Rh(I)-Catalyzed Intramolecular Decarbonylation of Thioesters

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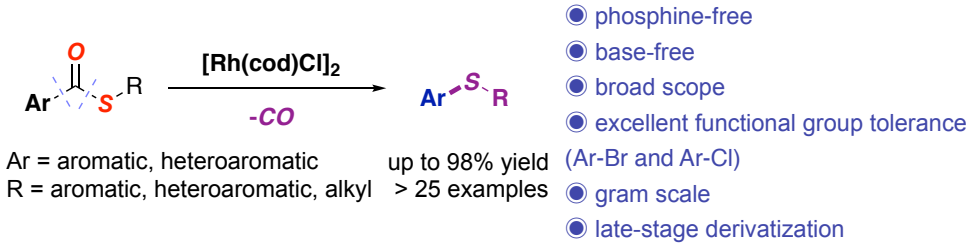


Decarbonylative synthesis of thioethers from thioesters proceeds in the presence of a catalytic amount of $[Rh(cod)Cl]_2$ (2 mol%). The protocol represents the first Rh-catalyzed decarbonylative thioetherification of thioesters to yield valuable thioethers. Notable features include the absence of phosphine ligands, inorganic bases and other additives and excellent group tolerance to aryl chlorides and bromides that are problematic using other metals to promote decarbonylation. Gram scale synthesis, late-stage pharmaceutical derivatization and orthogonal site-selective cross-couplings by C–S/C–Br cleavage are reported.

Thioethers are fundamental sulfur containing motifs that have found wide application in organic synthesis, and are central component of bioactive compounds, including pharmaceuticals, natural products and agrochemicals (Figure 1A).[1,2] Methods for the synthesis of thioethers have gained increasing attention due to the privileged role of sulfur and diverse applications of thioesters.[3,4] In this regard, transition-metal-catalyzed cross-couplings are one of the most fundamental methods for C–S bond formation.[4a,b] Recently, decarbonylative couplings have attracted significant attention because carboxylic acids and their derivatives can be converted into C–C, C–B, C–Si, C–N, C–O and C–S bonds under redox neutral conditions with a concomitant loss of CO.[5–9]

In this context, our laboratory has been focused on the development of decarbonylative cross-coupling reactions as an orthogonal strategy to conventional cross-couplings of aryl halides and pseudohalides.[5b,6,7] Decarbonylative synthesis of sulfides represents an attractive strategy to harness thioesters as electrophilic substrates for homogenous catalysis[10] by CO extrusion as an orthogonal method to oxidative methods for decarboxylative C–S coupling (Figure 1B).[11] Decarbonylative thioetherification of thioesters has been reported by Ni and Pd catalysis by the groups of Wenkert,[12] Sanford,[13] Yamaguchi,[14] and our group.[15,16] Studies on the mechanism by Kambe[17] and early precedents by Yamamoto[18] are noteworthy. In consideration of significant advantages of Rh as catalysis platform for organic synthesis[19] and decarbonylative coupling,[5] we recently questioned whether Rh(I) can be catalytically employed to promote decarbonylative thioetherification of thioesters.

Herein, we report the first Rh-catalyzed decarbonylative thioetherification of thioesters (Figure 1C). Notable features include (1) practical catalyst system using $[Rh(cod)Cl]_2$ the absence of phosphine ligands, inorganic bases and other additives, and (2) excellent functional group tolerance to aryl halides, such as chlorides and bromides that are problematic using other metals to promote decarbonylation. Furthermore, we present gram scale synthesis, late-stage pharmaceutical derivatization and orthogonal site-selective cross-couplings by C–S/C–Br cleavage. The protocol should facilitate the synthesis of valuable thioethers under decarbonylative conditions.

The novelty of the present work should be compared and contrasted with (1) the use of aryl halides and pseudohalides for the synthesis of thioethers;[3,4] and (2) the use of Ni and Pd catalyzed protocols for intramolecular decarbonylation of thioesters.[12–16] Thus, in terms of using thioesters vs. aryl halides for the synthesis of thioethers, the ultimate pool of precursors is different; in the latter case, thioesters are formed from carboxylic acids, which represent a ubiquitous class of substrates in organic synthesis and are inherently present in many pharmaceuticals and natural products.[9] With respect to other protocols for decarbonylation of thioesters,[12–16] the present method provides the first example of using Rh for catalytic decarbonylative thioetherification. Development of new metal catalysts for functional group interconversions is one of the most fundamental aspects of catalysis. The advantages can be identified as follows: (1) functional group tolerance to aryl bromides. This chemoselectivity cannot be easily achieved using low valent Ni or Pd systems, while the bromide handle is extremely useful for sequential transformations; (2) the Rh system is very practical in that phosphine or NHC ligands are not required, while phosphines/NHCs are required for Ni or Pd systems; (3) additionally Rh system shows better chemoselectivity for carbonyl containing substrates and vinyl substrates; (4) furthermore, Rh(I) is well known to promote other decarbonylative processes,[5] which might open the door for sequential catalysis using Rh systems.

