Supporting Information

Oxaphosphiranes: isolable phosphorus-containing epoxide rings

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Table of Contents

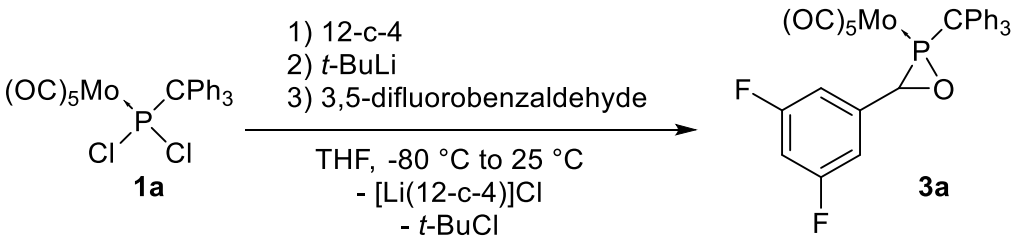
1 Experimental part

1.1 General working techniques

The syntheses of all compounds were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. Toluene, tetrahydrofuran, diethyl ether and *n*-pentane were dried over sodium wire, CH_2Cl_2 over CaH_2 and further purified by subsequent distillation. All NMR spectra were recorded on a Bruker AV I-300, Bruker AV I-400 or a Bruker AV III HD Prodigy 500 spectrometer. The ^{1}H and ^{13}C NMR spectra were referenced to the residual proton resonances and the ^{13}C NMR signals of the deuterated solvents and ^{19}F to $CFCl_3$ and ^{31}P to 85% H_3PO_4 as external standards, respectively. Mass spectrometric data were collected either on a MAT 95 XL Finnigan spectrometer using EI, 70 eV or on a MAT 90 for LIFDI-measurements. Exact masses were determined by peak-matching with perfluorokerosine on MAT 95 XL Finnigan spectrometer. IR spectra were measured on a Thermo Nicolet 380 spectrometer with a SMART iTR unit (diamond). Elemental analyses were determined on a gas chromatograph of type *Vario EL* from *Elementa*. Single crystal measurements were recorded on a STOE IPDS-2T-spectrometer at 123K. An X-ray tube with Mo-Kα - radiation (λ = 0,71073 Å) was used as the radiation source.

1.2 Analytical Data

1.2.1 Synthesis of [Pentacarbonyl{2-triphenylmethyl-3-(3,5-difluorophenyl)oxaphosphirane-κP}molybdenum(0)] 3a



316.5 mg (0.54 mmol, 1.00 eq) **1a** were dissolved in 32 mL of THF. 85 µl (0.54 mmol, 1.00 eq) 12-crown-4 were added and the solution was cooled to -80 °C. Then, 0.41 ml (0.70 mmol, 1.30 eq) *t*-BuLi (1.7 M in *n*-pentane) were added dropwise, and the solution turned intensely red. The solution was stirred for 30 min at -80 °C and subsequently 0.42 ml (2.14 mmol, 4.00 eq) 3,5-difluorobenzaldehyde were added, and the solution turned yellow. The solution was warmed up and the cooling bath was removed at -20 °C. The solvent was removed under reduced pressure (8 x 10^{-3} mbar) and a yellow-brown residue was obtained. The residue was filtered over Al_2O_3 (h = 3 cm, Ø = 2.5 cm) with 36 mL of Et_2O and a yellow filtrate was obtained. The solvent was removed under reduced pressure (8 x 10^{-3} mbar) and the resulting slightly green solid was washed five times with a total of 8 mL of *n*-pentane at -30 °C. The remaining solid was dried under reduced pressure (8 x 10^{-3} mbar) and the product was obtained as a colorless powder.

Yield: 168.7 mg (0.26 mmol, 48%).

Melting point: 142 °C

Elemental analysis: calculated: C 57.04 H 3.12 found.: C 57.07 H 2.94

MS (LIFDI): m/z (%) = 654.0 (100) $[M]^{+\bullet}$, 243.1 (35) $[CPh_3]^{+\bullet}$, 92.1 (10) $[CPh]^{+\bullet}$.

IR (ATR diamond): / cm^{-1} = 2076 (m, ν(CO)), 1960 (s, ν(CO)), 1950 (s, ν(CO)), 1931 (s, ν(CO)), 1618 (w, ν(C=C)), 1596 (w, ν(C=C)), 1580 (w, ν(C=C)), 1132 (s, ν(C-F)), 891 (m, $\delta(C^{ArF}\text{-}H)_{oop}$), 844 (w, $\delta(C^{ArF}\text{-}H)_{oop}$), 745 (m, $\delta(C^{Ar}\text{-}H)_{oop}$), 701 (s, $\delta(C^{Ar}\text{-}H)_{oop}$), 683 (m, $\delta(C^{Ar}\text{-}H)_{oop}$).

^{1}H-NMR (300.13 MHz, 298.5 K, C_6D_6): δ /ppm = 3.90 (d, 1H, $^{2}J_{P,H}$ = 1.90 Hz, PC(H)O), 6.38 (tq, 1H, $^{3}J_{F,H}$ = 8.9 Hz, $^{4}J_{H,H}$ = 2.1 Hz, *p*-Aryl^{F}), 6.68 (ddd, 2H, $^{3}J_{F,H}$ = 7.4 Hz, $^{4}J_{H,H}$ = 2.1 Hz, $^{5}J_{F,H}$ = 1.1 Hz, *o*-Aryl^{F}), 6.95 – 7.02 (m, 3H, *p*-CPh_3), 7.04 – 7.12 (m, 6H, *o*-CPh_3), 7.51 – 7.55 (m, 6H, *m*-CPh_3).

^{13}C{^{1}H}-NMR (75.48 MHz, 298.0 K, C_6D_6): δ /ppm = 58.3 (dt, $^{1}J_{P,C}$ = 18.9 Hz, $^{4}J_{C,F}$ = 2.8 Hz , PCO), 67.7 (d, $^{1}J_{P,C}$ = 14.5 Hz, Ph_3C-P), 104.1 (td, $^{2}J_{F,C}$ = 25.4 Hz, $^{5}J_{P,C}$ = 2.0 Hz, *p*-Aryl^{F}), 110.0 (m, *o*-Aryl^{F}), 128.2 (d, $^{5}J_{P,C}$ = 1.7 Hz, *p*-CPh_3), 129.1 (s, *o*-CPh_3), 130.1 (d, $^{4}J_{P,C}$ = 7.0 Hz, *m*-CPh_3), 139.0 (td, $^{3}J_{F,C}$ = 9.6 Hz, $^{2}J_{P,C}$ = 2.0 Hz, *ipso*-Aryl^{F}), 140.1 (d, $^{2}J_{P,C}$ = 2.9 Hz, *ipso*-CPh_3), 163.6 (ddd, $^{1}J_{F,C}$ = 250.7 Hz, $^{3}J_{F,C}$ = 12.6 Hz, $^{4}J_{P,C}$ = 1.9 Hz, *m*-Aryl^{F}), 165.3 (dd, $^{1}J_{F,C}$ = 12.7 Hz, $^{4}J_{P,C}$ = 1.8 Hz, *m*-Aryl^{F}), 203.4 (d, $^{2}J_{P,C}$ = 10.1 Hz, *cis*-CO), 207.2 (d, $^{2}J_{P,C}$ = 41.6 Hz, *trans*-CO).

^{19}F-NMR (282.4 MHz, 298.0 K, C_6D_6): δ /ppm = -108.4 (dd, $^{3}J_{F,H}$ = 7.7 Hz, $^{3}J_{F,H}$ = 7.7 Hz, *m*-Aryl^{F}).

^{31}P{^{1}H}-NMR (121.51 MHz, 298.0 K, C_6D_6): δ /ppm = 34.7.

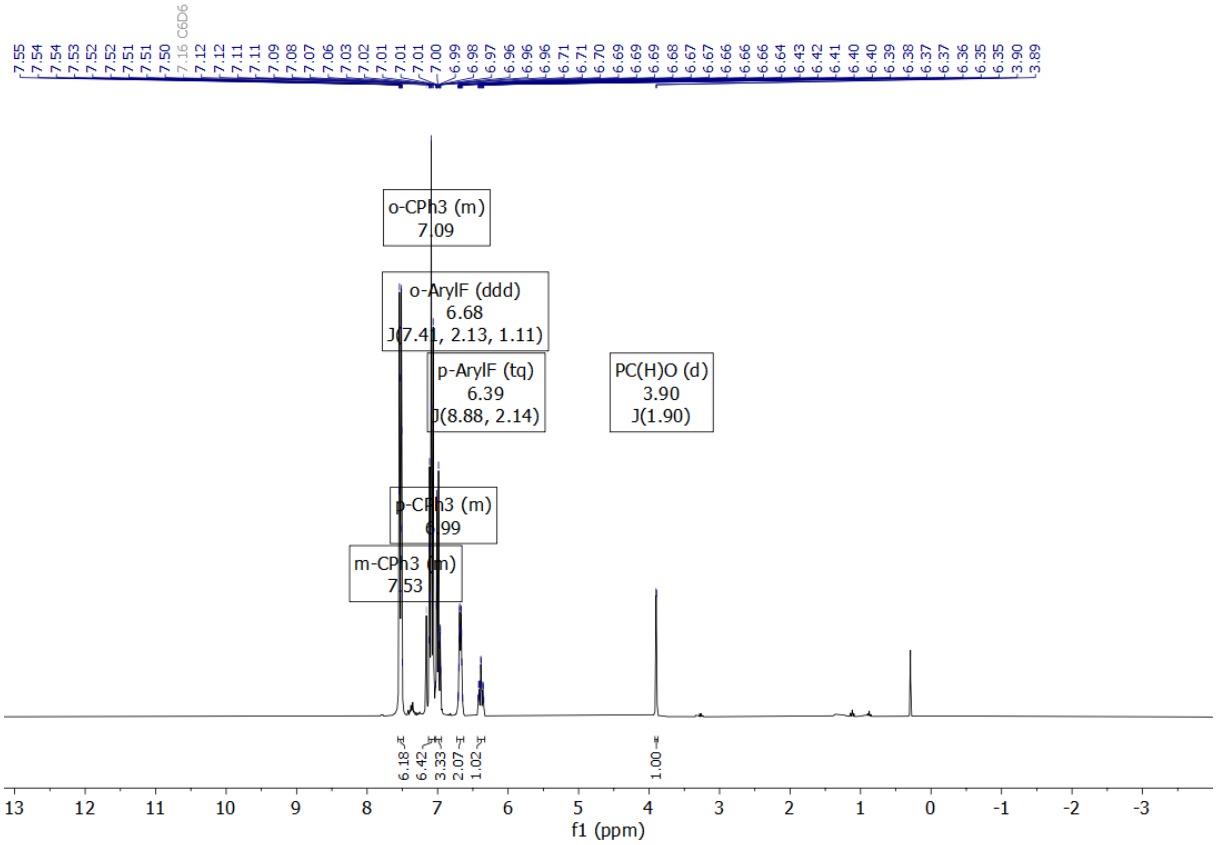


Figure S 1: ^{1}H-NMR spectrum in C_6D_6.

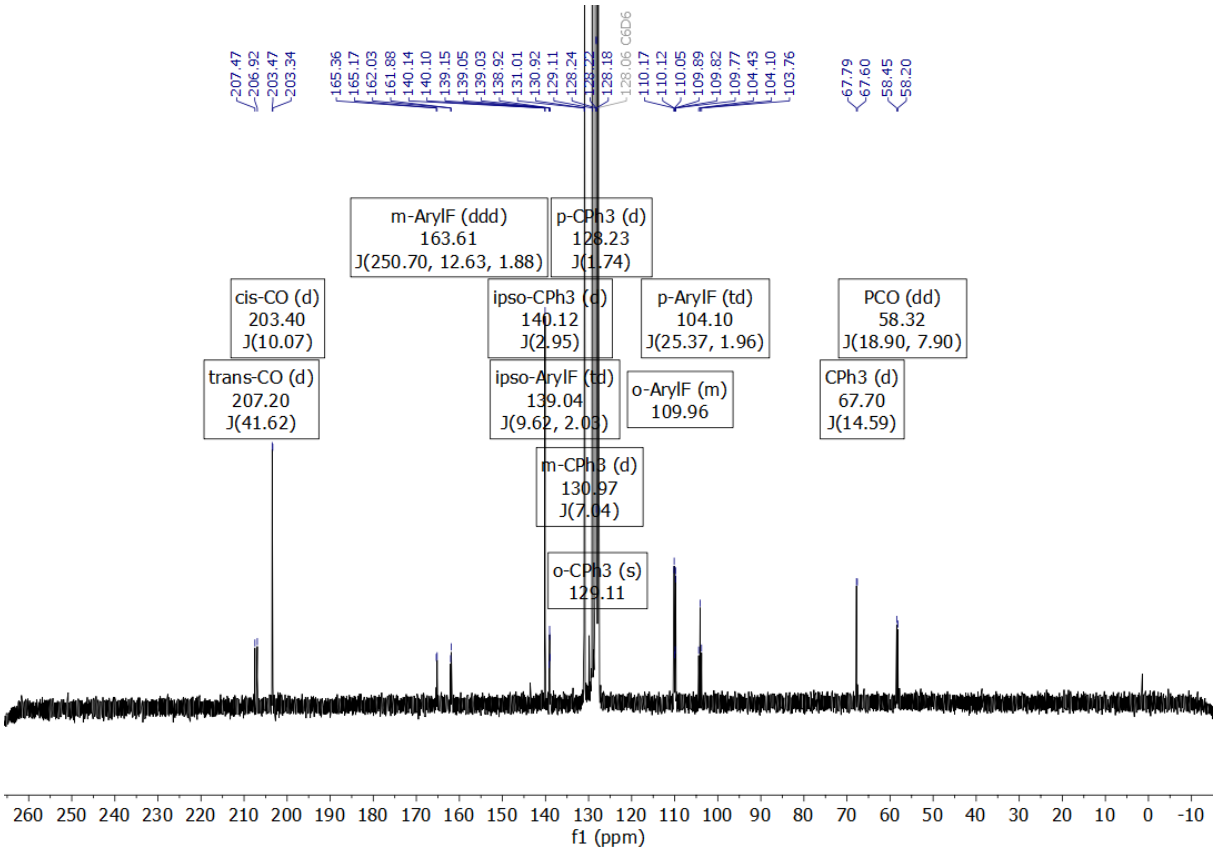


Figure S 2: $^{13}C\{^{1}H\}$-NMR spectrum in C_6D_6.

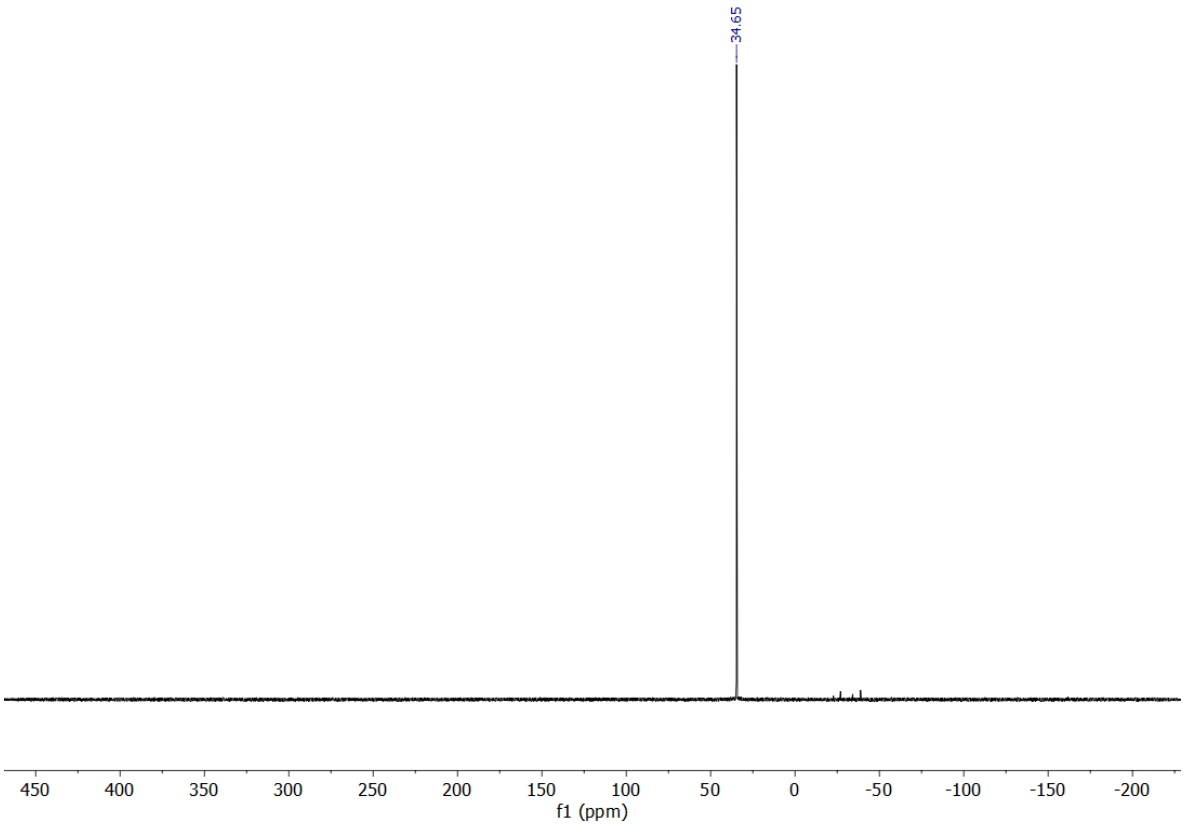


Figure S 3: $^{31}P\{^{1}H\}$-NMR spectrum in C_6D_6.

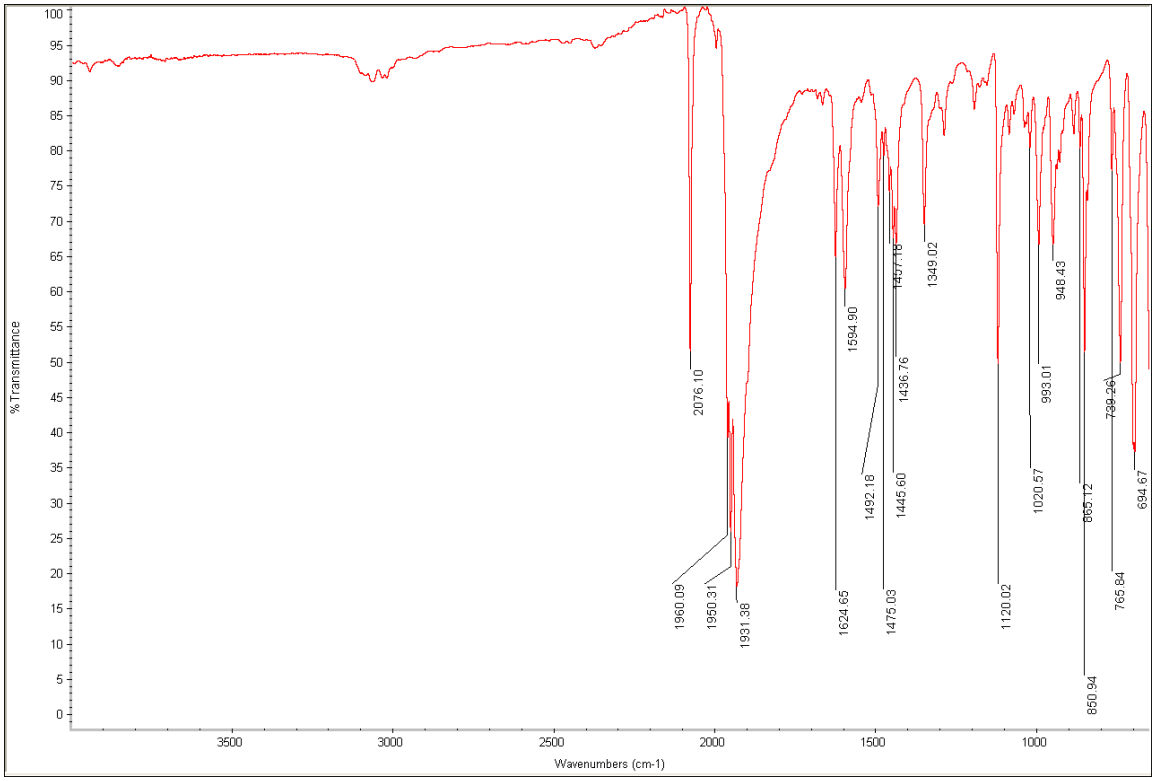
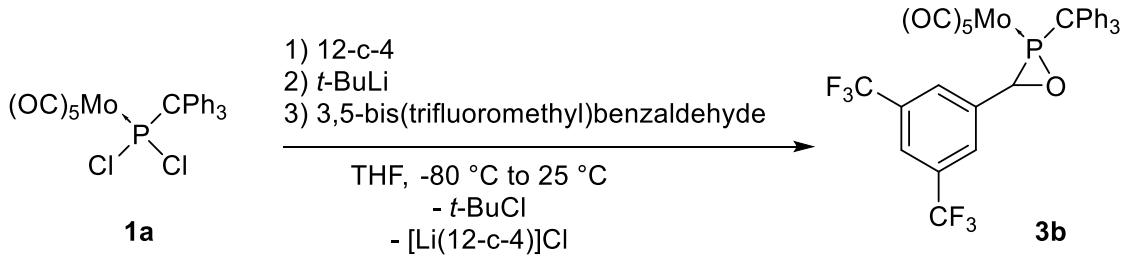


Figure S 4: IR spectrum of **3a**.

1.2.2 Synthesis of [Pentacarbonyl{2-triphenylmethyl-3-(3,5-bis(trifluoromethyl)phenyl)-oxaphosphirane-κP}molybdenum (0)] 3b



294.8 mg (0.51 mmol, 1.00 eq) **1a** were dissolved in 30 mL of THF. 81 µl (0.51 mmol, 1.00 eq) 12-crown-4 were added and the solution was cooled to -80 °C. Then, 0.39 ml (0.66 mmol, 1.30 eq) *t*-BuLi (1.7 M in *n*-pentane) were added dropwise, and the solution turned intensely red. The solution was stirred for 30 min at -80 °C and subsequently 0.33 ml (2.03 mmol, 4.00 eq) 3,5-bis(trifluoromethyl)benzaldehyde were added, and the solution turned yellow. The solution was warmed up and the cooling bath was removed at -20 °C. The solvent was removed under reduced pressure (8 x 10^{-3} mbar) and a yellow-brown residue was obtained. The residue was filtered over Al_2O_3 (h = 3 cm, Ø = 2.5 cm) with 36 mL of Et_2O and a yellow filtrate was obtained. The solvent was removed under reduced pressure (8 x 10^{-3} mbar) and the resulting slightly green solid was washed four times with a total of 6 mL of *n*-pentane at -30 °C. The remaining solid was dried under reduced pressure (8 x 10^{-3} mbar) and the product was obtained as a colorless powder.

Yield: 220 mg (0.28 mmol, 58%).

Melting point: 140 °C

Elemental analysis: calculated.: C 52.68 H 2.55 found: C 53.22 H 2.70

MS (LIFDI): m/z (%) = 754.1 (100) $[M]^{+\cdot}$, 243.1 (35) $[CPh_3]^{+\cdot}$, 92.0 (17) $[CPh]^{+\cdot}$.

IR (ATR diamond): / cm^{-1} = 2080 (m, ν(CO)), 1958 (s, ν(CO)), 1944 (s, ν(CO)), 1133 (s, ν(C-F)), 891 (m, $\delta(C^{ArCF3}\text{-}H)_{oop}$), 844 (w, $\delta(C^{ArCF3}\text{-}H)_{oop}$), 747 (m, $\delta(C^{Ar}\text{-}H)_{oop}$), 702 (s, $\delta(C^{Ar}\text{-}H)_{oop}$), 683 (m, $\delta(C^{Ar}\text{-}H)_{oop}$).

Single crystal x-ray analysis: GSTR716

^{1}H-NMR (300.13 MHz, 298.5 K, C_6D_6): δ /ppm = 3.95 (s, 1H, PC(H)O), 6.92 - 7.05 (m, 3H, *p*-CPh_3), 7.05 – 7.15 (m, 6H, *m*-CPh_3), 7.49 – 7.58 (m, 6H, *o*-CPh_3), 7.61 (s, 2H, *o*-$Aryl^{CF3}$), 7.69 (s, 1H, *p*-$Aryl^{CF3}$).

^{13}C{^{1}H}-NMR (75.48 MHz, 298.0 K, C_6D_6): δ /ppm = 58.1 (d, $^{1}J_{P,C}$ = 19.5 Hz, PCO), 68.0 (d, $^{1}J_{P,C}$ = 14.3 Hz, $Ph_3\underline{C}$-P), 122.2 – 122.4 (m, *p*-$Aryl^{CF3}$), 123.6 (q, $^{1}J_{F,C}$ = 273.0 Hz, CF_3), 127.3 (s, *o*-$Aryl^{CF3}$), 128.4 (s, *p*-CPh_3), 129.2 (s, *m*-CPh_3), 131.0 (d, $^{3}J_{P,C}$ = 7.0 Hz, *o*-CPh_3) , 132.3 (qd, $^{2}J_{F,C}$ = 33.5 Hz, $^{4}J_{P,C}$ = 1.2 Hz, *m*-$Aryl^{CF3}$), 138.2 (d, $^{2}J_{P,C}$ = 2.0 Hz, *ipso*-$Aryl^{CF3}$), 140.0 (d, $^{2}J_{P,C}$ = 2.8 Hz, *ipso*-CPh_3), 203.2 (d, $^{2}J_{P,C}$ = 10.0 Hz, *cis*-CO), 206.7 (d, $^{2}J_{P,C}$ = 41.5 Hz, *trans*-CO).

^{19}F{^{1}H}-NMR: δ /ppm = -63.0 ppm.

^{31}P{^{1}H}-NMR (121.51 MHz, 298.0 K, C_6D_6): δ /ppm = 35.0.

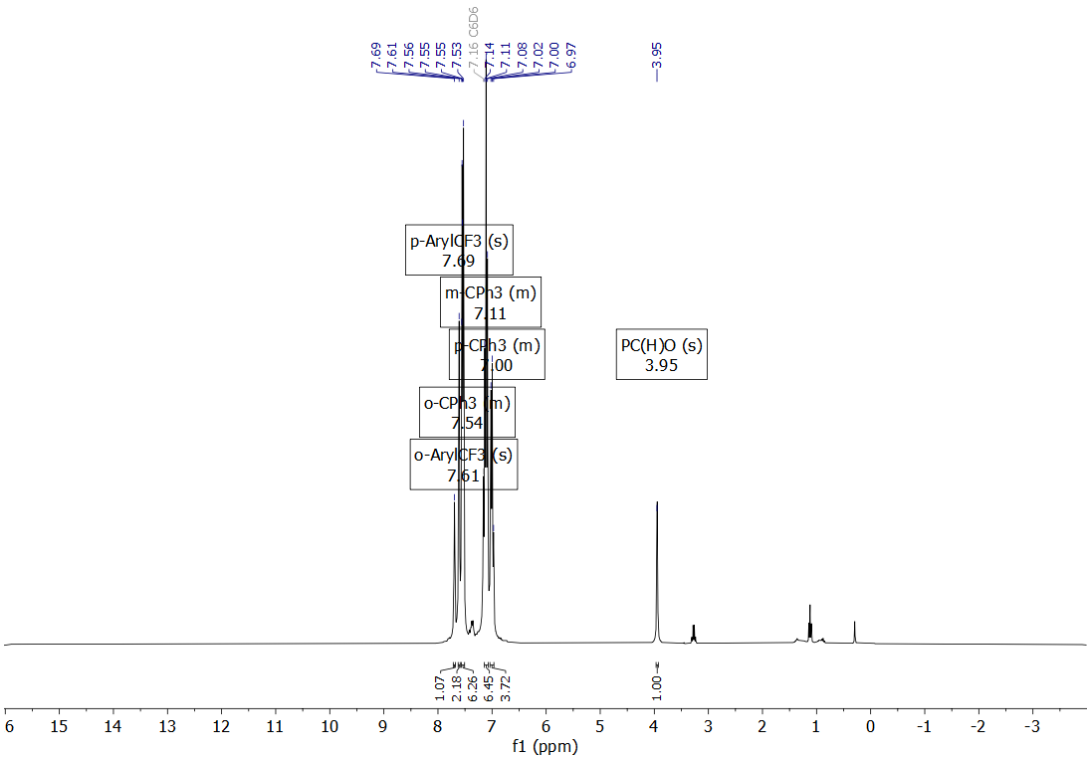


Figure S 5: ^{1}H-NMR spectrum in C_6D_6.

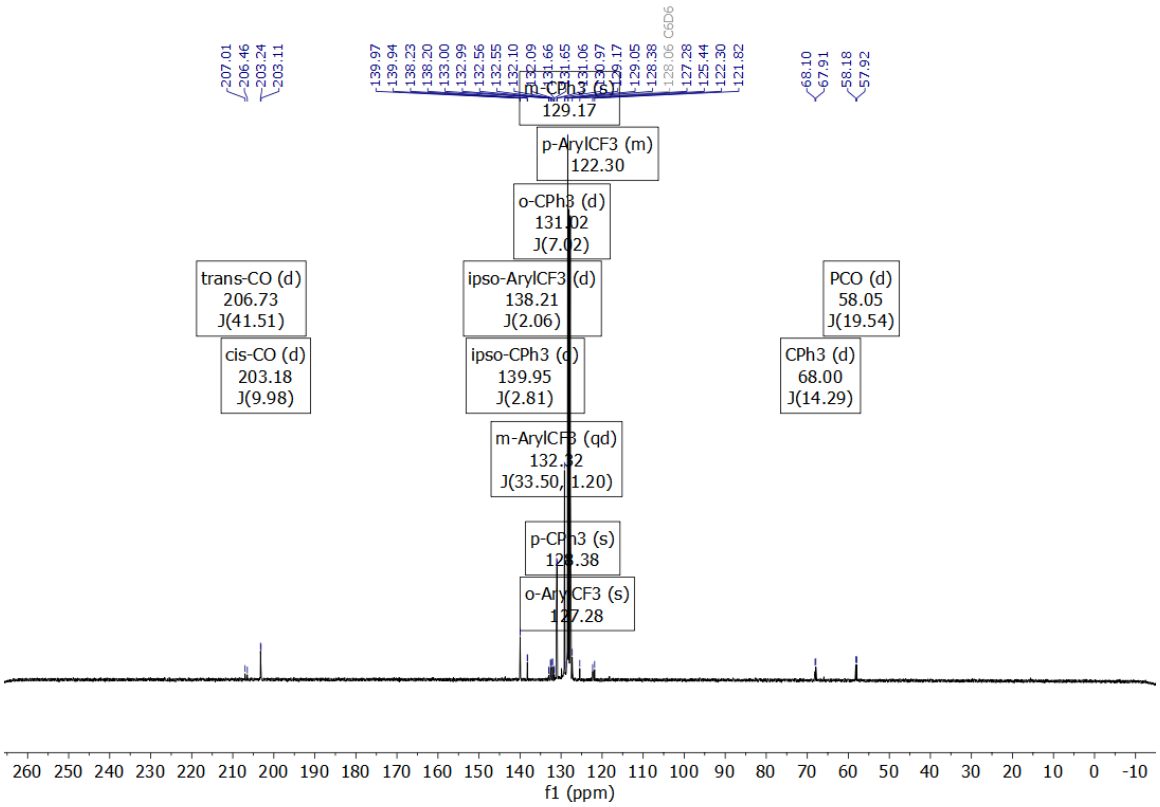


Figure S 6: $^{13}C\{^{1}H\}$-NMR spectrum in C_6D_6.

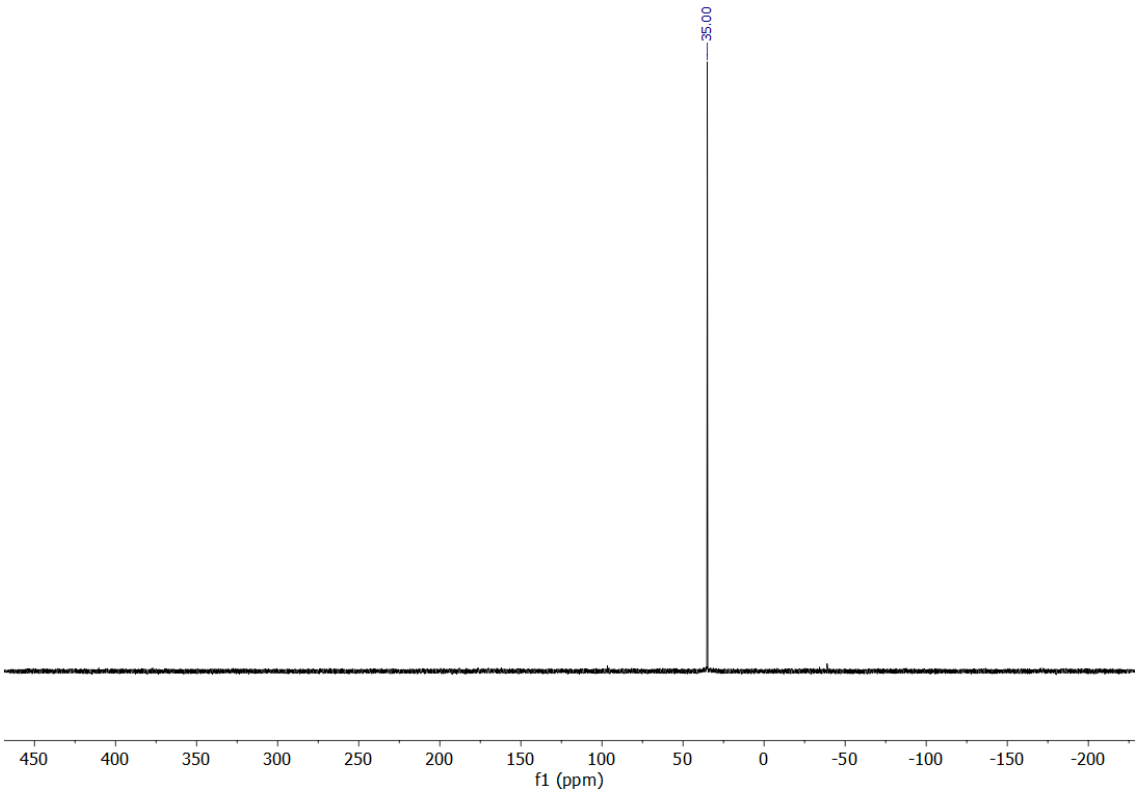


Figure S 7: $^{31}P\{^{1}H\}$-NMR spectrum in C_6D_6.

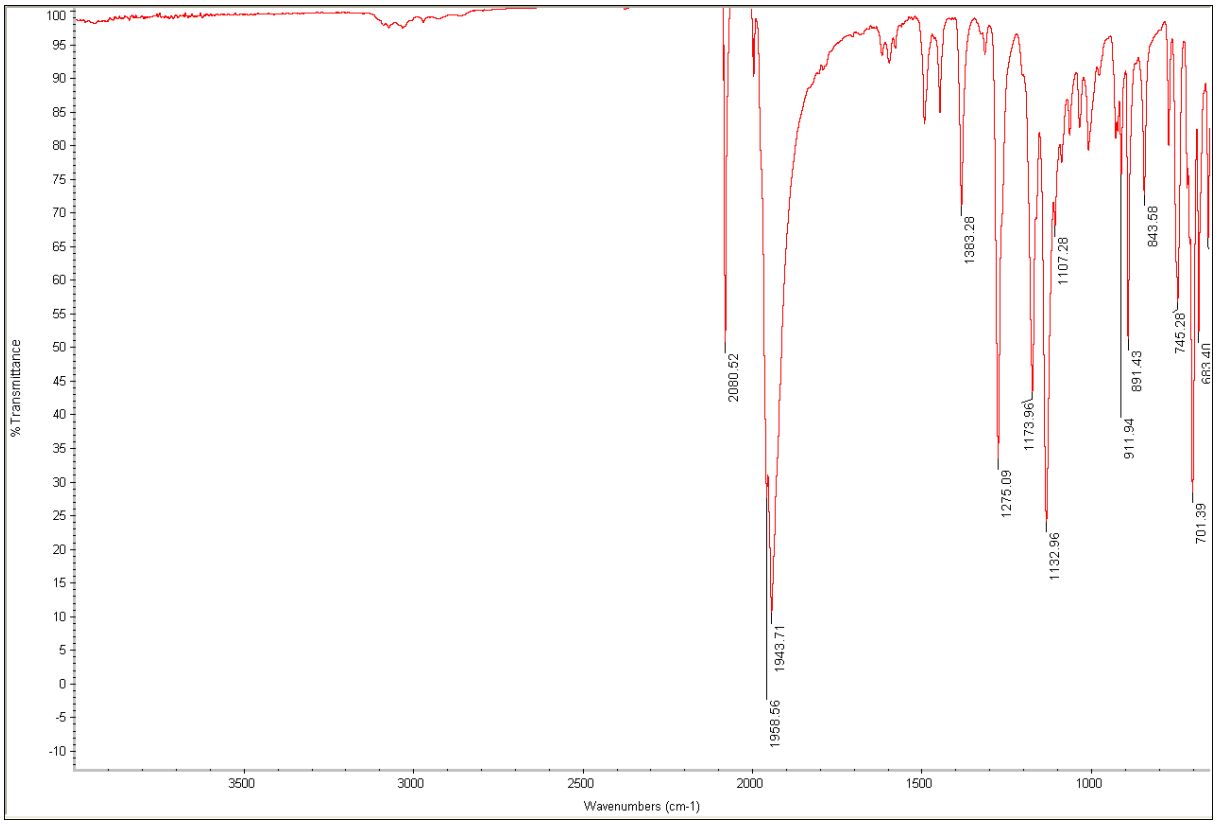


Figure S 8: IR spectrum of **3b**.

Molecular structure of 3b

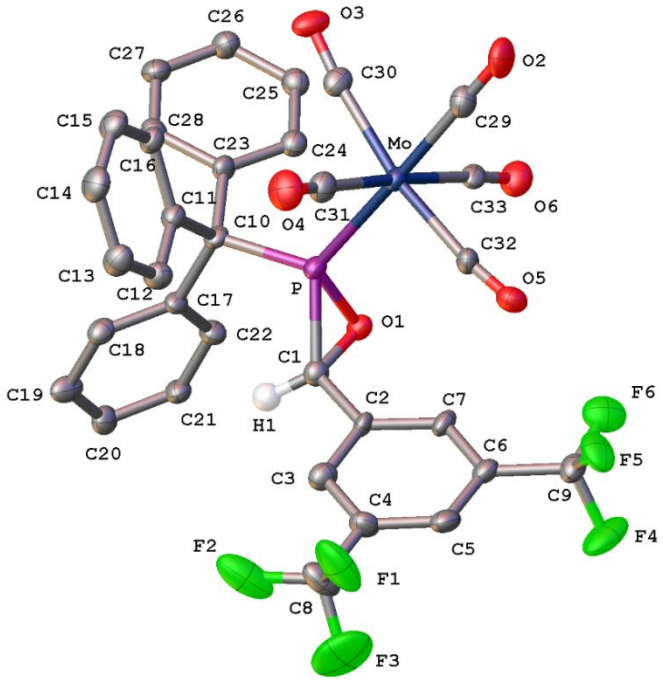


Figure S 9: Molecular structure of **3b** of the (2*R*,3*R*)-enantiomer in the single crystal (50% probability level). The hydrogen atoms, except the hydrogen atom of the oxaphosphirane ring, are omitted for clarity.

