**Supporting Information**

# Mechanistic investigation of Palladium Catalyzed Allylic C-H Activation

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**General Information**

GCMS analysis was performed on a Shimadzu QP5000 GCMS instrument using electron impact as the ionization method and a 30 m x 0.25 mm x 0.25 μm Supelco Equity-1 capillary column.
Flash column chromatography was performed with silica gel 60 (35-70 μm) with solvents of HPLC quality. $^{1}H$ and $^{13}C$ NMR spectra were recorded at 25 °C on a Varian Mercury 300 at 300 MHz and 75 MHz, respectively. Chemical shifts (δ) are represented in parts per million (ppm). $^{1}H$ NMR spectra are referenced to residual $CHCl_3$ (7.26 ppm). $^{13}C$ NMR spectra are referenced to $CDCl_3$ (77.0 ppm).
Dodecane, Pd[1,2-bis(phenylsulfonyl)ethane]$(OAc)_2$, 2,6-dimethyl benzoquinone, 4-allyltoluene and 1-allyl-4-methoxybenzene were purchased from Sigma-Aldrich and used without further purification. Allylbenzene and methyl nitroacetate were distilled before use.

**GC retention times**

Injector temperature 200 °C, detector temperature 200 °C.

**Table S1 Programmed oven temperature: start 60 °C for 5 min, ramp 20 °C/min to 250 °C, 6 min @ 250 °C.**

| ***Compound*** | ***Retention Time*** |
|---|---:|
| Methyl nitroacetate | 6.5 min |
| Allylbenzene | 6.9 min |
| 1-allyl-4-(trifluoromethyl)benzene | 7.6 min |
| 1-allyl-4-Methylbenzene | 8.5 min |
| 2,6-dimethylbenzoquinone | 9.3 min |
| 1-allyl-4-chlorobenzene | 9.5 min |
| Dodecane (Int. Std.) | 10.0 min |
| 1-allyl-4-Methoxybenzene | 10.1 min |
| 4-allylbenzonitrile | 10.8 min |
| Methyl 4-allylbenzoate | 11.7 min |

**Table S2 Programmed oven temperature: start 60 °C for 5 min, ramp 10 °C/min to 300 °C, 5 min @ 300 °C.**

| ***Compound*** | ***Retention Time*** |
|---|---|
| Methyl nitroacetate | 6.7 min |
| $d_2$-allylbenzene | 7.3 min |
| Allylbenzene | 7.3 min |
| 2,6-dimethylbenzoquinone | 11.1 min |
| Dodecane (Int. Std.) | 12.5 min |
| Methyl N-tosylcarbamate | 19.1 min |

**Table 3 Programmed oven temperature: start 60 °C for 5 min, ramp 12 °C/min to 280 °C, 2 min @ 280 °C.**

| ***Compound*** | ***Retention Time*** |
|---|---|
| Methyl nitroacetate | 6.6 min |
| $d_2$-allylbenzene | 7.2 min |
| 1-allyl-4-Methylbenzene | 9.4 min |
| 2,6-dimethylbenzoquinone | 10.6 min |
| Dodecane (Int. Std.) | 11.8 min |
| Methyl N-tosylcarbamate | 17.3 min |

**Competition experiments for the Hammett Study**

**General**

To a screw-cap vial was added Pd[1,2-bis(phenylsulfonyl)ethane](OAc)$_2$ (0.05 mmol, 25 mg), 2,6-dimethylbenzoquinone (0.75 mmol, 102 mg) and a stir bar. Allylbenzene (0.25 mmol, 30 mg), *para*-substituted allylbenzene (0.25 mmol) under investigation, methyl nitroacetate (1.5 mmol, 178 mg), AcOH (0.25 mmol, 15 mg) and dodecane as internal standard (0.125 mmol, 21 mg) were weighed out in a 1.0 ml vial and transferred to the catalyst mixture using dioxane:DMSO (4:1) (1.5 mL). The reaction was sealed with a screw cap fitted with a PTFE septum and placed in an aluminum block preheated to 45 ºC. Samples of 0.05 mL each were withdrawn from the reaction mixture after 0, 0.5, 1, 2, 4, 6, 8, and 24 hrs reaction time, diluted with diethylether (1 mL) and analyzed by GCMS.

**Table S4 Data for the competition experiment involving allylbenzene and 1-allyl-4-methoxybenzene.**

| Reaction time (min) | Conversion allylbenzene | Conversion 1-allyl-4-methoxybenzene | Kinetics allylbenzene | Kinetics 1-allyl-4-methoxybenzene |
|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0 | 0 |
| 40 | 0.27 | 0.27 | 0.310 | 0.319 |
| 60 | 0.39 | 0.37 | 0.496 | 0.467 |
| 120 | 0.60 | 0.57 | 0.921 | 0.839 |
| 250 | 0.81 | 0.78 | 1.651 | 1.500 |
| 360 | 0.89 | 0.85 | 2.172 | 1.911 |
| 480 | 0.93 | 0.91 | 2.608 | 2.385 |
| 1410 | 0.96 | 0.94 | 3.220 | 2.869 |

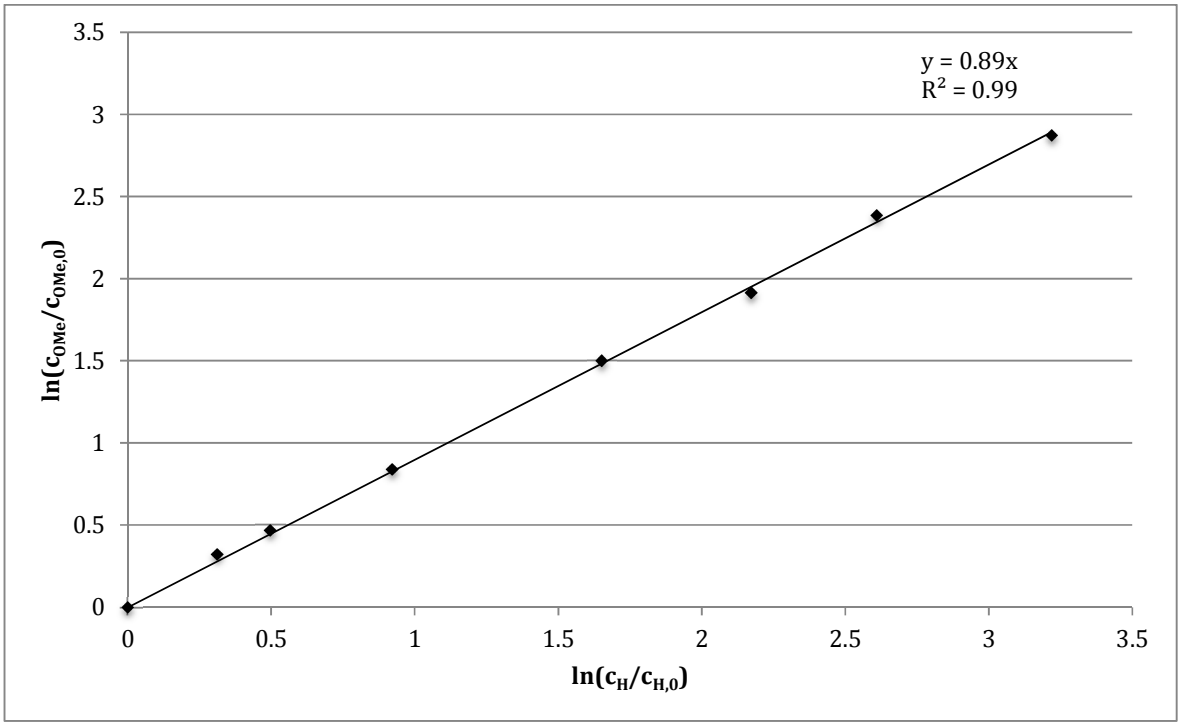



**Figure S1 Kinetic plot for the competition experiment with allylbenzene and 1-allyl-4-methoxybenzene. The slope represents the reactivity of 1-allyl-4-methoxybenzene relative to allylbenzene.**

**Table S5 Data for the competition experiment involving allylbenzene and 1-allyl-4-(trifluoromethyl)benzene.**

| Reaction time (min) | Conversion allylbenzene | Conversion 1-allyl-4-(trifluoromethyl)benzene | Kinetics allylbenzene | Kinetics 1-allyl-4-(trifluoromethyl)benzene |
|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0 | 0 |
| 30 | 0.21 | 0.29 | 0.234 | 0.339 |
| 70 | 0.31 | 0.43 | 0.370 | 0.568 |
| 120 | 0.41 | 0.56 | 0.528 | 0.820 |
| 240 | 0.51 | 0.66 | 0.705 | 1.093 |
| 360 | 0.54 | 0.69 | 0.767 | 1.167 |
| 480 | 0.54 | 0.70 | 0.782 | 1.188 |
| 1335 | 0.56 | 0.71 | 0.829 | 1.225 |

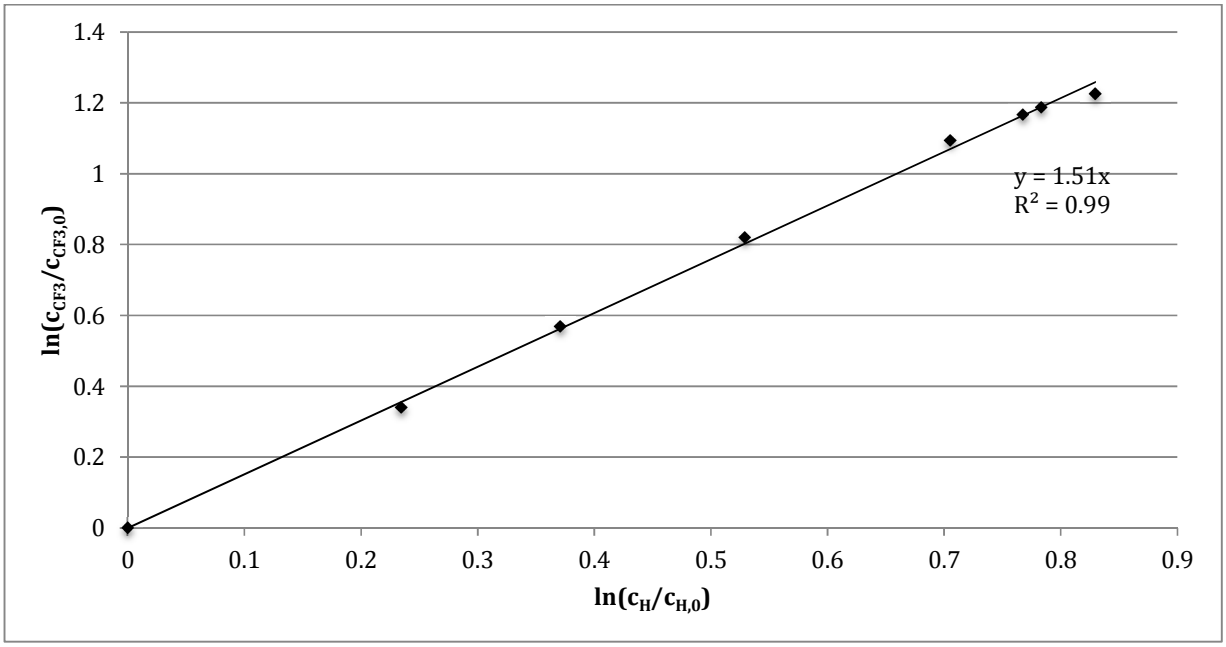



**Figure S2 Kinetic plot for the competition experiment with allylbenzene and 1-allyl-4-(trifluoromethyl)benzene. The slope represents the reactivity of 1-allyl-4-(trifluoromethyl)benzene relative to allylbenzene.**

**Table S6 Data for the competition experiment involving allylbenzene and 1-allyl-4-chlorobenzene.**

| Reaction time (min) | Conversion allylbenzene | Conversion 1-allyl-4-chlorobenzene | Kinetics allylbenzene | Kinetics 1-allyl-4-chlorobenzene |
|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0 | 0 |
| 30 | 0.20 | 0.20 | 0.217 | 0.228 |
| 60 | 0.32 | 0.33 | 0.382 | 0.402 |
| 120 | 0.50 | 0.52 | 0.683 | 0.738 |
| 240 | 0.68 | 0.70 | 1.129 | 1.214 |
| 367 | 0.76 | 0.78 | 1.410 | 1.512 |
| 480 | 0.78 | 0.81 | 1.530 | 1.662 |
| 1329 | 0.81 | 0.83 | 1.672 | 1.768 |

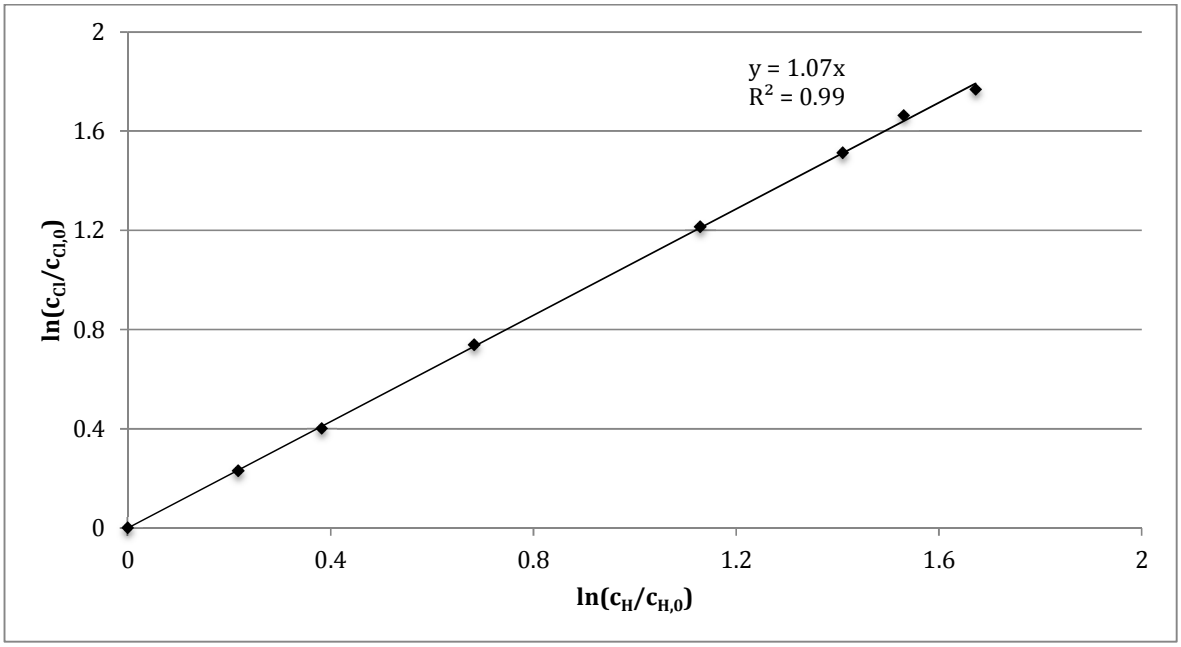



**Figure S3 Kinetic plot for the competition experiment with allylbenzene and 1-allyl-4-chlorobenzene. The slope represents the reactivity of 1-allyl-4-chlorobenzene relative to allylbenzene.**

**Table S7 Data for the competition experiment involving allylbenzene and 1-allyl-4-methylbenzene.**

| Reaction time (min) | Conversion allylbenzene | Conversion 1-allyl-4-methylbenzene | Kinetics allylbenzene | Kinetics 1-allyl-4-methylbenzene |
|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0 | 0 |
| 38 | 0.28 | 0.28 | 0.333 | 0.335 |
| 60 | 0.42 | 0.41 | 0.544 | 0.533 |
| 120 | 0.61 | 0.60 | 0.934 | 0.914 |
| 240 | 0.80 | 0.80 | 1.606 | 1.595 |
| 360 | 0.87 | 0.87 | 2.046 | 2.041 |
| 420 | 0.89 | 0.89 | 2.232 | 2.197 |
| 1560 | 0.93 | 0.92 | 2.604 | 2.581 |

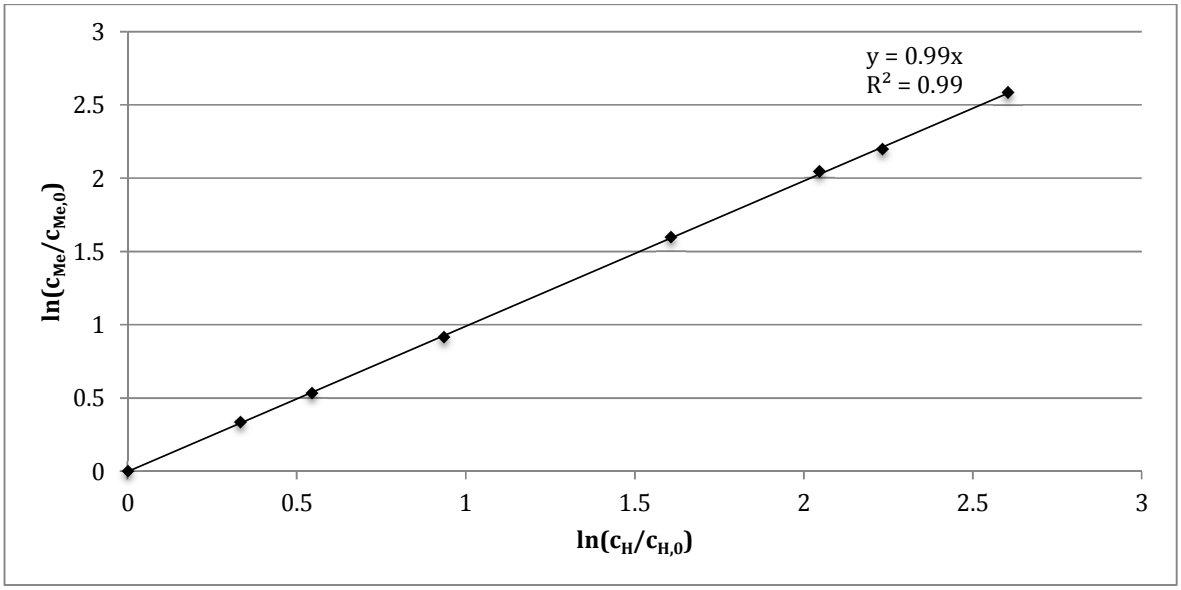



**Figure S4 Kinetic plot for the competition experiment with allylbenzene and 1-allyl-4-methylbenzene. The slope represents the reactivity of 1-allyl-4-methylbenzene relative to allylbenzene.**

**Table S8 Data for the competition experiment involving allylbenzene and 4-allylbenzonitrile.**

| Reaction time (min) | Conversion allylbenzene | Conversion 4-allylbenzonitrile | Kinetics allylbenzene | Kinetics 4-allylbenzonitrile |
|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0 | 0 |
| 5 | 0.03 | 0.03 | 0.026 | 0.029 |
| 10 | 0.08 | 0.12 | 0.085 | 0.127 |
| 15 | 0.11 | 0.19 | 0.112 | 0.210 |
| 30 | 0.19 | 0.36 | 0.215 | 0.452 |
| 60 | 0.35 | 0.65 | 0.427 | 1.048 |
| 90 | 0.46 | 0.80 | 0.622 | 1.595 |
| 120 | 0.54 | 0.87 | 0.774 | 2.003 |

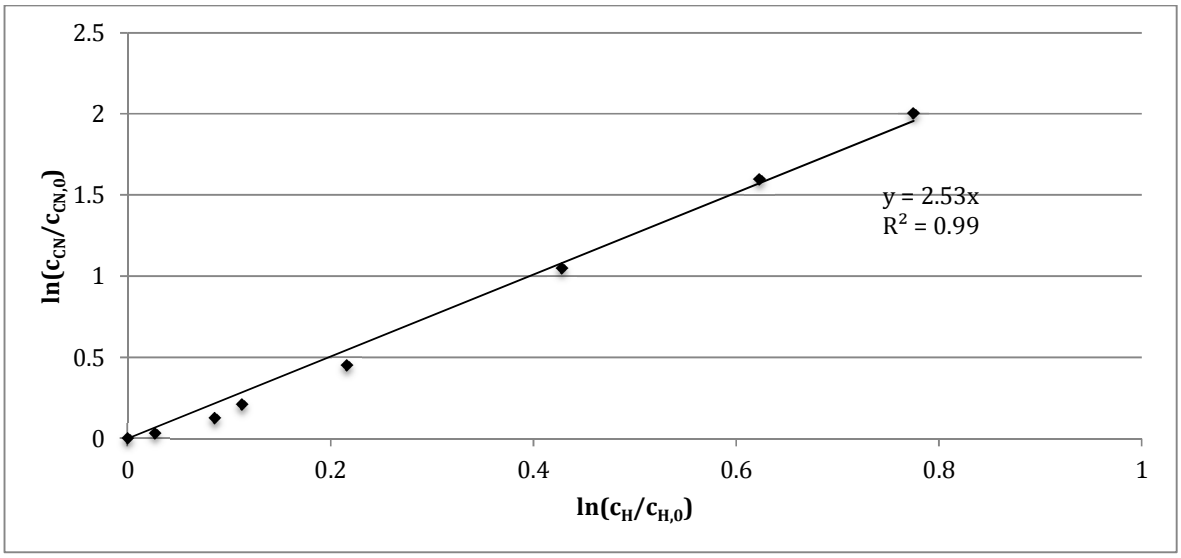



**Figure S5 Kinetic plot for the competition experiment with allylbenzene and 4-allylbenzonitrile. The slope represents the reactivity of 4-allylbenzonitrile relative to allylbenzene.**

**Table S9 Data for the competition experiment involving 1-allyl-4-methylbenzene and methyl 4-allylbenzoate. Due to overlap between peaks during the reaction, a competitive experiment between allylbenzene and methyl 4-allylbenzoate could not be preformed. Therefore a competitive experiment between 1-allyl-4-methylbenzene and methyl 4-allylbenzoate was performed and the obtained values for the kinetics of methyl 4-allylbenzoate were corrected afterwards.**

| Reaction time (min) | Conversion 1-allyl-4-methylbenzene | Conversion methyl 4-allylbenzoate | Kinetics 1-allyl-4-methylbenzene | Kinetics methyl 4-allylbenzoate | Corrected kinetic methyl 4-allylbenzoate values |
|---|---|---|---|---|---|
| 0 | 0.00 | 0.00 | 0 | 0 | 0 |
| 5 | 0.05 | 0.02 | 0.048 | 0.022 | 0.022 |
| 10 | 0.16 | 0.27 | 0.169 | 0.315 | 0.311 |
| 15 | 0.21 | 0.37 | 0.237 | 0.457 | 0.453 |
| 30 | 0.28 | 0.49 | 0.330 | 0.667 | 0.660 |
| 60 | 0.47 | 0.74 | 0.637 | 1.334 | 1.320 |
| 90 | 0.57 | 0.82 | 0.839 | 1.732 | 1.715 |
| 120 | 0.66 | 0.90 | 1.079 | 2.322 | 2.298 |