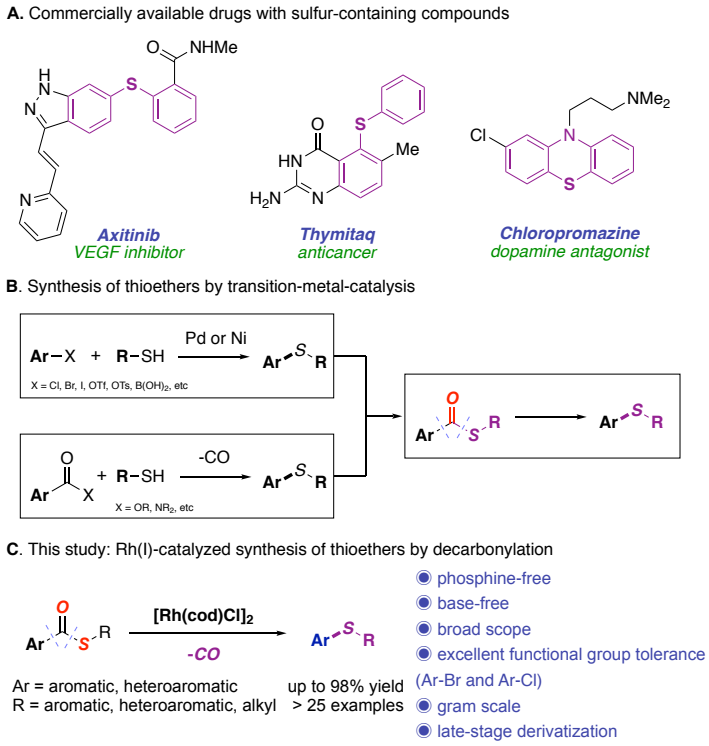
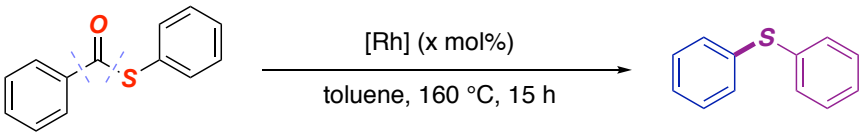


Figure 1. Context of the present study: intramolecular decarbonylation of thioesters.

The optimization was conducted using PhCOSPh **1a** as a modular, unbiased substrate. Selected results are summarized in Table 1. First, we screened various combinations of $[Rh(PPh_3)_3Cl]$ with inorganic bases, which furnished the desired product in 70-88% yields (Table 1, entries 1-3). Next, we found that the base is not needed for the reaction, furnishing the desired thioether product in excellent 87% yield (Table 1, entry 4). Various rhodium catalysts were tested, including $[Rh(PPh_3)_3Cl]$, $[Rh(cod)Cl]_2$, $[Rh(cod)_2]BF_4$ and $[RhCp^*Cl_2]_2$, and the catalytic system in the presence of $[Rh(cod)Cl]_2$ as catalyst shows the optimal condition (Table 1, entries 4-7). Control experiments indicated that lower catalyst loading resulted in a lower but promising reactivity (Table 1, entries 8-9). Interestingly, toluene was found as the preferred solvent over the more typically used dioxane in this cross-coupling manifold[5–8] (Table 1, entry 10). Finally, we found that the reaction proceeds at the temperatures as low as 120 °C (Table 1, entries 11-12), consistent with high efficiency of decarbonylation under these conditions.

Table 1. Summary of Optimization Studies[a]



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entry	catalyst	base	yield (%)[b]
1	$Rh(PPh_3)_3Cl$	Na_2CO_3	88
2	$Rh(PPh_3)_3Cl$	K_2CO_3	72
3	$Rh(PPh_3)_3Cl$	K_3PO_4	70
4	$Rh(PPh_3)_3Cl$	-	87
5	$[Rh(cod)Cl]_2$	-	97
6	$[Rh(cod)_2]BF_4$	-	65
7	$[RhCp^*Cl_2]_2$	-	75
8[c]	$[Rh(cod)Cl]_2$	-	51
9[d]	$[Rh(cod)Cl]_2$	-	39
10[e]	$[Rh(cod)Cl]_2$	-	56
11[f]	$[Rh(cod)Cl]_2$	-	77
12[g]	$[Rh(cod)Cl]_2$	-	43

[a]Conditions: thioester (1.0 equiv), catalyst (2 mol%), base (1.5 equiv), toluene, 160 °C, 15 h. [b]GC/^{1}H NMR yields. [c]catalyst (1 mol%). [d]catalyst (0.5 mol%). [e]dioxane as solvent. [f]140 °C. [g]120 °C.

With the optimal conditions in hand, the scope of the reaction was next investigated. As shown, this protocol shows very broad substrate scope to afford aryl-aryl, aryl-heteroaryl, vinyl-aryl and aryl-alkyl thioether products (Figure 2). Thus, a range of electronically-diverse thioesters can be utilized, including electron-neutral (**2a-c**), electron-donating (**2d**), and electron-withdrawing substrates (**2e**). Furthermore, halide-containing substrates, such as fluoro- (**2f**) and chloro- (**2g**) thioesters are well accommodated. Moreover, electrophilic substrates that would be problematic under traditional organometallic conditions, such as cyano (**2h**), ester (**2i**) and ketone (**2j**) are perfectly compatible with this method.

These findings are consistent with the high chemoselectivity exhibited by Rh[19] and attest to the high practicality of this method. Furthermore, sterically-hindered substrates (**2k-l**) are well tolerated in this protocol. As expected, meta-substitution (**2m**) is also well compatible. Moreover, this protocol can be employed to incorporate heterocyclic thioesters, such as furyl and thienyl in excellent yields (**2n-o**). Finally, vinyl thioesters are also well accommodated, delivering vinyl-aryl thioesters by this protocol (**2p**).

