This ESI has been updated with new NMR spectra for compounds 3a, 3i, 3k, 3m, 3n, 3o, 3q, 3v, 3y, 3aa, 3ad and 3al. This ESI replaces the original version published on 22 June 2021.

Decarbonylative Sulfide Synthesis from Carboxylic Acids and Thioesters

Liu and Szostak

Decarbonylative Sulfide Synthesis from Carboxylic Acids and Thioesters via Cross-Over C–S Activation and Acyl Capture

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List of Known Compounds/General Methods

All starting materials reported in the manuscript have been prepared according to the method reported previously.¹⁻⁶ Unless stated otherwise, all compounds reported in this manuscript have been previously reported. Spectroscopic data matched literature values. All experiments involving palladium 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 ¹H 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 ¹H NMR and/or GC or GC/MS using an internal standard (optimization) and isolated yields (preparative runs) unless stated otherwise. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on Bruker spectrometers at 500 (¹H NMR) and 125 MHz (¹³C NMR). All shifts are reported in parts per million (ppm) relative to residual CHCl₃ peak (7.27 and 77.2 ppm, ¹H NMR and ¹³C 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. ¹H NMR and ¹³C NMR data are given for all compounds in the Supporting Information. ¹H NMR, ¹³C NMR and HRMS data are reported for all new compounds.

Experimental Procedures

General Procedure for Decarbonylative Sulfide Synthesis from Carboxylic Acids. An ovendried vial equipped with a stir bar was charged with carboxylic acid substrate (neat, 1.0 equiv), thioester 1.0 equiv), $Pd(OAc)_2$ 5 mol%) 1.3-(typically, (typically, and bis(diphenylphosphino)propane (typically, 10 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 CH₂Cl₂ (10 mL), filtered, and concentrated. The sample was analyzed by ¹H NMR (CDCl₃, 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 Decarbonylative Sulfide Synthesis from Carboxylic Acids. An oven-dried vial equipped with a stir bar was charged with 2-naphthoic acid (172.2 mg, 1.0 mmol, 1.0 equiv), S-phenyl benzothioate (neat, 214.3 mg, 1.0 mmol, 1.0 equiv), Pd(OAc)₂ (11.2 mg, 0.05 mmol, 0.05 equiv) and 1,3-bis(diphenylphosphino)propane (41.2 mg, 0.10 mmol, 0.10 equiv), placed under a positive pressure of argon, and subjected to three evacuation/backfilling cycles under high vacuum. Toluene (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 CH₂Cl₂ (20 mL), filtered, and concentrated. A sample was analyzed by ¹H NMR (CDCl₃, 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 95% (244.3 mg). Colorless oil. Characterization data are included in the section below.

\sim	, al	Pd(OAc) ₂ (5 mol%) L (10 mol%)	SPh
ОТ ОН	* SPh	toluene, 160 °C, 15 h	
Entry	[Pd]	Ligand	Yield (%)
1	-	-	<2
2	$Pd(OAc)_2$	DPPM	81
3	$Pd(OAc)_2$	DPPE	82
4	Pd(OAc) ₂	DPPP	>95
5	$Pd(OAc)_2$	DPPB	63
6	Pd(OAc) ₂	DPPPent	30
7	Pd(OAc) ₂	XantPhos	65
8	Pd(OAc) ₂	DPPF	73
9	Pd(OAc) ₂	PCy ₃	<2
10	Pd(OAc) ₂	PPh ₃	<2
11^{b}	Pd(OAc) ₂	DPPP	68
12 ^c	Pd(OAc) ₂	DPPP	70
13 ^d	$Pd(OAc)_2$	DPPP	81
14^{e}	Pd(OAc) ₂	DPPP	48
15 ^f	$Pd(OAc)_2$	DPPP	75

Table S1. Summary of Optimization Experiments Referred to from the Main Manuscript

^aConditions: carboxylic acid (1.0 equiv), thioester (1.0 equiv), Pd(OAc)₂ (5 mol%), ligand (10 mol%), toluene (0.20 M), 160 °C, 15 h. ^bPd(OAc)₂ (1 mol%), DPPP (2 mol%). ^cdioxane. ^d140 °C. ^e120 °C. ^f1 h.

Characterization Data





S-Phenyl 4-methylbenzothioate (2b).¹ White solid. <u>¹H NMR (500)</sup></u> <u>MHz, CDCl₃)</u> δ 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). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 189.75, 144.61, 135.15, 134.11, 29.22 127 59 21 78

130.28, 129.43, 129.24, 129.22, 127.59, 21.78.



S-Phenyl 4-(dibenzo[*b,d*]**thiophen-4-yl)benzothioate (2c)**.¹ Yellow solid. <u>¹H NMR (500 MHz, CDCl₃)</u> 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). ¹³C NMR

(125 MHz, CDCl₃) 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.



S-Phenyl (*E*)-3-phenylprop-2-enethioate (2d).¹ Yellow solid. <u>¹H</u> <u>NMR (500 MHz, CDCl₃)</u> 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). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 187.98, 141.55, 134.64,

134.05, 130.78, 129.47, 129.23, 129.03, 128.52, 127.65, 124.17.



129.75, 129.41, 129.21, 127.70, 113.97, 55.58.



S-Phenyl 4-(trifluoromethyl)benzothioate (2f).¹ White solid. <u>¹H</u> <u>NMR (500 MHz, CDCl₃)</u> δ 8.16 (s, 2 H), 7.79 (s, 2 H), 7.55 (s, 2 H), 7.51 (s, 3 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 189.40, 139.47, 135.01, 134.95 (q, J^2 = 32.9 Hz), 129.89, 129.44, 127.84, 126.59, 125.87 (q, J^3

= 3.4 Hz), 123.51 (q, J^1 = 270.7 Hz), <u>¹⁹F NMR (471 MHz, CDCl₃)</u> δ -63.06.



