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SUPPLEMENTARY INFORMATION

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Catalytic chemoselective functionalization of methane in a metal–organic framework

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Supplementary Information

Catalytic Chemo-Selective Functionalization of Methane in a Metal-Organic Framework

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■ Supplementary Methods

Chemicals used in this work

All manipulations of air-sensitive materials were performed with rigorous exclusion of O_2 and moisture in oven-dried Schlenk-type glassware on a dual manifold Schlenk line and in Ar- or N_2-filled atmospheres glove box with a high capacity recirculator (<1 ppm O_2). Solvents were sparged with N_2, dried using activated alumina columns and transferred into the glovebox, and stored over 4 Å molecular sieves prior to use. Unless specified, all chemicals and other solvents were purchased and used as received from Sigma-Aldrich, Acros Organics, Combi-blocks and Strem Chemicals. The carboxylation reaction using N-formylsaccharin as the carbonyl precursor was adapted from the literature. [1]

Analytical techniques

Nuclear magnetic resonance (NMR) spectra (^{1}H) were collected on a Bruker Avance III 500 MHz system equipped with DCH CryoProbeand automated with a BACS-60 autosampler and analyzed using MestReNova (v11.0.1, MestreLab Research S. L., Santiago de Compostela, Spain) software. Chemical shifts for ^{1}H spectra were referenced using internal solvent resonances and reported relative to tetramethylsilane (TMS).

Inductively coupled plasma–Atomic emission spectroscopy (ICP–AES) was conducted on an iCAP™ 7600 ICP-AES Analyzer (Thermo Scientific™) over the 166–847nm spectral range. Samples (2–3 mg) were digested in a small amount (1 mL) of a mixture of 10:3 v/v conc. HNO_3:H_2O_2 (30 wt % in H_2O) by heating in a Biotage (Uppsala, Sweden) SPX microwave reactor (software version 2.3, build 6250) at 150 °C for 5 minutes. The acidic solution was then diluted to a final volume of 15 mL with Millpore H_2O and analyzed for Ir (204.419, 236.804 and 263.971 nm) and Zr (327.305, 339.198, and 343.823 nm) content as compared to standard solutions.

Powder X-ray Diffraction (PXRD) patterns were recorded on a Rigaku X-ray Diffractometer Model SmartLab equipped with an 18 kW Cu rotating anode, an MLO monochromator, and a high-count-rate scintillation detector. Measurements were made over the range $3° < 2\theta < 30°$ in 0.05° step width with a 5°/min scanning speed.

Brunauer–Emmett–Teller (BET) Surface Area Analysis. The acetone exchanged MOFs were activated by heating at 120 ˚C for 18-24 h under high vacuum on a Micromeritics Smart Vacprep. N_2 adsorption and desorption isotherms were measured on a Micromeritics Tristar II 3020 (Micromeritics, Norcross, GA) instrument at 77 K. Pore-size distributions were obtained using DFT calculations using a carbon slit-pore model with a N_2 kernel. Before each run, samples were activated at 120 °C for 12–24 h Around 30 mg of sample was used in each measurement and BET surface area was calculated in the region $P/P_0 = 0.005–0.05$.

Thermogravimetric analysis (TGA). TGA was performed on a TA Instruments Discovery TGA equipped with a Stanford Research Systems QMS200 gas analyzer (MS). Samples were run under a nitrogen flow (5 mL/min) with a heating rate of 10 °C/min running from room temperature to 650 °C.

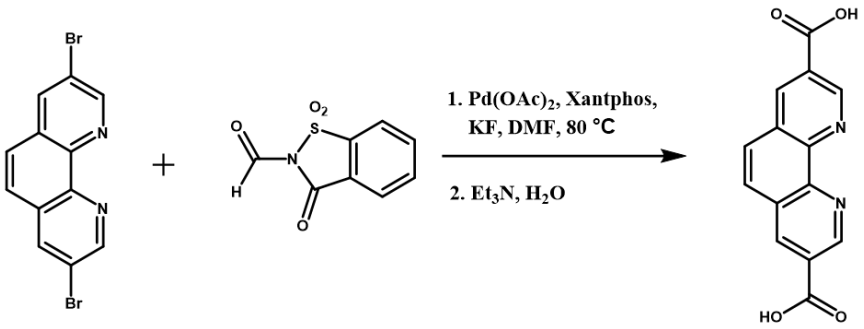
Diffuse Reflectance Infrared Fourier Transform (DRIFTS) measurements. Infrared (IR) spectra were collected were recorded on a Nicolet 6700 FTIR spectrometer (Thermo Scientific) equipped with an MCT detector and a Harrick praying mantis accessory. Samples were activated at 150 °C under high vacuum for 24 h before each measurement. The spectra were collected at 1 cm^{-1} resolution over 64 scans. A sample of solid KBr was utilized as the background.

Scanning electron microscopy (SEM) images were collected on a Hitachi SU8030 FE-SEM (Dallas, TX) microscope at Northwestern University's EPIC/NUANCE facility.

