Supporting Information

Arylation of Axially Chiral Phosphorothioate Salts by Dinuclear Pd\textsuperscript{I} Catalysis

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1. General Experimental Details

All reagents and starting materials were commercially available and used as received. Anhydrous toluene was dried using an Innovative Technology PS-MD-5 solvent purification system. Solvents used in work up and purification were distilled prior to use. Thin layer chromatography (TLC) was performed on Merck Kieselgel 60 F254 aluminium plates with unmodified silica and visualized either under UV light or stained with potassium permanganate. Flash column chromatography was performed with Merck silica gel 60 (35 – 70 mesh). Preparative HPLC was performed on a Gilson-Abimed HPLC (employing UV detector model 117) using a Merck LiChrosorb Si60 column (porosity 7 μm, 250 x 25 mm).

All 1H, 13C and 31P NMR spectra were recorded on Varian VNMRS 600 or Varian VNMRS 400 spectrometers or Varian Mercury 300 spectrometer at ambient temperature. Chemical shifts (δ) are reported in parts per million (ppm) and were referenced either to residual solvent peak (CDCl3; for 1H and 13C spectra) or P(O)(OMe)3 (δ = 3.05 ppm, added as an internal standard for 31P). Coupling constants (J) are given in Hertz (Hz).

Gas chromatography coupled with mass spectrometry (GC-MS) was performed on an Agilent Technologies 5975 series MSD mass spectrometer under electrospray ionization (EI) mode coupled with an Agilent Technologies 7820A gas chromatograph employing an Agilent 19091s-433 HP-5MS column (30 m x 0.250 μm x 0.250 μm). High-resolution mass spectrometry (HRMS) was performed using a Thermo Scientific LTQ Orbitrap XL spectrometer. IR spectra were recorded on a Spectrum 100 spectrometer with an UATR Diamond/KRS-5 crystal with attenuated total reflectance (ATR).

Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (Daicel AD).

Colourless prism-shaped crystals of compound 30 were obtained by slow diffusion from a mixture of hexane/ethyl acetate/dichloromethane/iso-propanol = 10:1:1:1. Suitable crystals were selected and mounted on a glass fibre with grease on a Bruker APEX-II CCD diffractometer. The crystals were kept at T = 296(2) K during data collection. The structures were solved with the ShelXT[1] structure solution program using the intrinsic phasing solution method and by using Olex2[2] as the graphical interface. The model was refined with ShelXL[3] using least squares minimization.
2. General Procedures

General procedure for Pd(I)-dimer catalyzed phosphorothioation of ArI. (Procedure A)

The Pd(I)-dimer catalyst \([\text{Pd(μ-I)PtBu}_3]^2\) (4.5 mg, 0.005 mmol) was added to a mixture of aryl iodide (0.1 mmol) and \((\text{Me}_4\text{N})\text{S}\text{P(O)(OR')}^2\) (0.15 mmol) in toluene (0.5 mL). The reaction was stirred at 100°C for the indicated time (typically overnight). The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (pentane/EtOAc as the eluent, typically 20:1-2:1) to furnish the corresponding products.

General procedure for the synthesis of \((\text{Me}_4\text{N})\text{S}\text{P(O)(OR')}^2\). (Procedure B)

To a stirred solution of \(\text{HP(O)(OR')}^2\) (16.0 mmol, 1.0 equiv) in dry DCM (30.0 mL) was added anhydrous Et₃N (2.8 mL, 19.4 mmol, 1.2 equiv) at 0°C under argon atmosphere. To the cold solution freshly distilled TMSCl (2.6 mL, 19.4 mol, 1.2 equiv) was added drop wise while maintaining the reaction temperature at 0°C. After complete addition of TMSCl, the reaction mixture was allowed to warm up to room temperature and stirring was continued for overnight. The formed Et₃N·HCl salt was filtered off under argon, and the solvent was then removed under vacuum. The residue was redissolved in dry diethyl ether to precipitate the remaining salt. After filtration and evaporation, the procedure was repeated until there was no more salt formation. The obtained TMSOP(OR')₂ was used directly for the next step without further purification.

Under inert atmosphere, 0.4 g of elemental sulfur (12.5 mmol) was dissolved in 50 mL of THF at room temperature, followed by the addition of TMSOP(OR')₂ (12 mmol). The solution was subsequently cooled to -78°C and 0.93 g of tetramethylammonium fluoride (10 mmol) was added under nitrogen flow to the stirred mixture. The reaction was stirred overnight, while allowing it to warm to room temperature. A white solid was subsequently filtered off under inert atmosphere and washed with THF and diethyl ether. Under inert atmosphere, the obtained solid was dissolved in a minimal amount of acetonitrile, the solution filtered and the product precipitated using an excess of THF. A white precipitate was filtered off, washed with THF and diethyl ether and dried in vacuo and stored in glovebox.
Reaction monitoring of the formation of mixed Pd(I)-I/SP(O)(OR')₂ dimer

To Pd(I)-iodo dimer (30 mg, 0.035 mmol, 1.0 equiv.) and NMe₄[SP(=O)(OPh)₂] (47 mg, 0.14 mmol, 4.0 equiv.) was added toluene (1 mL). The reaction was stirred at room temperature for 0.5-2 h. The crude mixture was filtered through celite under air atmosphere to afford the samples. Samples for ³¹P NMR were taken at 0.5 h and 2 h reaction time. ³¹P NMR (121 MHz, toluene-d₈) 97.9, 13.6.

³¹P NMR analysis conducted with (MeO)₃P=O as the internal standard

Figure S1. Reaction monitoring of the formation of mixed Pd(I)-I/SP(O)(OR')₂ dimer in toluene over time. The ratio of the signals at 97.9 (PtBu₃) to 13.6 (-SP(O)(OPh)₂) of 2:1 is in line with the exchange of only one iodide bridging unit with SP(O)(OPh)₂ rather than a double exchange.
Initial studies with Pd\(^{0}\)/Pd\(^{II}\) precatalyst.

In an argon-filled glove-box, the Pd catalyst [Pd(PPh\(_3\))\(_4\) (5.8 mg, 0.005 mmol) or Pd\(_2\)dba\(_3\) (4.6 mg, 0.005 mmol) or Pd\(_2\)dba\(_3\)/dppf (4.6 mg, 0.005 mmol/5.5 mg, 0.01 mmol)] was added to a mixture of PhI (20.4 mg, 0.1 mmol) and (Me\(_4\)N)SP(O)(OPh)\(_2\) (50.9 mg, 0.15 mmol) in toluene (0.5 mL). The reaction was stirred at 100°C overnight. No or only a trace amount of product was observed.

The Pd complex Pd(Ph\(_3\))\(_2\)PhI\(^{[4]}\) (41.7 mg, 0.05 mmol) was added to a toluene (0.5 mL) solution of (Me\(_4\)N)SP(O)(OPh)\(_2\) (33.9 mg, 0.1 mmol) with or without PhI (20.4 mg, 0.1 mmol) and the mixed solution was stirred at rt or 100°C for the period of time indicated above. The reaction mixture was concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel (pentane/EtOAc as the eluent, typically 20:1-2:1).
3. Compound Characterization Data

**Tetramethylammonium O,O-diphenyl phosphorothioate:** Procedure B was followed for the synthesis of the product as a white solid. IR (neat): 3022, 1588, 1480, 1178, 1017, 868, 765, 725 cm⁻¹. **¹H NMR** (400 MHz, CD₂CN): δ 7.31 – 7.25 (m, 8H), 7.08 – 7.04 (m, 2H), 3.07 (s, 12H). **¹³C NMR** (151 MHz, CD₂CN): δ 154.4 (d, J = 8.2 Hz), 129.8 (d, J = 6.0 Hz), 123.7 (d, J = 8.7 Hz), 121.8 (t, J = 4.6 Hz), 55.9 (m). **³¹P NMR** (243 MHz, CD₃CN): δ 49.3. **HRMS** (ESI): m/z [M-((CH₃)₄N)]⁻ calcd for C₁₂H₂₀O₃PS: 265.00828; found: 265.00870.

**Tetramethylammonium O,O-bis((S)-2-methylbutyl) phosphorothioate:** Procedure B was followed for the synthesis of the product as a white solid. IR (neat): 1494, 1462, 1162, 1013, 957, 782 cm⁻¹. **¹H NMR** (300 MHz, CD₂CN): δ 3.68 – 3.52 (m, 4H), 3.19 (s, 12H), 1.63 – 1.57 (m, 2H), 1.51 – 1.42 (m, 2H), 1.18 – 1.08 (m, 2H), 0.93 – 0.88 (m, 12H). **¹³C NMR** (151 MHz, CD₂CN): δ 70.1 (d, J = 6.4 Hz), 55.9 (m), 36.6 (d, J = 8.3 Hz), 26.7 (d, J = 9.3 Hz), 16.9, 11.6. **³¹P NMR** (243 MHz, CD₃CN): δ 56.7. **HRMS** (ESI): m/z [M-((CH₃)₄N)]⁻ calcd for C₁₀H₂₂O₃PS: 253.10218; found: 253.10248.

**Tetramethylammonium (3aR,8aR)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-1,3-dioxolo[4,5-e][1,3,2]dioxaphosphepine-6-thiolate 6-oxide:** Procedure B was followed for the synthesis of the product as a white solid. IR (neat): 1488, 1447, 1181, 1043, 1017, 890, 841, 744, 697, 674 cm⁻¹. **¹H NMR** (600 MHz, DMSO) δ 7.68 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 7.4 Hz, 2H), 7.32 – 7.14 (m, 16H), 5.53 (d, J = 8.4 Hz, 1H), 4.73 (d, J = 8.4 Hz, 1H), 3.03 (s, 12H), 1.12 (s, 3H), 0.21 (s, 3H). **¹³C NMR** (151 MHz, DMSO) δ 147.3, 147.1 (d, J = 9.4 Hz), 142.5, 142.1 (d, J = 10.0 Hz), 129.1, 128.9, 127.5, 127.54, 127.51, 127.1, 126.9, 126.84, 126.83, 126.76, 126.5, 126.4, 110.3 (d, J = 9.7 Hz), 82.8 (d, J = 12.0 Hz), 82.1, 80.1, 54.4 (t, J = 3.8 Hz), 27.5, 25.4. **³¹P NMR** (121 MHz, DMSO) δ 46.5. **HRMS** (ESI): m/z [M-((CH₃)₄N)]⁻ calcd for C₂₁H₂₂O₃P: 543.13896; found: 543.13898.

**O,O,S-Triphenyl phosphorothioate (2):** Procedure A was followed for the synthesis of the product 2 as a yellow oil (28.4 mg, 83%). IR (neat): 2921, 1590, 1486, 1273, 1183, 937, 764, 689, 616, 491 cm⁻¹. **¹H NMR** (400 MHz, CDCl₃) δ 7.51 – 7.48 (m, 2H), 7.38 – 7.31 (m, 7H), 7.21 – 7.17 (m, 6H). **¹³C NMR** (101 MHz, CDCl₃) δ 150.5 (d, J = 8.9 Hz), 135.4 (d, J = 5.4 Hz), 129.9, 129.8 (d, J = 3.1 Hz), 129.6 (d, J = 2.5 Hz), 125.7, 125.2, 120.6 (d, J = 4.9 Hz). **³¹P NMR** (121 MHz, CDCl₃) δ 14.9. **HRMS** (ESI): m/z [M+Na]⁺ calcd for C₁₈H₁₅O₃NaPS: 365.03717; found: 365.03726.
**O,O-Diphenyl S-(p-tolyl) phosphorothioate (3):** Procedure A was followed for the synthesis of the product 3 as a yellow oil (32.8 mg, 92%). **IR** (neat): 2921, 1590, 1487, 1273, 1184, 937, 810, 766, 688, 615, 497 cm\(^{-1}\). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 7.39 – 7.33 (m, 6H), 7.22 – 7.20 (m, 6H), 7.15 – 7.14 (m, 2H), 2.36 (d, \(J = 1.6\) Hz, 3H). **\(^13\)C NMR** (151 MHz, CDCl\(_3\)) \(\delta\) 150.5 (d, \(J = 8.4\) Hz), 140.1 (d, \(J = 3.5\) Hz), 135.4 (d, \(J = 5.3\) Hz), 130.4 (d, \(J = 2.7\) Hz), 130.0, 125.6, 121.4, 120.6 (d, \(J = 5.1\) Hz), 21.4. **\(^{31}\)P NMR** (243 MHz, CDCl\(_3\)) \(\delta\) 15.3. **HRMS** (ESI): \(m/z\) [M+Na\(^+\)] calcd for C\(_{19}\)H\(_{17}\)O\(_3\)NaPS: 379.05282; found: 379.05270. These data are in agreement with those reported previously in the literature.\([5]\)

**S-(4-Butylphenyl) O,O-diphenyl phosphorothioate (4):** Procedure A was followed for the synthesis of the product 4 as a yellow oil (32.0 mg, 80%). **IR** (neat): 2924, 1590, 1487, 1383, 1274, 1184, 936, 766, 688, 615 cm\(^{-1}\). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 7.41 – 7.39 (m, 2H), 7.36 – 7.33 (m, 4H), 7.22 – 7.19 (m, 6H), 1.32 (s, 9H). **\(^13\)C NMR** (151 MHz, CDCl\(_3\)) \(\delta\) 150.6 (d, \(J = 8.3\) Hz), 135.4 (d, \(J = 5.3\) Hz), 130.0, 129.8 (d, \(J = 2.6\) Hz), 125.6, 121.5 (d, \(J = 7.8\) Hz), 120.6 (d, \(J = 5.1\) Hz), 35.4, 33.5, 22.4, 14.1. **\(^{31}\)P NMR** (121 MHz, CDCl\(_3\)) \(\delta\) 15.2. **HRMS** (ESI): \(m/z\) [M+H\(^+\)] calcd for C\(_{22}\)H\(_{24}\)O\(_3\)PS: 399.11783; found: 399.11783.

**S-(4-(Tert-butyl)phenyl) O,O-diphenyl phosphorothioate (5):** Procedure A was followed for the synthesis of the product 5 as a yellow oil (35.0 mg, 88%). **IR** (neat): 2962, 1487, 1274, 1185, 938, 767, 688, 615 cm\(^{-1}\). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 7.47 – 7.44 (m, 2H), 7.36 – 7.34 (m, 4H), 7.23 – 7.20 (m, 6H), 7.04 – 7.01 (m, 2H). **\(^13\)C NMR** (151 MHz, CDCl\(_3\)) \(\delta\) 163.8 (d, \(J = 251.1\) Hz), 150.4 (d, \(J = 8.5\) Hz), 137.8 (dd, \(J = 8.6, 5.2\) Hz), 123.0, 125.8, 120.5 (d, \(J = 5.0\) Hz), 120.2 (dd, \(J = 7.9, 3.5\) Hz), 116.9 (dd, \(J = 22.2, 2.5\) Hz). **\(^{31}\)P NMR** (121 MHz, CDCl\(_3\)) \(\delta\) 14.5 (dd, \(J = 6.1, 1.9\) Hz). **HRMS** (ESI): \(m/z\) [M+Na\(^+\)] calcd for C\(_{18}\)H\(_{17}\)FO\(_3\)NaPS: 383.02775; found: 383.02774.

**S-(4-Fluorophenyl) O,O-diphenyl phosphorothioate (6):** Procedure A was followed for the synthesis of the product 6 as a yellow oil (30.6 mg, 85%). **IR** (neat): 2920, 1588, 1486, 1182, 936, 765, 687, 615 cm\(^{-1}\). **\(^1\)H NMR** (600 MHz, CDCl\(_3\)) \(\delta\) 7.47 – 7.44 (m, 2H), 7.37 – 7.34 (m, 4H), 7.23 – 7.20 (m, 6H), 7.04 – 7.01 (m, 2H). **\(^13\)C NMR** (151 MHz, CDCl\(_3\)) \(\delta\) 163.8 (d, \(J = 251.1\) Hz), 150.4 (d, \(J = 8.5\) Hz), 137.8 (dd, \(J = 8.6, 5.2\) Hz), 123.0, 125.8, 120.5 (d, \(J = 5.0\) Hz), 120.2 (dd, \(J = 7.9, 3.5\) Hz), 116.9 (dd, \(J = 22.2, 2.5\) Hz). **\(^{31}\)P NMR** (121 MHz, CDCl\(_3\)) \(\delta\) 14.5 (dd, \(J = 6.1, 1.9\) Hz). **HRMS** (ESI): \(m/z\) [M+Na\(^+\)] calcd for C\(_{18}\)H\(_{17}\)FOSNaPS: 383.02775; found: 383.02774.
**S-(4-Chlorophenyl) O,O-diphenyl phosphorothioate (7):** Procedure A was followed for the synthesis of the product 7 as a yellow oil (32.0 mg, 85%). IR (neat): 2920, 1587, 1481, 1384, 1181, 937, 765, 610 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.29 (m, 8H), 7.24 – 7.18 (m, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 150.4 (d, J = 5.4 Hz), 136.7 (d, J = 5.5 Hz), 130.0, 129.8 (d, J = 2.7 Hz), 125.8, 123.6 (d, J = 7.6 Hz), 120.6 (d, J = 5.2 Hz), 115.4. ³¹P NMR (121 MHz, CDCl₃) δ 14.9. HRMS (ESI): m/z [M+H]⁺ calcd for C₃₈H₃₅ClO₃PS: 377.01626; found: 377.01645.

