Supporting Information

Synthesis of Di- and Trinuclear Iridium Polyhydride Complexes surrounded by Light-Absorbing Ligands.

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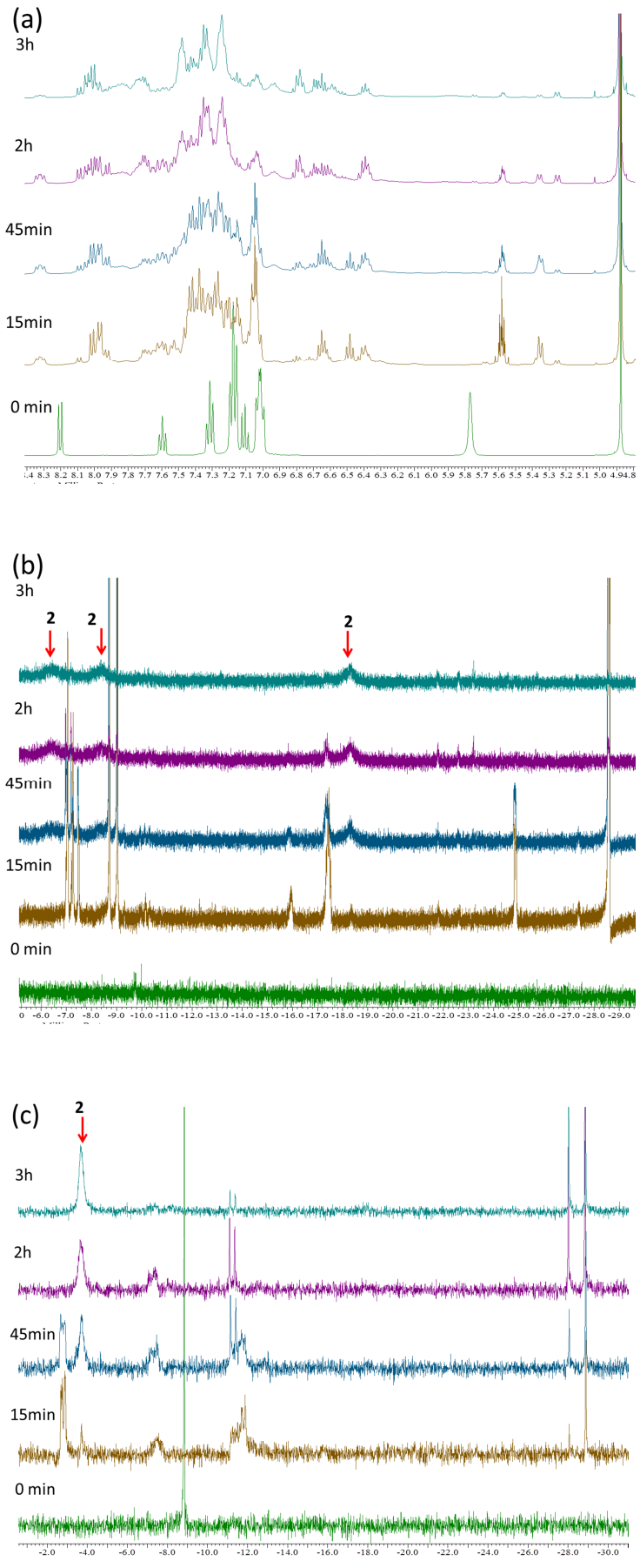

Figure S1. ^{1}H NMR spectra (400 MHz, CD_3OD) of (a) lower field region, (b) higher field region, and (c) ^{31}P NMR spectra (162 MHz, CD_3OD) of complexes after treatment of atmospheric pressure of H_2 with **1**.

Experimental Procedures

General. All experiments were carried out under a nitrogen atmosphere using standard Schlenk techniques. All solvents were treated with appropriate drying agents, distilled, and stored under a nitrogen atmosphere. All the chemicals were purchased from common commercial suppliers. ^{1}H, ^{31}P, and ^{13}C NMR spectra were acquired on a JEOL JNM-AL400 FT-NMR spectrometers. Solvents for NMR measurements (CD_3OD, $(CD_3)_2CO$ CD_2Cl_2) were dried over molecular sieves, degassed, and stored under N_2. Electrospray ionization (ESI) mass spectra were recorded on a Bruker MicroTOF II mass spectrometer. UV−vis absorption and steady-state emission spectra were obtained on a JASCO V-670 and SHIMADZU RF-5300PC spectrometer, respectively.

Computational Details. DFT calculations were performed using the Gaussian-16 Revision A.03 quantum chemistry program package[i] at the B3LYP/LanL2DZ level[ii,iii]. We used the LanL2DZ pseudo-potential for Ir, 6-31G(d)[iv] split-valence basis set for P, and 3-21G[v] for C and H. The orbital energies were determined by using minimized singlet geometries to approximate the ground state.

Preparation and spectral data of 1.

To a acetone (6 mL) solution of $[Ir(cod)_2]BF_4$ (0.17 g, 0.35 mmol), a solution of diphosphine ligand (0.19 g, 0.35 mmol) in THF (4 mL) was added. After stirring for 1.5 h, the blue-purple solution was concentrated under vacuum and Et_2O was added for recrystallization. **1^{Ph}** was obtained as blue-purple crystals (0.28 g, 0.31 mmol, 88%)

^{1}H NMR (400 MHz, acetone-d_6, δ/ ppm) 8.27 (d, J = 7.60 Hz, 2H), 7.62 (t, J = 7.60 Hz, 2H), 7.35 (t, J = 7.60 Hz, 4H), 7.23 (t, J = 6.80 Hz, 8H), 7.15-7.07 (m, 12H), 5.84 (s, 4H), 2.69-2.53 (m, 8H). $^{31}P\{^{1}H\}$ NMR (162 MHz, acetone-d_6, δ/ ppm) -8.83. $^{13}C\{^{1}H\}$ NMR (100.8 MHz, acetone-d_6, δ/ ppm) 140.6-140.4 (m, Ar), 135.1-134.9 (m, Ar), 131.9 (s), 130.1-129.0 (m, Ar), 128.9-128.8 (m, Ar), 121.6 (s, Ar), 91.2-91.1 (m, -*C*H= (cod)), 76.7 (t, $J_{C\text{-}P}$ = 24.1 Hz, Ar), 68.4 (s, -*C*H_2- (cod)). Anal. Calcd. for $C_{45}H_{40}IrP_2BF_4 \cdot CH_2Cl_2 \cdot C_4H_8O$ (THF): C, 55.67; H, 4.67. Found: C, 55.85; H, 4.34.

Preparation of 2 and 3.

To a stainless autoclave, **1** (62.2 mg, 0.0675 mmol) was added and dissolved in MeOH (3 mL) under a hydrogen atmosphere. The reaction mixture was stirred under H_2 (10 atm) for 30 minutess, and it was allowed to stand for 1 week to obtain **3** as yellow crystals (10.7 mg, 0.00470 mmol, 20.9%) and **2** dissolved in a mother liquid. The mother liquid was separated and the solvent was removed under reduced pressure to obtain **2** as a yellow powder (39.2 mg, 0.0254 mmol, 75.2%).

Complex **2**.

^{1}H NMR (400 MHz, CD_2Cl_2, 203 K, δ / ppm) 8.15–5.55 (br, 56 H), -3.90 (S, 1 H), -6.51 (d, J =

74.8 Hz, 2 H), -8.36 (t, J = 65.0 Hz, 1H), -8.94 (t, J = 49.8 Hz, 2H), -16.3 (s, 2H), -18.5 (s, 2H).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 203 K, δ / ppm), -4.07 (s), -4.80 (s).

Anal. Calcd. for $C_{74}H_{61}Ir_2P_4BF_4 \cdot CH_2Cl_2$: C, 55.25; H,3.89. Found: C, 55.26; H, 3.98.

Complex **3**.

