Supporting Information

New Journal of Chemistry

Ligand's Electronegativity Controls Sense of Enantioselectivity in BIFOP-X Palladium-Catalyzed Allylic Alkylations

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§ X-Ray analysis

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Experimental

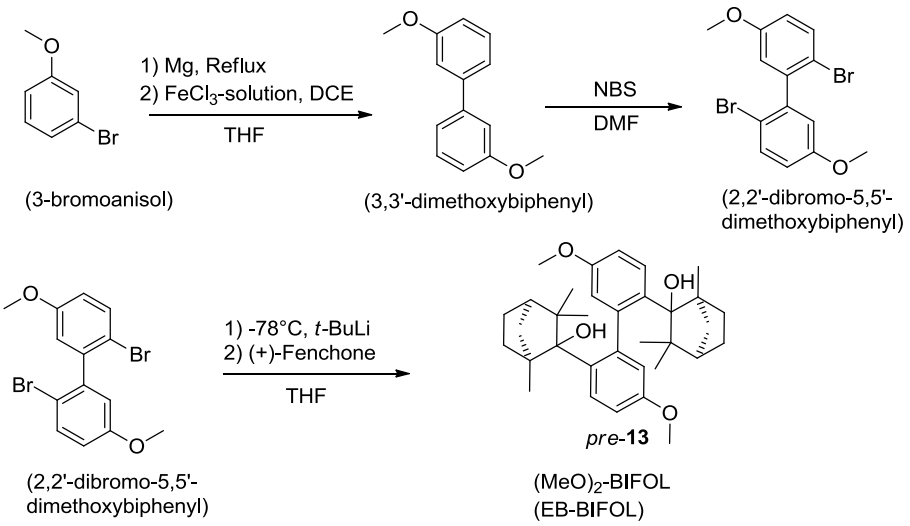
General Methods

All actions are carried out under an argon (*Air Products* RT Ar BIP) atmosphere using oven dried glassware and using standard *Schlenk* techniques. All solvents are reagent grade and are dried and distilled prior to use, if necessary. Column chromatography is performed on silica gel (SiO_2) (Silica gel for chromatography from *Acros Organics*, size 35-70 µm, 60 Å). TLC is performed on a TLC silica gel 60/Kieselguhr F254 from *Merck*. Components are visualized by a universal UV-lamp from *Lamag* 29,200 and staining with a solution of a mixture of $KMnO_4$ (5.0 g) and K_2CO_3 (5.0 g) in H_2O (250 mL). GC-MS are recorded on a *Varian* 4000 with an *Agilent* DB35-HT column (30 m, 25 µm, 0.25 mm). ^{1}H-, ^{13}C-, and ^{31}P-NMR are recorded on a *Bruker* AV300 (300, 75 and 125.5 MHz, respectively) using $CDCl_3$ as solvent. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: d = 7.26 ppm for ^{1}H, d = 77.0 ppm for ^{13}C). Data are reported as follows: chemical shifts, multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet, br = broad), coupling constants (Hz), and integration. Optical rotations are measured in $CHCl_3$ on a polarimeter (Polartronic MH8) with a 10 cm cell (c is given in g/100 mL). Conversion of the reaction is determined by ^{1}H-NMR. Enantiomeric excess values are determined by HPLC analysis using a *VWR Hitachi* L-2130 pump *EliteLaChrom* HPLC equipped with a *VWR Hitachi* L-2400 UV detector and a *VWR Chromaster* 5310 column oven.

Chemicals and solvents

Toluene, Tetrahydrofuran (THF) and diethylether (Et_2O) are distilled over Na/benzophenone. Dichloromethane (CH_2Cl_2) are distilled over phosphor pentaoxide. The ligands are synthesized using common methods. The palladium salt ($[(C_3H_5)PdCl]_2$, 98% purity) is purchased from *Sigma-Aldrich* as well as the *trans*-1,3-diphenyl-propen-1-ol (>98% purity), the 2-cyclohexen-1-ol (95% purity) and the 3-bromoanisol (>98% purity). (+)-Fenchone (98% purity) is purchased from *Alfa Aesar*. The PCl_3 (99% purity), the *n*-BuLi (2.5 M in hexane) and the *t*-BuLi (1.9 M in pentane) is purchased from *Acros Organics*.

General procedure for the synthesis of 5,5'-dimethoxybiphenyl-2,2'.bisfenchol ($(MeO)_2$-BIFOL; EB-BIFOL)



Mg (0.27 mol, 6.5 g, 1.0 eq.) is put together with THF (100 mL) in an appropriate Ar flushed *Schlenk* flask with a high reflux condenser and a dripping funnel. 3-bromoanisol (0.27 mol, 50 g = 34 mL, 1.0 eq.) is given into the dripping funnel together with THF (20 mL). The Grignard (organomagnesium reagent) is started by dropping one quarter (13.5 mL) of the 3-bromoanisol / THF solution to the Mg. After start of the Grignard (bubbling) a dripping speed is chosen that the rest of the 3-bromoanisol / THF solution is given to the Mg in about 1-2 h. The dripping funnel can be separated and exchanged by a dry tube. The Grignard is refluxed for further 6 h. Now, the Grignard must be filtered through a frit into another appropriate *Schlenk* flask. The *Schlenk* flask is again equipped with the high reflux condenser but the apparatus has to stay. 1,2-dichloroethane (DCE, 0.16 mol, 11 mL, 0.6 eq.) is given immediately to the Grignard reagent and $FeCl_3$-2-MTHF solution (0.2 M, 1.0 mmol, 0.2 mL, 0.004 mol%) is carefully added. A very heavy reaction is taking place while the Grignard reagent is homo-coupled (Cahiez-coupling [1], when the temperature is to low it does not taking place; but careful when the Grignard begins to react or is to hot). The mixture is stirred at room temperature for 2 h and then carefully quenched with 1 M aqueos HCl (100 mL). The mixture is extracted with dichloromethane (CH_2Cl_2, 3x 50 mL) and the combined organic layers are dried with $MgSO_4$ and evaporated under *vacuo*. Purification by flash chromatography over silica gel, using Et_2O:*n*-hexane 1:10 afforded the homo-coupled product 3,3'-dimethoxybiphenyl ([1], 0.17 mol, 31.5 g, 63% yield). The purified product is putted into a dried appropriate normal flask with dry tube (0.17 mol, 31.5 g, 1.0 eq.) together with (patent instructions [2]) dry acetonitrile (MeCN, 120 mL). The solution is cooled by an ice bath and N-bromosuccinimide (NBS, 0.24 mol, 60.6 g, 2.0 eq.) is added portionwise. The mixture stirs over night at 0°C to room temperature and is quenched with ice water. The precipitate is suction filtrated over a Büchner funnel and purified by washing with hot water (100 mL) and hot *n*-hexane (100 mL) yielding the 2,2'-dibromo-5,5'-dimethoxybiphenyl product ([2], 0.125 mol, 46.5 g, 74% yield). 2,2'-dibromo-5,5'-dimethoxybiphenyl ([2], 19.0 mmol, 7.0 g, 1.0 eq.) is given into an appropriate Ar-flushed *Schlenk* flask with dripping funnel and dissolved with THF (40 mL). The mixture is cooled to -78°C and the dripping funnel is filled with *t*-BuLi (1.9 M, 77.1 mmol, 40.6 mL, 4.1 eq.) and dropped over 1 h to the mixture. The mixture is warmed to room temperature and stirred for further 10 min. (+)-Fenchone (38.0 mmol, 6 mL, 2.0 eq.) is added dropwise under Ar-flushing. The mixture is stirred for 6 h and quenched with saturated aqueous NH_4Cl solution (25 mL). The mixture is

separated and the water layer is extracted with DCM (2×25 mL). The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by crystallization and recrystallization from acetone/*n*-hexane afforded the desired product 5,5'-dimethoxybiphenyl-2,2'-bisfenchol (*pre*-**13**, EB-BIFOL, 6.7 mmol, 3.5 g, 36% yield) in fine needles.

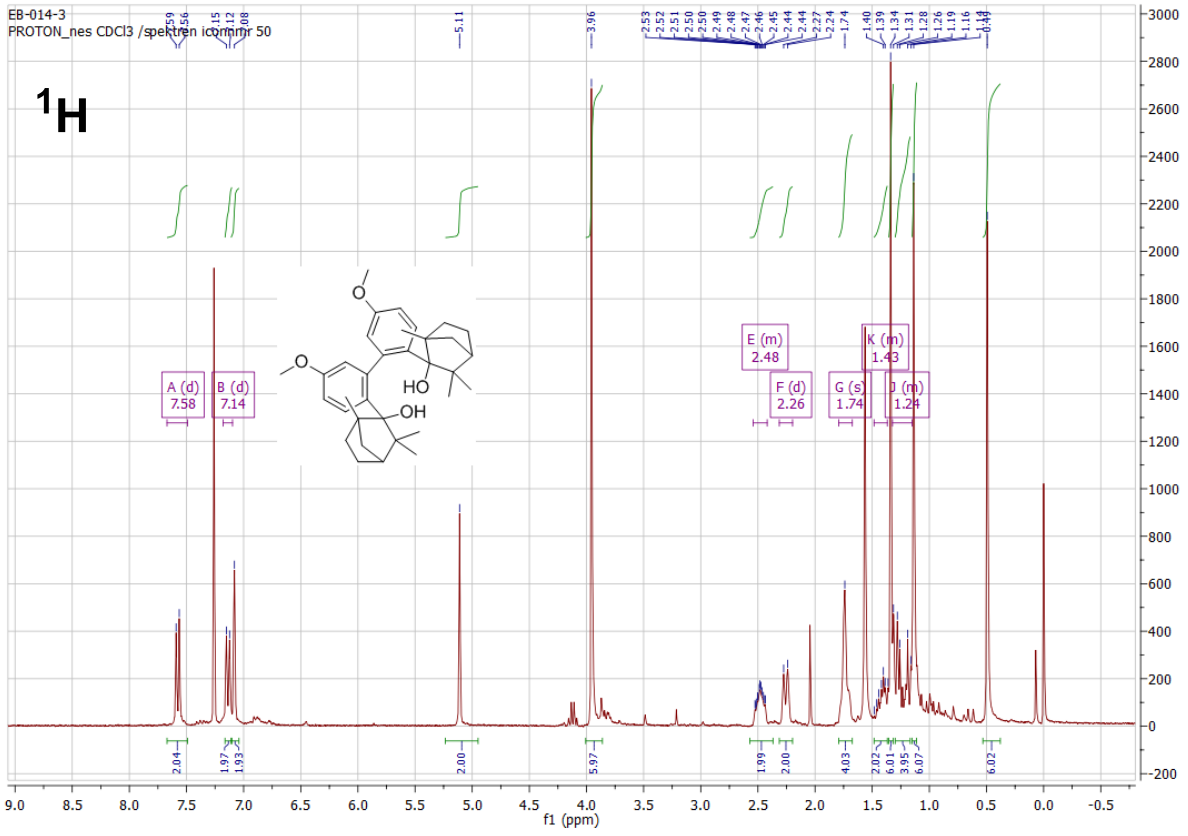
^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.51 (d, 2H, ^3J = *9.0* Hz), 6.79 (dd, 2H, ^3J = *8.9, 2.8* Hz) 6.49 (d, 2H, ^3J = *2.9* Hz), 3.79 (s, 6H), 2.86 (s, 2H), 2.38 (d, 2H, ^3J = *10.3* Hz), 1.44–1.27 (m, 4H), 1.11 (s, 6H), 0.77 (s, 6H), 0.70 (s, 6H).

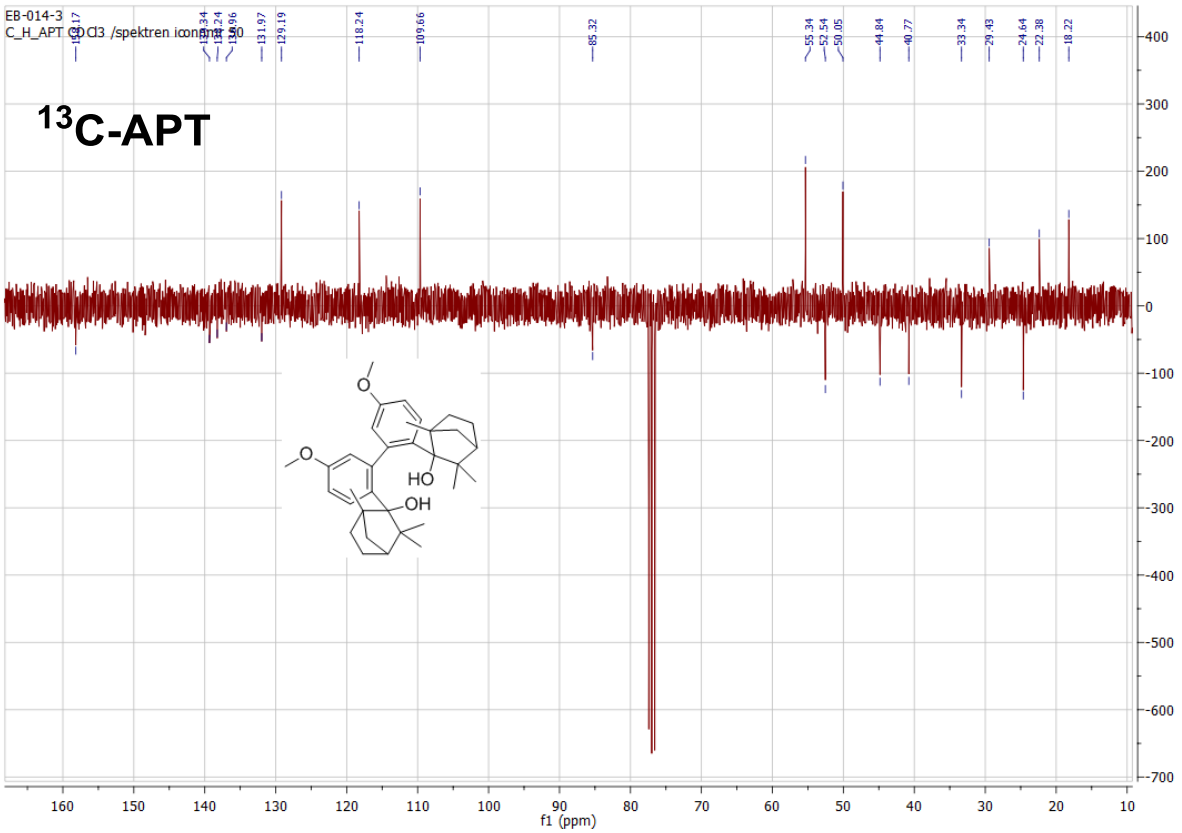
^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 155.46, 145.09, 133.62, 130.86, 116.25, 110.17, 85.01, 55.01, 54.64, 49.17, 46.43, 42.40, 33.93, 30.22, 23.78, 21.33, 17.61.

E.A.: calc. C: 78.72 found C: 78.68

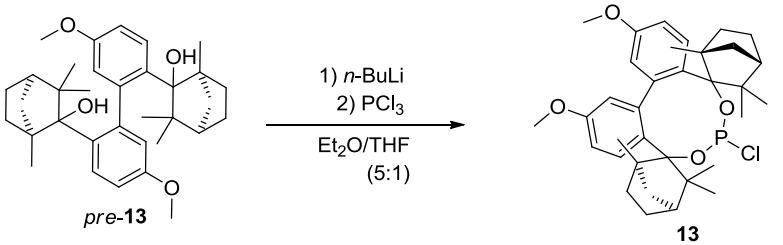
calc. H: 8.94 found H: 8.92

calc. N: 0.00 found N: 0.00





General procedure for the synthesis of 5,5'-dimethoxybiphenyl-2,2'-bisfenchol-chloro phosphite ($(MeO)_2$-BIFOP-Cl; EB-BIFOP-Cl)



pre-**13**
$(MeO)_2$-BIFOL
(EB-BIFOL)

13
$(MeO)_2$-BIFOP-Cl
(EB-BIFOP-Cl)

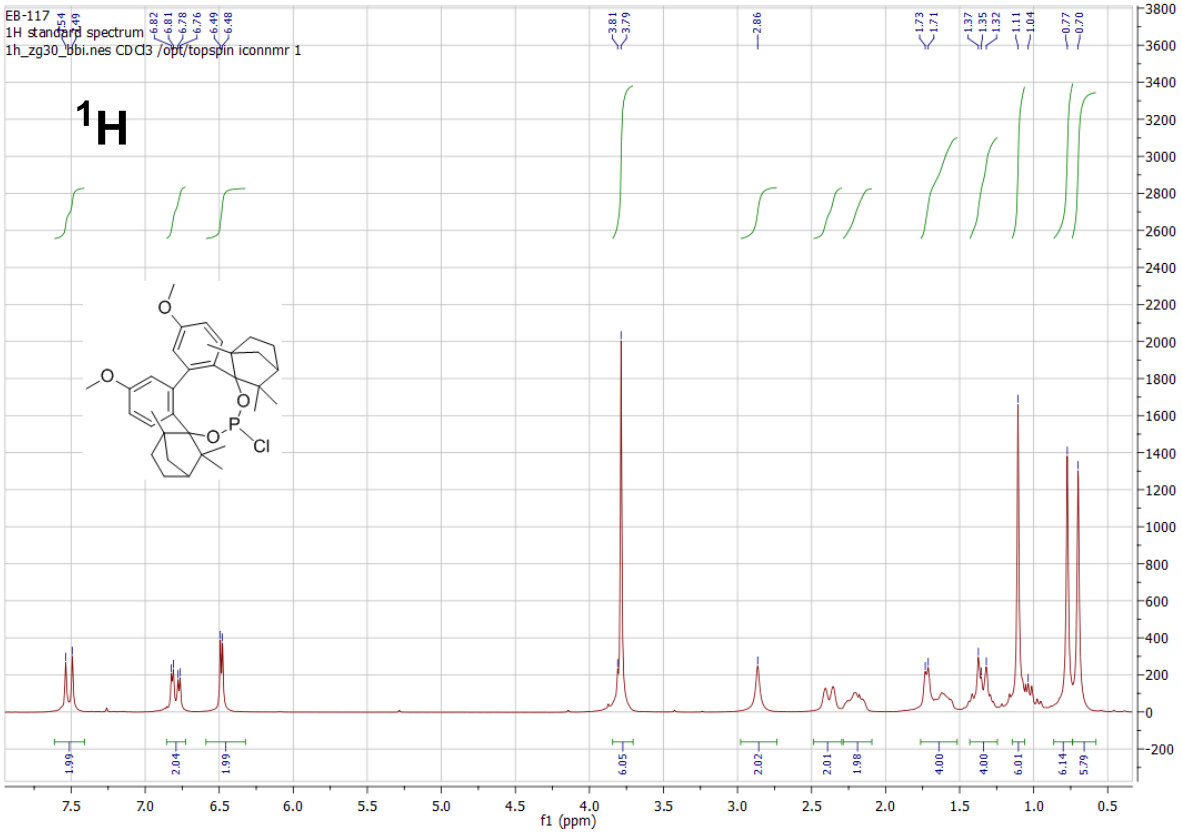
5,5'-dimethoxybiphenyl-2,2'-bisfenchol (*pre*-**13**, EB-BIFOL, 6.7 mmol, 3.5 g, 1.0 eq.) is dissolved in an appropriate dried and Ar-flushed *Schlenk* flask with dried and absolute Et_2O (20 mL). To the mixture *n*-BuLi (2.5 M, 14.1 mmol, 5.7 mL, 2.1 eq.) is added carefully and stirred for 2 h at room temperature. The slight pink solution (can be black with excess of *n*-BuLi) is cooled with an ice bath to 0°C and PCl_3 (7.1 mmol, 0.6 mL, 1.1 eq.) is added dropwise. The mixture is stirred for 10 min at 0°C then the ice bath is separated and the solution stirred over night, filtered over 2 cm of dried celite with the help of a reverse frit washed with dried and absolute Et_2O (10 mL). The product is highly unstable in the presence of air and moist. The solvent of the filtered solution is evaporated into a cooling trap under *vacuo* to receive the desired product 5,5'-dimethoxybiphenyl-2,2'-bisfenchol-chloro phosphite (**13**, EB-BIFOP-Cl) as a colorless white powder (3.9 mmol, 2.3 g, 58% yield).

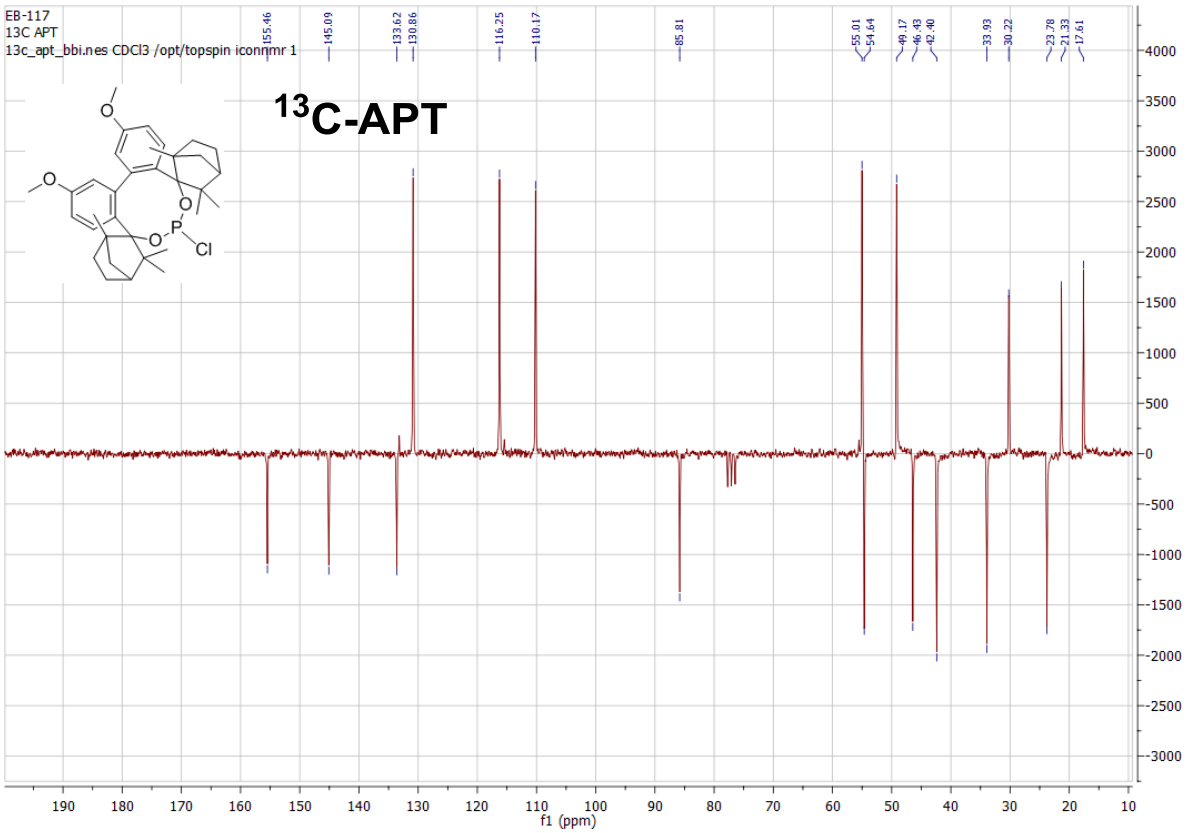
^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.58 (d, 2H, ^{3}J = *8.2* Hz), 7.14 (d, 2H, ^{3}J = *8.2* Hz), 7.08 (s, 2H), 5.11 (s, 2H), 3.96 (s, 6H), 2.53–2.44 (m, 2H), 2.26 (d, 2H, ^{3}J = *10.5* Hz), 1.74 (s, 4H), 1.48–1.36 (m, 2H), 1.34 (s, 6H), 1.31–1.16 (m, 4H), 1.14 (s, 6H), 0.49 (s, 6H).

^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 158.17, 139.34, 138.24, 136.96, 131.97, 129.19, 118.24, 109.66, 85.32, 55.34, 52.54, 50.05, 44.84, 40.77, 33.34, 29.43, 24.64, 22.38, 18.22.

^{31}P-NMR: (125.5 MHz, $CDCl_3$): δ [ppm] = 154.3; ^{1}J(P-Cl) = *6.6* Hz.

E.A.:	calc. C: 70.03	found C: 70.17
	calc. H: 8.94	found H: 9.12
	calc. N: 0.00	found N: 0.00

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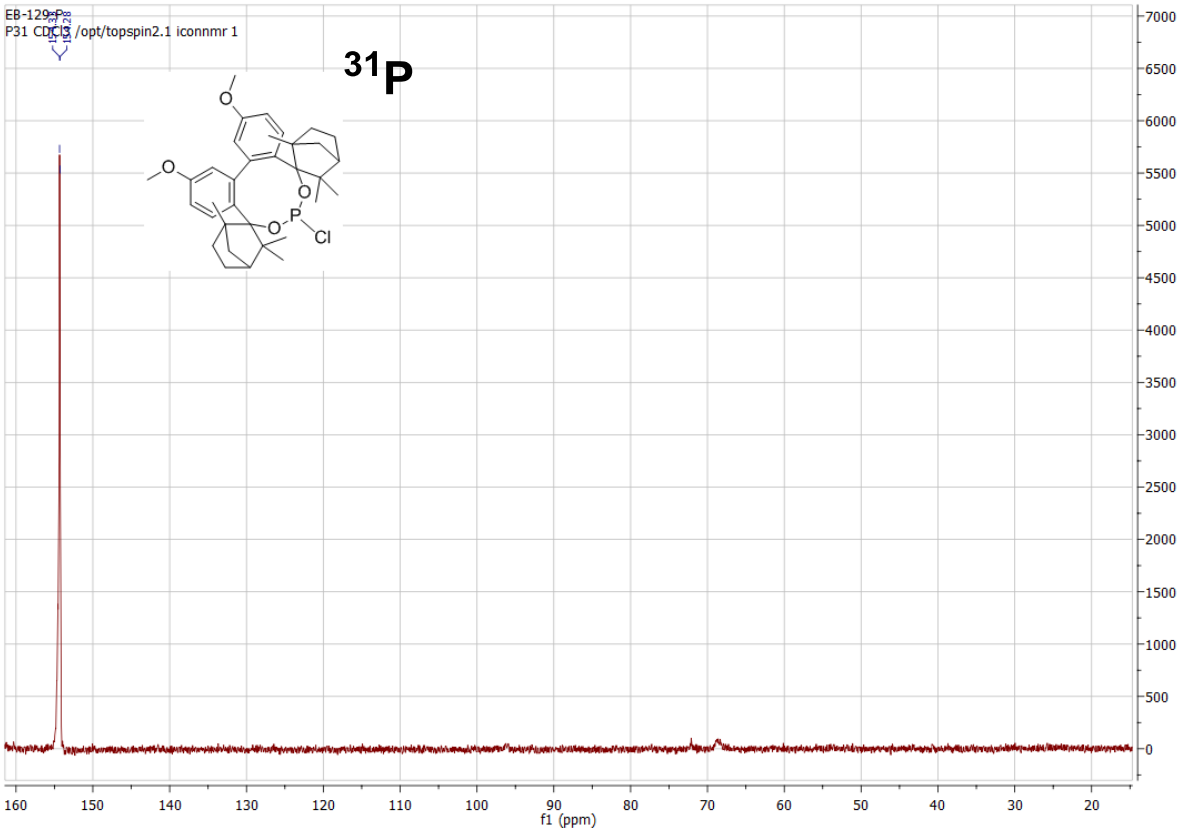
145.09
133.62
130.86
116.25
110.17
85.81
55.01
54.64
49.17
46.43
42.40
33.93
30.22
23.78
21.33
17.61
13C-APT
f1 (ppm)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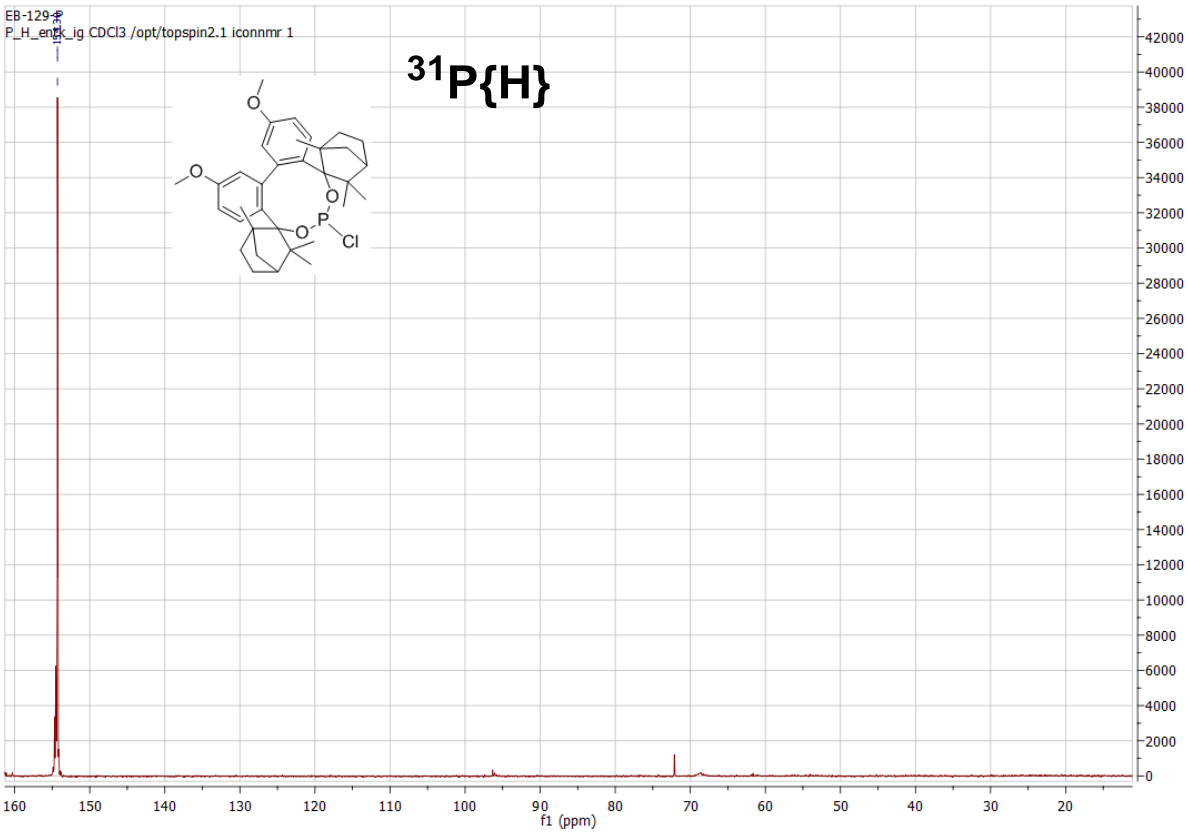
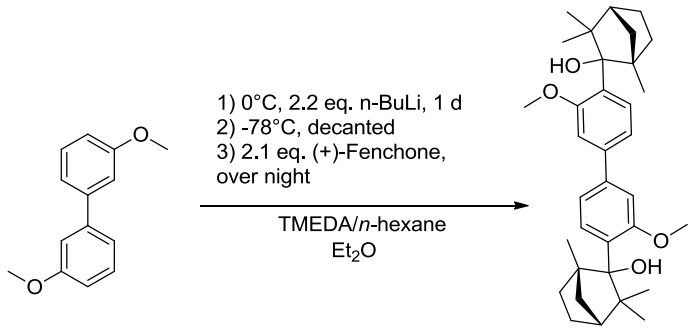
31P
f1 (ppm)



General procedure for the synthesis of 3,3'-dimethoxybiphenyl-4,4'-bisfenchol (DIME-BIFOL)



(3,3'-dimethoxybiphenyl)

22

(DIME-BIFOL)

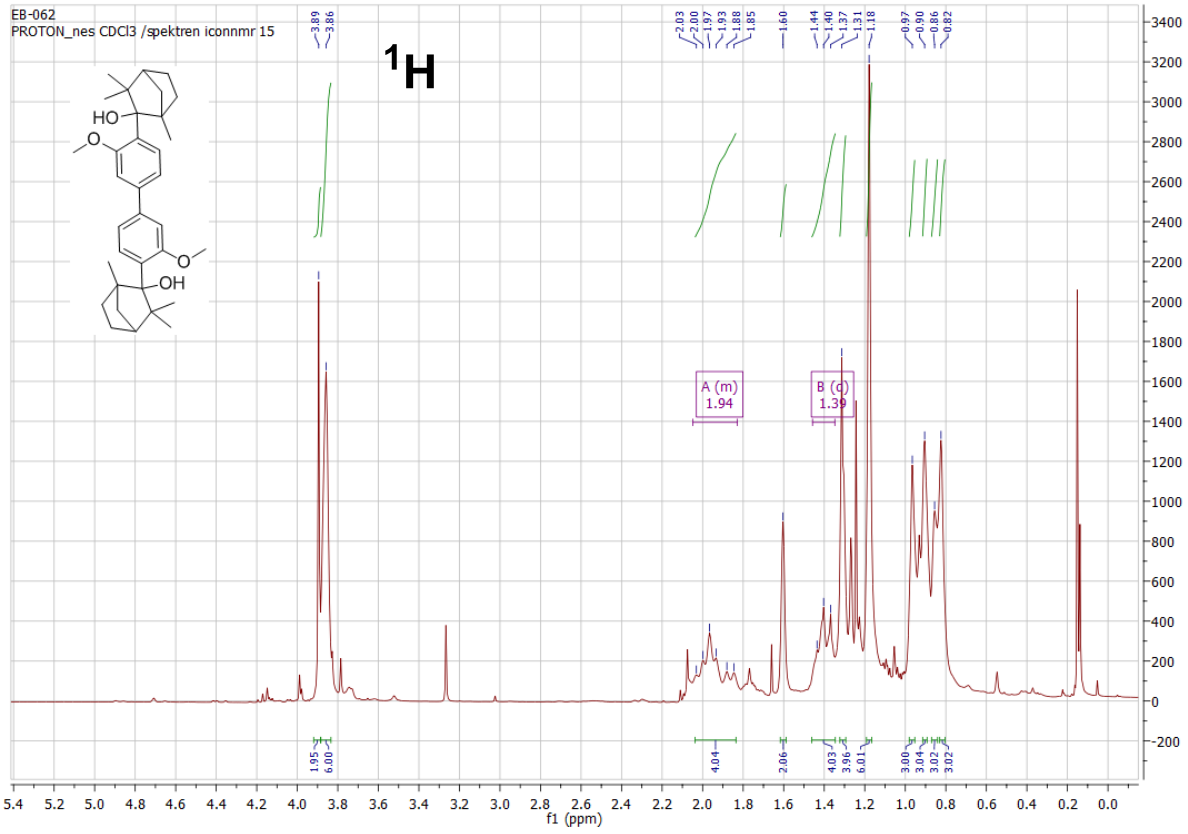
3,3'-dimethoxybiphenyl ([1], 21.9 mmol, 4.7 g, 1.0 eq.) is added in an appropriate dried and Ar-flushed *Schlenk* flask with dripping flunnel and is dissolved in dried TMEDA (48.0 mmol, 7.2 mL, 2.2 eq.) and cooled with an ice bath to 0°C. *n*-BuLi (2.5 M, 48.0 mmol, 19.2 mL, 2.2 eq.) is putted into the dripping funnel and dropped within 1 h to the mixture at 0°C. After 1 d, the the solution is taken to the cooler and kept there for 4 h at -20°C. A cooling bath with -78°C is prepared for the *Schlenk* flask and the solution is separated from the yellow crystals (the crystals can be freezed to the bottom of the flask so that the solution can easily be decanted and the rest of the remaining solution can be separated *via* a syringe, 9.5 mmol, 4.4 g, 43% yield). The crystals are dissolved in 15 mL dried and absolute Et_2O. To the solution (+)-Fenchone (46.0 mmol, 7.4 mL, 2.1 eq.) is added dropwise and the solution turned to a green (petrol) color. The mixture is stirred over night at room temperature and

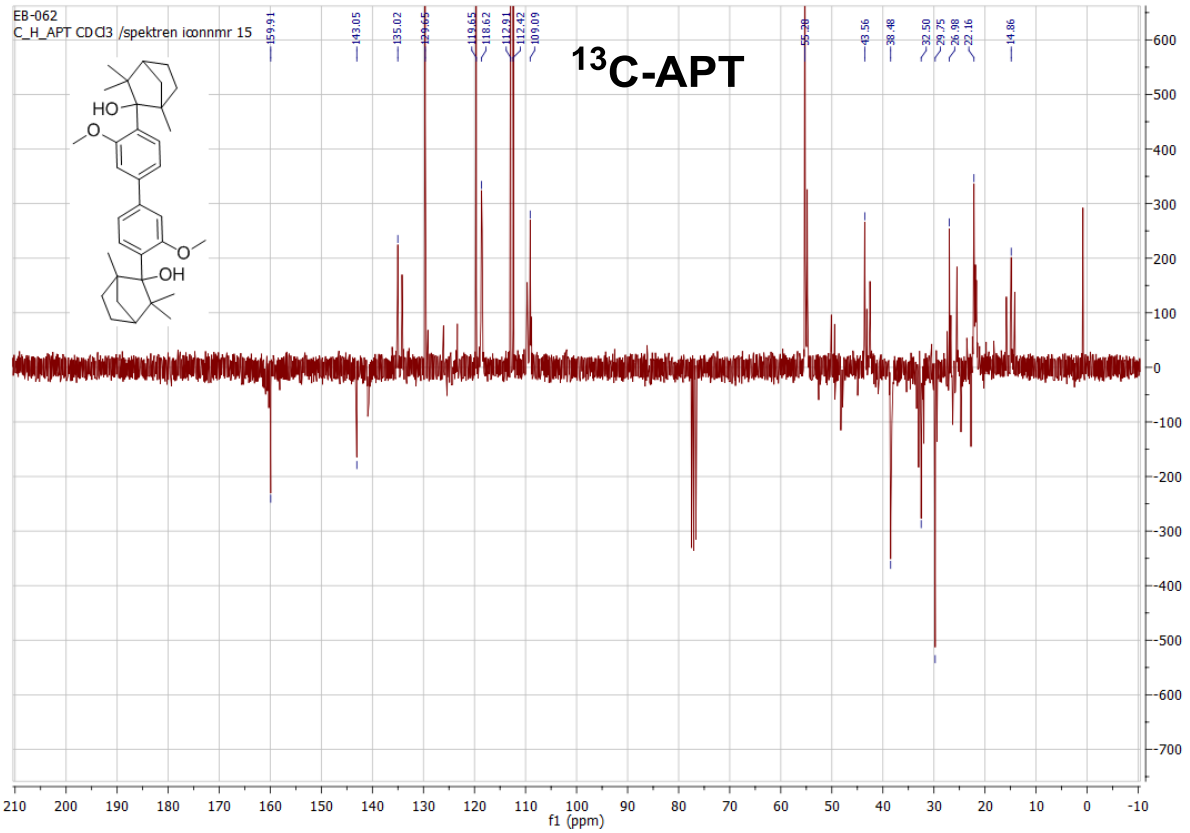
quenched with saturated aqueous NH_4Cl solution (10 mL). The mixture is separated and the water layer is extracted with DCM (2×10 mL). The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by crystallization and recrystallization from acetone afforded the desired product 3,3'-dimethoxybiphenyl-4,4'-bisfenchol (**22**) as fine colorless needles (2.3 mmol, 1.2 g, 11% yield).

^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.30–7.16 (m, 3H), 7.14–7.10 (m, 3H) 3.89 (s, 2H), 3.86 (s, 6H), 2.03–1.85 (m, 4H), 1.60 (s, 2H), 1.39 (t, 4H, ^{3}J = *10.5* Hz), 1.31 (s, 4H), 1.18 (s, 6H), 0.97 (s, 3H), 0.90 (s, 3H), 0.86 (s, 3H), 0.82 (s, 3H).

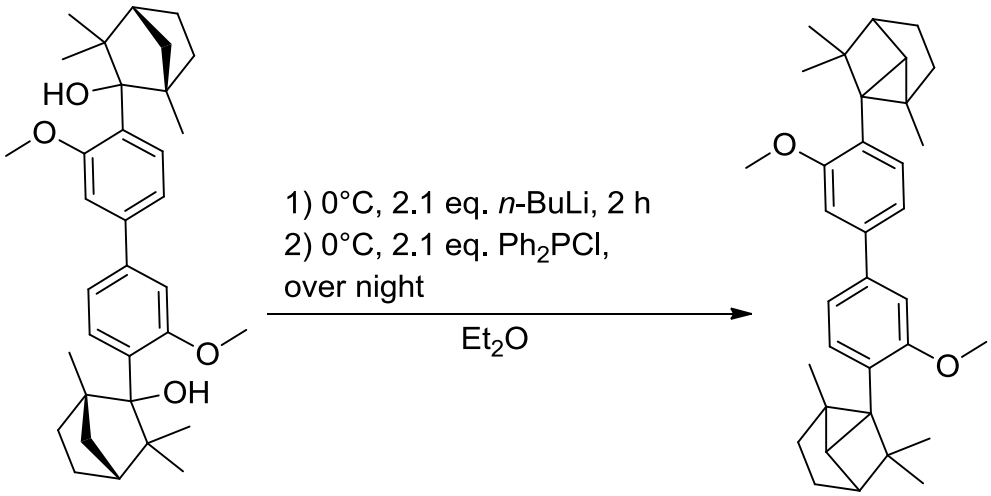
^{13}C-NMR: ($CDCl_3$): δ [ppm] = 159.91, 143.05, 135.02, 129.66, 119.65, 118.62, 112.91, 112.42, 109.09, 55.20, 43.56, 38.48, 32.50, 29.75, 26.98, 22.16, 14.86.

E.A.:	calc. C: 78.72	found C: 78.92
	calc. H: 8.94	found H: 9.15
	calc. N: 0.00	found N: 0.00





Synthesis attempt of 3,3'-dimethoxybiphenyl-4,4'-bisfenchol phosphite (DIME-BIFOP-Ph_2) gave a carbocationic rearranged product



22 **23**

3,3'-dimethoxybiohenyl-4,4'-bisfenchol (**22**, 2.3 mmol, 1.2 g, 1.0 eq.) is dissolved in dried and absolute Et_2O (10 mL). The mixture is cooled with an ice bath to 0°C and *n*-BuLi (2.5 M, 4.8 mmol, 1.9 mL, 2.1 eq.) is added dropwise, the ice bath is separated and the solution is stirred for 2 h at room temperature. The slight pink solution (can be black with excess of *n*-BuLi) is cooled again with an ice bath to 0°C and Ph_2PCl (4.8 mmol, 0.9 mL, 2.1 eq.) is added dropwise and stirred over night at room temperature and quenched with saturated aqueous NH_4Cl solution (5 mL) and separated, where the water layer is extracted with DCM (2×5 mL).

The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by crystallization and recrystallization from acetone afforded a carbocationic rearranged product 3,3'-dimethoxy-4,4'-bis(2,6,6-trimethyltricyclo[3.2.0.0^{2,7}]heptane (**23**, 2.0 mmol, 0.96 g, 87% yield).

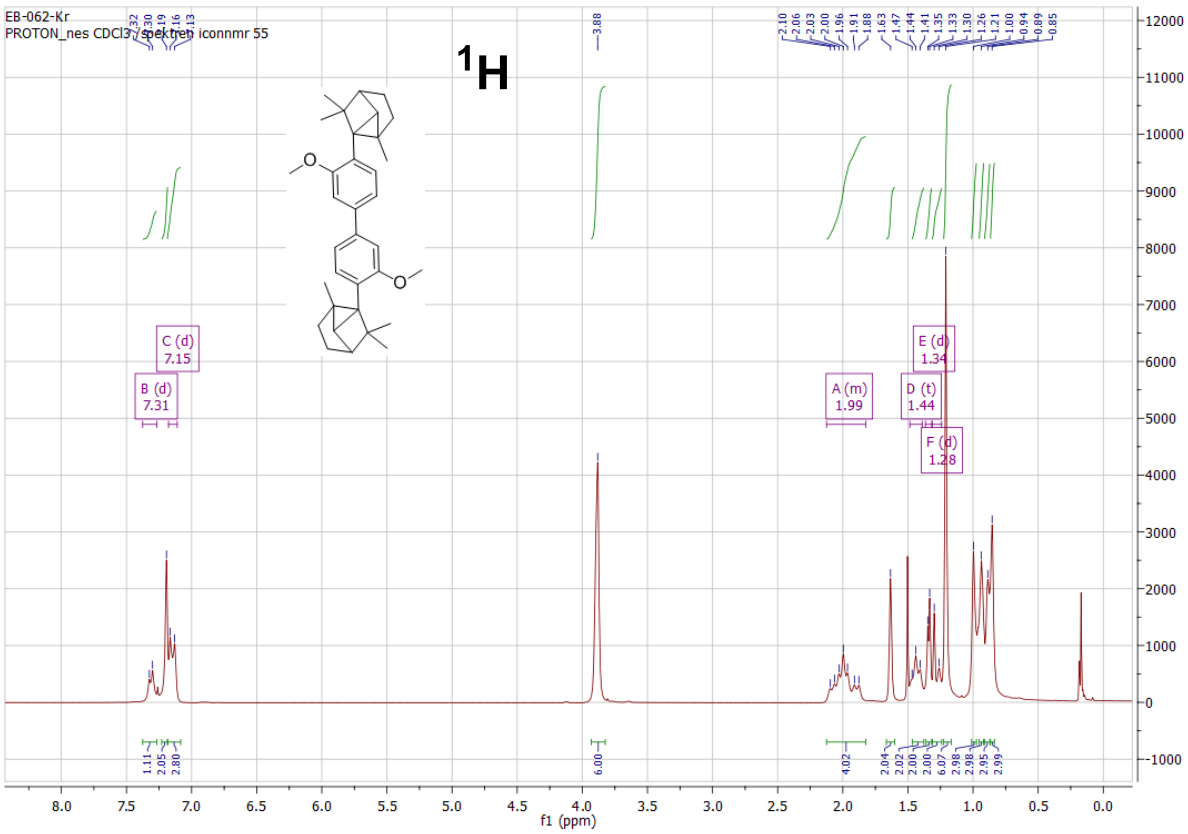
^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.31 (d, 1H, ^{3}J = *7.3* Hz), 7.19 (s, 2H), 7.15 (d, 3H, ^{3}J = *10.4* Hz), 3.88 (s, 6H), 2.10–1.88 (m, 4H), 1.63 (s, 2H), 1.44 (t, 2H, ^{3}J = *7.3* Hz), 1.35–1.26 (m, 4H), 1.21 (s, 6H), 1.00 (s, 3H), 0.94 (s, 3H), 0.89 (s, 3H), 0.85 (s, 3H).

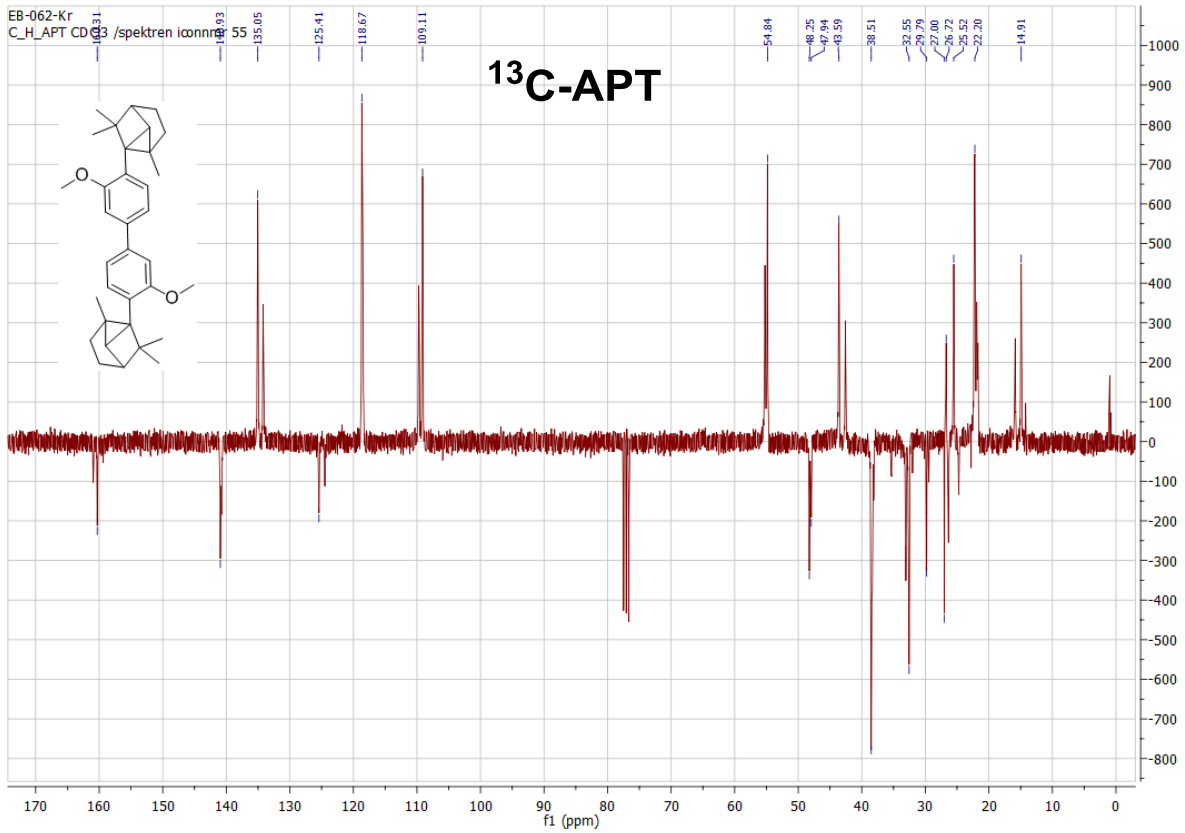
^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 160.31, 140.93, 135.06, 125.41, 118.67, 109.11, 54.84, 48.25, 47.94, 43.59, 38.51, 32.55, 29.79, 27.00, 26.72, 25.52, 22.20, 14.91.

E.A.: calc. C: 84.60 found C: 84.73

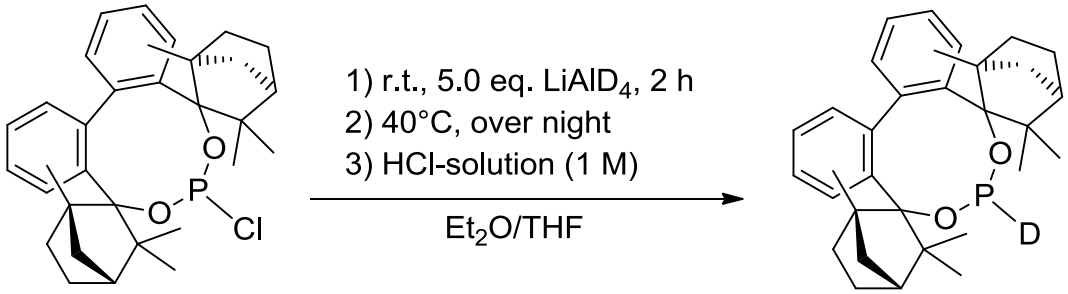
calc. H: 8.77 found H: 8.93

calc. N: 0.00 found N: 0.00





General procedure for the synthesis of biphenyl-2,2'-bisfenchol-deutero phosphite (BIFOP-D)



7 **10**

Biphenyl-2,2'-bisfenchol-chloro phosphite (**7** [3], 9.6 mmol, 5.0 g, 1.0 eq.) is dissolved in an appropriate dried and Ar-flushed *Schlenk* flask with reflux condenser and drying tube with dried and absolute Et_2O (60 mL) and dried and absolute THF (10 mL). To the mixture solid $LiAlD_4$ (48.0 mmol, 2.0 g, 5.0 eq.) is added portionwise during Ar-flushing and stirred for 2 h at room temperature. Then the mixture is heated to 40°C over night and carefully quenched with 1 M aqueous HCl solution (20 mL) and separated, where the water layer is extracted with DCM (2×20 mL). The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by crystallization and recrystallization from DCM afforded the desired product biphenyl-2,2'-bisfenchol-deutero phosphite (**10**) as fine colorless needles (7.8 mmol, 3.8 g, 81% yield).

m.p.: 180°C.

$[\alpha]^{589}_{20}$: +39.1° (c = 0.5, $CHCl_3$).

^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.64 (d, 2H, ^3J = *8.1* Hz), 7.24 (d, 2H, ^3J = *7.5* Hz), 7.14 (t, 2H, ^3J = *7.4* Hz), 6.94 (d, 2H, ^3J = *7.4* Hz), 2.89 (s, 1H), 2.44 (d, 2H, ^3J = *10.3* Hz), 2.22 (t, 2H, ^3J = *10.2* Hz), 1.74 (d, 2H, ^3J = *3.6* Hz), 1.66 (d, 1H, ^3J = *3.6* Hz), 1.38 (m, 4H), 1.14 (s, 6H), 1.07 (td, 2H, ^3J = *12.3*, *4.8* Hz), 0.74 (s, 6H), 0.69 (s, 6H).

^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 144.07, 141.21, 131.11, 129.92, 124.78, 124.37, 68.14, 54.71, 49.20, 46.49, 42.53, 34.06, 30.06, 23.72, 21.23, 17.93.

^{31}P-NMR: (125.5 MHz, $CDCl_3$): δ [ppm] = 138.0; ^1J(P-H) = *213.5* Hz.

E.A.:

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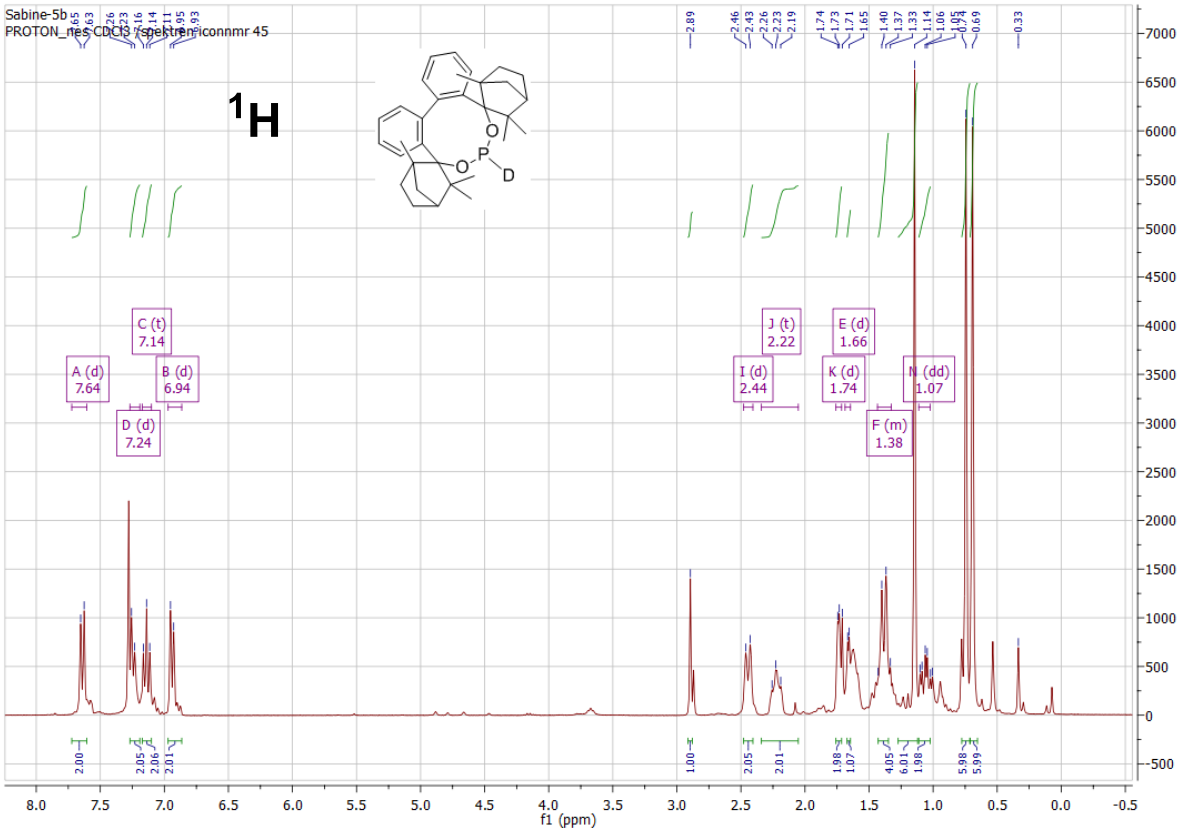
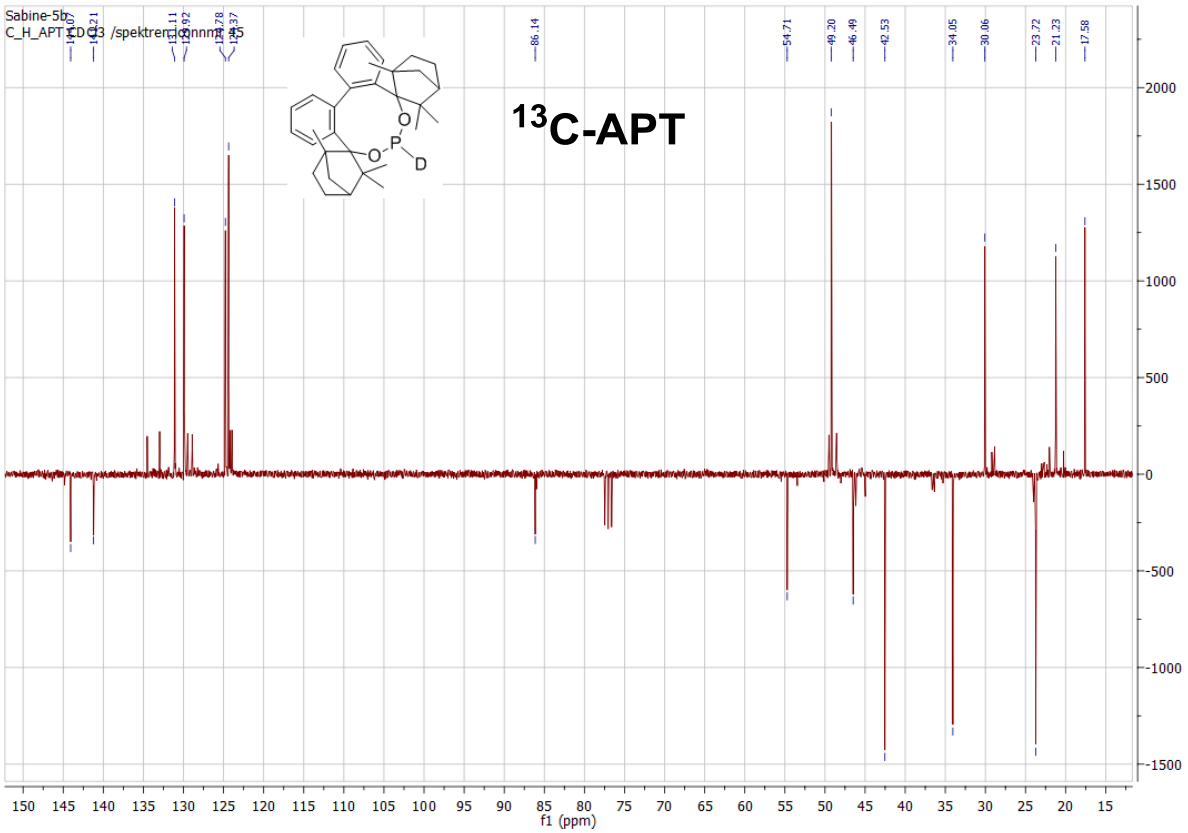
calc. H: 8.65	found H: 8.81
calc. N: 0.00	found N: 0.00

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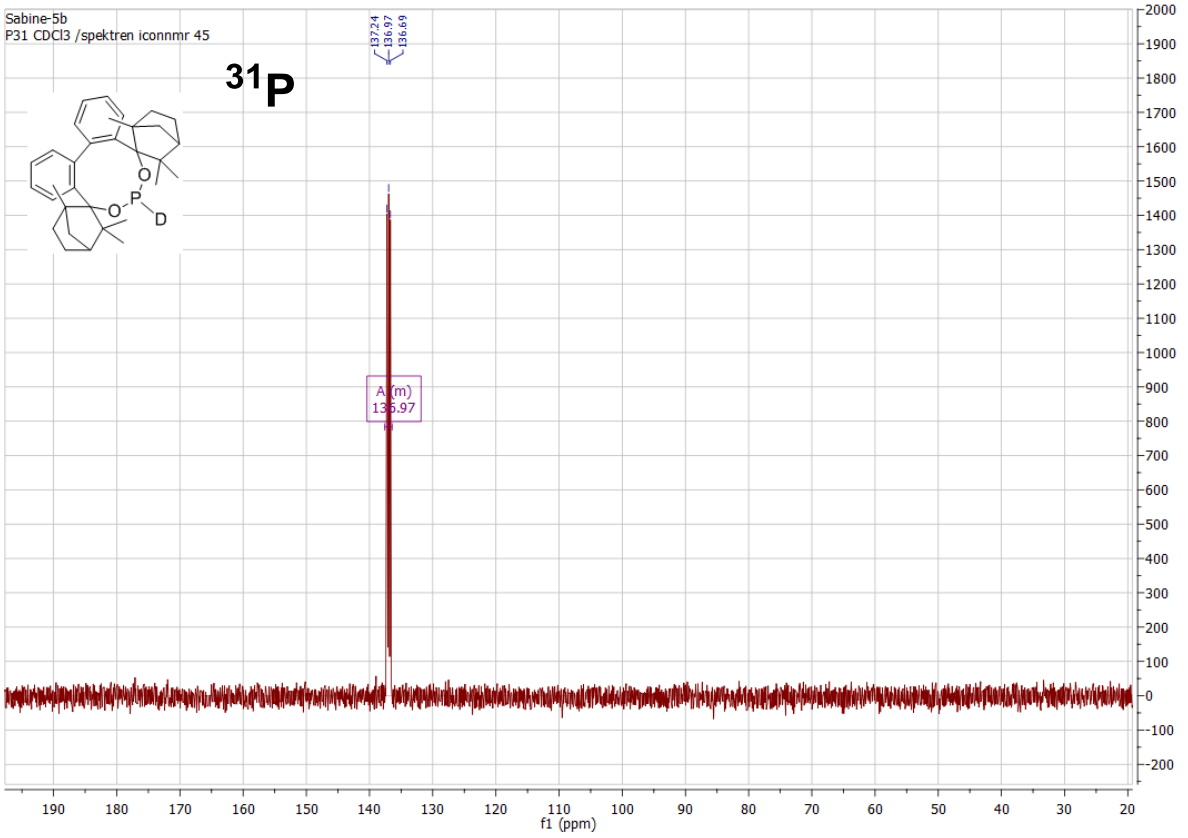
^{13}C-APT
f1 (ppm)


Sabine-5b
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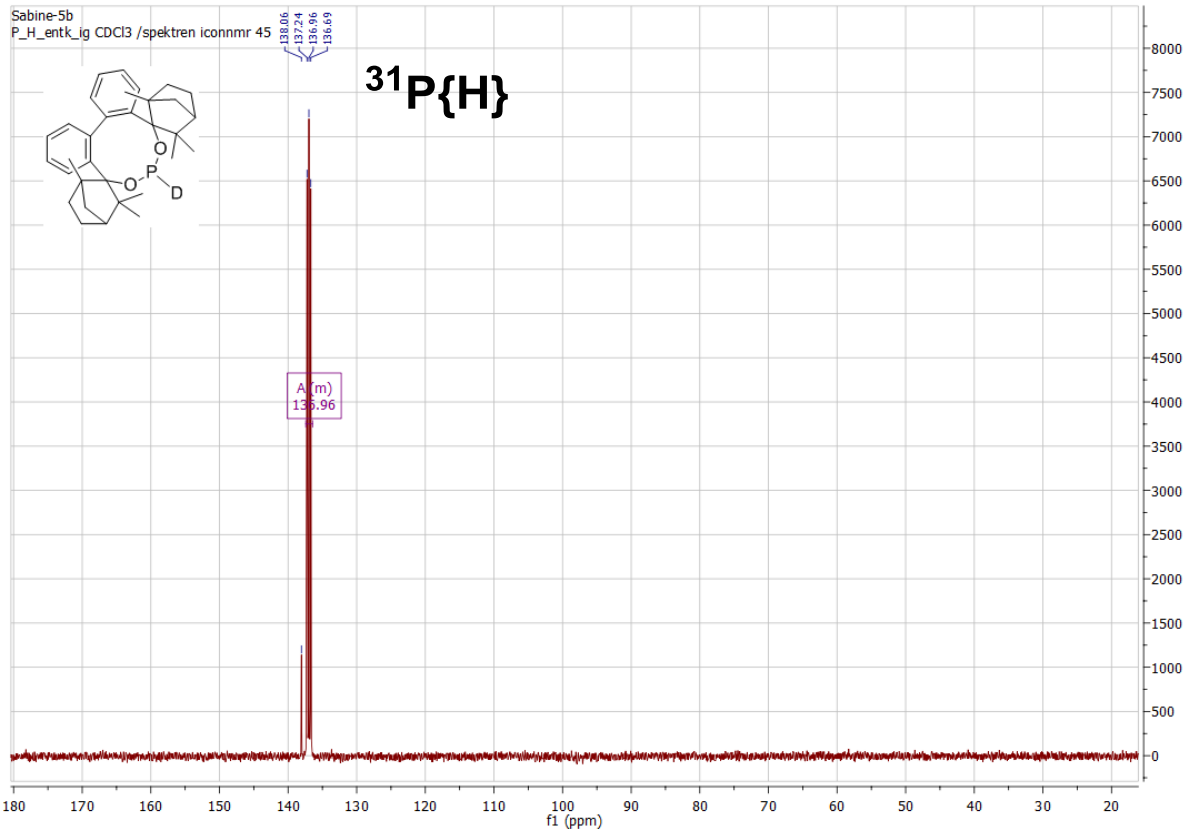
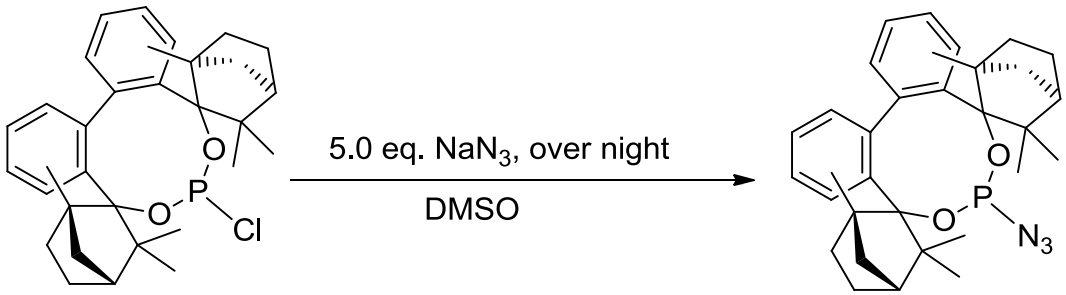
^{31}P
A (m)
135.97
f1 (ppm)



General procedure for the synthesis of biphenyl-2,2'-bisfenchol-azido phosphite (BIFOP-N_3)



7 **11**

Biphenyl-2,2'-bisfenchol-chloro phosphite (**7** [3], 9.6 mmol, 5.0 g, 1.0 eq.) is dissolved in an appropriate dried and Ar-flushed *Schlenk* flask with dried DMSO (40 mL). To the mixture NaN_3 (48.0 mmol, 3.1 g, 5.0 eq.) is added and stirred over night at room temperature. The solution is quenched with saturated aqueous NH_4Cl solution (20 mL) and separated, where the water layer is extracted with EtOAc/cyclohexane (1:1, 2×30 mL). The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by crystallization and recrystallization from acetone afforded the desired product biphenyl-2,2'-bisfenchol-azido phosphite (**11**) as colorless crystals (7.2 mmol, 3.8 g, 75% yield).

m.p.: 147°C.