**S-[(1,1'- Biphenyl)-4-yl] O,O-diphenyl phosphorothioate (8):** Procedure A was followed for the synthesis of the product 8 as a yellow oil (35.0 mg, 84%). IR (neat): 3064, 1590, 1485, 1273, 1183, 936, 763, 691, 615 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.59 – 7.76 (m, 6H), 7.48 – 7.45 (m, 2H), 7.40 – 7.35 (m, 5H), 7.25 – 7.21 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 150.5 (d, J = 8.4 Hz), 142.7 (d, J = 3.5 Hz), 139.9, 135.8 (d, J = 5.4 Hz), 130.0, 129.1, 128.3 (d, J = 2.5 Hz), 128.1, 127.2, 125.7, 123.8 (d, J = 7.7 Hz), 120.6 (d, J = 5.1 Hz). ³¹P NMR (121 MHz, CDCl₃) δ 14.8 (d, J = 1.9 Hz). HRMS (ESI): m/z [M+H]⁺ calcd for C₃₈H₃₅ClO₃PS: 419.08653; found: 419.08661.

**S-(3-Chlorophenyl) O,O-diphenyl phosphorothioate (9):** Procedure A was followed for the synthesis of the product 9 as a yellow oil (25.2 mg, 67%). IR (neat): 2921, 1585, 1484, 1384, 1274, 1182, 938, 768, 685, 613 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) δ 7.42 – 7.40 (m, 1H), 7.39 – 7.33 (m, 5H), 7.25 – 7.19 (m, 8H). ¹³C NMR (101 MHz, CDCl₃) δ 150.4, 135.0, 133.4, 130.5, 130.5, 130.0, 127.0, 125.9, 120.6 (d, J = 5.1 Hz). ³¹P NMR (121 MHz, CDCl₃) δ 13.7 (d, J = 1.7 Hz). HRMS (ESI): m/z [M+Na]⁺ calcd for C₃₈H₃₄ClO₃NaPS: 398.99820; found: 398.99814.

**S-(2-Methoxyphenyl) O,O-diphenyl phosphorothioate (10):** Procedure A was followed for the synthesis of the product 10 as a yellow oil (24.0 mg, 65%). IR (neat): 2921, 1584, 1459, 1384, 1267, 1160, 1023, 927, 754, 686, 609 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.53 (d, J = 7.6 Hz), 1H, 7.38 – 7.33 (m, 5H), 7.26 – 7.18 (m, 6H), 6.94 – 6.91 (m, 1H), 6.86 (d, J = 8.3 Hz, 1H), 3.65 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 159.9 (d, J = 5.3 Hz), 150.7 (d, J = 8.1 Hz), 137.6 (d, J = 4.9 Hz), 131.7 (d, J = 3.2 Hz), 129.8, 125.4, 121.4, 120.6 (d, J = 5.2 Hz), 113.1 (d, J = 8.0 Hz), 111.6 (d, J = 2.5 Hz), 55.8 (d, J = 3.1 Hz). ³¹P NMR (121 MHz, CDCl₃) δ 14.9. HRMS (ESI): m/z [M+Na]⁺ calcd for C₃₉H₃₃O₄NaPS: 395.04774; found: 395.04712.

**O,O-Diphenyl S-(o-tolyl) phosphorothioate (11):** Procedure A was followed for the synthesis of the product 11 as a yellow oil (33.4 mg, 94%). IR (neat): 2921, 1586, 1454, 1384, 1182, 934, 758, 687, 610
For the larger scale reaction Procedure A was also followed, using 1-iodo-2-methylbenzene (218 mg, 1.0 mmol, 1.0 equiv.), (Me3N)SP(O)(OPh)2 (509 mg, 1.5 mmol, 1.5 equiv.), Pd(I)-dimer 1 (44.5 mg, 0.05 mmol, 0.05 equiv.) in toluene (5.0 mL). After reaction completion (overnight) the product was obtained after purification by column chromatography (pentane/EtOAc = 20/1-5/1) as a yellow oil (300 mg, 84%) and characterized as described above.

**S-[[1,1’-Biphenyl]-2-yl] O,O-diphenyl phosphorothioate (12):** Procedure A was followed for the synthesis of the product 12 as a yellow oil (30.9 mg, 74%). IR (neat): 3061, 1590, 1487, 1274, 1183, 938, 760, 691, 614, 498 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.58 – 7.56 (m, 1H), 7.35 – 7.29 (m, 5H), 7.25 – 7.16 (m, 8H), 2.33 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 150.5 (d, J = 8.9 Hz), 143.0 (d, J = 5.8 Hz), 136.8 (d, J = 4.4 Hz), 131.2 (d, J = 2.8 Hz), 130.1 (d, J = 3.3 Hz), 129.9, 127.0 (d, J = 2.9 Hz), 125.6, 124.5 (d, J = 7.8 Hz), 120.5 (d, J = 5.0 Hz), 21.4. ³¹P NMR (243 MHz, CDCl₃) δ 15.3. HRMS (ESI): m/z [M+Na]⁺ calcd for C₁₉H₁₇O₃NaPS: 379.05282; found: 379.05276.

**S-[(3,5-Dimethylphenyl) O,O-diphenyl phosphorothioate (13):** Procedure A was followed for the synthesis of the product 13 as a yellow oil (31.1 mg, 84%). IR (neat): 3232, 2921, 1588, 1485, 1383, 1183, 935, 765, 686, 614, 495 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.37 – 7.34 (m, 4H), 7.26 – 7.21 (m, 6H), 7.06 (s, 2H), 7.00 (s, 1H), 2.26 (s, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 150.6 (d, J = 8.3 Hz), 139.2 (d, J = 2.6 Hz), 133.1 (d, J = 5.4 Hz), 131.6 (d, J = 3.3 Hz), 130.0, 125.6, 124.1 (d, J = 7.6 Hz), 120.6 (d, J = 5.2 Hz), 21.2. ³¹P NMR (243 MHz, CDCl₃) δ 15.2. HRMS (ESI): m/z [M+Na]⁺ calcd for C₂₀H₂₃O₃NaPS: 393.06847; found: 393.06863.

**S-[(2,5-Dimethylphenyl) O,O-diphenyl phosphorothioate (14):** Procedure A was followed for the synthesis of the product 14 as a yellow oil (32.3 mg, 87%). IR (neat): 2921, 1588, 1485, 1383, 1271, 1182, 933, 755, 687, 615 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.35 – 7.33 (m, 4H), 7.29 (s, 1H), 7.26 – 7.20 (m, 6H), 7.11 – 7.09 (m, 2H), 2.28 (s, 3H), 2.25 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 150.6 (d, J = 8.5 Hz), 139.8 (d, J = 5.9 Hz), 137.4 (d, J = 4.4 Hz), 136.6 (d, J = 3.1 Hz), 131.0 (d, J = 3.5 Hz), 130.0, 125.6, 123.9 (d, J = 7.8 Hz), 120.6 (d, J = 5.1 Hz), 20.9. ³¹P NMR (243 MHz, CDCl₃) δ 15.4. HRMS (ESI): m/z [M+Na]⁺ calcd for C₂₀H₂₃O₃NaPS: 393.06847; found: 393.06863.
S-(Naphthalen-1-yl) O,O-diphenyl phosphorothioate (15): Procedure A was followed for the synthesis of the product 15 as a red oil (34.8 mg, 89%). IR (neat): 1588, 1486, 1271, 1176, 930, 762, 686 cm\(^{-1}\). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.26 (d, \(J = 8.3\) Hz, 1H), 7.91 (dd, \(J = 8.2, 2.3\) Hz, 1H), 7.85 – 7.82 (m, 2H), 7.51 – 7.40 (m, 3H), 7.29 – 7.24 (m, 4H), 7.18 – 7.09 (m, 6H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 150.6 (d, \(J = 8.7\) Hz), 136.2 (d, \(J = 6.1\) Hz), 135.3, 134.4 (d, \(J = 2.4\) Hz), 131.1 (d, \(J = 4.0\) Hz), 129.8, 128.7, 127.4, 126.7, 126.1, 125.8 (d, \(J = 3.8\) Hz), 125.6 (d, \(J = 1.3\) Hz), 122.3 (d, \(J = 8.8\) Hz), 120.5 (d, \(J = 5.1\) Hz). \(^{31}\)P NMR (121 MHz, CDCl\(_3\)) \(\delta\) 14.5. HRMS (ESI): \(m/z\) [M+Na]\(^+\) calcd for C\(_{22}\)H\(_{13}\)O\(_3\)N\(_2\)PS: 415.05282; found: 415.05264.

S-(Phenanthren-9-yl) O,O-diphenyl phosphorothioate (16): Procedure A was followed for the synthesis of the product 16 as a red oil (36.0 mg, 81%). IR (neat): 3065, 1590, 1486, 1272, 1183, 935, 757, 688, 617 cm\(^{-1}\). \(^1^H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.68 (dd, \(J = 12.3, 8.4\) Hz, 2H), 8.39 (d, \(J = 8.2\) Hz, 1H), 8.07 (d, \(J = 4.0\) Hz, 1H), 7.77 – 7.53 (m, 5H), 7.31 – 7.28 (m, 4H), 7.19 – 7.14 (m, 6H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 150.6 (d, \(J = 8.4\) Hz), 138.2 (d, \(J = 7.2\) Hz), 132.2 (d, \(J = 3.1\) Hz), 131.4 (d, \(J = 3.4\) Hz), 131.3, 129.9, 129.0, 128.4, 127.29, 127.25, 127.1, 125.6, 123.0, 122.8, 121.1 (d, \(J = 9.1\) Hz), 120.5 (d, \(J = 5.2\) Hz). \(^{31}\)P NMR (121 MHz, CDCl\(_3\)) \(\delta\) 14.3 (d, \(J = 1.8\) Hz). HRMS (ESI): \(m/z\) [M+Na]\(^+\) calcd for C\(_{26}\)H\(_{15}\)O\(_3\)N\(_2\)PS: 465.06847; found: 465.06824.

Methyl 4-((diphenoxophosphoryl)thio)benzoate (17): Procedure A was followed for the synthesis of the product 17 as a yellow oil (30.5 mg, 76%). IR (neat): 2922, 1724, 1589, 1484, 1277, 1180, 938, 763, 688, 610 cm\(^{-1}\). \(^1^H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (d, \(J = 8.2\) Hz, 2H), 7.56 (dd, \(J = 8.6, 1.9\) Hz, 2H), 7.35 – 7.31 (m, 4H), 7.24 – 7.17 (m, 6H), 3.91 (s, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 166.3, 150.3 (d, \(J = 8.4\) Hz), 134.8 (d, \(J = 5.8\) Hz), 131.3 (d, \(J = 7.6\) Hz), 131.1, 130.5, 130.0, 125.9, 120.6 (d, \(J = 5.1\) Hz), 52.6. \(^{31}\)P NMR (121 MHz, CDCl\(_3\)) \(\delta\) 14.9. HRMS (ESI): \(m/z\) [M+Na]\(^+\) calcd for C\(_{26}\)H\(_{15}\)O\(_3\)NaPS: 423.04265; found: 423.04166.

Ethyl 3-((diphenoxophosphoryl)thio)benzoate (18): Procedure A was followed for the synthesis of the product 18 as a yellow oil (24.0 mg, 58%). IR (neat): 1717, 1585, 1481, 1261, 1159, 931, 745, 682 cm\(^{-1}\). \(^1^H\) NMR (600 MHz, CDCl\(_3\)) \(\delta\) 8.16 (d, \(J = 1.6\) Hz, 1H), 8.07 (d, \(J = 7.7\) Hz, 1H), 7.68 (d, \(J = 7.7\) Hz, 1H), 7.43 – 7.41 (m, 1H), 7.35 (dd, \(J = 7.9, 7.9\) Hz, 4H), 7.23 – 7.21 (m, 6H), 4.38 (q, \(J = 7.2\) Hz, 2H), 1.39 (t, \(J = 7.1\) Hz, 3H). \(^{13}\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 165.5, 150.4 (d, \(J = 8.3\) Hz), 139.5 (d, \(J = 5.0\) Hz), 136.3 (d, \(J = 5.5\) Hz), 132.0, 130.8, 130.0, 129.6, 125.9 (d, \(J = 7.7\) Hz), 125.8, 120.5 (d, \(J = 5.2\) Hz), 61.5, 14.4. \(^{31}\)P NMR (243 MHz, CDCl\(_3\)) \(\delta\) 14.0. HRMS (ESI): \(m/z\) [M+Na]\(^+\) calcd for C\(_{26}\)H\(_{15}\)O\(_3\)NaPS: 437.05830; found: 437.05835.
**S-(4-Morpholinophenyl) O,O-diphenyl phosphorothioate (19):** Procedure A was followed for the synthesis of the product 19 as a red oil (33.3 mg, 77%). IR (neat): 1591, 1491, 1267, 1238, 1185, 934, 678, 689, 617 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.38 – 7.33 (m, 6H), 7.23 – 7.19 (m, 6H), 6.82 (d, J = 8.7 Hz, 2H), 3.85 (t, J = 4.8 Hz, 4H), 3.19 (t, J = 4.8 Hz, 4H). ¹³C NMR (151 MHz, CDCl₃) δ 152.2, 150.6 (d, J = 4.9 Hz), 130.0, 125.5, 120.6 (d, J = 5.0 Hz), 115.9, 112.9, 66.8, 48.4. ³¹P NMR (243 MHz, CDCl₃) δ 15.7. HRMS (ESI): m/z [M+H]⁺ calcd for C₂₃H₂₅NO₄PS: 428.10799; found: 428.10883.

**O,O-Bis(2-methylbutyl) S-phenyl phosphorothioate (20):** Procedure A was followed for the synthesis of the product 20 as a colourless oil (26.7 mg, 81%). IR (neat): 2962, 1463, 1381, 1259, 993, 862, 746, 691 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.58 – 7.56 (m, 2H), 7.33 (d, J = 6.7 Hz, 3H), 4.00 – 3.86 (m, 4H), 1.69 – 1.66 (m, 2H), 1.40 – 1.39 (m, 2H), 1.14 – 1.13 (m, 2H), 0.89 – 0.85 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 134.7 (d, J = 5.2 Hz), 129.4 (d, J = 1.8 Hz), 129.0 (d, J = 2.5 Hz), 126.7 (d, J = 7.0 Hz), 72.5 (dd, J = 7.1, 1.8 Hz), 35.5 (d, J = 7.4 Hz), 25.6 (d, J = 0.9 Hz), 16.1 (d, J = 3.0 Hz), 11.3. ³¹P NMR (243 MHz, CDCl₃) δ 22.9. HRMS (ESI): m/z [M+Na]⁺ calcd for C₁₆H₂₂O₃NaPS: 353.13107; found: 353.13208.

**O,O-Bis(2-methylbutyl) S-(o-tolyl) phosphorothioate (21):** Procedure A was followed for the synthesis of the product 21 as a colourless oil (33.4 mg, 97%). IR (neat): 2961, 1462, 1258, 993, 863, 753, 707 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.61 (d, J = 7.5 Hz, 1H), 7.26 – 7.24 (m, 2H), 7.16 – 7.14 (m, 1H), 3.98 – 3.81 (m, 4H), 2.51 (s, 3H), 1.69 – 1.66 (m, 2H), 1.40 – 1.39 (m, 2H), 1.14 – 1.12 (m, 2H), 0.89 – 0.85 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 142.3 (d, J = 5.4 Hz), 136.2, 130.9 (d, J = 2.4 Hz), 129.4 (d, J = 2.8 Hz), 126.8 (d, J = 2.5 Hz), 126.0 (d, J = 7.5 Hz), 72.5 (d, J = 7.1 Hz), 35.5 (d, J = 6.8 Hz), 25.6, 21.6, 16.1 (d, J = 5.0 Hz), 11.2. ³¹P NMR (243 MHz, CDCl₃) δ 23.1 (d, J = 2.0 Hz). HRMS (ESI): m/z [M+Na]⁺ calcd for C₁₇H₂₃O₃NaPS: 367.14672; found: 367.14767.