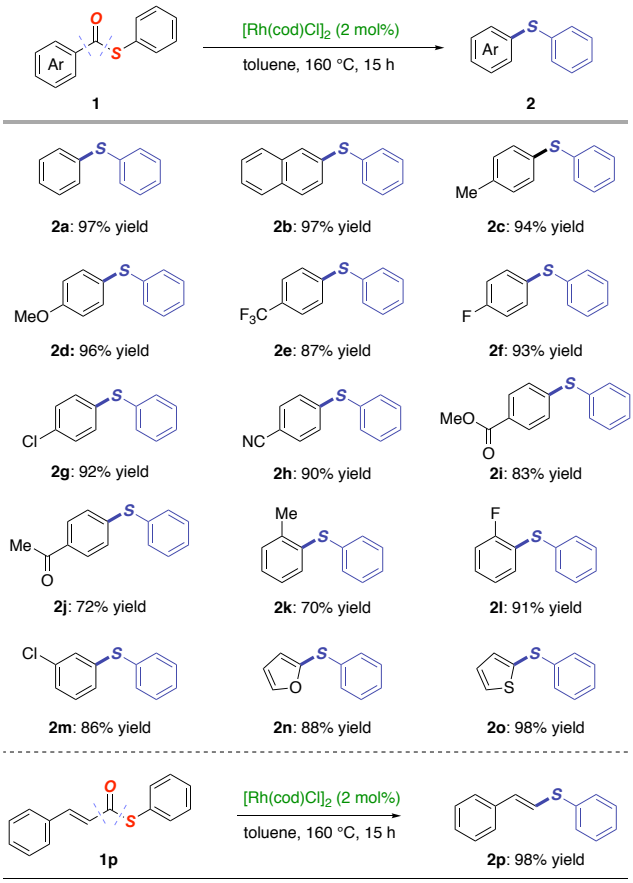

Figure 2. Scope of Rhodium-Catalyzed Intramolecular Decarbonylation of Thioesters. Conditions: thioester (1.0 equiv), $[Rh(cod)Cl]_2$ (2 mol %), toluene, 160 °C, 15 h. Isolated yields.

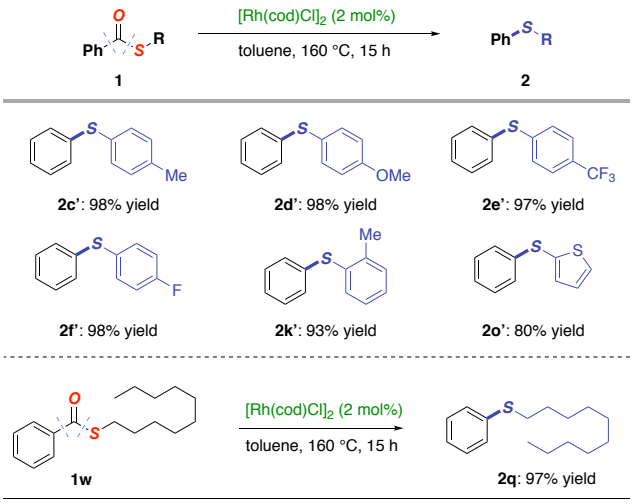

Figure 3. Scope of Rhodium-Catalyzed Intramolecular Decarbonylation of Thioesters. Conditions: thioester (1.0 equiv), $[Rh(cod)Cl]_2$ (2 mol %), toluene, 160 °C, 15 h. Isolated yields.

We were pleased to find that the scope of the thiophenol group is also broad (Figure 3). As shown high yields are achieved using electron-neutral (**2c'**), electron-rich (**2d'**) and electron-deficient (**2e'-f'**) substrates. Moreover, sterically-hindered (**2k'**) and heterocyclic thioester substrates (**2o'**) can be readily employed to afford the desired products in high yields. Finally, we demonstrated that this Rh(I)-catalyzed strategy is also amenable for the synthesis of challenging aryl-alkyl thioesters (**2q**) in the absence of β-hydride elimination.

To illustrate the utility of this Rh(I)-catalyzed intramolecular decarbonylation of thioesters, we conducted intramolecular selectivity studies and gram scale synthesis (Figure 4). Thus, intramolecular decarbonylation of thioesters by C–S cleavage is possible with full chemoselectivity in the presence of activated phenolic ester (Figure 4A).[20] This result is consistent with the fact that even activated ester carbonyl groups are well accommodated under these Rh(I) conditions, while the carbonyl group in the ester moiety remains fully intact and C–O cleavage is not observed. At this stage of reaction development, preliminary mechanistic studies have been done (not shown). As such, intermolecular competitions using PhCOS-4-Tol with external 4-F-C_6H_4-SH showed that the electron deficient product is favored (Ph-S-4-F-C_6H_4:Ph-S-4-Tol = 56:44), while the use of external 4-MeO-C_6H_4-SH showed that electron-donating product is less favored (Ph-S-4-MeO-C_6H_4:Ph-S-4-Tol = 41:59). These results are

consistent with the ease of oxidative addition. Importantly, this protocol is easily scalable as demonstrated by gram scale coupling conducted under the standard condition, which resulted in 90% yield (0.81 g) of the desired product, demonstrating the scalability of the method (Figure 4B).

