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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. 1,3,5-Tris(methylamino)-2,4,6-triethylbenzene, 1,1′-diformylferrocene, tris(4-aminophenyl)amine and 1,1′-bis(4-formylphenyl)ferrocene were prepared according to the literature.[S1-4] 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, a Bruker Avance DRX 500 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: $\delta(CDCl_3)$ = 7.26 ppm; $^{13}C\{^{1}H\}$: $\delta(CDCl_3)$ = 77.16 ppm). Splitting patterns are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), quintet (p), heptet (hept), multiplet (m), and broad (br). ^{1}H DOSY (Diffusion Ordered Spectroscopy) NMR experiments were performed using a stimulated echo sequence incorporating bipolar gradient pulses and with convection compensation. The gradient strength was logarithmically incremented in 20 steps from 25% up to 95% of the maximum gradient strength.

IR

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

TOF-HRMS(ESI)

ESI-HRMS (TOF) measurements were performed with a Q-Exactive ThermoScientific spectrometer.

Ball Milling

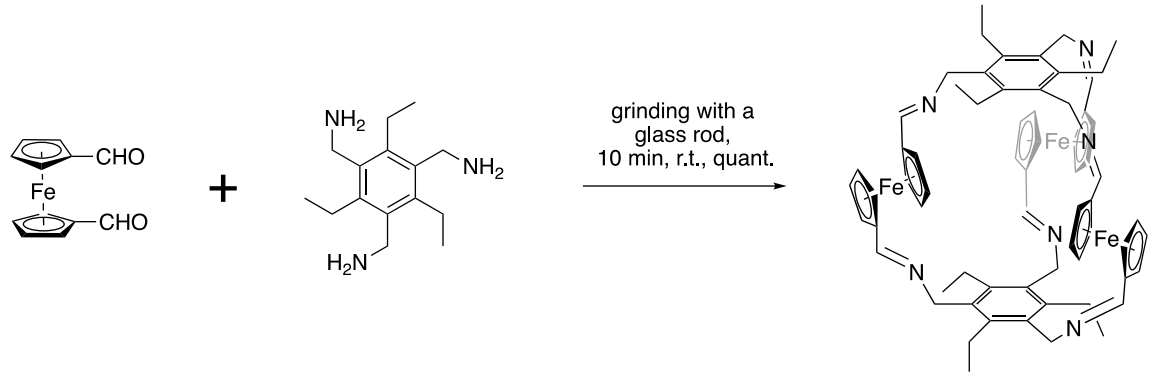
Ball milling experiments were conducted using a MM400 (Retsch GmbH, Haan, Deutschland) with 5x Ø 3 mm steel balls.

PXRD

PXRD measurements were obtained using a Rigaku Miniflex 600 (Rigaku Americas Holding Company Inc., Texas, USA) with Cu-Kα radiation (40 kV, 15mA).

II. Experimental details

Synthesis of FcC1

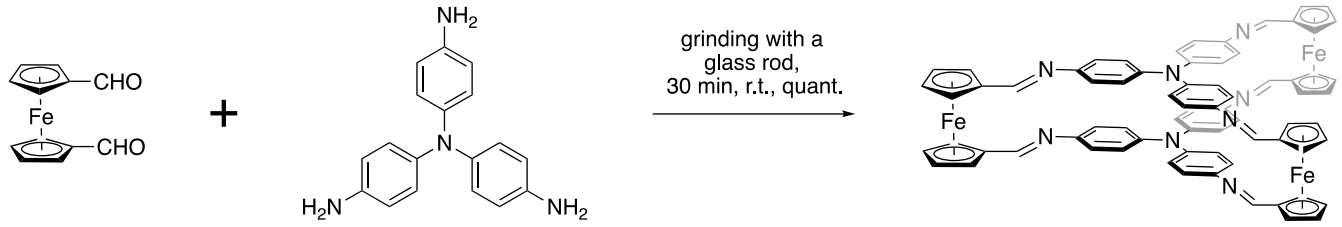


1,1′-Diformylferrocene (36.30 mg, 0.15 mmol, 1.50 eq.) and 1,3,5-triethyl-2,4,6-tris(aminomethyl)benzene (24.9 mg, 0.10 mmol, 1.00 eq) were added to a reaction tube (Ø 1 cm, length 10 cm). Both dry powders were ground by hand, using a glass rod (Ø 0.7 cm) for 10 minutes. During the grinding process, the mixture became sticky. To be able to continue grinding, residues from the side wall of the tube were scraped off with a spatula in regular intervals. After 10 minutes of grinding, the resulting dark red glue-like substance was dissolved in $CDCl_3$ and was subjected to NMR analysis immediately.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (s, 6H, C**H**N), 4.73 (s, 12H, C**H$_2$**-NCH), 4.67 (s, 12H, **H$_{Fc}$**), 4.34–4.20 (m, 12H, **H$_{Fc}$**), 2.63 (d, *J* = 7.6 Hz, 12H, C_{Ar}-C**H$_2$**-CH_3), 1.27 (t, *J* = 7.4 Hz, 18H, C_{Ar}-CH_2-C**H$_3$**); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 159.9 (s, C_{Fc}-**C**HN), 143.6 (s, **C$_{Ar}$**-CH_2-N), 132.5 (s, **C$_{Ar}$**-CH_2-CH_3), 81.8 (s, **C$_{Fc}$**-CHN), 72.5 (s, **C$_{Fc}$**-H), 68.7 (s, **C$_{Fc}$**-H), 56.0 (s, **C**H_2-N) 23.5 (s, C_{Ar}-**C**H_2-CH_3), 16.2 (s, C_{Ar}-CH_2-**C**H_3); **HR-MS (MALDI)**: calc. for $[C_{66}H_{72}Fe_3N_6+H]^+$ = 1117.394 m/z, found: 1117.423 m/z; **TOF-HRMS (ESI)**: calc. for $[C_{66}H_{72}Fe_3N_6+H]^+$ = 1117.3940 m/z, found: 1117.3917 m/z; **FT-IR (ATR)**: $\tilde{\nu}$(cm^{-1}) = 2975 (w), 2914 (w), 2874 (w), 1684 (s), 1657 (s), 1625 (s), 1454 (m), 1366 (m), 1235 (s), 1036 (m), 824 (s), 736 (s).

Synthesis of FcC2

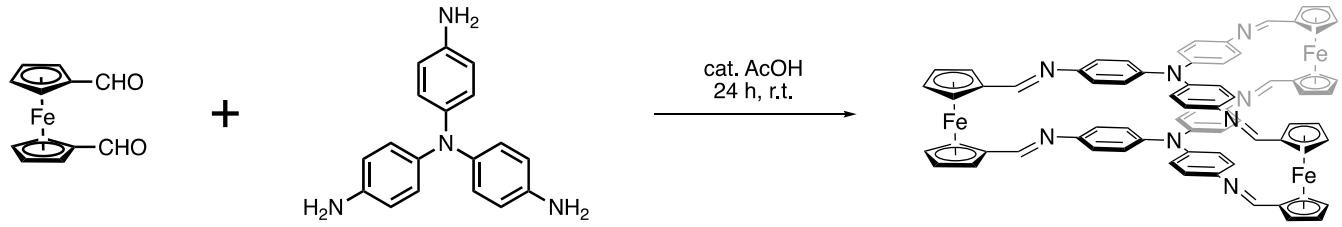
a) *via* grinding



1,1′-Diformylferrocene (36.30 mg, 0.15 mmol, 1.50 eq.) and tris(4-aminophenyl)amine (29.0 mg, 0.10 mmol, 1.00 eq.) were added to a reaction tube (Ø 1 cm, length 10 cm). Both dry powders were then ground using a glass rod (Ø 0.7 cm) for 30 minutes by hand. During the grinding process, residues from the side wall of the tube were scraped off with a spatula in regular intervals. After 30 minutes of grinding, the resulting dark orange-red solid was dissolved in $CDCl_3$ and was subjected to NMR analysis immediately.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.19 (s, 6H, C**H**N), 6.93-6.90 (m, 12H, Ar-**H**), 6.85–6.82 (m, 12H, Ar-**H**), 4.99–4.98 (t, J = 1.9 Hz, 12H, $\mathbf{H_{Fc}}$), 4.47–4.46 (t, J = 1.9 Hz, 12H, $\mathbf{H_{Fc}}$); **^{13}C{^{1}H} NMR** (75 MHz, $CDCl_3$): δ 157.9 (s, C_{Fc}-**C**HN), 146.1 (s, $\mathbf{C_{Ar}}$), 144.9 (s, $\mathbf{C_{Ar}}$), 124.2 (s, $\mathbf{C_{Ar}}$), 122.6 (s, $\mathbf{C_{Ar}}$), 122.0 (s, $\mathbf{C_{Ar}}$), 121.9 (s, $\mathbf{C_{Ar}}$), 83.6 (s, $\mathbf{C_{Fc}}$-Ar), 71.2 (s, $\mathbf{C_{Fc}}$-H), 69.5 (s, $\mathbf{C_{Fc}}$-H); **FT-IR (ATR):** $\tilde{\nu}$(cm^{-1}) = 3070 (w), 3010 (w), 2970 (w), 2880 (w), 1630 (s), 1506 (s), 1472 (m), 1310 (m), 1268 (m), 1036 (w), 840 (s); **TOF-HRMS (ESI):** calc. for $[C_{72}H_{54}Fe_3N_8+H]^+$ = 1199.2593 m/z, found: 1199.2582 m/z.

