Arylation and Heteroarylation of Thienylsulfonamides with Organotrifluoroborates

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Supporting Information

ABSTRACT: A mild, practical protocol has been developed for the Suzuki cross-coupling of unprotected thienylsulfonamides from air- and bench-stable organotrifluoroborates in the absence of a protecting group on the sulfonamide nitrogen. The developed synthetic method can be applied to the preparation of various arylated and heteroarylated thienylsulfonamides under conditions that are tolerant of a broad range of functional groups.

Substituted thiophenes are important motifs in biologically active molecules and are routinely utilized as heterocyclic building blocks.1−6 Their structural rigidity and electronic features also make them abundant in organic light-emitting diodes, organic field-effect transistors, and organic solar cells.7−11 Thienylsulfonamides have been of particular interest in medicinal chemistry and are abundant in many biologically active compounds.12 Thienylsulfonamide I (Figure 1), the first drug-like compound selective to AT2 receptor agonist M024/C21, was reported in 2004.13 Additionally, Lawrence and co-workers reported the design and synthesis of a novel class of proteasome inhibitors, and their screening efforts led to the identification of PI 8182 (compound II, Figure 1) containing a thienylsulfonamide.14 Further, Waters and co-workers identified substituted thienylsulfonamides as drug targets against malarial and mammalian cyclin dependent protein kinases.15 Finally, compound III (Tasfulam, LY573636·Na, Figure 1) is a novel anticancer agent that was classified as a cytotoxic compound and shown to initiate apoptosis.16

To date, the most common access to arylated thienylsulfonamides is by Suzuki−Miyaura cross-coupling of protected thienylsulfonamides using arylboronic acids.17−19 However, the need for protection of the sulfonamide nitrogen and the homocoupling of the boronic acid as a significant side reaction are perceived shortcomings of this protocol.18 An alternative method toward protected arylated thienylsulfonamides involves sulfonylation of arylated thiophenes with sulfuric acid in the presence of Ac2O, thus requiring very stable substrates.20 Therefore, a general coupling method requiring no nitrogen protection and tolerating a broader scope of functional groups would be greatly desired.

Arylated thienylsulfonamides prepared by methods using aryltriﬂuoroborates have never been examined. Triﬂuoroborates21−28 are increasingly important reagents because of their favorable physical and chemical properties; additionally, they offer an alternative to toxic organometallic species such as organostannanes. The tetracoordinate nature of the triﬂuoroborates makes them resistant to a variety of reaction conditions. This characteristic allows one to build complexity into a molecule while leaving the carbon−boron bond intact. Unlike boronic acids, which are susceptible to undesired side reactions, organotriﬂuoroborates have proven to be air-, moisture-, and bench-stable reagents. The conventional preparation of aryltriﬂuoroborates includes (i) transmetalation, (ii) Miyaura borylation, and (iii) C−H activation.21−28 Herein, we report an effective and practical protocol for the preparation of unprotected thienylsulfonamides from various aryl- and heteroaryltriﬂuoroborates in the presence of a simple palladium catalyst and in the absence of a protecting group on the sulfonamide nitrogen, under conditions that are tolerant of a broad range of functional groups.

In initial screening, 5-bromothienyl-2-sulfonamide (1) was treated with phenyltriﬂuoroborate (1.1 equiv) in the presence of inexpensive Pd(PPh3)4 (5 mol %) under an argon atmosphere for 12 h, examining a variety of bases and solvents

Figure 1. Biologically active thienylsulfonamides.
be ineffective in the absence of base. Under the conditions tested, K2PO4 proved to be the best base for this reaction, affording the highest yield. Lowering the temperature below 100 °C gave lower yields. The nature of the solvent proved to be critical, with toluene (entries 6 and 7) being ineffective, while dioxane afforded the best results.

Under the conditions developed, the scope of the Suzuki coupling was evaluated. Various aryl- and heteroaryltrifluoroborates were employed, for which the results are described herein. The coupling reaction between 5-bromothienyl-2-sulfonamide (1a) and trifluoroborates took place efficiently, giving good to excellent yields (Table 2, 3a–3e) of arylated thienylsulfonamides, thus demonstrating the feasibility of this general method. Both electron-donating and electron-withdrawing groups were well-tolerated in this reaction and thus aldehydes, esters, methoxy, hydroxyl, and nitrile groups afforded good to excellent yields. In addition, there was no ortho steric effect on the yield of the reaction, with methyl, aldehyde, methoxy, and hydroxyl groups at that position leading to no discernible diminution of yield (Table 2, 3f,g,i,p,t,z,bb).

