Electronic Supplementary Information
for

Oxidative Addition of Aromatic *ortho* C–H Bond of Tetraphosphine to Asymmetric Diiridium(I) Centers

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Appendix 14. Cartesian coordinates of the optimized structure of $\mathbf{TS_{C\text{-}M2}}$.

Synthesis and Structure of mononuclear iridium complex $[Ir_2(H)((dpmppp)–\kappa P^3)(^tBuNC)_2)](PF_6)_2$ **(4).**

A similar reaction using ^{t}BuNC instead of the aromatic isocyanides gave only a mononuclear iridium(III) complex, $[Ir_2(H)((dpmppp)–\kappa P^3)(^tBuNC)_2)](PF_6)_2$ (**4**) in 18% yield; the ESI mass spectrum of the reaction solution did not show the formation of any diiridium hydride complex analogous to **2** and **3**. The solid state structure of **4** was determined by X-ray crystallography (Fig. S1 and Table S8 in ESI). The iridium centre is six-coordinate with three P atoms of dpmppp in meridional mode, *cis*-disposed two ^{t}BuNC, and a hydride to form a distorted octahedral geometry (Ir1–P1 = 2.325(3) Å, Ir1–P2 = 2.305(3) Å, Ir1–P3 = 2.335(3) Å, Ir–C1 = 1.985(10) Å, Ir–C2 = 2.046(9) Å, P1–Ir1–P2 = 71.91(8) °, P2–Ir1–P3 = 93.28(8) °, C1–Ir1–C2 = 89.5(4) °). The distance of Ir–C1 bond is slightly shorter than that of Ir–C2 bond due to large *trans* influence of the hydride ligand, which was determined from difference Fourier maps (Ir1–H1 = 1.51(10) Å). The $^{31}P\{^1H\}$ NMR spectrum of **4** showed four resonances at δ −25.7 (dd, J = 54 Hz, 6 Hz, 1P, P_D), −34.3 (ddd, J = 255 Hz, 54 Hz, 23 Hz, 1P, P_C), −52.3 (ddd, J = 256 Hz, 53 Hz, 6 Hz, 1P, P_A), and −70.2 (dd, J = 53 Hz, 23 Hz, 1P, P_B) (Fig. 3d), which were assignable as indicated in experimental section by the ^{31}P –^{31}P COSY spectrum (Fig. S16). In the ^{1}H NMR spectrum, the hydride peak was observed at δ −10.09 (q, J_{PH} = 16 Hz) (Fig. S14). The presence of two terminal ^{t}BuNC ligands were confirmed by ν(CN) frequency of 2224 and 2209 cm^{-1} as well as the singlets of ^{1}H NMR spectrum at 0.89 and 1.50 ppm. The ESI mass spectrum in methanol showed monovalent parent peak at m/z 1161.348 (**4**), corresponding to $\{Ir(H)(dpmppp)(^tBuNC)_2)(PF_6)\}^+$ (m/z 1161.456) (Fig. S20).

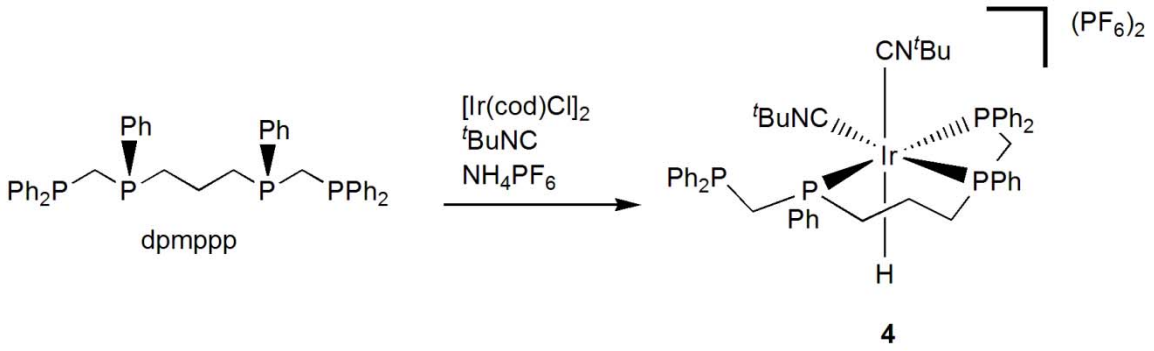

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Table S1. Crystallographic Data of Complexes **1**·CH_2Cl_2 and **2**·1.5CH_2Cl_2

Compound	**1**·CH_2Cl_2	**2**·1.5CH_2Cl_2
formula	$C_{44}H_{40}ClF_6Ir_2O_{18}P_5 \cdot CH_2Cl_2$	$C_{77}H_{76}F_{12}Ir_2N_4P_6 \cdot 1.5CH_2Cl_2$
formula wt	1390.48	1983.14
cryst. syst	monoclinic	triclinic
space group	$P2_1/n$	$P1$-
a, Å	15.512(5)	12.196(3)
b, Å	16.476(5)	17.953(5)
c, Å	19.316(6)	19.765(5)
α, deg		99.843(2)
β, deg	96.487(4)	96.204(3)
γ, deg		100.923(3)
V, Å^3	4905(3)	4142.2(19)
Z	4	2
temp, °C	-120	-120
D_{calcd}, g cm^{-1}	1.883	1.590
μ, mm^{-1} (Mo Kα)	5.824	3.502
2θ range, deg	6–55	6–55
R_{int}	0.028	0.026
no. of reflns collected	44785	39032
no. of unique reflns	11092	18411
no. of obsd reflns ($I > 2\sigma(I)$)	10002	16036
no. of variables	609	997
$R1$[a]	0.033	0.037
$wR2$[b]	0.081	0.100
GOF	1.045	1.011

[a] $R1 = \Sigma \| |F_o| - |F_c| | / \Sigma |F_o|$ (for obsd. refs with $I > 2\sigma(I)$). [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^2)^2]^{1/2}$ (for all refs).

Table S2. Crystallographic Data of Complexes **3** and **4**·3THF

Compound	**3**	**4**·3THF
formula	$C_{81}H_{84}F_{12}Ir_2N_4P_6$	$C_{51}H_{59}F_{12}IrN_2P_6$·3THF
formula wt	1911.85	1522.40
cryst. syst	monoclinic	orthorhombic
space group	$P2_1/n$	$P2_12_12_1$
a, Å	12.103(2)	13.058(3)
b, Å	20.671(3)	18.478(4)
c, Å	34.721(5)	28.214(6)
α, deg		
β, deg	95.920(2)	
γ, deg		
V, Å^3	8640(2)	6808(3)
Z	4	4
temp, °C	-150	-120
D_{calcd}, g cm^{-1}	1.470	1.485
μ, mm^{-1} (Mo Kα)	3.266	2.185
2θ range, deg	6–55	6–55
R_{int}	0.063	0.071
no. of reflns collected	40205	79705
no. of unique reflns	19408	7049
no. of obsd reflns ($I > 2\sigma(I)$)	14358	4943
no. of variables	952	787
$R1$[a]	0.068	0.066
$wR2$[b]	0.202	0.180
GOF	1.086	1.106

[a] $R1 = \Sigma\big||F_o| - |F_c|\big|/\Sigma|F_o|$ (for obsd. refs with $I > 2\sigma(I)$). [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (for all refs).

Table S3. Crystallographic Data of Complexes **5** and **6**·0.5CH_2Cl_2·2CH_3OH

Compound	**5**	**6**·0.5CH_2Cl_2·2CH_3OH
formula	$C_{76}H_{78}N_3F_{12}P_6Ir_2$	$C_{79.5}H_{85}N_4F_{12}P_6ClIr_2$
formula wt	1832.74	1962.29
cryst. syst	triclinic	triclinic
space group	*P*1-	*P*1-
a, Å	12.672(2)	13.7832(17)
b, Å	16.834(3)	14.612(2)
c, Å	20.346(4)	21.817(3)
α, deg	75.827(10)	81.004(6)
β, deg	74.185(10)	74.071(5)
γ, deg	75.401(11)	81.207(6)
V, Å^3	3968.0(13)	4145.3(10)
Z	2	2
temp, °C	-120	-120
D_{calcd}, g cm^{-1}	1.533	1.572
μ, mm^{-1} (Mo Kα)	3.551	3.438
2θ range, deg	6–55	6–55
R_{int}	0.028	0.036
no. of reflns collected	48606	50204
no. of unique reflns	18075	18838
no. of obsd reflns ($I > 2\sigma(I)$)	13852	14795
no. of variables	908	999
*R*1[a]	0.052	0.057
*wR*2[b]	0.139	0.177
GOF	1.106	1.081

[a] $R1 = \Sigma\big|\,|F_o| - |F_c|\,\big|/\Sigma|F_o|$ (for obsd. refs with $I > 2\sigma(I)$). [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (for all refs).

Table S4. Crystallographic Data of Complex **8**·CH_2Cl_2

Compound	**8**·CH_2Cl_2
formula	$C_{46}H_{42}Cl_3F_6Ir_2O_4P_5$
formula wt	1418.49
cryst. syst	triclinic
space group	*P*1-
a, Å	12.621(3)
b, Å	14.450(3)
c, Å	14.580(3)
α, deg	67.321(8)
β, deg	85.710(8)
γ, deg	88.282(9)
V, Å^3	2446.6(10)
Z	2
temp, °C	-120
D_{calcd}, g cm^{-1}	1.925
μ, mm^{-1} (Mo Kα)	5.842
2θ range, deg	6–55
R_{int}	0.028
no. of reflns collected	17171
no. of unique reflns	10475
no. of obsd reflns ($I > 2\sigma(I)$)	7617
no. of variables	585
$R1$[a]	0.039
$wR2$[b]	0.105
GOF	0.925

[a] $R1 = \Sigma\big|\,|F_o| - |F_c|\,\big|/\Sigma|F_o|$ (for obsd. refs with $I > 2\sigma(I)$). [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (for all refs).

Table S5. Selected Bond Lengths (Å) and Angles (deg) for Complex **1** [a]

Ir1–Ir2	2.80444(17)	Ir1–Cl1	2.4559(10)
Ir1–P2	2.2701(9)	Ir1–P3	2.3570(9)
Ir1–C1	1.902(3)	Ir1–C10	2.123(3)
Ir2–P1	2.3073(10)	Ir2–P4	2.3388(10)
Ir2–C2	1.964(4)	Ir2–C3	1.934(3)
Ir2–H1	1.56(3)	C1–O1	1.123(4)
C2 –O2	1.128(4)	C3–O3	1.133(5)
P2– Ir1–P3	96.35(3)	P3–Ir1–C10	174.03(10)
P2–Ir1–Cl1	175.23(3)	Ir2–Ir1–Cl1	90.13(2)
Ir2–Ir1–C1	178.51(11)	P1–Ir2–P4	164.87(3)
C2–Ir2–H1	173.7(13)	Ir1–Ir2–C2	86.40(10)
Ir1–Ir2–C3	175.27(12)	Ir1-Ir2-H1	87.8(13)
Ir1–C1–O1	178.7(3)	Ir2–C2–O2	174.7(3)
Ir2–C3–O3	176.4(3)		

[a] The atomic numbering schemes are shown in Figure 1.

Table S6. Selected Bond Lengths (Å) and Angles (deg) for Complex **2** [a]

Ir1–Ir2	2.85685(18)	Ir1–P2	2.3416(9)
Ir1–P3	2.3445(10)	Ir1–C1	1.963(3)
Ir1–C2	1.973(3)	Ir1–C43	2.132(3)
Ir2–P1	2.2904(10)	Ir2–P4	2.3160(10)
Ir2–C3	2.014(3)	Ir2–C4	1.956(3)
Ir2–H1	1.75(5)	C1–N1	1.133(4)
C2–N2	1.153(4)	C3–N3	1.151(5)
C4–N4	1.159(4)		
P2– Ir1–P3	96.33(3)	P3–Ir1–C43	176.51(11)
P2–Ir1–C2	169.15(11)	Ir2–Ir1–C1	177.75(11)
P1–Ir2–P4	165.15(3)	C3–Ir2–H1	171.2(15)
Ir1–Ir2–C4	165.39(12)	Ir1-Ir2-H1	77.4(14)
Ir1–C1–N1	175.4(3)	Ir1–C2–N2	172.2(3)
Ir2–C3–N3	175.3(3)	Ir2–C4–N4	173.2(3)

[a] The atomic numbering schemes are shown in Figure 2.

Table S7. Selected Bond Lengths (Å) and Angles (deg) for Complex **3** [a]

Ir1–Ir2	2.8527(7)	Ir1–P2	2.3383(18)
Ir1–P3	2.3410(17)	Ir1–C1	1.976(9)
Ir1–C2	1.973(8)	Ir1–C47	2.130(7)
Ir2–P1	2.2955(19)	Ir2–P4	2.3125(19)
Ir2–C3	2.010(8)	Ir2–C4	1.971(8)
Ir2–H1	1.56(6)	C1–N1	1.099(11)
C2–N2	1.172(10)	C3–N3	1.160(10)
C4–N4	1.140(10)		
P2– Ir1–P3	96.16(6)	P3–Ir1–C47	177.0(2)
P2–Ir1–C2	167.7(2)	Ir2–Ir1–C1	177.4(2)
P1–Ir2–P4	165.07(7)	C3–Ir2–H1	172 (3)
Ir1–Ir2–C4	165.7(2)	Ir1-Ir2-H1	80(2)
Ir1–C1–N1	174.6(7)	Ir1–C2–N2	170.5(6)
Ir2–C3–N3	178.3(7)	Ir2–C4–N4	174.1(7)

[a] The atomic numbering schemes are shown in Figure S2.

Table S8. Selected Bond Lengths (Å) and Angles (deg) for Complex **4** [a]

Ir1–P1	2.325(3)	Ir1–P2	2.305(3)
Ir1–P3	2.335(3)	Ir1–C1	1.985(10)
Ir1–C2	2.046(9)	Ir1–H1	1.51(10)
C1–N1	1.168(12)	C2–N2	1.138(12)
P1– Ir1–P2	71.91(8)	P1–Ir1–P3	158.50(8)
P1–Ir1–C1	97.3(3)	P1–Ir1–C2	95.0(3)
P1–Ir1–H1	85(4)	P2–Ir1–P3	93.28(8)
P2–Ir1–C1	167.9(3)	P2–Ir1–C2	96.8(3)
P2–Ir1–H1	87(4)	P3–Ir1–C1	95.5(3)
P3–Ir1–C2	102.3(3)	P3–Ir1–H1	79(4)
Ir1–C1–N1	176.7(8)	Ir1–C2–N2	174.5(8)

[a] The atomic numbering schemes are shown in Figure S1.

Table S9. Selected Bond Lengths (Å) and Angles (deg) for **5** [a]

Ir1–P1	2.3287(17)	Ir1–P2	2.2999(14)
Ir1–P3	2.3542(14)	Ir1–C4	2.264(5)
Ir1–C5	2.265(6)	Ir1–C8	2.181(8)
Ir1-C9	2.173(8)	Ir2-P4	2.3321(15)
Ir2–C1	1.957(5)	Ir2–C2	1.944(6)
Ir2–C3	1.937(6)	C1–N1	1.155(7)
C2–N2	1.155(8)	C3–N3	1.157(8)
P1– Ir1–P2	71.60(5)	P1–Ir1–P3	107.28(6)
P2–Ir1–P3	94.22(5)	P4–Ir2–C1	97.43(16)
P4–Ir2–C2	178.4(2)	P4–Ir2–C3	90.79(18)
C1–Ir2–C2	84.0(2)	C1–Ir2–C3	168.5(2)
C2–Ir2–C3	87.7(2)		

[a] The atomic numbering schemes are shown in Figure S3.

Table S10. Selected Bond Lengths (Å) and Angles (deg) for **6** [a]

Ir1–Ir2	2.7990(5)	Ir1–P2	2.322(2)
Ir1–P3	2.3334(14)	Ir1–C1	2.023(7)
Ir1–C2	1.982(8)	Ir1–C3	1.997(5)
Ir2–P1	2.2893(18)	Ir2–P4	2.2928(14)
Ir2–C4	1.876(8)	C1–N1	1.082(9)
C2–N2	1.155(11)	C3–N3	1.138(7)
C4–N4	1.109(10)		
P2– Ir1–P3	93.65(6)	Ir2–Ir1–C1	175.54(16)
P2–Ir1–C2	162.22(19)	P3–Ir1–C3	175.1(2)
P1–Ir2–P4	168.89(6)	Ir1–Ir2–C4	174.1(2)
Ir1–C1–N1	176.3(8)	Ir1–C2–N2	175.1(5)
Ir2–C3–N3	171.2(6)	Ir2–C4–N4	176.1(8)

[a] The atomicnumbering schemes are shown in Figure 8.

