Supporting Information

Framework Adaptability and Concerted Structural Response in a Bismuth Metal-Organic Framework Catalyst.

E. P. Gómez-Oliveira, D. Reinares-Fisac, L. M. Aguirre-Díaz, F. Esteban-Betegón, M. Pintado-Sierra, E. Gutiérrez-Puebla, M. Iglesias, M. Ángeles Monge*, F. Gándara*
Supporting Information

S1. Experimental procedure  S-3
   • General
   • Synthesis of materials
   • Catalytic activity experiments procedure

S2. Single crystal X-ray Diffraction data including framework – guest studies  S-5
   • General information
   • Table S 2.1 InPF-60
   • Table S 2.2 BiPF-5
   • Table S 2.3 BiPF-7
   • Table S 2.4 BiPF-7_acetophenone
   • Table S 2.5 BiPF-7_aniline
   • Table S 2.6 BiPF-7_aniline_acetophenone
   • Table S 2.7 BiPF-7_BrBenzene
   • Figure S.2.1 Simulation of guest molecules location

S3. Powder X-ray diffraction data  S-13
   • Figure S3.1 InPF-60 as-synthesized, activated, simulated
   • Figure S3.2 InPF-60 phase transformation
- Figure S3.3 InPF-60 Pawley of transformed phase
- Figure S3.4 BiPF-5 as-synthesized, activated, simulated
- Figure S3.5 BiPF-7 as-synthesized, activated, simulated

S4. IR Spectra
   - Figure S4.1 IR of InPF-60
   - Figure S4.2 IR of BiPF-5
   - Figure S4.3 IR of BiPF-7

S5. Thermogravimetric analysis
   - Figure S5.1a, b TG Curve of InPF-60 and PXRD residue
   - Figure S5.2a, b TG Curve of BiPF-5 and PXRD residue
   - Figure S5.3a, b TG Curve of BiPF-7 and PXRD residue

S6. Gas sorption analysis
   - Figure S6.1 N\textsubscript{2} sorption isotherms
   - Figure S6.2 Ar isotherm micropore of BiPF-7
   - Figure S6.3 InPF-60 CO\textsubscript{2} isotherm
   - Figure S6.4 BiPF-5 CO\textsubscript{2} isotherm
   - Figure S6.5BiPF-7 CO\textsubscript{2} isotherm

S7 Catalytic activity experiments background

S8 Catalytic activity

S9 Recycle reactions

S10 Characterization of the Strecker 3C reaction products

S11 Spectra for characterized compounds
S1. EXPERIMENTAL PROCEDURE

1.1. General

The reagents and solvents employed were commercially available and used as received without further purification. Bismuth nitrate (III) pentahydrate, Bi(NO₃)₃·5H₂O (from Strem Chemicals); indium acetate, In(OAc)₃ (from PURATREM); dichloromethane (DCM, obtained from Labkem); ethanol absolute (EtOH, obtained from Scharlau); acetone, 99.5% (purchased from Labkem). The organic linker 4,4′,4″,4‴-methanetetrayltetrabenzoic acid, H₄MTBA was synthesized following reported procedures, as well as used from commercial sources (98% TCI and ChemScn}. NMR spectra were recorded in a Bruker Advance 300-II equipment using CDCl₃ as solvent. IR spectra were recorded from KBr pellets in the range 4000-450 cm⁻¹ on a Bruker Vertex 70V spectrophotometer, with a resolution of 2 cm⁻¹. Thermogravimetric and differential thermal analysis (TGA-DTA) was performed using a SDT Q600 from TA Instruments equipment in a temperature range between 30 and 800 °C in air (100 mL/min flow) atmosphere and heating rate of 10 °C/min. A CNHS PERKIN ELMER 2400 analyzer was employed for the elemental analysis. Powder X-ray diffraction (PXRD) patterns were measured with a Bruker D8 diffractometer with a copper source operated at 1600 W, with step size = 0.02° and exposure time = 0.5 s/step. PXRD measurements were used to check the purity of the obtained microcrystalline products by a comparison of the experimental results with the simulated patterns obtained from single-crystal X-ray diffraction data. N₂ sorption isotherms were measured at 77K and CO₂ sorption isotherms were measured at 274K with an Autosorb-1 from Quantachrome Instruments in the relative pressure range of 10⁻² to 1. Before adsorption measurements, the samples were activated and outgassed at different temperatures overnight.

1.2 Synthesis of materials

1.2.1 Synthesis of InPF-60

\[([\text{In(MTB)}]_2[\text{CH}_3\text{NH}_2]^+ \cdot 0.75\text{DMF} \cdot \text{H}_2\text{O})\]: In a Teflon vessel, 44 mg of In(OAc)₃ (0.15 mmol) and 50 mg of 4,4′,4″,4‴-methanetetrayltetrabenzoic (H₄MTBA; 0.10 mmol) were added. Later, we dissolved them in 2.5 mL of N,N-dimethylformamide and finally, 0.9 mL of nitric acid were added. Next, the vessel was sealed and placed in a preheated oven at 120°C for a time of 48 hours and cooled to room temperature. Pure, white, needle-like crystals were obtained after being centrifuged and washed with DMF, water, ethanol and acetone. Powder X-ray diffraction supported the purity of the sample. Yield: 42 mg, 64%. Elemental analysis, found (calculated): C, 54.50% (55.46%); H, 4.37% (3.86%); N, 1.68% (2.09%). IR (KBr, cm⁻¹): 3455 v(O-H), 3129 and 3058 v(CSP2-H), 2969 and 2925 v(CSP3-H), 1680 v(C=O), 1604 v(C=O), 1537 and 1415 scissoring(C-H), 1187, 1017, 875, 775 and 723 v(C-C) 552, 519, 496 and 448 v(In-O).