$[\alpha]^{589}_{20}$: +56.5° (c = 0.5, $CHCl_3$).

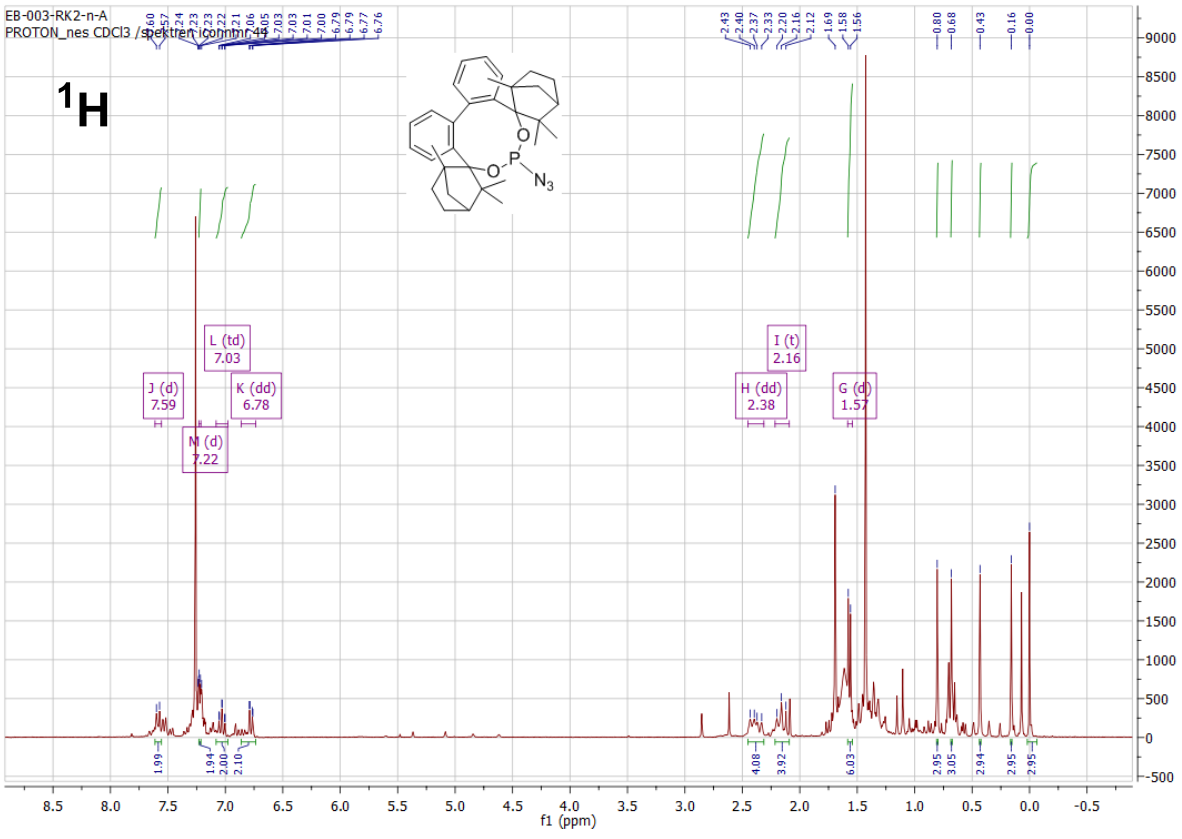
^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.59 (d, 2H, ^3J = *8.1* Hz), 7.22 (d, 2H, ^3J = *3.3* Hz), 7.03 (td, 2H, ^3J = *7.7*, *1.2* Hz), 6.78 (dd, 2H, ^3J = *7.7*, *1.5* Hz), 2.38 (dd, 4H, ^3J = *18.6*, *11.4* Hz), 2.16 (t, 4H, ^3J = *11.7* Hz), 1.57 (d, 6H, ^3J = *5.9* Hz), 0.80 (s, 3H), 0.68 (s, 3H), 0.43 (s, 3H), 0.16 (s, 3H), 0.00 (s, 3H).

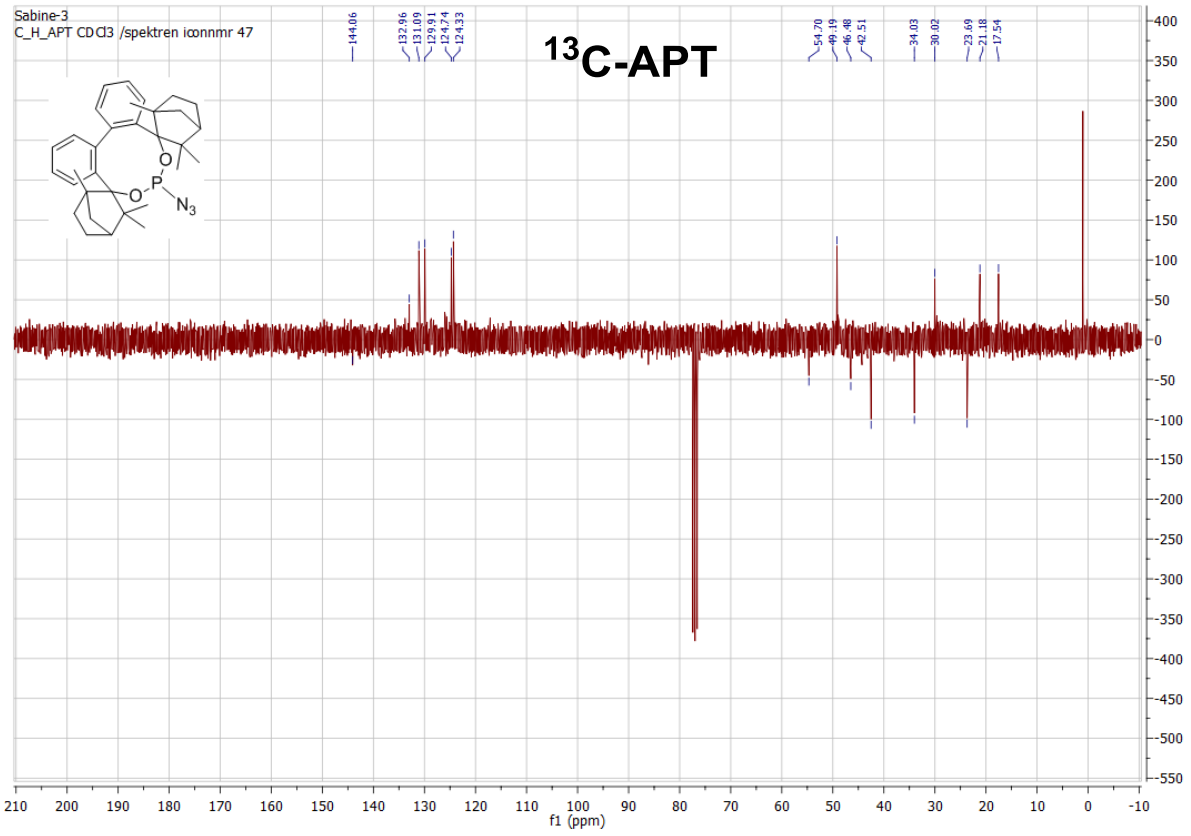
^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 145.14, 143.47, 141.43, 139.37, 136.21, 133.86, 129.15, 128.59, 126.00, 125.48, 125.10, 124.30, 94.27, 94.12, 56.10, 53.16, 51.13, 51.06, 50.31, 49.17, 48.03, 45.35, 44.74, 41.23, 36.14, 29.40, 28.56, 24.12, 23.78, 22.61, 20.53, 19.86.

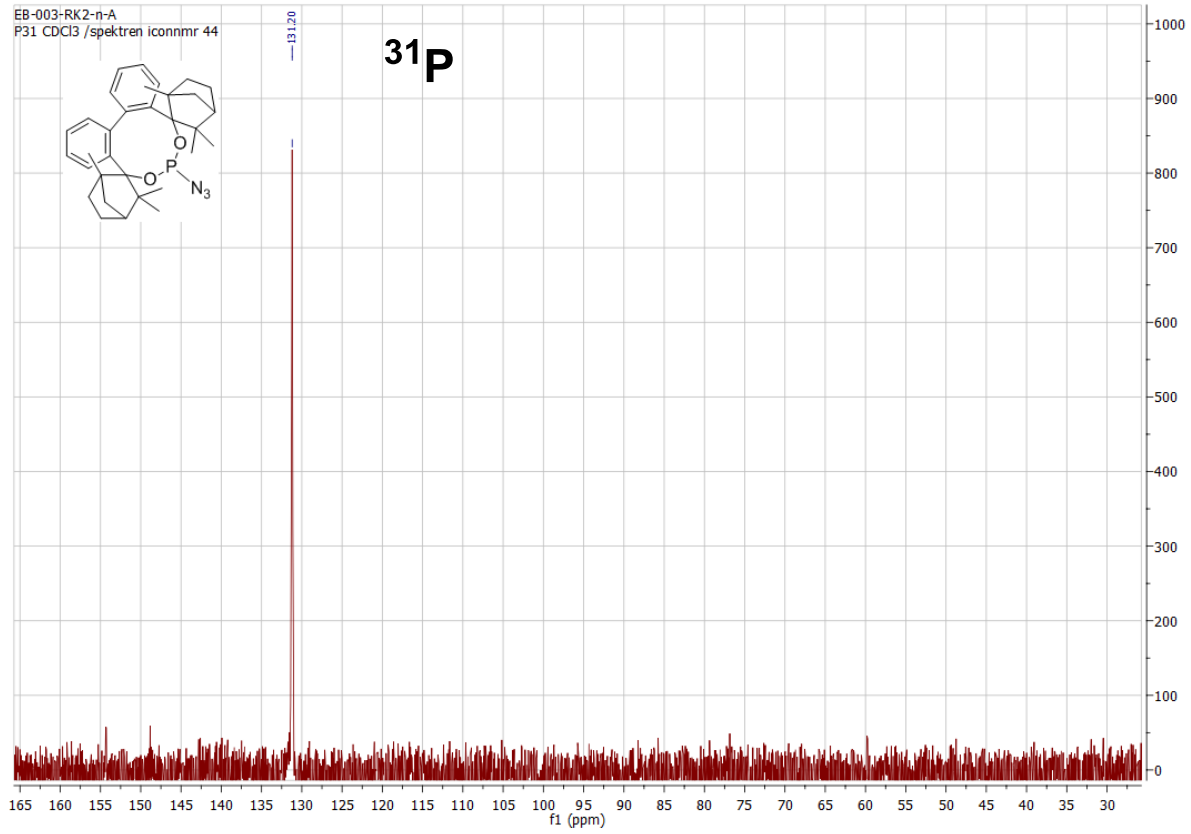
^{31}P-NMR: (125.5 MHz, $CDCl_3$): δ [ppm] = 131.2.

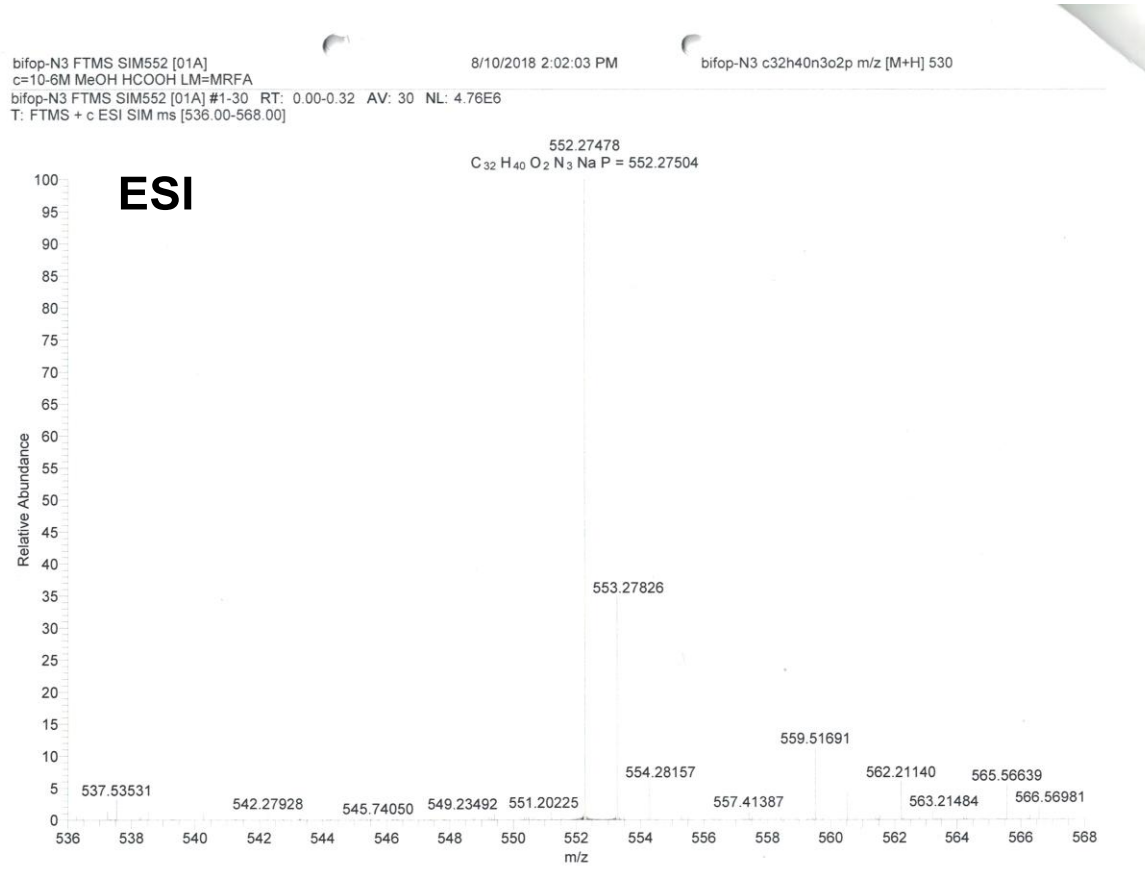
HR-mass: $[M + Na]^+(C_{32}H_{40}N_3O_2P)$ [u] = calc. mass: 552.27504; measured mass: 552.27478.

E.A.:	calc. C: 72.56	found C: 72.73
	calc. H: 7.61	found H: 7.80
	calc. N: 7.93	found N: 7.88

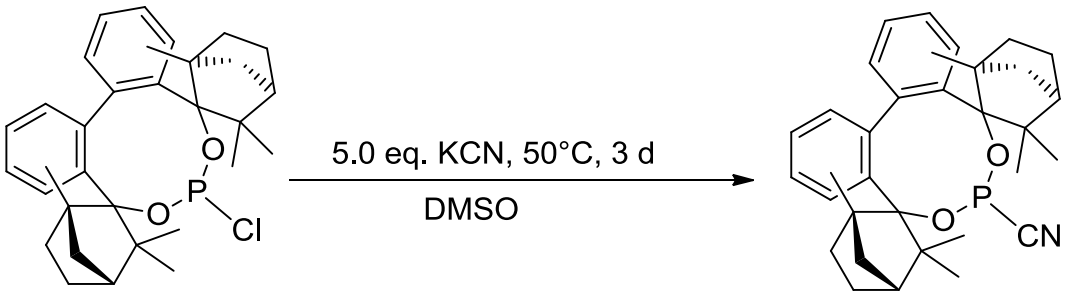



Sabine-3
C_H_APT CDCl3 /spektren iconnmr 47
144.06
132.96
131.09
129.91
124.74
124.33
54.70
49.19
46.48
42.51
34.03
30.02
23.69
21.18
17.54
13C-APT
f1 (ppm)


EB-003-RK2-n-A
P31 CDCl3 /spektren iconnmr 44
131.20
31P
f1 (ppm)



General procedure for the synthesis of biphenyl-2,2'-bisfenchol-cyanido phosphite (BIFOP-CN)



7 **12**

Biphenyl-2,2'-bisfenchol-chloro phosphite (**7** [3], 9.6 mmol, 5.0 g, 1.0 eq.) is dissolved in an appropriate dried and Ar-flushed *Schlenk* flask with dried DMSO (40 mL). To the mixture KCN (48.0 mmol, 3.1 g, 5.0 eq.) is added and stirred for 3 d at 50°C. The solution is quenched with saturated aqueous NH_4Cl solution (20 mL) and separated, where the water layer is extracted with EtOAc/cyclohexane (1:1, 2×30 mL). The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by crystallization and recrystallization from EtOAc/cyclohexane afforded the desired product niphenyl-2,2'-bisfenchol-cyanido phosphite (**12**) as colorless crystals (7.8 mmol, 4.0 g, 81% yield).

m.p.: 169-170°C.

$[\alpha]^{589}_{20}$: +52.8° (c = 0.5, $CHCl_3$).

^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.68 (d, 1H, ^3J = *8.1* Hz), 7.62–7.57 (m, 1H), 7.32 (d, 2H, ^3J = *4.6* Hz), 7.28–722 (m, 2H), 7.06 (td, 1H, ^3J = *7.7*, *1.0* Hz), 6.77 (dd, 1H, ^3J = *7.6*, *1.5* Hz), 2.53–2.27 (m, 4H), 1.87 (s, 3H), 1.85 (s, 3H), 1.51 (d, 4H, ^3J = *7.6* Hz), 1.43–1.27 (m, 4H), 0.88 (s, 3H), 0.74 (s, 3H), 0.39 (s, 3H), 0.05 (s, 3H).

^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 193.79, 174.55, 167.02, 162.64, 132.53, 126.60, 125.70, 125.09, 124.21, 50.31, 48.41, 17.40.

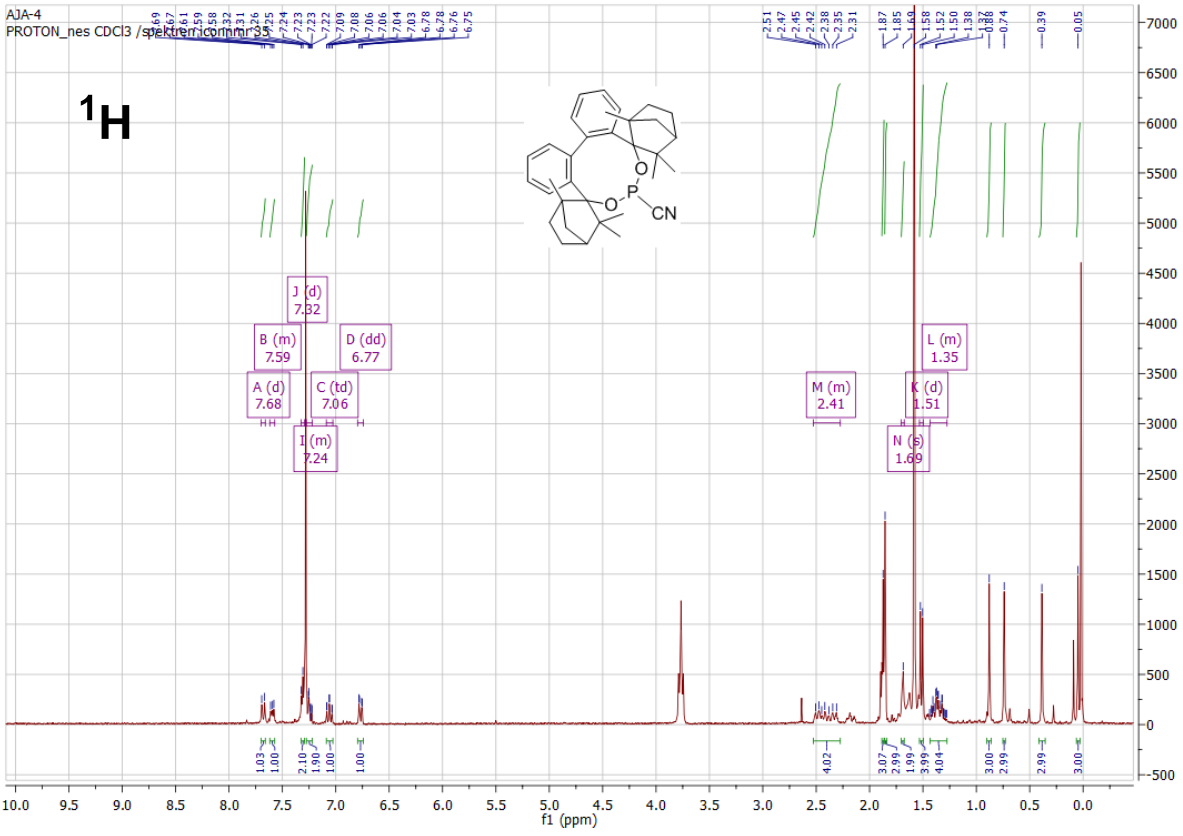
^{31}P-NMR: (125.5 MHz, $CDCl_3$): δ [ppm] = 104.8; ^1J(P-CN) = (t, *11.3* Hz).

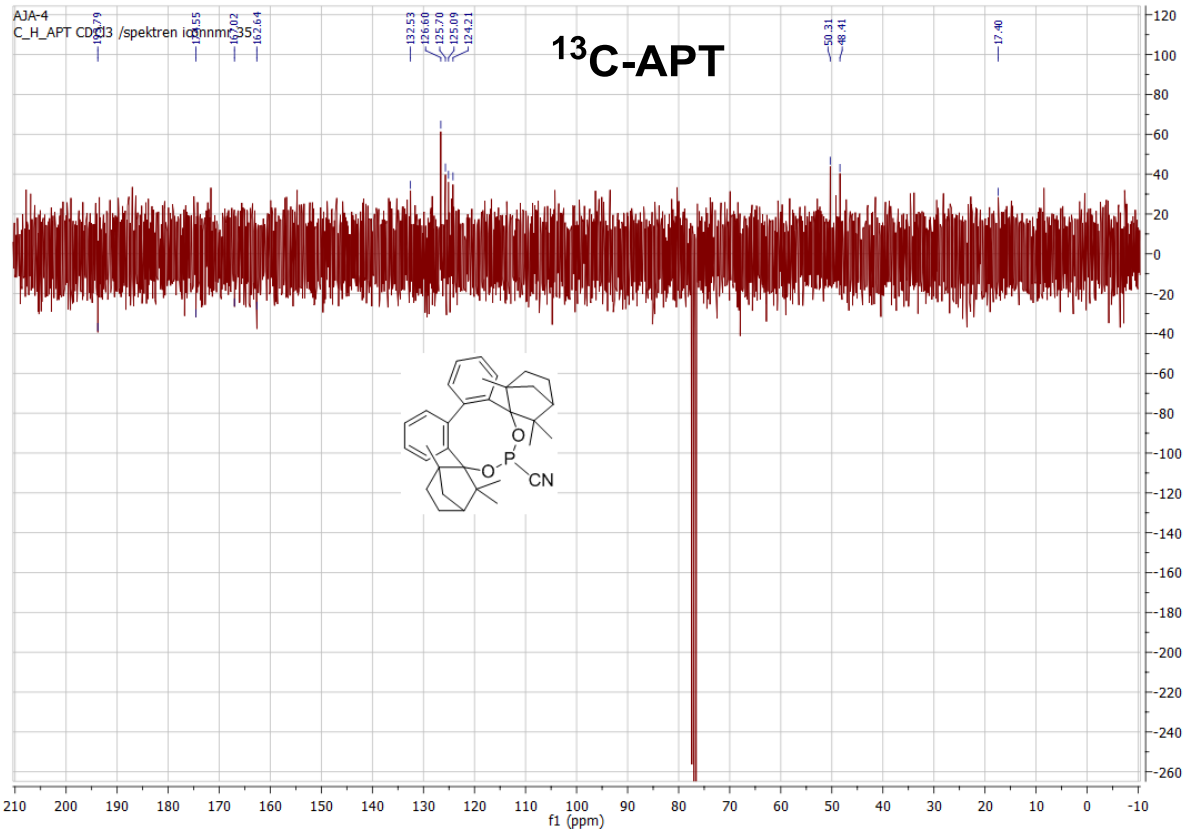
HR-mass: $[M + Na]^+(C_{33}H_{40}NO_2P)$ [u] = calc. mass: 536.26889; measured mass: 536.26911.

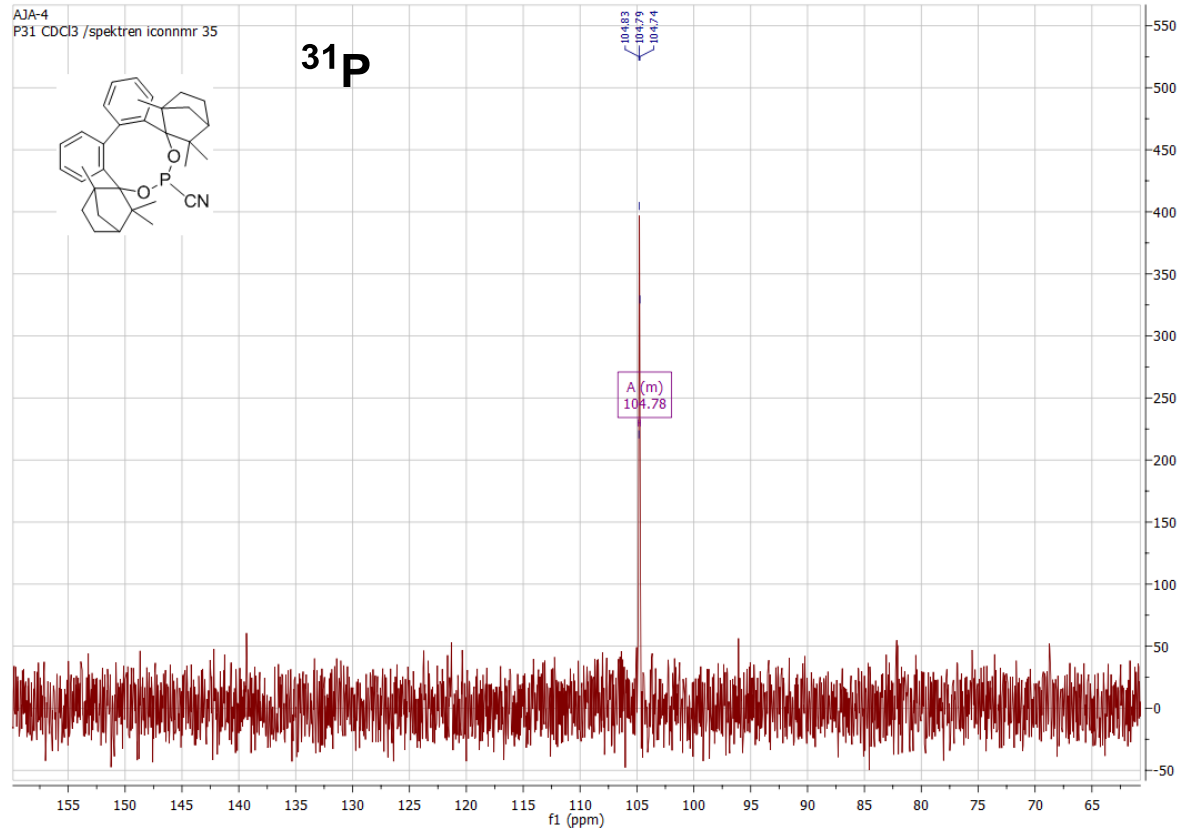
E.A.: calc. C: 77.16 found C: 77.23

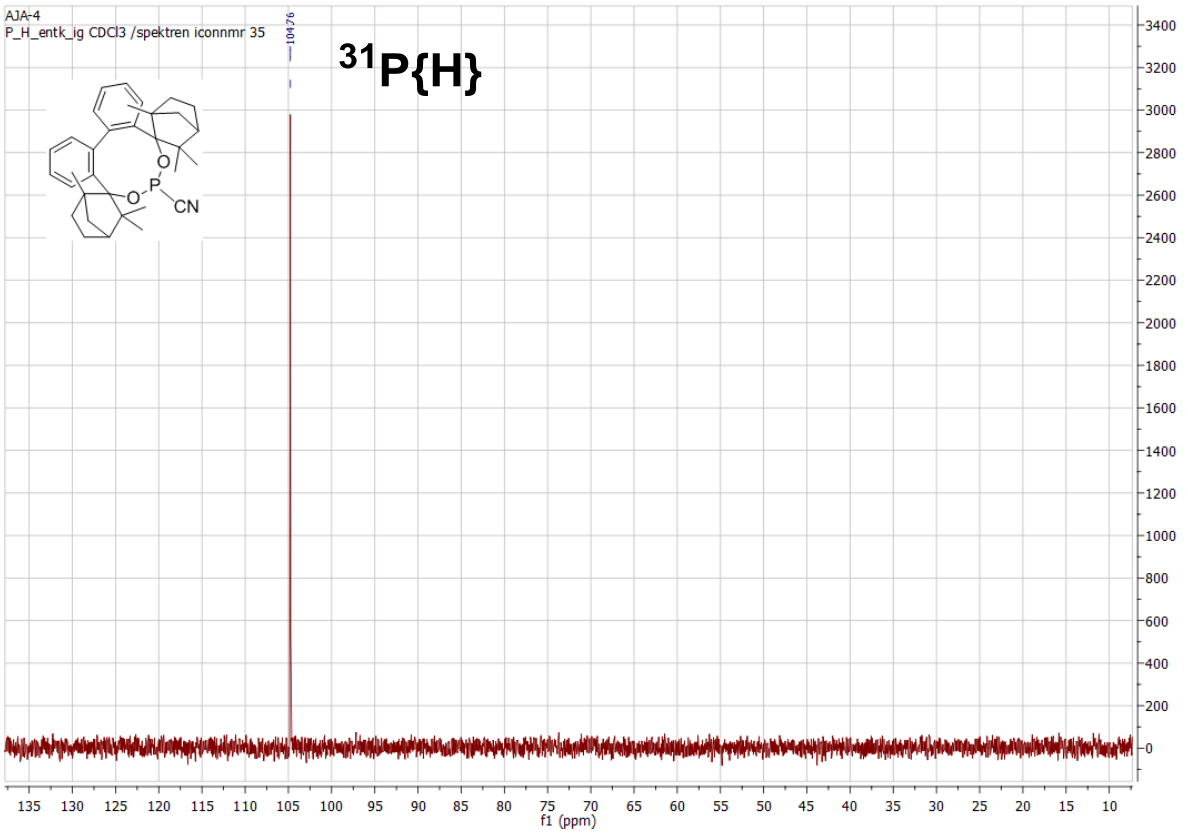
calc. H: 7.85 found H: 7.92

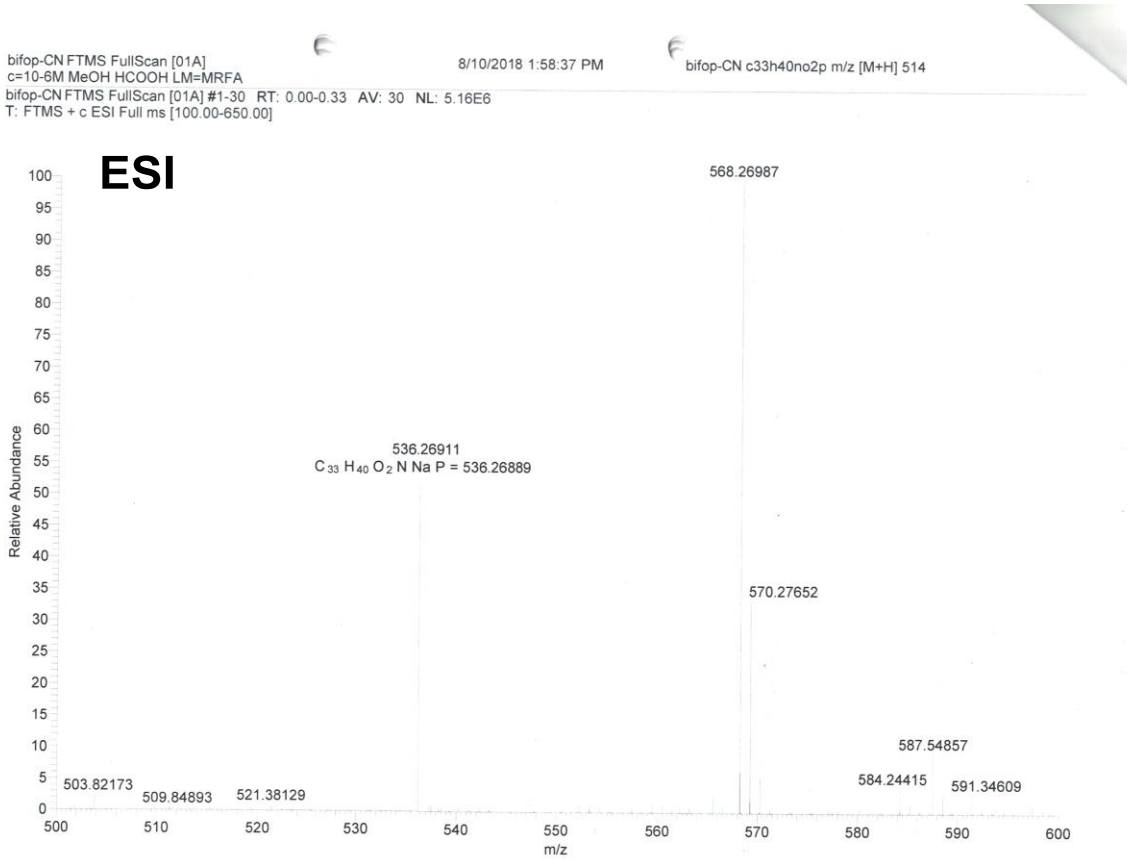
calc. N: 2.73 found N: 2.72



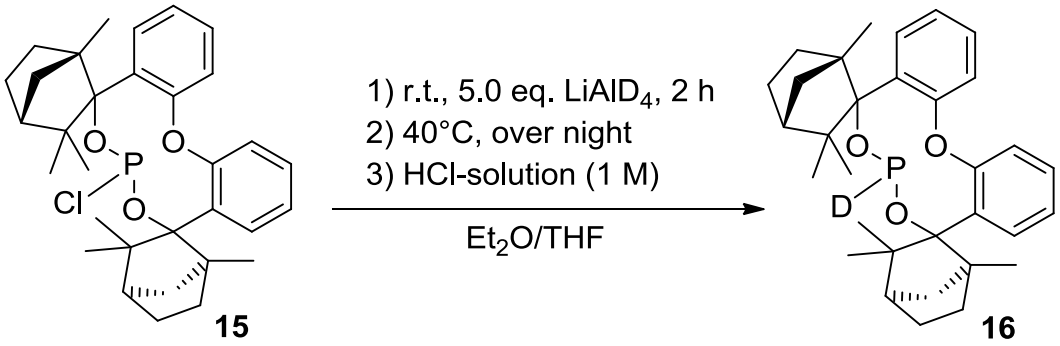

AJA-4
C_H_APT CDCl3 /spektren iconnmr 35
^{13}C-APT
132.53
126.60
125.70
125.09
124.21
50.31
48.41
17.40
O
O
P
CN
f1 (ppm)


AJA-4
P31 CDCl3 /spektren iconnmr 35
^{31}P
104.83
104.79
104.74
A (m)
104.78
O
O
P
CN
f1 (ppm)


AJA-4
P_H_entk_ig CDCl3 /spektren iconnmr 35
31P{H}
O
P
O
CN
f1 (ppm)


bifop-CN FTMS FullScan [01A]
c=10-6M MeOH HCOOH LM=MRFA
8/10/2018 1:58:37 PM
bifop-CN c33h40no2p m/z [M+H] 514
bifop-CN FTMS FullScan [01A] #1-30 RT: 0.00-0.33 AV: 30 NL: 5.16E6
T: FTMS + c ESI Full ms [100.00-650.00]
ESI
568.26987
536.26911
C33 H40 O2 N Na P = 536.26889
570.27652
587.54857
584.24415
591.34609
503.82173
509.84893
521.38129
Relative Abundance
m/z

General procedure for the synthesis of biphenyl-2,2'-bisfenchol-deutero phosphite (O-BIFOP-D)



Biphenylether-2,2'-bisfenchol-chloro phosphite (**15**, 9.3 mmol, 5.0 g, 1.0 eq.) is dissolved in an appropriate dried and Ar-flushed *Schlenk* flask with reflux condenser and drying tube with dried and absolute Et_2O (60 mL) and dried and absolute THF (10 mL). To the mixture solid $LiAlD_4$ (46.5 mmol, 1.9 g, 5.0 eq.) is added portionwise during Ar-flushing and stirred for 2 h at room temperature. Then the mixture is heated to 40°C over night and carefully quenched with 1 M aqueous HCl solution (20 mL) and separated, where the water layer is extracted with DCM (2×20 mL). The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by crystallization and recrystallization from DCM afforded the desired product **16** as fine colorless needles (7.3 mmol, 3.7 g, 79% yield).

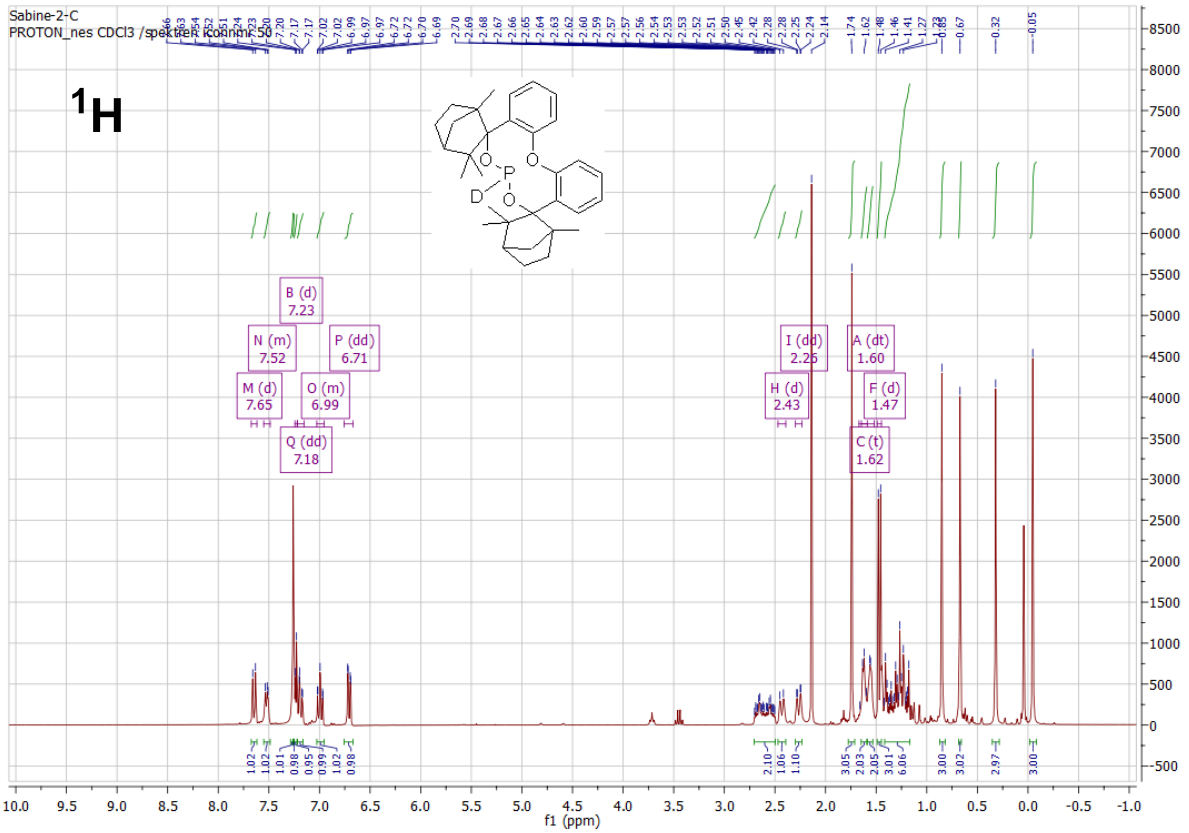
$[\alpha]^{589}_{20}$: +54.0° (c = 0.5, $CHCl_3$).

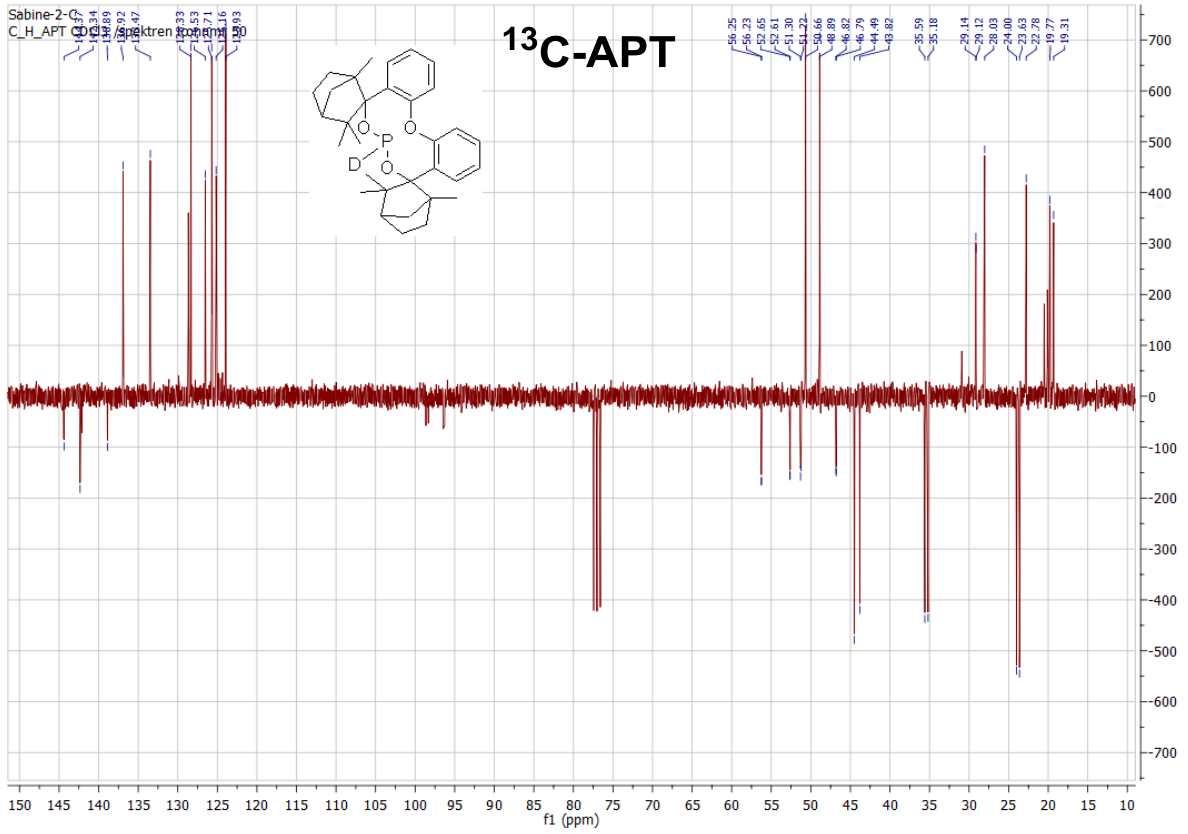
^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.65 (d, 1H, ^3J = *8.2* Hz), 7.55–7.49 (m, 1H), 7.23 (d, 1H, ^3J = *3.2* Hz), 7.18 (dd, 1H, ^3J = *8.3*, 1.4 Hz), 7.03–6.95 (m, 1H), 6.71 (dd, 1H, ^3J = *7.7*, *1.5* Hz), 2.71–2.49, (m, 2H), 2.43 (d, 1H, ^3J = *10.6* Hz), 2.26 (dd, 1H, *J* = *10.6*, *1.7* Hz), 1.74 (s, 3H), 1.62 (t, 2H, ^3J = *5.6* Hz), 1.60 (dt, 2H, ^3J = 12.1, 4.8 Hz), 1.47 (d, 3H, ^3J = *6.9* Hz), 1.42–1.16 (m, 6 H), 0.85 (s, 3H), 0.67 (s, 3H), 0.32 (s, 3H), 0.05 (s, 3H).

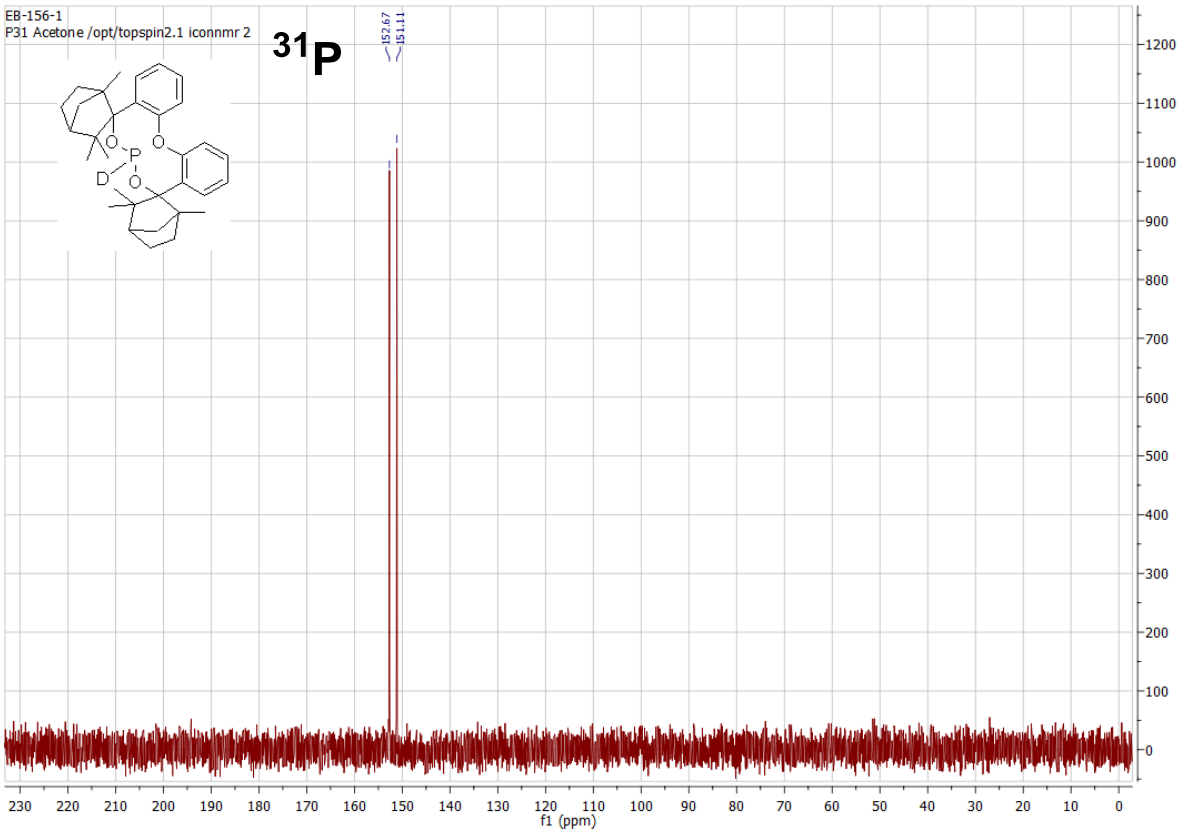
^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 144.37, 142.34, 138.89, 136.92, 133.47, 128.33, 126.53, 125.71, 125.16, 123.93, 56.25, 56.23, 52.65, 52.61, 51.30, 51.22, 50.66, 48.89, 46.82, 46.79, 44.49, 43.82, 35.59, 35.18, 29.14, 29.12, 28.03, 24.00, 23.63, 22.78, 19.77, 19.31

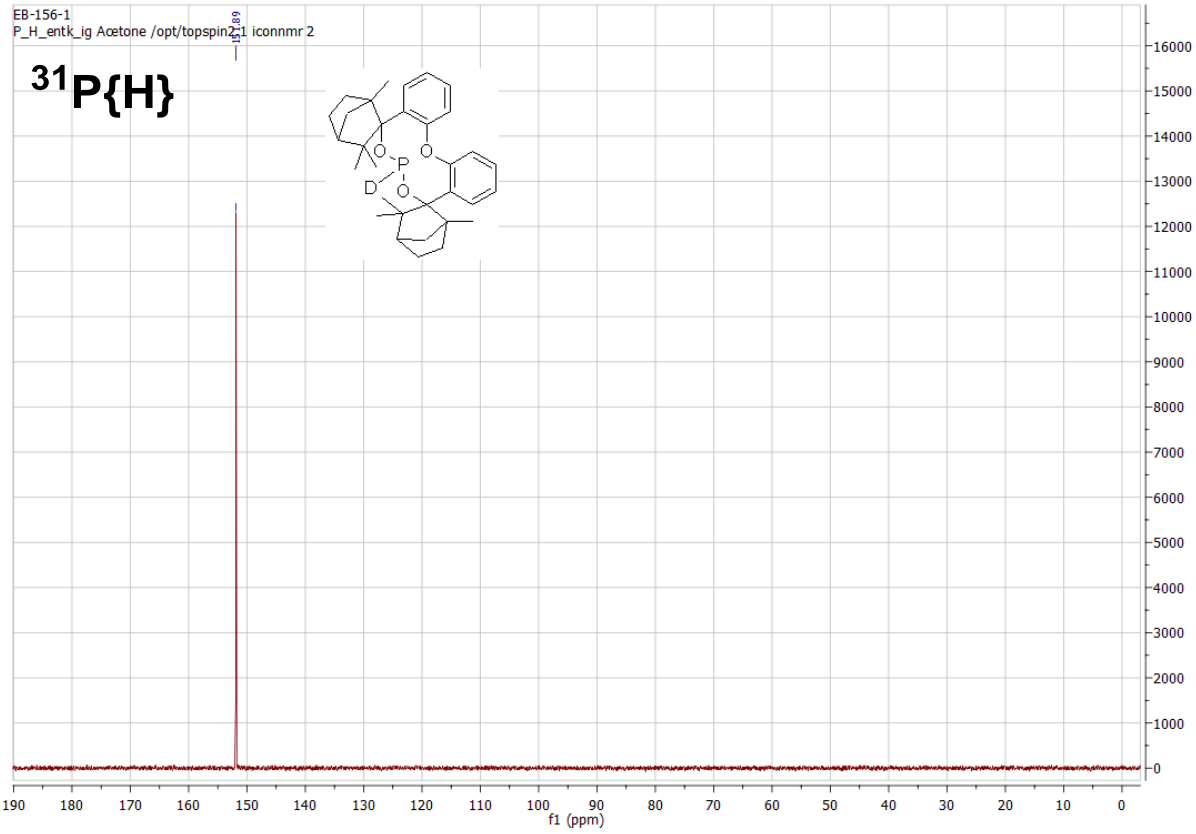
^{31}P-NMR: (125.5 MHz, $CDCl_3$): δ [ppm] = 151.9; ^1J(P-H) = *189.8* Hz.

