Supporting Information

Site-Selective C–S Bond Formation at C–Br over C–OTf and C–Cl Enabled by an Air-Stable, Easily Recoverable, and Recyclable Palladium(I) Catalyst

Thomas Scattolin, Erdem Senol, Guoyin Yin, Qianqian Guo, and Franziska Schoenebeck*

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1. General experimental details

Reagents. Pd(I)-Iodo dimer was prepared according to the corresponding literature procedure.\[^{[1]}\] Unless otherwise stated, all starting materials were commercially available and used as received.

Solvents. Toluene, Et\(_2\)O and THF were purified by a solvent drying system from Innovative Technology Pure Solvent PS-MD-5.

Experimental Techniques. All reactions were carried out under argon atmosphere unless otherwise stated.

Characterization. All \(^1\)H NMR, \(^{13}\)C NMR, \(^{19}\)F NMR and \(^{31}\)P NMR spectra were recorded at ambient temperature either on Varian V-NMRS 600 or Varian V-NMRS 400 spectrometers. Chemical shifts (\(\delta\)) are quoted in parts per million (ppm) and were referenced to the residual solvent peak in the case of \(^1\)H and \(^{13}\)C NMR spectra, and to triethyl phosphate (+0.800 ppm) in the case of \(^{31}\)P NMR. Coupling constants (J) are given in Hz. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sex (sextet), hept (heptet), m (multiplet), dd (doublet of doublets) and br (broad). The peak observed at 83.3 ppm in \(^{13}\)C NMR measured at 151 MHz is an artifact from the instrument.

High Resolution Mass spectrometric analysis were performed on a Thermo Scientific LTQ Orbitrap XL (ESI), and on a Finnigan SSQ 7000, EI: 70 eV (EI).
All reactions were followed with an Agilent Technologies 5975 series MSD mass spectrometer coupled with an Agilent Technologies 7820A gas chromatograph (with an Agilent 19091s-433 HP-SMS column (30 m x 0.250 \(\mu\)m x 0.25 \(\mu\)m)).

(GC-MS Conditions: Front inlet mode: split; Temperature: 250°C; Pressure: 10.42 psi; Total flow 22.7 ml/min; Split ratio: 20:1; Split flow: 20 ml/min; Run time: 25.5 min; Oven Program: 60°C for 0.5 min then 10°C/min to 280°C for 3 min; Flow 1.2 ml/min.)
2. General experimental procedures and compounds characterization data

2.1. Procedure for the synthesis of sodium aryl or alkyl thiolates:

\[
\text{R-SH} \xrightarrow{\text{NaH, r.t., 1h, THF}} \text{R-SNa}
\]

Under argon atmosphere, to a suspension of NaH (300 mg, 12.50 mmol, 0.98 equiv.) in THF (30 mL) was slowly added a solution of the corresponding thiol (12.71 mmol, 1 equiv.) in THF (3 mL) at room temperature. **Careful:** strong gas evolution (H₂)! The reaction was stirred at the same temperature for 1h. To the generated white suspension in THF (sometimes addition of hexane was necessary to see white suspension) was added 50 mL of dry hexane. The solid was then collected and dried under vacuum to afford the corresponding sodium thiolate salt in quantitative yield. The salt were used without further purification.

The following sodium thiolate salts were prepared: sodium ethanethiolate, sodium benzenethiolate, sodium 2-chlorobenzenethiolate and sodium (4-chlorophenyl)methanethiolate.

2.2. Procedure for the synthesis of the different Pd(I) dimers:

\[
\begin{align*}
\text{rBu}_3\text{P-} & \text{Pd} \quad \text{SNa} \\
\text{Ph} & \text{Ph}
\end{align*}
\]

To Pd(I)-iodo dimer (100 mg, 0.115 mmol, 1 equiv.) and sodium benzenethiolate (36 mg, 0.242 mmol, 2.1 equiv.) was added toluene (1 mL). The reaction was stirred at room temperature for 2 h. Samples for \(^{31}\)P NMR were taken at 0.5 h, 1 h and 2 h reaction time. The crude mixture was filtered through celite under air atmosphere to afford after evaporation of the solvent 88 mg (0.105 mmol) of the Pd(I)-SPh dimer in 91% yield. \(^1\)H NMR (600 MHz, C\(_6\)D\(_6\)) δ 7.77 – 7.73 (m, 4H), 7.05 – 7.01 (m, 4H), 6.89 – 6.85 (m, 2H), 1.27 – 1.23 (m, 54H). \(^{31}\)P NMR (243 MHz, C\(_6\)D\(_6\)) δ 97.19.

The Pd(I)-SEt dimer was prepared in the same manner in 80% isolated yield.
2.3. Procedure for the stoichiometric reaction in Scheme 1:

To a solution of 4-iodoaniline (44 mg, 0.2 mmol, 2 equiv.) in toluene (1 mL) was added Pd(I)-SEt dimer (74 mg, 0.1 mmol, 1 equiv.). The reaction was stirred at 40°C for 1h. The crude mixture was filtered through a short plug of celite and concentrated under reduced pressure. The obtained crude material was purified by column chromatography on silica gel using hexane/EtOAc (98/2) to isolate the Pd(I)-iodo dimer (62 mg) in 71% yield; and hexane/EtOAc (80/20) to isolate the 4-(ethylthio)aniline (25.8 mg) as a pale yellow liquid in 84% yield.
2.4. Procedure for the kinetic study experiments:

![Chemical structure](image)

A stock solution was prepared by weighing 5-iodoindole (486 mg, 2.0 mmol) and mesitylene (298.4 mg) in benzene-$d_6$ (10 mL). Quantities of Pd(I)-iodo dimer 1 (8.7 mg [2.5 mol%], 17.4 mg [5.0 mol%], 26.1 mg [7.5 mol%] and 34.8 mg [10 mol%]) were separately weighed into four different 10 mL flasks with stirring bar, and to each of these flasks was added sodium ethanethiolate (40.4 mg, 0.48 mmol, 1.2 equiv.). To these mixtures, 2 mL of the stock solution (5-iodoindole: 97.2 mg, 0.4 mmol, 1.0 equiv.; mesitylene: 59.9 mg) was added and the reaction mixtures were stirred at 40°C. Aliquots (0.1 mL) of the reaction were taken every 5 min, diluted with 0.8 mL benzene-$d_6$ and filtered through celite. The reaction progress was monitored by the formation of 5-(ethylthio)-1H-indole 14 ($^1$H NMR: $\delta$ 1.53 ppm [t, $J = 7.2$ Hz, 3H]) as compared to an internal standard (mesitylene, $^1$H NMR: $\delta$ 2.16 ppm [s, 9H]) via $^1$H NMR using the following parameters on 400 MHz: repetitions: # = 32, relaxation delay: $T = 10$ sec, pulse angle: $\nu = 45^\circ$C, acquisition time: $t = 6:42$ min.
Integral of the product 5-(ethylthio)-1H-indole (14) *

| Time (min) | 1 [2.5 mol%] | 1 [5.0 mol%] | 1 [7.5 mol%] | 1 [10.0 mol%] |
|-----------|--------------|--------------|--------------|--------------|
| 5         | 0.0015       | 0.0230       | 0.0061       | 0.0212       |
| 10        | 0.0158       | 0.0329       | 0.0471       | 0.0438       |
| 15        | 0.0301       | 0.0729       | 0.0883       | 0.1756       |
| 20        | 0.0516       | 0.1012       | 0.1517       | 0.1932       |
| 25        | 0.0611       | 0.0150       | 0.1728       | 0.2864       |
| 30        | 0.0666       | 0.1662       | 0.2373       | 0.3515       |
| 35        | 0.0653       | 0.1663       | 0.2163       | 0.3694       |
| 40        | 0.0676       | 0.1783       | 0.2425       | 0.3915       |
| 45        | 0.0705       | 0.1688       | 0.2266       | 0.4351       |
| 50        | 0.0715       | 0.1773       | 0.2334       | 0.4415       |
| 55        | 0.0719       | 0.1678       | 0.2319       | 0.4552       |
| 60        | 0.0751       | 0.2077       | 0.2494       | 0.4605       |

*compared to internal standard, integral = 9 (in 1H NMR)

**Pd(I)-iodo dimer (1) study:**

Figure S2. Rate of formation of 5-(ethylthio)-1H-indole with different initial concentrations of Pd(I)-iodo dimer 1 (quantified by integration of the signal at 1.53 ppm (t, J = 7.2 Hz) against the -CH₃ signal of the internal standard at 2.16 ppm).
We studied the catalytic C-S bond formation between 5-iodoindole and sodium ethanethiolate with Pd(I)-iodo dimer 1 with the method of initial rate kinetics. To determine the reaction order in Pd(I)-iodo dimer, four kinetic runs were performed with varying concentrations of 1. Each of these was performed for a period of 1h via quantitative $^1$H NMR with an internal standard as reference and analyzed to approximately 10% conversion. Aliquots of the reaction mixture were taken approximately every 5 min and were quenched immediately. The rate of 14 was found to increase linearly with increasing concentration of 1. Figure S3 illustrates the logarithmic plot of the rate against the initial concentration of 1, indicating a straight line with a slope of 1.13. These data suggest that the C-S bond formation is first-order in 1.

| $[1]_0$ (mM) | $R^2$ | $d[14]/dt$ (mM) |
|--------------|-------|-----------------|
| 0.5          | 0.9731| 0.2284          |
| 1.0          | 0.9761| 0.5181          |
| 1.5          | 0.9895| 0.7551          |
| 2.0          | 0.9620| 1.1335          |

Table S1. $R^2$ values, demonstrating the “fit” of the data to applied linear trendlines in Figure S2, and values for the gradient of the trendline for each $[1]_0$.

Figure S3. Logarithmic plot of the initial concentration of 1 (mmol/L) against the rate of formation of 14.
2.5. **General procedure for the C-S bond forming reactions:**

A 5 mL vial equipped with a stirring bar was charged with the aryl halide (0.4 mmol, 1 equiv.), the sodium thiolate (0.48 mmol, 1.2 equiv.), Pd(I)-dimer (17.4 mg, 0.02 mmol, 0.05 equiv.). Toluene (2 mL) was added and the reaction mixture was stirred at the mentioned temperature for the indicated time. The aryl halide was adding together with toluene if it was a liquid. The crude mixture was filtered through a short plug of celite and concentrated under reduced pressure. The obtained crude material was purified by column chromatography on silica gel using the indicated solvent system.

2.6. **Compounds from Table 1:**

**4-(Ethylthio)aniline 4:** The title compound was obtained as a pale yellow oil after 3h at 40°C in 92% yield (56.4 mg) using 4-iodoaniline (87.6 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (80/20), R<sub>f</sub> = 0.36) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.25 – 7.20 (m, 2H), 6.63 – 6.57 (m, 2H), 3.67 (brs, 2H), 2.77 (q, J = 7.3 Hz, 2H), 1.21 (t, J = 7.3 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.8, 133.9, 123.3, 115.5, 30.3, 14.7. MS (70eV, EI): m/z (%): 153 (68) [M<sup>+</sup>], 124 (100), 80 (23). These data are in agreement with those reported previously in the literature.<sup>2</sup>

**1-(Ethylthio)-4-methylbenzene 5:** The title compound was obtained as a colourless oil after 3h at 40°C in 95% yield (57.0 mg) using 4-iodotoluene (87.2 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% pentane, R<sub>f</sub> = 0.20) following the general procedure. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 – 7.28 (m, 2H), 7.14 – 7.08 (m, 2H), 2.91 (q, J = 7.4 Hz, 2H), 2.33 (s, 3H), 1.29 (t, J = 7.4 Hz, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 136.1, 132.8, 130.9, 129.7, 28.5, 21.1, 14.6. MS (70eV, EI): m/z (%): 152 (100) [M<sup>+</sup>], 137 (52), 124 (26), 91 (63), 65 (9). HRMS (EI) calculated for C<sub>9</sub>H<sub>12</sub>S: 152.0654 [M<sup>+</sup>], Found: 152.0650. These data are in agreement with those reported previously in the literature.<sup>3</sup>
4-(Ethylthio)benzonitrile 6: The title compound was obtained as an orange oil after 12 h at 40°C in 92% yield (60.0 mg) using 4-iodobenzonitrile (91.6 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (pentane/EtOAc (98/2), R<sub>f</sub> = 0.35) following the general procedure. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.54 – 7.48 (m, 2H), 7.31 – 7.23 (m, 2H), 3.00 (q, J = 7.4 Hz, 2H), 1.36 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.1, 132.3, 126.7, 119.0, 108.0, 26.0, 13.8. MS (70eV, EI): m/z (%): 163 (100) [M⁺], 148 (65), 135 (91), 108 (14), 91 (14), 69 (10). HRMS (ESI) calculated for C<sub>9</sub>H<sub>10</sub>NS: 164.0528 [M+H]⁺, Found: 164.0526.

5-(Ethylthio)furan-2-carbaldehyde 7: The title compound was obtained as a yellow liquid after 12 h at 40°C in 87% yield (54.7 mg) using 5-iodofuran-2-carbaldehyde (88.8 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (85/15), R<sub>f</sub> = 0.30) following the general procedure. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.51 (s, 1H), 7.20 (d, J = 3.6 Hz, 1H), 6.48 (d, J = 3.6 Hz, 1H), 3.02 (q, J = 7.4 Hz, 2H), 1.34 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.3, 156.2, 154.1, 123.1, 114.2, 28.3, 15.2. HRMS (ESI) calculated for C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>NaS: 179.0138 [M+Na]⁺, Found: 179.0137.