1.2.2 Synthesis of BiPF-5

\[[\text{Bi(MTB)}(\text{H}_2\text{O})]_2[\text{CH}_3\text{NH}_2]^-\cdot 1\text{DMF})\]: In a glass vial, 10.2 mg of Bi(NO₃)₃·5H₂O (0.021 mmol) and 10 mg of tetrakis(4-carboxyphenyl)methane (H₄MTBA; 0.02 mmol) were added. Later, we dissolved them in 1 mL of N,N-dimethylformamide (DMF), 1 mL of ethanol (EtOH) and 1 mL of water. Next, the glass vial was sealed and placed in a preheated heating plate at 90°C for a time of 6 days and cooled to room temperature. Pure, white, needle-like crystals were obtained after being washed with DMF, toluene (x2), ethanol and toluene again, allowing it to dry in the air or under N₂ flow. Powder X-ray diffraction supported the purity of the sample. Yield: 10 mg, 61 %. Elemental analysis, found (calculated): C, 45.35% (49.5%); H, 4.28% (3.68%); N, 2.86% (3.30%).

---

1 Grimm, M.; Kirste, B.; Kurreck, H. 13C-ENDOR Investigation of an Organic Tetraradical in the Quintet State; Synthesis of a Fourfold 13C-Labeled Tetrakisgalvinol. Angew. Chemie Int. Ed. English 1996, 25 (12), 1097–1098. https://doi.org/10.1002/anie.19961097).

2 Zimmermann, T.; Müller, T. Convenient Syntheses of Tetraarylmethylene Starting Materials. Synthesis (Stuttg). 2002, 2002 (09), 1157–1162. https://doi.org/10.1055/s-2002-32526.
1.2.3 Synthesis of BiPF-7

{[Bi₆(MTB)₆(H₂O)₆]·4DMF}: In a glass vial, 29.1 mg of Bi(NO₃)₃·5H₂O (0.06 mmol) and 20 mg of tetrakis(4-carboxyphenyl)methane (H₄MTBA; 0.04 mmol) were added. Later, we dissolved them in 2.5 mL of N,N-dimethylformamide (DMF) and finally, 0.9 mL of nitric acid were added. Next, the vessel was sealed and placed in a preheated heating plate at 90°C for a time of 6 days and cooled to room temperature. Pure, colourless crystals with the shape of a hexagonal prism were obtained after being centrifuged and washed with DMF, water, ethanol, and acetone. Powder X-ray diffraction supported the purity of the sample. Yield: 40 mg, xx %. Elemental analysis, found (calculated): C, 41.66% (43.09%); H, 2.77% (2.92%); N, 2.46% (1.08%). IR (KBr, cm⁻¹): 3446 v(O-H), 3171, 3123 and 3062 v(C₉H₈-O), 1701 v(C=O), 1606 v(C-O), 1534 and 1383 scissoring(C-H), 1189, 1112, 1018, 847 and 772 v(C-C), 553, 528, 503, 485, 459 and 430 v(Bi-O).

1.3. Catalytic activity experiments procedure

Catalysts were activated under vacuum for a period of 18 hours. Then, the mixture of ketone, amine and trimethylsilyl cyanide (TMSCN) was added to a Schlenk tube (1.89 mmol of ketone, 1.89 mmol of amine and 1.98 mmol of TMSCN), where the MOF has been previously introduced. The mixture (in solvent-free conditions) was stirred (210 rpm) at 25 °C for 4 hours, under N₂ atmosphere. For comparative purpose, the same standard reaction conditions were used for all tested substrates, and therefore the reaction parameters were not further optimized for each one of them. The progress of the reactions was monitored by ¹H-NMR, and isolated yields calculated. When reaction was completed and samples were taken, the content of the Schlenk tube was mixed with DCM in order to dissolve the Strecker α-aminonitrile and recover the catalyst by centrifugation. X-ray diffraction patterns were obtained before and after each experiment to ensure crystallinity, purity, and recyclability of the MOF.

Catalysts were reused at least in 9 cycles. In each case, after recovery, the catalysts were washed with DCM and dried overnight following the same procedure described above, without significant loss of activity (yield of 64% in the nineth run).

The leaching test was performed. The mixture remained 5 minutes within the conditions previously described. After that, part of the liquid was separated and transferred to an empty Schlenk. After 4 hours, no progress is observed in the reaction. After 24 hours, different products were found in the mixture, mainly composed of unreacted acetophenone (20%) and aniline (22%), a small amount of aminonitrile (15%), and other undetermined products (scheme 1 shows the main possible products). This proved that the presence of the catalyst is necessary in order to selectively complete the organic transformation.

![Scheme S1 Strecker reaction and possible by-products: α-aminonitrile, imine, cyanohdride and silanamine.](image-url)
2.1 General information

Tables S2.1, S2.2 and S2.3 summarizes the main crystal and refinement data for InPF-60, BiPF-5 and BiPF-7, respectively. Tables S2.4, S2.5 and S2.6 summarizes the main crystal and refinement for BiPF-7 with acetophenone, aniline and the mixture of both, respectively. Crystals were selected under a polarizing optical microscope for a single-crystal X-ray diffraction experiment. Single-crystal X-ray data were obtained in a Bruker four circle kappa diffractometer equipped with a Cu INCOATED microsource, operated at 30 W power (45kV, 0.60mA) to generate Cu Kα radiation (λ = 1.54178 Å), and a Bruker VANTEC 500 area detector (microgap technology). Diffraction data were collected exploring over a hemisphere of the reciprocal space in a combination of φ and ω scans to reach a resolution of 0.85 Å, using a Bruker APEX3 software suite (each exposure, depending on ω, was of 56, 90 or 140 s covering 1º in ω or φ). Unit cell dimensions were determined for least-squares fit of reflections with I>4σ. The structures were solved by intrinsic phase methods. The hydrogen atoms were fixed at their calculated positions using distances and angle constraints. All calculations were performed using APEX3 software for data collection and OLEX2-1.23 and SHELXTL4 to resolve and refine the structure.

