

# **Decarbonylative Thioetherification by Nickel Catalysis using Air- and Moisture-Stable Nickel Precatalysts**

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## **Electronic Supplementary Information**

<b>Table of Contents</b>	<b>1</b>
List of Known Compounds/General Methods	2
Experimental Procedures and Characterization Data	3
• General Procedures	3
• Characterization Data of Starting Materials	5
• Characterization Data of Decarbonylation Products	13
References	23
<sup>1</sup> H and <sup>13</sup> C NMR Spectra	24

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### List of Known Compounds/General Methods

All starting materials reported in the manuscript have been prepared by the method reported previously.<sup>1-8</sup> All compounds reported in this manuscript have been previously reported, unless stated otherwise. All experiments involving nickel 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 and <sup>13</sup>C NMR spectra were recorded in CDCl<sub>3</sub> on Bruker spectrometers at 500 (<sup>1</sup>H NMR) and 125 MHz (<sup>13</sup>C NMR). All shifts are reported in parts per million (ppm) relative to residual CHCl<sub>3</sub> peak (7.27 and 77.2 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 HP6890 GC System and Agilent 5973A inert XL EI/CI 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). High-resolution mass spectra (HRMS) were measured on a 7T Bruker Daltonics FT-MS instrument (for HRMS). Melting point was measured on MeltEMP (laboratory devices). 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 Supplementary Information for characterization purposes. <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS data are reported for all new compounds.

## Experimental Procedures and Characterization Data

**General Procedure for Thioester Synthesis.** An oven-dried flask (25 mL) equipped with a stir bar was charged with thiophenol (typically, 5.0 mmol, 1.0 equiv), acyl chloride (typically, 1.0 equiv), 4-(dimethylamino)pyridine (typically, 0.005 equiv), and dichloromethane (typically, 0.50 M). Triethylamine (typically, 2.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the resulting reaction mixture was stirred for 15 h at room temperature. After the indicated time, the reaction mixture was diluted with ethyl acetate (30 mL). The reaction mixture was washed with HCl (1 x 10 mL), brine (1 x 10 mL), H<sub>2</sub>O (1 x 10 mL), dried, and concentrated. The crude product was washed with hexane or purified by chromatography on silica gel (EtOAc/hexanes) to give analytically pure product.

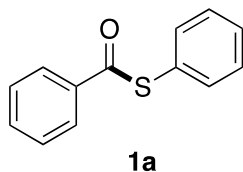
**General Procedure for Decarbonylation of Thioesters.** An oven-dried vial equipped with a stir bar was charged with a thioester substrate (neat, 1.0 equiv), Ni(dppp)Cl<sub>2</sub> (typically, 10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (typically, 1.5 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (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<sub>2</sub>Cl<sub>2</sub> (10 mL), filtered, and concentrated. The sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 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 Thioesters. 1.0 mmol Scale.** An oven-dried vial equipped with a stir bar was charged with *S*-phenyl benzothioate (neat, 214.3 mg, 1.0 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%, 0.10 mmol, 54.2 mg) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv, 1.5 mmol, 159.0 mg), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. 1,4-Dioxane (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<sub>2</sub>Cl<sub>2</sub> (10 mL), filtered, and concentrated. A sample was analyzed by <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz) and GC-MS to obtain conversion, yield and selectivity using internal

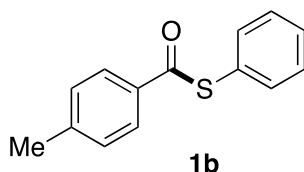
standard and comparison with authentic samples. Purification by chromatography on silica gel (hexanes/ethyl acetate) afforded the title product. Yield 98% (182.0 mg). White solid. Characterization data are included in the section below.

## Characterization Data for Starting Materials

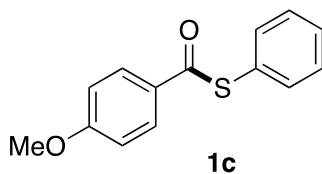
**Note:** All starting materials have been prepared according to the previously published procedures.<sup>1</sup> Unless stated otherwise, all starting materials reported in the manuscript have been previously described in literature and prepared by the method reported previously. <sup>1</sup>H NMR and <sup>13</sup>C NMR data for all starting materials used are given for characterization purposes.



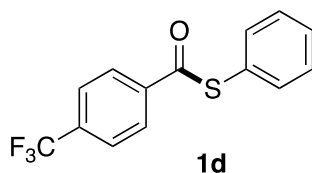
**S-Phenyl benzothioate (1a).**<sup>2</sup> Yield 97% (1.039 g). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (s, 2 H), 7.68 (s, 2 H), 7.64-7.62 (d,  $J$  = 6.2 Hz, 1 H), 7.53 (s, 5 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  189.90, 136.80, 135.32, 133.90, 129.70, 129.47, 129.00, 127.67.



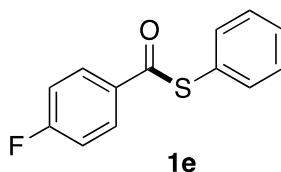
**S-Phenyl 4-methylbenzothioate (1b).**<sup>2</sup> Yield 75% (0.856 g). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.05-8.03 (d,  $J$  = 7.6 Hz, 2 H), 7.97-7.95 (d,  $J$  = 7.7 Hz, 1 H), 7.54 (s, 1 H), 7.48 (s, 2 H), 7.31-7.30 (d,  $J$  = 7.4 Hz, 2 H), 2.46 (s, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  189.75, 144.61, 135.15, 134.11, 130.28, 129.43, 129.24, 129.22, 127.59, 21.78.



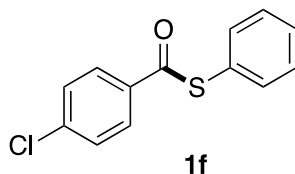
**S-Phenyl 4-methoxybenzothioate (1c).**<sup>2</sup> Yield 95% (1.161 g). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.06-8.04 (d,  $J$  = 8.8 Hz, 2 H), 7.57-7.54 (m, 2 H), 7.51-7.46 (m, 3 H), 7.00-6.98 (d,  $J$  = 8.8 Hz, 2 H), 3.90 (s, 3 H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  188.60, 164.04, 135.23, 132.38, 129.75, 129.41, 129.21, 127.70, 113.97, 55.58.



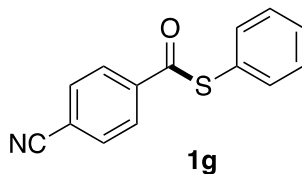
**S-Phenyl 4-(trifluoromethyl)benzothioate (1d).**<sup>2</sup> Yield 88% (1.242 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.16 (s, 2 H), 7.79 (s, 2 H), 7.55 (s, 2 H), 7.51 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.40, 139.47, 135.01, 134.95 (q,  $J^F = 32.9$  Hz), 129.89, 129.44, 127.84, 126.59, 125.87 (q,  $J^F = 3.4$  Hz), 123.51 (q,  $J^F = 270.7$  Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -63.06.



