Supporting Information

Engineering Catalytic Coordination Space in a Chemical Stable Ir-Porphyrin MOF with Confinement Effect Inverting Conventional Si-H Insertion Chemoselectivity

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Contents

1. General Information

All the reagents in the present work were obtained from the commercial source and used directly without further purification. The metalloporphyrin ligands Ir(TCPPCO_2Me)(CO)Cl and Ir(TCPP)Cl were synthesized according to our recent work.[1] The elemental analyses were performed with Perkin-Elmer 240 elemental analyzer. HRESI-MS was performed by using a Bruker Daltonics ESI-Q-TOF maXis4G. Infrared spectra on KBr pellets were collected with a Nicolet/Nexus-670 FT-IR spectrometer in the region of 4000-400 cm^{-1}. UV-vis spectra were tested on a Shimadzu/UV-3600 spectrophotometer. ^{1}H and ^{13}C NMR were recorded on Bruker AVANCE III 400MHz. PXRD patterns were recorded on SmartLab X-ray powder diffractometer (Rigaku Co.) at 40 kV and 30 mA with a Cu target tube. Thermogravimetric (TG) analyses were performed under an air atmosphere at a heating rate of 2 °C min^{-1} by using a NETZSCH TG 209 system. X-ray photoelectron spectroscopy (XPS) was performed on a ULVAC PHI Quantera microprobe. Binding energies (BE) were calibrated by setting the measured BE of C 1s to 284.65 eV. The sorption isotherms for N_2 (77 K) gas were measured with an Autosorb-iQ2-MP gas sorption analyzer (Quantachrome, USA).

Cautions! Although we have not experienced any problem in the handling of the diazo compounds, extreme care should be taken when manipulating them due to their explosive nature.

References:

(1) H. Cui, Y. Wang, Y. Wang, Y.-Z. Fan, L. Zhang and C.-Y. Su, *CrystEngComm,* 2016, **18**, 2203.

2. Crystal Structure Data of Ir-PMOF-1(Hf)

Table S1. Crystal data and structure refinement parameters for Ir-PMOF-**1**(Hf).

MOF Code	Ir-PMOF-**1**(Hf)
Formula	$C_{144}H_{72}Cl_3Ir_3N_{12}O_{64}Hf_{12}$
Fw	5818.96
T/K	150(10)
Crystal system	cubic
Space group	*I*m-3m
a/Å	38.3207(2)
b/Å	38.3207(2)
c/Å	38.3207(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	56273.0(9)
Z	4
ρ_{calc}g/cm^3	0.687
μ/mm^{-1}	5.633
F(000)	10712
Reflections collected	18019
Independent reflections	4361
Data/restraints/parameters	4361 / 97 / 102
R_{int}	0.0398
Goodness-of-fit on F^2	1.017
R1, *wR*2 [I>=2σ (I)]	0.0991, 0.2464
R1, *wR*2 [all data]	0.1011, 0.2476

Table S2. Selected bond lengths (Å) and bond Angles (º) for Ir-PMOF-**1**(Hf).