S-Phenyl 4-fluorobenzothioate (2g).¹ White solid. <u>¹H NMR (500</u> <u>MHz, CDCl₃)</u> 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). <u>¹³C NMR (125 MHz,</u> <u>CDCl₃)</u> δ 188.72, 166.10 (d, $J^{l} =$ 253.9 Hz), 135.12, 132.99 (d, $J^{4} =$ 3.0

Hz), 130.09 (d, $J^3 = 9.3$ Hz), 129.67, 129.32, 127.08, 115.95 (d, $J^2 = 22.0$ Hz),. <u>19F NMR (471 MHz, CDCl_3)</u> δ -104.10.



S-(4-Methoxyphenyl) benzothioate (2h).¹ Yellow solid. <u>¹H NMR</u>
(500 MHz, CDCl₃) 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). <u>¹³C NMR (125</u>

<u>MHz, CDCl</u>₃) δ 191.07, 160.82, 136.66, 133.58, 130.60, 128.74, 127.48, 117.91, 115.00, 55.41.



S-(4-Fluorophenyl) benzothioate (2i).¹ White solid. <u>¹H NMR (500</u> <u>MHz, CDCl₃)</u> 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). <u>¹³C NMR (125</u> <u>MHz, CDCl₃)</u> δ 189.81, 163.68 (d, *J*¹ = 248.4 Hz), 137.29 (d, *J*³ = 8.5

Hz), 136.47, 133.91,128.92, 127.58, 122.87 (d, $J^4 = 3.4$ Hz), 116.58 (d, $J^2 = 21.9$ Hz). <u>19F NMR</u> (471 MHz, CDCl₃) δ -110.55.

 $S-(o-Tolyl) \text{ benzothioate (2j).}^{1} \text{ Colorless oil. } \frac{1\text{H NMR (500 MHz, CDCl}_{3})}{1 \text{ Me}}$ $S-(o-Tolyl) \text{ benzothioate (2j).}^{1} \text{ Colorless oil. } \frac{1\text{H NMR (500 MHz, CDCl}_{3})}{1 \text{ Solution}}$ $\delta 8.12-8.11 \text{ (d, } J = 8.0 \text{ Hz, 2 H), 7.67-7.64 (t, } J = 7.4 \text{ Hz, 1 H), 7.55-7.52 (m, } 3 \text{ H), 7.43-7.42 (m, 2 H), 7.34-7.31 (t, } J = 7.4 \text{ Hz, 1 H), 2.46 (s, 3 H). } \frac{1^{3}\text{C}}{130.28, 128.79, 127.60, 126.87, 126.73, 20.89.}$



S-Decyl benzothioate (2k).¹ Yellow oil. <u>¹H NMR (500 MHz, CDCl₃)</u> 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). <u>¹³C NMR</u>

(125 MHz, CDCl₃) δ 192.16, 137.31, 133.19, 128.56, 127.19, 31.91, 29.58, 29.56, 29.53, 29.32, 29.18, 29.08, 28.97, 22.70, 14.13.

CF₃ S-(4-(Trifluoromethyl)phenyl) benzothioate (2l).¹ White solid. $\frac{1}{H}$ NMR (500 MHz, CDCl₃) 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). ¹³C NMR (125 MHz, CDCl₃) δ 188.92, 136.25, 135.23, 134.07, 132.19, 131.47 (q, $J^2 = 32.6$ Hz), 128.91, 127.59, 126.02 (q, $J^3 = 3.7$ Hz), 123.86 (q, $J^1 = 270.8$ Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -62.78.

2-Naphthoic acid and S-phenyl benzothioate (2a, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (1.0 mmol), *S*-phenyl benzothioate (1.0 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 95% yield (244.3 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.76 (s, 1 H), 7.74-7.72 (t, *J* = 5.1 Hz, 1 H), 7.70-7.68 (d, *J* = 8.7 Hz, 1 H), 7.67-7.65 (t, *J* = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-phenyl 4-methylbenzothioate (2b, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), *S*-phenyl 4methylbenzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 64% yield (30.3 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.76 (s, 1 H), 7.74-7.72 (t, *J* = 5.1 Hz, 1 H), 7.70-7.68 (d, *J* = 8.7 Hz, 1 H), 7.67-7.65 (t, *J* = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). <u>¹³C NMR (100</u> <u>MHz, CDCl₃)</u> δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-phenyl [1,1'-biphenyl]-4-carbothioate (2c, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), S-phenyl [1,1'-biphenyl]-4-carbothioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1.3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 63% yield (29.8 mg). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1 H), 7.74-7.72 (t, J = 5.1 Hz, 1 H), 7.70-7.68 (d, J = 8.7 Hz, 1 H), 7.67-7.65 (t, J = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.22 (m, 2 H), 7.20-77.16 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-phenyl (E)-3-phenylprop-2-enethioate (2d, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), S-phenyl (E)-3-phenylprop-2-enethioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1,3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 54% yield (25.6 mg). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1 H), 7.74-7.72 (t, J = 5.1 Hz, 1 H), 7.70-7.68 (d, J = 8.7 Hz, 1 H), 7.67-7.65 (t, J = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-phenyl 4-methoxybenzothioate (2e, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), *S*-phenyl 4methoxybenzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 32% yield (15.2 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.76 (s, 1 H), 7.74-7.72 (t, *J* = 5.1 Hz, 1 H), 7.70-7.68 (d, *J* = 8.7 Hz, 1 H), 7.67-7.65 (t, *J* = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). <u>¹³C NMR (100</u> <u>MHz, CDCl₃)</u> δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-phenyl 4-(trifluoromethyl)benzothioate (2f, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), S-phenyl 4-(trifluoromethyl)benzothioate (0.20)mmol), (5 mol%) $Pd(OAc)_2$ and 1.3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 27% yield (12.8 mg). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1 H), 7.74-7.72 (t, J = 5.1 Hz, 1 H), 7.70-7.68 (d, J = 8.7 Hz, 1 H), 7.67-7.65 (t, J = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). ¹³C NMR (100 MHz, CDCl₃) δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-phenyl 4-fluorobenzothioate (2g, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), *S*-phenyl 4-fluorobenzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 29% yield (13.7 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.76 (s, 1 H), 7.74-7.72 (t, *J* = 5.1 Hz, 1 H), 7.70-7.68 (d, *J* = 8.7 Hz, 1 H), 7.67-7.65 (t, *J* = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-(4-methoxyphenyl) benzothioate (2h, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), S-(4methoxyphenyl) benzothioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1,3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 90% yield (48.0 mg). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.79-7.78 (d, J = 7.7 Hz, 1 H), 7.74-7.72 (d, J = 8.6 Hz, 1 H), 7.70-7.68 (d, *J* = 7.7 Hz, 1 H), 7.63 (s, 1 H), 7.49-7.42 (m, 4 H), 7.33-7.31 (m, 1 H), 6.95-6.94 (d, *J* = 8.7 Hz, 2 H), 3.86 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 159.87, 135.91, 135.22, 133.78, 131.75, 128.55, 127.70, 127.16, 126.74, 126.51, 126.49, 125.63, 124.46, 115.06, 55.40. The spectral data matched those reported in the literature.²