**O,O-Bis(2-methylbutyl) S-(p-tolyl) phosphorothioate (22):** Procedure A was followed for the synthesis of the product 22 as a colourless oil (29.5 mg, 86%). IR (neat): 2962, 1461, 1258, 993, 809 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.44 (dd, J = 8.2, 1.9 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 4.01 – 3.83 (m, 4H), 2.33 (d, J = 1.4 Hz, 3H), 1.70 – 1.66 (m, 2H), 1.40 – 1.39 (m, 2H), 1.15 – 1.14 (m, 2H), 0.89 – 0.86 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 139.3 (d, J = 3.0 Hz), 134.7 (dd, J = 5.0, 2.3 Hz), 130.2 (d, J = 2.2 Hz), 122.9 (d, J = 7.1 Hz), 72.4 (dd, J = 7.0, 2.0 Hz), 35.5 (d, J = 7.3 Hz), 25.6, 21.3, 16.1 (d, J = 3.5 Hz), 11.3. ³¹P NMR (243 MHz, CDCl₃) δ 23.3. HRMS (ESI): m/z [M+Na]⁺ calcd for C₁₇H₂₃O₃NaPS: 367.14752.
S-(3,5-Dimethylphenyl) O,O-bis(2-methylbutyl) phosphorothioate (23): Procedure A was followed for the synthesis of the product 23 as a colourless oil (32.9 mg, 92%). IR (neat): 2961, 1461, 1258, 993, 848, 791, 685 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 7.18 (s, 2H), 6.96 (s, 1H), 4.01 – 3.85 (m, 4H), 2.28 (s, 6H), 1.71 – 1.66 (m, 2H), 1.43 – 1.40 (m, 2H), 1.16 – 1.14 (m, 2H), 0.90 – 0.86 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 139.0 (d, J = 2.2 Hz), 132.4 (q, J = 4.8 Hz), 130.8, 125.8 (d, J = 3.0 Hz), 123.9 (d, J = 2.6 Hz), 129.0 (d, J = 7.5 Hz), 11.3. ³¹P NMR (243 MHz, CDCl₃) δ 23.3. HRMS (ESI): m/z [M+Na]⁺ calcd for C₁₉H₂₉O₂PS: 381.16237; found: 381.16245.

O,O-Bis(2-methylbutyl) S-(naphthalen-1-yl) phosphorothioate (24): Procedure A was followed for the synthesis of the product 24 as a yellow oil (36.0 mg, 95%). IR (neat): 2961, 1461, 1257, 993, 798, 771 cm⁻¹. ¹H NMR (600 MHz, CDCl₃) δ 8.54 (d, J = 8.5 Hz, 1H), 7.91 – 7.64 (m, 3H), 7.61 – 7.58 (m, 1H), 7.54 – 7.51 (m, 1H), 7.46 – 7.43 (m, 1H), 3.96 – 3.79 (m, 4H), 1.57 – 1.54 (m, 2H), 1.30 – 1.25 (m, 2H), 1.06 – 1.00 (m, 2H), 0.80 – 0.77 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 135.3 (t, J = 2.6 Hz), 134.9 (d, J = 3.7 Hz), 134.4 (d, J = 2.1 Hz), 130.3 (d, J = 3.3 Hz), 128.6, 127.2, 126.5, 126.2, 125.7 (d, J = 3.2 Hz), 123.9 (d, J = 8.3 Hz), 72.6 (d, J = 6.1 Hz), 35.4 (dd, J = 7.3, 2.1 Hz), 25.5, 16.0 (d, J = 9.1 Hz), 11.2 (d, J = 3.2 Hz). ³¹P NMR (243 MHz, CDCl₃) δ 22.7. HRMS (ESI): m/z [M+Na]⁺ calcd for C₂₀H₂₅O₂PS: 403.14672; 403.14603.

O,O-Bis((S)-2-methylbutyl) S-phenyl phosphorothioate (25): Procedure A was followed for the synthesis of the product 25 as a colourless oil (27.6 mg, 82%). ¹H NMR (300 MHz, CDCl₃) δ 7.59 – 7.55 (m, 2H), 7.34 – 7.26 (m, 3H), 4.03 – 3.82 (m, 4H), 1.73 – 1.47 (m, 2H), 1.45 – 1.36 (m, 2H), 1.16 – 1.09 (m, 2H), 0.93 – 0.84 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 134.7 (d, J = 5.2 Hz), 129.4 (d, J = 1.8 Hz), 129.0 (d, J = 2.5 Hz), 126.7 (d, J = 7.0 Hz), 72.5 (dd, J = 7.1, 1.8 Hz), 35.5 (d, J = 7.4 Hz), 25.6 (d, J = 0.9 Hz), 16.1 (d, J = 3.0 Hz), 11.3. ³¹P NMR (121 MHz, CDCl₃) δ 22.9.

O,O-Bis((S)-2-ethylbutyl) S-(p-tolyl) phosphorothioate (26): Procedure A was followed for the synthesis of the product 26 as a colourless oil (30.3 mg, 88%). ¹H NMR (300 MHz, CDCl₃) δ 7.44 (dd, J = 8.2, 2.0 Hz, 2H), 7.14 (d, J = 8.0 Hz, 2H), 4.03 – 3.81 (m, 4H), 2.33 (d, J = 1.8 Hz, 3H), 1.71 – 1.65 (m, 2H), 1.45 – 1.38 (m, 2H), 1.25 – 1.11 (m, 2H), 0.96 – 0.85 (m, 12H). ¹³C NMR (151 MHz, CDCl₃) δ 139.3 (d, J = 3.0 Hz), 134.8 (d, J = 5.1 Hz), 130.2 (d, J = 2.2 Hz), 122.9 (d, J = 7.3 Hz), 72.5 – 72.4 (m), 35.5 (d, J = 7.2 Hz), 25.6, 21.3, 16.1 (d, J = 3.3 Hz), 11.3. ³¹P NMR (121 MHz, CDCl₃) δ 23.3.
S-(3,5-Dimethylphenyl) O,O-bis([S]-2-methylbutyl) phosphorothioate (27): Procedure A was followed for the synthesis of the product 27 as a colourless oil (34.0 mg, 95%). 1H NMR (600 MHz, CDCl3) δ 7.18 (s, 2H), 6.96 (s, 1H), 4.01 – 3.86 (m, 4H), 2.28 (s, 6H), 1.71 – 1.67 (m, 2H), 1.43 – 1.40 (m, 2H), 1.16 – 1.13 (m, 2H), 0.90 – 0.86 (m, 12H). 13C NMR (151 MHz, CDCl3) δ 139.0 (d, J = 2.2 Hz), 132.4 (d, J = 7.9 Hz, 1H), 5.09 (d, J = 5.5 Hz), 129.8, 129.3 (d, J = 8.0 Hz, 1H), 0.72 (s, 3H), 0.50 (s, 3H).

(3aR,8aR)-2,2-Dimethyl-4,4,8,8-tetraphenyl-6-(phenylthio)tetrahydro-[1,3]dioxolo[4,5-e][1,3]dioxaphosphepine 6-oxide (28): Procedure A was followed for the synthesis of the product 28 as a white solid (58.9 mg, 95%). [α]D25 -200.1 (c 1.0, DCM); 99% ee as determined by HPLC (AD, 90:10 n-heptane/i-PrOH, 0.7 mL/min), tr maj = 8.0 min, tr min = 9.4 min. IR (neat): 1494, 1445, 1254, 1013, 971, 745, 696, 658 cm⁻¹. 1H NMR (600 MHz, CDCl3) δ 7.56 – 7.54 (m, 2H), 7.48 – 7.45 (m, 4H), 7.40 – 7.39 (m, 5H), 7.35 – 7.17 (m, 12H), 6.97 – 6.96 (m, 2H), 5.39 (d, J = 7.9 Hz, 1H), 5.10 (d, J = 7.9 Hz, 1H), 0.73 (s, 3H), 0.51 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 143.9 (d, J = 5.9 Hz), 143.2, 139.6 (d, J = 11.1 Hz), 139.5 (d, J = 3.6 Hz), 135.7 (d, J = 5.5 Hz), 129.8, 129.3 (d, J = 2.8 Hz), 129.2 (d, J = 3.5 Hz), 128.7, 128.5, 128.33, 128.30, 127.9, 127.82, 127.77 127.31, 127.29, 126.7, 126.1, 126.0, 114.1, 91.9 (d, J = 13.5 Hz), 88.9 (d, J = 9.9 Hz), 79.2, 79.0, 27.0, 26.6. 31P NMR (243 MHz, CDCl3) δ 15.2. HRMS (ESI): m/z [M+Na]^+ calcd for C37H35O8SNaPS: 643.16785; found: 643.16675.

(3aS,8aS)-2,2-Dimethyl-4,4,8,8-tetraphenyl-6-(phenylthio)tetrahydro-[1,3]dioxolo[4,5-e][1,3]dioxaphosphepine 6-oxide (29): Procedure A was followed for the synthesis of the product 29 as a white solid (52.7 mg, 85%). [α]D25 +168.9 (c 1.0, DCM); 99% ee as determined by HPLC (AD, 90:10 n-heptane/i-PrOH, 0.7 mL/min), tr maj = 9.4 min, tr min = 8.0 min. 1H NMR (600 MHz, CDCl3) δ 7.55 – 7.53 (m, 2H), 7.48 – 7.44 (m, 4H), 7.40 – 7.39 (m, 5H), 7.35 – 7.17 (m, 12H), 6.97 – 6.96 (m, 2H), 5.38 (d, J = 7.9 Hz, 1H), 5.09 (d, J = 7.9 Hz, 1H), 0.72 (s, 3H), 0.50 (s, 3H). 13C NMR (151 MHz, CDCl3) δ 143.9 (d, J = 5.9 Hz), 143.2, 139.7 (d, J = 11.2 Hz), 139.5 (d, J = 3.4 Hz), 135.7 (d, J = 5.4 Hz), 129.8, 129.3 (d, J = 2.5 Hz), 129.2 (d, J = 3.2 Hz), 128.7, 128.5, 128.33, 128.31, 127.9, 127.82, 127.77 127.31, 127.29, 126.7, 126.1, 126.0, 114.1, 91.9 (d, J = 13.6 Hz), 88.9 (d, J = 9.8 Hz), 79.2, 79.0, 27.0, 26.6. 31P NMR (243 MHz, CDCl3) δ 15.2.
(3aR,8aR)-2,2-Dimethyl-4,4,8,8-tetraphenyl-6-(p-tolylthio)tetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (30): Procedure A was followed for the synthesis of the product 30 as a white solid (57.7 mg, 91%). [α]Dm, c 1.0, DCM); 99% ee as determined by HPLC (AD, 90:10 n-heptane/i-PrOH, 1.0 mL/min), t<sub>maj</sub> = 5.6 min, t<sub>min</sub> = 7.5 min. IR (neat): 2924, 1493, 1447, 1254, 1008, 967, 744, 696 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.54 (dd, J = 7.8, 1.5 Hz, 2H), 7.48 – 7.44 (m, 4H), 7.44 – 7.39 (m, 3H), 7.32 – 7.18 (m, 11H), 6.99 (dd, J = 6.8, 5.3 Hz, 4H), 5.38 (d, J = 7.9 Hz, 1H), 5.09 (d, J = 7.9 Hz, 1H), 5.09 (d, J = 7.9 Hz, 1H), 2.87 (s, 3H), 0.72 (s, 3H), 0.51 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.0 (d, J = 5.8 Hz), 143.2, 139.7 (d, J = 11.1 Hz), 139.6 (d, J = 3.5 Hz), 139.4 (d, J = 3.5 Hz), 135.6 (d, J = 5.2 Hz), 130.03, 130.01, 129.8, 128.7, 128.4, 128.30, 128.28, 127.8, 127.7, 127.27, 127.25, 126.7, 122.43, 122.38, 114.1, 91.8 (d, J = 13.6 Hz), 88.8 (d, J = 10.0 Hz), 79.2, 79.1, 27.0, 26.6, 21.4. <sup>31</sup>P NMR (243 MHz, CDCl<sub>3</sub>) δ 15.5. HRMS (ESI): m/z [M+Na]<sup>+</sup> calcd for C<sub>38</sub>H<sub>35</sub>O<sub>3</sub>NaPS: 657.18350; found: 657.18213.

(3aS,8aS)-2,2-Dimethyl-4,4,8,8-tetraphenyl-6-(p-tolylthio)tetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (31): Procedure A was followed for the synthesis of the product 31 as a white solid (53.3 mg, 84%). [α]D<sup>25</sup> +179.2 (c 1.0, DCM); 99% ee as determined by HPLC (AD, 90:10 n-heptane/i-PrOH, 1.0 mL/min), t<sub>maj</sub> = 7.5 min, t<sub>min</sub> = 5.6 min. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.54 (dd, J = 7.8, 1.5 Hz, 2H), 7.48 – 7.43 (m, 4H), 7.40 – 7.39 (m, 3H), 7.30 – 7.17 (m, 11H), 6.99 – 6.97 (m, 4H), 5.37 (d, J = 7.9 Hz, 1H), 5.08 (d, J = 7.9 Hz, 1H), 2.36 (d, J = 1.8 Hz, 1H), 0.71 (s, 3H), 0.50 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.0 (d, J = 5.9 Hz), 143.3, 139.7 (d, J = 11.1 Hz), 139.6 (d, J = 3.5 Hz), 139.5 (d, J = 3.6 Hz), 135.6 (d, J = 5.3 Hz), 130.05, 130.03, 129.8, 128.7, 128.4, 128.33, 128.29, 127.9, 127.8, 127.29, 127.26, 122.5, 122.4, 114.1, 91.8 (d, J = 13.6 Hz), 88.8 (d, J = 10.0 Hz), 79.2, 79.1, 27.0, 26.6, 21.4. <sup>31</sup>P NMR (243 MHz, CDCl<sub>3</sub>) δ 15.5.

(3aR,8aR)-6-(4-Butylphenyl)thio)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (32): Procedure A was followed for the synthesis of the product 32 as a white solid (57.5 mg, 85%). [α]D<sup>25</sup> -173.0 (c 1.0, DCM); 99% ee as determined by HPLC (AD, 95:5 n-heptane/i-PrOH, 1.0 mL/min), t<sub>maj</sub> = 8.0 min, t<sub>min</sub> = 12.3 min. IR (neat): 2927, 1492, 1448, 1255, 992, 924, 743, 695 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.56 – 7.54 (m, 2H), 7.46 – 7.38 (m, 7H), 7.31 – 7.18 (m, 11H), 7.00 (dd, J = 14.3, 7.8 Hz, 4H), 5.39 (d, J = 7.9 Hz, 1H), 5.08 (d, J = 7.9 Hz, 1H), 2.61 (t, J = 7.6 Hz, 2H), 1.62 – 1.58 (m, 2H), 1.39 – 1.38 (m, 2H), 0.96 (t, J = 7.3 Hz, 3H), 0.72 (s, 3H), 0.51 (s, 3H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 144.4 (d, J = 3.5 Hz), 144.0 (d, J = 5.9 Hz), 143.3, 139.7 (d, J = 11.0 Hz), 139.6 (d, J = 3.4 Hz), 135.7 (d, J = 5.3 Hz), 129.8, 129.35, 129.33, 128.7, 128.4, 128.3, 127.9, 127.8, 127.3, 127.2, 126.7, 122.44,
(3a5,8a5)-6-[(4-Butylphenyl)thio]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (33): Procedure A was followed
for the synthesis of the product 33 as a white solid (60.1 mg, 89%). \([\alpha]_D^{25} +152.8\) (c
1.0, DCM); 99% ee as determined by HPLC (AD, 95:5 n-heptane/\(i\)-PrOH, 1.0 mL/min),
\(t_{maj} = 12.3\) min, \(t_{min} = 8.0\) min. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.66 – 7.56 (m, 2H), 7.47 – 7.46 (m, 4H), 7.40 – 7.39 (m,
3H), 7.31 – 7.18 (m, 11H), 7.00 (dd, \(J = 15.0, 7.8\) Hz, 4H), 5.39 (d, \(J = 7.9\) Hz, 1H), 5.08 (d, \(J = 7.9\)
Hz, 1H), 2.62 (t, \(J = 7.6\) Hz, 2H), 1.64 – 1.58 (m, 2H), 1.40 – 1.35 (m, 2H), 0.97 (t, \(J = 7.3\)
Hz, 3H), 0.73 (s, 3H), 0.51 (s, 3H). \(^1^3\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 144.4 (d, \(J = 3.5\)
Hz), 144.0 (d, \(J = 5.9\) Hz), 143.3, 139.7 (d, \(J = 11.0\) Hz), 139.6 (d, \(J = 3.2\) Hz), 135.7 (d, \(J =
5.3\) Hz), 129.8, 129.34, 129.33, 128.7, 128.4, 128.3, 127.82, 127.75, 127.3, 127.2,
126.7, 122.5, 122.4, 114.0, 91.8 (d, \(J = 13.7\) Hz), 88.7 (d, \(J = 9.9\) Hz), 79.2, 79.1, 35.5, 33.6,
27.0, 26.6, 22.4, 14.1. \(^3^1^P\) NMR (243 MHz, CDCl\(_3\)) \(\delta\) 15.7.