Bond Length (Å)		Bond Angle (º)	
Hf(1)-O(2)#1	2.067(8)	O(2)#1-Hf(1)-O(2)#2	116.9(7)
Hf(1)-O(2)#2	2.0678)	O(2)#1-Hf(1)-O(3)	72.4(3)
Hf(1)-O(4)	2.221(8)	O(2)#2-Hf(1)-O(3)	72.4(3)
Hf(1)-O(1)#3	2.234(8)	O(2)#1-Hf(1)-O(1)#3	75.6(4)
Hf(1)-O(1)	2.234(8)	O(2)#2-Hf(1)-O(1)#3	141.4(4)
Hf(1)-O(3) #3	2.290(13)	O(3)-Hf(1)-O(1)#3	142.6(2)
Hf(1)-O(3)	2.290(13)	O(2)#1-Hf(1)-O(1)	141.4(4)
Hf(1)-O(2)	2.305(14)	O(2)#2-Hf(1)-O(1)	75.6(4)
Hf(1)-Hf(1)#2	3.478(2)	O(3)-Hf(1)-O(1)	142.6(2)
Hf(1)-Hf(1)#1	3.478(2)	O(1)#3-Hf(1)-O(1)	74.4(5)
Hf(1)-Hf(1)#4	3.4810(11)	O(2)#1-Hf(1)-O(4)	76.2(6)
Hf(1)-Hf(1)#5	3.4810(11)	O(2)#2-Hf(1)-O(4)	140.6(5)
O(1)-C(8)	1.202(11)	O(3)-Hf(1)-O(4)	77.6(4)
O(2)-Hf(1)#2	2.067(8)	O(1)#3-Hf(1)-O(4)	76.3(5)
O(2)-Hf(1)#1	2.067(8)	O(1)-Hf(1)-O(4)	118.8(6)
O(4)-Hf(1)#4	2.221(8)	O(2)#1-Hf(1)-O(4)#3	140.6(5)
O(4)-Hf(1)#5	2.221(8)	O(2)#2-Hf(1)-O(4)#3	76.2(6)
N(1)-C(1)#9	1.348(11)	O(3)-Hf(1)-O(4)#3	77.6(4)
N(1)-C(1)	1.348(11)	O(1)#3-Hf(1)-O(4)#3	118.8(6)
N(1)-Ir(1)	2.024(8)	O(1)-Hf(1)-O(4)#3	76.4(5)
C(8)-O(1)#10	1.202(11)	O(4)-Hf(1)-O(4)#3	72.8(11)
C(1)-C(3)	1.359(12)	O(2)#1-Hf(1)-O(2)	74.9(3)
C(1)-C(2)	1.449(16)	O(2)#2-Hf(1)-O(2)	74.9(3)
C(2)-C(2)#9	1.42(3)	O(3)-Hf(1)-O(2)	114.9(3)
C(3)-C(4)	1.392(5)	O(1)#3-Hf(1)-O(2)	73.8(4)
C(4)-C(5)	1.388(5)	O(1)-Hf(1)-O(2)	73.8(4)
C(5)-C(4)#6	1.388(5)	O(4)-Hf(1)-O(2)	142.6(5)
C(5)-C(6)	1.495(8)	O(4)#3-Hf(1)-O(2)	142.6(5)
C(6)-C(7)#6	1.378(5)	N(1)#9-Ir(1)-N(1)#10	178.4(5)
C(7)-C(6)	1.378(5)	N(1)#9-Ir(1)-N(1)#11	90.011(7)
C(7)-C(8)	1.54(2)	N(1)#10-Ir(1)-N(1)#11	90.011(7)
C(8)-C(8)#8	1.352(8)	N(1)#9-Ir(1)-N(1)	90.011(7)
Ir(1)-N(1)#6	2.001(10)	N(1)#10-Ir(1)-N(1)	90.011(7)
Ir(1)-N(1)#7	2.001(10)	N(1)#11-Ir(1)-N(1)	178.4(5)
Ir(1)-N(1)#8	2.001(10)	N(1)#9-Ir(1)-Cl(1)#10	89.2(2)
Ir(1)-Cl(1)#7	2.47(4)	N(1)#11-Ir(1)-Cl(1)#10	90.8(2)
Ir(1)-Cl(1)	2.47(4)	Cl(1)#10-Ir(1)-Cl(1)	180

Symmetry transformations used to generate equivalent atoms: #1 -y+1/2,-z+1/2,-x+1/2, #2 -z+1/2,-x+1/2,-y+1/2,#3 y,x,z,#4 z,x,y , #5 y,z,x,#6 -z+1/2,-y+1/2,-x+1/2,#7 -x+1/2,-z+1/2,-y+1/2 #8 -x+1,y,z, #9 z+1/2,-y+1/2,-x+1/2,#10 -z+1/2,-y+1/2,x-1/2,#11 x,y,-z

3. Physical Characterizations of Ir-PMOF-1(Hf)

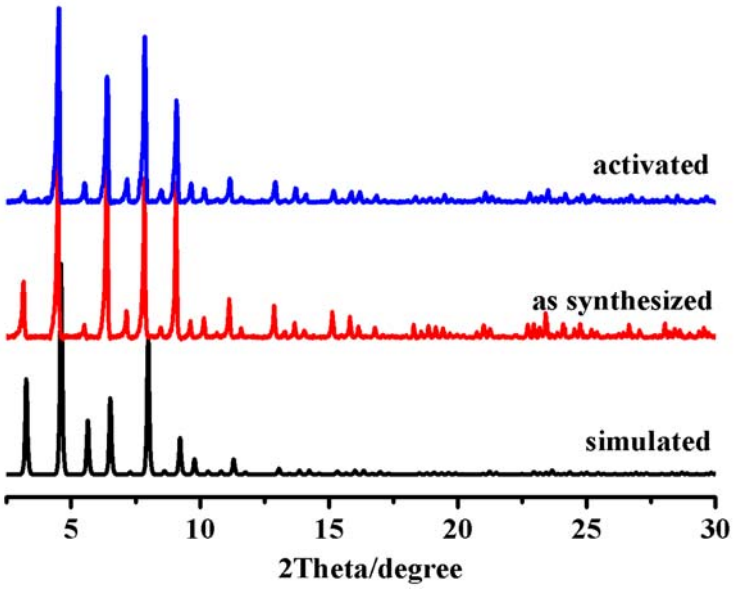


Figure S1. The PXRD patterns of the simulated, as synthesized and activated Ir-PMOF-**1**(Hf).