Bond lengths in Å

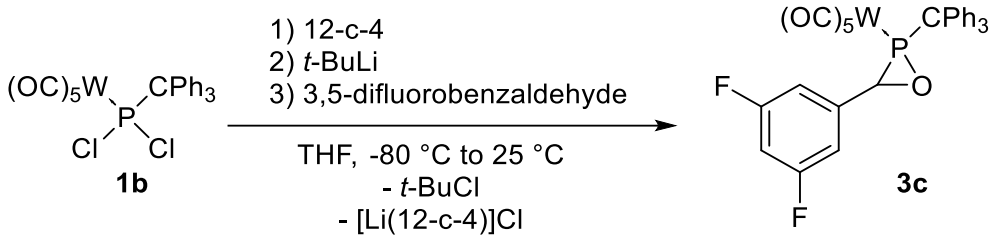
Mo	P	2.4872(14)		C4	C8	1.495(8)
Mo	C29	2.022(6)		C5	C6	1.390(8)
Mo	C30	2.059(6)		C6	C7	1.393(7)
Mo	C31	2.061(6)		C6	C9	1.496(8)
Mo	C32	2.044(5)		C10	C11	1.536(7)
Mo	C33	2.067(5)		C10	C17	1.547(7)
P	O1	1.673(4)		C10	C23	1.540(7)
P	C1	1.802(5)		C11	C12	1.382(8)
P	C10	1.911(5)		C11	C16	1.403(7)
F1	C8	1.342(8)		C12	C13	1.410(8)
F2	C8	1.312(7)		C13	C14	1.383(8)
F3	C8	1.336(8)		C14	C15	1.379(9)
F4	C9	1.331(6)		C15	C16	1.382(7)
F5	C9	1.348(7)		C17	C18	1.403(7)
F6	C9	1.324(7)		C17	C22	1.392(7)
O1	C1	1.458(6)		C18	C19	1.393(7)
O2	C29	1.148(7)		C19	C20	1.387(8)
O3	C30	1.138(6)		C20	C21	1.390(8)
O4	C31	1.134(7)		C21	C22	1.398(8)
O5	C32	1.136(6)		C23	C24	1.382(7)
O6	C33	1.126(6)		C23	C28	1.416(7)
C1	C2	1.483(7)		C24	C25	1.396(8)
C2	C3	1.399(8)		C25	C26	1.396(8)
C2	C7	1.383(7)		C26	C27	1.374(8)
C3	C4	1.398(7)		C27	C28	1.378(7)
C4	C5	1.384(8)				

Bond angles in °

C29	Mo	P	176.03(17)	F3	C8	C4	112.2(6)
C29	Mo	C30	85.0(2)	F4	C9	F5	105.6(5)
C29	Mo	C31	89.5(2)	F4	C9	C6	112.0(5)
C29	Mo	C32	84.5(2)	F5	C9	C6	111.7(5)
C29	Mo	C33	91.0(2)	F6	C9	F4	107.4(5)
C30	Mo	P	92.05(16)	F6	C9	F5	106.3(5)
C30	Mo	C31	91.0(2)	F6	C9	C6	113.4(5)
C30	Mo	C33	92.1(2)	C11	C10	P	99.4(3)
C31	Mo	P	93.27(17)	C11	C10	C17	113.5(4)
C31	Mo	C33	176.8(2)	C11	C10	C23	114.1(4)
C32	Mo	P	98.37(15)	C17	C10	P	112.8(3)
C32	Mo	C30	169.5(2)	C23	C10	P	112.0(3)
C32	Mo	C31	89.4(2)	C23	C10	C17	105.3(4)
C32	Mo	C33	87.5(2)	C12	C11	C10	118.8(5)
C33	Mo	P	86.40(15)	C12	C11	C16	118.4(5)
O1	P	Mo	118.83(14)	C16	C11	C10	122.7(5)
O1	P	C1	49.5(2)	C11	C12	C13	121.0(5)
O1	P	C10	108.9(2)	C14	C13	C12	119.4(5)
C1	P	Mo	129.45(18)	C15	C14	C13	119.8(5)
C1	P	C10	105.3(2)	C14	C15	C16	120.9(5)

C10	P	Mo	122.48(15)		C15	C16	C11	120.4(5)
C1	O1	P	69.9(2)		C18	C17	C10	122.3(4)
O1	C1	P	60.7(2)		C22	C17	C10	119.5(5)
O1	C1	C2	116.5(4)		C22	C17	C18	118.1(5)
C2	C1	P	124.5(4)		C19	C18	C17	120.2(5)
C3	C2	C1	117.8(5)		C20	C19	C18	121.3(5)
C7	C2	C1	122.9(5)		C19	C20	C21	118.7(5)
C7	C2	C3	119.3(5)		C20	C21	C22	120.2(5)
C4	C3	C2	120.0(5)		C17	C22	C21	121.3(5)
C3	C4	C8	120.1(5)		C24	C23	C10	124.5(4)
C5	C4	C3	120.2(5)		C24	C23	C28	118.0(5)
C5	C4	C8	119.7(5)		C28	C23	C10	117.3(4)
C4	C5	C6	119.8(5)		C23	C24	C25	120.9(5)
C5	C6	C7	120.1(5)		C26	C25	C24	120.2(5)
C5	C6	C9	118.7(5)		C27	C26	C25	119.1(5)
C7	C6	C9	121.2(5)		C26	C27	C28	121.1(5)
C2	C7	C6	120.6(5)		C27	C28	C23	120.6(5)
F1	C8	C4	111.5(5)		O2	C29	Mo	179.5(5)
F2	C8	F1	106.7(6)		O3	C30	Mo	173.1(5)
F2	C8	F3	106.7(6)		O4	C31	Mo	175.7(6)
F2	C8	C4	114.7(5)		O5	C32	Mo	171.9(5)
F3	C8	F1	104.4(5)		O6	C33	Mo	176.8(5)

1.2.3 Synthesis of [Pentacarbonyl{2-triphenylmethyl-3-(3,5-difluorophenyl)oxaphosphirane-κP}tungsten(0)] 3c



345.0 mg (0.52 mmol, 1.00 eq) **1b** were dissolved in 23 mL of THF. 74 µl (0.47 mmol, 0.90 eq) 12-crown-4 were added and the solution was cooled to -80 °C. Then, 0.36 ml (0.61 mmol, 1.18 eq) *t*-BuLi (1.7 M in *n*-pentane) were added dropwise, and the solution turned intensely red. The solution was stirred for 30 min at -80 °C and subsequently 0.17 ml (1.86 mmol, 3.62 eq) 3,5-difluorobenzaldehyde were added, and the solution turned yellow. The solution was warmed up and the cooling bath was removed at -20 °C. The solvent was removed under reduced pressure (8 x 10^{-3} mbar) and a yellow-brown residue was obtained. The residue was filtered over Al_2O_3 (h = 3 cm, Ø = 2.5 cm) with 40 mL of Et_2O and a yellow filtrate was obtained. The solvent was removed under reduced pressure (8 x 10^{-3} mbar) and the resulting slightly yellow solid was washed five times with a total of 2 mL of *n*-pentane at -30 °C. The remaining solid was dried under reduced pressure (8 x 10^{-3} mbar) and the product was obtained as a colorless powder.

Yield: 248.1 mg (0.34 mmol, 65%).

Melting point: 130 °C

Elemental analysis: calculated.: C 50.30 H 2.59 found: C 50.54 H 2.96

MS (LIFDI): m/z (%) = 740.1 (100) $[M]^{+\cdot}$, 597.9 (2) $[M\text{-}5\ CO]^{+\cdot}$, 243.1 (100) $[CPh_3]^{+\cdot}$.

IR (ATR diamond): / cm^{-1} = 2075 (m, ν(CO)), 1953 (s, ν(CO)), 1942 (s, ν(CO)), 1928 (s, ν(CO)), 1625 (w, ν(C=C)), 1595 (w, ν(C=C)), 1120 (m, ν(C-F)), 851 (m, $\delta(C^{ArF}\text{-}H)_{oop}$), 741 (m, $\delta(C^{Ar}\text{-}H)_{oop}$), 700 (m, $\delta(C^{Ar}\text{-}H)_{oop}$).

^{1}H-NMR (500.04 MHz, 298.0 K, $CDCl_3$): δ /ppm = 3.93 (br s, 1H, PC(H)O), 6.73 (tq, 1H, $^3J_{F,H}$ = 8.9 Hz, $^4J_{H,H}$ = 2.0 Hz, *p*-Aryl^F), 6.84 – 6.90 (m, 2H, *o*-Aryl^F), 7.31 – 7.36 (m, 3H, *p*-CPh_3), 7.38 – 7.44 (m, 6H, *o*-CPh_3), 7.51 – 7.56 (m, 6H, *m*-CPh_3).

^{13}C{^{1}H}-NMR (125.75 MHz, 298.0 K, $CDCl_3$): δ /ppm = 59.0 (d, $^1J_{P,C}$ = 23.3 Hz, PCO), 67.6 (d, $^1J_{P,C}$ = 7.4 Hz, Ph_3C-P), 104.0 (t, $^2J_{F,C}$ = 25.5 Hz, *p*-Aryl^F), 109.7 (m, *o*-Aryl^F), 128.0 (d, $^5J_{P,C}$ = 1.6 Hz, *p*-CPh_3), 128.9 (s, *o*-CPh_3), 130.7 (d, $^4J_{P,C}$ = 6.9 Hz, *m*-CPh_3), 138.5 (t, $^3J_{F,C}$ = 9.4 Hz, *ipso*-Aryl^F), 139.5 (d, $^2J_{P,C}$ = 2.1 Hz, *ipso*-CPh_3), 163.5 (dd, $^1J_{F,C}$ = 250.2 Hz, $^3J_{F,C}$ = 12.7 Hz, *m*-Aryl^F, $^4J_{P,C}$ = 1.9 Hz), 193.8 (d, $^1J_{W,C}$ = 8.5 Hz, $^2J_{P,C}$ = 8.0 Hz, *cis*-CO), 193.4 (d, $^2J_{P,C}$ = 41.6 Hz, *trans*-CO).

^{19}F{^{1}H}-NMR: δ /ppm = -108.3.

^{31}P{^{1}H}-NMR (202.44 MHz, 298.0 K, $CDCl_3$): δ /ppm = 16.9 (s_{sat}, $^1J_{P,W}$ = 315.7 Hz).

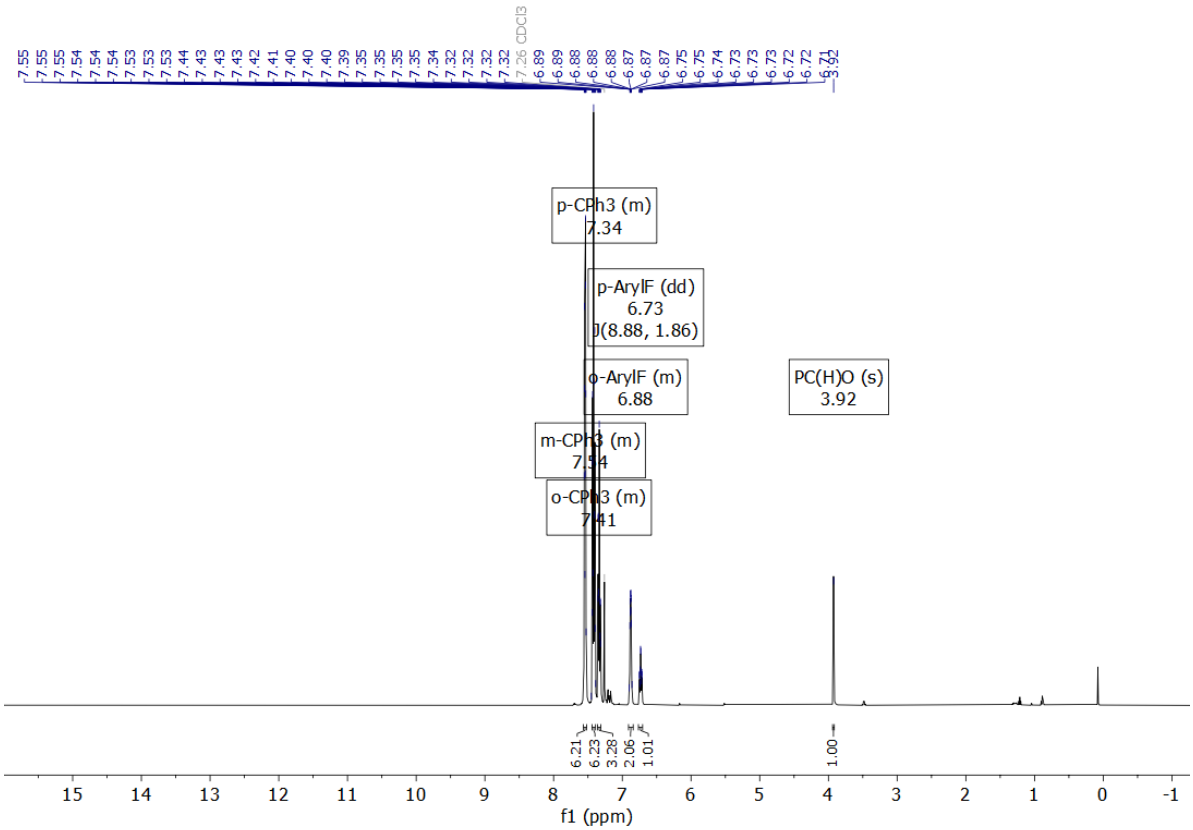


Figure S 10: ^{1}H-NMR spectrum in $CDCl_3$.

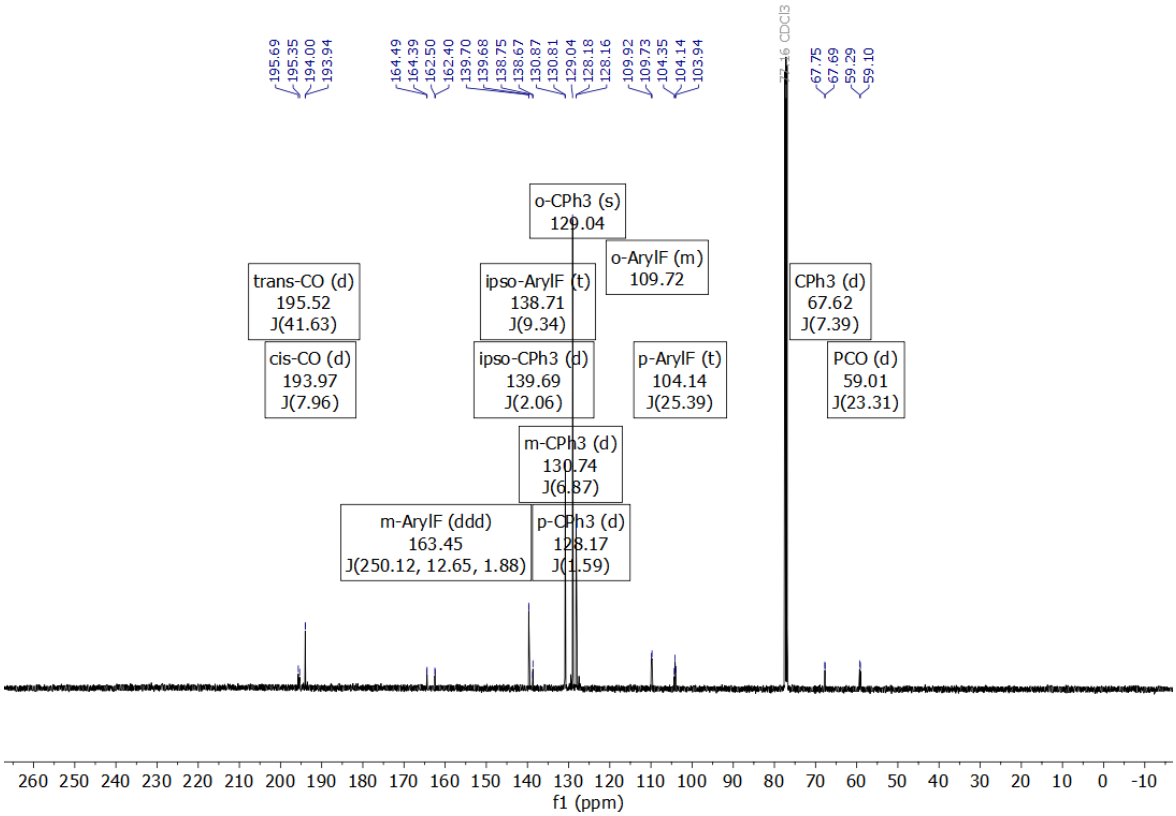


Figure S 11: $^{13}C\{^{1}H\}$-NMR spectrum in $CDCl_3$.

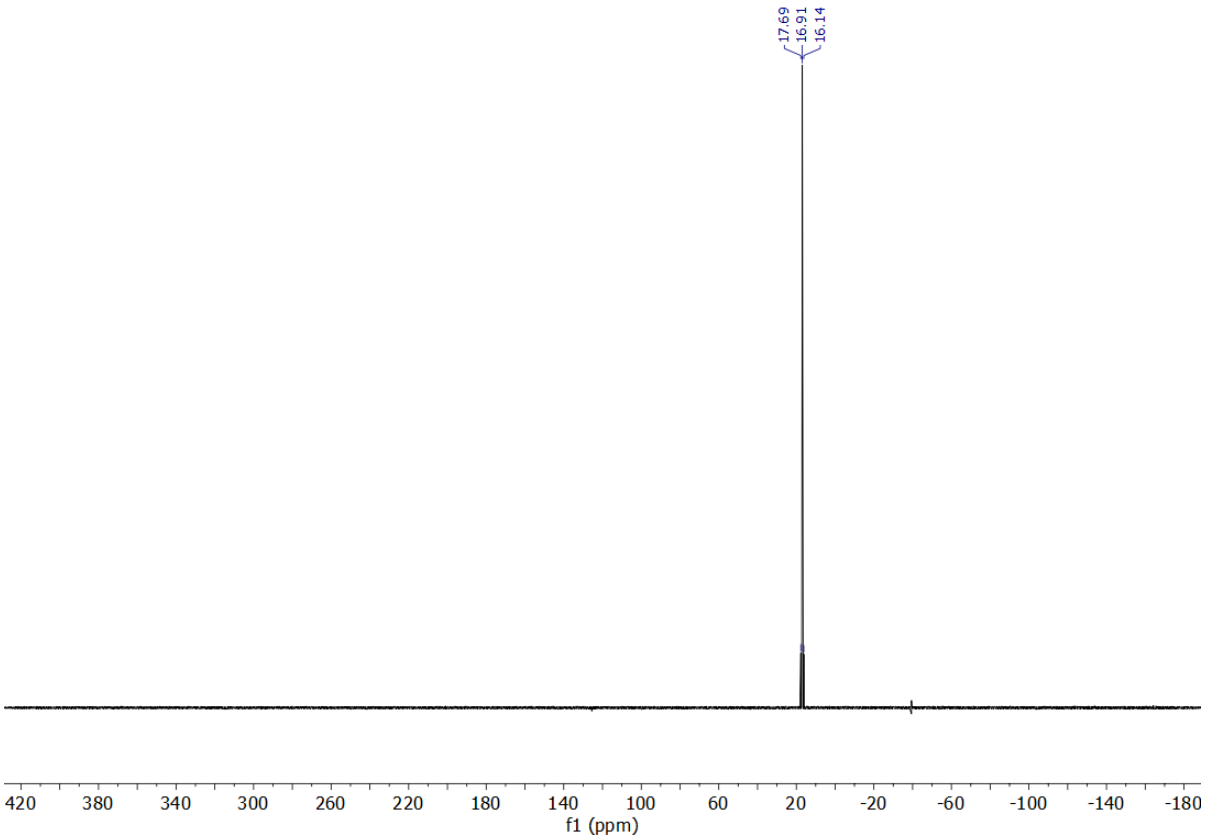


Figure S 12: $^{31}P\{^{1}H\}$-NMR spectrum in $CDCl_3$.

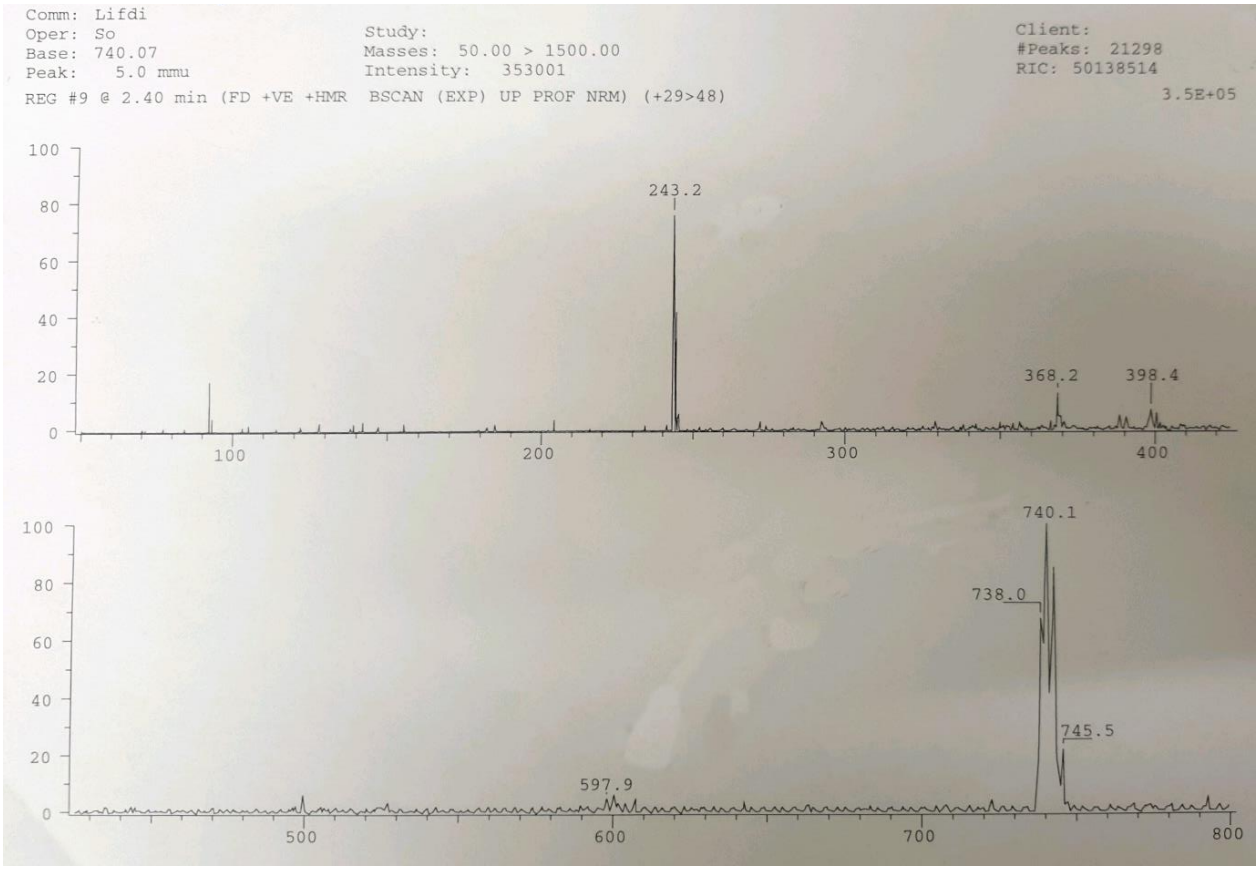


Figure S 13: MS spectrum (LIFDI) of **3c**.

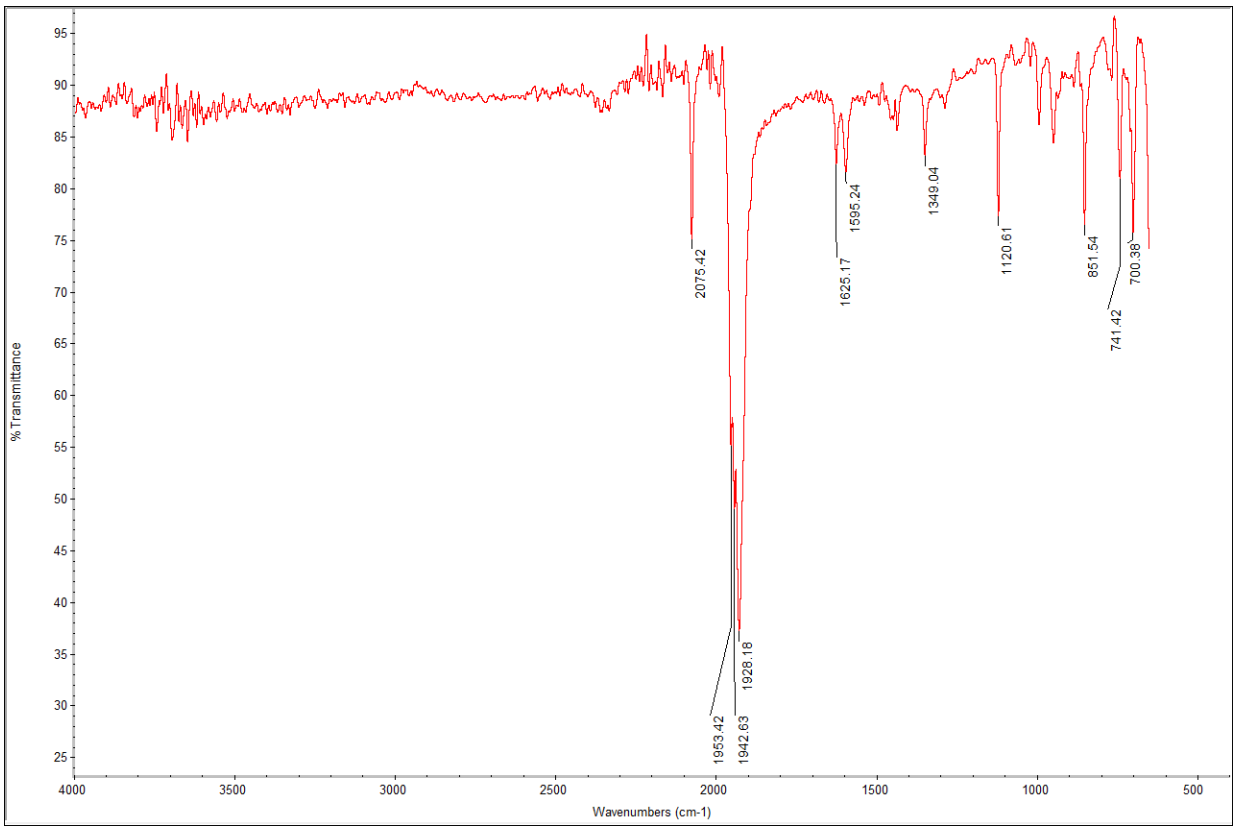


Figure S 14: IR spectrum of **3c**.

Molecular structure of 3c

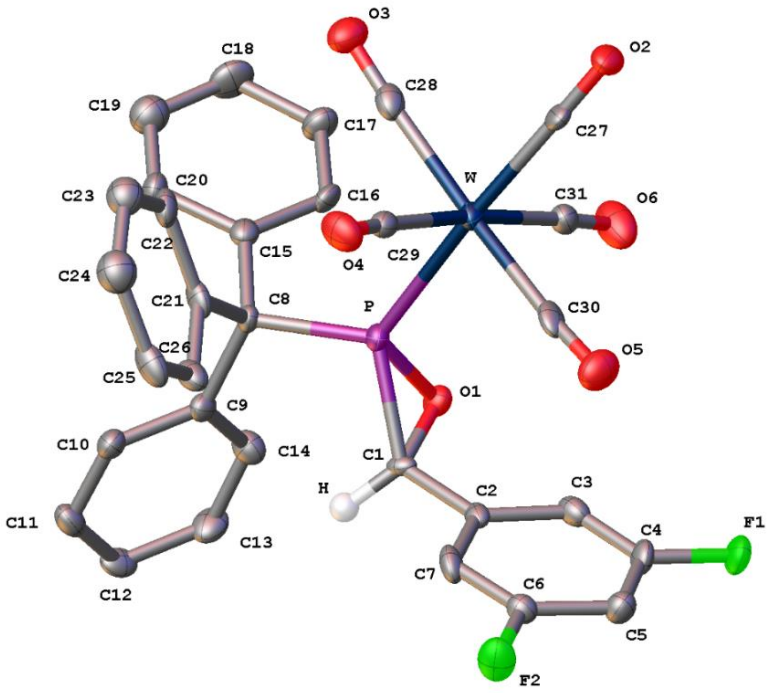


Figure S 15: Molecular structure of **3c** of the (2*R*,3*R*)-enantiomer in the single crystal (50% probability level). The hydrogen atoms, except the hydrogen atom of the oxaphosphirane ring, are omitted for clarity. Details for this and the following structures can be obtained from the CCDC data base by citing the numbers 2382051-2382055.

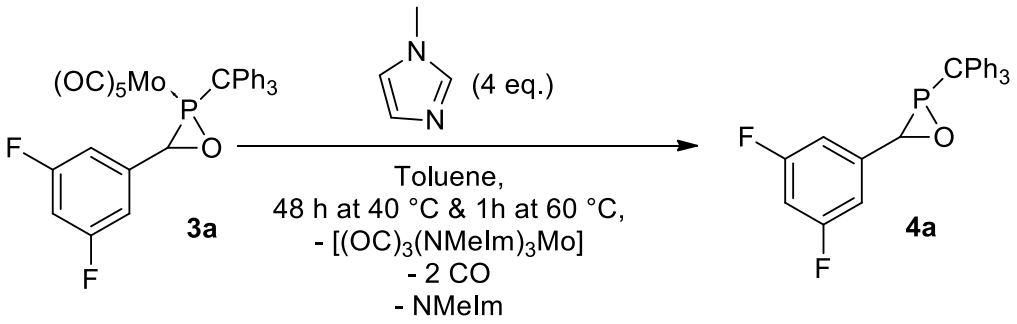
Bond lengths in Å

W	P	2.4715(13)		C6	C7	1.366(8)
W	C27	2.013(5)		C8	C9	1.546(7)
W	C28	2.053(7)		C8	C15	1.537(9)
W	C29	2.048(6)		C8	C21	1.554(7)
W	C30	2.042(8)		C9	C10	1.397(8)
W	C31	2.053(6)		C9	C14	1.394(7)
P	O1	1.669(4)		C10	C11	1.390(7)
P	C1	1.790(5)		C11	C12	1.377(8)
P	C8	1.893(5)		C12	C13	1.402(8)
F1	C4	1.360(6)		C13	C14	1.368(7)
F2	C6	1.359(7)		C15	C16	1.398(8)
O1	C1	1.481(7)		C15	C20	1.397(8)
O2	C27	1.149(6)		C16	C17	1.377(8)
O3	C28	1.140(7)		C17	C18	1.389(8)
O4	C29	1.135(7)		C18	C19	1.375(9)
O5	C30	1.161(8)		C19	C20	1.379(10)
O6	C31	1.129(7)		C21	C22	1.383(8)
C1	C2	1.495(8)		C21	C26	1.392(9)
C2	C3	1.385(7)		C22	C23	1.387(8)
C2	C7	1.370(9)		C23	C24	1.356(9)
C3	C4	1.366(9)		C24	C25	1.406(9)
C4	C5	1.372(9)		C25	C26	1.384(8)

Bond angles in °

C27	W	P	173.99(16)		C6	C7	C2	119.3(5)
C27	W	C28	88.0(2)		C9	C8	P	115.1(4)
C27	W	C29	91.5(2)		C9	C8	C21	112.2(4)
C27	W	C30	86.2(2)		C15	C8	P	110.2(3)
C27	W	C31	89.6(2)		C15	C8	C9	106.9(5)
C28	W	P	92.69(16)		C15	C8	C21	114.2(4)
C28	W	C31	94.4(2)		C21	C8	P	98.3(4)
C29	W	P	94.45(14)		C10	C9	C8	121.8(4)
C29	W	C28	90.6(2)		C14	C9	C8	120.2(5)
C29	W	C31	174.8(2)		C14	C9	C10	117.8(5)
C30	W	P	93.74(14)		C11	C10	C9	120.3(5)
C30	W	C28	171.7(2)		C12	C11	C10	121.3(5)
C30	W	C29	83.6(2)		C11	C12	C13	118.4(5)
C30	W	C31	91.4(2)		C14	C13	C12	120.3(5)
C31	W	P	84.43(15)		C13	C14	C9	121.7(5)
O1	P	W	117.02(13)		C16	C15	C8	122.5(5)
O1	P	C1	50.5(2)		C20	C15	C8	119.9(5)
O1	P	C8	107.9(2)		C20	C15	C16	117.4(6)
C1	P	W	126.14(18)		C17	C16	C15	121.0(5)
C1	P	C8	107.0(2)		C16	C17	C18	121.0(6)
C8	P	W	124.55(16)		C19	C18	C17	118.1(7)
C1	O1	P	69.0(2)		C18	C19	C20	121.5(6)
O1	C1	P	60.5(3)		C19	C20	C15	120.9(6)
O1	C1	C2	116.4(4)		C22	C21	C8	123.8(6)
C2	C1	P	123.4(4)		C22	C21	C26	118.3(5)
C3	C2	C1	119.7(5)		C26	C21	C8	117.8(5)
C7	C2	C1	120.4(5)		C21	C22	C23	119.6(7)
C7	C2	C3	120.0(6)		C24	C23	C22	121.9(6)
C4	C3	C2	118.9(6)		C23	C24	C25	119.8(6)
F1	C4	C3	119.9(6)		C26	C25	C24	118.0(7)
F1	C4	C5	116.5(6)		C25	C26	C21	122.3(5)
C3	C4	C5	123.6(5)		O2	C27	W	179.3(6)
C4	C5	C6	115.5(6)		O3	C28	W	176.0(5)
F2	C6	C5	117.6(5)		O4	C29	W	174.5(5)
F2	C6	C7	119.6(5)		O5	C30	W	172.5(5)
C7	C6	C5	122.8(6)		O6	C31	W	177.2(6)

1.2.4 Synthesis of 2-Triphenylmethyl-3-(3,5-difluorophenyl)oxaphosphirane 4a



To a solution of 749.4 mg **3a** (1.149 mmol, 1.00 eq) in 55 mL of toluene, 0.37 mL 1-methylimidazole (4.595 mmol, 4.00 eq) were added. The solution was stirred for 48h at 40 °C and 1h at 60 °C, and the solution turned from slightly yellow to yellow and a yellow solid precipitated out of solution. The solvent was removed under reduced pressure (1 x 10^{-2} mbar) and a brown-yellow residue was obtained. The residue was dissolved in 10 mL of CH_2Cl_2 and purified by column chromatography (h = 10 cm, Ø = 3 cm, Al_2O_3, Eluent: PE:Et_2O (50:50), -20 °C). After collecting 150 mL of a yellow fraction, the solvent was removed under reduced pressure (1 x 10^{-2} mbar) and a yellow residue was obtained. The residue was washed eight times with 1 mL of -pentane at -50 °C and after drying under reduced pressure (1 x 10^{-2} mbar), the product was obtained as a slightly yellow powder.

Yield: 318.0 mg (0.76 mmol, 66 %).

Melting point: 118 °C.

Elemental analysis: calculated.: C 75.00 H 4.60 found: C 73.48 H 4.74 N 0.15.

MS (LIFDI): m/z (%) = 243.2 $[CPh_3]^{+\bullet}$ (100), 173.1 $[M\text{-}CPh_3]^{+\bullet}$ (16).

IR (ATR diamond): / cm^{-1} = 1624 (m, ν(C=C), 1593 (m, ν(C=C), 1116 (m, ν(C-F)), 861 (m, $\delta(C^{ArF}\text{-}H)_{oop}$)), 836 (m, $\delta(C^{ArF}\text{-}H)_{oop}$)), 729 (m, $\delta(C^{Ar}\text{-}H)_{oop}$)), 704 (m, $\delta(C^{Ar}\text{-}H)_{oop}$)).

^{1}H-NMR (500.04 MHz, 298.0 K, $CDCl_3$): δ /ppm = 3.20 (s, 1H, PC(H)O), 6.67 (tt, $^3J_{F,H}$ = 8.8 Hz, $^4J_{H,H}$ = 2.3 Hz, 1H, *p*-Aryl^F), 6.69 – 6.73 (m, 2 H, *o*-Aryl^F), 7.21 – 7.25 (m, 6H, *o*-CPh_3), 7.28 – 7.34 (m, 3H, *p*-CPh_3), 7.34 – 7.40 (m, 6H, *m*-CPh_3).

^{13}C{^{1}H}-NMR (125.75 MHz, 298.0 K, $CDCl_3$): δ /ppm = 55.2 (dt, $^1J_{P,C}$ = 15.3 Hz, $^4J_{F,C}$ = 2.7 Hz, PCO), 62.4 (d, $^1J_{P,C}$ = 59.2 Hz, $Ph_3\underline{C}$-P), 103.1 (t, $^2J_{F,C}$ = 25.5 Hz, *p*-Aryl^F), 108.2 (ddd, $^2J_{F,C}$ = 20.1 Hz, $^4J_{F,C}$ = 6.3 Hz, $^3J_{P,C}$ = 3.0 Hz, *o*-Aryl^F), 127.4 (s, *p*-CPh_3), 128.7 (s, *o*-CPh_3), 130.1 (d, $^4J_{P,C}$ = 7.9 Hz, *m*-CPh_3), 141.4 (d, $^1J_{P,C}$ = 9.0 Hz, *ipso*- CPh_3), 142.9 (q, $^2J_{P,C}$ = 9.0 Hz, $^4J_{F,C}$ = 9.0 Hz, *ipso*-Aryl^F), 163.3 (dd, $^1J_{F,C}$ = 249.0 Hz, $^4J_{P,C}$ = 12.8 Hz, *m*-Aryl^F).

^{19}F-NMR (470.44 MHz, 298.0 K, $CDCl_3$): δ /ppm = -109.3 (dd, $^3J_{F,H}$ = 8.0 Hz, $^3J_{F,H}$ = 8.0 Hz).

