Electronic Supplementary Material (ESI) for ChemComm.


# Electronic Supplementary Information

## Enhanced Emission by Stacking of Crown Ether Side Chains in A 2D Covalent Organic Framework

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# 1. General Procedure

All reagents were purchased from commercial sources without further purification. Compound **1**,[S1] **2**,[S2] **3**, [S2] **4** [S2] and **M2OMe** [S1] are synthesized according to reported methods.

$^{1}H$ and $^{13}C$ NMR spectra were recorded using 400 MHz Bruker spectrometer in $(CD_3)_2CO$ and $CD_3Cl$ with tetramethylsilane (TMS) as the internal standard. The chemical shift was recorded in ppm and the following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. HR ESI mass spectra were recorded on a MicrOTOFQII instrument.

Thermogravimetric analysis (TGA) was performed on a TGA 500 thermogravimetric analyzer by heating the samples at 5 $^{o}C$ $min^{-1}$ to 800 $^{o}C$ in a nitrogen atmosphere.

Fourier transform infrared (FT-IR) spectra were recorded as KBr-pellet on a Bruker OPUS/IR PS15 spectrometer.

Scanning Electron Microscopy (SEM) imaging of the COF pristine materials were performed using a JEOL JSM-6701F Field-Emission.

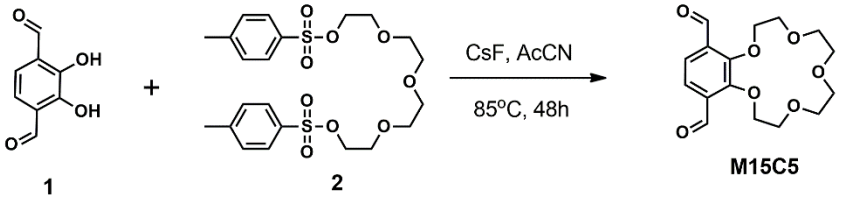
Powder X-ray Diffraction (PXRD) measurements were performed on Bruker D8 Focus Powder X-ray diffractometer using Cu Kα radiation (40 kV, 40 mA) at room temperature.

Gas Sorption measurements: Gas sorption analyses were performed by using Quantachrome Instruments Autosorb-iQ (Boynton Beach, Florida USA) with extra-high pure gases. The samples were activated and outgassed at 120 $^{o}C$ for 8 h before the measurements. The Brunauer-Emmett-Teller (BET) surface area and total pore volume were calculated from the $N_2$ sorption isotherms at 77 K, and the pore size distribution was calculated based on the $N_2$ sorption isotherm by using Non-Local Density Functional Theory (NL-DFT, a carbon model containing slit/cylindrical pore) model in the Quantachrome ASiQwin 5.0 software package.

Fluorescence Quantum Yield & Lifetime：The fluorescence data and lifetimes were measured using a Horiba Fluorolog-3 spectrofluorometer equipped with a 365 nm nanoLED for excitation and a FluoroHub R-928 detector. Absolute quantum yields were measured on the HORIBA Fluorolog-3 Photon Counting Spectrofluorometer System with Quanta-ϕ 6-inch integrating sphere.

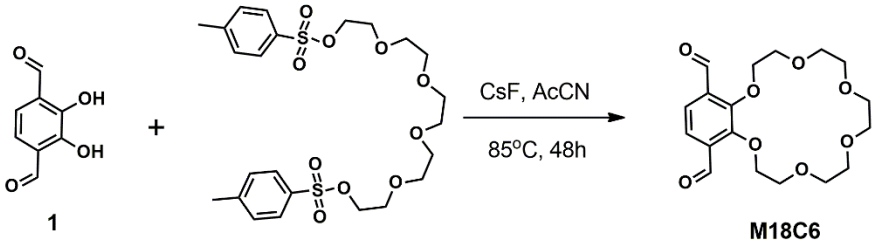
Structural Modelling Method: Molecular modelling and Pawley refinement were carried out using Reflex, a software package for crystal determination from Powder XRD pattern, implemented in BIOVIA Materials Studio modelling version 2016. All of the four COF models were constructed initially with a P1 space group using Materials Studio Visualizer and their geometries were optimized using the Forcite module (ultra-fine, Universal force fields, Ewald summations). Pawley refinement was then performed to optimize the lattice parameters until the RWP value converges.

## 2. Synthesis



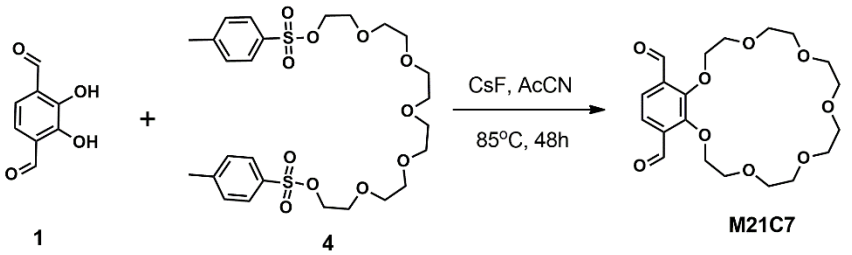

1 2 M15C5

Synthesis of compound **M15C5**: Compound **1** (498.4 mg, 3 mmol), compound **2** (1.66 g, 3.3 mmol) and CsF (1.82 g, 12 mmol) were added to a three-neck flask containing 20 mL dry acetonitrile. The mixture was heated to reflux and stirred for 48 h under $N_2$ protection. After cooling to room temperature, solvents were removed under vacuum. The residue was extracted by DCM and washed by water. The organic phase was collected and dried over sodium sulfate. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, MeOH: DMC=1:100) to give a white solid (409 mg, yield 42%). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.44 (s, 2H), 7.65 (s, 2H), 4.37 (t, *J* = 5.2 Hz, 4H), 4.02 (t, *J* = 5.2 Hz, 4H), 3.81 – 3.69 (m, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.2, 156.1, 134.3, 123.2, 75.3, 71.1, 70.7, 70.1. HR MS (ESI): calcd for $C_{16}H_{20}O_7$ $(M+Na)^+$: 347.1101, found: 347.1103 (error: 0.57 ppm) mp: 83°C.



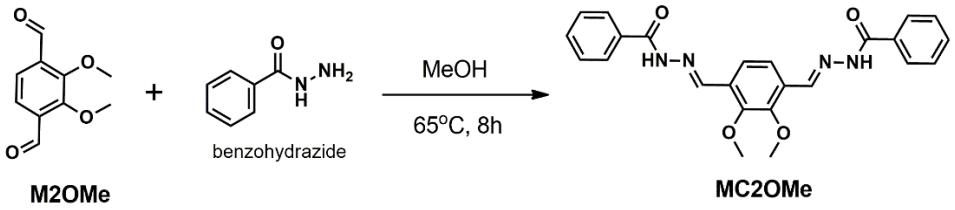

1 3 M18C6

Synthesis of compound **M18C6**: Compound **1** (498.4 mg, 3 mmol), compound **3** (1.80 g, 3.3 mmol) and CsF (1.82 g, 12 mmol) were added to a three-neck flask containing 20 mL dry acetonitrile. The mixture was heated to reflux and stirred for 48 h under $N_2$ protection. After cooling to room temperature, solvents were removed under vacuum. The residue was extracted by DCM and washed by water. The organic phase was collected and dried over sodium sulfate. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, MeOH: DMC=1:80) to give a white solid (497 mg, yield 45%). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.47 (s, 2H), 7.64 (s, 2H), 4.40 (t, *J* = 5.2 Hz, 4H), 3.96 (t, *J* = 5.2 Hz, 4H), 3.75 (td, $^3J$ = 5.6 Hz, $^4J$ = 2.3 Hz, 8H), 3.68 (s, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 189.5, 155.9, 134.5, 122.9, 75.1, 71.2, 70.8, 70.6, 70.1. HR MS (ESI): calcd for $C_{18}H_{24}O_8$ $(M+Na)^+$: 391.1363, found: 391.1365 (error: 0.51 ppm). Mp: 48°C.



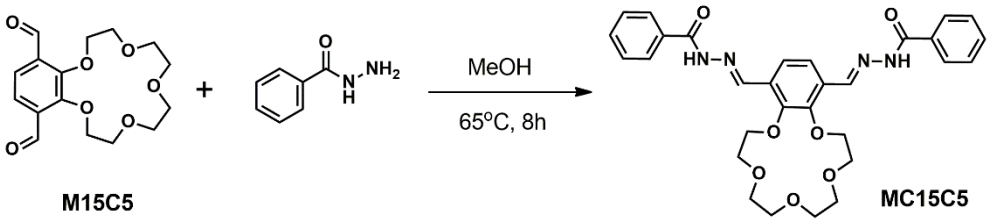

1 4 M21C7

Synthesis of compound **M21C7**: Compound **1** (498.4 mg, 3 mmol), compound **4** (1.95 g, 3.3 mmol) and CsF (1.82 g, 12 mmol) were added to a three-neck flask containing 20 mL dry acetonitrile. The mixture was heated to reflux and stirred for 48 h under $N_2$ protection. After cooling to room temperature, solvents were removed under vacuum. The residue was extracted by DCM and washed by water. The organic phase was collected and dried over sodium sulfate. The solvent was removed under vacuum and the residue was purified by column chromatography (silica gel, MeOH: DMC=1:50) to give a white solid (631 mg, yield 51%). $^1$H NMR (400 MHz, $CDCl_3$) δ 10.49 (s, 2H), 7.63 (s, 2H), 4.51 – 4.30 (m, 4H), 3.99 – 3.82 (m, 4H), 3.70 (dd, $^3J$ = 15.6 Hz, $^4J$ = 4.2 Hz, 8H), 3.65 (s, 8H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 190.0, 155.0, 134.5, 122.7, 74.4, 71.4, 70.8, 70.7, 70.38, 70.35. HR MS (ESI): calcd for $C_{20}H_{28}O_9$ $(M+Na)^+$: 435.1626, found: 435.1638 (error: 2.76). mp: 76°C.

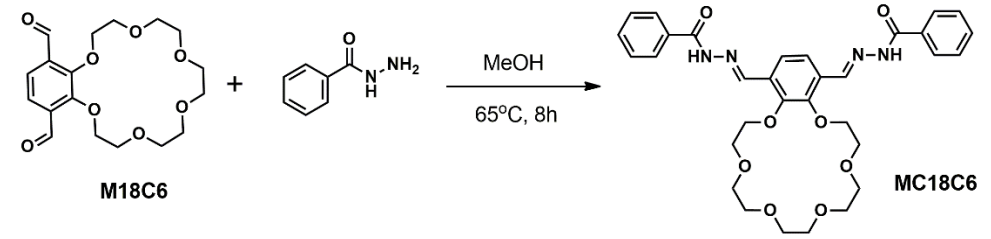



M2OMe MC2OMe

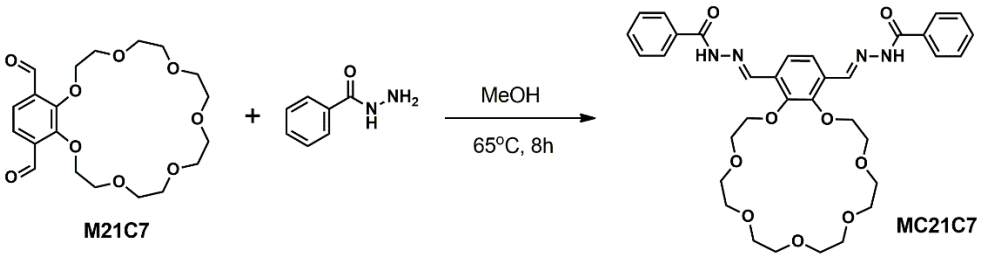
Synthesis of compound **MC2OMe**: Compound **M2OMe** (582.5 mg, 3 mmol) and benzohydrazide (1.22 g, 9 mmol) were added to a two-neck flask containing 10 mL methanol. The mixture was heated to reflux and stirred for 8 h under $N_2$ protection. After cooling to room temperature, a white precipitate was obtained by filtration. The solid was washed with methanol (3 x 10 mL) and dried in vacuum overnight to get the pure compound (813 mg, yield 63%). $^1$H NMR (400 MHz, $(CD_3)_2CO$) δ 11.15 (s, 2H), 8.80 (s, 2H), 8.00 (d, $J$ = 7.3 Hz, 4H), 7.86 (s, 2H), 7.59 (t, $J$ = 7.3 Hz, 2H), 7.55 – 7.47 (m, 4H), 3.92 (s, 6H). $^{13}$C NMR (100 MHz, $(CD_3)_2SO$) δ 163.2, 152.2, 142.6, 133.3, 131.9, 129.9, 128.5, 127.7, 120.9, 61.8. HR MS (ESI): calcd for $C_{24}H_{23}N_4O_4$ $(M+H)^+$: 431.1719, found: 431.1710 (error: -2.09 ppm). mp. 141°C.




Synthesis of compound **MC15C5**: This compound was synthesized by using similar procedure for that of **MC2OMe.** $^{1}$H NMR (400 MHz, $(CD_3)_2SO$) δ11.96 (s, 2H), 8.73 (s, 2H), 7.94 (d, *J* = 7.3 Hz, 4H), 7.77 (s, 2H), 7.61 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 4H), 4.15 (t, *J* = 4.6 Hz, 4H), 3.95 (t, *J* = 4.8 Hz, 4H), 3.65 (dd, $^{3}J$ = 10.4 Hz, $^{4}J$ = 5.4 Hz, 8H). $^{13}$C NMR (100 MHz, $(CD_3)_2SO$) δ 163.2, 151.7, 142.6, 133.4, 131.8, 130.0, 128.5, 127.7, 121.0, 74.2, 70.4, 69.7, 69.6. HR MS (ESI): calcd for $C_{30}H_{32}N_4O_7$ $(M+Na)^+$: 583.2163, found: 583.2181 (error: 3.09 ppm). mp. 127°C.




Synthesis of compound **MC18C6**: This compound was synthesized by using similar procedure for that of **MC2OMe.** $^{1}$H NMR (400 MHz, $(CD_3)_2SO$) δ 11.99 (s, 2H), 8.73 (s, 2H), 7.94 (d, *J* = 7.3 Hz, 4H), 7.77 (s, 2H), 7.62 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 4H), 4.16 (t, *J* = 4.6 Hz, 4H), 3.88 (t, *J* = 4.7 Hz, 4H), 3.69 – 3.61 (m, 8H), 3.58 (s, 4H). $^{13}$C NMR (100 MHz, $(CD_3)_2SO$) δ 163.2, 151.4, 142.6, 133.4, 131.8, 130.1, 128.5, 127.7, 121.0, 73.8, 70.1, 70.0, 69.8, 69.5. HR MS (ESI): calcd for $C_{32}H_{36}N_4O_8$ $(M+Na)^+$: 627.2425, found: 627.2441 (error: 2.55 ppm). mp. 98°C.




Synthesis of compound **MC21C7**: This compound was synthesized by using similar procedure for that of **MC2OMe**. $^{1}$H NMR (400 MHz, $(CD_3)_2SO$) δ11.97 (s, 2H), 8.75 (s, 2H), 7.93 (d, *J* = 7.2 Hz, 4H), 7.76 (s, 2H), 7.65 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 4H), 4.21 (t, *J* = 4.6 Hz, 4H), 3.88 (t, *J* = 4.7 Hz, 4H), 3.62 (td, $^{3}J$ = 5.2 Hz, $^{4}J$ = 3.4 Hz, 8H), 3.55 (s, 8H). $^{13}$C NMR (100 MHz, $(CD_3)_2SO$) δ 163.3, 151.2, 142.9, 133.4, 131.8, 130.1, 128.5, 127.7, 120.8, 73.2, 70.3, 70.0, 69.7, 69.6. HR MS (ESI): calcd for $C_{34}H_{40}N_4O_9$ $(M+Na)^+$: 671.2687, found: 671.2695 (error: 1.30

ppm). mp. 101°C.

