Supporting information for

# Mechanistic Studies of Palladium-Catalyzed S,O-Ligand promoted C–H Olefination of Aromatic compounds

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## 1. General information

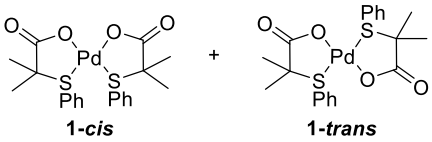
Chromatography: Silicycle Silica Flash P60 size 40–63 µm (230–400 mesh), TLC: Merck silica gel 60 (0.25mm). Visualization of the TLC was performed by UV, phosphomolybdic acid and $KMnO_4$ staining. Mass spectra were recorded on a AccuTOF GC v 4g, JMS-T100GCV mass spectrometers. $^1H$, $^{13}C$ and $^{31}P$ NMR were recorded on a Bruker DRX 500, Bruker AMX 400 and Bruker DRX 300. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 for $^1H$, δ 77.16 for $^{13}C$, $C_6D_6$: δ 7.16 for $^1H$, δ 128.06 for $^{13}C$, THF-$d_8$: δ 3.58 for $^1H$, δ 67.57 for $^{13}C$; AcOD-$d_4$: δ 2.04 for $^1H$). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, bs = broad singlet, m = multiplet), coupling constants (Hz) and integration. Infrared spectra were recorded on a Bruker IFS 28 FT-spectrophotometer and wavelengths are reported in $cm^{-1}$. GC analysis was performed on a Shimadzu GC-2010 Plus Gas Chromatograph using SH-Rxi-5HT (30 m, 0.25 mm, D 0.25 µm) column. All reagents and solvents that were not mentioned were used as received. $Pd(OAc)_2$ was purchased from Strem. 3-Methyl-2-(phenylthio)butanoic acid (**L1**) and 2-methyl-2-(phenylthio)propanoic acid (**L2**) were prepared according to the literature.[1]

## 2. Identification of active palladium complexes

**Procedure for the synthesis of complexes 1-*cis* and 1-*trans***

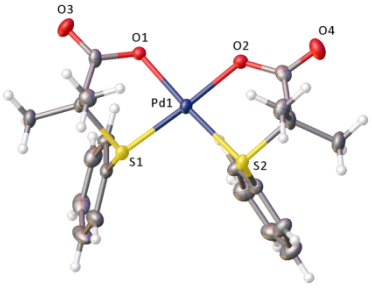
A solution of $Pd(OAc)_2$ (22.5 mg, 0.1 mmol, 1 equiv) and ligand **L2** (39.3 mg, 0.2 mmol, 2 equiv) in $CH_2Cl_2$ (3 mL) was stirred at room temperature overnight. The reaction was filtrated through a pad of Celite and evaporated to dryness to afford palladium complexes **1-*cis*** and **1-*trans*** as an organge solid (50.3 mg, quantitative yield). Single crystal suitable for X-ray crystallography was obtained by crystallization with a two-solvent system ($CHCl_3$/*n*-heptane).

**Complexes 1-*cis* and 1-*trans***




$^1H$ NMR (500 MHz, $CDCl_3$) δ = 8.01 – 7.87 (m, $4H_{cis+trans}$), 7.65 – 7.16 (m, $16H_{cis+trans}$), 1.92 (s, $6H_{cis}$), 1.75 (s, $6H_{trans}$), 1.22 (s, $6H_{cis}$), 1.20 (s, $6H_{trans}$); IR ν = 1649, 1287, 1177, 746, 686, 494 $cm^{-1}$; HRMS (FD) calcd for $C_{20}H_{22}O_4PdS_2$ $[M]^+$: 495.9994; found: 495.9972.

Crystal structure information of complex **1-*cis***




| | |
|---|---|
| CCDC Number | 1567101 |
| Empirical formula | $C_{20}H_{22}O_4S_2Pd$ |
| Formula weight | 496.94 |
| Temperature/K | N/A |
| Crystal system | triclinic |
| Space group | P-1 |

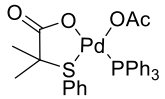
| | |
|---|---|
| a/Å | 9.0235(3) |
| b/Å | 10.1775(4) |
| c/Å | 11.8976(5) |
| α/° | 81.443(2) |
| β/° | 73.982(2) |
| γ/° | 76.298(2) |
| Volume/Å$^3$ | 1016.25(7) |
| Z | 2 |
| $\rho_{calc}$g/cm$^3$ | 1.6239 |
| μ/mm$^{-1}$ | 1.141 |
| F(000) | 502.7 |
| Crystal size/mm$^3$ | 0.479 x 0.178 x 0.114 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.22 to 50.08 |
| Index ranges | -10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -14 ≤ l ≤ 14 |
| Reflections collected | 15109 |
| Independent reflections | 3577 [$R_{int}$ = 0.0346, $R_{sigma}$ = 0.0279] |
| Data/ restraints/ parameters | 3577/0/248 |
| Goodness-of-fit on $F^2$ | 0.913 |
| Final R indexes [I>2σ (I)] | $R_1$ = 0.0266, $wR_2$ = 0.0916 |
| Final R indexes [all data] | $R_1$ = 0.0347, $wR_2$ = 0.1103 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.62/-0.68 |

**Table S1.** Fractional atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$×10$^3$) for **1-*cis***. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Pd1 | 2968.6(3) | 5559.8(2) | 3054.7(2) | 17.75(13) |
| S1 | 4291.4(10) | 3988.7(8) | 4169.7(7) | 18.6(2) |
| S2 | 4356.2(10) | 7195.2(8) | 2872.8(7) | 18.7(2) |
| O1 | 1637(3) | 4182(2) | 3167(2) | 17.1(5) |
| O2 | 1734(3) | 6870(2) | 2021(2) | 19.5(5) |
| O3 | 916(3) | 2283(3) | 4021(2) | 32.3(6) |
| O4 | 1186(3) | 8939(3) | 1183(2) | 33.1(6) |
| C1 | 1681(4) | 3143(3) | 3934(3) | 20.7(7) |
| C2 | 2698(4) | 3032(3) | 4809(3) | 19.5(7) |
| C15 | 5905(4) | 6954(3) | 1552(3) | 19.9(7) |
| C12 | 2791(4) | 8625(3) | 2526(3) | 24.1(8) |
| C3 | 3388(4) | 1558(3) | 5161(3) | 25.1(8) |
| C4 | 1698(4) | 3787(4) | 5868(3) | 26.9(8) |
| C5 | 5722(4) | 2955(3) | 3131(3) | 20.5(7) |
| C6 | 5393(4) | 2532(4) | 2194(3) | 24.7(8) |
| C11 | 1850(4) | 8129(4) | 1830(3) | 21.8(7) |
| C16 | 6007(4) | 6009(4) | 793(3) | 27.3(8) |
| C17 | 7315(5) | 5768(4) | -138(4) | 35.3(9) |

| | | | | |
|---|---|---|---|---|
| C10 | 7248(4) | 2603(4) | 3294(3) | 31.4(9) |
| C14 | 3489(5) | 9825(4) | 1879(4) | 32.2(9) |
| C7 | 6579(4) | 1726(4) | 1428(3) | 30.5(9) |
| C20 | 7094(5) | 7671(4) | 1377(3) | 30.6(9) |
| C19 | 8389(5) | 7442(5) | 423(4) | 40.6(10) |
| C13 | 1696(4) | 8957(4) | 3739(3) | 29.2(8) |
| C8 | 8088(4) | 1358(4) | 1589(4) | 35.5(10) |
| C18 | 8499(5) | 6491(5) | -340(4) | 37.2(10) |
| C9 | 8426(5) | 1805(5) | 2508(4) | 39.1(10) |

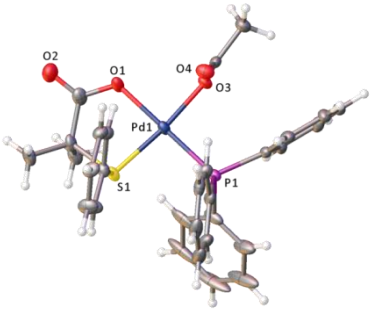
**Procedure for the synthesis of complex 2**



**2**

A solution of $Pd(OAc)_2$ (56.1 mg, 0.25 mmol, 1 equiv), ligand **L2** (49.0 mg, 0.25 mmol, 1 equiv) and $PPh_3$ (65.6 mg, 0.25 mmol, 1 equiv) in $CH_2Cl_2$ (8 mL) was stirred at room temperature for 1 h. The reaction was filtrated through a pad of Celite and evaporated to dryness to afford palladium complex **2** as an orange solid (131.5 mg, 84% yield). Single crystal suitable for X-ray crystallography was obtained by crystallization with a two-solvent system (THF/*n*-heptane). $^1$H NMR (400 MHz, $CDCl_3$) δ = 7.59 (dd, *J* = 12.1, 7.7 Hz, 8H), 7.44 (t, *J* = 7.4 Hz, 4H), 7.33 – 7.27 (m, 8H), 2.02 (s, 3H), 1.75 (bs, 3H), 1.10 (s, 3H); $^{13}$C NMR (101 MHz, $CDCl_3$) δ = 179.7, 179.7, 134.2, 134.1, 134.0, 131.7, 131.7, 131.6, 129.9, 128.7, 128.6, 127.0, 126.4, 126.4, 63.1, 27.7, 25.6, 21.7; $^{31}$P NMR (162 MHz, $CDCl_3$) δ = 26.45 (s); IR ν = 3055, 2925, 1645, 1436, 1302, 1098, 691, 536 cm$^{-1}$; HRMS (FD) calcd for $C_{30}H_{29}O_4PPdS$ $[M]^+$: 622.0559; found: 622.0543.

Crystal structure information of complex **2**




| | |
|---|---|
| CCDC number | 1969711 |
| Empirical formula | $C_{30}H_{29}O_4PPdS$ |
| Formula weight | 622.96 |
| Temperature/K | 100(2) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 10.1765(4) |
| b/Å | 28.3513(11) |
| c/Å | 9.7423(4) |
| α/° | 90 |
| β/° | 106.9510(10) |
| γ/° | 90 |
| Volume/Å$^3$ | 2688.70(19) |

| | |
|---|---|
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.539 |
| $\mu$/mm$^{-1}$ | 0.862 |
| F(000) | 1272.0 |
| Crystal size/mm$^3$ | 0.23 x 0.17 x 0.05 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.85 to 52.912 |
| Index ranges | -12 ≤ h ≤ 12, -34 ≤ k ≤ 35, -12 ≤ l ≤ 12 |
| Reflections collected | 35241 |
| Independent reflections | 5489 [$R_{int}$ = 0.0620, $R_{sigma}$ = 0.0381] |
| Data/ restraints/ parameters | 5489/0/337 |
| Goodness-of-fit on $F^2$ | 1.149 |
| Final R indexes [I>2σ (I)] | $R_1$ = 0.0440, $wR_2$ = 0.0808 |
| Final R indexes [all data] | $R_1$ = 0.0585, $wR_2$ = 0.0852 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.92/-1.06 |

**Table S2.** Fractional atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$×10$^3$) for **2**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

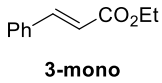
| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| Pd1 | 6811.8(3) | 6472.5(2) | 6676.7(3) | 17.49(8) |
| S1 | 5116.3(9) | 6820.7(3) | 4935.4(10) | 20.5(2) |
| P1 | 8060.0(10) | 6296.9(3) | 5194.7(10) | 17.7(2) |
| O1 | 5622(3) | 6614.2(10) | 8006(3) | 25.8(6) |
| O2 | 3730(3) | 6951.1(11) | 8232(3) | 36.6(7) |
| O3 | 8240(3) | 6190.6(9) | 8402(3) | 20.3(5) |
| O4 | 7013(3) | 5531.6(10) | 7732(3) | 27.3(6) |
| C1 | 4576(4) | 6888.1(14) | 7570(4) | 27.2(9) |
| C2 | 4411(4) | 7168.2(14) | 6177(4) | 24.4(9) |
| C3 | 5349(4) | 7607.4(15) | 6502(5) | 30.8(10) |
| C30 | 8892(4) | 5533.7(15) | 9900(4) | 29.2(9) |
| C29 | 7943(4) | 5754.4(14) | 8565(4) | 20.0(8) |
| C4 | 2925(4) | 7300.9(15) | 5440(5) | 31.3(10) |
| C5 | 3878(4) | 6370.2(13) | 4242(4) | 19.9(8) |
| C6 | 3603(4) | 6012.9(13) | 5088(4) | 20.8(8) |
| C7 | 2664(4) | 5667.3(14) | 4460(4) | 24.4(9) |
| C8 | 2016(4) | 5674.3(15) | 2990(4) | 26.0(9) |
| C9 | 2300(4) | 6029.1(16) | 2145(4) | 32.4(10) |
| C10 | 3225(4) | 6380.2(15) | 2775(4) | 27.8(9) |
| C11 | 7000(4) | 5950.2(14) | 3708(4) | 20.9(8) |
| C12 | 6300(4) | 5564.4(14) | 4053(4) | 21.1(8) |
| C13 | 5397(4) | 5304.9(15) | 2966(5) | 27.4(9) |
| C14 | 5172(4) | 5433.5(17) | 1551(5) | 35.1(11) |
| C15 | 5840(4) | 5817.3(19) | 1198(4) | 38.4(12) |
| C17 | 9607(4) | 5966.2(13) | 6097(4) | 18.6(8) |
| C16 | 6761(4) | 6079.5(16) | 2277(4) | 28.4(9) |

| | | | | |
|---|---|---|---|---|
| C18 | 9627(4) | 5478.9(14) | 6128(4) | 22.6(8) |
| C19 | 10784(4) | 5244.9(15) | 6967(4) | 24.3(9) |
| C20 | 11910(4) | 5493.3(15) | 7787(4) | 25.9(9) |
| C21 | 11906(4) | 5978.2(15) | 7754(4) | 26.3(9) |
| C22 | 10751(4) | 6216.1(14) | 6902(4) | 23.7(8) |
| C23 | 8683(4) | 6797.3(16) | 4414(5) | 32.4(11) |
| C24 | 8351(5) | 7248.5(16) | 4722(5) | 42.2(13) |
| C25 | 8856(6) | 7636(2) | 4147(7) | 69(2) |
| C26 | 9659(7) | 7566(3) | 3261(8) | 94(3) |
| C27 | 9986(5) | 7120(3) | 2945(7) | 82(3) |
| C28 | 9520(4) | 6726(2) | 3531(5) | 48.0(14) |

**Reactivity of Pd complexes in the C–H olefination of benzene**

Pd catalyst (12.5 µmol, 5 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (0.25 mL, 2.8 mmol, 11.2 equiv) and AcOH (1.25 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a screw cap and the reaction was placed in a 100 °C pre-heated oil bath and stirred for 2 h. The resulting mixture was diluted with EtOAc, filtered through a plug of Celite and concentrated under reduced pressure. The $^1$H NMR yield was determined by adding $CH_2Br_2$ (17.5 µL, 0.25 mmol, 1 equiv) as an internal standard.

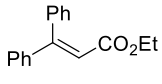
**Ethyl cinnamate (3-mono)**



**3-mono**

$^1$H NMR spectra data matched with the spectra data reported in the literature for this compound.[2] $^1$H NMR (300 MHz) δ = 7.69 (d, *J* = 16.0 Hz, 1H), 7.54 - 7.51 (m, 2H), 7.40 - 7.36 (m, 3H), 6.44 (d, *J* = 16.0 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H).

**Ethyl 3,3-diphenylacrylate (3-di)**



**3-di**

$^1$H NMR spectra data matched with the spectra data reported in the literature for this compound.[3] $^1$H NMR (400 MHz) δ = 7.42 – 7.33 (m, 8H), 7.26 – 7.23 (m, 2H), 6.40 (s, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 1.14 (t, *J* = 7.1 Hz, 3H).

**Table S3.** The amount of catalyst.

| Entry | Amount of catalyst |
|---|---|
| 1 | $Pd(OAc)_2$ 2.8 mg |
| 2 | $Pd(OAc)_2$ 2.8 mg and **L2** 2.5 mg |
| 3 | $Pd(OAc)_2$ 2.8 mg and **L2** 4.9 mg (25 µmol, 10 mol%) |
| 4 | Complexes **1-*cis*** and **1-*trans*** 6.2 mg |
| 5 | $Pd(OAc)_2$ 2.8 mg, **L2** 2.5 mg and $PPh_3$ 3.3 mg |
| 6 | Complex **2** 7.8 mg |

**Kinetic profile of the C–H olefination of benzene with different Pd-catalyst**

Pd catalyst (5 mol%), *t*-butyl peroxybenzoate (1 equiv), ethyl acrylate (1 equiv), benzene (11.2 equiv) and AcOH (0.2 M) were added into a pressure tube. The pressure tube was sealed with a crimp cap with septa and the reaction was placed in a 100 °C pre-heated oil bath. The reaction

was followed during the indicated time by sampling 50 µL. PhCl (10 µL) was added in each sample as an internal standard for quantitative GC analysis. The reaction mixture was diluted with EtOAc (1 mL). The organic layer was quenched with saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was filtered through a plug of anh. $MgSO_4$ and analyzed by GC.

$Pd(OAc)_2$ (5.6 mg, 25 µmol, 5 mol%), *t*-butyl peroxybenzoate (94 µL, 0.5 mmol, 1 equiv), ethyl acrylate (53 µL, 0.5 mmol, 1 equiv), benzene (0.5 mL, 5.6 mmol, 11.2 equiv) and AcOH (2.5 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a crimp cap with septa and the reaction was placed in a 100 °C pre-heated oil bath. The reaction was followed during the indicated time by sampling 50 µL. PhCl (10 µL) was added in each sample as an internal standard for quantitative GC analysis. The reaction mixture was diluted with EtOAc (1 mL). The organic layer was quenched with saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was filtered through a plug of anh. $MgSO_4$ and analyzed by GC.

Parallel reaction using $Pd(OAc)_2$ and ligand **L2** was performed to compare the kinetic profile. $Pd(OAc)_2$ (5.6 mg, 25 µmol, 5 mol%), ligand **L2** (4.9 mg, 25 µmol, 5 mol%), *t*-butyl peroxybenzoate (94 µL, 0.5 mmol, 1 equiv), ethyl acrylate (53 µL, 0.5 mmol, 1 equiv), benzene (0.5 mL, 5.6 mmol, 11.2 equiv) and AcOH (2.5 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a crimp cap with septa and the reaction was placed in a 100 °C pre-heated oil bath. The reaction was followed during the indicated time by sampling 50 µL. PhCl (10 µL) was added in each sample as an internal standard for quantitative GC analysis. The reaction mixture was diluted with EtOAc (1 mL). The organic layer was quenched with saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was filtered through a plug of anh. $MgSO_4$ and analyzed by GC.

Parallel reaction using complexes **1-*cis*** and **1-*trans*** was performed to compare the kinetic profile. Complexes **1-*cis*** and **1-*trans*** (12.4 mg, 25 µmol, 5 mol%), *t*-butyl peroxybenzoate (94 µL, 0.5 mmol, 1 equiv), ethyl acrylate (53 µL, 0.5 mmol, 1 equiv), benzene (0.5 mL, 5.6 mmol, 11.2 equiv) and AcOH (2.5 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a crimp cap with septa and the reaction was placed in a 100 °C pre-heated oil bath. The reaction was followed during the indicated time by sampling 50 µL. PhCl (10 µL) was added in each sample as an internal standard for quantitative GC analysis. The reaction mixture was diluted with EtOAc (1 mL). The organic layer was quenched with saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was filtered through a plug of anh. $MgSO_4$ and analyzed by GC.

Parallel reaction using complex **2** was performed to compare the kinetic profile. Complex **2** (15.6 mg, 25 µmol, 5 mol%), *t*-butyl peroxybenzoate (94 µL, 0.5 mmol, 1 equiv), ethyl acrylate (53 µL, 0.5 mmol, 1 equiv), benzene (0.5 mL, 5.6 mmol, 11.2 equiv) and AcOH (2.5 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a crimp cap with septa and the reaction was placed in a 100 °C pre-heated oil bath. The reaction was followed during the indicated time by sampling 50 µL. PhCl (10 µL) was added in each sample as an internal standard for quantitative GC analysis. The reaction mixture was diluted with EtOAc (1 mL). The organic layer was quenched with saturated aqueous $NaHCO_3$ solution (1 mL). The organic layer was filtered through a plug of anh. $MgSO_4$ and analyzed by GC.

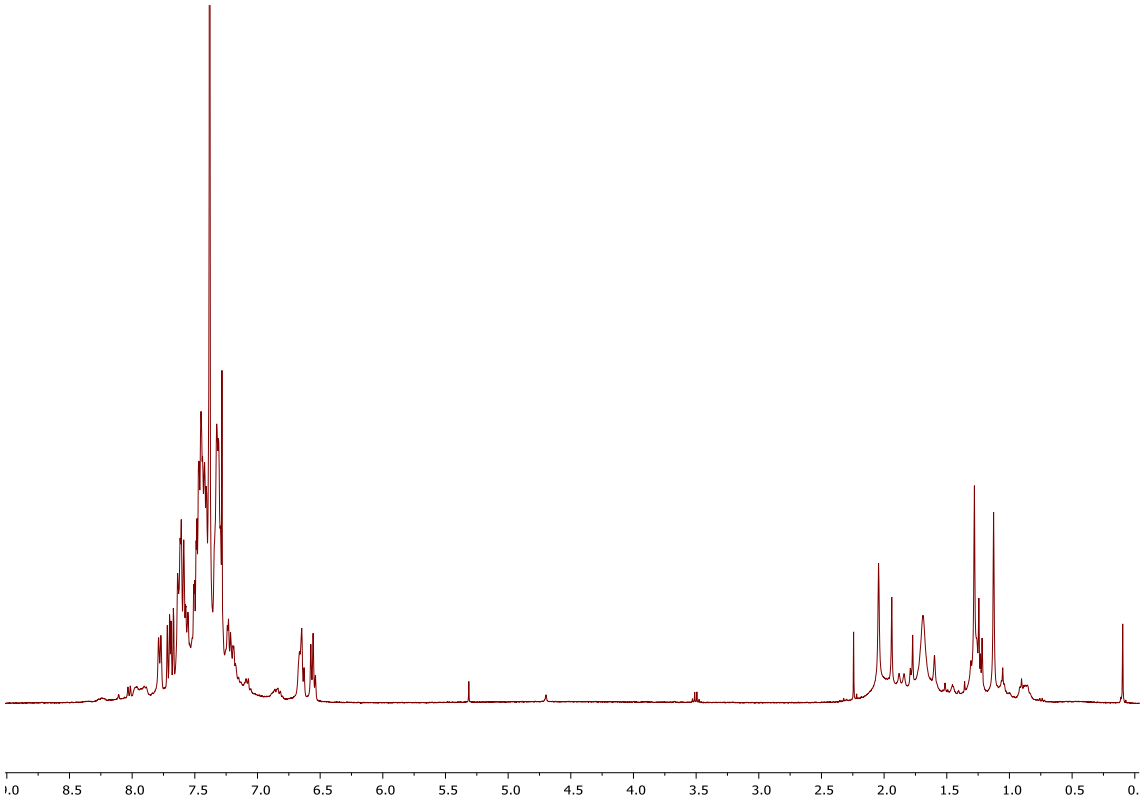
**Table S4.** Kinetic profile of the Pd-catalyzed C–H olefination of benzene.

| Entry | Reaction time | GC yield | | | |
|---|---|---|---|---|---|
| | | $Pd(OAc)_2$ | $Pd(OAc)_2$ + ligand L2 | Complexes 1-*cis* and 1-*trans* | Complex 2 |
| 1 | 15 min | 1% | 17% | 9% | 22% |
| 2 | 30 min | 3% | 40% | 21% | 42% |
| 3 | 45 min | 4% | 57% | 31% | 57% |
| 4 | 1 h | 6% | 74% | 40% | 74% |
| 5 | 1.5 h | 10% | 84% | 52% | 90% |
| 6 | 2 h | 14% | 80% | 62% | 83% |

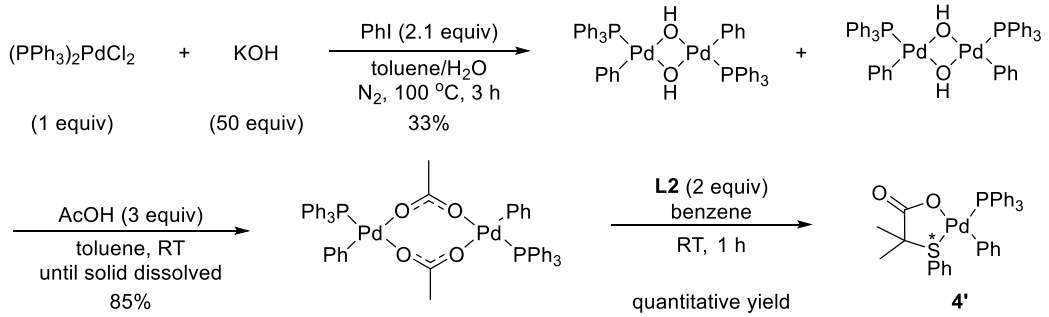
Note: The reactions were performed at the same time to compare the kinetic profiles.

**Procedure for the reaction of complex 2 and benzene**

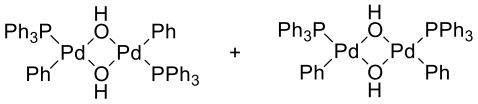
Complex **2** (30 mg, 48.0 µmol, 1 equiv) and benzene (0.25 mL) were added into a pressure tube. The pressure tube was sealed with a screw cap and the reaction was placed in a 100 °C pre-heated oil bath and stirred for 10 minutes. The reaction was cooled down to room temperature. The resulting mixture was diluted with $CH_2Cl_2$, filtered through a plug of Celite and concentrated under reduced pressure. The resulting crude was measured by $^1H$ NMR.



**Procedure for the synthesis of complex 4'**

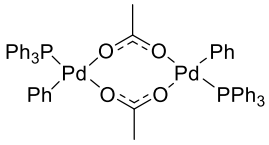



**Complex [PhPd(PPh$_3$)(μ-OH)]$_2$**



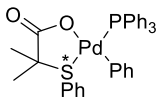
Complex [PhPd(PPh$_3$)(μ-OH)]$_2$ was prepared following the procedure described in the literature.[4] Degassed toluene (20 mL) and degassed water (4 mL) were added to Pd(PPh$_3$)$_2$Cl$_2$ (1.00 g, 1.42 mmol, 1 equiv) and KOH (4.00g, 71 mmol, 50 equiv) under nitrogen atmosphere followed by PhI (0.34 mL, 3.00 mmol, 2.1 equiv). The reaction was heated at 100 °C for 3 h with vigorous stirred. The hot solution was filtered through a short pad of Celite. The filtrated was separated and extracted with toluene (3 x 20 mL). The combined organic layers were dried over anh. MgSO$_4$, filtered and concentrated under reduced pressure to obtain a yellow solid. The resulting solid was triturated with acetone (5 mL) overnight and the obtained solid was filtered and washed with acetone (2 x 3 mL) to obtain a white solid (0.44 g, 33% yield). $^1$H and $^{31}$P NMR spectra data matched with the spectra data reported in the literature for this compound.[4a] $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.50 – 7.46 (m, 10H), 7.41 – 7.31 (m, 8H), 7.26 – 7.19 (m, 12H), 7.06 – 7.04 (m, 4H), 6.68 – 6.60 (m, 6H); $^{31}$P NMR (162 MHz, CDCl$_3$) δ = 33.54 (s, *trans*), 32.85 (s, *cis*).