b) *via* solution-based synthesis

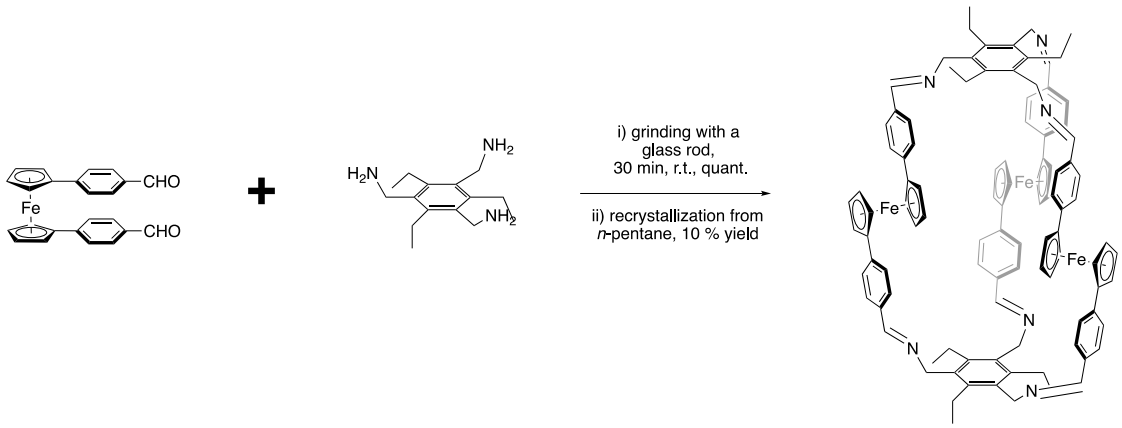


1,1′-Diformylferrocene (14.5 mg, 0.06 mmol) and tris(4-aminophenyl)amine (11.6 mg, 0.04 mmol) were dissolved in EtOH (99.8%; 15 mL). Glacial acetic acid (30 µL) was added, and the

reaction mixture was stirred at room temperature for 24 hours. The formed solid was filtered off, washed with MeOH, and dried at room temperature for 24 hours, to give the cage product as orange-red solid (22.6 mg; 94%).

Mp: >300 °C; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 8.19 (s, 6H; CH=N), 6.93–6.90 (m, 12H; Ar-H), 6.85–6.82 (m, 12 H; Ar-H), 4.99–4.98 (t-like m, *J* = 1.9 Hz, 12 H; H-Cp), 4.47–4.46 (t-like m, *J* = 1.9 Hz, 12 H; H-Cp);**^{13}C{^{1}H} NMR** (125 MHz, CDCl3): δ 157.9 (s, C_{Fc}-**C**HN), 146.1 (s, **C_{Ar}**), 144.9 (s, **C_{Ar}**), 124.2 (s, **C_{Ar}**), 122.6 (s, **C_{Ar}**), 122.0 (s, **C_{Ar}**), 121.9 (s, **C_{Ar}**), 83.6 (s, **C_{Fc}**-Ar), 71.2 (s, **C_{Fc}**-H), 69.5 (s, **C_{Fc}**-H); **ESI-HRMS** (TOF): calc. for $[C_{72}H_{54}Fe_3N_8+H]^+$ = 1198.2514 m/z, found: 1198.2512 m/z.

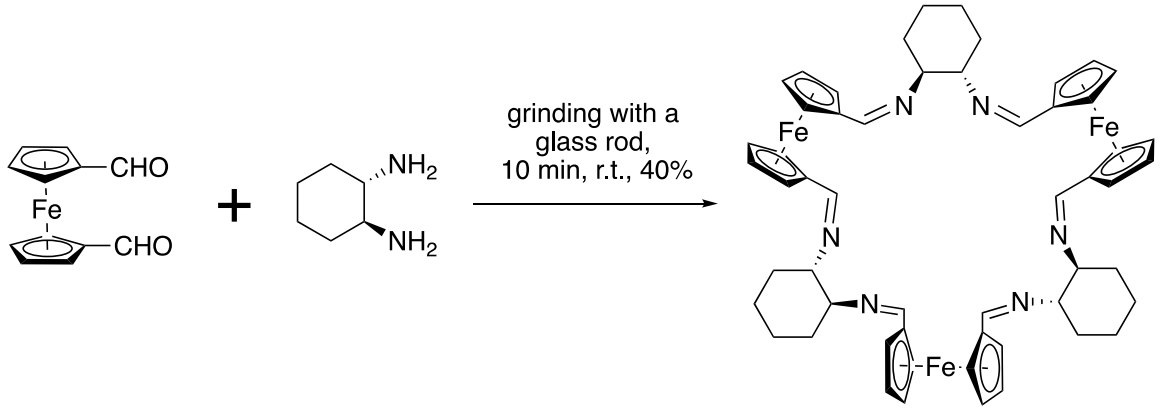
Synthesis of FcC3



1,1′-Bis(4-formylphenyl)ferrocene (29.57 mg, 0.08 mmol, 1.50 eq.) and 1,3,5-triethyl-2,4,6-tris(aminomethyl)benzene (12.45 mg, 0.05 mmol, 1.00 eq.) were added to a reaction tube (Ø 1 cm, length 10 cm). Both dry powders were then ground using a glass rod (Ø 0.7 cm) for 30 minutes by hand. During the grinding process, the mixture became sticky. In order to be able to continue to grind, residues from the side wall of the tube were scraped off with a spatula in regular intervals. After 30 minutes, the resulting mixture was dissolved in $CHCl_3$ (1 mL) and filtered through a syringe filter (pore Ø: 0.45 µm) into a 2.5 mL vial. This vial was then transferred into a larger vial (25 mL) filled with 10 mL of *n*-pentane. The larger vial was sealed and put into the refrigerator (4°C) for 16 hours. Red brick-like crystals formed on the side walls of the smaller vial, which could be isolated after decantation of the supernatant, yielding **FcC3** (4 mg, 0.03 mmol, 10%).

^{1}H NMR(300 MHz, $CDCl_3$): δ 7.98 (s, 6H, C**H**=N), 7.57 (d, *J* = 7.9 Hz, 12H, C$\mathbf{H}_{\mathbf{Aryl}}$-C-Fc), 7.41 (d, *J* = 8.0 Hz, 12H, C$\mathbf{H}_{\mathbf{Aryl}}$-C-CHN), 5.06–5.00 (m, 12H,C$\mathbf{H_2}$-N=CH), 4.62 (t, *J* = 1.9 Hz, 12H, $\mathbf{H}_{\mathbf{Fc}}$), 4.07 (t, *J* = 1.8 Hz, 12H, $\mathbf{H}_{\mathbf{Fc}}$), 2.67–2.56 (m, 12H, C$\mathbf{H_2}$-CH_3), 1.30 (t, *J* = 7.4 Hz, 18H, -C$\mathbf{H_3}$); due to the very low solubility in common NMR solvents, no meaningful $^{13}C\{^1H\}$ NMR and even DOSY spectra could be obtained. This structure, as any new structure reported herein, was additionally assigned by SC-XRD; **FT-IR (ATR):** $\tilde{\nu}$(cm-1) = 3088 (w), 2963 (m), 2928 (w), 2869 (w), 2830 (w), 2365 (w), 2356 (w), 2339 (w), 1636 (s), 1605 (s), 1562 (w), 1525 (w), 1314 (w), 1300 (w), 1175 (w), 825 (m), 754 (m); **HRMS (ESI):** calc. for $[C_{102}H_{94}Fe_3N_6+3H]^{3+}$ = 524.8614 m/z, found: 524.8616 m/z.

