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Supporting Information

The chemistry of phosphirane-substituted phosphinidene complexes

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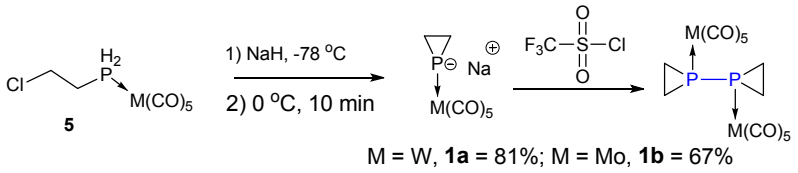
General information

All reactions were performed under nitrogen using solvents dried by standard methods except for special statement. Tetrahydrofuran (THF), toluene and ether were dried with sodium and distilled before use. NMR spectra were obtained using Bruker AV300 spectrometer. All spectra were recorded in $CDCl_3$. All coupling constants (*J* values) were reported in hertz (Hz). Chemical shifts were expressed in parts per million (ppm) downfield from internal TMS (^1H). HRMS spectra were obtained on an Agilent 1290-6540 UHPLC Q-T of HRMS spectrometer. Element analyses were performed on a Thermo Flash EA 1112 automatic element analyzer. X-ray crystallographic analyses were performed on an Oxford diffraction Gemini E diffractometer. Silica gel (200-300 mesh) was used for the chromatographic separations. All commercially available reagents were used without further purification. All new compounds were synthetic in small scale, and were purified by column chromatography. The purities of the new compounds are acceptable according to NMR spectra analysis.

Experimental Procedures and Characterization Data

The preparation of 1a and 1b



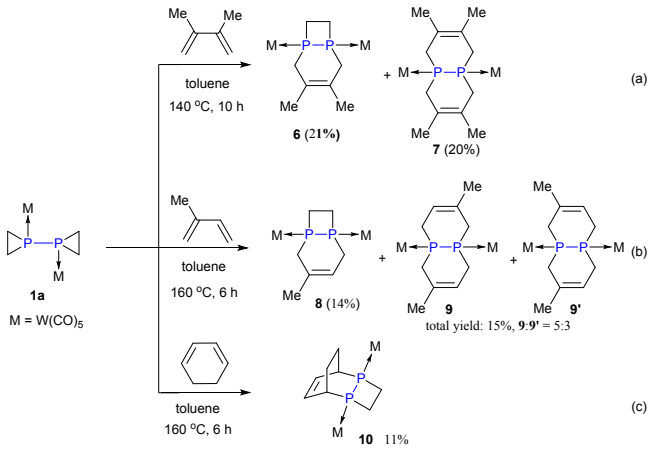
M = W, **1a** = 81%; M = Mo, **1b** = 67%

NaH (160 mg, 4 mmol, 60% dispersion in mineral oil) was added to the solution of 2-chloroethylphosphine $M(CO)_5$ complex **5** (1 mmol) in THF (20 mL) at -78 °C. Then the mixture was stirred vigorously in an ice bath for 10 min, produced phosphiranide complex. Trifluoromathanesulfonyl chloride (4 mmol, 426 μL) was added to the solution of phosphiranide complex at -50 °C. The solution was warmed

slowly to r.t. The solvent was removed by rotary evaporation. Purification was performed via column chromatography on silica using 10/1 petroleum ether /dichloromethane, to give a light green solid **1a** (311 mg, 81%), whiteness solid **1b** (200 mg, 67%)

1a: ^{31}P NMR ($CDCl_3$): δ -193.1 (J_{PW1} = 153.1 Hz, J_{PW2} = 99.6 Hz), ^{1}H NMR ($CDCl_3$): δ 1.57-1.61 (m, 4H, CH_2), 1.74-1.76 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 13.3 (t, *J* = 9.8 Hz, CH_2), 194.5 (t, *J* = 2.3 Hz CO *cis*), 195.7 (t, *J* = 13.6 Hz, CO *trans*). HRMS: m/z calcd for $C_{14}H_9O_{10}P_2W_2$ $[M+H]^+$ 766.8684, found 766.8680.

1b: ^{31}P NMR ($CDCl_3$): δ -171.1. ^{1}H NMR ($CDCl_3$): δ 1.39-1.48 (m, 4H, CH_2), 1.63-1.68 (m, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 11.8 (t, *J* = 7.6 Hz, CH_2), 203.68 (t, *J* = 9.1 Hz, CO *cis*), 207.08 (t, *J* = 18.9 Hz, CO *trans*). Anal. Calcd for $C_{14}H_8Mo_2O_{10}P_2$: C, 28.50; H, 1.37. Found: C, 28.25; H, 1.584.



General procedure for the thermolysis of 1,1'-biphosphirane $W(CO)_5$ complex **1a** with conjugated dienes.

A solution of biphosphirane $W(CO)_5$ complex **1a** (0.5 mmol) and conjugated diene (2 mmol) in toluene (10 mL) was stirred at 140 °C for 10 h (2,3-dimethyl-1,3-butadiene) or 160 °C for 6 h (2-methyl-1,3-butadiene and 1,3-cyclohexadiene) in a heavy wall pressure tube. The solution was cooled to room temperature. All volatile were

removed by rotary evaporation. The products were purified by chromatography on silica gel (petroleum ether/dichloromethane: 5/1). Single crystals of **6** and **7** suitable for X-ray analysis were grown from a mixture of *n*-hexane and ethyl acetate.

6: yellow solid, Yield: 86 mg (21 %)**.** ^{31}P NMR ($CDCl_3$): δ 21.33 (J_{PW1} = 267.3 Hz, J_{PW2} = 196.8 Hz), ^{1}H NMR ($CDCl_3$): δ 2.05 (s, 6H, CH_3), 2.58-2.64 (m, 2H, CH_2), 2.82-2.93 (m, 4H, CH_2), 3.07-3.15 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 22.5 (s, CH_3), 27.8 (dd, *J* = 13.4, 12.2 Hz), 41.2 (s, CH_2), 128.4 (t, *J* = 6.0, =C), 195.8 (t, *J* = 2.2 Hz, CO *cis*), 198.3 (t, *J* = 9.8 Hz, CO *trans*). HRMS: m/z calcd for $C_{18}H_{15}O_{10}P_2W_2$ $[M+H]^+$ 820.9154, found 820.9152.

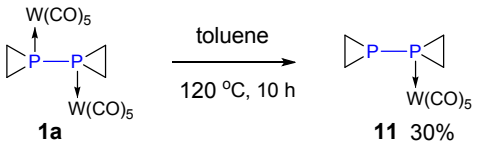
7: yellow solid**,** Yield: 87 mg (20 %). ^{31}P NMR ($CDCl_3$): δ -27.45 (J_{PW1} = 157.9 Hz, J_{PW2} = 94.5 Hz). ^{1}H NMR ($CDCl_3$): δ 1.86 (s, 12H, CH_3), 2.70 (d, *J* = 15.0 Hz, 4H, CH_2), 2.96 (d, *J* = 9.0 Hz, 4H, CH_2). ^{13}C NMR ($CDCl_3$): δ 22.0 (s, CH_3), 36.4 (s, CH_2), 125.5 (s, =C), 196.6 (t, *J* = 3.0 Hz, CO *cis*), 197.5 (d, *J* = 10.5 Hz, CO *trans*). HRMS: m/z calcd for $C_{22}H_{21}O_{10}P_2W_2$ $[M+H]^+$ 874.9623, found 874.9628.

8: brown solid, Yield: 56 mg (14 %). ^{31}P NMR ($CDCl_3$): δ 20.18 (d, J_{pp} = 41.0 Hz, J_{PW1} = 269.7, J_{PW2} = 183.5), 23.81 (d, J_{pp} = 41.3 Hz, J_{PW1} = 269.7, J_{PW2} = 184.7). ^{1}H NMR ($CDCl_3$): δ 2.08 (d, *J* = 1.6 Hz, 3H, CH_3), 2.58-2.81 (m, 2H, CH_2), 2.84-2.95 (m, 4H, CH_2), 3.02-3.18 (m, 2H, CH_2), 6.05 (bs, 1H, =CH). ^{13}C NMR ($CDCl_3$): δ 26.4 (t, *J* = 2.4 Hz, CH_3), 27.3 (dd, *J* = 30.1 Hz, *J* = 3.8 Hz, CH_2), 28.3 (dd, *J* = 30.0 Hz, *J* = 4.5 Hz, CH_2), 34.3 (t, *J* = 3.3 Hz, CH_2), 39.3 (t, *J* = 2.1 Hz, CH_2), 121.0 (t, *J* = 8.5 Hz, =CH), 137.4-137.6 (m, =C), 195.8 (tt, *J* = 6.75 Hz, *J* = 1.5 Hz CO *cis*), 198.0-198.7(m, CO *trans*). HRMS: m/z calcd for $C_{17}H_{11}O_{10}P_2W_2$ $[M-H]^-$ 804.8852, found 804.8867.

9 and **9'** were isolated as a mixture**:** light pink solid, Yield: 64 mg (15 %). ^{31}P NMR ($CDCl_3$): **9**, δ -52.08 (J_{PW1} = 162.1 Hz, J_{PW2} = 82.2 Hz). **9'**, δ -55.86 (d, J_{PP} = 151.3 Hz), - 48.84 (d, J_{PP} = 151.3 Hz). ^{1}H NMR ($CDCl_3$): 1.86 (s, 6H, CH_3), 2.62-2.77 (m, 4H, CH_2), 2.91-3.07 (m, 4H, CH_2), 5.61 (d, *J* = 16.6 Hz, 1H, =CH). ^{13}C NMR

($CDCl_3$): **9**, δ 27.02 (d, J = 2.7 Hz, CH_3), 28.1 (*pseudo*-t, J = 8.0 Hz, CH_2), 32.0 (*pseudo*-t, J = 7.6 Hz, CH_2), 117.3 (d, J = 2.3 Hz, CH), 131.4 (d, J = 1.3 Hz, C), 195.9 (d, J = 2.6 Hz, CO *cis*), 197.2 (d, J = 13.2 Hz, CO *trans*). **9'**, 26.95 (d, J = 2.0 Hz, CH_3), 27.5 (d, J = 15.8 Hz, CH_2), 32.6 (d, J = 15.4 Hz, CH_2), 117.5 (d, J = 6.8 Hz, CH), 131.1 (dd, J = 8.5 Hz, J =5.7 Hz, C), 195.8 (d, J = 2.6 Hz, CO *cis*), 196.9 (d, J = 20.6 Hz, CO *trans*). HRMS: m/z calcd for $C_{20}H_{15}O_{10}P_2W_2$ $[M-H]^-$ 844.9165, found 844.9168.

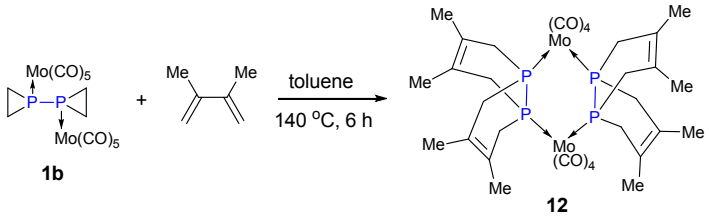
10: yellow solid, Yield: 45 mg (11 %). ^{31}P NMR ($CDCl_3$): δ 31.01 (J_{PW1} = 292.8 Hz, J_{PW2} = 183.5 Hz). ^1H NMR ($CDCl_3$): δ 1.77-1.91 (m, 4H, CH_2), 2.64-2.78 (m, 4H, CH_2), 3.53 (s, 2H, CH), 6.79-6.82 (m, 2H, CH). ^{13}C NMR ($CDCl_3$): δ 21.5 (t, J = 5.3 Hz, CH_2), 29.6 (t, J = 10.6 Hz, CH_2), 38.8 (s, CH), 132.5 (s, CH), 195.6 (t, J = 2.3 Hz, CO *cis*), 197.9 (t, J = 9.8 Hz, CO *trans*). HRMS: m/z calcd for $C_{18}H_{13}O_{10}P_2W_2$ $[M+H]^+$ 818.8997, found 818.9005.



1a **11** 30%

A solution of biphosphirane $W(CO)_5$ complex **1a** (383 mg, 0.5 mmol) in toluene (10 mL) was stirred at 120 °C for 10 h in a heavy wall pressure tube. The solution was cooled to room temperature. The solvent was removed by rotary evaporation. The products were purified by chromatography on silica gel (petroleum ether / dichloromethane: 15 / 1), to give **11** as a yellow oil (66 mg, 30%).

11: ^{31}P NMR ($CDCl_3$): δ -278.3 (d, J_{pp}= 277.1), -205.7 (d, J_{pp}= 277.1, J_{pw}= 219.0). ^1H NMR ($CDCl_3$): δ 1.21-1.33 (m, 4H, CH_2), 1.38-1.46 (m, 2H, CH_2), 1.58-1.65 (m, 2H, CH_2). ^{13}C NMR ($CDCl_3$): δ 9.2 (d, J = 42.3 Hz, CH_2), 11.1 (dd, J = 15.0 Hz, J = 12.8 Hz, CH_2), 195.4 (d, J = 7.3 Hz, CO *cis*), 196.8 (d, J = 31.3 Hz, CO *trans*).



A solution of biphosphirane $Mo(CO)_5$ complex **1b** (297 mg, 0.5 mmol) and 2,3-dimethyl-1,3-butadiene (0.23 mL, 2 mmol) in toluene (10 mL) was stirred at 140 °C for 6 h in a heavy wall pressure tube. The solution was cooled to room temperature. All volatiles were removed by rotary evaporation. The product was purified by chromatography on silica gel (petroleum ether / dichloromethane: 5 / 1). Single crystal of **12** suitable for X-ray analysis was grown from a mixture of n-hexane and ethyl acetate.

12: yellow solid, Yield: 96 mg (22 %). ^{31}P NMR ($CDCl_3$): δ -18.96. ^{1}H NMR ($CDCl_3$): δ 1.86 (s, 24H, CH_3), 2.47 (d, J = 14.1 Hz, CH_2, 8H), 2.70 (d, J = 14.1 Hz, CH_2, 8H). ^{13}C NMR ($CDCl_3$): δ 21.4 (s, CH_3), 35.7 (s, CH_2), 126.2 (s, =C), 207.8 - 208.1 (m, CO *cis*), 213.1-213.3 (m, CO *trans*). HRMS: m/z calcd for $C_{32}H_{41}Mo_2O_8P_4$ $[M+H]^+$ 872.9855, found 872.9845.

X-ray Diffraction Data

X-ray crystallographic data of 6

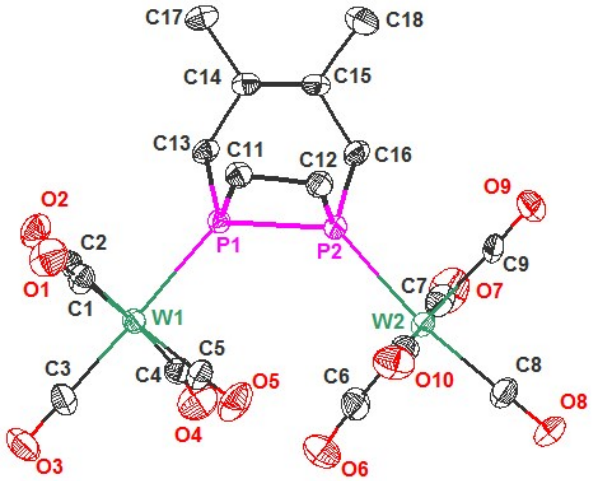


Figure S1 X-ray structure of **6**

Table S1 Crystal data and structure refinement for 6.

Identification code	**6**
Empirical formula	$C_{18}H_{14}O_{10}P_2W_2$
Formula weight	819.93
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	25.4396(4)
b/Å	10.82292(16)
c/Å	18.9442(3)
α/°	90
β/°	111.4853(19)
γ/°	90
Volume/Å^3	4853.46(15)
Z	8
ρ_{calc}g/cm^3	2.244
μ/mm^{-1}	18.960
F(000)	3040.0
Crystal size/mm^3	0.3321 × 0.1992 × 0.1181
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.47 to 134.142

Index ranges	$-30 \le h \le 30, -7 \le k \le 12, -22 \le l \le 22$
Reflections collected	20747
Independent reflections	8648 [R_{int} = 0.0536, R_{sigma} = 0.0592]
Data/restraints/parameters	8648/0/581
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0412, wR_2 = 0.0989
Final R indexes [all data]	R_1 = 0.0525, wR_2 = 0.1085
Largest diff. peak/hole / e $Å^{-3}$	1.19/-1.09

Table S2 Bond Lengths for 6

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	O1	1.128(12)	C1'	O1'	1.134(12)
C1	W1	2.040(10)	C1'	W1'	2.038(10)
C2	O2	1.136(11)	C2'	O2'	1.129(12)
C2	W1	2.034(9)	C2'	W1'	2.052(10)
C3	O3	1.154(11)	C3'	O3'	1.116(11)
C3	W1	1.992(9)	C3'	W1'	2.015(9)
C4	O4	1.119(11)	C4'	O4'	1.123(12)
C4	W1	2.059(9)	C4'	W1'	2.047(9)
C5	O5	1.110(11)	C5'	O5'	1.127(13)
C5	W1	2.059(9)	C5'	W1'	2.035(10)
C6	O6	1.134(12)	C6'	O6'	1.118(14)
C6	W2	2.050(10)	C6'	W2'	2.057(13)
C7	O7	1.102(13)	C7'	O7'	1.116(13)
C7	W2	2.067(11)	C7'	W2'	2.061(11)
C8	O8	1.130(11)	C8'	O8'	1.150(13)
C8	W2	2.008(10)	C8'	W2'	1.990(10)
C9	O9	1.112(11)	C9'	O9'	1.139(13)
C9	W2	2.047(9)	C9'	W2'	2.013(11)
C10	O10	1.111(12)	C10'	O10'	1.117(15)
C10	W2	2.046(10)	C10'	W2'	2.037(12)
C11	C12	1.566(11)	C11'	C12'	1.551(13)
C11	P1	1.864(8)	C11'	P1'	1.877(9)
C12	P2	1.850(8)	C12'	P2'	1.858(9)
C13	C14	1.494(11)	C13'	C14'	1.516(12)
C13	P1	1.850(8)	C13'	P1'	1.837(8)
C14	C15	1.353(13)	C14'	C15'	1.324(13)

C14	C17	1.510(12)	C14'	C17'	1.517(13)
C15	C16	1.512(12)	C15'	C16'	1.501(14)
C15	C18	1.517(13)	C15'	C18'	1.511(14)
C16	P2	1.856(9)	C16'	P2'	1.853(10)
P1	P2	2.225(3)	P1'	P2'	2.225(3)
P1	W1	2.498(2)	P1'	W1'	2.472(2)
P2	W2	2.495(2)	P2'	W2'	2.493(2)

Table S3 Bond Angles for 6

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	W1	175.5(10)	O1'	C1'	W1'	179.1(11)
O2	C2	W1	177.1(8)	O2'	C2'	W1'	178.1(9)
O3	C3	W1	178.5(9)	O3'	C3'	W1'	178.7(10)
O4	C4	W1	174.2(9)	O4'	C4'	W1'	178.1(10)
O5	C5	W1	178.1(10)	O5'	C5'	W1'	177.6(13)
O6	C6	W2	175.3(10)	O6'	C6'	W2'	176.2(11)
O7	C7	W2	178.0(12)	O7'	C7'	W2'	178.5(11)
O8	C8	W2	179.1(11)	O8'	C8'	W2'	179.5(14)
O9	C9	W2	179.5(9)	O9'	C9'	W2'	179.6(12)
O10	C10	W2	178.1(9)	O10'	C10'	W2'	178.5(16)
C12	C11	P1	99.6(5)	C12'	C11'	P1'	99.2(6)
C11	C12	P2	100.7(5)	C11'	C12'	P2'	101.5(6)
C14	C13	P1	115.7(6)	C14'	C13'	P1'	116.8(6)
C13	C14	C17	115.8(8)	C13'	C14'	C17'	116.0(8)
C15	C14	C13	120.5(8)	C15'	C14'	C13'	120.2(9)
C15	C14	C17	123.7(8)	C15'	C14'	C17'	123.8(9)
C14	C15	C16	120.3(8)	C14'	C15'	C16'	121.0(9)
C14	C15	C18	125.4(9)	C14'	C15'	C18'	124.4(10)
C16	C15	C18	114.3(9)	C16'	C15'	C18'	114.5(9)
C15	C16	P2	117.2(6)	C15'	C16'	P2'	115.5(7)
C11	P1	P2	79.8(3)	C11'	P1'	P2'	79.9(3)
C11	P1	W1	119.4(3)	C11'	P1'	W1'	124.8(3)
C13	P1	C11	105.9(4)	C13'	P1'	C11'	105.0(4)
C13	P1	P2	100.2(3)	C13'	P1'	P2'	101.0(3)
C13	P1	W1	117.3(3)	C13'	P1'	W1'	115.7(3)
P2	P1	W1	127.27(10)	P2'	P1'	W1'	123.62(11)

C12	P2	C16	104.3(4)	C12'	P2'	P1'	79.2(3)
C12	P2	P1	79.7(3)	C12'	P2'	W2'	118.3(3)
C12	P2	W2	119.4(3)	C16'	P2'	C12'	106.0(5)
C16	P2	P1	100.0(3)	C16'	P2'	P1'	98.8(3)
C16	P2	W2	112.5(3)	C16'	P2'	W2'	114.8(3)
P1	P2	W2	134.53(11)	P1'	P2'	W2'	132.99(12)
C1	W1	C4	174.2(4)	C1'	W1'	C2'	86.4(4)
C1	W1	C5	89.8(4)	C1'	W1'	C4'	175.8(4)
C1	W1	P1	90.7(3)	C1'	W1'	P1'	89.9(3)
C2	W1	C1	89.0(4)	C2'	W1'	P1'	91.3(3)
C2	W1	C4	89.9(4)	C3'	W1'	C1'	90.0(4)
C2	W1	C5	176.9(4)	C3'	W1'	C2'	89.3(4)
C2	W1	P1	88.0(2)	C3'	W1'	C4'	90.3(4)
C3	W1	C1	86.9(4)	C3'	W1'	C5'	92.6(4)
C3	W1	C2	91.8(4)	C3'	W1'	P1'	179.4(3)
C3	W1	C4	87.4(4)	C4'	W1'	C2'	89.4(4)
C3	W1	C5	91.0(4)	C4'	W1'	P1'	89.8(3)
C3	W1	P1	177.6(3)	C5'	W1'	C1'	95.0(5)
C4	W1	C5	91.5(4)	C5'	W1'	C2'	177.6(4)
C4	W1	P1	95.0(3)	C5'	W1'	C4'	89.2(5)
C5	W1	P1	89.2(3)	C5'	W1'	P1'	86.8(3)
C6	W2	C7	89.9(4)	C6'	W2'	C7'	91.2(5)
C6	W2	P2	98.7(3)	C6'	W2'	P2'	98.0(3)
C7	W2	P2	90.2(3)	C7'	W2'	P2'	89.0(3)
C8	W2	C6	89.6(4)	C8'	W2'	C6'	88.7(5)
C8	W2	C7	89.7(4)	C8'	W2'	C7'	90.7(5)
C8	W2	C9	88.2(4)	C8'	W2'	C9'	89.0(5)
C8	W2	C10	90.6(4)	C8'	W2'	C10'	90.3(6)
C8	W2	P2	171.7(3)	C8'	W2'	P2'	173.3(4)
C9	W2	C6	177.8(4)	C9'	W2'	C6'	177.3(4)
C9	W2	C7	89.5(4)	C9'	W2'	C7'	90.1(5)
C9	W2	P2	83.4(2)	C9'	W2'	C10'	89.1(5)
C10	W2	C6	89.4(4)	C9'	W2'	P2'	84.3(3)
C10	W2	C7	179.3(4)	C10'	W2'	C6'	89.6(6)
C10	W2	C9	91.2(4)	C10'	W2'	C7'	178.7(5)
C10	W2	P2	89.7(3)	C10'	W2'	P2'	89.9(4)

X-ray crystallographic data of 7

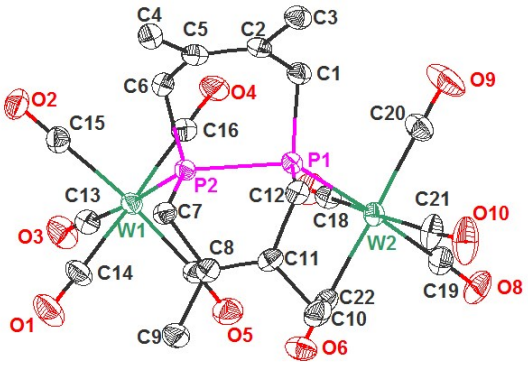


Figure S2 X-ray structure of **7**

Table S4 Crystal data and structure refinement for 7.