X-ray absorption near-edge structure and extended X-ray absorption fine structure (XANES and EXAFS) data collection and analysis: X-ray absorption measurements were acquired on the insertion device (ID) beam line of the Materials Research Collaborative Access Team (MRCAT, sector 10) at the Advanced Photon Source, Argonne National Laboratory. Photon energies were selected using a water-cooled, double-crystal Si(111) monochromator. High harmonics were rejected with a Rh coated harmonic rejection mirror strip set at cutoff energy of 13000 eV. Measurements were made in transmission quick scan mode using pure nitrogen in both the incident ionization chamber and the transmission ionization chamber. The detector settling time was 0.1 s prior to each measurement with a beam size of 0.5 mm by 0.5 mm. An Ir foil spectrum (edge energy 11217 eV) was acquired simultaneously with each measurement for energy calibration. All the samples were grinded then pressed into a cylindrical sample holder consisting of six wells, forming a self-supporting wafer which was then placed in a quartz tube (2.5 cm. OD, 10.0 cm. length) sealed with Kapton windows by two Ultra-Torr fittings. Demeter software package was used for data processing and fitting.[2]

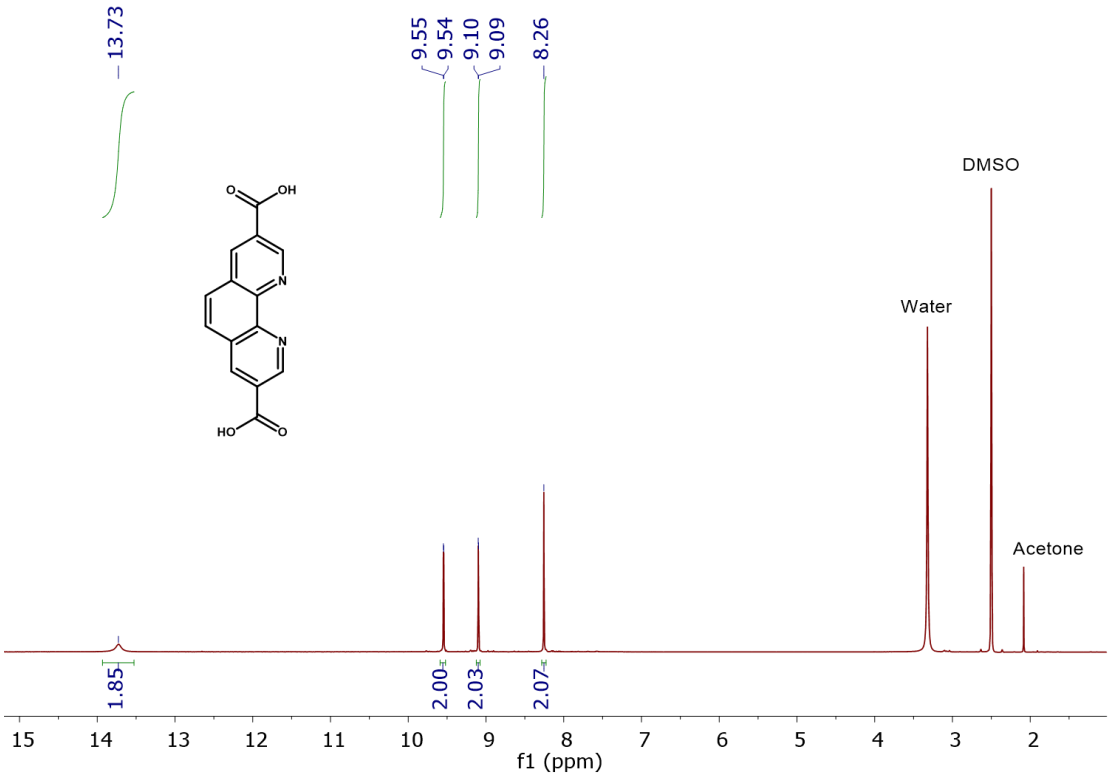
X-ray photoelectron spectroscopy (XPS) measurements were carried out at the KECK-II/NUANCE facility at NU on a Thermo Scientific ESCALAB 250 Xi (Al Kα radiation, hν = S5 1486.6 eV) equipped with an electron flood gun. XPS data was analyzed using Thermo Scientific Avantage Data System software and all spectra were referenced to the C1s peak (284.8 eV).

Synthesis of organic linker

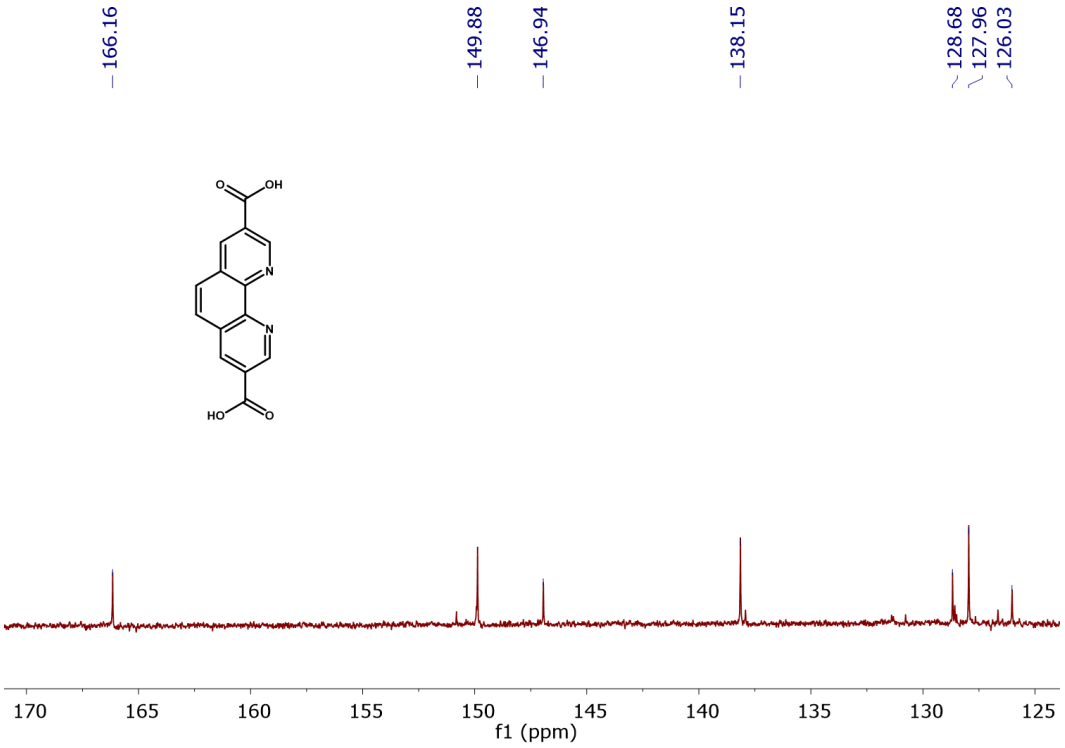


Synthetic path for 1,10-phenanthroline-3,8-dicarboxylic acid (PhenDC).