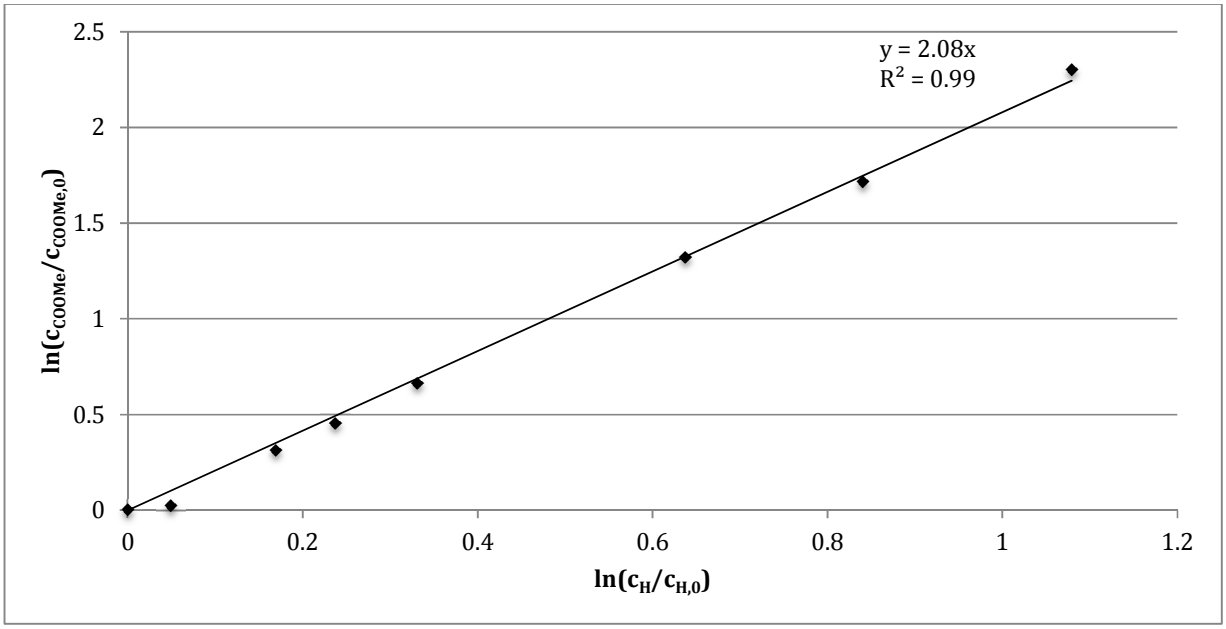



**Figure S6 Kinetic plot for the competition experiment with 1-allyl-4-methylbenzene and methyl 4-allylbenzoate. The slope represents the reactivity of methyl 4-allylbenzoate relative to allylbenzene.**

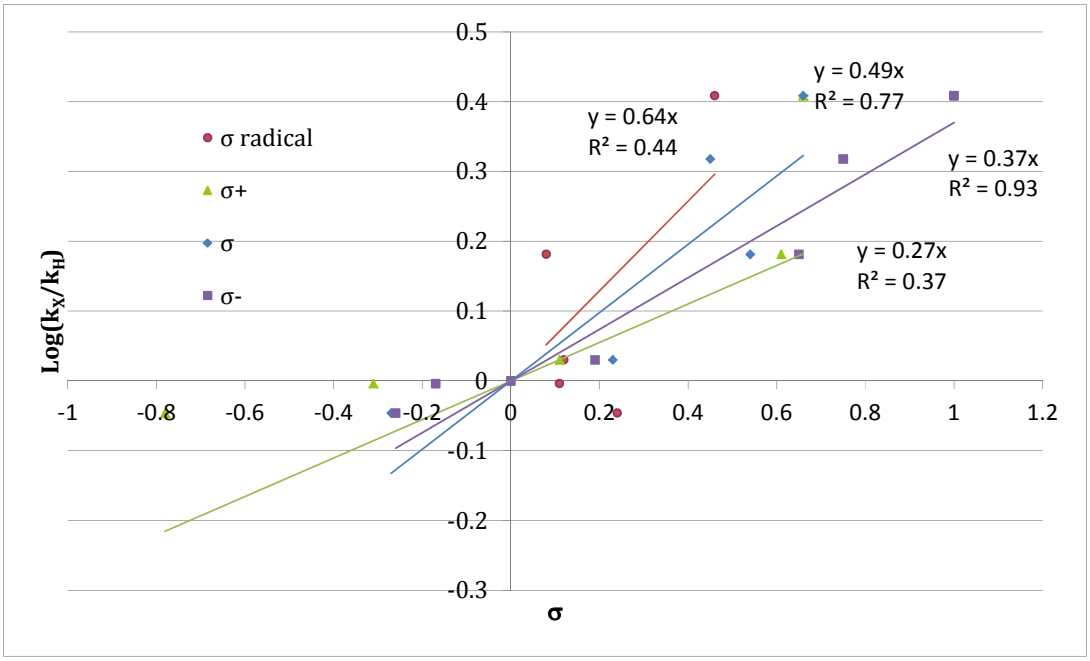



**Figure S7 Hammett plots for the alkylation of *para*-substituted allylbenzenes using σ values from the literature. σ• gives a slope of 0.64, σ gives 0.77, $\sigma^-$ gives 0.37 and $\sigma^+$ gives a slope of 0.27.**

**KIE determination and deuterium experiments**

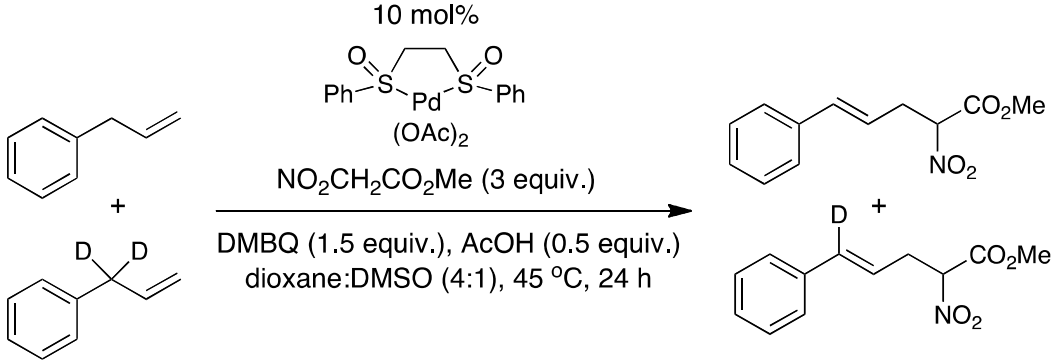
Synthesis of $d_2$-allylbenzene (**2**):
Methyl benzoate was reduced with $LiAlD_4$ [1] to the corresponding benzylic alcohol and then halogenated with $Br_2$ and $PPh_3$[2] to benzyl bromide with deuterium in both benzylic positions. $d_2$-allylbenzene was then obtained by a Kumada-Corriu reaction with vinylmagnesium bromide[3].

Synthesis of deuterium marked (E)-methyl 2-nitro-5-phenylpent-4-enoate (**SI-1**):
To a 7 mL screw-cap vial was added Pd[1,2-bis(phenylsulfonyl)ethane]$(OAc)_2$ (0.05 mmol, 25 mg) and 2,6-dimethylbenzoquinone (0.75 mmol, 102 mg). $d_2$-allylbenzene (0.5 mmol, 60 mg), methyl nitroacetate (1.5 mmol, 178 mg), and AcOH (0.25 mmol, 15 mg) were weighed out in a 1.0 mL vial and transferred to the catalyst mixture using dioxane (3 x 0.4 mL). DMSO (0.3 mL) was added followed by a stir bar. The reaction was sealed with a screw cap fitted with a PTFE septum and placed in an aluminum block preheated to 45 ºC. The reaction mixture was stirred for 96 h, before the vial was allowed to cool to room temperature. The reaction mixture was diluted with saturated aqueous $NH_4Cl$ (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified using silica-gel chromatography (15% EtOAc/hexane) giving the pure linear product (48 mg, 41 % yield) as a pale yellow oil. GC-MS: m/z 236. $^1$H NMR (300 MHz, $CDCl_3$) δ 7.32 (m, 4H), 7.25 (m, 1H), 6.07 (m, 1H), 5.23 (dd, $J$ = 9.0, 5.6 Hz, 1H), 3.85 (s, 3H), 3.10 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 164.7, 136.3, 135.1 (t, $J$ = 92 Hz), 128.8, 128.2, 126.6, 121.1, 87.7, 53.9, 33.9.

Synthesis of bis[chloro($d_2$-1,2,3-*trihapto*-allylbenzene)palladium (II)] (**SI-2**):
Procedure reported by White and coworkers[4] was utilized with $d_2$-allylbenzene, and a longer reaction time of 5 h, affording the product as a yellow solid (32 mg, 62 % yield).
$^1$H NMR (300 MHz, $CDCl_3$) δ 7.47-7.40 (m, 2H), 7.30-7.17 (m, 3H), 5.73 (dd, $J$ = 11.9, 6.9 Hz, 1H), 3.90 (d, $J$ = 6.9 Hz, 1H), 2.97 (d, $J$ = 11.9 Hz, 1H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 136.8, 128.9, 128.4, 127.8, 105.7, 81.5 (t, $J$ = 86.6 Hz), 59.3.

Synthesis of (E)-methyl 5-(4-chlorophenyl)-2-nitropent-4-enoate (**SI-3**):
To a 7 mL screw-cap vial was added Pd[1,2-bis(phenylsulfonyl)ethane](OAc)$_2$ (0.05 mmol, 25 mg) and 2,6-dimethylbenzoquinone (0.75 mmol, 102 mg). 1-allyl-4-chlorobenzene (0.5 mmol, 66 mg), methyl nitroacetate (1.5 mmol, 178 mg), and AcOH (0.25 mmol, 15 mg) were weighed out in a 1.0 mL vial and transferred to the catalyst mixture using dioxane (3 x 0.4 mL). DMSO (0.3 mL) was added followed by a stir bar. The reaction was sealed with a screw cap fitted with a PTFE septum and placed in an aluminum block preheated to 45 ºC. The reaction mixture was stirred for 24 h, before the vial was allowed to cool to room temperature. The reaction mixture was diluted with saturated aqueous $NH_4Cl$ (20 mL) and extracted with EtOAc (3 x 20 mL). The combined organics were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified using silica-gel chromatography (15% EtOAc/hexane) giving the pure linear product (73 mg, 54 % yield) as a pale yellow oil. GC-MS: m/z 269 ($^{35}$Cl), 271 ($^{37}$Cl). $^1$H NMR (300 MHz, $CDCl_3$) δ 7.3-7.2 (m, 4H), 6.51 (dd, *J* = 15.8, 1.2 Hz, 1H), 6.07 (dt, *J* = 15.8, 7.2 Hz, 1H), 5.24 (dd, *J* = 9.0, 5.6 Hz, 1H), 3.85 (s, 3H), 3.25 – 2.94 (m, 2H); $^{13}$C NMR (75 MHz, $CDCl_3$) δ 164.5, 134.7, 134.3, 133.8, 128.9, 127.7, 121.8, 87.4, 53.8, 33.8.

Procedure for determining the deuterium-isotope-effect of allylbenzene in Palladium Catalyzed Allylic CH Alkylation
To a screw-cap vial was added Pd[1,2-bis(phenylsulfonyl)ethane](OAc)$_2$ (0.05 mmol, 25 mg), 2,6-dimethylbenzoquinone (0.75 mmol, 102 mg) and a stir bar. Allylbenzene (0.25 mmol, 30 mg), $d_2$-allylbenzene (0.25 mmol, 30 mg), methyl nitroacetate (1.5 mmol, 178 mg), AcOH (0.25 mmol, 15 mg) and dodecane as internal standard (0.125 mmol, 21 mg) were weighed out in a 1.0 ml vial and transferred to the catalyst mixture using dioxane:DMSO (4:1) (1.5 mL). The reaction was sealed with a screw cap fitted with a PTFE septum and placed in an aluminum block preheated to 45 ºC. Samples of 0.05 mL each were withdrawn from the reaction mixture after 0, 0.5, 1, 2, 4, 6, 8, and 24 hrs reaction time, diluted with diethylether (1 mL) and analyzed by GCMS.




**Scheme S1 The experiment for determination of the kinetic isotope effect ($k_H/k_D$) for allylbenzene in the allylic CH alkylation reaction.**

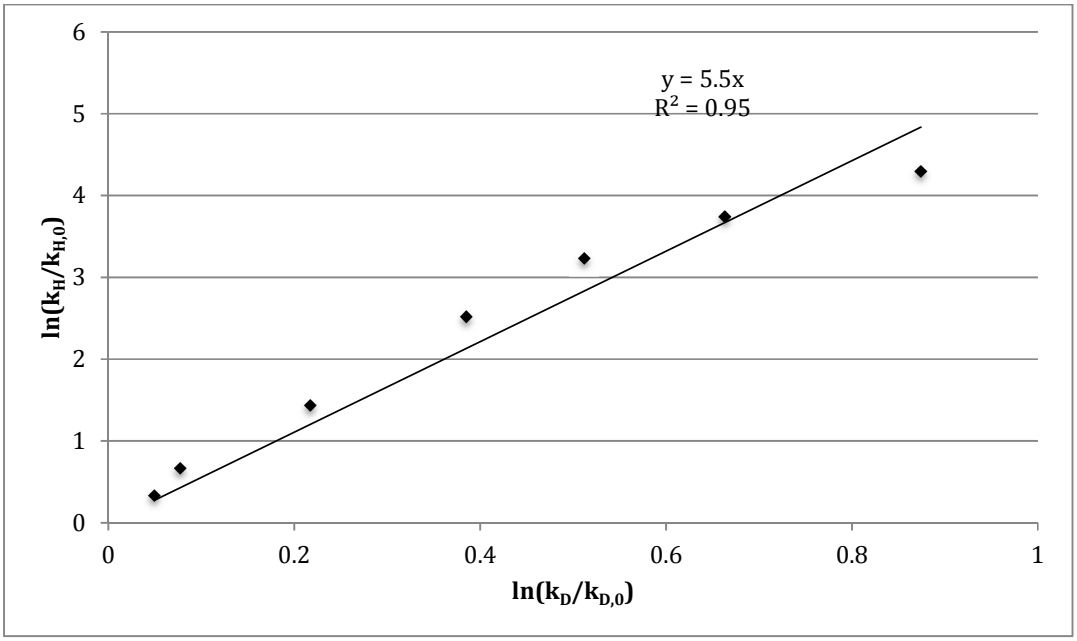



**Figure S8 Deuterium-isotope-effect of allylbenzene in the allylic CH alkylation reaction.**

Due to overlap in retention time between allylbenzene and $d_2$-allylbenzene the deuterium-isotope-effect was determined from a distinct molecular ion of each of the substrates, m/z=115 and m/z=120 respectively, by SIM (Single Ion Monitoring).

The deuterium-isotope-effect was also determined by two separate experiments run in parallel, one with allylbenzene and the other with $d_2$-allylbenzene as the substrate. Samples were taken every 10 minutes for the first two hours reaction time to determine the initial reaction rates. The resulting KIE was determined from the average of two runs.

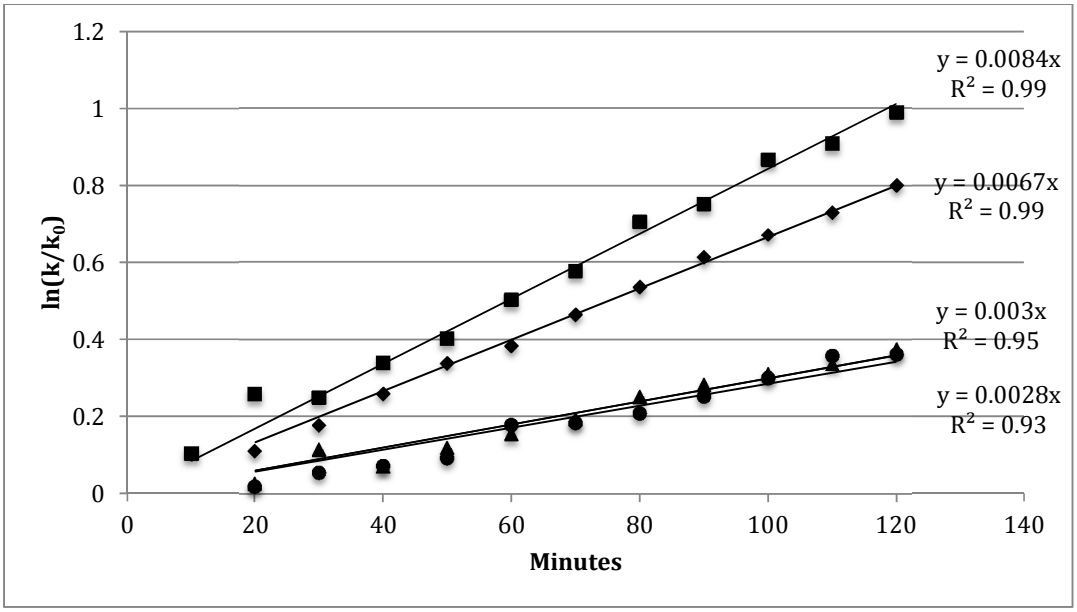
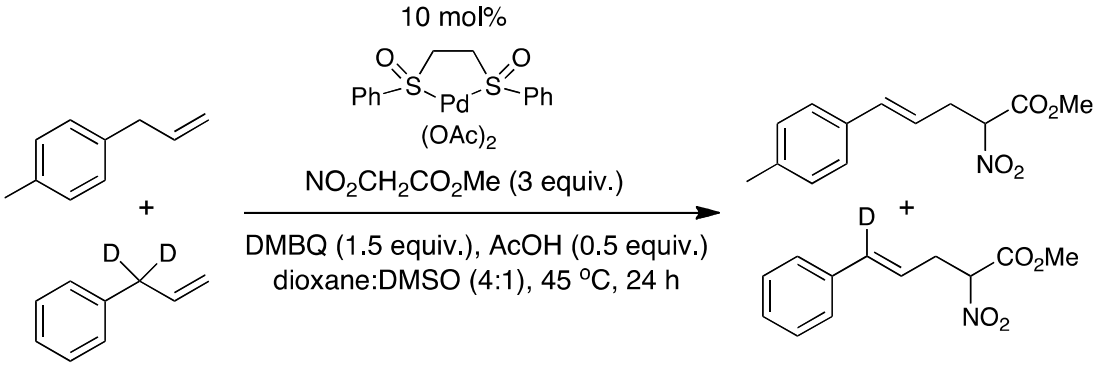



**Figure S9 Deuterium-isotope-effect determined from two separate experiments run in parallel. The two top lines are experiments with allylbenzene and the two others are experiments with $d_2$-allylbenzene.**

The competitive experiment between $d_2$-allylbenzene and 4-allyltoluene (0.25 mmol, 33 mg) in the allylic CH alkylation reaction was performed with the same conditions as the reaction between allylbenzene and $d_2$-allylbenzene.




**Scheme S2 Kinetic isotope effect ($k_H/k_D$) for allylbenzene determined by comparison to 4-allyltoluene in the allylic CH alkylation reaction.**

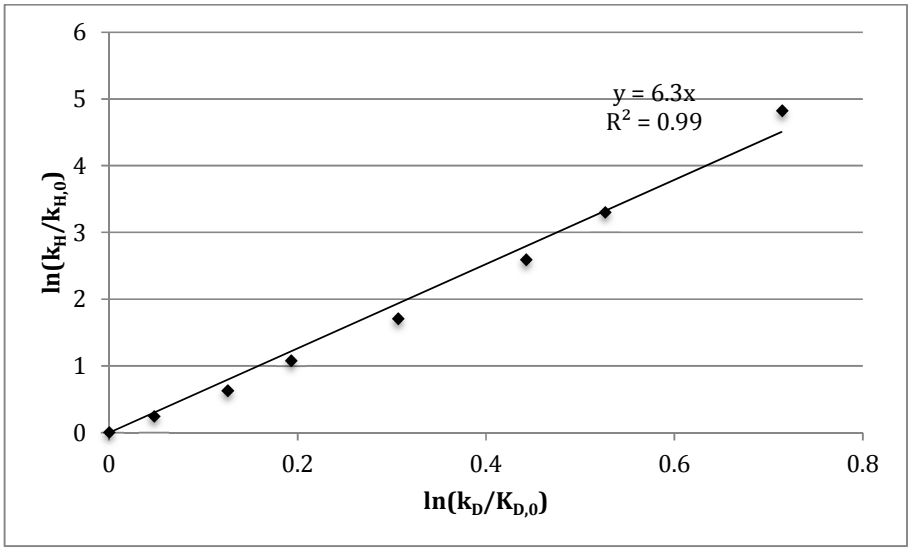



**Figure S10 Deuterium-isotope-effect of allylbenzene based on comparison with 4-allyltoluene in the allylic CH alkylation reaction.**

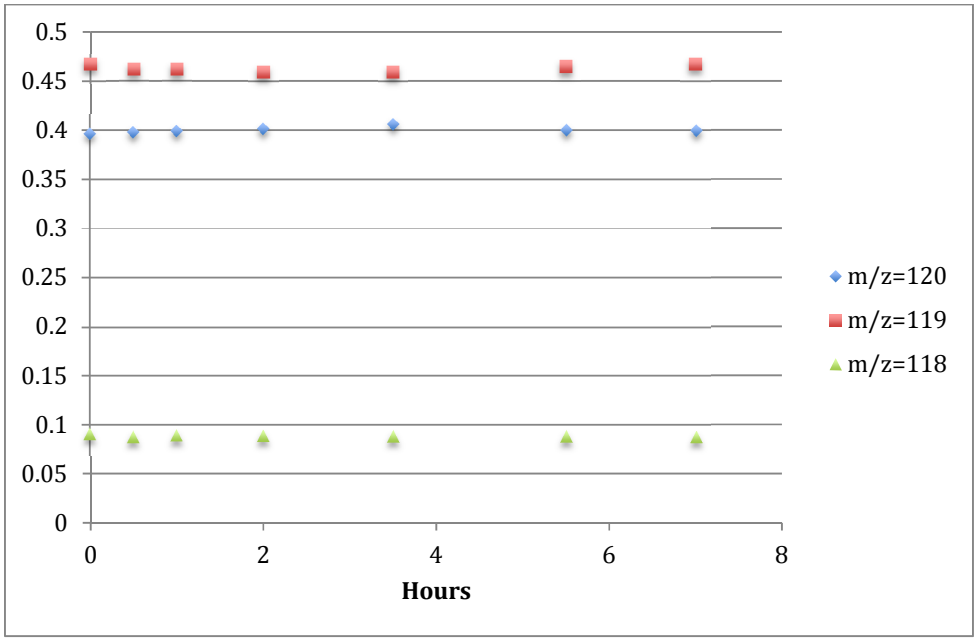



**Figure S11 GC-MS data showing that the $d_2$-allylbenzene (m/z=120) loses no deuterium content during the reaction.**

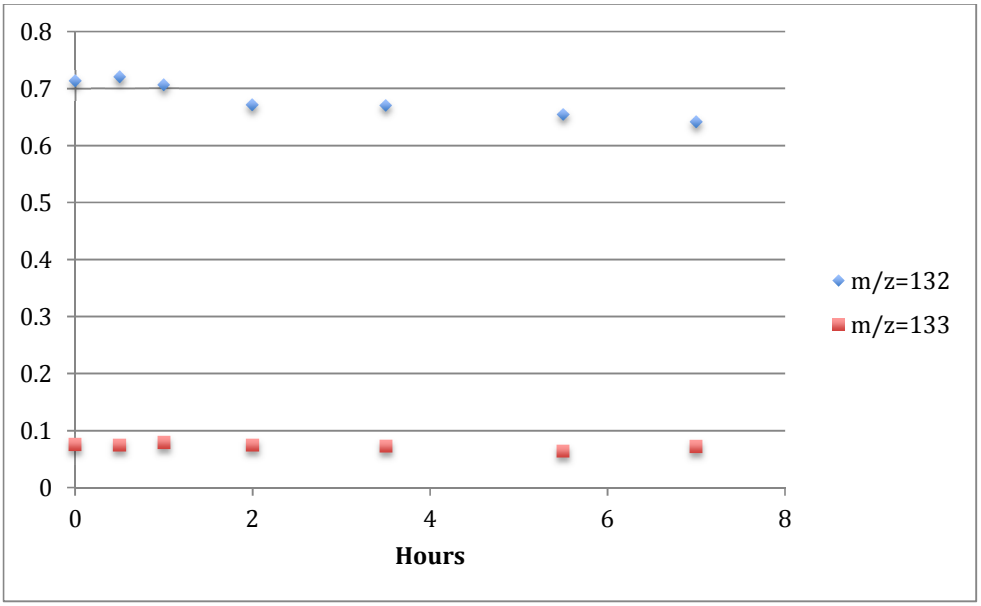
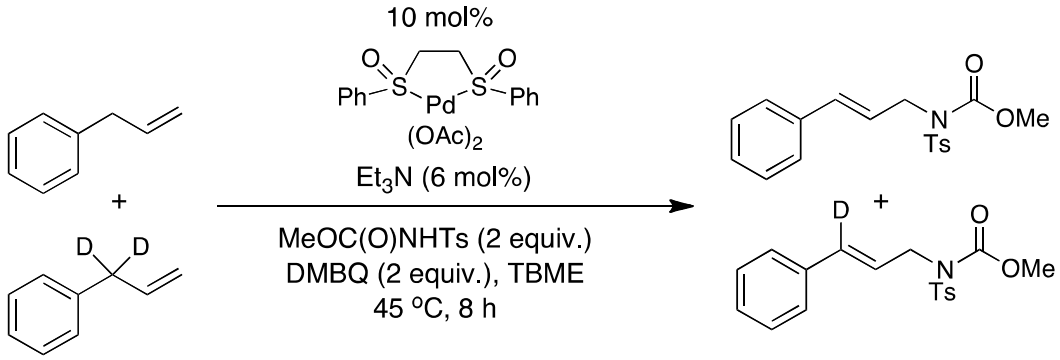



**Figure S12 GC-MS data showing that no deuterium is incorporated in 4-allyltoluene (m/z=132) during the reaction.**

Procedure for determining the deuterium-isotope-effect of allylbenzene in Palladium Catalyzed Allylic CH Amination

To a screw-cap vial was added Pd[1,2-bis(phenylsulfonyl)ethane](OAc)$_2$ (0.05 mmol, 25 mg), methyl tosylcarbamate (1.0 mmol, 229 mg), 2,6-dimethylbenzoquinone (1 mmol, 136 mg) and a stir bar. Allylbenzene (0.25 mmol, 30 mg), $d_2$-allylbenzene (0.25 mmol, 30 mg), $Et_3N$ (0.03 mmol, 4 µL) and dodecane as internal standard (0.125 mmol, 21 mg) were weighed out in a 1.0 ml vial and

transferred to the catalyst mixture using *tert*-butyl methyl ether (1.0 mL). The reaction was sealed with a screw cap fitted with a PTFE septum and placed in an aluminum block preheated to 45 ºC. Samples of 0.05 mL each were withdrawn from the reaction mixture after 0, 0.5, 1, 2, 3, 4, 6 and 8 hrs reaction time, diluted with diethylether (1 mL) and analyzed by GCMS.