Identification code	**7**
Empirical formula	$C_{22}H_{20}O_{10}P_2W_2$
Formula weight	874.02
Temperature/K	200.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.8615(2)
b/Å	14.1665(2)
c/Å	17.7114(3)
α/°	90
β/°	90.165(2)
γ/°	90
Volume/Å^3	2725.23(8)
Z	4
ρ_{calc}g/cm^3	2.130
μ/mm^{-1}	16.937
F(000)	1640.0
Crystal size/mm^3	0.4 × 0.3 × 0.2
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.992 to 146.786
Index ranges	$-13 \le h \le 13$, $-17 \le k \le 13$, $-21 \le l \le 21$
Reflections collected	22522
Independent reflections	5377 [R_{int} = 0.0586, R_{sigma} = 0.0364]
Data/restraints/parameters	5377/0/329

Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0551, wR_2 = 0.1493
Final R indexes [all data]	R_1 = 0.0585, wR_2 = 0.1567
Largest diff. peak/hole / e $Å^{-3}$	2.33/-1.74

Table S5 Bond Lengths for 7.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	P2	2.5243(15)	O3	C13	1.137(9)
W1	C13	2.010(8)	O4	C16	1.125(8)
W1	C14	2.058(7)	O5	C17	1.140(9)
W1	C15	2.047(8)	O6	C22	1.125(8)
W1	C16	2.037(7)	O7	C18	1.118(8)
W1	C17	2.040(7)	O8	C19	1.126(9)
W2	P1	2.5213(15)	O9	C20	1.119(9)
W2	C18	2.068(7)	O10	C21	1.120(10)
W2	C19	2.016(8)	C1	C2	1.494(9)
W2	C20	2.054(8)	C2	C3	1.523(8)
W2	C21	2.044(8)	C2	C5	1.355(9)
W2	C22	2.060(7)	C4	C5	1.502(10)
P1	P2	2.237(2)	C5	C6	1.488(9)
P1	C1	1.860(6)	C7	C8	1.497(8)
P1	C12	1.849(6)	C8	C9	1.499(9)
P2	C6	1.862(7)	C8	C11	1.346(9)
P2	C7	1.864(7)	C10	C11	1.517(8)
O1	C14	1.119(9)	C11	C12	1.505(9)
O2	C15	1.135(9)			

Table S6 Bond Angles for 7

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C13	W1	P2	175.0(2)	C12	P1	P2	98.1(2)
C13	W1	C14	92.6(3)	C12	P1	C1	103.5(3)
C13	W1	C15	87.3(3)	P1	P2	W1	123.15(8)
C13	W1	C16	92.5(3)	C6	P2	W1	109.6(2)
C13	W1	C17	83.6(3)	C6	P2	P1	99.3(2)
C14	W1	P2	90.7(2)	C6	P2	C7	103.2(3)
C15	W1	P2	89.1(2)	C7	P2	W1	119.1(2)
C15	W1	C14	88.3(3)	C7	P2	P1	99.3(2)

C16	W1	P2	84.0(2)	C2	C1	P1	112.9(4)
C16	W1	C14	174.1(3)	C1	C2	C3	115.3(6)
C16	W1	C15	88.8(3)	C5	C2	C1	120.6(6)
C16	W1	C17	93.5(3)	C5	C2	C3	123.9(6)
C17	W1	P2	100.1(2)	C2	C5	C4	125.6(6)
C17	W1	C14	90.2(3)	C2	C5	C6	118.6(6)
C17	W1	C15	170.7(3)	C6	C5	C4	115.8(6)
C18	W2	P1	98.6(2)	C5	C6	P2	116.5(5)
C19	W2	P1	175.9(2)	C8	C7	P2	113.9(4)
C19	W2	C18	84.8(3)	C7	C8	C9	116.2(6)
C19	W2	C20	92.1(3)	C11	C8	C7	118.9(6)
C19	W2	C21	87.9(3)	C11	C8	C9	124.9(6)
C19	W2	C22	89.8(3)	C8	C11	C10	123.6(6)
C20	W2	P1	90.4(2)	C8	C11	C12	119.6(5)
C20	W2	C18	86.5(3)	C12	C11	C10	116.8(6)
C20	W2	C22	178.1(3)	C11	C12	P1	110.9(4)
C21	W2	P1	88.9(2)	O3	C13	W1	179.8(8)
C21	W2	C18	171.7(3)	O1	C14	W1	178.5(8)
C21	W2	C20	89.8(4)	O2	C15	W1	175.5(7)
C21	W2	C22	90.3(3)	O4	C16	W1	176.1(7)
C22	W2	P1	87.77(18)	O5	C17	W1	173.6(6)
C22	W2	C18	93.7(3)	O7	C18	W2	172.7(6)
P2	P1	W2	124.64(7)	O8	C19	W2	178.9(8)
C1	P1	W2	115.7(2)	O9	C20	W2	177.6(9)
C1	P1	P2	98.7(2)	O10	C21	W2	176.8(8)
C12	P1	W2	112.9(2)	O6	C22	W2	178.7(7)

X-ray crystallographic data of 9

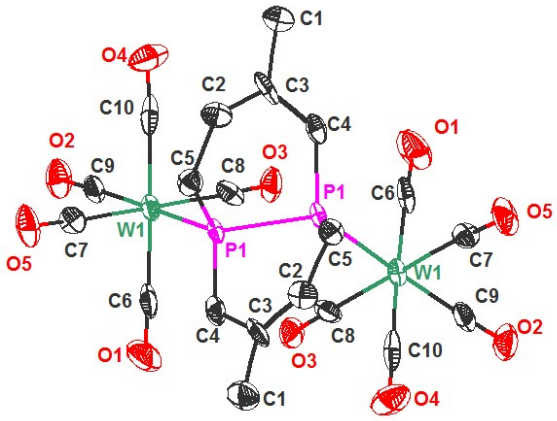


Figure S3 X-ray structure of **9**

Table S7 Crystal data and structure refinement for 9.

Identification code	**9**
Empirical formula	$C_{10}H_8O_5PW$
Formula weight	422.98
Temperature/K	300.13
Crystal system	tetragonal
Space group	$P4_12_12$
a/Å	15.924(5)
b/Å	15.924(5)
c/Å	9.853(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2498.4(17)
Z	8
ρ_{calc}g/cm^3	2.249
μ/mm^{-1}	9.380
F(000)	1576.0
Crystal size/mm^3	0.3 × 0.15 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.862 to 55.102
Index ranges	-20 ≤ h ≤ 20, -20 ≤ k ≤ 20, -12 ≤ l ≤ 11
Reflections collected	26658
Independent reflections	2880 [R_{int} = 0.1267, R_{sigma} = 0.0698]
Data/restraints/parameters	2880/0/155
Goodness-of-fit on F^2	1.121

Final R indexes [I>=2σ (I)]	R_1 = 0.0582, wR_2 = 0.1022
Final R indexes [all data]	R_1 = 0.0898, wR_2 = 0.1107
Largest diff. peak/hole / e Å^{-3}	1.35/-0.90
Flack parameter	0.076(14)

Table S8 Bond Lengths for 9.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
W1	P1	2.509(5)	O2	C9	1.18(2)
W1	C9	1.97(2)	O5	C7	1.14(2)
W1	C8	2.07(2)	C2	C3	1.33(3)
W1	C6	2.01(3)	C2	C5^1	1.51(3)
W1	C10	1.97(3)	C4	C3	1.53(3)
W1	C7	2.05(2)	O1	C6	1.17(3)
P1	P1^1	2.175(8)	C3	C1	1.46(3)
P1	C4	1.80(2)	O4	C10	1.20(3)
P1	C5	1.84(2)	C5	C2^1	1.51(3)
O3	C8	1.10(2)			

Table S9 Bond Angles for 9

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	W1	P1	176.1(6)	C4	P1	W1	118.9(7)
C9	W1	C8	89.3(8)	C4	P1	P1^1	97.3(7)
C9	W1	C6	90.1(10)	C4	P1	C5	103.0(9)
C9	W1	C7	91.3(8)	C5	P1	W1	112.0(7)
C8	W1	P1	94.6(6)	C5	P1	P1^1	99.3(7)
C6	W1	P1	90.3(7)	O2	C9	W1	178.2(17)
C6	W1	C8	91.5(9)	C3	C2	C5^1	133(2)
C6	W1	C7	89.4(9)	O3	C8	W1	179(2)
C10	W1	P1	91.9(7)	C3	C4	P1	123.7(15)
C10	W1	C9	87.6(9)	C2	C3	C4	122(2)
C10	W1	C8	88.9(9)	C2	C3	C1	122(2)
C10	W1	C6	177.7(10)	C1	C3	C4	116.4(18)
C10	W1	C7	90.3(9)	O1	C6	W1	177(2)
C7	W1	P1	84.9(6)	C2^1	C5	P1	113.4(14)
C7	W1	C8	179.0(8)	O4	C10	W1	177(2)
P1^1	P1	W1	122.9(2)	O5	C7	W1	177(2)

X-ray crystallographic data of 12

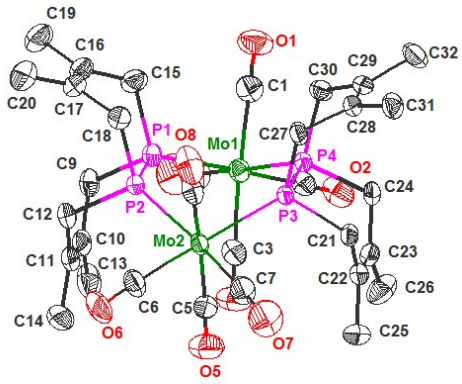


Figure S4 X-ray structure of **12**

Table S10 Crystal data and structure refinement for 12

Identification code	12
Empirical formula	$C_{32}H_{40}Mo_2O_8P_4$
Formula weight	868.40
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.1297(4)
b/Å	17.3992(6)
c/Å	18.9772(7)
α/°	87.053(3)
β/°	85.059(3)
γ/°	74.342(3)
Volume/Å^3	3840.5(2)
Z	4
ρ_{calc}g/cm^3	1.502
μ/mm^{-1}	7.296
F(000)	1760.0
Crystal size/mm^3	0.2783 × 0.2328 × 0.2024

Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	6.95 to 134.156
Index ranges	$-14 \leq h \leq 10$, $-20 \leq k \leq 20$, $-21 \leq l \leq 22$
Reflections collected	30703
Independent reflections	13720 [R_{int} = 0.0422, R_{sigma} = 0.0554]
Data/restraints/parameters	13720/0/846
Goodness-of-fit on F^2	1.027
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.1147
Final R indexes [all data]	R_1 = 0.0575, wR_2 = 0.1295
Largest diff. peak/hole / e $Å^{-3}$	0.66/-0.92

Table S11 Bond Lengths for 12

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	Mo1	2.029(6)	C1'	Mo1'	2.033(6)
C1	O1	1.144(7)	C1'	O1'	1.136(7)
C2	Mo1	1.992(6)	C2'	Mo1'	1.999(6)
C2	O2	1.140(7)	C2'	O2'	1.120(7)
C3	Mo1	2.032(6)	C3'	Mo1'	1.980(6)
C3	O3	1.133(7)	C3'	O3'	1.132(7)
C4	Mo1	1.986(6)	C4'	Mo1'	2.037(6)
C4	O4	1.147(7)	C4'	O4'	1.126(7)
C5	Mo2	2.040(6)	C5'	Mo2'	2.044(8)
C5	O5	1.132(7)	C5'	O5'	1.126(9)
C6	Mo2	1.985(5)	C6'	Mo2'	2.001(7)
C6	O6	1.137(7)	C6'	O6'	1.122(8)
C7	Mo2	1.981(6)	C7'	Mo2'	2.005(8)
C7	O7	1.126(7)	C7'	O7'	1.119(10)
C8	Mo2	2.041(6)	C8'	Mo2'	2.062(8)
C8	O8	1.131(7)	C8'	O8'	1.118(9)
C9	C10	1.510(8)	C9'	C10'	1.492(8)
C9	P1	1.865(5)	C9'	P1'	1.862(5)
C10	C11	1.317(9)	C10'	C11'	1.328(10)
C10	C13	1.531(8)	C10'	C13'	1.493(9)
C11	C12	1.509(7)	C11'	C12'	1.503(9)
C11	C14	1.512(8)	C11'	C14'	1.523(10)
C12	P2	1.859(5)	C12'	P2'	1.866(5)
C15	C16	1.486(8)	C15'	C16'	1.510(8)

C15	P1	1.859(5)	C15'	P1'	1.854(5)
C16	C17	1.324(8)	C16'	C17'	1.301(10)
C16	C19	1.516(7)	C16'	C19'	1.506(8)
C17	C18	1.506(7)	C17'	C18'	1.499(9)
C17	C20	1.517(8)	C17'	C20'	1.507(8)
C18	P2	1.858(5)	C18'	P2'	1.863(6)
C21	C22	1.499(7)	C21'	C22'	1.516(7)
C21	P3	1.856(4)	C21'	P3'	1.856(4)
C22	C23	1.320(8)	C22'	C23'	1.334(8)
C22	C25	1.506(7)	C22'	C25'	1.509(7)
C23	C24	1.512(7)	C23'	C24'	1.509(7)
C23	C26	1.524(8)	C23'	C26'	1.497(8)
C24	P4	1.857(4)	C24'	P4'	1.863(4)
C27	C28	1.497(6)	C27'	C28'	1.502(6)
C27	P3	1.865(5)	C27'	P3'	1.862(5)
C28	C29	1.322(7)	C28'	C29'	1.318(8)
C28	C31	1.523(6)	C28'	C31'	1.508(7)
C29	C30	1.516(7)	C29'	C30'	1.500(7)
C29	C32	1.508(7)	C29'	C32'	1.529(7)
C30	P4	1.854(5)	C30'	P4'	1.851(5)
Mo1	P1	2.5311(13)	Mo1'	P1'	2.5141(12)
Mo1	P4	2.5283(11)	Mo1'	P3'	2.5391(11)
Mo2	P2	2.5318(12)	Mo2'	P2'	2.5242(14)
Mo2	P3	2.5235(11)	Mo2'	P4'	2.5170(12)
P1	P2	2.2299(18)	P1'	P2'	2.2226(19)
P3	P4	2.2277(16)	P3'	P4'	2.2275(15)

Table S12 Bond Angles for 12

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	C1	Mo1	178.1(6)	O1'	C1'	Mo1'	171.7(6)
O2	C2	Mo1	175.8(5)	O2'	C2'	Mo1'	177.1(6)
O3	C3	Mo1	174.3(5)	O3'	C3'	Mo1'	177.3(7)
O4	C4	Mo1	176.4(7)	O4'	C4'	Mo1'	173.6(6)
O5	C5	Mo2	170.0(6)	O5'	C5'	Mo2'	171.0(7)
O6	C6	Mo2	176.7(6)	O6'	C6'	Mo2'	176.1(7)
O7	C7	Mo2	176.9(6)	O7'	C7'	Mo2'	177.0(11)
O8	C8	Mo2	173.1(6)	O8'	C8'	Mo2'	173.1(8)

C10	C9	P1	111.4(4)	C10'	C9'	P1'	111.2(4)
C9	C10	C13	114.8(6)	C9'	C10'	C13'	117.7(7)
C11	C10	C9	120.0(5)	C11'	C10'	C9'	117.9(6)
C11	C10	C13	125.2(6)	C11'	C10'	C13'	124.3(7)
C10	C11	C12	118.8(5)	C10'	C11'	C12'	120.9(6)
C10	C11	C14	124.5(6)	C10'	C11'	C14'	125.0(8)
C12	C11	C14	116.7(6)	C12'	C11'	C14'	114.1(8)
C11	C12	P2	109.8(3)	C11'	C12'	P2'	113.2(4)
C16	C15	P1	116.4(4)	C16'	C15'	P1'	113.9(4)
C15	C16	C19	116.5(6)	C17'	C16'	C15'	120.4(5)
C17	C16	C15	119.3(5)	C17'	C16'	C19'	124.6(7)
C17	C16	C19	124.1(6)	C19'	C16'	C15'	115.0(7)
C16	C17	C18	119.9(5)	C16'	C17'	C18'	120.2(5)
C16	C17	C20	125.2(6)	C16'	C17'	C20'	123.9(7)
C18	C17	C20	114.9(6)	C18'	C17'	C20'	115.9(7)
C17	C18	P2	114.6(4)	C17'	C18'	P2'	115.7(4)
C22	C21	P3	111.5(3)	C22'	C21'	P3'	110.9(3)
C21	C22	C25	115.9(6)	C23'	C22'	C21'	118.9(5)
C23	C22	C21	119.3(5)	C23'	C22'	C25'	124.6(6)
C23	C22	C25	124.7(6)	C25'	C22'	C21'	116.5(5)
C22	C23	C24	119.0(5)	C22'	C23'	C24'	118.9(5)
C22	C23	C26	125.0(6)	C22'	C23'	C26'	124.4(5)
C24	C23	C26	116.0(6)	C26'	C23'	C24'	116.7(5)
C23	C24	P4	111.0(3)	C23'	C24'	P4'	110.4(3)
C28	C27	P3	114.4(3)	C28'	C27'	P3'	115.3(3)
C27	C28	C31	114.4(4)	C27'	C28'	C31'	114.6(5)
C29	C28	C27	120.5(4)	C29'	C28'	C27'	120.2(4)
C29	C28	C31	125.0(4)	C29'	C28'	C31'	125.2(5)
C28	C29	C30	120.1(4)	C28'	C29'	C30'	119.9(4)
C28	C29	C32	125.2(5)	C28'	C29'	C32'	125.4(5)
C32	C29	C30	114.7(5)	C30'	C29'	C32'	114.8(5)
C29	C30	P4	115.2(3)	C29'	C30'	P4'	115.7(3)
C1	Mo1	C3	176.3(2)	C1'	Mo1'	C4'	170.6(2)
C1	Mo1	P1	91.86(18)	C1'	Mo1'	P1'	91.61(16)
C1	Mo1	P4	87.99(17)	C1'	Mo1'	P3'	98.74(17)
C2	Mo1	C1	88.5(2)	C2'	Mo1'	C1'	89.6(2)
C2	Mo1	C3	87.9(2)	C2'	Mo1'	C4'	88.7(2)
C2	Mo1	P1	173.46(16)	C2'	Mo1'	P1'	176.47(17)
C2	Mo1	P4	89.97(16)	C2'	Mo1'	P3'	89.65(16)

C3	Mo1	P1	91.79(16)	C3'	Mo1'	C1'	86.7(2)
C3	Mo1	P4	91.24(16)	C3'	Mo1'	C2'	86.1(3)
C4	Mo1	C1	88.7(3)	C3'	Mo1'	C4'	84.0(2)
C4	Mo1	C2	84.6(3)	C3'	Mo1'	P1'	90.7(2)
C4	Mo1	C3	91.7(3)	C3'	Mo1'	P3'	173.06(19)
C4	Mo1	P1	88.8(2)	C4'	Mo1'	P1'	89.62(18)
C4	Mo1	P4	173.7(2)	C4'	Mo1'	P3'	90.48(16)
P4	Mo1	P1	96.57(4)	P1'	Mo1'	P3'	93.44(4)
C5	Mo2	C8	171.5(2)	C5'	Mo2'	C8'	173.1(3)
C5	Mo2	P2	96.72(16)	C5'	Mo2'	P2'	97.2(2)
C5	Mo2	P3	96.37(16)	C5'	Mo2'	P4'	94.1(2)
C6	Mo2	C5	86.5(2)	C6'	Mo2'	C5'	86.6(3)
C6	Mo2	C8	87.8(2)	C6'	Mo2'	C7'	85.9(4)
C6	Mo2	P2	89.20(18)	C6'	Mo2'	C8'	87.7(3)
C6	Mo2	P3	174.28(18)	C6'	Mo2'	P2'	173.9(2)
C7	Mo2	C5	86.8(3)	C6'	Mo2'	P4'	90.3(2)
C7	Mo2	C6	85.9(3)	C7'	Mo2'	C5'	86.3(5)
C7	Mo2	C8	86.6(3)	C7'	Mo2'	C8'	89.4(4)
C7	Mo2	P2	173.8(2)	C7'	Mo2'	P2'	89.6(3)
C7	Mo2	P3	89.31(19)	C7'	Mo2'	P4'	176.1(3)
C8	Mo2	P2	89.48(18)	C8'	Mo2'	P2'	88.2(2)
C8	Mo2	P3	88.78(16)	C8'	Mo2'	P4'	89.9(2)
P3	Mo2	P2	95.35(4)	P4'	Mo2'	P2'	94.16(4)
C9	P1	Mo1	114.31(19)	C9'	P1'	Mo1'	114.23(19)
C9	P1	P2	98.6(2)	C9'	P1'	P2'	99.1(2)
C15	P1	C9	102.6(3)	C15'	P1'	C9'	102.6(2)
C15	P1	Mo1	113.8(2)	C15'	P1'	Mo1'	115.1(2)
C15	P1	P2	99.52(19)	C15'	P1'	P2'	98.8(2)
P2	P1	Mo1	124.80(6)	P2'	P1'	Mo1'	123.67(6)
C12	P2	Mo2	113.53(19)	C12'	P2'	Mo2'	115.2(2)
C12	P2	P1	98.96(19)	C12'	P2'	P1'	98.6(2)
C18	P2	C12	103.6(2)	C18'	P2'	C12'	101.6(3)
C18	P2	Mo2	114.04(18)	C18'	P2'	Mo2'	112.50(19)
C18	P2	P1	98.09(19)	C18'	P2'	P1'	99.5(2)
P1	P2	Mo2	125.42(6)	P1'	P2'	Mo2'	125.77(6)
C21	P3	C27	101.8(2)	C21'	P3'	C27'	103.2(2)
C21	P3	Mo2	114.72(16)	C21'	P3'	Mo1'	115.94(16)
C21	P3	P4	98.52(16)	C21'	P3'	P4'	98.60(17)
C27	P3	Mo2	112.23(15)	C27'	P3'	Mo1'	110.63(15)

C27	P3	P4	99.83(16)	C27'	P3'	P4'	99.68(16)
P4	P3	Mo2	126.20(5)	P4'	P3'	Mo1'	125.62(5)
C24	P4	Mo1	114.10(17)	C24'	P4'	Mo2'	114.84(17)
C24	P4	P3	98.78(17)	C24'	P4'	P3'	98.95(16)
C30	P4	C24	102.4(2)	C30'	P4'	C24'	103.6(2)
C30	P4	Mo1	114.72(16)	C30'	P4'	Mo2'	114.23(16)
C30	P4	P3	99.22(17)	C30'	P4'	P3'	98.64(17)
P3	P4	Mo1	124.30(5)	P3'	P4'	Mo2'	123.50(5)

DFT calculations

Computational Methods

All of the calculations were carried out by using Gaussian09.[1] The optimized structures were illustrated using CYLView.[2] The density functional theory (DFT) calculations were performed with the B3LYP[3, 4] functional using the integral equation formalism polarizable continuum model IEF-PCM[5] in toluene solvent, and basis set 6-31G(d) was employed for H, C, O, N, and P atoms, while LANL2DZ for W was used.[6] Then, frequency calculations at the same level of theory were carried out to identify all of the stationary points as minima (zero imaginary frequency) or transition state (only one frequency), and to provide corrections for free energies. The intrinsic reaction coordinate (IRC) [7, 8] calculations were performed for the transition states at the same level to confirm that each transition state links the corresponding reactant and product well. To value whether the aforementioned computational method (i.e. B3LYP) is proper and reliable, we have additionally re-optimized all the stationary points such as reactants, intermediates, transition states by employing multiple DFT methods and levels including L1 (B3LYP/6-31G(d)/LANL2DZ//IEF-$PCM_{Toluene}$), L2 (B3LYP/def2-tzvp//IEF-$PCM_{Toluene}$), L3 (ωB97XD/def2-tzvp//IEF-$PCM_{Toluene}$), L4 (M06L/def2-tzvp//IEF-$PCM_{Toluene}$) and L5 (B3LYP-D3/6-31G(d)/LANL2DZ//IEF-$PCM_{Toluene}$), and then the frequencies were computed at the same levels.

References

[1]G.W. Trucks, M.J. Frisch, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr, J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, O. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox , Revision D.01, (2010).

[2] C. Y. Legault, CYLview, 1.0 b, Universit´e de Sherbrooke, 2009, http://www.cylview.org.

[3] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

[4] C.T. Lee, W.T. Yang, R.G. Parr, *Phys. Rev. B.*, 1988, **37**, 785.

[5] (a) B. Mennucci and J. Tomasi, *J. Chem. Phys.*, 1997, **106**, 5151–5158; (b) V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995–2001.

[6] P. J. Hay, W. R. Wadt, *J. Chem. Phys.,* 1985, **82**, 299.

[7] C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523-5527.

[8] C. Gonzalez and H. B. Schlegel, *J. Chem. Phys.*, 1989, **90**, 2154-2161.