Synthesis of FcM1

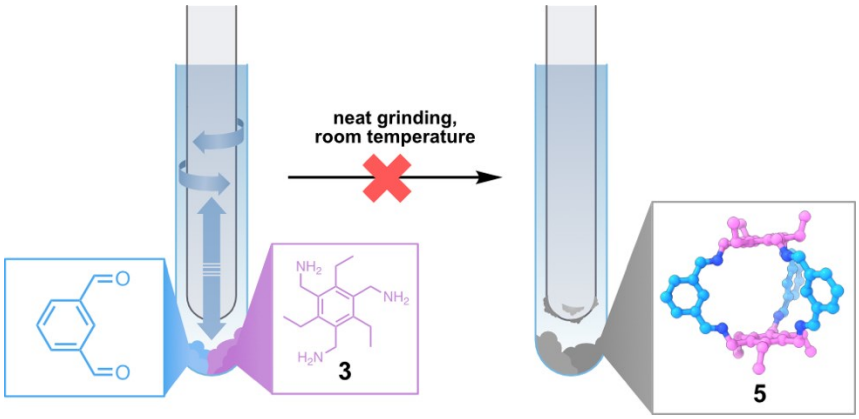


1,1'-Diformylferrocene (29.07 mg, 0.12 mmol, 1.00 eq.) and (1R,2R)-(−)-1,2-diaminocyclohexane (13.70 mg, 0.12 mmol, 1.00 eq) were added to a reaction tube (Ø 1 cm, length 10 cm). Both dry powders were then ground using a glass rod (Ø 0.7 cm) for 10 minutes. During the grinding process, the mixture became sticky. In order to be able to continue to grind, residues from the side wall of the tube were scraped off with a spatula in regular intervals. After 10 minutes of grinding, the resulting dark red glue-like substance was dissolved in chloroform (0.10 mL) and the resulting mixture was filtered. The deep red solution was then poured into hexane (20 mL). The resulting orange precipitate was filtered off to yield **FcM1** as a light-orange powder (15.00 mg, 0.02 mmol, 40%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 6H, C**H**=N), 4.53–4.33 (m, 12H, $\mathbf{H_{Fc}}$), 4.05–3.92 (m, 12H, $\mathbf{H_{Fc}}$), 3.42 (s, 6H, C**H**-N=CH), 2.31 (s, 12H, $\mathbf{H_{cyclohexyl}}$), 1.94–1.66 (m, 12H, $\mathbf{H_{cyclohexyl}}$); **HR-MS (MALDI)**: calc. for $[C_{54}H_{60}Fe_3N_6+H]^+$ = 961.300 m/z, found: 961.304 m/z.

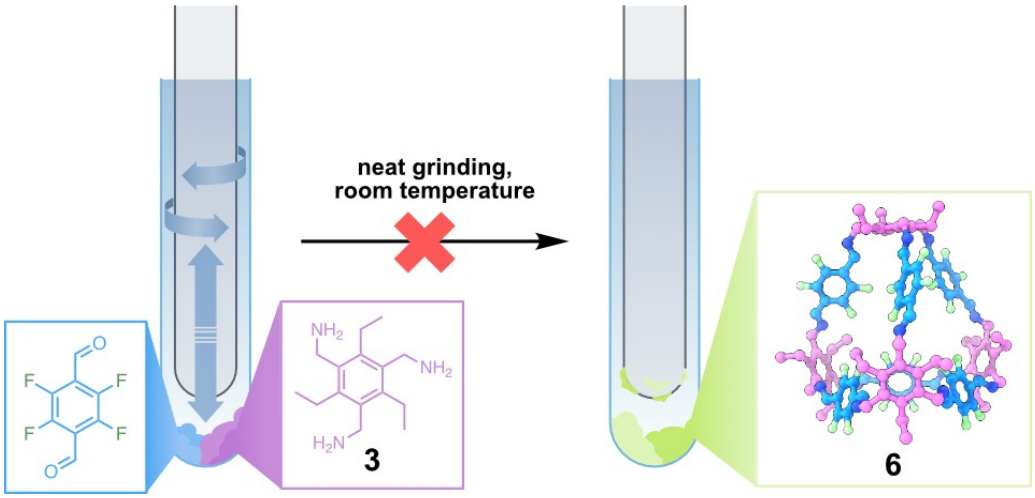
The analytical data was in accordance with previously published data.[S5]

Attempted synthesis of hydrogenated Tri^2Di^3 cage 5 from grinding



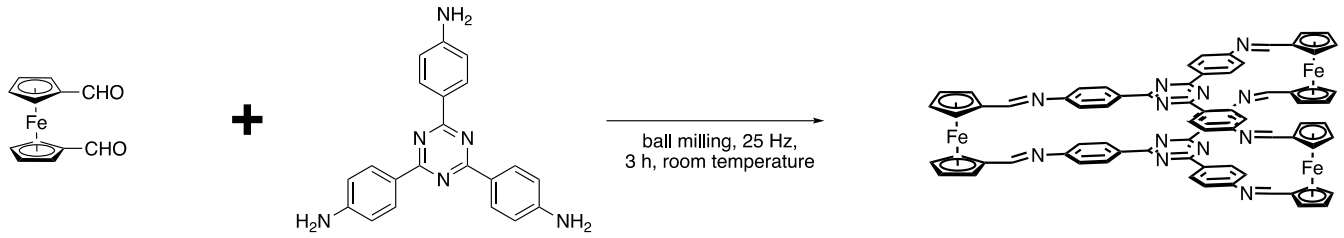
Isopthalaldehyde (0.15 mmol, 20.10 mg, 1.50 eq.) and 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene (0.10 mmol, 24.90 mg, 1.00 eq.) were added to a reaction tube (Ø 1 cm, length 10 cm). Both dry powders were then ground using a glass rod (Ø 0.7 cm) for 30 minutes by hand. No visual or haptic change was noted. The mixture was subjected to NMR analysis by dissolving in $CDCl_3$ and filtration, showing only the presence of the starting materials.

Attempted synthesis of Tri^4Di^6 cage 6 by grinding



Tetrafluoroterephthalaldehyde (0.15 mmol, 31.00 mg, 1.50 eq.) and 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene (0.10 mmol, 24.90 mg, 1.00 eq.) were added to a reaction tube (Ø 1 cm, length 10 cm). Both dry powders were then ground using a glass rod (Ø 0.7 cm) for 30 minutes. No visual or haptic change was noted. The mixture was subjected to NMR analysis by dissolving in $CDCl_3$ and quick filtration, showing only the presence of the starting materials.

Ball-Milling synthesis of FcC4



1,1′-Diformylferrocene (0.15 mmol, 36.30 mg, 1.50 eq.) and 1,3,5-tris(4-aminophenyl)-2,4,6-triazine (**7**) (0.10 mmol, 35.40 mg, 1.0 eq.) were added to a 2 mL Eppendorf tube together with 5x Ø 3 mm steel balls. The tube was shaken at 25 Hz for 3 hours. All solids were washed off the balls using $CDCl_3$.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.97–8.70 (m, 12H, C**H**$_{\textbf{Aryl}}$-$C_{Triazine}$), 8.35 (s, 6H, C**H**=N), 7.00–6.68 (m, 12H, C**H**$_{\textbf{Aryl}}$-C-N), 4.97 (s, 12H, **H**$_{\textbf{Fc}}$), 4.60 (s, 12H, **H**$_{\textbf{Fc}}$); **MALDI-MS** calc. for $[C_{78}H_{54}Fe_3N_{12}+H]^+$ = 1328.274 m/z, found: 1328.681 m/z.

Obtained data of **FcC4** are in accordance with the literature.[S6]