3-(Ethylthio)thiophene 8: The title compound was obtained as a colourless oil after 10 h at 40°C in 95% yield (54.8 mg) using 3-iodothiophene (84.0 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% pentane, R<sub>f</sub> = 0.33) following the general procedure. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.32 (dd, J = 5.0, 3.0 Hz, 1H), 7.14 (dd, J = 3.0, 1.3 Hz, 1H), 7.03 (dd, J = 5.0, 1.3 Hz, 1H), 2.87 (q, J = 7.4 Hz, 2H), 1.29 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 132.0, 129.9, 126.1, 123.5, 29.5, 14.8. MS (70eV, EI): m/z (%): 144 (87) [M⁺], 129 (17), 126.1, 29.5, 14.8 MS (70eV, EI): m/z (%): 144 (87) [M⁺], 129 (17), 116 (100) 71 (44).

Ethyl-3-((tert-butylthio)benzoate 9: The title compound was obtained as a pale-yellow liquid after 6 h at 40°C in 96% yield (90.8 mg) using ethyl 3-iodobenzoate (110.4 mg) with sodium 2-methyl-2-propanethiolate (53.8 mg) after purification by column chromatography on silica gel (hexane/EtOAc (97/3), R<sub>f</sub> = 0.30) following the general procedure. ¹H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 – 8.19 (m, 1H), 8.06 – 8.01 (m, 1H), 7.74 – 7.69 (m, 1H), 7.44 – 7.38 (m, 1H), 4.39 (q, J = 7.1 Hz, 2H), 1.40 (t, J = 7.1 Hz, 3H), 1.30 (s, 9H). ¹³C NMR (101 MHz, CDCl<sub>3</sub>) δ 166.3, 141.8, 138.3, 133.5, 131.1, 129.9, 128.6, 61.3, 46.4, 31.1, 14.5. MS (70eV, EI): m/z (%): 238 (10) [M⁺], 193 (10), 182 (100), 154 (45), 137 (41), 109 (22), 57 (41). These data are in agreement with those reported previously in the literature.[4]
**Ethyl-3-(ethylthio)benzoate 10:** The title compound was obtained as a pale-yellow liquid after 6 h at 40°C in 92% yield (77.1 mg) using ethyl 3-iodobenzoate (110.4 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (97/3), Rf = 0.30) following the general procedure. ¹H NMR (400 MHz, CDCl₃) δ 8.17 – 8.12 (m, 1H), 8.02 – 7.96 (m, 1H), 7.68 – 7.63 (m, 1H), 7.56 – 7.48 (m, 1H), 4.54 (q, J = 7.1 Hz, 2H), 3.15 (q, J = 7.4 Hz, 2H), 1.56 (t, J = 7.1 Hz, 3H), 1.49 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 137.6, 133.1, 131.3, 129.6, 128.9, 126.9, 61.3, 27.6, 14.5, 14.4. HRMS (ESI) calculated for C₁₁H₁₄O₂NaS: 233.0609 [M+Na]+, Found: 233.0606.

**Ethyl(4-methoxyphenyl)sulphide 11:** The title compound was obtained as a colourless oil after 3 h at 40°C in 92% yield (61.4 mg) using 4-iodoanisole (93.6 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% hexane, Rf = 0.30) following the general procedure.

1H NMR (400 MHz, CDCl₃) δ 7.37 – 7.29 (m, 2H), 6.85 – 6.80 (m, 2H), 3.77 (s, 3H), 2.82 (q, J = 7.3 Hz, 2H), 1.23 (t, J = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 158.9, 133.3, 126.6, 114.6, 55.4, 29.9, 14.7. MS (70eV, EI): m/z (%): 168 (100) [M⁺], 153 (38), 139 (60), 125 (30), 96 (17), 69 (10). HRMS (EI) calculated for C₉H₁₂OS: 168.0603 [M⁺], Found: 168.0604. These data are in agreement with those reported previously in the literature.[⁵]

**1-(4-Ethylthiophenyl)pyrrole 12:** The title compound was obtained as a white solid after 6 h at 40°C in 94% yield (76.2 mg) using 1-(4-iodophenyl)pyrrole (107.6 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% hexane, Rf = 0.25) following the general procedure. M.p. = 81 – 83 °C. ¹H NMR (600 MHz, CDCl₃) δ 7.42 – 7.38 (m, 2H), 7.34 – 7.31 (m, 2H), 7.09 – 7.05 (m, 2H), 6.37 – 6.32 (m, 2H), 2.95 (q, J = 7.4 Hz, 2H), 1.33 (t, J = 7.4 Hz, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 139.1, 133.6, 130.9, 121.1, 119.4, 110.6, 28.5, 14.6. HRMS (ESI) calculated for C₁₂H₁₄NS: 204.0842 [M+H]+, Found: 204.0841.

**1-Benzyl-5-(ethylthio)-1H-indole 13:** The title compound was obtained as a yellow oil after 3 h at 40°C in 91% yield (97.3 mg) using 1-benzyl-5-iodo-1H-indole (133.3 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (pentane/EtOAc (98/2), Rf = 0.50) following the general procedure. ¹H NMR (400 MHz, CDCl₃) δ 7.80 – 7.73 (m, 1H), 7.35 – 7.19 (m, 5H), 7.17 – 7.08 (m, 3H), 6.55 – 6.50 (m, 1H), 5.30 (s, 2H), 2.92 (q, J = 7.3 Hz, 2H), 1.29 (t, J = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 137.4, 135.6, 129.5, 129.1, 128.9, 127.8, 126.9, 126.2, 125.4, 125.0, 110.2, 101.5, 50.3, 30.4, 14.9. MS (70eV,
EI: \( m/z \) (%): 267 (91) [M\(^+\)], 238 (26), 204 (5), 176 (6), 148 (5), 91 (100), 65 (12). HRMS (EI) calculated for C\(_{17}\)H\(_{17}\)NS: 267.1076 [M\(^+\)], Found: 267.1075.

5-(Ethylthio)-1H-indole 14: The title compound was obtained as a light-brown oil after 6 h at 40°C in 99% yield (70.0 mg) using 5-iodo-1H-indole (97.2 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (80/20), \( R_f = 0.40 \)) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.13 (brs, 1H), 7.75 – 7.74 (m, 1H), 7.33 – 7.27 (m, 2H), 7.20 – 7.17 (m, 1H), 6.52 – 6.48 (m, 1H), 2.90 (q, \( J = 7.3 \) Hz, 2H), 1.26 (t, \( J = 7.3 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 135.0, 128.6, 126.5, 125.5, 124.8, 124.6, 111.4, 102.4, 30.3, 14.7. HRMS (ESI) calculated for C\(_{17}\)H\(_{17}\)NS: 267.1076 [M\(^+\)], Found: 267.1075.

5-(tert-Butylthio)-1H-indole 15: The title compound was obtained as a beige solid after 6 h at 40°C in 98% yield (81.1 mg) using 5-iodo-1H-indole (97.2 mg) with sodium 2-methyl-2-propanethiolate (53.8 mg) after purification by column chromatography on silica gel (hexane/EtOAc (80/20), \( R_f = 0.45 \)) following the general procedure. M.p. = 62 – 64 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.21 (brs, 1H), 7.88 – 7.82 (m, 1H), 7.40 – 7.31 (m, 2H), 7.25 – 7.19 (m, 1H), 6.60 – 6.51 (m, 1H), 1.29 (s, 9H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 136.0, 131.6, 130.5, 128.4, 124.9, 122.8, 110.9, 103.0, 45.6, 31.0. HRMS (E SI) calculated for C\(_{12}\)H\(_{15}\)NS: 205.0921 [M\(^+\)], Found: 205.0919.

1-(Ethylthio)naphthalene 16: The title compound was obtained as a colourless oil after 3 h at 40°C in 95% yield (71.5 mg) using 2-iodonaphthalene (101.6 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% pentane, \( R_f = 0.40 \)) following the general procedure. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \( \delta \) 7.87 – 7.71 (m, 4H), 7.55 – 7.39 (m, 3H), 3.07 (q, \( J = 7.4 \) Hz, 2H), 1.39 (t, \( J = 7.4 \) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \( \delta \) 134.3, 133.9, 131.7, 128.4, 127.8, 127.3, 127.1, 126.6, 126.5, 125.6, 27.6, 14.4. MS (70eV, EI): \( m/z \) (%): 188 (100) [M\(^+\)], 173 (24), 160 (70), 128 (29), 115 (78). These data are in agreement with those reported previously in the literature.\(^{[6]}\)

Phenyl(4-methoxyphenyl)sulphide 17: The title compound was obtained as a colourless oil after 6 h at 60°C in 92% yield (79.6 mg) using 4-iodoanisole (93.6 mg) with sodium benzenethiolate (63.4 mg) after purification by column chromatography on silica gel (100% pentane, \( R_f = 0.35 \)) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.45 – 7.38 (m, 2H), 7.25 – 7.21 (m, 2H), 7.20 – 7.10 (m, 3H), 6.91 – 6.87 (m, 2H), 3.81 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta \) 159.9, 138.7, 135.5, 129.0, 128.3, 125.9, 124.4, 115.1, 55.5. MS
S12

(70eV, EI): \textit{m/z} (%) : 216 (100) [M\textsuperscript{+}], 200 (52), 171 (15), 129 (13), 77 (10), 51 (9). HRMS (EI) calculated for C\textsubscript{13}H\textsubscript{12}OS: 216.0603 [M\textsuperscript{+}], Found: 216.0604. These data are in agreement with those reported previously in the literature.\textsuperscript{[7]}

1-(Phenylothio)-4-methylbenzene 18: The title compound was obtained as a colourless liquid after 6 h at 60°C in 92% yield (73.8 mg) using 4-iodotoluene (87.2 mg) with sodium benzenethiolate (63.4 mg) after purification by column chromatography on silica gel (100% pentane, R\textsubscript{f} = 0.25) following the general procedure. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.35 – 7.31 (m, 2H), 7.31 – 7.27 (m, 1H), 7.24 – 7.19 (m, 4H), 7.18 – 7.14 (m, 2H), 2.35 (s, 3H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 137.7, 137.2, 132.4, 131.4, 130.2, 129.9, 129.2, 126.5, 21.3. MS (70eV, EI): \textit{m/z} (%) : 200 (100) [M\textsuperscript{+}], 184 (35), 167 (13), 91 (18), 65 (10). These data are in agreement with those reported previously in the literature.\textsuperscript{[7]}

4-(Phenylothio)aniline 19: The title compound was obtained as a beige solid after 6 h at 60°C in 99% yield (79.8 mg) using 4-iodoaniline (87.6 mg) with sodium benzenethiolate (63.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (80/20), R\textsubscript{f} = 0.20) following the general procedure. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.33 – 7.27 (m, 2H), 7.22 – 7.16 (m, 2H), 7.14 – 7.05 (m, 3H), 6.69 – 6.64 (m, 2H), 3.80 (brs, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 147.1, 139.8, 136.3, 128.9, 127.4, 125.4, 120.6, 116.0. MS (70eV, EI): \textit{m/z} (%) : 201 (100) [M\textsuperscript{+}], 200(50), 169 (20), 124 (17), 80 (14). These data are in agreement with those reported previously in the literature.\textsuperscript{[8]}

1-(Phenylothio)naphthalene 20: The title compound was obtained as a colourless oil after 10 h at 60°C in 95% yield (89.7 mg) using 2-iodonaphthalene (101.6 mg) with sodium benzenethiolate (63.4 mg) after purification by column chromatography on silica gel (100% pentane, R\textsubscript{f} = 0.40) following the general procedure. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.90 – 7.87 (m, 1H), 7.85 – 7.82 (m, 1H), 7.81 – 7.78 (m, 1H), 7.78 – 7.75 (m, 1H), 7.53 – 7.48 (m, 2H), 7.47 – 7.44 (m, 1H), 7.44 – 7.40 (m, 2H), 7.37 – 7.32 (m, 2H), 7.32 – 7.27 (m, 1H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 136.0, 133.9, 133.1, 132.4, 131.1, 130.0, 129.4, 129.0, 128.9, 127.9, 127.5, 127.2, 126.7, 126.3. MS (70eV, EI): \textit{m/z} (%) : 236 (100) [M\textsuperscript{+}], 202 (17), 115 (20). HRMS (EI) calculated for C\textsubscript{16}H\textsubscript{12}S: 236.0654 [M\textsuperscript{+}], Found: 236.0654. These data are in agreement with those reported previously in the literature.\textsuperscript{[7]}

5-((4,6-dimethylpyrimidin-2-ylthio)-1H-indole 21: The title compound was obtained as a pale-orange solid after 3 h at 40°C in 97% yield (95.8 mg)
using 5-iodo-1H-indole (97.2 mg) with sodium 4,6-dimethylpyrimidine-2-thiolate (77.8 mg) after purification by column chromatography on silica gel (CH$_2$Cl$_2$/MeOH (99/1), R$_f$ = 0.20) following the general procedure. M.p. = 142 – 144 °C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ 11.31 (brs, 1H), 7.79 – 7.73 (m, 1H), 7.49 – 7.38 (m, 2H), 7.27 – 7.19 (m, 1H), 6.91 (s, 1H), 6.50 – 6.44 (m, 1H), 2.24 (s, 6H). $^{13}$C NMR (101 MHz, DMSO-d$_6$) δ 171.5, 167.0, 136.0, 128.3, 128.2, 127.6, 126.3, 117.9, 116.1, 112.1, 101.4, 23.4. HRMS (ESI) calculated for C$_{14}$H$_{13}$N$_3$NaS: 278.0722 [M+Na]$^+$, Found: 278.0722.