(3aR,8aR)-6-[(1,1',Biphenyl]-4-ylthio]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (34): Procedure A was followed
for the synthesis of the product 34 as a white solid (61.9 mg, 89%). \([\alpha]_D^{25} -131.4\)
(c 1.0, DCM); 99% ee as determined by HPLC (AD, 95:5 n-heptane/\(i\)-PrOH, 1.0 mL/min),
\(t_{maj} = 13.6\) min, \(t_{min} = 19.2\) min. IR (neat): 1484, 1448, 1255, 982, 914, 731, 697 cm\(^{-1}\).
\(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.60 – 7.40 (m, 18H), 7.32 – 7.16 (m, 9H), 7.01 – 6.93 (m, 2H),
5.41 (d, \(J = 7.9\) Hz, 1H), 5.14 (d, \(J = 7.9\) Hz, 1H), 0.72 (s, 3H), 0.52 (s, 3H). \(^1^3\)C NMR (151
MHz, CDCl\(_3\)) \(\delta\) 144.0 (d, \(J = 5.8\) Hz), 143.2, 142.2 (d, \(J = 3.5\) Hz), 140.1, 139.7, 139.5
(d, \(J = 3.7\) Hz), 136.0 (d, \(J = 5.4\) Hz), 129.8, 129.1, 128.7, 128.5, 128.39, 128.37 128.3,
128.0, 127.9, 127.88, 127.86, 127.8, 127.3, 127.2, 126.8, 124.93, 124.87, 114.1, 92.0 (d,
\(J = 13.6\) Hz), 88.9 (d, \(J = 9.9\) Hz), 79.2, 79.1, 27.0, 26.6. \(^3^1^P\) NMR (243 MHz, CDCl\(_3\)) \(\delta\)
15.1. HRMS (ESI): \(m/z\) [M+Na]\(^+\) calcd for C\(_{44}H\(_{37}\)O\(_3\)N\(_2\)PS: 719.19915; found: 719.19867.

(3a5,8a5)-6-[(1,1',Biphenyl]-4-ylthio]-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (35): Procedure A was followed
for the synthesis of the product 35 as a white solid (57.4 mg, 82%). \([\alpha]_D^{25} +140.3\)
(c 1.0, DCM); 99% ee as determined by HPLC (AD, 95:5 n-heptane/\(i\)-PrOH, 1.0 mL/min),
\(t_{maj} = 19.2\) min, \(t_{min} = 13.6\) min. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\) 7.61 – 7.41 (m, 18H), 7.32 – 7.17 (m, 9H),
7.02 (d, \(J = 7.6\) Hz, 2H), 5.42 (d, \(J = 7.9\) Hz, 1H), 5.15 (d, \(J = 7.9\) Hz, 1H), 0.73 (s, 3H), 0.53 (s, 3H). \(^1^3\)C NMR (151 MHz, CDCl\(_3\)) \(\delta\) 144.0 (d, \(J = 5.7\) Hz), 143.2, 142.2.
(3aR,8aR)-6-((3,5-Dimethylphenyl)thio)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (36): Procedure A was followed for
the synthesis of the product 36 as a white solid (60.9 mg, 94%). [a]D25° -198.6 (c 1.0,
DCM); 99% ee as determined by HPLC (AD, 97:3 n-heptane/i-PrOH, 0.7 mL/min), t_rmaj =
13.9 min, t_rmin = 16.2 min. IR (neat): 1495, 1257, 993, 948, 735, 696, 662 cm⁻¹. 1H NMR
(600 MHz, CDCl₃) δ 7.66 – 7.54 (m, 2H), 7.48 – 7.47 (m, 4H), 7.37 – 7.17 (m, 12H), 7.08 (s, 2H), 7.01 – 6.98 (m, 3H), 5.42 (d, J = 8.0 Hz, 1H),
5.08 (d, J = 7.9 Hz, 1H), 2.18 (s, 6H), 0.75 (s, 3H), 0.52 (s, 3H). 13C NMR (151 MHz, CDCl₃) δ 144.1 (d, J = 6.1 Hz),
143.4, 139.8, 139.7 (d, J = 3.4 Hz), 139.0 (d, J = 2.8 Hz), 133.0 (d, J = 5.6 Hz), 131.01, 130.99, 129.7, 128.7, 128.3,
127.82, 127.76, 127.6, 127.32, 127.30, 126.8, 125.44, 125.39, 113.9, 91.5 (d, J = 13.2 Hz), 88.7 (d, J = 9.8 Hz), 79.5,
79.3, 27.0, 26.6, 21.3. 31P NMR (243 MHz, CDCl₃) δ 15.4. HRMS (ESI): m/z [M+Na]+ calcd for C₉₈H₇₇O₆S₇P:
671.19915; found: 671.19800.

(3aS,8aS)-6-((3,5-Dimethylphenyl)thio)-2,2-dimethyl-4,4,8,8-tetraphenyltetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (37): Procedure A was followed for
the synthesis of the product 37 as a white solid (61.6 mg, 95%). [a]D25° +184.5 (c 1.0,
DCM); 99% ee as determined by HPLC (AD, 97:3 n-heptane/i-PrOH, 0.7 mL/min), t_rmaj = 16.2 min, t_rmin = 13.9 min.
1H NMR (600 MHz, CDCl₃) δ 7.56 – 7.54 (m, 2H), 7.48 – 7.46 (m, 4H), 7.37 – 7.27 (m, 12H), 7.07 – 6.98 (m, 5H), 5.41
(d, J = 7.9 Hz, 1H), 5.08 (d, J = 8.0 Hz, 1H), 2.18 (s, 6H), 0.75 (s, 3H), 0.52 (s, 3H). 13C NMR (151 MHz, CDCl₃) δ 144.1
(d, J = 6.1 Hz), 143.4, 139.8, 139.7 (d, J = 3.4 Hz), 139.0 (d, J = 2.7 Hz), 133.0 (d, J = 5.5 Hz), 131.01, 130.99, 129.7,
128.7, 128.3, 127.81, 127.75, 127.6, 127.32, 127.30, 126.8, 125.44, 125.39, 113.9, 91.5 (d, J = 13.6 Hz), 88.7 (d, J =
9.8 Hz), 79.5, 79.3, 27.0, 26.6, 21.3. 31P NMR (243 MHz, CDCl₃) δ 15.4.

(3aR,8aR)-2,2-Dimethyl-6-(naphthalen-1-ylthio)-4,4,8,8-tetraphenyltetrahydro-
[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (38): Procedure A was followed for
the synthesis of the product 38 as a white solid (57.9 mg, 86%). [a]D25° -254.2 (c 1.0, DCM);
99% ee as determined by HPLC (AD, 97:3 n-heptane/i-PrOH, 0.7 mL/min), t_rmaj = 22.9 min,
t_rmin = 28.2 min. IR (neat): 1595, 1448, 1259, 995, 949, 853, 737, 695 cm⁻¹. 1H NMR (600 MHz, CDCl₃) δ 8.62 (d, J =
7.9 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.39 – 7.24 (m, 18H), 7.06 – 7.03 (m, 2H), 6.92 (t, J = 7.8 Hz, 2H), 6.51 (d, J = 7.6 Hz, 2H), 5.37 (d, J = 7.9 Hz, 1H), 4.87 (d, J = 7.9 Hz, 1H), 0.71 (s, 3H), 0.42 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 144.0 (d, J = 6.7 Hz), 143.3, 139.6, 139.2 (d, J = 11.1 Hz), 136.1 (d, J = 6.0 Hz), 135.18, 135.12, 134.3, 130.28, 130.26, 130.0, 128.4, 128.27, 128.25, 127.9, 127.8, 127.4, 127.3, 127.0, 126.7, 126.5, 125.7, 125.8, 125.7, 123.3, 123.2, 114.0, 92.3 (d, J = 14.1 Hz), 88.6 (d, J = 9.8 Hz), 79.1, 78.9, 27.0, 26.5. $^{31}$P NMR (243 MHz, CDCl$_3$) $\delta$ 16.3. HRMS (ESI): m/z [M+Na]$^+$ calcld for $\text{C}_{41}$H$_{35}$O$_5$NaPS: 693.18350; found: 693.18262.

(3aS,8aS)-2,2-Dimethyl-6-(naphthalen-1-ylthio)-4,4,8,8-tetraphenyltetrahydro-[1,3]dioxolo[4,5-e][1,3,2]dioxaphosphepine 6-oxide (39): Procedure A was followed for the synthesis of the product 39 as a white solid (63.0 mg, 94%). $\left[\alpha\right]_D^{25}$ +252.1 (c 1.0, DCM); 99% ee as determined by HPLC (AD, 97:3 $n$-heptane/$i$-PrOH, 0.7 mL/min), $t$ maj = 28.2 min, $t$ min = 22.9 min. $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 8.62 (d, J = 7.9 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.51 – 7.25 (m, 18H), 7.08 – 7.04 (m, 2H), 6.92 (t, J = 7.8 Hz, 2H), 6.52 – 6.50 (m, 2H), 5.37 (d, J = 7.9 Hz, 1H), 4.87 (d, J = 7.9 Hz, 1H), 0.71 (s, 3H), 0.42 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 144.0 (d, J = 6.7 Hz), 143.3, 139.6, 139.2 (d, J = 11.1 Hz), 136.1 (d, J = 6.0 Hz), 135.18, 135.12, 134.3, 130.28, 130.26, 130.0, 128.4, 128.27, 128.25, 127.9, 127.8, 127.4, 127.3, 127.0, 126.7, 126.5, 125.8, 125.7, 123.3, 123.2, 114.0, 92.3 (d, J = 14.3 Hz), 88.6 (d, J = 9.7 Hz), 79.1, 78.9, 27.0, 26.5. $^{31}$P NMR (243 MHz, CDCl$_3$) $\delta$ 16.3.
4. X-Ray Structure of Compound 30

Figure S2. Crystal structure of compound 30. Thermal ellipsoids drawn at 50% probability.
Table S1. Crystal data and structure refinement for compound 30.

| Compound | 30 |
|----------|----|
| CCDC     | 1911726 |
| Formula  | C_{38}H_{35}O_{5}PS |
| Formula Weight | 634.69 |
| Colour   | colourless |
| Shape    | prism |
| Size/mm^3 | 0.70×0.29×0.17 |
| Temperature/K | 296(2) |
| Crystal System | orthorhombic |
| Space Group | P2_{1}2_{1}2_{1} |
| Flack Parameter | -0.01(3) |
| Hooft Parameter | -0.01(3) |
| a/Å     | 11.5259(9) |
| b/Å     | 31.459(2) |
| c/Å     | 9.3490(6) |
| α°      | 90 |
| β°      | 90 |
| γ°      | 90 |
| V/Å^3   | 3389.9(4) |
| Z       | 4 |
| Z'      | 1 |
| \(\rho_{calc}/g\ cm^{-3}\) | 1.244 |
| \(\mu/\text{mm}^{-1}\) | 0.184 |
| Radiation type | MoK\(\alpha\) |
| Wavelength/Å | 0.71073 |
| \(\theta_{min}/\text{°}\) | 1.882 |
| \(\theta_{max}/\text{°}\) | 35.668 |
| Measured Refl. | 61637 |
| Independent Refl. | 15602 |
| Reflections with I > 2(I) | 9211 |
| \(R_{int}\) | 0.0588 |
| Parameters | 409 |
| Restraints | 0 |
| Largest Peak/eÅ^{-3} | 0.379 |
| Largest Hole/eÅ^{-3} | -0.325 |
| Goof on F^2 | 1.009 |
| \(wR_2\) (all data) | 0.1269 |
| \(wR_2\) | 0.1058 |
| \(R_1\) (all data) | 0.1009 |
| \(R_1\) | 0.0483 |
5. NMR Spectra
6. HPLC Data

Sample Name: Chen mi rac
Data file: E:\CHN\CHN\M1R2AD.D
Sample Info: Mobile phase: n-Heptan/iPrOH 9:1;
The sample is solved in MP

Method file: AD.M
Column-info: Chiralpak AD (250x4.6)mm
Operator: Analytical Lab 4.03 - 4.04

Injection Time: 09:53:30
Injection Date: 16.01.2019

Instrument Conditions: At Start At Stop
Temperature in °C: 30.0 30.0
Pressure in bar: 21.0 21.0
Flow in ml/min: 0.70 0.70
Sample Name: Chen m2 rac
Data file: E:\GONZO\CHEN\M2R1AD.D
Sample Info: Mobile phase: n-Heptan/iPrOH 9:1;
The sample is solved in MP
Method file: AD.M
Column-info: Chiralpak AD (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04
Injection Time: 16:15:22
Injection Date: 15.01.2019
Instrument Conditions: At Start At Stop
Temperature in °C: 30.0 30.0
Pressure in bar: 28.9 29.5
Flow in ml/min: 1.00 1.00
Sample Name: Chen m3 mix
Data file: D:\GONIO\CHEN\M3R1AD,D
Sample Info: Mobile phase: n-Heptan/iPrOH 95:5;
The sample is solved in MP

Method file: AD.M
Column-info: Chiralpak AD (250x4.6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 14:38:21
Injektion Date: 22.01.2019

Instrument Conditions: At Start At Stop
Temperature in °C: 30.0 30.0
Pressure in bar: 28.3 29.1
Flow in ml/min: 1.00 1.00

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DAD1 D. Sig=250.16 Ref=360,100 (CHENM0R1AD,D)

DAD1 D. Sig=250.16 Ref=360,100 (CHENR33AD,D)

DAD1 D. Sig=250.16 Ref=360,100 (CHENN33AD,D)

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(R)-32 + (S)-33

(R)-32

(S)-33

---

- S104 -
Sample Name: Chen R6
Data file: D:\GQN020\CHEN\R6XAD.D
Sample Info: Mobile phase: n-Heptan/PrOH 97:3; The sample is solved in MP

Method file: AD.M
Column-info: Chiraipak AD (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04

Injektion Time: 14:15:41
Injektion Date: 21.01.2019

Instrument Conditions: At Start At Stop
Temperature in °C: 30.0 30.0
Pressure in bar: 19.8 20.0
Flow in ml/min: 0.70 0.70

### Retention Time Table

| # | Ret. Time (min) | Width (mAU) | Height (mAU) | Area (mAU*s) | Area % |
|---|-----------------|-------------|-------------|--------------|--------|
| 1 | 4.84 | 0.20 | 13.94 | 202.08 | 2.53 |
| 2 | 6.24 | 0.29 | 16.84 | 48.12 | 0.60 |
| 3 | 16.00 | 0.70 | 166.26 | 7742.07 | 96.87 |

Total 7992.27 100.00
Sample Name: Chen R7
Data file: D:\GQNZQ\CHEN\R7XAD.D
Sample Info: Mobile phase: n-Heptan/IPrOH 97:3;
The sample is solved in MP
Method file: AD.M
Column info: Chiralpak AD (250x4,6)mm
Operator: Analytical Lab 4.03 - 4.04
Injektion Time: 12:02:09
Injektion Date: 22.01.2019
Instrument Conditions: At Start At Stop
Temperature in °C: 30.0 30.0
Pressure in bar: 20.3 20.5
Flow in ml/min: 0.70 0.70

|    | Ret. Time | Width | Height | Area     | Area %  |
|----|-----------|-------|--------|----------|---------|
| #  | (min)     | (mAU) | (mAU)  | (mAU*e)  |         |
| 1  | 28.22     | 1.34  | 377.31 | 33373.79 | 100.00  |
|    |           |       |        |          |         |
Total | 33373.79 |       |        |          | 100.00  |
7. Computational Results

Computational methodology

All calculations were performed with the Gaussian 09 program package (revision D.01).\(^6\) Gas phase structural optimizations and frequency calculations were performed with B3LYP-D3 along with 6-31G(d) basis set on C, H, O, and P atoms, and the effective core potential (ECP) SDD on Pd, I and Fe. D3 corrections were applied using the original D3 damping functions proposed by Grimme and co-workers.\(^7\) Single point energy calculations were performed using M06L with basis set def2TZVP. Solvation energies of toluene were described using the SMD solvation model. Frequency calculations were performed to confirm whether the structure is a minimum or a transition state. Intrinsic reaction coordinate (IRC) analysis was used to confirm that the obtained transition states connected the corresponding reactants and products. Reported Gibbs free energies were determined by summing single-point electronic energies and Gibbs free energy corrections and converted to 1M standard state (by adding 1.89 kcal/mol to every species).