E.A.:	calc. C: 76.01	found C: 76.19
	calc. H: 8.37	found H: 8.51
	calc. N: 0.00	found N: 0.00

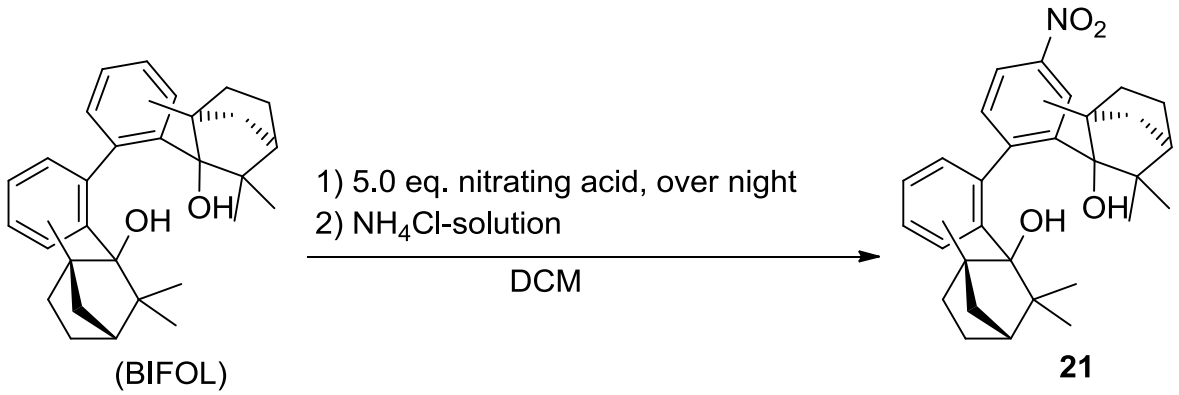

Sabine-2-C
PROTON_nes CDCl3 /spektren iconnmr 50
1H
B (d)
7.23
N (m)
7.52
P (dd)
6.71
M (d)
7.65
O (m)
6.99
Q (dd)
7.18
I (dd)
2.25
A (dt)
1.60
H (d)
2.43
F (d)
1.47
C (t)
1.62
f1 (ppm)


Sabine-2-C
C_H_APT CDCl3 /spektren iconnmr 50
13C-APT
f1 (ppm)


EB-156-1
P31 Acetone /opt/topspin2.1 iconnmr 2
31P
152.67
151.11
f1 (ppm)


EB-156-1
P_H_entk_ig Acetone /opt/topspin2.1 iconnmr 2
31P{H}
147.89
f1 (ppm)

General procedure for the synthesis of 4-nitrobiphenyl-2,2'-bisfenchol (NO_2-BIFOL)



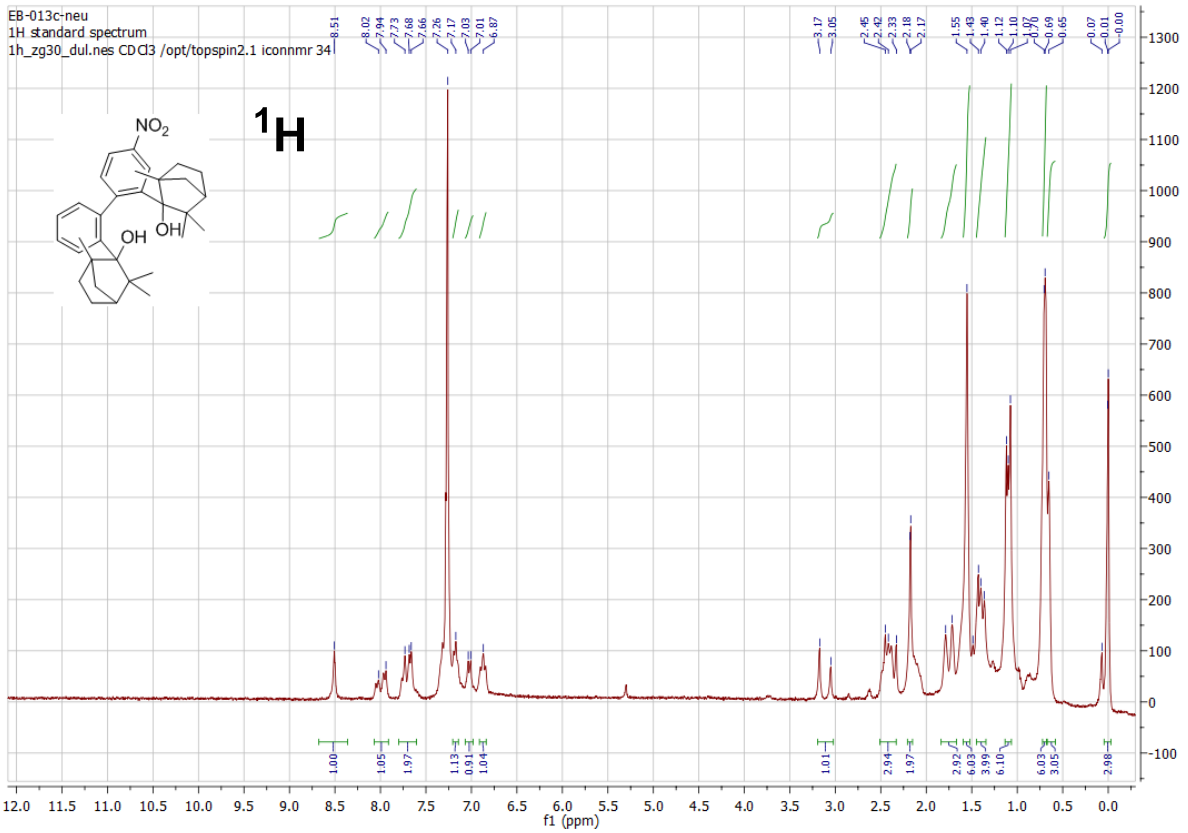
(BIFOL) **21**

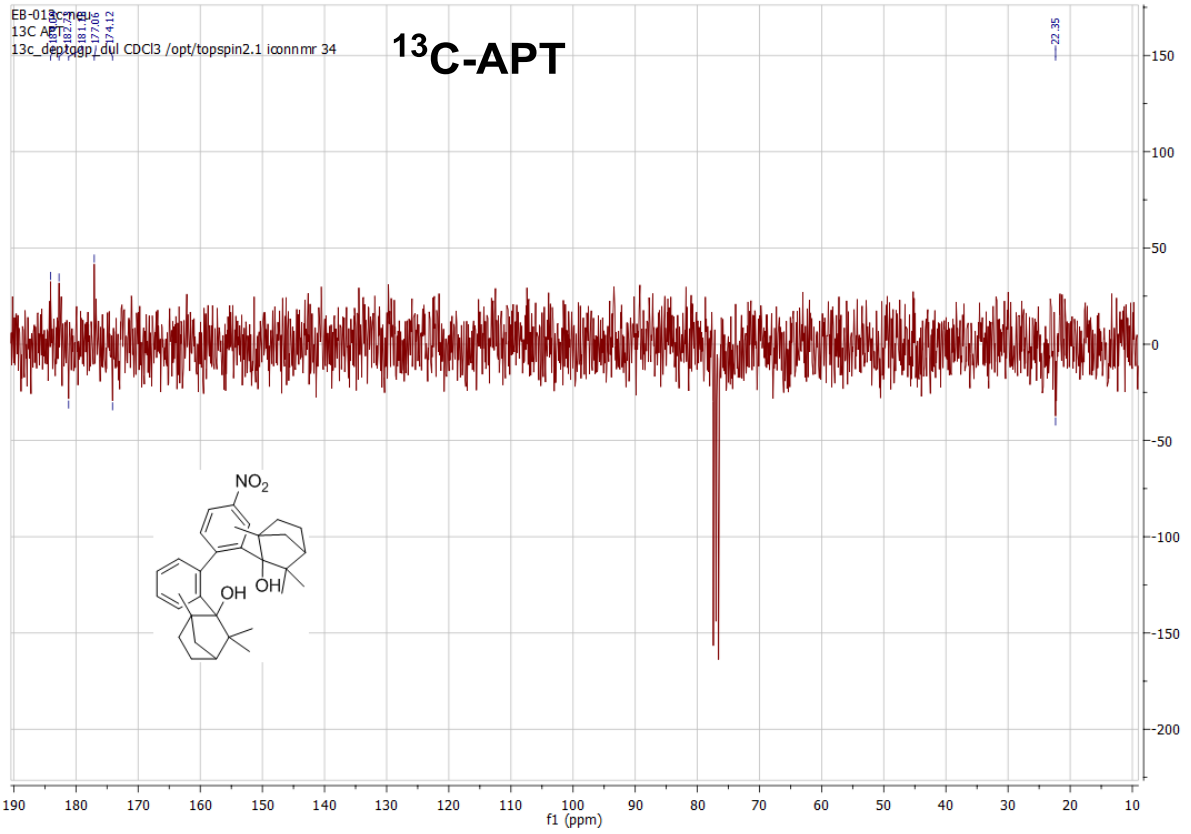
Biphenyl-2,2'-bisfenchol (9.6 mmol, 5.0 g, 1.0 eq.) is dissolved in an appropriate dried and Ar-flushed *Schlenk* flask with dried DCM (5 mL). To the mixture nitrating acid (7.0 mL (3 mL HNO_3 + 4 mL H_2SO_4), 5.0 eq.) is added dropwise and the mixture is stirred over night at room temperature. The orange solution is quenched with saturated aqueous NH_4Cl solution (7 mL) and separated, where the water layer is extracted with DCM (2×10 mL). The combined organic layers are dried over $MgSO_4$, filtered and the solvent is evaporated under *vacuo*. Purification by crystallization and recrystallization from acetone/n-hexane afforded the desired product as small yellow crystals (0.04 mmol, 0.02 g, <1% yield). The main product is reisolated BIFOL , 4.0 g, 89% yield).

^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 8.54 (t, 2H, ^3J = *2.6* Hz), 8.11 (dt, 1H, ^3J = *9.0*, *2.4* Hz), 8.00 (dt, 2H, ^3J = *8.6*, *2.6* Hz), 7.01 (t, 2H, ^3J = *8.9* Hz), 2.66 (s, 1.5H), 2.53 (s, 0.5H), 2.43 (dd, 3H, ^3J = *19.6*, *10.9* Hz), 2.09–1.98 (m, 3H), 1.79 (d, 2H, ^3J = *2.8* Hz), 1.47 (d, 2H, ^3J = *2.8* Hz), 1.26 (d, 2H, ^3J = *2.8* Hz), 1.08 (s, 3H), 1.08 (d, 3H, ^3J = *9.6* Hz), 0.73 (s, 3H), 0.71 (s, 3H), 0.68 (s, 6H).

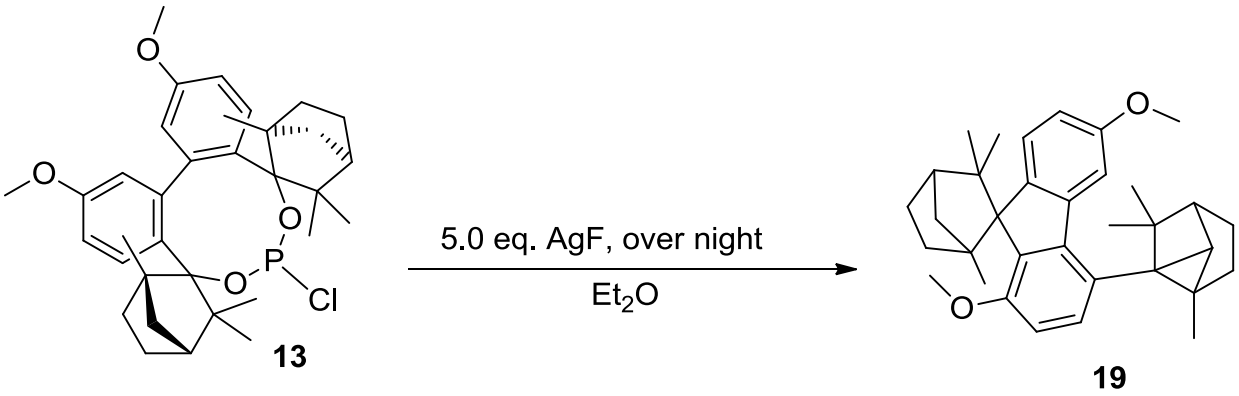
^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 184.09, 182.73, 181.18, 177.06, 174.12, 22.35.

E.A.:	calc. C: 76.31	found C: 76.38
	calc. H: 8.20	found H: 8.37
	calc. N: 2.78	found N: 2.82





Synthesis attempt of 5,5'-dimethoxybiphenyl-2,2'-bisfenchol-fluoro phosphite gave a carbocationic rearranged product

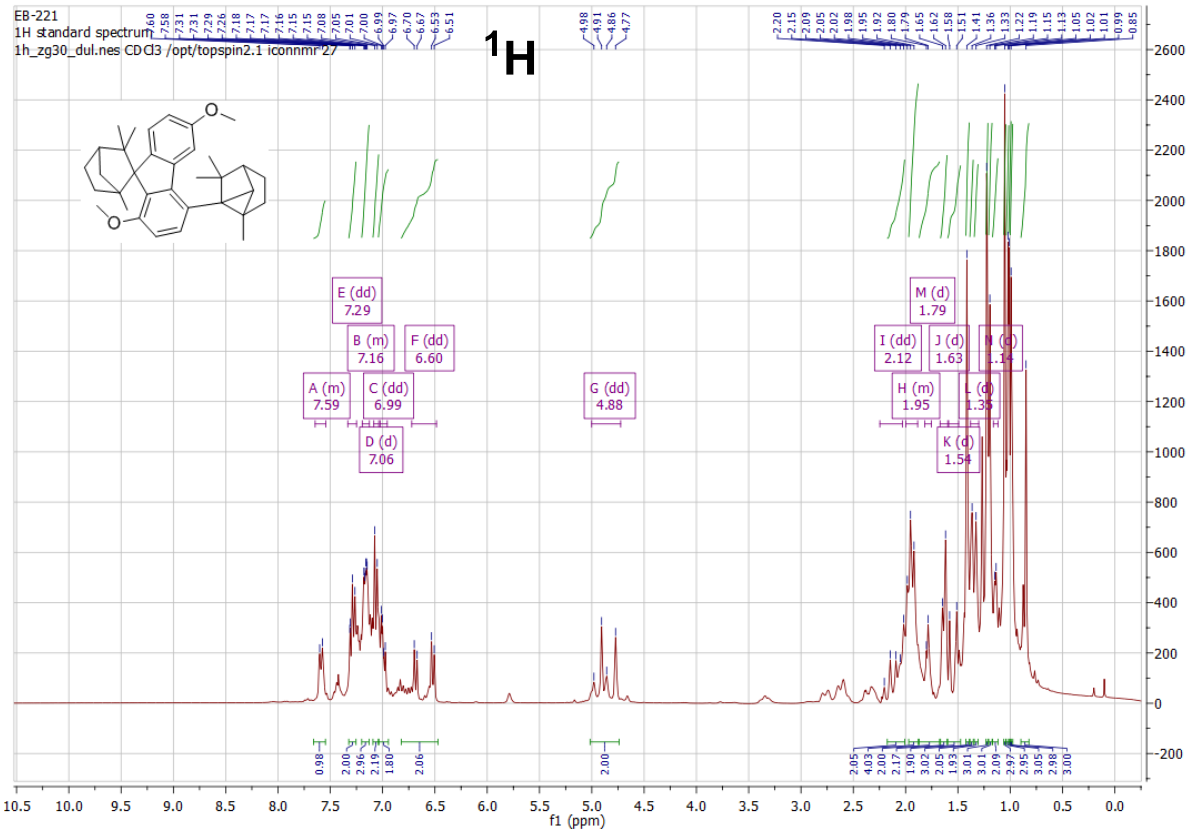


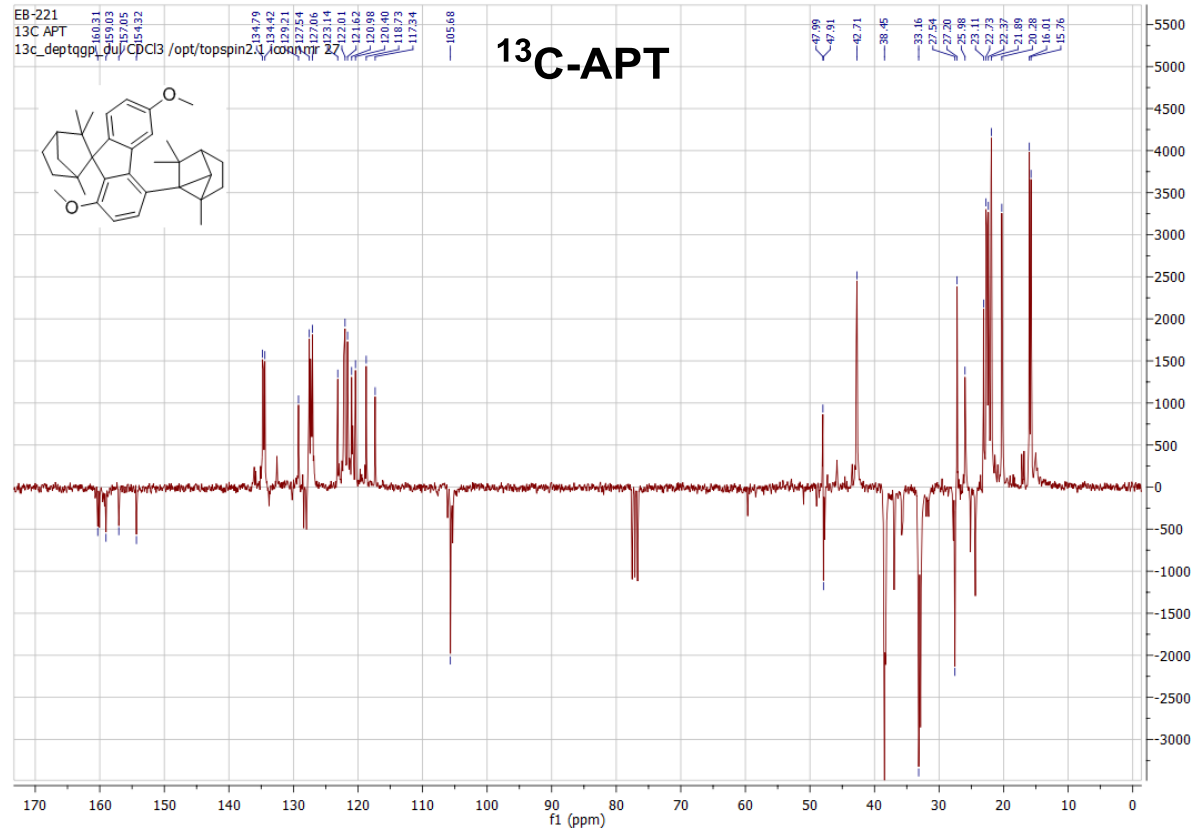
5,5'-dimethoxy-biphenyl-2,2'-bisfenchol-chloro phosphite (**13**, 1.7 mmol, 3.5 g, 1.0 eq.) is dissolved in an appropriate dried and Ar-flushed *Schlenk* flask with dried DMF (15 mL). To the mixture AgF (8.5 mmol, 1.1 g, 5.0 eq.) is added portionwise and the flask is veiled with kitchen foil (AgF is light sensitive) and stirred over night at room temperature. The mixture is filtered over 2 cm of dried celite with the help of a reverse frit (the Silversalts remain on top of the celite) and ished with dried and absolute Et_2O (10 mL). The solvent of the filtered solution is evaporated into a cooling trap under *vacuo*. Unfortunately the desired product is not isolated but a carbocationic rearranged product 5,5'-dimethoxy-2,2'-bis(2,6,6-trimethyltricyclo[3.2.0.0^{2,7}]heptanes (**19**, 1.2 mmol, 0.58 g, 71% yield).

^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.59 (dd, 1H, ^{3}J = *7.8*, *1.6* Hz), 7.29 (dd, 1H, ^{3}J = *10.4*, *4.5* Hz), 7.19–7.13 (m, 1H), 7.06 (d, 1H, ^{3}J = *7.4* Hz), 6.99 (dd, 1H, ^{3}J = *7.7*, *3.9* Hz), 6.60 (dd, 1H, ^{3}J = *49.4*, *7.9* Hz), 4.88 (dd, 1H, ^{3}J = *38.3*, *23.8* Hz), 2.12 (dd, 2H, ^{3}J = *31.3*, *15.0* Hz), 2.00–1.88 (m, 5H), 2.03–1.85 (m, 4H), 1.79 (d, 2H, ^{3}J = *4.8* Hz), 1.63 (d, 2H, ^{3}J = *8.9* Hz), 1.54 (d, 2H, ^{3}J = *20.3* Hz), 1.44 (s, 3H), 1.35 (d, 4H, ^{3}J = *11.4* Hz), 1.22 (s, 3H), 1.19 (s, 3H), 1.14 (d, 2H, ^{3}J = *4.3* Hz), 1.05 (s, 3H), 1.02 (s, 3H), 1.01 (s, 3H), 0.99 (s, 3H), 0.85 (s, 3H).

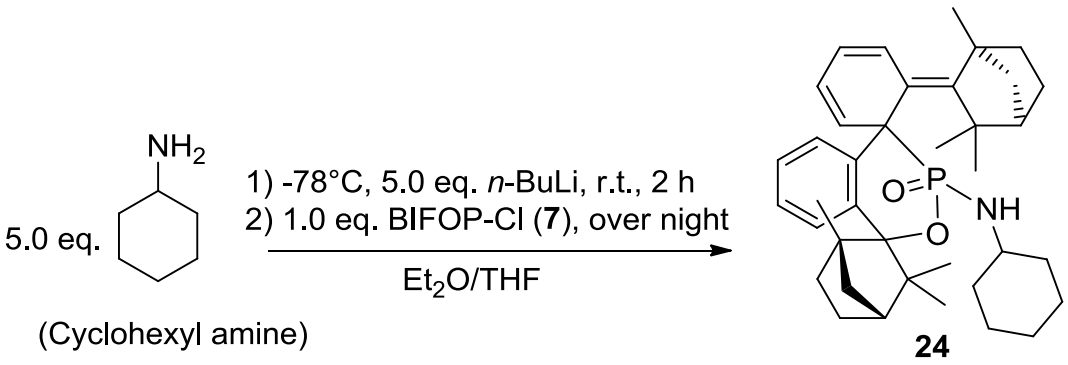
^{13}C-NMR: ($CDCl_3$): δ [ppm] = 160.31, 159.03, 157.05, 154.32, 134.79, 134.42, 129.21, 127.54, 127.06, 123.34, 122.01, 121.62, 120.98, 120.40, 118.73, 1117.34, 105.68, 47.99, 47.91, 42.71, 38.45, 33.16, 27.54, 27.20, 25.98, 23.11, 22.73, 22.37, 21.89, 20.28, 16.01, 15.76.

E.A.:	calc. C: 84.60	found C: 84.66
	calc. H: 8.77	found H: 8.81
	calc. N: 0.00	found N: 0.00


EB-221
1H standard spectrum
1h_zg30_dul.nes CDCl3 /opt/topspin2.1 iconnmr 27
1H
E (dd) 7.29
B (m) 7.16
F (dd) 6.60
A (m) 7.59
C (dd) 6.99
D (d) 7.06
G (dd) 4.88
M (d) 1.79
I (dd) 2.12
J (d) 1.63
H (m) 1.95
K (d) 1.54
f1 (ppm)


EB-221
13C APT
13c_deptqgp_dul/CDCl3 /opt/topspin2.1 iconnmr 27
13C-APT
f1 (ppm)

Synthesis attempt of biphenyl-2,2'-bisfenchol-cyclohexyl phosporamidite (BIFOP-NH-*c*-Hex) gave a carbocationic rearranged product

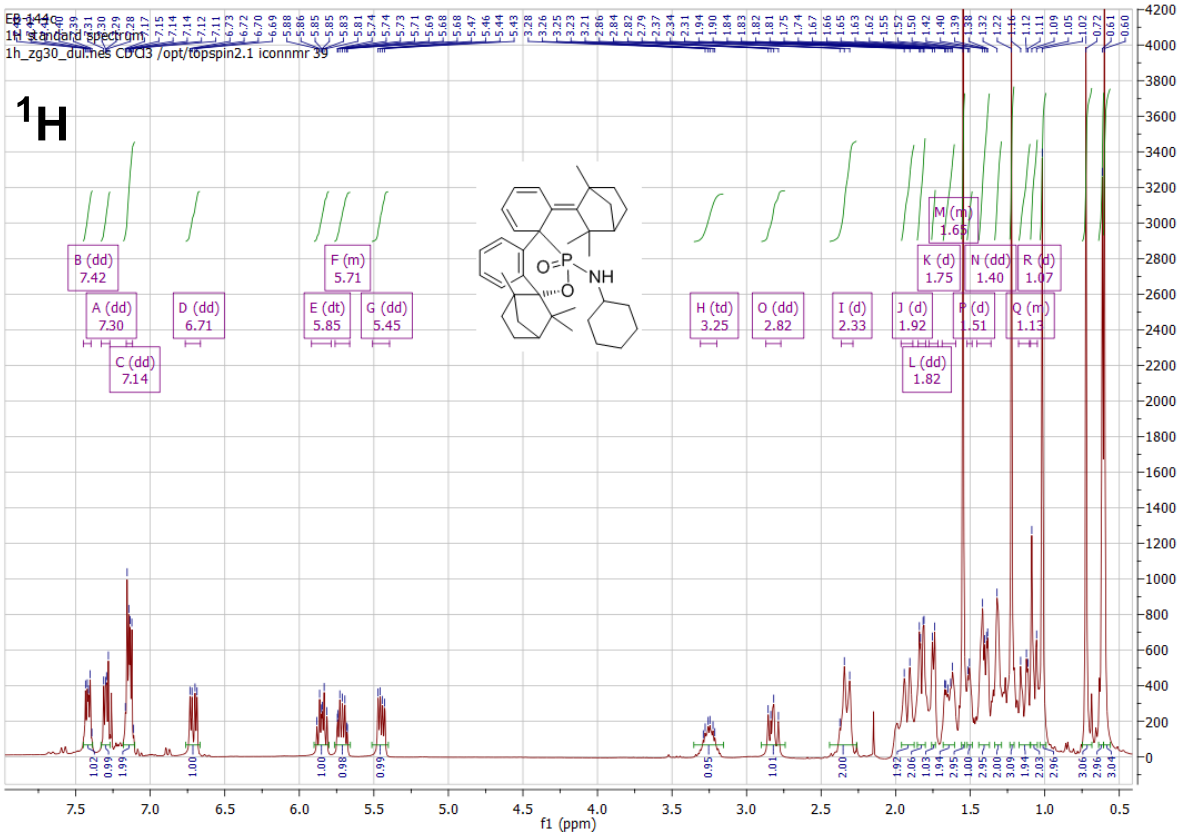


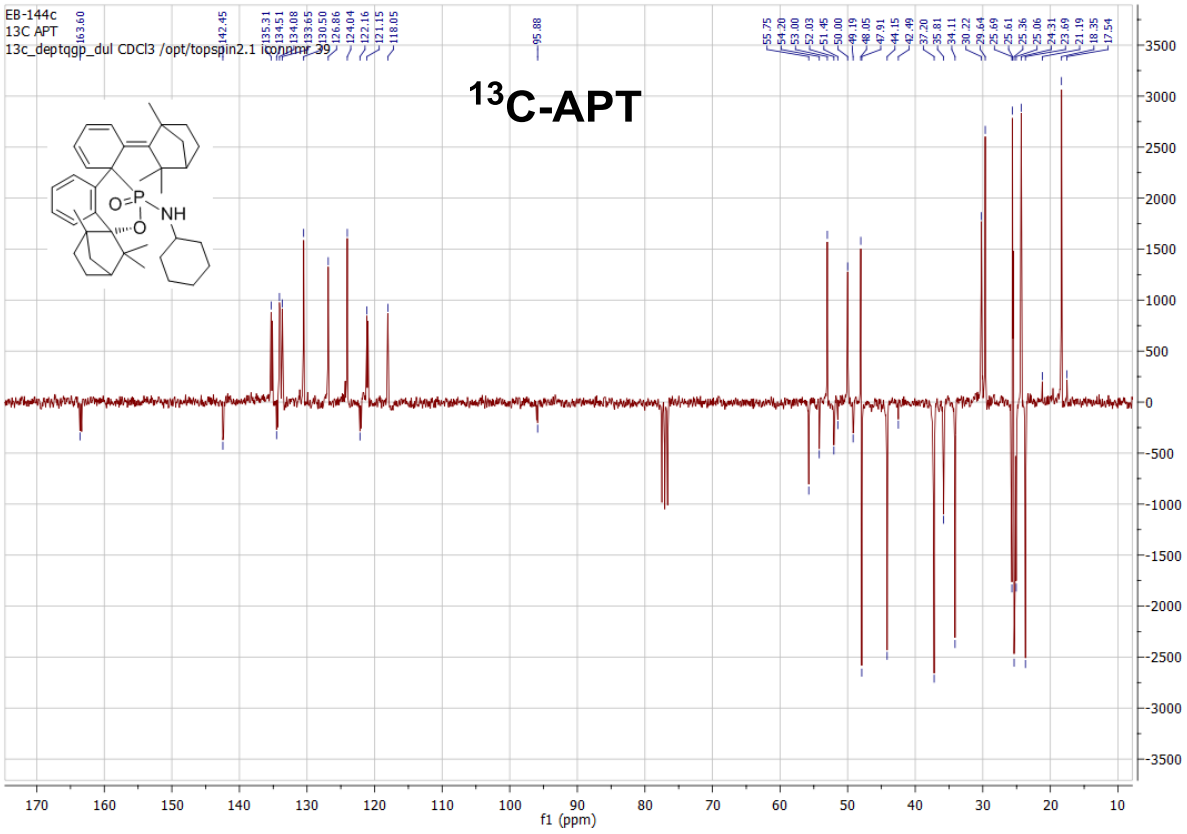
Cyclohexyl amine (19.0 mmol, 2.2 mL, 5.0 eq.) is dissolved in an appropriate dried and Ar-flushed *Schlenk* flask with dried and absolute Et_2O (40 mL) and dried and absolute THF (5 mL). To the mixture at -78°C *n*-BuLi (1.6 M, 19.2 mmol, 12.0 mL, 5.0 eq.) is added moderately the cooling bath is separated and the solution stirred for 2 h at room temperature. biphenyl-2,2'-bisfenchol-chloro phosphite (**7**, 3.8 mmol, 2.0 g, 1.0 eq.) is added portionwise. The mixture is stirred over night. It is quenched with saturated aqueous NH_4Cl solution (30 mL) and separated, where the water layer is extracted with DCM (2×20 mL). The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Unfortunately the desired product is not isolated but a carbocationic rearranged product 2-(fenchane-2-ylidene-1,2-dihydro)-[1,1'-biphenyl]-2'-(fenchol)-*N*-cyclohexylphosphonic amide (**24**). Purification by crystallization and recrystallization from DCM afforded colorless prism blocks (3.4 mmol, 2.0 g, 89% yield).

^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 7.42 (dd, 1H, ^3J = *6.0*, *3.5* Hz), 7.30 (dd, 1H, ^3J = *5.7*, *3.7* Hz), 7.14 (dd, 2H, ^3J = *6.0*, *3.5* Hz), 6.71 (dd, 1H, ^3J = *10.2*, *4.1* Hz), 5.85 (dt, 1H, ^3J = *9.3*, *5.5* Hz), 5.76–5.66 (m, 1H), 5.45 (dd, 1H, ^3J = *9.0*, *4.4* Hz), 3.25 (td, 1H, ^3J = *9.9*, *3.8* Hz), 2.82 (dd, 1H, ^3J = *5.7*, *3.7* Hz), 2.33 (d, 2H, ^3J = *10.8* Hz), 1.92 (d, 2H, ^3J = *11.3* Hz), 1.82 (dd, 2H, ^3J = *7.3*, *2.1* Hz), 1.75 (d, 1H, ^3J = *4.6* Hz), 1.69–1.60 (m, 2H), 1.55 (s, 3H), 1.51 (d, 1H, ^3J = *3.2* Hz), 1.44–1.36 (m, 3H), 1.32 (s, 2H), 1.22 (s, 3H), 1.18–1.10 (m, 2H), 1.09–1.04 (m, 2H), 1.02 (s, 3H), 0.72 (s, 3H), 0.61 (s, 3H), 0.60 (s, 3H).

^{13}C-NMR: (75MHz, $CDCl_3$): δ [ppm] = 163.60, 142.45, 135.31, 134.51, 134.08, 133.65, 130.50, 126.86, 124.04, 122.16, 121.15, 118.05, 95.88, 55.75, 54.20, 53.00, 52.03, 51.45, 50.00, 49.19, 48.05, 47.91, 44.15, 42.49, 37.20, 35.81, 34.11, 30.22, 29.64, 25.69, 25.61, 25.36, 25.06, 24.31, 23.69, 21.19, 18.35, 17.54.

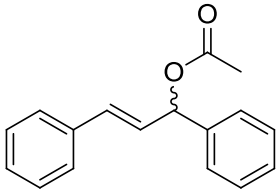
E.A.:	calc. C: 77.91	found C: 78.10
	calc. H: 8.95	found H: 9.08
	calc. N: 2.39	found N: 2.41


EB-144c
1H standard spectrum
1h_zg30_dul.nes CDCl3 /opt/topspin2.1 iconnmr 39
1H
B (dd) 7.42
A (dd) 7.30
C (dd) 7.14
D (dd) 6.71
F (m) 5.71
E (dt) 5.85
G (dd) 5.45
H (td) 3.25
O (dd) 2.82
I (d) 2.33
J (d) 1.92
L (dd) 1.82
M (m) 1.65
K (d) 1.75
N (dd) 1.40
P (d) 1.51
R (d) 1.07
Q (m) 1.13
O=P
O
NH
f1 (ppm)


EB-144c
13C APT
13c_deptqqp_dul CDCl3 /opt/topspin2.1 iconnmr 39
13C-APT
O=P
O
NH
f1 (ppm)

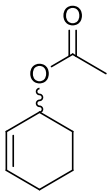
General procedure for the synthesis of the substrates

The presubstrate *trans*-1,3-diphenylpropen-1-ol (5.2 mmol, 1.1 g, 1.0 eq.) or 2-cyclohexen-1-ol (5.1 mmol, 5.0 mL, 1.0 eq.) is dissolved in pyridine (10 mL) and stirred for 30 min. To the mixture acetic anhydride (8.2 mmol, 8.6 mL, 1.6 eq.) is added dropwise. The reaction mixture is stirred over night and quenched with 1 M aqueous HCl solution (50 mL). The product is extracted with dichlormethane (CH_2Cl_2, 2x 50 mL) and the extract is washed with 1 M aqueous HCl solution (25 mL), 1 M aqueous Na_2CO_3-solution (25 mL) and the solvent is evaporated under *vacuo* to give the desired product *rac*-**1** or *rac*-**3** as stated in literature [4,5].



rac-**1**

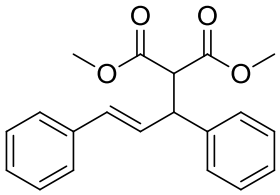
^{1}H-NMR: (300MHz, CDCl3): δ [ppm] = 7.41–7.33 (m, 6H), 7.25–7.33 (m, 3H), 7.23 (m, 1H), 6.61 (d, 1H, ^3J = *15.6* Hz), 6.43 (d, 1H, ^3J = *7.0* Hz), 6.35 (dd, 1H, ^3J = *15.6*, *6.8* Hz), 2.12 (s, 3H); compared with [4].



rac-**3**

^{1}H-NMR: (300MHz, CDCl3): δ [ppm] = 5.93 (m, 1H), 5.69 (m, 1H), 5.30 (m, 1H), 2.11 (s, 3H), 1.91–1.43 (m, 6H); compared with [5].

General procedure for the synthesis of *trans*-dimethyl-2-(1,3-diphenylallyl) malonate (2)



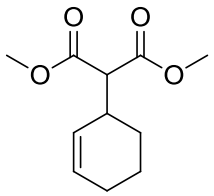
2

$[(C_3H_5)PdCl]_2$ (0.0014 mmol), 1.0 mg, 1 mol%) and **L** (0.0028 mmol, s.b., 2 mol%) are dissolved in dry dichloroethane (DCE, 3.0 mL) and the mixture is stirred at room temperature for 10 min. To the mixture *trans*-1,3-diphenylallyl acetate (*rac*-**1**, 1.0 mmol, 38 mg, 1.0 eq.) is added dropwise. The reaction mixture is stirred for another 10 min. Then the nucleophile sodium dimethyl malonate (1.0 mmol, 65 mg, 1.0 eq.) is added portionwise over 1 h (room temperature). The reaction mixture is stirred for 4 d (full conversion is determined) and quenched with saturated aqueous NH_4Cl solution (3 mL). The mixture is separated and the water layer is extracted with DCM (2×5 mL). The combined organic layers are dried over

Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by flash chromatography over silica gel, using EtOAc:*n*-hexane 1:10 afforded the desired product **2**.
L = PPh_3, 5.3 mg, racemic product is formed.
L = BIFOP-H, 9.8 mg, enantioselective (*S*)-**2**-product is formed.
L = BIFOP-F, 10.2 mg, enantioselective (*R*)-**2**-product is formed.

$[\alpha]^{589}_{20}$: -13.2° (*S*, c = 0.5, $CHCl_3$).
$[\alpha]^{589}_{20}$: +10.9° (*R*, c = 0.5, $CHCl_3$).
^{1}H-NMR: (300MHz, CDCl3): δ [ppm] = 7.33–7.20 (m, 10H), 6.49 (d, 1H, ^3J = *15.6* Hz), 6.33 (dd, 1H, ^3J = *15.6*, *8.0* Hz), 4.29 (dd, 1H, ^3J = *10.6*, *8.5* Hz), 3.97 (d, 1H, ^3J = *10.7* Hz), 3.70 (s, 3H), 3.51 (s, 3H); compared with [4].
HPLC: AD-H Chiralpack® AD-H column, t_R = 19.7-20.8 min (*R*), t_R = 26.1-26.3 min (*S*) [6].

General procedure for the synthesis of dimethyl-2-(cyclohexenyl)-1-malonate (4)



4

$[(C_3H_5)PdCl]_2$ (0.0014 mmol), 1.0 mg, 1 mol%) and **L** (0.0028 mmol, s.b., 2 mol%) are dissolved in dry dichloroethane (DCE, 3.0 mL) and the mixture is stirred at room temperature for 10 min. To the mixture 2-cyclohexenyl-1-acetate (*rac*-**3**, 1.0 mmol, 0.1 mL, 1.0 eq.) is added dropwise. The reaction mixture is stirred for another 10 min. Then the nucleophile sodium dimethyl malonate (1.0 mmol, 65 mg, 1.0 eq.) is added portionwise over 1 h (room temperature). The reaction mixture is stirred for 4 d (full conversion is determined) and quenched with saturated aqueous NH_4Cl solution (3 mL). The mixture is separated and the water layer is extracted with DCM (2×5 mL). The combined organic layers are dried over Na_2SO_4, filtered and the solvent is evaporated under *vacuo*. Purification by flash chromatography over silica gel, using EtOAc:*n*-hexane 1:10 afforded the desired product **4**.
L = PPh_3, 5.3 mg, racemic product is formed.
L = BIFOP-H, 9.8 mg, enantioselective (*R*)-**4**-product is formed.
L = BIFOP-F, 10.2 mg, enantioselective (*S*)-**4**-product is formed.

$[\alpha]^{589}_{20}$: +28.3° (*R*, c = 0.5, $CHCl_3$).
$[\alpha]^{589}_{20}$: -38.7° (*S*, c = 0.5, $CHCl_3$).
^{1}H-NMR: (300MHz, $CDCl_3$): δ [ppm] = 5.80 (m, 1H), 5.22 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.27 (d, 1H, ^3J = *9.6* Hz), 2.00 (m, 2H), 1.76 (m, 1H), 1.70 (m, 1H), 1.55 (m, 1H), 1.34 (m, 1H); compared with [5].
Chiral GC: CP-Chiralsil®-DEX-CB (25 m x 0.25 mm, 0.25 mm thickness) column, t_R = 22.4-22.8 min (*S*), t_R = 23.1-23.9 min (*R*) [5].

X-ray crystal structures

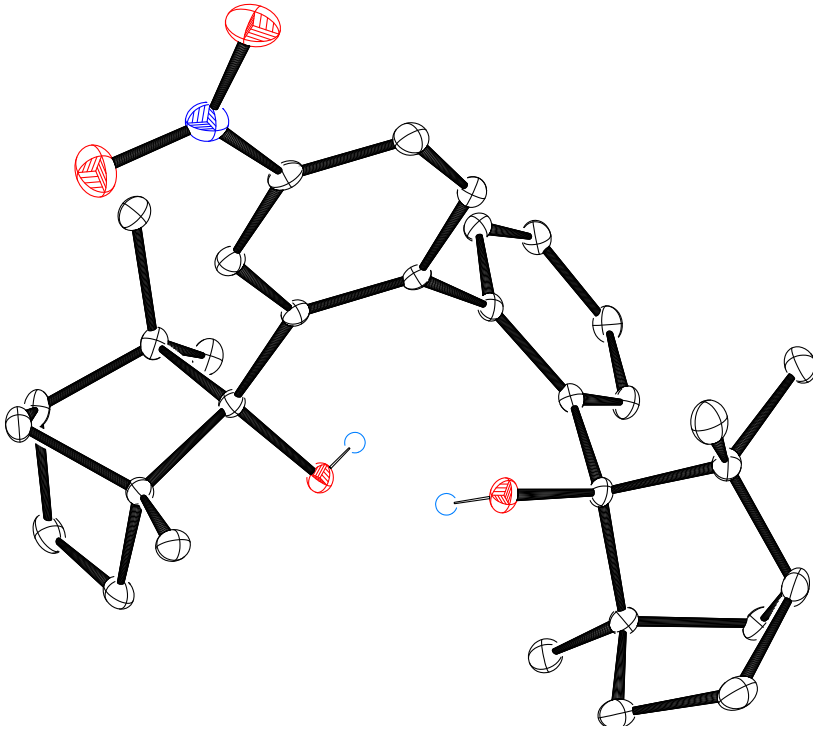


Table 1. Crystal data and structure refinement for eb013.

Identification code	eb013	
Empirical formula	C32 H41 N O4	
Moiety formula	C32 H41 N O4	
Formula weight	503.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.0376(5) Å	a= 97.302(3)°.
	b = 12.5422(9) Å	b= 98.335(4)°.
	c = 13.6773(8) Å	g = 94.869(4)°.
Volume	1345.65(15) $Å^3$	
Z	2	
Density (calculated)	1.243 Mg/m^3	
Absorption coefficient	0.081 mm^{-1}	
F(000)	544	
Crystal size	0.300 x 0.300 x 0.300 mm^3	
Theta range for data collection	1.520 to 27.492°.	
Index ranges	-10<=h<=10, -16<=k<=16, -16<=l<=17	
Reflections collected	9194	
Independent reflections	6151 [R(int) = 0.0315]	

Completeness to theta = 25.242°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6151 / 0 / 348
Goodness-of-fit on F^2	0.994
Final R indices [I>2sigma(I)]	R1 = 0.0536, wR2 = 0.1377
R indices (all data)	R1 = 0.1088, wR2 = 0.1619
Extinction coefficient	n/a
Largest diff. peak and hole	0.254 and -0.465 e.$Å^{-3}$

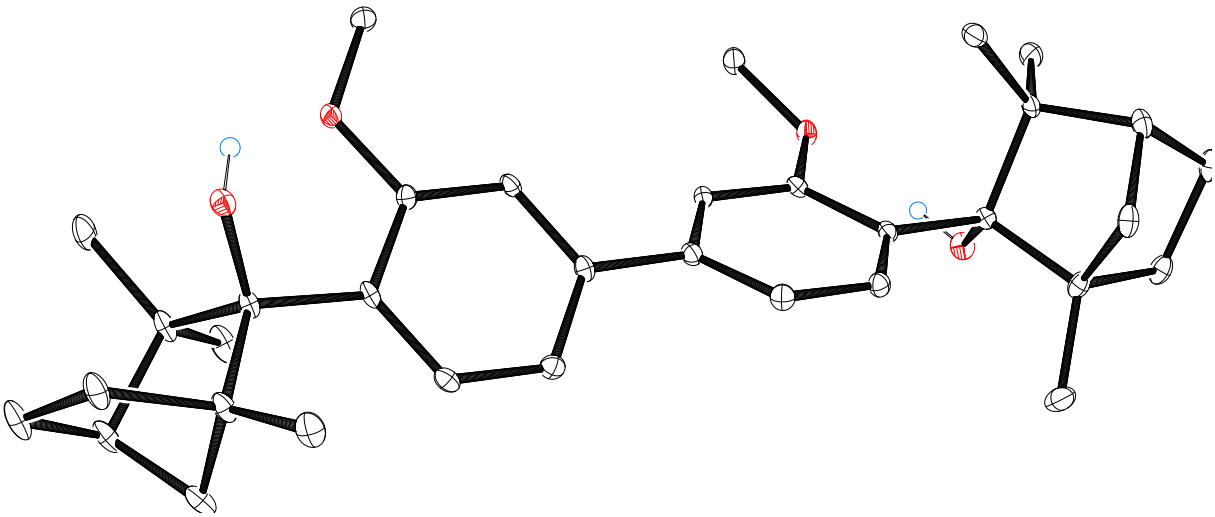


Table 2. Crystal data and structure refinement for eb79.

Identification code	eb79	
Empirical formula	C34 H46 O4	
Moiety formula	C34 H46 O4	
Formula weight	518.71	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	$P2_1$	
Unit cell dimensions	a = 7.7206(15) Å	a= 90°.
	b = 11.737(2) Å	b= 102.16(3)°.
	c = 16.646(3) Å	g = 90°.
Volume	1474.6(5) $Å^3$	
Z	2	
Density (calculated)	1.168 Mg/m^3	
Absorption coefficient	0.584 mm^{-1}	
F(000)	564	

Crystal size	0.400 x 0.200 x 0.050 mm^3
Theta range for data collection	4.645 to 72.165°.
Index ranges	-9<=h<=9, -14<=k<=13, -20<=l<=20
Reflections collected	13366
Independent reflections	5526 [R(int) = 0.0402]
Completeness to theta = 67.679°	98.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.5626
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5526 / 1 / 351
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0360, wR2 = 0.0906
R indices (all data)	R1 = 0.0375, wR2 = 0.0939
Absolute structure parameter	0.14(7)
Extinction coefficient	n/a
Largest diff. peak and hole	0.321 and -0.262 e.$Å^{-3}$

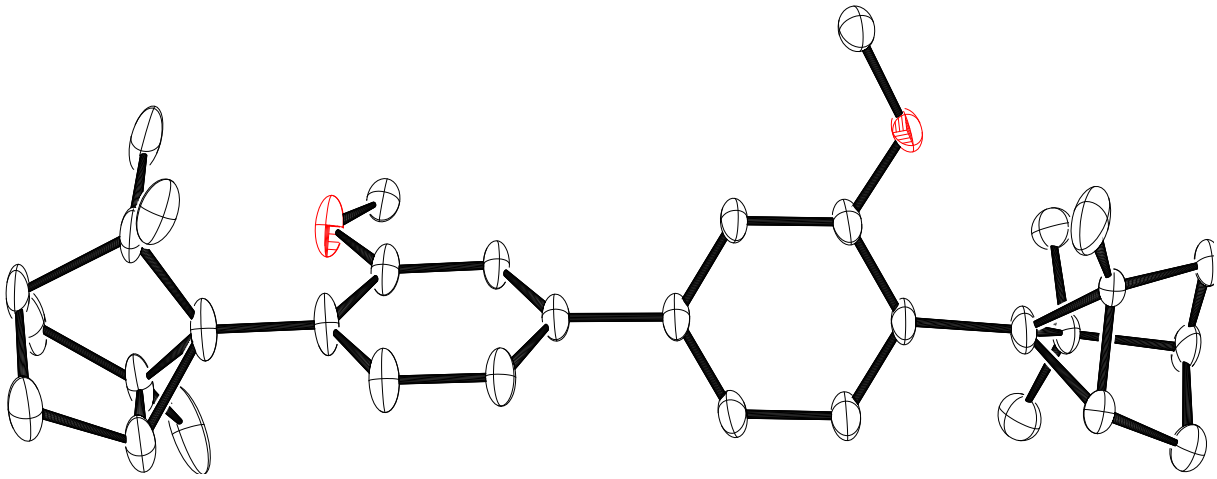


Table 3. Crystal data and structure refinement for eb15.

Identification code	eb15	
Empirical formula	C34 H42 N0 O2	
Moiety formula	C20 H20 N2 O4	
Formula weight	482.67	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	C2	
Unit cell dimensions	a = 13.1690(6) Å	a= 90°.
	b = 6.8675(3) Å	b= 101.802(2)°.

	c = 15.9197(7) Å g = 90°.
Volume	1409.31(11) Å^3
Z	2
Density (calculated)	1.137 Mg/m^3
Absorption coefficient	0.524 mm^{-1}
F(000)	524
Crystal size	0.200 x 0.200 x 0.100 mm^3
Theta range for data collection	2.836 to 65.042°.
Index ranges	-15<=h<=15, -8<=k<=8, -18<=l<=18
Reflections collected	5891
Independent reflections	2352 [R(int) = 0.0385]
Completeness to theta = 65.042°	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7526 and 0.5930
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2352 / 1 / 167
Goodness-of-fit on F^2	1.102
Final R indices [I>2sigma(I)]	R1 = 0.0745, wR2 = 0.1899
R indices (all data)	R1 = 0.0812, wR2 = 0.1976
Absolute structure parameter	-0.08(17)
Extinction coefficient	n/a
Largest diff. peak and hole	0.745 and -0.200 e.Å^{-3}

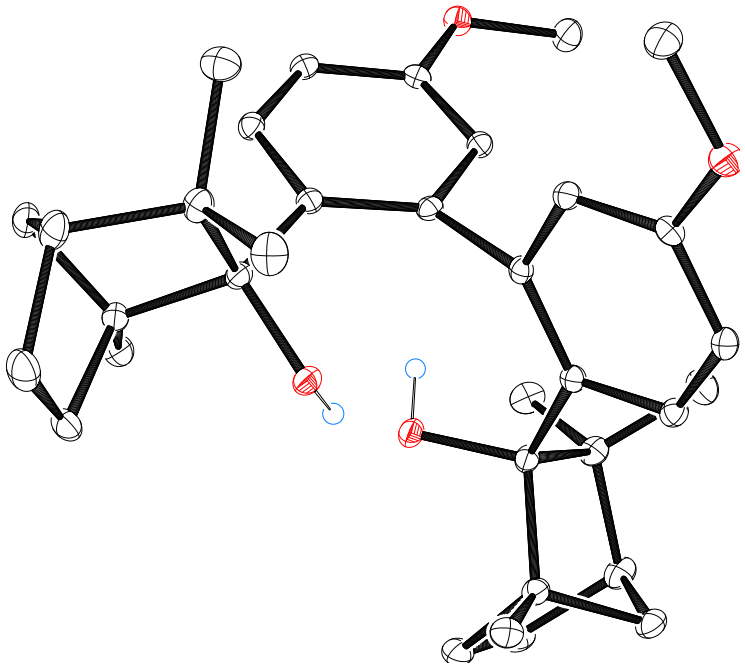


Table 4. Crystal data and structure refinement for eb127.

Identification code	eb127	
Empirical formula	C34 H46 O4	
Moiety formula	?	
Formula weight	518.71	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12$	
Unit cell dimensions	a = 12.2984(6) Å	a= 90°.
	b = 14.6289(7) Å	b= 90°.
	c = 7.9467(4) Å	g = 90°.
Volume	1429.71(12) $Å^3$	
Z	2	
Density (calculated)	1.205 Mg/m^3	
Absorption coefficient	0.602 mm^{-1}	
F(000)	564	
Crystal size	0.200 x 0.200 x 0.200 mm^3	
Theta range for data collection	6.050 to 72.192°.	
Index ranges	-14<=h<=11, -17<=k<=18, -9<=l<=9	
Reflections collected	13860	
Independent reflections	2776 [R(int) = 0.0455]	
Completeness to theta = 67.679°	99.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7536 and 0.5647	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2776 / 2 / 185	
Goodness-of-fit on F^2	1.153	
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.1005	
R indices (all data)	R1 = 0.0377, wR2 = 0.1014	
Absolute structure parameter	0.22(7)	
Extinction coefficient	0.031(3)	
Largest diff. peak and hole	0.370 and -0.314 $e.Å^{-3}$	

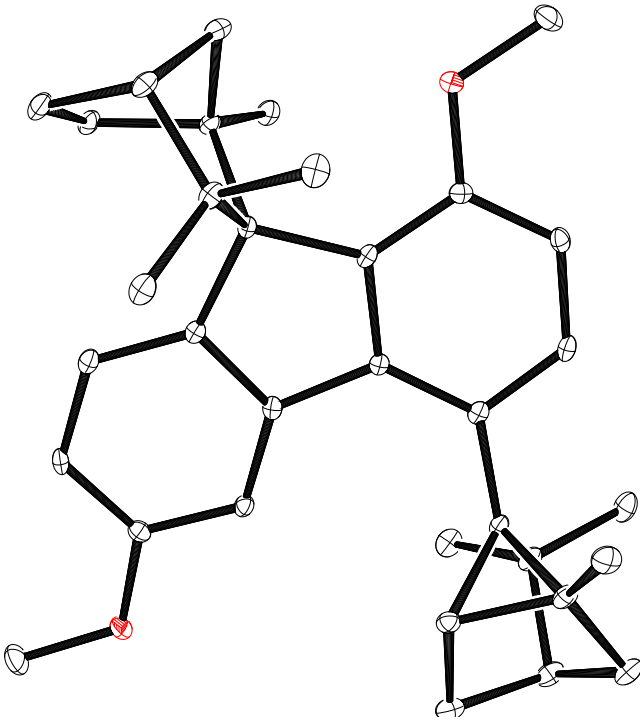


Table 5. Crystal data and structure refinement for eb-ox.

Identification code	eb-ox	
Empirical formula	C34 H42 O2	
Moiety formula	C34 H42 O2	
Formula weight	482.67	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.4531(13) Å	a= 90°.
	b = 16.561(6) Å	b= 90°.
	c = 22.022(7) Å	g = 90°.
Volume	2718.2(14) $Å^3$	
Z	4	
Density (calculated)	1.179 Mg/m^3	
Absorption coefficient	0.543 mm^{-1}	
F(000)	1048	
Crystal size	0.300 x 0.040 x 0.020 mm^3	
Theta range for data collection	3.339 to 72.347°.	
Index ranges	-8<=h<=9, -20<=k<=20, -27<=l<=27	
Reflections collected	26381	
Independent reflections	5335 [R(int) = 0.0527]	
Completeness to theta = 67.679°	99.4 %	

Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7536 and 0.5097
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5335 / 0 / 333
Goodness-of-fit on F^2	1.074
Final R indices [I>2sigma(I)]	R1 = 0.0400, wR2 = 0.1051
R indices (all data)	R1 = 0.0414, wR2 = 0.1064
Absolute structure parameter	0.07(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.363 and -0.408 e.$Å^{-3}$

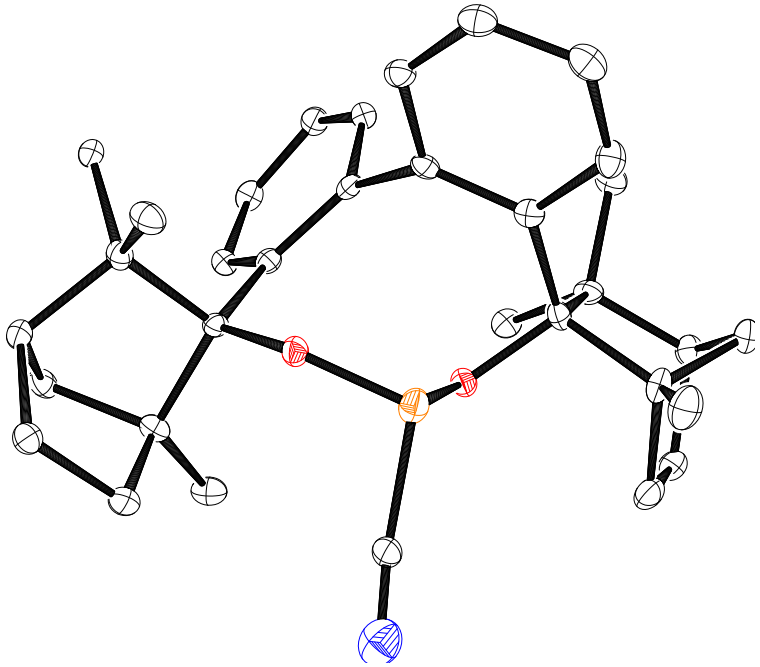


Table 6. Crystal data and structure refinement for eb-aja4.

Identification code	eb-aja4	
Empirical formula	C39 H52 N O2 P	
Moiety formula	C33 H40 N O2 P, C6 H12	
Formula weight	597.78	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 10.6897(4) Å	a= 90°.
	b = 15.7992(5) Å	b= 90°.
	c = 18.4623(6) Å	g = 90°.
Volume	3118.07(18) $Å^3$	

Z	4
Density (calculated)	1.273 Mg/m^3
Absorption coefficient	0.125 mm^{-1}
F(000)	1296
Crystal size	0.400 x 0.400 x 0.400 mm^3
Theta range for data collection	1.696 to 26.996°.
Index ranges	-13<=h<=10, -20<=k<=20, -23<=l<=23
Reflections collected	18022
Independent reflections	6803 [R(int) = 0.0437]
Completeness to theta = 25.242°	100.0 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6803 / 0 / 394
Goodness-of-fit on F^2	1.061
Final R indices [I>2sigma(I)]	R1 = 0.0547, wR2 = 0.1395
R indices (all data)	R1 = 0.0785, wR2 = 0.1525
Absolute structure parameter	0.08(4)
Extinction coefficient	n/a
Largest diff. peak and hole	0.798 and -0.463 $e.Å^{-3}$

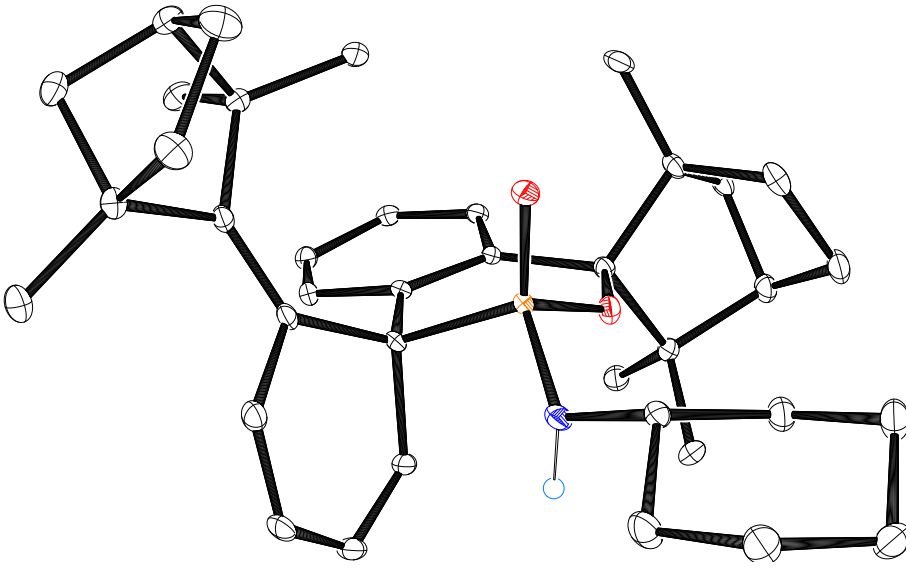
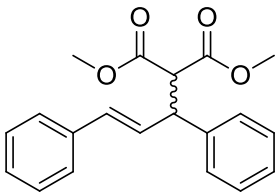


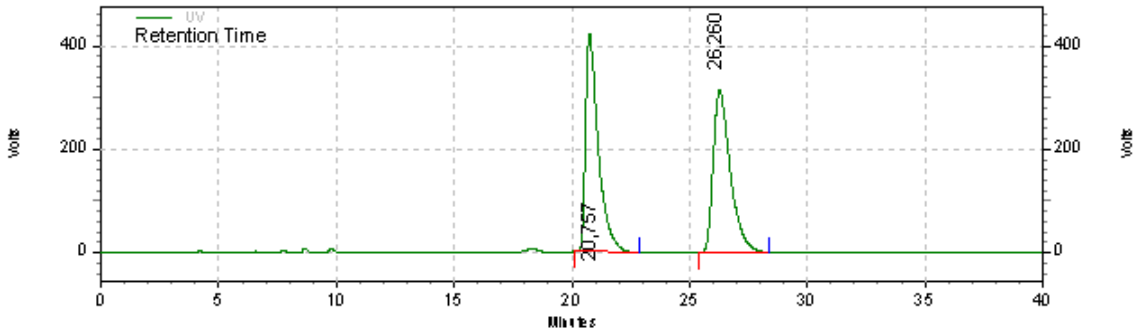
Table 7. Crystal data and structure refinement for **24**.

HPLC-chromatograms

rac-Standard of *trans*-dimethyl-2-(1,3-diphenylallyl) malonate (**2**)



rac-**2**

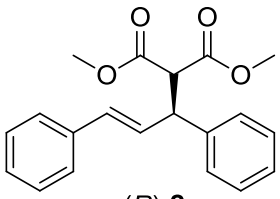


UV Results

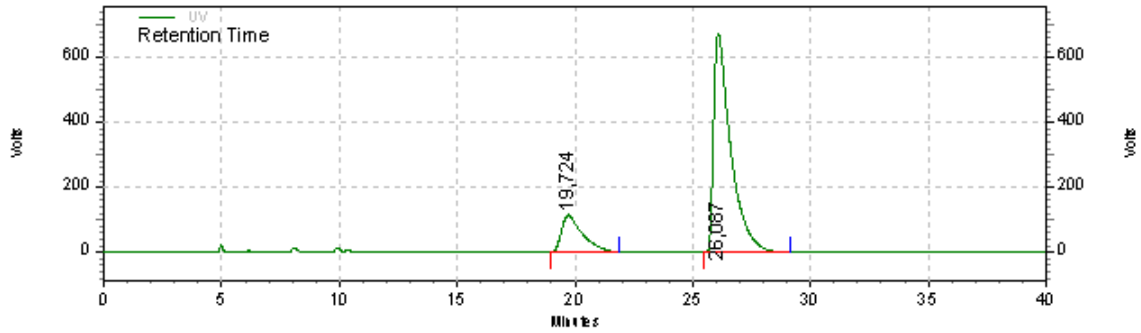
Retention Time	Area	Area %	Height	Height %
20,757	63567737	49,89	1687327	57,28
26,260	63860516	50,11	1258230	42,72

Totals	127428253	100,00	2945557	100,00

(*R*)-*trans*-dimethyl-2-(1,3-diphenylallyl) malonate ((*R*)-**2**)



(*R*)-**2**

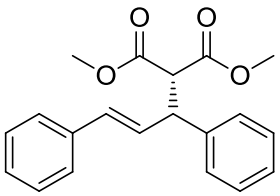


UV Results

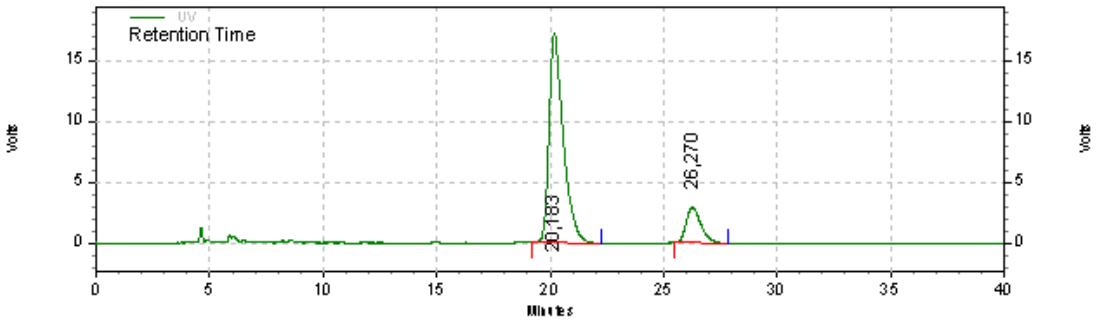
Retention Time	Area	Area %	Height	Height %
19,724	32322915	17,25	606586	16,62
26,087	155056303	82,75	3043148	83,38

Totals	187379218	100,00	3649734	100,00

(*S*)-*trans*-dimethyl-2-(1,3-diphenylallyl) malonate ((*S*)-**2**)



(*S*)-**2**

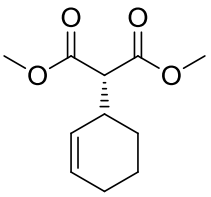


UV Results

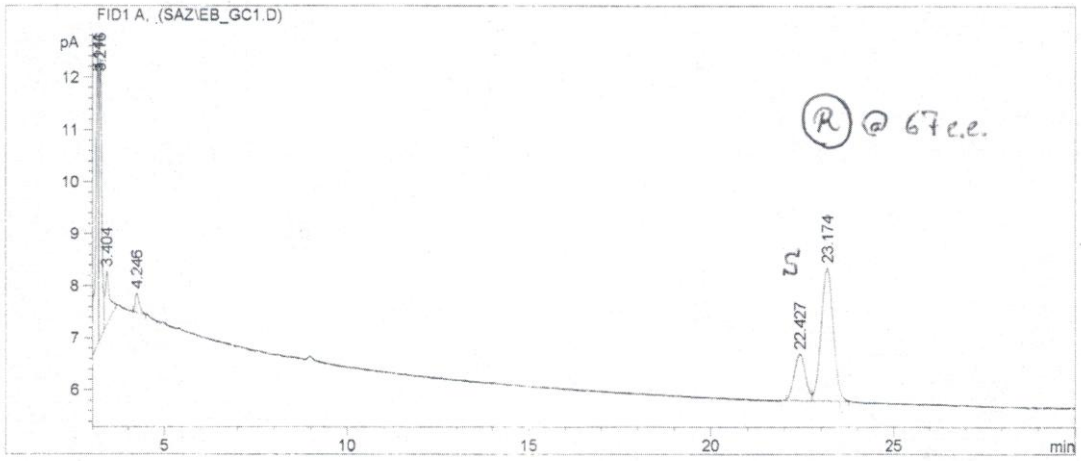
Retention Time	Area	Area %	Height	Height %
20,183	2996736	84,92	69123	85,53
26,270	532184	15,08	11698	14,47
Totals	3528920	100,00	80821	100,00

GC-chromatograms

(*R*)-*trans*-dimethyl-2-(cyclohexenyl)-1-malonate (*R*)-**4** after catalysis.

