Supplementary information

3D vs. turborstratic: controlling metal-organic framework dimensionality via N-heterocyclic carbene chemistry

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1. General notes

Materials:
All the commercially available chemicals were used as received without further purification. Cu(BF₄)₂·6H₂O (99 %) and n-octane (>99 %) were obtained from ABCR, CDCl₃ (>99.8 % D) was obtained from Acros, ethanol (A15 pharmaceutical grade) was obtained from Reactolab SA, anhydrous tetrahydrofuran (THF, >99.5 %) and trans-stilbene (>98.0 %) were obtained from TCI, [Ir(cod)(OMe)]₂ was obtained from Sigma-Aldrich (cat. #685062), anhydrous toluene (≥99.5 %), HNO₃ (69 %), HCl (37 %), ICP elemental standards for B and Cu were obtained from Carl Roth AG, Ir ICP elemental standard was obtained from Alfa Aesar.

X-Ray crystallography:
Laboratory single-crystal X-ray diffraction was performed at 100 K using a Bruker D8 Venture diffractometer equipped with a graphite monochromator and microfocused MoKα radiation source.
(λ = 0.71073 Å). The data was integrated with SAINT\textsuperscript{1} and corrected for adsorption with SADABS software. \textsuperscript{2} Synchrotron single crystal and powder X-ray diffraction data were collected using a multipurpose PILATUS@SNBL diffractometer with PILATUS 2M detector at the BM01 at European Synchrotron Radiation Facility (λ = 0.6866 Å). Single crystals were mounted on a Kapton loop and measured at 100 K. The structure solution and refinement were performed using ShelXT\textsuperscript{3} and ShelXL-2013\textsuperscript{4} operated through the Olex2 interface.\textsuperscript{5} First, non-hydrogen atoms were located and refined anisotropically, then H atoms were introduced with corresponding HFIX commands and refined isotropically. Powders were loaded in 1mm diameter glass capillaries and measured at 300 K in ambient conditions for \textit{ex situ} samples. For studies of \textit{in situ} material activation, the MOF sample was loaded in a capillary connected to a custom-built manifold and evacuated using a turbomolecular pump (< 10\textsuperscript{-2} mbar). Then, a temperature ramp was applied and the material was heated to 190 °C over 90 minutes, kept at that temperature for 20 minutes, and cooled down to room temperature over 50 minutes. The sample structure evolution was followed by measuring a powder pattern each minute. The data was visualized using MEDVEDED software.\textsuperscript{6} Laboratory powder X-ray diffraction was performed using Bruker D8 Discover instrument equipped with Cu Kα radiation source operated in Bragg–Brentano geometry. The scan step was 0.02 ° and the time per step was 1 s.

**FTIR measurements**

The \textit{in situ} FTIR data was collected using a PerkinElmer FTIR/FIR spectrometer. Ca. 20 mg of sample was mixed with ca. 200 mg of KBr and placed into a custom-built cell with diffuse reflectance Praying Mantis™ accessory. The sample was first activated by heating at 185 °C in vacuum for 15 h. Then the sample was cooled to −123 °C (150 K) and dosed with selected CO pressures using a custom-built gas manifold. The spectra were collected at 1 cm\textsuperscript{-1} resolution. All spectra were background-subtracted.

**TGA**

Thermogravimetric analysis (TGA) and decomposition temperatures were determined from TGA experiments on a TGA Q500 device from TA Instruments in 100 μl platinum pans with an empty pan of the same type as reference.
ICP
An exact amount of ca. 10 mg of MOF material was digested, inside a PTFE vial, in 1 mL of aqua regia (1:3 v/v HNO$_3$ 69 %+HCl 37 %) at 100 °C for 1h and further overnight at room temperature. The solution was diluted to 25 mL in a volumetric flask using 2 % HCl as a matrix, filtered through 0.22 μm syringe membrane filter and analyzed via ICP-OES using Agilent 5110 instrument. The averaged element concentrations and their standard deviations were extracted using 5 chosen, most intense and non-overlapping wavelengths.