^{1}H NMR (400 MHz, CD_2Cl_2, 203 K, δ / ppm) 8.30–5.40 (br, 84H), -3.21 (d, J = 36.0 Hz, 1H), -5.25 – -5.75 (m, 1H), -8.65 (d, J = 74.4 Hz, 1H), -10.1 – -10.8 (m, 1H), -11.4 – -12.1 (m, 2H), -12.8 – -13.5 (m, 4H), -20.2 (s, 2H).

$^{31}P\{^{1}H\}$ NMR (162 MHz, CD_2Cl_2, 203 K, δ / ppm) -4.13, -7.93, -12.5, -23.6 (br).

Anal. Calcd. for $C_{111}H_{90}Ir_3P_6BF_4 \cdot 3CH_2Cl_2$: C, 54.16; H,3.83. Found: C, 54.47; H, 3.82.

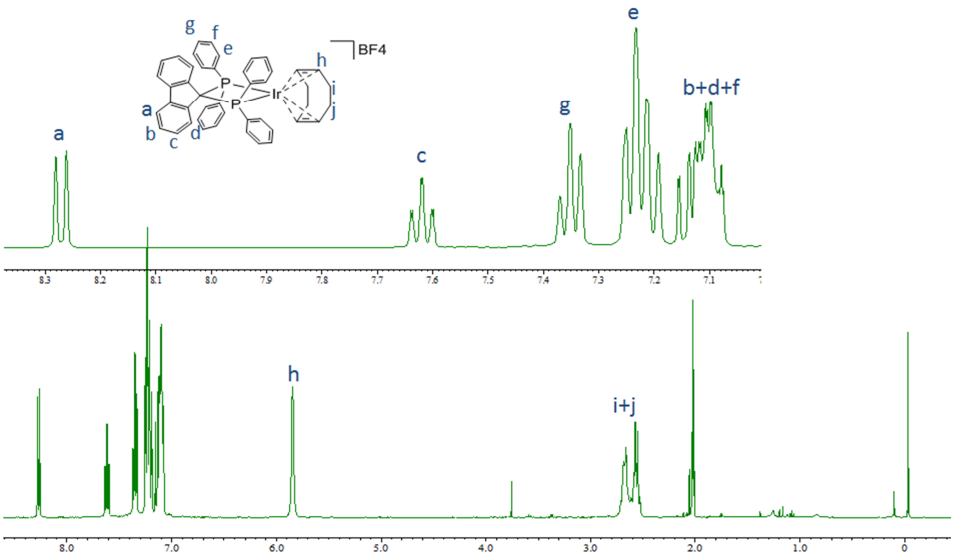

Figure S2. ^{1}H NMR spectrum of **1** (400 MHz, acetone-d_6).

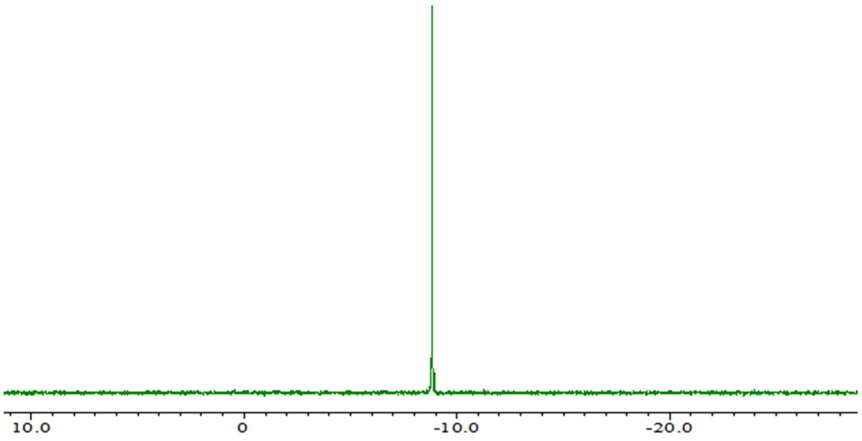

Figure S3. ^{31}P NMR spectrum of **1** (162 MHz, acetone-d_6)

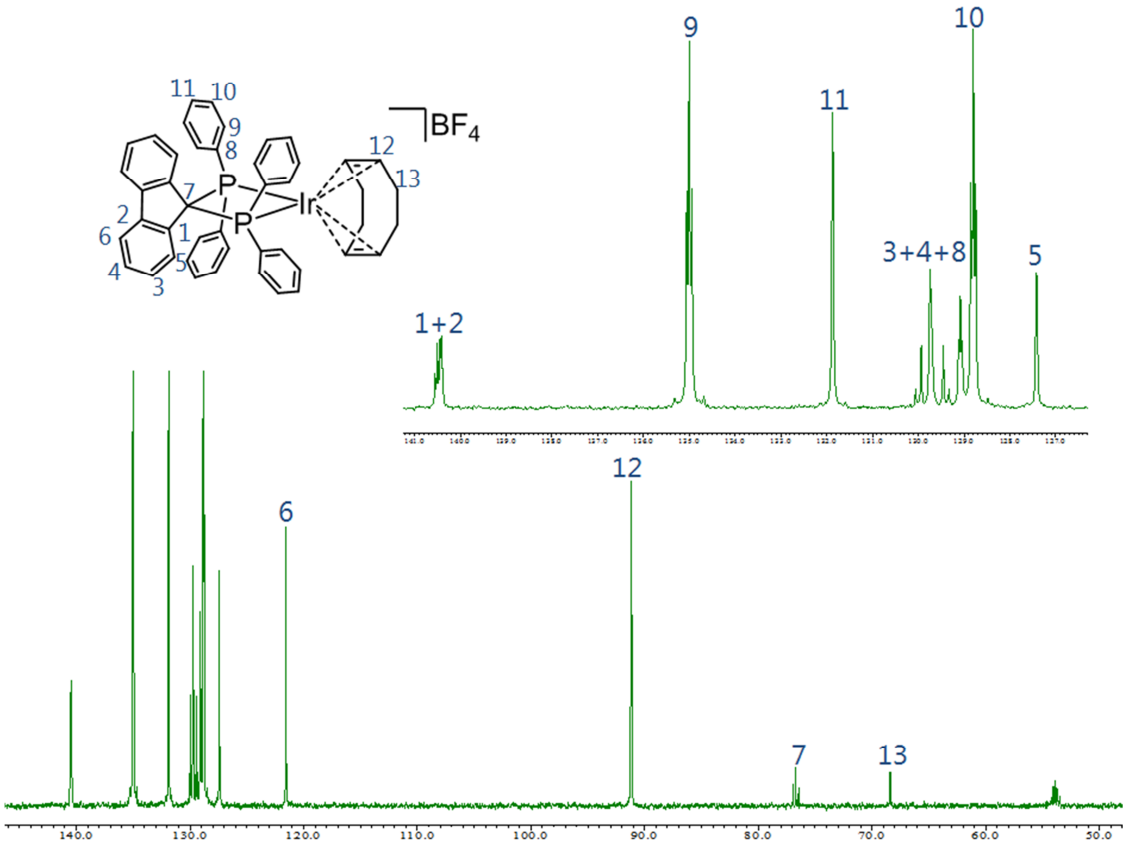

Figure S4. ^{13}C NMR spectrum of **1** (100.8 MHz, acetone-d_6).