Synthesis of **COF2OMe**: To a 10 mL schlenk storage tube was added benzene-1,3,5-tricarbohydrazide (15.1 mg. 0.06 mmol) and **M2OMe** (17.5 mg, 0.09 mmol). Then 2 mL mixed solvent of mesitylene:1, 4-dioxane (5:1, V:V) and acetic acid (aq. 9M, 0.24 mL) were added. The mixture was degassed by three freeze-pump-thaw cycles. The tube was sealed and heated at 105°C in an oven for 4 days. The precipitate was filtered through centrifugation, which was washed with anhydrous THF for 6 times. Then the precipitate was immersed in DMF (HPLC Grade) for 3 days. The obtained powder was extracted by Soxhlet extraction for 24h, using chloroform, acetone and THF solvent successively. Then the powder was dried at 120°C under vacuum for 12 h. Yellow solid (yield, 92%) FT-IR (KBr, $cm^{-1}$): 3219, 3061, 2993, 2940, 2832, 1665, 1548, 1459, 1405, 1363, 1283, 1253, 1050, 1019, 954, 822, 731. Anal. Calcd. For chemical formula $C_{48}H_{42}N_{12}O_{12}$: C 58.89; H 4.32; N 17.17; O 19.61; found: C 54.11; H 4.68; N 16.05.

Synthesis of **COF15C5**, **COF18C6**, **COF21C7**: The three COFs were synthesized using the same procedure as used for **COF2OMe** by reacting 0.06 mmol benzene-1,3,5-tricarbohydrazide and 0.09 mmol **M15C5**, **M18C6** and **M21C7** respectively. The only difference is a change of mesitylene:1, 4-dioxane ratio to 9:1 (V : V).

**COF15C5**: Yellow solid (yield, 95%) FT-IR (KBr, $cm^{-1}$): 3217, 3041, 2924, 2869, 1677, 1547, 1431, 1354, 1278, 1251, 1127, 1057, 934, 873, 830, 734. Anal. Calcd. For chemical formula $C_{66}H_{72}N_{12}O_{21}$: C 57.89; H 5.30; N 12.27; O 24.54; found: C 54.37; H 4.19; N 11.95.

**COF18C6**: Yellow solid (yield, 90%) FT-IR (KBr, $cm^{-1}$): 3204, 3042, 2919, 2870, 1677, 1548, 1431, 1350, 1251, 1111, 1059, 945, 874, 829, 732. Anal. Calcd. For chemical formula $C_{72}H_{84}N_{12}O_{24}$: C 57.59; H 5.64; N 11.19; O 25.57; found: C 55.32; H 5.38; N 10.99.

**COF21C7**: Yellow solid (yield, 91%) FT-IR (KBr, $cm^{-1}$): 3212, 3040, 2920, 2873, 1681, 1546, 1430, 1351, 1252, 1108, 1057, 950, 873, 828, 733. Anal. Calcd. For chemical formula $C_{84}H_{108}N_{12}O_{30}$: C 57.13; H 6.16; N 9.52; O 27.18; found: C 56.42; H 5.96; N 9.33.

## 3. Photoluminescence Property of Model Compound

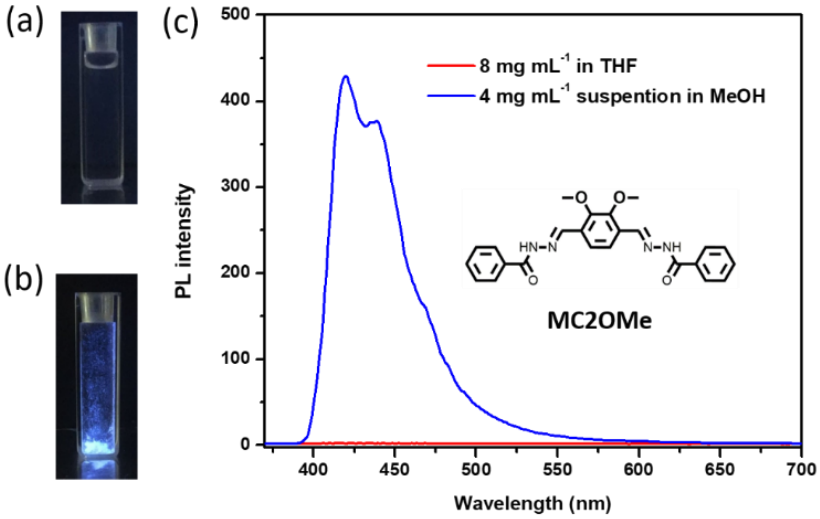



**Figure S1** Images of compound **MC2OMe** (a) 8 mg $mL^{-1}$ THF solution, and (b) crystalline powder in a cuvette under 365 nm irradiation; (c) Fluorescence spectra of **MC2OMe** solution in THF and suspension in methanol.

## 4. IR Spectra and Solid State $^{13}$C-NMR Spectra

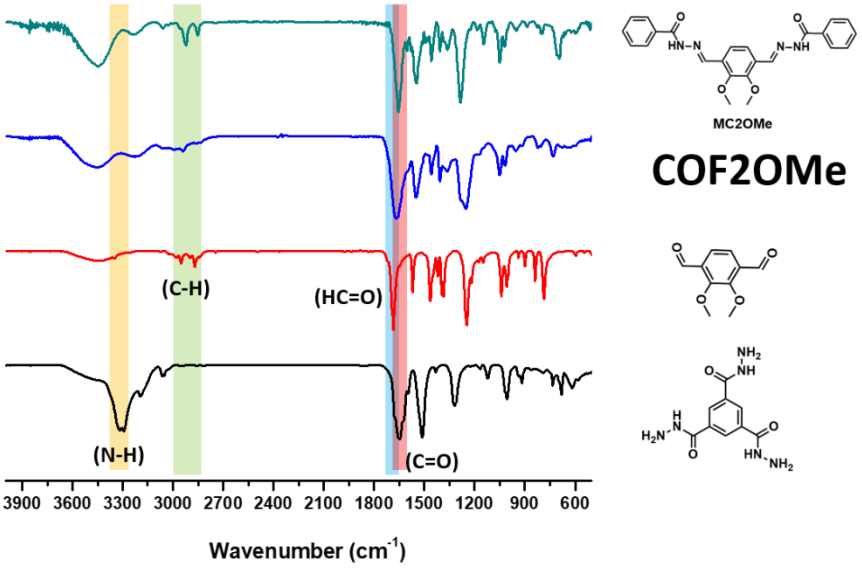



**Figure S2.** IR spectra of monomer compounds, **COF2OMe** and **MC2OMe**.

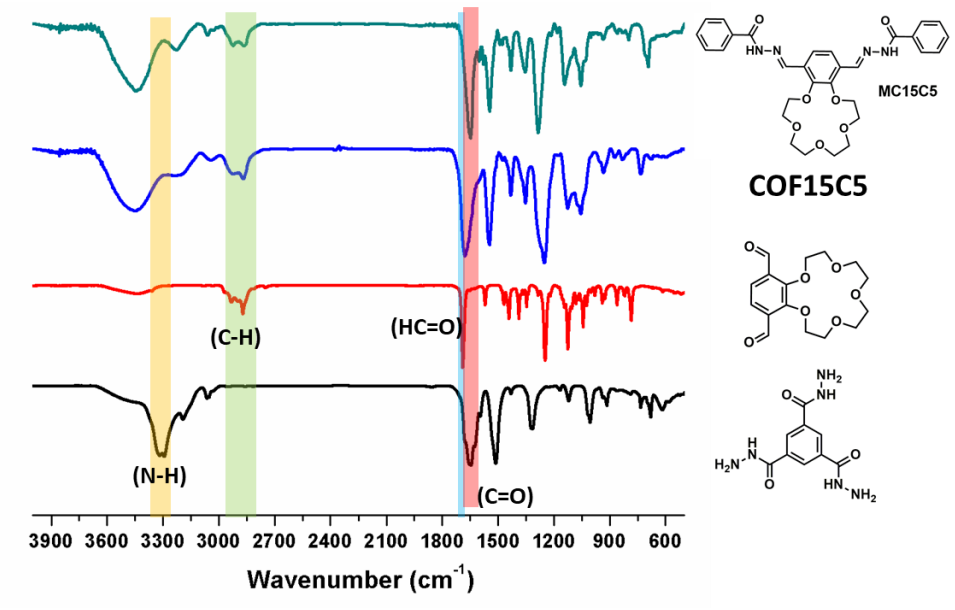



**Figure S3.** IR spectra of monomer compounds, **COF15C5** and **MC15C5**.

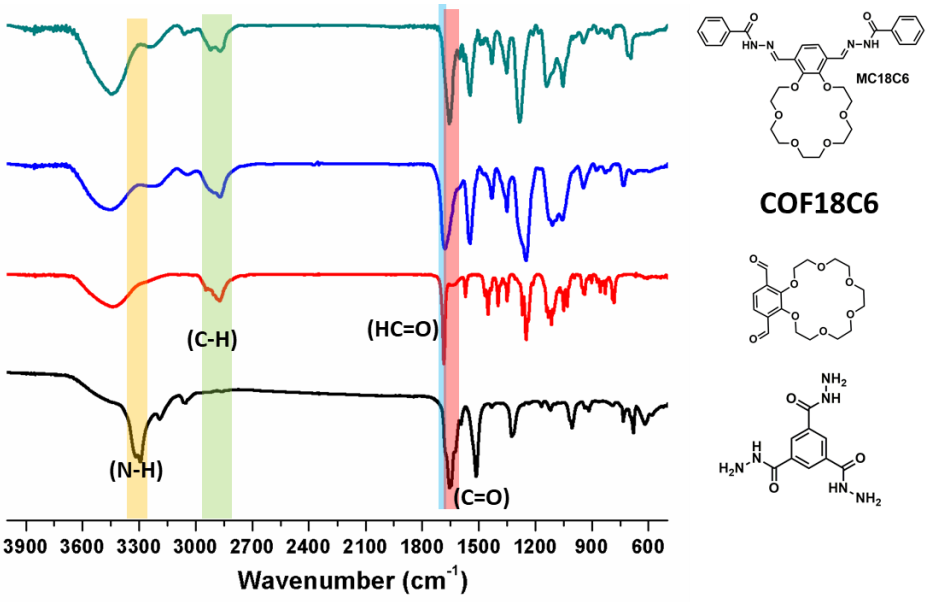



**Figure S4.** IR spectra of monomer compounds, **COF18C6** and **MC18C6**.

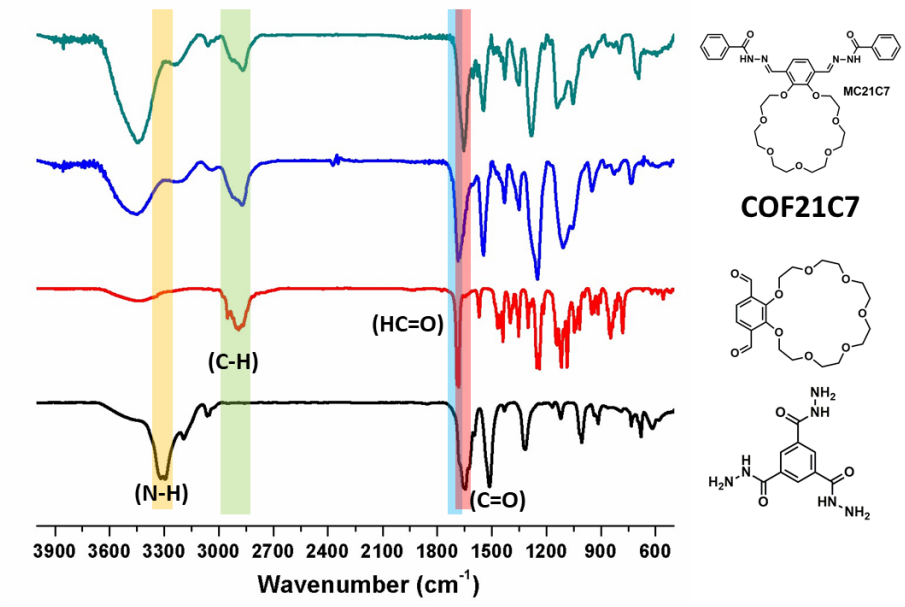



**Figure S5.** IR spectra of monomer compounds, **COF21C7** and **MC21C7**.

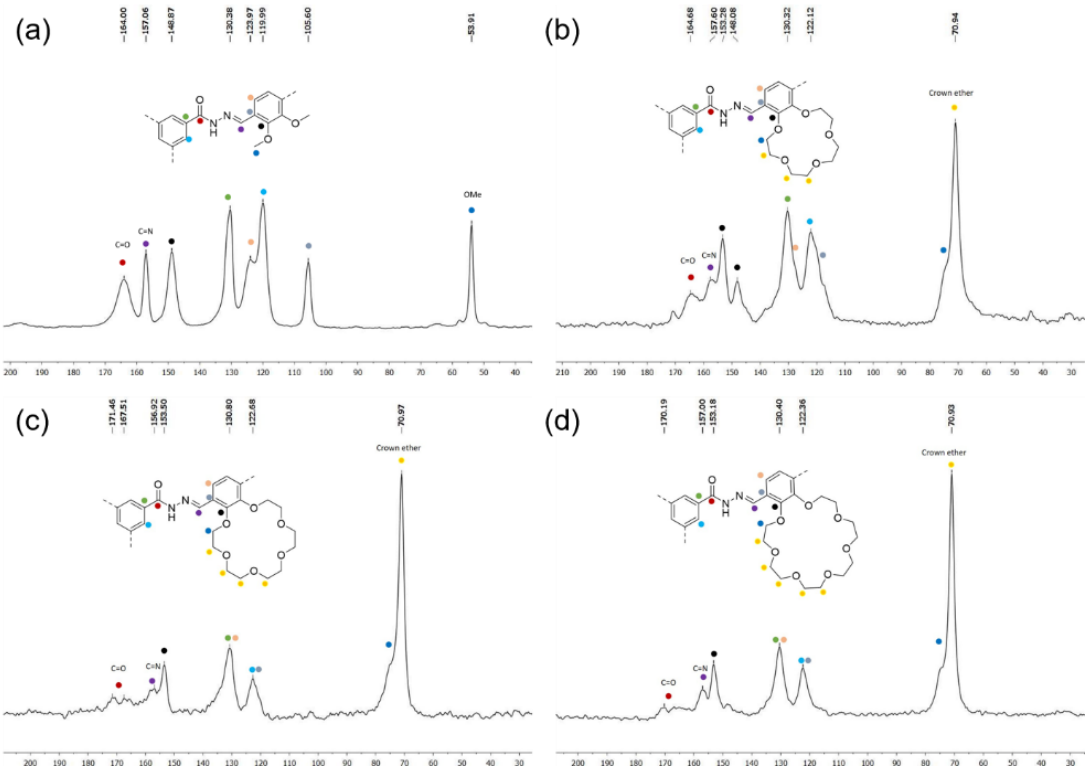



**Figure S6.** Solid state $^{13}$C-NMR spectra of (a) **COF2OMe**, (b) **COF15C5**, (c) **COF18C6** and (d) **COF21C7**.

## 5. $N_2$ Sorption Isotherm and Pore Size Distribution

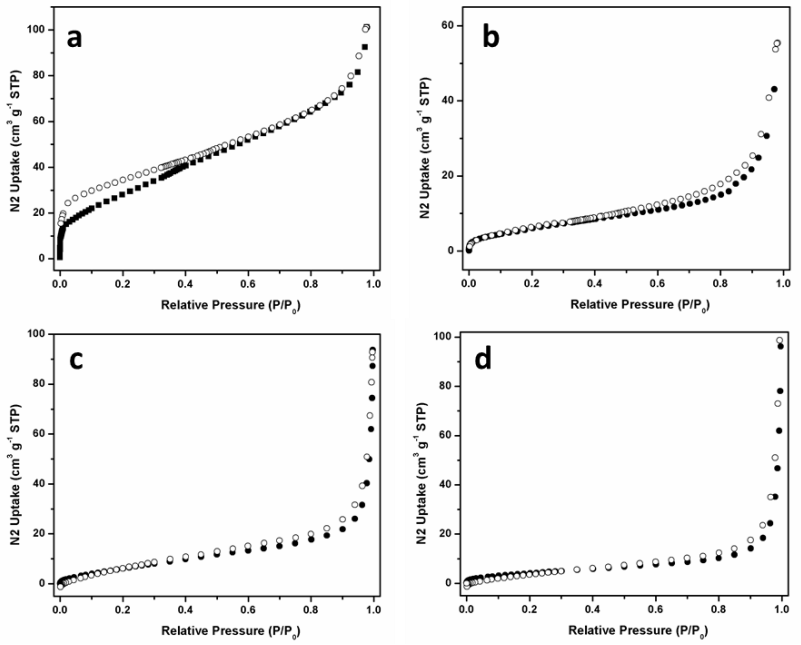



**Figure S7.** $N_2$ sorption isotherm of (a) **COF2OMe**, (b) **COF15C5**, (c) **COF18C6** and (d) **COF21C7**.

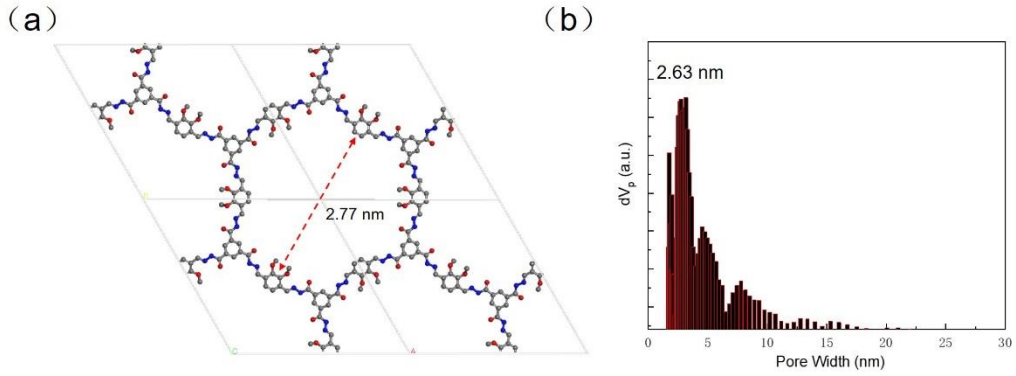



**Figure S8.** (a) Pore size measured form Pawley refined structure of **COF2OMe**, and (b) pore size distribution plot of **COF2OMe** calculated by nonlocal density functional theory.