NMR
Solution NMR spectra were recorded in CDCl$_3$ using a BRUKER AVIII HD 400 spectrometer; chemical shift values were referenced to 1 % TMS solution in CDCl$_3$ using the residual solvent signals as a secondary reference. Digestion NMR was performed in a mixture of D$_2$SO$_4$ (66 uL) and DMSO-d$_6$ (600 uL). The MOF was sonicated in this mixture until no solid was present. The Bruker Topspin software package (version 3.2) was used for measurements and Mestrenova software (version 12.0.0-20080) was used for processing of the spectra. Solid-state $^{13}$C NMR was performed at room temperature using a 500 MHz 3.2 mm LTMAS probe at 24 kHz MAS, with an Avance III Bruker console.

Electron microscopy
SEM images were acquired on a Thermo Scientific Teneo SEM instrument using an ETD detector at an accelerating voltage of 2.0 kV. Bright-field transmission electron microscopy (TEM) images were taken using the Thermo Scientific Tecnai G2 Spirit Twin instrument at an accelerating voltage of 120 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging was performed on a double Cs-corrected Thermo Scientific Titan Themis instrument operated in scanning mode at an accelerating voltage of 200 kV. This microscope is equipped with a high brightness X-FEG gun and four silicon drift Super-X EDX detectors.

X-ray photoelectron spectroscopy (XPS)
XPS measurements were carried out using a Kratos AXIS Supra spectrometer with an Al Kα X-ray source. All measurements are done with an emission current of 15 mA and all data was
collected with a pass energy of 40 eV and a step size of 0.1 eV. All binding energies were calibrated with respect to the C-C (C 1s) bond at 284.8 eV. Elemental fitting was done using ESCApe software by Kratos Analytical. All spectra were fit using a convolution of Gaussian and Lorentzian line shapes with a ratio of 70:30. A splitting of 3.0 eV with a ratio of 4:3 was used for the spin-orbit coupling of Ir 4f5/2 and 4f7/2 and a fixed FWHM was used. For metallic Ir, asymmetric line shape with an asymmetry of 0.5 was used.

X-ray absorption spectroscopy (XAS)
XAS spectra on Ir L_{III} absorption edges were acquired on an SNBL BM31 beamline of ESRF, Grenoble, France in transmission mode using two ionization chambers as detectors. The SNBL is equipped with a Si(111) double crystal monochromator for EXAFS data collection. The data was measured with a step size of 0.5 eV. Three reference materials, Ir metal (as a foil), [Ir(cod)(OMe)]_2 and Ir(acac)_3 (acac stands for acetylacetonate ligand) were measured in addition to the two samples. [Ir(cod)(OMe)]_2 and Ir(acac)_3 were diluted with cellulose prior to measurement, while other materials were measured neat.

2. Synthetic protocols
H_2Sp5-BF_4 and Cu-Sp5 were synthesized and characterized as previously described. Cu-Sp5-BF_4 large-scale synthesis. In a 500 mL Schott bottle, 1.761 g of Cu(BF_4)_2·6H_2O (5.100 mmol) was dissolved in 167 mL of ethanol. To this solution was added 1.435 g (3.604 mmol) of finely ground H_2Sp5-BF_4 and the mixture was sonicated for 10 minutes to form a well-dispersed pale blue slurry. The bottle was transferred into a temperature-programmed oven and the following program was applied: ramp to 80 °C over 8 h, stay at 80 °C for 72 h, turn off heating, and cool naturally inside the oven. The pale blue crystals were filtered on a G3 frit and washed with ethanol until the filtrate was clear and colorless. The material was further dried in vacuum (10^{-2} mbar) to produce Cu-Sp5-BF_4·EtOH. Anal. Calcd for Cu(C_{17}H_{13}N_{2}O_{4})(BF_4)(C_2H_5OH)_{1.6}(H_2O)_{0.6}: C, 44.59; H, 4.41; N, 5.15. Found: C, 44.65; H, 4.41; N, 5.17.

Cu-Sp5-BF_4 single crystal synthesis. In a 8 ml vial, 10.3mg (0.03 mmol) of Cu(BF_4)_2·6H_2O was dissolved in 3 mL of ethanol. To this was added 12 mg (0.03 mmol) of finely ground H_2Sp5-BF_4.
The mixture was sonicated for 10 minutes and transferred into a temperature-programmed oven and the following program was applied: ramp to 80 °C over 8 h, stay at 80 °C for 48 h, ramp to 25 °C during 8 h. The blue crystals were washed with ethanol by decantation until the supernatant was clear and colorless. The material was further dried in vacuum (10^-2 mbar) to produce Cu-Sp5-BF4-EtOH. Anal. Calcd for Cu(C17H13N2O4)(BF4)(C2H5OH)1.6(H2O)0.7: C, 44.44; H, 4.43; N, 5.13. Found: C, 44.52; H, 4.28; N, 4.93.

