Supporting Information

Amorphous zirconium metal-organic frameworks assembled from mixed porphyrins as solvent-free catalysts for Knoevenagel condensation

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EXPERIMENTAL METHODS

Materials and Characterization.

All chemicals were purchased from Aladdin-reagent (Shanghai, China), J&K (Beijing, China), CASmart (Beijing, China), and Integle (Shanghai, China). The HPLC-grade acetonitrile was purchased from Dikma (Beijing, China).

HPLC analysis was performed on a JASCO LC-1500 system using columns (Daicel Chiral Technologies Co., LTD, Shanghai, China) with a JASCO UV-2075 detector. The yields of the products were determined by HPLC analyses. HPLC detection method: column (C18), mobile phase (water–acetonitrile (50:50, v/v)) flowing at 1 mL/min, UV 254 nm. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded using a Bruker 600 MHz spectrometer in DMSO with TMS as an internal standard. Infrared spectra were measured in the 4000−400 cm^{-1} range on Fourier transform infrared (FT-IR) spectroscopy (EQUINOX55, Bruker, Germany). All in situ infrared spectra were obtained using an IN-SITU IR (ReactIR 15, Mettler Toledo, Redmond, VA) equipped with an ATR diamond sensor probe interfaced with the Mettler iC IR 4.0 synthesis workstation. Powder X-ray diffraction (PXRD) patterns of the dried samples were recorded on a multipurpose X-ray diffractometer (DX-2700BH, HAOYUAN, China) operated at 40 kV voltage and 30 mA current with CuKα radiation (λ=0.154nm). The scanning electron microscope (SEM) was measured by a HITACHI SU-70. Transmission electron microscopy (TEM) was carried out on a FEI talos F200x G2. Thermogravimetric analysis (TGA) was performed at a constant heating rate of 20 ℃ min^{-1} from 30 ℃ to 800 ℃ in nitrogen, on a TGA thermogravimetric analyzer (TGA 2 (SF), Mettler Toledo, Switzerland). Brunauer-Emmett-Teller (BET) surface area and pore volume distribution were performed using a Micromeritics ASAP 2020 instrument. X-ray photoelectron spectroscopy (XPS) with an Mg Kaanode (PHI5000 VersaprobeIII, ULVAC-PHI, Japan)

was used to determine the composition of the samples. Zirconium content analysis was performed by inductively coupled plasma optical emission spectrometry (ICP-OES, Thermo Fisher iCAP PRO).

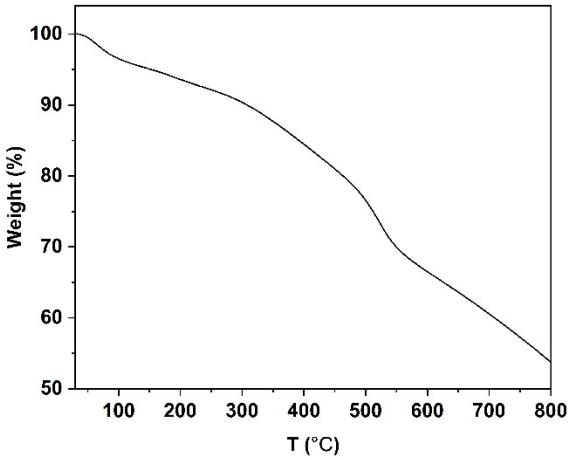
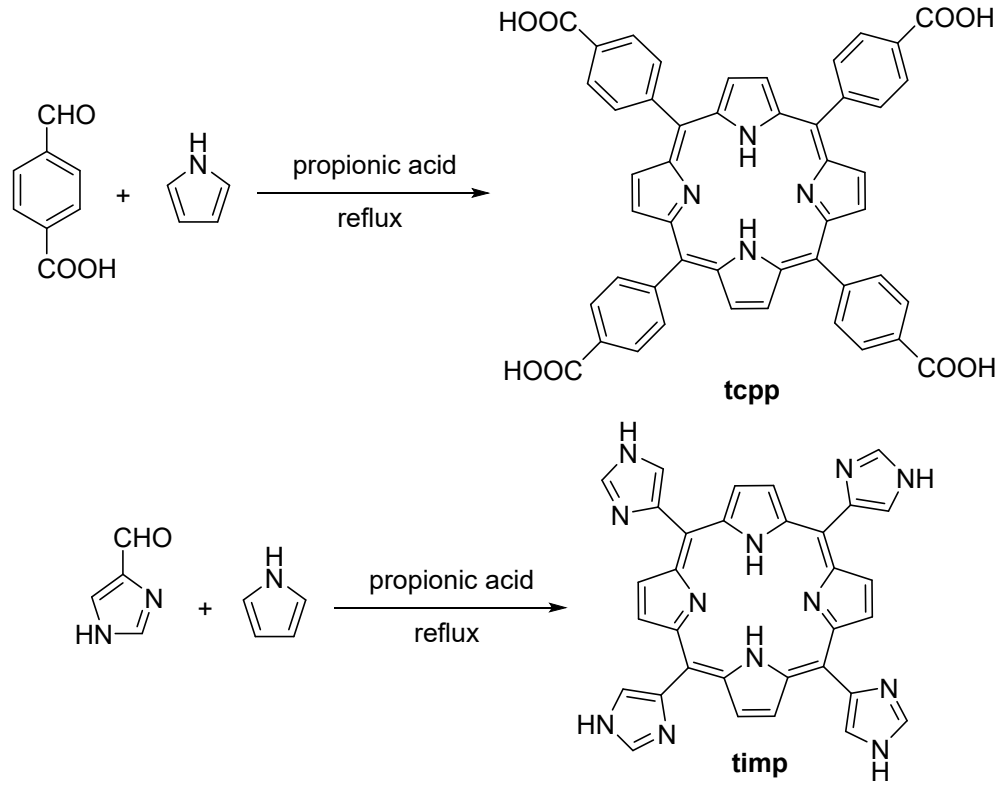


