General and Practical Intramolecular Decarbonylative Coupling of Thioesters via Palladium Catalysis Cao et al.

# General and Practical Intramolecular Decarbonylative Coupling of Thioesters via Palladium Catalysis

Han Cao,<sup>†</sup> Xuejing Liu,<sup>\*,†</sup> Fusheng Bie,<sup>†</sup> Yijun Shi,<sup>†</sup> Ying Han,<sup>†</sup> Peng Yan,<sup>†</sup> Michal Szostak,<sup>\*,‡</sup> and Chengwei Liu<sup>\*,‡</sup>

<sup>†</sup>Shandong Lunan Coal Chemical Research Institute of Engineering and Technology, Zaozhuang University, Zaozhuang, Shandong 277160, China <sup>‡</sup>Department of Chemistry, Rutgers University, 73 Warren Street, Newark, New Jersey 07102, United States

lxj3786749@126.com; michal.szostak@rutgers.edu; chengwei.liu@rutgers.edu

## Supporting Information

Table of Contents	SI-1
List of Known Compounds/General Methods	SI-2
Experimental Procedures	SI-3
General Procedures	SI-3
Characterization Data of Starting Materials	SI-4
Characterization Data of Products	SI-12
References	SI-25
<sup>1</sup> H NMR, <sup>13</sup> C NMR and <sup>19</sup> F NMR Spectra	SI-26

### **Corresponding Author:**

Prof. Dr. X. Liu	Prof. Dr. M. Szostak	Prof. Dr. C. Liu
Zaozhuang University	Rutgers University	Rutgers University
lxj3786749@126.com	michal.szostak@rutgers.edu	chengwei.liu@rutgers.edu

#### List of Known Compounds/General Methods

All starting materials reported in the manuscript have been prepared according to the method reported previously.<sup>1-6</sup> Spectroscopic data matched literature values. All experiments involving rhodium were performed using standard Schlenk techniques under argon atmosphere unless stated otherwise. All solvents were purchased at the highest commercial grade and used as received or after purification by passing through activated alumina columns or distillation from sodium/benzophenone under nitrogen. All solvents were deoxygenated prior to use. All other chemicals were purchased at the highest commercial grade and used as received. Reaction glassware was oven-dried at 140 °C for at least 24 h or flame-dried prior to use, allowed to cool under vacuum and purged with argon (three cycles). All products were identified using <sup>1</sup>H NMR analysis and comparison with authentic samples. GC and/or GC/MS analysis was used for volatile products. All yields refer to yields determined by <sup>1</sup>H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were recorded in CDCl<sub>3</sub> on Bruker spectrometers at 400 (<sup>1</sup>H NMR), 100 MHz (<sup>13</sup>C NMR) and 376 MHz (<sup>19</sup>F NMR). All shifts are reported in parts per million (ppm) relative to residual CHCl<sub>3</sub> peak (7.26 and 77.16 ppm, <sup>1</sup>H NMR and <sup>13</sup>C NMR, respectively). All coupling constants (J) are reported in hertz (Hz). Abbreviations are: s, singlet; d, doublet; t, triplet; q, quartet; brs, broad singlet. GC-MS chromatography was performed using Agilent 7890A GC System and Agilent 7000B inert XL EI MSD using helium as the carrier gas at a flow rate of 1 mL/min and an initial oven temperature of 50 °C. The injector temperature was 250 °C. The detector temperature was 250 °C. For runs with the initial oven temperature of 50 °C, temperature was increased with a 10 °C/min ramp after 50 °C hold for 3 min to a final temperature of 220 °C, then hold at 220 °C for 15 min (splitless mode of injection, total run time of 22.0 min). Infrared spectrum was measured on a Thermo Scientific Nicolet<sup>TM</sup> iS<sup>TM</sup> 50 Spectrometer. HRMS data were recorded on Agilent 6530 Accurate-Mass Q-TOF LCMS spectrometer by ESI in positive mode. Melting point was recorded on INESA (SGWX-4B) equipment without corrected. All flash chromatography was performed using silica gel, 60 Å, 300 mesh. TLC analysis was carried out on glass plates coated with silica gel 60 F254, 0.2 mm thickness. The plates were visualized using a 254 nm ultraviolet lamp or aqueous potassium permanganate solutions. <sup>1</sup>H NMR and <sup>13</sup>C NMR data are given for all compounds in the Supporting Information. <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS data are reported for all new compounds.

#### **Experimental Procedures**

General Procedure for Decarbonylation of Thioester. An oven-dried vial equipped with a stir bar was charged with thioester substrate (neat, 1.0 equiv),  $Pd(OAc)_2$  (typically, 3 mol%) and 1, 4-bis(diphenylphosphino)butane (typically, 6 mol%), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (typically, 0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for the indicated time at 160 °C. After the indicated time, the reaction mixture was diluted with  $CH_2Cl_2$  (10 mL), filtered, and concentrated. The sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title product.