Cu-Sp5-BF4 activation. In a 20 mL vial equipped with a septum cap, vacuum-dried pale blue Cu-Sp5-BF4-solvent was placed and connected to a vacuum line via needle. The vial was heated stepwise in an oil bath (80 °C → 120 °C →160 °C → 185 °C), staying for 1 h at each intermediate temperature, and kept at 185 °C overnight. The resulting dark green crystals of Cu-Sp5-BF4-A were cooled down under vacuum, dosed with N2 from the Schlenk line, and immediately transferred to a nitrogen-filled glove box. Anal. Calcd for Cu(C17H13N2O4)(BF4): C, 44.42; H, 2.85; N, 6.09. Found: C, 44.06; H, 2.08; N, 5.58. B:Cu molar ratio (ICP): 1.02(3):1.

Cu-Sp5-OMe synthesis. In a nitrogen-filled glovebox, 1.000 g of Cu-Sp5-BF4-A (2.176 mmol) was added to a solution of 123.5 mg sodium methoxide (2.286 mmol, 1.05 eq) in 300 mL anhydrous methanol in a 1L Schott bottle. The bottle was tightly capped and placed on a magnetic stirrer plate at 300 rpm speed. After stirring for 24 h under nitrogen at room temperature, the mixture was allowed to stand still for 30 minutes and most of the liquid was decanted. The solid was isolated using centrifugation (3 min, 6000 rpm) and washed 3 times with 100 mL methanol. The obtained material, Cu-Sp5-OMe, was vacuum dried and then activated at 120 °C in vacuum overnight to produce Cu-Sp5-OMe-A. Anal. Calcd for Cu(C17H13N2O4)(BF4)0.22(OCH3)0.78(H2O)2.4: C, 46.49; H, 4.42; N, 6.10. Found: C, 46.15; H, 4.33; N, 6.14. B:Cu molar ratio (ICP): 0.22(2):1.

Cu-Sp5-BF4-A methanol treatment.
100 mg of Cu-Sp5-BF4-A was placed in 30 mL of anhydrous methanol and stirred at 300 rpm speed under N2 for 24 hours. The resulting material was isolated using centrifugation (3 min, 6000 rpm) and washed 3 times with 30 mL methanol. B:Cu molar ratio (ICP): 1.01(2):1.
Cu-Sp5-OMe synthesis with 1.5 eq of MeONa. In a nitrogen-filled glovebox, 0.1 g of Cu-Sp5-BF4-A (0.2176 mmol) was added to a solution of 17.6 mg sodium methoxide (0.3258 mmol, 1.5 eq) in 30 mL anhydrous methanol in a 40 mL vial. The vial was tightly capped and stirred at 300 rpm speed. After stirring for 24 h under nitrogen at room temperature, the solid was isolated using centrifugation (3 min, 6000 rpm) and washed 3 times with 30 mL methanol. B:Cu molar ratio (ICP): 0.049(6):1.

Cu-Sp5-OMe treatment with 0.2 eq of MeONa. In a nitrogen-filled glovebox, 0.1 g of Cu-Sp5-OMe (0.24 mmol) was added to a solution of 2.6 mg sodium methoxide (0.0.048 mmol, 0.2 eq) in 6 mL anhydrous methanol in a 20 mL vial. The vial was tightly capped and stirred at 300 rpm speed. After stirring for 24 h under nitrogen at room temperature, the solid was isolated using centrifugation (3 min, 6000 rpm) and washed 3 times with 30 mL methanol. B:Cu molar ratio (ICP): 0.053(3):1.