2-Naphthoic acid and S-(4-fluorophenyl) benzothioate (2i, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), S-(4fluorophenyl) benzothioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1.3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 75% yield (38.2 mg). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.81-7.79 (m, 1 H), 7.77-7.75 (m, 2 H), 7.73-7.71 (m, 1 H), 7.49-7.45 (m, 2 H), 7.43-7.41 (m, 2 H), 7.36-7.34 (m, 1 H), 7.07-7.03 (t, J = 8.6 Hz, 2 H). <u>13C NMR (125</u> **MHz, CDCl₃**) δ 162.44 (q, J^{1} = 246.2 Hz), 133.99 (q, J^{3} = 8.1 Hz), 132.15, 130.32 (q, J^{4} = 3.3 Hz), 129.97, 129.21, 128.91, 128.70, 127.87, 127.76, 127.35, 126.70, 126.17, 116.49 (a. $J^2 =$ 21.8 Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -113.97. The spectral data matched those reported in the literature.³

2-Naphthoic acid and S-(o-tolyl) benzothioate (2j, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), *S*-(*o*-tolyl) benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 91% yield (45.6 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.82-7.81 (d, *J* = 6.9 Hz, 1 H), 7.78-7.76 (d, *J* = 8.6 Hz, 1 H), 7.73-7.71 (d, *J* = 8.7 Hz, 1 H), 7.68 (s, 1 H), 7.48-7.46 (m, 1 H), 7.37-7.32 (m, 3 H), 7.24-7.22 (m, 2 H), 7.19-7.17 (m, 1 H), 2.44 (s, 3 H). <u>¹³C</u> <u>NMR (125 MHz, CDCl₃)</u> δ 135.43, 133.89, 133.79, 133.52, 132.98, 132.01, 130.69, 130.34, 128.62, 128.11, 127.97, 127.75, 127.72, 127.34, 126.79, 126.72, 20.65. The spectral data matched those reported in the literature.²

2-Naphthoic acid and S-decyl benzothioate (2k, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), *S*-decyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 80% yield (48.1 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.81-7.79 (d, *J* = 8.1 Hz, 1 H), 7.77-7.74 (m, 3 H), 7.50-7.47 (t, *J* = 6.9 Hz, 1 H), 7.45-7.42 (m, 2 H), 3.05-3.02 (t, *J* = 7.4 Hz, 2 H), 1.75-1.69 (m, 2 H), 1.50-1.44 (m, 2 H), 1.33-1.28 (m, 12 H), 0.91-0.88 (t, *J* = 6.8 Hz, 3 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 134.64, 133.83, 131.62, 128.26, 127.71, 127.24, 126.98, 126.47, 126.31, 125.45, 33.50, 31.89, 29.55, 29.51, 29.31, 29.18, 29.11, 28.89, 22.68, 14.11. The spectral data matched those reported in the literature.⁴

2-Naphthoic acid and S-(4-(trifluoromethyl)phenyl) benzothioate (2l, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), *S*-(4-(trifluoromethyl)phenyl) benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 27% yield (16.5 mg). Colorless oil. <u>¹H NMR</u> (500 MHz, CDCl₃) δ 8.05-8.04 (d, J = 1.8 Hz, 1 H), 7.89-7.86 (m, 2 H), 7.85-7.82 (m, 1 H), 7.57-7.55 (m, 2 H), 7.52-7.49 (m, 3 H), 7.33-7.31 (d, J = 10.2 Hz, 2 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 141.74 (q, $J^3 = 1.8$ Hz), 133.97, 132.78, 131.99, 131.89, 129.13, 128.59, 128.42, 127.28, 126.78, 126.66, 125.96, 125.83, 124.80 (q, $J^2 = 4.6$ Hz), 123.03 (q, $J^1 = 337.6$ Hz). <u>¹⁹F NMR (471 MHz, CDCl₃)</u> δ -62.44. The spectral data matched those reported in the literature.⁵

2-Naphthoic acid and S-phenyl benzothioate (3a, Figure 3)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 95% yield (44.9 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.76 (s, 1 H), 7.74-7.72 (t, *J* = 5.1 Hz, 1 H), 7.70-7.68 (d, *J* = 8.7 Hz, 1 H), 7.67-7.65 (t, *J* = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