In an argon-filled glovebox, Xantphos (0.8 mmol, 468.5 mg) and Pd(OAc)2 (0.54 mmol, 121.2 mg) was added to a 150 mL heavy wall pressure vessel with a magnetic stir bar, followed by 75 mL of anhydrous N,N-dimethylformamide to dissolve the catalyst. Then 3,8-Dibromo-1,10-phenanthroline (8.9 mmol, 3.00 g), KF (45.1 mmol, 2.62 g) and N-formylsaccharin (22.5 mmol, 4.75 g) was added. The vessel was screw capped and heated with vigorous stirring at 80˚C in an oil bath for three days. After cooling to room temperature, 7 mL triethylamine and 10 mL water was added and the mixture was stirred at room temperature overnight. The solvent was removed under vacuum, the solid was suspended in water and filtered with copious amount of water. 1 g portions of the solid was heated and dissolved in 250 mL of 1 M NaOH aqueous solution and filtered through a cellulose membrane. The filtrate was acidified with 1 M HCl aqueous solution to about pH = 6 and the light orange precipitate was collected by filtration and washed with a large amount of water until the filtrate was neutral. The solid was rinsed with acetone and dried in vacuo to afford in total 1.93 g of light orange product (81 % yield). ^{1}H NMR (DMSO-d_6, 500 MHz) δ 13.73 (s, 2H), 9.55 (d, J = 2.1 Hz, 2H), 9.10 (d, J = 2.1 Hz, 2H), 8.26 (s, 2H). ^{13}C NMR (DMSO-d_6, 500 MHz) δ 166.16, 149.88, 146.94 138.15 128.68, 127.96, 126.03. HRMS (ESI) m/z Calcd for C14H9N2O4 $[M+H]^+$ 269.0563, found 269.0557.



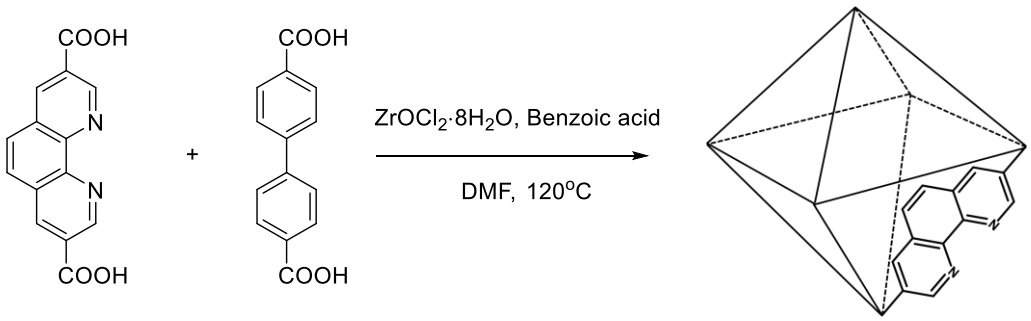
Supplementary Figure 1. ^{1}H NMR spectrum of the 1,10-phenanthroline-3,8-dicarboxylic acid (PhenDC).



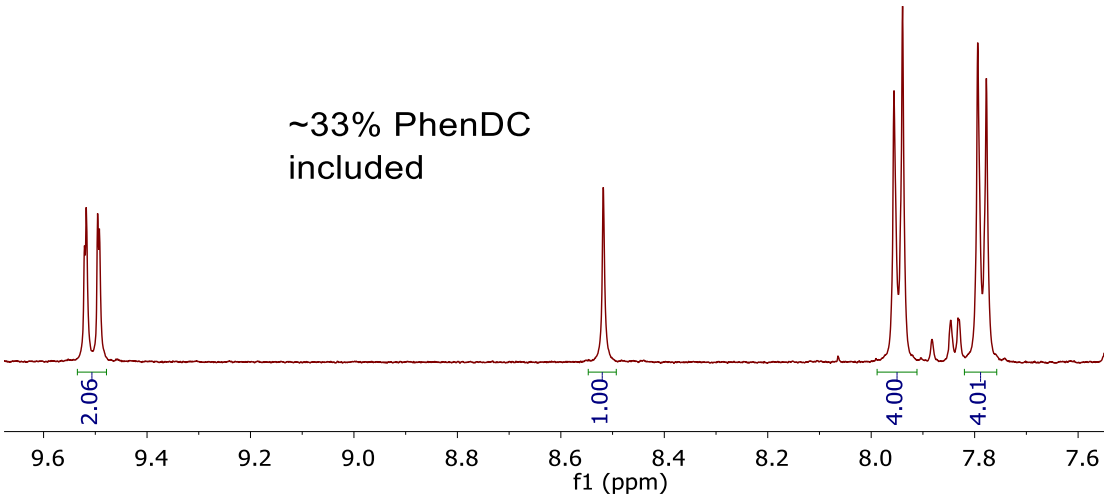
Supplementary Figure 2. ^{13}C NMR spectrum of the 1,10-phenanthroline-3,8-dicarboxylic acid (PhenDC).