2-((2-Methoxyphenyl)thio)-4,6-dimethylpyrimidine 22: The title compound was obtained as a light-orange oil after 3 h at 40°C in 97% yield (95.8 mg) using 2-iodoanisole (93.6 mg) with sodium 4,6-dimethylpyrimidine-2-thiolate (77.8 mg) after purification by column chromatography on silica gel (CH$_2$Cl$_2$/MeOH (99/1), R$_f$ = 0.15) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.63 – 7.58 (m, 1H), 7.43 – 7.36 (m, 1H), 7.02 – 6.93 (m, 2H), 6.66 (s, 1H), 3.79 (s, 3H), 2.31 (s, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.0, 167.1, 160.1, 136.8, 130.9, 121.0, 118.8, 116.1, 56.1, 24.0. HRMS (ESI) calculated for C$_{13}$H$_{14}$NO$_2$NaS: 269.0721 [M+Na]$^+$, Found: 269.0719.

1-Benzyl-5-(phenylthio)-1H-indole 23: The title compound was obtained as a yellow oil after 12 h at 60°C in 92% yield (116.0 mg) using 1-benzyl-5-iodo-1H-indole (133.3 mg) with sodium benzenethiolate (63.4 mg) after purification by column chromatography on silica gel (100% hexane, R$_f$ = 0.40) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.85 (m, 1H), 7.36 – 7.28 (m, 5H), 7.25 – 7.09 (m, 8H), 6.58 – 6.54 (m, 1H), 5.33 (s, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 139.8, 137.2, 136.3, 129.8, 129.3, 128.0, 127.9, 127.8, 127.6, 127.0, 125.4, 122.9, 110.9, 102.0, 50.4. MS (70eV, EI): m/z (%): 316 (100) [M+H]$^+$ (ESI), 273 (11), 241 (74), 219 (88), 207 (65), 163 (10). HRMS (ESI) calculated for C$_{21}$H$_{18}$NS: 316.1155 [M+H]$^+$, Found: 316.1165.

1-(Ethylthio)-2-methoxynaphthalene 24: The title compound was obtained as an orange oil after 12 h at 40°C in 85% yield (74.2 mg) using 1-bromo-2-methoxynaphthalene (94.8 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% pentane, R$_f$ = 0.22) following the general procedure. $^1$H NMR (600 MHz, CDCl$_3$) δ 8.68 – 8.64 (m, 1H), 7.88 – 7.83 (m, 1H), 7.82 – 7.77 (m, 1H), 7.59 – 7.52 (m, 1H), 7.40 – 7.35 (m, 1H), 7.31 – 7.27 (m, 1H), 4.04 (s, 3H), 2.89 (q, J = 7.4 Hz, 2H), 1.18 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 158.7, 136.6, 130.5, 129.4, 128.3, 127.1, 125.8, 123.9, 116.1, 113.1, 56.8, 29.1, 15.0. MS (70eV, EI): m/z (%): 218 (100) [M$^+$], 198 (16), 161 (17), 143 (26), 128
S14

HRMS (EI) calculated for C_{13}H_{14}OS: 218.0759 [M^+]\textsuperscript{+}, Found: 218.0757. These data are in agreement with those reported previously in the literature.\textsuperscript{[9]}

4-(Ethylthio)biphenyl 25: The title compound was obtained as a white solid after 5 h at 40°C in 91% yield (78.0 mg) using 4-bromobiphenyl (93.2 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% pentane, R\textsubscript{f} = 0.25) following the general procedure. M.p. = 72 - 74 °C. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.62 – 7.55 (m, 2H), 7.55 – 7.51 (m, 2H), 7.48 – 7.37 (m, 4H), 7.37 – 7.31 (m, 1H), 2.99 (q, \(J\) = 7.4 Hz, 2H), 1.36 (t, \(J\) = 7.3 Hz, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 140.6, 138.9, 135.9, 129.4, 128.9, 127.6, 127.4, 127.0, 27.8, 14.6. MS (70eV, EI): \(m/z\) (%): 214 (100) [M^+]\textsuperscript{+}, 185 (61), 166 (22), 152 (30), 115 (13). HRMS (EI) calculated for C\textsubscript{14}H\textsubscript{14}S: 218.0759 [M^+]\textsuperscript{+}, Found: 218.0757.

2-(Ethylthio)pyrimidine 26: The title compound was obtained as a pale-yellow liquid after 12 h at 40°C in 90% yield (50.3 mg) using 2-bromopyrimidine (63.6 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% CH\textsubscript{2}Cl\textsubscript{2}, R\textsubscript{f} = 0.30) following the general procedure. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.52 – 8.46 (m, 2H), 6.96 – 6.91 (m, 1H), 3.14 (q, \(J\) = 7.4 Hz, 2H), 1.39 (t, \(J\) = 7.4 Hz, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 172.8, 157.3, 116.4, 25.3, 14.5. HRMS (ESI) calculated for C\textsubscript{6}H\textsubscript{8}N\textsubscript{2}NaS: 163.0301 [M+Na]^+\textsuperscript{+}, Found 163.0300. These data are in agreement with those reported previously in the literature.\textsuperscript{[10]}

3-(Ethylthio)benzonitrile 27: The title compound was obtained as a pale-yellow liquid after 6 h at 40°C in 92% yield (59.7 mg) using 3-bromobenzonitrile (72.8 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (90/10), R\textsubscript{f} = 0.30) following the general procedure. \textsuperscript{1}H NMR (600 MHz, CDCl\textsubscript{3}) \(\delta\) 7.55 – 7.52 (m, 1H), 7.52 – 7.47 (m, 1H), 7.45 – 7.40 (m, 1H), 7.39 – 7.34 (m, 1H), 2.98 (q, \(J\) = 7.4 Hz, 2H), 1.34 (t, \(J\) = 7.4 Hz, 3H). \textsuperscript{13}C NMR (151 MHz, CDCl\textsubscript{3}) \(\delta\) 139.5, 132.4, 130.9, 129.5, 129.0, 118.6, 113.2, 27.2, 14.1. MS (70eV, EI): \(m/z\) (%): 163 (100) [M^+]\textsuperscript{+}, 148 (68), 135 (88), 108 (11), 91 (14). These data are in agreement with those reported previously in the literature.\textsuperscript{[11]}

5-(Ethylthio)-1,3-benzodioxole 28: The title compound was obtained as a yellow oil after 3 h at 40°C in 95% yield (69.2 mg) using 5-bromo-1,3-benzodioxole (80.4 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% pentane, R\textsubscript{f} = 0.25) following the general procedure. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 6.93 – 6.86 (m, 2H), 6.76 – 6.71 (m, 1H), 5.95 (s, 2H), 2.83 (q, \(J\) = 7.3 Hz, 2H), 1.25 (t, \(J\) = 7.3 Hz, 3H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) \(\delta\) 148.0, 147.0, 128.2, 125.3, 112.0, 108.7, 101.3, 29.9, 14.7. MS (70eV, EI):
m/z (%): 182 (100) [M⁺], 167 (17), 153 (70), 123 (10), 95 (26), 69 (15). HRMS (EI) calculated for C₉H₁₀O₂S: 182.0396 [M⁺], Found: 182.0993.

4-(Ethylthio)acetophenone 29: The title compound was obtained as a pale yellow solid after 3 h at 40°C in 93% yield (67.0 mg) using 4-bromoacetophenone (79.6 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (pentane/EtOAc (98/2), Rf = 0.30) following the general procedure. M.p. = 42 – 44 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.87 – 7.82 (m, 2H), 7.31 – 7.25 (m, 2H), 3.01 (q, J = 7.4 Hz, 2H), 2.55 (s, 3H), 1.36 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.3, 144.7, 133.9, 128.9, 126.4, 26.5, 26.2, 14.0. MS (70eV, EI): m/z (%): 180 (50) [M⁺], 165 (100), 137 (31), 109 (14), 69 (10). HRMS (EI) calculated for C₁₀H₁₂O₅: 180.0603 [M⁺], Found: 180.0605. These data are in agreement with those reported previously in the literature.[12]

9-(Ethythio)anthracene 30: The title compound was obtained as a pale-yellow oil after 3 h at 40°C in 90% yield (85.8 mg) using 9-bromoanthracene (102.9 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% pentane, Rf = 0.45) following the general procedure. ¹H NMR (400 MHz, CDCl₃) δ 9.03 – 8.97 (m, 2H), 8.48 (s, 1H), 8.06 – 7.99 (m, 2H), 7.65 – 7.57 (m, 2H), 7.55 – 7.48 (m, 2H), 2.91 (q, J = 7.4 Hz, 2H), 1.16 (t, J = 7.4 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 134.9, 131.9, 129.5, 129.1, 128.9, 127.4, 126.6, 125.4, 31.4, 15.3. MS (70eV, EI): m/z (%): 238 (71) [M⁺], 209 (100), 165 (72). HRMS (EI) calculated for C₁₆H₁₄S: 238.0810 [M⁺], Found: 238.0809. These data are in agreement with those reported previously in the literature.[13]

9-(Phenylthio)anthracene 31: The title compound was obtained as a pale-yellow solid after 10 h at 60°C in 89% yield (102.0 mg) using 9-bromoanthracene (102.9 mg) with sodium benzenethiolate (63.4 mg) after purification by column chromatography on silica gel (100% pentane, Rf = 0.30) following the general procedure. M.p. = 98 - 100 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.86 – 8.79 (m, 2H), 8.61 (s, 1H), 8.09 – 8.05 (m, 2H), 7.57 – 7.49 (m, 4H), 7.12 – 7.07 (m, 2H), 7.04 – 7.00 (m, 1H), 6.95 – 6.81 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.9, 135.2, 132.1, 130.4, 129.1, 129.0, 127.4, 127.0, 126.4, 125.7, 125.4, 125.0. MS (70eV, EI): m/z (%): 286 (100) [M⁺], 253 (25), 209 (8), 165 (40). These data are in agreement with those reported previously in the literature.[14]
5-(Phenylthio)-1,3-benzodioxole 32: The title compound was obtained as a brown oil after 12 h at 60°C in 90% yield (82.9 mg) using 5-bromo-1,3-benzodioxole (80.4 mg) with sodium benzenethiolate (63.4 mg) after purification by column chromatography on silica gel (100% pentane, Rf = 0.25) following the general procedure. $^1$H NMR (600 MHz, CDCl$_3$) δ 7.29 – 7.22 (m, 4H), 7.20 – 7.16 (m, 1H), 7.03 – 6.99 (m, 1H), 6.94 – 6.91 (m, 1H), 6.82 – 6.79 (m, 1H), 5.99 (s, 2H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 148.5, 148.0, 138.0, 129.1, 129.0, 127.5, 126.4, 126.3, 113.7, 109.1, 101.6. MS (70eV, EI): m/z (%): 230 (100) [M$^+$], 199 (16), 171 (45), 139 (8), 95 (17). HRMS (EI) calculated for C$_{13}$H$_{10}$O$_2$S: 230.0396 [M$^+$], Found: 230.0403. These data are in agreement with those reported previously in the literature.$^{[15]}$

2.7. Procedure for the recycling of the Pd(I) species from Scheme 2:

The general procedure for C-S bond forming reaction was followed with the conditions used for the coupling of 4-iodoaniline with sodium benzenethiolate (60°C for 6h) and the crude mixture was filtered through a short plug of celite and concentrated under reduced pressure. Column chromatography on silica gel was used with a gradient of hexane/EtOAc (98/2 to 80/20) to afford the Pd(I) species [Pd(I)-I/SEt or Pd(I)-SEt dimer] and 4-(phenylthio)aniline in an average of 95% isolated yield over 5 cycles. The Pd(I) species isolated were used in the following round of catalysis and recovered after each cycles (ratio of dimers recovered determined by quantitative $^{31}$P NMR).

2.8. Compounds from Scheme 3:

3-Chloro-5-(phenylthio)pyridine 33: The title compound was obtained as a pale yellow oil after 12h at 80°C in 93% yield (82.2 mg) using 3-bromo-5-chloropyridine (77.0 mg) with sodium benzenethiolate (63.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (98/2), Rf = 0.09) following the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.30 (d, $J$ = 2.2 Hz, 1H), 8.29 (d, $J$ = 2.2 Hz, 1H), 7.41 – 7.39 (m, 1H), 7.39 – 7.35 (m, 1H), 7.33 – 7.28 (m, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 147.5, 146.2, 135.9, 135.8, 133.0, 132.2, 132.0, 129.8, 128.8. MS (70eV, EI): m/z (%): 223 (38) [M$^+$, $^{37}$Cl], 221 (100) [M$^+$, $^{35}$Cl], 186 (16), 109 (27), 77 (50). HRMS (ESI) calculated for C$_{11}$H$_9$NCIS: 222.0138 [M+H]$^+$, Found: 222.0139 (for $^{35}$Cl).
3-Chloro-5-((2-chlorophenyl)(thio)phenyl trifluoromethanesulfonate 34: The title compound was obtained as a colourless oil after 12 h at 80°C in 92% yield (148.3 mg) using 3-bromo-5-chlorophenyl trifluoromethanesulfonate (135.8 mg) with sodium 2-chlorobenzenethiolate (80.0 mg) after purification by column chromatography on silica gel (100% pentane, Rf = 0.5) following the general procedure. 1H NMR (600 MHz, CDCl3) δ 7.54 – 7.51 (m, 1H), 7.47 – 7.45 (m, 1H), 7.38 – 7.35 (m, 1H), 7.32 – 7.28 (m, 1H), 7.20 – 7.18 (m, 1H), 7.14 – 7.12 (m, 1H), 6.95 – 6.93 (m, 1H). 13C NMR (151 MHz, CDCl3) δ 149.7, 140.6, 137.7, 136.2, 135.3, 132.6, 130.9, 130.8, 128.6, 128.1, 120.0, 119.9, 118.7 (q, J = 321.2 Hz). 19F NMR (564 MHz, CDCl3) δ -72.6. MS (70eV, EI): m/z (%): 406 (13) [M+ Cl, 2x 37Cl], 404 (56) [M+ 37Cl], 402 (74) [M+, 35Cl], 268 (12), 236 (39) [37Cl], 234 (100) [35Cl], 171 (93), 108 (21), 69 (41). HRMS (EI) calculated for C13H7O3Cl2F3S2: 401.9160 [M]+, Found: 401.9166 (for 35Cl).