**Representative Procedure for Decarbonylation of Thioester.** An oven-dried vial equipped with a stir bar was charged with *S*-phenyl benzothioate (neat, 42.9 mg, 0.20 mmol, 1.0 equiv),  $Pd(OAc)_2$  (1.3 mg, 0.006 mmol, 0.03 equiv) and 1, 4-bis(diphenylphosphino)butane (4.9 mg, 0.012 mmol, 0.06 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (1.0 mL, 0.20 M) was added with vigorous stirring at room temperature, the reaction mixture was placed in a preheated oil bath at 160 °C, and stirred for 15 h at 160 °C. After the indicated time, the reaction mixture was cooled down to room temperature, diluted with  $CH_2Cl_2$  (10 mL), filtered, and concentrated. A sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) and GC-MS to obtain conversion, yield and selectivity using internal standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title product. Yield 95% (35.4 mg, 0.190 mmol). White solid. Characterization data are included in the section below.

#### **Characterization Data of Starting Materials**

*Note:* All starting materials have been prepared according to the previously published procedure.<sup>1</sup> The yields have not been optimized.



*S*-Phenyl benzothioate (1a)<sup>1</sup> Yield 96% (1.029 g). White solid. <sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$ 8.05-8.03 (d, J = 7.2 Hz, 2H), 7.64-7.60 (t, J = 7.4 Hz, 1H), 7.54-7.46 (m, 7H). <sup>13</sup><u>C NMR (100</u> MHz, CDCl<sub>3</sub>)  $\delta$  190.32, 136.78, 135.25, 133.81, 129.68, 129.41, 128.90, 127.63, 127.48.



*S*-Phenyl naphthalene-2-carbothioate (1b)<sup>1</sup> Yield 70% (0.919 g). White solid. <sup>1</sup><u>H NMR (400</u> <u>MHz, CDCl<sub>3</sub>)</u> δ 8.63 (s, 1H), 8.05-8.00 (m, 2H), 7.94-7.89 (m, 2H), 7.65-7.56 (m, 4H), 7.51-7.47 (m, 3H). <sup>13</sup><u>C NMR (100 MHz, CDCl<sub>3</sub>)</u> δ 190.25, 136.03, 135.29, 134.06, 132.60, 129.76, 129.70, 129.43, 129.16, 128.79, 127.99, 127.57, 127.15, 123.40.



*S*-Phenyl 4-methylbenzothioate (1c)<sup>1</sup> Yield 81% (0.925 g). White solid. <sup>1</sup><u>H NMR (400 MHz,</u> <u>CDCl<sub>3</sub>)</u>  $\delta$  7.94-7.92 (d, J = 8.2 Hz, 2H), 7.53-7.51 (dd, J = 6.6, 3.1 Hz, 2H), 7.46-7.45 (m, 3H), 7.30-7.28 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H). <sup>13</sup><u>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  189.89, 144.74, 135.28, 134.22, 129.58, 129.56, 129.35, 127.71, 127.67, 21.87.



S-Phenyl 4-methoxybenzothioate (1d)<sup>1</sup> Yield 95% (1.158 g). White solid. <sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>)</u> δ 8.03-7.99 (m, 2H), 7.53-7.50 (m, 2H), 7.47-7.44 (m, 3H), 6.98-6.95 (m, 2H), 3.89 (s, 3H). <sup>13</sup><u>C NMR (100 MHz, CDCl<sub>3</sub>)</u> δ 188.78, 164.14, 135.35, 129.86, 129.53, 129.32, 127.77, 114.05, 55.70.



*S*-Phenyl 4-(trifluoromethyl)benzothioate (1e)<sup>1</sup> Yield 89% (1.253 g). White solid. <sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>) δ 8.15-8.13 (d, J = 7.9 Hz, 2H), 7.78-7.75 (d, J = 8.2 Hz, 2H), 7.55-7.48 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 189.55, 139.57, 135.14, 135.06 (d,  $J^2 = 33.0$  Hz), 130.02, 129.57, 127.97, 126.69, 125.99 (q,  $J^3 = 3.8$  Hz), 123.63 (d,  $J^1 = 272.6$  Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.10.