**Complex [PhPd(PPh$_3$)(μ-OAc)]$_2$**



Complex [PhPd(PPh$_3$)(μ-OAc)]$_2$ was prepared following the procedure described in the literature.[4a] AcOH (60 μL, 1.05 mmol, 3 equiv) was added to the suspension of complex [PhPd(PPh$_3$)(μ-OH)]$_2$ (324 mg, 0.35 mmol, 1 equiv) in toluene (10 mL). The reaction was stirred at room temperature until solid was completely dissolved. The reaction was then concentrated under reduced pressure. The solid was washed with petroleum ether (3 x 5 mL) and dried under vacuum to obtain a yellow powder (300 mg, 85% yield). $^1$H and $^{31}$P NMR spectra data matched with the spectra data reported in the literature for this compound.[4a] $^1$H NMR (400 MHz, C$_6$D$_6$) δ = 7.77 (bs, 4H), 7.52 – 7.47 (m, 12H), 6.93 – 6.83 (m, 24H), 1.59 (s, 6H); $^{31}$P NMR (162 MHz, C$_6$D$_6$) δ = 29.97 (s).

**Complex 4'**

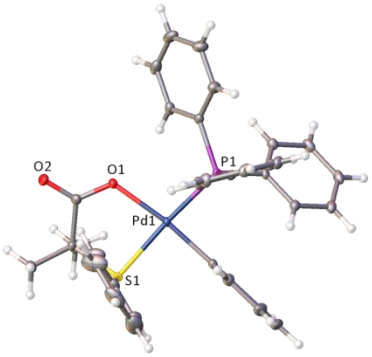


**4'**

Complex **4'** was prepared following a similar procedure to the one described in the literature.[4a] Complex [PhPd(PPh$_3$)(μ-OAc)]$_2$ (100 mg, 0.1 mmol, 1 equiv) and ligand **L2** (39.3 mg, 0.2 mmol, 2 equiv) were stirred in benzene at room temperature. After 1 h, the solvent was removed under reduced pressure to obtain a pale yellow solid (130 mg, quantitative yield). Single crystal suitable for X-ray crystallography was obtained by crystallization with a two-solvent system (THF/*n*-heptane). $^1$H NMR (400 MHz, THF-d$_8$) δ = 7.78 (d, *J* = 6.8 Hz, 2H), 7.52 – 7.37 (m, 12H), 7.30 – 7.28 (m, 6H),

6.64 (d, *J* = 6.6 Hz, 2H), 6.53 (t, *J* = 6.8 Hz, 1H), 6.45 (t, *J* = 7.2 Hz, 2H), 1.54 (s, 6H); $^{13}$C NMR (101 MHz, THF-$d_8$) δ = 179.1, 146.8 (d, *J* = 7.2 Hz), 136.7 (d, *J* = 3.8 Hz), 135.5, 135.4, 135.2, 131.7, 131.5 (d, *J* = 1.9 Hz), 131.2, 131.2, 130.5, 130.4, 129.4, 129.3, 129.2, 128.1, 123.5, 59.5, 27.7; $^{31}$P NMR (162 MHz, THF-$d_8$) δ = 24.48 (s); IR ν = 1620, 1303, 1097, 735, 690, 529 cm$^{-1}$; HRMS (FD) calcd for $C_{34}H_{31}O_2PPdS$ $[M]^+$: 640.0817; found: 640.1009.

Crystal structure information of complex **4'A**

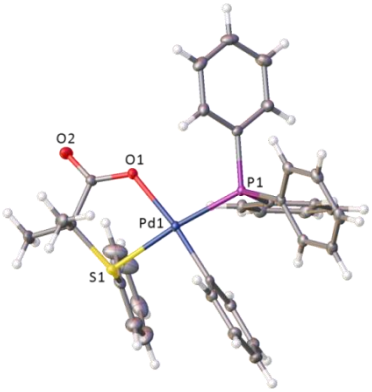



| | |
|---|---|
| CCDC number | 1969712 |
| Empirical formula | $C_{34}H_{31}O_2PPdS$ |
| Formula weight | 641.02 |
| Temperature/K | 100(2) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.7129(4) |
| b/Å | 11.8850(4) |
| c/Å | 24.9669(9) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2882.12(19) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.477 |
| μ/mm$^{-1}$ | 0.802 |
| F(000) | 1312.0 |
| Crystal size/mm$^3$ | 0.330 x 0.300 x 0.120 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.976 to 59.268 |
| Index ranges | -13 ≤ h ≤ 13, -16 ≤ k ≤ 16, -34 ≤ l ≤ 34 |
| Reflections collected | 53234 |
| Independent reflections | 8114 [$R_{int}$ = 0.0236, $R_{sigma}$ = 0.0172] |
| Data/ restraints/ parameters | 8114/0/354 |
| Goodness-of-fit on F$^2$ | 1.086 |
| Final R indexes [I>2σ (I)] | $R_1$ = 0.0163, w$R_2$ = 0.0389 |
| Final R indexes [all data] | $R_1$ = 0.0173, w$R_2$ = 0.0392 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.29/-0.51 |
| Flack parameter | -0.013(4) |

**Table S5.** Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **4'A**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| Pd1 | 7138.3(2) | 5911.4(2) | 6231.0(2) | 9.25(3) |
| S1 | 7842.2(5) | 7332.0(3) | 6825.9(2) | 12.71(8) |
| P1 | 6104.5(5) | 4611.4(4) | 5696.5(2) | 9.27(8) |
| O1 | 8217.0(14) | 4842.8(11) | 6758.2(5) | 14.1(3) |
| O2 | 9287.0(18) | 4660.2(12) | 7540.1(6) | 23.8(3) |
| C1 | 6177(2) | 7070.0(15) | 5790.7(7) | 11.9(3) |
| C2 | 4805(2) | 7374.3(17) | 5875.9(8) | 15.5(4) |
| C3 | 4196(2) | 8214.7(17) | 5564.9(9) | 20.5(4) |
| C4 | 4943(2) | 8746.9(17) | 5163.3(9) | 22.6(4) |
| C5 | 6318(2) | 8461.6(17) | 5083.0(8) | 19.7(4) |
| C6 | 6930.7(19) | 7637.3(15) | 5399.7(7) | 14.6(3) |
| C7 | 8857(2) | 5238.0(16) | 7166.1(7) | 13.6(3) |
| C8 | 9178(2) | 6520.9(16) | 7179.9(8) | 14.0(4) |
| C9 | 10474(2) | 6726.3(17) | 6839.7(9) | 20.3(4) |
| C10 | 9409(3) | 6977.5(18) | 7742.9(8) | 22.1(4) |
| C11 | 6327(2) | 7311.7(17) | 7230.8(8) | 17.2(4) |
| C12 | 5997(3) | 6439(2) | 7575.5(11) | 34.3(6) |
| C13 | 4743(3) | 6467(2) | 7853.1(13) | 44.9(8) |
| C14 | 3829(3) | 7345(2) | 7778.5(11) | 36.1(6) |
| C15 | 4160(3) | 8190(3) | 7433.0(11) | 36.7(6) |
| C16 | 5414(2) | 8192(2) | 7161.0(10) | 27.3(5) |
| C17 | 4301.9(19) | 4480.3(15) | 5887.2(7) | 11.1(3) |
| C18 | 4010.4(19) | 4552.0(17) | 6436.5(7) | 14.6(4) |
| C19 | 2696(2) | 4324.6(16) | 6624.9(7) | 17.1(4) |
| C20 | 1650.2(17) | 4042.4(17) | 6268.0(8) | 16.9(3) |
| C21 | 1926.8(17) | 3975.3(16) | 5723.4(7) | 15.7(3) |
| C22 | 3254.8(17) | 4189.2(16) | 5532.0(7) | 12.9(3) |
| C23 | 6158.1(18) | 4803.3(15) | 4972.0(7) | 11.3(3) |
| C24 | 5378.9(19) | 5653.2(15) | 4727.1(7) | 13.2(3) |
| C25 | 5459.8(19) | 5819.3(17) | 4175.8(7) | 15.9(3) |
| C26 | 6316(2) | 5154.7(17) | 3860.1(7) | 17.7(4) |
| C27 | 7099(2) | 4316.2(15) | 4101.8(7) | 17.0(3) |
| C28 | 7021.4(18) | 4139.3(16) | 4653.6(7) | 14.0(3) |
| C29 | 6717.5(19) | 3176.0(15) | 5789.0(7) | 11.9(3) |
| C30 | 8105.6(19) | 2986.7(16) | 5900.5(7) | 15.5(4) |
| C31 | 8587(2) | 1894.0(18) | 5974.6(8) | 20.1(4) |
| C32 | 7691(2) | 993.8(18) | 5940.7(8) | 22.3(4) |
| C33 | 6309(2) | 1172.7(17) | 5820.5(9) | 22.1(4) |
| C34 | 5824(2) | 2257.6(17) | 5744.8(8) | 17.8(4) |

Crystal structure information of complex **4'B**




| | |
|---|---|
| CCDC number | 1969713 |
| Empirical formula | $C_{34}H_{31}O_2PPdS$ |
| Formula weight | 641.02 |
| Temperature/K | 100(2) |
| Crystal system | orthorhombic |
| Space group | $P2_12_12_1$ |
| a/Å | 9.6976(5) |
| b/Å | 11.8942(7) |
| c/Å | 24.9749(15) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 2880.7(3) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.478 |
| μ/mm$^{-1}$ | 0.802 |
| F(000) | 1312.0 |
| Crystal size/mm$^3$ | 0.12 x 0.10 x 0.06 |
| Radiation | MoKα (λ = 0.71073) |
| 2Θ range for data collection/° | 5.974 to 54.388 |
| Index ranges | -12 ≤ h ≤ 12, -15 ≤ k ≤ 15, -32 ≤ l ≤ 32 |
| Reflections collected | 55231 |
| Independent reflections | 6397 [$R_{int}$ = 0.0281, $R_{sigma}$ = 0.0159] |
| Data/ restraints/ parameters | 6397/0/354 |
| Goodness-of-fit on F$^2$ | 1.085 |
| Final R indexes [I>2σ (I)] | $R_1$ = 0.0155, $wR_2$ = 0.0380 |
| Final R indexes [all data] | $R_1$ = 0.0164, $wR_2$ = 0.0385 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.25/-0.43 |
| Flack parameter | -0.030(4) |

**Table S6.** Fractional atomic coordinates (×10$^4$) and equivalent isotropic displacement parameters (Å$^2$×10$^3$) for **4'B**. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| Pd1 | 7139.5(2) | 5911.0(2) | 3769.0(2) | 9.73(4) |

| | | | | |
|---|---|---|---|---|
| S1 | 7843.5(6) | 7331.0(4) | 3174.0(2) | 13.23(10) |
| P1 | 6105.3(5) | 4612.0(5) | 4303.5(2) | 9.65(10) |
| O1 | 8218.2(16) | 4841.1(13) | 3242.2(6) | 14.3(3) |
| O2 | 9289(2) | 4659.6(14) | 2459.9(7) | 24.1(4) |
| C1 | 6178(2) | 7069.4(18) | 4210.3(9) | 12.4(4) |
| C2 | 4806(2) | 7374(2) | 4124.2(9) | 15.9(4) |
| C3 | 4198(2) | 8214(2) | 4435.6(10) | 21.2(5) |
| C4 | 4943(3) | 8744(2) | 4836.7(10) | 22.8(5) |
| C5 | 6317(3) | 8460(2) | 4915.9(10) | 20.4(5) |
| C6 | 6932(2) | 7637.5(18) | 4601.7(9) | 14.9(4) |
| C7 | 8858(2) | 5237.9(18) | 2833.3(9) | 13.6(4) |
| C8 | 9179(2) | 6522.0(19) | 2819.5(9) | 14.8(4) |
| C9 | 10479(2) | 6727(2) | 3159.6(10) | 21.0(5) |
| C10 | 9410(3) | 6977(2) | 2256.4(10) | 22.5(5) |
| C11 | 6326(2) | 7309(2) | 2769.3(9) | 17.7(5) |
| C12 | 5414(3) | 8191(2) | 2837.7(11) | 28.2(6) |
| C13 | 4161(3) | 8190(3) | 2566.0(12) | 36.7(7) |
| C14 | 3829(3) | 7343(3) | 2221.2(12) | 36.0(7) |
| C15 | 4743(4) | 6466(3) | 2146.1(14) | 45.4(9) |
| C16 | 5993(3) | 6439(2) | 2424.5(12) | 34.7(7) |
| C17 | 6717(2) | 3177.2(18) | 4212.4(8) | 12.5(4) |
| C18 | 5824(2) | 2257(2) | 4255.2(9) | 17.7(5) |
| C19 | 6307(3) | 1172(2) | 4179.5(10) | 22.4(5) |
| C20 | 7691(3) | 992(2) | 4060.1(9) | 22.7(5) |
| C21 | 8586(3) | 1894(2) | 4026.0(9) | 20.6(5) |
| C22 | 8105(2) | 2985.2(19) | 4098.7(9) | 15.8(5) |
| C23 | 6158(2) | 4803.6(18) | 5028.3(8) | 12.1(4) |
| C24 | 5380(2) | 5655.6(18) | 5273.0(9) | 14.0(4) |
| C25 | 5461(2) | 5819(2) | 5823.6(9) | 16.6(4) |
| C26 | 6317(2) | 5155.2(19) | 6139.7(9) | 18.0(5) |
| C27 | 7100(3) | 4316.4(18) | 5897.5(8) | 17.4(4) |
| C28 | 7021(2) | 4138.7(19) | 5347.2(8) | 14.4(4) |
| C29 | 4299(2) | 4479.4(18) | 4112.7(9) | 11.8(4) |
| C30 | 4012(2) | 4552(2) | 3564.6(9) | 15.3(4) |
| C31 | 2699(2) | 4324.7(19) | 3375.6(9) | 18.0(5) |
| C32 | 1650(2) | 4042(2) | 3731.2(9) | 17.1(4) |
| C33 | 1929(2) | 3975.8(19) | 4276.4(9) | 16.2(4) |
| C34 | 3253(2) | 4190.1(19) | 4467.7(8) | 13.6(4) |

**Procedure for the reaction of complex 4' and ethyl acrylate**

Complex **4'** (32 mg, 50.0 µmol, 1 equiv) and ethyl acrylate (0.25 mL, 2.35 mmol) were added into a pressure tube. The pressure tube was sealed with a screw cap and the reaction was placed in a 100 °C pre-heated oil bath and stirred for 2 h. The reaction was cooled down to room temperature. The resulting mixture was diluted with EtOAc, filtered through a plug of Celite and concentrated under reduced pressure. The $^{1}$H NMR yield was determined by adding $CH_2Br_2$ (6.0

µL, 85.0 µmol, 1.7 equiv) as an internal standard. The reaction provided the olefinated product in 90% $^{1}$H NMR yield.

**3. Identification of palladium complexes during the catalytic reaction**

**Procedure for the C–H olefination of benzene (the reaction is performed in an NMR tube)**

$Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 50 mol%), ligand **L2** (9.8 mg, 0.05 mmol, 50 mol%), $PPh_3$ (13.1 mg, 0.05 mmol, 50 mol%), *tert*-butyl peroxybenzoate (19 µL, 0.1 mmol, 1 equiv), ethyl acrylate (11 µL, 0.1 mmol, 1 equiv), benzene (0.1 mL, 1.12 mmol, 11.2 equiv) and AcOD-$d_4$ (0.5 mL) were added into an NMR tube. The NMR tube was sealed with a screw cap. The reaction was placed in a 100 °C pre-heated oil bath and followed during the indicated time. $^{1}$H and $^{31}$P NMR spectra were collected at room temperature.

**Procedure for the reaction of $Pd(OAc)_2$, ligand L2, $PPh_3$ and benzene (the reaction is performed in an NMR tube)**

$Pd(OAc)_2$ (11.2 mg, 0.05 mmol, 1 equiv), ligand **L2** (9.8 mg, 0.05 mmol, 1 equiv), $PPh_3$ (13.1 mg, 0.05 mmol, 1 equiv), benzene (0.1 mL) and AcOD-$d_4$ (0.5 mL) were added into an NMR tube. The NMR tube was sealed with a screw cap. The reaction was placed in a 100 °C pre-heated oil bath and followed during the indicated time. $^{1}$H and $^{31}$P NMR spectra were collected at room temperature.

**4. Kinetic investigations**

**Procedure for kinetic order of the reaction**

$Pd(OAc)_2$, ligand **L1**, *tert*-butyl peroxybenzoate, ethyl acrylate, benzene, NaOAc and AcOH (1.25 mL) were added into a pressure tube. The pressure tube was sealed with a crimp cap with septa and the reaction was placed in a 100 °C pre-heated oil bath. The reaction was followed during the indicated time by sampling 50 µL. PhCl (10 µL) was added in each sample as an internal standard for quantitative GC analysis. The reaction mixture was diluted with EtOAc (0.5 mL). The organic layer was quenched with saturated aqueous $NaHCO_3$ solution (0.5 mL). The organic layer was filtered through a plug of anh. $MgSO_4$ and analyzed by GC.

**Order of catalyst with ligand L1**

General procedure was followed using $Pd(OAc)_2$ (2.5–12.5 mol%), ligand **L1** (0.0843 M in AcOH) (2.5–12.5 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (0.25 mL, 0.28 mmol, 11.2 equiv) and AcOH (1.25 mL, 0.2 M). The reaction was sampling at 4, 8, 12, 16 and 20 min.

**Table S7.** Amount of catalyst.

| Entry | Amount of $Pd(OAc)_2$ | Amount of ligand L1 | AcOH (mL) | [catalyst] (mM) |
|---|---|---|---|---|
| 1 | 1.4 mg, 6.25 µmol, 2.5 mol% | 75 µL, 6.25 µmol, 2.5 mol% | 1.175 | 4.17 |
| 2 | 2.8 mg, 12.50 µmol, 5 mol% | 150 µL, 12.50 µmol, 5 mol% | 1.1 | 8.33 |
| 3 | 4.2 mg, 18.75 µmol, 7.5 mol% | 225 µL, 18.75 µmol, 7.5 mol% | 1.025 | 12.50 |
| 4 | 5.6 mg, 25.00 µmol, 10 mol% | 300 µL, 25.00 µmol, 10 mol% | 0.95 | 16.67 |
| 5 | 7.0 mg, 31.25 µmol, 12.5 mol% | 375 µL, 31.25 µmol, 12.5 mol% | 0.875 | 20.83 |

**Table S8.** Data used to determine the rate of the reactions with different concentrations of catalyst with ligand **L1**.

| Entry | [catalyst] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.07 h | 0.13 h | 0.2 h | 0.26 h | 0.33 h |
| 1 | 4.17 | 0.56 | 1.79 | 4.94 | 9.08 | 13.62 |
| 2 | 8.33 | 0.84 | 3.96 | 11.49 | 18.78 | 27.25 |
| 3 | 12.50 | 1.29 | 6.24 | 15.29 | 26.79 | 40.18 |
| 4 | 16.67 | 1.26 | 8.65 | 22.63 | 38.34 | 50.82 |
| 5 | 20.83 | 2.00 | 11.03 | 25.21 | 45.23 | 60.66 |

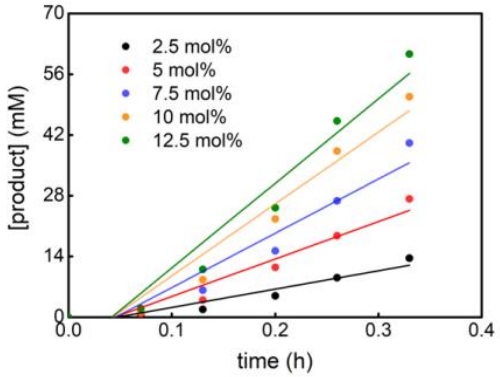



**Figure S1.** Plot of time (h) versus [product] (mM) with different concentrations of catalyst with ligand **L1** to determine the rate of the reactions.

**Table S9.** Data used to determine the order of catalyst with ligand **L1**.

| Entry | [catalyst] (mM) | *k* (mM/h) | $R^2$ | log[catalyst] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 4.17 | 42.26 | 0.9165 | 0.62 | 1.63 |
| 2 | 8.33 | 86.24 | 0.9349 | 0.92 | 1.94 |
| 3 | 12.50 | 125.01 | 0.9274 | 1.10 | 2.10 |
| 4 | 16.67 | 165.40 | 0.9438 | 1.22 | 2.22 |
| 5 | 20.83 | 194.96 | 0.9419 | 1.32 | 2.29 |

**Order of benzene with ligand L1**

General procedure was followed using $Pd(OAc)_2$ (2.8 mg, 12.5 µL, 5 mol%), ligand **L1** (0.0843 M in AcOH) (150 µL, 12.5 µmol, 5 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (6.7–24.7 equiv), $C_6F_6$ and AcOH (1.1 mL, 0.2 M). The reaction was sampling at 5, 10, 15, 20 and 25 min.

**Table S10.** Amount of benzene.

| Entry | Amount of benzene | Amount of $C_6F_6$ | [benzene] (mM) |
|---|---|---|---|
| 1 | 0.15 mL, 1.675 mmol, 6.7 equiv | 0.6 mL | 837.50 |
| 2 | 0.25 mL, 2.8 mmol, 11.2 equiv | 0.5 mL | 1400.00 |
| 3 | 0.35 mL, 3.925 mmol, 15.7 equiv | 0.4 mL | 1962.50 |
| 4 | 0.45 mL, 5.05 mmol, 20.2 equiv | 0.3 mL | 2525.00 |
| 5 | 0.55 mL, 6.175 mmol, 24.7 equiv | 0.2 mL | 3087.50 |

**Table S11.** Data used to determine the rate of the reactions with different concentrations of benzene with ligand **L1**.

| Entry | [benzene] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.08 h | 0.17 h | 0.25 h | 0.33 h | 0.42 h |
| 1 | 837.50 | 0 | 1.44 | 3.35 | 4.90 | 7.18 |
| 2 | 1400.00 | 1.01 | 2.10 | 5.43 | 9.39 | 13.47 |
| 3 | 1962.50 | 1.19 | 2.93 | 6.48 | 11.86 | 16.39 |
| 4 | 2525.00 | 0.84 | 4.15 | 10.78 | 19.72 | 27.10 |
| 5 | 3087.50 | 1.40 | 4.92 | 12.33 | 23.50 | 33.16 |

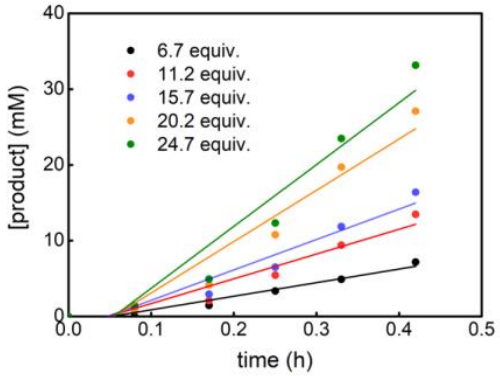



**Figure S2.** Plot of time (h) versus [product] (mM) with different concentrations of benzene with ligand **L1** to determine the rate of the reactions.

**Table S12.** Data used to determine the order of benzene with ligand **L1**.

| Entry | [benzene] (mM) | *k* (mM/h) | $R^2$ | log[benzene] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 837.50 | 17.93 | 0.9528 | 2.92 | 1.25 |
| 2 | 1400.00 | 32.69 | 0.9347 | 3.15 | 1.51 |
| 3 | 1962.50 | 40.07 | 0.9397 | 3.29 | 1.60 |
| 4 | 2525.00 | 67.80 | 0.9329 | 3.40 | 1.83 |
| 5 | 3087.50 | 81.71 | 0.9256 | 3.49 | 1.91 |

**Order of oxidant with ligand L1**

General procedure was followed using $Pd(OAc)_2$ (2.8 mg, 12.5 µL, 5 mol%), ligand **L1** (0.0843 M in AcOH) (150 µL, 12.5 µmol, 5 mol%), *tert*-butyl peroxybenzoate (0.5–1.25 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (0.25 mL, 2.8 mmol, 11.2 equiv) and AcOH (1.1 mL, 0.2 M). The reaction was sampling at 5, 10, 15, 20 and 25 min.

**Table S13.** Amount of oxidant.

| Entry | Amount of oxidant | [oxidant] (mM) |
|---|---|---|
| 1 | 24 µL, 0.125 mmol, 0.5 equiv | 83.33 |
| 2 | 36 µL, 0.188 mmol, 0.75 equiv | 125.00 |
| 3 | 47 µL, 0.25 mmol, 1 equiv | 166.67 |
| 4 | 59 µL, 0.313 mmol, 1.25 equiv | 208.33 |

**Table S14.** Data used to determine the rate of the reactions with different concentrations of oxidant with ligand **L1**.

| Entry | [oxidant] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.08 h | 0.17 h | 0.25 h | 0.33 h | 0.42 h |
| 1 | 83.33 | 1.49 | 8.86 | 20.05 | 33.13 | 39.79 |
| 2 | 125.00 | 1.74 | 7.63 | 18.34 | 29.21 | 38.82 |
| 3 | 166.67 | 1.23 | 7.44 | 18.30 | 29.36 | 39.17 |
| 4 | 208.33 | 1.14 | 6.97 | 16.17 | 27.35 | 36.43 |

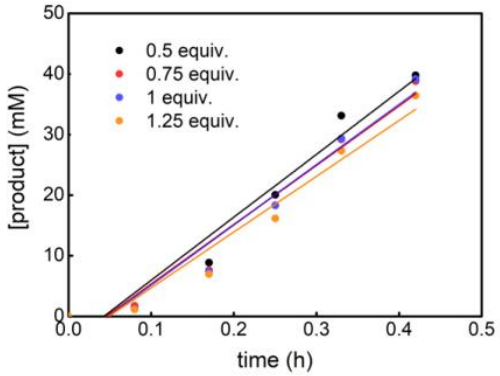



**Figure S3.** Plot of time (h) versus [product] (mM) with different concentrations of oxidant with ligand **L1** to determine the rate of the reactions.