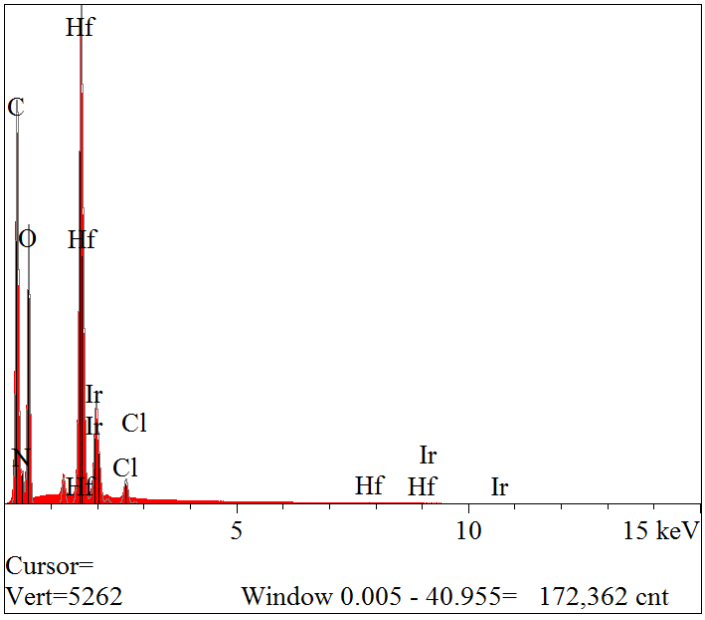
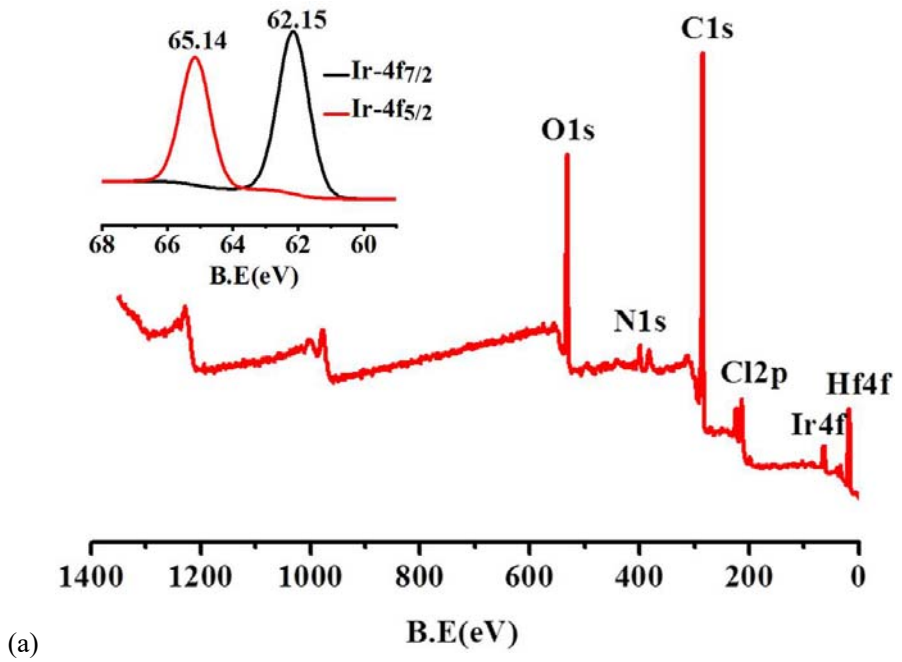


Figure S2. EDS spectrum of Ir-PMOF-**1**(Hf).