Iridium grafting procedure. In a nitrogen-filled glovebox, a solution of 252 mg [Ir(cod)(OMe)]2 (0.380 mmol = 0.760 mmol Ir, 1 eq Ir) in 35 mL anhydrous THF was prepared in a 100 mL Schlenk flask. To this solution, 350 mg of either Cu-Sp5-BF4-A (0.760 mmol) or Cu-Sp5-OMe-A (0.841 mmol) was added. The Schlenk flask was connected to a reflux condenser under nitrogen and the mixture was allowed to stir for 16 h at room temperature. After this soaking step, the mixture was heated to reflux (oil bath temperature 75 °C) for 24 h. Upon cooling, the mixture was separated using a centrifuge and the solid was washed with THF until the supernatant was colorless (5x50 mL). The materials were dried in vacuum overnight and stored in a nitrogen-filled glovebox, to produce Ir/Cu-Sp5-BF4-A and Ir/Cu-Sp5-OMe accordingly. Ir/Cu-Sp5-BF4-A: B:Cu ratio (ICP): 1.02(3):1. Ir(wt. %): 0.82(1). Ir/Cu-Sp5-OMe: B:Cu ratio (ICP): 0.23(1):1. Ir(wt. %): 2.47(6).

3. Catalysis protocols
Catalytic test protocol. In a nitrogen-filled glovebox, a stock solution of 2.143 g trans-stilbene and 0.676 g n-octane (internal standard) in anhydrous toluene was prepared in a 25 mL volumetric flask. 2.918 mL of this solution (corresponding to 0.250 g trans-stilbene, 1.387 mmol) was added
into a Parr pressure vessel. To this solution, an amount of catalyst corresponding to 0.25 mol% Ir (25.6 mg for Ir/MOF-OMe, 77.4 mg for Ir/MOF) was added, the vessel was sealed and removed from the glovebox and subsequently pressurized with 5 bar H₂ after 3 purges. The reaction was run at 40 °C for 24 hours. To stop the reaction, the vessel was cooled down in an ice bath and subsequently depressurized. The solid catalyst was removed using centrifugation and washed with THF 3 times. It was later dried in vacuum and stored in the glovebox for further characterization and recycle test. The liquid toluene solution was analyzed using ¹H NMR in CDCl₃ to determine the yield and the conversion.

**Split test protocol.** A catalytic reaction was run as described above for a period of 2 hours instead of 24 hours. Afterward, upon stopping the reaction and centrifugation, the supernatant was additionally filtered using a 0.22 μm syringe membrane filter to ensure the removal of all the solid material. A sample of the solution was taken for ¹H NMR and the rest of it was loaded in the reactor again and the reaction was run for extra 20 hours as described above. Upon stopping the reaction, the solution was analyzed again using ¹H NMR spectroscopy.
Table S1. Crystallographic data for **Cu-Sp5-BF₄-EtOH** and **Cu-Sp5-BF₄-A**

| Material     | Cu-Sp5-BF₄-EtOH                              | Cu-Sp5-BF₄-A                              |
|--------------|----------------------------------------------|-------------------------------------------|
| Empirical formula | C₁₉H₁₄BCuF₄N₂O₅                        | C₁₇H₁₃BCuF₄N₂O₄                        |
| Formula weight | 500.67                                      | 459.64                                    |
| Temperature/K | 100(2)                                      | 99.99                                     |
| Crystal system | monoclinic                                  | monoclinic                                |
| Space group   | P₂₁/n                                       | P₂₁/c                                     |
| a/Å           | 6.6391(5)                                   | 14.932(3)                                 |
| b/Å           | 33.5424(9)                                  | 31.562(5)                                 |
| c/Å           | 11.4021(9)                                  | 14.861(3)                                 |
| α/°           | 90                                          | 90                                        |
| β/°           | 106.155(8)                                  | 98.450(6)                                 |
| γ/°           | 90                                          | 90                                        |
| Volume/Å³     | 2438.9(3)                                   | 6928(2)                                   |
| Z             | 4                                           | 12                                        |
| ρcalc/g/cm³   | 1.364                                       | 1.322                                     |
| μ/mm⁻¹        | 0.873                                       | 0.999                                     |
| F(000)        | 1008.0                                      | 2772.0                                    |
| Crystal size/mm³ | 0.15 × 0.03 × 0.03                          | 0.1 × 0.02 × 0.02                         |
| Radiation     | synchrotron (λ = 0.6866)                    | MoKα (λ = 0.71073)                        |
| 2Θ range for data collection/° | 3.78 to 65.1                       | 1.29 to 46.848                           |
| Index ranges  | -6 ≤ h ≤ 6, -51 ≤ k ≤ 51, -17 ≤ l ≤ 17     | -16 ≤ h ≤ 16, -35 ≤ k ≤ 35, -15 ≤ l ≤ 16 |
| Reflections collected | 22331                                      | 79663                                     |
| Independent reflections | 5858 [Rint = 0.2689, Rsigma = 0.1810]     | 9973 [Rint = 0.1906, Rsigma = 0.1227]   |
| Data/restraints/parameters | 5858/3/345                                 | 9973/459/495                             |
| Goodness-of-fit on F² | 1.047                                      | 1.488                                     |
| Final R indexes [I>2σ (I)] | R₁ = 0.0779, wR₂ = 0.2260 | R₁ = 0.1261, wR₂ = 0.3637 |
| Final R indexes [all data] | R₁ = 0.0882, wR₂ = 0.2403 | R₁ = 0.2099, wR₂ = 0.4251 |
| Largest diff. peak/hole / e Å⁻³ | 1.65/-1.54                              | 1.86/-1.51                               |
Figure S1. Comparison of (a) **Cu-Sp5-H$_2$O** and (b) **Cu-Sp5-BF$_4$-EtOH** structures

