Supporting Information for

A Mild, Non-basic Synthesis of Thioethers. The Copper-Catalyzed Coupling of Boronic Acids with *N*-Thio(alkyl, aryl, heteroaryl)imides.

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GENERAL METHODS

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a Varian Inova 400MHz (400 MHz ^{1}H, 100.0 MHz ^{13}C, 376.3 MHz ^{19}F) spectrometer in deuteriochloroform ($CDCl_3$) or deuterio-DMSO ($(CD_6)_2SO$) with either chloroform (7.26 ppm ^{1}H, 77.00 ppm) or DMSO (2.50 ppm, ^{1}H) as internal reference unless otherwise stated. ^{19}F NMR spectra was referenced with trifluoromethyltoluene in benzene (-63.7 ppm) as external standard. Data are reported in the following order: chemical shifts are given ( ); multiplicities are indicated (br (broadened), s (singlet), d (doublet), t (triplet), q (quartet), pent (pentuplet), hex (hextet), hept (heptet), m (multiplet), exch (exchangeable), app (apparent)); coupling constants, J, are reported (Hz); integration is provided. Infrared spectra were recorded on a ASI ReactIR 1000FT-IR spectrometer with a silicone probe. Peaks are reported (cm^{-1}) with the following relative intensities: s (strong, 67-100%), m (medium, 40-67%), w (weak, 20-40%) and br (broad). GC-MS spectra were recorded on a Shimadzu Gas Chromatograph GC-17A, Mass Spectrometer QP-5000. GC/MS analysis was carried out on a bonded 5% diphenylsiloxane capillary column (30m, 0.25mm id, 0.25 m df). Elementary analyses were performed by Atlantic Microlab, Inc., Norcross, Georgia. Melting points were taken on a Thomas-Hoover melting point apparatus in open capillary tubes and are uncorrected. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel 60 plates, 0.25 mm thick with F-254 indicator. Visualization was accomplished by UV light, 5% phosphomolybdic acid solution in ethanol. Flash column chromatography was performed by the method of Still with 32-63 m silica gel (Woelm). Rotary chromatography was performed with a Chromatotron from Harrison Research using 4 mm PF-254 silica rotors. Preparative plate

chromatography was performed on Merck silica gel 60 plates, 0.5 mm thick with F-254 indicator. Solvents for extraction and chromatography were reagent grade and used as received. Dried solvents (THF, toluene, CH_3CN, benzene, DMA) used as reaction media were purchased from Aldrich and dried over 4Å molecular sieves and titrated for water level prior to use with a Fisher Coulomatic K-F titrator. Et_3N and pyridine were dried over 4Å molecular sieves. All solvents, unless otherwise noted were sparged with nitrogen for several hours. All reactions were performed under an atmosphere of dry nitrogen,. "Brine" refers to a saturated aqueous solution of NaCl. Unless otherwise specified, solutions of HCl, NH_4Cl, and $NaHCO_3$ refer to aqueous solutions.

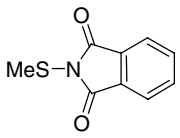
STARTING MATERIALS

N-Chlorosuccimide (NCS), *N*-bromosuccinimide (NBS), thiocresol, dodecylthiol, dimethyldisulfide, 4-nitrobenzenethiol, 3-methylsalicylic acid, thiophene-2-carboxylic acid, phenylboronic acid, and Cu_2O were purchased from Aldrich Chemical Co. and used as received. Other boronic acid reagents were obtained from Frontier Scientific.

Copper (I)-3-methylsalicylate, CuMeSal.

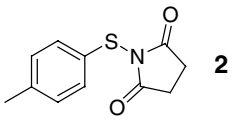
Cu_2O (6.9 g, 0.09 mol of Cu, 1.0 equiv) and 3-methylsalicylic acid (23.0 g, 0.15 mol, 1.6 equiv) were introduced into a 1000 mL round-bottomed flask, which was equipped with a Dean-Stark apparatus. Under argon, dry and degassed toluene (200 mL) was added and the mixture was refluxed for 2 days. CuMeSal was filtered under argon, washed with dry and degassed toluene (2 x 100 mL), MeOH (50 mL), ether (200 mL) and dried for 2 h. CuMeSal (16.7 g, 0.08 mol, 88%) was obtained as a beige powder. Mp 205 °C (decomp). IR (KBr pellet, cm^{-1}): 3210 (br), 1873 (s), 1734 (s), 1597 (s). ^1H NMR (d_6 DMS, 400 MHz): 14.35 (br s, 1 H), 7.75 (d, J = 6.8 Hz,1 H), 7.08 (d, J = 6.4 Hz,1 H), 6.58 (t, J = 6.8 Hz, 1 H), 2.21 (s, 3 H). Anal. Calcd for $C_8H_7O_3Cu$: C, 44.75; H, 3.29; O, 22.36; Found: C, 44.55; H, 3.18; O, 22.22.