**Scheme S3 The experiment for determination of the kinetic isotope effect ($k_H/k_D$) for allylbenzene in the allylic CH acetoxylation reaction.**

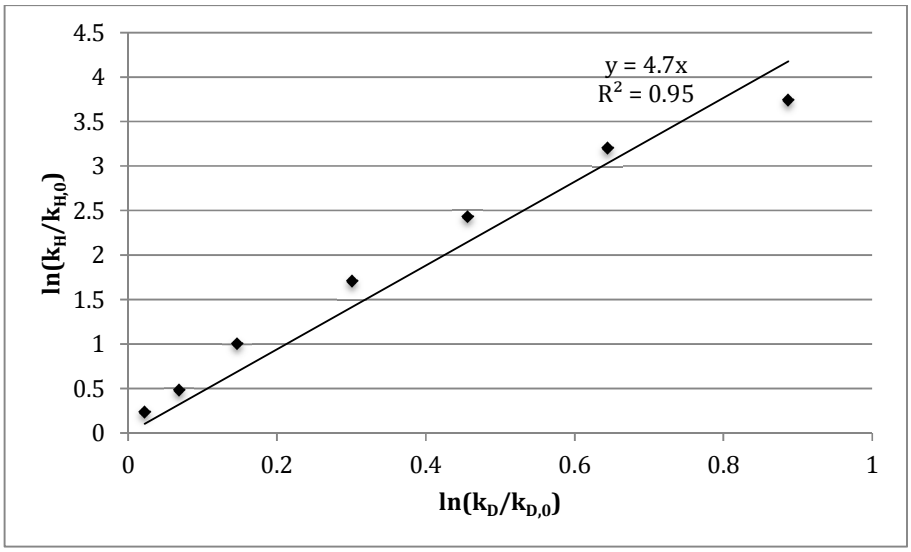
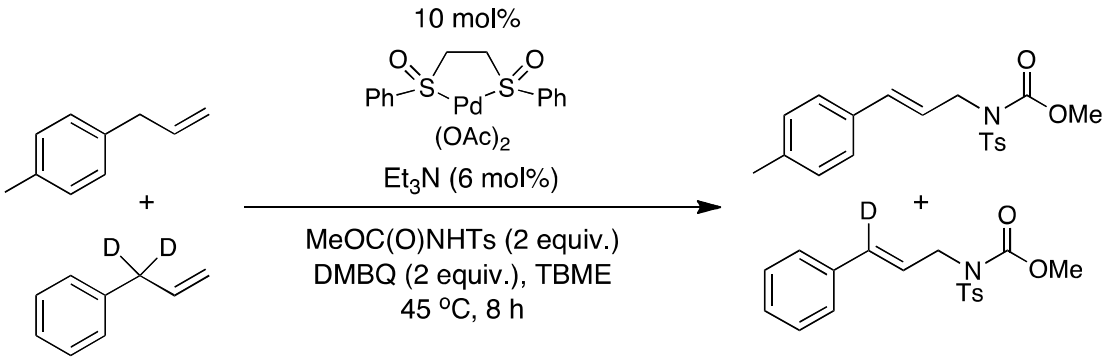



**Figure S13 Deuterium-isotope-effect of allylbenzene in the allylic CH amination reaction.**

Competitive experiment between $d_2$-allylbenzene and 4-allyltoluene (0.25 mmol, 33 mg) in the allylic CH amination reaction was performed with the same conditions as the reaction between allylbenzene and $d_2$-allylbenzene.




**Scheme S4 Competitive experiment between $d_2$-allylbenzene and 4-allyltoluene in the allylic CH amination reaction.**

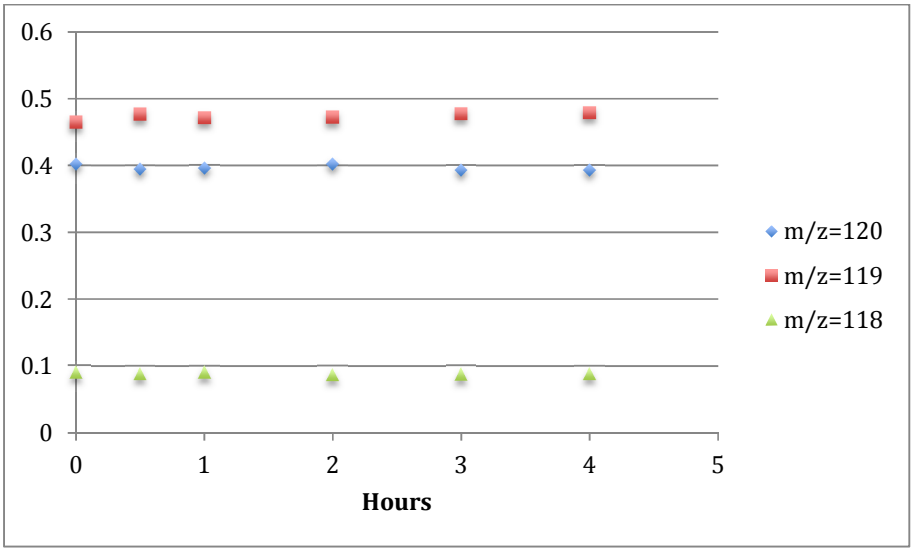



**Figure S14 GC-MS data showing that the $d_2$-allylbenzene (m/z=120) loses no deuterium content during the reaction.**

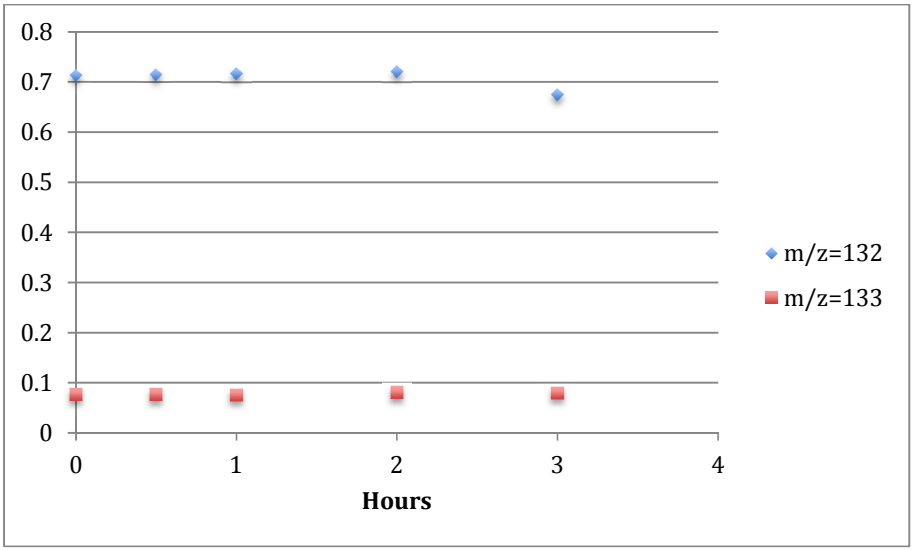
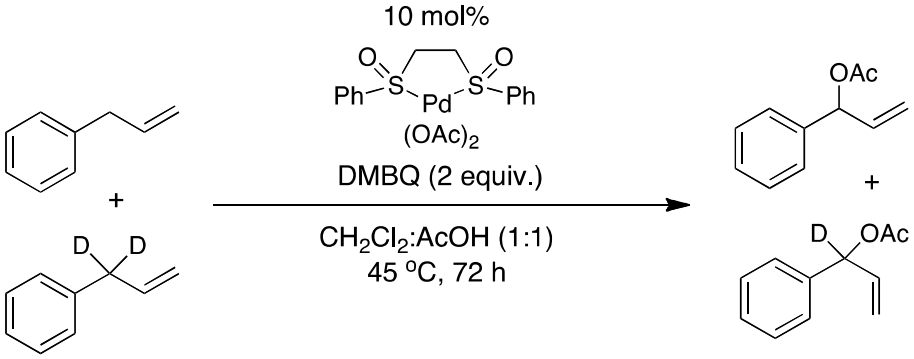



**Figure S15 GC-MS data showing that no deuterium is incorporated in 4-allyltoluene (m/z=132) during the reaction.**

Procedure for determining the deuterium-isotope-effect of allylbenzene in Palladium Catalyzed Allylic CH Acetoxylation

To a screw-cap vial was added Pd[1,2-bis(phenylsulfonyl)ethane](OAc)$_2$ (0.05 mmol, 25 mg), 2,6-dimethylbenzoquinone (1 mmol, 136 mg) and a stir bar. Allylbenzene (0.25 mmol, 30 mg), $d_2$-allylbenzene (0.25 mmol, 30 mg) and dodecane as internal standard (0.125 mmol, 21 mg) were weighed out in a 1.0 ml vial and transferred to the catalyst mixture using $CH_2Cl_2$:AcOH (3 mL). The reaction was sealed with a screw cap fitted with a PTFE septum and placed in an aluminum block preheated to 45 ºC. Samples of 0.05 mL each were withdrawn from the reaction mixture after 0, 1, 3, 6, 24, 28, 32 and 48 hrs reaction time, diluted with diethylether (1 mL) and analyzed by GCMS.




**Scheme S5 The experiment for determination of the kinetic isotope effect ($k_H/k_D$) for allylbenzene in the allylic CH amination reaction.**

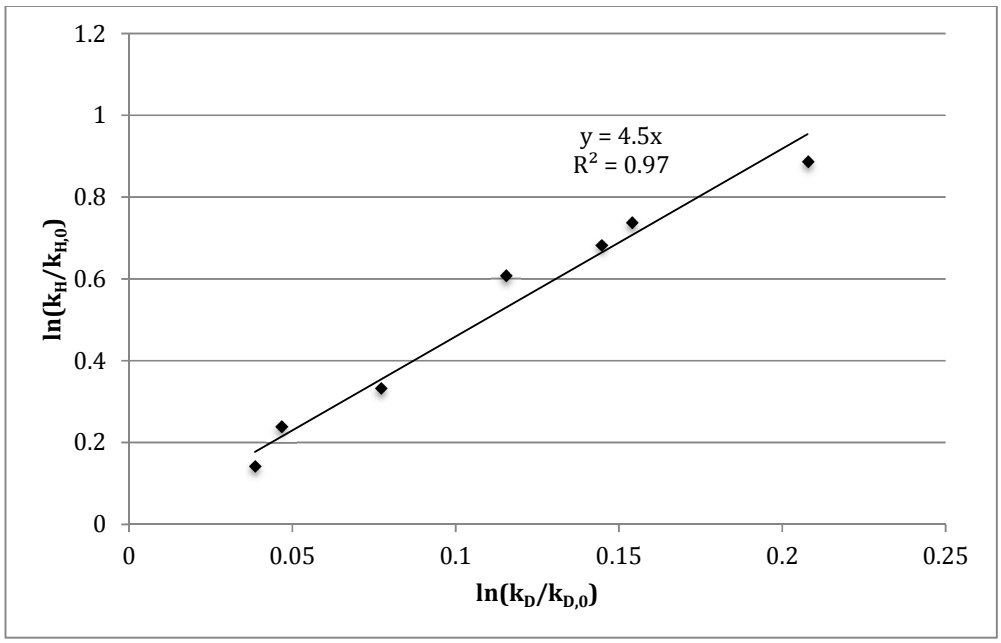



**Figure S16 Deuterium-isotope-effect of allylbenzene in the allylic CH acetoxylation reaction.**

Competitive experiment between $d_2$-allylbenzene and 4-allyltoluene (0.25 mmol, 33 mg) in the allylic CH acetoxylation reaction was performed with the same conditions as the reaction between allylbenzene and $d_2$-allylbenzene.

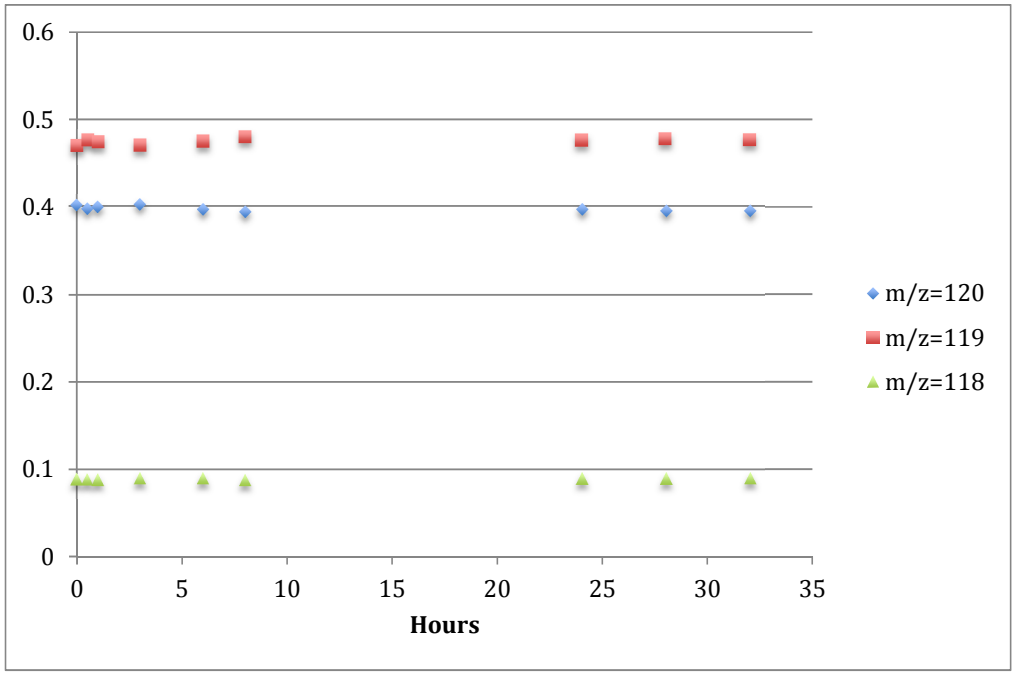



**Figure S17 GC-MS data showing that the $d_2$-allylbenzene (m/z=120) loses no deuterium content during the reaction.**

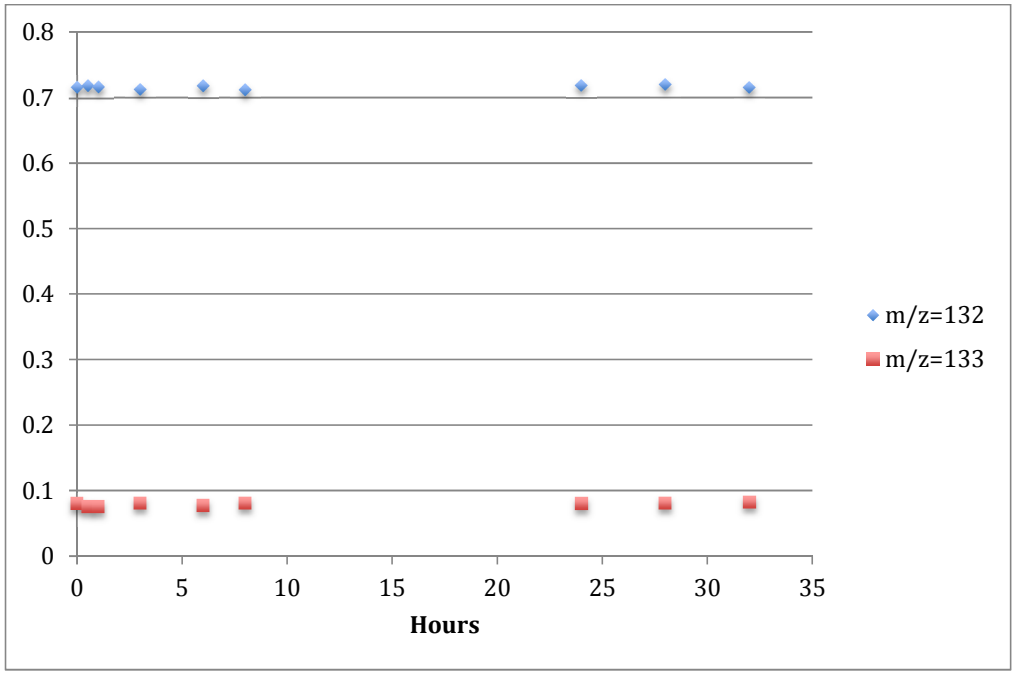
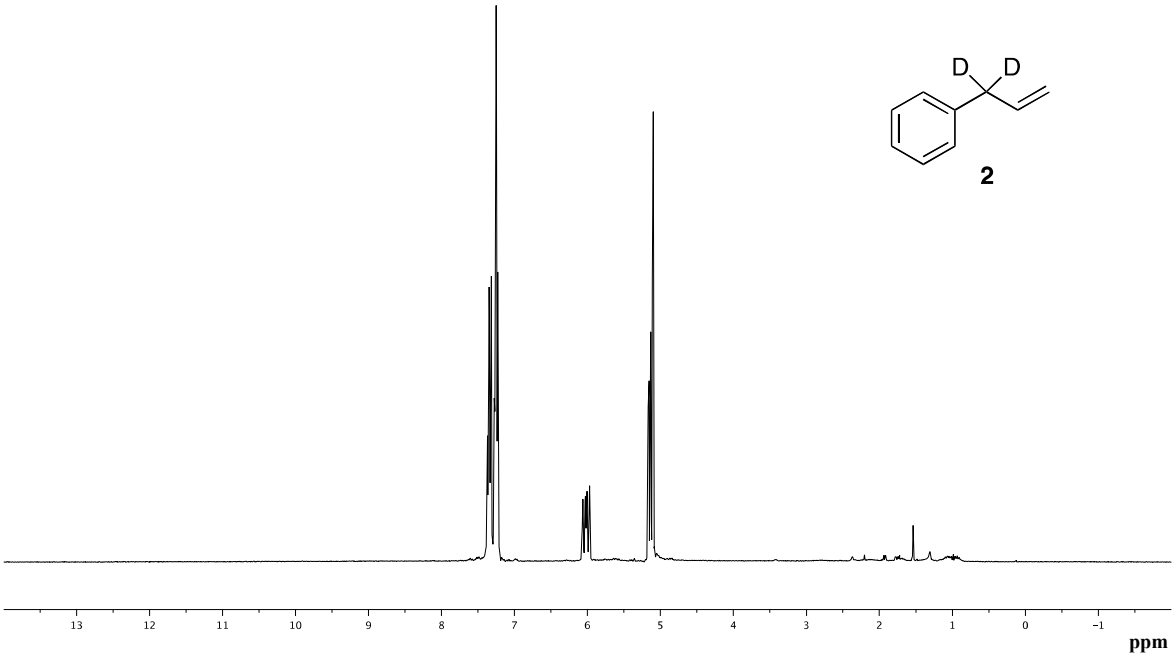
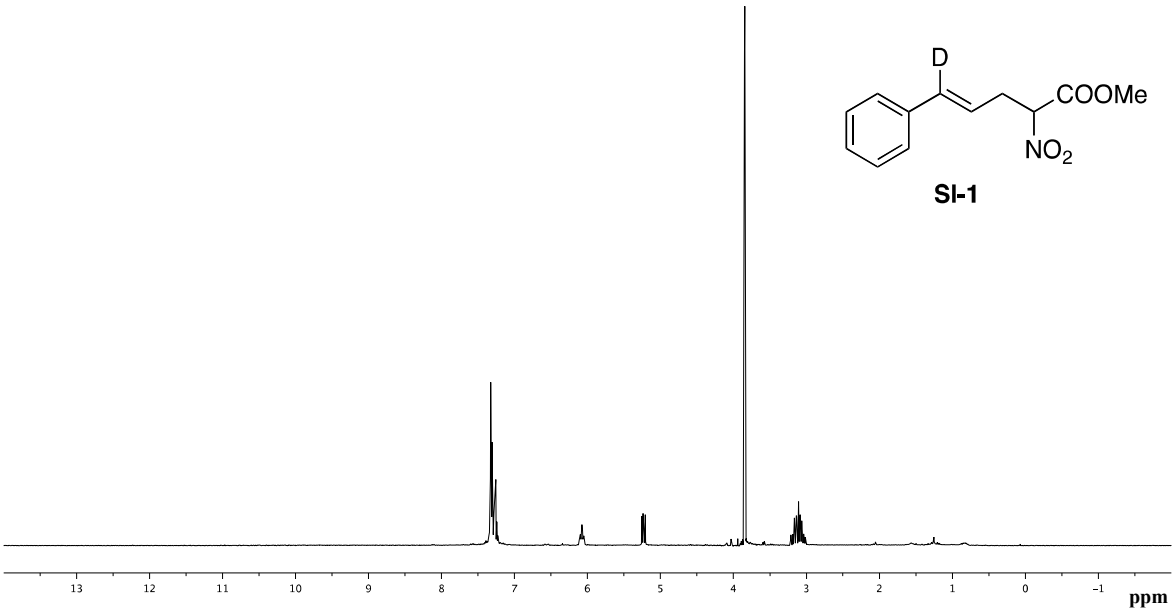
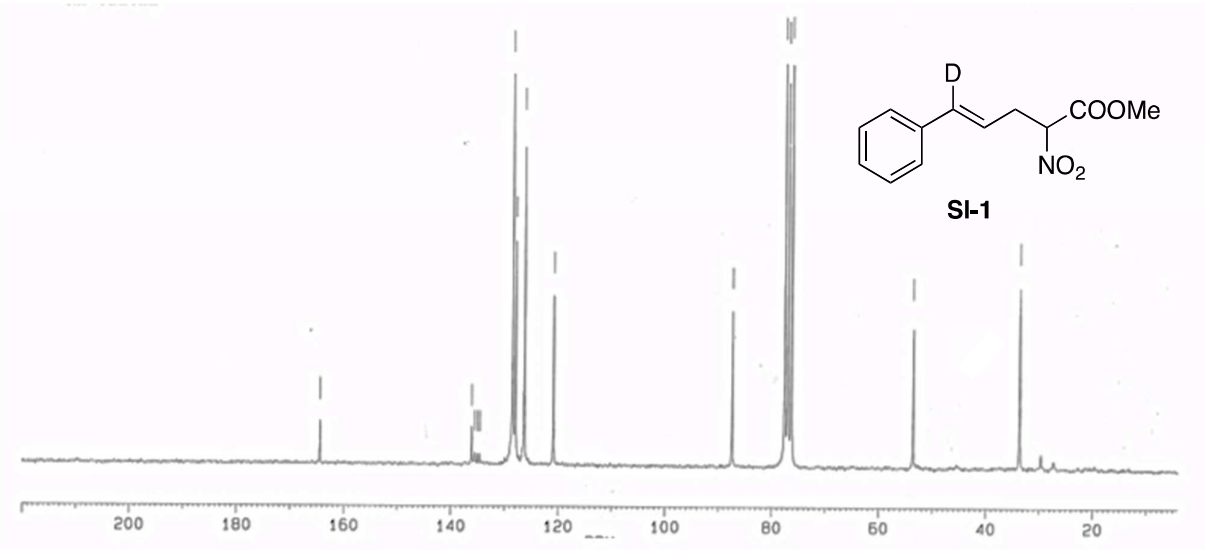