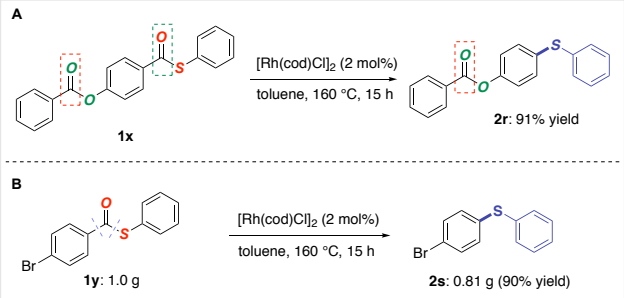

Figure 4. A Selectivity Study: C–S vs. C–O Coupling. B Gram Scale Reaction.

To further demonstrate the utility of this Rh(I)-catalyzed intramolecular decarbonylative thioester synthesis we conducted additional selectivity studies (Figure 5). First, we employed this method for late-stage derivatization of pharmaceuticals as demonstrated by probenecid (antihyperuricemic), which could be readily converted to the corresponding thioether in 87% yield (Figure 5A). One of the most important advantages of this robust Rh(I) is highlighted by the fact that this method readily tolerates aryl halides, such as Ar–Br, which are not compatible by other decarbonylative protocols for thioether synthesis (Figure 5B).[12–18] Thus, sequential C–S/C–Br cross-coupling is readily feasible by our standard catalytic system, leaving the bromide bond in thioether **2s** fully intact. This sets ups the C–Br bond for Buchwald-Hartwig amination by standard $Pd_2(dba)_3$/P*t*-Bu_3 catalytic system, which highlights the orthogonal nature of this process.

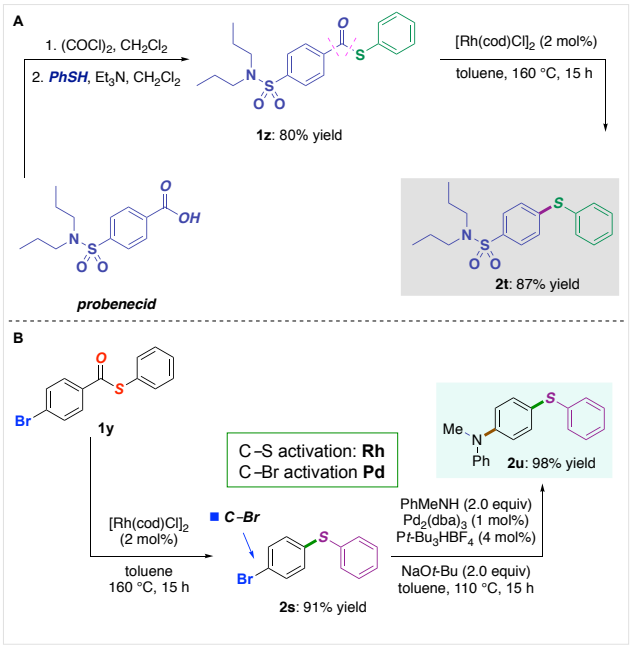

Figure 5. A Facile Synthesis of Probenecid Thioether; B Chemoselective C–N/C–Br Sequential Cleavage.

Conclusions

In conclusion, we have reported the first rhodium-catalyzed method for decarbonylative thioetherification of thioesters. The catalytic system employs commercially-available $[Rh(cod)Cl]_2$ in the absence of phosphine ligands, inorganic bases or other additives. The method proceeds with excellent functional group tolerance to furnish aryl–aryl, aryl–alkyl and vinyl–aryl thioether products. Gram scale synthesis, late-stage pharmaceutical derivatization and orthogonal sequential cross-couplings by C–S/C–Br cleavage have been demonstrated, highlighting the practicality of the method. We anticipate that this Rh(I)-catalyzed strategy will provide facile means for decarbonylative thioether synthesis. Further studies on decarbonylative cross-couplings are underway in our laboratory and will be reported in due course.

Experimental Section

General Methods. All starting materials reported in the manuscript have been prepared according to the method reported previously.[14] All compounds reported in this manuscript have been previously

reported or are commercially available. Spectroscopic data matched literature values. General methods have been published.[14]

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), and dichloromethane (typically, 0.50 M), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Triethylamine (typically, 2.0 equiv) was added dropwise to the reaction mixture with vigorous stirring at 0 °C, and the reaction mixture was stirred for 12 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_2O (1 x 10 mL), dried, and concentrated. The crude product was washed with hexane to give analytically pure product.

General Procedure for Decarbonylation of Thioester. An oven-dried vial equipped with a stir bar was charged with thioester substrate (neat, 1.0 equiv) and $[Rh(cod)Cl]_2$ (typically, 2 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 1H NMR ($CDCl_3$, 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) and $[Rh(cod)Cl]_2$ (1.0mg, 0.004 mmol, 0.02 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 ^1H NMR ($CDCl_3$, 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 97% (36.1 mg, 0.194 mmol). White solid. Characterization data are included in the section below.

***S*-Phenyl benzothioate (1a)**.[15] Yield 96% (1.029 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 190.3, 136.8, 135.3, 133.8, 129.7, 129.4, 128.9, 127.6, 127.5.

***S*-Phenyl naphthalene-2-carbothioate (1b)**.[15] Yield 70% (0.919 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 190.3, 136.0, 135.3, 134.1, 132.6, 129.8, 129.7, 129.4, 129.2, 128.8, 128.0, 127.6, 127.2, 123.4.

***S*-Phenyl 4-methylbenzothioate (1c)**.[15] Yield 81% (0.925 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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), 7.29 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 189.9, 144.7, 135.3, 134.2, 129.6, 129.6, 129.4, 127.7, 127.7, 21.9.