Table S11. Selected Bond Lengths (Å) and Angles (deg) for Complex **8** [a]

Ir1–Ir2	2.8894(2)		
Ir1–P2	2.324(2)	Ir1–P3	2.361(2)
Ir1–C1	2.611(6)	Ir1–C3	1.912(8)
Ir1–C4	1.904(7)	Ir2–Cl1	2.439(1)
Ir2–P1	2.348(2)	Ir2–P4	2.345(2)
Ir2–C1	1.881(7)	Ir2–C2	2.002(5)
Ir2– Ir1–C3	113.4(2)	Ir2– Ir1–C4	112.3(2)
P2– Ir1–P3	94.34(5)	P2–Ir1–C3	158.5(2)
P2–Ir1–C4	85.6(2)	P3–Ir1–C3	87.7(2)
P3–Ir1–C4	159.8(2)	C3–Ir1–C4	85.2(3)
Ir2–Ir2–C1	62.2(2)	Ir1–Ir2–C2	163.5(2)
Cl1–Ir2–P1	86.12(5)	Cl1–Ir2–P4	85.05(5)
Cl1–Ir2–C1	158.0(2)	Cl1–Ir2–C2	100.6(2)
P1–Ir2–P4	168.57(4)	P1–Ir2–C1	92.8(2)
P1–Ir2–C2	93.2(2)	P4–Ir2–C1	92.7(2)
P4–Ir2–C2	95.6(2)	C1–Ir2–C2	101.3(2)

[a] The atomic numbering schemes are shown in Figure S4.

Table S12. Thermodynamic Parameters Derived from DFT Calculations with B3LYP/lanl2dz for Ir/6-311+G(d,p) for Phenyl Group/6-31G(d) for Others on the Optimized (a) GS and (b) TS Model Structures with B3LYP/lanl2dz for Ir/6-31G(d) for Others.

(a) For the GS structures

stable structures		M6	M8	M2	A	B	C
E_{elec} + ZPE	Hartree	-2379.150151	-2379.159121	-2379.164819	-2379.082107	-2379.12822	-2379.141284
	kcal/mol	-1492939.322	-1492944.95	-1492948.526	-1492896.623	-1492925.56	-1492933.758
⊿E	kcal/mol		-5.6	-9.2	42.7	13.8	5.6
E (corrected thermal energies)	Hartree	-2379.117986	-2379.126468	-2379.133661	-2379.050277	-2379.096439	-2379.110158
	kcal/mol	-1492919.138	-1492924.46	-1492928.974	-1492876.65	-1492905.617	-1492914.226
⊿E	kcal/mol		-5.3	-9.8	42.5	13.5	4.9
H (corrected enthalpies)	Hartree	-2379.117042	-2379.125524	-2379.132716	-2379.049332	-2379.095495	-2379.109213
	kcal/mol	-1492918.545	-1492923.868	-1492928.381	-1492876.057	-1492905.025	-1492913.633
⊿H	kcal/mol		-5.3	-9.8	42.5	13.5	4.9
G (corrected Gibbs's free energies)	Hartree	-2379.213463	-2379.225251	-2379.224329	-2379.144922	-2379.190695	-2379.202573
	kcal/mol	-1492979.051	-1492986.448	-1492985.869	-1492936.04	-1492964.763	-1492972.217
⊿G	kcal/mol		-7.4	-6.8	43.0	14.3	6.8

(b) For the TS Structures

transition states		**TS-M6-to-M8**	**TS-M8-to-B**	**TS-B-to-M2**	**TS-M8-to-C**	**TS-C-to-M2**
E_{elec} + ZPE	Hartree	-2379.142643	-2379.090095	-2379.083809	-2379.103068	-2379.130102
	kcal/mol	-1492934.61	-1492901.636	-1492897.691	-1492909.777	-1492926.741
⊿E	kcal/mol	4.7	37.7	41.6	29.5	12.6
E (corrected thermal energies)	Hartree	-2379.111341	-2379.058317	-2379.052657	-2379.072201	-2379.099514
	kcal/mol	-1492914.968	-1492881.695	-1492878.143	-1492890.407	-1492907.546
⊿E	kcal/mol	4.2	37.4	41.0	28.7	11.6
H (corrected enthalpies)	Hartree	-2379.110397	-2379.057373	-2379.051713	-2379.071257	-2379.09857
	kcal/mol	-1492914.376	-1492881.103	-1492877.551	-1492889.815	-1492906.954
⊿H	kcal/mol	4.2	37.4	41.0	28.7	11.6
G (corrected Gibbs's free energies)	Hartree	-2379.204291	-2379.152045	-2379.143954	-2379.163104	-2379.189523
	kcal/mol	-1492973.295	-1492940.51	-1492935.433	-1492947.45	-1492964.028
⊿G	kcal/mol	5.8	38.5	43.6	31.6	15.0

Figure S1. ORTEP diagram for **4** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% probability level, and the C–H hydrogen atoms are omitted for clarity.

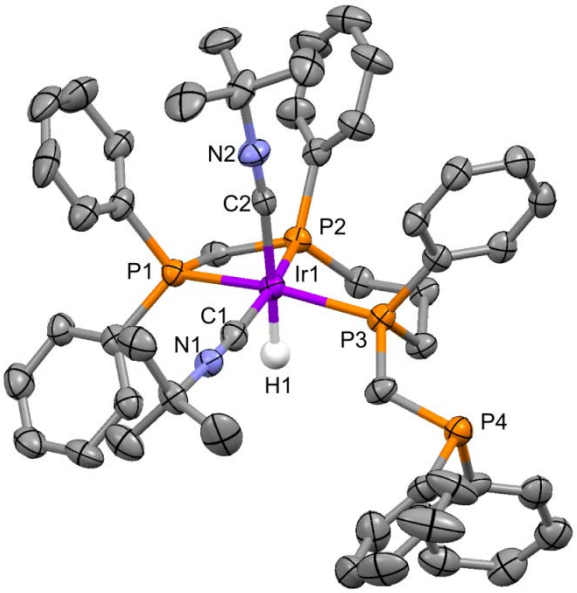


Figure S2. ORTEP diagram for **3** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% probability level, and the C–H hydrogen atoms are omitted for clarity.

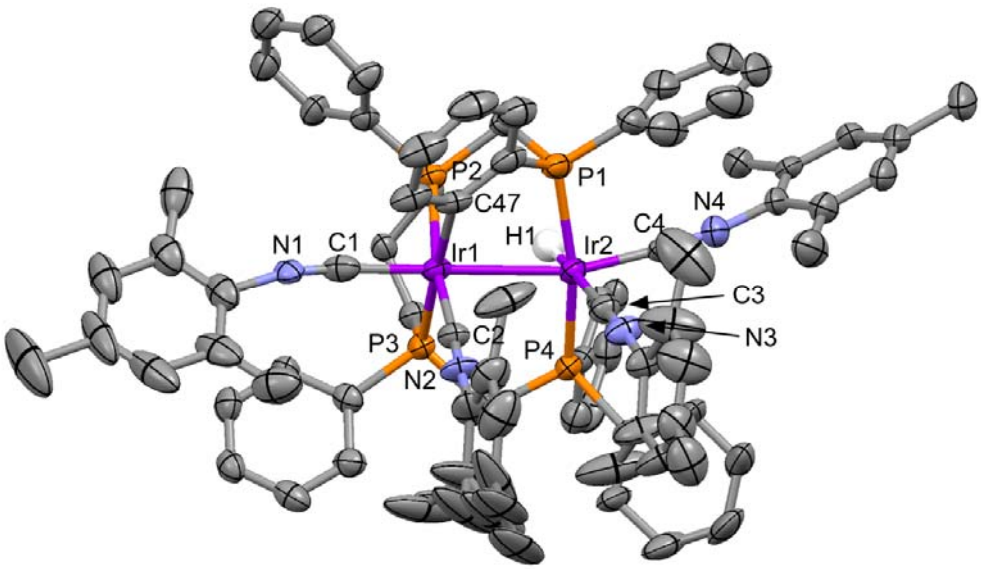


Figure S3. ORTEP diagram for **5** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% probability level, and the C–H hydrogen atoms are omitted for clarity.

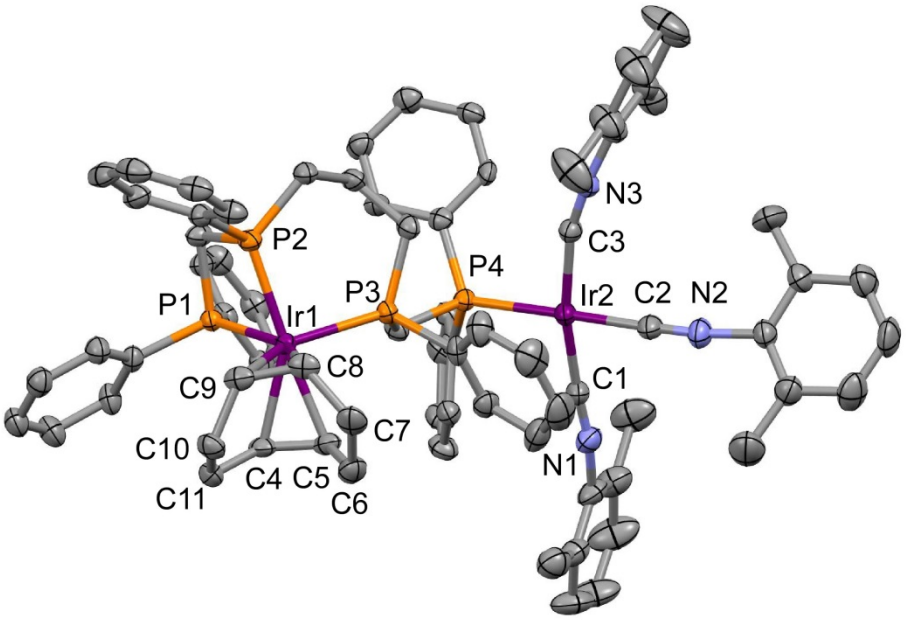


Figure S4. ORTEP diagram for **8** with the atomic numbering scheme. The thermal ellipsoids are drawn at the 40% probability level, and the C–H hydrogen atoms are omitted for clarity.

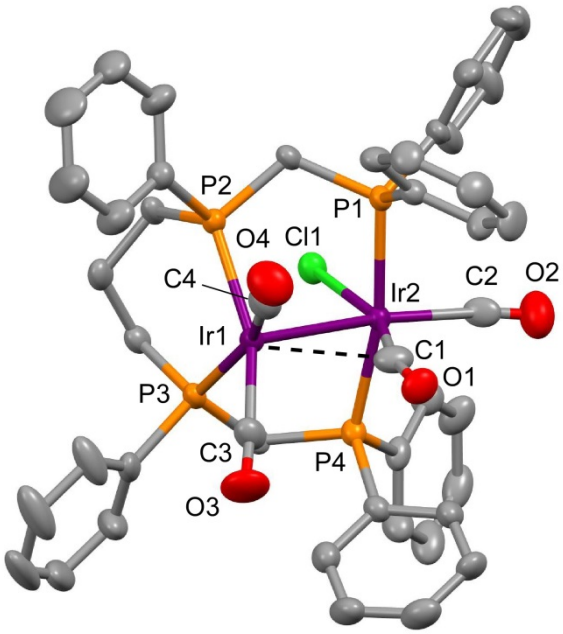


Figure S5. $^{1}H–^{1}H$ COSY spectra of **1** in acetone-d_6 at room temperature. (a) Correlation for methylene protons. (b) Correlation for methylene proton and hydride.

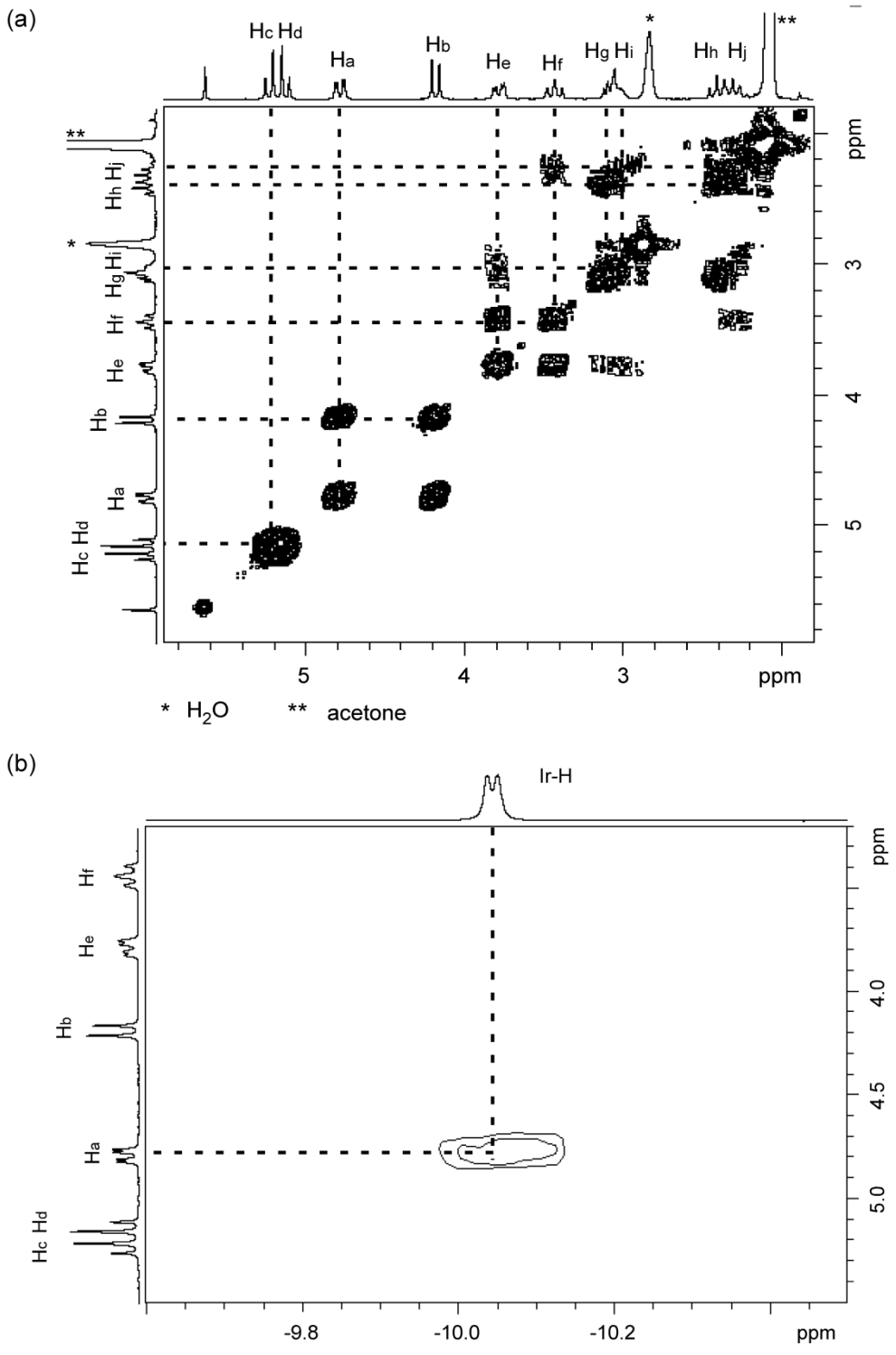


Figure S6. (a) $^{1}H\{^{31}P\}$ NMR and (b) ^{1}H NMR spectra for the methylene region of **2** in acetone-d_6 at room temperature.

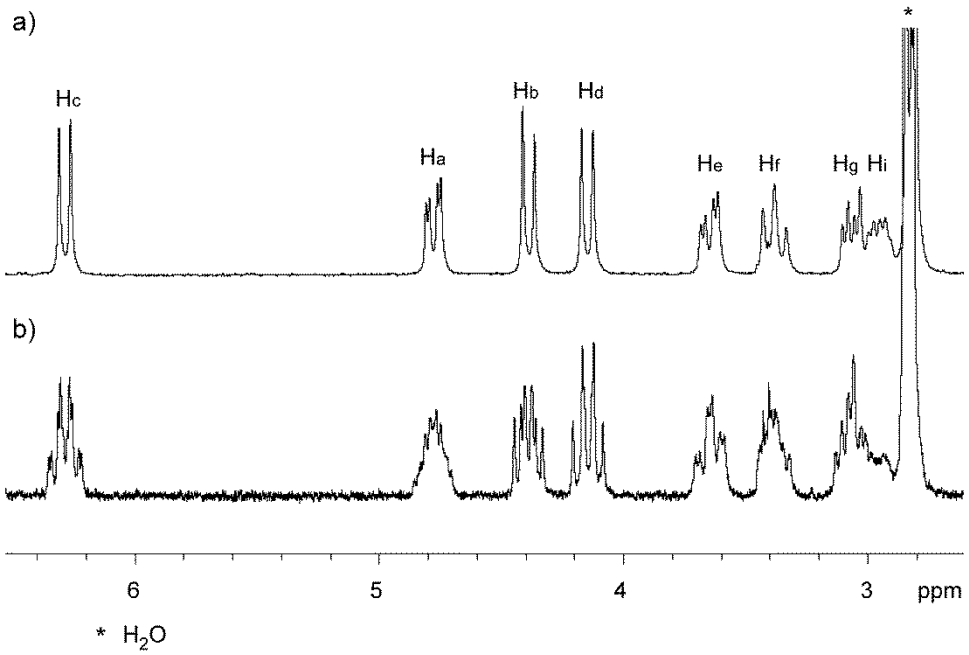


Figure S7. (a) $^{1}H\{^{31}P\}$ NMR and (b) ^{1}H NMR spectra for the hydride peak of **2** in acetone-d_6 at room temperature.