Free energy profiles

![Figure S3. Free energy profile of coupling of PhI with [SP(O)(OPh)]\(_2\) under Pd\(^0\)/Pd\(^{II}\) catalysis using dppf as ligand. The data were calculated at SMD (Toluene) M06L/def2-TZVP//B3LYP-D3/6-31G(d,p), SDD for I, Fe and Pd. Note: 1,5-Cyclooctadiene (cod) was used as an olefinic ligand to model dibenzylideneacetone (dba) present in the experimentally employed Pd-precursor Pd\(_2\)dba\(_3\). This was to overcome the challenge of adequately modeling the multitude of possible conformations of dba upon coordination at Pd.](image)
Figure S4. Free energy profile of reductive elimination of Ph-SPh from Pd(II) using dppf as ligand (cod = 1,5-cyclooctadiene). The data were calculated at SMD (Toluene) M06L/def2-TZVP//B3LYP-D3/6-31G(d,p), SDD for I, Fe and Pd.

Figure S5. Free energy profile of coupling of PhI with [SP(O)(OPh)2] under Pd0/PdII catalysis using PPh3 as ligand. The data were calculated at SMD (Toluene) M06L/def2-TZVP//B3LYP-D3/6-31G(d,p), SDD for I and Pd.
Figure S6. Free energy profile of coupling of PhI with [SP(O)(OPh)$_2$]$_2$ under Pd dimer catalysis. The data were calculated at SMD (Toluene) M06L/def2-TZVP//B3LYP-D3/6-31G(d,p), SDD for I and Pd.
Structures and energies

$\text{(dpf)Pd(cod)}$

|   | C     | H     |
|---|-------|-------|
| P | 1.82606 | -0.44621 | -0.19459 |
| C | 2.78014 | 0.17829 | 1.26446 |
| C | 2.15326 | 1.08949 | 2.12792 |
| H | 1.14991 | 1.43519 | 1.89259 |
| C | 2.81278 | 1.56713 | 3.26161 |
| H | 2.31390 | 2.27464 | 3.91799 |
| C | 4.11489 | 1.14695 | 3.54018 |
| H | 4.63330 | 1.52244 | 4.41790 |
| C | 4.75407 | 0.25115 | 2.67899 |
| H | 5.77096 | -0.07098 | 2.88572 |
| C | 4.09192 | -0.23023 | 1.54835 |
| H | 4.59959 | -0.92080 | 0.88166 |
| C | 3.14528 | -0.69837 | -1.46385 |
| C | 3.87733 | -1.88890 | -1.59189 |
| H | 3.66983 | -2.72488 | -0.93077 |
| C | 4.86970 | -2.00665 | -2.56733 |
| H | 5.42843 | -2.93421 | -2.65798 |
| C | 5.14375 | -0.93789 | -3.42331 |
| H | 5.91566 | -1.03183 | -4.18197 |
| C | 4.41597 | 0.24885 | -3.30636 |
| H | 4.61853 | 1.08089 | -3.97510 |
| C | 3.41803 | 0.36482 | -2.33863 |
| H | 2.83428 | 1.27639 | -2.25846 |
| P | -1.93308 | -0.28691 | -1.32852 |
| C | -3.46117 | 0.63997 | 0.33104 |
| C | -3.97613 | 0.66479 | 1.63369 |
| H | -3.51688 | 0.06039 | 2.40963 |
| C | -5.08035 | 1.46491 | 1.94252 |
| H | -5.46856 | 1.47485 | 2.95739 |
| C | -5.68577 | 2.24181 | 0.95492 |
| H | -6.54389 | 2.86221 | 1.19697 |
| C | -5.18048 | 2.21940 | -0.34925 |
| H | -5.64460 | 2.82298 | -1.12431 |
| C | -4.07426 | 1.43063 | -0.65641 |
| H | -3.67504 | 1.43020 | -1.66749 |
| C | -2.57425 | -1.38884 | -1.46930 |
| C | -1.78749 | -1.58638 | -2.61360 |
| H | -0.83637 | -1.06583 | -2.69665 |
| C | -2.22204 | -2.43218 | -3.63697 |
| H | -1.60209 | -2.57691 | -4.51728 |
| C | -3.45357 | -3.08102 | -3.53106 |
| H | -3.79420 | -3.73715 | -4.32705 |
| C | -4.25541 | -2.87268 | -2.40489 |
| H | -5.22129 | -3.36393 | -2.32590 |
| C | -3.82133 | -2.02771 | -1.38311 |
| H | -4.45633 | -1.85372 | -0.51907 |
| Fe | -0.14286 | -2.73783 | 1.44253 |
| C | 1.49527 | -2.17359 | 0.32253 |
| C | 1.92201 | -2.86646 | 1.50480 |
| H | 2.52988 | -2.44206 | 2.29081 |
| C | 1.35605 | -4.17546 | 1.48846 |
| H | 1.45705 | -4.91906 | 2.26766 |
| C | 0.58376 | -4.03060 | 0.29537 |
| H | -0.00498 | -5.16972 | 0.00961 |

Thermal correction to Gibbs free energy = 0.623049
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -3699.44782314

cod =

|   | C     | H     |
|---|-------|-------|
| C | 0.66241 | -3.07915 | -0.41963 |
| H | 0.14888 | -2.84957 | -1.34153 |
| C | -1.72552 | -1.43018 | 1.27929 |
| C | -0.91509 | -1.10310 | 2.42190 |
| H | -0.37129 | -0.17977 | 2.55487 |
| C | -0.90713 | -2.22058 | 3.30480 |
| H | -0.35033 | -2.29333 | 4.22905 |
| C | -1.70211 | -3.25082 | 2.71791 |
| H | -1.85201 | -4.24440 | 3.11877 |
| C | -2.20897 | -2.76756 | 1.47596 |
| H | -2.80708 | -3.32769 | 0.77212 |
| Pd | -0.01034 | 0.92546 | -0.68121 |
| C | 0.72462 | 2.91467 | -1.38110 |
| C | -0.65913 | 2.99232 | -1.15081 |
| H | 1.02842 | 2.76055 | -2.41890 |
| C | 1.78475 | 3.59314 | -0.53089 |
| H | -1.31015 | 2.91218 | -2.02304 |
| C | -1.29304 | 3.72067 | 0.02123 |
| H | 2.76314 | 3.16990 | -0.78663 |
| H | 1.63587 | 3.38173 | 0.53129 |
| C | 1.81425 | 5.14450 | -0.73535 |
| H | -2.32739 | 3.38030 | 0.12491 |
| H | -0.78617 | 3.46587 | 0.95810 |
| C | -1.26932 | 5.27537 | -0.15736 |
| H | 2.85330 | 5.48308 | -0.81371 |
| H | 1.33670 | 5.37799 | -1.69485 |
| C | 1.13857 | 5.91029 | 0.38171 |
| H | -0.17622 | 5.96459 | 0.62795 |
| H | -1.16157 | 5.49871 | -1.22771 |
| H | -2.23647 | 5.68991 | 0.14819 |
| H | 1.80144 | 6.43733 | 1.06770 |
| H | -0.50138 | 6.53309 | 1.49910 |

Thermal correction to Gibbs free energy = 0.623049
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -3699.44782314

cod =

- S114 -
Ph\textsuperscript{-1}l

\[
\begin{bmatrix}
    [\text{dpfPd}]- \\
    \text{Ph}
\end{bmatrix}^\dagger
\]

\begin{align*}
\text{I} & : -1.88004 -2.84660 -1.29631 \\
Pd & : -0.32833 -0.90423 0.47019 \\
C & : -1.91433 -2.09189 1.07760 \\
C & : -1.05584 -2.86923 1.88847 \\
H & : -0.22751 -3.42329 1.46099 \\
H & : -1.37156 -3.01078 3.25606 \\
C & : -0.71352 -3.59716 3.89244 \\
C & : -2.54646 -2.47401 3.76465 \\
H & : -2.79918 -2.60930 4.81215 \\
C & : -3.44215 -1.80210 2.90902 \\
C & : -4.57005 -1.39749 3.30510 \\
C & : -3.15286 -1.62949 1.56346 \\
P & : -1.36036 1.17272 -0.07986 \\
C & : -0.94999 2.58753 1.02775 \\
C & : -0.05578 2.36632 2.08537 \\
H & : 0.33669 1.38697 2.25284 \\
C & : 0.34274 3.41776 2.91404 \\
H & : 1.04714 3.22684 3.71867 \\
C & : -0.16420 4.70122 2.70436 \\
H & : 0.14337 5.52144 3.34683 \\
C & : -1.08272 4.92667 1.67407 \\
H & : -0.49438 5.92020 1.51980 \\
C & : -1.47689 3.87686 0.84410 \\
H & : -2.20811 4.05468 0.06127 \\
C & : -3.18561 1.26441 -0.24629 \\
C & : -3.79842 0.72068 -1.38766 \\
H & : -3.18966 0.37524 -2.21699 \\
C & : -5.18660 0.60447 -1.45658 \\
H & : -5.64525 0.18208 -2.34593 \\
C & : -5.98322 1.02132 -0.38687 \\
H & : -7.06377 0.92600 -0.44127 \\
C & : -5.38190 1.55831 0.75353 \\
H & : -5.99334 1.88416 1.59052 \\
C & : -3.99338 1.67528 0.82734 \\
H & : -3.53773 2.08373 1.72388 \\
P & : 1.98063 -0.41855 0.24683 \\
C & : 2.79343 -0.01706 1.85591 \\
C & : 3.90749 0.82769 1.97852 \\
H & : 4.34150 1.28157 1.09067 \\
C & : 4.45059 1.10770 3.23095 \\
C & : 5.31105 1.76629 3.31020 \\
C & : 3.88833 0.54855 4.38072 \\
H & : 4.30955 0.77197 5.35682 \\
C & : 2.77915 -0.29344 4.27156 \\
H & : 2.32300 -0.72634 5.16192 \\
C & : 2.23235 -0.57139 3.01826 \\
H & : 1.35305 -1.20611 2.93698 \\
C & : 3.01128 -1.77680 -0.46047 \\
C & : 2.36112 -2.82269 -1.13077 \\
H & : 1.27631 -2.83173 -1.19369 \\
C & : 3.10143 -3.85510 -1.71291 \\
C & : 2.58562 -4.65952 -2.22935 \\
C & : 4.49363 -3.85465 -1.62231 \\
C & : 5.06941 -4.66029 -2.06912 \\
C & : 5.14802 -2.81757 -0.94984 \\
H & : 6.23177 -2.81669 -0.87331 \\
C & : 4.41240 -1.78212 -0.37510 \\
H & : 4.92841 -0.98178 0.14633 \\
Fe & : 1.23895 1.93285 -2.17711 \\
C & : -0.75812 1.69598 -1.72387 \\
C & : -0.52324 3.05001 -2.62856 \\
C & : -0.67243 3.94020 -1.74660 \\
C & : 0.01177 2.85657 -3.57785 \\
C & : 0.36323 3.66242 -4.22278 \\
C & : 0.11288 1.46147 -3.86203 \\
C & : 0.52303 1.02340 -4.76166 \\
C & : 0.35492 0.74479 -2.72557 \\
C & : -0.37624 -0.32900 -2.60073 \\
C & : 2.49000 0.99145 -0.80983 \\
C & : 2.34281 2.38750 -0.49924 \\
C & : 1.92616 2.78941 0.41228 \\
C & : 2.81857 3.14415 -1.60967 \\
C & : 2.80774 4.22271 -1.68966 \\
C & : 3.24340 2.22993 -2.61991 \\
C & : 3.61344 2.49168 -3.60195 \\
C & : 3.04270 0.90629 -2.12984 \\
C & : 3.24397 -0.01191 -2.66305 \\
C & : -3.83293 -1.10186 0.90697 \\
\end{align*}

Thermal correction to Gibbs free energy = 0.148656
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -312.094709137

\[
\begin{align*}
\text{I} & : 529.57427252 \\
\text{dpfPd} & : 532.083583 \\
\text{Ph} & : 529.57427252
\end{align*}
\]
|    | C    | H    | C    | H    |
|----|------|------|------|------|
| C  | -3.77242 | -3.18110 | 1.39066 |
| H  | -4.12792 | -3.47800 | 2.37474 |
| C  | -4.51995 | -3.48890 | 0.25282 |
| H  | -5.46361 | -4.01974 | 0.34415 |
| C  | -4.04145 | -3.11451 | -1.00501 |
| H  | -4.61313 | -3.35233 | -1.89862 |
| C  | -2.83012 | -2.42786 | -1.12369 |
| P  | -1.64977 | 0.84209 | -0.05967 |
| C  | -1.69152 | 1.66867 | 1.58139 |
| C  | -0.84567 | 1.21044 | 2.60171 |
| H  | -0.20101 | 0.35619 | 2.42480 |
| C  | -0.81857 | 1.85269 | 3.84135 |
| H  | -0.15092 | 1.48950 | 4.61705 |
| C  | -1.64683 | 2.95142 | 4.07608 |
| H  | -1.62736 | 3.45259 | 5.03949 |
| C  | -2.51531 | 3.39630 | 3.07445 |
| H  | -3.17565 | 4.23834 | 3.26079 |
| C  | -2.54438 | 2.75491 | 1.83628 |
| H  | -3.24315 | 3.08500 | 1.07368 |
| C  | -3.42448 | 0.70749 | -0.51053 |
| C  | -3.85068 | 0.97058 | -1.81968 |
| H  | -3.14520 | 1.32794 | -2.56268 |
| C  | -5.18508 | 0.76990 | -2.17687 |
| H  | -5.50582 | 0.97819 | -3.19357 |
| H  | -6.10101 | 0.30209 | -1.23412 |
| H  | -7.17315 | 0.13846 | -1.51589 |
| C  | -5.68090 | 0.03994 | 0.07200 |
| H  | -6.38477 | -0.33678 | 0.80774 |
| C  | -4.35157 | 0.24299 | 0.43441 |
| H  | -4.02916 | 0.01138 | 1.44318 |
| P  | 1.87904 | 0.00433 | 0.11691 |
| C  | 2.57122 | -0.19858 | 1.81594 |
| C  | 3.49273 | 0.71706 | 2.35159 |
| H  | 3.83019 | 1.55946 | 1.75657 |
| C  | 3.97055 | 0.56235 | 3.65333 |
| H  | 4.68318 | 1.27841 | 4.05291 |
| C  | 5.33098 | -0.50488 | 4.43957 |
| H  | 3.90000 | -0.62195 | 5.45459 |
| C  | 2.61683 | -1.42050 | 3.91506 |
| H  | 2.27306 | -2.25674 | 4.51691 |
| C  | 2.13829 | -1.27159 | 2.61216 |
| H  | 1.44082 | -1.99812 | 2.20918 |
| C  | 3.15237 | -0.62528 | -1.04885 |
| C  | 2.73000 | -1.02856 | -2.32320 |
| H  | 1.66925 | -1.06963 | -2.54895 |
| C  | 3.66386 | -1.41610 | -3.28386 |
| H  | 3.32622 | -1.73404 | -4.26586 |
| C  | 5.02528 | -1.42235 | -2.97200 |
| H  | 5.75211 | -1.73670 | -3.71551 |
| C  | 5.44991 | -1.03764 | -1.69821 |
| H  | 6.50687 | -1.05287 | -1.44818 |
| C  | 4.51834 | -0.63450 | -0.74027 |
| H  | 4.85618 | -0.33729 | 0.24740 |
| Fe | 0.79069 | 2.95770 | -1.21608 |
| C  | -1.05319 | 2.09355 | -1.23874 |
| C  | -1.18740 | 3.52409 | -1.21131 |
| H  | -1.64076 | 4.10051 | -0.41857 |
| C  | -0.55285 | 4.05165 | -2.37255 |
| H  | -0.44107 | 5.10116 | -2.60900 |
| C  | -0.02873 | 2.96137 | -3.13045 |
| H  | 0.54685 | 3.03879 | -4.04250 |
| C  | -0.33662 | 1.75546 | -2.43980 |
| H  | -0.04947 | 0.75369 | -2.72887 |
| C  | 2.10147 | 1.80898 | -0.13798 |
| H  | 1.56083 | 2.86067 | 0.68094 |
| H  | 0.96831 | 2.72477 | 1.57290 |
| C  | 1.91409 | 4.10984 | 0.09468 |
| H  | 1.61712 | 5.08380 | 0.45930 |
| C  | 2.66637 | 3.84809 | -1.08910 |
| H  | 3.04327 | 4.58845 | -1.78153 |
| C  | 2.79032 | 2.43579 | -1.23049 |
| H  | 3.28125 | 1.91332 | -2.03853 |
| H  | -2.47622 | -2.13942 | -2.10957 |
| I  | 0.84721 | -3.52203 | -0.29778 |