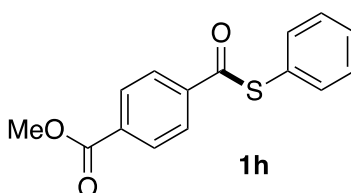
**S-Phenyl 4-fluorobenzothioate (1e).**<sup>3</sup> Yield 96% (1.115 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.10-8.07 (m, 2 H), 7.55-7.53 (m, 2 H), 7.50-7.48 (t,  $J = 3.3$  Hz, 3 H), 7.21-7.18 (t,  $J = 8.5$  Hz, 2 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 188.72, 166.10 (d,  $J^F = 253.9$  Hz), 135.12, 132.99 (d,  $J^F = 3.0$  Hz), 130.09 (d,  $J^F = 9.3$  Hz), 129.67, 129.32, 127.08, 115.95 (d,  $J^F = 22.0$  Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -104.10.



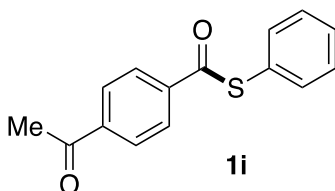
**S-Phenyl 4-chlorobenzothioate (1f).**<sup>4</sup> Yield 86% (1.070 g). Yellow solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.00 (s, 2 H), 7.54 (s, 2 H), 7.49 (s, 5 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.08, 140.10, 135.08, 134.99, 129.72, 129.35, 129.10, 128.85, 126.93.



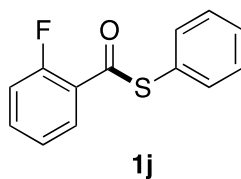
**S-Phenyl 4-cyanobenzothioate (1g).**<sup>5</sup> Yield 82% (0.981 g). Yellow solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.15-8.13 (d, *J* = 8.3 Hz, 2 H), 7.83-7.81 (d, *J* = 8.3 Hz, 2 H), 7.55-7.51 (m, 5 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.11, 139.82, 134.96, 132.65, 130.04, 129.51, 127.93, 126.23, 117.79, 116.92.



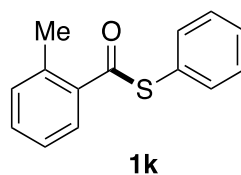
**Methyl 4-((phenylthio)carbonyl)benzoate (1h).**<sup>2</sup> Yield 81% (1.103 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.18-8.17 (d, *J* = 8.4 Hz, 2 H), 8.11-8.09 (d, *J* = 8.3 Hz, 2 H), 7.56-7.54 (m, 2 H), 7.50-7.49 (m, 3 H), 3.99 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.75, 166.09, 139.98, 135.01, 134.44, 129.99, 129.79, 129.39, 127.42, 126.83, 52.56.



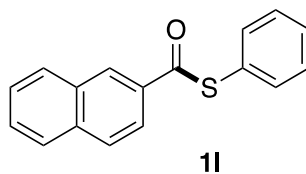
**S-Phenyl 4-acetylbenzothioate (1i).**<sup>5</sup> Yield 67% (0.859 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.14-8.12 (d, *J* = 8.4 Hz, 2 H), 8.09-8.07 (d, *J* = 8.2 Hz, 2 H), 7.56-7.54 (m, 2 H), 7.51-7.50 (d, *J* = 3.1 Hz, 3 H), 2.68 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 197.29, 189.70, 140.65, 139.94, 135.00, 129.82, 129.41, 128.65, 127.71, 126.79, 26.92.



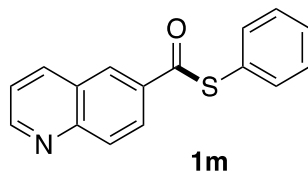
**S-Phenyl 2-fluorobenzothioate (1j).**<sup>4</sup> Yield 93% (1.080 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  7.96-7.93 (t,  $J$  = 7.8 Hz, 1 H), 7.60-7.55 (m, 3 H), 7.50-7.49 (t,  $J$  = 3.8 Hz, 3 H), 7.30-7.27 (t,  $J$  = 7.2 Hz, 1 H) 7.24-7.20 (m, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  187.17, 160.53 (d,  $J^F$  = 256.6 Hz), 135.01, 134.64 (d,  $J^F$  = 8.8 Hz), 129.90, 129.73, 129.31, 127.27 (d,  $J^F$  = 4.2 Hz), 125.18 (d,  $J^F$  = 11.5 Hz), 124.37 (d,  $J^F$  = 3.6 Hz), 117.01 (d,  $J^F$  = 22.0 Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)**  $\delta$  -109.71.



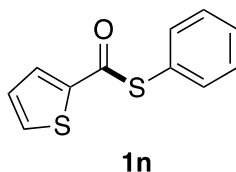
**S-Phenyl 2-methylbenzothioate (1k).**<sup>2</sup> Yield 89% (1.016 g). Colorless oil. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.09 (s, 1 H), 7.67 (s, 2 H), 7.56-7.50 (m, 4 H), 7.40-7.36 (m, 2 H), 2.64 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  192.09, 137.54, 136.88, 135.07, 132.20, 131.94, 129.60, 129.42, 128.80, 128.42, 126.06, 20.99.



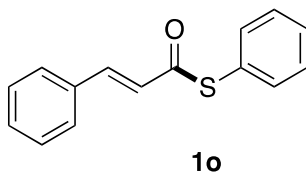
**S-Phenyl naphthalene-2-carbothioate (1l).**<sup>4</sup> Yield 70% (0.925 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)**  $\delta$  8.65 (s, 1 H), 8.07-8.02 (m, 2 H), 7.96-7.92 (m, 2 H), 7.67-7.59 (m, 4 H), 7.52-7.51 (m, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)**  $\delta$  190.09, 135.92, 135.17, 133.97, 132.50, 129.64, 129.57, 129.31, 129.04, 128.68, 128.67, 127.88, 127.48, 127.04, 123.30.



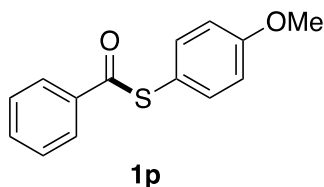
**S-Phenyl quinoline-6-carbothioate (1m).** Yield 80% (1.062 g). *New compound.* White solid. **Mp** = 116-118 °C. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.06-9.05 (d, *J* = 4.1 Hz, 1 H), 8.61 (s, 1 H), 8.34-8.29 (m, 2 H), 8.23-8.21 (d, *J* = 8.8 Hz, 1 H), 7.59-7.58 (m, 2 H), 7.54-7.50 (m, 4 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.60, 152.83, 150.39, 137.56, 135.11, 134.48, 130.39, 129.75, 129.39, 128.77, 127.52, 127.07, 127.01, 122.18. **HRMS** calcd for C<sub>16</sub>H<sub>11</sub>NOSNa (M<sup>+</sup> + Na) 288.0454, found 288.0442.