Fig. S1 TGA curve of **SPUZ-1**.

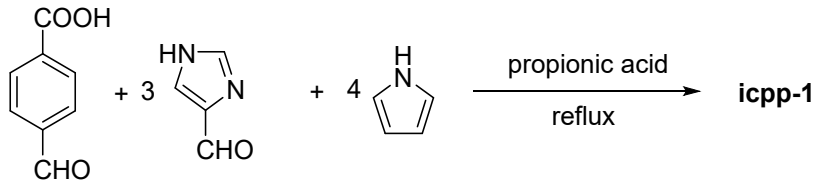
Synthesis of tcpp and timp.



Tetrakis(4-carboxyphenyl)porphyrin (**tcpp**) and tetrakis(4-imidazoyl)porphyrin (**timp**) were synthesized using the Adler–Longo method by mixing pyrrole with 4-formylbenzoic acid and 4-

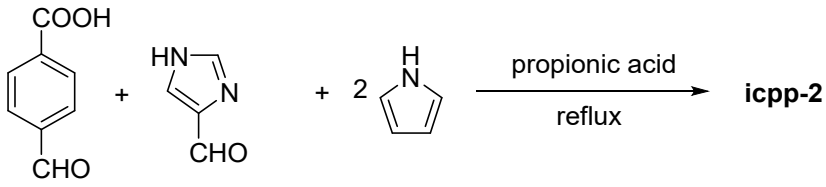
imidazolecarboxaldehyde, respectively , in propionic acid under reflux conditions.[1-3]

Synthesis of icpp-1.



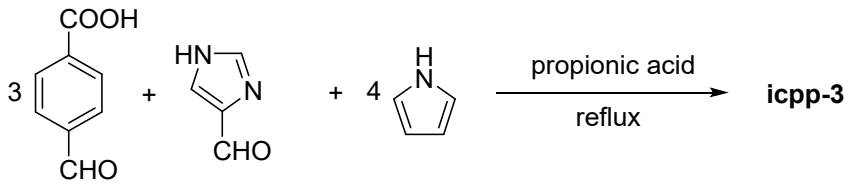
The mixture of 4-imidazolecarboxaldehyde (0.72 g, 7.5 mmol), 4-formylbenzoic acid (0.38 g, 2.5 mmol) and propanoic acid (50 mL) were heated to 80 ℃, and then the freshly distilled pyrrole (0.69 mL, 10 mmol) was added. The mixture was heated to reflux and stirred for 2h before it was cooled to ambient temperature, and then placed in the freezer overnight. The mixture was filtered and then a dark purple solid was collected, washed with 5x50 mL of DCM and dried overnight in vacco to give 0.51 g of **icpp-1** (33% yield).

Synthesis of icpp-2.



Icpp-2 was synthesized under the same procedure, with 4-imidazolecarboxaldehyde (0.48 g, 5.0 mmol) and 4-formylbenzoic acid (0.75 g, 5.0 mmol) to give 0.92 of the product as a dark purple solid (54% yield).

Synthesis of icpp-3.



Icpp-3 was synthesized under the same procedure, with 4-imidazolecarboxaldehyde (0.24 g, 2.5 mmol) and 4-formylbenzoic acid (1.13 g, 7.5 mmol) to give 1.16 g of the product as a dark purple solid (63% yield).

Synthesis of SPUZ (1-5).

In a typical procedure, **icpp-1** (80 mg), $ZrCl_4$ (0.1 g), benzoic acid (2.5 g) and H_2O (2 mL) were dissolved in DMF (20 mL) and transferred to a 75 mL Teflon-lined stainless-steel hydrothermal reaction vessel, and then heated at 120 ℃ for 24 h. The products were separated via centrifugation at 10000 rpm for 5 minutes and further purified with ethanol for several times to give **SPUZ-1** as a black powder. **SPUZ-2**, **SPUZ-3**, **SPUZ-4** and **SPUZ-5** could be synthesized as black powders using the same amount of **icpp-2, icpp-3**, **timp** and **tcpp**, respectively.

Synthesis of Zr-icpp-1.