**Table S15.** Data used to determine the order of oxidant with ligand **L1**.

| Entry | [oxidant] (mM) | *k* (mM/h) | $R^2$ | log[oxidant] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 83.33 | 103.99 | 0.9583 | 1.92 | 2.02 |
| 2 | 125.00 | 97.96 | 0.9572 | 2.10 | 1.99 |
| 3 | 166.67 | 99.31 | 0.9541 | 2.22 | 2.00 |
| 4 | 208.33 | 92.11 | 0.9511 | 2.32 | 1.96 |

**Order of olefin with ligand L1**

General procedure was followed using $Pd(OAc)_2$ (2.8 mg, 12.5 µL, 5 mol%), ligand **L1** (0.0843 M in AcOH) (150 µL, 12.5 µmol, 5 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (0.5–1.5 equiv), benzene (0.25 mL, 2.8 mmol, 11.2 equiv) and AcOH (1.1 mL, 0.2 M). The reaction was sampling at 5, 10, 15, 20 and 25 min.

**Table S16.** Amount of olefin.

| Entry | Amount of olefin | [olefin] (mM) |
|---|---|---|
| 1 | 14 µL, 0.125 mmol, 0.5 equiv | 83.33 |
| 2 | 27 µL, 0.25 mmol, 1 equiv | 166.67 |
| 3 | 34 µL, 0.313 mmol, 1.25 equiv | 208.33 |
| 4 | 41 µL, 0.375 mmol, 1.5 equiv | 250.00 |

**Table S17.** Data used to determine the rate of the reactions with different concentrations of olefin with ligand **L1**.

| Entry | [olefin] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.08 h | 0.17 h | 0.25 h | 0.33 h | 0.42 h |
| 1 | 83.33 | 1.35 | 9.53 | 20.12 | 33.14 | 42.25 |
| 2 | 166.67 | 1.20 | 9.34 | 18.05 | 30.97 | 42.25 |
| 3 | 208.33 | 1.03 | 7.86 | 16.46 | 25.77 | 35.76 |
| 4 | 250.00 | 1.55 | 6.83 | 17.11 | 25.43 | 34.36 |

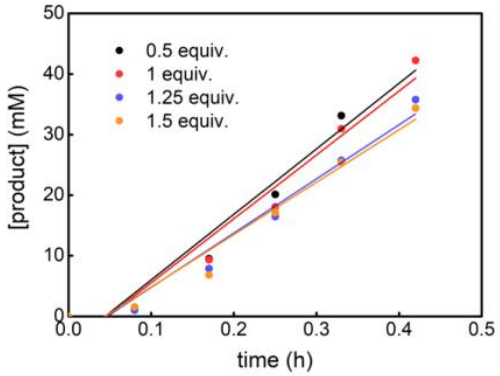



**Figure S4.** Plot of time (h) versus [product] (mM) with different concentrations of olefin with ligand **L1** to determine the rate of the reactions.

**Table S18.** Data used to determine the order of olefin with ligand **L1**.

| Entry | [olefin] (mM) | *k* (mM/h) | $R^2$ | log[olefin] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 83.33 | 108.20 | 0.9612 | 1.92 | 2.03 |
| 2 | 166.67 | 105.56 | 0.9553 | 2.22 | 2.02 |
| 3 | 208.33 | 89.32 | 0.9607 | 2.32 | 1.95 |
| 4 | 250.00 | 85.56 | 0.9605 | 2.40 | 1.93 |

**Order of NaOAc with ligand L1**

General procedure was followed using $Pd(OAc)_2$ (2.8 mg, 12.5 µL, 5 mol%), ligand **L1** (0.0843 M in AcOH) (150 µL, 12.5 µmol, 5 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (0.25 mL, 2.8 mmol, 11.2 equiv), NaOAc (0.5–2.5 equiv) and AcOH (1.1 mL, 0.2 M). The reaction was sampling at 5, 10, 15, 20 and 25 min.

**Table S19.** Amount of NaOAc.

| Entry | Amount of NaOAc | [NaOAc] (mM) |
|---|---|---|
| 1 | 10.3 mg, 0.125 mmol, 0.5 equiv | 83.33 |
| 2 | 20.5 mg, 0.25 mmol, 1 equiv | 166.67 |
| 3 | 30.8 mg, 0.375 mmol, 1.5 equiv | 250.00 |
| 4 | 41.0 mg, 0.5 mmol, 2 equiv | 333.33 |
| 5 | 51.3 mg, 0.625 mmol, 2.5 equiv | 416.67 |

**Table S20.** Data used to determine the rate of the reactions with different concentrations of NaOAc with ligand **L1**.

| Entry | [NaOAc] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.08 h | 0.17 h | 0.25 h | 0.33 h | 0.42 h |
| 1 | 83.33 | 3.81 | 13.38 | 20.99 | 28.27 | 35.10 |
| 2 | 166.67 | 2.33 | 6.85 | 9.55 | 14.69 | 18.55 |
| 3 | 250.00 | 2.09 | 5.47 | 8.49 | 13.14 | 15.86 |
| 4 | 333.33 | 1.80 | 4.89 | 7.06 | 10.07 | 13.32 |
| 5 | 416.67 | 1.68 | 3.74 | 6.50 | 9.34 | 10.21 |

**Figure S5.** Plot of time (h) versus [product] (mM) with different concentrations of NaOAc with ligand **L1** to determine the rate of the reactions.

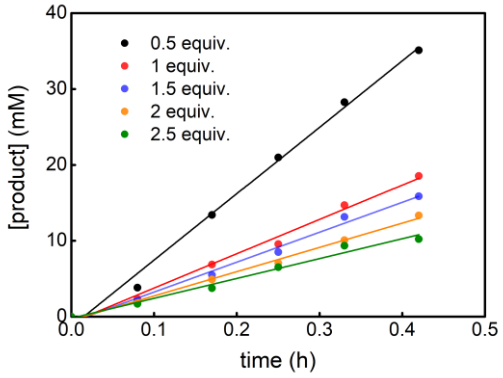



**Table S21.** Data used to determine the order of NaOAc with ligand **L1**.

| Entry | [NaOAc] (mM) | *k* (mM/h) | $R^2$ | log[NaOAc] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 83.33 | 87.56 | 0.9936 | 1.92 | 1.94 |
| 2 | 166.67 | 45.24 | 0.9912 | 2.22 | 1.66 |
| 3 | 250.00 | 39.39 | 0.9894 | 2.40 | 1.60 |
| 4 | 333.33 | 31.96 | 0.9948 | 2.52 | 1.50 |
| 5 | 416.67 | 26.17 | 0.9821 | 2.62 | 1.42 |

**Order of catalyst without ligand**

General procedure was followed using $Pd(OAc)_2$ (1–10 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (0.25 mL, 0.28 mmol, 11.2 equiv) and AcOH (1.25 mL, 0.2 M). The reaction was sampling at 30, 45, 60, 75 and 90 min.

**Table S22.** Amount of catalyst.

| Entry | Amount of $Pd(OAc)_2$ | [catalyst] (mM) |
|---|---|---|
| 1 | 0.6 mg, 2.50 µmol, 1 mol% | 1.67 |
| 2 | 1.4 mg, 6.25 µmol, 2.5 mol% | 4.17 |
| 3 | 2.8 mg, 12.50 µmol, 5 mol% | 8.33 |
| 4 | 4.2 mg, 18.75 µmol, 7.5 mol% | 12.50 |
| 5 | 5.6 mg, 25.00 µmol, 10 mol% | 16.67 |

**Table S23.** Data used to determine the rate of the reactions with different concentrations of catalyst without ligand.

| Entry | [catalyst] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.5 h | 0.75 h | 1 h | 1.25 h | 1.5 h |
| 1 | 1.67 | 4.47 | 5.90 | 7.62 | 11.44 | 12.86 |
| 2 | 4.17 | 5.13 | 7.33 | 10.66 | 14.48 | 18.16 |
| 3 | 8.33 | 6.18 | 8.89 | 12.06 | 16.61 | 21.44 |
| 4 | 12.50 | 7.13 | 10.87 | 13.81 | 19.35 | 24.65 |
| 5 | 16.67 | 8.03 | 12.87 | 17.74 | 22.30 | 29.29 |

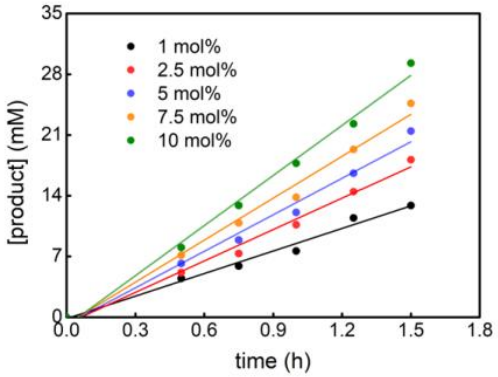



**Figure S6.** Plot of time (h) versus [product] (mM) with different concentrations of catalyst without ligand to determine the rate of the reactions.

**Table S24.** Data used to determine the order of catalyst without ligand.

| Entry | [catalyst] (mM) | *k* (mM/h) | $R^2$ | log[catalyst] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 1.67 | 8.66 | 0.9849 | 0.22 | 0.94 |
| 2 | 4.17 | 12.06 | 0.9878 | 0.62 | 1.08 |
| 3 | 8.33 | 14.01 | 0.9857 | 0.92 | 1.15 |
| 4 | 12.50 | 16.13 | 0.9876 | 1.10 | 1.21 |
| 5 | 16.67 | 19.22 | 0.9917 | 1.22 | 1.28 |

**Order of benzene without ligand**

General procedure was followed using $Pd(OAc)_2$ (2.8 mg, 12.5 µL, 5 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (6.7–24.7 equiv), $C_6F_6$ and AcOH (1.1 mL, 0.2 M). The reaction was sampling at 30, 45, 60, 75 and 90 min.

**Table S25.** Amount of benzene.

| Entry | Amount of benzene | Amount of $C_6F_6$ | [benzene] (mM) |
|---|---|---|---|
| 1 | 0.15 mL, 1.675 mmol, 6.7 equiv | 0.6 mL | 837.50 |
| 2 | 0.25 mL, 2.8 mmol, 11.2 equiv | 0.5 mL | 1400.00 |
| 3 | 0.35 mL, 3.925 mmol, 15.7 equiv | 0.4 mL | 1962.50 |
| 4 | 0.45 mL, 5.05 mmol, 20.2 equiv | 0.3 mL | 2525.00 |

**Table S26.** Data used to determine the rate of the reactions with different concentrations of benzene without ligand.

| Entry | [benzene] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.5 h | 0.75 h | 1 h | 1.25 h | 1.5 h |
| 1 | 837.50 | 1.94 | 2.88 | 3.98 | 4.67 | 5.57 |
| 2 | 1400.00 | 3.49 | 5.07 | 7.44 | 9.78 | 11.40 |
| 3 | 1962.50 | 4.35 | 7.34 | 9.37 | 12.27 | 16.52 |
| 4 | 2525.00 | 6.28 | 8.57 | 11.95 | 14.92 | 19.30 |

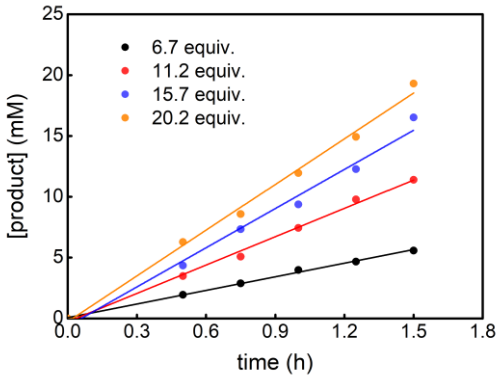



**Figure S7.** Plot of time (h) versus [product] (mM) with different concentrations of benzene without ligand to determine the rate of the reactions.

**Table S27.** Data used to determine the order of benzene without ligand.

| Entry | [benzene] (mM) | *k* (mM/h) | $R^2$ | log[benzene] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 837.50 | 3.73 | 0.9976 | 2.92 | 0.57 |
| 2 | 1400.00 | 7.77 | 0.995 | 3.15 | 0.89 |
| 3 | 1962.50 | 10.72 | 0.9855 | 3.29 | 1.03 |
| 4 | 2525.00 | 12.53 | 0.994 | 3.40 | 1.10 |

**Order of oxidant without ligand**

General procedure was followed using $Pd(OAc)_2$ (2.8 mg, 12.5 µL, 5 mol%), *tert*-butyl peroxybenzoate (0.5–2.5 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (0.25 mL, 2.8 mmol, 11.2 equiv) and AcOH (1.1 mL, 0.2 M). The reaction was sampling at 30, 45, 60, 75 and 90 min.

**Table S28.** Amount of oxidant.

| Entry | Amount of oxidant | [oxidant] (mM) |
|---|---|---|
| 1 | 24 µL, 0.125 mmol, 0.5 equiv | 83.33 |
| 2 | 47 µL, 0.25 mmol, 1 equiv | 166.67 |
| 3 | 71 µL, 0.375 mmol, 1.5 equiv | 250.00 |
| 4 | 94 µL, 0.5 mmol, 2 equiv | 333.33 |
| 5 | 118 µL, 0.625 mmol, 2.5 equiv | 416.67 |

**Table S29.** Data used to determine the rate of the reactions with different concentrations of oxidant without ligand.

| Entry | [oxidant] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.5 h | 0.75 h | 1 h | 1.25 h | 1.5 h |
| 1 | 83.33 | 7.04 | 13.39 | 19.86 | 27.17 | 34.91 |
| 2 | 166.67 | 7.06 | 13.29 | 19.70 | 25.51 | 33.94 |
| 3 | 250.00 | 6.73 | 11.66 | 17.98 | 23.73 | 30.85 |
| 4 | 333.33 | 6.26 | 10.57 | 14.82 | 19.70 | 24.46 |
| 5 | 416.67 | 6.71 | 10.51 | 15.61 | 20.45 | 25.61 |

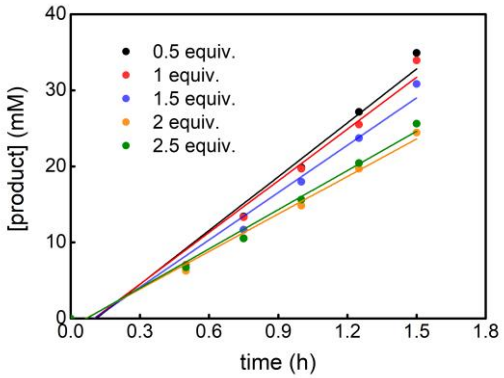



**Figure S8.** Plot of time (h) versus [product] (mM) with different concentrations of oxidant without ligand to determine the rate of the reactions.

**Table S30.** Data used to determine the order of oxidant without ligand.

| Entry | [oxidant] (mM) | *k* (mM/h) | $R^2$ | log[oxidant] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 83.33 | 23.62 | 0.9758 | 1.92 | 1.37 |
| 2 | 166.67 | 22.68 | 0.9780 | 2.22 | 1.36 |
| 3 | 250.00 | 20.73 | 0.9784 | 2.40 | 1.32 |
| 4 | 333.33 | 16.47 | 0.9912 | 2.52 | 1.22 |
| 5 | 416.67 | 17.20 | 0.9896 | 2.62 | 1.24 |

**Order of olefin without ligand**

General procedure was followed using $Pd(OAc)_2$ (2.8 mg, 12.5 µL, 5 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (0.5–1.5 equiv), benzene (0.25 mL, 2.8 mmol, 11.2 equiv) and AcOH (1.1 mL, 0.2 M). The reaction was sampling at 30, 45, 60, 75 and 90 min.

**Table S31.** Amount of olefin.

| Entry | Amount of olefin | [olefin] (mM) |
|---|---|---|
| 1 | 14 µL, 0.125 mmol, 0.5 equiv | 83.33 |
| 2 | 20 µL, 0.188 mmol, 0.75 equiv | 125.00 |
| 3 | 27 µL, 0.25 mmol, 1 equiv | 166.67 |
| 4 | 34 µL, 0.313 mmol, 1.25 equiv | 208.33 |
| 5 | 41 µL, 0.375 mmol, 1.5 equiv | 250.00 |

**Table S32.** Data used to determine the rate of the reactions with different concentrations of olefin without ligand.

| Entry | [olefin] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.5 h | 0.75 h | 1 h | 1.25 h | 1.5 h |
| 1 | 83.33 | 6.93 | 9.35 | 13.80 | 18.01 | 23.15 |
| 2 | 125.00 | 6.60 | 10.65 | 16.30 | 21.57 | 28.10 |
| 3 | 166.67 | 6.10 | 10.23 | 15.26 | 21.20 | 28.05 |
| 4 | 208.33 | 5.97 | 10.13 | 16.03 | 22.39 | 30.65 |
| 5 | 250.00 | 6.27 | 11.42 | 15.69 | 23.90 | 31.21 |

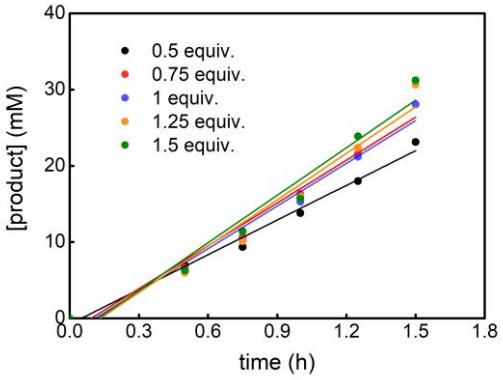



**Figure S9.** Plot of time (h) versus [product] (mM) with different concentrations of olefin without ligand to determine the rate of the reactions.

**Table S33.** Data used to determine the order of olefin without ligand.

| Entry | [olefin] (mM) | *k* (mM/h) | $R^2$ | log[olefin] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 83.33 | 15.18 | 0.9884 | 1.92 | 1.18 |
| 2 | 125.00 | 18.75 | 0.9802 | 2.10 | 1.27 |
| 3 | 166.67 | 18.65 | 0.9716 | 2.22 | 1.27 |
| 4 | 208.33 | 20.30 | 0.9583 | 2.32 | 1.31 |
| 5 | 250.00 | 20.80 | 0.9620 | 2.40 | 1.32 |

**Order of NaOAc without ligand**

General procedure was followed using $Pd(OAc)_2$ (2.8 mg, 12.5 µL, 5 mol%), *tert*-butyl peroxybenzoate (47 µL, 0.25 mmol, 1 equiv), ethyl acrylate (27 µL, 0.25 mmol, 1 equiv), benzene (0.25 mL, 2.8 mmol, 11.2 equiv), NaOAc (0.1–3.5 equiv) and AcOH (1.25 mL, 0.2 M). The reaction was sampling at 30, 45, 60, 75 and 90 min.

**Table S34.** Amount of NaOAc.

| Entry | Amount of NaOAc | [NaOAc] (mM) |
|---|---|---|
| 1 | 2.1 mg, 0.025 mmol, 0.1 equiv | 16.67 |
| 2 | 6.2 mg, 0.075 mmol, 0.3 equiv | 50.00 |
| 3 | 10.3 mg, 0.125 mmol, 0.5 equiv | 83.33 |
| 4 | 20.5 mg, 0.25 mmol, 1 equiv | 166.67 |
| 5 | 30.8 mg, 0.375 mmol, 1.5 equiv | 250.00 |
| 6 | 41.0 mg, 0.5 mmol, 2 equiv | 333.33 |

| | | |
|---|---|---|
| 7 | 51.3 mg, 0.625 mmol, 2.5 equiv | 416.67 |
| 8 | 61.5 mg, 0.75 mmol, 3 equiv | 500.00 |
| 9 | 71.8 mg, 0.875 mmol, 3.5 equiv | 583.33 |

**Table S35.** Data used to determine the rate of the reactions with different concentrations of NaOAc without ligand.

| Entry | [NaOAc] (mM) | [product] (mM) | | | | |
|---|---|---|---|---|---|---|
| | | 0.5 h | 0.75 h | 1 h | 1.25 h | 1.5 h |
| 1 | 16.67 | 8.16 | 12.66 | 16.19 | 21.96 | 29.78 |
| 2 | 50.00 | 10.49 | 16.54 | 22.99 | 39.06 | 41.76 |
| 3 | 83.33 | 13.48 | 21.06 | 28.64 | 39.15 | 47.95 |
| 4 | 166.67 | 17.37 | 24.11 | 32.55 | 43.19 | 50.12 |
| 5 | 250.00 | 14.93 | 22.67 | 33.76 | 39.31 | 46.06 |
| 6 | 333.33 | 9.66 | 13.82 | 18.38 | 23.74 | 27.14 |
| 7 | 416.67 | 7.88 | 12.35 | 14.86 | 19.60 | 22.59 |
| 8 | 500.00 | 6.17 | 9.16 | 11.54 | 14.31 | 17.44 |
| 9 | 583.33 | 5.41 | 7.85 | 11.18 | 12.20 | 16.05 |

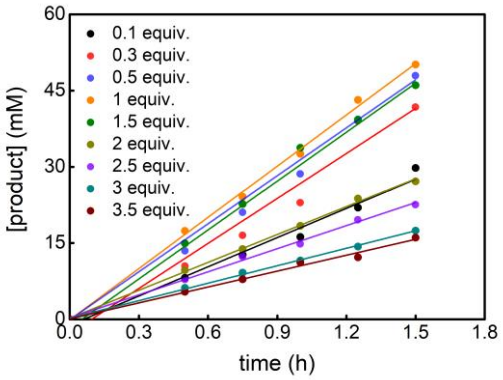



**Figure S10.** Plot of time (h) versus [product] (mM) with different concentrations of NaOAc without ligand to determine the rate of the reactions.

**Table S36.** Data used to determine the order of NaOAc without ligand.

| Entry | [NaOAc] (mM) | *k* (mM/h) | $R^2$ | log[NaOAc] (mM) | log*k* (mM/h) |
|---|---|---|---|---|---|
| 1 | 16.67 | 19.15 | 0.9807 | 1.22 | 1.28 |
| 2 | 50.00 | 29.53 | 0.9575 | 1.70 | 1.47 |
| 3 | 83.33 | 32.10 | 0.9926 | 1.92 | 1.51 |
| 4 | 166.67 | 33.62 | 0.9976 | 2.22 | 1.53 |
| 5 | 250.00 | 31.43 | 0.9945 | 2.40 | 1.50 |
| 6 | 333.33 | 18.29 | 0.9982 | 2.52 | 1.26 |
| 7 | 416.67 | 15.12 | 0.9964 | 2.62 | 1.18 |
| 8 | 500.00 | 11.45 | 0.9985 | 2.70 | 1.06 |
| 9 | 583.33 | 10.42 | 0.9911 | 2.77 | 1.02 |

**Procedure for the reaction using an excess of NaOAc with the aim to detect $[L2Pd(OAc)_2]^-$ (the reaction is performed in an NMR tube)**

$Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 1 equiv), **L2** (2.0 mg, 0.01 mmol, 1 equiv) and AcOD-$d_4$ (0.5 mL) were added into an NMR tube. The NMR tube was sealed with a screw cap and the reaction was placed in a 100 °C pre-heated oil bath for 20 minutes until solid was dissolved. The reaction was cooled down to room temperature and the $^1$H NMR spectrum was collected. Then, NaOAc (16.4 mg, 0.2 mmol, 20 equiv) was added to the NMR tube. The NMR tube was again placed in a 100 °C pre-heated oil bath for 2 h. The reaction was cooled down to room temperature and the $^1$H NMR spectrum was collected.

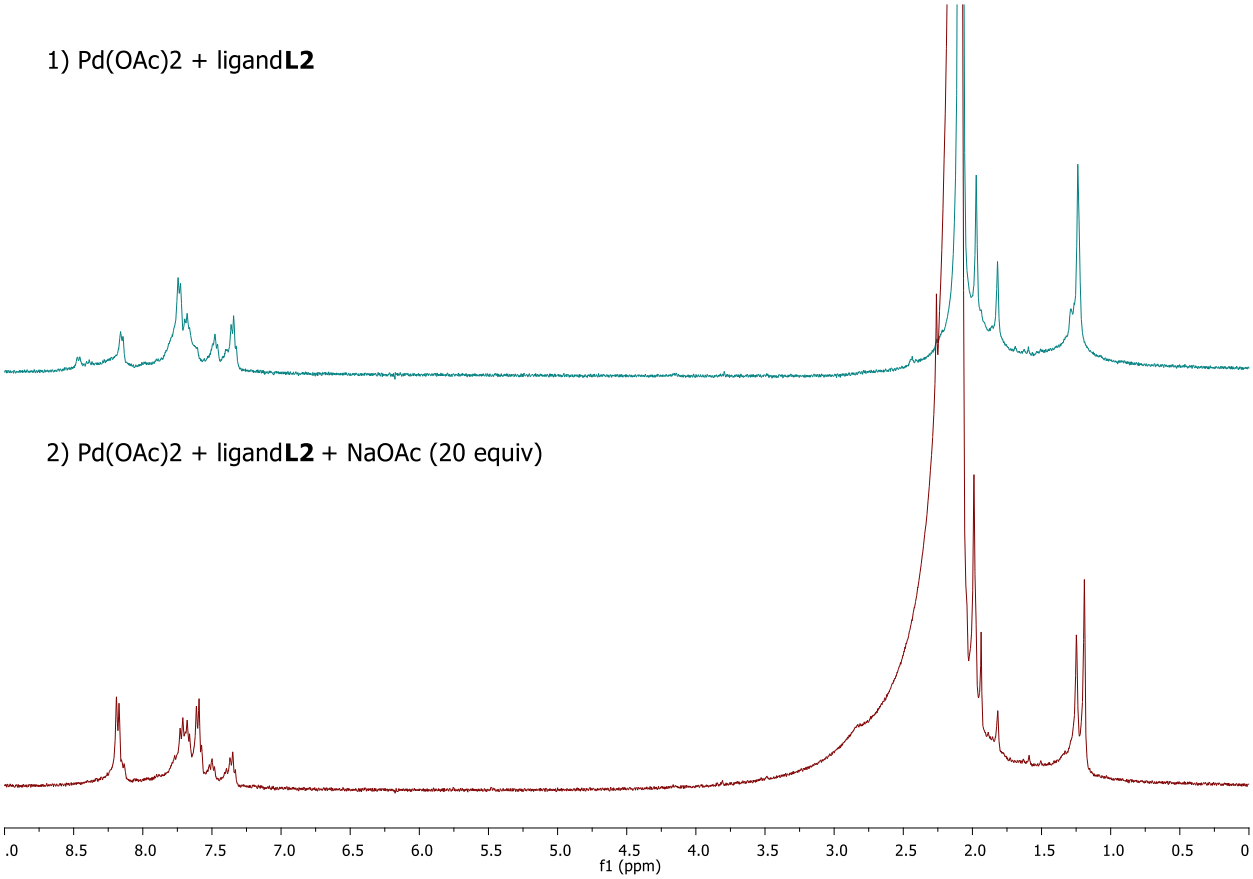



**Figure S11.** $^1$H NMR spectra of the mixture of $Pd(OAc)_2$ and ligand **L2** in AcOD-$d_4$, 1) before and 2) after the addition of 20 equiv of NaOAc.