Table S2.1 InPF-60. Main crystallographic data for InPF-60 compound. Data recovered from InPF-60 crystal after evacuation.

| Identification code | InPF-60          |
|---------------------|------------------|
| CCDC number        | 2150203          |
| Empirical formula  | C_{31}H_{21.67}InN_{0.58} |
| Formula weight     | 660.30           |
| Temperature/K      | 296.15           |
| Crystal system     | Monoclinic       |
| Space group        | Cc               |
| a/Å                | 21.3537(10)      |
| b/Å                | 14.9688(6)       |
| c/Å                | 15.0505(7)       |
| α/°                | 90               |
| β/°                | 132.912(2)       |
| γ/°                | 90               |
| Volume/Å³          | 3523.4(3)        |
| Z                   | 4                |
| \(\rho_{calc}\)/g/cm³ | 1.245          |
| \(\mu\)/mm⁻¹       | 5.743            |
| F(000)             | 1329             |
| Crystal size/mm³   | 0.15 x 0.15 x 0.15 |
| Radiation          | CuKα (λ = 1.54178) |
| 2θ range for data collection/° | 8.176 to 149.272 |
| Index ranges       | -25 ≤ h ≤ 26, -18 ≤ k ≤ 18, -18 ≤ l ≤ 17 |
| Reflections collected | 16313         |
| Independent reflections | 6259 [R_{int} = 0.0670, R_{sigma} = 0.1007] |
| Data/restraints/parameters | 6259/3/364    |
| Goodness-of-fit on F² | 0.930           |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0772, wR₂ = 0.2009 |
| Final R indexes [all data] | R₁ = 0.0983 wR₂ = 0.2473 |
| Largest diff. peak/hole / e Å³ | 1.45/-1.04 |
Table S2.2 BiPF-5. Main crystallographic data for BiPF-5 compound. Data recovered from BiPF-5 crystal after evacuation.

| Identification code       | BiPF-5         |
|---------------------------|----------------|
| CCDC number               | 2150204        |
| Empirical formula         | C_{126}H_{72}Bi_{4}N_{4}O_{41} |
| Formula weight            | 3133.79        |
| Temperature/K             | 296.15         |
| Crystal system            | orthorhombic   |
| Space group               | Pnna           |
| a/Å                       | 28.0290(15)    |
| b/Å                       | 18.5193(8)     |
| c/Å                       | 15.0920(7)     |
| α/°                       | 90             |
| β/°                       | 90             |
| γ/°                       | 90             |
| Volume/Å³                  | 7833.9(6)      |
| Z                         | 2              |
| ρ calc/g/cm³              | 1.329          |
| μ/mm²                     | 9.235          |
| F(000)                    | 3032.0         |
| Crystal size/mm³          | 0.16 × 0.08 × 0.02 |
| Radiation                 | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 6.652 to 127.634 |
| Index ranges              | -32 ≤ h ≤ 30, -21 ≤ k ≤ 21, -17 ≤ l ≤ 17 |
| Reflections collected     | 78901          |
| Independent reflections   | 6459 [R_{int} = 0.1325, R_{sigma} = 0.1100] |
| Data/restraints/parameters| 6459/0/386     |
| Goodness-of-fit on F²     | 0.924          |
| Final R indexes [I>=2σ(I)]| R₁ = 0.0611, wR₂ = 0.1645 |
| Final R indexes [all data]| R₁ = 0.0819, wR₂ = 0.1900 |
| Largest diff. peak/hole / e Å³ | 1.43/-1.58   |
Table S2.3 BiPF-7. Main crystallographic data for BiPF-7 compound. Data collected from as made BiPF-7 crystal.

| Identification code   | BiPF-7_as made                  |
|-----------------------|---------------------------------|
| CCDC number           | 2150208                         |
| Empirical formula     | C$_{174}$H$_{96}$Bi$_8$O$_{63}$ |
| Formula weight        | 4866.34                         |
| Temperature/K         | 296.15                          |
| Crystal system        | trigonal                        |
| Space group           | R-3c                            |
| a/A                   | 39.4805(13)                     |
| b/A                   | 39.4805(13)                     |
| c/A                   | 24.6270(10)                     |
| α/°                   | 90                              |
| β/°                   | 90                              |
| γ/°                   | 120                             |
| Volume/Å$^3$           | 33244(3)                        |
| Z                     | 6                               |
| ρ_g/cm$^3$             | 1.458                           |
| μ/mm$^{-1}$            | 12.801                          |
| F(000)                | 13848.0                         |
| Crystal size/mm$^3$    | 0.6 × 0.1 × 0.06                |
| Radiation             | Cu Kα (λ = 1.54178)             |
| 2Θ range for data collection/° | 4.476 to 130.336               |
| Index ranges          | -46 ≤ h ≤ 44, -46 ≤ k ≤ 46, -28 ≤ l ≤ 28 |
| Reflections collected | 126859                          |
| Independent reflections| 6320 [R$_{int} = 0.1310$, R$_{sigma} = 0.0357$] |
| Data/restraints/parameters | 6320/0/369                  |
| Goodness-of-fit on F$^2$ | 1.019                          |
| Final R indexes [I>2σ (I)] | R$_1 = 0.0664$, wR$_2 = 0.1796$ |
| Final R indexes [all data] | R$_1 = 0.0841$, wR$_2 = 0.2037$ |
| Largest diff. peak/hole / e Å$^3$ | 6.41/-4.07                   |
Table S2.4 BiPF-7_acetophenone. Main crystallographic data for BiPF-7 compound with acetophenone coordinated. Data collected from BiPF-7 crystal after soaking various hours in the acetophenone.

