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# I. General

Solvents and commercial starting materials were purchased from Sigma Aldrich, TCI, Fisher Scientific, J&K scientific and abcr GmbH and used as received. Dry solvents were obtained from an MBraun solvent purification system. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel plates (ALUGRAM® Xtra SIL G/UV254, Macherey Nagel) using UV light for detection. Column chromatography was carried out with silica gel (Silica 60 M, 0.04-0.063 mm, Macherey Nagel) using eluents as specified. Flash column chromatography was carried out on a Biotage® Selekt system using the SNAP Sphär60 columns.

**NMR measurements**

NMR spectra were recorded on a Bruker Avance III 300 and a Bruker Avance III 600 spectrometer at 25 °C using residual protonated solvent signals as internal standards for $^{1}$H and $^{13}$C{$^{1}$H} spectra ($^{1}$H: δ($CDCl_3$) = 7.26 ppm; $^{13}$C{$^{1}$H}: δ($CDCl_3$) = 77.16 ppm). Hexafluorobenzene was used as internal standard for $^{19}$F titration spectra ($^{19}$F spectra δ($CDCl_3$) = 0.00 ppm). Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (p), heptet (hept), multiplet (m), and broad (br).

**IR**

Infrared spectra were recorded with a Shimadzu IR Affinity-1 with ATR technique.

**Mass spectrometry (MALDI)**

Matrix-assisted Laser Desorption/Ionization mass spectrometry was performed on a MALDI-TOF/TOF UltrafleXtreme (Bruker Daltonics, Billerica, Massachusetts) using dithranol as matrix.

**Mass spectrometry (CI)**

Samples ionized by chemical ionization were measured using a Finnigan Trace DSQ Single Quadrupole GC/MS by Thermo Fisher Scientific (Waltham, Massachusetts, US). The samples were heated either to 40 °C or to 300 °C.

**Mass spectrometry (ESI)/MS-CID-experiments**

High resolution mass spectra were obtained on an Agilent 6210 ESI-TOF (Agilent Technologies, Santa Clara, CA, USA) using a flow rate of 4 µL/min, a spray voltage of 4 kV and desolvation gas pressure of 15 psi (1 bar). Additional MS measurements and collision-induced dissociation (CID) tandem MS experiments were conducted on a Synapt G2-S HDMS (Waters Co., Milford, MA, USA) with a flow rate of 10 µL/min, a spray voltage of 2.63 kV, source temperature of 80 °C, sample cone voltage of 121 V and source offset of 64 V, respectively. For CID, a nitrogen-containing trap cell was used with collision voltages between 0 and 60 V. All ions were generated by electrospray ionization (ESI) in the positive mode. Samples were sprayed from $CH_2Cl_2/CH_3CN$ (9:1) solutions at concentration of ~10 μM. Host-guest complexes were generated by addition of 20 μL of the corresponding aromatic guest to 1 mL of the 10 μM host solution and subsequent vortexing.

### BET measurements

Initially all samples of **FC1** were subjected to a single point BET surface analysis to check for sufficient porosity allowing a full gas adsorption analysis. These measurements were conducted using a Macsorb HM Model-1210 (Mountech Co., Ltd., Tokio, Japan). The samples were deaerated at 70°C for 1 hour. The consistency of the measurement was ensured by triplicate repetition.

The BET-surface of **FC1** samples, which were identified to be porous via single point BET measurements, was determined via BET-isothermal analysis on a QUANTACHROME Nova 4200e S/N (Quantachrome Instruments, Florida, USA). The samples were evacuated at 80 °C for 16 hours prior to the measurement.

### TGA

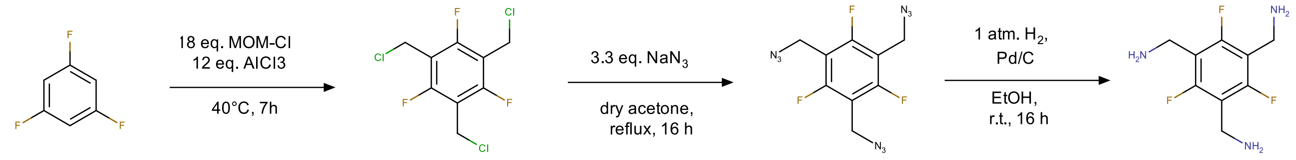
Thermogravimetric analysis was carried out under argon using a PerkinElmer Thermogravimetric Analyzer Pyris 1 in a temperature range from 30 °C to 800 °C at a step rate of 10 °C/min and holding a constant temperature at 800 °C for 5 minutes.

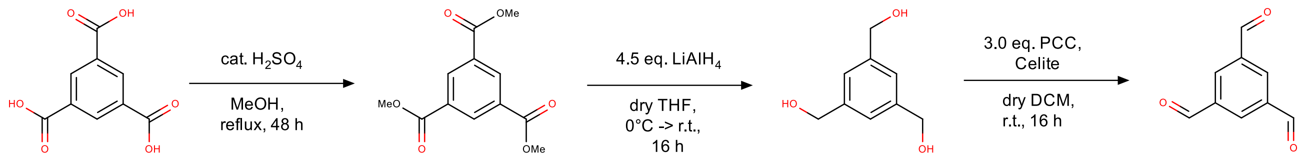
### SEM

Scanning electron microscopy was carried out using a REM Leo 1430 VP, (Carl Zeiss NTS GmbH, Oberkochen, Germany) using 12 kV acceleration voltage. The samples were coated with a monolayer of gold beforehand using an automatic sputter coater from Agar Scientific (Essex, UK).

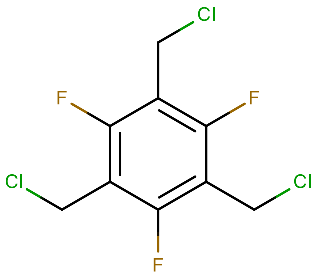
# II. Experimental details

## Synthetic overview





### Synthesis of 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene (3)

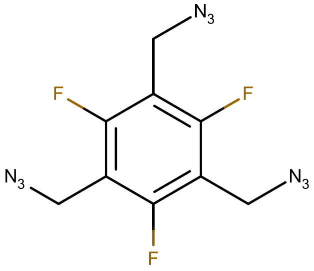


A two-neck round bottomed flask was charged with 1,3,5-trifluorobenzene (2.5 g, 24 mmol) and (chloromethyl)methylether (32.6 g, 430 mmol, 18 eq.) was added. The solution was degassed by bubbling with nitrogen before $AlCl_3$ (38.0 g, 288 mmol, 12 eq.) was added in 6 portions under a continuous nitrogen stream over 30 min at 0 °C. After complete addition of $AlCl_3$, the resulting orange mixture was stirred at 0 °C for 30 min and was then heated to 40 °C for 16 hours under a nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature, was poured onto ice and stirred for two additional hours. The resulting mixture was extracted with dichloromethane (3 x 150 mL). The combined organic phases were neutralized with saturated sodium bicarbonate solution and were dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to give 1,3,5-chloromethyl-2,4,6-trifluorobenzene (**3**) as an off-white solid (5.8 g, 21 mmol, 89% yield).

**$^{1}$H NMR** (300 MHz, $CDCl_3$): $\delta = 4.64$ ppm (s, 6H, C**$H_2$**); **$^{19}$F NMR** (282 MHz, $CDCl_3$): $\delta = -114.57$ ppm (s, 3F, Ar-**F**); **$^{13}$C{$^{1}$H} NMR** (75 MHz, $CDCl_3$) $\delta = 159.51$ (dt, $J = 257.6, 10.4$ Hz, C-**F**), 111.27 (dd, $J =$

24.4, 19.8 Hz, C-C**H$_2$**), 32.03 ppm (s); **IR**: $\tilde{\nu}$ = 3041.7, 2991.6, 2789.1, 1722.4, 1660.7, 1622.1, 1469.8, 1438.9, 1365.6, 1267.2, 1257.6, 1190.1, 1097.5, 995.3, 974.4, 937.4, 787.0, 760.0, 734.9, 713.7, 694.4, 667.4, 638.4, 615.3 cm$^{-1}$; **CI-MS**: [M-Cl+H]$^+$ calc.: 241 m/z; found: 241 m/z. This compound was reported previously.[1]

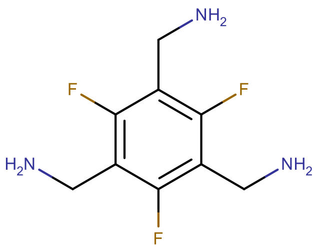
**Synthesis of 1,3,5-tris(azidomethyl)-2,4,6-trifluorobenzene (4)**



A 250 mL round-bottomed flask was charged with 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene (**3**) (5.6 g, 20 mmol) and sodium azide, (4.3 g, 66 mmol, 3.3 eq.) to which 80 mL of dry acetone was added. The resulting suspension was refluxed for 16 hours. The reaction mixture was allowed to cool to room temperature, before dry ethyl ether (80 mL) was added. The mixture was washed with water (3 x 80 mL) and the organic phase was washed with brine, (2 x 50 mL) before it was dried over anhydrous $MgSO_4$. The solvent was evaporated under reduced pressure to yield the azido compound (**4**) as a colourless oil (4.5 g, 15 mmol, 75%).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ = 4.45 ppm (s, 6H, C**H$_2$**); **$^{19}$F NMR** (282 MHz, $CDCl_3$): δ = -114.52 ppm (s, 3F, Ar-**F**); **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) δ = 160.04 (dt, *J* = 254.2, 10.9 Hz), 108.91 (dd, *J* = 25.6, 20.8 Hz), 42.05 – 41.61 ppm (m); **IR**: $\tilde{\nu}$ = 2467.0, 2420.7, 2090.8, 1722.4, 1626.0, 1467.8, 1450.5, 1342.5, 1251.8, 1219.0, 1097.5, 1008.8, 881.5, 858.3, 779.2, 752.2, 715. 6, 640.4, 625.0, 603.7 cm$^{-1}$; due to the very labile nature of triazide **4**, high-resolution MS data could not be obtained, ionization by different techniques led to unspecific fragments; **CI-MS**: [M-$N_3$+H]$^+$ calc.: 255 m/z; found: 255 m/z.

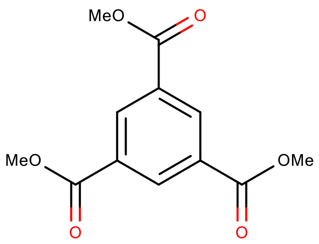
### Synthesis of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene (2)



In a 250 mL Schlenk flask 1,3,5-tris(azidomethyl)-2,4,6-trifluorobenzene (**4**) (2.4 g, 8.0 mmol) was dissolved in 100 mL absolute ethanol. To this solution 300 mg of palladium on carbon (10 w%) were added. The atmosphere inside the flask was exchanged with hydrogen gas twice before it was stirred for four hours under 1 bar of hydrogen gas. The resulting suspension was filtered through two filter papers and the solvent was evaporated under reduced pressure to give 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene (**2**) as an off-white hygroscopic solid (1.5 g, 6.8 mmol, 85%).

**$^1$H NMR** (300 MHz, $CDCl_3$) $\delta = 3.89$ (s, 6H, $\mathrm{C}\mathbf{H}_2$), 1.45 ppm (broad s, 6H, $\mathrm{N}\mathbf{H}_2$); **$^{19}$F NMR** (282 MHz, $CDCl_3$) $\delta = -123.61$ ppm (s, 3F, Ar-**F**); **$^{13}$C{$^1$H} NMR** (75 MHz, $CDCl_3$) $\delta = 158.4$ (dt, $J = 246.1, 12.1$ Hz, C3), 115.6 - 115.0 (m, C2), 34.3 ppm (s, C1); **IR**: $\tilde{\nu} = 3361.3$, 3289.4, 2951.5, 2885.0, 2667.1, 1621.8, 1457.0, 1383.7, 1312.3, 1170.6, 1089.6, 913.1, 821.5, 744.4, 622.9, 607.5, 537.1, 520.7 cm$^{-1}$; **ESI-HRMS**: calc. $[C_9H_{12}F_3N_3 + H]^+ = 220.1056$ m/z, found: 220.1059 m/z;

### Synthesis of trimethylbenzene-1,3,5-tricarboxylate (5)

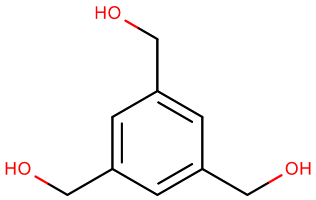


Benzene-1,3,5-tricarboxylic acid (10.00 g, 47.59 mmol) was suspended in a mixture of 150 mL methanol and concentrated sulfuric acid (3.1 mL, 58.16 mmol, 1.2 eq.) and heated to 60 °C for 21 hours. The suspension was allowed to cool to room temperature and saturated sodium hydrogen carbonate solution was added slowly. The mixture was filtered and the residue was washed with 150 mL water while the filtrate was extracted with diethyl ether (2 x 100 mL). The combined organic phases were dried over $Na_2SO_4$. The precipitate and the organic phase were combined and the solvent was removed under reduced pressure to give trimethyl-1,3,5-benzenetricarboxylate (**5**) as a colourless solid (11.26 g, 44.74 mmol, 94 %).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ = 8.86 (s, 3H, Ar-**H**), 3.98 ppm (s, 9H, C**$H_3$**-O).

This compound was reported previously.[2]

**Synthesis of 1,3,5-tris(hydroxymethyl)benzene (6)**

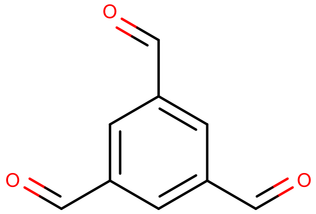


Trimethyl-1,3,5-benzenetricarboxylate (**5**) (10.57 g, 41.9 mmol) in 170 mL dry THF was added dropwise to a suspension of $LiAlH_4$ (7.10 g, 187.1 mmol, 4.5 eq.) in 80 mL dry THF at 0 °C. After addition, the mixture was allowed to warm to room temperature while stirring for 14 hours under a nitrogen atmosphere. 100 g of a 1:1 mixture of Celite and $NaHSO_4$ were added in small portions. At 0 °C, 7 mL water and 7 mL 15 % NaOH solution were added dropwise. The mixture was diluted with THF and filtered and the residue was washed with diethyl ether. The solvent was removed under reduced pressure yielding 1,3,5-tris(hydroxymethyl)benzene (**6**) as a pale-yellow solid (6.49 g, 38.6 mmol, 92 %).

**$^1$H NMR** (300 MHz, $D_2O$): δ = 7.32 (s, 3H, Ar-**H**), 4.65 ppm (s, 6H, C**$H_2$**).

This compound was reported previously.[2]

**Synthesis of 1,3,5-triformylbenzene (1)**



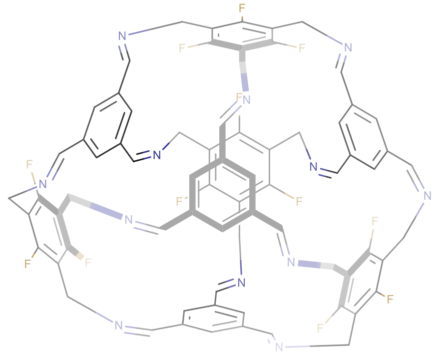
1,3,5-tris(hydroxymethyl)benzene (**6**) (4.082 g, 24.27 mmol) was suspended in 240 mL $CH_2Cl_2$. 7.5 g Celite were added and the suspension was stirred for 15 minutes. PCC (15.70 g, 72.81 mmol, 3.0 eq.) was added and the mixture was stirred overnight. The reaction mixture was diluted with diethyl ether (80 mL) and stirred for another 30 minutes. The precipitate was filtered off. The residue was extracted with $CH_2Cl_2$. The solvent was removed under reduced pressure. The crude product was dissolved in $CH_2Cl_2$

and filtered over silica gel to give 1,3,5-triformylbenzene (**1**) as a colourless solid (3.402 g, 20.87 mmol, (86 %).

**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ = 10.21 (s, 3H, C**H**O), 8.64 ppm (s, 3H, Ar-**H**).

This compound was reported previously.[3]

### Synthesis of [4+4] imine-cages FC1



**Method A:**

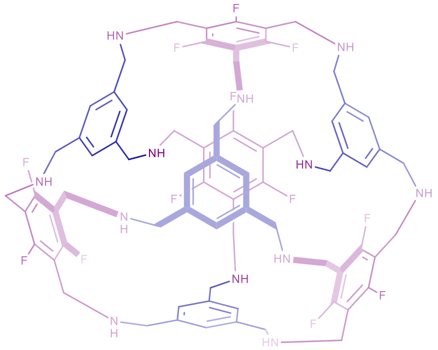
1,3,5-triformylbenzene (**1**) (104 mg, 6.4 mmol, 0.8 eq.) was dissolved in 100 mL of dry methanol inside a 250 mL round bottomed flask. A solution of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene (**2**) (175 mg, 8.0 mmol, 1.0 eq.) in 100 mL dry methanol was added dropwise over the period of one hour. The resulting solution was stirred for two days at room temperature. The resulting precipitate was filtered off and washed with 50 mL of cold methanol to give the [4+4] imine cage **FC1** as a white solid (200 mg, 1.5 mmol, 95%).

**Method B:**

1,3,5-Triformylbenzene (**1**) (104 mg, 6.4 mmol, 0.8 eq.) was dissolved in 100 mL of DCM/methanol 3:1 inside a 250 mL Erlenmeyer flask. A solution of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene **(2)** (175 mg, 8.0 mmol, 1.0 eq.) in 100 mL DCM/methanol 3:1 was carefully layered on top of the formylbenzene **1** solution. The resulting bi-layered solution was left standing without stirring for three days. The resulting precipitate was filtered off and washed with cold methanol (50 mL) to yield the [4+4] imine cage **FC1** as transparent thin needles (140 mg, 1.1 mmol, 67%).

**$^{1}$H NMR** (300 MHz, $CDCl_3$): δ = 8.37 (s, 12H, Ar-**H**), 7.97 (s, 12H, C**H**N), 4.76 ppm (s, 24H, C**$H_2$**-N); **$^{19}$F NMR** (282 MHz, $CDCl_3$): δ = -119.17 ppm (s, 12F, Ar-**F**); due to the poor solubility of **FC1** no $^{13}C\{^{1}H\}$ could be obtained, we provided an elemental analysis additionally; **IR**: $\tilde{\nu}$ = 2987.7, 2968.5, 2868.2, 1672.3, 1643.4, 1624.1, 1464.0, 1452.0, 1388.8, 1365.6 1330.9, 1253.7, 1224.8, 1149.6, 1041.6, 1018.4, 993.3, 970.2, 891.1, 866.0, 702.1, 684.7, 655.8, 611.4 $cm^{-1}$; **ESI-HRMS**: calc. $[C_{72}H_{48}F_{12}N_{12} + H]^+$ = 1309.4006 m/z, found: 1309.3985 m/z; **Anal. Calcd.** for $C_{72}H_{48}F_{12}N_{12}$ x 4.5 $H_2O$: C: 62.20, H: 4.13, N: 12.09; found: C: 62.36, H: 4.30, N: 12.41.

### Reduction of [4+4] imine cage, FC1$_L$



Cage **FC1** (100 mg, 0.80 mmol) was suspended in 200 mL of methanol and sodium borohydride (500 mg, excess) was added in portions at room temperature. After one hour, the reaction mixture was heated to reflux and more sodium borohydride (300 mg) was added. The resulting mixture was refluxed for two days. After allowing the mixture to cool to room temperature, the solvent was evaporated and the residue was taken up with 100 mL of 2M HCl and made basic with 4M KOH again. The aqueous phase was extracted with DCM (3 x 100mL) and the combined organic phases were dried over $MgSO_4$. The solvent was evaporated under reduced pressure to yield the locked cage **FC1$_L$** as a white solid (24 mg, 0.18 mmol, 23% yield).

**$^1$H NMR** (300 MHz, $CDCl_3$): δ = 6.98 (s, 12H, Ar-**H**), 3.82 - 3.64 (m, 48H, C**$H_2$**-$NH_2$-C**$H_2$**), 1.58 ppm (br s, 24H, N**$H_2$**); **$^{19}$F NMR** (282 MHz, $CDCl_3$): δ = -120.65 ppm (s, 12F, Ar-**F**); Due to the low solubility of the compound sufficient $^{13}$C NMR data could not be obtained. **FT-IR (ATR):** $\tilde{v}(cm^{-1})$ = 2989.7, 2968.5, 2953.02, 2900.9, 2881.7, 2866.2, 2850.8, 2833.4, 1726.3, 1668.43, 1622.1, 1600.9, 1504.5, 1452.4, 1444.7, 1363.7, 1325.1, 1317.4, 1236.4, 1220.94, 1192.01, 1157.29, 1097.5, 1089.8, 1057.0, 995.3, 925.8, 854.5, 841.0, 748.4, 731.0, 719.5, 663.5, 619.2, 607.6; **ESI-HRMS**: calc. $[C_{72}H_{48}F_{12}N_{12} + 3H]^{3+}$ = 445.2010 m/z, found: 445.2007 m/z; calc. $[C_{72}H_{48}F_{12}N_{12} + 2H]^{2+}$ = 667.2978 m/z, found: 667.2968 m/z.

## III. DOSY experiments

DOSY NMR experiments were recorded at 298 K and calibrated using known self-diffusion values for the solvents used ($D_{solv}$).[4] The hydrodynamic radii were estimated using the unmodified Stokes-Einstein-equation. This equation was solved for $r_H$ using values for $\eta$ from the literature.[5]

$$D = \frac{k_B T}{6\pi\eta r_H}$$

| | |
|---|---|
| $D$ | is the measured diffusion coefficient ($m^2\ s^{-1}$) |
| $k_B$ | is the Boltzmann constant ($1.3806485 * 10^{-23}\ m^2\ kg\ s^{-2}\ K^{-1}$) |
| $T$ | is the temperature (K) |
| $r_H$ | is the hydrodynamic radius of the analyte (m) |
| $\eta$ | is the viscosity of the solvent at temperature T ($kg\ m^{-1}\ s^{-1}$) |

The hydrodynamic radii were estimated to be $r_H = 0.71$ nm for **FC1** and $r_H = 0.76$ nm for **FC1$_L$** respectively.