Synthesis of the catalyst

UiO-67-Mix. $ZrOCl_2 \cdot 8H_2O$ (515.6 mg, 1.6 mmol) and benzoic acid (5.85g, 48 mmol) was dissolved in 40 mL of DMF and heated at 90 ˚C for 1 h and cooled to room temperature. This solution was added to a solution of PhenDC (214.4 mg, 0.8 mmol) and BPDC (193.6 mg, 0.8 mmol) in 40 mL of DMF and the mixture was sonicated. The resulted clear solution was split into two 100 mL Pyrex bottles and heated in an oven at 120 ˚C for 36 h. After cooling to room temperature, the supernatant was decanted and the solid was washed three times by DMF in 24 h and then exchanged with acetone for three times in 24 h. After that the product was collected by centrifugation and dried in-vacuo to give 375 mg off-white solid (65% yield based on Zr).



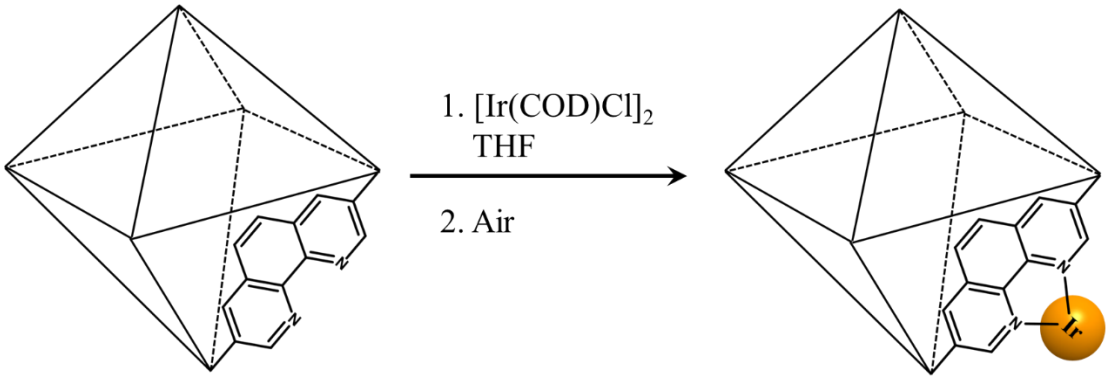
Synthetic scheme of the PhenDC/BPDC mixed-linkers UiO-67-Mix MOF.



Supplementary Figure 3. ^{1}H NMR spectrum of the acid digested PhenDC/BPDC mixed-linkers UiO-67-Mix MOF.

Metalation of the metal organic frameworks. In a glovebox, UiO-67-Mix (217.2 mg, 0.20 mmol equiv. of phen ligand) was added to a solution of $[Ir(COD)(\mu\text{-}Cl)]_2$ (67.2 mg, 0.20 mmol) in anhydrous THF (2 mL). Upon addition of the metal precursor, the MOF immediately turned from white to olive green. After exposing the suspension to the air at room temperature by the shaking table overnight, the green mixture gradually turned orange. The resulting orange solid of UiO-67-Mix-Ir was first soaked with anhydrous THF (2 x 5 mL in 12 h intervals) and then soaked with

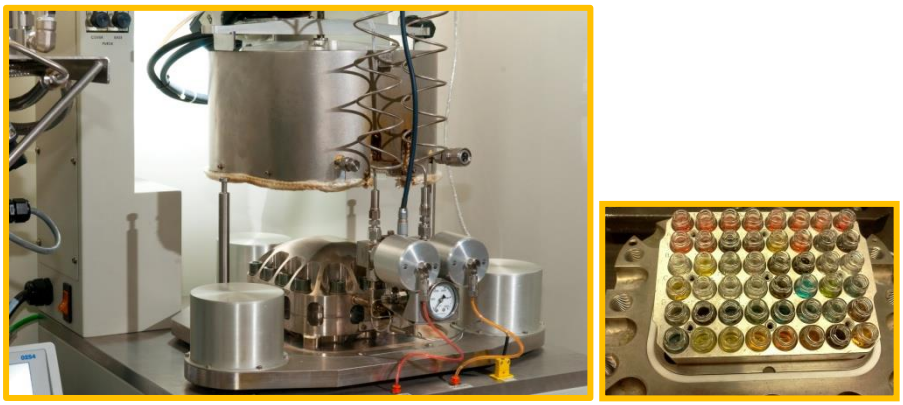
cyclohexane (2 x 5 mL in 12 h intervals). The obtained UiO-67-Mix-Ir was activated by heating at 150 ˚C in vacuo for 2 h.



UiO-67-Mix UiO-67-Mix-Ir

Reaction scheme for the metalation of the PhenDC/BPDC mixed-linkers UiO-67-Mix MOF.

High-Throughput methane borylation reactions



Supplementary Figure 4. Photographs of the reaction setup for the high-throughput experiments. The vials are not from the actual reactions.

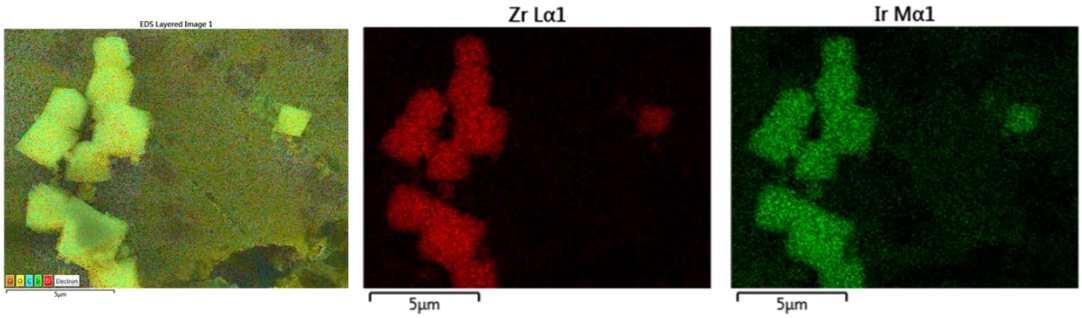
GC-MS analysis. The compositions of the reaction mixtures were determined using a Trace GC Ultra Gas Chromatograph system equipped with a Tri Plus RSH autosampler, and an ISQ MS detector. The column used for the MS detector was an Agilent J&W DB-5 column (30 m × 0.25 mm × 0.25 µm film thickness). GC data were analyzed using the Thermo Xcalibur 2.2 SP1.48 software. The following method was used: a 0.5 µL split injection with a split ratio of 100 run under a constant gas flow of 1 mL/min. The oven temperature profile was as follows: initial temperature = 40 °C, hold for 1 minute, ramp at 3 °C/min, final temperature = 200 °C. $TON = \frac{B2pin2\ (mol) \times CH3Bpin\ Yield\ (\%)}{Ir\ (mol) \times 100}$