A mixture of icpp-1 (0.983 g, 1.24 mmol, 1.00 equiv), $ZrCl_4$ (2.10 g, 10.6 mmol, 8.52 equiv), and DMF (150 mL) was refluxed for 12 h. A

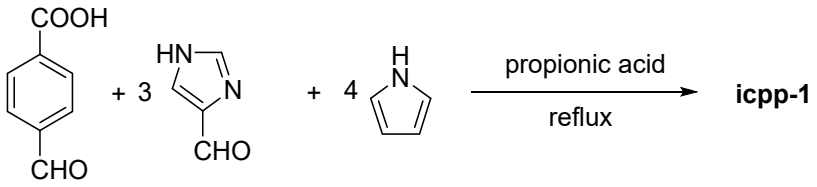
fter the reaction mixture was cooled to 23 °C, distilled H_2O (250 mL) was added. The precipitate was collected by filtration and washed with DMF, H_2O, methanol successively, and dried in vacuo to give the target product as a dark purple powder (0.923 g, 66% yield).

Catalytic Study for Knoevenagel Condensation Reactions.

In a typical procedure, aldehyde (1 mmol), malononitrile (2 mmol), and catalysts (0.01 mmol, 7 mg) were mixed and stirred at 60 °C for 30 min. After the reaction was completed, the mixture was dissolved with ethanol or CH_2Cl_2, and **SPUZ-1** could be isolated by filtration and reused for the next run. After removing the solvent of the filtrate, the crude product was obtained, followed by recrystallization in ethanol, and pure product was obtained. The yields were determined by HPLC.

Calculations of the statistical distributions of each porphyrin component in icpp (1-3).

According to literature, condensation of two different aldehydes and pyrrole afforded a statistical mixture of six porphyrins.[4, 5] The statistical distributions of each porphyrin component in **icpp-1**, **icpp-2** and **icpp-3** are calculated as follows.



timp % = 0.75^4 = 31.64%

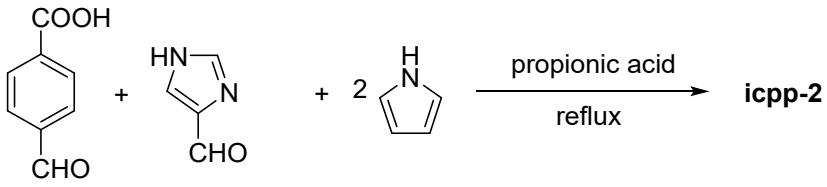
$i_3$cpp % = 0.25 * 0.75^3 * 4 = 42.19%

cis-i_2cp_2p % = 0.25^2 * 0.75^2 * 4 = 14.06%

trans-i_2cp_2p % = 0.25^2 * 0.75^2 * 2 = 7.03%

icp_3p % = 0.25^3 * 0.75 * 4 = 4.69%

tcpp % = 0.25^4 = 0.39%



timp % = 0.5^4 = 6.25%

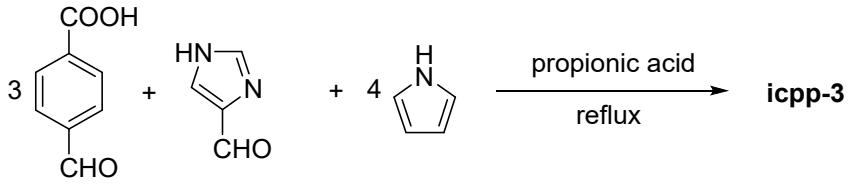
i_3cpp % = $0.5 * 0.5^3 * 4 = 25\%$

cis-i_2cp_2p % = $0.5^2 * 0.5^2 * 4 = 25\%$

trans-i_2cp_2p % = $0.5^2 * 0.5^2 * 2 = 12.5\%$

icp_3p % = $0.5^3 * 0.5 * 4 = 25\%$

tcpp % = $0.5^4 = 6.25\%$



timp % = $0.25^4 = 0.39\%$

i_3cpp % = $0.25^3 * 0.75 * 4 = 4.69\%$

cis-i_2cp_2p % = $0.25^2 * 0.75^2 * 4 = 14.06\%$

trans-i_2cp_2p % = $0.25^2 * 0.75^2 * 2 = 7.03\%$ icp_3p % = $0.25 * 0.75^3 * 4 = 42.19\%$

tcpp % = $0.75^4 = 31.64\%$

REFERENCES

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(4) Lindsey, J. S. Synthetic Routes to Meso-Patterned Porphyrins. *Acc. Chem. Res.* **2010,** *43*, 300-311.

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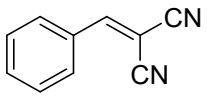
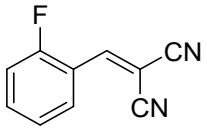
Spectral Data of the Products.



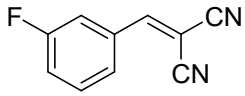
2-(phenylmethylene)malononitrile

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.55 (s, 1H), 8.01 – 7.92 (m, 2H), 7.75 – 7.57 (m, 3H).



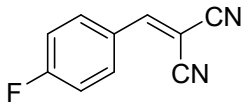
2-((2-fluorophenyl)methylene)malononitrile

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.60 (s, 1H), 8.07 (td, J = 7.7, 1.7 Hz, 1H), 7.76 (dddd, J = 8.7, 7.3, 5.5, 1.7 Hz, 1H), 7.50 – 7.43 (m, 2H).