*S*-Phenyl 4-fluorobenzothioate (1f)<sup>1</sup> Yield 96% (1.113 g). White solid. <sup>1</sup><u>H NMR (400 MHz,</u> <u>CDCl<sub>3</sub>)</u> δ 8.09-8.04 (ddd, J = 8.9, 5.2, 2.5 Hz, 2H), 7.53-7.46 (m, 5H), 7.20-7.14 (m, 2H). <sup>13</sup><u>C</u> <u>NMR (100 MHz, CDCl<sub>3</sub>)</u> δ 188.85, 166.21 (d,  $J^{l} = 255.7$  Hz), 135.24, 133.08 (d,  $J^{4} = 2.9$  Hz), 130.20 (d,  $J^{3} = 9.4$  Hz), 129.79, 129.45, 127.18, 116.07 (d,  $J^{2} = 21.9$  Hz). <sup>19</sup><u>F NMR (376 MHz,</u> <u>CDCl<sub>3</sub>)</u> δ -104.11.



*S*-Phenyl 4-chlorobenzothioate (1g)<sup>1</sup> Yield 80% (0.990 g). White solid. <sup>1</sup>H NMR (400 MHz, <u>CDCl<sub>3</sub></u>) δ 7.99-7.95 (m, 2H), 7.53-7.49 (m, 2H), 7.48-7.46 (m, 5H). <sup>13</sup>C NMR (100 MHz, <u>CDCl<sub>3</sub></u>) δ 189.26, 140.24, 135.22, 135.11, 129.87, 129.49, 129.23, 128.99, 127.05.



*S*-Phenyl 4-cyanobenzothioate (1h)<sup>1</sup> Yield 83% (0.988 g). White solid. <sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  8.13-8.10 (d, *J* = 8.6 Hz, 2H), 7.81-7.79 (d, *J* = 8.6 Hz, 2H), 7.52-7.48 (m, 5H). <sup>13</sup><u>C</u> <u>NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  189.26, 139.93, 135.09, 132.78, 130.17, 129.63, 128.05, 126.34, 117.93, 117.03.



Methyl 4-((phenylthio)carbonyl)benzoate (1i)<sup>1</sup> Yield 81% (1.105 g). White solid. <sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.16-8.14 (m, 2H), 8.09-8.07 (m, 2H), 7.54-7.47 (m, 5H), 3.96 (s, 3H). <sup>13</sup><u>C</u> NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  189.93, 166.23, 140.09, 135.15, 134.55, 130.12, 129.94, 129.53, 127.55, 126.93, 52.69.



*S*-Phenyl 4-acetylbenzothioate (1j)<sup>1</sup> Yield 66% (0.850 g). Orange solid. <u><sup>1</sup>H NMR (400 MHz,</u> <u>CDCl<sub>3</sub>)</u> δ 8.12-8.10 (m, 2H), 8.06-8.04 (m, 2H), 7.54-7.47 (m, 5H), 2.66 (s, 3H). <u><sup>13</sup>C NMR (100</u> <u>MHz, CDCl<sub>3</sub></u>) δ 197.44, 189.85, 140.76, 140.04, 135.13, 129.95, 129.53, 128.77, 127.83, 126.89, 27.05.



S-Phenyl 2-methylbenzothioate (1k)<sup>1</sup> Yield 88% (1.009 g). White solid. <sup>1</sup>H NMR (400 MHz, <u>CDCl<sub>3</sub></u>) δ 7.97-7.95 (d, J = 7.6 Hz, 1H), 7.55-7.52 (m, 2H), 7.50-7.42 (m, 4H), 7.33-7.27 (m, 2H), 2.50 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 192.32, 137.58, 136.87, 135.05, 132.16, 131.89, 129.61, 129.41, 128.78, 128.34, 126.00, 20.92.



S-Phenyl 2-fluorobenzothioate (11)<sup>1</sup> Yield 94% (1.091 g). White solid. <sup>1</sup>H NMR (400 MHz, <u>CDCl<sub>3</sub></u>)  $\delta$  7.95-7.91 (t, J = 7.5 Hz, 1H), 7.58-7.53 (m, 3H), 7.48-7.47 (m, 3H), 7.28-7.17 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  187.31 (d,  $J^5 = 5.2$  Hz), 160.61 (d,  $J^1 = 258.3$  Hz), 135.11, 134.75 (d,  $J^4 = 8.9$  Hz), 130.01, 129.83, 129.41, 127.34 (d, J = 4.3 Hz), 125.24 (d,  $J^3 = 11.6$  Hz), 124.46 (d,  $J^6 = 3.6$  Hz), 117.10 (d,  $J^2 = 22.4$  Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -109.75.



*S*-Phenyl 3-chlorobenzothioate (1m)<sup>2</sup> Yield 90% (1.119 g). White solid. <sup>1</sup><u>H NMR (400 MHz,</u> <u>CDCl<sub>3</sub>)</u> δ 8.00 (s, 1H), 7.93-7.91 (d, *J* = 7.9 Hz, 1H), 7.60-7.57 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.54-7.47 (m, 5H), 7.46-7.42 (t, *J* = 7.9 Hz, 1H). <sup>13</sup><u>C NMR (100 MHz, CDCl<sub>3</sub>)</u> δ 189.17, 138.26, 135.14, 133.67, 130.19, 129.89, 129.49, 127.59, 126.88, 125.70.