## 6. SEM Images of COF Materials

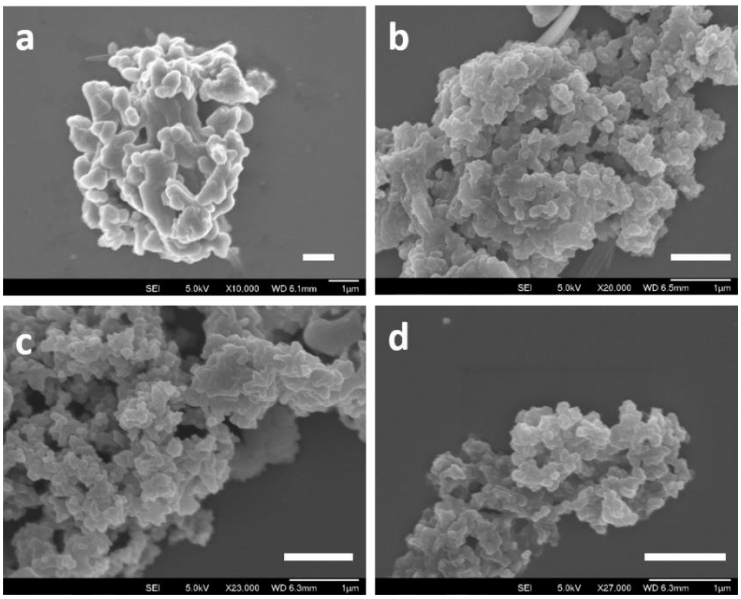



**Figure S9.** SEM images of (a) **COF2OMe**, (b) **COF15C5**, (c) **COF18C6** and (d) **COF21C7** (1μm for all scale bars).

## 7. Thermal Properties

Thermal gravimetric analysis (TGA) of the COFs and model compounds (Figures S10 and S11,) showed similar degradation temperatures (Table S1, with 5% weight loss) over 320°C for **COF2OMe** and **MC2OMe**. Slightly higher degradation temperatures (332°C-338°C) were measured for the crown ether COFs than their corresponding model compounds (309°C-328°C).

Table 1. Thermal stability data of COFs and model compounds.

| Degradation Temperature | | | |
|---|---|---|---|
| **MC2OMe** 325°C | **MC15C5** 309°C | **MC18C6** 328°C | **MC21C7** 327°C |
| **COF2OMe** 321°C | **COF15C5** 332°C | **COF18C6** 336°C | **COF21C7** 338°C |

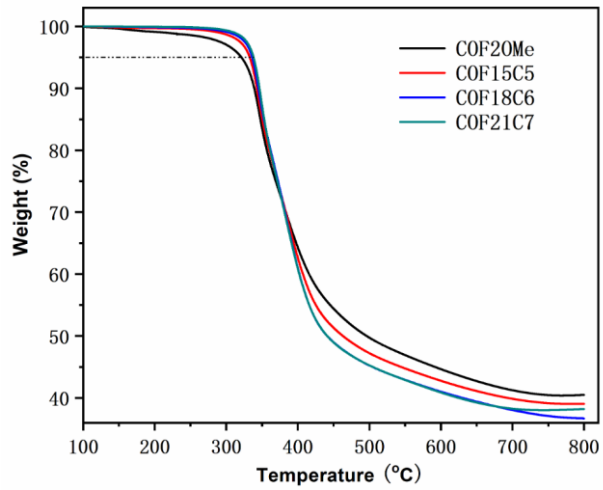



**Figure S10.** TGA profiles of **COF2OMe**, **COF15C5**, **COF18C6** and **COF21C7**.

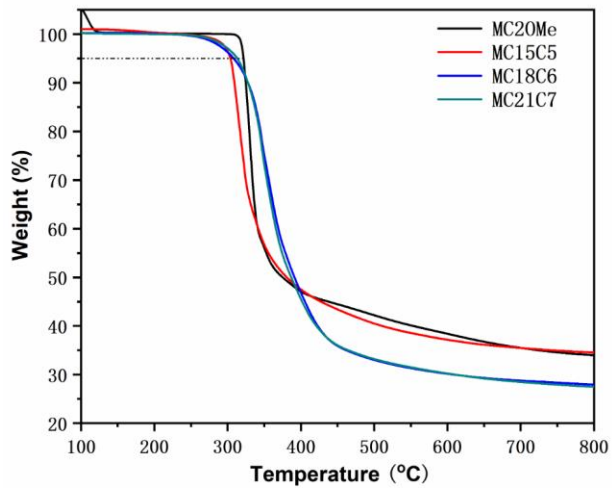



**Figure S11.** TGA profiles of **MC2OMe**, **MC15C5**, **MC18C6** and **MC21C7**.

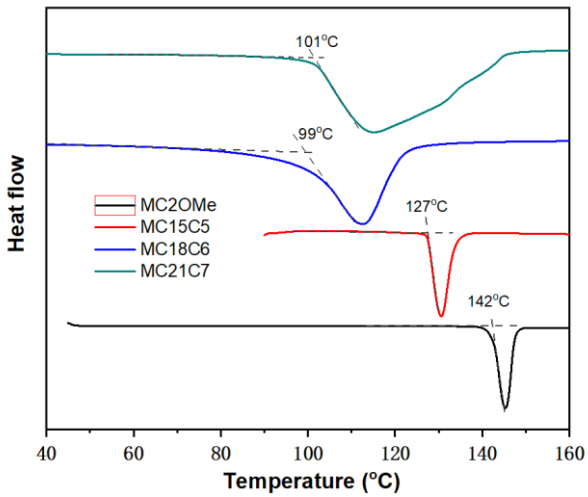



**Figure S12.** DSC heating thermograms of **MC2OMe**, **MC15C5**, **MC18C6** and **MC21C7** at 10°C/min.

## 8. PLQY of Model Compounds

The luminescence property of model compounds was also studied for comparison. Single crystals of these four compounds were not successfully grown, crystalline powders were obtained instead. Their PLQY were determined to be 18.4%, 13.2%, 12.8%, 11.4% for **MC2OMe**, **MC15C5**, **MC18C6**, **MC21C7**, respectively. As degree of crystallinity and packing mode had impact on the PLQY, their XRD pattern were measured (Figure S13). XRD results showed very similar pattern and intensity for **MC18C6** and **MC21C7**, indicating same packing mode and similar degree of crystallinity. PLQY of **MC18C6** was 1.4% higher than **MC21C7**, which was reasonable since the former had tighter packing, as seen from the right shifted diffraction peaks to slightly higher degrees. Quite different XRD patterns were found for **MC2OMe** and **MC15C5**. Their higher PLQY might be resulted from more closed packing of backbones due to shrinking of side chain bulkiness, especially for **MC2OMe**, which restricted backbone movement. This was in consistence with their higher melting points than **MC18C6** and **MC21C7**. DSC profiles of the crystalline model compounds (Figure S12) showed similar melting points of 101°C and 99°C for **MC21C7** and **MC18C6**, respectively, and notably increased melting points for **MC15C5** (127°C) and **MC2OMe** (142°C). Thus, we anticipated that the same RIR mechanism working in model compounds for PLQY enhancing as in COFs.

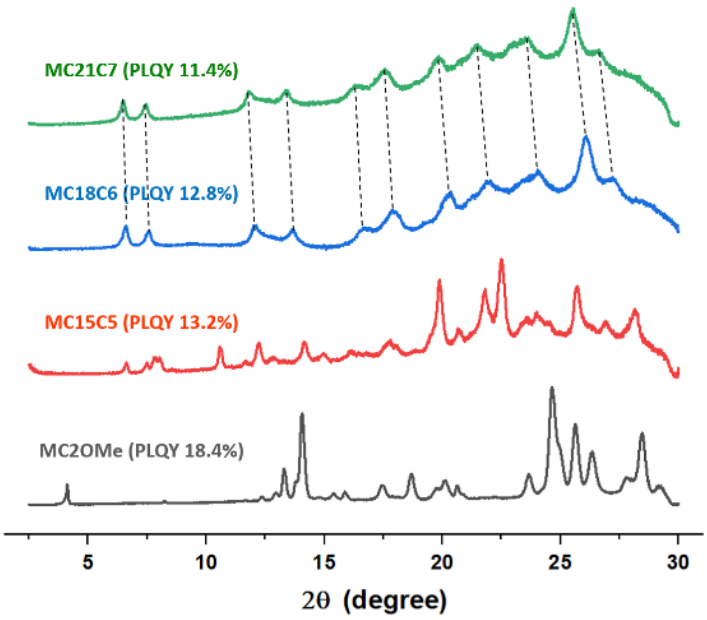



**Figure S13.** Normalized powder XRD patterns of crystalline model compounds and their corresponding PLQY.

## 9. Metal Ions Sensing

The PL intensity of **COF2OMe** is too low for metal ion sensing experiments. We have done PL sensing of 15 common metal ions using **COF15C5**, **COF18C6**, and **COF21C7** suspension, but no significant PL quenching was found for any metal ions (Figure S14).

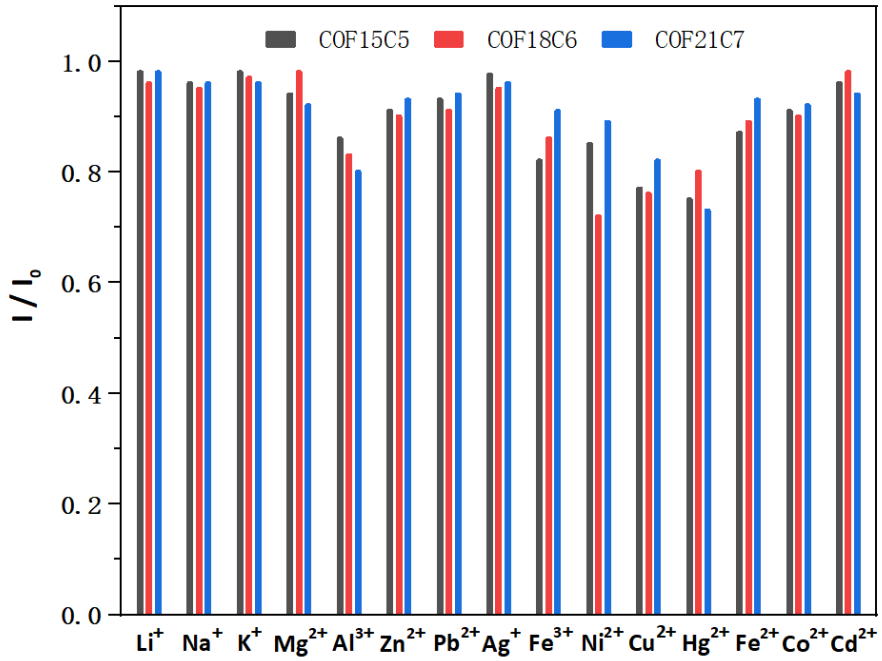



**Figure S14.** Fluorescence response of **COF2OMe**, **COF15C5**, **COF18C6** and **COF21C7** ($H_2O$ : ethanol in 1:1 ratio) suspension in the presence of different metal ions (100 μM) in water at $\lambda_{em}$ = 503 nm. I: PL intensity of COF suspension with metal ions; $I_0$: PL intensity of COF suspension. The concentration of COFs suspension is 0.2mg/mL.

## 10. Fractional Atomic Coordinates for the Unit Cells

**Table s2.** Atomistic coordinates for optimized unit cell of **COF2OMe** (space group P1, a = b = 30.068 Å, c = 3.739 Å, α = β = 90°, and γ = 120°).

| Atom | x | y | z |
|---|---|---|---|
| C1 | 1.28858 | -0.35317 | 0.32616 |
| C2 | 1.32187 | -0.3731 | 0.30475 |
| C3 | 1.37501 | -0.34021 | 0.27695 |
| C4 | 1.39479 | -0.28682 | 0.26806 |
| C5 | 1.36212 | -0.26619 | 0.28816 |
| C6 | 1.309 | -0.29964 | 0.31688 |
| C7 | 1.4095 | -0.36161 | 0.24394 |
| C8 | 1.38347 | -0.21003 | 0.26356 |
| C9 | 1.23262 | -0.38822 | 0.34271 |
| N10 | 1.43723 | -0.17694 | 0.20416 |
| O11 | 1.35531 | -0.19176 | 0.28682 |
| O12 | 1.21508 | -0.43481 | 0.3412 |
| N13 | 1.19861 | -0.36791 | 0.35296 |
| O14 | 1.45594 | -0.33288 | 0.23498 |
| N15 | 1.38864 | -0.41604 | 0.21439 |
| N16 | 1.42051 | -0.43676 | 0.1501 |
| N17 | 1.45788 | -0.12429 | 0.13653 |
| C18 | 1.53094 | -0.04005 | -5.7E-4 |
| C19 | 1.58407 | -0.01375 | -0.04422 |
| C20 | 1.61058 | 0.03856 | -0.12383 |
| C21 | 1.5847 | 0.06601 | -0.15927 |
| C22 | 1.50656 | -0.09557 | 0.07911 |
| C23 | 1.4717 | 0.063 | 0.13943 |
| C24 | 1.50331 | -0.01362 | -0.0442 |
| C25 | 1.53081 | 0.04063 | -0.11039 |
| O26 | 1.50606 | 0.06962 | -0.14251 |
| C27 | 1.42198 | -0.03489 | -0.28858 |
| O28 | 1.44971 | -0.04156 | -0.00657 |
| C29 | 1.51397 | -0.50832 | -0.0613 |
| C30 | 1.48668 | -0.48143 | 0.00123 |
| C31 | 1.4326 | -0.50981 | 0.03889 |
| C32 | 1.40099 | -0.48592 | 0.11253 |
| C33 | 1.43273 | -0.58906 | -0.08172 |
| C34 | 1.40636 | -0.56313 | -0.00546 |
| C35 | 1.62428 | -0.67217 | -0.33488 |
| C36 | 1.64439 | -0.70544 | -0.34449 |

| | | | |
|---|---|---|---|
| C37 | 1.6976 | -0.68481 | -0.31776 |
| C38 | 1.73059 | -0.63155 | -0.28215 |
| C39 | 1.70984 | -0.59888 | -0.27234 |
| C40 | 1.65674 | -0.61884 | -0.3002 |
| C41 | 1.60981 | -0.76167 | -0.36147 |
| C42 | 1.78628 | -0.61022 | -0.23924 |
| C43 | 1.63509 | -0.5844 | -0.27778 |
| N44 | 1.818 | -0.558 | -0.12642 |
| O45 | 1.80524 | -0.63738 | -0.29075 |
| O46 | 1.66353 | -0.5378 | -0.26093 |
| N47 | 1.58071 | -0.60551 | -0.26682 |
| O48 | 1.56361 | -0.77949 | -0.39535 |
| N49 | 1.6301 | -0.79554 | -0.32569 |
| N50 | 1.59761 | -0.84843 | -0.27102 |
| N51 | 1.87039 | -0.53781 | -0.05965 |
| N52 | 1.55958 | -0.5739 | -0.20547 |
| C53 | 1.51039 | -0.59369 | -0.18381 |
| C54 | 1.48605 | -0.5624 | -0.11215 |
| C55 | 1.6167 | -0.87831 | -0.23041 |
| C56 | 1.89736 | -0.49205 | 0.07205 |
| C57 | 2.02997 | -0.39024 | 0.32565 |
| C58 | 1.97723 | -0.41731 | 0.26642 |
| C59 | 1.9526 | -0.46846 | 0.1519 |
| C60 | 1.92987 | -0.58183 | 0.22777 |
| C61 | 2.03537 | -0.46589 | 0.16391 |
| C62 | 1.98158 | -0.4936 | 0.10546 |
| O63 | 1.95902 | -0.54363 | -0.03223 |
| C64 | 2.05092 | -0.53453 | 0.27691 |
| O65 | 2.06571 | -0.4881 | 0.0868 |
| N66 | 2.14596 | -0.39975 | 0.31107 |
| C67 | 2.1153 | -0.3813 | 0.32577 |
| C68 | 2.05945 | -0.41366 | 0.27161 |
| O69 | 1.51191 | 1.57229 | 0.04258 |
| O70 | 1.5677 | 1.51727 | -0.09037 |
| C71 | 1.54595 | 1.60073 | -0.23952 |
| C72 | 1.59486 | 1.55211 | 0.19143 |