| Identification code  | BiPF7aceto          |
|---------------------|---------------------|
| CCDC number         | 2150207             |
| Empirical formula   | C_{375}H_{216}Bi_{16}O_{114} |
| Formula weight      | 9889.54             |
| Temperature/K       | 296.15              |
| Crystal system      | trigonal            |
| Space group         | R-3c                |
| a/Å                 | 39.592(8)           |
| b/Å                 | 39.592(8)           |
| c/Å                 | 25.452(5)           |
| α/°                 | 90                  |
| β/°                 | 90                  |
| γ/°                 | 120                 |
| Volume/Å³           | 34553(16)           |
| Z                   | 3                   |
| ρ_{calc}/g/cm³      | 1.426               |
| μ/mm⁻¹              | 12.306              |
| F(000)              | 14118.0             |
| Crystal size/mm³    | 0.2 × 0.2 × 0.15    |
| Radiation           | CuKα (λ = 1.54184)  |
| 2Θ range for data collection/° | 4.464 to 131.628 |
| Index ranges        | -46 ≤ h ≤ 46, -46 ≤ k ≤ 46, -28 ≤ l ≤ 27 |
| Reflections collected | 102653              |
| Independent reflections | 6591 [R_{int} = 0.1156, R_{sigma} = 0.0388] |
| Data/restraints/parameters | 6591/11/376 |
| Goodness-of-fit on F² | 1.045               |
| Final R indexes [I>2σ (I)] | R₁ = 0.0728, wR₂ = 0.1922 |
| Final R indexes [all data] | R₁ = 0.0899, wR₂ = 0.2136 |
| Largest diff. peak/hole / e Å⁻³ | 3.19/-1.76          |
Table S2.5 BiPF-7_aniline. Main crystallographic data for BiPF-7 compound with aniline coordinated. Data collected from BiPF-7 crystal after soaking various hours in the aniline.

| Identification code | BiPF7-aniline |
|---------------------|---------------|
| CCDC number         | 2150205       |
| Empirical formula   | C_{192}H_{105}Bi_{8}N_{3}O_{54} |
| Formula weight      | 4989.62       |
| Temperature/K       | 296.15        |
| Crystal system      | trigonal      |
| Space group         | R-3c          |
| a/Å                 | 39.990(8)     |
| b/Å                 | 39.990(8)     |
| c/Å                 | 26.126(5)     |
| α/°                 | 90            |
| β/°                 | 90            |
| γ/°                 | 120           |
| Volume/Å³            | 36184(16)     |
| Z                    | 6             |
| ρ_{calc}g/cm³        | 1.374         |
| μ/mm⁻¹              | 11.751        |
| F(000)              | 14244.0       |
| Crystal size/mm³     | 0.2 × 0.2 × 0.1 |
| Radiation            | CuKα (λ = 1.54184) |
| 2θ range for data collection/° | 4.42 to 128.652 |
| Index ranges         | -46 ≤ h ≤ 46, -46 ≤ k ≤ 46, -30 ≤ l ≤ 30 |
| Reflections collected | 101454       |
| Independent reflections | 6687 [Rint = 0.0805, Rsigma = 0.0300] |
| Data/restraints/parameters | 6687/0/390     |
| Goodness-of-fit on F² | 1.065         |
| Final R indexes [I>2σ(I)] | R1 = 0.0670, wR2 = 0.1691 |
| Final R indexes [all data] | R1 = 0.0790, wR2 = 0.1842 |
| Largest diff. peak/hole / e Å⁻³ | 1.75/-2.02 |
Table S2.6 BiPF-7_aniline_acetophenone. Main crystallographic data for BiPF-7 compound with acetophenone and aniline coordinated. Data collected from BiPF-7 crystal after soaking various hours in a mixture of acetophenone and aniline.

| Identification code | BiPF-7_Ani_aceto |
|---------------------|------------------|
| CCDC number         | 2150206          |
| Empirical formula   | C_{202}H_{96}Bi_{8}N_{2}O_{55} |
| Formula weight      | 5102.54          |
| Temperature/K       | 293.5            |
| Crystal system      | trigonal         |
| Space group         | R-3c             |
| a/Å                 | 39.5629(10)      |
| b/Å                 | 39.5629(10)      |
| c/Å                 | 25.6030(8)       |
| α/°                 | 90               |
| β/°                 | 90               |
| γ/°                 | 120              |
| Volume/Å³           | 34705(2)         |
| Z                   | 6                |
| \( \rho_{\text{calc}} \)/g/cm³ | 1.465 |
| \( \mu \)/mm⁻¹      | 12.269           |
| F(000)              | 14556.0          |
| Crystal size/mm³    | 0.3 × 0.2 × 0.1  |
| Radiation           | CuKα (\( \lambda = 1.54178 \)) |
| 2θ range for data collection/° | 4.466 to 144.67 |
| Index ranges        | -46 ≤ h ≤ 46, -46 ≤ k ≤ 46, -27 ≤ l ≤ 29 |
| Reflections collected | 111193          |
| Independent reflections | 7492 [\( R_{\text{int}} = 0.0630, R_{\text{sigma}} = 0.0239 \)] |
| Data/restraints/parameters | 7492/13/391 |
| Goodness-of-fit on \( F^2 \) | 1.080 |
| Final R indexes [I>2σ(I)] | \( R_1 = 0.0665, wR_2 = 0.1563 \) |
| Final R indexes [all data] | \( R_1 = 0.0839, wR_2 = 0.1743 \) |
| Largest diff. peak/hole / e Å⁻³ | 1.59/-1.22 |
Table S2.7 BiPF-7_Bromobenzene. Main crystallographic data for BiPF-7 compound with bromobenzene. Data collected from BiPF-7 crystal after soaking overnight in bromobenzene.