4-(Ethylthio)phenyl trifluoromethanesulfonate 35: The title compound was obtained as a colourless liquid after 6 h at 40°C in 94% yield (108.0 mg) using 4-bromophenyl trifluoromethanesulfonate (122.0 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (99/1), Rf = 0.20) following the general procedure. 1H NMR (600 MHz, CDCl3) δ 7.38 – 7.32 (m, 2H), 7.21 – 7.16 (m, 2H), 2.96 (q, J = 7.4 Hz, 2H), 1.34 (t, J = 7.4 Hz, 3H). 13C NMR (151 MHz, CDCl3) δ 147.5, 138.3, 129.8, 121.9, 118.6 (q, J = 320.9 Hz), 27.6, 14.2. 19F NMR (564 MHz, CDCl3) δ -72.8 HRMS (EI) calculated for C9H9O3F3S2: 285.9942 [M]+, Found: 285.9939.

4-Chloro-2-((2-chlorophenyl)(thio)phenyl trifluoromethanesulfonate 36: The title compound was obtained as a colourless oil after 12 h at 80°C in 88% yield (141.4 mg) using 2-bromo-4-chlorophenyl trifluoromethanesulfonate (135.8 mg) with sodium 2-chlorobenzenethiolate (80.0 mg) after purification by column chromatography on silica gel (hexane/EtOAc (95/5), Rf = 0.47) following the general procedure. 1H NMR (600 MHz, CDCl3) δ 7.52 – 7.50 (m, 1H), 7.39 – 7.33 (m, 2H), 7.29 – 7.27 (m, 3H), 7.06 – 7.03 (m, 1H). 13C NMR (151 MHz, CDCl3) δ 146.2, 137.3, 134.7, 134.7, 132.0, 131.6, 130.8, 130.5, 130.5, 128.7, 128.1, 123.3, 118.5 (q, J = 320.7). 19F NMR (564 MHz, CDCl3) δ -73.3. MS (70eV, EI): m/z (%): 406 (3) [M+, 2x 37Cl], 404 (10) [M+, 37Cl], 402 (14) [M+, 35Cl], 236 (38) [37Cl], 234 (100) [35Cl], 171 (26), 95 (10), 69 (13). HRMS (ESI) calculated for C13H7O3Cl2F3NaS2: 424.9057 [M+Na]+, Found: 424.9058 (for 35Cl).
3-((4-Chlorobenzyl)thio)-4-(trifluoromethyl) phenyl trifluoromethane sulfonate 37: The title compound was obtained as a colourless oil after 12 h at 80°C in 89% yield (159.4 mg) using 4-bromo-3-((trifluoromethyl)phenyl trifluoromethanesulfonate (149.2 mg) with sodium (4-chlorophenyl)methanethiolate (86.7 mg) after purification by column chromatography on silica gel (100% pentane, Rt = 0.25) following the general procedure. \(^1\)H NMR (600 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 7.57 – 7.55 (m, 1H), 7.48 – 7.46 (m, 1H), 7.39 – 7.36 (m, 1H), 7.30 – 7.25 (m, 4H), 4.18 (s, 2H). \(^13\)C NMR (151 MHz, CD\(_2\)Cl\(_2\)) \(\delta\) 147.7, 137.4, 134.9, 134.0, 133.7, 131.9 (q, \(J = 31.6\) Hz), 130.9, 129.4, 125.4, 123.2 (q, \(J = 274.3\) Hz), 120.9 (q, \(J = 5.9\) Hz), 119.2 (q, \(J = 320.9\) Hz), 39.0. \(^19\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -62.0, -72.9. MS (70eV, EI): \(m/z\) (%): 452 (1) [M\(^+\), \(^{37}\)Cl], 450 (2) [M\(^+\), \(^{35}\)Cl], 261 (2), 127 (33) [\(^{37}\)Cl], 125 (100) [\(^{35}\)Cl], 69 (22). HRMS (EI) calculated for C\(_{13}\)H\(_9\)O\(_2\)Cl\(_3\)F\(_2\): 449.9580 [M\(^+\)], Found: 449.9598 (for \(^{35}\)Cl).

2-Chloro-4-(ethylthio)phenyl trifluoromethanesulfonate 38: The title compound was obtained as a yellow oil after 12 h at 40°C in 90% yield (115.5 mg) using 4-bromo-2-chlorophenyl trifluoromethanesulfonate (135.8 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (100% pentane, \(R_t = 0.32\)) following the general procedure. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.43 – 7.39 (m, 1H), 7.29 – 7.26 (m, 1H), 7.25 – 7.20 (m, 1H), 3.00 (q, \(J = 7.4\) Hz, 2H), 1.38 (t, \(J = 7.4\) Hz, 3H). \(^13\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 143.2, 140.0, 129.6, 127.7, 127.3, 123.2, 118.7 (q, \(J = 320.6\) Hz), 27.4, 14.1. \(^19\)F NMR (564 MHz, CDCl\(_3\)) \(\delta\) -74.4. MS (70eV, EI): \(m/z\) (%): 322 (6) [M\(^+\), \(^{37}\)Cl], 320 (14) [M\(^+\), \(^{35}\)Cl], 189 (37) [\(^{37}\)Cl], 187 (100) [\(^{35}\)Cl], 161 (16) [\(^{37}\)Cl], 159 (46) [\(^{35}\)Cl], 133 (7) [\(^{37}\)Cl], 131 (19) [\(^{35}\)Cl], 95 (20), 69 (44). HRMS (EI) calculated for C\(_9\)H\(_7\)O\(_2\)Cl\(_3\)F\(_2\): 319.9550 [M\(^+\)], Found: 319.9544 (for \(^{35}\)Cl).

3-(tert-Butylthio)-4-chlorophenyl trifluoromethanesulfonate 39: The title compound was obtained as a colourless liquid after 6 h at 40°C in 91% yield (127.1 mg) using 4-chloro-3-bromophenyl trifluoromethanesulfonate (135.8 mg) with sodium 2-methyl-2-propanethiolate (53.8 mg) after purification by column chromatography on silica gel (hexane/EtOAc (99/1), \(R_t = 0.30\)) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.62 – 7.53 (m, 2H), 7.25 – 7.18 (m, 1H), 1.36 (s, 9H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 147.0, 141.0, 135.3, 131.7, 131.4, 122.8, 118.7 (q, \(J = 320.6\) Hz), 49.7, 31.1. \(^19\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -72.6. MS (70eV, EI): \(m/z\) (%): 350 (2) [M\(^+\), \(^{37}\)Cl], 348 (5) [M\(^+\), \(^{35}\)Cl], 294 (14) [\(^{37}\)Cl], 292 (33) [\(^{35}\)Cl], 161 (3) [\(^{37}\)Cl], 159 (8) [\(^{35}\)Cl], 95 (15), 69 (18), 57 (100). HRMS (EI) calculated for C\(_{11}\)H\(_{12}\)O\(_2\)Cl\(_3\)F\(_2\): 347.9852 [M\(^+\)], Found: 347.9863 (for \(^{35}\)Cl).
4-((4-Chlorobenzyl)thio)-3-methylphenyltrifluoromethanesulfonate 40: The title compound was obtained as a colourless oil after 12 h at 80°C in 91% yield (144.1 mg) using 4-bromo-3-methylphenyl trifluoromethanesulfonate (127.6 mg) with sodium (4-chlorophenyl)methanethiolate (86.7 mg) after purification by column chromatography on silica gel (100% pentane, Rf = 0.32) following the general procedure. \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.33 – 7.20 (m, 5H), 7.13 – 7.02 (m, 2H), 4.07 (s, 2H), 2.37 (s, 3H). \(^13\)C NMR (101 MHz, CDCl\(_3\)) δ 147.8, 140.6, 136.4, 135.2, 133.5, 130.4, 130.2, 128.9, 122.8, 119.2, 118.8 (q, J = 320.9 Hz), 37.7, 20.6. \(^19\)F NMR (376 MHz, CDCl\(_3\)) δ -72.9. MS (70eV, EI): m/z (%): 398 (4) [M\(^+\), \(^{37}\)Cl], 396 (9) [M\(^+\), \(^{35}\)Cl], 127 (35) [\(^{37}\)Cl], 125 (100) [\(^{35}\)Cl], 89 (12), 69 (9). HRMS (EI) calculated for C\(_{15}\)H\(_{12}\)O\(_3\)ClF\(_3\)S\(_2\): 395.9863 [M\(^+\)], Found: 395.9857 (for \(^{35}\)Cl).
2.9. Procedure for the comparison of different catalytic systems from Scheme 3:

Procedure with [Pd_{2}dba_{3}/ DPEPhos]: In an argon filled glove-box, an oven-dried 20 mL vial, equipped with a stir bar was charged with Pd_{2}dba_{3} (10 mg, 10 μmol, 0.01 equiv.), DPEPhos (10.8 mg, 20 μmol, 0.02 equiv.) and toluene (8 mL). The reaction mixture was stirred for 3 min. After addition of 5-bromo-4-methylpyridine-2-yl trifluoromethanesulfonate (320 mg, 1.0 mmol, 1.0 equiv.), ethanethiol (74 μL, 1.00 mmol, 1.0 equiv.) and KOTBu (120 mg, 1.1 mmol, 1.1 equiv.), the reaction mixture was allowed to stir in the glove-box at 100°C for 2 h.

The reaction with [Pd(I)-Br dimer and Pd(I)-I dimer] as catalyst were performed following the general C-S bond forming procedure.

5-(Ethylthio)-4-methylpyridine-2-yl trifluoromethanesulfonate: The title compound was obtained as a yellow liquid after 12 h at 40°C in 91% yield (110.0 mg) using 5-bromo-4-methylpyridine-2-yl trifluoromethanesulfonate (128.0 mg) with sodium ethanethiolate (40.4 mg) after purification by column chromatography on silica gel (hexane/EtOAc (95/5), R_E = 0.47) following the general procedure. $^1$H NMR (600 MHz, CDCl₃) δ 8.15 (s, 1H), 6.98 (s, 1H), 2.99 (q, J = 7.4 Hz, 2H), 2.41 (s, 3H), 1.36 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (151 MHz, CDCl₃) δ 154.0, 151.9, 145.8, 134.9, 118.6 (q, J = 320.5 Hz), 115.7, 27.0, 20.5, 14.2. $^{19}$F NMR (564 MHz, CDCl₃) δ -73.2. HRMS (ESI) calculated for C₉H₁₀O₃NF₃NaS₂: 323.9946 [M+Na]⁺, Found: 323.9946. The impurity observed at 1.5 ppm in $^1$H NMR is tri-tert-butylphosphine related and integrate for less than 1%.
As a result, the following chromatograms were obtained by qualitative GC/MS analysis, describing the relative selectivity of the tested Pd-(pre-)catalysts.

*The chromatogram with the Pd(I)-Iodo dimer was obtained using a different method on the GC/MS instrument therefore displaying different retention time.*
2.10. Crystallographic study for \([\text{PtBu}_3\text{Pd}^I\text{SPh}]_2\):

Crystals suitable for X-ray crystallography were grown from a solution of 2 in pentane at -30 °C. The diffraction experiment was performed with a Bruker D8 goniometer equipped with an Incoatec microsource (Mo-Kα, λ = 0.71073 Å, multilayer optics) and an APEX CCD detector; a sample temperature of 100(2) K was maintained with an Oxford Cryostream 700 instrument. Intensity data were integrated with SAINT+ and corrected for absorption by multi-scan methods using the program SADABS. The phase problem was solved with Direct methods, and refinements were accomplished with full matrix least-squares procedures as implemented in SHELXL-13. All non-hydrogen atoms were assigned anisotropic displacement parameters; hydrogen atoms were placed in idealized positions and included as riding with constrained isotropic displacement parameters. Crystal data and refinement results have been compiled in Table 1. Additional crystallographic information has been deposited in CIF format and is available from the CCDC, deposition number 1841115.