**Figure S18 GC-MS data showing that no deuterium is incorporated in 4-allyltoluene (m/z=132) during the reaction.**

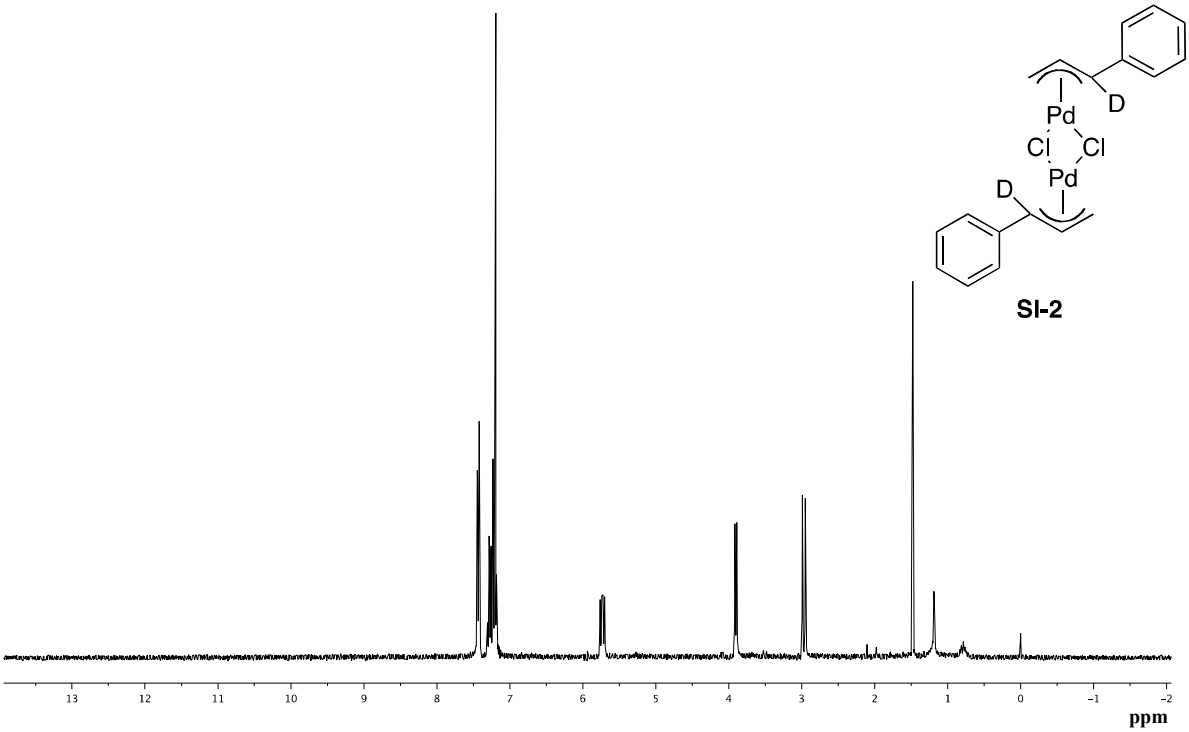
**NMR data**


D
D
2
13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
ppm

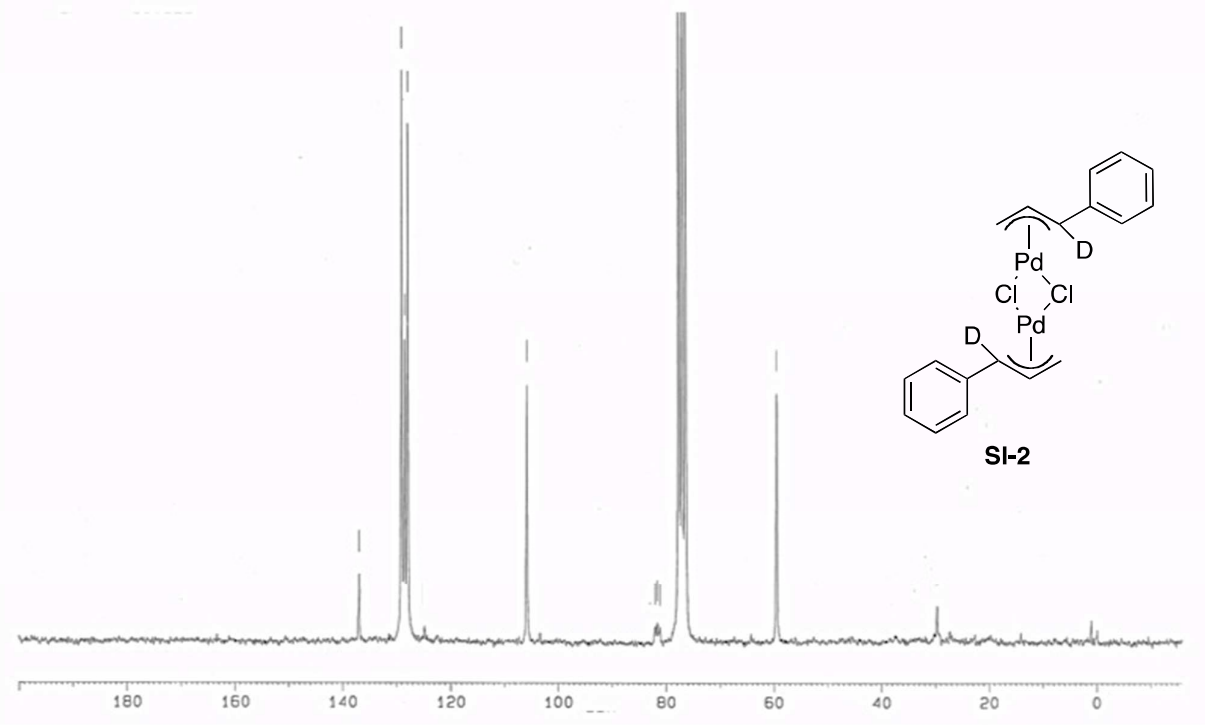

D
COOMe
NO2
SI-1
13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1
ppm


D
COOMe
NO2
200
180
160
140
120
100
80
60
40
20
ppm

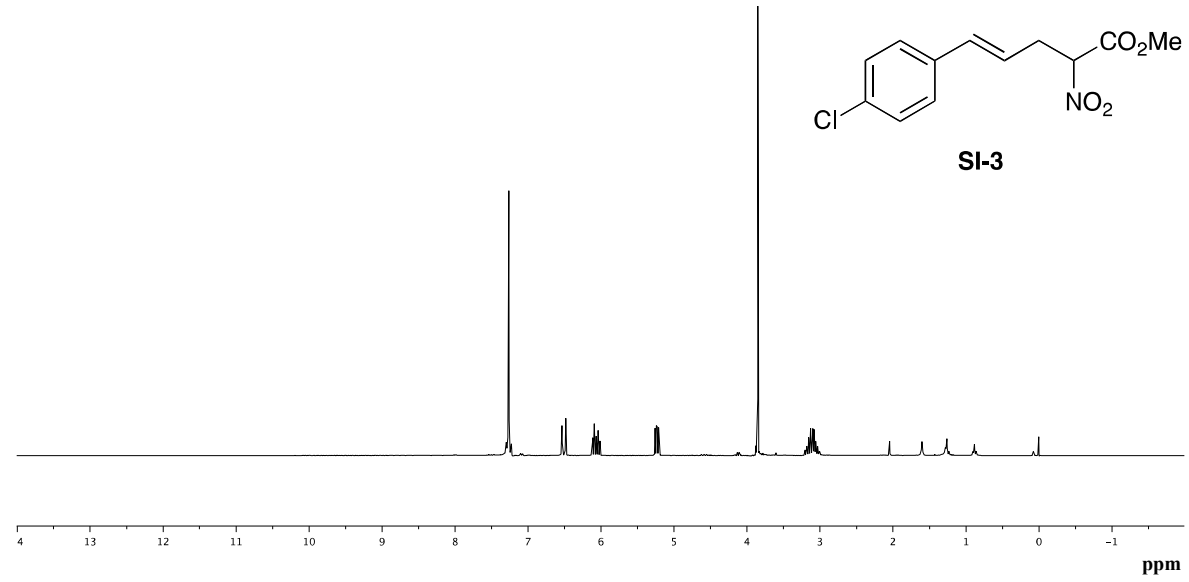
**SI-1**


D
Pd
Cl
Cl
Pd
D
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
−2
ppm

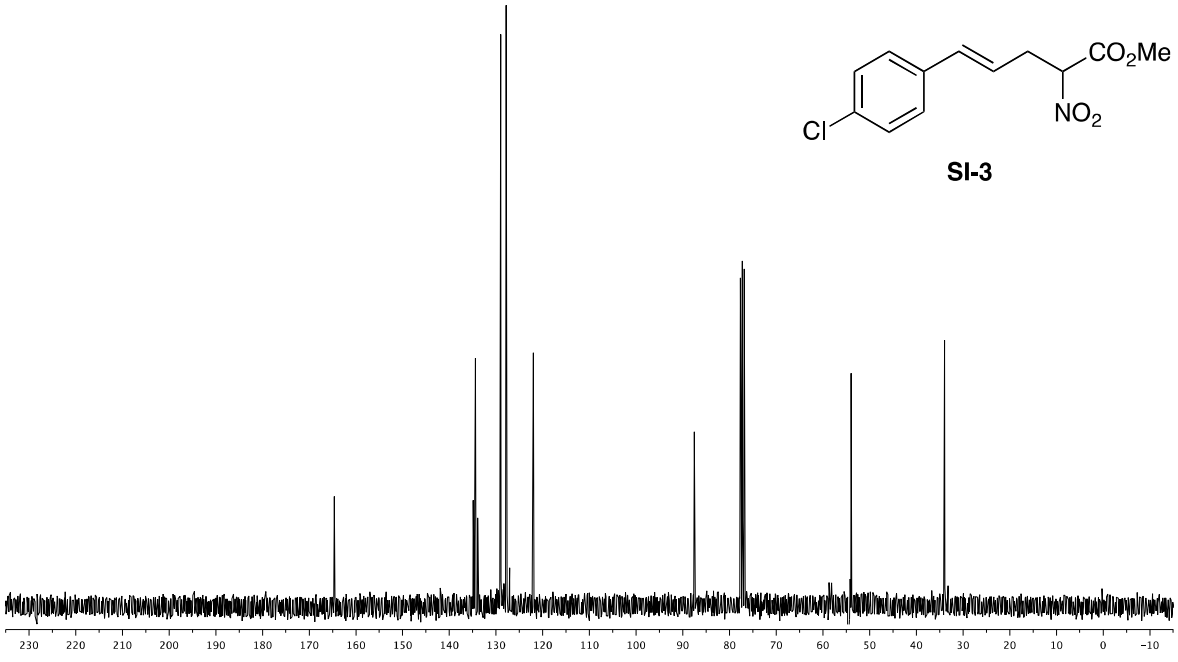
**SI-2**


D
Pd
Cl
Cl
Pd
D
180
160
140
120
100
80
60
40
20
0
ppm

**SI-2**


CO2Me
NO2
Cl
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
ppm

**SI-3**

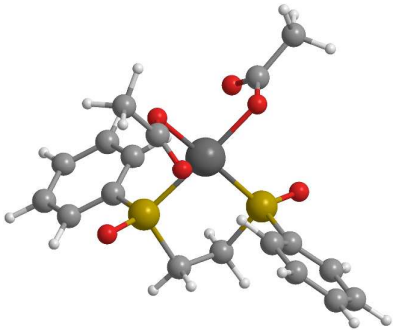

CO2Me
NO2
Cl
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
ppm

**SI-3**

**XYZ coordinates and energies from computational study**

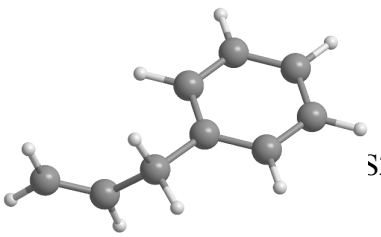
The description of the computational method is included in the main text of the manuscript.

Pd_Bisulfoxide_2Acetate
E_scf (B3LYP/LACVP*) = -2072.35905820344 a.u.
E_scf (M06/LACVP*) = -2071.57851982228 a.u.
E_Gibbs = -2072.067993 a.u.
E_Gibbs(318K) = -2072.074334 a.u.
E_solv = -2072.40209458304 a.u.
ZPE = 222.482 kcal/mol



| | | | |
|---|---|---|---|
| Pd | 0.17330 | -0.35000 | -0.04100 |
| S | 0.21020 | 1.35800 | 1.57480 |
| S | -2.13920 | -0.02230 | -0.31880 |
| O | 0.89750 | 1.35880 | 2.90030 |
| O | -2.90670 | 0.09040 | -1.59500 |
| C | 0.63750 | 2.86890 | 0.67650 |
| C | 0.95300 | 3.99760 | 1.43760 |
| C | 1.28310 | 5.17900 | 0.77740 |
| C | 1.30440 | 5.21770 | -0.62020 |
| C | 1.01070 | 4.07380 | -1.36330 |
| C | 0.68030 | 2.87740 | -0.72100 |
| C | -1.59620 | 1.62920 | 1.89750 |
| C | -2.43910 | 1.53890 | 0.63760 |
| C | -2.92860 | -1.24950 | 0.74870 |
| C | -4.30140 | -1.45290 | 0.58270 |
| C | -4.94100 | -2.39240 | 1.38840 |
| C | -4.20970 | -3.11850 | 2.33360 |
| C | -2.83570 | -2.91800 | 2.46920 |
| C | -2.17380 | -1.98310 | 1.66900 |
| H | 0.96370 | 3.93540 | 2.52200 |
| H | 1.53350 | 6.06600 | 1.35270 |
| H | 1.56720 | 6.14070 | -1.13010 |
| H | 1.05070 | 4.09740 | -2.44850 |
| H | 0.49530 | 1.97750 | -1.30790 |
| H | -1.85280 | 0.85290 | 2.62550 |
| H | -1.68990 | 2.60970 | 2.37430 |
| H | -2.20210 | 2.33350 | -0.07720 |
| H | -3.50880 | 1.57240 | 0.86560 |
| H | -4.84300 | -0.90300 | -0.18140 |
| H | -6.00710 | -2.56600 | 1.27130 |
| H | -4.71240 | -3.85450 | 2.95540 |
| H | -2.26330 | -3.49880 | 3.18650 |
| H | -1.09310 | -1.86420 | 1.75110 |
| O | 2.13390 | -0.75220 | 0.34840 |
| O | 1.23390 | -1.98060 | 2.01170 |
| O | 0.13920 | -1.70480 | -1.56650 |
| O | 0.36200 | 0.16160 | -2.81220 |
| C | 2.20500 | -1.57060 | 1.37110 |
| C | 3.63120 | -1.98280 | 1.70560 |
| C | 0.27280 | -1.06390 | -2.70330 |
| C | 0.31750 | -1.99090 | -3.90880 |
| H | 4.24520 | -1.09570 | 1.89190 |
| H | 3.63210 | -2.62770 | 2.58650 |
| H | 4.07200 | -2.51490 | 0.85570 |
| H | -0.54040 | -2.67040 | -3.89680 |
| H | 1.22410 | -2.60460 | -3.86700 |
| H | 0.31620 | -1.40150 | -4.82770 |

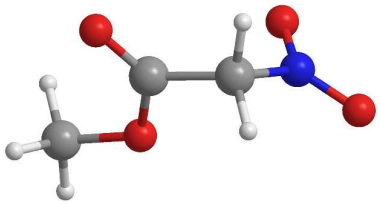
Allylbenzene
E_scf (B3LYP/LACVP*) = -348.94958989188 a.u.



E_scf (M06/LACVP*) = -348.65922367329 a.u.
E_Gibbs = -348.820936 a.u.
E_Gibbs(318K) = -348.823816 a.u.
E_solv = -348.95003655272 a.u.
ZPE = 101.89 kcal/mol

| | | | |
|---|---|---|---|
| C | 0.00020 | -0.00030 | 0.00110 |
| C | 0.00100 | 0.00060 | 1.40300 |
| C | 1.23210 | 0.00020 | 2.06850 |
| C | 2.43330 | 0.00670 | 1.35620 |
| C | 2.41950 | 0.01170 | -0.03840 |
| C | 1.19710 | 0.00770 | -0.71400 |
| H | -0.94850 | -0.01260 | -0.53030 |
| H | 1.25180 | -0.00320 | 3.15650 |
| H | 3.37910 | 0.00660 | 1.89250 |
| H | 3.35290 | 0.01620 | -0.59550 |
| H | 1.17630 | 0.00900 | -1.80110 |
| C | -1.30980 | 0.01410 | 2.17810 |
| H | -1.08280 | -0.06950 | 3.25020 |
| H | -1.81360 | 0.98110 | 2.04220 |
| C | -2.25220 | -1.09330 | 1.77680 |
| H | -1.86270 | -2.10590 | 1.88860 |
| C | -3.48530 | -0.91530 | 1.29980 |
| H | -3.91000 | 0.07810 | 1.16760 |
| H | -4.11970 | -1.75470 | 1.02780 |

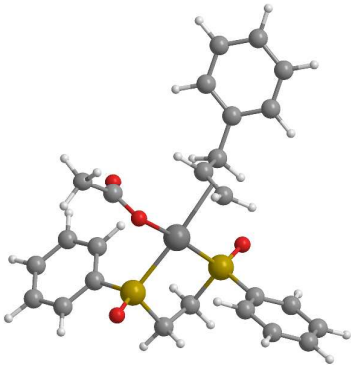
Methyl_Nitroacetate



E_scf (B3LYP/LACVP*) = -472.86630684448 a.u.
E_scf (M06/LACVP*) = -472.62177095945 a.u.
E_Gibbs = -472.807334 a.u.
E_Gibbs(318K) = -472.810306 a.u.
E_solv = -472.88312714186 a.u.
ZPE = 58.922 kcal/mol

| | | | |
|---|---|---|---|
| C | 0.00000 | 0.00000 | 0.00000 |
| H | 0.00000 | 0.00000 | 1.09020 |
| N | 1.44460 | 0.00000 | -0.43920 |
| O | 1.65900 | -0.29460 | -1.60970 |
| O | 2.28030 | 0.33100 | 0.39140 |
| C | -0.75440 | -1.19430 | -0.57030 |
| O | -0.13800 | -2.33900 | -0.24750 |
| O | -1.78820 | -1.10370 | -1.18820 |
| C | -0.74850 | -3.53870 | -0.76330 |
| H | -0.12450 | -4.35730 | -0.40620 |
| H | -1.77020 | -3.63540 | -0.38790 |
| H | -0.76460 | -3.51170 | -1.85550 |
| H | -0.44130 | 0.91940 | -0.38660 |

Pd_Bisulfoxide_Allylbenzene_Acetate
E_scf (B3LYP/LACVP*) = -2192.62716360606 a.u.
E_scf (M06/LACVP*) = -2191.68601439312 a.u.
E_Gibbs = -2192.2284 a.u.
E_Gibbs(318K) = -2192.2353 a.u.
E_solv = -2192.70663936665 a.u.
ZPE = 293.109 kcal/mol

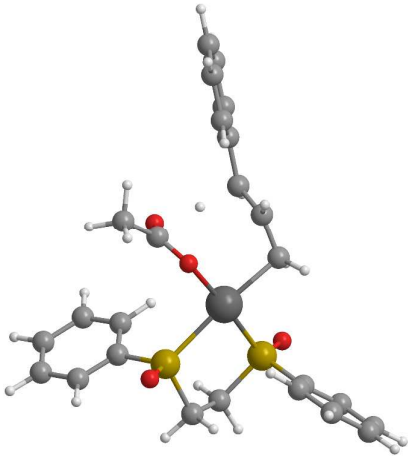


| | | | |
|---|---|---|---|
| O | 0.51030 | -0.10320 | -0.82940 |
| H | -0.56850 | 0.69510 | 2.30510 |
| C | 0.29650 | 0.50450 | 2.95030 |
| C | 1.48070 | 0.13100 | 2.11060 |
| C | 2.77460 | 0.58380 | 2.28080 |
| C | -1.07000 | -2.83710 | 4.22080 |

| | | | |
|---|---|---|---|
| O | 0.81410 | 3.77100 | 2.98410 |
| C | -0.41640 | -2.95820 | 5.44860 |
| C | -0.84930 | -1.71810 | 3.41830 |
| C | 0.02090 | -0.70540 | 3.84150 |
| C | 0.68010 | -0.83770 | 5.07070 |
| C | 0.45780 | -1.95570 | 5.87320 |
| H | -0.58930 | -3.82980 | 6.07360 |
| H | -1.75480 | -3.61260 | 3.88890 |
| H | -1.36420 | -1.62520 | 2.46430 |
| H | 1.35940 | -0.05730 | 5.40750 |
| H | 0.96490 | -2.04370 | 6.83000 |
| Pd | 2.17760 | 1.86860 | 0.50280 |
| S | 1.78970 | 3.76850 | 1.85250 |
| S | 2.13810 | 3.35180 | -1.41710 |
| O | 3.26300 | 3.33450 | -2.39420 |
| C | 3.38570 | 4.38800 | 2.41030 |
| C | 3.40510 | 5.16860 | 3.56890 |
| C | 4.63130 | 5.65750 | 4.01970 |
| C | 5.80650 | 5.36340 | 3.32300 |
| C | 5.77030 | 4.56900 | 2.17400 |
| C | 4.55460 | 4.06560 | 1.71100 |
| C | 1.25550 | 5.05740 | 0.63230 |
| C | 2.09770 | 5.03610 | -0.62890 |
| C | 0.55070 | 3.31690 | -2.25920 |
| C | 0.49030 | 3.89440 | -3.53230 |
| C | -0.73800 | 3.91860 | -4.18920 |
| C | -1.87230 | 3.37100 | -3.58090 |
| C | -1.78530 | 2.77970 | -2.31940 |
| C | -0.56240 | 2.73770 | -1.64710 |
| H | 2.48510 | 5.36830 | 4.10970 |
| H | 4.66830 | 6.26300 | 4.92010 |
| H | 6.75720 | 5.74530 | 3.68280 |
| H | 6.68650 | 4.32990 | 1.64270 |
| H | 4.52960 | 3.42220 | 0.83430 |
| H | 0.20190 | 4.82840 | 0.44080 |
| H | 1.32360 | 6.01930 | 1.15020 |
| H | 3.14820 | 5.27580 | -0.43770 |
| H | 1.70610 | 5.72780 | -1.38050 |
| H | 1.38600 | 4.29250 | -3.99960 |
| H | -0.80820 | 4.35800 | -5.17970 |
| H | -2.82510 | 3.39070 | -4.10190 |
| H | -2.66140 | 2.32830 | -1.86410 |
| H | -0.47360 | 2.21610 | -0.69960 |
| O | 2.70450 | 0.36200 | -0.74880 |
| C | 1.66600 | -0.31720 | -1.19680 |
| C | 2.03780 | -1.38450 | -2.20940 |
| H | 2.84610 | -2.01450 | -1.82660 |
| H | 2.40140 | -0.90840 | -3.12660 |
| H | 1.15990 | -1.99190 | -2.43560 |
| H | 1.30270 | -0.66190 | 1.39050 |
| H | 0.48880 | 1.40150 | 3.54390 |
| H | 3.02210 | 1.25750 | 3.09850 |
| H | 3.60150 | 0.06650 | 1.80050 |

