Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2022

# Synthesis of azadiphosphiridine complexes. Theoretical studies on ring formation, the P-to-P' metal shift and the resulting nitrogen geometry

Alexander Schmer,[a]$ Antonio García Alcaraz,[b]$ Andreas Wolfgang Kyri,[a] Gregor Schnakenburg,[a] Arturo Espinosa Ferao,*[b] and Rainer Streubel*[a]

[a] Institute for Inorganic Chemistry, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Str. 1, 53121 Bonn, Germany.

[b] Departamento de Química Orgánica, Universidad de Murcia, Campus de Espinardo, 30071 Murcia, Spain

$ These authors contributed equally to this work

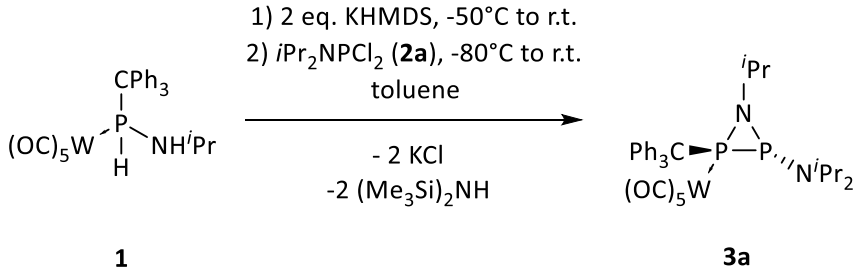
## Table on Contents

1. Experimental details and devices ..... 2
2. Experimental procedure for 3a ..... 2
3. Experimental procedure for 4b ..... 5
4. Experimental procedure for 4c ..... 8
5. Crystallographic Data for 3a and 4b ..... 13
6. Computational Details ..... 15
7. Base-free formation of azadiphosphiridine complex $3d'_N{\cdot}H^+$ ..... 16
8. Detailed analysis of the P-W bonds ..... 17
9. Calculated structures ..... 19
10. References ..... 52

## 1. Experimental details and devices

The syntheses of all compounds were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Tetrahydrofuran, toluene and petrol ether were dried over sodium wire and benzophenone. Dichloromethane was dried over $CaH_2$. Complex **1** was prepared according to literature procedure[1] and the dichlorophosphanes (*i*$Pr_2NPCl_2$, *t*$BuPCl_2$ and $PhPCl_2$) were purchased and used without further purification. The solvents were freshly distilled before usage. The NMR spectra were recorded on a Bruker AVI-300 (300.1 MHz for $^1H$ NMR, 75.5 MHz for $^{13}C$ NMR, 59.6 MHz and 121.5 MHz for $^{31}P$ NMR) and Bruker AV III HD Prodigy 500 (500.2 MHz for $^1H$ NMR, 125.8 MHz for $^{13}C$ NMR, and 202.5 MHz for $^{31}P$ NMR) spectrometers at 25 °C. The $^1H$ and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual proton resonances and the $^{13}C$ NMR signals of the deuterated solvents; the $^{31}P$ NMR spectra were referenced to 85 % $H_3PO_4$ as external standards, respectively. Melting points were determined in one-side melted off capillaries using a Büchi Type Sor a Carl Roth Type MPM-2 apparatus and are uncorrected. Elemental analyses were carried out on a Vario EL gas chromatograph. Mass spectrometric data were collected on a Thermo Finnigan MAT 90 and MAT 95 XL device using 70 eV voltage. The IR spectra were recorded on a Thermo Nicolet 380 FT-IR spectrometer with an attenuated total reflection (ATR) attachment or a Bruker Alpha Diamond ATR FTIR spectrometer.

## 2. Experimental procedure for 3a




**1** **3a**

***Scheme S 1**. Synthesis of complex **3a**.*

The aminophosphane complex **1** (329 mg, 0.5 mmol, 1.00 eq.) was dissolved in 40 mL of toluene and a solution of KHMDS (209 mg, 1.05 mmol, 2.10 eq.) in 2.5 mL of toluene was added to the solution at -50 °C while stirring. After five minutes, the cooling bath was removed. The solution was stirred for 30 minutes at ambient temperature and subsequently, the yellow solution was cooled to -80 °C. To the solution i-$Pr_2NPCl_2$ (0.10 mL, 0.54 mmol, 1.09 eq.) was added at low temperature. After ten minutes the colour changed from yellow to red/orange. The solution was allowed slowly warming up to ambient temperature overnight. All volatiles were removed under reduced pressure ($5\cdot10^{-2}$ mbar) and the crude product was filtered over $Al_2O_3$ (ø = 1 cm, h = 1 cm) using 50 mL of toluene. After removing of the toluene under reduced pressure ($5\cdot10^{-2}$ mbar), the product was washed with *n*-pentane

(five times 1 mL) at -30°C. Drying for 2h under reduced pressure ($5 \cdot 10^{-2}$ mbar) yielded the product **3a** as a yellow solid in 46 % yield (176 mg, 0.23 mmol).

m.p. 141°C; $^{1}$H NMR (500.1 MHz, 298 K, $C_6D_6$): δ / ppm = 0.88 (d, $^{3}J_{HH}$ = 6.8 Hz, 6H, $CH_3$), 0.92 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, $CH_3$), 1.13 (d, $^{3}J_{HH}$ = 6.7 Hz, 6H, $CH_3$), 1.47 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, $CH_3$), 3.32 (dhept, $^{3}J_{HH}$ = 6.8 Hz, $^{3}J_{PH}$ = 3.5 Hz, 2H, CH), 3.43 (dhept, $^{3}J_{HH}$ = 6.5 Hz, $^{3}J_{PH}$ = 3.5 Hz, 2H, CH), 7.02-7.08 (m, 3H, *para*-C), 7.11-7.20 (m, 6H, *meta*-C), 7.40-7.61 (m, 6H, *ortho*-C); $^{13}$C{$^{1}$H} NMR (125.8 MHz, 298 K, $C_6D_6$): δ / ppm = 22.4 (d, $^{3}J_{PC}$ = 7.8 Hz, $CH_3$), 24.0 (s, $CH_3$), 24.1 (d, $^{3}J_{PC}$ = 7.3 Hz, $CH_3$), 24.6 (dd, $^{3}J_{PC}$ = 11.5 Hz, $^{4}J_{PC}$ = 2.2 Hz, $CH_3$), 44.8 (d, $^{2}J_{PC}$ = 8.5 Hz, CH), 50.7 (d, $^{2}J_{PC}$ = 4.6 Hz, CH), 70.8 (d, $^{1}J_{PC}$ = 36.8 Hz, $CPh_3$), 127.3 (s, *para*-C), 128.4 (s, *meta*-C), 132.0 (br s, *ortho*-C), 143.4 (br s, *ipso*-C), 198.2 (d, $^{2}J_{PC}$ = 32.8 Hz, *trans*-CO), 198.5 ($d_{sat}$, $^{2}J_{PC}$ = 6.7 Hz, $^{1}J_{WC}$ = 127.0 Hz, *cis*-CO); $^{31}$P{$^{1}$H} NMR (202.5 MHz, 298 K, $C_6D_6$): δ / ppm = -44.6 ($d_{sat}$, $^{1}J_{PP}$ = 200.5 Hz, $^{1}J_{WP}$ = 253.3, $PCPh_3$), -20.8 (d, $^{1}J_{PP}$ = 200.5 Hz, $PNiPr_2$); IR (ATR Diamant): ν /cm$^{-1}$ = 2064 (vs, CO), 1974 (w, CO), 1951 (m, CO), 1928 (s, CO), 1913 (vs, CO), 1899 (vs, CO); MS (LIFDI): m/z (%) = 786.1 (40) $[M]^{+\cdot}$, 542.9 (30) $[M\text{-}CPh_3]^{+}$, 243.1 (100) $[CPh_3]^{+}$; elemental analysis calcd. (%) for $C_{33}H_{36}N_2O_5P_2W$: C 50.40, H 4.61, N 3.56; found C 51.65, H 4.76, N 3.34.

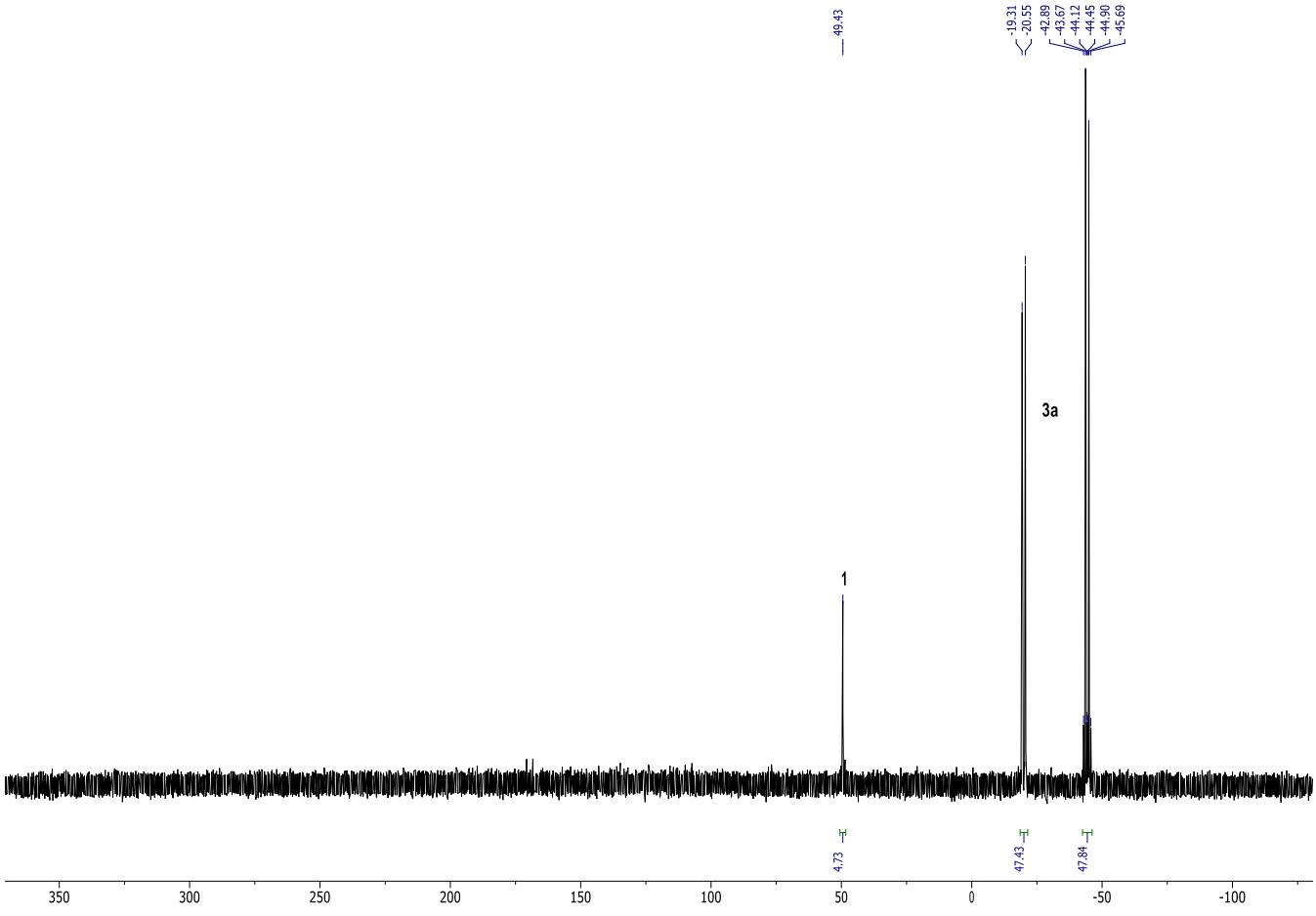



***Figure S 1.*** *$^{31}$P{$^{1}$H} NMR spectrum of the reaction mixture containing **1** (5 %) and **3a** (95 %).*

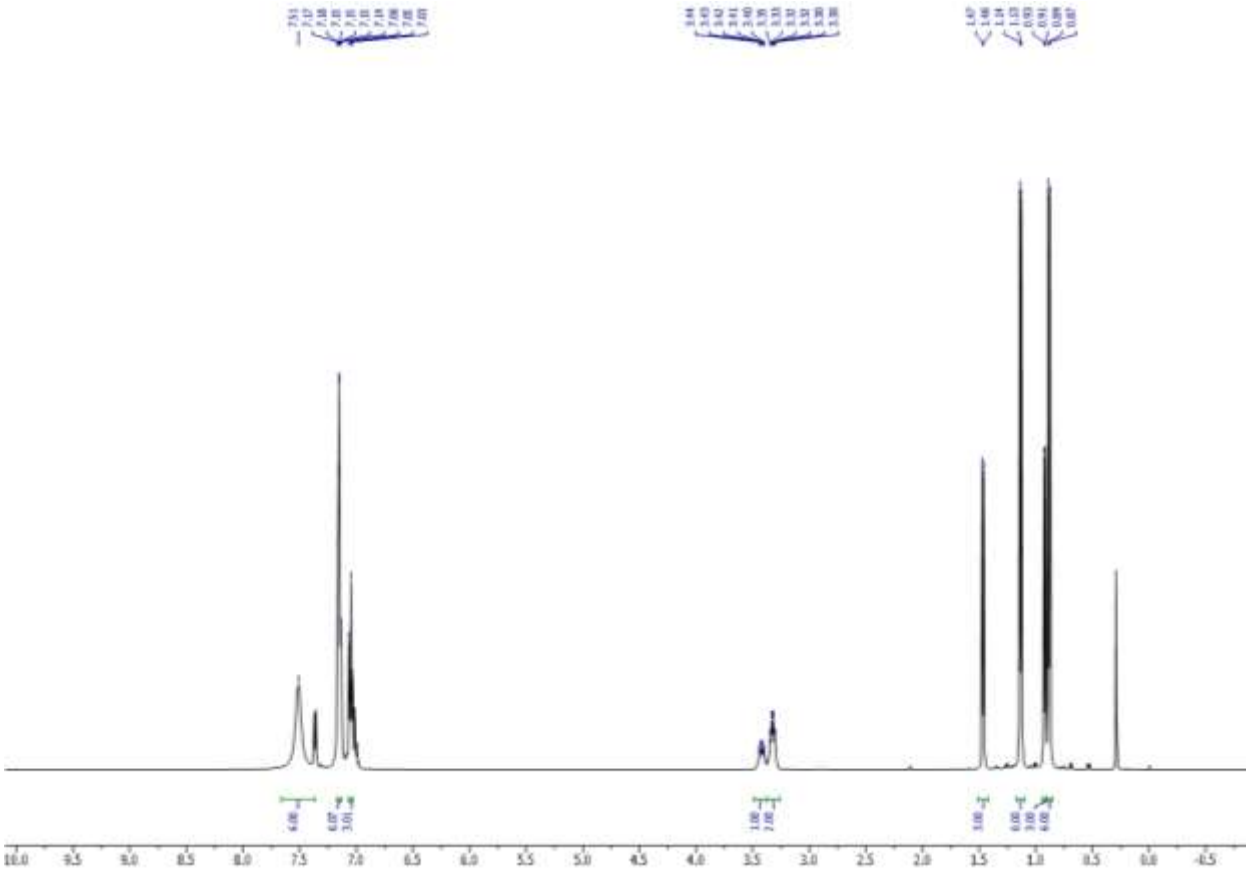


***Figure S 2***. *$^{1}$H NMR spectrum of **3a** in $C_6D_6$.*

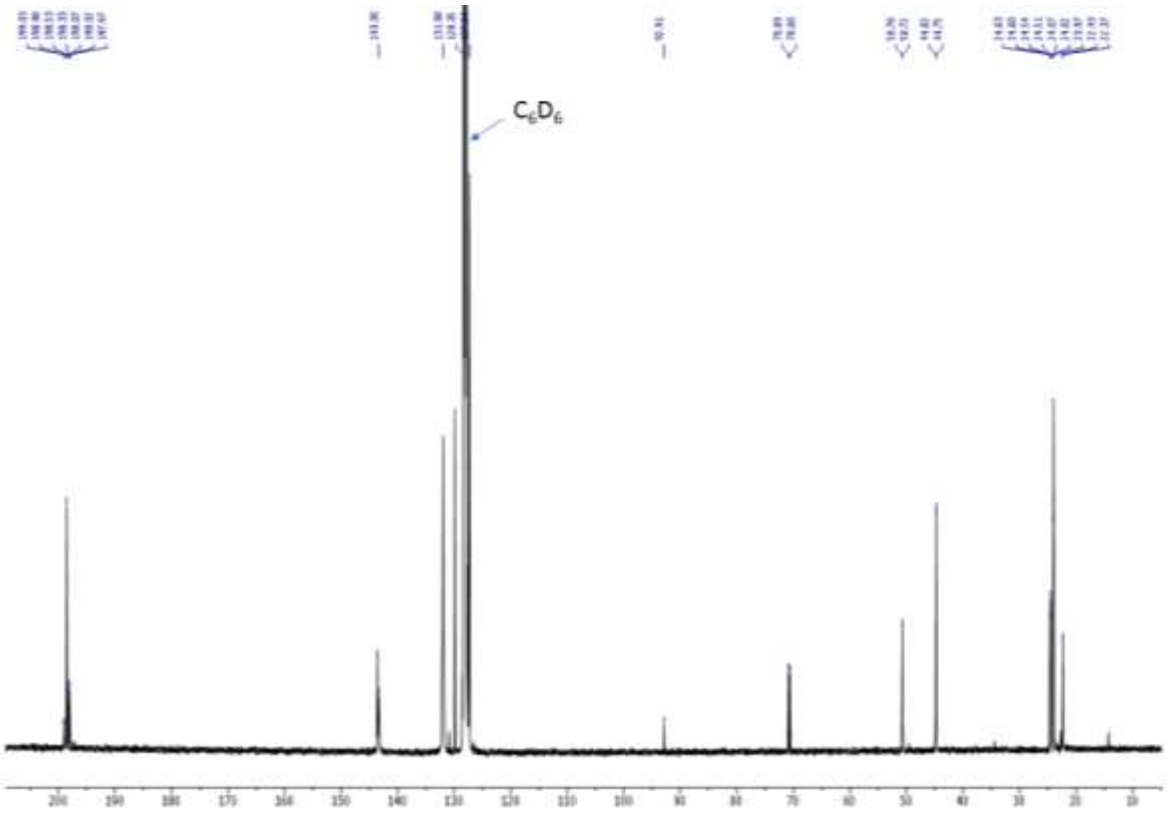



***Figure S 3***. *$^{13}C\{^{1}H\}$ NMR spectrum of **3a** in $C_6D_6$.*

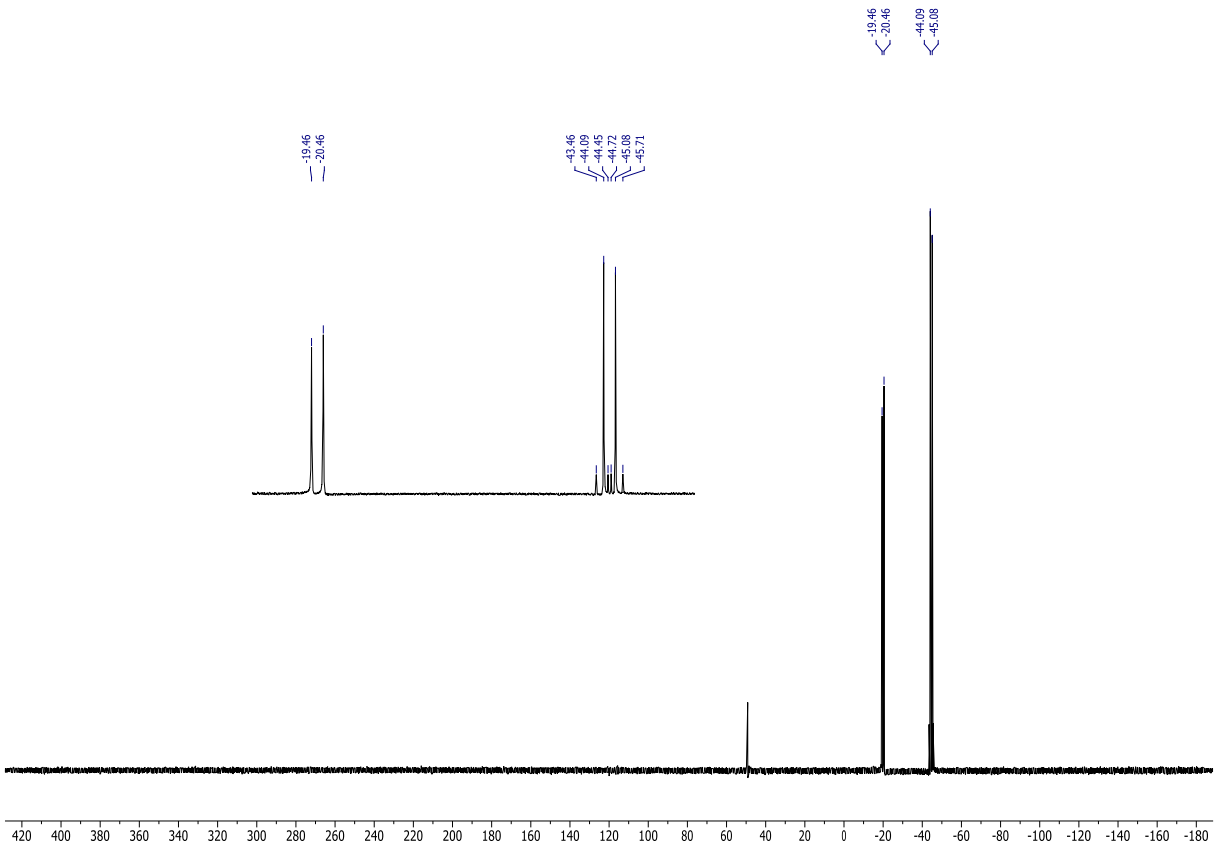
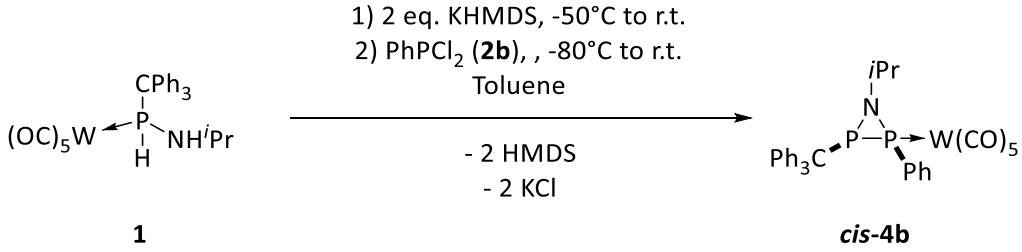



***Figure S 4**. $^{31}P\{^{1}H\}$ NMR spectrum of **3a** in $C_6D_6$.*

## 3. Experimental procedure for 4b




**1** ***cis*-4b**

***Scheme S 2**. Synthesis of complex **cis-4b**.*

The aminophosphane complex **1** (329 mg, 0.5 mmol, 1.00 eq.) was dissolved in 40 mL of toluene and a solution of KHMDS (209 mg, 1.05 mmol, 2.10 eq.) in 2.5 mL of toluene was added to the solution at -50 °C while stirring. After five minutes, the cooling bath was removed. The solution was stirred for 30 minutes at ambient temperature and subsequently, the yellow solution was cooled to -80 °C. To the solution $PhPCl_2$ (72.0 µL, 0.53 mmol, 1.06 eq.) was added at low temperature. After addition, the colour changed from yellow to red/brown. The solution was allowed slowly warming up to ambient temperature overnight. All volatiles were removed under reduced

pressure ($5 \cdot 10^{-2}$ mbar) and the crude product was filtered over $Al_2O_3$ (ø = 1 cm, h = 1 cm) using 50 mL of toluene. After removing of the toluene under reduced pressure ($5 \cdot 10^{-2}$ mbar), the product was washed with *n*-pentane (five times 1 mL) at -30°C. Drying for 2h under reduced pressure ($5 \cdot 10^{-2}$ mbar) yielded the product ***cis-4b*** as a colorless solid in 22 % yield (84 mg, 0.11 mmol).

m.p. 138 °C; $^{1}$H NMR (500.1 MHz, 298 K, $C_6D_6$): δ / ppm = 0.93 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, $CH_3$), 1.36 (d, $^{3}J_{HH}$ = 6.2 Hz, 3H, $CH_3$), 3.05 (dhept, $^{3}J_{HH}$ = 6.2 Hz, $^{3}J_{PH}$ = 13.1 Hz, 1H, CH), 6.65-6.73 (m, 3H, Ph), 6.86.-6.95 (m, 9H, $CPh_3$), 7.07-7.14 (m, 2H, Ph), 7.17-7.20 (m, 6H, $CPh_3$); $^{13}$C{$^{1}$H} NMR (125.8 MHz, 298 K, $C_6D_6$): δ / ppm = 22.4 (t, $^{3}J_{PC}$ = 9.3 Hz, $CH_3$), 25.7 (s, $CH_3$), 54.2 (d, $^{2}J_{PC}$ = 11.8 Hz, CH), 65.3 (d, $^{1}J_{PC}$ = 75.4 Hz, $CPh_3$), 127.1 (s, *para*-C), 128.0 (s, *meta*-C), 128.5 (d, $^{3}J_{PC}$ = 10.6 Hz, *meta*-C), 129.1 (d, $^{4}J_{PC}$ = 2.0 Hz, *para*-C), 129.7 (d, $^{2}J_{PC}$ = 13.6 Hz, *ortho*-C), 131.4 (d, $^{3}J_{PC}$ = 7.6 Hz, *ortho*-C), 136.6 (d, $^{1}J_{PC}$ = 19.6 Hz, *ipso*-C), 142.5 (d, $^{2}J_{PC}$ = 9.5 Hz, *ipso*-C), 196.2 ($d_{sat}$, $^{2}J_{PC}$ = 7.3 Hz, $^{1}J_{WC}$ = 126.6 Hz, *cis*-CO), 198.2 (d, $^{2}J_{PC}$ = 29.8 Hz, *trans*-CO); $^{31}$P{$^{1}$H} NMR (202.5 MHz, 298 K, $C_6D_6$): δ / ppm = -16.3 (d, $^{1}J_{PP}$ = 172.8 Hz, $PCPh_3$), -30.5 ($d_{sat}$, $^{1}J_{PP}$ = 172.8 Hz, $^{1}J_{WP}$ = 268.6 Hz, PPh); IR (ATR Diamant): ν /cm$^{-1}$ = 2068 (s, CO), 1986 (m, CO), 1915 (vs, CO); MS (LIFDI): m/z (%) = 519.9 (3) $[M\text{-}CPh_3]^{+\cdot}$, 243.1 (100) $[CPh_3]^{+}$; elemental analysis calcd. (%) $C_{33}H_{27}NO_5P_2W$: C 51.92, H 3.57, N 1.83; found C 52.31, H 3.98, N 1.73.