S-Phenyl furan-2-carbothioate (1n)<sup>3</sup> Yield 87% (0.887 g). Pale yellow solid. <sup>1</sup>H NMR (400 <u>MHz, CDCl<sub>3</sub></u>) δ 7.62 (s, 1H), 7.53-7.49 (m, 2H), 7.47-7.44 (m, 3H), 7.27-7.26 (d, J = 4.3 Hz, 1H), 6.58-6.57 (dd, J = 3.7, 1.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 178.80, 150.46, 146.61, 135.27, 129.79, 129.39, 126.27, 116.40, 112.56.



*S*-Phenyl thiophene-2-carbothioate (10)<sup>1</sup> Yield 76% (0.835 g). Pale yellow solid. <sup>1</sup><u>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92-7.91 (dd, J = 3.8, 1.2 Hz, 1H), 7.67-7.66 (d, J = 5.0 Hz, 1H), 7.55-7.52 (m, 2H), 7.46-7.45 (m, 3H), 7.17-7.15 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  182.19, 141.50, 135.19, 133.37, 131.73, 129.79, 129.39, 128.15, 127.02.



*S*-Phenyl (*E*)-3-phenylprop-2-enethioate (1p)<sup>1</sup> Yield 84% (1.012 g). Pale yellow solid. <sup>1</sup><u>H</u> <u>NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.70-7.66 (d, *J* = 15.8 Hz, 1H), 7.58-7.56 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.51-7.48 (m, 2H), 7.46-7.40 (m, 6H), 6.82-6.78 (d, *J* = 15.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, <u>CDCl<sub>3</sub></u>)  $\delta$  188.15, 141.68, 134.78, 134.15, 130.92, 129.61, 129.37, 129.15, 128.65, 127.74, 124.27.



*S*-(*p*-Tolyl) benzothioate (1q)<sup>1</sup> Yield 77% (0.881 g). White solid. <sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  8.05-8.03 (d, *J* = 7.0 Hz, 2H), 7.63-7.59 (t, *J* = 7.4 Hz, 1H), 7.51-7.47 (t, *J* = 7.7 Hz, 2H), 7.42-7.40 (d, *J* = 7.9 Hz, 2H), 7.29-7.27 (d, *J* = 7.6 Hz, 2H), 2.42 (s, 3H). <sup>13</sup><u>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  190.73, 139.94, 136.82, 135.16, 133.71, 130.24, 128.84, 127.59, 123.87, 21.51.



*S*-(4-Methoxyphenyl) benzothioate (1r)<sup>1</sup> Yield 87% (1.062 g). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl\_3)</u>  $\delta$  8.04-8.02 (d, *J* = 7.3 Hz, 2H), 7.62-7.59 (t, *J* = 7.4 Hz, 1H), 7.50-7.47 (t, *J* = 7.7 Hz, 2H), 7.44-7.40 (m, 2H), 7.01-6.97 (m, 2H), 3.85 (s, 3H). <u><sup>13</sup>C NMR (100 MHz, CDCl\_3)</u>  $\delta$  191.24, 160.93, 136.79, 133.72, 128.87, 127.60, 118.01, 115.12, 55.53.



*S*-(4-(Trifluoromethyl)phenyl) benzothioate (1s)<sup>1</sup> Yield 83% (1.177 g). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04-8.02 (dd, J = 8.4, 1.2 Hz, 2H), 7.73-7.62 (m, 5H), 7.53-7.50 (t, J = 7.7 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  189.07, 136.36, 135.37, 134.20, 132.30, 131.59 (q,  $J^2 = 33.0$  Hz), 129.04, 127.71, 126.14 (q,  $J^3 = 3.8$  Hz), 123.98 (d,  $J^1 = 272.4$  Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.82.



*S*-(4-Fluorophenyl) benzothioate (1t)<sup>1</sup> Yield 96% (1.115 g). White solid. <sup>1</sup>H NMR (400 MHz, <u>CDCl<sub>3</sub></u>)  $\delta$  8.03-8.01 (d, *J* = 7.2 Hz, 2H), 7.62-7.60 (t, *J* = 7.4 Hz, 1H), 7.52-7.47 (m, 4H), 7.19-7.13 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  190.29, 163.78 (d, *J<sup>l</sup>* = 250.0 Hz), 137.31 (d, *J<sup>3</sup>* = 8.6 Hz), 136.53, 133.96, 128.95, 127.64, 122.74 (d, *J<sup>4</sup>* = 3.6 Hz), 116.70 (d, *J<sup>2</sup>* = 22.3 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -111.02.