Preparation of N-Thioimides



1

2-Methylsulfanyl-1*H*-isoindole-1,3(2*H*)-dione, **1**, was prepared by a literature procedure.[1] TLC (dichloromethane, $R_f = 0.40$); Mp 167-168 °C (dichloromethane/hexanes, lit.{175-176 °C[1]}); IR (neat): 1787 (m), 1745 (s), 1718 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.93-7.91 (m, 2 H), 7.78-7.76 (m, 2 H), 2.53 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 168.1, 134.6, 132.0, 123.8, 22.4.



2

N-(*p*-Tolylthio)succinimide, **2**, was prepared by a literature procedure.[2] TLC (CH_2Cl_2-ethanol, 20:1, $R_f = 0.74$) Mp 111-112 °C (ethanol; lit.{113 °C,[2] 114-115 °C [3]}; IR (CCl_4, KCl, cm^{-1}): 2914 (w), 2848 (m), 1731 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.59 (d, J = 8.4 Hz, 2 H), 7.15 (d, J = 8.4 Hz, 2 H), 2.78 (s, 3 H), 2.24 (s, 4 H).

General Procedure for the Preparation of Aryl/Alkylthiosuccinimides 3 – 6. *N*-Chlorosuccimide (1.0 equiv) was added to a mixture of thiol (1.0 equiv) in dry, degassed benzene or toluene at room temperature. The mixture was stirred for 30–120 min. Et_3N (1.0 equiv) in dry and degassed benzene (30 mL) was then added then over 30 min and the reaction mixture was stirred for 4-12 h. Depending on the solubility of the substrate, different work-up procedures were used. *Method A*: ether:hexanes (4:1) was added and the resulting solid was filtered. The filtrate was evaporated, and the resulting solid was washed with ether and hexanes. *Method B*: 1:4 ether:hexanes was added and the resulting solid was filtered. The solid was washed with water and then recrystallized from

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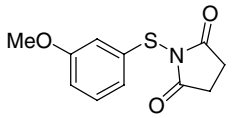
[1] Klose, J.; Reese, C. B.; Song, Q. *Tetrahedron.* **1997**, *53*, 42, 14411-14416.

[2] Reaction of disulfide and trisulfide with *N*-chlorocarboxamide. Furukawa, M.; Fujino, Y.; Kojima, Y.; Ono, M.; Hayashi, S. *Chem. Pharm. Bull.* **1972**, *26*, 9, 2024-2028.

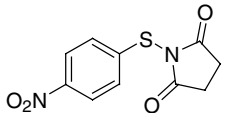
[3] The preparation of *N*-(alkylthio)- and *N*-(arylthio)succinimide. Abe, Y.; Nakabayashi, T.; Tsurugi, J. *Bull. Chem. Soc. Jap.* **1973,** *46*, 1898-1899.

dichloromethane-hexanes or ethanol; the *N*-thiosuccinimides were obtained as white needles. The reaction time and conditions were not optimized.