^{31}P{^{1}H}-NMR (202.44 MHz, 298.0 K, $CDCl_3$): δ /ppm = -26.0.

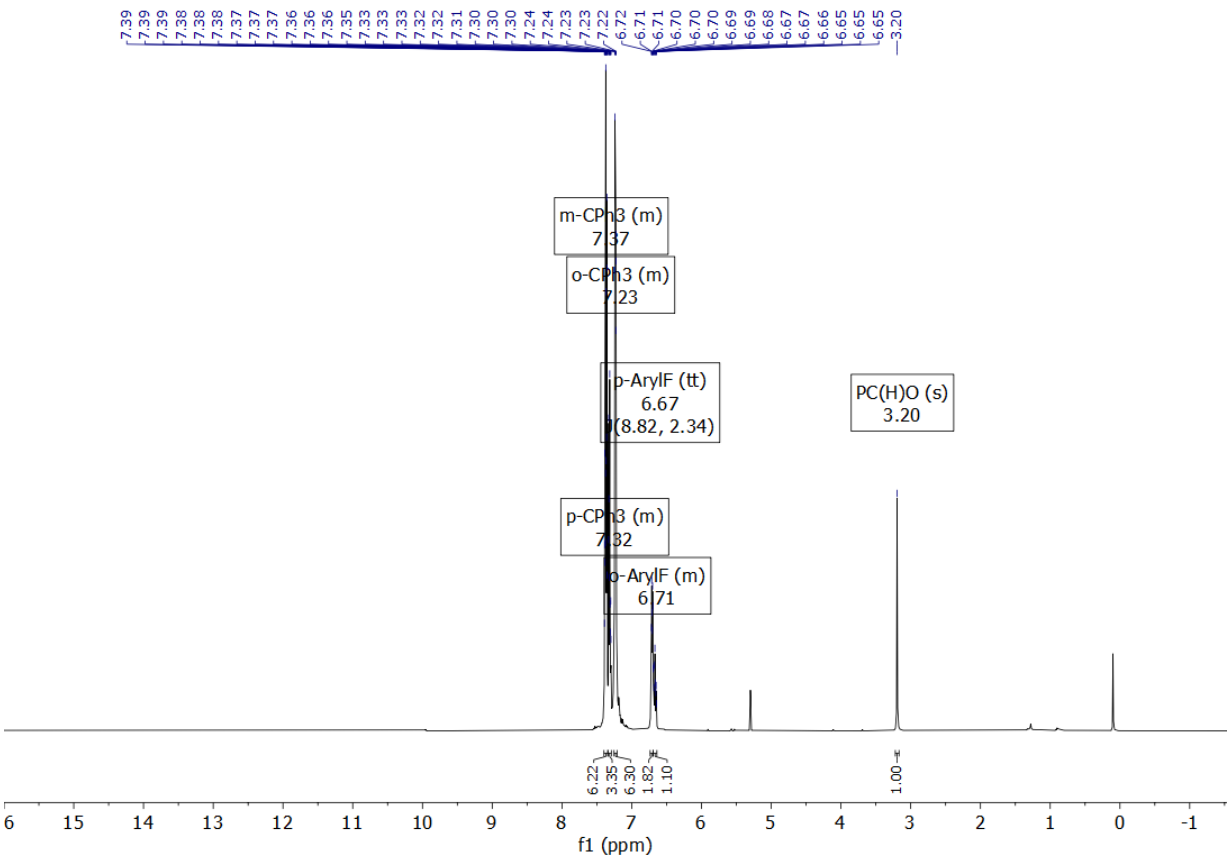


Figure S 16: ^{1}H-NMR spectrum in $CDCl_3$.

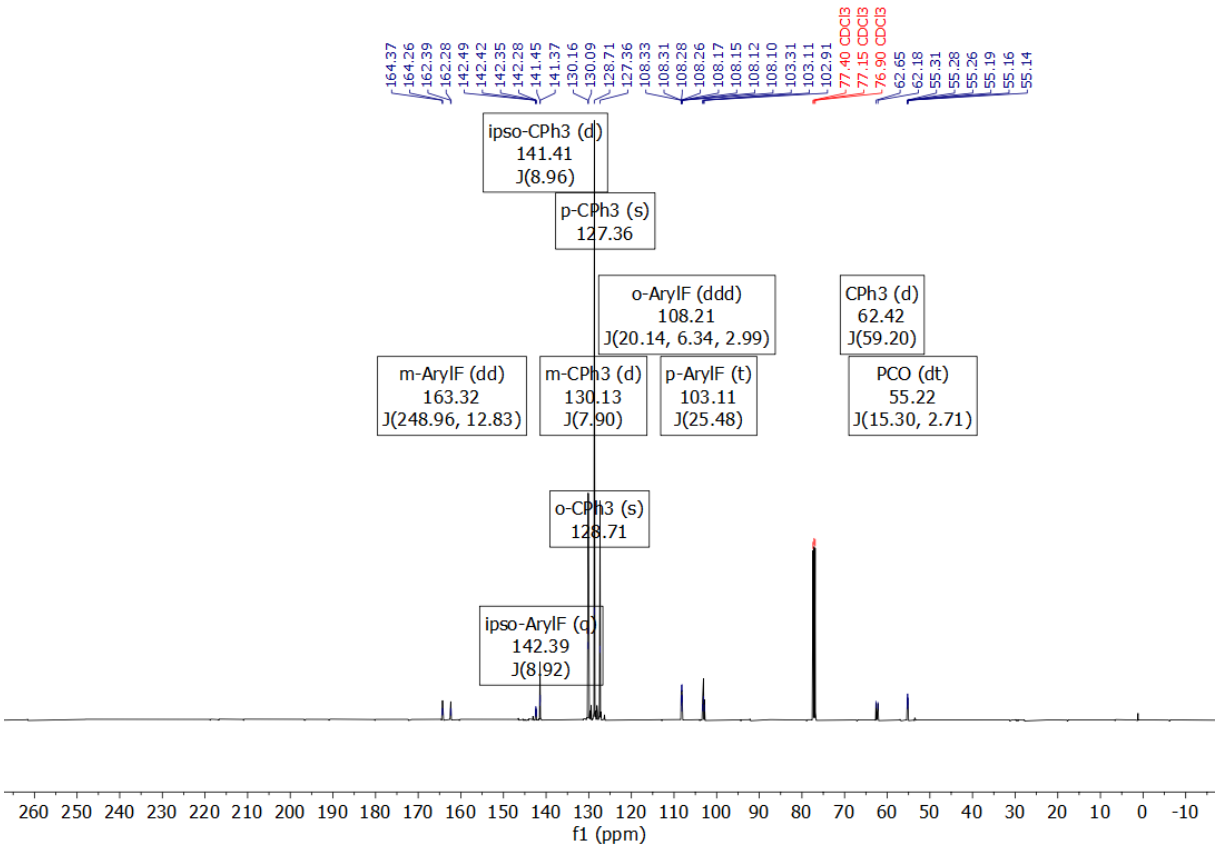


Figure S 17: $^{13}C\{^{1}H\}$-NMR spectrum in $CDCl_3$.

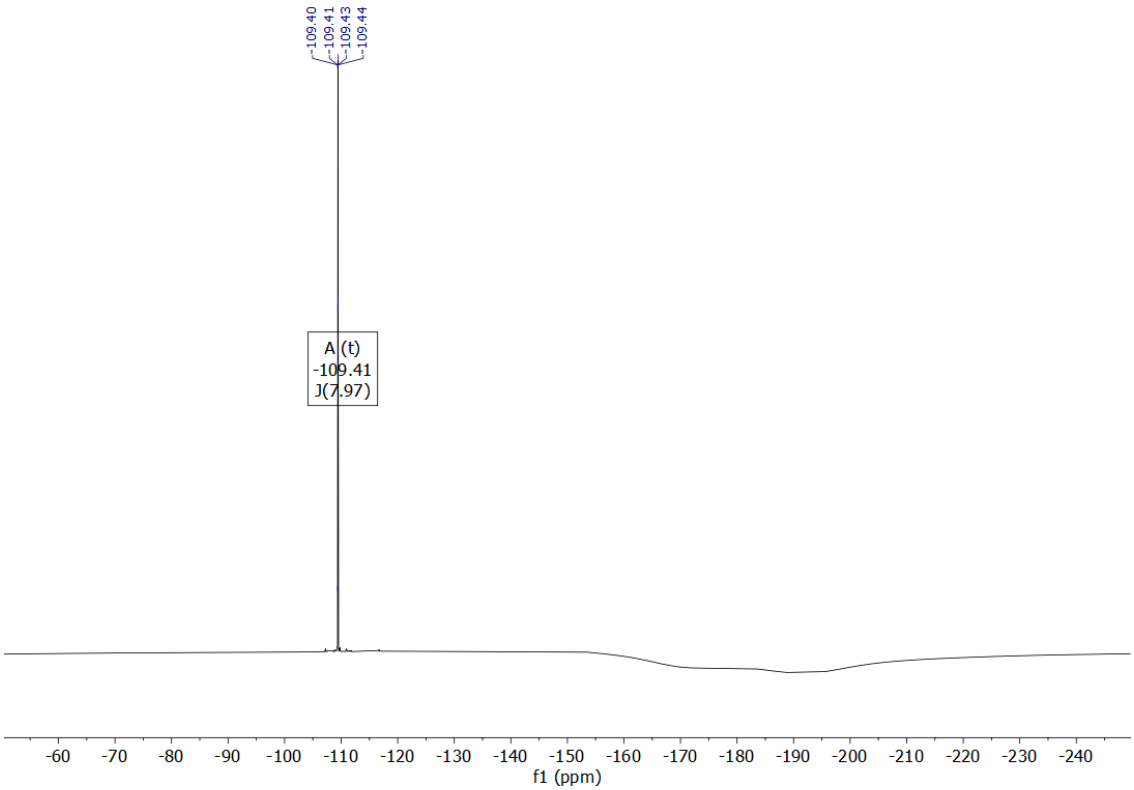


Figure S 18: $^{19}F\{^{1}H\}$-NMR spectrum in $CDCl_3$.

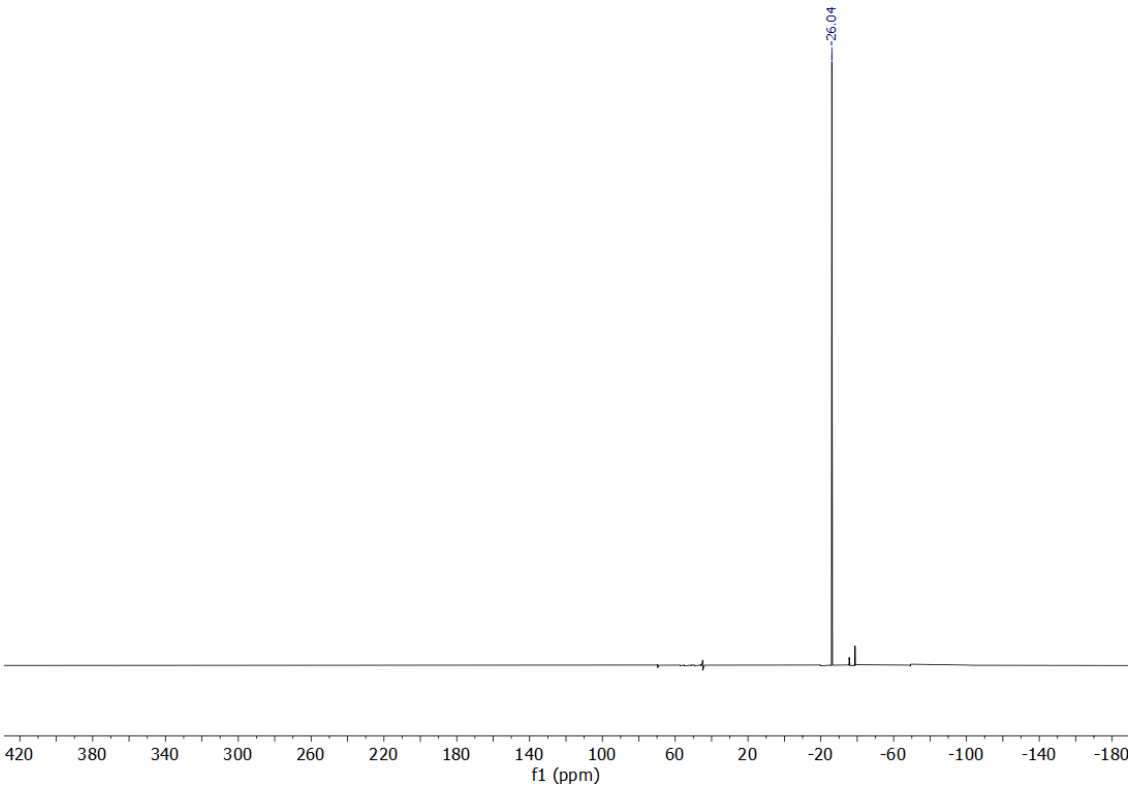


Figure S 19: $^{31}P\{^{1}H\}$-NMR spectrum in $CDCl_3$.

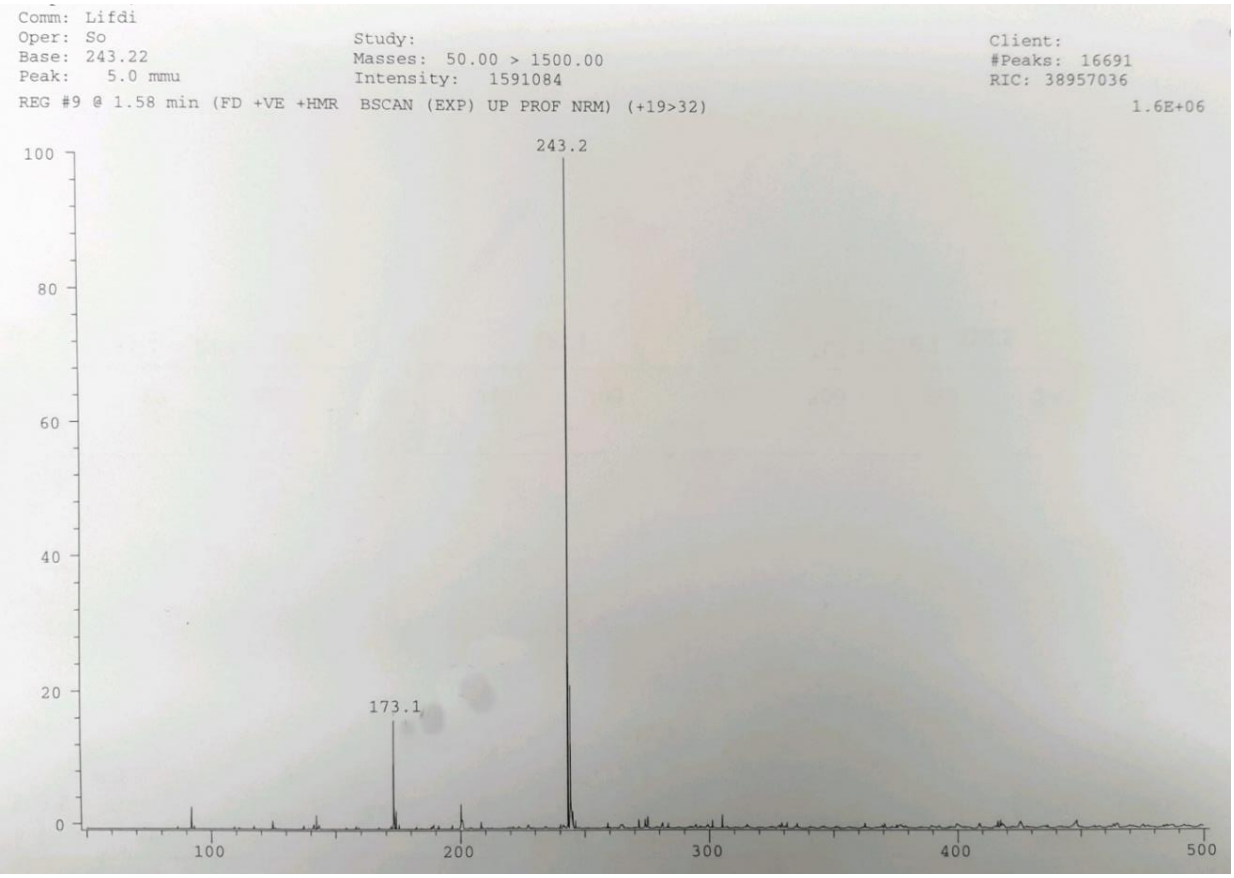


Figure S 20: MS spectrum (LIFDI) of **4a**.

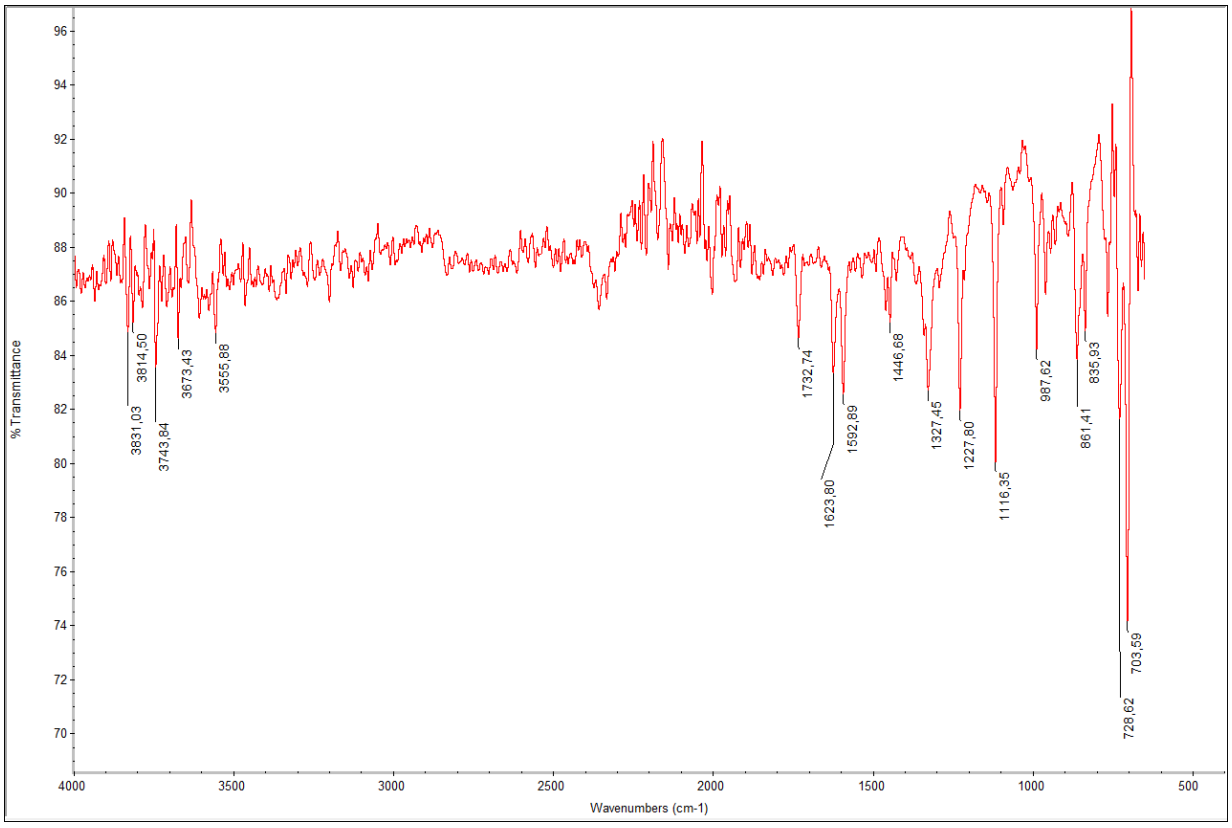


Figure S 21: IR spectrum of **4a**.

Molecular structure of 4a

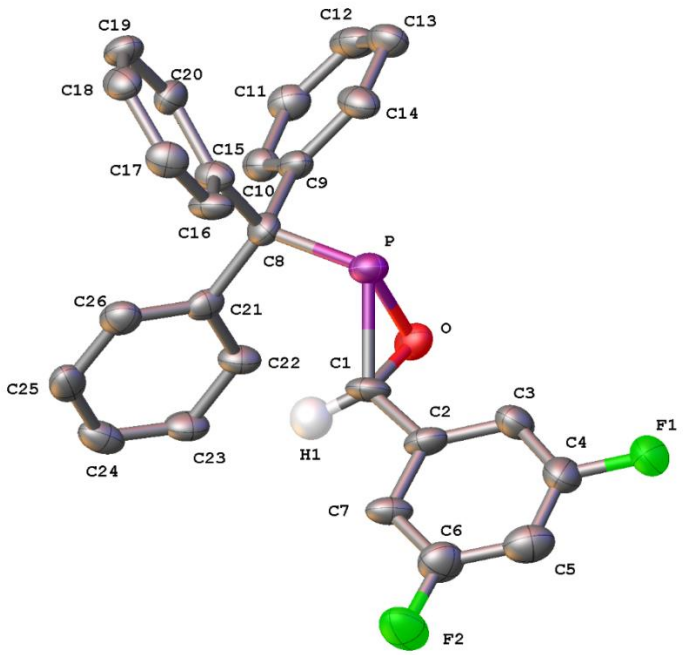


Figure S 22: Molecular structure of **4a** of the (2*S*,3*R*)-enantiomer in the single crystal (50% probability level). The hydrogen atoms, except the hydrogen atom of the oxaphosphirane ring, are omitted for clarity.

Bond lengths in Å

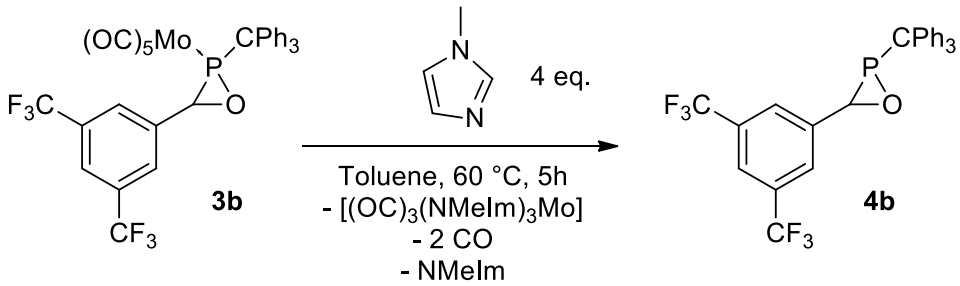
P	O	1.685(7)		C9	C14	1.393(13)
P	C1	1.835(8)		C10	C11	1.412(13)
P	C8	1.916(9)		C11	C12	1.378(15)
F1	C4	1.361(11)		C12	C13	1.366(16)
F2	C6	1.334(13)		C13	C14	1.386(14)
O	C1	1.456(11)		C15	C16	1.381(13)
C1	C2	1.500(13)		C15	C20	1.399(12)
C2	C3	1.379(14)		C16	C17	1.399(13)
C2	C7	1.373(13)		C17	C18	1.380(13)
C3	C4	1.396(14)		C18	C19	1.376(13)
C4	C5	1.347(16)		C19	C20	1.417(13)
C5	C6	1.371(17)		C21	C22	1.431(12)
C6	C7	1.390(13)		C21	C26	1.374(13)
C8	C9	1.540(12)		C22	C23	1.383(13)
C8	C15	1.551(11)		C23	C24	1.378(15)
C8	C21	1.539(12)		C24	C25	1.404(15)
C9	C10	1.356(14)		C25	C26	1.382(14)

Bond angles in °

O	P	C1	48.6(4)		C10	C9	C8	122.8(8)
O	P	C8	104.2(4)		C10	C9	C14	118.6(8)
C1	P	C8	107.8(4)		C14	C9	C8	118.5(9)
C1	O	P	71.1(4)		C9	C10	C11	121.2(9)
O	C1	P	60.3(4)		C12	C11	C10	118.6(9)

O	C1	C2	115.7(8)		C13	C12	C11	121.2(9)
C2	C1	P	121.3(7)		C12	C13	C14	119.1(9)
C3	C2	C1	120.5(8)		C13	C14	C9	121.3(10)
C7	C2	C1	118.1(9)		C16	C15	C8	121.1(8)
C7	C2	C3	121.4(9)		C16	C15	C20	117.7(8)
C2	C3	C4	115.5(8)		C20	C15	C8	121.2(8)
F1	C4	C3	116.2(9)		C15	C16	C17	122.1(8)
C5	C4	F1	118.9(10)		C18	C17	C16	119.3(8)
C5	C4	C3	124.8(10)		C19	C18	C17	120.6(8)
C4	C5	C6	118.0(10)		C18	C19	C20	119.5(8)
F2	C6	C5	120.5(9)		C15	C20	C19	120.7(8)
F2	C6	C7	119.5(10)		C22	C21	C8	117.9(8)
C5	C6	C7	119.9(10)		C26	C21	C8	122.7(8)
C2	C7	C6	120.2(10)		C26	C21	C22	119.3(8)
C9	C8	P	105.6(6)		C23	C22	C21	118.6(9)
C9	C8	C15	109.2(7)		C24	C23	C22	121.1(9)
C15	C8	P	103.4(6)		C23	C24	C25	120.2(8)
C21	C8	P	113.9(6)		C26	C25	C24	119.0(9)
C21	C8	C9	113.9(8)		C21	C26	C25	121.6(9)
C21	C8	C15	110.2(7)					

1.2.5 2-Triphenylmethyl-3-(3,5-bis(trifluormethyl)phenyl)oxaphosphirane 4b



To a solution of 417.9 mg **3b** (0.56 mmol, 1.00 eq) in 30 mL of toluene, 0.18 mL 1-methylimidazole (2.22 mmol, 4.00 eq) were added. The solution was stirred for 5h at 60 °C, and the solution turned from slightly yellow to yellow and a yellow solid precipitated out of solution. The solvent was removed under reduced pressure (1 x 10^{-2} mbar) and a brown-yellow residue was obtained. The residue was dissolved in 10 mL of CH_2Cl_2 and purified by column chromatography (h = 9 cm, Ø = 3 cm, Al_2O_3, eluent: petroleum ether:Et_2O (50:50), -20 °C). After collecting 150 mL of a yellow fraction, the solvent was removed under reduced pressure (1 x 10^{-2} mbar) and a yellow residue was obtained. The residue was washed five times with 1 mL of -pentane at -50 °C and after drying under reduced pressure (1 x 10^{-2} mbar), the product was obtained as a colorless powder.

Yield: 214.3 mg (0.415 mmol, 75%).

Melting point: 132 °C.

Elemental analysis: calculated.: C 65.12 H 3.71 found: C 65.55 H 4.06

MS (LIFDI): m/z (%) = 273.2 $[M\text{-}CPh_3]^{+\bullet}$ (16), 243.2 $[CPh_3]^{+\bullet}$ (100).

IR (ATR diamond): / cm^{-1} = 1131 (s, ν(C-F)), 900 (m, δ(C^{ArF}-H)$_{oop}$)), 843 (m, δ(C^{ArF}-H)$_{oop}$)), 729 (w, δ(C^{Ar}-H)$_{oop}$)), 705 (m, δ(C^{Ar}-H)$_{oop}$)), 682 (w, δ(C^{Ar}-H)$_{oop}$)).

^{1}H-NMR (300.13 MHz, 299.4 K, C_6D_6): δ /ppm = 3.46 (s, 1H, PC(H)O), 7.00 - 7.12 (m, 9H, *o*- and *p*-CPh_3), 7.30 - 7.36 (m, 6H, *m*-CPh_3), 7.39 (s, 2H, *o*-Ar^{CF3}), 7.51 (s, 1H, *p*-Ar^{CF3}).

^{13}C{^{1}H}-NMR (75.48 MHz, 299.4 K, C_6D_6): δ /ppm = 55.1 (dd, $^{1}J_{P,C}$ = 16.2 Hz, $^{5}J_{F,C}$ = 2.7 Hz , PCO), 62.9 (d, $^{1}J_{P,C}$ = 59.8 Hz, Ph_3C-P), 121.3 (t, $^{5}J_{P,C}$ = 3.7 Hz, *p*-$Aryl^{CF3}$), 123.7 (q, $^{1}J_{F,C}$ = 272.9 Hz, CF_3), 125.3 (m, *o*-$Aryl^{CF3}$), 127.7 (d, $^{5}J_{P,C}$ = 1.1 Hz, *p*-CPh_3), 129.0 (s, *o*-CPh_3), 130.4 (d, $^{4}J_{P,C}$ = 7.9 Hz, *m*-CPh_3), 132.0 (q, $^{2}J_{F,C}$ = 33.3 Hz, *m*-$Aryl^{CF3}$), 141.6 (d, $^{2}J_{P,C}$ = 7.5 Hz, *ipso*-$Aryl^{CF3}$), 141.7 (d, $^{2}J_{P,C}$ = 9.1 Hz, *ipso*-CPh_3).

^{19}F{^{1}H}-NMR (282.4 MHz, 298.4 K, C_6D_6): δ /ppm = -109.3.

^{31}P{^{1}H}-NMR (121.51 MHz, 299.4 K, C_6D_6): δ /ppm = -25.5.

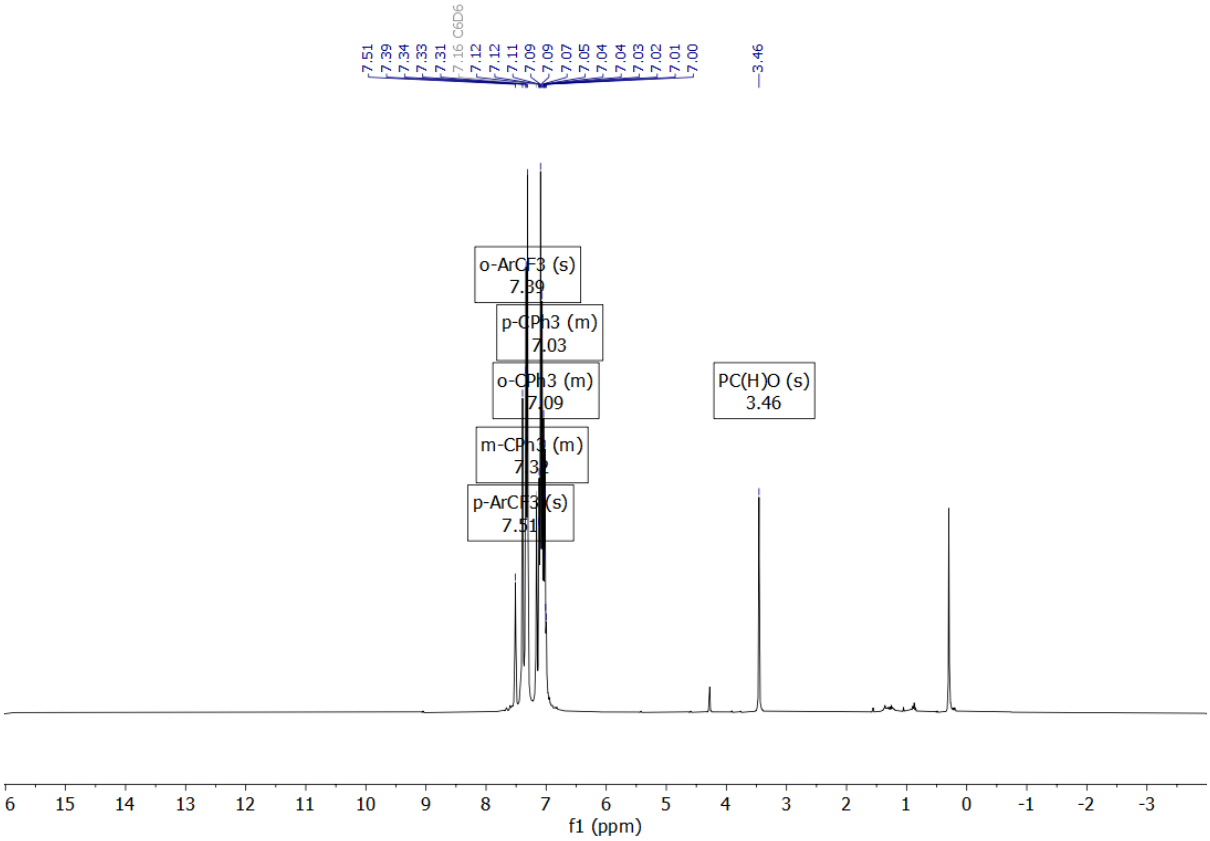


Figure S 23: ^{1}H-NMR spectrum in C_6D_6.

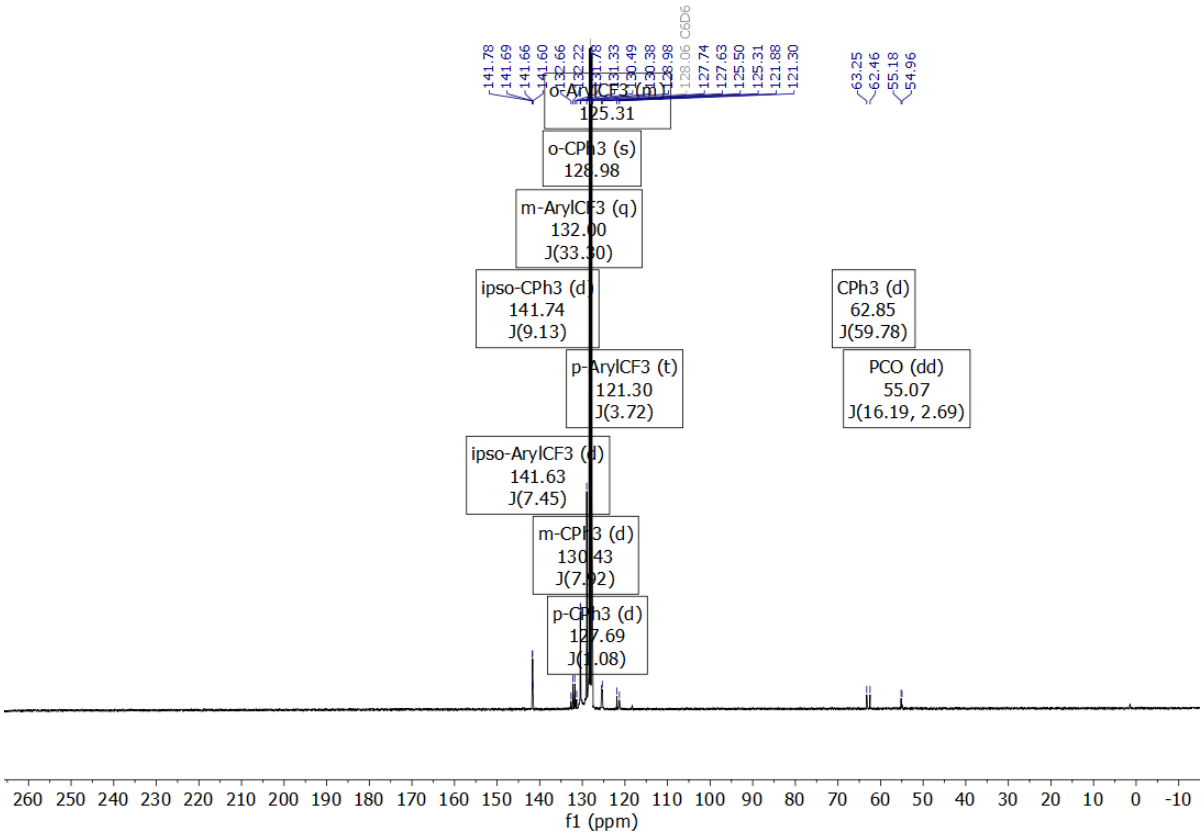


Figure S 24: $^{13}C\{^{1}H\}$-NMR spectrum in C_6D_6.

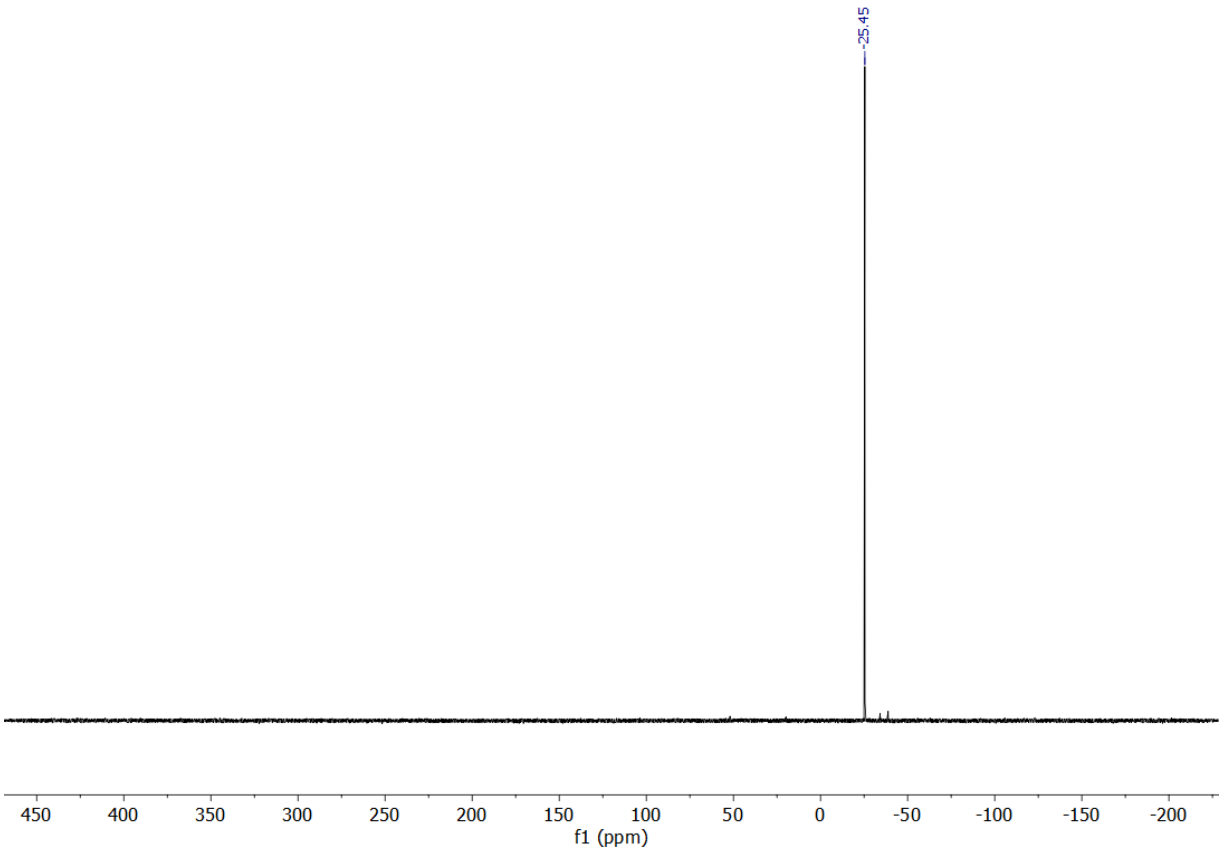


Figure S 25: $^{31}P\{^{1}H\}$-NMR spectrum in C_6D_6.