*S*-(*o*-Tolyl) benzothioate (1u)<sup>1</sup> Yield 93% (1.065 g). Colorless oil. <sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>)</u> δ 8.08-8.06 (d, *J* = 7.5 Hz, 2H), 7.64-7.60 (t, *J* = 7.4 Hz, 1H), 7.52-7.48 (m, 3H), 7.41-7.36 (m, 2H), 7.30-7.27 (m, 1H), 2.41 (s, 3H). <sup>13</sup><u>C NMR (100 MHz, CDCl<sub>3</sub>)</u> δ 189.82, 142.80, 136.91, 136.54, 133.72, 130.97, 130.37, 128.87, 127.68, 126.91, 126.81, 20.95.



*S*-(Thiophen-2-yl) benzothioate  $(1v)^4$  Yield 73% (0.804 g). Brown solid. <sup>1</sup><u>H NMR (400 MHz,</u> <u>CDCl<sub>3</sub>)</u>  $\delta$  8.03-8.01 (dd, J = 8.4, 1.0 Hz, 2H), 7.65-7.61 (m, 2H), 7.52-7.48 (t, J = 7.8 Hz, 2H), 7.27-7.26 (dd, J = 3.6, 1.2 Hz, 1H), 7.18-7.16 (dd, J = 5.3, 3.6 Hz, 1H). <sup>13</sup><u>C NMR (100 MHz,</u> <u>CDCl<sub>3</sub>)</u>  $\delta$  189.98, 136.47, 136.07, 134.10, 132.30, 129.00, 128.06, 127.74, 124.30.



**S-Decyl benzothioate (1w)**<sup>1</sup> Yield 90% (1.259 g). Yellow oil. <sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>)</u> δ 7.98-7.96 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.58-7.54 (t, *J* = 7.4 Hz, 1H), 7.46-7.42 (t, *J* = 7.7 Hz, 2H), 3.09-3.05 (t, *J* = 8.0 Hz, 2H), 1.71-1.63 (p, *J* = 7.3 Hz, 2H), 1.46-1.39 (p, *J* = 6.7 Hz, 2H), 1.321.26 (m, 12H), 0.90-0.86 (t, J = 6.9 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  192.33, 137.41, 133.33, 128.68, 127.31, 32.02, 29.69, 29.68, 29.64, 29.44, 29.30, 29.19, 29.08, 22.82, 14.25.



**4-((Phenylthio)carbonyl)phenyl benzoate (1x)**<sup>1</sup> Yield 94% (1.571 g). White solid. <u><sup>1</sup>H NMR</u> (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.23-8.21 (d, J = 9.5 Hz, 2H), 8.14-8.12 (d, J = 8.8 Hz, 2H), 7.69-7.65 (t, J= 6.8 Hz, 1H), 7.56-7.52 (m, 4H), 7.48-7.46 (m, 3H), 7.38-7.36 (d, J = 8.8 Hz, 2H). <u><sup>13</sup>C NMR</u> (100 MHz, CDCl<sub>3</sub>)  $\delta$  189.24, 155.27, 135.27, 134.34, 134.14, 130.44, 129.78, 129.45, 129.30, 129.12, 128.86, 127.29, 122.31.



*S*-Phenyl 4-(N,N-dipropylsulfamoyl)benzothioate (1y)<sup>5</sup> Yield 80% (1.510 g). Pale yellow solid. <sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  8.14-8.12 (d, *J* = 8.6 Hz, 2H), 7.93-7.91 (d, *J* = 8.6 Hz, 2H), 7.53-7.47 (m, 5H), 3.13-3.09 (t, *J* = 7.6 Hz, 4H), 1.61-1.52 (dq, *J* = 14.9, 7.6 Hz, 4H), 0.90-0.86 (t, *J* = 7.4 Hz, 6H). <sup>13</sup><u>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  189.43, 144.89, 139.54, 135.12, 130.07, 129.59, 128.20, 127.54, 126.63, 50.11, 22.10, 11.30.

#### **Characterization Data of Products**





According to the general procedure, the reaction of *S*-phenyl benzothioate (0.20 mmol),  $Pd(OAc)_2$  (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 95% yield (35.4 mg). Yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.33 (m, 4H), 7.32-7.28 (m, 4H), 7.25-7.22 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.91, 131.18, 129.33, 127.19.

#### Naphthalen-2-yl(phenyl)sulfane (2b, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl naphthalene-2-carbothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 70% yield (33.1 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.84 (s, 1H), 7.81-7.72 (m, 3H), 7.49-7.44 (m, 2H), 7.42-7.36 (m, 3H), 7.32-7.29 (t, *J* = 7.2 Hz, 2H), 7.27-7.24 (m, 1H). <u><sup>13</sup>C NMR</u> (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.98, 133.92, 133.14, 132.42, 131.09, 130.02, 129.37, 129.00, 128.89, 127.88, 127.56, 127.21, 126.74, 126.35.