1-Naphthoic acid and S-phenyl benzothioate (3g, Figure 3)



According to the general procedure, the reaction of benzoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 91% yield (43.0 mg) Yellow oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 8.42-8.40 (m, 1 H), 7.92-7.88 (m, 2 H), 7.70-7.69 (d, J = 7.2 Hz, 1 H), 7.56-7.53 (m, 2 H), 7.48-7.45 (t, J = 7.9 Hz, 1 H), 7.27-7.17 (m, 5 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 136.94, 134.26, 133.62, 132.58, 131.26, 129.22, 129.09, 129.01, 128.58, 126.96, 126.44, 126.15, 125.84, 125.65. The spectral data matched those reported in the literature.²

Benzoic acid and S-phenyl benzothioate (3h, Figure 3)



According to the general procedure, the reaction of benzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 98% yield (36.5 mg) Yellow oil. <u>¹H NMR (500 MHz, CDCl₃)</u> 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). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 135.80, 131.05, 129.20, 127.05. The spectral data matched those reported in the literature.¹

4-(Trifluoromethyl)benzoic acid and S-phenyl benzothioate (3i, Figure 3)



According to the general procedure, the reaction of 4-(trifluoromethyl)benzoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 66% yield (33.6 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.41-7.39 (m, 5 H), 7.33-7.29 (m, 3 H), 7.20 (s, 1 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 141.81, 132.52, 131.44, 129.98, 128.65, 127.63, 127.23, 124.78 (q, $J^2 = 3.7$ Hz), 123.05 (q, $J^1 = 270.2$ Hz). <u>¹⁹F</u> <u>NMR (377 MHz, CDCl₃)</u> δ -62.46. The spectral data matched those reported in the literature.¹

4-(Trifluoromethoxy)benzoic acid and S-phenyl benzothioate (3j, Figure 3)



According to the general procedure, the reaction of 4-(trifluoromethoxy)benzoic acid (0.20 mmol), S-phenyl benzothioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1.3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 64% yield (34.6 mg). New compound. Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.40-7.30 (m, 7 H), 7.17-7.15 (d, J = 8.3 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ 148.12, 135.09, 134.76, 131.75, 131.71, 129.43, 127.68, 121.69, 120.43 (q, $J^{1} = 255.8$ Hz). ¹⁹F NMR (471 MHz, CDCl₃) δ -57.94. HRMS calcd for C₁₃H₉F₃OS (M⁺) 270.0321, found 270.0342.

4-Methoxybenzoic acid and S-phenyl benzothioate (3k, Figure 3)



According to the general procedure, the reaction of 4-methoxybenzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 45% yield (19.5 mg). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.34 (d, *J* = 8.6 Hz, 2 H), 7.16-7.15 (d, *J* = 7.4 Hz, 2 H), 7.10-7.05 (m, 3 H), 6.84-6.82 (d, *J* = 8.6 Hz, 2 H), 3.75 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 158.79, 137.57, 134.35, 127.89, 127.15, 124.72, 123.25, 113.95, 54.34. The spectral data matched those reported in the literature.¹

4-(Tosyloxy)benzoic acid and S-phenyl benzothioate (31, Figure 3)



According to the general procedure, the reaction of 4-(tosyloxy)benzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 61% yield (43.5 mg). *New compound*. Colorless oil. ¹H NMR (500 MHz, <u>CDCl₃</u>) δ 7.74-7.72 (d, *J* = 8.3 Hz, 2 H), 7.37-7.30 (m, 7 H), 7.21-7.20 (d, *J* = 8.8 Hz, 2 H), 6.93-6.91 (d, *J* = 8.8 Hz, 2 H), 2.47 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 148.37, 145.48, 135.59, 134.50, 132.34, 131.86, 131.23, 129.81, 129.41, 128.54, 127.74, 123.13, 21.74. <u>HRMS</u> calcd for C₁₉H₁₆O₃S₂ (M⁺) 356.0535, found 356.0553.

4-Cyanobenzoic acid and S-phenyl benzothioate (3m, Figure 3)



According to the general procedure, the reaction of 4-cyanobenzoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 72% yield (30.5 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.46-7.43 (m, 2 H), 7.42-7.40 (d, *J* = 8.4 Hz, 2 H), 7.37-7.36 (m, 3 H), 7.10-7.08 (d, *J* = 8.4 Hz, 2 H). <u>¹³C</u> <u>NMR (100 MHz, CDCl₃)</u> δ 144.73, 133.50, 131.35, 129.79, 128.90, 128.38, 126.27, 117.79, 107.66. The spectral data matched those reported in the literature.¹

4-(Methoxycarbonyl)benzoic acid and S-phenyl benzothioate (3n, Figure 3)



According to the general procedure, the reaction of 4-(methoxycarbonyl)benzoic acid (0.20 mmol), S-phenyl benzothioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1.3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 74% yield (36.2 mg). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.83-7.81 (d, J = 8.7 Hz, 2 H), 7.43-7.41 (m, 2 H), 7.34-7.31 (m, 3 H), 7.14-7.12 (d, J = 8.6 Hz, 2 H), 3.82 (s, 3 H). ¹³C NMR (100 MHz, CDCl₃) δ 165.67, 143.36, 132.68, 131.32, 129.06, 128.62, 127.64, 126.52, 126.43, 51.07. The spectral data matched those reported in the literature.¹

4-Acetylbenzoic acid and S-phenyl benzothioate (30, Figure 3)