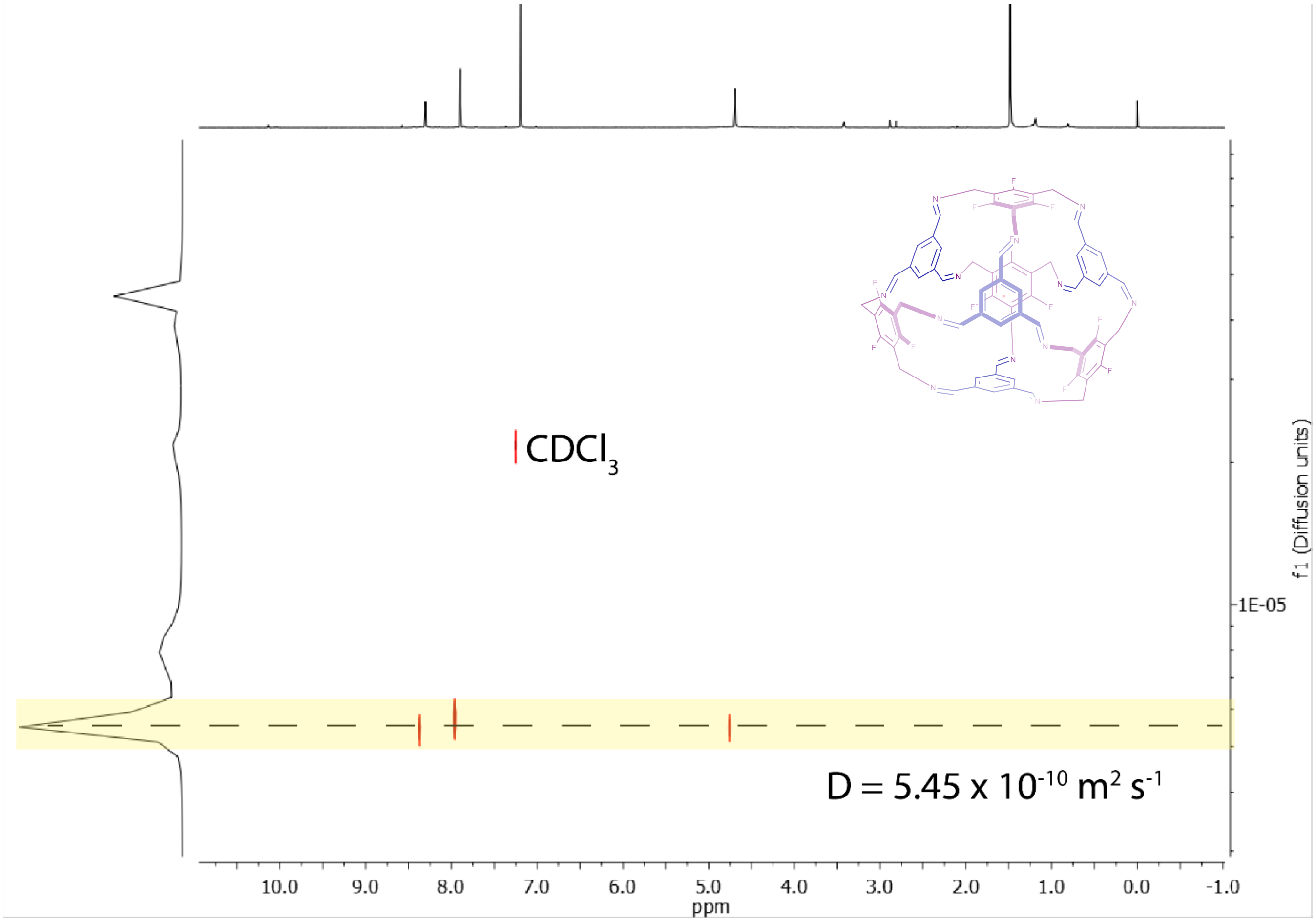


**Figure S1:** DOSY NMR spectrum (600 MHz, CDCl$_3$, 298 K) of **FC1**.

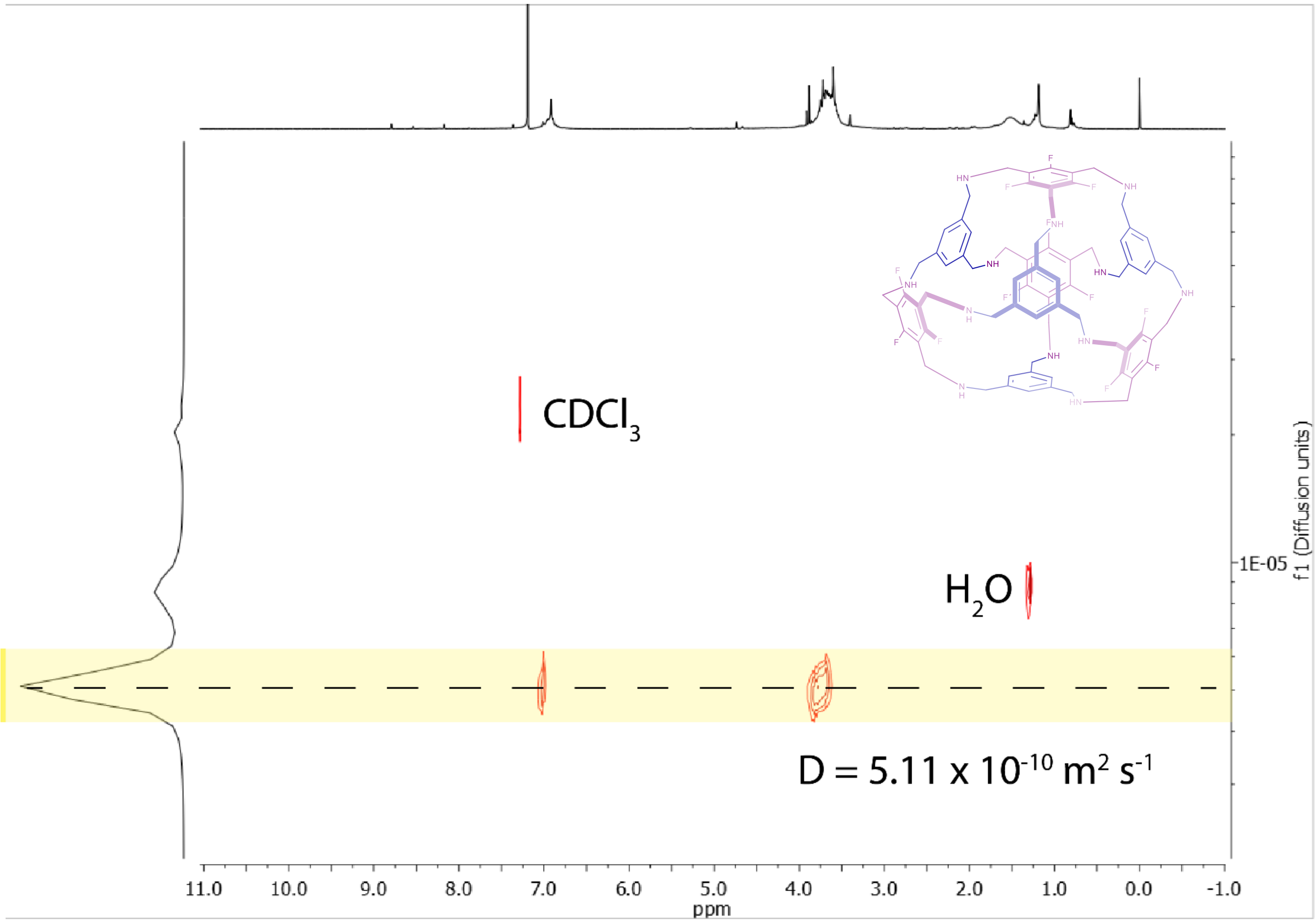


**Figure S2:** DOSY NMR spectrum (600 MHz, $CDCl_3$, 298 K) of **FC1$_L$**. The hydrodynamic radius of **FC1** is comparable to structurally similar [4+4]-cages previously reported in the literature.[3]

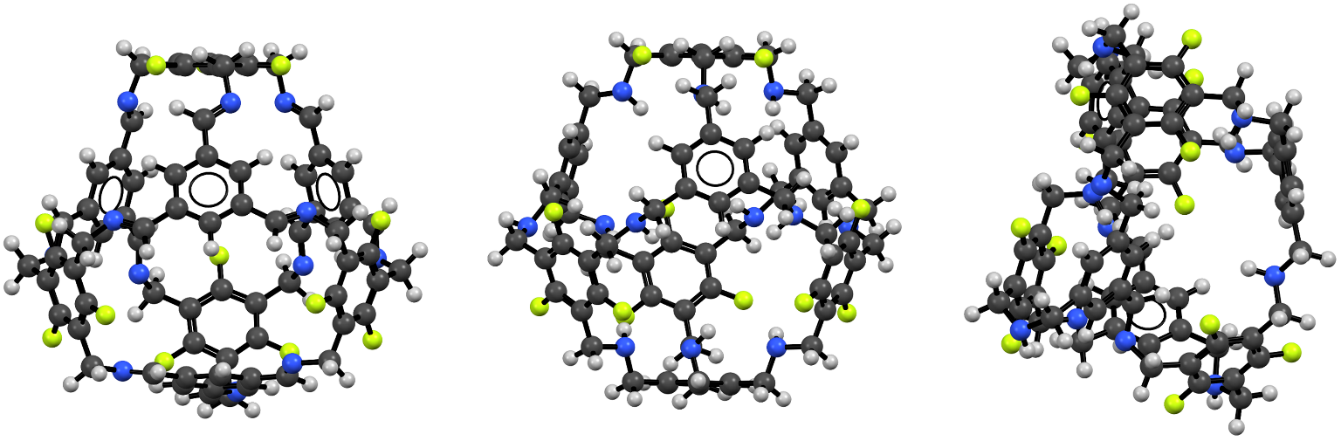
**Table S1**: Hydrodynamic radii of different structurally related [4+4]-imine cages.

| | **FC1** | **3-Et-Et** | **3-Et-H** |
|---|---|---|---|
| **hydrodynamic radius $r_H$ (nm)** | 0.71 | 0.89 | 0.87 |

The hydrodynamic radius is lower for **FC1** because of the missing bulky substituents that are required for the synthesis of the **3-Et-Et** and **3-Et-H** cages.

## IV. Computational details

Quantum mechanical calculations were performed by applying density functional theory All geometry optimizations were performed with the Gaussian16 program.[11] Geometries were optimized using first B3LYP, followed by M062X functionals and the def2-TZVP basis set for H, C, N and F atoms. Stationary points were characterized by vibrational analyses. Figure **S3** gives an overview of all optimized structures. The geometries are nearly equivalent for B3LYP and M062X, therefore only M062X-optimized ones are shown.



**FC1** -4627.556679 Hartree

**FC1$_{\mathrm{Lpuffy}}$** -4642,071543 Hartree

**FC1$_{\mathrm{Lcollapsed}}$** -4642,085841 Hartree

**Figure S3:** DFT-optimized geometries of **FC1**, **FC1$_{\mathrm{Lpuffy}}$** and **FC1$_{\mathrm{Lcollapsed}}$** (from left to right) using M062X/def2-TZVP level of theory. The collapsed geometry of **FC1$_{\mathrm{L}}$** is more stable than the puffy geometry of **FC1$_{\mathrm{L}}$** by 9.6 kcal mol$^{-1}$.

## MM2 calculations

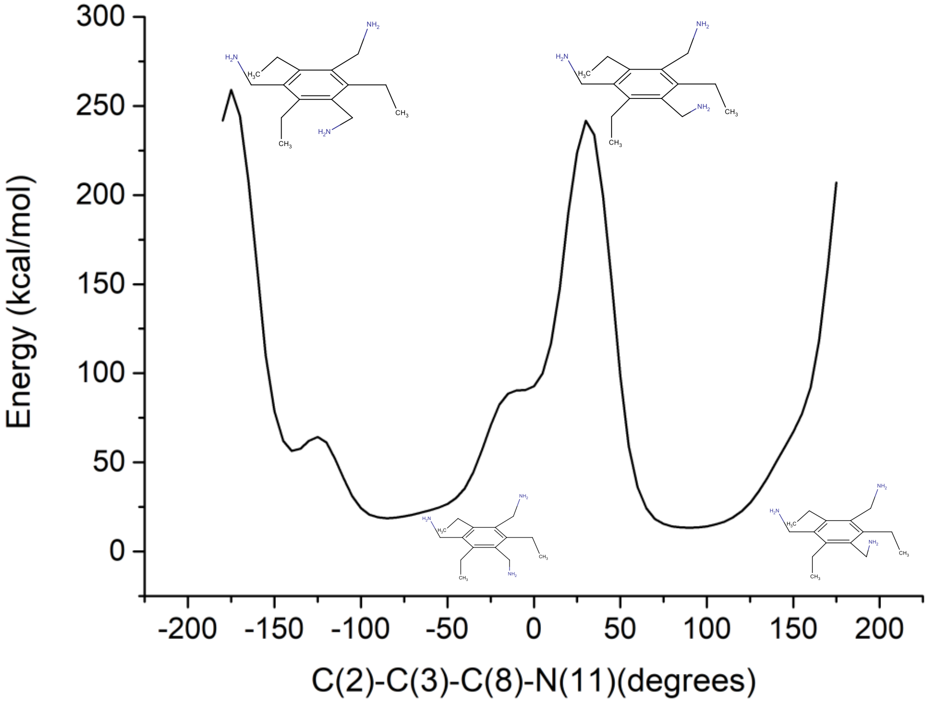


**Figure S4:** Energy plot of the rotation around the $C_{sp2}$-$C_{sp3}$-bond of an aminomethyl substituent of 1,3,5-triethyl-2,4,6-tris(aminomethyl)benzene (MM2 calculation).

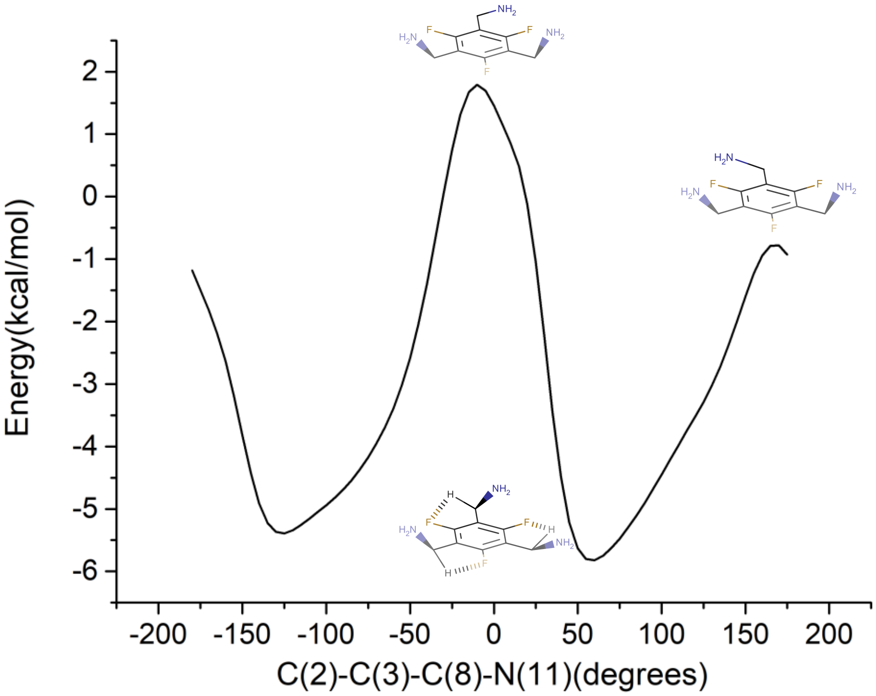


**Figure S5:** Rotational energy around the $C_{sp2}$-$C_{sp3}$-bond of an aminomethyl substituent of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene (**2**) (MM2 calculations).

## V. Thermogravimetrical analysis

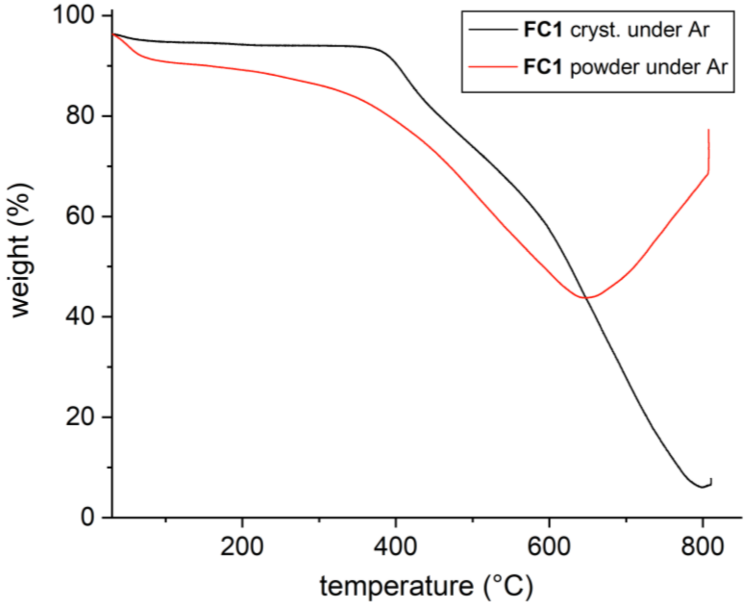


**Figure S6:** Thermogravimetric curves of a crystalline sample of **FC1** (black line) and of a powdered sample of **FC1** (red line). The initial dip in the red curve stems from remaining moisture, even though the sample was previously evacuated at 40 °C and $10^{-2}$ mbar for 24 hours. The increase in weight starting at about 680 °C is caused by a corrosion of the instruments by release of HF due to the moisture in the gas flow. Onset decomposing temperatures are 361.5 °C (powdered **FC1**) and 373.1 °C (crystalline **FC1**).

# VI. Gas adsorption analysis

**Table S2:** Gas uptake of differently processed samples of **FC1**.

| Gas | **FC1** (cryst.) | | **FC1** (powder) | |
|---|---|---|---|---|
| | uptake (mmol/g) | in weight % | uptake (mmol/g) | in weight % |
| $N_2$ | 7.6 | 22.14 | 6.8 | 19.10 |
| $H_2$ | 7.5 | 1.51 | 5.4 | 11.42 |
| $CO_2$ | 4.2 | 18.98 | 2.6 | 1.06 |

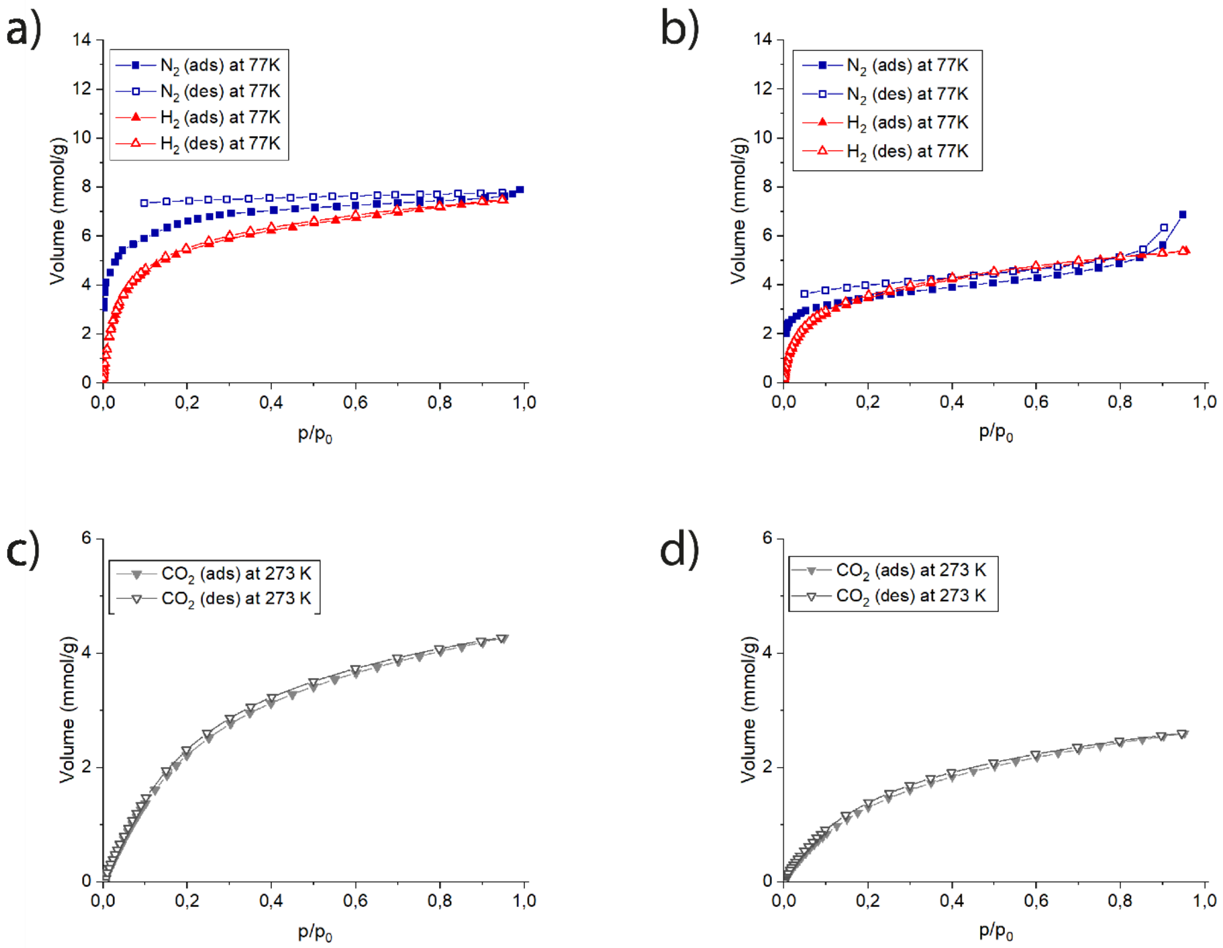


**Figure S7:** a) adsorption (solid symbol) and desorption (hollow symbol) of nitrogen (blue) and hydrogen (red) for a crystalline **FC1** sample; b) adsorption (solid symbol) and desorption (hollow symbol) of nitrogen (blue) and hydrogen (red) for a powdered **FC1** sample; c) adsorption (solid symbol) and desorption (hollow symbol) for carbon dioxide of a crystalline **FC1** sample; d) adsorption (solid symbol) and desorption (hollow symbol) for carbon dioxide of a powdered **FC1** sample.

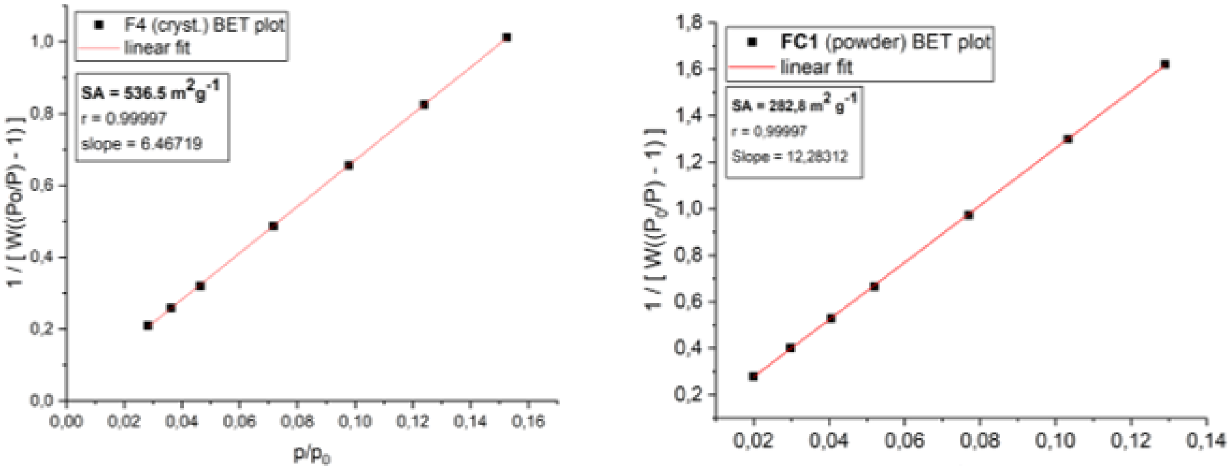


**Figure S8:** BET plots of a crystalline (left) and a powdered (right) **FC1** sample.

## VII. Crystallographic details

Single crystals used directly as obtained from the synthetic mixture were mounted using a microfabricated polymer film crystal-mounting tool (dual-thickness MicroMount, MiTeGen) using low viscosity oil perfluoropolyether PFO-XR75 to reduce the X-ray absorption and scattering. A data set of a colourless needle with dimensions of 157.0 x 34.0 x 33.4 µm of **FC1** was collected at the P11 beamline at PETRA III, DESY[6,7] in August 2019 with a wavelength of 0.619900 Å and a PILATUS detector, using P11 Crystallography Control GUI at 200(2) K. Initial data reduction was carried out using XDS (V. 1 Nov 2016). The structure was then refined by full-matrix least-squares methods on $F^2$ (SHELXL-2014).[8-10] The hydrogen atoms were placed at calculated positions and refined by using a riding model.

Because of the inherent difficulty to obtain a suitable data set, hampered by disorder of the imine bonds, disordered solvents within the cavities and poor diffraction phenomena, it was decided together with the crystallographic expert team of the Max-Planck-Institut für Kohlenforschung not to submit the data set to the Cambridge Crystallographic Data Centre, therefore neither the CCDC number nor checkcif is supplied with this supporting material. It is of course available from the author by request, as is the raw data.

The structure was refined using (geometrical) constraints including simu, delu, isor, dfix and affix 66 for parts of the **FC1** cage. Imine bonds show disorder to some extent, which was treated with fvar refinement, if sufficient electron density was present. Inside the cavity, neither chloroform nor methanol molecules could be located from the electron density map. The cavities are filled with partially or completely disorded solvent, which were not removed using SQUEEZE but refined as oxygen atoms to remove electron density from system and enable further cage refinement. This is common for large supramolecular systems and sufficient to discuss cage geometry and packing within the crystal but no bond length or intermolecular contacts are given.