**Table s3.** Atomistic coordinates for optimized unit cell of **COF15C5** (space group P1, a = b = 29.714 Å, c = 3.8004 Å, α = β = 90°, and γ = 120°).

| Atom | x | y | z |
|---|---|---|---|
| C1 | 1.48387 | -0.10821 | 0.13185 |

| | | | |
|---|---|---|---|
| C2 | 1.59296 | 0.10867 | -0.24205 |
| N3 | 1.57342 | 0.13882 | -0.26447 |
| C4 | 1.50738 | -0.05312 | 0.02946 |
| C5 | 1.55916 | -0.02879 | -0.07871 |
| C6 | 1.5858 | 0.02365 | -0.16823 |
| C7 | 1.56126 | 0.05311 | -0.15227 |
| C8 | 1.31065 | -0.00449 | -0.03988 |
| C9 | 1.26908 | -0.05054 | -0.24187 |
| C10 | 1.44172 | 0.04424 | -0.24065 |
| C11 | 1.39624 | 0.04007 | -0.03388 |
| O12 | 1.35359 | 0.02444 | -0.25582 |
| O13 | 1.23419 | -0.08743 | -0.00493 |
| C14 | 1.2211 | -0.13571 | -0.15016 |
| C15 | 1.25446 | -0.15605 | 0.01 |
| O16 | 1.30204 | -0.13458 | -0.16592 |
| C17 | 1.33919 | -0.10291 | 0.08104 |
| C18 | 1.39278 | -0.07841 | -0.08271 |
| C19 | 1.5085 | 0.02927 | -0.04948 |
| O20 | 1.48502 | 0.05979 | -0.01377 |
| O21 | 1.43052 | -0.04616 | 0.1695 |
| C22 | 1.48125 | -0.02418 | 0.0405 |
| C23 | 1.37698 | -0.49547 | 0.13156 |
| C24 | 1.40857 | -0.51889 | 0.02918 |
| C25 | 1.40686 | -0.59724 | -0.16853 |
| C26 | 1.38104 | -0.57068 | -0.07902 |
| C27 | 1.48478 | -0.60424 | -0.24227 |
| C28 | 1.46091 | -0.57262 | -0.15251 |
| C29 | 0.87957 | -0.49731 | -0.24277 |
| C30 | 0.93513 | -0.47337 | -0.15305 |
| C31 | 1.01711 | -0.39341 | -0.07956 |
| C32 | 0.96466 | -0.4193 | -0.16907 |
| C33 | 1.09646 | -0.38921 | 0.13107 |
| C34 | 1.04136 | -0.42087 | 0.02865 |
| N35 | 0.84936 | -0.54707 | -0.2651 |
| C36 | 1.2648 | -0.36367 | 0.45059 |
| C37 | 1.2976 | -0.38487 | 0.4497 |
| C38 | 1.35172 | -0.35254 | 0.45079 |
| C39 | 1.373 | -0.29848 | 0.44993 |
| C40 | 1.34075 | -0.27669 | 0.45083 |
| C41 | 1.28667 | -0.30956 | 0.44973 |
| C42 | 1.3858 | -0.37509 | 0.42717 |
| C43 | 1.36338 | -0.21998 | 0.42724 |

| | | | |
|---|---|---|---|
| C44 | 1.20808 | -0.39783 | 0.42676 |
| N45 | 1.41684 | -0.18775 | 0.33431 |
| O46 | 1.33607 | -0.20064 | 0.47239 |
| O47 | 1.18867 | -0.44455 | 0.47184 |
| N48 | 1.17593 | -0.37661 | 0.33369 |
| O49 | 1.43253 | -0.34772 | 0.47241 |
| N50 | 1.36451 | -0.42854 | 0.3341 |
| N51 | 1.39683 | -0.44871 | 0.25192 |
| N52 | 1.4371 | -0.13519 | 0.25213 |
| N53 | 1.12336 | -0.409 | 0.25144 |
| N54 | 1.53453 | -0.58463 | -0.26468 |
| C55 | 1.01234 | -0.47602 | 0.03972 |
| C56 | 0.95889 | -0.5023 | -0.05024 |
| O57 | 1.03424 | -0.50478 | 0.16875 |
| O58 | 0.9283 | -0.55637 | -0.01451 |
| O59 | 1.49254 | -0.44195 | 0.16929 |
| C60 | 1.46372 | -0.49268 | 0.04026 |
| C61 | 1.48992 | -0.51985 | -0.0497 |
| O62 | 1.54398 | -0.49629 | -0.01396 |
| C63 | 1.63206 | -0.63024 | -0.38411 |
| C64 | 1.68601 | -0.60987 | -0.38353 |
| C65 | 1.70694 | -0.64288 | -0.38422 |
| C66 | 1.67328 | -0.69684 | -0.38344 |
| C67 | 1.61926 | -0.71786 | -0.38401 |
| C68 | 1.59898 | -0.68427 | -0.38333 |
| C69 | 1.76365 | -0.62105 | -0.36704 |
| C70 | 1.5843 | -0.77458 | -0.36662 |
| C71 | 1.61032 | -0.59535 | -0.36681 |
| N72 | 1.6054 | -0.80834 | -0.34065 |
| O73 | 1.53724 | -0.79283 | -0.3662 |
| O74 | 1.63919 | -0.54828 | -0.3665 |
| N75 | 1.55538 | -0.61654 | -0.34082 |
| O76 | 1.78183 | -0.64987 | -0.36669 |
| N77 | 1.79748 | -0.5661 | -0.34119 |
| C78 | 0.65339 | 0.67624 | -0.04 |
| C79 | 0.64893 | 0.71775 | -0.24199 |
| C80 | 0.57085 | 0.54513 | -0.24082 |
| C81 | 0.61223 | 0.59064 | -0.03403 |
| O82 | 0.63931 | 0.63331 | -0.25596 |
| O83 | 0.64696 | 0.75261 | -0.00504 |
| C84 | 0.61175 | 0.76561 | -0.15027 |
| C85 | 0.55797 | 0.73218 | 0.00987 |

| | | | |
|---|---|---|---|
| O86 | 0.53179 | 0.6846 | -0.16607 |
| C87 | 0.52626 | 0.64746 | 0.08088 |
| C88 | 0.49711 | 0.59388 | -0.08291 |
| C89 | 0.9923 | 1.33348 | -0.04064 |
| C90 | 1.03831 | 1.33802 | -0.24262 |
| C91 | 0.94378 | 1.41586 | -0.24139 |
| C92 | 0.94786 | 1.37452 | -0.03462 |
| O93 | 0.96343 | 1.3475 | -0.25657 |
| O94 | 1.07517 | 1.34005 | -0.00567 |
| C95 | 1.12347 | 1.37532 | -0.15087 |
| C96 | 1.14389 | 1.42908 | 0.00929 |
| O97 | 1.1225 | 1.45521 | -0.16663 |
| C98 | 1.09087 | 1.46068 | 0.08032 |
| C99 | 1.06645 | 1.48976 | -0.08345 |

**Table s4.** Atomistic coordinates for optimized unit cell of **COF18C6** (space group P1, a = b = 29.458 Å, c = 3.7834 Å, α = β = 90°, and γ = 120°).

| Atom | x | y | z |
|---|---|---|---|
| C1 | 0.68055 | -2.70796 | -0.48296 |
| C2 | 0.71349 | -2.65387 | -0.49562 |
| C3 | 0.69179 | -2.62158 | -0.4569 |
| C4 | 0.63779 | -2.64279 | -0.40709 |
| C5 | 0.60543 | -2.69688 | -0.39543 |
| C6 | 0.62644 | -2.72977 | -0.43501 |
| C7 | 0.77067 | -2.63106 | -0.52397 |
| C8 | 0.61567 | -2.60863 | -0.34696 |
| C9 | 0.59242 | -2.7865 | -0.40447 |
| N10 | 0.56324 | -2.63001 | -0.21952 |
| O11 | 0.64253 | -2.56188 | -0.39512 |
| O12 | 0.54499 | -2.80549 | -0.38449 |
| N13 | 0.61492 | -2.81932 | -0.38383 |
| O14 | 0.78962 | -2.65912 | -0.55982 |
| N15 | 0.80424 | -2.57606 | -0.49567 |
| C16 | 0.07819 | -2.51636 | -0.29077 |
| O17 | 0.06634 | -2.59994 | -0.15235 |
| C18 | 0.10291 | -2.5469 | -0.1504 |
| O19 | 0.01755 | -2.70344 | -0.42977 |
| C20 | 0.06343 | -2.68118 | -0.2296 |
| C21 | 0.09394 | -2.62289 | -0.28905 |
| O22 | -0.08854 | -2.7849 | -0.42623 |
| C23 | -0.04999 | -2.78599 | -0.63397 |
| C24 | 0.00288 | -2.75589 | -0.45322 |

| | | | |
|---|---|---|---|
| C25 | -0.0494 | -2.5953 | -0.35373 |
| C26 | -0.08884 | -2.6517 | -0.27858 |
| O27 | -0.07773 | -2.684 | -0.48319 |
| C28 | -0.12561 | -2.73027 | -0.50757 |
| C29 | -0.11743 | -2.77286 | -0.6611 |
| C30 | 0.10768 | -2.39804 | -0.06177 |
| C31 | 0.05218 | -2.42937 | -0.16581 |
| C32 | -0.02516 | -2.42718 | -0.35758 |
| C33 | 0.028 | -2.40165 | -0.27631 |
| C34 | -0.11184 | -2.50487 | -0.40746 |
| C35 | -0.05552 | -2.48108 | -0.32811 |
| O36 | -0.06366 | -2.56356 | -0.15689 |
| C37 | -0.03192 | -2.51022 | -0.22098 |
| C38 | 0.02238 | -2.48446 | -0.146 |
| O39 | 0.0447 | -2.5138 | -0.03105 |
| C40 | 0.40713 | -2.08295 | -0.13965 |
| O41 | 0.31658 | -2.13951 | -0.26195 |
| C42 | 0.35136 | -2.10528 | -0.01112 |
| O43 | 0.24548 | -2.10644 | -0.37846 |
| C44 | 0.22745 | -2.1587 | -0.30143 |
| C45 | 0.2683 | -2.16411 | -0.08893 |
| O46 | 0.29367 | -2.01688 | 0.0344 |
| C47 | 0.24466 | -2.03375 | -0.11869 |
| C48 | 0.21609 | -2.0924 | -0.16316 |
| C49 | 0.49095 | -1.92707 | 0.16494 |
| C50 | 0.45245 | -1.90821 | 0.10167 |
| O51 | 0.40142 | -1.94983 | 0.13457 |
| C52 | 0.37066 | -1.93429 | -0.05106 |
| C53 | 0.31465 | -1.96353 | 0.08386 |
| N54 | -0.14203 | -2.55462 | -0.43406 |
| C55 | 0.4993 | -2.11464 | 0.19986 |
| C56 | 0.52314 | -2.05979 | 0.09082 |
| C57 | 0.60215 | -1.98176 | -0.09235 |
| C58 | 0.57678 | -2.0334 | 0.01939 |
| C59 | 0.60501 | -1.90058 | -0.24974 |
| C60 | 0.57448 | -1.95534 | -0.13704 |
| O61 | 0.48971 | -1.95811 | -0.12366 |
| C62 | 0.52001 | -1.9815 | -0.06444 |
| C63 | 0.49441 | -2.0337 | 0.04629 |
| O64 | 0.44182 | -2.05707 | 0.1448 |
| C65 | 0.49707 | -2.61762 | 0.01358 |
| C66 | 0.47336 | -2.5861 | 0.11807 |

| | | | |
|---|---|---|---|
| C67 | 0.39403 | -2.58795 | 0.31059 |
| C68 | 0.42127 | -2.61365 | 0.22872 |
| C69 | 0.38584 | -2.51021 | 0.36119 |
| C70 | 0.41817 | -2.53403 | 0.28212 |
| C71 | 0.5413 | -2.41998 | 0.29472 |
| O72 | 0.49332 | -2.45149 | 0.11465 |
| O73 | 0.60762 | -2.3317 | 0.3791 |
| C74 | 0.55976 | -2.36349 | 0.21353 |
| O75 | 0.71333 | -2.25872 | 0.47024 |
| C76 | 0.6782 | -2.24358 | 0.34911 |
| C77 | 0.63277 | -2.28848 | 0.15777 |
| O78 | 0.74251 | -2.31228 | -0.00146 |
| C79 | 0.77973 | -2.26796 | 0.17746 |
| C80 | 0.75739 | -2.23268 | 0.25408 |
| C81 | 0.47118 | -2.50497 | 0.17575 |
| C82 | 0.49929 | -2.53099 | 0.09895 |
| O83 | 0.55111 | -2.502 | -0.01809 |
| C84 | 0.58729 | -2.4993 | 0.24131 |
| C85 | 0.64273 | -2.46939 | 0.09848 |
| O86 | 0.65922 | -2.41646 | 0.07928 |
| C87 | 0.70179 | -2.39302 | 0.31034 |
| C88 | 0.75039 | -2.35228 | 0.11867 |
| N89 | 0.54283 | -2.59791 | -0.13009 |
| C90 | 0.3606 | -2.3617 | 0.4476 |
| C91 | 0.38196 | -2.30763 | 0.43644 |
| C92 | 0.34965 | -2.286 | 0.38942 |
| C93 | 0.29556 | -2.31903 | 0.34916 |
| C94 | 0.27361 | -2.37311 | 0.3591 |
| C95 | 0.3064 | -2.39415 | 0.40814 |
| C96 | 0.37248 | -2.22931 | 0.36061 |
| C97 | 0.21711 | -2.40732 | 0.29786 |
| C98 | 0.395 | -2.3843 | 0.47548 |
| N99 | 0.18623 | -2.3859 | 0.17101 |
| O100 | 0.19692 | -2.4541 | 0.3446 |
| O101 | 0.44221 | -2.35609 | 0.51052 |
| N102 | 0.37336 | -2.43928 | 0.44794 |
| O103 | 0.34391 | -2.21062 | 0.34296 |
| N104 | 0.42798 | -2.19617 | 0.33797 |
| N105 | 0.44946 | -2.14372 | 0.2477 |
| N106 | 0.13346 | -2.4179 | 0.08172 |
| N107 | 0.40569 | -2.46046 | 0.38668 |
| N108 | 0.58414 | -1.87166 | -0.28914 |

**Table s5.** Atomistic coordinates for optimized unit cell of **COF21C7** (space group P1, a = b = 29.737 Å, c = 3.8190 Å, α = β = 90°, and γ = 120°).