According to the general procedure, the reaction of 4-acetylbenzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 82% yield (37.5 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.76-7.74 (d, *J* = 8.7 Hz, 2 H), 7.44-7.42 (m, 2 H), 7.35-7.32 (m, 3 H), 7.15-7.13 (d, *J* = 8.7 Hz, 2 H), 2.49 (s, 3 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 196.14, 143.92, 133.44, 132.87, 131.04, 128.67, 127.88, 127.79, 126.42, 25.47. The spectral data matched those reported in the literature.¹

4-Formylbenzoic acid and S-phenyl benzothioate (3p, Figure 3)



According to the general procedure, the reaction of 4-formylbenzoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 79% yield (33.9 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 9.93 (s, 1 H), 7.75-7.73 (d, *J* = 8.4 Hz, 2 H), 7.56-7.54 (m, 2 H), 7.45-7.44 (t, *J* = 3.8 Hz, 3 H), 7.27-7.25 (m, 2 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 191.18, 147.25, 134.39, 133.77, 131.37, 130.15, 129.83, 129.18, 127.28. The spectral data matched those reported in the literature.³

4-Chlorobenzoic acid and S-phenyl benzothioate (3q, Figure 3)



According to the general procedure, the reaction of 4-chlorobenzoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 87% yield (38.4 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.26-7.18 (m, 9 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 134.07, 133.60, 131.96, 130.98, 130.29, 128.31, 128.29, 126.41. The spectral data matched those reported in the literature.¹

3-Chlorobenzoic acid and S-phenyl benzothioate (3r, Figure 3)



According to the general procedure, the reaction of **3-chlorobenzoic acid** (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 63% yield (27.8 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.44-7.31 (m, 6 H), 7.27 (s, 1 H), 7.23-7.17 (m, 2 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 138.85, 134.90, 133.92, 131.06, 130.09, 129.49, 129.46, 129.21, 127.99, 127.89. The spectral data matched those reported in the literature.⁶

3-Methylbenzoic acid and S-phenyl benzothioate (3s, Figure 3)



According to the general procedure, the reaction of 3-methylbenzoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 73% yield (29.3 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.86-7.85 (m, 2 H), 7.55-7.53 (m, 2 H), 7.48-7.47 (m, 3 H), 7.45-7.43 (m, 1 H), 7.41-7.38 (m, 1 H), 2.46 (s, 3 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 138.68, 136.71, 135.10, 134.43, 129.48, 129.24, 128.64, 127.96, 127.54, 124.72, 21.36. The spectral data matched those reported in the literature.⁷

3-(Methoxycarbonyl)benzoic acid and S-phenyl benzothioate (3t, Figure 3)



According to the general procedure, the reaction of 3-(methoxycarbonyl)benzoic acid (0.20 mmol), S-phenyl benzothioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1.3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 76% yield (37.2 mg). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 8.03 (s, 1 H), 7.92-7.90 (d, J = 7.8 Hz, 1 H), 7.50-7.48 (m, 1 H), 7.41-7.29 (m, 6 H), 3.91 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 166.47, 137.12, 134.74, 134.65, 131.72, 131.46, 131.18, 129.41, 129.17, 127.99, 127.65, 52.26. The spectral data matched those reported in the literature.⁸

3-Acetylbenzoic acid and S-phenyl benzothioate (3u, Figure 3)



According to the general procedure, the reaction of 3-acetylbenzoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 86% yield (39.3 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.92 (s, 1 H), 7.83-7.81 (d, J = 7.7 Hz, 1 H), 7.49-7.48 (d, J = 7.8 Hz, 1 H), 7.42-7.31 (m, 6 H), 2.57 (s, 3 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 197.44, 137.98, 137.58, 134.64, 134.43, 131.89, 130.01, 129.47, 129.38, 127.79, 126.58, 26.65. The spectral data matched those reported in the literature.⁹

2-Methylbenzoic acid and S-phenyl benzothioate (3v, Figure 3)



According to the general procedure, the reaction of 2-methylbenzoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 77% yield (30.9 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.23-7.05 (m, 9 H), 2.31 (s, 3 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 138.95, 135.10, 132.71, 131.95, 129.56, 128.60, 128.10, 126.87, 125.68, 125.31, 19.57. The spectral data matched those reported in the literature.¹

2-Methoxybenzoic acid and S-phenyl benzothioate (3w, Figure 3)



According to the general procedure, the reaction of 2-methoxybenzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 82% yield (35.5 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.38-7.36 (m, 2 H), 7.34-7.31 (t, *J* = 7.2 Hz, 2 H), 7.29-7.24 (m, 2 H), 7.12-7.10 (m, 1 H), 6.94-6.92 (d, *J* = 8.2 Hz, 1 H), 6.91-6.88 (t, *J* = 7.6 Hz, 1 H), 3.90 (s, 3 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 157.36, 134.54, 131.65, 131.50, 129.15, 128.35, 127.07, 124.14, 121.27, 110.90, 55.91. The spectral data matched those reported in the literature.⁹

2-(Methylthio)benzoic acid and S-phenyl benzothioate (3x, Figure 3)



According to the general procedure, the reaction of 2-(methylthio)benzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 68% yield (31.6 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.32-7.29 (m, 6 H), 7.25-7.24 (m, 2 H), 7.12-7.09 (m, 1 H), 2.48 (s, 3 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 141.78, 135.38, 133.32, 132.86, 130.11, 129.18, 128.41, 126.77, 125.68, 125.37, 15.90. The spectral data matched those reported in the literature.¹⁰

Quinoline-6-carboxylic acid and S-phenyl benzothioate (3y, Figure 3)