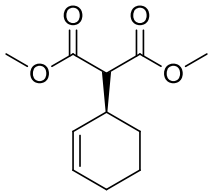


(*R*)-**4**

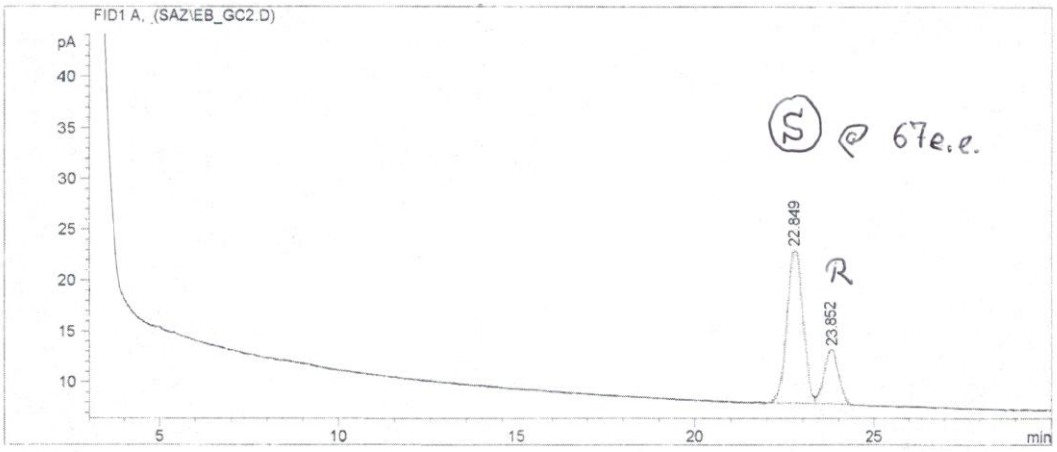


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	0.878	BV	9.10e-3	291.84952	515.62781	0.08028
2	0.900	VB S	0.0360	3.62987e5	1.68018e5	99.85041
3	1.869	BB	0.0479	13.83400	4.15004	0.00381
4	2.540	BB	0.0477	4.09056e-1	1.09128e-1	0.00011
5	3.141	BV	0.0811	31.89195	5.63226	0.00877
6	3.216	VV	0.0738	27.07394	5.36987	0.00745
7	3.404	VB	0.1090	8.76034	1.02732	0.00241
8	4.246	BB	0.1006	3.07410	3.63595e-1	0.00085
9	22.427	BV	0.2531	19.10950	8.96907e-1	0.00526
10	23.174	VB	0.2727	58.72195	2.56880	0.01615
11	49.179	BB	0.0803	2.25826	3.40891e-1	0.00062
12	50.570	BV	0.0835	1.85656	2.74181e-1	0.00051
13	51.047	VV	0.2532	4.69823	2.21261e-1	0.00129
14	51.334	VV	0.0973	5.67713	7.29098e-1	0.00156
15	51.574	VB	0.0694	3.40530	6.58051e-1	0.00094
16	51.884	BB	0.0650	6.46252e-1	1.25676e-1	0.00018
17	54.791	BBA	0.6648	70.55415	1.24371	0.01941
Totals :				3.63531e5	1.68557e5	

(*S*)-*trans*-dimethyl-2-(cyclohexenyl)-1-malonate (*S*)-**4** after catalysis.



(*S*)-**4**



Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area
1	22.849	BV	0.3425	1570.34460	23.06024	0.83461
2	23.852	VB	0.3179	311.17925	13.02911	0.16539
Totals :				1881.52385	36.08935	

Computational structures

All computations are performed with GAUSSIAN 16 Revision B.01 [7a]. The transitions states are computed by using the B3LYP functional [7b-e] with the def2-SVP basis set [7f] and Grimme's dispersion (D3) with Becke-Johnson damping (BJ) [7g]. The energies are refined by using the M06-2X functional [1g] with the def2-TZVP basis set [7f] and Grimme's dispersion (D3) [7h]. The NBO-analyzes are done with NBO6. Everything is implemented in the program package of GAUSSIAN 16.

Table 8. Computed transition structures of the nucleophilic attack of NH_3 to allyl • Pd • BIFOP-(H,F)[a].

TS *pro*(*R*/*S*)	Imag. freq. [cm^{-1}]	Hartree	ΔG_{rel} [kcal/mol]
H: TS-2 (*S*)	**-301.94**	**-2499.369863**	**0.0**
TS-**1** (*R*)	-282.73	-2499.368257	1.0
TS-**3** (*S*)	-311.86	-2499.367852	1.3
TS-**4** (*R*)	-294.38	-2499.367502	1.5
TS-**6** (*R*)	-301.94	-2499.352387	11.0
TS-**7** (*S*)	-311.86	-2499.352177	11.1
TS-**5** (*R*)	-282.73	-2499.351540	11.5
TS-**8** (*S*)	-294.38	-2499.349864	12.5
F: TS-1 (*R*)	**-291.93**	**-2598.677484**	**0.0**
TS-**2** (*S*)	-302.23	-2598.676031	0.9
TS-**4** (*R*)	-289.62	-2598.675574	1.2
TS-**3** (*S*)	-311.86	-2598.675311	1.4
TS-**6** (*R*)	-302.23	-2598.661255	10.2
TS-**7** (*R*)	-320.94	-2598.660552	10.6
TS-**5** (*S*)	-291.93	-2598.660376	10.7
TS-**8** (*S*)	-289.62	-2598.659592	11.2
H: TS-1b (*R*)	**-307.38**	**-2153.998540**	**0.0**
TS-**4b** (*R*)	-322.47	-2153.997689	0.5

TS-**2b** (*S*)	-308.51	-2153.995975	1.6
TS-**3b** (*S*)	-322.44	-2153.993890	2.9
F: TS-2b (*S*)	**-307.33**	**-2253.306249**	**0.0**
TS-**1b** (*R*)	-308.72	-2253.305033	0.8
TS-**3b** (*S*)	-324.23	-2253.303786	1.5
TS-**4b** (*R*)	-321.17	-2253.302106	2.6
20-H *(trans-exo*)	**-87.61**	**-872.489779**	**0.0**
20-H (*trans-endo*)	-87.61	-872.489573	0.1
20-H (*cis-endo*)	-185.37	-872.485357	2.8
20-H (*cis-exo*)	-185.37	-872.484730	3.2
20-F *(trans-endo*)	**-103.32**	**-971.804468**	**0.0**
20-F (*trans-exo*)	-103.32	-971.803311	0.7
20-F (*cis-exo*)	-196.66	-971.803169	0.8
20-F (*cis-endo*)	-196.66	-971.800922	2.2
20-Cl *(trans-exo*)	**-102.74**	**-1332.134742**	**0.0**
20-Cl (*trans-endo*)	-102.74	-1332.134256	0.3
20-Cl (*cis-exo*)	-196.63	-1332.133470	0.8
20-Cl (*cis-endo*)	-196.63	-1332.133230	0.9

[a] M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP, T = 293.15 K, p = 1 bar, gas phase [1].

Table 9. NBO-analyzes of model (**20**-X, X = H, Cl, F) and "real" (TS-**1**(**b**) to TS-**4**(**b**): allyl•Pd•BIFOP-X, X = H, F) complex. **NBO** in [kcal/mol][a].

TS (**20**-X, X = H, Cl, F, **model**; TS-**1**(**b**) to TS-**4**(**b**), "**real**")	**Imag. Freq.** [cm^{-1}]	NBO lp(**O**)→σ*(**P-O**)	NBO[b] lp(**O**)→σ*(**P-X**)	**NBO(!)** lp(**Pd**)→σ*(**P-O**)	NBO[b] lp(**Pd**)→σ*(**P-X**)	**NBO(!)** lp(**Pd**)→σ*(**allyl**)	NBO[c] lp(**X**)→σ*(**P-O**)	NBO **Σ**	**NBO** **ΔE_{rel}, stab.**
20-H (*trans-endo*)	-87.61	9.1	17.0	8.5	2.8	4.0	0.0	41.4	0.0
20-H (*trans-exo*)	-87.61	9.3	16.9	8.4	2.9	**4.4**	0.0	41.9	**+0.5**
20-H (*cis-endo*)	-185.37	9.8	18.2	**8.0**	2.5	**1.2**	0.0	39.7	**+1.0**
20-H (*cis-exo*)	-185.37	9.8	17.9	7.8	2.5	0.7	0.0	38.7	0.0
20-Cl (*trans-endo*)	-102.74	9.4	30.2	8.3	3.6	4.1	4.1	59.7	0.0
20-Cl (*trans-exo*)	-102.74	9.2	31.0	8.3	3.5	**4.3**	4.3	60.6	**+0.9**
20-Cl (*cis-endo*)	-195.63	9.9	29.7	**7.9**	3.7	0.6	0.6	52.4	**+0.6**
20-Cl (*cis-exo*)	-195.63	9.8	29.5	7.7	3.4	0.7	0.7	51.8	0.0
20-F (*trans-endo*)	-103.32	7.6	31.9	**7.5**	3.8	**7.5**	4.2	62.5	**+0.4**
20-F (*trans-exo*)	-103.32	8.0	31.6	7.2	3.9	7.2	4.2	62.1	0.0
20-F (*cis-endo*)	-195.66	8.3	31.3	5.6	3.7	5.6	1.4	55.9	0.0
20-F (*cis-exo*)	-195.66	7.7	32.2	**7.5**	3.8	**7.5**	0.6	59.3	**+3.4**
H: TS-**1**	-301.94	22.5	14.3	3.2	2.3	2.7	0.0	45.0	0.0

TS-**2**	-282.73	23.0	13.9	**7.7**	2.2	2.8	0.0	49.6	**+4.6**
TS-**3**	-311.86	20.5	13.1	**8.1**	1.5	1.9	0.0	45.1	**+2.7**
TS-**4**	-294.38	21.8	13.2	4.0	1.3	2.1	0.0	42.4	0.0
F: TS-**1**	-291.93	20.6	25.9	**8.0**	2.6	3.1	18.8	79.0	**+1.8**
TS-**2**	-302.23	22.8	23.9	6.6	3.0	3.2	17.7	77.2	0.0
TS-**3**	-320.94	18.2	25.3	7.0	1.5	0.5	18.5	71.0	0.0
TS-**4**	-289.62	19.4	25.0	**7.8**	3.2	0.5	18.5	74.4	**+3.4**
H: TS-**1b**	-307.38	20.9	14.1	**7.9**	2.0	2.0	0.0	46.9	+**3.4**
TS-**2b**	-308.51	19.4	12.8	7.1	2.3	1.9	0.0	43.5	0.0
TS-**3b**	-322.44	20.7	13.3	3.4	0.0	2.0	0.0	39.4	0.0
TS-**4b**	-322.47	22.5	12.4	**7.6**	1.6	0.6	0.0	44.7	+**5.3**
F: TS-**1b**	-308.72	18.2	25.5	4.5	0.0	4.0	19.4	71.6	0.0
TS-**2b**	-307.33	23.1	23.7	**7.3**	3.3	5.3	18.4	81.1	**+9.5**
TS-**3b**	-324.23	25.6	23.2	6.3	2.7	**4.1**	18.6	80.5	**+7.3**
TS-**4b**	-321.17	19.3	24.8	7.3	2.8	0.5	18.5	73.2	0.0
H: TS-**1c**	-173.12	19.6	12.8	**10.1**	2.9	0.0	0.0	45.4	**+1.6**

TS-**2c**	-218.71	20.5	12.6	8.8	1.3	0.6	0.0	43.8	0.0
F: TS-**1c**	-195.76	20.0	22.2	4.9	3.6	0.0	18.2	68.9	0.0
TS-**2c**	-291.04	17.8	23.8	**9.2**	0.9	0.6	19.3	71.6	**+2.7**
H: TS-**1d**	-235.93	20.2	12.7	10.7	1.9	1.3	0.0	46.8	0.0
TS-**2d**	-239.21	19.6	12.3	**13.3**	3.1	**1.9**	0.0	50.2	**+3.4**
F: TS-**1d**	-241.76	17.4	23.8	**9.2**	5.6	0.8	19.1	75.9	**+2.4**
TS-**2d**	-230.67	20.3	22.5	8.0	4.6	1.2	16.9	73.5	0.0

[a] M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP, T = 293.15 K, p = 1 bar, gas phase [1]. [b] σ*(**P-X**): X = H, Cl, F. [c] lp(**X**): X = Cl, F.

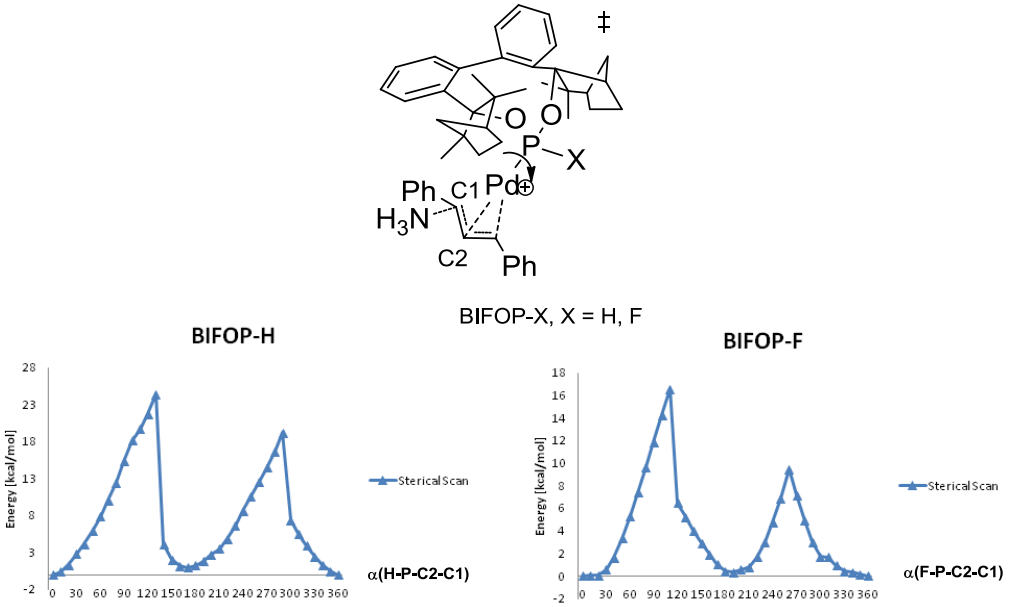


Figure 1. Computational rotatory analysis (B3LYP-D3(BJ)/def2-SVP) rotatory analysis α(X-P-C2-C1) of dihedral angle α(X-P-C2-C1) of the sterical hinderance of BIFOP-X (X = H, F).

The NBO-analyzes [8] of Pd^0 and Pd^{II} connected to different model ligand (L) systems showing a hyperconjugation (Pd(lp)->σ*(P-X, X = H, C, O, F, Table 11). The F-substituted P-ligands receive more stabilizing energy from the stabilizing hyperconjugation effect than the non-F-substituted P-ligands which applies for both Pd^0 and Pd^{II} (Table 10). These precatalysts resemble different electronic properties (CO, PH_3, PMe_3, $POMe_3$, PFH_2, $PFMe_2$, $PF(OMe)_2$, Table 10). The NPA-charge of Pd shows that Pd^0 functions more as acceptor to the P-ligands (negative charge: -0.10 to -0.24, Table 10) while Pd^{II} functions more as donator to the P-ligands (charge < 1: 0.98 to 0.75, Table 10). The P-hybridization of the P-nucleus at Pd^0 is almost below sp^2 ($sp^{1.82}$ - $sp^{1.97}$) except for PMe_3 and $PFMe_2$ where it is higher than sp^2 ($sp^{2.65}$ and $sp^{2.30}$, Table 10). At Pd^{II} the hybridization of the P-nucleus changes drastically depending on the apparent ligand and ranges from $sp^{5.11}$ to $sp^{8.69}$ (Table 10) with lesser s- and more p-character. Obviously, the F-substituent has no significant influence at the P-hybridization of the P-Pd bond, because the hybridization pattern is nearly equal to the corresponding non-F-substituted corresponding ligands (Table 10). Thus, electrophilic Pd-species governs the p-character. The bond-energies of the F-substituted P-ligands at the Pd^{II} are lesser than the bond-energies of the corresponding non-F-substituted P-ligands. The cause might be that the F-group demands more p-character from the P-F bond according to Bent's rule [9].

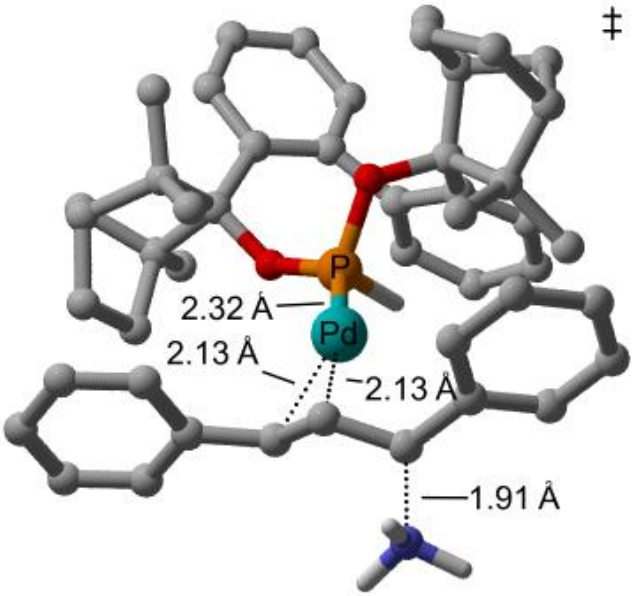
Table 10. Computation of DFT-NBO-analyzes to Pd^0/Pd^{II}•L (L = model ligand)[a].

Pd^0/Pd^{II}•L[b]	NPA Pd-charge	ΔG_{rel} NBO[c] (Pd(lp) -> σ*(P-X) X = H, C, O, F	P-hybri-dization (P-Pd)	ΔG [kcal/mol][d]
CO	0.06 / 1.39	-	-	58.0 / 145.1
PH_3	-0.10 / 0.98	4.7 / 1.5	$sp^{1.97}$ / $sp^{6.62}$	50.8 / 223.7
PMe_3	-0.24 / 0.75	4.8 / 2.3	$sp^{2.65}$ / $sp^{8.69}$	58.1 / 304.2
$POMe_3$	-0.23 / 0.75	5.7 / 3.3	$sp^{1.93}$ / $sp^{5.55}$	59.8 / 312.4
PH_2F	-0.13 / 0.93	8.1 / 4.1	$sp^{1.90}$ / $sp^{5.67}$	57.5 / 224.5
PMe_2F	-0.22 / 0.79	7.4 / 4.3	$sp^{2.30}$ / $sp^{7.33}$	60.2 / 282.2
$P(OMe)_2F$	-0.19 / 0.75	6.7 / 3.7	$sp^{1.82}$ / $sp^{5.11}$	57.7 / 282.5

[a] TPSS-D3(BJ)/def2-TZVP, ZPE scaled by 1.0020 [27] in kcal/mol, 293.15 K, 1 bar. [b] The values are stated as Pd^0/Pd^{II}. [c] Stabilizing energy in [kcal/mol]; the energy for PH_3, PMe_3 and $POMe_3$ is divided by 3. For PH_2F, PMe_2F and $P(OMe)_2F$ only the σ*(P-F) is given (higher electronegativity of F). [d] Bonding energy of Pd^0/Pd^{II}•L.

Important: The optimized structures and single points are computed in gas phase, T = 293.15 K, p = 1 bar.

H: TS-**8** (*exo-cis*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -294.38 cm^{-1}

Optimization: -2498.325569

Single point: -2499.349864

1 1

Pd	1.93164	0.49472	0.17962
C	3.88778	1.34094	0.21783
C	2.97533	2.21734	0.88309
C	4.55199	0.28223	0.93525
H	4.22828	1.5751	-0.79408
H	2.92534	2.146	1.97638
C	4.92594	-0.99543	0.2726
C	4.99339	-2.16587	1.04613
C	5.16847	-1.07593	-1.10934
C	5.29089	-3.39382	0.45332
H	4.78536	-2.11764	2.11865

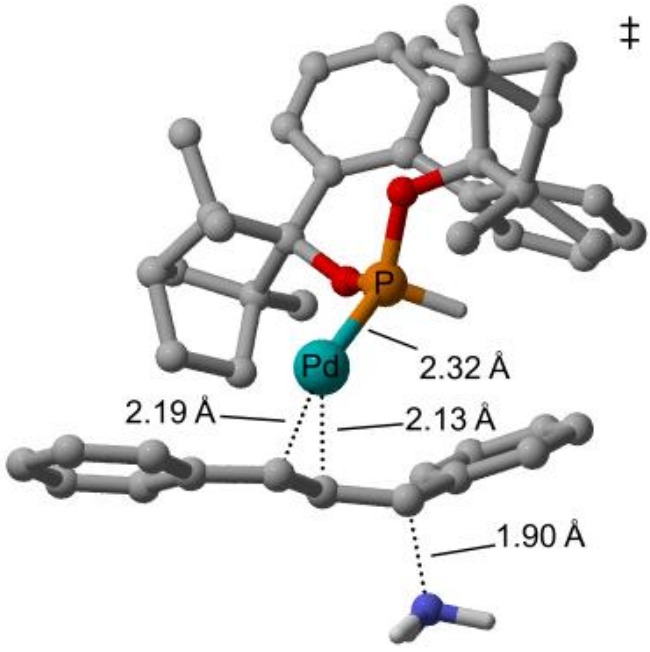
C	5.47187	-2.30214	-1.70013
H	5.10254	-0.18291	-1.73326
C	5.53189	-3.46354	-0.92167
H	5.32894	-4.29816	1.06411
H	5.65448	-2.35507	-2.77541
H	5.76249	-4.42319	-1.38906
C	2.52442	3.5153	0.35322
C	2.0501	4.48998	1.25084
C	2.5691	3.83389	-1.0186
C	1.66161	5.7515	0.80014
H	1.99299	4.25301	2.3163
C	2.17735	5.09258	-1.46836
H	2.89388	3.08393	-1.74277
C	1.72916	6.05953	-0.5606
H	1.29967	6.49501	1.51337
H	2.21531	5.32213	-2.53551
H	1.42136	7.04474	-0.91692
H	4.19721	0.14375	1.9606
N	6.26586	0.94075	1.45207
H	6.80372	1.10669	0.59751
H	6.16062	1.82821	1.95115
H	6.78376	0.27749	2.03528
P	-0.30358	-0.01288	0.55954
O	-0.88873	-1.11687	-0.52778
O	-1.53131	1.0202	0.73361
C	-1.01946	-2.51845	-0.19153
C	-2.58229	1.49376	-0.13092
C	-1.81619	-2.52659	1.14231
C	-1.72427	-3.30943	-1.35936

C	-3.66556	0.39728	-0.24262
C	-2.02775	2.15701	-1.51067
C	-3.1539	2.77147	0.63538
C	-1.55116	-3.469	2.14582
C	-2.77484	-1.50342	1.46274
C	-1.02321	-2.96312	-2.7054
C	-1.18122	-4.72487	-1.06803
C	-3.23286	-3.2258	-1.47254
C	-3.7239	-0.8093	0.50284
C	-4.8083	0.70744	-1.01246
C	-2.33805	3.67211	-1.28468
C	-2.69686	1.67129	-2.81296
C	-0.52944	1.93251	-1.74493
C	-3.66679	3.65813	-0.51835
C	-4.10952	2.44889	1.77232
C	-1.94538	3.63719	1.09441
C	-2.0145	-3.34674	3.45761
H	-0.94432	-4.33354	1.91224
C	-3.16836	-1.3565	2.80373
C	0.25084	-3.84339	-2.71614
H	-0.81156	-1.88775	-2.77261
H	-1.69371	-3.21017	-3.54059
C	0.29019	-4.36277	-1.26991
H	-1.43408	-5.08618	-0.06158
H	-1.54884	-5.46353	-1.79617
H	-3.73076	-3.53396	-0.54594
H	-3.57122	-2.2144	-1.72974
H	-3.56638	-3.90519	-2.27259
C	-4.93488	-1.54649	0.49443

C	-5.96523	-0.05956	-1.04972
H	-4.82046	1.61363	-1.59733
H	-2.33353	4.22549	-2.2353
C	-1.40917	4.27363	-0.21473
H	-2.08111	2.0016	-3.66295
H	-2.76448	0.57509	-2.85258
H	-3.69742	2.08361	-2.98286
H	-0.32743	0.89084	-2.03501
H	-0.20165	2.57279	-2.57813
H	0.09652	2.18647	-0.88622
H	-3.95106	4.65694	-0.15237
H	-4.52351	3.2647	-1.07226
H	-3.61318	1.80999	2.51959
H	-4.42296	3.37546	2.27764
H	-5.01295	1.92868	1.42588
H	-2.31975	4.4059	1.78672
H	-1.19413	3.0503	1.63312
C	-2.76981	-2.23437	3.81125
H	-1.75993	-4.11169	4.19428
H	-3.87206	-0.55579	3.0389
H	1.15648	-3.30907	-3.0296
H	0.13548	-4.69598	-3.40221
C	0.49524	-3.18687	-0.25817
H	1.0202	-5.16927	-1.10727
C	-6.04436	-1.20277	-0.26121
H	-4.98035	-2.44699	1.10815
H	-6.80382	0.2579	-1.67313
H	-1.51914	5.36808	-0.20077
H	-0.34881	4.07076	-0.39077

H	-3.10371	-2.08127	4.83974
C	1.13632	-3.72382	1.03504
C	1.53785	-2.19768	-0.8181
H	-6.94607	-1.81774	-0.23299
H	0.7441	-4.69842	1.3484
H	2.21135	-3.87129	0.84664
H	1.03989	-3.02338	1.87739
H	1.179	-1.57675	-1.64341
H	1.92076	-1.54548	0.00244
H	2.42432	-2.75274	-1.15584
H	-0.44307	-0.7006	1.79098

H: TS-**7** (*endo-cis*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -311.86 cm^{-1}

Optimization: -2498.326171

Single point: -2499.352177

1 1

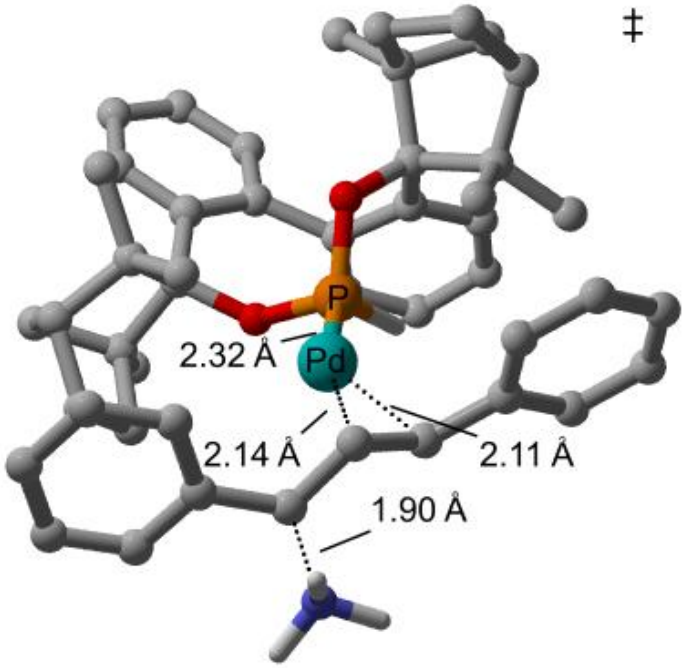
Pd	2.05678	-0.82162	-0.53011
C	3.50061	-1.37084	0.94035
C	2.76739	-2.51944	1.44262
C	4.15635	-1.39772	-0.30725
H	3.64954	-0.52975	1.62158
H	2.68669	-3.35082	0.7376
C	5.03137	-0.34516	-0.83662
C	5.26675	0.86823	-0.15739
C	5.63225	-0.53178	-2.09789
C	6.06878	1.85589	-0.72372
H	4.81644	1.04768	0.81982
C	6.4338	0.45874	-2.66359
H	5.46071	-1.46672	-2.63783
C	6.65435	1.6578	-1.9795
H	6.23823	2.78965	-0.18295
H	6.88958	0.29472	-3.64245
H	7.28162	2.43501	-2.42104
C	1.57127	-2.35289	2.3089
C	0.57026	-3.33769	2.28594
C	1.39001	-1.21473	3.11371
C	-0.59156	-3.1861	3.04545
H	0.68748	-4.21372	1.64217
C	0.22968	-1.06476	3.86982
H	2.13909	-0.42207	3.12696
C	-0.76208	-2.05081	3.84028
H	-1.3748	-3.94492	3.00227
H	0.08996	-0.16475	4.47168
H	-1.67607	-1.92449	4.42003

H	4.20122	-2.3548	-0.84184
N	3.95401	-3.41595	2.62161
H	4.84136	-3.6153	2.15142
H	4.13315	-2.79902	3.41831
H	3.54816	-4.28686	2.97514
P	-0.16532	-0.33565	-0.07314
O	-1.3308	-0.31742	-1.24122
O	-0.38936	1.04907	0.73492
C	-2.45975	-1.22583	-1.21676
C	-0.58926	2.4294	0.39437
C	-3.10734	-1.04168	0.18343
C	-3.42581	-0.90229	-2.4205
C	-2.11201	2.63704	0.30652
C	0.27274	2.98176	-0.88228
C	0.08402	3.22087	1.60315
C	-3.75104	-2.11667	0.81934
C	-3.03558	0.1834	0.92811
C	-2.58578	-0.78657	-3.72604
C	-4.09804	-2.27923	-2.60086
C	-4.38372	0.2594	-2.25549
C	-3.09167	1.61961	0.42321
C	-2.58409	3.96255	0.185
C	1.35685	3.84932	-0.17266
C	-0.52686	3.8666	-1.86318
C	0.90076	1.91798	-1.79103
C	0.56809	4.53378	0.95108
C	-0.77517	3.30113	2.85411
C	1.46915	2.56916	1.8734
C	-4.14014	-2.10502	2.15844

H	-3.96295	-3.01171	0.25112
C	-3.34365	0.14346	2.30221
C	-2.32025	-2.25314	-4.14745
H	-1.6676	-0.20994	-3.55664
H	-3.16957	-0.24659	-4.48505
C	-2.80437	-3.03261	-2.91501
H	-4.62941	-2.62537	-1.7037
H	-4.81306	-2.27942	-3.43747
H	-5.038	0.12623	-1.38574
H	-3.85489	1.21512	-2.14854
H	-5.02539	0.3266	-3.14774
C	-4.45586	1.99698	0.34364
C	-3.925	4.30684	0.09506
H	-1.8722	4.7765	0.18127
H	1.86148	4.51872	-0.88422
C	2.32797	2.9769	0.64809
H	0.11957	4.09988	-2.72186
H	-1.41699	3.34655	-2.24256
H	-0.84862	4.82488	-1.44613
H	0.13501	1.30437	-2.2845
H	1.48179	2.42153	-2.57781
H	1.60768	1.25555	-1.26913
H	1.21335	5.10373	1.63738
H	-0.21596	5.2153	0.60743
H	-1.04197	2.28809	3.19569
H	-0.22379	3.8003	3.66613
H	-1.70875	3.85489	2.68738
H	1.87215	2.9988	2.80306
H	1.39346	1.48618	2.01112

C	-3.86443	-0.98338	2.93334
H	-4.64117	-2.97709	2.58428
H	-3.25138	1.07471	2.86457
H	-1.27737	-2.45186	-4.42372
H	-2.93504	-2.53221	-5.01631
C	-1.91438	-2.72314	-1.66713
H	-2.8989	-4.11495	-3.08556
C	-4.88607	3.30044	0.15411
H	-5.20419	1.21439	0.46987
H	-4.21062	5.35633	-0.00215
H	3.20261	3.57301	0.94918
H	2.71336	2.11495	0.0899
H	-4.11782	-0.95185	3.99569
C	-2.0195	-3.89213	-0.66812
C	-0.42456	-2.69144	-2.05906
H	-5.95257	3.52687	0.09493
H	-3.02734	-4.31681	-0.58921
H	-1.37546	-4.70811	-1.03156
H	-1.67609	-3.6185	0.3386
H	-0.14065	-1.82944	-2.67065
H	0.22565	-2.70097	-1.1681
H	-0.18955	-3.60511	-2.62563
H	-0.74686	-1.20327	0.88368

H: TS-**6** (*exo-trans*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -301.94 cm^{-1}

Optimization: -2498.328896

Single point: -2499.352387

1 1

Pd	1.82947	0.68993	-0.08412
C	3.77703	1.55797	-0.22598
C	4.52684	0.47549	-0.80863
C	2.83519	2.29869	-1.01119
H	4.09511	1.93511	0.74921
H	4.20073	0.19574	-1.81532
C	2.29305	3.62389	-0.66391
C	2.47951	4.22076	0.59775
C	1.52545	4.31305	-1.62136
C	1.91857	5.46292	0.88695
H	3.05648	3.70597	1.3682

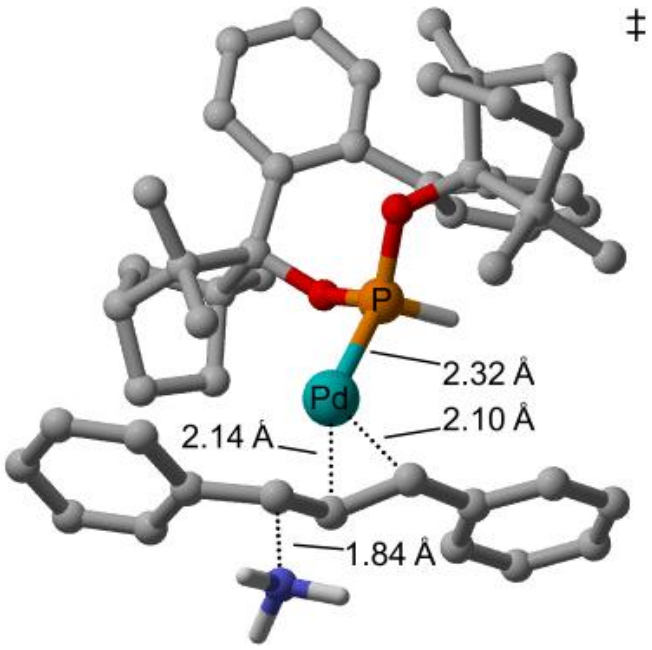
C	0.95779	5.55272	-1.32937
H	1.366	3.86055	-2.60368
C	1.15252	6.13383	-0.07308
H	2.07368	5.91054	1.87115
H	0.36222	6.06871	-2.08558
H	0.71082	7.10542	0.15814
C	4.99442	-0.68745	-0.00751
C	5.42776	-1.84452	-0.67749
C	4.97918	-0.68031	1.39736
C	5.84593	-2.9672	0.0364
H	5.41459	-1.87403	-1.77103
C	5.39323	-1.80489	2.11108
H	4.61659	0.19495	1.93773
C	5.82879	-2.94898	1.43382
H	6.17076	-3.86256	-0.49732
H	5.37012	-1.79172	3.20276
H	6.14732	-3.82908	1.9964
H	2.80618	2.07882	-2.08569
N	6.18642	1.21014	-1.38428
H	6.01246	2.02026	-1.98527
H	6.68461	1.52339	-0.54709
H	6.77736	0.53534	-1.87791
P	-0.40488	0.21987	-0.50788
O	-1.55701	0.4196	0.64609
O	-0.52589	-1.35586	-0.90467
C	-2.74759	1.23206	0.42144
C	-0.71516	-2.54734	-0.12798
C	-3.34705	0.7013	-0.90989
C	-3.71567	1.12444	1.66082

C	-2.22924	-2.69296	0.14507
C	0.30224	-2.71464	1.14482
C	-0.2058	-3.7161	-1.08334
C	-3.98214	1.57023	-1.81047
C	-3.2093	-0.66347	-1.33748
C	-2.89784	1.35659	2.96525
C	-4.46805	2.46445	1.51476
C	-4.6114	-0.09288	1.76608
C	-3.23821	-1.89709	-0.45521
C	-2.67195	-3.81692	0.87597
C	1.17001	-3.94279	0.71034
C	-0.37131	-2.98728	2.50704
C	1.21172	-1.51121	1.4336
C	0.19464	-4.8192	-0.08485
C	-1.1717	-4.08356	-2.19671
C	1.20307	-3.31815	-1.61519
C	-4.28984	1.22677	-3.12771
H	-4.24141	2.56806	-1.48534
C	-3.45497	-0.96883	-2.68777
C	-2.73374	2.89401	3.05263
H	-1.94174	0.81829	2.93146
H	-3.46152	0.95936	3.82154
C	-3.22827	3.34559	1.67032
H	-4.98787	2.56592	0.5517
H	-5.20814	2.60773	2.31667
H	-5.23829	-0.21738	0.87549
H	-4.03779	-1.01559	1.92017
H	-5.28202	0.03312	2.63054
C	-4.58263	-2.33328	-0.36177

C	-4.00266	-4.19542	1.00162
H	-1.95042	-4.45848	1.35726
H	1.65233	-4.4163	1.57827
C	2.15264	-3.56093	-0.41188
H	0.36502	-2.81819	3.30715
H	-1.22076	-2.31252	2.68145
H	-0.71932	-4.018	2.62907
H	0.65217	-0.67181	1.86944
H	1.97819	-1.81125	2.1636
H	1.78763	-1.20334	0.53312
H	0.70247	-5.65244	-0.59471
H	-0.62889	-5.24892	0.49063
H	-1.36065	-3.21223	-2.84204
H	-0.74123	-4.88004	-2.82323
H	-2.13653	-4.43915	-1.80989
H	1.45533	-3.97252	-2.46246
H	1.22085	-2.28547	-1.98227
C	-3.94945	-0.03668	-3.59817
H	-4.77286	1.9591	-3.77804
H	-3.32055	-2.00455	-3.00423
H	-1.71234	3.21692	3.28911
H	-3.38856	3.31741	3.82927
C	-2.28952	2.81664	0.53829
H	-3.38717	4.43074	1.59037
C	-4.98233	-3.45349	0.34982
H	-5.34162	-1.73792	-0.87066
H	-4.259	-5.08192	1.58563
H	2.83048	-4.40657	-0.60248
H	2.79447	-2.70385	-0.17729

H	-4.12873	-0.32147	-4.63718
C	-2.41794	3.73608	-0.6921
C	-0.8122	2.94107	0.94643
H	-6.03627	-3.73516	0.39343
H	-3.4435	4.07206	-0.88805
H	-1.82889	4.64408	-0.49441
H	-2.01667	3.28218	-1.60925
H	-0.50464	2.26093	1.74614
H	-0.14717	2.77303	0.08891
H	-0.62112	3.97151	1.27723
H	-1.02438	0.77387	-1.65653

H: TS-**5** (*endo-trans*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -282.73 cm^{-1}

Optimization: -2498.326175

Single point: -2499.351540

1 1

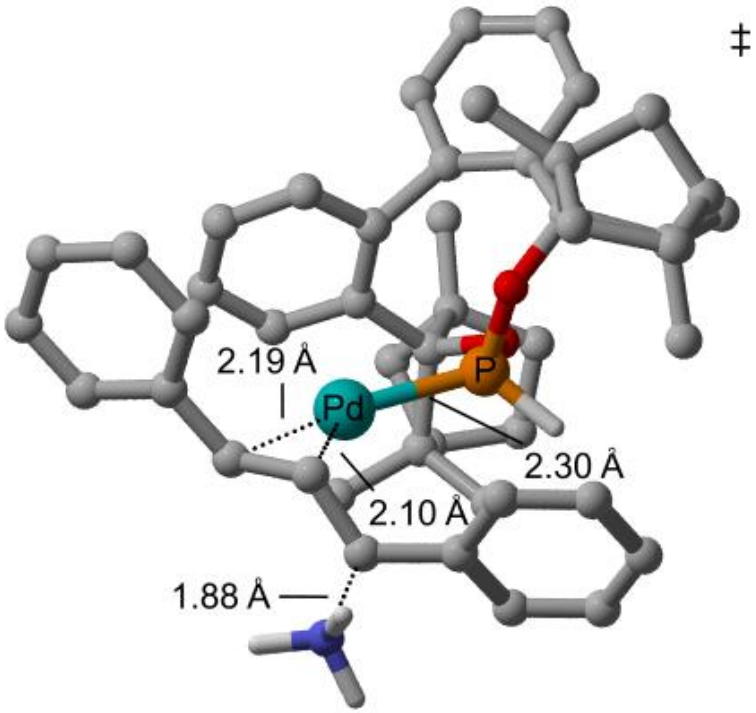
Pd	1.89799	-0.61459	-0.07087
C	3.79955	-1.53784	0.23815
C	2.75634	-2.51728	0.18769
C	4.48513	-1.09659	-0.95471
H	4.20234	-1.22426	1.20478
H	2.61798	-3.04386	-0.76531
C	4.941	0.32035	-1.08
C	4.99162	0.90983	-2.35313
C	5.27376	1.09624	0.0435
C	5.36251	2.2479	-2.50387
H	4.71512	0.32202	-3.23313
C	5.64719	2.43113	-0.10755
H	5.21991	0.66718	1.04552
C	5.6915	3.01087	-1.38072
H	5.3876	2.69639	-3.49917
H	5.89649	3.02633	0.77333
H	5.97793	4.05846	-1.49478
C	2.19542	-3.23454	1.34913
C	1.44306	-4.40267	1.12934
C	2.33427	-2.76876	2.67176
C	0.84217	-5.08104	2.19103
H	1.32341	-4.77776	0.11025
C	1.74007	-3.4497	3.73169
H	2.89044	-1.85056	2.87184
C	0.98797	-4.60747	3.49677
H	0.25847	-5.98357	1.99664
H	1.85523	-3.07148	4.74994
H	0.51775	-5.13467	4.32949

H	4.04483	-1.47768	-1.88211
N	6.06933	-2.0255	-1.0923
H	6.58071	-1.81266	-1.95436
H	6.65668	-1.76055	-0.29651
H	5.8843	-3.03159	-1.04126
P	-0.3837	-0.34957	0.22169
O	-1.46027	-0.34054	-1.01822
O	-0.6203	1.0422	1.04351
C	-2.61155	-1.23341	-1.03529
C	-0.75264	2.40587	0.62309
C	-3.35419	-0.96949	0.30137
C	-3.47732	-0.9592	-2.32451
C	-2.1965	2.58724	0.10132
C	0.48519	2.96502	-0.30084
C	-0.53945	3.26374	1.94799
C	-4.06693	-2.00154	0.93281
C	-3.32156	0.29285	0.98549
C	-2.5389	-0.93348	-3.56698
C	-4.16597	-2.33147	-2.47833
C	-4.42092	0.22518	-2.30529
C	-3.257	1.6736	0.35189
C	-2.55786	3.82741	-0.4656
C	1.08851	4.09527	0.60253
C	0.10571	3.523	-1.68943
C	1.58701	1.9407	-0.61675
C	-0.11633	4.63155	1.38316
C	-1.70347	3.24936	2.92203
C	0.7957	2.80452	2.60774
C	-4.57011	-1.91365	2.23022

H	-4.23796	-2.92584	0.39945
C	-3.78273	0.34057	2.31387
C	-2.28342	-2.42618	-3.89117
H	-1.62091	-0.37051	-3.35474
H	-3.04874	-0.42036	-4.39492
C	-2.87114	-3.12527	-2.65557
H	-4.76774	-2.61674	-1.60487
H	-4.81892	-2.36372	-3.36373
H	-5.12677	0.17033	-1.46821
H	-3.88123	1.17851	-2.24509
H	-5.00816	0.2295	-3.23698
C	-4.58234	2.11096	0.11905
C	-3.86515	4.21115	-0.74211
H	-1.79352	4.55681	-0.6835
H	1.64755	4.82842	0.00236
C	1.90038	3.4948	1.76496
H	1.01107	3.56436	-2.31426
H	-0.62814	2.88308	-2.19955
H	-0.28686	4.54508	-1.66324
H	1.2825	1.26396	-1.43039
H	2.48357	2.47308	-0.96676
H	1.91557	1.38317	0.28774
H	0.18012	5.32228	2.18735
H	-0.88107	5.13591	0.78671
H	-1.87519	2.2316	3.30048
H	-1.47424	3.89359	3.78491
H	-2.6342	3.61335	2.46521
H	0.81436	3.14652	3.65257
H	0.8784	1.71097	2.62363

C	-4.36412	-0.74816	2.95926
H	-5.10446	-2.76261	2.66172
H	-3.74822	1.30134	2.82677
H	-1.2291	-2.66295	-4.08145
H	-2.8439	-2.73832	-4.78533
C	-2.06363	-2.76141	-1.36754
H	-2.97778	-4.21367	-2.77172
C	-4.90575	3.34743	-0.42
H	-5.39071	1.42432	0.37168
H	-4.05883	5.19253	-1.18034
H	2.3777	4.31027	2.32876
H	2.70782	2.8191	1.4536
H	-4.70843	-0.65689	3.99166
C	-2.25183	-3.87537	-0.31755
C	-0.55142	-2.76759	-1.65315
H	-5.94926	3.62333	-0.58441
H	-3.26909	-4.28273	-0.28273
H	-1.59941	-4.71672	-0.598
H	-1.96379	-3.56349	0.69598
H	-0.20848	-1.94436	-2.28676
H	0.02545	-2.7375	-0.71903
H	-0.29283	-3.71609	-2.14871
H	-1.00883	-1.21705	1.15298

H: TS-**4** (*exo-cis*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -294.38 cm^{-1}

Optimization: -2498.346716

Single point: -2499.367502

1 1

Pd	-1.7604	-0.042	0.31923
C	-3.24454	1.39729	-0.06547
C	-3.87704	0.13784	-0.23046
C	-3.18123	2.06776	1.21825
H	-2.97473	1.98464	-0.94686
H	-4.44012	-0.27122	0.6167
C	-2.08415	3.02617	1.5291
C	-1.65432	3.16661	2.85761
C	-1.45659	3.78513	0.52589
C	-0.61339	4.04118	3.17985
H	-2.12349	2.56868	3.6435

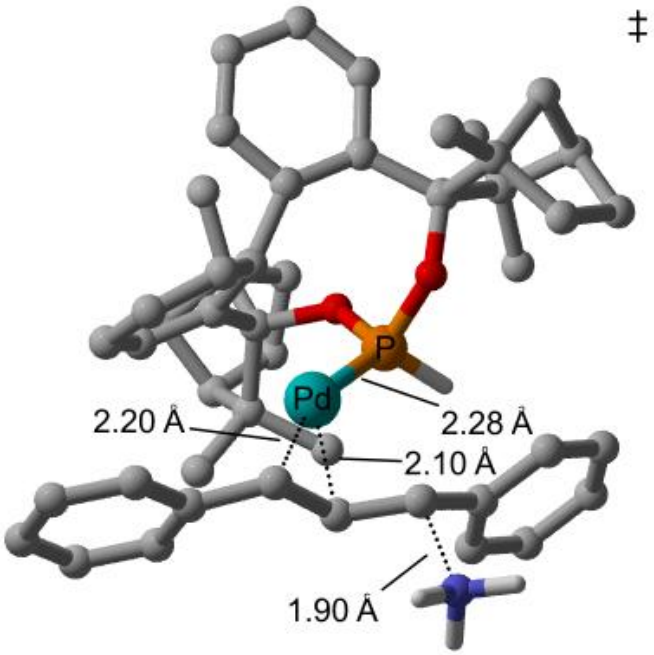
C	-0.42624	4.66568	0.85001
H	-1.75501	3.67613	-0.51812
C	-0.0003	4.79565	2.1772
H	-0.27983	4.12999	4.21576
H	0.05628	5.24503	0.06067
H	0.81501	5.47814	2.42528
C	-4.17262	-0.47122	-1.53368
C	-5.04527	-1.57407	-1.59978
C	-3.5805	-0.02152	-2.73167
C	-5.32799	-2.1967	-2.81495
H	-5.50506	-1.94569	-0.68013
C	-3.87289	-0.63627	-3.94794
H	-2.86668	0.80411	-2.71325
C	-4.7473	-1.72703	-3.99762
H	-6.01001	-3.04962	-2.84172
H	-3.40519	-0.26907	-4.86434
H	-4.97229	-2.20971	-4.95098
H	-3.47876	1.4516	2.07096
N	-4.68431	3.20057	1.29322
H	-4.57518	3.91732	0.5708
H	-5.53121	2.66036	1.09528
H	-4.77633	3.6677	2.1997
P	0.41481	0.58528	0.74387
O	1.39796	-0.60254	1.34646
O	1.11574	1.03277	-0.64258
C	0.73401	-1.86626	1.59258
C	2.45548	0.98678	-1.16606
C	-0.0129	-2.17218	0.25501
C	1.78476	-2.97271	2.00252

C	2.86894	-0.49022	-1.36786
C	2.33612	1.69473	-2.59147
C	3.46826	1.99982	-0.38814
C	-1.25751	-2.84143	0.24874
C	0.52775	-1.81511	-1.04069
C	2.74754	-2.36618	3.06381
C	0.89508	-3.88898	2.86718
C	2.54304	-3.69975	0.91062
C	1.98601	-1.60779	-1.41613
C	4.1914	-0.7263	-1.79724
C	1.55724	3.03038	-2.40597
C	3.76029	2.2428	-2.79977
C	1.74631	0.8262	-3.68995
C	3.78754	3.05679	-1.49958
C	2.82652	2.68196	0.82901
C	4.7777	1.3958	0.16218
C	-2.00088	-3.09049	-0.91073
H	-1.64728	-3.22813	1.17923
C	-0.28667	-2.00466	-2.17245
C	1.94502	-2.41205	4.38673
H	3.06152	-1.35451	2.77803
H	3.65529	-2.98378	3.12019
C	0.54651	-2.823	3.90369
H	0.03181	-4.29648	2.32022
H	1.46347	-4.73436	3.28322
H	1.8723	-4.13675	0.16024
H	3.26062	-3.04525	0.40355
H	3.11113	-4.52487	1.368
C	2.4585	-2.80272	-2.01255

C	4.65044	-1.9316	-2.31614
H	4.90764	0.07863	-1.7636
C	2.5845	3.98618	-1.74375
H	0.64628	2.88843	-1.81309
H	1.2516	3.39678	-3.39719
H	4.53721	1.47879	-2.89321
H	3.81778	2.87905	-3.6965
H	2.35012	-0.07061	-3.88489
H	0.7285	0.50387	-3.42099
H	1.68064	1.40069	-4.62692
H	4.72198	3.59431	-1.28234
H	1.82058	3.06605	0.64262
H	2.79107	2.00011	1.69054
H	3.45651	3.53642	1.12103
H	5.56177	1.26613	-0.59294
H	5.19304	2.08745	0.91042
H	4.60687	0.42952	0.65758
C	-1.53812	-2.62003	-2.13032
H	-2.94841	-3.6255	-0.83788
H	0.12308	-1.71029	-3.13919
H	1.96202	-1.46845	4.9465
H	2.33797	-3.18697	5.06195
C	-0.10513	-1.71344	3.02148
H	-0.12462	-3.13527	4.71695
C	3.75772	-2.98615	-2.46216
H	1.76195	-3.6374	-2.0915
H	5.69288	-2.02313	-2.62832
H	2.20956	4.47174	-0.8343
H	2.87982	4.79127	-2.43302

H	-2.12087	-2.75264	-3.04189
C	-1.62905	-1.93346	3.04764
C	0.09592	-0.31958	3.64476
H	4.06137	-3.9382	-2.90174
H	-2.15895	-1.33187	2.28901
H	-1.92801	-2.98349	2.93933
H	-1.99753	-1.61075	4.03357
H	-0.54479	0.43042	3.15437
H	-0.21706	-0.35769	4.69922
H	1.12903	0.03831	3.61093
H	0.75357	1.62377	1.63547

H: TS-**3** (*endo-cis*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -311.86 cm^{-1}

Optimization: -2498.346601

Single point: -2499.367852

1 1

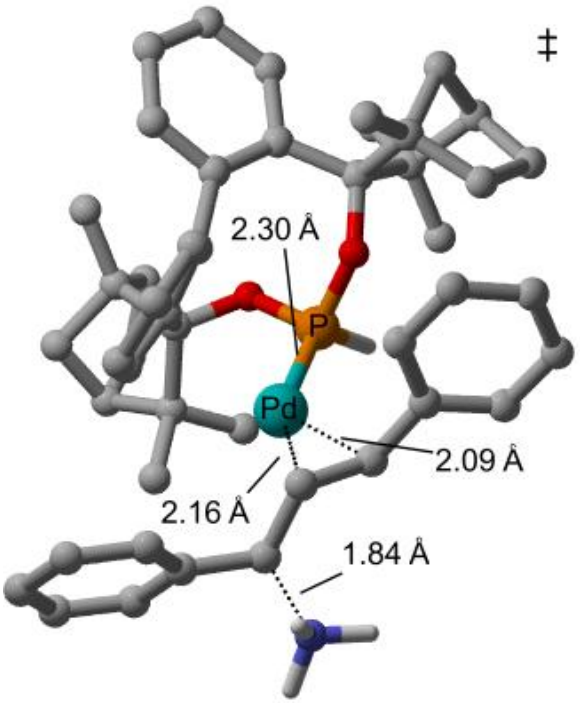
Pd	-1.39981	0.72682	-0.50244
C	-2.78784	2.25134	-0.09314
C	-1.86377	3.35729	-0.24059
C	-3.30294	1.56173	-1.22672
H	-3.2397	2.10028	0.89099
C	-4.41175	0.60048	-1.19353
C	-5.01434	0.20026	-2.40166
C	-4.87143	0.00893	0.00019
C	-6.03123	-0.75373	-2.41983
H	-4.67184	0.6447	-3.34
C	-5.889	-0.94346	-0.01694
H	-4.42191	0.28461	0.95522
C	-6.47398	-1.33287	-1.22652
H	-6.48353	-1.04583	-3.37041
H	-6.22632	-1.38885	0.92188
H	-7.27059	-2.07972	-1.2384
C	-0.88318	3.70549	0.825
C	0.36178	4.23612	0.45312
C	-1.15153	3.48678	2.18671
C	1.32581	4.53385	1.41869
H	0.58925	4.39035	-0.60445
C	-0.18985	3.78823	3.15095
H	-2.10629	3.05847	2.49826
C	1.0514	4.3118	2.77027
H	2.29425	4.93287	1.11127
H	-0.4061	3.60688	4.20582
H	1.80442	4.53963	3.52743
H	-3.07972	1.97676	-2.2167

H	-1.46447	3.48039	-1.25075
N	-2.91826	4.93382	-0.29332
H	-2.36184	5.76958	-0.49299
H	-3.65017	4.82934	-1.00129
H	-3.36029	5.05148	0.62197
P	0.56413	0.54655	0.64795
O	0.99014	-0.94024	1.21856
O	1.69256	0.88537	-0.46188
C	0.00701	-1.9983	1.34142
C	2.91276	0.25764	-0.86494
C	-0.72486	-2.07095	-0.01849
C	0.7492	-3.3314	1.74451
C	2.60164	-1.16625	-1.37905
C	3.44047	1.17213	-2.065
C	4.08268	0.45555	0.24354
C	-1.98043	-2.65779	-0.17925
C	-0.1331	-1.46949	-1.19933
C	1.74628	-3.0093	2.89238
C	-0.37098	-4.05545	2.51973
C	1.39082	-4.12508	0.62197
C	1.32118	-1.74827	-1.60467
C	3.7077	-1.89819	-1.86091
C	3.28376	2.65867	-1.63594
C	4.97332	1.04349	-1.94364
C	2.79558	0.88312	-3.41091
C	5.03289	1.47151	-0.47131
C	3.56191	1.02457	1.57151
C	4.86807	-0.8109	0.63718
C	-2.75037	-2.5206	-1.34701

H	-2.4108	-3.22642	0.63644
C	-0.98875	-1.19312	-2.29707
C	0.8524	-2.85978	4.15067
H	2.33841	-2.11415	2.6686
H	2.45028	-3.84771	2.99625
C	-0.566	-2.95137	3.56288
H	-1.25879	-4.27806	1.91294
H	-0.01622	-5.00302	2.95276
H	0.67158	-4.37436	-0.16913
H	2.22809	-3.58085	0.16577
H	1.7862	-5.07001	1.02591
C	1.26047	-2.94852	-2.36192
C	3.62578	-3.09473	-2.56062
H	4.69945	-1.50194	-1.70928
C	4.39084	2.86949	-0.56877
H	2.27574	2.87181	-1.26728
H	3.45767	3.29086	-2.5195
H	5.38479	0.0531	-2.15729
H	5.48536	1.75428	-2.61072
H	3.01648	-0.12957	-3.77397
H	1.7002	0.98545	-3.34206
H	3.15459	1.59997	-4.16549
H	6.03115	1.47756	-0.01016
H	2.91959	1.9019	1.45062
H	3.01145	0.25959	2.13655
H	4.42287	1.33035	2.18551
H	5.59383	-1.13856	-0.11597
H	5.44672	-0.59494	1.54779
H	4.19672	-1.65239	0.85827

C	-2.28975	-1.71824	-2.3775
H	-3.73101	-2.99442	-1.40618
H	-0.54077	-0.72832	-3.17827
H	1.03883	-1.93696	4.71424
H	1.01134	-3.69386	4.8503
C	-0.89779	-1.70902	2.6793
H	-1.3456	-3.1286	4.31798
C	2.372	-3.62331	-2.8423
H	0.27864	-3.38723	-2.54365
H	4.5395	-3.58965	-2.89602
H	4.00627	3.2413	0.38905
H	5.14204	3.59601	-0.91268
H	-2.90177	-1.52924	-3.25929
C	-2.42148	-1.60712	2.49584
C	-0.49578	-0.39548	3.37079
H	2.25255	-4.54854	-3.40923
H	-2.68983	-0.93182	1.67259
H	-2.91332	-2.57156	2.32485
H	-2.85425	-1.20053	3.42284
H	-0.90277	0.47377	2.82863
H	-0.94048	-0.37425	4.37743
H	0.58473	-0.2602	3.47885
H	0.97722	1.35626	1.73246

H: TS-**2** (*exo-trans*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -301.94 cm^{-1}

Optimization: -2498.345100

Single point: -2499.369863

1 1

Pd	1.36428	0.69934	-0.5289
C	2.82569	2.23957	-0.14793
C	4.05891	1.74142	-0.70871
C	1.75677	2.70442	-0.98459
H	2.82415	2.49018	0.91626
H	3.97822	1.4118	-1.74947
C	0.6919	3.61325	-0.50958
C	0.28931	3.6553	0.84045
C	0.0573	4.47347	-1.42262
C	-0.6855	4.55494	1.26302
H	0.72311	2.95563	1.55775