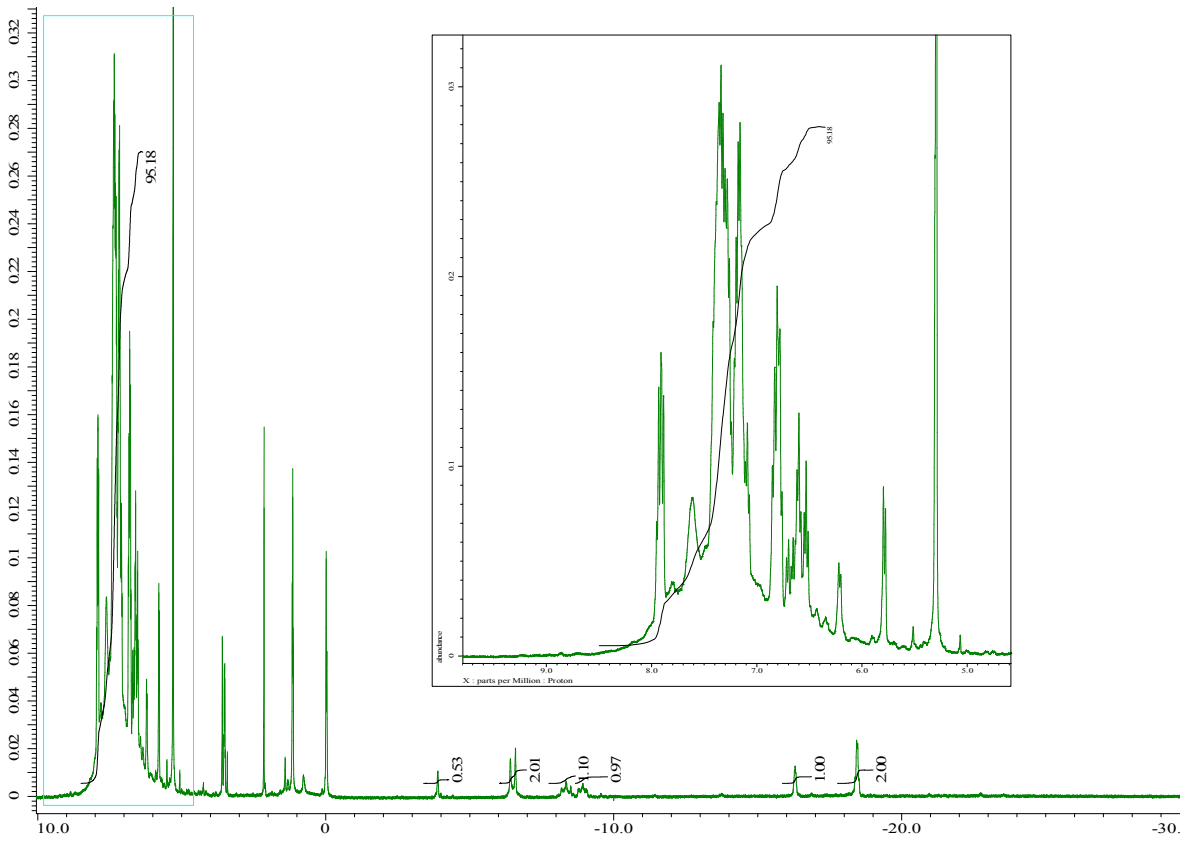

Figure S5. ^{1}H NMR spectra of **2** at 203K (400 MHz, CD_2Cl_2).

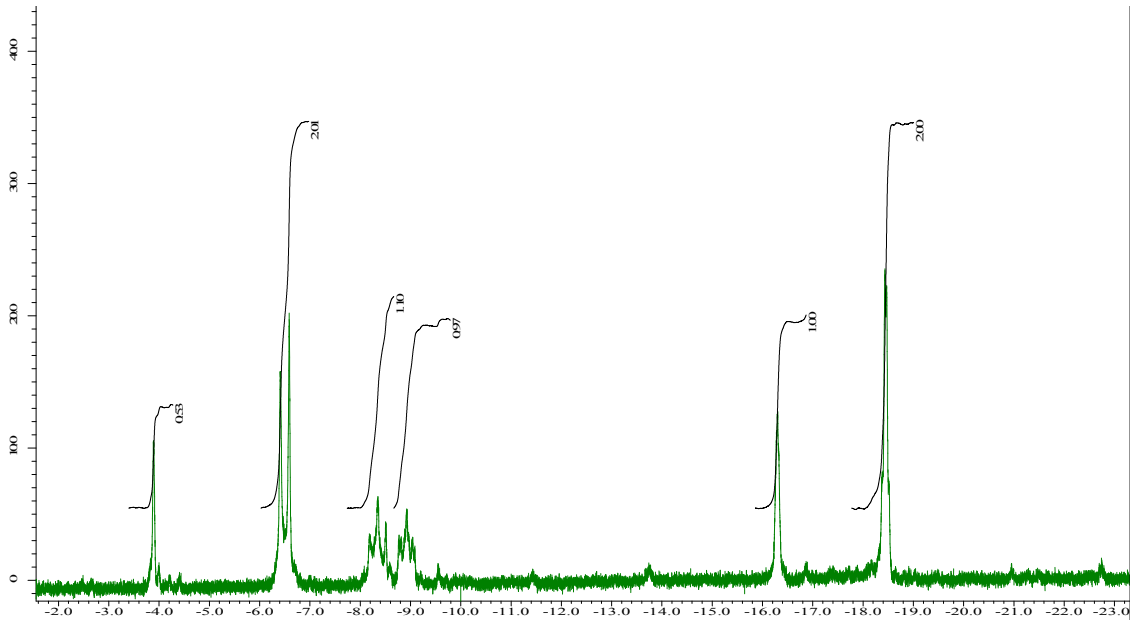

Figure S6. ^{1}H NMR spectra of hydride region of **2** at 203K (400 MHz, CD_2Cl_2).

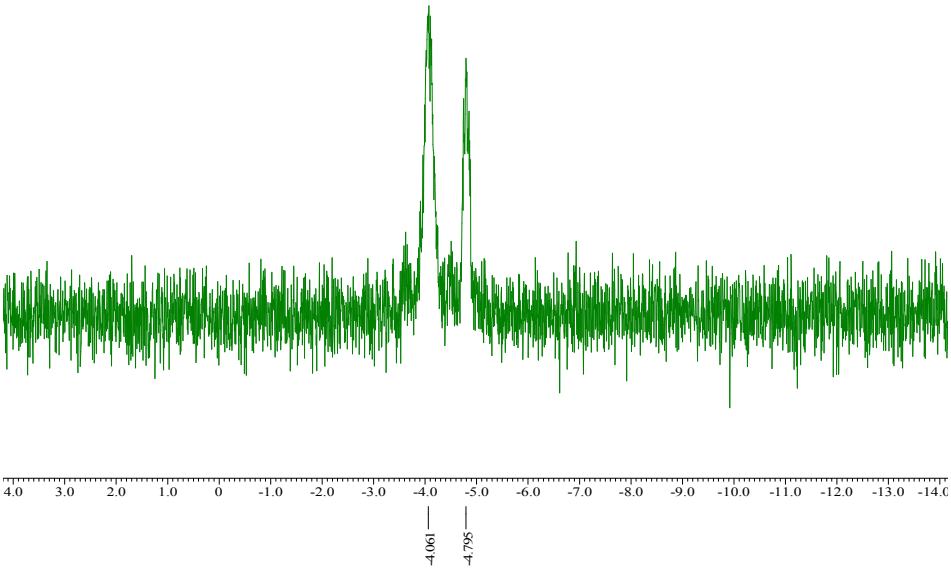

Figure S7. ^{31}P NMR spectra of **2** at 203K (161.8 MHz, CD_2Cl_2).