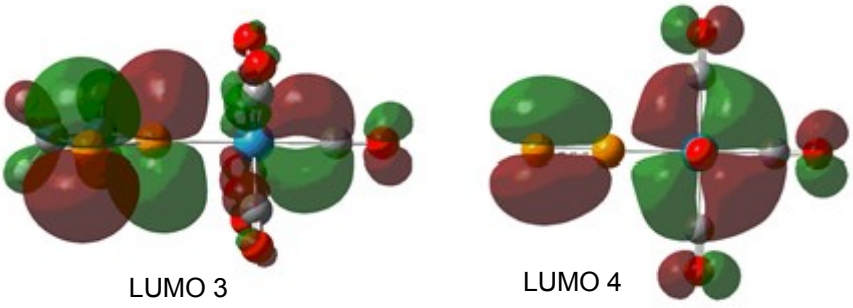


Figure S5 Selected frontier orbitals

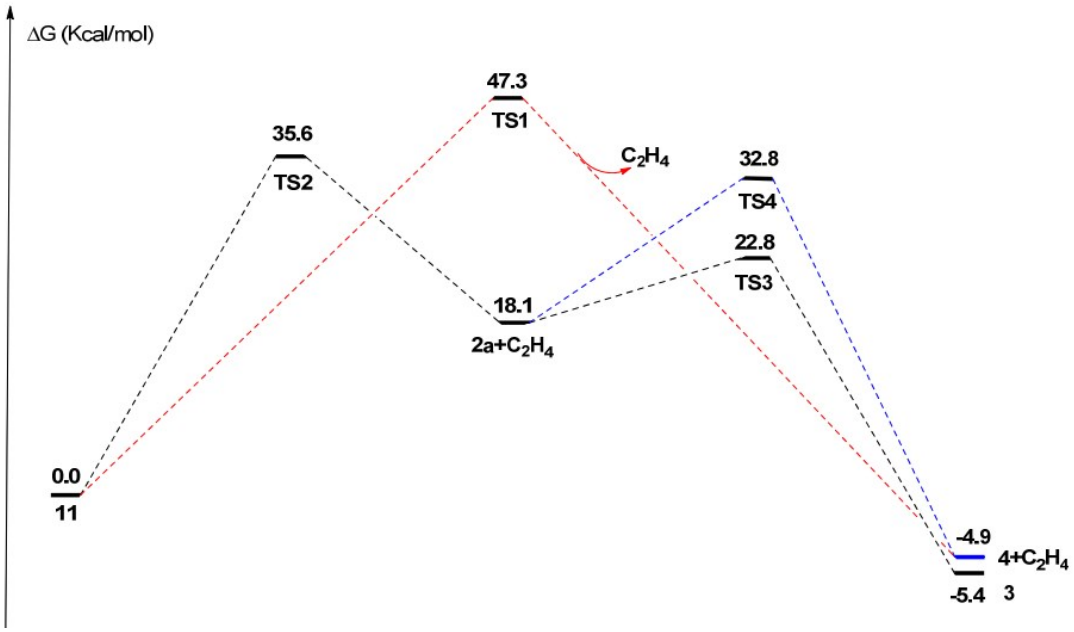


Figure S6 Computed energy profile (Kcal/mol) for the reaction with **11** at the L2 (B3LYP/def2-tzvp//IEF-PCM$_{Toluene}$) level

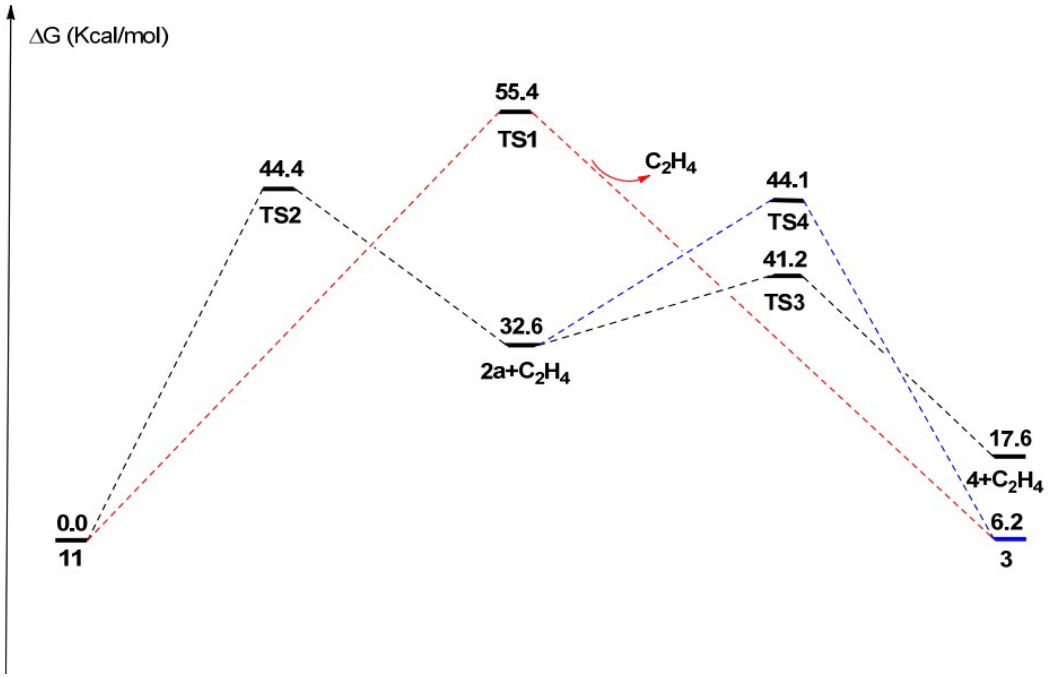


Figure S7 Computed energy profile (Kcal/mol) for the reaction with **11** at the L3 (ωB97XD/def2-tzvp//IEF-PCM$_{Toluene}$) level

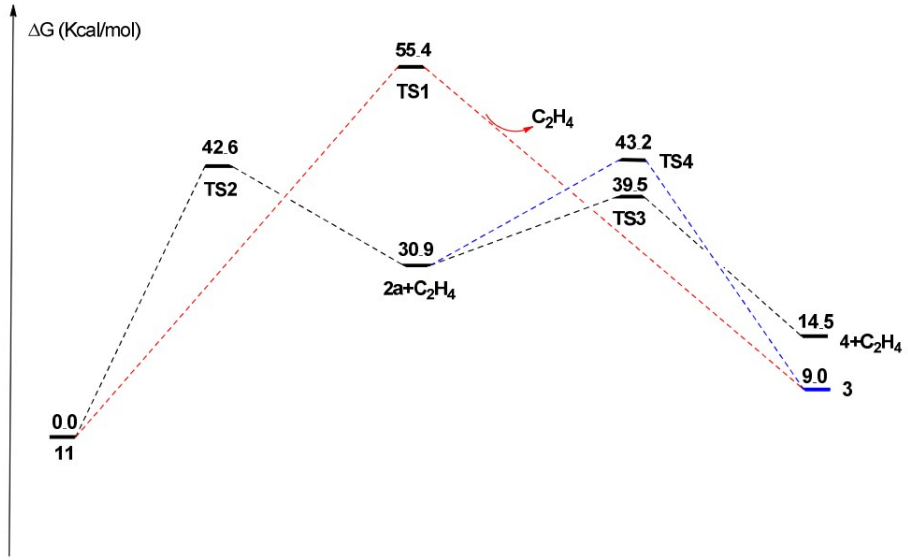


Figure S8 Computed energy profiles (Kcal/mol) for the reaction with **11** at the L4 (M06L/def2-tzvp//IEF-PCM$_{Toluene}$) level

Table S13 Gibbs free energy barriers (Kcal/mol) for the reaction with **11** calculated at the **L1** (B3LYP/6-31G(d)/LanL2DZ//IEF-PCM$_{Toluene}$) level and the **L5** (B3LYP-D3/6-31G(d)/Lan2LDZ//IEF-PCM$_{Toluene}$)

Computational level	$\Delta G^{\ddagger}_{TS1}$	$\Delta G^{\ddagger}_{TS2}$	$\Delta G^{\ddagger}_{TS3}$	$\Delta G^{\ddagger}_{TS4}$
L1	49.2	34.4	5.1	15.4
L5	49.2	34.6	3.8	14.4

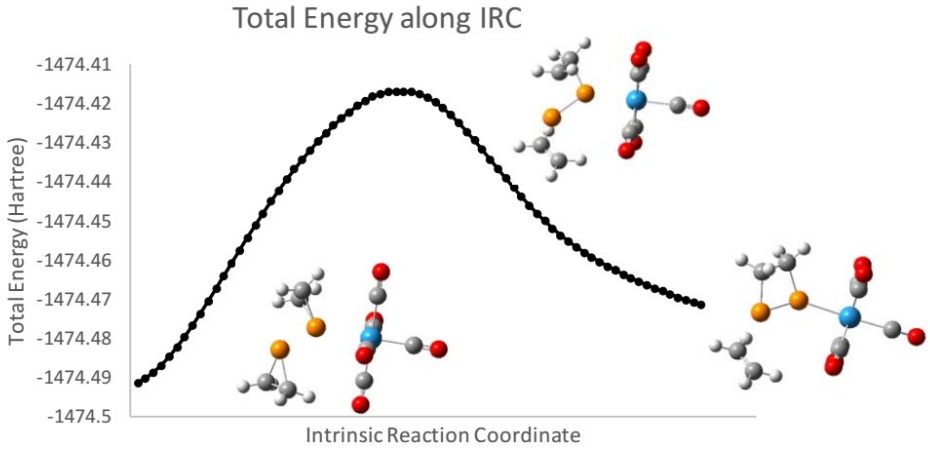


Figure S9 The IRC plots of TS1 calculated at the L1 (B3LYP/6-31G(d)/LanL2DZ) level

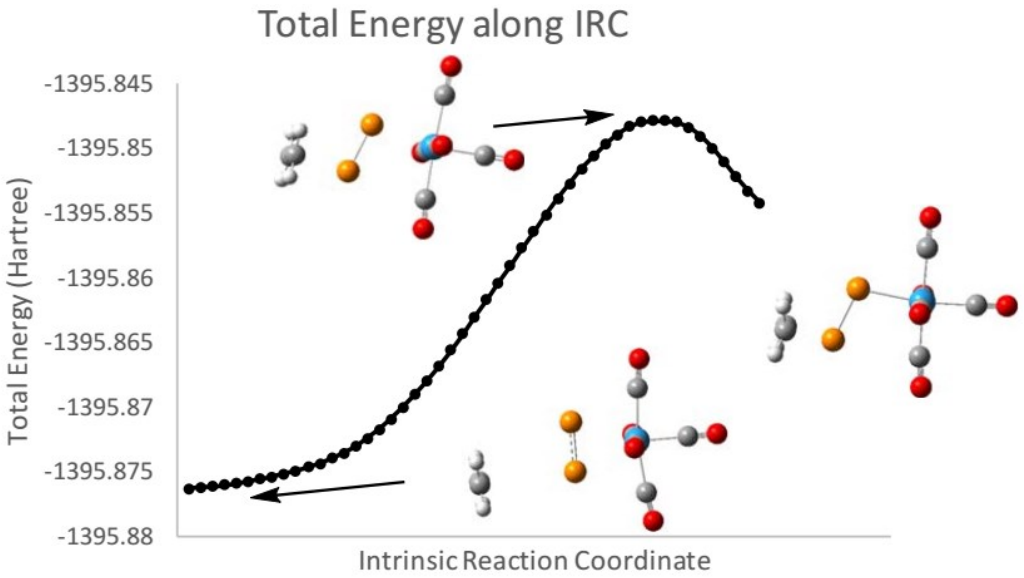


Figure S10 The IRC plots of TS3 calculated at the L1 (B3LYP/6-31G(d)/LanL2DZ) level

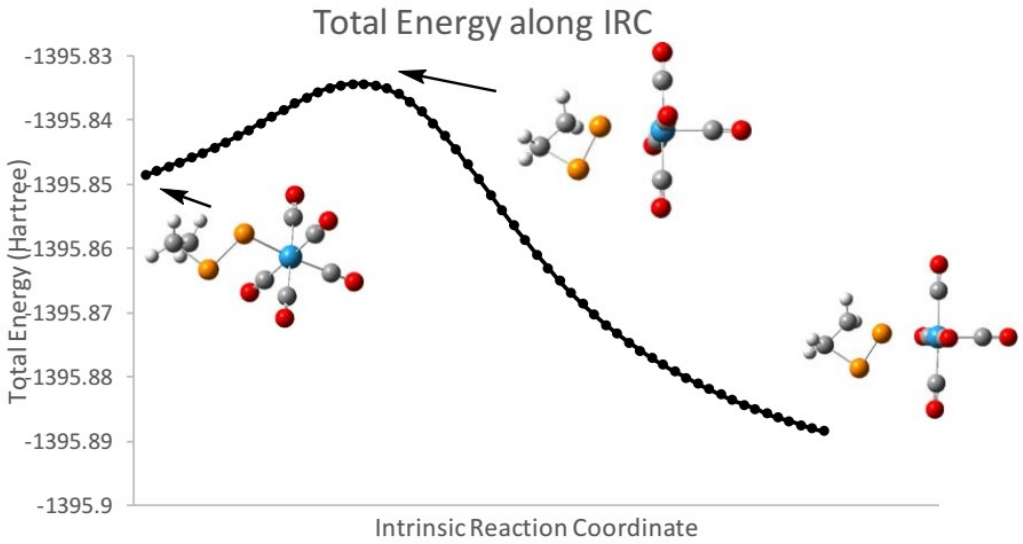


Figure S11 The IRC plots of TS4 calculated at the L1 (B3LYP/6-31G(d)/LanL2DZ) level

Energies and Geometrical Coordinates of the Listed Complexes

11 (L1)

Zero-point correction= 0.154668 (Hartree/Particle)
Thermal correction to Energy= 0.175525
Thermal correction to Enthalpy= 0.176469

Thermal correction to Gibbs Free Energy= 0.101457
Sum of electronic and zero-point Energies= -1474.345596
Sum of electronic and thermal Energies= -1474.324739
Sum of electronic and thermal Enthalpies= -1474.323795
Sum of electronic and thermal Free Energies= -1474.398807

0 1

P	-1.54080900	0.88909700	0.00731600
W	0.85966400	-0.10039600	0.00034700
C	0.38163000	-1.51085000	-1.41461200
C	0.41176700	-1.42118300	1.50889000
C	2.76063800	-0.75127800	-0.00294600
C	1.34275300	1.31746000	1.40901100
C	1.30149700	1.22987000	-1.50392500
O	0.14218600	-2.30889600	-2.21691900
O	0.18407300	-2.16882000	2.36143300
O	3.86015200	-1.12011700	-0.00465400
O	1.60929600	2.11893700	2.19730800
O	1.54355800	1.98277900	-2.34617600
P	-3.57860900	-0.02802000	0.05828300
C	-1.90019600	2.56438200	0.73401000
H	-2.84812600	2.69079700	1.25206400
H	-1.06123300	3.05014800	1.22604000
C	-1.91993200	2.53637300	-0.77143900
H	-2.88069700	2.64429900	-1.26959900
H	-1.09336000	3.00171300	-1.30275700
C	-3.28670700	-1.68588800	-0.77843500
H	-2.36699400	-1.82424100	-1.33855800
H	-4.16669100	-2.08760100	-1.27605200
C	-3.22438700	-1.75419400	0.71119000
H	-2.26196500	-1.93885700	1.17841700
H	-4.06126700	-2.20232200	1.24237300

3 (L1)
Zero-point correction= 0.099766 (Hartree/Particle)
Thermal correction to Energy= 0.117835
Thermal correction to Enthalpy= 0.118779
Thermal correction to Gibbs Free Energy= 0.048734
Sum of electronic and zero-point Energies= -1395.796247
Sum of electronic and thermal Energies= -1395.778178
Sum of electronic and thermal Enthalpies= -1395.777234
Sum of electronic and thermal Free Energies= -1395.847279

0 1

W	0.69743700	-0.00444100	0.00000200
C	0.70624400	1.45912400	1.44982900
C	0.70623200	1.45689700	-1.45208800
C	2.72935200	-0.01952300	-0.00001700
C	0.67419200	-1.47233400	-1.45058600
C	0.67426100	-1.47008200	1.45287500
O	0.71371700	2.28023700	2.26057200
O	0.71373300	2.27678800	-2.26406200
O	3.88554000	-0.02615300	-0.00003700
O	0.66211900	-2.29252300	-2.26055900
O	0.66220700	-2.28901800	2.26411400

C	-3.00077300	1.45626300	0.00008600
H	-2.90703900	2.09478500	-0.88528900
H	-2.90696400	2.09480300	0.88543800
C	-4.26504800	0.55892400	0.00011000
H	-4.89388600	0.70432800	0.88463500
H	-4.89410500	0.70454300	-0.88422300
P	-1.78038000	0.04837900	-0.00001400
P	-3.44986000	-1.16038200	-0.00013300

2a (L1)

Zero-point correction= 0.098138 (Hartree/Particle)
Thermal correction to Energy= 0.116953
Thermal correction to Enthalpy= 0.117897
Thermal correction to Gibbs Free Energy= 0.046982
Sum of electronic and zero-point Energies= -1395.759478
Sum of electronic and thermal Energies= -1395.740664
Sum of electronic and thermal Enthalpies= -1395.739719
Sum of electronic and thermal Free Energies= -1395.810634

0 1

W	-0.73203600	0.00428100	0.00002100
C	-0.16342800	1.37992600	-1.43270500
C	-0.16416000	1.37964600	1.43336700
C	-2.65851500	0.75799400	-0.00020200
C	-1.27605100	-1.38052800	1.43540300
C	-1.27603100	-1.38006000	-1.43591000
O	0.16754300	2.14796200	-2.22504200
O	0.16635100	2.14757500	2.22599600
O	-3.72707700	1.19220500	-0.00037500
O	-1.58479600	-2.15864000	2.22736800
O	-1.58483200	-2.15785600	-2.22815100
C	4.48010000	-0.46786200	-0.72621100
H	5.17025900	0.18311200	-1.25732300
H	4.20138500	-1.37388000	-1.25504000
C	4.47957700	-0.46668500	0.72708600
H	4.20073300	-1.37188900	1.25722500
H	5.16938300	0.18530000	1.25742700
P	2.99682800	0.58119100	-0.00084100
P	1.49666700	-0.99745800	0.00036200

4 (L1)

Zero-point correction= 0.044397 (Hartree/Particle)
Thermal correction to Energy= 0.059978
Thermal correction to Enthalpy= 0.060922
Thermal correction to Gibbs Free Energy= -0.002063
Sum of electronic and zero-point Energies= -1317.238376
Sum of electronic and thermal Energies= -1317.222795
Sum of electronic and thermal Enthalpies= -1317.221851
Sum of electronic and thermal Free Energies= -1317.284836

0 1

P	-3.98846000	0.00079200	-0.00043300
P	-2.08384800	0.00095300	-0.00049700
W	0.36144800	0.00003000	-0.00000500
C	0.37662000	2.06723100	-0.05633400

C	0.37563500	-0.05621300	-2.06719800
C	2.39337000	-0.00205500	0.00112600
C	0.37313700	-2.06717100	0.05630900
C	0.37397300	0.05643300	2.06720700
O	0.39636400	3.21746700	-0.08754800
O	0.39544200	-0.08705200	-3.21744600
O	3.54722600	-0.00282800	0.00133200
O	0.39081700	-3.21745500	0.08715500
O	0.39278600	0.08765200	3.21745900

C_2H_4 (L1)

Zero-point correction= 0.051200 (Hartree/Particle)
Thermal correction to Energy= 0.054242
Thermal correction to Enthalpy= 0.055186
Thermal correction to Gibbs Free Energy= 0.029669
Sum of electronic and zero-point Energies= -78.535165
Sum of electronic and thermal Energies= -78.532123
Sum of electronic and thermal Enthalpies= -78.531179
Sum of electronic and thermal Free Energies= -78.556696

0 1

C	0.00000000	-0.66589500	0.00000000
H	-0.92396300	-1.23983600	0.00000000
H	0.92392300	-1.23988300	0.00000000
C	0.00000000	0.66589500	0.00000000
H	0.92396300	1.23983600	0.00000000
H	-0.92392300	1.23988300	0.00000000

TS1 (L1)

Zero-point correction= 0.151269 (Hartree/Particle)
Thermal correction to Energy= 0.173211
Thermal correction to Enthalpy= 0.174155
Thermal correction to Gibbs Free Energy= 0.096423
Sum of electronic and zero-point Energies= -1474.265611
Sum of electronic and thermal Energies= -1474.243669
Sum of electronic and thermal Enthalpies= -1474.242725
Sum of electronic and thermal Free Energies= -1474.320456

0 1

P	1.41295900	0.77567500	0.31463600
W	-0.90962300	-0.12171000	-0.00583600
C	-1.48223700	1.65240900	-0.88553200
C	-1.39369000	0.64056500	1.83946900
C	-2.79214300	-0.84091200	-0.23634200
C	-0.33742500	-1.90374900	0.85056600
C	-0.34821800	-0.85606400	-1.84857800
O	-1.80343000	2.64572000	-1.37883000
O	-1.65616300	1.07727400	2.87643900
O	-3.86819600	-1.24666800	-0.36573600
O	-0.01437300	-2.90884400	1.32019300
O	-0.02529700	-1.26643400	-2.87665800
P	3.22402300	0.45191400	-0.65546800
C	2.22270800	2.60191000	-0.42039900
H	3.21174600	3.02258200	-0.57010700
H	1.50550300	2.91402100	-1.17597100
C	1.69867200	2.46732500	0.99018800
H	2.45858200	2.54991400	1.76585600

H	0.78596800	3.01821500	1.22850000
C	4.30206100	-1.55770400	0.86337300
H	3.85989700	-1.36402100	1.83625000
H	5.34567500	-1.28184700	0.74291100
C	3.60930000	-2.16444000	-0.12434700
H	2.58599200	-2.49912400	0.01945800
H	4.06949500	-2.41146900	-1.07621500

TS2 (L1)

Zero-point correction= 0.151125 (Hartree/Particle)
Thermal correction to Energy= 0.173323
Thermal correction to Enthalpy= 0.174268
Thermal correction to Gibbs Free Energy= 0.095580
Sum of electronic and zero-point Energies= -1474.288409
Sum of electronic and thermal Energies= -1474.266210
Sum of electronic and thermal Enthalpies= -1474.265266
Sum of electronic and thermal Free Energies= -1474.343954

0 1

W	-0.90433500	-0.03039300	0.03052600
C	-0.08077200	-1.06395800	1.60771200
C	-1.14693200	-1.83542100	-0.95692300
C	-2.80319000	-0.24393000	0.77521500
C	-1.65733400	1.02424800	-1.56962400
C	-0.68448000	1.74016700	1.07117400
O	0.37151800	-1.63965300	2.50007900
O	-1.28232600	-2.84585300	-1.49274100
O	-3.87231500	-0.36558000	1.19669600
O	-2.07536200	1.62267700	-2.46311100
O	-0.55429800	2.72894100	1.65128500
C	3.43226900	-1.25733600	1.00474900
H	3.67776600	-2.18096400	1.52552700
H	3.09599200	-0.46093300	1.66377100
C	4.28466200	-0.85831800	-0.18947200
H	4.54555400	0.19313000	-0.27886700
H	5.09603300	-1.52729900	-0.47064900
P	2.57895800	-1.43544200	-0.63735800
P	1.27157000	0.24539100	-1.12454900
C	2.90820700	2.52438300	0.63898100
C	2.58596600	2.84660200	-0.62229500
H	2.23089700	2.70823100	1.46779700
H	3.86972100	2.07973500	0.87981300
H	3.27535700	2.69507100	-1.44763600
H	1.64345200	3.33004300	-0.86486300

TS3 (L1)

Zero-point correction= 0.097197 (Hartree/Particle)
Thermal correction to Energy= 0.116011
Thermal correction to Enthalpy= 0.116955
Thermal correction to Gibbs Free Energy= 0.045467
Sum of electronic and zero-point Energies= -1395.750663
Sum of electronic and thermal Energies= -1395.731849
Sum of electronic and thermal Enthalpies= -1395.730905
Sum of electronic and thermal Free Energies= -1395.802393

0 1

W	-0.71849300	0.00251400	0.00000600
C	-0.17087400	-1.98807000	0.00032800
C	-0.68199000	-0.03713700	-2.06424300
C	-2.66801100	-0.54606300	0.00012200
C	-1.36703000	1.95629600	-0.00032300
C	-0.68190600	-0.03642100	2.06426800
O	0.03653200	-3.12524400	0.00049400
O	-0.65447700	-0.07418800	-3.21688600
O	-3.78762400	-0.84324000	0.00018500
O	-1.74531600	3.04651100	-0.00050600
O	-0.65433400	-0.07307200	3.21692200
C	4.78393800	0.25806300	0.68689100
H	5.15240800	-0.59339200	1.25169200
H	4.55579300	1.15695000	1.24967500
C	4.78400700	0.25768400	-0.68702100
H	4.55590500	1.15625500	-1.25032700
H	5.15251300	-0.59408800	-1.25131900
P	2.70112200	-0.57750300	0.00013700
P	1.57919700	1.11456800	-0.00026800

TS4 (L1)

Zero-point correction= 0.097886 (Hartree/Particle)
Thermal correction to Energy= 0.115788
Thermal correction to Enthalpy= 0.116732
Thermal correction to Gibbs Free Energy= 0.048408
Sum of electronic and zero-point Energies= -1395.736545
Sum of electronic and thermal Energies= -1395.718644
Sum of electronic and thermal Enthalpies= -1395.717700
Sum of electronic and thermal Free Energies= -1395.786024

0 1

W	0.69548400	-0.00513600	-0.01713300
C	-0.07892200	0.20583500	-1.90675800
C	0.36448700	-2.03177700	-0.13698000
C	2.57079100	-0.20409800	-0.75632000
C	1.39021700	-0.22350100	1.91114400
C	0.98689800	2.02726400	0.13312700
O	-0.55309200	0.32110200	-2.95488500
O	0.15560700	-3.16666100	-0.19632300
O	3.63949200	-0.32247600	-1.18844200
O	1.78273600	-0.34337100	2.99071800
O	1.15583600	3.16688700	0.22057300
C	-3.34391600	1.19011500	-0.26427600
H	-3.22330100	1.23457600	-1.34426600
H	-3.21415600	2.16244300	0.20241800
C	-4.40282800	0.26418000	0.27440800
H	-4.71417300	0.49166000	1.29290700
H	-5.24619600	0.06354200	-0.38962400
P	-3.00114000	-0.93661900	0.04673700
P	-1.62772600	0.39101100	0.95374200

11 (L2)

Zero-point correction= 0.152601 (Hartree/Particle)
Thermal correction to Energy= 0.173812

Thermal correction to Enthalpy= 0.174756
Thermal correction to Gibbs Free Energy= 0.097603
Sum of electronic and zero-point Energies= -1474.035960
Sum of electronic and thermal Energies= -1474.014749
Sum of electronic and thermal Enthalpies= -1474.013805
Sum of electronic and thermal Free Energies= -1474.090958

0 1

P	-1.57310800	0.87441000	-0.00259600
W	0.83962200	-0.08394000	0.00042900
C	0.35447700	-2.09649600	-0.04375000
C	0.78584600	-0.12241100	2.06979400
C	2.77373200	-0.65873100	0.00551900
C	1.50448200	1.87245200	0.04008400
C	0.81896700	-0.04478100	-2.06919800
O	0.17541100	-3.22875100	-0.07000700
O	0.75951400	-0.14561400	3.21484400
O	3.87946000	-0.97399000	0.01082300
O	1.90867800	2.94167800	0.06097600
O	0.81038900	-0.02716500	-3.21323900
P	-3.57906400	-0.08917500	-0.00070800
C	-1.97273500	2.50824900	0.75168400
H	-2.92811800	2.60543100	1.25300900
H	-1.15550700	3.00725500	1.25832500
C	-1.97274000	2.50841100	-0.75566800
H	-2.92580200	2.60638600	-1.25986000
H	-1.15535200	3.00579000	-1.26091500
C	-3.18437000	-1.74784300	-0.74513200
H	-2.23784600	-1.86418400	-1.25812600
H	-4.01820200	-2.21516000	-1.25630900
C	-3.18224200	-1.74682300	0.74691300
H	-2.23467900	-1.86091300	1.25450600
H	-4.01404400	-2.21298400	1.25850400