Poisoning experiment. For the poisoning experiment, tricyclohexylphosphine was used. A solution of tricyclohexylphosphine in dodecane was prepared and added to UiO-67-Mix-Ir MOF and B_2Pin_2 so that the tricyclohexylphosphine : Ir molar ratio is 1. The reaction was conducted in 750 µL of dry dodecane, at 150 °C, 34 atm CH_4 for 14 h.

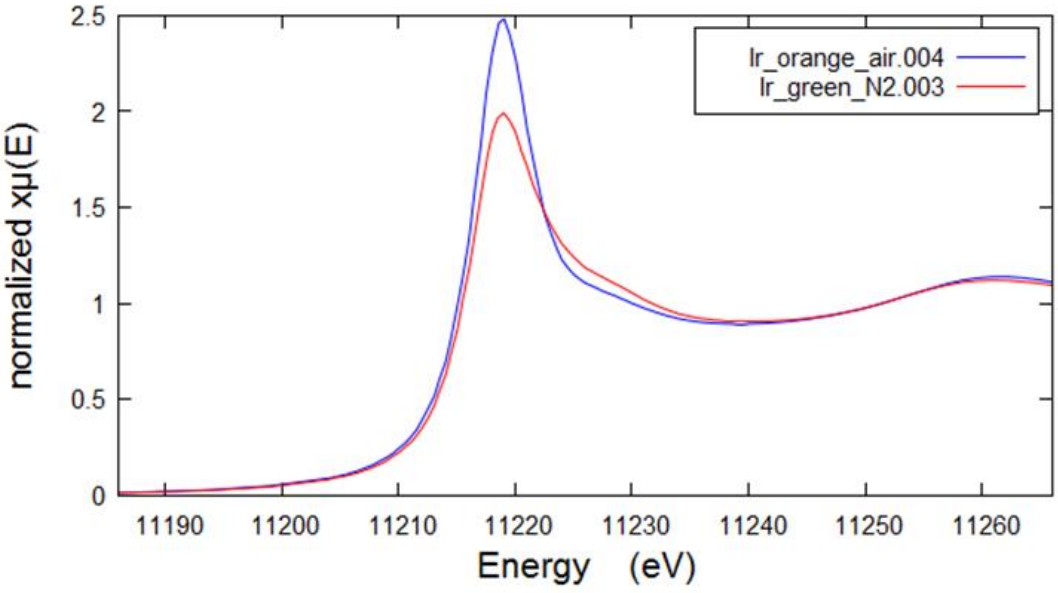
Leaching test. For the leaching experiment, 1.7 mg of Ir-MOF- catalyst, and 13.7 mg of B_2pin_2 were used with 0.75 mL of dodecane. After the first reaction (150 °C, 500 psi CH_4, 14 h) was carried out (100% conversion); the supernatant was filtered from the catalyst and split into 2 samples; one for GC analyses and one for a second reaction. 13.4 mg of B_2pin_2 was added to the supernatant and then reacted at the same conditions. No conversion was observed in the second reaction.

Recyclability test. For the recyclability test, after the first reaction (750 µL of dry dodecane, 150 °C, 34 atm CH_4 for 14 h), the UiO-67-Mix-Ir MOF catalyst was washed 3 times with dodecane. The supernatant was then removed, and fresh dodecane and B_2pin_2 were added. A second reaction was then performed at the same condition.

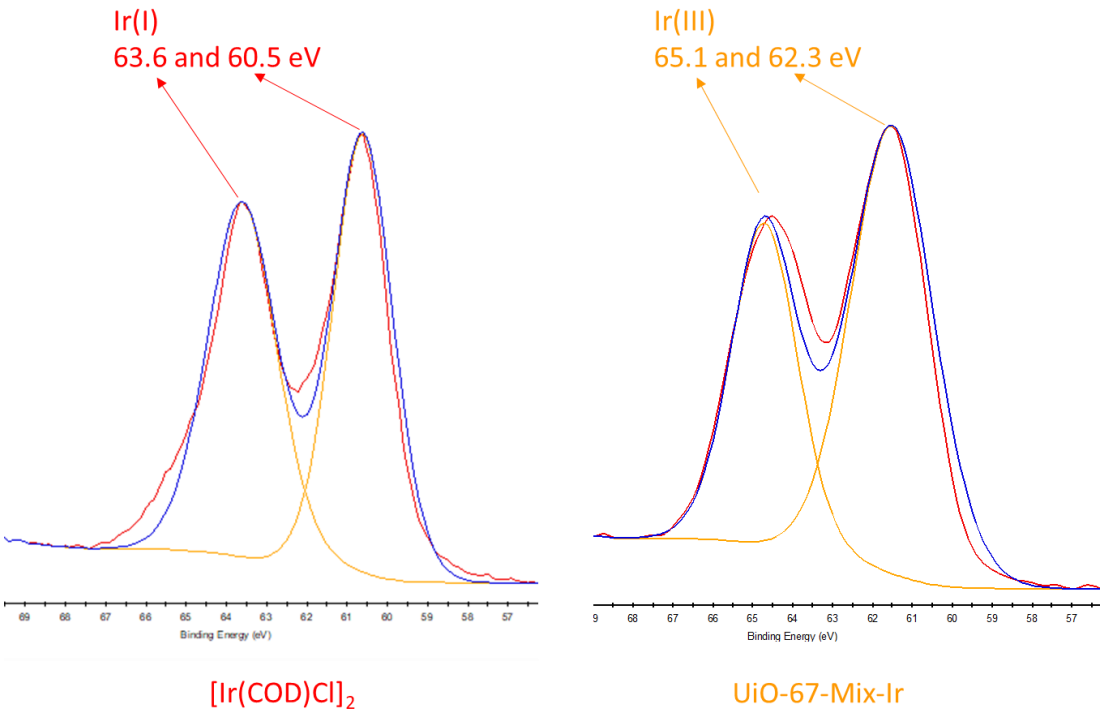
Characterization of the catalyst: SEM(EDS), ICP, XPS, DRIFTS, EXAFS