Pd_Bisulfoxide_Allylbenzene_Acetate_Abstraction_TS (**A**)

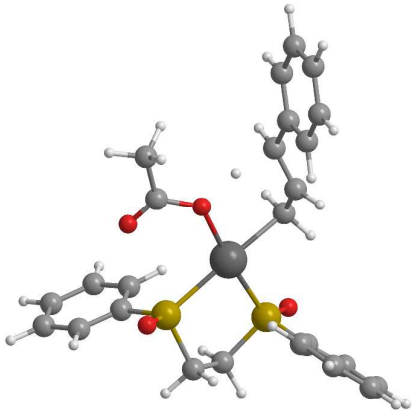
E_scf (B3LYP/LACVP*) = -2192.59758069590 a.u.
E_scf (M06/LACVP*) = -2191.6529988305 a.u.
E_Gibbs = -2192.205317 a.u.
E_Gibbs(318K) = -2192.211977 a.u.
E_solv = -2192.67481266168 a.u.
ZPE = 289.469 kcal/mol



| | | | |
|---|---|---|---|
| O | 0.03180 | -0.00940 | 0.01320 |
| H | 0.00920 | 0.01240 | 1.49290 |
| C | 0.19930 | 0.00430 | 2.79910 |
| C | -0.26550 | 1.33240 | 2.88800 |
| C | -1.63950 | 1.71300 | 2.96910 |
| C | 3.23750 | -2.09900 | 3.59670 |
| O | -4.83400 | 0.74560 | 2.82690 |
| C | 4.28870 | -1.24690 | 3.25720 |
| C | 1.91810 | -1.67780 | 3.43940 |
| C | 1.62980 | -0.39410 | 2.95210 |
| C | 2.69500 | 0.45080 | 2.60070 |
| C | 4.01240 | 0.02890 | 2.75750 |
| H | 5.31760 | -1.57450 | 3.37570 |
| H | 3.44320 | -3.09310 | 3.98350 |
| H | 1.10300 | -2.34710 | 3.70560 |
| H | 2.50430 | 1.44360 | 2.19890 |
| H | 4.82700 | 0.69470 | 2.48570 |
| Pd | -2.33230 | 1.90660 | 0.94120 |
| S | -4.48990 | 1.75910 | 1.78630 |
| S | -3.35400 | 2.13420 | -1.31630 |
| O | -3.00920 | 3.24960 | -2.24980 |
| C | -5.03000 | 3.39400 | 2.31200 |
| C | -6.02300 | 3.45770 | 3.29240 |
| C | -6.45170 | 4.71360 | 3.72270 |
| C | -5.89000 | 5.87320 | 3.18160 |
| C | -4.88680 | 5.79010 | 2.21230 |
| C | -4.43990 | 4.54320 | 1.77450 |
| C | -5.54420 | 1.43260 | 0.29680 |
| C | -5.15840 | 2.29170 | -0.89350 |
| C | -3.34350 | 0.56120 | -2.19360 |
| C | -3.60970 | 0.57990 | -3.56600 |
| C | -3.62190 | -0.63020 | -4.25760 |
| C | -3.36440 | -1.82830 | -3.58390 |
| C | -3.07730 | -1.82550 | -2.21740 |
| C | -3.05490 | -0.62240 | -1.50980 |
| H | -6.42920 | 2.54560 | 3.71890 |
| H | -7.21890 | 4.78480 | 4.48780 |
| H | -6.22610 | 6.84690 | 3.52570 |
| H | -4.44090 | 6.69280 | 1.80560 |
| H | -3.63520 | 4.47480 | 1.04610 |
| H | -5.41170 | 0.36250 | 0.10600 |
| H | -6.57750 | 1.61220 | 0.61010 |
| H | -5.30220 | 3.35980 | -0.70170 |
| H | -5.72840 | 2.01300 | -1.78460 |
| H | -3.78060 | 1.52270 | -4.07720 |
| H | -3.82510 | -0.63730 | -5.32430 |
| H | -3.37290 | -2.76670 | -4.13040 |
| H | -2.85220 | -2.75480 | -1.70290 |
| H | -2.78360 | -0.60960 | -0.45760 |
| O | -0.46190 | 2.18430 | 0.04810 |
| C | 0.21310 | 1.17910 | -0.38310 |
| C | 1.29200 | 1.46270 | -1.40000 |
| H | 2.26980 | 1.23410 | -0.96100 |
| H | 1.26490 | 2.50110 | -1.73400 |
| H | 1.15960 | 0.79000 | -2.25400 |
| H | 0.46270 | 2.13530 | 2.78010 |

| | | | |
|---|---|---|---|
| H | -0.52240 | -0.75880 | 3.10590 |
| H | -2.31310 | 0.96660 | 3.39300 |
| H | -1.80560 | 2.72390 | 3.34650 |

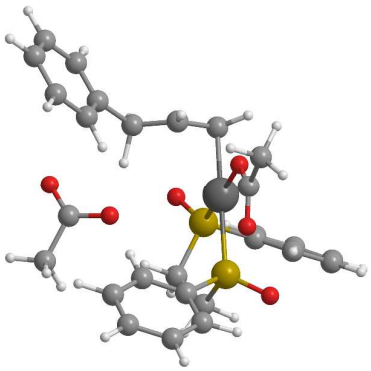
Pd_Bisulfoxide_Allylbenzene_Acetate_Abstraction_6Membered_TS (**B**)
E_scf (B3LYP/LACVP*) = -2192.60235869582 a.u.
E_scf (M06/LACVP*) = -2191.65784538658 a.u.
E_Gibbs = -2192.206611 a.u.
E_Gibbs(318K) = -2192.213173 a.u.
E_solv = -2192.68085368379 a.u.
ZPE = 289.490 kcal/mol



| | | | |
|---|---|---|---|
| O | -0.00690 | 0.00240 | -0.00370 |
| H | -0.01670 | 0.00240 | 1.41630 |
| C | 0.54290 | 0.00230 | 2.67770 |
| O | -0.53800 | 1.01470 | -1.92780 |
| C | 1.46450 | -0.96770 | 2.22500 |
| C | 2.52850 | -0.71210 | 1.31830 |
| C | -2.14260 | -1.67680 | 4.79120 |
| O | 4.94030 | -1.76270 | -0.79550 |
| C | -2.52690 | -0.61820 | 5.61960 |
| C | -1.15160 | -1.49380 | 3.83050 |
| C | -0.51850 | -0.24760 | 3.68770 |
| C | -0.92210 | 0.81240 | 4.51630 |
| C | -1.91390 | 0.62770 | 5.47740 |
| H | -3.30340 | -0.76320 | 6.36500 |
| H | -2.62320 | -2.64610 | 4.89010 |
| H | -0.88220 | -2.32420 | 3.18140 |
| H | -0.44510 | 1.78490 | 4.41470 |
| H | -2.20690 | 1.45720 | 6.11480 |
| Pd | 1.67780 | -0.98280 | -0.69920 |
| S | 3.58810 | -2.20090 | -1.25340 |
| S | 0.96220 | -1.22790 | -3.05150 |
| O | -0.38190 | -1.74000 | -3.45030 |
| C | 3.33300 | -3.93280 | -0.81390 |
| C | 4.47230 | -4.69730 | -0.55280 |
| C | 4.30930 | -6.04030 | -0.21130 |
| C | 3.03010 | -6.59710 | -0.13100 |
| C | 1.90060 | -5.81260 | -0.38060 |
| C | 2.04360 | -4.46570 | -0.71690 |
| C | 3.58760 | -2.25400 | -3.10410 |
| C | 2.19900 | -2.47540 | -3.67220 |
| C | 1.43740 | 0.19890 | -4.04770 |
| C | 0.78230 | 0.37740 | -5.26550 |
| C | 1.14780 | 1.46240 | -6.06260 |
| C | 2.14300 | 2.34540 | -5.63690 |
| C | 2.77430 | 2.15950 | -4.40470 |
| C | 2.41520 | 1.08410 | -3.59190 |
| H | 5.45670 | -4.24160 | -0.59910 |
| H | 5.18370 | -6.64900 | -0.00200 |
| H | 2.91170 | -7.64240 | 0.13760 |
| H | 0.90690 | -6.24370 | -0.30520 |
| H | 1.16600 | -3.84540 | -0.88450 |
| H | 4.01530 | -1.29100 | -3.40170 |
| H | 4.27960 | -3.05280 | -3.38800 |
| H | 1.78020 | -3.44510 | -3.38630 |
| H | 2.20330 | -2.40260 | -4.76360 |
| H | -0.00870 | -0.30350 | -5.56490 |
| H | 0.64660 | 1.62250 | -7.01250 |
| H | 2.41790 | 3.19060 | -6.26090 |
| H | 3.53220 | 2.86010 | -4.06690 |
| H | 2.86960 | 0.96120 | -2.61120 |
| C | -0.77200 | 0.83230 | -0.75240 |

| | | | |
|---|---|---|---|
| C | -1.91050 | 1.47240 | 0.01020 |
| H | -1.53020 | 2.05340 | 0.85800 |
| H | -2.57740 | 0.70020 | 0.40920 |
| H | -2.46810 | 2.12780 | -0.66020 |
| H | 1.28570 | -2.00810 | 2.49890 |
| H | 0.91150 | 1.03230 | 2.64760 |
| H | 2.85460 | 0.32540 | 1.21710 |
| H | 3.35170 | -1.42200 | 1.35030 |

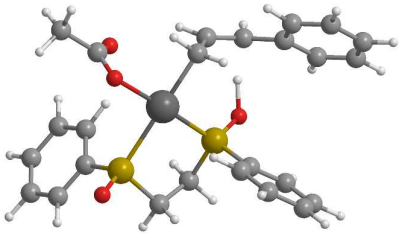
Pd_Bisulfoxide_Allylbenzene_Acetate_External_Acetate_Abstraction_TS (**C**)
E_scf (B3LYP/LACVP*) = -2421.28149348030 a.u.
E_scf (M06/LACVP*) = -2420.23362721681 a.u.
E_Gibbs = -2420.843169 a.u.
E_Gibbs(318K) = -2420.850349 a.u.
E_solv = -2421.3179288444 a.u.
ZPE = 321.551 kcal/mol



| | | | |
|---|---|---|---|
| O | -0.01470 | -0.01380 | -0.00070 |
| H | -0.00150 | -0.01240 | 1.45920 |
| C | 0.33620 | -0.00880 | 2.75600 |
| O | -5.71850 | -1.16100 | 1.63460 |
| C | -0.96080 | -0.20240 | 3.26570 |
| C | -1.58350 | -1.46660 | 3.50250 |
| C | 1.18780 | 3.70340 | 3.03470 |
| O | 0.16380 | -3.30750 | 1.16800 |
| C | 2.55200 | 3.64610 | 3.33110 |
| C | 0.45630 | 2.53510 | 2.82830 |
| C | 1.07800 | 1.28030 | 2.92900 |
| C | 2.45200 | 1.23330 | 3.20870 |
| C | 3.18260 | 2.40400 | 3.41130 |
| H | 3.11880 | 4.56050 | 3.48670 |
| H | 0.69000 | 4.66620 | 2.94870 |
| H | -0.58690 | 2.59630 | 2.53810 |
| H | 2.95010 | 0.26840 | 3.27620 |
| H | 4.24550 | 2.34330 | 3.63210 |
| Pd | -2.73480 | -1.64600 | 1.72450 |
| S | -1.31230 | -3.33300 | 0.90690 |
| S | -3.87170 | -1.89780 | -0.46680 |
| O | -4.73960 | -3.08630 | -0.79160 |
| C | -1.95790 | -4.92870 | 1.47920 |
| C | -1.05060 | -5.79770 | 2.08100 |
| C | -1.52330 | -7.00640 | 2.59630 |
| C | -2.88020 | -7.32260 | 2.51120 |
| C | -3.77410 | -6.43300 | 1.90790 |
| C | -3.32250 | -5.21990 | 1.38820 |
| C | -1.64250 | -3.41970 | -0.93390 |
| C | -2.30860 | -2.14460 | -1.43400 |
| C | -4.54140 | -0.42220 | -1.25660 |
| C | -5.60750 | -0.59520 | -2.13690 |
| C | -6.14110 | 0.53230 | -2.76120 |
| C | -5.61120 | 1.79770 | -2.49720 |
| C | -4.55110 | 1.94630 | -1.59980 |
| C | -4.00850 | 0.83220 | -0.95720 |
| H | -0.00240 | -5.52170 | 2.14200 |
| H | -0.82920 | -7.69670 | 3.06780 |
| H | -3.24430 | -8.26150 | 2.91920 |
| H | -4.83060 | -6.67750 | 1.84390 |
| H | -4.02040 | -4.53080 | 0.91730 |
| H | -0.64700 | -3.55450 | -1.36710 |
| H | -2.26050 | -4.30110 | -1.11940 |
| H | -2.58250 | -2.24210 | -2.48950 |
| H | -1.66800 | -1.27220 | -1.27330 |
| H | -6.01040 | -1.58890 | -2.30630 |

| | | | |
|---|---|---|---|
| H | -6.97480 | 0.42160 | -3.44930 |
| H | -6.03260 | 2.67220 | -2.98600 |
| H | -4.13910 | 2.92830 | -1.38520 |
| H | -3.19490 | 0.96390 | -0.24800 |
| O | -3.90130 | -0.17710 | 2.54660 |
| C | -5.18790 | -0.28970 | 2.32400 |
| C | -6.00200 | 0.80500 | 3.00610 |
| H | -5.72230 | 1.78150 | 2.59530 |
| H | -5.78560 | 0.82780 | 4.07930 |
| H | -7.06720 | 0.63030 | 2.84360 |
| H | -1.58520 | 0.67590 | 3.41920 |
| H | 0.97360 | -0.89670 | 2.77130 |
| H | -0.91630 | -2.32490 | 3.57830 |
| H | -2.39580 | -1.45450 | 4.22810 |
| C | -0.53130 | 1.11630 | -0.39390 |
| O | -1.25500 | 1.85400 | 0.28650 |
| C | -0.21740 | 1.48530 | -1.84540 |
| H | -1.11570 | 1.33870 | -2.45860 |
| H | 0.03980 | 2.54750 | -1.89920 |
| H | 0.59730 | 0.88250 | -2.25300 |

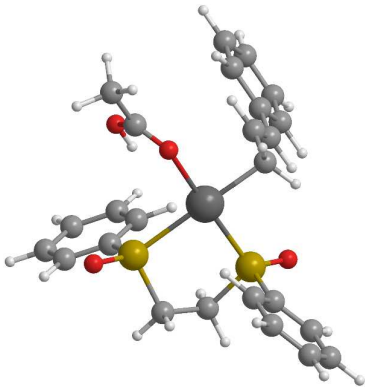
Pd_Bisulfoxide_Allylbenzene_Acetate_Sulfoxide_Abstraction_TS (**D**)
E_scf (B3LYP/LACVP*) = -2192.58810788547 a.u.
E_scf (M06/LACVP*) = -2191.64522399195 a.u.
E_Gibbs = -2192.194628 a.u.
E_Gibbs(318K) = -2192.201555 a.u.
E_solv = -2192.66925785363 a.u.
ZPE = 289.597 kcal/mol



| | | | |
|---|---|---|---|
| C | -0.04780 | 0.07070 | 0.04430 |
| C | -0.01580 | 0.12020 | 1.43910 |
| C | 1.07840 | 0.01350 | -0.85270 |
| H | 0.90800 | -0.52040 | -1.78500 |
| H | 0.29390 | 1.52780 | 1.40450 |
| O | 0.70930 | 2.67520 | 1.53930 |
| H | 2.05690 | -0.17990 | -0.41570 |
| H | -1.01190 | 0.20970 | -0.44320 |
| C | 3.06510 | -1.38910 | 4.04300 |
| C | 2.87200 | -1.97280 | 2.79020 |
| C | 1.88850 | -1.48480 | 1.93100 |
| C | 1.08260 | -0.39720 | 2.31020 |
| C | 1.27520 | 0.16870 | 3.58300 |
| C | 2.25820 | -0.32030 | 4.43970 |
| H | 3.82650 | -1.77690 | 4.71400 |
| H | 3.47490 | -2.82430 | 2.48690 |
| H | 1.71690 | -1.98080 | 0.98040 |
| H | 0.64410 | 0.99410 | 3.90510 |
| H | 2.38900 | 0.12590 | 5.42180 |
| H | -0.99300 | 0.17940 | 1.92580 |
| Pd | 1.12140 | 1.97730 | -1.69970 |
| S | 1.57590 | 3.06950 | 0.29670 |
| S | 1.26760 | 4.27460 | -2.77640 |
| O | 2.23530 | 4.61650 | -3.86420 |
| C | 3.28260 | 3.11640 | 0.80490 |
| C | 3.61500 | 3.56670 | 2.08810 |
| C | 4.96080 | 3.59860 | 2.44480 |
| C | 5.94220 | 3.19180 | 1.53360 |
| C | 5.58950 | 2.73940 | 0.26070 |
| C | 4.24690 | 2.68890 | -0.11470 |
| C | 1.11320 | 4.82840 | -0.00730 |
| C | 1.73960 | 5.32190 | -1.30130 |
| C | -0.35850 | 4.96430 | -3.13080 |
| C | -0.41560 | 6.16640 | -3.84420 |

| | | | |
|---|---|---|---|
| C | -1.66450 | 6.72250 | -4.11030 |
| C | -2.82820 | 6.07870 | -3.67450 |
| C | -2.75140 | 4.86650 | -2.98790 |
| C | -1.50820 | 4.28790 | -2.71700 |
| H | 2.84380 | 3.85670 | 2.79490 |
| H | 5.24470 | 3.93670 | 3.43660 |
| H | 6.98850 | 3.22080 | 1.82300 |
| H | 6.35370 | 2.41480 | -0.43860 |
| H | 3.95650 | 2.32120 | -1.09580 |
| H | 0.01880 | 4.81690 | -0.04280 |
| H | 1.44620 | 5.40100 | 0.86350 |
| H | 2.83360 | 5.28670 | -1.27470 |
| H | 1.42430 | 6.34840 | -1.50790 |
| H | 0.49640 | 6.63560 | -4.20250 |
| H | -1.73150 | 7.65320 | -4.66590 |
| H | -3.79850 | 6.51670 | -3.88980 |
| H | -3.65700 | 4.35190 | -2.68080 |
| H | -1.45200 | 3.30640 | -2.25220 |
| O | 0.66490 | 1.10500 | -3.49570 |
| O | -1.42020 | 1.07960 | -2.65800 |
| C | -0.61900 | 0.84540 | -3.57130 |
| C | -1.04160 | 0.21110 | -4.88420 |
| H | -0.60570 | -0.79080 | -4.96640 |
| H | -0.66830 | 0.79760 | -5.72890 |
| H | -2.12960 | 0.13880 | -4.92570 |

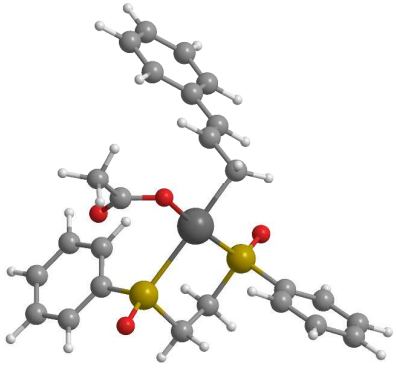
Pd_Bisulfoxide_Phenallyl_AcOH
E_scf (B3LYP/LACVP*) = -2192.64497188532 a.u.
E_scf (M06/LACVP*) = -2191.70998657237 a.u.
E_Gibbs = -2192.249059 a.u.
E_Gibbs(318K) = 2192.256157 a.u.
E_solv = -2192.71630543964 a.u.
ZPE = 292.843 kcal/mol



| | | | |
|---|---|---|---|
| O | 0.00000 | 0.00000 | 0.00000 |
| H | 0.00000 | 0.00000 | 0.97840 |
| C | 3.33970 | 0.00000 | 3.50520 |
| C | 3.11410 | 0.78840 | 2.40820 |
| C | 2.89280 | 2.21370 | 2.49580 |
| C | 4.00760 | -3.41640 | 4.89190 |
| O | 1.77620 | 2.28570 | 5.77290 |
| C | 4.01110 | -4.20920 | 3.74210 |
| C | 3.78520 | -2.04670 | 4.79000 |
| C | 3.56080 | -1.43590 | 3.53720 |
| C | 3.56850 | -2.25400 | 2.38480 |
| C | 3.79120 | -3.62120 | 2.49000 |
| H | 4.18870 | -5.27820 | 3.81720 |
| H | 4.18270 | -3.86520 | 5.86550 |
| H | 3.78850 | -1.42920 | 5.68530 |
| H | 3.41070 | -1.81740 | 1.40300 |
| H | 3.80000 | -4.23630 | 1.59450 |
| Pd | 0.78230 | 2.19470 | 2.52900 |
| S | 0.79890 | 2.87300 | 4.79780 |
| S | -1.74920 | 1.91930 | 2.77750 |
| O | -2.79950 | 2.43570 | 1.83700 |
| C | 0.80680 | 4.67250 | 4.93850 |
| C | 1.22310 | 5.23280 | 6.14820 |
| C | 1.23420 | 6.62220 | 6.26780 |
| C | 0.83850 | 7.42450 | 5.19370 |
| C | 0.43990 | 6.84660 | 3.98610 |
| C | 0.43130 | 5.45820 | 3.84640 |
| C | -0.90390 | 2.46380 | 5.41610 |
| C | -1.99960 | 2.77570 | 4.40930 |

| | | | |
|---|---|---|---|
| C | -2.15890 | 0.21710 | 3.24400 |
| C | -3.47630 | -0.20890 | 3.06500 |
| C | -3.80680 | -1.52300 | 3.39620 |
| C | -2.82980 | -2.39290 | 3.88940 |
| C | -1.51140 | -1.95920 | 4.04530 |
| C | -1.16400 | -0.64780 | 3.71310 |
| H | 1.55030 | 4.59340 | 6.96260 |
| H | 1.55950 | 7.07840 | 7.19790 |
| H | 0.85400 | 8.50570 | 5.29390 |
| H | 0.15000 | 7.47330 | 3.14810 |
| H | 0.15700 | 4.99860 | 2.89890 |
| H | -0.85030 | 1.39770 | 5.65840 |
| H | -1.04060 | 3.02750 | 6.34420 |
| H | -2.03690 | 3.83940 | 4.15220 |
| H | -2.98160 | 2.47210 | 4.78520 |
| H | -4.21400 | 0.47510 | 2.65560 |
| H | -4.82720 | -1.87020 | 3.26300 |
| H | -3.09490 | -3.41530 | 4.14240 |
| H | -0.75060 | -2.63950 | 4.41650 |
| H | -0.13370 | -0.31180 | 3.82100 |
| O | 0.84910 | 2.06820 | 0.29650 |
| C | 0.46530 | 1.16430 | -0.44870 |
| C | 0.46880 | 1.26720 | -1.94390 |
| H | 0.90780 | 0.36690 | -2.38360 |
| H | 1.01820 | 2.15550 | -2.25470 |
| H | -0.56680 | 1.33430 | -2.29720 |
| H | 3.09310 | 0.34220 | 1.41600 |
| H | 3.36060 | 0.49990 | 4.47400 |
| H | 3.24150 | 2.69340 | 3.40960 |
| H | 3.08380 | 2.79900 | 1.59590 |