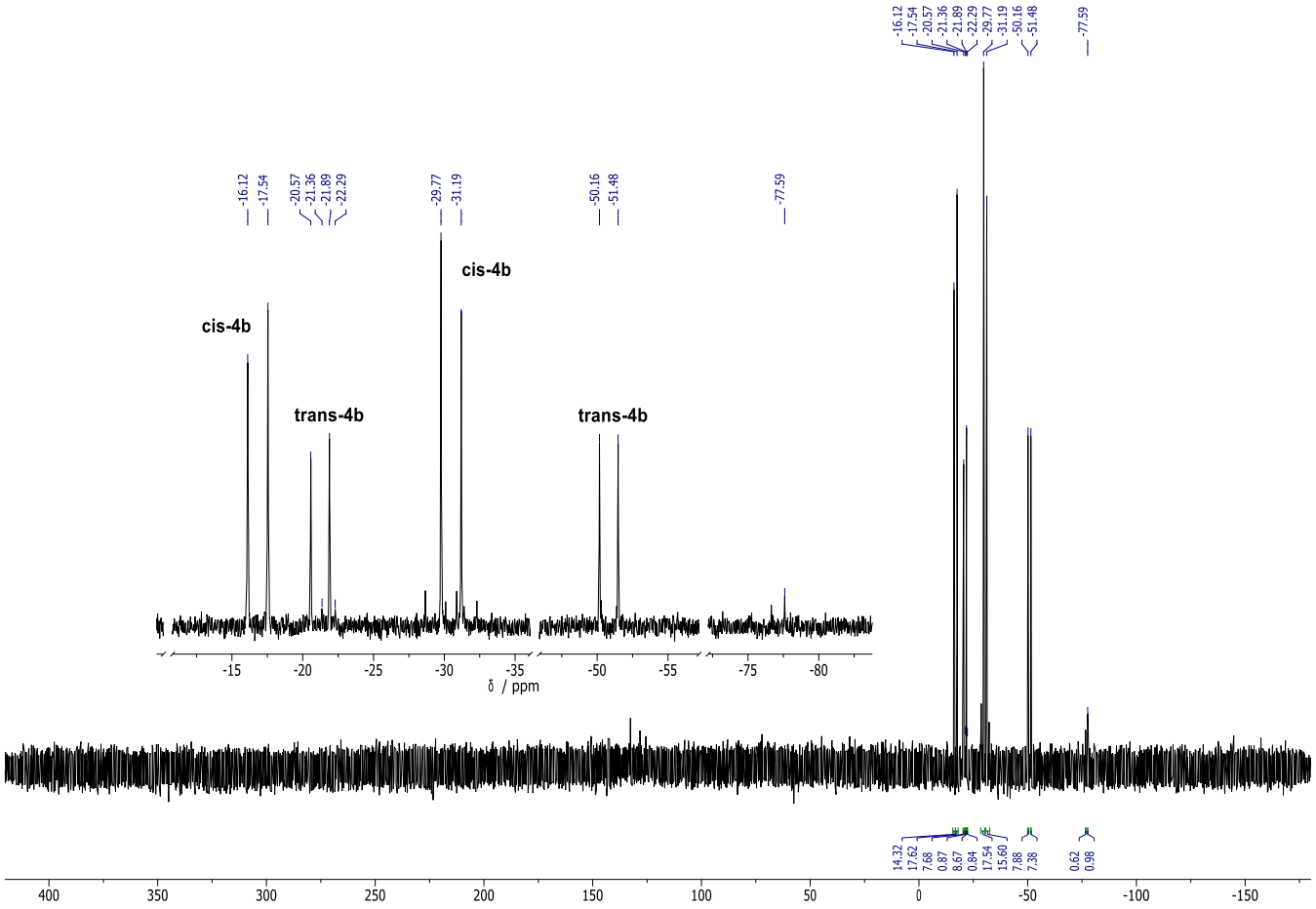



***Figure S 5.*** *$^{31}$P{$^{1}$H} NMR spectrum of the reaction mixture containing **cis-4b** (66 %) and **trans-4b** (32 %).*

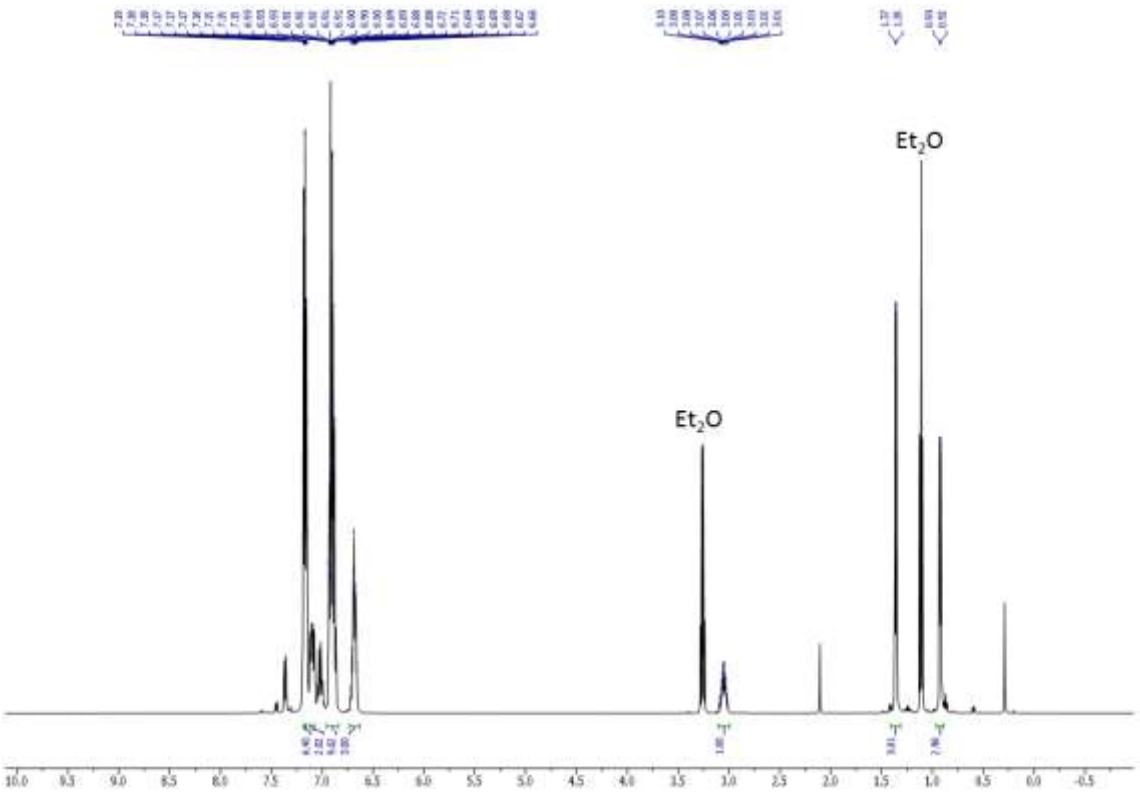



***Figure S 6**. [1]H NMR spectrum of **cis-4b** ($C_6D_6$).*

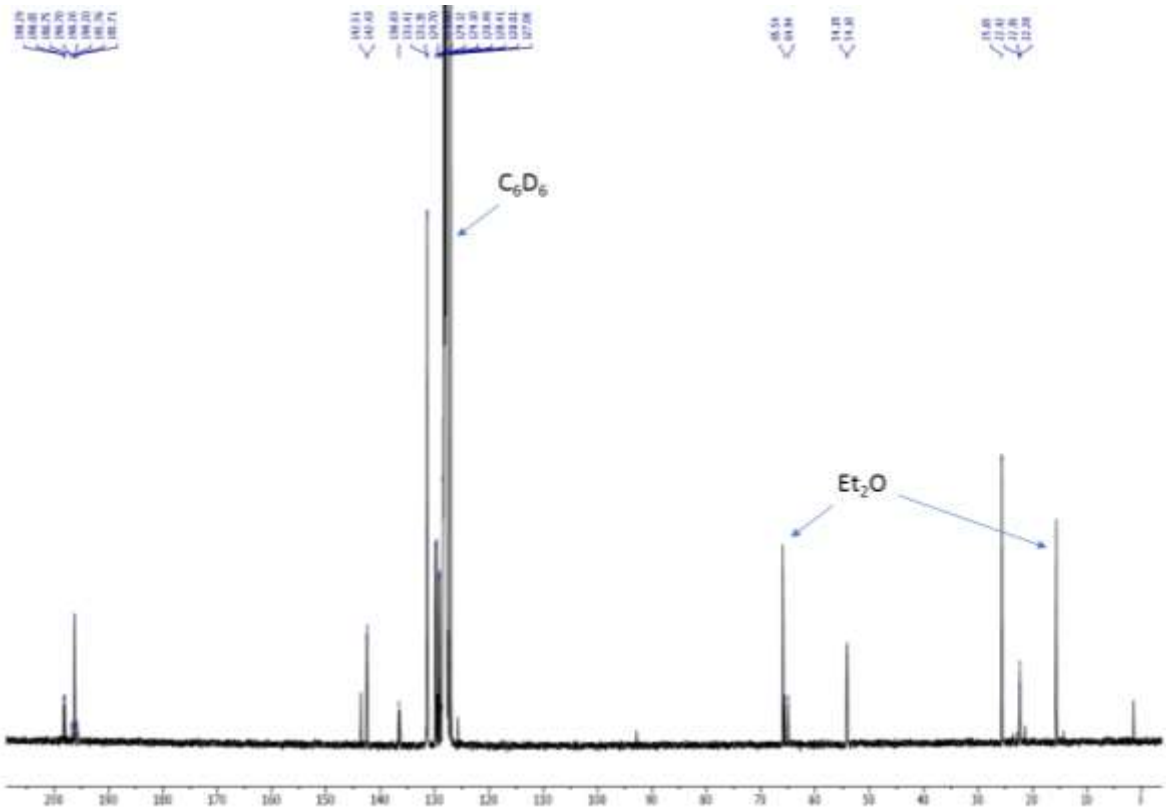



***Figure S 7**. [13]C NMR spectrum of **cis-4b** ($C_6D_6$).*

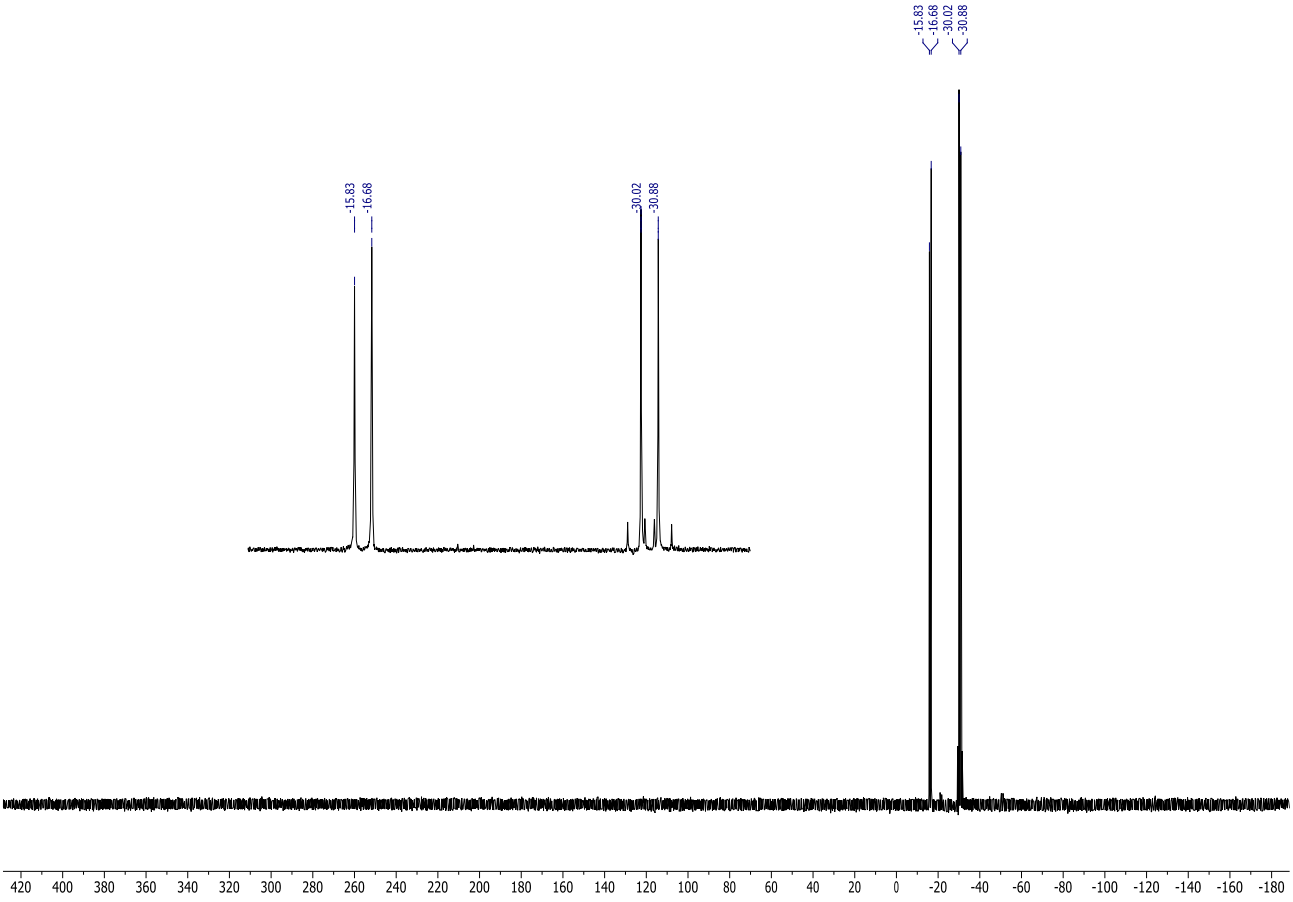
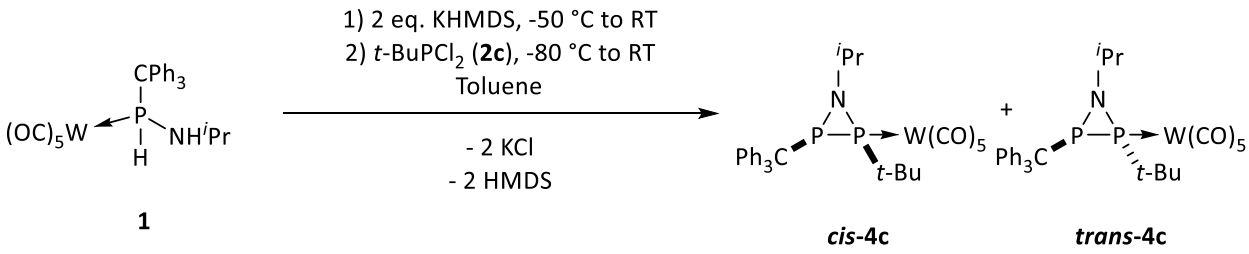



***Figure S 8**. $^{31}P\{^{1}H\}$ NMR spectrum of **cis-4b** in $C_6D_6$.*

## 4. Experimental procedure for 4c




***Scheme S 3**. Synthesis of complexes **cis-4c** and **trans-4c***

The aminophosphane complex **1** (329 mg, 0.5 mmol, 1.00 eq.) was dissolved in 40 mL of toluene and a solution of KHMDS (209 mg, 1.05 mmol, 2.10 eq.) in 2.5 mL of toluene was added to the solution at -50 °C while stirring. After five minutes, the cooling bath was removed. The solution was stirred for 30 minutes at ambient temperature and subsequently, the yellow solution was cooled to -80 °C. To the solution *t*BuPCl$_2$ (84 mg, 0.53 mmol, 1.06 eq.) was added at low temperature. After addition, the colour changed from yellow to red/orange. The solution was

allowed slowly warming up to ambient temperature overnight. All volatiles were removed under reduced pressure ($5 \cdot 10^{-2}$ mbar) and the crude product was filtered over $Al_2O_3$ (ø = 1 cm, h = 1 cm) using 50 mL of toluene. After removing of the toluene under reduced pressure ($5 \cdot 10^{-2}$ mbar), the product was washed with *n*-pentane (five times 1 mL) at -30°C. Drying for 2h under reduced pressure ($5 \cdot 10^{-2}$ mbar) yielded the products ***cis-4c*** *and* ***trans-4c*** as a yellow solid, containing both isomers, in 46 % yield (173 mg, 0.23 mmol).

m.p. 140 °C; isomeric ratio (isomer 1: isomer 2) = 10 : 1; Isomer 1: $^{1}$H NMR (500.1 MHz, 298 K, $C_6D_6$): $\delta$ / ppm = 0.75 (d, $^{3}J_{HH}$ = 6.4 Hz, 3H, $CH_3$), 1.05 (d, $^{3}J_{PH}$ = 14.5 Hz, 9H, tBu), 1.21 (d, $^{3}J_{HH}$ = 6.3 Hz, 3H, $CH_3$), 3.27 (dhept, $^{3}J_{HH}$ = 6.3 Hz, $^{3}J_{PH}$ = 2.9 Hz, 1H, CH), 7.00-7.05 (m, 3H, $CPh_3$), 7.10-7.17 (m, 6H, $CPh_3$), 7.33-7.39 (m, 6H, $CPh_3$); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, 298 K, $C_6D_6$): $\delta$ / ppm = 23.3 (s, $CH_3$), 24.2 (dd, $^{3}J_{PC}$ = 6.5 Hz, $^{3}J_{PC}$ = 2.8 Hz, $CH_3$), 29.8 (dd, $^{2}J_{PC}$ = 9.8 Hz, $^{3}J_{P,C}$ = 6.1 Hz, tBu), 45.3 (dd, $^{1}J_{PC}$ = 15.5 Hz, $^{2}J_{PC}$ = 5.6 Hz, tBu), 52.0 (dd, $^{2}J_{PC}$ = 10.1 Hz, $^{2}J_{PC}$ = 4.6 Hz, CH), 64.1 (dd, $^{1}J_{PC}$ = 84.7 Hz, $^{2}J_{PC}$ = 3.5 Hz, $CPh_3$), 127.3 (s, *para*-C), 128.7 (s, *meta*-C), 131.7 (d, $^{3}J_{PC}$ = 6.5 Hz, *ortho*-C), 143.5 (d, $^{2}J_{PC}$ = 11.9 Hz, *ipso*-C), 197.0 (d, $^{2}J_{PC}$ = 33.6 Hz, *trans*-CO), 197.0 ($d_{sat}$, $^{2}J_{PC}$ = 7.7 Hz, $^{1}J_{WC}$ = 126.7 Hz, *cis*-CO); $^{31}P\{^{1}H\}$ NMR (202.5 MHz, 298 K, $C_6D_6$): $\delta$ / ppm = -26.6 (d, $^{1}J_{PP}$ = 167.9 Hz, $PCPh_3$), -21.4 ($d_{sat}$, $^{1}J_{PP}$ = 167.9 Hz, $^{1}J_{WP}$ = 273.0, PtBu). Isomer 2: $^{1}$H NMR (500.1 MHz, 298 K, $C_6D_6$): $\delta$ / ppm = 0.76 (d, $^{3}J_{PH}$ = 18.2 Hz, 9H, tBu), 0.82 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, $CH_3$), 1.20 (d, $^{3}J_{HH}$ = 6.5 Hz, 3H, $CH_3$), 2.93 (m, 1H, CH), 6.95-7.08 (m, 3H, $CPh_3$), 7.10-7.17 (m, 6H, $CPh_3$), 7.33-7.39 (m, 6H, $CPh_3$); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, 298 K, $C_6D_6$): $\delta$ / ppm = 21.4 (s, $CH_3$), 25.3 (s, $CH_3$), 28.3 (d, $^{2}J_{PC}$ = 8.2 Hz, tBu), 41.2 (d, $^{1}J_{PC}$ = 6.5 Hz, $^{2}J_{PC}$ = 1.1 Hz, tBu), 56.1 (d, $^{2}J_{PC}$ = 11.6 Hz, CH), 127.2 (s, *para*-C), 129.9 (s, *meta*-C), 131.9 (d, $^{3}J_{P,C}$ = 6.9 Hz, *ortho*-C), 143.6 (d, $^{2}J_{PC}$ = 15.9 Hz, *ipso*-C), the CO-signals for the minor isomer were not observed due to their low intensity; $^{31}P\{^{1}H\}$ NMR (202.5 MHz, 298 K, $C_6D_6$): $\delta$ / ppm = 30.9 (d, $^{1}J_{PP}$ = 183.4 Hz, $PCPh_3$), 41.4 ($d_{sat}$, $^{1}J_{PP}$ = 183.4 Hz, $^{1}J_{WP}$ = 244.9, PtBu); IR (ATR Diamant): ν /$cm^{-1}$ = 2070 (s, CO), 1916 (vs, CO); MS (LIFDI): m/z (%) = 499.9 (10) $[M\text{-}CPh_3]^{+\cdot}$, 243.1 (100) $[CPh_3]^{+}$; elemental analysis calcd. (%) $C_{31}H_{31}NO_5P_2W$: C 50.09, H 4.20, N 1.88; found C 50.24, H 4.42, N 1.71.

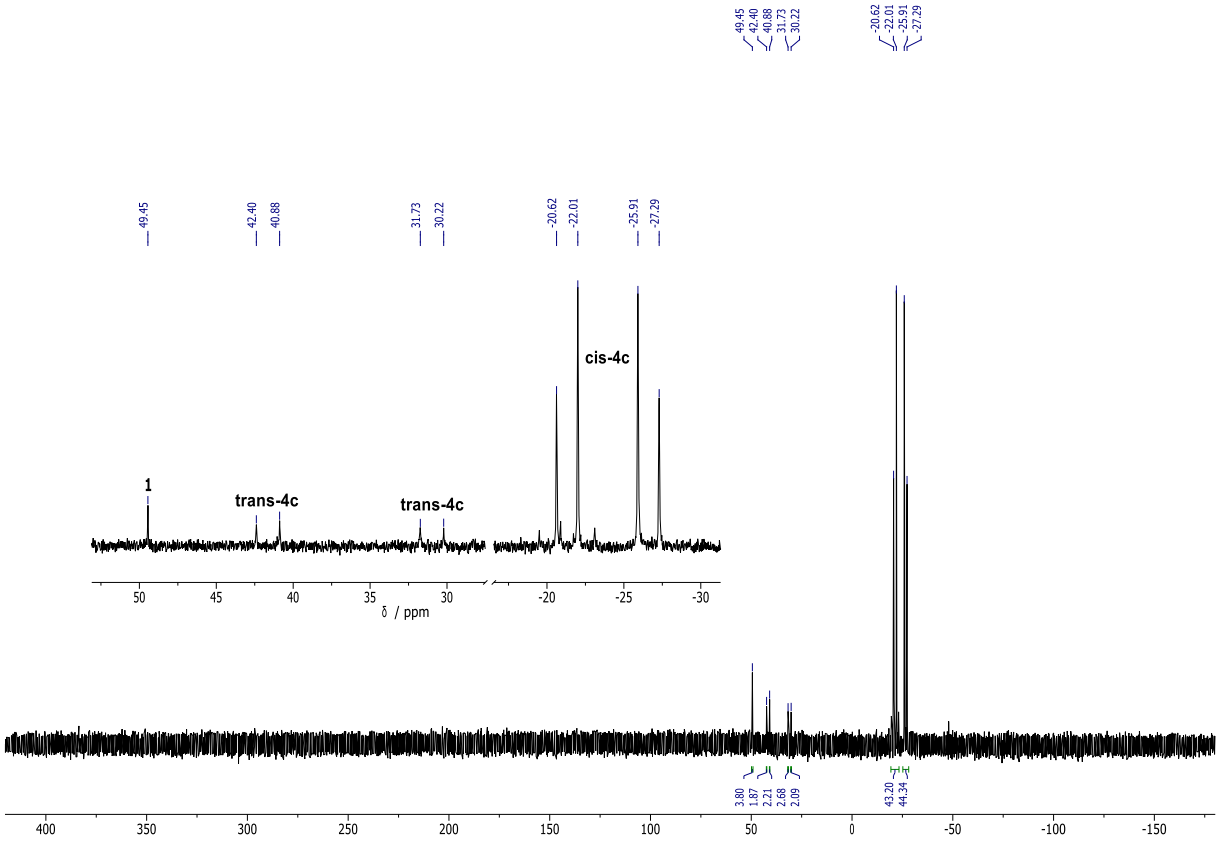



***Figure S 9.*** *$^{31}P\{^{1}H\}$ NMR spectrum of the reaction mixture containing **cis-4c** (88 %), **trans-4c** (8 %) and **1** (4 %).*