3

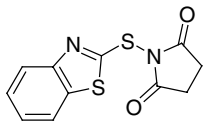
*1-(3-Methoxy-phenylsulfanyl)-pyrrolidine-2, 5-dione, **3**.* *N*-Chlorosuccinimide (1.90 g, 0.014 mol, 1.0 equiv) was added to 3-methoxythiophenol (2.00 g, 0.014 mol, 1.0 equiv) in dry benzene (60 mL). The reaction mixture changed from colorless to yellow. After 30 min. at room temperature, Et_3N (2.0 mL, 0.014 mmol, 1.0 equiv) in dry benzene (40 mL) was added over a 30 min. period. After stirring for 12 hr, Et_2O was added and the resulting white precipitate was filtered. After evaporation of the filtrate, the solid obtained was washed with ether (100 mL) and hexanes (40 mL). After recrystallization from dichloromethane-hexanes, product **3** (2.6 g, 0.011 mol, 78%) was obtained as white crystals. TLC (dichloromethane, $R_f = 0.12$); Mp 149-150 °C (dichloromethane/hexanes); IR (neat): 3083 (w), 2999 (w), 2941 (w), 2841 (w), 1725 (s), 1590 (s), 1580 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.24 (t, *J* = 8.4 Hz, 1 H), 7.13 (app d, *J* = 8.0 Hz, 1 H), 7.09 (t, *J* = 1.6 Hz, 1 H), 6.86 (dd, *J* = 7.6, 1.6 Hz, 1 H), 3.74 (s, 3H), 2.81 (s, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 176.4, 159.8, 134.9, 130.1, 123.6, 116.4, 115.7, 55.3, 28.5. Anal. Calcd for $C_{11}H_{11}O_3NS$: C, 55.68; H, 4.67; S, 13.51; N, 5.90; Found: C, 55.58; H, 4.61; S, 13.57; N, 5.92. LRMS (FAB+), m/z (relative intensity) 244 (11), 219 (10), 166 (10), 160 (100). HRMS (FAB+) Calcd for $C_{11}H_{11}O_3NSLi$: 244.0602. Found: 244.0627.



4

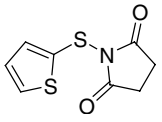
*1-(4-Nitrophenylsulfanyl)-pyrrolidine-2, 5-dione, **4**.* *N*-Chlorosuccinimide (0.90 g, 0.007 mol, 1.0 equiv) was added to 4-nitrothiophenol (1.20 g, 0.007 mol, 1.0 equiv) in dry toluene (60 mL). After 30 min. at room temperature, Et_3N (0.9 mL, 0.006 mmol, 0.9 equiv) in dry benzene (10 mL) was added over a 30 min. period. After 12 hr, addition of Et_2O gave a white precipitate that was filtered and washed with water. SiO_2 chromatography (Chromatotron, 4 mm thick, dichloromethane as

eluant) and recrystallization of the solid from $CHCl_3$ gave product **4** (0.75 g, 0.003 mol, 43 %) as white crystals. TLC (dichloromethane, R_f =0.15); Mp 170-171 °C (ethanol; lit.{160-171 °C[4]}); IR (neat, cm^{-1}): 3013 (w), 2933 (w), 2853 (w), 1729 (s), 1598 (m). ^{1}H NMR ($CDCl_3$, 400 MHz): 8.17 (d, *J* = 8.8 Hz, 2 H), 7.44 (d, *J* = 8.8 Hz, 2 H), 2.97 (s, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 175.6, 147.2, 142.9, 127.4, 124.4, 28.7.



5

1-(Benzothiazol-2-ylsulfanyl)-pyrrolidine-2, 5-dione, ***5***. *N*-Chlorosuccinimide (7.07 g, 0.053 mol, 1.0 equiv) was added to benzothiazole (8.69 g, 0.052 mol, 1.0 equiv) in dry benzene (220 mL). After 30 min. at room temperature, Et_3N (7.3 mL, 0.052 mmol, 1.0 equiv) in dry benzene (75 mL) was added over a 30 min. period After 12 hr, Et_2O was added and the resulting white precipitate was filtered and washed with water. Recrystallization of the solid from EtOH gave product **5** (6.00 g, 0.02 mol, 45 %) as white crystals. TLC (dichloromethane, R_f =0.23); Mp 143-145 °C (ethanol); IR (neat): 3083 (w), 2937 (w), 1737 (s), 1714 (s), 1652 (w). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.88 (app d, *J* = 8.0 Hz, 1 H), 7.76 (app d, *J* = 8.0 Hz, 1 H), 7.44 (dt, *J* = 7.2, 1.2 Hz, 1 H); 7.34 (dt, *J* = 7.2, 1.2 Hz, 1 H), 3.03 (s, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 175.0, 163.0, 152.9, 135.4, 126.5, 125.2, 122.7, 121.2, 28.8. Anal. Calcd for $C_{11}H_8O_2N_2S_2$. ½ H_2O: C, 48.34; H, 3.32; S, 23.46; N, 10.25; Found: C, 48.38; H, 3.37; S, 23.54; N, 9.93. LRMS (EI), m/z (relative intensity) 264 (20), 224 (11), 166 (60), 122 (17), 108 (35), 99 (39), 69 (14). HRMS (EI) Calcd for $C_{11}H_8O_2N_2S_2$: 264.0027. Found: 264.0026.