| Identification code       | BiPF-7_BrBenz |
|---------------------------|---------------|
| CCDC number               | 2179344       |
| Empirical formula         | C₁₉₂H₉₆Bi₈Br₃O₅₆.75 |
| Formula weight            | 5222.25       |
| Temperature/K             | 293.5         |
| Crystal system            | trigonal      |
| Space group               | R-3c          |
| a/Å                       | 39.5856(14)   |
| b/Å                       | 39.5856(14)   |
| c/Å                       | 25.2176(13)   |
| α/°                       | 90            |
| β/°                       | 90            |
| γ/°                       | 120           |
| Volume/Å³                 | 34222(3)      |
| Z                         | 6             |
| ρ calc/g/cm³              | 1.520         |
| µ/mm⁻¹                    | 13.051        |
| F(000)                    | 14826.0       |
| Crystal size/mm³          | 0.1 × 0.1 × 0.07 |
| Radiation                 | CuKα (λ = 1.54178) |
| 2Θ range for data collection/° | 4.464 to 131.568 |
| Index ranges              | -46 ≤ h ≤ 46, -46 ≤ k ≤ 46, -29 ≤ l ≤ 29 |
| Reflections collected     | 135112        |
| Independent reflections   | 6543 [R_{int} = 0.1494, R_{sigma} = 0.0482] |
| Data/restraints/parameters| 6543/7/383    |
| Goodness-of-fit on F²     | 1.031         |
| Final R indexes [I>=2σ (I)] | R₁ = 0.0818, wR₂ = 0.2224 |
| Final R indexes [all data]| R₁ = 0.1111, wR₂ = 0.2612 |
| Largest diff. peak/hole / e Å³ | 5.83/-2.79   |
To corroborate that aniline can diffuse through the pores of BiPF-7, we have completed a simulated annealing process with the use of the adsorption locator module of Materials Studio, employing a universal forcefield, and including 33 molecules per unit cell. In addition, we have also used aminonaphthalene in the simulation, to check whether larger molecules could also fit in the pores. To this end, the simulated annealing process was carried out with 24 molecules per unit cell.

*Figure S2.1:* Location of aniline (top) and aminonaphthalene (bottom) molecules in the pores of BiPF-7. For the sake of clarity, guest molecule atoms are shown with CPK radii, and framework atoms are shown as white sticks.
• S3. POWDER X-RAY DIFFRACTION DATA

Figure S3.1 From top to bottom, InPF-60 as-synthesized (red), activated (blue), and simulated from single crystal data (black).

Figure S3.2 From top to bottom, InPF-60 as-after 3 days at 125 °C (pink), after 1 day at 125 °C (red), synthesized (blue), and simulated profile from single-crystal diffraction structure data (black).
**Figure S3.3** Pawley refinement in the C2 monoclinic space group of InPF-60 after heating the crystals for 3 days at 125 °C.

**Figure S3.4** From top to bottom, BiPF-5 as-synthesized (red), activated (blue), and simulated from single crystal data (black).
Figure S3.5 From top to bottom, BiPF-7 as-synthesized (red), activated (blue), and simulated from single crystal data (black).
• S.4 IR SPECTRA

**Figure S4.1** Infrared transmittance spectra of MOF InPF-60.

**Figure S4.2** Infrared transmittance spectra of MOF BiPF-5.
Figure S4.3 Infrared transmittance spectra of MOF BiPF-7.
S.5 THERMOGRAVIMETRIC ANALYSIS (TGA)

Figure S5.1a TG-DTA curve for as-synthesized InPF-60 in air. Pores are filled with residual DMF, acetone and water molecules, which evacuates from 60 to 150 °C, corresponding to a loss of 4 % of the total weight. The structure finally collapses when temperature reaches 424 °C. The final residue is a cubic indium oxide (In$_2$O$_3$).

Figure S5.1b Powder X-ray diffraction of residues after thermogravimetric analysis (red), fitting according to In$_2$O$_3$, PXRD ICSD pattern 252371 (black).
Figure S5.2a TG-DTA curve for as-synthesized BiPF-5 in air. Pores are filled with ethanol molecules, which evacuates at 80 °C, corresponding to a loss of 4 % of the total weight. A second loss of mass occurs at 260 °C, which coincides with the evacuation of the counterion, dimethylammonium. The structure finally collapses when temperature reaches 382 °C. The final residue is a cubic Bi$_{13}$O$_{20}$.

Figure S5.2b Powder X-ray diffraction of residues after thermogravimetric analysis (red), fitting according to Bi$_{13}$O$_{20}$, PXRD PDF 04-020-2230 (black).
Figure S5.3a TG-DTA curve for as-synthesized BiPF-7 in air. Pores are filled with acetone molecules, which evacuates at 80 °C, corresponding to a loss of 6 % of the total weight. A second loss of mass occurs at 240 °C, which coincides with the evacuation of coordinated water molecules. The structure finally collapses when temperature reaches 395 °C. The final residue is a cubic Bi$_{12.8}$O$_{19.2}$.

Figure S5.3b Powder X-ray diffraction of residues after thermogravimetric analysis (red), fitting according to Bi$_{12.8}$O$_{19.2}$, PXRD ICSD pattern 71917 (black).
S6 GAS SORPTION ANALYSIS

Figure S6.1: Top: Nitrogen sorption isotherms for InPF-60, BiPF-5, and BiPF-7. Filled and empty symbols represent adsorption and desorption curves, respectively. Bottom: Pore size distribution.

Figure S6.2: Micropore isotherm analysis of BiPF-7 at 87 K. The measurement of Ar adsorption (black) was obtained after evacuating the sample overnight at 90 °C under vacuum. The experimental BET area obtained is 425 m²/g, and the experimental micropore area is 425 m²/g.
Figure S6.3 CO$_2$ isotherm (273K) sorption analysis of InPF-60 recorded at 273 K.

Figure S6.4 CO$_2$ isotherm (273K) sorption analysis of BiPF-5.
Figure S6.5 CO$_2$ isotherm (273K) sorption analysis of BiPF-7.
S7. CATALYTIC ACTIVITY EXPERIMENTS BACKGROUND

Table S7.1 Catalytic activity of several homogeneous and heterogeneous catalysts used in the acetophenone mediated 3C-Strecker reaction.

| Catalyst        | Type          | Reaction conditions | Time and yield | Reference                        |
|-----------------|---------------|---------------------|----------------|----------------------------------|
| InBr3           | homogeneous   | 10 mol%, 80ºC, toluene | 27 h; 85 %    | Org. Lett. 2016 18 (7), 1634-1637. |
| InI3            | homogeneous   | 10 mol%, 80ºC, toluene | 27 h; 80 %    | J. Saudi Chem. Soc. 2016, 20 (1), S202-S210. |
| Bi(NO₃)₃        | homogeneous   | 10%, r.t., MeCN      | 1 h; 94 %     | Chem. A Eur. J. 2017, 23, 1568 – 1575. |
| Bismuth perfluoroalkylphosphinates | homogeneous | 7 mol%, r.t., DCM | 30 min; 97 % | Inorg. Chem. 2020, 59, 3, 1653–1659. |
| In₁₂-GL         | heterogeneous | 6 mol%, 50ºC, MeOH   | 24 h; 99 %    |                                  |

