Cooperative P–H Bond Activation with Ruthenium and Iridium Carbene Complexes

Julia Weismann, Lennart T. Scharf and Viktoria H. Gessner*

Institut für Anorganische Chemie, Julius-Maximilians-Universität Würzburg, Am Hubland, 97074 Würzburg, Germany.

Present address: Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, Universitätsstraße 150, D-44780 Bochum, Germany.

Index

Synthesis and Characterization of Complexes 3a-3f.

General procedure: In a *J. Young* NMR tube, 30.0 mg (49.5 µmol) of ruthenium carbene complex **1** were dissolved in 0.7 mL dry C_6D_6 (for reactions at room temperature) or dry toluene (for reactions at –78 °C) and the purple solution was treated with one equivalent (49.5 µmol) of the appropriate phosphine. Subsequently, a color change to red/orange occurred, and the reaction mixture was screened by $^{31}P\{^1H\}$ NMR spectroscopy, indicating a complete conversion of the starting materials. Thus, the NMR spectroscopic studies confirmed the presence of more than one main product and consequently the desired activation products **3a-3f** could not be isolated and fully characterized. ^1H and $^{31}P\{^1H]$ NMR data were determined out of the spectra of the reaction mixtures.

$^{31}P\{^1H\}$ and ^1H NMR data of Complexes 3b-3f.

3b: ^1H NMR (400.1 MHz, C_6D_6): δ = 1.06 (d, $^3J_{HH}$ = 6.99 Hz, 3 H; CH(CH_3)$_2$), 1.16 (d, $^3J_{HH}$ = 6.94 Hz, 3 H; CH(CH_3)$_2$), 1.60 (s, 3 H; CH_3), 2.88-2.98 (sept., $^3J_{HH}$ = 6.77 Hz, 1 H; CH(CH$_3$)$_2$), 3.56 (dd, $^2J_{PH}$ = 10.5, $^3J_{PH}$ = 4.18 Hz, 1 H; PCHS), 5.09 (d, $^3J_{HH}$ = 5.24 Hz, 1 H; CH_{Cymene}), 5.27 (d, $^3J_{HH}$ = 5.82 Hz, 1 H; CH_{Cymene}), 5.38 (br., 2 H; CH_{Cymene}), 6.16-8.32 (C$H_{arom.}$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ = 39.0 (d, $^3J_{PP}$ = 2.89 Hz), 56.7 (d, $^3J_{PP}$ = 3.74 Hz; *P*S).

3c: ^1H NMR (400.1 MHz, C_6D_6): δ = 1.00 (d, $^3J_{HH}$ = 7.00 Hz, 3 H; CH(CH_3)$_2$), 1.18 (d, $^3J_{HH}$ = 6.81 Hz, 3 H; CH(CH_3)$_2$), 1.63 (s, 3 H; CH_3), 2.70-2.80 (sept., $^3J_{HH}$ = 7.00 Hz, 1 H; CH(CH$_3$)$_2$), 3.61 (dd, $^2J_{PH}$ = 10.1, $^3J_{PH}$ = 4.21 Hz, 1 H; PCHS), 5.07 (d, $^3J_{HH}$ = 5.88 Hz, 1 H; CH_{Cymene}), 5.19 (d, $^3J_{HH}$ = 5.70 Hz, 1 H; CH_{Cymene}), 5.25 (d, $^3J_{HH}$ = 5.76 Hz, 1 H; CH_{Cymene}), 5.56 (d, $^3J_{HH}$ = 5.95 Hz, 1 H; CH_{Cymene}), 6.57-6.75 (m, 8 H; C$H_{arom.}$), 7.03-7.11 (m, 5 H; C$H_{arom.}$), 7.52-7.54 (m, 2 H; C$H_{arom.}$), 7.83 (dd, *J* = 1.90, 4.36 Hz, 4 H; C$H_{arom.}$), 8.15-8.21 (m, 2 H; C$H_{P(S)Ph,ortho}$. $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ = 35.5 (br.), 59.5 (d, $^3J_{PP}$ = 14.8 Hz; *P*S).

3d: ^1H NMR (400.1 MHz, C_6D_6): δ = 0.79 (d, $^3J_{HH}$ = 6.90 Hz, 3 H; CH(CH_3)$_2$), 1.03 (d, $^3J_{HH}$ = 6.91 Hz, 3 H; CH(CH_3)$_2$), 1.84 (s, 3 H; CH_3), 2.68-2.78 (sept., $^3J_{HH}$ = 6.85 Hz, 1 H; CH(CH$_3$)$_2$), 3.17 (s, 3 H; OCH_3), 3.24 (s, 3 H; OCH_3), 3.86 (dd, $^2J_{PH}$ = 8.57, $^3J_{PH}$ = 6.87 Hz, 1 H; PCHS), 5.47 (d, $^3J_{HH}$ = 5.86 Hz, 1 H; CH_{Cymene}), 5.65 (d, $^3J_{HH}$ = 6.18 Hz, 1 H; CH_{Cymene}), 6.23 (d, $^3J_{HH}$ = 5.59 Hz, 1 H; CH_{Cymene}), 6.46-8.09 (C$H_{arom.}$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ = 36.5 (d, $^3J_{PP}$ = 2.95 Hz; *P*O), 56.6 (d, $^3J_{PP}$ = 3.75 Hz; *P*S).

3e: ^1H NMR (400.1 MHz, C_6D_6): δ = 0.83 (d, $^3J_{HH}$ = 6.91 Hz, 3 H; CH(CH_3)$_2$), 1.29 (d, $^3J_{HH}$ = 6.80 Hz, 3 H; CH(CH_3)$_2$), 1.92 (s, 3 H; CH_3), 2.70-2.78 (sept., $^3J_{HH}$ = 6.94 Hz, 1 H; CH(CH$_3$)$_2$), 4.04 (dd, $^2J_{PH}$ = 8.36, $^3J_{PH}$ = 6.71 Hz, 1 H; PCHS), 5.57 (d, $^3J_{HH}$ = 6.05 Hz, 1 H; CH_{Cymene}), 5.72 (d, $^3J_{HH}$ = 6.32 Hz, 1 H; CH_{Cymene}), 5.96 (dd, $^3J_{HH}$ = 2.23, 9.06 Hz, 1 H; CH_{Cymene}), 6.21-8.40 (C$H_{arom.}$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ = 34.3 (br.), 56.5 (d, $^3J_{PP}$ = 3.90 Hz; *P*S).

3f: ^1H NMR (400.1 MHz, C_6D_6): δ = 0.96 (d, $^3J_{HH}$ = 6.97 Hz, 3 H; CH(CH_3)$_2$), 1.01 (d, $^3J_{HH}$ = 6.84 Hz, 3 H; CH(CH_3)$_2$), 1.63 (s, 3 H; CH_3), 2.54-2.64 (sept., $^3J_{HH}$ = 6.88 Hz, 1 H; CH(CH$_3$)$_2$), 3.90 (dd, $^2J_{PH}$ = 9.29, $^3J_{PH}$ = 2.49 Hz, 1 H; PCHS), 4.92 (d, $^3J_{HH}$ = 5.80 Hz, 1 H; CH_{Cymene}), 4.97 (d, $^3J_{HH}$ = 5.68 Hz, 1 H; CH_{Cymene}), 5.20 (d, $^3J_{HH}$ = 5.80 Hz, 1 H; CH_{Cymene}), 5.83 (d, $^3J_{HH}$ = 5.99 Hz, 1 H; CH_{Cymene}), 6.50-6.55 (m, 2 H; CH_{arom}), 6.61-6.74 (m, 6 H; C$H_{arom.}$), 7.02-7.10 (m, 3 H; CH_{arom}), 7.40 (d, $^2J_{HH}$ = 7.19 Hz, 2 H; CH_{arom}), 7.64 (s, 2 H; CH_{arom}), 7.99-8.06 (m, 2 H; CH_{arom}), 8.40 (d, $^3J_{HH}$ = 3.35 Hz, 4 H; C$H_{arom.}$). $^{31}P\{^1H\}$ NMR (162.0 MHz, C_6D_6): δ = 24.4 (br.), 62.8 (d, $^3J_{PP}$ = 14.0 Hz; *P*S).

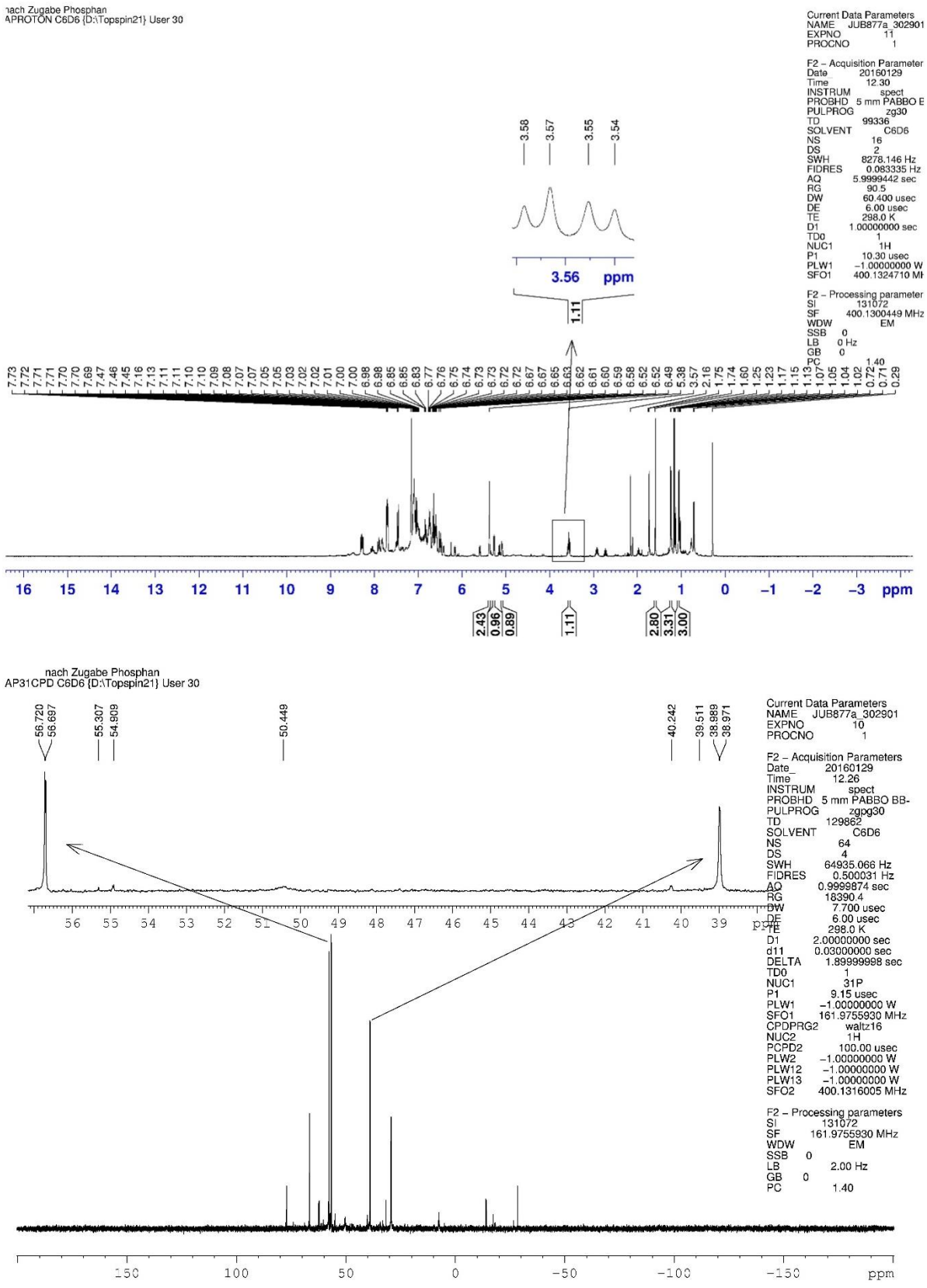


Figure S1. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **3b** in C_6D_6.

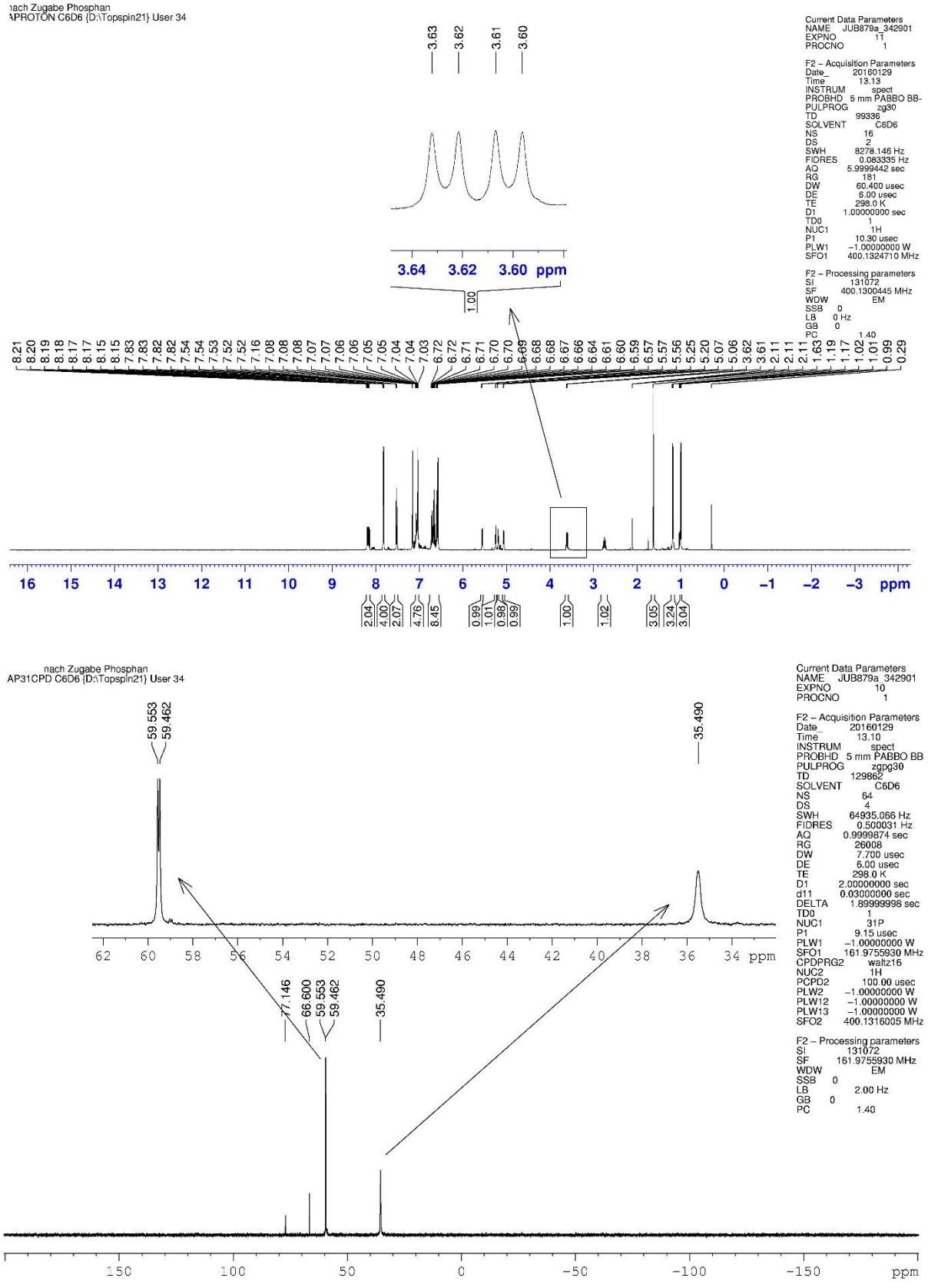


Figure S2. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **3c** in C_6D_6.

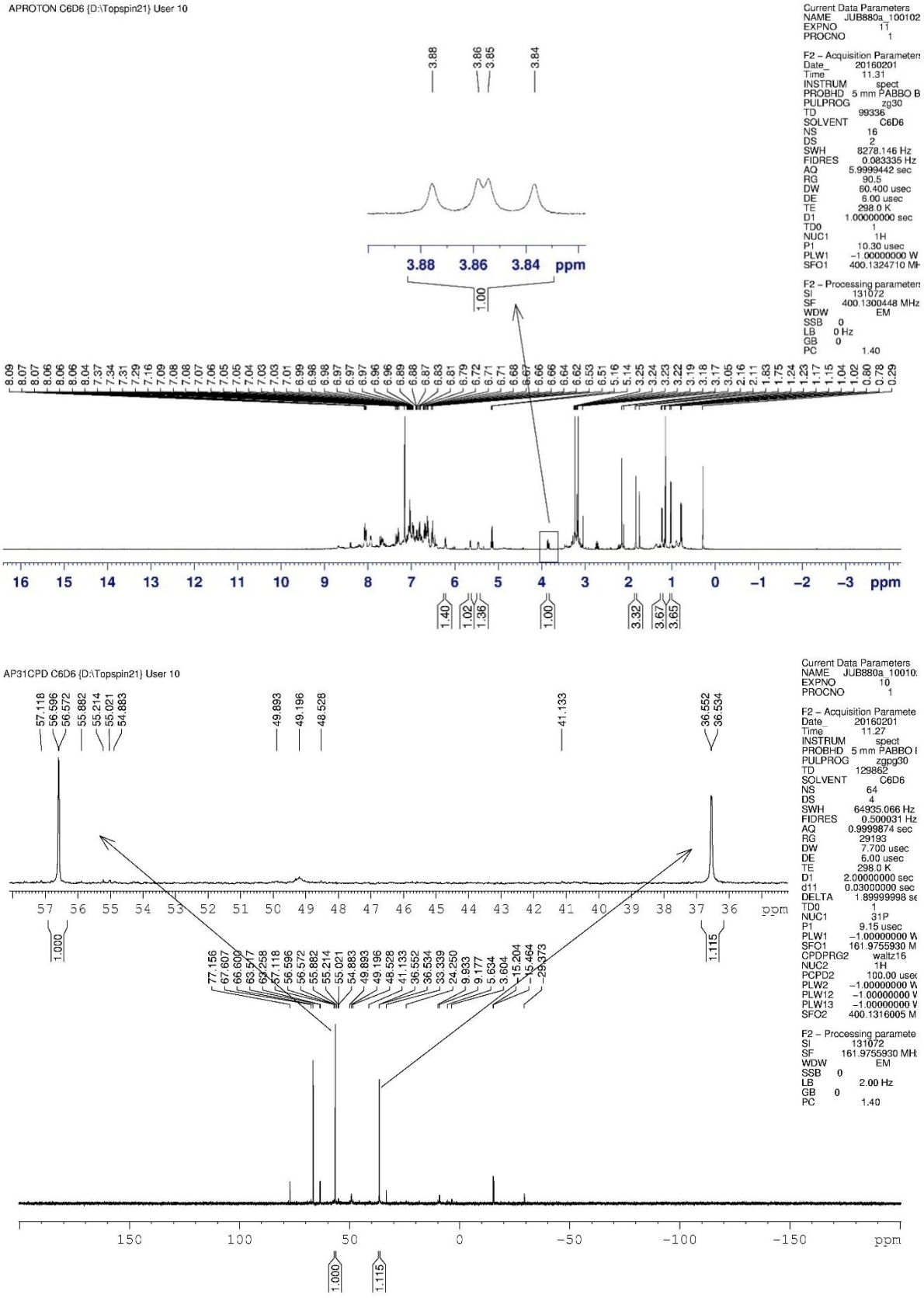


Figure S3. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **3d** in C_6D_6.

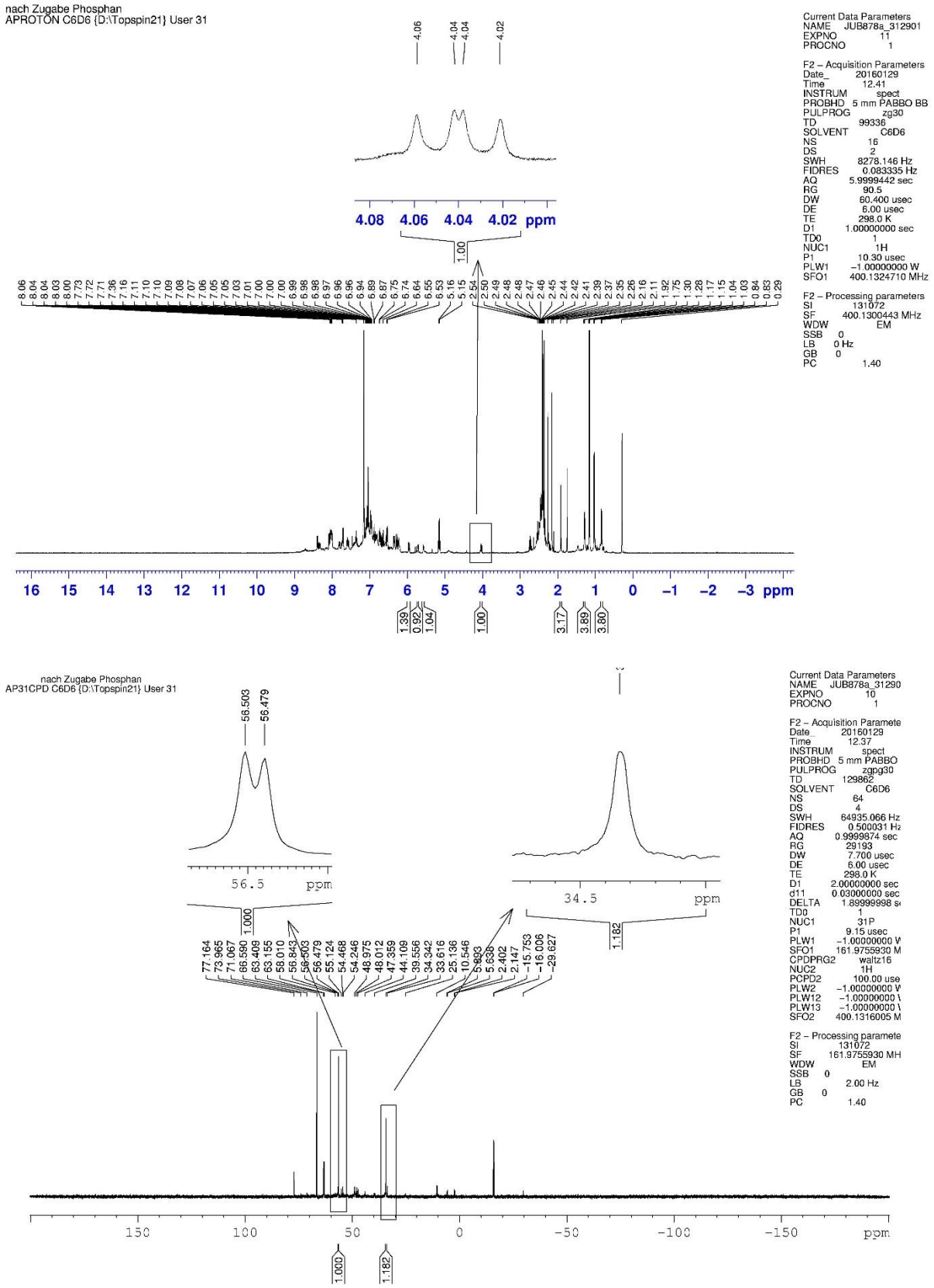


Figure S4. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **3e** in C_6D_6.