Thermal correction to Gibbs free energy = 0.533826

SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -3916.95283726

\[
\theta_I = 0.00000 \quad 0.00000 \quad 0.00000
\]

Thermal correction to Gibbs free energy = -0.016848

SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -298.013236398

\[
\theta_I = 0.00000 \quad 0.00000 \quad 0.00000
\]

Thermal correction to Gibbs free energy = 0.151296
SCF Energy (SMD(Toluene), M06L/def2-TZVP) = - 1428.9859577

|   |   |   |   |
|---|---|---|---|
| Fe | 2.08265 | -1.29543 | -2.65872 |
| C  | 0.11454 | 2.27061 | 1.65233 |
| C  | 0.86566 | 2.62209 | 2.78131 |
| H  | 1.55101 | 1.90681 | 3.23098 |
| C  | 0.74358 | 3.89681 | 3.34788 |
| H  | 1.33415 | 4.15448 | 4.22415 |
| C  | -0.13285 | 4.83040 | 2.79255 |
| H  | -0.22821 | 5.82016 | 3.23078 |
| C  | -0.88547 | 4.48197 | 1.66869 |
| H  | -1.57152 | 5.19901 | 1.22529 |
| C  | -0.75726 | 3.21335 | 1.09935 |
| P  | 1.89332 | 1.39879 | -0.55598 |
| C  | 3.65741 | 1.24711 | -0.07011 |
| C  | 3.99218 | 0.49018 | 1.06136 |
| H  | 3.20874 | 0.03451 | 1.65591 |
| C  | 5.32881 | 0.30862 | 1.42333 |
| H  | 5.56938 | -0.29198 | 2.29458 |
| C  | 6.34183 | 0.89651 | 0.66321 |
| H  | 7.38247 | 0.75660 | 0.94118 |
| C  | 6.01512 | 1.68186 | -0.44710 |
| H  | 6.80037 | 2.15831 | -1.02693 |
| C  | 4.68052 | 1.86311 | -0.80890 |
| H  | 4.43108 | 2.49914 | -1.65264 |
| C  | 1.69665 | 3.18907 | -0.90492 |
| C  | 0.86299 | 3.61418 | -1.94852 |
| H  | 0.39867 | 2.86818 | -2.60604 |
| C  | 0.61725 | 4.97468 | -2.13842 |
| H  | -0.03070 | 5.29542 | -2.94908 |
| C  | 1.19698 | 5.91759 | -1.28841 |
| H  | 0.99751 | 6.97556 | -1.43224 |
| C  | 2.02892 | 5.49743 | -0.24806 |
| H  | 2.47155 | 6.22505 | 0.45236 |
| C  | 2.27946 | 4.14089 | -0.05563 |
| H  | 2.90111 | 3.82133 | 0.77361 |
| P  | 0.99289 | -1.96605 | 0.48350 |
| C  | 2.06359 | -2.49780 | 1.88966 |
| C  | 3.05587 | -3.48051 | 1.75056 |
| H  | 3.19602 | -3.97640 | 0.79584 |
| C  | 3.87385 | -3.81850 | 2.82995 |
| H  | 4.4092 | -4.57773 | 2.70594 |
| C  | 3.70824 | -3.18400 | 4.06295 |
| H  | 3.48357 | -3.44523 | 4.90065 |
| C  | 2.71385 | -2.21520 | 4.21590 |
| H  | 2.57385 | -1.72079 | 5.17275 |
| C  | 1.89643 | -1.87364 | 3.13786 |
| H  | 1.13258 | -1.11282 | 3.26459 |
| C  | -0.35259 | -3.21215 | 0.40778 |
| C  | -1.41203 | -2.97491 | -0.48214 |
| H  | -1.47912 | -2.03247 | -1.01436 |
| C  | -2.41053 | -3.93295 | -0.65064 |
| H  | -3.23349 | -3.73604 | -1.32868 |

SCF Energy (SMD(Toluene), M06L/def2-TZVP) = - 5047.88131458

Thermal correction to Gibbs free energy = 0.715894
|    | x     | y     | z     |
|----|-------|-------|-------|
| Pd | 0.50557 | 0.31458 | 0.85950 |
| C  | -0.83206 | 1.71698 | 1.80433 |
| C  | -0.21342 | 1.82450 | 3.07454 |
| H  | 0.06778 | 0.93139 | 3.62531 |
| C  | 0.03866 | 3.08701 | 3.61745 |
| H  | 0.54830 | 3.15771 | 4.57502 |
| C  | -0.83866 | 4.24251 | 2.95964 |
| H  | -0.20423 | 5.22046 | 3.39535 |
| C  | -1.07070 | 4.12510 | 1.74296 |
| H  | -1.40900 | 5.01420 | 1.21352 |
| C  | -1.31673 | 2.88308 | 1.16957 |
| P  | 1.45688 | 1.66699 | -0.85062 |
| C  | 3.00474 | 2.55103 | -0.38109 |
| C  | 3.50978 | 2.35741 | 0.91326 |
| H  | 2.96466 | 1.71677 | 1.60213 |
| C  | 4.69531 | 2.97767 | 1.31497 |
| H  | 5.07510 | 2.81547 | 2.31974 |
| C  | 5.38447 | 3.80706 | 0.42889 |
| H  | 6.30631 | 4.29079 | 0.73940 |
| C  | 4.87779 | 4.02638 | -0.85563 |
| H  | 5.40214 | 4.68467 | -1.54280 |
| C  | 3.69337 | 3.40772 | -1.25591 |
| H  | 3.28947 | 3.60521 | -2.24430 |
| C  | 0.43241 | 2.99024 | -1.62399 |
| C  | -0.59643 | 2.62430 | -2.50873 |
| H  | -0.72271 | 1.58765 | -2.79751 |
| C  | -1.49127 | 3.58132 | -2.98539 |
| H  | -2.28420 | 3.27955 | -3.66381 |
| C  | -1.37789 | 4.29125 | -2.58746 |
| H  | -2.07811 | 5.65927 | -2.95888 |
| C  | -0.36324 | 5.28641 | -1.70374 |
| H  | -0.26828 | 6.32036 | -1.38273 |
| C  | 0.53119 | 4.33019 | -1.21897 |
| H  | 1.29931 | 4.62981 | -0.51393 |
| P  | 1.67822 | -1.74894 | 0.88277 |
| C  | 2.39240 | -2.22410 | 2.51588 |
| C  | 3.68532 | -2.74003 | 2.67979 |
| H  | 4.32322 | -2.88691 | 1.81366 |
| C  | 4.15964 | -3.06269 | 3.95436 |
| H  | 5.16511 | -3.45832 | 4.06950 |
| C  | 3.34642 | -2.88272 | 5.07406 |
| C  | 3.71715 | -3.13512 | 6.06346 |
| C  | 2.05393 | -2.37226 | 4.91842 |
| H  | 1.41633 | -2.22763 | 5.78615 |
| C  | 1.58410 | -2.03746 | 3.64988 |
| H  | 0.58413 | -1.62741 | 3.52920 |
| C  | 0.67095 | -3.23094 | 0.43853 |
| C  | -0.47134 | -3.05614 | -0.35664 |
| H  | -0.76149 | -2.06196 | -0.67395 |
| C  | -1.24883 | -4.15552 | -0.73777 |
| H  | -2.12978 | -4.00241 | -1.34700 |
| C  | -0.88535 | -5.43910 | -0.32314 |
| H  | -1.48980 | -6.29407 | -0.61316 |
| C  | 0.24844 | -5.62181 | 0.47384 |

\[
\begin{pmatrix}
\text{dpf}^2 & \text{Pd} & \text{S} \\
\end{pmatrix}
\]
|       |       |       |       |       |
|-------|-------|-------|-------|-------|
| C     | 4.13792 | -0.12908 | -0.97874 | C     | -1.96543 | 2.02039 | 1.79215 |
| C     | 3.38474 | 1.03964 | 1.01557 | H     | -1.07729 | 1.48829 | 2.11769 |
| C     | 5.27498 | -0.55804 | -0.29311 | C     | -2.45255 | 3.08696 | 2.55023 |
| H     | 3.97483 | -0.41706 | -2.01188 | H     | -1.93747 | 3.37545 | 3.46183 |
| C     | 4.51592 | 0.58906 | 1.69558 | C     | -3.59620 | 3.77226 | 2.13641 |
| H     | 2.63885 | 1.64438 | 1.51796 | H     | -3.97748 | 4.60135 | 2.72545 |
| C     | 5.46372 | -0.20243 | 1.04332 | H     | -5.16031 | 3.90032 | 0.65496 |
| H     | 6.00632 | -1.17861 | -0.80220 | C     | -4.26034 | 3.38013 | 0.97012 |
| H     | 6.34618 | -0.54340 | 1.57647 | H     | -4.31078 | 1.99517 | -0.67682 |
| S     | 1.77791 | 1.27884 | -1.26029 | C     | -3.38043 | -0.71659 | -0.87239 |
| P     | 0.24619 | 0.34099 | -0.18154 | H     | -3.49266 | -1.24980 | -2.16381 |
| O     | 0.35513 | -1.21230 | -0.67651 | H     | -2.75000 | -1.01322 | -2.91901 |
| O     | -1.05254 | 0.86969 | -1.00700 | C     | -4.55952 | -2.09086 | -2.48605 |
| O     | 0.21372 | 0.54002 | 1.28611 | H     | -4.63847 | -2.49685 | -3.49053 |
| C     | -0.69171 | -2.07478 | -0.31504 | C     | -5.51802 | -2.40898 | -1.52326 |
| C     | -1.53364 | -2.53097 | -1.32643 | H     | -6.34262 | -3.07030 | -1.77325 |
| C     | -0.86550 | -2.45936 | 1.01389 | H     | -5.41023 | -1.87949 | -0.23519 |
| C     | -2.57389 | -3.40100 | -0.99792 | H     | -6.14253 | -2.13463 | 0.52457 |
| H     | -1.36757 | -2.19328 | -2.34311 | C     | -4.35007 | -1.03677 | 0.08972 |
| C     | -1.91469 | -3.32500 | 1.32803 | H     | -4.25890 | -0.65619 | 1.10065 |
| H     | -0.20263 | -2.06316 | 1.77368 | P     | 1.63088 | 0.78292 | 0.42168 |
| C     | -2.76786 | -3.79711 | 0.32770 | C     | 1.92956 | 1.56170 | 2.06651 |
| H     | -3.23665 | -3.76226 | -1.7834 | H     | 2.62907 | 2.77482 | 2.17512 |
| H     | -2.06420 | -3.62818 | 2.35982 | H     | 3.02106 | 3.25394 | 1.28320 |
| H     | -3.58135 | -4.47021 | 0.58021 | H     | 2.81998 | 3.37282 | 3.42045 |
| C     | -2.14701 | 1.46836 | -0.36587 | C     | 3.36319 | 4.31098 | 3.48998 |
| C     | -3.06370 | 0.67535 | 0.31940 | C     | 2.31169 | 2.76871 | 4.57341 |
| C     | -2.31471 | 2.84306 | -0.49412 | C     | 2.45752 | 3.23715 | 5.54266 |
| C     | -4.17727 | 1.28727 | 0.89506 | C     | 1.61937 | 1.56069 | 4.47622 |
| H     | -2.89883 | -0.39364 | 0.39628 | H     | 1.22751 | 1.08114 | 5.36851 |
| C     | -3.43567 | 3.44106 | 0.08348 | C     | 1.43144 | 0.95718 | 3.23101 |
| H     | -1.57462 | 3.41968 | -1.03830 | C     | 0.90495 | 0.01138 | 3.16423 |
| C     | -4.36663 | 2.66627 | 0.77836 | C     | 3.26453 | 0.14584 | -0.12041 |
| H     | -4.89824 | 0.68163 | 1.43570 | C     | 3.36944 | -0.40369 | -1.40800 |
| H     | -3.57798 | 4.51344 | -0.00928 | H     | 2.49802 | -0.44778 | -2.05170 |
| H     | -5.23618 | 3.13546 | 1.22816 | H     | 4.58275 | -0.91668 | -1.86213 |

Thermal correction to Gibbs free energy = 0.23413

SCF Energy(SMD(Toluene), M06L/def2-TZVP) = 1660.50870352
\[
\begin{bmatrix}
\text{dpf}^{\text{Pd}} & \text{dpf}^{\text{Ph}}
\end{bmatrix}
\]

Thermal correction to Gibbs free energy = 0.620516
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -4248.95541876

-0.239884 0.36833
-1.75233 -1.44882 1.67837
-1.12553 -1.4983 2.94139
-0.10798 -1.86454 3.03394
-1.82123 -1.07468 4.07895
-1.32209 -1.09395 5.04479
-3.15283 -0.66545 3.98453
-3.69527 -0.35203 4.87148
-3.79223 -0.69505 2.73933
-4.83371 -0.3928 2.65958
-3.10788 -1.09455 1.59237
-1.04017 -1.39286 -0.19886
-1.36828 2.54911 1.19587
-1.00734 2.15755 2.49200
-0.57999 1.17328 2.65396
-1.23058 3.00948 3.57639
-0.95545 2.68773 4.57658
-1.81988 4.25789 3.37576
-1.99596 4.91990 4.21897
-2.20087 4.64977 2.08822
-2.67473 5.61455 1.92999
-1.98312 3.79828 1.00590
-2.30354 4.09531 0.01159
-2.62659 1.45433 -1.14118
-2.63829 1.38763 -2.54410
-1.70467 1.40926 -3.09703
-3.84432 1.30650 -3.24115
-3.83445 1.26785 -4.32707
-5.05773 1.27897 -2.54948
-5.99568 1.21103 -3.09290
-5.05602 1.34315 -1.15490
-5.99431 1.32520 -0.60750

-0.619108

-0.385278 1.43376 -0.45466
-0.386506 1.48692 0.62852
-0.214387 -0.72554 0.09145
-0.307819 -1.61488 1.41567
-0.420210 -1.08327 2.05049
-0.457833 -0.10743 1.75901
-0.84469 -1.80056 3.06306
-0.51834 -1.37680 3.55080
-0.436876 -3.05517 3.44639
-0.486911 -3.61041 4.23468
-0.32473 -3.59285 2.81582
-0.28642 -4.56724 3.11137
-0.259367 -2.87609 1.81181
-0.171094 -3.29252 1.33484
-0.281997 -1.48313 -1.44569
-0.191887 -1.86524 -2.45086
-0.085294 -1.74454 -2.28259
-0.238745 -2.42591 -3.64194
-0.168107 -2.72181 -4.41234
-0.375648 -2.61875 -3.83311
-0.412072 -3.05802 -4.75750
-0.65877 -2.26309 -2.82555
-0.572345 -2.42882 -2.96479
-0.419301 -1.70394 -1.63584
-0.489428 -1.44738 -0.84661
-0.210747 2.50071 -0.93682
-0.08719 2.33984 -1.28405
-0.47152 3.72294 -1.24236
-0.12726 4.44817 -0.52000
-0.143744 3.95245 -2.26579
-0.194914 4.88667 -2.45364
-0.16592 2.72139 -2.95265
-0.236654 2.55526 -3.75358
-0.083623 1.72755 -2.34881
-0.081243 0.67870 -2.60839
-0.290711 0.93117 0.11685
-0.246106 1.96285 1.01376
-0.167663 1.85514 1.74950
-0.31790 3.15671 0.71925
-0.303266 4.11628 1.19600
-0.406845 2.88135 -0.36321
-0.471661 3.59668 -0.85144
-0.390842 1.51298 -0.73242
-0.440851 1.00881 -1.54647
-0.360817 -1.09381 0.63105
-0.97037 -3.05713 0.31356
-0.245488 -3.15796 -0.66933
-0.334523 -4.21909 -0.44265
-0.275887 -2.20843 -1.65794
-0.451062 -4.33165 -1.20102
-0.312339 -4.94512 0.33349
-0.393885 -2.31164 -2.39451
-0.208175 -1.37679 -1.82147
-0.481544 -3.37653 -2.17438
-0.519085 -5.15915 -1.01801
-0.417118 -1.54967 -3.13180
-0.573124 -3.45937 -2.75277