NMR experiments comparing grinding to solution mixing

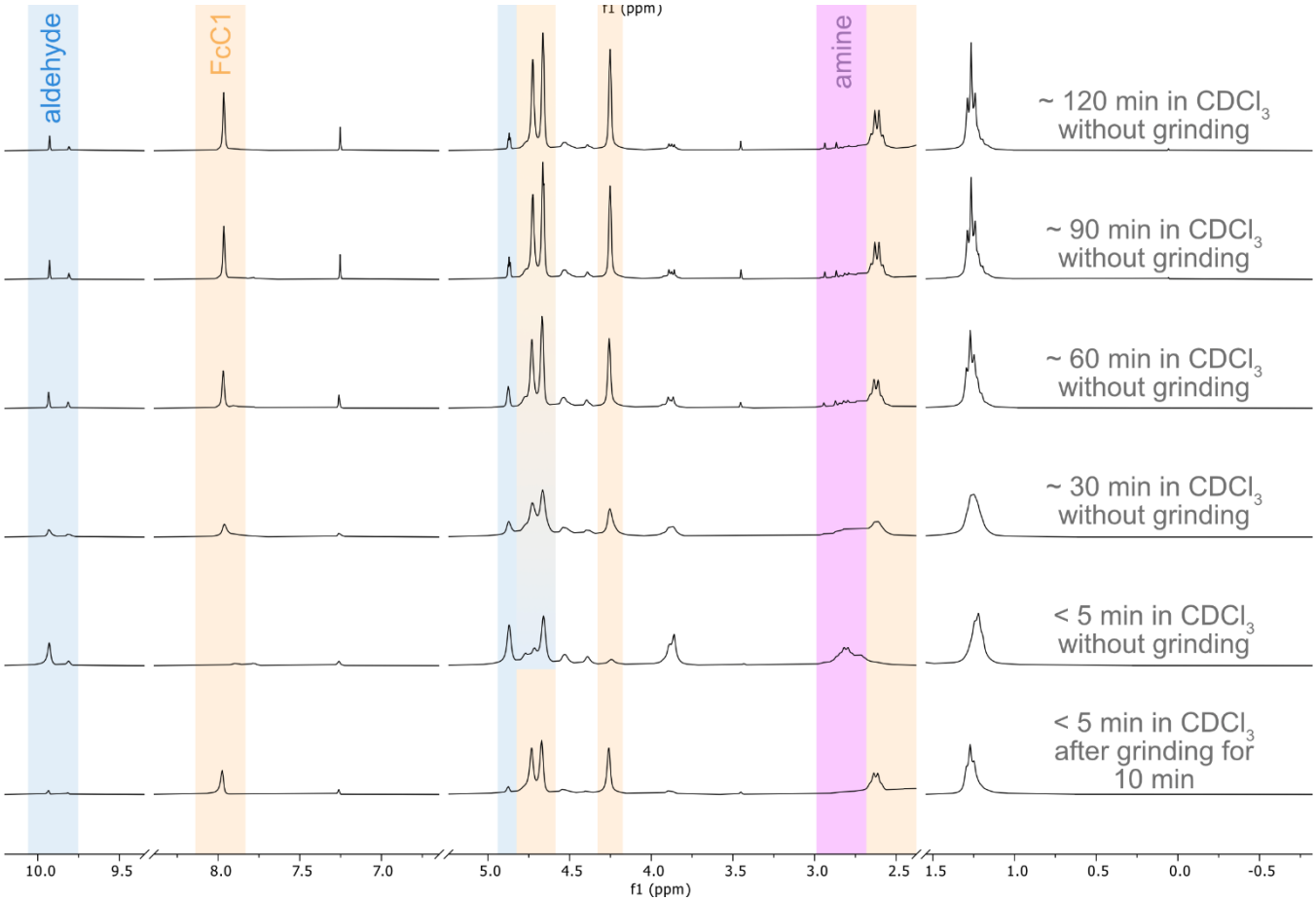


Figure S1: ^{1}H NMR spectra of the starting materials in an NMR tube in solution $CDCl_3$ after <5, 30, 60, 90, and 120 min (top, "without grinding"). Comparison with a sample prepared by grinding after <5 min in CDCl3 (bottom, "after grinding"). The signals corresponding to the different observed species are highlighted in orange (**FcC1**), blue (1,1′-diformylferrocene) and purple (1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene). The top sample for NMR monitoring was prepared by adding 1,1′-diformylferrocene (18.2 mg, 0.075 mmol, 1.50 eq.) and 1,3,5-triethyl-2,4,6-tris(aminomethyl)benzene (12.5 mg, 0.05 mmol, 1.00 eq.) to an NMR tube, dissolved in 0.7 mL $CDCl_3$ and the homogenous solution was subjected to NMR analysis immediately (<5 min until spectrum was obtained).

Ball Milling Comparison of FcC4 ^{1}H NMR with literature

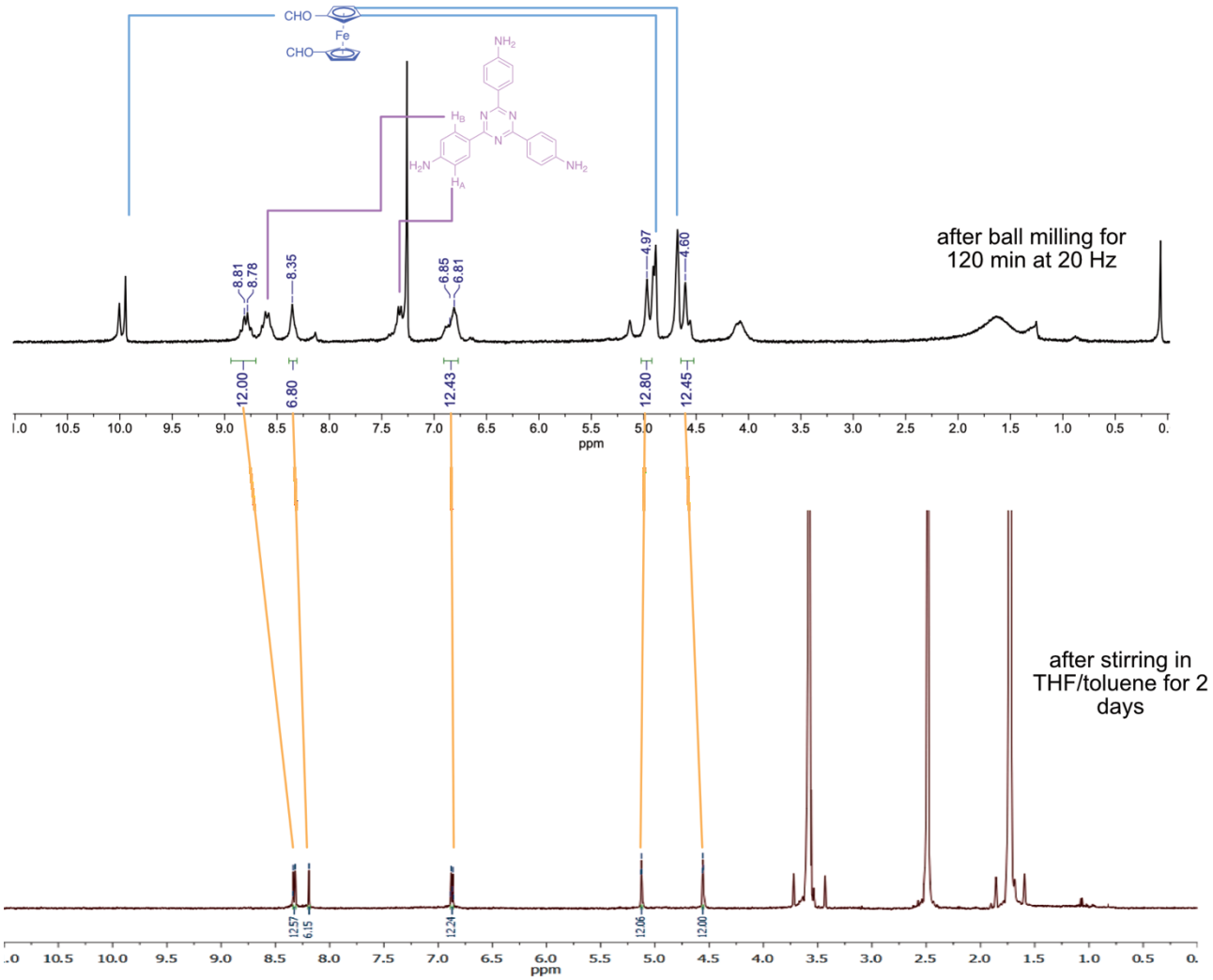


Figure S2: ^{1}H NMR spectra of the mixture obtained from ball milling for 120 minutes at room temperature and 120 Hz in $CDCl_3$ (top) and from the solid isolated after reacting the starting materials in THF/toluene for 2 days and several washing steps in THF-d_8 (bottom). Orange lines show the corresponding cage signals in both NMR spectra, while the blue (aldehyde) and purple lines (amine) show the signals corresponding to remaining starting materials in the ball milling experiment.

III. DOSY experiments

DOSY NMR experiments were recorded at 298 K and calibrated using known self-diffusion values for the solvents used (D_{solv}).[S7] The hydrodynamic radii were estimated using the unmodified Stokes-Einstein-equation. This equation was solved for r_H using values for η from the literature.[S8]

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

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)

η is the viscosity of the solvent at temperature T ($kg\ m^{-1}\ s^{-1}$)