C_2H_4 (L2)

Zero-point correction= 0.050910 (Hartree/Particle)
Thermal correction to Energy= 0.053948
Thermal correction to Enthalpy= 0.054893
Thermal correction to Gibbs Free Energy= 0.029391
Sum of electronic and zero-point Energies= -78.573429
Sum of electronic and thermal Energies= -78.570390
Sum of electronic and thermal Enthalpies= -78.569446
Sum of electronic and thermal Free Energies= -78.594947

0 1

C	0.00000000	0.66269600	0.00000000
H	0.92155700	1.23273500	0.00000000
H	-0.92155500	1.23273600	0.00000000
C	0.00000000	-0.66269600	0.00000000
H	-0.92155700	-1.23273500	0.00000000
H	0.92155500	-1.23273600	0.00000000

3 (L2)

Zero-point correction= 0.098598 (Hartree/Particle)
Thermal correction to Energy= 0.116850
Thermal correction to Enthalpy= 0.117795
Thermal correction to Gibbs Free Energy= 0.046885

Sum of electronic and zero-point Energies= -1395.453657
Sum of electronic and thermal Energies= -1395.435405
Sum of electronic and thermal Enthalpies= -1395.434460
Sum of electronic and thermal Free Energies= -1395.505370

0 1

W	0.69275800	-0.00475400	0.00001200
C	0.71163100	1.46669800	1.45894900
C	0.71166800	1.46433700	-1.46131900
C	2.73693700	-0.02254600	0.00002300
C	0.67165400	-1.48223000	-1.45952600
C	0.67173800	-1.47987500	1.46194300
O	0.72983900	2.28012900	2.26217800
O	0.72991300	2.27649600	-2.26582900
O	3.88263100	-0.02941200	-0.00004800
O	0.66525300	-2.29531000	-2.26139500
O	0.66538500	-2.29168500	2.26509700
C	-2.99759600	1.44972400	0.00027600
H	-2.90414100	2.08664600	-0.88109900
H	-2.90415600	2.08630300	0.88190100
C	-4.25846600	0.55629100	0.00007500
H	-4.88575400	0.69870500	0.88138100
H	-4.88577000	0.69910700	-0.88115300
P	-1.78913300	0.05066900	-0.00000500
P	-3.44778700	-1.14767800	-0.00029400

2a (L2)

Zero-point correction= 0.096865 (Hartree/Particle)
Thermal correction to Energy= 0.115962
Thermal correction to Enthalpy= 0.116906
Thermal correction to Gibbs Free Energy= 0.044746
Sum of electronic and zero-point Energies= -1395.415057
Sum of electronic and thermal Energies= -1395.395960
Sum of electronic and thermal Enthalpies= -1395.395016
Sum of electronic and thermal Free Energies= -1395.467176

0 1

W	0.72550700	-0.00343900	-0.00006400
C	0.18892300	-1.40325600	-1.44338100
C	0.18933900	-1.40324000	1.44342100
C	2.68051100	-0.72545100	-0.00022100
C	1.25571600	1.39816300	1.44230000
C	1.25544500	1.39802500	-1.44267700
O	-0.10788500	-2.17519000	-2.22958600
O	-0.10722200	-2.17521700	2.22967600
O	3.74792900	-1.13325300	-0.00019300
O	1.55428500	2.17372200	2.22504600
O	1.55381700	2.17346200	-2.22561700
C	-4.47619400	0.45686600	-0.72463100
H	-5.16165400	-0.19483600	-1.25205300
H	-4.19638300	1.35743000	-1.25236100
C	-4.47605800	0.45652000	0.72554300
H	-4.19614400	1.35683300	1.25364800
H	-5.16141400	-0.19543400	1.25278800
P	-3.00766000	-0.58320500	0.00007300
P	-1.51270200	0.98030900	0.00032800

4 (L2)

Zero-point correction=	0.043835 (Hartree/Particle)
Thermal correction to Energy=	0.059593
Thermal correction to Enthalpy=	0.060537
Thermal correction to Gibbs Free Energy=	-0.003171
Sum of electronic and zero-point Energies=	-1316.862734
Sum of electronic and thermal Energies=	-1316.846976
Sum of electronic and thermal Enthalpies=	-1316.846032
Sum of electronic and thermal Free Energies=	-1316.909739

0 1

P	-3.97944900	0.00016200	0.00018600
P	-2.08856000	0.00029200	0.00021000
W	0.35600400	0.00005600	0.00002900
C	0.37638200	1.18099900	1.71278800
C	0.37597500	1.71280500	-1.18092400
C	2.40155100	-0.00051900	-0.00045300
C	0.37507800	-1.18086700	-1.71273400
C	0.37554500	-1.71272500	1.18093400
O	0.40393100	1.82795300	2.65116900
O	0.40310700	2.65114800	-1.82795300
O	3.54476800	-0.00121500	-0.00073800
O	0.40186100	-1.82790200	-2.65108400
O	0.40241600	-2.65112500	1.82789000

TS1 (L2)

Zero-point correction=	0.149511 (Hartree/Particle)
Thermal correction to Energy=	0.171815
Thermal correction to Enthalpy=	0.172760
Thermal correction to Gibbs Free Energy=	0.092747
Sum of electronic and zero-point Energies=	-1473.958780
Sum of electronic and thermal Energies=	-1473.936475
Sum of electronic and thermal Enthalpies=	-1473.935531
Sum of electronic and thermal Free Energies=	-1474.015544

0 1

P	1.41488600	0.81605900	0.27912500
W	-0.90341400	-0.11973400	-0.00842900
C	-1.53118800	1.59585300	-0.99239000
C	-1.41905000	0.72599500	1.80438700
C	-2.78052400	-0.89500000	-0.19438900
C	-0.31777000	-1.85624500	0.95759600
C	-0.33421400	-0.94736800	-1.82480200
O	-1.89016400	2.53533600	-1.53693800
O	-1.70328200	1.19710000	2.80823700
O	-3.83809900	-1.32689400	-0.29495100
O	-0.01062100	-2.82312800	1.48687000
O	-0.02409800	-1.40520700	-2.82422000
P	3.22884800	0.50718500	-0.64298400
C	2.18820900	2.61587600	-0.40567200
H	3.17258600	3.03074900	-0.57144800
H	1.46150300	2.94202800	-1.14017400
C	1.69707600	2.46552800	1.01614100
H	2.47698700	2.52701800	1.76680100

H	0.79855400	3.01746700	1.28219600
C	4.30426300	-1.59272600	0.86255900
H	3.80462400	-1.46236400	1.81369500
H	5.33636400	-1.27091000	0.81062200
C	3.69197100	-2.16520200	-0.18282600
H	2.67677900	-2.53389700	-0.11660900
H	4.20671600	-2.33631700	-1.11907600

TS2 (L2)

Zero-point correction=	0.149918 (Hartree/Particle)
Thermal correction to Energy=	0.172125
Thermal correction to Enthalpy=	0.173069
Thermal correction to Gibbs Free Energy=	0.094506
Sum of electronic and zero-point Energies=	-1473.978746
Sum of electronic and thermal Energies=	-1473.956540
Sum of electronic and thermal Enthalpies=	-1473.955596
Sum of electronic and thermal Free Energies=	-1474.034158

0 1

W	0.89821100	-0.04670100	0.03168400
C	1.11040200	1.98511000	0.37816700
C	1.70549000	0.25253100	-1.85681800
C	2.79486100	-0.38044400	0.74973200
C	0.72802600	-2.09176600	-0.30013800
C	0.05302600	-0.33031300	1.90478000
O	1.23683000	3.10721600	0.56265500
O	2.15806000	0.42743600	-2.89136500
O	3.85093100	-0.56775600	1.15345800
O	0.65849000	-3.21919100	-0.46779900
O	-0.41552400	-0.48661600	2.93598900
C	-4.35175300	-0.68293000	-0.24441400
H	-5.18033400	-1.29706000	-0.57733300
H	-4.55493000	0.37854800	-0.29948600
C	-3.54958800	-1.18038000	0.94658400
H	-3.20900000	-0.44533100	1.66304800
H	-3.84753200	-2.12098400	1.39512900
P	-2.67051000	-1.29054100	-0.66939000
P	-1.30847800	0.35227800	-1.07203800
C	-2.55416900	2.73877100	-0.54194800
C	-2.54562300	2.43491200	0.76216200
H	-1.73962300	3.28246600	-1.00260700
H	-3.41154200	2.53755000	-1.17022000
H	-3.38821000	1.95004000	1.23857000
H	-1.70594100	2.68292500	1.39755300

TS3 (L2)

Zero-point correction=	0.096155 (Hartree/Particle)
Thermal correction to Energy=	0.115134
Thermal correction to Enthalpy=	0.116079
Thermal correction to Gibbs Free Energy=	0.044273
Sum of electronic and zero-point Energies=	-1395.407837
Sum of electronic and thermal Energies=	-1395.388857
Sum of electronic and thermal Enthalpies=	-1395.387913
Sum of electronic and thermal Free Energies=	-1395.459719

0 1

W	-0.70918700	0.00365900	0.00000200
C	-0.18240200	-2.00529500	0.00016800
C	-0.68141300	-0.04191200	-2.07799800
C	-2.67390600	-0.53101900	0.00001400
C	-1.36776400	1.96649800	-0.00016700
C	-0.68144700	-0.04157100	2.07801600
O	0.00288000	-3.13553800	0.00025400
O	-0.66387200	-0.08525800	-3.21970300
O	-3.78695300	-0.81247900	0.00001900
O	-1.75835700	3.04103000	-0.00026400
O	-0.66392000	-0.08473200	3.21972800
C	4.75051500	0.26626200	0.68510100
H	5.12810700	-0.57894200	1.24541800
H	4.51886200	1.15994200	1.24600200
C	4.75047900	0.26619000	-0.68518700
H	4.51880800	1.15981600	-1.24616600
H	5.12804900	-0.57906900	-1.24543600
P	2.71831600	-0.57490700	0.00004800
P	1.59258100	1.10213300	-0.00004400

TS4 (L2)

Zero-point correction= 0.096662 (Hartree/Particle)
Thermal correction to Energy= 0.114790
Thermal correction to Enthalpy= 0.115735
Thermal correction to Gibbs Free Energy= 0.046455
Sum of electronic and zero-point Energies= -1395.393524
Sum of electronic and thermal Energies= -1395.375395
Sum of electronic and thermal Enthalpies= -1395.374451
Sum of electronic and thermal Free Energies= -1395.443731

0 1

W	0.68878000	-0.00387300	-0.01294200
C	-0.02460700	0.15222500	-1.94658600
C	0.41459900	-2.05483200	-0.10574400
C	2.59323000	-0.18370600	-0.69963100
C	1.35237400	-0.17724900	1.94293700
C	0.95760000	2.04572500	0.09541100
O	-0.43710900	0.23309500	-3.01181600
O	0.26148800	-3.18798700	-0.15530100
O	3.66703300	-0.28595000	-1.09550700
O	1.72852600	-0.27279600	3.01950300
O	1.11925900	3.17748500	0.15541000
C	-3.35273100	1.16505100	-0.29549200
H	-3.23554100	1.18292500	-1.37255000
H	-3.23065400	2.14685900	0.14259000
C	-4.41766000	0.25531500	0.25905400
H	-4.72250000	0.50111100	1.27051200
H	-5.26025000	0.04871500	-0.39731700
P	-3.02762500	-0.93605500	0.04903500
P	-1.66378700	0.39478900	0.91872800

11 (L3)

Zero-point correction= 0.155486 (Hartree/Particle)
Thermal correction to Energy= 0.176094
Thermal correction to Enthalpy= 0.177038
Thermal correction to Gibbs Free Energy= 0.102710

Sum of electronic and zero-point Energies= -1473.767345
Sum of electronic and thermal Energies= -1473.746738
Sum of electronic and thermal Enthalpies= -1473.745793
Sum of electronic and thermal Free Energies= -1473.820122

0 1

P	-1.55319300	0.86642600	-0.00005900
W	0.80690200	-0.07768700	0.00004600
C	0.38813200	-2.09391100	0.00012400
C	0.73960000	-0.07372600	2.05780200
C	2.74400700	-0.61705000	0.00029700
C	1.44968700	1.87297300	-0.00040000
C	0.73987700	-0.07457100	-2.05766300
O	0.25310800	-3.22684400	0.00006900
O	0.69093300	-0.07178100	3.19635700
O	3.85183700	-0.90629400	0.00038200
O	1.84259100	2.94372500	-0.00057000
O	0.69132100	-0.07321900	-3.19623400
P	-3.49840400	-0.14907000	0.00006800
C	-1.94632400	2.48371800	0.75364100
H	-2.90091400	2.59153000	1.25306000
H	-1.12368300	2.97771500	1.25509200
C	-1.94629900	2.48336400	-0.75454300
H	-2.90093200	2.59085400	-1.25396000
H	-1.12373900	2.97721500	-1.25627100
C	-2.99108900	-1.76296900	-0.74497400
H	-2.03549800	-1.80929400	-1.25197900
H	-3.78735200	-2.29252500	-1.25293600
C	-2.99101200	-1.76287000	0.74532600
H	-2.03533000	-1.80901300	1.25218600
H	-3.78711700	-2.29241400	1.25354000

C_2H_4 (L3)
Zero-point correction= 0.051319 (Hartree/Particle)
Thermal correction to Energy= 0.054351
Thermal correction to Enthalpy= 0.055295
Thermal correction to Gibbs Free Energy= 0.029806
Sum of electronic and zero-point Energies= -78.538299
Sum of electronic and thermal Energies= -78.535268
Sum of electronic and thermal Enthalpies= -78.534324
Sum of electronic and thermal Free Energies= -78.559813
0 1

C	0.00000000	0.66123900	0.00000000
H	0.92300100	1.22935100	0.00000000
H	-0.92300000	1.22935200	0.00000000
C	0.00000000	-0.66123900	0.00000000
H	-0.92300100	-1.22935100	0.00000000
H	0.92300000	-1.22935200	0.00000000

3 (L3)
Zero-point correction= 0.100082 (Hartree/Particle)
Thermal correction to Energy= 0.118112
Thermal correction to Enthalpy= 0.119056
Thermal correction to Gibbs Free Energy= 0.049252
Sum of electronic and zero-point Energies= -1395.199591

Sum of electronic and thermal Energies= -1395.181562
Sum of electronic and thermal Enthalpies= -1395.180618
Sum of electronic and thermal Free Energies= -1395.250421

0 1

W	-0.68442600	-0.00554800	0.00014200
C	-0.67816900	1.53253600	-1.36840200
C	-0.67530800	1.37424700	1.52799000
C	-2.72118900	0.00414100	0.00499800
C	-0.66593200	-1.55066400	1.37073100
C	-0.68209800	-1.39262600	-1.53016300
O	-0.67461100	2.38691800	-2.12170400
O	-0.67061200	2.14193400	2.36999200
O	-3.86204400	0.01415300	0.00868300
O	-0.65614400	-2.40161300	2.12720300
O	-0.68139300	-2.15927200	-2.37296200
C	2.94113800	1.43461500	-0.01137700
H	2.84152500	2.07452500	0.86767800
H	2.84274600	2.06520900	-0.89845200
C	4.20461000	0.54741500	-0.00445600
H	4.83070000	0.69075300	-0.88844100
H	4.82815400	0.70202800	0.87632200
P	1.75802700	0.03412900	-0.00524800
P	3.39694200	-1.14592100	0.00570000

2a (L3)

Zero-point correction= 0.098476 (Hartree/Particle)
Thermal correction to Energy= 0.117327
Thermal correction to Enthalpy= 0.118271
Thermal correction to Gibbs Free Energy= 0.046391
Sum of electronic and zero-point Energies= -1395.156213
Sum of electronic and thermal Energies= -1395.137362
Sum of electronic and thermal Enthalpies= -1395.136417
Sum of electronic and thermal Free Energies= -1395.208298

0 1

W	0.71596900	-0.00553100	-0.00208100
C	0.11277000	-1.32465100	-1.48132600
C	0.22397600	-1.48007900	1.37080200
C	2.66643900	-0.72733000	-0.06214300
C	1.27759300	1.33691700	1.46332600
C	1.21237700	1.44229000	-1.40213500
O	-0.22350900	-2.04968900	-2.28886700
O	-0.06042900	-2.29419000	2.10988500
O	3.73134200	-1.12454300	-0.08849500
O	1.58598000	2.08951700	2.25801100
O	1.48395900	2.24287000	-2.16094600
C	-4.38449300	0.58029300	-0.66635600
H	-5.08970000	0.04607700	-1.29098200
H	-4.09508900	1.55506700	-1.03435200
C	-4.41221600	0.35056500	0.77456500
H	-4.14137500	1.16148600	1.43671000
H	-5.14116900	-0.34429000	1.17313200
P	-2.98323100	-0.56342600	-0.08006200
P	-1.47222200	0.96417600	0.16355400

4 (L3)

Zero-point correction= 0.044708 (Hartree/Particle)
Thermal correction to Energy= 0.060380
Thermal correction to Enthalpy= 0.061324
Thermal correction to Gibbs Free Energy= -0.002399
Sum of electronic and zero-point Energies= -1316.625270
Sum of electronic and thermal Energies= -1316.609597
Sum of electronic and thermal Enthalpies= -1316.608653
Sum of electronic and thermal Free Energies= -1316.672376

0 1

P	-3.93175000	0.00017300	-0.00004200
P	-2.06206600	0.00018300	-0.00025500
W	0.34855300	0.00000900	-0.00002300
C	0.37095600	0.87287900	-1.87503700
C	0.36990900	-1.87507000	-0.87283800
C	2.38684900	-0.00023000	0.00012800
C	0.37012100	-0.87291000	1.87503100
C	0.37073300	1.87501800	0.87295300
O	0.39751800	1.35379000	-2.90355900
O	0.39663300	-2.90365200	-1.35361700
O	3.52503600	-0.00040700	0.00027200
O	0.39668900	-1.35376500	2.90357700
O	0.39698900	2.90352000	1.35391600

TS1 (L3)

Zero-point correction= 0.151684 (Hartree/Particle)
Thermal correction to Energy= 0.173649
Thermal correction to Enthalpy= 0.174593
Thermal correction to Gibbs Free Energy= 0.096176
Sum of electronic and zero-point Energies= -1473.676280
Sum of electronic and thermal Energies= -1473.654315
Sum of electronic and thermal Enthalpies= -1473.653371
Sum of electronic and thermal Free Energies= -1473.731788

0 1

P	1.39569200	0.83446400	0.29520700
W	-0.85975500	-0.11021400	-0.01493900
C	-0.31174700	-1.74748200	1.10899800
C	-0.19173500	-1.05825400	-1.72402500
C	-2.71544300	-0.91657300	-0.22653600
C	-1.43036300	1.52025300	-1.14621700
C	-1.45148900	0.86825900	1.69037900
O	-0.01738300	-2.65657200	1.73013500
O	0.18039900	-1.58195300	-2.66267800
O	-3.75825400	-1.36681500	-0.34082300
O	-1.74318800	2.42164500	-1.76773400
O	-1.76837400	1.41927800	2.63681700
P	3.18745300	0.54420200	-0.61595300
C	2.12426100	2.58098500	-0.37864600
H	3.10037700	3.01181700	-0.56109200
H	1.37958700	2.92387500	-1.08862900
C	1.67435200	2.44773100	1.06649800
H	2.48052500	2.51600200	1.78742800
H	0.77878400	2.99483100	1.34804300
C	3.89595400	-1.78016800	0.89385500

H	3.31681300	-1.61671400	1.79463400
H	4.96184400	-1.60072100	0.96133500
C	3.32854700	-2.21427000	-0.23097900
H	2.26862300	-2.43023800	-0.28685200
H	3.90853600	-2.41057900	-1.12387300

TS2 (L3)

Zero-point correction= 0.152614 (Hartree/Particle)
Thermal correction to Energy= 0.174253
Thermal correction to Enthalpy= 0.175197
Thermal correction to Gibbs Free Energy= 0.098757
Sum of electronic and zero-point Energies= -1473.695554
Sum of electronic and thermal Energies= -1473.673915
Sum of electronic and thermal Enthalpies= -1473.672971
Sum of electronic and thermal Free Energies= -1473.749412

0 1

W	0.87300700	-0.04408600	0.03026200
C	1.00241900	1.99273600	0.32084300
C	1.74779600	0.22222100	-1.82148700
C	2.74636700	-0.29647600	0.83152000
C	0.76035600	-2.09505400	-0.22879600
C	-0.03328600	-0.29542100	1.86826300
O	1.07063100	3.11968800	0.47273000
O	2.23471600	0.38126000	-2.83729300
O	3.78857600	-0.43620600	1.27246900
O	0.70683600	-3.22362700	-0.35449600
O	-0.53150600	-0.43275300	2.88279500
C	-4.24317100	-0.63986700	-0.25303300
H	-5.10716100	-1.23753900	-0.51797000
H	-4.40167700	0.42484800	-0.36505900
C	-3.41720500	-1.09922800	0.93339100
H	-3.02526200	-0.33765300	1.59361000
H	-3.73724500	-1.99921000	1.44503800
P	-2.60919400	-1.33030500	-0.69333300
P	-1.24233000	0.27364400	-1.15114500
C	-2.48375900	2.69810200	-0.52255300
C	-2.52381000	2.32430800	0.75480200
H	-1.61767900	3.19559400	-0.94133500
H	-3.33672900	2.57906000	-1.17890200
H	-3.41130200	1.87906700	1.18735200
H	-1.68088400	2.47331300	1.41773100

TS3 (L3)

Zero-point correction= 0.097495 (Hartree/Particle)
Thermal correction to Energy= 0.116349
Thermal correction to Enthalpy= 0.117293
Thermal correction to Gibbs Free Energy= 0.044522
Sum of electronic and zero-point Energies= -1395.141743
Sum of electronic and thermal Energies= -1395.122889
Sum of electronic and thermal Enthalpies= -1395.121944
Sum of electronic and thermal Free Energies= -1395.194716

0 1

W	0.68704200	-0.00574500	-0.00018700
C	0.16637300	1.99135400	0.01742600

C	0.62971600	0.07410700	-2.06359200
C	2.63079800	0.54479400	-0.00211000
C	1.39594600	-1.94193800	-0.01851200
C	0.64505400	0.04007400	2.06430700
O	-0.00660200	3.11953500	0.02746200
O	0.58799700	0.14387700	-3.19930700
O	3.73851900	0.83132200	-0.00328200
O	1.82370600	-2.99696700	-0.02927400
O	0.61161300	0.09045800	3.20104900
C	-4.67353100	-0.21684200	0.68275900
H	-5.00712700	0.65901800	1.22598700
H	-4.47710900	-1.10930700	1.26085700
C	-4.67169700	-0.24310500	-0.67946700
H	-4.47309300	-1.15803800	-1.22076400
H	-5.00312700	0.61027600	-1.25800600
P	-2.60814800	0.53047900	-0.00474500
P	-1.56908500	-1.16869700	0.00659400

TS4 (L3)

Zero-point correction=	0.097995 (Hartree/Particle)
Thermal correction to Energy=	0.115995
Thermal correction to Enthalpy=	0.116939
Thermal correction to Gibbs Free Energy=	0.046556
Sum of electronic and zero-point Energies=	-1395.138642
Sum of electronic and thermal Energies=	-1395.120642
Sum of electronic and thermal Enthalpies=	-1395.119697
Sum of electronic and thermal Free Energies=	-1395.190081

0 1

W	0.66939600	-0.00605600	-0.01141800
C	-0.11136400	0.08740800	-1.90766200
C	0.47445100	-2.05764300	-0.05470900
C	2.54158500	-0.13152700	-0.75367000
C	1.40022700	-0.11173700	1.91278500
C	0.86791200	2.04113000	0.02731900
O	-0.56356300	0.13916900	-2.95448200
O	0.36120100	-3.19172600	-0.08267700
O	3.60247000	-0.19856200	-1.18027500
O	1.81727800	-0.16979900	2.97207400
O	0.99088300	3.17505300	0.04249300
C	-3.18153400	1.14517700	-0.22546700
H	-3.02541500	1.20447300	-1.29800000
H	-3.10486500	2.12642200	0.22887400
C	-4.32805700	0.25980600	0.23850100
H	-4.65470100	0.48756500	1.24739100
H	-5.15032000	0.13254300	-0.46063500
P	-2.96991400	-0.93208900	0.02725300
P	-1.64644800	0.33664500	0.99459000

11 (L4)

Zero-point correction=	0.153433 (Hartree/Particle)
Thermal correction to Energy=	0.174497
Thermal correction to Enthalpy=	0.175441
Thermal correction to Gibbs Free Energy=	0.098781
Sum of electronic and zero-point Energies=	-1473.947482

Sum of electronic and thermal Energies= -1473.926418
Sum of electronic and thermal Enthalpies= -1473.925474
Sum of electronic and thermal Free Energies= -1474.002134

0 1

P	-1.57401500	0.85198000	0.00251100
W	0.82246700	-0.07343200	0.00230300
C	0.39612900	-2.08871000	-0.21995200
C	0.68201000	-0.28484600	2.05537300
C	2.77190800	-0.58350700	0.02351800
C	1.37999400	1.90254500	0.21228300
C	0.83257500	0.13528300	-2.05576500
O	0.24042800	-3.21988000	-0.34550500
O	0.58712200	-0.41001100	3.19233800
O	3.89205200	-0.85304700	0.03926400
O	1.69757500	3.00056500	0.32534200
O	0.82153500	0.25510100	-3.19710800
P	-3.50639400	-0.19465100	0.03463200
C	-2.00113600	2.46541300	0.74087900
H	-2.95602000	2.54355900	1.24439500
H	-1.19681300	2.98453400	1.24540100
C	-2.00254500	2.45422900	-0.75713200
H	-2.95626400	2.53095100	-1.26291700
H	-1.19333700	2.95970800	-1.26893700
C	-2.96554900	-1.75438100	-0.78636400
H	-2.03119100	-1.73256100	-1.33385200
H	-3.75458900	-2.29656700	-1.29087300
C	-2.90796700	-1.80949000	0.69398600
H	-1.93284000	-1.82692600	1.16728300
H	-3.65755700	-2.38967500	1.21631200