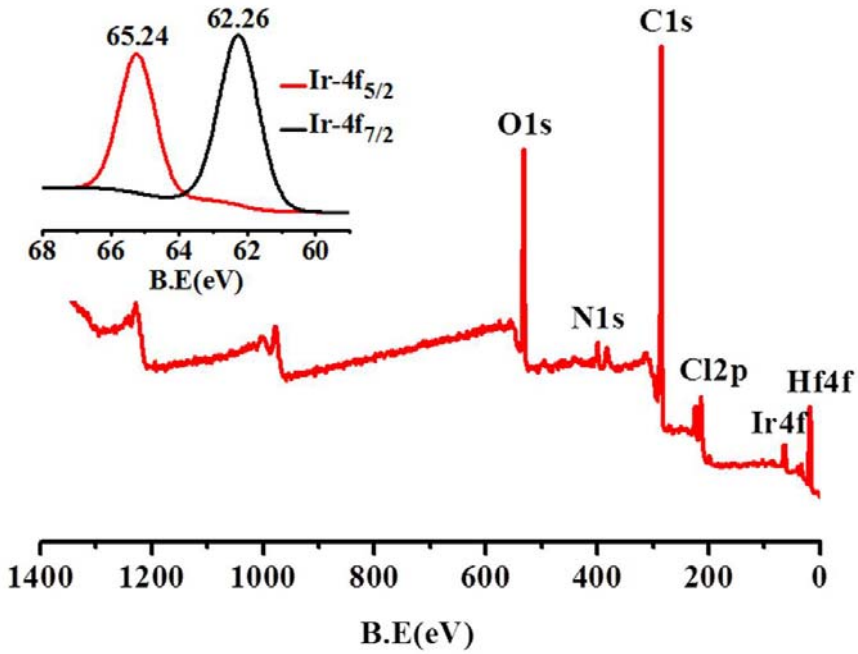
Table S3. Elemental analysis of Ir-PMOF-**1**(Hf) based on EDS experiment.

Element	Weight %	Atomic %
Hf	29.44	3.47
Ir	8.00	0.88
Cl	1.10	0.65

[a]The calculated molar ratio of Hf : Ir : Cl = 3.9 : 1 : 0.7.



(a)



(b)

Figure S3. XPS spectra of Ir-PMOF-**1**(Hf) before (a) and after (b) catalysis. The inserts show the peaks related to the Ir(III) atoms.

Table S4. Elemental analysis of Ir-PMOF-**1**(Hf) based on XPS experiment.

Element	Peak	Bond Energy (eV)	Atomic %
Hf	Hf 4f	17.32	2.47
Ir	Ir 4f	62.19	0.65
Cl	Cl 2p	197.82	0.85

[a]The calculated molar ratio of Hf : Ir : Cl = 3.8 : 1 : 1.3.

4. Stability Study of Ir-PMOF-1(Hf)

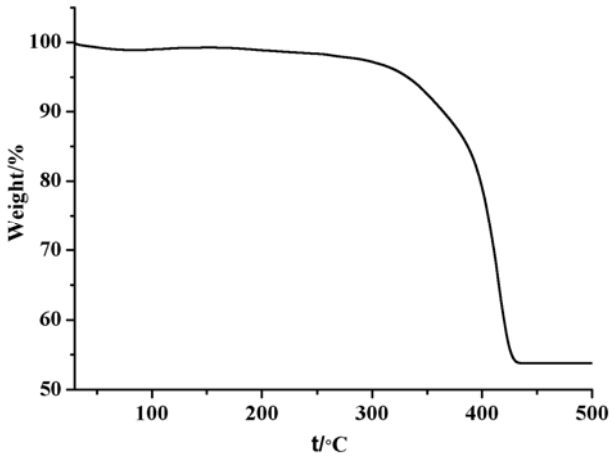


Figure S4 The TG curve of activated Ir-PMOF-**1**(Hf) sample.

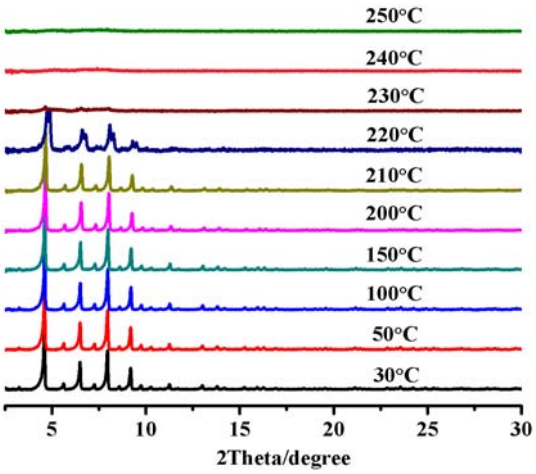


Figure S5. Variable-temperature PXRD patterns of Ir-PMOF-**1**(Hf) from 30 to 250°C.