Figure S2. ORTEP of 2 at 50% probability levels. Hydrogens are omitted for clarity. Selected bond distances [Å] and angles [deg]: Pd1-P1, 2.303(3); Pd1-S1, 2.342(2); Pd1-S2, 2.368(2); Pd2-P2, 2.304(2); Pd2-S1, 2.355(2); Pd2-S2, 2.355(2); S1-Pd1-P1, 124.53(8); P1-Pd1-S2, 121.08(8); S2-Pd1-S1, 114.35(8); S1-Pd2-P2, 120.83(8); P2-Pd2-S2, 124.75(8); S1-Pd2-S2, 114.33(8).
Table 1. Crystal data and refinement results for 2.

| Identification code | CCDC-1841115 (2) |
|---------------------|------------------|
| Empirical formula   | C_{36}H_{64}P_2PdS_6 |
| Formula weight      | 835.73 g/mol |
| Temperature         | 100(2) K |
| Wavelength          | 0.71073 Å |
| Crystal system      | monoclinic |
| Space group         | P2_1/n |
| Unit cell dimensions| a = 8.335(4) Å  
|                     | b = 20.005(9) Å  
|                     | c = 23.533(11) Å |
| Volume              | 3923(3) Å³ |
| Z                   | 4 |
| Density (calculated)| 1.415 Mg/m³ |
| Absorption coefficient | 1.128 mm⁻¹ |
| F(000)              | 1736 |
| Theta range for data collection | 1.336 to 25.809° |
| Index ranges        | -7<=h<=10, -23<=k<=24, -27<=l<=28 |
| Reflections collected | 22220 |
| Independent reflections | 7477 [R(int) = 0.1451] |
| Completeness to theta = 25.809° | 98.9 % |
| Absorption correction | multi-scan |
| Refinement method   | Full-matrix least-squares on F² |
| Data / restraints / parameters | 7477/0/397 |
| Goodness-of-fit on F² | 1.032 |
| Final R indices [I>2sigma(I)] | R_1 = 0.0760, wR_2 = 0.1459 |
| R indices (all data) | R_1 = 0.1219, wR_2 = 0.1673 |
| Largest diff. peak and hole | 1.144 and -1.019 (e Å⁻³) |
3. Computational studies

All calculations were performed with the Gaussian 09 program package. Structural optimizations and frequency calculations were performed with B3LYP along with 6-31G(d) basis set on all atoms except Pd, I and the effective core potential (ECP) LANL2DZ on Pd and I atoms. Single point energy calculations were performed with M06L functional and 6-311++G(d,p) basis set on all atoms except Pd, I and the Stuttgart-Dresden (SDD) ECP on Pd and I atoms or def2-TZVP on all atoms. Solvent effects of toluene were taken into account for single point energy calculation using the CPCM solvation model, optimization were performed in the gas phase. Energies of all structures are converted to 1M standard state (with the addition of 1.89 kcal/mol).

Figure S3. Free-energy path of I → SET exchange on 4-iodoaniline calculated at CPCM (toluene) M06L/6-311++G(d,p) [SDD for Pd,I] or CPCM (toluene) M06L/def2TZVP (in parentheses). Geometries were optimized at B3LYP/6-31G(d) [with LANL2DZ for Pd,I]. Values are in kcal.mol⁻¹ at 298K.
3.1. Coordinates of the computed structures:

\[
\begin{array}{cccc}
\text{Pd} & -1.30862800 & 0.01665500 & -0.11279900 \\
Pd & 1.31212800 & 0.04553900 & -0.12685500 \\
P & 3.69144600 & -0.01955700 & 0.00550400 \\
C & 4.17784400 & -0.85899200 & 1.68922400 \\
C & 4.44687300 & -1.07227500 & -1.46280500 \\
C & 5.63728300 & -0.66493500 & 2.14899500 \\
C & 3.22818600 & -0.30561100 & 2.78088200 \\
C & 3.88799900 & -2.37431500 & 1.61835600 \\
C & 5.89028400 & -1.57447600 & -1.25426100 \\
C & 4.18801100 & 2.49465800 & 1.24956600 \\
C & 6.04904900 & 1.76985900 & -0.27023600 \\
C & 3.86319600 & 2.57581800 & -1.19365600 \\
H & 5.87419400 & 0.37931500 & 2.36759600 \\
H & 5.79107300 & -1.22842900 & 3.07947700 \\
H & 6.36531900 & -1.03490400 & 1.42214100 \\
H & 2.18063000 & -0.47262500 & 2.51197400 \\
H & 3.42760900 & -0.83978200 & 3.72001900 \\
H & 3.36550800 & 0.75852000 & 2.97546100 \\
H & 4.00179300 & -2.79381500 & 2.62671200 \\
H & 2.86114700 & -2.57130800 & 1.29666200 \\
H & 4.57993400 & -2.91456500 & 0.96796400 \\
H & 3.49253000 & -2.97845000 & -0.85864200 \\
H & 2.49647000 & -1.95695600 & -1.90325000 \\
H & 3.88458500 & -2.84251000 & -2.57434700 \\
H & 5.14122800 & 0.54795100 & -2.79929300 \\
H & 4.62335100 & -0.92640600 & -3.60992100 \\
H & 3.40866400 & 0.17696700 & 2.94820200 \\
H & 6.20930300 & -2.11815700 & -2.15435900 \\
H & 6.60365400 & -0.76175200 & -1.09701700 \\
H & 5.97560100 & -2.26892200 & -0.41510600 \\
H & 3.11382600 & 2.47744200 & 1.46061500 \\
H & 4.48865300 & 3.54490500 & 1.14035700 \\
H & 4.72124100 & 2.09819500 & 2.11642200 \\
H & 6.33831400 & 1.39288800 & -1.25468100 \\
H & 6.39894000 & 2.80981000 & -0.21186100 \\
H & 6.59333000 & 1.20018700 & 0.48586300 \\
H & 4.12444900 & 2.22586000 & -2.19229600 \\
H & 2.77373300 & 2.57453700 & -1.11107900 \\
H & 4.21465500 & 3.61368700 & -1.11137600 \\
P & -3.68701800 & 0.05230800 & 0.00296100 \\
C & -4.39776000 & -1.71442100 & -0.43773700 \\
C & -4.21492800 & 0.48901000 & 1.82176900 \\
\end{array}
\]
Zero-point correction= 0.884397 (Hartree/Particle)
Thermal correction to Energy= 0.936399
Thermal correction to Enthalpy= 0.937344
Thermal correction to Gibbs Free Energy= 0.801635
Sum of electronic and zero-point Energies= -2837.318054
Sum of electronic and thermal Energies= -2837.266051
Sum of electronic and thermal Enthalpies= -2837.265107
Sum of electronic and thermal Free Energies= -2837.400815

CPCM(Toluene) M06L/def2-TZVP E = -2840.90005831
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -2841.07733156

\[
\begin{array}{c}
\text{I} \\
\text{NH}_2
\end{array}
\]

| C      | -0.18820700 | 0.00000800 | -0.00474600 |
| C      | -0.88281200 | 1.20893500 | -0.00582800 |
| C      | -2.27620000 | 1.20674100 | -0.00649500 |
| C      | -2.99678200 | 0.00000500 | -0.00709500 |
| C      | -2.27619100 | -1.20673900 | -0.00650000 |
| C      | -0.88281300 | -1.20893100 | -0.00582600 |
| H      | -0.35021800 | 2.15406500 | -0.00367700 |
| H      | -2.81174200 | 2.15350600 | -0.01189600 |
| H      | -2.81174400 | -2.15349700 | -0.01192200 |
| H      | -0.35020600 | -2.15405400 | -0.00367400 |
| I      | 1.95763000  | -0.00000100 | 0.00262000 |
| N      | -4.39095400 | -0.00001600 | -0.06563300 |
| H      | -4.83786900 | -0.83759300 | 0.28541400 |
| H      | -4.83788400 | 0.83762300  | 0.28524800 |

Zero-point correction= 0.106902 (Hartree/Particle)
Thermal correction to Energy= 0.114291
Thermal correction to Enthalpy= 0.115235
Thermal correction to Gibbs Free Energy= 0.073494
Sum of electronic and zero-point Energies= -298.267075
Sum of electronic and thermal Energies= -298.259686
Sum of electronic and thermal Enthalpies= -298.258741
Sum of electronic and thermal Free Energies= -298.300483

CPCM(Toluene) M06L/def2-TZVP E = -584.944747903
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -298.445248644
Zero-point correction=                           0.991322 (Hartree/Particle)
Thermal correction to Energy=                    1.052563
Thermal correction to Enthalpy=                  1.053508
Thermal correction to Gibbs Free Energy=         0.895301
Sum of electronic and zero-point Energies=       -3135.528932
Sum of electronic and thermal Energies=          -3135.467690
Sum of electronic and thermal Enthalpies=        -3135.466746
Sum of electronic and thermal Free Energies=     -3135.624953

CPCM(Toluene) M06L/def2-TZVP E = -3425.98371437
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -3139.31534718
|   |   |   |   |   |   |
|---|---|---|---|---|---|
| C | 1.96172700 | -3.78110600 | -0.87568800 |
| C | 3.19136600 | -2.31047700 | -2.45179500 |
| C | 4.40528800 | -4.07763600 | -1.14112400 |
| C | 5.72443000 | 0.09592000 | 1.14761500 |
| C | 6.27152200 | -2.31203200 | 0.95853500 |
| C | 5.91857100 | -0.89450000 | -1.09421700 |
| H | 1.97143300 | -4.41602000 | 0.01295600 |
| H | 1.09671600 | -3.11844800 | -0.83149000 |
| H | 1.82146200 | -4.44593400 | -1.73892500 |
| H | 4.10879100 | -1.79145200 | -2.73392100 |
| H | 2.98840700 | -3.06419200 | -3.22424500 |
| H | 2.37521900 | -1.58381600 | -2.46376500 |
| H | 4.13120900 | -4.80906800 | -1.91324500 |
| H | 5.37828400 | -3.67173600 | -1.42181200 |
| H | 4.51622500 | -4.62904900 | -0.20352000 |
| H | 5.39826000 | 0.99414700 | 0.63188400 |
| H | 5.29864700 | 0.10592700 | 2.14856000 |
| H | 6.18164900 | 0.15033700 | 1.25671600 |
| H | 6.11139500 | -3.29776100 | 0.52419500 |
| H | 7.32797800 | -2.05591800 | 0.80123700 |
| H | 6.12439300 | -2.38415000 | 2.03953500 |
| H | 5.96385300 | -1.77916600 | -1.73123200 |
| H | 5.31196900 | -0.13159400 | -1.59005900 |
| H | 6.94047500 | -0.50019500 | -1.02029600 |
| Pd | 1.82019400 | 0.19960700 | -0.28058500 |
| Pd | -2.12555500 | 0.65096800 | -0.34066000 |
| P | -4.02949300 | -0.81656100 | 0.40036300 |
| C | -3.45977700 | -1.94060300 | 1.89568800 |
| C | -5.70043100 | 0.05734300 | 0.97254900 |
| C | -4.48337700 | -1.96738200 | -1.11391100 |
| C | -4.30570300 | -3.21345800 | 2.11786400 |
| C | -1.99548900 | -2.36792600 | 1.68014400 |
| C | -3.46270200 | -1.11493400 | 3.20162600 |
| C | -5.40076800 | 1.21581100 | 1.95140600 |
| C | -6.39912800 | 0.69218100 | -0.25312800 |
| C | -6.71033200 | -0.88035600 | 1.67345100 |
| C | -3.41282500 | -3.06231800 | -1.31160300 |
| C | -5.84864300 | -2.68589900 | -1.04132700 |
| C | -4.45125700 | -1.07308600 | -2.37644700 |
| C | -5.36378500 | -3.00796800 | 2.28107600 |
| H | -4.21942500 | -3.92193600 | 1.29147900 |
| H | -3.92995800 | -3.72296700 | 3.01574400 |
| H | -1.33679800 | -1.49061100 | 1.63558900 |
| H | -1.68794800 | -2.98351000 | 2.53641000 |
| H | -1.83855500 | -2.95284900 | 0.77512200 |
| H | -2.92071700 | -1.68426000 | 3.96803500 |
| H | -2.94986400 | -0.15498100 | 3.08195500 |
| H | -4.46621400 | -0.93190900 | 3.58948800 |
| H | -4.98265300 | 0.88493100 | 2.90105600 |
| H | -4.73430400 | 1.94483100 | 1.49511200 |
| H | -6.35083900 | 1.72024100 | 2.17395400 |
| H | -6.79943700 | -0.04536300 | -0.95087000 |
| H | -7.25081500 | 1.28086500 | 0.11281700 |
| H | -5.73609800 | 1.37711600 | -0.78439700 |
| H | -7.63704000 | -0.31262800 | 1.83088900 |
| H | -6.96896800 | -1.76687900 | 1.09355300 |
| H | -6.36745600 | -1.20067600 | 2.66042800 |
H  -2.39954900  -2.65816000  -1.32780600
H  -3.46523900  -3.84599700  -0.55153700
H  -3.59853200  -3.54653200  -2.28005100
H  -6.69983400  -2.00393400  -2.51242100
H  -5.94468000  -3.32170000  -1.93189100
H  -5.93420800  -3.33991700  -0.16952800
H  -5.18854000  -0.26936600  -2.35258600
H  -3.46697000  -0.61606900  -3.25590800
H  -3.46697000  -0.16952800  -2.83800900
S  -3.41924000  2.66040300  -0.48350400
S  -0.39095700  -1.08737200  -1.00480800
C  -0.49143700  -1.98590300  -3.69414300
H  -1.44101400  -2.50028500  -3.51797500
H  -0.44437500  -1.71797900  -4.75817700
H  0.31588600  -2.69589300  -3.48941700
C  -3.53799500  5.17782400  0.65672400
H  -4.63168900  5.11069900  0.66213100
H  -3.23452400  5.86335300  1.45864600
H  -3.23079900  5.61335600  -0.29978400
H  0.55970700  -0.19191200  -3.06610300
H  -1.18511900  -0.03499700  -3.05416100
H  -1.80314300  3.89586600  0.86475300
H  -3.19201100  3.39476800  1.83728400