| Atom | x | y | z |
|---|---|---|---|
| C1 | -0.12856 | 0.48979 | -0.1325 |
| C2 | -0.07397 | 0.51231 | -0.24237 |
| C3 | 0.00338 | 0.59005 | -0.45275 |
| C4 | -0.04899 | 0.56434 | -0.36236 |
| C5 | 0.08776 | 0.59529 | -0.51099 |
| C6 | 0.03203 | 0.5643 | -0.42598 |
| N7 | -0.15486 | 0.44319 | 0.00211 |
| C8 | 0.62158 | 0.26865 | 0.3483 |
| C9 | 0.5993 | 0.30101 | 0.3561 |
| C10 | 0.63034 | 0.35593 | 0.32541 |
| C11 | 0.68415 | 0.37839 | 0.2842 |
| C12 | 0.70693 | 0.3465 | 0.27697 |
| C13 | 0.67534 | 0.29169 | 0.30763 |
| C14 | 0.60628 | 0.38931 | 0.3105 |
| C15 | 0.76303 | 0.36979 | 0.21688 |
| C16 | 0.58866 | 0.21084 | 0.35406 |
| O17 | 0.78352 | 0.34295 | 0.2565 |
| O18 | 0.54295 | 0.19048 | 0.43433 |
| N19 | 0.60969 | 0.17855 | 0.24737 |
| O20 | 0.63342 | 0.43732 | 0.30835 |
| C21 | -0.04587 | 0.485 | -0.22147 |
| C22 | 0.00739 | 0.51118 | -0.31291 |
| C23 | 0.48439 | 0.87847 | -0.35169 |
| C24 | 0.50923 | 0.9341 | -0.23987 |
| C25 | 0.59018 | 1.01628 | -0.17294 |
| C26 | 0.56307 | 0.9635 | -0.2713 |
| C27 | 0.59647 | 1.09731 | 0.04992 |
| C28 | 0.56412 | 1.04108 | -0.04263 |
| C29 | 0.47923 | 0.37421 | 0.14227 |
| C30 | 0.45462 | 0.4047 | 0.02769 |
| C31 | 0.37564 | 0.40202 | -0.16066 |
| C32 | 0.40145 | 0.37645 | -0.0394 |
| C33 | 0.37118 | 0.4799 | -0.33622 |
| C34 | 0.40237 | 0.45641 | -0.21882 |
| N35 | 0.57725 | 1.12488 | 0.17567 |
| C36 | 0.36763 | 0.68363 | -0.55366 |
| C37 | 0.33562 | 0.70596 | -0.56645 |
| C38 | 0.28175 | 0.67275 | -0.58911 |

| | | | |
|---|---|---|---|
| C39 | 0.25991 | 0.61778 | -0.60057 |
| C40 | 0.29256 | 0.59606 | -0.58571 |
| C41 | 0.34649 | 0.62878 | -0.56376 |
| C42 | 0.35843 | 0.76352 | -0.53411 |
| C43 | 0.20312 | 0.58327 | -0.60639 |
| C44 | 0.38066 | 0.60608 | -0.52947 |
| N45 | 0.17017 | 0.60579 | -0.59231 |
| O46 | 0.18405 | 0.53538 | -0.61349 |
| O47 | 0.42761 | 0.63503 | -0.52728 |
| N48 | 0.35923 | 0.55052 | -0.48505 |
| O49 | 0.33066 | 0.78319 | -0.53915 |
| N50 | 0.41315 | 0.79632 | -0.48633 |
| N51 | 0.43474 | 0.84929 | -0.38871 |
| N52 | 0.11705 | 0.57436 | -0.5241 |
| N53 | 0.39093 | 0.53002 | -0.38526 |
| N54 | 0.55118 | 0.36559 | 0.28193 |
| N55 | 0.52877 | 0.39596 | 0.18691 |
| C56 | 0.48141 | 0.95748 | -0.09892 |
| C57 | 0.50932 | 1.01226 | -0.00956 |
| C58 | 0.67229 | 0.81085 | -0.0516 |
| C59 | 0.61976 | 0.80721 | -0.08829 |
| C60 | 0.73136 | 0.74086 | 0.05062 |
| C61 | 0.71679 | 0.77895 | 0.21424 |
| O62 | 0.66653 | 0.76572 | 0.1148 |
| C63 | 0.45627 | 0.48623 | -0.14846 |
| C64 | 0.48258 | 0.45987 | -0.02994 |
| C65 | 0.68569 | 0.60254 | 0.13158 |
| C66 | 0.71907 | 0.66011 | 0.02899 |
| O67 | 0.70033 | 0.69028 | 0.18743 |
| O68 | 0.53539 | 0.48866 | 0.05073 |
| C69 | 0.56758 | 0.50224 | -0.24958 |
| C70 | 0.62411 | 0.53271 | -0.14049 |
| O71 | 0.63601 | 0.58204 | -0.00941 |
| C72 | 0.5501 | 0.62903 | -0.06992 |
| C73 | 0.51623 | 0.57252 | 0.05488 |
| O74 | 0.48333 | 0.54061 | -0.22038 |
| C75 | 0.52979 | 0.6898 | 0.07244 |
| O76 | 0.51927 | 0.65026 | -0.17226 |
| O77 | 0.58662 | 0.76285 | -0.28687 |
| C78 | 0.53918 | 0.73995 | -0.11035 |
| O79 | 0.42724 | 0.92464 | -0.05595 |
| N80 | 0.79328 | 1.42309 | 1.09843 |

| | | | |
|---|---|---|---|
| C81 | 1.02982 | 1.22487 | 0.59954 |
| C82 | 1.07884 | 1.27117 | 0.74718 |
| C83 | 0.90073 | 1.19769 | 0.44766 |
| C84 | 0.94528 | 1.19369 | 0.60919 |
| O85 | 0.99239 | 1.23953 | 0.54103 |
| C86 | 0.8282 | 1.25512 | 0.79443 |
| C87 | 0.84079 | 1.21644 | 0.61635 |
| O88 | 0.8943 | 1.23604 | 0.62131 |
| O89 | 0.93175 | 1.4344 | 0.92014 |
| C90 | 0.90019 | 1.39483 | 0.67392 |
| C91 | 0.88151 | 1.34101 | 0.83461 |
| O92 | 0.84865 | 1.3018 | 0.60177 |
| C93 | 1.06253 | 1.43882 | 0.35472 |
| C94 | 1.0184 | 1.43874 | 0.55281 |
| O95 | 1.03712 | 1.48686 | 0.74042 |
| C96 | 1.08179 | 1.37607 | 0.4335 |
| O97 | 1.09005 | 1.42359 | 0.57536 |
| O98 | 1.10438 | 1.3092 | 0.48833 |
| C99 | 1.11265 | 1.35646 | 0.63534 |
| C100 | 1.20679 | 1.02254 | 1.02916 |
| C101 | 1.19758 | 0.97526 | 1.24784 |
| C102 | 1.31949 | 1.14829 | 0.8972 |
| C103 | 1.26741 | 1.10683 | 1.04364 |
| O104 | 1.25996 | 1.05647 | 0.98167 |
| C105 | 1.44514 | 1.16328 | 0.92711 |
| C106 | 1.40396 | 1.17875 | 0.87342 |
| O107 | 1.35943 | 1.14469 | 1.0624 |
| O108 | 1.48371 | 1.03751 | 1.12502 |
| C109 | 1.46847 | 1.06098 | 0.85949 |
| C110 | 1.44062 | 1.08678 | 1.02762 |
| O111 | 1.42904 | 1.11396 | 0.77673 |
| C112 | 1.34322 | 0.90169 | 1.16709 |
| C113 | 1.40034 | 0.94283 | 1.15918 |
| C114 | 1.27734 | 0.91657 | 1.14753 |
| O115 | 1.31673 | 0.92068 | 1.36618 |
| O116 | 1.21665 | 0.94638 | 1.07573 |
| C117 | 1.25473 | 0.94856 | 1.29954 |