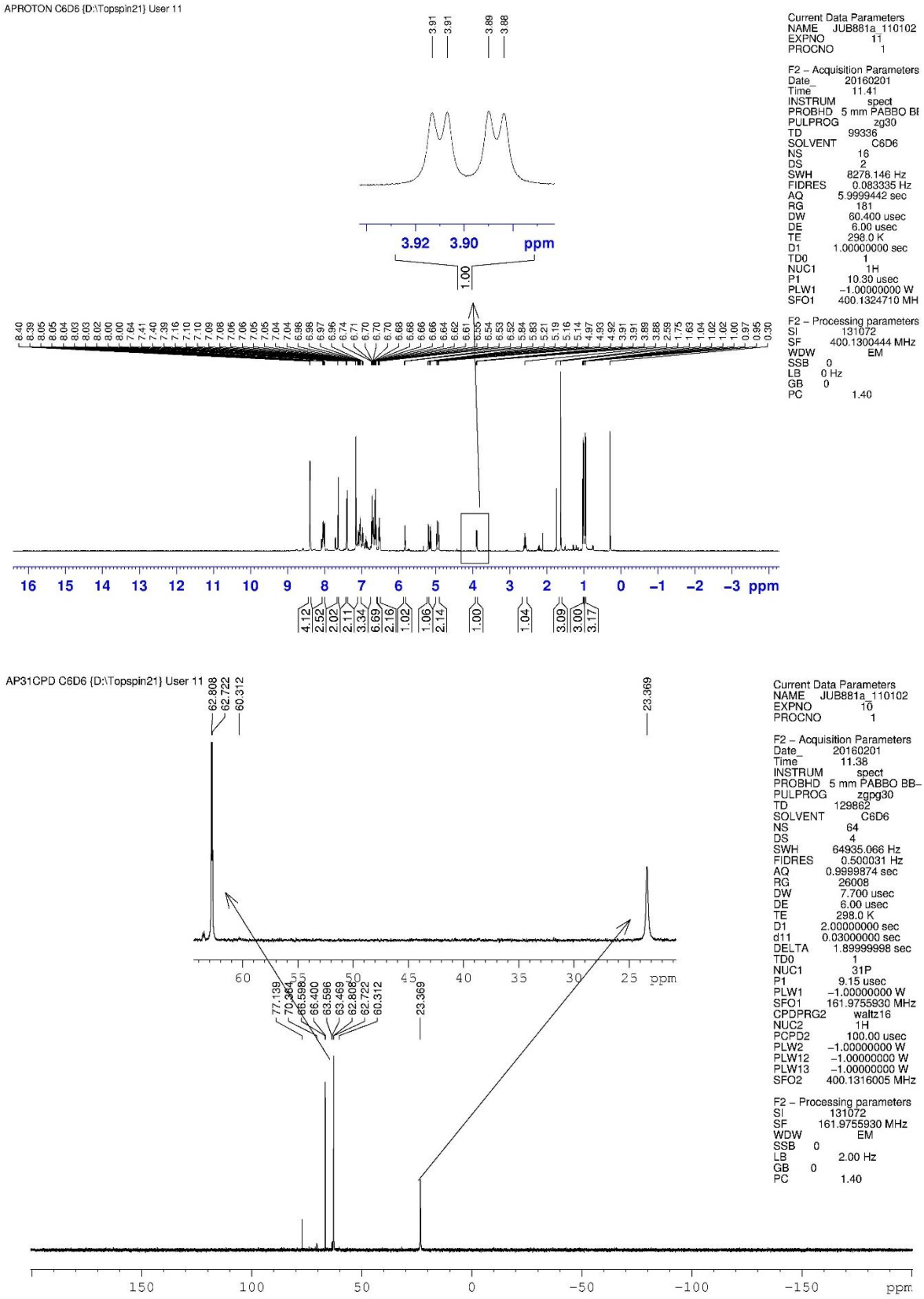


Figure S5. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **3f** in C_6D_6.

2. NMR spectra of the isolated complexes

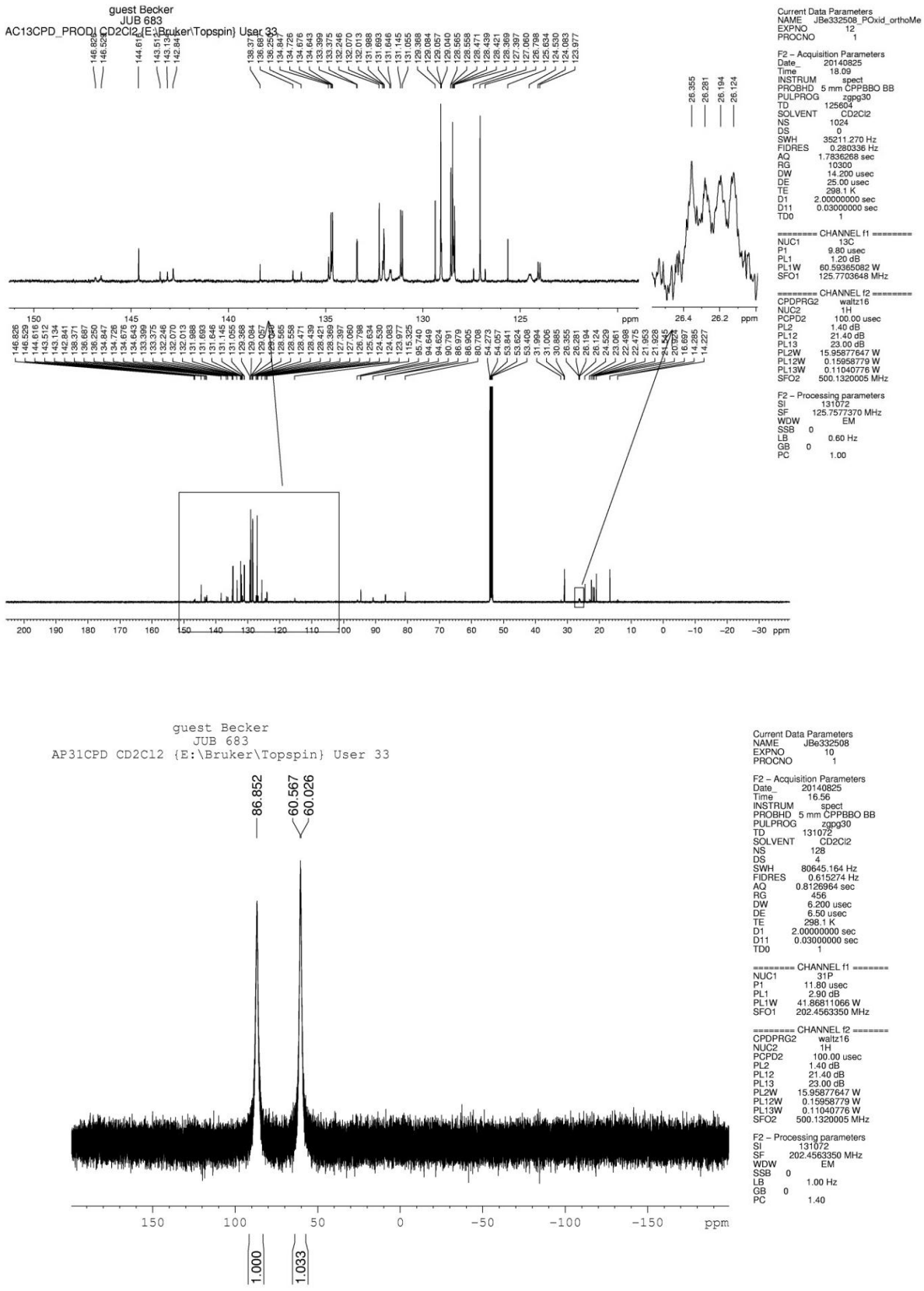


Figure S6. $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of **4a** in CD_2Cl_2.

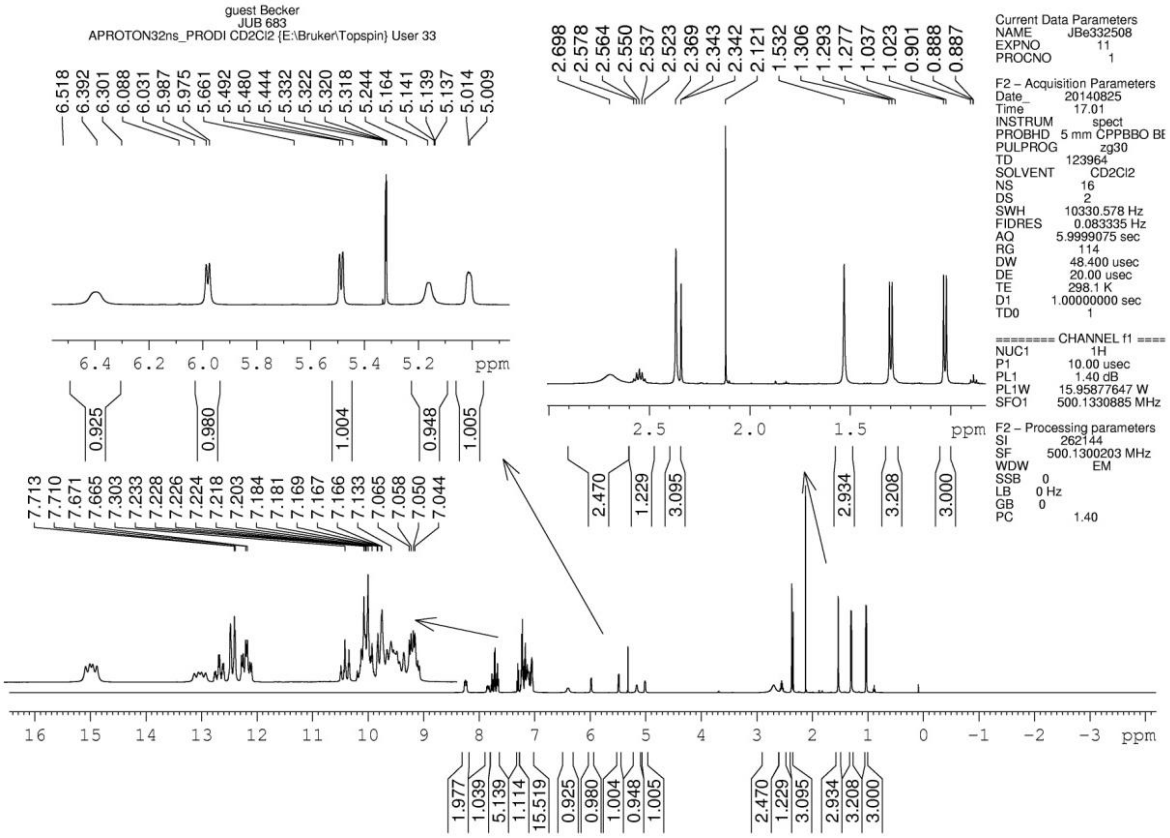


Figure S7. ^{1}H NMR spectrum of **4a** in CD_2Cl_2.

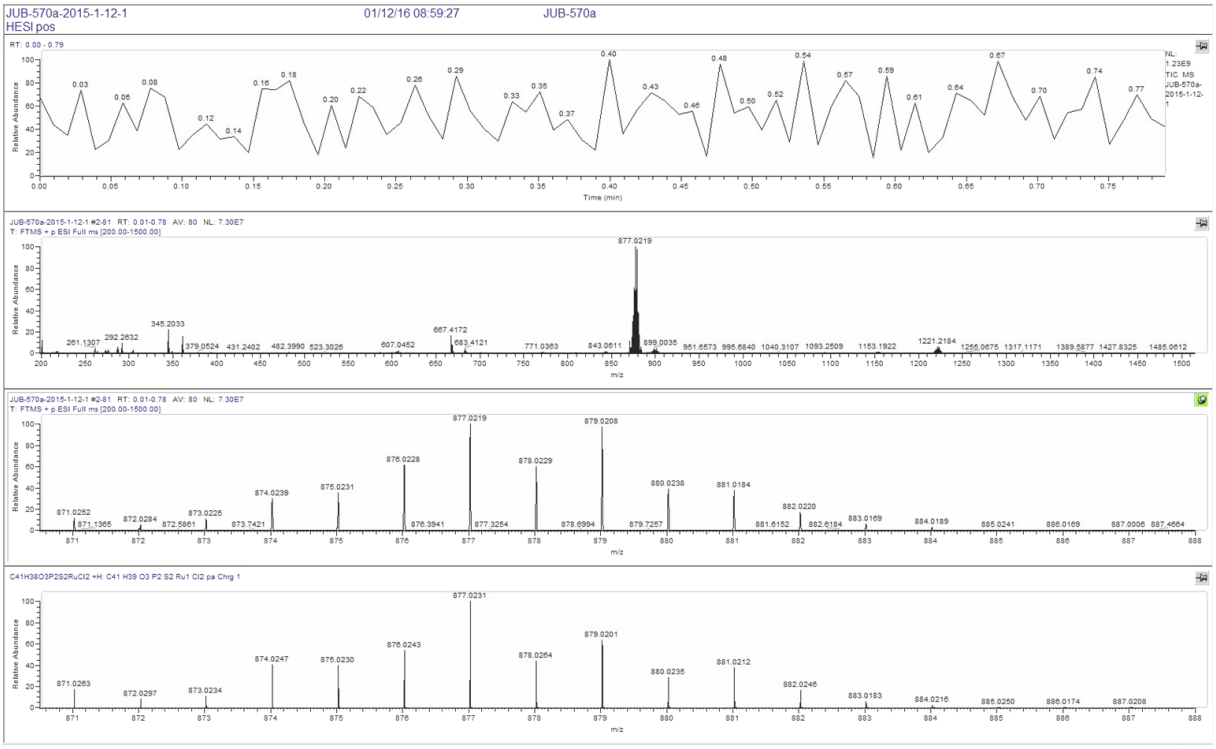


Figure S8. ESI-HR MS spectra of complex **4b**.

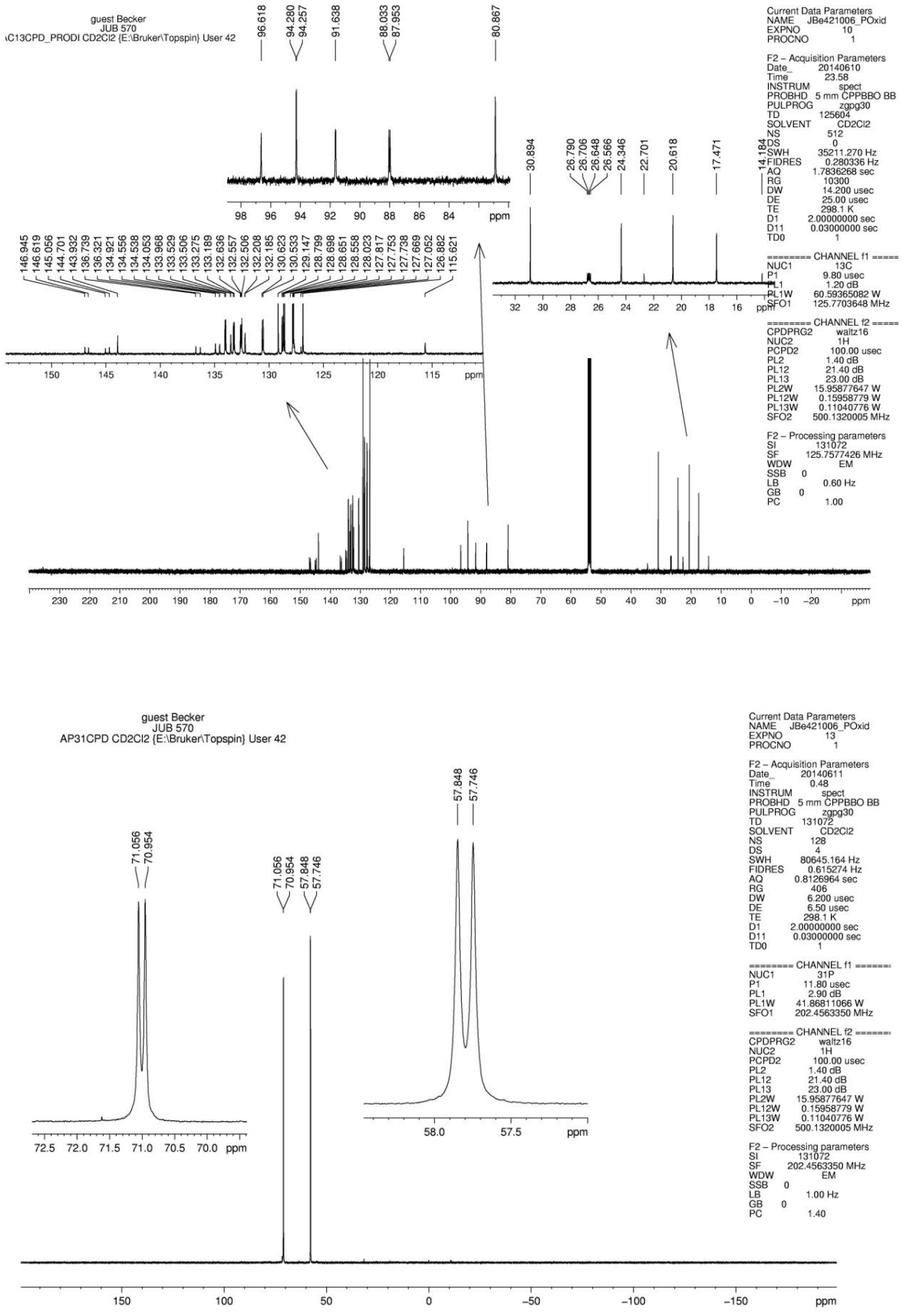


Figure S9. $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra of **4b** in CD_2Cl_2.

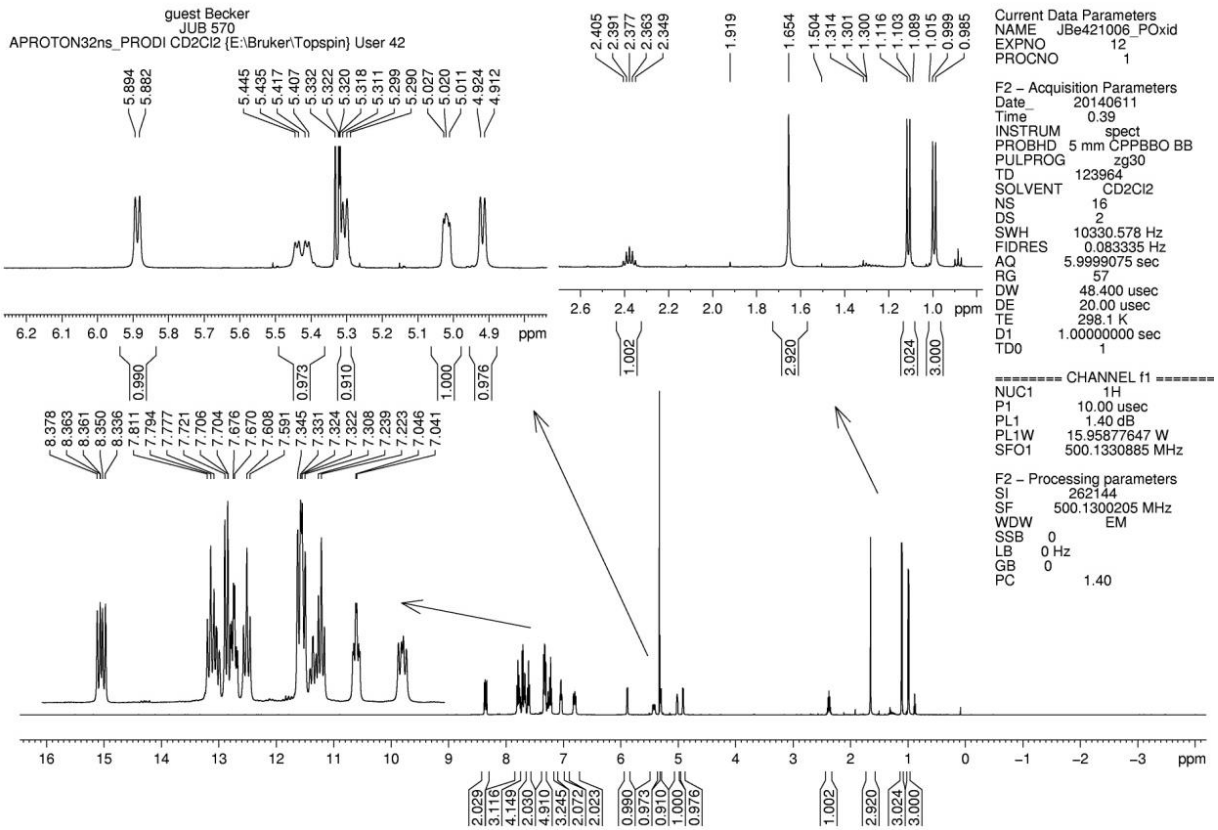


Figure S10. ^{1}H NMR spectrum of **4b** in CD_2Cl_2.

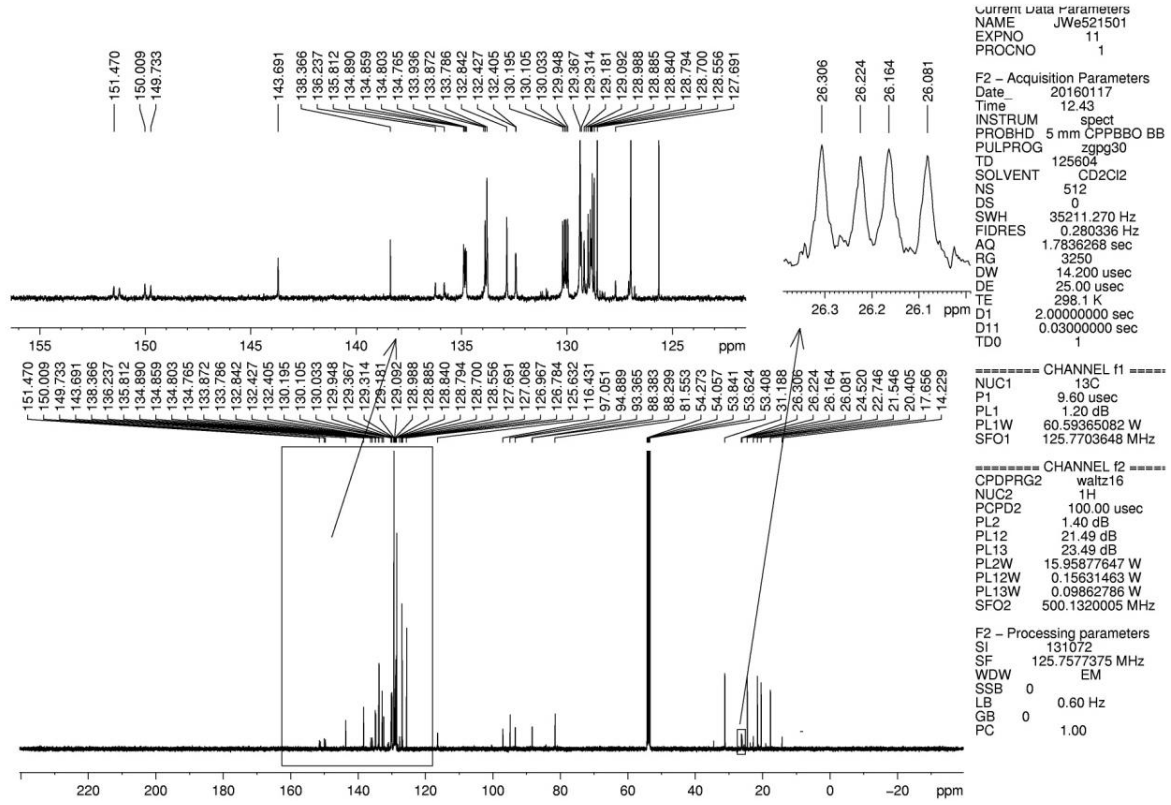
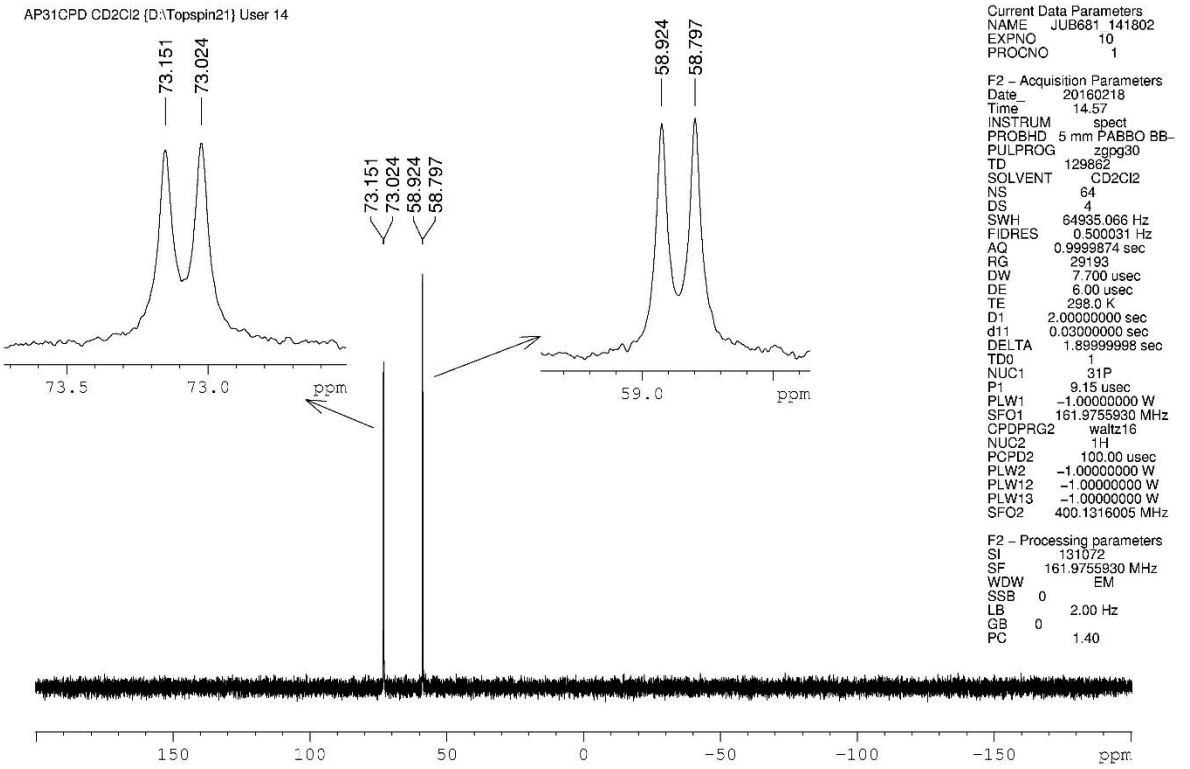


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of **4c** in CD_2Cl_2.