6

1-(Thiophene-2-ylsulfanyl)-pyrrolidine-2, 5-dione, ***6***. *N*-Chlorosuccinimide (2.50 g, 0.019 mol, 1.0 equiv) was added to 2-mercaptothiophene (2.20 g, 0.019 mol, 1.0 equiv) in dry toluene (65 mL). After 30 min. at room temperature, Et_3N (2.6 mL, 0.019 mmol, 1.0 equiv) in dry toluene (10

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[4] LaLonde R. T.; Eckert, T. S. *Can. J. Chem.* **1981**, *59*, 2298-2302.

mL) was added over a 30 min. period. After 12 hr, Et_2O (80 mL) was added, and the resulting white precipitate filtered. Evaporation of the filtrate and recrystallization of the solid from EtOH gave product **6** (1.10 g, 0.005 mol, 27%) as white crystals. TLC (dichloromethane, R_f=0.26); Mp 107-108 °C (dichloromethane/hexanes); IR (neat): 3083 (w), 2999 (w), 2941 (w), 1725 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.58 (dd, *J* = 3.6, 1.2 Hz, 1 H), 7.54 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.03 (dd, *J* = 5.2, 3.6 Hz, 1 H); 2.77 (s, 4 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 175.9, 139.4, 134.4, 131.0, 127.7, 28.5. Anal. Calcd for $C_8H_7O_2NS_2$: C, 45.05; H, 3.31; N, 6.57; S, 30.07; Found: C, 44.51; H, 3.38; N, 6.25; S, 30.43. LRMS (FAB+), m/z (relative intensity) 214 (80), 213 (20), 197 (100). HRMS (FAB+) Calcd for $C_8H_8O_2NS_2$: 213.9996. Found: 213.9995.

General Procedure for the Copper-catalyzed Coupling of N-Thioimides and Boronic Acids:

The *N*-thioimide derivative (1.0 equiv), boronic acid (1.5-2.0 equiv) and CuMeSal (20-30%) were introduced into a 25 mL Schlenck tube. After a vacuum/argon cycle, dry and degassed THF was added. The reaction mixture was stirred under argon at 45-50 °C for 2.5-12 h with monitoring by TLC and GC/MS. Upon completion of the reaction, the reaction mixture was diluted with dichloromethane (20-40 mL) and then quenched with 2N HCl (20 mL) or, for acid senstitive substrates, with sat'd aqueous NH_4Cl (20 mL). The organic layer was dried (Na_2SO_4 or $MgSO_4$), filtered, and then evaporated to dryness. The crude product was then purified by SiO_2 chromatography (Chromatotron, 4mm thick plate of silica gel, or preparative thin layer plate). The reactions were run only once and are not optimized.

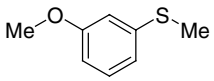

Table Entry 1. 1-Methoxy-3-methylsulfanyl-benzene.[5] THF (1.0 mL) was added to 2-methylsulfanyl-1*H*-isoindole-1,3(2*H*)-dione (35 mg, 0.18 mmol, 1.0 equiv), 3-methoxyphenylboronic

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[5] Oxidation of alkylthio substituted tricarbonyl(η^6-arene)chromium(0) complexes to alkylsulfinyl substituted tricarbonyl(η^6-arene)chromium(0) complexes Perez-Encabo, A.; Perrio, S.; Slawin, A. M. Z.; Thomas, S. E.; Wierzchleyski, A. T.; William, D. J. *J. Chem. Soc. Perkin Trans1* **1994**, *6*, 629-642.

acid (50 mg, 0.33 mmol, 1.8 equiv) and CuMeSal (12 mg, 0.06 mmol, 31 %). The reaction was stirred for 4 h at 45-50 °C. After preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant), product (22 mg, 0.14 mmol, 79%) was obtained as a colorless oil. TLC (1:1 hexanes:dichloromethane, $R_f = 0.48$); IR (neat, cm^{-1}): 3000 (w), 2961 (w), 2922 (w), 2837 (w), 1590 (s), 1478 (s). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.20 (t, J = 8.1 Hz, 1 H), 6.84 (td, J = 7.8, 0.6 Hz, 1 H), 6.80 (app t, J = 2.1 Hz, 1 H), 6.68 (dd, J = 8.4, 2.4 Hz, 1 H), 3.80 (s, 3 H), 2.48 (s, 3 H).