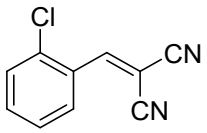
2-((3-fluorophenyl)methylene)malononitrile

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.57 (s, 1H), 7.83 – 7.77 (m, 1H), 7.74 (dt, J = 9.9, 2.1 Hz, 1H), 7.70 (td, J = 8.1, 5.9 Hz, 1H), 7.58 (tdd, J = 8.5, 2.6, 0.9 Hz, 1H).



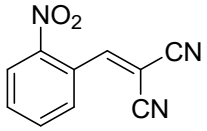
2-((4-fluorophenyl)methylene)malononitrile

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.55 (s, 1H), 8.08 – 8.02 (m, 2H), 7.54 – 7.47 (m, 2H).



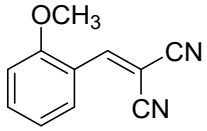
2-((2-chlorophenyl)methylene)malononitrile

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.68 (s, 1H), 8.03 (dd, J = 7.8, 1.5 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.62 – 7.56 (m, 1H).



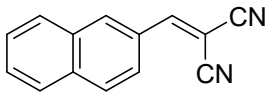
2-((2-nitrophenyl)methylene)malononitrile

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.98 (s, 1H), 8.35 (dd, J = 8.2, 1.2 Hz, 1H), 8.02 (td, J = 7.5, 1.2 Hz, 1H), 7.96 (dt, J = 7.6, 1.1 Hz, 1H), 7.94 – 7.87 (m, 1H).



2-((2-methoxyphenyl)methylene)malononitrile

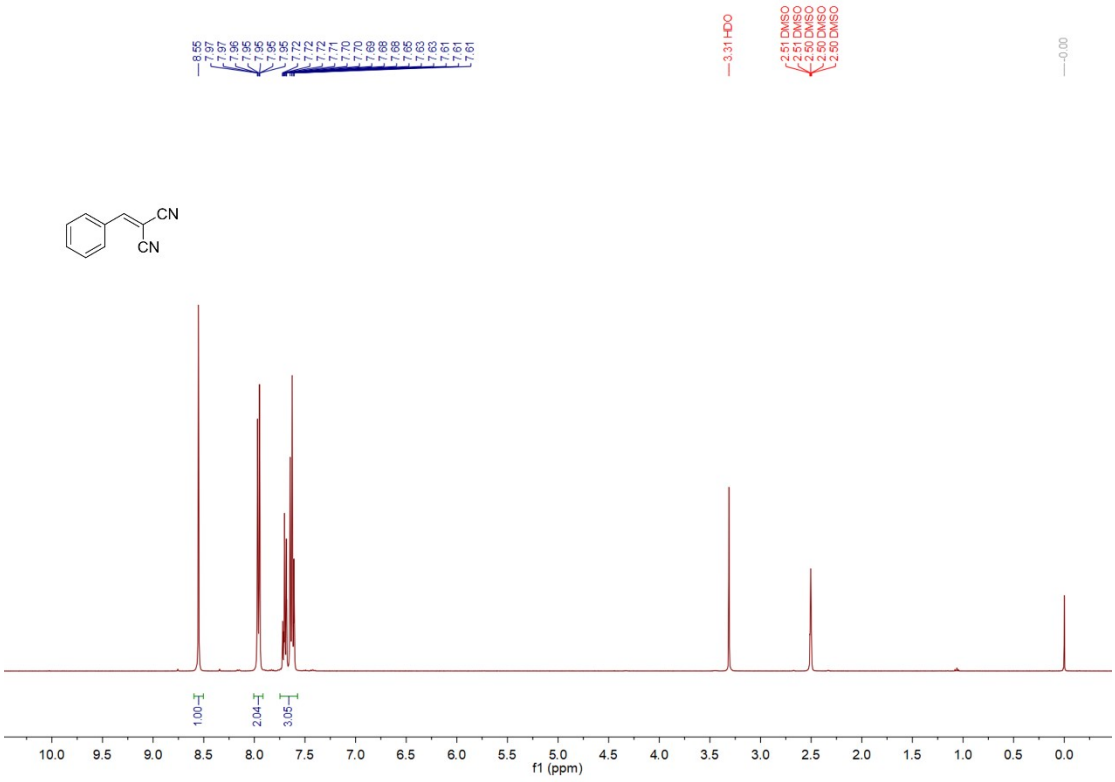
^{1}H NMR (600 MHz, DMSO-d_6) δ 8.48 (s, 1H), 7.97 (dd, J = 7.9, 1.6 Hz, 1H), 7.68 (ddd, J = 8.7, 7.3, 1.7 Hz, 1H), 7.24 (dd, J = 8.5, 1.0 Hz, 1H), 7.18 – 7.12 (m, 1H), 3.91 (s, 3H).

