Electronic Supplementary Material (ESI) for New Journal of Chemistry
This journal is © The Royal Society of Chemistry and The Centre National de la Recherche Scientifique 2013

SUPPORTING INFORMATION

Efficient Desulfinylative Cross-Coupling of Heteroaromatic Sulfinates with Aryl Bromides in Water

*Stéphane Sévigny and Pat Forgione**

Department of Chemistry and Biochemistry, Concordia University, 7141 Sherbrooke Street West, Montréal, Québec, Canada H4B 1R6

e-mail: s_sevign@live.concordia.ca; pat.forgione@concordia.ca

Table of Contents

Electronic Supplementary Material (ESI) for New Journal of Chemistry
This journal is © The Royal Society of Chemistry and The Centre National de la Recherche Scientifique 2013

I. GENERAL

All anhydrous flasks were flame-dried while under high-vacuum and purged with argon unless otherwise stated. Solids were weighed on a balance open to air and added to a round bottom flask or microwave vial unless otherwise noted. Liquids were transferred using a glass syringe with a stainless steel needle or a micropipette for µL volumes unless noted otherwise. Manual flash chromatography columns were carried out using 40-63 µm silica gel from Silicycle.

All reagents were purchased from Sigma-Aldrich or Alfa Aesar and used without further purification unless otherwise noted. All solvents were purchased as ACS grade from Fischer Scientific or JT Baker unless otherwise noted. Anhydrous solvents were dried and stored in a flame-dried Schlenk flask using 3 Å molecular sieves, which were activated by heating at 150 ºC under high vacuum overnight. Distilled water was obtained from an in-house distillery.

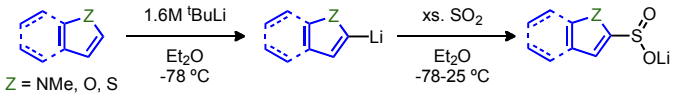
Unless otherwise noted, reactions were performed using a Biotage Initiator 2.3 build 6250 microwave reactor. Purifications by flash column chromatography were performed using a Teledyne Isco CombiFlash® R_f unless mentioned otherwise. Proton nuclear magnetic resonance spectra (^{1}H-NMR) were measured using a 500 MHz Varian VNMRS-500 in chloroform-d unless stated otherwise. Carbon nuclear magnetic resonance spectra (^{13}C-NMR) were measured at 125 MHz using the Varian VNMRS-500 in chloroform-d unless stated otherwise. The chemical shifts are reported in parts per million (ppm) and referenced from either residual solvent or tetramethylsilane (TMS) signal. The multiplicity is represented as; s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet which is indicated in parentheses along with the number of protons and coupling constants (in Hz). Gas chromatograph-mass spectral analyses (GC-MS) were obtained using an Agilent 7890A GC system and Agilent 5975C VL MSD with Triple-Axis Detector MS with a HP-588 column coated with (5%-phenyl)-methylpolysiloxane.

II. EXPERIMENTAL PROCEDURES

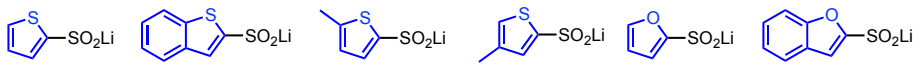
General procedure for the generation of anhydrous sulfur dioxide

To a three-neck flask equipped with a magnetic stir bar, sodium sulfite or sodium metabisulfite (1.0 equiv.) and water were added. Concentrated sulfuric acid (1.0 equiv.) was added drop-wise, with stirring, from a capped pressure-equalized addition funnel. The gas generated was then scrubbed twice *via* diffusion through concentrated sulfuric acid.