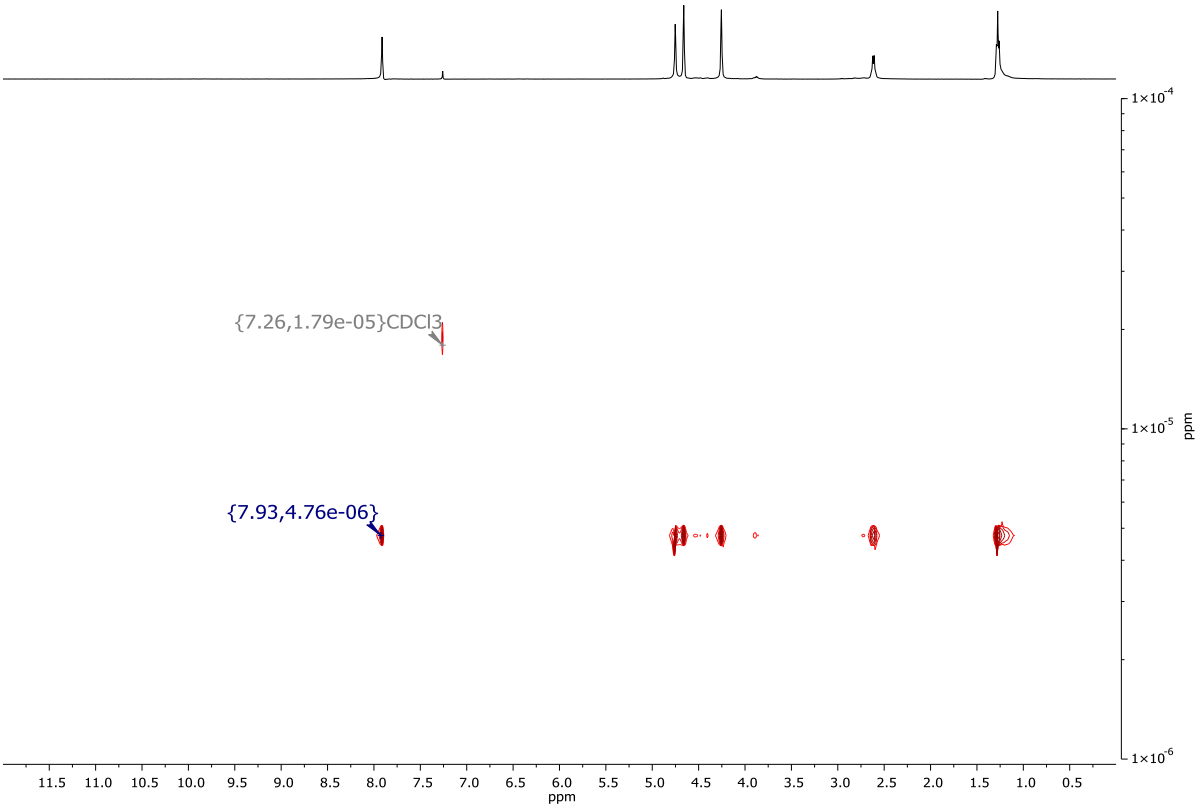


Figure S3: ^1H DOSY NMR spectrum of **FcC1** in $CDCl_3$ (500 MHz).

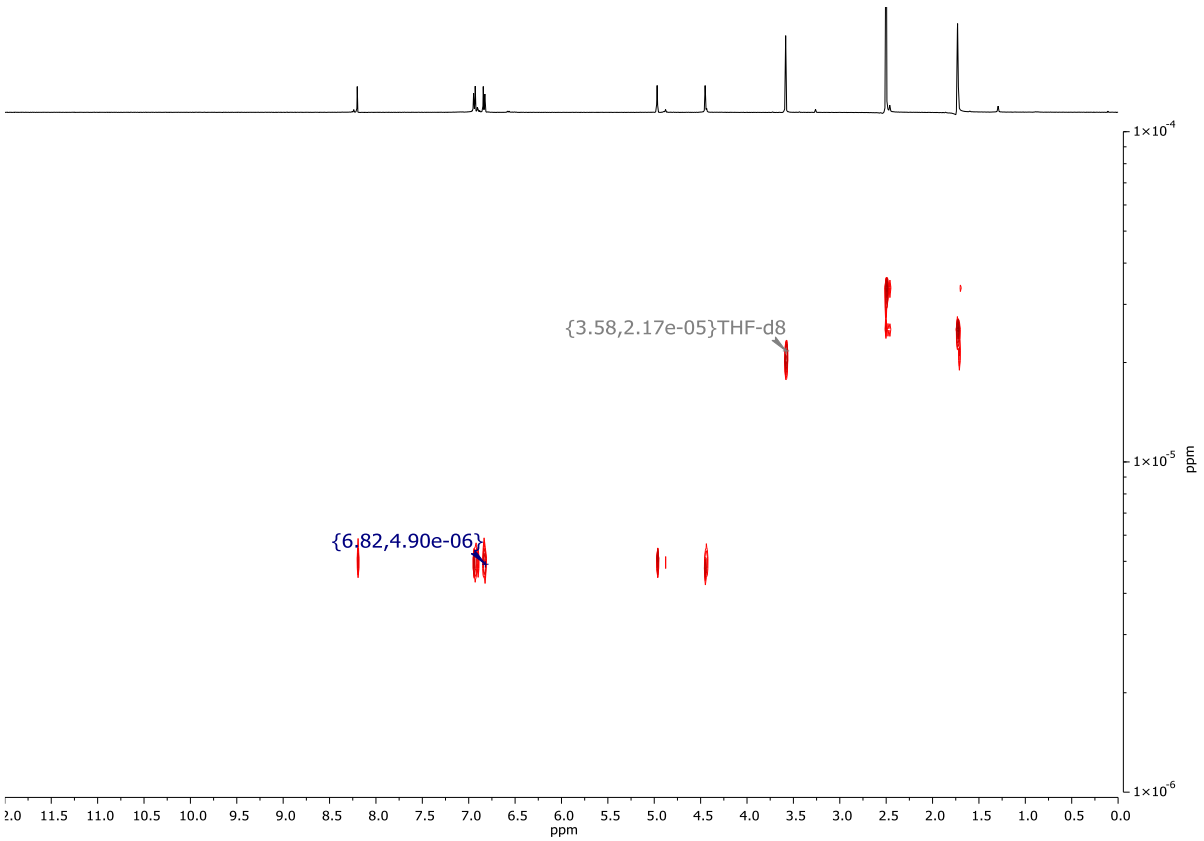


Figure S4: ^{1}H DOSY NMR spectrum of **FcC2** in THF-d^{8} (500 MHz).

IV. Crystallographic details

Single-crystals were mounted using a microfabricated polymer film crystal-mounting tool (dual-thickness MicroMount, MiTeGen) or a cactus needle, using low viscosity oil (perfluoropolyalkylether; viscosity 1800 cSt, ABCR). A Rigaku XtaLAB Synergy diffractometer or a Rigaku Oxford Diffraction Gemini ultra single-crystal X-ray diffractometer using Mo-K_α (λ = 0.71073 Å) radiation were used for data collection at the temperature stated for each compound. The structures were refined by full-matrix least-squares methods on F^2 (SHELXL-2018).[S9] The hydrogen atoms were placed at calculated positions and refined by using a riding model. CCDC 2122280 (**FcC1**), CCDC 2085773 (**FcC2**), CCDC 2122279 (**FcC3**) and CCDC 2117653 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. Raw diffraction data are available at 10.5281/zenodo.5470707 (**FcC2**) and 10.5281/zenodo.5596197 (**2**).

FcC1

Crystals of **FcC1** were grown by vapour diffusion of *n*-pentane into a chloroform solution. An orange brick-like fragment was mounted and the structure was obtained at 100 K using Mo-K_α radiation. Crystals of **FcC1** are heavily solvated and three chloroform molecules and one water molecule were modelled. One additional chloroform molecule showed rotational disorder and was ultimately removed using the SQUEEZE procedure implemented in Platon software.[S10] The solvent accessible volume found (SAV) was 435 Å^3 with 87 electrons (per unit cell). One imine bond, N1–C34 (N3–C1), shows a minor rotational disorder that was modelled accordingly.

FcC2

Crystals of **FcC2** were grown by slow evaporation of a chloroform benzene solution. A colourless needle was mounted and the structure was obtained at 293 K using Mo-K_α radiation. The crystal contains a molecule of benzene and water in the asymmetric unit, filling small discreet voids in the structure, as well as channels running parallel to the crystallographic [100] direction which contain heavily disordered solvent molecules. Their modelling was impossible and the SQUEEZE procedure implemented in Platon software was applied.[S10] The solvent accessible volume found (SAV) was 301 Å^3 with 93 electrons (per unit cell). The electron density was attributed to two benzene molecules because (1) it was used in crystallization and Q-peaks in the SAV were lying on planes; (2) SQUEEZE is known to overestimate the

number of solvent electrons. **FcC2** crystallizes in the triclinic $P\bar{1}$ (No. 2) space group and its molecules exhibit C_1 point group. Peripheral phenyl rings within the molecules are disordered. The distance between central nitrogen atoms is 4.890(3) Å. Peripheral phenyl rings are twisted in **FcC2** with all angles between average ring plane normal vectors exceeding 59° and reaching 71°. Imine moieties exhibit *E* configuration and the intramolecular distances between imine nitrogen atoms from adjacent "molecular sides" are 3.668(2)–4.176(3) Å.

FcC3

Crystals of **FcC3** were grown by vapour diffusion of *n*-pentane into a chloroform solution. A red-orange brick-like fragment was mounted and the structure was obtained at 100 K using Mo-K_α radiation.