# 11. NMR and Mass Spectra

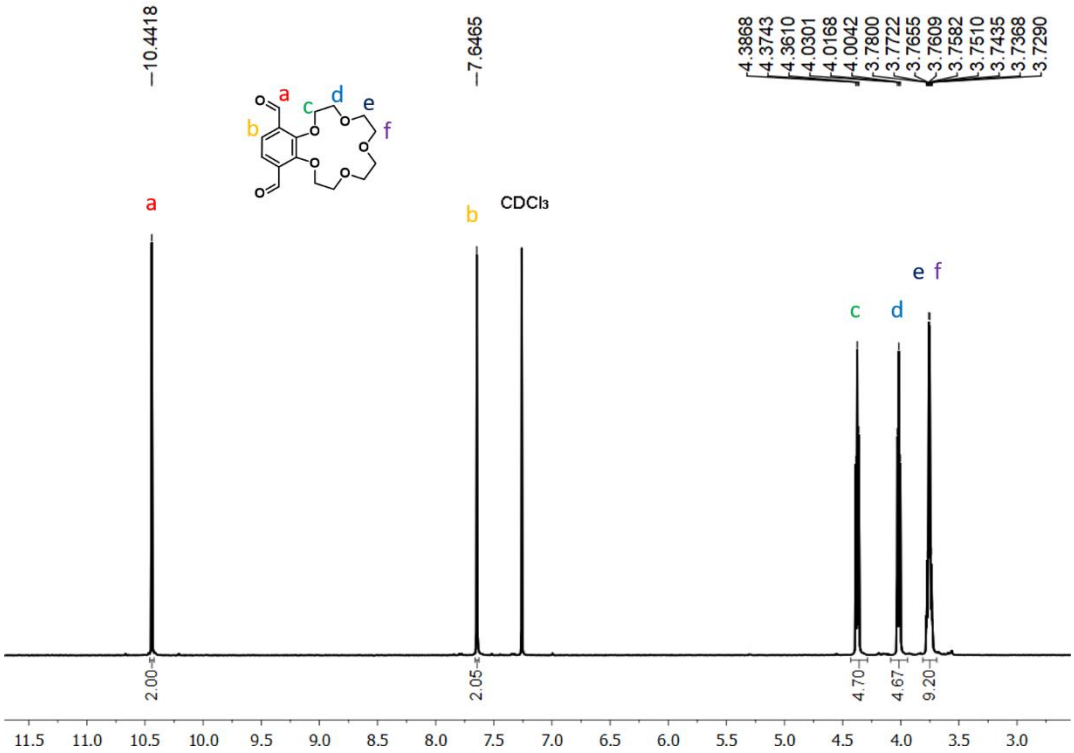



**Figure S15.** $^{1}$H NMR spectrum of **M15C5** (400 MHz, $CDCl_3$).

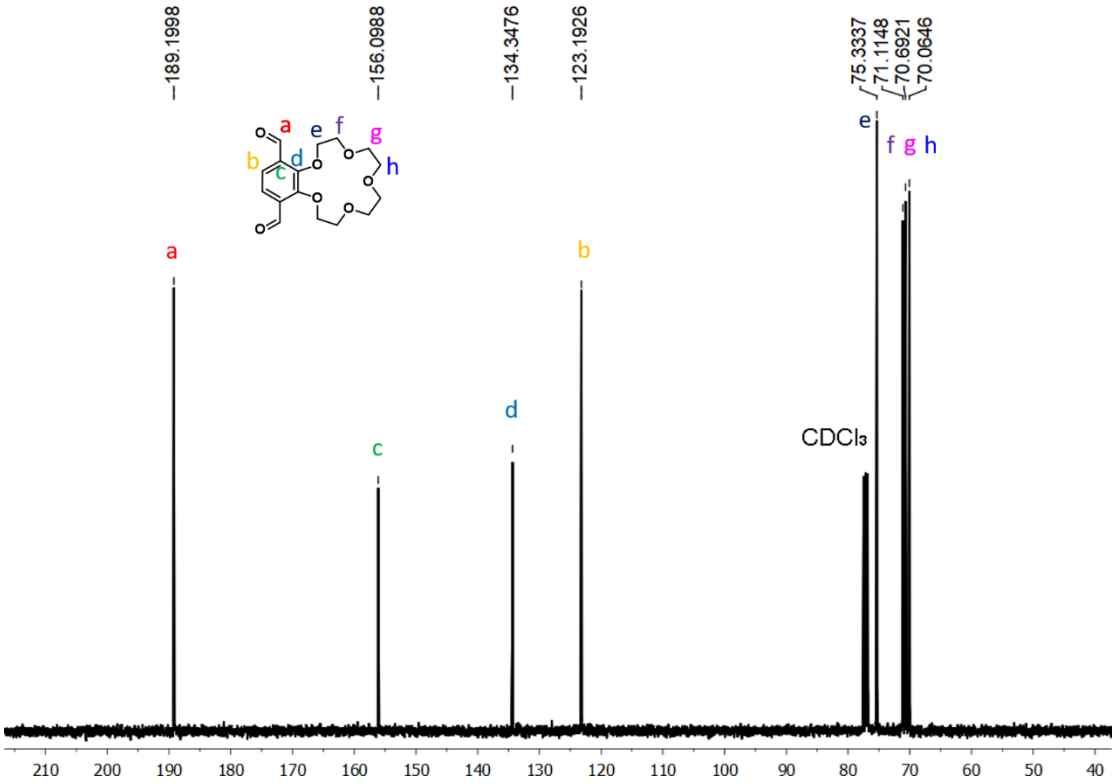



**Figure S16.** $^{13}$C NMR spectrum of **M15C5** (100 MHz, $CDCl_3$).

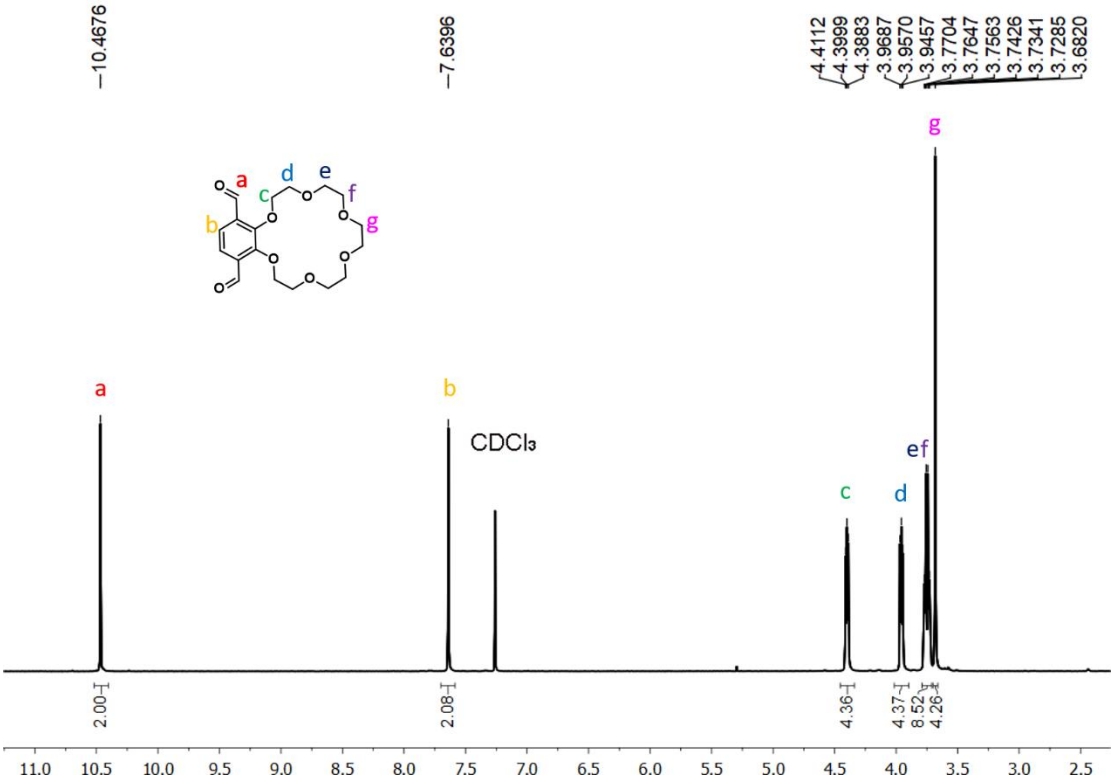



**Figure S17.** $^{1}$H NMR spectrum of **M18C6** (400 MHz, $CDCl_3$).

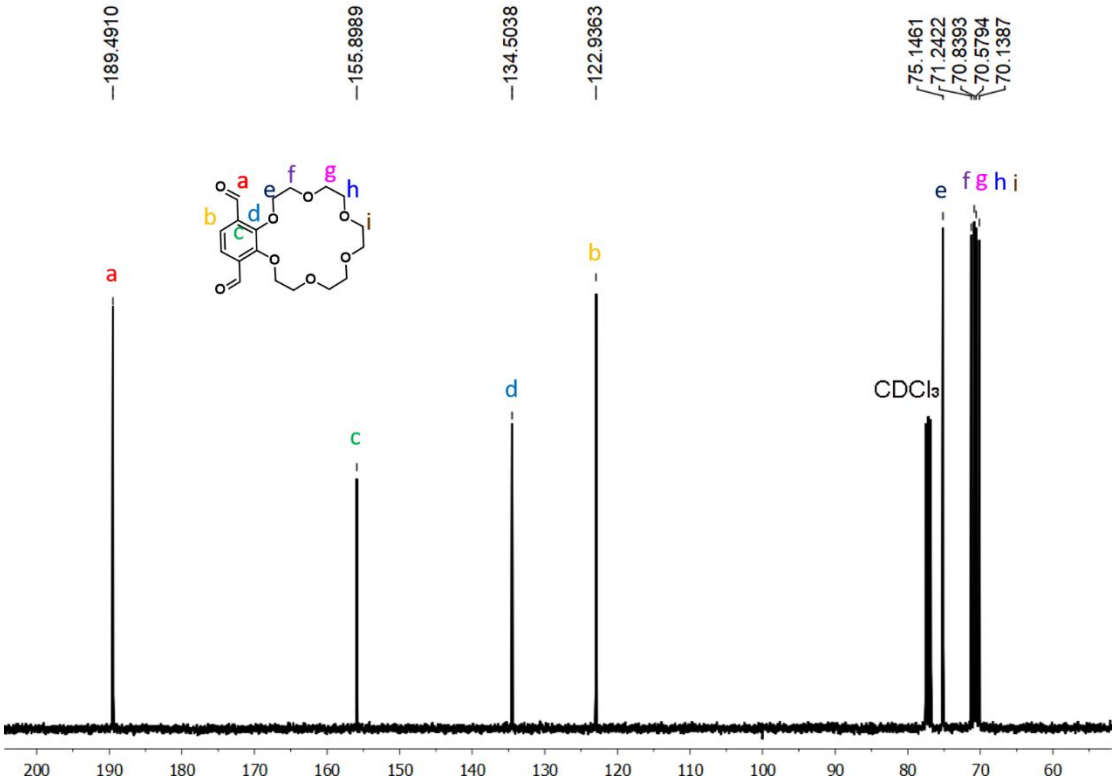



**Figure S18.** $^{13}$C NMR spectrum of **M18C6** (100 MHz, $CDCl_3$).

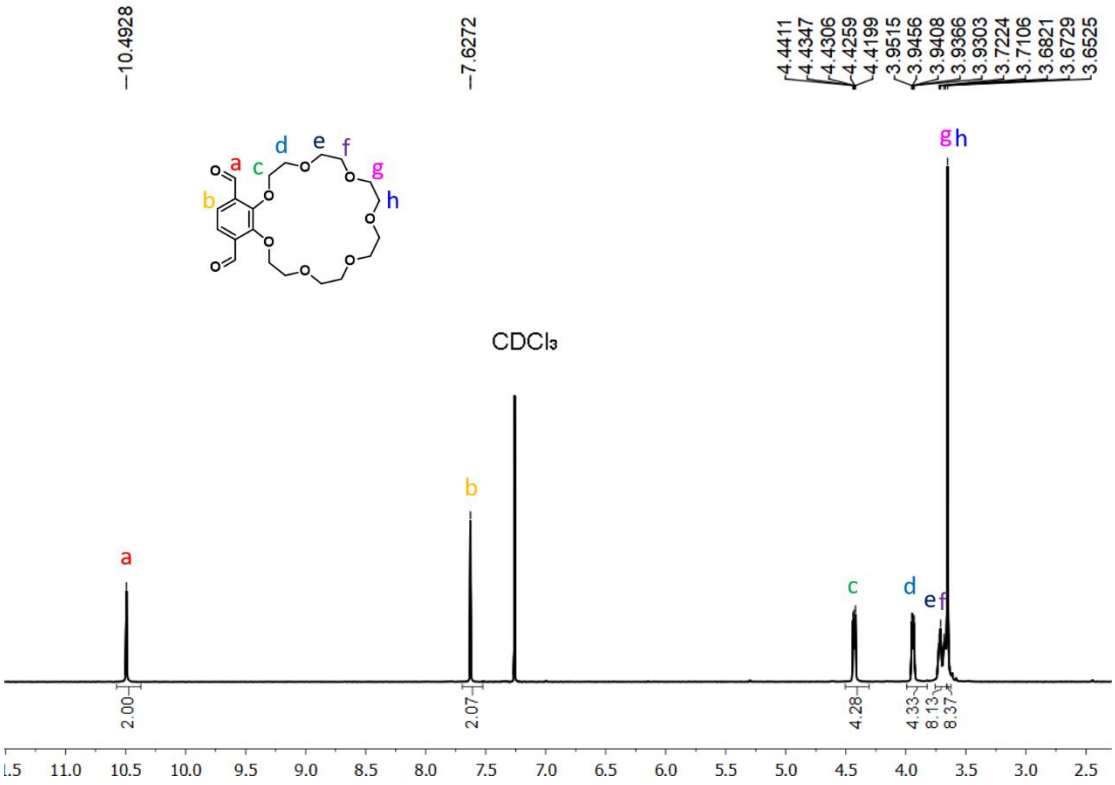



**Figure S19.** $^{1}$H NMR spectrum of **M21C7** (400 MHz, $CDCl_3$).

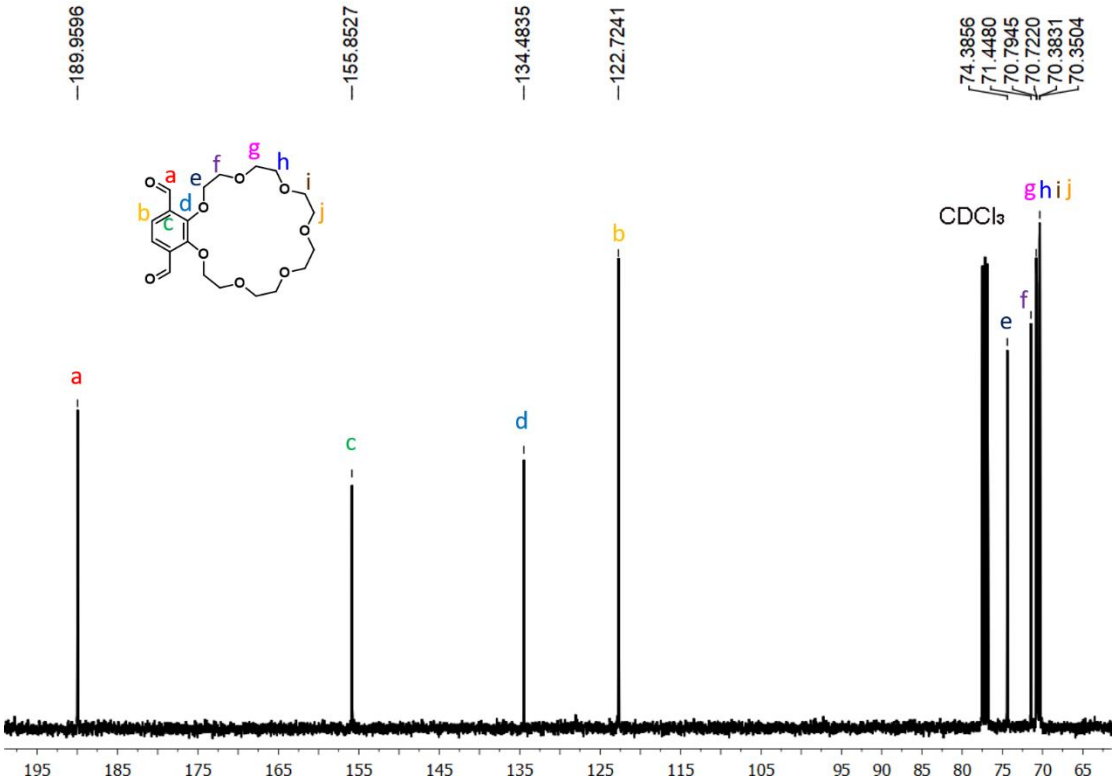



**Figure S20**. $^{13}$C NMR spectrum of **M21C7** (100 MHz, $CDCl_3$).

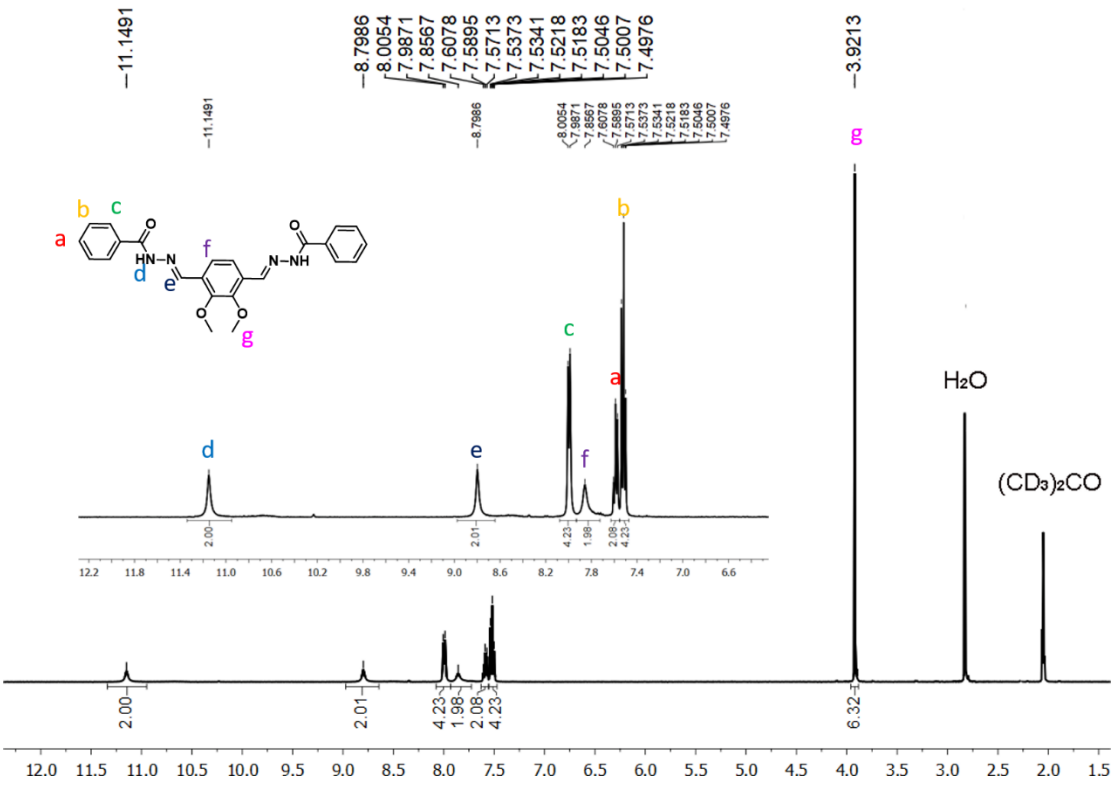



**Figure S21.** $^{1}$H NMR spectrum of **MC2OMe** (400 MHz, $(CD_3)_2CO$).

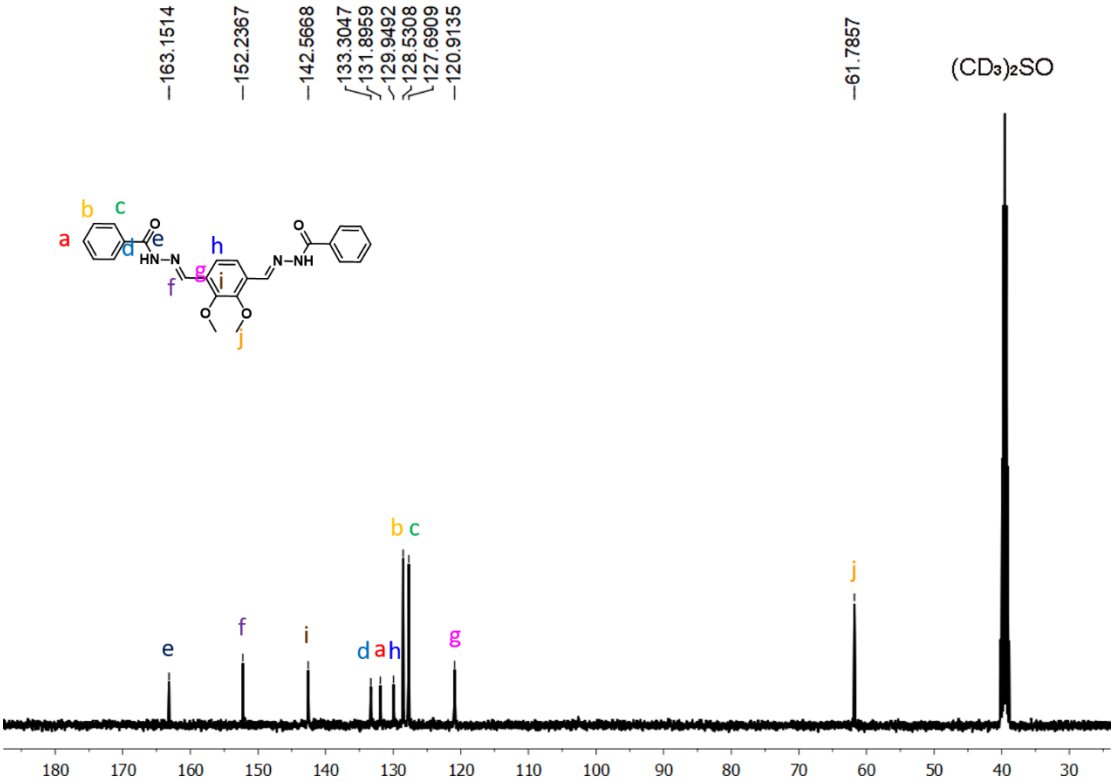