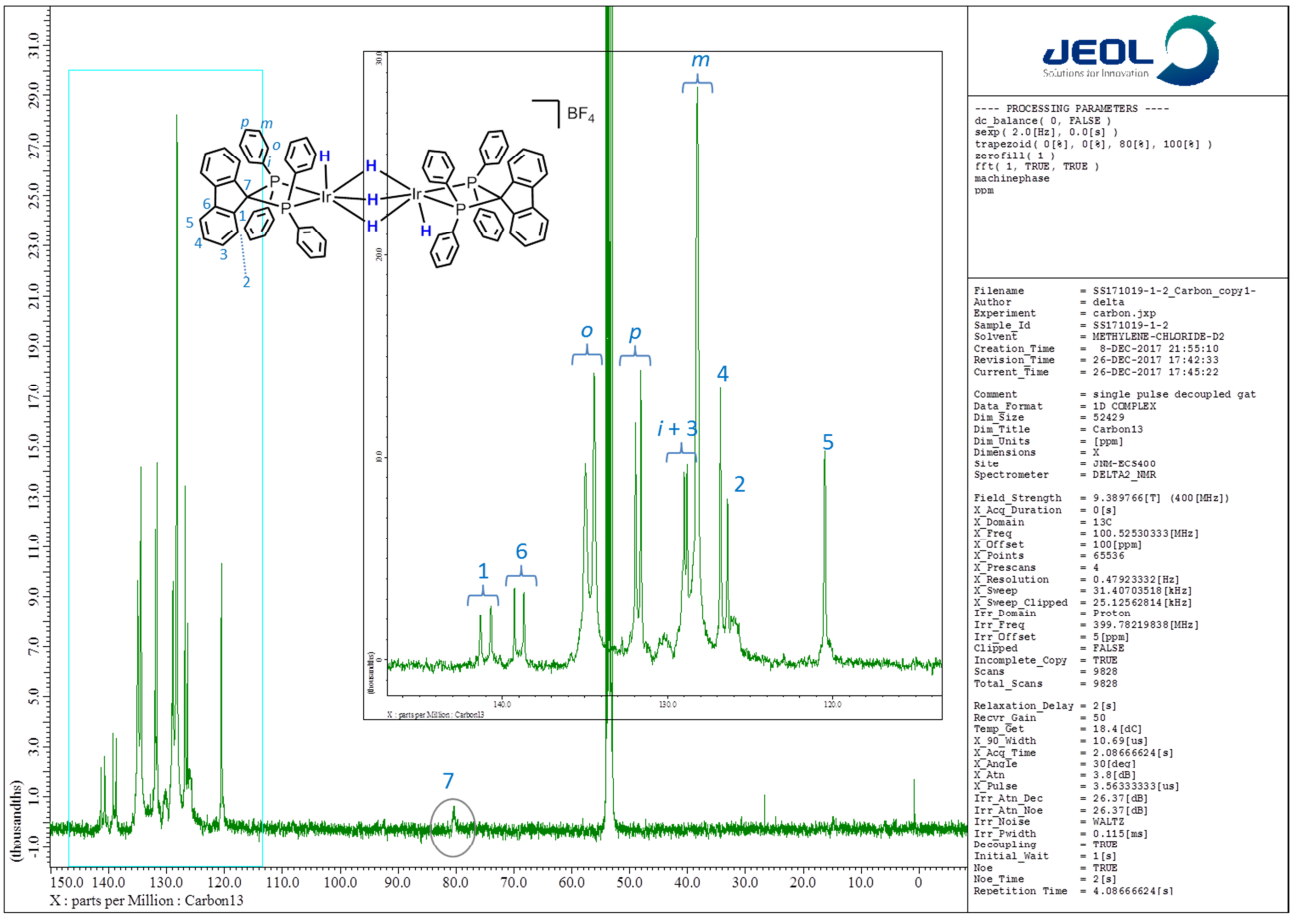

Figure S8. ^{13}C NMR spectra of **2** at 291 K (100 MHz, CD_2Cl_2).

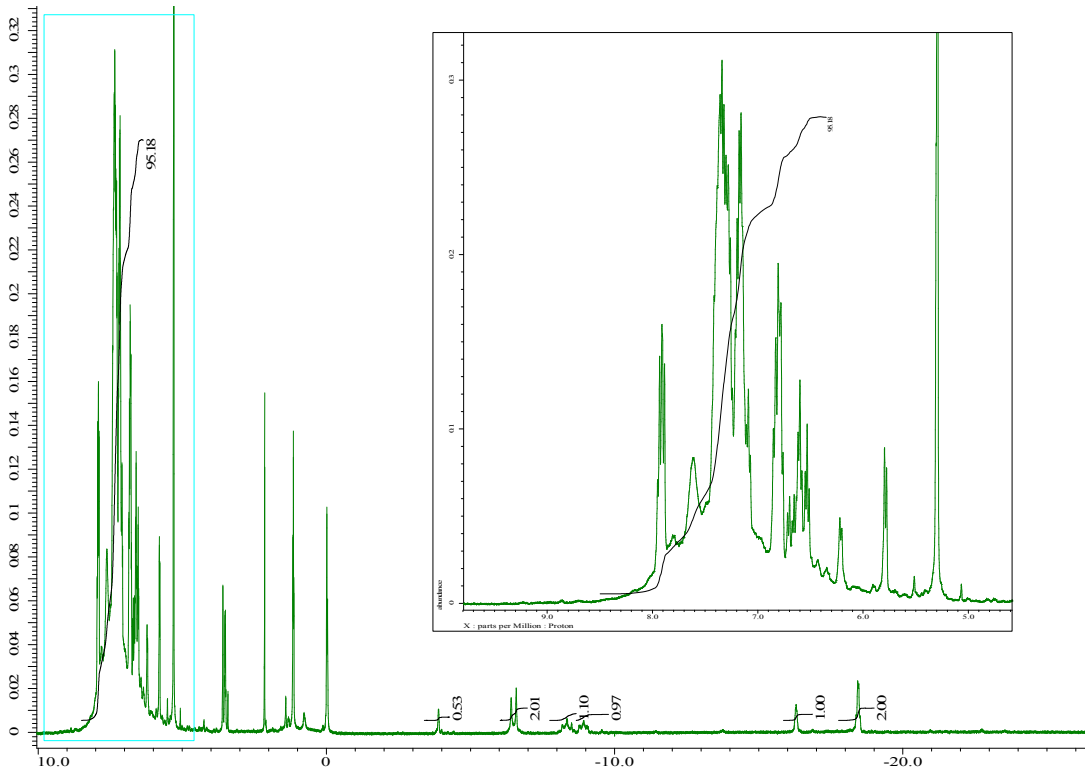

Figure S9. ^{1}H NMR spectra of **3**at 203K (400 MHz, CD_2Cl_2).

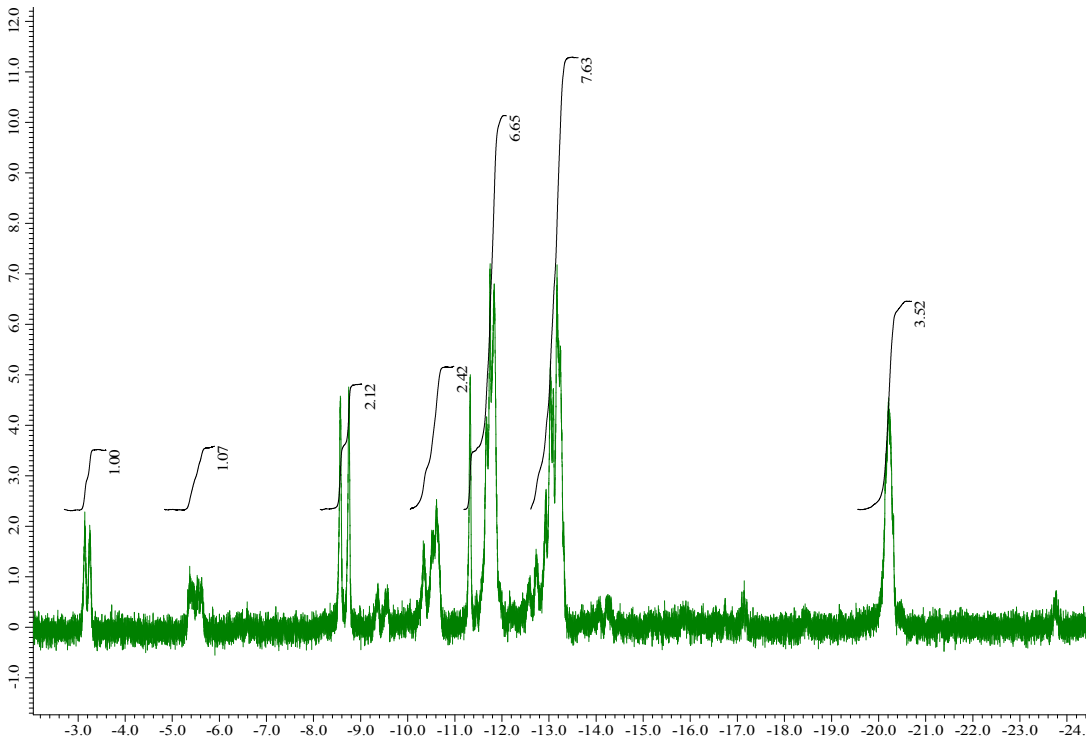

Figure S10. ^{1}H NMR spectra of hydride region of **3** at 203K (400 MHz, CD_2Cl_2).