1,1′-bis(4-formylphenyl)ferrocene 2

Crystals of **2** were grown by vapour diffusion of *n*-hexane into a chloroform solution. An orange block was chosen, and the diffraction data were collected at 293 K using Mo-K_α radiation. Due to excellent crystal and diffraction data quality, Hirshfeld atom refinement (HAR) of the structure was viable which allowed for the free refinement of hydrogen atom positions and their anisotropic displacement parameters.[S11] HAR was carried out using NoSphereA2 module of the Olex2 package. [S12, S13]

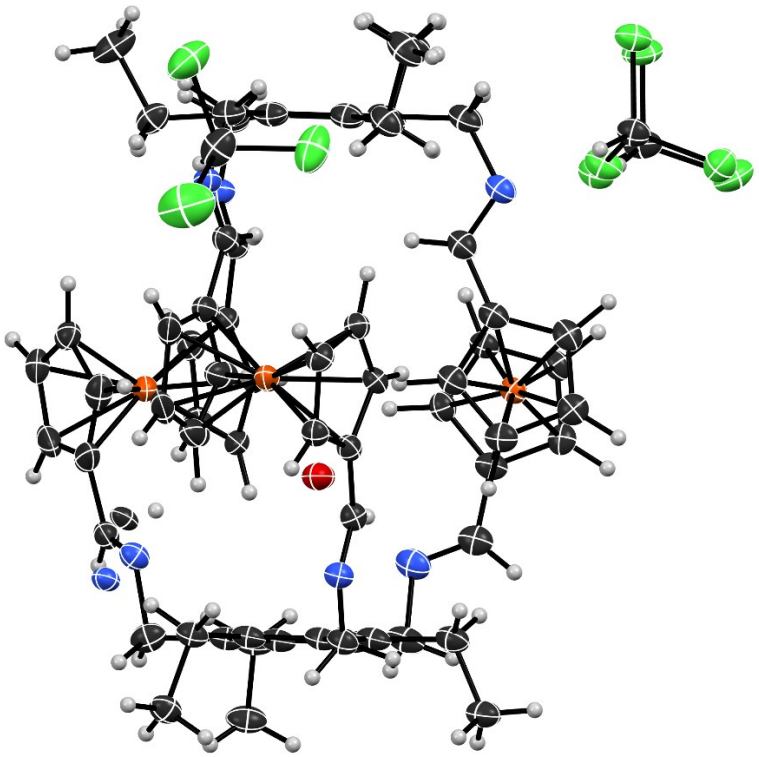


Figure S5: Data set of **FcC1** showing the asymmetric unit bearing one unique **FcC1** molecule including three unique chloroform molecules with thermal ellipsoids set at 50% probability. The structure was measured at 100 K and solved in the monoclinic space group $P\bar{1}$ with $R_{int} = 0.070$, $R_1 = 0.061$ and $wR_2 = 0.1822$.

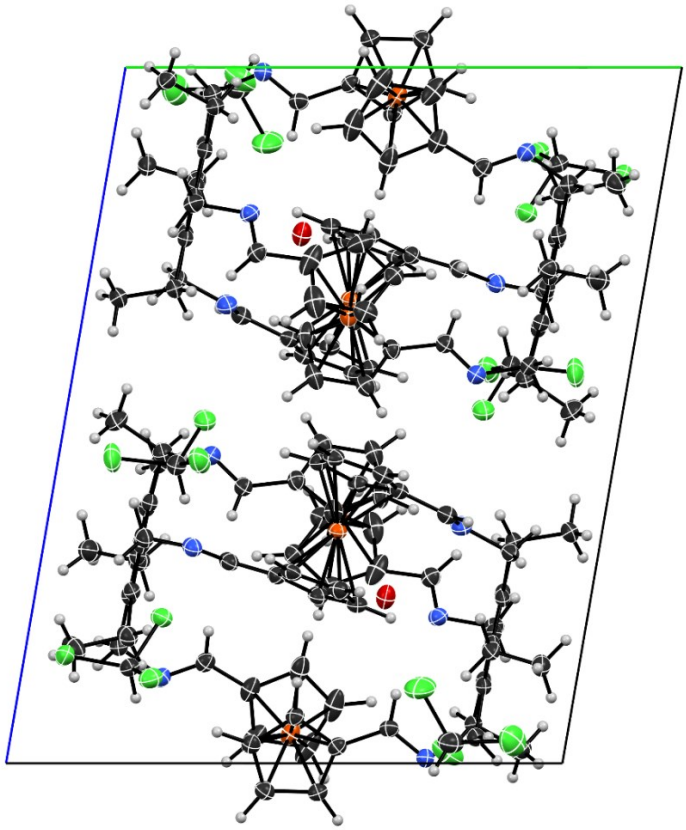


Figure S6: View of the unit cell of **FcC1** along the crystallographic *a* axis.

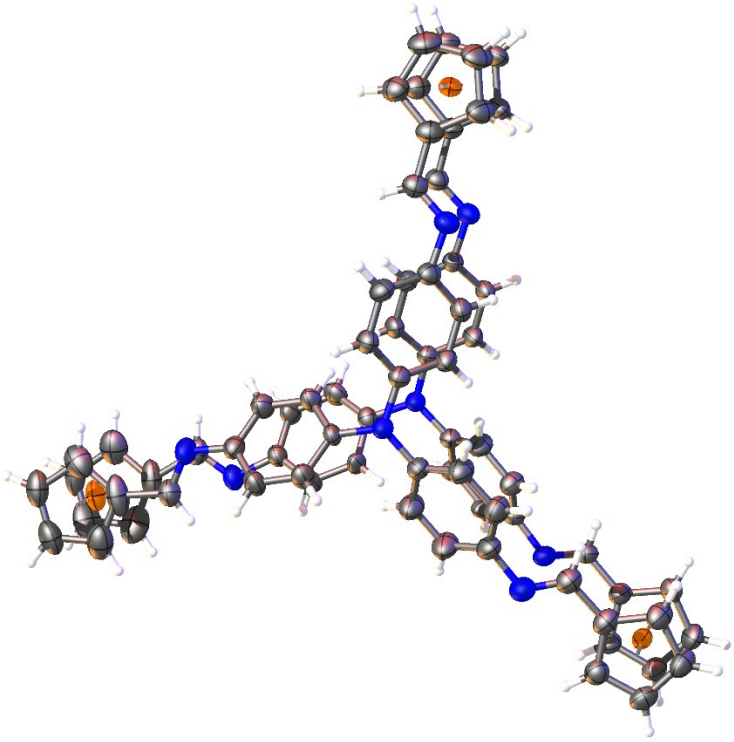


Figure S7: Molecular structure of compound **FcC**2 with only the major disorder component shown. Thermal ellipsoids are drawn at 50% probability level. The structure was measured at 293 K and solved in the triclinic space group $P\bar{1}$ with $R_{int} = 0.029$, $R_1 = 0.041$ and $wR_2 = 0.1178$.

