-(phenylsulfonyl)-2-(trifluoromethyl)benzonitrile (CAS: 2383030-86-0) <sup>1</sup>**

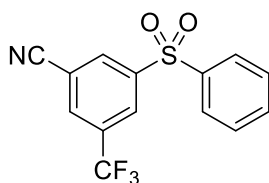
Following the General Procedure with 4-bromo-2-(trifluoromethyl)benzonitrile (49.8 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3j** was obtained as white solid (51.0

mg, 82%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.04 – 7.95 (m, 3H), 7.68 (t, *J* = 7.4 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.6, 139.3, 135.9, 134.6, 134.2 (d, *J* = 34.0 Hz), 131.3, 130.0, 128.2, 125.8 (q, *J* = 4.7 Hz), 121.5 (d, *J* = 275.8 Hz), 114.5, 114.0.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.10 (s).



3-(phenylsulfonyl)-5-(trifluoromethyl)benzonitrile

Chemical Formula: C<sub>14</sub>H<sub>8</sub>F<sub>3</sub>NO<sub>2</sub>S

Exact Mass: 311.0228

Molecular Weight: 311.2782

**(3k) 3-(phenylsulfonyl)-5-(trifluoromethyl)benzonitrile<sup>1</sup>**

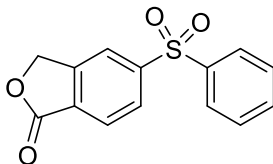
Following the General Procedure with 3-bromo-5-(trifluoromethyl)benzonitrile (40.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3k** was obtained as white solid (34.8 mg, 56%). This product of interest is

purified by silica gel flash chromatography (PE: EA = 5:1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 10.4 Hz, 2H), 8.08 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.68 (m, 1H), 7.60 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.1, 139.3, 134.6, 134.3, 133.5 (d, *J* = 35.0 Hz), 133.0 (d, *J* = 3.6 Hz), 130.2, 128.3 (q, *J* = 3.6), 128.2, 127.7, 122.0 (d, *J* = 274.8 Hz), 115.7, 115.2.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.06 (s).



5-(phenylsulfonyl)isobenzofuran-1(3H)-one

Chemical Formula: C<sub>14</sub>H<sub>10</sub>O<sub>4</sub>S

Exact Mass: 274.0300

Molecular Weight: 274.2900

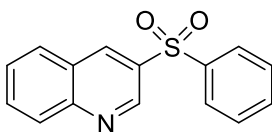
**(3l) 5-(phenylsulfonyl)isobenzofuran-1(3H)-one (CAS: 2232133-50-3)<sup>3</sup>**

Following the General Procedure with 5-bromoisobenzofuran-1(3H)-one (42.4 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3l** was obtained as white solid (27.4 mg, 50%). This product of interest is purified by silica gel flash

chromatography (PE: EA = 5:1)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.99 – 7.96 (m, 2H), 7.64 (m, 1H), 7.55 (t, *J* = 7.8 Hz, 2H), 5.39 (s, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 169.1, 147.3, 147.2, 140.3, 134.0, 129.8, 129.7, 128.6, 128.0, 126.9, 122.0, 69.6.



3-(phenylsulfonyl)quinoline  
Chemical Formula: C<sub>15</sub>H<sub>11</sub>NO<sub>2</sub>S

Exact Mass: 269.0510

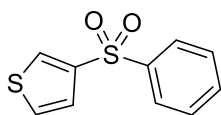
Molecular Weight: 269.3180

**(3m) 3-(phenylsulfonyl)quinoline (CAS: 117620-35-6)<sup>1</sup>**

Following the General Procedure with methyl 1-bromo-4-nitrobenzene (40.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3m** was obtained as white solid (22.6 mg, 42%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.28 (d, *J* = 2.0 Hz, 1H), 8.83 (d, *J* = 2.0 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 1H), 8.07 – 8.01 (m, 2H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.87 (m, 1H), 7.68 (m, 1H), 7.63 – 7.57 (m, 1H), 7.54 (m, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 149.4, 147.1, 141.0, 137.0, 134.7, 133.8, 132.8, 129.6, 129.2, 128.4, 127.8, 126.4.

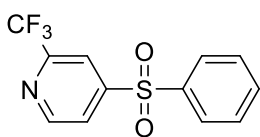


3-(phenylsulfonyl)thiophene  
Chemical Formula:  $C_{10}H_8O_2S_2$   
Exact Mass: 223.9966  
Molecular Weight: 224.2920

**(3n) 3-(phenylsulfonyl)thiophene (CAS: 89770-30-9) <sup>4</sup>**

Following the General Procedure with 3-iodothiophene (40.0 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (44.6 mg, 0.4 mmol, 2.0 equiv), **3n** was obtained as white solid (25.0 mg, 56%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.13 – 8.08 (m, 1H), 7.97 (d,  $J$  = 7.2 Hz, 2H), 7.59 (t,  $J$  = 6.8 Hz, 1H), 7.52 (t,  $J$  = 7.4 Hz, 2H), 7.41 – 7.36 (m, 1H), 7.36 – 7.32 (m, 1H).  
 $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  142.0, 141.6, 133.3, 131.6, 129.3, 128.4, 127.5, 125.9.