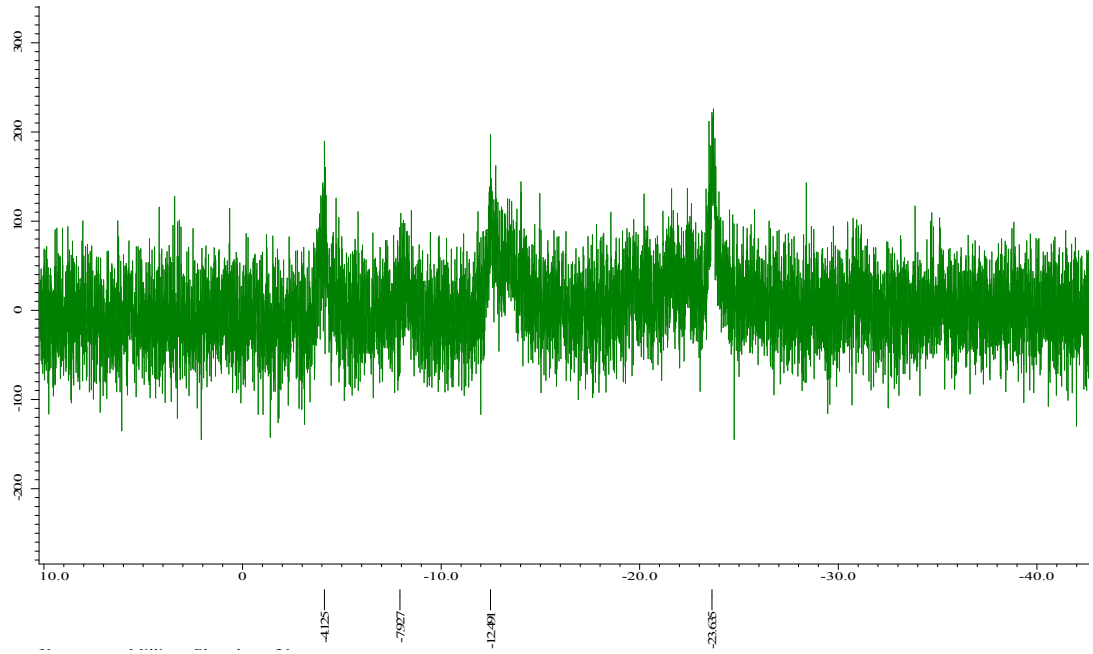

Figure S11. ^{31}P NMR spectra of **3** at 203K (161.8 MHz, CD_2Cl_2).

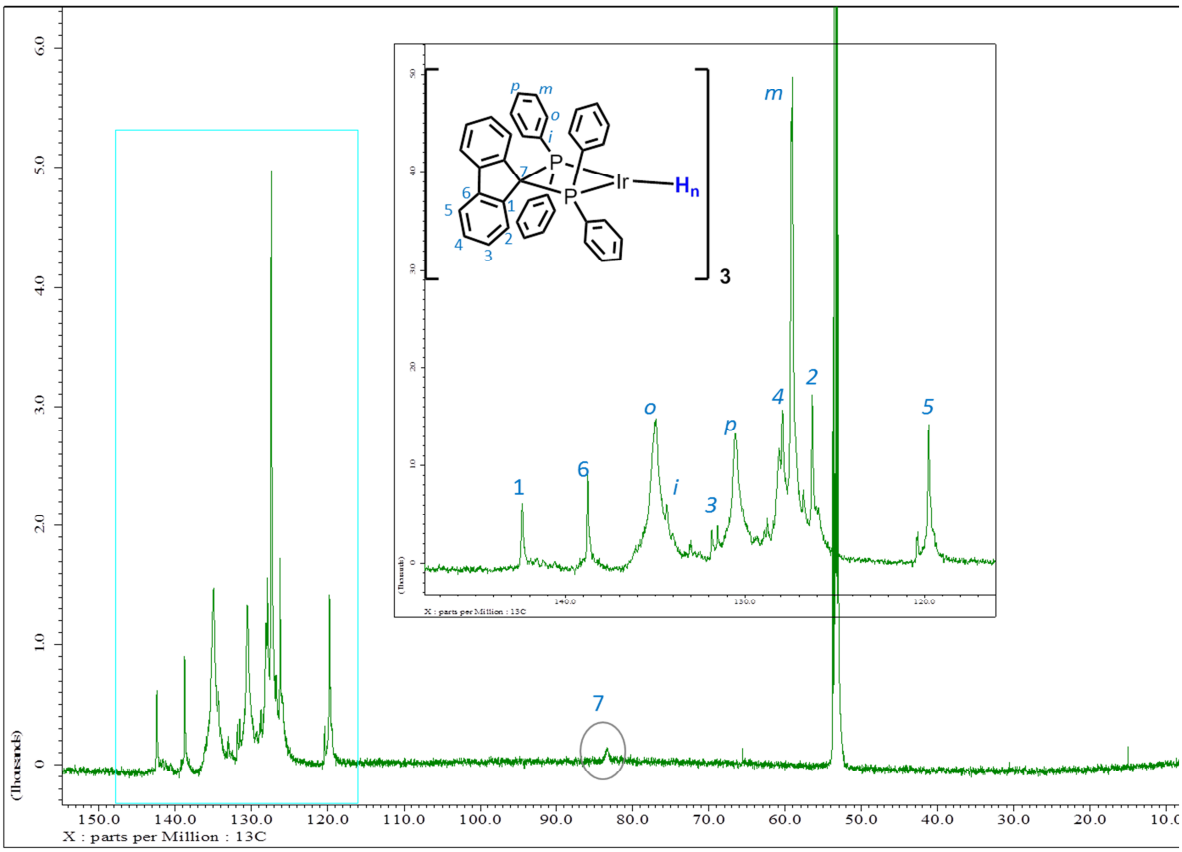

Figure S12. ^{13}C NMR spectra of **3** at 300 K (150 MHz, CD_2Cl_2).