***S*-Phenyl 4-methoxybenzothioate (1d)**.[15] Yield 95% (1.158 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 188.8, 164.1, 135.4, 129.9, 129.5, 129.3, 127.8, 114.1, 55.7.

***S*-Phenyl 4-(trifluoromethyl)benzothioate (1e)**.[15] Yield 89% (1.253 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 189.6, 139.6, 135.1, 135.1 (d, J^2 = 33.0 Hz), 130.0, 129.6, 128.0, 126.7, 126.0 (q, J^3 = 3.8 Hz), 123.6 (d, J^1 = 272.6 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -63.10.

***S*-Phenyl 4-fluorobenzothioate (1f)**.[15] Yield 96% (1.113 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 188.6, 166.2 (d, J^1 = 255.7 Hz), 135.2, 133.1 (d, J^4 = 2.9 Hz), 130.2 (d, J^3 = 9.4 Hz), 129.8, 129.5, 127.2, 116.1 (d, J^2 = 21.9 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -104.11.

***S*-Phenyl 4-chlorobenzothioate (1g)**.[15] Yield 80% (0.990 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.99-7.95 (m, 2H), 7.53-7.49 (m, 2H), 7.48-7.46 (m, 5H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 189.3, 140.2, 135.2, 135.1, 129.9, 129.5, 129.2, 129.0, 127.1.

***S*-Phenyl 4-cyanobenzothioate (1h)**.[15] Yield 83% (0.988 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 189.3, 139.9, 135.1, 132.8, 130.2, 129.6, 128.1, 126.3, 117.9, 117.0.

Methyl 4-((phenylthio)carbonyl)benzoate (1i).[15] Yield 81% (1.105 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16-8.14 (m, 2H), 8.09-8.07 (m, 2H), 7.54-7.47 (m, 5H), 3.96 (s, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 189.9, 166.2, 140.1, 135.2, 134.6, 130.1, 129.9, 129.5, 127.6, 126.9, 52.7.

***S*-Phenyl 4-acetylbenzothioate (1j)**.[15] Yield 66% (0.850 g). Orange solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.12-8.10 (m, 2H), 8.06-8.04 (m, 2H), 7.54-7.47 (m, 5H), 2.66 (s, 3H). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 197.4, 189.9, 140.8, 140.0, 135.1, 130.0, 129.5, 128.8, 127.8, 126.9, 27.1.

***S*-Phenyl 2-methylbenzothioate (1k)**.[15] Yield 88% (1.009 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 192.3, 137.6, 136.9, 135.1, 132.2, 131.9, 129.6, 129.4, 128.8, 128.3, 126.0, 20.9.

***S*-Phenyl 2-fluorobenzothioate (1l)**.[15] Yield 94% (1.091 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 187.3 (d, J^5 = 5.2 Hz), 160.6 (d, J^1 = 258.3 Hz), 135.1, 134.8 (d, J^4 = 8.9 Hz),

130.0, 129.8, 129.4, 127.3 (d, J^6 = 4.3 Hz), 125.2 (d, J^3 = 11.6 Hz), 124.5 (d, J^7 = 3.6 Hz), 117.1 (d, J^2 = 22.4 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -109.75.

***S*-Phenyl 3-chlorobenzothioate (1m)**.[16] Yield 90% (1.119 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 189.2, 138.3, 135.1, 133.7, 130.2, 129.9, 129.5, 127.6, 126.9, 125.7.

***S*-Phenyl furan-2-carbothioate (1n)**.[16] Yield 87% (0.887 g). Pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 178.8, 150.5, 146.6, 135.3, 129.8, 129.4, 126.3, 116.4, 112.6.

***S*-Phenyl thiophene-2-carbothioate (1o)**.[16] Yield 76% (0.835 g). Pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 182.2, 141.5, 135.2, 133.4, 131.7, 129.8, 129.4, 128.2, 127.0.

***S*-Phenyl (E)-3-phenylprop-2-enethioate (1p)**.[15] Yield 84% (1.012 g). Pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 188.2, 141.7, 134.8, 134.2, 130.9, 129.6, 129.4, 129.2, 128.7, 127.7, 124.3.

***S*-(*p*-Tolyl) benzothioate (1q)**.[15] Yield 77% (0.881 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 190.7, 139.9, 136.8, 135.2, 133.7, 130.2, 128.8, 127.6, 123.9, 21.5.

***S*-(4-Methoxyphenyl) benzothioate (1r)**.[15] Yield 87% (1.062 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 191.2, 160.9, 136.8, 133.7, 128.9, 127.6, 118.0, 115.1, 55.5.

***S*-(4-(Trifluoromethyl)phenyl) benzothioate (1s)**.[15] Yield 83% (1.177 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 189.1, 136.4, 135.4, 134.2, 132.3, 131.6 (q, J^2 = 33.0 Hz), 129.0, 127.7, 126.1 (q, J^3 = 3.8 Hz), 124.0 (d, J^1 = 272.4 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -62.82.

***S*-(4-Fluorophenyl) benzothioate (1t)**.[15] Yield 96% (1.115 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 190.3, 163.8 (d, J^1 = 250.0 Hz), 137.3 (d, J^3 = 8.6 Hz), 136.5, 134.0, 129.0, 127.6, 122.7 (d, J^4 = 3.6 Hz), 116.7 (d, J^2 = 22.3 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -111.02.