Zero-point correction=     0.994045 (Hartree/Particle)
Thermal correction to Energy=       1.054952
Thermal correction to Enthalpy=      1.055896
Thermal correction to Gibbs Free Energy= 0.899566
Sum of electronic and zero-point Energies=  -3135.570386
Sum of electronic and thermal Energies=  -3135.509478
Sum of electronic and thermal Enthalpies=  -3135.508534
Sum of electronic and thermal Free Energies=  -3135.664865

CPCM(Toluene) M06L/def2-TZVP E = -3426.01907257
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -3139.35081508
|   |   |   |   |   |
|---|---|---|---|---|
| C | -4.73126 | 1.14886 | 2.22572 | 500 |
| C | -6.16459 | 0.43165 | 0.33018 | 000 |
| C | -6.11050 | -0.32169 | 2.41041 | 100 |
| C | -3.30346 | -3.328 | -1.00476 | 100 |
| C | -5.68266 | -2.985 | -0.36043 | 100 |
| C | -4.54961 | -1.4169 | -1.97420 | 800 |
| H | -4.79588 | -3.10959 | 2.83563 | 300 |
| H | -3.79765 | -4.10345 | 1.76637 | 900 |
| H | -3.28884 | -3.80930 | 3.42531 | 300 |
| H | -0.85757 | 0.89969 | 3.08027 | 600 |
| H | -1.13452 | -3.19854 | 2.57741 | 800 |
| H | -1.51154 | -3.2128 | 0.85101 | 400 |
| H | -2.11813 | -1.77822 | 4.10870 | 400 |
| H | -2.17723 | -0.30032 | 3.14030 | 000 |
| H | -3.65198 | -0.94333 | 3.89274 | 200 |
| H | -4.10126 | 0.89969 | 3.08027 | 600 |
| H | -4.18331 | 1.83416 | 1.57781 | 100 |
| H | -5.60685 | 1.68736 | 2.61264 | 500 |
| H | -6.71592 | -0.36564 | -0.17232 | 600 |
| H | -6.90979 | 1.09088 | 0.79442 | 100 |
| H | -5.62928 | 1.02365 | -0.41259 | 600 |
| H | -6.97572 | -0.31943 | 2.69647 | 900 |
| H | -6.49992 | -1.84561 | 1.95481 | 800 |
| H | -5.59604 | -1.20005 | 3.33563 | 000 |
| H | -2.31881 | -2.89629 | 1.19486 | 200 |
| H | -3.20983 | -4.07566 | -0.21246 | 200 |
| H | -3.61978 | -3.86190 | -1.91149 | 900 |
| H | -6.53282 | -2.31108 | -0.24809 | 800 |
| H | -5.91608 | -3.65934 | -1.19592 | 200 |
| H | -5.61149 | -3.60054 | 0.53994 | 400 |
| H | -5.29261 | -0.62530 | -1.87391 | 100 |
| H | -3.61092 | -0.94738 | -2.28161 | 120 |
| H | -4.87861 | -2.08552 | 2.78138 | 800 |
| I | -3.4111 | 2.65857 | -1.05657 | 800 |
| C | -0.08117 | 3.22301 | 0.47229 | 500 |
| C | -0.40592 | -0.80581 | -2.85141 | 110 |
| N | 4.92660 | 5.33233 | 1.66070 | 900 |
| H | 5.28624 | 5.29279 | 2.60705 | 800 |
| H | 5.63391 | 5.67617 | 1.02195 | 900 |
| S | 0.03147 | 1.83245 | -0.75957 | 300 |
| S | -0.24216 | -1.21920 | -1.03441 | 900 |
| C | -0.42545 | -2.06149 | -3.7231 | 100 |
| H | -1.26811 | -2.71181 | -3.46698 | 100 |
| H | -0.52558 | -1.77591 | -4.77828 | 300 |
| H | 0.49424 | 2.64450 | -3.61722 | 200 |
| H | -1.33239 | -0.24149 | -2.97896 | 300 |
| H | 0.41567 | -0.14321 | -3.13426 | 500 |
| C | 0.16184 | 4.57024 | -0.20461 | 400 |
| H | 1.16056 | 4.61597 | -0.64934 | 300 |
| H | -0.58292 | 4.75268 | -0.98486 | 300 |
| H | 0.08465 | 5.37133 | 0.54211 | 300 |
| H | -1.08427 | 3.17969 | 0.89803 | 500 |
| H | 0.65103 | 3.03539 | 1.25767 | 600 |
Zero-point correction= 0.995794 (Hartree/Particle)
Thermal correction to Energy= 1.055972
Thermal correction to Enthalpy= 1.056917
Thermal correction to Gibbs Free Energy= 0.904693
Sum of electronic and zero-point Energies= -3135.587120
Sum of electronic and thermal Energies= -3135.526941
Sum of electronic and thermal Enthalpies= -3135.525997
Sum of electronic and thermal Free Energies= -3135.678221

CPCM(Toluene) M06L/def2-TZVP E = -3426.03643499
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -3139.37185037

C                  4.31607800    4.25254100    -0.45639400
C                  2.33934600    3.13106700    0.41758900
C                  2.31039000    2.26001400    -0.69240100
C                  3.26982100    2.43992100    -1.70410200
H                  3.26346300    1.81785600    -2.59167400
H                  1.56004600    3.05337300    1.16968600
C                  4.26303600    3.41333800    -1.58028900
C                  3.30165000    4.09453100    0.53914600
H                  5.00935500    3.51884900    -2.36553000
C                  3.33795700    4.74959000    1.40842300
Pd                  1.71277300    0.20615000    -0.32566400
Pd                 -1.56813600    0.29997100    -0.08213300
H                  4.16829800    0.12139700    3.99474500
C                  3.59705100    -0.46353700    3.26187300
C                  4.46515400    -0.63722900    1.99483500
H                  2.67607200    0.08885700    3.04730200
H                  3.33525000    -1.40923200    3.74094600
C                  3.36527900    -1.39063400    0.57413000
C                  5.73145800    -1.43899500    2.36219000
C                  4.89802300    0.79159800    1.59363200
C                  2.47265000    -2.97213800    1.28747500
C                  4.53730300    -1.96165400    -0.87326600
H                  6.46190600    -1.44906000    1.54869000
H                  6.21784400    -0.95572100    3.22077400
H                  5.52236200    -2.47232000    2.64499600
H                  5.56919200    0.82025700    0.73588700
H                  4.03859500    1.42468700    1.36955100
H                  5.43546300    1.23887900    2.44115400
C                  3.31829900    -3.86717900    2.21797900
C                  1.21753700    -2.49141300    2.05410300
C                  1.94455600    -3.85209200    0.13289400
C                  3.66160700    -2.16119000    -2.13320500
C                  5.52441000    -0.82426100    -1.21619000
C                  5.35646200    -3.24373400    -0.61763100
H   -4.20594700  -3.64640300  1.05003900
I   -1.09166700  -1.87323500  -1.8055500
C   0.31939900   1.87578000  -3.05761000
S   0.27225900   1.80268800  -1.19990100
C   0.90695500   0.71587800  -3.85223700
H   1.94727800   0.51804700  -3.57969100
H   0.33924500  -0.20155200  -3.69171500
H   0.87929800   0.96756400  -4.92097800
H   -0.73309100  2.02671900  -3.32084000
H   0.84768700   2.81195600  -3.27106400
N   5.33710000   5.19383100  -0.30676500
H   5.75903300   5.51089000  -1.17100600
H   5.11606800   5.97029500  -0.30459700
S   -0.98523200  1.83053800  -1.66820000
C   -0.86663100  0.76121300  -3.16520700
H   -1.83388000  0.28108800  -3.34838600
H   -0.13271500  -0.02854500  2.98776900
C   -0.46358100  1.59809500  -4.38324100
H   -1.20385400  2.37874700  -4.58974100
H   -0.37997400  0.96104900  -5.27339700
H   0.50397400  2.08712700  -4.22386300

Zero-point correction= 0.992664 (Hartree/Particle)
Thermal correction to Energy= 1.053349
Thermal correction to Enthalpy= 1.054293
Thermal correction to Gibbs Free Energy= 0.898866
Sum of electronic and zero-point Energies= -3135.547501
Sum of electronic and thermal Energies= -3135.486816
Sum of electronic and thermal Enthalpies= -3135.485872
Sum of electronic and thermal Free Energies= -3135.641299

CPCM(Toluene) M06L/def2-TZVP E = -3425.99967764
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -3139.33244724

\[ fBu_3P - Pd - Ph - PrBu_3 \]

Pd  1.33088500  -0.02368600  0.06102400
Pd  -1.34352000  0.04081400  0.05490700
P  -3.71460100  0.14779800  -0.16515100
C  -4.31236000  -1.40076300  -1.19467200
C  -4.54067000  0.08465500  1.59713400
C  -4.33651600  1.75490300  -1.08168200
C  -5.75023400  -1.32725000  -1.74934900
C  -3.32500500  -1.59367100  -2.37236300
C  -4.19716200  -2.67758900  -0.33334300
C  -3.74511200  -0.92344600  2.46125000
C  -4.37894600  1.45393100  2.29351900
C  -6.03401400  -0.29918600  1.61974000
C  -3.95468000  1.66456800  -2.57619900
C  -5.85043500  2.03679600  -0.97001600
C  -3.57273700  2.98509400  -0.53875000
H  -5.87854100  -0.53596200  -2.49116000
H  -5.97835900  -2.27602500  -2.25381400
H  -6.50090300  -1.18821600  -0.96663300
H  -2.29469700  -1.68644800  -2.01547000
H  -3.58574300  -2.52292800  -2.89691200
H  -3.36025900  -0.78631000  -3.10440900
H  -4.36349000  -3.54556400  -0.98456000
H  -3.20709000  -2.78603500  0.10715300
H  -4.94581700  -2.72619900  0.46068400
H  -3.82840900  -1.95309600  2.11347600
H  -2.68098200  -0.66880300  2.49146000
H  -4.13658400  -0.88904500  3.48718300
H  -5.01347200  1.79687400  2.65601300
H  -4.67346400  1.34452000  3.34542800
H  -3.33914900  1.79687400  2.27742600
H  -6.39595300  -0.25171100  2.65601300
H  -6.65399600  0.37737100  1.02678300
H  -6.21025800  -1.31856200  1.26836800
H  -2.89513300  1.42233300  -2.70735700
H  -4.12782100  2.64536600  -3.03838700
H  -4.55389500  0.93971900  -3.13099400
H  -6.05210400  2.28546800  0.05115300
H  -6.09286400  2.90726500  -1.59479600
H  -6.46980200  1.20640900  -1.31511600
H  -3.74728300  3.17468400  0.52035900
H  -2.49723300  2.88389300  -0.70048100
H  -3.91533400  3.87180500  -1.08937700
P  3.71028900  0.07346100  -0.17194200
C  4.50239500  0.56844300  1.53814900
C  4.52401400  1.60364400  -0.75809800
C  4.15346000  1.44356200  -1.49205500
C  5.93415300  1.13938500  1.47608500
C  3.57268600  1.60813700  2.20725700
C  4.50614100  -0.65380300  2.48363500
C  3.88871800  -2.78201600  0.01557000
C  4.16950800  -1.84712400  -2.24173000
C  6.05719100  -1.68335500  -0.59297800
C  3.86386000  2.84057000  -0.90345400
C  5.60479100  1.43372600  -2.01464900
C  3.18643000  1.28554100  -2.69138100
H  5.98577100  2.09041000  0.93939500
H  6.28321800  1.33098600  2.50017300
H  6.64516100  0.44960000  1.01503600
H  2.59923600  1.20833100  2.31613700
H  3.96264500  1.83575400  3.20881100
H  3.50856700  2.54868200  1.65900600
H  4.77317400  -0.30883500  3.49123500
H  3.52009400  -1.12460400  2.54740900
H  5.23973700  -1.41165300  2.20049700
H  4.05510700  -2.74144000  1.09158900
H  2.81243100  -2.83944000  -0.15693900
H  4.34000700  -3.71405200  -0.35083000
H  4.70167400  -1.18329800  -2.92644800
S

H                  4.45645400  -2.87426900  -2.50208000  
H                  3.09352600  -1.75273500  -2.42035900  
H                  6.40672100  -2.63193300  -1.02286800  
H                  6.58934000  -0.87918700  -1.10529300  
H                  6.36362800  -1.67922000  0.45638000  
H                  6.34428800  -1.54970900  -1.21800000  
H                  3.34913200  -2.12432500  -3.38182700  

C                  -0.10366300  0.00000000  -0.42012800  
C                  0.59949000  1.20409000  -0.26966700  
C                  1.95780200  1.20830700  0.03173900  
C                  2.66008700  0.00000100  0.18923500  
C                  1.95780400  -1.20830500  0.03173400  
C                  0.59949100  -1.20408900  -0.26966900  
H                  0.07492400  2.14659800  -0.39782600  
H                  2.48454100  2.15323700  0.14734400  
H                  2.48454500  -2.15323600  0.14733300  
H                  0.07492700  -2.14659700  -0.39783200  
N                  4.00904300  0.00000400  0.54501700  
H                  4.52051500  -0.83778200  0.29749200  