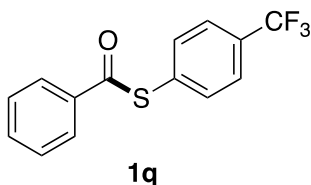
**S-Phenyl thiophene-2-carbothioate (1n).**<sup>2</sup> Yield 71% (0.782 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.95 (s, 1 H), 7.65 (s, 1 H), 7.60 (s, 2 H), 7.49 (s, 3 H), 7.15 (s, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 182.00, 141.39, 135.18, 133.56, 131.86, 129.79, 129.41, 129.27, 128.26, 127.09.



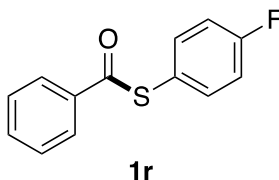
**S-Phenyl (E)-3-phenylprop-2-enethioate (1o).**<sup>2</sup> Yield 85% (1.022 g). Yellow solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.73-7.69 (d, *J* = 15.8 Hz, 1 H), 7.60-7.59 (m, 2 H), 7.54-7.52 (m, 2 H), 7.49-7.41 (m, 6 H), 6.84-6.81 (d, *J* = 15.8 Hz, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 187.98, 141.55, 134.64, 134.05, 130.78, 129.47, 129.23, 129.03, 128.52, 127.65, 124.17.



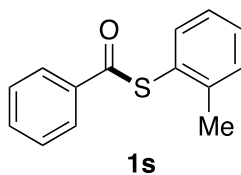
***S*-(4-Methoxyphenyl) benzothioate (1p).**<sup>2</sup> Yield 87% (1.063 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.06-8.05 (d, *J* = 7.7 Hz, 2 H), 7.64-7.61 (t, *J* = 7.2 Hz, 1 H), 7.52-7.49 (t, *J* = 7.5 Hz, 2 H), 7.46-7.44 (d, *J* = 8.6 Hz, 2 H), 7.03-7.01 (d, *J* = 8.6 Hz, 2 H), 3.88 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 191.07, 160.82, 136.66, 133.58, 130.60, 128.74, 127.48, 117.91, 115.00, 55.41.



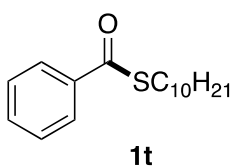
***S*-(4-(Trifluoromethyl)phenyl) benzothioate (1q).**<sup>2</sup> Yield 83% (1.172 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.06-8.05 (d, *J* = 8.1 Hz, 2 H), 7.75-7.73 (d, *J* = 8.2 Hz, 2 H), 7.69-7.65 (m, 3 H), 7.55-7.52 (t, *J* = 7.7 Hz, 2 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 188.92, 136.25, 135.23, 134.07, 132.19, 131.47 (q, *J<sup>F</sup>* = 32.6 Hz), 128.91, 127.59, 126.02 (q, *J<sup>F</sup>* = 3.7 Hz), 123.86 (q, *J<sup>F</sup>* = 270.8 Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -62.78.



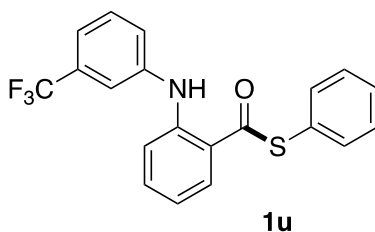
***S*-(4-Fluorophenyl) benzothioate (1r).**<sup>2</sup> Yield 96% (1.115 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.10-8.08 (d, *J* = 8.1 Hz, 2 H), 7.62-7.59 (t, *J* = 7.3 Hz, 1 H), 7.54-7.47 (m, 4 H), 7.19-7.16 (t, *J* = 8.6 Hz, 2 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.81, 163.68 (d, *J<sup>F</sup>* = 248.4 Hz), 137.29 (d, *J<sup>F</sup>* = 8.5 Hz), 136.47, 133.91, 128.92, 127.58, 122.87 (d, *J<sup>F</sup>* = 3.4 Hz), 116.58 (d, *J<sup>F</sup>* = 21.9 Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -110.55.



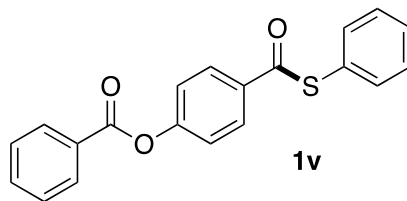
***S*-(*o*-Tolyl) benzothioate (1s).**<sup>4</sup> Yield 93% (1.062 g). Colorless oil. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.12-8.11 (d, *J* = 8.0 Hz, 2 H), 7.67-7.64 (t, *J* = 7.4 Hz, 1 H), 7.55-7.52 (m, 3 H), 7.43-7.42 (m, 2 H), 7.34-7.31 (t, *J* = 7.4 Hz, 1 H), 2.46 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.66, 142.71, 136.85, 136.47, 133.63, 130.89, 130.28, 128.79, 127.60, 126.87, 126.73, 20.89.



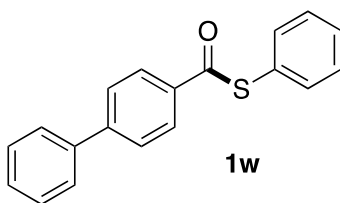
***S*-Decyl benzothioate (1t).** Yield 90% (1.253 g).<sup>6</sup> Yellow oil. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.00-7.99 (d, *J* = 7.5 Hz, 2 H), 7.60-7.57 (t, *J* = 7.4 Hz, 1 H), 7.48-7.45 (t, *J* = 7.6 Hz, 2 H), 3.11-3.08 (t, *J* = 7.2 Hz, 2 H), 1.73-1.67 (m, 2 H), 1.46-1.42 (m, 2 H), 1.32-1.29 (m, 12 H), 0.92-0.89 (t, *J* = 5.9 Hz, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 192.16, 137.31, 133.19, 128.56, 127.19, 31.91, 29.58, 29.56, 29.32, 29.18, 29.08, 28.97, 22.70, 14.13.