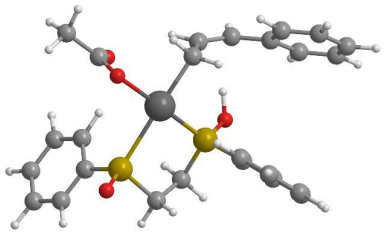
Pd_Bisulfoxide_Phenallyl_Acetate
E_scf (B3LYP/LACVP*) = -2192.23937937424 a.u.
E_scf (M06/LACVP*) = -2192.40522504855 a.u.
E_Gibbs = -2191.854087 a.u.
E_Gibbs(318K) = -2191.860639 a.u.
E_solv = -2192.27515767617 a.u.
ZPE = 285.096 kcal/mol



| | | | |
|---|---|---|---|
| C | -0.24690 | -0.37230 | 0.04290 |
| O | 1.47340 | -2.62130 | 4.33380 |
| C | 0.32150 | -1.55810 | 0.37890 |
| C | -0.39150 | -2.83150 | 0.39760 |
| C | 2.26530 | 2.45300 | 0.42050 |
| O | -3.51750 | -1.38110 | 1.26140 |
| C | 1.52110 | 3.53470 | -0.06180 |
| C | 1.71210 | 1.17760 | 0.46540 |
| C | 0.39250 | 0.94360 | 0.02610 |
| C | -0.34320 | 2.04650 | -0.45130 |
| C | 0.21170 | 3.32340 | -0.49670 |
| H | 1.95760 | 4.52950 | -0.09470 |
| H | 3.28430 | 2.60700 | 0.76720 |
| H | 2.30710 | 0.35540 | 0.85200 |
| H | -1.36460 | 1.88900 | -0.79110 |
| H | -0.38010 | 4.15480 | -0.87200 |
| Pd | -0.79480 | -3.10040 | 2.43370 |
| S | -3.03930 | -2.50500 | 2.13670 |
| S | -1.32850 | -3.25140 | 4.97120 |
| O | -1.04870 | -4.37900 | 5.92550 |
| C | -3.98630 | -3.99220 | 1.71570 |
| C | -5.22880 | -3.82740 | 1.10170 |
| C | -5.96580 | -4.96180 | 0.76150 |
| C | -5.45910 | -6.23620 | 1.03040 |

| | | | |
|---|---|---|---|
| C | -4.20700 | -6.38510 | 1.63040 |
| C | -3.45540 | -5.25860 | 1.96890 |
| C | -3.69320 | -2.17200 | 3.83910 |
| C | -3.19260 | -3.16480 | 4.87450 |
| C | -1.06750 | -1.67030 | 5.81880 |
| C | -1.19410 | -1.64250 | 7.20720 |
| C | -1.02440 | -0.42960 | 7.87410 |
| C | -0.72870 | 0.73080 | 7.15390 |
| C | -0.58300 | 0.68130 | 5.76600 |
| C | -0.73850 | -0.52920 | 5.08760 |
| H | -5.58980 | -2.82820 | 0.87700 |
| H | -6.93240 | -4.85080 | 0.27810 |
| H | -6.03580 | -7.11600 | 0.75860 |
| H | -3.80500 | -7.37570 | 1.82290 |
| H | -2.46120 | -5.36040 | 2.39920 |
| H | -3.36100 | -1.15060 | 4.05240 |
| H | -4.78470 | -2.17770 | 3.75590 |
| H | -3.49830 | -4.18990 | 4.64120 |
| H | -3.56040 | -2.91090 | 5.87310 |
| H | -1.39630 | -2.56320 | 7.74740 |
| H | -1.11590 | -0.39130 | 8.95620 |
| H | -0.59570 | 1.67330 | 7.67820 |
| H | -0.32680 | 1.57880 | 5.21000 |
| H | -0.57130 | -0.59160 | 4.01610 |
| O | 1.13190 | -3.87740 | 2.49180 |
| C | 1.85130 | -3.43640 | 3.48500 |
| C | 3.25190 | -4.03970 | 3.54330 |
| H | 3.88180 | -3.45610 | 4.21810 |
| H | 3.70060 | -4.08250 | 2.54630 |
| H | 3.18590 | -5.06730 | 3.91970 |
| H | 1.36530 | -1.59710 | 0.68450 |
| H | -1.29780 | -0.38160 | -0.24670 |
| H | -1.33170 | -2.83390 | -0.15760 |
| H | 0.22180 | -3.71030 | 0.19980 |

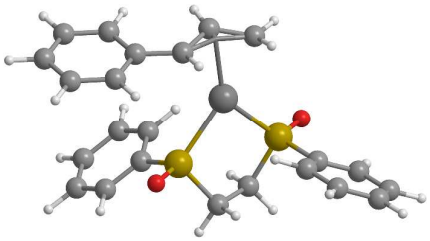
Pd_Bisulfoxide_OH_Phenallyl_Acetate
E_scf (B3LYP/LACVP*) = -2192.59551642752 a.u.
E_scf (M06/LACVP*) = -2191.65696166141 a.u.
E_Gibbs = -2192.19613 a.u.
E_Gibbs(318K) = -2192.202887 a.u.
E_solv = -2192.68157277337 a.u.
ZPE = 292.323 kcal/mol



| | | | |
|---|---|---|---|
| C | -0.01690 | -0.01430 | 0.00890 |
| C | -0.02060 | -0.05670 | 1.37630 |
| C | 1.13770 | 0.00220 | -0.89310 |
| H | 1.06890 | -0.68180 | -1.73770 |
| H | 0.23880 | 1.90360 | 1.09650 |
| O | 0.53070 | 2.87590 | 1.12580 |
| H | 2.12040 | -0.02540 | -0.42210 |
| H | -0.98230 | 0.03390 | -0.49180 |
| C | 3.18000 | -0.61240 | 4.17660 |
| C | 3.23870 | -1.24650 | 2.93390 |
| C | 2.21270 | -1.07480 | 2.00670 |
| C | 1.10570 | -0.25700 | 2.30600 |
| C | 1.04650 | 0.34830 | 3.57710 |
| C | 2.07640 | 0.18170 | 4.49820 |
| H | 3.97700 | -0.75680 | 4.90070 |
| H | 4.07490 | -1.89760 | 2.69450 |
| H | 2.24070 | -1.62480 | 1.07150 |
| H | 0.18010 | 0.95120 | 3.84190 |
| H | 2.01220 | 0.65790 | 5.47280 |
| H | -0.99900 | 0.00540 | 1.85610 |

| | | | |
|---|---|---|---|
| Pd | 1.05380 | 1.80780 | -1.99270 |
| S | 1.43610 | 3.15030 | -0.18770 |
| S | 1.05000 | 4.06770 | -3.35850 |
| O | 2.01070 | 4.40110 | -4.45830 |
| C | 3.09470 | 3.36560 | 0.41050 |
| C | 3.34220 | 4.07950 | 1.59080 |
| C | 4.66340 | 4.22740 | 2.00150 |
| C | 5.70450 | 3.67880 | 1.24230 |
| C | 5.43650 | 2.96730 | 0.07150 |
| C | 4.11930 | 2.79510 | -0.35400 |
| C | 0.83900 | 4.83370 | -0.63450 |
| C | 1.44880 | 5.25570 | -1.96270 |
| C | -0.60440 | 4.65950 | -3.76720 |
| C | -0.71270 | 5.80490 | -4.56340 |
| C | -1.98410 | 6.27750 | -4.87930 |
| C | -3.11970 | 5.60750 | -4.40960 |
| C | -2.99100 | 4.45140 | -3.63960 |
| C | -1.72380 | 3.95520 | -3.31820 |
| H | 2.52820 | 4.48170 | 2.18590 |
| H | 4.88280 | 4.76850 | 2.91660 |
| H | 6.73150 | 3.80300 | 1.57240 |
| H | 6.24700 | 2.53740 | -0.50850 |
| H | 3.89110 | 2.23230 | -1.25560 |
| H | -0.25020 | 4.73020 | -0.68260 |
| H | 1.11050 | 5.50340 | 0.18710 |
| H | 2.54290 | 5.28580 | -1.92880 |
| H | 1.07900 | 6.24520 | -2.24540 |
| H | 0.17960 | 6.29190 | -4.94670 |
| H | -2.09070 | 7.16200 | -5.50030 |
| H | -4.10780 | 5.97980 | -4.66410 |
| H | -3.87380 | 3.91420 | -3.30570 |
| H | -1.62360 | 3.01100 | -2.78660 |
| O | 0.65050 | 0.63750 | -3.64410 |
| O | -1.42730 | 0.81350 | -2.81490 |
| C | -0.63530 | 0.39740 | -3.67390 |
| C | -1.08770 | -0.45980 | -4.84170 |
| H | -0.72720 | -1.48540 | -4.70200 |
| H | -0.66100 | -0.08960 | -5.77830 |
| H | -2.17740 | -0.46630 | -4.89760 |

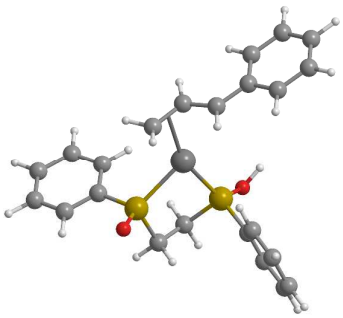
Pd_Bisulfoxide_Phenallyl
E_scf (B3LYP/LACVP*) = -1963.56308152005 a.u.
E_scf (M06/LACVP*) = -1962.74654372455 a.u.
E_Gibbs = -1963.219033 a.u.
E_Gibbs(318K) = -1963.224925 a.u.
E_solv = -1963.63786665601 a.u.
ZPE = 253.174 kcal/mol



| | | | |
|---|---|---|---|
| C | 0.01570 | 0.35520 | -0.01560 |
| S | 2.53740 | 0.00500 | -3.86360 |
| S | -0.76280 | 0.63220 | -3.55750 |
| O | 3.85910 | 0.71130 | -3.90050 |
| O | -2.09640 | -0.04800 | -3.54600 |
| C | 2.73800 | -1.70180 | -4.41170 |
| C | 3.84880 | -2.00810 | -5.19990 |
| C | 4.01190 | -3.32120 | -5.64130 |
| C | 3.07950 | -4.30270 | -5.29180 |
| C | 1.98290 | -3.98270 | -4.48790 |
| C | 1.80990 | -2.67480 | -4.03270 |
| C | 1.50150 | 0.68240 | -5.25280 |
| C | 0.05180 | 0.22950 | -5.18190 |
| C | -0.98720 | 2.41510 | -3.72690 |

| | | | |
|---|---|---|---|
| C | -2.21650 | 2.87070 | -4.20600 |
| C | -2.40900 | 4.24530 | -4.34730 |
| C | -1.38860 | 5.13810 | -4.00950 |
| C | -0.16940 | 4.66620 | -3.51600 |
| C | 0.03620 | 3.29460 | -3.36180 |
| H | 4.57340 | -1.23620 | -5.44220 |
| H | 4.87020 | -3.57900 | -6.25480 |
| H | 3.21380 | -5.32280 | -5.63940 |
| H | 1.26700 | -4.74960 | -4.20760 |
| H | 0.97340 | -2.42420 | -3.38360 |
| H | 1.60240 | 1.76870 | -5.16260 |
| H | 1.97300 | 0.36460 | -6.18770 |
| H | -0.04990 | -0.85690 | -5.26970 |
| H | -0.55340 | 0.70170 | -5.96180 |
| H | -3.00350 | 2.16100 | -4.44260 |
| H | -3.35960 | 4.61880 | -4.71620 |
| H | -1.54740 | 6.20680 | -4.12010 |
| H | 0.61700 | 5.36310 | -3.24150 |
| H | 0.97380 | 2.92360 | -2.95190 |
| C | 1.12190 | -0.49670 | 0.18320 |
| C | 2.42430 | -0.03210 | -0.10370 |
| H | 0.12060 | 1.43190 | 0.11670 |
| H | 2.57270 | 1.04910 | -0.08960 |
| H | 0.94830 | -1.55670 | 0.34740 |
| Pd | 0.99970 | 0.15090 | -1.95710 |
| H | -0.99280 | -0.03630 | 0.07930 |
| C | 6.07940 | -2.22280 | -0.23710 |
| C | 4.88370 | -2.90710 | 0.01230 |
| C | 3.67840 | -2.21780 | 0.05230 |
| C | 3.64910 | -0.82120 | -0.14860 |
| C | 4.86160 | -0.14670 | -0.39870 |
| C | 6.06520 | -0.84180 | -0.44400 |
| H | 7.01900 | -2.76730 | -0.26730 |
| H | 4.89690 | -3.98020 | 0.17920 |
| H | 2.76280 | -2.76640 | 0.25310 |
| H | 4.85110 | 0.92780 | -0.56310 |
| H | 6.99070 | -0.30820 | -0.63820 |

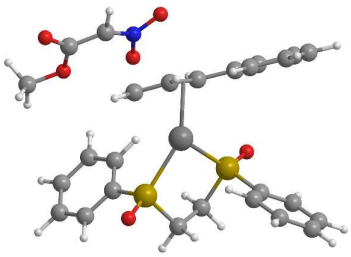
Pd_Bisulfoxide_OH_Phenallyl
E_scf (B3LYP/LACVP*) = -1963.81591428391 a.u.
E_scf (M06/LACVP*) = -1962.99107432339 a.u.
E_Gibbs = -1963.463286 a.u.
E_Gibbs(318K) = -1963.469386 a.u.
E_solv = -1964.04817028426 a.u.
ZPE = 259.856 kcal/mol



| | | | |
|---|---|---|---|
| S | 13.53570 | -0.16530 | 0.35560 |
| S | 16.81510 | -0.01820 | -0.30060 |
| O | 12.79700 | -0.82060 | 1.47540 |
| O | 17.88590 | 0.26160 | -1.53620 |
| C | 12.39370 | 0.38860 | -0.91840 |
| C | 11.13140 | -0.20960 | -0.95650 |
| C | 10.23440 | 0.20340 | -1.94230 |
| C | 10.60050 | 1.19270 | -2.85960 |
| C | 11.86270 | 1.79000 | -2.79530 |
| C | 12.77010 | 1.39700 | -1.81070 |
| C | 14.47650 | -1.50270 | -0.54920 |
| C | 15.62970 | -0.95350 | -1.37200 |
| C | 17.56430 | -1.25200 | 0.72690 |
| C | 18.23590 | -2.34710 | 0.15820 |
| C | 18.78120 | -3.29810 | 1.01410 |
| C | 18.64700 | -3.15910 | 2.40230 |
| C | 17.98160 | -2.05950 | 2.95100 |

| | | | |
|---|---|---|---|
| C | 17.44310 | -1.08350 | 2.11470 |
| H | 10.85560 | -0.96050 | -0.22210 |
| H | 9.24610 | -0.24360 | -1.98780 |
| H | 9.89380 | 1.51060 | -3.62020 |
| H | 12.13380 | 2.57070 | -3.49960 |
| H | 13.74040 | 1.88450 | -1.73020 |
| H | 14.80810 | -2.18710 | 0.23830 |
| H | 13.77180 | -2.02960 | -1.20000 |
| H | 15.30970 | -0.23480 | -2.13290 |
| H | 16.20950 | -1.74970 | -1.84900 |
| H | 18.35460 | -2.44310 | -0.91690 |
| H | 19.31110 | -4.15030 | 0.60020 |
| H | 19.07040 | -3.91300 | 3.05920 |
| H | 17.88640 | -1.95880 | 4.02750 |
| H | 16.92720 | -0.22050 | 2.52790 |
| C | 15.15790 | 3.67010 | 1.70980 |
| C | 16.21100 | 3.56590 | 2.63950 |
| C | 13.97420 | 2.90290 | 1.85470 |
| H | 13.10450 | 3.14490 | 1.24880 |
| H | 16.04270 | 2.88240 | 3.47290 |
| H | 13.75670 | 2.40650 | 2.80090 |
| H | 15.21720 | 4.39780 | 0.90470 |
| Pd | 15.24440 | 1.52210 | 0.84960 |
| C | 19.76420 | 5.82410 | 3.00200 |
| C | 18.93130 | 6.04660 | 1.89230 |
| C | 17.77330 | 5.30640 | 1.73510 |
| C | 17.42150 | 4.31820 | 2.69580 |
| C | 18.28230 | 4.10610 | 3.80750 |
| C | 19.43930 | 4.85400 | 3.95820 |
| H | 20.66700 | 6.41650 | 3.12170 |
| H | 19.19340 | 6.80840 | 1.16480 |
| H | 17.12970 | 5.49710 | 0.88170 |
| H | 18.01390 | 3.36300 | 4.55460 |
| H | 20.08460 | 4.69610 | 4.81650 |
| H | 18.51420 | 0.96750 | -1.27610 |

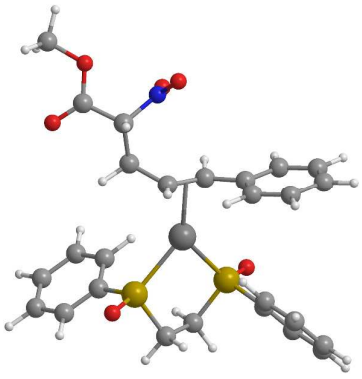
Pd_Bisulfoxide_Liniar_Product_TS
E_scf (B3LYP/LACVP*) = -2435.98718418631 a.u.
E_scf (M06/LACVP*) = -2434.93766112862 a.u.
E_Gibbs = -2435.574805 a.u.
E_Gibbs(318K) = -2435.58222 a.u.
E_solv = -2436.03861411663 a.u.
ZPE = 304.374 kcal/mol



| | | | |
|---|---|---|---|
| C | 0.04440 | 0.07590 | 0.11060 |
| C | -0.14590 | -0.06370 | 2.69080 |
| S | 3.89750 | 0.02960 | -2.79750 |
| S | 1.26270 | 2.22300 | -2.88740 |
| O | 5.19330 | -0.30950 | -2.11270 |
| O | 0.12480 | 2.67920 | -3.76250 |
| C | 3.89650 | -0.75330 | -4.43390 |
| C | 5.12470 | -1.12230 | -4.98370 |
| C | 5.14270 | -1.73840 | -6.23470 |
| C | 3.94630 | -1.98530 | -6.91380 |
| C | 2.72340 | -1.62930 | -6.34120 |
| C | 2.69120 | -1.01740 | -5.08670 |
| C | 4.04470 | 1.81110 | -3.31340 |
| C | 2.78420 | 2.36670 | -3.95410 |
| C | 1.63210 | 3.53530 | -1.68660 |
| C | 1.23010 | 4.83410 | -2.00520 |
| C | 1.48760 | 5.85990 | -1.09660 |
| C | 2.12680 | 5.58250 | 0.11640 |
| C | 2.50090 | 4.27470 | 0.43190 |

| | | | |
|---|---|---|---|
| C | 2.24890 | 3.23740 | -0.46950 |
| H | 6.03780 | -0.94590 | -4.42250 |
| H | 6.09050 | -2.03380 | -6.67640 |
| H | 3.96670 | -2.46960 | -7.88620 |
| H | 1.79340 | -1.83880 | -6.86210 |
| H | 1.74250 | -0.76620 | -4.61640 |
| H | 4.29880 | 2.33180 | -2.38420 |
| H | 4.90070 | 1.87210 | -3.99340 |
| H | 2.51500 | 1.82750 | -4.86820 |
| H | 2.89490 | 3.42820 | -4.19720 |
| H | 0.70480 | 5.02030 | -2.93770 |
| H | 1.17940 | 6.87520 | -1.33080 |
| H | 2.31880 | 6.38570 | 0.82250 |
| H | 2.96770 | 4.04560 | 1.38500 |
| H | 2.51100 | 2.21650 | -0.20250 |
| C | 0.47990 | -1.19870 | -0.27900 |
| C | 1.84350 | -1.57080 | -0.19330 |
| H | 0.71130 | 0.79230 | 0.57490 |
| H | 2.47750 | -0.96860 | 0.45610 |
| H | -0.24790 | -1.88450 | -0.70560 |
| Pd | 1.65890 | 0.04350 | -1.76360 |
| H | -0.97500 | 0.38590 | -0.09400 |
| C | 3.60500 | -5.30330 | -1.31800 |
| C | 2.25820 | -5.06900 | -1.61160 |
| C | 1.66230 | -3.86310 | -1.25710 |
| C | 2.40300 | -2.86470 | -0.59540 |
| C | 3.75770 | -3.11560 | -0.30590 |
| C | 4.35220 | -4.32180 | -0.66450 |
| H | 4.06690 | -6.24720 | -1.59620 |
| H | 1.67070 | -5.83190 | -2.11600 |
| H | 0.61410 | -3.70210 | -1.49350 |
| H | 4.33970 | -2.35110 | 0.20080 |
| H | 5.39900 | -4.49620 | -0.43120 |
| C | -0.77160 | 1.23310 | 2.86220 |
| O | 0.01370 | 2.31840 | 2.61000 |
| O | -1.95360 | 1.34330 | 3.16580 |
| H | -0.74820 | -0.91890 | 2.95700 |
| N | 1.20320 | -0.35500 | 2.59240 |
| O | 2.04690 | 0.53210 | 2.28280 |
| O | 1.53540 | -1.56320 | 2.69840 |
| C | -0.64980 | 3.57420 | 2.78410 |
| H | 0.08580 | 4.33190 | 2.50850 |
| H | -1.53240 | 3.64780 | 2.14160 |
| H | -0.96620 | 3.70920 | 3.82300 |