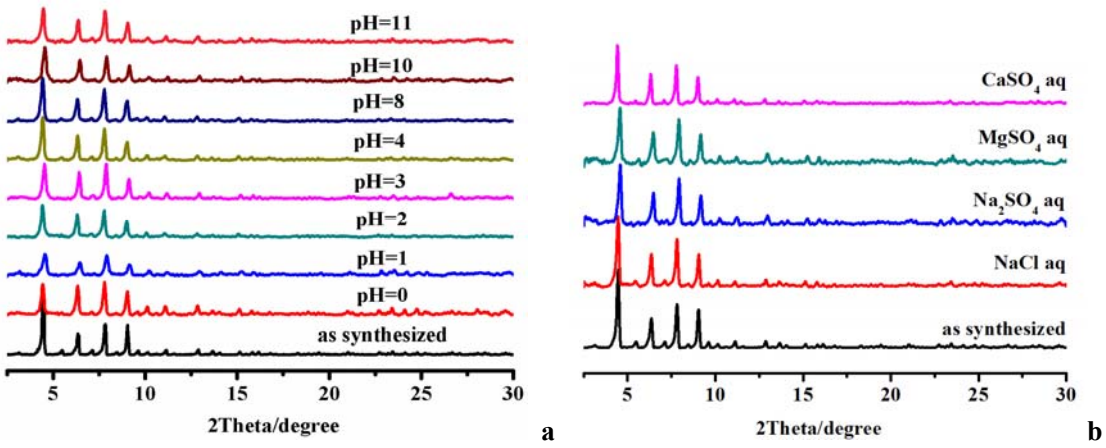


Figure S6. The PXRD patterns upon treatments in different pH (0-11) (a) and salts (b) aqueous solutions of Ir-PMOF-**1**(Hf).

5. Gas Adsorption of Ir-PMOF-1(Hf).

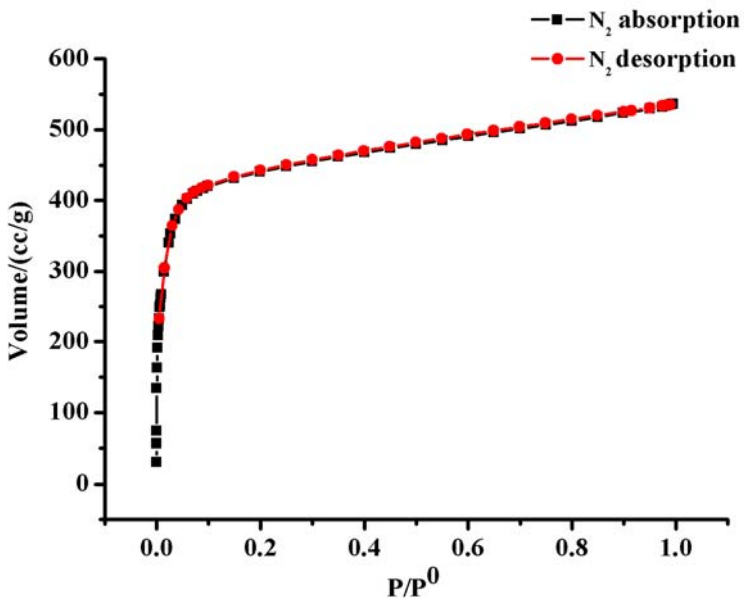


Figure S7. Nitrogen adsorption-desorption isotherms of Ir-PMOF-**1**(Hf) at 77K.

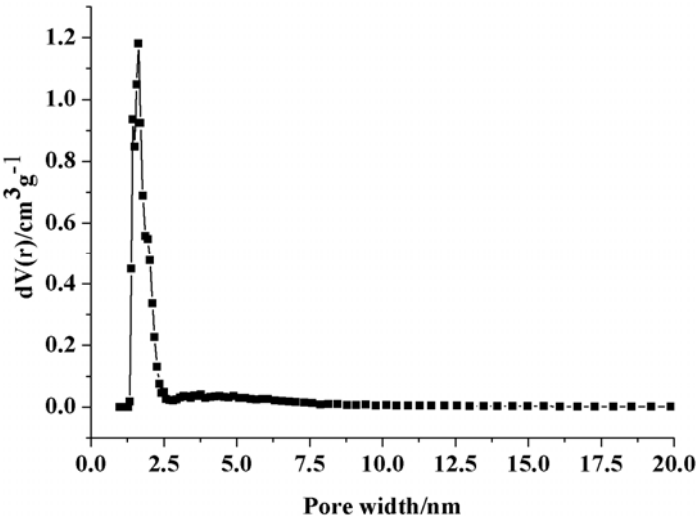
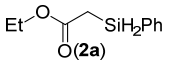


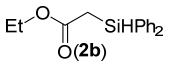
Figure S8. The Density Functional Theory pore distribution plot of Ir-PMOF-**1**(Hf)