***S*-Phenyl 2-((3-(trifluoromethyl)phenyl)amino)benzothioate (1u).** Yield 88% (1.643 g). *New compound.* Yellow oil. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.05-8.03 (d, *J* = 7.3 Hz, 1 H), 7.69-7.58 (m, 2 H), 7.54-7.53 (m, 2 H), 7.47 (s, 3 H), 7.42-7.35 (m, 5 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.66, 141.56, 137.59, 135.03, 134.79, 134.51, 133.53, 133.22, 131.44 (q, *J<sup>F</sup>* = 63.0 Hz), 130.56, 129.99, 129.69 (q, *J<sup>F</sup>* = 30.9 Hz), 129.43, 129.36, 129.20, 127.56 (q, *J<sup>F</sup>* = 270.2 Hz), 123.71 (q, *J<sup>F</sup>* = 3.3 Hz), 123.04 (q, *J<sup>F</sup>* = 3.7 Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -62.52. **HRMS** calcd for C<sub>20</sub>H<sub>14</sub>F<sub>3</sub>NOSNa (M<sup>+</sup> + Na) 396.0640, found 396.0629.

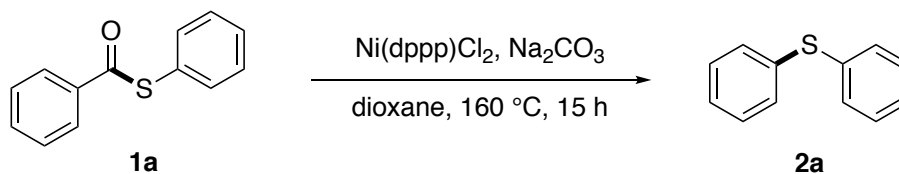


**4-((Phenylthio)carbonyl)phenyl benzoate (1v).**<sup>7</sup> Yield 94% (1.572 g). Yellow solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.25-8.24 (d, *J* = 7.9 Hz, 2 H), 8.16-8.14 (d, *J* = 8.4 Hz, 2 H), 7.71-7.68 (t, *J* = 7.4 Hz, 1 H), 7.58-7.55 (m, 4 H), 7.50 (s, 3 H), 7.40-7.39 (d, *J* = 8.4 Hz, 2 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.06, 164.56, 155.14, 135.13, 134.23, 133.99, 130.31, 129.63, 129.31, 129.16, 129.01, 128.72, 127.19, 122.17.

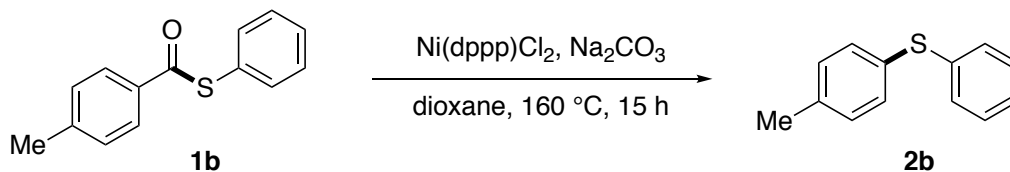


**S-Phenyl 4-(dibenzo[*b,d*]thiophen-4-yl)benzothioate (1w).**<sup>8</sup> Yield 95% (1.379 g). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.14-8.13 (d, *J* = 8.2 Hz, 2 H), 7.75-7.73 (d, *J* = 8.2 Hz, 2 H), 7.68-7.66 (d, *J* = 7.6 Hz, 2 H), 7.58-7.56 (m, 2 H), 7.53-7.50 (m, 5 H), 7.46-7.43 (t, *J* = 7.3 Hz, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 189.69, 146.45, 139.76, 135.35, 135.14, 129.55, 129.29, 129.02, 128.37, 128.08, 127.40, 127.31.

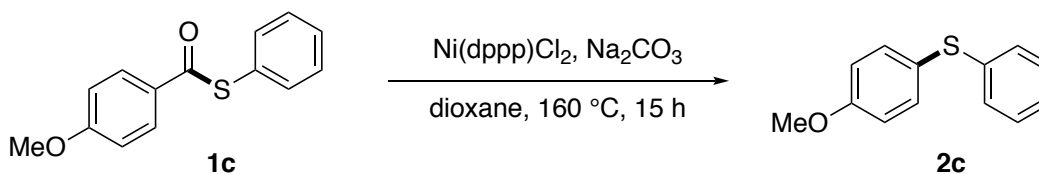
## Characterization Data for Decarbonylation Products

***S*-Phenyl benzothioate (1a, Scheme 1, Entry 1)**

According to the general procedure, the reaction of *S*-phenyl benzothioate (1.0 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (182.0 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.38-7.36 (d, *J* = 7.2 Hz, 4 H), 7.34-7.31 (t, *J* = 7.2 Hz, 4 H), 7.28-7.25 (t, *J* = 7.0 Hz, 2 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 135.80, 131.05, 129.20, 127.05.

***S*-Phenyl 4-methylbenzothioate (1b, Scheme 1, Entry 2)**

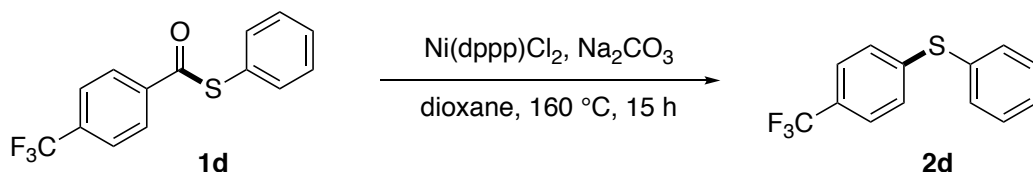
According to the general procedure, the reaction of *S*-phenyl 4-methylbenzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 91% yield (36.5 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.38-7.29 (m, 6 H), 7.25-7.12 (m, 3 H), 2.37 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 137.62, 137.13, 132.29, 131.29, 130.08, 129.79, 129.05, 126.42, 21.15.

***S*-Phenyl 4-methoxybenzothioate (1c, Scheme 1, Entry 3)**

According to the general procedure, the reaction of *S*-phenyl 4-methoxybenzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160

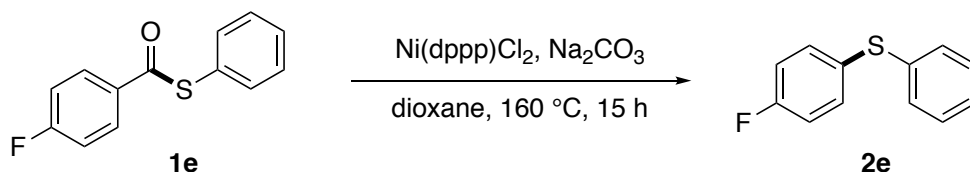
°C, afforded after work-up and chromatography the title compound in 81% yield (35.1 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.45-7.43 (d, *J* = 8.4 Hz, 2 H), 7.28-7.24 (t, *J* = 7.5 Hz, 2 H), 7.20-7.15 (m, 3 H), 6.93-6.92 (d, *J* = 8.4 Hz, 2 H), 3.85 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 159.85, 138.61, 135.38, 128.94, 128.22, 125.77, 124.33, 115.00, 55.38.