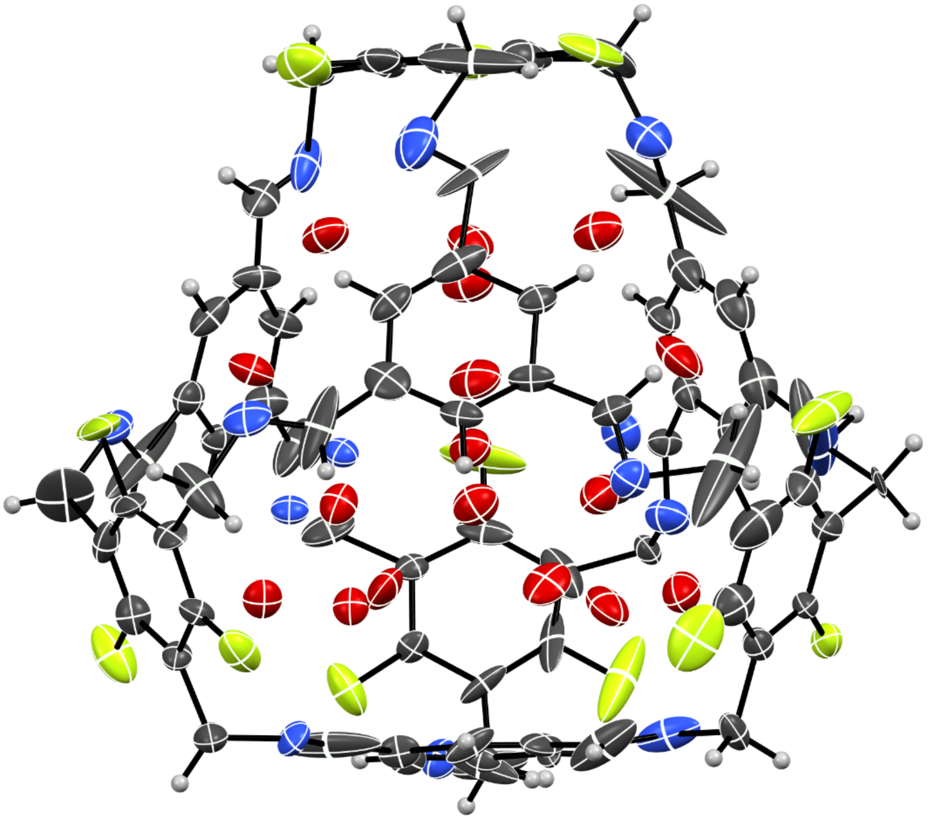


**Figure S9:** Synchrotron data set of **FC1** showing the asymmetric unit with thermal ellipsoids set at 50% probability. The structure was measured at 200 K and solved in the monoclinic space group $P2_1$ with $R_{Int} = 0.0693$, $R_1 = 0.2287$ and $wR_2 = 0.5134$. The structure shows various C-H···F contacts between alternating hydrogenated and fluorinated ports of the windows.

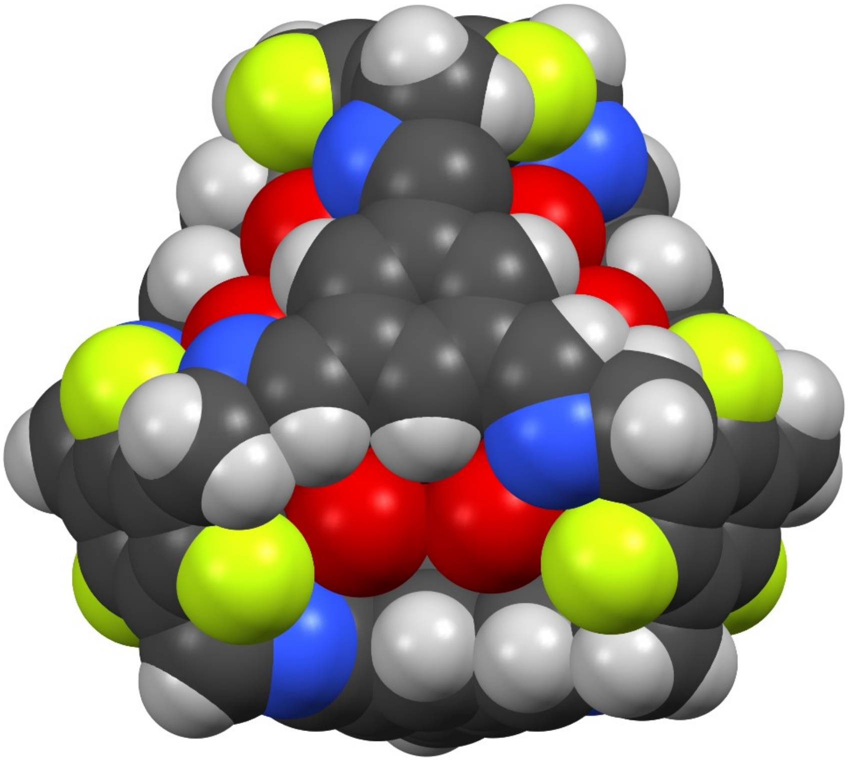


**Figure S10:** Asymmetric unit of **FC1** showing the asymmetric unit with a space-filling representation.

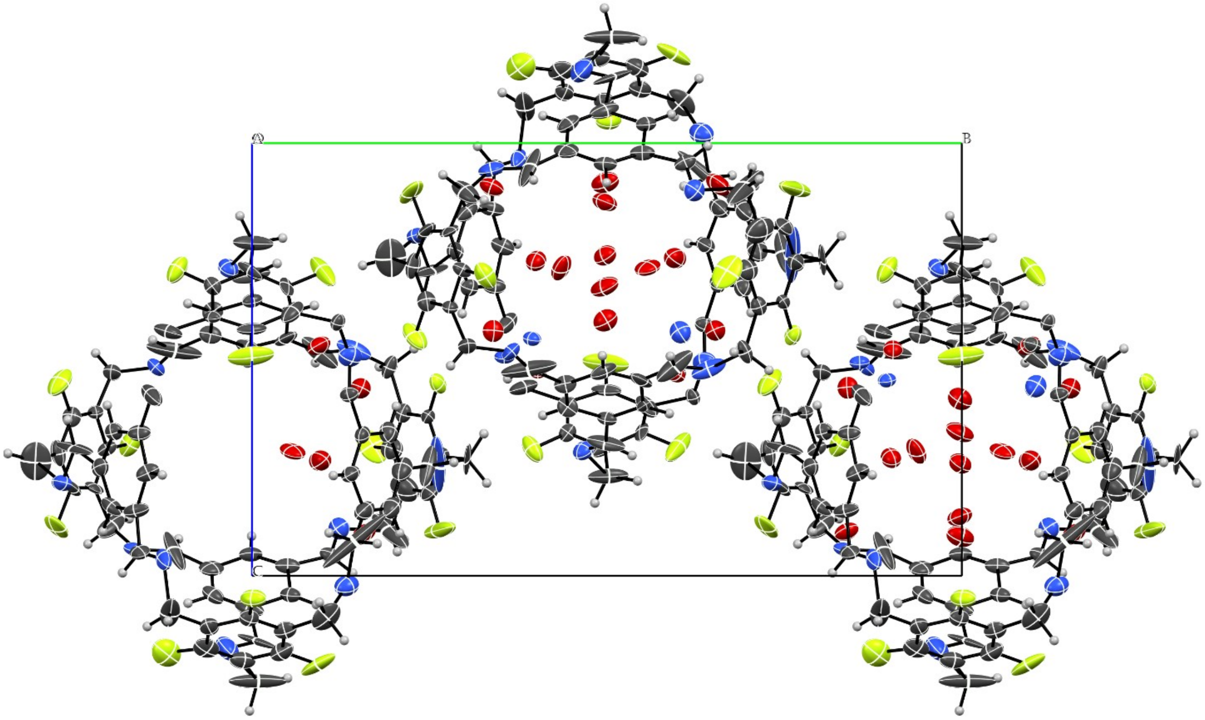


**Figure S11:** View of the unit cell of **FC1** along the crystallographic *a* axis. The infinite pores along the cages can be clearly seen.

## PXRD

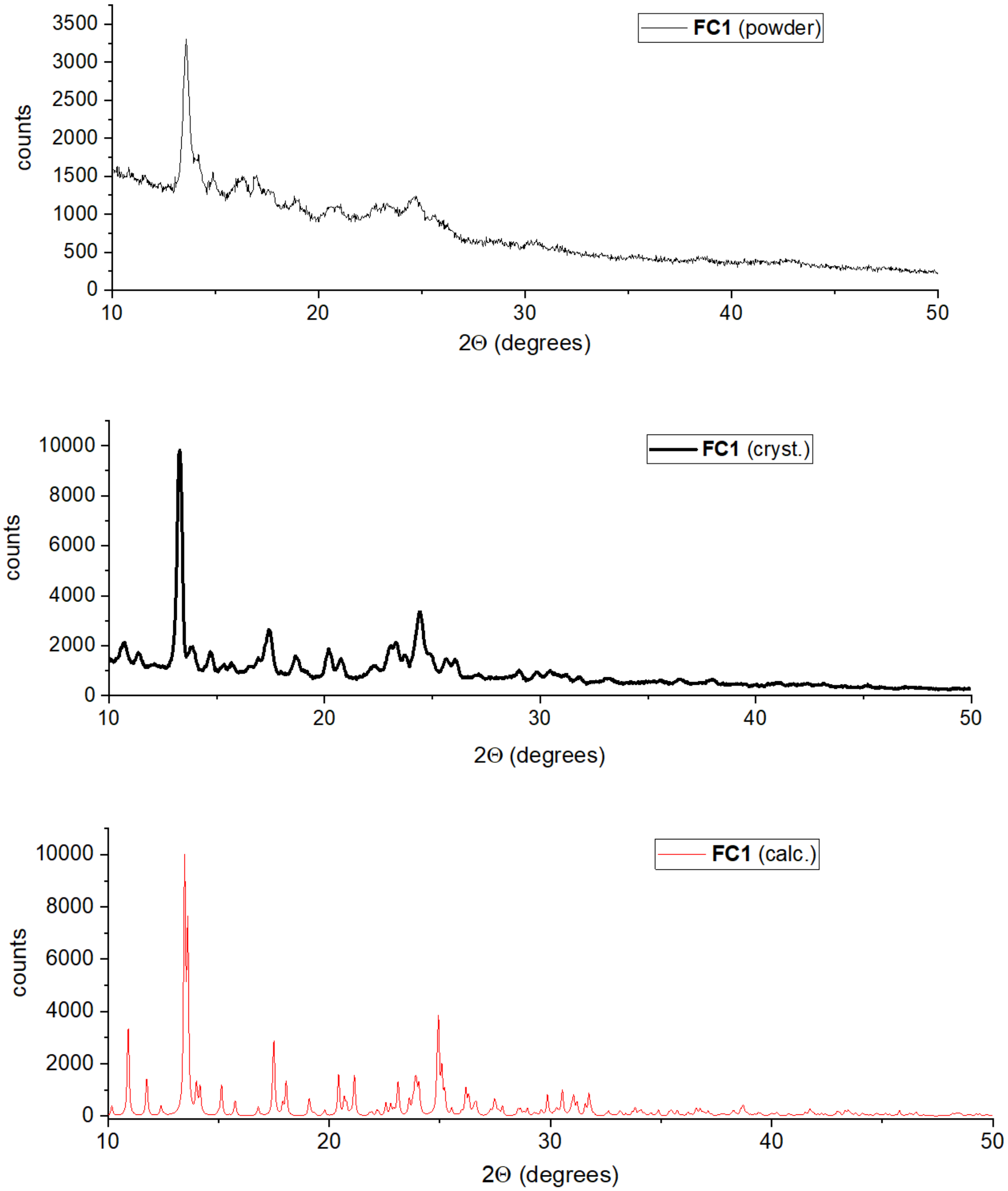


**Figure S12:** Powder XRD spectra of a powder (top) and crystalline (middle) **FC1** sample. The spectra at the bottom was calculated from the single-crystal XRD data and is in good agreement with the crystalline sample. As can be seen by the broader signals and the noise in the spectrum in the top the crystallinity of the powdered sample is the lowest.

# VIII. MS and CID experiments

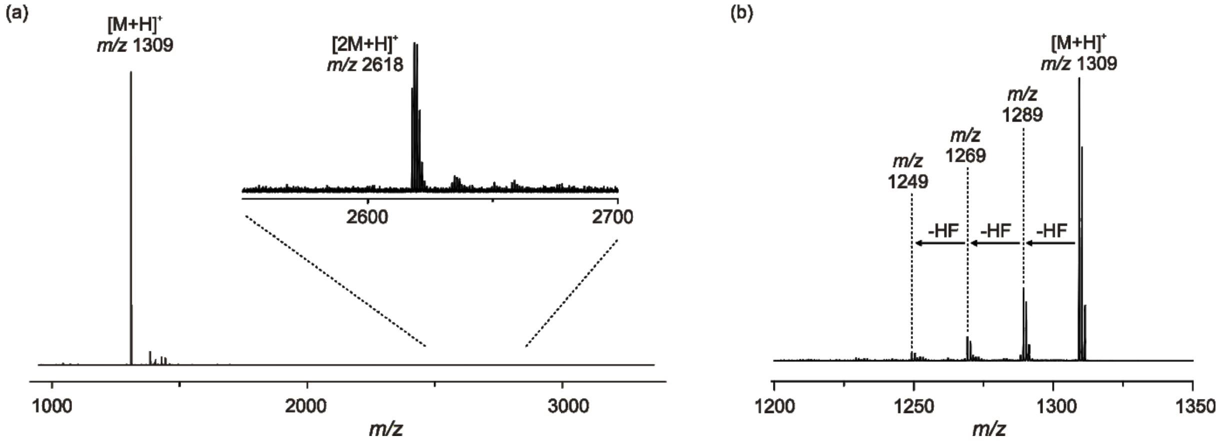


**Figure S13:** (a) ESI-MS spectrum ($CH_2Cl_2/CH_3CN$ = 9:1) of the protonated imine cage [**FC1**+H]$^+$, inlet showing the weak dimer signal at *m/z* 2618. (b) CID Experiment (collision voltage: 60 V) of the mass-selected signal *m/z* 1309.

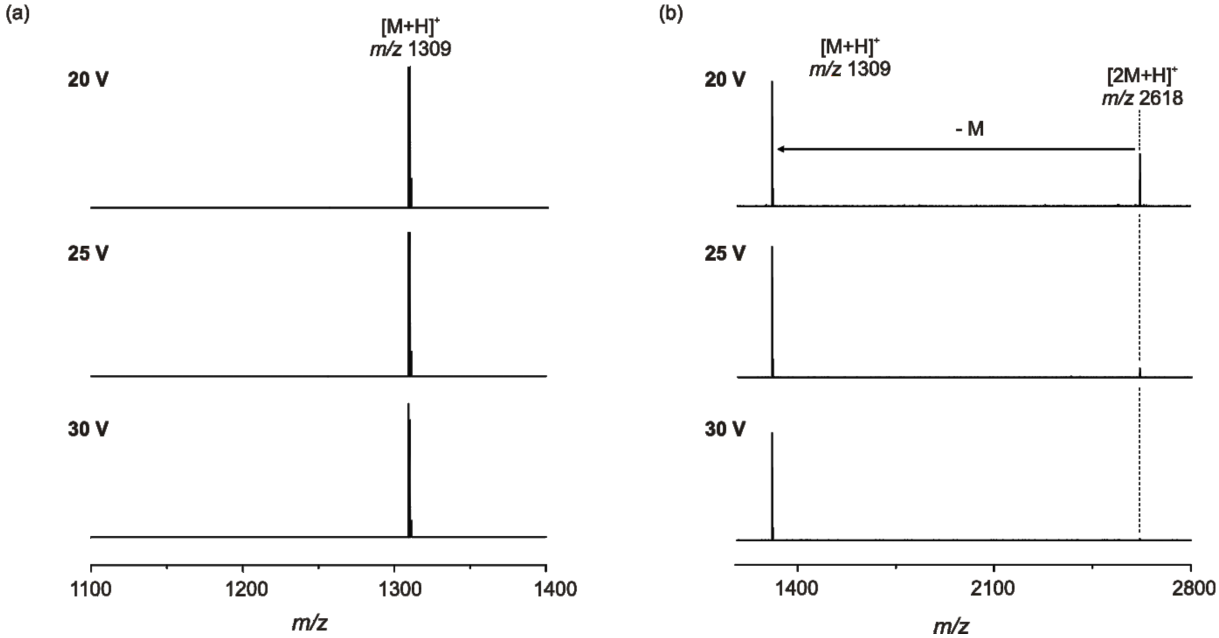


**Figure S14:** CID experiments of the imine cage **FC1** with mass selected signals (a) *m/z* 1309 and (b) *m/z* 2618 at different collision voltages.

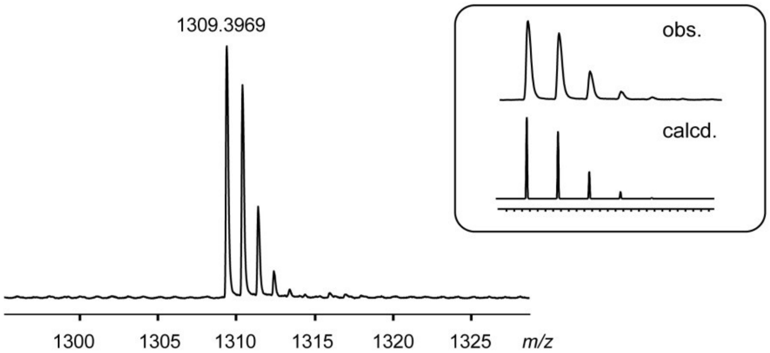


**Figure S15:** High resolution mass spectrum of the protonated imine cage [**FC1**+H]$^+$ *m/z* calcd. for $C_{72}H_{48}N_{12}F_{12}$: 1309.4006 [**FC1**+H]$^+$, found: 1309.3969 ($\Delta$ = 2.8 ppm).

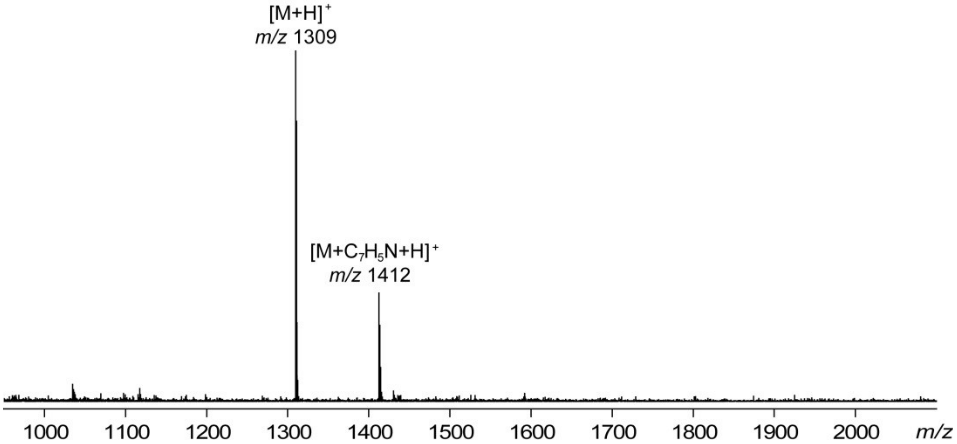


**Figure S16:** ESI-MS spectrum ($CH_2Cl_2$/$CH_3CN$ = 9:1) of the protonated imine cage [**FC1**+H]$^+$ and its benzonitrile complex.

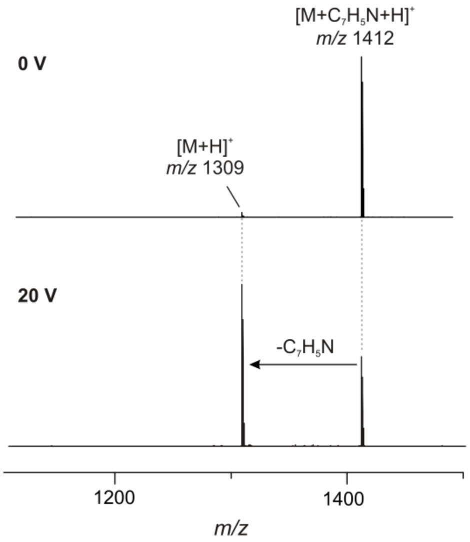


**Figure S17:** CID experiments with imine cage **FC1** and its benzonitrile complex: mass-selected signal for the protonated host-guest complex at *m/z* 1412 before (top) and after increase of collision voltage to 20 V (bottom).

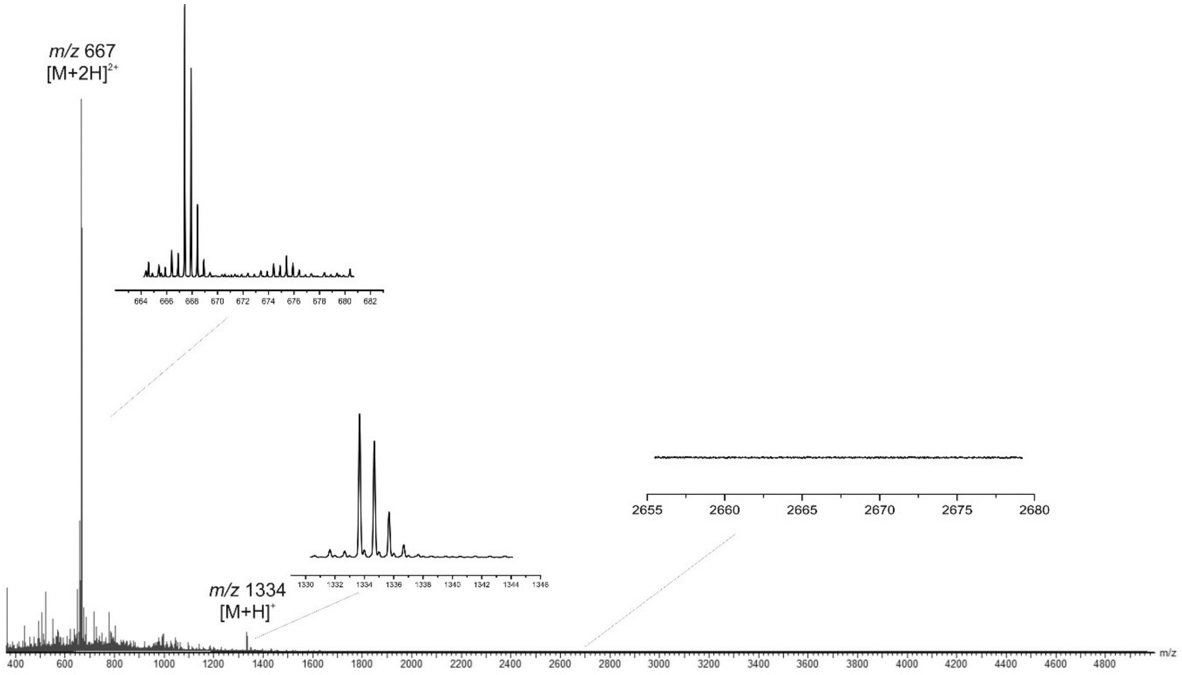
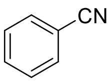
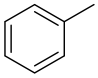
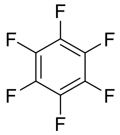
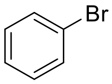
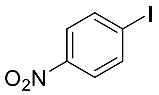
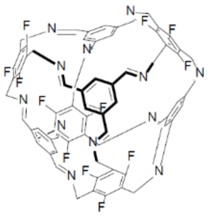
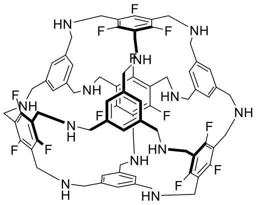


**Figure S18:** ESI-MS spectrum $H_2O$/iPrOH/HCOOH (50:50:1) of the protonated amine cage [$\mathbf{FC1_L}$+2H]$^{2+}$ *m/z* at 667, inlet showing the weak single charged ion [$\mathbf{FC1_L}$+H]$^{+}$ signal at *m/z* 1334.

**Table S3:** Qualitative screening of guests for the imine cage **FC1** and amine cage **FC1$_L$**.

| |  |  |  |  |  |
|---|---|---|---|---|---|
| **FC1**<br> | ✓<br>*m/z* 1412 | ✗ | ✓<br>*m/z* 1495 | ✗ | ✓<br>*m/z* 1558<br>(weak) |
| **FC1$_L$**<br> | ✗ | ✗ | ✗ | ✗ | ✗ |

For NMR titration experiments, the same substrates as listed above were used. A stock solution of **FC1** in CDCl$_3$ (c = 0.16 mM) was mixed with a stock solution of the substrates (1 and 10 eq.) in CDCl$_3$. The mixture was sonicated at room temperature for 30 min and the corresponding solutions were then subjected to NMR analysis. In neither case, a shift in neither $^1$H nor $^{19}$F NMR could be observed for the substrates.