C_2H_4 (L4)
Zero-point correction= 0.050994 (Hartree/Particle)
Thermal correction to Energy= 0.054039
Thermal correction to Enthalpy= 0.054983
Thermal correction to Gibbs Free Energy= 0.029480
Sum of electronic and zero-point Energies= -78.551608
Sum of electronic and thermal Energies= -78.548563
Sum of electronic and thermal Enthalpies= -78.547619
Sum of electronic and thermal Free Energies= -78.573121

0 1

C	0.00000000	0.66066300	0.00000000
H	0.91899700	1.23364900	0.00000000
H	-0.91899500	1.23365000	0.00000000
C	0.00000000	-0.66066300	0.00000000
H	-0.91899700	-1.23364900	0.00000000
H	0.91899500	-1.23365000	0.00000000

3 (L4)
Zero-point correction= 0.099278 (Hartree/Particle)
Thermal correction to Energy= 0.117567
Thermal correction to Enthalpy= 0.118511
Thermal correction to Gibbs Free Energy= 0.047996
Sum of electronic and zero-point Energies= -1395.363441

Sum of electronic and thermal Energies= -1395.345151
Sum of electronic and thermal Enthalpies= -1395.344207
Sum of electronic and thermal Free Energies= -1395.414722

0 1

W	0.69450400	-0.00786000	0.00000500
C	0.65305200	1.46864200	1.45099700
C	0.65324500	1.46756600	-1.45209500
C	2.73997400	0.03477000	0.00004900
C	0.69479600	-1.49054600	-1.45399500
C	0.69488100	-1.48946700	1.45511100
O	0.62177800	2.29141500	2.24883100
O	0.62216700	2.28968000	-2.25061400
O	3.88789700	0.06551300	0.00007800
O	0.68747100	-2.30978400	-2.25382500
O	0.68760700	-2.30817000	2.25548800
C	-2.93456900	1.42138000	0.00012600
H	-2.82894700	2.06137800	-0.87708600
H	-2.82892600	2.06118500	0.87747700
C	-4.19673300	0.55465100	0.00005100
H	-4.82617200	0.71035100	0.87662500
H	-4.82617300	0.71051400	-0.87649300
P	-1.76176900	0.01762300	-0.00001800
P	-3.43598700	-1.15049100	-0.00011900

2a (L4)

Zero-point correction= 0.097165 (Hartree/Particle)
Thermal correction to Energy= 0.116293
Thermal correction to Enthalpy= 0.117237
Thermal correction to Gibbs Free Energy= 0.044614
Sum of electronic and zero-point Energies= -1395.327293
Sum of electronic and thermal Energies= -1395.308165
Sum of electronic and thermal Enthalpies= -1395.307221
Sum of electronic and thermal Free Energies= -1395.379843

0 1

W	0.72568500	-0.00992400	-0.00001100
C	0.09687600	-1.38465700	-1.42936200
C	0.09724800	-1.38528200	1.42890000
C	2.64461700	-0.82195800	-0.00032000
C	1.30324900	1.38618100	1.42834700
C	1.30290500	1.38673400	-1.42798100
O	-0.27240500	-2.14061200	-2.20470400
O	-0.27149600	-2.14175500	2.20399100
O	3.69168600	-1.28678800	-0.00044000
O	1.61905500	2.16805300	2.20218400
O	1.61872800	2.16876800	-2.20164500
C	-4.38455100	0.48366900	-0.72415400
H	-5.08042700	-0.15674600	-1.25170000
H	-4.10674800	1.38605400	-1.25018000
C	-4.38446800	0.48240400	0.72501700
H	-4.10659700	1.38386700	1.25258600
H	-5.08030600	-0.15892000	1.25150900
P	-2.95320800	-0.53947700	-0.00053400
P	-1.47788900	1.02322600	0.00059000

4 (L4)

Zero-point correction= 0.043685 (Hartree/Particle)
Thermal correction to Energy= 0.059539
Thermal correction to Enthalpy= 0.060484
Thermal correction to Gibbs Free Energy= -0.003771
Sum of electronic and zero-point Energies= -1316.785283
Sum of electronic and thermal Energies= -1316.769429
Sum of electronic and thermal Enthalpies= -1316.768485
Sum of electronic and thermal Free Energies= -1316.832740

0 1

P	-3.95342600	0.00024300	0.00049600
P	-2.06134700	0.00076800	0.00089300
W	0.35444300	0.00002300	0.00002000
C	0.36953100	0.20020600	2.06998300
C	0.36913000	2.06997000	-0.20025900
C	2.40421900	-0.00102200	-0.00134900
C	0.36684100	-0.20015100	-2.06992100
C	0.36733100	-2.06993400	0.20010100
O	0.38751700	0.30908900	3.20767100
O	0.38626400	3.20767200	-0.30912600
O	3.54984000	-0.00140100	-0.00173700
O	0.38363300	-0.30914300	-3.20761900
O	0.38405300	-3.20763100	0.30910400

TS1 (L4)

Zero-point correction= 0.150333 (Hartree/Particle)
Thermal correction to Energy= 0.172211
Thermal correction to Enthalpy= 0.173155
Thermal correction to Gibbs Free Energy= 0.096245
Sum of electronic and zero-point Energies= -1473.859764
Sum of electronic and thermal Energies= -1473.837887
Sum of electronic and thermal Enthalpies= -1473.836943
Sum of electronic and thermal Free Energies= -1473.913852

0 1

P	1.39813600	0.81363700	0.29615300
W	-0.88531200	-0.12107200	-0.01875800
C	-0.30809200	-1.82023400	1.01794000
C	-0.23404900	-0.99742900	-1.78252700
C	-2.76250300	-0.88642200	-0.25103800
C	-1.41114200	1.60656800	-1.03646100
C	-1.43033000	0.77985500	1.75597800
O	0.01790700	-2.75852800	1.59247700
O	0.14934000	-1.48426700	-2.74616300
O	-3.82391900	-1.30770800	-0.38047200
O	-1.67927500	2.57752300	-1.58570000
O	-1.71057000	1.29344500	2.74361700
P	3.20888400	0.52588000	-0.59411200
C	2.11985000	2.52041400	-0.40953900
H	3.08817400	2.96314700	-0.60754400
H	1.38224400	2.83648800	-1.14027900
C	1.65969000	2.44792700	1.03047300
H	2.45944700	2.54069000	1.75452700
H	0.76551200	3.01042800	1.28645000
C	3.97028300	-1.70398000	0.92006000
H	3.36790500	-1.54823200	1.80648900

H	5.02820000	-1.49811900	1.01799100
C	3.43908500	-2.15526500	-0.21964000
H	2.38909000	-2.40475000	-0.30417000
H	4.04257700	-2.34536600	-1.09753200

TS2 (L4)

Zero-point correction= 0.150645 (Hartree/Particle)
Thermal correction to Energy= 0.172538
Thermal correction to Enthalpy= 0.173483
Thermal correction to Gibbs Free Energy= 0.096415
Sum of electronic and zero-point Energies= -1473.880007
Sum of electronic and thermal Energies= -1473.858113
Sum of electronic and thermal Enthalpies= -1473.857169
Sum of electronic and thermal Free Energies= -1473.934237

0 1

W	-0.88687100	-0.05112700	-0.03471600
C	-1.14578800	1.99927800	-0.13421000
C	-1.77168700	-0.00617100	1.84364700
C	-2.73088800	-0.39239200	-0.85916600
C	-0.56848400	-2.10031100	0.08511000
C	0.04034600	-0.07989100	-1.88707800
O	-1.26750100	3.14000500	-0.17690000
O	-2.26820500	0.02793200	2.87535600
O	-3.76299000	-0.58546000	-1.32719000
O	-0.38981400	-3.23055900	0.13907800
O	0.57106400	-0.08742700	-2.90451800
C	4.25327000	-0.58786700	0.19126800
H	5.13073600	-1.14327700	0.49831800
H	4.41662500	0.48178500	0.16640200
C	3.39308100	-1.18612600	-0.89974800
H	2.97633300	-0.51199000	-1.63578500
H	3.70168800	-2.13859200	-1.31370300
P	2.64375700	-1.21372800	0.76141400
P	1.27021700	0.38648000	1.13076700
C	2.48663900	2.65938400	0.48775300
C	2.35976100	2.26649600	-0.78510900
H	1.72921500	3.25861700	0.97696700
H	3.38659100	2.47562400	1.05991200
H	3.14381900	1.72557600	-1.30073600
H	1.47589300	2.49407200	-1.36647300

TS3 (L4)

Zero-point correction= 0.095792 (Hartree/Particle)
Thermal correction to Energy= 0.114982
Thermal correction to Enthalpy= 0.115926
Thermal correction to Gibbs Free Energy= 0.043172
Sum of electronic and zero-point Energies= -1395.313432
Sum of electronic and thermal Energies= -1395.294243
Sum of electronic and thermal Enthalpies= -1395.293299
Sum of electronic and thermal Free Energies= -1395.366052

0 1

W	0.67517400	-0.00061000	-0.00153000
C	0.57943200	-0.03541300	2.07511800
C	0.07947600	1.98942800	0.06248300
C	2.60944400	0.62350300	0.06196700

C	0.65439200	0.12028400	-2.07788300
C	1.45308900	-1.91894700	-0.06005400
O	0.50884900	-0.03608600	3.21818300
O	-0.12404100	3.11935300	0.10049500
O	3.71261700	0.94885300	0.10078700
O	0.62681700	0.20597500	-3.21950400
O	1.91700100	-2.96623800	-0.08872200
C	-4.60668200	-0.24952900	0.67425000
H	-4.92693800	0.58584300	1.28239500
H	-4.41951600	-1.17954000	1.19140000
C	-4.61707800	-0.18216000	-0.69059000
H	-4.43854800	-1.05644900	-1.29963900
H	-4.94677900	0.70862700	-1.20862700
P	-2.55412200	0.48782700	0.01014600
P	-1.53077800	-1.23923800	-0.07774600

TS4 (L4)

Zero-point correction= 0.096753 (Hartree/Particle)
Thermal correction to Energy= 0.114921
Thermal correction to Enthalpy= 0.115865
Thermal correction to Gibbs Free Energy= 0.046266
Sum of electronic and zero-point Energies= -1395.309656
Sum of electronic and thermal Energies= -1395.291488
Sum of electronic and thermal Enthalpies= -1395.290543
Sum of electronic and thermal Free Energies= -1395.360143

0 1

W	0.67798800	-0.01645700	-0.01397100
C	-0.17298300	0.00846800	-1.89187200
C	0.39519700	-2.06902800	0.03422400
C	2.52844300	-0.19814300	-0.81314000
C	1.44275200	-0.05891900	1.91143400
C	0.92009400	2.03843200	-0.03937700
O	-0.68175500	0.01446400	-2.92240600
O	0.21260700	-3.20155300	0.06252400
O	3.57787200	-0.29477500	-1.27955500
O	1.87202300	-0.08063500	2.97541500
O	1.06094900	3.17762300	-0.05255000
C	-3.13048000	1.12064200	-0.29953300
H	-2.95686500	1.06730100	-1.37096700
H	-3.07676200	2.15770600	0.01802500
C	-4.30159500	0.30724200	0.21939800
H	-4.62993100	0.62702500	1.20144500
H	-5.12369200	0.14529200	-0.47164800
P	-2.95091700	-0.90440300	0.12295100
P	-1.63615000	0.46489000	0.98790000

11 (L5)

Zero-point correction= 0.154817 (Hartree/Particle)
Thermal correction to Energy= 0.175541
Thermal correction to Enthalpy= 0.176485
Thermal correction to Gibbs Free Energy= 0.102142
Sum of electronic and zero-point Energies= -1474.378581
Sum of electronic and thermal Energies= -1474.357857
Sum of electronic and thermal Enthalpies= -1474.356913
Sum of electronic and thermal Free Energies= -1474.431255

0 1

P	1.51908400	0.91406700	-0.01896400
W	-0.83477800	-0.09711200	-0.00301400
C	-0.26868400	-1.82563900	0.95167500
C	-0.46452400	-0.96700200	-1.82836500
C	-2.73399200	-0.76842000	-0.01493300
C	-1.44175200	1.62469800	-0.94862800
C	-1.10534200	0.80580100	1.82560700
O	0.01032200	-2.80853300	1.49390700
O	-0.24112300	-1.45914500	-2.85002300
O	-3.83041800	-1.14498400	-0.02363000
O	-1.76721500	2.59928100	-1.47748700
O	-1.22848200	1.32973200	2.84773800
P	3.49437200	-0.09338400	-0.23198100
C	1.84139300	2.62377700	-0.66211600
H	2.77067200	2.79139100	-1.20219100
H	0.98081200	3.12791200	-1.09498700
C	1.91370600	2.50870600	0.84183700
H	2.88899100	2.60279500	1.31408700
H	1.09657300	2.92715600	1.42509700
C	3.20973200	-1.59428400	0.86940300
H	2.37244600	-1.56691400	1.56055100
H	4.11973500	-2.00794300	1.29857900
C	2.92690300	-1.85428700	-0.57179400
H	1.89351300	-2.00195400	-0.87356700
H	3.63970900	-2.44728000	-1.14051100

3 (L5)

Zero-point correction=	0.099712 (Hartree/Particle)
Thermal correction to Energy=	0.117827
Thermal correction to Enthalpy=	0.118771
Thermal correction to Gibbs Free Energy=	0.047462
Sum of electronic and zero-point Energies=	-1395.817535
Sum of electronic and thermal Energies=	-1395.799419
Sum of electronic and thermal Enthalpies=	-1395.798475
Sum of electronic and thermal Free Energies=	-1395.869785

0 1

W	-0.69661200	-0.00508900	-0.00007600
C	-0.68329200	1.45116000	-1.45854400
C	-0.68352500	1.46804600	1.44137600
C	-2.73184400	0.00113700	-0.00054300
C	-0.68274400	-1.46564000	1.46007300
C	-0.68092200	-1.48256300	-1.44253100
O	-0.66990600	2.26925800	-2.27217300
O	-0.66975700	2.29576800	2.24523200
O	-3.88777200	0.00744500	-0.00047700
O	-0.66988200	-2.28156100	2.27388700
O	-0.66748000	-2.30812300	-2.24718300
C	2.97239700	1.45052700	0.00144800
H	2.87110100	2.08688000	0.88798800
H	2.87117600	2.08833700	-0.88351700
C	4.24353600	0.55999700	0.00050000
H	4.87110000	0.71036800	-0.88426000

H	4.87160700	0.70887800	0.88524600
P	1.76763300	0.03530900	0.00037400
P	3.43643600	-1.16705500	-0.00069300

2a (L5)

Zero-point correction= 0.098087 (Hartree/Particle)
Thermal correction to Energy= 0.116906
Thermal correction to Enthalpy= 0.117850
Thermal correction to Gibbs Free Energy= 0.047079
Sum of electronic and zero-point Energies= -1395.780358
Sum of electronic and thermal Energies= -1395.761540
Sum of electronic and thermal Enthalpies= -1395.760596
Sum of electronic and thermal Free Energies= -1395.831367

0 1

W	0.73510400	-0.00458600	0.00001100
C	0.14379200	-1.37450800	-1.43058300
C	0.14372500	-1.37392700	1.43114400
C	2.65271300	-0.78283900	0.00036600
C	1.29505600	1.37466900	1.43629300
C	1.29533800	1.37392100	-1.43690000
O	-0.20827500	-2.13825900	-2.21782200
O	-0.20835600	-2.13730100	2.21874200
O	3.71501400	-1.23207300	0.00034900
O	1.61174100	2.14949900	2.22825700
O	1.61223000	2.14835800	-2.22916400
C	-4.48165000	0.47202100	-0.72710200
H	-5.16781500	-0.18380300	-1.25785000
H	-4.21020400	1.38004900	-1.25711100
C	-4.48159500	0.47202500	0.72699200
H	-4.21012500	1.38005100	1.25699300
H	-5.16770800	-0.18381700	1.25778500
P	-2.99188800	-0.56857100	-0.00011100
P	-1.48977600	1.01236900	-0.00020700

4 (L5)

Zero-point correction= 0.044296 (Hartree/Particle)
Thermal correction to Energy= 0.059945
Thermal correction to Enthalpy= 0.060889
Thermal correction to Gibbs Free Energy= -0.002494
Sum of electronic and zero-point Energies= -1317.253980
Sum of electronic and thermal Energies= -1317.238331
Sum of electronic and thermal Enthalpies= -1317.237387
Sum of electronic and thermal Free Energies= -1317.300770

0 1

P	3.98336300	0.00009700	-0.00012800
P	2.08094400	0.00030300	-0.00010500
W	-0.35959700	-0.00000600	0.00000800
C	-0.37510200	0.36544300	-2.03673300
C	-0.37514100	2.03676200	0.36535400
C	-2.39312900	-0.00039600	0.00031300
C	-0.37447500	-0.36539500	2.03677800
C	-0.37451300	-2.03675100	-0.36548300
O	-0.39510400	0.56802800	-3.16934500

O	-0.39493500	3.16939900	0.56781500
O	-3.54689400	-0.00059800	0.00044300
O	-0.39410900	-0.56791300	3.16940600
O	-0.39399300	-3.16936100	-0.56812600

C_2H_4 (L5)

Zero-point correction= 0.051197 (Hartree/Particle)
Thermal correction to Energy= 0.054237
Thermal correction to Enthalpy= 0.055181
Thermal correction to Gibbs Free Energy= 0.029666
Sum of electronic and zero-point Energies= -78.536015
Sum of electronic and thermal Energies= -78.532975
Sum of electronic and thermal Enthalpies= -78.532031
Sum of electronic and thermal Free Energies= -78.557546

0 1

C	0.00000000	0.66611200	0.00000000
H	0.92401600	1.24017200	0.00000000
H	-0.92401000	1.24017800	0.00000000
C	0.00000000	-0.66611200	0.00000000
H	-0.92401600	-1.24017200	0.00000000
H	0.92401000	-1.24017800	0.00000000

TS1 (L5)

Zero-point correction= 0.151231 (Hartree/Particle)
Thermal correction to Energy= 0.173151
Thermal correction to Enthalpy= 0.174095
Thermal correction to Gibbs Free Energy= 0.095940
Sum of electronic and zero-point Energies= -1474.297563
Sum of electronic and thermal Energies= -1474.275643
Sum of electronic and thermal Enthalpies= -1474.274699
Sum of electronic and thermal Free Energies= -1474.352853

0 1

P	1.40770400	0.78219700	0.37296800
W	-0.88004100	-0.11533200	-0.01085100
C	-1.25385000	1.49664100	-1.24199800
C	-1.51259800	0.97565200	1.61073000
C	-2.75865300	-0.82495200	-0.32930000
C	-0.45554500	-1.72701100	1.20149400
C	-0.13240200	-1.17211900	-1.61333100
O	-1.43712100	2.40669800	-1.92837900
O	-1.83927400	1.60702000	2.52161900
O	-3.83056600	-1.22077400	-0.50957600
O	-0.19608100	-2.63466600	1.86708800
O	0.31518100	-1.76623900	-2.49491300
P	3.19001000	0.44789100	-0.62526800
C	2.19355000	2.60818300	-0.37739300
H	3.18021100	3.03671400	-0.52449300
H	1.47384600	2.90943100	-1.13558600
C	1.66889900	2.47836100	1.03533000
H	2.42418600	2.58348600	1.81286700
H	0.74032000	3.00641900	1.26396200
C	3.98591000	-1.73932000	0.87181500
H	3.55136600	-1.49773100	1.83753000

H	5.06343400	-1.63218500	0.78411100
C	3.23082100	-2.19593500	-0.15056800
H	2.16272700	-2.36262100	-0.03913200
H	3.66733000	-2.49357900	-1.09915500

TS2 (L5)

Zero-point correction= 0.151794 (Hartree/Particle)
Thermal correction to Energy= 0.173554
Thermal correction to Enthalpy= 0.174498
Thermal correction to Gibbs Free Energy= 0.097788
Sum of electronic and zero-point Energies= -1474.322049
Sum of electronic and thermal Energies= -1474.300289
Sum of electronic and thermal Enthalpies= -1474.299345
Sum of electronic and thermal Free Energies= -1474.376055

0 1

W	-0.89514400	-0.03266500	0.03059200
C	0.02376900	-0.92011400	1.64396200
C	-1.18604300	-1.91978900	-0.78121600
C	-2.75132500	-0.16412900	0.89831300
C	-1.72341800	0.88748600	-1.61625800
C	-0.61372600	1.82030600	0.89011800
O	0.54470100	-1.40698700	2.55157700
O	-1.34101700	-2.97350500	-1.21887800
O	-3.79547500	-0.24213900	1.38701600
O	-2.17635900	1.41576600	-2.53646900
O	-0.43989600	2.85848500	1.36404600
C	3.40286300	-1.01854300	1.00174600
H	3.70138200	-1.84029600	1.65005300
H	2.99695000	-0.16496100	1.53822300
C	4.24015700	-0.74557800	-0.23503900
H	4.40988600	0.29162300	-0.51030100
H	5.09982800	-1.38995200	-0.40953200
P	2.57308500	-1.48273900	-0.59758200
P	1.23031300	0.13203400	-1.22775100
C	2.82806500	2.40489300	0.60565500
C	2.45564400	2.69986000	-0.64982200
H	2.14038000	2.50054600	1.44010700
H	3.83639900	2.07395600	0.83868900
H	3.14829500	2.63901400	-1.48419100
H	1.46504200	3.08852500	-0.86993300

TS3 (L5)

Zero-point correction= 0.097131 (Hartree/Particle)
Thermal correction to Energy= 0.115987
Thermal correction to Enthalpy= 0.116932
Thermal correction to Gibbs Free Energy= 0.043437
Sum of electronic and zero-point Energies= -1395.771540
Sum of electronic and thermal Energies= -1395.752684
Sum of electronic and thermal Enthalpies= -1395.751739
Sum of electronic and thermal Free Energies= -1395.825234

0 1

W	0.72843400	-0.00355200	-0.00105700

C	0.18605900	1.98442500	0.12008200
C	0.63083000	0.14880800	-2.05852000
C	2.68266700	0.52996500	-0.02881200
C	1.35411700	-1.96210700	-0.11614600
C	0.74540100	-0.06962500	2.06402400
O	-0.03167900	3.11753100	0.19013500
O	0.56247000	0.25130800	-3.20537900
O	3.80393400	0.82036800	-0.04624800
O	1.71721600	-3.05569300	-0.17950500
O	0.74521600	-0.08951300	3.21737000
C	-4.80322300	-0.28092300	0.68878800
H	-5.19477300	0.56173800	1.25178200
H	-4.56093800	-1.17614200	1.25248900
C	-4.79666800	-0.28054600	-0.68632900
H	-4.54858900	-1.17547500	-1.24781000
H	-5.18233700	0.56243200	-1.25288800
P	-2.73287800	0.59656000	0.01289600
P	-1.58644700	-1.08200600	0.01144500

TS4 (L5)

Zero-point correction=	0.097773 (Hartree/Particle)
Thermal correction to Energy=	0.115668
Thermal correction to Enthalpy=	0.116612
Thermal correction to Gibbs Free Energy=	0.048353
Sum of electronic and zero-point Energies=	-1395.758992
Sum of electronic and thermal Energies=	-1395.741098
Sum of electronic and thermal Enthalpies=	-1395.740153
Sum of electronic and thermal Free Energies=	-1395.808412

0 1

W	0.69313600	-0.00760100	-0.02100500
C	-0.19534200	0.36207500	-1.83196600
C	0.34664200	-2.01990000	-0.28584600
C	2.52598000	-0.13716200	-0.87477900
C	1.46639600	-0.38525100	1.85401800
C	1.00477100	2.00448300	0.28645600
O	-0.75960500	0.56875200	-2.82065400
O	0.12572900	-3.14565000	-0.42212700
O	3.56828200	-0.21478700	-1.37522700
O	1.89733500	-0.59381300	2.90492800
O	1.18293100	3.13231600	0.46298900
C	-3.24065400	1.17423700	-0.23022900
H	-3.07574500	1.22121700	-1.30495900
H	-3.10871200	2.14472800	0.24172400
C	-4.35368400	0.28115900	0.26503200
H	-4.69237800	0.51767900	1.27313800
H	-5.17932000	0.11209300	-0.42940800
P	-2.97574700	-0.95021000	0.07395400
P	-1.60278100	0.34450300	1.03794600