Figure S2. PXRD data for **Cu-Sp5-BF$_4$-EtOH**
Figure S3. TGA curve for Cu-Sp5-BF₄-EtOH (air, 5 °C/min)

Figure S4. Comparison of PXRD patterns for Cu-Sp5-BF₄-EtOH and Cu-Sp5-BF₄-A
Figure S5. Structure of **Cu-Sp5-BF₄-EtOH** (left) and its activated counterpart, **Cu-Sp5-BF₄-A** (right), as viewed along the *a* axis (top) and the *c* axis (bottom). The number of Cu atoms along the *a* axis is the same in both pictures. Hydrogen atoms are omitted for clarity.

Figure S6. *In situ* PXRD data for **Cu-Sp5-BF₄** activation.
Figure S7. Synchrotron PXRD data for Cu-Sp5-BF4-A.

Figure S8. In situ DRIFTS spectra of (a) Cu-Sp5-BF4-A and (b) Cu-Sp5 upon CO dosage at 150 K.
Figure S9. Gas adsorption isotherms (CO$_2$, 195 K and N$_2$, 77 K) for Cu-Sp5-BF$_4$-A. Closed symbols represent adsorption, open symbols represent desorption.

Figure S10. (a) Gas adsorption isotherms of CO$_2$ (top) and N$_2$ (bottom) for Cu-Sp5-BF$_4$-A at 283 K, 298 K, and 313 K (b) Isosteric heat of adsorption of CO$_2$ for Cu-Sp5-BF$_4$-A.
Figure S11. Solid-state $^{13}$C MAS of Cu-Sp5-BF$_4$-A (bottom) and Cu-Sp5-OMe (top)
Figure S12. PXRD of **Cu-Sp5-OMe** and **Cu-Sp5-BF$_4$-A**

Figure S13. TGA curves of vacuum-dried **Cu-Sp5-OMe** and **Cu-Sp5-BF$_4$-A**
Figure S14. $^1$H digestion NMR of vacuum-dried Cu-Sp5-OMe in DMSO-d6 + D$_2$SO$_4$.

Figure S15. Light microscope image of Cu-Sp5-OMe particles.
Figure S16. A photo of Cu-Sp5-BF$_4$ crystal mounted on the goniometer, after unit cell indexing and crystal orientation determination.

Figure S17. Gas adsorption isotherms (CO$_2$, 195K) of Cu-Sp5-OMe and Cu-Sp5-BF$_4$-A and the corresponding Langmuir surface areas.
Figure S18. Gas adsorption isotherms (N$_2$, 77K) of Cu-Sp5-OMe and Cu-Sp5-BF$_4$-A

Figure S19. Powder diffraction patterns of materials obtained by treating Cu-Sp5-OMe and Cu-Sp5-BF$_4$-A under different conditions.
Figure S20. SEM images (a, b) and photos before (c) and after (d) air drying of Cu-Sp5-BF$_4$-A treated with MeOH for 24h

Figure S21. SEM images (a, b) and a photo (c) of Cu-Sp5-BF$_4$-A treated with 1.5 eq of NaOMe in MeOH for 24h