# IX. IR spectra

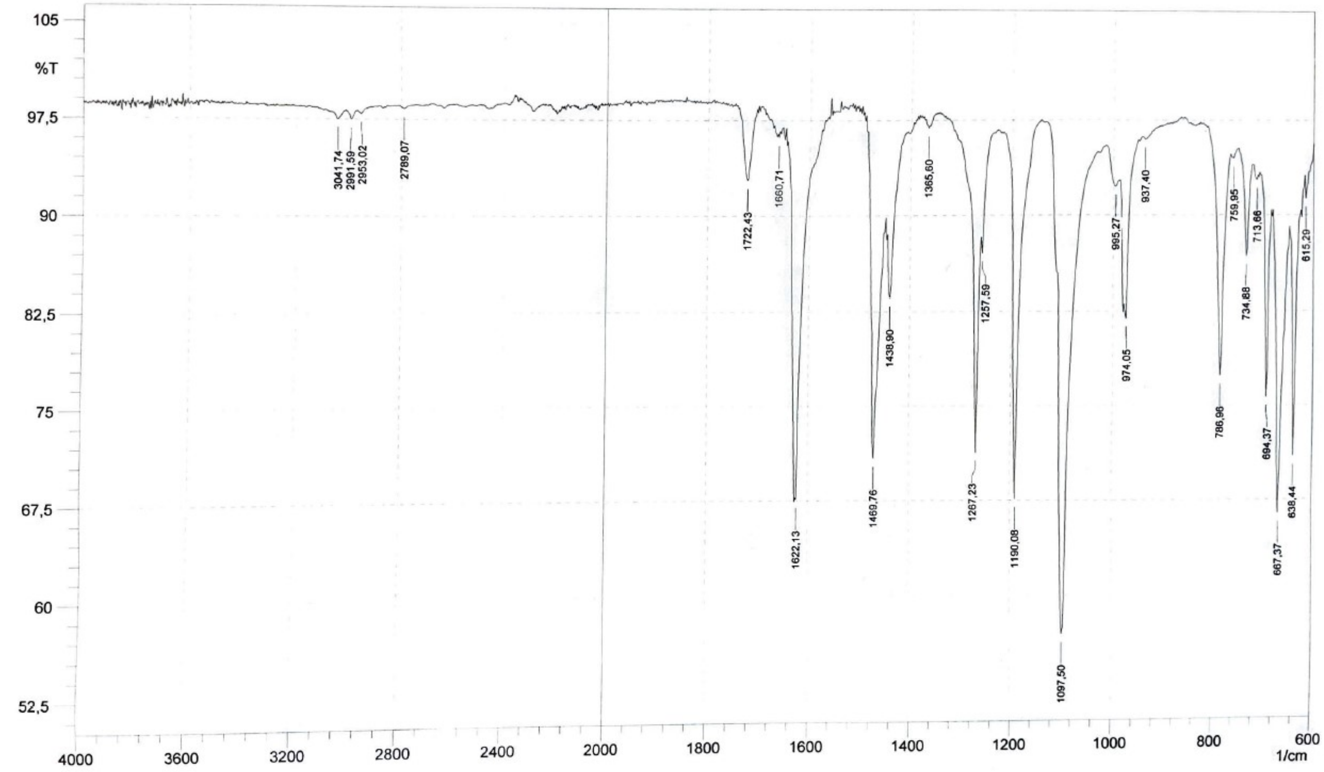


**Figure S19:** AT-IR spectrum of 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene **3**.

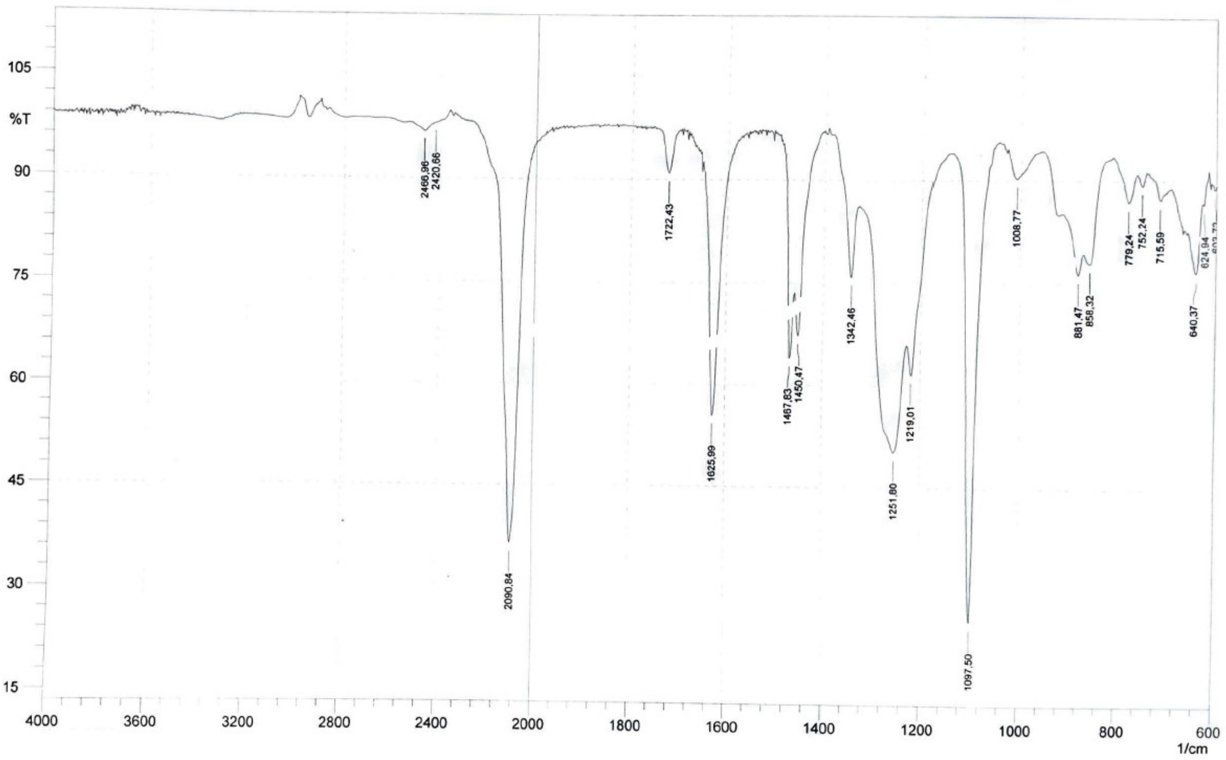


**Figure S20:** AT-IR spectrum of 1,3,5-tris(azidomethyl)-2,4,6-trifluorobenzene **4**.

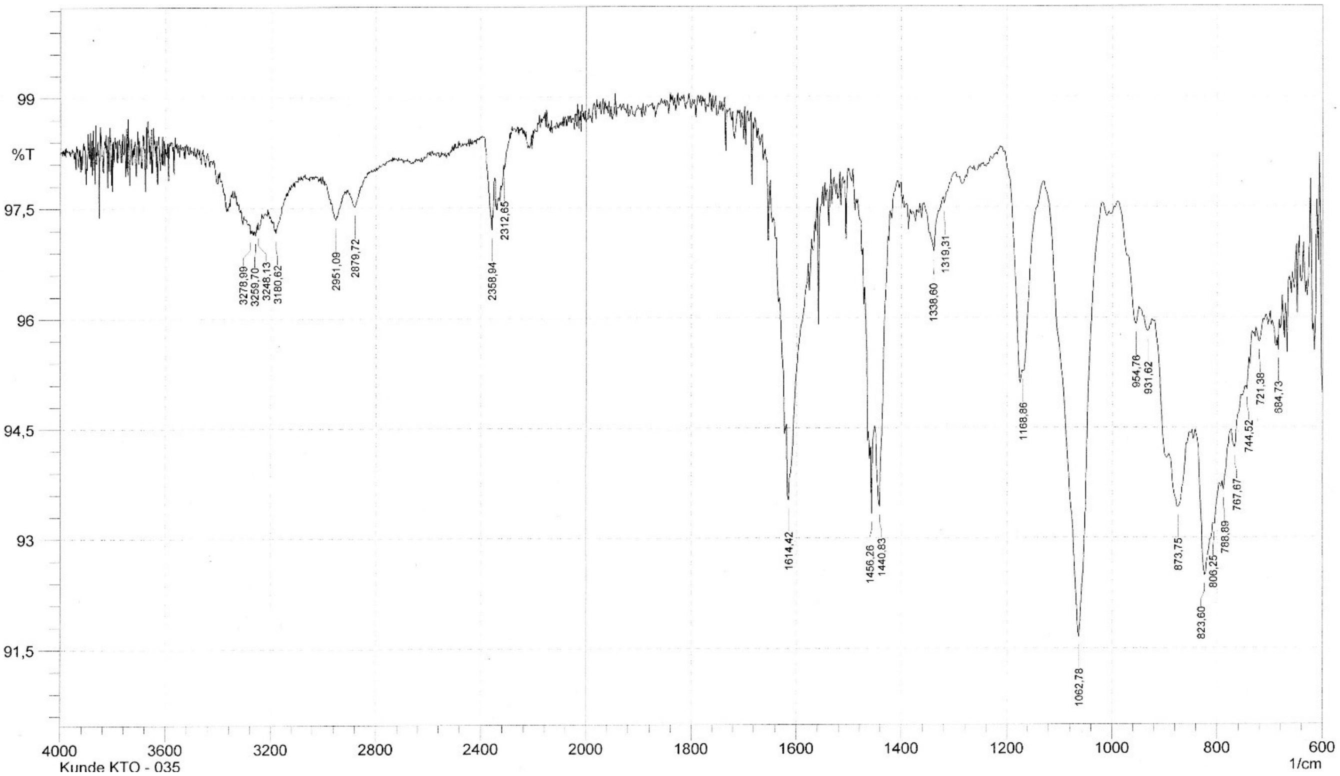


**Figure S21:** AT-IR spectrum of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene **2**.

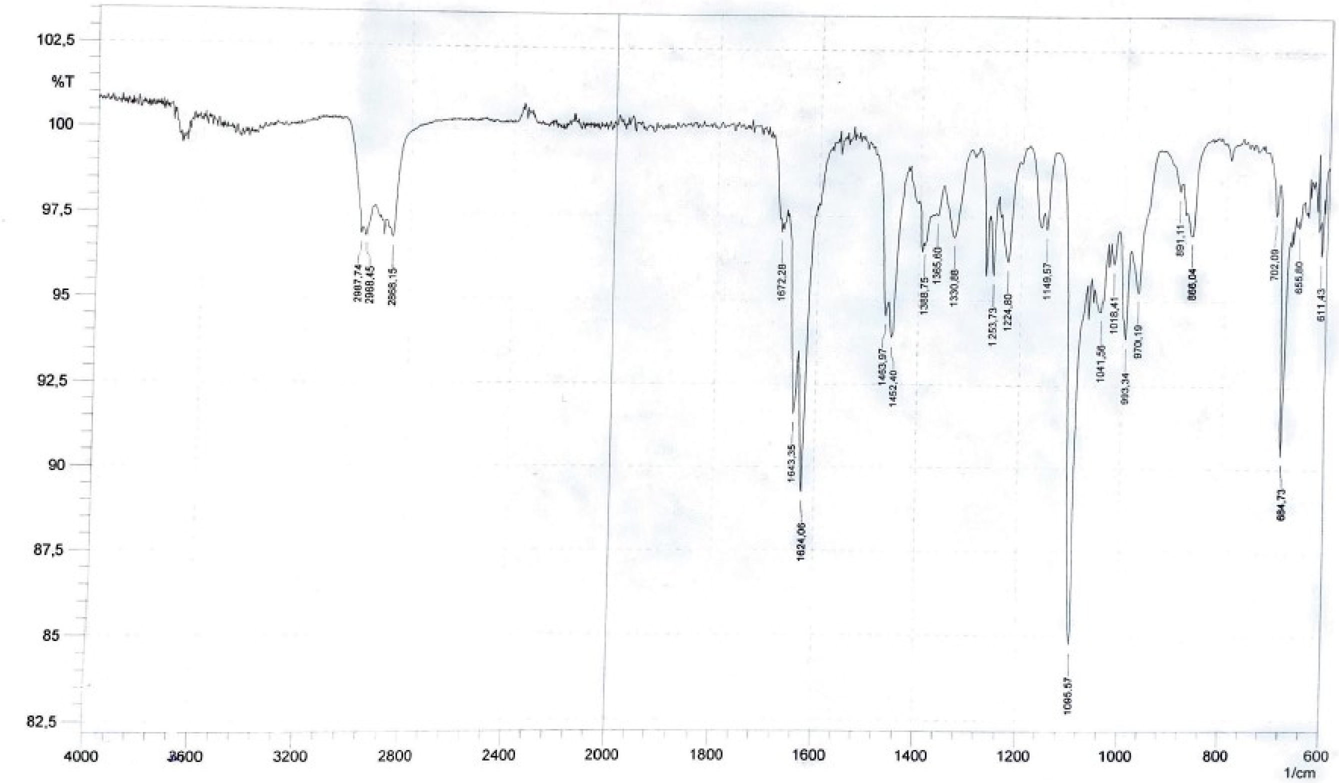


**Figure S22:** AT-IR spectrum of **FC1** in crystalline form.

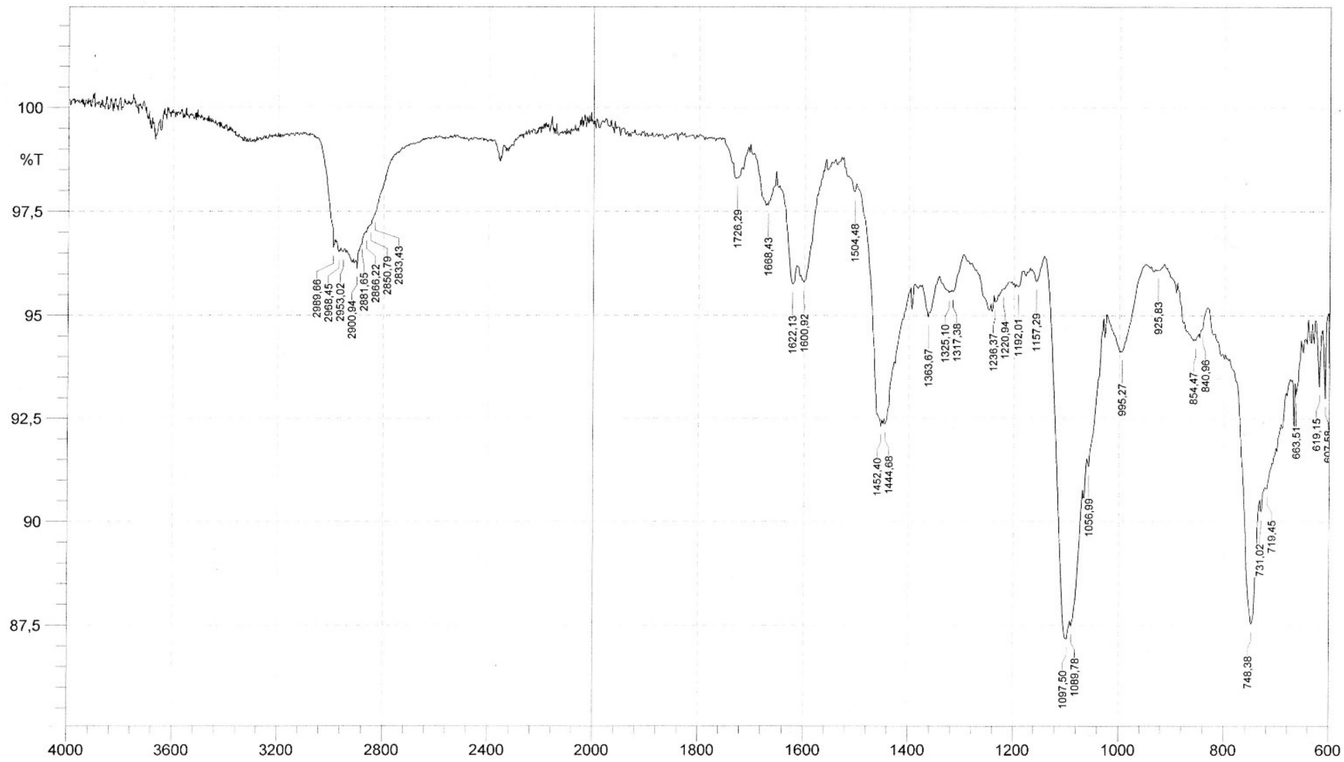


**Figure S23:** AT-IR spectrum of amine cage **FC1$_L$**.

## X. NMR spectra

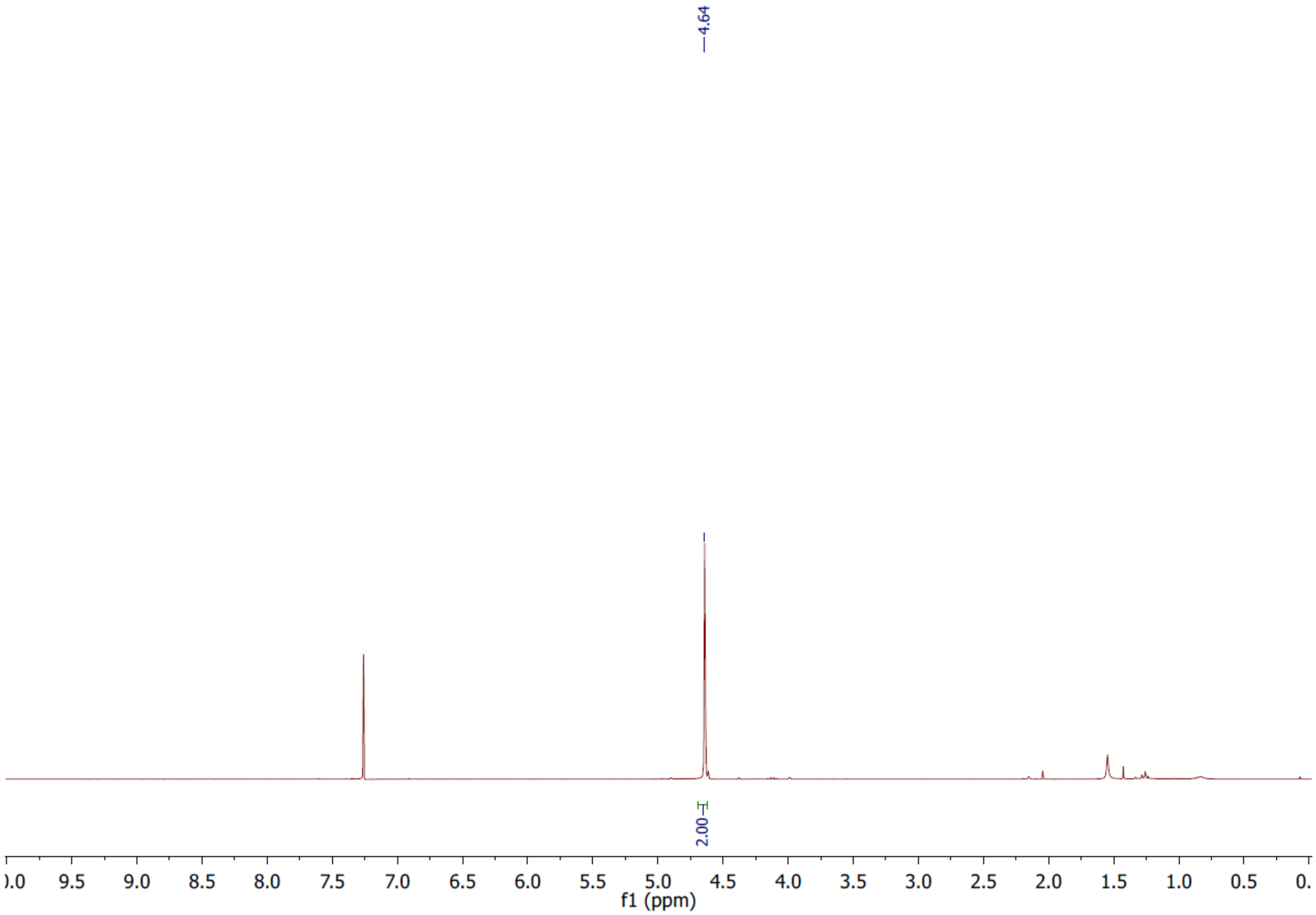


**Figure S24**: $^{1}H$ NMR spectrum (300 MHz, $CDCl_3$) of 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene **3**. *water

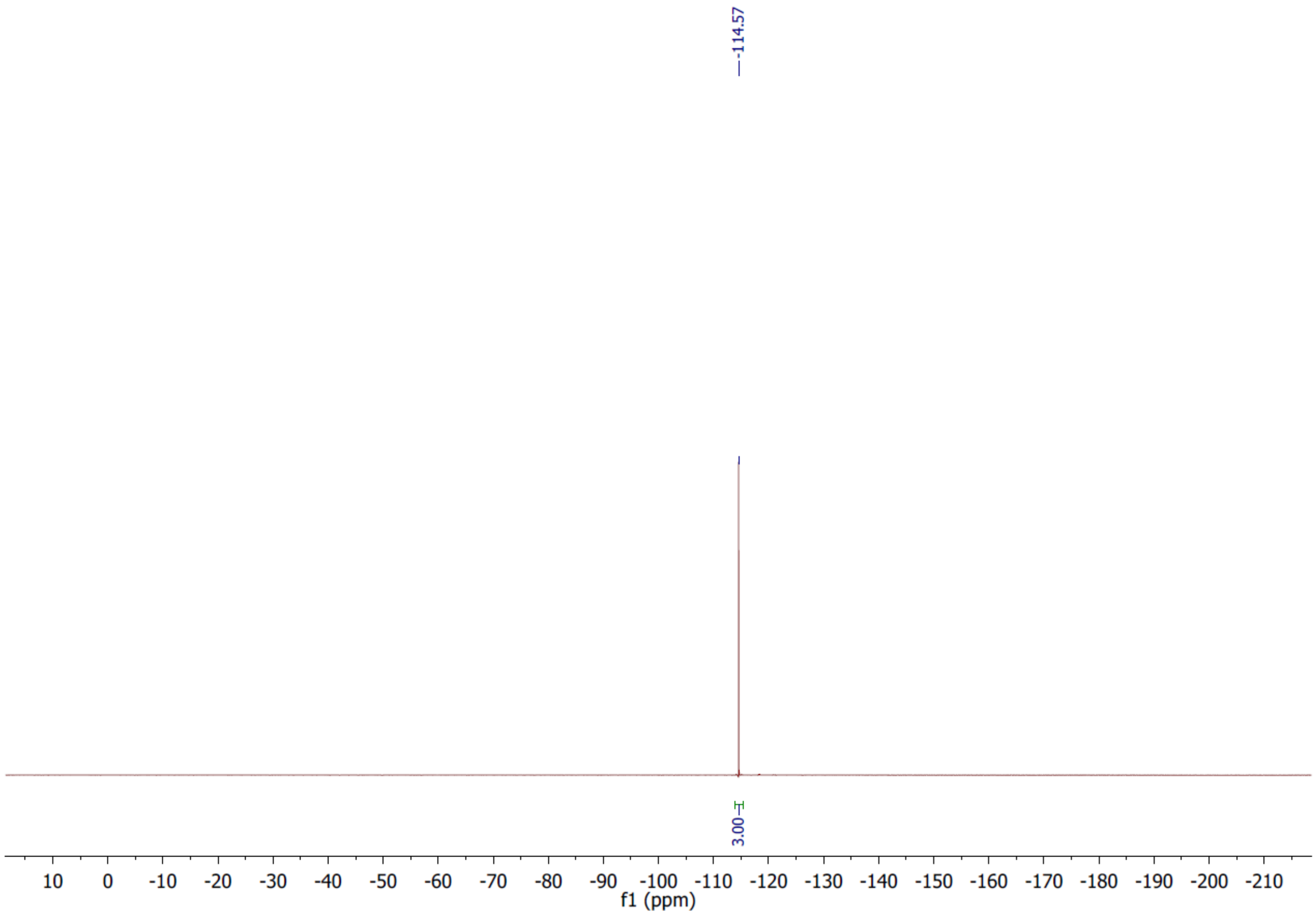


**Figure S25**: $^{19}$F NMR spectrum (282 MHz, $CDCl_3$) of 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene **3**.