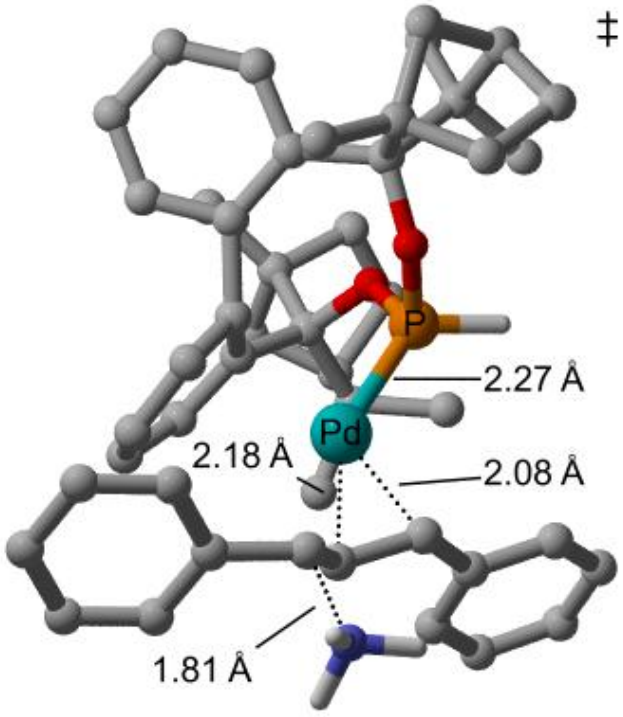
C	-0.92393	5.37201	-0.99875
H	0.3453	4.44272	-2.47701
C	-1.2911	5.42334	0.34736
H	-0.98889	4.5705	2.31206
H	-1.40212	6.03514	-1.72304
H	-2.05841	6.12494	0.68114
C	4.94594	0.87048	0.11302
C	5.50036	-0.28513	-0.45716
C	5.22419	1.17057	1.457
C	6.29685	-1.14028	0.30722
H	5.28812	-0.52846	-1.50078
C	6.03555	0.32665	2.21497
H	4.7954	2.06138	1.92252
C	6.56684	-0.83537	1.64402
H	6.71073	-2.04469	-0.1436
H	6.24796	0.56967	3.25827
H	7.19453	-1.50005	2.2413
H	1.95996	2.78242	-2.06057
N	5.1507	3.18493	-1.05426
H	6.02204	2.92106	-1.52478
H	4.64098	3.86394	-1.62674
H	5.38594	3.62495	-0.16042
P	-0.67792	-0.0666	-1.26359
O	-0.93776	-1.68802	-1.02931
O	-1.8522	0.6552	-0.41952
C	0.16476	-2.42018	-0.44658
C	-3.17858	0.26429	-0.01417
C	0.55348	-1.57885	0.81061
C	-0.26428	-3.90451	-0.11279

C	-3.06839	-0.88667	1.01446
C	-3.7611	1.55222	0.72428
C	-4.21044	0.12484	-1.26784
C	1.8973	-1.451	1.22322
C	-0.43129	-0.88108	1.61166
C	-1.02474	-4.48334	-1.34101
C	1.10198	-4.61241	-0.219
C	-1.00233	-4.18372	1.18062
C	-1.90315	-1.21743	1.76525
C	-4.27154	-1.47721	1.45192
C	-3.53909	2.7839	-0.20089
C	-5.27899	1.35421	0.557
C	-3.23273	1.78235	2.13014
C	-5.23914	1.2717	-0.97455
C	-3.54596	0.35362	-2.63532
C	-4.94023	-1.22649	-1.42114
C	2.31069	-0.63963	2.28835
H	2.65743	-2.03854	0.72946
C	0.02657	-0.01319	2.61909
C	0.09097	-4.87118	-2.34111
H	-1.73636	-3.75143	-1.74315
H	-1.60664	-5.3604	-1.02374
C	1.33803	-4.26081	-1.68587
H	1.85353	-4.20806	0.47598
H	1.01643	-5.69406	-0.03587
H	-0.47303	-3.78639	2.05568
H	-2.01996	-3.77823	1.16896
H	-1.08145	-5.27467	1.30888
C	-2.06728	-1.95097	2.96485

C	-4.39554	-2.26187	2.59376
H	-5.17979	-1.29273	0.90116
C	-4.63137	2.64943	-1.29314
H	-2.51958	2.81791	-0.59826
H	-3.6774	3.6976	0.39356
H	-5.68824	0.47852	1.06845
H	-5.83781	2.23271	0.91492
H	-3.47058	0.95403	2.8116
H	-2.14121	1.91753	2.10932
H	-3.67404	2.70118	2.54641
H	-6.19919	1.08381	-1.47697
H	-2.85898	1.20581	-2.65873
H	-3.01163	-0.54629	-2.97027
H	-4.33725	0.54794	-3.3753
H	-5.81225	-1.3391	-0.76622
H	-5.32626	-1.30156	-2.44877
H	-4.26495	-2.07796	-1.25386
C	1.37234	0.12841	2.96172
H	3.36688	-0.6127	2.55565
H	-0.72613	0.521	3.19927
H	-0.09053	-4.51859	-3.36402
H	0.20894	-5.96375	-2.39907
C	1.26722	-2.70256	-1.66111
H	2.28229	-4.61318	-2.12609
C	-3.28009	-2.46922	3.39563
H	-1.17719	-2.15123	3.56186
H	-5.37054	-2.67475	2.86108
H	-4.24438	2.74577	-2.31466
H	-5.4063	3.42193	-1.17672

H	1.66501	0.79897	3.77267
C	2.70539	-2.17259	-1.52904
C	0.76991	-2.1472	-3.00855
H	-3.33969	-3.03888	4.32501
H	2.73654	-1.09595	-1.29293
H	3.31546	-2.71288	-0.79424
H	3.20304	-2.30573	-2.50217
H	0.93396	-1.05959	-3.07424
H	1.36286	-2.60141	-3.81674
H	-0.28615	-2.34967	-3.20872
H	-1.12387	0.01415	-2.59739

H: TS-**1** (*endo-trans*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -282.73 cm^{-1}

Optimization: -2498.343495

Single point: -2499.368257

1 1

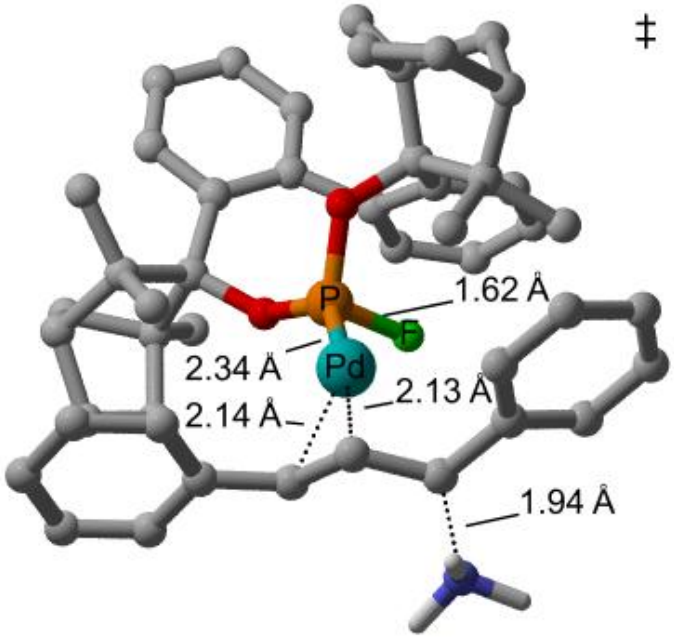
Pd	-1.382	-0.01879	-0.50165
C	-3.51793	-0.09321	-0.93344
C	-2.76763	0.65124	-1.90487
C	-3.84862	-1.48384	-1.15953
H	-4.06879	0.428	-0.14688
H	-2.52455	0.13156	-2.84166
C	-4.23367	-2.34697	-0.00497
C	-3.65792	-3.61882	0.12849
C	-5.14792	-1.90438	0.9648
C	-3.97492	-4.42845	1.22135
H	-2.93794	-3.96703	-0.61681
C	-5.47738	-2.71958	2.04797
H	-5.59809	-0.91158	0.88571
C	-4.8873	-3.98125	2.18141
H	-3.50958	-5.41105	1.32315
H	-6.1898	-2.36695	2.79671
H	-5.13951	-4.61534	3.03393
C	-2.76262	2.12438	-2.03503
C	-2.03249	2.70883	-3.08828
C	-3.42414	2.97631	-1.13272
C	-1.95358	4.09361	-3.22704
H	-1.51035	2.06103	-3.79789
C	-3.34836	4.36211	-1.27375
H	-3.99786	2.557	-0.30446
C	-2.61055	4.92857	-2.31743
H	-1.37787	4.52493	-4.04905
H	-3.86869	5.00603	-0.561

H	-2.55136	6.01371	-2.42396
H	-3.17225	-1.99007	-1.85671
N	-5.3147	-1.55394	-2.21026
H	-6.10066	-1.14996	-1.69284
H	-5.15174	-0.98634	-3.04737
H	-5.5644	-2.51007	-2.48398
P	0.73277	0.64719	-1.00665
O	1.64527	1.25216	0.22348
O	1.49121	-0.7166	-1.42649
C	1.0534	1.71207	1.46315
C	2.7131	-1.3535	-1.04675
C	0.11799	0.58368	1.94433
C	2.22024	2.05943	2.46857
C	2.67908	-1.65001	0.46876
C	2.70939	-2.71786	-1.87958
C	4.0049	-0.5888	-1.66514
C	-0.89469	0.78144	2.88061
C	0.23604	-0.75226	1.38807
C	3.2931	2.88343	1.70459
C	1.55306	3.16386	3.31386
C	2.81727	0.90039	3.245
C	1.58626	-1.48442	1.36662
C	3.80286	-2.33271	0.982
C	2.26797	-2.39009	-3.33458
C	4.21102	-2.96822	-2.13275
C	1.88322	-3.83247	-1.25782
C	4.47541	-1.59537	-2.766
C	3.65557	0.77784	-2.27072
C	5.1608	-0.30455	-0.68585

C	-1.89907	-0.16989	3.13677
H	-0.93697	1.71524	3.42907
C	-0.88455	-1.61357	1.50767
C	2.66435	4.29362	1.55771
H	3.55067	2.41789	0.74645
H	4.211	2.91356	2.30972
C	1.25191	4.09146	2.13267
H	0.66882	2.8266	3.87108
H	2.25813	3.59854	4.03871
H	2.05534	0.34634	3.80928
H	3.33534	0.19277	2.58417
H	3.55435	1.28635	3.96618
C	1.68778	-2.0754	2.65488
C	3.8946	-2.86773	2.25957
H	4.65662	-2.48221	0.34006
C	3.48535	-1.64591	-3.94638
H	1.33894	-1.8113	-3.3652
H	2.08245	-3.34093	-3.85634
H	4.81205	-3.19672	-1.2481
H	4.36068	-3.79562	-2.84364
H	2.27551	-4.15481	-0.28379
H	0.84269	-3.49898	-1.10945
H	1.86556	-4.70877	-1.9242
H	5.51326	-1.39709	-3.07065
H	2.80149	0.74652	-2.95366
H	3.45035	1.51582	-1.48297
H	4.52026	1.14172	-2.84624
H	5.75949	-1.18706	-0.43246
H	5.85107	0.40975	-1.15898

H	4.80057	0.14761	0.2488
C	-1.95179	-1.32852	2.38092
H	-2.65835	0.04025	3.8925
H	-0.79912	-2.615	1.07978
H	2.66952	4.67	0.52718
H	3.20491	5.03323	2.16704
C	0.38174	3.18572	1.20779
H	0.73616	5.03227	2.37366
C	2.80381	-2.75731	3.11344
H	0.84834	-1.95149	3.34012
H	4.80828	-3.38006	2.56788
H	3.23269	-0.65883	-4.35256
H	3.92851	-2.22209	-4.77215
H	-2.76048	-2.04834	2.50042
C	-1.10018	3.362	1.58193
C	0.471	3.61086	-0.26578
H	2.81793	-3.17698	4.12117
H	-1.73077	2.57135	1.15294
H	-1.27914	3.41102	2.66246
H	-1.44739	4.3174	1.16262
H	-0.27967	3.08515	-0.87595
H	0.22753	4.68093	-0.34377
H	1.45876	3.45988	-0.71232
H	1.11401	1.52734	-2.05139

F: TS-**8** (*exo-cis*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -289.62 cm^{-1}

Optimization: -2597.531080

Single point: -2598.659592

1 1

F	-0.17935	-0.84866	1.86665
Pd	1.95928	0.58686	0.13799
C	3.91268	1.42968	0.18137
C	2.97775	2.39234	0.66808
C	4.49736	0.45686	1.06743
H	4.32056	1.52438	-0.82795
H	2.86315	2.47805	1.75516
C	4.92317	-0.88114	0.58785
C	4.84949	-1.97168	1.47012
C	5.35248	-1.0983	-0.7331
C	5.18904	-3.25552	1.04143

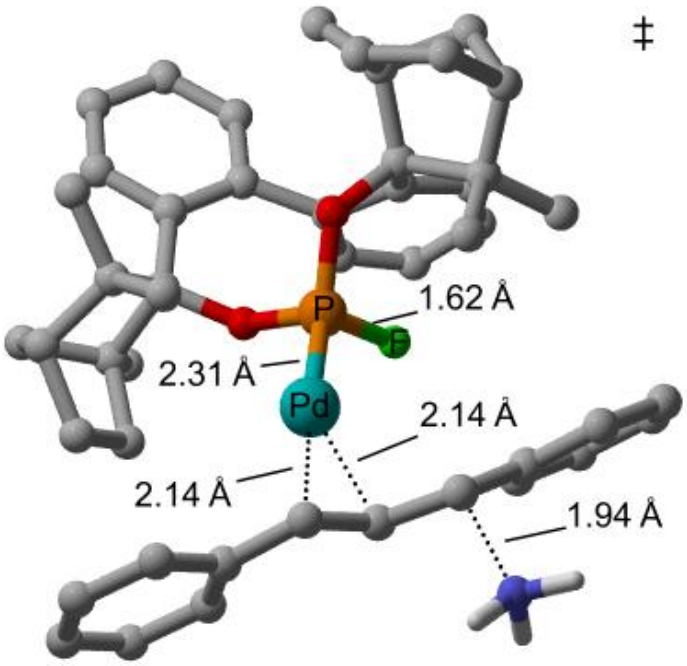
H	4.49563	-1.81631	2.49287
C	5.6996	-2.38009	-1.15803
H	5.40365	-0.26789	-1.43987
C	5.61651	-3.46147	-0.27329
H	5.11495	-4.09712	1.73305
H	6.03002	-2.53964	-2.1865
H	5.8821	-4.4653	-0.61145
C	2.54602	3.58384	-0.07955
C	1.9692	4.65809	0.62153
C	2.67426	3.68825	-1.47922
C	1.53631	5.80201	-0.04964
H	1.85387	4.58887	1.70616
C	2.2428	4.83013	-2.14852
H	3.08992	2.8581	-2.05374
C	1.67	5.89195	-1.43717
H	1.0872	6.62347	0.51235
H	2.34424	4.89259	-3.23423
H	1.32824	6.7846	-1.96529
H	4.07035	0.44236	2.07378
N	6.20035	1.18402	1.65876
H	6.81346	1.24578	0.84222
H	6.06652	2.12354	2.04147
H	6.65385	0.59042	2.35843
P	-0.27881	0.01202	0.49444
O	-0.82626	-1.04472	-0.61905
O	-1.56528	0.88365	0.85451
C	-0.90647	-2.49108	-0.4831
C	-2.68158	1.47597	0.14578
C	-1.80605	-2.71649	0.75989

C	-1.47261	-3.12311	-1.81145
C	-3.66964	0.36371	-0.26273
C	-2.17245	2.5303	-0.9886
C	-3.35852	2.45105	1.20817
C	-1.61357	-3.82362	1.59685
C	-2.80498	-1.77121	1.16722
C	-0.66403	-2.5748	-3.02389
C	-0.90722	-4.55246	-1.67122
C	-2.96693	-3.05197	-2.04925
C	-3.70768	-0.95985	0.25225
C	-4.77014	0.75782	-1.05493
C	-2.66509	3.89558	-0.40362
C	-2.72044	2.34022	-2.41924
C	-0.65097	2.52566	-1.162
C	-3.97866	3.53271	0.30067
C	-4.27001	1.77077	2.2152
C	-2.23801	3.28898	1.88865
C	-2.18769	-3.93689	2.86409
H	-0.97662	-4.63385	1.26803
C	-3.31715	-1.86772	2.47155
C	0.63634	-3.416	-3.03465
H	-0.48595	-1.49589	-2.92251
H	-1.24635	-2.71683	-3.94519
C	0.56224	-4.12934	-1.67501
H	-1.24045	-5.06313	-0.75819
H	-1.1762	-5.18506	-2.53048
H	-3.53205	-3.50933	-1.22919
H	-3.314	-2.01877	-2.17677
H	-3.20792	-3.60461	-2.97083

C	-4.86718	-1.73686	0.00675
C	-5.87324	-0.042	-1.3245
H	-4.79447	1.75342	-1.4677
H	-2.73014	4.66434	-1.18732
C	-1.81658	4.31981	0.80849
H	-2.0803	2.90752	-3.11129
H	-2.70146	1.28692	-2.7322
H	-3.73628	2.72535	-2.56361
H	-0.31538	1.62584	-1.70228
H	-0.35475	3.39173	-1.77117
H	-0.09641	2.59217	-0.22467
H	-4.38166	4.36622	0.8964
H	-4.7831	3.18315	-0.35282
H	-3.70185	1.05151	2.82398
H	-4.69845	2.5212	2.89728
H	-5.10061	1.23601	1.73429
H	-2.66701	3.78661	2.77067
H	-1.41232	2.66053	2.24072
C	-2.98933	-2.90679	3.3409
H	-1.98331	-4.82011	3.47303
H	-4.06487	-1.13507	2.77804
H	1.54717	-2.82338	-3.18755
H	0.61298	-4.16777	-3.83781
C	0.63026	-3.09961	-0.49725
H	1.30386	-4.93212	-1.55222
C	-5.93782	-1.31312	-0.76489
H	-4.90489	-2.73375	0.4471
H	-6.68215	0.34562	-1.94742
H	-2.09178	5.34298	1.10651

H	-0.74041	4.32913	0.6083
H	-3.41432	-2.93916	4.34638
C	1.16631	-3.78735	0.77298
C	1.68817	-2.02502	-0.81902
H	-6.79939	-1.96511	-0.92207
H	0.7989	-4.81132	0.90517
H	2.261	-3.86463	0.68262
H	0.94088	-3.21184	1.68068
H	1.39182	-1.31846	-1.60175
H	1.96354	-1.48304	0.1149
H	2.62031	-2.51352	-1.13471

F: TS-**7** (*endo-cis*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -320.94 cm^{-1}

Optimization: -2597.535382

Single point: -2598.660552

1 1

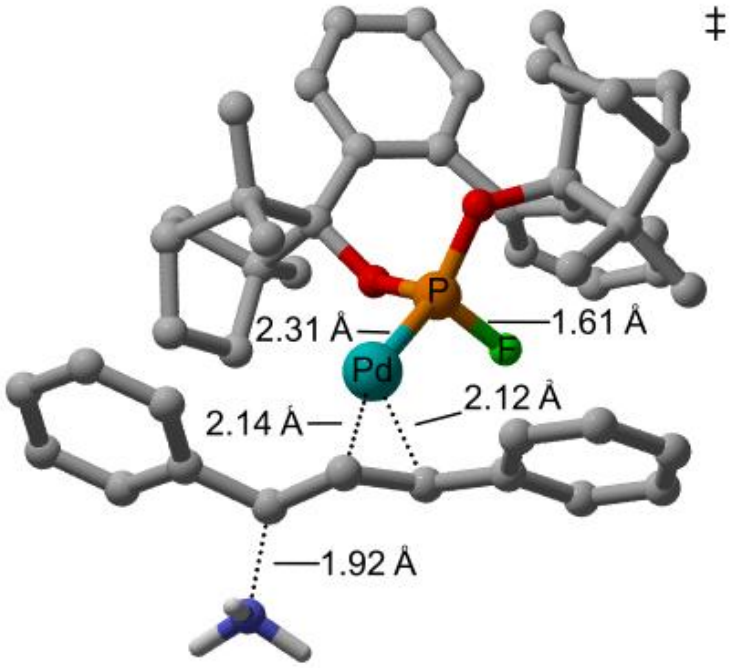
F	0.46667	1.04799	1.36815
Pd	-2.03355	0.39228	-0.61856
C	-3.61583	1.55736	0.22294
C	-3.2553	2.90365	-0.15855
C	-4.16059	0.64017	-0.70971
H	-3.67659	1.34677	1.29319
H	-3.25257	3.0944	-1.23571
C	-4.78424	-0.64532	-0.36231
C	-4.77837	-1.1656	0.94876
C	-5.3685	-1.41945	-1.38451
C	-5.34548	-2.40759	1.22356
H	-4.31477	-0.60388	1.76135
C	-5.9295	-2.66551	-1.10834
H	-5.37654	-1.03417	-2.40752
C	-5.92309	-3.16372	0.19792
H	-5.32945	-2.79411	2.24486
H	-6.37678	-3.25003	-1.91525
H	-6.36368	-4.13873	0.41625
C	-2.27321	3.71016	0.60343
C	-1.84164	4.93825	0.06914
C	-1.76074	3.28787	1.84118
C	-0.93899	5.73827	0.76631
H	-2.20848	5.2622	-0.90943
C	-0.84846	4.0838	2.53236
H	-2.04049	2.31802	2.25164
C	-0.44235	5.31164	2.00231
H	-0.60912	6.68793	0.34032
H	-0.43922	3.73404	3.4819

H	0.27675	5.92942	2.54413
H	-4.37366	1.0051	-1.72254
N	-4.86873	3.93443	0.15327
H	-4.76923	4.91162	-0.13397
H	-5.6619	3.50912	-0.334
H	-5.0475	3.91114	1.16046
P	0.16357	0.14486	0.05897
O	1.48847	0.29945	-0.86345
O	0.3415	-1.31489	0.69982
C	2.62415	1.19391	-0.66542
C	0.67751	-2.63368	0.22026
C	3.12757	0.87292	0.76691
C	3.68259	0.94997	-1.80678
C	2.21522	-2.76053	0.26049
C	-0.05398	-3.05103	-1.18393
C	-0.04148	-3.61104	1.2484
C	3.681	1.87491	1.57597
C	2.95309	-0.41187	1.37903
C	2.95808	0.95377	-3.18434
C	4.37509	2.3292	-1.81108
C	4.61745	-0.23327	-1.66035
C	3.12092	-1.77447	0.72628
C	2.77217	-4.01504	-0.07664
C	-1.05412	-4.15682	-0.71356
C	0.88874	-3.61757	-2.26764
C	-0.79701	-1.92372	-1.91306
C	-0.29368	-4.87908	0.40542
C	0.68651	-3.76137	2.57345
C	-1.51462	-3.1298	1.41641

C	3.84858	1.74249	2.95542
H	3.98115	2.81198	1.12708
C	3.04559	-0.50053	2.7782
C	2.73588	2.45294	-3.5027
H	2.0261	0.37508	-3.14411
H	3.60275	0.47184	-3.93315
C	3.11794	3.12143	-2.1737
H	4.82168	2.59215	-0.84199
H	5.16394	2.38921	-2.57611
H	5.18365	-0.19177	-0.72263
H	4.07952	-1.18936	-1.69648
H	5.34182	-0.22253	-2.48965
C	4.494	-2.11812	0.81974
C	4.1238	-4.31926	-0.00424
H	2.12228	-4.81492	-0.39642
H	-1.38052	-4.78223	-1.55733
C	-2.21558	-3.55952	0.10031
H	0.3338	-3.68904	-3.21474
H	1.7574	-2.96532	-2.43203
H	1.2567	-4.62459	-2.05018
H	-0.111	-1.15462	-2.29268
H	-1.33048	-2.34647	-2.7768
H	-1.5933	-1.46757	-1.28693
H	-0.9313	-5.59359	0.94826
H	0.59711	-5.42672	0.08804
H	0.79127	-2.7817	3.06528
H	0.11757	-4.41944	3.24819
H	1.69121	-4.18829	2.44878
H	-1.94964	-3.64473	2.28552

H	-1.58096	-2.05368	1.61093
C	3.44268	0.56834	3.57974
H	4.27262	2.56891	3.52995
H	2.87787	-1.47789	3.23522
H	1.71992	2.68594	-3.84539
H	3.42211	2.79478	-4.29216
C	2.12548	2.72343	-1.03351
H	3.23322	4.21274	-2.24485
C	5.01117	-3.34928	0.45302
H	5.17403	-1.36237	1.21411
H	4.46964	-5.31591	-0.28638
H	-2.96853	-4.33836	0.2868
H	-2.74832	-2.74149	-0.39769
H	3.50572	0.45184	4.66387
C	2.16291	3.803	0.06347
C	0.67049	2.74515	-1.53705
H	6.08065	-3.54985	0.54304
H	3.16953	4.18613	0.26865
H	1.57556	4.66248	-0.2918
H	1.71136	3.46058	1.00278
H	0.42968	1.95465	-2.25459
H	-0.03679	2.67763	-0.69958
H	0.48412	3.71411	-2.02461

F: TS-**6** (*exo-trans*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -302.23 cm^{-1}

Optimization: -2597.534118

Single point: -2598.661255

1 1

F	-0.87629	0.89061	-1.77679
Pd	1.8723	0.67636	-0.0234
C	3.81197	1.55476	-0.21732
C	4.54228	0.45041	-0.78218
C	2.85805	2.27582	-1.00127
H	4.14439	1.9536	0.74421
H	4.20186	0.14633	-1.77672
C	2.31267	3.60357	-0.67667
C	2.51816	4.23305	0.56616
C	1.52275	4.26095	-1.63834
C	1.95523	5.47919	0.83243

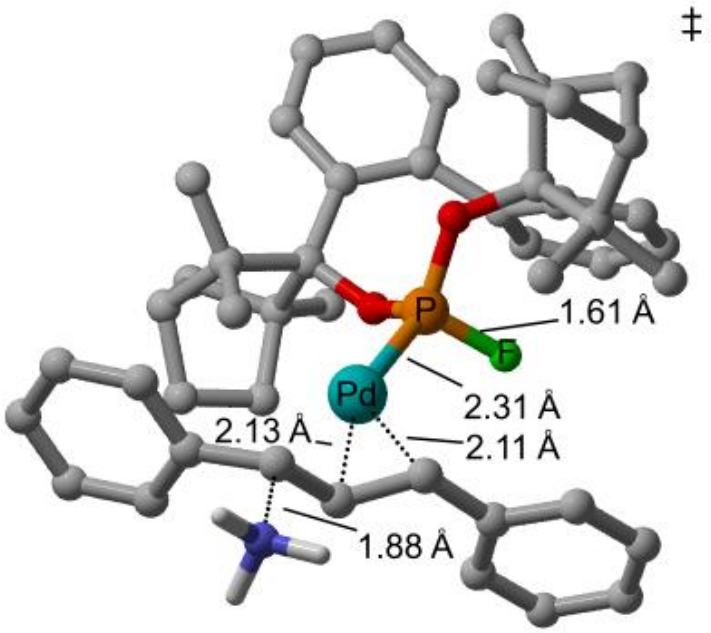
H	3.11235	3.74191	1.33907
C	0.9542	5.50503	-1.36897
H	1.34222	3.77766	-2.60182
C	1.16911	6.12004	-0.13224
H	2.12441	5.9538	1.80151
H	0.34016	5.99654	-2.12656
H	0.7258	7.09496	0.0813
C	5.02506	-0.68746	0.04241
C	5.42027	-1.87285	-0.60122
C	5.06198	-0.63034	1.44622
C	5.84978	-2.97542	0.13684
H	5.36775	-1.93986	-1.69179
C	5.48888	-1.73416	2.18404
H	4.73274	0.26867	1.9688
C	5.88449	-2.90753	1.53243
H	6.1444	-3.89312	-0.37605
H	5.50758	-1.68183	3.27462
H	6.21346	-3.77124	2.11412
H	2.79674	2.02099	-2.06646
N	6.20801	1.16795	-1.41674
H	6.78416	0.47437	-1.9014
H	6.028	1.96052	-2.03885
H	6.72503	1.50236	-0.59954
P	-0.35351	0.19472	-0.41779
O	-1.54478	0.41386	0.65477
O	-0.51163	-1.35013	-0.83709
C	-2.74516	1.23648	0.49278
C	-0.70717	-2.59555	-0.13972
C	-3.42414	0.68117	-0.78597

C	-3.62748	1.14353	1.79421
C	-2.21128	-2.74179	0.17489
C	0.35451	-2.83117	1.08725
C	-0.23079	-3.70396	-1.17964
C	-4.1444	1.52881	-1.63875
C	-3.27487	-0.67824	-1.21659
C	-2.73266	1.41081	3.04012
C	-4.39964	2.47455	1.66823
C	-4.49972	-0.08199	1.97487
C	-3.24616	-1.91427	-0.33281
C	-2.619	-3.90235	0.86951
C	1.22575	-4.00845	0.53912
C	-0.26168	-3.21724	2.45022
C	1.24412	-1.62746	1.43192
C	0.22695	-4.85397	-0.26045
C	-1.24197	-4.02485	-2.26684
C	1.14861	-3.26639	-1.75344
C	-4.52433	1.17302	-2.93372
H	-4.40979	2.52068	-1.29878
C	-3.59605	-0.99429	-2.54739
C	-2.58029	2.95142	3.08601
H	-1.77414	0.88135	2.9589
H	-3.23712	1.02547	3.93776
C	-3.15937	3.36733	1.72514
H	-4.98241	2.55124	0.74018
H	-5.0869	2.62936	2.51379
H	-5.18429	-0.22254	1.13045
H	-3.90573	-0.99705	2.09599
H	-5.11039	0.04505	2.88243

C	-4.58708	-2.33674	-0.15097
C	-3.94152	-4.27295	1.07171
H	-1.87411	-4.5787	1.25796
H	1.75542	-4.52387	1.3538
C	2.15012	-3.5393	-0.59986
H	0.50327	-3.09199	3.23101
H	-1.11597	-2.57696	2.70902
H	-0.58461	-4.26158	2.50832
H	0.67313	-0.82413	1.91954
H	2.02491	-1.94885	2.13676
H	1.79927	-1.25268	0.54537
H	0.72025	-5.6512	-0.8375
H	-0.56472	-5.32556	0.32767
H	-1.46252	-3.12605	-2.86221
H	-0.83418	-4.78812	-2.94741
H	-2.18744	-4.40507	-1.85649
H	1.37204	-3.88988	-2.6314
H	1.1406	-2.22268	-2.08719
C	-4.17326	-0.07873	-3.42548
H	-5.06935	1.88905	-3.55246
H	-3.45927	-2.0277	-2.87035
H	-1.55064	3.28883	3.25696
H	-3.19412	3.38441	3.89031
C	-2.28269	2.8177	0.5524
H	-3.33113	4.44901	1.6284
C	-4.95353	-3.48021	0.54017
H	-5.37108	-1.7143	-0.58328
H	-4.1683	-5.18887	1.62147
H	2.84694	-4.35076	-0.85878

H	2.77224	-2.67379	-0.34325
H	-4.4073	-0.37025	-4.45161
C	-2.48162	3.69826	-0.69658
C	-0.78651	2.96146	0.87799
H	-6.00656	-3.74642	0.65133
H	-3.5155	4.03537	-0.83794
H	-1.87711	4.60844	-0.56535
H	-2.14082	3.20239	-1.61486
H	-0.42696	2.29986	1.67218
H	-0.17262	2.79203	-0.01447
H	-0.59043	3.99799	1.18554

F: TS-**5** (*endo-trans*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -291.93 cm^{-1}

Optimization: -2597.531046

Single point: -2598.660376

1 1

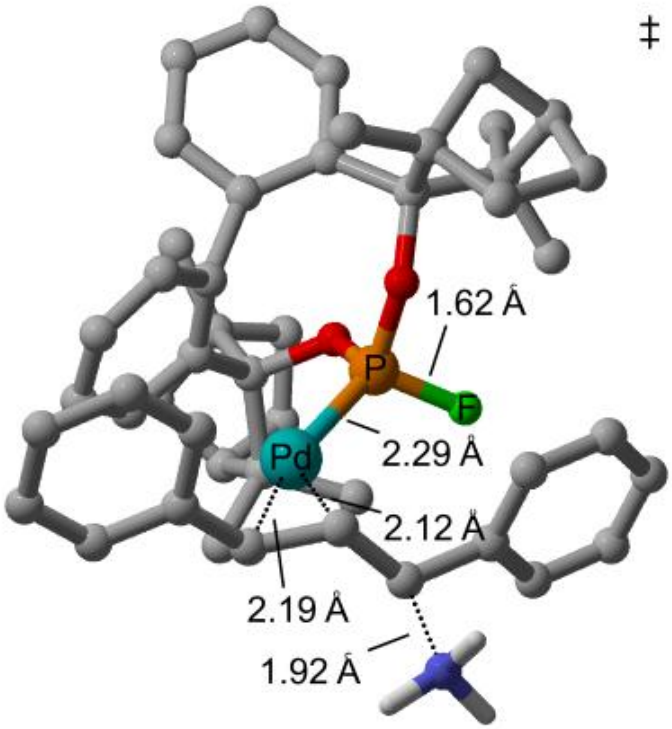
F	-0.89992	-1.32552	1.34272
Pd	1.93609	-0.56876	-0.06612
C	3.86309	-1.4582	0.15708
C	2.85151	-2.46716	0.10384
C	4.48015	-0.94188	-1.04009
H	4.2907	-1.17146	1.1214
H	2.6894	-2.95678	-0.8648
C	4.90543	0.48455	-1.1243
C	4.908	1.12086	-2.37614
C	5.25513	1.22588	0.0176
C	5.24872	2.47044	-2.48782
H	4.61819	0.55946	-3.26895
C	5.59864	2.5725	-0.09483
H	5.2394	0.75953	1.00412
C	5.5954	3.19853	-1.34672
H	5.23713	2.9552	-3.4662
H	5.86235	3.14031	0.79981
H	5.85888	4.25499	-1.4302
C	2.35999	-3.24432	1.25567
C	1.69842	-4.46326	1.02234
C	2.4837	-2.79172	2.5841
C	1.17315	-5.20734	2.07946
H	1.59023	-4.82616	-0.00238
C	1.96396	-3.53698	3.63896
H	2.96183	-1.83203	2.79165
C	1.3036	-4.74685	3.39149
H	0.65879	-6.14941	1.87741
H	2.0614	-3.16818	4.66236

H	0.88901	-5.32422	4.22051
H	4.02646	-1.3044	-1.96793
N	6.11085	-1.83703	-1.27965
H	6.58229	-1.57524	-2.15045
H	6.7202	-1.58686	-0.4961
H	5.95552	-2.84898	-1.26351
P	-0.33836	-0.31212	0.22122
O	-1.43684	-0.38155	-0.96229
O	-0.63068	1.06578	1.00497
C	-2.5926	-1.27493	-1.03966
C	-0.79552	2.4456	0.63187
C	-3.42559	-0.95821	0.22753
C	-3.35211	-1.02304	-2.39754
C	-2.22013	2.61113	0.05859
C	0.46948	3.04395	-0.2293
C	-0.63906	3.26053	1.98966
C	-4.21204	-1.95711	0.8195
C	-3.40024	0.3133	0.89007
C	-2.32574	-1.05301	-3.56817
C	-4.05291	-2.3885	-2.55967
C	-4.27084	0.17828	-2.47959
C	-3.28528	1.68458	0.23662
C	-2.55948	3.85902	-0.50663
C	1.03102	4.14675	0.73181
C	0.14499	3.64725	-1.61362
C	1.58152	2.02892	-0.53814
C	-0.20806	4.64867	1.48159
C	-1.8386	3.20669	2.91763
C	0.67492	2.79567	2.68694

C	-4.79602	-1.83348	2.07987
H	-4.37251	-2.88609	0.29029
C	-3.94622	0.39641	2.1833
C	-2.07778	-2.55947	-3.82831
H	-1.41383	-0.50023	-3.30716
H	-2.76322	-0.55609	-4.44588
C	-2.76284	-3.20775	-2.61511
H	-4.7237	-2.63546	-1.72632
H	-4.6383	-2.43784	-3.49037
H	-5.04138	0.15446	-1.70025
H	-3.7194	1.12333	-2.39516
H	-4.78207	0.17244	-3.45499
C	-4.59438	2.11003	-0.09569
C	-3.84737	4.23279	-0.87017
H	-1.79183	4.60196	-0.65375
H	1.60543	4.90306	0.17678
C	1.80447	3.51492	1.90327
H	1.0758	3.70788	-2.19806
H	-0.56667	3.0266	-2.17597
H	-0.248	4.66859	-1.5699
H	1.29786	1.37108	-1.37523
H	2.48575	2.5685	-0.85437
H	1.88491	1.44624	0.35736
H	0.05011	5.31736	2.31689
H	-0.95475	5.16381	0.87112
H	-2.01408	2.17704	3.26021
H	-1.64894	3.82862	3.806
H	-2.75446	3.57532	2.43509
H	0.65032	3.11487	3.73869

H	0.76823	1.70306	2.68419
C	-4.59971	-0.66495	2.8055
H	-5.38296	-2.65936	2.48718
H	-3.92452	1.36498	2.68177
H	-1.01779	-2.82009	-3.93873
H	-2.58207	-2.8894	-4.74914
C	-2.04001	-2.81322	-1.2853
H	-2.87993	-4.29763	-2.70193
C	-4.89485	3.34695	-0.64568
H	-5.41079	1.41338	0.09508
H	-4.02233	5.22081	-1.30123
H	2.25913	4.31444	2.5071
H	2.62488	2.8515	1.59912
H	-5.00622	-0.54736	3.81226
C	-2.31727	-3.88043	-0.20735
C	-0.51198	-2.85606	-1.46921
H	-5.92716	3.60916	-0.88588
H	-3.33809	-4.27941	-0.23446
H	-1.65285	-4.73682	-0.4006
H	-2.10262	-3.51543	0.80504
H	-0.10858	-2.059	-2.10172
H	-0.00252	-2.8219	-0.49866
H	-0.24578	-3.82069	-1.92789

F: TS-**4** (*exo-cis*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -289.62 cm^{-1}

Optimization: -2597.551266

Single point: -2598.675574

1 1

F	0.65257	1.69864	1.81578
Pd	-1.76947	-0.04163	0.29686
C	-3.26864	1.38592	-0.14084
C	-3.87959	0.11311	-0.25514
C	-3.2154	2.10826	1.11265
H	-3.00246	1.9384	-1.045
H	-4.42587	-0.27425	0.61319
C	-2.15974	3.11358	1.38751
C	-1.82034	3.39522	2.72
C	-1.4707	3.77081	0.35343

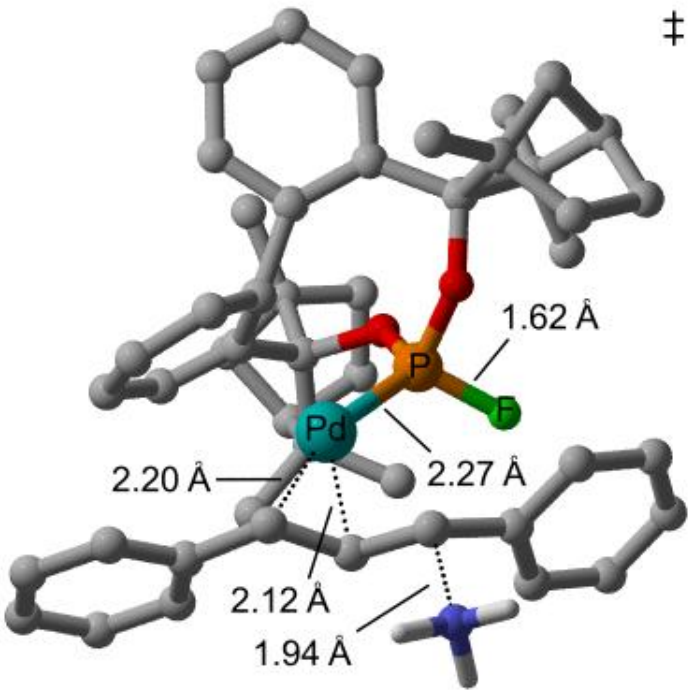
C	-0.80562	4.30503	3.01695
H	-2.33409	2.87122	3.53092
C	-0.46273	4.68455	0.65105
H	-1.69948	3.55278	-0.6908
C	-0.1248	4.95082	1.98269
H	-0.53706	4.50066	4.05693
H	0.07331	5.18079	-0.16006
H	0.67629	5.65658	2.21175
C	-4.17925	-0.55115	-1.53024
C	-5.01169	-1.68648	-1.53603
C	-3.63835	-0.11768	-2.75794
C	-5.30659	-2.35637	-2.72289
H	-5.43102	-2.04471	-0.59216
C	-3.94271	-0.78015	-3.94562
H	-2.95927	0.73639	-2.78676
C	-4.77789	-1.90268	-3.93561
H	-5.95755	-3.23335	-2.70386
H	-3.51701	-0.42462	-4.88668
H	-5.01309	-2.42191	-4.86705
H	-3.51973	1.5322	1.99039
N	-4.78128	3.22652	1.12452
H	-4.67781	3.90896	0.36931
H	-5.62218	2.66855	0.95397
H	-4.8769	3.73555	2.00723
P	0.40996	0.51906	0.7328
O	1.38825	-0.64179	1.34722
O	1.18884	1.0513	-0.54836
C	0.73785	-1.9233	1.59782
C	2.48922	0.96002	-1.17727

C	-0.00246	-2.2398	0.25872
C	1.81492	-3.00572	1.99683
C	2.85994	-0.52447	-1.39746
C	2.28472	1.6622	-2.59458
C	3.56394	1.96478	-0.47305
C	-1.21713	-2.95846	0.25093
C	0.50892	-1.83875	-1.03488
C	2.73508	-2.40232	3.09808
C	0.93242	-3.97355	2.81149
C	2.61815	-3.67165	0.89861
C	1.96316	-1.6317	-1.43157
C	4.16722	-0.7751	-1.86463
C	1.56059	3.02275	-2.36837
C	3.70764	2.16225	-2.90636
C	1.59439	0.80714	-3.64359
C	3.84678	2.99175	-1.62305
C	2.99366	2.67784	0.75912
C	4.88713	1.34466	0.02738
C	-1.97176	-3.19899	-0.90098
H	-1.57999	-3.37963	1.17694
C	-0.3215	-2.01533	-2.15867
C	1.91407	-2.53237	4.40339
H	3.01062	-1.36759	2.85818
H	3.66784	-2.98207	3.14555
C	0.53482	-2.95133	3.87375
H	0.09363	-4.38854	2.2337
H	1.51594	-4.81557	3.2129
H	1.97587	-4.13044	0.13705
H	3.30374	-2.97151	0.40731

H	3.22538	-4.47385	1.34608
C	2.41079	-2.83231	-2.03732
C	4.60148	-1.98359	-2.39639
H	4.89181	0.02187	-1.84846
C	2.66239	3.95802	-1.80472
H	0.69807	2.91502	-1.70089
H	1.18474	3.38335	-3.33736
H	4.45144	1.37172	-3.04143
H	3.72237	2.78427	-3.81467
H	2.1516	-0.11256	-3.86861
H	0.58385	0.52586	-3.30867
H	1.49037	1.37719	-4.57967
H	4.8105	3.49989	-1.47549
H	1.99362	3.0889	0.61365
H	2.95816	2.00342	1.62421
H	3.6676	3.50912	1.01731
H	5.6414	1.20212	-0.75594
H	5.33837	2.03507	0.75503
H	4.72567	0.38418	0.53676
C	-1.55119	-2.67091	-2.11304
H	-2.89596	-3.7736	-0.82941
H	0.0647	-1.68725	-3.12389
H	1.90093	-1.61767	5.00834
H	2.31422	-3.33171	5.04508
C	-0.11356	-1.81461	3.02102
H	-0.15012	-3.30394	4.6584
C	3.69648	-3.03033	-2.51717
H	1.70378	-3.65946	-2.10074
H	5.63448	-2.08348	-2.73602

H	2.36861	4.47573	-0.88371
H	2.9345	4.73511	-2.53453
H	-2.14589	-2.7953	-3.01779
C	-1.63861	-2.03309	3.01357
C	0.07026	-0.4488	3.70711
H	3.97948	-3.98619	-2.96216
H	-2.15114	-1.42595	2.24702
H	-1.94187	-3.08079	2.89646
H	-2.02624	-1.71112	3.99201
H	-0.5971	0.31077	3.27751
H	-0.2103	-0.55764	4.76555
H	1.08999	-0.05742	3.66256

F: TS-**3** (*endo-cis*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -320.94 cm^{-1}

Optimization: -2597.554071

Sinlge point: -2598.675311

1 1

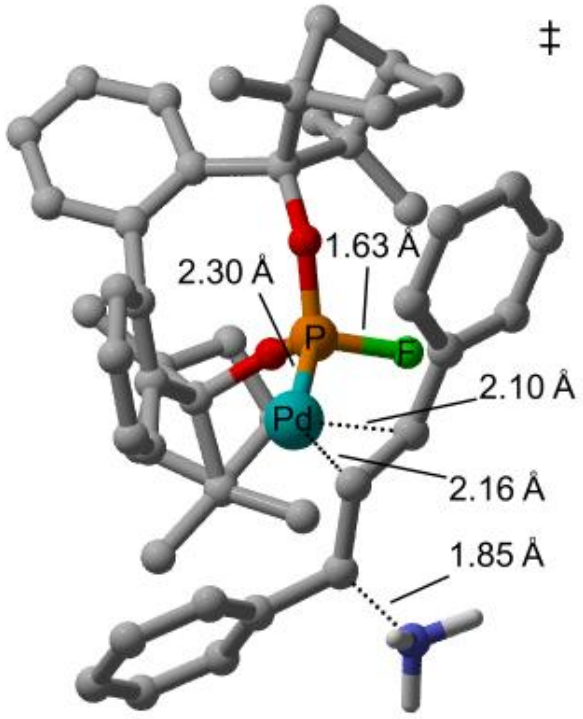
F	0.86815	1.43435	1.89938
Pd	-1.41291	0.70068	-0.52131
C	-2.82718	2.23375	-0.1533
C	-1.94309	3.35816	-0.36299
C	-3.33309	1.47861	-1.24695
H	-3.26008	2.11131	0.84288
C	-4.42054	0.49579	-1.15118
C	-5.07711	0.07332	-2.32244
C	-4.80753	-0.088	0.07152
C	-6.07966	-0.89516	-2.2772
H	-4.79096	0.51244	-3.28191
C	-5.80899	-1.05619	0.11764
H	-4.31115	0.20545	0.99769
C	-6.45011	-1.46678	-1.05603
H	-6.57685	-1.20464	-3.19937
H	-6.08894	-1.49712	1.0771
H	-7.23466	-2.22548	-1.0185
C	-1.01052	3.83258	0.68537
C	0.23133	4.35854	0.29566
C	-1.31362	3.73316	2.05369
C	1.16597	4.75225	1.25301
H	0.47922	4.42707	-0.76641
C	-0.38538	4.14046	3.00868
H	-2.26856	3.31461	2.37855
C	0.85859	4.64309	2.61137
H	2.13826	5.13553	0.93736
H	-0.62409	4.0507	4.07031

H	1.59003	4.94574	3.36359
H	-3.14018	1.85907	-2.25697
H	-1.54678	3.44486	-1.37791
N	-3.1005	4.91083	-0.54325
H	-3.55119	5.0681	0.36133
H	-2.57256	5.75174	-0.79052
H	-3.82254	4.73688	-1.24699
P	0.53225	0.47414	0.63542
O	0.9691	-0.99087	1.20614
O	1.73286	0.85946	-0.33765
C	0.0262	-2.09857	1.30404
C	2.92319	0.24997	-0.86368
C	-0.71359	-2.14259	-0.05366
C	0.83785	-3.41154	1.63445
C	2.56945	-1.11363	-1.49621
C	3.41727	1.28368	-1.97944
C	4.13557	0.3156	0.2173
C	-1.94508	-2.77049	-0.22863
C	-0.157	-1.47211	-1.21613
C	1.82308	-3.09976	2.79565
C	-0.24171	-4.2297	2.3722
C	1.51173	-4.11602	0.47204
C	1.29046	-1.7122	-1.67767
C	3.65305	-1.77449	-2.11608
C	3.26579	2.71811	-1.39965
C	4.95514	1.16395	-1.90853
C	2.73778	1.12891	-3.33058
C	5.0451	1.42697	-0.39981
C	3.67408	0.69115	1.63017

C	4.94781	-0.98263	0.39806
C	-2.73472	-2.61237	-1.3816
H	-2.34409	-3.39051	0.56478
C	-1.03776	-1.18004	-2.29324
C	0.93043	-3.06677	4.06272
H	2.36577	-2.16348	2.62117
H	2.57221	-3.90293	2.85013
C	-0.48392	-3.19394	3.47283
H	-1.12034	-4.46372	1.75626
H	0.16213	-5.18033	2.75208
H	0.79977	-4.37116	-0.32355
H	2.31256	-3.50649	0.03345
H	1.96293	-5.05393	0.83087
C	1.21163	-2.88295	-2.48103
C	3.55557	-2.93406	-2.87083
H	4.63837	-1.34552	-2.02739
C	4.37572	2.81463	-0.31964
H	2.26163	2.90054	-1.00738
H	3.44251	3.43362	-2.21688
H	5.37936	0.21125	-2.23859
H	5.43944	1.95215	-2.50556
H	2.95148	0.16054	-3.80246
H	1.64384	1.2167	-3.22314
H	3.07314	1.92174	-4.01687
H	6.05502	1.40067	0.03399
H	3.0491	1.58389	1.66694
H	3.11698	-0.13289	2.09478
H	4.56475	0.88048	2.24832
H	5.6205	-1.2147	-0.43529

H	5.58532	-0.86962	1.28718
H	4.29511	-1.85089	0.56503
C	-2.31952	-1.75056	-2.3814
H	-3.69692	-3.12154	-1.4498
H	-0.61355	-0.67691	-3.16518
H	1.07451	-2.16894	4.67607
H	1.13372	-3.93097	4.71257
C	-0.87701	-1.92017	2.66094
H	-1.25166	-3.44685	4.21825
C	2.30233	-3.50112	-3.06951
H	0.23199	-3.34229	-2.61687
H	4.45446	-3.37228	-3.30917
H	3.98542	3.05314	0.67746
H	5.11002	3.59437	-0.5711
H	-2.94776	-1.55062	-3.24905
C	-2.4062	-1.88141	2.49125
C	-0.53441	-0.63498	3.42942
H	2.168	-4.40619	-3.6649
H	-2.71642	-1.18208	1.70388
H	-2.85629	-2.85904	2.28234
H	-2.84595	-1.53685	3.43945
H	-0.99723	0.24507	2.95907
H	-0.9551	-0.71498	4.44344
H	0.53685	-0.43851	3.52112

F: TS-**2** (*exo-trans*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -301.94 cm^{-1}

Optimization: -2597.551382

Single point: -2598.676031

1 1

F	-0.42496	0.78361	-2.34046
Pd	1.73101	0.63314	-0.01689
C	3.46568	1.92031	-0.14653
C	4.44154	0.99461	-0.67086
C	2.39048	2.37743	-0.97409
H	3.6656	2.38822	0.8207
H	4.15688	0.55571	-1.63219
C	1.51001	3.52686	-0.68658
C	1.45651	4.15414	0.57263
C	0.65581	3.99254	-1.70379

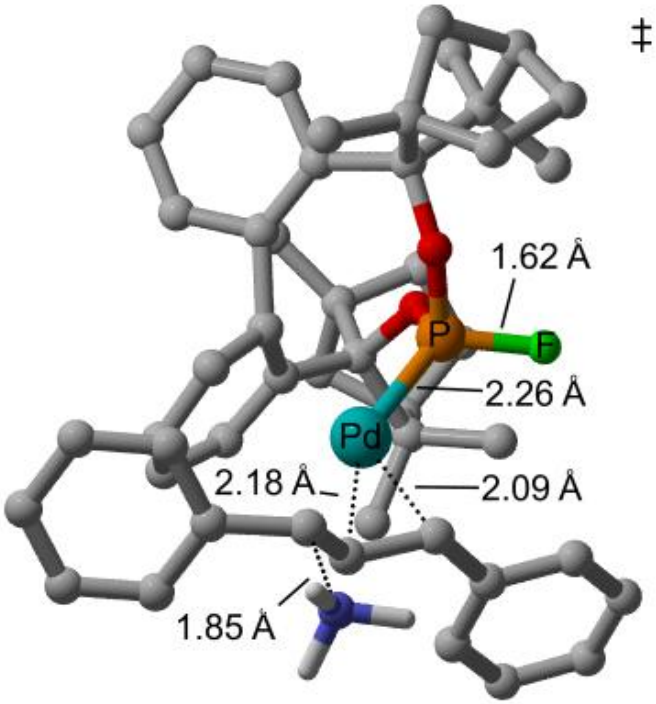
C	0.58655	5.21957	0.79892
H	2.09074	3.80045	1.38802
C	-0.21577	5.05652	-1.47524
H	0.6695	3.49965	-2.67873
C	-0.25151	5.67705	-0.22359
H	0.55761	5.69493	1.78191
H	-0.87353	5.40078	-2.27622
H	-0.93568	6.5084	-0.04162
C	5.10296	0.01255	0.23401
C	5.19915	-1.32747	-0.17155
C	5.57429	0.37844	1.50554
C	5.73615	-2.29052	0.6854
H	4.82424	-1.62157	-1.15541
C	6.12354	-0.58153	2.35586
H	5.49754	1.41462	1.84454
C	6.19985	-1.91905	1.95036
H	5.79168	-3.33293	0.36472
H	6.48662	-0.28847	3.34319
H	6.62156	-2.67016	2.62145
H	2.44628	2.12654	-2.04082
N	5.878	1.96288	-1.32339
H	6.57389	1.37389	-1.79116
H	5.53414	2.67282	-1.9764
H	6.33202	2.43646	-0.53764
P	-0.37817	0.18537	-0.82895
O	-0.92123	-1.31036	-1.18422
O	-1.61269	0.84545	-0.07087
C	-0.37904	-2.52842	-0.56911
C	-3.02243	0.68407	0.25678

C	0.11463	-1.98793	0.80732
C	-1.53476	-3.64908	-0.6835
C	-3.22031	-0.55738	1.16573
C	-3.36067	2.00915	1.08693
C	-3.97886	0.85956	-1.04981
C	1.513	-1.82384	0.98987
C	-0.71909	-1.2663	1.71252
C	-2.38512	-3.26879	-1.92067
C	-0.80398	-4.86927	-1.28884
C	-2.37143	-4.03338	0.52297
C	-2.21707	-1.30696	1.83845
C	-4.54689	-0.83338	1.56608
C	-2.73915	3.22214	0.341
C	-4.84738	2.24178	0.7503
C	-2.95974	1.97359	2.55228
C	-4.64539	2.24704	-0.77036
C	-3.21179	0.87154	-2.37382
C	-5.07972	-0.20688	-1.24507
C	2.08333	-1.03051	1.99307
H	2.19937	-2.33019	0.33036
C	-0.12538	-0.4923	2.73618
C	-1.38705	-3.42631	-3.09803
H	-2.8293	-2.27271	-1.8481
H	-3.20786	-3.99576	-1.99545
C	-0.15943	-4.09337	-2.43309
H	-0.10552	-5.36706	-0.60587
H	-1.5362	-5.61944	-1.62132
H	-1.76249	-4.16333	1.42733
H	-3.16762	-3.3148	0.73362

H	-2.85482	-5.00008	0.31111
C	-2.58368	-2.14906	2.91345
C	-4.89677	-1.71444	2.5822
H	-5.36139	-0.31014	1.09224
C	-3.63529	3.403	-0.91137
H	-1.68183	3.0739	0.10682
H	-2.80044	4.09799	1.0034
H	-5.54034	1.48402	1.12784
H	-5.1905	3.2144	1.13551
H	-3.44538	1.15954	3.10767
H	-1.86909	1.85712	2.64697
H	-3.23417	2.92382	3.03566
H	-5.55251	2.37891	-1.3777
H	-2.40173	1.59877	-2.40112
H	-2.79273	-0.11699	-2.60638
H	-3.9148	1.13079	-3.17965
H	-5.95501	-0.0691	-0.59952
H	-5.45069	-0.13179	-2.27734
H	-4.70271	-1.22847	-1.10253
C	1.24578	-0.34922	2.88362
H	3.16845	-0.98991	2.09329
H	-0.7931	0.02637	3.42382
H	-1.14301	-2.46534	-3.57001
H	-1.7874	-4.0813	-3.88566
C	0.72115	-3.10755	-1.61203
H	0.45561	-4.67023	-3.13839
C	-3.89686	-2.36637	3.29781
H	-1.78346	-2.671	3.44105
H	-5.95112	-1.86008	2.82632

H	-3.07141	3.38493	-1.8517
H	-4.17163	4.36336	-0.88226
H	1.65764	0.27493	3.67889
C	1.86001	-3.97831	-0.99899
C	1.37555	-2.0392	-2.49188
H	-4.13109	-3.03611	4.12744
H	2.81181	-3.43176	-0.93698
H	1.63928	-4.37523	-0.00077
H	2.04704	-4.83886	-1.658
H	1.95441	-1.31512	-1.89332
H	2.07364	-2.52957	-3.18875
H	0.65059	-1.4726	-3.08596

F: TS-**1** (*endo-trans*), optimized transition structure of the active catalyst system (1,3-diphenylallyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP)



Imaginary frequency: -291.93 cm^{-1}

Optimization: -2597.551727

Single point: -2598.677484

1 1

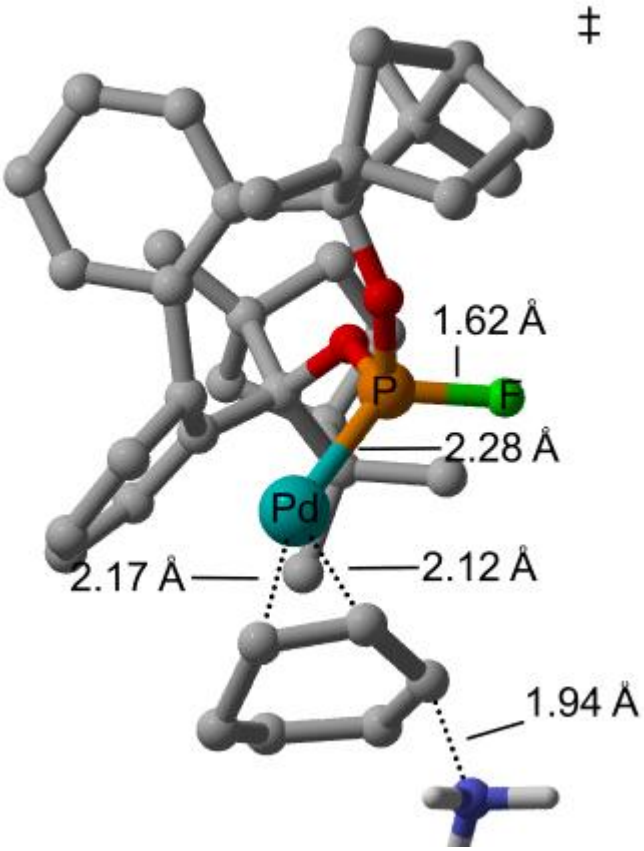
Pd	-1.43332	-0.0357	-0.45698
C	-3.56817	-0.12357	-0.89562
C	-2.83274	0.65704	-1.84662
C	-3.82979	-1.52388	-1.12411
H	-4.13258	0.36708	-0.09932
H	-2.57317	0.17084	-2.79604
C	-4.18562	-2.40705	0.02105
C	-3.53832	-3.64326	0.16445
C	-5.13542	-2.0161	0.97912
C	-3.81839	-4.46606	1.25741
H	-2.79186	-3.95087	-0.5726
C	-5.42878	-2.84643	2.06106
H	-5.64334	-1.05236	0.89041
C	-4.76593	-4.07026	2.20595
H	-3.29772	-5.41956	1.36755
H	-6.1704	-2.5352	2.79973
H	-4.99006	-4.71573	3.05777
C	-2.84771	2.13336	-1.92148
C	-2.13958	2.76535	-2.96116
C	-3.50801	2.93977	-0.9767
C	-2.08478	4.15489	-3.04893
H	-1.60602	2.15364	-3.69253
C	-3.45665	4.33057	-1.06762
H	-4.0618	2.48174	-0.15527
C	-2.74327	4.945	-2.10117
H	-1.52239	4.62495	-3.85857
H	-3.97504	4.93997	-0.3239

H	-2.70143	6.03415	-2.16831
H	-3.14707	-1.99811	-1.83637
N	-5.32828	-1.65896	-2.19908
H	-6.1304	-1.29113	-1.68049
H	-5.19146	-1.08551	-3.03634
H	-5.53423	-2.62484	-2.47262
P	0.68137	0.58562	-0.96008
O	1.63198	1.24036	0.19112
O	1.48391	-0.71926	-1.39366
C	1.09888	1.74857	1.44994
C	2.65549	-1.44853	-0.99598
C	0.14702	0.65203	1.9783
C	2.31444	2.06215	2.40566
C	2.58677	-1.75098	0.51599
C	2.56721	-2.79614	-1.85064
C	4.00161	-0.75906	-1.58933
C	-0.84306	0.89792	2.92533
C	0.21138	-0.69922	1.44925
C	3.37584	2.86213	1.60044
C	1.70605	3.17796	3.27982
C	2.91269	0.88818	3.15838
C	1.52768	-1.49071	1.4298
C	3.6548	-2.52839	1.01641
C	2.14467	-2.41924	-3.29942
C	4.05007	-3.1332	-2.11837
C	1.67458	-3.86778	-1.24499
C	4.39582	-1.76442	-2.72003
C	3.76551	0.64998	-2.14576
C	5.17286	-0.60265	-0.5986