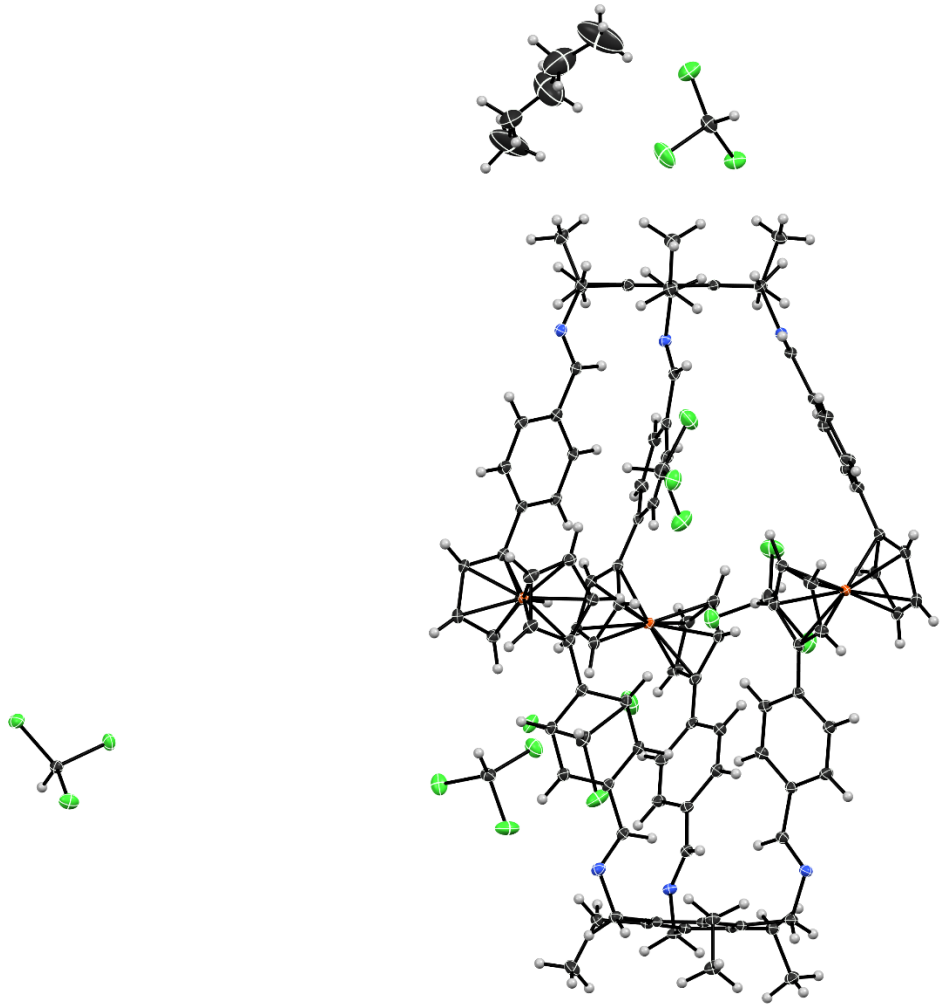


Figure S8: Data set of **FcC3** showing the asymmetric unit bearing one unique **FcC3** molecule including six unique chloroform molecules and one additional *n*-pentane solvent molecule with thermal ellipsoids set at 50% probability. The structure was measured at 100 K and solved in the triclinic space group $P\bar{1}$ with $R_{int} = 0.042$, $R_1 = 0.065$ and $wR_2 = 0.2010$.

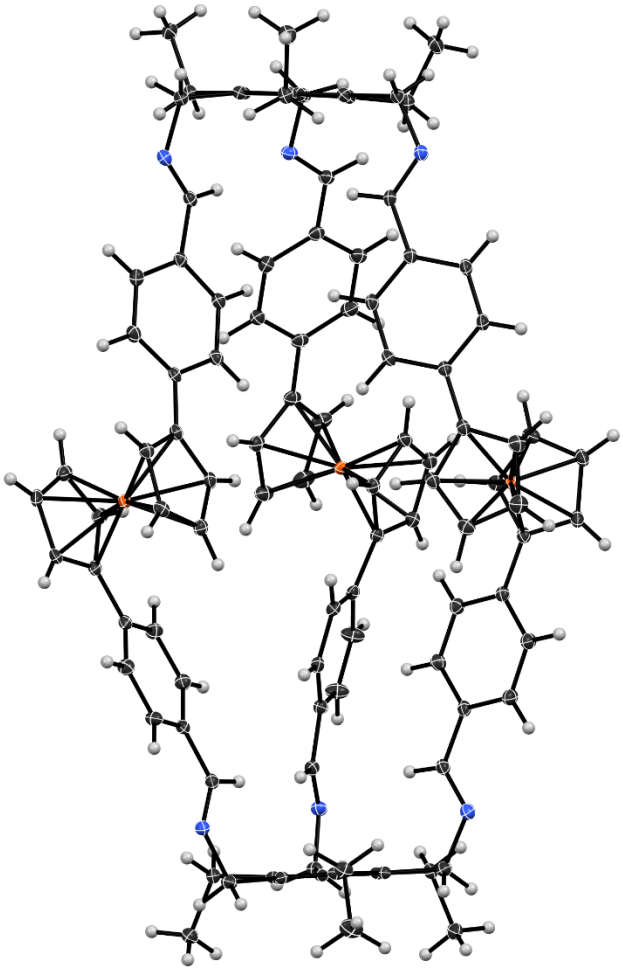


Figure S9: Data set of **FcC3** showing the molecular structure of one cage with all solvent molecules omitted for clarity.

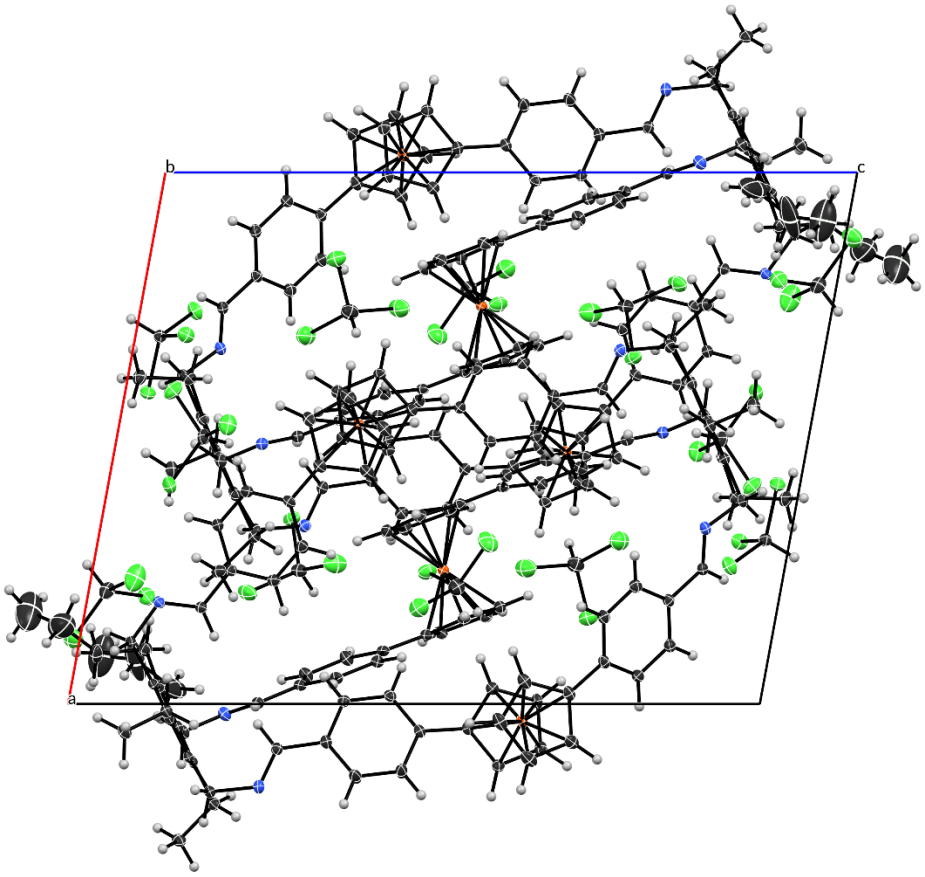


Figure S10: View of the unit cell of **FcC3** along the crystallographic *b* axis.

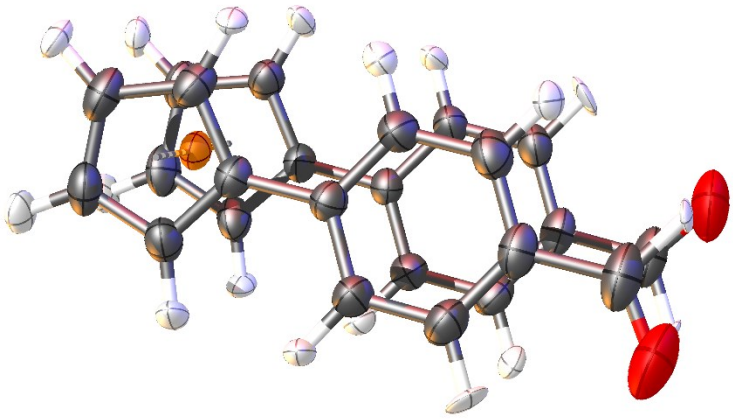


Figure S11: Molecular structure of 1,1′-bis(4-formylphenyl)ferrocene **2**. Thermal ellipsoids are drawn at 50% probability level. Carbon, hydrogen, nitrogen, and iron atoms are drawn as dark grey, light grey blue and orange ellipsoids, respectively. Note anisotropic refinement of hydrogen atoms possible thanks to excellent crystal and diffraction data quality as well as application of Hirshfeld atom refinement. The structure was measured at 293 K and solved in the orthorhombic space group *Fdd*2 with R_{int} = 0.0231, R_1 = 0.0138 and wR_2 = 0.0316.