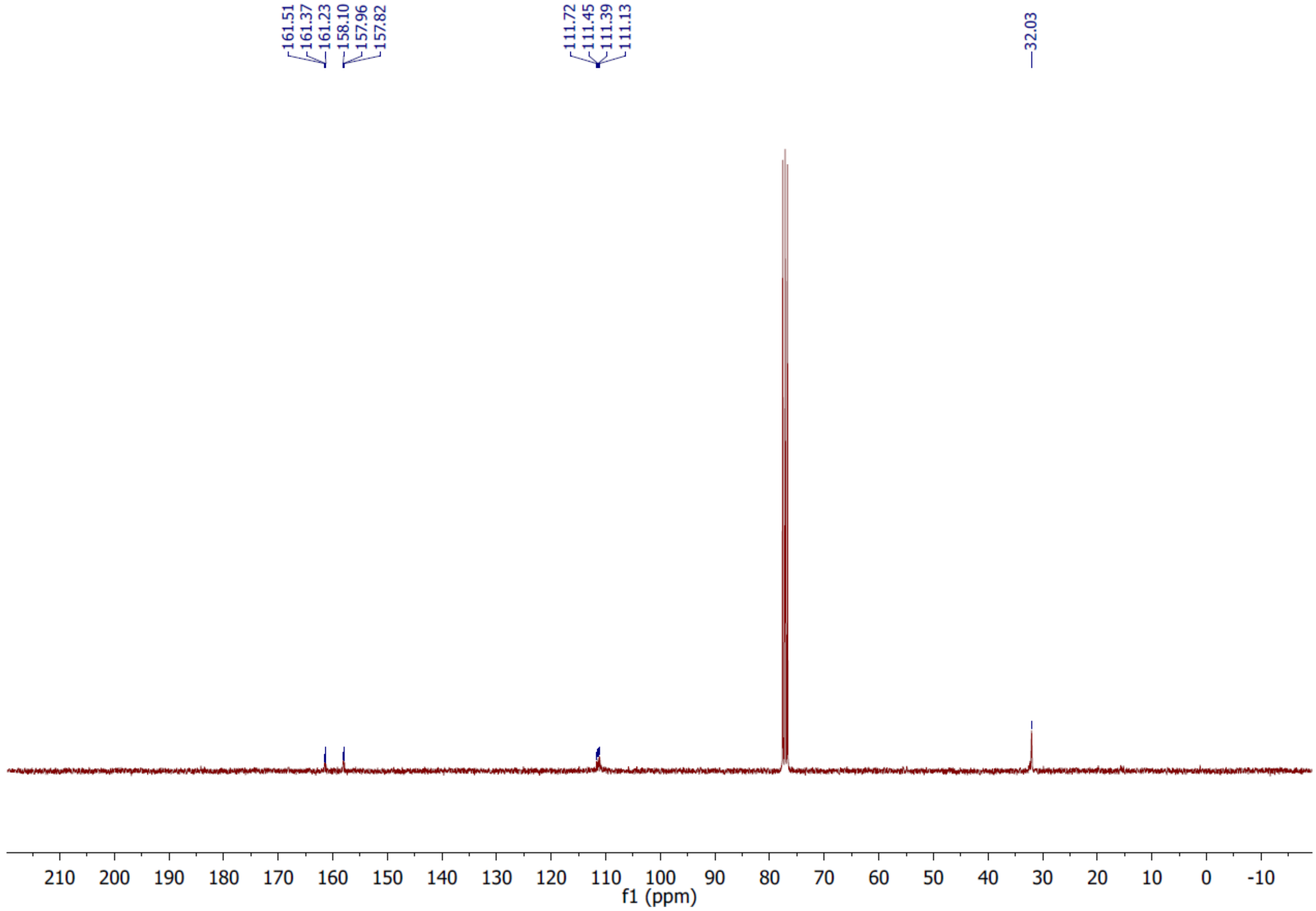


**Figure S26:** $^{13}C\{^{1}H]$ NMR spectrum (80 MHz, $CDCl_3$) of 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene **3**.

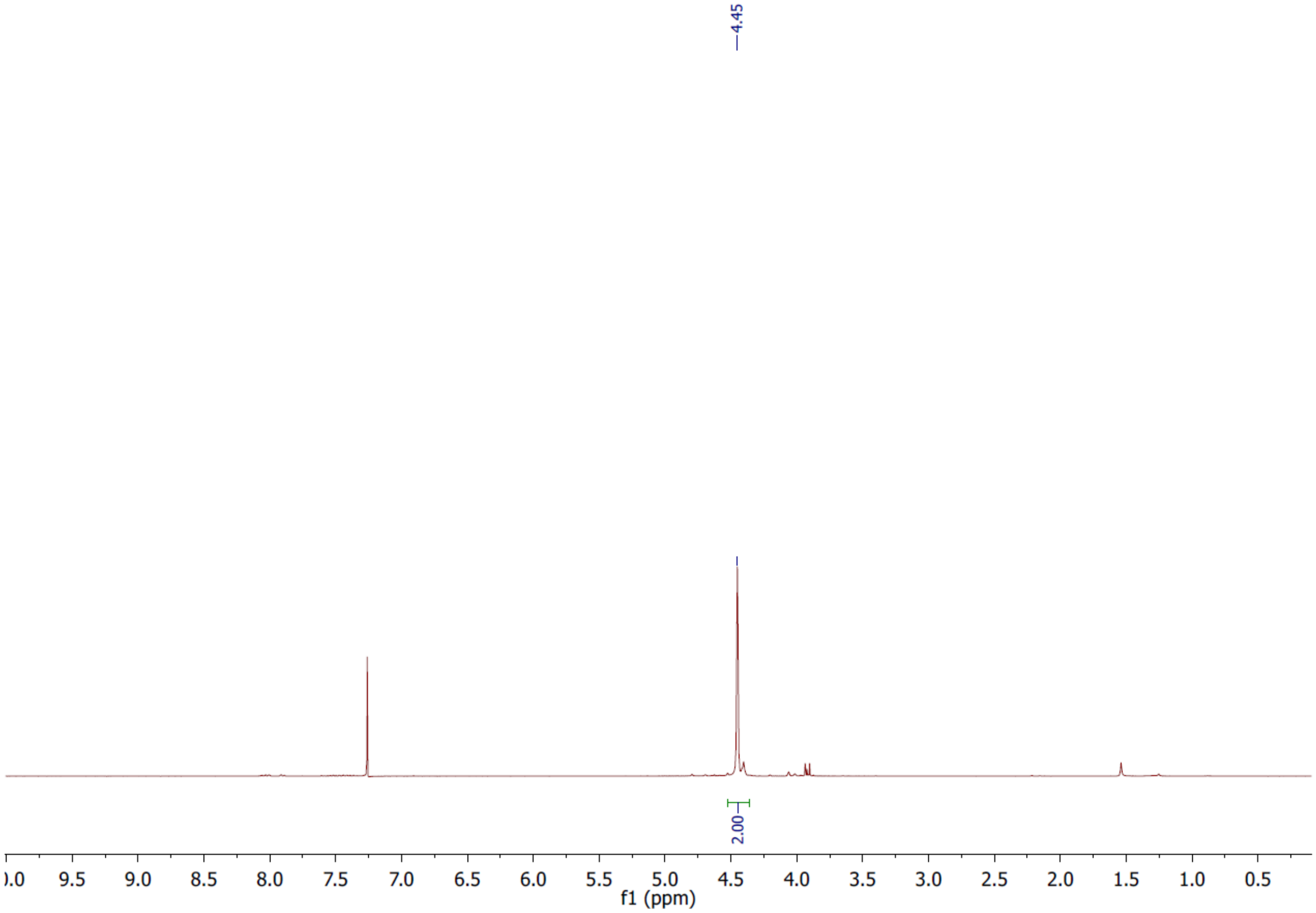


**Figure S27:** $^1$H NMR spectrum (300 MHz, $CDCl_3$) of 1,3,5-tris(azidomethyl)-2,4,6-trifluorobenzene **4**. *water

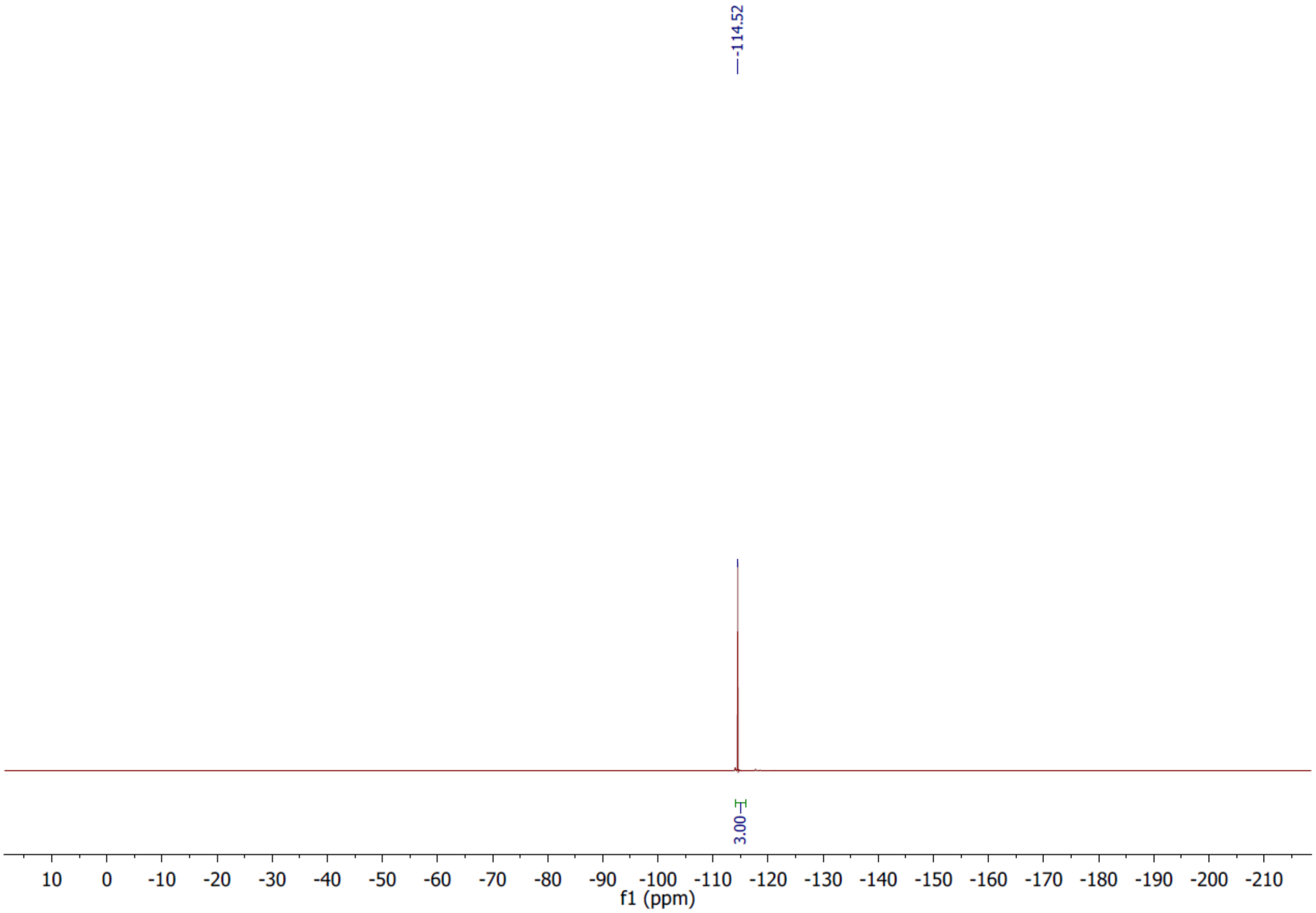


**Figure S28:** $^{19}$F NMR spectrum (282 MHz, $CDCl_3$) of 1,3,5-tris(azidomethyl)-2,4,6-trifluorobenzene **4**.

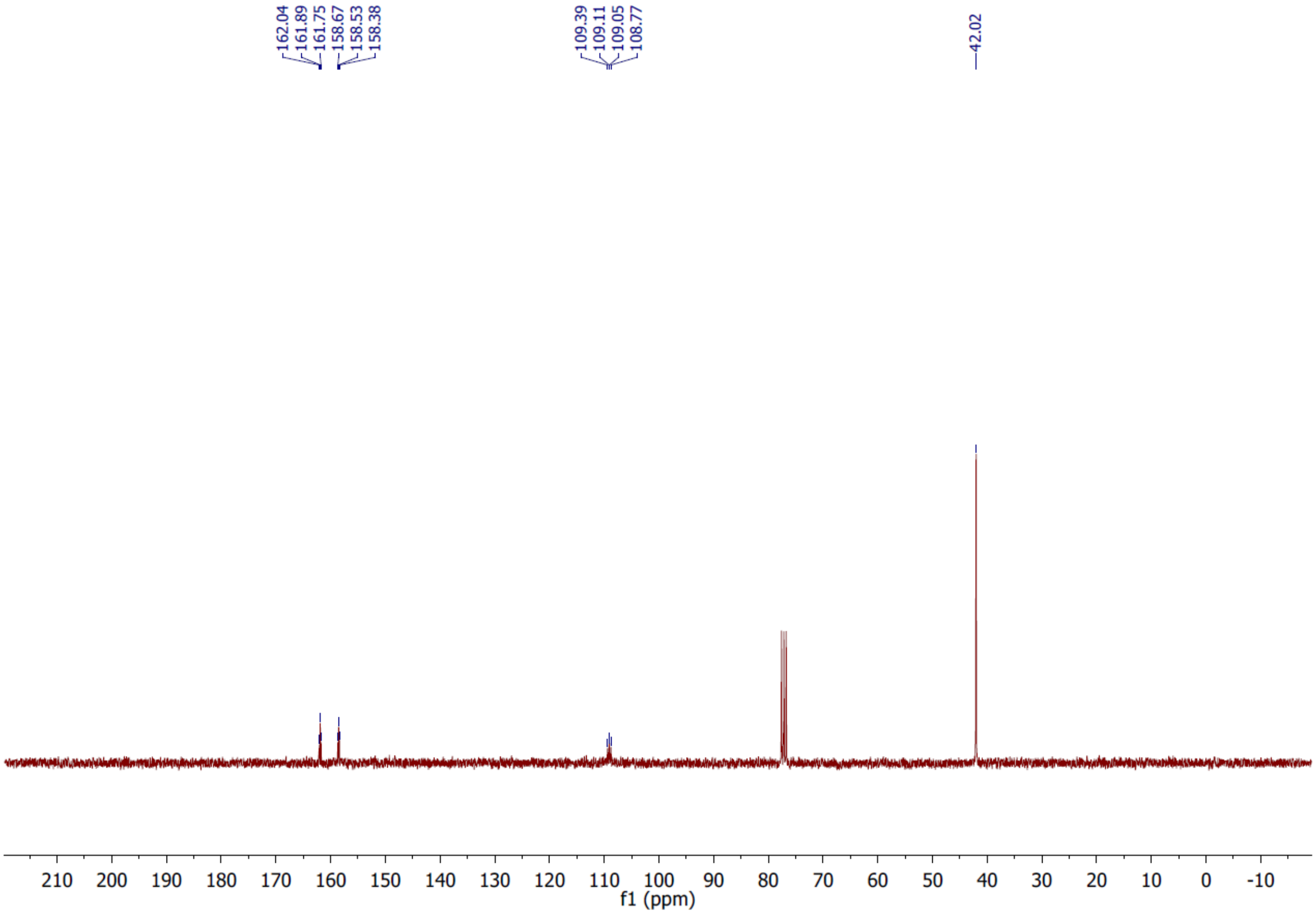


**Figure S29:** $^{13}C\{^1H]$ NMR spectrum (80 MHz, $CDCl_3$) of 1,3,5-tris(azidomethyl)-2,4,6-trifluorobenzene **4**.

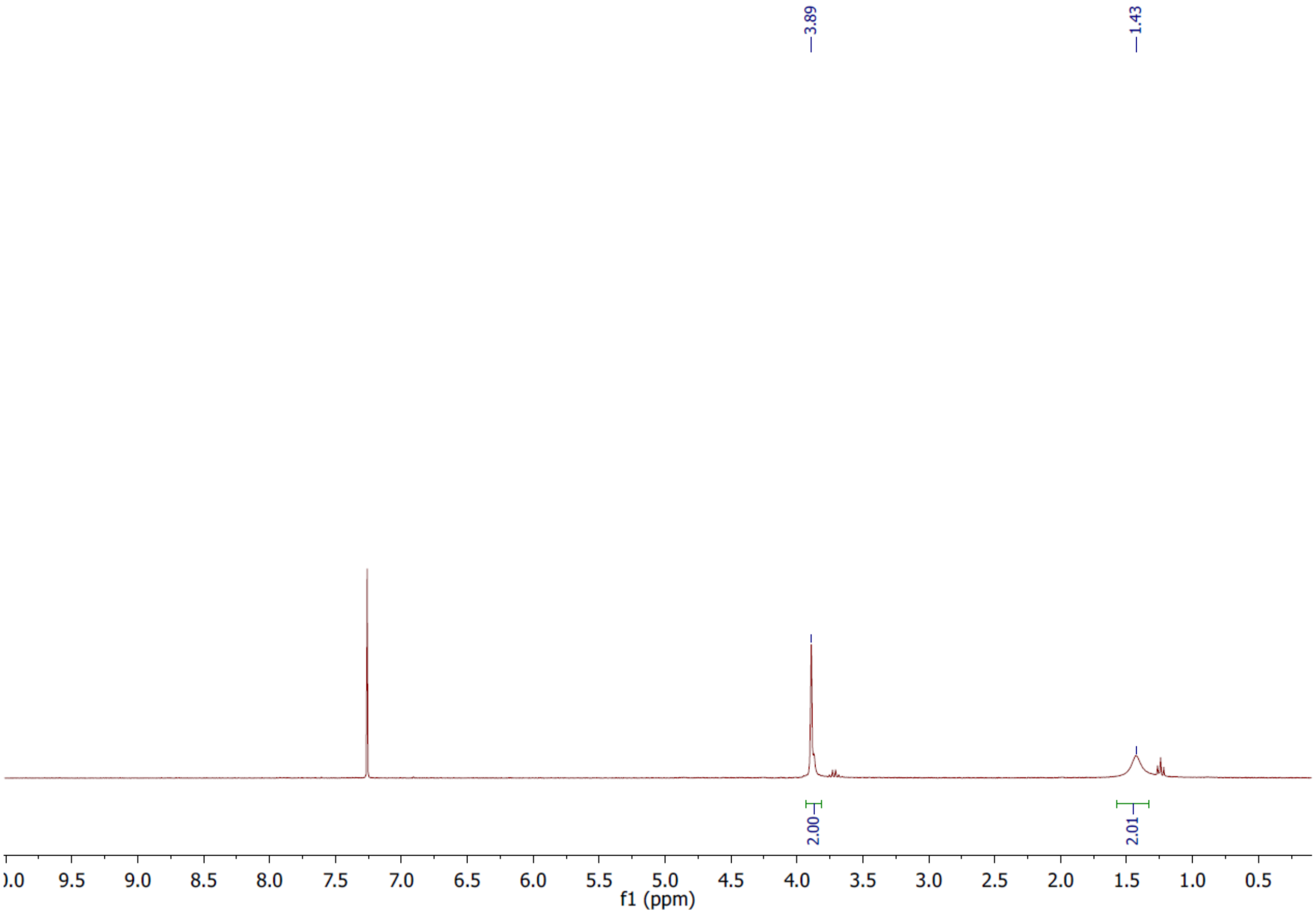


**Figure S30**: $^1$H NMR spectrum (300 MHz, $CDCl_3$) of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene **2**. *ethanol

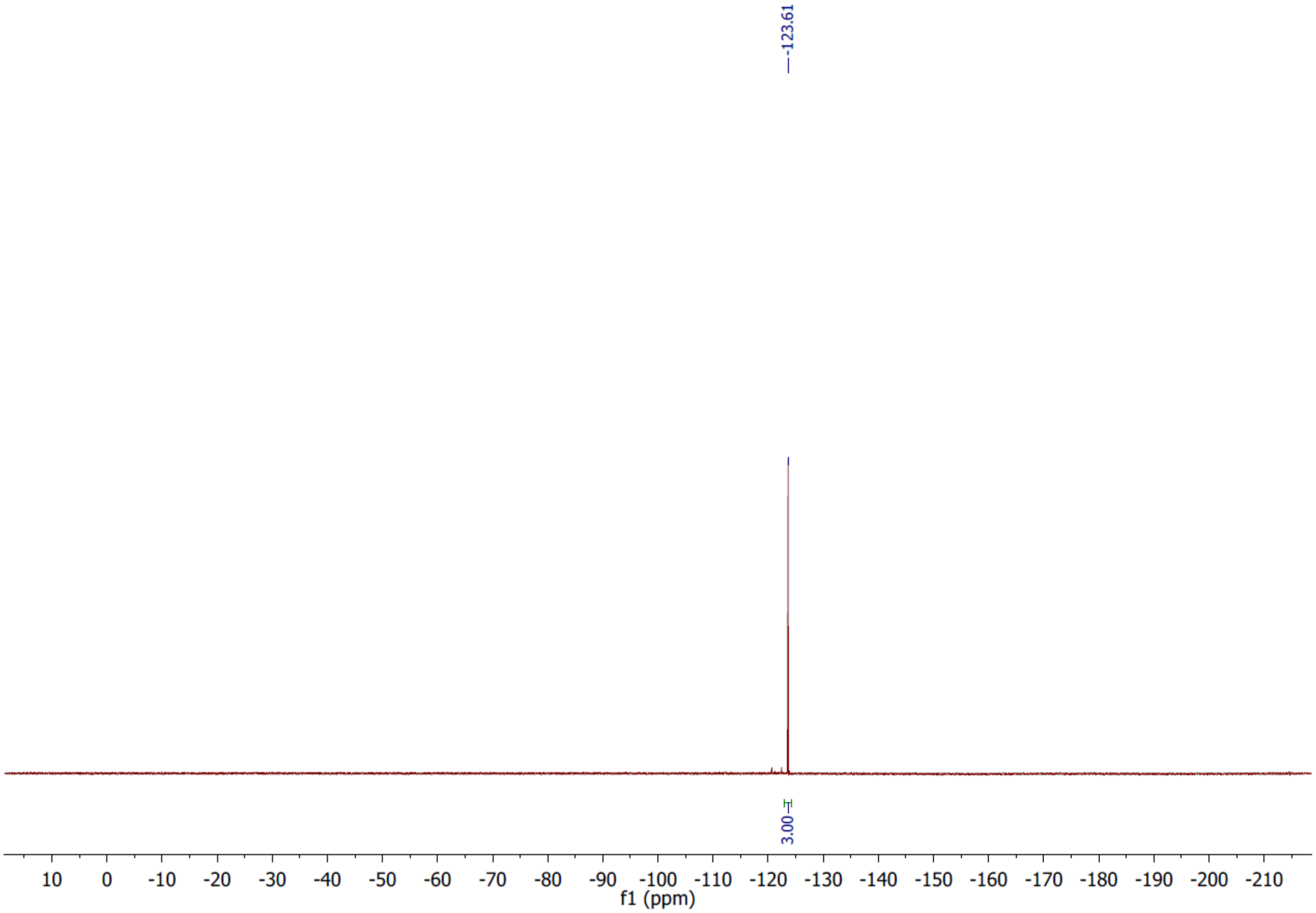


**Figure S31**: $^{19}$F NMR spectrum (282 MHz, $CDCl_3$) of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene **2**.

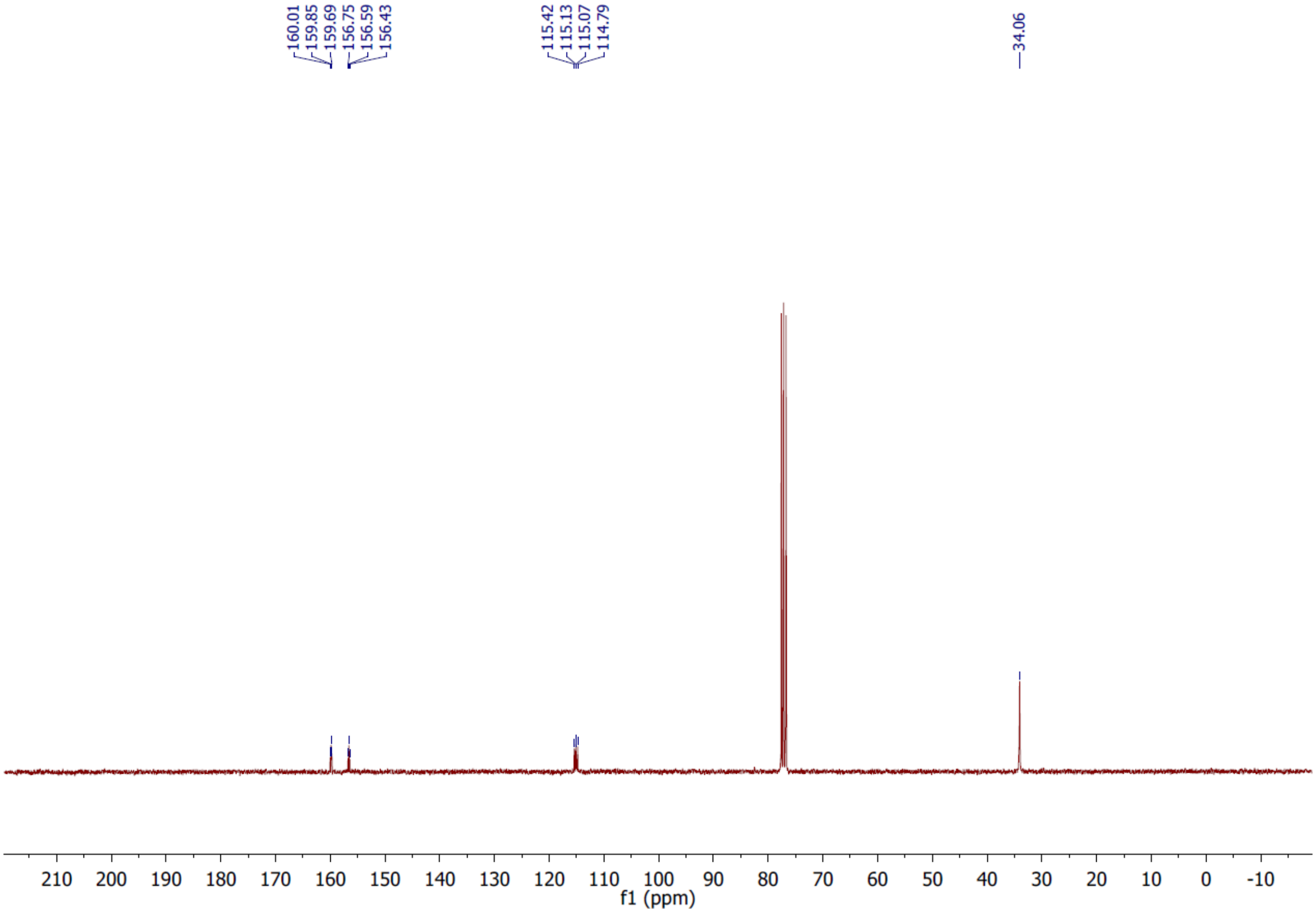


**Figure S32:** $^{13}C\{^{1}H]$ NMR spectrum (80 MHz, $CDCl_3$) of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene **2**.