## Phenyl(*p*-tolyl)sulfane (2c, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 4-methylbenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 91% yield (36.5 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.32-7.30 (d, *J* = 8.1 Hz, 2H), 7.28-7.27 (d, *J* = 4.4 Hz, 4H), 7.23-7.18 (m, 1H), 7.16-7.14 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  137.75, 137.26, 132.42, 131.40, 130.21, 129.90, 129.18, 126.54, 21.27.

## (4-Methoxyphenyl)(phenyl)sulfane (2d, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 4-methoxybenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 75% yield (32.4 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.45-7.41 (m, 2H), 7.27-7.23 (m, 2H), 7.19-7.13 (m, 3H), 6.93-6.89 (m, 2H), 3.83 (s, 3H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  159.97, 138.75, 135.53, 129.07, 128.33, 125.89, 124.42, 115.12, 55.51.

## Phenyl(4-(trifluoromethyl)phenyl)sulfane (2e, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 4-(trifluoromethyl)benzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (49.8 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49-7.47 (m, 5H), 7.40-7.38 (m, 3H), 7.28 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.99, 133.70, 132.62, 129.83, 128.81, 128.41, 128.16 (d,  $J^2 = 32.7$  Hz), 125.96 (q,  $J^3 = 3.9$  Hz), 124.23 (d,  $J^1 = 271.9$  Hz). <sup>19</sup>F NMR (376 MHz, Chloroform-d)  $\delta$  -62.46.

#### (4-Fluorophenyl)(phenyl)sulfane (2f, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 4-fluorobenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (39.2 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.40-7.35 (m, 2H), 7.30-7.24 (m, 4H), 7.23-7.19 (m, 1H), 7.05-6.99 (m, 2H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  162.54 (d, *J<sup>l</sup>* = 247.6 Hz), 136.78, 134.24 (d, *J<sup>3</sup>* = 8.1 Hz), 130.33 (d, *J<sup>4</sup>* = 3.6 Hz), 130.08, 129.33, 126.91, 116.56 (d, *J<sup>2</sup>* = 21.8 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -114.02.

#### (4-Chlorophenyl)(phenyl)sulfane (2g, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 4-chlorobenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 97% yield (42.8 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.22 (m, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.25, 134.78, 133.13, 132.16, 131.46, 129.49, 129.46, 127.58.

#### 4-(Phenylthio)benzonitrile (2h, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 4-cyanobenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (41.4 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.53-7.50 (m, 2H), 7.49-7.47 (d, *J* = 8.6 Hz, 2H), 7.45-7.43 (m, 3H), 7.17-7.15 (d, *J* = 8.5 Hz, 2H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  145.90, 134.67, 132.53, 130.98, 130.08, 129.55, 127.46, 118.96, 108.85.

## Methyl 4-(phenylthio)benzoate (2i, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of methyl 4-((phenylthio)carbonyl)benzoate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 77% yield (37.6 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.90-7.88 (d, *J* = 8.6 Hz, 2H), 7.50-7.48 (m, 2H), 7.40-7.38 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.22-7.19 (m, 2H), 3.89 (s, 3H). <sup>13</sup>C

<u>NMR (100 MHz, CDCl<sub>3</sub>)</u> δ 166.85, 144.54, 133.85, 132.50, 130.24, 129.79, 128.81, 127.70, 127.60, 52.23.

#### 1-(4-(Phenylthio)phenyl)ethan-1-one (2j, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 4-acetylbenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 82% yield (37.4 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.83-7.81 (d, *J* = 8.6 Hz, 2H), 7.51-7.49 (m, 2H), 7.41-7.39 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.22-7.20 (d, *J* = 8.6 Hz, 2H), 2.55 (s, 3H). <u><sup>13</sup>C NMR</u> (100 MHz, CDCl<sub>3</sub>)  $\delta$  197.34, 145.10, 134.62, 134.04, 132.22, 129.84, 129.05, 128.96, 127.60, 26.62.

#### Phenyl(*o*-tolyl)sulfane (2k, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 2-methylbenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (39.3 mg). White solid. <sup>1</sup><u>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.30-7.14 (m, 9H), 2.38 (s, 3H). <sup>13</sup><u>C NMR</u> (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.12, 136.27, 133.88, 133.13, 131.18, 130.74, 129.77, 129.27, 128.04, 126.86, 126.48, 20.73.