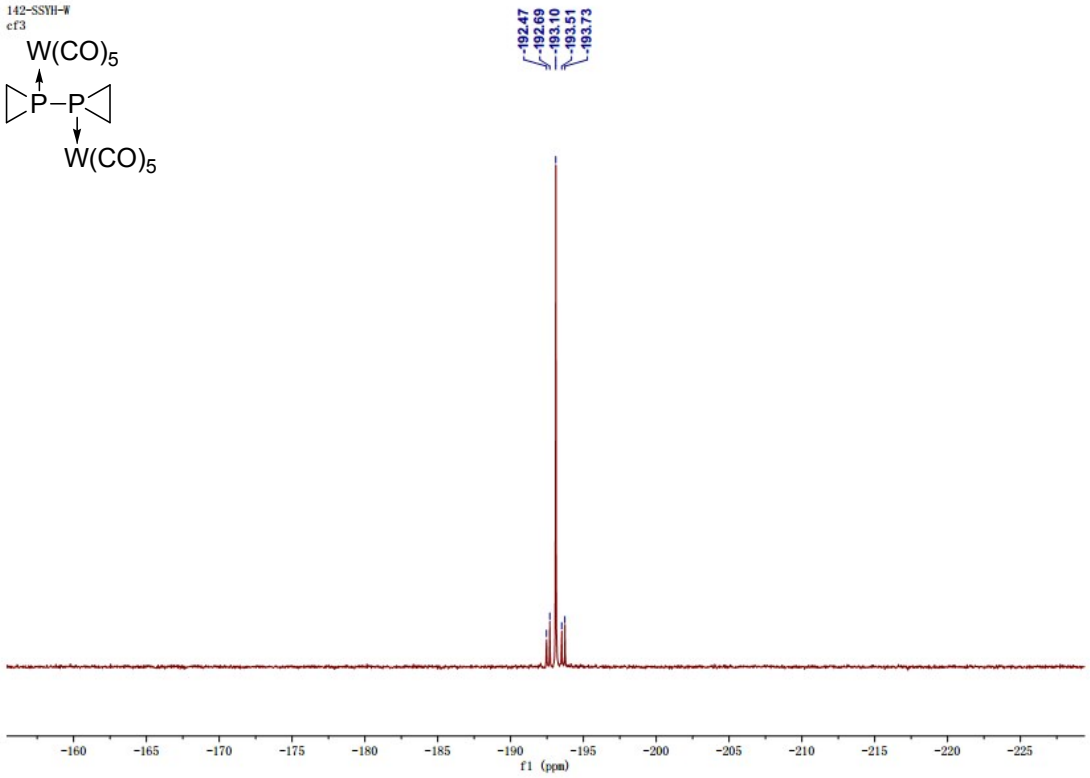
2b

0 1

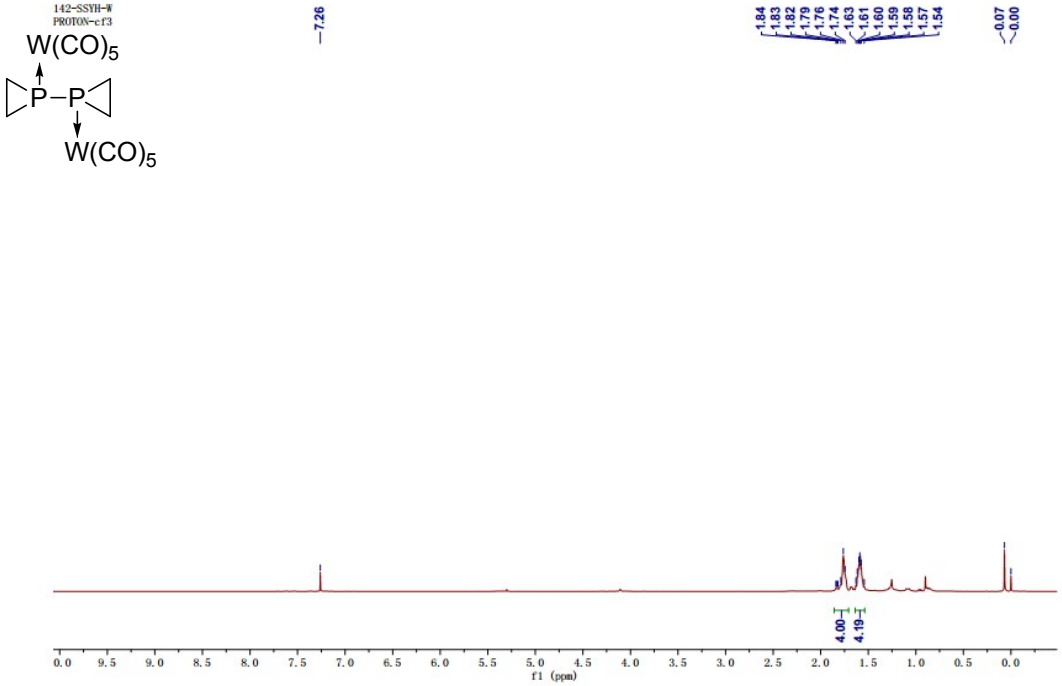
Mo	0.88077800	-0.00529900	-0.00010000
C	0.31341600	-1.38641700	-1.44339200
C	0.31394000	-1.38662300	1.44320000
C	2.82649500	-0.75591100	-0.00043900

C	1.41434000	1.38970100	1.44690000
C	1.41383700	1.38986500	-1.44714100
O	-0.01264300	-2.15350600	-2.23648300
O	-0.01187800	-2.15385500	2.23625100
O	3.89428300	-1.18593700	-0.00070700
O	1.71743400	2.16815000	2.23829800
O	1.71661700	2.16835700	-2.23861600
C	-4.33638900	0.46525200	-0.72527000
H	-5.02230500	-0.18975900	-1.25683900
H	-4.05555800	1.36951800	-1.25572600
C	-4.33644600	0.46555200	0.72583900
H	-4.05565700	1.37004400	1.25593100
H	-5.02239100	-0.18923700	1.25764200
P	-2.84720100	-0.58492800	0.00056400
P	-1.34762600	0.98678300	0.00044200

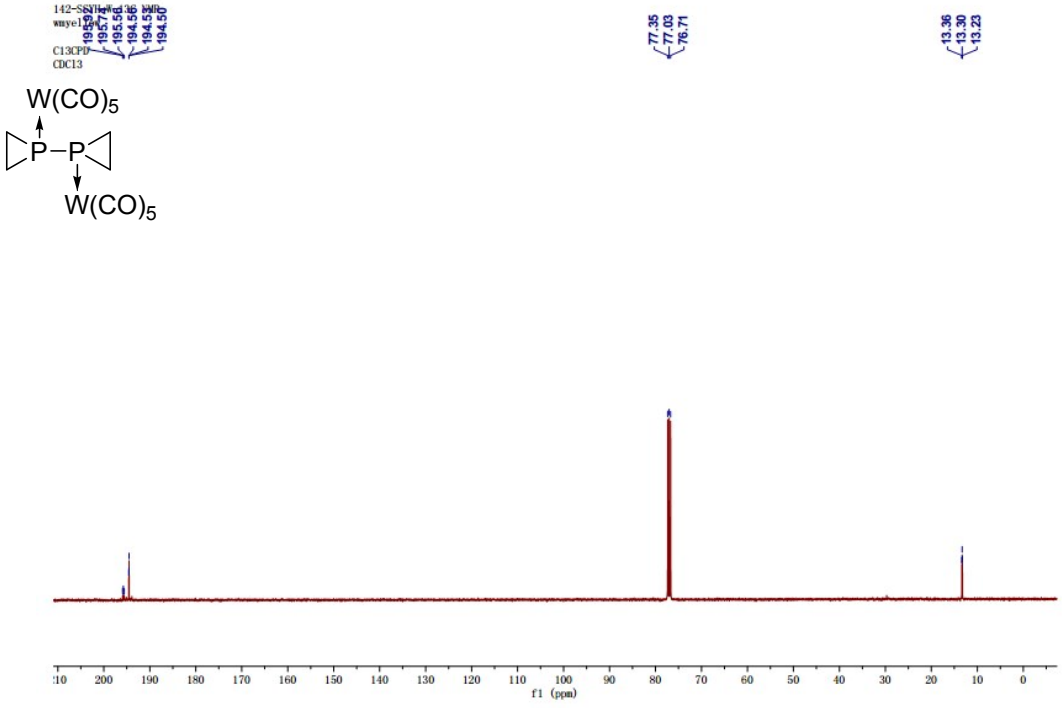
NMR spectra



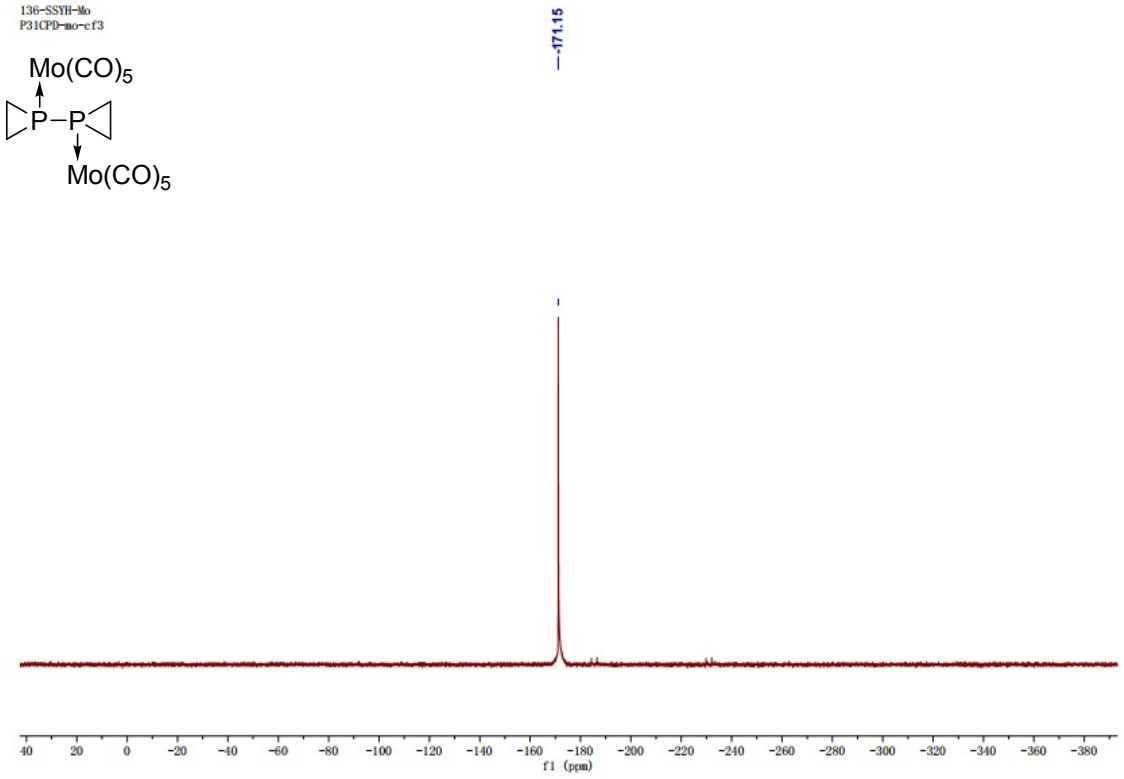
^{31}P $\{^{1}H\}$ NMR of Compound **1a**



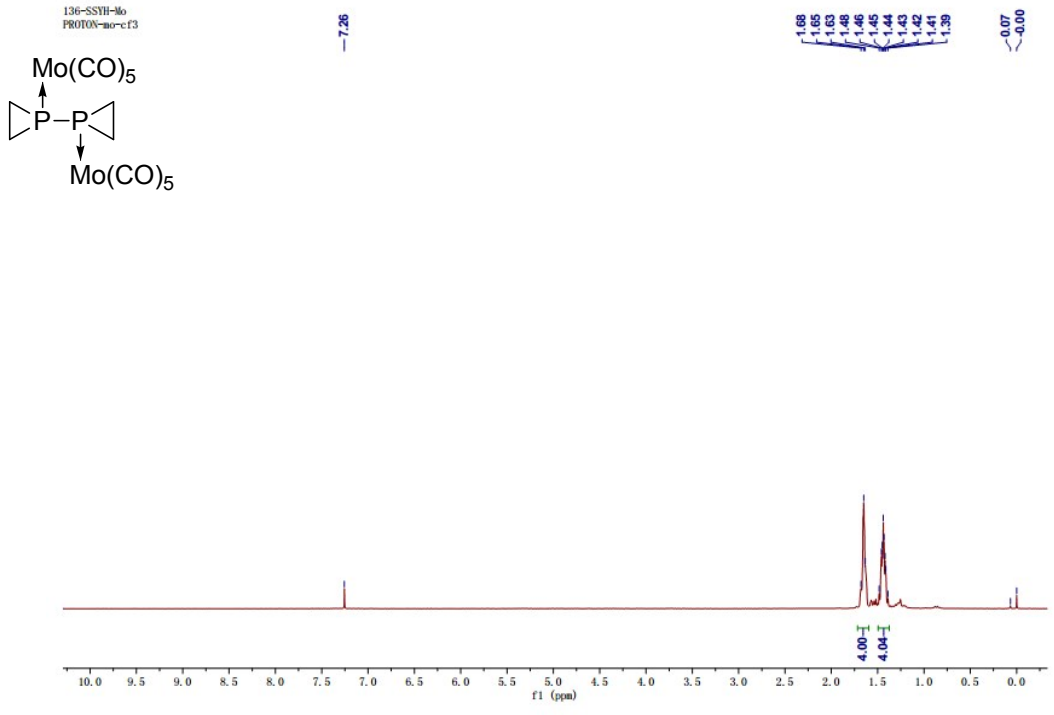
^{1}H NMR of Compound **1a**



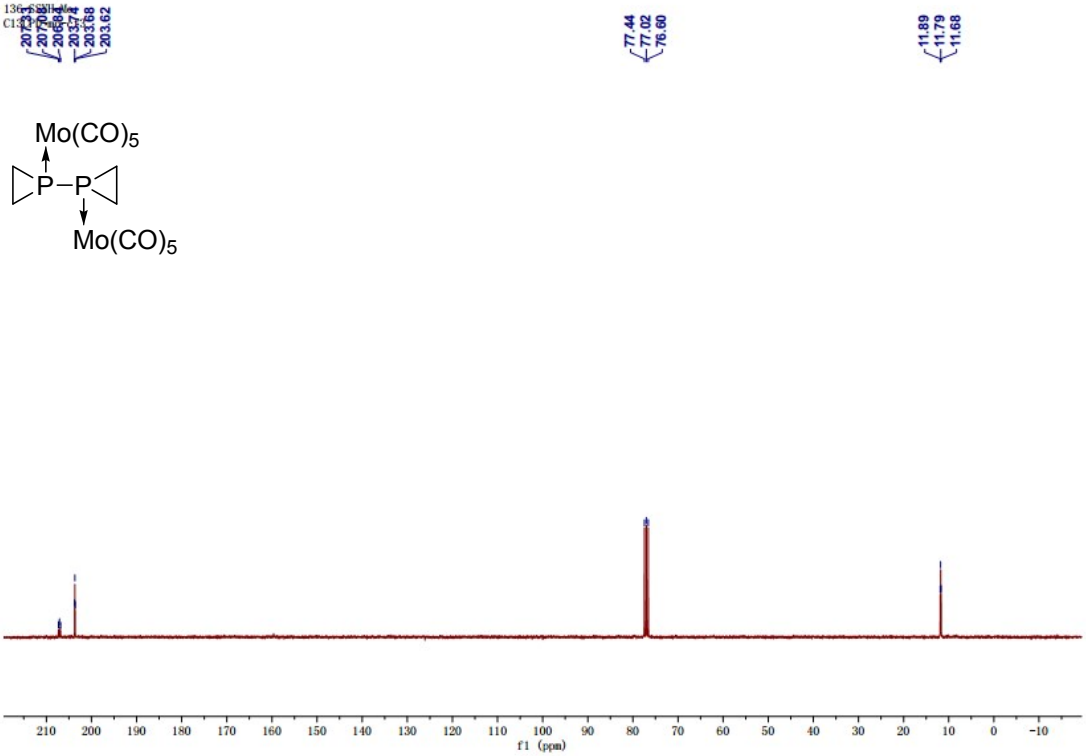
^{13}C {^{1}H} NMR of Compound **1a**



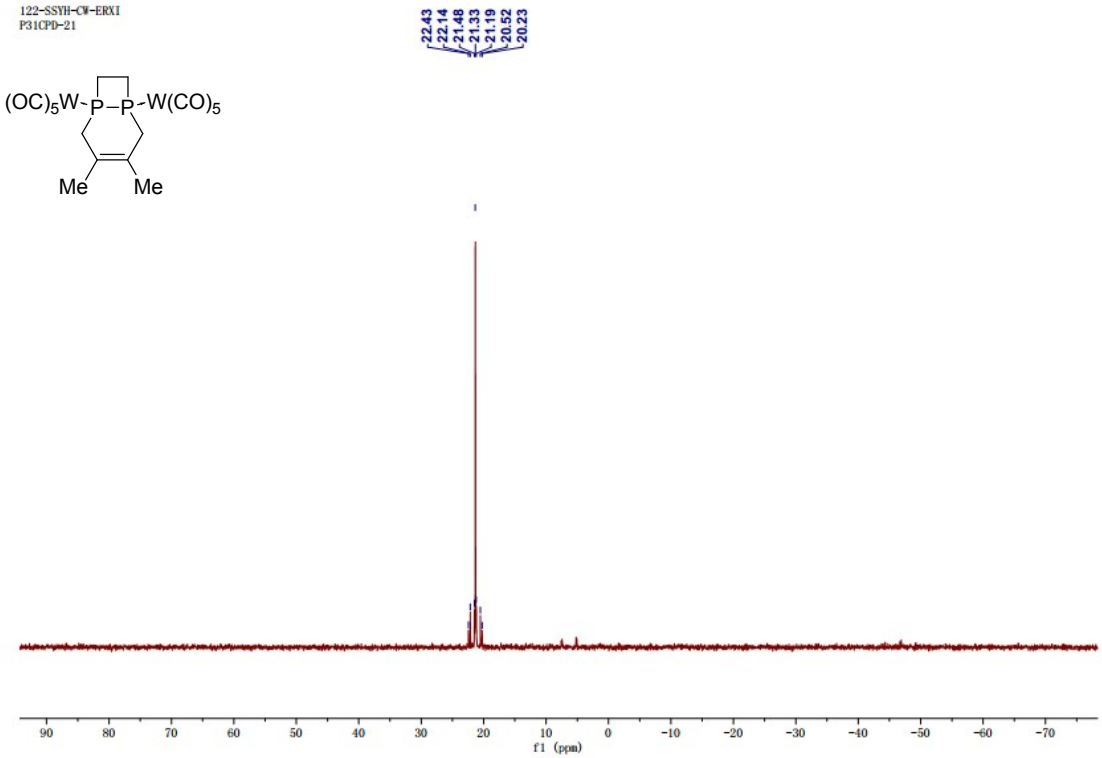
^{31}P $\{^{1}H\}$ NMR of Compound **1b**