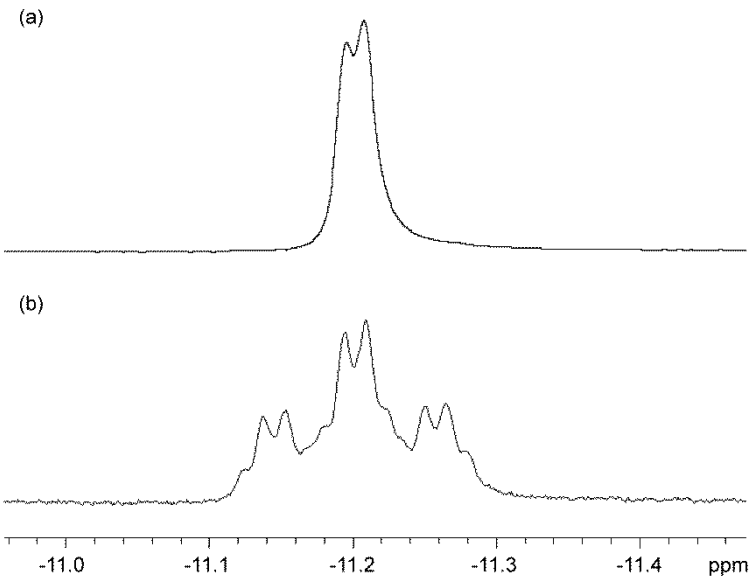


Figure S8. $^{1}H–^{31}P$ HMQC spectrum displaying correlation of the hydride peak and the phosphorous peaks of **2** in acetone-d_6 at room temperature.

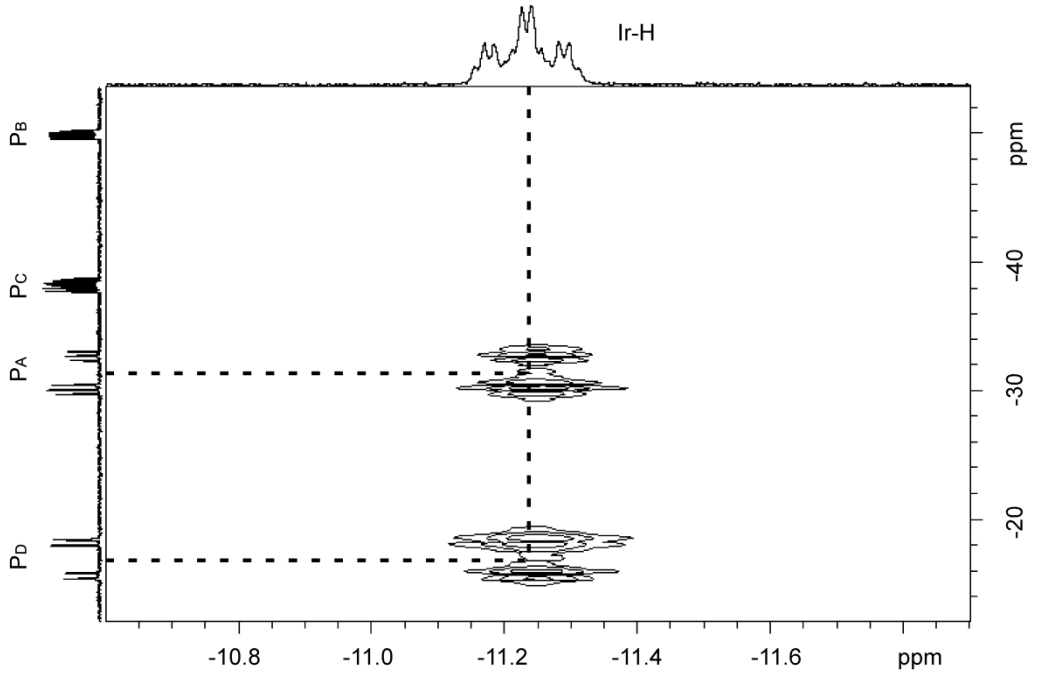


Figure S9. $^{1}H–^{31}P$ HMBC spectrum of **2** in acetone-d_6 at room temperature.

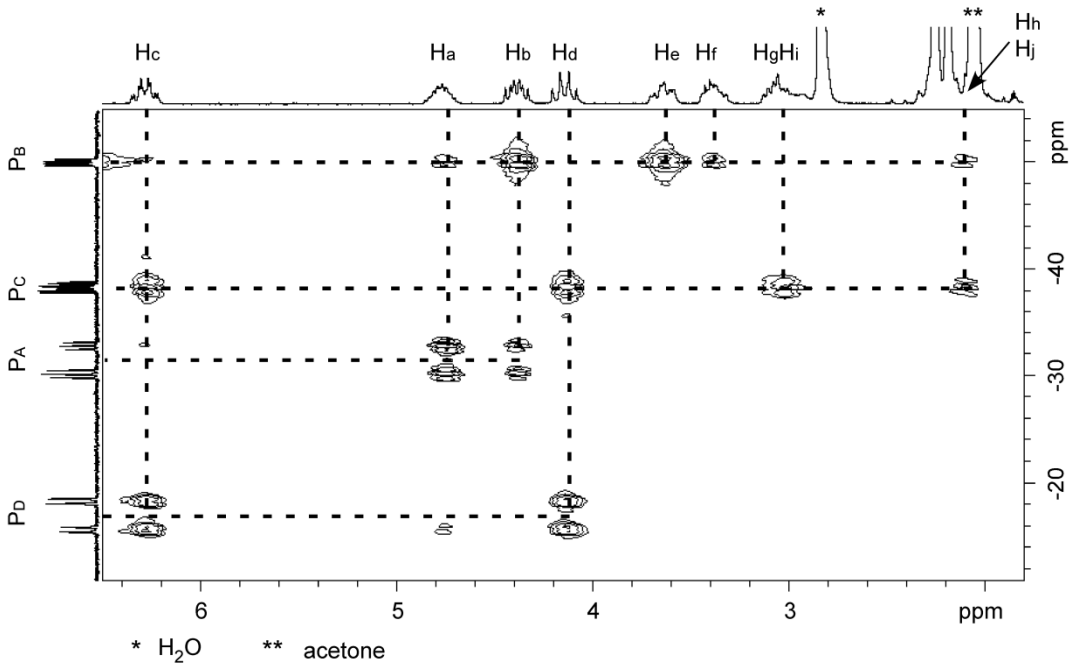


Figure S10. $^{1}H–^{1}H$ COSY spectra of **2** in acetone-d_6 at room temperature. (a) Correlation for methylene protons. (b) Correlation for methylene proton and hydride.

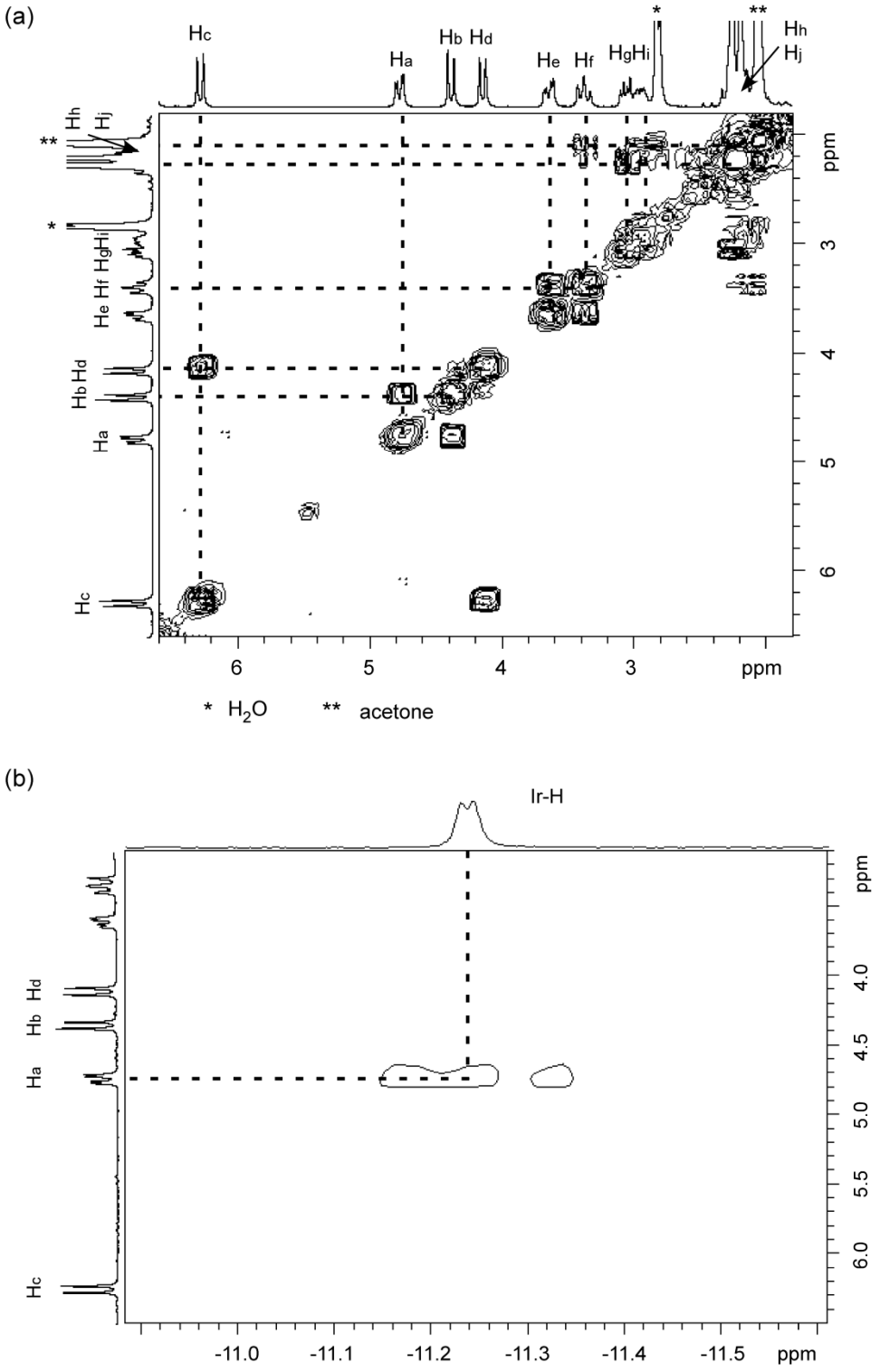


Figure S11. $^{1}H–^{1}H$ ROESY spectrum of **2** in acetone-d_6 at room temperature.

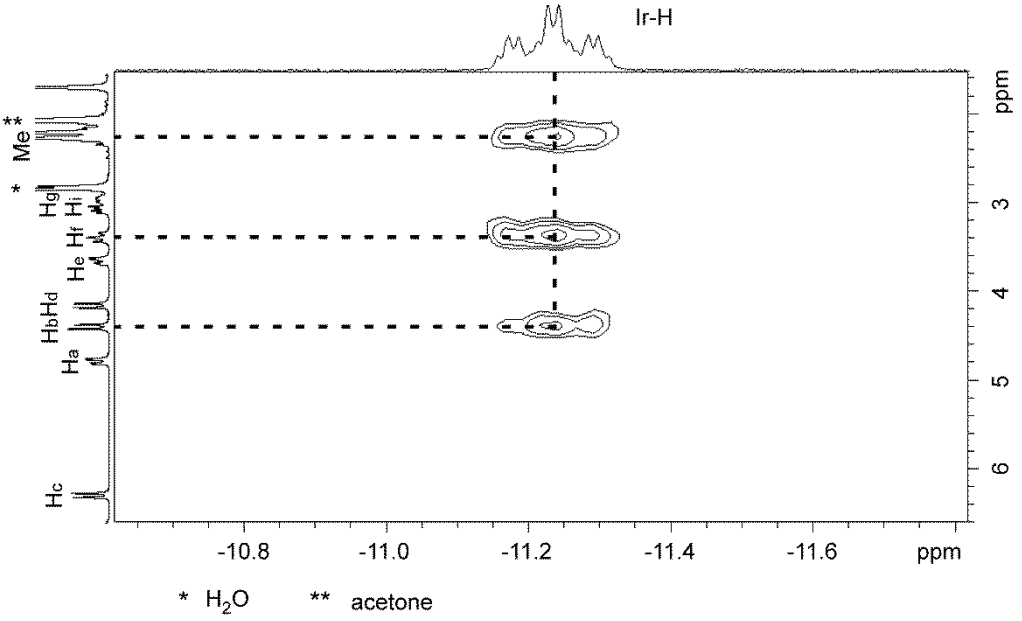


Figure S12. (a) $^{1}H\{^{31}P\}$ NMR and (b) ^{1}H NMR spectra for the methylene region of **3** in acetone-d_6 at room temperature.

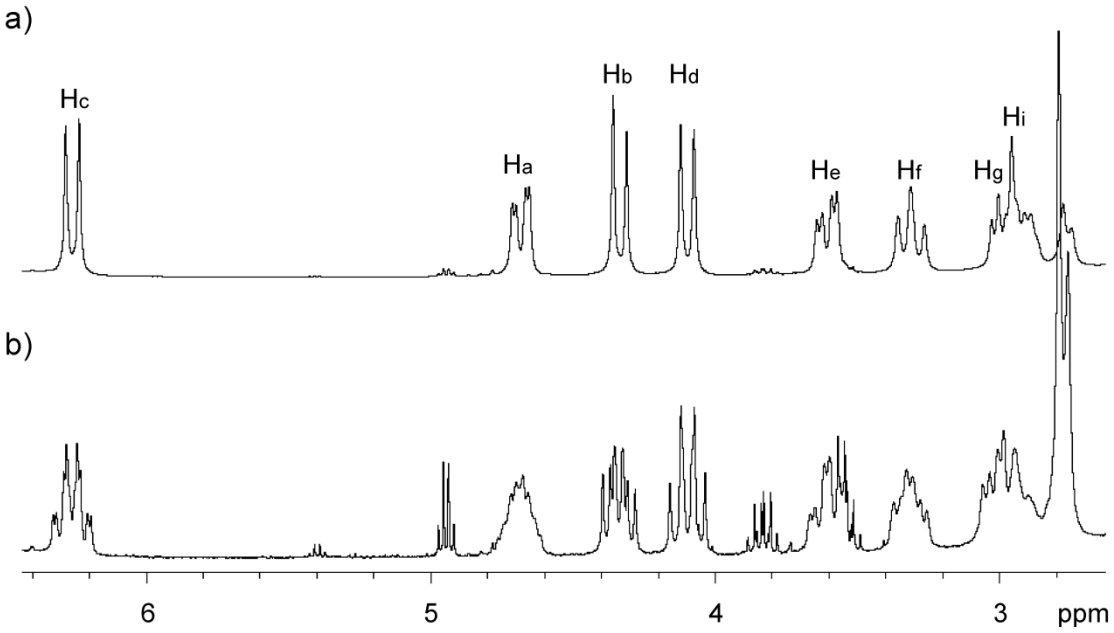


Figure S13. (a) $^{1}H\{^{31}P\}$ NMR and (b) ^{1}H NMR spectra for the hydride peak of **3** in acetone-d_6 at room temperature.

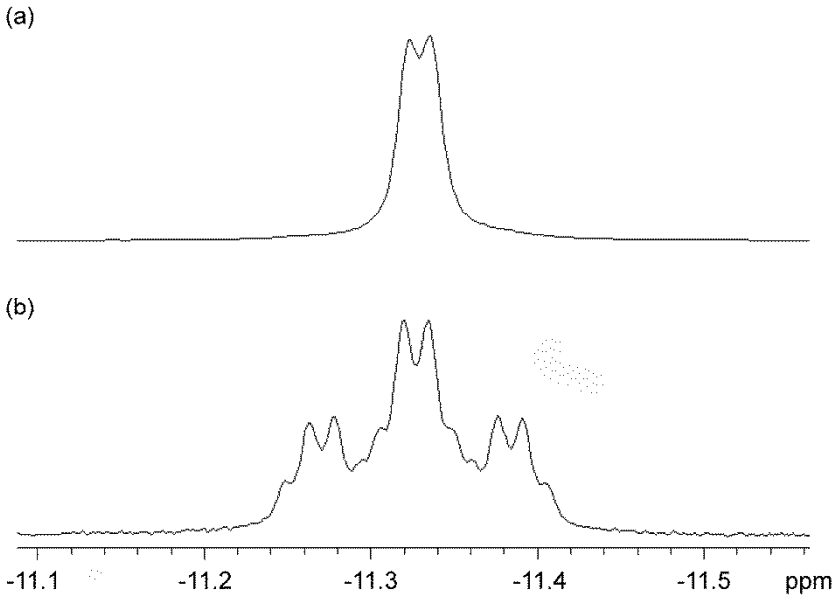


Figure S14. (a) $^{1}H\{^{31}P\}$ NMR and (b) ^{1}H NMR spectra for the hydride peak of **4** in acetone-d_6 at room temperature.