**Figure S22.** $^{13}$C NMR spectrum of **MC2OMe** (100 MHz, $(CD_3)_2SO$).

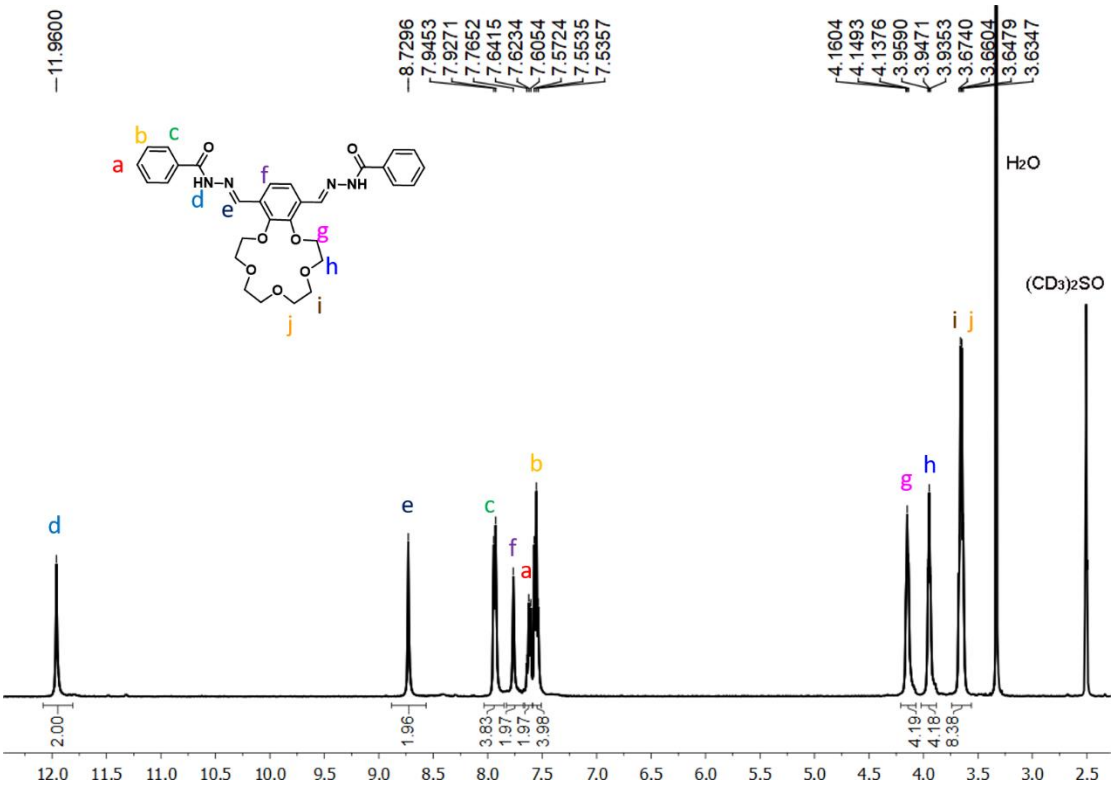



**Figure S23.** $^{1}$H NMR spectrum of **MC15C5** (400 MHz, $(CD_3)_2SO$).

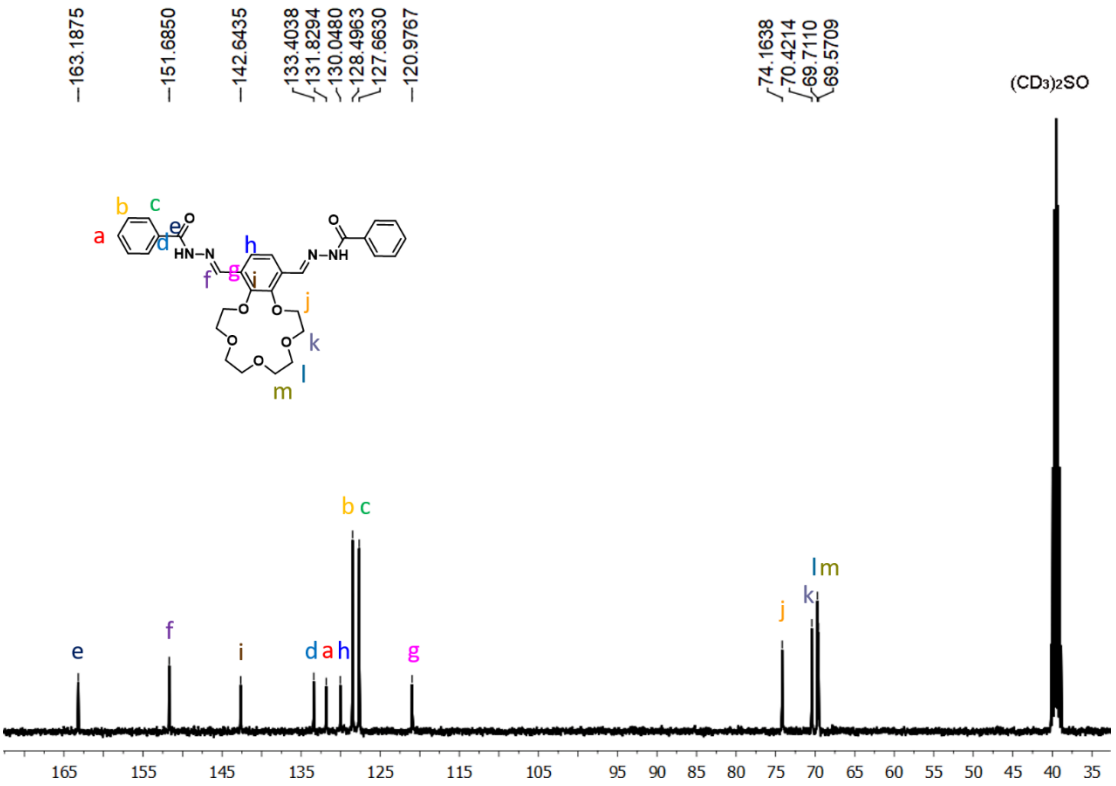



**Figure S24.** $^{13}$C NMR spectrum of **MC15C5** (100 MHz, $(CD_3)_2SO$).

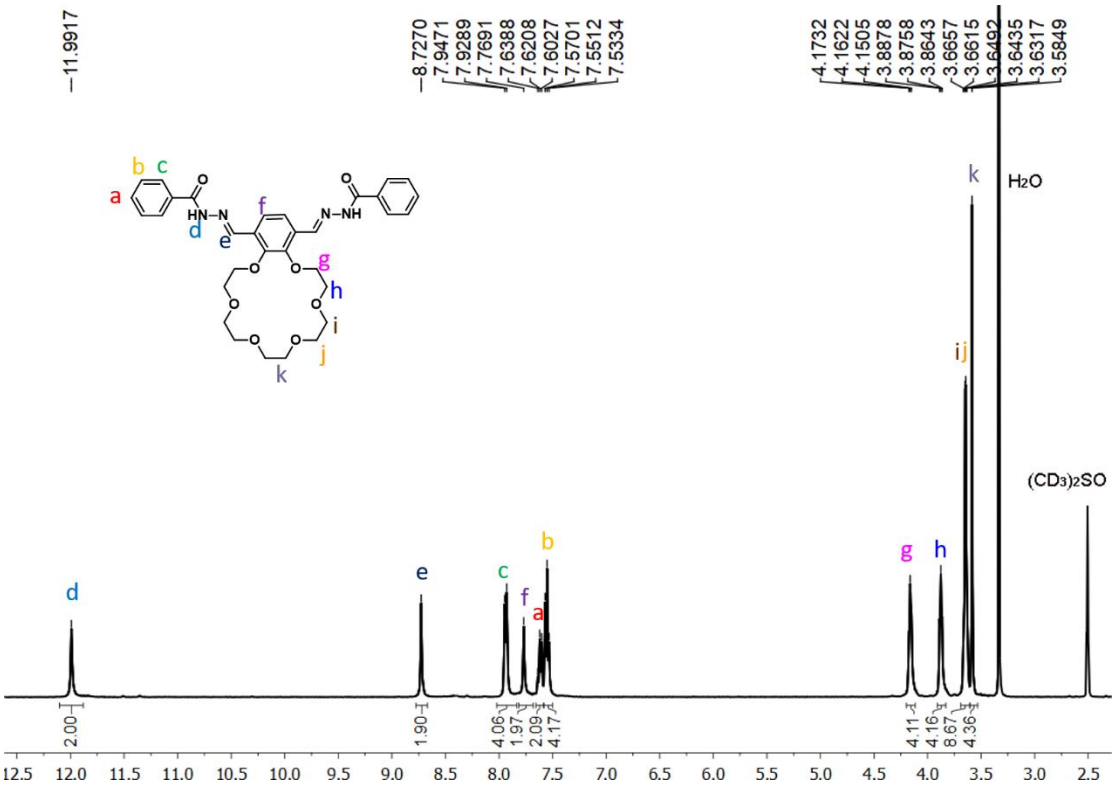



**Figure S25.** $^{1}$H NMR spectrum of **MC18C6** (400 MHz, $(CD_3)_2SO$).

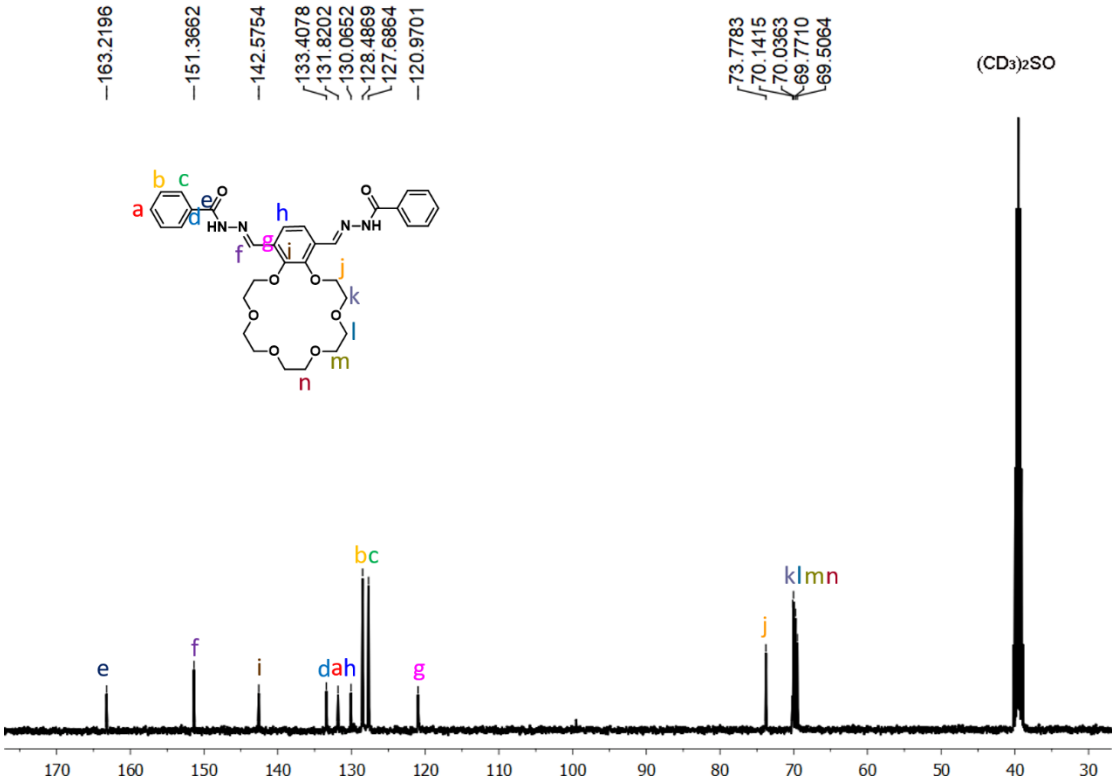



**Figure S26.** $^{13}$C NMR spectrum of **MC18C6** (100 MHz, $(CD_3)_2SO$).

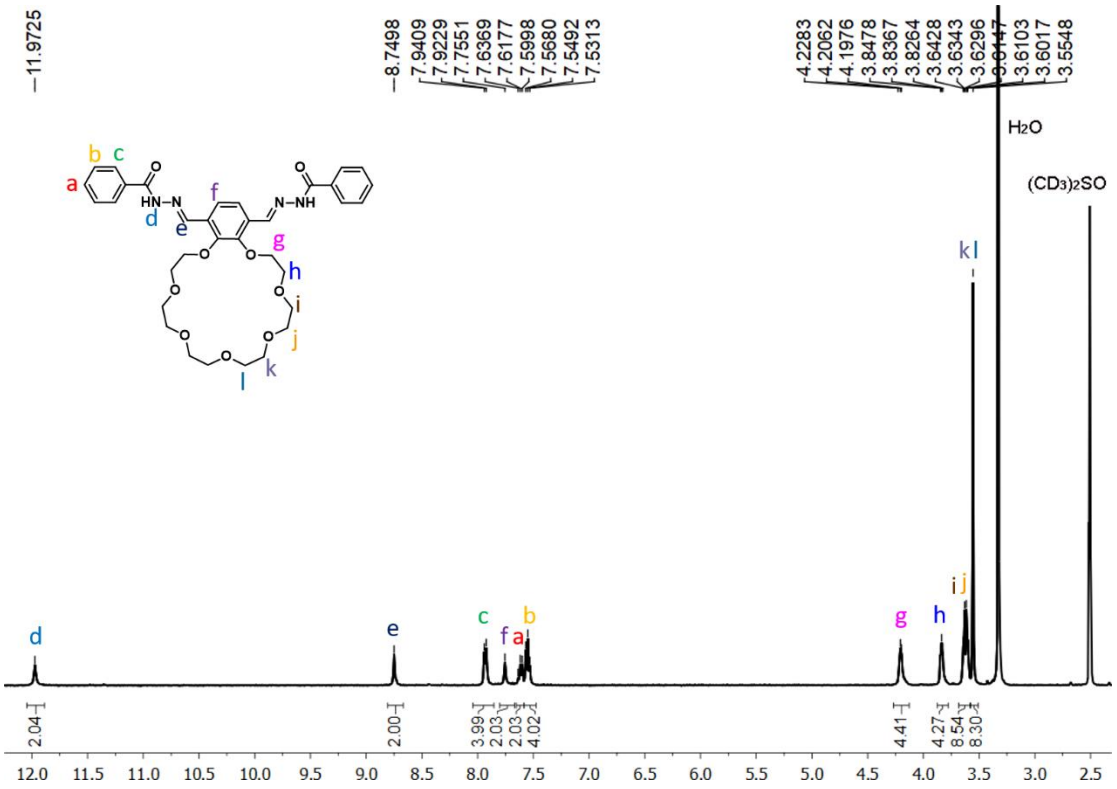



**Figure S27.** $^{1}$H NMR spectrum of **MC21C7** (400 MHz, $(CD_3)_2SO$).

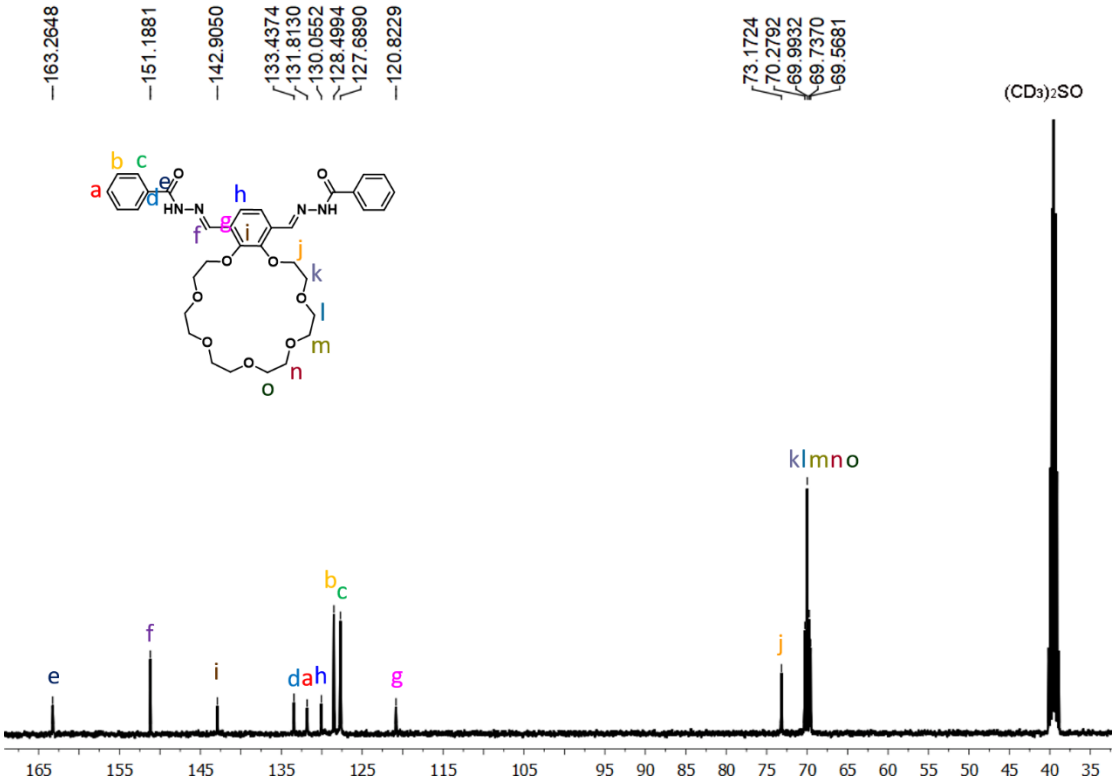



**Figure S28.** $^{13}$C NMR spectrum of **MC21C7** (100 MHz, $(CD_3)_2SO$).

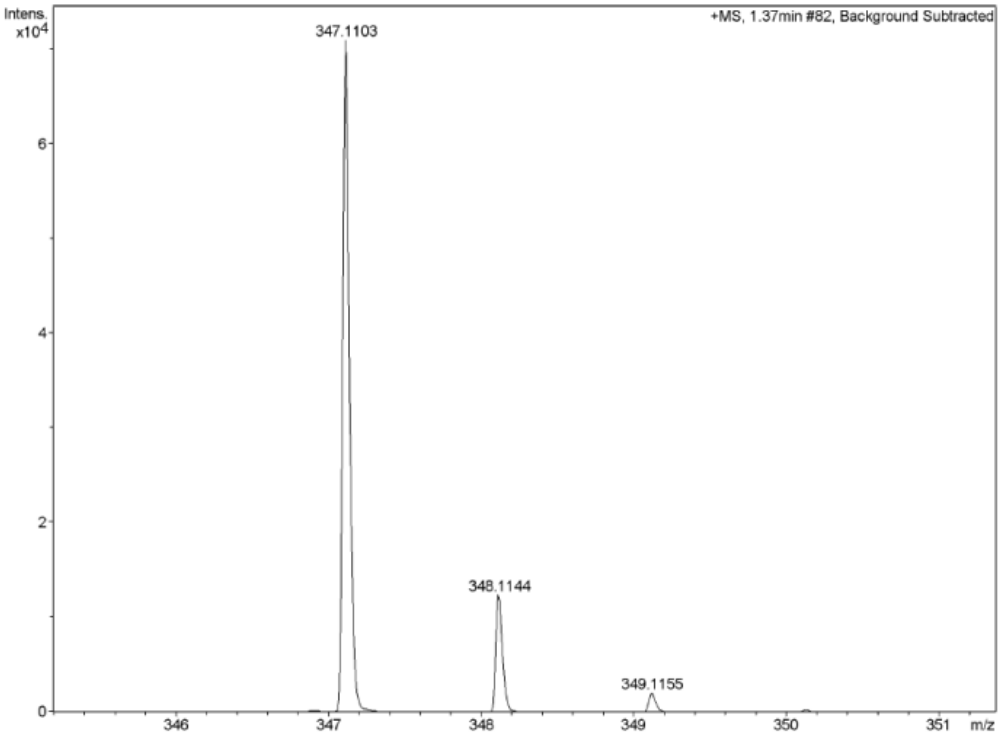



**Figure S29.** HR mass spectrum (ESI) of compound **M15C5**.

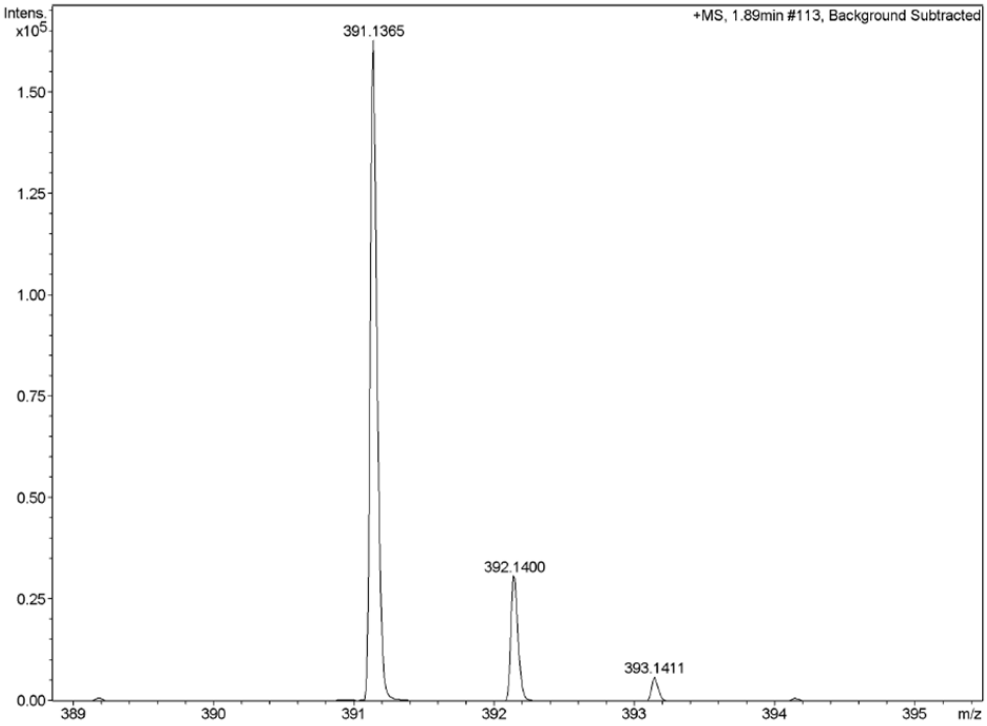