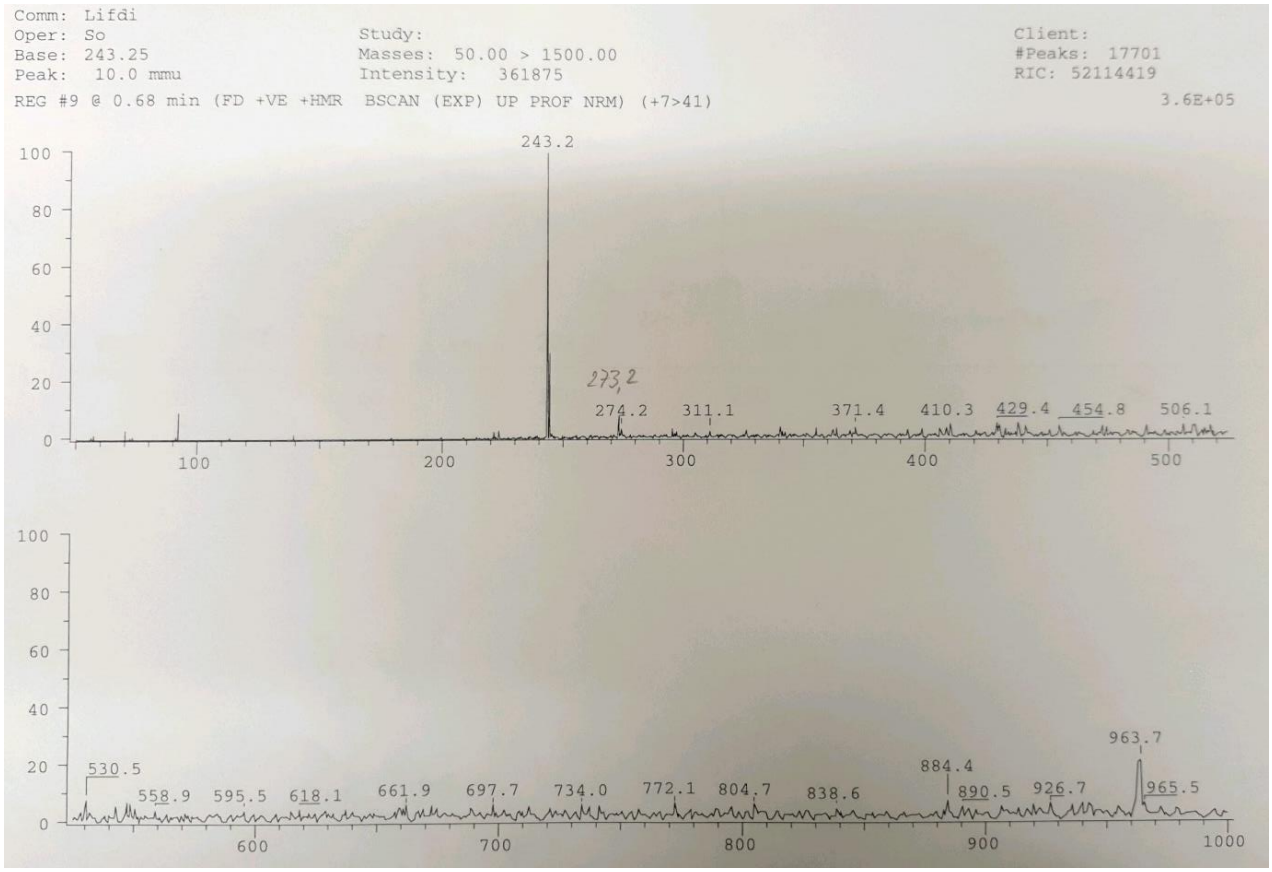


Figure S 26: MS spectrum (LIFDI) of **4b**.

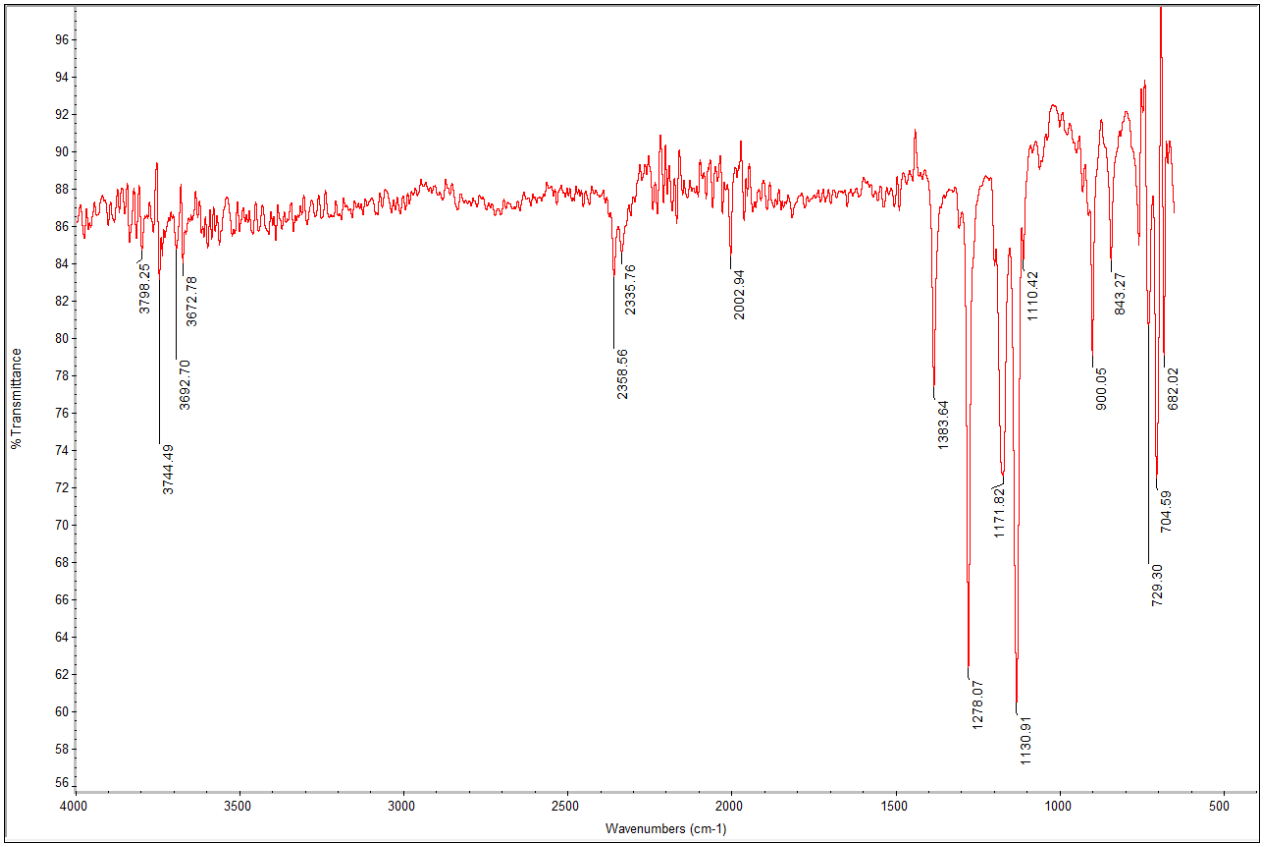


Figure S 27: IR spectrum of **4b**.

Molecular structure of 4b

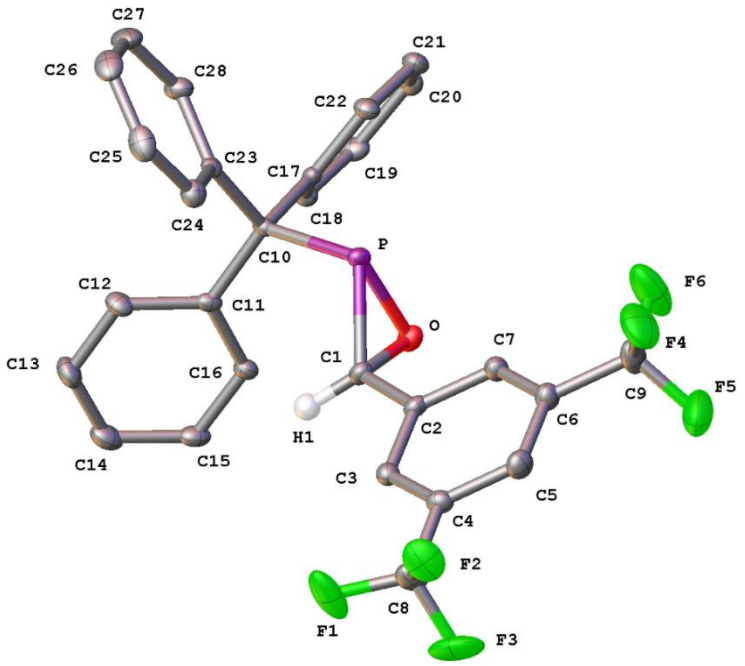


Figure S 28: Molecular structure of **4b** of the (2*S*,3*R*)-enantiomer in the single crystal (50% probability level). The hydrogen atoms, except the hydrogen atom of the oxaphosphirane ring, are omitted for clarity.

Bond lengths in Å

P	O	1.682(3)		C10	C17	1.538(5)
P	C1	1.819(4)		C10	C23	1.537(5)
P	C10	1.917(4)		C11	C12	1.402(6)
F1	C8	1.334(6)		C11	C16	1.400(6)
F2	C8	1.323(6)		C12	C13	1.405(6)
F3	C8	1.337(6)		C13	C14	1.371(7)
F4	C9	1.330(6)		C14	C15	1.384(6)
F5	C9	1.332(6)		C15	C16	1.393(6)
F6	C9	1.326(6)		C17	C18	1.396(6)
O	C1	1.458(5)		C17	C22	1.400(6)
C1	C2	1.486(5)		C18	C19	1.392(6)
C2	C3	1.394(6)		C19	C20	1.403(6)
C2	C7	1.395(5)		C20	C21	1.374(6)
C3	C4	1.391(6)		C21	C22	1.387(6)
C4	C5	1.387(6)		C23	C24	1.397(6)
C4	C8	1.509(6)		C23	C28	1.390(6)
C5	C6	1.398(6)		C24	C25	1.387(6)
C6	C7	1.387(5)		C25	C26	1.388(7)
C6	C9	1.495(6)		C26	C27	1.383(7)
C10	C11	1.534(5)		C27	C28	1.388(6)

Bond angles in °

O	P	C1	49.04(16)		C11	C10	P	115.9(3)

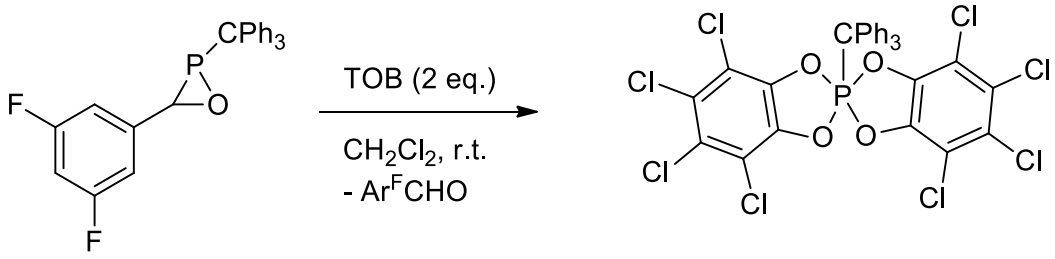
O	P	C10	104.99(16)		C11	C10	C17	114.7(3)
C1	P	C10	110.74(18)		C11	C10	C23	111.5(3)
C1	O	P	70.4(2)		C17	C10	P	100.2(2)
O	C1	P	60.57(19)		C23	C10	P	101.6(2)
O	C1	C2	113.5(3)		C23	C10	C17	111.8(3)
C2	C1	P	118.0(3)		C12	C11	C10	120.6(4)
C3	C2	C1	121.0(4)		C16	C11	C10	121.1(3)
C3	C2	C7	119.3(4)		C16	C11	C12	118.2(4)
C7	C2	C1	119.6(4)		C11	C12	C13	120.2(4)
C4	C3	C2	119.6(4)		C14	C13	C12	120.7(4)
C3	C4	C8	120.5(4)		C13	C14	C15	119.7(4)
C5	C4	C3	121.5(4)		C14	C15	C16	120.5(4)
C5	C4	C8	118.0(4)		C15	C16	C11	120.7(4)
C4	C5	C6	118.5(4)		C18	C17	C10	123.5(3)
C5	C6	C9	118.5(4)		C18	C17	C22	117.9(4)
C7	C6	C5	120.6(4)		C22	C17	C10	118.6(3)
C7	C6	C9	120.9(4)		C19	C18	C17	120.7(4)
C6	C7	C2	120.4(4)		C18	C19	C20	120.4(4)
F1	C8	F3	107.2(4)		C21	C20	C19	119.1(4)
F1	C8	C4	111.8(4)		C20	C21	C22	120.6(4)
F2	C8	F1	107.1(4)		C21	C22	C17	121.3(4)
F2	C8	F3	106.1(4)		C24	C23	C10	119.4(4)
F2	C8	C4	112.3(4)		C28	C23	C10	122.0(4)
F3	C8	C4	112.0(4)		C28	C23	C24	118.6(4)
F4	C9	F5	104.5(4)		C25	C24	C23	121.0(4)
F4	C9	C6	112.2(4)		C24	C25	C26	119.8(4)
F5	C9	C6	112.2(5)		C27	C26	C25	119.6(4)
F6	C9	F4	105.8(5)		C26	C27	C28	120.7(5)
F6	C9	F5	108.2(4)		C27	C28	C23	120.3(4)
F6	C9	C6	113.3(4)					

Torsion angles in °

P	O	C1	C2	-110.1(3)		C10	P	C1	C2	-165.2(3)
P	C1	C2	C3	141.6(4)		C10	C11	C12	C13	178.6(4)
P	C1	C2	C7	-38.2(5)		C10	C11	C16	C15	-178.2(4)
P	C10	C11	C12	124.4(4)		C10	C17	C18	C19	-176.5(4)
P	C10	C11	C16	-58.4(4)		C10	C17	C22	C21	176.6(4)
P	C10	C17	C18	126.1(3)		C10	C23	C24	C25	-176.3(4)
P	C10	C17	C22	-52.3(4)		C10	C23	C28	C27	175.6(4)
P	C10	C23	C24	-48.1(4)		C11	C10	C17	C18	1.3(5)
P	C10	C23	C28	134.1(3)		C11	C10	C17	C22	-177.1(4)
O	P	C1	C2	102.6(4)		C11	C10	C23	C24	75.9(4)
O	C1	C2	C3	-150.5(4)		C11	C10	C23	C28	-101.8(4)
O	C1	C2	C7	29.7(5)		C11	C12	C13	C14	-1.8(7)
C1	C2	C3	C4	-178.2(4)		C12	C11	C16	C15	-0.9(6)
C1	C2	C7	C6	177.7(4)		C12	C13	C14	C15	1.8(7)
C2	C3	C4	C5	-0.9(6)		C13	C14	C15	C16	-1.3(7)
C2	C3	C4	C8	-178.6(4)		C14	C15	C16	C11	0.9(6)
C3	C2	C7	C6	-2.1(6)		C16	C11	C12	C13	1.3(6)

C3	C4	C5	C6	0.7(7)		C17	C10	C11	C12	-119.5(4)
C3	C4	C8	F1	-14.7(6)		C17	C10	C11	C16	57.7(5)
C3	C4	C8	F2	-135.1(4)		C17	C10	C23	C24	-154.2(3)
C3	C4	C8	F3	105.6(5)		C17	C10	C23	C28	28.1(5)
C4	C5	C6	C7	-1.2(7)		C17	C18	C19	C20	-1.2(6)
C4	C5	C6	C9	-179.9(4)		C18	C17	C22	C21	-1.9(6)
C5	C4	C8	F1	167.5(4)		C18	C19	C20	C21	0.4(7)
C5	C4	C8	F2	47.1(6)		C19	C20	C21	C22	-0.4(7)
C5	C4	C8	F3	-72.2(6)		C20	C21	C22	C17	1.2(7)
C5	C6	C7	C2	1.9(7)		C22	C17	C18	C19	1.9(6)
C5	C6	C9	F4	-56.9(6)		C23	C10	C11	C12	8.9(5)
C5	C6	C9	F5	60.5(6)		C23	C10	C11	C16	-173.9(4)
C5	C6	C9	F6	-176.6(4)		C23	C10	C17	C18	-127.0(4)
C7	C2	C3	C4	1.6(6)		C23	C10	C17	C22	54.6(5)
C7	C6	C9	F4	124.5(5)		C23	C24	C25	C26	-0.6(6)
C7	C6	C9	F5	-118.1(5)		C24	C23	C28	C27	-2.1(6)
C7	C6	C9	F6	4.8(7)		C24	C25	C26	C27	0.1(7)
C8	C4	C5	C6	178.5(4)		C25	C26	C27	C28	-0.7(7)
C9	C6	C7	C2	-179.5(4)		C26	C27	C28	C23	1.7(7)
C10	P	O	C1	-104.7(2)		C28	C23	C24	C25	1.6(6)
C10	P	C1	O	92.2(2)						

1.2.6 Synthesis of 4,4',5,5',6,6',7,7'-octachloro-2-triphenylmethyl-2,2'-spirobis[1,3,2-benzodioxaphosphole] 5



4a **5**

30.0 mg of **4a** (0.072 mmol, 1.00 eq) were dissolved in 1 mL of DCM and 17.7 mg of tetrachloro-*ortho*-benzoquinone (TOB) were dissolved in 0.5 mL of DCM. The TOB-solution was added to the oxaphosphirane-solution and the stirred for two hours at room temperature, and the solution turned from red to brown. Subsequently, after stirring for 1h each, four times 4.4 mg TOB (0.018 mmol, 0.25 eq) were added. The solvent was removed under reduced pressure (1 x 10^{-2} mbar) and a brown residue was obtained. The residue was washed five times with 1 mL of Et_2O and after drying under reduced pressure (1 x 10^{-2} mbar) the product was obtained as a slightly yellow powder.

Yield: 17.8 mg (32%, 0.023 mmol).

Melting point: 185 °C.

IR (ATR Diamond): / cm^{-1} = 1698 (w, ν(C=C), 1623 (m, ν(C=C), 1595 (m, ν(C=C)), 1118 (m, ν(P-O-C^{Ar})), 986 (m, ν(C^{Ar}-Cl)), 747 (m, δ(C^{Ar}-H)$_{oop}$)), 718 (m, δ(C^{Ar}-H)$_{oop}$)), 699 (s, δ(C^{Ar}-H)$_{oop}$)), 681(m, δ(C^{Ar}-H)$_{oop}$)), 669 (w, δ(C^{Ar}-H)$_{oop}$)).

MS (EI): m/z = 765.8 (0.6) $[M]^{+\bullet}$, 535.9 (0.4) $[M\text{-}C_6Cl_4O]^{+\bullet}$, 523.7 (2) $[M–CPh_3]^{+\bullet}$, 293.8 (4) $[M\text{-}C_{25}H_{15}Cl_4O]^{+\bullet}$ 243.1 (100) $[CPh_3]^{+\bullet}$, 165.0 (64) $[CPh_2]^{+\bullet}$.

HRMS (EI): calculated.: 761.8211 found.: 761.81925.

^{1}H-NMR (300.13 MHz, 298.0 K, CD_2Cl_2): δ /ppm = 7.16 - 7.26 (m, 9H, *o*- and *p*-CPh_3), 7.46 - 7.53 (m, 6H, *m*-CPh_3).

^{13}C{^{1}H}-NMR (75.48 MHz, 298.0 K, CD_2Cl_2): δ /ppm = 77.4 (d, $^{1}J_{P,C}$ = 150.4 Hz, $\underline{C}Ph_3$), 115.2 (d, $^{2}J_{P,C}$ = 14.0 Hz, *ipso*-CPh_3), 126.0 (s, $Aryl^{OP}$), 127.7 (d, $^{5}J_{P,C}$ = 2.8 Hz, *p*-CPh_3), 128.3 (d, $^{3}J_{P,C}$ = 1.9 Hz, *o*-CPh_3), 130.8 (d, $^{4}J_{P,C}$ = 9.4 Hz, *m*-CPh_3), 140.7 (d, $^{x}J_{P,C}$ = 6.0 Hz, $Aryl^{Cl}$), 141.5 (d, $^{x}J_{P,C}$ = 2.0 Hz, $Aryl^{Cl}$).

^{31}P{^{1}H}-NMR (121.51 MHz, 298.0 K, CD_2Cl_2): δ /ppm = 1.7.

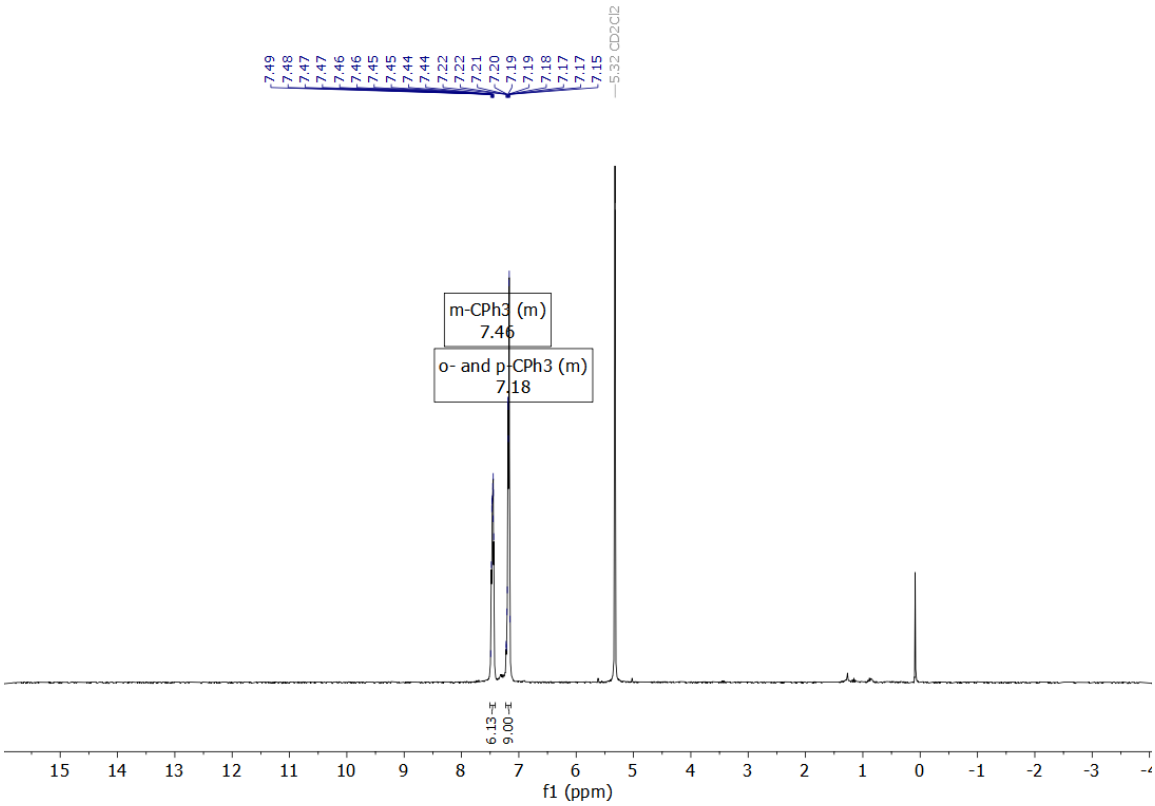


Figure S 29: ^{1}H-NMR spectrum in CD_2Cl_2.

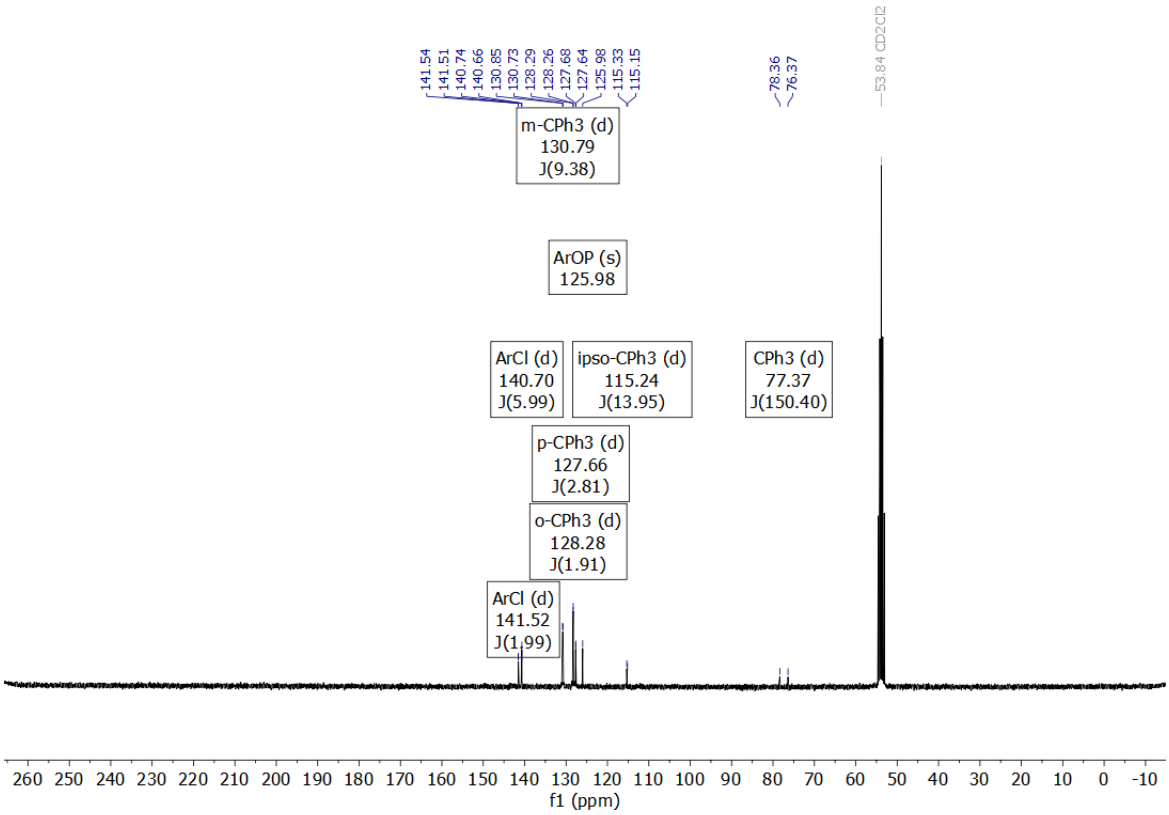


Figure S 30: $^{13}C\{^{1}H\}$-NMR spectrum in CD_2Cl_2.

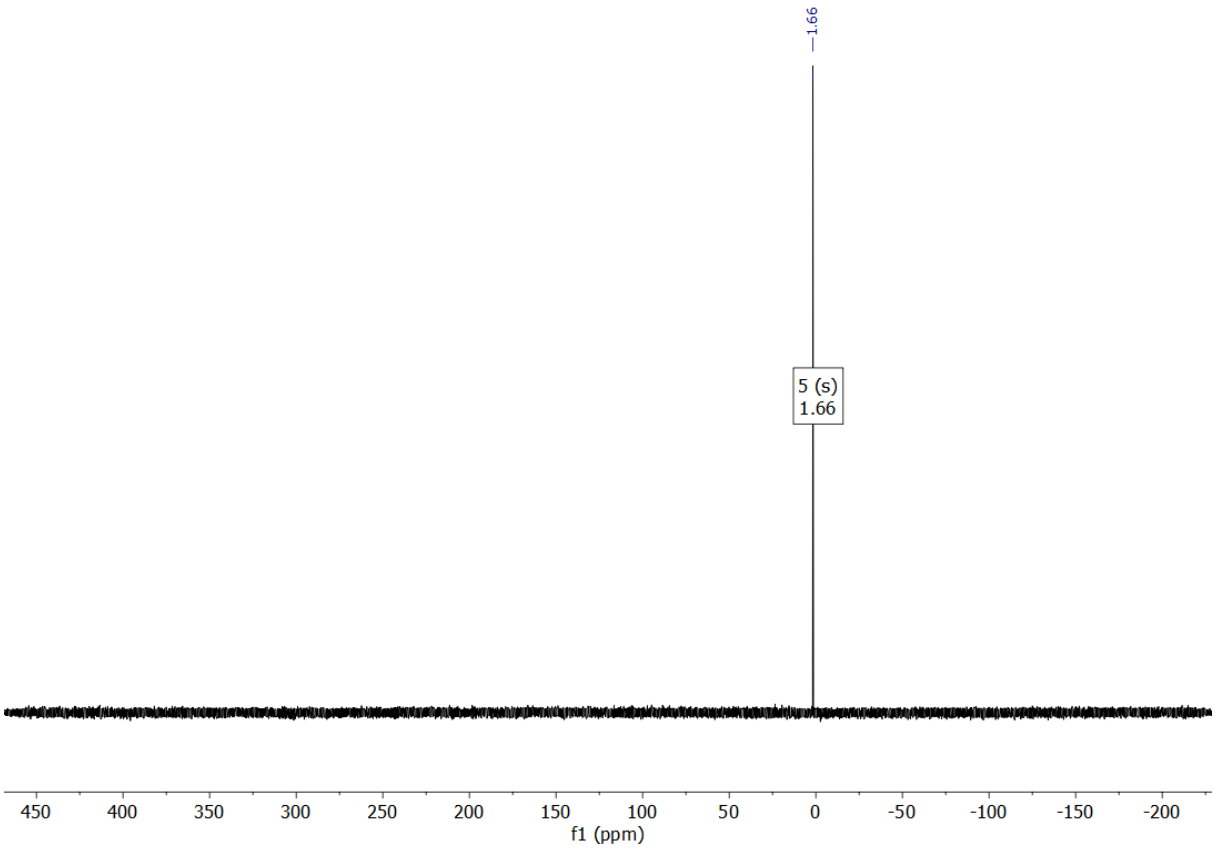


Figure S 31: $^{31}P\{^{1}H\}$-NMR spectrum in CD_2Cl_2.

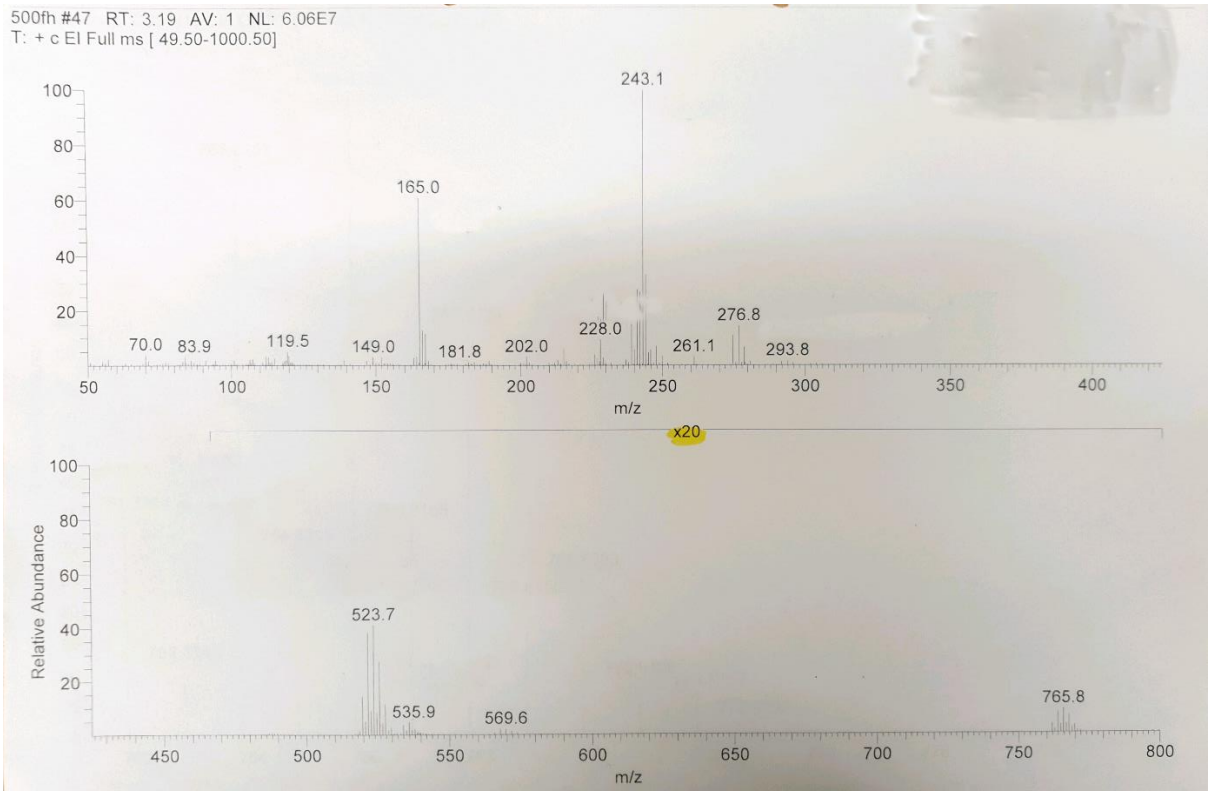


Figure S 32: MS spectrum (EI) of **5**.

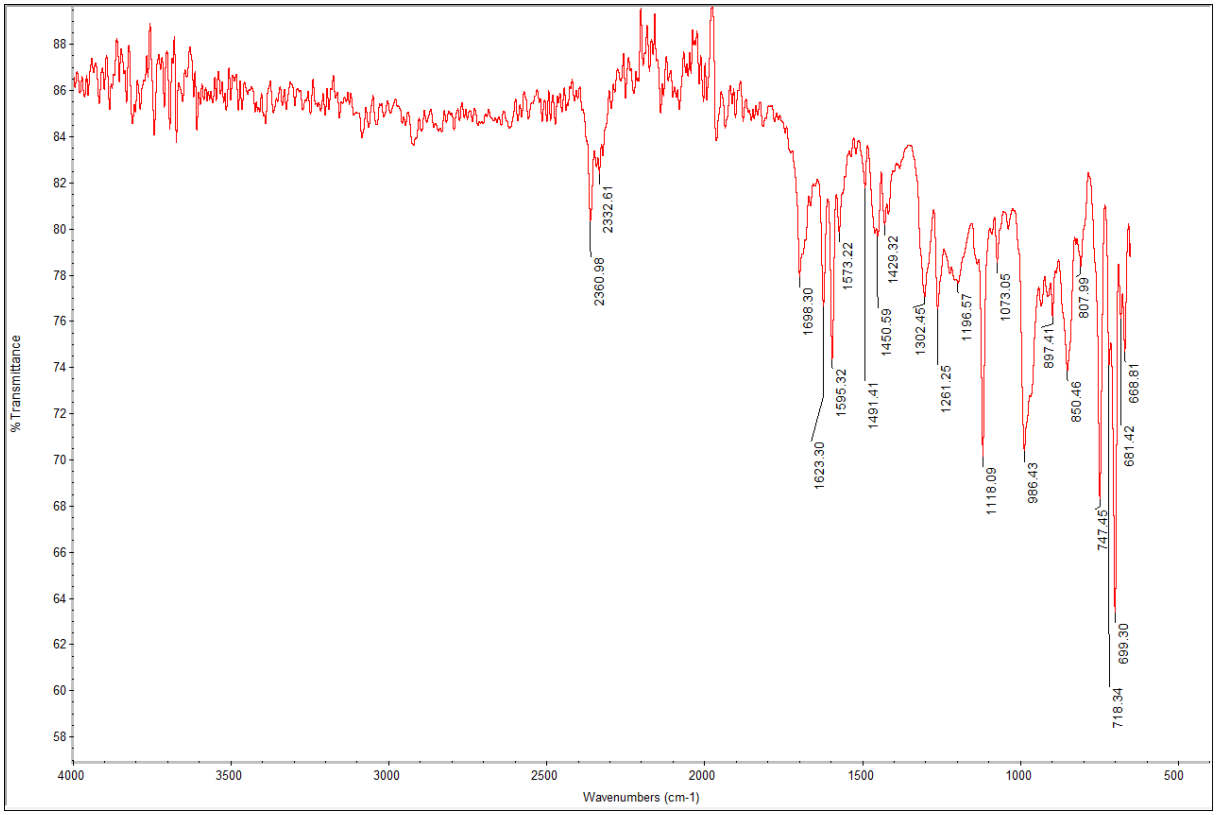
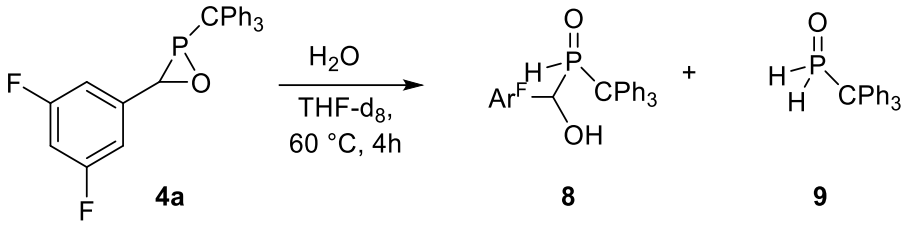


Figure S 33: IR spectrum of **5**.

1.2.7 Product mixture of {2-hydroxy-1-(3,5-difluorphenyl)methyl}(1-triphenylmethyl)-phosphaneoxide 8 (two diastereomers) and 1-triphenylmethylphosphaneoxide 9 in a ratio of 1.00 : 0.19 : 0.13.



13.4 mg of **4a** (0.032 mmol, 1.00 eq) were dissolved in 0.5 mL THF-d_8 in a Young NMR tube. To the solution 0.01 mL of degassed, distilled water were added. After keeping the solution for 16h at room temperature, 2h at 40 °C, 4h at 60 °C and additionally 12 days at room temperature the reaction was completed. The solution was transferred to a Schlenk tube and the solvent was removed under reduced pressure (1 x 10^{-2} mbar). The colorless residue was washed three times with 0.3 mL of *n*-pentane and a product mixture of **8** (two diastereomers) and **9** in a ratio of 1.00 : 0.19 : 0.13 was obtained as a colorless powder. The following analytical data refer to the product mixture.

IR (ATR diamond): / cm^{-1} = 3744 (w, ν(OH)), 3693 (w, ν(OH)), 2356 (m, ν(P-H)), 1620 (m, ν(C=C), 1594 (m, ν(C=C)), 1118 (m, ν(C-F)), 899 (m, $\delta(C^{ArF}\text{-}H)_{oop}$)), 851 (m, $\delta(C^{ArF}\text{-}H)_{oop}$)), 769 (m, $\delta(C^{Ar}\text{-}H)_{oop}$)), 745 (m, $\delta(C^{Ar}\text{-}H)_{oop}$)), 700 (s, $\delta(C^{Ar}\text{-}H)_{oop}$)), 681 (m, $\delta(C^{Ar}\text{-}H)_{oop}$)).