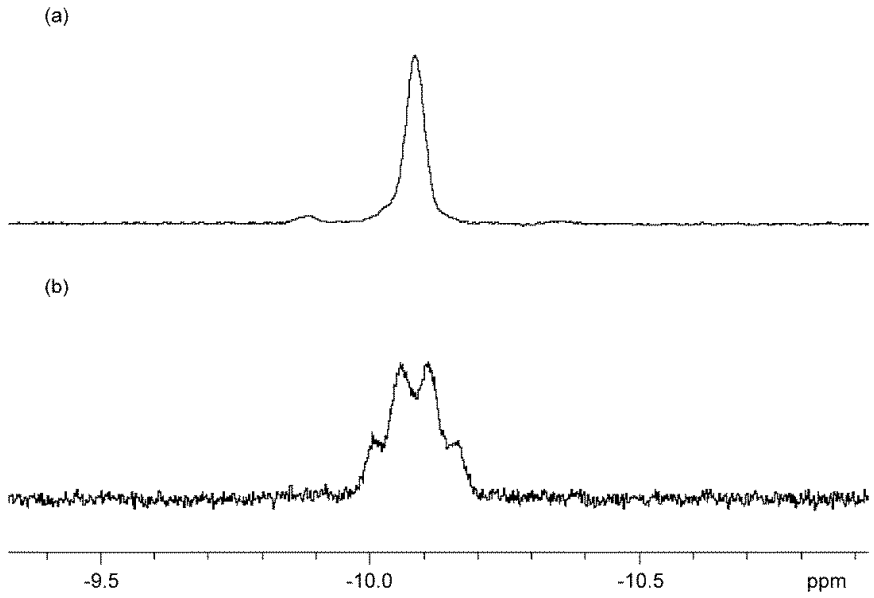


Figure S15. ^{1}H– ^{1}H COSY spectra of **4** in acetone-d_6 at room temperature.

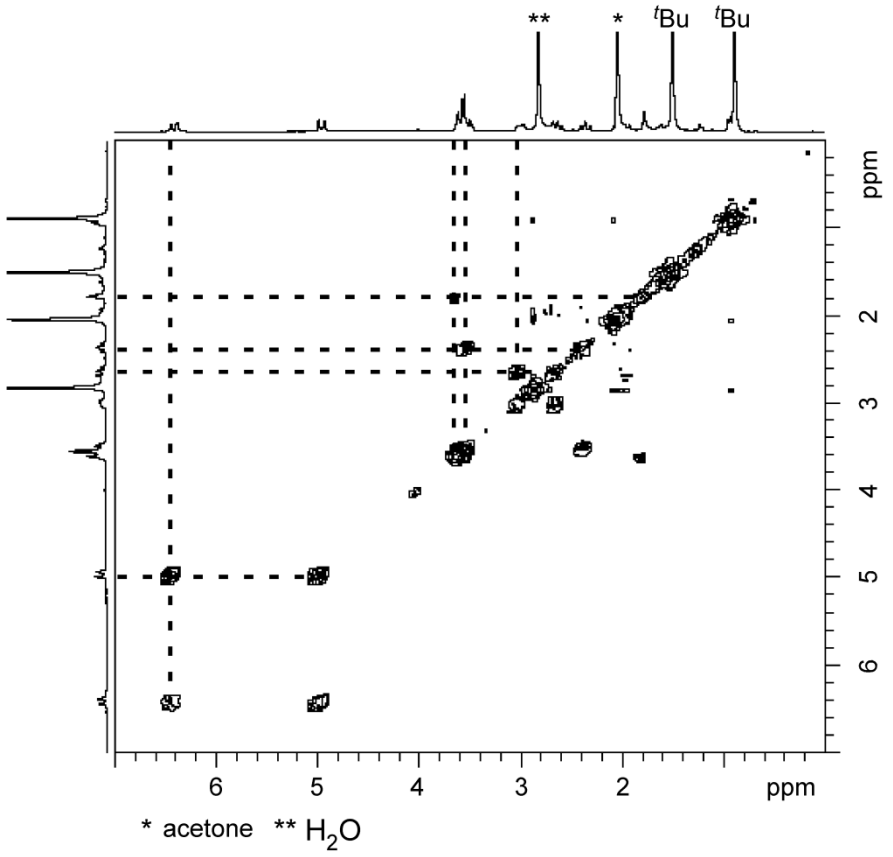


Figure S16. ^{31}P– ^{31}P COSY spectra of **4** in acetone-d_6 at room temperature.

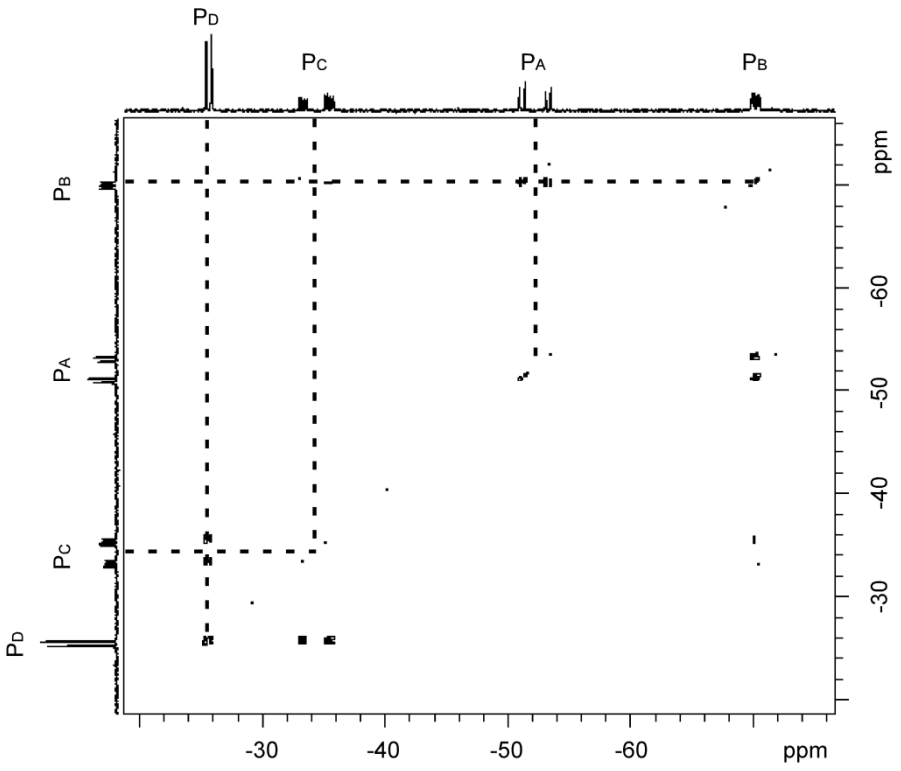


Figure S17. ESI–TOF mass spectra of **1** in MeOH.

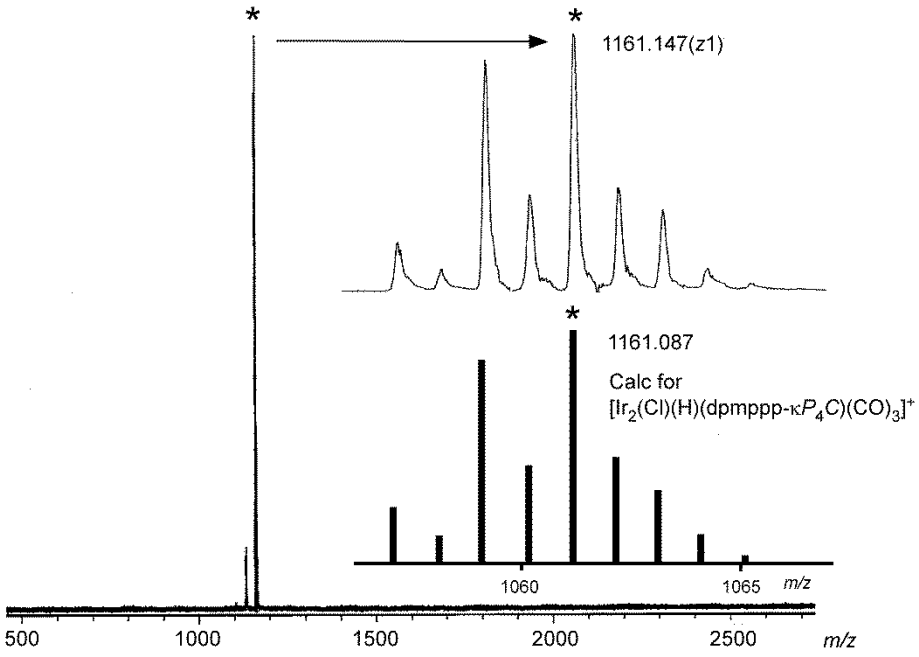


Figure S18. ESI–TOF mass spectra of **2** in MeOH.

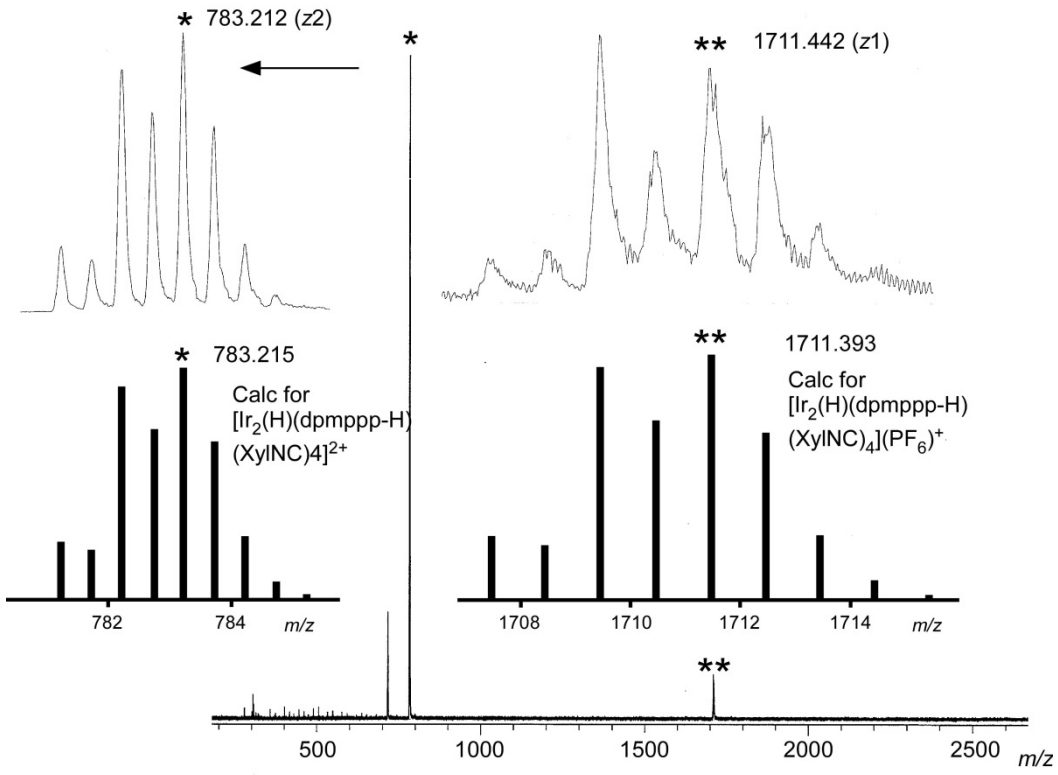


Figure S19. ESI–TOF mass spectra of **3** in MeOH.

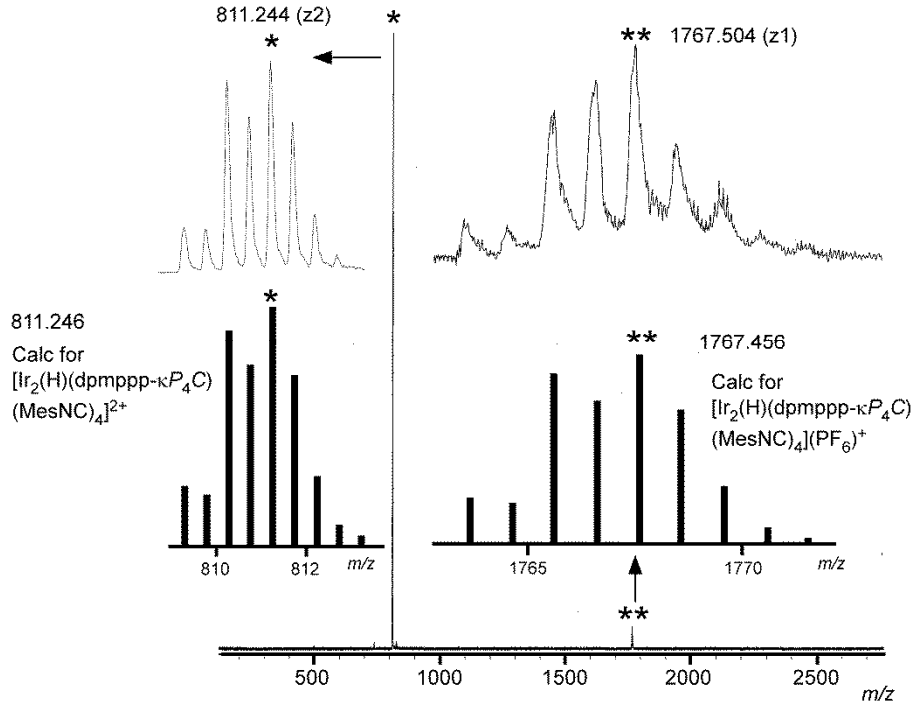


Figure S20. ESI–TOF mass spectra of **4** in MeOH.

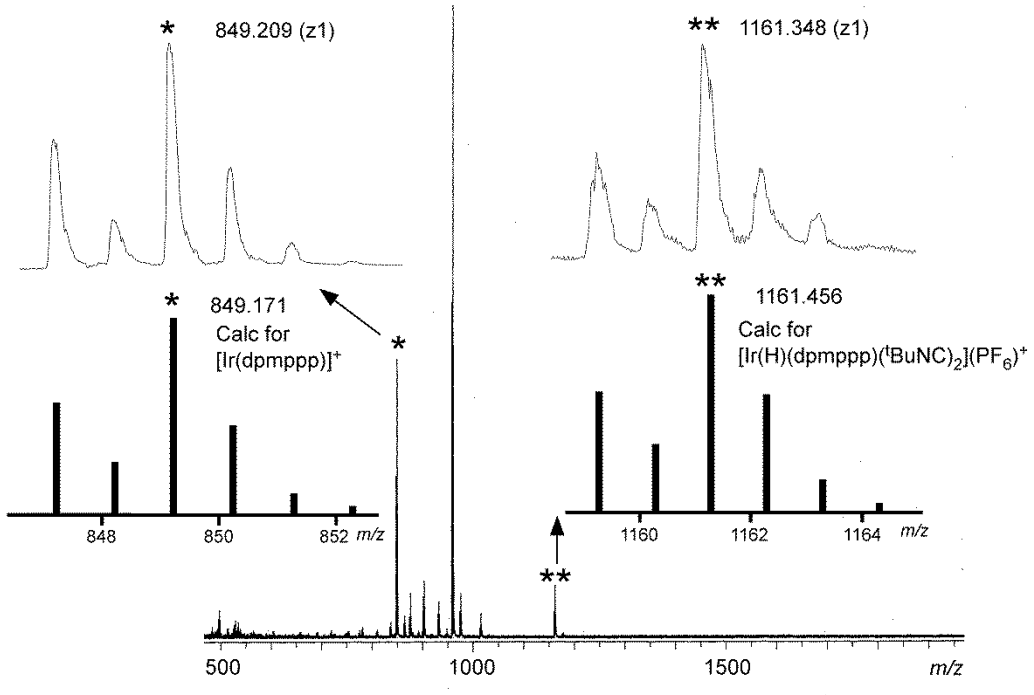


Figure S21. DFT optimized structures of (a) $\mathbf{1}_{opt}$ and (b) $\mathbf{2^*}_{opt}$ using B3LYP functionals and lanl2dz basis set.