C	-1.8831	-0.00926	3.20465
H	-0.84571	1.84033	3.4598
C	-0.93768	-1.51902	1.59595
C	2.78449	4.29161	1.49483
H	3.57446	2.40018	0.62664
H	4.32198	2.85699	2.16104
C	1.3878	4.11915	2.11497
H	0.83444	2.85898	3.86706
H	2.44782	3.58938	3.98111
H	2.16194	0.35917	3.76021
H	3.37936	0.16265	2.47897
H	3.69245	1.25574	3.84314
C	1.61651	-2.05208	2.73311
C	3.73419	-3.04161	2.30258
H	4.47157	-2.77084	0.35548
C	3.39573	-1.71751	-3.8926
H	1.24191	-1.80039	-3.32483
H	1.92164	-3.35235	-3.83835
H	4.64329	-3.42025	-1.24527
H	4.14269	-3.95132	-2.84935
H	2.04623	-4.22971	-0.27677
H	0.65606	-3.47355	-1.08942
H	1.60208	-4.73025	-1.92542
H	5.44197	-1.62535	-3.02842
H	2.93176	0.7138	-2.84571
H	3.58466	1.368	-1.33503
H	4.67319	0.9716	-2.6784
H	5.68984	-1.53875	-0.35872
H	5.92517	0.05643	-1.05608

H	4.85112	-0.136	0.34299
C	-1.98987	-1.17586	2.46811
H	-2.627	0.24484	3.96215
H	-0.88783	-2.53445	1.19696
H	2.76553	4.68148	0.46994
H	3.36641	5.00583	2.09634
C	0.46789	3.2426	1.20902
H	0.90169	5.06982	2.37738
C	2.68537	-2.80838	3.18453
H	0.80469	-1.84734	3.43213
H	4.60522	-3.63021	2.59773
H	3.19124	-0.70226	-4.25271
H	3.80051	-2.28201	-4.74564
H	-2.8269	-1.86051	2.6017
C	-0.99975	3.46321	1.61679
C	0.53436	3.67847	-0.26153
H	2.69335	-3.19886	4.20396
H	-1.66321	2.69019	1.20585
H	-1.15532	3.52832	2.70026
H	-1.32742	4.42466	1.19573
H	-0.26002	3.20572	-0.85515
H	0.35401	4.76295	-0.3108
H	1.49119	3.47207	-0.74794
F	0.9708	1.5436	-2.23474

F: TS-**4b** (*exo-cis*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -321.17 cm^{-1}

Optimization: -2252.368747

Single point: -2253.302106

1 1

Pd	-1.63950000	-1.14691600	0.34311800
C	-3.03816900	-2.60436700	-0.30349600
C	-3.34108500	-2.29178700	1.05231200
C	-3.80761100	-1.99647500	-1.36657100
H	-2.45191000	-3.49314500	-0.55760600
N	-5.25237100	-3.25766300	-1.66559200
H	-5.17813100	-3.97718500	-0.94181200
H	-6.17652800	-2.82390300	-1.59962400

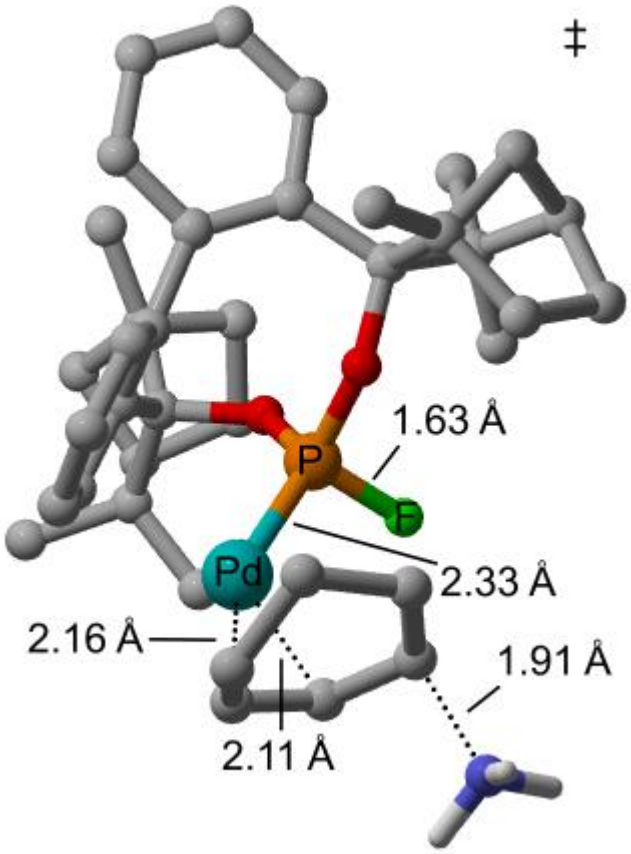
H	-5.17139400	-3.70979000	-2.58044000
P	-0.00524000	-0.41440300	-1.06641400
O	0.55315900	1.10959900	-0.93698300
O	1.25505500	-1.31148800	-0.70741000
C	-0.18555100	2.18758500	-0.29120300
C	2.55535500	-1.12975400	-0.12712800
C	-0.75839100	1.59652200	1.01405000
C	0.81067300	3.39618300	-0.06746900
C	2.43950900	-0.28256800	1.15857400
C	3.03519900	-2.61659900	0.21097800
C	3.61684700	-0.68121300	-1.27124100
C	-1.77670900	2.19240400	1.73496700
C	-0.23618700	0.32776500	1.53250900
C	1.62224600	3.60699800	-1.37494500
C	-0.16303600	4.59024700	-0.13715800
C	1.69275800	3.34170600	1.16596700
C	1.27204700	0.18966900	1.82644200
C	3.66001700	-0.09018600	1.84258000
C	2.64774700	-3.53009600	-0.98682900
C	4.55922800	-2.54807900	-0.02973900
C	2.53196900	-3.15583900	1.54043300
C	4.44973600	-1.99154700	-1.45545900
C	2.94141700	-0.25385100	-2.58128400
C	4.55465500	0.48555700	-0.90374800
C	-2.44715300	1.55199900	2.80745500
H	-2.11073500	3.18832700	1.46707500
C	-1.05291700	-0.37960800	2.46714100
C	0.61957600	4.27728400	-2.34942600
H	2.03392100	2.66501900	-1.75271900

H	2.47349000	4.26785400	-1.15597800
C	-0.68793200	4.27119300	-1.53920500
H	-0.92658900	4.59196200	0.65222100
H	0.37402600	5.54914800	-0.08223300
H	1.10716000	3.22981400	2.08767500
H	2.41433900	2.51617200	1.11610700
H	2.26316500	4.28006800	1.24329700
C	1.43147800	0.77105600	3.11336300
C	3.79323400	0.50479500	3.08844100
H	4.56844200	-0.44909400	1.38556800
C	3.61535800	-3.10311800	-2.12307700
H	1.58994600	-3.44385600	-1.25544700
H	2.82712900	-4.57269200	-0.68491400
H	5.12939600	-1.92811000	0.66850400
H	5.00758200	-3.55313900	-0.00167100
H	2.91511900	-2.58842700	2.39930000
H	1.43024600	-3.12189000	1.57744500
H	2.83872200	-4.20571600	1.66377500
H	5.40165900	-1.78856100	-1.96687900
H	2.19742400	-0.96367900	-2.94668600
H	2.45195400	0.72252000	-2.47115500
H	3.71555400	-0.15182800	-3.35674400
H	5.34589300	0.22051900	-0.19295700
H	5.06231300	0.82229700	-1.81956500
H	4.00042300	1.34282200	-0.49678000
C	-2.14848400	0.24584000	3.11811200
H	-3.22941600	2.09147600	3.34477200
H	-0.62244100	-1.27444000	2.92308300
H	0.54035600	3.76334600	-3.31533400

H	0.91102400	5.31569100	-2.56596300
C	-1.24583000	2.82524300	-1.36473000
H	-1.45550700	4.95071900	-1.93686100
C	2.65040000	0.93818100	3.74962800
H	0.54124700	1.14330600	3.62068400
H	4.78379800	0.60972200	3.53554000
H	3.09687500	-2.77476000	-3.03181400
H	4.27459000	-3.93359900	-2.41600000
H	-2.68559400	-0.29151600	3.90180800
C	-2.71803200	2.91580300	-0.92690700
C	-1.26907000	2.05881700	-2.69389100
H	2.69779200	1.40349100	4.73597800
H	-3.09238800	1.96291500	-0.53122200
H	-2.91278800	3.69601700	-0.18192100
H	-3.32229700	3.17326100	-1.80965600
H	-1.82842400	1.11518500	-2.60039000
H	-1.79380100	2.67127000	-3.44288000
H	-0.27913200	1.81581600	-3.08740100
F	-0.04321000	-0.62313500	-2.67593600
C	-4.56683500	-1.45332900	1.34444700
H	-5.46671900	-2.10105400	1.31571200
H	-4.52409200	-1.05437400	2.36769600
H	-3.03161400	-3.00158800	1.82535500
H	-3.39696200	-2.11044600	-2.37395100
C	-4.70660700	-0.28847500	0.35750600
H	-5.67329800	0.21827200	0.49477900
H	-3.93203300	0.44964000	0.61297300
C	-4.53369300	-0.68638300	-1.12586300
H	-3.94562800	0.08600800	-1.64680700

H	-5.49774200	-0.69813200	-1.65866200

F: TS-**3b** (*endo-cis*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -324.23 cm^{-1}

Optimization: -2252.366864

Single point: -2253.303786

1 1

F	0.71311000	0.01806600	-2.42466900
Pd	2.33762300	-0.89696000	0.19483800
C	4.16434600	-0.49888700	-0.78045500
C	4.18034900	0.93254700	-1.02380500
C	4.47300700	-1.01665600	0.50441200
H	4.17365700	-1.14899500	-1.66188600

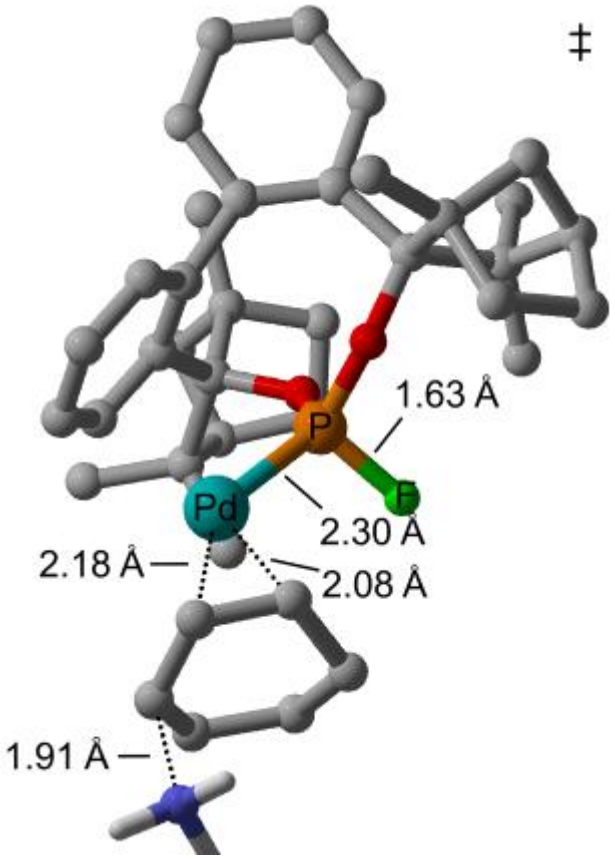
N	5.90496800	1.24698400	-1.77495300
H	6.41862300	0.36221300	-1.73915100
H	5.83848500	1.54289700	-2.75303700
H	6.43598500	1.95281000	-1.25830800
P	0.37790600	-0.17964200	-0.84379700
O	-0.99017600	-1.04249900	-1.01668200
O	-0.16812500	1.24406000	-0.35845800
C	-1.33749500	-2.17394000	-0.14117300
C	-1.36701400	2.05483100	-0.19172700
C	-0.60061500	-1.77829300	1.17534800
C	-2.94059600	-2.33139300	-0.21325500
C	-2.28732000	1.43722100	0.89602600
C	-2.03780100	2.48672900	-1.61255900
C	-0.78323100	3.45068700	0.32530100
C	0.60447400	-2.46515100	1.47991700
C	-0.79314200	-0.53701300	1.84868100
C	-3.36858400	-1.78285900	-1.59702700
C	-3.14668400	-3.83589200	-0.50281500
C	-3.82569700	-1.84734200	0.92050700
C	-1.97963100	0.38354000	1.79857700
C	-3.48394100	2.13528800	1.17543700
C	-1.71111200	4.01693400	-1.66903800
C	-3.56464800	2.28615700	-1.74157200
C	-1.44695500	1.75029000	-2.81699400
C	-1.81700900	4.46419800	-0.20509700
C	-0.43710200	3.48908600	1.80439000
C	0.42696200	3.83667200	-0.57456300
C	1.55950100	-2.00379400	2.39530700
H	0.81919400	-3.40091600	0.98803300

C	0.16068300	-0.10554600	2.80121200
C	-2.70342600	-2.77006600	-2.59167900
H	-3.08399400	-0.73925800	-1.75318900
H	-4.46614900	-1.83967500	-1.65225700
C	-2.16576600	-3.88979500	-1.66979700
H	-2.91172400	-4.49809500	0.33863700
H	-4.19064900	-4.02335800	-0.79350900
H	-3.43512700	-2.13460200	1.90557400
H	-3.98368100	-0.76578100	0.90392400
H	-4.81380200	-2.32082100	0.80944200
C	-2.78557600	0.19054200	2.94428000
C	-4.30115700	1.89313900	2.27286100
H	-3.79371500	2.93695200	0.52535300
H	-2.36805400	4.53612800	-2.38134600
C	-0.21274600	4.26885600	-1.92049300
H	-3.82860500	2.33630800	-2.80767000
H	-3.89171000	1.30791500	-1.36557900
H	-4.16041500	3.06176400	-1.24649800
H	-1.72986800	0.68909800	-2.81785600
H	-1.85258800	2.20237900	-3.73450400
H	-0.36113100	1.80922200	-2.87605700
H	-1.47123000	5.49850300	-0.05362700
H	-2.81389000	4.39255900	0.23768100
H	0.33638900	2.73996400	2.03669400
H	-0.03582400	4.47886000	2.07161700
H	-1.30693300	3.29295400	2.44606000
H	0.95674300	4.67400100	-0.09591400
H	1.13828000	3.00970600	-0.67610400
C	1.32743400	-0.80014900	3.07547200

H	2.43582600	-2.61650000	2.61490300
H	-0.03843400	0.83106600	3.32197900
H	-1.91175200	-2.29504000	-3.18612200
H	-3.43404200	-3.18678500	-3.30026700
C	-0.85491500	-3.51009700	-0.92214700
H	-2.05605300	-4.85682800	-2.18036700
C	-3.93438700	0.92123700	3.19906300
H	-2.49189400	-0.59642600	3.64103700
H	-5.20673000	2.48802900	2.40859500
H	-0.04879900	5.33985700	-2.11137800
H	0.18616600	3.72755600	-2.78679500
H	2.04161000	-0.42243700	3.80968200
C	-0.51488300	-4.74014700	-0.02602700
C	0.31963800	-3.28562500	-1.87828800
H	-4.53191300	0.72713300	4.09175600
H	-0.92011800	-4.68414100	0.99177400
H	-0.92777600	-5.64751700	-0.49027100
H	0.56820200	-4.90991000	0.05208400
H	0.10397300	-2.53911700	-2.65033100
H	1.23081100	-2.96517000	-1.34549500
H	0.55498800	-4.23499800	-2.38378900
C	4.16593500	1.26221400	1.54554600
H	3.13525100	1.06769500	1.87990400
H	4.59736000	1.98170700	2.25768600
H	3.64051700	1.25180700	-1.92006600
H	4.81207000	-2.05490100	0.57740500
C	4.09984700	1.90620100	0.14545700
H	4.87845500	2.67797300	0.03504300
H	3.15166800	2.45516700	0.04000800

C	4.93494500	-0.06473900	1.58970800
H	6.02426800	0.11491900	1.48493100
H	4.80835000	-0.52897300	2.57986700

F: TS-**2b** (*exo-trans*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -307.33 cm^{-1}

Optimization: -2252.369305

Single point: -2253.306249

1 1

F	-0.77297300	-0.73265600	-2.11279400
Pd	-2.25595700	-0.48775500	0.67853200
C	-4.15369000	-1.52577400	0.97710100
C	-5.26677400	-0.68541500	0.61803700
C	-3.35232600	-2.08258700	-0.07461900

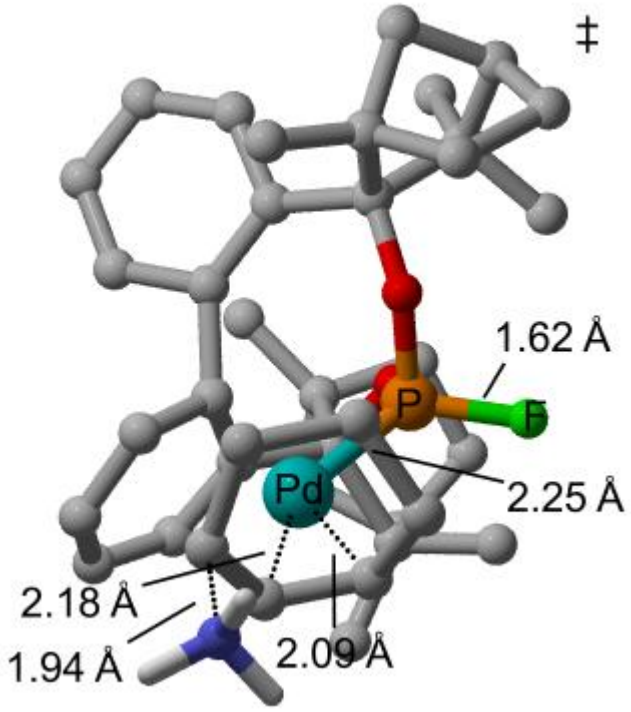
H	-4.14889300	-1.96715800	1.97837100
N	-6.73563000	-1.86628600	0.32578200
H	-6.36348600	-2.81851100	0.36821800
H	-7.44857700	-1.76733100	1.05377100
H	-7.18409700	-1.73276100	-0.58450900
P	-0.34891800	-0.32947200	-0.59504700
O	0.40620200	1.06420600	-0.96607100
O	0.85215400	-1.30274700	-0.21470700
C	0.32750600	2.27946700	-0.14236900
C	2.30274300	-1.45853000	-0.23206400
C	0.03301500	1.67542100	1.26335900
C	1.66199700	3.13288500	-0.45325000
C	2.95972600	-0.41914000	0.71439600
C	2.89421200	-1.61808200	-1.74102600
C	2.51548200	-2.92978900	0.35634900
C	-1.29844600	1.76998200	1.75008900
C	0.85635200	0.69628400	1.89177800
C	2.09602100	2.74725400	-1.88902300
C	1.12679300	4.55008800	-0.76181900
C	2.81633400	3.17079600	0.53140300
C	2.31616000	0.41800100	1.66580200
C	4.36884200	-0.46346300	0.81008200
C	3.30734700	-3.12764900	-1.76365900
C	4.12210200	-0.74819100	-2.09197700
C	1.87095900	-1.30909500	-2.83638400
C	3.81606800	-3.38101000	-0.33869400
C	2.44589100	-3.03004400	1.87119000
C	1.51158500	-3.88862500	-0.34689200
C	-1.80211200	0.99473400	2.80091900

H	-1.97476900	2.48287500	1.30520500
C	0.33694600	-0.05974800	2.96940400
C	0.92818400	3.27033900	-2.76609000
H	2.29224000	1.67891600	-2.00709100
H	3.03140400	3.28324900	-2.10939800
C	0.07661900	4.08861600	-1.76700300
H	0.73827900	5.09013400	0.10950300
H	1.92374700	5.16393800	-1.20607200
H	2.47707000	3.31653500	1.56524100
H	3.44290500	2.27644400	0.48720600
H	3.45722600	4.02838600	0.27318100
C	3.08130800	1.02341300	2.68934600
C	5.11426300	0.18949400	1.78418100
H	4.92778800	-1.06476500	0.11186200
H	4.02178100	-3.32948700	-2.57459900
C	2.07715200	-4.05419800	-1.78234800
H	4.23274400	-0.73574800	-3.18576400
H	4.00867900	0.29182200	-1.75901100
H	5.06919500	-1.13422000	-1.69721700
H	1.62633200	-0.23886200	-2.86998200
H	2.31084600	-1.57865700	-3.80822000
H	0.94103100	-1.86673800	-2.73436000
H	4.01734400	-4.44587500	-0.14497700
H	4.71648000	-2.82879500	-0.05589300
H	1.45580600	-2.71063200	2.23232300
H	2.59243300	-4.07522100	2.18402200
H	3.20910500	-2.41795100	2.37105800
H	1.51935900	-4.84537500	0.19602400
H	0.48517300	-3.50764300	-0.31957700

C	-0.96593500	0.06098300	3.42528500
H	-2.82118500	1.16348100	3.15476600
H	1.00337700	-0.78074800	3.44293200
H	0.36243500	2.45596600	-3.23798000
H	1.28789100	3.92408400	-3.57400100
C	-0.80492200	3.21274800	-0.83126900
H	-0.52571300	4.87153000	-2.24910300
C	4.46082900	0.92531500	2.76832100
H	2.54878300	1.61995300	3.43212900
H	6.20190700	0.09254300	1.78164200
H	2.40218600	-5.08950800	-1.96334200
H	1.35159600	-3.80986200	-2.56745200
H	-1.32553600	-0.55432400	4.25204900
C	-1.53352600	4.21561400	0.11478000
C	-1.87317200	2.42899900	-1.59679600
H	5.00972600	1.42123600	3.57106600
H	-1.01253800	4.40429500	1.06132500
H	-1.63725500	5.18300900	-0.39779500
H	-2.55639700	3.89190700	0.35459900
H	-1.45526400	1.80823200	-2.39675100
H	-2.44653400	1.76908900	-0.92553400
H	-2.58345500	3.13679300	-2.05184900
C	-4.39335300	-0.55159100	-1.82145600
H	-3.54162100	0.10283400	-2.04928300
H	-4.99810400	-0.59556600	-2.73948800
H	-5.74607400	-0.14806600	1.44276400
H	-2.79369800	-3.00006000	0.14342600
C	-5.21505800	0.09901400	-0.67711700
H	-6.23826800	0.35344500	-0.99689500

H	-4.76231900	1.06671000	-0.40664100
C	-3.83596000	-1.94733700	-1.50251100
H	-4.60878000	-2.72365900	-1.67698700
H	-3.02020100	-2.17994300	-2.20151700

F: TS-**1b** (*endo-trans*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -308.72 cm^{-1}

Optimization -2252.371164

Single point: -2253.305033

1 1

Pd	1.82339900	-0.92726100	-0.11216600
C	3.91850500	-1.53812400	-0.13727600
C	3.45560600	-1.06993100	-1.41191900
C	4.68531100	-0.65580800	0.69549100
H	3.94801900	-2.60830700	0.08825100
N	6.52784200	-0.92416600	0.14740100

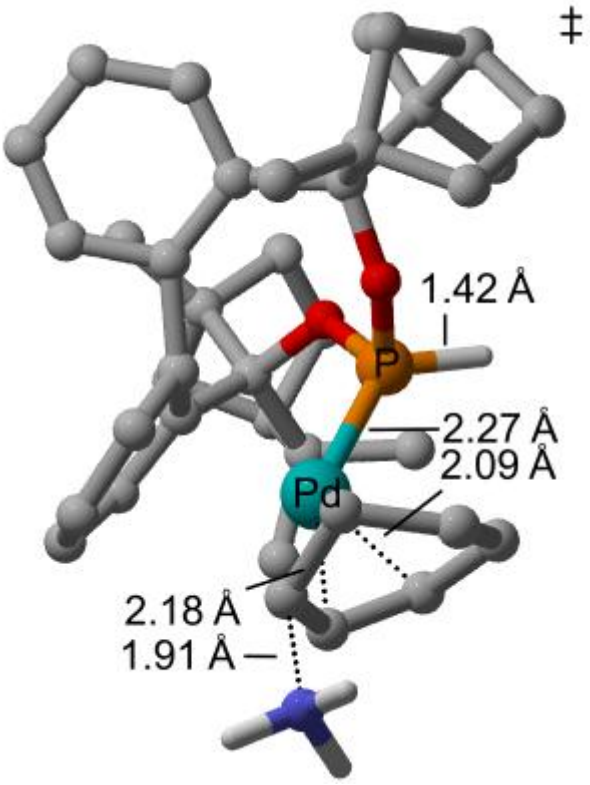
H	7.07276300	-1.39951300	0.87197800
H	6.50175400	-1.52667200	-0.67905100
H	7.01134800	-0.05694100	-0.10007300
P	0.05894600	-0.03810700	-1.18348500
O	-1.44545400	-0.54534700	-0.83658500
O	0.05235100	1.48975700	-0.73771000
C	-1.72074300	-1.83384600	-0.20774600
C	-0.79993200	2.37637200	0.00345900
C	-0.72394000	-1.95704600	0.96491700
C	-3.23479400	-1.85162900	0.23662000
C	-1.19681400	1.71909600	1.34466300
C	0.11459300	3.66493400	0.23692100
C	-1.97579500	2.96513400	-0.95019000
C	-0.41775600	-3.16293600	1.57403600
C	-0.00711500	-0.77755500	1.44607500
C	-4.10093600	-1.35024500	-0.95302300
C	-3.52205600	-3.36683600	0.19076300
C	-3.57250300	-1.15528500	1.54188300
C	-0.77940700	0.47543400	1.90139700
C	-1.97471800	2.54049300	2.19063800
C	0.86481700	3.97050900	-1.09268700
C	-0.90422400	4.82522600	0.19973800
C	1.05552000	3.55830100	1.42671200
C	-1.50119600	4.44048900	-1.16069300
C	-2.09932800	2.21777600	-2.28442400
C	-3.39583600	2.95402300	-0.35112900
C	0.66892300	-3.32901400	2.46274500
H	-1.00554200	-4.04326900	1.34264700
C	1.18574800	-0.99749900	2.19286100

C	-4.14159700	-2.54910300	-1.93551900
H	-3.68607200	-0.43824800	-1.39713700
H	-5.10416500	-1.09954000	-0.57903100
C	-3.16043000	-3.54009100	-1.28680600
H	-2.91610600	-3.95890800	0.88883600
H	-4.57978100	-3.58167800	0.40548700
H	-2.99153700	-1.55363900	2.38391200
H	-3.39450100	-0.07316300	1.48526500
H	-4.63879500	-1.30791300	1.76878500
C	-1.15559700	0.18559100	3.24103000
C	-2.34905500	2.22558400	3.48841600
H	-2.29670800	3.50125700	1.82199500
C	-0.23884500	4.50786300	-2.04234400
H	1.39010000	3.09741800	-1.49139900
H	1.62001900	4.74288900	-0.88332300
H	-1.61902300	4.86688900	1.02645800
H	-0.39138300	5.79911300	0.17455200
H	0.52046200	3.48373800	2.38298600
H	1.69435800	2.66407800	1.33049000
H	1.71415500	4.43912100	1.47250700
H	-2.32365800	5.07486300	-1.52085800
H	-1.15183200	2.09334700	-2.81127600
H	-2.53931700	1.22301300	-2.13771700
H	-2.77426600	2.78595800	-2.94211000
H	-3.56204600	3.70514700	0.42944900
H	-4.11141200	3.17964100	-1.15536400
H	-3.65723400	1.96865500	0.05930100
C	1.52362800	-2.27466400	2.70167700
H	0.84868400	-4.30898200	2.90870400

H	1.67575200	-0.11715200	2.61595800
H	-3.88155400	-2.27882800	-2.96598200
H	-5.14505100	-2.99881000	-1.96892400
C	-1.69395600	-3.00700300	-1.34924300
H	-3.23353500	-4.56086200	-1.68850600
C	-1.92394000	1.02057800	4.03506500
H	-0.84589300	-0.77156100	3.66171600
H	-2.95668300	2.92808100	4.06237500
H	-0.32283800	3.93501800	-2.97335400
H	-0.04301900	5.55194500	-2.32773500
H	2.40873200	-2.39074200	3.33048900
C	-0.71393100	-4.17388200	-1.13109400
C	-1.35288600	-2.46069700	-2.74380600
H	-2.18420600	0.72720400	5.05382400
H	0.30365800	-3.82263000	-0.90507900
H	-1.02339700	-4.87605400	-0.34831300
H	-0.66494100	-4.75527700	-2.06382500
H	-0.27256400	-2.28534200	-2.84991400
H	-1.62610600	-3.22129100	-3.49078600
H	-1.86984700	-1.53266000	-3.00173100
F	0.01497300	0.14981500	-2.78966800
C	3.96256700	0.27167900	-1.90310600
H	4.98753600	0.13873900	-2.30531300
H	3.35497800	0.62095000	-2.75113300
H	3.24436300	-1.81563900	-2.18537800
H	4.86518800	-0.99830100	1.71899000
C	3.95135100	1.33342500	-0.79462900
H	4.49005400	2.23377000	-1.12512000
H	2.90655000	1.63875800	-0.63972100

C	4.52109000	0.84603300	0.56093600
H	3.83612300	1.14515600	1.37128500
H	5.47105800	1.34428400	0.81092000

H: TS-**1b** (*endo-trans*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -307.38 cm^{-1}

Optimization: -2153.164468

Single point: -2153.998540

1 1

Pd	1.44777200	-1.45112500	0.05853700
C	3.23583000	-2.37935800	-0.64938600
C	3.83076700	-1.29971100	-1.41040700
C	3.27184600	-2.37579200	0.77230200
H	2.91259600	-3.27215700	-1.19369000
N	5.47634700	-1.98284400	-2.11177000

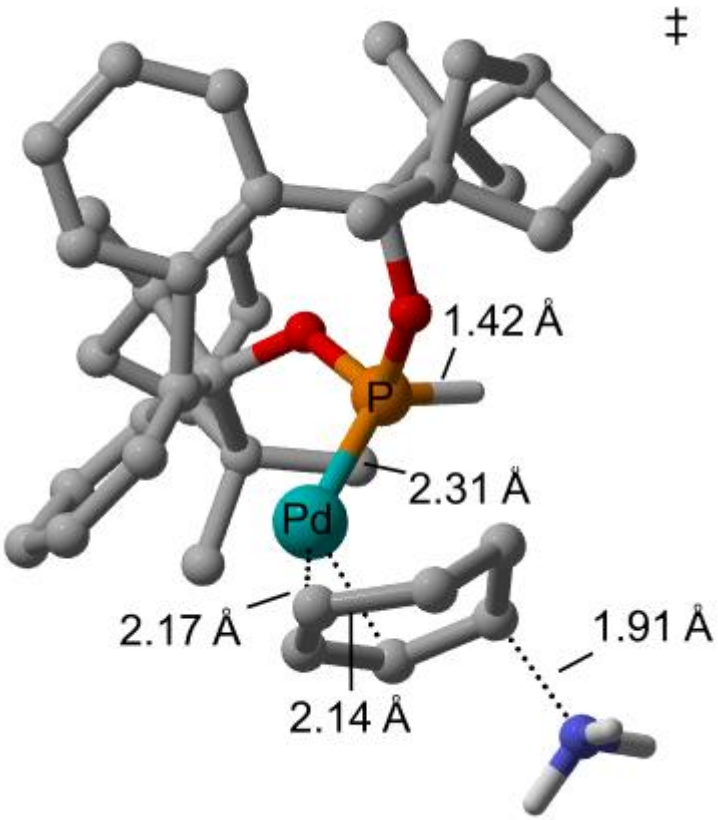
H	5.58031000	-2.94283900	-1.77395500
H	5.46764000	-1.99812100	-3.13508000
H	6.28928300	-1.44360300	-1.80250900
P	0.08295200	-0.13408300	-1.25916900
O	-1.53071800	-0.11154400	-0.94683300
O	0.62367300	1.29699200	-0.72129600
C	-2.21627300	-1.23825100	-0.34518800
C	0.02721100	2.43677900	-0.10024600
C	-1.39551600	-1.64072000	0.89417000
C	-3.69899700	-0.79994700	-0.02564300
C	-0.71781400	2.00056600	1.18295900
C	-0.76709600	3.34534300	-1.18601300
C	1.27506400	3.36858000	0.25764000
C	-1.53221700	-2.86132900	1.53243600
C	-0.37828100	-0.73080700	1.41793100
C	-4.27009200	-0.06217800	-1.26874200
C	-4.42736700	-2.15567400	-0.13237100
C	-3.91585100	-0.02788300	1.26250900
C	-0.75635100	0.71308500	1.79212200
C	-1.30191900	3.05052900	1.92491800
C	0.17102300	4.59156400	-1.30846000
C	-2.18705000	3.79485800	-0.79074300
C	-0.93793100	2.63426800	-2.53606300
C	0.69323200	4.79201600	0.12135200
C	1.98810500	2.99223500	1.54687300
C	2.23227800	3.38482800	-0.96975200
C	-0.62769300	-3.32858100	2.51512200
H	-2.34756500	-3.52085000	1.25820100
C	0.61910100	-1.28840200	2.26700200

C	-4.57160800	-1.19391500	-2.28567500
H	-3.56879500	0.69008000	-1.64774700
H	-5.18707400	0.46835900	-0.97371800
C	-4.00474700	-2.43673900	-1.57791500
H	-4.09298400	-2.90240400	0.59933200
H	-5.51547900	-2.03951500	-0.01493300
H	-3.54900600	-0.57795500	2.13896300
H	-3.41580900	0.94971000	1.23866500
H	-4.99310600	0.14987000	1.40423500
C	-1.32122500	0.60749400	3.09112100
C	-1.87551600	2.91720300	3.18151400
H	-1.29464100	4.04555300	1.50912300
H	-0.35736700	5.44768900	-1.75204300
C	1.48713900	4.24047700	-2.02902700
H	-2.68739400	4.19608000	-1.68475500
H	-2.78994700	2.95470300	-0.41874200
H	-2.21137000	4.59325300	-0.04031600
H	-1.69347300	1.83980100	-2.46617200
H	-1.29197700	3.36346600	-3.28050600
H	-0.01000700	2.19994600	-2.92055700
H	1.48765700	5.55248400	0.17594800
H	-0.06361000	5.07186700	0.85897100
H	2.31788500	1.94012500	1.50985600
H	2.88048900	3.62143100	1.68816600
H	1.34762100	3.10858800	2.43139900
H	3.17354000	3.86443800	-0.66138300
H	2.47495400	2.37723600	-1.32175800
C	0.49101000	-2.58731200	2.82099100
H	-0.80287900	-4.29877100	2.98384500

H	1.31733300	-0.59005900	2.73397800
H	-4.14232500	-1.01620000	-3.27959000
H	-5.65527300	-1.31868300	-2.42847700
C	-2.44731000	-2.38278500	-1.49283000
H	-4.35214100	-3.38674900	-2.00903100
C	-1.87319500	1.66827200	3.79090900
H	-1.35297900	-0.37916000	3.55448100
H	-2.30422600	3.79086000	3.67669100
H	2.04090100	5.16400300	-2.25384100
H	1.34152700	3.72003000	-2.98350900
H	1.23918500	-2.94852900	3.52929400
C	-1.90102800	-3.79094700	-1.19921500
C	-1.81648600	-1.98286500	-2.83618000
H	-2.29929700	1.51206300	4.78376500
H	-2.48227500	-4.34310900	-0.45195000
H	-1.95284500	-4.38031000	-2.12718900
H	-0.85040800	-3.76787800	-0.87467600
H	-2.02750000	-0.95231000	-3.13810500
H	-0.72301600	-2.12534200	-2.81231900
H	-2.20060600	-2.64941300	-3.62308600
H	0.04738300	0.11925200	-2.65761300
H	3.01883900	-3.30856600	1.28387400
H	3.40031400	-1.11164800	-2.39731300
C	4.31117000	-0.08654000	-0.64229700
H	3.42429100	0.52926100	-0.41927400
H	4.96018300	0.53943900	-1.27492100
C	4.13183400	-1.38788900	1.55058600
H	3.49626900	-0.74623100	2.18142600
H	4.77354100	-1.94211700	2.25557500

C	5.01362300	-0.50422600	0.65363700
H	5.34007800	0.39042700	1.20363000
H	5.93766100	-1.05564400	0.40194300

H: TS-**3b** (*endo-cis*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -322.44 cm^{-1}

Energy: -2153.160763

Single point: -2153.993890

1 1

Pd	1.44777200	-1.45112500	0.05853700
C	3.23583000	-2.37935800	-0.64938600
C	3.83076700	-1.29971100	-1.41040700
C	3.27184600	-2.37579200	0.77230200
H	2.91259600	-3.27215700	-1.19369000

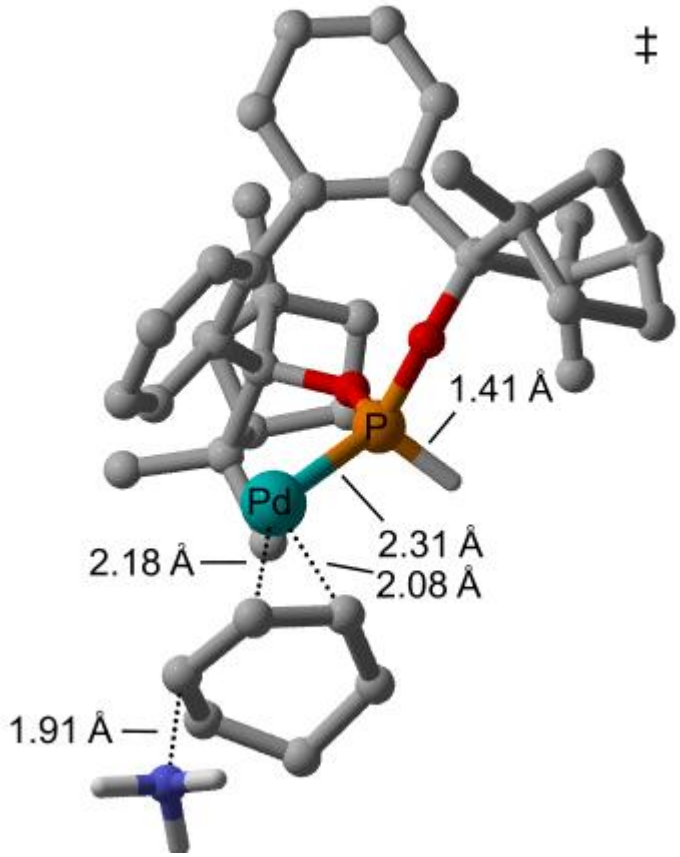
N	5.47634700	-1.98284400	-2.11177000
H	5.58031000	-2.94283900	-1.77395500
H	5.46764000	-1.99812100	-3.13508000
H	6.28928300	-1.44360300	-1.80250900
P	0.08295200	-0.13408300	-1.25916900
O	-1.53071800	-0.11154400	-0.94683300
O	0.62367300	1.29699200	-0.72129600
C	-2.21627300	-1.23825100	-0.34518800
C	0.02721100	2.43677900	-0.10024600
C	-1.39551600	-1.64072000	0.89417000
C	-3.69899700	-0.79994700	-0.02564300
C	-0.71781400	2.00056600	1.18295900
C	-0.76709600	3.34534300	-1.18601300
C	1.27506400	3.36858000	0.25764000
C	-1.53221700	-2.86132900	1.53243600
C	-0.37828100	-0.73080700	1.41793100
C	-4.27009200	-0.06217800	-1.26874200
C	-4.42736700	-2.15567400	-0.13237100
C	-3.91585100	-0.02788300	1.26250900
C	-0.75635100	0.71308500	1.79212200
C	-1.30191900	3.05052900	1.92491800
C	0.17102300	4.59156400	-1.30846000
C	-2.18705000	3.79485800	-0.79074300
C	-0.93793100	2.63426800	-2.53606300
C	0.69323200	4.79201600	0.12135200
C	1.98810500	2.99223500	1.54687300
C	2.23227800	3.38482800	-0.96975200
C	-0.62769300	-3.32858100	2.51512200
H	-2.34756500	-3.52085000	1.25820100

C	0.61910100	-1.28840200	2.26700200
C	-4.57160800	-1.19391500	-2.28567500
H	-3.56879500	0.69008000	-1.64774700
H	-5.18707400	0.46835900	-0.97371800
C	-4.00474700	-2.43673900	-1.57791500
H	-4.09298400	-2.90240400	0.59933200
H	-5.51547900	-2.03951500	-0.01493300
H	-3.54900600	-0.57795500	2.13896300
H	-3.41580900	0.94971000	1.23866500
H	-4.99310600	0.14987000	1.40423500
C	-1.32122500	0.60749400	3.09112100
C	-1.87551600	2.91720300	3.18151400
H	-1.29464100	4.04555300	1.50912300
H	-0.35736700	5.44768900	-1.75204300
C	1.48713900	4.24047700	-2.02902700
H	-2.68739400	4.19608000	-1.68475500
H	-2.78994700	2.95470300	-0.41874200
H	-2.21137000	4.59325300	-0.04031600
H	-1.69347300	1.83980100	-2.46617200
H	-1.29197700	3.36346600	-3.28050600
H	-0.01000700	2.19994600	-2.92055700
H	1.48765700	5.55248400	0.17594800
H	-0.06361000	5.07186700	0.85897100
H	2.31788500	1.94012500	1.50985600
H	2.88048900	3.62143100	1.68816600
H	1.34762100	3.10858800	2.43139900
H	3.17354000	3.86443800	-0.66138300
H	2.47495400	2.37723600	-1.32175800
C	0.49101000	-2.58731200	2.82099100

H	-0.80287900	-4.29877100	2.98384500
H	1.31733300	-0.59005900	2.73397800
H	-4.14232500	-1.01620000	-3.27959000
H	-5.65527300	-1.31868300	-2.42847700
C	-2.44731000	-2.38278500	-1.49283000
H	-4.35214100	-3.38674900	-2.00903100
C	-1.87319500	1.66827200	3.79090900
H	-1.35297900	-0.37916000	3.55448100
H	-2.30422600	3.79086000	3.67669100
H	2.04090100	5.16400300	-2.25384100
H	1.34152700	3.72003000	-2.98350900
H	1.23918500	-2.94852900	3.52929400
C	-1.90102800	-3.79094700	-1.19921500
C	-1.81648600	-1.98286500	-2.83618000
H	-2.29929700	1.51206300	4.78376500
H	-2.48227500	-4.34310900	-0.45195000
H	-1.95284500	-4.38031000	-2.12718900
H	-0.85040800	-3.76787800	-0.87467600
H	-2.02750000	-0.95231000	-3.13810500
H	-0.72301600	-2.12534200	-2.81231900
H	-2.20060600	-2.64941300	-3.62308600
H	0.04738300	0.11925200	-2.65761300
H	3.01883900	-3.30856600	1.28387400
H	3.40031400	-1.11164800	-2.39731300
C	4.31117000	-0.08654000	-0.64229700
H	3.42429100	0.52926100	-0.41927400
H	4.96018300	0.53943900	-1.27492100
C	4.13183400	-1.38788900	1.55058600
H	3.49626900	-0.74623100	2.18142600

H	4.77354100	-1.94211700	2.25557500
C	5.01362300	-0.50422600	0.65363700
H	5.34007800	0.39042700	1.20363000
H	5.93766100	-1.05564400	0.40194300

H: TS-**2b** (*exo-trans*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -308.51 cm^{-1}

Optimization: -2153.162229

Single point: -2153.995975

1 1

Pd	-2.20893900	-0.67922800	0.50427800
C	-4.07287500	-1.80111700	0.68643100
C	-5.12890400	-0.82927300	0.69535900
C	-3.34773800	-2.09474000	-0.51735800

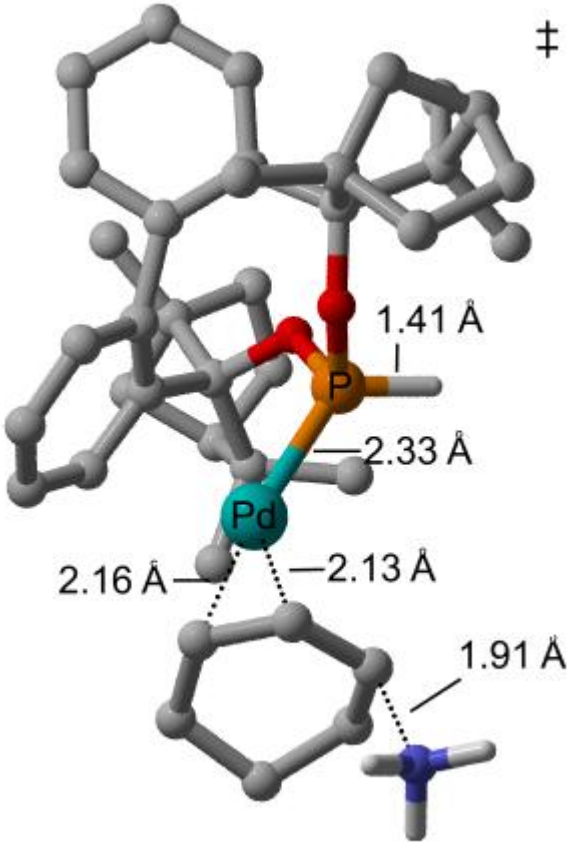
H	-3.93808500	-2.42885300	1.57274100
N	-6.78659000	-1.78691100	0.73436200
H	-7.30493100	-1.61009700	1.59929500
H	-7.40042900	-1.57300600	-0.05646200
H	-6.55357400	-2.78230000	0.69776700
P	-0.26941300	-0.42399700	-0.72916600
O	0.38541400	1.05670400	-1.00628700
O	0.96803100	-1.32078700	-0.19863800
C	0.17900500	2.21116800	-0.12920200
C	2.41394600	-1.36312900	-0.28425400
C	-0.07630800	1.53013700	1.24746000
C	1.42824700	3.20613300	-0.36807900
C	3.01098800	-0.27781000	0.65007200
C	2.97743300	-1.47554700	-1.80844200
C	2.77627100	-2.81042800	0.29445400
C	-1.41384200	1.49468300	1.72657700
C	0.82619800	0.61253100	1.86057400
C	1.93073800	2.93365700	-1.80725500
C	0.76253900	4.57747800	-0.62292900
C	2.55346400	3.30945900	0.64475600
C	2.30499800	0.46606800	1.63423900
C	4.41863800	-0.18532000	0.71781800
C	3.53490500	-2.93765600	-1.84232900
C	4.10314100	-0.49276100	-2.19836000
C	1.90238700	-1.27782700	-2.88374500
C	4.09735000	-3.13655800	-0.42948200
C	2.75334000	-2.92153500	1.80973500
C	1.84581500	-3.85383900	-0.38815400
C	-1.85366600	0.65138100	2.75462800

H	-2.14452100	2.16486300	1.30222300
C	0.36909800	-0.20958400	2.91747900
C	0.74168600	3.39101300	-2.69177600
H	2.22551300	1.89364900	-1.96761300
H	2.81802200	3.56224800	-1.97614900
C	-0.21161800	4.06760500	-1.67928600
H	0.30044000	5.03029400	0.26231400
H	1.50407400	5.28975900	-1.01323500
H	2.18164000	3.36579800	1.67604200
H	3.26821300	2.48623800	0.56992400
H	3.10902700	4.23932800	0.44528300
C	3.02390100	1.09432800	2.67605600
C	5.11341600	0.49885600	1.70894300
H	5.02061900	-0.70106000	-0.01337100
H	4.24651000	-3.07085100	-2.67003500
C	2.40028900	-3.97874600	-1.83195800
H	4.18336300	-0.47358500	-3.29515400
H	3.89920100	0.53226400	-1.86204200
H	5.09279800	-0.78536000	-1.82896400
H	1.58416400	-0.22751500	-2.94414300
H	2.33304100	-1.54727100	-3.86003600
H	1.02135100	-1.90904600	-2.74027500
H	4.40658600	-4.17615200	-0.24083900
H	4.94448000	-2.49647500	-0.16759000
H	1.74621000	-2.70018200	2.19487500
H	3.00715200	-3.94909100	2.11246800
H	3.46637500	-2.24091800	2.29469800
H	1.93934600	-4.80490300	0.15665100
H	0.79251800	-3.55663200	-0.34346300

C	-0.94187800	-0.21816900	3.36438000
H	-2.88444400	0.72435200	3.10738300
H	1.09437100	-0.87818300	3.38099200
H	0.27013600	2.55486700	-3.22539200
H	1.05703700	4.12071400	-3.45194200
C	-1.02588200	3.06280200	-0.81427700
H	-0.87607300	4.81167600	-2.14110100
C	4.40835600	1.12051300	2.73547600
H	2.44971900	1.60971400	3.44807200
H	6.20513000	0.51196700	1.68737100
H	2.82224800	-4.97906400	-2.00969700
H	1.64199200	-3.81765300	-2.60830000
H	-1.24924600	-0.88185700	4.17465100
C	-1.88813100	3.94221400	0.14107900
C	-1.98398600	2.21576200	-1.65594900
H	4.92112700	1.62928400	3.55395500
H	-1.41336800	4.16100700	1.10495600
H	-2.09321700	4.90641800	-0.34681500
H	-2.87124100	3.49425400	0.34551700
H	-1.48114400	1.69953200	-2.48236300
H	-2.49344400	1.45423300	-1.04283900
H	-2.75767700	2.86753100	-2.09121800
H	-0.40839300	-0.76448100	-2.09385600
H	-2.77644000	-3.02878000	-0.53547400
H	-5.32185500	-0.32935200	1.64921500
C	-5.30614900	0.01877200	-0.54728400
H	-4.53522700	0.80608700	-0.52010500
H	-6.27442600	0.54326300	-0.52483900
C	-3.83076400	-1.60353100	-1.87833900

H	-3.05243800	-0.97738300	-2.34458100
H	-3.95030500	-2.46665600	-2.55408600
C	-5.15760600	-0.82727800	-1.81667900
H	-5.26732000	-0.18821900	-2.70503700
H	-5.99446900	-1.54720900	-1.86209400

H: TS-**4b** (*exo-cis*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-H, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -322.47 cm^{-1}

Energy: -2153.160787

Single point: -2153.997689

1 1

Pd	-1.94660000	-0.68026900	0.33053000
C	-3.25644800	-2.34837000	0.53151100
C	-3.67468900	-1.34272600	1.43650300

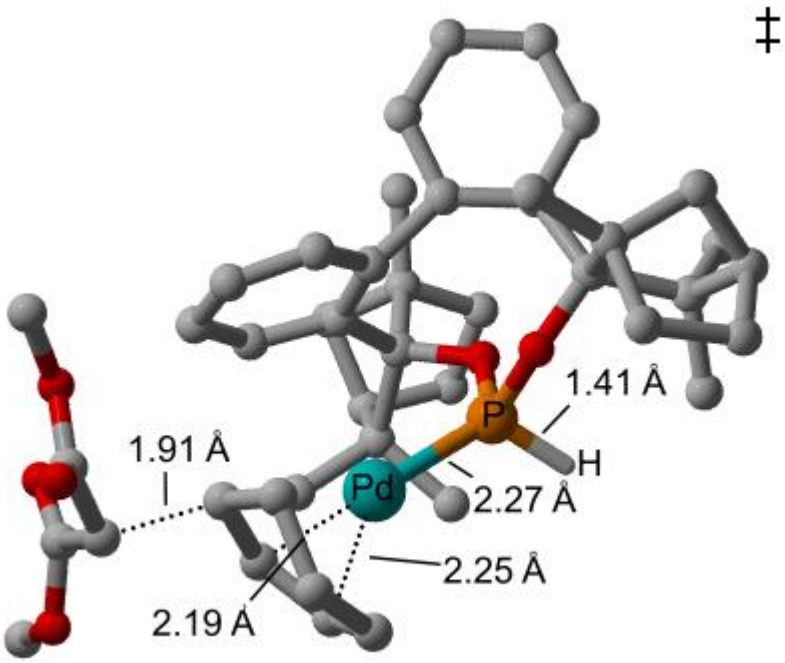
C	-3.84493200	-2.44586100	-0.79105700
H	-2.60592300	-3.16402600	0.86221400
N	-5.00806200	-3.96558300	-0.72843000
H	-4.69149700	-4.70163300	-1.36533700
H	-4.98772900	-4.33161500	0.22675700
H	-5.97569700	-3.72769200	-0.96203300
P	-0.03741300	-0.46768900	-0.98398600
O	0.56902100	1.07361800	-1.07125800
O	1.15004900	-1.33656900	-0.30664300
C	-0.19644600	2.08643600	-0.37918100
C	2.58505700	-1.21251800	-0.27273900
C	-0.40049600	1.49141000	1.05068500
C	0.57088300	3.47047300	-0.39010500
C	2.96068100	0.05616000	0.52985300
C	3.07819500	-2.48947200	0.54976700
C	3.27557800	-1.48776600	-1.72465900
C	-1.59701800	1.70397000	1.77122600
C	0.61713700	0.70493000	1.71662900
C	1.10671100	3.72074000	-1.82933700
C	-0.62078300	4.44655900	-0.31833200
C	1.63781500	3.73327300	0.65310400
C	2.11439900	0.72259200	1.46420000
C	4.32356300	0.41391500	0.56669700
C	2.39798900	-3.75180900	-0.05697900
C	4.51309400	-2.66921200	0.02127500
C	2.89721200	-2.40166300	2.05566900
C	4.10459300	-2.79062100	-1.45177400
C	2.25786200	-1.74227800	-2.84935000
C	4.18959800	-0.37752600	-2.28554500

C	-1.85517900	1.15227700	3.03349800
H	-2.33999100	2.37358900	1.36285000
C	0.29156900	0.10445300	2.94718700
C	-0.12573800	4.22040600	-2.62091200
H	1.55444900	2.81014100	-2.24642100
H	1.89815300	4.48270400	-1.79047000
C	-1.26823500	3.98814100	-1.62206200
H	-1.24376100	4.30378400	0.57772300
H	-0.28983600	5.49569400	-0.33831700
H	1.27553200	3.55613700	1.67352900
H	2.53498300	3.12809400	0.48543000
H	1.93541500	4.79151500	0.58724700
C	2.72249800	1.53510000	2.45093100
C	4.88673100	1.28006800	1.49835500
H	5.00444200	-0.03125000	-0.14072800
C	3.18506800	-4.02234100	-1.36619900
H	1.32471300	-3.59383200	-0.21592500
H	2.50342200	-4.58437100	0.65411000
H	5.19297400	-1.84591700	0.25791000
H	4.96960300	-3.59307200	0.40871600
H	3.45600500	-1.56642400	2.49931900
H	1.83315300	-2.28192400	2.30972100
H	3.25049100	-3.33210200	2.52635500
H	4.92383700	-2.90077100	-2.17705700
H	1.43032200	-2.39898800	-2.56089800
H	1.84716200	-0.79789400	-3.23218400
H	2.78415300	-2.22346100	-3.68781300
H	5.20492200	-0.38516000	-1.87180900
H	4.30743900	-0.53404600	-3.36828300

H	3.75841200	0.62287500	-2.13661000
C	-0.91960800	0.30595400	3.60971200
H	-2.79528500	1.38647800	3.53705500
H	1.06253800	-0.49520600	3.43097500
H	-0.26793200	3.71334300	-3.58350100
H	-0.04748000	5.29609600	-2.83900900
C	-1.49516400	2.46941300	-1.34994800
H	-2.20566400	4.48944400	-1.90356300
C	4.08019100	1.81883100	2.49275500
H	2.07519100	1.99627500	3.19709200
H	5.95631300	1.49627300	1.45648200
H	2.54318500	-4.16627000	-2.24375800
H	3.80249400	-4.92858000	-1.27650700
H	-1.10145800	-0.16607400	4.57739500
C	-2.92953100	2.30822000	-0.81684300
C	-1.47403400	1.66258200	-2.66113600
H	4.48629100	2.46483000	3.27346900
H	-3.11180900	1.30180300	-0.40960000
H	-3.21010300	3.05446500	-0.06249400
H	-3.62133400	2.44983000	-1.66133600
H	-1.85122000	0.63890100	-2.50412000
H	-2.15645100	2.14091700	-3.37985300
H	-0.48591000	1.59658700	-3.12532100
H	0.06626900	-0.77605100	-2.35592700
H	-3.20368300	-2.86382500	-1.57143400
H	-3.34733900	-1.43028600	2.47702900
C	-4.79815700	-1.35038700	-1.22069500
H	-4.18436700	-0.50599200	-1.57247900
H	-5.38898500	-1.67501900	-2.09204600

C	-4.90278500	-0.48337400	1.18352200
H	-5.56152600	-0.52475200	2.06688200
H	-4.61012100	0.57543100	1.09347700
C	-5.69781700	-0.91470900	-0.05897900
H	-6.35999000	-1.75585400	0.21573900
H	-6.36433600	-0.10436800	-0.38849400

H: TS-**2c** (*endo-trans*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-H with dimethylmalonate, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -218.71 cm^{-1}

Energy: -2592.034385

Single point: -2593.321249

0 1

Pd	-1.01989200	-0.02916100	-1.41020600
C	-3.20354000	-0.15885300	-1.42918900
C	-2.79141100	-0.62550500	-2.67125600

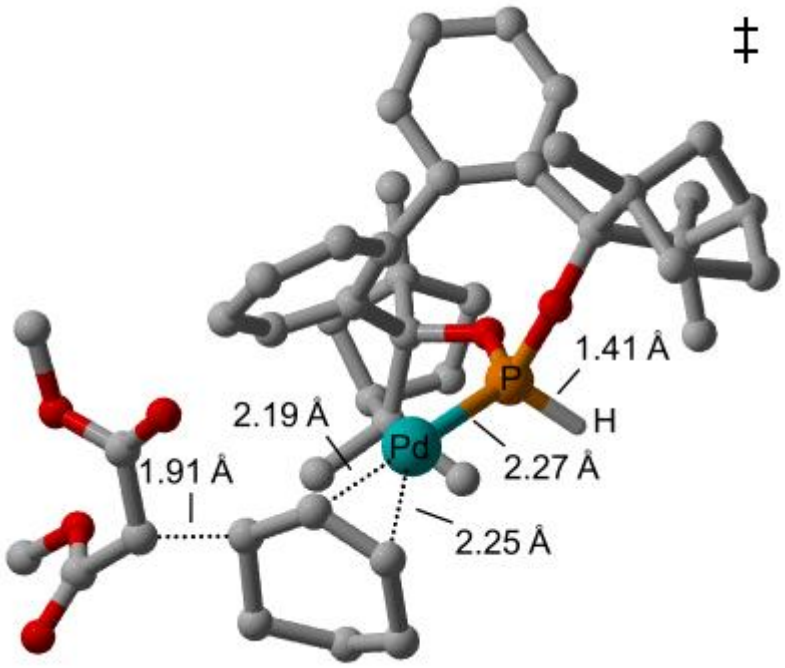
C	-3.51888400	-1.07324100	-0.30137500
H	-3.46564300	0.89799900	-1.31192000
P	1.24353400	0.10558900	-1.39481300
O	2.02880100	1.36078500	-0.62071800
O	1.93014900	-1.22181500	-0.73126400
C	1.22782000	2.32297900	0.09040000
C	3.18470800	-1.51179100	-0.11788000
C	0.33204700	1.47042500	1.03267100
C	2.16503900	3.34622700	0.85273900
C	3.30349700	-0.71928300	1.20755400
C	3.10150300	-3.06886300	0.24394600
C	4.42864700	-1.50884200	-1.17569600
C	-0.96652700	1.87515000	1.38643200
C	0.77617600	0.20733500	1.56274500
C	3.27739900	3.82179400	-0.12689300
C	1.24132500	4.58019900	0.90840300
C	2.74132100	2.94441200	2.19659000
C	2.20701200	-0.15864600	1.92520600
C	4.52774900	-0.79018100	1.90452900
C	2.62793200	-3.83413800	-1.02753900
C	4.58653900	-3.47518500	0.27367000
C	2.26093400	-3.40707500	1.46464500
C	4.88449500	-3.00968900	-1.15804100
C	4.01608800	-1.10755600	-2.60291600
C	5.62080800	-0.58121300	-0.85263400
C	-1.87137900	1.06341800	2.07368300
H	-1.30659300	2.86362600	1.10720500
C	-0.17234700	-0.62053800	2.19166100
C	2.58289900	4.88731500	-1.01221500

H	3.68036900	2.97483000	-0.70027800
H	4.11070600	4.25519600	0.45021300
C	1.10853600	4.73145400	-0.60653400
H	0.29252000	4.38669000	1.43440400
H	1.73447000	5.44040000	1.39338700
H	1.96036900	2.61781200	2.89873200
H	3.48617700	2.14148900	2.10169800
H	3.24812200	3.82033800	2.64117400
C	2.38356600	0.10751300	3.30488800
C	4.69564300	-0.44832400	3.24331700
H	5.40379900	-1.16716400	1.39894400
C	3.89034300	-3.89912600	-1.92933000
H	1.77652800	-3.33017600	-1.50355500
H	2.29283600	-4.84236000	-0.73269500
H	5.17888400	-2.99526200	1.06085300
H	4.70242100	-4.56655000	0.39321800
H	2.64470300	-2.93861700	2.38494000
H	1.21882300	-3.07680500	1.31608700
H	2.24955000	-4.50106400	1.61779200
H	5.92742400	-3.11531000	-1.49841500
H	3.07038400	-1.55367900	-2.93510200
H	3.94206600	-0.01312500	-2.69915800
H	4.80626800	-1.44120400	-3.29883000
H	6.32896000	-1.00247300	-0.12406200
H	6.20168900	-0.41601900	-1.77654400
H	5.28346600	0.40256100	-0.48603700
C	-1.48790300	-0.22654000	2.42697200
H	-2.88591600	1.41831400	2.26960800
H	0.17147300	-1.58388400	2.57407500