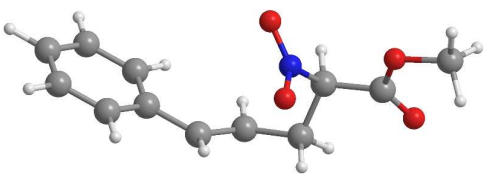
Pd_Bisulfoxide_Liniar_Product
E_scf (B3LYP/LACVP*) = -2436.04886058496 a.u.
E_scf (M06/LACVP*) = -2435.00696745586 a.u.
E_Gibbs = -2435.632045 a.u.
E_Gibbs(318K) = -2435.639506 a.u.
E_solv = -2436.08617857517 a.u.
ZPE = 305.822 kcal/mol



| | | | |
|---|---|---|---|
| C | 0.00000 | 0.00000 | 0.00000 |
| C | 0.00000 | 0.00000 | 1.54620 |
| S | 2.66530 | 0.00000 | -4.86600 |
| S | -0.38880 | -1.29160 | -4.25190 |
| O | 3.33880 | 1.31590 | -5.22400 |
| O | -1.17470 | -2.58830 | -4.12890 |
| C | 3.80790 | -1.33380 | -5.30310 |
| C | 4.64630 | -1.17320 | -6.41140 |
| C | 5.55920 | -2.18270 | -6.71740 |
| C | 5.63320 | -3.33090 | -5.91920 |

| | | | |
|---|---|---|---|
| C | 4.79840 | -3.47220 | -4.80780 |
| C | 3.88280 | -2.46500 | -4.48840 |
| C | 1.37880 | -0.23950 | -6.18300 |
| C | 0.45150 | -1.40860 | -5.90330 |
| C | -1.58120 | 0.03040 | -4.59120 |
| C | -2.81110 | -0.30700 | -5.16140 |
| C | -3.74700 | 0.70330 | -5.38860 |
| C | -3.45060 | 2.02740 | -5.04480 |
| C | -2.21950 | 2.34850 | -4.46490 |
| C | -1.27810 | 1.34400 | -4.22410 |
| H | 4.59950 | -0.26880 | -7.01230 |
| H | 6.21800 | -2.07070 | -7.57510 |
| H | 6.35210 | -4.11060 | -6.15910 |
| H | 4.86730 | -4.35680 | -4.18000 |
| H | 3.24730 | -2.55030 | -3.61010 |
| H | 0.84120 | 0.71470 | -6.21040 |
| H | 1.89880 | -0.37090 | -7.13740 |
| H | 0.98790 | -2.36320 | -5.86190 |
| H | -0.33080 | -1.47940 | -6.66600 |
| H | -3.03570 | -1.34200 | -5.40490 |
| H | -4.71010 | 0.45490 | -5.82790 |
| H | -4.18550 | 2.80890 | -5.22000 |
| H | -1.99520 | 3.37510 | -4.18640 |
| H | -0.32940 | 1.57770 | -3.74330 |
| C | 1.17770 | -0.75910 | -0.58060 |
| C | 2.42100 | -0.14640 | -0.82430 |
| H | -0.01970 | 1.03880 | -0.34310 |
| H | 2.46090 | 0.94060 | -0.73910 |
| H | 1.15790 | -1.82890 | -0.37030 |
| Pd | 1.41770 | -0.52580 | -2.74250 |
| H | -0.94720 | -0.46080 | -0.29300 |
| C | 6.35300 | -1.89650 | -0.58830 |
| C | 5.22550 | -2.71630 | -0.47610 |
| C | 3.94330 | -2.17430 | -0.55870 |
| C | 3.75430 | -0.79380 | -0.76170 |
| C | 4.90000 | 0.01770 | -0.86890 |
| C | 6.18240 | -0.52370 | -0.78410 |
| H | 7.35170 | -2.32180 | -0.51760 |
| H | 5.34520 | -3.78540 | -0.31290 |
| H | 3.08390 | -2.83300 | -0.45710 |
| H | 4.77670 | 1.08980 | -1.01520 |
| H | 7.04940 | 0.12880 | -0.86550 |
| C | -1.26320 | 0.64200 | 2.13390 |
| O | -1.03230 | 1.24800 | 3.29490 |
| O | -2.34790 | 0.54820 | 1.59800 |
| H | 0.08190 | -1.01460 | 1.94690 |
| N | 1.22330 | 0.72700 | 2.05630 |
| O | 1.38810 | 1.88400 | 1.67260 |
| O | 1.98670 | 0.11770 | 2.79670 |
| C | -2.17640 | 1.85510 | 3.95280 |
| H | -1.78110 | 2.28060 | 4.87480 |
| H | -2.60010 | 2.63430 | 3.31570 |
| H | -2.92960 | 1.09390 | 4.16810 |

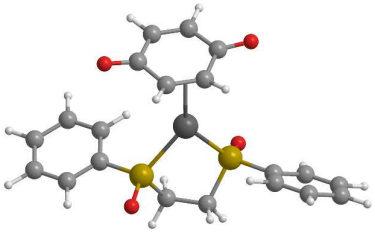
Liniar_Product
E_scf (B3LYP/LACVP*) = -820.6294486975 a.u.
E_scf (M06/LACVP*) = -820.10962683226 a.u.
E_Gibbs = -820.424305 a.u.
E_Gibbs(318K) = -820.428596 a.u.
E_solv = -820.63883802547 a.u.
ZPE = 148.447 kcal/mol



| | | | |
|---|---|---|---|
| C | 0.00000 | 0.00000 | 0.00000 |

| | | | |
|---|---|---|---|
| C | 0.00000 | 0.00000 | 1.54620 |
| C | 1.17770 | -0.75910 | -0.58060 |
| C | 2.42100 | -0.14640 | -0.82430 |
| H | -0.01970 | 1.03880 | -0.34310 |
| H | 2.46090 | 0.94060 | -0.73910 |
| H | 1.15790 | -1.82890 | -0.37030 |
| H | -0.94720 | -0.46080 | -0.29300 |
| C | 6.35300 | -1.89650 | -0.58830 |
| C | 5.22550 | -2.71630 | -0.47610 |
| C | 3.94330 | -2.17430 | -0.55870 |
| C | 3.75430 | -0.79380 | -0.76170 |
| C | 4.90000 | 0.01770 | -0.86890 |
| C | 6.18240 | -0.52370 | -0.78410 |
| H | 7.35170 | -2.32180 | -0.51760 |
| H | 5.34520 | -3.78540 | -0.31290 |
| H | 3.08390 | -2.83300 | -0.45710 |
| H | 4.77670 | 1.08980 | -1.01520 |
| H | 7.04940 | 0.12880 | -0.86550 |
| C | -1.26320 | 0.64200 | 2.13390 |
| O | -1.03230 | 1.24800 | 3.29490 |
| O | -2.34790 | 0.54820 | 1.59800 |
| H | 0.08190 | -1.01460 | 1.94690 |
| N | 1.22330 | 0.72700 | 2.05630 |
| O | 1.38810 | 1.88400 | 1.67260 |
| O | 1.98670 | 0.11770 | 2.79670 |
| C | -2.17640 | 1.85510 | 3.95280 |
| H | -1.78110 | 2.28060 | 4.87480 |
| H | -2.60010 | 2.63430 | 3.31570 |
| H | -2.92960 | 1.09390 | 4.16810 |

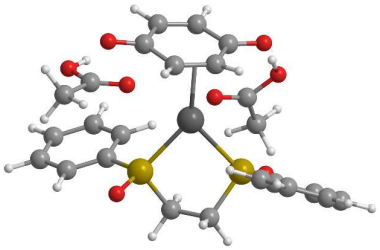
Pd_Bisulfoxide_Quinone
E_scf (B3LYP/LACVP*) = -1996.87729924803 a.u.
E_scf (M06/LACVP*) = -1996.10776602681 a.u.
E_Gibbs = -1996.600239 a.u.
E_Gibbs(318K) = -1996.606031 a.u.
E_solv = -1996.91290368969 a.u.
ZPE = 210.888 kcal/mol



| | | | |
|---|---|---|---|
| O | 0.04670 | -0.17830 | -0.11090 |
| S | 0.04780 | -0.08450 | 1.39370 |
| Pd | 2.16850 | -0.06260 | 2.64440 |
| C | 0.42400 | 2.63770 | 1.70230 |
| C | -0.66200 | 1.57690 | 1.82490 |
| S | 1.71920 | 2.33140 | 2.99740 |
| H | 0.03040 | 3.64020 | 1.89960 |
| H | -1.47590 | 1.74710 | 1.11260 |
| H | -1.06530 | 1.53130 | 2.84140 |
| H | 0.90350 | 2.61710 | 0.71830 |
| C | 3.28340 | -1.92780 | 2.75490 |
| C | 4.06880 | -0.89600 | 3.31400 |
| C | 4.15510 | -0.70980 | 4.78370 |
| C | 3.28250 | -1.58170 | 5.62170 |
| H | 3.32390 | -1.39440 | 6.69190 |
| C | 2.52970 | -2.56080 | 5.09130 |
| H | 1.92150 | -3.22180 | 5.70420 |
| C | 2.50650 | -2.84520 | 3.62740 |
| H | 4.86980 | -0.42990 | 2.74500 |
| H | 3.45870 | -2.28780 | 1.74400 |
| O | 4.91940 | 0.09610 | 5.30590 |
| O | 1.88540 | -3.81000 | 3.19080 |
| C | 4.92260 | 5.27990 | 1.57870 |
| C | 4.76410 | 4.06230 | 0.90970 |
| C | 3.79000 | 3.15600 | 1.32830 |

| | | | |
|---|---|---|---|
| C | 2.97430 | 3.49780 | 2.40810 |
| C | 3.12640 | 4.69930 | 3.09540 |
| C | 4.10960 | 5.59480 | 2.66960 |
| H | 5.69000 | 5.97760 | 1.25570 |
| H | 5.40660 | 3.81220 | 0.07010 |
| H | 3.67440 | 2.19470 | 0.83180 |
| H | 2.49180 | 4.90740 | 3.95170 |
| H | 4.24410 | 6.53580 | 3.19580 |
| C | -3.29230 | -2.78260 | 2.97740 |
| C | -2.42940 | -2.15650 | 3.88180 |
| C | -1.40960 | -1.32820 | 3.41550 |
| C | -1.28540 | -1.12670 | 2.03980 |
| C | -2.12620 | -1.75250 | 1.12340 |
| C | -3.13890 | -2.58500 | 1.60410 |
| H | -4.07850 | -3.43570 | 3.34600 |
| H | -2.54240 | -2.32300 | 4.94930 |
| H | -0.71720 | -0.85680 | 4.10990 |
| H | -1.97090 | -1.59090 | 0.06100 |
| H | -3.80330 | -3.08400 | 0.90420 |
| O | 1.15340 | 2.84660 | 4.29630 |

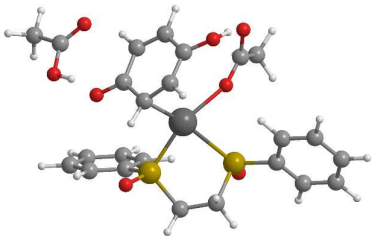
Pd_Bisulfoxide_Quinone_2AcOH (Poli_A)
E_scf (B3LYP/LACVP*) = -2455.06242530146 a.u.
E_scf (M06/LACVP*) = -2454.06065277806 a.u.
E_Gibbs = -2454.671081 a.u.
E_Gibbs(318K) = -2454.679407 a.u.
E_solv = -2455.09599236341 a.u.
ZPE = 290.546 kcal/mol



| | | | |
|---|---|---|---|
| O | 0.00000 | 0.00000 | 0.00000 |
| S | 0.00000 | 0.00000 | 1.50690 |
| Pd | 2.04260 | 0.00000 | 2.85990 |
| C | 0.22890 | 2.70310 | 2.03590 |
| C | -0.80480 | 1.58590 | 2.04690 |
| S | 1.47640 | 2.38420 | 3.37480 |
| O | 0.90460 | 2.96830 | 4.64450 |
| H | -0.21570 | 3.67460 | 2.27520 |
| H | -1.60810 | 1.76820 | 1.32570 |
| H | -1.23050 | 1.43640 | 3.04390 |
| H | 0.75060 | 2.76430 | 1.07580 |
| C | 3.52930 | -1.61600 | 2.67930 |
| C | 3.93480 | -0.68800 | 3.66380 |
| C | 3.59370 | -0.89830 | 5.08180 |
| C | 2.84110 | -2.13240 | 5.42710 |
| H | 2.59870 | -2.26220 | 6.47760 |
| C | 2.50050 | -3.04120 | 4.49850 |
| H | 1.97000 | -3.95630 | 4.74750 |
| C | 2.83820 | -2.85700 | 3.06470 |
| H | 4.70270 | 0.05380 | 3.46060 |
| H | 3.95210 | -1.60780 | 1.67660 |
| O | 3.91340 | -0.09110 | 5.96690 |
| O | 2.55430 | -3.75280 | 2.25620 |
| H | 2.56850 | 0.44040 | 6.99030 |
| O | 1.81150 | 0.89350 | 7.44730 |
| C | 0.67980 | 0.68310 | 6.77390 |
| O | 0.59230 | -0.06540 | 5.80870 |
| C | -0.47060 | 1.48660 | 7.32740 |
| H | -0.38720 | 1.60410 | 8.41080 |
| H | -0.43150 | 2.47930 | 6.86520 |
| H | -1.41820 | 1.01210 | 7.06440 |
| O | 4.42890 | -2.18820 | -0.38860 |
| C | 3.89760 | -3.10880 | -0.98760 |

| | | | |
|---|---|---|---|
| O | 3.05730 | -3.98510 | -0.43210 |
| H | 2.93450 | -3.78190 | 0.53480 |
| C | 4.11240 | -3.39500 | -2.45780 |
| H | 4.46260 | -4.42370 | -2.59330 |
| H | 3.16250 | -3.30120 | -2.99550 |
| H | 4.84020 | -2.69410 | -2.86870 |
| C | 4.86800 | 5.14510 | 2.01880 |
| C | 4.61800 | 3.96640 | 1.30940 |
| C | 3.58240 | 3.11990 | 1.70320 |
| C | 2.79920 | 3.48290 | 2.80130 |
| C | 3.04020 | 4.64680 | 3.52600 |
| C | 4.08460 | 5.48220 | 3.12390 |
| H | 5.68300 | 5.79570 | 1.71400 |
| H | 5.23550 | 3.69920 | 0.45650 |
| H | 3.39680 | 2.18790 | 1.17310 |
| H | 2.42400 | 4.87330 | 4.39070 |
| H | 4.28920 | 6.39310 | 3.67960 |
| C | -3.17650 | -2.97810 | 2.90830 |
| C | -2.39290 | -2.31560 | 3.85780 |
| C | -1.42010 | -1.39970 | 3.45630 |
| C | -1.26700 | -1.15830 | 2.08840 |
| C | -2.02810 | -1.81480 | 1.12530 |
| C | -2.99330 | -2.73130 | 1.54680 |
| H | -3.92630 | -3.69530 | 3.23210 |
| H | -2.53190 | -2.51660 | 4.91670 |
| H | -0.79870 | -0.89640 | 4.19600 |
| H | -1.85180 | -1.60880 | 0.07370 |
| H | -3.59660 | -3.25520 | 0.81040 |

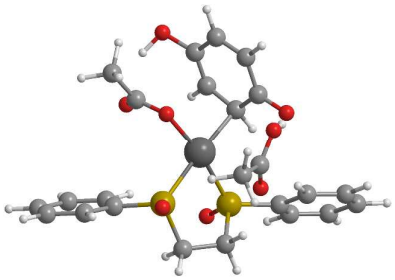
Pd_Bisulfoxide_Quinone_2AcOH (Poli_A-B)
E_scf (B3LYP/LACVP*) = -2455.03418236377 a.u.
E_scf (M06/LACVP*) = -2454.0309695028 a.u.
E_Gibbs = -2454.646965 a.u.
E_Gibbs(318K) = -2454.6544 a.u.
E_solv = -2455.06910045294 a.u.
ZPE = 288.711 kcal/mol



| | | | |
|---|---|---|---|
| O | -0.52040 | -0.18640 | 2.85750 |
| H | -0.11310 | -0.47850 | 4.14160 |
| O | 6.85970 | -1.45570 | 3.65200 |
| S | 5.97850 | -1.01360 | 2.51800 |
| Pd | 3.69280 | -0.67780 | 2.92370 |
| C | 5.87860 | 1.78700 | 2.25800 |
| C | 6.68190 | 0.56880 | 1.82070 |
| S | 4.17330 | 1.61830 | 1.55260 |
| O | 4.36120 | 1.70060 | 0.05170 |
| H | 6.32150 | 2.70270 | 1.85240 |
| H | 7.70590 | 0.58540 | 2.20650 |
| H | 6.69760 | 0.48590 | 0.73160 |
| H | 5.79330 | 1.87010 | 3.34660 |
| C | 3.69270 | -2.14180 | 4.46710 |
| C | 2.67200 | -1.44960 | 5.16320 |
| O | 1.65900 | 0.08910 | 2.31720 |
| C | 0.01480 | 0.35500 | 0.60340 |
| C | 1.34910 | -1.58630 | 4.72490 |
| H | -1.06740 | 0.46930 | 0.51700 |
| C | 1.00080 | -2.68070 | 3.81460 |
| H | 0.52080 | 1.25750 | 0.24700 |
| H | -0.05210 | -2.79710 | 3.57540 |
| H | 0.34200 | -0.47350 | -0.03600 |
| C | 1.93010 | -3.50770 | 3.28680 |
| H | 4.05430 | -5.42940 | 2.12050 |
| H | 1.67850 | -4.34190 | 2.63640 |

| | | | |
|---|---|---|---|
| O | 4.15930 | -6.20860 | 1.50480 |
| C | 3.34900 | -3.31970 | 3.61630 |
| C | 2.97060 | -6.59150 | 1.02970 |
| H | 2.91030 | -0.68670 | 5.89720 |
| O | 1.91220 | -6.05370 | 1.30740 |
| H | 4.70970 | -2.14530 | 4.85600 |
| C | 3.08820 | -7.78340 | 0.10420 |
| O | 0.42710 | -0.72980 | 5.06800 |
| H | 3.78140 | -7.56020 | -0.71360 |
| O | 4.23330 | -4.09840 | 3.21850 |
| H | 3.49520 | -8.64110 | 0.65100 |
| H | 2.10580 | -8.03520 | -0.29740 |
| C | 0.42280 | 0.06390 | 2.04100 |
| C | 2.28370 | 5.50440 | 3.04900 |
| C | 3.10900 | 5.52500 | 1.92040 |
| C | 3.69420 | 4.34630 | 1.46090 |
| C | 3.44720 | 3.16010 | 2.15450 |
| C | 2.60020 | 3.11480 | 3.26370 |
| C | 2.02640 | 4.30490 | 3.71540 |
| H | 1.82580 | 6.42550 | 3.39920 |
| H | 3.28970 | 6.45840 | 1.39440 |
| H | 4.31150 | 4.33190 | 0.56700 |
| H | 2.36590 | 2.16640 | 3.73810 |
| H | 1.36230 | 4.28800 | 4.57490 |
| C | 6.36990 | -3.99270 | -0.91780 |
| C | 6.96810 | -4.25630 | 0.31420 |
| C | 6.88170 | -3.32400 | 1.35050 |
| C | 6.19300 | -2.13600 | 1.12100 |
| C | 5.57050 | -1.85840 | -0.10110 |
| C | 5.67550 | -2.79640 | -1.12580 |
| H | 6.43350 | -4.72530 | -1.71770 |
| H | 7.48990 | -5.19420 | 0.47880 |
| H | 7.32120 | -3.51100 | 2.32450 |
| H | 5.01170 | -0.93730 | -0.25390 |
| H | 5.20410 | -2.59660 | -2.08390 |

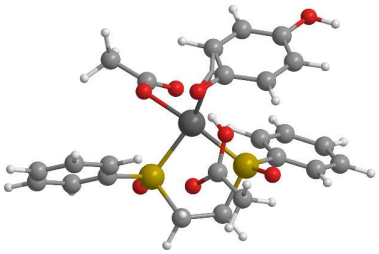
Pd_Bisulfoxide_Quinone_2AcOH (Poli_B)
E_scf (B3LYP/LACVP*) = -2455.04534352613 a.u.
E_scf (M06/LACVP*) = -2454.0456716079 a.u.
E_Gibbs = -2454.653343 a.u.
E_Gibbs(318K) = -2454.66087 a.u.
E_solv = -2455.0798515766 a.u.
ZPE = 291.586 kcal/mol



| | | | |
|---|---|---|---|
| O | 1.36190 | 1.12940 | 2.97480 |
| S | 1.63910 | 0.13520 | 1.87670 |
| Pd | -0.01050 | 0.17820 | 0.19220 |
| C | 2.83760 | 2.06990 | 0.36520 |
| C | 3.14070 | 0.70350 | 0.96600 |
| S | 1.40410 | 1.96780 | -0.82430 |
| O | 1.94100 | 1.88640 | -2.22530 |
| H | 3.67470 | 2.43990 | -0.23480 |
| H | 3.94760 | 0.76770 | 1.70290 |
| H | 3.35730 | -0.05180 | 0.20460 |
| H | 2.58170 | 2.79840 | 1.13850 |
| C | -1.15070 | -1.46920 | 1.13550 |
| C | -2.42710 | -0.83880 | 1.32830 |
| C | -3.42730 | -1.02150 | 0.41330 |
| C | -3.28530 | -2.00740 | -0.62110 |
| H | -4.13400 | -2.15490 | -1.28480 |
| C | -2.12980 | -2.71030 | -0.79460 |
| H | -2.03050 | -3.45610 | -1.57760 |
| C | -0.99370 | -2.50410 | 0.08200 |

| | | | |
|---|---|---|---|
| H | -2.55340 | -0.12770 | 2.13850 |
| H | -0.54130 | -1.65060 | 2.01830 |
| O | -4.55290 | -0.24590 | 0.38420 |
| O | 0.06870 | -3.17090 | -0.02650 |
| H | -4.24570 | 0.67390 | 0.53210 |
| O | -2.64200 | 1.84260 | -0.03870 |
| C | -2.33350 | 1.35540 | -1.13800 |
| O | -1.33350 | 0.55650 | -1.36490 |
| C | -3.19220 | 1.63120 | -2.36920 |
| H | -3.49680 | 2.68180 | -2.37460 |
| H | -2.67230 | 1.38060 | -3.29580 |
| H | -4.10020 | 1.02050 | -2.29410 |
| H | 0.80800 | -3.02740 | -1.51860 |
| O | 1.15080 | -2.77430 | -2.43000 |
| C | 2.07640 | -1.83090 | -2.32560 |
| O | 2.52070 | -1.42940 | -1.25200 |
| C | 2.52590 | -1.27650 | -3.65550 |
| H | 2.10050 | -1.83570 | -4.49050 |
| H | 2.20960 | -0.22880 | -3.70500 |
| H | 3.61880 | -1.29200 | -3.70670 |
| C | 2.98680 | -3.75820 | 3.84240 |
| C | 2.92320 | -3.68480 | 2.44860 |
| C | 2.52310 | -2.50670 | 1.81760 |
| C | 2.20830 | -1.40780 | 2.62030 |
| C | 2.25560 | -1.45790 | 4.01420 |
| C | 2.65290 | -2.64890 | 4.62330 |
| H | 3.28750 | -4.68600 | 4.32170 |
| H | 3.16720 | -4.55350 | 1.84380 |
| H | 2.43700 | -2.44770 | 0.73770 |
| H | 1.98090 | -0.58270 | 4.59460 |
| H | 2.69380 | -2.71020 | 5.70730 |
| C | -0.50630 | 6.07730 | -0.26250 |
| C | -0.58070 | 5.13660 | 0.76900 |
| C | 0.00470 | 3.88120 | 0.61600 |
| C | 0.67570 | 3.60240 | -0.57650 |
| C | 0.74980 | 4.51870 | -1.62210 |
| C | 0.15310 | 5.76970 | -1.45410 |
| H | -0.97510 | 7.04990 | -0.13960 |
| H | -1.11070 | 5.37180 | 1.68730 |
| H | -0.06910 | 3.13410 | 1.40220 |
| H | 1.25710 | 4.24320 | -2.54150 |
| H | 0.19950 | 6.50040 | -2.25680 |