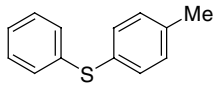

Table Entry 2. 1-Methyl-4-phenylsulfanyl-benzene.[6] THF (1.5 mL) was added to *N*-(*p*-tolylthio)succinimide (104 mg, 0.47 mmol, 1.0 equiv), phenylboronic acid (113 mg, 0.93 mmol, 2.0 equiv) and CuMeSal (30 mg, 0.14 mmol, 29%). After 3 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant) gave product (56 mg, 0.28 mmol, 60 %) as a colorless oil. TLC (hexanes, $R_f = 0.50$); ^{1}H NMR ($CDCl_3$, 400 MHz): 7.33 (d, J = 8.0 Hz, 2 H), 7.22-7.30 (m, 5H), 7.15 (d, J = 8.0 Hz, 2 H), 2.36 (s, 3 H).

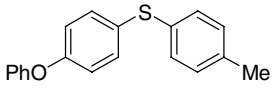

Table Entry 3. 1-Phenoxy-4-methylphenylsulfanyl-benzene. THF (3.0 mL) was added to *N*-(*p*-tolylthio)succinimide (104 mg, 0.47 mmol, 1.0 equiv), 4-phenoxyphenylboronic acid (176 mg, 0.83 mmol, 1.8 equiv) and CuMeSal (30 mg, 0.14 mmol, 30 %). After 4 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant) gave product (96 mg, 0.33 mmol, 70 %) as a white solid. TLC (1:1 hexanes:dichloromethane, R_f =0.75); Mp 42-43 °C (lit.{41-42°C (ethanol)[7]});

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[6] Reduction of aryl thiocyanates with SmI_2 and Pd-catalyzed coupling wuth aryl halides as a route to mixed aryl sulfides Still, I. W. J.; Toste, F. D. *J. Org. Chem.* **1996**, *61*, 7677-7680.

[7] Spettri nel vicino u.v. del *p*-(fenossi)-difenilsolfone e corrispondenti metil-, cloro-, nitro-, amino- ed acetilamino-derivati Arcoria, A.; Marziano, N.; Passerini, R. *Gazz. Chim. Ital.* **1961**, *91*, 223-241.

^{1}H NMR ($CDCl_3$, 400 MHz): 7.38-7.32 (m, 4 H), 7.26 (td, *J* = 8.0, 1.2 Hz, 2H), 7.16-7.12 (m, 3H), 7.02 (qd, *J* = 8.8, 1.2 Hz, 2 H), 6.93 (td, *J* = 9.2, 2.4 Hz, 2H), 2.33 (s, 3 H).

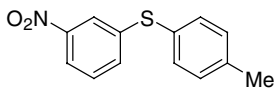

Table Entry 4. 1-Methyl-4-(3-nitro)-phenylsulfanyl-benzene. THF (1.7 mL) was added to *N*-(*p*-tolylthio)succinimide (100 mg, 0.45 mmol, 1.0 equiv), 3-nitrophenylboronic acid (140 mg, 0.84 mmol, 1.9 equiv) and CuMeSal (29 mg, 0.14 mmol, 30%). After 4 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes:dichloromethane, 3:1 as eluant) gave product (56 mg, 0.22 mmol, 51 %) as yellow needles. TLC (3:2 hexanes:EtOAc, R_f = 0.78); Mp 59-61 °C (ethanol, lit.{60-61°C (ethanol)[8]}); ^{1}H NMR ($CDCl_3$, 400 MHz): 7.97-7.95 (m, 2 H), 7.45-7.36 (m, 4H), 7.23 (d, *J* = 8.0 Hz, 2 H), 2.40 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 148.7, 141.6, 139.6, 134.2, 133.3, 130.7, 129.5, 127.8, 122.2, 120.4, 21.3.