6. Catalytic Results

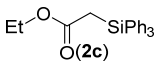
Typical Procedure for Si-H Insertion. A solution of ethyl 2-diazoacetate (45.6 mg, 0.4 mmol, 1.0 eq) in DCM (1.0 mL) was added slowly to the mixture of phenylsilane (216.4 mg, 2.0 mmol, 5.0 eq) and activated Ir-PMOF-**1**(Hf) (6.4 mg, 0.0032 mmol, 0.8 mol [Ir]%) in DCM (1 mL). The resulting suspension was stirred at room temperature for 3 min until EDA was completely consumed. The undissolved catalyst was removed through centrifugation, and washed with DCM (3 × 8 mL). The combined supernatant was evaporated to dryness, and the residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR to determine the conversion of EDA to ethyl 2-(phenylsilyl)acetate (**2a**, 93%).



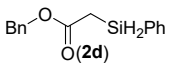
^1H NMR (400 MHz, $CDCl_3$) of ethyl 2-(phenylsilyl)acetate (**2a**): δ 7.59 (d, 2H, J = 7.6 Hz), 7.37 (m, 3H), 4.50 (t, 2H, J = 3.2 Hz), 4.05 (q, 2H, J = 7.2 Hz), 2.23 (t, 2H, J = 3.2 Hz), 1.14 (t, 3H, J = 7.2 Hz). HRMS ([M-H]) Calcd. for $C_{10}H_{14}O_2Si$: 193.0679; Found: 193.0683.



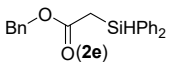
^1H NMR (400 MHz, $CDCl_3$) of ethyl 2-(diphenylsilyl)acetate (**2b**): δ 7.58 (d, 2H, J = 6.8 Hz), 7.38 (m, 6H), 5.05 (t, 1H, J = 3.2 Hz), 3.94 (q, 2H, J = 7.2 Hz), 2.46 (d, 2H, J = 3.2 Hz), 1.02 (t, 3H, J = 7.2 Hz). HRMS ([M+Na]) Calcd. for $C_{16}H_{18}O_2Si$: 293.0668; Found: 293.0669.



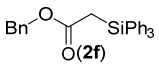
^1H NMR (400 MHz, $CDCl_3$) of ethyl 2-(triphenylsilyl)acetate (**2c**): δ 7.54 (d, 2H, J = 7.2 Hz), 7.41 (m, 3H), 7.35 (m, 6H), 3.82 (q, 2H, J = 7.2 Hz), 2.86 (s, 2H), 0.90 (t, 3H, J = 7.2 Hz). HRMS ([M+Na]) Calcd. for $C_{22}H_{22}O_2Si$: 369.1281; Found: 369.1289.



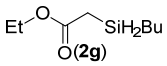
^1H NMR (400 MHz, $CDCl_3$) of benzyl 2-(phenylsilyl)acetate (**2d**): δ 7.61 (d, 2H, J = 7.2 Hz), 7.48 (m, 8H), 5.11 (s, 2H), 4.56 (t, 2H, J = 3.6 Hz), 2.37 (t, 2H, J = 3.6 Hz). HRMS ([M+Na]) Calcd. for $C_{15}H_{16}O_2Si$: 279.0812; Found: 279.0812.



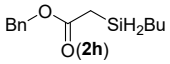
^1H NMR (400 MHz, $CDCl_3$) of benzyl 2-(diphenylsilyl)acetate (**2e**): δ 7.26-7.58 (m, 15H), 5.06 (t, 1H, J = 3.2 Hz), 4.95 (s, 2H), 2.52 (d, 2H, J = 3.6 Hz). HRMS ([M-H]) Calcd. for $C_{21}H_{20}O_2Si$: 371.0864; Found: 371.0873.



^{1}H NMR (400 MHz, $CDCl_3$) of benzyl 2-(triphenylsilyl)acetate (**2f**): δ 7-8 (m, 20H), 5.03 (s, 2H), 2.99 (s, 2H). HRMS ([M-H]) Calcd. for $C_{27}H_{24}O_2Si$: 447.1177; Found: 447.1179.



^{1}H NMR (400 MHz, $CDCl_3$) of ethyl 2-(butylsilyl)acetate (**2g**): δ 4.08 (q, 2H, J = 7.2 Hz), 3.82 (t, 2H, J = 3.2 Hz), 1.99 (t, 2H, J = 3.2 Hz), 1.35 (m, 4H), 1.21 (t, 3H, J = 7.2 Hz), 0.86 (t, 3H, J = 6.4 Hz), 0.75 (br, 2H). HRMS ([M-H]) Calcd. for $C_8H_{18}O_2Si$: 173.0992; Found: 173.0992.