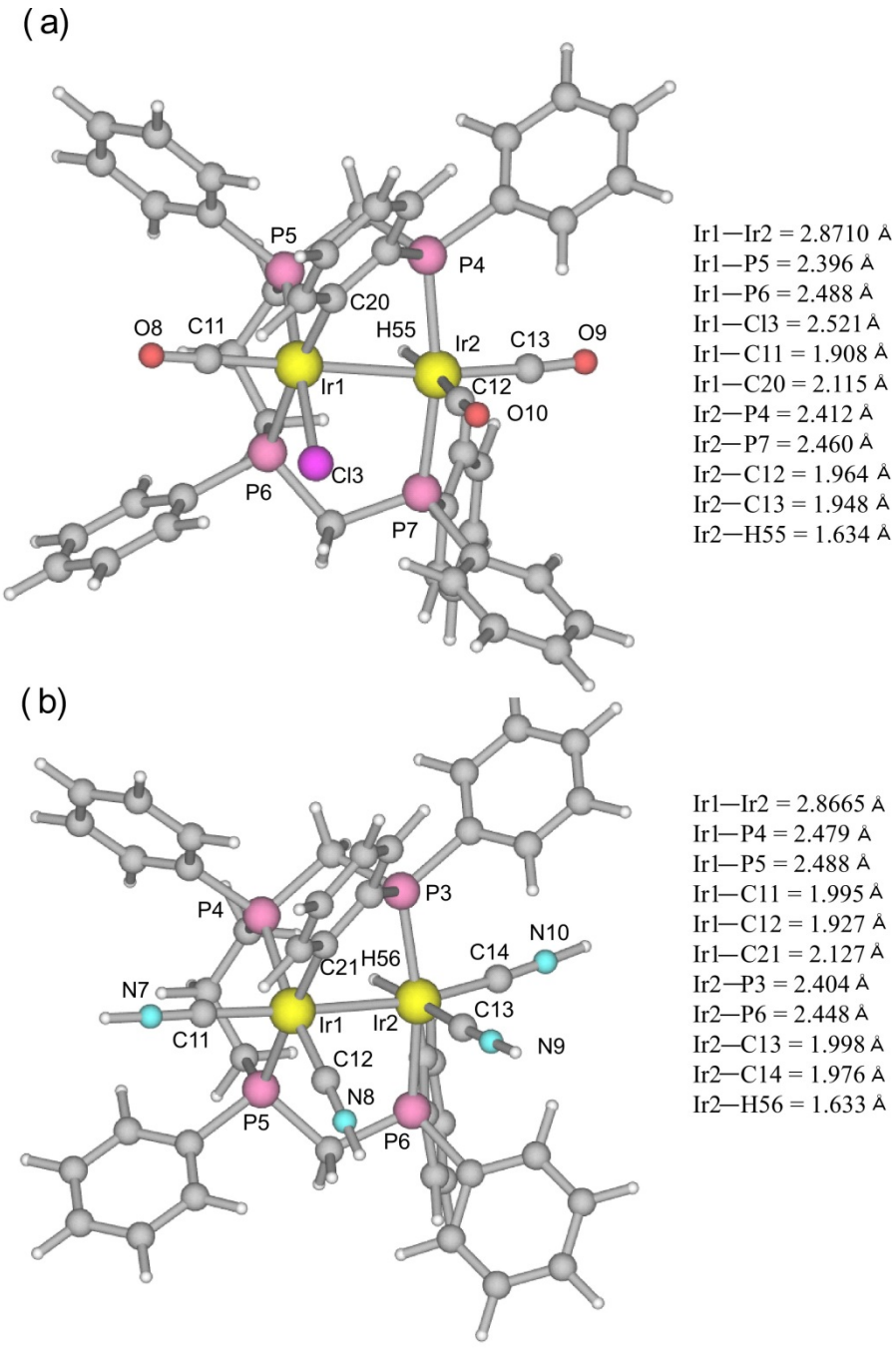
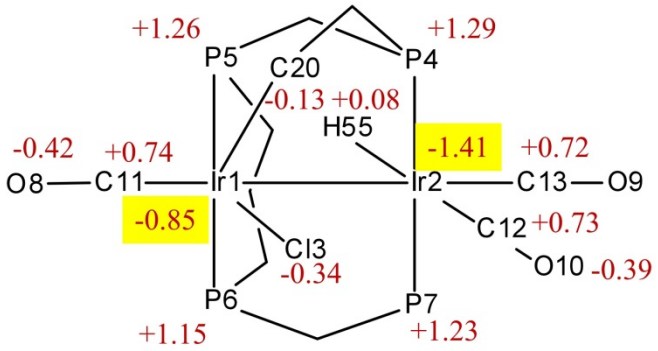
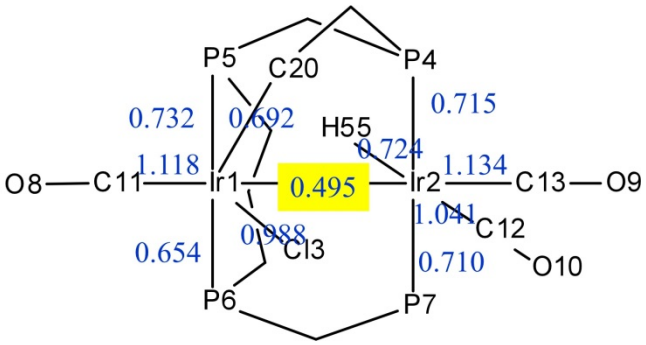


Figure S22. Natural population analyses of $\mathbf{1}_{opt}$ showing natural charge, Wiberg bond indices, and NBO analysis for Ir–Ir and Ir–H bonds.

Natural Charge



Wiberg Bond Index



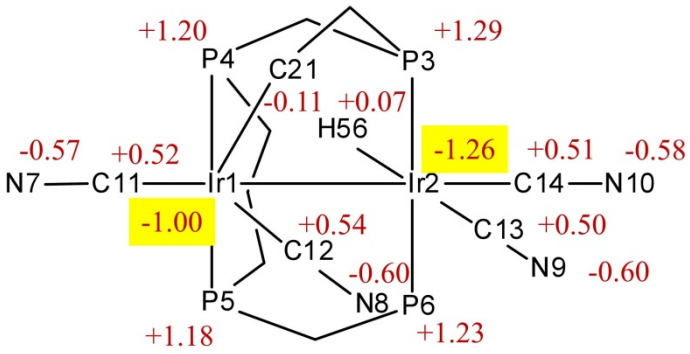
Natural Bond Orbital Analysis

Ir1-Ir2 (1.569)
Ir1 (41.7%) (s 11.9, p 50.5, d 37.6%)
Ir2 (58.3%) (s 10.5, p 50.3, d 39.2%)

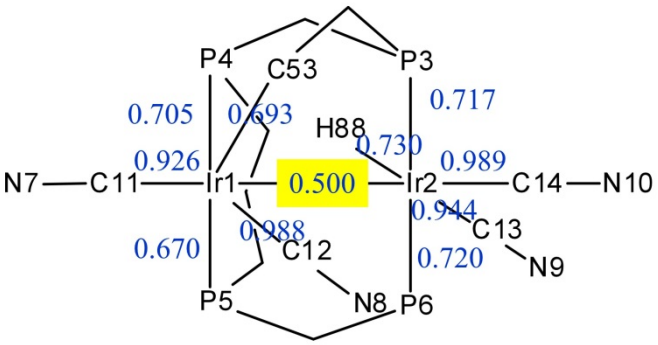
Ir2-H55 (1.786)
Ir2 (51.3%) (s 14.2, p 49.6, d 36.2%)
H88 (48.7%) (s 100%)

Figure S23. Natural population analyses of **2*$_{opt}$** showing natural charge, Wiberg bond indices, and NBO analysis for Ir–Ir and Ir–H bonds.

Natural Charge



Wiberg Bond Index



Natural Bond Orbital Analysis

Ir1-Ir2 (1.552)
Ir1 (50.5%) (s 12.1, p 49.6, d 38.3%)
Ir2 (49.5%) (s 10.6, p 50.8, d 38.6%)

Ir2-H88 (1.780)
Ir2 (50.3%) (s 14.5, p 49.5, d 36.0%)
H88 (49.8%) (s 100%)

Figure S24. (a) DFT optimized structure of **6*$_{opt}$** using B3LYP functionals and lanl2dz basis set. Natural population analyses of **6*$_{opt}$** showing (b) natural charge and (c) Wiberg bond indices. (d) MO diagrams of **6*$_{opt}$**.

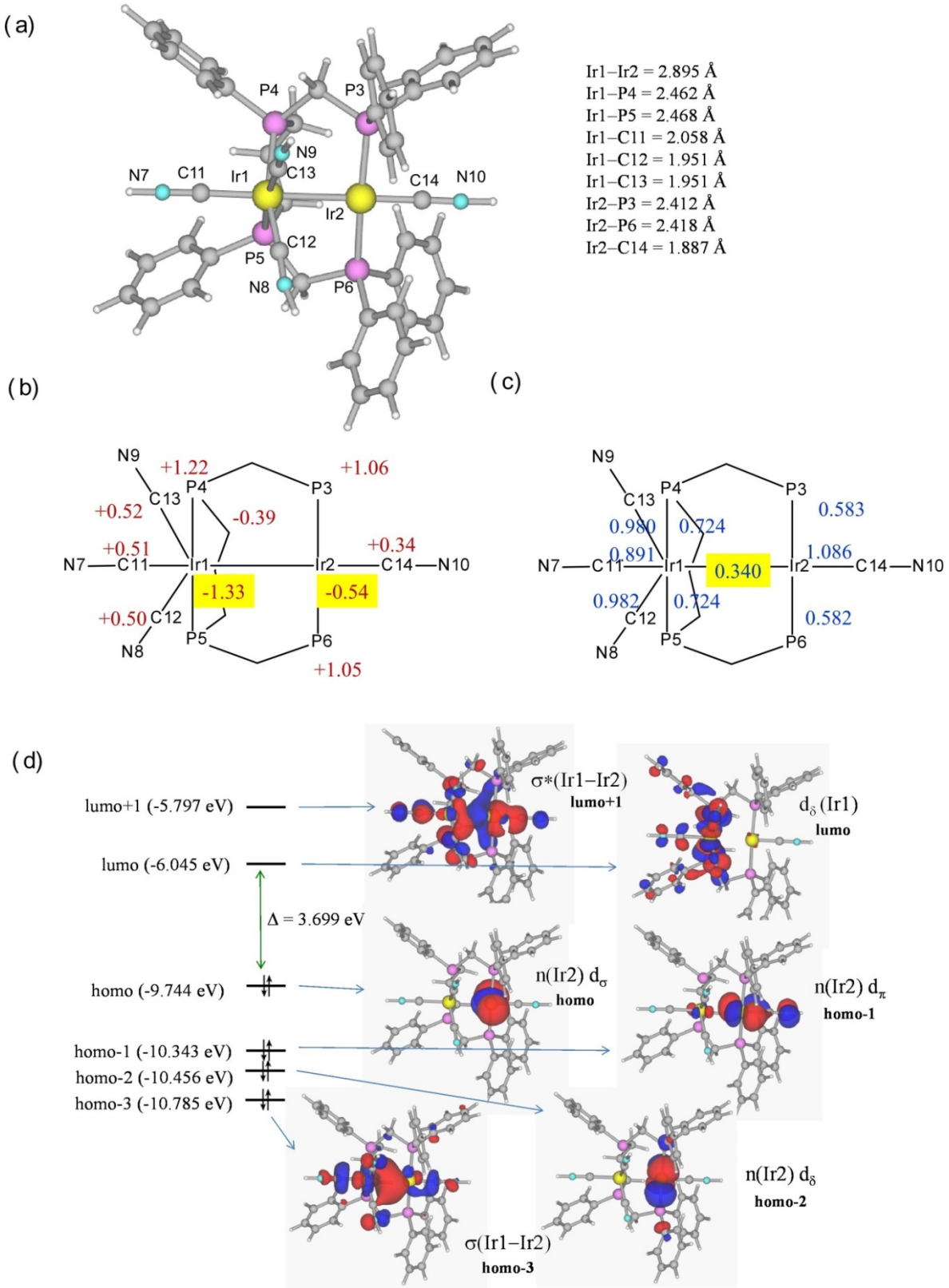


Figure S25. $^{31}P\{^{1}H\}$ NMR spectra of (a) **5** and (b) **6** in CD_2Cl_2 at room temperature (121 MHz). Peaks with asterisk correspond to **6** as impurity.

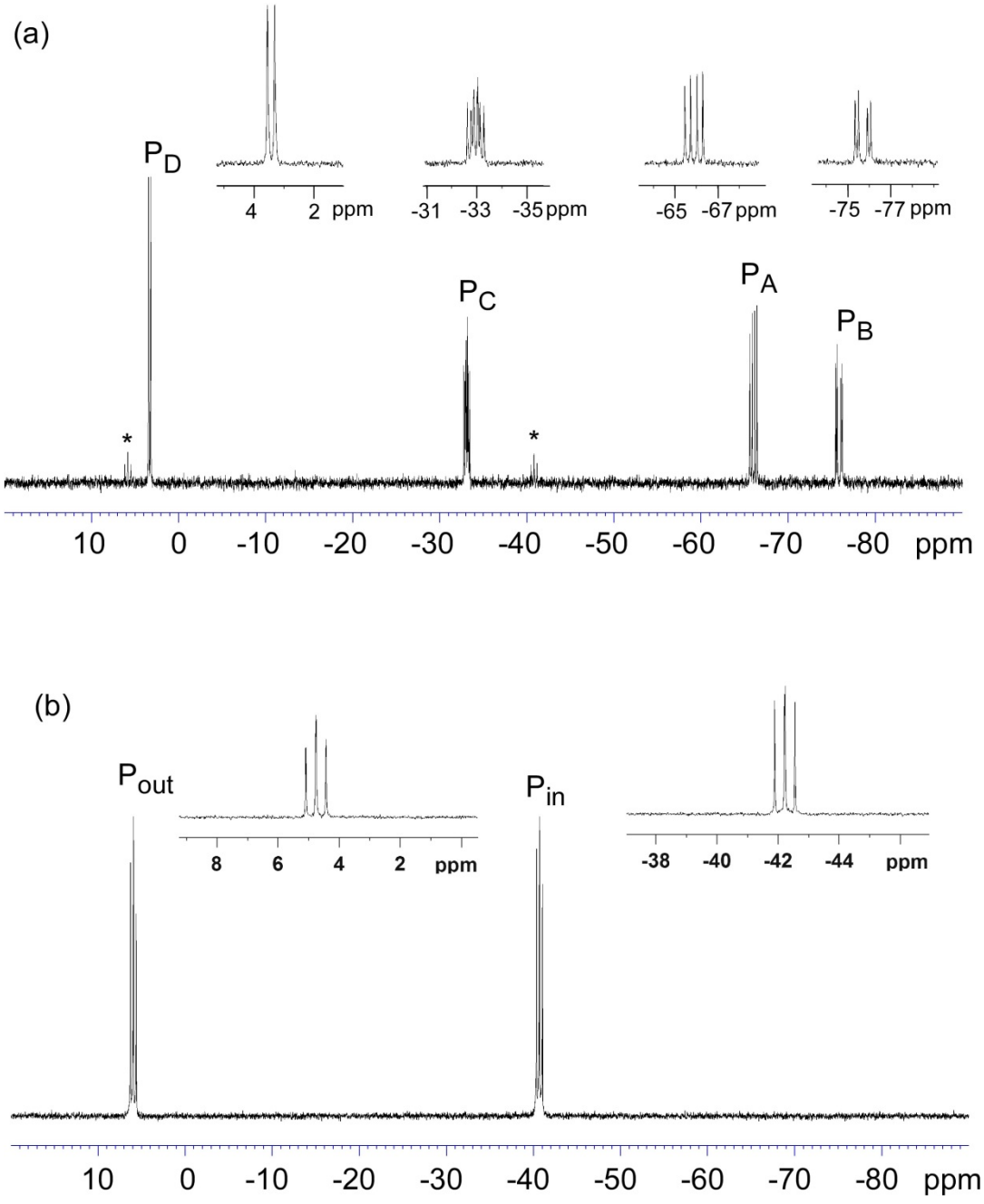


Figure S26. $^{31}P–^{1}H$ HMBC Spectrum of **6** in CD_2Cl_2.

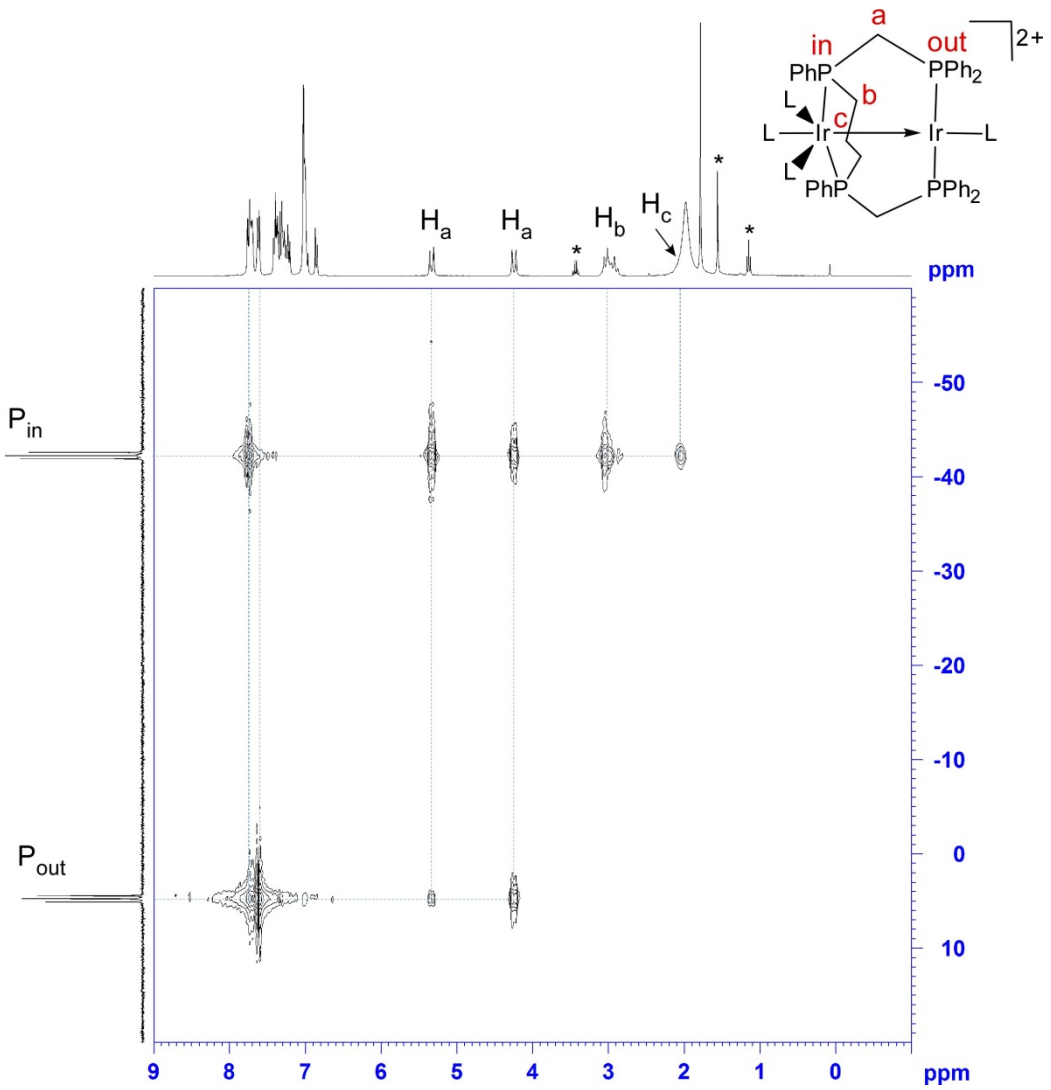


Figure S27. ESI–TOF mass spectra of **5** (a) and **6** (b) in MeOH.