**KIE for Pd-catalyzed C–H olefination of benzene with ligand L1**

$Pd(OAc)_2$ (5.6 mg, 25.0 µmol, 5 mol%), a stock solution of ligand **L1** (0.0846 M in AcOH) (300 µL, 25.0 µmol, 5 mol%), *tert*-butyl peroxybenzoate (94 µL, 0.5 mmol, 1 equiv), ethyl acrylate (53 µL, 0.5 mmol, 1 equiv), benzene (0.5 mL, 5.6 mmol, 11.2 equiv) or benzene-$d_6$ (0.5 mL, 5.6 mmol, 11.2 equiv) and AcOH (2.2 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a crimp cap with septa and the reaction was placed in a 100 °C pre-heated oil bath. The reaction was followed during the time (5, 10, 15, 30 and 45 min) by sampling 100 µL. PhCl (20 µL) was added in each sample as an internal standard for quantitative GC analysis. The reaction mixture was diluted with EtOAc (0.5 mL). The organic layer was quenched with saturated aqueous $NaHCO_3$ solution (0.5 mL). The organic layer was filtered through a plug of anh. $MgSO_4$ and analyzed by GC.

**Table S37.** Data used to determine KIE for C–H olefination of benzene with ligand **L1**.

| Entry | Time (h) | [product] (mM) | |
|---|---|---|---|
| | | Benzene | Benzene-$d_6$ |
| 1 | 0.08 | 2.63 | 1.10 |
| 2 | 0.17 | 10.16 | 2.93 |
| 3 | 0.25 | 19.39 | 5.50 |
| 4 | 0.50 | 47.31 | 12.60 |
| 5 | 0.75 | 71.08 | 17.60 |

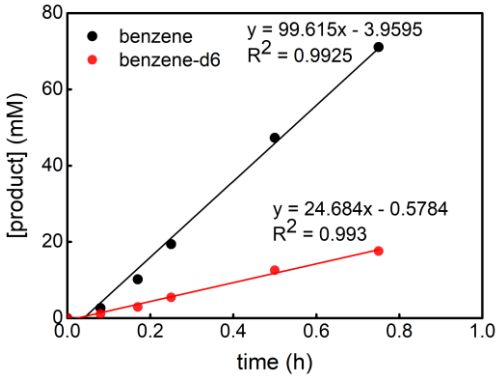



**Figure S12.** Plot of time (h) versus [product] (mM) to determine KIE for C–H olefination of benzene with ligand **L1**.

**KIE for Pd-catalyzed C–H olefination of benzene without ligand**

$Pd(OAc)_2$ (5.6 mg, 25.0 µmol, 5 mol%), *tert*-butyl peroxybenzoate (94 µL, 0.5 mmol, 1 equiv), ethyl acrylate (53 µL, 0.5 mmol, 1 equiv), benzene (0.5 mL, 5.6 mmol, 11.2 equiv) or benzene-$d_6$ (0.5 mL, 5.6 mmol, 11.2 equiv) and AcOH (2.5 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a crimp cap with septa and the reaction was placed in a 100 °C pre-heated oil bath. The reaction was followed during the time (5, 10, 15, 30 and 45 min) by sampling 100 µL. PhCl (20 µL) was added in each sample as an internal standard for quantitative GC analysis. The reaction mixture was diluted with EtOAc (0.5 mL). The organic layer was quenched with saturated aqueous $NaHCO_3$ solution (0.5 mL). The organic layer was filtered through a plug of anh. $MgSO_4$ and analyzed by GC.

**Table S38.** Data used to determine KIE for C–H olefination of benzene without ligand.

| Entry | Time (h) | [product] (mM) | |
|---|---|---|---|
| | | Benzene | Benzene-$d_6$ |
| 1 | 0.08 | 0.99 | 0.74 |
| 2 | 0.17 | 2.17 | 1.13 |
| 3 | 0.25 | 2.77 | 1.25 |
| 4 | 0.50 | 7.03 | 1.82 |
| 5 | 0.75 | 12.85 | 2.66 |

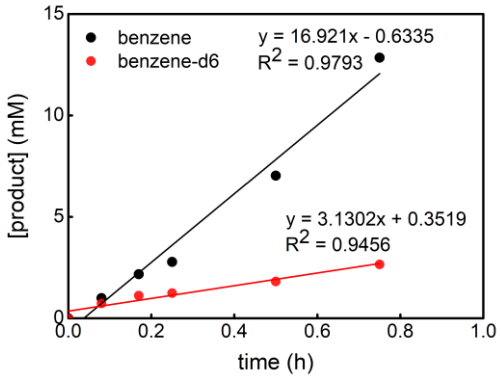



**Figure S13.** Plot of time (h) versus [product] (mM) to determine KIE for C–H olefination of benzene without ligand.

**Procedure for one-pot intermolecular competition experiment of *p*-xylene and 1,4-bis(trifluoromethyl)benzene with ligand L1**

$Pd(OAc)_2$ (2.8 mg, 12.5 μmol, 5 mol%), a stock solution of ligand **L1** (0.0846 M in DCE) (150 μL, 12.5 μmol, 5 mol%), *tert*-butyl peroxybenzoate (47 μL, 0.25 mmol, 1 equiv), ethyl acrylate (27 μL, 0.25 mmol, 1 equiv), *p*-xylene (0.15 mL, 1.25 mmol, 5 equiv), 1,4-bis(trifluoromethyl)benzene (0.19 mL, 1.25 mmol, 5 equiv) and AcOH (1.10 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a screw cap and the reaction was placed in a 100 °C pre-heated oil bath and stirred for 3 h. The resulting mixture was diluted with EtOAc, filtered through a plug of Celite and concentrated under reduced pressure. The $^1$H NMR yield was determined by adding $CH_2Br_2$ (17.5 μL, 0.25 mmol, 1 equiv) as an internal standard. The reaction provided the olefinated product in 84% $^1$H NMR yield (**5**:**6** = 84%:traces).

**Procedure for one-pot intermolecular competition experiment of *p*-xylene and 1,4-bis(trifluoromethyl)benzene without ligand**

$Pd(OAc)_2$ (2.8 mg, 12.5 μmol, 5 mol%), *tert*-butyl peroxybenzoate (47 μL, 0.25 mmol, 1 equiv), ethyl acrylate (27 μL, 0.25 mmol, 1 equiv), *p*-xylene (0.15 mL, 1.25 mmol, 5 equiv), 1,4-bis(trifluoromethyl)benzene (0.19 mL, 1.25 mmol, 5 equiv) and AcOH (1.25 mL, 0.2 M) were added into a pressure tube. The pressure tube was sealed with a screw cap and the reaction was placed in a 100 °C pre-heated oil bath and stirred for 3 h. The resulting mixture was diluted with EtOAc, filtered through a plug of Celite and concentrated under reduced pressure. The $^1$H NMR yield was determined by adding $CH_2Br_2$ (17.5 μL, 0.25 mmol, 1 equiv) as an internal standard. The reaction provided the olefinated product in 22% $^1$H NMR yield (**5**:**6** = 22%:traces).

**Procedure for the H/D exchange experiment with ligand L1 (the reaction is performed in an NMR tube)**

$Pd(OAc)_2$ (1.1 mg, 5.0 μmol, 5 mol%), ligand **L1** (1.1 mg, 5.0 μmol, 5 mol%), *tert*-butyl peroxybenzoate (19 μL, 0.1 mmol, 1 equiv), ethyl acrylate (11 μL, 0.1 mmol, 1 equiv), mesitylene (0.14 mL, 1.0 mmol, 10 equiv) and AcOD-$d_4$ (0.5 mL, 0.2 M) were mixed in a vial. The solution was transferred into an NMR tube, sealed with a screw cap and $^1$H NMR spectrum was collected. The NMR tube was placed in a 100 °C pre-heated oil bath for 6 h. The reaction was cooled down to room temperature and the $^1$H NMR spectrum was collected.

**Procedure for the H/D exchange experiment without ligand (the reaction is performed in an NMR tube)**

$Pd(OAc)_2$ (2.2 mg, 10.0 µmol, 10 mol%), *tert*-butyl peroxybenzoate (19 µL, 0.1 mmol, 1 equiv), ethyl acrylate (11 µL, 0.1 mmol, 1 equiv), mesitylene (0.14 mL, 1.0 mmol, 10 equiv) and AcOD-$d_4$ (0.5 mL, 0.2 M) were mixed in a vial. The solution was transferred into an NMR tube, sealed with a screw cap and $^1$H NMR spectrum was collected. The NMR tube was placed in a 100 °C pre-heated oil bath for 16 h. The reaction was cooled down to room temperature and the $^1$H NMR spectrum was collected.

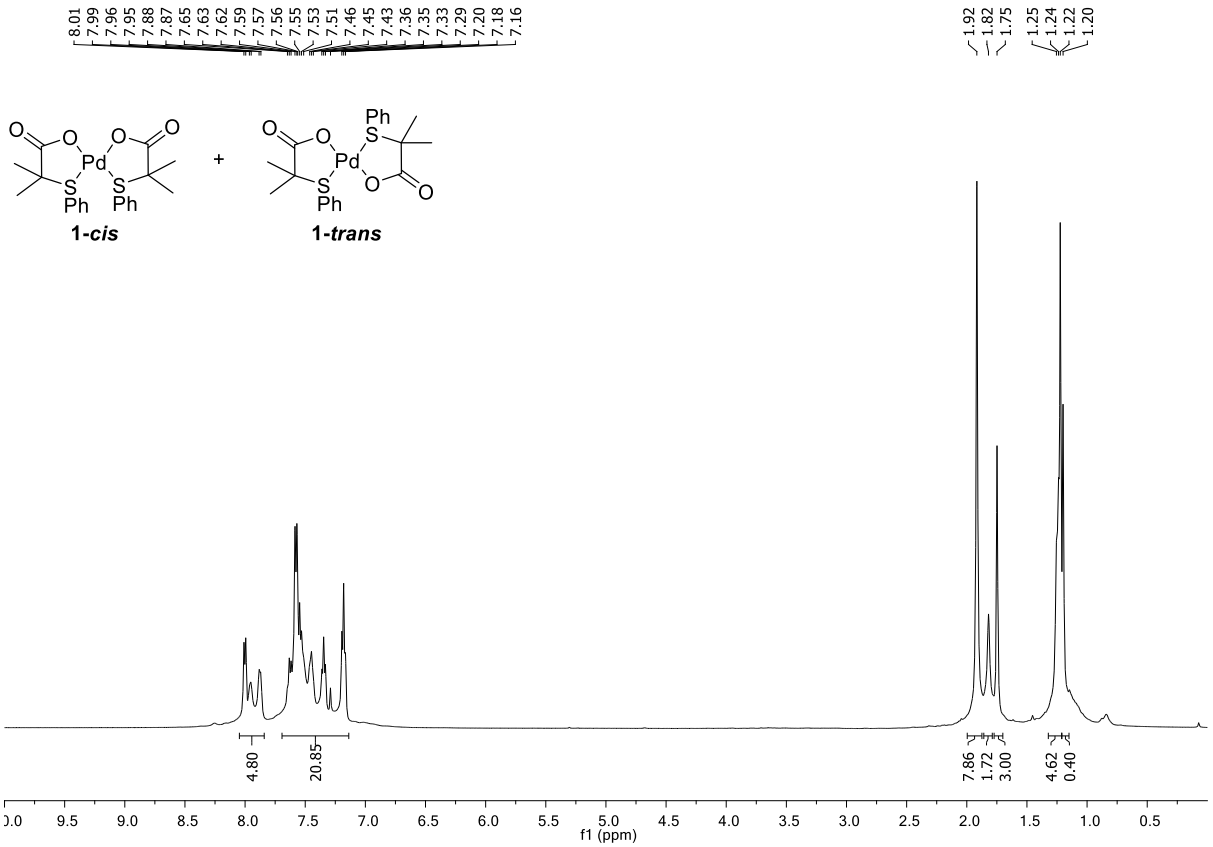
**Procedure for the reaction of ligand L2 and oxidant**

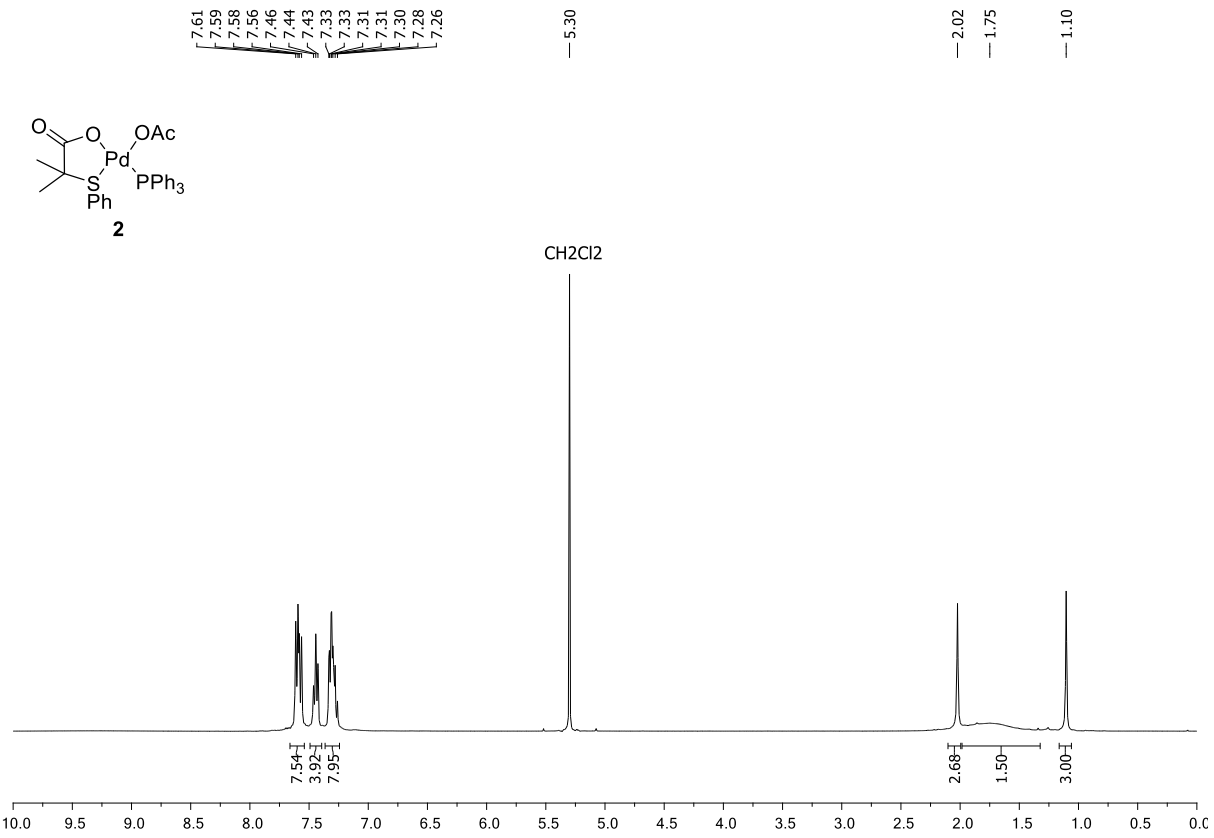
Ligand **L2** (19.6 mg, 0.1 mmol, 1 equiv), *tert*-butyl peroxybenzoate (0.38 mL, 2.0 mmol, 20 equiv), benzene (2 mL, excess) and AcOH (10 mL) were added into a pressure tube. The pressure tube was sealed with a screw cap and the reaction was placed in a 100 °C pre-heated oil bath and stirred for 2 h. The reaction was cooled down to room temperature and concentrated under reduced pressure. The resulting crude was basified (2 M aqueous NaOH solution) until pH = 14. The aqueous layer was washed with $CH_2Cl_2$ (3 x 10 mL). The aqueous layer was acidified (6 M aqueous HCl solution) until pH = 1 and extracted with $CH_2Cl_2$ (3 x 15 mL). The combined organic layers were dried over anh. $MgSO_4$, filtered, concentrated under reduced pressure and analyzed by $^1$H NMR.

**Procedure for the reaction of complex 1 and oxidant**

Complex **1** (15.5 mg, 0.03 mmol, 1 equiv) and *tert*-butyl peroxybenzoate (22 µL, 0.12 mmol, 4 equiv) were added into a pressure tube. The pressure tube was sealed with a screw cap and the reaction was placed in a 100 °C pre-heated oil bath and stirred for 2 h. The reaction was cooled down to room temperature, diluted with $CH_2Cl_2$, filtered through a plug of Celite, concentrated under reduced pressure and analyzed by $^1$H NMR.

## 5. NMR spectra

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7.33
7.31
7.31
7.30
7.28
7.26
5.30
2.02
1.75
1.10
OAc
Pd
PPh3
S
Ph
O
2
CH2Cl2
7.54
3.92
7.95
2.68
1.50
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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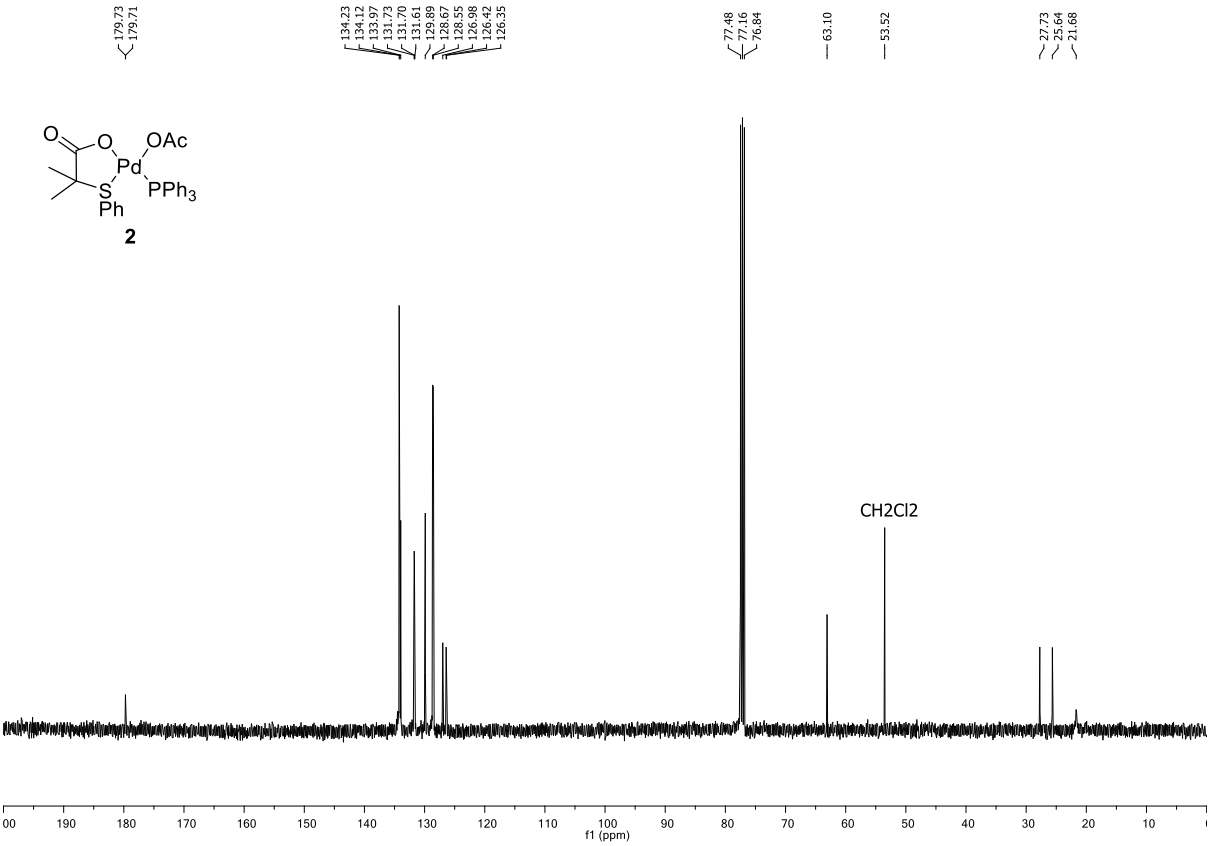
0.0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133.97
131.73
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131.61
129.89
128.67
128.55
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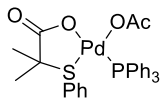
126.35
77.48
77.16
76.84
63.10
53.52
27.73
25.64
21.68
OAc
Pd
PPh3
S
Ph
O
2
CH2Cl2
f1 (ppm)


O
O
OAc
Pd
S
PPh3
Ph

**2**


26.45
50
45
40
35
30
25
20
15
10
5


7.71
7.67
7.54
7.54
7.53
7.53
7.53
7.52
7.51
7.51
7.40
7.40
7.39
7.39
7.39
7.38
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4.26
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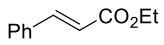
1.32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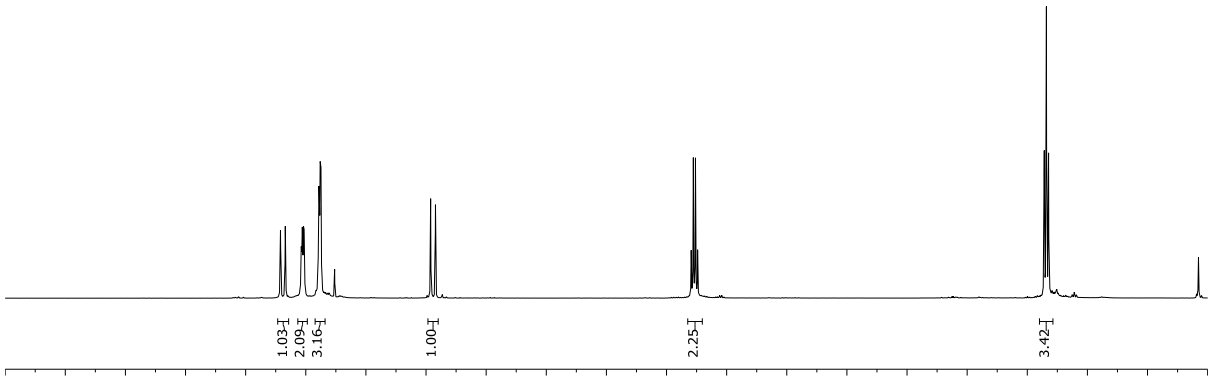
CO2Et

**3-mono**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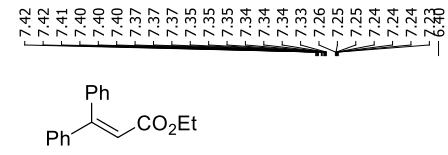
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7.24
7.24
7.24
7.23
6.40
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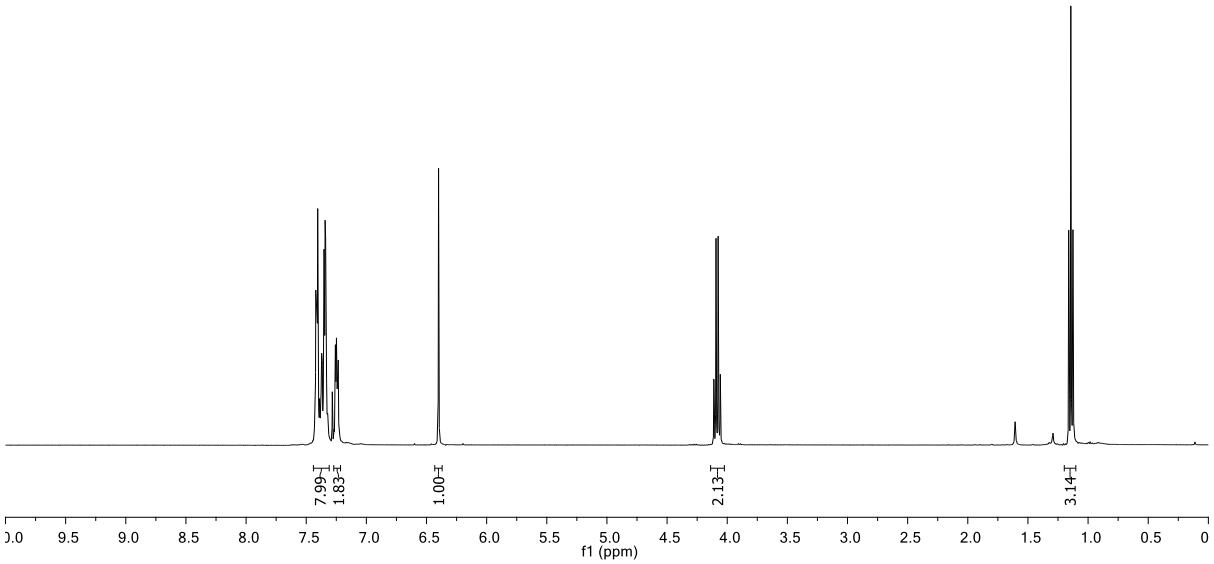
4.09
4.08
4.06
1.16
1.14
1.13
Ph
Ph
CO2Et