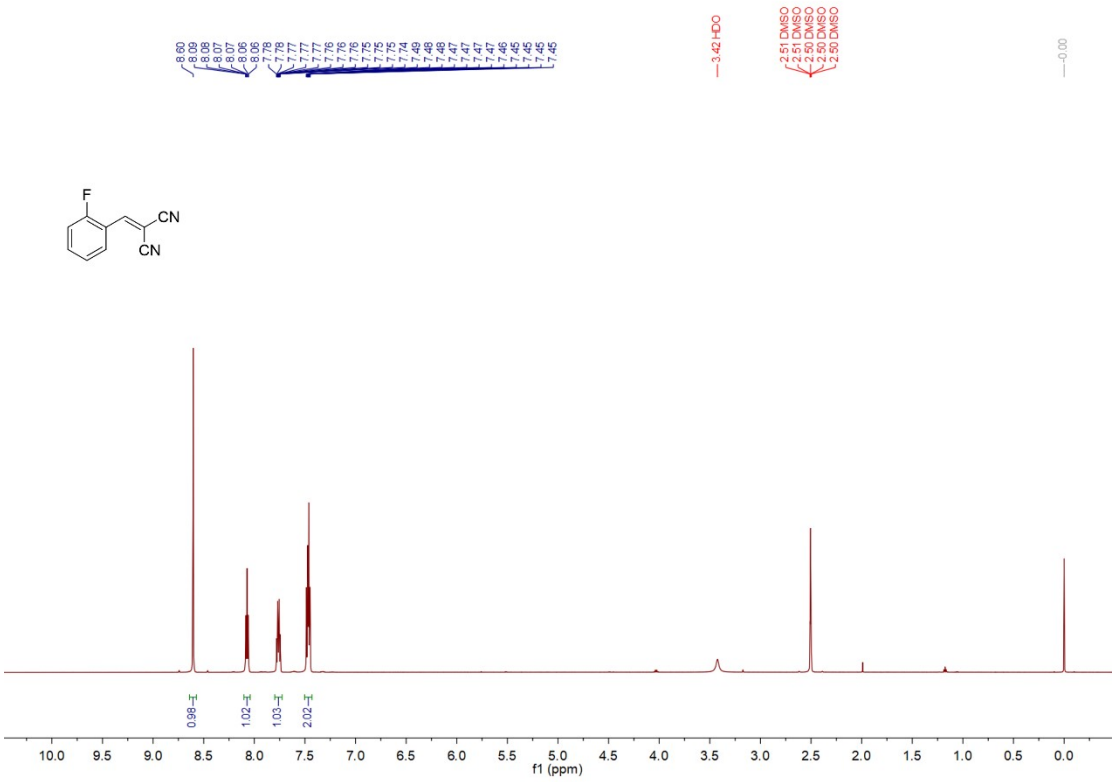


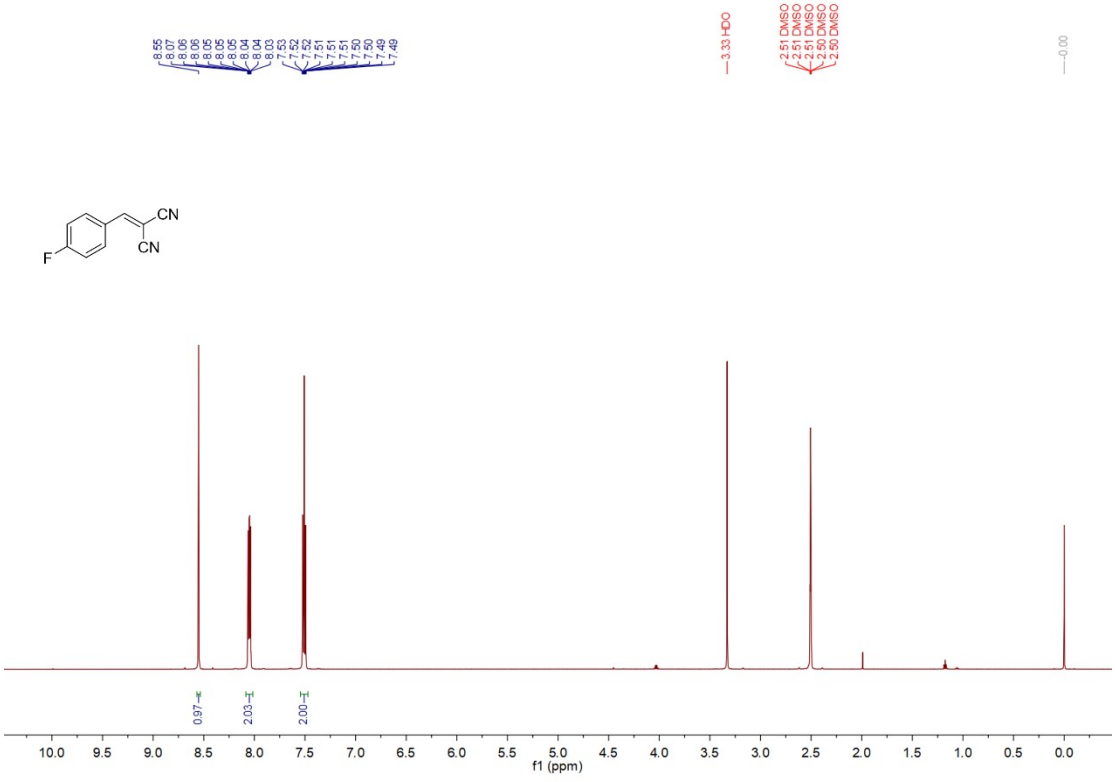
2-(naphthalen-2-ylmethylene)malononitrile