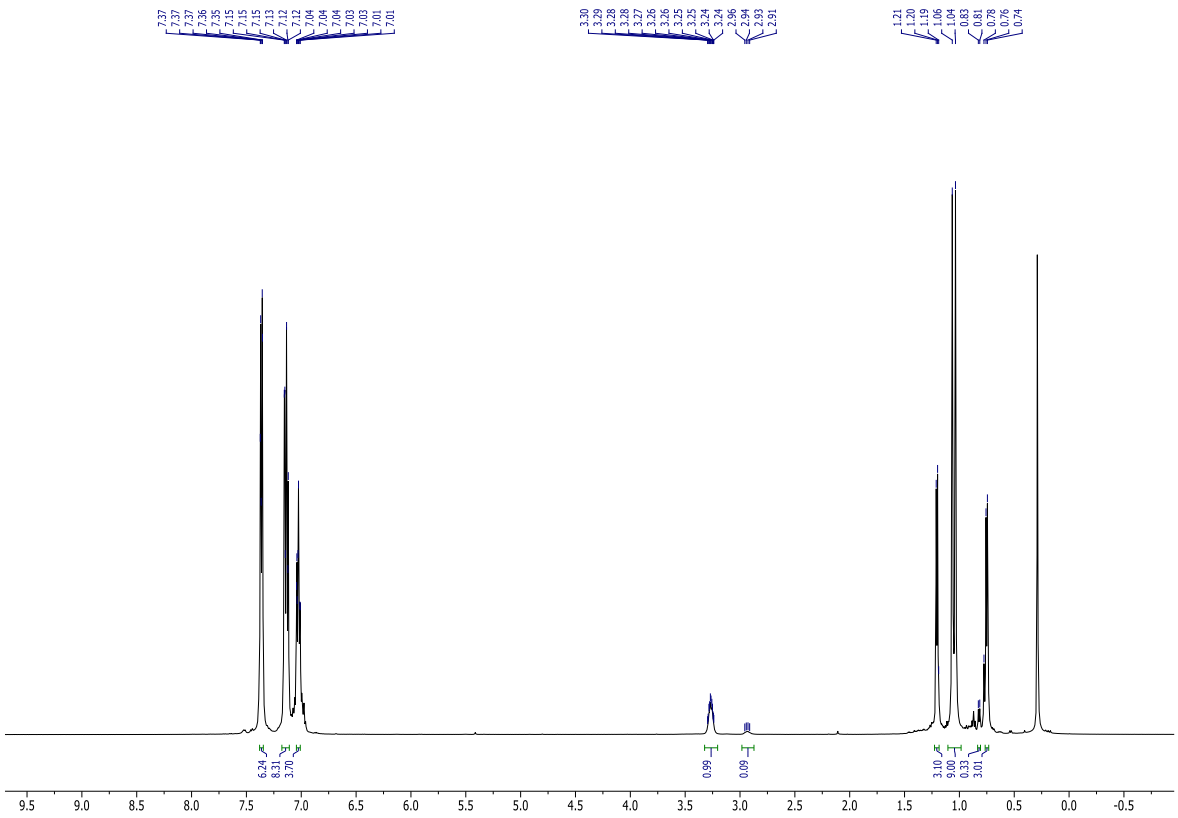


***Figure S 10***. *$^{1}$H NMR spectrum of the isomeric mixture of **cis-4c** and **trans-4c** in $C_6D_6$.*

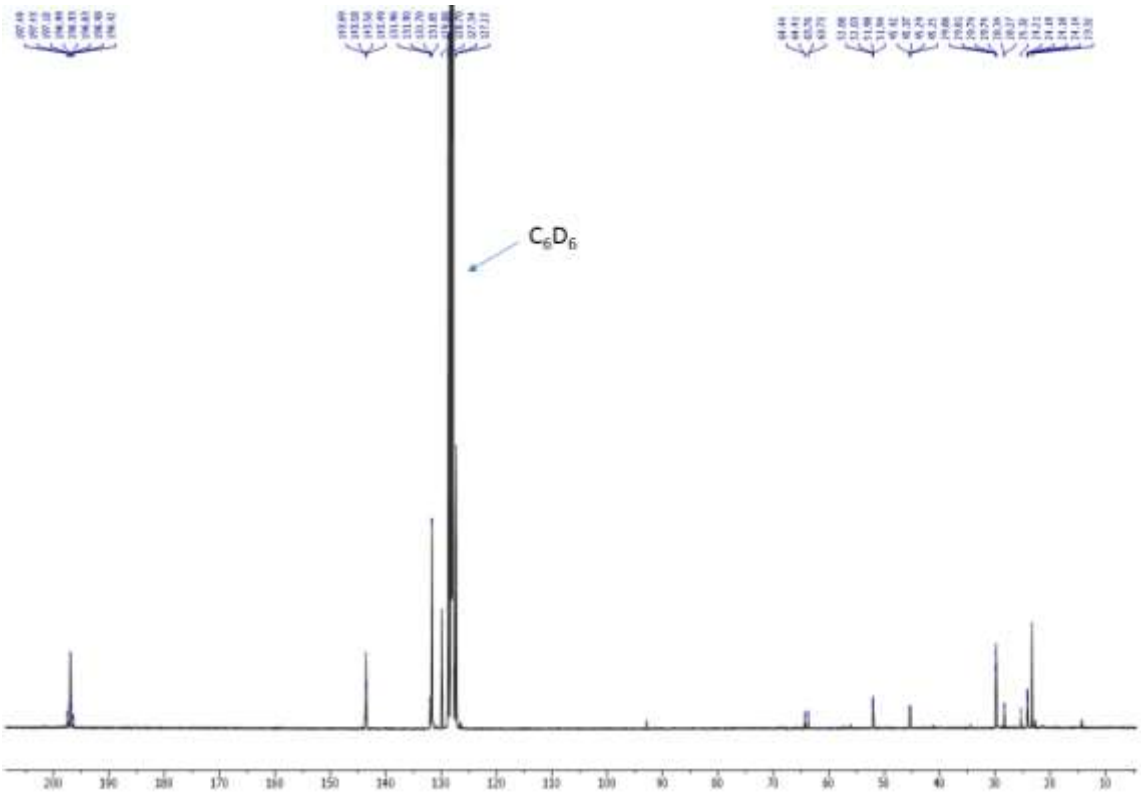



***Figure S 11***. *$^{13}C\{^{1}H\}$ NMR spectrum of the isomeric mixture of **cis-4c** and **trans-4c** in $C_6D_6$.*

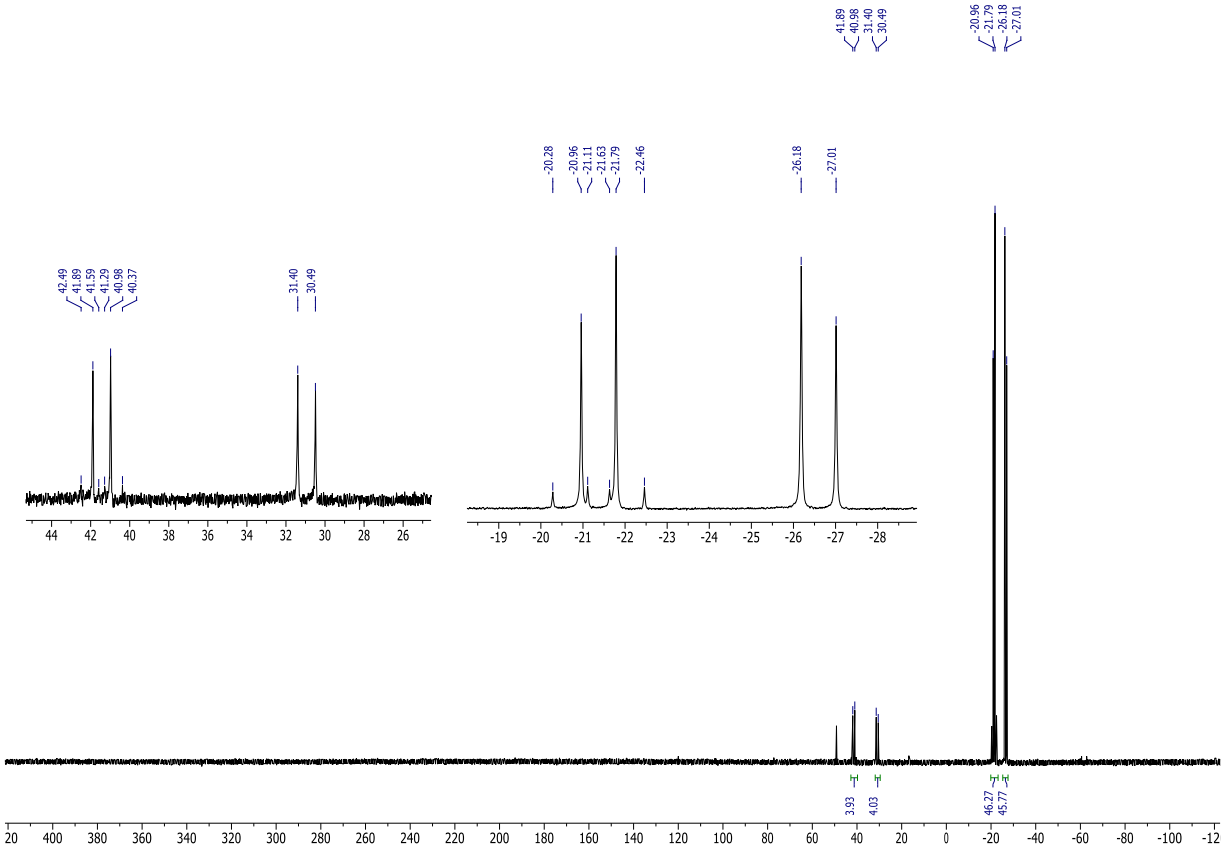



***Figure S 12***. *$^{31}P\{^{1}H\}$ NMR spectrum of the isomeric mixture of **cis-4c** and **trans-4c** in $C_6D_6$.*

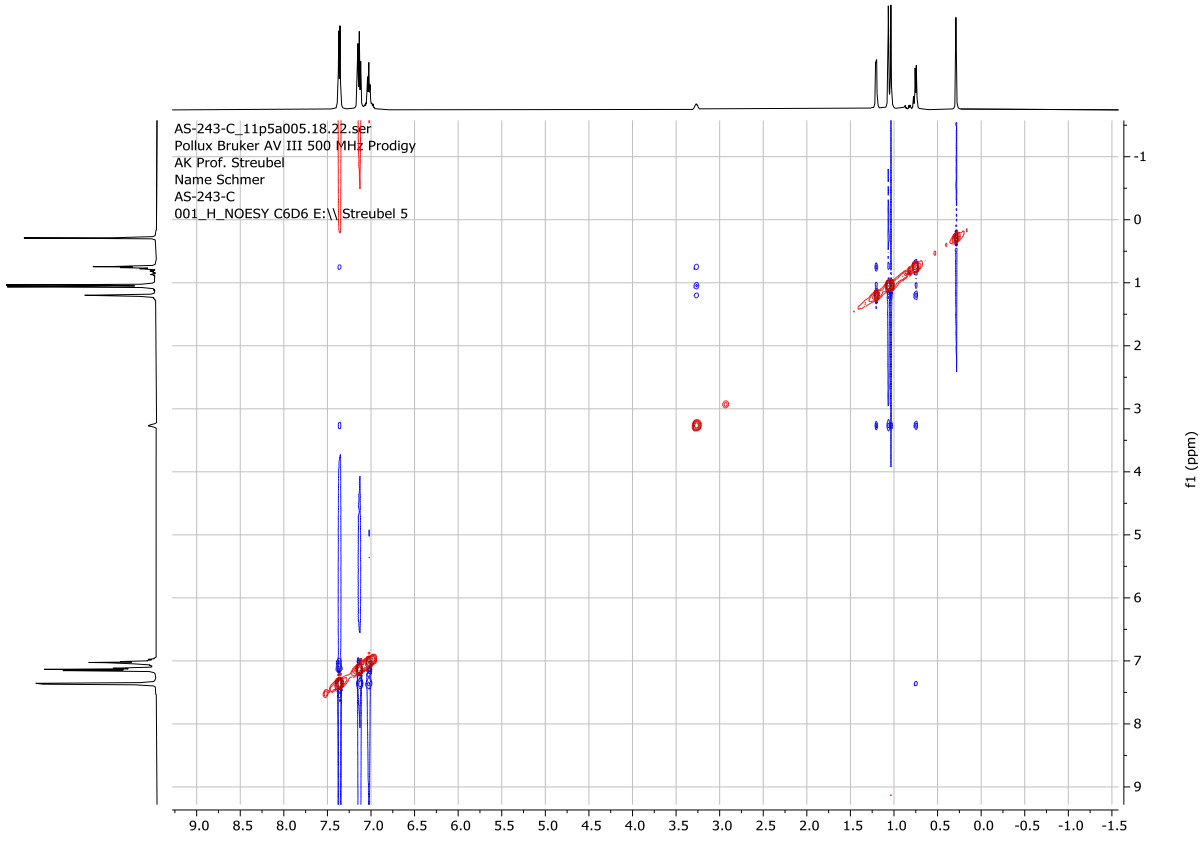



***Figure S 13***. *NOESY NMR spectrum of the isomeric mixture of **cis-4c** and **trans-4c** in $C_6D_6$.*

## 5. Crystallographic Data for 3a and 4b

Data of **3a** were collected with a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device at 100 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical formula: $C_{33}H_{36}N_2O_5P_2W$ formula weight M = 786.43 g·mol$^{-1}$, crystal system triclinic, space group $P\bar{1}$, unit cell dimensions a = 10.5675(6) Å, b = 16.9702(11) Å, c = 18.6599(10) Å, α = 100.746(4) °, β = 90.409(3) °, γ = 97.893(4) °, volume V = 3254.7(3) Å$^3$, Z = 4, calculated density $\rho_{calcd.}$ = 1.605 g·cm$^{-3}$, absorption coefficient μ = 3.690 mm$^{-1}$, crystal size 0.09 × 0.09 × 0.04 mm, transmission factors (min/max) 0.6152/ 0.7461, 2Θ range for data collection 3.62 to 55.998 °, completeness to theta 0. 997, reflections collected 139084, independent reflections 15651 [$R_{int}$ = 0.0979, $R_{sigma}$ = 0.0590], Goodness-of-fit on $F^2$ 1.027, final R indexes [I>=2σ (I)] $R_1$ = 0.0352, $wR_2$ = 0.0668, final R indexes [all data] $R_1$ = 0.0584, $wR_2$ = 0.0749, largest diff. peak and hole 1.31/-1.52 e A$^{-3}$. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures (CCDC 2091682).

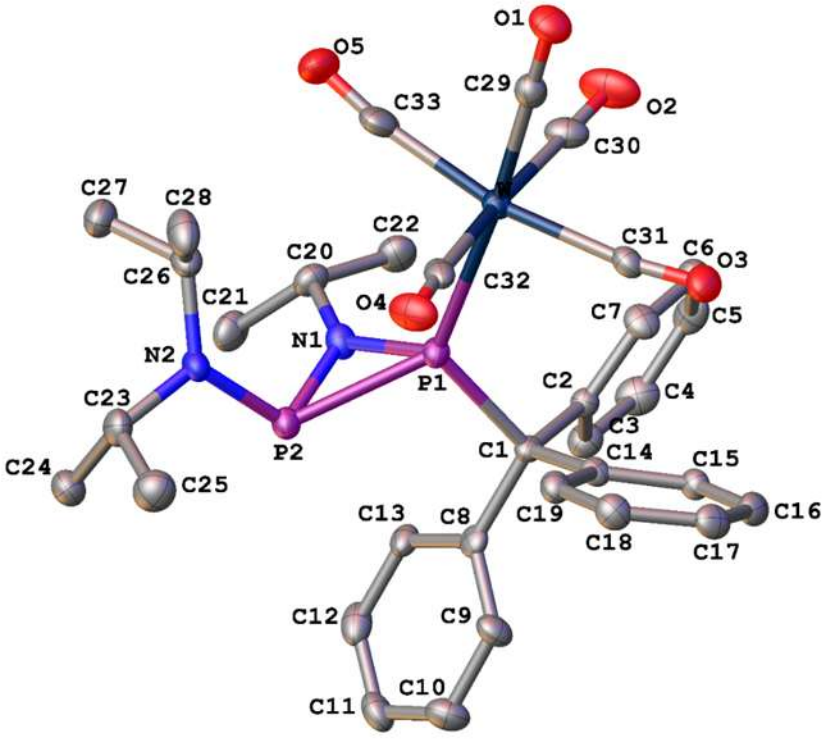



***Figure S 14**. Molecular structure of trans-**3a**. All hydrogen atoms are omitted for clarity. The thermal ellipsoids are set at 50 % probability.*

Data of **4b** were collected with a Bruker X8-KappaApexII diffractometer equipped with a low-temperature device at 100 K by using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Empirical formula: $C_{70}H_{64}N_2O_{11}P_4W_2$ (=2 molecules and 1 $Et_2O$), formula weight M = 1600.81 g·mol$^{-1}$, crystal system triclinic, space group $P\bar{1}$, unit cell dimensions a = 9.2415(5) Å, b = 13.4694(8) Å, c = 14.4358(8) Å, α = 86.110(4) °, β = 76.077(3) °, γ = 72.024(4) °,

volume V = 1658.41(17) $Å^3$, Z = 1, calculated density $\rho_{calcd.}$ = 1.603 $g \cdot cm^{-3}$, absorption coefficient $\mu$ = 3.623 $mm^{-1}$, crystal size 0.22 × 0.09 × 0.05 mm, transmission factors (min/max) 0.4717/ 0.7461, 2Θ range for data collection 6.362 to 55.998°, completeness to theta 0.997, reflections collected 50896, independent reflections 7983 [$R_{int}$ = 0.0574, $R_{sigma}$ = 0.0402], Goodness-of-fit on $F^2$ 1.022, final R indexes [I>=2σ (I)] $R_1$ = 0.0260, $wR_2$ = 0.0528, final R indexes [all data] $R_1$ = 0.0357, $wR_2$ = 0.0569, largest diff. peak and hole 1.55/-1.30 e $A^{-3}$. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures (CCDC 2091683)

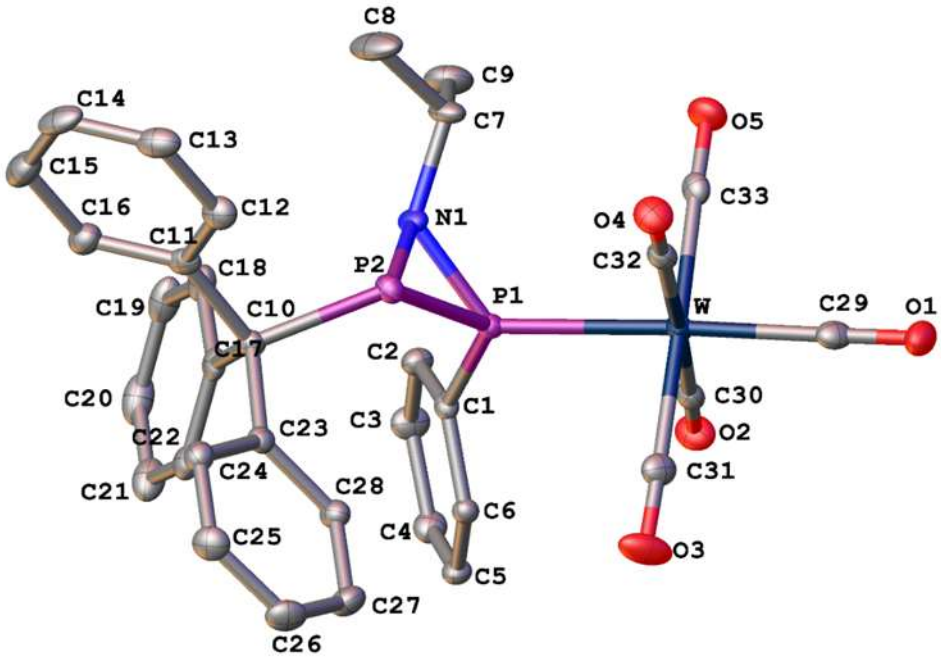



***Figure S 15****. Molecular structure of* ***cis-4b****. All hydrogen atoms are omitted for clarity. The thermal ellipsoids are set at 50 % probability.*

## 6. Computational Details

Quantum chemical calculations were performed with the ORCA electronic structure program package (version 4.2.1).[2] For the mechanistic study, all geometry optimizations were run in redundant internal coordinates with tight convergence criteria using Grimme's dispersion-corrected composite PBEh-3c level. Compounds ***trans*-3a**, ***cis*/*trans*-4b**, ***cis*/*trans*-4c**, **8'e-g** and **8''e-g** were further re-optimized using the B3LYP functional[3][4] with the D3 dispersion correction[5][6] and the def2-TZVP basis set[7][8] together with the powerful speeding up RIJCOSX algorithm.[9] Solvent (toluene) effects were taken into consideration with the CPCM solvation method as implemented in ORCA. Harmonic frequency calculations verified the nature of ground states or transition states (TS) having all positive frequencies or only one imaginary frequency, respectively. TS structures were confirmed by following the intrinsic reaction path in both directions of the negative eigenvector. From these optimized geometries, all reported data were obtained by means of single point (SP) calculations using the hybrid-meta-GGA PW6B95[10] functional with the D4 dispersion correction,[11][12] the def2-QZVP basis set[8] and speeding up the calculation by means of the RI-JK approach.[13] For W atoms, the def2-ECP(28] effective core potential (ECP) was used in all cases.[14] The rest of the compounds **9a-d** were optimized in the gas phase at the B3LYP-D4/def2-TZVP level of theory. Ring strain energies (RSEs) were obtained by means of the linear scaling-domain-based local pair natural orbital (DLPNO) method to achieve coupled cluster theory with single-double and perturbative triple excitations (CCSD(T)) using the more polarized def2-TZVPP basis set. Wiberg bond indices (WBI) were obtained from the natural bond orbital (NBO) population analysis.[15,16] The topological analysis of the electronic charge density, ρ(r), within Bader's atoms-in-molecules (AIM) theory,[17,18] was conducted by using the Multiwfn software.[19] Figure S17 was plotted with Chimera[20] and Figure S18 with Aimall.[21]

## 7. Base-free formation of azadiphosphiridine complex 3d'$_N$·H$^+$

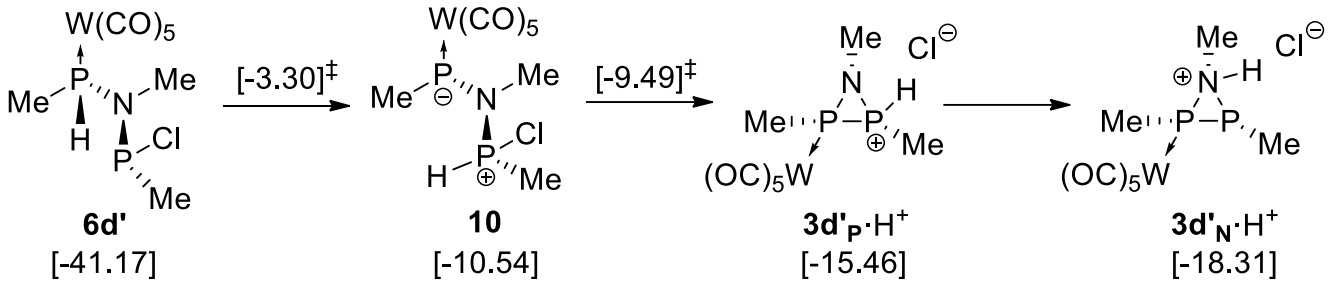



***Figure S 16**. Formation of azadiphosphiridine complex **3d'$_N$**·H$^+$ via transprotonation of **6d'**.*

## 8. Detailed analysis of the P-W bonds

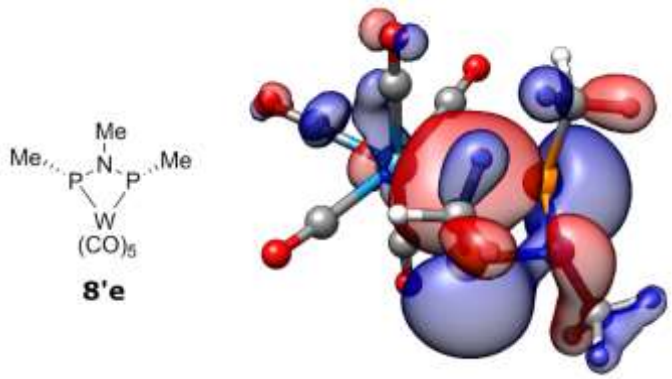



***Figure S 17**. Kohn-Sham isosurface (0.03 au) of HOMO-4 for **8'e** at the CPCMtol/B3LYP-D3/def2-TZVP(ecp) level of theory.*

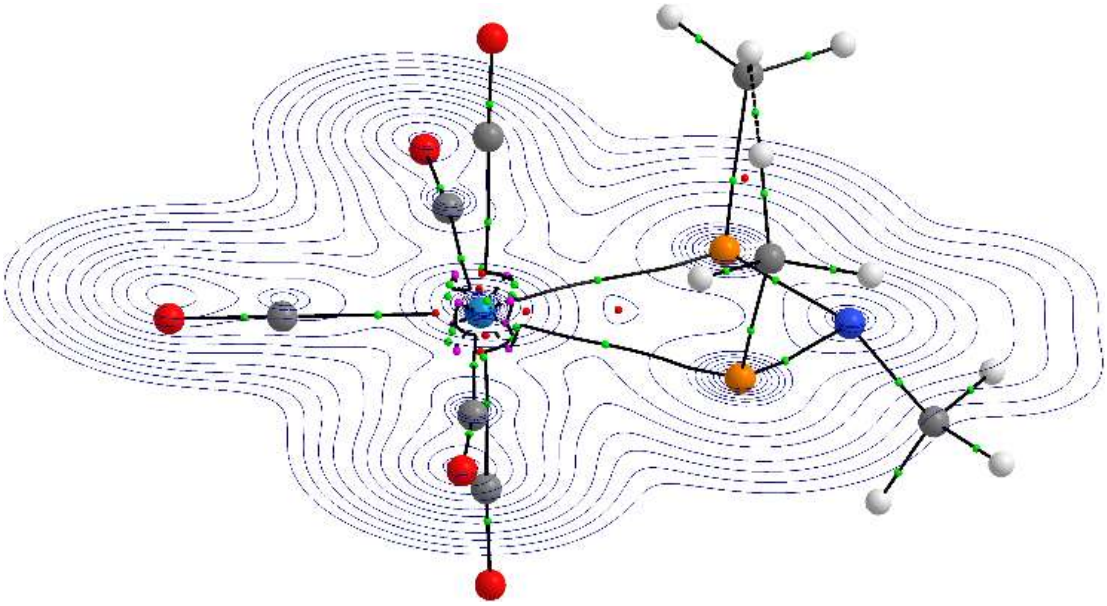


***Figure S 18**. Computed (CPCM$_{tol}$/RIJCOSX-B3LYP-D3/def2-TZVP) structure for **8'e** highlighting with small spheres BCP (green), RCP (red) and non-attractive atomic critical points around the W atom (pink), as well as bond paths (black lines). An electron isodensity contour map in the plane formed by the two P atoms and the chelate RCP is also depicted.*

In the central part of the W-P bond path (Figure S15), the $\nabla^2\rho$ function displays a pronounced minimum corresponding to a valence-shell charge concentration VSCC$_P$ owing to the electron-donating atom (in this case the P atom), and another shoulder VSCC$_W$ corresponding to the accepting W atom. Both are located within the basin of the donor atom (an inflection point for the transition between VSCC$_W$ and VSCC$_P$ can be envisaged in the positive side of the bond path), which is a signature of dative bonds. The same holds for precursor **3'e** (Figure S15) with

$VSCC_W$ roughly located at the interbasins border. All of this aside, the comparatively higher $\nabla^2\rho$ value for chelate **8'e** indicates an increased P-W covalent bond character, only the vanishing value displayed by **3'e** fully confirming its dative bonding character. The relatively large P-W bond lengths ($d_{P-W}$ = 2.842, 2.847 Å) and smaller bond orders ($WBI_{P-W}$ = 0.511, 0.507) in **8'e** compared to the **3'e** precursor ($d_{P-W}$ = 2.516 Å, $WBI_{P-W}$ = 0.772) could arise from either steric crowding at the metal center and higher p character (89.01 and 89.07%) of the P atomic orbitals (engaged in hetero-allylic P-N-P system) in binding to W. In contrast, **3'e** displays a more compact lone pair with high s character (44.43%). The higher P-W bond distances in **8'e** may also arise from the low population of σ(P-W) bonds (1.55e) due to a high electronic transfer to the corresponding σ*(P-W) with asso-ciated energy of $E_{SOPT}$ = 194.11 and 192.69 kcal $mol^{-1}$, as obtained from the second-order perturbation theory (SOPT) of Fock matrix in the natural bond orbital (NBO) basis.