***S*-(*o*-Tolyl) benzothioate (1u)**.[15] Yield 93% (1.065 g). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 189.8, 142.8, 136.9, 136.5, 133.7, 131.0, 130.4, 128.9, 127.7, 126.9, 126.8, 21.0.

***S*-(Thiophen-2-yl) benzothioate (1v)**.[16] Yield 73% (0.804 g). Brown solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 190.0, 136.5, 136.1, 134.1, 132.3, 129.0, 128.1, 127.7, 124.3.

***S*-Decyl benzothioate (1w)**.[15] Yield 90% (1.259 g). Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** 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), 1.32-1.26 (m, 12H), 0.90-

0.86 (t, *J* = 6.9 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 192.3, 137.4, 133.3, 128.7, 127.3, 32.0, 29.7, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 22.8, 14.3.

4-((Phenylthio)carbonyl)phenyl benzoate (1x).[15] Yield 94% (1.571 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 189.2, 164.7, 155.3, 135.3, 134.3, 134.1, 130.4, 129.8, 129.5, 129.3, 129.1, 128.9, 127.3, 122.3.

***S*-Phenyl 4-bromobenzothioate (1y)**.[21] Yield 78% (1.143 g). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91-7.88 (m, 2H), 7.65-7.62 (m, 2H), 7.53-7.46 (m, 5H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 189.5, 135.5, 135.2, 132.2, 129.9, 129.5, 129.1, 128.9, 127.0.

***S*-Phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzothioate (1z).**[15] Yield 80% (1.510 g). Pale yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 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). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 189.4, 144.9, 139.5, 135.1, 130.1, 129.6, 128.2, 127.5, 126.6, 50.1, 22.1, 11.3.

Diphenylsulfane (2a, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 97% yield (36.1 mg). Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36-7.33 (m, 4H), 7.32-7.28 (m, 4H), 7.26-7.22 (m, 2H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 135.9, 131.2, 129.3, 127.2.

Naphthalen-2-yl(phenyl)sulfane (2b, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl naphthalene-2-carbothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 97% yield (45.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.85 (s, 1H), 7.82-7.73 (m, 3H), 7.50-7.45 (m,

2H), 7.43-7.37 (m, 3H), 7.34-7.24 (m, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 136.0, 133.9, 133.1, 132.4, 131.1, 130.0, 129.4, 129.0, 128.9, 127.9, 127.6, 127.2, 126.7, 126.4.

Phenyl(p-tolyl)sulfane (2c, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 4-methylbenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 94% yield (37.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.30 (d, J = 8.1 Hz, 2H), 7.28-7.27 (d, J = 4.4 Hz, 4H), 7.23-7.17 (m, 1H), 7.16-7.14 (d, J = 7.9 Hz, 2H), 2.35 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 137.8, 137.3, 132.4, 131.4, 130.2, 129.9, 129.2, 126.5, 21.3.

(4-Methoxyphenyl)(phenyl)sulfane (2d, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 4-methoxybenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 96% yield (41.5 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.40 (m, 2H), 7.25-7.22 (m, 2H), 7.18-7.12 (m, 3H), 6.92-6.88 (m, 2H), 3.82 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 160.0, 138.8, 135.5, 129.1, 128.3, 125.9, 124.4, 115.1, 55.5.

Phenyl(4-(trifluoromethyl)phenyl)sulfane (2e, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 4-(trifluoromethyl)benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 87% yield (44.2 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50-7.47 (m, 5H), 7.41-7.38 (m, 3H), 7.28 (s, 1H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 143.0, 133.7, 132.6, 129.8, 128.8, 128.4, 128.2 (d, J^2 = 32.7 Hz), 126.0 (q, J^3 = 3.8 Hz), 124.2 (d, J^1 = 271.8 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -62.46.

(4-Fluorophenyl)(phenyl)sulfane (2f, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 4-fluorobenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 93% yield (38.0

mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.39-7.35 (m, 2H), 7.30-7.21 (m, 5H), 7.04-7.00 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 162.6 (d, J^1 = 247.8 Hz), 136.8, 134.3 (d, J^3 = 8.0 Hz), 130.3 (d, J^4 = 3.4 Hz), 130.1, 129.3, 126.9, 116.6 (d, J^2 = 21.8 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -114.02.

(4-Chlorophenyl)(phenyl)sulfane (2g, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 4-chlorobenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 92% yield (40.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36-7.30 (m, 4H), 7.29-7.23 (m, 5H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 135.3, 134.8, 133.1, 132.2, 131.5, 129.5, 129.5, 127.6.

4-(Phenylthio)benzonitrile (2h, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 4-cyanobenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 90% yield (38.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53-7.50 (m, 2H), 7.49-7.47 (d, J = 8.7 Hz, 2H), 7.44-7.43 (m, 3H), 7.18-7.15 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 145.9, 134.7, 132.5, 130.97, 130.1, 129.6, 127.5, 119.0, 108.8.

Methyl 4-(phenylthio)benzoate (2i, Figure 2).[15] According to the general procedure, the reaction of Methyl 4-((phenylthio)carbonyl)benzoate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 83% yield (40.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91-7.88 (m, 2H), 7.50-7.48 (m, 2H), 7.42-7.38 (m, 3H), 7.22-7.19 (m, 2H), 3.89 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.7, 144.5, 133.9, 132.50, 130.2, 129.8, 128.8, 127.7, 127.6, 52.2.