CPCM(Toluene) M06L/def2-TZVP E = -2661.53874469
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -2374.90323769
H  4.52052900  0.83776500  0.29743900
S  -1.84305100  0.00000000  -0.84685300
C  -2.62262100  -0.00013000  0.83028600
H  -2.27939200  0.88616400  1.37381900
H  -2.27941400  -0.88621300  1.37381900
C  -4.14413300  0.00000800  0.69325000
H  -4.49494300  -0.88643000  0.15364100
H  -4.49494300  0.88647000  0.15366500

Zero-point correction=                           0.175155 (Hartree/Particle)
Thermal correction to Energy=                    0.185693
Thermal correction to Enthalpy=                  0.186637
Thermal correction to Gibbs Free Energy=         0.138077
Sum of electronic and zero-point Energies=      -764.232751
Sum of electronic and thermal Energies=          -764.222213
Sum of electronic and thermal Enthalpies=        -764.221269
Sum of electronic and thermal Free Energies=     -764.269829

CPCM(Toluene) M06L/def2-TZVP E = -764.508542626
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -764.4701567
| Atom | X    | Y    | Z    |
|------|------|------|------|
| H    | -4.95345500 | 3.54200300 | 1.21365500 |
| H    | -4.33838500 | 4.05493100 | 2.78158400 |
| H    | -3.64069900 | 4.72419400 | 1.30630400 |
| H    | -4.50606200 | 1.02278400 | 1.86499800 |
| H    | -2.93719800 | 0.62219600 | 2.57676600 |
| H    | -4.05556000 | 1.70518800 | 3.43221100 |
| C    | -1.44833300 | 4.94799000 | -0.25271300 |
| C    | 0.34068600  | 3.28842500 | 0.28908900  |
| C    | -0.63549100 | 3.31063500 | -1.96894000 |
| C    | -3.22399900 | 1.32046600 | -2.47520300 |
| C    | -4.91709700 | 1.36529900 | -0.67728000 |
| C    | -4.18578500 | 3.51150500 | -1.71737900 |
| H    | -2.39554800 | 5.17980800 | -0.74282800 |
| H    | -1.54012700 | 5.20119000 | 0.80616300  |
| H    | -0.68945500 | 5.62049600 | -0.67610900 |
| H    | 0.78154000  | 2.31197000 | 0.06120200  |
| H    | 1.04891700  | 4.06267600 | -0.03815500 |
| H    | 0.22455600  | 3.36546500 | 1.37151700  |
| H    | 0.22455600  | 3.95438800 | -2.19828300 |
| H    | -0.34923200 | 2.28107800 | -2.20414600 |
| H    | -1.44390000 | 3.61434100 | -2.63741300 |
| H    | -2.41398000 | 1.80288300 | -3.02149300 |
| H    | -2.88496100 | 0.32159000 | -2.19401600 |
| H    | -4.06993800 | 1.21273200 | -3.16860400 |
| H    | -5.43248800 | 1.91304600 | 0.11511300  |
| H    | -5.64140400 | 1.22040000 | -1.49023600 |
| H    | -4.64512100 | 0.37782600 | -0.30148100 |
| H    | -5.03204800 | 3.36557100 | -2.40342500 |
| H    | -4.53691200 | 4.14486000 | -0.89889900 |
| H    | -3.42088500 | 4.06004600 | -2.27112400 |
| P    | 3.80384800  | 0.14782700 | -0.18479100 |
| C    | 4.71268000  | 0.96215900 | 1.35881000  |
| C    | 4.45872200  | 1.68546800 | -0.37939600 |
| C    | 4.38823700  | 1.18390200 | -1.75189200 |
| C    | 6.20330200  | 1.30627900 | 1.13487700  |
| C    | 3.98394700  | 2.26304900 | 1.77264600  |
| C    | 4.63122900  | 0.01352600 | 2.57341600  |
| C    | 3.65517200  | -2.57197700 | 0.60030900  |
| C    | 4.15404900  | -2.21732500 | -1.79681300 |
| C    | 5.96628000  | -1.88677500 | -0.11373600 |
| C    | 4.23476200  | 2.69621700  | -1.47461300 |
| C    | 5.84805600  | 0.90451100  | -2.17882100 |
| C    | 3.48694500  | 0.89802400  | -2.96829900 |
| H    | 6.80551800  | 0.45266800  | 0.81876900  |
| H    | 6.34829700  | 2.11684000  | 0.41803400  |
| H    | 6.61254700  | 1.65493800  | 2.09248000  |
| H    | 2.94301700  | 2.07017500  | 2.03334800  |
| H    | 4.48339900  | 2.65659900  | 2.66869400  |
| H    | 4.02399800  | 3.04366900  | 1.01429600  |
| H    | 5.02022300  | 0.54859300  | 3.44964100  |
| H    | 3.60128100  | -0.26349200 | 2.79348400  |
| H    | 5.23432300  | -0.88912300 | 2.45636600  |
| H    | 3.81805800  | -2.31244700 | 1.64765900  |
| H    | 2.58163800  | -2.51360800 | 0.39519000  |
| H    | 3.97095000  | -3.61527200 | 0.46528800  |
| H    | 4.77480900  | -1.75449000 | -2.56733200 |
| H    | 4.37815400  | -3.29223800 | -1.80829500 |
Zero-point correction = 0.923852 (Hartree/Particle)
Thermal correction to Energy = 0.981851
Thermal correction to Enthalpy = 0.982795
Thermal correction to Gibbs Free Energy = 0.831788

Sum of electronic and zero-point Energies = -2669.598895
Sum of electronic and thermal Energies = -2669.540896
Sum of electronic and thermal Enthalpies = -2669.539952
Sum of electronic and thermal Free Energies = -2669.690959

CPCM(Toluene) M06L/def2-TZVP E = -3246.4568532
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -2673.3297943

C  4.68539600  3.99968800  1.20871400
C  3.26634800  2.09718800  1.75521600
C  3.16382500  1.74200600  0.40464200
C  3.80402700  2.55207400  -0.54114500
H  3.72029000  2.33193400  -1.60239700
H  2.75372300  1.51626600  2.51780100
C  4.56134400  3.65935800  -0.14787000
C  4.02099400  3.20169700  2.15489600
Zero-point correction= 0.926472 (Hartree/Particle)
Thermal correction to Energy= 0.984218
Thermal correction to Enthalpy= 0.985162
Thermal correction to Gibbs Free Energy= 0.835743

Sum of electronic and zero-point Energies= -2669.638855
Sum of electronic and thermal Energies= -2669.581110
Sum of electronic and thermal Enthalpies= -2669.580165
Sum of electronic and thermal Free Energies= -2669.729585

CPCM(Toluene) M06L/def2-TZVP E = -3246.48292627
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -2673.35775542
| Element | x      | y      | z     |
|---------|--------|--------|-------|
| H       | 7.13918300 | 0.26013100 | -0.63866900 |
| Pd      | 1.91515100 | 0.23663000 | -0.24195100 |
| Pd      | -3.90270400 | -0.96073000 | 0.47677200 |
| C       | -3.32410900 | -2.53354600 | 1.49332900 |
| C       | -5.24745800 | -0.06281700 | 1.59783900 |
| C       | -4.78735200 | -1.56437300 | -1.14968300 |
| C       | -4.35968200 | -3.67852000 | 1.56057700 |
| C       | -2.03216700 | -3.11488000 | 0.88572900 |
| C       | -2.94159200 | -2.11268500 | 2.93070100 |
| C       | -4.52163400 | 0.77855900 | 2.67568400 |
| C       | -6.09771000 | 0.91680600 | 0.75672700 |
| C       | -6.23468500 | -1.00850000 | 2.32078000 |
| C       | -3.94431600 | -2.64437000 | -1.86172300 |
| C       | -6.09661000 | -2.13763000 | -0.96682300 |
| C       | -4.84340900 | -0.35136100 | -2.10830600 |
| H       | -5.33229900 | -3.37053500 | 1.94300600 |
| H       | -4.51038800 | -4.15242700 | 0.58747600 |
| H       | -3.97234800 | -4.45339100 | 2.23605900 |
| H       | -1.20667500 | -2.40637500 | 0.95562100 |
| H       | -1.75835400 | -4.01088500 | 1.45980700 |
| H       | -2.12798100 | -3.40803000 | -0.15872600 |
| H       | -2.42000200 | -2.95343900 | 3.40655800 |
| H       | -2.25719300 | -1.25778300 | 2.93548500 |
| H       | -3.80158800 | -1.87445800 | 3.55810700 |
| H       | -3.98328100 | 0.17073200 | 3.40327800 |
| H       | -3.82562300 | 1.49048300 | 2.23663600 |
| H       | -5.27900200 | 1.35050100 | 3.22818300 |
| H       | -6.78691400 | 0.40894900 | 0.07877600 |
| H       | -6.70946000 | 1.50800200 | 1.45064700 |
| H       | -5.48759400 | 1.61843300 | 0.18866500 |
| H       | -6.96614900 | -0.38418200 | 2.85103400 |
| H       | -6.79566800 | -1.65131900 | 1.63841900 |
| H       | -5.75381800 | -1.63751600 | 3.07230200 |
| H       | -2.91203500 | -2.32758000 | -2.02634300 |
| H       | -3.94248700 | -3.60093100 | -1.33351900 |
| H       | -4.38853300 | -2.82452300 | -2.84951900 |
| H       | -6.92333900 | -1.40380000 | -0.59003000 |
| H       | -6.57581200 | -2.46474200 | -1.94922900 |
| H       | -6.23372900 | -3.00837500 | -0.30686000 |
| H       | -5.43688800 | 0.47791200 | -1.72252500 |
| H       | -3.84046300 | 0.02913500 | -2.32430600 |
| H       | -5.29611200 | -0.67406000 | -3.05564100 |
| I       | -3.07682000 | 2.99912000 | -0.09327100 |
| I       | -0.25151100 | -1.25797900 | -1.66321500 |
| C       | 0.15028100 | 2.53146200 | -2.04412700 |
| N       | 4.91986900 | 5.48594900 | 1.35399200 |
| H       | 5.11127000 | 5.60592200 | 2.34130300 |
| H       | 5.73660800 | 5.70333200 | 0.79585500 |
| S       | 0.10769000 | 1.84666900 | -0.30767600 |
| C       | 0.55838900 | 4.00288000 | -2.04439600 |
| H       | 0.56853900 | 4.37248700 | -3.07838100 |
| H       | -0.15483900 | 4.60258400 | -1.47186500 |
| H       | 1.55514300 | 4.14848200 | -1.61773000 |
| H       | 0.82941400 | 1.91416900 | -2.63281000 |
| H       | -0.85871300 | 2.40877800 | -2.43861700 |
Zero-point correction = 0.925953 (Hartree/Particle)
Thermal correction to Energy = 0.984029
Thermal correction to Enthalpy = 0.984973
Thermal correction to Gibbs Free Energy = 0.833225
Sum of electronic and zero-point Energies = -2669.648097
Sum of electronic and thermal Energies = -2669.590021
Sum of electronic and thermal Enthalpies = -2669.589077
Sum of electronic and thermal Free Energies = -2669.740825

CPCM(Toluene) M06L/def2-TZVP E = -3246.48380016
CPCM(Toluene) M06L/6-31++G(d,p) with SDD (for Pd, I) E = -2673.3599941