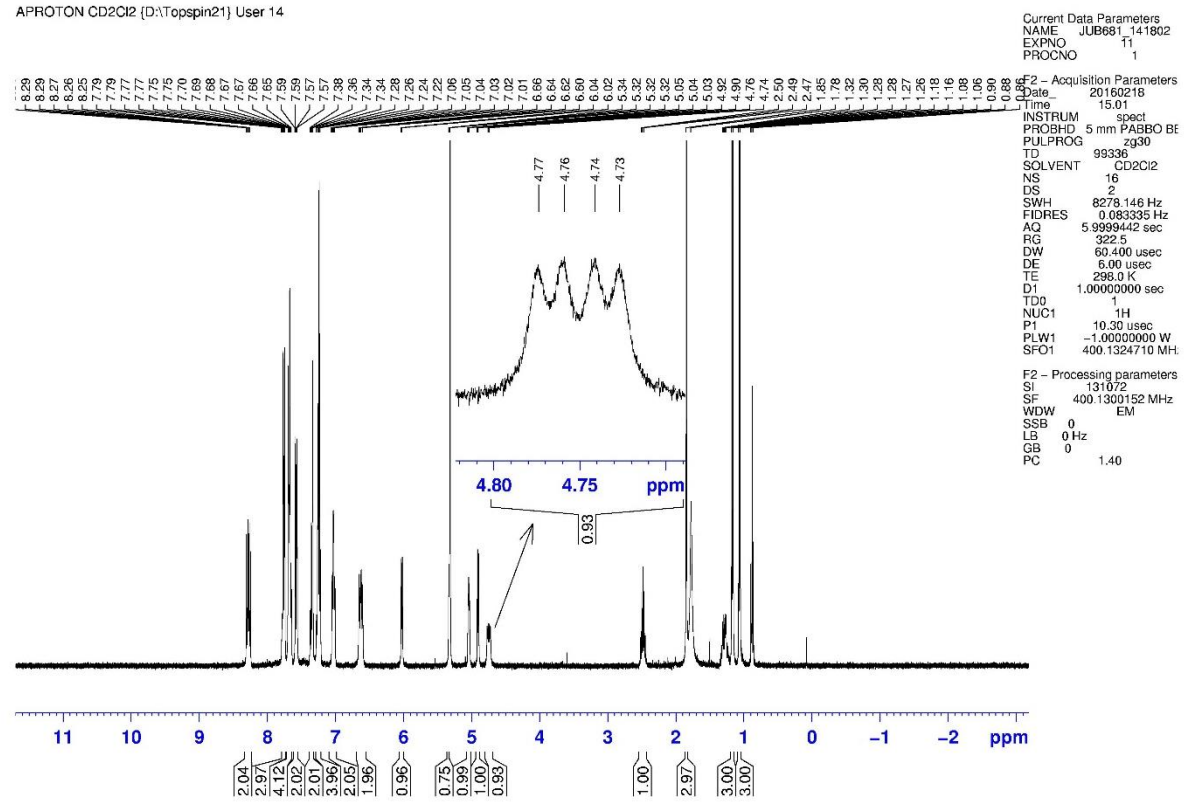


Figure S12. $^{31}P\{^{1}H\}$ and ^{1}H NMR spectra of **4c** in CD_2Cl_2.

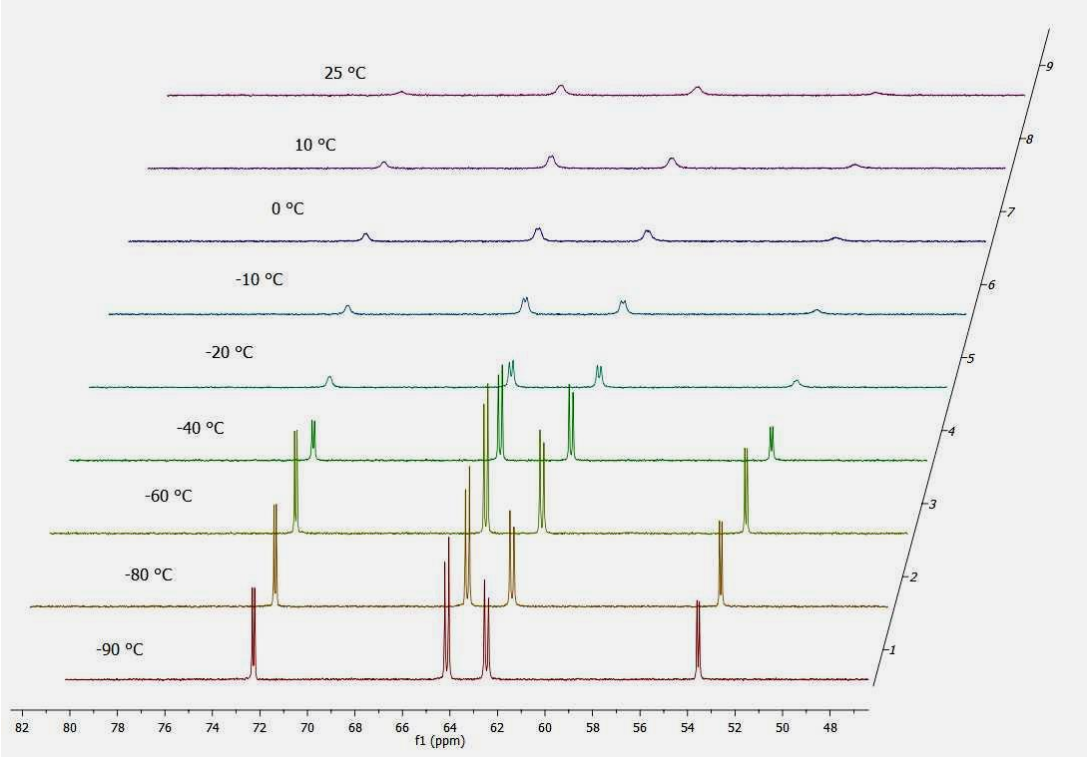


Figure S13a. VT $^{31}P\{^{1}H\}$ NMR spectra of **5a** in CD_2Cl_2 at low temperatures.

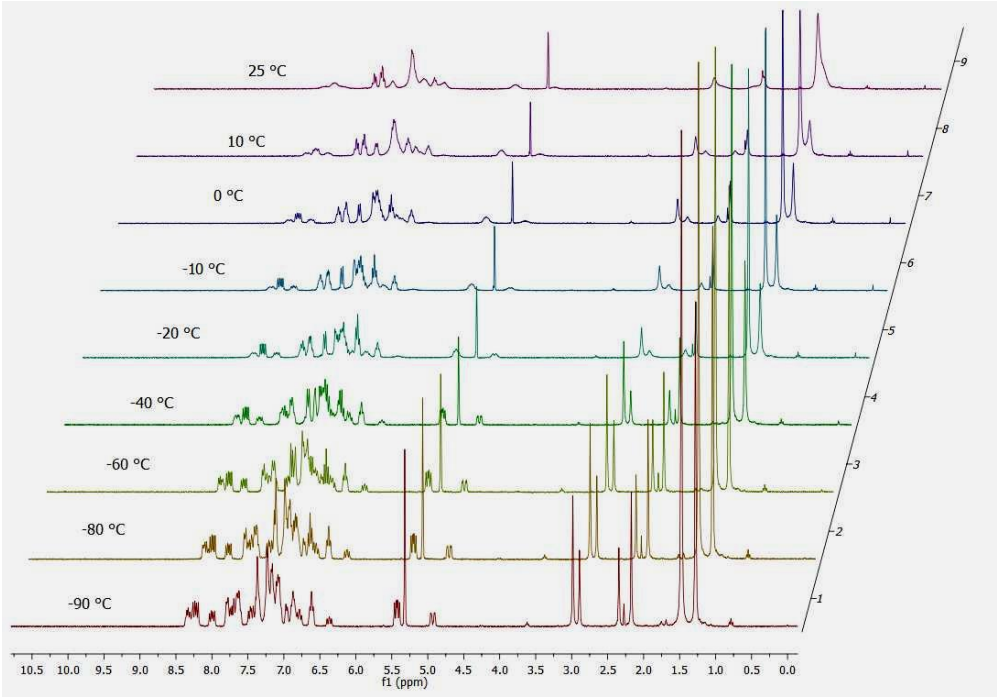


Figure S13b. VT ^{1}H NMR spectra of **5a** in CD_2Cl_2 at low temperatures.

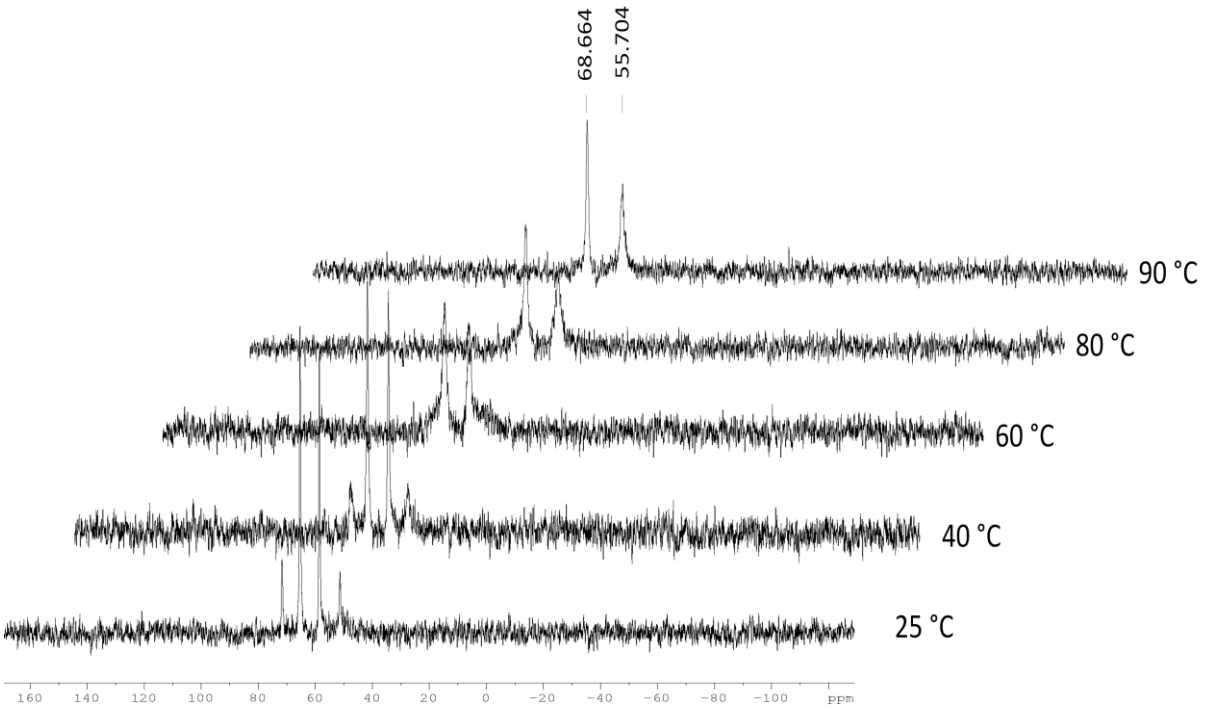


Figure 14a. VT $^{31}P\{^{1}H\}$ NMR spectra of **5a** in CD_2Cl_2 at elevated temperatures.

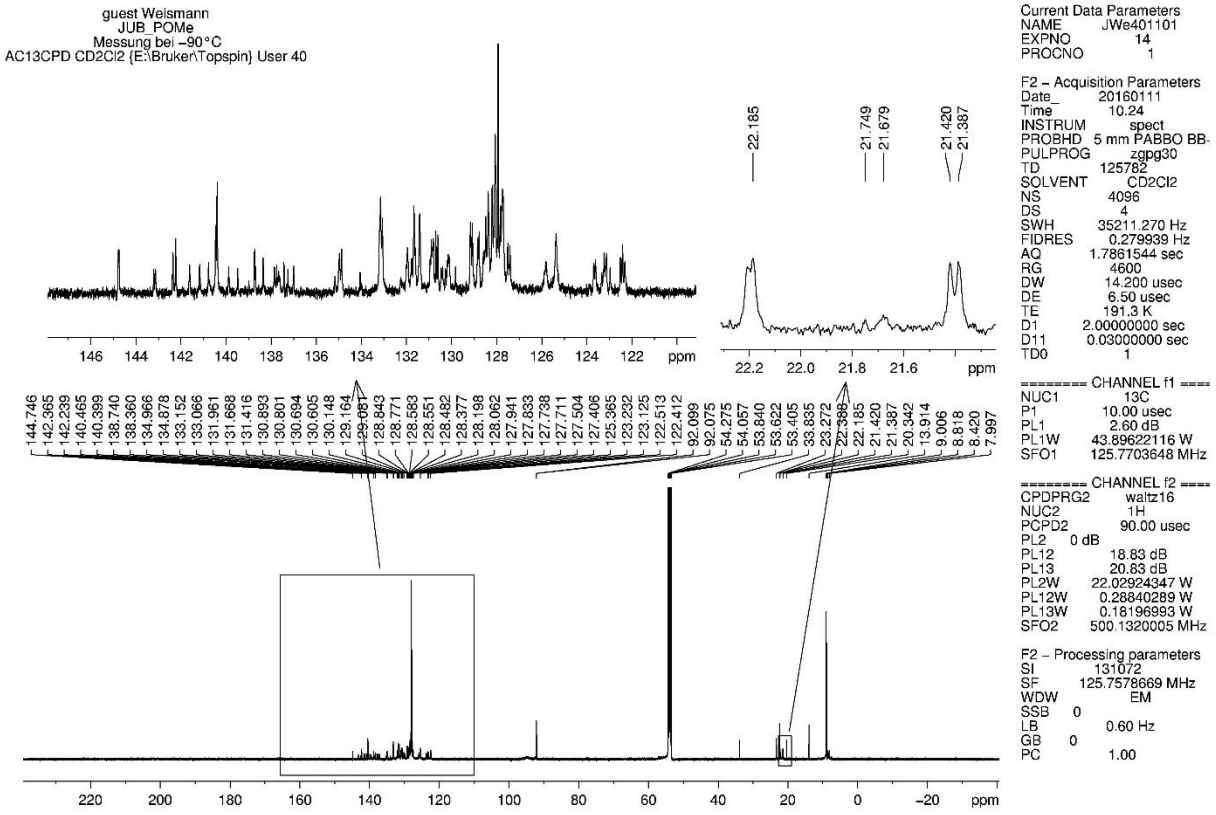


Figure S15. $^{13}C\{^{1}H\}$ NMR spectra of **5a** in CD_2Cl_2.

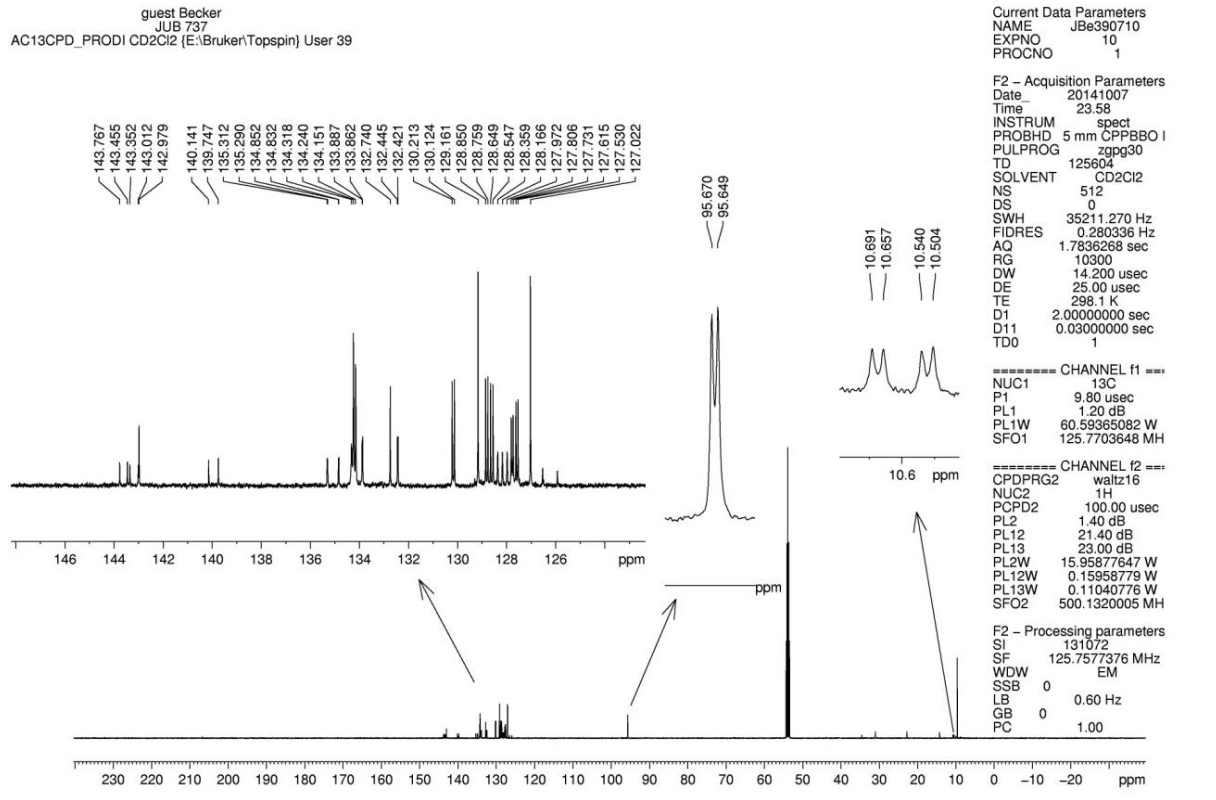


Figure S16. $^{13}C\{^{1}H\}$ spectrum of **5b** in CD_2Cl_2.

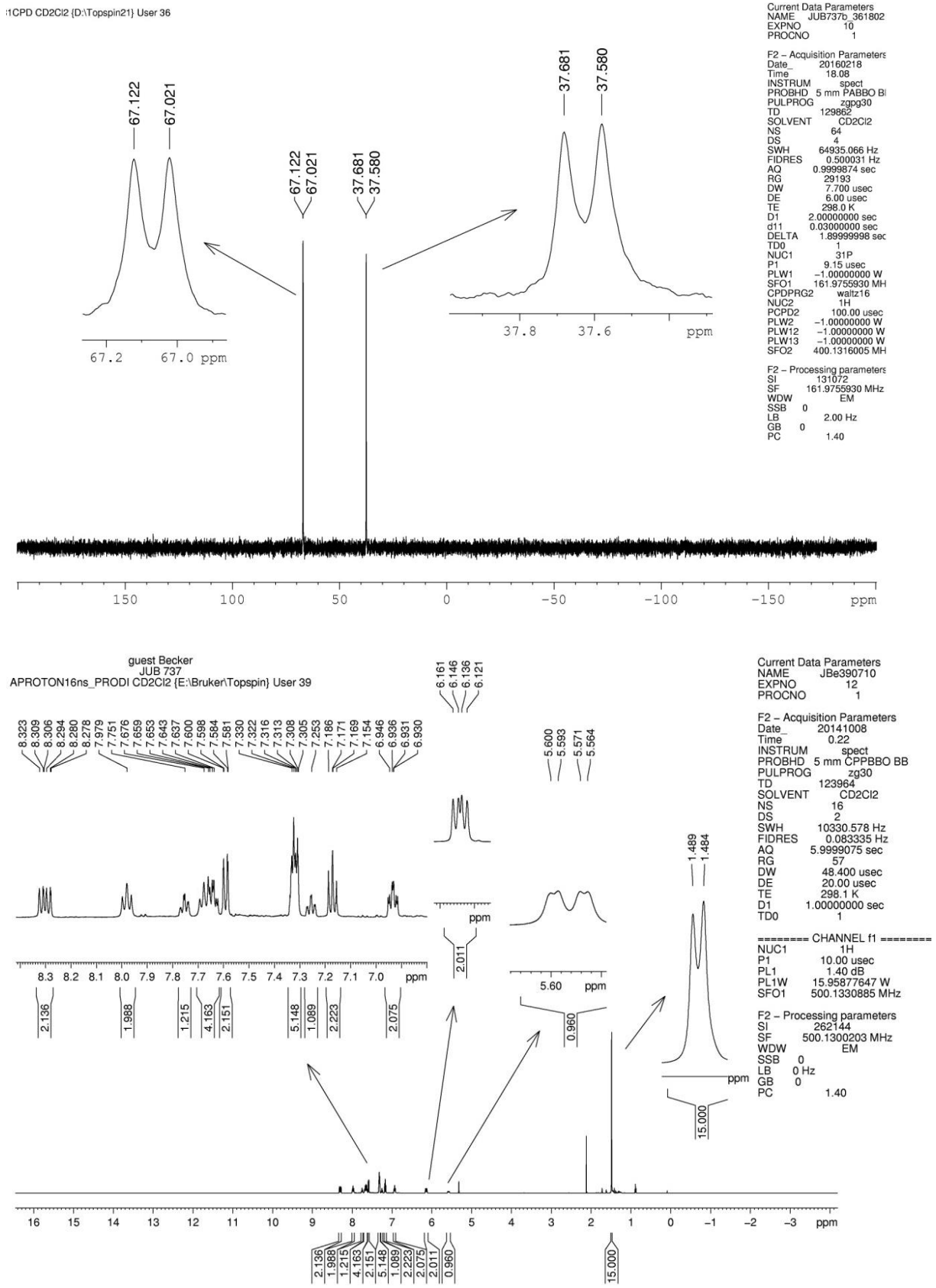


Figure S17. ^{1}H and $^{31}P\{^{1}H\}$ NMR spectra of **5b** in CD_2Cl_2.

3. Crystal Structure Determination

Table S1a. Data collection and structure refinement details for compounds **4a** and **4b**.