According to the general procedure, the reaction of quinoline-6-carboxylic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 85% yield (40.4 mg). Colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 8.80-8.80 (d, *J* = 2.6 Hz, 1 H), 7.96-7.93 (t, *J* = 5.3 Hz, 2 H), 7.63 (s, 1 H), 7.54-7.51 (d, *J* = 8.8 Hz, 1 H), 7.38-7.36 (d, *J* = 6.9 Hz, 2 H), 7.33-7.25 (m, 4 H). ¹³C NMR (100 MHz, CDCl₃) δ 149.32, 146.14, 134.28, 134.22, 133.38, 131.08, 130.44, 129.23, 128.45, 127.64, 126.93, 126.81, 120.66. The spectral data matched those reported in the literature.¹

Picolinic acid and S-phenyl benzothioate (3z, Figure 3)



According to the general procedure, the reaction of picolinic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 74% yield (27.8 mg). Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 8.45-8.45 (d, *J* = 4.0 Hz, 1 H), 7.63-7.61 (m, 2 H), 7.49-7.44 (m, 4 H), 7.03-7.00 (m, 1 H), 6.92-6.90 (d, *J* = 8.1 Hz, 1 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 161.57, 149.55, 136.76, 134.98, 131.07, 129.65, 129.12, 121.40, 119.90. The spectral data matched those reported in the literature.⁹

Cinnamic acid and S-phenyl benzothioate (3aa, Figure 3)



According to the general procedure, the reaction of cinnamic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 73% yield (31.0 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.35-7.18 (m, 10 H), 6.83-6.80 (d, J = 15.4 Hz, 1 H), 6.68-6.64 (d, J = 15.5 Hz, 1 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 135.48, 134.19, 130.78, 128.79, 128.13, 127.66, 126.56, 125.92, 124.99, 122.35. The spectral data matched those reported in the literature.¹

(E)-3-(4-Methoxyphenyl)acrylic acid and S-phenyl benzothioate (3ab, Figure 3)



According to the general procedure, the reaction of (E)-3-(4-methoxyphenyl)acrylic acid (0.20) mmol), S-phenyl benzothioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1.3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 70% yield (34.0 mg). Colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 7.43-7.41 (m, 2 H), 7.36-7.32 (m, 4 H), 7.28-7.25 (m, 1 H), 6.90-6.88 (d, J = 8.7 Hz, 2 H), 6.77-6.76 (d, J = 7.1 Hz, 2 H), 3.84 (s, 3 H). ¹³C NMR (125 MHz, CDCl₃) δ 159.40, 135.96, 130.19, 129.41, 129.28, 129.10, 127.39, 126.61, 120.10, 114.16, 55.34. The spectral data matched those reported in the literature.¹¹

(E)-3-(4-(Trifluoromethyl)phenyl)acrylic acid and S-phenyl benzothioate (3ac, Figure 3)



According to the general procedure, the reaction of (E)-3-(4-(trifluoromethyl)phenyl)acrylic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 76% yield (42.6 mg). Yellow oil. <u>¹H NMR</u> (500 MHz, CDCl₃) δ 7.58-7.57 (d, *J* = 8.2 Hz, 2 H), 7.49-7.48 (d, *J* = 7.2 Hz, 2 H), 7.43-7.40 (m, 3 H), 7.36-7.31 (m, 2 H), 7.06-7.03 (d, *J* = 15.5 Hz, 1 H), 6.69-6.65 (d, *J* = 15.5 Hz, 1 H). <u>¹³C</u> NMR (125 MHz, CDCl₃) δ 139.98, 134.01, 130.80, 129.36, 129.08, 128.40, 127.66, 127.55, 125.95, 125.66 (q, *J*² = 3.8 Hz), 124.20 (q, *J*¹ = 270.1 Hz). <u>¹⁹F NMR (471 MHz, CDCl₃)</u> δ - 62.47. The spectral data matched those reported in the literature.¹¹

4-(Benzoyloxy)benzoic acid and S-phenyl benzothioate (3ad, Figure 3)



According to the general procedure, the reaction of 4-(benzoyloxy)benzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 81% yield (49.7 mg). Yellow oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 8.14-8.11 (m, 2 H), 7.59-7.56 (t, *J* = 7.4 Hz, 1 H), 7.47-7.43 (t, *J* = 7.5 Hz, 2 H), 7.36-7.33 (m, 2 H), 7.30-7.23 (m, 4 H), 7.20-7.18 (m, 1 H), 7.13-7.09 (m, 2 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 163.99, 149.14, 134.82, 132.71, 131.92, 131.45, 129.80, 129.17, 128.28, 128.23, 127.60, 126.07, 121.56. The spectral data matched those reported in the literature.¹

4-(*N*,*N*-Dipropylsulfamoyl)benzoic acid and *S*-phenyl benzothioate (3ae, Figure 3)



According to the general procedure, the reaction of 4-(*N*,*N*-dipropylsulfamoyl)benzoic acid (0.20 mmol), S-phenyl benzothioate (0.20)mmol), $Pd(OAc)_2$ (5 mol%) and 1.3bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 90% yield (63.0 mg). Yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 7.67-7.65 (d, J = 8.5 Hz, 2 H), 7.52-7.50 (m, 2 H), 7.45-7.42 (m, 3 H), 7.25-7.23 (d, J = 8.5 Hz, 2 H), 3.08-3.05 (t, J = 7.6 Hz, 4 H), 1.60-1.53 (m, 4 H), 0.90-0.87 (t, J= 7.4 Hz, 6 H). ¹³C NMR (125 MHz, CDCl₃) δ 144.08, 137.25, 133.99, 131.77, 129.79, 128.99, 127.71, 127.59, 50.08, 22.08, 11.20. The spectral data matched those reported in the literature.¹²

6-(3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-4-methoxyphenyl)-2-naphthoic acid and S-phenyl benzothioate (3af, Figure 3)