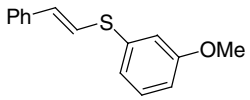

Table Entry 5. 1-Methoxy-3-((E)-phenylacetylenesulfanyl)-benzene. THF (2.0 mL) was added to 1-(3-methoxyphenyl)-pyrrolidine-2,5-dione (105 mg, 0.44 mmol, 1.0 equiv), *trans*-β-styrylboronic acid (132 mg, 0.89 mmol, 2.0 equiv) and CuMeSal (29 mg, 0.13 mmol, 30%). After 4 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant) gave product (77 mg, 0.33 mmol, 72 %) as a yellowish oil. TLC (1:1 hexanes:dichloromethane, R_f =0.57); IR (neat): 1590 (s). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.38-7.24 (m, 6 H), 7.01 (td, *J* = 7.6, 1.6 Hz, 1 H), 6.96 (t , *J* = 2.4 Hz, 1 H), 6.91 (d, *J* = 15.2 Hz, 1 H), 6.81 (ddd, *J* = 8.0, 2.4, 0.4 Hz, 1 H), 6.77 (d, *J* = 15.2 Hz, 1 H), 3.81 (s, 3 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 160.0, 136.6, 136.4, 132.1, 129.9, 128.7 127.6, 126.0, 122.9, 121.8, 114.8, 112.7, 55.3. Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82; S, 13.23; Found: C, 74.16; H, 5.81; S, 12.97.

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[8] Passerini. *Boll. Sci. Fac. Chim. Ind. Bologna.* **1950**, *8*, 1-122.

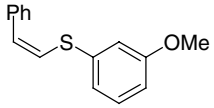

Table Entry 6. 1-Methoxy-3-((Z)-phenylacetylenesulfanyl)-benzene. THF (2 mL) was added to 1-(3-methoxyphenyl)-pyrrolidine-2,5-dione (55 mg, 0.22 mmol, 1.0 equiv), *cis*-β-styrylboronic acid (66 mg, 0.44 mmol, 2.0 equiv) and CuMeSal (14 mg, 0.07 mmol, 30%). After 48 h at 45-50 °C, only a trace of product was seen by gc/ms. From tlc analysis, it appeared that the *cis*-β-styrylboronic acid was unreacted. Neither longer reaction times nor additional CuMeSal affected the reaction outcome.

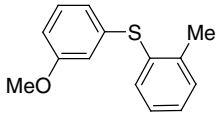

Table Entry 7. 3-Methoxyphenyl-2-methylphenyl sulfide. THF (2 mL) was added to 1-(3-methoxyphenyl)-pyrrolidine-2,5-dione (55 mg, 0.22 mmol, 1.0 equiv), 2-methylphenylboronic acid (60 mg, 0.44 mmol, 2.0 equiv) and CuMeSal (16 mg, 0.67 mmol, 30%). After 18 h at 45-50 °C, preparative plate chromatography (SiO_2, 1.0 mm thick, hexanes as eluant) gave product (42 mg, 0.18 mmol, 83 %) as a colorless oil. ^{1}H NMR ($CDCl_3$, 400 MHz): 7.34 (app d, J = 8.4 Hz, 1H), 7.27–7.14 (m, 4H), 6.77 (app d, J = 8.0 Hz, 1H), 6.75–6.72 (m, 2H), 3.75 (s, 3H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): 160, 140, 138, 133, 133, 131, 130, 128, 127, 121, 114, 112, 55, 21. HRMS (EI) Calcd for $C_{14}H_{14}OS$: 230.07654. Found: 230.07701.

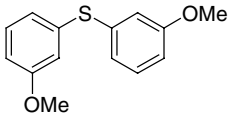

Table Entry 8. Bis-(3-Methoxy-phenyl)-sulfide.[9] THF (3.5 mL) was added to 1-(3-methoxyphenyl)-pyrrolidine-2,5-dione (151 mg, 0.63 mmol, 1.0 equiv), 3-methoxyphenylboronic acid (194 mg, 1.27 mmol, 2.0 equiv) and CuMeSal (39 mg, 0.18 mmol, 29%). After 2.5 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant) gave product (110 mg, 0.45