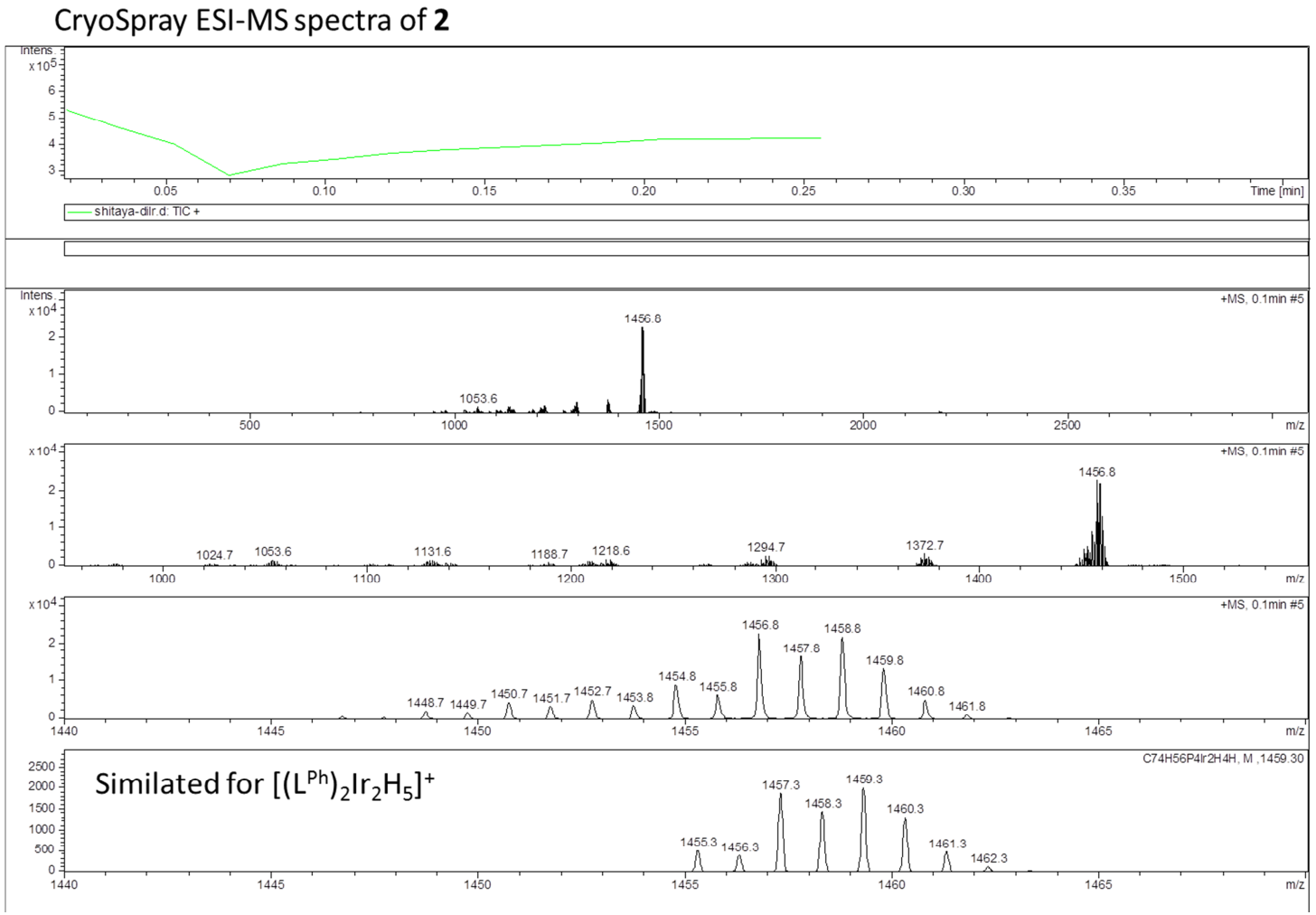

Figure S13. CryoSpray ESI-MS spectra of **2**.

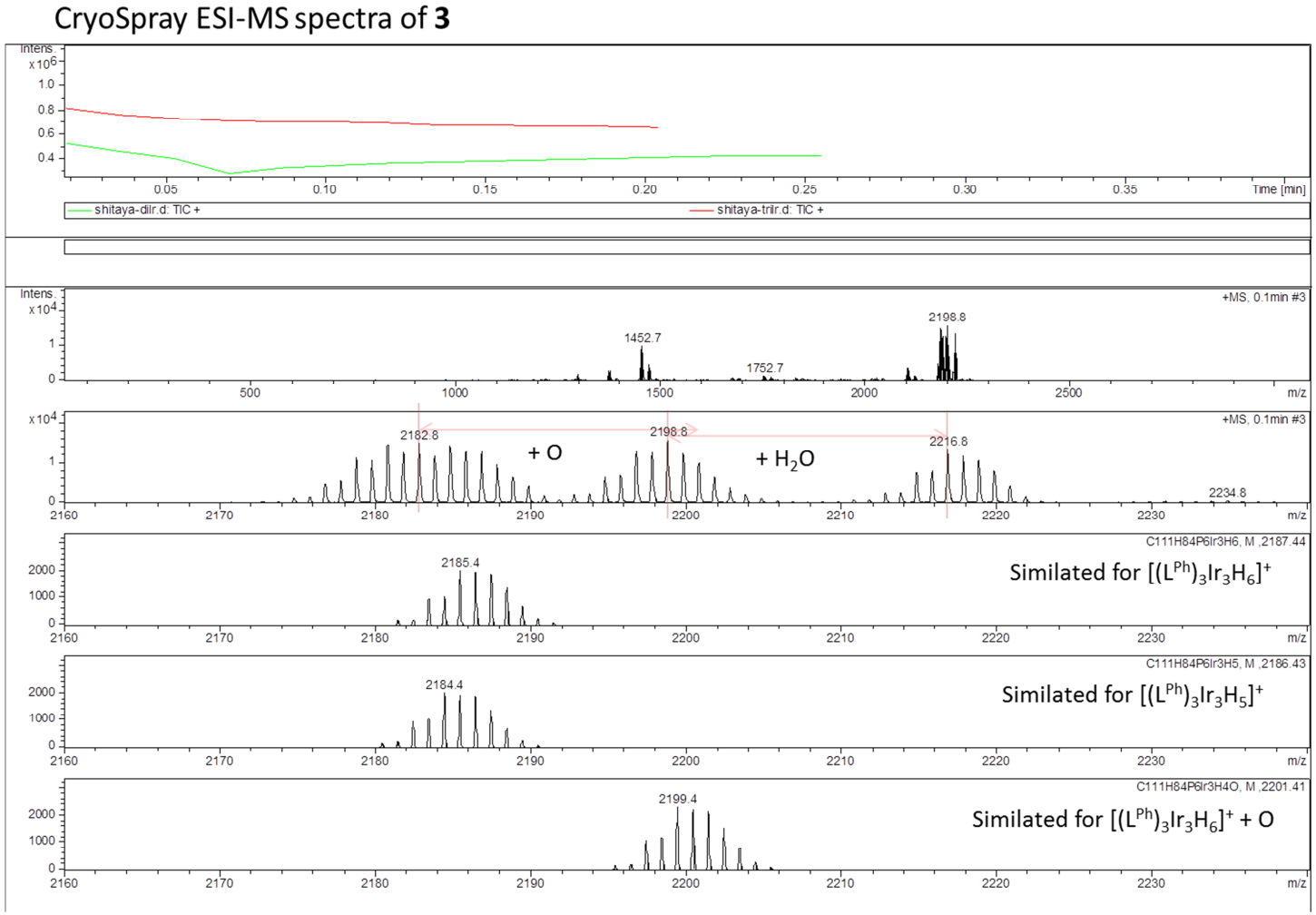

Figure S14. CryoSpray ESI-MS spectra of **3**.

X-ray Structural Determinations.

The diffraction data of **1- 3** were collected on a Rigaku XtaLAB P100 diffractometer with graphite monochromated MoKα(λ=0.71073Å). The data were collected at a temperature of -180 ± 1°C to a maximum 2θ value of 55.1°. The crystal-to-detector distance was 45.00 mm. Readout was performed in the 0.172 mm pixel mode. Data were collected and processed using CrystalClear (Rigaku).[1] An empirical absorption correction was applied The data were corrected for Lorentz and polarization effects.

The crystal structures were solved by direct method (SHELXS-97[2] or SHELXT[3]) and expanded using Fourier techniques, which are subsequently completed by Fourier recycling using the SHELXL 2014 program.[3] Non-hydrogen atoms were refined by anisotropic displacement parameters. Crystallographic data, data collection and refinement parameters for **1**–**3** are listed in Tables S1 in the ESI.

(1) CrystalClear: Data Collection and Processing Software, Rigaku Corporation (1998-2015). Tokyo 196-8666, Japan.
(2) SHELXS Version 2013/1: Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.
(3) SHELXT Version 2014/5: Sheldrick, G. M. (2014). Acta Cryst. A70, C1437.

Table S1. Crystal data and structure refinement for **1** and **3**.