**3-di**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1.00
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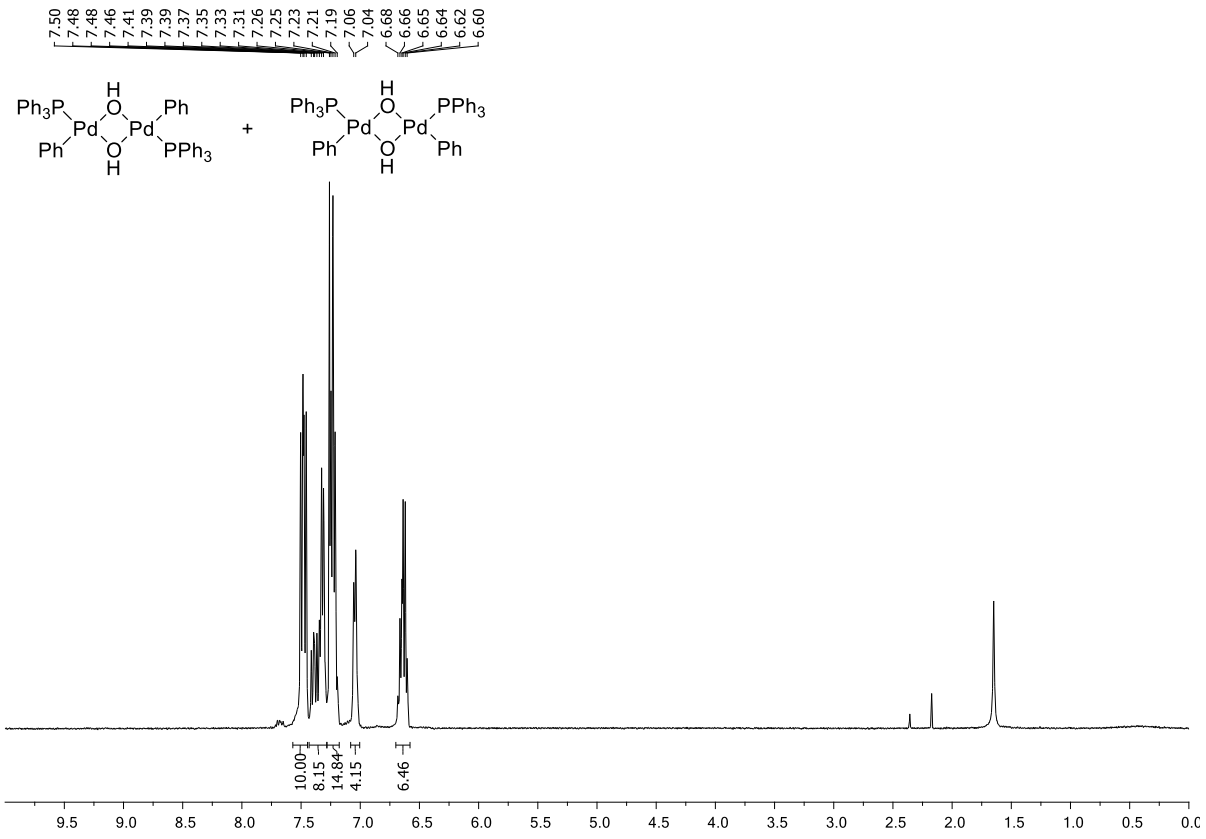
3.14
f1 (ppm)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7.23
7.21
7.19
7.06
7.04
6.68
6.66
6.65
6.64
6.62
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Pd
O
H
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+
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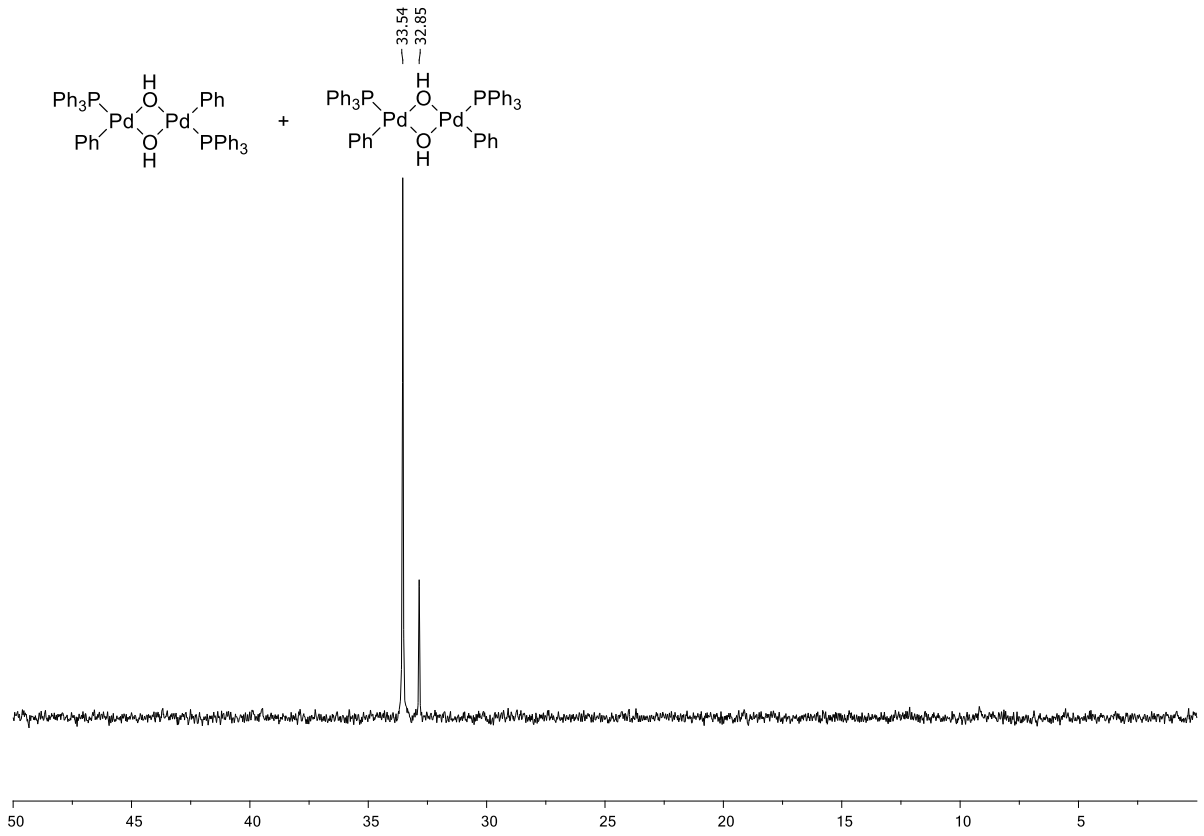
14.84
4.15
6.46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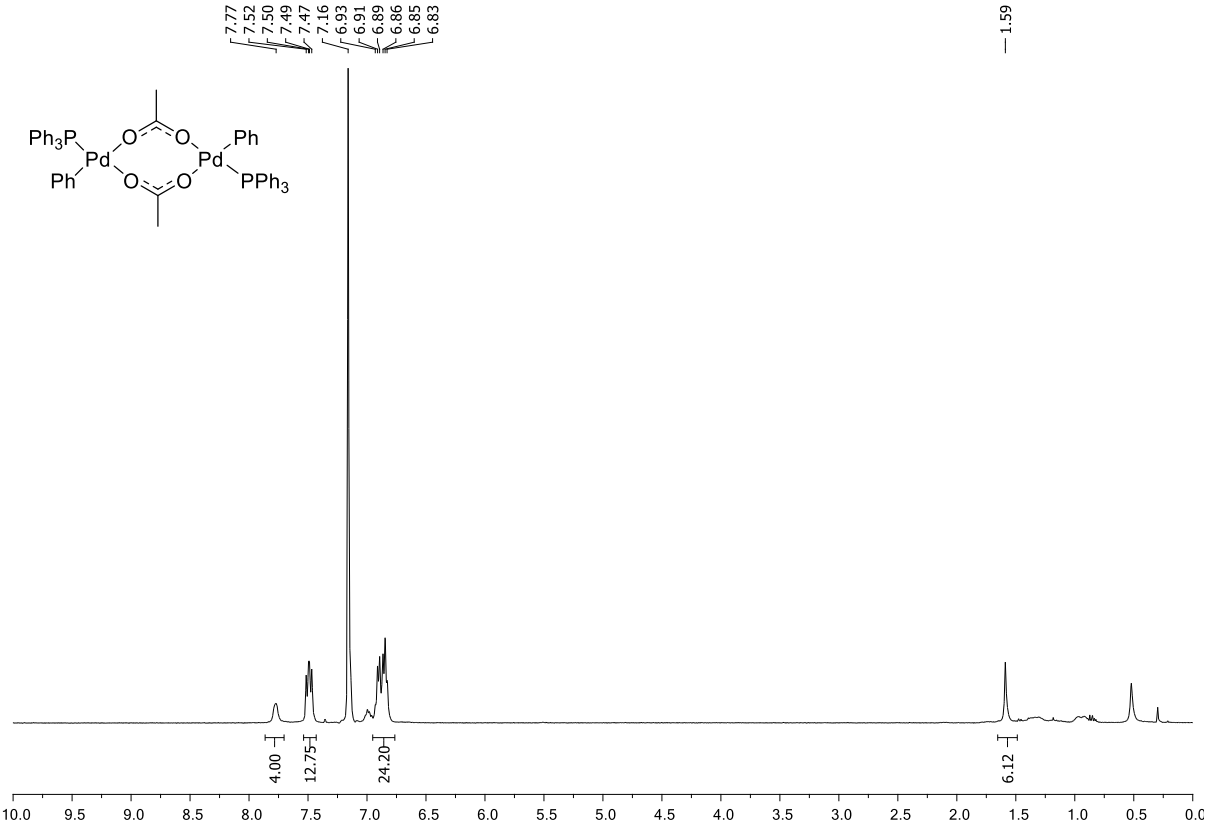
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PPh3
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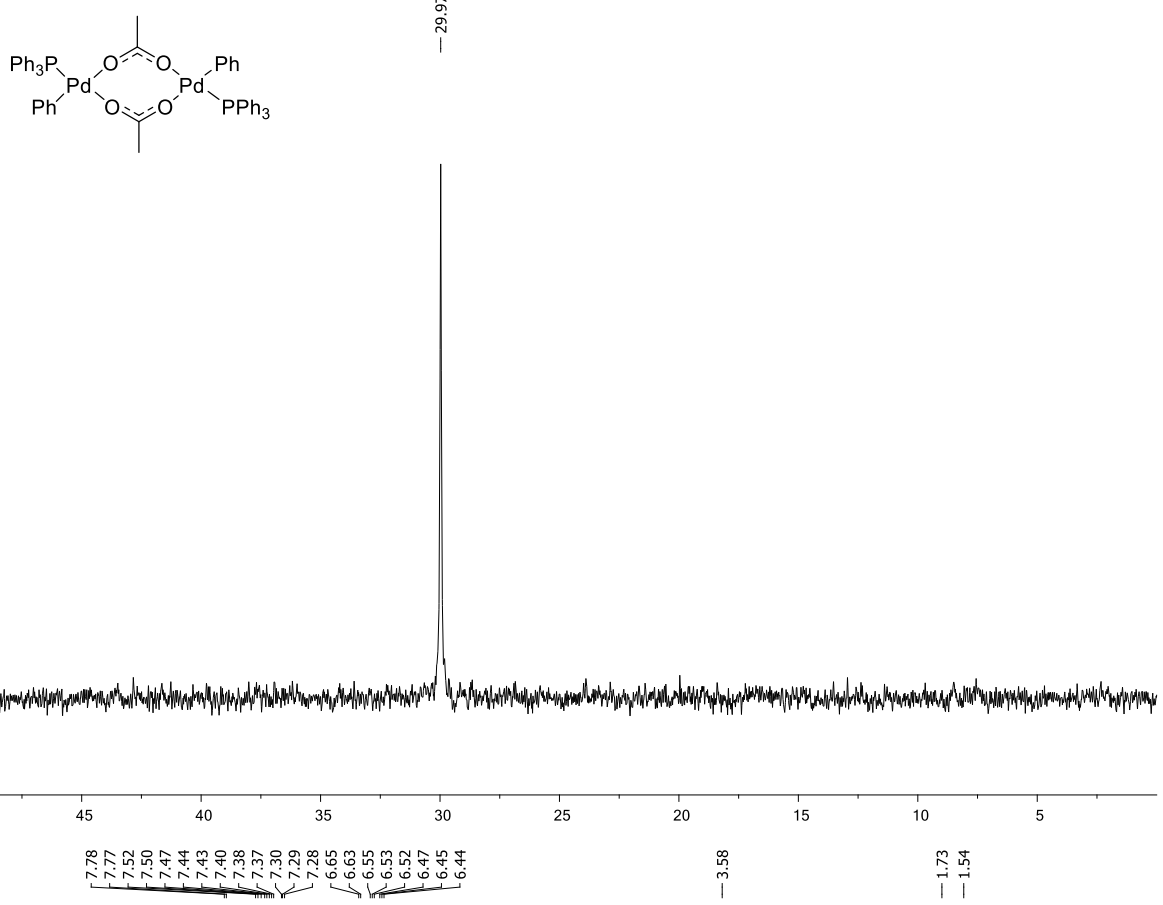
6.12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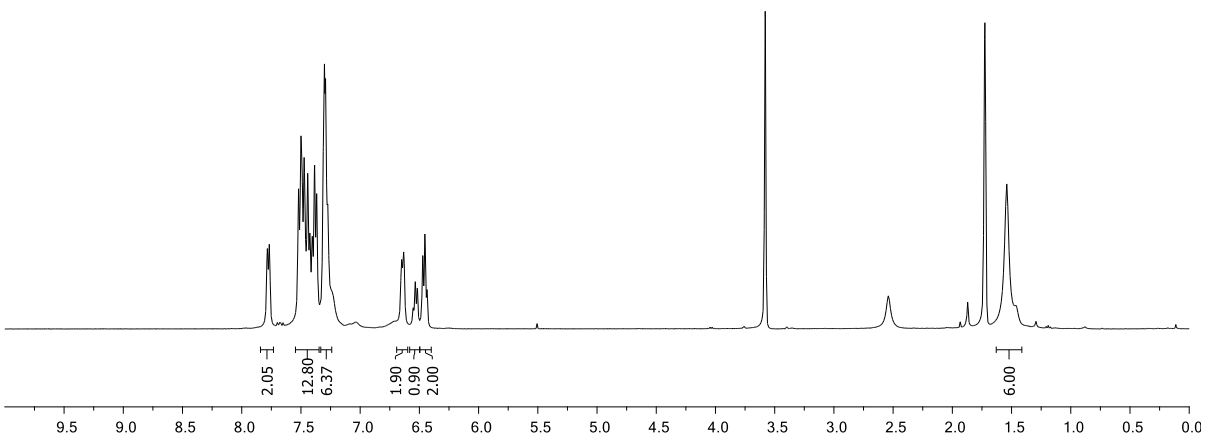
1.73
1.54

**4'**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6.5
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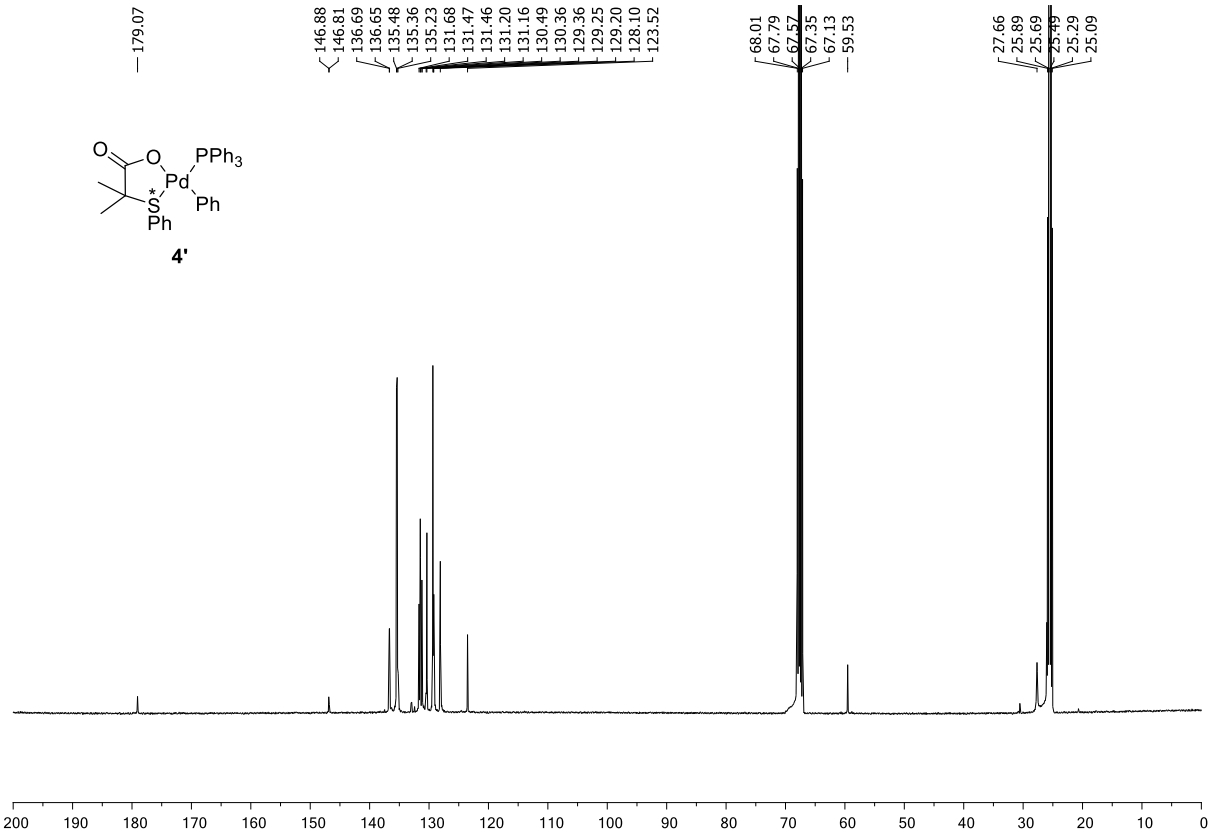
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67.35
67.13
59.53
27.66
25.89
25.69
25.49
25.29
25.09
O
O
PPh3
Pd
S*
Ph
Ph
Ph
200
190
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10
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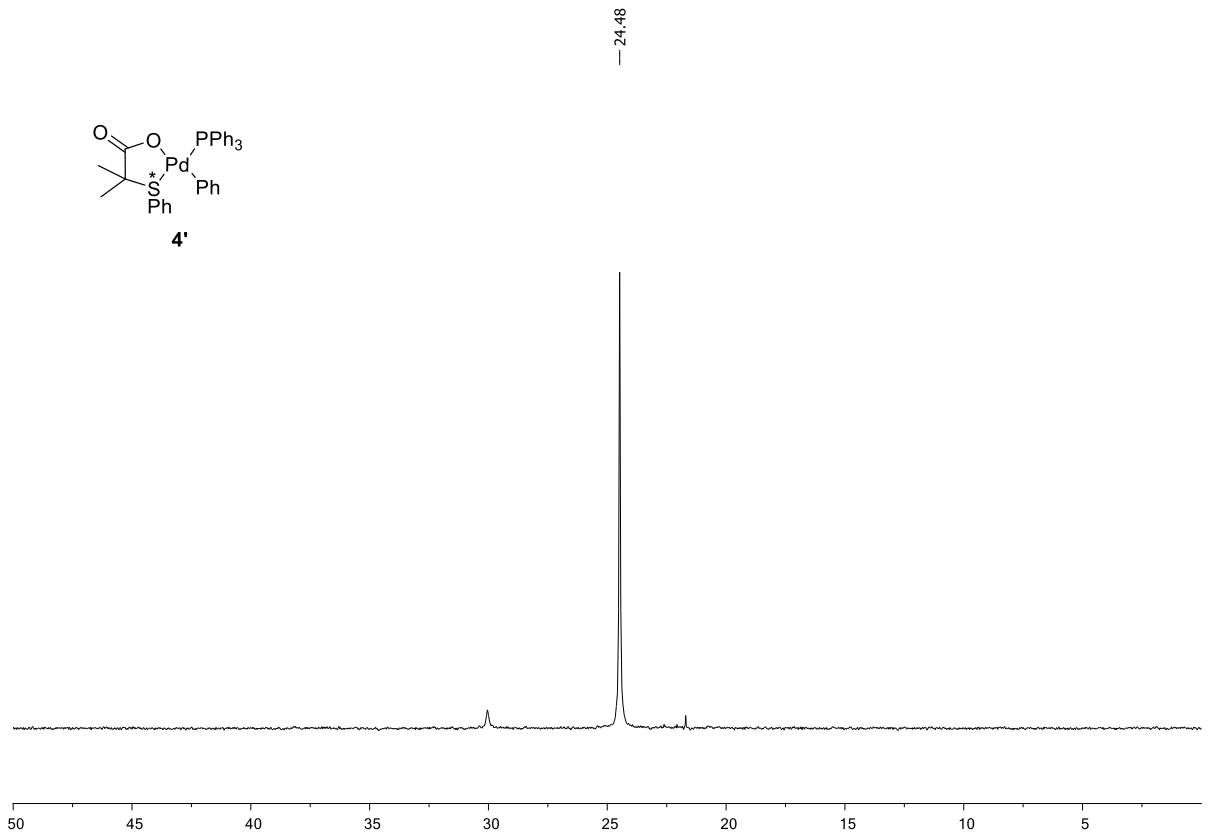
24.48
50
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30
25
20
15
10
5

**4'**

**6. Mass spectrometric measurements**

The mass spectra were recorded on a linear ion trap (LTQ) instrument with an electrospray ionization (ESI) source.[5] General conditions used were as follows: 4 to 5 kV spray voltage, 200 to 275 ℃ capillary temperature and 1 to 20 psi sheath gas. For positive mode, 0 to 20 V capillary voltage and 25 to 70 V tube lens while for the negative mode 0 to -20 V capillary voltage and -25 to -75 V tube lens.

Energy resolved collision induced dissociation (CID) experiments were performed on LCQ Deca mass spectrometer with an ESI source.[6] The calibration was performed using the thermometer ions using the Schroder's method to correlate the collision energy and the appearance energies of the ions.[7]

In general, 1 mM fresh stock solution was prepared in the desired solvent (sonication used if turbidity observed followed by filtration, filtrate used). From these stock solutions after mixing/addition, by appropriate dilution with the desired solvent final concentration of 50 to 200 µM was injected directly into the ESI–MS inlet with the help of a silica capillary using the nitrogen overpressure in the vial.

[Pd(**L2**)($PPh_2Ph^{SO3}$)OAc ]Na i.e. the negatively charge tagged analog of 'complex **2**' was synthesized according to the "Procedure for the synthesis of complex **2**" described above with the exception that instead of triphenylphosphine, 3-(diphenylphosphino)benzenesulfonic acid sodium salt i.e. $PPh_2Ph^{SO3}Na$ was used and dark yellowish solid of [Pd(**L2**)($PPh_2Ph^{SO3}$)OAc ]Na was obtained. This was then used further for the mass spectrometry analysis.

High resolution mass spectra were recorded with a timsTOF instrument from Bruker Daltonik (Bremen, Germany) equipped with an ESI source. Calibration was performed using an Agilent ESI low concentration tune mix before the experiment. The sample and the calibration solutions were injected in the timsTOF using a glass syringe pump with 0.5 mL volume and flow rate of 0.3 µL. The timsTOF was operated in the negative ion mode in a mass range of *m/z* 50 to 1500 with the spray voltage of 4.5 kV. The end plate offset of -500 V with a $N_2$ nebulizer pressure of 0.3 bar and a dry gas flow of 1.5 L $min^{-1}$ at 275 ℃.

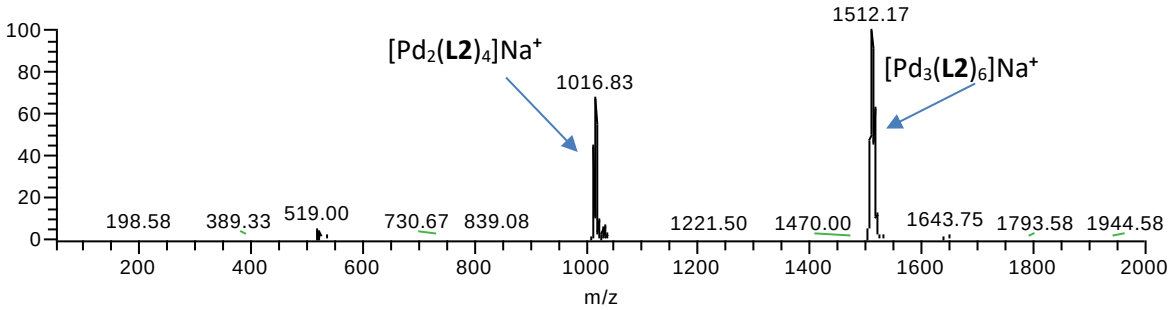


**Figure S14.** ESI mass spectrum (positive mode) of a mixture of $Pd(OAc)_2$ and **L2** in benzene and ethyl acetate.

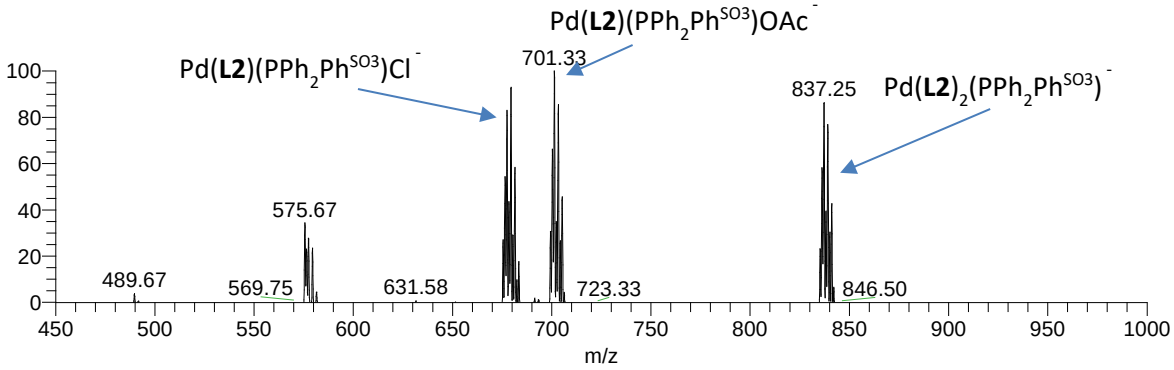


**Figure S15.** ESI mass spectrum (negative mode) of a mixture of $Pd(OAc)_2$, **L2**, $(PPh_2Ph^{SO3-})Na$ and acetic acid in benzene and deuterated benzene.

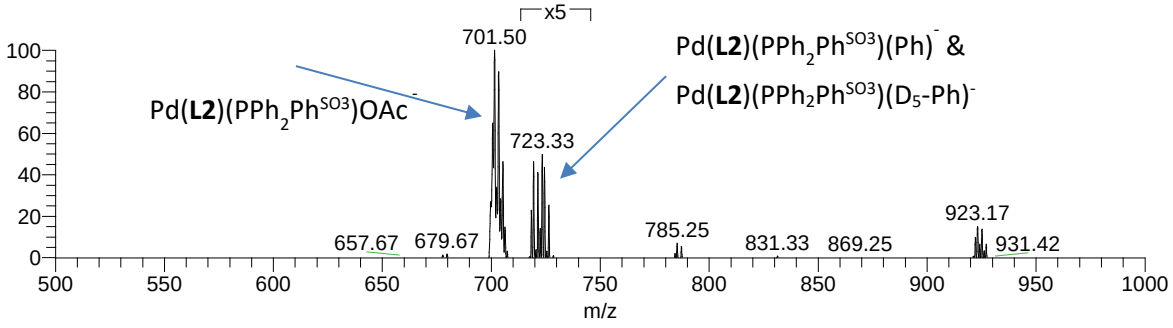


**Figure S16.** ESI mass spectrum (negative mode) of $[Pd(\mathbf{L2})(PPh_2Ph^{SO3})OAc]Na$ in benzene and deuterated benzene (heated for 5 min at 80 °C and filtered, filtrate injected).