[9] Arylation of phenols and thiophenes under conditions of microwave heating El'tsov, A. V.; Martynova, V. P.; Sokolova, N. B.; Dmitrieva, N. M.; Brykov, A. S. *Russ. J. Gen. Chem.* **1994**, *64*, 9, 1581-1582.

mmol, 71 %) as a colorless oil. TLC (1:1 hexanes:dichloromethane, R_f = 0.55); ^{1}H NMR ($CDCl_3$, 400 MHz): 7.24 (t, *J* = 8.0 Hz, 2 H), 6.97 (dd, *J* = 7.6, 0.8 Hz, 2H), 6.93 (t, *J* = 1.6 Hz, 2H), 6.82 (dd, *J* = 8.4, 0.8 Hz, 2 H), 3.78 (s, 6 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 160.0, 136.6, 129.9, 123.2, 116.2, 112.9, 55.2. LRMS (FAB+), m/z (relative intensity) 247 (51), 246 (100), 154 (13), 139 (12). HRMS (FAB+) Calcd for $C_{14}H_{15}O_2S$: 247.0793. Found: 247.0795 (+0.9 ppm error, [M+H]), Calcd for $C_{14}H_{14}O_2S$: 246.0715. Found: 246.0707.

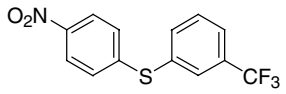

Table Entry 9. (3-Trifluoromethylphenyl)-(4-nitro-phenyl)-sulfide. THF (1 mL) was added to 4-nitrophenylsulfensuccinimide (30 mg, 0.12 mmol, 1.0 equiv), 3-trifluoromethylphenylboronic acid (47 mg, 0.25 mmol, 2.0 equiv) and CuMeSal (8 mg, 0.04 mmol, 30 %). After 4 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant) gave product (25 mg, 0.083 mmol, 69 %) as a yellowish oil. TLC (1:1 hexanes:dichloromethane, R_f =0.40); ^{1}H NMR ($CDCl_3$, 400 MHz): 8.12 (td, *J* = 9.2, 2.8 Hz, 2 H), 7.78 (br s, 1 H), 7.69 (d , *J* = 8.0 Hz, 2 H), 7.57 (d, *J* = 7.6 Hz, 1 H), 7.26 (td, *J* = 8.8, 2.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 146.3, 146.0, 137.1, 132.8, 132.5 (q, *J* = 32.2 Hz), 130.5 (q, *J* = 3.6 Hz), 130.4, 127.8, 126.1 (q, *J* = 3.6 Hz), 124.3, 123.4 (q, *J* = 272.4 Hz). ^{19}F NMR ($CDCl_3$, 376 MHz): -64.1. Anal. Calcd for $C_{13}H_8O_2FNS$: C, 52.17; H, 2.69; S, 10.71; N, 4.68; Found: C, 52.36; H, 2.86; S, 10.74; N, 4.80.

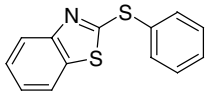

Table Entry 10. 2-Phenylsulfanyl-benzothiazole.[10] THF (2.0 mL) was added to 1-(benzothiazol-2-sulfanyl)-pyrrolidine-2, 5-dione (107 mg, 0.41 mmol, 1.0 equiv), phenylboronic acid (93 mg, 0.76 mmol, 1.8 equiv) and CuMeSal (26 mg, 0.12 mmol, 29%). After 12 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, dichloromethane as eluant) gave product (57

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[10] Synthesis of alkylthio- and arylthioheteroarenes by regioselective Grignard reaction of thiocyanatoheteroarenes Nagasaki, I.; Matsumoto, M.; Yamashita, M.; Miyashita, A. *Heterocycles* **1999**, *51*, 5, 1015-1024.

mg, 0.23 mmol, 57 %) as a yellowish oil. TLC (dichloromethane, R_f =0.52). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.88 (d, *J* = 8.4 Hz, 1 H), 7.75 (td , *J* = 7.6, 1.2 Hz, 2 H), 7.66 (d, *J* = 7.6 Hz, 1 H), 7.53-7.47 (m, 3 H), 7.41 (dt, *J* = 8.0 Hz, 1H), 7.27 (dt, *J* = 8.0, 1.2 Hz, 1H).