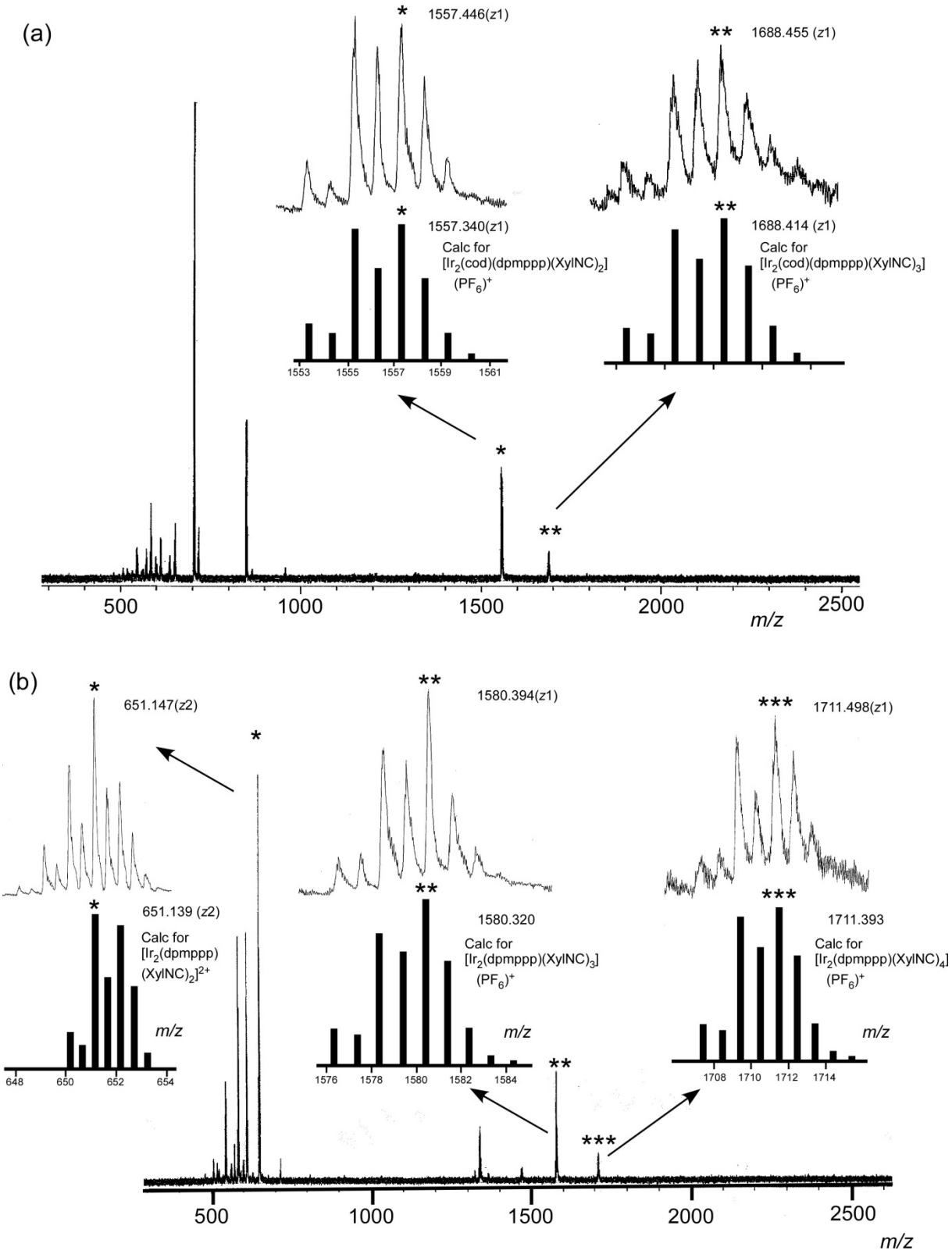


Figure S28. ESI–TOF mass spectra of **7** in MeOH.

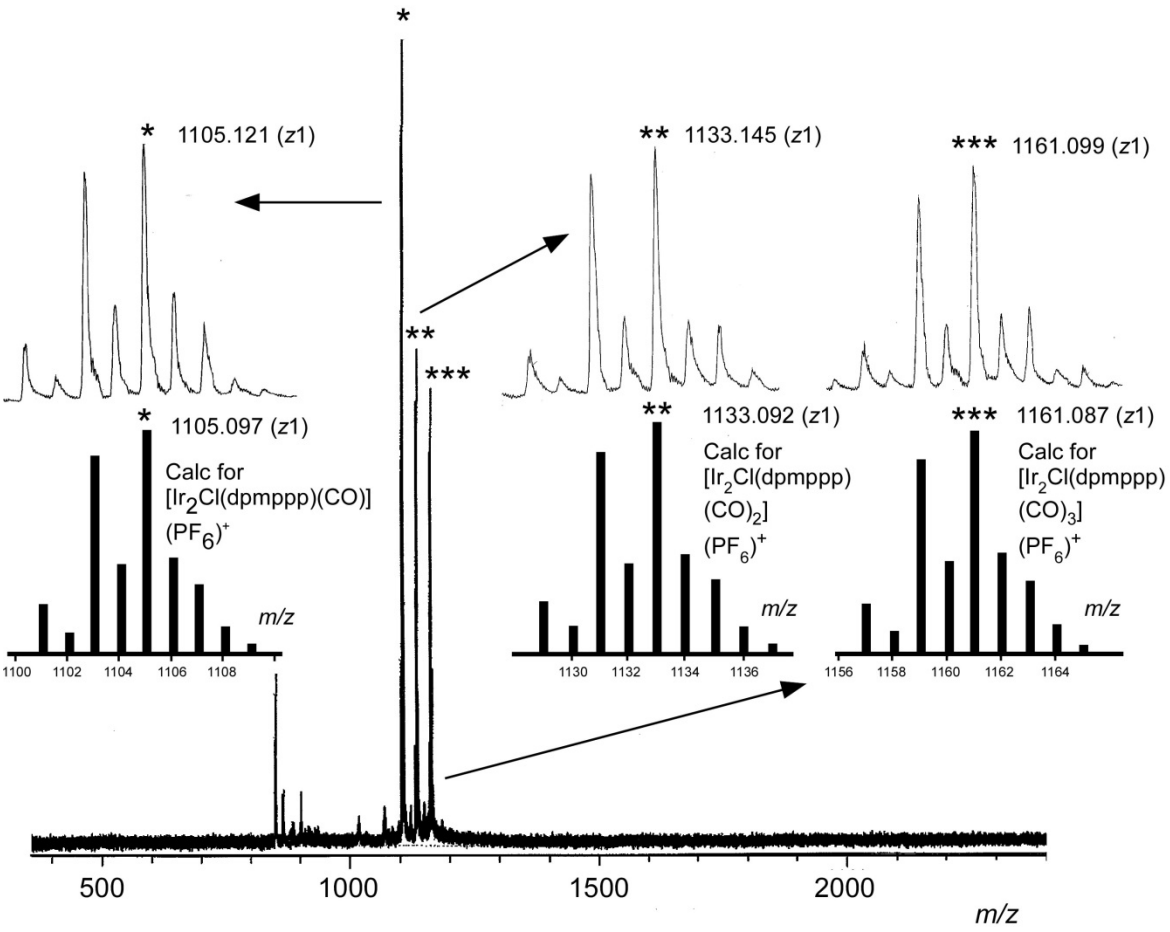
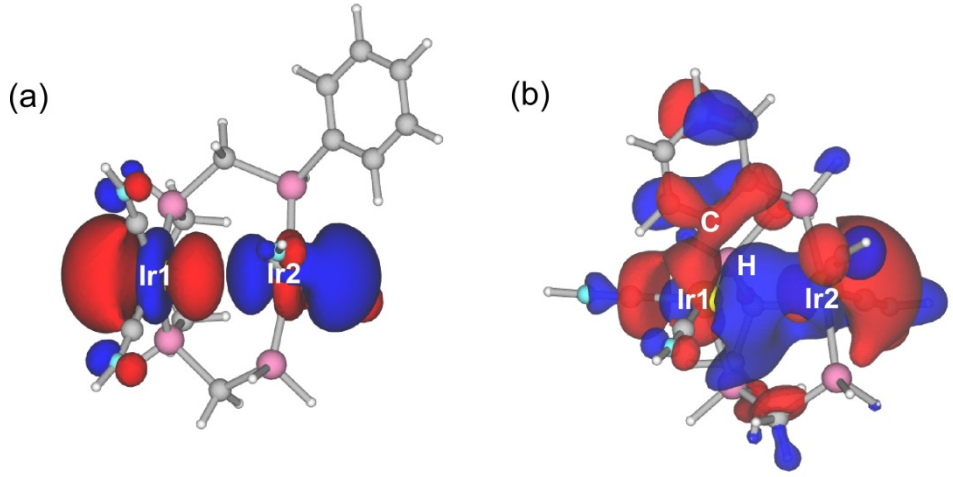


Figure S29. MO diagrams for the HOMOs of (a) **M8** and (b) $\mathbf{TS_{M8\text{-}C}}$.



Appendix 1. Cartesian coordinates of the optimized structure of **1*$_{opt}$**.

Ir 0	11.203130	3.579772	6.309703
Ir 0	8.884625	3.782899	4.628590
Cl 0	12.735048	4.161730	4.393827
P 0	8.306124	5.207360	6.486459
P 0	9.708519	3.048648	8.105946
P 0	11.427552	1.213904	5.574992
P 0	9.671450	2.011245	3.114029
O 0	13.724803	3.441665	8.076028
O 0	6.122088	4.063549	3.201805
O 0	10.353527	6.117746	3.148375
C 0	12.759951	3.485775	7.408988
C 0	9.852154	5.220182	3.703803
C 0	7.171749	3.926958	3.711668
C 0	8.176676	4.170616	8.052556
C 0	8.950012	1.311035	8.135356
C 0	9.879492	0.132614	7.756403
C 0	10.132631	0.005142	6.233521
C 0	11.243442	1.135359	3.698020
C 0	9.764660	6.299027	6.824530
C 0	11.020119	5.645446	6.723623
C 0	12.164313	6.463015	6.907493
C 0	12.051963	7.838180	7.187301
C 0	10.788556	8.449449	7.303738
C 0	9.633315	7.673004	7.115831
C 0	6.760284	6.247707	6.405206
C 0	5.787243	6.213850	7.426535
C 0	4.636320	7.018768	7.330551
C 0	4.453493	7.862749	6.219682
C 0	5.425330	7.900633	5.200289
C 0	6.573017	7.094592	5.289559
C 0	10.416971	3.317157	9.822783
C 0	10.605807	2.247276	10.723197
C 0	11.160275	2.483631	11.995471
C 0	11.528158	3.786682	12.376496
C 0	11.345432	4.855384	11.477370
C 0	10.798411	4.623840	10.203666
C 0	13.079655	0.354625	5.862875
C 0	14.257960	1.012054	5.439285
C 0	15.512164	0.405583	5.628912
C 0	15.606763	-0.854127	6.251025
C 0	14.437668	-1.505465	6.684448
C 0	13.178402	-0.906288	6.490596
C 0	10.051523	2.601844	1.371806
C 0	9.080570	2.469272	0.354885
C 0	9.341092	2.968559	-0.934033
C 0	10.565939	3.603813	-1.214036
C 0	11.526690	3.748628	-0.195360
C 0	11.271490	3.257505	1.097974
C 0	8.479343	0.573700	2.867512
C 0	7.256268	0.487556	3.560233
C 0	6.403089	-0.615672	3.360650
C 0	6.768621	-1.641527	2.470690
C 0	7.991726	-1.559643	1.774946
C 0	8.842167	-0.458059	1.969657
H 0	8.310536	2.564525	5.553159
H 0	7.277639	3.548056	8.025401
H 0	8.153100	4.812171	8.937218
H 0	8.540216	1.169289	9.142726
H 0	8.104701	1.342177	7.440380
H 0	9.385150	-0.789128	8.093158
H 0	10.828901	0.185398	8.306629
H 0	9.204051	0.194896	5.687145
H 0	10.445964	-1.012953	5.977499
H 0	12.107439	1.661506	3.287603
H 0	11.247371	0.099941	3.344196
H 0	13.157604	6.037944	6.802328
H 0	12.954284	8.432907	7.308791
H 0	10.706244	9.511002	7.520231
H 0	8.651151	8.135247	7.177552
H 0	5.909160	5.575691	8.297125
H 0	3.890075	6.986849	8.119767
H 0	3.564340	8.483165	6.147474
H 0	5.289547	8.550187	4.340132
H 0	7.313186	7.133679	4.493436
H 0	10.332284	1.230346	10.457773
H 0	11.304327	1.653380	12.681599
H 0	11.955934	3.967265	13.358890
H 0	11.634808	5.863400	11.761256
H 0	10.685642	5.458041	9.516212
H 0	14.203855	1.993274	4.974198
H 0	16.410269	0.920100	5.298074
H 0	16.577806	-1.318827	6.399884
H 0	14.501988	-2.475529	7.170511
H 0	12.296807	-1.438438	6.835228
H 0	8.131976	1.977350	0.551742
H 0	8.590725	2.860662	-1.712624
H 0	10.766169	3.986837	-2.211145
H 0	12.468189	4.251265	-0.398854
H 0	12.011305	3.415898	1.878259
H 0	6.964597	1.269803	4.253199
H 0	5.457581	-0.667259	3.893996
H 0	6.108909	-2.490957	2.314997
H 0	8.278009	-2.344263	1.079804
H 0	9.771149	-0.400456	1.406706

Appendix 2. Cartesian coordinates of the optimized structure of **2*$_{opt}$**.

Ir 0	9.553891	1.916981	6.366312	C 0	13.596282	-1.249032	1.513978
Ir 0	8.490851	0.930014	3.893936	C 0	13.169080	-0.884500	0.224725
P 0	6.861168	2.591850	4.493922	C 0	11.826786	-0.522076	0.012119
P 0	7.297808	1.486157	7.299498	C 0	10.918910	-0.519344	1.084165
P 0	10.301345	-0.402666	6.864422	H 0	7.655895	-0.071695	4.877394
P 0	10.069090	-0.936491	3.759562	H 0	10.926687	3.275202	10.070696
N 0	10.597080	2.949095	9.181278	H 0	13.076066	2.937757	4.515515
N 0	12.220588	2.627083	4.929810	H 0	10.676390	3.689899	1.633744
N 0	10.181270	3.020466	2.188654	H 0	6.133269	-0.389643	0.731002
N 0	6.738045	-0.095575	1.474129	H 0	5.381313	2.860587	6.472926
C 0	10.187936	2.559046	8.145046	H 0	5.315256	1.192841	5.840262
C 0	11.203705	2.315795	5.454922	H 0	5.901681	-0.301426	8.215525
C 0	9.578656	2.235918	2.842864	H 0	6.560164	-0.736930	6.636934
C 0	7.433529	0.265258	2.363297	H 0	8.283934	-0.718410	9.184974
C 0	5.971930	2.040307	6.056412	H 0	7.359359	-2.110586	8.658576
C 0	6.818313	-0.319640	7.614973	H 0	8.578833	-2.092869	6.434881
C 0	7.878646	-1.214163	8.294443	H 0	9.561015	-2.523738	7.836446
C 0	9.012884	-1.702884	7.360356	H 0	12.026337	-0.504518	5.161036
C 0	11.127985	-1.103928	5.321007	H 0	11.424605	-2.146887	5.473763
C 0	7.757380	4.116324	5.054081	H 0	10.525729	4.908149	6.869742
C 0	8.914259	3.875923	5.839374	H 0	9.777478	7.177837	6.290624
C 0	9.626844	5.022020	6.269537	H 0	7.704496	7.533486	4.938607
C 0	9.202093	6.324450	5.945059	H 0	6.411090	5.560919	4.143559
C 0	8.036836	6.528843	5.183122	H 0	6.986760	3.708752	1.779853
C 0	7.309260	5.415452	4.737295	H 0	5.276800	4.375945	0.114182
C 0	5.542292	3.079603	3.272175	H 0	2.854668	4.120263	0.632650
C 0	5.935466	3.593687	2.018397	H 0	2.154814	3.204567	2.841428
C 0	4.968830	3.970041	1.071207	H 0	3.842190	2.554673	4.521407
C 0	3.602014	3.827717	1.364346	H 0	7.119308	4.364945	7.959990
C 0	3.207425	3.311557	2.609200	H 0	6.523455	5.619968	10.003697
C 0	4.173350	2.938734	3.562383	H 0	5.947232	4.406480	12.111034
C 0	6.857827	2.405044	8.874824	H 0	5.959689	1.911487	12.145014
C 0	6.861290	3.818109	8.862878	H 0	6.520224	0.639455	10.113274
C 0	6.530934	4.534629	10.026160	H 0	10.328281	-1.296655	9.733853
C 0	6.206073	3.850787	11.214409	H 0	12.083016	-1.450252	11.450403
C 0	6.212435	2.445344	11.233192	H 0	14.443932	-0.839091	10.908730
C 0	6.535306	1.723495	10.068762	H 0	15.018444	-0.067298	8.605684
C 0	11.658407	-0.582066	8.160612	H 0	13.279489	0.104102	6.873762
C 0	11.341572	-1.012287	9.468409	H 0	7.272320	-2.033542	4.033267
C 0	12.340960	-1.104400	10.453969	H 0	6.318510	-4.317408	3.819593
C 0	13.670794	-0.762032	10.149234	H 0	7.792258	-6.240494	3.223792
C 0	13.993394	-0.327237	8.851504	H 0	10.229298	-5.858897	2.833268
C 0	12.994408	-0.233894	7.865150	H 0	11.186155	-3.588932	3.022848
C 0	9.298573	-2.647785	3.571345	H 0	13.041637	-1.565295	3.565857
C 0	7.921939	-2.864866	3.782416	H 0	14.626647	-1.543306	1.682610
C 0	7.381504	-4.159044	3.659436	H 0	13.868919	-0.892216	-0.605017
C 0	8.210711	-5.242987	3.323115	H 0	11.488939	-0.249494	-0.983484
C 0	9.585273	-5.027984	3.103866	H 0	9.885787	-0.242843	0.902209
C 0	10.128427	-3.737137	3.223589				
C 0	11.342732	-0.883368	2.380167				
C 0	12.687461	-1.253675	2.587377				

Appendix 3. Cartesian coordinates of the optimized structure of **6*$_{opt}$**.