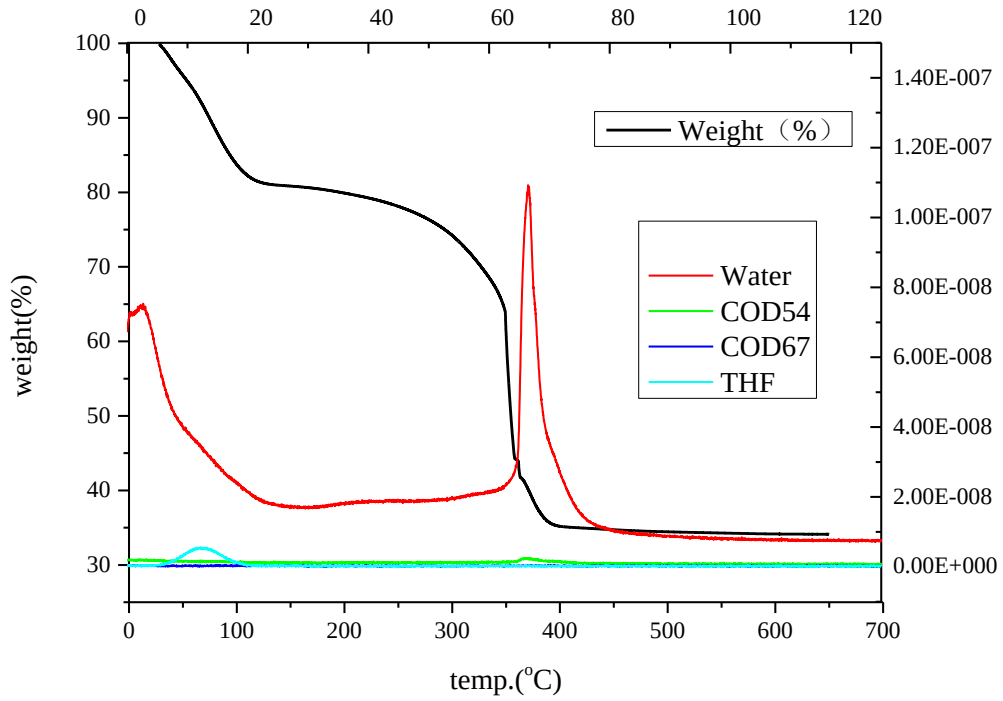
Supplementary Figure 5. SEM-EDS layered image (left) and the Zr (middle, red) and Ir (right, green) SEM-EDS mapping of UiO-67-Mix-Ir.



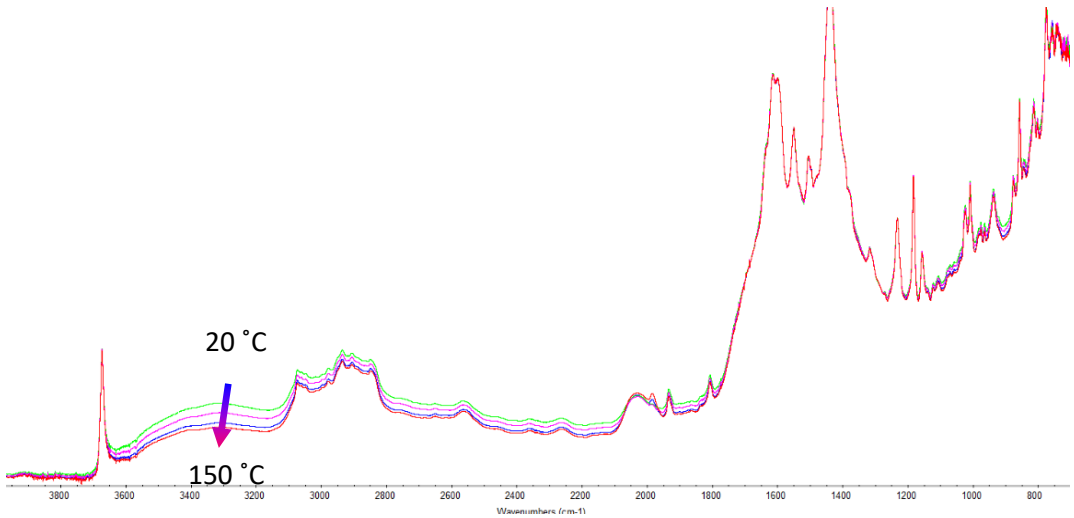
Supplementary Figure 6. Normalized Ir L^3-edge XANES spectra of UiO-67-Mix-Ir-green and the orange precatalyst UiO-67-Mix-Ir. The higher white line intensity of the latter (blue line) indicates higher e_g orbital vacancy, which is attributed to oxidation from Ir(I) to Ir(III). No energy shift is observed.