General procedure for the synthesis of heteroaromatic lithium sulfinates



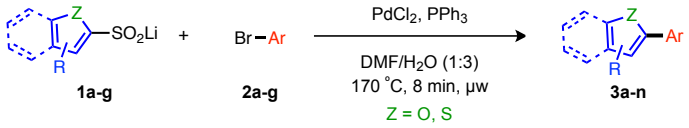
To a dried, rubber septum capped flask, under an argon stream, equipped with a magnetic stir bar and cooled to -78 ºC (in an EtOAc/$N_{2(l)}$ bath) was added the heteroaromatic (1.0 equiv.) with anhydrous diethyl ether (0.3 M). After 20 minutes, with stirring, *tert*-butyl lithium (0.9 equiv.) was added slowly with a glass syringe over 5 minutes. The reaction was stirred for 2 hours while maintaining a temperature of -78 ºC in an EtOAc/$N_{2(l)}$ bath. The reaction was then quenched by bubbling SO_2 produced from general procedure (A) for an hour, while warming to 23 ºC, precipitating the sulfinate salt. The salt was isolated *via* vacuum filtration, washed thoroughly with diethyl ether followed by acetone, and dried under vacuum. The solid was then ground to a fine powder, to which diethyl ether was added, and sonicated for 10 minutes, followed by vacuum filtration and drying under high vacuum.



1a, 94 % **1b, 85 %** **1c, 98 %** **1d, 75 %** **1f, 80 %** **1g, 78 %**

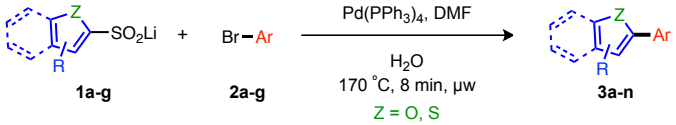
This journal is © The Royal Society of Chemistry and The Centre National de la Recherche Scientifique 2013

General procedure (A) for the arylation of thiophene- and furan-2-sulfinates



To a 5 mL conical microwave vial equipped with a spin-vein was added heteroaromatic sulfinate (0.30 mmol, 1.5 equiv.), aryl halide (0.20 mmol, 1.0 equiv.), $PdCl_2$ (0.01 mmol, 0.05 equiv.) and PPh_3 (0.05 mmol, 0.25 equiv.). H_2O/DMF (2 mL, 3:1 ratio) was then added and the vial was pre-stirred for 30 s at 23 ºC followed by heating at 170 ºC, for 8 min with stirring. The crude cross-coupling solution was diluted with EtOAc (25 mL). The organic layer was washed with a saturated NaCl aqueous solution (2x 50 mL), saturated $NaHCO_3$ aqueous solution (2x 25 mL), distilled H_2O (1x 25 mL), and saturated NaCl aqueous solution (1x 25 mL). The combined aqueous phases were washed with EtOAc (25 mL). The combined organic phases were dried over Na_2SO_4 and after filtration the solvent evaporated under reduced pressure and the solid residue was purified by flash column chromatography.

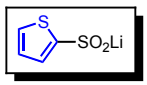
General procedure (B) for the arylation of thiophene- and furan-2-sulfinates



To a 5 mL conical microwave vial equipped with a spin-vein was added heteroaromatic sulfinate (0.40 mmol, 2.0 equiv.), aryl halide (0.20 mmol, 1.0 equiv.), $Pd(PPh_3)_4$ (0.01 mmol, 0.05 equiv.) and DMF (1.2 mmol, 6.0 equiv.). H_2O (2 mL) was then added and the vial was pre-stirred for 30 s at 23 ºC followed by heating at 170 ºC, for 8 min with stirring. The crude cross-coupling solution was diluted with EtOAc (25 mL). The organic layer was washed with a saturated NaCl aqueous solution (2x 25 mL), saturated $NaHCO_3$ aqueous solution (2x 25 mL), distilled H_2O (1x 25 mL), and saturated NaCl aqueous solution (1x 25 mL). The combined aqueous phases were washed with EtOAc 25 mL). The combined organic phases were dried over Na_2SO_4 and after filtration the solvent evaporated under reduced pressure and the solid residue was purified by flash column chromatography.