***S*-Phenyl 4-(trifluoromethyl)benzothioate (1d, Scheme 1, Entry 4)**

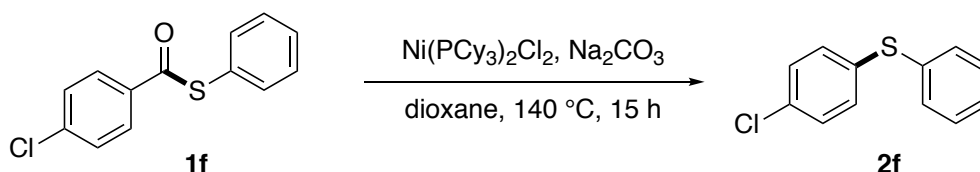


According to the general procedure, the reaction of *S*-phenyl 4-(trifluoromethyl)benzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (49.9 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.51-7.46 (m, 5 H), 7.42-7.38 (m, 3 H), 7.30 (s, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 142.84, 133.55, 131.03, 129.69, 129.02 (q, *J*<sup>F</sup> = 63.0 Hz), 128.66, 128.29, 125.82 (q, *J*<sup>F</sup> = 3.8 Hz), 124.09 (q, *J*<sup>F</sup> = 270.1 Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -62.42.

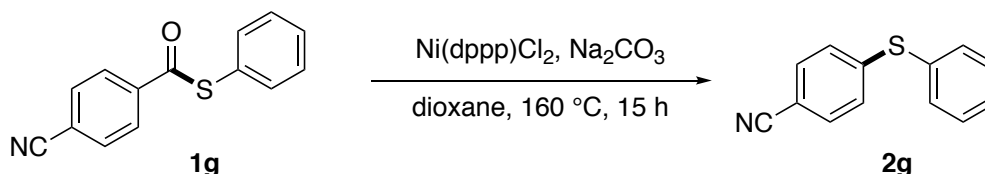
***S*-Phenyl 4-fluorobenzothioate (1e, Scheme 1, Entry 5)**



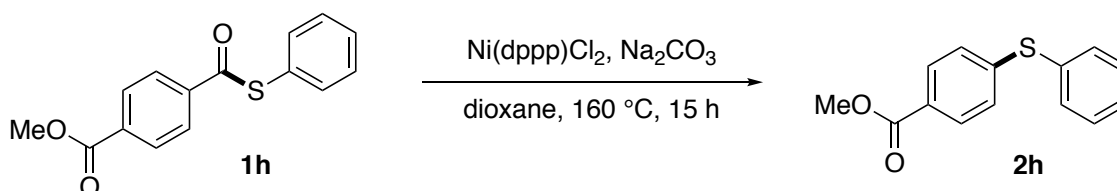
According to the general procedure, the reaction of *S*-phenyl 4-fluorobenzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 87% yield (35.6 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.42-7.39 (m, 2 H), 7.36-7.29 (m, 4 H), 7.26-7.23 (m, 1 H), 7.07-7.03 (t, *J* = 8.6 Hz, 2 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 162.42 (d, *J*<sup>F</sup> = 246.2 Hz), 136.64, 134.10 (d, *J*<sup>F</sup> = 8.1 Hz), 131.05, 129.96, 129.19, 126.77, 116.42 (d, *J*<sup>F</sup> = 21.8 Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -113.99.

**S-Phenyl 4-chlorobenzothioate (1f, Scheme 1, Entry 6)**

According to the general procedure, the reaction of *S*-phenyl 4-chlorobenzothioate (0.20 mmol),  $\text{Ni}(\text{PCy}_3)_2\text{Cl}_2$  (10 mol%) and  $\text{Na}_2\text{CO}_3$  (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at  $140^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 84% yield (37.1 mg). White solid.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.39-7.25 (m, 9 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  132.03, 131.48, 131.34, 131.18, 129.36, 129.33, 129.32, 127.46.

**S-Phenyl 4-cyanobenzothioate (1g, Scheme 1, Entry 7)**

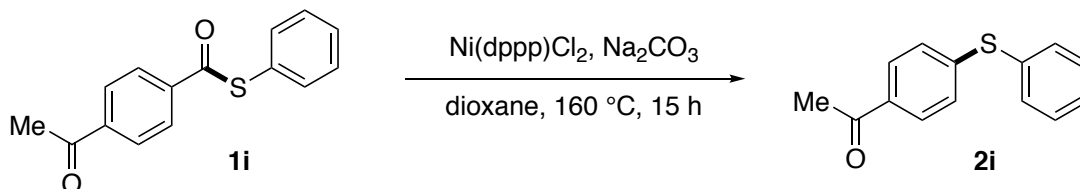
According to the general procedure, the reaction of *S*-phenyl 4-cyanobenzothioate (0.20 mmol),  $\text{Ni}(\text{dppp})\text{Cl}_2$  (10 mol%) and  $\text{Na}_2\text{CO}_3$  (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at  $160^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 72% yield (30.5 mg). White solid.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.54 (s, 2 H), 7.51-7.49 (d,  $J = 8.3$  Hz, 2 H), 7.46-7.46 (d,  $J = 2.7$  Hz, 3 H), 7.20-7.18 (d,  $J = 8.3$  Hz, 2 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  145.75, 134.53, 132.39, 130.86, 129.94, 129.42, 127.34, 118.82, 108.73.

**Methyl 4-((phenylthio)carbonyl)benzoate (1h, Scheme 1, Entry 8)**

According to the general procedure, the reaction of *S*-phenyl 4-((phenylthio)carbonyl)benzoate (0.20 mmol),  $\text{Ni}(\text{dppp})\text{Cl}_2$  (10 mol%) and  $\text{Na}_2\text{CO}_3$  (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at  $160^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 90% yield (44.0 mg). White solid.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.93-7.91 (d,  $J = 8.4$  Hz, 2 H),

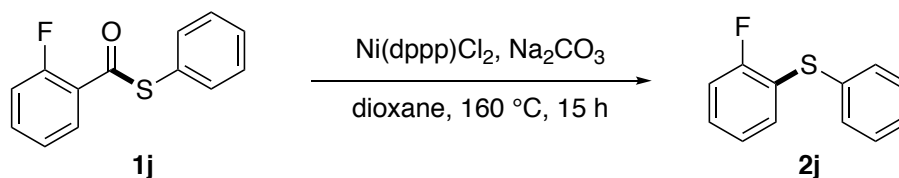
7.52-7.51 (m, 2 H), 7.44-7.39 (m, 3 H), 7.24-7.22 (d,  $J = 8.4$  Hz, 2 H), 3.91 (s, 3 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  166.70, 144.39, 133.71, 132.40, 130.10, 129.65, 128.67, 127.59, 127.50, 52.10.