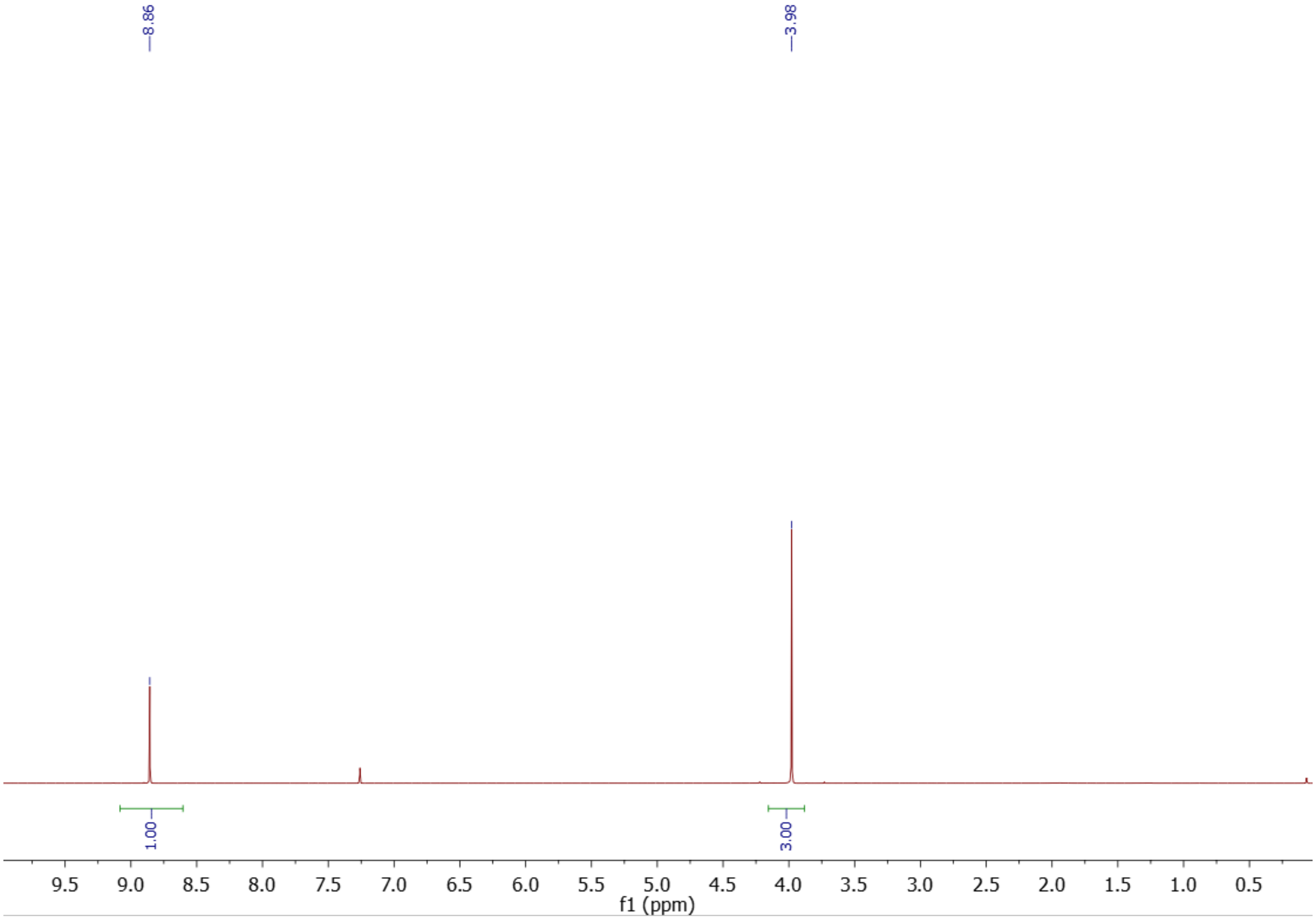


**Figure S33**: $^1$H NMR spectrum (300 MHz, $CDCl_3$) of 1,3,5-tris(methylcarboxylate)benzene **5**.

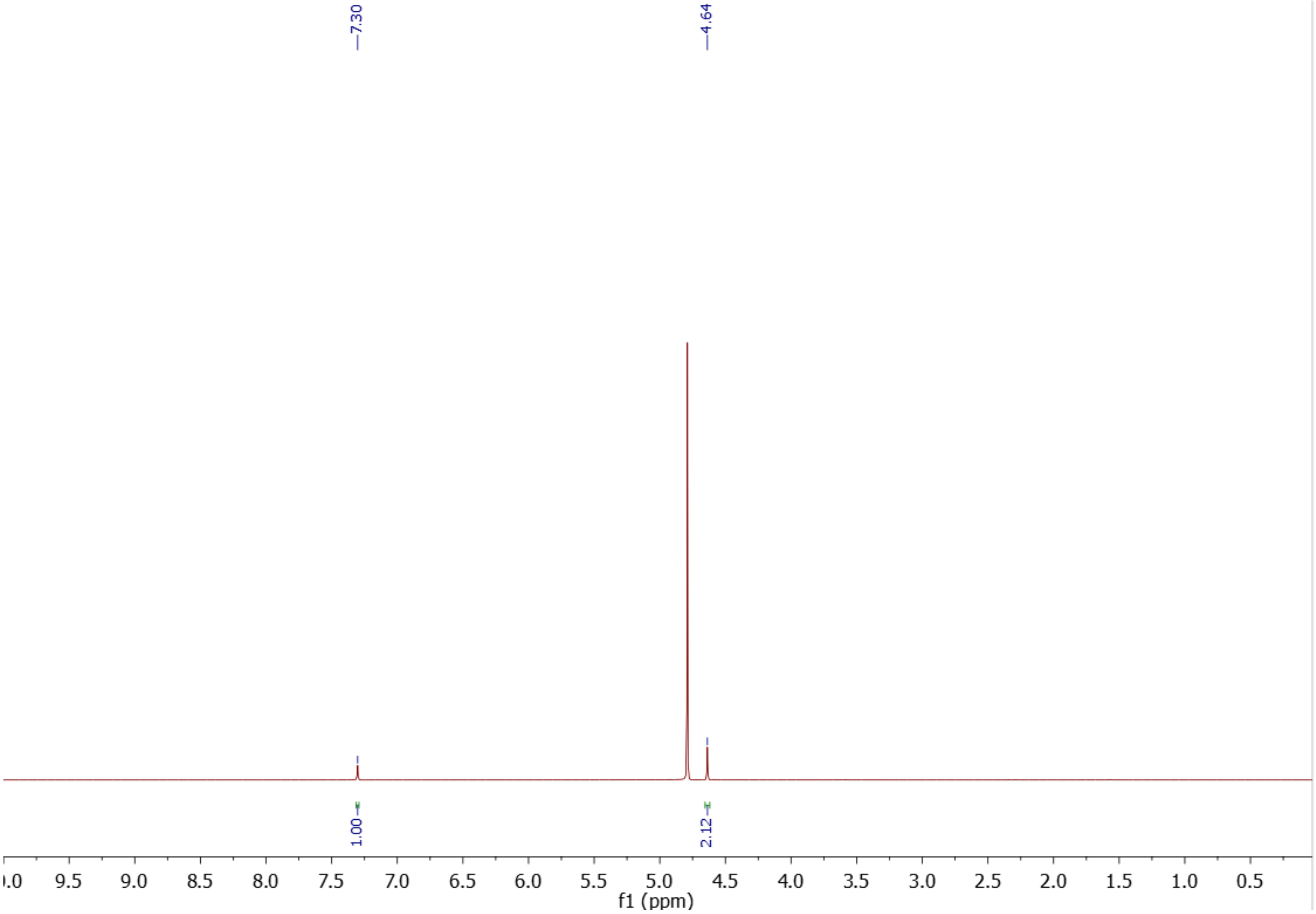


**Figure S34**: $^1$H NMR spectrum (300 MHz, $D_2O$) of 1,3,5-tris(hydroxymethyl)benzene **6**.

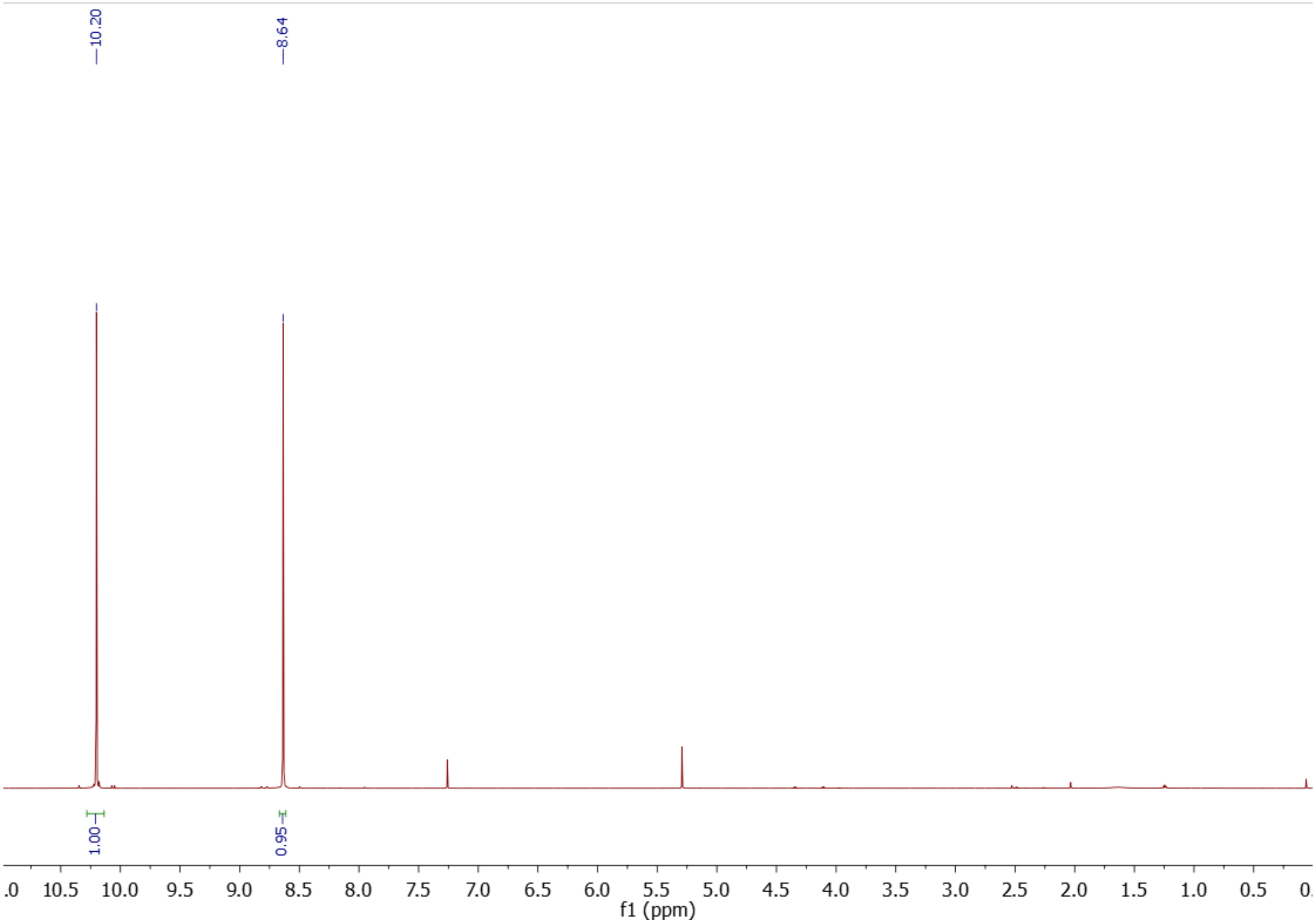


**Figure S35**: $^1$H NMR spectrum (300 MHz, $CDCl_3$) of 1,3,5-triformylbenzene **1**. *$CH_2Cl_2$

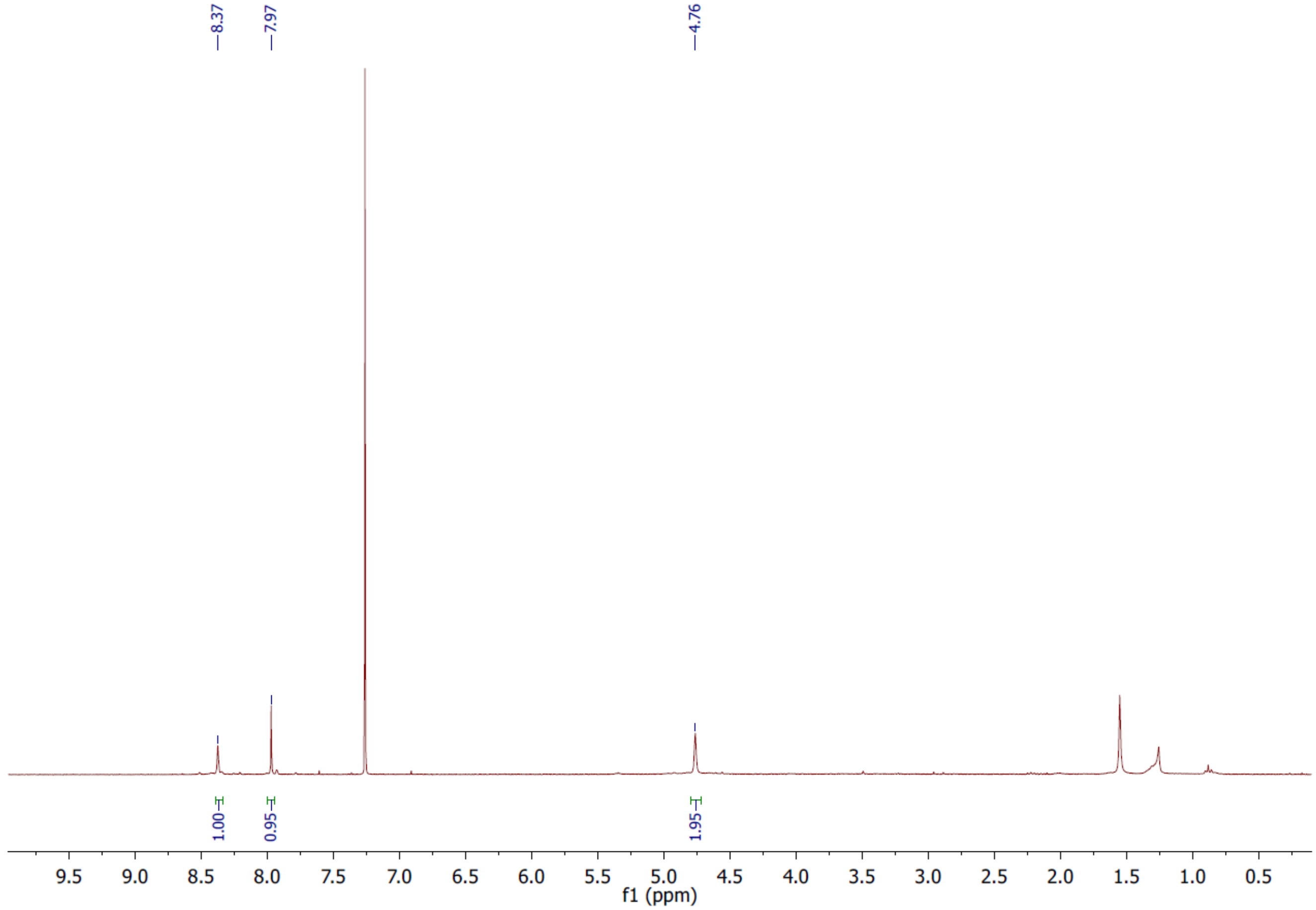


**Figure S36:** $^1$H NMR spectrum (300 MHz, $CDCl_3$) of [4+4] imine cage **FC1**. * water

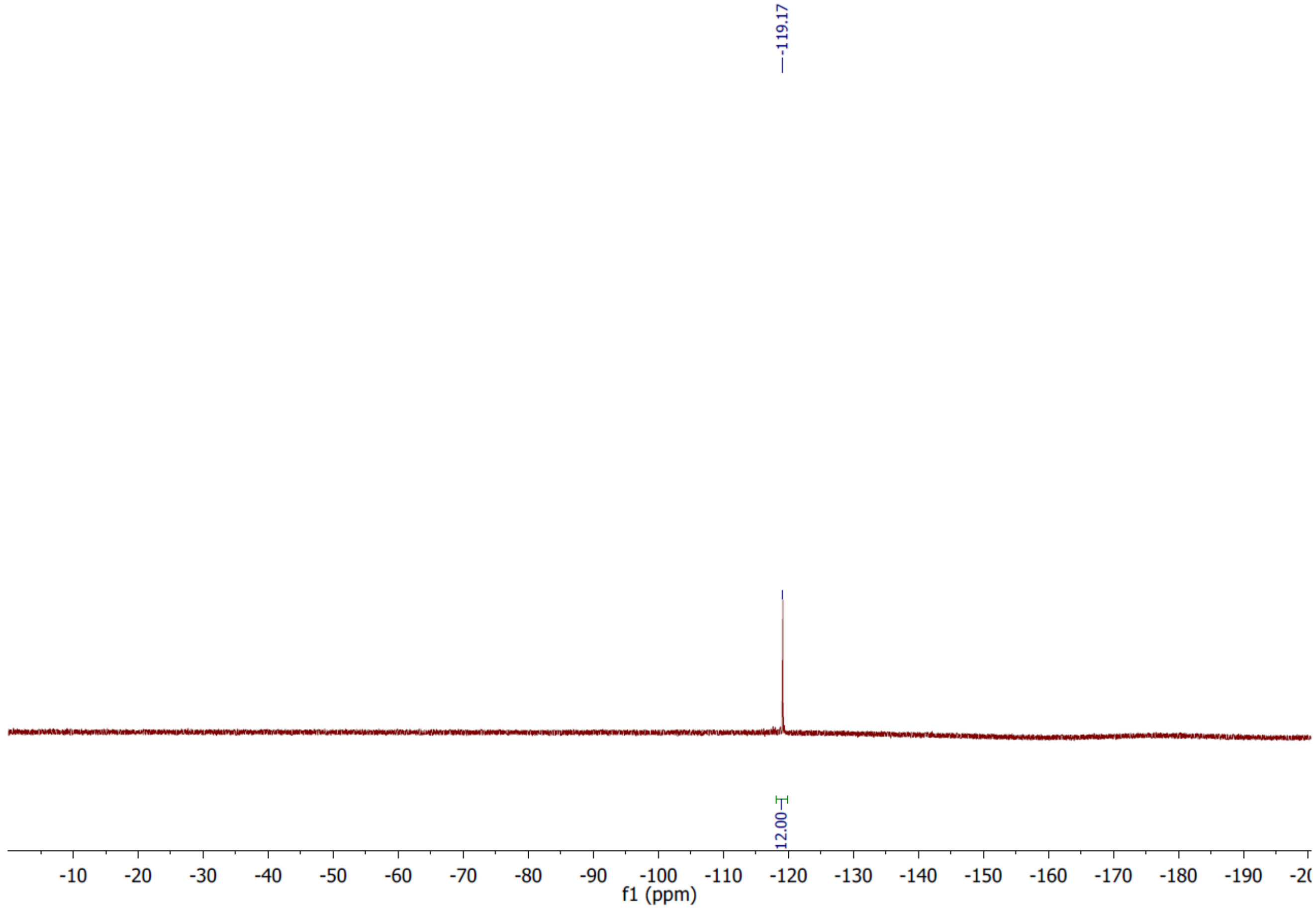


**Figure S37:** $^{19}$F NMR spectrum (282 MHz, $CDCl_3$) of [4+4] imine cage **FC1**.

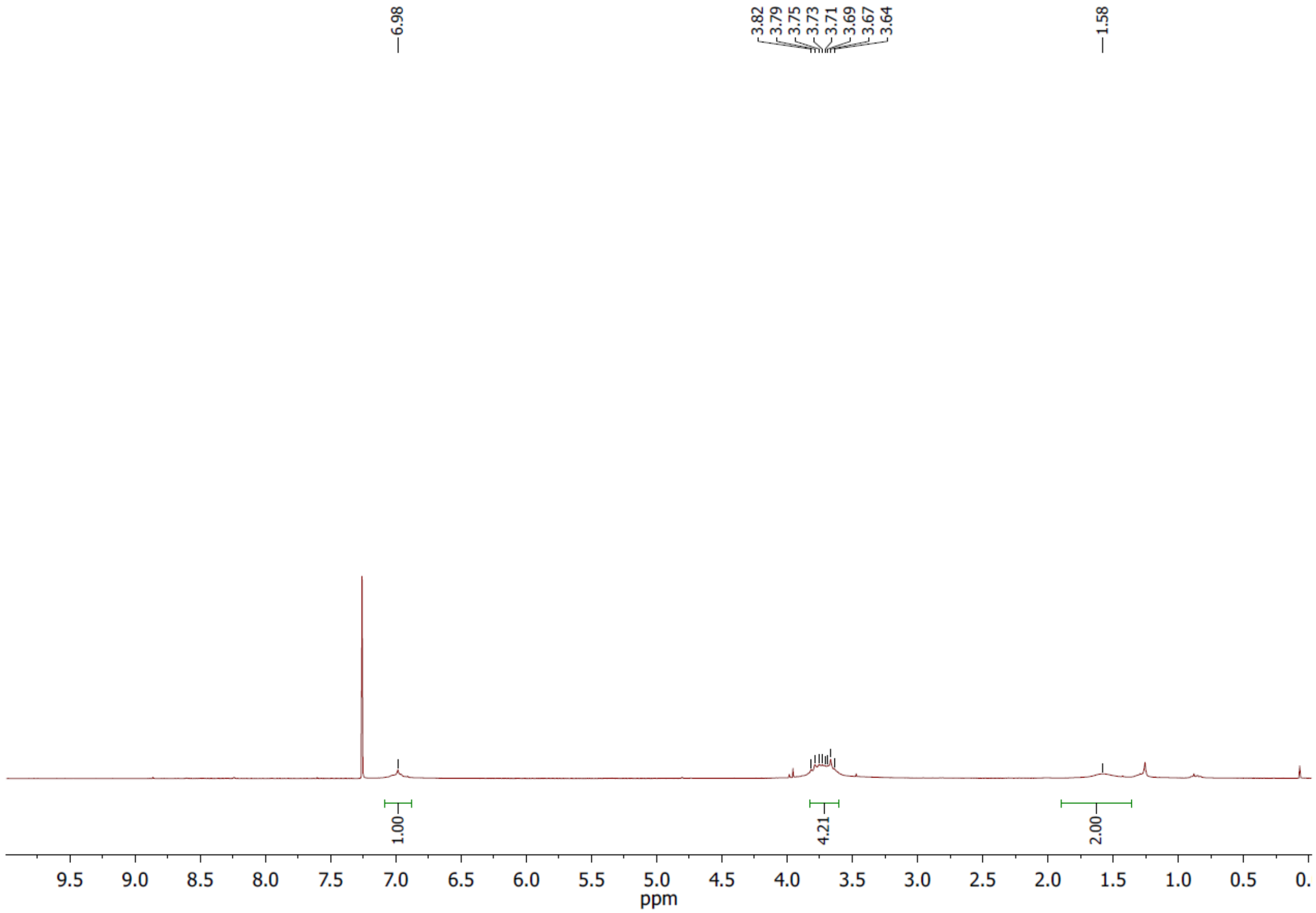


**Figure S38:** $^1$H NMR spectrum (282 MHz, CDCl$_3$) of [4+4] amine cage **FC1$_L$**.

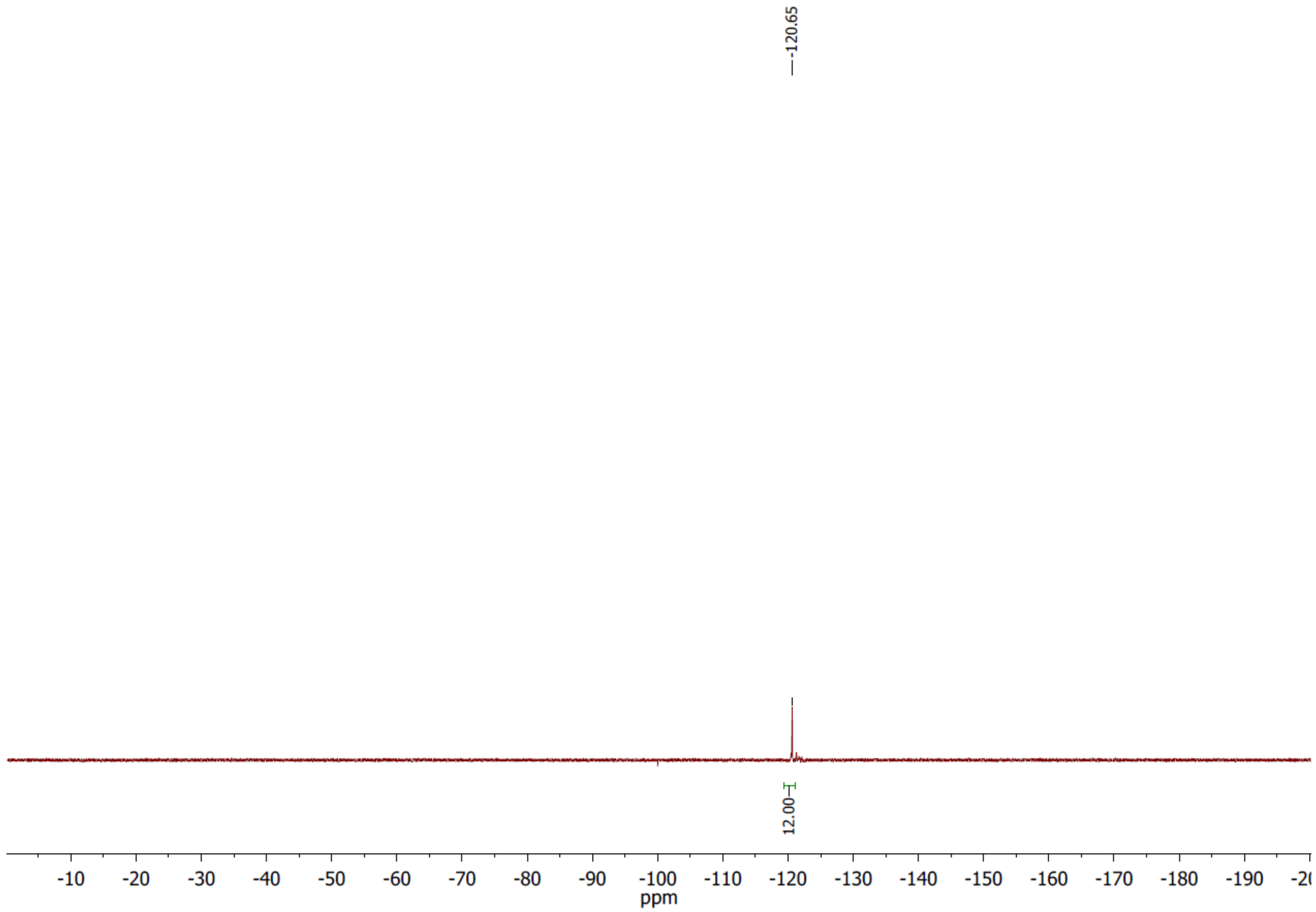


**Figure S39:** $^{19}$F NMR spectrum (282 MHz, $CDCl_3$) of [4+4] amine cage **FC1**.

## XI. MS spectra

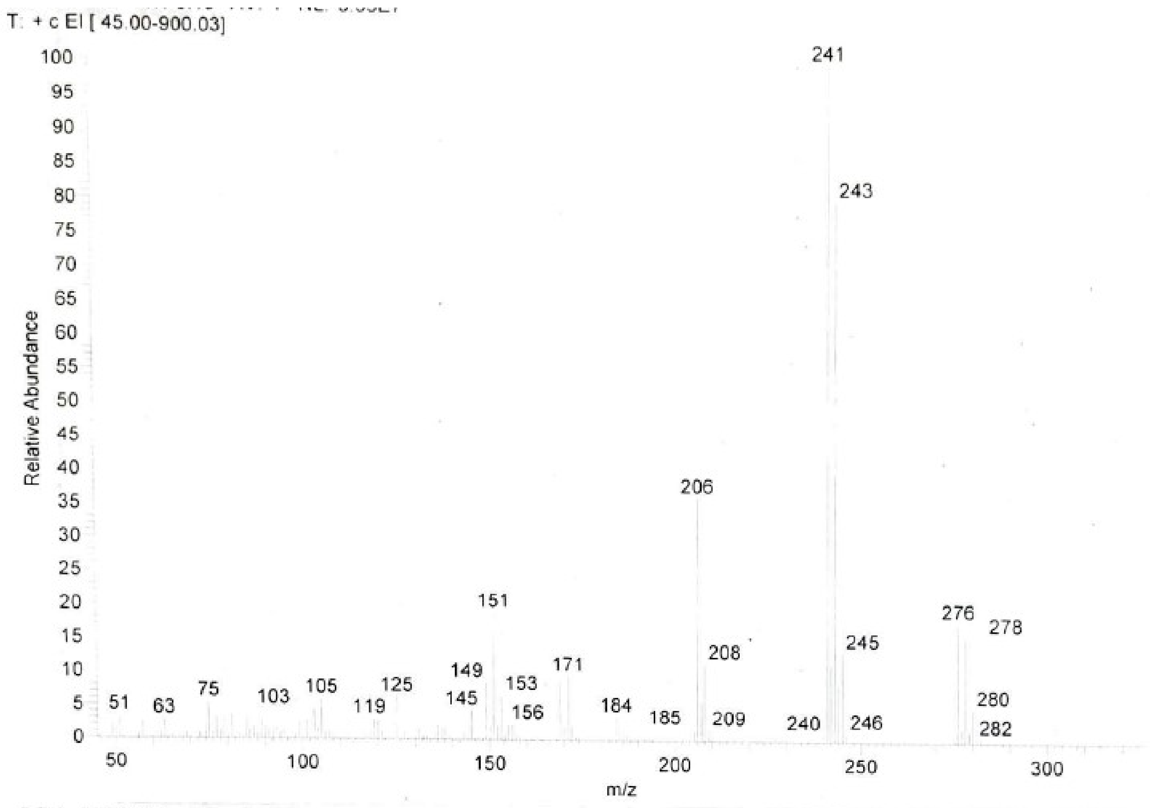


**Figure S40:** CI-MS spectrum of 1,3,5-tris(chloromethyl)-2,4,6-trifluorobenzene **3** at 300°C. The corresponding $[M+H]^+$ ion (276 m/z) shows a loss of an Cl-fragment (35 m/z) resulting in a fragmented ion of $[M-Cl+H]^+$ (241 m/z).

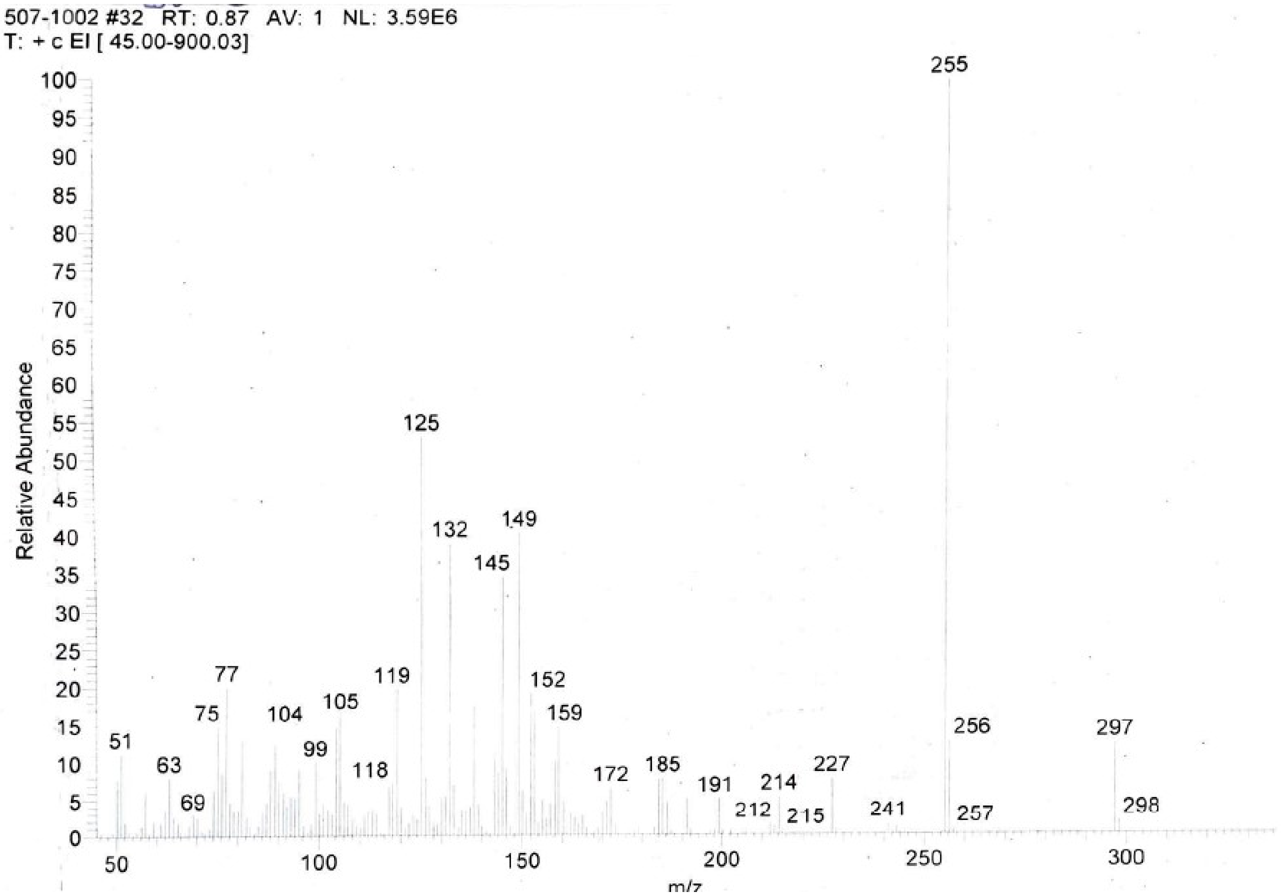


**Figure S41:** CI-MS spectrum of 1,3,5-tris(azidomethyl)-2,4,6-trifluorobenzene **4** at 40°C. The corresponding $[M+H]^+$ ion (297 m/z) shows a loss of an $N_3$-fragment (42 m/z) resulting in a fragmented ion of $[M-N_3+H]^+$ (255 m/z).

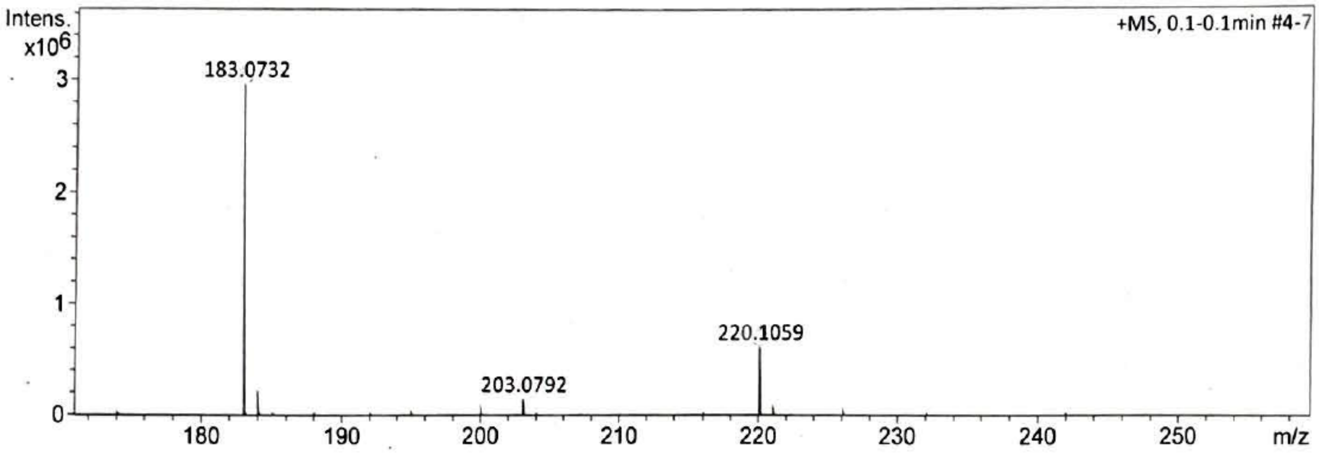


**Figure S42:** ESI-MS spectrum of 1,3,5-tris(aminomethyl)-2,4,6-trifluorobenzene **2**. The corresponding $[M+H]^+$ ion (found 220.1059 m/z) shows a good correspondence to the theoretical value of calc. 220.1056 m/z.

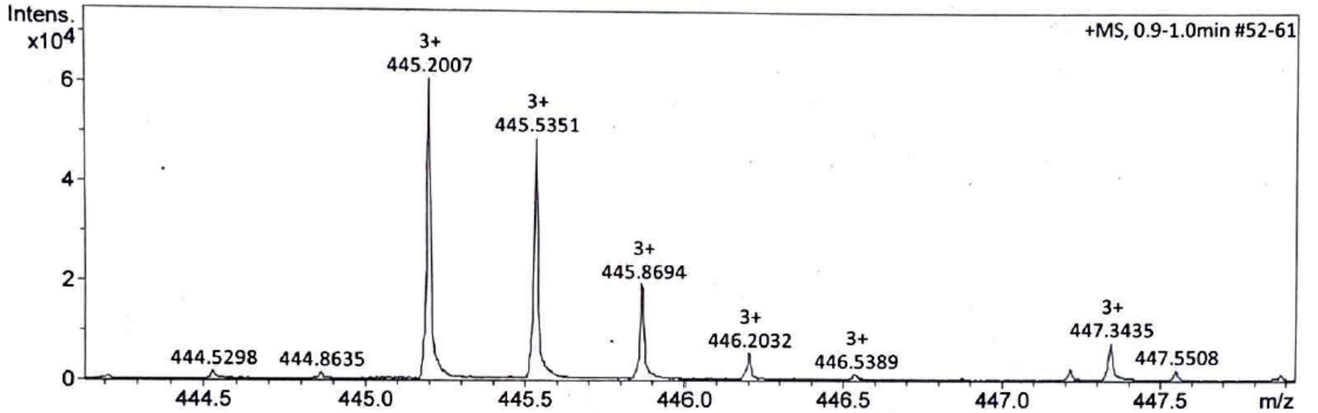


**Figure S43:** ESI-HRMS spectrum of **FC1$_L$**. The found $[M+3H]^{3+}$ ion mass: 445.2007 m/z corresponds very well to the calculated triply charged m/z = 445.2010.

# XI. References

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[11] Frisch, M. J. *et al.*; Gaussian16 Revision B.01. (**2016**).

## XII. Cartesian coordinates of calculated POCs FC1, FC1$_{\mathrm{Lpuffy}}$ and FC1$_{\mathrm{Lcollapsed}}$

### Cartesian coordinates of **FC1** M062X/def2-TZVP

| Symbol | **X** | **Y** | **Z** |
|---|---|---|---|
| C | -26.606.010 | -33.513.990 | 30.932.160 |
| C | -33.208.370 | -38.808.580 | 19.872.950 |
| C | -26.326.480 | -47.291.650 | 11.317.820 |
| C | -12.823.230 | -50.069.570 | 13.347.120 |
| C | -0.6256180 | -44.577.940 | 24.276.430 |
| C | -13.220.090 | -36.445.350 | 33.215.050 |
| C | -0.6729190 | -31.151.430 | 45.365.210 |
| C | -47.217.950 | -35.428.130 | 16.886.000 |
| C | -0.5933080 | -58.820.610 | 0.3696740 |
| N | 0.5652030 | -32.237.690 | 47.514.870 |
| N | -53.314.280 | -26.037.990 | 22.716.090 |
| N | 0.6633850 | -59.509.030 | 0.2845510 |
| C | 12.059.920 | -68.286.980 | -0.7441470 |
| C | 10.726.490 | -27.049.460 | 60.128.380 |
| C | -66.674.310 | -11.151.250 | 0.9218980 |
| C | -65.225.850 | -12.373.680 | -0.4503570 |
| C | -64.534.030 | -0.1670200 | -13.275.350 |
| C | -65.190.170 | 10.890.640 | -0.7461670 |
| C | -66.616.050 | 13.147.230 | 0.6141260 |
| C | -67.183.170 | 0.1811620 | 14.082.840 |
| F | -64.555.870 | -24.720.340 | -0.9657400 |
| F | -64.526.620 | 21.592.510 | -15.485.140 |
| C | -62.997.080 | -0.3504480 | -28.142.810 |
| C | -66.824.310 | 27.037.270 | 11.971.310 |
| C | -66.890.240 | -23.190.730 | 18.265.250 |
| N | -49.072.280 | -0.5941900 | -31.771.640 |
| C | -42.526.580 | 0.3932840 | -36.117.960 |
| C | -28.551.120 | 0.2942960 | -40.760.860 |
| C | -22.526.250 | -0.9398690 | -43.199.810 |
| C | -0.9734650 | -0.9918730 | -48.596.500 |
| C | -0.2945950 | 0.1935400 | -51.367.730 |
| C | -0.8640520 | 14.247.460 | -48.450.580 |
| C | -21.560.100 | 14.679.520 | -43.284.410 |
| C | -0.3101830 | -22.695.720 | -51.783.680 |
| C | -0.0978540 | 26.583.410 | -50.892.250 |
| C | 16.412.470 | -60.100.210 | -19.308.990 |