8 (major diastereomer): ^{1}H-NMR (500.04 MHz, 298.0 K, THF-d_8): δ /ppm = 2.86 (s, 1H, OH), 4.34 (s, 1H, CH), 6.51 (m, *o*-Aryl^F), 6.61 (d, $^1J_{P,H}$ = 481.3 Hz, 1H, PH), 6.80 (m, *p*- Aryl^F), 7.23 – 7.37 (m, 15H, CPh_3).

$^{13}C\{^1H\}$-NMR (125.75 MHz, 298.0 K, THF-d_8): δ /ppm = 64.7 (d, $^1J_{P,C}$ = 50.2 Hz, $\underline{C}Ph_3$), 69.2 (dt, $^1J_{P,C}$ = 65.4 Hz, $^4J_{F,C}$ = 2.2 Hz, CH), 103.7 (td, $^2J_{F,C}$ = 25.8 Hz, $^5J_{P,C}$ = 2.9 Hz, *p*-Aryl^F), 110.3 (m, *o*-Aryl^F), 127.4 (d, $^5J_{P,C}$ = 1.9 Hz, *p*-$C\underline{Ph}_3$), 128.3 (d, $^3J_{P,C}$ = 1.4 Hz, *o*-$C\underline{Ph}_3$), 130.6 (d, $^4J_{P,C}$ = 6.1 Hz, *m*-$C\underline{Ph}_3$), 142.1 (d, $^2J_{P,C}$ = 1.4 Hz *ipso*-CPh_3), 146.4 (td, $^3J_{F,C}$ = 8.5 Hz, $^2J_{P,C}$ = 2.2 Hz, *ipso*-Aryl^F), 164.1 (ddd, $^1J_{F,C}$ = 248.3 Hz, $^2J_{F,C}$ = 12.8 Hz, $^4J_{P,C}$ = 2.7 Hz, *m*-Aryl^F).

^{31}P-NMR (202.44 MHz, 298.0 K, THF-d_8): δ /ppm = 50.3 (d, $^1J_{P,H}$ = 481.3 Hz).

8' (minor diastereomer): ^{1}H-NMR (500.04 MHz, 298.0 K, THF-d_8): δ /ppm = 2.88 (s, 1H, OH), 4.55 (s, 1H, CH), 6.51 (m, *o*-Aryl^F), 6.80 (m, *p*-Aryl^F), 7.23 – 7.37 (m, 15H, CPh_3), 7.37 (dd, $^1J_{P,H}$ = 481.3 Hz, $^3J_{H,H}$ = 1.2 Hz, 1H, PH).

$^{13}C\{^1H\}$-NMR (125.75 MHz, 298.0 K, THF-d_8): δ /ppm = 63.4 (d, $^1J_{P,C}$ = 50.5 Hz, $\underline{C}Ph_3$), 72.3 (dt, $^1J_{P,C}$ = 73.6 Hz, $^4J_{F,C}$ = 2.0 Hz, CH), 103.7 (td, $^2J_{F,C}$ = 25.8 Hz, $^5J_{P,C}$ = 2.9 Hz, *p*- Aryl^F), 112.9 (m, *o*-Aryl^F), 128.2 – 131.8 (m, $C\underline{Ph}_3$), 142.5 (d, $^2J_{P,C}$ = 2.0 Hz, *ipso*-CPh_3), 144.1 – 144.2 (m, *ipso*-Aryl^F), 164.3 (dd, $^1J_{F,C}$ = 249.9 Hz, $^2J_{F,C}$ = 11.8 Hz, *m*-Aryl^F).

^{31}P-NMR (202.44 MHz, 298.0 K, THF-d_8): δ /ppm = 49.3 (d, $^1J_{P,H}$ = 481.8 Hz).

9: ^{1}H-NMR (500.04 MHz, 298.0 K, THF-d_8): δ /ppm = 7.05 (d, $^1J_{P,H}$ = 480.5 Hz, 2H, PH), 7.28 – 7.37 (m, 15H, CPh_3).

$^{13}C\{^1H\}$-NMR (125.75 MHz, 298.0 K, THF-d_8): δ /ppm = 63.6 (d, $^1J_{P,C}$ = 50.2 Hz, $\underline{C}Ph_3$), 128.2 – 131.8 (m, $C\underline{Ph}_3$), 141.7 (s, *ipso*-$C\underline{Ph}_3$).

^{31}P-NMR (202.44 MHz, 298.0 K, THF-d_8): δ /ppm = 19.9 (t, $^{1}J_{P,H}$ = 480.8 Hz).

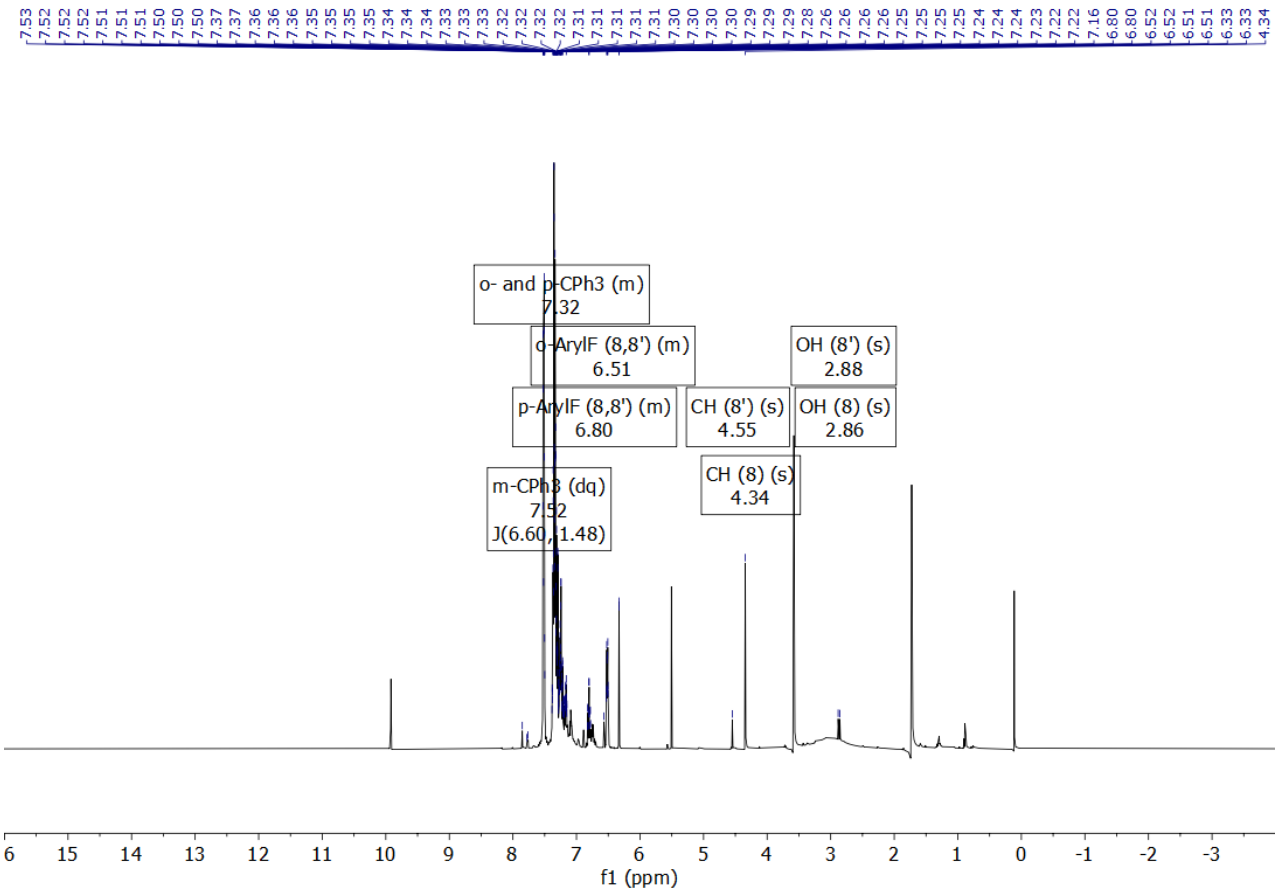


Figure S 34: ^{1}H-NMR spectrum in THF-d_8.

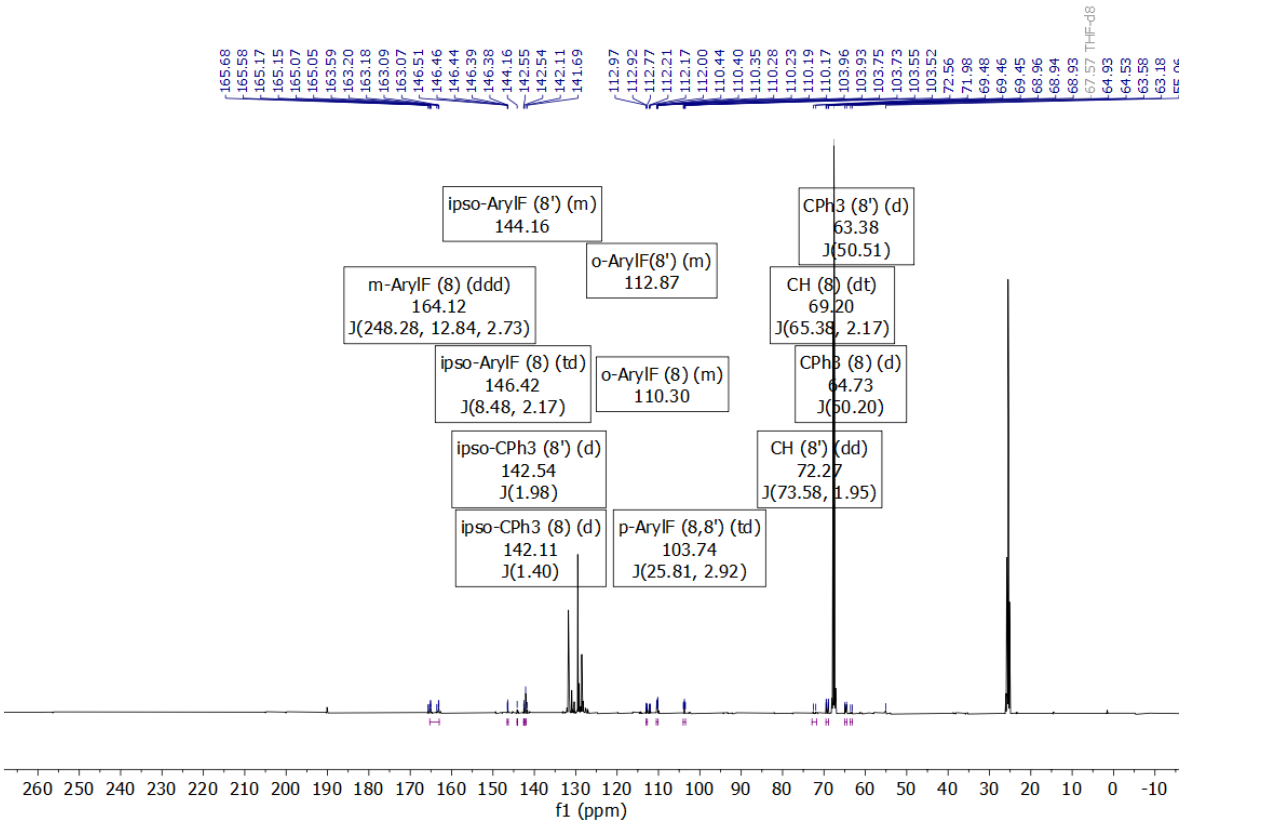


Figure S 35: ^{13}C{^{1}H}-NMR spectrum in THF-d_8.

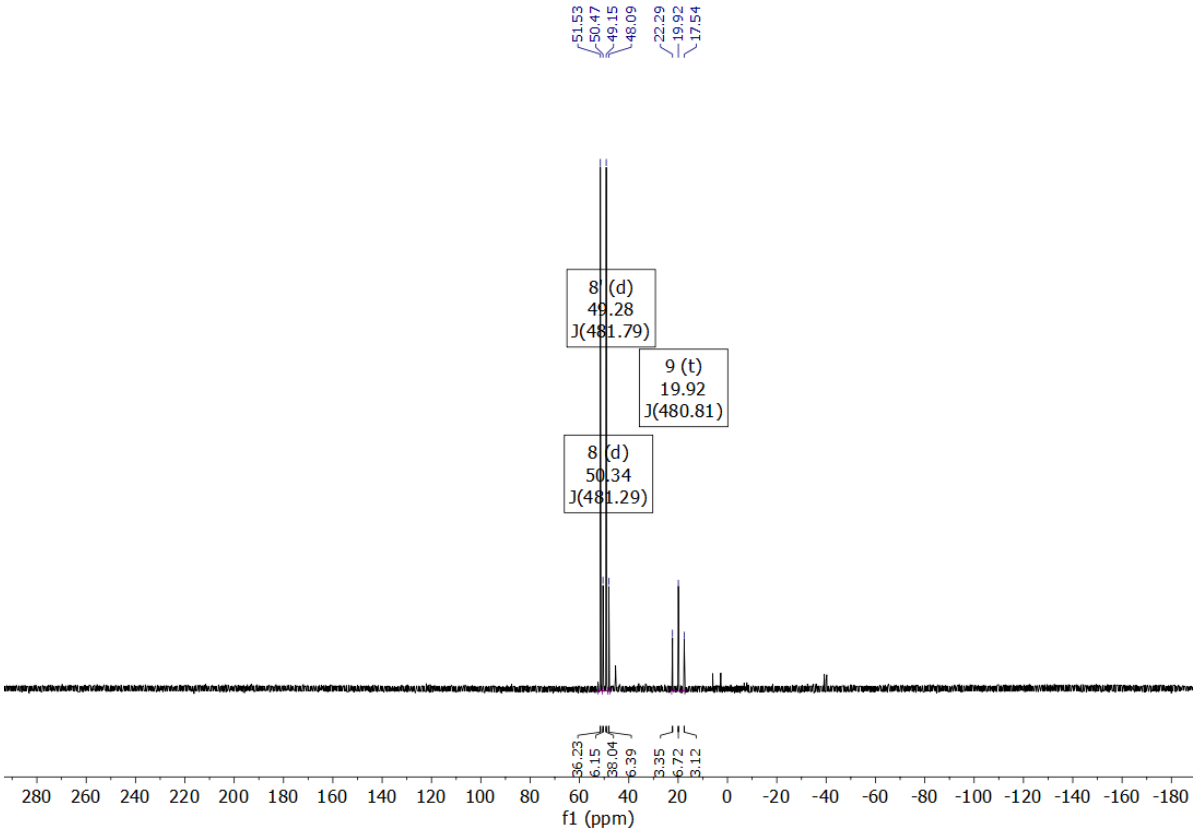


Figure S 36: ^{31}P-NMR spectrum in THF-d_8.

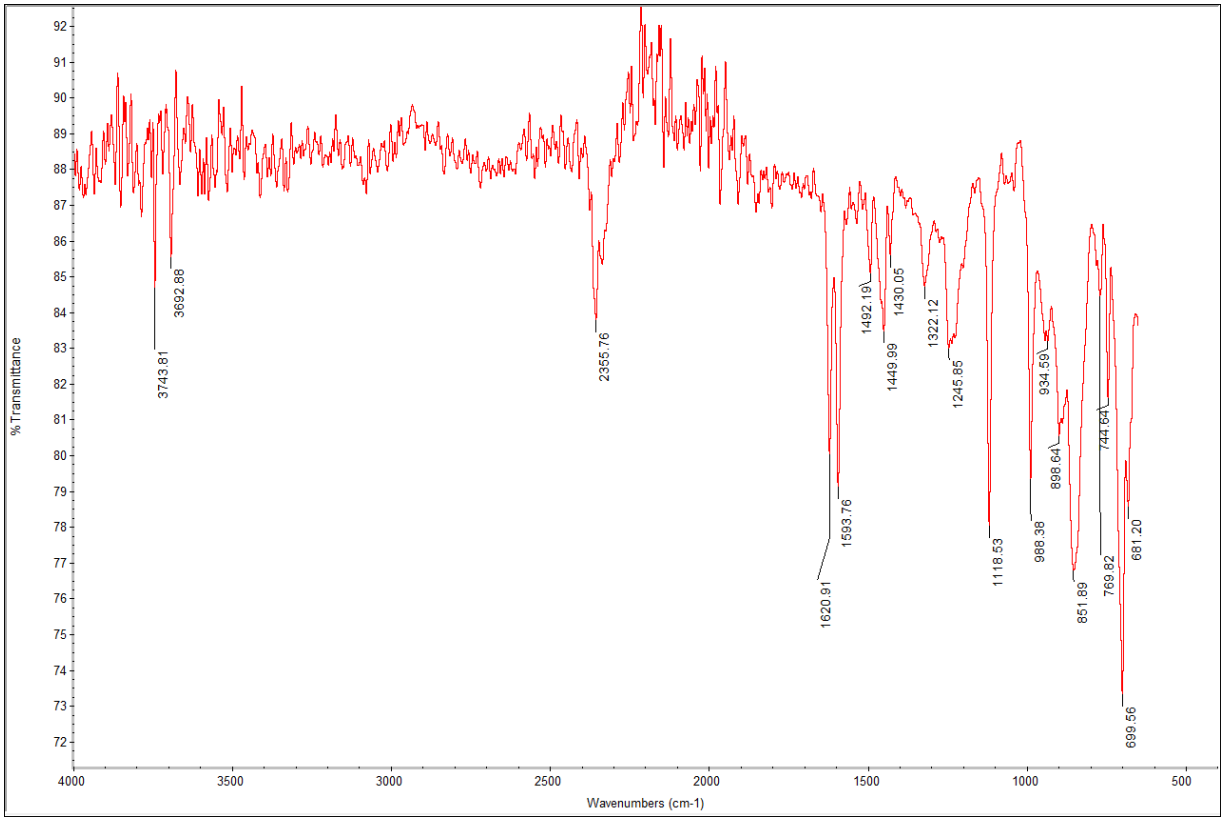


Figure S 37: IR spectrum of the product mixture **8** & **9**.

Molecular structure of 8

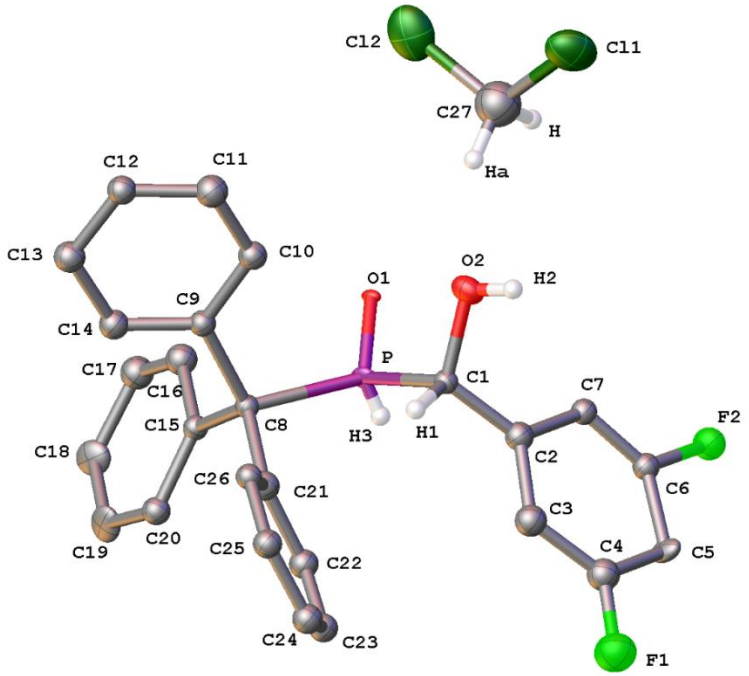


Figure S 38: Molecular structure of **8** of the (1*R*,2*S*)-diastereomer with cocrystalized CH_2Cl_2 in the single crystal (50% probability level). The structural not relevant hydrogen atoms are omitted for clarity.

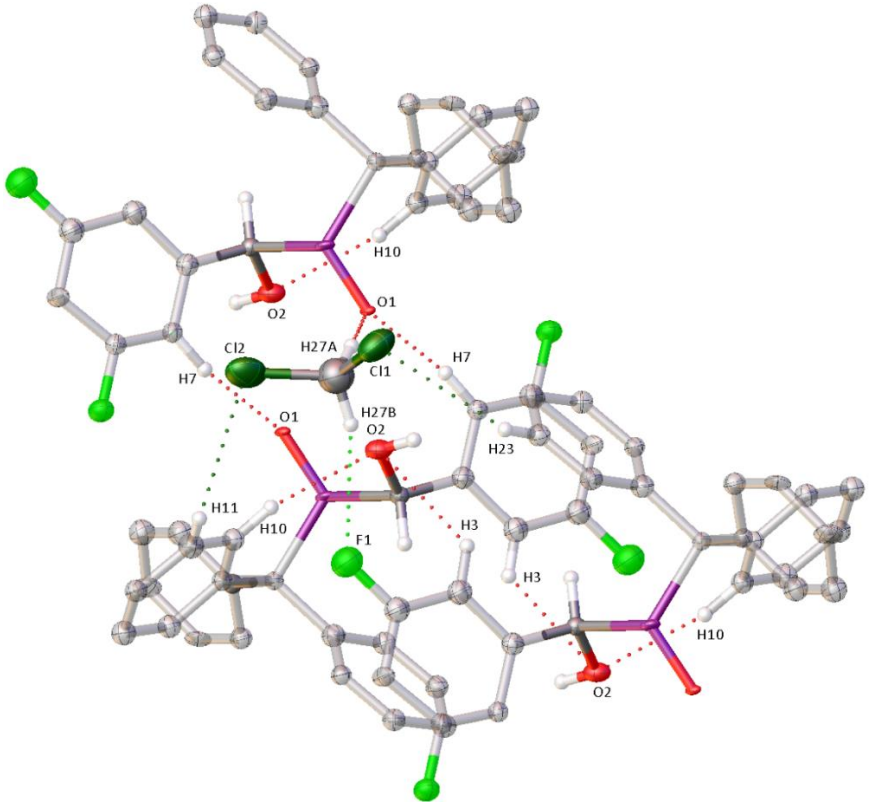


Figure S 39: Secondary structural motif of the molecular structure of three molecules of **8** with cocrystalized CH_2Cl_2 in the single crystal (50% probability level). The structural not relevant hydrogen atoms are omitted for clarity.

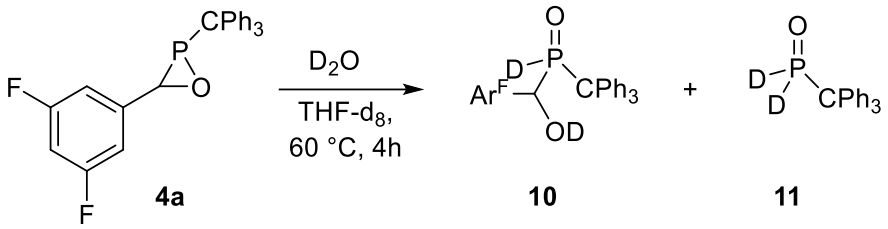
Bond lengths in Å

Cl1	C27	1.82(2)		C9	C10	1.42(2)
Cl2	C27	1.74(2)		C9	C14	1.34(2)
P	O1	1.491(8)		C10	C11	1.34(2)
P	C1	1.892(14)		C11	C12	1.36(2)
P	C8	1.891(13)		C12	C13	1.41(2)
F1	C4	1.336(19)		C13	C14	1.41(2)
F2	C6	1.401(15)		C15	C16	1.42(2)
O2	C1	1.464(17)		C15	C20	1.40(2)
C1	C2	1.42(2)		C16	C17	1.31(2)
C2	C3	1.43(2)		C17	C18	1.47(2)
C2	C7	1.421(19)		C18	C19	1.41(2)
C3	C4	1.41(2)		C19	C20	1.40(2)
C4	C5	1.41(2)		C21	C22	1.39(2)
C5	C6	1.44(2)		C21	C26	1.44(2)
C6	C7	1.29(2)		C22	C23	1.32(2)
C8	C9	1.598(19)		C23	C24	1.43(2)
C8	C15	1.515(19)		C24	C25	1.35(2)
C8	C21	1.557(19)		C25	C26	1.34(2)

Bond angles in °

Cl2	C27	Cl1	110.0(13)		C10	C9	C8	122.9(12)
O1	P	C1	113.8(5)		C14	C9	C8	116.3(13)
O1	P	C8	115.0(5)		C14	C9	C10	120.6(14)
C8	P	C1	112.8(6)		C11	C10	C9	120.3(14)
O2	C1	P	107.4(9)		C10	C11	C12	119.9(15)
C2	C1	P	110.2(10)		C11	C12	C13	121.4(15)
C2	C1	O2	115.6(11)		C14	C13	C12	117.6(14)
C1	C2	C3	120.0(12)		C9	C14	C13	120.0(15)
C7	C2	C1	123.3(13)		C16	C15	C8	118.8(13)
C7	C2	C3	116.7(13)		C20	C15	C8	121.6(12)
C4	C3	C2	119.8(13)		C20	C15	C16	119.5(14)
F1	C4	C3	120.0(13)		C17	C16	C15	122.3(16)
F1	C4	C5	117.0(13)		C16	C17	C18	121.7(15)
C5	C4	C3	123.0(14)		C19	C18	C17	114.9(16)
C4	C5	C6	112.6(12)		C20	C19	C18	123.6(16)
F2	C6	C5	111.7(11)		C15	C20	C19	117.9(14)
C7	C6	F2	121.0(12)		C22	C21	C8	121.5(13)
C7	C6	C5	127.1(12)		C22	C21	C26	117.8(13)
C6	C7	C2	120.4(13)		C26	C21	C8	120.4(13)
C9	C8	P	110.1(9)		C23	C22	C21	120.0(14)
C15	C8	P	106.8(8)		C22	C23	C24	122.2(14)
C15	C8	C9	109.5(11)		C25	C24	C23	117.7(14)
C15	C8	C21	115.9(12)		C26	C25	C24	121.8(14)
C21	C8	P	101.3(9)		C25	C26	C21	120.3(13)
C21	C8	C9	112.8(11)					

1.2.8 Product mixture of {1-deuterooxide-1-(3,5-difluorphenyl)methyl}(1-triphenylmethyl)-phosphaneoxide 10 (two diastereomers) and 1,1-dideuterio-1-triphenylmethyl-phosphaneoxide 11 in a ratio of 1.00 : 0.26 : 0.27



15.2 mg of **4a** (0.032 mmol, 1.00 eq) were dissolved in 0.5 mL THF-d_8 in a Young NMR tube. To the solution three drops of D_2O were added and the solution was heated for 4h at 60 °C. The solution was transferred to a Schlenk tube and the solvent was removed under reduced pressure (1 x 10^{-2} mbar). The colorless residue was washed three times with 0.3 mL of *n*-pentane and a product mixture of **10** (two diastereomers) and **11** in a ratio of 1.00 : 0.26 : 0.27 was obtained as a colorless powder. The following analytical data refers to the product mixture.

IR (ATR Diamond): / cm^{-1} = 2165 (w, ν(P-D)), 1620 (m, ν(C=C)), 1594 (m, ν(C=C)), 1120 (m, ν(C=C)), 844 (m, $\delta(C^{ArF}\text{-}H)_{oop}$)), 800 (m, $\delta(C^{Ar}\text{-}H)_{oop}$)), 742 (m, $\delta(C^{Ar}\text{-}H)_{oop}$)), 700 (s, $\delta(C^{Ar}\text{-}H)_{oop}$)).

10: Isomer 1 (major, 80%): ^{1}H-NMR (500.04 MHz, 298.0 K, THF-d_8): δ /ppm = 2.87 (s, 1H, OH), 4.30 (s, 1H, CH), 6.58 (m, *o*-Aryl^F), 6.80 (m, *p*- Aryl^F), 7.23 – 7.55 (m, 15H, CPh_3).

^{31}P-NMR (121.51 MHz, 298.0 K, THF-d_8): δ /ppm = 50.2 (t*, $^1J_{P,D}$ = 73.7 Hz).

10‘: Isomer 2 (minor, 20%): ^{1}H-NMR (500.04 MHz, 298.0 K, THF-d_8): δ /ppm = 2.91 (s, 1H, OH), 4.61 (s, 1H, CH), 6.58 (m, *o*- Aryl^F), 6.72(m, *p*- Aryl^F), 7.23 – 7.55 (m, 15H, CPh_3).

^{31}P-NMR (121.51 MHz, 298.0 K, THF-d_8): δ /ppm = 49.5 (t*, $^1J_{P,D}$ = 74.0 Hz).

11: ^{1}H-NMR (500.04 MHz, 298.0 K, THF-d_8): δ /ppm = 7.23 – 7.55 (m, 15H, CPh_3).

^{31}P-NMR (121.51 MHz, 298.0 K, THF-d_8): δ /ppm = 19.5 (quint*, $^1J_{P,D}$ = 74.4 Hz).

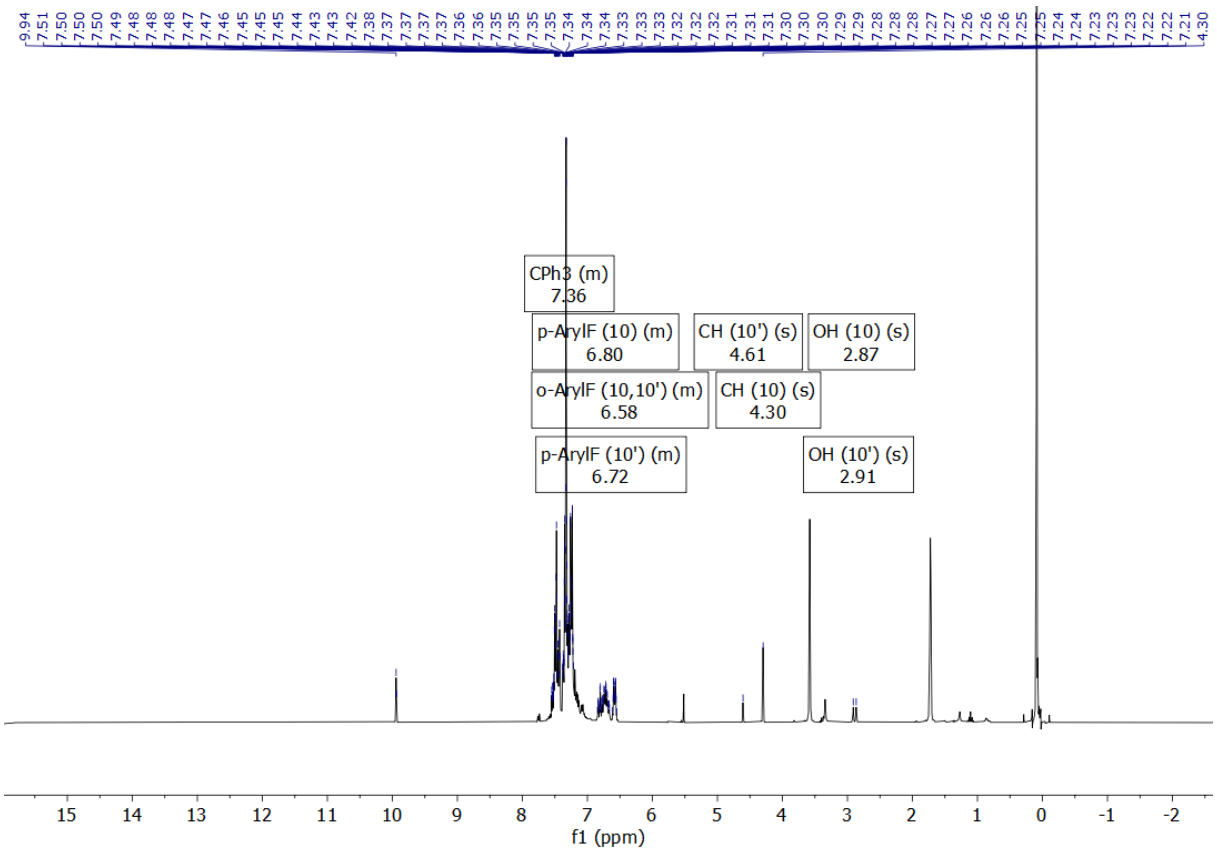


Figure S 40: ^{1}H-NMR spectrum in THF-d_8.

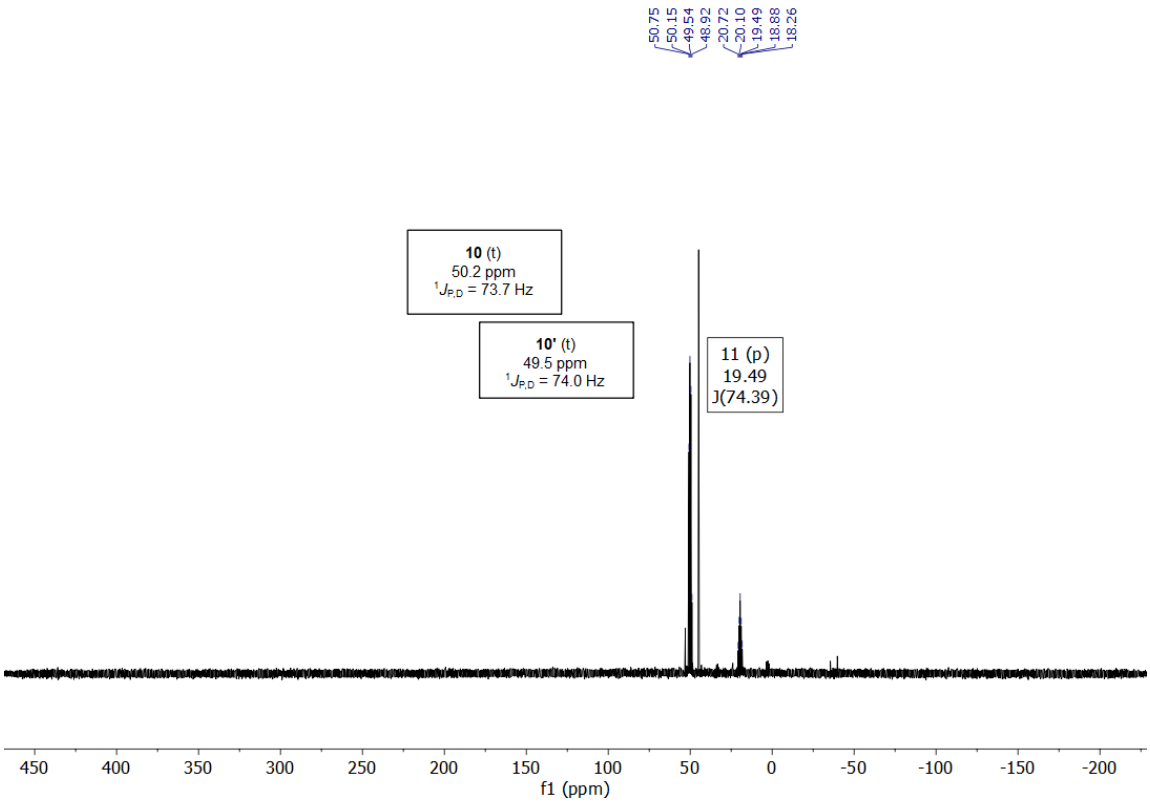


Figure S 41: ^{31}P{^{1}H}-NMR spectrum in THF-d_8.

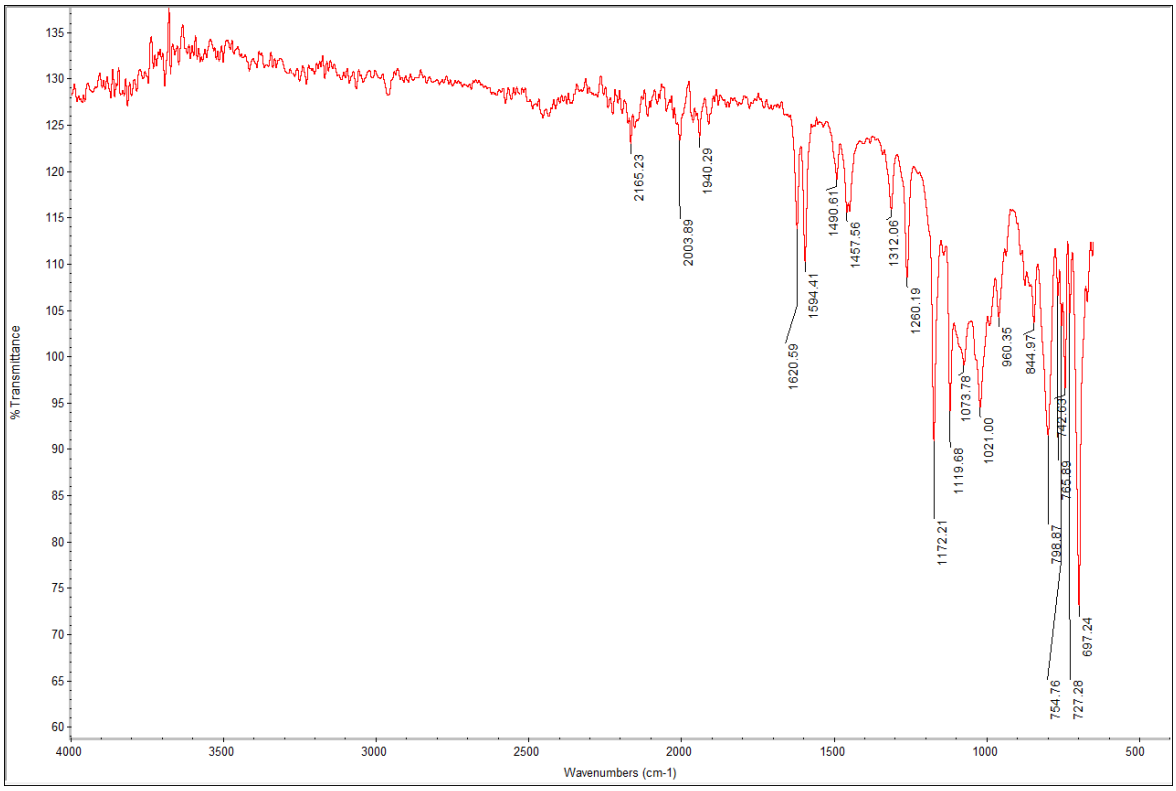


Figure S 42: IR spectrum of the product mixture **10** & **11**.