## (2-Fluorophenyl)(phenyl)sulfane (2l, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl 2-fluorobenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (40.0 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.36-7.23 (m, 7H), 7.12-7.05 (m, 2H). <u><sup>13</sup>C</u> <u>NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  161.29 (d, *J*<sup>*l*</sup> = 246.9 Hz), 134.31, 133.56, 131.08, 129.49 (d, *J*<sup>*d*</sup> = 7.9 Hz), 129.42, 127.44, 124.86 (d, *J*<sup>5</sup> = 3.7 Hz), 122.88 (d, *J*<sup>3</sup> = 17.5 Hz), 116.08 (d, *J*<sup>2</sup> = 22.0 Hz). <u><sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)</u>  $\delta$  -108.75.

## (3-Chlorophenyl)(phenyl)sulfane (2m, Scheme 1)<sup>6</sup>



According to the general procedure, the reaction of *S*-phenyl 3-chlorobenzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (43.3 mg). Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.42-7.39 (m, 2H), 7.38-7.31 (m, 3H), 7.25-7.23 (m, 1H), 7.21-7.14 (m, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 138.97, 135.02, 134.03, 132.47, 130.22, 129.62, 129.58, 128.12, 128.01, 126.86.

#### 2-(Phenylthio)furan (2n, Scheme 1)<sup>3</sup>



According to the general procedure, the reaction of *S*-phenyl furan-2-carbothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 97% yield (34.2 mg). <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.59-7.58 (dd, *J* = 1.9, 0.9 Hz, 1H), 7.36-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.18-7.15 (m, 3H), 6.76-6.75 (dd, *J* = 3.2, 0.9 Hz, 1H), 6.49-6.47 (dd, *J* = 3.2, 2.0 Hz, 1H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  146.69, 143.22, 136.46, 131.18, 129.21, 127.67, 127.19, 126.48, 119.68, 112.03.

#### 2-(Phenylthio)thiophene (20, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl thiophene-2-carbothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (37.7 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49-7.48 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.37-7.28 (m, 2H), 7.24 (s, 1H), 7.21-7.14 (m, 3H), 7.10-7.07 (dd, *J* = 5.4, 3.5 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.80, 136.23, 131.45, 131.18, 129.33, 129.11, 128.08, 127.24, 126.19.

## (E)-Phenyl(styryl)sulfane (2p, Scheme 1)<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl (E)-3-phenylprop-2-enethioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 84% yield (35.7 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.43-7.41 (d, *J* = 7.2 Hz, 2H), 7.36-7.23 (m, 8H), 6.91-6.87 (d, *J* = 15.5 Hz, 1H), 6.75-6.72 (d, *J* = 15.5 Hz, 1H). <u><sup>13</sup>C NMR</u> (100 MHz, CDCl<sub>3</sub>)  $\delta$  136.66, 135.36, 131.95, 129.97, 129.31, 128.84, 127.74, 127.10, 126.17, 123.53.

## Phenyl(*p*-tolyl)sulfane (2c', Scheme 2)<sup>1</sup>



According to the general procedure, the reaction of *S*-(*p*-tolyl) benzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 94% yield (37.7 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.32-7.30 (d, *J* = 8.1 Hz, 2H), 7.28-7.27 (d, *J* = 4.4 Hz, 4H), 7.23-7.18 (m, 1H), 7.16-7.14 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  137.75, 137.26, 132.42, 131.40, 130.21, 129.90, 129.18, 126.54, 21.27.

### (4-Methoxyphenyl)(phenyl)sulfane (2d', Scheme 2)<sup>1</sup>



According to the general procedure, the reaction of *S*-(4-methoxyphenyl) benzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 66% yield (28.6 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.45-7.41 (m, 2H), 7.27-7.23 (m, 2H), 7.19-7.13 (m, 3H), 6.93-6.89 (m, 2H), 3.83 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  159.97, 138.75, 135.53, 129.07, 128.33, 125.89, 124.42, 115.12, 55.51.

### Phenyl(4-(trifluoromethyl)phenyl)sulfane (2e', Scheme 2)<sup>1</sup>



According to the general procedure, the reaction of *S*-(4-(trifluoromethyl)phenyl) benzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 90% yield (45.8 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.49-7.47 (m, 5H), 7.40-7.38 (m, 3H), 7.28 (s, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.99, 133.70, 132.62, 129.83, 128.81, 128.41, 128.16 (d,  $J^2 = 32.7$  Hz), 125.96 (q,  $J^3 = 3.9$  Hz), 124.23 (d,  $J^I = 271.9$  Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)  $\delta$  -62.46.