Figure S22. SEM images (a, b) and a photo (c) of Cu-Sp5-OMe treated with 0.2 eq of NaOMe in MeOH for 24h
Scheme S1. Iridium modification on Cu-Sp5-BF4-A

Figure S23. TEM images of Ir/Cu-Sp5-OMe
Figure S24. XPS spectrum of **Ir/Cu-Sp5-OMe**

Table S2. XPS fitting details for **Ir/Cu-Sp5-OMe**

|                  | Ir(III) 7/2 | Ir(III) 5/2 | Ir(I) 7/2 | Ir(I) 5/2 |
|------------------|-------------|-------------|-----------|-----------|
| Peak energy (eV)| 62.30       | 65.30       | 61.58     | 64.58     |
| FWHM             | 2.11        | 2.11        | 1.27      | 1.27      |
| Area (%)         | 52.07       | 39.04       | 5.08      | 3.81      |
| Algorithm        | Gauss/Lorentz | Gauss/Lorentz | Gauss/Lorentz | Gauss/Lorentz |
| Blend            | 0.3        | 0.3        | 0.3       | 0.3       |
| Asymmetry        | none       | none       | none      | none      |
Table S3. Structures of complexes used for EXAFS fits and detailed information on the corresponding starting fit parameters

| Entry # | Structure | 1 | 2 | 3 | 4 |
|---------|-----------|---|---|---|---|
| Name    | Mono-NHC-Ir(I) | Bis-NHC-Ir(I) | Tris-cyclometalated-Ir(III) | Bis-cyclometalated-Ir(III) |
| Atom    | C(NHC), C.N. 1, 2.06 Å | C(NHC), C.N. 2, 2.02 Å | C(NHC), C.N. 3, 2.03 Å | C(NHC), C.N. 2, 2.06 |
| Atom 2  | C(cod), C.N. 2, 2.11 Å | C(cod), C.N. 4, 2.11 Å | C(benzene), C.N. 3, 2.08 Å | C(benzene), C.N. 2, 1.99 Å |
| Atom 3  | C(cod), C.N. 2, 2.20 Å | - | - | O(acac), C.N. 2, 2.17 Å |
| Atom 4  | O(solvent), C.N. 1, 2.11 Å | - | - | - |
| CSD code| GARSAW | AZDCRH | KUNYAU | ASIHUG |
| Reference| 8 | 9 | 10 | 11 |

Atom colors: Ir, dark blue; C, grey; O, red; N, blue; H, white. C.N. stands for Coordination Number.

EXAFS fitting details for **Ir/Cu-Sp5-OMe** before catalysis:

Athena and Artemis software were used for the data analysis (background subtraction, normalization, etc.) of the Ir L-III edge XAS data and EXAFS fitting, respectively. The amplitude reduction factor, $S_0^2$, was determined for the Ir metal reference ($S_0^2 = 0.70059$) and transferred to the sample to fit in order to reduce the number of refined parameters, while the coordination number (C.N.) was fixed to be the same for the three different atoms (C1, C2, O1). Iridium bis-cyclometalated complex model structure was taken from literature. $\Delta E_0$ denotes the energy shift, $\Delta R_C$ and $\Delta R_O$ denote the adjustment in the half path length during the refinement for C and O atoms, respectively, and $\sigma^2$ denotes the Debye-Waller factor.
Goodness of fit parameters:

Reduced chi-square : 504.7882647
R-factor : 0.0184169

Fit results:
C.N. = 2.6 ± 0.3
ΔE₀ = 9.0 ± 1.4
ΔR_C = 0.08 ± 0.08
ΔR_O = -0.08 ± 0.08
σ² = 0.004 ± 0.002

Figure S25. (a) Normalized EXAFS spectrum of Ir/Cu-Sp5-OMe, (b) Fitted EXAFS spectrum of Ir/Cu-Sp5-OMe in k-space
Figure S26. PXRD of Ir/Cu-Sp5-OMe compared to those of Cu-Sp5-OMe and Cu-Sp5-BF4-A

Figure S27. Gas adsorption isotherm (N2, 77K) of Ir/Cu-Sp5-OMe
Figure S28. Distances between centers of neighboring NHC ligands in Cu-Sp5-BF4-A structure. Hydrogen atoms and BF4⁻ ions are omitted for clarity. Atom colors: C, gray; O, red; N, blue; Cu, orange

Figure S29. HAADF-STEM images of Ir/Cu-Sp5-OMe
Figure S30. $^1$H NMR (CDCl$_3$) spectrum of the solution after a catalytic run with a bare Cu-Sp5-OMe as a catalyst. No internal standard was used in this run.