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|---|---|---|---|
| C | 0.7549270 | -56.755.780 | -29.422.670 |
| C | 10.817.910 | -49.083.720 | -40.475.750 |
| C | 23.901.370 | -44.528.850 | -40.935.550 |
| C | 33.499.100 | -47.330.120 | -31.350.730 |
| C | 29.233.890 | -55.036.610 | -20.643.850 |
| F | -0.5004590 | -61.354.560 | -28.494.240 |
| F | 27.570.840 | -37.008.160 | -51.408.930 |
| C | 47.550.230 | -41.972.260 | -32.222.510 |
| C | 0.0764970 | -45.541.210 | -51.116.000 |
| N | -0.6904070 | -33.784.280 | -47.121.300 |
| C | 20.593.290 | 0.9893030 | 58.212.510 |
| C | 13.525.780 | -0.1917150 | 59.781.740 |
| C | 18.857.790 | -14.567.560 | 57.948.850 |
| C | 32.112.490 | -14.960.690 | 53.912.890 |
| C | 39.922.600 | -0.3706850 | 51.787.200 |
| C | 33.711.570 | 0.8484170 | 53.997.290 |
| F | 40.869.640 | 19.647.980 | 52.072.660 |
| F | 0.0650230 | -0.1000920 | 63.543.570 |
| F | 37.754.110 | -26.919.050 | 52.118.980 |
| C | 54.047.160 | -0.4645950 | 46.641.760 |
| C | 14.305.430 | 23.300.410 | 60.935.980 |
| N | -53.244.350 | 32.335.370 | 12.463.390 |
| C | -25.442.300 | 30.601.370 | 35.550.220 |
| C | -32.897.020 | 35.193.280 | 24.782.240 |
| C | -26.920.580 | 43.725.450 | 15.539.410 |
| C | -13.593.960 | 47.391.940 | 16.919.360 |
| C | -0.6043500 | 42.302.210 | 27.481.620 |
| C | -11.970.610 | 33.937.600 | 36.847.910 |
| C | -0.4423910 | 28.612.110 | 48.338.730 |
| C | -0.7804300 | 56.946.790 | 0.7275530 |
| C | -46.882.210 | 30.842.900 | 23.260.180 |
| C | 0.7592990 | 59.233.620 | -25.956.780 |
| C | 15.016.530 | 62.338.770 | -14.674.440 |
| C | 28.186.420 | 58.027.060 | -14.733.320 |
| C | 33.987.900 | 50.922.630 | -25.134.430 |
| C | 25.704.740 | 48.149.450 | -35.881.150 |
| C | 12.532.520 | 52.329.150 | -36.896.140 |
| F | -0.5179050 | 63.253.450 | -26.396.520 |
| C | 0.4031330 | 49.184.450 | -48.922.890 |
| F | 30.785.980 | 40.994.850 | -46.072.090 |
| C | 48.256.010 | 46.130.220 | -24.535.510 |
| F | 35.816.650 | 61.004.230 | -0.4203550 |
| C | 0.8902580 | 69.474.760 | -0.2911500 |

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|---|---|---|---|
| N | 0.8175020 | 28.737.180 | 48.906.240 |
| C | 52.878.890 | 12.496.730 | 0.1999390 |
| C | 51.623.060 | 11.319.580 | -11.879.110 |
| C | 51.243.050 | -0.1242830 | -17.672.720 |
| C | 52.095.410 | -12.715.240 | -0.9719560 |
| C | 53.396.730 | -11.450.390 | 0.3996860 |
| C | 53.720.510 | 0.1200790 | 0.9935750 |
| C | 54.687.520 | 0.2635400 | 24.569.420 |
| C | 51.533.750 | -26.174.350 | -15.683.720 |
| C | 50.653.100 | 23.354.740 | -20.333.630 |
| N | 53.699.520 | -0.7280080 | 32.313.200 |
| N | 47.947.820 | -28.137.260 | -27.629.680 |
| F | 38.110.300 | -57.865.460 | -11.015.110 |
| F | -68.345.450 | 0.3443890 | 27.342.060 |
| N | -0.4510930 | 37.726.640 | -46.146.970 |
| N | 0.4490470 | 59.771.450 | 0.7035120 |
| N | 49.316.760 | 34.881.670 | -15.382.130 |
| H | -32.109.290 | -27.079.680 | 37.697.930 |
| H | -31.447.440 | -51.595.760 | 0.2770640 |
| H | 0.4212240 | -46.739.220 | 25.977.130 |
| H | -13.447.690 | -26.309.480 | 52.585.320 |
| H | -51.979.210 | -41.380.680 | 0.8983910 |
| H | -12.485.720 | -64.624.830 | -0.2931910 |
| H | 20.695.840 | -73.468.490 | -0.3305450 |
| H | 0.4738290 | -75.731.070 | -10.736.400 |
| H | 0.2662690 | -24.861.310 | 67.199.080 |
| H | 17.166.350 | -34.698.260 | 64.477.090 |
| H | -68.794.900 | -12.190.830 | -31.249.860 |
| H | -66.999.940 | 0.5328310 | -33.199.250 |
| H | -72.776.880 | 33.543.530 | 0.5577110 |
| H | -71.439.590 | 26.679.750 | 21.875.700 |
| H | -72.991.760 | -21.007.600 | 27.017.590 |
| H | -71.317.450 | -31.639.340 | 12.901.200 |
| H | -47.008.620 | 13.929.230 | -36.899.610 |
| H | -27.933.020 | -18.552.520 | -41.167.860 |
| H | 0.7003400 | 0.1511230 | -55.687.310 |
| H | -26.064.670 | 24.341.270 | -41.332.890 |
| H | 0.5559580 | -21.943.560 | -58.498.490 |
| H | 0.8123300 | 25.476.400 | -56.943.120 |
| H | 54.168.560 | -48.405.540 | -26.358.130 |
| H | 50.811.700 | -42.175.840 | -42.615.160 |
| H | 0.6030000 | -43.933.030 | -60.569.080 |
| H | -0.6183070 | -53.833.060 | -52.368.790 |