Table S7.2 Catalytic activity of different MOFs in the 3C-Strecker reaction with acetophenone, aniline and trimethylsilyl cyanide.

| Catalyst        | Type          | Reaction conditions | Time and yield | Reference                        |
|-----------------|---------------|---------------------|----------------|----------------------------------|
| InGaPF-1        | heterogeneous | 1 mol%, r.t., Solvent-free | 0.42 h; 50 %  |                                  |
| InGaPF-2        | heterogeneous | 1 mol%, r.t., Solvent-free | 0.75 h; 67 %  | Journal of the American Chemical Society 2015, 137 (19), 6132-6135. |
| InGaPF-3        | heterogeneous | 1 mol%, r.t., Solvent-free | 2 h; 80 %     |                                  |
| InPF-11α        | heterogeneous | 2.5 mol%, 80ºC, Solvent-free | 4 h; 65 %    |                                  |
| InPF-11β        | heterogeneous | 1 mol%, r.t., Solvent-free | 0.67 h; 67 %  |                                  |
| GaPF-1          | heterogeneous | 1 mol%, r.t., Solvent-free | 0.63 h; 67 %  |                                  |
| AIPF-1          | heterogeneous | 1 mol%, r.t., Solvent-free | 8 h; 75 %     |                                  |
| InPF-110        | heterogeneous | 0.5 mol%, r.t., Solvent-free | 3.5 h; 99 %  | Journal of the American Chemical Society. 2016, 138, 29, 9089–9092. |
| In-pbpta        | heterogeneous | 0.5 mol%, r.t., Solvent-free | 65 min; 84 % | ACS Applied Materials & Interfaces. 2021, 13, 44, 52023–52033. |
**S8. CATALYTIC ACTIVITY DATA**

Table S8.1 Screening of catalyst loadings and scaled up in the Strecker one-pot three component reaction using acetophenone, aniline and TMSCN (1:1:1.1).

![Chemical structure](image)

| Entry | Catalyst loading (mol%) | Catalyst | Conversion (%) | Selectivity (%) | Yield (%) |
|-------|-------------------------|----------|---------------|----------------|-----------|
|       |                         |          |                | A   | B   | C   |           |           |
| 1     | 0,5                     | InPF-60  | 67            | ≥ 99 | –   | –   | 67         |           |
| 2     | 1                       | BiPF-5   | 46            | –   | ≥ 99| –   |  0         |           |
| 3     | 1                       | BiPF-7   | 49            | 83  | 3   | 14  | 41         |           |
| 4     | 1                       | InPF-60  | 96            | ≥ 99 | –   | –   | 96         |           |
| 5     | 1                       | BiPF-5   | 83            | –   | ≥ 99| –   |  0         |           |
| 6     | 1                       | BiPF-7   | 97            | ≥ 99 | –   | –   | 97         |           |
| 7     | 1                       | InPF-60* | 96            | ≥ 99 | –   | –   | 96         |           |
| 8     | 1                       | BiPF-7*  | 88            | 93  | –   |  7  | 82         |           |
| 9     | 1                       | InPF-60**| 67            | 89  | –   | 11  | 60         |           |
| 10    | 1                       | BiPF-7** | 61            | ≥ 99 | –   | –   | 61         |           |
| 11    | –                       | –        | 4             | 59  | 6   | 35  |  2         |           |

*a Reaction conditions: acetophenone, amine, TMSCN (1:1:1.1), mol% catalyst based on the crystallographic formula of different catalysts, N2 atmosphere, 25 °C, without solvent; catalyst washed with dichloromethane. b Conversion and selectivity calculated by 1H NMR. c Yield calculated with the A product. * Scaled up x3. ** Scaled up x5.*

Table S8.2 Results of the catalytic activity of InPF-60 and BiPF-7 for differently substituted ketones and amines.

| Entry | Ketone | Amine | Conv. (%) | Selectivity to Strecker product (%) | Selectivity to cyanosylilation product (%) | Selectivity to imine product (%) | Strecker product yield (%) |
|-------|--------|-------|-----------|-------------------------------------|------------------------------------------|---------------------------------|---------------------------|
|       |        |       | InPF-60   | BiPF-7 | InPF-60 | BiPF-7 | InPF-60 | BiPF-7 | InPF-60 | BiPF-7 | InPF-60 | BiPF-7 | InPF-60 | BiPF-7 |
| 1     | ![Image](image) |       | 95        | 97     | ≥99     | ≥99     | –       | –       | –       | –       | –       | –       | –       | –       | –       | –       | 95      | 97      |
| 2     | ![Image](image) | ![Image](image) | 83        | 68     | ≥99     | ≥99     | –       | –       | –       | –       | –       | –       | –       | 83      | 68      |
| 3     | ![Image](image) |       | 10        | 5      | 43      | 60      | 8       | –       | 49      | 40      | 4       | 3       | 4       | 3       | 4       | 3       | ≥99     | ≥99     |
| 4     | ![Image](image) |       | ≥99       | ≥99    | ≥99     | ≥99     | –       | –       | –       | –       | –       | –       | –       | –       | –       | –       | ≥99     | ≥99     |

S-25
| a |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
| 5 | ![Structure](image5.png) | 87 | 84 | ≥99 | ≥99 | - | - | - | 87 | 84 |
| 6 | ![Structure](image6.png) | 95 | 57 | 63 | 85 | - | - | 37 | 15 | 60 | 48 |
| 7 | ![Structure](image7.png) | 6 | 38 | 11 | - | 89 | ≥99 | - | - | 1 | 0 |
| 8 | ![Structure](image8.png) | ≥99 | 94 | 15 | - | 85 | ≥99 | - | - | 15 | 0 |
| 9 | ![Structure](image9.png) | 65 | 70 | 82 | 77 | - | - | 18 | 23 | 53 | 54 |

*Reaction conditions: r.t., solvent free, 1 mol% catalyst, 4h.*

---

**Figure S8.1** InPF-60 as-synthesized (blue), activated (red) and after standard catalytic reaction (black).
Figure S8.2 BiPF-5 as-synthesized (blue), activated (red) and after standard catalytic reaction (black).