\[
\begin{align*}
\text{C} & \quad -5.16847400 \quad -3.44401600 \quad 0.20689000 \\
\text{C} & \quad -2.92745800 \quad -2.78366600 \quad 0.89048600 \\
\text{C} & \quad -2.74565600 \quad -2.06668000 \quad -0.31042000 \\
\text{C} & \quad -3.78013800 \quad -2.08570700 \quad -1.26328600 \\
\text{H} & \quad -3.67468700 \quad -1.55383600 \quad -2.19959800 \\
\text{H} & \quad -2.12437400 \quad 2.81819100 \quad 1.61954000 \\
\text{C} & \quad -4.97751400 \quad -2.74998100 \quad -1.00092700 \\
\text{C} & \quad -4.11793600 \quad -3.44853500 \quad 1.14708100 \\
\text{H} & \quad -5.77305900 \quad -2.73423000 \quad -1.74338700 \\
\text{H} & \quad -4.23614100 \quad -3.99664700 \quad 2.07960400 \\
Pd & \quad -1.64837500 \quad -0.20180700 \quad -0.30728200 \\
Pd & \quad 1.34102400 \quad -0.50867800 \quad -0.17156500 \\
\text{H} & \quad -3.11691300 \quad 1.41152900 \quad 4.15990900 \\
\text{C} & \quad -2.62113800 \quad 1.67923000 \quad 3.21735100 \\
\text{C} & \quad -3.69052700 \quad 1.70916800 \quad 2.10168800 \\
\text{H} & \quad -1.85023200 \quad 0.92576100 \quad 3.02649000 \\
\text{H} & \quad -2.13841100 \quad 2.64610100 \quad 3.37557800 \\
P & \quad -2.81084200 \quad 1.86169400 \quad 0.37054300 \\
\text{C} & \quad -4.71730200 \quad 2.81358000 \quad 2.42822700 \\
\text{C} & \quad -4.39952700 \quad 0.33732800 \quad 2.17259800 \\
\text{C} & \quad -1.52755000 \quad 3.32485600 \quad 0.47081800 \\
\text{C} & \quad -4.14759700 \quad 2.31491200 \quad -0.96953000 \\
\text{H} & \quad -5.58188100 \quad 2.79333900 \quad 1.75963600 \\
\text{H} & \quad -5.09729800 \quad 2.64802500 \quad 3.44576700 \\
\text{H} & \quad -4.29056300 \quad 3.81864400 \quad 2.40152000 \\
\text{H} & \quad -4.82304600 \quad 0.21986500 \quad 3.17949100 \\
\text{H} & \quad -5.21839500 \quad 0.23139400 \quad 1.46081000 \\
\text{H} & \quad -3.69808400 \quad -0.48180300 \quad 2.00430000 \\
\text{C} & \quad -2.01096100 \quad 4.58532200 \quad 1.21781600 \\
\text{C} & \quad -0.25170700 \quad 2.78802400 \quad 1.16275000 \\
\text{C} & \quad -1.08594600 \quad 3.74374000 \quad -0.94936700 \\
\text{C} & \quad -3.54092300 \quad 1.99827600 \quad -2.35762700 \\
\text{C} & \quad -5.37480200 \quad 1.38878700 \quad -0.81864200
\end{align*}
\]
| Atoms | X       | Y       | Z       |
|-------|---------|---------|---------|
| C     | -4.64710500 | 3.77430100 | -0.95757200 |
| H     | -2.91212300 | 5.02189800 | 0.77908500  |
| H     | -2.20200100 | 4.39990400 | 2.27709100  |
| H     | -1.22134400 | 5.34716700 | 1.16356900  |
| H     | 0.17072500  | 1.93573300 | 0.61924400  |
| H     | 0.50058200  | 3.58887500 | 1.16875800  |
| H     | -0.40785300 | 2.47532100 | -1.53928300 |
| H     | -0.24300000 | 4.44035200 | -0.85025600 |
| H     | -0.73187700 | 2.89388200 | -1.50745600 |
| H     | -2.69990200 | 2.63971500 | -2.61971600 |
| H     | -3.19291400 | 0.96130300 | -2.40807800 |
| H     | -4.31637700 | 2.13902100 | -3.12310000 |
| H     | -5.97758100 | 1.62147300 | 0.06234400  |
| H     | -2.91212300 | 5.02189800 | 0.77908500  |
| C     | 3.88840500  | 0.09355500 | 0.31199000  |
| C     | 4.50461900  | -0.31987000 | 2.13508400 |
| C     | 4.80632500  | -1.14185500 | 0.00360500 |
| C     | 4.52375300  | 1.90943000 | -0.06890700 |
| C     | 5.97496500  | 0.03949700 | 2.44883300  |
| C     | 3.63432600  | 0.43918500 | 3.16827400  |
| C     | 4.32238900  | -1.83405500 | 2.38728000 |
| C     | 3.99394200  | -2.45858100 | -0.92782600 |
| C     | 4.79394200  | -0.59892600 | -2.35105700 |
| H     | 6.69954900  | -0.43778700 | 1.78807800 |
| H     | 6.15290500  | 1.11725200 | 2.43558900  |
| H     | 6.19102900  | -0.30352900 | 3.46994700 |
| H     | 2.57082400  | 0.40465000 | 2.93768800  |
| C     | 3.76639400  | -0.03928300 | 4.14718100 |
| C     | 3.93578200  | 1.48077300 | 3.27925500  |
| C     | 4.51357900  | -2.03134900 | 3.45000300 |
| C     | 3.30620700  | -2.17065900 | 2.17441400 |
| C     | 5.02762500  | -2.44371100 | 1.81800900 |
| C     | 3.92569100  | -2.94420300 | 0.04653700 |
| H     | 2.97478800  | -2.28445300 | -1.28834800 |
| H     | 4.48142200  | -3.16024800 | -1.61870000 |
| H     | 5.45332600  | 0.26086100 | -2.48844900 |
| H     | 5.16300200  | -1.39387900 | -3.01331500 |
| H     | 3.79130300  | -0.30352900 | 3.46994700 |
| H     | 6.67760100  | -2.11710600 | -1.34200100 |
| H     | 6.90792300  | -0.58570500 | -0.49949800 |
| H     | 6.37008200  | -2.02236200 | 0.38745600  |
| H     | 3.10002900  | 2.73338400 | 1.40000000  |
| H     | 4.78093000  | 2.71797500 | 1.97607600 |
| H     | 4.27840900  | 3.88479500 | 0.75899400 |
| H     | 6.35896200  | 1.52835900 | -1.23474600 |
| H     | 6.29057300  | 3.09236400 | -0.43215900 |
| H     | 6.65158800  | 1.64363700 | 0.50558400  |
| H     | 3.94447500  | 1.88571800 | -2.20908500 |
Zero-point correction= 0.925253 (Hartree/Particle)
Thermal correction to Energy= 0.982800
Thermal correction to Enthalpy= 0.983744
Thermal correction to Gibbs Free Energy= 0.834109

Sum of electronic and zero-point Energies= -2669.617939
Sum of electronic and thermal Energies= -2669.560392
Sum of electronic and thermal Enthalpies= -2669.559447
Sum of electronic and thermal Free Energies= -2669.709083

CPCM(Toluene) M06L/def2-TZVP E = -3246.46833592
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -2673.34423808

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**Diagram**

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**Table**

| Element | X    | Y    | Z    |
|---------|------|------|------|
| Pd      | -1.36139900 | 0.00064400 | 0.06607600 |
| Pd      | 1.36144300  | 0.00065100  | -0.06606700 |
| I       | -0.00007300 | 2.40299200  | -0.00002200 |
| I       | 0.00003000  | -2.39208700 | -0.00000700 |
| P       | 3.75219200  | -0.00270600 | -0.01201800 |
| C       | 4.23561000  | -0.47097100 | 1.81650000  |
| C       | 4.56218100  | -1.29483700 | -1.22978700 |
| C       | 4.49106100  | 1.75577800  | -0.42519800 |
| C       | 5.68374100  | -0.13977700 | 2.23217000  |
| C       | 3.25732600  | 0.26113300  | 2.76802900  |
| C       | 3.99540600  | -1.97964000 | 2.04593100  |
| C       | 3.71807000  | -2.58978800 | -1.23319200 |
| C       | 4.49462300  | -0.75699900 | -2.67656600 |
| C       | 6.02609500  | -1.66304200 | -0.90645900 |
| C       | 4.15889700  | 2.74010700  | 0.71894000  |
| C       | 6.01682500  | 1.79155500  | -0.66239700 |
| C       | 3.78411300  | 2.31148500  | -1.68560500 |
| H       | 5.88883500  | 0.93328100  | 2.22270800  |
| H       | 5.84108800  | -0.48708200 | 3.26235900  |

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S49
H  -4.42373700  3.75255500  -0.38780300
H  -4.72842500  2.54358800  -1.63028900
H  -6.31710100  1.23811200  1.55539900
H  -6.32056800  2.83559000  0.81769100
H  -6.59104800  1.40975700  -0.18539000
H  -4.01105000  1.75072700  2.59206500
H  -2.69896600  2.33541200  1.56158200
H  -4.12713400  3.34238300  1.84604700

Zero-point correction=                           0.749549 (Hartree/Particle)
Thermal correction to Energy=                    0.795415
Thermal correction to Enthalpy=                  0.796359
Thermal correction to Gibbs Free Energy=         0.671950
Sum of electronic and zero-point Energies=       -1905.447011
Sum of electronic and thermal Energies=          -1905.401145
Sum of electronic and thermal Enthalpies=         -1905.400201
Sum of electronic and thermal Free Energies=      -1905.524610

CPCM(Toluene) M06L/def2-TZVP E = -2481.99430463
CPCM(Toluene) M06L/6-311++G(d,p) with SDD (for Pd, I) E = -1908.89892589
4. References

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5. NMR spectra

1H

[Scheme 1] 600 MHz, C₆D₆

31P

[Scheme 1] 243 MHz, C₆D₆
$^{31}$P NMR of the crude mixture from Scheme 1, bottom showing only presence of Pd$_2$-iodo dimer (and P(OMe)$_3$ as internal standard).

Entry 4.
[Table 1] 400 MHz, CDCl$_3$
Entry 4.
[Table 1] 101 MHz, CDCl₃

Entry 5.
[Table 1] 400 MHz, CDCl₃
Entry 5.
[Table 1] 101 MHz, CDCl$_3$

Entry 6.
[Table 1] 400 MHz, CDCl$_3$
Entry 6.
[Table 1] 101 MHz, CDCl₃

Entry 7.
[Table 1] 400 MHz, CDCl₃
Entry 7.
(Table 1) 101 MHz, CDCl₃

Entry 8.
(Table 1) 400 MHz, CDCl₃
Entry 8.
[Table 1] 101 MHz, CDCl₃

Entry 9.
[Table 1] 400 MHz, CDCl₃
Entry 9.
[Table 1] 101 MHz, CDCl₃

Entry 10.
[Table 1] 400 MHz, CDCl₃
Entry 10.
[Table 1] 101 MHz, CDCl₃

Entry 11.
[Table 1] 400 MHz, CDCl₃
13C

Entry 11.
[Table 1] 101 MHz, CDCl₃

---

1H

Entry 12.
[Table 1] 600 MHz, CDCl₃
Entry 12.
[Table 1] 151 MHz, CDCl$_3$

Entry 13.
[Table 1] 400 MHz, CDCl$_3$
Entry 13.
[Table 1] 101 MHz, CDCl₃

Entry 14.
[Table 1] 400 MHz, CDCl₃
Entry 14.
[Table 1] 101 MHz, CDCl$_3$

Entry 15.
[Table 1] 400 MHz, CDCl$_3$
13C

Entry 15.
[Table 1] 101 MHz, CDCl₃

1H

Entry 16.
[Table 1] 600 MHz, CDCl₃
Entry 16.
[Table 1] 151 MHz, CDCl₃

Entry 17.
[Table 1] 400 MHz, CDCl₃
Entry 17.
[Table 1] 101 MHz, CDCl₃

Entry 18.
[Table 1] 400 MHz, CDCl₃
Entry 18.
[Table 1] 101 MHz, CDCl₃

Entry 19.
[Table 1] 400 MHz, CDCl₃
Entry 19.
[Table 1] 101 MHz, CDCl₃

Entry 20.
[Table 1] 600 MHz, CDCl₃
Entry 20.
[Table 1] 151 MHz, CDCl$_3$

Entry 21.
[Table 1] 400 MHz, DMSO-d$_6$
Entry 21.
[Table 1] 101 MHz, DMSO-d$_6$

Entry 22.
[Table 1] 400 MHz, CDCl$_3$
Entry 22.
[Table 1] 151 MHz, CDCl₃

Entry 23.
[Table 1] 400 MHz, CDCl₃
Entry 23.
[Table 1] 101 MHz, CDCl₃

Entry 24.
[Table 1] 600 MHz, CDCl₃
Entry 24.
[Table 1] 151 MHz, CDCl$_3$

Entry 25.
[Table 1] 400 MHz, CDCl$_3$
Entry 25.
[Table 1] 101 MHz, CDCl₃

Entry 26.
[Table 1] 400 MHz, CDCl₃
Entry 26.
[Table 1] 101 MHz, CDCl₃

Entry 27.
[Table 1] 600 MHz, CDCl₃
13C

Entry 27.
[Table 1] 151 MHz, CDCl$_3$

---

1H

Entry 28.
[Table 1] 400 MHz, CDCl$_3$
Entry 28.
[Table 1] 101 MHz, CDCl₃

Entry 29.
[Table 1] 400 MHz, CDCl₃
Entry 29.
[Table 1] 101 MHz, CDCl$_3$

Entry 30.
[Table 1] 400 MHz, CDCl$_3$
Entry 30.
[Table 1] 101 MHz, CDCl₃

Entry 31.
[Table 1] 400 MHz, CDCl₃
Entry 31.
[Table 1] 101 MHz, CDCl₃

Entry 32.
[Table 1] 600 MHz, CDCl₃
Entry 32.
[Table 1] 151 MHz, CDCl₃

Entry 33.
[Scheme 3] 400 MHz, CDCl₃
Entry 33.
(Scheme 3) 151 MHz, CDCl₃

Entry 34.
(Scheme 3) 600 MHz, CDCl₃
Entry 34.

[Scheme 3] 151 MHz, CDCl₃

Entry 34.

[Scheme 3] 564 MHz, CDCl₃
Entry 35.

[Scheme 3] 600 MHz, CDCl₃

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Entry 35.

[Scheme 3] 151 MHz, CDCl₃
Entry 35.
[Scheme 3] 564 MHz, CDCl₃

Entry 36.
[Scheme 3] 600 MHz, CDCl₃
Entry 36.

[Scheme 3] 151 MHz, CDCl₃

Entry 36.

[Scheme 3] 564 MHz, CDCl₃
Entry 37.
[Scheme 3] 600 MHz, CD₂Cl₂

Entry 37.
[Scheme 3] 151 MHz, CD₂Cl₂
Entry 37.
[Scheme 3] 564 MHz, CD₂Cl₂

Entry 38.
[Scheme 3] 600 MHz, CDCl₃
Entry 38.

[Scheme 3] 151 MHz, CDCl₃

Entry 38.

[Scheme 3] 564 MHz, CDCl₃
Entry 39.
[Scheme 3] 400 MHz, CDCl₃

Entry 39.
[Scheme 3] 101 MHz, CDCl₃
Entry 39.
[Scheme 3] 376 MHz, CDCl$_3$

Entry 40.
[Scheme 3] 400 MHz, CDCl$_3$
Entry 40.

[Scheme 3] 101 MHz, CDCl₃

Entry 40.

[Scheme 3] 376 MHz, CDCl₃
[Scheme 3] 600 MHz, CDCl₃
[Scheme 3] 600 MHz, CDCl₃