^{1}H NMR (600 MHz, DMSO-d_6) δ 8.68 (s, 1H), 8.51 – 8.47 (m, 1H), 8.14 (d, J = 8.7 Hz, 1H), 8.11 – 8.06 (m, 2H), 8.04 (dd, J = 8.2, 1.1 Hz, 1H), 7.75 (ddd, J = 8.2, 6.8, 1.3 Hz, 1H), 7.68 (ddd, J = 8.1, 6.8, 1.2 Hz, 1H).

^{1}H-NMR Spectra of Compounds



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7.49
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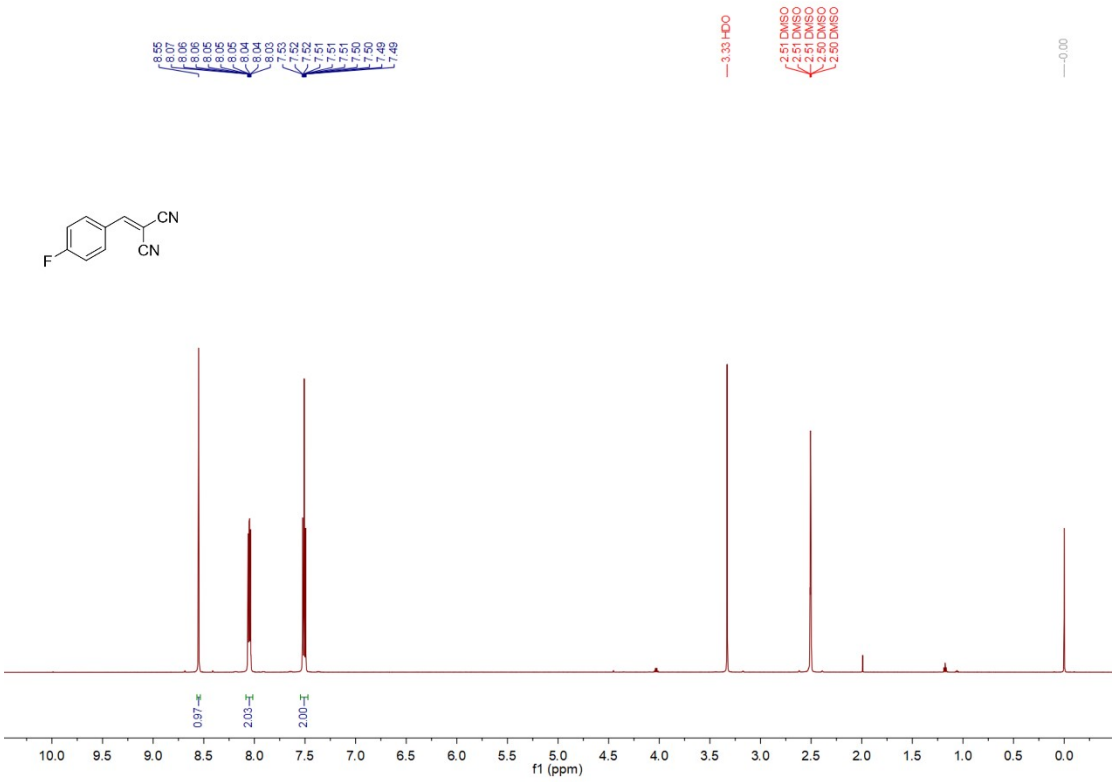
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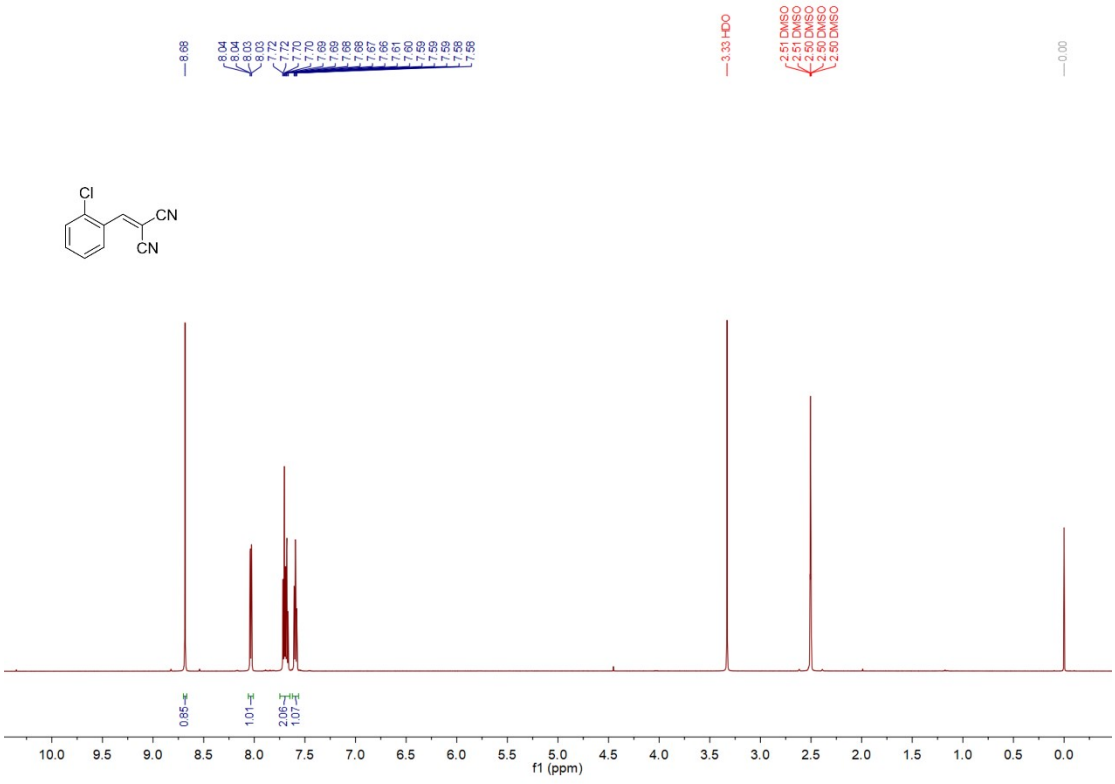
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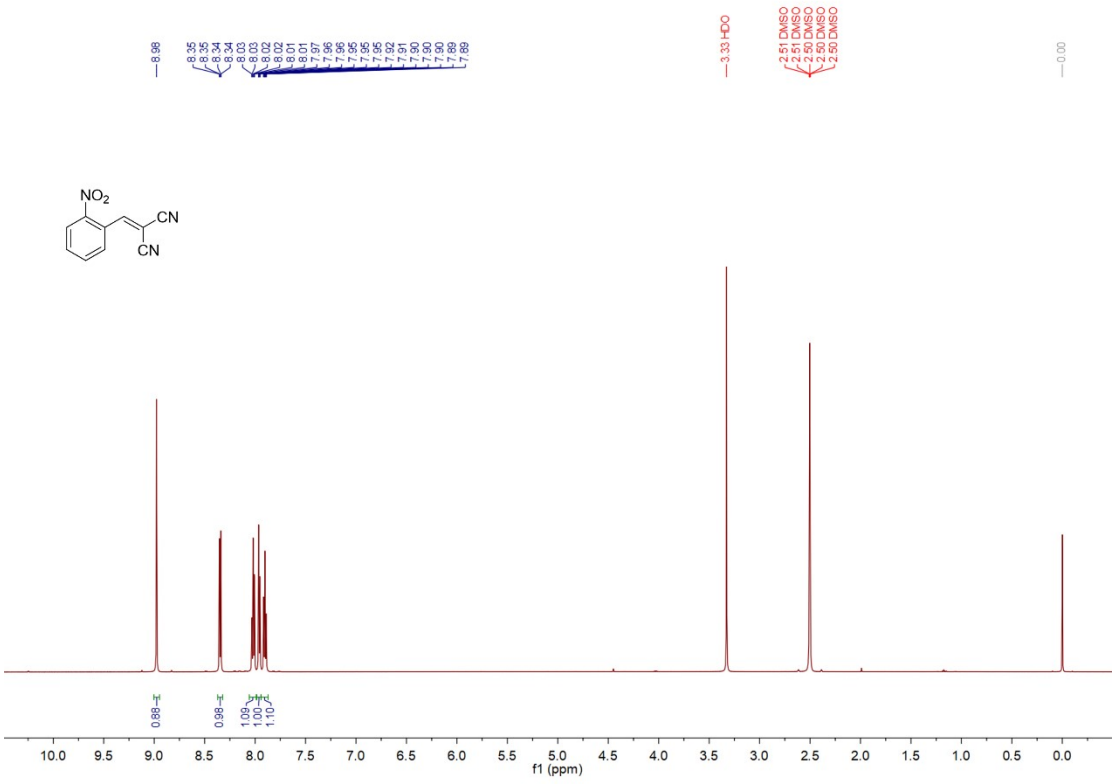
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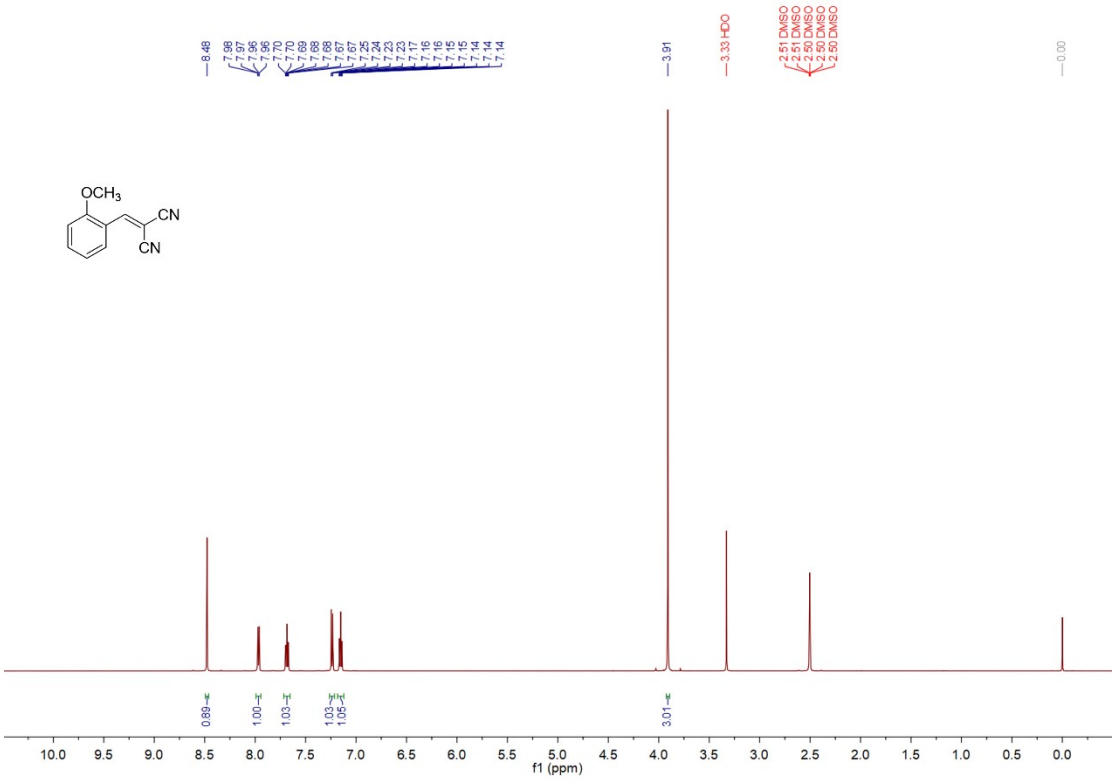