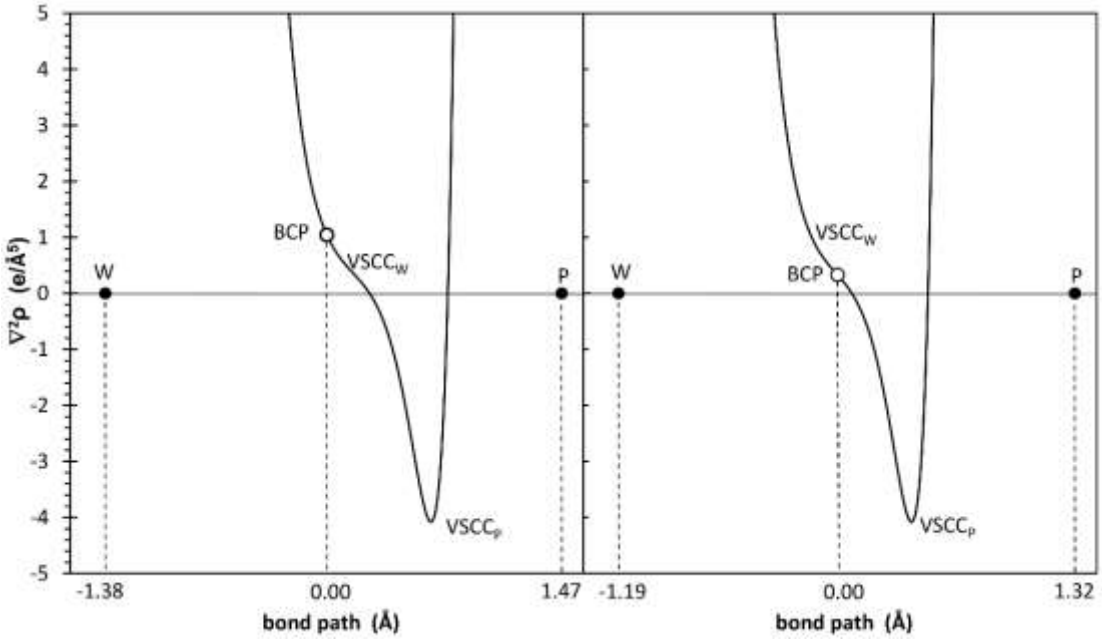
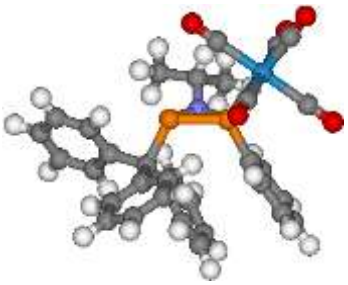



***Figure S 19**. Computed (B3LYP-D3/def2-TZVPecp) variation of the Laplacian of electron density $\nabla^2\rho$ for **8'e** (left) and **3'e** (right) along the W-P bond paths*

## 9. Calculated structures

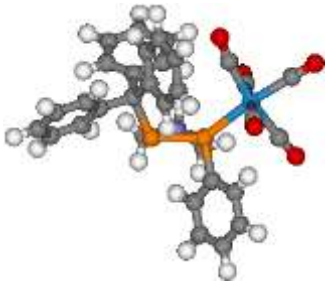
Cartesian coordinates (in Å), G correction (G-E) and zero-point energy (ZPE) correction (in hartrees) for minima and transition states were computed at $CPCM_{tol}$/PBEh-3c(ecp) whereas electronic energies (in hartrees) were quoted at the $CPCM_{tol}$/PW6B95-D4/def2-QZVP(ecp) level unless otherwise stated. In some cases, where explicitly indicated, geometries and ZPE were obtained at the $CPCM_{tol}$/B3LYP-D4/def2-TZVP and electronic energies at the DLPNO-CCSD(T)/def2-TZVPP level of theory. Imaginary frequencies were obtained upon frequency calculation (at the optimization level).



***Cis*-4b:** E = -2454.360340622169 au ($CPCM_{tol}$/B3LYP-D4/def2-TZVP)
P-P = 2.168 Å; P-C(Trt) = 1.942 Å; P-W = 2.518 Å

| | | | | | |
|---|---|---|---|---|---|
| W | 3.402888 | 6.405932 | 2.188248 |
| P | 4.982415 | 4.677731 | 3.115735 |
| P | 4.250464 | 2.662979 | 3.442559 |
| O | 1.359001 | 8.603175 | 1.141888 |
| O | 5.375523 | 8.702207 | 3.253730 |
| O | 1.924048 | 6.287795 | 5.034158 |
| O | 1.495463 | 4.079989 | 1.069929 |
| O | 4.919481 | 6.490810 | -0.638541 |
| N | 5.444001 | 3.250248 | 2.312366 |
| C | 6.354233 | 5.267338 | 4.132583 |
| C | 7.669026 | 5.211498 | 3.679213 |
| H | 7.904923 | 4.679499 | 2.769582 |
| C | 8.677222 | 5.831420 | 4.404499 |
| H | 9.698308 | 5.783512 | 4.048634 |
| C | 8.381250 | 6.500749 | 5.585390 |
| H | 9.171259 | 6.980338 | 6.149275 |
| C | 7.069039 | 6.553055 | 6.043627 |
| H | 6.832597 | 7.071733 | 6.963892 |
| C | 6.056846 | 5.947600 | 5.314795 |
| H | 5.035571 | 6.016349 | 5.667125 |
| C | 5.464997 | 3.009662 | 0.857387 |
| H | 4.598155 | 3.501155 | 0.398851 |
| C | 5.364282 | 1.515513 | 0.584651 |
| H | 6.230904 | 0.983916 | 0.981927 |
| H | 5.317786 | 1.337743 | -0.490615 |
| H | 4.465430 | 1.090757 | 1.035174 |
| C | 6.733003 | 3.618611 | 0.274376 |
| H | 6.801347 | 4.683130 | 0.502184 |
| H | 6.740711 | 3.510007 | -0.811478 |
| H | 7.615967 | 3.122374 | 0.681982 |
| C | 5.191367 | 1.646663 | 4.803722 |
| C | 4.978839 | 0.194466 | 4.339323 |
| C | 3.685367 | -0.234948 | 4.015297 |
| H | 2.854088 | 0.453174 | 4.087939 |
| C | 3.434988 | -1.541221 | 3.622424 |
| H | 2.424038 | -1.839269 | 3.374166 |
| C | 4.473567 | -2.463973 | 3.558366 |
| H | 4.282176 | -3.484694 | 3.252380 |
| C | 5.755286 | -2.062212 | 3.908114 |
| H | 6.572526 | -2.772609 | 3.888354 |
| C | 6.004201 | -0.748886 | 4.294790 |
| H | 7.008134 | -0.472401 | 4.576892 |
| C | 6.652991 | 2.025231 | 4.941775 |
| C | 7.547122 | 1.797465 | 3.890349 |
| H | 7.188883 | 1.372012 | 2.967251 |
| C | 8.897909 | 2.080042 | 4.019804 |
| H | 9.566425 | 1.881692 | 3.190937 |
| C | 9.391071 | 2.617299 | 5.202696 |
| H | 10.445357 | 2.841266 | 5.305444 |
| C | 8.512616 | 2.877193 | 6.244662 |
| H | 8.875696 | 3.311138 | 7.167597 |
| C | 7.160604 | 2.583921 | 6.114954 |
| H | 6.501226 | 2.789034 | 6.944849 |
| C | 4.406643 | 1.876145 | 6.100098 |
| C | 4.278408 | 0.843466 | 7.032022 |
| H | 4.699021 | -0.128724 | 6.816316 |

| | | |
|---|---|---|
| C | 3.621785 | 1.045048 | 8.238146 |
| H | 3.542103 | 0.228655 | 8.945129 |
| C | 3.065151 | 2.284477 | 8.537853 |
| H | 2.544429 | 2.438528 | 9.474419 |
| C | 3.183589 | 3.320129 | 7.621469 |
| H | 2.757268 | 4.292166 | 7.835316 |
| C | 3.852269 | 3.115104 | 6.419908 |
| H | 3.945613 | 3.941882 | 5.733786 |
| C | 2.098939 | 7.809165 | 1.518462 |
| C | 4.668998 | 7.884571 | 2.879134 |
| C | 2.442816 | 6.339814 | 4.014378 |
| C | 2.177873 | 4.903892 | 1.477348 |
| C | 4.383785 | 6.449801 | 0.372704 |



***Trans*-4b:** E = -2454.353936777287 au ($CPCM_{tol}$/B3LYP-D4/def2-TZVP)

P-P = 2.211 Å; P-C(Trt) = 1.967 Å; P-W = 2.559 Å

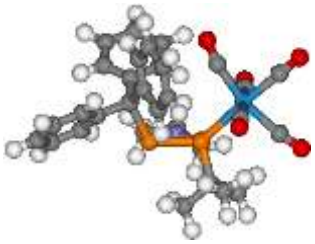
| | | | |
|---|---|---|---|
| W | 2.983084 | 5.964059 | 3.809204 |
| P | 4.888316 | 4.299660 | 3.425695 |
| P | 5.252769 | 2.121651 | 3.308785 |
| O | 0.894160 | 8.323362 | 4.129381 |
| O | 5.057802 | 8.316792 | 3.155173 |
| O | 3.592176 | 5.964257 | 6.961159 |
| O | 0.420199 | 4.129309 | 4.386060 |
| O | 2.282844 | 5.722889 | 0.691959 |
| N | 4.995685 | 3.300337 | 2.086046 |
| C | 6.573618 | 4.920183 | 3.785840 |
| C | 7.689054 | 4.424512 | 3.106342 |
| H | 7.562283 | 3.690670 | 2.323720 |
| C | 8.964871 | 4.864851 | 3.428412 |
| H | 9.818392 | 4.477923 | 2.886044 |
| C | 9.147384 | 5.796696 | 4.445489 |
| H | 10.143066 | 6.140063 | 4.695988 |
| C | 8.045850 | 6.282933 | 5.139396 |
| H | 8.177376 | 7.004296 | 5.935738 |
| C | 6.768285 | 5.848437 | 4.809725 |
| H | 5.925048 | 6.241423 | 5.358227 |
| C | 5.038439 | 3.403039 | 0.621270 |
| H | 4.006005 | 3.426162 | 0.264084 |
| C | 5.708472 | 2.166195 | 0.040418 |
| H | 6.739691 | 2.076068 | 0.389533 |
| H | 5.718067 | 2.228192 | -1.048611 |
| H | 5.164565 | 1.262129 | 0.317480 |
| C | 5.720645 | 4.694471 | 0.184781 |
| H | 5.283310 | 5.562304 | 0.680719 |
| H | 5.590992 | 4.829340 | -0.890191 |
| H | 6.788537 | 4.679081 | 0.403571 |
| C | 3.641682 | 1.026146 | 3.577315 |
| C | 4.281794 | -0.330366 | 3.892827 |
| C | 5.240793 | -0.871269 | 3.026413 |
| H | 5.513491 | -0.341673 | 2.122995 |
| C | 5.848759 | -2.090100 | 3.287959 |
| H | 6.583577 | -2.480779 | 2.595241 |
| C | 5.517223 | -2.803261 | 4.435097 |
| H | 5.991488 | -3.753562 | 4.645132 |
| C | 4.573971 | -2.279264 | 5.308083 |
| H | 4.304714 | -2.820515 | 6.206543 |
| C | 3.966754 | -1.055651 | 5.041597 |
| H | 3.239586 | -0.672333 | 5.741201 |
| C | 2.799846 | 1.498778 | 4.760192 |
| C | 3.357232 | 2.178448 | 5.842665 |
| H | 4.402402 | 2.455491 | 5.832714 |
| C | 2.594763 | 2.502348 | 6.957962 |
| H | 3.050925 | 3.042944 | 7.777431 |
| C | 1.257261 | 2.133010 | 7.021639 |
| H | 0.660727 | 2.385428 | 7.889094 |
| C | 0.693263 | 1.439374 | 5.958159 |
| H | -0.348350 | 1.145516 | 5.991664 |
| C | 1.456217 | 1.130402 | 4.840356 |
| H | 0.999881 | 0.591769 | 4.021234 |
| C | 2.831087 | 1.020885 | 2.289103 |
| C | 2.670302 | -0.105281 | 1.482911 |
| H | 3.122402 | -1.044491 | 1.763221 |
| C | 1.915319 | -0.048082 | 0.314684 |
| H | 1.805750 | -0.939761 | -0.290145 |
| C | 1.300505 | 1.134994 | -0.070032 |
| H | 0.714884 | 1.179143 | -0.979548 |
| C | 1.436014 | 2.261642 | 0.735863 |
| H | 0.955602 | 3.191180 | 0.458630 |
| C | 2.189070 | 2.198024 | 1.895966 |
| H | 2.281031 | 3.076257 | 2.513521 |

| | | | | | |
|---|---|---|---|---|---|
| C | 1.643422 | 7.459148 | 4.016430 | C | 1.392288 4.697600 4.193916 |
| C | 4.354758 | 7.447017 | 3.398973 | C | 2.543021 5.818047 1.802985 |
| C | 3.389406 | 5.975143 | 5.834725 | | |

***Cis*-4c:** E = -2380.552057280566 au ($CPCM_{tol}$/B3LYP-D4/def2-TZVP)

P-P = 2.181 Å; P-C(Trt) = 1.960 Å; P-W = 2.562 Å

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| W | 3.269295 | 6.120470 | 2.052161 | C | 9.513887 | 1.826710 | 5.607893 |
| P | 5.151490 | 4.816388 | 3.201285 | H | 10.583444 | 1.883124 | 5.766274 |
| P | 4.458374 | 2.795983 | 3.644510 | C | 8.636229 | 1.960929 | 6.674980 |
| O | 0.877568 | 7.607030 | 0.589363 | H | 9.016418 | 2.121806 | 7.676127 |
| O | 4.009009 | 9.001118 | 3.242341 | C | 7.262554 | 1.887910 | 6.469833 |
| O | 1.569621 | 5.504278 | 4.704157 | H | 6.603334 | 1.994051 | 7.318398 |
| O | 2.105691 | 3.434928 | 0.735734 | C | 4.440922 | 1.833828 | 6.240356 |
| O | 5.255643 | 6.580581 | -0.422379 | C | 4.062145 | 0.774102 | 7.067114 |
| N | 5.666371 | 3.336570 | 2.508986 | H | 4.295178 | -0.241345 | 6.778671 |
| C | 5.741179 | 3.008196 | 1.071352 | C | 3.395010 | 1.004334 | 8.262667 |
| H | 4.972339 | 3.580601 | 0.541245 | H | 3.117100 | 0.165733 | 8.888866 |
| C | 5.462379 | 1.528627 | 0.848127 | C | 3.081710 | 2.301813 | 8.654916 |
| H | 6.226659 | 0.902009 | 1.310661 | H | 2.552576 | 2.479933 | 9.582425 |
| H | 5.450313 | 1.314557 | -0.221349 | C | 3.452335 | 3.365193 | 7.842825 |
| H | 4.492646 | 1.241769 | 1.257995 | H | 3.215280 | 4.381593 | 8.130665 |
| C | 7.102360 | 3.432539 | 0.535701 | C | 4.128684 | 3.128809 | 6.651813 |
| H | 7.270923 | 4.498525 | 0.694784 | H | 4.420033 | 3.970649 | 6.041867 |
| H | 7.163319 | 3.242149 | -0.537376 | C | 1.741500 | 7.068392 | 1.123558 |
| H | 7.901976 | 2.881742 | 1.034728 | C | 3.784263 | 7.953724 | 2.833062 |
| C | 5.241412 | 1.575031 | 4.962920 | C | 2.153952 | 5.736938 | 3.748119 |
| C | 4.827576 | 0.227649 | 4.346342 | C | 2.558507 | 4.369979 | 1.217310 |
| C | 3.476241 | 0.002677 | 4.046177 | C | 4.530497 | 6.421195 | 0.450824 |
| H | 2.740339 | 0.760886 | 4.274160 | C | 6.559589 | 5.735706 | 4.042350 |
| C | 3.051935 | -1.187985 | 3.476700 | C | 7.075884 | 6.763654 | 3.020236 |
| H | 2.001886 | -1.327191 | 3.252214 | H | 7.861726 | 7.357451 | 3.494187 |
| C | 3.967408 | -2.198871 | 3.203427 | H | 7.510088 | 6.275745 | 2.146413 |
| H | 3.639598 | -3.129756 | 2.758346 | H | 6.302713 | 7.447913 | 2.679514 |
| C | 5.303248 | -2.004437 | 3.525309 | C | 5.959805 | 6.451370 | 5.260414 |
| H | 6.026834 | -2.789314 | 3.343119 | H | 5.701715 | 5.743428 | 6.048533 |
| C | 5.727639 | -0.805474 | 4.089735 | H | 6.698843 | 7.146623 | 5.666082 |
| H | 6.770594 | -0.692709 | 4.340273 | H | 5.069066 | 7.028689 | 5.012651 |
| C | 6.732867 | 1.684814 | 5.194012 | C | 7.716323 | 4.843229 | 4.467310 |
| C | 7.631692 | 1.546595 | 4.131234 | H | 8.511144 | 5.474680 | 4.873773 |
| H | 7.258508 | 1.385286 | 3.133884 | H | 7.424158 | 4.136934 | 5.237180 |
| C | 9.001077 | 1.614230 | 4.332855 | H | 8.121344 | 4.285450 | 3.626862 |
| H | 9.670681 | 1.506483 | 3.488396 | | | | |



***Trans*-4c:** E = -2380.552186888799 au ($CPCM_{tol}$/B3LYP-D4/def2-TZVP)

P-P = 2.217 Å; P-C(Trt) = 1.975 Å; P-W = 2.600 Å

| | | | | | |
|---|---|---|---|---|---|
| W | 3.093188 | 5.947500 | 3.793974 | | |
| P | 5.039974 | 4.282350 | 3.352387 | | |
| P | 5.250518 | 2.077512 | 3.259387 | | |
| O | 0.853125 | 8.147626 | 4.175621 | | |
| O | 4.869582 | 8.600334 | 3.753103 | | |
| O | 3.589574 | 5.747731 | 6.957855 | | |
| O | 0.486715 | 4.115105 | 4.082943 | | |
| O | 2.716513 | 5.985833 | 0.610918 | | |
| N | 5.082059 | 3.253817 | 2.020634 | | |
| C | 5.060247 | 3.279729 | 0.552535 | | |
| H | 4.031043 | 3.465686 | 0.236912 | | |
| C | 5.478683 | 1.918616 | 0.014157 | | |
| H | 6.491631 | 1.666254 | 0.335989 | | |
| H | 5.457786 | 1.932746 | -1.076262 | | |
| H | 4.796627 | 1.137609 | 0.349961 | | |
| C | 5.931191 | 4.399540 | 0.002348 | | |
| H | 5.637144 | 5.367522 | 0.408113 | | |
| H | 5.819158 | 4.448426 | -1.082187 | | |
| H | 6.984303 | 4.227546 | 0.231540 | | |
| C | 3.584994 | 1.061456 | 3.566754 | | |
| C | 4.195184 | -0.304557 | 3.904158 | | |
| C | 5.082283 | -0.912674 | 3.005772 | | |
| H | 5.308890 | -0.433320 | 2.062784 | | |
| C | 5.672453 | -2.135553 | 3.286215 | | |
| H | 6.350922 | -2.579239 | 2.568343 | | |
| C | 5.396051 | -2.785691 | 4.484725 | | |
| H | 5.857356 | -3.739028 | 4.709476 | | |
| C | 4.523532 | -2.195744 | 5.388154 | | |
| H | 4.296297 | -2.688093 | 6.325527 | | |
| C | 3.932902 | -0.967921 | 5.102108 | | |
| H | 3.260036 | -0.533576 | 5.825729 | | |
| C | 2.759301 | 1.568128 | 4.744225 | | |
| C | 3.339630 | 2.232948 | 5.823435 | | |
| H | 4.391911 | 2.481477 | 5.805368 | | |
| C | 2.592471 | 2.572049 | 6.944086 | | |
| H | 3.066520 | 3.095965 | 7.763581 | | |
| C | 1.244480 | 2.243059 | 7.011864 | | |
| H | 0.659832 | 2.509711 | 7.883160 | | |
| C | 0.656041 | 1.569420 | 5.949019 | | |
| H | -0.393916 | 1.307186 | 5.985150 | | |
| C | 1.406710 | 1.237082 | 4.829645 | | |
| H | 0.931655 | 0.712967 | 4.012056 | | |
| C | 2.756377 | 1.036207 | 2.289354 | | |
| C | 2.441032 | -0.137955 | 1.605273 | | |
| H | 2.798023 | -1.090195 | 1.967685 | | |
| C | 1.655533 | -0.109063 | 0.456934 | | |
| H | 1.426126 | -1.036730 | -0.052702 | | |
| C | 1.162100 | 1.093992 | -0.029305 | | |
| H | 0.553095 | 1.115918 | -0.924159 | | |
| C | 1.451058 | 2.270063 | 0.655619 | | |
| H | 1.066257 | 3.217648 | 0.299675 | | |
| C | 2.234544 | 2.233539 | 1.797096 | | |
| H | 2.449694 | 3.152000 | 2.316693 | | |
| C | 1.662360 | 7.341486 | 4.041933 | | |
| C | 4.315154 | 7.595535 | 3.738527 | | |
| C | 3.410829 | 5.805418 | 5.829326 | | |
| C | 1.489694 | 4.652024 | 3.974025 | | |
| C | 2.849668 | 5.983464 | 1.748721 | | |
| C | 6.792119 | 4.904731 | 3.757857 | | |
| C | 6.740731 | 5.371184 | 5.219997 | | |
| H | 6.096432 | 6.238100 | 5.355334 | | |
| H | 6.395327 | 4.578794 | 5.887712 | | |
| H | 7.746708 | 5.657072 | 5.537094 | | |
| C | 7.850076 | 3.806206 | 3.617720 | | |
| H | 7.721290 | 3.015039 | 4.354878 | | |
| H | 7.842092 | 3.354848 | 2.624879 | | |
| H | 8.837079 | 4.251638 | 3.770539 | | |
| C | 7.183907 | 6.072348 | 2.842143 | | |
| H | 8.068242 | 6.565475 | 3.255426 | | |
| H | 7.437234 | 5.722380 | 1.843956 | | |
| H | 6.405410 | 6.824018 | 2.747896 | | |

**1':** E = -1112.57710905017 au

ZPE = 0.14945781 au

$G_{corr}$ = 0.10291744 au

| | | | |
|---|---|---|---|
| P-5.929421-0.149701 | -1.190247 | C-3.2877970.027936 | -0.660913 |
| W-6.596389-2.136401 | 0.214774 | H-3.4587640.834339 | 0.052499 |
| C-4.972734-3.199377 | -0.468272 | H-3.235343-0.911053 | -0.099454 |
| O-4.079013-3.798740 | -0.849812 | H-2.3128920.203989 | -1.112659 |
| C-7.705131-2.830101 | -1.373576 | C-6.3280401.491817 | -0.498036 |
| O-8.317099-3.203841 | -2.261125 | H-5.9881432.284809 | -1.161914 |
| C-5.484505-1.396832 | 1.777994 | H-7.4056821.571651 | -0.360564 |
| O-4.873952-0.983249 | 2.650095 | H-5.8594131.610763 | 0.477923 |
| C-8.231189-1.087629 | 0.890866 | H-6.550405-0.064338 | -2.449720 |
| O-9.141328-0.511430 | 1.268654 | N-4.3034830.054884 | -1.700205 |
| C-7.157573-3.726477 | 1.333059 | H-4.077506-0.586372 | -2.449886 |
| O-7.478192-4.625572 | 1.965103 | | |

**2d:** E = -1302.88042443607 au

ZPE = 0.04217587 au

$G_{corr}$ = 0.01228486 au

| | | | |
|---|---|---|---|
| Cl-7.1338592.849909 | -3.956431 | H-4.9735522.869574 | -1.655360 |
| P-5.5771701.537435 | -3.566229 | H-3.5491652.170139 | -2.436111 |
| Cl-4.5559551.584990 | -5.369769 | H-4.3236123.610415 | -3.136200 |
| C-4.5007112.670518 | -2.617355 | | |

KHMDS**:** E = -1474.8421058666 au

ZPE = 0.23276744 au

$G_{corr}$ = 0.19016236 au

| | | | |
|---|---|---|---|
| N-3.7373600.949432 | -5.268131 | H-0.4408912.503058 | -6.796434 |
| Si-5.2098421.576956 | -5.787566 | H-1.4785561.329288 | -7.605593 |
| Si-2.1909751.610150 | -5.207675 | C-5.8137173.115810 | -4.846301 |
| K-3.861064-1.439228 | -4.411782 | H-5.8635652.932911 | -3.770538 |
| C-1.9977543.112165 | -4.056455 | H-5.1340383.958128 | -4.994847 |
| H-0.9635063.461033 | -4.001622 | H-6.8058783.437205 | -5.172912 |
| H-2.6062413.951171 | -4.401764 | C-5.2873112.037139 | -7.631725 |
| H-2.3220362.881294 | -3.039181 | H-6.2823522.375225 | -7.931725 |
| C-0.9776940.293343 | -4.532541 | H-4.5863732.841981 | -7.864707 |
| H-1.238790-0.025256 | -3.517482 | H-5.0216361.189523 | -8.267518 |
| H-0.942911-0.597135 | -5.169311 | C-6.5710220.256889 | -5.533690 |
| H0.044760 0.674204 | -4.479987 | H-6.674525-0.025706 | -4.480578 |
| C-1.4711712.149220 | -6.883938 | H-7.5515470.616460 | -5.853802 |
| H-2.0578992.961623 | -7.318967 | H-6.372701-0.652862 | -6.110541 |

TS(**1'+**KHMDS→**5'**)**:** E = -2587.43311630999 au

ZPE = 0.37916186 au

$G_{corr}$ = 0.31367198 au

ν = -1216.75 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| P | -5.893762 | -0.166178 | -1.194616 | H | -2.211950 | 3.973192 | -2.603413 |
| W | -6.608246 | -2.146362 | 0.238833 | H | -3.907452 | 3.629062 | -2.937123 |
| C | -5.011499 | -3.073860 | -0.602613 | H | -3.057949 | 2.723813 | -1.695156 |
| O | -4.102778 | -3.538038 | -1.136554 | C | -0.739316 | 1.228883 | -3.526170 |
| C | -7.784131 | -2.775879 | -1.325440 | H | -0.733127 | 0.731445 | -2.552403 |
| O | -8.431680 | -3.116946 | -2.201816 | H | -0.382770 | 0.508776 | -4.267627 |
| C | -5.460941 | -1.471040 | 1.806797 | H | 0.001926 | 2.029338 | -3.473009 |
| O | -4.839080 | -1.103012 | 2.691660 | C | -2.247456 | 2.822112 | -5.620757 |
| C | -8.203930 | -1.059496 | 0.977577 | H | -3.185258 | 3.259950 | -5.968941 |
| O | -9.080799 | -0.447051 | 1.372988 | H | -1.537419 | 3.642266 | -5.491458 |
| C | -7.122544 | -3.780777 | 1.307838 | H | -1.866607 | 2.183894 | -6.419294 |
| O | -7.407341 | -4.716064 | 1.906750 | C | -6.243213 | 1.505788 | -5.154847 |
| C | -3.314795 | 0.046925 | -0.631222 | H | -6.718601 | 1.503884 | -4.171602 |
| H | -3.414941 | 0.980631 | -0.062496 | H | -5.905998 | 2.527694 | -5.344134 |
| H | -3.299844 | -0.769185 | 0.102039 | H | -7.013827 | 1.273970 | -5.893266 |
| H | -2.314405 | 0.084859 | -1.075546 | C | -4.138808 | 0.316507 | -7.010636 |
| C | -6.378129 | 1.500120 | -0.590230 | H | -4.887678 | -0.097912 | -7.689899 |
| H | -6.029854 | 2.269645 | -1.279540 | H | -3.904272 | 1.320918 | -7.363121 |
| H | -7.462088 | 1.567013 | -0.496052 | H | -3.233700 | -0.285875 | -7.115913 |
| H | -5.942619 | 1.682674 | 0.391771 | C | -5.487636 | -1.459906 | -4.997110 |
| H | -6.535138 | -0.153306 | -2.448098 | H | -5.775133 | -1.689612 | -3.967945 |
| N | -3.594042 | 0.594132 | -4.032125 | H | -6.387873 | -1.590717 | -5.601458 |
| Si | -4.787114 | 0.298538 | -5.232469 | H | -4.788709 | -2.232132 | -5.335913 |
| Si | -2.459526 | 1.888749 | -3.989357 | N | -4.300828 | -0.134038 | -1.672487 |
| K | -2.857770 | -1.935831 | -3.174474 | H | -4.011785 | 0.340634 | -2.828110 |
| C | -2.948424 | 3.170856 | -2.684863 | | | | |