Molecular structure of 10

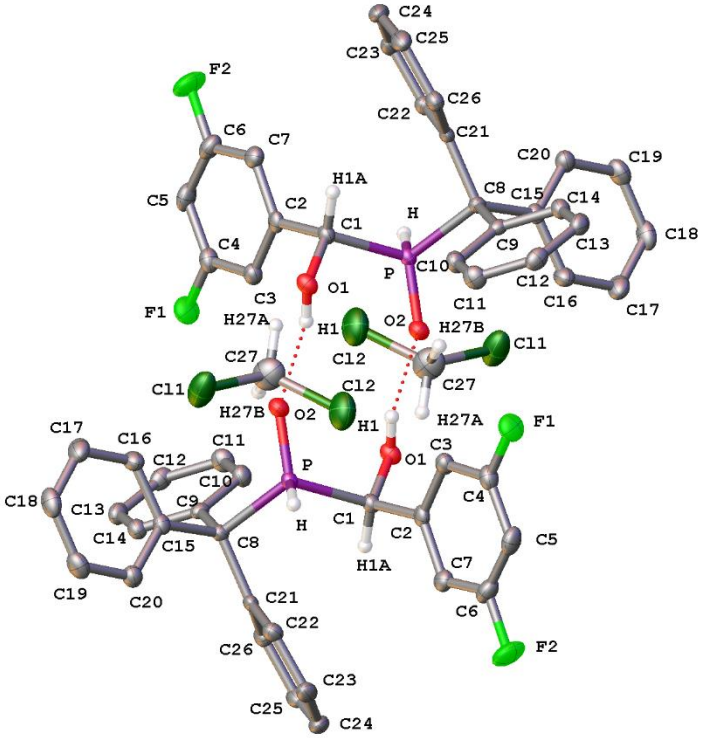


Figure S 43: D-bridging dimer of the molecular structure of **10** (enantiomers 1*R*,2*S* and 1*S*,2*R*)-diastereomer with cocrystalized CH_2Cl_2 in the single crystal (50% probability level). The structural not relevant hydrogen atoms are omitted for clarity.

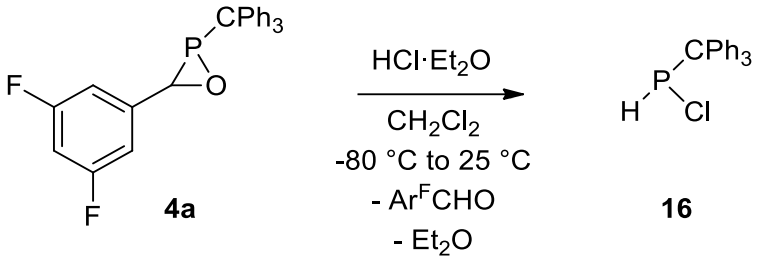
Bond lengths in Å

Cl1	C27	1.745(2)		C9	C10	1.391(2)
Cl2	C27	1.756(3)		C9	C14	1.396(2)
P	O1	1.4895(12)		C10	C11	1.386(3)
P	C1	1.8774(18)		C11	C12	1.380(3)
P	C8	1.8746(17)		C12	C13	1.385(3)
F1	C4	1.352(2)		C13	C14	1.388(3)
F2	C6	1.359(2)		C15	C16	1.399(2)
O2	C1	1.413(2)		C15	C20	1.395(2)
C1	C2	1.514(2)		C16	C17	1.387(3)
C2	C3	1.393(3)		C17	C18	1.386(3)
C2	C7	1.393(2)		C18	C19	1.382(3)
C3	C4	1.375(3)		C19	C20	1.389(3)
C4	C5	1.382(3)		C21	C22	1.400(2)
C5	C6	1.373(3)		C21	C26	1.396(3)
C6	C7	1.377(3)		C22	C23	1.389(3)
C8	C9	1.534(2)		C23	C24	1.382(3)
C8	C15	1.537(2)		C24	C25	1.382(3)
C8	C21	1.541(2)		C25	C26	1.389(3)

Bond angles in °

Cl1	C27	Cl2	111.99(12)		C10	C9	C8	122.75(15)
O1	P	C1	111.08(7)		C10	C9	C14	118.40(16)
O1	P	C8	116.34(7)		C14	C9	C8	118.77(15)
C8	P	C1	111.41(8)		C11	C10	C9	120.77(16)
O2	C1	P	109.91(11)		C12	C11	C10	120.34(17)
O2	C1	C2	113.77(14)		C11	C12	C13	119.72(17)
C2	C1	P	109.32(12)		C12	C13	C14	120.08(17)
C3	C2	C1	120.00(15)		C13	C14	C9	120.68(17)
C7	C2	C1	119.52(16)		C16	C15	C8	118.56(15)
C7	C2	C3	120.47(16)		C20	C15	C8	123.48(15)
C4	C3	C2	118.17(16)		C20	C15	C16	117.83(17)
F1	C4	C3	119.05(16)		C17	C16	C15	121.17(17)
F1	C4	C5	117.54(16)		C18	C17	C16	120.26(18)
C3	C4	C5	123.42(18)		C19	C18	C17	119.18(19)
C6	C5	C4	116.21(17)		C18	C19	C20	120.80(18)
F2	C6	C5	117.79(17)		C19	C20	C15	120.74(17)
F2	C6	C7	118.52(18)		C22	C21	C8	120.02(16)
C5	C6	C7	123.69(17)		C26	C21	C8	121.56(15)
C6	C7	C2	118.04(18)		C26	C21	C22	118.19(15)
C9	C8	P	111.70(11)		C23	C22	C21	120.69(18)
C9	C8	C15	109.71(13)		C24	C23	C22	120.30(18)
C9	C8	C21	111.51(14)		C23	C24	C25	119.71(17)
C15	C8	P	105.89(11)		C24	C25	C26	120.32(19)
C15	C8	C21	114.95(14)		C25	C26	C21	120.78(18)
C21	C8	P	102.78(11)					

1.2.9 Synthesis of chloro(triphenylmethyl)phosphane 16



22.1 mg of **4a** (0.053 mmol, 1.00 eq) and 0.026 mL HCl·Et_2O (0.053 mmol, 1.00 eq, 2M in Et_2O) were each dissolved in 3 mL of DCM and cooled to -80 °C. The oxaphosphirane solution was transferred with a transfer cannula to the HCl-solution and the solution was warmed up to room temperature. After stirring for 22h at room temperature the solvent was removed under reduced pressure (1 x 10^{-2} mbar) and a colorless residue was obtained. The residue was washed three times with 0.5 mL of *n*-pentane at -30 °C. After drying under reduced pressure (1 x 10^{-2} mbar) the product was obtained as a colorless powder.

Yield: 12.8 mg (0.041 mmol, 78 %) (Lit.: 11.1 g (65.9 %)).

Melting point: 122 °C.

IR (ATR diamond): / cm^{-1} = 2310 (w, ν(P-H)).

^{1}H-NMR (500.04 MHz, 298.0 K, $CDCl_3$): δ /ppm = 5.70 (d, 1H, $^1J_{P,H}$ = 189.9 Hz, PH), 7.22 – 7.25 (m, 6H, *o*-CPh_3), 7.27 – 7.31 (m, 3H, *p*-CPh_3), 7.31 – 7.36 (m, 6H, *m*-CPh_3).

^{13}C{^{1}H}-NMR (125.75 MHz, 298.0 K, $CDCl_3$): δ /ppm = 60.7 (d, $^1J_{P,C}$ = 34.7 Hz, $\underline{C}Ph_3$), 127.3 (d, $^3J_{P,C}$ = 1.6 Hz, *o*-CPh_3), 128.6 (s, *p*-CPh_3), 129.8 (d, $^4J_{P,C}$ = 8.2 Hz, *m*-CPh_3), 142.8 (d, $^2J_{P,C}$ = 10.1 Hz, *ipso*-CPh_3).

^{31}P-NMR (202.44 MHz, 298.0 K, $CDCl_3$): δ /ppm = 44.9 (d, $^1J_{P,H}$ = 189.9 Hz).

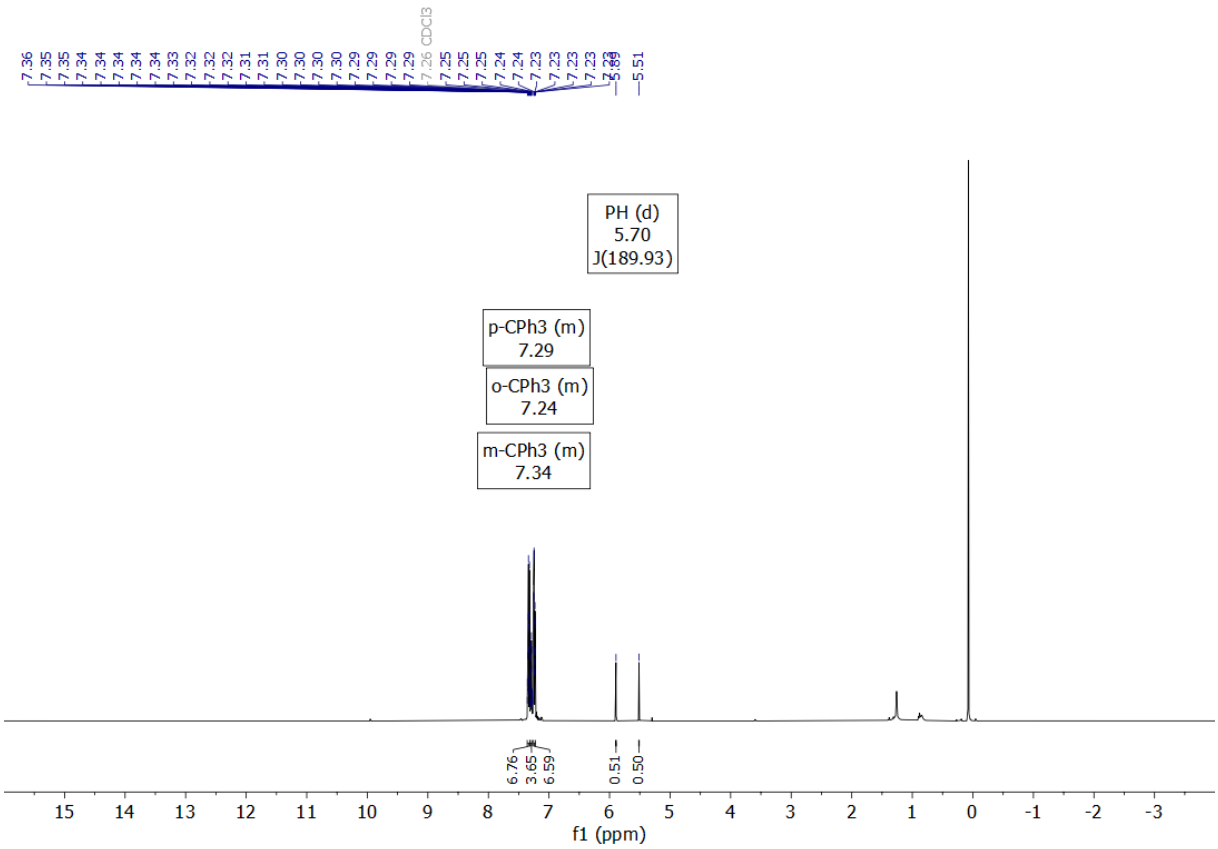


Figure S 44: ^{1}H-NMR spectrum in $CDCl_3$.

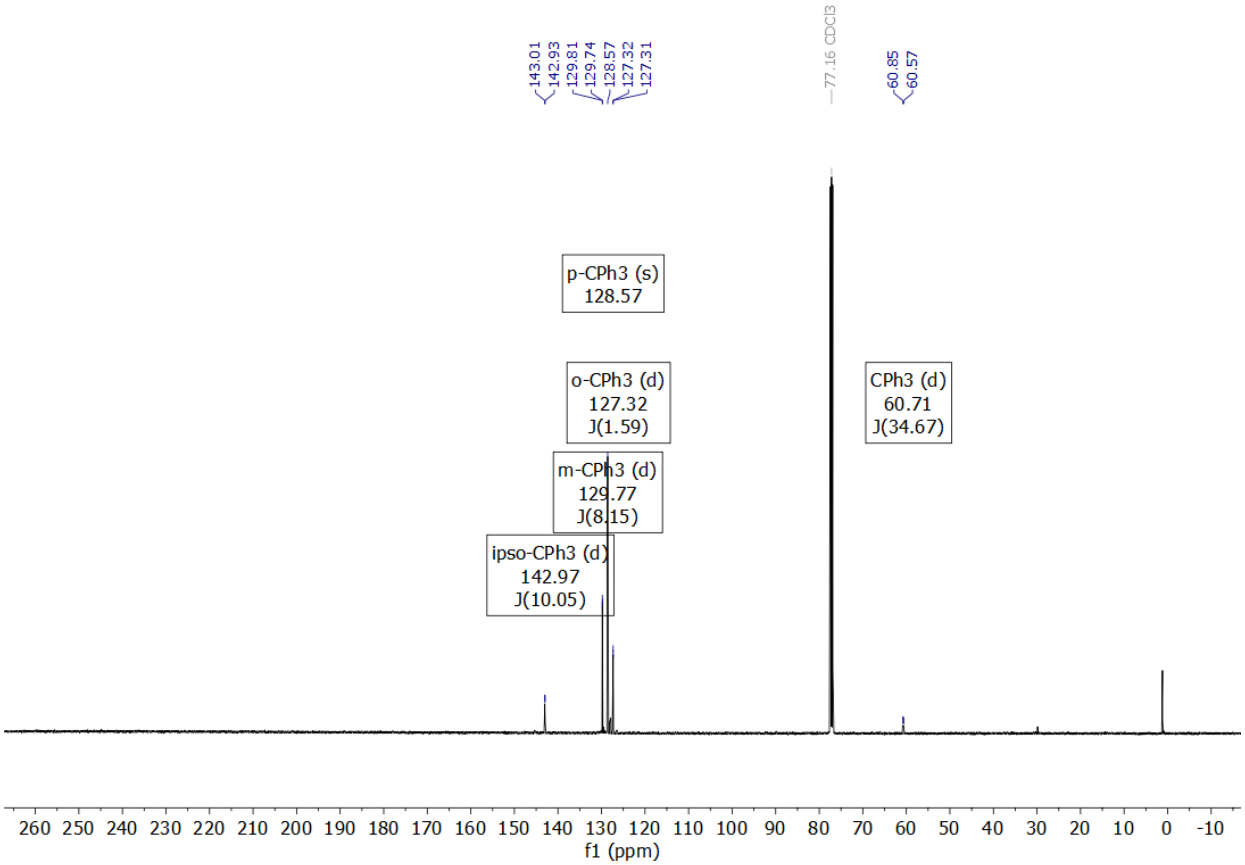


Figure S 45: $^{13}C\{^{1}H\}$-NMR spectrum in $CDCl_3$.

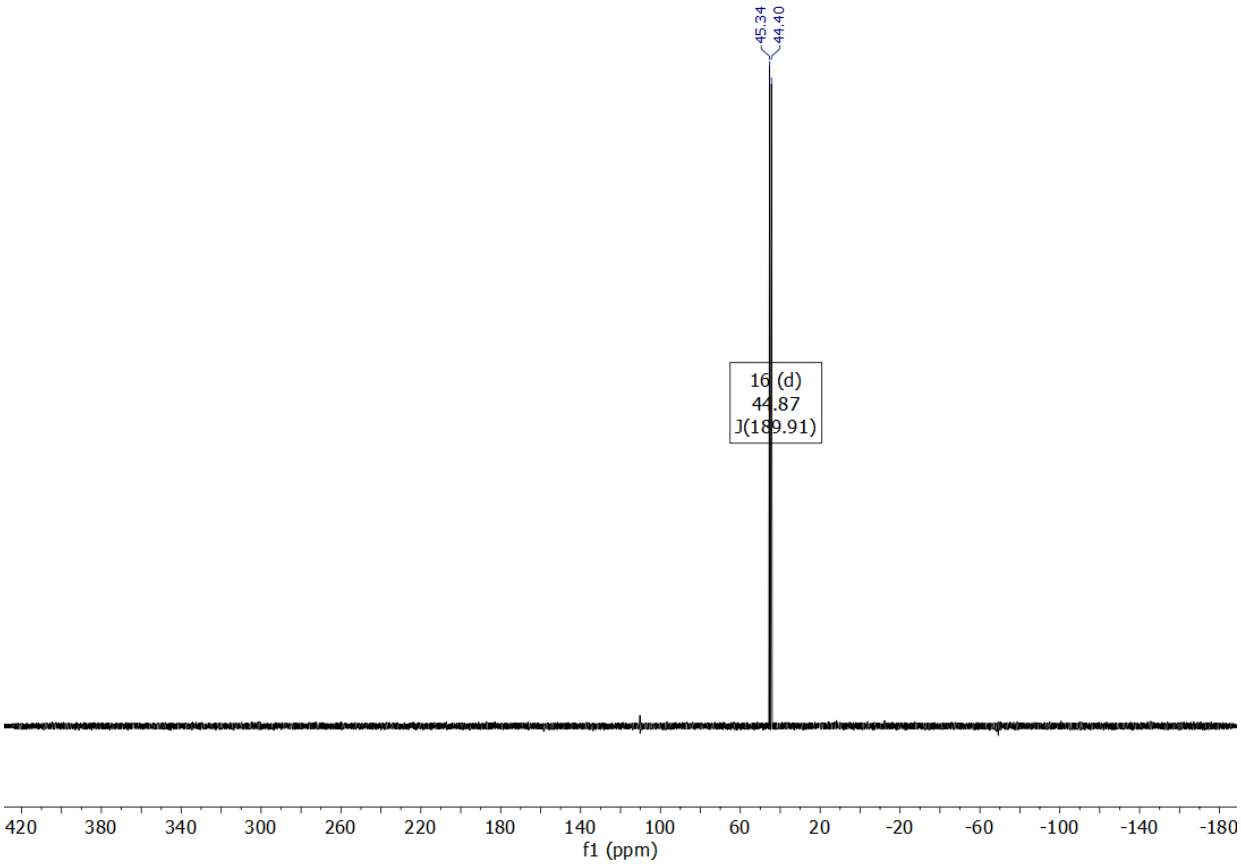
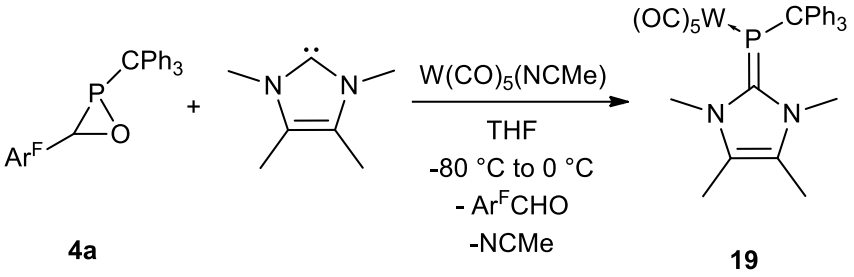


Figure S 46: ^{31}P-NMR spectrum in $CDCl_3$.

Figure S 47: IR spectrum of **16**.

1.2.10 Synthesis of compound 19



0.192 g (0.46 mmol) of **4a** was dissolved in a minimum volume of THF in a Schlenk tube. To this, 0.056 g (0.46 mmol) of NHC carbene (IMe4) in minimum volume of THF were slowly added at -80 °C. After ten minutes of stirring at -80 °C, 0.168 g (0.46 mmol) of $W(CO)_5(NCMe)$ in THF, which was precooled to -80 °C, was slowly added to the solution. After ten minutes of stirring at -80 °C, the solution was warmed up to 0 °C and the solvent was removed under reduced pressure and a yellow-red oily residue was obtained. The residue was redissolved in minimum volume of diethylether and purified *via* column chromatography (Ø = 3 cm, h = 5 cm, 25 °C, Al_2O_3, eluent Et_2O). The yellow fractions obtained after column chromatography were concentrated to a minimum volume and layered with *n*-pentane and stored at 5 °C. Dark orange crystals which were suitable for X-ray crystallography were obtained after two weeks.

^{1}H-NMR (300.13 MHz, 298.0 K, CD_2Cl_2): δ /ppm = 7.36-7.21 (m, 15H, CPh_3), 3.21 (s, 6H, NCH_3), 2.16 (s, 6H, CCH_3).

$^{31}P\{^1H\}$-NMR (121.51 MHz, 298.0 K, CD_2Cl_2): δ /ppm = -37.7 (s_{sat}, $^1J_{P\text{-}W}$ = 114.1 Hz).

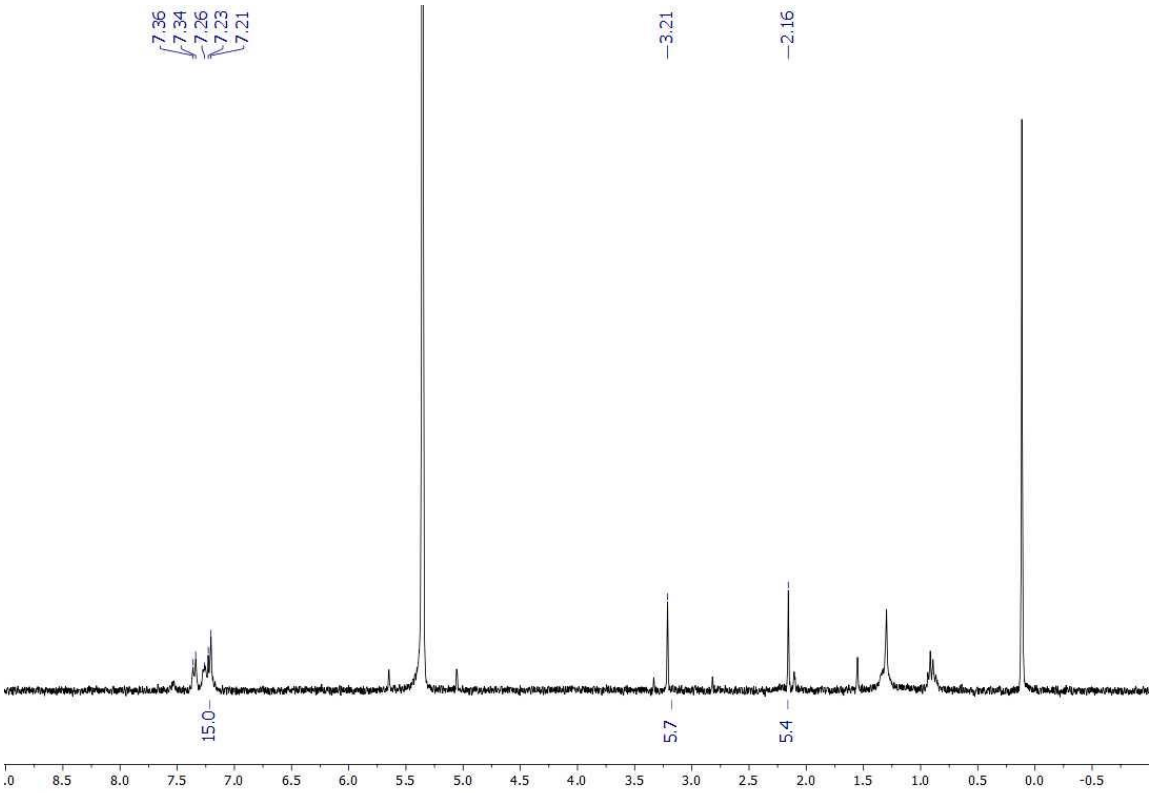


Figure S 48: ^{1}H-NMR spectrum in CD_2Cl_2.

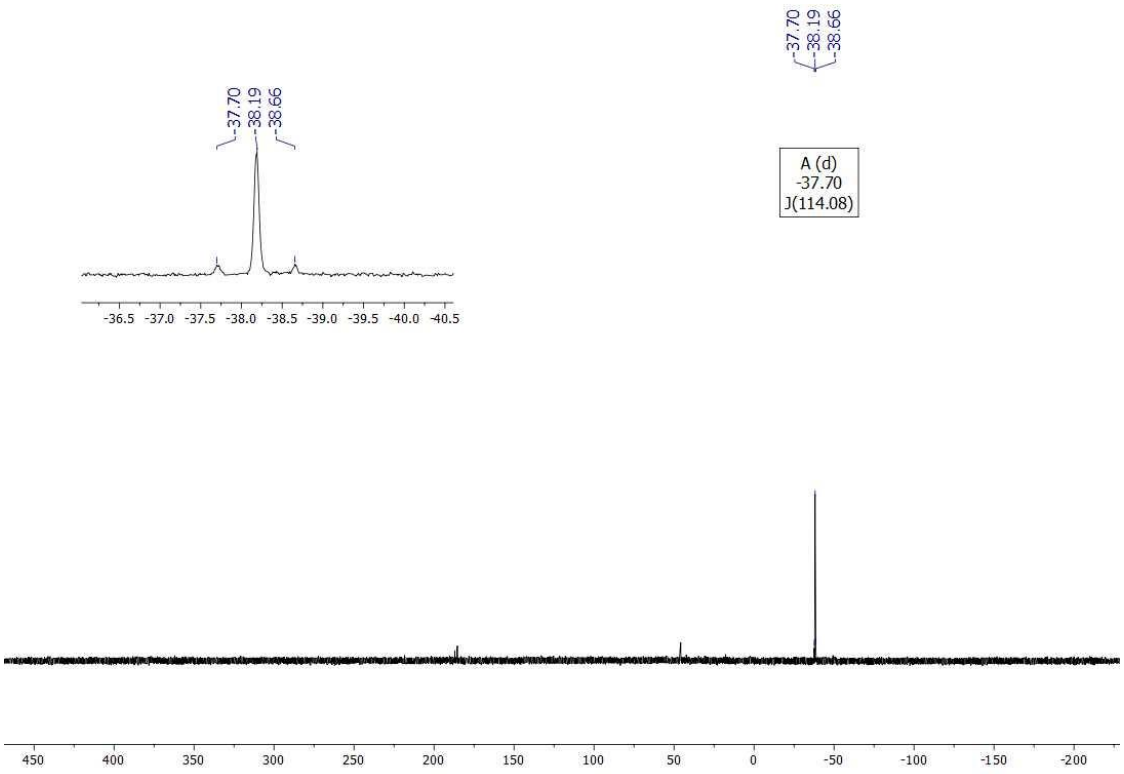


Figure S 49: $^{31}P\{^{1}H\}$-NMR spectrum in CD_2Cl_2.

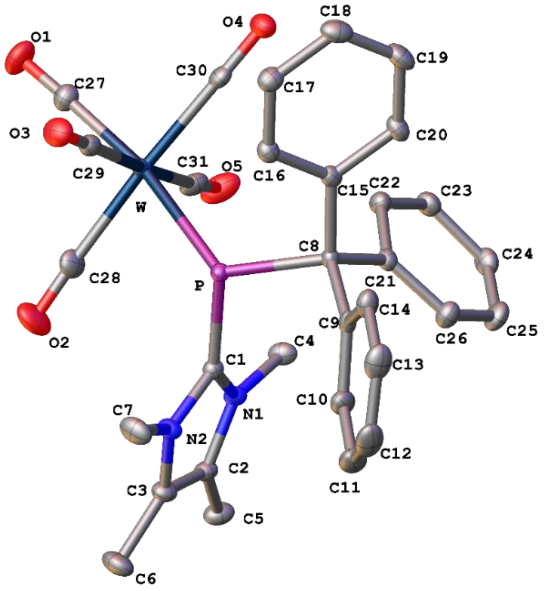


Figure S 50: Molecular structure of **19** in the single crystal (50% probability level). The hydrogen atoms are omitted for clarity.

Bond lengths in Å

W	P	2.6146(5)		C8	C9	1.538(2)
W	C27	1.983(2)		C8	C15	1.548(2)

W	C28	2.033(2)		C8	C21	1.533(2)
W	C29	2.047(2)		C9	C10	1.400(3)
W	C30	2.0468(19)		C9	C14	1.396(3)
W	C31	2.041(2)		C10	C11	1.391(3)
P	C1	1.8502(18)		C11	C12	1.383(4)
P	C8	1.9549(17)		C12	C13	1.381(3)
O1	C27	1.154(3)		C13	C14	1.394(3)
O2	C28	1.143(3)		C15	C16	1.399(3)
O3	C29	1.141(3)		C15	C20	1.397(2)
O4	C30	1.143(2)		C16	C17	1.390(3)
O5	C31	1.144(3)		C17	C18	1.388(3)
N1	C1	1.353(2)		C18	C19	1.385(3)
N1	C2	1.387(2)		C19	C20	1.392(3)
N1	C4	1.456(2)		C21	C22	1.402(3)
N2	C1	1.362(2)		C21	C26	1.391(3)
N2	C3	1.384(2)		C22	C23	1.391(3)
N2	C7	1.462(2)		C23	C24	1.391(3)
C2	C3	1.353(3)		C24	C25	1.380(3)
C2	C5	1.489(3)		C25	C26	1.399(3)
C3	C6	1.491(3)				

Bond angles in °

C27	W	P	168.23(6)		C9	C8	C15	109.49(14)
C27	W	C28	92.23(8)		C15	C8	P	103.56(11)
C27	W	C29	88.81(8)		C21	C8	P	113.89(12)
C27	W	C30	91.43(8)		C21	C8	C9	113.13(14)
C27	W	C31	87.73(8)		C21	C8	C15	110.45(14)
C28	W	P	79.69(6)		C10	C9	C8	121.28(17)
C28	W	C29	89.44(8)		C14	C9	C8	121.70(16)
C28	W	C30	176.33(7)		C14	C9	C10	117.01(17)
C28	W	C31	92.39(8)		C11	C10	C9	121.4(2)
C29	W	P	82.60(5)		C12	C11	C10	120.4(2)
C30	W	P	96.71(5)		C13	C12	C11	119.2(2)
C30	W	C29	90.82(7)		C12	C13	C14	120.4(2)
C31	W	P	101.06(5)		C13	C14	C9	121.41(19)
C31	W	C29	176.15(7)		C16	C15	C8	121.25(15)
C31	W	C30	87.58(8)		C20	C15	C8	120.88(16)
C1	P	W	108.98(6)		C20	C15	C16	117.65(17)
C1	P	C8	106.50(8)		C17	C16	C15	121.33(17)
C8	P	W	122.37(5)		C18	C17	C16	120.38(18)
C1	N1	C2	110.92(15)		C19	C18	C17	118.90(18)
C1	N1	C4	126.41(15)		C18	C19	C20	120.85(18)
C2	N1	C4	122.67(15)		C19	C20	C15	120.84(18)
C1	N2	C3	110.74(15)		C22	C21	C8	119.46(16)
C1	N2	C7	126.34(15)		C26	C21	C8	123.05(16)
C3	N2	C7	122.85(16)		C26	C21	C22	117.49(17)
N1	C1	P	133.43(13)		C23	C22	C21	121.46(17)
N1	C1	N2	104.85(15)		C22	C23	C24	120.10(18)
N2	C1	P	121.08(13)		C25	C24	C23	119.10(18)

N1	C2	C5	122.33(17)		C24	C25	C26	120.70(18)
C3	C2	N1	106.73(16)		C21	C26	C25	121.03(18)
C3	C2	C5	130.91(17)		O1	C27	W	178.44(18)
N2	C3	C6	122.68(17)		O2	C28	W	176.10(17)
C2	C3	N2	106.77(16)		O3	C29	W	177.93(18)
C2	C3	C6	130.53(18)		O4	C30	W	177.74(16)
C9	C8	P	105.78(11)		O5	C31	W	175.48(17)

1.3 Computational Details

DFT calculations were performed with the ORCA electronic structure program package (version 4.2.1).[1] All geometry optimizations were run in redundant internal coordinates with tight convergence criteria and using Grimme's dispersion-corrected composite PBEh-3c level.[2] Solvent (THF, CH_2Cl_2 or toluene) effects were taken into consideration with the CPCM solvation method[3] as implemented in ORCA. Harmonic frequency calculations verified the nature of ground 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, reported final energies were obtained by means of single-point (SP) calculations using the double-hybrid-meta-GGA functional PWPB95[4] using the RI-JK[5] approximation for Coulomb and exchange integrals, Grimme's semiempirical atom-pair-wise London dispersion correction D3[6] and the higher quality def2-QZVPP basis set,[7] and include the Gibbs free energy (G) correction term at the optimization level.

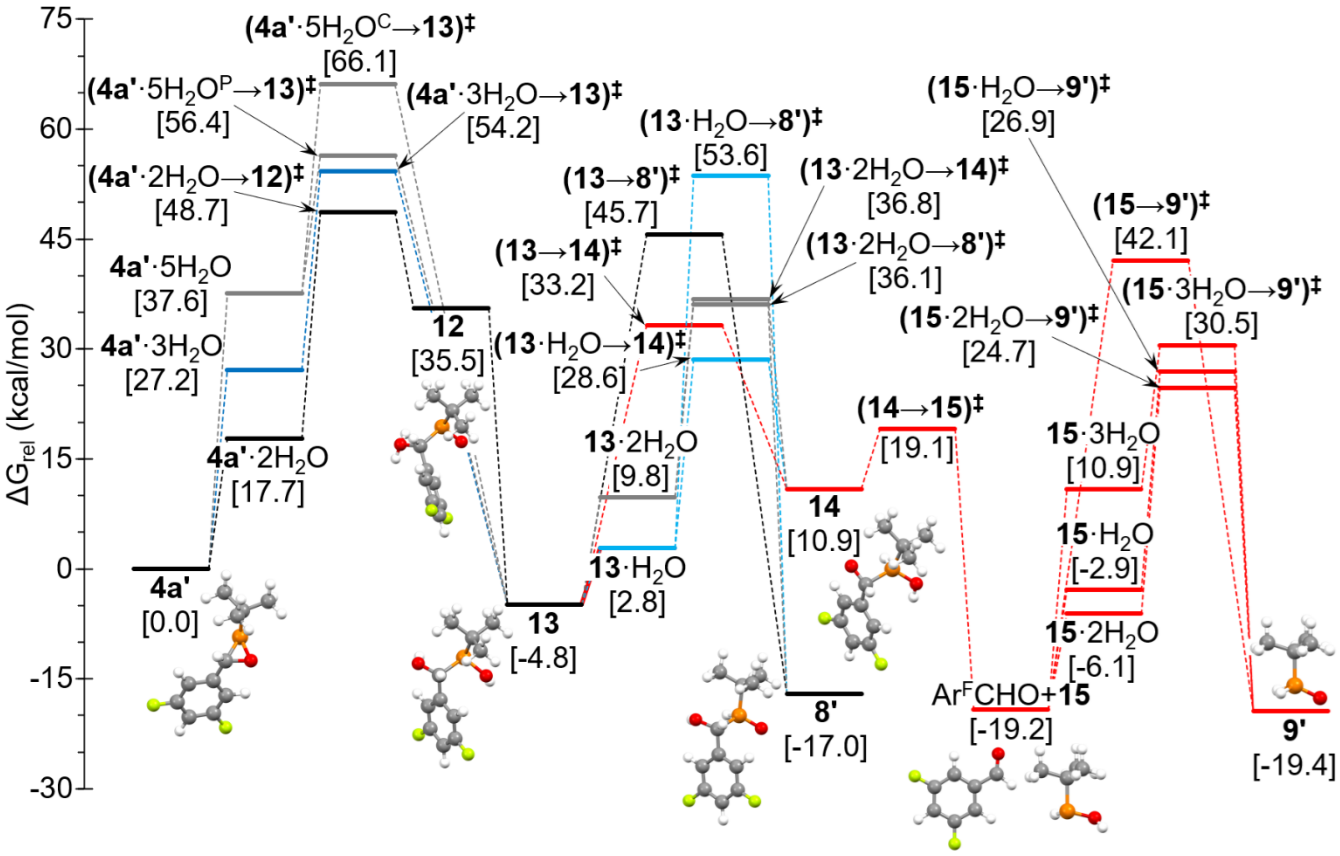


Figure S 51: Computed ($CPCM_{THF}$/PWPB95-D3(def2-QZVPP//$CPCM_{THF}$/PBEh-3c) full Gibbs energy profile for the hydrolysis of model **4a'**.

1.4 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 the $CPCM_{solvent}$/PBEh-3c, whereas electronic energies (in hartrees) were quoted at the $CPCM_{solvent}$/PWPB95-D4/def2-QZVPP level. Imaginary frequencies were obtained upon frequency calculation at the optimization level.