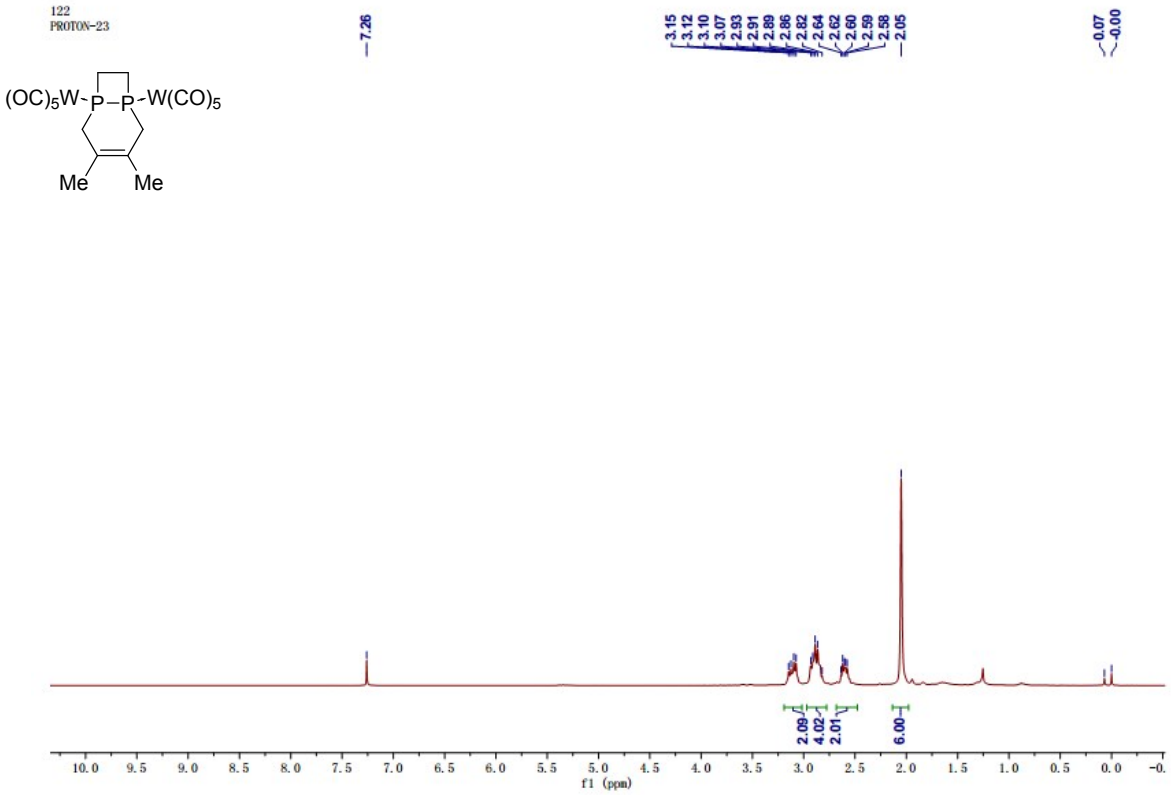
^{1}H NMR of Compound **1b**



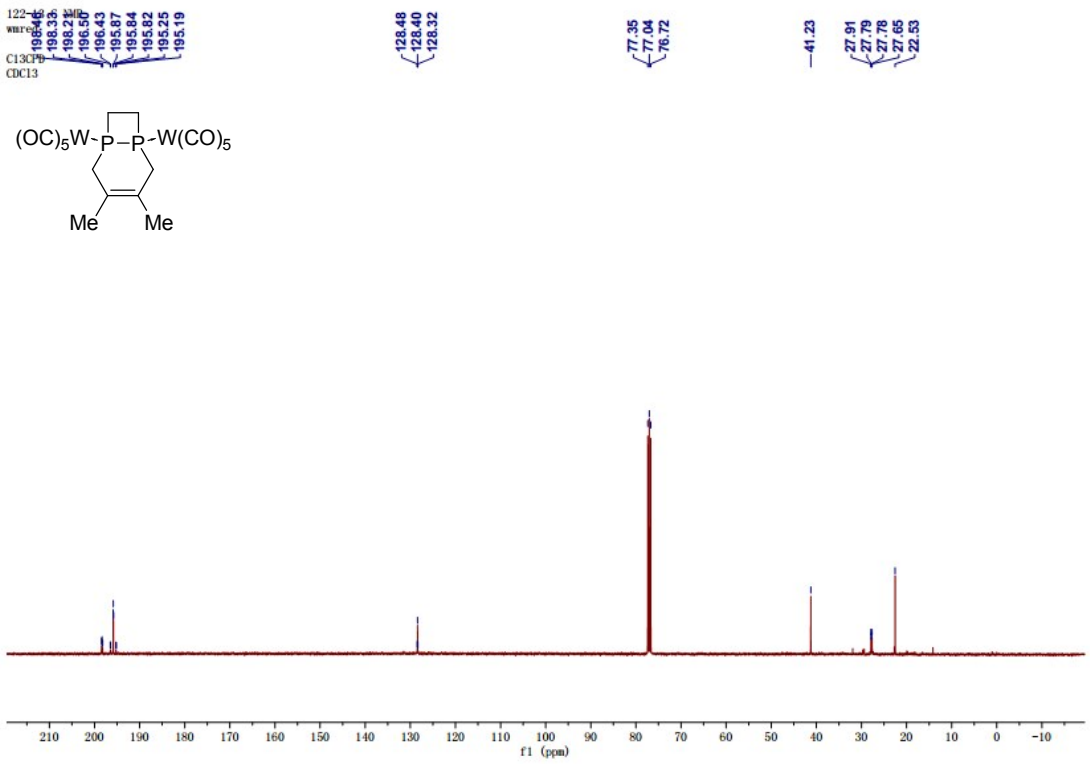
^{13}C {^{1}H} NMR of Compound **1b**



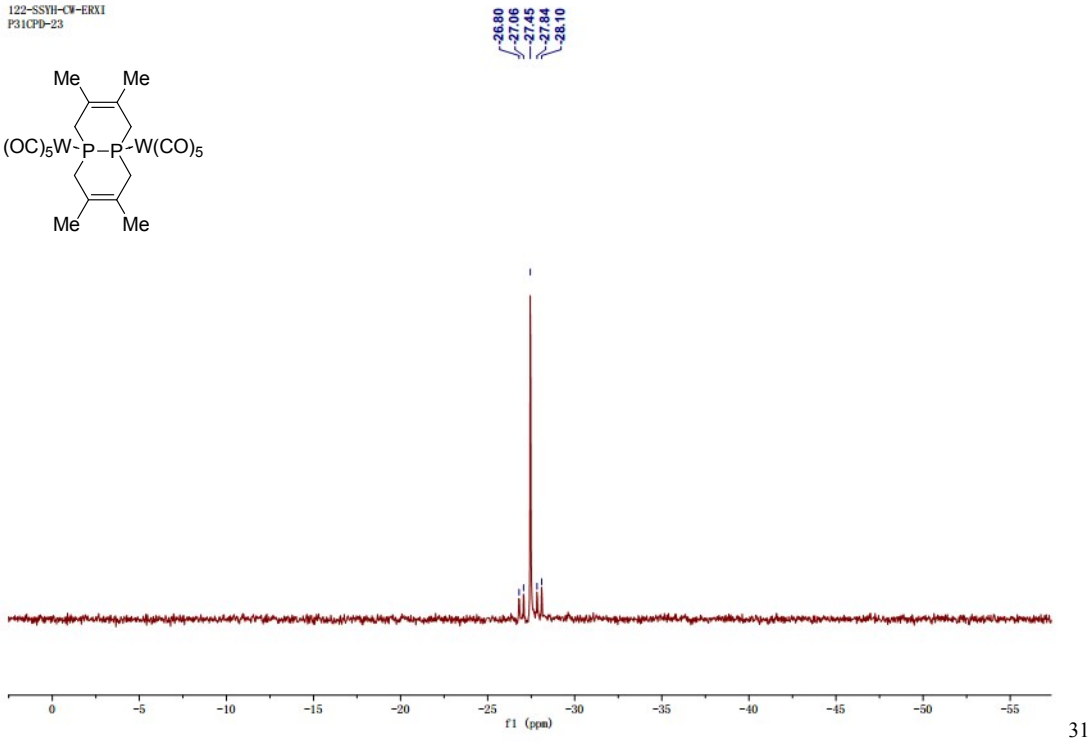
^{31}P {^{1}H} NMR of Compound **6**



^{1}H NMR of Compound **6**

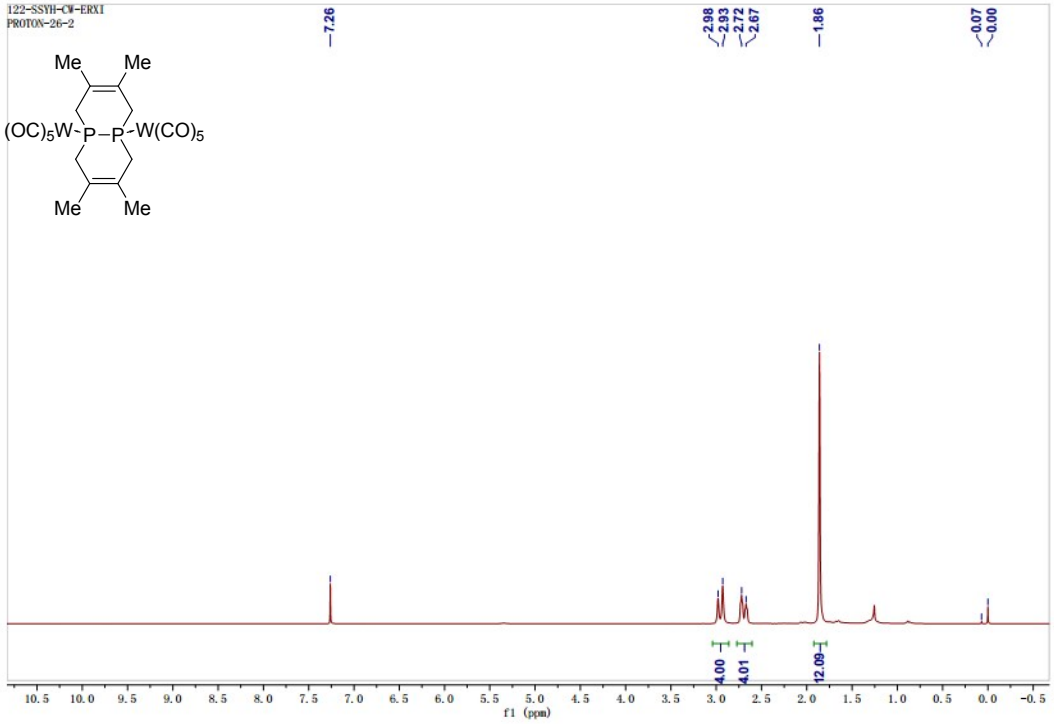


^{13}C {^{1}H} NMR of Compound **6**

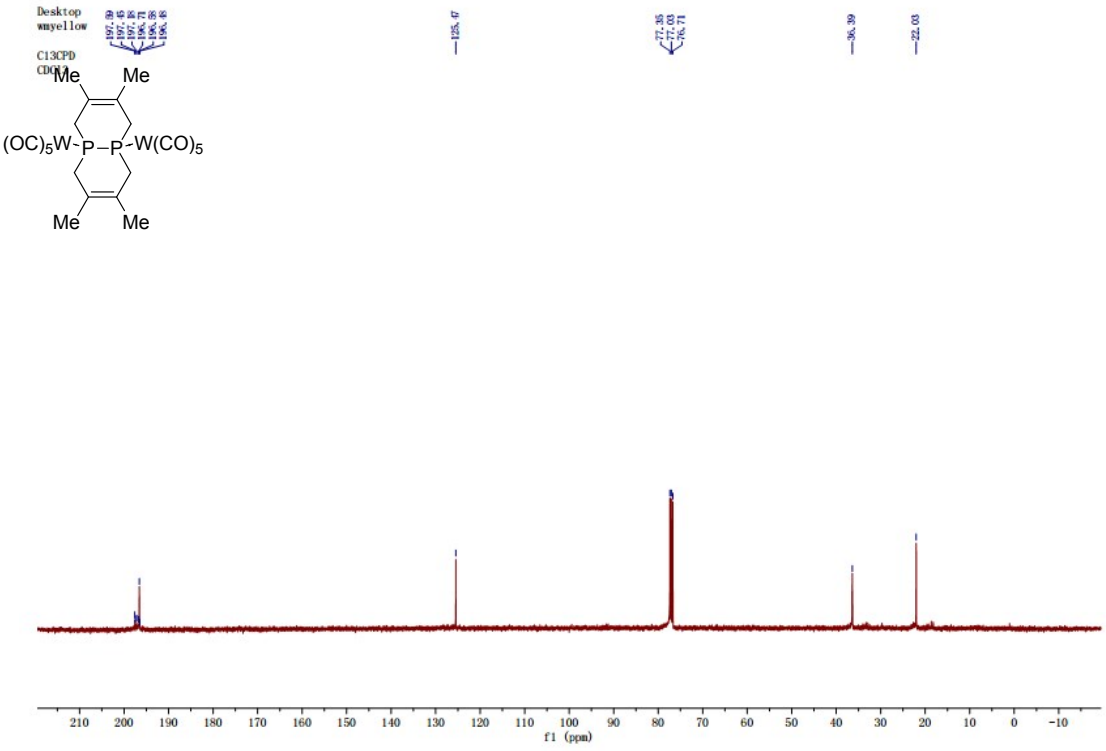


31

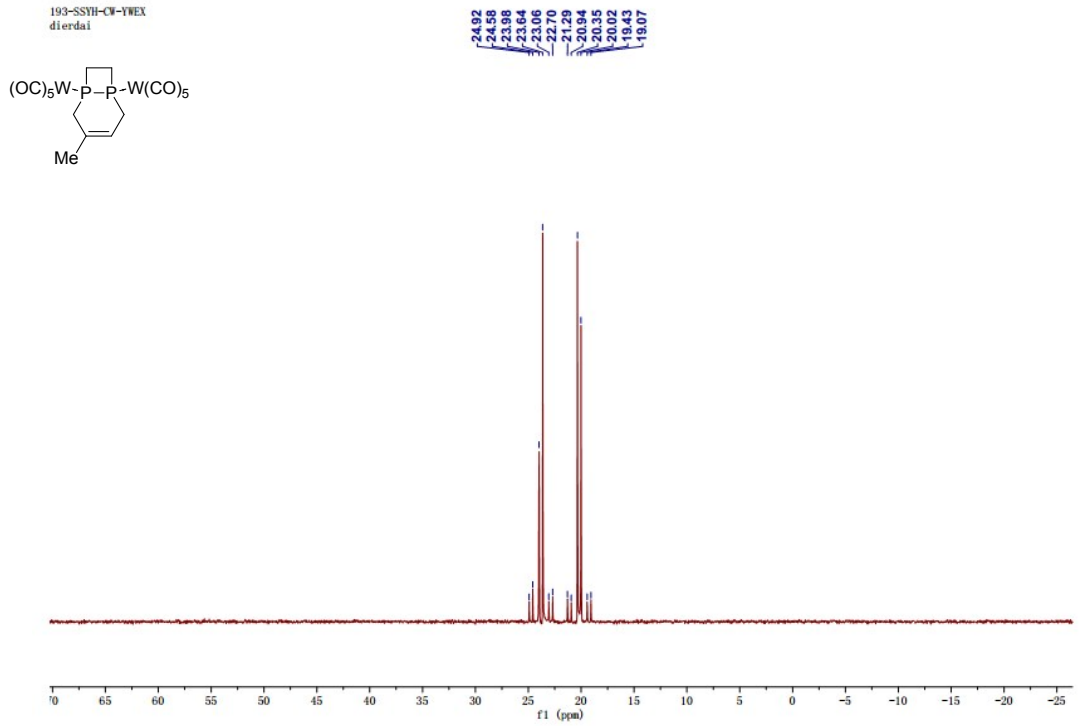
P {^{1}H} NMR of Compound **7**



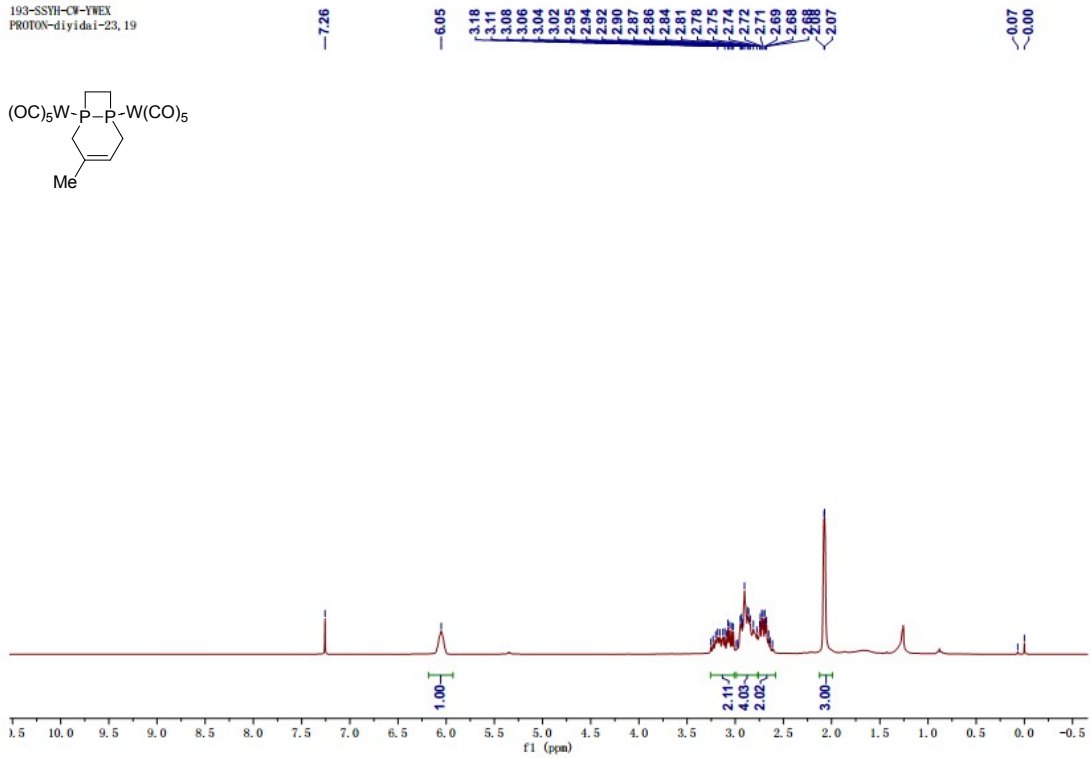
^{1}H NMR of Compound **7**



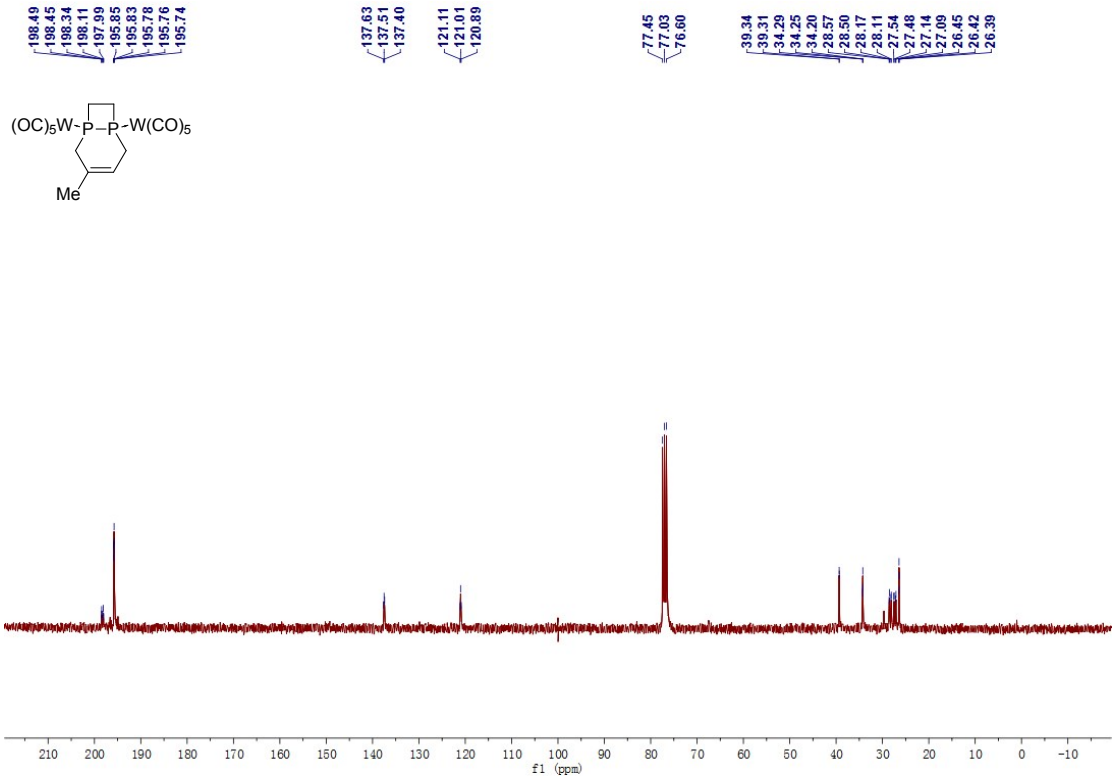
^{13}C {^{1}H} NMR of Compound **7**



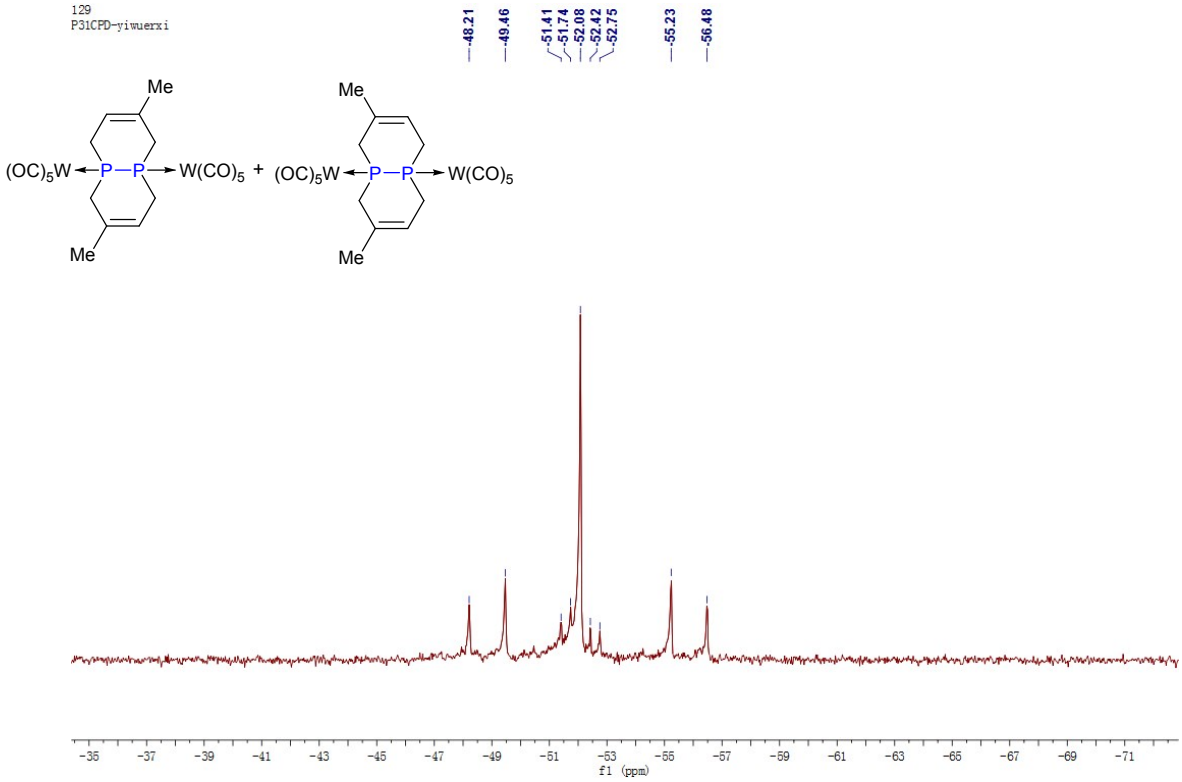
^{31}P {^{1}H} NMR of Compound **8**



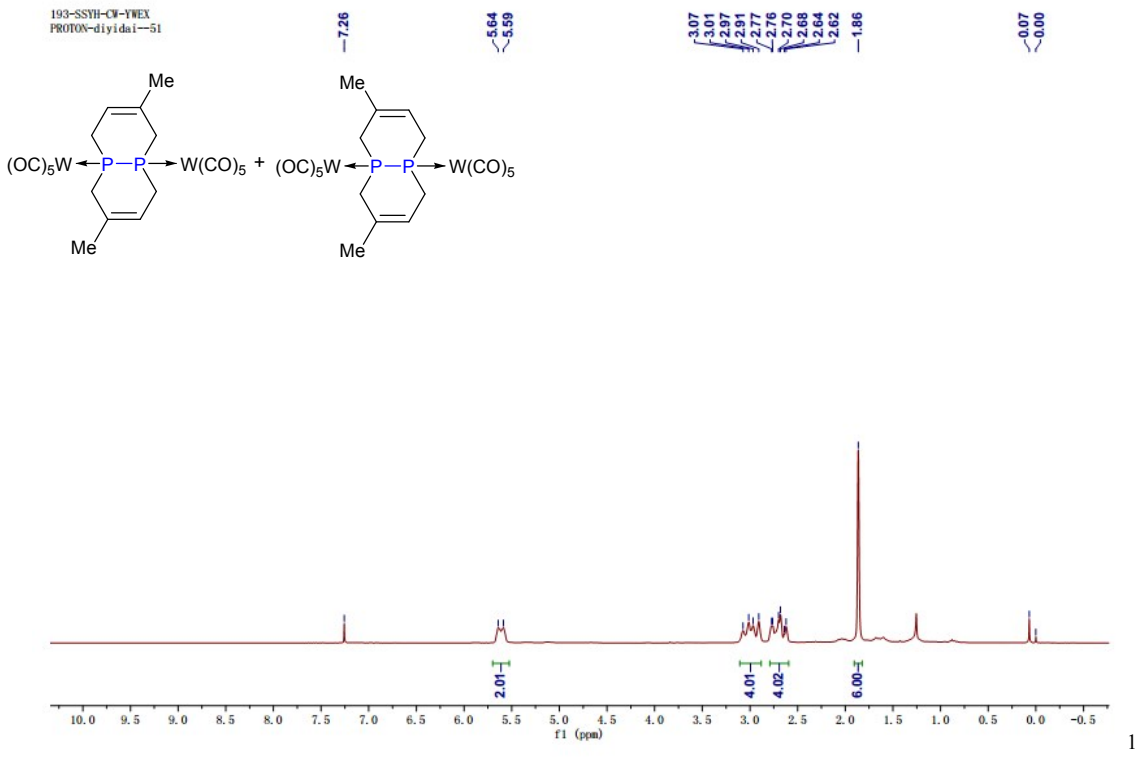
^{1}H NMR of Compound **8**



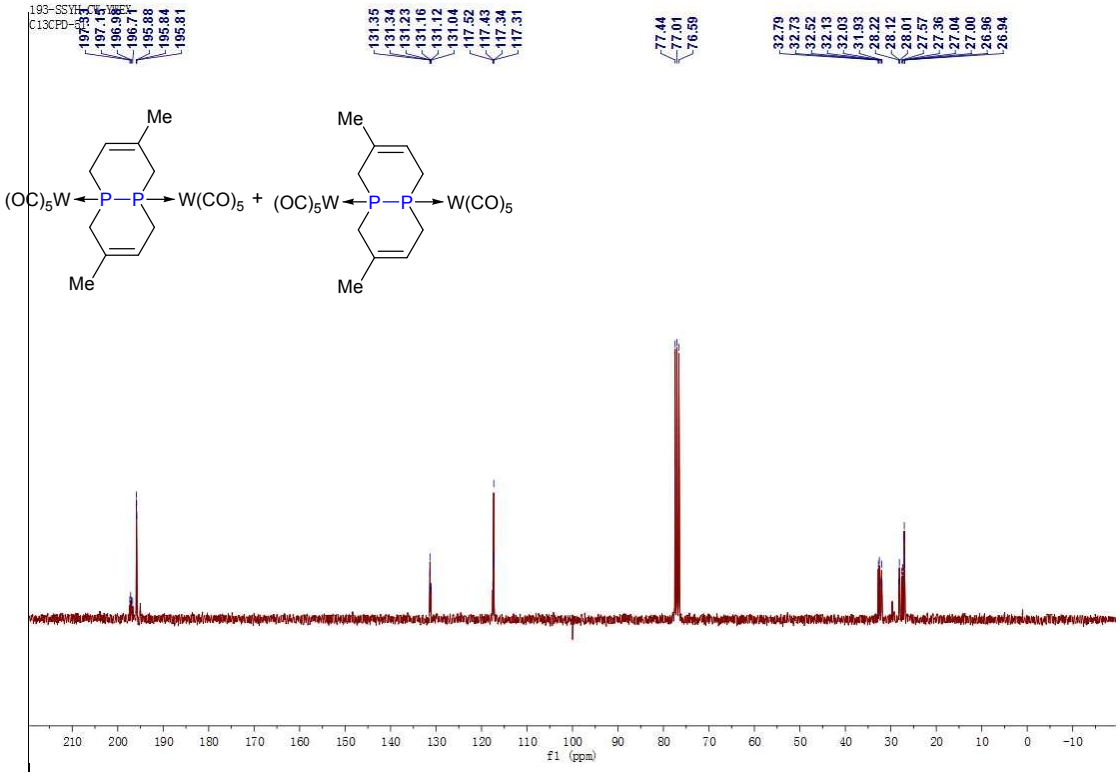
^{13}C {^{1}H} NMR of Compound **8**



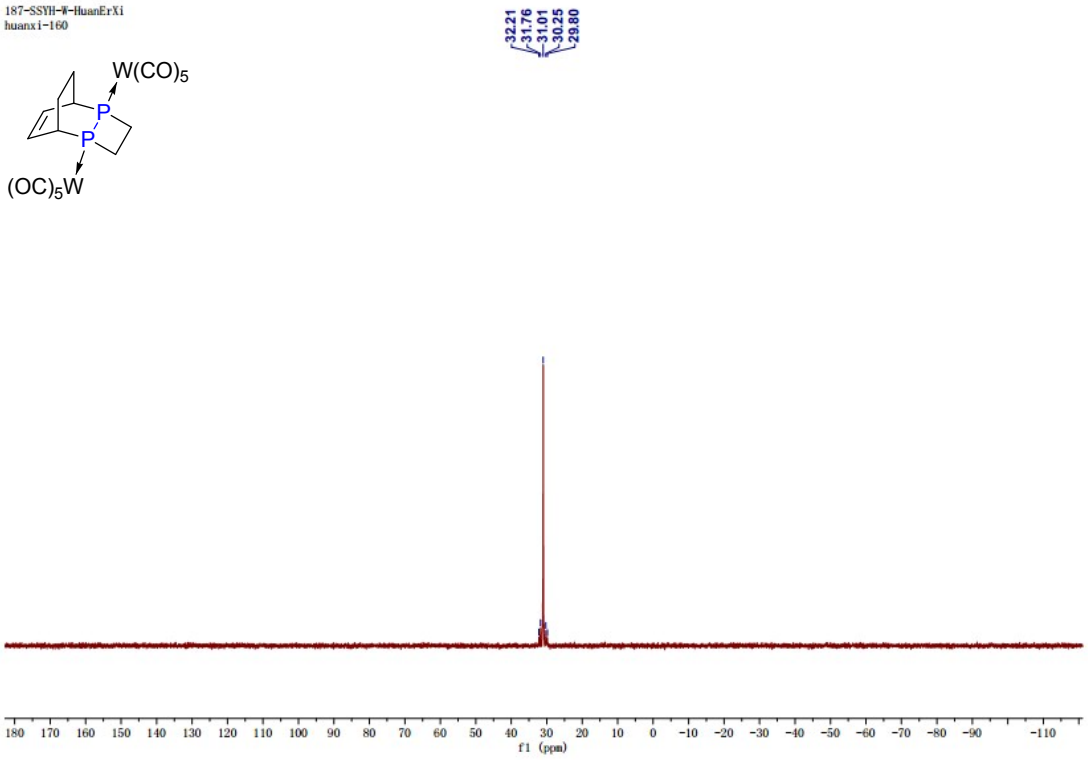
^{31}P $\{^{1}H\}$ NMR of Compound **9** and **9'**