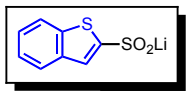
III. COMPOUNDS SYNTHESIZED

Lithium thiophene-2-sulfinate (1a)



The above compound was synthesized following general procedure (B) on a 128.84 mmol (20.01 g) scale. Yield 94% colourless powder. ^{1}H NMR (500 MHz, DMSO) δ 7.41 (ddd, J = 4.9, 1.2, 0.5 Hz, 1H), 7.00 (ddd, J = 3.4, 1.3, 0.5 Hz, 1H), 6.95 (ddd, J = 4.9, 3.4, 0.5 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 166.96, 126.56, 125.72, 123.48.

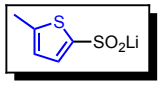
Lithium benzo[b]thiophene-2-sulfinate (1b)



The above compound was synthesized following general procedure (B) on a 18.7 mmol (3.82 g) scale. Yield 85% colourless powder. ^{1}H NMR (500 MHz, DMSO) δ 7.88 (d, J = 7.8 Hz, 1H), 7.77 (d, J = 7.3 Hz, 1H), 7.33 – 7.25 (m, 3H). ^{13}C NMR (126 MHz, DMSO) δ 166.76, 140.09, 140.05, 124.61, 124.52, 124.40, 123.14, 120.27.

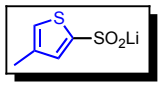
This journal is © The Royal Society of Chemistry and The Centre National de la Recherche Scientifique 2013

Lithium 5-methylthiophene-2-sulfinate (1c)



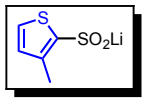
The above compound was synthesized following general procedure (B) on a 20.81 mmol (3.50 g) scale. Yield 98% colourless powder. ^{1}H NMR (500 MHz, DMSO) δ 6.76 (d, J = 3.2 Hz, 1H), 6.61 (d, J = 1.8 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 164.53, 139.05, 124.79, 123.13, 15.30.

Lithium 4-methylthiophene-2-sulfinate (1d)



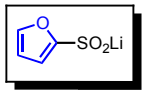
The above compound was synthesized following general procedure (B) on a 20.70 mmol (4.12 g) scale. Yield 75% colourless powder. ^{1}H NMR (500 MHz, DMSO) δ 6.96 (s, 1H), 6.79 (s, 1H), 2.14 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 166.70, 136.45, 125.61, 120.94, 105.94, 15.55.

Lithium 3-methylthiophene-2-sulfinate (1e)



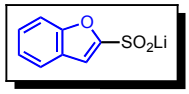
To a dry flask under argon atmosphere, equipped with a magnetic stir bar, 1.57 g (8.88 mmol, 1 equiv.) 2-bromo-3-methylthiophene synthesized by bromination of 3-methylthiophene,[1] was added along with 30 mL anhydrous diethyl ether. The flask was cooled to -78 ºC (using an EtOAc/$N_{2(l)}$ bath) and 10.5 mL (17.85 mmol, 2 equiv.) 1.7M *tert*-butyl lithium was added drop-wise over 5 minutes, with stirring. The reaction was stirred for two hours at -78 ºC in an EtOAc/$N_{2(l)}$ bath, and then quenched by bubbling SO_2 produced from general procedure (A) for an hour, while warming to 23 ºC, precipitating the sulfinate salt. The salt was isolated *via* vacuum filtration, washed thoroughly with diethyl ether, and dried under vacuum. The solid was then ground to a fine powder, to which diethyl ether is added, and sonicated for 10 minutes, followed by vacuum filtration, and dried under high vacuum. Yield 78% colourless powder. ^{1}H NMR (500 MHz, DMSO) δ 7.20 (d, J = 4.8 Hz, 1H), 6.71 (d, J = 4.8 Hz, 1H), 2.22 (s, 3H). ^{13}C NMR (126 MHz, DMSO) δ 160.55, 132.32, 130.03, 123.32, 13.50.

Lithium furan-2-sulfinate (1f)



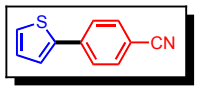
The above compound was synthesized following general procedure (B) on a 34.38 mmol (4.75 g) scale. Yield 80% light yellow powder. ^{1}H NMR (500 MHz, DMSO) δ 7.52 (s, 1H), 6.36 (dd, J = 3.1, 1.7 Hz, 1H), 6.31 (d, J = 3.1 Hz, 1H). ^{13}C NMR (126 MHz, DMSO) δ 169.63, 152.20, 141.97, 109.86, 105.23.