Ir 0	0.706809	1.236178	-0.924484
Ir 0	-0.676143	-1.150028	-0.044907
P 0	-2.758159	0.057805	0.114631
P 0	-0.646413	2.287432	0.843439
P 0	2.423810	0.517924	0.695576
P 0	1.385377	-2.398589	0.145096
N 0	2.353703	3.917714	-1.692672
N 0	1.895224	-0.710886	-3.074265
N 0	-1.547902	1.786531	-3.027424
N 0	-2.219188	-3.705310	0.718198
C 0	1.754304	2.948001	-1.379742
C 0	1.447010	-0.013012	-2.226999
C 0	-0.735820	1.556731	-2.197852
C 0	-1.612405	-2.709906	0.454195
C 0	-2.480655	1.881836	0.603233
C 0	-0.301029	1.720773	2.608177
C 0	1.183116	1.738495	3.042662
C 0	1.982148	0.519888	2.531233
C 0	2.914084	-1.276534	0.377612
C 0	-3.973774	-0.545005	1.424258
C 0	-3.699783	-0.338715	2.793968
C 0	-4.583938	-0.817731	3.776830
C 0	-5.746251	-1.518931	3.400291
C 0	-6.016465	-1.736867	2.036819
C 0	-5.135024	-1.252968	1.050643
C 0	-3.812926	0.150146	-1.438078
C 0	-4.867177	1.082396	-1.559242
C 0	-5.638500	1.127018	-2.736031
C 0	-5.370320	0.231214	-3.792102
C 0	-4.331207	-0.712373	-3.664781
C 0	-3.552750	-0.751826	-2.491102
C 0	-0.650584	4.167430	0.904335
C 0	-0.386789	4.885707	2.090171
C 0	-0.430781	6.293559	2.090300
C 0	-0.743273	6.993955	0.911166
C 0	-1.005596	6.280998	-0.275679
C 0	-0.953062	4.876403	-0.280630
C 0	4.065864	1.426868	0.567656
C 0	4.771255	1.376669	-0.656397
C 0	6.011190	2.025210	-0.789148
C 0	6.553857	2.742512	0.295899
C 0	5.848867	2.806585	1.511448
C 0	4.610025	2.150377	1.649707
C 0	1.490752	-3.524361	1.655871
C 0	0.721838	-3.204598	2.796014
C 0	0.818008	-3.990951	3.958624
C 0	1.674910	-5.107920	3.987594
C 0	2.428941	-5.439357	2.845698
C 0	2.338986	-4.651908	1.682180
C 0	1.864489	-3.483169	-1.316027
C 0	0.832734	-3.983430	-2.140632
C 0	1.139809	-4.811231	-3.237467
C 0	2.479495	-5.140910	-3.523341
C 0	3.511980	-4.643259	-2.703811
C 0	3.206517	-3.821742	-1.601415
H 0	2.874670	4.741253	-1.936551
H 0	2.160663	-1.436534	-3.715635
H 0	-2.309858	1.829281	-3.680661
H 0	-2.705405	-4.513928	1.050572
H 0	-2.862963	2.531427	-0.188945
H 0	-3.027493	2.118617	1.521552
H 0	-0.906407	2.347091	3.274050
H 0	-0.683722	0.696247	2.669294
H 0	1.668908	2.681389	2.758133
H 0	1.206736	1.705511	4.140220
H 0	1.406946	-0.394539	2.706742
H 0	2.924879	0.417302	3.081376
H 0	3.524353	-1.294539	-0.528603
H 0	3.526120	-1.637705	1.210243
H 0	-2.803835	0.189697	3.110713
H 0	-4.369387	-0.644732	4.828094
H 0	-6.431962	-1.886109	4.158816
H 0	-6.912311	-2.274417	1.738119
H 0	-5.366710	-1.424537	0.003666
H 0	-5.109076	1.759223	-0.742599
H 0	-6.452305	1.841791	-2.822042
H 0	-5.975198	0.258424	-4.694392
H 0	-4.135382	-1.417053	-4.468560
H 0	-2.743459	-1.471897	-2.393266
H 0	-0.153508	4.377054	3.020598
H 0	-0.228802	6.837433	3.008879
H 0	-0.785271	8.079480	0.916306
H 0	-1.252494	6.816305	-1.188543
H 0	-1.149884	4.346315	-1.210397
H 0	4.366031	0.839456	-1.511870
H 0	6.552901	1.968397	-1.729418
H 0	7.514131	3.240415	0.195143
H 0	6.261922	3.357293	2.351973
H 0	4.096558	2.212346	2.604526
H 0	0.029146	-2.366672	2.762889
H 0	0.219858	-3.741488	4.831218
H 0	1.745909	-5.719034	4.883218
H 0	3.079342	-6.309684	2.856655
H 0	2.913430	-4.938955	0.806845
H 0	-0.201583	-3.724310	-1.930934
H 0	0.339446	-5.200352	-3.861021
H 0	2.715769	-5.783657	-4.366867
H 0	4.546113	-4.904279	-2.911681
H 0	4.021229	-3.463923	-0.976198

Appendix 4. Cartesian coordinates of the optimized structure of **M6**.

Ir 0	-1.238983	-1.037442	-0.404389
Ir 0	0.435257	1.307241	-0.119359
P 0	2.018181	0.150413	1.155139
P 0	-0.525671	-1.339877	1.858449
P 0	-2.925593	0.519097	0.279416
P 0	-1.218013	2.566305	-1.150236
N 0	-3.105507	-3.667102	-0.401795
N 0	-1.803604	-0.377271	-3.423199
N 0	1.385819	-2.399719	-1.441464
N 0	2.043290	3.870800	0.387493
C 0	-2.447066	-2.704679	-0.389237
C 0	-1.600976	-0.591767	-2.293166
C 0	0.433324	-1.855516	-1.026519
C 0	1.459053	2.871444	0.137543
C 0	1.310953	-1.354635	2.028232
C 0	-1.123427	-0.198780	3.182429
C 0	-2.611110	0.184645	3.110704
C 0	-2.924338	1.198241	1.996975
C 0	-2.975818	2.009632	-0.816537
C 0	3.581860	-0.417527	0.397795
C 0	4.559863	-1.077097	1.161653
C 0	5.744008	-1.504329	0.560734
C 0	5.962739	-1.274625	-0.800942
C 0	4.999274	-0.609223	-1.563825
C 0	3.810940	-0.178038	-0.967950
H 0	2.472489	0.884550	2.271795
H 0	-0.884207	-2.601713	2.384062
H 0	-4.247064	0.031306	0.166000
H 0	-1.285434	3.939764	-0.838423
H 0	-1.225810	2.676761	-2.559884
H 0	-3.655081	-4.507643	-0.441124
H 0	-1.965688	-0.287263	-4.409785
H 0	2.341439	-2.490789	-1.745857
H 0	2.725226	4.586360	0.209402
H 0	1.691752	-2.259461	1.544699
H 0	1.601920	-1.393764	3.083175
H 0	-0.905319	-0.695687	4.134926
H 0	-0.505103	0.704722	3.130340
H 0	-3.246694	-0.706549	3.025825
H 0	-2.879490	0.648760	4.065961
H 0	-2.190608	2.012468	2.020356
H 0	-3.915121	1.640176	2.153431
H 0	-3.567177	2.807928	-0.356148
H 0	-3.467081	1.738774	-1.755861
H 0	4.410972	-1.251183	2.224525
H 0	6.498685	-2.008993	1.156168
H 0	6.888370	-1.603901	-1.263317
H 0	5.179587	-0.411310	-2.616547
H 0	3.067066	0.359685	-1.551175

Appendix 5. Cartesian coordinates of the optimized structure of **M8**.

Ir 0	0.702520	1.184495	-0.534469
Ir 0	-1.836019	-1.138789	-0.055094
P 0	2.164429	0.060531	0.935353
P 0	-0.505414	-1.245922	1.914578
P 0	-2.821200	0.922255	0.577515
P 0	-1.096741	2.148267	-1.693880
C 0	1.330911	-1.439980	1.663990
C 0	-0.703220	0.030718	3.249334
C 0	-2.109264	0.656206	3.338848
C 0	-2.406777	1.675465	2.221605
C 0	-2.635407	2.316328	-0.656436
C 0	3.823209	-0.467357	0.408816
C 0	4.358233	0.057203	-0.778889
C 0	5.651588	-0.290015	-1.172807
C 0	6.411238	-1.160419	-0.389158
C 0	5.883198	-1.682815	0.795750
C 0	4.595142	-1.337272	1.199715
C 0	-3.071037	-1.221348	-1.550767
N 0	-3.824336	-1.288845	-2.448039
C 0	-1.191306	-2.916418	-0.508481
N 0	-0.820518	-3.997137	-0.775512
C 0	0.968977	-0.163385	-1.947195
N 0	1.189964	-0.883856	-2.843041
C 0	0.881280	2.786437	0.546637
N 0	1.043382	3.775814	1.164381
H 0	2.403111	0.805336	2.110159
H 0	-0.774577	-2.434291	2.627962
H 0	-4.227310	0.836614	0.657414
H 0	-0.978520	3.444714	-2.239351
H 0	-1.567369	1.458964	-2.827366
H 0	1.809258	-1.718891	2.609049
H 0	1.470032	-2.268412	0.960917
H 0	0.038003	0.820814	3.083697
H 0	-0.446680	-0.453112	4.197857
H 0	-2.175312	1.184869	4.296203
H 0	-2.881412	-0.122716	3.374857
H 0	-1.544445	2.336250	2.081072
H 0	-3.255300	2.307822	2.504478
H 0	-2.598584	3.272214	-0.122649
H 0	-3.513628	2.343199	-1.309327
H 0	3.771762	0.743918	-1.383009
H 0	6.065703	0.122405	-2.087856
H 0	7.417371	-1.428937	-0.696573
H 0	6.477468	-2.353763	1.408389
H 0	4.206803	-1.740745	2.130912
H 0	-4.571622	-1.513180	-3.079193
H 0	-0.722728	-4.983777	-0.930027
H 0	1.488113	-1.413035	-3.640559
H 0	1.433094	4.655498	1.455581

Appendix 6. Cartesian coordinates of the optimized structure of **M2**.

Ir 0	1.377366	-0.968037	0.050944
Ir 0	-0.841861	0.840569	-0.349993
P 0	-0.243503	-1.736761	1.551206
P 0	-0.790601	1.113175	2.027334
P 0	0.822107	2.551880	-0.673326
P 0	2.805559	0.326327	-1.317610
C 0	-0.517157	-0.504846	2.904156
C 0	0.398318	2.305454	2.811312
C 0	0.726868	3.567881	1.993561
C 0	1.662177	3.307744	0.795699
C 0	2.185972	2.011653	-1.807452
C 0	-1.853533	-1.888183	0.765564
C 0	-2.204375	-0.794167	-0.053894
C 0	-3.466828	-0.853275	-0.662677
C 0	-4.323655	-1.943204	-0.469234
C 0	-3.950590	-3.010184	0.349848
C 0	-2.707335	-2.980859	0.978630
C 0	-0.836179	0.342250	-2.238242
N 0	-0.875707	0.074235	-3.377687
C 0	-2.367971	2.101123	-0.524999
N 0	-3.261250	2.846949	-0.631158
C 0	0.767650	-2.235759	-1.384365
N 0	0.447641	-3.011042	-2.199144
C 0	2.856582	-2.121639	0.697895
N 0	3.711566	-2.795986	1.120525
H 0	1.813100	0.105634	1.209492
H 0	-0.034487	-2.948590	2.245430
H 0	-2.027151	1.540085	2.552653
H 0	0.377298	3.707975	-1.353788
H 0	4.056712	0.616990	-0.740592
H 0	3.244908	-0.194433	-2.552433
H 0	0.368734	-0.437614	3.543279
H 0	-1.379678	-0.781286	3.517686
H 0	1.320665	1.751932	3.018069
H 0	-0.031850	2.584214	3.779698
H 0	1.233978	4.269443	2.665047
H 0	-0.189938	4.078923	1.671210
H 0	2.478951	2.642958	1.100015
H 0	2.117795	4.246017	0.460848
H 0	3.002222	2.739932	-1.858908
H 0	1.750187	1.928321	-2.808893
H 0	-3.804737	-0.046577	-1.307346
H 0	-5.291697	-1.954930	-0.962634
H 0	-4.618715	-3.852768	0.497490
H 0	-2.403585	-3.804659	1.620072
H 0	-1.069484	-0.139086	-4.337552
H 0	-4.058851	3.448358	-0.727274
H 0	0.189273	-3.750198	-2.824957
H 0	4.443604	-3.377953	1.483524

Appendix 7. Cartesian coordinates of the optimized structure of **A**.

Ir 0	2.485158	0.422802	-0.315924
Ir 0	-1.839674	-0.710845	0.031174
P 0	-1.826155	0.839474	1.802592
P 0	1.343050	0.606745	1.878686
P 0	1.540063	-1.724787	-0.721629
P 0	-1.309594	-1.453787	-2.124526
C 0	4.170561	-0.490772	0.146451
C 0	1.592604	1.166532	-1.864895
C 0	3.412925	2.136984	-0.098756
C 0	-3.394041	-1.888667	0.576783
C 0	-0.202325	1.661713	2.166526
C 0	1.002292	-0.992659	2.806876
C 0	1.397330	-2.288192	2.074197
C 0	0.681496	-2.523013	0.724788
C 0	0.440952	-2.117706	-2.181091
C 0	-2.938635	1.778689	0.727916
C 0	-3.641527	2.983908	0.786587
C 0	-4.457666	3.307474	-0.300519
C 0	-4.561116	2.441141	-1.395072
C 0	-3.855248	1.227814	-1.449087
C 0	-3.040760	0.910000	-0.371216
N 0	-4.319379	-2.531693	0.881410
N 0	1.009699	1.650116	-2.789962
N 0	3.967194	3.154657	0.039649
N 0	5.175989	-1.031848	0.444998
H 0	-0.627811	0.287438	-0.419698
H 0	-2.404094	0.649756	3.074765
H 0	2.170812	1.268874	2.810855
H 0	2.537929	-2.693706	-0.954990
H 0	-2.005658	-2.456116	-2.832761
H 0	-1.297795	-0.430255	-3.086987
H 0	-0.121012	2.529011	1.503115
H 0	-0.207461	2.024742	3.199359
H 0	1.540172	-0.944706	3.758980
H 0	-0.064856	-1.035046	3.054981
H 0	2.483870	-2.323064	1.929696
H 0	1.156314	-3.125972	2.737613
H 0	-0.367501	-2.152671	0.808427
H 0	0.594159	-3.594572	0.512788
H 0	0.378291	-3.209615	-2.244879
H 0	0.940454	-1.767823	-3.089997
H 0	-3.567401	3.645463	1.645000
H 0	-5.022629	4.234141	-0.292946
H 0	-5.208030	2.708385	-2.225997
H 0	-3.969783	0.572108	-2.306861
H 0	-5.129578	-3.069278	1.130701
H 0	1.197821	1.861835	-3.761408
H 0	4.505942	3.999923	0.067511
H 0	6.099552	-1.382317	0.252072

Appendix 8. Cartesian coordinates of the optimized structure of **B**.