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|---|---|---|---|
| H | 59.360.150 | 0.4614390 | 49.000.460 |
| H | 59.132.500 | -12.957.260 | 51.511.250 |
| H | 0.7048430 | 22.207.200 | 69.065.000 |
| H | 22.079.760 | 30.228.220 | 64.142.100 |
| H | -30.095.340 | 24.137.440 | 42.925.870 |
| H | -32.871.790 | 47.453.040 | 0.7284750 |
| H | 0.4377460 | 45.048.870 | 28.483.960 |
| H | -10.509.730 | 24.432.810 | 56.476.180 |
| H | -14.946.060 | 61.556.290 | 0.0321760 |
| H | -51.365.030 | 25.945.210 | 32.011.740 |
| H | -0.2389670 | 57.727.080 | -51.059.890 |
| H | 10.539.860 | 47.459.500 | -57.545.090 |
| H | 51.630.140 | 43.594.330 | -34.627.650 |
| H | 54.532.550 | 54.172.440 | -20.681.070 |
| H | 16.426.370 | 75.847.340 | 0.1717560 |
| H | 0.0662220 | 75.751.560 | -0.6430650 |
| H | 53.080.930 | 22.408.420 | 0.6375090 |
| H | 50.240.360 | -0.2407650 | -28.401.220 |
| H | 54.032.010 | -20.200.900 | 10.357.670 |
| H | 56.054.690 | 12.864.270 | 28.317.410 |
| H | 54.285.520 | -34.450.130 | -0.9016120 |
| H | 51.089.210 | 21.683.150 | -31.182.260 |

Cartesian coordinates of **FC1**$_{\mathbf{Lpuffy}}$ M062X/def2-TZVP

| **Symbol** | **X** | **Y** | **Z** |
|---|---|---|---|
| C | 17.011.010 | -28.262.610 | -45.941.190 |
| C | 0.9504410 | -37.943.670 | -39.260.550 |
| C | -0.4076020 | -38.881.560 | -41.903.730 |
| C | -10.249.380 | -30.334.960 | -51.003.710 |
| C | -0.2631490 | -20.742.250 | -57.482.960 |
| C | 11.035.650 | -19.659.960 | -55.045.580 |
| C | 19.020.020 | -0.8772390 | -61.681.720 |
| C | 15.814.640 | -47.171.930 | -29.129.300 |
| C | -25.098.200 | -31.353.740 | -53.253.540 |
| N | 17.535.050 | 0.3720080 | -54.295.610 |
| N | 29.976.580 | -49.232.790 | -31.720.090 |
| N | -32.172.680 | -27.789.020 | -41.040.200 |
| C | -46.661.030 | -28.480.520 | -42.317.480 |
| C | 24.969.470 | 14.712.900 | -60.322.260 |
| C | 37.609.520 | -53.575.710 | -0.8834420 |
| C | 29.556.740 | -57.529.590 | 0.1705130 |
| C | 30.980.930 | -53.038.870 | 14.773.810 |

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|---|---|---|---|
| C | 41.084.690 | -43.815.810 | 16.864.620 |
| C | 49.654.030 | -39.169.450 | 0.6971790 |
| C | 47.459.040 | -44.294.070 | -0.5700260 |
| F | 19.898.320 | -66.478.580 | -0.0743490 |
| F | 42.952.420 | -39.288.760 | 29.325.260 |
| C | 22.256.380 | -57.961.010 | 25.951.850 |
| C | 60.625.420 | -29.371.760 | 0.9966480 |
| C | 36.110.350 | -58.983.720 | -22.811.770 |
| N | 0.9910650 | -50.264.610 | 26.974.070 |
| C | 0.2220260 | -54.227.940 | 38.717.220 |
| C | -10.266.080 | -45.972.450 | 40.259.130 |
| C | -21.393.990 | -48.444.240 | 32.290.950 |
| C | -33.094.040 | -41.132.720 | 33.896.990 |
| C | -33.452.610 | -30.972.900 | 43.397.010 |
| C | -22.421.140 | -28.185.070 | 51.352.140 |
| C | -10.905.610 | -35.824.820 | 49.737.020 |
| C | -45.259.610 | -43.986.730 | 25.518.210 |
| C | -22.747.710 | -16.992.480 | 61.386.910 |
| C | -52.969.100 | -23.948.510 | -29.470.630 |
| C | -53.185.950 | -32.106.830 | -18.238.100 |
| C | -58.107.350 | -28.224.250 | -0.5892940 |
| C | -62.863.240 | -15.215.540 | -0.5168200 |
| C | -63.212.320 | -0.6360070 | -15.799.880 |
| C | -58.047.730 | -11.186.870 | -27.747.880 |
| F | -48.504.400 | -44.541.560 | -19.494.060 |
| F | -67.423.850 | -10.937.510 | 0.6741630 |
| C | -68.217.710 | 0.7723760 | -14.444.030 |
| C | -57.865.900 | -37.278.370 | 0.6072370 |
| N | -45.351.120 | -35.860.150 | 13.410.870 |
| C | 34.128.520 | 41.758.260 | -34.781.180 |
| C | 34.621.660 | 30.851.050 | -43.374.310 |
| C | 24.198.500 | 26.874.600 | -51.554.530 |
| C | 12.635.010 | 34.531.180 | -50.688.580 |
| C | 11.152.080 | 45.549.150 | -42.449.190 |
| C | 22.170.780 | 48.711.920 | -34.602.740 |
| F | 21.139.430 | 59.281.930 | -26.446.120 |
| F | 46.013.110 | 23.830.310 | -43.788.070 |
| F | 0.2311270 | 31.058.390 | -58.465.670 |
| C | -0.1640740 | 53.359.720 | -41.683.460 |
| C | 45.681.380 | 45.249.690 | -25.858.620 |
| N | 55.428.270 | -15.856.930 | 11.686.250 |
| C | 61.334.320 | 16.897.110 | 0.4828220 |
| C | 60.956.360 | 0.7754470 | 15.246.190 |

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|---|---|---|---|
| C | 55.581.140 | 11.669.510 | 27.493.300 |
| C | 50.979.720 | 24.594.190 | 29.449.510 |
| C | 51.585.580 | 33.649.140 | 18.860.990 |
| C | 56.644.920 | 29.908.000 | 0.6507380 |
| C | 56.761.440 | 39.519.310 | -0.5061610 |
| C | 45.110.350 | 28.872.790 | 42.616.250 |
| C | 66.233.300 | -0.6217640 | 13.410.740 |
| C | 0.2942170 | 20.127.430 | 59.476.020 |
| C | 0.9573690 | 31.065.940 | 54.147.060 |
| C | 0.1520600 | 40.499.880 | 47.978.770 |
| C | -12.292.000 | 39.696.820 | 47.150.570 |
| C | -17.961.480 | 28.387.670 | 52.802.490 |
| C | -10.801.660 | 18.381.690 | 59.187.690 |
| F | 10.284.340 | 10.632.090 | 65.445.760 |
| C | -17.320.980 | 0.6245870 | 65.138.550 |
| F | -31.296.270 | 27.130.850 | 52.148.080 |
| C | -20.578.900 | 50.196.750 | 40.341.320 |
| F | 0.7524760 | 51.195.810 | 42.565.000 |
| C | 24.501.430 | 32.507.900 | 54.655.470 |
| N | 46.204.040 | 36.109.480 | -14.516.200 |
| C | -27.170.820 | 55.813.860 | -0.5229920 |
| C | -34.793.010 | 52.317.690 | 0.5801160 |
| C | -46.038.670 | 44.269.740 | 0.3958560 |
| C | -49.625.590 | 39.728.940 | -0.8636210 |
| C | -41.864.950 | 43.470.980 | -19.589.060 |
| C | -30.729.170 | 51.579.170 | -18.029.890 |
| C | -22.565.500 | 55.834.460 | -29.941.100 |
| C | -61.476.210 | 30.659.610 | -10.521.720 |
| C | -31.059.890 | 56.847.160 | 19.649.070 |
| N | -0.9544090 | 49.288.380 | -30.116.140 |
| N | -57.054.810 | 16.983.630 | -12.968.620 |
| F | -58.037.430 | -0.2914310 | -38.277.700 |
| F | 55.549.090 | -40.310.380 | -15.600.270 |
| N | -18.261.470 | -0.4496760 | 55.321.490 |
| N | 30.683.970 | 26.683.940 | 42.815.440 |
| N | -22.489.290 | 47.039.770 | 26.241.260 |
| H | 27.631.700 | -27.483.190 | -43.906.210 |
| H | -10.104.750 | -46.278.630 | -36.740.640 |
| H | -0.7337440 | -13.915.970 | -64.481.420 |
| H | 15.289.680 | -0.7059630 | -71.817.170 |
| H | 29.544.120 | -11.857.580 | -62.570.240 |
| H | 14.834.010 | -42.782.410 | -19.141.450 |
| H | 10.183.810 | -56.621.040 | -28.894.200 |

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|---|---|---|---|
| H | -27.998.330 | -25.105.760 | -61.830.210 |
| H | -27.813.930 | -41.663.630 | -55.727.830 |
| H | 20.562.690 | 0.2343630 | -44.704.230 |
| H | 31.236.720 | -52.215.260 | -41.329.390 |
| H | -29.382.300 | -18.494.900 | -38.067.180 |
| H | -50.548.810 | -22.461.070 | -50.627.090 |
| H | -49.357.530 | -38.889.180 | -44.240.640 |
| H | 35.503.760 | 12.244.570 | -62.146.580 |
| H | 20.394.010 | 16.913.420 | -69.997.040 |
| H | 19.531.630 | -68.358.080 | 24.033.030 |
| H | 28.057.470 | -57.763.090 | 35.276.390 |
| H | 65.480.830 | -32.225.460 | 19.331.630 |
| H | 68.198.260 | -29.993.250 | 0.2047560 |
| H | 46.042.480 | -61.246.770 | -26.702.860 |
| H | 30.461.460 | -68.375.020 | -22.307.660 |
| H | 12.053.800 | -40.353.380 | 27.489.440 |
| H | -0.0477080 | -64.750.850 | 37.435.520 |
| H | 0.8174120 | -53.564.060 | 47.952.270 |
| H | -20.946.390 | -56.292.690 | 24.818.460 |
| H | -42.557.840 | -25.213.120 | 44.740.090 |
| H | -0.2329090 | -33.953.390 | 56.134.440 |
| H | -45.309.440 | -54.486.420 | 22.479.230 |
| H | -54.290.010 | -42.347.390 | 31.608.620 |
| H | -32.963.900 | -15.475.340 | 64.970.240 |
| H | -16.628.480 | -19.713.870 | 70.126.360 |
| H | -75.283.620 | 0.8243910 | -0.6060830 |
| H | -73.667.100 | 10.505.110 | -23.491.890 |
| H | -66.647.060 | -35.189.880 | 12.338.620 |
| H | -58.627.380 | -47.640.560 | 0.2734480 |
| H | -43.847.510 | -26.120.760 | 15.847.700 |
| H | 0.0678670 | 63.971.380 | -40.540.190 |
| H | -0.7105100 | 52.190.230 | -51.130.230 |
| H | 55.015.350 | 44.159.660 | -31.428.570 |
| H | 44.864.370 | 55.762.360 | -22.823.050 |
| H | 49.790.800 | -13.255.070 | 0.3654810 |
| H | 65.380.310 | 13.955.070 | -0.4802110 |
| H | 55.063.060 | 0.4488660 | 35.606.080 |
| H | 48.125.970 | 43.836.660 | 20.358.380 |
| H | 55.886.200 | 49.834.180 | -0.1332140 |
| H | 66.287.300 | 38.833.980 | -10.395.790 |
| H | 49.489.730 | 23.035.580 | 50.754.070 |
| H | 47.655.350 | 39.427.260 | 44.466.240 |
| H | 71.838.420 | -0.9196840 | 22.319.370 |

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|---|---|---|---|
| H | 73.309.300 | -0.6375040 | 0.4984020 |
| H | -11.676.460 | 0.3226950 | 74.067.440 |
| H | -27.435.070 | 0.8780740 | 68.364.060 |
| H | -30.107.780 | 51.262.320 | 45.708.330 |
| H | -15.409.740 | 59.788.090 | 40.953.150 |
| H | 27.016.860 | 43.134.280 | 55.879.950 |
| H | 28.332.920 | 27.219.970 | 63.398.970 |
| H | 37.250.980 | 36.039.680 | -0.9730730 |
| H | -18.337.460 | 61.976.670 | -0.3952660 |
| H | -52.156.830 | 41.628.050 | 12.537.360 |
| H | -44.675.640 | 39.988.070 | -29.473.230 |
| H | -28.291.780 | 53.958.930 | -39.146.680 |
| H | -20.766.160 | 66.617.560 | -29.467.350 |
| H | -68.130.590 | 31.401.680 | -0.1788690 |
| H | -67.267.520 | 33.841.180 | -19.239.560 |
| H | -25.570.660 | 66.285.720 | 19.154.870 |
| H | -40.247.230 | 58.744.120 | 25.420.600 |
| H | -10.807.400 | 39.214.730 | -30.180.510 |
| H | -51.035.260 | 13.958.200 | -0.5375690 |
| H | -0.9216640 | -0.5944360 | 50.940.680 |
| H | 26.534.760 | 30.674.270 | 34.452.230 |
| H | -26.576.660 | 37.792.730 | 25.314.410 |

Cartesian coordinates of **FC1$_{\mathbf{Lcollapsed}}$** M062X/def2-TZVP

| **Symbol** | **X** | **Y** | **Z** |
|---|---|---|---|
| C | -49.164.620 | 25.616.140 | -21.142.810 |
| C | -38.460.630 | 31.017.780 | -28.165.440 |
| C | -26.100.320 | 24.693.750 | -27.452.770 |
| C | -24.192.760 | 13.451.360 | -19.493.470 |
| C | -35.086.130 | 0.8141870 | -12.711.090 |
| C | -47.630.070 | 14.086.490 | -13.559.800 |
| C | -59.342.860 | 0.7504070 | -0.6832240 |
| C | -40.543.330 | 43.586.270 | -36.314.850 |
| C | -10.417.250 | 0.7534700 | -17.616.070 |
| N | -65.382.240 | -0.2234490 | -15.944.160 |
| N | -43.536.810 | 55.211.390 | -27.898.800 |
| N | -10.213.970 | -0.6936340 | -19.131.210 |
| C | -0.9742810 | -11.891.680 | -32.905.880 |
| C | -73.626.290 | -12.239.090 | -0.9305760 |
| C | -21.408.760 | 56.950.680 | -17.226.220 |
| C | -10.005.010 | 51.818.160 | -23.070.590 |

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|---|---|---|---|
| C | 0.0016720 | 44.961.320 | -16.356.090 |
| C | -0.1690170 | 43.872.370 | -0.2671260 |
| C | -12.656.660 | 48.898.480 | 0.4267450 |
| C | -22.312.440 | 55.137.580 | -0.3472310 |
| F | -0.8508420 | 53.172.700 | -36.398.630 |
| F | 0.7925970 | 37.826.800 | 0.4390240 |
| C | 11.709.930 | 39.092.610 | -23.933.510 |
| C | -13.510.620 | 48.226.500 | 19.256.920 |
| C | -32.156.070 | 63.915.880 | -25.151.780 |
| N | 22.472.030 | 48.420.970 | -27.001.190 |
| C | 30.892.200 | 51.760.560 | -15.624.930 |
| C | 39.882.390 | 40.179.470 | -11.792.830 |
| C | 43.252.970 | 30.468.130 | -21.137.570 |
| C | 51.294.980 | 19.685.900 | -17.635.840 |
| C | 56.280.220 | 18.778.630 | -0.4719130 |
| C | 53.179.730 | 28.493.780 | 0.4741670 |
| C | 44.906.520 | 39.069.990 | 0.1127820 |
| C | 53.270.890 | 0.8560270 | -27.572.000 |
| C | 58.027.510 | 27.039.280 | 19.021.950 |
| C | 0.3323490 | -18.749.580 | -36.107.620 |
| C | 15.202.860 | -11.645.400 | -36.544.450 |
| C | 27.772.340 | -17.102.990 | -38.561.140 |
| C | 27.779.960 | -30.789.150 | -40.736.250 |
| C | 16.507.450 | -38.840.140 | -40.866.820 |
| C | 0.4492410 | -32.396.220 | -38.382.480 |
| F | 14.350.570 | 0.1742400 | -34.959.220 |
| F | 39.614.530 | -36.845.260 | -42.860.030 |
| C | 17.750.920 | -53.783.810 | -43.258.630 |
| C | 40.324.420 | -0.8754700 | -38.821.210 |
| N | 41.466.270 | -0.0103310 | -27.139.780 |
| C | -57.607.740 | -25.141.740 | 23.128.270 |
| C | -65.559.610 | -18.278.530 | 14.087.250 |
| C | -65.900.450 | -20.820.230 | 0.0481180 |
| C | -57.547.410 | -31.005.240 | -0.3839760 |
| C | -49.386.520 | -38.633.640 | 0.4350230 |
| C | -49.748.440 | -35.212.750 | 17.777.600 |
| F | -41.788.130 | -42.012.980 | 26.235.060 |
| F | -73.219.930 | -0.8341250 | 18.816.700 |
| F | -57.289.120 | -33.618.120 | -17.039.950 |
| C | -40.596.070 | -49.692.810 | -0.1135600 |
| C | -56.204.970 | -20.783.290 | 37.417.310 |
| N | -14.923.650 | 34.617.440 | 24.284.130 |
| C | -28.966.890 | 14.075.610 | 45.984.620 |

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|---|---|---|---|
| C | -16.879.010 | 20.775.870 | 44.541.850 |
| C | -0.5109020 | 14.437.330 | 48.396.610 |
| C | -0.5333900 | 0.1641290 | 53.809.420 |
| C | -17.545.800 | -0.4880950 | 55.132.180 |
| C | -29.405.760 | 0.1207700 | 51.231.890 |
| C | -42.329.430 | -0.6466400 | 51.602.460 |
| C | 0.7405860 | -0.5040510 | 58.271.280 |
| C | -16.480.590 | 34.682.500 | 38.806.240 |
| C | 50.534.680 | -0.1252540 | 41.273.290 |
| C | 40.231.660 | -10.521.130 | 41.185.270 |
| C | 39.803.790 | -18.897.920 | 30.159.640 |
| C | 48.924.620 | -18.685.710 | 19.739.470 |
| C | 59.073.900 | -0.9325800 | 20.977.070 |
| C | 60.276.820 | -0.0292520 | 31.452.550 |
| F | 51.077.560 | 0.7339970 | 51.562.420 |
| C | 71.068.930 | 10.242.490 | 31.652.010 |
| F | 68.434.410 | -0.9104310 | 11.380.880 |
| C | 47.689.690 | -27.503.190 | 0.7481150 |
| F | 29.785.510 | -27.854.870 | 29.618.490 |
| C | 29.856.280 | -11.240.960 | 52.004.900 |
| N | -45.350.760 | -11.073.750 | 38.097.050 |
| C | 0.4587750 | -29.697.180 | 0.1051610 |
| C | 17.835.250 | -30.177.640 | -0.3381990 |
| C | 22.200.250 | -41.440.180 | -10.137.020 |
| C | 13.487.430 | -51.943.340 | -12.961.770 |
| C | 0.0313960 | -51.100.990 | -0.8797380 |
| C | -0.4269200 | -40.025.730 | -0.1658860 |
| C | -18.562.460 | -39.672.010 | 0.3287160 |
| C | 18.315.260 | -63.991.220 | -20.806.030 |
| C | 26.915.870 | -18.179.230 | -0.1558370 |
| N | -27.659.210 | -45.674.120 | -0.6339980 |
| N | 25.198.090 | -61.357.940 | -33.346.860 |
| F | -0.6702710 | -39.779.190 | -38.227.600 |
| F | -33.102.880 | 60.141.130 | 0.2658290 |
| N | 69.934.770 | 18.781.450 | 19.939.740 |
| N | 17.842.950 | -0.3930580 | 48.183.100 |
| N | 40.881.720 | -21.285.970 | -0.3744480 |
| H | -58.864.000 | 30.446.400 | -21.648.190 |
| H | -17.728.240 | 28.660.660 | -33.114.860 |
| H | -33.702.470 | -0.0790550 | -0.6688700 |
| H | -66.948.030 | 14.877.890 | -0.4138080 |
| H | -55.823.210 | 0.2879010 | 0.2486270 |
| H | -31.802.900 | 45.353.680 | -42.701.410 |

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|---|---|---|---|
| H | -49.062.370 | 42.001.490 | -42.955.830 |
| H | -0.7088330 | 0.9806850 | -0.7443050 |
| H | -0.3469650 | 12.598.490 | -24.437.040 |
| H | -58.087.700 | -0.6813120 | -21.303.150 |
| H | -50.899.340 | 60.737.730 | -32.063.270 |
| H | -0.2835680 | -11.135.530 | -13.655.570 |
| H | -17.899.340 | -18.876.810 | -34.770.010 |
| H | -11.155.740 | -0.3446310 | -39.714.790 |
| H | -81.698.770 | -0.7153670 | -0.4037610 |
| H | -78.120.230 | -18.583.690 | -16.936.630 |
| H | 0.7983230 | 34.929.470 | -33.310.230 |
| H | 15.908.360 | 30.835.830 | -18.175.870 |
| H | -0.4207210 | 52.206.920 | 23.412.780 |
| H | -21.608.530 | 54.822.290 | 22.616.140 |
| H | -35.808.770 | 72.399.880 | -19.356.260 |
| H | -27.577.910 | 67.813.110 | -34.326.920 |
| H | 18.787.360 | 56.751.550 | -31.393.620 |
| H | 25.146.430 | 54.817.730 | -0.6756770 |
| H | 37.079.010 | 60.300.230 | -18.491.230 |
| H | 39.321.100 | 31.309.480 | -31.210.400 |
| H | 62.615.160 | 10.483.840 | -0.1837650 |
| H | 42.211.880 | 46.529.130 | 0.8550750 |
| H | 54.790.580 | 12.775.040 | -37.620.320 |
| H | 62.115.480 | 0.2633140 | -25.096.620 |
| H | 50.094.880 | 22.147.270 | 24.759.710 |
| H | 59.321.890 | 36.967.220 | 23.510.920 |
| H | 22.601.920 | -55.242.640 | -52.930.760 |
| H | 0.7755790 | -58.070.030 | -43.981.420 |
| H | 48.942.890 | -15.427.480 | -39.004.950 |
| H | 40.552.710 | -0.2952140 | -48.181.590 |
| H | 33.306.950 | 0.5868380 | -26.553.350 |
| H | -38.894.420 | -56.999.660 | 0.6780780 |
| H | -46.004.670 | -54.742.940 | -0.9134100 |
| H | -65.390.720 | -15.935.180 | 40.743.950 |
| H | -54.502.370 | -29.519.050 | 43.843.780 |
| H | -22.921.830 | 30.097.150 | 19.957.930 |
| H | -38.213.250 | 18.860.450 | 42.910.180 |
| H | 0.4405400 | 19.484.950 | 47.168.020 |
| H | -17.822.600 | -14.924.770 | 59.239.290 |
| H | -41.492.130 | -14.780.920 | 58.756.370 |
| H | -50.554.520 | -0.0085270 | 54.951.470 |
| H | 11.127.110 | -0.0202590 | 67.366.200 |
| H | 0.5249100 | -15.497.400 | 60.932.920 |

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|---|---|---|---|
| H | -0.7872710 | 40.007.640 | 42.928.850 |
| H | -25.463.050 | 40.215.160 | 41.949.540 |
| H | 70.505.490 | 15.647.270 | 41.166.370 |
| H | 80.822.700 | 0.5360200 | 31.205.070 |
| H | 57.660.280 | -30.474.230 | 0.4252540 |
| H | 42.250.520 | -36.569.350 | 10.182.980 |
| H | 27.763.530 | -21.797.970 | 54.230.570 |
| H | 33.811.390 | -0.6707290 | 61.101.800 |
| H | -36.964.850 | -15.107.740 | 34.036.710 |
| H | 0.1122760 | -21.017.780 | 0.6615300 |
| H | 32.471.580 | -41.695.120 | -13.613.780 |
| H | -0.6693410 | -59.008.760 | -11.189.010 |
| H | -19.243.510 | -45.601.400 | 12.464.210 |
| H | -21.250.990 | -29.357.880 | 0.6001640 |
| H | 25.130.080 | -69.864.820 | -14.601.290 |
| H | 0.9734510 | -70.405.710 | -22.978.340 |
| H | 24.961.030 | -13.646.570 | 0.8279900 |
| H | 24.172.590 | -10.624.130 | -0.8985760 |
| H | -28.623.640 | -39.766.100 | -14.522.990 |
| H | 34.357.280 | -57.342.950 | -31.847.840 |
| H | 78.358.760 | 24.155.750 | 18.477.420 |
| H | 14.357.670 | -0.7499620 | 39.336.800 |
| H | 45.740.140 | -13.211.950 | -0.7472950 |