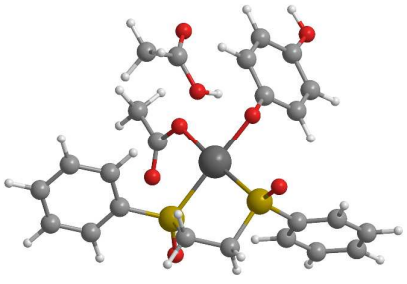
Pd_Bisulfoxide_Quinone_2AcOH (Poli_B-C)
E_scf (B3LYP/LACVP*) = -2455.01951872337 a.u.
E_scf (M06/LACVP*) = -2454.02215163565 a.u.
E_Gibbs = -2454.627321 a.u.
E_Gibbs(318K) = -2454.634625 a.u.
E_solv = -2455.06233453529 a.u.
ZPE = 290.555 kcal/mol



| | | | |
|---|---|---|---|
| Pd | 0.19070 | -0.07250 | 0.06780 |
| S | 0.16360 | 0.05340 | 2.39350 |
| O | 1.30470 | 0.09920 | 3.37220 |
| S | -0.82870 | 1.98250 | -0.02710 |
| O | -2.31010 | 2.05840 | -0.22690 |
| C | -0.82820 | 1.62000 | 2.64750 |
| C | -0.42490 | 2.67620 | 1.62960 |
| H | -0.58700 | 1.92640 | 3.66970 |
| H | -1.88880 | 1.36390 | 2.57190 |
| H | -1.02200 | 3.58770 | 1.73570 |
| H | 0.64870 | 2.89380 | 1.65780 |
| O | -0.36860 | -0.17920 | -1.90090 |

| | | | |
|---|---|---|---|
| C | -1.48810 | -0.84260 | -2.07530 |
| O | -2.12590 | -1.40480 | -1.18520 |
| C | 1.32980 | -2.32270 | -0.74820 |
| C | 2.17450 | -1.53850 | 0.12380 |
| C | 0.84470 | -3.58030 | -0.37290 |
| C | 2.47500 | -2.12900 | 1.41310 |
| C | 1.17100 | -4.10890 | 0.86810 |
| H | 0.21840 | -4.15520 | -1.04720 |
| C | 1.99440 | -3.36990 | 1.75500 |
| H | 1.16890 | -1.94790 | -1.75180 |
| H | 3.50190 | 0.29940 | 0.70100 |
| O | 4.12720 | 0.69900 | 1.45200 |
| C | 3.63870 | 1.80880 | 1.95850 |
| O | 2.67520 | 2.42180 | 1.49640 |
| C | 4.36930 | 2.26830 | 3.20180 |
| H | 4.00380 | 1.67830 | 4.05080 |
| H | 5.44470 | 2.09290 | 3.10980 |
| H | 4.16750 | 3.32430 | 3.39090 |
| H | 3.10460 | -1.56960 | 2.09560 |
| H | 2.24280 | -3.79430 | 2.72750 |
| C | -1.94070 | -0.86940 | -3.53120 |
| H | -2.86510 | -1.44370 | -3.62110 |
| H | -2.10340 | 0.15240 | -3.89010 |
| H | -1.16350 | -1.31570 | -4.16110 |
| O | 0.68280 | -5.33900 | 1.19860 |
| H | 0.98770 | -5.57550 | 2.08860 |
| O | 2.64740 | -0.39060 | -0.24950 |
| C | 1.13450 | 4.67670 | -3.12750 |
| C | -0.25700 | 4.59570 | -3.04180 |
| C | -0.85150 | 3.78580 | -2.07450 |
| C | -0.02300 | 3.07850 | -1.20380 |
| C | 1.37010 | 3.13190 | -1.27540 |
| C | 1.94220 | 3.95160 | -2.24750 |
| H | 1.59270 | 5.30210 | -3.88930 |
| H | -0.88150 | 5.15590 | -3.73220 |
| H | -1.92920 | 3.68800 | -1.99270 |
| H | 1.98710 | 2.56520 | -0.58330 |
| H | 3.02420 | 4.01310 | -2.32110 |
| C | -2.89120 | -2.96070 | 3.97690 |
| C | -1.87980 | -2.47810 | 4.81160 |
| C | -0.94220 | -1.56970 | 4.32030 |
| C | -1.04680 | -1.15420 | 2.99260 |
| C | -2.03590 | -1.63880 | 2.13260 |
| C | -2.96460 | -2.54730 | 2.64490 |
| H | -3.61850 | -3.66980 | 4.36370 |
| H | -1.81950 | -2.80930 | 5.84490 |
| H | -0.13670 | -1.18920 | 4.94120 |
| H | -2.07530 | -1.34610 | 1.08290 |
| H | -3.73890 | -2.93750 | 1.99070 |

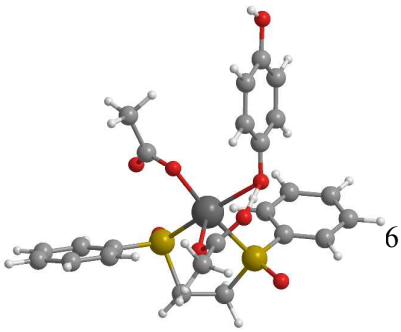
Pd_Bisulfoxide_Quinone_2AcOH (Poli_C)
E_scf (B3LYP/LACVP*) = -2455.04725149665 a.u.
E_scf (M06/LACVP*) = -2454.03291604582 a.u.
E_Gibbs = -2454.657418 a.u.
E_Gibbs(318K) = -2454.665029 a.u.
E_solv = -2455.09371181012 a.u.
ZPE = 291.316 kcal/mol



| | | | |
|---|---|---|---|
| Pd | -0.53930 | 0.09530 | 0.16470 |
| S | -1.71020 | 0.65770 | 2.17330 |
| O | -1.69540 | 2.02170 | 2.79020 |
| S | -2.58850 | -0.90200 | -0.56140 |

| | | | |
|---|---|---|---|
| O | -3.06490 | -2.26740 | -0.16220 |
| C | -3.47460 | 0.17420 | 1.79920 |
| C | -3.74040 | 0.27250 | 0.30400 |
| H | -4.07740 | 0.88150 | 2.37660 |
| H | -3.64170 | -0.84230 | 2.16380 |
| H | -4.75940 | -0.04640 | 0.06320 |
| H | -3.56380 | 1.27890 | -0.08900 |
| O | 0.57520 | -0.32560 | -1.49970 |
| C | 0.34600 | -1.44200 | -2.13640 |
| O | -0.59710 | -2.20970 | -1.92470 |
| C | 1.38690 | -1.73330 | -3.21230 |
| H | 1.42520 | -0.90760 | -3.93070 |
| H | 2.37740 | -1.81010 | -2.75170 |
| H | 1.14100 | -2.66440 | -3.72660 |
| H | 2.94570 | 1.46110 | -0.96950 |
| O | 1.05900 | 1.16240 | 0.84830 |
| O | 6.01680 | -1.25990 | 1.06870 |
| H | 6.55920 | -1.00150 | 0.30710 |
| H | 4.14110 | -1.55820 | 2.79910 |
| C | 2.25830 | 0.55070 | 0.86010 |
| H | 0.66890 | 2.45320 | -0.31810 |
| C | 3.20570 | 0.79180 | -0.15610 |
| O | 0.14080 | 3.08270 | -0.88570 |
| C | 2.61100 | -0.30440 | 1.92700 |
| C | 0.88660 | 3.53880 | -1.90480 |
| C | 4.46420 | 0.20350 | -0.09330 |
| O | 2.04380 | 3.22470 | -2.10280 |
| C | 3.86250 | -0.90060 | 1.98090 |
| C | 0.11240 | 4.50650 | -2.77570 |
| H | 1.88240 | -0.48530 | 2.71270 |
| H | -0.78810 | 4.02510 | -3.17300 |
| C | 4.79650 | -0.64890 | 0.96670 |
| H | -0.21440 | 5.36650 | -2.18110 |
| H | 5.19600 | 0.40580 | -0.87490 |
| H | 0.74430 | 4.84390 | -3.59840 |
| C | -0.48960 | -2.38800 | 5.35890 |
| C | -0.52960 | -1.02600 | 5.66320 |
| C | -0.92410 | -0.10030 | 4.69420 |
| C | -1.27930 | -0.56850 | 3.43170 |
| C | -1.23470 | -1.92670 | 3.10040 |
| C | -0.84170 | -2.83630 | 4.08150 |
| H | -0.17650 | -3.10290 | 6.11450 |
| H | -0.24850 | -0.67920 | 6.65350 |
| H | -0.95220 | 0.96570 | 4.89780 |
| H | -1.49800 | -2.27320 | 2.10320 |
| H | -0.80320 | -3.89520 | 3.84260 |
| C | -3.73040 | 0.00980 | -4.88360 |
| C | -2.95460 | 0.92690 | -4.16950 |
| C | -2.59050 | 0.66090 | -2.84940 |
| C | -3.03050 | -0.52960 | -2.26870 |
| C | -3.79250 | -1.46340 | -2.96420 |
| C | -4.14520 | -1.18150 | -4.28460 |
| H | -4.00250 | 0.22050 | -5.91430 |
| H | -2.62030 | 1.84520 | -4.64420 |
| H | -1.95720 | 1.35130 | -2.29690 |
| H | -4.07680 | -2.39210 | -2.47970 |
| H | -4.73560 | -1.89860 | -4.84810 |

Pd_Bisulfoxide_Quinone_2AcOH (Poli_C-D)
E_scf (B3LYP/LACVP*) = -2455.03646923901 a.u.
E_scf (M06/LACVP*) = -2454.02291978903 a.u.
E_Gibbs = -2454.649746 a.u.
E_Gibbs(318K) = -2454.657231 a.u.

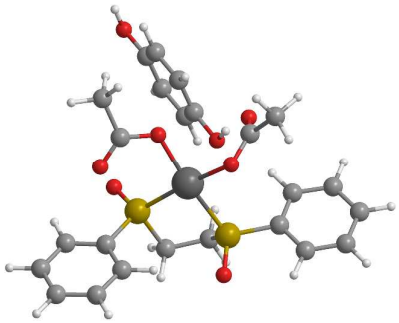


E_solv = -2455.07938681832 a.u.
ZPE = 288.577 kcal/mol

| | | | |
|---|---|---|---|
| Pd | 0.58780 | -0.05140 | -0.01110 |
| S | 1.89480 | 1.20610 | -1.50550 |
| O | 2.12190 | 2.67260 | -1.32870 |
| S | 2.32050 | -1.66930 | -0.05640 |
| O | 2.56300 | -2.67490 | -1.14340 |
| C | 3.53770 | 0.31890 | -1.50390 |
| C | 3.70900 | -0.44240 | -0.19830 |
| H | 4.27700 | 1.11720 | -1.61860 |
| H | 3.57250 | -0.35070 | -2.36680 |
| H | 4.64180 | -1.01480 | -0.19280 |
| H | 3.65760 | 0.21370 | 0.67630 |
| O | -0.71630 | -1.04200 | 1.14520 |
| C | -0.78740 | -2.34810 | 1.08800 |
| O | -0.46260 | 2.72770 | 1.61100 |
| O | 0.01120 | -3.08550 | 0.51060 |
| C | 0.59090 | 2.26250 | 2.17340 |
| O | 1.28470 | 1.30910 | 1.73750 |
| C | 0.97530 | 2.92830 | 3.48480 |
| H | 1.99610 | 2.66700 | 3.77140 |
| H | 0.86990 | 4.01360 | 3.40100 |
| H | 0.28720 | 2.59130 | 4.26980 |
| C | -1.99050 | -2.89780 | 1.84620 |
| H | -1.87730 | -2.69070 | 2.91620 |
| H | -2.90440 | -2.39970 | 1.50870 |
| C | -2.39440 | 1.10410 | -0.38990 |
| H | -2.06430 | -3.97540 | 1.68790 |
| C | -3.19550 | 1.16350 | 0.76220 |
| H | -2.77380 | 1.55280 | 1.68280 |
| C | -2.94650 | 0.59430 | -1.57770 |
| O | -1.11120 | 1.54610 | -0.39120 |
| C | -4.52200 | 0.73930 | 0.71720 |
| O | -6.35690 | -0.20590 | -0.56940 |
| C | -4.26490 | 0.15980 | -1.61890 |
| H | -6.78910 | -0.10100 | 0.29230 |
| H | -2.32130 | 0.54650 | -2.46490 |
| H | -4.69850 | -0.23550 | -2.53270 |
| C | -5.06180 | 0.23280 | -0.46930 |
| H | -0.80890 | 2.13290 | 0.57580 |
| H | -5.13970 | 0.79860 | 1.61270 |
| C | 0.30990 | 0.48840 | -5.73210 |
| C | 0.58270 | 1.78460 | -5.29090 |
| C | 1.08500 | 1.99850 | -4.00540 |
| C | 1.30920 | 0.89470 | -3.18660 |
| C | 1.03010 | -0.41150 | -3.60120 |
| C | 0.53390 | -0.60550 | -4.88990 |
| H | -0.08490 | 0.32830 | -6.73140 |
| H | 0.39980 | 2.63350 | -5.94340 |
| H | 1.29310 | 2.99550 | -3.63010 |
| H | 1.19210 | -1.26010 | -2.94020 |
| H | 0.31460 | -1.61320 | -5.23060 |
| C | 3.30780 | -3.47610 | 4.01220 |
| C | 2.85760 | -2.15550 | 3.93900 |
| C | 2.54370 | -1.58290 | 2.70570 |
| C | 2.70520 | -2.36600 | 1.56100 |
| C | 3.14060 | -3.68740 | 1.60770 |
| C | 3.44710 | -4.24000 | 2.85140 |
| H | 3.54150 | -3.91440 | 4.97890 |
| H | 2.73990 | -1.56800 | 4.84550 |
| H | 2.16900 | -0.56280 | 2.63980 |
| H | 3.21530 | -4.26250 | 0.69050 |

| | | | |
|---|---|---|---|
| H | 3.78530 | -5.27060 | 2.91300 |

Pd_Bisulfoxide_Quinone_2AcOH (Poli_D)
E_scf (B3LYP/LACVP*) = -2455.05169440408 a.u.
E_scf (M06/LACVP*) = -2454.03155458226 a.u.
E_Gibbs = -2454.66157 a.u.
E_Gibbs(318K) = -2454.672228 a.u.
E_solv = -2455.09685599479 a.u.
ZPE = 291.906 kcal/mol



| | | | |
|---|---|---|---|
| Pd | -1.14580 | 0.25390 | 0.48950 |
| S | -1.43580 | -1.39790 | 2.14050 |
| O | -2.82680 | -1.89950 | 2.41270 |
| S | -1.23070 | -1.54130 | -1.09110 |
| O | -0.21810 | -1.70440 | -2.17300 |
| C | -0.45340 | -2.74160 | 1.35490 |
| C | -1.11160 | -3.05850 | 0.02060 |
| H | -0.47250 | -3.60440 | 2.02840 |
| H | 0.56330 | -2.35200 | 1.23970 |
| H | -0.51140 | -3.76120 | -0.56430 |
| H | -2.11980 | -3.45520 | 0.15810 |
| O | -0.68390 | 1.72230 | -0.82270 |
| C | -1.22370 | 1.69330 | -2.01320 |
| O | -1.96590 | 0.80850 | -2.43680 |
| C | 2.74900 | -0.19230 | -0.28960 |
| C | 2.83230 | 1.02900 | -0.96360 |
| C | 3.54940 | -1.26330 | -0.69670 |
| C | 3.71330 | 1.17150 | -2.03630 |
| C | 4.42320 | -1.12120 | -1.77140 |
| H | 3.48260 | -2.20710 | -0.16230 |
| C | 4.50870 | 0.09920 | -2.44660 |
| H | 3.77500 | 2.12560 | -2.55850 |
| C | -0.83050 | 2.89550 | -2.86410 |
| H | -1.07450 | 3.82580 | -2.34120 |
| H | 0.25150 | 2.88500 | -3.03400 |
| H | -1.35340 | 2.85610 | -3.82150 |
| H | 2.19840 | 1.85530 | -0.65620 |
| O | 1.89120 | -0.37930 | 0.76920 |
| O | 5.39080 | 0.18430 | -3.49810 |
| H | 5.32800 | 1.07230 | -3.88190 |
| H | 5.04670 | -1.94810 | -2.09810 |
| H | 1.54110 | 0.49920 | 1.08150 |
| O | 1.02430 | 1.90490 | 1.91070 |
| C | -0.11040 | 2.29920 | 2.21930 |
| O | -1.23260 | 1.72780 | 1.90100 |
| C | -0.28880 | 3.57080 | 3.03500 |
| H | 0.63690 | 3.80840 | 3.56320 |
| H | -0.52740 | 4.39370 | 2.35080 |
| H | -1.11910 | 3.47200 | 3.73910 |
| C | 0.54820 | -0.72050 | 6.20090 |
| C | -0.81530 | -1.00530 | 6.10530 |
| C | -1.40130 | -1.21820 | 4.85690 |
| C | -0.59660 | -1.14120 | 3.72030 |
| C | 0.76870 | -0.85130 | 3.78890 |
| C | 1.33430 | -0.64720 | 5.04790 |
| H | 0.99930 | -0.55080 | 7.17460 |
| H | -1.42780 | -1.05940 | 7.00090 |
| H | -2.45830 | -1.44110 | 4.75480 |
| H | 1.38300 | -0.77390 | 2.89760 |
| H | 2.39380 | -0.41950 | 5.12120 |
| C | -5.42410 | -2.19140 | -2.78300 |
| C | -4.30530 | -2.28790 | -3.61230 |
| C | -3.02550 | -2.08930 | -3.09240 |

| | | | |
|---|---|---|---|
| C | −2.89840 | −1.80850 | −1.73700 |
| C | −4.00010 | −1.70000 | −0.88820 |
| C | −5.27180 | −1.89700 | −1.42570 |
| H | −6.41870 | −2.33750 | −3.19580 |
| H | −4.42700 | −2.50560 | −4.66980 |
| H | −2.14050 | −2.12600 | −3.71920 |
| H | −3.87900 | −1.46910 | 0.16730 |
| H | −6.14290 | −1.81460 | −0.78170 |

**Calculation of theoretical KIE**

The calculation of the theoretical KIE was performed using the Hessian calculated in gas phase for the complexes **A**, **B** and **C**. To allow comparison with experimental results the Gibbs free energy was evaluated at T=318 K (=45 °C).

This gave the following results:

| | |
|---|---|
| (**A**) Pd_Bisulfoxide_Allylbenzene_Acetate_Abstraction_TS | -2192.212272 a.u. |
| Pd_Bisulfoxide_Allylbenzene_Acetate_Abstraction_TS_D | -2192.21407 a.u. |
| (**B**) Pd_Bisulfoxide_Allylbenzene_Acetate_Abstraction_6Membered_TS | -2192.213173 a.u. |
| Pd_Bisulfoxide_Allylbenzene_Acetate_Abstraction_6Membered_TS_D | -2192.214928 a.u. |
| (**C**) Pd_Bisulfoxide_Allylbenzene_Acetate_External_Acetate_Abstraction_TS | -2420.850806 a.u. |
| Pd_Bisulfoxide_Allylbenzene_Acetate_External_Acetate_Abstraction_TS_D | -2420.852142 a.u. |

From this we find the activation energies and differences in energy.

**A**: Activation energy of 60.5 kJ/mol (proton) and 64.9 kJ/mol (deuterium). Energy difference of 4.4 kJ/mol.
**B**: Activation energy of 58.1 kJ/mol (proton) and 62.6 kJ/mol (deuterium). Energy difference of 4.5 kJ/mol.
**C**: Activation energy of 15.6 kJ/mol (proton) and 20.3 kJ/mol (deuterium). Energy difference of 4.7 kJ/mol.

These results corresponds to the following differences in reaction rates, when using a Boltzmann expression evaluated at T=318K.

**A**: Reaction rate of 5.3
**B**: Reaction rate of 5.5
**C**: Reaction rate of 5.9

Performing a similar analysis using differences in zero-point energies (ZPE) resulted in the following calculated KIE values:

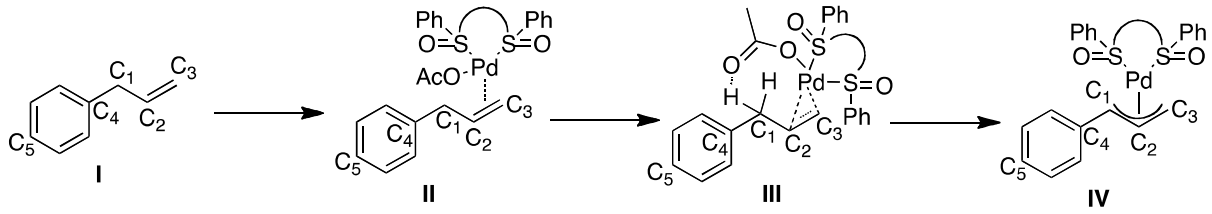
**A**: KIE value of 5.7
**B**: KIE value of 5.9
**C**: KIE value of 3.7

Thus documenting that the observed effect arises mainly from the differences in bond strengths, as expected.
The results for **C** are obtained with a starting point structure where the O-H distance between substrate and acetate is set to 1.6Å. If a starting point with 1.5Å is used the following results are obtained:

Reaction rate from Gibbs free energy (T=318K) = 3.9
KIE value from ZPE = 2.5

## Calculated charges

The electrostatic potential (esp) charges for the structures shown here were calculated. The various carbons in the allylbenzene substrate are marked.




**Scheme S6 Numbering of the carbon atoms used for the calculation of charges.**

In the figure the absolute charges of the marked carbons in the structures are plotted.

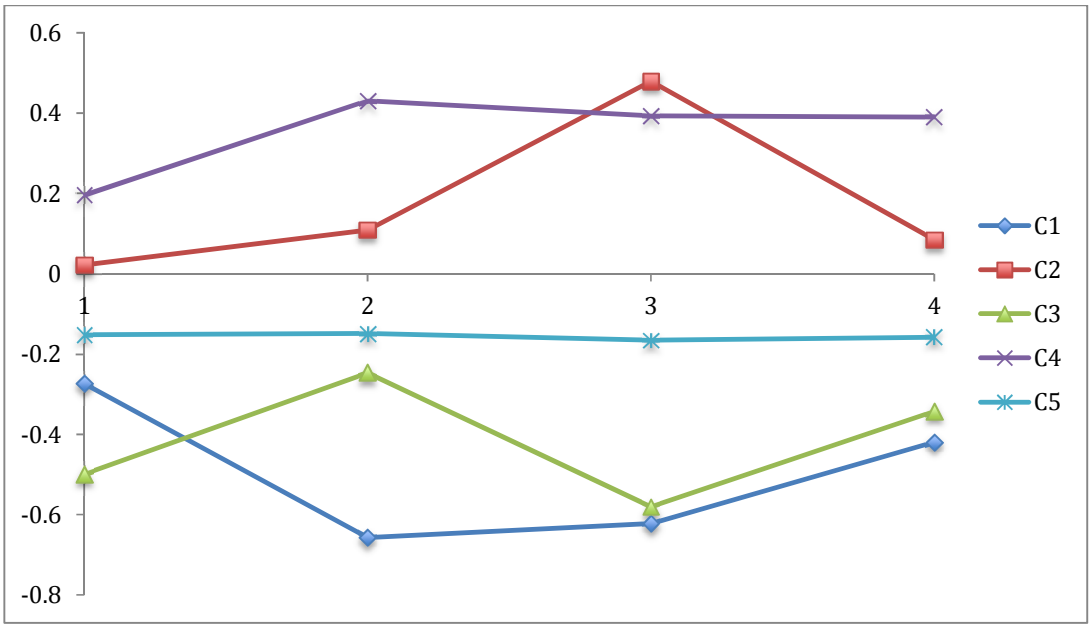



**Figure S19 Calculated charges for the carbon atoms along the C-H activation pathway.**


(1) Biellmann, J.; d'Orchymont, H. *J. Org. Chem.* **1982**, *47*, 2882-2886.
(2) Bialecki, J.; Ruzicka, J.; Attygalle, A. *J. Mass Spectrom.* **2006**, *41*, 1195-1204.
(3) López-Pérez, A.; Adrio, J.; Carretero, J. C. *Org. Lett.* **2009**, *11*, 5514-5517.
(4) Young, A. J.; White, M. C. *J. Am. Chem. Soc.* **2008**, *130*, 14090-14091.