***S*-Phenyl 4-acetylbenzothioate (1i, Scheme 1, Entry 9)**



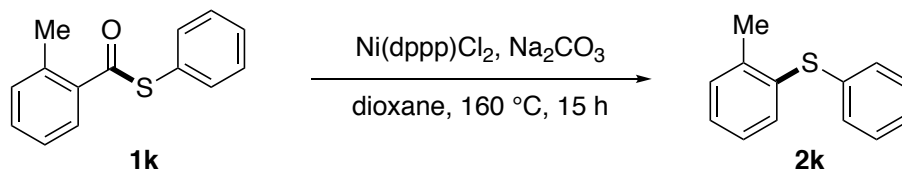
According to the general procedure, the reaction of *S*-phenyl 4-acetylbenzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (44.8 mg). White solid.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.85-7.84 (d,  $J = 8.4$  Hz, 2 H), 7.53-7.52 (m, 2 H), 7.45-7.40 (m, 3 H), 7.25-7.22 (d,  $J = 8.4$  Hz, 2 H), 3.91 (s, 3 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  197.14, 144.93, 134.51, 133.89, 132.12, 129.70, 128.91, 128.81, 127.49, 26.49.

***S*-Phenyl 2-fluorobenzothioate (1j, Scheme 1, Entry 10)**



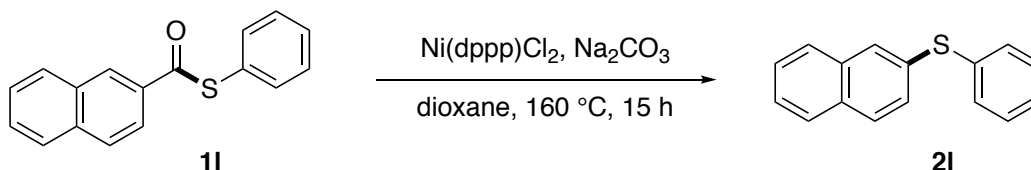
According to the general procedure, the reaction of *S*-phenyl 2-fluorobenzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 92% yield (37.6 mg). White solid.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.38-7.30 (m, 6 H), 7.28-7.27 (m, 1 H), 7.14-7.08 (m, 2 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  161.16 (d,  $J^F = 245.6$  Hz), 134.19, 133.43 (d,  $J^F = 0.9$  Hz), 130.95, 130.13 (d,  $J^F = 231.9$  Hz), 129.35 (d,  $J^F = 7.8$  Hz), 129.28, 127.30, 124.72 (d,  $J^F = 3.8$  Hz), 115.95 (d,  $J^F = 22.0$  Hz).  **$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**  $\delta$  -108.67.

***S*-Phenyl 2-methylbenzothioate (1k, Scheme 1, Entry 11)**



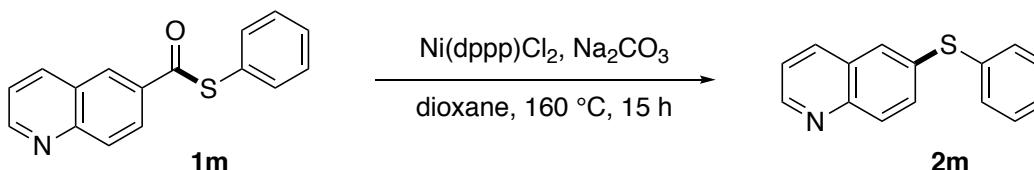
According to the general procedure, the reaction of *S*-phenyl 2-methylbenzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 97% yield (38.9 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.33-7.28 (m, 3 H), 7.26-7.16 (m, 6 H), 2.41 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 140.00, 136.17, 133.77, 133.01, 130.61, 129.65, 129.14, 127.92, 126.73, 126.36, 20.61.

### *S*-Phenyl naphthalene-2-carbothioate (**1l**, Scheme 1, Entry 12)



According to the general procedure, the reaction of *S*-phenyl naphthalene-2-carbothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 95% yield (44.9 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.88 (s, 1 H), 7.85-7.84 (d, *J* = 6.4 Hz, 1 H), 7.81-7.80 (d, *J* = 8.6 Hz, 1 H), 7.78-7.76 (d, *J* = 8.3 Hz, 1 H), 7.52-7.50 (t, *J* = 3.8 Hz, 2 H), 7.46-7.42 (m, 3 H), 7.37-7.34 (t, *J* = 7.3 Hz, 2 H), 7.31-7.28 (t, *J* = 7.3 Hz, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 135.89, 133.83, 133.05, 132.33, 131.00, 129.92, 129.27, 128.90, 128.79, 127.77, 127.46, 127.10, 126.63, 126.24.

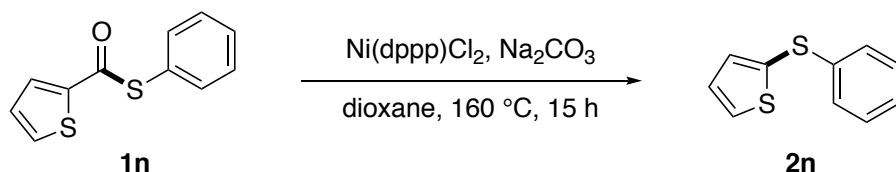
### *S*-Phenyl quinoline-6-carbothioate (**1m**, Scheme 1, Entry 13)



According to the general procedure, the reaction of *S*-phenyl quinoline-6-carbothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 94% yield (44.7 mg).

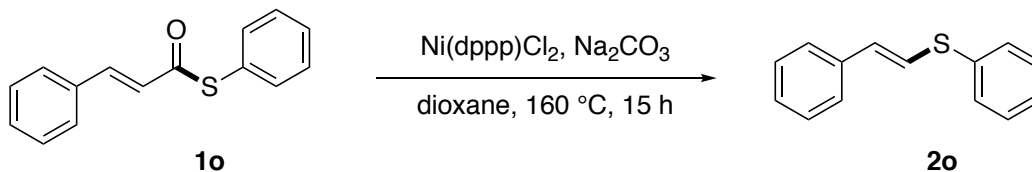
Colorless oil. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.90-8.89 (d, *J* = 3.8 Hz, 1 H), 8.05-8.02 (t, *J* = 6.1 Hz, 2 H), 7.73-7.72 (d, *J* = 1.7 Hz, 1 H), 7.63-7.61 (m, 1 H), 7.48-7.46 (d, *J* = 7.3 Hz, 2 H), 7.42-7.33 (m, 4 H), **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 150.37, 147.21, 135.30, 135.25, 134.45, 132.11, 131.49, 130.30, 129.49, 128.69, 128.00, 127.85, 121.69.