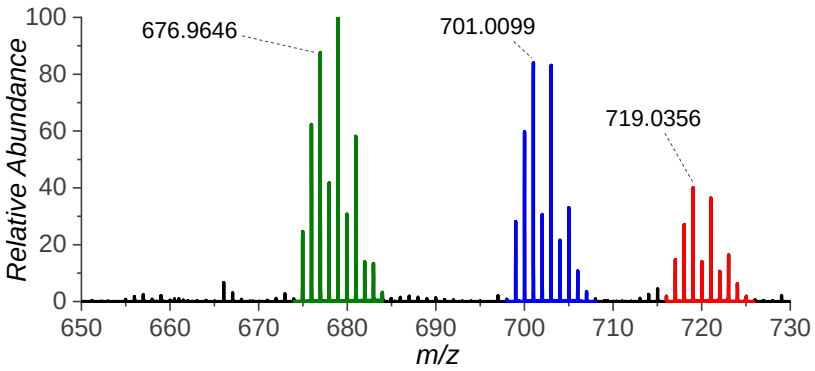


**Figure S17.** High resolution mass spectrum (negative mode) of [Pd(**L2**)($PPh_2Ph^{SO3}$)OAc]Na in benzene and DCM (heated for 5min at 60 ℃ and filtered, filtrate injected); [($PPh_2Ph^{SO3-}$)Pd(**L2**)(X)]$^-$ ions highlighted, where X = Cl (*m/z* 677, green), AcO (*m/z* 701, blue), or Ph (*m/z* 719, red).

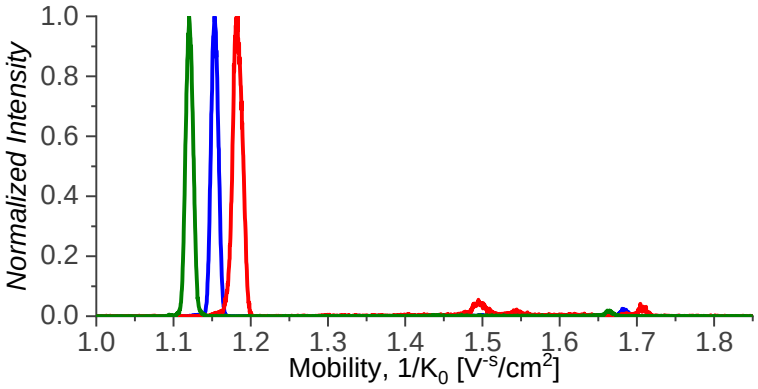


**Figure S18.** Mobilogram of [($PPh_2Ph^{SO3-}$)Pd(**L2**)(X)]$^-$, where X = Cl (*m/z* 677, green), AcO (*m/z* 701, blue), or Ph (*m/z* 719, red). Note that the minor peaks at the higher values of mobility originate from fragmentations of larger clusters; i.e., they do not correspond to isomers of the monopalladium complexes.

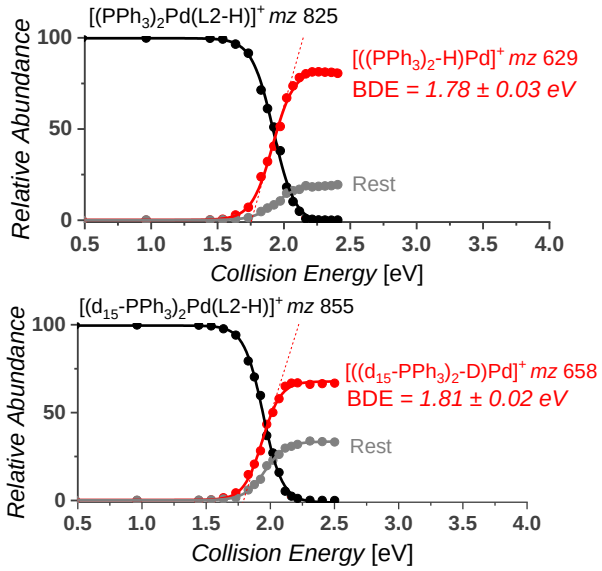


**Figure S19.** Energy resolved CIDs of $[(PPh_3)_2Pd(\mathbf{L2})]^+$ *m/z*=825 (left) and $[(P(C_6D_5)_3)_2Pd(\mathbf{L2})]^+$ *m/z*=855 (right).

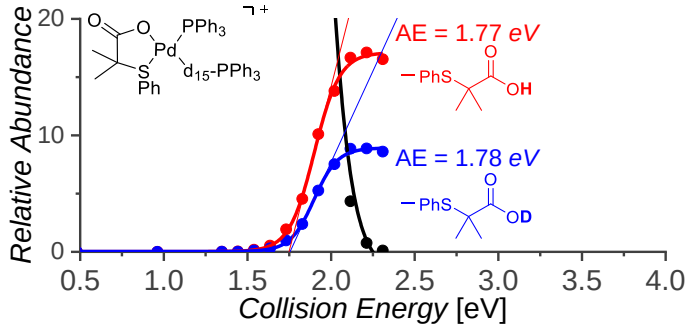


**Figure S20.** Energy resolved CID of $[(PPh_3)(d_{15}\text{-}PPh_3)Pd(\mathbf{L2})]^+$ (*m/z*=840).

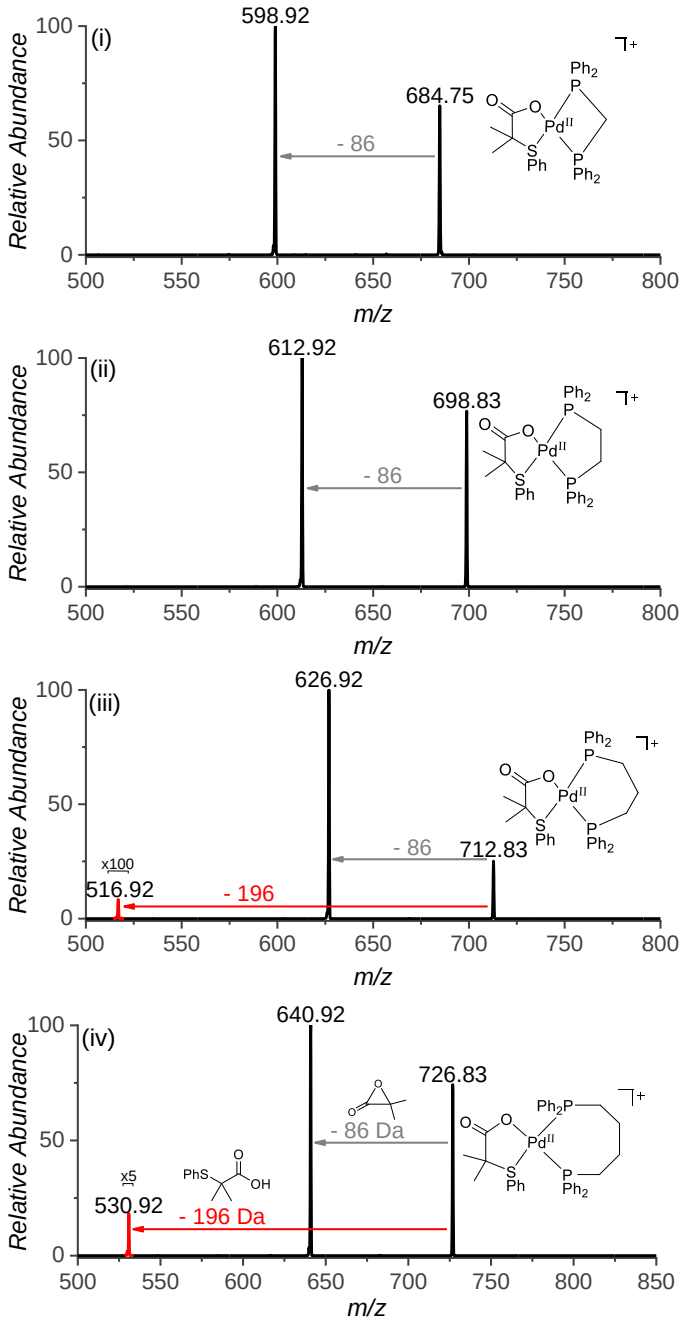


**Figure S21.** CID mass spectra of (i) [(dppm)Pd(**L2**)]$^+$ (*m/z*=685), (ii) [(dppe)Pd(**L2**)]$^+$ (*m/z*=699), (iii) [(dppp)Pd(**L2**)]$^+$ (*m/z*=713) and (iv) [(dppb)Pd(**L2**)]$^+$ (*m/z*=727).

## 7. DFT calculations

All structures were optimized using density functional theory (DFT) as implemented in Gaussian 16,[8] with B3LYP[9] as functional, 6-31G(d,p) as basis set for non-metallic atoms, and SDD[10] as basis set for palladium. Final energies were obtained performing single-point calculations on the previously optimized structures at M06[11]/def2tzvpp[12] level of theory, introducing solvation factors with the IEF-PCM[13] method, and acetic acid as solvent. The stationary points were characterized by frequency calculations in order to verify that they have the right number of imaginary frequencies.

**Table S39**. Energies of the structures included in the main Manuscript

| Compound | E (B3LYP) | Correction to G | G (M06) | $\Delta G$ (kcal/mol) | Imaginary freq. ($cm^{-1}$) |
|---|---|---|---|---|---|
| **$Pd_3(OAc)_6$** | -1754.741193 | 0.242712 | -1754.498481 | 0 | |
| **I** ($Pd(OAc)_2$) | -584.877443 | 0.064476 | -584.812967 | +12.5 | |
| HOAc | -229.064385 | 0.034877 | -229.029508 | | |
| Ligand **L2** | -936.787272 | 0.159941 | -936.627331 | | |
| **II** | -1292.625462 | 0.193240 | -1292.432222 | -0.9 | |
| **III** | -2000.373320 | 0.320370 | -2000.052950 | -15.3 | |
| Benzene | -232.143505 | 0.07314 | -232.070365 | | |
| **IV** | -817.026177 | 0.156968 | -816.869209 | +8.9 | |
| **V** | -1392.258978 | 0.270498 | -1391.988480 | | |
| **VI** | -1624.423646 | 0.365825 | -1624.057821 | +0.6 | |
| **VII** | -2100.004899 | 0.398180 | -2099.606719 | | |
| **VIII** | -2332.177308 | 0.495660 | -2331.681648 | -2.9 | |
| **TS-A** | -2332.116435 | 0.488351 | -2331.628084 | +33.6 | -1415.5 |
| **IX** | -2332.156985 | 0.496851 | -2331.660134 | +13.5 | |
| **TS-B** | -2332.110667 | 0.485327 | -2331.625340 | +35.3 | -582.0 |
| **VIII-OAc** | -2560.785447 | 0.538731 | -2560.246716 | -7.5 | |
| **TS-C** | -2560.769467 | 0.535771 | -2560.233696 | +0.7 | -838.7 |

Cartesian coordinates of the optimized structures are shown below, as well as their single point energy and correction to Gibbs free energy (in Hartrees).

**$Pd_3(OAc)_6$**:

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -0.041846 | -1.870081 | -0.000251 |
| 2 | 8 | 0 | -2.385559 | 0.020794 | -1.613349 |
| 3 | 6 | 0 | -2.329656 | -1.222021 | -1.863010 |
| 4 | 8 | 0 | -1.605465 | -2.092314 | -1.293891 |
| 5 | 6 | 0 | -3.259194 | -1.729598 | -2.945940 |
| 6 | 1 | 0 | -2.806630 | -2.573690 | -3.468142 |
| 7 | 1 | 0 | -4.185984 | -2.073188 | -2.474105 |
| 8 | 1 | 0 | -3.504648 | -0.926283 | -3.641598 |
| 9 | 8 | 0 | 1.510466 | -2.160647 | 1.294178 |
| 10 | 6 | 0 | 2.271565 | -1.323111 | 1.863913 |
| 11 | 8 | 0 | 2.381506 | -0.083685 | 1.614832 |
| 12 | 6 | 0 | 3.178700 | -1.868661 | 2.947344 |
| 13 | 1 | 0 | 2.719612 | -2.733074 | 3.428385 |
| 14 | 1 | 0 | 4.119203 | -2.186301 | 2.484513 |
| 15 | 1 | 0 | 3.404421 | -1.089905 | 3.677208 |
| 16 | 46 | 0 | -1.601387 | 0.972211 | 0.004679 |
| 17 | 46 | 0 | 1.643544 | 0.900921 | -0.005037 |
| 18 | 8 | 0 | -1.107771 | 2.100211 | 1.624504 |
| 19 | 6 | 0 | 0.022650 | 2.618353 | 1.875229 |
| 20 | 8 | 0 | 1.123510 | 2.391125 | 1.289510 |
| 21 | 6 | 0 | 0.071036 | 3.602233 | 3.025861 |
| 22 | 1 | 0 | 0.815158 | 4.374877 | 2.825614 |
| 23 | 1 | 0 | -0.911675 | 4.043305 | 3.194940 |
| 24 | 1 | 0 | 0.377346 | 3.064499 | 3.929454 |
| 25 | 8 | 0 | -2.626414 | -0.225561 | 1.302239 |
| 26 | 6 | 0 | -2.270188 | -1.294439 | 1.883224 |
| 27 | 8 | 0 | -1.260725 | -2.016382 | 1.621816 |
| 28 | 6 | 0 | -3.139496 | -1.744290 | 3.039201 |
| 29 | 1 | 0 | -2.987604 | -2.803955 | 3.245251 |
| 30 | 1 | 0 | -2.864744 | -1.164711 | 3.926757 |
| 31 | 1 | 0 | -4.188302 | -1.538459 | 2.817477 |
| 32 | 8 | 0 | 2.614080 | -0.342685 | -1.300291 |
| 33 | 6 | 0 | 2.210190 | -1.393869 | -1.882617 |
| 34 | 8 | 0 | 1.168464 | -2.069161 | -1.623209 |
| 35 | 6 | 0 | 3.062370 | -1.882128 | -3.035742 |
| 36 | 1 | 0 | 4.119623 | -1.763774 | -2.790265 |
| 37 | 1 | 0 | 2.834443 | -2.921804 | -3.270931 |
| 38 | 1 | 0 | 2.852170 | -1.260322 | -3.912142 |
| 39 | 8 | 0 | 1.202019 | 2.049776 | -1.625545 |
| 40 | 6 | 0 | 0.094632 | 2.614566 | -1.877731 |
| 41 | 8 | 0 | -1.015122 | 2.435710 | -1.291923 |
| 42 | 6 | 0 | 0.086328 | 3.600680 | -3.027599 |
| 43 | 1 | 0 | -0.327706 | 3.102645 | -3.910550 |
| 44 | 1 | 0 | -0.562177 | 4.445188 | -2.786740 |
| 45 | 1 | 0 | 1.097627 | 3.940887 | -3.250885 |

**$Pd(OAc)_2$**:

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | 0.000017 | -0.000075 | -0.000104 |
| 2 | 8 | 0 | 1.762329 | 1.088029 | 0.017933 |
| 3 | 6 | 0 | 2.436426 | -0.000016 | 0.017634 |
| 4 | 8 | 0 | 1.762594 | -1.088157 | 0.018119 |
| 5 | 6 | 0 | 3.931471 | 0.000253 | -0.013596 |
| 6 | 1 | 0 | 4.317007 | -0.899216 | 0.469775 |
| 7 | 1 | 0 | 4.264866 | 0.002529 | -1.057065 |
| 8 | 1 | 0 | 4.316617 | 0.897978 | 0.473361 |
| 9 | 8 | 0 | -1.762470 | -1.088086 | -0.018105 |
| 10 | 6 | 0 | -2.436408 | -0.000082 | -0.017475 |
| 11 | 8 | 0 | -1.762503 | 1.088137 | -0.017909 |
| 12 | 6 | 0 | -3.931535 | 0.000182 | 0.013976 |
| 13 | 1 | 0 | -4.317301 | -0.897427 | -0.472696 |
| 14 | 1 | 0 | -4.264740 | -0.001603 | 1.057498 |
| 15 | 1 | 0 | -4.316563 | 0.899764 | -0.469614 |

Ligand **L2**:

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -1.415433 | -0.011049 | 0.476247 |
| 2 | 6 | 0 | -0.986180 | 1.219633 | 1.274472 |
| 3 | 1 | 0 | -1.649352 | 1.345608 | 2.135826 |
| 4 | 1 | 0 | 0.036440 | 1.101409 | 1.638377 |
| 5 | 1 | 0 | -1.048287 | 2.126153 | 0.670198 |
| 6 | 6 | 0 | -2.833753 | 0.205157 | -0.058118 |
| 7 | 8 | 0 | -3.510196 | 1.190594 | 0.133533 |
| 8 | 8 | 0 | -3.279789 | -0.853190 | -0.775411 |
| 9 | 6 | 0 | 1.303281 | -0.079256 | -0.501755 |
| 10 | 6 | 0 | 1.966434 | 1.155971 | -0.544697 |
| 11 | 6 | 0 | 1.997799 | -1.217222 | -0.064725 |
| 12 | 6 | 0 | 3.297725 | 1.252988 | -0.138979 |
| 13 | 1 | 0 | 1.435037 | 2.032324 | -0.900600 |
| 14 | 6 | 0 | 3.328233 | -1.114755 | 0.343904 |
| 15 | 1 | 0 | 1.495370 | -2.178832 | -0.060844 |
| 16 | 6 | 0 | 3.978939 | 0.119644 | 0.309221 |
| 17 | 1 | 0 | 3.803244 | 2.213543 | -0.176243 |
| 18 | 1 | 0 | 3.857794 | -2.001005 | 0.681216 |
| 19 | 1 | 0 | 5.015884 | 0.196902 | 0.622643 |
| 20 | 16 | 0 | -0.381749 | -0.224667 | -1.101576 |
| 21 | 6 | 0 | -1.358128 | -1.286983 | 1.332447 |
| 22 | 1 | 0 | -2.001371 | -1.178517 | 2.214109 |
| 23 | 1 | 0 | -1.683637 | -2.160465 | 0.765960 |

| | | | | | |
|---|---|---|---|---|---|
| 24 | 1 | 0 | -0.335731 | -1.452128 | 1.683147 |
| 25 | 1 | 0 | -4.171037 | -0.614328 | -1.081643 |

**$PPh_3$**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 15 | 0 | 0.000572 | -0.000303 | -1.208857 |
| 2 | 6 | 0 | -1.209555 | -1.151830 | -0.404320 |
| 3 | 6 | 0 | -2.458107 | -1.299632 | -1.031732 |
| 4 | 6 | 0 | -0.949852 | -1.898507 | 0.754801 |
| 5 | 6 | 0 | -3.427653 | -2.151866 | -0.504586 |
| 6 | 1 | 0 | -2.668158 | -0.745408 | -1.943087 |
| 7 | 6 | 0 | -1.916506 | -2.760806 | 1.276320 |
| 8 | 1 | 0 | 0.011984 | -1.809749 | 1.249621 |
| 9 | 6 | 0 | -3.157720 | -2.887111 | 0.651317 |
| 10 | 1 | 0 | -4.388562 | -2.250148 | -1.001658 |
| 11 | 1 | 0 | -1.698130 | -3.333759 | 2.173292 |
| 12 | 1 | 0 | -3.907838 | -3.559143 | 1.058198 |
| 13 | 6 | 0 | 1.602702 | -0.471584 | -0.403476 |
| 14 | 6 | 0 | 2.111215 | 0.117858 | 0.763874 |
| 15 | 6 | 0 | 2.362576 | -1.469241 | -1.037051 |
| 16 | 6 | 0 | 3.340832 | -0.287089 | 1.287121 |
| 17 | 1 | 0 | 1.546807 | 0.898612 | 1.263579 |
| 18 | 6 | 0 | 3.585157 | -1.881779 | -0.508351 |
| 19 | 1 | 0 | 1.993863 | -1.921363 | -1.954355 |
| 20 | 6 | 0 | 4.078659 | -1.289156 | 0.655545 |
| 21 | 1 | 0 | 3.721413 | 0.181503 | 2.190502 |
| 22 | 1 | 0 | 4.156841 | -2.657203 | -1.010327 |
| 23 | 1 | 0 | 5.035418 | -1.601948 | 1.063753 |
| 24 | 6 | 0 | -0.392136 | 1.622969 | -0.403584 |
| 25 | 6 | 0 | 0.104972 | 2.778620 | -1.029452 |
| 26 | 6 | 0 | -1.170109 | 1.770472 | 0.754710 |
| 27 | 6 | 0 | -0.148957 | 4.043942 | -0.501607 |
| 28 | 1 | 0 | 0.691212 | 2.684208 | -1.940092 |
| 29 | 6 | 0 | -1.434241 | 3.038375 | 1.276859 |
| 30 | 1 | 0 | -1.574928 | 0.892653 | 1.248154 |
| 31 | 6 | 0 | -0.922149 | 4.176925 | 0.653417 |
| 32 | 1 | 0 | 0.247118 | 4.925626 | -0.997445 |
| 33 | 1 | 0 | -2.040822 | 3.135050 | 2.173092 |
| 34 | 1 | 0 | -1.129569 | 5.162249 | 1.060797 |

**II**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | 1.337631 | 0.205851 | -0.172156 |
| 2 | 8 | 0 | -0.093344 | 3.979161 | 0.450914 |
| 3 | 6 | 0 | 0.016987 | 2.781876 | 0.256866 |
| 4 | 8 | 0 | 1.169741 | 2.161127 | 0.179339 |
| 5 | 6 | 0 | -1.281349 | 1.924181 | 0.178601 |
| 6 | 8 | 0 | 3.353910 | -0.253318 | 0.330600 |
| 7 | 6 | 0 | 3.136783 | -1.462800 | 0.001756 |
| 8 | 8 | 0 | 1.953872 | -1.767086 | -0.401834 |
| 9 | 6 | 0 | 4.204625 | -2.510989 | 0.089908 |
| 10 | 1 | 0 | 4.233562 | -3.087915 | -0.838046 |
| 11 | 1 | 0 | 5.173381 | -2.048071 | 0.280834 |
| 12 | 1 | 0 | 3.965411 | -3.202856 | 0.904053 |
| 13 | 16 | 0 | -0.834236 | 0.422330 | -0.897648 |
| 14 | 6 | 0 | -1.662723 | 1.510790 | 1.605754 |
| 15 | 1 | 0 | -1.839480 | 2.426267 | 2.178584 |
| 16 | 1 | 0 | -2.576421 | 0.910892 | 1.618541 |
| 17 | 1 | 0 | -0.862992 | 0.950186 | 2.096519 |
| 18 | 6 | 0 | -2.408226 | 2.694537 | -0.507999 |
| 19 | 1 | 0 | -2.560536 | 3.629626 | 0.036905 |
| 20 | 1 | 0 | -2.152550 | 2.947334 | -1.540022 |
| 21 | 1 | 0 | -3.339846 | 2.119695 | -0.501788 |
| 22 | 6 | 0 | -1.856936 | -0.936950 | -0.314735 |
| 23 | 6 | 0 | -3.114049 | -1.097861 | -0.912948 |
| 24 | 6 | 0 | -1.415933 | -1.833061 | 0.665812 |
| 25 | 6 | 0 | -3.940201 | -2.146092 | -0.506974 |
| 26 | 1 | 0 | -3.437649 | -0.414854 | -1.692039 |
| 27 | 6 | 0 | -2.247201 | -2.883590 | 1.056068 |
| 28 | 1 | 0 | -0.430085 | -1.717396 | 1.102432 |
| 29 | 6 | 0 | -3.508201 | -3.038084 | 0.476674 |
| 30 | 1 | 0 | -4.915892 | -2.269470 | -0.967003 |
| 31 | 1 | 0 | -1.904889 | -3.582932 | 1.812784 |
| 32 | 1 | 0 | -4.150169 | -3.857755 | 0.784960 |

**III**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -0.019451 | -1.161272 | -0.033966 |
| 2 | 6 | 0 | 2.885425 | -1.104571 | -1.181449 |
| 3 | 6 | 0 | 4.265704 | -0.471514 | -1.327399 |
| 4 | 1 | 0 | 4.510583 | 0.175882 | -0.482862 |
| 5 | 1 | 0 | 4.999869 | -1.280467 | -1.343211 |

| | | | | | |
|---|---|---|---|---|---|
| 6 | 1 | 0 | 4.341111 | 0.105099 | -2.254738 |
| 7 | 6 | 0 | 2.794930 | -2.006470 | 0.083937 |
| 8 | 8 | 0 | 1.627276 | -2.124823 | 0.663330 |
| 9 | 8 | 0 | 3.802567 | -2.588784 | 0.450761 |
| 10 | 16 | 0 | 1.549400 | 0.232750 | -1.067516 |
| 11 | 6 | 0 | 2.520497 | -1.942613 | -2.420220 |
| 12 | 1 | 0 | 1.515870 | -2.368828 | -2.345769 |
| 13 | 1 | 0 | 2.588694 | -1.346626 | -3.335565 |
| 14 | 1 | 0 | 3.233208 | -2.769874 | -2.488679 |
| 15 | 6 | 0 | 2.155705 | 1.363574 | 0.202743 |
| 16 | 6 | 0 | 2.487300 | 2.659508 | -0.210854 |
| 17 | 6 | 0 | 2.278993 | 0.990572 | 1.548599 |
| 18 | 6 | 0 | 2.945667 | 3.587195 | 0.726419 |
| 19 | 1 | 0 | 2.387116 | 2.937223 | -1.255419 |
| 20 | 6 | 0 | 2.744901 | 1.925919 | 2.473719 |
| 21 | 1 | 0 | 2.021213 | -0.014815 | 1.863760 |
| 22 | 6 | 0 | 3.075510 | 3.221244 | 2.067191 |
| 23 | 1 | 0 | 3.203693 | 4.592014 | 0.405608 |
| 24 | 1 | 0 | 2.847510 | 1.637488 | 3.515460 |
| 25 | 1 | 0 | 3.434713 | 3.943057 | 2.794656 |
| 26 | 8 | 0 | -1.207104 | -2.546256 | 0.844821 |
| 27 | 6 | 0 | -2.505332 | -2.434595 | 0.932934 |
| 28 | 8 | 0 | -3.239329 | -3.298663 | 1.383307 |
| 29 | 6 | 0 | -3.160894 | -1.075773 | 0.529012 |
| 30 | 6 | 0 | -3.210147 | -0.193701 | 1.782720 |
| 31 | 1 | 0 | -3.675200 | 0.774362 | 1.578679 |
| 32 | 1 | 0 | -3.814652 | -0.719418 | 2.528106 |
| 33 | 1 | 0 | -2.216166 | -0.030603 | 2.207215 |
| 34 | 6 | 0 | -4.552673 | -1.287749 | -0.065415 |
| 35 | 1 | 0 | -5.037539 | -0.331430 | -0.287372 |
| 36 | 1 | 0 | -4.512614 | -1.886832 | -0.978519 |
| 37 | 1 | 0 | -5.152842 | -1.834578 | 0.665984 |
| 38 | 16 | 0 | -2.047165 | -0.337364 | -0.821877 |
| 39 | 6 | 0 | -2.219547 | 1.448032 | -0.690552 |
| 40 | 6 | 0 | -3.137661 | 2.067818 | -1.549052 |
| 41 | 6 | 0 | -1.461712 | 2.213000 | 0.204444 |
| 42 | 6 | 0 | -3.304296 | 3.452379 | -1.499492 |
| 43 | 1 | 0 | -3.709887 | 1.470514 | -2.251832 |
| 44 | 6 | 0 | -1.631505 | 3.597482 | 0.241895 |
| 45 | 1 | 0 | -0.746185 | 1.730631 | 0.860925 |
| 46 | 6 | 0 | -2.552462 | 4.217244 | -0.605547 |
| 47 | 1 | 0 | -4.016834 | 3.931395 | -2.164125 |
| 48 | 1 | 0 | -1.039863 | 4.189400 | 0.933581 |
| 49 | 1 | 0 | -2.680524 | 5.295047 | -0.572691 |