**5'**: E = -1712.37813185956 au

ZPE = 0.13641272 au

$G_{corr}$ = 0.08756568 au

| | | | | | |
|---|---|---|---|---|---|
| P | -5.826012 | -0.156375 | -1.197515 | O | -7.433477 | -4.699248 | 1.924601 |
| W | -6.577826 | -2.148287 | 0.261588 | C | -3.292441 | 0.000504 | -0.617958 |
| C | -4.972218 | -3.078621 | -0.545076 | H | -3.281636 | 0.956566 | -0.072533 |
| O | -4.062668 | -3.543565 | -1.082501 | H | -3.382855 | -0.781025 | 0.157199 |
| C | -7.702129 | -2.761588 | -1.337146 | H | -2.275537 | -0.098846 | -1.022265 |
| O | -8.316439 | -3.087550 | -2.245671 | C | -6.416274 | 1.474449 | -0.567203 |
| C | -5.465858 | -1.450947 | 1.847600 | H | -6.095613 | 2.275249 | -1.234341 |
| O | -4.870096 | -1.069132 | 2.745334 | H | -7.503745 | 1.489237 | -0.489413 |
| C | -8.189753 | -1.049398 | 0.941981 | H | -6.002849 | 1.658951 | 0.424347 |
| O | -9.079780 | -0.433277 | 1.303482 | H | -6.515526 | -0.175172 | -2.428863 |
| C | -7.125680 | -3.768194 | 1.326747 | K | -3.194206 | -1.847164 | -3.213517 |

N-4.264721-0.076361 -1.682117

HMDS**:** E = -875.049890427244 au

ZPE = 0.24447833 au

$G_{corr}$ = 0.20311313 au

| | | | |
|---|---|---|---|
| N-3.7454070.904902 | -5.156365 | H-1.3962810.394548 | -7.351861 |
| Si-5.2807311.607067 | -5.599304 | C-5.9198892.791312 | -4.278312 |
| Si-2.1368001.572026 | -5.274528 | H-6.0525682.285305 | -3.320197 |
| C-2.1638893.392228 | -4.787909 | H-5.2275143.619619 | -4.116037 |
| H-1.1621853.823460 | -4.841479 | H-6.8836603.221714 | -4.558857 |
| H-2.8021703.988040 | -5.443266 | C-5.1020822.559100 | -7.215431 |
| H-2.5269943.524854 | -3.767428 | H-6.0572022.993848 | -7.517108 |
| C-1.0266260.607971 | -4.098487 | H-4.3889933.381965 | -7.136314 |
| H-1.3631230.697483 | -3.064313 | H-4.7643951.908892 | -8.024124 |
| H-1.003381-0.454776 | -4.348064 | C-6.5165560.202717 | -5.812652 |
| H0.001653 0.971343 | -4.142358 | H-6.628025-0.377571 | -4.894425 |
| C-1.4442421.434348 | -7.023052 | H-7.5049480.585444 | -6.073340 |
| H-2.0626521.975061 | -7.742042 | H-6.211142-0.484704 | -6.603171 |
| H-0.4346171.845988 | -7.086464 | H-3.795826-0.027381 | -4.768258 |

**6d':** E = -1954.26539044336 au

ZPE = 0.18043921 au

$G_{corr}$ = 0.12819286 au

| | | | |
|---|---|---|---|
| W-5.980192-2.445474 | 2.647410 | H-2.086830-0.987678 | 1.513986 |
| C-4.105271-3.244569 | 2.317342 | C-5.8106711.247453 | 2.318814 |
| O-3.080866-3.717177 | 2.157832 | H-5.6204562.110744 | 1.683602 |
| C-6.610375-3.230300 | 0.847005 | H-6.8554061.249091 | 2.629447 |
| O-6.957447-3.658163 | -0.150549 | H-5.1967271.318153 | 3.216155 |
| C-5.323280-1.626095 | 4.411565 | N-3.859803-0.055465 | 0.819147 |
| O-4.951957-1.166207 | 5.389104 | P-3.641657-0.185393 | -0.853041 |
| C-7.864310-1.703981 | 2.994665 | C-2.0219720.634345 | -1.080454 |
| O-8.913589-1.300941 | 3.195059 | H-2.1382831.698257 | -0.869394 |
| C-6.501513-4.154404 | 3.600485 | H-1.2276640.226956 | -0.457739 |
| O-6.805839-5.116159 | 4.140079 | H-1.7318630.524801 | -2.124671 |
| C-2.756741-0.166296 | 1.770427 | Cl-2.949019-2.180670 | -1.091378 |
| H-2.1838390.759642 | 1.808924 | P-5.451476-0.312416 | 1.440228 |
| H-3.133615-0.359778 | 2.774974 | H-6.162724-0.110989 | 0.243138 |

**6d'':** E = -1954.26351585103 au

ZPE = 0.1804005 au

$G_{corr}$ = 0.12866017 au

| | | | |
|---|---|---|---|
| P-6.050299-0.691524 | -0.257138 | H-3.533552-1.135952 | 1.203070 |
| W-6.693163-2.556857 | 1.296457 | H-2.484182-0.129833 | 0.204599 |
| C-4.879964-3.517481 | 1.061351 | C-6.6318130.985380 | 0.178446 |
| O-3.891903-4.074054 | 0.950828 | H-6.3100711.719510 | -0.558294 |
| C-7.404415-3.573528 | -0.350750 | H-7.7204900.980051 | 0.227391 |
| O-7.796500-4.124442 | -1.268034 | H-6.2568451.269944 | 1.160477 |
| C-5.956043-1.499750 | 2.895352 | H-6.567162-0.806696 | -1.556097 |
| O-5.545981-0.905341 | 3.780443 | N-4.379664-0.438766 | -0.631824 |
| C-8.522993-1.659853 | 1.542529 | P-3.617808-0.892627 | -2.076155 |
| O-9.545673-1.172109 | 1.686248 | C-4.631979-0.088883 | -3.370843 |
| C-7.293957-4.053270 | 2.518002 | H-5.693916-0.325024 | -3.342057 |
| O-7.642027-4.896633 | 3.208661 | H-4.4999870.990143 | -3.281827 |
| C-3.511641-0.274372 | 0.534181 | H-4.242078-0.398662 | -4.340094 |
| H-3.7984950.610998 | 1.103173 | Cl-4.316155-2.868106 | -2.402789 |

KCl**:** E = -1061.05301340126 au

ZPE = 0.00057241 au

$G_{corr}$ = -0.02288867 au

| | | | |
|---|---|---|---|
| K-3.514131-1.680741 | -6.291564 | Cl-3.8047420.646666 | -4.879771 |

TS(**6d'→7d'**)**:** E = -3429.11733192071 au

ZPE = 0.41261595 au

$G_{corr}$ = 0.34406635 au

ν = -696.05 $cm^{-1}$

| | | | |
|---|---|---|---|
| W-6.059546-2.438651 | 2.423731 | P-3.453619-1.135801 | -1.047337 |
| C-4.053287-2.744180 | 2.775373 | C-1.870556-0.314703 | -1.450378 |
| O-2.963956-2.959504 | 3.036778 | H-2.0753020.720605 | -1.723548 |
| C-5.971219-3.621896 | 0.779592 | H-1.153908-0.335699 | -0.631419 |
| O-5.915554-4.220722 | -0.202683 | H-1.428468-0.817477 | -2.309366 |
| C-6.089425-1.053665 | 3.956754 | Cl-2.593917-2.992613 | -0.398678 |
| O-6.093338-0.267204 | 4.782714 | P-5.636044-0.529021 | 0.770004 |
| C-8.103782-2.274334 | 2.266660 | H-6.352335-0.476263 | -0.621401 |
| O-9.245353-2.246288 | 2.255350 | Si-8.824652-0.652928 | -1.680282 |
| C-6.397586-3.989755 | 3.664869 | Si-6.7274161.111135 | -2.840365 |
| O-6.589917-4.875928 | 4.366468 | C-9.5463720.272067 | -0.192293 |
| C-3.0069710.084067 | 1.376386 | H-9.5667101.347107 | -0.382315 |
| H-2.6471951.093076 | 1.172425 | H-10.567476-0.043573 | 0.031710 |
| H-3.4942120.093043 | 2.351130 | H-8.9561930.119213 | 0.712487 |
| H-2.150228-0.585247 | 1.457466 | C-9.045745-2.513889 | -1.347121 |
| C-6.0374661.165693 | 1.340310 | H-10.068326-2.724839 | -1.027304 |
| H-5.8382051.892490 | 0.552833 | H-8.878570-3.121396 | -2.243000 |
| H-7.1007391.198846 | 1.577572 | H-8.394655-2.891318 | -0.556705 |
| H-5.4868411.446606 | 2.236772 | C-9.983427-0.292361 | -3.139975 |
| N-3.940731-0.359367 | 0.346363 | H-9.684937-0.838988 | -4.037318 |

| | | | | | |
|---|---|---|---|---|---|
| H | -11.005962 | -0.593714 | -2.899633 | H | -4.5983801.623822 | -1.574689 |
| H | -10.0139630.766858 | | -3.402007 | H | -4.2475540.784731 | -3.087575 |
| C | -6.9513090.911170 | | -4.717047 | C | -7.6720082.680069 | -2.336816 |
| H | -7.9940240.744309 | | -4.991703 | H | -8.7457112.596354 | -2.516871 |
| H | -6.6084981.796193 | | -5.258689 | H | -7.5421342.892396 | -1.272983 |
| H | -6.3773310.060810 | | -5.096902 | H | -7.3189113.553041 | -2.890743 |
| C | -4.8909651.535715 | | -2.622799 | K | -5.991827 | -2.628270 | -2.587442 |
| H | -4.6665542.489921 | | -3.105232 | N | -7.169048 | -0.294183 | -1.960042 |

TS(**6d''→7d''**): E = -3429.09960103111 au

ZPE = 0.41313507 au

$G_{corr}$ = 0.34467398 au

ν = -1050.62 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| W | -5.935973 | -2.523250 | 1.624767 | Si | -9.388146 | -1.352366 | -2.218404 |
| C | -3.894445 | -2.737823 | 1.855547 | Si | -7.5556260.514770 | -3.694946 |
| O | -2.799840 | -2.925127 | 2.110849 | C | -6.3944241.852371 | -3.020295 |
| C | -5.923386 | -3.694820 | -0.023634 | H | -6.0768172.518957 | -3.825341 |
| O | -5.899692 | -4.287165 | -1.014884 | H | -6.9216072.467301 | -2.287174 |
| C | -5.850057 | -1.132687 | 3.151962 | H | -5.4953011.484199 | -2.527677 |
| O | -5.789643 | -0.349576 | 3.978748 | C | -6.794562 | -0.144495 | -5.316176 |
| C | -7.980251 | -2.403313 | 1.725648 | H | -5.819886 | -0.624865 | -5.188465 |
| O | -9.112159 | -2.357989 | 1.880181 | H | -7.463066 | -0.869231 | -5.791523 |
| C | -6.089870 | -4.085175 | 2.882984 | H | -6.6440820.660874 | -6.038909 |
| O | -6.198992 | -4.980381 | 3.591943 | C | -9.0871121.490658 | -4.244090 |
| C | -3.9340891.044237 | | 0.749935 | H | -9.7179441.782290 | -3.402002 |
| H | -4.6519451.798923 | | 1.065751 | H | -8.7680652.411087 | -4.739392 |
| H | -3.6821180.416899 | | 1.608847 | H | -9.7118760.946085 | -4.951821 |
| H | -3.0273071.568295 | | 0.443062 | C | -10.368443 | -0.315681 | -0.976076 |
| C | -6.9979760.823084 | | 0.556107 | H | -9.954843 | -0.364266 | 0.031788 |
| H | -6.9224701.678977 | | -0.114082 | H | -10.3921270.735845 | -1.268731 |
| H | -8.0339620.486384 | | 0.552245 | H | -11.402764 | -0.661215 | -0.911588 |
| H | -6.7509271.131156 | | 1.569525 | C | -9.309181 | -3.124462 | -1.519187 |
| N | -4.4528870.251182 | | -0.361674 | H | -9.213052 | -3.891464 | -2.295650 |
| P | -3.285610 | -0.095202 | -1.521848 | H | -8.514491 | -3.282713 | -0.791161 |
| C | -4.173459 | -1.240071 | -2.642644 | H | -10.245808 | -3.351677 | -1.005463 |
| H | -4.516586 | -2.121857 | -2.104224 | C | -10.514317 | -1.561717 | -3.737782 |
| H | -5.006153 | -0.721582 | -3.111486 | H | -11.349941 | -2.220620 | -3.487978 |
| H | -3.473698 | -1.553607 | -3.416829 | H | -10.941486 | -0.622564 | -4.087941 |
| Cl | -2.030972 | -1.617060 | -0.674595 | H | -9.991705 | -2.013987 | -4.585788 |
| N | -7.807202 | -0.771700 | -2.576553 | P | -5.978558 | -0.574543 | -0.061634 |
| K | -6.770012 | -3.121711 | -3.469323 | H | -6.792076 | -0.730178 | -1.438059 |

**7d':** E = -2554.08716177091 au

ZPE = 0.1705489 au

$G_{corr}$ = 0.11683637 au

| | | | |
|---|---|---|---|
| W-5.935441-2.455918 | 2.582702 | H-2.532351-1.101695 | 1.927444 |
| C-4.183254-3.292474 | 1.897748 | C-5.9540181.212597 | 2.435125 |
| O-3.230118-3.805885 | 1.532979 | H-5.8025552.164869 | 1.925827 |
| C-6.855311-3.092762 | 0.906449 | H-6.9970931.162318 | 2.750106 |
| O-7.356778-3.370126 | -0.097363 | H-5.3397271.198209 | 3.336571 |
| C-4.948055-1.627590 | 4.200318 | N-3.9150630.140587 | 0.898698 |
| O-4.409401-1.156500 | 5.090028 | P-3.6974440.236911 | -0.736045 |
| C-7.706845-1.674053 | 3.258501 | C-1.8987190.527121 | -0.937616 |
| O-8.705087-1.255792 | 3.629397 | H-1.6572561.522515 | -0.561257 |
| C-6.321991-4.157111 | 3.572154 | H-1.276760-0.209548 | -0.432493 |
| O-6.551354-5.127690 | 4.144516 | H-1.6714480.503884 | -2.002463 |
| C-2.860947-0.062866 | 1.876675 | Cl-3.614906-1.887871 | -1.448420 |
| H-1.9947250.561296 | 1.658585 | P-5.620012-0.202867 | 1.289966 |
| H-3.2223730.229004 | 2.860205 | K-6.629342-1.159425 | -1.688403 |

**7d'':** E = -2554.08246377134 au

ZPE = 0.17053031 au

$G_{corr}$ = 0.11670217 au

| | | | |
|---|---|---|---|
| P-6.146546-0.755448 | -0.511183 | H-3.550285-1.403781 | 1.066560 |
| W-6.745599-2.545035 | 1.317887 | H-2.511955-0.250300 | 0.230574 |
| C-5.027466-3.590731 | 0.882420 | C-6.5966470.922804 | 0.135009 |
| O-4.097708-4.197558 | 0.612568 | H-6.3075321.697033 | -0.577055 |
| C-7.708051-3.659907 | -0.046944 | H-7.6797010.969440 | 0.255157 |
| O-8.252647-4.276415 | -0.862560 | H-6.1487771.155723 | 1.101856 |
| C-5.806863-1.358308 | 2.743099 | N-4.389535-0.526299 | -0.680362 |
| O-5.327709-0.705968 | 3.546070 | P-3.578353-0.610304 | -2.128286 |
| C-8.481433-1.497089 | 1.620172 | C-4.6543670.284738 | -3.307484 |
| O-9.462170-0.926773 | 1.767168 | H-5.7135320.061599 | -3.186728 |
| C-7.242993-3.865908 | 2.741787 | H-4.5090961.351481 | -3.126367 |
| O-7.526136-4.617021 | 3.564696 | H-4.3361860.065193 | -4.325560 |
| C-3.544603-0.469446 | 0.506801 | Cl-4.053468-2.619736 | -2.919643 |
| H-3.8791970.329635 | 1.168772 | K-7.104733-2.697477 | -2.894301 |

TS(**7d'→3d'**): E = -2554.07640716152 au

ZPE = 0.16964625 au

$G_{corr}$ = 0.11666545 au

ν = -35.24 $cm^{-1}$

| | | | |
|---|---|---|---|
| W-6.286695-2.369776 | 2.697411 | C-7.885245-1.121660 | 3.155221 |
| C-4.739070-3.546403 | 2.174766 | O-8.764617-0.440046 | 3.399272 |
| O-3.881362-4.209134 | 1.773391 | C-7.130766-3.879051 | 3.718700 |
| C-7.145894-2.931914 | 0.943419 | O-7.606983-4.746091 | 4.303384 |
| O-7.513421-3.253308 | -0.097904 | C-2.596123-0.913756 | 1.336229 |
| C-5.237355-1.707368 | 4.348230 | H-1.800246-1.370666 | 0.747097 |
| O-4.626668-1.342568 | 5.240303 | H-2.2348470.052446 | 1.698969 |

| | | | |
|---|---|---|---|
| H-2.779877-1.541131 | 2.208411 | C-3.0937421.632324 | -0.684690 |
| C-4.8223551.009779 | 2.500190 | H-3.7519442.304723 | -0.133372 |
| H-4.4582781.891010 | 1.970295 | H-2.1484291.540206 | -0.152888 |
| H-5.7073081.312617 | 3.062408 | H-2.9083122.071801 | -1.664057 |
| H-4.0643450.705208 | 3.222589 | Cl-2.291410-0.974520 | -1.970944 |
| N-3.821557-0.812015 | 0.564317 | P-5.353223-0.338637 | 1.343822 |
| P-3.9620530.028570 | -0.911837 | K-4.276248-3.231504 | -0.922803 |

TS(**7d''→3d''**)**:** E = -2554.04469765139 au

ZPE = 0.16842223 au

$G_{corr}$ = 0.11358166 au

ν = -35.24 $cm^{-1}$

| | | | |
|---|---|---|---|
| W-6.286695-2.369776 | 2.697411 | H-2.779877-1.541131 | 2.208411 |
| C-4.739070-3.546403 | 2.174766 | C-4.8223551.009779 | 2.500190 |
| O-3.881362-4.209134 | 1.773391 | H-4.4582781.891010 | 1.970295 |
| C-7.145894-2.931914 | 0.943419 | H-5.7073081.312617 | 3.062408 |
| O-7.513421-3.253308 | -0.097904 | H-4.0643450.705208 | 3.222589 |
| C-5.237355-1.707368 | 4.348230 | N-3.821557-0.812015 | 0.564317 |
| O-4.626668-1.342568 | 5.240303 | P-3.9620530.028570 | -0.911837 |
| C-7.885245-1.121660 | 3.155221 | C-3.0937421.632324 | -0.684690 |
| O-8.764617-0.440046 | 3.399272 | H-3.7519442.304723 | -0.133372 |
| C-7.130766-3.879051 | 3.718700 | H-2.1484291.540206 | -0.152888 |
| O-7.606983-4.746091 | 4.303384 | H-2.9083122.071801 | -1.664057 |
| C-2.596123-0.913756 | 1.336229 | Cl-2.291410-0.974520 | -1.970944 |
| H-1.800246-1.370666 | 0.747097 | P-5.353223-0.338637 | 1.343822 |
| H-2.2348470.052446 | 1.698969 | K-4.276248-3.231504 | -0.922803 |

**3d':** E = -1493.01680165071 au

ZPE = 0.16751056 au

$G_{corr}$ = 0.11865545 au

| | | | |
|---|---|---|---|
| W-6.605013-1.491347 | 2.902453 | H-2.863342-3.144194 | 0.775746 |
| C-5.408926-2.799512 | 3.942803 | H-2.715634-2.549513 | -0.878380 |
| O-4.740796-3.523418 | 4.519922 | C-3.2042210.045859 | 2.709086 |
| C-6.819013-2.888023 | 1.395337 | H-2.2768170.153794 | 2.152347 |
| O-6.929348-3.656394 | 0.562037 | H-3.4971761.022292 | 3.096277 |
| C-6.344658-0.084144 | 4.375432 | H-3.027061-0.610900 | 3.561014 |
| O-6.1938550.697904 | 5.193698 | N-3.977814-1.448661 | 0.345455 |
| C-7.772190-0.164949 | 1.834806 | P-4.4157750.111005 | -0.321402 |
| O-8.4078750.570953 | 1.240828 | C-2.8893731.176137 | -0.255217 |
| C-8.238695-2.214014 | 3.853232 | H-2.9604051.951161 | 0.507832 |
| O-9.159006-2.627377 | 4.393603 | H-1.9776940.603788 | -0.087173 |
| C-2.791468-2.244109 | 0.165142 | H-2.7964361.669957 | -1.222376 |
| H-1.865838-1.724998 | 0.435352 | P-4.581932-0.649386 | 1.719247 |

**3d'':** E = -1493.0226150659 au

ZPE = 0.167919 au

$G_{corr}$ = 0.11826314 au

| | | | |
|---|---|---|---|
| P-5.828108-0.679923 | -0.170462 | H-3.4919950.437108 | 1.668102 |
| W-6.552633-2.494513 | 1.393576 | H-3.132260-1.214755 | 1.147529 |
| C-4.856823-3.584590 | 0.958771 | H-2.2809130.151164 | 0.421102 |
| O-3.927350-4.203341 | 0.728456 | C-6.9733230.686316 | -0.550786 |
| C-7.519385-3.387778 | -0.193038 | H-6.5654521.391894 | -1.269308 |
| O-8.053425-3.883306 | -1.069931 | H-7.9038720.271881 | -0.937522 |
| C-5.585826-1.599910 | 2.976224 | H-7.1949761.219092 | 0.374591 |
| O-5.063149-1.112480 | 3.865515 | N-4.2509250.001014 | -0.221577 |
| C-8.250208-1.421625 | 1.834118 | P-4.319117-0.994937 | -1.681773 |
| O-9.194412-0.831839 | 2.084640 | C-4.5466530.262833 | -3.005937 |
| C-7.186291-3.967986 | 2.623143 | H-5.0466771.169204 | -2.673997 |
| O-7.549756-4.801463 | 3.317878 | H-3.5626350.534494 | -3.391047 |
| C-3.244276-0.181479 | 0.806000 | H-5.111506-0.181932 | -3.825708 |

**3'e:** E = -1493.022585753 au

ZPE = 0.16790727 au

$G_{corr}$ = 0.11822015 au

| | | | |
|---|---|---|---|
| C-4.0127970.232658 | 0.192412 | O-6.9574742.414369 | -4.996857 |
| H-3.8092291.292256 | 0.011701 | C-3.2370743.110937 | -4.733588 |
| H-4.2280580.108406 | 1.253126 | O-2.7153973.900861 | -5.376527 |
| H-3.108414-0.331309 | -0.033997 | C-3.7799690.311194 | -5.059572 |
| N-5.118195-0.302014 | -0.578816 | O-3.563783-0.460764 | -5.871675 |
| P-6.7023030.481546 | -0.650837 | C-2.3634021.260525 | -2.708195 |
| C-5.674823-1.665327 | -2.992276 | O-1.3568891.017452 | -2.229179 |
| H-6.225108-1.534616 | -3.923550 | C-4.5395333.131052 | -2.155907 |
| H-4.717719-2.133885 | -3.223785 | O-4.7419243.929921 | -1.368088 |
| H-6.233413-2.322290 | -2.331355 | C-7.852122-0.930847 | -0.384329 |
| P-5.354845-0.027693 | -2.258855 | H-8.085634-0.984107 | 0.680065 |
| W-4.1612891.712661 | -3.604501 | H-8.783196-0.738228 | -0.918052 |
| C-5.9620342.163827 | -4.500817 | H-7.450639-1.891947 | -0.695401 |

**3'f:** E = -1587.85116723198 au

ZPE = 0.21509383 au

$G_{corr}$ = 0.16271637 au

| | | | |
|---|---|---|---|
| C-3.848663-0.079077 | 0.051069 | N-5.083713-0.299230 | -0.669872 |
| H-3.4447230.927735 | -0.081793 | P-6.5952000.483674 | -0.453382 |
| H-4.020765-0.237309 | 1.115015 | C-5.883966-1.496117 | -3.124777 |
| H-3.096761-0.795488 | -0.278155 | H-6.439092-1.270015 | -4.035161 |

| | | | |
|---|---|---|---|
| H-4.972281-2.024293 | -3.405070 | W-4.1784821.830004 | -3.578658 |
| H-6.491122-2.141029 | -2.496222 | C-5.9751482.637039 | -4.188165 |
| N-7.633661-0.737260 | 0.055964 | O-6.9687823.083479 | -4.525544 |
| C-8.998044-0.348806 | 0.339815 | C-3.1684613.231594 | -4.622860 |
| H-9.691417-0.685228 | -0.436975 | O-2.5923684.022901 | -5.217747 |
| H-9.324659-0.772896 | 1.292456 | C-4.1666990.604913 | -5.229632 |
| H-9.0801090.736418 | 0.413743 | O-4.158190-0.071145 | -6.149182 |
| C-7.398968-2.159956 | 0.026974 | C-2.3991251.004554 | -2.958677 |
| H-7.684846-2.602622 | 0.984616 | O-1.4071730.547867 | -2.626059 |
| H-7.982200-2.657489 | -0.755039 | C-4.1947013.070318 | -1.934024 |
| H-6.344175-2.365886 | -0.137521 | O-4.1963833.773939 | -1.035641 |
| P-5.4590730.082622 | -2.307253 | | |

**3'g:** E = -1685.1094417672 au

ZPE = 0.22360572 au

$G_{corr}$ = 0.17085943 au

| | | | |
|---|---|---|---|
| C-4.0462220.123322 | 0.155433 | O-4.230939-0.470887 | -5.921922 |
| H-3.5784691.094122 | -0.031340 | C-2.4066210.802057 | -2.847101 |
| H-4.2166350.032126 | 1.227299 | O-1.4658560.294821 | -2.448225 |
| H-3.345604-0.656111 | -0.141834 | C-3.9888493.145871 | -2.110960 |
| N-5.304031-0.072170 | -0.539713 | O-3.9264693.942705 | -1.297966 |
| P-6.6351551.075233 | -0.453837 | C-8.057416-0.023182 | -0.156292 |
| C-6.409499-1.152823 | -2.903319 | C-9.3290790.530741 | -0.301135 |
| H-6.911168-0.854910 | -3.823538 | C-7.929816-1.343430 | 0.269492 |
| H-5.653209-1.898635 | -3.150043 | C-10.458248-0.232376 | -0.045410 |
| H-7.136756-1.592022 | -2.224171 | H-9.4418231.562230 | -0.616477 |
| P-5.5865470.305834 | -2.192165 | C-9.061383-2.100037 | 0.537094 |
| W-4.0874721.723026 | -3.600153 | H-6.943968-1.775125 | 0.387065 |
| C-5.7693042.645652 | -4.357583 | C-10.325754-1.548876 | 0.375787 |
| O-6.6971153.157111 | -4.777992 | H-11.4412350.202380 | -0.169791 |
| C-2.9152632.870577 | -4.782361 | H-8.955541-3.124119 | 0.870791 |
| O-2.2549433.518738 | -5.455224 | H-11.206423-2.142843 | 0.581769 |
| C-4.1829540.309802 | -5.091448 | | |