Compound	**4a**	**4b**
CCDC No.	CCDC 1450798	CCDC 1450797
Formula	$C_{43}H_{43}O_3P_2RuS_2 \cdot 0.5\ C_7H_8$	$C_{44}H_{41}O_3P_2RuS_2Cl_2$
Formula weight [g·mol^{-1}]	880.97	915.80
Temperature [K]	100(2)	100(2)
Wave length [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/c	*C*2/c
a [Å]	25.0763(13)	27.165(3)
b [Å]	12.6879(7)	13.074(1)
c [Å]	26.8084(14)	25.394(4)
α [°]	90	90
β [°]	109.414(2)	118.508(3)
γ [°]	90	90
Volume [Å^3]	8044.5(7)	7925.2(17)
Z	8	8
Calc. density [Mg·m^{-3}]	1.455	1.535
μ ($Mo_{K\alpha}$) [mm^{-1}]	0.615	0.758
F(000)	3648	3752
Crystal dimensions [mm]	0.21 x 0.19 x 0.09	0.19 x 0.18 x 0.07
Theta range [°]	1.61 to 25.00	2.90 to 25
Index ranges	$-29 \le h \le 29$	$-32 \le h \le 32$
	$-15 \le k \le 15$	$-15 \le k \le 15$
	$-31 \le l \le 31$	$-30 \le l \le 30$
Reflections collected	59370	44370
Independent reflections	7089 [R_{int} = 0.0496]	6950 [R_{int} = 0.0969]
Data/Restraints/Parameter	7089 / 0 / 517	6950 / 0 / 494
Goodness-of-fit on F^2	1.097	1.100
Final R indices [I>2sigma(I)]	*R*1 = 0.0413 w*R*2 = 0.1229	*R*1 = 0.0381 w*R*2 = 0.0661
R indices (all data)	*R*1 = 0.0486 w*R*2 = 0.1275	*R*1 = 0.0738 w*R*2 = 0.0774
Largest diff. peak and hole	0779 und –0.793	0.417 und –0.428

Table S1b. Data collection and structure refinement details for compounds **5a** and **5b**.

Compound	**5a**	**5b**
CCDC No.	CCDC 1450796	CCDC 1450795
Formula	$C_{43}H_{45}O_3P_2IrS_2$	$C_{41}H_{39}Cl_2IrO_3P_2S_2 \cdot 1.5\ C_6H_6$
Formula weight [g·mol^{-1}]	928.05	1086.05
Temperature [K]	100(2)	100(2)
Wave length [Å]	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$/c	$P2_1$/n
a [Å]	11.5779(12)	13.0190(6)
b [Å]	19.1195(19)	23.4383(10)

c [Å]	17.1015(17)	18. 9496(7)
α [°]	90	90
β [°]	96.535(3)	95.295(2)°
γ [°]	90	90
Volume [$Å^3$]	3761.1(7)	4542.3(4)
Z	4	4
Calc. density [$Mg \cdot m^{-3}$]	1.639	1.588
μ ($Mo_{K\alpha}$) [mm^{-1}]	3.787	3.262
F(000)	1864	2180
Crystal dimensions [mm]	0.31 x 0.28 x 0.21	0.21 x 0.20 x 0.11
Theta range [°]	1.60 to 26.44	1.62 to 25.00
Index ranges	$-13 \le h \le 13$ $-22 \le k \le 22$ $-20 \le l \le 20$	$-15 \le h \le 15$ $-27 \le k \le 27$ $-17 \le l \le 17$
Reflections collected	45901	74061
Independent reflections	6633 [R_{int} = 0.0426]	8005 [R_{int} = 0.0352]
Data/Restraints/Parameter	6633 / 0 / 461	8005 / 0 / 550
Goodness-of-fit on F^2	1.044	1.013
Final R indices [I>2sigma(I)]	$R1$ = 0.0198 w$R2$ = 0.0425	$R1$ = 0.0201 w$R2$ = 0.0468
R indices (all data)	$R1$ = 0.0255 w$R2$ = 0.0445	$R1$ = 0.0249 w$R2$ = 0.0493
Largest diff. peak and hole	0.467 and –0.397	0.797 and –0.366

3.1 Crystal Structure Determination of **4a**

All hydrogen atoms were refined on ideal positions except for H1 at C1, which was found in the difference Fourier map and refined independently.

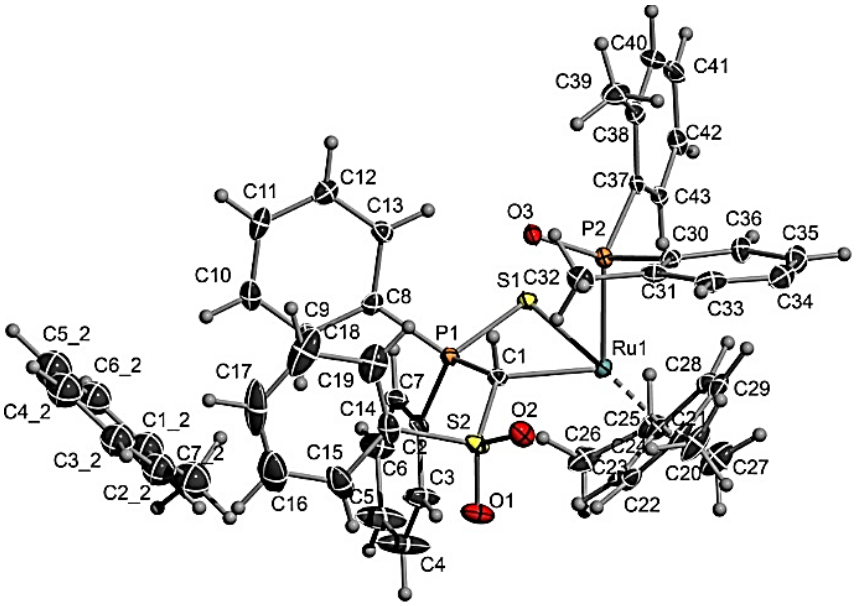


Figure S18. ORTEP Plot of complex **4a.** Ellipsoids are drawn at the 50% probability level.

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **4a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	8207(1)	10758(1)	8434(1)	12(1)
S(1)	8063(1)	9027(1)	7999(1)	13(1)
S(2)	8819(1)	9992(1)	9721(1)	16(1)
P(1)	8545(1)	8536(1)	8723(1)	12(1)
P(2)	7262(1)	10441(1)	8417(1)	12(1)
O(1)	9393(1)	10233(2)	9767(1)	24(1)
O(2)	8509(1)	10800(2)	9885(1)	21(1)
O(3)	7194(1)	9515(2)	8748(1)	15(1)
C(1)	8412(2)	9630(3)	9079(1)	13(1)
C(2)	9245(2)	8241(3)	8716(1)	16(1)
C(3)	9742(2)	8722(3)	9020(2)	30(1)
C(4)	10242(2)	8484(5)	8928(2)	56(2)
C(5)	10247(2)	7766(4)	8540(2)	52(2)
C(6)	9753(2)	7275(3)	8248(2)	30(1)
C(7)	9252(2)	7503(3)	8334(2)	20(1)
C(8)	8288(2)	7335(3)	8927(1)	16(1)
C(9)	8649(2)	6687(3)	9306(1)	19(1)
C(10)	8431(2)	5849(3)	9507(2)	24(1)
C(11)	7856(2)	5644(3)	9318(2)	24(1)
C(12)	7499(2)	6283(3)	8935(2)	22(1)
C(13)	7708(2)	7142(3)	8744(2)	18(1)
C(14)	8837(2)	8885(3)	10127(1)	22(1)
C(15)	8335(2)	8469(3)	10142(2)	34(1)
C(16)	8361(3)	7619(4)	10483(2)	48(1)
C(17)	8885(3)	7252(4)	10798(2)	55(2)
C(18)	9377(3)	7686(4)	10781(2)	53(2)
C(19)	9360(2)	8508(4)	10441(2)	36(1)
C(20)	8238(2)	12993(3)	9157(2)	34(1)
C(21)	8385(2)	12409(3)	8739(2)	22(1)
C(22)	8897(2)	11829(3)	8861(2)	20(1)
C(23)	9075(2)	11345(3)	8467(2)	17(1)
C(24)	8722(2)	11394(3)	7935(1)	16(1)
C(25)	8888(2)	10926(3)	7490(2)	22(1)
C(26)	9353(2)	10109(3)	7664(2)	27(1)
C(27)	9046(2)	11825(4)	7183(2)	36(1)
C(28)	8200(2)	11944(3)	7807(2)	19(1)
C(29)	8038(2)	12435(3)	8203(2)	23(1)
C(30)	6959(2)	11639(3)	8602(1)	15(1)
C(31)	6944(2)	11829(3)	9114(2)	18(1)
C(32)	7096(2)	11027(3)	9548(2)	23(1)
C(33)	6777(2)	12831(3)	9225(2)	23(1)
C(34)	6625(2)	13627(3)	8854(2)	26(1)
C(35)	6615(2)	13418(3)	8342(2)	26(1)
C(36)	6774(2)	12434(3)	8223(2)	19(1)
C(37)	6768(1)	10228(3)	7738(1)	14(1)
C(38)	6201(2)	9927(3)	7647(2)	19(1)
C(39)	5941(2)	9911(3)	8080(2)	25(1)
C(40)	5865(2)	9662(3)	7139(2)	24(1)
C(41)	6065(2)	9693(3)	6717(2)	23(1)
C(42)	6614(2)	10012(3)	6801(1)	20(1)
C(43)	6955(2)	10275(3)	7307(1)	14(1)
C12	9972(3)	4946(4)	9878(2)	51(5)
C22	9941(3)	5524(4)	10312(3)	47(3)
C32	9704(3)	5069(6)	10666(2)	46(3)
C42	9498(3)	4035(6)	10585(2)	49(3)
C52	9529(3)	3457(4)	10150(3)	53(3)
C62	9766(3)	3912(4)	9797(2)	43(3)
C72	10230(4)	5440(7)	9494(3)	55(3)

Table S3. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **4a**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	13(1)	10(1)	13(1)	-1(1)	5(1)	0(1)
S(1)	14(1)	13(1)	12(1)	-1(1)	3(1)	0(1)
S(2)	14(1)	19(1)	13(1)	-4(1)	2(1)	1(1)
P(1)	11(1)	11(1)	13(1)	-1(1)	2(1)	0(1)
P(2)	13(1)	12(1)	12(1)	1(1)	4(1)	2(1)
O(1)	14(1)	33(2)	23(2)	-11(1)	4(1)	-2(1)
O(2)	22(1)	22(1)	19(1)	-5(1)	5(1)	4(1)
O(3)	14(1)	15(1)	16(1)	3(1)	5(1)	3(1)
C(1)	13(2)	12(2)	12(2)	-3(1)	2(2)	0(1)
C(2)	12(2)	15(2)	20(2)	0(2)	3(2)	5(1)
C(3)	16(2)	33(2)	37(2)	-21(2)	5(2)	-2(2)
C(4)	15(2)	71(4)	75(4)	-53(3)	8(2)	-7(2)
C(5)	16(2)	67(4)	72(4)	-44(3)	13(2)	2(2)
C(6)	21(2)	31(2)	37(3)	-18(2)	7(2)	4(2)
C(7)	15(2)	19(2)	23(2)	-4(2)	2(2)	0(2)
C(8)	22(2)	13(2)	14(2)	-5(2)	5(2)	-1(2)
C(9)	23(2)	16(2)	15(2)	-3(2)	1(2)	0(2)
C(10)	38(2)	17(2)	13(2)	-1(2)	4(2)	3(2)
C(11)	40(2)	13(2)	24(2)	2(2)	18(2)	1(2)
C(12)	23(2)	18(2)	28(2)	-4(2)	14(2)	-1(2)
C(13)	16(2)	17(2)	19(2)	-1(2)	4(2)	3(2)
C(14)	33(2)	21(2)	12(2)	1(2)	7(2)	5(2)
C(15)	52(3)	30(2)	30(2)	0(2)	27(2)	5(2)
C(16)	88(4)	31(3)	45(3)	-2(2)	50(3)	-5(3)
C(17)	113(5)	30(3)	20(3)	10(2)	21(3)	21(3)
C(18)	73(4)	40(3)	30(3)	5(2)	-3(3)	8(3)
C(19)	41(3)	33(3)	23(2)	-2(2)	-4(2)	9(2)
C(20)	56(3)	17(2)	42(3)	-8(2)	34(2)	-8(2)
C(21)	34(2)	9(2)	30(2)	-5(2)	21(2)	-8(2)
C(22)	26(2)	16(2)	14(2)	-1(2)	4(2)	-9(2)
C(23)	13(2)	14(2)	24(2)	0(2)	4(2)	-6(2)
C(24)	19(2)	11(2)	21(2)	-1(2)	8(2)	-4(2)
C(25)	26(2)	20(2)	23(2)	-3(2)	13(2)	-6(2)
C(26)	25(2)	28(2)	36(2)	-9(2)	21(2)	-6(2)
C(27)	50(3)	33(3)	34(3)	-6(2)	29(2)	-11(2)
C(28)	21(2)	17(2)	19(2)	1(2)	7(2)	-6(2)
C(29)	27(2)	14(2)	34(2)	5(2)	17(2)	-3(2)
C(30)	13(2)	16(2)	17(2)	-1(2)	6(2)	-1(1)
C(31)	14(2)	23(2)	18(2)	-2(2)	6(2)	-2(2)
C(32)	24(2)	32(2)	15(2)	0(2)	9(2)	1(2)
C(33)	17(2)	28(2)	27(2)	-11(2)	11(2)	-4(2)
C(34)	20(2)	19(2)	44(3)	-4(2)	15(2)	2(2)
C(35)	24(2)	20(2)	39(2)	7(2)	16(2)	6(2)
C(36)	21(2)	17(2)	21(2)	2(2)	8(2)	3(2)
C(37)	13(2)	10(2)	16(2)	2(1)	2(2)	3(1)
C(38)	17(2)	17(2)	23(2)	4(2)	7(2)	3(2)
C(39)	16(2)	31(2)	31(2)	1(2)	11(2)	-4(2)
C(40)	13(2)	25(2)	29(2)	2(2)	1(2)	-1(2)
C(41)	21(2)	20(2)	18(2)	-1(2)	-4(2)	2(2)
C(42)	25(2)	16(2)	15(2)	1(2)	4(2)	6(2)
C(43)	13(2)	13(2)	16(2)	3(1)	4(2)	2(1)
C12	18(5)	64(8)	54(14)	27(10)	-13(7)	9(5)
C22	26(6)	44(8)	57(8)	-3(6)	-7(5)	9(5)
C32	44(7)	37(7)	37(7)	1(5)	-13(5)	13(5)
C42	41(6)	40(6)	48(7)	17(5)	-10(5)	7(5)
C52	61(7)	44(6)	34(6)	17(5)	-9(5)	-5(5)
C62	25(5)	39(6)	45(6)	-1(5)	-13(5)	2(4)
C72	46(7)	63(9)	45(8)	20(7)	-1(6)	12(7)

3.2 Crystal Structure Determination of **4b**

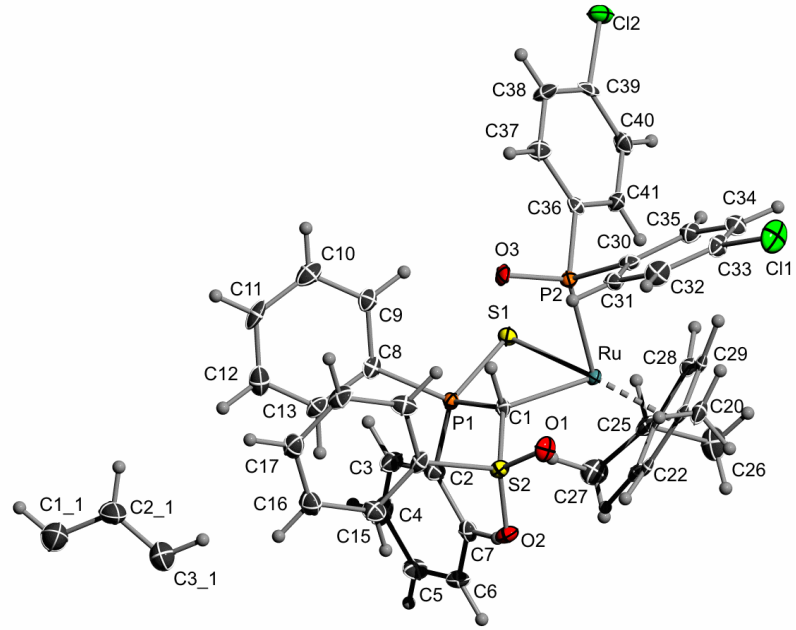


Figure. S19. ORTEP Plot of complex **4b.** Ellipsoids are drawn at the 50% probability level.

Table S4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **4b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ru(1)	8343(1)	9957(1)	8516(1)	11(1)
Cl(1)	6506(1)	13688(1)	8986(1)	31(1)
S(1)	8207(1)	8232(1)	8093(1)	14(1)
P(1)	8690(1)	7813(1)	8955(1)	12(1)
O(1)	8678(1)	10212(2)	10084(1)	18(1)
C(1)	8580(2)	8942(3)	9276(2)	12(1)
Cl(2)	5524(1)	8648(1)	5778(1)	24(1)
S(2)	8975(1)	9343(1)	10017(1)	13(1)
P(2)	7445(1)	9643(1)	8406(1)	13(1)
O(2)	9561(1)	9477(2)	10195(1)	16(1)
C(2)	9382(2)	7495(3)	9086(2)	15(1)
O(3)	7395(1)	8838(2)	8809(1)	15(1)
C(3)	9434(2)	6578(3)	8835(2)	22(1)
C(4)	9934(2)	6324(3)	8845(2)	27(1)
C(5)	10383(2)	6984(3)	9103(2)	22(1)
C(6)	10337(2)	7889(3)	9350(2)	18(1)
C(7)	9838(2)	8149(3)	9346(2)	15(1)
C(8)	8425(2)	6704(3)	9164(2)	14(1)
C(9)	7848(2)	6540(3)	8886(2)	17(1)
C(10)	7629(2)	5748(3)	9076(2)	24(1)
C(11)	7982(2)	5122(3)	9537(2)	23(1)
C(12)	8554(2)	5281(3)	9824(2)	23(1)
C(13)	8778(2)	6063(3)	9634(2)	18(1)
C(14)	8911(2)	8332(3)	10442(2)	14(1)
C(15)	9370(2)	7736(3)	10801(2)	18(1)

C(16)	9301(2)	6919(3)	11107(2)	24(1)
C(17)	8780(2)	6706(3)	11053(2)	22(1)
C(18)	8324(2)	7321(3)	10703(2)	22(1)
C(19)	8390(2)	8142(3)	10396(2)	19(1)
C(20)	8318(2)	12217(3)	9196(2)	21(1)
C(21)	8479(2)	11604(3)	8798(2)	14(1)
C(22)	8996(2)	11087(3)	9032(2)	15(1)
C(23)	9185(2)	10597(3)	8664(2)	15(1)
C(24)	8834(2)	10547(3)	8041(2)	14(1)
C(25)	9004(2)	10068(3)	7613(2)	19(1)
C(26)	9157(2)	10923(3)	7301(2)	31(1)
C(27)	9472(2)	9282(3)	7892(2)	25(1)
C(28)	8298(2)	11020(3)	7801(2)	15(1)
C(29)	8128(2)	11542(3)	8167(2)	16(1)
C(30)	7139(2)	10805(3)	8530(2)	13(1)
C(31)	7190(2)	10947(3)	9096(2)	16(1)
C(32)	6991(2)	11827(3)	9236(2)	21(1)
C(33)	6744(2)	12574(3)	8807(2)	19(1)
C(34)	6681(2)	12460(3)	8235(2)	19(1)
C(35)	6871(2)	11564(3)	8101(2)	17(1)
C(36)	6925(2)	9309(3)	7636(2)	12(1)
C(37)	6461(2)	8735(3)	7558(2)	20(1)
C(38)	6034(2)	8518(3)	6990(2)	22(1)
C(39)	6074(2)	8871(3)	6497(2)	16(1)
C(40)	6539(2)	9398(3)	6565(2)	20(1)
C(41)	6962(2)	9615(3)	7135(2)	17(1)
C1A1	9716(2)	3429(4)	12328(2)	40(1)
C2A1	9428(2)	4344(4)	12155(2)	38(1)
C3A1	9719(2)	5254(3)	12336(2)	31(1)

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for **4b**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ru(1)	11(1)	11(1)	12(1)	1(1)	6(1)	-1(1)
Cl(1)	39(1)	21(1)	46(1)	-8(1)	31(1)	3(1)
S(1)	16(1)	14(1)	11(1)	-1(1)	6(1)	-1(1)
P(1)	12(1)	11(1)	12(1)	-1(1)	6(1)	-1(1)
O(1)	24(2)	14(2)	21(2)	-5(1)	14(1)	0(1)
C(1)	12(2)	13(2)	11(2)	3(2)	6(2)	-1(2)
Cl(2)	16(1)	26(1)	22(1)	-5(1)	3(1)	-1(1)
S(2)	14(1)	14(1)	12(1)	-1(1)	6(1)	-2(1)
P(2)	12(1)	13(1)	15(1)	1(1)	7(1)	0(1)
O(2)	13(2)	21(2)	15(1)	-3(1)	7(1)	-5(1)
C(2)	13(2)	17(2)	16(2)	2(2)	9(2)	1(2)
O(3)	16(2)	15(1)	19(2)	6(1)	11(1)	-1(1)
C(3)	20(2)	20(2)	28(2)	-5(2)	13(2)	-5(2)
C(4)	30(3)	16(2)	43(3)	-8(2)	25(2)	-1(2)
C(5)	15(2)	26(2)	28(2)	4(2)	14(2)	6(2)

C(6)	13(2)	22(2)	17(2)	-1(2)	6(2)	-2(2)
C(7)	19(2)	15(2)	11(2)	-1(2)	7(2)	1(2)
C(8)	20(2)	10(2)	14(2)	-6(2)	10(2)	-1(2)
C(9)	20(2)	14(2)	19(2)	-2(2)	11(2)	0(2)
C(10)	22(2)	25(2)	30(3)	-4(2)	18(2)	-6(2)
C(11)	35(3)	16(2)	30(2)	-3(2)	25(2)	-9(2)
C(12)	36(3)	19(2)	13(2)	0(2)	11(2)	1(2)
C(13)	21(2)	18(2)	17(2)	-5(2)	10(2)	-6(2)
C(14)	20(2)	16(2)	10(2)	-3(2)	10(2)	-6(2)
C(15)	17(2)	22(2)	19(2)	2(2)	10(2)	1(2)
C(16)	22(2)	27(2)	19(2)	6(2)	7(2)	3(2)
C(17)	29(3)	21(2)	16(2)	0(2)	12(2)	-6(2)
C(18)	21(2)	28(2)	21(2)	2(2)	14(2)	-6(2)
C(19)	18(2)	25(2)	17(2)	-2(2)	10(2)	2(2)
C(20)	23(2)	12(2)	29(2)	0(2)	15(2)	-2(2)
C(21)	17(2)	6(2)	22(2)	-1(2)	12(2)	-5(2)
C(22)	16(2)	12(2)	17(2)	4(2)	8(2)	-5(2)
C(23)	15(2)	11(2)	21(2)	4(2)	10(2)	-2(2)
C(24)	18(2)	9(2)	20(2)	1(2)	12(2)	-7(2)
C(25)	20(2)	19(2)	20(2)	-3(2)	12(2)	-5(2)
C(26)	43(3)	33(3)	30(3)	4(2)	29(2)	1(2)
C(27)	28(3)	28(2)	26(2)	-2(2)	18(2)	0(2)
C(28)	17(2)	14(2)	15(2)	1(2)	8(2)	-4(2)
C(29)	14(2)	9(2)	22(2)	5(2)	7(2)	-3(2)
C(30)	10(2)	17(2)	13(2)	-1(2)	7(2)	-2(2)
C(31)	11(2)	20(2)	14(2)	2(2)	5(2)	-2(2)
C(32)	26(2)	26(2)	18(2)	-5(2)	16(2)	-5(2)
C(33)	18(2)	14(2)	29(2)	-4(2)	15(2)	0(2)
C(34)	18(2)	17(2)	26(2)	2(2)	13(2)	2(2)
C(35)	16(2)	21(2)	16(2)	0(2)	10(2)	-1(2)
C(36)	11(2)	11(2)	16(2)	1(2)	8(2)	5(2)
C(37)	19(2)	22(2)	20(2)	-1(2)	10(2)	-1(2)
C(38)	16(2)	24(2)	26(2)	-6(2)	10(2)	-10(2)
C(39)	9(2)	16(2)	18(2)	-2(2)	2(2)	5(2)
C(40)	22(2)	21(2)	15(2)	6(2)	8(2)	0(2)
C(41)	15(2)	15(2)	19(2)	2(2)	6(2)	-6(2)
C1A1	40(3)	34(3)	40(3)	5(2)	15(3)	-5(2)
C2A1	20(3)	42(3)	43(3)	15(2)	9(2)	0(2)
C3A1	31(2)	31(3)	33(3)	4(2)	17(2)	4(2)

3.3 Crystal Structure Determination of **5a**

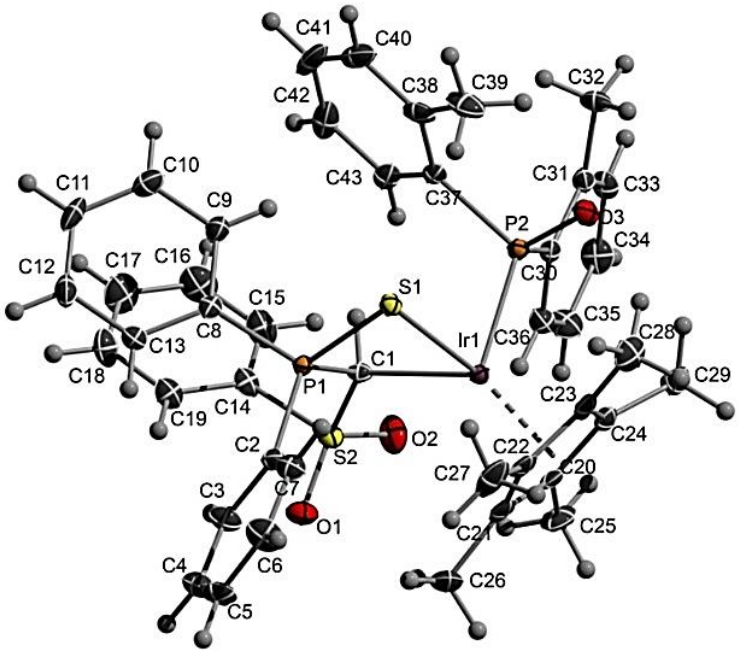


Figure S20. ORTEP Plot of complex **5a.** Ellipsoids are drawn at the 50% probability level.