Figure S31. $^1$H NMR (CDCl$_3$) spectrum of the solution after a catalytic run with a bare Cu-Sp5-BF$_4$-A as a catalyst. No internal standard was used in this run.
Figure S32. $^1$H NMR (CDCl$_3$) spectrum of the starting material used for the Ir-catalyzed reactions (solution of trans-stilbene in toluene with n-hexane as an internal standard).

Figure S33. $^1$H NMR (CDCl$_3$) spectrum of the solution after a catalytic run with a fresh Ir/Cu-Sp5-OMe catalyst.
Figure S34. $^1$H NMR (CDCl$_3$) spectrum of the solution after a catalytic run with a fresh Ir/Cu-Sp5-BF$_4$-A catalyst.

Figure S35. $^1$H NMR (CDCl$_3$) spectrum of the solution after a catalytic run with a recycled Ir/Cu-Sp5-OMe catalyst.
Figure S36. $^1$H NMR (CDCl$_3$) spectrum of the solution after a catalytic run with a recycled \textit{Ir/Cu-Sp5-BF$_4$-A} catalyst

Figure S37. Catalyst separation test results for \textit{Ir/Cu-Sp5-BF$_4$-A} and \textit{Ir/Cu-Sp5-OMe}
Table S4. Comparison of **Ir/Cu-Sp5-OMe** catalytic performance with reported supported Ir-NHC catalysts

| Material                        | Substrate          | Reaction parameters                                             | Yield | Ref  |
|---------------------------------|--------------------|-----------------------------------------------------------------|-------|------|
| Ir/Cu-Sp5-OMe                   | stilbene           | 5 bar H\(_2\), 0.25 mol. % catalyst, 24h, 40 °C                | >99%  | This work |
| Ir-NHC grafted on silica        | stilbene           | 3 bar H\(_2\), 0.1 mol. % catalyst, 18 h, 40 °C                | >99%  | 14   |
| Ir-NHC grafted on MCM-41        | diethyl 2-benzylidene succinate | 4 bar H\(_2\), 0.01 mol. % catalyst, 1 h, 40 °C              | 72.5  | 15   |
| Ir-NHC grafted on MM clay       | cyclohexene        | 1 bar H\(_2\), 0.1 mol. % catalyst, 3.7 h, 17 °C              | 83    | 16   |

Figure S38. XPS spectra of **Ir/Cu-Sp5-OMe** before and after catalysis

Table S5. XPS fitting details for **Ir/Cu-Sp5-OMe** after catalysis

|                  | Ir(III) 7/2 | Ir(III) 5/2 | Ir(I) 7/2 | Ir(I) 5/2 | Ir(0) 7/2 | Ir(0) 5/2 |
|------------------|-------------|-------------|-----------|-----------|-----------|-----------|
| Peak energy (eV) | 62.422      | 65.422      | 61.670    | 64.670    | 60.900    | 63.900    |
| FWHF             | 2.113       | 2.113       | 1.479     | 1.479     | 1.056     | 1.056     |
| Area (%)         | 37.49       | 28.12       | 16.18     | 12.13     | 3.47      | 2.60      |
| Algorithm        | Gauss/Lorentz| Gauss/Lorentz| Gauss/Lorentz| Gauss/Lorentz| Asymmetric| Asymmetric|
| Blend            | 0.3         | 0.3         | 0.3       | 0.3       | 0.3       | 0.3       |
| Asymmetry        | none        | none        | none      | none      | 0.5       | 0.5       |
Figure S39. (a) XANES spectra of Ir/Cu-Sp5-OMe before and after catalysis (solid lines) and reference materials Ir metal and [Ir(cod)(OMe)]$_2$ (dashed lines). (b) First derivative of the spectra.

Figure S40. (a) R-space EXAFS spectra of Ir/Cu-Sp5-OMe before and after catalysis (b) R-space EXAFS spectrum of iridium foil.
Figure S41. HAADF-STEM images of Ir/Cu-Sp5-OMe sample after catalytic cycle
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