According to the general procedure, the reaction of 6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoic acid (0.20 mmol),*S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 80% yield (76.3 mg).*New compound* $. Colorless oil. <u>1H NMR (500 MHz, CDCl_3)</u> <math>\delta$ 7.97 (s, 1 H), 7.89 (s, 1 H), 7.85-7.83 (d, J = 8.6 Hz, 1 H), 7.81-7.80 (d, J = 8.6 Hz, 1 H), 7.76-7.75 (d, J = 8.5 Hz, 1 H), 7.60-7.60 (d, J = 1.9 Hz, 1 H), 7.55-7.53 (d, J = 8.3 Hz, 1 H), 7.46-7.44 (d, J = 8.6 Hz, 1 H), 7.41-7.39 (m, 2 H), 7.35-7.32 (t, J = 7.3 Hz, 2 H), 7.29-7.26 (m, 1 H), 7.02-7.00 (d, J = 8.4 Hz, 1 H), 3.92 (s, 3 H), 2.21 (s, 6 H), 2.13 (s, 3 H), 1.83 (s, 6 H). <u>13C NMR (125 MHz, CDCl_3)</u> δ 158.70, 139.46, 138.96, 136.20, 132.90, 132.75, 132.59, 132.31, 130.72, 130.02, 129.29, 129.22, 129.03, 127.80,

126.94, 126.45, 125.88, 125.58, 124.83, 112.13, 55.19, 40.64, 37.22, 37.16, 29.15. <u>**HRMS**</u> calcd for $C_{33}H_{32}OSNa$ (M⁺ + Na) 499.2072, found 499.2098.

4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoic acid and *S*-phenyl benzothioate (3ag, Figure 3)



According to the general procedure, the reaction of 4-(1-(3,5,5,8,8-pentamethyl-5,6,7,8-tetrahydronaphthalen-2-yl)vinyl)benzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 57% yield (47.1 mg). <u>New compound.</u> Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.99-7.97 (d, *J* = 8.4 Hz, 2 H), 7.55-7.53 (m, 2 H), 7.48-7.47 (m, 3 H), 7.40-7.39 (d, *J* = 8.3 Hz, 2 H), 7.16 (s, 1 H), 7.11 (s, 1 H), 5.87 (s, 1 H), 5.38 (s, 1 H), 1.98 (s, 3 H), 1.73 (s, 4 H), 1.33 (s, 6 H), 1.31 (s, 6 H). <u>¹³C NMR (125 MHz, CDCl₃)</u> δ 149.01, 146.37, 144.48, 142.41, 137.86, 135.12, 134.98, 132.71, 129.49, 129.24, 129.10, 129.08, 128.14, 127.64, 126.90, 117.17, 46.96, 35.23, 35.21, 34.03, 33.92, 31.96, 31.90, 27.44, 19.95. <u>HRMS</u> calcd for C₂₉H₃₂SNa (M⁺ + Na) 435.2117, found 435.2113.

4-((((*R*)-2,5,7,8-Tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl) benzoic acid and *S*-phenyl benzothioate (3ah, Figure 3)

$$\begin{array}{c|c} & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & & \\ & &$$

According to the general procedure, the reaction of 4-((((*R*)-2,5,7,8-tetramethyl-2-((4*S*,8*S*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl) benzoic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 77% yield (96.9 mg). <u>New compound</u>. Colorless oil. <u>¹H NMR (500 MHz, CDCl₃)</u> δ 7.47-7.45 (d, *J* = 8.1 Hz, 2 H), 7.42-7.41 (m, 3 H), 7.40-7.37 (m, 2 H), 7.34-7.31 (t, *J* =

7.9 Hz, 2 H), 4.69 (s, 2 H), 2.62-2.60 (t, J = 6.6 Hz, 2 H), 2.23 (s, 3 H), 2.18 (s, 3 H), 2.12 (s, 3 H), 1.88-1.76 (m, 2 H), 1.62-1.51 (m, 4 H), 1.43-1.39 (m, 3 H), 1.34 (s, 8 H), 1.32-1.28 (m, 3 H), 1.18-1.14 (m, 3 H), 1.12-1.09 (m, 3 H), 0.90-0.86 (m, 12 H). ¹³C NMR (125 MHz, CDCl₃) δ 148.00, 137.16, 135.99, 135.06, 134.98, 131.33, 130.89, 129.20, 129.07, 128.55, 127.87, 127.00, 123.00, 117.65, 74.87, 74.16, 40.10, 39.39, 37.48, 37.44, 37.41, 37.31, 32.82, 32.72, 31.33, 28.00, 27.44, 24.83, 24.46, 23.91, 22.64, 21.07, 20.70, 19.77, 12.88, 12.02, 11.83. <u>HRMS</u> calcd for C₄₂H₆₀O₂S (M⁺) 628.4309, found 628.4292.

2-Naphthoic acid and S-phenyl benzothioate (2a, Figure 4)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), S-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 95% yield (44.9 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.76 (s, 1 H), 7.74-7.72 (t, *J* = 5.1 Hz, 1 H), 7.70-7.68 (d, *J* = 8.7 Hz, 1 H), 7.67-7.65 (t, *J* = 5.2 Hz, 1 H), 7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-phenyl ethanethioate (2n, Figure 4)



According to the general procedure, the reaction of 2-naphthoic acid (0.20 mmol), S-phenyl ethanethioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 38% yield (18.0 mg). Colorless oil. <u>¹H NMR (400 MHz, CDCl₃)</u> δ 7.76 (s, 1 H), 7.74-7.72 (t, *J* = 5.1 Hz, 1 H), 7.70-7.68 (d, *J* = 8.7 Hz, 1 H), 7.67-7.65 (t, *J* = 5.2 Hz, 1 H),

7.42-7.37 (m, 2 H), 7.34-7.29 (m, 3 H), 7.26-7.22 (m, 2 H), 7.20-7.16 (m, 1 H). <u>¹³C NMR (100</u> <u>MHz, CDCl₃)</u> δ 134.80, 132.74, 131.96, 131.25, 129.91, 128.85, 128.20, 127.83, 127.71, 126.70, 126.39, 126.03, 125.58, 125.17. The spectral data matched those reported in the literature.¹

2-Naphthoic acid and S-phenyl dimethylcarbamothioate (20, Figure 4)



According to the general procedure, 2-naphthoic acid (0.20 mmol) was reacted with *S*-phenyl dimethylcarbamothioate (0.20 mmol), $Pd(OAc)_2$ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C. Analysis of the reaction mixture by ¹H NMR (500 MHz) and GC-MS indicated <2% of the title product.