1-(4-(Phenylthio)phenyl)ethan-1-one (2j, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 4-acetylbenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (ethyl acetate/hexane = 1/15) the title compound in 72% yield (32.9 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.83-7.80 (m, 2H), 7.51-7.49 (m,

2H), 7.42-7.39 (m, 3H), 7.23-7.19 (m, 2H), 2.55 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 197.3, 145.1, 134.6, 134.0, 132.2, 129.8, 129.1, 129.0, 127.6, 26.6.

Phenyl(o-tolyl)sulfane (2k, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 2-methylbenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 70% yield (28.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35-7.13 (m, 9H), 2.38 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 140.1, 136.3, 133.9, 133.1, 131.2, 130.7, 129.8, 129.3, 128.1, 126.9, 126.5, 20.7.

(2-Fluorophenyl)(phenyl)sulfane (2l, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl 2-fluorobenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (ethyl acetate/hexane = 1/15) the title compound in 91% yield (37.2 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36-7.23 (m, 7H), 7.13-7.05 (m, 2H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 161.3 (d, J^1 = 247.1 Hz), 134.3, 133.6, 131.1, 129.5 (d, J^4 = 7.9 Hz), 129.4, 127.4, 124.9 (d, J^5 = 3.7 Hz), 122.9 (d, J^3 = 17.5 Hz), 116.1 (d, J^2 = 22.4 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -108.75.

(3-Chlorophenyl)(phenyl)sulfane (2m, Figure 2).[16] According to the general procedure, the reaction of *S*-phenyl 3-chlorobenzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 86% yield (38.0 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42-7.39 (m, 2H), 7.38-7.31 (m, 3H), 7.25-7.22 (m, 1H), 7.21-7.14 (m, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 139.0, 135.0, 134.0, 132.5, 130.2, 129.6, 129.6, 128.1, 128.0, 126.9.

2-(Phenylthio)furan (2n, Figure 2).[16] According to the general procedure, the reaction of *S*-phenyl furan-2-carbothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 88% yield (31.0 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.59-7.58 (dd, J = 1.9, 0.8 Hz, 1H), 7.36-7.27 (m, 1H), 7.24 (s, 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* = 3.3, 2.0 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 146.7, 143.2, 136.5, 131.2, 129.2, 127.7, 127.2, 126.5, 119.7, 112.0.

2-(Phenylthio)thiophene (2o, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl thiophene-2-carbothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 98% yield (37.7 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49-7.47 (dd, *J* = 5.4, 1.2 Hz, 1H), 7.37-7.28 (m, 2H), 7.24 (s, 1H), 7.21-7.14 (m, 3H), 7.09-7.07 (dd, *J* = 5.4, 3.6 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 138.8, 136.2, 131.4, 131.2, 129.3, 129.1, 128.1, 127.3, 126.2.

(*E*)-Phenyl(styryl)sulfane (2p, Figure 2).[15] According to the general procedure, the reaction of *S*-phenyl (*E*)-3-phenylprop-2-enethioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (ethyl acetate/hexane = 1/15) the title compound in 98% yield (41.6 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43-7.41 (m, 2H), 7.36-7.22 (m, 8H), 6.91-6.87 (d, *J* = 15.5 Hz, 1H), 6.75-6.72 (d, *J* = 15.5 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 136.7, 135.4, 132.0, 130.0, 129.3, 128.8, 127.7, 127.1, 126.2, 123.5.

Phenyl(p-tolyl)sulfane (2c', Figure 3).[15] According to the general procedure, the reaction of *S*-(*p*-tolyl) benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 98% yield (39.3 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.32-7.30 (d, *J* = 8.1 Hz, 2H), 7.28-7.27 (d, *J* = 4.4 Hz, 4H), 7.23-7.17 (m, 1H), 7.16-7.14 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 137.8, 137.3, 132.4, 131.4, 130.2, 129.9, 129.2, 126.5, 21.3.

(4-Methoxyphenyl)(phenyl)sulfane (2d', Figure 3).[15] According to the general procedure, the reaction of *S*-(4-methoxyphenyl) benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 98% yield (42.4 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.40 (m, 2H), 7.25-7.22 (m, 2H), 7.18-7.12

(m, 3H), 6.92-6.88 (m, 2H), 3.82 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 160.0, 138.8, 135.5, 129.1, 128.3, 125.9, 124.4, 115.1, 55.5.

Phenyl(4-(trifluoromethyl)phenyl)sulfane (2e', Figure 3).[15] According to the general procedure, the reaction of *S*-(4-(trifluoromethyl)phenyl) benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 97% yield (49.3 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50-7.47 (m, 5H), 7.41-7.38 (m, 3H), 7.28 (s, 1H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 143.0, 133.7, 132.6, 129.8, 128.8, 128.4, 128.2 (d, J^2 = 32.7 Hz), 126.0 (q, J^3 = 3.8 Hz), 124.2 (d, J^1 = 271.8 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -62.46.

(4-Fluorophenyl)(phenyl)sulfane (2f', Figure 3).[15] According to the general procedure, the reaction of *S*-(4-fluorophenyl) benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 98% yield (40.0 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40-7.35 (m, 2H), 7.29-7.21 (m, 5H), 7.05-7.01 (m, 2H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 162.6 (d, J^1 = 247.8 Hz), 136.8, 134.3 (d, J^3 = 8.0 Hz), 130.3 (d, J^4 = 3.4 Hz), 130.1, 129.3, 126.9, 116.6 (d, J^2 = 21.8 Hz). **^{19}F (376 MHz, $CDCl_3$)** δ -114.02.