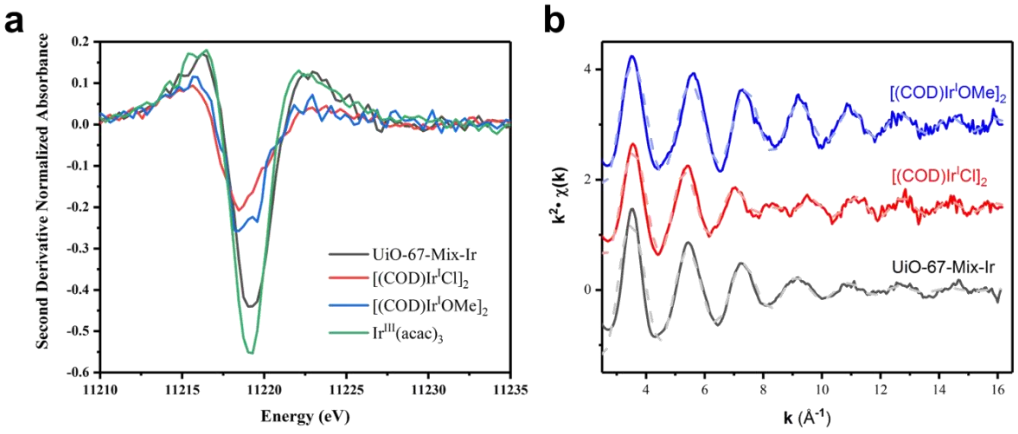
Supplementary Figure 7. XPS spectra showing the binding energy of the metal precursor $[Ir(COD)Cl]_2$ (left) and UiO-67-Mix-Ir MOF (right) at the Ir 4f region.



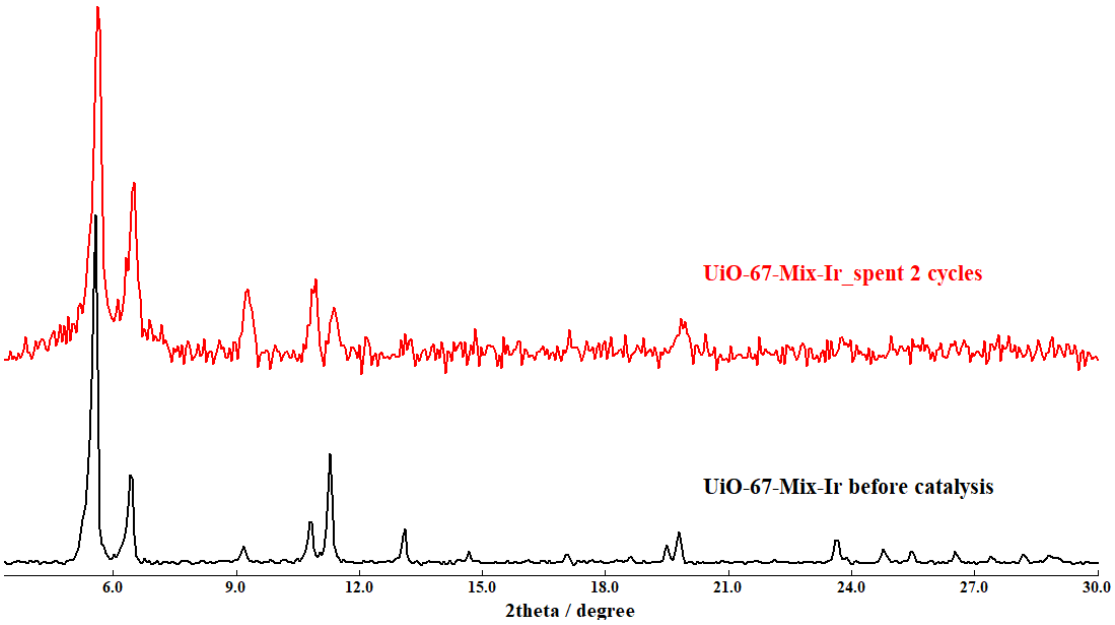
Supplementary Figure 8. TGA-MS plot of UiO-67-Mix-Ir before thermal activation at 150 ˚C showing no loss of COD until 350 ˚C.