***S*-Phenyl thiophene-2-carbothioate (1n, Scheme 1, Entry 14)**



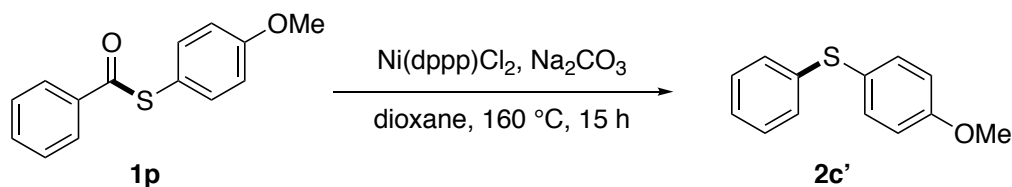
According to the general procedure, the reaction of *S*-phenyl thiophene-2-carbothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 95% yield (36.6 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.51-7.50 (d, *J* = 4.9 Hz, 1 H), 7.32 (s, 1 H), 7.29-7.26 (m, 2 H), 7.23-7.21 (m, 2 H), 7.20-7.17 (t, *J* = 7.2 Hz, 1 H), 7.11 (s, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 138.67, 136.08, 131.30, 131.16, 128.99, 127.95, 127.15, 126.07.

***S*-Phenyl (*E*)-3-phenylprop-2-enethioate (1o, Scheme 1, Entry 15)**



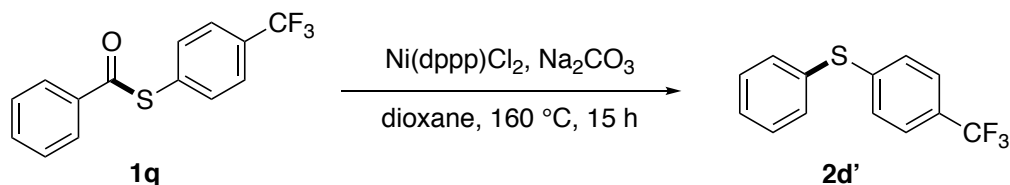
According to the general procedure, the reaction of *S*-phenyl (*E*)-3-phenylprop-2-enethioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 97% yield (41.2 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.46-7.44 (d, *J* = 7.5 Hz, 2 H), 7.39-7.33 (m, 6 H), 7.31-7.26 (m, 2 H), 6.94-6.91 (d, *J* = 15.5 Hz, 1 H), 6.79-6.76 (d, *J* = 15.5 Hz, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 136.55, 135.25, 131.83, 129.86, 129.18, 128.71, 127.61, 126.98, 126.05, 123.42.

***S*-(4-Methoxyphenyl) benzothioate (1p, Table 2, Entry 2)**



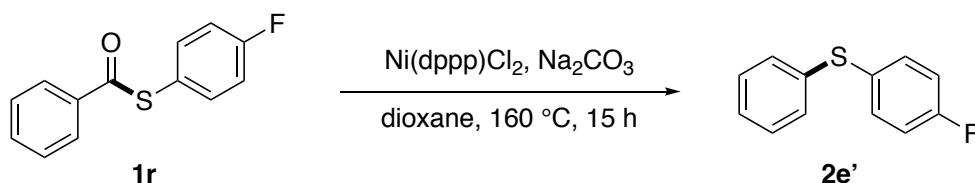
According to the general procedure, the reaction of *S*-(4-methoxyphenyl) benzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 85% yield (36.8 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.45-7.43 (d, *J* = 8.4 Hz, 2 H), 7.28-7.24 (t, *J* = 7.5 Hz, 2 H), 7.20-7.15 (m, 3 H), 6.93-6.92 (d, *J* = 8.4 Hz, 2 H), 3.85 (s, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 159.85, 138.61, 135.38, 128.94, 128.22, 125.77, 124.33, 115.00, 55.38.

***S*-(4-(Trifluoromethyl)phenyl) benzothioate (1q, Table 2, Entry 3)**



According to the general procedure, the reaction of *S*-(4-(trifluoromethyl)phenyl) benzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (49.9 mg). White solid. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 7.51-7.46 (m, 5 H), 7.42-7.38 (m, 3 H), 7.30 (s, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 142.84, 133.55, 131.03, 129.69, 129.02 (q, *J*<sup>F</sup> = 63.0 Hz), 128.66, 128.29, 125.82 (q, *J*<sup>F</sup> = 3.8 Hz), 124.09 (q, *J*<sup>F</sup> = 270.1 Hz). **<sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)** δ -62.42.

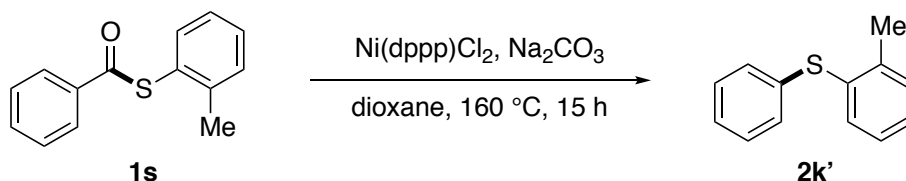
***S*-(4-Fluorophenyl) benzothioate (1r, Table 2, Entry 4)**



According to the general procedure, the reaction of *S*-(4-fluorophenyl) benzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 91% yield (37.2 mg).

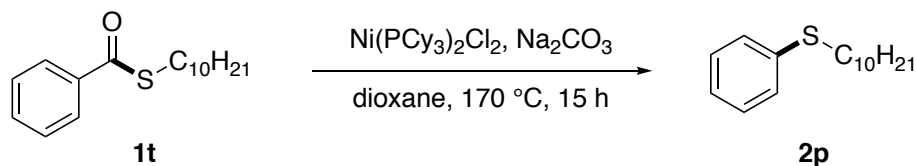
White solid.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.42-7.39 (m, 2 H), 7.36-7.29 (m, 4 H), 7.26-7.23 (m, 1 H), 7.07-7.03 (t,  $J = 8.6$  Hz, 2 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  162.42 (q,  $J^F = 246.2$  Hz), 136.64, 134.10 (q,  $J^F = 8.1$  Hz), 131.05, 129.96, 129.19, 126.77, 116.42 (q,  $J^F = 21.8$  Hz).  **$^{19}\text{F}$  NMR (471 MHz,  $\text{CDCl}_3$ )**  $\delta$  -113.99.

### *S*-(*o*-Tolyl) benzothioate (1s, Table 2, Entry 5)



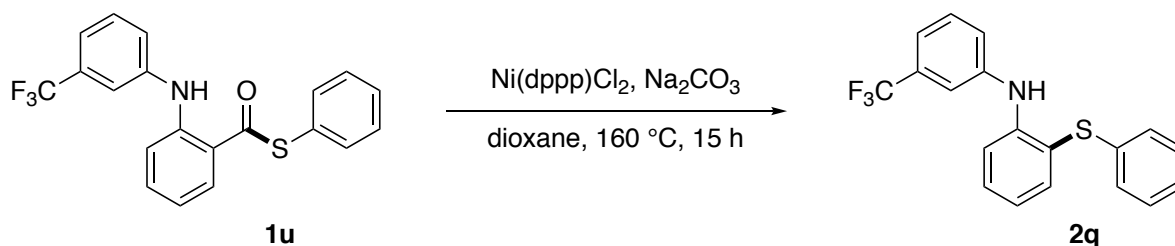
According to the general procedure, the reaction of *S*-(*o*-tolyl) benzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (38.5 mg). White solid.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.33-7.28 (m, 3 H), 7.26-7.16 (m, 6 H), 2.41 (s, 3 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  140.00, 136.17, 133.77, 133.01, 130.61, 129.65, 129.14, 127.92, 126.73, 126.36, 20.61.