In those instances where modest yields were obtained, typically unreacted starting material was recovered together with negligible amounts of protodeboronation.

Under the same optimized conditions, heteroaryltrifluoroborates were also investigated (Table 3), demonstrating the effectiveness of this protocol. Diverse nitrogen-, oxygen-, and sulfur-containing heteroaryltrifluoroborates of various ring sizes were successfully cross-coupled with 5-bromothienyl-2-sulfonamide (1a). Isoquinolinyl (5a), pyridinyl (5b,c,h,j), furyl (5o–q), thienyl (5d,f,g,k,m), isoaxazolyl (5e), indolyl (5i,n), and dibenzothienyl (5l) trifluoroborates were all examined under the reaction conditions and afforded the desired products in good to excellent yields. Of note, chloride, nitro, and aldehyde substituents on the heteroaryltrifluoroborate were well-tolerated.

In conclusion, the results described herein reveal that the approach developed serves as a general, versatile method for the synthesis of diversely substituted NH2-free thienylsulfonamides from stable, commercially available, aryl- and heteroaryltrifluoroborates using inexpensive Pd(PPh3)4 as a catalyst.

### EXPERIMENTAL SECTION

**General.** Melting points (°C) are uncorrected. All known compounds were characterized by 1H and 13C NMR and melting point determination (for solids) and compared with literature values. All new compounds were characterized by 1H, 13C, 19F NMR spectra, high-resolution mass spectrometry (HRMS), and melting point determination (for solids). 1H, 13C, and 19F NMR spectra were recorded at 500.4, 125.8, and 470.8 MHz, respectively. HRMS (CI) data were obtained in positive mode, using ethane as the ionizing gas. HRMS (ESI) data were obtained in positive or negative mode. Reactions were performed using sealed biotage microwave vials purged with argon several times before use. Reactions were monitored by thin-layer chromatography carried out on silica plates using UV light for visualization. Chromatography was performed on a Combiflash RF 200 using hexanes and ethyl acetate as eluent.

**General Experimental Procedure for Suzuki–Miyaura Cross-Coupling Reaction of 3-Bromothienyl-2-sulfonamide with Aryl- and Heteroaryltrifluoroborates.** To 5-bromothienyl-2-sulfonamide (242.1 mg, 1.00 mmol) was added ary/ heteroaryltrifluoroborate (1.1 mmol), K2PO4 (636 mg, 3.00 mol), and Pd(PPh3)4 (58 mg, 0.05 mmol) in a vial, which was sealed and purged with argon three times. Then, 1a-dioxane (5 mL) was added, followed by the addition of H2O (1.25 mL). The solution was stirred at 100 °C, and the reaction was monitored by GCMS/TLC. After the reaction was complete, it was cooled to rt. Extraction was performed with EtOAc (30 mL × 3) to obtain the organic layer, which was filtered and dried (Na2SO4). The solvent was removed under reduced pressure. The residue obtained was purified by CombiFlash column chromatography using EtOAc and hexanes to obtain the desired product. The product was characterized by spectroscopic techniques.