Thermal correction to Gibbs free energy = 0.619108
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -4248.92145585

\[ \text{Ph-S} \]

C -2.54510 1.41642 -0.94663
C -1.41229 0.60662 -0.89193
C -1.40151 -0.52531 -0.06368
C -2.53652 -0.84257 0.69308
C -3.67588 -0.03884 0.61338
C -3.68261 1.09454 -0.20027
H -2.54338 2.29574 -1.58465
H -0.53333 0.85233 -1.47885
H -2.52347 -1.71004 1.34600
H -4.55250 -0.29338 1.20227
H -4.56546 1.72473 -0.25217
S 0.00000 1.64201 -0.00003
C 1.40151 -0.52526 0.06366
C 2.53667 -0.84268 -0.69282
C 1.41213 0.60686 0.89166
C 3.67600 -0.03892 -0.61308
H 2.52375 -1.71029 -1.34555
C 2.54494 1.41667 0.94639
H 0.53307 0.85269 1.47837
C 3.68250 1.09464 0.20031
H 4.55273 -0.29359 -1.20176
H 2.54309 2.29613 1.58423
C 4.56542 1.72485 0.25224

Thermal correction to Gibbs free energy = 0.122680
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -709.145517919

\[ \text{Ph₃P} \rightarrow \text{Pd} \rightarrow \text{PPH₃} \]

Pd 0.11543 -0.08412 -0.52278
P 2.39656 -0.45046 -0.26624
P -0.70629 2.09369 -0.20164
C 3.59242 0.72661 -1.03921
C 3.34876 1.09855 -2.37113
C 4.69249 1.28347 -0.37217
C 4.18766 2.00111 -3.02375
H 2.47809 0.69532 -2.88318
C 5.52650 2.19686 -1.02145
H 4.89088 1.01409 0.66042
C 5.27811 2.55677 -2.34735
H 3.98385 2.28169 -4.05339
H 6.37003 2.62791 -0.48918
H 5.92699 3.26815 -2.85057
C 2.69804 -0.24072 1.54751
C 3.02889 -1.31082 2.39109
C 2.42592 1.01525 2.12180
C 3.06767 -1.13352 3.77786
H 3.24543 -2.28699 1.96937
C 2.47608 1.19100 3.50268
H 2.16948 1.85510 1.48560
C 2.78797 0.11364 4.33833
H 3.32263 -1.97416 4.41777

H 2.26093 2.16955 3.92269
H 2.81673 0.24770 5.41601
C 3.18637 -2.08919 -0.61487
C 4.55125 -2.25600 -0.89611
C 2.35927 -3.22116 -0.57775
C 5.07044 -3.52887 -1.13796
H 5.20803 -1.39232 -0.93140
C 2.87902 -4.49475 -0.81251
H 1.30136 -3.09658 -0.37785
C 4.23713 -4.65028 -1.09646
H 6.12787 -3.64521 -1.36002
H 2.21602 -5.35501 -0.79176
H 4.64513 -5.63845 -1.29065
C -1.82736 2.09679 1.27087
C -3.05186 2.77766 1.31269
C -1.46834 1.27887 2.35642
C -3.91035 2.62015 2.40411
H -3.34911 3.40942 0.48202
C -2.32536 1.12076 3.44401
C -0.53002 0.73422 2.32980
C -3.55536 1.78526 3.46587
H -4.86291 3.14323 2.41787
H -2.04367 0.45321 4.25298
H -4.23435 1.64906 4.30297
C -1.75358 2.86661 -1.50799
C -1.80047 4.24807 -1.74937
C -2.56845 2.01256 -2.26887
C -2.64925 4.76347 -2.73119
H -1.17463 4.91960 -1.16936
C -3.42720 2.53158 -3.23731
C -2.53515 0.94261 -2.09328
C -3.46716 3.90782 -3.47322
H -2.67482 5.83463 -2.91260
H -4.06193 1.85627 -3.80356
H -4.13001 4.31248 -4.23319
C 0.50224 3.42976 0.20925
C 1.58655 3.60580 -0.66685
C 0.45911 4.18462 1.39044
C 2.60621 4.50711 -0.36955
H 1.64892 3.00659 -1.56902
C 1.48806 5.08121 1.69402
H -0.37045 4.06345 2.07959
C 2.56348 5.24260 0.81893
H 3.44474 4.60804 -1.05172
C 1.44672 5.65306 2.61730
C 3.36656 5.93230 1.06320
H -1.52610 -1.72726 -0.22347
C -1.69976 -2.19706 1.55750
C -3.24888 -1.25869 -0.70642
C -1.30704 -3.35241 -1.08296
H -0.56612 -2.06859 2.37581
C -2.90007 -2.63955 2.13496
H -3.78513 -1.62492 -1.95075
C -3.96189 -0.34574 0.09168
H -1.74574 -4.57963 -0.56519
H -0.62304 -3.33912 -2.30926
H -0.62853 -2.36621 3.73697
H 0.36328 -1.70695 1.94960
| C     | -2.96469 | -2.93378 | 3.49835 |
|-------|----------|----------|---------|
| H     | -3.79195 | -2.73431 | 1.52354 |
| C     | -4.99607 | -1.08347 | -2.38974|
| H     | -3.25524 | -2.33083 | -2.58295|
| C     | -5.17229 | 0.18691  | -0.34652|
| H     | -3.56502 | -0.03970 | 1.05291 |
| C     | -1.50162 | -5.76663 | -1.25857|
| H     | -2.26600 | -6.41156 | 0.38690 |
| C     | -0.39478 | -4.52329 | -3.01090|
| H     | -0.24104 | -2.39471 | -2.69003|
| C     | -1.83117 | -2.79544 | 4.30333 |
| H     | 0.26098  | -2.24285 | 4.34819 |
| C     | -3.90339 | -3.26728 | 3.93229 |
| H     | -5.39518 | -1.37809 | -3.35672|
| H     | -5.69769 | 0.89759  | 0.28476 |
| C     | -0.83010 | -5.74128 | -2.48357|
| H     | -1.83721 | -6.71237 | -0.84169|
| C     | 0.14103  | -4.49665 | -3.95544|
| H     | -1.88711 | -3.01823 | 5.36535 |
| C     | -6.63154 | 0.24979  | -1.93710|
| H     | -0.64012 | -6.66680 | -3.01990|

Thermal correction to Gibbs free energy = 0.732839
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -3237.5190099

$\text{PPh}_3$

| P     | -0.00069 | 0.00049  | -1.26479 |
|-------|----------|----------|---------|
| C     | 0.43705  | -1.59839 | -0.43975|
| C     | -0.06505 | -2.77567 | -1.01916|
| C     | 1.22891  | -1.70084 | 0.71439 |
| C     | 0.20170  | -4.02131 | -0.45120|
| H     | -0.66866 | -2.71470 | -1.92155|
| C     | 1.50531  | -2.94917 | 1.27620 |
| C     | 1.62978  | -0.80369 | 1.17527 |
| C     | 0.99061  | -4.11107 | 0.69811 |
| H     | -0.19826 | -4.92133 | -0.90988|
| H     | 2.12166  | -3.01249 | 2.16890 |
| C     | 1.20661  | -5.08101 | 1.13711 |
| C     | 1.16602  | -1.17853 | -0.44038|
| C     | 0.85991  | 1.91585  | 0.71385 |
| C     | 2.43638  | 1.33159  | -1.02053|
| C     | 1.80360  | 2.77895  | 1.27495 |
| H     | -0.11716 | 1.81518  | 1.17553 |
| C     | 3.38261  | 2.18497  | -0.45322|
| H     | 2.68457  | 0.77801  | -1.92293|
| C     | 3.06696  | 2.91338  | 0.69615 |
| H     | 1.55109  | 3.34467  | 2.16770 |
| H     | 4.36185  | 2.28791  | -0.91244|
| C     | 3.79957  | 3.58501  | 1.13472 |
| C     | -1.60391 | 0.42063  | -0.43895|
| C     | -2.08073 | -0.20413 | 0.72382 |
| C     | -2.37993 | 1.43382  | -1.02616|
| C     | -3.29976 | 0.18019  | 1.28631 |
| H     | -1.49823 | -0.99201 | 1.19069 |
| C     | -3.59208 | 1.82520  | -0.45770|
| H     | -2.03137 | 1.91811  | -1.93517|
| C     | -4.05635 | 1.19671  | 0.70014 |

H     | -3.65673 | -0.31425 | 2.18570 |
| H     | -4.17759 | 2.61352  | -0.92259|
| H     | -5.00420 | 1.49427  | 1.13969 |

Thermal correction to Gibbs free energy = 0.227515
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -1036.4636573

\[
\begin{pmatrix}
Pd \\
P \\
PPh_3 \\
PPh_3 \text{Ph}
\end{pmatrix}
\]
Ph₃P[Pd₉]II

Thermal correction to Gibbs free energy = 0.559532
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -2730.59486214

| Atomic Number | X | Y | Z | Atomic Number | X | Y | Z |
|---------------|---|---|---|---------------|---|---|---|
| C             | 4.15472 | -0.80834 | 1.18352 | C             | 0.25053 | 4.47921 | -0.14762 |
| C             | 3.83488 | -1.49885 | -1.11082 | H             | 0.15771 | 2.83675 | 1.22644 |
| C             | 5.18722 | -1.74191 | 1.31321 | C             | -0.24224 | 5.03496 | -1.32915 |
| H             | 3.88440 | -0.18466 | 2.02930 | H             | -1.63052 | 4.79101 | -2.96155 |
| C             | 4.87086 | -2.42037 | -0.98282 | H             | 1.01363 | 4.99383 | 0.42847 |
| H             | 3.30505 | -1.40933 | -2.05617 | H             | 0.13458 | 5.98996 | -1.68336 |
| C             | 5.54929 | -2.54743 | 0.23396 | C             | -3.38425 | 0.68037 | -0.56720 |
| H             | 5.70928 | -1.83505 | 2.26147 | C             | -4.52588 | 0.95256 | 0.19666 |
| H             | 5.14564 | -3.04473 | -1.82839 | C             | -3.53486 | 0.25479 | -1.89628 |
| H             | 6.35145 | -3.27231 | 0.33779 | H             | -5.79629 | 0.80532 | -0.36303 |
| C             | 2.02714 | 1.50318 | 1.25032 | H             | -4.43154 | 1.26448 | 1.23089 |
| C             | 1.31132 | 1.05968 | 2.37602 | C             | -4.80837 | 0.11281 | -2.45325 |
| C             | 2.60875 | 2.77805 | 1.72531 | H             | -2.65922 | -0.00642 | -2.48100 |
| C             | 1.16336 | 1.88022 | 3.49361 | C             | -5.93851 | 0.38715 | -1.68650 |
| H             | 0.83287 | 0.08552 | 2.35757 | H             | -6.67516 | 1.01159 | 0.24116 |
| C             | 2.45822 | 3.59996 | 2.39474 | H             | -4.90516 | -0.23428 | -3.47698 |
| H             | 3.15334 | 3.14300 | 0.41073 | H             | -6.92856 | 0.26327 | -2.11560 |
| C             | 1.73004 | 3.15777 | 3.50159 | C             | 2.24804 | 1.26348 | -1.71595 |
| H             | 0.57819 | 1.53087 | 4.33920 | C             | 3.52650 | 1.76460 | -2.01816 |
| H             | 2.90256 | 4.59162 | 2.39647 | C             | 1.17937 | 1.57770 | -2.56439 |
| C             | 1.59968 | 3.80694 | 4.36281 | C             | 3.71635 | 2.59639 | -3.12034 |
| I             | 0.47176 | -3.13389 | 1.31036 | H             | 4.37432 | 1.48913 | -1.39791 |
| C             | -0.72142 | -2.77984 | -0.71385 | C             | 1.37009 | 2.41083 | -3.66815 |
| H             | 0.07215 | -2.92856 | -1.8007 | H             | 0.19692 | 1.17020 | -2.35922 |
| C             | -2.08546 | -3.12897 | -0.72100 | C             | 2.63600 | 2.92675 | -3.94396 |
| C             | -0.56503 | -3.27762 | -3.07773 | C             | 4.70823 | 2.98000 | -3.34178 |
| H             | 1.15104 | -2.83658 | -1.82010 | H             | 0.52703 | 2.65570 | -4.30706 |
| C             | -2.67544 | -3.50329 | -1.91992 | H             | 2.78550 | 3.57458 | -4.80306 |
| H             | -2.66930 | -3.05314 | 0.18906 | C             | 3.46396 | -0.88253 | -0.32430 |
| C             | -1.92130 | -3.56263 | -3.10521 | C             | 4.49014 | -0.80491 | 0.62341 |
| H             | 0.03824 | -3.37093 | -3.98013 | C             | 3.57519 | -1.79252 | -1.38696 |
| H             | -3.73951 | -3.71991 | -1.94115 | C             | 5.61625 | -1.62453 | 0.50655 |
| H             | -2.39729 | -3.86052 | -4.03475 | H             | 4.41602 | -0.11103 | 1.45409 |

Ph₃P[Pd₉][Pd₉]II

Ph₃P[Pd₉][Pd₉]II

Pd  -0.20756  -0.97518  -0.22906
P   1.67593  0.84587  0.09451
P   1.95968  0.17410 -0.25805
C  -1.86876  1.00322  1.92342
C  -1.53927 -0.08503  2.74645
C  -2.33850  2.18718  2.51585
C  -1.67850  0.00847  4.13176
H  -1.14905 -0.99802  2.30506
C  -2.47183  2.72928  3.90139
C  -2.58587  3.04270  1.89550
C  -2.14227  1.19023  4.71205
H  -1.41451 -0.84205  4.75341
H  -2.83053  3.20777  4.34666
C  -2.24433  1.26468  5.79998
C  -1.20249  2.55209 -0.42718
C  -1.70776  3.12667 -1.60377
C  -0.22772  3.24986  0.30293
C  -1.22915  4.35916 -2.04911
H  -2.47540  2.61601 -2.17492

Thermal correction to Gibbs free energy = 0.559532
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -2730.59486214
C  -3.04620  -3.74884  -3.33652
H  -4.85183  -3.31788  0.54438
H  -4.95680  -4.16943  -1.79270
I  0.88846  -3.29153  0.68913

Thermal correction to Gibbs free energy = 0.56411
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -2730.63258411

\[
\begin{array}{c}
\text{Ir}^{1}\text{Pd}^{3}\text{PhPPh}_3^3 \\
\text{Ph}_3\text{PPh}_3^3 \\
\end{array}
\]