**Figure S30.** HR mass spectrum (ESI) of compound **M18C6**.

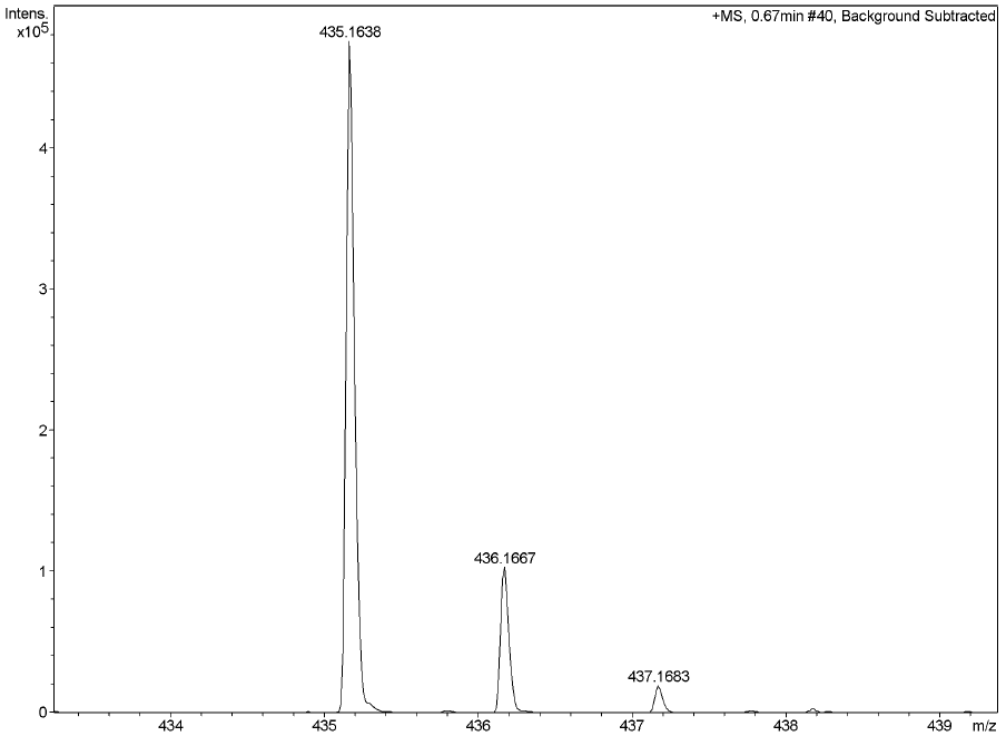



**Figure S31.** HR mass spectrum (ESI) of compound **M21C7**.

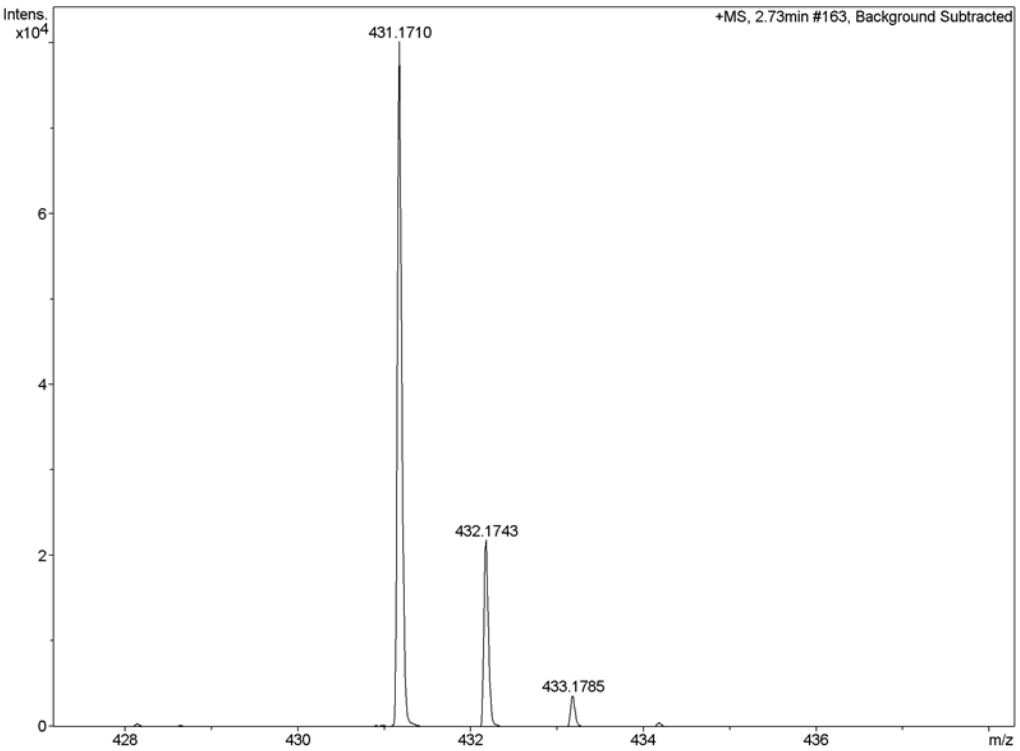



**Figure S32.** HR mass spectrum (ESI) of compound **MC2OMe**.

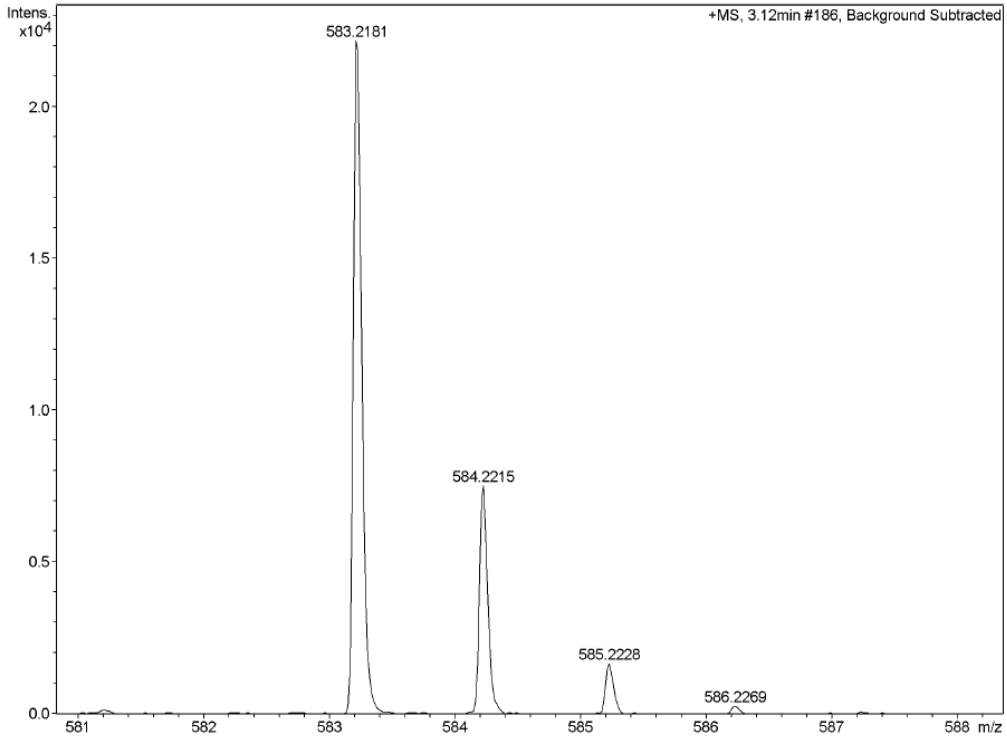



**Figure S33.** HR mass spectrum (ESI) of compound **MC15C5**.

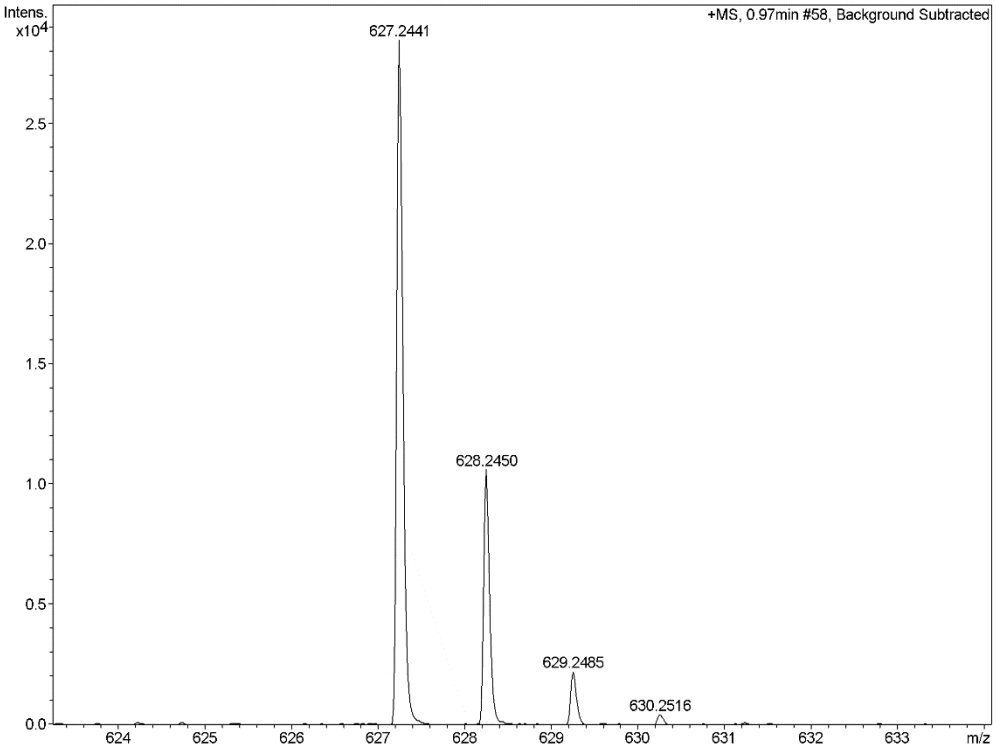



**Figure S34.** HR mass spectrum (ESI) of compound **MC18C6**.

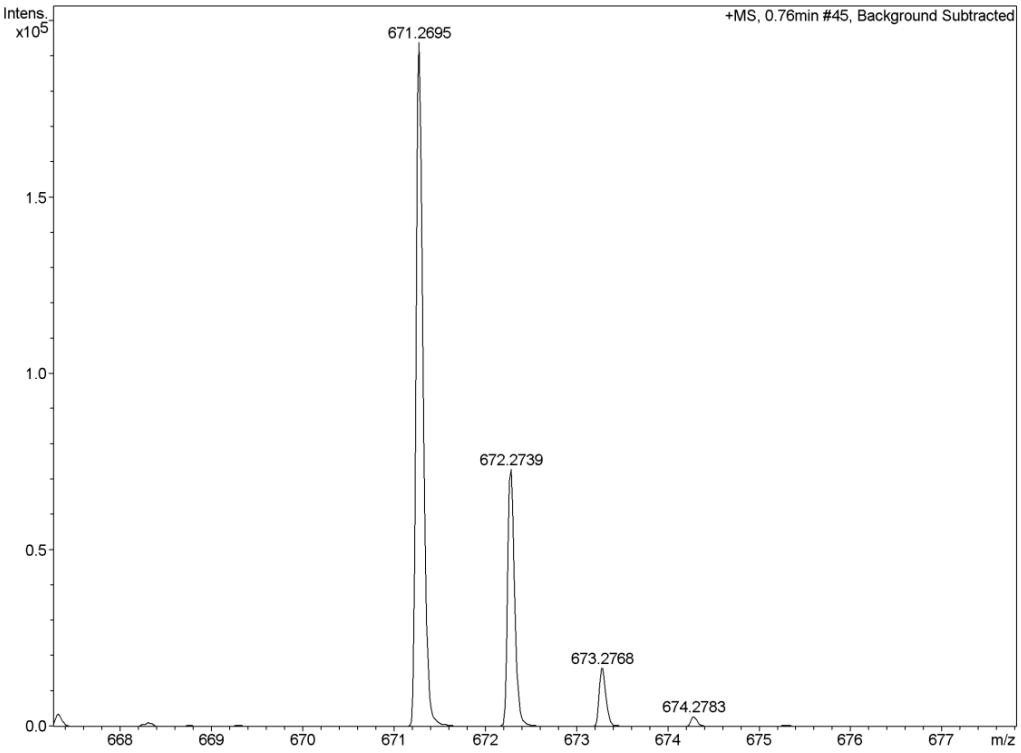



**Figure S35.** HR mass spectrum (ESI) of compound **MC21C7**.

# 12. References

S1. H. Nagae, R. Aoki, S.-n. Akutagawa, J. Kleemann, R. Tagawa, T. Schindler, G. Choi, T. P. Spaniol, H. Tsurugi, J. Okuda and K. Mashima, *Angew. Chem., Int. Ed*., **2018**, 57, 2492–2496.

S2. S. Ito, K. Koizumi, K. Fukuda, N. Kameta, T. Ikeda, T. Oba, K. Hiratani, *Tetrahedron Lett.*, **2006**, 47, 8563 – 8566.