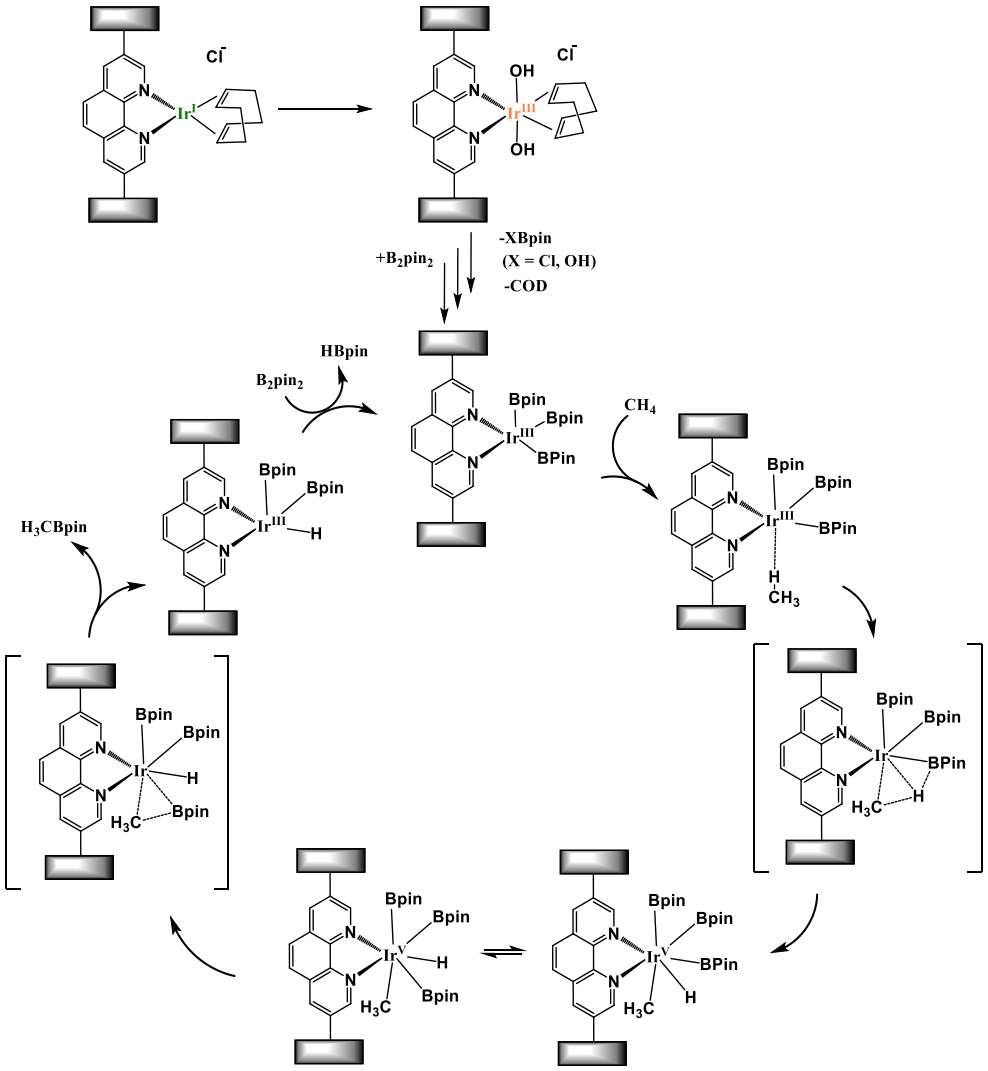
Supplementary Figure 9. Variable temperature (20 to 150 ˚C) DRIFTS spectra of UiO-67-Mix-Ir after thermal activation at 150 ˚C showing no loss of COD.



Supplementary Figure 10. (**a**) Second derivative XANES for UiO-67-Mix-Ir, $Ir(acac)_3$, $[(COD)Ir(\mu\text{-}Cl)]_2$, $[(COD)Ir(\mu\text{-}OMe)]_2$. (**b**) k^2-weighting k-space spectrum.



Supplementary Figure 11. Powder X-ray diffraction (PXRD) patterns of the catalyst UiO-67-Mix-Ir before and after 2 cycles of catalysis.



Supplementary Figure 12. Proposed catalytic cycle of UiO-67-Mix-Ir for the borylation of methane.

Supplementary Table 1. Variations of the reaction conditions for the catalytic borylation of methane.

Entry	B_2pin_2 (mg)	mol B_2pin_2	Cat (mg)	% w/w Ir	Ir (mg)	mol Ir	moles of B_2pin_2 converted	Conversion (%)	Yield of 1 (%)	TON	Ratio 1:2
1				5 mol %					2.3	-	4
2	13.2	5.19808E-05	0.2	5 mol %	0.01	5.20237E-08	2.91092E-06	100	5.6	23	-
3	13.3	5.23746E-05	0.2	0	0	0	0	0.7	0	0	0
4	13.3	5.23746E-05	2.9	1.8	0.0522	2.71564E-07	8.79893E-06	100	16.8	32	14.8
5	13.7	5.39498E-05	3.15	1.8	0.0567	2.94975E-07	1.78034E-06	18.7	3.3	6	57.5
6	13.2	5.19808E-05	2.8	1.8	0.0504	2.622E-07	1.97527E-06	98.2	3.8	7.5	41.8
7	13.8	5.43435E-05	1.7	1.8	0.0306	1.59193E-07	1.0597E-05	100	19.5	67	0
8	13.8	5.43435E-05	1.7	1.8	0.0306	1.59193E-07	1.0597E-05	100	19.5	67	0
9	13.2	5.19808E-05	3.1	1.8	0.0558	2.90292E-07	8.47287E-06	100	16.3	29	0
10	13.3	5.23746E-05	5.8	1.8	0.1044	5.43128E-07	3.40435E-06	100	6.5	6	0
11	13.8	5.43435E-05	1.7	1.8	0.0306	1.59193E-07	1.0597E-05	100	19.5	67	0
12	13.9	5.47373E-05	2.9	1.8	0.0522	2.71564E-07	1.00169E-05	85.1	18.3	37	22.3
13	13.9	5.47373E-05	2.9	1.8	0.0522	2.71564E-07	1.97054E-06	99.2	3.6	7	0
14	13.9	5.47373E-05	2.9	1.8	0.0522	2.71564E-07	3.83161E-07	12.9	0.7	1	0
15	13.8	5.43435E-05	1.7	1.8	0.0306	1.59193E-07	1.0597E-05	100	19.5	67	0
16	13.9	5.47373E-05	2.9	1.8	0.0522	2.71564E-07	4.32425E-06	100	7.9	16	0
17	13.8	5.43435E-05	1.7	1.8	0.0306	1.59193E-07	1.0597E-05	100	19.5	67	0
18	13.9	5.47373E-05	2.9	1.8	0.0522	2.71564E-07	1.52443E-05	100	27.85	56	0
19	13.3	5.23746E-05	2.9	1.8	0.0522	2.71564E-07	5.04367E-06	54.14	9.63	18	83.2

■ Supplementary References

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