H	2.76410100	4.75328100	-2.08821200
H	2.92677300	5.90342900	-0.75340200
C	0.53971500	3.34029300	-1.02884000
H	0.46635500	5.55363300	-0.96084500
C	3.59020200	-0.03432400	3.97670000
H	1.52181100	0.48493100	3.85869300
H	5.68317000	-0.54139600	3.70460900
H	3.70779500	-3.57925000	-2.96443000
H	4.28979800	-4.92613300	-1.98051400
H	-2.19257900	-0.90435600	2.91529900
C	-0.99478700	3.45428300	-1.10591400
C	0.97649600	2.97923000	-2.46227800
H	3.66224700	0.20173200	5.04207400
H	-1.47845600	2.46337200	-1.15340000
H	-1.43549100	4.03624400	-0.28202900
H	-1.24905000	3.99346900	-2.03556900
H	0.39149000	2.12338600	-2.84354300
H	0.75854700	3.83541000	-3.12452800
H	2.04330100	2.74105000	-2.55451200
H	1.95939800	0.24233700	-2.60471500
H	-3.11384500	-0.71116000	0.64900600
H	-2.73101200	0.08661300	-3.50156800
C	-3.19531500	-2.53481300	-0.56282800
H	-2.10706600	-2.66236300	-0.39704500
H	-3.70791200	-3.18593100	0.16430300
C	-2.79793900	-2.09972100	-3.03249000
H	-3.26920100	-2.22096700	-4.02596800
H	-1.76139300	-2.46638000	-3.14381800
C	-3.55130100	-2.94400400	-1.99433000

H	-4.64027500	-2.81559400	-2.13761500
H	-3.33779100	-4.01549000	-2.14956900
C	-5.37442500	-0.89517500	0.13634900
H	-5.93443600	-1.28860500	-0.71544600
C	-5.54095700	-1.78137900	1.32381300
C	-5.54081000	0.57966600	0.29584900
O	-4.94918300	-1.29932700	2.43254800
O	-6.14769000	1.09896300	-0.79441400
O	-6.08170400	-2.86360700	1.28472700
O	-5.14474400	1.26555000	1.20906800
C	-5.03095100	-2.11969700	3.59342500
H	-4.52768700	-1.55887700	4.39437800
H	-6.08254200	-2.31434200	3.86254500
H	-4.52766500	-3.08709700	3.42529800
C	-6.25572700	2.51868100	-0.83033100
H	-5.25612700	2.98652200	-0.80812800
H	-6.76930900	2.75992000	-1.77229000
H	-6.83521100	2.89020800	0.03126400

H: TS-**1c** (*exo-trans*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-H with dimethylmalonate, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -173.12 cm^{-1}

Energy: -2592.033944

Single point: -2593.321970

0 1

Pd	-0.81247200	-1.11569500	-1.11135900
C	-2.82745400	-1.96017800	-0.90131200
C	-3.78909400	-0.82320900	-0.80001200
C	-2.34773600	-2.41410900	-2.12318800
H	-2.68361200	-2.56674300	-0.00068500
P	1.26946300	-0.24402100	-1.32320900
O	1.69705600	1.27571800	-0.76639500
O	2.38393300	-1.18378100	-0.58357700
C	0.71307200	2.10397500	-0.12272200
C	3.66166000	-0.98186400	0.01650200
C	0.07345200	1.19290300	0.95839200
C	1.40430300	3.40598000	0.45081600
C	3.50312200	-0.11233100	1.28753800

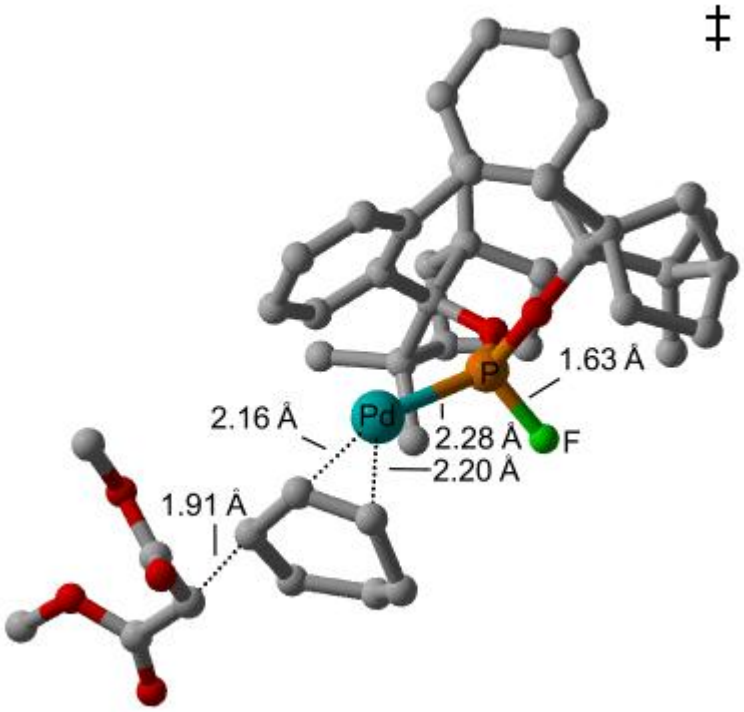
C	4.82739100	-0.60528200	-1.05798500
C	4.11490500	-2.45120000	0.46234900
C	-1.26740000	1.31670300	1.34777800
C	0.80977400	0.10637200	1.54883400
C	2.34171000	3.99006000	-0.64469000
C	0.21869800	4.39190700	0.40803400
C	2.09525300	3.31834100	1.79871300
C	2.27428300	0.16857800	1.94735500
C	4.67519900	0.22070800	1.99981700
C	5.74295100	-1.87637500	-1.01207600
C	5.65984800	0.66181000	-0.76259700
C	4.29404000	-0.38389500	-2.48179700
C	5.65227600	-2.34624400	0.44682100
C	3.45228800	-2.96524700	1.73100300
C	3.90026900	-3.40677500	-0.74825600
C	-1.95068600	0.33103500	2.06620200
H	-1.82820500	2.19556900	1.05463400
C	0.08922300	-0.91253600	2.19466800
C	1.38485300	4.72033700	-1.62215100
H	2.92802000	3.19302100	-1.12351100
H	3.05464900	4.68990700	-0.17837700
C	0.00173400	4.29447800	-1.10275900
H	-0.63996600	4.06338200	1.01583200
H	0.51173100	5.40143400	0.74486300
H	1.42781300	2.92038900	2.57733800
H	2.99715800	2.69002800	1.76018800
H	2.40615100	4.33318700	2.10721100
C	2.32139800	0.59728600	3.29713200
C	4.69716400	0.70698700	3.30302300

H	5.63792000	0.06633400	1.53657800
H	6.75448200	-1.65472300	-1.38961800
C	5.07173600	-3.07383500	-1.71286700
H	6.16778200	0.97561200	-1.69092200
H	5.02359300	1.49753200	-0.42753000
H	6.45608700	0.50955300	-0.01951700
H	3.82210000	0.60741900	-2.57436800
H	5.14759200	-0.40956600	-3.18262800
H	3.57666100	-1.14600800	-2.80786700
H	6.12234500	-3.33344700	0.59964800
H	6.08087800	-1.66433900	1.18960100
H	2.35544000	-2.98729300	1.60790300
H	3.78925400	-3.99619100	1.94036500
H	3.68758200	-2.34451800	2.61037500
H	3.96135900	-4.44794700	-0.39031800
H	2.90932500	-3.27029800	-1.19923100
C	-1.28746500	-0.84250300	2.41235100
H	-3.01044100	0.47459600	2.29128100
H	0.65271900	-1.75962500	2.59302100
H	1.55745100	4.46883800	-2.67839700
H	1.48684800	5.81543600	-1.53292100
C	-0.24224500	2.76631500	-1.30217700
H	-0.82579400	4.89274800	-1.51679800
C	3.49653000	0.85976000	3.98711100
H	1.36939200	0.76598900	3.80494100
H	5.65600100	0.93308100	3.77860400
H	5.79016400	-3.90904400	-1.76951400
H	4.74688400	-2.86633500	-2.74192000
H	-1.81659900	-1.67693300	2.87779100

C	-1.75976100	2.50871100	-1.26507500
C	0.19786200	2.30783200	-2.70536700
H	3.46568200	1.20001500	5.02596700
H	-2.28724400	3.09032800	-0.49371700
H	-2.18555900	2.82243400	-2.23424100
H	-1.98882100	1.44111900	-1.13139000
H	1.28410000	2.32428400	-2.85724600
H	-0.16757200	1.28632500	-2.91224300
H	-0.26310100	2.97240600	-3.45715400
H	1.83464800	-0.07638800	-2.60905200
H	-1.84309400	-3.38626600	-2.16162100
H	-3.42072400	-0.00341100	-0.17265200
C	-4.37031200	-0.34852200	-2.13057700
H	-4.76773600	0.67397000	-2.02227700
H	-5.22475900	-0.99405200	-2.40489300
C	-2.79494500	-1.82580500	-3.43961000
H	-1.95978200	-1.83575400	-4.16138900
H	-3.58346600	-2.47987500	-3.86948900
C	-3.34327800	-0.40691000	-3.27118400
H	-2.50365200	0.27658800	-3.05490800
H	-3.81572300	-0.06212700	-4.20810000
C	-5.27952100	-1.36986500	0.27065500
H	-5.65391600	-2.26106200	-0.24499500
C	-6.26701500	-0.24957000	0.16579600
C	-4.78122500	-1.74808700	1.63147600
O	-7.38351600	-0.35245400	-0.28263700
O	-4.07564300	-2.70526900	1.85682300
O	-5.74048500	0.92756500	0.56428300
O	-5.21781600	-0.91994000	2.60118900

C	-4.84195600	-1.24207900	3.93840900
H	-5.43491700	-0.57922000	4.58505300
H	-5.05858900	-2.29955300	4.16058300
H	-3.76640500	-1.05642500	4.09611500
C	-6.60275700	2.05672000	0.48618900
H	-7.49601800	1.91047100	1.11658300
H	-6.01488600	2.91294700	0.84813300
H	-6.93056400	2.22750400	-0.55334200

F: TS-**2c** (*endo-trans*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-F with dimethylmalonate, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -291.04 cm^{-1}

Energy: -2691.239340

Single point: -2692.621735

0 1

Pd	0.74177100	-0.84553100	-0.34772300

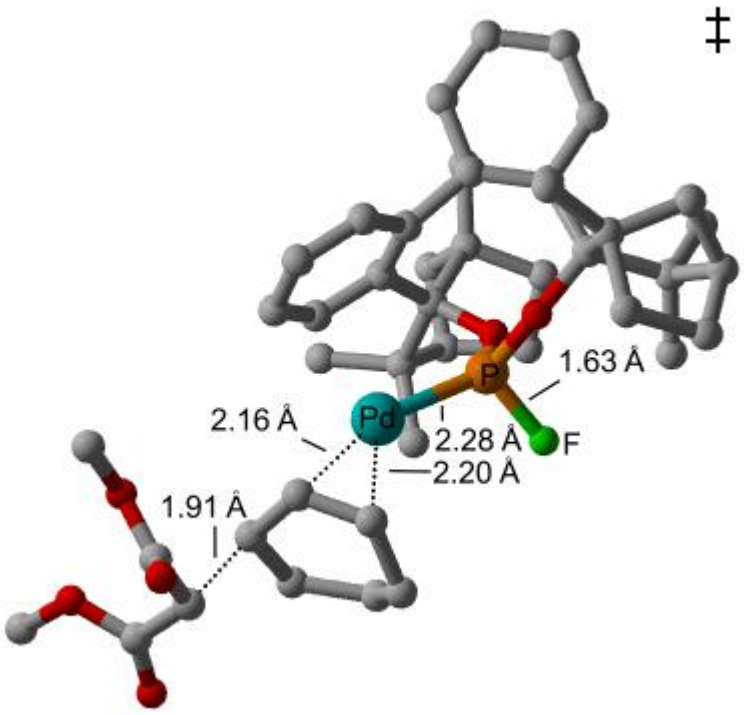
C	2.87502600	-1.35516600	-0.32688800
C	2.50085600	-1.05278400	-1.64258400
C	3.66265600	-0.40535200	0.49354800
H	2.89217900	-2.40097000	-0.00188400
P	-1.15595600	-0.07528100	-1.31452700
O	-2.59965200	-0.59582100	-0.72119200
O	-1.16986800	1.47993000	-0.91556100
C	-2.74522800	-1.85718200	-0.01875800
C	-1.87274400	2.37529100	-0.06137600
C	-1.60385900	-1.92369800	1.02352400
C	-4.19214300	-1.89207100	0.61501000
C	-2.06644100	1.75880500	1.34305200
C	-0.92284700	3.66349700	0.00728400
C	-3.17926500	2.96285600	-0.83371600
C	-1.21641600	-3.08671500	1.66122500
C	-0.83180500	-0.71145300	1.32217400
C	-5.21742400	-1.46316300	-0.47327400
C	-4.44713800	-3.41255500	0.67202300
C	-4.38051900	-1.14080300	1.92105300
C	-1.56999600	0.52884000	1.86079800
C	-2.71029200	2.60579700	2.27430100
C	-0.36014900	3.91855200	-1.42049100
C	-1.92457800	4.83778300	0.07479800
C	0.17367200	3.58119700	1.05958100
C	-2.71473400	4.41624200	-1.17292000
C	-3.52876800	2.16735800	-2.09914400
C	-4.49167300	3.01191300	-0.02316500
C	-0.02107500	-3.19889500	2.41887800
H	-1.81095200	-3.98793800	1.55168600

C	0.45564300	-0.89137200	1.92338000
C	-5.35092100	-2.70775100	-1.39121900
H	-4.88055300	-0.56525100	-1.00791900
H	-6.17500800	-1.21630900	0.01431300
C	-4.26595200	-3.64565500	-0.83192600
H	-3.74180300	-3.96014800	1.31321300
H	-5.46825400	-3.63927800	1.02460700
H	-3.68390000	-1.48996300	2.69806000
H	-4.22918100	-0.05704500	1.79284800
H	-5.40982600	-1.29872100	2.29028700
C	-1.76642800	0.26335000	3.24306400
C	-2.90207400	2.31802800	3.61772100
H	-3.06938200	3.56675000	1.93765900
C	-1.58806600	4.42256300	-2.22841100
H	0.11048500	3.02783600	-1.85127300
H	0.41354900	4.70097900	-1.34488100
H	-2.51718400	4.91259800	0.99453800
H	-1.41031400	5.80571600	-0.05650000
H	-0.22777700	3.55322700	2.08492100
H	0.78212600	2.67082000	0.91044000
H	0.84642600	4.45335000	0.97875200
H	-3.57045700	5.05710600	-1.43994300
H	-2.67655900	1.99484300	-2.76122400
H	-3.94919100	1.18411600	-1.83653300
H	-4.29427700	2.72509500	-2.66705200
H	-4.52637400	3.80799400	0.73409600
H	-5.32375900	3.21044300	-0.72018500
H	-4.69630300	2.05171800	0.47766400
C	0.85184700	-2.13778900	2.47819100

H	0.22145400	-4.15379100	2.89280500
H	0.97710100	0.00977800	2.26021700
H	-5.23073500	-2.47829000	-2.45919100
H	-6.33980700	-3.18260000	-1.27421400
C	-2.83432500	-3.08259300	-1.10269500
H	-4.36192300	-4.68724300	-1.17795700
C	-2.41660500	1.11543100	4.12061100
H	-1.39844700	-0.68796100	3.63226200
H	-3.41649900	3.03964200	4.25874400
H	-1.80934200	3.80090300	-3.10676700
H	-1.43024700	5.45110100	-2.59410600
H	1.81294800	-2.21512100	2.99429100
C	-1.80003200	-4.21550900	-0.96085700
C	-2.68897600	-2.59615500	-2.55376900
H	-2.53696200	0.83949500	5.17186800
H	-0.77471200	-3.82386400	-0.85734600
H	-1.99963900	-4.89591800	-0.12081500
H	-1.83618400	-4.83215500	-1.87572600
H	-1.63230500	-2.40398700	-2.80261100
H	-3.03900100	-3.39746400	-3.22844400
H	-3.25471400	-1.68577400	-2.78045800
F	-1.53195800	0.09788800	-2.89357000
C	2.89852500	0.27692900	-2.24511600
H	3.92551900	0.17735900	-2.64743200
H	2.24185000	0.52854200	-3.09524100
H	2.28368700	-1.87346200	-2.33415700
H	3.50183200	-0.53927100	1.57005800
C	2.85386600	1.38989100	-1.19335900
H	3.19968200	2.34552600	-1.62531600

H	1.79711700	1.53457500	-0.90615500
C	3.69383000	1.06668100	0.05763500
H	3.34625300	1.69419200	0.89738100
H	4.73720400	1.36216900	-0.13043000
C	5.47423300	-1.10212900	0.48950200
H	5.29782600	-2.12419100	0.83558000
C	5.91261600	-1.13086600	-0.93264500
C	6.12569400	-0.32101000	1.57897800
O	5.78317700	-2.10551100	-1.63930200
O	5.96938600	-0.58942300	2.75056400
O	6.83141300	0.74802400	1.16746200
O	6.39037300	0.04299700	-1.39415500
C	7.38971200	1.55775600	2.19724300
H	8.07439900	0.96967800	2.83112400
H	7.93599400	2.36285900	1.68439600
H	6.59578800	1.97836500	2.83771300
C	6.80283200	0.06424700	-2.75567700
H	7.30556000	1.03170500	-2.90316600
H	7.49250300	-0.76858800	-2.97001900
H	5.93371200	-0.01615100	-3.43330700

F: TS-**1c** (*exo-trans*), optimized transition structure of the active catalyst system (cyclohexenyl • Pd • BIFOP-F with dimethylmalonate, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -195.76 cm^{-1}

Energy: -2691.235584

Single point: -2692.620586

0 1

F	0.93858300	-0.22615200	-2.57366700
Pd	-1.22201100	-0.54133100	-0.20639600
C	-3.28310900	-1.18599800	-0.15752900
C	-4.24438000	-0.07609000	-0.40573600
C	-2.66843600	-1.84699000	-1.22851300
H	-3.36445900	-1.69068900	0.81133100
P	0.91055900	-0.19676600	-0.94237100
O	1.71862200	1.23652000	-0.80431600
O	2.07165500	-1.22849200	-0.50582300
C	1.39227700	2.25641800	0.18336500
C	3.47583300	-1.38013900	-0.21579400
C	0.81443500	1.39908700	1.34916100

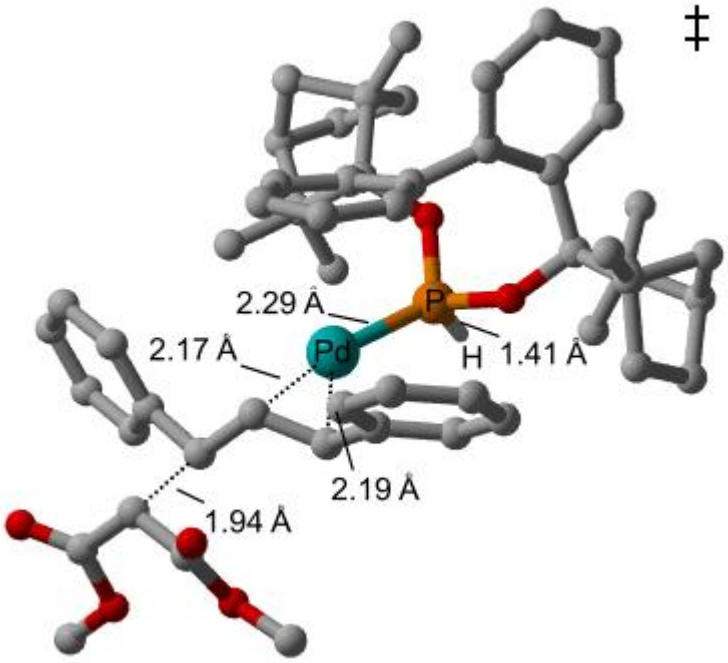
C	2.72607000	3.15481700	0.36853800
C	3.87356800	-0.55200300	1.03967500
C	4.41029700	-1.26325100	-1.54998000
C	3.61294800	-2.94092000	0.12723400
C	-0.58696800	1.41595800	1.55780900
C	1.51789600	0.30532400	1.93735200
C	3.50109000	3.05350800	-0.96855600
C	2.22316300	4.60923100	0.21681100
C	3.61714100	2.99757500	1.58888100
C	3.00253300	0.06571900	1.97980400
C	5.23100100	-0.61199400	1.42989900
C	4.87608800	-2.74448900	-1.74955800
C	5.65418900	-0.34805900	-1.45525100
C	3.65139600	-0.75571800	-2.77955100
C	5.05423700	-3.26333000	-0.31572200
C	3.20066600	-3.32560600	1.53963200
C	2.83101600	-3.74492900	-0.95211500
C	-1.27523900	0.46023900	2.31359300
H	-1.18606700	2.19153100	1.10651800
C	0.81051800	-0.63176800	2.72245600
C	2.54676300	3.74167200	-1.98207200
H	3.75555300	2.02357400	-1.23687800
H	4.44280600	3.61790500	-0.85725600
C	1.45188800	4.35491400	-1.07497300
H	1.62083600	4.97388900	1.06023000
H	3.07882100	5.29452000	0.09494600
H	3.03609800	2.91736200	2.52046900
H	4.28821900	2.13387100	1.51720300
H	4.25293200	3.89792600	1.67103300

C	3.50704500	0.43603200	3.24894000
C	5.72310800	-0.18301600	2.65746500
H	5.95542000	-1.05013600	0.76175300
H	5.76629500	-2.79607200	-2.39692000
C	3.71973100	-3.64743200	-2.22222500
H	5.99271800	-0.11536100	-2.47875000
H	5.43493700	0.60666300	-0.95312200
H	6.51370200	-0.81488600	-0.95176600
H	3.39897700	0.31170000	-2.68227600
H	4.30283500	-0.87037000	-3.66386800
H	2.72569200	-1.29808400	-2.97725100
H	5.24611100	-4.34987700	-0.28059300
H	5.84589800	-2.77681700	0.26550400
H	2.14075300	-3.07022200	1.71211300
H	3.31019200	-4.41584900	1.67855000
H	3.80728600	-2.82227900	2.30969500
H	2.74392900	-4.78880600	-0.60735400
H	1.81461300	-3.35929300	-1.09639400
C	-0.56315100	-0.58071100	2.91282700
H	-2.35691400	0.55146100	2.44038500
H	1.38317600	-1.43991100	3.18124200
H	2.13923900	3.03231400	-2.71704800
H	3.05766500	4.54089800	-2.54466400
C	0.41212500	3.32025100	-0.55621300
H	0.94805200	5.22105700	-1.53190700
C	4.84075800	0.32233900	3.60791000
H	2.79989400	0.86248500	3.96428600
H	6.79203600	-0.27690500	2.86962600
H	4.12052300	-4.63550800	-2.50462000

H	3.18429500	-3.25894700	-3.09915700
H	-1.07208900	-1.34556600	3.50502100
C	-0.55583900	4.12803400	0.36439400
C	-0.42618500	2.71401400	-1.68345300
H	5.18114600	0.63577500	4.59864400
H	-0.27380400	4.13183600	1.42748400
H	-0.58285700	5.17860700	0.02834900
H	-1.59244000	3.76066300	0.29393300
H	0.18173600	2.24661600	-2.46908600
H	-1.11977400	1.94484500	-1.30040400
H	-1.03496700	3.50927700	-2.15016100
C	-3.14219000	0.08311800	-2.76736000
H	-2.13202300	0.51290100	-2.66336900
H	-3.49921900	0.34883600	-3.77751500
H	-4.37114300	0.57076400	0.47146500
H	-2.28578200	-2.86300500	-1.07909000
C	-4.07940700	0.71414400	-1.71043700
H	-5.07502700	0.88754700	-2.14884100
H	-3.69446600	1.71751900	-1.45360600
C	-2.99244600	-1.43635300	-2.64440000
H	-3.93435400	-1.94047600	-2.94951600
H	-2.20994700	-1.79120500	-3.33661000
C	-5.96546100	-0.89447400	-0.41602000
H	-5.99090400	-1.48200600	-1.33855600
C	-6.02457500	-1.80788700	0.77005900
C	-6.94228700	0.22789700	-0.51016500
O	-6.29578800	-2.98319600	0.71154100
O	-7.29378700	0.72781200	-1.55653200
O	-7.35408600	0.68387700	0.68867200

O	-5.68394800	-1.19378900	1.92207400
C	-8.24551200	1.79397600	0.66161800
H	-9.16680400	1.54413200	0.10888500
H	-8.47765900	2.02060000	1.71255100
H	-7.77230000	2.66414500	0.17570400
C	-5.70579900	-2.00619500	3.08950700
H	-5.42402400	-1.34667600	3.92367900
H	-6.71164300	-2.42689400	3.25648400
H	-4.98896200	-2.84065700	2.99953800

H: TS-**2d** (*exo-trans*), optimized transition structure of the active catalyst system (diphenylallyl • Pd • BIFOP-H with dimethylmalonate, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -239.21 cm^{-1}

Energy: -2937.195812

Single point: -2938.681830

0 1

Pd	-0.87215200	-0.01116300	-0.32977200

C	-2.75582600	-0.73989700	0.46393900
C	-3.87984000	-0.08742700	-0.25013300
C	-2.06999300	-1.82706700	-0.09466100
H	-2.70067400	-0.58820600	1.54793000
H	-3.96170700	-0.42235000	-1.29053400
C	-1.33194700	-2.84964500	0.68044400
C	-1.68732900	-3.16703900	2.00380900
C	-0.27718900	-3.56362700	0.08307300
C	-0.98203100	-4.13800700	2.71863200
H	-2.54457700	-2.67163100	2.46332400
C	0.41211600	-4.54798100	0.78900500
H	0.01069900	-3.32230700	-0.94323300
C	0.07383700	-4.83003000	2.11800000
H	-1.27529000	-4.36988000	3.74727800
H	1.22397900	-5.09459400	0.30269700
H	0.61942000	-5.59786900	2.67469800
C	-4.06808200	1.38368200	-0.10662000
C	-4.42179500	2.15311600	-1.22453800
C	-3.93370700	2.02565900	1.13518700
C	-4.63034100	3.52999400	-1.10990400
H	-4.53029200	1.66213600	-2.19649200
C	-4.14436200	3.39850700	1.25343400
H	-3.65807200	1.44410200	2.01874100
C	-4.49334300	4.15739200	0.13051900
H	-4.90241300	4.11443400	-1.99398300
H	-4.03692400	3.88233300	2.22897600
H	-4.65898400	5.23465500	0.22452000
H	-2.33770100	-2.11926100	-1.11778600
P	1.22704900	0.24520700	-1.21690400

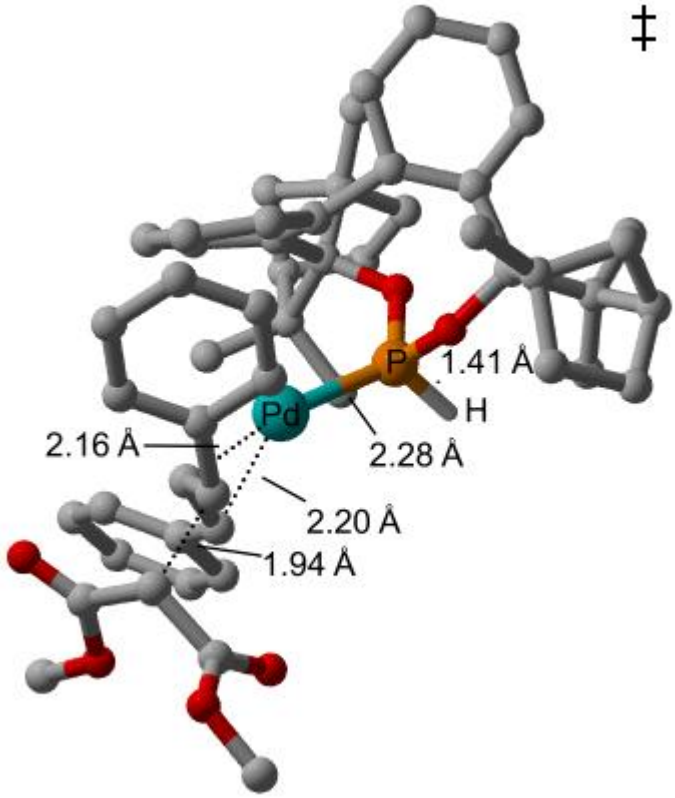
O	2.15085500	1.56070900	-0.75321400
O	2.23826900	-1.00936900	-0.92448700
C	1.59000100	2.44071500	0.24009900
C	3.66619400	-1.10260600	-0.86268000
C	1.17693500	1.49601100	1.40538700
C	2.63843400	3.54691600	0.66084900
C	4.18554700	-0.28199800	0.34523100
C	3.96734500	-2.64305400	-0.54938000
C	4.37877200	-0.94233300	-2.32388100
C	0.04129800	1.73706800	2.19531400
C	1.90365100	0.28384000	1.68317300
C	3.27680700	4.13810300	-0.62924600
C	1.67929000	4.67738800	1.09149900
C	3.68785200	3.20401100	1.70100900
C	3.39192100	0.07995900	1.47324300
C	5.58006400	-0.15550300	0.50786300
C	3.15731600	-3.50397600	-1.56336500
C	5.39026500	-2.81400300	-1.11400900
C	3.75034100	-3.07161400	0.89309700
C	5.03430700	-2.35268200	-2.53181700
C	3.39077500	-0.66744200	-3.47294900
C	5.43909200	0.17256700	-2.45910500
C	-0.48561400	0.80097800	3.09013900
H	-0.47283600	2.68531400	2.11103000
C	1.31858000	-0.66653800	2.53681600
C	2.21668300	5.13536600	-1.16222000
H	3.51887600	3.33873300	-1.34433600
H	4.22047800	4.64659000	-0.37200700
C	1.00318800	4.82451800	-0.27068700

H	1.00108800	4.37836400	1.90734400
H	2.22601900	5.58100600	1.41189600
H	3.24423000	2.76022700	2.60407300
H	4.44814200	2.51393600	1.30794600
H	4.20391500	4.13394600	2.00226200
C	4.04997500	0.31212200	2.70351200
C	6.20678000	0.16220700	1.71078600
H	6.23274400	-0.35278900	-0.32940100
C	3.97002400	-3.41030800	-2.88284900
H	2.12830700	-3.13774500	-1.66233900
H	3.10539400	-4.54129500	-1.19425100
H	6.15869300	-2.22393000	-0.60248700
H	5.70953300	-3.87027700	-1.08177000
H	4.40868900	-2.53494700	1.59387700
H	2.70547100	-2.90176000	1.19628300
H	3.95741200	-4.15230500	0.99294400
H	5.86463800	-2.30533200	-3.25499800
H	2.45985900	-1.24504200	-3.40813300
H	3.13825000	0.40227500	-3.53301000
H	3.88562900	-0.93476600	-4.42344000
H	6.43417100	-0.11286300	-2.08713600
H	5.57400700	0.40792600	-3.52900800
H	5.12329300	1.09688100	-1.94731800
C	0.12036300	-0.44347000	3.21324200
H	-1.38714700	1.04942000	3.65758000
H	1.85750200	-1.59989100	2.70930600
H	2.01599100	5.03315000	-2.23830300
H	2.53409500	6.17861400	-0.99319100
C	0.45912100	3.38415700	-0.52299100

H	0.20147900	5.57703400	-0.34057400
C	5.43121700	0.34089700	2.84989600
H	3.42766000	0.52823200	3.57439700
H	7.29789000	0.23063200	1.74866900
H	3.35600400	-3.16272500	-3.75961000
H	4.47340200	-4.36573700	-3.10778800
H	-0.30055000	-1.22325300	3.85172300
C	-1.00009500	3.32584900	-0.05172700
C	0.38942100	3.08115700	-2.03331200
H	5.88149900	0.53714500	3.82692000
H	-1.38559400	2.29110800	0.01741200
H	-1.18128000	3.82562000	0.91000300
H	-1.63127100	3.84673200	-0.79032900
H	-0.21201200	2.17429100	-2.22557200
H	-0.13322300	3.91448600	-2.53427600
H	1.36947400	2.95533700	-2.50954000
H	1.40336900	0.44765700	-2.60274100
C	-5.50975900	-0.86773000	0.45825700
H	-5.53970800	-0.54929700	1.50302700
C	-5.25891600	-2.33733200	0.39419200
C	-6.57276000	-0.16211900	-0.30916700
O	-7.17495100	0.79567900	0.11661700
O	-5.13945400	-3.02234600	1.38597600
O	-6.72182800	-0.62219700	-1.56802200
O	-5.07932200	-2.81404400	-0.84751700
C	-7.64916600	0.09090700	-2.37955600
H	-7.64593400	-0.41354000	-3.35705700
H	-8.65945700	0.06596700	-1.93756000
H	-7.34169500	1.14516600	-2.48638900

C	-4.73481800	-4.19545700	-0.93758900
H	-4.66665500	-4.41739500	-2.01255300
H	-3.76899500	-4.38698800	-0.44032000
H	-5.50718500	-4.82270100	-0.46268500

H: TS-**1d** (*endo-trans*), optimized transition structure of the active catalyst system (diphenylallyl • Pd • BIFOP-H with dimethylmalonate, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -235.93 cm^{-1}

Energy: -2937.195654

Single point: -2938.680788

0 1

Pd	-0.83117700	0.30846000	-0.19108200
C	-2.90244000	0.10691300	0.38479100
C	-2.87008200	0.85563300	-0.79782100
C	-3.19119300	-1.35036300	0.36183700

H	-3.02806100	0.60328900	1.35239200
H	-3.04217000	0.32213600	-1.73899000
C	-2.71843700	-2.11788300	1.55604500
C	-1.65917000	-3.02712000	1.41857300
C	-3.27533700	-1.91055000	2.82893400
C	-1.16328300	-3.71783400	2.52797300
H	-1.20608600	-3.17827200	0.43383400
C	-2.78538300	-2.60681800	3.93604800
H	-4.10674200	-1.20802800	2.93924500
C	-1.72586400	-3.51070800	3.79078200
H	-0.33217400	-4.41846900	2.40324600
H	-3.23285700	-2.44184300	4.92103100
H	-1.34144400	-4.05267600	4.66009100
C	-2.99030500	2.32232400	-0.87727700
C	-2.76626700	2.96405100	-2.11073300
C	-3.33650000	3.12115600	0.23014500
C	-2.86093100	4.35048000	-2.23085600
H	-2.49975700	2.35543600	-2.98016800
C	-3.43385100	4.50738500	0.11036400
H	-3.54548800	2.64909500	1.19287500
C	-3.19254300	5.13224500	-1.11838200
H	-2.67510300	4.82541800	-3.19915500
H	-3.70490300	5.10686600	0.98494900
H	-3.26836300	6.21978300	-1.20952200
H	-2.87394200	-1.80609600	-0.58095100
P	1.22016400	0.30107300	-1.18849900
O	2.51321800	1.23328900	-0.69594000
O	1.79677300	-1.22231500	-1.04227600
C	2.30123600	2.18458500	0.36714100

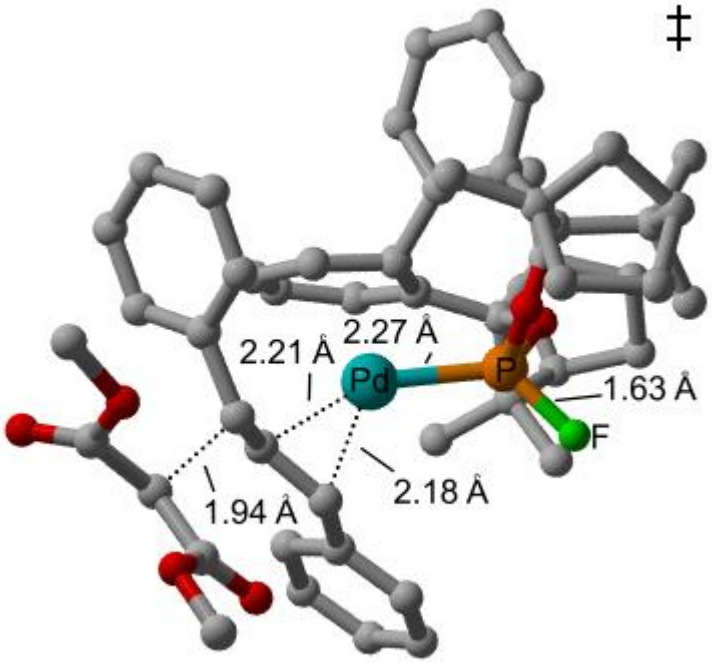
C	3.07853600	-1.84256700	-0.99199100
C	1.65892600	1.36149600	1.51639400
C	3.67246200	2.86964300	0.74593600
C	3.82510500	-1.37901600	0.28197100
C	2.75246700	-3.40334500	-0.84971400
C	3.85179400	-1.81261200	-2.42684900
C	0.75356100	1.92870400	2.42436200
C	1.88830400	-0.05358600	1.64481400
C	4.38521600	3.30915500	-0.56577800
C	3.16484900	4.21949000	1.29421000
C	4.60949200	2.12080800	1.67443600
C	3.21929700	-0.74638300	1.40343100
C	5.14723800	-1.83559400	0.46811100
C	1.68200400	-3.77087800	-1.91854800
C	3.99693800	-4.05859200	-1.47837200
C	2.34721300	-3.84968100	0.54615100
C	3.87144700	-3.32835500	-2.82306200
C	3.11245900	-0.99086600	-3.49467900
C	5.28715700	-1.24277200	-2.43487200
C	-0.06605200	1.16855400	3.26436700
H	0.64748900	3.00557500	2.46453900
C	0.99923500	-0.80379800	2.43269500
C	3.65752200	4.61343900	-0.98238200
H	4.32809800	2.51718000	-1.32600200
H	5.45260200	3.49008200	-0.35711300
C	2.47444800	4.65191800	-0.00104400
H	2.49042100	4.11147900	2.15868200
H	3.99707800	4.88215400	1.58911500
H	4.11327400	1.83356400	2.61334900

H	5.01386900	1.21217200	1.20391100
H	5.46227000	2.77595700	1.92992100
C	3.91872100	-0.75454000	2.63484900
C	5.84118000	-1.77354400	1.67246000
H	5.66888600	-2.29907500	-0.35577100
C	2.47294500	-3.81153800	-3.25494300
H	0.85232300	-3.05195000	-1.92207700
H	1.26274400	-4.76077800	-1.67241700
H	4.93387600	-3.88794400	-0.93586200
H	3.86892100	-5.15060200	-1.57871200
H	3.13735700	-3.67289500	1.29321300
H	1.44074100	-3.31125900	0.87031900
H	2.11564600	-4.93004300	0.54246800
H	4.65850500	-3.53798300	-3.56555900
H	2.03366100	-1.18326600	-3.53290000
H	3.27258200	0.08830500	-3.34023800
H	3.53136800	-1.24637700	-4.48436800
H	6.05139200	-1.95517600	-2.09134100
H	5.55867400	-0.98433200	-3.47303100
H	5.36488100	-0.32571400	-1.82790100
C	-0.00562700	-0.21907900	3.20546300
H	-0.77645500	1.67326500	3.92523100
H	1.15290400	-1.88221900	2.49463500
H	3.35682400	4.63155300	-2.03964000
H	4.29926100	5.49572100	-0.81640600
C	1.47858000	3.47771400	-0.25778500
H	1.95415200	5.62274000	0.02374200
C	5.20271600	-1.25695000	2.79424800
H	3.42102600	-0.30834500	3.49845800

H	6.86432400	-2.15691600	1.72619800
H	2.01703200	-3.20875000	-4.05248900
H	2.54902200	-4.84235500	-3.64028500
H	-0.68428700	-0.84784500	3.78475800
C	0.10982500	3.84685700	0.34108600
C	1.20257500	3.30245600	-1.76409000
H	5.69394300	-1.22355100	3.77075000
H	-0.54535700	2.96831600	0.44434400
H	0.17747600	4.36387600	1.31052600
H	-0.39492300	4.54546200	-0.34674200
H	0.33139900	2.64368600	-1.92510600
H	0.93171300	4.28448800	-2.18914100
H	2.05432200	2.90732000	-2.33192300
H	1.38468100	0.54866400	-2.57131400
C	-5.10750600	-1.61468100	0.20307300
H	-5.37038500	-2.36139400	0.95853000
C	-5.69552100	-0.28803700	0.55542700
C	-5.34144900	-2.09749700	-1.19905400
O	-5.76536700	0.13828000	1.68674900
O	-4.73816900	-1.74153800	-2.18353000
O	-6.31942700	-3.02371100	-1.23449200
O	-6.07839700	0.39777600	-0.53511700
C	-6.63198900	-3.55509800	-2.52020800
H	-5.74819000	-4.04160300	-2.96648400
H	-7.43453300	-4.28936800	-2.35836800
H	-6.97205800	-2.75541600	-3.19960700
C	-6.56630800	1.73082600	-0.37924700
H	-7.56433000	1.77971700	-0.84466800
H	-6.62456400	1.99312200	0.68728700

H	-5.87436400	2.41133700	-0.89987200

F: TS-**1d** (*endo-trans*), optimized transition structure of the active catalyst system (diphenylallyl • Pd • BIFOP-F with dimethylmalonate, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -235.93 cm^{-1}

Energy: -3036.404276

Single point: -3037.986316

0 1

Pd	-0.47934800	0.71220400	0.06334500
C	-2.60304900	1.30270500	0.22871900
C	-2.01399400	1.93313500	-0.87746000
C	-3.44661600	0.09087500	0.06989100
H	-2.71313800	1.84346900	1.17368200
H	-2.21218200	1.51288300	-1.86643300
C	-3.41707500	-0.88847700	1.19802000
C	-3.08052600	-2.22596400	0.94425600

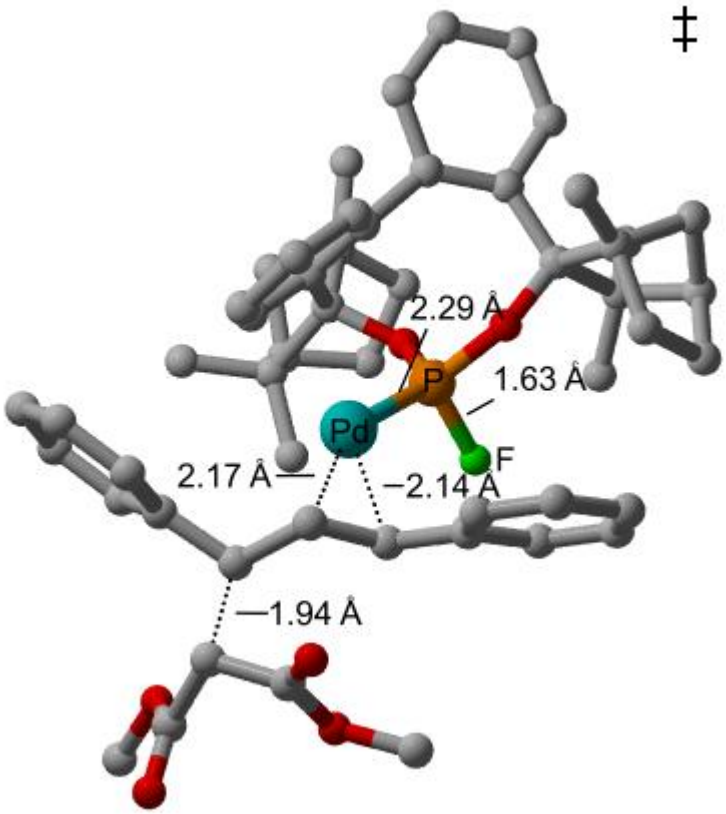
C	-3.68822100	-0.50394800	2.51946700
C	-2.97671800	-3.15088700	1.98495400
H	-2.88463700	-2.53863200	-0.08464400
C	-3.59813000	-1.42817700	3.56255300
H	-3.98398800	0.52595100	2.73470100
C	-3.23148100	-2.75280100	3.30138900
H	-2.69104000	-4.18413600	1.76649000
H	-3.81537300	-1.11156000	4.58700200
H	-3.15118600	-3.47332600	4.12063600
C	-1.47610600	3.30997700	-0.88517200
C	-0.86653100	3.79638000	-2.05764300
C	-1.52940600	4.16324500	0.23358600
C	-0.32651000	5.08091800	-2.11113700
H	-0.80544500	3.14087000	-2.93161200
C	-0.99411600	5.45045500	0.17930900
H	-1.99363400	3.81757500	1.16016000
C	-0.38772800	5.91743600	-0.99139600
H	0.14736700	5.43141100	-3.03307300
H	-1.04763300	6.09452900	1.06240800
H	0.03436100	6.92595900	-1.03047200
H	-3.26791200	-0.40631700	-0.88978000
P	1.35603300	0.27952100	-1.20163900
O	2.83534300	0.46399000	-0.50747800
O	1.30222700	-1.30734000	-1.44810400
C	3.05576700	1.33803900	0.63068300
C	2.00692100	-2.47820800	-1.04738600
C	1.94083000	1.02770100	1.65616400
C	4.51537800	1.06468600	1.17062500
C	2.25920600	-2.47129900	0.47815200

C	1.01928900	-3.67521600	-1.44633700
C	3.26641400	-2.73792600	-2.04491700
C	1.63126300	1.85589300	2.71642900
C	1.10679800	-0.17009300	1.47883700
C	5.49262100	1.05036400	-0.03877300
C	4.85519400	2.43177200	1.79991600
C	4.68955800	-0.14205400	2.07612100
C	1.79782400	-1.54640400	1.45809800
C	2.90843200	-3.62480000	0.97411200
C	0.40061000	-3.34065000	-2.83325700
C	1.98406900	-4.79869900	-1.88509600
C	-0.03617000	-3.98598200	-0.39607200
C	2.74484200	-3.93625500	-2.90265300
C	3.59706200	-1.52028200	-2.91911300
C	4.60419200	-3.11822700	-1.37583700
C	0.45740100	1.70925100	3.50221700
H	2.27407500	2.69828000	2.95005300
C	-0.15895200	-0.18769700	2.14762900
C	5.66200800	2.54642900	-0.41686400
H	5.10223800	0.43742500	-0.86159500
H	6.44904100	0.60373300	0.28014600
C	4.64880300	3.23816200	0.51308100
H	4.19718100	2.71635800	2.63338000
H	5.89584400	2.46054400	2.16725200
H	4.02517900	-0.09572900	2.95236900
H	4.48151800	-1.08373800	1.54355100
H	5.73208400	-0.18101600	2.44016000
C	2.01743800	-1.86509400	2.82532300
C	3.12694400	-3.90514300	2.31528900

H	3.24798100	-4.37054000	0.27117300
C	1.58324000	-3.51142900	-3.82711700
H	-0.05188800	-2.34242500	-2.85876500
H	-0.39590700	-4.07628100	-3.03619200
H	2.60395700	-5.23575400	-1.09302000
H	1.43521000	-5.63019300	-2.36069800
H	0.39742900	-4.39297200	0.53113300
H	-0.58927400	-3.06888500	-0.12902700
H	-0.76223200	-4.72155800	-0.78662500
H	3.57031900	-4.43519100	-3.43559200
H	2.72780600	-1.08922700	-3.42185800
H	4.06153300	-0.72333600	-2.31826500
H	4.32076000	-1.82889200	-3.69421400
H	4.64288100	-4.14894700	-0.99535100
H	5.40623300	-3.03593000	-2.12921900
H	4.85235000	-2.43559000	-0.54697400
C	-0.47199300	0.75380100	3.16590500
H	0.27862500	2.40406600	4.32729200
H	-0.73183000	-1.11815100	2.11981600
H	5.49116100	2.74889900	-1.48342900
H	6.67917700	2.90260300	-0.18066900
C	3.17981700	2.88906900	0.11632600
H	4.79539100	4.32721200	0.59277600
C	2.66468600	-3.00630000	3.27058700
H	1.67581900	-1.14667500	3.57280000
H	3.64307400	-4.82668800	2.59947500
H	1.79495400	-2.60119000	-4.40448800
H	1.37913100	-4.31402100	-4.55569800
H	-1.41637900	0.65357400	3.70490100

C	2.21846300	3.91080000	0.75021000
C	2.95566000	3.02893500	-1.39764400
H	2.80443100	-3.18014100	4.34116800
H	1.17646800	3.55675800	0.74357900
H	2.48835200	4.19604500	1.77742700
H	2.24803700	4.83545400	0.14982900
H	1.88132600	2.99826400	-1.64211700
H	3.32398200	4.02092500	-1.71397100
H	3.46360400	2.26683400	-1.99886700
F	1.68284100	0.73725000	-2.73565200
C	-5.45476300	0.86671200	-1.63683300
C	-6.14960500	-0.27183400	0.58212000
C	-6.71843600	0.28831100	-3.53306400
H	-5.83883000	-0.06588100	-4.09671400
H	-7.59362100	-0.34038800	-3.75202500
H	-6.91556500	1.33667900	-3.81361000
C	-6.74984800	-2.52959500	0.81415300
H	-6.28687500	-2.62683100	1.81083300
H	-7.82162500	-2.30131500	0.93698500
H	-6.61701100	-3.45877100	0.24116000
O	-6.09685400	-1.51110000	0.06457200
O	-6.49643000	0.17427900	-2.13011200
O	-6.75918100	0.00267400	1.59023000
O	-4.74918200	1.56794200	-2.32469900
C	-5.27910700	0.68823300	-0.15916400
H	-5.27902800	1.66187300	0.34187300

F: TS-**1d** (*endo-trans*), optimized transition structure of the active catalyst system (diphenylallyl • Pd • BIFOP-F with dimethylmalonate, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -235.93 cm^{-1}

Energy: -3036.403945

Single point: -3037.985167

0 1

F	-0.73803600	0.76322000	-2.21138000
Pd	0.97754800	0.13043800	0.40886600
C	3.03014400	0.78325500	0.67673500
C	3.94565100	-0.29713600	0.22826400
C	2.38164000	1.60104200	-0.27106900
H	3.15315900	1.13839100	1.70518600
H	3.80741900	-0.52712400	-0.83150300
C	1.83449900	2.95392500	-0.03072700
C	2.10400100	3.68940600	1.13773700
C	1.01673000	3.54387900	-1.01531900
C	1.54930400	4.95743300	1.32534300

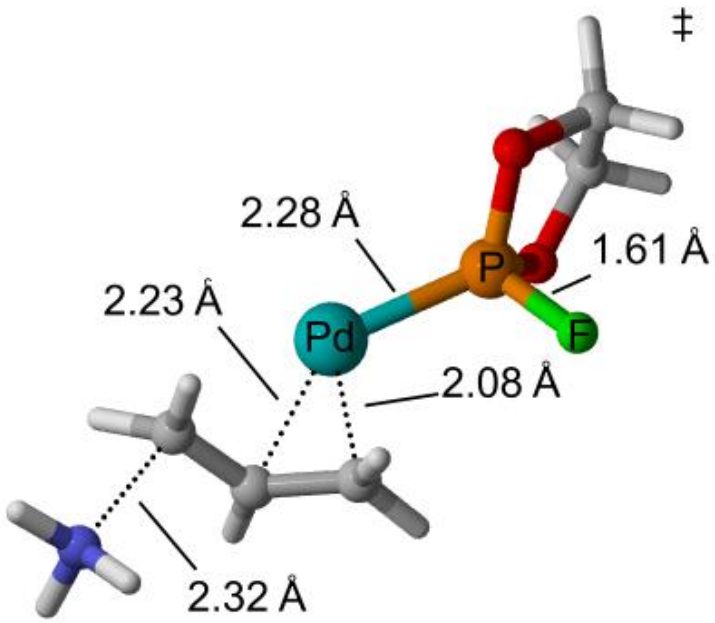
H	2.77926500	3.27760500	1.89073100
C	0.46636400	4.81075100	-0.82848700
H	0.79085500	2.97803500	-1.92383600
C	0.72434400	5.52377100	0.34806400
H	1.77409800	5.51343100	2.24083800
H	-0.17742200	5.24175600	-1.60147200
H	0.29112000	6.51706800	0.49841300
C	3.96468100	-1.53826400	1.06144300
C	3.65766700	-2.77727400	0.48001800
C	4.22653800	-1.49266600	2.44087100
C	3.59271900	-3.93803300	1.25640800
H	3.45566800	-2.82310500	-0.59382000
C	4.17109300	-2.65116500	3.21827300
H	4.47023700	-0.53532100	2.91139900
C	3.84688600	-3.87928200	2.62979100
H	3.34204100	-4.89362900	0.78565400
H	4.37684800	-2.59553000	4.29150300
H	3.79716700	-4.78630700	3.23928900
H	2.54892700	1.36736600	-1.32985700
P	-1.02139500	0.17950200	-0.71116200
O	-1.88327600	-1.13318400	-1.21428400
O	-2.19795200	1.12257400	-0.14652800
C	-1.75579800	-2.44867600	-0.59564900
C	-3.62372900	1.30390100	-0.03925400
C	-1.36967700	-2.07472600	0.86719700
C	-3.11938900	-3.24522700	-0.94195900
C	-4.26661500	0.14463300	0.77396000
C	-3.76243200	2.66760900	0.79431200
C	-4.30185500	1.72674100	-1.46223700

C	-0.02354400	-2.26241600	1.26641000
C	-2.13293800	-1.16933800	1.66435500
C	-3.64572700	-2.64470200	-2.26914700
C	-2.62863700	-4.60194900	-1.49828400
C	-4.20713800	-3.42644400	0.10262900
C	-3.59609900	-0.83589100	1.55679600
C	-5.66751300	0.20164800	0.95376700
C	-2.75668800	3.69730200	0.20666300
C	-5.07839400	3.26462400	0.25552400
C	-3.61142600	2.52292900	2.30050100
C	-4.64944500	3.23274300	-1.21813200
C	-3.35815500	1.56661000	-2.65758800
C	-5.58467400	0.96794200	-1.87573600
C	0.55988200	-1.63537900	2.37310400
H	0.62803500	-2.90179300	0.69238100
C	-1.53957200	-0.56995300	2.79684900
C	-2.54280600	-3.03056900	-3.29205200
H	-3.82946300	-1.56731500	-2.20714300
H	-4.60333600	-3.13872300	-2.50722600
C	-1.63688900	-3.99479400	-2.48700100
H	-2.19112000	-5.27193700	-0.74549200
H	-3.46343000	-5.13830200	-1.98011900
H	-3.79728300	-3.70766000	1.08492700
H	-4.83096200	-2.53325400	0.22493300
H	-4.87152900	-4.24583200	-0.22732500
C	-4.32632300	-1.56781100	2.52204400
C	-6.38097500	-0.57201300	1.86244000
H	-6.24606400	0.91380300	0.38625800
C	-3.38165700	4.10912600	-1.15337900

H	-1.74411500	3.28956300	0.11764000
H	-2.69957600	4.55708400	0.89453100
H	-5.98669400	2.69741300	0.49102800
H	-5.22922800	4.29190800	0.63032700
H	-4.35843500	1.84278600	2.74068500
H	-2.60537800	2.14291000	2.54824500
H	-3.72281900	3.51019600	2.78288500
H	-5.39476400	3.59034700	-1.94686000
H	-2.38963700	2.04817800	-2.51651300
H	-3.17408600	0.50474700	-2.88454300
H	-3.83474300	2.02427000	-3.54242800
H	-6.49573900	1.32285400	-1.37199200
H	-5.75162200	1.13021400	-2.95378600
H	-5.49847800	-0.11759500	-1.71253800
C	-0.21276600	-0.76961800	3.15208500
H	1.59931000	-1.85175900	2.62331800
H	-2.15951000	0.09727800	3.39799100
H	-1.99813100	-2.15199500	-3.66750800
H	-2.96364800	-3.55475600	-4.16640800
C	-0.68213500	-3.27670100	-1.48940300
H	-1.07949000	-4.69762500	-3.12603400
C	-5.69732600	-1.45631100	2.69223500
H	-3.76964400	-2.27562800	3.14086900
H	-7.46585800	-0.45205000	1.93398600
H	-2.70011700	3.96546300	-2.00325100
H	-3.67246000	5.17323900	-1.15395200
H	0.21496500	-0.25853900	4.01842600
C	0.09192400	-4.41789400	-0.75805200
C	0.35354200	-2.39914000	-2.19949700

H	-6.21702600	-2.05484400	3.44547900
H	1.12842000	-4.12881300	-0.52511700
H	-0.37599500	-4.75426400	0.17871500
H	0.15911400	-5.29438900	-1.42509500
H	0.98710300	-1.84633700	-1.48151900
H	1.01719300	-3.04571600	-2.80198400
H	-0.10086000	-1.66040500	-2.87277100
C	5.76919400	0.36740400	0.20815300
H	6.17025400	0.11691600	1.19655600
C	5.61700300	1.84629900	0.09378900
C	6.59549400	-0.28094400	-0.87425200
O	7.74406400	0.01092900	-1.09844600
O	5.55320100	2.60411200	1.03298900
O	5.44785600	2.22909300	-1.18546700
O	5.93870500	-1.24140800	-1.55048000
C	5.20286500	3.61938900	-1.40058600
H	5.11300000	3.74340600	-2.48940400
H	4.27158400	3.92921400	-0.89943800
H	6.03994400	4.22275800	-1.01211800
C	6.68321700	-1.91104800	-2.56491000
H	6.00480700	-2.66549200	-2.98928700
H	7.00524200	-1.19953500	-3.34358100
H	7.57781900	-2.39319200	-2.13680800

F: 20-**F** (*endo-trans*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -103.32 cm^{-1}

Optimization: -971.4810828

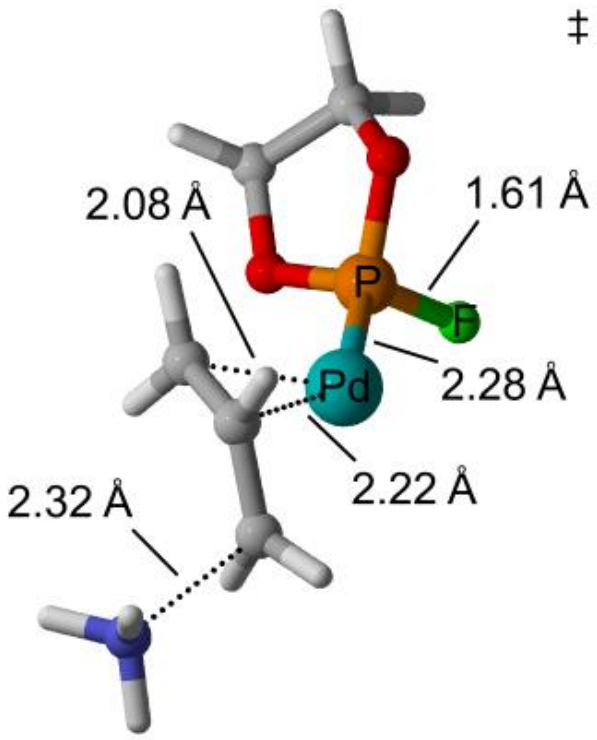
Single point: -971.804468

1 1

O	-2.61621500	-0.02158400	-1.11614700
O	-2.46823700	-0.32488600	1.27521400
P	-1.54046700	0.22253300	0.06768700
C	2.64596600	0.26937900	-0.73336700
C	1.72854800	1.29813300	-0.36012200
C	3.23491500	-0.56061700	0.22347300
H	2.84324900	0.08152100	-1.79348100
H	1.76388700	1.72646000	0.64883300
H	3.05917100	-0.40185300	1.28883800
N	5.41314600	0.13638700	0.59841300
H	5.94963000	0.08342400	-0.26993300
H	5.41802400	1.11174600	0.90349200
H	5.90969500	-0.41307600	1.30345400

H	3.67778700	-1.51291800	-0.06728800
H	1.31966000	1.96138000	-1.12782900
C	-3.90785500	-0.44762800	-0.61208500
H	-4.68629800	0.15158200	-1.10212600
H	-4.03694400	-1.50674700	-0.87896500
C	-3.86898500	-0.22728100	0.90897000
H	-4.41419800	-0.99780900	1.46751500
H	-4.23869700	0.76916200	1.19514100
Pd	0.62385400	-0.45509600	-0.14949700
F	-1.59635400	1.81874300	0.25236100

F: 20-**F** (*exo-trans*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -103.32 cm^{-1}