^{1}H NMR (400 MHz, $CDCl_3$) of *tert*-butyl 2-(phenylsilyl)acetate (**2h**): δ 7.34 (m, 5H), 5.09 (s, 2H), 3.86 (t, 2H, J = 3.2 Hz), 2.07 (t, 2H, J = 2.8 Hz), 1.34 (m, 4H), 0.86 (t, 3H, J = 7.2 Hz), 0.75 (m, 2H).

7. Chemical Stability Study of Ir-PMOF-1(Hf) during Catalytic Reactions.

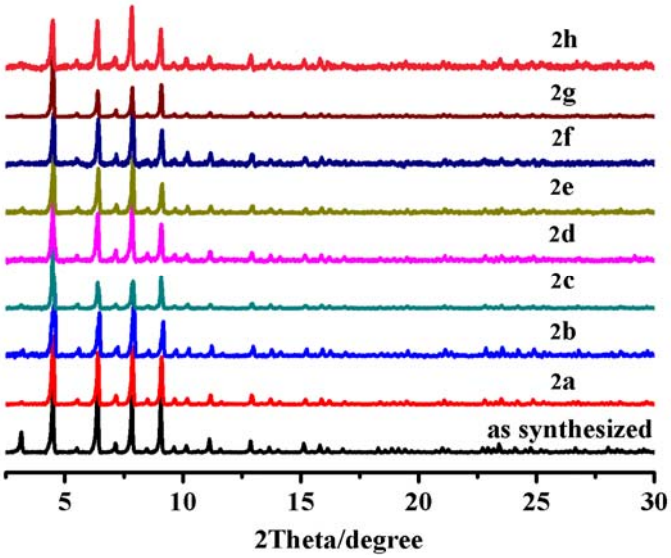


Figure S9. The PXRD patterns for Ir-PMOF-**1**(Hf) after catalytic reactions in the formation of the products **2a-h**.

8. Competition Experiments.

Method 1: The procedure is according to the literature.[2] A solution of EDA (45.6 mg, 0.4 mmol, 1.0 eq) in DCM (1.0 mL) was added slowly to the mixture of phenylsilane (33.9 mg, 0.36 mmol, 0.9 eq), diphenylsilane (99.4 mg, 0.54 mmol, 1.35 eq), triphenylsilane (281 mg, 1.08 mmol, 2.7 eq) and activated Ir-PMOF-**1**(Hf) (6.4 mg, 0.0032 mmol, 0.8 mol [Ir]%) in DCM (1 mL). The resulting suspension was stirred at room temperature for 30 min until EDA was completely consumed. The undissolved catalyst was removed through centrifugation, and washed with DCM (0.2 × 3 mL). The combined supernatant was evaporated to dryness, and the residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR to determine the ratio of ethyl 2-(phenylsilyl)acetate (**2a**), ethyl 2-(diphenylsilyl)acetate (**2b**) and ethyl 2-(triphenylsilyl)acetate (**2c**). The molar ratio of **2a**:**2b**:**2c** is 1 : 0.66 : 0.27.

Method 2: A solution of EDA (45.6 mg, 0.4 mmol, 1.0 eq) in DCM (1.0 mL) was added slowly to the mixture of phenylsilane (72 mg, 0.67 mmol, 1.67 eq), diphenylsilane (123 mg, 0.67 mmol, 1.67 eq), triphenylsilane (173 mg, 0.67 mmol, 1.67 eq) and activated Ir-PMOF-**1**(Hf) (6.4 mg, 0.0032 mmol, 0.8 mol [Ir]%) in DCM (1 mL). The resulting suspension was stirred at room temperature for 30 min until EDA was completely consumed. The following procedure is similar to **Method 1**. The molar ratio of **2a**:**2b**:**2c** is 1 : 0.5 : 0.1.

Method 3: A solution of EDA (45.6 mg, 0.4 mmol, 1.0 eq) in DCM (1.0 mL) was added slowly to the mixture of phenylsilane (96.4 mg, 0.8 mmol, 2.0 eq), diphenylsilane (221 mg, 1.2 mmol, 3.0 eq) and activated Ir-PMOF-**1**(Hf) (6.4 mg, 0.0032 mmol, 0.8 mol [Ir]%) in DCM (1 mL). The resulting suspension was stirred at room temperature for 5 min until EDA was completely consumed. The following procedure is similar to **Method 1**. The molar ratio of **2a**:**2b** is 1 : 0.7.