Lithium benzo[b]furan-2-sulfinate (1g)



The above compound was synthesized following general procedure (B) on a 18.15 mmol (3.42 g) scale. Yield 78% colourless powder. ^{1}H NMR (500 MHz, DMSO) δ 7.60 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 8.2 Hz, 1H), 7.26 (t, J = 7.1 Hz, 1H), 7.20 (t, J = 7.4 Hz, 1H), 6.75 (s, 1H). ^{13}C NMR (126 MHz, DMSO) δ 172.11, 154.64, 127.79, 124.06, 122.64, 121.59, 111.35, 101.53.

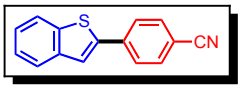
4-(Thiophen-2-yl)benzonitrile (3a, CAS: 15961-46-3)[2]



The above compound was prepared from the general procedure (A) on a 0.20 mmol (37.05 mg) scale, starting from lithium thiophene-2-sulfinate and 4-bromobenzonitrile. The target compound was isolated in 98% yield (36.31 mg) as a colourless solid using 1% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 185.0) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.62 (m, 4H), 7.42 (dd, J = 3.5, 0.9 Hz, 1H), 7.40 (dd, J = 5.1, 1.0 Hz, 1H), 7.13 (dd, J = 5.0, 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.20, 138.78, 132.85, 128.65, 127.19, 126.21, 125.23, 118.95, 110.70.

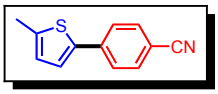
This journal is © The Royal Society of Chemistry and The Centre National de la Recherche Scientifique 2013

4-(Benzo[b]thiophen-2-yl)benzonitrile (3b, CAS: 132932-64-0)[3]



The above compound was prepared from the general procedure (A) on a 0.20 mmol (47.06 mg) scale, starting from lithium benzo[*b*]thiophene-2-sulfinate and 4-bromobenzonitrile. The target compound was isolated in 86% yield (40.47 mg) as a colourless solid using 1% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 235.1) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.74 (m, 4H), 7.71 – 7.65 (m, 2H), 7.64 (s, 1H), 7.43 – 7.34 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.75, 140.39, 140.06, 138.70, 132.80, 126.82, 125.47, 125.07, 124.27, 122.50, 121.88, 118.78, 111.47.

4-(5-Methylthiophen-2-yl)benzonitrile (3c, CAS: 1186368-93-3)

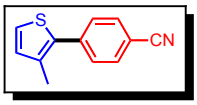


The above compound was prepared from the general procedure (A) on a 0.20 mmol (39.85 mg) scale, starting from lithium 5-methylthiophene-2-sulfinate and 4-bromobenzonitrile. The target compound was isolated in 97% yield (38.66 mg) as a colourless solid using 1% ethyl acetate in hexanes as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 – 7.57 (s, 4H), 7.22 (d, *J* = 3.6 Hz, 1H), 6.80 – 6.75 (m, 1H), 2.53 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.34, 139.71, 139.06, 132.78, 126.95, 125.64, 125.25, 119.10, 110.05, 15.70.

4-(4-Methylthiophen-2-yl)benzonitrile (3d, CAS: 1101167-54-7)[3]

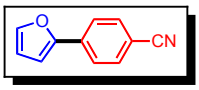
The above compound was prepared from the general procedure (A) on a 0.20 mmol (39.85 mg) scale, starting from lithium 4-methylthiophene-2-sulfinate and 4-bromobenzonitrile. The target compound was isolated in 73% yield (29.10 mg) as a colourless solid using 1% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 199.1) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 4H), 7.23 (m, 1H), 6.97 (m, 1.0 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.78, 139.34, 138.94, 132.79, 127.51, 125.93, 122.64, 119.00, 110.48, 15.89.