Pd  -0.01090  0.07000  -0.45096
P  2.32190  0.04489  -0.06290
P  -2.34545  -0.06601  -0.08859
C  2.56956  0.11345  1.75769
C  1.50848  0.52943  2.57738
C  3.78747  -0.25781  2.35237
H  1.66368  0.57557  3.96326
C  0.56058  0.81565  2.13438
C  3.94108  -0.20261  3.73765
H  4.60881  -0.60730  1.73455
C  2.87917  0.21285  4.54534
H  0.82591  0.88871  4.57881
H  4.88757  -0.49129  4.18572
C  2.99940  0.24760  5.62452
C  3.27127  -1.44799  -0.58471
C  3.94951  -1.47296  -1.81190
C  3.22563  -2.61822  0.18974
C  4.56161  -2.64603  -2.25705
C  4.00871  -0.57779  -2.42160
C  3.83713  -3.78675  -0.25803
C  2.69226  -2.62428  1.13253
C  4.50515  -3.80607  -1.48419
H  5.08583  -2.64828  -3.20857
C  3.77884  -4.68569  0.34821
H  4.97827  -4.71915  -1.83409
C  3.29443  1.41870  -0.79712
C  4.35845  2.03872  -0.13158
C  2.96790  1.82286  -2.10058
C  5.09182  3.04236  -0.76710
H  4.60854  1.75565  0.88491
C  3.71374  2.81193  -2.73899
H  2.11048  1.38245  -2.60042
C  4.77656  3.42531  -2.07169
H  5.90849  3.52624  -0.23908
C  3.44932  3.11966  -3.74628
H  5.34897  4.20698  -2.56282
C  -3.31112  -1.56394  -0.54983
C  -4.83815  -1.92481  0.13448
C  -2.93418  -2.29188  -1.68526
C  -5.24192  -3.01339  -0.29295
C  -4.80267  -1.35935  1.00397
C  -3.69747  -3.37849  -2.11413
H  -2.03324  -2.02235  -2.22167
C  -4.84827  -3.74541  -1.41613
H  -6.14232  -3.28756  0.24929
H  -3.38455  -3.94108  -2.98874
H  -5.43873  -4.59555  -1.74565
C  -3.43479  1.25621  -0.74680

\[
\begin{array}{c}
\text{RS}^{1}\text{Pd}^{3}\text{PhPPh}_3^3 \\
\text{Ph}_3\text{PPh}_3^3 \\
\end{array}
\]

Pd  1.07244  0.27002  -0.66843
P  0.38162  2.48285  -0.09026
P  1.73537  -2.00603  -0.49249
C  -0.02865  2.52058  1.70171
C  -0.30744  1.31998  2.36853
C  -0.07252  3.72533  2.42014
C  -0.61644  1.32009  3.72710
C  -0.29050  0.38831  1.81935
C  -0.39122  3.72513  3.77904
C  -0.66091  2.52244  4.43552
C  -0.81644  0.37746  4.22839
C  -0.42331  4.66424  4.32389
C  -0.90183  2.52341  5.49489
C  1.63768  3.83182  -0.26042
C  1.64055  4.70465  -1.35907
C  2.65481  3.95610  0.70135
C  2.63695  5.67363  -1.49360
C  0.85828  4.64773  -2.10690
Thermal correction to Gibbs free energy = 0.746598
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -3861.56052882

\[
\begin{align*}
\text{Pd} & \quad 0.63822 \quad 0.42490 \quad -0.91422 \\
P & \quad 2.05012 \quad 1.36512 \quad 0.75922 \\
P & \quad 0.86844 \quad -1.97583 \quad -0.81622 \\
O & \quad 1.31071 \quad 1.34844 \quad 2.45089 \\
O & \quad -0.06767 \quad 1.59802 \quad 2.54219 \\
C & \quad 2.04245 \quad 1.13625 \quad 3.62929 \\
C & \quad -0.70025 \quad 1.62632 \quad 3.76068 \\
H & \quad -0.65842 \quad 1.76016 \quad 1.64664 \\
C & \quad 1.40300 \quad 1.14511 \quad 4.87080 \\
H & \quad 3.11091 \quad 0.95487 \quad 3.58090 \\
C & \quad 0.03016 \quad 1.38792 \quad 4.95332 \\
H & \quad -1.76589 \quad 1.83337 \quad 3.83334 \\
H & \quad 1.98079 \quad 0.96719 \quad 5.77359 \\
H & \quad -0.46462 \quad 1.39841 \quad 5.92062 \\
C & \quad 3.65034 \quad 0.45031 \quad 0.94611 \\
C & \quad 4.80008 \quad 0.87327 \quad 0.25810 \\
C & \quad 3.69580 \quad -0.77558 \quad 1.63247 \\
C & \quad 5.95397 \quad 0.08731 \quad 0.24765 \\
H & \quad 4.79749 \quad 1.81887 \quad -0.27387 \\
C & \quad 4.85106 \quad -1.55633 \quad 1.62249 \\
H & \quad 2.89225 \quad -1.12868 \quad 2.17648 \\
C & \quad 5.98368 \quad -1.13286 \quad 0.92565 \\
H & \quad 6.83199 \quad 0.43416 \quad -0.29055 \\
H & \quad 4.85289 \quad -2.50374 \quad 2.15330 \\
H & \quad 6.87976 \quad -1.74646 \quad 0.91064 \\
\end{align*}
\]
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -3861.52064587

Thermal correction to Gibbs free energy = 0.742991

L-Pd-Pd-L

Pd 1.34260 0.00661 -0.19553
Pd -1.34259 -0.00659 -0.19548
I -0.01823 2.36980 -0.06411
H 3.86030 -2.23889 3.09077
C 3.79852 -2.00746 2.02059
C 4.04828 -0.49400 1.83809
H 2.80141 -2.29755 1.67868
H 4.54107 -2.62754 1.51619
H 3.66714 0.00338 0.00188
C 5.47159 -0.16764 2.33382
C 3.01820 0.21434 2.75395
C 4.53466 -1.26622 -1.18062
C 4.42494 1.75740 -0.34040
H 5.66997 0.90518 2.35865
H 5.57854 -0.53664 3.36166
H 6.24880 -0.64541 1.73487
H 3.10061 1.29950 2.74559
H 1.99345 -0.04558 2.47232
H 3.18418 -0.12160 3.78533
C 5.97347 -1.64511 -0.77362
C 3.68368 -2.55520 -1.26081
C 4.55293 -0.69704 -2.61595
C 3.78799 2.34435 -1.62432
C 4.03036 2.71237 0.80762
C 5.95996 1.78760 -0.49562
H 6.63259 -0.78134 -0.67927
H 6.00311 -2.19986 0.16574

- S127 -
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -2482.00622308

\[ \begin{align*}
\text{Pd} & \quad 1.57773 \quad -0.35660 \quad -0.29176 \\
\text{Pd} & \quad -0.99685 \quad -1.09331 \quad -0.19615 \\
\text{H} & \quad 5.42100 \quad -2.49429 \quad 1.72568 \\
\text{C} & \quad 4.95177 \quad -2.15745 \quad 0.79352 \\
\text{C} & \quad 4.93433 \quad -0.61378 \quad 0.79412 \\
\text{H} & \quad 3.94346 \quad -2.57559 \quad 0.76651 \\
\text{H} & \quad 5.53304 \quad -2.57855 \quad -0.02804 \\
\text{P} & \quad 3.84696 \quad 0.04610 \quad -0.67363 \\
\text{C} & \quad 6.39399 \quad -0.11512 \quad 0.79483 \\
\text{C} & \quad 4.25750 \quad -0.20025 \quad 2.12225 \\
\text{C} & \quad 4.30978 \quad -0.94559 \quad -2.27549 \\
\text{C} & \quad 4.26908 \quad 1.91305 \quad -0.95038 \\
\text{H} & \quad 6.46756 \quad 0.96342 \quad 0.94057 \\
\text{H} & \quad 6.92457 \quad -0.58903 \quad 1.63012 \\
\text{H} & \quad 6.93006 \quad -0.37532 \quad -0.11970 \\
\text{P} & \quad 4.15615 \quad 0.87476 \quad 2.25204 \\
\text{H} & \quad 3.26215 \quad -0.63901 \quad 2.21137 \\
\text{H} & \quad 4.86665 \quad -0.57829 \quad 2.95341 \\
\text{C} & \quad 5.82045 \quad -1.16101 \quad -2.49673 \\
\text{C} & \quad 3.60421 \quad -2.32395 \quad -2.22390 \\
\text{C} & \quad 3.72701 \quad -0.22264 \quad -3.50938 \\
\text{C} & \quad 3.17004 \quad 2.56878 \quad -1.81843 \\
\text{C} & \quad 4.20527 \quad 2.64006 \quad 0.41036 \\
\text{C} & \quad 5.63625 \quad 2.17775 \quad -1.61409 \\
\text{H} & \quad 6.37792 \quad -0.22466 \quad -2.54744 \\
\text{H} & \quad 6.27022 \quad -1.78362 \quad -1.72182 \\
\text{H} & \quad 5.96548 \quad -1.68173 \quad -3.45161 \\
\text{H} & \quad 2.52001 \quad -2.21214 \quad -2.13272 \\
\text{H} & \quad 3.81341 \quad -2.85519 \quad -3.16111 \\
\text{H} & \quad 3.94054 \quad -2.95839 \quad -1.40651 \\
\text{H} & \quad 3.83915 \quad -0.88109 \quad -4.37928 \\
\text{H} & \quad 2.66047 \quad -0.01176 \quad -3.38853 \\
\text{C} & \quad 4.24586 \quad 0.70815 \quad -3.74322 \\
\text{H} & \quad 3.58990 \quad 2.23861 \quad 3.09102 \\
\text{H} & \quad 3.04661 \quad 2.11196 \quad -2.79771 \\
\text{H} & \quad 2.20372 \quad 2.57273 \quad -1.31984 \\
\text{H} & \quad 3.44814 \quad 3.61740 \quad -1.98032 \\
\text{H} & \quad 5.03711 \quad 2.39408 \quad 1.07251 \\
\text{H} & \quad 4.24545 \quad 3.72013 \quad 0.22628 \\
\text{H} & \quad 3.26641 \quad 2.43845 \quad 0.93164 \\
\text{H} & \quad 5.81417 \quad 3.26006 \quad -1.62482 \\
\text{H} & \quad 6.47267 \quad 1.71522 \quad -1.08977 \\
\text{H} & \quad 5.65637 \quad 1.84293 \quad -2.65340 \\
\text{P} & \quad -3.24293 \quad -1.73588 \quad -0.17890 \\
\text{C} & \quad -3.36317 \quad -3.65731 \quad 0.10616 \\
\text{C} & \quad -4.11822 \quad -0.83717 \quad 1.29748 \\
\text{C} & \quad -4.19294 \quad -1.31018 \quad -1.81615 \\
\text{C} & \quad -4.74911 \quad -4.27448 \quad -0.17053 \\
\text{C} & \quad -2.31679 \quad -4.36059 \quad -0.79414 \\
\text{C} & \quad -2.96373 \quad -3.99101 \quad 1.56094 \\
\text{C} & \quad -3.12245 \quad -0.78128 \quad 2.48207 \\
\end{align*} \]
| Element | X          | Y          | Z          |
|---------|------------|------------|------------|
| C       | 3.67272    | -2.78185   | -2.65065   |
| C       | 3.19997    | 0.58587    | -2.41982   |
| C       | 4.32232    | 1.54381    | -0.42265   |
| C       | 5.61435    | 0.04971    | -1.92892   |
| C       | 4.12524    | -2.61387   | 2.13898    |
| C       | 5.90749    | -0.98787   | 1.41451    |
| C       | 3.77754    | -0.19251   | 2.42618    |
| H       | 6.21441    | -2.41934   | -1.55532   |
| H       | 5.94134    | -3.38983   | -0.09970   |
| H       | 5.74620    | -4.11140   | -1.68765   |
| H       | 2.44295    | -3.82702   | 0.03198    |
| H       | 3.04993    | -4.79590   | -1.28761   |
| H       | 4.01234    | -4.62099   | 0.17966    |
| H       | 3.84621    | -3.76002   | -3.11367   |
| H       | 2.61910    | -2.54330   | -2.78176   |
| H       | 4.27527    | -2.05056   | -3.19677   |
| H       | 2.97743    | -0.27394   | -3.05183   |
| H       | 2.62687    | 0.96912    | -2.00672   |
| H       | 3.61422    | 1.37545    | -3.05854   |
| H       | 5.14675    | 1.50828    | 0.29073    |
| H       | 4.49787    | 2.40292    | -1.07790   |
| H       | 3.40253    | 1.74597    | 0.11729    |
| H       | 5.91972    | 0.98549    | -2.41211   |
| H       | 6.37906    | -0.19547   | -1.18954   |
| H       | 5.61427    | -0.72045   | -2.70077   |
| H       | 3.06310    | -2.87532   | 2.13057    |
| H       | 4.88756    | -3.42403   | 1.67741    |
| H       | 4.44379    | -2.55313   | 3.18622    |
| H       | 6.13812    | 0.03635    | 1.11887    |
| H       | 6.31696    | -1.13191   | 2.42208    |
| H       | 6.44128    | -1.66343   | 0.74916    |
| H       | 3.84418    | 0.82905    | 2.05995    |
| H       | 2.73231    | -0.40764   | 2.64646    |
| H       | 4.33162    | -0.24298   | 3.37236    |
| I       | 0.13240    | -3.09236   | -1.52498   |
| C       | -3.11013   | 0.03819    | -1.73190   |
| C       | -3.63428   | -1.15182   | -2.25968   |
| C       | -3.93183   | 1.15636    | -1.50762   |
| C       | -5.01164   | -1.25465   | -2.44722   |
| H       | -2.96914   | -1.97334   | -2.50155   |
| C       | -5.30728   | 1.03504    | -1.71656   |
| H       | -3.50591   | 2.09997    | -1.19001   |
| C       | -5.85067   | -0.16569   | -2.17879   |
| H       | -5.42779   | -2.18581   | -2.82173   |
| H       | -5.94673   | 1.89245    | -1.52721   |
| H       | -6.91944   | -0.24905   | -2.35125   |
| I       | -0.94722   | 0.68139    | -2.57091   |
| S       | 1.10076    | 1.04205    | 1.13909    |
| P       | 0.66315    | 2.80026    | 0.18549    |
| O       | -0.94907   | 2.96443    | 0.38752    |
| O       | 1.13061    | 3.94148    | 1.28491    |
| O       | 1.19616    | 3.05516    | -1.18161   |
| C       | 2.49669    | 4.12804    | 1.49059    |
| C       | 3.06003    | 3.65040    | 2.67361    |
| C       | 3.26839    | 4.78705    | 0.53357    |
| C       | 4.42452    | 3.83618    | 2.90069    |
| H       | 2.42684    | 3.13035    | 3.38365    |
| C       | 4.63168    | 4.96662    | 0.77270    |
| H       | 2.79836    | 5.11978    | -0.38418   |
| C       | 5.21311    | 4.49216    | 1.95148    |
| H       | 4.87068    | 3.46393    | 3.81839    |
| H       | 5.24114    | 5.47565    | 0.03164    |
| H       | 6.27477    | 4.63439    | 2.13043    |
| C       | -1.79152   | 3.88277    | -0.22557   |
| C       | -2.89600   | 4.28054    | 0.53061    |
| C       | -1.62372   | 4.31657    | -1.54297   |
| C       | -3.85880   | 5.10940    | -0.04531   |
| H       | -2.98575   | 3.92680    | 1.55117    |
| C       | -2.59281   | 5.15418    | -2.09982   |
| H       | -0.76038   | 3.99364    | -2.10877   |
| C       | -3.71323   | 5.54667    | -1.36434   |
| H       | -4.72062   | 5.41468    | 0.54124    |
| H       | -2.46920   | 5.49293    | -3.12438   |
| C       | -4.46310   | 6.19144    | -1.81253   |

Thermal correction to Gibbs free energy = 0.939687
SCF Energy(SMD(Toluene), M06L/def2-TZVP) = -4142.4908363
\[
\begin{bmatrix}
  \text{Pd} & R \\
  \text{L} & \text{L}
\end{bmatrix}^{\dagger}
\]

Pd  -1.40832  -1.27533  -0.01388
Pd  -0.12645  1.36421  0.30512
I  0.62479  0.57440  -2.0781
H  -5.67642  0.39470  1.99788
C  -5.07208  0.40654  1.08262
C  -4.98612  -1.04052  0.54920
H  -4.08902  0.79768  1.35184
H  -5.55807  1.09332  0.38867
P  -3.66119  -1.15788  -0.86191
C  -6.40320  -1.49734  0.14796
C  -4.48736  -1.88254  1.74436
C  -3.93886  0.34604  -2.05281
C  -3.95796  -2.79342  -1.86062
H  -6.45061  -2.56003  -0.09403
H  -7.07601  -1.33116  0.98845
H  -6.80417  -0.93573  -0.69736
H  -4.28208  -2.92402  1.50467
H  -3.57661  -1.44589  2.15748

\[ begin{tabular}{c|c|c|c|c}
Pd & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\text{L} & \text{L} & \text{L} & \text{L} & \text{L} \\
\end{tabular}\]
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