H_2O (THF):

E = -76.4358707077 au
ZPE = 0.02192289 au
G_{corr} = 0.00428347 au

O-0.072978-0.096030	0.000000	H-0.3177480.831755	0.000000
H0.886469-0.083389	0.000000		

TOB (toluene):

E = -2219.720218136100 au
ZPE = 0.04919847 au
G_{corr} = 0.01162888 au

C-0.071143-0.066113	-0.000504	O-0.659489-1.109535	-0.001325
C1.466218-0.066196	0.000912	O2.054452-1.109677	0.003813
C2.143743 1.238024	-0.000403	Cl3.8410011.206126	0.000425
C1.433801 2.380924	-0.001301	Cl2.2230763.884082	-0.002703
C-0.0384582.381001	-0.001124	Cl-0.8275853.884230	-0.001408
C-0.7485211.238178	-0.000708	Cl-2.4457841.206460	-0.001377

Me_2O (CH_2Cl_2):

E = -154.9949154134au
ZPE = 0.05655405 au
G_{corr} = 0.08190337 au

O-0.460105-1.189277	-0.000408	C0.941749-1.223849	0.000548
C-0.9606610.120633	-0.000596	H1.367297-0.737554	0.887459
H-0.6435970.684900	-0.886746	H1.255345-2.267436	-0.001131
H-2.0490730.067915	0.000162	H1.368450-0.734523	-0.884114
H-0.6425460.685409	0.884827		

$Me_2O{\cdot}HCl$ (CH_2Cl_2):

E = -615.7945124494 au
ZPE = 0.06046991 au
G_{corr} = 0.09110727 au

Cl3.525237-0.710894	-2.125031	H5.554363-2.639658	1.566679
H3.705427-1.295262	-0.920996	C3.256471-3.270683	0.388178
O3.960707-2.039732	0.387485	H2.206115-3.050095	0.210250
C5.355900-2.194033	0.589587	H3.620476-3.941735	-0.394999
H5.806522-2.822237	-0.183977	H3.356608-3.768755	1.354970
H5.805887-1.204191	0.553457		

NHC^{Me2} (toluene): E = -304.724784572 au
ZPE = 0.13063368 au
G_{corr} = 0.09987190 au

C	-0.005759	-0.001062	-0.004658	H	-2.062479	-0.002235	1.459326
N	-0.007406	-0.000071	1.349445	C	1.836679	-0.000120	-1.634891
C	1.261509	0.000815	1.887459	H	2.448723	-0.882762	-1.820075
C	2.109433	0.000537	0.839126	H	0.996015	-0.005137	-2.321884
N	1.318105	-0.000490	-0.289314	H	2.440456	0.887612	-1.822998
C	-1.214877	0.000155	2.137783	H	1.457401	0.001450	2.946736
H	-1.269226	-0.883762	2.773168	H	3.186266	0.000942	0.809354
H	-1.271357	0.886545	2.769542				

4a' (THF): E = -1043.1175109804 au
ZPE = 0.22441953 au
G_{corr} = 0.18386429 au

C	0.364549	0.033457	-0.107977	H	0.306546	1.295392	2.538281
O	1.761850	-0.136874	-0.211771	H	1.886738	0.506248	2.425582
P	1.369800	1.506268	-0.439530	H	1.703568	1.999299	3.337252
H	-0.037981	-0.105910	0.893652	C	-0.463233	-0.549862	-1.188153
C	1.709043	2.309391	1.210414	C	0.114998	-1.017738	-2.364322
C	3.201981	2.656856	1.201566	C	-1.843912	-0.610306	-1.013259
H	3.452244	3.237834	2.092460	C	-0.711691	-1.529018	-3.345217
H	3.824372	1.760406	1.206067	H	1.185580	-0.994539	-2.515854
H	3.480610	3.255655	0.331734	C	-2.618969	-1.129434	-2.029000
C	0.876474	3.595038	1.199313	H	-2.306906	-0.258177	-0.100139
H	1.104652	4.190878	2.085967	C	-2.084868	-1.600066	-3.214045
H	1.088829	4.217955	0.327159	H	-2.710198	-2.007450	-3.997021
H	-0.194705	3.384747	1.209280	F	-3.945651	-1.186437	-1.864069
C	1.378048	1.471059	2.437679	F	-0.160348	-1.982573	-4.477019

4a' (CH_2Cl_2): E = -1043.117822916839 au
ZPE = 0.22438963 au
G_{corr} = 0.18383245 au

C	1.180369	0.841005	0.129375	C	-1.605402	-0.939881	-1.798807
O	0.836346	2.063328	-0.487158	H	-2.538314	-0.711418	-1.278017
H	1.801296	0.184091	-0.476980	H	-1.871759	-1.394864	-2.755505
P	-0.551397	1.082210	-0.352493	H	-1.068785	-1.689510	-1.214160
C	-0.754205	0.310658	-2.039327	C	1.558949	0.896400	1.559767
C	-1.547961	1.328341	-2.866411	C	2.125494	-0.233694	2.145116
H	-1.807139	0.895637	-3.835665	C	1.343549	2.044048	2.316830
H	-2.480601	1.618549	-2.377843	C	2.454201	-0.192794	3.483793
H	-0.969774	2.234912	-3.053072	H	2.307004	-1.130502	1.566358
C	0.535493	-0.053811	-2.762103	C	1.695123	2.026265	3.652162
H	1.075587	-0.856127	-2.258454	H	0.919458	2.937993	1.880166
H	0.300141	-0.406574	-3.769261	C	2.252210	0.924832	4.272041
H	1.204510	0.801441	-2.865463	H	2.520777	0.937355	5.319796

F	1.492261	3.128325	4.383873	F	2.996581 -1.277867 4.048868

4a' (toluene): E = -1043.114580991872 au
ZPE = 0.22471016 au
G_{corr} = 0.18424067 au

C	1.174117	0.841707	0.132367	H	-2.542972	-0.721693	-1.291305
O	0.818456	2.060333	-0.480999	H	-1.871569	-1.396476	-2.770269
H	1.799392	0.191511	-0.477155	H	-1.074949	-1.700176	-1.228108
P	-0.561319	1.071509	-0.344781	C	1.556836	0.896951	1.561720
C	-0.756256	0.305682	-2.037948	C	2.120503	-0.233708	2.148041
C	-1.545755	1.328223	-2.862963	C	1.348222	2.046869	2.316213
H	-1.801237	0.903125	-3.836639	C	2.454005	-0.192121	3.485497
H	-2.480385	1.616378	-2.377044	H	2.296589	-1.133340	1.572147
H	-0.966342	2.235703	-3.040465	C	1.703395	2.031626	3.650620
C	0.536584	-0.053039	-2.757890	H	0.927666	2.940791	1.876584
H	1.072585	-0.862012	-2.260273	C	2.257996	0.928741	4.270329
H	0.308538	-0.394695	-3.770616	H	2.529806	0.942917	5.316972
H	1.207350	0.802374	-2.847018	F	1.507690	3.134767	4.380022
C	-1.608241	-0.946296	-1.810420	F	2.993307	-1.277304	4.050805

4a'' (toluene): E = -925.217019679 au
ZPE = 0.13734830 au
G_{corr} = 0.10063213 au

C	0.055772	-0.027929	0.025886	C	-1.120288	-2.330958	-2.668273
O	0.048531	-0.032761	1.434148	H	-0.503470	-0.285106	-2.592138
P	1.658765	-0.045830	0.877628	C	-1.360545	-3.517647	-2.001535
H	-0.253620	0.913625	-0.429465	H	-1.714356	-4.398005	-2.520532
C	2.101432	1.737904	0.932017	F	-1.334576	-2.288260	-3.987307
C	-0.449499	-1.241020	-0.654923	F	-1.363074	-4.652827	0.036304
C	-0.685046	-2.414884	0.053536	H	2.504055	1.984213	1.915074
C	-0.674013	-1.193552	-2.028577	H	2.888387	1.925636	0.199547
C	-1.132854	-3.522465	-0.639108	H	1.259585	2.396532	0.722148
H	-0.534150	-2.468277	1.122943				

4a'·2H_2O: E = -1195.9948981950 au
ZPE = 0.27291443 au
G_{corr} = 0.22636341 au

C	0.458758	0.095653	-0.049444	H	-1.481331	3.193601	-1.144417
O	1.829227	0.185518	-0.385978	C	3.156268	2.703957	1.231053
P	1.130903	1.752605	-0.312905	H	3.501437	3.226091	2.126644
H	0.260986	-0.229660	0.970526	H	3.747768	1.792822	1.135469
C	1.658486	2.402144	1.358421	H	3.378365	3.345357	0.375151
O	3.698665	-1.216495	1.419101	C	0.884456	3.711024	1.544272
H	3.179384	-0.773967	0.738182	H	1.226225	4.210622	2.453487
H	3.203214	-2.012259	1.620296	H	1.043321	4.403507	0.714341
O	-1.784974	2.700434	-0.378818	H	-0.187957	3.540443	1.635086
H	-2.043995	1.845906	-0.734015	C	1.416075	1.474548	2.541741

H	0.355214	1.268295	2.689113	H	1.007117	-0.522544	-2.664478
H	1.950897	0.529236	2.440672	C	-2.617857	-1.287784	-1.653164
H	1.783043	1.950293	3.454820	H	-2.105689	-0.622018	0.315031
C	-0.444694	-0.491189	-1.064091	C	-2.226989	-1.529166	-2.956637
C	-0.012102	-0.724975	-2.365136	H	-2.912696	-1.933241	-3.688827
C	-1.759799	-0.777908	-0.699568	F	-3.877888	-1.563520	-1.305601
C	-0.914530	-1.238529	-3.276148	F	-0.503617	-1.468393	-4.526105

4a'·3H_2O:

E = -1272.4363373670 au
ZPE = 0.30051950 au
G_{corr} = 0.25121276 au

C	0.277486	0.866666	-0.541238	H	3.968457	2.719282	-1.593015
O	0.066868	1.329413	0.787963	H	3.682027	0.995472	-1.405581
P	1.674122	0.773455	0.599183	H	2.412591	2.033593	-2.057096
H	0.264548	1.667923	-1.281452	C	1.956235	3.575777	0.166821
C	2.713135	2.255591	0.103912	H	1.095568	3.601059	-0.502867
O	1.645666	1.881326	3.392105	H	1.607605	3.791997	1.176073
H	1.507048	1.035175	3.861057	H	2.622245	4.388159	-0.135087
H	0.778217	2.290174	3.358255	C	-0.482451	-0.339723	-0.963390
O	1.063218	-0.537111	4.605016	C	-1.760009	-0.585908	-0.471112
H	0.339375	-0.737350	3.978717	C	0.083355	-1.197114	-1.902398
H	0.623973	-0.349110	5.438653	C	-2.442136	-1.697139	-0.930151
O	-0.913236	-0.790163	2.714605	H	-2.234782	0.083964	0.233423
H	-0.724496	-0.031274	2.147102	C	-0.645815	-2.287500	-2.329634
H	-0.775494	-1.557327	2.151597	H	1.080325	-1.021640	-2.285975
C	3.919391	2.291085	1.047314	C	-1.914308	-2.571820	-1.858630
H	4.476947	1.351805	1.024595	H	-2.466186	-3.436760	-2.201496
H	4.604717	3.083560	0.737557	F	-0.103730	-3.115271	-3.229272
H	3.618951	2.479033	2.075600	F	-3.671251	-1.936033	-0.459938
C	3.212933	1.979079	-1.318659				

4a'·5H_2O:

E = -1425.3280560303 au
ZPE = 0.35158077au
G_{corr} = 0.29636524 au

C	0.311631	0.271411	-0.287631	H	2.358084	-1.705417	3.157952
O	1.672695	-0.120613	-0.304435	H	2.662096	-1.071431	4.531656
P	1.539933	1.557886	-0.621699	O	-0.408824	-0.557372	4.482374
H	-0.151724	0.245639	0.695870	H	0.470301	-0.954959	4.289811
C	1.908584	2.387407	1.006517	H	-0.829171	-1.160801	5.100700
O	-2.212816	2.301218	1.231146	C	1.422222	1.672090	2.258889
H	-2.166421	1.436619	1.680471	H	1.772095	2.214328	3.140915
H	-3.126786	2.577594	1.330925	H	0.335391	1.636873	2.317712
O	-2.097926	-0.167897	2.443000	H	1.807842	0.655619	2.336325
H	-1.447740	-0.319838	3.168633	C	3.432808	2.543273	1.051426
H	-2.058020	-0.948174	1.885186	H	3.823510	3.051691	0.167431
O	3.008241	-1.812465	1.550309	H	3.717912	3.136468	1.923399
H	2.535819	-1.265616	0.903562	H	3.934627	1.576789	1.131987
H	3.917861	-1.502794	1.524822	C	1.240361	3.761681	0.889560
O	2.029848	-1.636735	4.080293	H	1.518070	4.378082	1.747649

H	1.551139	4.300772	-0.008837		
H	0.152761	3.674403	0.879053		
C	-0.535863	-0.251473	-1.385656		
C	-0.004755	-1.078195	-2.369623		
C	-1.883639	0.103298	-1.413052		
C	-0.845062	-1.535725	-3.366620		
H	1.036484	-1.369398	-2.362233		
C	-2.670581	-0.383461	-2.434393		
H	-2.297066	0.770682	-0.665930		
C	-2.184821	-1.210281	-3.431312		
H	-2.822340	-1.581578	-4.222429		
F	-3.964686	-0.043390	-2.470572		
F	-0.340455	-2.335909	-4.313625		

TS(**4a'**+TOB→**6'**): E = -3262.831648080847 au
ZPE = 0.27523081 au
G_{corr} = 0.22334821 au
ν = -376.78 cm^{-1}

C	-0.555301	0.080202	1.458637		
O	0.390666	0.034280	2.574976		
P	1.012434	-0.731956	1.211073		
H	-1.434008	-0.530406	1.628218		
C	-0.820079	1.406075	0.855679		
C	-1.957313	1.556886	0.060378		
C	0.062785	2.472597	1.030068		
C	-2.170181	2.767143	-0.566040		
H	-2.657207	0.745266	-0.081572		
C	-0.209933	3.661521	0.381955		
H	0.939475	2.382784	1.654156		
C	-1.312678	3.845039	-0.433075		
H	-1.496521	4.783188	-0.935875		
F	0.639710	4.695822	0.540343		
F	-3.257490	2.905584	-1.350525		
C	0.950055	-2.593099	1.531122		
C	1.735357	-2.812369	2.830956		
H	1.284491	-2.281777	3.669876		
H	1.732359	-3.880087	3.062975		
H	2.774242	-2.492007	2.733296		
C	1.626496	-3.315385	0.361288		
H	1.663465	-4.382035	0.597496		
H	1.069118	-3.182640	-0.563337		
H	2.649432	-2.969815	0.208049		
C	-0.502551	-3.046153	1.686402		
H	-1.082549	-2.850218	0.785679		
H	-0.503045	-4.125852	1.863191		
H	-0.986572	-2.573117	2.541938		
O	-0.802317	-1.506726	-1.350908		
O	1.612132	-0.485333	-0.640822		
C	0.867479	0.149597	-1.473681		
C	1.254800	1.417268	-1.985820		
C	-0.415952	-0.461043	-1.871622		
C	0.482005	2.059233	-2.915426		
C	-1.168910	0.255453	-2.889864		
C	-0.744498	1.458562	-3.373684		
Cl	2.717227	2.101461	-1.388817		
Cl	0.964588	3.582715	-3.547602		
Cl	-1.689227	2.309430	-4.531683		
Cl	-2.661983	-0.450086	-3.367396		

6': E = -3262.935726948132 au
ZPE = 0.27872230 au
G_{corr} = 0.22594791 au

C	0.054426	-0.161013	-0.109909		
O	1.440259	-0.264667	0.316672		
P	1.183666	-0.972063	-1.179878		
H	-0.651854	-0.735026	0.492616		
C	-0.433760	1.195180	-0.470642		
C	-1.761958	1.337753	-0.863219		
C	0.419400	2.291724	-0.450500		
C	-2.210509	2.588925	-1.229829		
H	-2.434666	0.490021	-0.884134		
C	-0.087753	3.522158	-0.823321		
H	1.450908	2.198644	-0.140356		
C	-1.396593	3.706754	-1.221307		
H	-1.769014	4.680039	-1.510594		
F	0.722764	4.583699	-0.798559		
F	-3.483804	2.733364	-1.608038		
C	1.660653	-2.724578	-0.888011		
C	2.901093	-2.756756	0.009566		
H	2.717361	-2.322964	0.989975		
H	3.194077	-3.797806	0.155009		
H	3.748465	-2.239873	-0.442334		
C	1.978281	-3.428450	-2.210635		
H	2.322824	-4.438565	-1.983382		
H	1.110747	-3.519485	-2.861151		
H	2.780933	-2.939004	-2.764748		
C	0.485769	-3.422721	-0.195983		
H	-0.420555	-3.405593	-0.802586		

H	0.748781	-4.468452	-0.027303	C	2.836920 0.581032 -5.488486
H	0.262023	-2.984503	0.777133	C	0.767516 -0.606348 -5.050359
O	0.365035	-1.116668	-2.715776	C	1.658129 -0.001550 -5.944438
O	2.407830	-0.121824	-1.925867	Cl	4.581993 1.273009 -3.513530
C	2.263875	-0.030039	-3.265447	Cl	3.920811 1.314370 -6.590245
C	3.149613	0.572509	-4.123549	Cl	1.285917 0.008246 -7.613929
C	1.085319	-0.605404	-3.710484	Cl	-0.687628 -1.337713 -5.566327

TS(**6'**→Ar^{F}CHO+**7'**): E = -3262.899233621381 au
ZPE = 0.27638640 au
G_{corr} = 0.22495804 au
ν = -220.74 cm^{-1}

C	0.143607	-0.187901	0.173672	C	2.006323 -3.719776 -2.031580
O	1.195517	-0.261971	0.898763	H	2.472719 -4.655795 -1.719687
P	0.888815	-1.325262	-1.269292	H	1.141391 -3.971792 -2.642744
H	-0.797659	-0.674764	0.495759	H	2.730037 -3.191132 -2.653233
C	-0.158243	1.081522	-0.597894	C	0.566260 -3.669402 0.038844
C	-1.320774	1.177867	-1.356850	H	-0.348107 -3.833678 -0.534157
C	0.776281	2.106562	-0.589721	H	0.949752 -4.649306 0.327281
C	-1.517057	2.312974	-2.114671	H	0.313301 -3.133102 0.953700
H	-2.055468	0.381278	-1.362563	O	0.252547 -1.526665 -2.819595
C	0.527103	3.222575	-1.364503	O	2.141749 -0.376600 -1.799840
H	1.676835	2.024173	0.003270	C	1.865439 0.065334 -3.051162
C	-0.606115	3.353836	-2.144171	C	2.522505 1.084199 -3.696082
H	-0.777007	4.234839	-2.747983	C	0.800763 -0.597029 -3.635463
F	1.418517	4.217540	-1.372737	C	2.103008 1.415995 -4.989564
F	-2.625519	2.417770	-2.854493	C	0.370646 -0.280294 -4.901891
C	1.640776	-2.934851	-0.767864	C	1.041837 0.739861 -5.585819
C	2.898025	-2.720233	0.081278	Cl	3.791450 1.903108 -2.907882
H	2.678402	-2.210569	1.014190	Cl	2.900261 2.674483 -5.825927
H	3.315866	-3.702795	0.310488	Cl	0.534535 1.157632 -7.163077
H	3.661472	-2.155365	-0.452230	Cl	-0.952493 -1.116905 -5.578451

$C_6H_3F_2$-CHO (THF): E = -544.0016040614 au
ZPE = 0.06362732 au
G_{corr} = 0.09650243 au

C	-1.838040	0.030112	0.710143	H	-1.589510 0.413752 -1.976448
H	-1.983779	-0.366871	1.729608	C	-2.395085 -3.224719 -1.011991
O	-1.588093	1.193587	0.520033	H	-2.389536 -2.568037 1.030417
C	-1.975424	-0.973912	-0.364971	C	-2.245154 -2.903123 -2.346320
C	-1.816164	-0.607116	-1.698907	H	-2.349536 -3.652414 -3.120116
C	-2.266302	-2.285412	-0.007765	F	-2.674260 -4.489701 -0.688000
C	-1.955684	-1.585042	-2.658521	F	-1.808172 -1.260997 -3.945699

$C_6H_3F_2$-CHO (CH_2Cl_2): E = -544.001950541765 au
ZPE = 0.09648854 au
G_{corr} = 0.06361152 au

C	1.302186	0.954265	0.128871	H	2.559445	-0.981948	1.479953
O	0.731801	1.850629	-0.440417	C	1.613907	2.007034	3.701528
H	1.622824	0.045095	-0.408149	H	0.769504	2.910030	1.950399
C	1.630232	0.964474	1.569206	C	2.271156	0.929724	4.272563
C	2.290586	-0.136834	2.101482	H	2.519020	0.918666	5.325951
C	1.283079	2.052996	2.365542	F	1.292930	3.037432	4.488435
C	2.597309	-0.128630	3.448087	F	3.231361	-1.177926	3.977467

$C_6H_3F_2$-CHO (toluene): E = -543.998517645016 au
ZPE = 0.09662622 au
G_{corr} = 0.06377042 au

C	1.300919	0.956746	0.128208	H	2.560205	-0.982664	1.482255
O	0.732170	1.852412	-0.439108	C	1.613733	2.007351	3.701752
H	1.621265	0.046548	-0.410221	H	0.769668	2.907402	1.947377
C	1.630460	0.963763	1.569584	C	2.271140	0.929770	4.272297
C	2.290701	-0.136904	2.102612	H	2.519031	0.919247	5.325451
C	1.283357	2.051941	2.365394	F	1.293083	3.036707	4.487908
C	2.597943	-0.129438	3.449158	F	3.231666	-1.177871	3.978250

7': E = -2718.924313657508 au
ZPE = 0.17842989 au
G_{corr} = 0.13477619 au

P	1.251877	-0.866181	-1.211504	H	0.047639	-2.866203	0.409697
C	1.733794	-2.649317	-0.977252	O	0.361105	-0.924716	-2.653676
C	2.796184	-2.640406	0.135491	O	2.620696	-0.232725	-1.985289
H	2.441056	-2.129643	1.034451	C	2.424009	-0.186234	-3.330021
H	3.035182	-3.669876	0.414584	C	3.349807	0.230296	-4.259869
H	3.718266	-2.156960	-0.191591	C	1.147395	-0.578492	-3.708218
C	2.271636	-3.329966	-2.235600	C	2.968042	0.256579	-5.610407
H	2.537572	-4.364740	-2.001716	C	0.757471	-0.568359	-5.028622
H	1.526063	-3.354204	-3.031294	C	1.685152	-0.140006	-5.991605
H	3.169927	-2.837726	-2.610314	Cl	4.916898	0.702306	-3.724366
C	0.458678	-3.351536	-0.479326	Cl	4.102950	0.793637	-6.794209
H	-0.316671	-3.372632	-1.247513	Cl	1.218465	-0.101719	-7.652950
H	0.695362	-4.384431	-0.211211	Cl	-0.840021	-1.069581	-5.431157

TS(**7'**+TOB→**5'**): E = -4938.636998161290 au
ZPE = 0.22885534 au
G_{corr} = 0.17240629 au
ν = -233.14 cm^{-1}

C	0.530101	-1.785507	0.612499	H	-0.938886	-2.685239	-0.739755
C	2.027895	-1.935623	0.906305	H	0.691110	-2.587147	-1.420251
H	2.353892	-1.315050	1.740099	C	-0.267992	-2.124154	1.874685
H	2.217388	-2.974908	1.182767	H	-1.344826	-2.067971	1.719902
H	2.650393	-1.709684	0.043274	H	-0.037366	-3.155771	2.149957
C	0.123255	-2.745146	-0.506301	H	-0.001223	-1.508367	2.733699
H	0.325215	-3.763727	-0.166930	O	-0.682164	-0.253245	-1.830572

O	1.914049	-0.200674	-1.804111	O	-1.364187	0.294018	0.613676
C	1.358613	0.277046	-2.789663	O	0.831424	0.775957	1.552494
C	2.041030	0.995010	-3.839834	C	-0.173386	1.199464	2.331476
C	-0.112753	0.240430	-2.815972	C	-1.423062	0.911178	1.804526
C	1.336386	1.522483	-4.874236	C	-1.207215	2.221906	4.219523
C	-0.809500	0.923435	-3.866261	C	-2.577190	1.259200	2.467192
C	-0.109359	1.486421	-4.888546	C	-2.460933	1.925376	3.692435
Cl	3.738800	1.062543	-3.757110	C	-0.043149	1.858148	3.533536
Cl	2.143733	2.266872	-6.174731	Cl	1.515886	2.189982	4.145771
Cl	-0.927351	2.191681	-6.202076	Cl	-1.074391	3.035549	5.717991
Cl	-2.510975	0.918667	-3.815491	Cl	-3.878461	2.371349	4.538793
P	0.236940	0.014569	0.129705	Cl	-4.091742	0.870931	1.781533

5':

E = -4938.751246250255 au
ZPE = 0.23334925 au
G_{corr} = 0.17859671 au

C	1.774844	-2.460749	-0.881760	C	0.650804	-0.465218	-5.026411
C	3.192810	-2.537566	-0.300095	C	1.556896	-0.182256	-6.055234
H	3.278332	-2.045530	0.667531	Cl	4.962492	0.494961	-4.041419
H	3.439315	-3.590048	-0.151811	Cl	3.984834	0.454683	-7.033302
H	3.945293	-2.117997	-0.966167	Cl	1.014199	-0.215915	-7.676189
C	1.727023	-3.259805	-2.190075	Cl	-0.985399	-0.843627	-5.327166
H	2.000122	-4.292152	-1.966550	P	1.348039	-0.691007	-1.217992
H	0.733753	-3.278157	-2.636595	O	-0.151200	-0.436233	-0.459805
H	2.440111	-2.902825	-2.934074	O	2.086315	0.186336	0.023406
C	0.786658	-3.074055	0.115894	C	1.264553	0.442471	1.051295
H	-0.238218	-3.073356	-0.252169	C	-0.036608	0.081181	0.767953
H	1.074299	-4.113245	0.282885	C	0.595993	1.204874	3.197860
H	0.806660	-2.581368	1.088784	C	-1.047974	0.264741	1.680449
O	0.409593	-0.666889	-2.622802	C	-0.717521	0.838446	2.913656
O	2.677593	-0.164753	-2.133608	C	1.611234	1.007640	2.254654
C	2.437511	-0.142770	-3.449686	Cl	3.235722	1.432784	2.556738
C	3.342609	0.141236	-4.444306	Cl	0.987551	1.897863	4.710989
C	1.119999	-0.435510	-3.735704	Cl	-1.947146	1.077795	4.077132
C	2.886481	0.116768	-5.767443	Cl	-2.640053	-0.206819	1.288096

TS(**4a'**·2H_2O→***l*-12**):

E = -1195.9471407325 au
ZPE = 0.27327421 au
G_{corr} = 0.22791046 au
ν = -386.89 cm^{-1}

C	-0.463181	-0.088847	-0.069525	H	-1.971951	1.724436	-0.718189
O	1.608880	-0.785426	-0.109868	H	-2.770107	0.757200	0.174396
P	1.156366	0.710715	-0.388743	C	2.999928	1.782722	1.254379
H	-0.611328	-0.433519	0.949239	H	3.299104	2.407484	2.099772
C	1.471298	1.694736	1.179279	H	3.452049	0.799222	1.391909
O	0.793862	-2.696037	1.655985	H	3.428992	2.225969	0.352023
H	1.130256	-1.995977	1.059740	C	0.890565	3.095138	0.990815
H	0.745536	-3.476875	1.100716	H	1.176744	3.739521	1.826450
O	-1.922414	1.218187	0.103607	H	1.256542	3.565578	0.075323

H	-0.199573	3.084260	0.949051	C	-1.562504	-1.408479	-3.387720
C	0.939448	1.057798	2.456704	H	-0.483243	0.329241	-2.755876
H	-0.150428	1.082024	2.505980	C	-2.227976	-2.932291	-1.712241
H	1.263352	0.020853	2.559250	H	-1.693336	-2.447625	0.307409
H	1.309213	1.600598	3.331064	C	-2.195392	-2.591395	-3.050451
C	-1.036099	-0.957994	-1.108455	H	-2.641664	-3.225919	-3.804885
C	-0.980917	-0.582454	-2.450379	F	-2.828244	-4.072306	-1.361086
C	-1.665610	-2.141902	-0.730131	F	-1.518165	-1.058637	-4.675543

***l*-12**:

E = -1119.5165113113 au
ZPE = 0.25002010 au
G_{corr} = 0.20789559 au

C	-0.961887	0.939883	-0.514577	C	0.919677	0.041581	1.896421
O	1.703670	0.332417	-1.206415	H	-0.153336	-0.157918	1.928585
P	0.909846	1.465504	-0.549887	H	1.389606	-0.753413	1.315662
H	-1.474979	1.204565	0.406512	H	1.289317	-0.031395	2.923681
C	1.235784	1.411779	1.304500	C	-1.287297	-0.434275	-0.951727
O	-1.538488	1.942019	-1.509928	C	-0.827137	-0.928895	-2.172477
H	-0.777530	2.514686	-1.798716	C	-2.025731	-1.255077	-0.100459
H	-1.970237	1.542087	-2.288359	C	-1.139040	-2.228926	-2.514994
C	2.734527	1.688625	1.452312	H	-0.218919	-0.330880	-2.835692
H	3.016427	1.691387	2.508676	C	-2.282647	-2.554963	-0.483871
H	3.331493	0.927756	0.948575	H	-2.400326	-0.884831	0.844927
H	3.010802	2.660309	1.035219	C	-1.859431	-3.073322	-1.692469
C	0.451487	2.513340	2.011134	H	-2.081671	-4.091892	-1.981519
H	0.731557	2.562700	3.066976	F	-2.988031	-3.342567	0.335274
H	0.651258	3.493855	1.573013	F	-0.712151	-2.703481	-3.690383
H	-0.628100	2.351828	1.979155				

***l*-13**:

E = -1119.5817306524 au
ZPE = 0.25143484 au
G_{corr} = 0.20878437 au

C	-0.936442	0.694151	-0.361794	H	1.419193	-0.376042	2.307805
P	0.938786	0.938171	-0.413911	H	1.214560	1.005693	3.378343
H	-1.278411	0.539631	0.665175	C	-1.316858	-0.507746	-1.178543
C	1.328037	1.559942	1.300137	C	-1.618821	-0.384034	-2.530933
O	-1.524312	1.890842	-0.808835	C	-1.323387	-1.764669	-0.579250
H	-0.984486	2.274485	-1.509678	C	-1.921405	-1.523423	-3.251071
C	2.844211	1.779951	1.339476	H	-1.636102	0.577635	-3.025752
H	3.134016	2.186003	2.311688	C	-1.634483	-2.867996	-1.345210
H	3.394431	0.849388	1.194280	H	-1.099145	-1.880590	0.473202
H	3.170289	2.487972	0.575127	C	-1.939098	-2.785261	-2.691290
C	0.618567	2.902222	1.488262	H	-2.184756	-3.662975	-3.273836
H	0.938429	3.352303	2.430996	F	-1.648395	-4.075175	-0.765493
H	0.859588	3.608406	0.690808	F	-2.214734	-1.402944	-4.552347
H	-0.465823	2.798773	1.528343	O	1.516284	-0.608421	-0.275275
C	0.926061	0.590299	2.409301	H	1.863018	-0.918883	-1.117592
H	-0.150915	0.419374	2.444811				

***u*-13**:

E = -1119.5836231911 au
ZPE = 0.25159948 au
G_{corr} = 0.20895945 au

C	-0.936442	0.694151	-0.361794	H	1.419193	-0.376042	2.307805
P	0.938786	0.938171	-0.413911	H	1.214560	1.005693	3.378343
H	-1.278411	0.539631	0.665175	C	-1.316858	-0.507746	-1.178543
C	1.328037	1.559942	1.300137	C	-1.618821	-0.384034	-2.530933
O	-1.524312	1.890842	-0.808835	C	-1.323387	-1.764669	-0.579250
H	-0.984486	2.274485	-1.509678	C	-1.921405	-1.523423	-3.251071
C	2.844211	1.779951	1.339476	H	-1.636102	0.577635	-3.025752
H	3.134016	2.186003	2.311688	C	-1.634483	-2.867996	-1.345210
H	3.394431	0.849388	1.194280	H	-1.099145	-1.880590	0.473202
H	3.170289	2.487972	0.575127	C	-1.939098	-2.785261	-2.691290
C	0.618567	2.902222	1.488262	H	-2.184756	-3.662975	-3.273836
H	0.938429	3.352303	2.430996	F	-1.648395	-4.075175	-0.765493
H	0.859588	3.608406	0.690808	F	-2.214734	-1.402944	-4.552347
H	-0.465823	2.798773	1.528343	O	1.516284	-0.608421	-0.275275
C	0.926061	0.590299	2.409301	H	1.863018	-0.918883	-1.117592
H	-0.150915	0.419374	2.444811				

TS(**4a'**·3H2O→***u*-13**):

E = -1272.3934582354 au
ZPE = 0.29798322 au
G_{corr} = 0.25146066 au
v = -315.68 cm^{-1}

C	-0.575887	0.234720	-0.768817	H	3.007698	1.901446	-1.926167
O	-0.811152	0.627003	0.612761	H	2.678529	0.192043	-1.666673
P	0.878682	0.085009	0.563867	H	1.391270	1.264451	-2.209179
H	-0.725184	1.084650	-1.431538	C	1.234978	2.866522	0.006312
C	1.926342	1.509051	-0.096483	H	0.320709	2.915134	-0.585599
O	1.076437	0.506554	2.286425	H	0.979589	3.131383	1.034725
H	0.062164	-0.320504	3.384212	H	1.902621	3.648572	-0.364691
H	1.015451	1.449574	2.490688	C	-1.212326	-0.993086	-1.225447
O	-0.695601	-0.736188	3.868744	C	-1.487361	-2.069012	-0.370764
H	-1.860797	-0.371647	2.960804	C	-1.476137	-1.141576	-2.594181
H	-0.750199	-0.280089	4.714443	C	-2.006138	-3.233685	-0.899251
O	-2.462301	-0.046220	2.196257	H	-1.270878	-2.031047	0.688315
H	-1.681150	0.265073	1.310737	C	-1.985717	-2.331108	-3.062581
H	-3.039403	-0.773777	1.932170	H	-1.284835	-0.328173	-3.282755
C	3.247564	1.544148	0.685147	C	-2.273121	-3.408733	-2.242599
H	3.734841	0.566926	0.703703	H	-2.682936	-4.331186	-2.630335
H	3.934741	2.241786	0.200304	F	-2.232449	-2.454203	-4.374711
H	3.125814	1.873423	1.715672	F	-2.263758	-4.252420	-0.066196
C	2.259900	1.195185	-1.557320				

TS(**4a'**·5H2O→***l*-13**):

E = -1425.2862869942 au
ZPE = 0.35308322 au
G_{corr} = 0.30006304 au

ν = -302.91 cm^{-1}

C	0.270330	0.669356	0.167079	H	1.139535 1.802977 2.639769
O	2.192615	0.083977	-0.358203	H	2.611121 0.861817 2.318949
P	1.686873	1.598580	-0.483277	C	3.833407 2.738613 0.681652
H	0.367907	0.290468	1.178606	H	3.994104 3.232915 -0.279317
C	2.343049	2.556636	0.989003	H	4.304301 3.356326 1.450523
O	-1.213248	1.896333	0.790932	H	4.359138 1.782340 0.656364
H	-1.927303	1.331168	1.219625	C	1.649000 3.917797 0.998658
H	-1.605478	2.288174	0.003432	H	2.092912 4.563719 1.760866
O	-2.978187	0.377122	1.923540	H	1.749031 4.429730 0.038981
H	-2.511059	-0.327481	2.441966	H	0.585464 3.826948 1.222168
H	-3.496523	-0.095415	1.266847	C	-0.524821 -0.156787 -0.759055
O	2.509787	-1.753223	1.498792	C	-0.756655 0.279665 -2.062773
H	2.416287	-1.060667	0.794564	C	-1.073844 -1.356844 -0.313257
H	3.446787	-1.794371	1.702651	C	-1.529385 -0.501868 -2.894919
O	0.922694	-1.221575	3.557849	H	-0.325376 1.203764 -2.426235
H	1.530005	-1.445871	2.807854	C	-1.835155 -2.102922 -1.190512
H	1.197928	-0.357882	3.872574	H	-0.900170 -1.716933 0.691874
O	-1.675692	-1.553615	3.161904	C	-2.085556 -1.700519 -2.488129
H	-0.711116	-1.420671	3.329237	H	-2.684229 -2.301270 -3.159695
H	-2.040081	-1.927581	3.967033	F	-2.358242 -3.257958 -0.772293
C	2.186111	1.866192	2.335971	F	-1.756447 -0.089664 -4.144505
H	2.711800	2.428805	3.112433		

TS(**4a'**·5H2O→***u*-13**): E = -1425.3001888847 au

ZPE = 0.35023992 au

G_{corr} = 0.29849622 au

ν = -429.39 cm^{-1}

C	0.275432	-0.430784	-0.737790	H	0.191258 1.288676 2.262222
O	1.588223	-0.458920	-1.119058	H	1.515879 0.245091 1.731409
P	0.262169	1.386561	-0.885313	C	2.762240 2.076873 0.071492
H	0.059968	-0.803986	0.278649	H	2.875891 2.580784 -0.890275
C	1.301342	2.054057	0.535849	H	3.360303 2.626560 0.802970
O	-1.343151	1.859666	-0.170400	H	3.174367 1.076387 -0.023772
H	-1.828049	1.302413	0.727090	C	0.862875 3.508636 0.756126
H	-1.989545	2.083153	-0.852252	H	1.566393 3.990586 1.438928
O	-2.308555	0.767245	1.725609	H	0.867997 4.083508 -0.172970
H	-1.979097	-0.173552	1.962852	H	-0.128560 3.590338 1.198252
H	-3.273116	0.752009	1.700367	C	-0.692657 -1.079347 -1.694827
O	2.690070	-1.979050	0.569565	C	-0.253933 -1.422644 -2.968815
H	2.292074	-1.361030	-0.143795	C	-2.019198 -1.312317 -1.334889
H	3.442678	-1.502446	0.929438	C	-1.151904 -1.986995 -3.852332
O	0.953858	-2.382413	2.527672	H	0.776181 -1.254528 -3.251386
H	1.593730	-2.233243	1.778750	C	-2.874363 -1.875711 -2.258486
H	1.376285	-2.004807	3.303865	H	-2.384658 -1.073036 -0.345496
O	-1.531362	-1.549118	2.382124	C	-2.474912 -2.227758 -3.534237
H	-0.570183	-1.818597	2.403790	H	-3.160110 -2.673037 -4.242925
H	-1.997566	-2.267068	1.943638	F	-4.149226 -2.100732 -1.907426
C	1.197836	1.279902	1.844537	F	-0.728519 -2.321379 -5.079451
H	1.851615	1.740051	2.590701		

***l*-13**·H2O: E = -1196.0242308993 au
ZPE = 0.27678862 au
G_{corr} = 0.23230402 au

C	0.179037	0.173169	0.067771	C	-0.714364	1.269678	-0.451215
P	-0.024281	0.083541	1.946325	C	-2.040470	1.006983	-0.784431
H	1.213639	0.434831	-0.174072	C	-0.217872	2.565685	-0.562015
C	1.558205	-0.710101	2.535661	C	-2.834504	2.048504	-1.221870
O	-0.079741	-1.079465	-0.499771	H	-2.461435	0.012940	-0.714308
C	2.820788	-0.014395	2.033445	C	-1.055399	3.568021	-1.005703
H	3.700438	-0.482874	2.482554	H	0.812196	2.789148	-0.317318
H	2.935591	-0.093786	0.951750	C	-2.376069	3.345424	-1.346020
H	2.841179	1.042193	2.301200	H	-3.015992	4.144016	-1.696535
C	1.512816	-0.646630	4.066648	F	-0.572028	4.812121	-1.119145
H	2.385155	-1.157556	4.481541	F	-4.109870	1.794825	-1.543629
H	1.526101	0.379796	4.434201	O	0.277159	1.658231	2.370052
H	0.622979	-1.137604	4.466383	H	-0.524044	2.083152	2.691351
C	1.552596	-2.176517	2.097862	H	-0.837884	-1.509915	-0.054881
H	0.647045	-2.695179	2.421238	O	-2.171009	-2.196824	0.929793
H	1.634983	-2.286412	1.017580	H	-2.071746	-1.647007	1.717574
H	2.401979	-2.694198	2.549905	H	-1.940731	-3.086281	1.215485