Optimization: -971.4803746

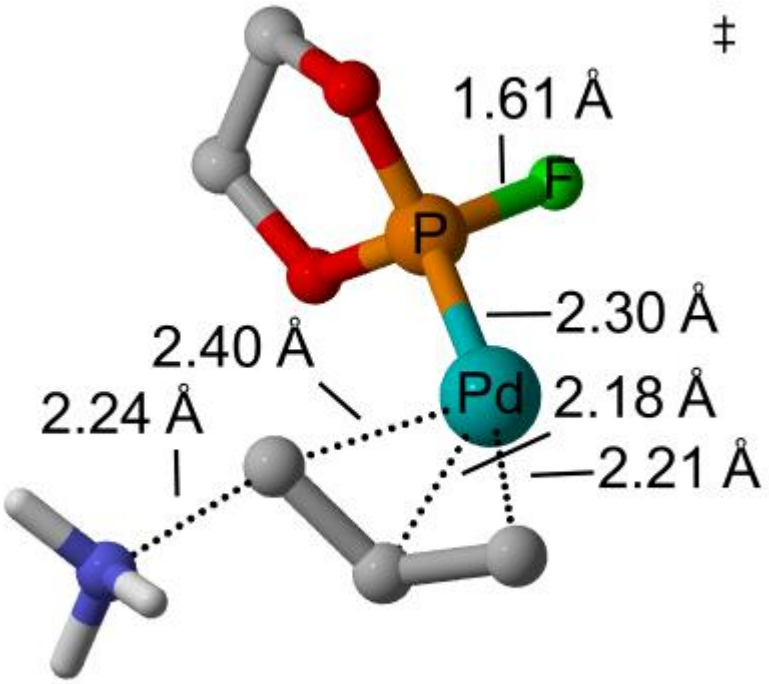
Single point: -971.803311

1 1

O	2.11245000	0.87668000	-1.10478800
O	2.54925000	-0.00831800	1.09737000
P	1.59029200	-0.33416300	-0.16419500
C	-2.52077700	0.47961000	0.75594800
C	-1.46081500	1.34583300	0.34995000
C	-3.24044600	-0.27344400	-0.17592100
H	-2.73139400	0.34758200	1.82191100
H	-1.44171900	1.75267900	-0.66818600
H	-3.05731500	-0.16605900	-1.24641700
N	-5.29861600	0.72634000	-0.54396200
H	-5.82634900	0.77280800	0.33009500
H	-5.17034400	1.68371700	-0.87762800

H	-5.87517100	0.23194100	-1.22858800
H	-3.81472000	-1.14342000	0.14199400
H	-0.94924700	1.95332100	1.10226400
C	3.26731600	1.55226100	-0.54460600
H	4.03467700	1.63697400	-1.32515900
H	2.94616200	2.55775900	-0.23530800
C	3.73370800	0.69550800	0.64486400
H	4.10682200	1.29465300	1.48433300
H	4.49400600	-0.04423000	0.35162700
Pd	-0.65309000	-0.56823500	0.17349700
F	2.28835100	-1.61736900	-0.83146600

F: 20-**F** (*endo-cis*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



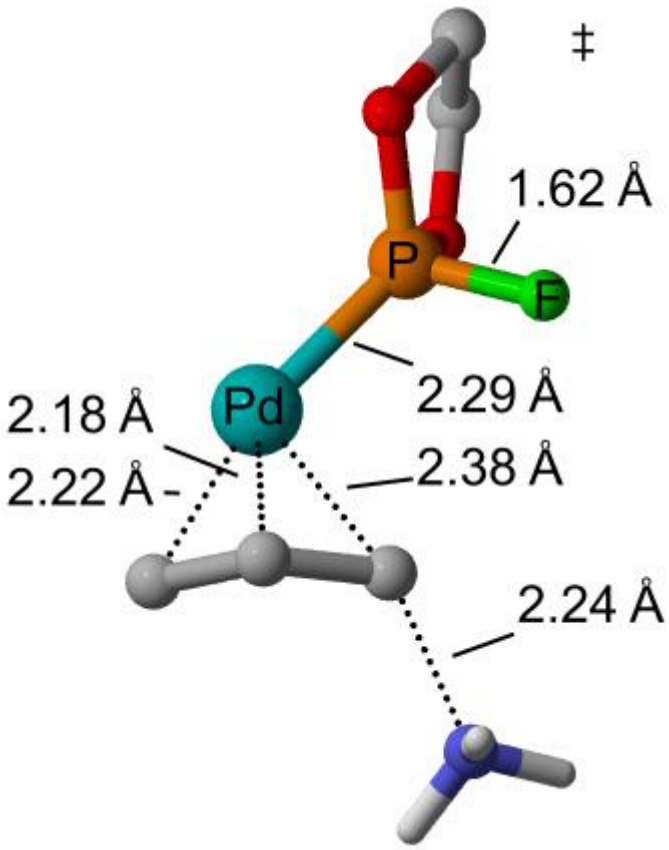
Imaginary frequency: -196.66 cm^{-1}

Single point: -971.800922

1 1

O	-2.02278900	0.65692400	1.20516000
O	-2.09962800	0.57749900	-1.20292100
P	-1.47741000	-0.29641200	0.01274100
F	-2.47958700	-1.55013600	0.09237200
Pd	0.73239100	-0.92531500	-0.04122900
C	2.60835400	-0.00744300	0.57582600
C	2.92450200	-1.17164600	-0.12115700
C	2.01287700	1.10558600	-0.09335100
H	2.71228200	0.03083200	1.66499600
H	3.04810300	-1.16240000	-1.21038900
H	1.98042100	1.15959300	-1.18141300
N	3.65566600	2.63043800	-0.14104900
H	3.94390200	2.89597400	0.80344700
H	4.47264200	2.23923800	-0.61526500
H	3.38543000	3.48383700	-0.63567900
H	1.42957800	1.83541800	0.46504700
H	3.32347800	-2.03991700	0.40972100
C	-2.97532700	1.64245600	0.73381500
H	-3.87430100	1.59079500	1.36208900
H	-2.50941500	2.63270800	0.84464200
C	-3.26917600	1.29481100	-0.73718300
H	-3.39262400	2.18187800	-1.37040800
H	-4.14976200	0.64291200	-0.84099600

F: 20-**F** (*exo-cis*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -196.66 cm^{-1}

Optimization: -971.480950

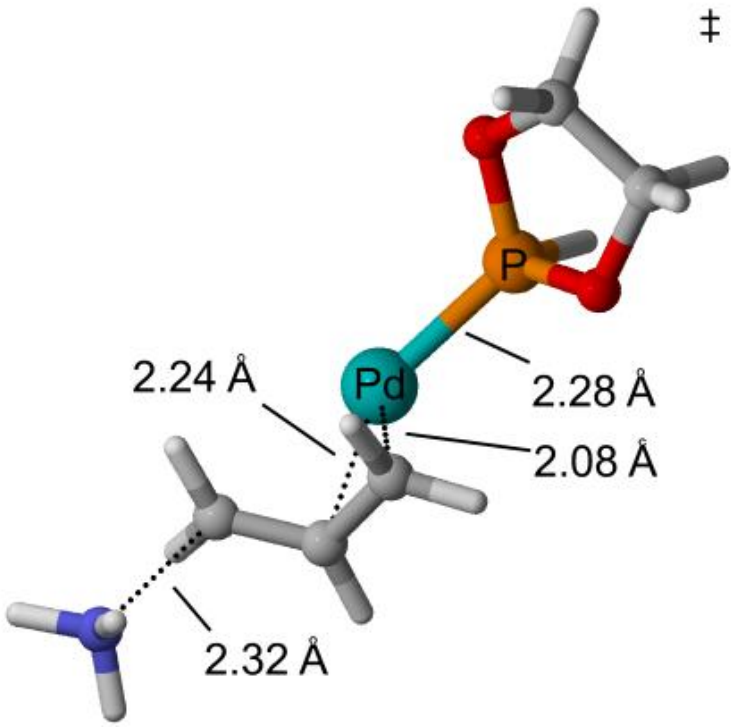
Single point: -971.803311

1 1

O	2.34692600	0.30122400	1.23073000
O	2.45681500	-0.11363200	-1.14484200
P	1.33717000	0.25117200	-0.03489300
F	1.06411100	1.82089000	-0.30143100
Pd	-0.64849000	-0.89290600	0.04094900
C	-2.64870900	-0.29174400	-0.56657800
C	-2.78231500	-1.49689700	0.11967200
C	-2.22395400	0.89261200	0.11430300
H	-2.76042600	-0.25905200	-1.65518300
H	-2.90301100	-1.51633900	1.20895000

H	-2.21286600	0.94017100	1.20327400
N	-4.05855200	2.18071300	0.14969100
H	-4.36799400	2.40951400	-0.79756800
H	-4.82651200	1.69637100	0.61959100
H	-3.89154400	3.06028900	0.64395700
H	-1.73915800	1.70335200	-0.42633600
H	-3.04644800	-2.41050500	-0.41898800
C	3.73565800	0.15638900	0.83879100
H	4.32384300	0.92998600	1.34952100
H	4.07309600	-0.83770500	1.16687300
C	3.76715400	0.30959800	-0.69040100
H	4.51197400	-0.33684700	-1.17035400
H	3.92797700	1.35335400	-1.00081000

H: 20-**H** (*endo-trans*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -87.61 cm^{-1}

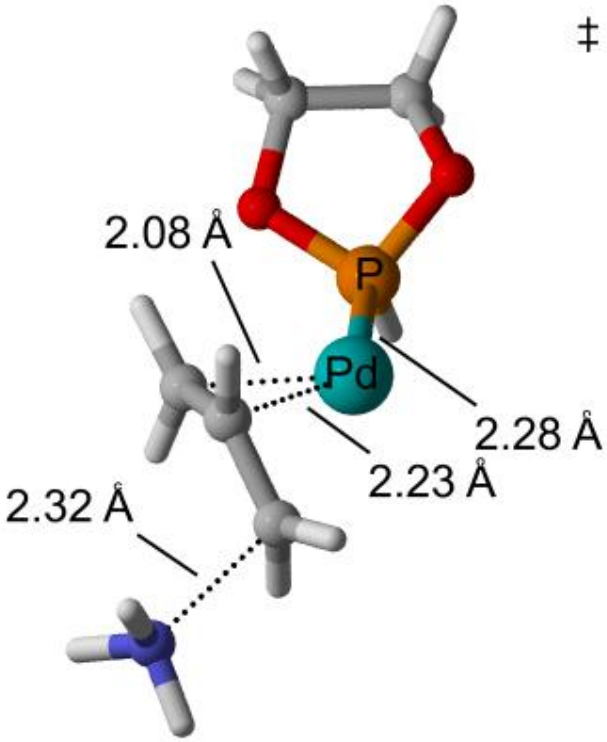
Optimization: -872.2714028

Single point: -872.489573

1 1

O	-2.59578600	-0.25848200	1.21807800
O	-2.21297500	0.81890900	-0.93981300
P	-1.75471600	-0.54983600	-0.15955400
C	2.35211100	0.30532100	-0.76596400
C	1.17926500	1.11592200	-0.65188800
C	3.05450200	-0.12165300	0.36059200
H	2.66592800	-0.04943500	-1.75269900
H	1.04081400	1.75123000	0.23167500
H	2.76713300	0.20811600	1.36043300
N	4.96141500	1.16984100	0.61907700
H	5.55632100	1.07666900	-0.20683500
H	4.70971800	2.15674600	0.70329800
H	5.52728300	0.92433900	1.43469000
H	3.74275100	-0.96395100	0.29776400
H	0.67604300	1.47190700	-1.55525700
C	-3.47858100	0.87652600	1.06630900
H	-4.47157900	0.60453400	1.45025900
H	-3.07190400	1.70735000	1.66277200
C	-3.50724700	1.20871700	-0.43494500
H	-3.63899600	2.28007800	-0.63346000
H	-4.29145400	0.64118400	-0.96471100
Pd	0.51740100	-0.76051000	-0.06200600
H	-2.55189100	-1.55908100	-0.78661100

H: 20-**H** (*exo-trans*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -87.61 cm^{-1}

Optimization: -872.2713683

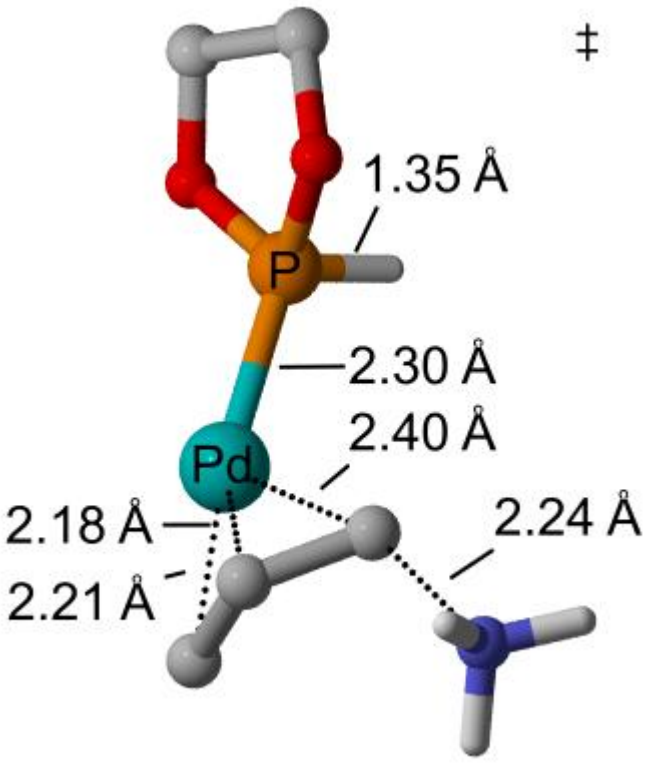
Single point: -872.489779

1 1

O	2.18146700	1.29268300	-0.39619400
O	2.82981700	-0.93174400	0.38217500
P	1.67510600	-0.26143800	-0.56362500
C	-2.29668700	0.55881100	0.69616800
C	-1.33141100	1.31112900	-0.04398900
C	-3.14484400	-0.35318100	0.06825000
H	-2.32709100	0.64755600	1.78669800
H	-1.49869000	1.51095800	-1.10943500
H	-3.13937700	-0.47073200	-1.01655300
N	-5.24921900	0.58790100	-0.17061800

H	-5.62828300	0.82625300	0.74817500
H	-5.18618200	1.45452300	-0.70861300
H	-5.92946200	-0.01689600	-0.63663000
H	-3.65208200	-1.12565500	0.64550900
H	-0.71104700	2.05160100	0.46897200
C	3.45580000	1.35512300	0.28644800
H	4.12170800	2.02836600	-0.27099000
H	3.28265900	1.76298500	1.29389800
C	3.99629400	-0.08392500	0.33807700
H	4.59321300	-0.28389200	1.23703500
H	4.59201000	-0.32964800	-0.55781200
Pd	-0.50402000	-0.59324100	0.03690600
H	2.12029500	-0.57533000	-1.88677900

H: 20-**H** (*exo*-*cis*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



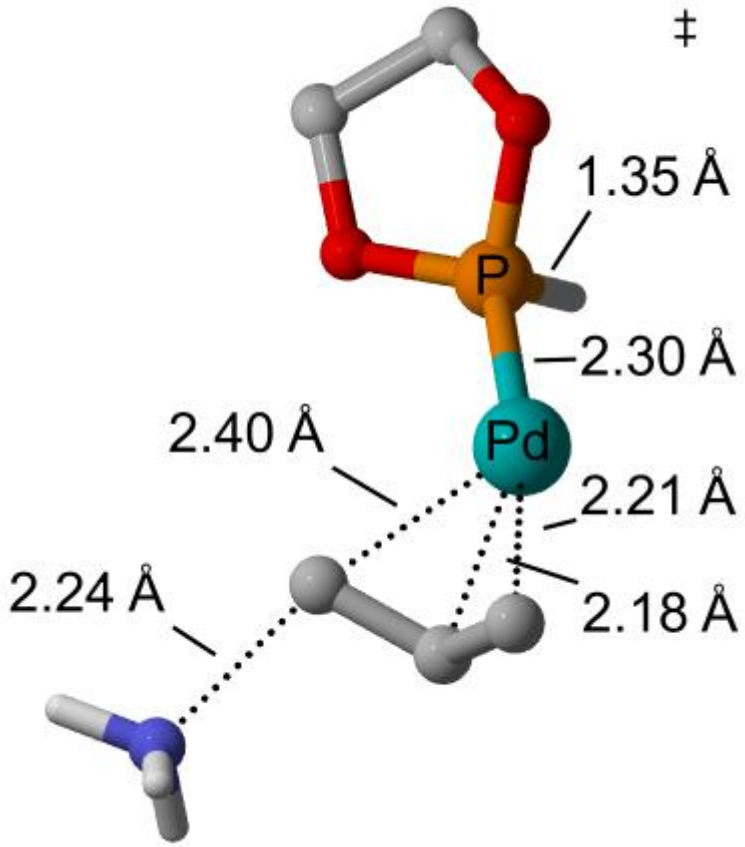
Imaginary frequency: -185.37 cm^{-1}

Single point: -872.484730

1 1

O	-2.84550500	-0.76630400	-0.14748500
O	-1.95087400	1.43335700	0.26747600
P	-1.49849600	0.07027600	-0.48490300
Pd	0.56526200	-0.84541700	-0.05587900
C	2.44468700	-0.09370900	0.74735100
C	2.67636600	-1.38929700	0.29031600
C	2.14367800	0.96093000	-0.16826600
H	2.38373900	0.11162600	1.82098000
H	2.96673800	-1.57829600	-0.74975800
H	2.28877000	0.83649600	-1.24125900
N	3.99459100	2.22565600	-0.14008000
H	4.17173400	2.60454100	0.79304900
H	4.80266200	1.65629100	-0.40125700
H	3.94266100	3.01272400	-0.79108200
H	1.60410500	1.84430900	0.16818900
H	2.84588500	-2.20187200	1.00157600
C	-3.89511000	0.07141300	0.39779200
H	-4.81550400	-0.10060800	-0.17565000
H	-4.05377600	-0.23447800	1.44240300
C	-3.39686800	1.52379200	0.28208800
H	-3.68529900	2.14498200	1.13884500
H	-3.73168100	2.00374400	-0.64996800
H	-1.67225500	0.38081800	-1.78715900

H: 20-**H** (*endo-cis*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -185.37 cm^{-1}

Optimization: -872.268568

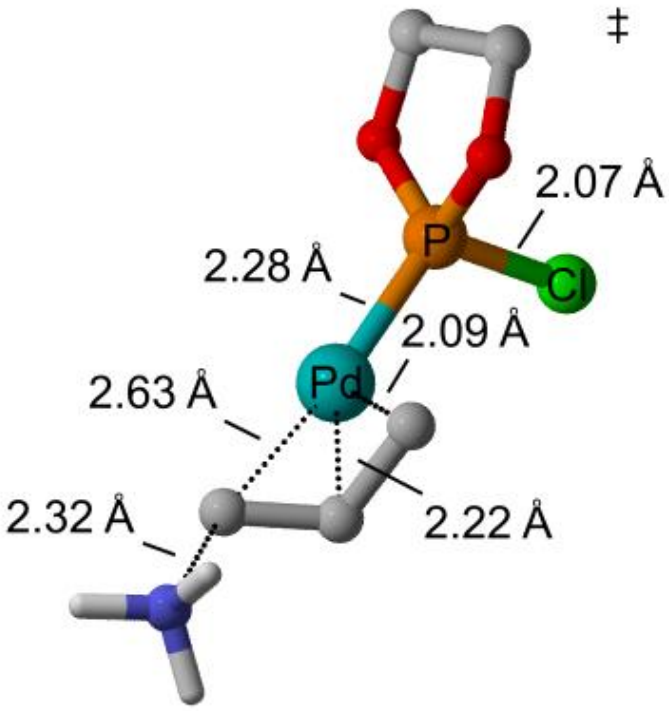
Single point: -872.485357

1 1

O	-1.89605300	1.40609100	0.36445200
O	-2.78346500	-0.67835300	-0.45935400
P	-1.54199100	-0.17344600	0.45307100
Pd	0.58834700	-0.90484400	-0.00340300
C	2.59231800	-0.16251600	0.41556500
C	2.72355800	-1.25283900	-0.44180000
C	1.98322000	1.04974400	-0.03237300
H	2.85589300	-0.25611600	1.47401900

H	2.68779100	-1.12381500	-1.52985500
H	1.79664700	1.23107100	-1.09074900
N	3.70179900	2.48319300	-0.16621000
H	4.14176000	2.62229000	0.74634100
H	4.41251000	2.10802100	-0.79827400
H	3.42138300	3.40093900	-0.51988200
H	1.53850200	1.73902200	0.68304400
H	3.13529900	-2.19616900	-0.07369000
C	-3.20346300	1.64855500	-0.21231300
H	-3.76484900	2.31377400	0.45692600
H	-3.05085300	2.14894300	-1.17992700
C	-3.87405300	0.27084000	-0.36479100
H	-4.47333700	0.18517500	-1.27946100
H	-4.49410600	0.01299000	0.50712000
H	-1.94667500	-0.48857800	1.70183900

CI: 20-**CI** (*endo-trans*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -102.74 cm^{-1}

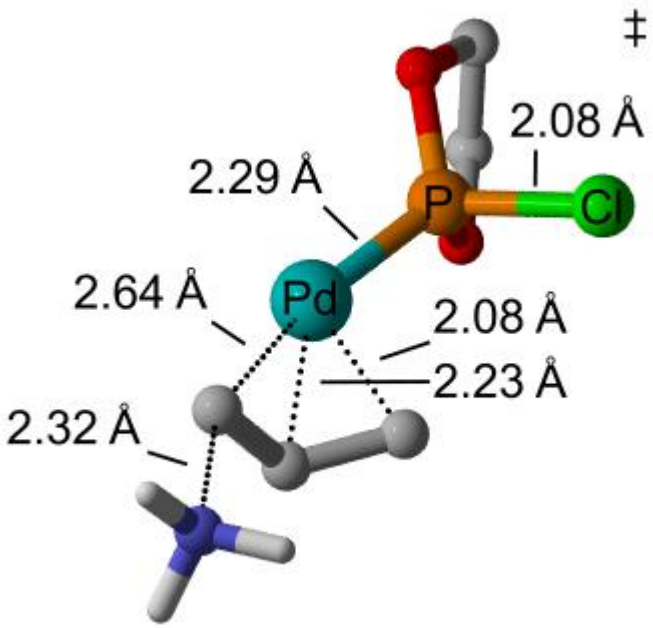
Single point: -1332.134256

1 1

O	-2.47131400	-0.60924200	-1.17937900
O	-1.83528200	-0.95445800	1.12748900
P	-1.45766800	0.05166100	-0.09524800
C	2.72209300	0.55047100	0.52354500
C	1.68443000	0.02307700	1.35043500
C	3.35804000	-0.23862500	-0.43822900
H	2.98023100	1.61181700	0.59467500
H	1.62983400	-1.05457500	1.54514300
H	3.12732400	-1.30081300	-0.53466300
N	5.43690300	-0.87760200	0.36247300
H	6.00544100	-0.04897200	0.54911100

H	5.33073000	-1.38182100	1.24502100
H	5.96394300	-1.47665800	-0.27700900
H	3.91001900	0.22356500	-1.25629100
H	1.24173700	0.65560100	2.12530600
C	-3.36820300	-1.57698300	-0.57816800
H	-4.39416800	-1.34507400	-0.89330900
H	-3.08236900	-2.56962100	-0.95548000
C	-3.18209900	-1.45333000	0.94416100
H	-3.25425800	-2.41650400	1.46399900
H	-3.88768800	-0.73634900	1.39142500
Pd	0.77678900	0.27448500	-0.51181200
Cl	-2.37230400	1.83901800	0.41420500

Cl: 20-**Cl** (*exo-trans*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -102.74 cm^{-1}

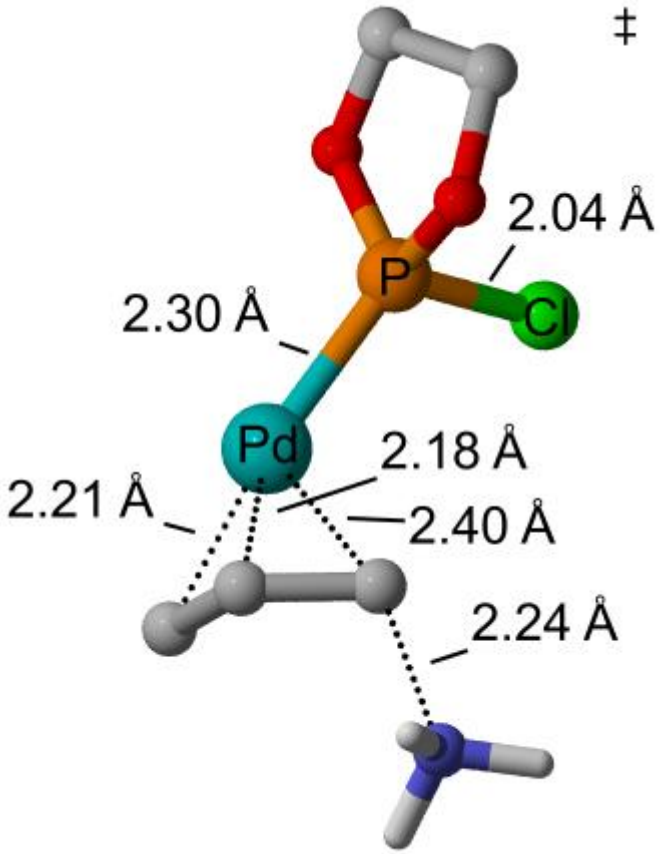
Optimization: -1331.781436

Single point: -1331.134742

1 1

O	2.38188900	-0.35087800	1.20076500
O	2.46292200	-0.51354500	-1.20922400
P	1.45215200	0.05103700	-0.06927100
C	-2.72401300	-0.10598900	0.82598900
C	-1.76986400	0.95472700	0.88140100
C	-3.36053300	-0.44728600	-0.36992300
H	-2.91444700	-0.70765100	1.72025600
H	-1.79794700	1.76114500	0.13881300
H	-3.19353000	0.13251600	-1.27930200
N	-5.51277600	0.41224700	-0.35814900
H	-6.03932800	0.02471600	0.42746300
H	-5.48156400	1.42649100	-0.23674100
H	-6.04069900	0.21669600	-1.21172800
H	-3.83803600	-1.42007500	-0.48491000
H	-1.32356800	1.22793800	1.84208500
C	3.70035300	-0.80193700	0.79981700
H	4.44980800	-0.25977800	1.39143700
H	3.76203700	-1.87693400	1.02319200
C	3.82106200	-0.50898600	-0.70585300
H	4.37977000	-1.28063500	-1.24942100
H	4.26448100	0.47914100	-0.90292800
Pd	-0.74231400	-0.58663400	-0.06904100
Cl	1.64506500	2.11661900	-0.17512700

Cl: 20-**Cl** (*exo-cis*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -196.63 cm^{-1}

Optimization: -1332.780559

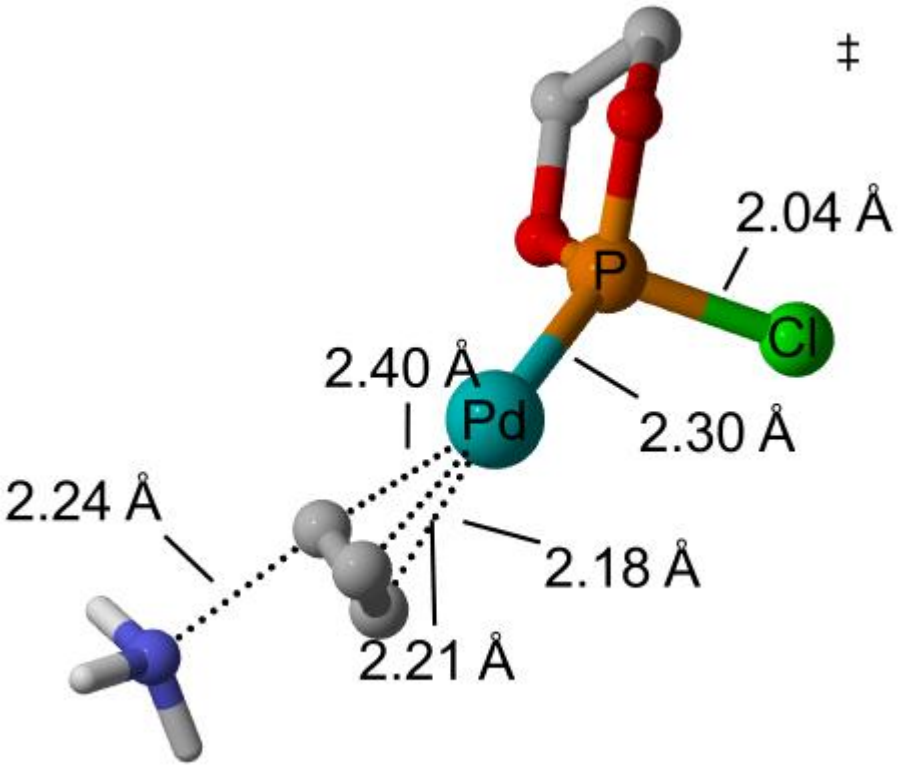
Single point: -1332.133470

1 1

O	2.59678400	-0.97606700	-0.13273100
O	1.72578000	1.06975200	-1.06388200
P	1.31476600	-0.00625900	0.07716000
Pd	-0.80647800	-0.88998400	0.10889800
C	-2.73635700	-0.28671300	-0.69987400
C	-2.95608800	-1.39145000	0.12011300
C	-2.31467700	0.96122000	-0.14663500

H	-2.77931300	-0.38884200	-1.78903900
H	-3.14423800	-1.27029500	1.19329000
H	-2.35322100	1.14543600	0.92687700
N	-4.12314400	2.26884600	-0.36056600
H	-4.38376600	2.38506200	-1.34251900
H	-4.91588800	1.83875000	0.12103800
H	-3.98348400	3.20074500	0.03697100
H	-1.78790500	1.68667800	-0.76382500
H	-3.21951900	-2.35797800	-0.31730600
C	3.60823200	-0.37997500	-0.98268100
H	4.57708400	-0.43757900	-0.46930100
H	3.65125500	-0.97010400	-1.90996300
C	3.16472800	1.07313300	-1.23331900
H	3.38156000	1.41737800	-2.25193600
H	3.60579500	1.77220400	-0.50672300
Cl	1.78909300	0.97194200	1.80335100

Cl: 20-**Cl** (*endo-cis*), optimized transition structure of the active catalyst system (allyl • Pd • BIFOP-F, M06-2X-D3/def2-TZVP//B3LYP-D3(BJ)/def2-SVP



Imaginary frequency: -196.63 cm^{-1}

Single point: --1332.133230

1 1

O	-1.58945500	1.53527500	0.22558400
O	-2.46001600	-0.27661400	-1.10492400
P	-1.31562600	-0.04942400	0.02089500
Pd	0.82100000	-0.81232000	-0.34580500
C	2.79052700	-0.30369900	0.43185500
C	2.97654000	-1.20454500	-0.61455800
C	2.29089300	1.01152200	0.18328800
H	2.92213900	-0.62638500	1.46969400
H	3.07593300	-0.85628000	-1.64926600
H	2.23937100	1.41483900	-0.82791400

N	4.07231600	2.32597800	0.53675700
H	4.40610600	2.24852400	1.50021300
H	4.83663700	2.04022800	-0.07930100
H	3.87505600	3.31270000	0.35388300
H	1.79381800	1.56982800	0.97443400
H	3.30127300	-2.22784000	-0.40883600
C	-2.80754100	1.97491300	-0.42538000
H	-3.41587600	2.52673100	0.30330200
H	-2.51988400	2.64930700	-1.24538100
C	-3.51294700	0.70368200	-0.93273900
H	-4.00227100	0.84427800	-1.90428200
H	-4.24265800	0.31643600	-0.20559200
Cl	-2.16685600	-0.85568700	1.69031000

Single point energy of Pd^{0}/Pd^{II} (TPSS-D3(BJ)/def2-TZVP)

Single point (Pd^{0}): -127.815437

0 1

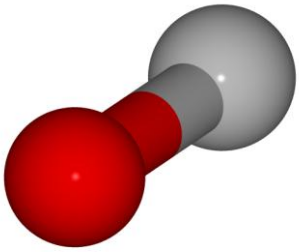
Pd 0.00000000 0.00000000 0.00000000

Single point (Pd^{II}): -126.701478

2 1

Pd 0.00000000 0.00000000 0.00000000

Optimized (TPSS-D3(BJ)/def2-TZVP) structure of CO

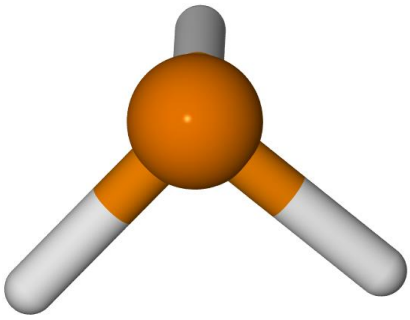


Energy: -113.374959

0 1

C	0.00000000	0.00000000	-0.64831600
O	0.00000000	0.00000000	0.48623700

Optimized (TPSS-D3(BJ)/def2-TZVP) structure of PH_3

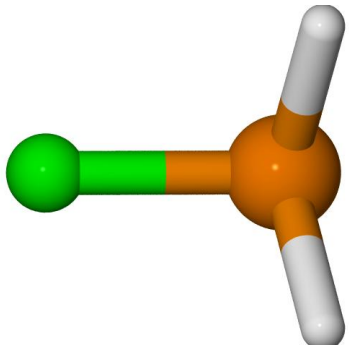


Energy: -343.182062

0 1

P	0.00000000	0.12894800	0.00000000
H	-1.19114000	-0.64469100	0.00000000
H	0.59557000	-0.64476700	1.03159000
H	0.59557000	-0.64476700	-1.03159000

Optimized (TPSS-D3(BJ)/def2-TZVP) structure of PH_2F

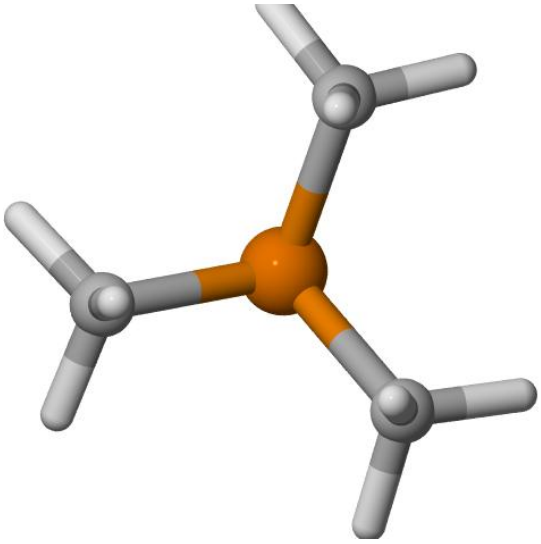


Energy: -442.494417

0 1

P	0.53722800	-0.00002000	-0.12938100
F	-1.07823900	-0.00003900	0.03239900
H	0.82323500	-1.02208700	0.82483600
H	0.82250300	1.02273900	0.82428300

Optimized (TPSS-D3(BJ)/def2-TZVP) structure of PMe_3



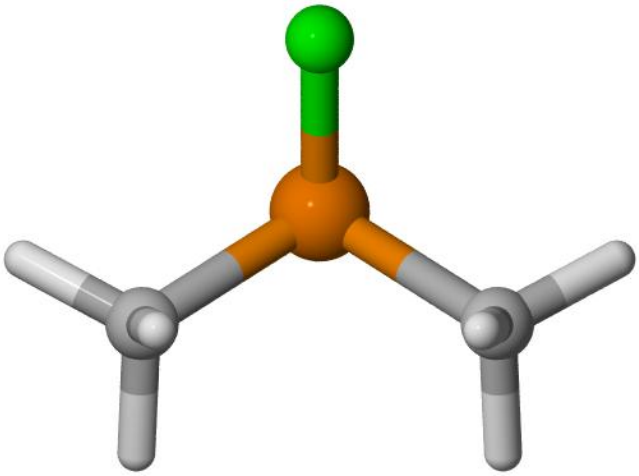
Energy: -461.212540

0 1

P	0.00001600	0.00009500	-0.60801900
C	-1.06047100	1.23666600	0.28159000
H	-0.97984800	1.14218900	1.37166600
H	-0.76315900	2.24932700	-0.00986200

H	-2.10653300	1.09758000	-0.01032000
C	1.60129700	0.29994500	0.28148900
H	1.47918800	0.27801800	1.37158300
H	2.32923100	-0.46440800	-0.00954300
H	2.00442600	1.27502800	-0.01092800
C	-0.54085000	-1.53673200	0.28139700
H	0.10259600	-2.37314600	-0.01047800
H	-0.49952000	-1.41981900	1.37150600
H	-1.56648100	-1.78547700	-0.01020000

Optimized (TPSS-D3(BJ)/def2-TZVP) structure of PMe_2F



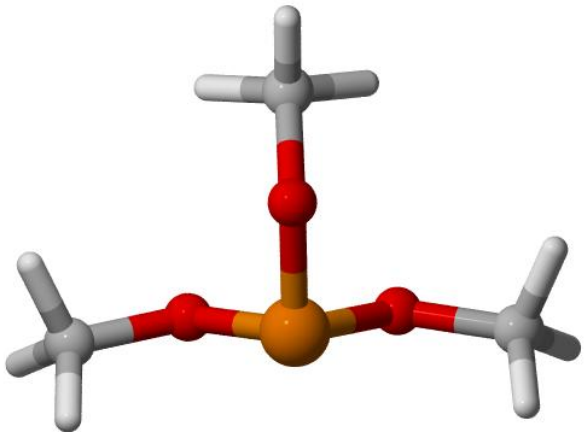
Energy: -521.194381

0 1

P	0.00000000	0.11981900	-0.56899100
F	0.00000000	1.46264400	0.36731300
C	-1.39710400	-0.76845500	0.24124300
H	-1.44750500	-1.78453400	-0.16839300
H	-1.27017400	-0.82270900	1.32795700
H	-2.33864500	-0.26256900	0.00750300
C	1.39710400	-0.76845500	0.24124300
H	2.33864500	-0.26256900	0.00750300

H	1.27017500	-0.82270900	1.32795700
H	1.44750500	-1.78453400	-0.16839300

Optimized (TPSS-D3(BJ)/def2-TZVP) structure of $P(OMe)_3$

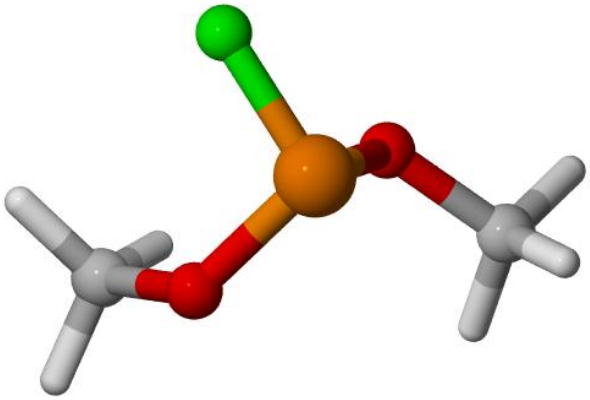


Energy: -687.041489

0 1

P	-0.00017200	-0.39463700	-0.55327100
O	1.18494300	-0.66443700	0.55986200
O	0.00008700	1.23770300	-0.71198900
C	2.53067300	-0.71584400	0.04936500
H	3.12000400	-1.27907000	0.77554700
H	2.56586200	-1.22006900	-0.92440800
H	2.94053000	0.29549200	-0.05384000
C	0.00086200	2.10735300	0.44628700
H	0.89549500	1.93429800	1.05122200
H	-0.00390700	3.12878900	0.06238600
H	-0.88844300	1.92811200	1.05723600
O	-1.18530200	-0.66404400	0.55994300
C	-2.53106900	-0.71500600	0.04947500
H	-3.12047200	-1.27843100	0.77544500
H	-2.94072300	0.29645100	-0.05329400
H	-2.56637200	-1.21882100	-0.92450700

Optimized (TPSS-D3(BJ)/def2-TZVP) structure of $P(OMe)_2F$

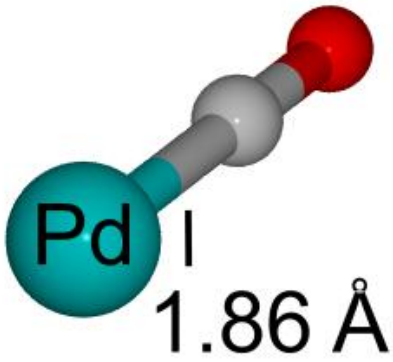


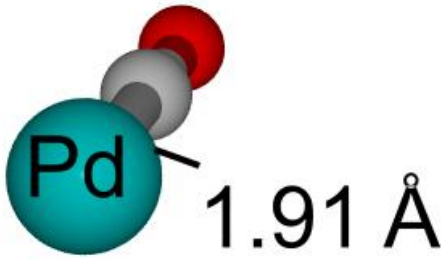
Energy: -671.757889

0 1

P	-0.03115300	0.60749500	-0.54772200
F	0.71436500	1.54391200	0.53714700
O	-1.09349700	0.00765100	0.55563700
O	1.06643400	-0.57270700	-0.71043700
C	-2.24821500	-0.68589700	0.03669600
H	-3.06406400	-0.51645900	0.74174100
H	-2.52835800	-0.30057500	-0.95143100
H	-2.03721000	-1.75766600	-0.03800400
C	1.65839100	-1.25368700	0.42780600
H	0.89133300	-1.48801000	1.17060900
H	2.10412500	-2.16952300	0.03775400
H	2.42763100	-0.61745400	0.87223100

Optimized Pd^0/Pd^{II} complexes with CO and their NBO-analyzes (Table 8, TPSS-D3(BJ)/def2-TZVP)





Energy (Pd^0•CO): -241.282780

0 1

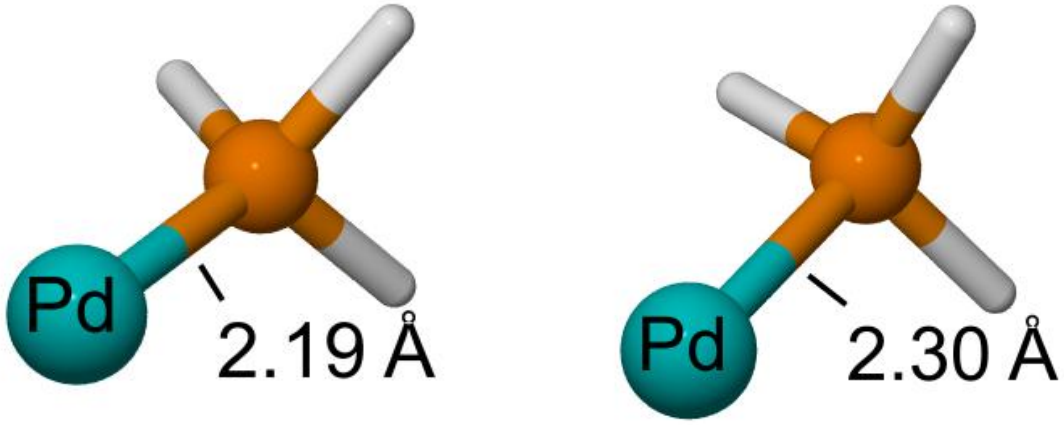
Pd	0.00000000	0.00000000	0.58606700
C	0.00000000	0.00000000	-1.27089400
O	0.00000000	0.00000000	-2.41671400

Energy (Pd^{II}•CO): -240.307670

2 1

Pd	0.00000000	0.00000000	0.59404800
C	0.00000000	0.00000000	-1.31514000
O	0.00000000	0.00000000	-2.42942300

Optimized Pd^0/Pd^{II} complexes with PH_3 and their NBO-analyzes (Table 8, TPSS-D3(BJ)/def2-TZVP)



Energy (Pd^0•PH_3): -471.078511

0 1

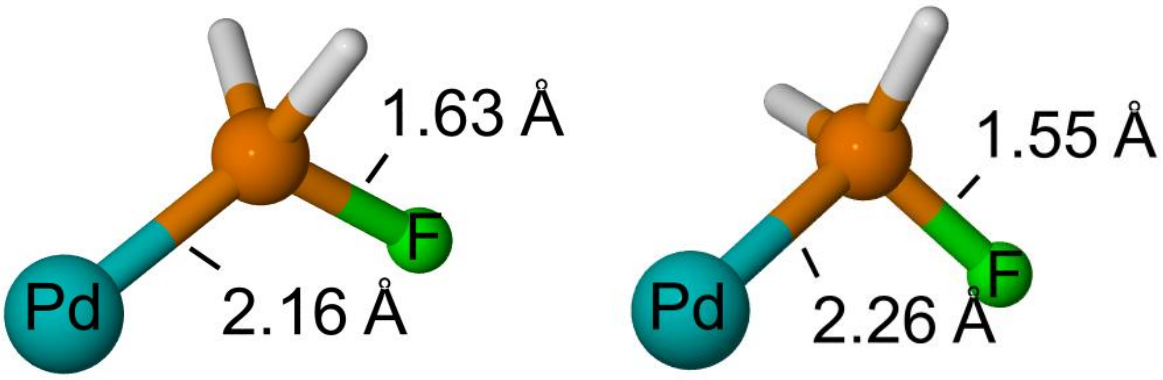
Pd	-0.00000700	0.64999600	0.00000000
P	-0.00000700	-1.53897700	0.00000000
H	-1.22229600	-2.27174800	0.00000000
H	0.61136700	-2.27171300	1.05850200
H	0.61136700	-2.27171300	-1.05850200

Energy (Pd^{II}•PH_3): -470.240017

2 1

Pd	-0.00000100	0.66658500	0.00000000
P	-0.00000100	-1.63794300	0.00000000
H	-1.36804900	-2.03126900	0.00000000
H	0.68406200	-2.03125300	1.18484100
H	0.68406200	-2.03125300	-1.18484100

Optimized Pd^0/Pd^{II} complexes with PH_2F and their NBO-analyzes (Table 8, TPSS-D3(BJ)/def2-TZVP)



Energy (Pd^0•PH_2F): -570.401408

0 1

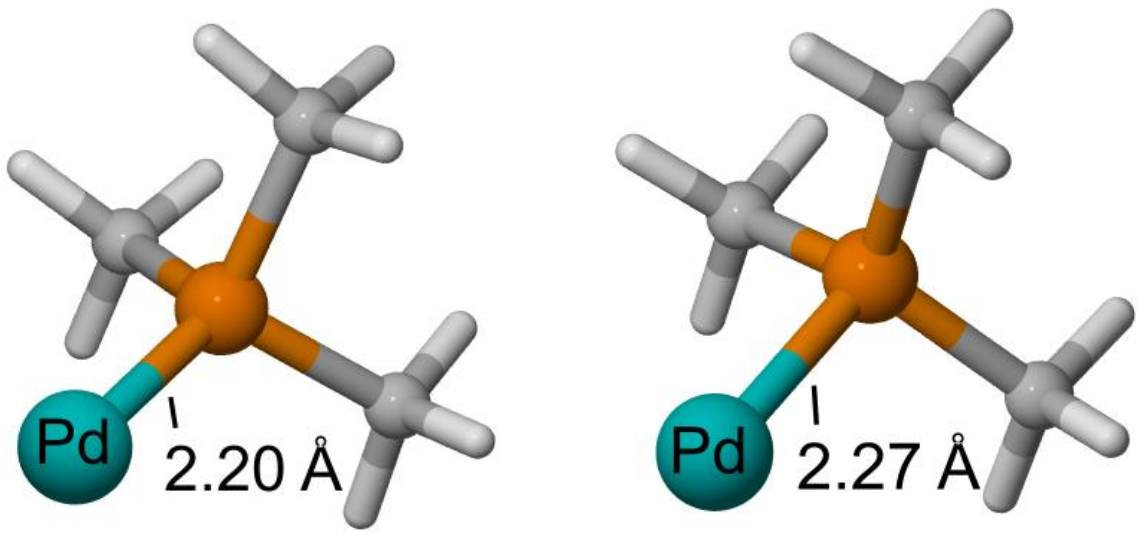
Pd	-0.91141200	-0.06146100	-0.00000300
P	1.18549600	0.46072200	-0.00004600
F	2.29651700	-0.73001500	-0.00003100
H	1.73722700	1.24387300	-1.05752700
H	1.73661600	1.24264900	1.05865600

Energy (Pd^{II}•PH_2F): -569.553719

2 1

Pd	-0.88554800	0.04647500	0.00000000
P	1.30623100	-0.50962400	0.00000100
F	1.99159100	0.87643100	-0.00000600
H	1.60875600	-1.19064900	1.21734100
H	1.60869700	-1.19071600	-1.21731600

Optimized Pd^0/Pd^{II} complexes with PMe_3 and their NBO-analyzes (Table 8, TPSS-D3(BJ)/def2-TZVP)



Energy (Pd^0•PMe_3): -589.120538

0 1

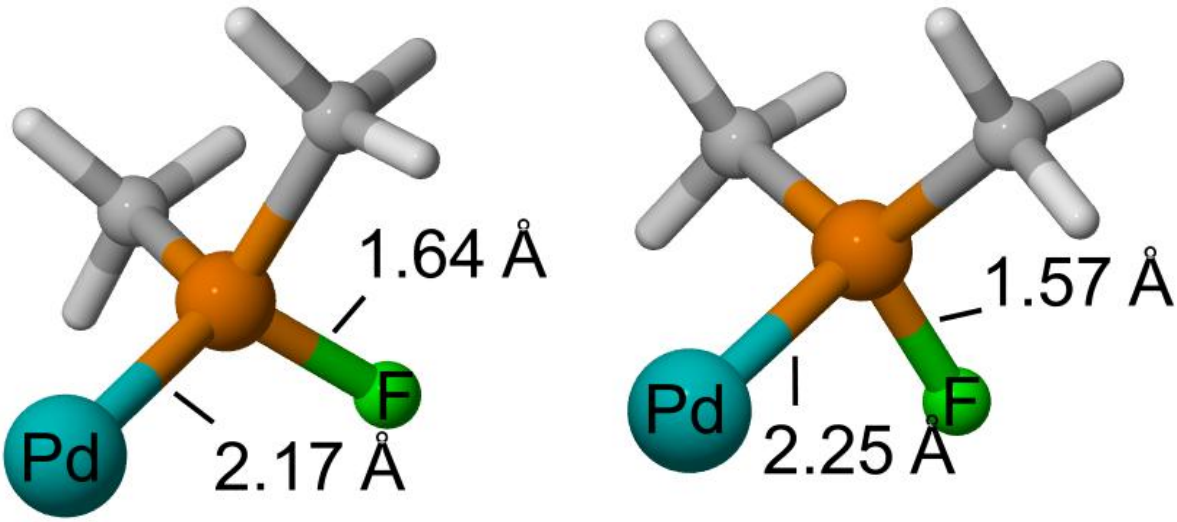
Pd	1.32031400	-0.00001000	0.00000800
P	-0.87551200	0.00001700	0.00000200
C	-1.71074000	-0.43134800	1.59095400
H	-2.80875100	-0.40418700	1.48919200
H	-1.39697100	-1.43797500	1.90255900
H	-1.39765300	0.28043700	2.36825100
C	-1.71068700	-1.16216800	-1.16905700
H	-2.80871700	-1.08759400	-1.09484600
H	-1.39670400	-0.92886200	-2.19659100
H	-1.39769000	-2.19120800	-0.94108200
C	-1.71062800	1.59354700	-0.42194100
H	-1.39766000	1.91068100	-1.42709500
H	-2.80864100	1.49196100	-0.39440400
H	-1.39664500	2.36675900	0.29388200

Energy (Pd^{II}•PMe_3): -588.401560

2 1

Pd	-1.22883400	0.00002400	-0.00001000
P	1.04418500	0.00000000	-0.00001600
C	1.47056200	1.64736800	-0.57544400
H	2.58210100	1.69671700	-0.59271100
H	1.10845300	1.82357000	-1.60189500
H	1.10849800	2.42427400	0.11817000
C	1.47038200	-1.32211800	-1.13890700
H	2.58191300	-1.36197800	-1.17288500
H	1.10805000	-2.29906900	-0.77826900
H	1.10844700	-1.10986300	-2.15857500
C	1.47035900	-0.32535900	1.71441300
H	1.10810100	-1.31441200	2.04047900
H	2.58189000	-0.33527000	1.76587400
H	1.10833300	0.47557900	2.38015200

Optimized Pd^0/Pd^{II} complexes with PMe_2F and their NBO-analyzes (Table 8, TPSS-D3(BJ)/def2-TZVP)



Energy (Pd^{0}•PMe_2F): -649.105688

0 1

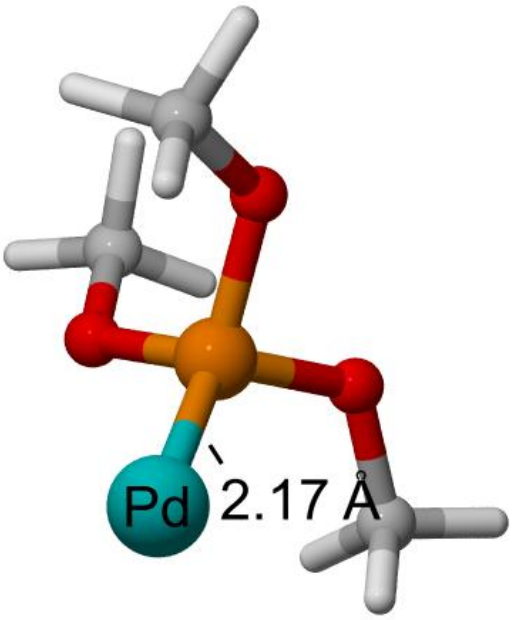
Pd	-1.30276900	0.00000000	-0.02523000
P	0.86555400	0.00000100	0.03860100
F	1.56308200	-0.00000900	1.52183300
C	1.76996400	-1.42409300	-0.67892500
H	1.53435200	-1.48694800	-1.75244700
H	2.85672500	-1.31255200	-0.53731800
H	1.42730400	-2.34907400	-0.19419800
C	1.76996400	1.42410100	-0.67891300
H	1.42730400	2.34908500	-0.19419200
H	2.85672400	1.31255600	-0.53730000
H	1.53435600	1.48695100	-1.75243600

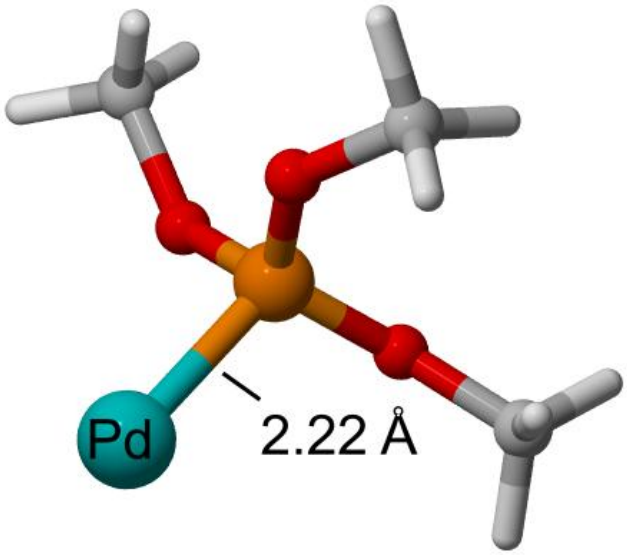
Energy (Pd^{II}•PMe_2F): -648.345640

2 1

Pd	1.22185800	0.00000300	-0.05239800
P	-1.02433000	0.00000800	0.01690800
F	-1.17374700	-0.00008300	1.57747200
C	-1.62952300	1.54612000	-0.62992500
H	-1.49507300	1.58683800	-1.72504100
H	-2.71648000	1.56408800	-0.38511300
H	-1.14973100	2.40684700	-0.13011900
C	-1.62951600	-1.54607000	-0.63002000
H	-1.15003400	-2.40678900	-0.12990500
H	-2.71656800	-1.56380600	-0.38561600
H	-1.49468200	-1.58699400	-1.72508100

Optimized Pd^0/Pd^{II} complexes with $P(OMe)_3$ and their NBO-analyzes (Table 8, TPSS-D3(BJ)/def2-TZVP)





Energy (Pd^0•$P(OMe_3)$): -814.952220

0 1

Pd	1.65871700	-0.00014900	0.22289300
P	-0.48443400	0.00012300	-0.11211600
O	-1.19259600	-1.20095500	-0.98257300
O	-1.36783600	0.00032400	1.27347700
C	-0.74593600	-2.53587700	-0.80393800
H	-1.15539600	-3.13092500	-1.63221500
H	0.35678400	-2.59566200	-0.82277300
H	-1.10421400	-2.95507700	0.15222100
C	-2.79362900	-0.00035600	1.24455100
H	-3.17913600	-0.89453600	0.72958200
H	-3.13846500	0.00079600	2.28765500
H	-3.17993700	0.89217500	0.72732800
O	-1.19221600	1.20134000	-0.98266400
C	-0.74561000	2.53622000	-0.80357100

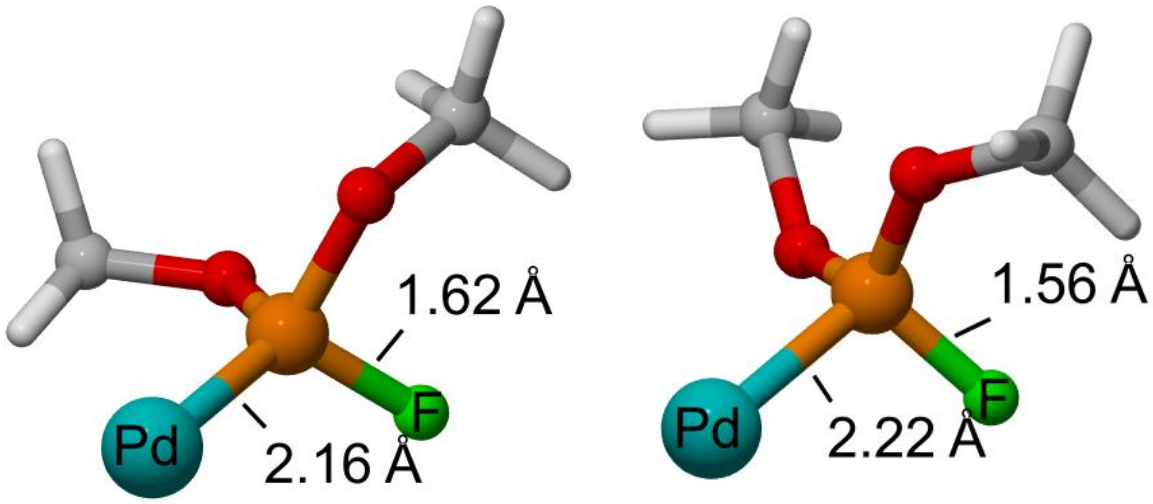
H	-1.15457700	3.13142900	-1.63197800
H	-1.10442000	2.95527500	0.15245600
H	0.35712300	2.59596300	-0.82178700

Energy (Pd^{II}•$P(OMe_3)$): -814.240825

2 1

Pd	-1.57821700	-0.25085400	0.23682100
P	0.55450400	0.16505600	-0.20716900
O	0.32091800	1.52394600	-0.91401500
O	1.26494200	0.29516200	1.16580100
C	0.79875400	2.91353600	-0.63291800
H	-0.08340100	3.55389200	-0.73602300
H	1.22744600	2.95245100	0.37503500
H	1.53890600	3.12155900	-1.41678100
C	2.38502500	-0.40741800	1.85435000
H	3.13558100	-0.69224300	1.10699700
H	2.77571700	0.33618900	2.55860600
H	1.96771700	-1.27015800	2.38704900
O	1.08117400	-0.86153200	-1.23605800
C	1.44569300	-2.30074000	-1.26968500
H	2.40791400	-2.32832500	-1.79635100
H	1.52887900	-2.69359700	-0.24930800
H	0.66855300	-2.80917100	-1.85173500

Optimized Pd^0/Pd^{II} complexes with $P(OMe)_2F$ and their NBO-analyzes (Table 8, TPSS-D3(BJ)/def2-TZVP)



Energy (Pd^0•$P(OMe_2)F$): -799.665304

0 1

Pd	1.59772400	-0.21415500	-0.11334400
P	-0.53146100	-0.10980700	0.22367900
F	-1.12983100	-0.67503700	1.61980100
O	-1.30024800	1.33723500	0.31192800
O	-1.46523800	-0.94366000	-0.81201500
C	-0.73173300	2.51188900	-0.24801200
H	-1.05814800	3.36660500	0.36146700
H	0.37175800	2.46249300	-0.24366000
H	-1.07603900	2.65504000	-1.28556100
C	-2.88694700	-1.00669500	-0.68128600
H	-3.32024800	0.00411400	-0.62808300
H	-3.26803900	-1.52647700	-1.57028500
H	-3.16823600	-1.56799300	0.22303800

Energy (Pd^{II}•$P(OMe_2)F$): -798.909583

2 1

Pd	1.54005600	-0.03242300	-0.16293400
P	-0.62931100	0.01274000	0.30242600
F	-0.66278100	-0.47395800	1.78067600
O	-0.94275400	1.50805600	0.22975500
O	-1.41500500	-0.91334500	-0.63363300
C	-1.91754400	2.40533100	-0.50554300
H	-1.29771200	3.15425400	-1.00975700
H	-2.49868400	1.78820200	-1.19976700
H	-2.52178300	2.84493200	0.29918300
C	-2.03775500	-2.28891800	-0.54379000
H	-2.00641900	-2.62007100	0.50065800
H	-3.06088100	-2.13155200	-0.90945200
H	-1.45851500	-2.92595300	-1.22134000

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