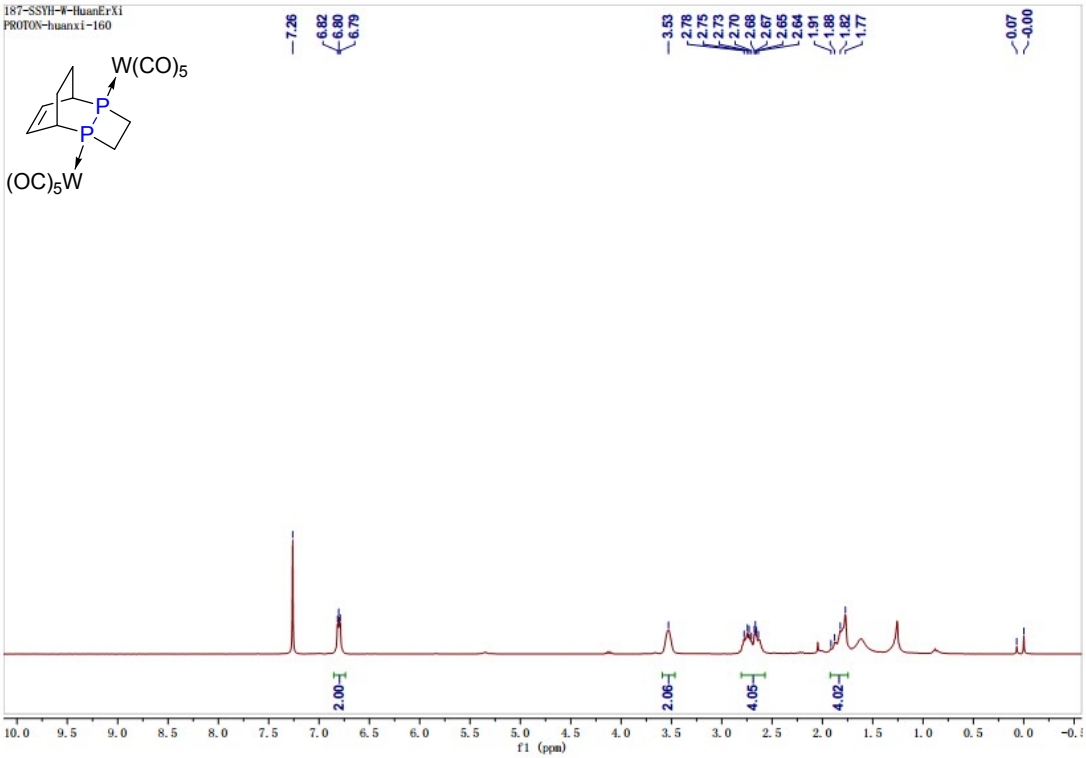
H NMR of Compound **9** and **9'**



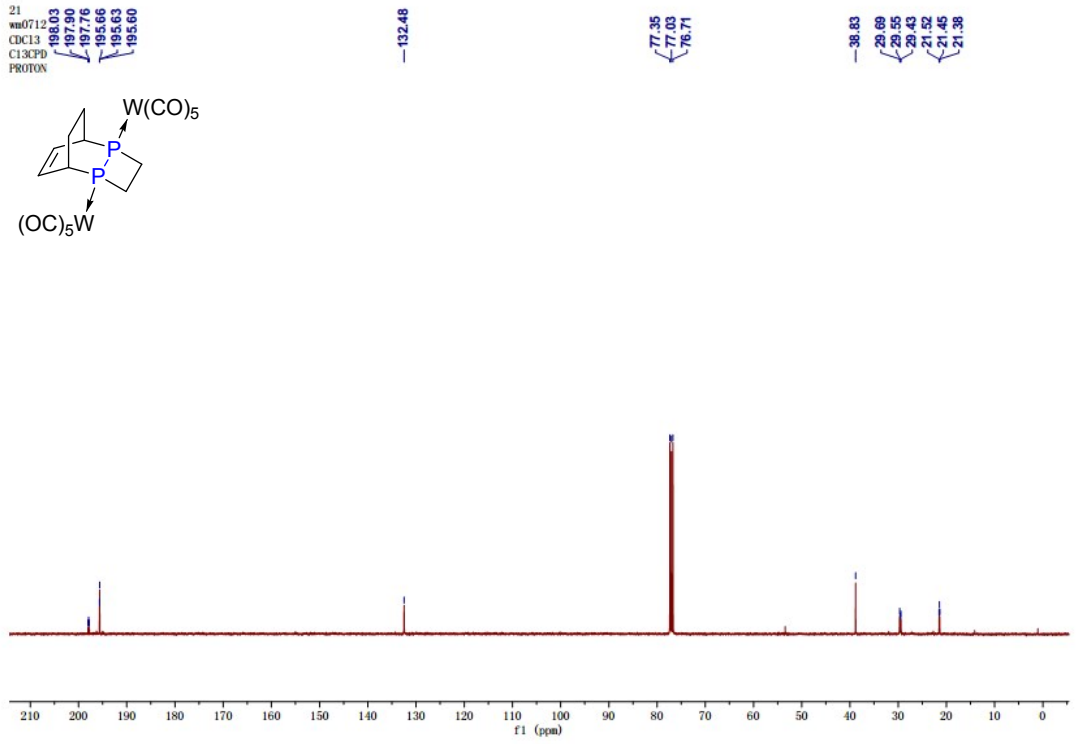
^{13}C {^{1}H} NMR of Compound **9** and **9'**



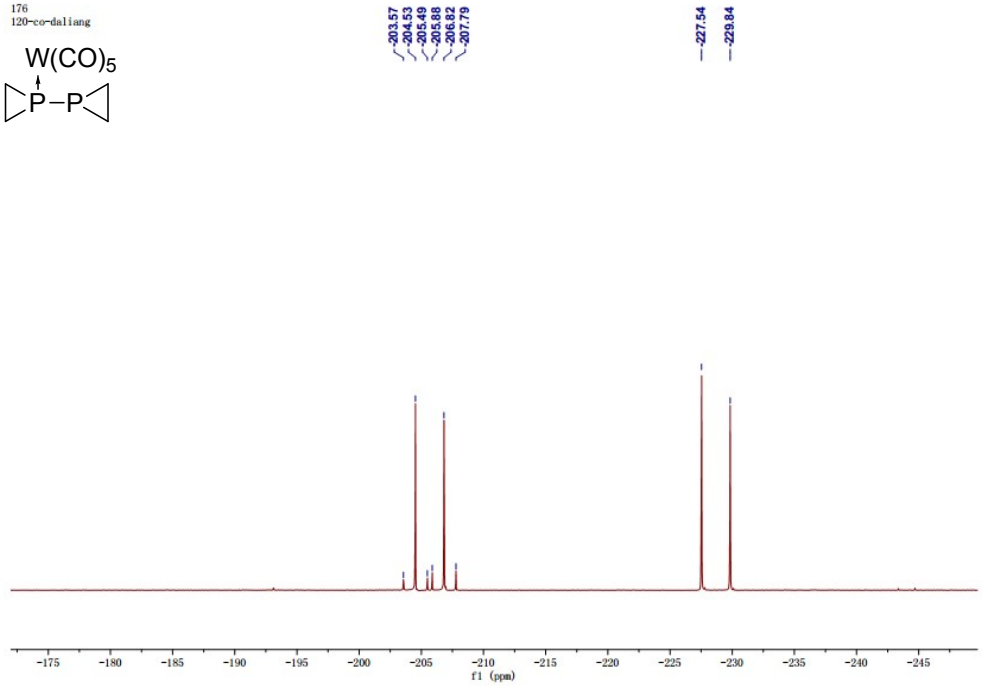
^{31}P {^{1}H} NMR of Compound **10**



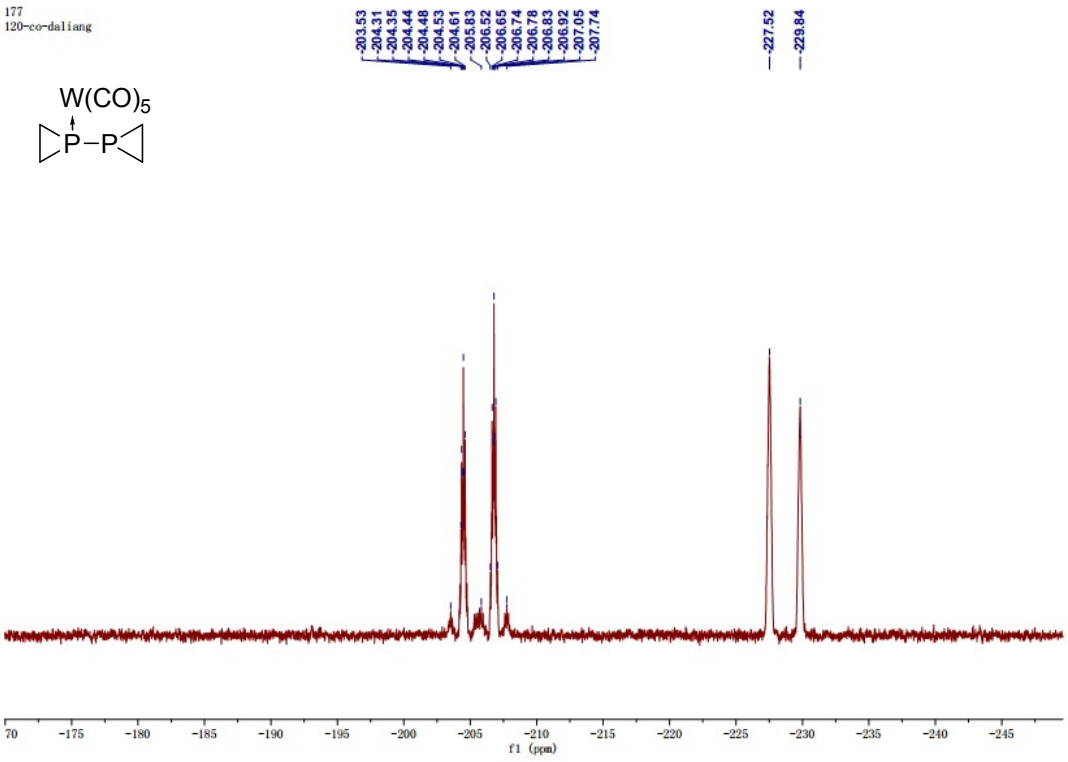
^{1}H NMR of Compound **10**



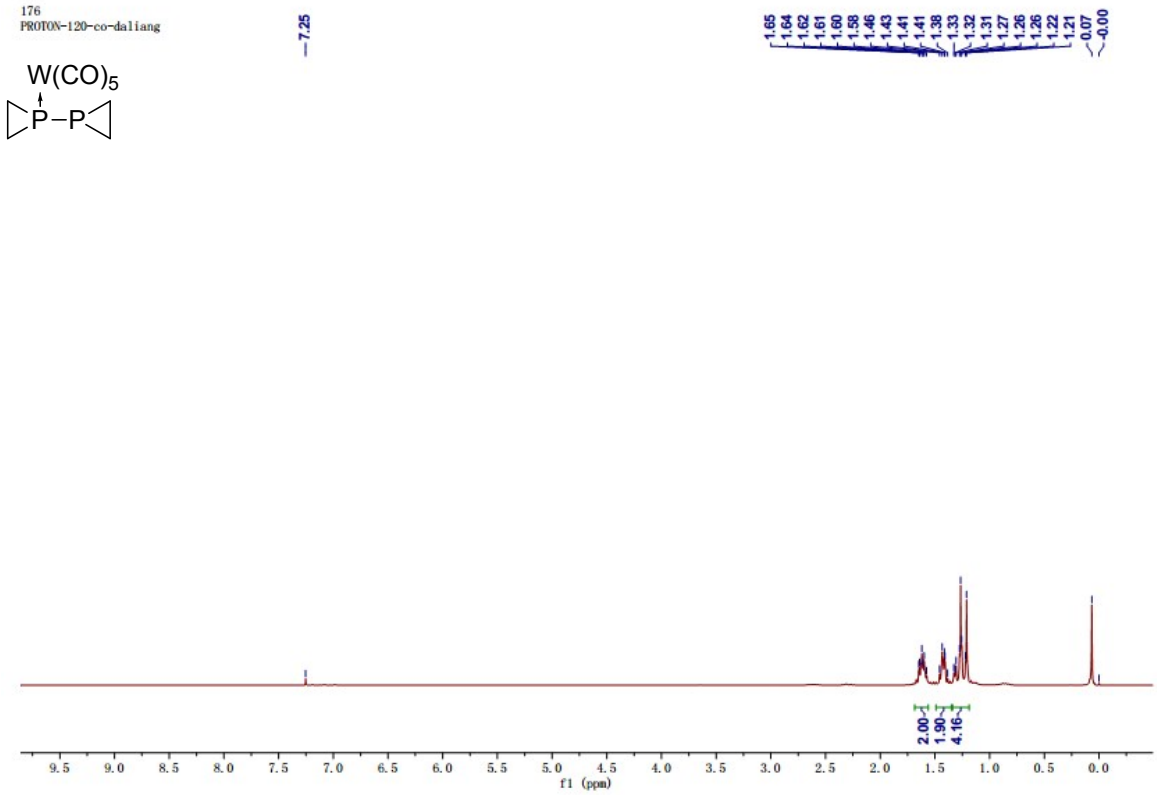
^{13}C {^{1}H} NMR of Compound **10**



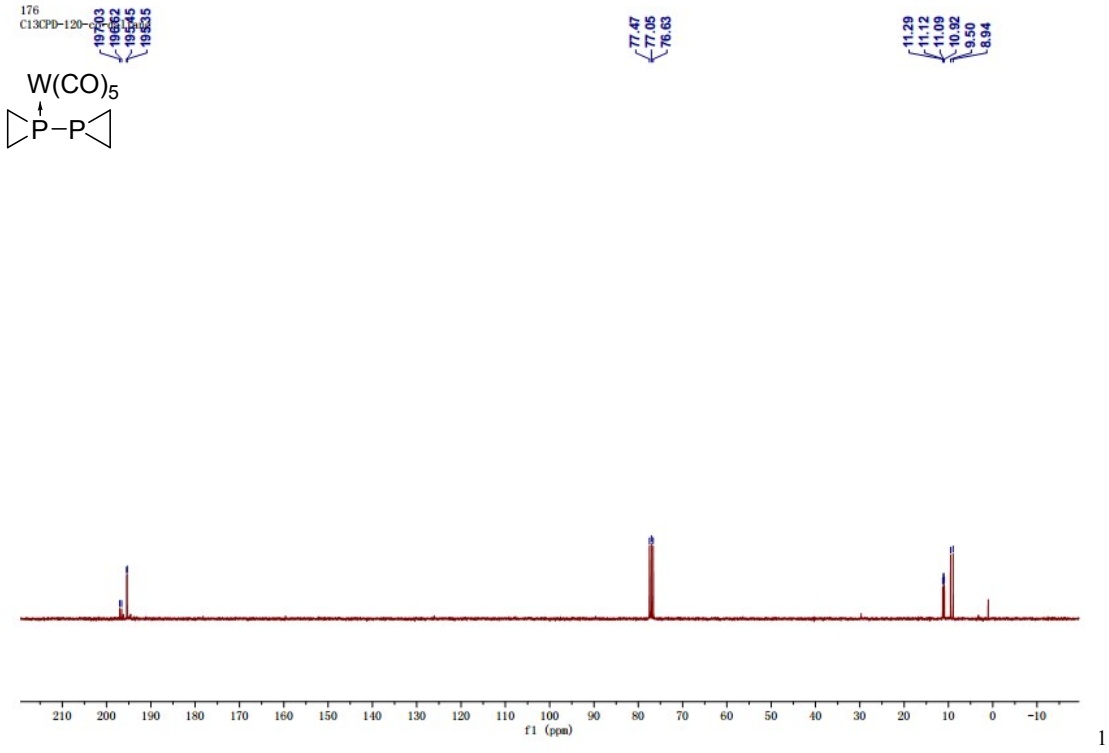
^{31}P $\{^{1}H\}$ NMR of Compound **11**



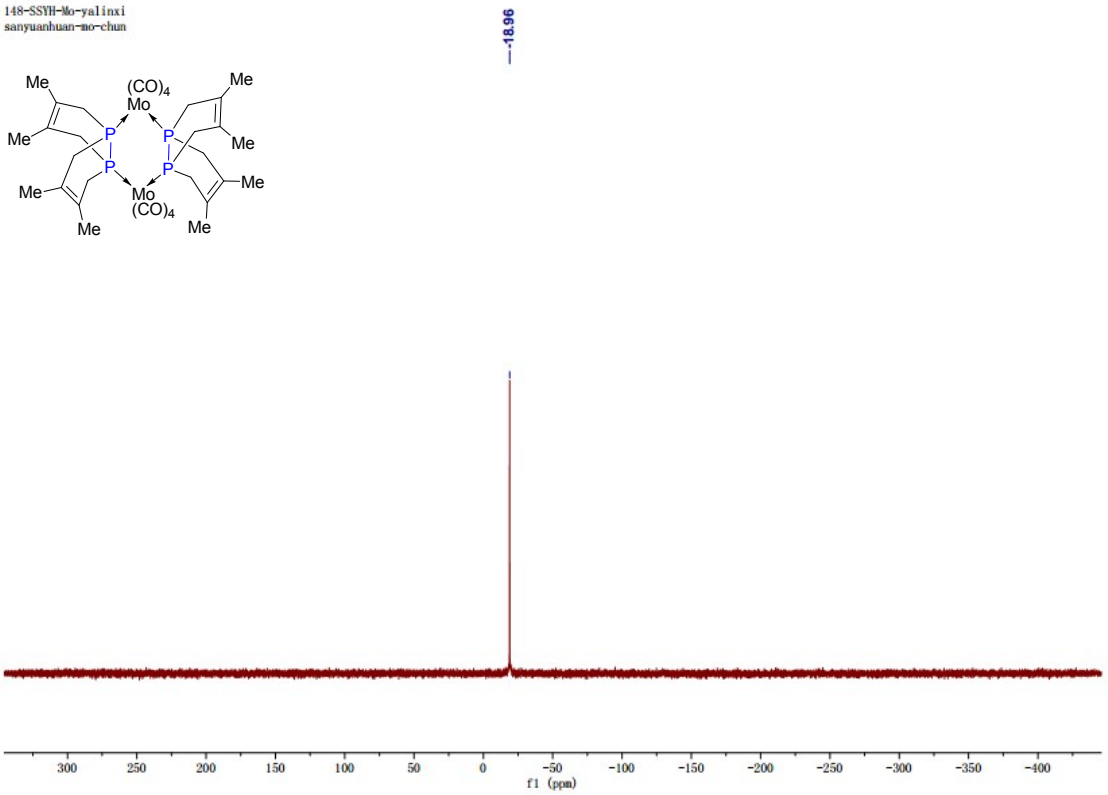
^{1}P NMR of Compound **11**



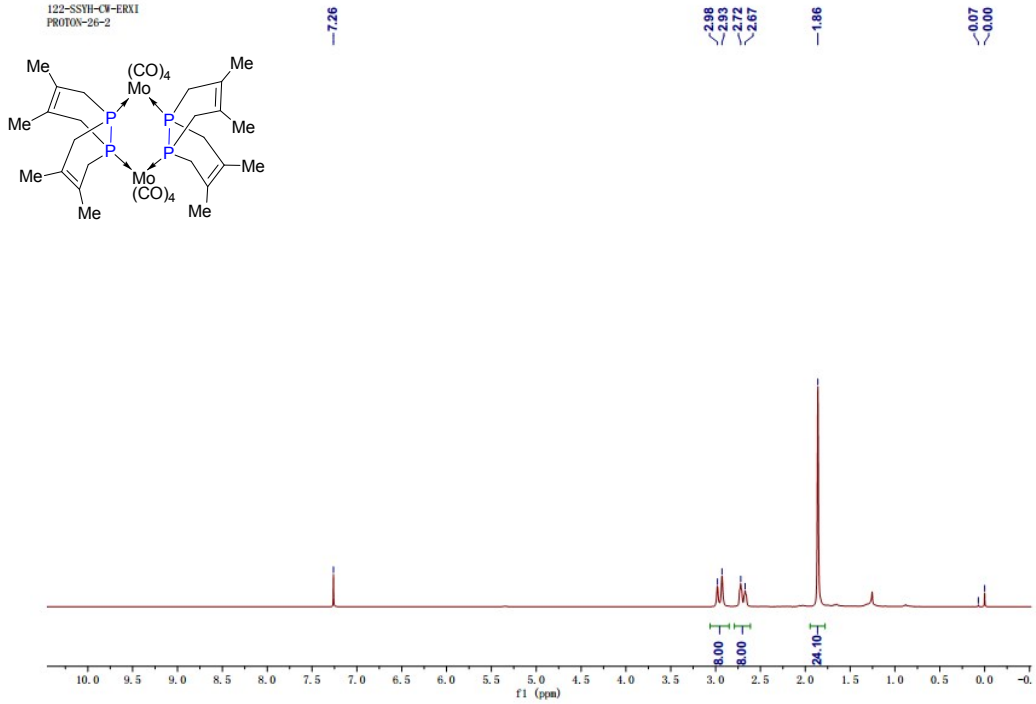
^{1}H NMR of Compound **11**



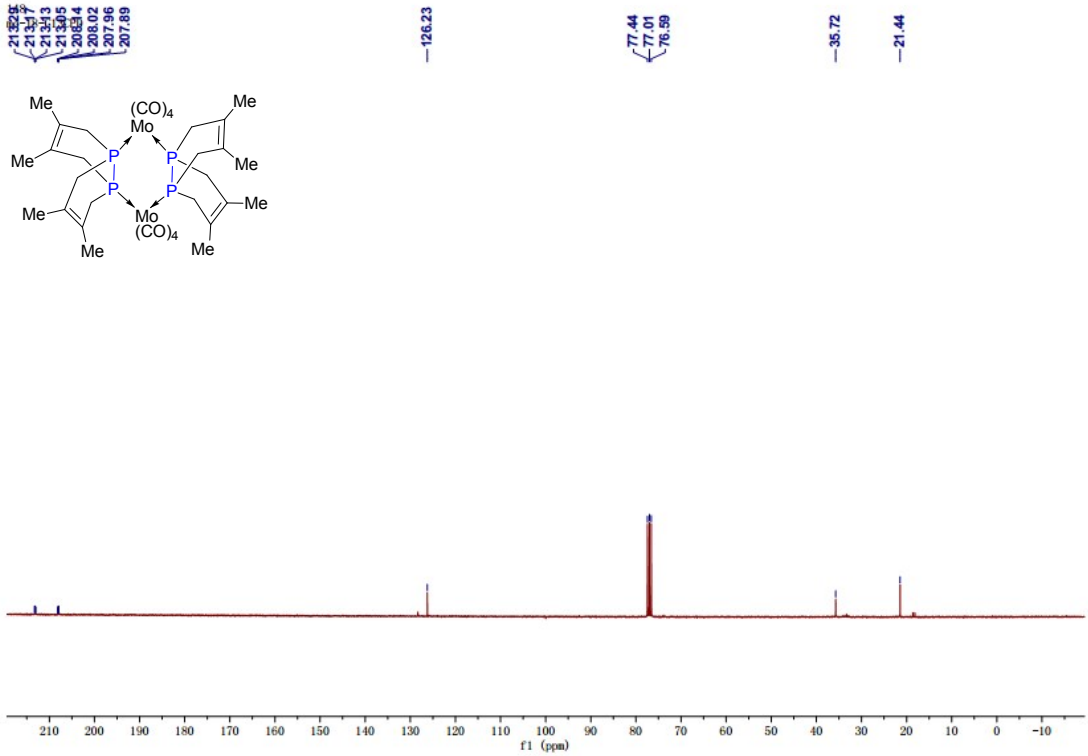
^{3}C {^{1}H} NMR of Compound **11**



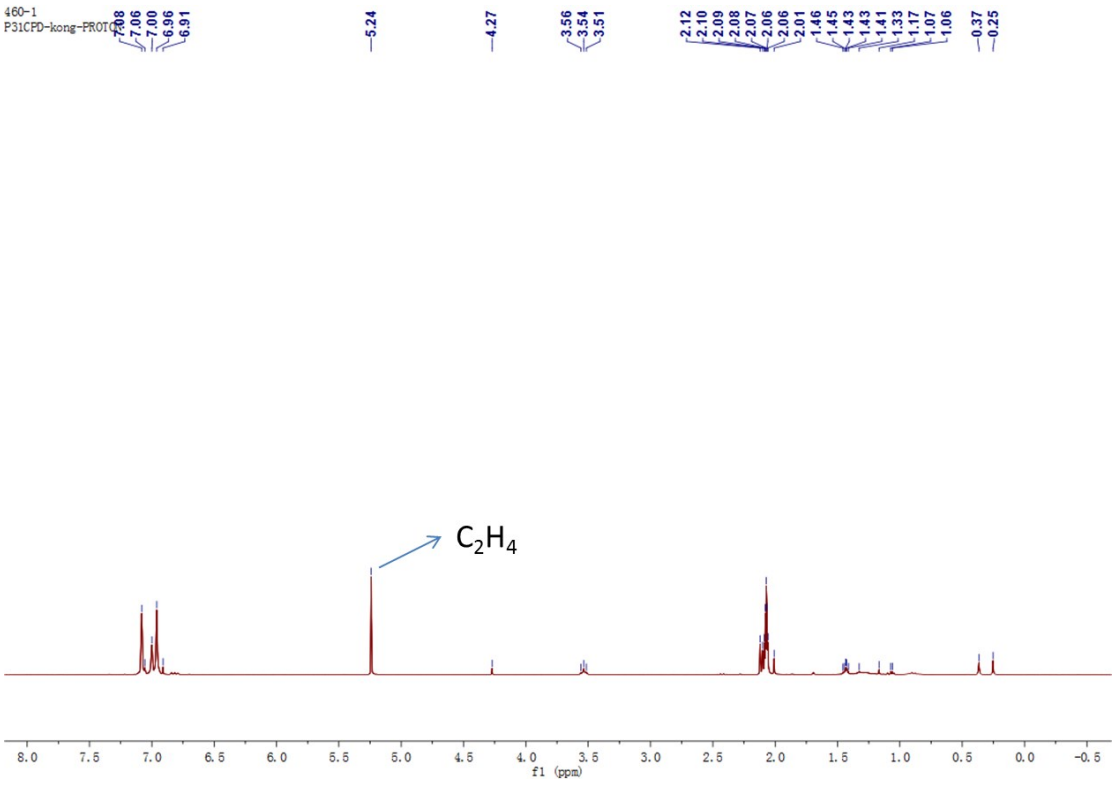
^{31}P {^{1}H} NMR of Compound **12**



^{1}H NMR of Compound **12**



^{13}C {^{1}H} NMR of Compound **12**



^{1}H NMR of the thermolysis reaction of **1a** in toluene-d8