Phenyl(o-tolyl)sulfane (2k', Figure 3).[15] According to the general procedure, the reaction of *S*-(*o*-tolyl) benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 93% yield (37.3 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.35-7.13 (m, 9H), 2.38 (s, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 140.1, 136.3, 133.9, 133.1, 131.2, 130.7, 129.8, 129.3, 128.1, 126.9, 126.5, 20.7.

2-(Phenylthio)thiophene (2o', Figure 3).[15] According to the general procedure, the reaction of *S*-(thiophen-2-yl) benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 80% yield (30.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49-7.47 (dd, J = 5.4, 1.2 Hz, 1H), 7.37-7.28 (m,

2H), 7.24 (s, 1H), 7.21-7.14 (m, 3H), 7.09-7.07 (dd, *J* = 5.4, 3.6 Hz, 1H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 138.8, 136.2, 131.4, 131.2, 129.3, 129.1, 128.1, 127.3, 126.2.

Decyl(phenyl)sulfane (2q, Figure 3).[15] According to the general procedure, the reaction of *S*-decyl benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 97% yield (48.6 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.33-7.25 (m, 4H), 7.18-7.14 (m, 1H), 2.93-2.90 (m, 2H), 1.68-1.61 (p, *J* = 7.3 Hz, 2H), 1.45-1.38 (p, *J* = 6.8 Hz, 2H), 1.26 (s, 12H), 0.90-0.86 (t, *J* = 6.8 Hz, 3H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 137.2, 129.0, 125.8, 33.7, 32.0, 29.7, 29.7, 29.5, 29.3, 29.3, 29.0, 22.8, 14.3.

4-(Phenylthio)phenyl benzoate (2r, Figure 4A).[15] According to the general procedure, the reaction of 4-((phenylthio)carbonyl)phenyl benzoate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (ethyl acetate/hexane = 1/15) the title compound in 91% yield (55.8 mg). Colorless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.21-8.18 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.67-7.63 (t, *J* = 7.4 Hz, 1H), 7.54-7.50 (t, *J* = 7.7 Hz, 2H), 7.43-7.40 (m, 2H), 7.37-7.30 (m, 4H), 7.27-7.25 (m, 1H), 7.20-7.16 (m, 2H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 165.2, 150.3, 136.0, 133.9, 133.1, 132.6, 131.0, 130.4, 129.5, 129.4, 128.8, 127.3, 122.7.

(4-Bromophenyl)(phenyl)sulfane (2s, Figure 4B).[22] According to the general procedure, the reaction of *S*-phenyl 4-bromobenzothioate (1.0 g, 3.41 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 90% yield (0.81 g). Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42-7.39 (m, 2H), 7.37-7.22 (m, 5H), 7.19-7.16 (m, 2H). **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 135.6, 135.0, 132.4, 132.2, 131.7, 131.6, 131.3, 129.5, 127.7, 121.0.

4-(Phenylthio)-*N*,*N*-dipropylbenzenesulfonamide (2t, Figure 5A).[16] According to the general procedure, the reaction of *S*-phenyl 4-(*N*,*N*-dipropylsulfamoyl)benzothioate (0.20 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (ethyl acetate/hexane = 1/15) the title compound in 87% yield (60.8 mg). White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66-7.62 (m, 2H), 7.51-7.48 (m, 2H), 7.42-7.40 (m, 3H), 7.23-7.20 (m, 2H), 3.06-3.02 (m, 4H), 1.57-1.50 (m, 4H), 0.88-0.84 (t, *J* = 7.4 Hz, 6H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 144.2, 137.3, 134.2, 131.8, 129.9, 129.2, 127.8, 127.7, 50.2, 22.2, 11.3.

(4-Bromophenyl)(phenyl)sulfane (2s, Figure 5B).[16] According to the general procedure, the reaction of *S*-phenyl 4-bromobenzothioate (0.2 mmol) and $[Rh(cod)Cl]_2$ (2 mol%) in tolunene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography (hexane) the title compound in 91% yield (48.3 mg). Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42-7.39 (m, 2H), 7.37-7.22 (m, 5H), 7.19-7.16 (m, 2H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 135.6, 135.0, 132.4, 132.2, 131.7, 131.6, 131.3, 129.5, 127.7, 121.0.

***N*-Methyl-*N*-phenyl-4-(phenylthio)aniline (2u, Figure 5B).** The reaction of (4-bromophenyl)(phenyl)sulfane (0.20 mmol), *N*-methylaniline (0.40 mmol), $Pd_2(dba)_3$ (1 mol%), tri-*tert*-butylphosphonium tetrafluoroborate (4 mol%) and sodium *tert*-butoxide (0.4 mmol) in tolunene (0.20 M) for 15 h at 110 °C, afforded after work-up and chromatography (ethyl acetate/hexane = 1/15) the title compound in 98% yield (57.1 mg). Pale solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.36-7.32 (m, 4H), 7.27-7.19 (m, 4H), 7.16-7.14 (d, *J* = 7.6 Hz, 3H), 7.11-7.07 (t, *J* = 7.3 Hz, 1H), 6.92-6.87 (m, 2H), 3.34 (s, 3H). **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 149.2, 148.4, 139.0, 135.0, 129.7, 129.0, 128.2, 125.8, 123.6, 123.5, 122.5, 118.3, 40.4. ESI-MS (m/z): Calcd for $C_{19}H_{18}NS$ (M^++H) 292.1160, Found 292.1157.

Supporting Information Available. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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