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	1859(1)	1312(1)	8491(1)	12(1)
S(1)	2992(1)	360(1)	9141(1)	14(1)
P(1)	4333(1)	870(1)	8748(1)	12(1)
O(1)	4631(2)	2447(1)	7835(1)	25(1)
C(1)	3450(2)	1265(1)	7922(2)	14(1)
S(2)	3971(1)	1940(1)	7353(1)	18(1)
P(2)	879(1)	506(1)	7643(1)	13(1)
O(2)	3018(2)	2189(1)	6818(1)	27(1)
C(2)	5089(2)	1442(1)	9485(2)	16(1)
O(3)	-126(2)	188(1)	8002(1)	20(1)
C(3)	5895(3)	1945(2)	9305(2)	22(1)
C(4)	6520(3)	2320(2)	9896(2)	25(1)
C(5)	6349(3)	2207(2)	10669(2)	25(1)
C(6)	5580(3)	1704(2)	10853(2)	29(1)
C(7)	4955(3)	1319(2)	10267(2)	21(1)
C(8)	5436(2)	285(1)	8459(2)	14(1)
C(9)	5064(3)	-246(2)	7933(2)	20(1)
C(10)	5867(3)	-689(2)	7652(2)	26(1)
C(11)	7027(3)	-600(2)	7885(2)	27(1)
C(12)	7408(3)	-83(2)	8413(2)	26(1)
C(13)	6613(2)	358(2)	8709(2)	19(1)
C(14)	4924(2)	1501(2)	6770(2)	18(1)
C(15)	4469(3)	1258(2)	6041(2)	28(1)
C(16)	5183(3)	887(2)	5591(2)	35(1)
C(17)	6327(3)	765(2)	5875(2)	36(1)
C(18)	6777(3)	1011(2)	6601(2)	28(1)
C(19)	6075(3)	1388(2)	7057(2)	22(1)
C(20)	1123(2)	2377(1)	8432(2)	19(1)
C(21)	1976(3)	2372(2)	9127(2)	22(1)

C(22)	1630(3)	1864(2)	9650(2)	22(1)
C(23)	565(3)	1538(2)	9299(2)	19(1)
C(24)	228(2)	1888(2)	8570(2)	19(1)
C(25)	1054(3)	2918(2)	7804(2)	30(1)
C(26)	2966(3)	2872(2)	9271(2)	35(1)
C(27)	2191(3)	1687(2)	10454(2)	34(1)
C(28)	-146(3)	1021(2)	9692(2)	29(1)
C(29)	-932(3)	1805(2)	8097(2)	24(1)
C(30)	312(2)	855(2)	6662(2)	15(1)
C(31)	-409(2)	439(2)	6119(2)	16(1)
C(32)	-771(3)	-296(2)	6295(2)	21(1)
C(33)	-787(3)	726(2)	5383(2)	22(1)
C(34)	-510(3)	1402(2)	5185(2)	26(1)
C(35)	173(3)	1805(2)	5721(2)	27(1)
C(36)	591(3)	1526(2)	6448(2)	20(1)
C(37)	1798(2)	-205(1)	7308(2)	15(1)
C(38)	1888(3)	-874(2)	7651(2)	22(1)
C(39)	1298(3)	-1072(2)	8359(2)	31(1)
C(40)	2542(3)	-1381(2)	7310(2)	30(1)
C(41)	3120(3)	-1241(2)	6674(2)	34(1)
C(42)	3054(3)	-583(2)	6335(2)	29(1)
C(43)	2388(2)	-73(2)	6651(2)	20(1)

Table S7. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5a**. The anisotropicdisplacement factor exponent takes the form: $-2p^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$.

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	12(1)	11(1)	13(1)	-2(1)	0(1)	1(1)
S(1)	13(1)	14(1)	14(1)	1(1)	2(1)	0(1)
P(1)	12(1)	11(1)	13(1)	0(1)	1(1)	0(1)
O(1)	27(1)	17(1)	32(1)	0(1)	3(1)	-5(1)
C(1)	16(2)	12(2)	14(2)	1(1)	0(1)	-1(1)
S(2)	17(1)	17(1)	19(1)	6(1)	1(1)	-1(1)
P(2)	13(1)	14(1)	13(1)	-2(1)	2(1)	-1(1)
O(2)	21(1)	30(1)	29(1)	17(1)	0(1)	3(1)
C(2)	16(2)	13(2)	17(2)	-2(1)	-2(1)	1(1)
O(3)	20(1)	21(1)	19(1)	-4(1)	7(1)	-4(1)
C(3)	26(2)	23(2)	17(2)	1(1)	-1(1)	-4(1)
C(4)	26(2)	19(2)	28(2)	1(1)	-4(1)	-6(1)
C(5)	27(2)	21(2)	25(2)	-7(1)	-10(1)	-2(1)
C(6)	35(2)	35(2)	14(2)	0(1)	-5(1)	-4(2)
C(7)	22(2)	19(2)	21(2)	3(1)	-1(1)	-1(1)
C(8)	17(2)	13(2)	13(2)	4(1)	4(1)	1(1)
C(9)	17(2)	20(2)	23(2)	-1(1)	1(1)	3(1)
C(10)	33(2)	21(2)	24(2)	-5(1)	3(1)	5(1)
C(11)	26(2)	25(2)	32(2)	4(1)	15(2)	13(1)
C(12)	15(2)	28(2)	37(2)	6(2)	5(1)	2(1)
C(13)	17(2)	16(2)	24(2)	-1(1)	3(1)	-2(1)
C(14)	18(2)	22(2)	15(2)	7(1)	4(1)	-5(1)
C(15)	24(2)	39(2)	21(2)	9(1)	2(1)	-4(2)
C(16)	38(2)	46(2)	20(2)	-3(2)	4(2)	-6(2)
C(17)	37(2)	48(2)	26(2)	-3(2)	14(2)	-1(2)
C(18)	20(2)	40(2)	26(2)	4(2)	7(1)	-1(2)
C(19)	22(2)	26(2)	17(2)	4(1)	4(1)	-4(1)
C(20)	22(2)	9(2)	25(2)	-4(1)	4(1)	8(1)
C(21)	23(1)	18(1)	23(1)	-13(1)	1(1)	7(1)
C(22)	23(1)	18(1)	23(1)	-13(1)	1(1)	7(1)
C(23)	20(2)	20(2)	17(2)	-7(1)	4(1)	7(1)
C(24)	18(2)	17(2)	20(2)	-6(1)	1(1)	6(1)

C(25)	37(2)	12(2)	41(2)	4(1)	6(2)	6(1)
C(26)	28(2)	22(2)	52(2)	-18(2)	-1(2)	-2(1)
C(27)	37(2)	42(2)	21(2)	-14(2)	-5(2)	19(2)
C(28)	32(2)	31(2)	26(2)	0(1)	14(2)	2(2)
C(29)	19(2)	26(2)	27(2)	-5(1)	0(1)	8(1)
C(30)	11(2)	19(2)	14(2)	-2(1)	1(1)	2(1)
C(31)	13(2)	19(2)	17(2)	-1(1)	1(1)	1(1)
C(32)	24(2)	20(2)	18(2)	-6(1)	-2(1)	-5(1)
C(33)	18(2)	29(2)	18(2)	-4(1)	0(1)	1(1)
C(34)	27(2)	35(2)	15(2)	6(1)	-1(1)	3(1)
C(35)	31(2)	22(2)	27(2)	8(1)	2(1)	-3(1)
C(36)	18(2)	20(2)	22(2)	0(1)	2(1)	-2(1)
C(37)	15(2)	17(2)	11(2)	-6(1)	-5(1)	1(1)
C(38)	23(2)	16(2)	25(2)	-3(1)	-11(1)	-3(1)
C(39)	37(2)	18(2)	36(2)	7(1)	-7(2)	-10(2)
C(40)	34(2)	18(2)	34(2)	-7(1)	-15(2)	6(1)
C(41)	31(2)	36(2)	33(2)	-23(2)	-13(2)	18(2)
C(42)	21(2)	49(2)	15(2)	-12(1)	-4(1)	9(2)
C(43)	20(2)	25(2)	13(2)	-6(1)	-2(1)	3(1)

3.4 Crystal Structure Determination of **5b**

All hydrogen atoms were refined on ideal positions except for H1 at C1, which was found in the difference Fourier map and refined independently.

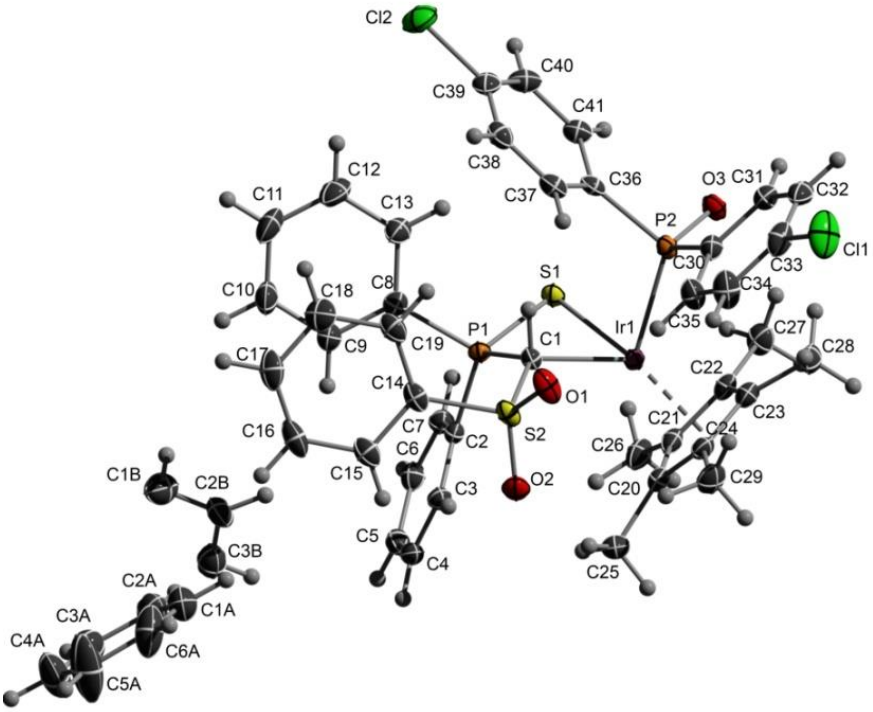


Figure S21. ORTEP Plot of complex **5b.** Ellipsoids are drawn at the 50% probability level.

Table S8. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **5b**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	6533(1)	4410(1)	8379(1)	16(1)
Cl(1)	10160(1)	1874(1)	8144(1)	46(1)
Cl(2)	3394(1)	1950(1)	10218(1)	39(1)
S(1)	5029(1)	4532(1)	9211(1)	19(1)
S(2)	5334(1)	3699(1)	6503(1)	21(1)
P(1)	4293(1)	4370(1)	8003(1)	17(1)
P(2)	6948(1)	3675(1)	9360(1)	18(1)
O(1)	6041(1)	3225(1)	6523(1)	29(1)
O(2)	5495(1)	4164(1)	5902(1)	26(1)
O(3)	7356(1)	3874(1)	10282(1)	23(1)
C(1)	5308(2)	3938(1)	7616(2)	16(1)
C(2)	3904(2)	5021(1)	7426(2)	18(1)
C(3)	3448(2)	5422(1)	7957(2)	22(1)
C(4)	2992(2)	5906(1)	7573(2)	25(1)
C(5)	2995(2)	5994(1)	6660(2)	26(1)
C(6)	3466(2)	5607(1)	6132(2)	24(1)
C(7)	3911(2)	5115(1)	6510(2)	21(1)
C(8)	3089(2)	3995(1)	8090(2)	21(1)
C(9)	2197(2)	4132(1)	7552(2)	26(1)
C(10)	1297(2)	3831(1)	7635(2)	35(1)
C(11)	1283(2)	3398(1)	8253(2)	39(1)
C(12)	2165(2)	3256(1)	8787(2)	36(1)
C(13)	3068(2)	3554(1)	8708(2)	27(1)
C(14)	4083(2)	3426(1)	6199(2)	21(1)
C(15)	3727(2)	2965(1)	6664(2)	27(1)
C(16)	2738(2)	2765(1)	6446(2)	34(1)
C(17)	2120(2)	3022(1)	5760(2)	34(1)
C(18)	2485(2)	3469(1)	5289(2)	32(1)
C(19)	3466(2)	3680(1)	5508(2)	26(1)
C(20)	7591(2)	5075(1)	8926(2)	22(1)
C(21)	6887(2)	5356(1)	8267(2)	23(1)
C(22)	6989(2)	5115(1)	7416(2)	23(1)
C(23)	7746(2)	4662(1)	7535(2)	22(1)
C(24)	8165(2)	4671(1)	8455(2)	22(1)
C(25)	7810(2)	5243(1)	9890(2)	30(1)
C(26)	6202(2)	5841(1)	8482(2)	30(1)
C(27)	6527(2)	5335(1)	6532(2)	32(1)
C(28)	8174(2)	4343(1)	6787(2)	32(1)
C(29)	9100(2)	4367(1)	8845(2)	28(1)
C(30)	7876(2)	3169(1)	8964(2)	21(1)
C(31)	7886(2)	3013(1)	8071(2)	27(1)
C(32)	8576(2)	2608(1)	7818(2)	34(1)
C(33)	9269(2)	2369(1)	8460(2)	29(1)
C(34)	9291(2)	2525(1)	9351(2)	28(1)
C(35)	8590(2)	2921(1)	9596(2)	25(1)
C(36)	5905(2)	3167(1)	9529(2)	19(1)
C(37)	5586(2)	2719(1)	8949(2)	22(1)
C(38)	4820(2)	2342(1)	9151(2)	25(1)
C(39)	4369(2)	2413(1)	9942(2)	25(1)
C(40)	4669(2)	2847(1)	10532(2)	27(1)
C(41)	5435(2)	3219(1)	10327(2)	22(1)
C11	8719(3)	6707(2)	8134(3)	56(1)
C41	10016(3)	5852(2)	7655(2)	45(1)
C51	10220(3)	6132(2)	8448(3)	63(1)
C61	9556(3)	6554(2)	8692(3)	86(2)
C21	8511(3)	6426(2)	7347(2)	45(1)
C31	9155(3)	6000(2)	7104(2)	45(1)

C12	10225(3)	4438(1)	5164(2)	41(1)
C22	9286(3)	4589(2)	4748(2)	39(1)
C32	9058(3)	5151(2)	4588(2)	42(1)

Table S9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **5b**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Ir(1)	14(1)	19(1)	15(1)	-1(1)	2(1)	1(1)
Cl(1)	31(1)	35(1)	73(1)	-17(1)	3(1)	12(1)
Cl(2)	46(1)	30(1)	42(1)	3(1)	10(1)	-15(1)
S(1)	19(1)	23(1)	15(1)	-2(1)	2(1)	0(1)
S(2)	21(1)	26(1)	15(1)	-4(1)	0(1)	4(1)
P(1)	17(1)	18(1)	15(1)	-1(1)	2(1)	0(1)
P(2)	18(1)	22(1)	15(1)	-1(1)	0(1)	2(1)
O(1)	27(1)	34(1)	25(1)	-9(1)	-2(1)	14(1)
O(2)	26(1)	35(1)	16(1)	0(1)	5(1)	-1(1)
O(3)	26(1)	28(1)	16(1)	-2(1)	-2(1)	0(1)
C(1)	15(1)	17(1)	15(1)	-1(1)	-1(1)	0(1)
C(2)	14(1)	20(1)	20(1)	1(1)	1(1)	-3(1)
C(3)	22(2)	24(2)	18(1)	-2(1)	3(1)	0(1)
C(4)	22(2)	23(2)	30(2)	-3(1)	1(1)	0(1)
C(5)	22(2)	23(2)	33(2)	5(1)	-5(1)	-1(1)
C(6)	24(2)	28(2)	20(2)	5(1)	0(1)	-7(1)
C(7)	19(1)	24(2)	19(1)	0(1)	3(1)	0(1)
C(8)	22(2)	21(2)	19(1)	-4(1)	4(1)	0(1)
C(9)	22(2)	28(2)	27(2)	1(1)	2(1)	-2(1)
C(10)	18(2)	38(2)	46(2)	2(2)	-2(1)	-2(1)
C(11)	22(2)	36(2)	60(2)	0(2)	12(2)	-7(1)
C(12)	33(2)	26(2)	50(2)	9(1)	11(2)	-3(1)
C(13)	25(2)	22(2)	33(2)	2(1)	5(1)	2(1)
C(14)	24(2)	22(2)	17(1)	-9(1)	-2(1)	5(1)
C(15)	31(2)	26(2)	23(2)	-5(1)	-5(1)	2(1)
C(16)	42(2)	26(2)	34(2)	-7(1)	2(1)	-6(1)
C(17)	27(2)	31(2)	42(2)	-15(1)	-6(1)	0(1)
C(18)	30(2)	34(2)	30(2)	-12(1)	-12(1)	10(1)
C(19)	31(2)	25(2)	22(2)	-6(1)	-3(1)	3(1)
C(20)	19(1)	21(2)	26(2)	-2(1)	3(1)	-6(1)
C(21)	17(1)	20(1)	34(2)	2(1)	5(1)	-3(1)
C(22)	16(1)	26(2)	26(2)	6(1)	4(1)	-4(1)
C(23)	19(2)	26(2)	22(1)	1(1)	6(1)	-5(1)
C(24)	18(1)	23(2)	26(2)	0(1)	5(1)	-4(1)
C(25)	32(2)	32(2)	27(2)	-8(1)	2(1)	-7(1)
C(26)	23(2)	24(2)	44(2)	0(1)	8(1)	0(1)
C(27)	28(2)	38(2)	31(2)	13(1)	2(1)	-5(1)
C(28)	26(2)	44(2)	28(2)	-4(1)	12(1)	-2(1)
C(29)	16(2)	30(2)	36(2)	2(1)	0(1)	0(1)
C(30)	18(1)	22(2)	25(2)	0(1)	1(1)	-2(1)
C(31)	23(2)	33(2)	25(2)	-6(1)	-1(1)	4(1)
C(32)	25(2)	40(2)	35(2)	-15(1)	1(1)	4(1)
C(33)	22(2)	20(2)	47(2)	-7(1)	7(1)	1(1)
C(34)	23(2)	24(2)	37(2)	11(1)	3(1)	1(1)
C(35)	21(2)	27(2)	25(2)	5(1)	4(1)	-1(1)
C(36)	22(2)	20(1)	15(1)	3(1)	-1(1)	6(1)
C(37)	26(2)	24(2)	17(1)	1(1)	-1(1)	6(1)
C(38)	28(2)	20(2)	26(2)	0(1)	-4(1)	2(1)

C(39)	27(2)	18(2)	30(2)	6(1)	2(1)	0(1)
C(40)	36(2)	24(2)	22(2)	3(1)	8(1)	4(1)
C(41)	29(2)	18(1)	19(1)	-1(1)	2(1)	2(1)
C11	33(2)	53(2)	80(3)	-23(2)	-4(2)	-2(2)
C41	41(2)	50(2)	44(2)	0(2)	6(2)	1(2)
C51	44(2)	98(3)	46(2)	-7(2)	-12(2)	12(2)
C61	48(3)	134(5)	72(3)	-63(3)	-17(2)	13(3)
C21	33(2)	59(2)	43(2)	8(2)	-2(2)	-4(2)
C31	40(2)	62(2)	33(2)	-7(2)	2(2)	-12(2)
C12	37(2)	40(2)	49(2)	10(2)	14(2)	10(2)
C22	32(2)	51(2)	34(2)	-4(2)	0(1)	-5(2)
C32	27(2)	66(3)	34(2)	14(2)	-4(1)	7(2)

4. Computational studies

4.1. Thermodynamics of different isomers

Table S10. Calculated energies [in kJ/mol] of the optimized structures [M062x//6-311+g(d)/LANL2TZ(f)]; energy differences, reaction enthalpies and activation energies are given relative to the energetically most favoured isomer.

Compound	SCF	Enthalpy[a]	Free energy[a]	ΔH	ΔG
Iridium complex + $Ph_2P(O)H$					
cis-isomer (*cis*-**5**)	-8916469,36	-8914433,13	-8914764,78	0	0
cis-isomer (H-bond) (*cis*-**5'**)	-8916458,34	-8914421,11	-8914755,52	12,02	9,25
trans-isomer (*trans*-**5**)	-8916437,04	-8914401,58	-8914737,14	31,57	27,65
Iridium complex + $Tol_2P(O)H$					
cis-isomer (*cis*-**5a**)	-9122847,25	-9120655,13	-9121005,98	0	0
cis-isomer (H-bond) (*cis*-**5a'**)	-9122838,16	-9120645,46	-9120991,62	9,67	14,36
Ruthenium complex + $Ph_2P(O)H$					
cis-isomer (*cis*-**4**)	-8680068,05	-8678219,17	-8678540,46	3,95	3,60
cis-isomer (H-bond) (*cis*-**4'**)	-8680072,281	-8678223,12	-8678544,06	0	0

[a] Thermal corrections were calculated using the 6-31+G(d) (for all non-metal atoms) and LANL2DZ (for Ir and Ru) basis set.