Figure S8.3 BiPF-7 as-synthesized (blue), activated (red) and after standard catalytic reaction (black).
Figure S8.4 N$_2$ sorption isotherm of InPF-60 sample before and after catalytic test.

Figure S8.5 N$_2$ sorption isotherm of BiPF-7 sample before and after catalytic test.
S9. RECYCLE REACTIONS

9.1 Recycle reactions for InPF-60

**Table S9.1** Strecker one-pot three component reaction using acetophenone, aniline and TMSCN (1:1:1.1) up to 9 cycles.

| Run | Yield (%) | TON |
|-----|-----------|-----|
| 1   | 96        | 96  |
| 2   | 95        | 95  |
| 3   | 97        | 97  |
| 4   | 97        | 97  |
| 5   | 97        | 97  |
| 6   | 98        | 98  |
| 7   | 96        | 96  |
| 8   | 95        | 95  |
| 9   | 96        | 96  |

*a Reaction conditions: N2 atmosphere, without solvent, at room temperature (25°C), in 4 hours, with a catalyst loading of 1 mol%. b Yield calculated by 1H NMR from reaction crude. c TON = (mol substrate/ mol catalyst).

**Figure S9.1a** Graph with recycle run yields obtained, from the first to the nineth.
**Figure S9.1b** From top to bottom InPF-60 as-after nineth cycle (pink), after first cycle (red), synthesized (blue), and simulated profile from single-crystal diffraction structure data (black).

### 9.2 Recycle reactions for BiPF-7

**Table S9.2** Strecker one-pot three component reaction using acetophenone, aniline and TMSCN (1:1:1.1) up to 9 cycles.

![Reaction Diagram]

| Run | Yield (%) | TON  |
|-----|-----------|------|
| 1   | 97        | 97   |
| 2   | 95        | 95   |
| 3   | 97        | 97   |
| 4   | 95        | 95   |
| 5   | 95        | 95   |
| 6   | 97        | 97   |
| 7   | 96        | 96   |
| 8   | 94        | 94   |
| 9   | 92        | 92   |

*a Reaction conditions: N2 atmosphere, without solvent, at room temperature (25°C), in 4 hours, with a catalyst loading of 1 mol%. *b Yield calculated by $^1$H NMR from reaction crude. *c TON = (mol substrate/ mol catalyst).
Figure S9.2a Graph with recycle run yields obtained, from the first to the nineth run.

Figure S9.2b BiPF-7 as-after ninth cycle (pink), after first cycle (red), synthesized (blue), and simulated profile from single-crystal diffraction structure data (black).
Figure S 9.3: Comparative of recycling experiments for the Strecker reaction using InPF-60 and BiPF-7 as catalysts.
10.1 2-Phenyl-2-(phenylamino)propanenitrile

White solid: $^1$H NMR (300 MHz, CDCl$_3$): $\delta = 1.94$ (s, 3H), 4.33 (brs, 1H, NH), 6.55 (d, 2H), 6.81 (t, 1H), 7.13 (t, 2H), 7.40 (m, 3H), 7.64 (m, 2H); which corresponds with the spectrum reported for compound with CAS No. 17424-68-9. This compound is known.

Figure S10.1 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S8.1, entry 1; Table S8.2, entry 1; table S7, entry 4).
10.2 Characterization of 3C Strecker Reaction ketone and amine scope

Table S8.2, entry 2. 2-(phenylamino)-2-(p-tolyl)propanitrile
CAS Registry Number: 17424-69-0.
$^1$H NMR (300 MHz; CDCl$_3$): δ = 1.95 (s, 3H), 2.38 (s, 3H), 4.27 (brs, 1H, NH), 6.58 (d, 2H), 6.83 (t, 1H), 7.11-7.17 (m, 2H), 7.23 (d, 2H), 7.52 (d, 2H).

Table S8.2, entry 3. 2-(4-chlorophenyl)-2-(phenylamino)propanitrile
CAS Registry Number: 17424-70-3.
$^1$H NMR (300 MHz; CDCl$_3$): δ = 1.94 (s, 3H), 4.28 (brs, 1H, NH), 6.52-6.55 (d, 2H), 6.81-6.86 (t, 1H), 7.12-7.17 (m, 2H), 7.37-7.40 (d, 2H), 7.56-7.59 (d, 2H).

Table S8.2, entry 4. 1-(phenylamino)cyclohexanecarbonitrile
CAS Registry Number: 64269-06-3.
$^1$H NMR (300 MHz; CDCl$_3$): δ = 1.26-1.37 (m, 1H), 1.61-1.82 (m, 7H), 2.32-2.41 (m, 2H), 3.26 (brs, 1H, NH), 6.93 (m, 3H), 7.25 (m, 2H).

Table S8.2, entry 5. 2-methyl-2-(phenylamino)octanenitrile
CAS Registry Number: New Product.
$^1$H NMR (300 MHz; CDCl$_3$): δ = 0.90 (t, 3H), 1.33 (m, 7H), 1.55 (m, 3H), 1.64 (s, 3H), 3.69 (brs, 1H, NH), 6.91 (m, 3H), 7.26 (td, m, 2H).
Table S8.2, entry 6. 2-((4-chlorophenyl)amino)-2-phenylpropanenitrile
CAS Registry Number: 81512-04-1.
$^1$H NMR (300 MHz; CDCl$_3$): $\delta = 1.94$ (s, 3H), 4.30 (brs, 1H, NH), 6.47 (d, 2H), 7.06 (d, 2H), 7.40 (m, 3H), 7.59 (d, 2H).