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**IV**

Standard orientation:

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -0.124445 | 0.289172 | -0.213089 |
| 2 | 8 | 0 | -0.030835 | 2.418359 | -0.208837 |
| 3 | 6 | 0 | 1.211873 | 2.341680 | 0.064811 |
| 4 | 8 | 0 | 1.727035 | 1.170367 | 0.163706 |
| 5 | 6 | 0 | 2.037193 | 3.571329 | 0.293895 |
| 6 | 1 | 0 | 3.096504 | 3.349450 | 0.154733 |
| 7 | 1 | 0 | 1.717153 | 4.366749 | -0.382475 |
| 8 | 1 | 0 | 1.880932 | 3.917382 | 1.321298 |
| 9 | 6 | 0 | 0.120804 | -1.885104 | 0.589488 |
| 10 | 6 | 0 | 0.309088 | -1.912652 | -0.818145 |
| 11 | 6 | 0 | 1.252108 | -1.934566 | 1.442736 |
| 12 | 6 | 0 | 1.622416 | -1.997448 | -1.348232 |
| 13 | 1 | 0 | -0.547900 | -2.024902 | -1.473805 |
| 14 | 6 | 0 | 2.523445 | -2.005225 | 0.904646 |
| 15 | 1 | 0 | 1.104293 | -1.925644 | 2.517804 |
| 16 | 6 | 0 | 2.709589 | -2.035958 | -0.495391 |
| 17 | 1 | 0 | 1.760984 | -2.042204 | -2.423895 |
| 18 | 1 | 0 | -0.873943 | -1.947820 | 1.017702 |
| 19 | 8 | 0 | -2.562548 | -0.314263 | 1.444171 |
| 20 | 6 | 0 | -2.873509 | -0.215582 | 0.260604 |
| 21 | 8 | 0 | -2.017257 | -0.082630 | -0.734252 |
| 22 | 6 | 0 | -4.318995 | -0.221167 | -0.212944 |
| 23 | 1 | 0 | -4.964445 | -0.587062 | 0.586552 |
| 24 | 1 | 0 | -4.612985 | 0.801141 | -0.472266 |
| 25 | 1 | 0 | -4.435621 | -0.834491 | -1.109840 |
| 26 | 1 | 0 | 3.715318 | -2.097626 | -0.900147 |
| 27 | 1 | 0 | 3.388931 | -2.043397 | 1.559327 |

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**V**

Standard orientation:

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -1.459845 | -0.191579 | -0.293091 |
| 2 | 8 | 0 | -3.570700 | -0.303041 | -0.636713 |
| 3 | 6 | 0 | -3.369606 | 0.076174 | -1.835306 |
| 4 | 8 | 0 | -2.146268 | 0.313453 | -2.177464 |
| 5 | 15 | 0 | 0.764895 | 0.026337 | 0.047740 |
| 6 | 6 | 0 | -0.046727 | -0.185209 | 1.655231 |
| 7 | 6 | 0 | -0.868242 | -1.351298 | 1.753756 |
| 8 | 6 | 0 | -0.181439 | 0.846925 | 2.616258 |
| 9 | 6 | 0 | -1.794245 | -1.461347 | 2.813399 |
| 10 | 1 | 0 | -0.671318 | -2.222310 | 1.132704 |
| 11 | 6 | 0 | -1.081777 | 0.699438 | 3.657740 |
| 12 | 1 | 0 | 0.429179 | 1.740244 | 2.536476 |
| 13 | 6 | 0 | -1.898822 | -0.446323 | 3.750419 |
| 14 | 1 | 0 | -2.402856 | -2.355714 | 2.895467 |
| 15 | 1 | 0 | -1.162896 | 1.477437 | 4.410459 |

| | | | | | |
|---|---|---|---|---|---|
| 16 | 1 | 0 | -2.604126 | -0.535990 | 4.570328 |
| 17 | 6 | 0 | 1.864249 | -1.351054 | -0.344959 |
| 18 | 6 | 0 | 2.015237 | -1.727824 | -1.691699 |
| 19 | 6 | 0 | 2.565604 | -2.032596 | 0.665385 |
| 20 | 6 | 0 | 2.870483 | -2.777600 | -2.020690 |
| 21 | 1 | 0 | 1.467130 | -1.209908 | -2.473614 |
| 22 | 6 | 0 | 3.416519 | -3.082794 | 0.322174 |
| 23 | 1 | 0 | 2.453069 | -1.745529 | 1.706331 |
| 24 | 6 | 0 | 3.568263 | -3.453922 | -1.016202 |
| 25 | 1 | 0 | 2.987076 | -3.071155 | -3.058876 |
| 26 | 1 | 0 | 3.960749 | -3.609363 | 1.099664 |
| 27 | 1 | 0 | 4.230408 | -4.273607 | -1.276917 |
| 28 | 6 | 0 | 1.584291 | 1.620216 | -0.139987 |
| 29 | 6 | 0 | 0.802908 | 2.778968 | -0.307439 |
| 30 | 6 | 0 | 2.987998 | 1.707184 | -0.132851 |
| 31 | 6 | 0 | 1.426968 | 4.017071 | -0.441607 |
| 32 | 1 | 0 | -0.280370 | 2.708964 | -0.345370 |
| 33 | 6 | 0 | 3.599335 | 2.951740 | -0.269344 |
| 34 | 1 | 0 | 3.594525 | 0.814077 | -0.023541 |
| 35 | 6 | 0 | 2.821938 | 4.103031 | -0.421583 |
| 36 | 1 | 0 | 0.826482 | 4.911272 | -0.573790 |
| 37 | 1 | 0 | 4.682238 | 3.021980 | -0.260601 |
| 38 | 1 | 0 | 3.304612 | 5.068859 | -0.533864 |
| 39 | 6 | 0 | -4.475745 | 0.219773 | -2.827897 |
| 40 | 1 | 0 | -4.234613 | 0.994454 | -3.558153 |
| 41 | 1 | 0 | -4.595726 | -0.729591 | -3.361714 |
| 42 | 1 | 0 | -5.411508 | 0.446850 | -2.314265 |

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## VI

Standard orientation:

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -1.110453 | -1.178450 | -0.204084 |
| 2 | 6 | 0 | 2.471117 | -2.946152 | -0.897985 |
| 3 | 6 | 0 | 2.412396 | -3.039826 | 0.508281 |
| 4 | 6 | 0 | 1.311764 | -2.967663 | -1.655526 |
| 5 | 6 | 0 | 1.193879 | -3.163845 | 1.153661 |
| 6 | 6 | 0 | 0.058881 | -3.109282 | -1.017284 |
| 7 | 1 | 0 | 1.357905 | -2.926748 | -2.739163 |
| 8 | 6 | 0 | -0.000456 | -3.210881 | 0.398432 |
| 9 | 1 | 0 | 3.436897 | -2.873393 | -1.386840 |
| 10 | 1 | 0 | -0.821842 | -3.330371 | -1.614602 |
| 11 | 1 | 0 | -0.926198 | -3.514396 | 0.880689 |
| 12 | 1 | 0 | 1.149529 | -3.274576 | 2.232563 |
| 13 | 1 | 0 | 3.332676 | -3.027457 | 1.083071 |
| 14 | 8 | 0 | -2.865492 | -0.034629 | -0.198445 |
| 15 | 6 | 0 | -3.592893 | -1.097162 | -0.276103 |
| 16 | 8 | 0 | -2.986505 | -2.217246 | -0.344839 |
| 17 | 15 | 0 | 0.313505 | 0.624468 | 0.042215 |
| 18 | 6 | 0 | 2.107392 | 0.414513 | 0.320079 |
| 19 | 6 | 0 | 2.965054 | 0.253266 | -0.784007 |
| 20 | 6 | 0 | 2.650706 | 0.427287 | 1.616001 |
| 21 | 6 | 0 | 4.340950 | 0.132351 | -0.592265 |
| 22 | 1 | 0 | 2.564072 | 0.248692 | -1.792164 |
| 23 | 6 | 0 | 4.026867 | 0.294454 | 1.800231 |
| 24 | 1 | 0 | 2.008999 | 0.569050 | 2.478397 |
| 25 | 6 | 0 | 4.873908 | 0.150971 | 0.698807 |
| 26 | 1 | 0 | 4.996298 | 0.030070 | -1.451866 |
| 27 | 1 | 0 | 4.437998 | 0.321633 | 2.804583 |
| 28 | 1 | 0 | 5.946045 | 0.063047 | 0.845503 |
| 29 | 6 | 0 | 0.171476 | 1.735923 | -1.402967 |
| 30 | 6 | 0 | 1.082992 | 2.795543 | -1.572603 |
| 31 | 6 | 0 | -0.870048 | 1.567619 | -2.330109 |
| 32 | 6 | 0 | 0.947248 | 3.668100 | -2.651257 |
| 33 | 1 | 0 | 1.897030 | 2.938726 | -0.869741 |
| 34 | 6 | 0 | -0.993416 | 2.441253 | -3.411033 |
| 35 | 6 | 0 | -0.087708 | 3.490437 | -3.572772 |
| 36 | 1 | 0 | 1.652895 | 4.483965 | -2.772977 |
| 37 | 1 | 0 | -1.799110 | 2.300885 | -4.124720 |
| 38 | 1 | 0 | -0.186645 | 4.168907 | -4.414451 |
| 39 | 1 | 0 | -1.589990 | 0.767087 | -2.203820 |
| 40 | 6 | 0 | -0.369025 | 1.484503 | 1.506360 |
| 41 | 6 | 0 | -0.642425 | 0.741678 | 2.669716 |
| 42 | 6 | 0 | -0.642892 | 2.860326 | 1.484813 |
| 43 | 6 | 0 | -1.157244 | 1.373404 | 3.800368 |
| 44 | 1 | 0 | -0.460783 | -0.329464 | 2.691309 |
| 45 | 6 | 0 | -1.162713 | 3.484453 | 2.619590 |
| 46 | 1 | 0 | -0.457543 | 3.443581 | 0.589909 |
| 47 | 6 | 0 | -1.417588 | 2.745955 | 3.776055 |
| 48 | 1 | 0 | -1.362762 | 0.794083 | 4.695132 |
| 49 | 1 | 0 | -1.371559 | 4.549388 | 2.595913 |
| 50 | 1 | 0 | -1.824642 | 3.236260 | 4.654868 |
| 51 | 6 | 0 | -5.083111 | -1.001072 | -0.253827 |
| 52 | 1 | 0 | -5.520663 | -1.842353 | -0.794423 |
| 53 | 1 | 0 | -5.424165 | -1.045398 | 0.786600 |
| 54 | 1 | 0 | -5.410868 | -0.051448 | -0.680797 |

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## VII

Standard orientation:

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | 0.337379 | -0.319336 | 0.161497 |
| 2 | 8 | 0 | 2.088695 | -2.147076 | -3.031045 |
| 3 | 6 | 0 | 1.834751 | -1.760181 | -1.908946 |
| 4 | 8 | 0 | 0.729729 | -1.072446 | -1.652052 |
| 5 | 6 | 0 | 2.770115 | -2.144885 | -0.735000 |

| | | | | | |
|---|---|---|---|---|---|
| 6 | 6 | 0 | 2.272333 | -3.475493 | -0.135500 |
| 7 | 1 | 0 | 2.932527 | -3.811478 | 0.668615 |
| 8 | 1 | 0 | 1.252892 | -3.397177 | 0.255142 |
| 9 | 1 | 0 | 2.275219 | -4.230251 | -0.927130 |
| 10 | 6 | 0 | 4.222219 | -2.253759 | -1.194678 |
| 11 | 1 | 0 | 4.602964 | -1.306092 | -1.580074 |
| 12 | 1 | 0 | 4.866526 | -2.592341 | -0.378388 |
| 13 | 1 | 0 | 4.263047 | -2.981882 | -2.008334 |
| 14 | 16 | 0 | 2.604708 | -0.887443 | 0.665044 |
| 15 | 6 | 0 | 3.560925 | 0.549731 | 0.147778 |
| 16 | 6 | 0 | 3.235635 | 1.303708 | -0.989274 |
| 17 | 6 | 0 | 4.654649 | 0.899706 | 0.949249 |
| 18 | 6 | 0 | 4.021741 | 2.407307 | -1.321314 |
| 19 | 1 | 0 | 2.390614 | 1.028872 | -1.611596 |
| 20 | 6 | 0 | 5.426248 | 2.012815 | 0.610170 |
| 21 | 1 | 0 | 4.903106 | 0.304950 | 1.822624 |
| 22 | 6 | 0 | 5.112195 | 2.764273 | -0.523239 |
| 23 | 1 | 0 | 3.779789 | 2.988395 | -2.205766 |
| 24 | 1 | 0 | 6.275692 | 2.284840 | 1.228727 |
| 25 | 1 | 0 | 5.717413 | 3.625783 | -0.787333 |
| 26 | 15 | 0 | -1.889032 | 0.227706 | 0.002872 |
| 27 | 6 | 0 | -1.417956 | 0.340797 | 1.757889 |
| 28 | 6 | 0 | -0.311967 | 1.195905 | 2.041075 |
| 29 | 6 | 0 | -1.869213 | -0.560940 | 2.749562 |
| 30 | 6 | 0 | 0.299104 | 1.147170 | 3.311232 |
| 31 | 1 | 0 | -0.040729 | 1.994616 | 1.354407 |
| 32 | 6 | 0 | -1.259716 | -0.578079 | 3.994789 |
| 33 | 1 | 0 | -2.700171 | -1.224795 | 2.534358 |
| 34 | 6 | 0 | -0.169583 | 0.267584 | 4.275331 |
| 35 | 1 | 0 | 1.120200 | 1.821784 | 3.531581 |
| 36 | 1 | 0 | -1.628859 | -1.250772 | 4.762835 |
| 37 | 1 | 0 | 0.294400 | 0.238553 | 5.256033 |
| 38 | 6 | 0 | -2.383111 | 1.844522 | -0.643389 |
| 39 | 6 | 0 | -2.143666 | 2.114301 | -2.002665 |
| 40 | 6 | 0 | -3.003991 | 2.807965 | 0.170176 |
| 41 | 6 | 0 | -2.533872 | 3.339167 | -2.541384 |
| 42 | 1 | 0 | -1.655107 | 1.374773 | -2.631063 |
| 43 | 6 | 0 | -3.385551 | 4.031575 | -0.380158 |
| 44 | 1 | 0 | -3.190813 | 2.605759 | 1.220460 |
| 45 | 6 | 0 | -3.152114 | 4.295916 | -1.731948 |
| 46 | 1 | 0 | -2.350527 | 3.547875 | -3.590523 |
| 47 | 1 | 0 | -3.866778 | 4.776103 | 0.246210 |
| 48 | 1 | 0 | -3.451293 | 5.249893 | -2.154874 |
| 49 | 6 | 0 | -3.172861 | -1.011327 | -0.281790 |
| 50 | 6 | 0 | -2.797607 | -2.355682 | -0.451023 |
| 51 | 6 | 0 | -4.527865 | -0.641720 | -0.348915 |
| 52 | 6 | 0 | -3.777322 | -3.324883 | -0.660346 |
| 53 | 1 | 0 | -1.748113 | -2.633394 | -0.438496 |
| 54 | 6 | 0 | -5.497906 | -1.619568 | -0.558949 |
| 55 | 1 | 0 | -4.820691 | 0.398279 | -0.244773 |
| 56 | 6 | 0 | -5.124110 | -2.957707 | -0.712265 |
| 57 | 1 | 0 | -3.488477 | -4.362000 | -0.797376 |
| 58 | 1 | 0 | -6.544524 | -1.336586 | -0.608566 |
| 59 | 1 | 0 | -5.883994 | -3.713896 | -0.883343 |

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**VIII**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -0.368695 | -0.937323 | -0.036191 |
| 2 | 6 | 0 | 0.590586 | -2.429322 | -1.780030 |
| 3 | 6 | 0 | 0.922366 | -2.991072 | -0.521246 |
| 4 | 6 | 0 | -0.438507 | -3.007736 | -2.551879 |
| 5 | 6 | 0 | 0.222696 | -4.123809 | -0.053372 |
| 6 | 6 | 0 | -1.119990 | -4.115398 | -2.073223 |
| 7 | 1 | 0 | -0.675358 | -2.594921 | -3.527351 |
| 8 | 6 | 0 | -0.788792 | -4.674488 | -0.823555 |
| 9 | 1 | 0 | 1.231102 | -1.672932 | -2.220702 |
| 10 | 1 | 0 | -1.909693 | -4.565114 | -2.666480 |
| 11 | 1 | 0 | -1.327077 | -5.547806 | -0.469512 |
| 12 | 1 | 0 | 0.497215 | -4.570423 | 0.897050 |
| 13 | 1 | 0 | 1.819926 | -2.669459 | -0.005642 |
| 14 | 8 | 0 | -2.096954 | -2.018825 | -0.104119 |
| 15 | 6 | 0 | -3.109969 | -1.826478 | 0.711995 |
| 16 | 8 | 0 | -4.112152 | -2.516991 | 0.705372 |
| 17 | 6 | 0 | -2.976616 | -0.697791 | 1.763914 |
| 18 | 6 | 0 | -4.320964 | -0.046492 | 2.075209 |
| 19 | 1 | 0 | -4.227467 | 0.699069 | 2.870357 |
| 20 | 1 | 0 | -4.766849 | 0.420728 | 1.195598 |
| 21 | 1 | 0 | -4.997430 | -0.839262 | 2.404798 |
| 22 | 6 | 0 | -2.335165 | -1.279504 | 3.036182 |
| 23 | 1 | 0 | -1.370806 | -1.754722 | 2.832641 |
| 24 | 1 | 0 | -2.204595 | -0.510108 | 3.802709 |
| 25 | 1 | 0 | -3.006996 | -2.048270 | 3.428753 |
| 26 | 16 | 0 | -1.756095 | 0.595831 | 1.102329 |
| 27 | 6 | 0 | -2.692068 | 1.483817 | -0.155961 |
| 28 | 6 | 0 | -2.953082 | 2.833792 | 0.106963 |
| 29 | 6 | 0 | -3.158476 | 0.874406 | -1.328784 |
| 30 | 6 | 0 | -3.693851 | 3.579125 | -0.811908 |
| 31 | 1 | 0 | -2.584341 | 3.294672 | 1.017580 |
| 32 | 6 | 0 | -3.900519 | 1.631580 | -2.235236 |
| 33 | 1 | 0 | -2.954228 | -0.172581 | -1.523489 |
| 34 | 6 | 0 | -4.167873 | 2.979856 | -1.979901 |
| 35 | 1 | 0 | -3.902716 | 4.624859 | -0.609454 |
| 36 | 1 | 0 | -4.273559 | 1.164029 | -3.141266 |
| 37 | 1 | 0 | -4.748354 | 3.560516 | -2.690116 |
| 38 | 15 | 0 | 1.545558 | 0.444802 | 0.086711 |
| 39 | 6 | 0 | 2.978172 | -0.063150 | -0.954745 |
| 40 | 6 | 0 | 3.169442 | 0.451821 | -2.247526 |

| | | | | | |
|---|---|---|---|---|---|
| 41 | 6 | 0 | 3.875273 | -1.031133 | -0.466416 |
| 42 | 6 | 0 | 4.232408 | 0.003546 | -3.033473 |
| 43 | 1 | 0 | 2.507639 | 1.216559 | -2.638229 |
| 44 | 6 | 0 | 4.935215 | -1.474354 | -1.256911 |
| 45 | 1 | 0 | 3.767354 | -1.420011 | 0.541589 |
| 46 | 6 | 0 | 5.113864 | -0.961215 | -2.543300 |
| 47 | 1 | 0 | 4.374801 | 0.418101 | -4.026673 |
| 48 | 1 | 0 | 5.624493 | -2.215186 | -0.863732 |
| 49 | 1 | 0 | 5.940787 | -1.305336 | -3.156535 |
| 50 | 6 | 0 | 1.109013 | 2.143254 | -0.456722 |
| 51 | 6 | 0 | 0.377433 | 2.294863 | -1.648732 |
| 52 | 6 | 0 | 1.487998 | 3.285965 | 0.263987 |
| 53 | 6 | 0 | 0.065235 | 3.566309 | -2.128306 |
| 54 | 1 | 0 | 0.041351 | 1.420516 | -2.199264 |
| 55 | 6 | 0 | 1.161160 | 4.555961 | -0.215061 |
| 56 | 1 | 0 | 2.034484 | 3.192504 | 1.195376 |
| 57 | 6 | 0 | 0.459368 | 4.699025 | -1.412788 |
| 58 | 1 | 0 | -0.495567 | 3.669917 | -3.051802 |
| 59 | 1 | 0 | 1.460245 | 5.433504 | 0.349862 |
| 60 | 1 | 0 | 0.213729 | 5.689187 | -1.784114 |
| 61 | 6 | 0 | 2.246471 | 0.553347 | 1.775689 |
| 62 | 6 | 0 | 1.557816 | 0.007738 | 2.869294 |
| 63 | 6 | 0 | 3.489306 | 1.178528 | 1.991593 |
| 64 | 6 | 0 | 2.091341 | 0.095669 | 4.156621 |
| 65 | 1 | 0 | 0.609940 | -0.495809 | 2.715715 |
| 66 | 6 | 0 | 4.014739 | 1.269193 | 3.279325 |
| 67 | 1 | 0 | 4.050378 | 1.584932 | 1.155962 |
| 68 | 6 | 0 | 3.316471 | 0.729597 | 4.363247 |
| 69 | 1 | 0 | 1.551290 | -0.334839 | 4.994156 |
| 70 | 1 | 0 | 4.972706 | 1.755406 | 3.435382 |
| 71 | 1 | 0 | 3.731558 | 0.797640 | 5.364029 |

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**TS-A**

Standard orientation:

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -0.301544 | -0.834892 | -0.111735 |
| 2 | 6 | 0 | -2.937351 | -1.791543 | 1.417580 |
| 3 | 6 | 0 | -4.387936 | -2.067004 | 0.999456 |
| 4 | 1 | 0 | -4.514231 | -2.079655 | -0.084428 |
| 5 | 1 | 0 | -4.672015 | -3.048421 | 1.391189 |
| 6 | 1 | 0 | -5.063569 | -1.318876 | 1.422529 |
| 7 | 6 | 0 | 3.286092 | -3.675405 | -1.917643 |
| 8 | 6 | 0 | 3.106354 | -3.597841 | -0.531318 |
| 9 | 6 | 0 | 2.366717 | -3.083847 | -2.791435 |
| 10 | 6 | 0 | 2.002795 | -2.922446 | -0.015517 |
| 11 | 6 | 0 | 1.265610 | -2.405242 | -2.276724 |
| 12 | 1 | 0 | 2.509444 | -3.159318 | -3.865036 |
| 13 | 6 | 0 | 1.049364 | -2.325700 | -0.878166 |
| 14 | 1 | 0 | 4.143743 | -4.207811 | -2.318971 |
| 15 | 1 | 0 | 0.546379 | -1.959684 | -2.958549 |
| 16 | 1 | 0 | -0.220893 | -2.811927 | -0.614656 |
| 17 | 1 | 0 | 1.858111 | -2.880405 | 1.060204 |
| 18 | 1 | 0 | 3.819002 | -4.070743 | 0.137475 |
| 19 | 6 | 0 | -2.020013 | -2.894934 | 0.810771 |
| 20 | 8 | 0 | -1.456857 | -2.588971 | -0.384885 |
| 21 | 8 | 0 | -1.866926 | -3.954377 | 1.365860 |
| 22 | 16 | 0 | -2.374554 | -0.038200 | 0.898533 |
| 23 | 6 | 0 | -2.789818 | -1.806868 | 2.947916 |
| 24 | 1 | 0 | -1.780927 | -1.523449 | 3.264366 |
| 25 | 1 | 0 | -3.503798 | -1.121336 | 3.409699 |
| 26 | 1 | 0 | -2.977102 | -2.821673 | 3.305261 |
| 27 | 6 | 0 | -3.430091 | 0.454829 | -0.476791 |
| 28 | 6 | 0 | -4.337036 | 1.492405 | -0.226625 |
| 29 | 6 | 0 | -3.351972 | -0.132185 | -1.747858 |
| 30 | 6 | 0 | -5.168057 | 1.943914 | -1.254173 |
| 31 | 1 | 0 | -4.389572 | 1.942449 | 0.759461 |
| 32 | 6 | 0 | -4.190780 | 0.325355 | -2.764460 |
| 33 | 1 | 0 | -2.658643 | -0.944884 | -1.932802 |
| 34 | 6 | 0 | -5.095849 | 1.362275 | -2.520785 |
| 35 | 1 | 0 | -5.873271 | 2.746077 | -1.060179 |
| 36 | 1 | 0 | -4.137820 | -0.131579 | -3.747880 |
| 37 | 1 | 0 | -5.745099 | 1.712980 | -3.316916 |
| 38 | 15 | 0 | 1.179708 | 0.903110 | 0.194264 |
| 39 | 6 | 0 | 2.233793 | 0.608690 | 1.662654 |
| 40 | 6 | 0 | 1.745670 | -0.181761 | 2.716122 |
| 41 | 6 | 0 | 3.503740 | 1.198150 | 1.776410 |
| 42 | 6 | 0 | 2.512430 | -0.378338 | 3.864483 |
| 43 | 1 | 0 | 0.766731 | -0.646081 | 2.635272 |
| 44 | 6 | 0 | 4.267051 | 0.997702 | 2.927287 |
| 45 | 1 | 0 | 3.897835 | 1.808598 | 0.970674 |
| 46 | 6 | 0 | 3.774376 | 0.210537 | 3.970253 |
| 47 | 1 | 0 | 2.127164 | -0.992701 | 4.672449 |
| 48 | 1 | 0 | 5.247880 | 1.456160 | 3.006819 |
| 49 | 1 | 0 | 4.373150 | 0.054548 | 4.862289 |
| 50 | 6 | 0 | 2.333807 | 1.238312 | -1.194037 |
| 51 | 6 | 0 | 2.255096 | 2.418068 | -1.950450 |
| 52 | 6 | 0 | 3.326618 | 0.290569 | -1.500377 |
| 53 | 6 | 0 | 3.151776 | 2.641512 | -2.997400 |
| 54 | 1 | 0 | 1.508563 | 3.169555 | -1.721789 |
| 55 | 6 | 0 | 4.222909 | 0.524943 | -2.540676 |
| 56 | 1 | 0 | 3.408201 | -0.624099 | -0.922804 |
| 57 | 6 | 0 | 4.135354 | 1.698565 | -3.294336 |
| 58 | 1 | 0 | 3.082988 | 3.559218 | -3.573229 |
| 59 | 1 | 0 | 4.989867 | -0.210440 | -2.763256 |
| 60 | 1 | 0 | 4.833876 | 1.877370 | -4.105982 |
| 61 | 6 | 0 | 0.286612 | 2.475565 | 0.499765 |
| 62 | 6 | 0 | -0.735088 | 2.862174 | -0.385911 |

| | | | | | |
|---|---|---|---|---|---|
| 63 | 6 | 0 | 0.605409 | 3.304840 | 1.585647 |
| 64 | 6 | 0 | -1.411906 | 4.066452 | -0.196012 |
| 65 | 1 | 0 | -1.001565 | 2.226864 | -1.225946 |
| 66 | 6 | 0 | -0.082496 | 4.504901 | 1.775042 |
| 67 | 1 | 0 | 1.387428 | 3.020911 | 2.281020 |
| 68 | 6 | 0 | -1.086963 | 4.888845 | 0.885762 |
| 69 | 1 | 0 | -2.195160 | 4.357284 | -0.889036 |
| 70 | 1 | 0 | 0.171243 | 5.139894 | 2.618207 |
| 71 | 1 | 0 | -1.616732 | 5.824611 | 1.035348 |