**3''e:** E = -1493.0233155254 au

ZPE = 0.16793895 au

$G_{corr}$ = 0.11841161 au

| | | | |
|---|---|---|---|
| C-3.797201-0.436173 | -0.013741 | C-4.1602871.317208 | -2.763530 |
| H-3.2403590.501803 | -0.100251 | H-3.2481870.822942 | -3.099180 |
| H-3.938504-0.646853 | 1.045688 | H-4.5524761.899984 | -3.596561 |
| H-3.186058-1.235127 | -0.434473 | H-3.9188031.997109 | -1.947896 |
| N-5.087296-0.427174 | -0.671959 | W-6.161889-1.592005 | -3.999650 |
| P-6.2840880.858153 | -0.488288 | C-6.352953-2.992270 | -2.495129 |
| P-5.4021880.056722 | -2.288429 | O-6.453126-3.764370 | -1.663532 |

| | | | |
|---|---|---|---|
| C-8.135122-1.036290 | -3.769876 | C-6.702157-2.964025 | -5.383156 |
| O-9.226807-0.727540 | -3.656551 | O-7.000025-3.743024 | -6.166566 |
| C-5.949699-0.169601 | -5.467252 | C-7.828401-0.109900 | -0.243922 |
| O-5.8277760.620311 | -6.282066 | H-7.947510-0.318189 | 0.820162 |
| C-4.192490-2.131852 | -4.248513 | H-8.6802550.490205 | -0.564803 |
| O-3.100635-2.430309 | -4.392203 | H-7.831984-1.054612 | -0.783802 |

**3''f:** E = -1587.85265219684 au

ZPE = 0.21494826 au

$G_{corr}$ = 0.1623526 au

| | | | |
|---|---|---|---|
| C-3.705193-1.028032 | -0.177986 | C-4.2170921.241985 | -2.604465 |
| H-3.014833-0.180214 | -0.197590 | H-3.2844570.784431 | -2.936623 |
| H-3.793984-1.372055 | 0.851651 | H-4.5900001.866642 | -3.415706 |
| H-3.270083-1.837294 | -0.765005 | H-4.0079761.878577 | -1.744162 |
| N-5.016686-0.712764 | -0.696930 | W-6.194064-1.508311 | -4.143725 |
| P-6.1306930.483895 | -0.182457 | C-6.098004-3.175335 | -2.937520 |
| N-7.465346-0.378416 | 0.356863 | O-6.033568-4.105927 | -2.281130 |
| C-8.5854260.402038 | 0.838617 | C-8.174448-1.227717 | -3.653793 |
| H-9.3880630.470485 | 0.097864 | O-9.273031-1.066458 | -3.390655 |
| H-8.997172-0.047820 | 1.744657 | C-6.2699290.158383 | -5.344977 |
| H-8.2682751.416122 | 1.085439 | O-6.3098791.078992 | -6.018758 |
| C-7.767723-1.758030 | 0.060990 | C-4.206261-1.753014 | -4.614080 |
| H-8.180383-2.242936 | 0.948593 | O-3.102697-1.884041 | -4.874363 |
| H-8.502310-1.854978 | -0.744110 | C-6.716580-2.662891 | -5.711887 |
| H-6.863535-2.288088 | -0.223576 | O-7.005299-3.320199 | -6.604672 |
| P-5.461754-0.055430 | -2.223381 | | |

**3''g:** E = -1685.11043924274 au

ZPE = 0.22354282 au

$G_{corr}$ = 0.17120095 au

| | | | |
|---|---|---|---|
| C-3.919245-0.495213 | 0.194871 | C-8.290651-1.165736 | -3.356050 |
| H-3.2552740.364809 | 0.068160 | O-9.392681-0.957729 | -3.163691 |
| H-4.115623-0.616548 | 1.259282 | C-6.349108-0.088296 | -5.230148 |
| H-3.395193-1.385375 | -0.153487 | O-6.3637870.744516 | -6.010593 |
| N-5.179090-0.381027 | -0.510214 | C-4.381324-2.029545 | -4.350015 |
| P-6.2516021.005580 | -0.417079 | O-3.308702-2.279316 | -4.652270 |
| P-5.4077350.028894 | -2.160605 | C-6.957479-2.922675 | -5.200085 |
| C-4.0311381.130305 | -2.659631 | O-7.309399-3.681646 | -5.981180 |
| H-3.1512010.532843 | -2.900304 | C-7.8729030.204793 | -0.210931 |
| H-4.3247151.671216 | -3.558894 | C-9.0006761.016807 | -0.320138 |
| H-3.7702651.853310 | -1.888025 | C-8.026375-1.149384 | 0.073949 |
| W-6.314487-1.588605 | -3.825566 | C-10.2679830.474801 | -0.173411 |
| C-6.271952-3.063447 | -2.385093 | H-8.8930622.076027 | -0.526939 |
| O-6.240932-3.882259 | -1.592691 | C-9.295115-1.685809 | 0.232446 |

| | | | | | |
|---|---|---|---|---|---|
| H | -7.150810 | -1.776277 | 0.175189 | H | -9.408430 -2.739068 0.454304 |
| C | -10.416499 | -0.877843 | 0.101827 | H | -11.405678 -1.300742 0.218320 |
| H | -11.139633 | 1.108322 | -0.271763 | | |

TS(**3'e→8'e**): E = -1492.99326560103 au

ZPE = 0.16743029 au

$G_{corr}$ = 0.11852666 au

ν = -94.89 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | 0.985548 | -0.728233 | 2.979708 | O | -2.384417 1.577876 -2.030997 |
| H | 1.539249 | 0.200356 | 2.808195 | C | 1.099179 2.673074 -2.558702 |
| H | 0.462383 | -0.638786 | 3.931274 | O | 1.345135 3.470724 -3.349869 |
| H | 1.704535 | -1.543137 | 3.054703 | C | 0.928840 -0.094823 -2.716649 |
| N | 0.013995 | -1.047664 | 1.940429 | O | 1.073727 -0.816891 -3.588502 |
| P | -1.010967 | 0.212925 | 1.348910 | C | 2.706126 1.175304 -0.754835 |
| C | -0.340746 | -2.393340 | -0.525389 | O | 3.819979 1.128485 -0.524633 |
| H | -1.252189 | -2.067440 | -1.024621 | C | 0.481702 2.797159 0.186014 |
| H | 0.316218 | -2.832254 | -1.276305 | O | 0.372131 3.665234 0.914917 |
| H | -0.583814 | -3.158316 | 0.210025 | C | -2.560046 -0.700812 0.958592 |
| P | 0.570325 | -1.013958 | 0.277264 | H | -3.340984 -0.314030 1.615322 |
| W | 0.691340 | 1.289264 | -1.214700 | H | -2.879182 -0.516762 -0.067373 |
| C | -1.294307 | 1.447091 | -1.715054 | H | -2.463760 -1.771042 1.122274 |

TS(**3'f→8'f**): E = -1587.82799813738 au

ZPE = 0.21495151 au

$G_{corr}$ = 0.16387945 au

ν = -42.22 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | 1.999885 | -1.049818 | 2.262191 | H | -2.568482 -2.093830 2.482360 |
| H | 2.599474 | -0.137204 | 2.197867 | H | -2.580354 -2.375139 0.736615 |
| H | 1.659266 | -1.163614 | 3.290968 | H | -1.066575 -2.513293 1.645466 |
| H | 2.641906 | -1.893898 | 2.013724 | P | 1.147685 -0.842910 -0.359790 |
| N | 0.849887 | -1.061754 | 1.369281 | W | 1.135242 1.592766 -1.487954 |
| P | -0.251722 | 0.208496 | 1.336336 | C | -0.904400 1.618498 -1.721617 |
| C | -0.124103 | -1.929971 | -1.123830 | O | -2.038014 1.641962 -1.866433 |
| H | -1.133092 | -1.519787 | -1.076604 | C | 1.319815 3.201615 -2.630628 |
| H | 0.140286 | -2.046236 | -2.175336 | O | 1.428315 4.126683 -3.305753 |
| H | -0.115604 | -2.917765 | -0.663990 | C | 1.300714 0.485158 -3.213240 |
| N | -1.729053 | -0.552701 | 1.353091 | O | 1.406338 -0.075618 -4.202156 |
| C | -2.907480 | 0.283618 | 1.222563 | C | 3.182561 1.511302 -1.234971 |
| H | -3.473757 | 0.031405 | 0.324413 | O | 4.314216 1.470828 -1.105417 |
| H | -3.559848 | 0.157083 | 2.089037 | C | 1.009646 2.860288 0.131186 |
| H | -2.629636 | 1.335838 | 1.161344 | O | 0.943638 3.608011 0.990772 |
| C | -1.996757 | -1.960014 | 1.560504 | | |

TS(**3'g→8'g**): E = -1685.07977435008 au

ZPE = 0.22360572 au

$G_{corr}$ = 0.171075 au

ν = -78.32 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | 2.515677 | -1.025849 | 2.241976 | O | 1.966288 | -0.472496 | -4.102488 |
| H | 3.180401 | -0.179630 | 2.045192 | C | 3.551470 | 1.520482 | -1.287852 |
| H | 2.235130 | -1.000193 | 3.294308 | O | 4.676559 | 1.529215 | -1.111099 |
| H | 3.068801 | -1.944881 | 2.053132 | C | 1.293633 | 3.017476 | -0.237947 |
| N | 1.302632 | -1.029518 | 1.432752 | O | 1.174834 | 3.894792 | 0.479697 |
| P | 0.396965 | 0.420252 | 1.268978 | C | -1.311664 | -0.178379 | 1.252670 |
| C | 0.205394 | -2.026260 | -0.972472 | C | -2.296190 | 0.767622 | 0.963697 |
| H | 0.461556 | -2.222262 | -2.013922 | C | -1.688033 | -1.474134 | 1.606052 |
| H | 0.237935 | -2.968129 | -0.426641 | C | -3.636715 | 0.416495 | 0.999298 |
| H | -0.808827 | -1.629631 | -0.935685 | H | -2.019395 | 1.786938 | 0.718374 |
| P | 1.465329 | -0.876590 | -0.304968 | C | -3.029585 | -1.817722 | 1.653446 |
| W | 1.515811 | 1.518392 | -1.641302 | H | -0.928114 | -2.205776 | 1.846786 |
| C | -0.508054 | 1.484057 | -2.012403 | C | -4.004201 | -0.876850 | 1.344197 |
| O | -1.620961 | 1.483298 | -2.263535 | H | -4.392810 | 1.153661 | 0.764649 |
| C | 1.722993 | 2.944630 | -2.986600 | H | -3.316722 | -2.823253 | 1.931676 |
| O | 1.846836 | 3.765917 | -3.782265 | H | -5.050459 | -1.150572 | 1.378531 |
| C | 1.793487 | 0.198896 | -3.196233 | | | | |

TS(**3''e→8''e**): E = -1492.98532520327 au

ZPE = 0.16764138 au

$G_{corr}$ = 0.11893482 au

ν = -116.43 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | -3.931296 | 0.599239 | 0.328052 | O | -6.732532 | -4.365627 | -2.328973 |
| H | -3.624783 | 1.525017 | -0.166715 | C | -8.319354 | -1.073357 | -3.446384 |
| H | -4.366451 | 0.859830 | 1.291997 | O | -9.427721 | -0.819858 | -3.336760 |
| H | -3.041111 | -0.002910 | 0.512297 | C | -6.193684 | 0.212290 | -4.867332 |
| N | -4.893992 | -0.189572 | -0.418021 | O | -6.102372 | 1.213566 | -5.403923 |
| P | -6.283404 | 0.466418 | -1.196000 | C | -4.598309 | -2.249142 | -4.708097 |
| P | -4.543331 | -0.756406 | -2.031374 | O | -3.648739 | -2.631216 | -5.208517 |
| C | -3.578353 | 0.624036 | -2.802532 | C | -7.198157 | -2.384192 | -5.528508 |
| H | -2.630315 | 0.742623 | -2.276097 | O | -7.656146 | -2.846593 | -6.476278 |
| H | -3.347750 | 0.357555 | -3.833213 | C | -7.554848 | -0.623249 | -0.432755 |
| H | -4.098320 | 1.581905 | -2.799755 | H | -7.550840 | -0.382549 | 0.633269 |
| W | -6.390221 | -1.601971 | -3.914429 | H | -8.547772 | -0.404140 | -0.818349 |
| C | -6.602742 | -3.381762 | -2.887291 | H | -7.343733 | -1.684811 | -0.539790 |

TS(**3''f→8''f**): E = -1587.82811714337 au

ZPE = 0.21423192 au

$G_{corr}$ = 0.16189897 au

ν = -120.26 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | -4.118056 | -0.715346 | 0.522286 | C | -3.469547 | 0.715831 | -2.828843 |
| H | -3.055040 | -0.527325 | 0.369177 | H | -2.640255 | 0.828712 | -2.129852 |
| H | -4.441204 | -0.153676 | 1.398246 | H | -3.054914 | 0.500563 | -3.813238 |
| H | -4.253175 | -1.778877 | 0.723155 | H | -4.006017 | 1.664054 | -2.885077 |
| N | -4.861352 | -0.276472 | -0.635925 | W | -6.302625 | -1.486046 | -4.080066 |
| P | -6.277279 | 0.496833 | -0.923528 | C | -5.813569 | -3.420787 | -3.571815 |
| N | -7.468733 | -0.362757 | -0.139490 | O | -5.543193 | -4.490496 | -3.282160 |
| C | -8.758394 | 0.275231 | 0.040978 | C | -8.040610 | -1.690771 | -3.008227 |
| H | -9.560027 | -0.331649 | -0.380487 | O | -9.063241 | -1.857361 | -2.523594 |
| H | -8.965851 | 0.432804 | 1.101854 | C | -6.724078 | 0.496846 | -4.447501 |
| H | -8.773633 | 1.248619 | -0.449940 | O | -6.950958 | 1.600216 | -4.627094 |
| C | -7.342625 | -1.693229 | 0.414609 | C | -4.703987 | -1.411256 | -5.374252 |
| H | -7.240374 | -1.665066 | 1.502605 | O | -3.856114 | -1.399358 | -6.138301 |
| H | -8.227232 | -2.283780 | 0.173024 | C | -7.369436 | -2.087800 | -5.644626 |
| H | -6.477405 | -2.202699 | -0.002868 | O | -7.976527 | -2.428472 | -6.560332 |
| P | -4.559297 | -0.674885 | -2.301592 | | | | |

TS(**3''g→8''g**): E = -1685.07329762274 au

ZPE = 0.22288772 au

$G_{corr}$ = 0.17103943 au

ν = -99.4 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | -4.203054 | 0.242444 | 0.648786 | O | -7.580695 | 1.332267 | -4.573268 |
| H | -3.616943 | 1.077888 | 0.256502 | C | -4.864638 | -1.214625 | -5.019535 |
| H | -4.753550 | 0.593742 | 1.520345 | O | -4.017085 | -1.053558 | -5.767610 |
| H | -3.514983 | -0.537836 | 0.975197 | C | -7.355420 | -2.250659 | -5.440962 |
| N | -5.141165 | -0.319573 | -0.302761 | O | -7.854086 | -2.652949 | -6.395760 |
| P | -6.206936 | 0.589088 | -1.278947 | C | -7.826661 | 0.012866 | -0.692146 |
| P | -4.645437 | -1.052874 | -1.804076 | C | -8.946670 | 0.705709 | -1.153910 |
| C | -3.324439 | 0.084989 | -2.431551 | C | -7.982933 | -0.988608 | 0.264399 |
| H | -2.562185 | 0.216261 | -1.662356 | C | -10.209318 | 0.386892 | -0.679457 |
| H | -2.839266 | -0.376098 | -3.289697 | H | -8.835829 | 1.501925 | -1.881593 |
| H | -3.693798 | 1.067801 | -2.724661 | C | -9.245731 | -1.299548 | 0.740819 |
| W | -6.481957 | -1.571199 | -3.811936 | H | -7.112665 | -1.520253 | 0.626938 |
| C | -5.801576 | -3.487876 | -3.422621 | C | -10.359576 | -0.616779 | 0.267526 |
| O | -5.435408 | -4.549260 | -3.237758 | H | -11.074249 | 0.924432 | -1.044776 |
| C | -8.243339 | -2.061729 | -2.839368 | H | -9.364201 | -2.079747 | 1.481345 |
| O | -9.244765 | -2.402039 | -2.420238 | H | -11.344761 | -0.865395 | 0.639645 |
| C | -7.175427 | 0.309985 | -4.266972 | | | | |

**8'e**: E = -1492.99685545382 au

ZPE = 0.16780847 au

$G_{corr}$ = 0.11975138 au

| | | | | | |
|---|---|---|---|---|---|
| C | -4.032684 | -0.500602 | 0.752104 | H | -3.285390 | 0.293051 | 0.650825 |

| | | | | | |
|---|---|---|---|---|---|
| H | -4.622758 | -0.295654 | 1.645227 | C | -4.085277 | 2.965938 | -4.845882 |
| H | -3.505602 | -1.443294 | 0.898257 | O | -3.855090 | 3.704799 | -5.691918 |
| N | -4.930028 | -0.630423 | -0.389942 | C | -4.160124 | 0.224762 | -4.799178 |
| P | -5.714465 | 0.812405 | -0.948205 | O | -3.959750 | -0.504055 | -5.654212 |
| C | -5.294205 | -1.974380 | -2.790898 | C | -2.476350 | 1.681108 | -2.866823 |
| H | -6.164944 | -1.542618 | -3.282186 | O | -1.368896 | 1.695788 | -2.608773 |
| H | -4.707169 | -2.493326 | -3.548845 | C | -4.743420 | 3.350228 | -2.182725 |
| H | -5.629435 | -2.702624 | -2.053139 | O | -4.878353 | 4.298337 | -1.569210 |
| P | -4.198527 | -0.748242 | -1.960200 | C | -7.395555 | 0.182332 | -1.335758 |
| W | -4.485122 | 1.679064 | -3.382066 | H | -7.774772 | -0.298187 | -0.432674 |
| C | -6.449368 | 1.717214 | -3.977637 | H | -8.039220 | 1.030762 | -1.565669 |
| O | -7.520789 | 1.775291 | -4.366533 | H | -7.457966 | -0.533038 | -2.152799 |

**8’e:**

E = -1490.985586654784 au (CPCM(tol)/B3LYP-D3/def2-TZV(ecp))

ZPE = 0.16117855 au

$G_{corr}$ = 0.11143138 au

| | | | | | |
|---|---|---|---|---|---|
| C | -3.964475 | -0.940338 | 0.629993 | O | -7.326431 | 0.813669 | -4.604740 |
| H | -3.046725 | -0.344552 | 0.593833 | C | -4.141066 | 2.869096 | -4.972328 |
| H | -4.489852 | -0.711478 | 1.558386 | O | -3.959642 | 3.573583 | -5.861545 |
| H | -3.692712 | -1.996894 | 0.632260 | C | -3.555039 | 0.230471 | -4.667594 |
| N | -4.868725 | -0.687137 | -0.498914 | O | -3.060216 | -0.491157 | -5.403005 |
| P | -5.345407 | 0.947502 | -0.807644 | C | -2.636638 | 2.073421 | -2.552432 |
| C | -5.585335 | -1.874607 | -2.890617 | O | -1.638179 | 2.322020 | -2.057416 |
| H | -6.577432 | -1.436393 | -2.801719 | C | -5.324695 | 3.259474 | -2.513893 |
| H | -5.346223 | -2.007693 | -3.946738 | O | -5.806554 | 4.189183 | -2.056058 |
| H | -5.592420 | -2.852077 | -2.402887 | C | -7.162273 | 0.763367 | -1.017891 |
| P | -4.249408 | -0.886439 | -2.103053 | H | -7.566610 | 0.462732 | -0.048451 |
| W | -4.459543 | 1.618582 | -3.428727 | H | -7.584684 | 1.730909 | -1.293119 |
| C | -6.299926 | 1.097692 | -4.186179 | H | -7.455054 | 0.021701 | -1.758378 |

**8’f:**

E = -1587.82947303986 au

ZPE = 0.21554129 au

$G_{corr}$ = 0.16394839 au

| | | | | | |
|---|---|---|---|---|---|
| C | -3.515123 | -1.192060 | 0.443584 | C | -8.156447 | 0.842565 | -0.427479 |
| H | -2.775493 | -0.386990 | 0.425880 | H | -8.843946 | 0.699002 | -1.261943 |
| H | -3.910026 | -1.272399 | 1.456360 | H | -8.727452 | 0.782740 | 0.501945 |
| H | -3.005087 | -2.123321 | 0.199954 | H | -7.741657 | 1.848272 | -0.501008 |
| N | -4.613794 | -1.003787 | -0.493708 | C | -7.557690 | -1.521510 | -0.308635 |
| P | -5.536050 | 0.402656 | -0.459909 | H | -8.097294 | -1.641283 | 0.634553 |
| C | -5.562768 | -1.865811 | -2.955529 | H | -8.234978 | -1.790485 | -1.121646 |
| H | -6.559727 | -1.438933 | -2.853105 | H | -6.713250 | -2.203562 | -0.312944 |
| H | -5.352412 | -1.968046 | -4.020620 | P | -4.231967 | -0.833179 | -2.206778 |
| H | -5.555711 | -2.863150 | -2.514605 | W | -4.663218 | 1.676854 | -3.264487 |
| N | -7.102654 | -0.153967 | -0.441126 | C | -6.666626 | 1.393312 | -3.601608 |

O-7.7788751.243905 -3.817481
C-4.6468313.207762 -4.526365
O-4.6337774.082563 -5.271695
C-4.2382330.524924 -4.920124
O-3.990826-0.033262 -5.884099
C-2.6393041.887727 -2.899404
O-1.5234382.003417 -2.702323
C-5.0456203.080739 -1.810086
O-5.2586753.908515 -1.053324

**8'f:**

E = -1585.647480278664 au (CPCM(tol)/B3LYP-D3/def2-TZV(ecp))

ZPE = 0.20757311 au

$G_{corr}$ = 0.15500234 au

C-3.613855-1.420671 0.468471
H-2.739855-0.766022 0.531494
H-4.101882-1.451098 1.444179
H-3.275999-2.426427 0.216132
N-4.578194-0.980759 -0.543329
P-5.4135770.460577 -0.389428
C-5.335638-1.966011 -3.030655
H-6.362508-1.619792 -2.941185
H-5.085556-2.027730 -4.091263
H-5.251913-2.963933 -2.596071
N-7.0144950.017944 -0.340454
C-7.9900921.098851 -0.241245
H-8.5936561.165133 -1.149073
H-8.6521180.921389 0.609499
H-7.4814772.050618 -0.088822
C-7.583469-1.316411 -0.451336
H-8.210599-1.514824 0.421971
H-8.204894-1.400257 -1.346638
H-6.786025-2.051753 -0.492974
P-4.093483-0.854248 -2.226620
W-4.7486251.644214 -3.277771
C-6.7076021.093453 -3.546523
O-7.7991650.763018 -3.673241
C-4.9061253.141362 -4.598681
O-4.9983543.987996 -5.374995
C-4.1843750.510401 -4.915651
O-3.870940-0.041308 -5.868248
C-2.7608852.039775 -2.847741
O-1.6658202.241354 -2.588437
C-5.2842443.060332 -1.881354
O-5.5835303.898036 -1.157771

**8'g:**

E = -1685.08462700506 au

ZPE = 0.22341197 au

$G_{corr}$ = 0.17121956 au

C-3.669656-1.058981 0.509435
H-2.839113-0.366245 0.344293
H-4.031280-0.918227 1.527859
H-3.284708-2.074828 0.421467
N-4.780663-0.890413 -0.418090
P-5.4956450.672419 -0.547902
C-5.813201-1.930077 -2.766824
H-5.688281-2.046425 -3.843419
H-5.754243-2.918855 -2.308886
H-6.803687-1.520117 -2.574234
P-4.432301-0.908794 -2.117271
W-4.9375431.638404 -3.180789
C-6.9113121.258670 -3.631821
O-7.9917211.049253 -3.924013
C-4.8662183.026328 -4.613426
O-4.8247453.819537 -5.438915
C-4.3914350.370184 -4.710272
O-4.072078-0.251594 -5.610586
C-2.9452851.918049 -2.713893
O-1.8448422.066158 -2.464570
C-5.3994993.246206 -1.969412
O-5.6322634.180794 -1.361600
C-7.2676040.263333 -0.512168
C-8.1844251.308146 -0.652954
C-7.740887-1.010518 -0.198227
C-9.5426681.078668 -0.515370
H-7.8434112.314387 -0.865897
C-9.102367-1.237260 -0.056298
H-7.038120-1.820904 -0.058702
C-10.006018-0.197348 -0.220405

H-10.2400921.897094 -0.634756
H-9.456995-2.231024 0.184324
H-11.067462-0.377219 -0.111949

**8'g:**

E = -1682.696193592751 au (CPCM(tol)/B3LYP-D3/def2-TZV(ecp))
ZPE = 0.21519880 au
$G_{corr}$ = 0.16231525 au

C-3.660595-1.107901 0.507647
H-2.824565-0.417430 0.357300
H-4.036993-0.980620 1.523368
H-3.292373-2.128163 0.392740
N-4.765101-0.896571 -0.435771
P-5.4703190.671525 -0.526134
C-5.811611-1.939543 -2.783564
H-5.703112-2.009481 -3.866783
H-5.733804-2.941011 -2.355091
H-6.793016-1.531391 -2.547482
P-4.416273-0.935907 -2.131668
W-4.9378441.641031 -3.190791
C-6.8932861.173657 -3.648818
O-7.9644920.897547 -3.935419
C-4.8966793.036727 -4.633909
O-4.8781123.833913 -5.461953
C-4.3424320.368793 -4.705530
O-4.011210-0.273155 -5.592212
C-2.9599591.973696 -2.680530
O-1.8656632.146326 -2.401790
C-5.4853703.233989 -1.987501
O-5.7724534.161886 -1.384790
C-7.2511290.285112 -0.490392
C-8.1601271.342935 -0.628430
C-7.741051-0.990540 -0.195286
C-9.5226721.125039 -0.495420
H-7.8051612.343136 -0.840581
C-9.107435-1.205762 -0.058893
H-7.043511-1.806193 -0.068736
C-10.001503-0.152087 -0.213304
H-10.2127661.950823 -0.611795
H-9.473531-2.199462 0.166969
H-11.065618-0.322114 -0.110723