Complex	**1**	**2**	**3**
Empirical formula	C45H40BF4IrP2	C78H71BF4Ir2OP4	C113H98BF4Ir3O2P6
Formula weight	921.72	1619.44	2337.14
Temperature	93(2) K	93(2) K	93(2) K
Wavelength	0.71075 Å	0.71075 Å	0.71075 Å
Crystal system	Monoclinic	monoclinic	Monoclinic
Space group	*P*21	*P*21/n	*P*21/n
Unit cell dimensions	a = 20.390(2) Å b = 14.7529(14) Å c = 26.785(3) Å	a = 17.2579(11) Å b = 14.7857(8) Å c = 27.6572(18) Å	a = 15.1654(10) Å b = 25.1723(16) Å c = 25.6917(18) Å
	α= 90°. β = 109.515(3)° γ = 90°.	α= 90°. β= 107.0026(12)°. γ = 90°.	α = 90°. β =99.7007(17)° γ = 90°.
Volume	7594.4(13) Å^3	6748.8(7) Å^3	9667.5(11) Å^3
Z	8	4	4
Density (calculated)	1.612 Mg/m^3	1.594 Mg/m^3	1.606 Mg/m^3
Absorption coefficient	3.653 mm^{-1}	4.091 mm^{-1}	4.278 mm^{-1}
F(000)	3664	3208	4616
Crystal size	0.14 x 0.10 x 0.04 mm^3	0.18 x 0.18 x 0.05 mm^3	0.46 x 0.22 x 0.20 mm^3
Theta range for data collection	3.01 to 27.49°.	3.02 to 27.53°.	3.03 to 27.54°.
Index ranges	-24<=h<=26, -19<=k<=17, -34<=l<=34	-22<=h<=22, -18<=k<=19, -27<=l<=35	-19<=h<=18, -30<=k<=32, -28<=l<=32
Reflections collected	61158	53434	80204
Independent reflections	27079 [R(int) = 0.0524]	14487 [R(int) = 0.0420]	20107 [R(int) = 0.0391]
Completeness to theta = 27.50°	90.1 %	93.2 %	90.1 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	27079 / 1 / 1909	14487 / 0 / 806	20107 / 0 / 1164
Goodness-of-fit on F^2	1.046	1.147	1.113
Final R indices [I>2sigma(I)]	*R*1 = 0.0455, *wR*2 = 0.1099	*R*1 = 0.0298, *wR*2 = 0.0819	*R*1 = 0.0344, *wR*2 = 0.0892
R indices (all data)	*R*1 = 0.0565, *wR*2 = 0.1139	*R*1 = 0.0359, *wR*2 = 0.0923	*R*1 = 0.0394, *wR*2 = 0.0903
Largest diff. peak and hole	1.863 and -1.190 e.Å^{-3}	1.844 and -0.921 e.Å^{-3}	2.238 and -1.792 e.Å^{-3}

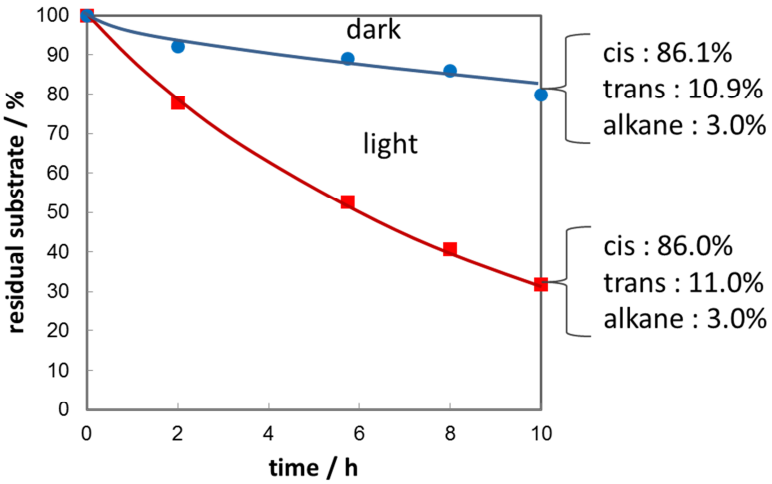

Figure S15. Catalytic hydrogenation of diphenylacetylene by **2** w/ or w/o light irradiation.

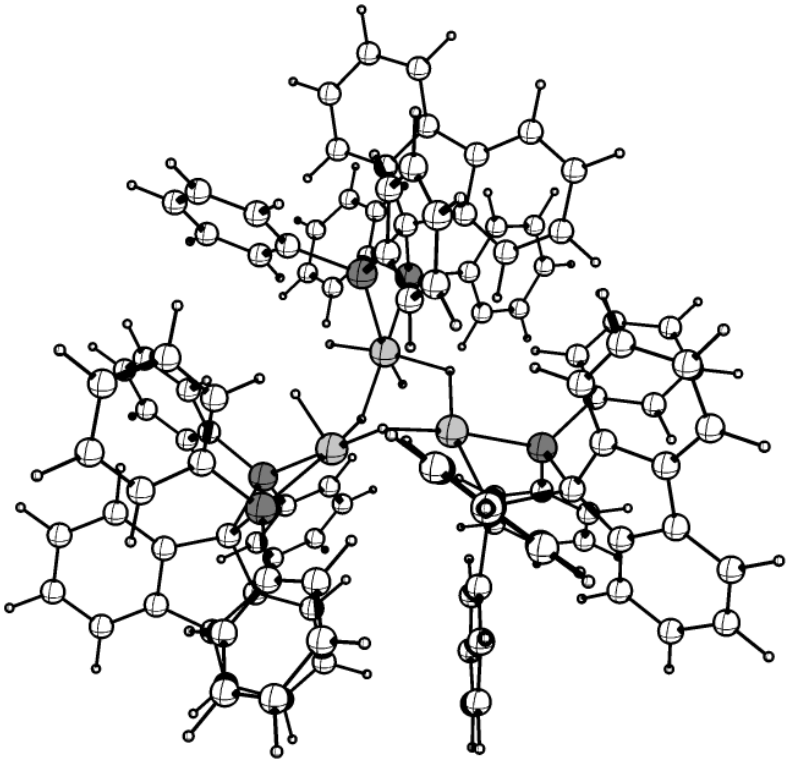

Figure S16. Optimized structure of **3**.

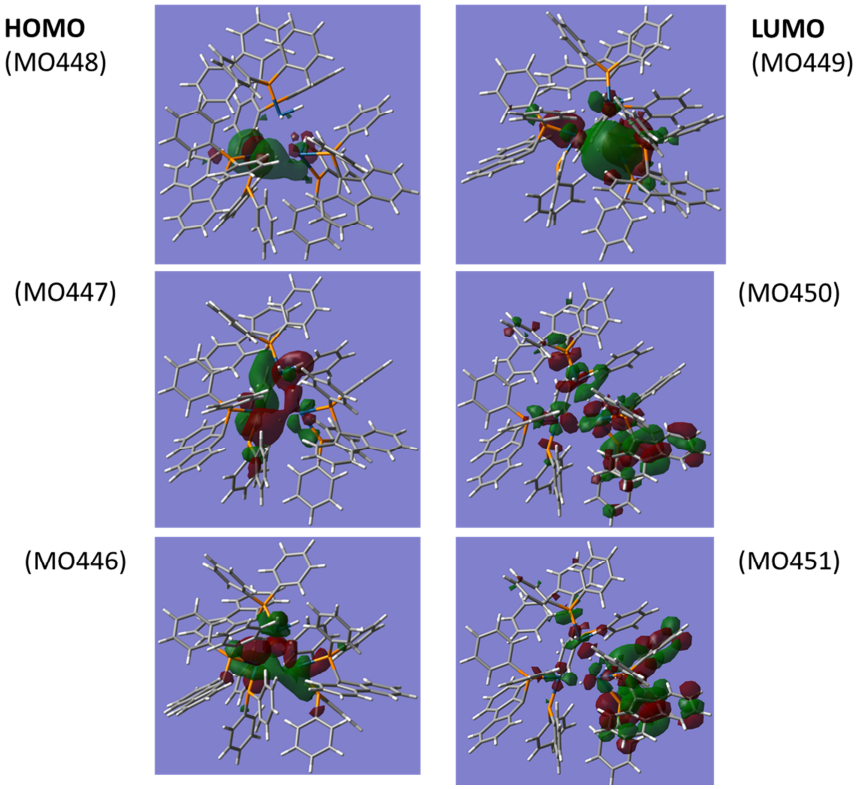

Figure S17. Frontier molecular orbitals of **3**.