Method 4: A solution of EDA (45.6 mg, 0.4 mmol, 1.0 eq) in DCM (1.0 mL) was added slowly to the mixture of phenylsilane (54 mg, 0.5 mmol, 1.25 eq), triphenylsilane (390 mg, 1.5 mmol, 3.75 eq) and activated Ir-PMOF-**1**(Hf) (6.4 mg, 0.0032 mmol, 0.8 mol [Ir]%) in DCM (1 mL). The resulting suspension was stirred at room temperature for 14 min until EDA was completely consumed. The following procedure is similar to **Method 1**. The molar ratio of **2a**:**2c** is 1 : 0.2.

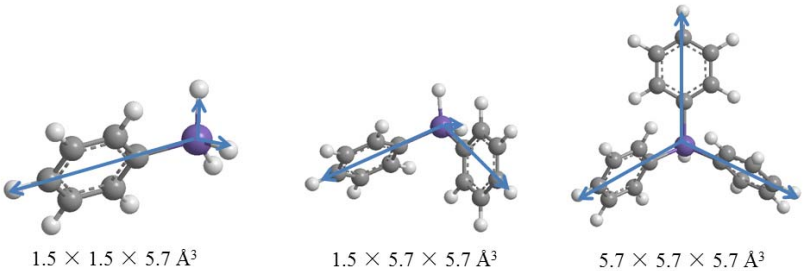


Figure S10. The molecular sizes of $PhSiH_3$ (the left), Ph_2SiH_2 (the middle) and Ph_3SiH (the right). The molecular sizes were calculated based on the MM2 energy minimization mode of the Chem3D program followed by measuring the longest atom-to-atom separations in two dimensions.

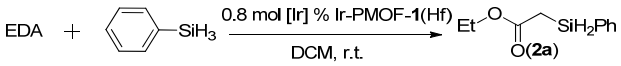
References:

(2) Iglesias, M. J.; Nicasio, M. C.; Caballero, A.; Pérez, P. J. *Dalton Trans.* **2013**, *42*, 1191-1195.

9. Recycling Experiments

A solution of ethyl 2-diazoacetate (228 mg, 2 mmol, 1 eq) in DCM (5 mL) was added slowly to the mixture of phenylsilane (1.08 g, 10 mmol, 5 eq) and activated Ir-PMOF-**1**(Hf) (32 mg, 0.016 mmol, 0.8 mol [Ir]%) in DCM (5 mL). The resulting suspension was stirred at room temperature for 9 min until EDA was completely consumed. The undissolved catalyst was removed through centrifugation, and washed with DCM (3 × 8 mL). The combined supernatant was evaporated to dryness, and the residue was dissolved in $CDCl_3$ and analyzed by ^1H NMR to determine the conversion of EDA to ethyl 2-(phenylsilyl)acetate (**2a**, 92%). The recycled catalyst was collected, air-dried and then used for the successive runs.

Table S5. Recycling experiments of Si-H insertion.



Run	Conversion (%)	Reaction Time (min)
1	92	9
2	91	9
3	89	9
4	86	10
5	83	13
6	90	12
7	84	26
8	75	55
9	83	90
10	74	200

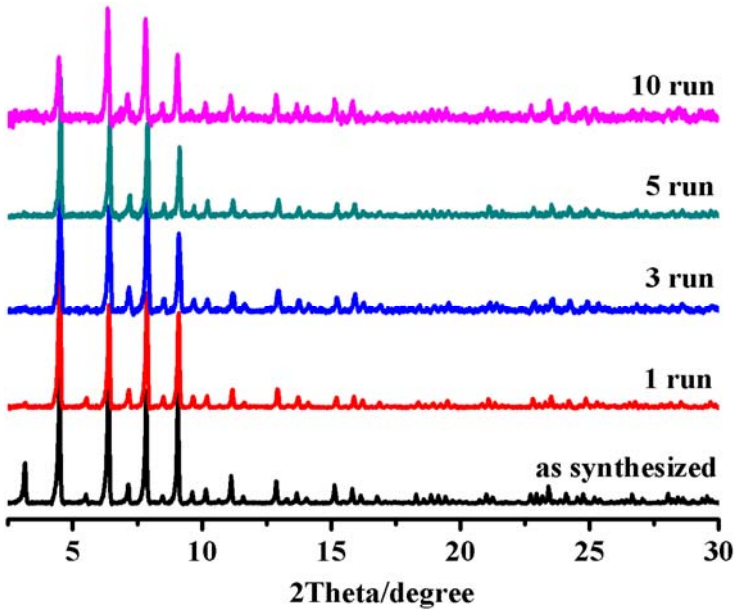


Figure S11. The PXRD patterns for Ir-PMOF-**1**(Hf) of the as-synthesized sample and after the 1st, 3rd, 5th and 10th runs of the catalytic Si-H insertion reactions.