Table S8.2, entry 7. 2-((4-methoxyphenyl)amino)-2-phenylpropanenitrile
CAS Registry Number: 81512-12-1.
$^1$H NMR (300 MHz; CDCl$_3$): $\delta = 2.02$ (s, 3H), 3.71 (s, 3H), 3.80 (brs, 1H, NH), 6.68 (m, 4H), 7.40 (m, 3H), 7.66 (m, 2H).

Table S8.2, entry 8. 2-phenyl-2-((trimethylsilyl)oxy)propanenitrile
CAS Registry Number: 127462-20-8.
$^1$H NMR (300 MHz; CDCl$_3$): $\delta = 0.17$ (s, 9H), 1.86 (s, 3H), 7.39 (m, 3H), 7.54 (m, 2H).
• S11. SPECTRAS FOR CHARACTERIZED COMPOUNDS

Figure S11.1 $^1$H NMR spectra of 2-phenyl-2-(phenylamino)propanenitrile (Table S8.1, entry 1; Table S8.2, entry 1 (InPF-60); Table S7, entry 4).

Figure S11.2 $^1$H NMR spectra of 2-phenyl-2-((trimethylsilyl)oxy)propanenitrile (Table S8.1, entry 2; Table S8.2, entry 1 (BiPF-5); Table S7, entry 5).
Figure S11.3 $^1$H NMR spectra of 2-phenyl-2-(phenylamino)propanenitrile (Table S8.1, entry 3; Table S8.2, entry 1 (BiPF-7); Table S7, entry 6).

Figure S11.4 $^1$H NMR spectra of 2-phenyl-2-(phenylamino)propanenitrile (Table S8.1, entry 4; Table S7, entry 11).
Figure S11.5 $^1$H NMR spectra of 2-(phenylamino)-2-(p-tolyl)propanenitrile (Table S8.2, entry 2 (InPF-60)).

Figure S11.6 $^1$H NMR spectra of 2-(4-chlorophenyl)-2-(phenylamino)propanenitrile (Table S8.2, entry 3 (InPF-60)).
Figure S11.7 $^1$H NMR spectra of 1-(phenylamino)cyclohexanecarbonitrile (Table S8.2, entry 4 (InPF-60)).

Figure S11.8 $^1$H NMR spectra of 2-methyl-2-(phenylamino)octanenitrile, (Table S8.2, entry 5 (InPF-60)).
Figure S11.9 $^1$H NMR spectra of 2-((4-chlorophenyl)amino)-2-phenylpropanenitrile$^6$, (Table S8.2, entry 6 (InPF-60)).

Figure S11.10 $^1$H NMR spectra of 2-((4-methoxyphenyl)amino)-2-phenylpropanenitrile (Table S8.2, entry 7 (InPF-60)).
Figure S11.11 $^1$H NMR spectra of 2-phenyl-2-((trimethylsilyl)oxy)propanenitrile (Table S8.2, entry 8 (InPF-60)).

Figure S11.12 $^1$H NMR spectra of 2-phenyl-2-(α-tolylamino)propanenitrile (Table S8.2, entry 9 (InPF-60)).
Figure S11.13 $^1$H NMR spectra 2-(phenylamino)-2-(p-tolyl)propanenitrile (Table S8.2, entry 2 (BiPF-7)).

Figure S11.14 $^1$H NMR spectra of 2-(4-chlorophenyl)-2-(phenylamino)propanenitrile (Table S8.2, entry 3 (BiPF-7)).
Figure S11.15 $^1$H NMR spectra 1-(phenylamino)cyclohexanecarbonitrile (Table S8.2, entry 4 (BiPF-7)).

Figure S11.16 $^1$H NMR spectra of 2-methyl-2-(phenylamino)octanenitrile, (Table S8.2, entry 5 (BiPF-7)).
Figure S11.17 ¹H NMR spectra of 2-((4-chlorophenyl)amino)-2-phenylpropanenitrile, (Table S8.2, entry 6 (BiPF-7)).
Figure S11.18 $^1$H NMR spectra of 2-((4-methoxyphenyl)amino)-2-phenylpropanenitrile (Table S8.2, entry 7 (BiPF-7)).

Figure S11.19 $^1$H NMR spectra of 2-phenyl-2-((trimethylsilyl)oxy)propanenitrile (Table S8.2, entry 8 (BiPF-S-45))
Figure S11.20 $^1$H NMR spectra of 2-phenyl-2-((trimethylsilyl)oxy)propanenitrile (Table S8.2, entry 9 (BIPF-7))
Figure S11.21 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S7, entry 1).

Figure S11.22 $^1$H NMR spectra of 2-phenyl-2-((trimethylsilyl)oxy)propanenitrile. (Table S7, entry 2).
Figure S11.23 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S7, entry 3).

Figure S11.24 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S7, entry 7).
Figure S11.25 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S7, entry 8).

Figure S11.26 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S7, entry 9).
Figure S11.27 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S7, entry 10).

Figure S11.28 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.1, recycle run 1).
Figure S11.29 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.1, recycle run 2).

Figure S11.30 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile (Table 9.1, recycle run 3).
Figure S11.31 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table 9.1, recycle run 4).

Figure S11.32 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table 9.1, recycle run 5).
Figure S11.33 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table 9.1, recycle run 6).

Figure S11.34 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table 9.1, recycle run 7).
Figure S11.35 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table 9.1, recycle run 8).

Figure S11.36 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table 9.1, recycle run 9).
Figure S11.37 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.2, recycle run 1).

Figure S11.38 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.2, recycle run 2).
Figure S11.39 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile (Table S9.2, recycle run 3).

Figure S11.40 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.2, recycle run 4).
Figure S11.41 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.2, recycle run 5).

Figure S11.42 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.2, recycle run 6).
Figure S11.43 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.2, recycle run 7).

Figure S11.44 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.2, recycle run 8).
Figure S11.45 $^1$H NMR spectra of 2-Phenyl-2-(phenylamino)propanenitrile. (Table S9.2, recycle run 9).