### *S*-Decyl benzothioate (1t, Scheme 2)



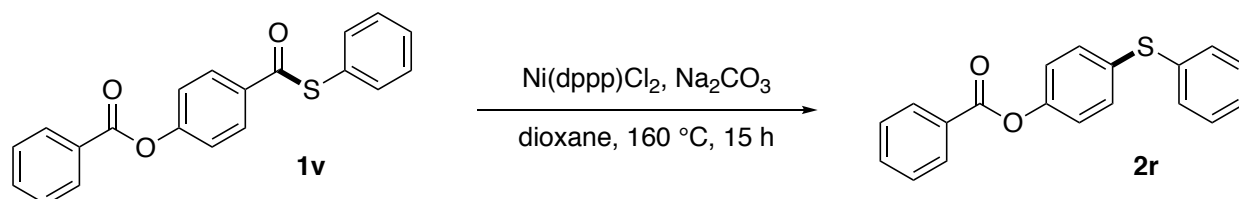
According to the general procedure, the reaction of *S*-decyl benzothioate (0.20 mmol), Ni(PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 170 °C, afforded after work-up and chromatography the title compound in 97% yield (48.6 mg). Colorless oil.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.35-7.34 (d,  $J = 7.6$  Hz, 2 H), 7.31-7.30 (d,  $J = 7.4$  Hz, 2 H), 7.20-7.17 (t,  $J = 7.3$  Hz, 1 H), 2.95-2.92 (t,  $J = 7.5$  Hz, 2 H), 1.70-1.64 (m, 2 H), 1.47-1.41 (m, 2 H), 1.33-1.28 (m, 12 H), 0.92-0.89 (t,  $J = 6.8$  Hz, 3 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  137.06, 128.83, 128.81, 125.62, 33.59, 31.89, 30.95, 29.54, 29.51, 29.31, 29.17, 28.86, 22.69, 14.12.

### *S*-Phenyl 2-((3-(trifluoromethyl)phenyl)amino)benzothioate (1u, Scheme 3)



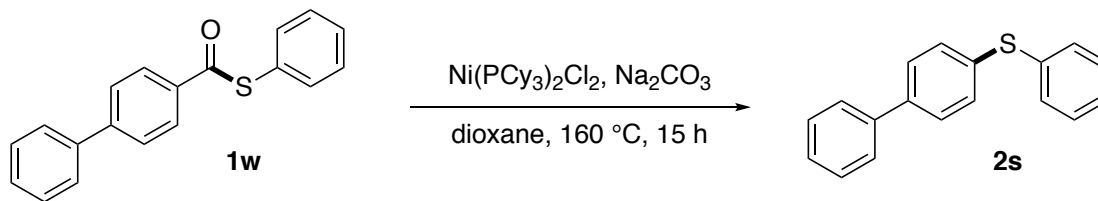
According to the general procedure, the reaction of *S*-phenyl 2-((3-(trifluoromethyl)phenyl)amino)benzothioate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 96% yield (66.4 mg). *New compound*. Yellow oil. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 9.61 (s, 1 H), 8.19-8.17 (d, *J* = 8.1 Hz, 1 H), 7.57-7.55 (m, 2 H), 7.52-7.51 (m, 3 H), 7.45-7.42 (t, *J* = 7.5 Hz, 3 H), 7.37-7.36 (d, *J* = 8.7 Hz, 1 H), 7.33-7.31 (d, *J* = 8.4 Hz, 2 H), 6.94-6.91 (t, *J* = 8.0 Hz, 1 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 144.81, 141.03, 135.63, 134.92, 131.81 (q, *J*<sup>F</sup> = 32.2 Hz), 130.86, 129.92, 129.82, 129.36, 129.08, 127.44, 126.06 (q, *J*<sup>F</sup> = 277.3 Hz), 124.89, 120.01 (q, *J*<sup>F</sup> = 3.8 Hz), 119.76, 118.46 (q, *J*<sup>F</sup> = 3.8 Hz) 114.72. **HRMS** calcd for C<sub>19</sub>H<sub>14</sub>F<sub>3</sub>NSNa (M<sup>+</sup> + Na) 368.0691, found 368.0688.

#### 4-((Phenylthio)carbonyl)phenyl benzoate (1v, Scheme 4)



According to the general procedure, the reaction of 4-((phenylthio)carbonyl)phenyl benzoate (0.20 mmol), Ni(dppp)Cl<sub>2</sub> (10 mol%) and Na<sub>2</sub>CO<sub>3</sub> (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 81% yield (49.7 mg). *New compound*. Colorless oil. **<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)** δ 8.07-8.06 (d, *J* = 8.1 Hz, 2 H), 7.66-7.63 (t, *J* = 7.3 Hz, 1 H), 7.57-7.45 (m, 8 H), 7.36-7.27 (m, 3 H). **<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)** δ 165.22, 151.00, 133.61, 130.77, 130.21, 129.63, 129.53, 129.50, 129.46, 129.11, 128.60, 127.54, 121.75. **HRMS** calcd for C<sub>19</sub>H<sub>14</sub>O<sub>2</sub>SNa (M<sup>+</sup> + Na) 329.0607, found 329.0611.

#### *S*-Phenyl [1,1'-biphenyl]-4-carbothioate (1w, Scheme 5)



According to the general procedure, the reaction of *S*-phenyl [1,1'-biphenyl]-4-carbothioate (0.20 mmol),  $\text{Ni}(\text{PCy}_3)_2\text{Cl}_2$  (10 mol%) and  $\text{Na}_2\text{CO}_3$  (1.5 equiv) in 1,4-dioxane (0.20 M) for 15 h at  $160\text{ }^\circ\text{C}$ , afforded after work-up and chromatography the title compound in 92% yield (48.3 mg). White solid.  **$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )**  $\delta$  7.61-7.60 (d,  $J = 8.0$  Hz, 2 H), 7.57-7.55 (d,  $J = 8.1$  Hz, 2 H), 7.48-7.42 (m, 6 H), 7.39-7.33 (m, 4 H).  **$^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )**  $\delta$  140.33, 139.99, 135.69, 134.91, 131.30, 131.18, 129.27, 128.86, 127.87, 127.50, 127.17, 126.98.

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