### Table 1. Optimization of Reaction Conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Yield (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>K2PO4 (2 equiv)</td>
<td>dioxane</td>
<td>100</td>
<td>74</td>
</tr>
<tr>
<td>2</td>
<td>K2PO4 (2 equiv)</td>
<td>dioxane</td>
<td>100</td>
<td>84</td>
</tr>
<tr>
<td>3</td>
<td>K2PO4 (3 equiv)</td>
<td>dioxane</td>
<td>100</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>K2PO4 (3 equiv)</td>
<td>dioxane</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>5</td>
<td>K2CO3 (3 equiv)</td>
<td>dioxane</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>K2CO3 (3 equiv)</td>
<td>dioxane</td>
<td>100</td>
<td>n.r.</td>
</tr>
<tr>
<td>7</td>
<td>K2PO4 (2 equiv)</td>
<td>toluene</td>
<td>100</td>
<td>87</td>
</tr>
<tr>
<td>8</td>
<td>K2PO4 (3 equiv)</td>
<td>toluene</td>
<td>100</td>
<td>n.r.</td>
</tr>
<tr>
<td>9</td>
<td>K2PO4 (3 equiv)</td>
<td>dioxane</td>
<td>90</td>
<td>77</td>
</tr>
<tr>
<td>10</td>
<td>K2PO4 (3 equiv)</td>
<td>dioxane</td>
<td>75</td>
<td>38</td>
</tr>
<tr>
<td>11</td>
<td>KOAc (3 equiv)</td>
<td>dioxane</td>
<td>100</td>
<td>n.r.</td>
</tr>
<tr>
<td>12</td>
<td>Cs2CO3 (3 equiv)</td>
<td>dioxane</td>
<td>100</td>
<td>&lt;10</td>
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5-(2-Methoxyphenyl)thienyl-2-sulfonamide (3f). Obtained as a yellow solid (248 mg, 92%). mp 180–181 °C; 1H NMR (500 MHz, acetone-d6) δ 7.85–7.75 (m, 1H), 7.65–7.50 (m, 2H), 7.40–7.30 (m, 1H), 7.20–7.10 (m, 1H), 7.10–7.00 (m, 1H), 6.85 (br s, 2H), 3.98 (s, 3H); 13C NMR (125.8 MHz, acetone-d6) δ 156.0, 144.8, 144.5, 130.4, 130.1, 128.2, 124.6, 121.8, 121.5, 112.5, 55.7; HRMS (TOF MS ES+) m/z calcd. for C11H12NO3S2 [M + H]+, 270.0259; found, 270.0254.

5-(2-Formylphenyl)thienyl-2-sulfonamide (3g). Obtained as a yellow solid (246 mg, 92%). mp 177–178 °C; 1H NMR (500 MHz, acetone-d6) δ 10.18 (s, 1H), 7.99 (d, J = 7.5 Hz, 1H), 7.79–7.74 (m, 1H), 7.68–7.62 (m, 3H), 7.26 (dd, J = 7.8, 3.8 Hz, 1H), 7.01 (br s, 2H); 13C NMR (125.8 MHz, acetone-d6) δ 191.3, 147.7, 144.5, 136.7, 135.2, 134.7, 132.3, 131.4, 130.3, 130.2, 128.9; HRMS (TOF MS ES+) m/z calcd. for C11H9NO3S2Na [M + Na]+, 289.9922; found, 289.9924.