Ir 0	-2.260111	-0.144376	0.057926
Ir 0	2.133078	0.002713	0.007391
P 0	1.212975	0.916112	-1.988316
P 0	-1.276375	-1.082854	-1.887832
P 0	-1.154559	-1.681301	1.497346
P 0	1.868639	-0.806356	2.195575
C 0	-0.066522	-0.071188	-2.906094
C 0	-0.530792	-2.786960	-1.769728
C 0	-1.056960	-3.636312	-0.594290
C 0	-0.469180	-3.260414	0.781643
C 0	0.107276	-1.051407	2.742514
C 0	0.496223	2.173984	-0.921158
C 0	0.923147	1.721187	0.347611
C 0	0.582170	2.501445	1.456238
C 0	-0.156662	3.678880	1.277754
C 0	-0.562842	4.102760	0.005628
C 0	-0.233263	3.347889	-1.121416
C 0	3.234498	-1.547068	-0.636645
N 0	3.873816	-2.442762	-1.029384
C 0	3.747131	1.208815	0.231416
N 0	4.657654	1.923472	0.366053
C 0	-3.219094	0.534701	1.605069
N 0	-3.810727	0.942080	2.530340
C 0	-3.390271	0.943829	-1.084019
N 0	-4.094823	1.584121	-1.767310
H 0	0.774512	-0.871176	-0.159776
H 0	1.944114	1.479594	-3.056709
H 0	-2.243742	-1.284107	-2.894753
H 0	-2.081003	-2.191245	2.431442
H 0	2.440534	-2.065816	2.465866
H 0	2.387561	-0.078611	3.286036
H 0	0.447891	-0.736936	-3.610061
H 0	-0.657119	0.632944	-3.504255
H 0	0.557192	-2.684717	-1.703519
H 0	-0.748881	-3.292731	-2.716360
H 0	-0.784351	-4.679110	-0.792952
H 0	-2.153286	-3.613444	-0.561864
H 0	0.619599	-3.172548	0.703272
H 0	-0.675625	-4.057818	1.502984
H 0	0.115936	-1.715658	3.613383
H 0	-0.263895	-0.075907	3.073358
H 0	0.908661	2.236675	2.459846
H 0	-0.403761	4.288858	2.142645
H 0	-1.116314	5.030244	-0.104636
H 0	-0.521542	3.680852	-2.115136
H 0	4.496407	-3.150663	-1.373302
H 0	5.435598	2.547516	0.478005
H 0	-4.437835	1.252493	3.247938
H 0	-4.829876	2.036084	-2.277503

Appendix 9. Cartesian coordinates of the optimized structure of **C**.

Ir 0	1.676461	-1.017152	-0.103756
Ir 0	-1.149711	0.823531	-0.323761
P 0	0.095372	-1.933447	1.392376
P 0	-0.617225	0.919071	2.016647
P 0	0.506249	2.506620	-0.894591
P 0	2.841715	0.442058	-1.524339
C 0	-0.156310	-0.718966	2.774609
C 0	0.633300	2.151116	2.613966
C 0	0.694944	3.465625	1.810841
C 0	1.448004	3.349171	0.470563
C 0	1.799400	1.891732	-2.094495
C 0	-1.592651	-2.095051	0.737120
C 0	-2.220774	-0.980604	0.127588
C 0	-3.563369	-1.140222	-0.243279
C 0	-4.250469	-2.342199	-0.042205
C 0	-3.609652	-3.432097	0.544222
C 0	-2.280760	-3.303523	0.942459
C 0	-1.632463	0.510243	-2.207392
N 0	-1.932137	0.306865	-3.315486
C 0	-2.723457	2.012406	0.001320
N 0	-3.661485	2.685633	0.169073
C 0	1.436270	-2.433434	-1.454020
N 0	1.365320	-3.309215	-2.233157
C 0	2.850328	-0.553092	1.331299
N 0	3.595660	-0.269717	2.225643
H 0	0.099019	-0.246428	-0.693783
H 0	0.317324	-3.149007	2.070450
H 0	-1.761414	1.274233	2.756937
H 0	0.025500	3.608327	-1.635866
H 0	3.977261	1.083227	-0.991235
H 0	3.377343	0.017262	-2.757877
H 0	0.762269	-0.604700	3.358081
H 0	-0.956353	-1.063123	3.436821
H 0	1.612986	1.661508	2.608315
H 0	0.385882	2.361552	3.660446
H 0	1.230669	4.198435	2.424157
H 0	-0.308671	3.883845	1.659869
H 0	2.385320	2.801898	0.623997
H 0	1.720780	4.345304	0.106225
H 0	2.453233	2.715841	-2.401211
H 0	1.256090	1.557148	-2.985393
H 0	-4.099530	-0.316809	-0.707096
H 0	-5.290114	-2.422509	-0.347046
H 0	-4.136670	-4.368348	0.698065
H 0	-1.781568	-4.146294	1.414116
H 0	-2.262753	0.078566	-4.235231
H 0	-4.489122	3.238630	0.301727
H 0	1.526956	-4.157733	-2.744403
H 0	4.438568	-0.638127	2.649277

Appendix 10. Cartesian coordinates of the optimized structure of $\mathbf{TS_{M6\text{-}M8}}$.

Ir 0	9.297355	11.204205	4.777526
Ir 0	11.596605	9.494751	5.777770
P 0	10.663206	13.029929	4.171868
P 0	12.579775	11.641756	6.114029
P 0	10.301765	9.659941	7.822392
P 0	8.025922	9.513991	5.798465
C 0	12.446316	12.735473	4.625750
C 0	12.078527	12.694912	7.555978
C 0	11.702067	11.933701	8.841114
C 0	10.323664	11.247563	8.775999
C 0	8.490314	9.260053	7.584771
C 0	10.657094	13.733349	2.497240
C 0	11.272316	14.974385	2.253163
C 0	11.276109	15.504718	0.964794
C 0	10.665980	14.806690	-0.082350
C 0	10.046525	13.578403	0.157265
C 0	10.039063	13.039930	1.444678
C 0	7.729990	12.328103	4.562168
N 0	6.770079	12.969679	4.368760
C 0	10.675612	9.935381	3.898004
N 0	10.917316	9.469405	2.800670
C 0	11.036636	7.619868	5.640625
N 0	10.739897	6.493066	5.547535
C 0	13.341382	8.921927	5.139425
N 0	14.388696	8.580649	4.739019
H 0	10.374557	14.150217	4.980149
H 0	13.977823	11.565580	6.278881
H 0	10.656199	8.722720	8.816840
H 0	6.624104	9.648600	5.869875
H 0	8.099801	8.210560	5.265033
H 0	12.976821	13.682242	4.773456
H 0	12.919259	12.206064	3.791240
H 0	11.233136	13.316770	7.239875
H 0	12.916407	13.372794	7.753450
H 0	11.670711	12.664571	9.656567
H 0	12.486170	11.216253	9.114830
H 0	9.591166	11.916281	8.308196
H 0	9.964947	11.023564	9.786491
H 0	7.875064	9.913477	8.212680
H 0	8.286924	8.228801	7.889727
H 0	11.739317	15.532048	3.061241
H 0	11.748571	16.464184	0.778392
H 0	10.668973	15.225391	-1.084098
H 0	9.565584	13.043213	-0.655845
H 0	9.543553	12.092339	1.635928
H 0	5.956757	13.504694	4.126288
H 0	10.418727	9.614577	1.926619
H 0	10.613169	5.501506	5.459950
H 0	15.306873	8.200435	4.601875

Appendix 11. Cartesian coordinates of the optimized structure of $\mathbf{TS_{M8\text{-}B}}$.

Ir 0	9.055670	11.655718	4.725951
Ir 0	11.901915	9.660528	5.564652
P 0	10.802549	13.114066	4.008991
P 0	12.616884	11.834943	6.234200
P 0	10.540229	9.371000	7.504144
P 0	8.148529	9.636785	5.523706
C 0	12.360121	13.241905	5.027574
C 0	12.037944	12.516284	7.856540
C 0	11.867483	11.461421	8.967907
C 0	10.564808	10.647589	8.854994
C 0	8.722108	9.037983	7.193835
C 0	10.995502	12.013134	2.583407
C 0	10.173153	10.906248	2.912483
C 0	9.990493	9.892760	1.970944
C 0	10.608192	10.011088	0.718054
C 0	11.395656	11.122430	0.397357
C 0	11.590217	12.147934	1.332810
C 0	8.570568	12.559505	6.352626
N 0	8.298214	13.141350	7.354495
C 0	7.541483	12.315829	3.522295
N 0	6.669513	12.678761	2.836175
C 0	13.277885	9.694344	4.197645
N 0	14.123452	9.698412	3.384743
C 0	11.603215	7.790689	5.159288
N 0	11.426001	6.656232	4.907210
H 0	10.648545	14.438142	3.547918
H 0	14.018543	11.920596	6.377999
H 0	10.876390	8.199646	8.214604
H 0	6.749569	9.499767	5.649649
H 0	8.423477	8.531562	4.696002
H 0	12.332303	14.187930	5.581524
H 0	13.217574	13.291811	4.346967
H 0	11.088914	13.035117	7.684807
H 0	12.770529	13.271452	8.161784
H 0	11.839946	11.991053	9.926723
H 0	12.740878	10.798930	9.017808
H 0	9.720606	11.325243	8.692902
H 0	10.373674	10.114398	9.792529
H 0	8.125804	9.542089	7.962170
H 0	8.522342	7.964717	7.281974
H 0	9.375807	9.024044	2.188843
H 0	10.461706	9.230865	-0.023512
H 0	11.853597	11.194943	-0.584227
H 0	12.179044	13.023927	1.073807
H 0	7.665939	13.807198	7.774724
H 0	5.919949	12.987668	2.243938
H 0	14.956242	9.547388	2.846612
H 0	11.570306	5.666290	4.820189
H 0	10.436989	10.525316	4.281893

Appendix 12. Cartesian coordinates of the optimized structure of $\mathbf{TS_{M8\text{-}C}}$.

Ir 0	1.058558	-1.422949	-0.122191
Ir 0	-0.700157	1.148519	-0.312429
P 0	-0.555752	-1.835388	1.546755
P 0	-0.237807	1.087863	2.053645
P 0	1.456585	2.050165	-0.789986
P 0	2.632365	-0.662483	-1.681393
C 0	-0.380528	-0.574813	2.889415
C 0	1.343984	1.811127	2.706217
C 0	1.985211	2.932070	1.870367
C 0	2.649190	2.428138	0.574613
C 0	2.426418	1.143808	-2.097954
C 0	-2.213605	-1.504863	0.886332
C 0	-2.301847	-0.462422	-0.064662
C 0	-3.538386	-0.249930	-0.695006
C 0	-4.653571	-1.017931	-0.351570
C 0	-4.559457	-2.020082	0.617160
C 0	-3.333363	-2.269608	1.234698
C 0	-1.083176	1.211771	-2.238299
N 0	-1.324006	1.258640	-3.380132
C 0	-1.810818	2.777729	0.023624
N 0	-2.495847	3.709478	0.190146
C 0	0.264696	-2.708237	-1.378793
N 0	-0.167740	-3.510759	-2.128265
C 0	2.424909	-1.341182	1.200770
N 0	3.289932	-1.290551	2.037744
H 0	-0.996725	-0.566860	-0.652400
H 0	-0.679962	-3.053507	2.245618
H 0	-1.207141	1.832600	2.756167
H 0	1.366946	3.312377	-1.419643
H 0	3.985085	-0.733729	-1.295797
H 0	2.721312	-1.252126	-2.958210
H 0	0.523194	-0.764895	3.477235
H 0	-1.246028	-0.592417	3.558720
H 0	2.055465	0.986379	2.817880
H 0	1.114298	2.176839	3.713267
H 0	2.767345	3.388746	2.486904
H 0	1.267453	3.735249	1.660028
H 0	3.233541	1.526371	0.786598
H 0	3.342124	3.182610	0.185927
H 0	3.389995	1.628158	-2.294026
H 0	1.834407	1.203385	-3.017606
H 0	-3.650474	0.523560	-1.447249
H 0	-5.603117	-0.830446	-0.844390
H 0	-5.428265	-2.617681	0.874310
H 0	-3.248825	-3.072221	1.962691
H 0	-1.615885	1.311592	-4.339017
H 0	-3.107616	4.494279	0.323575
H 0	-0.237311	-4.424435	-2.542513
H 0	3.958126	-1.966177	2.394406

Appendix 13. Cartesian coordinates of the optimized structure of $\mathbf{TS_{B\text{-}M2}}$.

Ir 0	-1.464238	-0.866812	0.008332
Ir 0	1.378770	0.620061	-0.292452
P 0	-1.476184	0.416962	1.996498
P 0	1.559743	0.082279	2.027109
P 0	2.125864	-1.552386	-0.957400
P 0	-0.726685	-1.797050	-2.047184
C 0	0.006863	0.186317	3.074111
C 0	2.294585	-1.549634	2.526979
C 0	3.366418	-2.110105	1.574127
C 0	2.773138	-2.754202	0.309330
C 0	0.938843	-2.600144	-1.981475
C 0	-1.366389	1.958560	1.102501
C 0	-0.801115	1.633353	-0.160425
C 0	-0.992950	2.584952	-1.180064
C 0	-1.594222	3.817055	-0.906436
C 0	-2.061723	4.138191	0.374628
C 0	-1.977126	3.183818	1.387707
C 0	-2.470199	-2.430824	0.567758
N 0	-3.076707	-3.365129	0.917142
C 0	-3.091515	0.063357	-0.825322
N 0	-4.050005	0.546361	-1.279214
C 0	1.545320	1.076343	-2.170632
N 0	1.660205	1.334801	-3.311722
C 0	2.253702	2.300869	0.145883
N 0	2.770781	3.329569	0.399493
H 0	-0.191883	-1.611347	0.680105
H 0	-2.550497	0.451142	2.909990
H 0	2.389256	0.985492	2.720329
H 0	3.206717	-1.499875	-1.862795
H 0	-1.520609	-2.785454	-2.669531
H 0	-0.616878	-0.880814	-3.109385
H 0	-0.105072	-0.726492	3.669465
H 0	0.077956	1.033026	3.765222
H 0	1.472245	-2.268807	2.621702
H 0	2.711360	-1.409108	3.530270
H 0	3.919929	-2.886270	2.114439
H 0	4.102301	-1.339755	1.313155
H 0	1.948275	-3.420227	0.589365
H 0	3.525695	-3.372748	-0.190897
H 0	0.817750	-3.588921	-1.526737
H 0	1.324176	-2.749147	-2.994822
H 0	-0.654636	2.391284	-2.192266
H 0	-1.698336	4.542488	-1.709304
H 0	-2.520080	5.103098	0.566312
H 0	-2.409325	3.377630	2.366425
H 0	-3.630901	-4.142965	1.224504
H 0	-4.864775	0.997091	-1.653981
H 0	2.005161	1.669020	-4.192751
H 0	3.530507	3.977739	0.511182

Appendix 14. Cartesian coordinates of the optimized structure of $\mathbf{TS_{C\text{-}M2}}$.

Ir 0	1.382489	-1.187978	-0.037570
Ir 0	-0.874798	0.933079	-0.337731
P 0	-0.256033	-1.773412	1.544938
P 0	-0.705000	1.214050	2.033045
P 0	0.925084	2.477236	-0.862486
P 0	2.802873	-0.008287	-1.496791
C 0	-0.389529	-0.438529	2.845518
C 0	0.612397	2.351658	2.682827
C 0	0.974968	3.556244	1.790316
C 0	1.852889	3.203223	0.569475
C 0	2.193934	1.702399	-1.986235
C 0	-1.917651	-1.785690	0.849006
C 0	-2.280913	-0.653890	0.086608
C 0	-3.585306	-0.638330	-0.427154
C 0	-4.478398	-1.691669	-0.197732
C 0	-4.095248	-2.798158	0.559265
C 0	-2.807643	-2.843401	1.090224
C 0	-0.948311	0.227994	-2.178255
N 0	-1.078209	-0.164547	-3.270397
C 0	-2.348783	2.205711	-0.582347
N 0	-3.198032	2.994822	-0.716279
C 0	0.828197	-2.542836	-1.373208
N 0	0.510867	-3.345532	-2.179944
C 0	2.779389	-1.315603	1.278373
N 0	3.625271	-1.351709	2.117781
H 0	0.748836	0.344601	0.340280
H 0	-0.161912	-2.943091	2.326999
H 0	-1.881854	1.666127	2.660033
H 0	0.590932	3.620267	-1.620270
H 0	4.098584	0.274742	-1.020953
H 0	3.137413	-0.527506	-2.764358
H 0	0.538979	-0.385068	3.422928
H 0	-1.208923	-0.682053	3.528752
H 0	1.505303	1.739659	2.854091
H 0	0.274575	2.700886	3.664771
H 0	1.545572	4.255563	2.411136
H 0	0.074578	4.103178	1.482097
H 0	2.628642	2.486440	0.864174
H 0	2.368285	4.098472	0.205148
H 0	3.050092	2.373430	-2.117476
H 0	1.709685	1.604587	-2.964215
H 0	-3.931630	0.196986	-1.028099
H 0	-5.479907	-1.641754	-0.615795
H 0	-4.788273	-3.614593	0.735700
H 0	-2.496852	-3.700578	1.682274
H 0	-1.250516	-0.602379	-4.156073
H 0	-3.953417	3.645522	-0.834276
H 0	0.567928	-4.250481	-2.616309
H 0	4.358529	-1.945453	2.478839