Table S2. XYZ coordinate of the optimized structure (**3**).

atom	x	y	z
6	3.413238000	-1.473355000	-5.746629000
6	4.521231000	-1.887713000	-5.001788000
6	0.018315000	3.876790000	-5.458679000
6	3.323146000	-6.127573000	-1.839314000
6	2.199187000	-1.219261000	-5.106486000
6	0.285716000	2.681513000	-4.786398000
6	2.853595000	-6.677445000	-0.645078000
6	-3.728761000	-6.276462000	-3.426048000
6	-0.695501000	4.893654000	-4.817816000
6	3.334279000	-4.743907000	-2.020230000
6	4.418234000	-2.052632000	-3.620483000
6	-2.500137000	-5.616664000	-3.388597000
6	2.087072000	-1.374522000	-3.722065000
6	3.196375000	-1.797618000	-2.969014000
6	-4.839244000	-5.711797000	-2.792486000
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6	-2.373520000	-4.402492000	-2.708254000
6	-0.145858000	2.508071000	-3.469496000
6	2.868605000	-3.889997000	-1.003647000
6	-1.135840000	4.724635000	-3.503774000
6	-5.111926000	-0.152373000	-4.312554000
6	-6.477742000	-0.199034000	-4.020660000
6	2.370540000	-4.454059000	0.184192000
6	-4.721511000	-4.496240000	-2.120250000
6	-0.846683000	3.536101000	-2.811495000
6	-4.185305000	-0.692123000	-3.418567000
6	-3.480085000	-3.833032000	-2.056939000
6	8.011827000	-4.091067000	0.015115000
6	3.405568000	4.381814000	-2.219811000
6	8.036349000	-2.865967000	-0.657538000
6	6.841891000	-4.532809000	0.640025000
6	0.458205000	7.912010000	-1.340804000
6	-6.914551000	-0.774603000	-2.824564000
6	7.481555000	0.048557000	-2.033503000
6	6.876640000	-2.092170000	-0.690532000
6	5.673487000	-3.759855000	0.610517000
6	6.992454000	1.272134000	-2.497996000
6	4.326102000	5.193860000	-1.550247000
6	6.627863000	-0.785651000	-1.313050000
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6	5.672160000	1.652521000	-2.239738000
6	5.289076000	-0.406008000	-1.064525000
6	2.363473000	3.775417000	-1.516200000
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6	-3.223332000	3.552317000	-1.292827000
6	-5.126627000	5.054799000	-1.380266000
6	2.192889000	4.012574000	-0.138599000
6	-4.584362000	-4.887498000	0.976829000
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6	3.584911000	-1.873071000	2.636577000
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6	2.352511000	-2.311970000	3.153944000
6	4.772774000	-2.289177000	3.267748000
6	2.310192000	-3.175505000	4.251087000
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6	6.336656000	2.527898000	3.128505000
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6	-3.364068000	-1.749193000	3.815046000
6	1.225865000	5.243334000	4.299332000
6	-1.928987000	0.587605000	4.361586000
6	1.160905000	2.864253000	4.728513000
6	-3.588797000	-1.051316000	5.000452000
6	1.299709000	4.172645000	5.195525000
6	-2.868246000	0.114948000	5.278419000
1	3.498326000	-1.350072000	-6.819917000
1	0.353710000	4.012830000	-6.480378000
1	3.684924000	-6.772932000	-2.631114000
1	5.466605000	-2.080036000	-5.495111000
1	1.334783000	-0.904826000	-5.680510000
1	-3.825748000	-7.218230000	-3.953477000
1	0.828348000	1.884129000	-5.281777000
1	2.854765000	-7.752095000	-0.504339000
1	-1.638526000	-6.039026000	-3.892969000
1	-0.916682000	5.815332000	-5.343327000
1	3.699652000	-4.330006000	-2.950414000
1	5.285138000	-2.363623000	-3.051741000
1	-5.798986000	-6.213756000	-2.826465000
1	-4.766939000	0.305498000	-5.232075000
1	1.140857000	-1.177548000	-3.231428000
1	-7.196348000	0.214597000	-4.718696000
1	-1.420941000	-3.887893000	-2.690083000
1	3.488650000	4.222075000	-3.289463000
1	1.102797000	8.333201000	-2.103115000
1	1.989202000	-6.252523000	1.286483000
1	0.051151000	1.582941000	-2.936504000
1	-1.706823000	5.509647000	-3.024257000
1	8.904767000	-4.703893000	0.049515000
1	-3.124643000	-0.652654000	-3.643934000
1	5.135301000	5.666728000	-2.094717000
1	8.942258000	-2.525489000	-1.145736000
1	6.833307000	-5.487538000	1.152020000
1	0.929708000	5.878099000	-1.873305000
1	8.508413000	-0.241985000	-2.224049000
1	-1.114734000	-0.987471000	-2.423996000
1	-5.595965000	-4.064083000	-1.652627000
1	-0.169167000	9.835264000	-0.604751000
1	7.644059000	1.935657000	-3.054171000
1	-7.972047000	-0.802341000	-2.588691000
1	1.662810000	3.144785000	-2.044489000
1	4.776249000	-4.125124000	1.087447000
1	1.987600000	-3.820110000	0.972764000

1	-0.736834000	-2.811752000	-1.231469000
1	5.308235000	2.613582000	-2.575427000
1	-0.679523000	-6.845003000	0.478419000
1	0.409787000	-0.917713000	-1.244485000
1	3.791014000	1.138768000	-1.325220000
1	-1.274930000	-4.549675000	-0.167909000
1	-3.164541000	5.647601000	-0.745855000
1	-6.345050000	-1.749781000	-0.997789000
1	1.042414000	-1.917970000	0.719647000
1	-5.546635000	6.042732000	-1.231001000
1	-3.673501000	-5.286780000	0.558518000
1	-5.390711000	-6.829222000	1.425249000
1	4.924194000	5.994235000	0.357129000
1	-1.701497000	0.388568000	-0.615741000
1	-1.641194000	8.893338000	1.161632000
1	-0.594838000	-7.491785000	2.882842000
1	-6.981800000	4.188868000	-2.050700000
1	-3.623429000	1.521374000	-1.914879000
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1	-7.487907000	-5.961430000	2.412808000
1	-6.000590000	1.924353000	-2.392091000
1	0.613311000	0.415758000	1.042007000
1	6.598586000	-0.317938000	1.289713000
1	5.730982000	-1.932920000	2.914632000
1	3.054359000	4.977466000	1.591938000
1	1.351133000	-3.510987000	4.627311000
1	-3.576306000	0.583075000	0.431685000
1	5.646805000	-3.467871000	4.835870000
1	-7.887470000	-3.511674000	2.548724000
1	3.463385000	-4.272657000	5.702949000
1	-3.023422000	7.473866000	2.804427000
1	3.070858000	1.785685000	2.599395000
1	-0.999620000	0.278632000	2.436544000
1	-1.103100000	-5.794019000	4.625232000
1	0.957060000	5.846591000	2.254375000
1	8.002657000	1.373026000	2.395176000
1	-2.221425000	2.638790000	1.843470000
1	-1.755378000	-3.510609000	3.981995000
1	-7.853394000	-0.961751000	2.487376000
1	0.822887000	1.610630000	3.007340000
1	-5.247999000	2.220905000	1.216597000
1	-3.946390000	-2.636253000	3.596632000
1	-7.374769000	1.465303000	2.243245000
1	-4.166974000	5.720167000	4.139837000
1	4.478174000	3.458220000	3.712346000
1	6.960965000	3.267466000	3.616000000
1	-3.766699000	3.318738000	3.657582000
1	-1.385591000	1.504415000	4.557917000
1	1.309047000	6.261211000	4.661985000
1	1.206264000	2.030101000	5.419353000

1	-4.334262000	-1.409656000	5.700825000
1	1.452730000	4.359307000	6.251989000
1	-3.048549000	0.655738000	6.200419000
77	-1.268097000	-1.343589000	-0.857047000
77	1.544952000	-0.647171000	-0.017908000
77	-0.390761000	1.462774000	-0.055903000
15	2.978070000	-2.067071000	-1.175073000
15	-3.360397000	-2.185388000	-1.234545000
15	-1.430650000	3.226608000	-1.096730000
15	3.616425000	-0.704233000	1.213867000
15	0.672275000	3.343273000	0.669427000
15	-2.112009000	-2.169258000	1.306104000

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