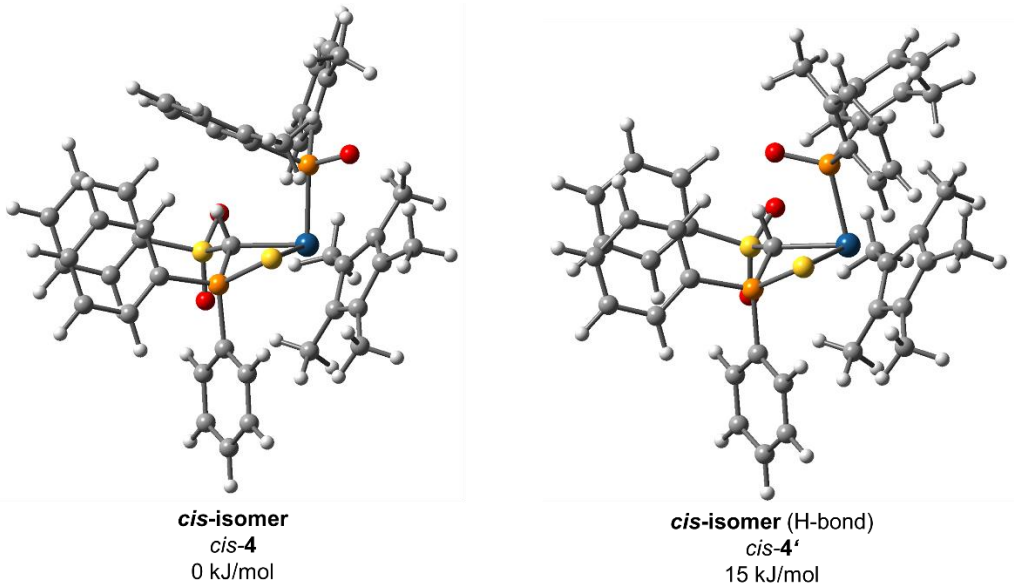


Figure S22. Structures of the energy-optimized *cis*-isomers of **5b** [M062X//6-311+G(d)/LANL2TZ(f)].

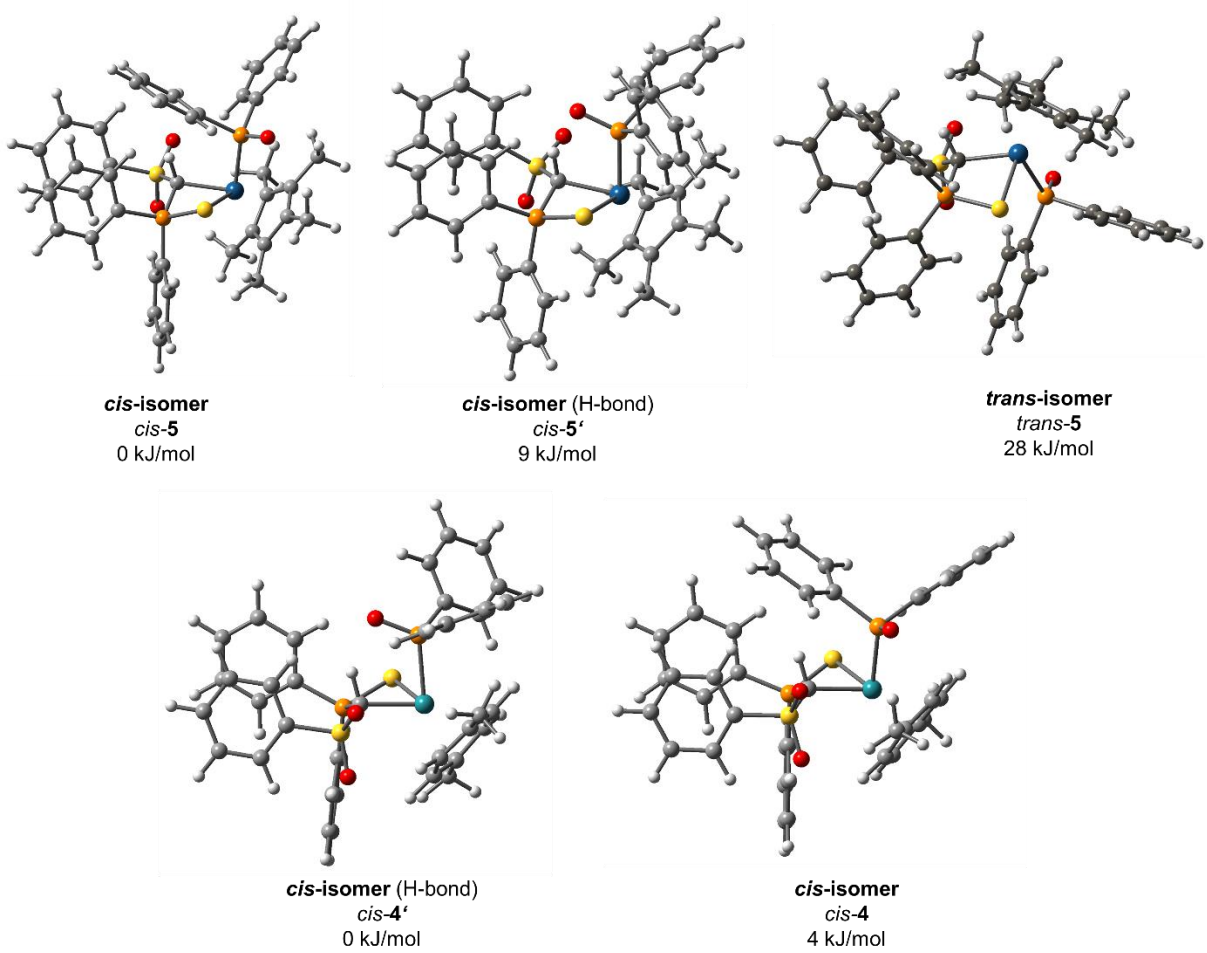


Figure S23. Structures of the energy-optimized isomers of the iridium and ruthenium complexes of the P-H activation of $Ph_2P(O)H$ [M062X//6-311+G(d)/LANL2TZ(f)].

Table S11. Cartesian coordinates of the *cis*-isomer *cis*-**5**.

Atomic symbol	x	y	z
Ir	-1.19375600	-0.92292700	-0.22032600
S	0.33015100	-0.78619300	-2.18328100
P	1.68161000	-0.64902200	-0.66976800
O	1.27142700	-0.74810000	2.92225700
C	0.54035800	0.13675600	0.48880500
S	0.89257800	0.46626000	2.19727300
P	-2.13303800	0.97185200	-1.10652400
O	-0.21703600	1.26696300	2.70883400
C	2.34666400	-2.29475300	-0.27078000
O	-2.83608400	0.68826900	-2.42001000
C	2.59554200	-2.74961600	1.02296300
C	3.17025200	-4.00591000	1.21092000
C	3.51079400	-4.79634900	0.12000500
C	3.27416600	-4.33501000	-1.17343000
C	2.68916900	-3.09180700	-1.36969100
C	3.13402200	0.37660100	-1.05802400
C	2.90230900	1.73040900	-1.32200300
C	3.97065700	2.57463600	-1.58960300
C	5.26985000	2.07175700	-1.60867800
C	5.50068400	0.72369200	-1.35700500
C	4.43566500	-0.12699400	-1.07559500

C	2.32608300	1.53494900	2.14359000
C	2.13048400	2.90791700	2.05845800
C	3.23875100	3.73528300	1.91712400
C	4.51610700	3.18529800	1.86089100
C	4.69654600	1.80825700	1.95895700
C	3.59595400	0.97179200	2.10346300
C	-2.41272700	-1.80090900	1.34431400
C	-1.35682300	-2.78150400	1.13378500
C	-1.40227800	-3.19761800	-0.20911200
C	-2.51050500	-2.51294600	-0.86432800
C	-3.18757900	-1.73834000	0.12783200
C	-2.78756300	-1.26204600	2.69008300
C	-0.50528000	-3.32604600	2.23556800
C	-0.51028100	-4.18693600	-0.88857400
C	-2.96491800	-2.70145000	-2.27853300
C	-4.52767400	-1.10278400	-0.06646800
C	-3.32206800	1.78573600	0.03585800
C	-4.48528300	2.31350300	-0.52706300
C	-5.43693500	2.92560800	0.28201000
C	-5.22925900	3.01780100	1.65647500
C	-4.06611500	2.49924700	2.21873400
C	-3.11494000	1.87940400	1.41125200
C	-0.96421900	2.38217400	-1.39511100
C	-0.55350100	2.61314000	-2.70950800
C	0.28777100	3.68177600	-3.00841200
C	0.72412700	4.53307400	-1.99611500
C	0.31728900	4.31113700	-0.68291900
C	-0.52573200	3.24259900	-0.38438300
H	0.48094900	1.15357300	0.09162400
H	2.31409000	-2.15124500	1.87994400
H	3.34426100	-4.36430000	2.21935800
H	3.95776100	-5.77207500	0.27445800
H	3.53386100	-4.94819100	-2.02868000
H	2.48039300	-2.74496600	-2.37654700
H	1.89228600	2.12917700	-1.32856300
H	3.78133700	3.62436700	-1.78486800
H	6.10319400	2.73225500	-1.82199200
H	6.51126900	0.33124000	-1.37510200
H	4.62403700	-1.17388700	-0.86467900
H	1.12612200	3.31027500	2.11795400
H	3.10467800	4.80910800	1.85221900
H	5.37756400	3.83311700	1.74247100
H	5.69329500	1.38477400	1.91731400
H	3.71908100	-0.10319400	2.18723300
H	-1.91977500	-0.84122100	3.20238700
H	-3.19746900	-2.06288500	3.31449200
H	-3.53906700	-0.47779600	2.60878500
H	-0.07798000	-2.53457400	2.85030800
H	0.30768700	-3.94182900	1.85340200
H	-1.12771800	-3.95575700	2.88032900
H	-0.11702600	-3.78063200	-1.82341000
H	-1.07334300	-5.09377500	-1.12890500
H	0.33861700	-4.46521600	-0.26259200
H	-3.30354700	-1.74901500	-2.69236000
H	-3.78090500	-3.42912700	-2.33203800
H	-2.14653600	-3.06433700	-2.90293100
H	-4.75337300	-0.36870900	0.70569000
H	-5.28659800	-1.89038700	-0.02249000
H	-4.59862100	-0.61342900	-1.03956800
H	-6.34380400	3.32670700	-0.15782600
H	-5.97331800	3.49176700	2.28771600
H	-3.90004700	2.56785700	3.28878100

H	-2.21965000	1.45762300	1.85650900
H	0.59545900	3.85556200	-4.03388100
H	1.36731100	5.37475200	-2.23117700
H	0.64270400	4.98065400	0.10672100
H	-0.85588100	3.08767900	0.63997500
H	-4.63755900	2.21576300	-1.59732600
H	-0.92057900	1.95593200	-3.49034400

Table S12. Cartesian coordinates of the *cis*-isomer *cis*-**5'**.

Atomic symbol	x	y	z
Ir	-0.88034900	0.90506000	-0.07093600
S	0.25341700	0.66214900	2.11082700
P	1.86103700	0.34990900	0.88796000
O	2.37464000	0.45557000	-2.60103300
C	0.86561000	-0.24668200	-0.47791300
S	1.50696700	-0.61009600	-2.08806300
P	-1.77198000	-1.19054700	0.38005400
O	0.38835000	-1.05480900	-2.91256000
C	2.81628200	1.87364100	0.61915100
O	-0.77201600	-2.35036300	0.37426400
C	3.75776800	1.96841700	-0.40990100
C	4.49491200	3.13579100	-0.56513600
C	4.31064300	4.20363200	0.30979600
C	3.39196600	4.10085000	1.34843500
C	2.64454500	2.93728000	1.50451300
C	3.02801700	-0.89775100	1.49588800
C	2.52507300	-2.19260500	1.67503000
C	3.37823500	-3.19839400	2.10803600
C	4.71832300	-2.91985400	2.36755300
C	5.21240100	-1.63128100	2.19810800
C	4.36859400	-0.61492400	1.76071700
C	2.52028200	-2.04944700	-1.76358200
C	1.86772700	-3.24942200	-1.49370200
C	2.63441800	-4.36483000	-1.18149200
C	4.02314000	-4.26701200	-1.12577400
C	4.65686400	-3.05626400	-1.38622300
C	3.90218200	-1.93362100	-1.71446100
C	-1.35928900	1.92702000	-1.93327900
C	-0.44153100	2.80932900	-1.22798100
C	-1.05635700	3.17611100	-0.00961500
C	-2.35883900	2.55407400	0.06885200
C	-2.56047800	1.83541200	-1.15333800
C	-1.21328300	1.47012900	-3.35062900
C	0.85381600	3.31812300	-1.78305600
C	-0.52511800	4.09516800	1.04430600
C	-3.40806000	2.89933300	1.08011100
C	-3.87192100	1.30846100	-1.63521100
C	-2.66502600	-1.26249100	1.98543300
C	-3.01233400	-2.53099900	2.45956800
C	-3.71559100	-2.66720500	3.65041900
C	-4.07247900	-1.53743900	4.38460800
C	-3.71234300	-0.27434700	3.92922200
C	-3.00770900	-0.14121300	2.73431300
C	-3.09376100	-1.63408700	-0.81498500
C	-2.67923400	-1.92134400	-2.12033400
C	-3.61286400	-2.25168000	-3.09547900
C	-4.96984700	-2.29956900	-2.77791700

C	-5.38530300	-2.02999200	-1.47888200
C	-4.44977300	-1.70235800	-0.49860700
H	0.59293900	-1.26011400	-0.14262100
H	3.88975800	1.15393500	-1.10919200
H	5.20947400	3.21263000	-1.37642700
H	4.88679000	5.11345800	0.18306600
H	3.25113600	4.92633200	2.03719400
H	1.91877300	2.85552300	2.30555500
H	1.47613700	-2.41072700	1.47857900
H	2.99491400	-4.20402400	2.23803600
H	5.37879500	-3.71117400	2.70503900
H	6.25403300	-1.41427800	2.40596300
H	4.75568900	0.38905300	1.62688500
H	0.78265600	-3.29426000	-1.49729700
H	2.14470800	-5.30809000	-0.96852000
H	4.61508800	-5.13929300	-0.87082200
H	5.73726400	-2.98406700	-1.33717300
H	4.37516500	-0.98560100	-1.94388300
H	-0.16641600	1.41036200	-3.64677200
H	-1.72011200	2.17830200	-4.01522500
H	-1.64684500	0.48110900	-3.49590400
H	1.44397200	2.52057600	-2.23530800
H	1.46536900	3.79273600	-1.01434000
H	0.64758000	4.06431600	-2.55722300
H	-0.49831800	3.60397100	2.02013100
H	-1.17576000	4.97074600	1.12850800
H	0.47992500	4.44142800	0.80918200
H	-4.15626700	2.11174100	1.17399500
H	-3.92492800	3.81866400	0.78467300
H	-2.97315900	3.07057800	2.06709800
H	-3.75773800	0.49527500	-2.35062800
H	-4.40164100	2.12768000	-2.13358900
H	-4.49651400	0.95322800	-0.81703800
H	-3.98305600	-3.65463400	4.01082700
H	-4.61974800	-1.64467300	5.31484800
H	-3.97085300	0.60669100	4.50707900
H	-2.70271000	0.83886200	2.38889000
H	-3.28218400	-2.46991100	-4.10533300
H	-5.69847600	-2.55464900	-3.53983200
H	-6.43871000	-2.07681700	-1.22416500
H	-4.78541500	-1.49249500	0.51206700
H	-2.71849100	-3.40558700	1.88797800
H	-1.62370300	-1.87061100	-2.37140300

Table S13. Cartesian coordinates of the *trans*-isomer *trans*-**5**.

Atomic symbol	x	y	z
Ir	-1.04606000	0.96678500	0.14882500
S	-0.38227900	-0.04091100	-2.04452000
P	1.43312000	-0.08509700	-1.15024200
O	1.12017000	-1.94205400	1.84278700
C	0.96538700	0.39936000	0.53577000
S	1.43091900	-0.52848600	1.98822000
P	-2.17643300	-0.95941300	0.74992300
O	0.94005300	0.24268100	3.12410500
C	2.38103200	-1.61548700	-1.36484800
O	-2.50588200	-1.04292200	2.22638400
C	1.81117600	-2.81674400	-0.93116500

C	2.54386000	-3.99389600	-1.02179500
C	3.83380100	-3.97810300	-1.54541700
C	4.39381000	-2.78473300	-1.99337300
C	3.67079300	-1.60092400	-1.90534800
C	2.50816000	1.25771900	-1.75817800
C	2.25226700	1.86271100	-2.98615000
C	3.07859100	2.88781700	-3.43870200
C	4.15461700	3.30970600	-2.66552000
C	4.41642300	2.69962800	-1.44034900
C	3.59862200	1.67198400	-0.98660500
C	3.22265800	-0.37698800	2.02351400
C	3.78201000	0.77402400	2.57269600
C	5.15992300	0.94832100	2.51856600
C	5.96144100	-0.02401300	1.92160400
C	5.39120700	-1.18177000	1.40108600
C	4.01209500	-1.36860800	1.45427800
C	-1.00053100	3.17113200	-0.31378400
C	-0.61897800	2.97581500	1.03573800
C	-1.68562500	2.28497400	1.73005100
C	-2.79016000	2.17401700	0.79943600
C	-2.35140900	2.65125400	-0.46744500
C	-0.21806900	3.83402700	-1.40429600
C	0.66146500	3.40019300	1.68095600
C	-1.76915100	1.96399000	3.18911600
C	-4.16872100	1.76348300	1.20620900
C	-3.16033400	2.78107300	-1.72036500
C	-3.78133000	-0.97690700	-0.18616600
C	-4.89144700	-1.47839300	0.49629600
C	-6.13980100	-1.51603800	-0.11602100
C	-6.29231500	-1.05932400	-1.42302400
C	-5.18870000	-0.56921100	-2.11475900
C	-3.94145800	-0.52630300	-1.49564800
C	-1.58268300	-2.62453500	0.20861500
C	-1.13285700	-3.48785700	1.20787000
C	-0.73429800	-4.78392200	0.89025700
C	-0.80190500	-5.23421100	-0.42512400
C	-1.27797300	-4.38742400	-1.42369400
C	-1.67141300	-3.09148500	-1.10629100
H	1.50072000	1.33591000	0.70785900
H	0.81891000	-2.83326800	-0.49937700
H	2.09775500	-4.91788300	-0.67354600
H	4.40242900	-4.89929600	-1.61103100
H	5.39356800	-2.77341500	-2.41254300
H	4.11643500	-0.67512800	-2.24944000
H	1.39820000	1.54370700	-3.57355500
H	2.87511700	3.36076300	-4.39259700
H	4.79208000	4.11333700	-3.01672300
H	5.25798100	3.02087800	-0.83701300
H	3.81781200	1.19157700	-0.03756400
H	3.13942800	1.50915600	3.04469000
H	5.60933300	1.83635400	2.94827200
H	7.03590100	0.11506100	1.87855100
H	6.01662200	-1.94632100	0.95447800
H	3.55275500	-2.27200800	1.06859900
H	0.85000000	3.85991700	-1.17975400
H	-0.55697400	4.86375600	-1.55538700
H	-0.34038000	3.29950100	-2.34910800
H	1.47194800	3.51830800	0.95753400
H	0.96422000	2.67824000	2.44204400
H	0.51649200	4.36482400	2.17556100
H	-2.18180100	0.96135500	3.32261400
H	-2.40747400	2.69312500	3.69933000

H	-0.78370600	1.97132400	3.65195400
H	-4.79339400	1.48875300	0.35697900
H	-4.63716200	2.60846900	1.72147600
H	-4.13456000	0.92099100	1.89916900
H	-2.60052600	2.43117000	-2.59120000
H	-3.41934500	3.83049300	-1.89156900
H	-4.08403900	2.20716300	-1.65936100
H	-6.99718400	-1.89782300	0.42803100
H	-7.26594600	-1.08598700	-1.90023100
H	-5.29942800	-0.21338500	-3.13408800
H	-3.09406000	-0.11903300	-2.03816300
H	-0.38037100	-5.44409600	1.67491300
H	-0.50261400	-6.24831200	-0.67076600
H	-1.35054000	-4.73786700	-2.44759100
H	-2.05746700	-2.45034300	-1.88949500
H	-4.76102000	-1.81284000	1.52092000
H	-1.09743200	-3.12933800	2.22899500

Table S14. Cartesian coordinates of the *cis*-isomer *cis*-**5b** (*o*-tolyl-substituted phosphine oxide).

Atomic symbol	x	y	z
Ir	-0.95158100	-1.19390500	-0.16394400
S	0.45803400	-0.72822900	-2.15325500
P	1.83428300	-0.43529000	-0.68573200
O	1.76128700	-0.77856900	2.80629100
C	0.62316600	0.10393000	0.54313600
S	1.05113700	0.37423000	2.24751700
P	-2.29050100	0.55698000	-0.85086800
O	-0.14376200	0.85648100	2.93162900
C	2.79219400	-1.95518400	-0.36558000
O	-3.18634100	0.12502600	-1.99639200
C	3.48260700	-2.19246200	0.82658000
C	4.29010100	-3.31775300	0.94727300
C	4.42840000	-4.20340800	-0.11724100
C	3.75597600	-3.96088200	-1.30988400
C	2.94049000	-2.84089800	-1.43541000
C	3.07196300	0.83657300	-1.08094400
C	2.59841300	2.13562700	-1.29235400
C	3.49429500	3.16197500	-1.55463400
C	4.86032600	2.89528200	-1.62193600
C	5.33039600	1.60042900	-1.43061100
C	4.43911200	0.56703400	-1.15593700
C	2.19517500	1.75289600	2.18506500
C	1.67103200	3.04039900	2.17920700
C	2.53736500	4.11849900	2.03816400
C	3.90561600	3.90116100	1.90596400
C	4.41801300	2.60715900	1.92779600
C	3.56058800	1.52232100	2.07006500
C	-1.71956800	-2.40381500	1.47011600
C	-0.60955200	-3.17927700	0.92971600
C	-0.90283900	-3.46491600	-0.41833900
C	-2.18865100	-2.88440000	-0.75532600
C	-2.72648800	-2.31131500	0.44357100
C	-1.87790600	-2.09107800	2.92609300
C	0.55010100	-3.67205100	1.73748800
C	-0.08908300	-4.26564700	-1.38296400
C	-2.91405900	-3.03811700	-2.05525400
C	-4.14239400	-1.84851700	0.58625100
C	-3.33748500	1.26192700	0.50264900
C	-4.46658200	2.04747300	0.19368500

C	-5.23391300	2.53858300	1.25241500
C	-4.89802500	2.29360200	2.58076500
C	-3.76391200	1.54933300	2.87668700
C	-2.99867400	1.03590000	1.83391500
C	-1.36758300	2.11335400	-1.31165600
C	-1.10747100	2.47849300	-2.64825000
C	-0.43543600	3.68340000	-2.88579900
C	-0.04116400	4.52768400	-1.85400400
C	-0.31432000	4.17382300	-0.53839000
C	-0.97446900	2.97646200	-0.28078100
H	0.37992400	1.11737400	0.21267600
H	3.35517700	-1.53730000	1.67578500
H	4.80467300	-3.50473900	1.88280900
H	5.05863400	-5.08001000	-0.01690800
H	3.85840300	-4.64483300	-2.14476700
H	2.40874000	-2.65954700	-2.36236300
H	1.53394000	2.34884500	-1.26371000
H	3.11909200	4.16769200	-1.70825600
H	5.55901400	3.69839100	-1.82955100
H	6.39250800	1.39163300	-1.49296100
H	4.81096800	-0.43952100	-0.99829400
H	0.60385500	3.18532000	2.30276800
H	2.14395000	5.12873000	2.03689000
H	4.57754700	4.74433500	1.79050600
H	5.48449000	2.44079000	1.83016800
H	3.94988100	0.51135500	2.09884500
H	-0.97377900	-1.64338500	3.34150600
H	-2.08249400	-3.01507300	3.47689900
H	-2.70507100	-1.40493700	3.10391100
H	0.97803800	-2.88027000	2.35343500
H	1.34267100	-4.07070400	1.10294700
H	0.21592700	-4.47470100	2.40341700
H	0.11214700	-3.69872100	-2.29470800
H	-0.64541700	-5.16375100	-1.66708300
H	0.86303600	-4.57381700	-0.95444000
H	-3.45574600	-2.12127700	-2.29295500
H	-3.61554200	-3.87764800	-2.00894900
H	-2.21241100	-3.22951500	-2.86943100
H	-4.29312100	-1.23707900	1.47403400
H	-4.78317600	-2.73274000	0.66357900
H	-4.45866500	-1.27419100	-0.28688400
H	-6.11165400	3.13692900	1.02680100
H	-5.51558100	2.69593600	3.37690100
H	-3.46747900	1.36846400	3.90450100
H	-2.10878200	0.46611300	2.06136900
H	-0.23324500	3.97032200	-3.91323700
H	0.46138000	5.46246100	-2.08021000
H	-0.03026300	4.82670500	0.27992200
H	-1.21124100	2.71496400	0.74768600
C	-1.57550600	1.67475300	-3.83500700
H	-1.13760300	2.07206500	-4.75241800
H	-2.66365600	1.70915200	-3.91140800
H	-1.32008700	0.62087100	-3.74633300
C	-4.86220200	2.39452000	-1.21971800
H	-5.69461200	3.10013500	-1.21672000
H	-5.13707300	1.50376200	-1.78384600
H	-4.02677900	2.84996400	-1.75914500

Table S15. Cartesian coordinates of the H-bonded *cis*-isomer *cis*-**5b'** (*o*-tolyl-substituted phosphine oxide).