f1 (ppm)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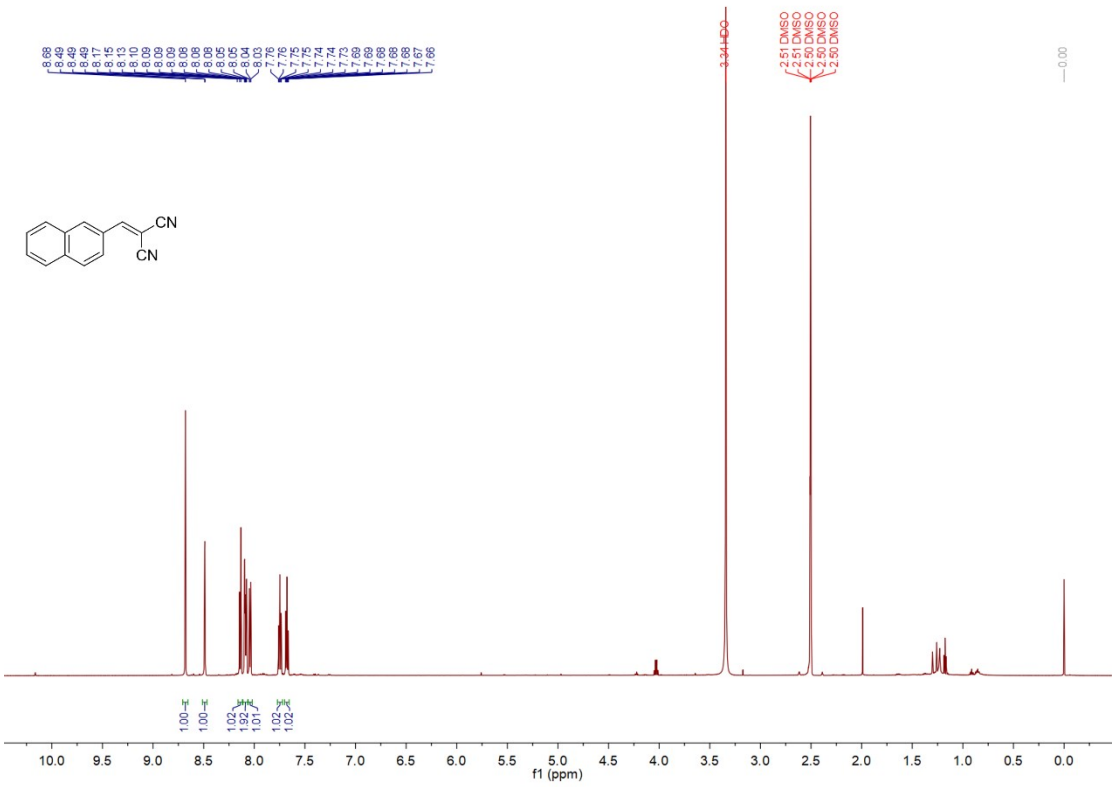
f1 (ppm)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7.69
7.68
7.68
7.67
7.66
3.34 HDO
2.51 DMSO
2.51 DMSO
2.50 DMSO
2.50 DMSO
2.50 DMSO
0.00
CN
CN
1.00
1.00
1.02
1.92
1.01
1.02
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)