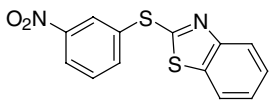

Table Entry 11. 2-(3-Nitrophenylsulfanyl)benzothiazole. THF (1.5 mL) was added to 1-(benzothiazol-2-sulfanyl)-pyrrolidine-2, 5-dione (49 mg, 0.19 mmol, 1.0 equiv), 3-nitrophenylboronic acid (61mg, 0.37 mmol, 2.0 equiv) and CuMeSal (11 mg, 0.05 mmol, 27%). After 12 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant) gave product (30 mg, 0.104 mmol, 56 %) as a yellowish solid. TLC (dichloromethane, R_f =0.62); Mp 85–87 °C (lit.{90.5-91 °C (methanol)[11]}); ^{1}H NMR ($CDCl_3$, 400 MHz): 8.58 (br s, 1 H); 8.32 (d, *J* = 8.0 Hz, 1 H), 8.02 (d , *J* = 8.0 Hz, 1 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.74 (d, *J* = 8.0 Hz, 1 H), 7.65 (t, *J* = 8.0, 1 H), 7.46 (t, *J* = 8.0, 1 H), 7.35 (d, *J* = 8.0, 1 H). ^{13}C NMR ($CDCl_3$, 100 MHz): 164.8, 153.5, 148.7, 139.8, 135.8, 132.9, 130.5, 128.7, 126.5, 125.1, 124.6, 122.5, 121.0.

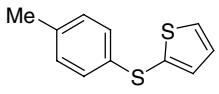

Table Entry 12. 2-p-Tolylsulfanyl-thiophene.[12] THF (1.0 mL) was added to 1-thiophenylpyrrolidine-2, 5-dione (38 mg, 0.18 mmol, 1.0 equiv), 4-methylphenylboronic acid (37 mg, 0.27 mmol, 1.5 equiv) and CuMeSal (9 mg, 0.04 mmol, 23 %). After 3 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant) gave product (26 mg, 0.12 mmol, 71%) as a colorless oil. TLC (hexanes, R_f =0.37). ^{1}H NMR ($CDCl_3$, 400 MHz): 7.43 (dd, *J* = 5.2, 1.2 Hz, 1 H), 7.26 (dd , *J* = 4.0, 1.2 Hz, 1 H), 7.15 (td, *J* = 8.4, 1.6 Hz, 2 H), 7.08-7.03 (m, 3 H), 2.30 (s, 3 H).

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[11] Syntheses of heterocyclic sulfones. I. Benzothiazolyl compounds Itai, T.; Yamamoto, S. *Chem. Abstr*. **1953**, 7491.

[12] Deryagina, E. N.; Papernaya, L. K.; Klyba, L. V.; Voronko, M. G. *Russ. J. Org. Chem.* **1997**, *33*, 9, 1296-1298.

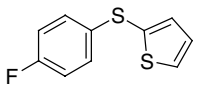

Table Entry 13. 2-(4-Fluoro-phenylsulfanyl)-thiophene.[13] THF (1.5 mL) was added to 1-thiophenylpyrrolidine-2, 5-dione (35 mg, 0.16 mmol, 1.0 equiv), 4-fluorophenylboronic acid (43 mg, 0.31 mmol, 1.9 equiv) and CuMeSal (10 mg, 0.05 mmol, 29%). After 3.5 h at 45-50 °C, preparative plate chromatography (SiO_2, 0.5 mm thick, hexanes as eluant) gave product (26 mg, 0.12 mmol, 76%) as a colorless oil. TLC (hexanes, R_f =0.45); ^{1}H NMR ($CDCl_3$, 400 MHz): 7.45 (dd, *J* = 5.6, 1.2 Hz, 1 H), 7.27 (dd , *J* = 3.2, 1.2 Hz, 1 H), 7.24-7.30 (m, 2 H), 7.05 (dd, *J* = 7.2, 3.2 Hz, 1 H), 6.96 (tt, *J* = 8.4, 2.0, 2 H). ^{19}F NMR ($CDCl_3$, 376 MHz): -57.7.

[13] A facile and convenient synthesis of 2-(arylthio)thiophenes, 2-(alkylthio)thiophene, and 2-(thiophenylthio)thiophene Lee, S. B.; Hong, J.-I. *Tetrahedron Lett.* **1995**, *36*, 46, 8439-8442.