***l*-13**·2H2O: E = -1272.4695356907 au
ZPE = 0.30332481 au
G_{corr} = 0.25671836 au

C	0.387439	0.255904	0.182844	C	0.043292	2.728133	-0.077073
P	-0.041592	-0.055925	1.993274	C	-2.402428	2.352708	-1.270350
H	1.444734	0.538006	0.137915	H	-2.064826	0.258732	-1.093341
C	1.219808	-1.307059	2.565588	C	-0.731066	3.798522	-0.475691
O	0.224701	-0.891990	-0.589461	H	1.010222	2.900297	0.376200
C	2.637567	-1.000322	2.091675	C	-1.965958	3.648673	-1.076536
H	3.338091	-1.707301	2.543857	H	-2.555537	4.500677	-1.387307
H	2.737022	-1.096749	1.010020	F	-0.267012	5.039499	-0.280040
H	2.957394	0.002714	2.377420	F	-3.592605	2.167220	-1.856364
C	1.167960	-1.282566	4.097551	O	0.583455	1.332562	2.650255
H	1.820170	-2.063613	4.495649	H	-0.101576	1.838311	3.097679
H	1.506243	-0.330430	4.505654	H	-0.628887	-1.345522	-0.399322
H	0.160536	-1.474596	4.474010	O	-2.086200	-2.203478	-0.133842
C	0.786294	-2.693329	2.082179	H	-2.426791	-0.523162	2.215847
H	-0.237286	-2.927172	2.383151	H	-1.905766	-3.105929	0.143180
H	0.855863	-2.791688	1.000441	O	-3.282625	-0.878234	1.920065
H	1.436809	-3.451277	2.525188	H	-2.606878	-1.800174	0.593947
C	-0.430907	1.435157	-0.285117	H	-3.757075	-0.116661	1.573155
C	-1.670725	1.245218	-0.890577				

TS(***l*-13**→**8'**): E = -1119.4960609157 au
ZPE = 0.20359628 au
G_{corr} = 0.24633843 au

ν = -1874.91 cm^{-1}

C	-1.021006	0.728827	-0.444798	H	1.228443	-0.426897	2.280008
P	0.850617	0.772811	-0.288272	H	1.134629	0.925193	3.403298
H	-1.444101	0.644150	0.561323	C	-1.432118	-0.478541	-1.235931
C	1.237414	1.547515	1.344209	C	-1.771427	-0.376174	-2.579553
O	-1.456497	1.953798	-0.964880	C	-1.432128	-1.720996	-0.608154
H	-0.897565	2.213791	-1.705793	C	-2.106624	-1.527601	-3.266298
C	2.755785	1.732448	1.390081	H	-1.795377	0.574972	-3.093652
H	3.042568	2.153017	2.356223	C	-1.777074	-2.836093	-1.341320
H	3.282598	0.785556	1.269397	H	-1.180253	-1.820132	0.439842
H	3.102077	2.415814	0.613038	C	-2.120140	-2.776611	-2.679460
C	0.534413	2.893696	1.494542	H	-2.390882	-3.663668	-3.236171
H	0.837370	3.352685	2.438110	F	-1.786726	-4.029980	-0.737014
H	0.801278	3.583890	0.692700	F	-2.437949	-1.430123	-4.559576
H	-0.551151	2.799446	1.512388	O	1.493469	-0.685528	-0.375762
C	0.796855	0.564053	2.429587	H	1.731134	0.317004	-1.363343
H	-0.288288	0.461993	2.482801				

TS(***l*-13→8'**)·H2O: E = -1195.9746104548 au

ZPE = 0.22761476 au

G_{corr} = 0.27188790 au

ν = -1480.15 cm^{-1}

C	0.038521	0.056657	-0.053395	H	3.850181	-0.553831	2.055081
P	0.182762	0.190455	1.815521	C	-0.691188	1.263248	-0.572347
H	1.040069	0.037385	-0.493620	C	-2.054726	1.214969	-0.838119
C	1.712156	-0.745304	2.281892	C	0.008882	2.454088	-0.743556
O	-0.571144	-1.165655	-0.377155	C	-2.686552	2.364381	-1.273031
H	-1.277374	-1.350984	0.252179	H	-2.626157	0.303389	-0.727298
C	1.773157	-0.716227	3.811834	C	-0.670937	3.568952	-1.183713
H	2.666469	-1.242874	4.155624	H	1.071112	2.510547	-0.544827
H	1.820321	0.303540	4.195210	C	-2.026445	3.561987	-1.458058
H	0.907580	-1.208461	4.260233	H	-2.540792	4.448031	-1.805154
C	1.627610	-2.191107	1.796466	F	0.004433	4.712287	-1.358129
H	2.489219	-2.749643	2.169901	F	-4.000049	2.316803	-1.531891
H	0.728982	-2.692105	2.161695	O	0.330795	1.685903	2.253699
H	1.636170	-2.266702	0.709495	H	-0.926745	1.694422	2.993647
C	2.945197	-0.051200	1.705004	O	-1.799798	1.162144	3.303515
H	2.963636	-0.080226	0.614158	H	-1.737142	1.008506	4.256024
H	3.001574	0.991739	2.017619	H	-1.295527	0.203556	2.718640

TS(***l*-13→8'**)·2H2O: E = -1272.4190702619 au

ZPE = 0.29488811 au

G_{corr} = 0.24818802au

ν = -1145.76 cm^{-1}

C	0.187119	0.128217	0.007454	O	-0.232302	-1.066708	-0.450927
P	0.090642	0.078616	1.882758	H	-1.386762	-1.667403	-0.008507
H	1.244811	0.348027	-0.235753	C	1.314224	-0.992028	4.066347
C	1.367917	-1.082117	2.537016	H	2.011615	-1.718096	4.489772

H	1.598025	-0.007141	4.435177	C	-0.832828	3.698051	-0.745329
H	0.320734	-1.228708	4.452695	H	0.956547	2.766564	-0.040152
C	1.012850	-2.507489	2.104848	C	-2.134246	3.572919	-1.194883
H	1.727620	-3.199569	2.555250	H	-2.717151	4.432883	-1.496253
H	0.017672	-2.801214	2.444348	F	-0.297152	4.925060	-0.689131
H	1.050965	-2.627657	1.024917	F	-3.901371	2.131820	-1.692262
C	2.760874	-0.706387	2.033321	O	0.594121	1.510973	2.499146
H	2.843974	-0.804297	0.950448	H	-0.128556	2.137053	2.621886
H	3.038912	0.311462	2.308197	O	-2.578771	-0.951126	2.468716
H	3.497768	-1.378921	2.478119	H	-1.433892	-0.394344	2.333671
C	-0.620193	1.339147	-0.427815	H	-3.265938	-0.278758	2.380069
C	-1.923590	1.173041	-0.883694	O	-2.284426	-2.142896	0.339521
C	-0.066358	2.617226	-0.362231	H	-2.567227	-1.521321	1.577469
C	-2.645486	2.291137	-1.252433	H	-2.084989	-3.077387	0.450464
H	-2.365526	0.190060	-0.970686				

***l*-8'**:

E = -1119.6006095286 au
ZPE = 0.25090165 au
G_{corr} = 0.20826203 au

C	-0.017297	-0.625738	-0.360699	H	2.334660	2.228345	-0.240448
P	1.845231	-0.654782	-0.260056	H	2.555386	2.577796	-1.949572
H	-0.351281	0.333718	-0.766584	C	-0.577105	-0.788736	1.028944
C	2.549199	0.468031	-1.522476	C	-0.895842	-2.047853	1.521873
O	-0.397597	-1.631027	-1.253213	C	-0.719983	0.336817	1.835396
H	0.224183	-2.369065	-1.177917	C	-1.359363	-2.148660	2.819652
C	4.072552	0.384930	-1.382320	H	-0.805981	-2.937903	0.914479
H	4.539984	1.043272	-2.117227	C	-1.184007	0.176466	3.124771
H	4.410581	0.703186	-0.394071	H	-0.484714	1.326969	1.464023
H	4.440257	-0.626002	-1.558000	C	-1.514941	-1.057626	3.651555
C	2.120980	0.005840	-2.915438	H	-1.882901	-1.163003	4.663304
H	2.597994	0.636814	-3.667874	F	-1.328839	1.257667	3.898310
H	2.422009	-1.024259	-3.108319	F	-1.672909	-3.358011	3.297100
H	1.042858	0.077570	-3.062785	O	2.286786	-2.091450	-0.348201
C	2.074384	1.894581	-1.247049	H	2.141455	0.001535	0.956431
H	0.997116	2.010071	-1.375976				

***u*-8'**:

E = -1119.6003964095 au
ZPE = 0.25109331 au
G_{corr} = 0.20928455 au

C	0.041387	-0.173653	-0.021327	C	-0.494982	-2.758528	2.485765
P	-0.030262	-0.100572	1.832858	H	-0.179679	-3.621200	3.076261
H	1.088596	-0.277653	-0.317044	H	-1.468440	-2.438872	2.858211
C	0.551160	-1.651703	2.618698	H	-0.618774	-3.093939	1.456852
O	-0.388720	1.083767	-0.482827	C	1.882723	-2.069043	1.995316
H	-1.218579	1.316805	-0.048372	H	1.772247	-2.386972	0.957993
C	0.750578	-1.311727	4.101290	H	2.624212	-1.267846	2.029624
H	1.096269	-2.201454	4.631233	H	2.294305	-2.914753	2.549742
H	1.499510	-0.530797	4.246062	C	-0.751779	-1.320961	-0.588214
H	-0.177665	-0.984570	4.570786	C	-0.097847	-2.333502	-1.280529

C-2.133948-1.370812	-0.418918	H-2.770651-4.309679	-2.021955
C-0.837904-3.390047	-1.776520	F-4.149415-2.502536	-0.775338
H0.972948-2.302382	-1.436971	F-0.206892-4.364287	-2.440122
C-2.823719-2.445484	-0.940050	O-1.3822720.391534	2.275463
H-2.669283-0.607753	0.130113	H1.039216 0.787380	2.102333
C-2.206490-3.477171	-1.623157		

TS(***I*-13→14**): E = -1119.524650408672 au
ZPE = 0.24610199 au
G_{corr} = 0.20407300 au
ν = -1397.78 cm^{-1}

C-1.2805080.228170	0.403274	H0.528357 2.710870	3.432795
P0.519002 0.719231	0.283651	C-1.601660-0.872336	-0.572395
H-1.538352-0.093565	1.425528	C-2.129750-0.552990	-1.816613
C1.128728 1.328276	1.913365	C-1.336699-2.200299	-0.242394
O-1.6617401.487335	0.074016	C-2.388803-1.577762	-2.706392
C1.299623 0.148381	2.873232	H-2.3442170.475047	-2.074848
H1.660304 0.521571	3.833986	C-1.612793-3.181691	-1.170358
H0.355725-0.367380	3.057037	H-0.932921-2.465877	0.727446
H2.023729-0.581049	2.512045	C-2.141024-2.905507	-2.419028
C2.473810 2.023903	1.674915	H-2.353194-3.691205	-3.131645
H2.838552 2.423234	2.623402	F-1.363499-4.459887	-0.857223
H3.232842 1.343130	1.290920	F-2.904343-1.276346	-3.905443
H2.379698 2.860128	0.980173	O1.692105-0.342219	-0.101491
C0.130159 2.333316	2.488764	H1.588534-0.703437	-0.991409
H-0.0245643.185995	1.828470	H-0.3038261.781070	-0.451548
H-0.8408691.885862	2.696302		

TS(***I*-13→*I*-14**)·H2O: E = -1195.9761153677 au
ZPE = 0.26911342 au
G_{corr} = 0.22504011 au
ν = -1324.31 cm^{-1}

C0.050073-0.011974	-0.043426	C-0.7697991.170708	-0.517444
P0.021925 0.000522	1.839543	C-2.0865580.982279	-0.920064
H1.093663 0.161502	-0.356294	C-0.2100142.446713	-0.533729
C1.564986-0.730303	2.508322	C-2.8155402.081325	-1.331184
O-0.408410-1.239064	-0.409819	H-2.532723-0.002675	-0.926652
C2.771705 0.130267	2.131701	C-0.9837573.507494	-0.955667
H3.675152-0.326879	2.540234	H0.820287 2.609305	-0.241835
H2.905011 0.202819	1.051521	C-2.2974383.361126	-1.361555
H2.702143 1.139273	2.537431	H-2.8866054.205527	-1.693324
C1.421592-0.810441	4.031589	F-0.4450564.733385	-0.980704
H2.314769-1.280010	4.448523	F-4.0838291.903940	-1.722824
H1.321435 0.173414	4.489256	O0.026389 1.500664	2.460232
H0.562623-1.414822	4.327717	H-0.8328641.937941	2.411037
C1.710817-2.139561	1.926916	H-1.292686-1.650232	0.370152
H0.857145-2.774429	2.168658	O-2.008587-1.865324	1.258575
H1.830987-2.134796	0.844741	H-1.214335-0.917168	1.989862
H2.598294-2.604266	2.360379	H-1.806348-2.748745	1.585541

TS(***l*-13→*l*-14**)·2H2O: E = -1272.4190460634 au

ZPE = 0.29486080 au

G_{corr} = 0.24931465 au

ν = -1144.91 cm^{-1}

C	0.306787	0.165230	0.064573	C	0.070686 2.676562 -0.121662
P	-0.000003	-0.036150	1.906391	C	-2.378335 2.424570 -1.341967
H	1.383269	0.403577	-0.038760	H	-2.109838 0.307441 -1.207737
C	1.188026	-1.268679	2.597813	C	-0.656621 3.785203 -0.501532
O	-0.047766	-0.988970	-0.532048	H	1.045552 2.799386 0.333127
C	2.629088	-0.891734	2.256643	C	-1.892911 3.697385 -1.114192
H	3.309047	-1.605787	2.726703	H	-2.445268 4.579255 -1.409733
H	2.815985	-0.923967	1.182842	F	-0.145914 5.003557 -0.276984
H	2.893913	0.101096	2.621678	F	-3.569984 2.301807 -1.942733
C	0.988383	-1.282206	4.117583	O	0.442782 1.333221 2.689798
H	1.625464	-2.055634	4.551986	H	-0.287490 1.952927 2.798386
H	1.256782	-0.333803	4.581126	H	-1.243049 -1.618390 -0.271920
H	-0.042578	-1.516606	4.390686	O	-2.171785 -2.114823 -0.065893
C	0.852916	-2.653097	2.035843	H	-1.569579 -0.518879 2.138111
H	-0.173980	-2.947079	2.261485	H	-1.979020 -3.054400 0.007998
H	0.990322	-2.699714	0.958341	O	-2.725513 -1.068496 2.089502
H	1.511661	-3.389917	2.500514	H	-2.604105 -1.576363 1.169581
C	-0.456444	1.407932	-0.361366	H	-3.392561 -0.382477 1.960318
C	-1.693168	1.279925	-0.984675		

***l*-14**: E = -1119.5532219341 au

ZPE = 0.24837183 au

G_{corr} = 0.20535447 au

C	-1.626640	0.018326	0.554422	H	0.723061 1.350948 4.114813
P	0.211822	0.166298	0.639529	C	-1.945680 -1.071316 -0.455687
H	-1.985031	-0.336547	1.546853	C	-2.280882 -0.699692 -1.749857
C	0.821253	1.275507	1.969746	C	-1.879046 -2.417676 -0.101043
O	-1.855884	1.273193	0.214008	C	-2.546292 -1.693565 -2.671643
C	2.355106	1.261469	1.925769	H	-2.340738 0.347173 -2.016098
H	2.723412	1.963980	2.675444	C	-2.150356 -3.367566 -1.063971
H	2.776916	0.284495	2.153963	H	-1.649550 -2.720504 0.914333
H	2.739859	1.586668	0.957525	C	-2.487397 -3.039399 -2.364970
C	0.329585	2.708137	1.756214	H	-2.701886 -3.800169 -3.103528
H	0.764516	3.336486	2.536282	F	-2.094230 -4.663689 -0.731903
H	0.649423	3.107902	0.793332	F	-2.876325 -1.345464 -3.921881
H	-0.752254	2.781475	1.809249	O	1.140764 -1.153376 0.839736
C	0.319855	0.733042	3.310618	H	0.915073 -1.870098 0.231346
H	-0.767609	0.771457	3.383536	H	0.548387 0.733034 -0.596953
H	0.642822	-0.292659	3.491626		

***u*-14**: E = -1119.5529407666 au

ZPE = 0.24863562 au

G_{corr} = 0.20627123 au

C	0.139465	-0.167056	0.118224	H	-3.261975	-1.629881	2.989710
P	-0.013111	-0.124330	1.955352	C	-0.502890	-1.417093	-0.456508
H	1.229588	-0.239132	-0.107912	C	0.068618	-2.671803	-0.259377
C	-1.719975	-0.183164	2.641905	C	-1.670248	-1.285263	-1.193367
O	-0.459218	0.995922	-0.075301	C	-0.562585	-3.775363	-0.791556
C	-1.593059	0.181229	4.129188	H	0.990648	-2.789814	0.297256
H	-2.592947	0.182226	4.566813	C	-2.257140	-2.424740	-1.709325
H	-0.989826	-0.530747	4.690239	H	-2.103938	-0.307170	-1.352627
H	-1.173851	1.178712	4.271591	C	-1.734107	-3.689036	-1.523443
C	-2.647010	0.824779	1.962738	H	-2.211193	-4.568500	-1.934737
H	-3.608955	0.793477	2.479121	F	-3.385325	-2.305423	-2.422047
H	-2.265099	1.842721	2.027704	F	-0.024516	-4.987456	-0.599886
H	-2.813216	0.593997	0.914889	O	0.737133	-1.226903	2.891908
C	-2.286258	-1.600137	2.501099	H	1.687382	-1.283500	2.730274
H	-2.432052	-1.882276	1.459307	H	0.528733	1.119896	2.295479
H	-1.658523	-2.352407	2.977271				

TS(***I*-14**→**15**+$C_6H_3F_2CHO$): E = -1195.9924651488 au
ZPE = 0.27228053 au
G_{corr} = 0.22603643 au
v = -191.03 cm^{-1}

C	-2.053005	0.194992	0.481168	C	-2.116460	-0.947542	-0.500643
P	0.156759	0.173820	0.679674	C	-2.212221	-0.685838	-1.861627
H	-2.281137	-0.150484	1.505421	C	-2.081065	-2.259387	-0.030728
C	0.920177	1.215381	1.986457	C	-2.261899	-1.757326	-2.731328
O	-2.370942	1.361021	0.134330	H	-2.249058	0.329179	-2.234622
C	2.437231	1.267955	1.801534	C	-2.138583	-3.290754	-0.946926
H	2.868084	1.915919	2.568546	H	-2.046486	-2.472166	1.032072
H	2.899794	0.286355	1.901580	C	-2.225681	-3.073259	-2.309286
H	2.712264	1.679535	0.829322	H	-2.271580	-3.894653	-3.011725
C	0.319204	2.616221	1.830429	F	-2.115762	-4.552241	-0.505123
H	0.774487	3.279197	2.568538	F	-2.352117	-1.519539	-4.043549
H	0.509830	3.037310	0.842200	O	0.972642	-1.236020	0.763385
H	-0.758173	2.622692	1.994263	H	0.457541	-1.978073	0.418283
C	0.561292	0.627543	3.351567	H	-1.441424	2.340257	-1.033356
H	-0.518374	0.585388	3.505679	O	-0.880354	2.877371	-1.621446
H	0.964079	-0.377144	3.482664	H	0.594326	0.801294	-0.507501
H	0.980965	1.256665	4.138883	H	-1.079467	3.784018	-1.378434

15: E = -575.5757446199 au
ZPE = 0.11787611 au
G_{corr} = 0.14974734 au

P	0.025602	0.207114	0.634949	C	0.282696	2.618709	1.846817
C	0.878463	1.213397	1.948949	H	0.713880	3.264316	2.615625
C	2.390500	1.266892	1.750121	H	0.492521	3.080156	0.879150
H	2.854072	1.866026	2.538940	H	-0.799932	2.616062	1.990649
H	2.838725	0.273639	1.786251	C	0.548565	0.601620	3.310629
H	2.653448	1.720450	0.792619	H	-0.528164	0.565935	3.488050

H	0.937391	-0.414334	3.399371	H	0.366335	-1.949265	0.756857
H	0.996873	1.195295	4.111115	H	0.624243	0.874545	-0.466507
O	0.934629	-1.189324	0.602124				

15·H2O: E = -652.0030226689 au
ZPE = 0.17486405 au
G_{corr} = 0.13957846 au

P	-0.024090	0.367210	0.080214	C	-0.885858	-1.059947	2.270990
C	0.004753	0.134830	1.929604	H	-1.908988	-0.915716	1.917417
C	1.416291	-0.097504	2.460087	H	-0.504811	-1.982743	1.829364
H	1.396600	-0.240894	3.544346	H	-0.927217	-1.207674	3.353138
H	1.870998	-0.984873	2.018870	O	0.875693	-0.903169	-0.475718
H	2.067847	0.753121	2.250851	H	0.308890	-1.464991	-1.048837
C	-0.581397	1.414078	2.527734	H	0.970733	1.381948	0.051094
H	-0.626184	1.335053	3.616758	O	-0.834053	-2.333894	-1.990654
H	0.027531	2.289348	2.289707	H	-1.539377	-2.664553	-1.426425
H	-1.595938	1.604473	2.170776	H	-1.269011	-1.715503	-2.585593

15·2H2O: E = -728.4608573025 au
ZPE = 0.19983544 au
G_{corr} = 0.16066210 au

P	-0.037170	0.420185	0.220598	H	1.548957	-0.281250	-2.170419
C	1.729139	0.029440	-0.018601	H	2.919752	-1.093145	-1.419471
C	2.496067	1.343992	-0.167138	O	-0.716700	1.166659	-0.905033
H	3.555041	1.133025	-0.327467	H	-1.202271	0.316268	-2.347286
H	2.140656	1.924160	-1.019353	H	-0.073775	1.099828	1.454580
H	2.414899	1.967064	0.725565	O	-1.451104	-0.277142	-3.085165
C	2.204901	-0.740929	1.213014	H	-1.253515	-1.868293	-2.231722
H	3.265763	-0.975169	1.107145	H	-2.394076	-0.139419	-3.207208
H	2.088954	-0.162119	2.131499	H	-0.622619	-0.819796	0.548572
H	1.673009	-1.686038	1.336297	O	-1.175830	-2.668823	-1.680220
C	1.871337	-0.822777	-1.280436	H	-1.888085	-2.590763	-1.042585
H	1.289957	-1.743663	-1.219447				

15·3H2O: E = -804.8916390709 au
ZPE = 0.22718892 au
G_{corr} = 0.18693597 au

P	0.447014	0.428354	-0.128063	C	-0.892038	-1.316590	1.516194
C	-0.032904	-0.054615	1.602954	H	-1.776960	-1.163312	0.894425
C	1.185862	-0.308979	2.484418	H	-0.331855	-2.157109	1.102704
H	0.873759	-0.611619	3.487889	H	-1.236471	-1.609375	2.510886
H	1.814272	-1.103448	2.080716	O	1.504326	-0.731739	-0.603168
H	1.800734	0.587352	2.585435	H	1.085602	-1.309478	-1.299323
C	-0.859841	1.107267	2.154104	H	1.354835	1.459311	0.222465
H	-1.204264	0.878362	3.165427	O	0.325737	-2.225017	-2.393752
H	-0.278046	2.030268	2.209309	H	-2.500919	-1.038188	-1.900105
H	-1.744270	1.303884	1.543634	H	0.496865	-1.874952	-3.272563

H	-1.673683	0.796149	-1.227248	O	-2.326689	-1.987513	-2.084280
O	-2.582761	0.663291	-1.549864	H	-0.653248	-2.167571	-2.275865
H	-2.628919	1.159585	-2.372602	H	-2.649265	-2.463995	-1.314841

TS(**15**→**9'**): E = -575.4729542440 au
ZPE = 0.14451319 au
G_{corr} = 0.11279587 au
ν = -1915.90 cm^{-1}

P	-0.621787	-0.998347	-1.224781	H	-1.801009	1.398721	0.032599
C	-0.021163	0.138554	0.090299	C	-0.339790	-0.481849	1.448776
C	1.490657	0.270273	-0.099504	H	-1.414790	-0.596798	1.596465
H	1.909531	0.884611	0.700757	H	0.123614	-1.462835	1.560060
H	1.988386	-0.700174	-0.063252	H	0.040846	0.158739	2.246945
H	1.740734	0.747487	-1.048653	O	0.120874	-2.415361	-1.197787
C	-0.718499	1.485970	-0.076181	H	-1.300422	-2.288534	-1.206914
H	-0.365007	2.181090	0.688218	H	-0.321556	-0.257505	-2.398154
H	-0.510619	1.935961	-1.048892				

TS(**15**→**9'**)·H2O: E = -651.9521948260 au
ZPE = 0.16986939 au
G_{corr} = 0.13624689 au
ν = -1609.15 cm^{-1}

P	0.118178	-0.131417	0.059127	C	-0.743297	-1.241599	2.404099
C	0.018623	-0.018084	1.896592	H	-1.757829	-1.280861	2.002680
C	1.427967	0.011572	2.485182	H	-0.237598	-2.169120	2.132204
H	1.378533	0.058780	3.576067	H	-0.818605	-1.211433	3.493428
H	1.992304	-0.882061	2.216311	O	0.944501	-1.388000	-0.404642
H	1.990471	0.881784	2.141576	H	-0.087058	-1.890509	-1.201698
C	-0.736142	1.265553	2.238909	H	0.826244	1.065720	-0.228759
H	-0.829281	1.365541	3.322662	O	-1.107148	-1.817276	-1.586320
H	-0.216221	2.153557	1.872972	H	-1.122670	-0.748191	-0.934199
H	-1.744337	1.268565	1.819865	H	-1.054224	-1.583918	-2.522331

TS(**15**→**9'**)·2H2O: E = -728.4105991832 au
ZPE = 0.19575852 au
G_{corr} = 0.15954489 au
ν = -892.30 cm^{-1}

P	0.025275	0.080092	-0.208301	C	2.396461	-0.710576	-1.330060
C	1.871463	-0.007054	-0.079034	H	2.005540	-1.726929	-1.415175
C	2.454992	1.400296	0.015592	H	2.121024	-0.169145	-2.236536
H	3.546951	1.359453	0.055931	H	3.486867	-0.777156	-1.301400
H	2.176214	2.004730	-0.848375	O	-0.387355	1.028993	-1.382587
H	2.109791	1.918404	0.912680	H	-1.245863	0.269049	-2.312011
C	2.212675	-0.816836	1.169719	H	-0.225698	0.737661	1.033763
H	3.296119	-0.912914	1.274944	O	-1.835964	-0.418300	-2.823847
H	1.837829	-0.339097	2.077749	H	-1.780626	-1.504243	-1.945958
H	1.796790	-1.825865	1.125397	H	-2.724806	-0.048858	-2.844638

H	-0.866742	-1.482252	-0.541299	H	-2.345624 -2.340089 -0.631906
O	-1.542023	-2.188067	-1.148927		

TS(**15**→**9'**)·3H2O: E = -804.8571306167 au
ZPE = 0.22184335 au
G_{corr} = 0.18364094 au
ν = -388.34 cm^{-1}

P	0.210018	0.249800	-0.084894	H	-1.045401 -1.520189 2.955181
C	-0.049613	-0.028363	1.734574	O	1.154423 -0.855404 -0.650587
C	1.293129	-0.176162	2.443914	H	0.550766 -1.808015 -1.629248
H	1.146865	-0.382285	3.508066	H	0.960875 1.462449 0.031164
H	1.875136	-0.996590	2.022266	O	0.121698 -2.432285 -2.320080
H	1.890703	0.734230	2.362155	H	-2.371894 -0.472760 -2.111594
C	-0.820490	1.169789	2.282913	H	0.657707 -2.347535 -3.113780
H	-1.023529	1.038897	3.348895	H	-1.449638 0.471856 -0.963451
H	-0.257893	2.099356	2.169662	O	-2.403957 0.452901 -1.527734
H	-1.782253	1.297896	1.780443	H	-2.395195 1.204369 -2.136995
C	-0.871246	-1.306874	1.897399	O	-2.233837 -1.623289 -2.777286
H	-1.847192	-1.223270	1.413305	H	-1.285581 -1.980887 -2.618005
H	-0.357340	-2.167768	1.466159	H	-2.841917 -2.287181 -2.434125

9': E = -575.5757446199 au
ZPE = 0.14913877 au
G_{corr} = 0.11757165 au

P	0.703791	-0.309908	0.839848	H	-1.084288 1.810265 1.802415
C	0.983436	1.115626	1.949531	C	0.851002 0.631941 3.393914
C	2.390753	1.654880	1.691835	H	-0.146856 0.240668 3.601557
H	2.588685	2.499824	2.354366	H	1.575543 -0.149625 3.624898
H	3.152902	0.898161	1.880818	H	1.028313 1.463649 4.078660
H	2.509456	2.006072	0.664933	O	1.638328 -1.474482 0.991285
C	-0.069697	2.176811	1.634526	H	-0.665146 -0.604923 1.034243
H	0.075965	3.042334	2.283866	H	0.679874 0.281829 -0.444002
H	-0.002211	2.528110	0.603020		

TS(**4a'**+HCl·OMe_2→**17**+Me_2O): E = -1658.9024341321 au
ZPE = 0.27348297 au
G_{corr} = 0.32080483 au
ν = -225.75 cm^{-1}

C	0.511535	-0.133438	0.581481	C	4.210416 1.900518 1.070869
O	0.647109	0.122282	1.967094	H	4.559617 2.935633 1.070244
P	2.184383	0.066663	1.166663	H	4.613139 1.419871 1.965600
H	0.055732	0.671205	0.003370	H	4.625228 1.397852 0.198818
C	2.678529	1.878579	1.057554	C	2.154106 2.566698 -0.198559
C	2.162345	2.597201	2.306357	H	2.470455 2.039793 -1.097579
H	2.550044	3.618847	2.311648	H	1.065420 2.636149 -0.202433
H	1.075362	2.654703	2.331018	H	2.541339 3.588223 -0.244218
H	2.496807	2.117439	3.228437	C	0.066046 -1.492638 0.190023

C	-0.326242	-2.418941	1.151129	H	3.416686	-1.739897	0.818124
C	0.078804	-1.840379	-1.159422	O	3.856340	-2.638761	0.947045
C	-0.713596	-3.678124	0.732698	C	5.296514	-2.507016	0.770649
H	-0.340449	-2.163886	2.202022	H	5.513808	-2.269483	-0.266525
C	-0.314741	-3.111748	-1.515915	H	5.614380	-1.705165	1.428885
H	0.415748	-1.137036	-1.909023	H	5.738510	-3.449497	1.075772
C	-0.716624	-4.062597	-0.593470	C	3.215026	-3.629764	0.092429
H	-1.022673	-5.054625	-0.897567	H	2.155891	-3.597290	0.326661
F	-0.301058	-3.455186	-2.810183	H	3.392664	-3.377735	-0.948871
F	-1.103781	-4.570180	1.652540	H	3.634827	-4.593772	0.358923
Cl	3.469583	-0.552391	-1.267589				

17: E = -1503.9266567044 au
ZPE = 0.19404210 au
G_{corr} = 0.23658120 au

C	0.419892	-0.160673	0.237691	H	1.106543	2.857313	-0.067994
O	0.648947	0.189113	1.602039	H	2.592166	3.792614	0.024465
P	2.100692	0.152204	0.644062	C	-0.014422	-1.549352	-0.057756
H	-0.099827	0.594162	-0.358434	C	-0.181881	-2.470493	0.969179
C	2.772115	1.857775	0.934010	C	-0.229812	-1.916131	-1.383354
C	2.354600	2.319235	2.332808	C	-0.573420	-3.753472	0.638765
H	2.809956	3.293840	2.516469	H	-0.020342	-2.196216	2.002839
H	1.277971	2.430607	2.432891	C	-0.614205	-3.212882	-1.651539
H	2.707291	1.641930	3.111960	H	-0.100684	-1.204991	-2.189008
C	4.300849	1.829643	0.861139	C	-0.796558	-4.161097	-0.661450
H	4.670765	2.809885	1.166167	H	-1.101783	-5.172328	-0.894891
H	4.730725	1.092800	1.541762	F	-0.822780	-3.575405	-2.922066
H	4.670828	1.630722	-0.140563	F	-0.745990	-4.645393	1.621022
C	2.193586	2.788531	-0.131092	Cl	3.252150	-0.325479	-1.221052
H	2.465610	2.473562	-1.137999	H	2.755871	-0.864159	1.336901

TS(**17**→**16'**+$C_6H_3F_2CHO$): E = -1503.9085645089 au
ZPE = 0.19231871 au
G_{corr} = 0.23489300 au
v = -136.29 cm^{-1}

C	0.214715	-0.104517	0.679058	H	2.699455	2.381664	-1.295562
O	0.202854	0.118627	1.951201	H	1.244977	2.785130	-0.372307
P	2.140256	0.101897	0.478097	H	2.719705	3.719057	-0.152569
H	-0.221778	0.646399	-0.010799	C	-0.093012	-1.494154	0.164668
C	2.795671	1.803807	0.814642	C	-0.190741	-2.537978	1.074096
C	2.265894	2.316775	2.156810	C	-0.268523	-1.718167	-1.197111
H	2.714346	3.296342	2.335060	C	-0.464609	-3.802880	0.591792
H	1.185680	2.428400	2.164811	H	-0.064460	-2.359523	2.133588
H	2.547637	1.665829	2.983878	C	-0.537602	-3.001812	-1.622343
C	4.324123	1.737096	0.872446	H	-0.203078	-0.906586	-1.911727
H	4.699211	2.730523	1.125628	C	-0.642582	-4.071600	-0.751394
H	4.673409	1.047668	1.642327	H	-0.859248	-5.070438	-1.106080
H	4.770806	1.450270	-0.077786	F	-0.710806	-3.230406	-2.930036
C	2.332428	2.713402	-0.324140	F	-0.565472	-4.818227	1.458782

Cl	3.181215	-0.535497	-1.191985	H	2.638385	-0.745234	1.473925

16': E = -959.9266298127 au
ZPE = 0.10432762 au
G_{corr} = 0.13664482 au

P	0.014406	-0.036144	0.047028	H	-0.314674	2.137674	2.150262
C	-0.045682	-0.009254	1.911077	H	-1.822958	1.220408	2.186865
C	1.432194	0.021859	2.319144	C	-0.696629	-1.303516	2.395463
H	1.507930	-0.007371	3.408340	H	-1.744088	-1.363583	2.096867
H	1.986560	-0.834276	1.929659	H	-0.183793	-2.186228	2.009261
H	1.931024	0.933065	1.982459	H	-0.661534	-1.349875	3.486092
C	-0.773001	1.203491	2.478606	Cl	-2.002176	0.207181	-0.467390
H	-0.734925	1.179781	3.570636	H	0.388163	1.317396	-0.129526

4a''·NHC^{Me2}: E = -1229.957666010 au
ZPE = 0.270087350 au
G_{corr} = 0.22488112 au

C	0.057022	-0.156420	-0.128201	H	3.450081	1.304479	0.576674
O	-0.009674	0.115538	1.235286	H	1.919978	2.027179	0.065702
P	1.680188	-0.395110	0.598927	C	2.941282	-0.829362	-1.061786
H	-0.102079	0.705900	-0.792018	N	3.690302	-1.944491	-1.088920
C	2.375246	1.312647	0.752620	C	4.140054	-2.211355	-2.359142
C	-0.650935	-1.364480	-0.634140	C	3.650167	-1.236482	-3.151453
C	-1.222330	-2.264537	0.259439	N	2.920430	-0.404107	-2.336524
C	-0.714533	-1.611939	-2.005031	C	4.031508	-2.749862	0.066631
C	-1.834748	-3.395582	-0.240723	H	3.964737	-3.804388	-0.190221
H	-1.187715	-2.074475	1.323466	H	5.042456	-2.526837	0.403012
C	-1.333316	-2.760829	-2.448942	H	3.332275	-2.533831	0.868893
H	-0.294570	-0.913774	-2.718482	C	2.263183	0.793286	-2.811783
C	-1.907245	-3.681112	-1.591378	H	1.609190	0.556643	-3.648838
H	-2.393297	-4.574536	-1.958762	H	1.667473	1.218926	-2.013290
F	-1.388499	-2.999842	-3.767259	H	2.998295	1.528961	-3.133186
F	-2.389177	-4.263590	0.615951	H	4.757707	-3.061639	-2.592229
H	2.191958	1.667195	1.765231	H	3.754745	-1.072758	-4.210366

TS(**4a''**·NHC^{Me2}→**18''**): E = -1229.958195202 au
ZPE = 0.27006599 au
G_{corr} = 0.22613857 au
ν = -77.46 cm^{-1}

C	0.061392	-0.140573	-0.169798	C	-1.758127	-3.422874	-0.050590
O	-0.080774	0.262119	1.136313	H	-1.293501	-1.885209	1.379983
P	1.719954	-0.300640	0.506990	C	-1.034950	-3.069405	-2.261209
H	-0.105849	0.632193	-0.941895	H	-0.001760	-1.243080	-2.667382
C	2.332492	1.440419	0.601950	C	-1.682027	-3.885667	-1.350972
C	-0.574196	-1.426873	-0.589671	H	-2.111754	-4.833988	-1.643420
C	-1.219421	-2.218107	0.353615	F	-0.944671	-3.484575	-3.533934
C	-0.486731	-1.853543	-1.914947	F	-2.385876	-4.188141	0.852928

H	2.190528	1.792273	1.621362	H	3.126059	-3.924141	-0.491317
H	3.396540	1.489223	0.369566	H	4.603191	-3.137694	0.102236
H	1.796271	2.120531	-0.059408	H	3.017644	-2.638837	0.720320
C	2.873373	-0.781695	-1.088887	C	2.529754	1.105993	-2.660909
N	3.444824	-1.990103	-1.206724	H	2.491899	1.187258	-3.743468
C	3.926119	-2.184061	-2.476818	H	1.532086	1.271987	-2.266362
C	3.640404	-1.063270	-3.171409	H	3.199726	1.868956	-2.271077
N	2.992355	-0.219819	-2.304055	H	4.419675	-3.091419	-2.779263
C	3.557389	-2.983938	-0.155421	H	3.838122	-0.803887	-4.197169

18“:

E = -685.964911969 au
ZPE = 0.17255463 au
G_{corr} = 0.13772435 au

P	-0.188436	0.103328	-0.136572	H	-2.987568	-0.340549	2.038841
C	-0.120931	-0.064786	1.685356	H	-2.496594	1.363600	1.932924
N	1.051547	-0.322721	2.293559	H	-2.832221	0.633902	3.503156
C	0.889730	-0.322871	3.653167	C	-1.981465	-0.160607	-0.522431
C	-0.414845	-0.081194	3.892131	H	-2.350825	-1.107976	-0.125158
N	-1.025266	0.077027	2.670939	H	-2.635608	0.652345	-0.216353
C	2.322475	-0.403397	1.607862	H	-2.031271	-0.224076	-1.609862
H	3.084584	-0.718326	2.314605	P	0.308122	2.181741	-0.281892
H	2.569103	0.576245	1.196469	C	1.636726	2.040737	-1.611922
H	2.263483	-1.119167	0.790963	H	2.438742	1.345342	-1.360382
H	1.707307	-0.493731	4.331071	H	1.244659	1.763536	-2.591455
H	-0.956722	-0.008835	4.818684	H	2.090703	3.028249	-1.717044
C	-2.416592	0.450789	2.516826				

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