## (4-Fluorophenyl)(phenyl)sulfane (2f', Scheme 2)<sup>1</sup>



According to the general procedure, the reaction of *S*-(4-Fluorophenyl) benzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 91% yield (37.2 mg). White solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.40-7.35 (m, 2H), 7.30-7.24 (m, 4H), 7.23-7.19 (m, 1H), 7.05-6.99 (m, 2H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  162.54 (d, *J<sup>t</sup>* = 247.6 Hz), 136.78, 134.24 (d, *J<sup>3</sup>* = 8.1 Hz), 130.33 (d, *J<sup>4</sup>* = 3.6 Hz), 130.08, 129.33, 126.91, 116.56 (d, *J<sup>2</sup>* = 21.8 Hz). <u><sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)</u>  $\delta$  -114.02.

#### **Phenyl(o-tolyl)sulfane (2k', Scheme 2)**<sup>1</sup>



According to the general procedure, the reaction of *S*-(o-Tolyl) benzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (39.3 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.30-7.14 (m, 9H), 2.38 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.12, 136.27, 133.88, 133.13, 131.18, 130.74, 129.77, 129.27, 128.04, 126.86, 126.48, 20.73.

### 2-(Phenylthio)thiophene (20', Scheme 2)<sup>1</sup>



According to the general procedure, the reaction of *S*-(thiophen-2-yl) benzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 83% yield (48.6 mg). <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.49-7.48 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.37-7.28 (m, 2H), 7.24 (s, 1H), 7.21-7.14 (m, 3H), 7.10-7.07 (dd, *J* = 5.4, 3.5 Hz, 1H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  138.80, 136.23, 131.45, 131.18, 129.33, 129.11, 128.08, 127.24, 126.19.

## Decyl(phenyl)sulfane (2q, Scheme 2)<sup>1</sup>



According to the general procedure, the reaction of *S*-decyl benzothioate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (49.1 mg). Colorless oil. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.33-7.25 (m, 4H), 7.18-7.13 (m, 1H), 2.93-2.89 (t, *J* = 8 Hz, 2H), 1.68-1.60 (p, *J* = 7.3 Hz, 2H), 1.45-1.38 (m, 2H), 1.26 (s, 12H), 0.89-0.86 (t, *J* = 6.8 Hz, 3H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  137.20, 128.95, 125.75, 33.69, 32.03, 29.68, 29.65, 29.45, 29.31, 29.28, 28.99, 22.82, 14.26.

### 4-(Phenylthio)phenyl benzoate (2r, Scheme 3A)<sup>1</sup>



According to the general procedure, the reaction of 4-((Phenylthio)carbonyl)phenyl benzoate (0.20 mmol), Pd(OAc)<sub>2</sub> (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 80% yield (49.0 mg). Colorless oil. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  8.20-8.19 (d, *J* = 7.1 Hz, 2H), 7.67-7.63 (t, *J* = 7.4 Hz, 1H), 7.54-7.50 (t, *J* = 7.7 Hz, 2H), 7.43-7.41 (d, *J* = 8.7 Hz, 2H), 7.37-7.30 (m, 4H), 7.27-7.25 (m, 1H), 7.19-7.17 (d, *J* = 8.7 Hz, 2H). <u><sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)</u>  $\delta$  165.18, 150.32, 135.99, 133.89, 133.10, 132.63, 130.98, 130.35, 129.46, 129.41, 128.77, 127.25, 122.73.

### **Diphenylsulfane (2a, Scheme 3B)**<sup>1</sup>



According to the general procedure, the reaction of *S*-phenyl benzothioate (1g, 4.67 mmol),  $Pd(OAc)_2$  (3 mol%) and 1, 4-bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 92% yield (0.80 g). Yellow solid. <u><sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)</u>  $\delta$  7.36-7.33 (m, 4H), 7.32-7.28 (m, 4H), 7.25-7.22 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  135.91, 131.18, 129.33, 127.19.



4-(Phenylthio)-N,N-dipropylbenzenesulfonamide (2s, Scheme 3C)<sup>5</sup>

procedure, According to the general the reaction of S-phenyl N-4-(N, dipropylsulfamoyl)benzothioate (0.20)mmol),  $Pd(OAc)_2$ (3 mol%) and 1. 4bis(diphenylphosphino)butane (6 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 89% yield (62.2 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.65-7.63 (d, J = 8.6 Hz, 2H), 7.51-7.48 (m, 2H), 7.42-7.40 (dd, J = 5.0, 1.7 Hz, 3H), 7.23-7.21 (d, J = 8.6 Hz, 2H), 3.06-3.02 (m, 4H), 1.60-1.50 (m, 4H), 0.88-0.84 (t, J= 7.4 Hz, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  144.24, 137.31, 134.15, 131.84, 129.93, 129.14, 127.81, 127.72, 50.20, 22.20, 11.33.

### References

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20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)



---111.02

07232020-ch-s-15.1.1.1r —

















-10 110 100 f1 (ppm) 



























08122020-ch-STM-106.1.1.1r —



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -22 f1 (ppm)