5-(3-Formyl-4-methoxyphenyl)thienyl-2-sulfonamide (3h). Obtained as a yellow solid (262 mg, 88%). mp 192–193 °C; 1H NMR (500 MHz, acetone-d6) δ 10.50–10.45 (m, 1H), 8.01–7.95 (m,
Table 3. Substrate Scope of Heteroarylated Thiencysulfonamides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>mp (°C)</th>
<th>1H NMR (500 MHz, acetone-d$_6$) δ</th>
<th>13C NMR (125.8 MHz, acetone-d$_6$) δ</th>
<th>HRMS (TOF MS ES+) m/z calcd. for</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-(6-Formylbenzo[d][1,3]dioxol-5-yl)thienyl-2-sulfonamide (3i)</td>
<td>88</td>
<td>210−212</td>
<td>9.94 (s, 1H), 7.63 (dd, $J = 4.0$, 1.5 Hz, 1H), 7.36 (s, 1H), 7.63 (dd, $J = 4.0$, 1.5 Hz, 1H), 7.07 (s, 1H), 6.99 (br s, 2H), 6.24 (s, 2H)</td>
<td>189.4, 153.4, 150.2, 147.8, 144.3, 133.9, 131.4, 130.8, 130.4, 111.6, 106.9, 104.1</td>
<td>333.9819</td>
<td>333.9817</td>
</tr>
<tr>
<td>5-(3-(Hydroxymethyl)phenyl)thienyl-2-sulfonamide (3j)</td>
<td>97</td>
<td>180−181</td>
<td>7.69 (s, 1H), 7.58−7.56 (m, 2H), 7.44−7.37 (m, 3H), 6.88 (br s, 2H), 4.69 (br s, 2H)</td>
<td>150.2, 145.1, 144.8, 133.8, 132.3, 130.1, 128.1, 125.4, 125.0, 124.1, 64.3</td>
<td>268.0103</td>
<td>268.0104</td>
</tr>
<tr>
<td>5-(3-Methoxyphenyl)thienyl-2-sulfonamide (3k)</td>
<td>74</td>
<td>170−171</td>
<td>7.60 (dd, $J = 8.5$, 4.5 Hz, 1H), 7.47 (dd, $J = 8.0$, 4.0 Hz, 1H), 7.42−7.36 (m, 1H), 7.30−7.22 (m, 2H), 7.01 (dd, $J = 8.0$, 2.5 Hz, 1H), 6.92 (br s, 2H), 3.89 (s, 3H)</td>
<td>161.2, 149.7, 145.1, 135.0, 132.1, 132.4, 126.7, 126.0, 125.8, 124.0, 114.4, 56.8</td>
<td>298.0208</td>
<td>298.0213</td>
</tr>
<tr>
<td>5-(Naphthalen-1-yl)thienyl-2-sulfonamide (3l)</td>
<td>98</td>
<td>243−244</td>
<td>8.17−8.15 (m, 1H), 8.04 (d, $J = 7.0$ Hz, 2H), 7.01 (d, $J = 4.0$ Hz, 1H), 7.65 (d, $J = 7.0$ Hz, 1H), 7.62−7.58 (m, 3H), 7.32−7.30 (m, 1H), 7.04 (br s, 1H)</td>
<td>147.5, 146.3, 143.9, 132.2, 131.5, 131.5, 130.4, 129.5, 129.3, 128.4, 128.0, 127.3, 126.3, 125.7</td>
<td>288.0153</td>
<td>288.0156</td>
</tr>
<tr>
<td>5-(4-(Benzyloxy)-2-formylphenyl)thienyl-2-sulfonamide (3m)</td>
<td>78</td>
<td>254−255</td>
<td>10.13 (s, 1H), 7.64 (d, $J = 4.0$ Hz, 1H), 7.60−7.50 (m, 4H), 7.45−7.32 (m, 4H), 7.17 (d, $J = 3.5$ Hz, 1H), 6.98 (br s, 2H), 5.28 (s, 2H)</td>
<td>191.0, 160.5, 147.3, 144.7, 137.7, 136.4, 133.9, 131.5, 129.9, 129.4, 129.2, 129.0, 128.6, 122.1, 113.4, 71.0</td>
<td>396.0340</td>
<td>396.0337</td>
</tr>
<tr>
<td>5-(6-Formylbenzo[d][1,3]dioxol-5-yl)thienyl-2-sulfonamide (3n)</td>
<td>72</td>
<td>235−236</td>
<td>8.25 (s, 1H), 8.01 (dd, $J = 8.0$, 1.0 Hz, 1H), 7.95 (d, $J = 7.5$ Hz, 1H), 7.62−7.57 (m, 2H), 7.53 (dd, $J = 4.0$, 1.5 Hz, 1H), 7.30−7.22 (m, 2H), 7.01 (dd, $J = 8.0$, 2.5 Hz, 1H), 6.92 (br s, 2H), 3.89 (s, 3H)</td>
<td>161.2, 149.7, 145.1, 135.0, 132.1, 132.4, 126.7, 126.0, 125.8, 124.0, 114.4, 56.8</td>
<td>298.0208</td>
<td>298.0213</td>
</tr>
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</table>
5-(3-Chloro-4-fluorophenyl)thienyl-2-sulfonamide (3d). Obtained as a yellow solid (323 mg, 84%). 1H NMR (500 MHz, acetone-\(\text{d}_6\)) \(\delta 7.75 (d, J = 7.5 Hz, 1H), 7.50 (m, 2H), 7.30 (m, 2H), 7.14 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 1.15 (t, J = 7.5 Hz, 3H); 13C NMR (125.8 MHz, acetone-\(\text{d}_6\)) \(\delta 155.4, 154.3, 149.3, 145.1, 134.5, 133.2, 129.0, 128.9, 128.7, 128.6, 126.4, 126.3, 53.1; HRMS (TOF MS ES+) m/z calcd. for C_{12}H_{12}NO_3S_2Na [M + Na]^+ 282.0259; found, 282.0259.