2-Bromonaphthalene and S-phenyl benzothioate (1ad, Figure 4)



According to the general procedure, the reaction of 2-bromonaphthalene (0.20 mmol) was reacted with *S*-phenyl benzothioate (0.20 mmol), $Pd(OAc)_2$ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C. Analysis of the reaction mixture by ¹H NMR (500 MHz) and GC-MS indicated <2% of the title product.

Naphthalen-2-yl 4-methylbenzenesulfonate and S-phenyl benzothioate (1ae, Figure 4)



According to the general procedure, naphthalen-2-yl 4-methylbenzenesulfonate (0.20 mmol) was reacted with *S*-phenyl benzothioate (0.20 mmol), $Pd(OAc)_2$ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C. Analysis of the reaction mixture by ¹H NMR (500 MHz) and GC-MS indicated <2% of the title product.

Naphthalen-2-yl pivalate and S-phenyl benzothioate (1af, Figure 4)



According to the general procedure, naphthalen-2-yl pivalate (0.20 mmol) was reacted with *S*-phenyl benzothioate (0.20 mmol), $Pd(OAc)_2$ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C. Analysis of the reaction mixture by ¹H NMR (500 MHz) and GC-MS indicated <2% of the title product.

Synthetic application: oxidative cleavage/thiolation (3al, Figure 4)



According to the general procedure,¹³ the reaction of methyl 4-methyl-1,1'-biphenyl (2.0 mmol), KMnO₄ (2.5 equiv), Na₂CO₃ (1.0 equiv) in H₂O (0.2 M) for 8 h at 120 °C. The reaction mixture was filtered through a pad of celite, and the filtrate was acidified with 6N HCl (5 mL). The precipitation was filtrated and washed with water (3 × 10 mL) to afforded [1,1'-biphenyl]-4-carboxylic acid **1ag** in 87% yield (344.9 mg). White solid. Then the reaction of [1,1'-biphenyl]-4-carboxylic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after

work-up and chromatography the title compound in 88% yield (46.2 mg). Colorless oil. <u>¹H NMR</u> (400 MHz, CDCl₃) δ 7.51-7.49 (m, 2 H), 7.47-7.45 (d, *J* = 8.4 Hz, 2 H), 7.38-7.29 (m, 6 H), 7.27-7.20 (m, 3 H), 7.20-7.17 (m, 1 H). <u>¹³C NMR (100 MHz, CDCl₃)</u> δ 139.27, 138.93, 134.62, 133.85, 130.25, 130.13, 128.22, 127.81, 126.82, 126.45, 126.12, 125.93. The spectral data matched those reported in the literature.¹

Synthetic application: classical cross-coupling/thiolation (3am, Figure 4)



According to the general procedure,¹⁴ the reaction of 2-bromobenzoate (1.0 mmol), phenylboronic acid (1.5 equiv), Pd₂(dba)₃ (1 mol%), SPhos (4 mol%) and K₃PO₄ (2.0 equiv) in toluene (0.20 M) for 15 h at 100 °C, afforded after work-up and chromatography methyl [1,1'-biphenyl]-2-carboxylate **1ah'** in 95% yield (201.7 mg). White solid. A 20 mL vial was charged with methyl [1,1'-biphenyl]-2-carboxylate (0.95 mmol), NaOH (10.0 equiv) in methanol (1 mL) and water (10 mL) for 12 h at 80 °C. The organic solvent was removed under vaccum and the reaction mixture was acidified with 6N HCl (5 mL). The precipitation was filtrated and washed with water (3 × 10 mL) to afforded [1,1'-biphenyl]-2-carboxylic acid **1ah** in 90% yield (169.5 mg). White solid. Then the reaction of [1,1'-biphenyl]-2-carboxylic acid (0.20 mmol), *S*-phenyl benzothioate (0.20 mmol), Pd(OAc)₂ (5 mol%) and 1,3-bis(diphenylphosphino)propane (10 mol%) in toluene (0.20 M) for 15 h at 160 °C, afforded after work-up and chromatography the title compound in 93% yield (48.8 mg). Colorless oil. **1H NMR (500 MHz, CDCl₃)** δ 7.44-7.29 (m, 11 H), 7.26-7.24 (m, 3 H). **1³C NMR (125 MHz, CDCl₃)** δ 143.05, 140.65, 135.64, 135.04, 131.88, 131.24, 130.57, 129.39, 129.15, 128.04, 127.96, 127.44, 127.14, 126.79. The spectral data matched those reported in the literature.¹⁵

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ESI-35




^{110 100} f1 (ppm) -10



ESI-38



ESI-39



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





ESI-42



f1 (ppm)



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



ESI-45



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



ESI-47



ESI-48



ESI-49



f1 (ppm)







f1 (ppm)



110 100 f1 (ppm) -10



110 100 f1 (ppm) -10





ESI-57









110 100 f1 (ppm)





ESI-63



-10 f1 (ppm)



110 100 f1 (ppm) -10 210 200 190 160 150 130 120











110 100 f1 (ppm) -10



ESI-71



fl (ppm)


100 f1 (ppm)