4-(3-Methylthiophen-2-yl)benzonitrile (3e, CAS: 1353717-30-2)



The above compound was prepared from the general procedure (A) on a 0.20 mmol (39.85 mg) scale, starting from lithium 3-methylthiophene-2-sulfinate and 4-bromobenzonitrile. The target compound was isolated in 58% yield (23.11 mg) as a colourless solid using 1% ethyl acetate in hexanes as the eluent. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 – 7.65 (m, 2H), 7.59 – 7.55 (m, 2H), 7.30 (d, *J* = 4.9 Hz, 1H), 6.96 (d, *J* = 5.0 Hz, 1H), 2.36 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.71, 135.86, 135.12, 132.46, 131.84, 129.37, 125.31, 118.99, 110.63, 15.33.

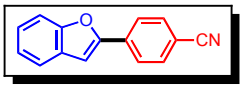
4-(Furan-2-yl)benzonitrile (3f, CAS: 64468-77-5)[2]



The above compound was prepared from the general procedure (B) on a 0.20 mmol (33.64 mg) scale, starting from lithium furan-2-sulfinate and 4-bromobenzonitrile. The target compound was isolated in 65% yield (21.87 mg) as a yellow solid using 1% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 169.1) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 – 7.73 (m, 2H), 7.68 – 7.62 (m, 2H), 7.55 – 7.52 (m, 1H), 6.84 – 6.79 (m, 1H), 6.55 – 6.50 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.11, 143.82, 134.78, 132.72, 124.08, 119.07, 112.37, 110.42, 108.29.

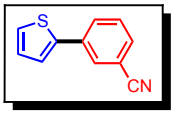
This journal is © The Royal Society of Chemistry and The Centre National de la Recherche Scientifique 2013

4-(Benzo[b]furan-2-yl)benzonitrile (3g, CAS: 41013-94-9)[3]



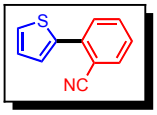
The above compound was prepared from the general procedure (A) on a 0.20 mmol (43.85 mg) scale, starting from lithium benzo[*b*]furan-2-sulfinate and 4-bromobenzonitrile. The target compound was isolated in 82% yield (35.96 mg) as a colourless solid using 1% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 219.1) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.74 – 7.69 (m, 2H), 7.64 – 7.62 (m, 1H), 7.54 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.38 – 7.33 (m, 1H), 7.30 – 7.26 (m, 1H), 7.17 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.38, 153.67, 134.58, 132.74, 128.79, 125.69, 125.24, 123.57, 121.63, 118.86, 111.65, 111.55, 104.47.

3-(Thiophen-2-yl)benzonitrile (3h, CAS: 380626-35-7)[4]



The above compound was prepared from the general procedure (A) on a 0.20 mmol (37.05 mg) scale, starting from lithium thiophene-2-sulfinate and 3-bromobenzonitrile. The target compound was isolated in 70% yield (25.94 mg) as a colourless solid using 1% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 185.0) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 – 7.85 (m, 1H), 7.83 – 7.80 (m, 1H), 7.55 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.48 (td, *J* = 7.8, 0.6 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.12 (dd, *J* = 5.0, 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.75, 135.79, 130.71, 130.11, 129.86, 129.30, 128.52, 126.47, 124.58, 118.68, 113.30.

2-(Thiophen-2-yl)benzonitrile (3i, CAS: 125610-77-7)[5]

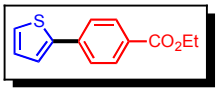


The above compound was prepared from the general procedure (B) on a 0.20 mmol (37.05 mg) scale, starting from lithium thiophene-2-sulfinate and 2-bromobenzonitrile. The target compound was isolated in 84% yield (31.12 mg) as a colourless solid using 1% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 185.0) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (ddd, *J* = 7.8, 1.3, 0.6 Hz, 1H), 7.65 – 7.57 (m, 3H), 7.44 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.38 (m, 1H), 7.16 (dd, *J* = 5.1, 3.7 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.53, 137.70, 134.43, 133.08, 129.82, 128.36, 127.73, 127.66, 127.45, 118.95, 110.18.