5-(3-Chloro-4-methoxyphenyl)thienyl-2-sulfonamide (3f). Obtained as a yellow solid (235 mg, 68%). 1H NMR (500 MHz, acetone-\(\text{d}_6\)) \(\delta 7.84 (d, J = 7.5 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 3.81 (s, 3H); 13C NMR (125.8 MHz, acetone-\(\text{d}_6\)) \(\delta 155.4, 149.3, 145.1, 134.5, 133.2, 128.9, 128.7, 128.6, 126.5, 125.7, 124.5, 122.7, 114.3, 111.7, 113.3, 114.1, 111.5, 113.6, 54.6; HRMS (TOF MS ES+) m/z calcd. for C_{12}H_{12}NO_3S_2Na [M + Na]^+ 368.0391; found, 368.0393.

5-(3-Chloro-4-fluorophenyl)thienyl-2-sulfonamide (3g). Obtained as a yellow solid (235 mg, 84%). 1H NMR (500 MHz, acetone-\(\text{d}_6\)) \(\delta 7.75 (d, J = 7.5 Hz, 1H), 7.50 (m, 2H), 7.30 (m, 2H), 7.14 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 1.15 (t, J = 7.5 Hz, 3H); 13C NMR (125.8 MHz, acetone-\(\text{d}_6\)) \(\delta 155.4, 149.3, 145.1, 134.5, 133.2, 129.0, 128.9, 128.7, 128.6, 126.4, 126.3, 53.1; HRMS (TOF MS ES+) m/z calcd. for C_{12}H_{12}NO_3S_2Na [M + Na]^+ 282.0259; found, 282.0259.

5-(2-Benzothiazol-2-yl)thienyl-2-sulfonamide (3h). Obtained as a yellow solid (235 mg, 68%). 1H NMR (500 MHz, acetone-\(\text{d}_6\)) \(\delta 7.84 (d, J = 7.5 Hz, 1H), 7.30 (d, J = 8.5 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 1.15 (t, J = 7.5 Hz, 3H); 13C NMR (125.8 MHz, acetone-\(\text{d}_6\)) \(\delta 155.4, 149.3, 145.1, 134.5, 133.2, 128.9, 128.7, 128.6, 126.5, 125.7, 124.5, 122.7, 114.3, 111.7, 113.3, 114.1, 111.5, 113.6, 54.6; HRMS (TOF MS ES+) m/z calcd. for C_{12}H_{12}NO_3S_2Na [M + Na]^+ 368.0391; found, 368.0393.

5-(3-Chloro-4-fluorophenyl)thienyl-2-sulfonamide (3i). Obtained as a yellow solid (235 mg, 84%). 1H NMR (500 MHz, acetone-\(\text{d}_6\)) \(\delta 7.75 (d, J = 7.5 Hz, 1H), 7.50 (m, 2H), 7.30 (m, 2H), 7.14 (d, J = 8.5 Hz, 1H), 7.07 (d, J = 8.0 Hz, 1H), 6.85 (d, J = 8.5 Hz, 1H), 6.75 (d, J = 7.5 Hz, 1H), 6.65 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 1.15 (t, J = 7.5 Hz, 3H); 13C NMR (125.8 MHz, acetone-\(\text{d}_6\)) \(\delta 155.4, 149.3, 145.1, 134.5, 133.2, 128.9, 128.7, 128.6, 126.4, 126.3, 53.1; HRMS (TOF MS ES+) m/z calcd. for C_{12}H_{12}NO_3S_2Na [M + Na]^+ 282.0259; found, 282.0259.
As a yellow solid (213 mg, 78%). mp 166–167 °C; 1H NMR (500 MHz, acetone-d6) δ 10.06 (s, 1H), 8.59 (d, J = 5.0 Hz, 1H), 7.85 (d, J = 5.0 Hz, 1H), 7.61 (dd, J = 8.5, 3.8 Hz, 1H), 7.41 (dd, J = 8.5, 4.0 Hz, 1H), 6.96 (br s, 2H); 13C NMR (125.8 MHz, acetone-d6) δ 185.6, 146.0, 141.5, 140.3, 139.9, 133.7, 131.3, 128.9, 128.2; HRMS (TOF MS ES+) m/z calcd. for C14H8N2O4S4 [M+Na]+: 285.8998; found: 285.8995.