Atomic symbol	x	y	z
Ir	-0.69258800	1.04078200	-0.08666000
S	0.37984400	0.61653300	2.10278300
P	1.98561200	0.24457500	0.89892600
O	2.59080800	0.48581100	-2.54704900
C	0.97672500	-0.21873400	-0.51004800
S	1.64521000	-0.54938800	-2.11469700
P	-1.77178000	-0.99742100	0.28536500
O	0.53328800	-0.89186400	-2.99472400
C	3.05163800	1.70921400	0.73214100
O	-0.83090700	-2.20703200	0.22548600
C	4.02871200	1.79413400	-0.26385600
C	4.84727100	2.91473700	-0.33396400
C	4.70922000	3.94419500	0.59373500
C	3.75406700	3.84944200	1.59984800
C	2.92521200	2.73383900	1.67023700
C	3.04763900	-1.10683300	1.47743400
C	2.45050700	-2.36830400	1.59256800
C	3.21839200	-3.44830700	2.00605500
C	4.56728200	-3.27628700	2.30927200
C	5.15511400	-2.02090000	2.20286300
C	4.39708700	-0.93102800	1.78591800
C	2.56200500	-2.06092900	-1.83004500
C	1.83085300	-3.23038600	-1.63938100
C	2.51740600	-4.40486900	-1.36007100
C	3.90695100	-4.39589600	-1.25771800
C	4.62035000	-3.21558600	-1.43931000
C	3.94593600	-2.03418400	-1.73493500
C	-0.97911700	2.19174300	-1.91714400
C	-0.06543200	2.96973500	-1.09791300
C	-0.74800500	3.30190100	0.09777500
C	-2.08454800	2.75715600	0.04818200
C	-2.23356900	2.12135700	-1.23063100
C	-0.76095800	1.80605700	-3.34610400
C	1.28417300	3.44009500	-1.54744000
C	-0.23146300	4.11643400	1.24165500
C	-3.18296000	3.09000000	1.01044200
C	-3.52102300	1.70400100	-1.86045300
C	-2.64773200	-1.07631100	1.90845300
C	-3.17687800	-2.29865900	2.36909700
C	-3.83217400	-2.31131300	3.60235800
C	-3.97540000	-1.16097300	4.37094600
C	-3.44468600	0.03892700	3.91634000
C	-2.77980100	0.06641900	2.69552800
C	-3.07255900	-1.30676700	-1.00002800
C	-2.50024600	-1.71580000	-2.21172000
C	-3.27707000	-1.98497600	-3.33043100
C	-4.65963700	-1.86506100	-3.24377300
C	-5.23568900	-1.46505800	-2.04567500
C	-4.46926700	-1.16872100	-0.91214100
H	0.61512600	-1.22097800	-0.22633100
H	4.12568700	1.01214500	-1.00473600
H	5.58942300	2.98579100	-1.12067200
H	5.34901500	4.81755600	0.53315600
H	3.64836700	4.64438500	2.32959900
H	2.17019800	2.66043700	2.44465800
H	1.39440900	-2.50154000	1.36207700
H	2.76191500	-4.42824100	2.08698600
H	5.16088200	-4.12486500	2.63151400
H	6.20343700	-1.88676500	2.44439500

H	4.85756500	0.04704600	1.70253400
H	0.74596600	-3.20892200	-1.67988000
H	1.96511700	-5.32538400	-1.20971000
H	4.43650400	-5.31403400	-1.02788600
H	5.70093500	-3.21257700	-1.35420300
H	4.48291300	-1.10763200	-1.90305200
H	0.29859100	1.69950800	-3.57718900
H	-1.17825500	2.58286900	-3.99644300
H	-1.24102100	0.85636000	-3.58007600
H	1.85282100	2.63974900	-2.02227100
H	1.87780800	3.83084400	-0.72030100
H	1.15998200	4.24350900	-2.28088500
H	-0.31427100	3.57233900	2.18563600
H	-0.81636200	5.03652200	1.33192000
H	0.81253000	4.39133500	1.09894500
H	-3.93820900	2.30461900	1.05366900
H	-3.68089800	4.01797800	0.71025700
H	-2.79772400	3.23564200	2.02163400
H	-3.39687700	0.86351800	-2.54260600
H	-3.90429500	2.55376200	-2.43605000
H	-4.27366200	1.43720600	-1.12044200
H	-4.24672700	-3.24768500	3.96347800
H	-4.49422100	-1.20702100	5.32242700
H	-3.53860300	0.94362600	4.50726000
H	-2.35918200	0.99909900	2.33925700
H	-2.80245500	-2.28510200	-4.25811500
H	-5.28735300	-2.07506900	-4.10312400
H	-6.31504700	-1.36214200	-1.98422400
H	-1.42182700	-1.80300900	-2.28316000
C	-3.09806000	-3.57563000	1.57107600
H	-3.60080900	-4.38613000	2.10086900
H	-2.06175500	-3.84768500	1.37509600
H	-3.57203900	-3.46056400	0.59171500
C	-5.21228400	-0.68935400	0.31362300
H	-6.21932800	-0.37278400	0.03587900
H	-4.71516100	0.14816500	0.80302300
H	-5.30556700	-1.47413200	1.06819800

Table S16. Cartesian coordinates of the ruthenium complex *cis*-**4**.

Atomic symbol	x	y	z
Ru	1.32984500	-0.99753100	0.27084200
S	0.51333800	-0.25146900	-2.02747600
P	-1.21757300	-0.39798800	-0.98517000
O	-0.77152000	0.81753600	3.08106700
C	-0.55611400	0.01707600	0.62913600
S	-1.44004700	-0.09113600	2.16062600
P	2.36846800	1.01270000	0.71473000
O	-1.64989600	-1.48461400	2.57069300
C	-1.95283600	-2.04954300	-1.18670100
O	2.72656800	1.20732600	2.17406800
C	-2.06994200	-2.51177000	-2.50179300
C	-2.62518100	-3.75943500	-2.75377700
C	-3.05876100	-4.55543800	-1.69555700
C	-2.93813700	-4.09821000	-0.38857900
C	-2.38801100	-2.84437200	-0.12732700
C	-2.47324600	0.78887000	-1.55488200
C	-2.05653700	2.11189700	-1.73130800

C	-2.97737900	3.08163200	-2.10388100
C	-4.31195300	2.73446400	-2.30358400
C	-4.72745900	1.42020700	-2.11861200
C	-3.81132200	0.44278500	-1.74005400
C	-3.06362500	0.57910700	1.80850400
C	-4.17260300	-0.25557100	1.82036300
C	-5.42217700	0.28381200	1.52289100
C	-5.54096900	1.63328800	1.21157900
C	-4.41626100	2.45732300	1.19928100
C	-3.16759900	1.93350300	1.50346300
C	1.60507800	-1.58822000	3.58161800
C	1.82016000	-2.09930600	2.18540900
C	0.86121800	-2.90718900	1.50618700
C	1.06544500	-3.35316000	0.19414200
C	2.23805400	-2.96792700	-0.51556500
C	2.40522500	-3.35508500	-1.95711600
C	3.24045400	-2.24286200	0.16001600
C	3.01344700	-1.79379500	1.48576400
C	3.93591800	1.06813900	-0.26663800
C	5.08119200	1.48662400	0.41201800
C	6.31409500	1.51570200	-0.23662600
C	6.41262600	1.12740700	-1.56829000
C	5.27461000	0.70332500	-2.25167800
C	4.04570700	0.66671600	-1.60114800
C	1.48513000	2.53360400	0.14614500
C	0.69667800	3.18533400	1.10097500
C	-0.00749100	4.33845700	0.76155000
C	0.08680300	4.86273200	-0.52552200
C	0.88295000	4.22700800	-1.47466400
C	1.57208900	3.06257800	-1.14259700
H	-0.40489100	1.09638100	0.53860500
H	-1.71212600	-1.90081600	-3.32465400
H	-2.71302800	-4.11326900	-3.77460000
H	-3.48605500	-5.53238300	-1.89215900
H	-3.26674400	-4.71817100	0.43799500
H	-2.27684900	-2.50857500	0.89589500
H	-1.01431200	2.38182600	-1.58440100
H	-2.64776100	4.10588400	-2.23926000
H	-5.03029700	3.49116400	-2.59988200
H	-5.76833900	1.15249000	-2.26239100
H	-4.14130300	-0.57937000	-1.58695700
H	-4.05638200	-1.30073200	2.08151400
H	-6.30040000	-0.35151000	1.53941500
H	-6.51440900	2.04905000	0.97557900
H	-4.51243300	3.50743700	0.94848000
H	-2.28224600	2.56266800	1.50628100
H	2.21396200	-2.16014700	4.28778400
H	0.55901800	-1.67872400	3.87223500
H	1.89598000	-0.53607400	3.63198300
H	-0.07626400	-3.11810700	2.00679600
H	0.29299600	-3.91816000	-0.31558100
H	3.10763700	-2.68936700	-2.46044300
H	4.14136200	-1.94293700	-0.36213100
H	3.74027300	-1.14767200	1.96639300
H	4.98701100	1.77846800	1.45315200
H	7.19874000	1.84039200	0.30061000
H	5.34713900	0.39556200	-3.28950300
H	3.16956500	0.31055700	-2.13449400
H	0.65004600	2.78037200	2.10848300
H	-0.61045500	4.84114200	1.51094600
H	0.97070700	4.63765100	-2.47498500
H	2.18945400	2.57753800	-1.89036500

H	-0.44527200	5.77258200	-0.78330500
H	7.37229100	1.15000000	-2.07312900
H	2.78750600	-4.37712300	-2.02874500
H	1.44974300	-3.30587600	-2.48149300

Table S17. Cartesian coordinates of the ruthenium complex *cis*-**4'** (H-bond).

Atomic symbol	x	y	z
Ru	0.99931300	1.03614700	-0.35698000
S	-0.00757800	1.02459400	1.93879000
P	-1.59574400	0.38828400	0.83762200
O	-0.29094400	-1.52158400	-2.77760100
C	-0.66552400	-0.29830800	-0.53188700
S	-1.31259900	-0.71828500	-2.11162800
P	2.05840700	-0.85918200	0.48369500
O	-1.83543200	0.45087000	-2.83256000
C	-2.71781100	1.79359700	0.53926100
O	1.16596800	-2.06363300	0.77664500
C	-3.03029700	2.56222400	1.66701000
C	-3.87536000	3.65717100	1.55294500
C	-4.40435100	4.00263800	0.31082700
C	-4.09375700	3.24213900	-0.80957400
C	-3.25670900	2.13198600	-0.70100300
C	-2.57472100	-0.89775200	1.66445200
C	-1.86315500	-1.97519500	2.20629500
C	-2.56222300	-3.02488800	2.78863200
C	-3.95526700	-3.00740600	2.82267200
C	-4.65733800	-1.94302400	2.26762600
C	-3.96891300	-0.88209200	1.68630700
C	-2.71234900	-1.76397800	-1.72433400
C	-3.99508400	-1.33903900	-2.04133800
C	-5.07634800	-2.13193900	-1.66412500
C	-4.86052700	-3.31785500	-0.97179500
C	-3.56533800	-3.72911400	-0.66008800
C	-2.47834800	-2.95406500	-1.03985000
C	3.09424000	0.65824600	-3.15364300
C	2.28538500	1.51160400	-2.22145500
C	0.93455100	1.77192700	-2.49995600
C	0.17894300	2.72374300	-1.75153500
C	0.73995500	3.35605700	-0.64365600
C	-0.05754900	4.29470500	0.21538900
C	2.08931500	3.02520500	-0.28645900
C	2.84815100	2.13666500	-1.06655700
C	3.39673600	-1.42966200	-0.64043600
C	3.01178300	-2.25849700	-1.69782500
C	3.95711200	-2.71436100	-2.60984700
C	5.29444000	-2.34751400	-2.47513300
C	5.68565900	-1.53182000	-1.41755400
C	4.74010700	-1.07624100	-0.50089500
C	3.00108100	-0.48454400	2.02315800
C	3.13340300	-1.52005000	2.94941100
C	3.85676300	-1.32627400	4.12204700
C	4.45321000	-0.09566300	4.38132300
C	4.31821200	0.94424900	3.46648500
C	3.59064200	0.74909100	2.29592600
H	-0.33285500	-1.26859600	-0.13433400
H	-2.59650000	2.31306900	2.63014600
H	-4.11230000	4.24730500	2.43077700
H	-5.05525700	4.86505200	0.21958100
H	-4.49871900	3.50970000	-1.77910400

H	-3.00502200	1.56023600	-1.58445700
H	-0.77577900	-1.99550200	2.14853600
H	-2.01698500	-3.86051300	3.21263400
H	-4.49519100	-3.82998500	3.27927500
H	-5.74150300	-1.93620000	2.28407200
H	-4.51635900	-0.05328600	1.24936300
H	-4.13510800	-0.41160400	-2.58404200
H	-6.08482500	-1.81945200	-1.91000900
H	-5.70505700	-3.92685800	-0.66868200
H	-3.40280300	-4.65008600	-0.11241500
H	-1.46328700	-3.25819000	-0.80038600
H	3.41233000	1.26863700	-4.00424000
H	2.49500200	-0.17012600	-3.53264000
H	3.98398300	0.25249800	-2.67476800
H	0.45549000	1.25334400	-3.32168100
H	-0.86011200	2.88948000	-2.00926000
H	-0.01872600	3.97809400	1.26028900
H	2.52055400	3.47357600	0.60158500
H	3.87079800	1.90330300	-0.78856900
H	1.96628000	-2.53097900	-1.80733800
H	3.64952500	-3.35472400	-3.42953300
H	6.72873500	-1.25849900	-1.29880000
H	5.05775200	-0.46041400	0.33497200
H	2.65387300	-2.47001600	2.73837300
H	3.95283200	-2.13619000	4.83720000
H	4.77246400	1.90835400	3.66900000
H	3.47280000	1.56856000	1.59497400
H	5.01567300	0.05521200	5.29625800
H	6.03101100	-2.70443700	-3.18678100
H	0.34607900	5.30847000	0.14814300
H	-1.10472300	4.31579400	-0.09215900

4.2 Mechanistic Studies

Table S18. Calculated energies [in kJ/mol] of the optimized structures and transition states [M062x//6-311+g(d)/LANL2TZ(f)]; energy differences, reaction enthalpies and activation energies are given relative to the Iridium complex 2' and the respective diphenylphosphine oxide.

Compound	SCF	Enthalpy	Free energy	ΔH	ΔG
Iridium complex 2'	-4578874.748	-4578249.006	-4578420.734	0.00	0.00
Diphenyl phosphine oxid	-2311416.030	-2310862.805	-2311002.356	0.00	0.00
Diphenyl phosphinous acid	-2311416.116	-2310860.369	-2311003.275	0.00	0.00
Path *via* Diphenyl phosphine oxid					
TS1	-6890246.648	-6889069.364	-6889314.822	42.45	108.27
Int1	-6890319.030	-6889136.617	-6889381.746	-24.81	41.34
TS2	-6890308.604	-6889131.710	-6889373.983	-19.90	49.11
5_{Me}	-6890483.160	-6889293.742	-6889533.873	-181.93	-110.78
Path *via* Diphenyl phosphinous acid					
TS1'	-6890333.182	-6889149.103	-6889402.168	-39.73	21.84
Int1'	-6890435.678	-6889249.505	-6889495.328	-140.13	-71.32
TS2'	-6890428.399	-6889252.987	-6889495.690	-143.61	-71.68
$5'_{Me}$	-6890498.303	-6889309.264	-6889552.766	-199.89	-128.76

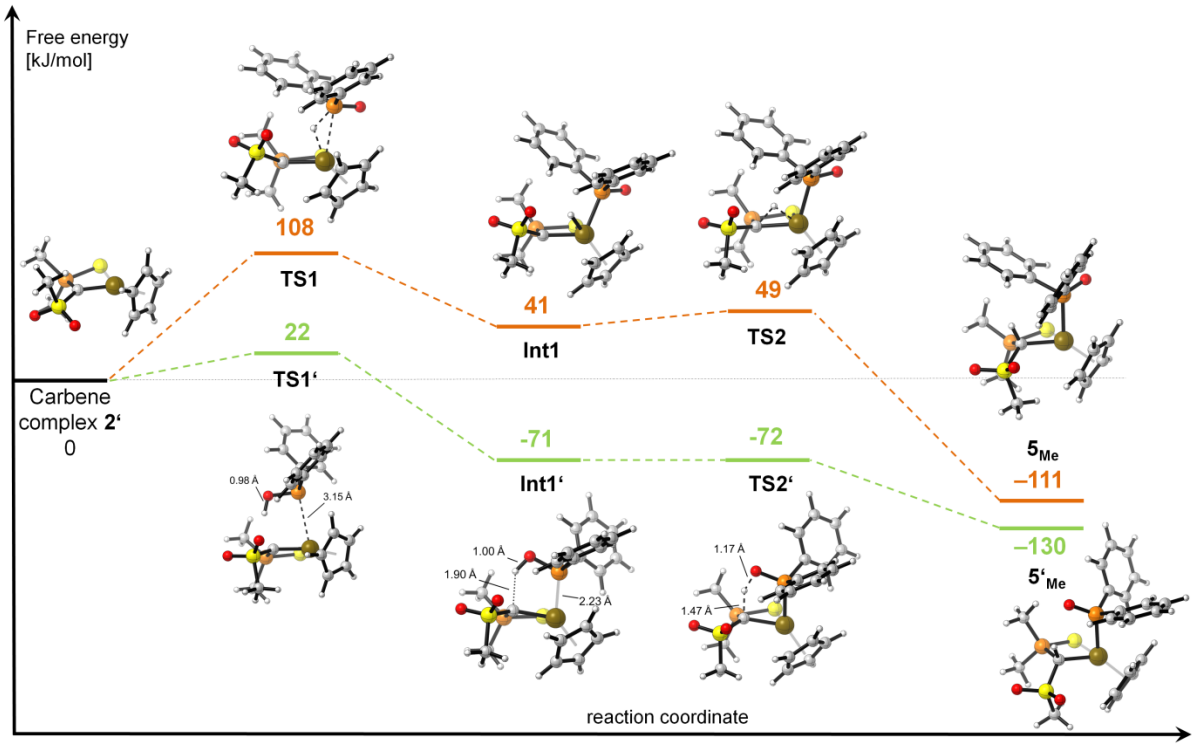


Figure S24. Reaction profile and structures of the optimized intermediates and transition states for the oxidative addition of the P–H bond to iridium (orange pathway) and for coordination of the phosphinous acid tautomer (green pathway) [M062X//6-311+G(d)/LANL2TZ(f)].

Table S19. Cartesian Coordinates of the iridium complex 2'.

Atomic symbol	x	y	z
Ir	0.94863900	-0.17471600	0.05247700
S	-0.00199300	-2.44209000	0.20658100
S	-1.76725800	1.68576900	-0.16186800
P	-1.72392100	-1.34466100	-0.02265600
O	-3.08394100	1.39698000	-0.75326500
O	-0.88995000	2.67173800	-0.79659800
C	-0.92960800	0.19294700	0.05892300
C	3.17463500	-0.41119800	0.06601800
C	2.72751500	0.47324300	1.08469300
C	2.04130800	1.58461900	0.45766900
C	2.01760400	1.33638000	-0.94498600
C	2.70016500	0.08077700	-1.17944200
H	3.67074500	-1.35612400	0.22485900
H	2.87933900	0.34336200	2.14509300
H	1.60499600	2.43751000	0.95361700
H	1.52731200	1.95495700	-1.68087300
H	2.81871600	-0.40038900	-2.13784500
C	-2.96325200	-1.66543000	1.26380000
H	-3.79863900	-0.97501400	1.12225200
H	-3.32554100	-2.69281100	1.19859300
H	-2.50542400	-1.50320800	2.23937400

C	-2.56685700	-1.68519100	-1.58873500
H	-2.95777200	-2.70397400	-1.59637900
H	-3.37266300	-0.95890200	-1.70859100
H	-1.84515600	-1.56140300	-2.39560900
C	-2.08905500	2.30928900	1.48836000
H	-2.61025600	3.25910100	1.36976200
H	-1.13524800	2.44842300	1.99326200
H	-2.71236200	1.59033100	2.01727800

Table S20. Cartesian Coordinates of TS1.

Atomic symbol	x	y	z
S	1.55688100	0.15384300	-2.09507400
S	1.54184700	-0.18732100	2.27902500
P	2.69572900	-0.40100200	-0.45306800
O	2.36071600	-1.40154000	2.46857400
O	0.12627000	-0.23495700	2.71035700
C	0.75194800	3.35545600	-0.55780200
C	0.10222700	3.12568200	0.70776800
C	-1.21808800	2.67197000	0.45282500
C	-1.43181500	2.68920800	-0.97950300
C	-0.23562600	3.11194900	-1.59110600
H	1.76056200	3.70738900	-0.70767800
H	0.56499000	3.20363700	1.67863300
H	-1.93678500	2.35841200	1.19518300
H	-2.32467800	2.36029600	-1.49091200
H	-0.05315400	3.15743000	-2.65407400
C	4.36945300	0.30844800	-0.58567300
H	4.93416700	0.05075000	0.31422900
H	4.88944800	-0.07756100	-1.46479000
H	4.27870700	1.39192900	-0.65909500
C	3.00422900	-2.18917400	-0.41661100
H	3.64759000	-2.45995200	-1.25666300
H	3.47405200	-2.44893400	0.53239300
H	2.05391300	-2.71345200	-0.49782400
C	1.67036400	0.34804100	0.69025400
H	-0.47386400	-0.16731100	0.05539700
Ir	0.22998800	1.31620600	-0.44056900
C	2.28080900	1.02096800	3.38802000
H	2.18348300	0.63145900	4.40106700
H	1.74524600	1.96302200	3.29001000
H	3.32773000	1.13616100	3.11376700
P	-1.46485600	-0.80594200	-0.96105300
C	-0.75924000	-2.43541900	-0.63679000
C	-0.42403000	-2.83713800	0.65853400
C	-0.51628800	-3.26745800	-1.73009300
C	0.13298800	-4.09490900	0.85875600
H	-0.56593900	-2.17258900	1.50531300
C	0.03992600	-4.52501000	-1.51872200
H	-0.75922000	-2.91718100	-2.72736000
C	0.35762700	-4.93819900	-0.22688800
H	0.41129100	-4.40136600	1.86006300
H	0.23033100	-5.17928200	-2.36188100

H	0.79654100	-5.91690300	-0.06679000
C	-2.91671300	-0.50322800	0.07602800
C	-2.81997200	-0.30950600	1.45650400
C	-4.15619600	-0.45909200	-0.56453000
C	-3.97919700	-0.09138600	2.19383800
H	-1.85062300	-0.30454900	1.94991300
C	-5.30814700	-0.23594500	0.18262400
H	-4.20500300	-0.59224400	-1.64006500
C	-5.21906000	-0.05625900	1.55978500
H	-3.91092000	0.05640600	3.26566400
H	-6.27311200	-0.20059300	-0.31019200
H	-6.11813200	0.11666800	2.14104800
O	-1.72818900	-0.54146900	-2.40096400

Table S21. Cartesian Coordinates of Int1.