2-(4-(Trifluoromethyl)phenyl)thiophene (3j, CAS: 115933-15-8)[2]

The above compound was prepared from the general procedure (B) on a 0.20 mmol (45.65 mg) scale, starting from lithium thiophene-2-sulfinate and 4-bromobenzotrifluoride. The target compound was isolated in 44% yield (20.09 mg) as a colourless solid using hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 228.0) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.8, 0.7 Hz, 2H), 7.63 (dd, *J* = 8.8, 0.6 Hz, 2H), 7.40 (dd, *J* = 3.6, 1.1 Hz, 1H), 7.36 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.61, 137.75, 128.29, 126.20, 125.95, 125.89, 125.86, 124.43. ^{19}F NMR (470 MHz, $CDCl_3$) δ -62.57.

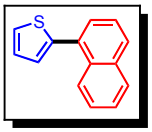
Ethyl 4-(thiophen-2-yl)benzoate (3k, CAS: 75601-33-1)[2]



The above compound was prepared from the general procedure (A) on a 0.20 mmol (46.46 mg) scale, starting from lithium thiophene-2-sulfinate and ethyl 4-bromobenzoate. The target compound was isolated in 65% yield (30.20 mg) as a colourless solid using 1-2% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 232.1) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.70 – 7.64 (m, 2H), 7.43 – 7.40 (m, 1H), 7.37 – 7.34 (m, 1H), 7.13 – 7.09 (m, 1H), 4.39 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.39, 143.26, 138.65, 130.36, 129.29, 128.42, 126.34, 125.61, 124.56, 61.11, 14.49.

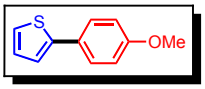
This journal is © The Royal Society of Chemistry and The Centre National de la Recherche Scientifique 2013

2-(Naphthalen-1-yl)thiophene (3l, CAS: 4632-51-3)[2]



The above compound was prepared from the general procedure (B) on a 0.20 mmol (42.06 mg) scale, starting from lithium thiophene-2-sulfinate and 2-bromonaphthalene. The target compound was isolated in 49% yield (20.61 mg) as a colourless solid using hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 210.1) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.20 (m, 1H), 7.93– 7.85 (m, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 7.0 Hz, 1H), 7.55 – 7.47 (m, 3H), 7.46 – 7.42 (m, 1H), 7.29 – 7.23 (m, 1H), 7.22 – 7.18 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.92, 134.00, 132.59, 132.04, 128.53, 128.45, 128.33, 127.52, 127.40, 126.57, 126.13, 125.90, 125.75, 125.37.

2-(4-Methoxyphenyl)thiophene (3m, CAS: 42545-43-7)[2]



The above compound was prepared from the general procedure (B) on a 0.20 mmol (38.06 mg) scale, starting from sodium thiophene-2-sulfinate and 4-bromoanisole. The target compound was isolated in 22% yield (8.37 mg) as a colourless solid using 5% ethyl acetate in hexanes as the eluent. The NMR spectrum was consistent with that found in the literature, and the mass obtained (m/z: 190.1) by GC-MS matched. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 1H), 7.23 – 7.19 (m, 1H), 7.05 (dd, J = 5.1, 3.6 Hz, 2H), 6.94 – 6.90 (m, 2H), 3.84 (s, 3H).

REFERENCES

(1). Hoffmann, K. J.; Carlsen, P. H. J., *Synth. Commun.* **1999,** *29*, 1607-10.
(2). Denmark, S. E.; Baird, J. D.; Regens, C. S., *J. Org. Chem.* **2008,** *73*, 1440-55.
(3). Molander, G. A.; Canturk, B.; Kennedy, L. E., *J. Org. Chem.* **2009,** *74*, 973-80.
(4). Yabe, Y.; Maegawa, T.; Monguchi, Y.; Sajiki, H., *Tetrahedron* **2010,** *66*, 8654-60.
(5). Cahiez, G.; Duplais, C.; Buendia, J., *Angew. Chem. Int. Ed.* **2009,** *121*, 6859-62.