**8''e:**

E = -1492.99490112882 au
ZPE = 0.16772103 au
$G_{corr}$ = 0.11875573 au

C-4.2546430.567300 0.117479
H-3.9451161.519764 -0.324261
H-4.8912340.786465 0.976149
H-3.3642630.058915 0.493512
N-4.956705-0.301019 -0.800042
P-6.4446960.171726 -1.532519
P-4.181355-1.076241 -2.121512
C-3.2330480.320448 -2.896276
H-2.4163250.605372 -2.229552
H-2.7856480.008901 -3.839416
H-3.8486261.203368 -3.074413
W-6.359026-1.395151 -3.764320
C-6.412943-3.162256 -2.696529
O-6.435671-4.129630 -2.098953
C-8.352248-1.067783 -3.335731
O-9.474655-0.916167 -3.221274
C-6.2343240.453113 -4.674308
O-6.1647221.479209 -5.160017
C-4.635637-1.946080 -4.761596
O-3.732128-2.288117 -5.362657
C-7.200663-2.273284 -5.380292
O-7.677419-2.776004 -6.287553
C-7.623363-0.653131 -0.367698
H-7.434463-0.242714 0.626679
H-8.658413-0.429086 -0.621801
H-7.488943-1.732795 -0.318574

**8''e:** E = -1490.983599010904 au (CPCM(tol)/B3LYP-D3/def2-TZV(ecp))

ZPE = 0.16097400 au

$G_{corr}$ = 0.11117677 au

| | | | | | |
|---|---|---|---|---|---|
| C | -4.279848 | 0.607287 | 0.139683 | O | -6.402177 | -4.147506 | -2.125177 |
| H | -3.964337 | 1.570377 | -0.275580 | C | -8.371994 | -1.097723 | -3.322685 |
| H | -4.942252 | 0.798673 | 0.986094 | O | -9.495228 | -0.946481 | -3.178339 |
| H | -3.397990 | 0.081508 | 0.513552 | C | -6.273275 | 0.465035 | -4.677703 |
| N | -4.964360 | -0.229547 | -0.832876 | O | -6.205335 | 1.504380 | -5.145278 |
| P | -6.474315 | 0.186730 | -1.532000 | C | -4.639489 | -1.883551 | -4.809657 |
| P | -4.188533 | -1.066835 | -2.103207 | O | -3.729410 | -2.177868 | -5.434127 |
| C | -3.159017 | 0.261892 | -2.895737 | C | -7.228724 | -2.295323 | -5.399611 |
| H | -2.367862 | 0.543517 | -2.196625 | O | -7.720052 | -2.811666 | -6.297844 |
| H | -2.688451 | -0.120458 | -3.801541 | C | -7.627628 | -0.646694 | -0.345290 |
| H | -3.744603 | 1.150462 | -3.138498 | H | -7.465959 | -0.185920 | 0.632516 |
| W | -6.378463 | -1.401499 | -3.790671 | H | -8.665212 | -0.480360 | -0.634408 |
| C | -6.398158 | -3.177013 | -2.726500 | H | -7.433606 | -1.716297 | -0.263969 |

**8''f:** E = -1587.83344750261 au

ZPE = 0.21524906 au

$G_{corr}$ = 0.16319612 au

| | | | | | |
|---|---|---|---|---|---|
| C | -4.346592 | -0.221574 | 0.377144 | C | -3.187883 | 0.206914 | -2.863861 |
| H | -3.382174 | 0.265579 | 0.226719 | H | -2.494916 | 0.460182 | -2.059716 |
| H | -4.913236 | 0.379442 | 1.088191 | H | -2.591964 | -0.172024 | -3.694165 |
| H | -4.167943 | -1.204258 | 0.815545 | H | -3.691761 | 1.117824 | -3.188830 |
| N | -5.051444 | -0.315048 | -0.885211 | W | -6.322929 | -1.363867 | -4.100198 |
| P | -6.581659 | 0.158229 | -1.243501 | C | -5.962960 | -3.366239 | -3.762672 |
| N | -7.529031 | -0.527711 | -0.064330 | O | -5.756260 | -4.470519 | -3.570760 |
| C | -8.862142 | 0.007089 | 0.139694 | C | -8.097043 | -1.626450 | -3.105731 |
| H | -9.618852 | -0.763593 | -0.011240 | O | -9.119242 | -1.816479 | -2.626362 |
| H | -8.966048 | 0.401169 | 1.152763 | C | -6.605241 | 0.660566 | -4.347062 |
| H | -9.056770 | 0.821718 | -0.557740 | O | -6.758297 | 1.783273 | -4.484063 |
| C | -7.201309 | -1.694299 | 0.728005 | C | -4.697687 | -1.282669 | -5.370671 |
| H | -7.038921 | -1.432089 | 1.775960 | O | -3.846294 | -1.274251 | -6.129402 |
| H | -8.020826 | -2.413717 | 0.679394 | C | -7.380382 | -1.747654 | -5.752441 |
| H | -6.305272 | -2.177443 | 0.346682 | O | -7.966656 | -1.966335 | -6.715296 |
| P | -4.373006 | -1.104166 | -2.299721 | | | | |

**8''f:** E = -1585.652725444814 au (CPCM(tol)/B3LYP-D3/def2-TZV(ecp))

ZPE = 0.20712856 au

$G_{corr}$ = 0.15425677 au

| | | | | | |
|---|---|---|---|---|---|
| C | -4.332452 | -0.205246 | 0.395846 | H | -4.158480 | -1.194459 | 0.824250 |
| H | -3.368609 | 0.286085 | 0.252502 | N | -5.033426 | -0.296813 | -0.880838 |
| H | -4.917499 | 0.388198 | 1.099066 | P | -6.558394 | 0.199661 | -1.233448 |

| | | | | | |
|---|---|---|---|---|---|
| N | -7.516341 | -0.491255 | -0.065355 | H | -3.652409 | 1.117625 | -3.156818 |
| C | -8.862176 | 0.042602 | 0.118591 | W | -6.332294 | -1.370270 | -4.090938 |
| H | -9.610131 | -0.716212 | -0.119105 | C | -5.936642 | -3.369845 | -3.745519 |
| H | -9.000238 | 0.366965 | 1.153228 | O | -5.709931 | -4.472614 | -3.542859 |
| H | -9.011189 | 0.902248 | -0.535270 | C | -8.068716 | -1.674327 | -3.031583 |
| C | -7.227947 | -1.712030 | 0.673301 | O | -9.063442 | -1.901795 | -2.503413 |
| H | -7.167258 | -1.513055 | 1.746587 | C | -6.643014 | 0.653534 | -4.340623 |
| H | -8.025587 | -2.438607 | 0.498936 | O | -6.808958 | 1.777765 | -4.485679 |
| H | -6.287145 | -2.138490 | 0.336522 | C | -4.715724 | -1.252381 | -5.377132 |
| P | -4.359155 | -1.097080 | -2.285949 | O | -3.862958 | -1.218474 | -6.139794 |
| C | -3.154972 | 0.190867 | -2.864800 | C | -7.428280 | -1.764337 | -5.729606 |
| H | -2.436165 | 0.405973 | -2.071599 | O | -8.041791 | -1.982906 | -6.680336 |
| H | -2.603420 | -0.199725 | -3.721040 | | | | |

**8’’g:**

E = -1685.08162962605 au

ZPE = 0.22292053 au

$G_{corr}$ = 0.17035377 au

| | | | | | |
|---|---|---|---|---|---|
| C | -4.637866 | 0.113347 | 0.431617 | O | -9.223382 | -0.185658 | -3.938752 |
| H | -3.896228 | 0.846826 | 0.100908 | C | -5.462775 | -0.013706 | -4.736728 |
| H | -5.364083 | 0.625927 | 1.064088 | O | -4.974436 | 0.862600 | -5.272846 |
| H | -4.132414 | -0.631602 | 1.049595 | C | -7.093551 | -2.396897 | -5.435530 |
| N | -5.323465 | -0.545450 | -0.656418 | O | -7.509527 | -2.862623 | -6.390661 |
| P | -6.324625 | 0.305940 | -1.754967 | C | -7.941048 | 0.204863 | -0.898321 |
| P | -4.599257 | -1.745122 | -1.648717 | C | -8.877838 | 1.207645 | -1.144188 |
| C | -3.051961 | -0.895012 | -2.223787 | C | -8.243344 | -0.795939 | 0.023983 |
| H | -2.385236 | -0.758217 | -1.369642 | C | -10.103873 | 1.200753 | -0.494108 |
| H | -2.520981 | -1.506457 | -2.952545 | H | -8.646789 | 2.006457 | -1.840242 |
| H | -3.247846 | 0.084628 | -2.662421 | C | -9.466208 | -0.800321 | 0.675697 |
| W | -6.352197 | -1.584474 | -3.736187 | H | -7.512041 | -1.566103 | 0.235997 |
| C | -4.740569 | -2.764484 | -4.264689 | C | -10.400633 | 0.195395 | 0.414961 |
| O | -3.899458 | -3.444750 | -4.617796 | H | -10.823654 | 1.984052 | -0.692814 |
| C | -7.198842 | -3.070976 | -2.576312 | H | -9.693449 | -1.582397 | 1.388647 |
| O | -7.660592 | -3.883770 | -1.929360 | H | -11.355329 | 0.189699 | 0.924499 |
| C | -8.195248 | -0.648492 | -3.793419 | | | | |

**8’’g:**

E = -1682.695022569899 au (CPCM(tol)/B3LYP-D3/def2-TZV(ecp))

ZPE = 0.21451100 au

$G_{corr}$ = 0.16080692 au

| | | | | | |
|---|---|---|---|---|---|
| C | -4.692916 | 0.292004 | 0.396074 | P | -4.692915 | -1.688237 | -1.612030 |
| H | -3.931034 | 1.031814 | 0.131480 | C | -3.007070 | -1.120830 | -2.144865 |
| H | -5.471483 | 0.789563 | 0.978020 | H | -2.407430 | -0.962707 | -1.244894 |
| H | -4.235930 | -0.473722 | 1.027350 | H | -2.520034 | -1.889270 | -2.745333 |
| N | -5.285754 | -0.332783 | -0.772589 | H | -3.047315 | -0.187246 | -2.708688 |
| P | -6.388093 | 0.411427 | -1.828031 | W | -6.368150 | -1.554869 | -3.815398 |

| | | | | | |
|---|---|---|---|---|---|
| C | -4.751931 | -2.763627 | -4.275324 | C | -8.981241 | 1.171161 | -1.134545 |
| O | -3.921101 | -3.476164 | -4.604352 | C | -8.152015 | -0.737185 | 0.081058 |
| C | -7.277123 | -3.039845 | -2.695412 | C | -10.175901 | 1.104409 | -0.427165 |
| O | -7.773690 | -3.852837 | -2.066891 | H | -8.840651 | 1.945682 | -1.879708 |
| C | -8.210024 | -0.605018 | -3.893900 | C | -9.343866 | -0.802670 | 0.789254 |
| O | -9.237720 | -0.130749 | -4.040878 | H | -7.362794 | -1.451793 | 0.277623 |
| C | -5.400998 | 0.007009 | -4.768619 | C | -10.359112 | 0.117597 | 0.535836 |
| O | -4.861583 | 0.874273 | -5.279501 | H | -10.961241 | 1.823068 | -0.624432 |
| C | -7.043784 | -2.326641 | -5.561092 | H | -9.485675 | -1.572900 | 1.537182 |
| O | -7.422977 | -2.768593 | -6.549360 | H | -11.288567 | 0.065584 | 1.088498 |
| C | -7.958623 | 0.249777 | -0.889825 | | | | |

TS(**8'e→4'e**): E = -1492.99324202369 au

ZPE = 0.16743816 au

$G_{corr}$ = 0.11855123 au

ν = -94.80 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | -0.188921 | -1.220269 | 2.971259 | O | -1.541747 | 2.926266 | -1.940168 |
| H | 0.659786 | -0.538512 | 3.086716 | C | 2.073261 | 2.871389 | -1.533796 |
| H | -1.008693 | -0.848391 | 3.584689 | O | 2.691152 | 3.683178 | -2.064712 |
| H | 0.109843 | -2.198128 | 3.347717 | C | 1.161803 | 0.315316 | -2.295605 |
| N | -0.654880 | -1.370212 | 1.597632 | O | 1.289137 | -0.299136 | -3.250325 |
| P | -0.971983 | 0.097608 | 0.690795 | C | 2.750080 | 0.707794 | 0.137604 |
| C | -0.373639 | -2.670628 | -0.839134 | O | 3.744674 | 0.310728 | 0.524878 |
| H | -0.377826 | -2.244349 | -1.842463 | C | 0.862049 | 2.729984 | 1.032961 |
| H | 0.173005 | -3.613725 | -0.890107 | O | 0.800193 | 3.430591 | 1.928044 |
| H | -1.394604 | -2.874956 | -0.527113 | C | -2.430363 | -0.323681 | -0.344647 |
| P | 0.518725 | -1.580844 | 0.345406 | H | -3.029422 | -1.088016 | 0.147384 |
| W | 0.994625 | 1.495008 | -0.622727 | H | -3.035634 | 0.577098 | -0.446498 |
| C | 0.660590 | 2.388083 | -1.453930 | H | -2.160033 | -0.662196 | -1.343856 |

TS(**8'f→4'f**): E = -1587.81518180678 au

ZPE = 0.21425087 au

$G_{corr}$ = 0.16286393 au

ν = -108.57 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | 2.283593 | -1.805254 | 1.437993 | N | -1.336389 | -0.384077 | 1.196037 |
| H | 3.065430 | -1.173810 | 1.006078 | C | -2.364456 | 0.605625 | 0.955983 |
| H | 2.216575 | -1.584644 | 2.502938 | H | -3.336492 | 0.109893 | 0.949028 |
| H | 2.585739 | -2.844971 | 1.317323 | H | -2.397132 | 1.393729 | 1.715892 |
| N | 0.972569 | -1.627469 | 0.828785 | H | -2.237121 | 1.070145 | -0.019605 |
| P | 0.275424 | -0.044301 | 0.792132 | C | -1.613281 | -1.267634 | 2.313112 |
| C | -0.811535 | -2.373311 | -1.140698 | H | -1.651760 | -0.732852 | 3.268303 |
| H | -1.606190 | -1.871064 | -0.585843 | H | -2.578733 | -1.753512 | 2.159361 |
| H | -1.043416 | -2.360825 | -2.205529 | H | -0.856731 | -2.045293 | 2.378967 |
| H | -0.762952 | -3.411879 | -0.810768 | P | 0.824312 | -1.583841 | -0.892976 |

| | | | | | |
|---|---|---|---|---|---|
| W | 0.827647 | 1.718270 | -1.245779 | | |
| C | -0.731357 | 1.095148 | -2.440153 | | |
| O | -1.585402 | 0.757977 | -3.117107 | | |
| C | 1.127690 | 3.268419 | -2.423433 | | |
| O | 1.291755 | 4.181541 | -3.103888 | | |
| C | 2.193562 | 0.718548 | -2.435710 | | |
| O | 2.963879 | 0.253653 | -3.134340 | | |
| C | 2.404233 | 2.296094 | -0.046158 | | |
| O | 3.277243 | 2.630456 | 0.605003 | | |
| C | -0.389846 | 2.986167 | -0.184266 | | |
| O | -1.006858 | 3.779069 | 0.359320 | | |

TS(**8'g→4'g**)**:** E = -1685.07895977059 au

ZPE = 0.2229363 au

$G_{corr}$ = 0.17076783 au

ν = -61.07 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | 2.652646 | -1.668784 | 1.512279 | | |
| H | 3.434161 | -1.063114 | 1.042793 | | |
| H | 2.613423 | -1.411061 | 2.569934 | | |
| H | 2.937972 | -2.716294 | 1.421624 | | |
| N | 1.326397 | -1.492072 | 0.931549 | | |
| P | 0.717871 | 0.142031 | 0.783976 | | |
| C | -0.440068 | -2.273404 | -1.081880 | | |
| H | -0.890054 | -1.862914 | -1.985795 | | |
| H | -0.239646 | -3.330922 | -1.266498 | | |
| H | -1.141914 | -2.187287 | -0.257414 | | |
| P | 1.182444 | -1.470130 | -0.791759 | | |
| W | 1.364395 | 1.618529 | -1.503894 | | |
| C | -0.201690 | 1.052416 | -2.709000 | | |
| O | -1.052804 | 0.765562 | -3.414027 | | |
| C | 1.746679 | 3.103880 | -2.742862 | | |
| O | 1.962658 | 3.977224 | -3.458483 | | |
| C | 2.671291 | 0.493204 | -2.641370 | | |
| O | 3.404465 | -0.066222 | -3.309727 | | |
| C | 2.965329 | 2.190965 | -0.325261 | | |
| O | 3.851714 | 2.523981 | 0.306551 | | |
| C | 0.176933 | 2.973751 | -0.501510 | | |
| O | -0.424354 | 3.802604 | 0.000942 | | |
| C | -1.045181 | -0.111465 | 1.152138 | | |
| C | -2.047181 | 0.558529 | 0.455821 | | |
| C | -1.394346 | -0.927594 | 2.229654 | | |
| C | -3.376921 | 0.413649 | 0.825167 | | |
| H | -1.803318 | 1.178215 | -0.396348 | | |
| C | -2.722735 | -1.067564 | 2.597964 | | |
| H | -0.627763 | -1.466206 | 2.771393 | | |
| C | -3.717639 | -0.397038 | 1.897516 | | |
| H | -4.145971 | 0.931655 | 0.267757 | | |
| H | -2.982315 | -1.704474 | 3.433377 | | |
| H | -4.754476 | -0.509651 | 2.185390 | | |

TS(**8''e→4''e**)**:** E = -1492.98929306283 au

ZPE = 0.16774437 au

$G_{corr}$ = 0.11907136 au

ν = -100.08 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| C | 1.228161 | -0.218738 | 3.071006 | | |
| H | 1.572759 | 0.779513 | 2.791370 | | |
| H | 0.499594 | -0.112855 | 3.873494 | | |
| H | 2.079804 | -0.778476 | 3.457954 | | |
| N | 0.624607 | -0.974128 | 1.988228 | | |
| P | -0.703746 | -0.319888 | 1.049976 | | |
| P | 1.299664 | -1.246007 | 0.437893 | | |
| C | 2.549717 | 0.109024 | 0.294610 | | |
| H | 3.333638 | -0.106869 | 1.025310 | | |
| H | 3.016743 | 0.092058 | -0.686958 | | |
| H | 2.169452 | 1.109413 | 0.489803 | | |
| W | -0.720014 | 0.666592 | -1.534420 | | |
| C | -1.412089 | -1.171176 | -2.153661 | | |
| O | -1.787391 | -2.183108 | -2.519987 | | |
| C | -2.598069 | 1.184098 | -0.849859 | | |
| O | -3.648794 | 1.492374 | -0.535115 | | |
| C | 0.032826 | 2.471819 | -0.881899 | | |
| O | 0.453414 | 3.471572 | -0.531713 | | |
| C | 1.035483 | 0.245771 | -2.509075 | | |
| O | 1.947062 | 0.037444 | -3.166135 | | |
| C | -1.286761 | 1.469141 | -3.243508 | | |
| O | -1.630976 | 1.940635 | -4.233660 | | |

| | | | |
|---|---|---|---|
| C-1.832963-1.770808 | 1.076426 | H-2.771701-1.517649 | 0.584675 |
| H-2.042551-2.022483 | 2.116375 | H-1.407869-2.647268 | 0.588869 |

TS(**8''f→4''f**)**:** E = -1587.81629347084 au

ZPE = 0.21446254 au

$G_{corr}$ = 0.16291168 au

ν = -119.46 $cm^{-1}$

| | | | |
|---|---|---|---|
| C-4.285541-0.313603 | -2.345274 | H-4.5932422.758882 | -2.770827 |
| H-3.4475350.340674 | -2.094427 | H-5.2889363.775741 | -1.524088 |
| H-4.016370-1.333373 | -2.074036 | H-4.1023132.531294 | -1.091559 |
| H-4.437762-0.277725 | -3.424114 | P-5.816340-0.001703 | -0.007631 |
| N-5.5188320.045320 | -1.678649 | W-6.2569962.123230 | 1.791912 |
| N-7.033572-1.152957 | 0.138779 | C-8.2035171.457734 | 1.883009 |
| C-8.148637-1.282656 | -0.770647 | O-9.2959731.137266 | 1.946081 |
| H-8.419587-2.335251 | -0.876751 | C-6.9465613.693119 | 0.662662 |
| H-9.031949-0.740111 | -0.417978 | O-7.3689594.610244 | 0.128686 |
| H-7.886379-0.910978 | -1.758791 | C-4.3316122.844429 | 1.671347 |
| C-7.197741-1.818021 | 1.412518 | O-3.2732653.266577 | 1.628253 |
| H-8.015425-1.408292 | 2.012515 | C-6.5926423.268940 | 3.350225 |
| H-7.407061-2.877292 | 1.245690 | O-6.7893463.932069 | 4.269911 |
| H-6.281540-1.764371 | 1.998517 | C-5.6220520.719386 | 3.162873 |
| P-6.3452731.551961 | -1.638492 | O-5.2752240.015604 | 3.990576 |
| C-4.9472522.765001 | -1.736626 | | |

TS(**8''g→4''g**)**:** E = -1685.07476808348 au

ZPE = 0.22310697 au

$G_{corr}$ = 0.17143697 au

ν = -94.01 $cm^{-1}$

| | | | |
|---|---|---|---|
| C2.471076 1.687509 | 1.759820 | C-0.8571041.173964 | -2.719420 |
| H3.097526 1.942127 | 0.902121 | O-1.4381992.091459 | -3.064728 |
| H1.964446 2.592200 | 2.092008 | C1.889062 0.326304 | -2.991432 |
| H3.117783 1.343468 | 2.566879 | O2.822077 0.786751 | -3.459321 |
| N1.476977 0.666139 | 1.490365 | C-0.281615-1.194491 | -4.008451 |
| P0.291718 0.826045 | 0.223947 | O-0.565057-1.571852 | -5.056795 |
| P1.721312-0.879046 | 0.800912 | C-1.2402250.467214 | 1.139468 |
| C3.312049-0.672011 | -0.117881 | C-2.4461010.861609 | 0.559871 |
| H4.104331-0.687612 | 0.635843 | C-1.255632-0.124560 | 2.401293 |
| H3.489616-1.510825 | -0.787026 | C-3.6471990.648761 | 1.217650 |
| H3.399914 0.255908 | -0.677850 | H-2.4574971.346310 | -0.408903 |
| W0.190367-0.532487 | -2.215322 | C-2.459053-0.342257 | 3.054570 |
| C1.166946-2.318970 | -1.959447 | H-0.328409-0.410687 | 2.879325 |
| O1.666346-3.345156 | -1.905908 | C-3.6563660.040192 | 2.464778 |
| C-1.498401-1.463420 | -1.471208 | H-4.5744800.960986 | 0.756049 |
| O-2.421950-2.021064 | -1.108999 | H-2.460937-0.811783 | 4.029541 |

H-4.593322-0.130724 2.978250

**4'e:**

E = -1493.02262772543 au

ZPE = 0.16793022 au

$G_{corr}$ = 0.11829061 au

C-3.450353-1.136439 0.080756
H-2.531153-0.823253 -0.423043
H-3.550138-0.557466 0.998401
H-3.341597-2.184787 0.356450
N-4.650603-0.981061 -0.717969
P-5.0354930.422266 -1.632529
C-6.421451-2.428321 -2.355272
H-6.856028-2.380346 -3.354150
H-6.263628-3.480388 -2.113238
H-7.123541-2.013093 -1.636780
P-4.783321-1.589782 -2.373439
W-3.4256202.258156 -2.181336
C-4.1857112.263463 -4.097560
O-4.6059612.266304 -5.157335
C-2.1623053.759467 -2.665638
O-1.4499754.611767 -2.940711
C-2.0073130.876896 -2.759092
O-1.2121820.128405 -3.086735
C-2.6702232.250531 -0.265751
O-2.2477442.265796 0.793911
C-4.8308993.646880 -1.612830
O-5.6053774.423563 -1.298075
C-6.7591000.836533 -1.208048
H-7.370631-0.041894 -1.021062
H-6.7544501.456190 -0.310689
H-7.1952801.416128 -2.021078

**4'f:**

E = -1587.84733949481 au

ZPE = 0.21497532 au

$G_{corr}$ = 0.16277424 au

C-3.006975-0.974362 -1.273367
H-2.529477-0.437798 -2.097946
H-2.849189-0.406869 -0.356835
H-2.506185-1.935426 -1.163867
N-4.423883-1.202962 -1.467441
P-5.591694-0.061596 -1.892050
C-6.264944-3.191810 -2.192746
H-6.945610-2.780953 -1.450394
H-6.854658-3.624310 -3.001633
H-5.685103-3.993759 -1.734636
N-6.769381-0.151672 -0.699196
C-8.0901050.366381 -0.977230
H-8.816429-0.440263 -1.117778
H-8.4371150.998425 -0.157031
H-8.0938330.971213 -1.883348
C-6.661815-0.929172 0.514772
H-6.844848-0.290525 1.382985
H-7.389910-1.745718 0.540167
H-5.669025-1.360411 0.606414
P-5.126632-1.938553 -2.921574
W-5.0556602.151528 -2.943377
C-6.6551881.934619 -4.224809
O-7.5362271.824288 -4.940351
C-4.6060103.916805 -3.813987
O-4.3513614.917332 -4.307909
C-3.8417191.182887 -4.297891
O-3.1600260.668347 -5.053173
C-3.4520772.407873 -1.679525
O-2.5649302.585937 -0.984421
C-6.2314533.137545 -1.571999
O-6.8674893.696188 -0.807579

**4'g:**

E = -1685.10869808946 au

ZPE = 0.22355355 au

$G_{corr}$ = 0.17101322 au

| | | | |
|---|---|---|---|
| C-3.422552-1.149655 | -1.132961 | O-2.8985040.641666 | -4.804218 |
| H-2.831786-0.644772 | -1.902791 | C-3.4858772.298295 | -1.422060 |
| H-3.296736-0.609448 | -0.195443 | O-2.6853942.374753 | -0.613218 |
| H-3.015349-2.151258 | -1.000456 | C-6.2073753.250022 | -1.654186 |
| N-4.835752-1.255060 | -1.442122 | O-6.9040873.839245 | -0.971113 |
| P-5.8032750.039856 | -2.010063 | C-7.297505-0.022417 | -0.991383 |
| C-6.763190-3.015621 | -2.471174 | C-8.4174550.694610 | -1.407577 |
| H-7.393643-3.227669 | -3.335169 | C-7.339867-0.737693 | 0.202797 |
| H-6.302583-3.952850 | -2.155138 | C-9.5703800.692969 | -0.638482 |
| H-7.385350-2.639567 | -1.661353 | H-8.3987541.252905 | -2.336269 |
| P-5.435139-1.858851 | -2.993687 | C-8.492253-0.726047 | 0.975243 |
| W-4.9275142.212442 | -2.891174 | H-6.473377-1.301657 | 0.522167 |
| C-6.3608642.154717 | -4.369556 | C-9.607590-0.013927 | 0.556088 |
| O-7.1524352.130336 | -5.190144 | H-10.4381111.246898 | -0.970805 |
| C-4.2456673.964375 | -3.629006 | H-8.518403-1.276448 | 1.906430 |
| O-3.8614254.956984 | -4.048965 | H-10.505404-0.008908 | 1.159794 |
| C-3.6261731.190579 | -4.119278 | | |