Atomic symbol	x	y	z
S	1.37537800	-0.09184000	-2.12276400
S	1.90118400	0.07483600	2.22409700
P	2.68767100	-0.50570900	-0.56717600
O	3.00236900	-0.88653800	2.41937000
O	0.59276300	-0.19790500	2.85170700
C	0.41274100	3.15404300	-1.53060500
C	0.68170900	3.36414700	-0.16884400
C	-0.47123700	2.95518900	0.57855200
C	-1.49179900	2.57577500	-0.35976800
C	-0.92672700	2.64817200	-1.66508800
H	1.11644000	3.27658400	-2.34063000
H	1.63089500	3.66075400	0.25132900
H	-0.59163500	2.99827200	1.65072400
H	-2.49737400	2.26955300	-0.11128000
H	-1.42311700	2.37554300	-2.58431200
C	4.35523600	0.14932000	-0.87896700
H	4.95765000	-0.02409900	0.01671400
H	4.82168900	-0.34888000	-1.73088700
H	4.28267300	1.21962800	-1.06802500
C	2.95475900	-2.29138000	-0.40363800
H	3.53967800	-2.64887500	-1.25413100
H	3.48422000	-2.47731700	0.53204200
H	1.99159700	-2.79778300	-0.38456100
C	1.75669500	0.37277500	0.56399200
H	-0.31666300	0.28684700	0.84069500
Ir	0.08891700	1.07290200	-0.43367300
C	2.44990300	1.59087400	3.01368500
H	2.52060000	1.39397100	4.08298300
H	1.71124000	2.36697700	2.81834800
H	3.42015900	1.85775100	2.59962900
P	-1.44490300	-0.58291300	-0.92323400
C	-0.76255900	-2.22228200	-0.50643700
C	-0.40518900	-2.58977200	0.79255900
C	-0.65245300	-3.14157000	-1.54975100
C	0.04325000	-3.88204100	1.04585600
H	-0.44926800	-1.88079700	1.61180200

C	-0.19278800	-4.43018600	-1.29172000
H	-0.93354600	-2.83502000	-2.55154300
C	0.14805300	-4.80260900	0.00584600
H	0.32432500	-4.16085900	2.05501800
H	-0.10672000	-5.14432600	-2.10319600
H	0.50126400	-5.80823800	0.20635900
C	-2.86666400	-0.35783300	0.21852400
C	-2.75836500	-0.19024000	1.60347100
C	-4.12711500	-0.35065000	-0.38050300
C	-3.90439700	-0.02734000	2.37365200
H	-1.79140100	-0.17690100	2.09968600
C	-5.27109200	-0.18068100	0.39575700
H	-4.19488900	-0.47425600	-1.45598800
C	-5.16108300	-0.01994800	1.77194400
H	-3.81401900	0.09612800	3.44706700
H	-6.24687400	-0.17435900	-0.07720600
H	-6.05103500	0.11183400	2.37740900
O	-1.92816500	-0.53015400	-2.34251200

Table S22. Cartesian Coordinates of TS2.

Atomic symbol	x	y	z
S	-1.43457300	0.15423600	-2.12853900
S	-1.87924600	-0.14905000	2.27333800
P	-2.65799400	0.57560500	-0.51020600
O	-3.01240300	0.76563000	2.49459900
O	-0.59591900	0.10066900	2.95203500
C	-0.62441500	-3.33555200	-0.14113800
C	0.57444300	-2.89032800	0.52191800
C	1.52344000	-2.53856500	-0.48715400
C	0.87265800	-2.64388900	-1.75540600
C	-0.44612800	-3.17232800	-1.52106700
H	-1.54009400	-3.63523700	0.34655200
H	0.76226700	-2.89518800	1.58546200
H	2.53840500	-2.21254000	-0.31449600
H	1.31408900	-2.40986500	-2.71205000
H	-1.19892900	-3.32779300	-2.27971400
C	-4.33304800	-0.10626200	-0.69068000
H	-4.86731600	0.06276100	0.24785800
H	-4.86781400	0.38181900	-1.50751000
H	-4.25704300	-1.17552100	-0.88505300
C	-2.92615200	2.35601700	-0.31497200
H	-3.59167000	2.71469300	-1.10325400
H	-3.37171900	2.52727700	0.66673900
H	-1.97023400	2.87267000	-0.38115000
C	-1.67193100	-0.28253900	0.59935400
H	-0.04611300	-0.03822900	0.67443400
Ir	-0.08907600	-1.06448700	-0.53354000
C	-2.41496100	-1.73826100	2.91332500
H	-2.54929500	-1.62599600	3.98875200
H	-1.63832800	-2.47241600	2.70368300
H	-3.35265900	-2.00359500	2.42856700
P	1.45941000	0.58917600	-0.94194600

C	0.78847400	2.23355900	-0.50265400
C	0.46521800	2.59663200	0.80716200
C	0.65641100	3.16092100	-1.53587900
C	0.02642800	3.88816000	1.08033400
H	0.54521800	1.88833200	1.62584600
C	0.20786600	4.44968000	-1.25883900
H	0.91656300	2.86121700	-2.54542000
C	-0.10071100	4.81534600	0.04875800
H	-0.22294500	4.16373100	2.09868100
H	0.10744800	5.17007900	-2.06311000
H	-0.44332700	5.82151000	0.26431900
C	2.82397200	0.33247400	0.25783500
C	2.63532900	0.05125900	1.61522400
C	4.11753000	0.41502300	-0.25878700
C	3.73749900	-0.13000300	2.44353600
H	1.63892300	-0.03690800	2.04009700
C	5.21699800	0.22558400	0.57492500
H	4.24677900	0.61920000	-1.31642400
C	5.02810400	-0.04532400	1.92539600
H	3.58623000	-0.34030000	3.49648600
H	6.21985400	0.28856200	0.16719700
H	5.88363400	-0.19294700	2.57526000
O	1.99265400	0.57818500	-2.34423700

Table S23. Cartesian Coordinates of 5_{Me}.

Atomic symbol	x	y	z
S	1.48306600	-0.99749300	-1.98208400
S	1.79077200	0.13093300	2.36707700
P	2.05195900	-1.59013500	-0.12311400
O	2.27717000	-1.06224100	3.06792300
O	0.81049600	0.99462100	3.02157100
C	1.91248900	2.69456400	-0.95926400
C	0.99602800	2.87931500	0.11949900
C	-0.33544500	2.86224900	-0.39878900
C	-0.24891500	2.65044100	-1.82088400
C	1.12389100	2.51168000	-2.14331600
H	2.99071100	2.69995300	-0.91430900
H	1.23593600	3.00788600	1.16566500
H	-1.23821400	3.00644800	0.17404300
H	-1.07957300	2.52939900	-2.50010900
H	1.51154500	2.27929300	-3.12433900
C	3.83968300	-1.38770500	0.11883800
H	4.11248100	-1.62194800	1.14950500
H	4.33702300	-2.08250900	-0.56061700
H	4.13857200	-0.37498700	-0.14844300
C	1.71814500	-3.30816600	0.32452900
H	2.32647600	-3.97684600	-0.28722200
H	1.96697400	-3.43390900	1.38154800
H	0.66315800	-3.52937200	0.16449500
C	1.05748100	-0.41745300	0.82970900
H	0.21678800	-0.98574000	1.24159000
Ir	0.52477900	0.89022900	-0.72948900

C	3.23158500	1.15351500	2.01167700
H	3.20824600	1.95549500	2.74812200
H	3.15906300	1.55698400	1.00547900
H	4.12455500	0.54750900	2.13569500
P	-1.53231000	-0.10962600	-0.92814100
C	-1.59137200	-1.89356200	-0.44622900
C	-1.80566400	-2.35205100	0.85652500
C	-1.49329400	-2.82327700	-1.48573100
C	-1.89526000	-3.71737900	1.12060600
H	-1.93960700	-1.64599900	1.67086300
C	-1.58652700	-4.18639600	-1.22293400
H	-1.37043700	-2.46076400	-2.50022700
C	-1.78308300	-4.63614500	0.08133300
H	-2.06818700	-4.05936100	2.13497600
H	-1.51814500	-4.89859000	-2.03803900
H	-1.86329200	-5.69844700	0.28461500
C	-2.68332300	0.62456400	0.30292800
C	-2.29819200	0.99089100	1.59545300
C	-4.00844000	0.79828600	-0.09723500
C	-3.23739200	1.50477000	2.48413600
H	-1.26255800	0.90310500	1.91273700
C	-4.94397100	1.32230500	0.79122500
H	-4.28769300	0.52848100	-1.11064300
C	-4.56110900	1.67054400	2.08276700
H	-2.93026100	1.78406600	3.48604400
H	-5.97172500	1.46051600	0.47343200
H	-5.29048700	2.07782000	2.77449100
O	-2.11258600	0.01753500	-2.31559300

Table S24. Cartesian Coordinates of TS1'.

Atomic symbol	x	y	z
S	-1.26059300	-2.20319300	1.36402300
S	-2.32488700	0.46414900	-2.04711000
P	-1.94613100	-2.09609500	-0.57523400
O	-2.56779800	-0.47117300	-3.15881600
O	-1.57712600	1.70232700	-2.30005400
C	-2.41625300	1.60265500	1.92059300
C	-1.52314200	2.31383600	1.03944700
C	-0.20095400	2.09960900	1.53041400
C	-0.26666800	1.34725800	2.75823000
C	-1.62380900	1.03645300	2.99253700
H	-3.49138800	1.54380700	1.84078900
H	-1.77490600	2.83617600	0.12782400
H	0.70385600	2.44223800	1.04923000
H	0.57826600	1.01882700	3.34257900
H	-2.00827800	0.41463300	3.78673600
C	-3.70044000	-2.56037200	-0.68305700
H	-4.05517400	-2.35910400	-1.69698300
H	-3.82039100	-3.62088100	-0.45534200
H	-4.26495400	-1.97335300	0.04158600
C	-1.10574600	-3.22368000	-1.71639300
H	-1.33891000	-4.26161700	-1.47270500

H	-1.44846400	-2.98581300	-2.72655800
H	-0.02996400	-3.05895700	-1.65176000
C	-1.58916000	-0.41018200	-0.77212900
H	0.20695500	-0.65110700	-1.64794900
Ir	-1.11765800	0.23105100	1.05481000
C	-3.95386500	1.01641900	-1.51744500
H	-4.38381400	1.56365000	-2.35620600
H	-3.83854900	1.67004200	-0.65497700
H	-4.56333400	0.14789300	-1.27501600
P	1.74624900	-0.23609300	-0.18263400
C	2.45910900	1.39517900	-0.62466600
C	3.63669900	1.87365700	-0.04611300
C	1.70126000	2.23882800	-1.44551600
C	4.05873900	3.17766800	-0.29070900
H	4.23640600	1.22268500	0.58369600
C	2.13108300	3.53919500	-1.69035200
H	0.77399000	1.88681700	-1.89096600
C	3.30667500	4.01237000	-1.11201700
H	4.98013600	3.53820600	0.15359600
H	1.54264000	4.18256000	-2.33529000
H	3.63826900	5.02666800	-1.30484000
C	3.24904700	-1.26327000	-0.03835800
C	3.65407800	-1.70081300	1.22147900
C	4.00973100	-1.59365600	-1.16368700
C	4.82187600	-2.44786700	1.36403200
H	3.04874500	-1.46538600	2.09210600
C	5.16621900	-2.34914200	-1.02178100
H	3.68336300	-1.25941300	-2.14276000
C	5.57582900	-2.77176500	0.24257800
H	5.13382100	-2.78476400	2.34631900
H	5.75396000	-2.60699600	-1.89589900
H	6.48154900	-3.35849900	0.34970600
O	1.18741200	-0.74190800	-1.64267600

.

Table S25. Cartesian Coordinates of Int1'.

Atomic symbol	x	y	z
S	-0.74588200	-2.40518800	0.56527200
S	-2.69617300	1.09522400	-1.34409100
P	-2.24120800	-1.74131200	-0.70147800
O	-3.48962000	0.47988200	-2.42650300
O	-1.91614900	2.31114100	-1.62235400
C	-0.86823600	0.05398200	3.14575400
C	-1.74286700	0.92400900	2.45375000
C	-0.93316300	1.90196400	1.76633300
C	0.43091100	1.62739600	2.08829800
C	0.47937100	0.47770100	2.94143400
H	-1.16969700	-0.83086400	3.68748800
H	-2.81801800	0.84039200	2.42352400
H	-1.27320400	2.71075100	1.13573800
H	1.28042100	2.19266700	1.73301300
H	1.36360000	0.03882100	3.37581300
C	-3.89081400	-2.08503800	-0.00320000

H	-4.64830800	-1.64415800	-0.65649500
H	-4.05589000	-3.16130800	0.07288800
H	-3.95020800	-1.64275200	0.99198900
C	-2.26002000	-2.59058300	-2.30279300
H	-2.56644500	-3.63223300	-2.19128400
H	-2.95802800	-2.05383600	-2.94938800
H	-1.25894500	-2.54514500	-2.73213100
C	-1.69378900	-0.11004600	-0.71124100
H	-0.34639300	-0.20790100	-2.05160000
Ir	-0.38669200	-0.01767500	0.91324100
C	-3.94551900	1.64646300	-0.16161000
H	-4.60404400	2.31981600	-0.70971300
H	-3.46656200	2.17998500	0.65595800
H	-4.50282200	0.78217300	0.19740700
P	1.21427800	-0.06525400	-0.63728500
C	2.10642400	1.51776900	-0.72601400
C	3.42527000	1.66520500	-0.29963100
C	1.37566500	2.63184500	-1.15640000
C	4.01730000	2.92725600	-0.30081400
H	3.99407400	0.80156000	0.02959700
C	1.97714200	3.88402500	-1.16305800
H	0.34027200	2.52007800	-1.47335000
C	3.29504700	4.03380700	-0.73197300
H	5.04379600	3.04105600	0.02930100
H	1.41437200	4.74582400	-1.50366700
H	3.75795000	5.01447100	-0.73571900
C	2.52194800	-1.31608100	-0.50206100
C	2.81207300	-1.92402400	0.71716700
C	3.27602300	-1.62968600	-1.63513000
C	3.86136500	-2.83348700	0.80967000
H	2.20401600	-1.69661700	1.58686700
C	4.31963700	-2.54257700	-1.54069900
H	3.03568400	-1.16440100	-2.58516100
C	4.61524600	-3.14072600	-0.31805500
H	4.08251200	-3.30976400	1.75814900
H	4.90169900	-2.78962300	-2.42131800
H	5.42955400	-3.85325600	-0.24722800
O	0.64934700	-0.28501000	-2.12814800

Table S26. Cartesian Coordinates of TS2'.

Atomic symbol	x	y	z
S	-0.70423700	-2.39600700	0.63165100
S	-2.73106200	1.04401300	-1.36136700
P	-2.17642000	-1.78854500	-0.67409800
O	-3.52662100	0.39212900	-2.41621000
O	-2.00794700	2.28357100	-1.66194600
C	-0.81237400	0.12874600	3.15277100
C	-1.72870700	0.96079000	2.46568700
C	-0.95865200	1.93826800	1.73122400
C	0.41961500	1.70540800	2.02129800
C	0.51861300	0.57844200	2.90073900
H	-1.07687300	-0.74829600	3.72571500

H	-2.80264500	0.86088100	2.48345400
H	-1.33076700	2.72455800	1.09033300
H	1.24507500	2.28014700	1.62708900
H	1.42447900	0.17084100	3.32057800
C	-3.83508100	-2.07996000	0.01466000
H	-4.58247500	-1.65133700	-0.65755100
H	-4.00532800	-3.15324900	0.11579300
H	-3.89786100	-1.61849500	1.00078100
C	-2.16439200	-2.66064400	-2.25851100
H	-2.41627600	-3.71443100	-2.12861800
H	-2.88948600	-2.16989300	-2.91187000
H	-1.16667500	-2.56538900	-2.68817600
C	-1.62953100	-0.13288400	-0.76872900
H	-0.57637500	-0.21599200	-1.78489900
Ir	-0.39117200	0.01163500	0.92153900
C	-3.94482300	1.51874100	-0.11693100
H	-4.67233000	2.13430400	-0.64560900
H	-3.46304200	2.10058100	0.66388900
H	-4.42716000	0.62923000	0.28413000
P	1.21128300	-0.07002500	-0.67133500
C	2.10083100	1.51523000	-0.77106700
C	3.40930000	1.68485900	-0.32215700
C	1.37186900	2.61303700	-1.24355400
C	3.99103700	2.95175600	-0.34028400
H	3.97873500	0.83323300	0.03656700
C	1.96079500	3.87105300	-1.26425100
H	0.34650200	2.48173300	-1.58316800
C	3.26810800	4.04255800	-0.80931800
H	5.01024400	3.08202200	0.00622800
H	1.39804400	4.72007600	-1.63583000
H	3.72261900	5.02703900	-0.82537900
C	2.51915900	-1.31798700	-0.49120400
C	2.85906600	-1.84857800	0.75124600
C	3.21830100	-1.71508600	-1.63261000
C	3.90458900	-2.76064500	0.85788600
H	2.29159500	-1.55927100	1.63018100
C	4.25949100	-2.63001600	-1.52436000
H	2.93449900	-1.31147700	-2.59890200
C	4.60559300	-3.14914800	-0.27943500
H	4.16445500	-3.17628700	1.82501300
H	4.79948200	-2.94069500	-2.41173700
H	5.41705400	-3.86378600	-0.19734900
O	0.55203500	-0.30383600	-2.08194300

Table S27. Cartesian Coordinates of 5'$_{Me}$.

Atomic symbol	x	y	z
S	0.79922000	2.18602800	0.85292300
S	3.29895800	-0.86532200	-0.85776200
P	1.97699800	1.85051600	-0.78301700
O	4.17431000	-0.23169000	-1.84812500
O	2.99692500	-2.28651400	-0.99425300
C	1.33203600	-1.14569400	2.61619500

C	1.17244900	-2.12912200	1.59986400
C	-0.21510800	-2.24991400	1.28544100
C	-0.93063400	-1.33163600	2.13453900
C	0.02479200	-0.63708700	2.91776300
H	2.25399400	-0.82949300	3.07793600
H	1.95183400	-2.68254800	1.09636100
H	-0.65127500	-2.93407700	0.57365900
H	-2.00058900	-1.19428300	2.15766000
H	-0.19369400	0.15309200	3.62157600
C	3.66565000	2.48270500	-0.53390000
H	4.30126700	2.18055400	-1.36610600
H	3.58834800	3.57156600	-0.49040300
H	4.08909300	2.13235200	0.40466400
C	1.44950500	2.64802200	-2.31446000
H	1.45040000	3.72971000	-2.16790700
H	2.16262900	2.37883100	-3.09802500
H	0.45473000	2.28011600	-2.56788100
C	1.75851500	0.04148900	-0.83890300
H	1.32997300	-0.20774000	-1.81596300
Ir	0.39187900	-0.22430600	0.74516100
C	4.06797400	-0.61859200	0.75999700
H	3.99159300	-1.54865900	1.31867200
H	3.55848000	0.18251100	1.29319900
H	5.10999000	-0.36652200	0.57112900
P	-1.21676200	0.20122000	-0.82406600
C	-2.23551600	-1.31840000	-1.00201400
C	-3.37483100	-1.58067300	-0.24143300
C	-1.79030900	-2.27235700	-1.92028300
C	-4.04602800	-2.79404100	-0.37668000
H	-3.75475200	-0.82963000	0.44520900
C	-2.46109400	-3.48278000	-2.05587200
H	-0.91860300	-2.05533800	-2.52980300
C	-3.58630300	-3.74835400	-1.27837100
H	-4.93406000	-2.98871800	0.21473600
H	-2.10909700	-4.21799200	-2.77110400
H	-4.10975700	-4.69207900	-1.38431000
C	-2.45210200	1.42496600	-0.23281700
C	-2.67503600	1.72423300	1.11038900
C	-3.22782500	2.05115900	-1.21025900
C	-3.67325500	2.62246300	1.47632400
H	-2.05348800	1.26849400	1.87461600
C	-4.22361400	2.95147500	-0.84591700
H	-3.03577400	1.82962700	-2.25513000
C	-4.45061400	3.23455200	0.49790900
H	-3.83751400	2.85282100	2.52335500
H	-4.82165900	3.43441800	-1.61092500
H	-5.22618200	3.93724500	0.78213700
O	-0.73584400	0.61139200	-2.20464500

Table S28. Cartesian Coordinates of Diphenyl phosphine oxid.

Atomic symbol	x	y	z
C	-1.45700100	0.34771500	-0.21789300
C	-2.05857200	-0.54670500	-1.10290300
C	-2.00253800	0.55092900	1.04998300
C	-3.19081900	-1.25493400	-0.71302500
H	-1.65362600	-0.68445400	-2.10183200
C	-3.13524000	-0.15602800	1.43558200
H	-1.54343500	1.27130700	1.71936900
C	-3.72570500	-1.06057400	0.55673000
H	-3.66057300	-1.94784500	-1.40176100
H	-3.56235300	0.00260500	2.41918700
H	-4.61108700	-1.60859900	0.85894900
C	1.44015900	0.18266600	-0.22934500
C	2.56646700	0.79352200	0.32064900
C	1.42163700	-1.19781300	-0.43501500
C	3.67662300	0.02389600	0.65496500
H	2.55516900	1.86500900	0.49087300
C	2.53410400	-1.96178400	-0.10390400
H	0.53736500	-1.68074500	-0.83982300
C	3.66127600	-1.35010400	0.43988000
H	4.55167700	0.49714600	1.08572100
H	2.52005200	-3.03434600	-0.26094600
H	4.52675700	-1.94878300	0.70122900
O	0.16414300	2.62042700	-0.07272200
P	0.04289500	1.25840700	-0.66323400
H	0.00112300	1.20447300	-2.07489700

Table S29. Cartesian Coordinates of Diphenyl phosphinous acid.

Atomic symbol	x	y	z
C	-1.39917900	0.37434600	-0.22370900
C	-2.32051200	-0.13193800	-1.13838500
C	-1.55225100	0.09382300	1.13696000
C	-3.37967000	-0.92750700	-0.70310100
H	-2.21582700	0.10025000	-2.19437600
C	-2.61517900	-0.68526500	1.57183000
H	-0.83619400	0.49591100	1.84676400
C	-3.52707600	-1.20134700	0.65063100
H	-4.09152700	-1.32201600	-1.41961700
H	-2.73349900	-0.89872300	2.62849400
H	-4.35372200	-1.81408000	0.99295700
C	1.37504500	0.27108900	-0.34135900
C	2.37185500	0.68061100	0.54282300
C	1.44521300	-1.00245300	-0.91312100
C	3.42264600	-0.17937200	0.85577200
H	2.31435200	1.66498200	0.99172400
C	2.49418200	-1.85644300	-0.60031600
H	0.66852400	-1.33463000	-1.59703600
C	3.48761800	-1.44513600	0.28591300
H	4.19141300	0.14340000	1.54942600

H	2.53642800	-2.84463200	-1.04474900
H	4.30704000	-2.11157600	0.53087200
O	0.17295700	2.47521500	0.42189200
P	0.00595200	1.38713600	-0.83853800
H	-0.07608400	3.36990500	0.17484900