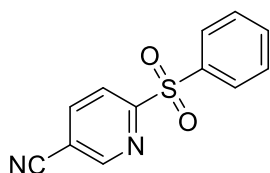


4-(phenylsulfonyl)-2-(trifluoromethyl)pyridine  
Chemical Formula:  $C_{12}H_8F_3NO_2S$   
Exact Mass: 287.0228  
Molecular Weight: 287.2562

**(3o) 4-(phenylsulfonyl)-2-(trifluoromethyl)pyridine <sup>5</sup> (CAS: 2412989-04-7)**

Following the General Procedure with 4-bromo-2-(trifluoromethyl)pyridine (44.9 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3o** was obtained as white solid (46.5 mg, 81%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.93 (d,  $J$  = 4.8 Hz, 1H), 8.13 (s, 1H), 7.99 (d,  $J$  = 8.0 Hz, 3H), 7.74 – 7.63 (m, 1H), 7.63 – 7.53 (m, 2H).  
 $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  152.2, 151.7, 150.0 (d,  $J$  = 36.1 Hz), 138.8, 134.7, 130.0, 128.3, 123.7, 120.7 (d,  $J$  = 275.8 Hz), 117.79 (d,  $J$  = 2.7 Hz).  
 $^{19}F$  NMR (376 MHz,  $CDCl_3$ )  $\delta$  -68.06 (s).



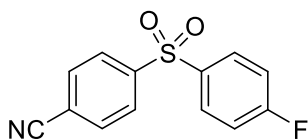
6-(phenylsulfonyl)nicotinonitrile  
Chemical Formula:  $C_{12}H_8N_2O_2S$   
Exact Mass: 244.0306  
Molecular Weight: 244.2680

**(3p) 6-(phenylsulfonyl)nicotinonitrile (205514-29-0)**

Following the General Procedure with 2-Bromo-4-cyanopyridine (36.6 mg, 0.2 mmol, 1.0 equiv), sodium benzenesulfinate (65.6 mg, 0.4 mmol, 2.0 equiv), **3p** was obtained as white solid (20.5 mg, 42%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

$^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.89 (d,  $J$  = 1.1 Hz, 1H), 8.34 (d,  $J$  = 8.0 Hz, 1H), 8.23 (dd,  $J$  = 8.4, 2.0 Hz, 1H), 8.06 (d,  $J$  = 7.2 Hz, 2H), 7.68 (t,  $J$  = 6.8 Hz, 1H), 7.58 (t,  $J$  = 7.6 Hz, 2H).  
 $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  161.7, 152.7, 141.9, 137.5, 134.6, 129.4, 129.4, 121.9, 115.1, 113.0.  
HRMS (ESI)  $m/z$  calcd for  $C_{12}H_8N_2O_2S^+ M+H^+$  245.0371, found 245.0371.  
IR: 3065, 2243, 1452, 325, 1161, 628.  
Melting point ( $^{\circ}C$ ): 119.1-120.1





4-((4-fluorophenyl)sulfonyl)benzonitrile  
 Chemical Formula:  $C_{13}H_8FNO_2S$   
 Exact Mass: 261.0260  
 Molecular Weight: 261.2704

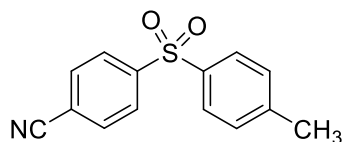
**(3q) 4-((4-fluorophenyl)sulfonyl)benzonitrile<sup>1</sup> (CAS: 1268049-80-4)**

Following the General Procedure with 4-Bromobenzonitrile (36.4 mg, 0.2 mmol, 1.0 equiv), 4-Fluorobenzenesulfinic acid sodium salt (91.0 mg, 0.4 mmol, 2.0 equiv), **3q** was obtained as white solid (20.8 mg, 40%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.4 Hz, 2H), 8.02 – 7.95 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.24 (dd, *J* = 16.0, 8.0 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.0 (d, *J* = 258.7 Hz), 145.7, 136.2, 133.2, 130.9 (d, *J* = 9.8 Hz), 128.2, 117.2, 117.1 (d, *J* = 3.7 Hz), 117.0.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -102.34 (s).



4-tosylbenzonitrile  
 Chemical Formula:  $C_{14}H_{11}NO_2S$   
 Exact Mass: 257.0510  
 Molecular Weight: 257.3070

**(3r) 4-tosylbenzonitrile<sup>1</sup> (CAS: 38111-56-7)**

Following the General Procedure with 4-Bromobenzonitrile (36.4 mg, 0.2 mmol, 1.0 equiv), 4-methylbenzenesulfinic acid sodium salt (71.2 mg, 0.4 mmol, 2.0 equiv), **3r** was obtained as white solid (27.8 mg, 54%). This product of interest is purified by silica gel flash chromatography (PE: EA = 5:1)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 6.8 Hz, 2H), 7.83 (d, *J* = 6.8 Hz, 2H), 7.81 – 7.76 (m, 2H), 7.34 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 146.3, 145.3, 137.1, 133.1, 130.3, 128.1, 128.0, 117.2, 116.7, 21.7.

### 3. References

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## **4. Copies of NMR spectra**