**4''e:**

E = -1493.0231416733 au

ZPE = 0.16811186 au

$G_{corr}$ = 0.11873135 au

| | | | |
|---|---|---|---|
| C-3.5261150.734652 | -0.373759 | O-4.693002-1.479005 | -5.724662 |
| H-2.8465270.897963 | -1.214036 | C-7.7363140.101590 | -4.100688 |
| H-4.0834891.655652 | -0.205105 | O-8.790131-0.307503 | -4.251717 |
| H-2.9208280.542063 | 0.512529 | C-6.5714782.361097 | -2.658125 |
| N-4.450762-0.359007 | -0.562591 | O-6.9750513.186569 | -1.982424 |
| P-5.605346-0.545487 | -1.815127 | C-3.9660281.714429 | -3.770365 |
| P-4.089303-1.963545 | -1.196697 | O-2.9379572.209977 | -3.764771 |
| C-2.804606-1.703538 | -2.502583 | C-6.1897482.022782 | -5.500099 |
| H-1.819693-1.700176 | -2.033725 | O-6.4002402.674464 | -6.416863 |
| H-2.839038-2.552071 | -3.186731 | C-7.145270-0.971176 | -0.931620 |
| H-2.914743-0.789221 | -3.082195 | H-6.935626-1.540952 | -0.028575 |
| W-5.8412700.873109 | -3.879049 | H-7.672659-0.055436 | -0.661963 |
| C-5.098469-0.640301 | -5.067856 | H-7.790569-1.559290 | -1.583380 |

**4''f:**

E = -1587.84814947618 au

ZPE = 0.21542218 au

$G_{corr}$ = 0.1634649 au

| | | | |
|---|---|---|---|
| C-3.7507371.162563 | 0.295111 | P-5.8230310.185503 | -1.463984 |
| H-3.1854270.659418 | 1.080960 | N-6.984907-0.655880 | -0.567774 |
| H-3.0521111.757119 | -0.297203 | C-8.350826-0.741708 | -1.042832 |
| H-4.4572051.841011 | 0.771843 | H-8.491082-1.485147 | -1.834657 |
| N-4.4666810.195734 | -0.493702 | H-8.994385-1.020095 | -0.207408 |

| | | | |
|---|---|---|---|
| H-8.7031620.220861 | -1.401286 | C-8.1759221.192851 | -3.710266 |
| C-6.588307-1.807693 | 0.220611 | O-9.0638500.702137 | -4.231935 |
| H-7.306037-1.952270 | 1.029515 | C-7.6706092.798733 | -1.261180 |
| H-6.555528-2.727660 | -0.373248 | O-8.2896373.166584 | -0.377285 |
| H-5.611423-1.651022 | 0.670614 | C-4.9398363.241781 | -2.219516 |
| P-3.974808-0.995961 | -1.676110 | O-4.0525803.888882 | -1.908939 |
| C-2.976331-0.042418 | -2.908528 | C-5.5067861.535824 | -4.532135 |
| H-1.928906-0.073655 | -2.603933 | O-4.9652571.209934 | -5.481439 |
| H-3.046815-0.527048 | -3.882631 | C-7.1273203.806673 | -3.886863 |
| H-3.2697801.001137 | -3.009547 | O-7.4531414.750054 | -4.447979 |
| W-6.5609582.161525 | -2.877330 | | |

**4''g:** E = -1685.10499641137 au

ZPE = 0.22346178 au

$G_{corr}$ = 0.17070199 au

| | | | |
|---|---|---|---|
| C-4.4089011.365748 | 0.714224 | O-6.2386694.310776 | -0.838893 |
| H-3.6873021.794599 | 0.012634 | C-3.7463242.299144 | -2.832993 |
| H-5.0541702.169526 | 1.066523 | O-2.6239702.477928 | -2.725253 |
| H-3.8575030.979698 | 1.571477 | C-5.6479663.540361 | -4.498293 |
| N-5.2190810.307394 | 0.158994 | O-5.5817024.361656 | -5.292176 |
| P-6.0525670.327100 | -1.328832 | C-7.720117-0.252064 | -0.914892 |
| P-4.675990-1.193255 | -0.597347 | C-8.529955-0.746707 | -1.934531 |
| C-3.125746-0.781304 | -1.531534 | C-8.201299-0.206218 | 0.389763 |
| H-2.543412-0.007337 | -1.031517 | C-9.813621-1.186125 | -1.652311 |
| H-2.516524-1.684605 | -1.558178 | H-8.158619-0.803636 | -2.951636 |
| H-3.310784-0.471032 | -2.558603 | C-9.491790-0.634867 | 0.665389 |
| W-5.7740072.094170 | -3.098791 | H-7.5658640.157247 | 1.186585 |
| C-5.4706020.637895 | -4.527613 | C-10.298219-1.125067 | -0.352314 |
| O-5.303887-0.168899 | -5.315460 | H-10.435294-1.575359 | -2.447526 |
| C-7.8060292.066428 | -3.450266 | H-9.866180-0.589982 | 1.679642 |
| O-8.9222472.108533 | -3.674069 | H-11.302619-1.462350 | -0.132981 |
| C-6.0745493.518023 | -1.641853 | | |

**9a:** E = -739.178712282657 au

ZPE = 0.03428816 au

$G_{corr}$ = 0.00781235 au

| | | | |
|---|---|---|---|
| N-0.0279670.071958 | -0.034102 | H-0.390957-0.755232 | -0.494732 |
| P-0.025140-0.059814 | 1.731262 | H-0.1295121.336103 | 1.993402 |
| P1.690433 0.061047 | 0.382010 | H1.945504-1.345909 | 0.474013 |

**9b:** E = -1289.442909965287 au

ZPE = 0.42999288 au

$G_{corr}$ = 0.38153486 au

| | | | | | |
|---|---|---|---|---|---|
| P | 5.510794 | 2.708182 | 10.153274 | C | 4.252338 | 2.459486 | 13.236063 |
| P | 3.547113 | 1.770292 | 10.480574 | H | 4.648486 | 3.317635 | 12.684884 |
| N | 3.941517 | 3.421507 | 10.145178 | C | 3.621704 | 3.016340 | 14.517461 |
| C | 5.993000 | 2.147290 | 8.397856 | H | 2.832631 | 3.735970 | 14.287969 |
| C | 3.278344 | 4.406461 | 9.297509 | H | 4.372529 | 3.524614 | 15.127112 |
| H | 3.284733 | 4.082544 | 8.247423 | H | 3.185028 | 2.224465 | 15.131648 |
| C | 1.825860 | 4.545817 | 9.737970 | C | 5.430158 | 1.547454 | 13.579632 |
| H | 1.305486 | 3.588479 | 9.670017 | H | 5.123719 | 0.721101 | 14.224804 |
| H | 1.300078 | 5.263001 | 9.104879 | H | 6.194476 | 2.113840 | 14.116155 |
| H | 1.774494 | 4.892584 | 10.772466 | H | 5.897577 | 1.132602 | 12.686574 |
| C | 4.023707 | 5.733107 | 9.394096 | C | 7.081353 | 1.089021 | 8.631021 |
| H | 3.993318 | 6.109762 | 10.418390 | H | 6.671298 | 0.195294 | 9.106210 |
| H | 3.570151 | 6.475857 | 8.734517 | H | 7.523874 | 0.789469 | 7.676089 |
| H | 5.070602 | 5.620498 | 9.108445 | H | 7.887487 | 1.468580 | 9.264245 |
| C | 2.606601 | 0.461533 | 12.808926 | C | 4.881573 | 1.563285 | 7.526774 |
| H | 2.643528 | 0.469138 | 13.903273 | H | 5.279727 | 1.323344 | 6.534492 |
| C | 1.134763 | 0.319686 | 12.408494 | H | 4.470494 | 0.649922 | 7.954889 |
| H | 0.532331 | 1.131680 | 12.821639 | H | 4.057238 | 2.263073 | 7.386403 |
| H | 0.720307 | -0.624987 | 12.768153 | C | 6.610242 | 3.370232 | 7.701633 |
| H | 1.020781 | 0.337825 | 11.321277 | H | 5.854726 | 4.122579 | 7.469035 |
| C | 3.393079 | -0.767162 | 12.332019 | H | 7.379625 | 3.843343 | 8.316755 |
| H | 3.302617 | -0.897415 | 11.250894 | H | 7.078249 | 3.069117 | 6.758789 |
| H | 2.998130 | -1.671030 | 12.801684 | C | 3.177867 | 1.821687 | 12.328442 |
| H | 4.452700 | -0.704023 | 12.571960 | H | 2.339442 | 2.529800 | 12.331417 |

**9c:**

E = -1923.334311950165 au

ZPE = 0.47380550 au

$G_{corr}$ = 0.41147843 au

| | | | | | |
|---|---|---|---|---|---|
| W | 7.850078 | 3.229755 | 11.210376 | H | 4.083100 | 6.650894 | 9.062720 |
| P | 5.687571 | 2.605973 | 9.968227 | H | 5.397555 | 5.503778 | 8.822938 |
| P | 3.683929 | 1.845283 | 10.463936 | C | 3.056001 | 0.196903 | 12.668480 |
| O | 10.413871 | 4.118801 | 12.852301 | H | 2.903900 | 0.185877 | 13.752458 |
| O | 8.125310 | 5.856935 | 9.397284 | C | 1.828431 | -0.472714 | 12.040430 |
| O | 9.895193 | 1.800812 | 9.202811 | H | 0.909855 | 0.054921 | 12.306672 |
| O | 7.836805 | 0.447562 | 12.813051 | H | 1.734887 | -1.504700 | 12.385369 |
| O | 6.131253 | 5.038449 | 13.223866 | H | 1.896907 | -0.493808 | 10.950289 |
| N | 4.252974 | 3.473639 | 10.235007 | C | 4.315428 | -0.622434 | 12.368428 |
| C | 5.875340 | 2.084814 | 8.146392 | H | 4.483193 | -0.705507 | 11.291071 |
| C | 3.584637 | 4.637568 | 9.651692 | H | 4.207627 | -1.637293 | 12.757008 |
| H | 3.182957 | 4.378140 | 8.663883 | H | 5.210435 | -0.192813 | 12.810873 |
| C | 2.415844 | 5.031056 | 10.548729 | C | 3.712629 | 2.664909 | 13.324594 |
| H | 1.720662 | 4.198462 | 10.674067 | H | 4.065880 | 3.548624 | 12.791747 |
| H | 1.863222 | 5.863120 | 10.108877 | C | 2.575066 | 3.121104 | 14.246675 |
| H | 2.773687 | 5.333072 | 11.534631 | H | 1.777961 | 3.610123 | 13.682167 |
| C | 4.579602 | 5.777790 | 9.488783 | H | 2.942809 | 3.830387 | 14.991170 |
| H | 5.003830 | 6.060905 | 10.453214 | H | 2.135122 | 2.276608 | 14.784948 |

| | | |
|---|---|---|
| C | 4.868345 | 2.125492 | 14.162985 |
| H | 4.565651 | 1.264138 | 14.761406 |
| H | 5.216973 | 2.895407 | 14.852636 |
| H | 5.713004 | 1.827954 | 13.550749 |
| C | 9.490340 | 3.796630 | 12.252209 |
| C | 8.004661 | 4.922430 | 10.047874 |
| C | 9.127569 | 2.285666 | 9.902001 |
| C | 7.802963 | 1.453953 | 12.269440 |
| C | 6.708893 | 4.343966 | 12.521827 |
| C | 6.476077 | 0.671458 | 8.186278 |
| H | 5.767681 | -0.043875 | 8.607352 |
| H | 6.720309 | 0.347874 | 7.170825 |
| H | 7.393633 | 0.624442 | 8.772059 |
| C | 4.550876 | 2.052308 | 7.375483 |
| H | 4.748017 | 1.698897 | 6.359279 |
| H | 3.821734 | 1.382158 | 7.825940 |
| H | 4.101842 | 3.041926 | 7.293437 |
| C | 6.826036 | 3.049914 | 7.426025 |
| H | 6.429465 | 4.065841 | 7.401746 |
| H | 7.813815 | 3.084327 | 7.876935 |
| H | 6.948968 | 2.720740 | 6.390455 |
| C | 3.161797 | 1.692201 | 12.259607 |
| H | 2.124620 | 2.019712 | 12.093464 |

**9d:**

E = -1939.401297736822 au

ZPE = 0.46199985 au

$G_{corr}$ = 0.39930609 au

| | | |
|---|---|---|
| W | 8.022161 | 3.248972 | 11.108492 |
| P | 5.874837 | 2.500895 | 9.904273 |
| P | 3.902563 | 1.658209 | 10.593640 |
| O | 10.680500 | 4.114508 | 12.608223 |
| O | 7.926854 | 5.957911 | 9.395214 |
| O | 10.041262 | 1.987352 | 8.963167 |
| O | 7.873246 | 0.436260 | 12.647943 |
| O | 6.522722 | 4.875514 | 13.422984 |
| N | 4.370752 | 3.243398 | 10.205068 |
| N | 3.642654 | 1.602889 | 12.252716 |
| C | 5.985624 | 2.114624 | 8.049105 |
| C | 3.701081 | 4.477434 | 9.780087 |
| H | 4.049543 | 4.709575 | 8.767865 |
| C | 2.194467 | 4.259479 | 9.728542 |
| H | 1.935215 | 3.444433 | 9.051216 |
| H | 1.694293 | 5.165172 | 9.382931 |
| H | 1.803781 | 4.015572 | 10.718689 |
| C | 4.083822 | 5.641035 | 10.689987 |
| H | 3.732277 | 5.468688 | 11.708576 |
| H | 3.640841 | 6.570881 | 10.326785 |
| H | 5.164770 | 5.772865 | 10.719744 |
| C | 2.975188 | 0.387145 | 12.781315 |
| H | 2.857002 | 0.564496 | 13.850134 |
| C | 1.572193 | 0.193128 | 12.200950 |
| H | 0.967258 | 1.089190 | 12.345681 |
| H | 1.073257 | -0.642303 | 12.696784 |
| H | 1.608905 | -0.022944 | 11.132452 |
| C | 3.841067 | -0.863392 | 12.617902 |
| H | 3.958141 | -1.122093 | 11.563122 |
| H | 3.380256 | -1.715839 | 13.122011 |
| H | 4.834095 | -0.708573 | 13.040029 |
| C | 4.030862 | 2.635766 | 13.224290 |
| H | 4.567104 | 3.383276 | 12.646982 |
| C | 2.802734 | 3.319343 | 13.829506 |
| H | 2.158477 | 3.726156 | 13.049383 |
| H | 3.113621 | 4.139312 | 14.479668 |
| H | 2.209800 | 2.627834 | 14.432302 |
| C | 4.967228 | 2.108681 | 14.310598 |
| H | 4.469285 | 1.387574 | 14.961845 |
| H | 5.307966 | 2.933605 | 14.936897 |
| H | 5.841466 | 1.626724 | 13.878443 |
| C | 9.717041 | 3.803665 | 12.066405 |
| C | 7.974410 | 4.991582 | 10.008520 |
| C | 9.275340 | 2.407689 | 9.704632 |
| C | 7.938679 | 1.447973 | 12.116015 |
| C | 7.005468 | 4.254576 | 12.589083 |
| C | 6.729031 | 0.776652 | 7.930887 |
| H | 6.145954 | -0.036101 | 8.367664 |
| H | 6.899817 | 0.542449 | 6.876363 |
| H | 7.701412 | 0.795605 | 8.420101 |
| C | 4.597875 | 1.973951 | 7.413972 |
| H | 4.716143 | 1.692364 | 6.363800 |
| H | 3.999547 | 1.201965 | 7.896877 |
| H | 4.036341 | 2.907429 | 7.440402 |
| C | 6.758057 | 3.223135 | 7.322401 |
| H | 6.264043 | 4.191550 | 7.419399 |
| H | 7.776140 | 3.328141 | 7.691318 |
| H | 6.816767 | 2.985641 | 6.255827 |

TS(**6d'→10**)**:** E = -1954.20168939079 au

ZPE = 0.17658748 au

$G_{corr}$ = 0.12483686 au

ν = -1049.8 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| W | -1.383389 | -1.600984 | 1.028923 | H | 2.065887 | -0.290693 | 0.825336 |
| C | 0.352939 | -2.525286 | 0.435436 | C | -1.323328 | 2.037665 | 0.476065 |
| O | 1.312322 | -3.057595 | 0.115213 | H | -1.033834 | 2.907396 | -0.114003 |
| C | -2.336643 | -2.382062 | -0.621334 | H | -2.407593 | 2.050137 | 0.592127 |
| O | -2.859926 | -2.807607 | -1.542322 | H | -0.886933 | 2.121598 | 1.472600 |
| C | -0.416039 | -0.738098 | 2.617879 | N | 0.903609 | 0.768273 | -0.584932 |
| O | 0.120960 | -0.242394 | 3.497948 | P | 1.172341 | 0.729939 | -2.191604 |
| C | -3.135216 | -0.702216 | 1.615574 | C | 2.536109 | 1.829313 | -2.653588 |
| O | -4.111665 | -0.210205 | 1.947524 | H | 2.271269 | 2.848776 | -2.377787 |
| C | -1.853078 | -3.221152 | 2.127622 | H | 3.454850 | 1.539015 | -2.143380 |
| O | -2.118492 | -4.138123 | 2.765353 | H | 2.698432 | 1.773618 | -3.728136 |
| C | 1.895613 | 0.725584 | 0.470885 | Cl | 1.887077 | -1.095399 | -2.820203 |
| H | 2.848109 | 1.133594 | 0.132096 | P | -0.853642 | 0.467243 | -0.365937 |
| H | 1.562573 | 1.332326 | 1.311009 | H | -0.362312 | 0.747337 | -2.288362 |

**10:** E = -1954.21746980023 au

ZPE = 0.18047378 au

$G_{corr}$ = 0.12908545 au

| | | | | | |
|---|---|---|---|---|---|
| W | -5.942012 | -2.512766 | 2.633398 | H | -2.695084 | -0.991938 | 2.423168 |
| C | -4.152192 | -3.273192 | 1.992297 | C | -6.116323 | 1.128643 | 2.259800 |
| O | -3.156053 | -3.712941 | 1.636413 | H | -5.906417 | 2.056313 | 1.726259 |
| C | -6.840064 | -3.305132 | 0.959666 | H | -7.191305 | 1.088284 | 2.441979 |
| O | -7.330926 | -3.732317 | 0.020897 | H | -5.624361 | 1.158733 | 3.232831 |
| C | -5.029313 | -1.609310 | 4.227888 | N | -3.909097 | 0.036487 | 1.020156 |
| O | -4.521496 | -1.088745 | 5.112536 | P | -3.588895 | -0.076983 | -0.545805 |
| C | -7.754699 | -1.773955 | 3.261663 | C | -1.905594 | 0.397264 | -0.945363 |
| O | -8.764927 | -1.373182 | 3.616181 | H | -1.717624 | 1.410321 | -0.591921 |
| C | -6.268407 | -4.192923 | 3.682323 | H | -1.194877 | -0.287977 | -0.486812 |
| O | -6.454315 | -5.149059 | 4.293667 | H | -1.775277 | 0.365999 | -2.025706 |
| C | -2.905733 | 0.017886 | 2.076993 | Cl | -3.759279 | -1.934854 | -1.348015 |
| H | -1.974006 | 0.481267 | 1.752980 | P | -5.672287 | -0.351797 | 1.241842 |
| H | -3.284162 | 0.599057 | 2.914616 | H | -4.488663 | 0.674104 | -1.291769 |

TS(**10→3d'$_P$·H$^+$**)**:** E = -1954.2152823828 au

ZPE = 0.17945929 au

$G_{corr}$ = 0.1285717 au

ν = -46.62 $cm^{-1}$

| | | | | | |
|---|---|---|---|---|---|
| W | -1.182445 | -1.593135 | 0.955460 | O | 1.697627 | -2.529521 | -0.074173 |
| C | 0.666102 | -2.213708 | 0.298744 | C | -2.038714 | -2.298928 | -0.791701 |

| | | | | | |
|---|---|---|---|---|---|
| O | -2.529268 | -2.711474 | -1.732986 | H | -1.289123 | 2.977117 | -0.198172 |
| C | -0.357520 | -0.901410 | 2.702438 | H | -2.671527 | 1.940683 | 0.200708 |
| O | 0.092921 | -0.519647 | 3.680777 | H | -1.465279 | 2.302265 | 1.435168 |
| C | -3.020257 | -0.899539 | 1.560478 | N | 0.982839 | 1.102466 | -0.213969 |
| O | -4.038295 | -0.504753 | 1.893623 | P | 0.713732 | 0.912175 | -1.838154 |
| C | -1.527145 | -3.378009 | 1.840520 | C | 2.411760 | 0.834635 | -2.512248 |
| O | -1.715538 | -4.386223 | 2.349647 | H | 2.991989 | 1.674713 | -2.128538 |
| C | 2.043484 | 1.299748 | 0.742527 | H | 2.898179 | -0.095736 | -2.221555 |
| H | 3.000735 | 1.375029 | 0.229246 | H | 2.383747 | 0.890469 | -3.598330 |
| H | 1.888538 | 2.216461 | 1.312886 | Cl | 0.051527 | -0.718716 | -3.101316 |
| H | 2.096887 | 0.460646 | 1.436955 | P | -0.680736 | 0.604042 | -0.121153 |
| C | -1.607671 | 2.104538 | 0.371880 | H | 0.203451 | 2.055814 | -2.478765 |

**3d'$_P$·H$^+$:** E = -1954.22344298117 au

ZPE = 0.17939061 au

$G_{corr}$ = 0.12721487 au

| | | | | | |
|---|---|---|---|---|---|
| W | -5.546730 | -2.439382 | 2.536536 | H | -2.536951 | -0.085946 | 3.244341 |
| C | -3.562386 | -2.889784 | 2.242898 | C | -6.332683 | 1.170968 | 2.012373 |
| O | -2.459468 | -3.132574 | 2.078612 | H | -5.985569 | 2.133329 | 1.641170 |
| C | -5.992153 | -3.130794 | 0.634899 | H | -7.277761 | 0.920026 | 1.529800 |
| O | -6.236411 | -3.537729 | -0.399021 | H | -6.505911 | 1.238538 | 3.086926 |
| C | -5.115759 | -1.779538 | 4.435527 | N | -3.570585 | 0.504631 | 1.525903 |
| O | -4.878447 | -1.419875 | 5.492033 | P | -4.079808 | 0.296248 | -0.123280 |
| C | -7.531556 | -1.962593 | 2.817472 | C | -2.897301 | -0.889575 | -0.810556 |
| O | -8.628855 | -1.697860 | 2.975469 | H | -1.950187 | -0.839124 | -0.277235 |
| C | -5.880627 | -4.300670 | 3.276994 | H | -3.307934 | -1.893912 | -0.723302 |
| O | -6.067592 | -5.344976 | 3.701163 | H | -2.746300 | -0.676830 | -1.865683 |
| C | -2.425794 | 0.588617 | 2.392671 | Cl | -5.579704 | -0.100433 | -1.810806 |
| H | -1.520882 | 0.295858 | 1.858243 | P | -5.128622 | -0.160285 | 1.675703 |
| H | -2.278607 | 1.599015 | 2.779032 | H | -3.898806 | 1.581939 | -0.635720 |

**3d'$_N$·H$^+$:** E = -1954.228299243 au

ZPE = 0.17972934 au

$G_{corr}$ = 0.1275224 au

| | | | | | |
|---|---|---|---|---|---|
| W | -5.077537 | -2.215517 | 3.001645 | O | -5.037382 | -4.279290 | 5.405700 |
| C | -3.020545 | -2.313191 | 2.977527 | C | -2.748362 | 0.670419 | 1.194180 |
| O | -1.885192 | -2.413112 | 3.006286 | H | -2.815285 | 1.028691 | 2.219013 |
| C | -5.160658 | -3.764947 | 1.641795 | H | -2.238219 | -0.286938 | 1.179605 |
| O | -5.206334 | -4.617797 | 0.888367 | H | -2.181410 | 1.387344 | 0.604083 |
| C | -4.978407 | -0.653205 | 4.348815 | C | -6.850361 | 0.502106 | 1.177434 |
| O | -4.920416 | 0.204516 | 5.094589 | H | -6.772096 | 1.331623 | 0.475215 |
| C | -7.134629 | -2.231061 | 3.148963 | H | -7.696995 | -0.128985 | 0.908701 |
| O | -8.267665 | -2.263157 | 3.255890 | H | -7.016289 | 0.902806 | 2.176910 |
| C | -5.044120 | -3.538852 | 4.537770 | N | -4.095814 | 0.592653 | 0.630949 |

| | | |
|---|---|---|
| P | -4.568902 | -0.408870 | -0.824053 |
| C | -3.307551 | -1.741996 | -0.819114 |
| H | -3.104969 | -2.201288 | 0.145772 |
| H | -3.675098 | -2.516157 | -1.494166 |
| H | -2.377358 | -1.359372 | -1.240121 |
| Cl | -4.920591 | 3.250763 | 0.011779 |
| P | -5.359977 | -0.542832 | 1.192654 |
| H | -4.461226 | 1.652936 | 0.445973 |

## 10. References


[1] P. K. Majhi, A. W. Kyri, A. Schmer, G. Schnakenburg, R. Streubel, *Chem. – A Eur. J.* **2016**, *22*, 15413–15419.

[2] F. Neese, *WIREs Comput. Mol. Sci.* **2018**, *8*, e1327.

[3] C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785–789.

[4] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[5] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104.

[6] S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456–1465.

[7] A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, *97*, 2571–2577.

[8] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297–3305.

[9] F. Neese, F. Wennmohs, A. Hansen, U. Becker, *Chem. Phys.* **2009**, *356*, 98–109.

[10] Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 5656–5667.

[11] E. Caldeweyher, C. Bannwarth, S. Grimme, *J. Chem. Phys.* **2017**, *147*, 34112.

[12] E. Caldeweyher, S. Ehlert, A. Hansen, H. Neugebauer, S. Spicher, C. Bannwarth, S. Grimme, *J. Chem. Phys.* **2019**, *150*, 154122.

[13] F. Weigend, *Phys. Chem. Chem. Phys.* **2006**, *8*, 1057–1065.

[14] D. Andrae, U. Häußermann, M. Dolg, H. Stoll, H. Preuß, *Theor. Chim. Acta* **1990**, *77*, 123–141.

[15] A. E. Reed, F. Weinhold, *J. Chem. Phys.* **1983**, *78*, 4066–4073.

[16] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.* **1985**, *83*, 735–746.

[17] R. F. W. Bader, *Atoms in Molecules: A Quantum Theory*, Oxford University Press: Oxford, UK, **1990**.

[18] R. F. W. Bader, *Chem. Rev.* **1991**, *91*, 893–928.

[19] T. Lu, F. Chen, *J. Comput. Chem.* **2012**, *33*, 580–592.

[20] E. F. Pettersen, T. D. Goddard, C. C. Huang, G. S. Couch, D. M. Greenblatt, E. C. Meng, T. E. Ferrin, *J. Comput. Chem.* **2004**, *25*, 1605–1612.

[21] T. A. Keith, *TK Gristmill Softw. Overl. Park KS, USA* **2014**.