**5-(5-Methylfuran-2-yl)thienyl-2-sulfonamide (5q).** Obtained as a yellow solid (213 mg, 78%). mp 166–167 °C; 1H NMR (500 MHz, acetone-d6) δ 10.06 (s, 1H), 8.59 (d, J = 5.0 Hz, 1H), 7.85 (d, J = 5.0 Hz, 1H), 7.61 (dd, J = 8.5, 3.8 Hz, 1H), 7.41 (dd, J = 8.5, 4.0 Hz, 1H), 6.96 (br s, 2H); 13C NMR (125.8 MHz, acetone-d6) δ 185.6, 146.0, 141.5, 140.3, 139.9, 133.7, 131.3, 128.9, 128.2; HRMS (TOF MS ES+) m/z calcd. for C14H8N2O4S4 [M+Na]+: 285.8998; found: 285.8995.

**5-(5-Methylfuran-2-yl)thienyl-2-sulfonamide (5q).** Obtained as a yellow solid (213 mg, 78%). mp 166–167 °C; 1H NMR (500 MHz, acetone-d6) δ 10.06 (s, 1H), 8.59 (d, J = 5.0 Hz, 1H), 7.85 (d, J = 5.0 Hz, 1H), 7.61 (dd, J = 8.5, 3.8 Hz, 1H), 7.41 (dd, J = 8.5, 4.0 Hz, 1H), 6.96 (br s, 2H); 13C NMR (125.8 MHz, acetone-d6) δ 185.6, 146.0, 141.5, 140.3, 139.9, 133.7, 131.3, 128.9, 128.2; HRMS (TOF MS ES+) m/z calcd. for C14H8N2O4S4 [M+Na]+: 285.8998; found: 285.8995.

**5-((2,2′-Bithiophen-4-yl)-1H-thienyl)-2-sulfonamide (5f).** Obtained as a yellow solid (223 mg, 78%). mp 202–203 °C; 1H NMR (500 MHz, acetone-d6) δ 9.02 (d, J = 1.5 Hz, 1H), 8.60–8.53 (m, 1H), 8.45–8.36 (m, 1H), 7.84 (d, J = 6.5 Hz, 1H), 7.71 (d, J = 6.5 Hz, 1H), 7.12 (br s, 2H); 13C NMR (125.8 MHz, acetone-d6) δ 157.1, 148.7, 146.5, 143.1, 137.8, 135.3, 132.4, 128.1, 119.5; HRMS (TOF MS ES+) m/z calcd. for C31H18N2O2S [M+H]+: 458.1172; found: 458.1173.

**5-((2,2′-Bithiophen-4-yl)-1H-thienyl)-2-sulfonamide (5f).** Obtained as a yellow solid (223 mg, 78%). mp 202–203 °C; 1H NMR (500 MHz, acetone-d6) δ 9.02 (d, J = 1.5 Hz, 1H), 8.60–8.53 (m, 1H), 8.45–8.36 (m, 1H), 7.84 (d, J = 6.5 Hz, 1H), 7.71 (d, J = 6.5 Hz, 1H), 7.12 (br s, 2H); 13C NMR (125.8 MHz, acetone-d6) δ 157.1, 148.7, 146.5, 143.1, 137.8, 135.3, 132.4, 128.1, 119.5; HRMS (TOF MS ES+) m/z calcd. for C31H18N2O2S [M+H]+: 458.1172; found: 458.1173.

**5-((2,2′-Bithiophen-4-yl)-1H-thienyl)-2-sulfonamide (5f).** Obtained as a yellow solid (223 mg, 78%). mp 202–203 °C; 1H N!M!R (500 MHz, acetone-d6) δ 9.02 (d, J = 1.5 Hz, 1H), 8.60–8.53 (m, 1H), 8.45–8.36 (m, 1H), 7.84 (d, J = 6.5 Hz, 1H), 7.71 (d, J = 6.5 Hz, 1H), 7.12 (br s, 2H); 13C NMR (125.8 MHz, acetone-d6) δ 157.1, 148.7, 146.5, 143.1, 137.8, 135.3, 132.4, 128.1, 119.5; HRMS (TOF MS ES+) m/z calcd. for C31H18N2O2S [M+H]+: 458.1172; found: 458.1173.

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REFERENCES


NOTE ADDED AFTER ASAP PUBLICATION

Table 1 entry 8 was corrected on July 15, 2014.