**IX**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | 0.064919 | 0.477070 | -0.609832 |
| 2 | 6 | 0 | -3.117377 | -1.913590 | -1.195225 |
| 3 | 6 | 0 | -4.075231 | -1.379661 | -2.261715 |
| 4 | 1 | 0 | -4.448758 | -0.386264 | -2.011015 |
| 5 | 1 | 0 | -3.558216 | -1.314858 | -3.225558 |
| 6 | 1 | 0 | -4.922397 | -2.061530 | -2.369689 |
| 7 | 6 | 0 | -1.758838 | 3.526853 | -1.186259 |
| 8 | 6 | 0 | -0.925714 | 3.322575 | -0.100747 |
| 9 | 6 | 0 | -1.324463 | 3.214784 | -2.494493 |
| 10 | 6 | 0 | 0.373555 | 2.788695 | -0.297430 |
| 11 | 6 | 0 | -0.059315 | 2.698130 | -2.711851 |
| 12 | 1 | 0 | -1.987850 | 3.395142 | -3.334227 |
| 13 | 6 | 0 | 0.808755 | 2.475865 | -1.613452 |
| 14 | 1 | 0 | -2.750820 | 3.940735 | -1.037691 |
| 15 | 1 | 0 | 0.286886 | 2.483456 | -3.717313 |
| 16 | 1 | 0 | 1.851070 | 2.246437 | -1.800971 |
| 17 | 1 | 0 | 1.082634 | 2.798560 | 0.522699 |
| 18 | 1 | 0 | -1.247255 | 3.587780 | 0.900825 |
| 19 | 6 | 0 | -1.943008 | -0.974314 | -0.994617 |
| 20 | 8 | 0 | -0.826010 | -1.412560 | -0.516338 |
| 21 | 8 | 0 | -2.014311 | 0.261161 | -1.281261 |
| 22 | 16 | 0 | -3.959614 | -2.092880 | 0.488419 |
| 23 | 6 | 0 | -2.631178 | -3.332822 | -1.528788 |
| 24 | 1 | 0 | -1.962146 | -3.723604 | -0.759874 |
| 25 | 1 | 0 | -3.488025 | -4.003762 | -1.628763 |
| 26 | 1 | 0 | -2.091939 | -3.322517 | -2.481388 |
| 27 | 6 | 0 | -4.663868 | -0.482806 | 0.848850 |
| 28 | 6 | 0 | -5.940393 | -0.141800 | 0.376145 |
| 29 | 6 | 0 | -3.977439 | 0.405280 | 1.690711 |
| 30 | 6 | 0 | -6.509623 | 1.085090 | 0.721216 |
| 31 | 1 | 0 | -6.485222 | -0.839391 | -0.251224 |
| 32 | 6 | 0 | -4.554916 | 1.627867 | 2.038984 |
| 33 | 1 | 0 | -3.001843 | 0.130333 | 2.079271 |
| 34 | 6 | 0 | -5.818089 | 1.971178 | 1.550925 |
| 35 | 1 | 0 | -7.496998 | 1.343030 | 0.350100 |
| 36 | 1 | 0 | -4.022298 | 2.307436 | 2.697998 |
| 37 | 1 | 0 | -6.267203 | 2.920987 | 1.825572 |
| 38 | 15 | 0 | 2.093678 | -0.185057 | 0.246130 |
| 39 | 6 | 0 | 1.730680 | -1.235282 | 1.696618 |
| 40 | 6 | 0 | 0.705872 | -0.860832 | 2.583758 |
| 41 | 6 | 0 | 2.468092 | -2.404707 | 1.940189 |
| 42 | 6 | 0 | 0.439293 | -1.637902 | 3.710277 |
| 43 | 1 | 0 | 0.109990 | 0.026556 | 2.390449 |
| 44 | 6 | 0 | 2.191124 | -3.178750 | 3.067460 |
| 45 | 1 | 0 | 3.252011 | -2.713382 | 1.257463 |
| 46 | 6 | 0 | 1.180866 | -2.796931 | 3.952345 |
| 47 | 1 | 0 | -0.352824 | -1.344147 | 4.391619 |
| 48 | 1 | 0 | 2.764463 | -4.082077 | 3.250181 |
| 49 | 1 | 0 | 0.966323 | -3.404944 | 4.825681 |
| 50 | 6 | 0 | 3.006219 | -1.190388 | -0.975401 |
| 51 | 6 | 0 | 4.402306 | -1.337962 | -0.889505 |
| 52 | 6 | 0 | 2.297804 | -1.866640 | -1.983927 |
| 53 | 6 | 0 | 5.075008 | -2.148672 | -1.803919 |
| 54 | 1 | 0 | 4.964133 | -0.824765 | -0.116714 |
| 55 | 6 | 0 | 2.980285 | -2.671879 | -2.895720 |
| 56 | 1 | 0 | 1.219072 | -1.773103 | -2.052486 |
| 57 | 6 | 0 | 4.366978 | -2.812421 | -2.808315 |
| 58 | 1 | 0 | 6.152408 | -2.257843 | -1.730644 |
| 59 | 1 | 0 | 2.427065 | -3.188009 | -3.673994 |
| 60 | 1 | 0 | 4.895054 | -3.438387 | -3.520889 |
| 61 | 6 | 0 | 3.221328 | 1.146231 | 0.791050 |
| 62 | 6 | 0 | 3.996835 | 1.840230 | -0.157033 |
| 63 | 6 | 0 | 3.279020 | 1.529318 | 2.141949 |
| 64 | 6 | 0 | 4.816217 | 2.894450 | 0.244145 |
| 65 | 1 | 0 | 3.985727 | 1.544758 | -1.201586 |
| 66 | 6 | 0 | 4.100079 | 2.586976 | 2.534064 |
| 67 | 1 | 0 | 2.698201 | 0.999110 | 2.888444 |
| 68 | 6 | 0 | 4.866840 | 3.271148 | 1.588652 |
| 69 | 1 | 0 | 5.417241 | 3.416901 | -0.493190 |
| 70 | 1 | 0 | 4.144154 | 2.869590 | 3.581070 |
| 71 | 1 | 0 | 5.506064 | 4.091831 | 1.898617 |

**TS-B**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | 0.484085 | -0.192110 | -0.008590 |
| 2 | 6 | 0 | 1.012854 | 4.448160 | -0.524694 |
| 3 | 6 | 0 | 1.596931 | 3.653411 | -1.521605 |
| 4 | 6 | 0 | 0.030117 | 3.924595 | 0.323285 |
| 5 | 6 | 0 | 1.208920 | 2.325999 | -1.661452 |

| | | | | | |
|---|---|---|---|---|---|
| 6 | 6 | 0 | -0.373050 | 2.600439 | 0.175815 |
| 7 | 1 | 0 | -0.430804 | 4.555393 | 1.077004 |
| 8 | 6 | 0 | 0.202764 | 1.770560 | -0.825461 |
| 9 | 1 | 0 | 1.317022 | 5.485704 | -0.419180 |
| 10 | 1 | 0 | -1.171984 | 2.207384 | 0.798196 |
| 11 | 1 | 0 | -0.667983 | 1.098226 | -1.429815 |
| 12 | 1 | 0 | 1.651833 | 1.716920 | -2.443556 |
| 13 | 1 | 0 | 2.344126 | 4.077611 | -2.185360 |
| 14 | 8 | 0 | -1.864169 | 0.507178 | -1.916876 |
| 15 | 6 | 0 | -2.276360 | -0.244003 | -0.991786 |
| 16 | 8 | 0 | -1.546300 | -0.649053 | -0.019039 |
| 17 | 6 | 0 | -3.754425 | -0.667713 | -1.004746 |
| 18 | 15 | 0 | 2.736064 | -0.330366 | 0.203365 |
| 19 | 6 | 0 | 3.600686 | 0.469665 | 1.582501 |
| 20 | 6 | 0 | 3.487272 | 1.861214 | 1.741690 |
| 21 | 6 | 0 | 4.384425 | -0.279535 | 2.477356 |
| 22 | 6 | 0 | 4.161254 | 2.495072 | 2.784868 |
| 23 | 1 | 0 | 2.875664 | 2.442873 | 1.058706 |
| 24 | 6 | 0 | 5.050998 | 0.364733 | 3.519241 |
| 25 | 1 | 0 | 4.473111 | -1.355614 | 2.363395 |
| 26 | 6 | 0 | 4.940314 | 1.748987 | 3.672409 |
| 27 | 1 | 0 | 4.072813 | 3.569753 | 2.908691 |
| 28 | 1 | 0 | 5.654994 | -0.214275 | 4.210709 |
| 29 | 1 | 0 | 5.459181 | 2.245722 | 4.486355 |
| 30 | 6 | 0 | 2.161641 | -1.988748 | 0.703367 |
| 31 | 6 | 0 | 2.387309 | -3.158020 | -0.054915 |
| 32 | 6 | 0 | 1.235133 | -2.024675 | 1.781028 |
| 33 | 6 | 0 | 1.723135 | -4.332704 | 0.273321 |
| 34 | 1 | 0 | 3.087368 | -3.139400 | -0.883455 |
| 35 | 6 | 0 | 0.558281 | -3.215167 | 2.082363 |
| 36 | 1 | 0 | 1.113260 | -1.162798 | 2.432713 |
| 37 | 6 | 0 | 0.801999 | -4.361036 | 1.332896 |
| 38 | 1 | 0 | 1.918293 | -5.236287 | -0.295837 |
| 39 | 1 | 0 | -0.142355 | -3.236599 | 2.910483 |
| 40 | 1 | 0 | 0.285378 | -5.285167 | 1.572107 |
| 41 | 6 | 0 | 3.826413 | -0.436665 | -1.242091 |
| 42 | 6 | 0 | 3.269853 | -0.770482 | -2.491105 |
| 43 | 6 | 0 | 5.203444 | -0.183030 | -1.136027 |
| 44 | 6 | 0 | 4.089291 | -0.868309 | -3.614040 |
| 45 | 1 | 0 | 2.201935 | -0.951057 | -2.583260 |
| 46 | 6 | 0 | 6.014297 | -0.278484 | -2.267080 |
| 47 | 1 | 0 | 5.639513 | 0.087211 | -0.180083 |
| 48 | 6 | 0 | 5.460718 | -0.621775 | -3.502201 |
| 49 | 1 | 0 | 3.657554 | -1.128650 | -4.575306 |
| 50 | 1 | 0 | 7.078643 | -0.083555 | -2.181979 |
| 51 | 1 | 0 | 6.096143 | -0.692300 | -4.379531 |
| 52 | 6 | 0 | -4.170847 | -1.100440 | -2.416998 |
| 53 | 1 | 0 | -5.244047 | -1.307893 | -2.436399 |
| 54 | 1 | 0 | -3.944735 | -0.324983 | -3.149136 |
| 55 | 1 | 0 | -3.645590 | -2.020053 | -2.703727 |
| 56 | 6 | 0 | -4.051480 | -1.753361 | 0.028132 |
| 57 | 1 | 0 | -3.775080 | -1.443207 | 1.036711 |
| 58 | 1 | 0 | -5.114115 | -2.004156 | 0.016373 |
| 59 | 1 | 0 | -3.485184 | -2.657285 | -0.220375 |
| 60 | 16 | 0 | -4.577226 | 0.991469 | -0.559809 |
| 61 | 6 | 0 | -6.138661 | 0.507764 | 0.173724 |
| 62 | 6 | 0 | -6.276604 | 0.446990 | 1.568137 |
| 63 | 6 | 0 | -7.253512 | 0.266272 | -0.643888 |
| 64 | 6 | 0 | -7.511786 | 0.133051 | 2.136067 |
| 65 | 1 | 0 | -5.417768 | 0.651823 | 2.199203 |
| 66 | 6 | 0 | -8.484665 | -0.054300 | -0.070450 |
| 67 | 1 | 0 | -7.155177 | 0.345960 | -1.721655 |
| 68 | 6 | 0 | -8.614811 | -0.122283 | 1.318374 |
| 69 | 1 | 0 | -7.613314 | 0.090646 | 3.216517 |
| 70 | 1 | 0 | -9.343722 | -0.240086 | -0.708231 |
| 71 | 1 | 0 | -9.575593 | -0.364874 | 1.762454 |

## VIII-OAc

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -0.218978 | -0.766091 | -0.438515 |
| 2 | 6 | 0 | 0.802605 | -0.951972 | -2.716147 |
| 3 | 6 | 0 | 1.469020 | -1.862718 | -1.862238 |
| 4 | 6 | 0 | -0.115433 | -1.428552 | -3.680171 |
| 5 | 6 | 0 | 1.209054 | -3.245222 | -1.995792 |
| 6 | 6 | 0 | -0.344341 | -2.789032 | -3.799392 |
| 7 | 1 | 0 | -0.607951 | -0.726151 | -4.345808 |
| 8 | 6 | 0 | 0.325593 | -3.701050 | -2.958098 |
| 9 | 1 | 0 | 1.111800 | 0.086202 | -2.753879 |
| 10 | 1 | 0 | -1.034650 | -3.159864 | -4.551341 |
| 11 | 1 | 0 | 0.143131 | -4.765508 | -3.070582 |
| 12 | 1 | 0 | 1.722896 | -3.938499 | -1.339220 |
| 13 | 8 | 0 | -1.456064 | -2.386742 | -0.753044 |
| 14 | 6 | 0 | -2.245641 | -2.866426 | 0.168616 |
| 15 | 8 | 0 | -2.920414 | -3.879684 | 0.012012 |
| 16 | 6 | 0 | -2.306584 | -2.143185 | 1.536071 |
| 17 | 6 | 0 | -3.710038 | -2.193449 | 2.138172 |
| 18 | 1 | 0 | -3.736086 | -1.694989 | 3.111676 |
| 19 | 1 | 0 | -4.461059 | -1.743438 | 1.486369 |
| 20 | 1 | 0 | -3.970398 | -3.246021 | 2.273379 |
| 21 | 6 | 0 | -1.275618 | -2.764457 | 2.495973 |
| 22 | 1 | 0 | -0.248369 | -2.714849 | 2.123220 |
| 23 | 1 | 0 | -1.331616 | -2.281208 | 3.476560 |
| 24 | 1 | 0 | -1.541646 | -3.818955 | 2.622235 |
| 25 | 16 | 0 | -1.775588 | -0.339477 | 1.288923 |
| 26 | 6 | 0 | -3.214422 | 0.428675 | 0.518467 |
| 27 | 6 | 0 | -3.891578 | 1.385474 | 1.283853 |
| 28 | 6 | 0 | -3.667892 | 0.085549 | -0.762383 |

| | | | | | |
|---|---|---|---|---|---|
| 29 | 6 | 0 | -5.033892 | 1.998403 | 0.764745 |
| 30 | 1 | 0 | -3.532582 | 1.644687 | 2.274428 |
| 31 | 6 | 0 | -4.813874 | 0.700897 | -1.266150 |
| 32 | 1 | 0 | -3.136965 | -0.653769 | -1.351025 |
| 33 | 6 | 0 | -5.496378 | 1.655782 | -0.506699 |
| 34 | 1 | 0 | -5.560362 | 2.739488 | 1.358023 |
| 35 | 1 | 0 | -5.171820 | 0.433240 | -2.255626 |
| 36 | 1 | 0 | -6.386671 | 2.131250 | -0.906727 |
| 37 | 15 | 0 | 0.974853 | 1.217717 | 0.008973 |
| 38 | 6 | 0 | 2.365985 | 1.662586 | -1.112583 |
| 39 | 6 | 0 | 2.303110 | 2.739252 | -2.011787 |
| 40 | 6 | 0 | 3.539117 | 0.888415 | -1.032574 |
| 41 | 6 | 0 | 3.399601 | 3.036841 | -2.823817 |
| 42 | 1 | 0 | 1.413640 | 3.355228 | -2.075683 |
| 43 | 6 | 0 | 4.626547 | 1.196170 | -1.850787 |
| 44 | 1 | 0 | 3.601797 | 0.044426 | -0.346590 |
| 45 | 6 | 0 | 4.560874 | 2.266398 | -2.746656 |
| 46 | 1 | 0 | 3.343890 | 3.875947 | -3.510899 |
| 47 | 1 | 0 | 5.528108 | 0.594391 | -1.785261 |
| 48 | 1 | 0 | 5.411729 | 2.500567 | -3.379659 |
| 49 | 6 | 0 | -0.248990 | 2.584680 | -0.140046 |
| 50 | 6 | 0 | -0.971409 | 2.697415 | -1.343027 |
| 51 | 6 | 0 | -0.514154 | 3.490810 | 0.897615 |
| 52 | 6 | 0 | -1.904032 | 3.718731 | -1.516836 |
| 53 | 1 | 0 | -0.807952 | 1.986182 | -2.147178 |
| 54 | 6 | 0 | -1.458493 | 4.505539 | 0.722624 |
| 55 | 1 | 0 | 0.010562 | 3.412571 | 1.842187 |
| 56 | 6 | 0 | -2.147429 | 4.627915 | -0.484078 |
| 57 | 1 | 0 | -2.445899 | 3.797327 | -2.454261 |
| 58 | 1 | 0 | -1.650956 | 5.200700 | 1.534214 |
| 59 | 1 | 0 | -2.876734 | 5.421042 | -0.617944 |
| 60 | 6 | 0 | 1.727214 | 1.327572 | 1.676648 |
| 61 | 6 | 0 | 1.706282 | 0.232806 | 2.551302 |
| 62 | 6 | 0 | 2.380502 | 2.514034 | 2.061716 |
| 63 | 6 | 0 | 2.295112 | 0.344549 | 3.814738 |
| 64 | 1 | 0 | 1.311441 | -0.728649 | 2.233884 |
| 65 | 6 | 0 | 2.959327 | 2.616760 | 3.324824 |
| 66 | 1 | 0 | 2.443846 | 3.354374 | 1.377143 |
| 67 | 6 | 0 | 2.908688 | 1.533429 | 4.207745 |
| 68 | 1 | 0 | 2.285761 | -0.512236 | 4.481780 |
| 69 | 1 | 0 | 3.455978 | 3.537565 | 3.615410 |
| 70 | 1 | 0 | 3.363927 | 1.613559 | 5.190573 |
| 71 | 8 | 0 | 3.591262 | -1.921952 | 0.455590 |
| 72 | 6 | 0 | 3.058640 | -2.708135 | 1.289384 |
| 73 | 8 | 0 | 1.832539 | -2.780261 | 1.592481 |
| 74 | 6 | 0 | 4.017741 | -3.653033 | 2.042825 |
| 75 | 1 | 0 | 4.810315 | -4.010588 | 1.379074 |
| 76 | 1 | 0 | 4.501431 | -3.098501 | 2.856533 |
| 77 | 1 | 0 | 3.486149 | -4.502511 | 2.479150 |
| 78 | 1 | 0 | 2.267463 | -1.566545 | -1.182475 |

**TS-C**

Standard orientation:

| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 46 | 0 | -0.252015 | -0.852948 | -0.223393 |
| 2 | 6 | 0 | 1.345625 | -1.309870 | -2.740299 |
| 3 | 6 | 0 | 1.105867 | -1.996251 | -1.526100 |
| 4 | 6 | 0 | 1.285456 | -1.970008 | -3.969410 |
| 5 | 6 | 0 | 0.820727 | -3.384011 | -1.603672 |
| 6 | 6 | 0 | 1.005803 | -3.337726 | -4.010890 |
| 7 | 1 | 0 | 1.464971 | -1.422358 | -4.890366 |
| 8 | 6 | 0 | 0.786785 | -4.048770 | -2.823383 |
| 9 | 1 | 0 | 1.592383 | -0.254268 | -2.729069 |
| 10 | 1 | 0 | 0.966545 | -3.853884 | -4.966400 |
| 11 | 1 | 0 | 0.589154 | -5.116436 | -2.857991 |
| 12 | 1 | 0 | 0.663737 | -3.926585 | -0.677398 |
| 13 | 1 | 0 | 1.801365 | -1.812452 | -0.478953 |
| 14 | 8 | 0 | -1.589054 | -2.443107 | -0.433767 |
| 15 | 6 | 0 | -2.538729 | -2.682294 | 0.423687 |
| 16 | 8 | 0 | -3.309923 | -3.634832 | 0.335899 |
| 17 | 6 | 0 | -2.666262 | -1.739752 | 1.649707 |
| 18 | 6 | 0 | -4.109140 | -1.631423 | 2.139856 |
| 19 | 1 | 0 | -4.173725 | -1.001466 | 3.032044 |
| 20 | 1 | 0 | -4.776986 | -1.232607 | 1.373977 |
| 21 | 1 | 0 | -4.452289 | -2.638035 | 2.389921 |
| 22 | 6 | 0 | -1.743226 | -2.254207 | 2.771114 |
| 23 | 1 | 0 | -0.708627 | -2.386513 | 2.441578 |
| 24 | 1 | 0 | -1.773817 | -1.585700 | 3.637263 |
| 25 | 1 | 0 | -2.118138 | -3.233551 | 3.085030 |
| 26 | 16 | 0 | -2.019371 | -0.031188 | 1.165310 |
| 27 | 6 | 0 | -3.311863 | 0.619887 | 0.089336 |
| 28 | 6 | 0 | -4.078967 | 1.677055 | 0.592949 |
| 29 | 6 | 0 | -3.557758 | 0.105975 | -1.190822 |
| 30 | 6 | 0 | -5.100402 | 2.220418 | -0.188595 |
| 31 | 1 | 0 | -3.879393 | 2.069719 | 1.584659 |
| 32 | 6 | 0 | -4.584328 | 0.654834 | -1.960235 |
| 33 | 1 | 0 | -2.958991 | -0.712007 | -1.574679 |
| 34 | 6 | 0 | -5.354246 | 1.710131 | -1.463074 |
| 35 | 1 | 0 | -5.696134 | 3.039774 | 0.201749 |
| 36 | 1 | 0 | -4.779864 | 0.255964 | -2.950984 |
| 37 | 1 | 0 | -6.150270 | 2.132957 | -2.068472 |
| 38 | 15 | 0 | 1.035803 | 1.097383 | 0.049315 |
| 39 | 6 | 0 | 2.478490 | 1.457653 | -1.046952 |
| 40 | 6 | 0 | 2.437349 | 2.466620 | -2.023249 |
| 41 | 6 | 0 | 3.656142 | 0.704402 | -0.886761 |
| 42 | 6 | 0 | 3.553746 | 2.717348 | -2.824249 |
| 43 | 1 | 0 | 1.546867 | 3.068574 | -2.158100 |
| 44 | 6 | 0 | 4.766296 | 0.964761 | -1.689982 |

| | | | | | |
|---|---|---|---|---|---|
| 45 | 1 | 0 | 3.695074 | -0.095923 | -0.154749 |
| 46 | 6 | 0 | 4.719748 | 1.968820 | -2.660163 |
| 47 | 1 | 0 | 3.508899 | 3.504394 | -3.571138 |
| 48 | 1 | 0 | 5.669319 | 0.376151 | -1.557603 |
| 49 | 1 | 0 | 5.586646 | 2.166399 | -3.283783 |
| 50 | 6 | 0 | -0.091032 | 2.532505 | -0.207091 |
| 51 | 6 | 0 | -0.839352 | 2.580430 | -1.397455 |
| 52 | 6 | 0 | -0.223349 | 3.573793 | 0.723045 |
| 53 | 6 | 0 | -1.673556 | 3.665020 | -1.665479 |
| 54 | 1 | 0 | -0.770499 | 1.768411 | -2.115744 |
| 55 | 6 | 0 | -1.072954 | 4.650679 | 0.457053 |
| 56 | 1 | 0 | 0.333526 | 3.552579 | 1.652748 |
| 57 | 6 | 0 | -1.791312 | 4.703288 | -0.738012 |
| 58 | 1 | 0 | -2.240018 | 3.691102 | -2.591130 |
| 59 | 1 | 0 | -1.167039 | 5.449774 | 1.186284 |
| 60 | 1 | 0 | -2.445864 | 5.544906 | -0.943672 |
| 61 | 6 | 0 | 1.733976 | 1.278982 | 1.737800 |
| 62 | 6 | 0 | 1.387460 | 0.378641 | 2.754922 |
| 63 | 6 | 0 | 2.624297 | 2.329125 | 2.024908 |
| 64 | 6 | 0 | 1.905580 | 0.536699 | 4.042621 |
| 65 | 1 | 0 | 0.741960 | -0.464416 | 2.538432 |
| 66 | 6 | 0 | 3.136397 | 2.485192 | 3.312508 |
| 67 | 1 | 0 | 2.921113 | 3.022681 | 1.244570 |
| 68 | 6 | 0 | 2.775433 | 1.591170 | 4.324162 |
| 69 | 1 | 0 | 1.635189 | -0.171632 | 4.819720 |
| 70 | 1 | 0 | 3.821093 | 3.301152 | 3.522982 |
| 71 | 1 | 0 | 3.179126 | 1.711543 | 5.325021 |
| 72 | 8 | 0 | 2.828632 | -1.915248 | 0.503858 |
| 73 | 6 | 0 | 2.534076 | -2.650623 | 1.527148 |
| 74 | 8 | 0 | 1.427117 | -3.173318 | 1.746481 |
| 75 | 6 | 0 | 3.677603 | -2.830354 | 2.526093 |
| 76 | 1 | 0 | 3.826657 | -1.891282 | 3.070785 |
| 77 | 1 | 0 | 3.445014 | -3.620741 | 3.242350 |
| 78 | 1 | 0 | 4.612136 | -3.059138 | 2.006504 |

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