V. NMR spectra

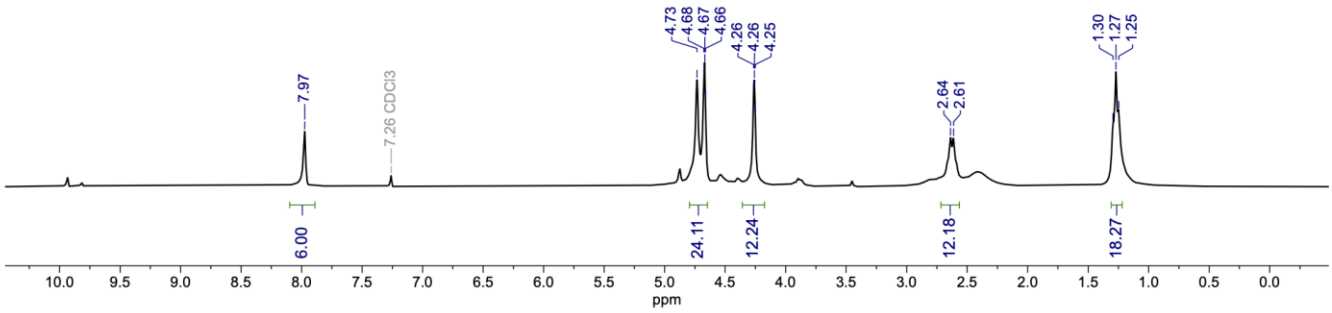


Figure S12: ^{1}H NMR spectrum of **FcC1** in $CDCl_3$ (300 MHz).

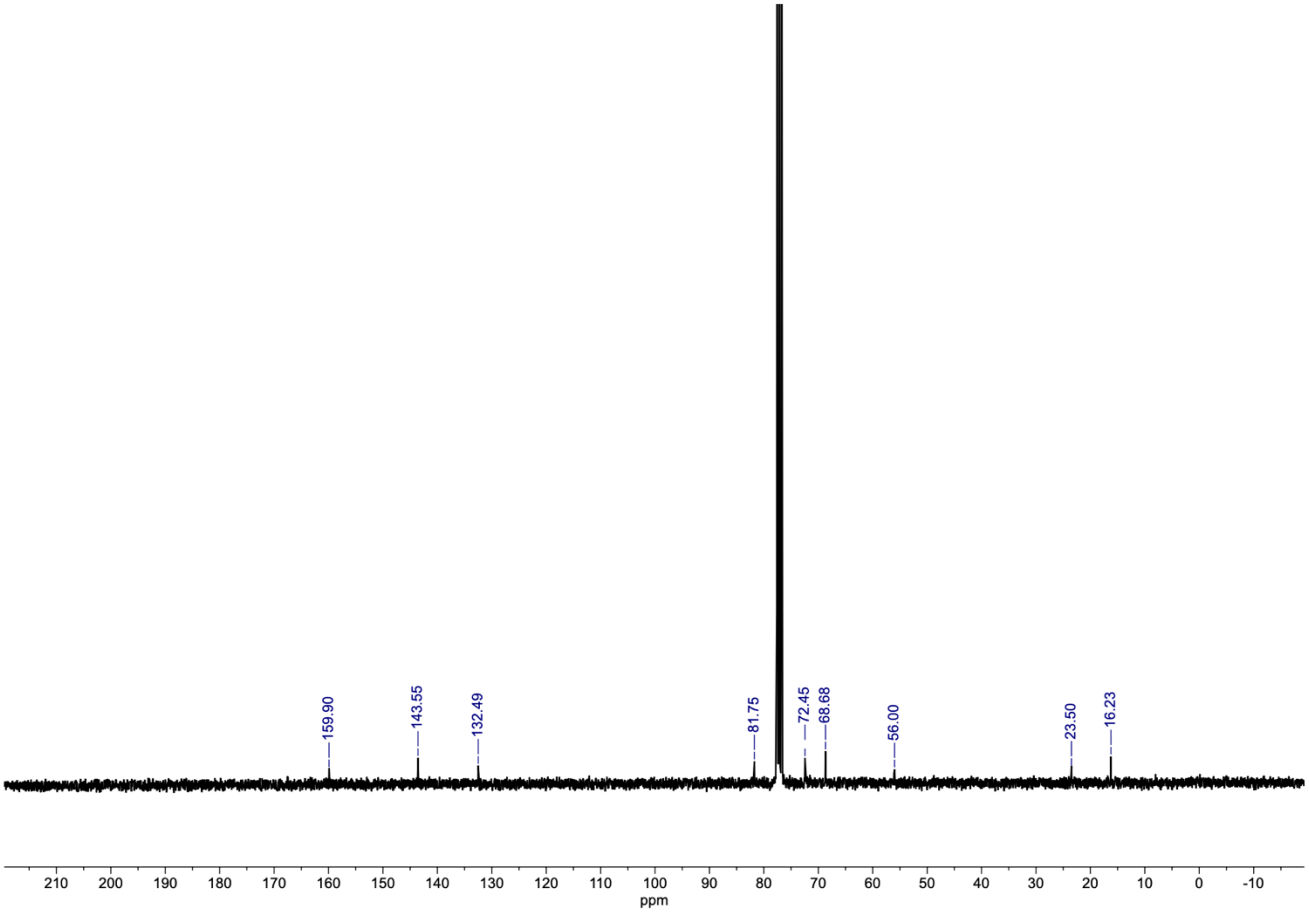


Figure S13: $^{13}C\{^{1}H\}$ NMR spectrum of **FcC1** in $CDCl_3$ (600 MHz).

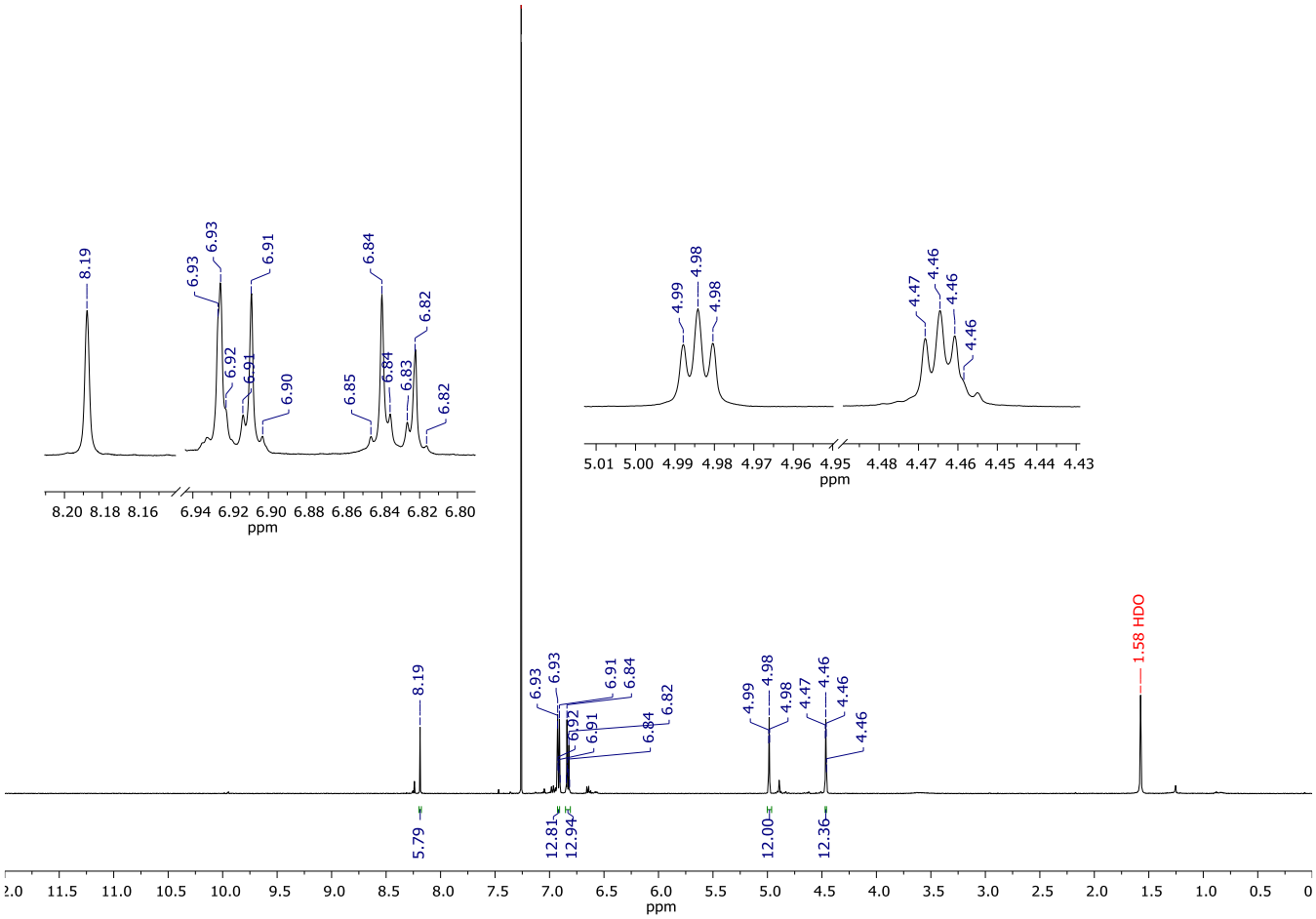


Figure S14: ^{1}H NMR spectrum of **FcC2** in $CDCl_3$ (500 MHz).

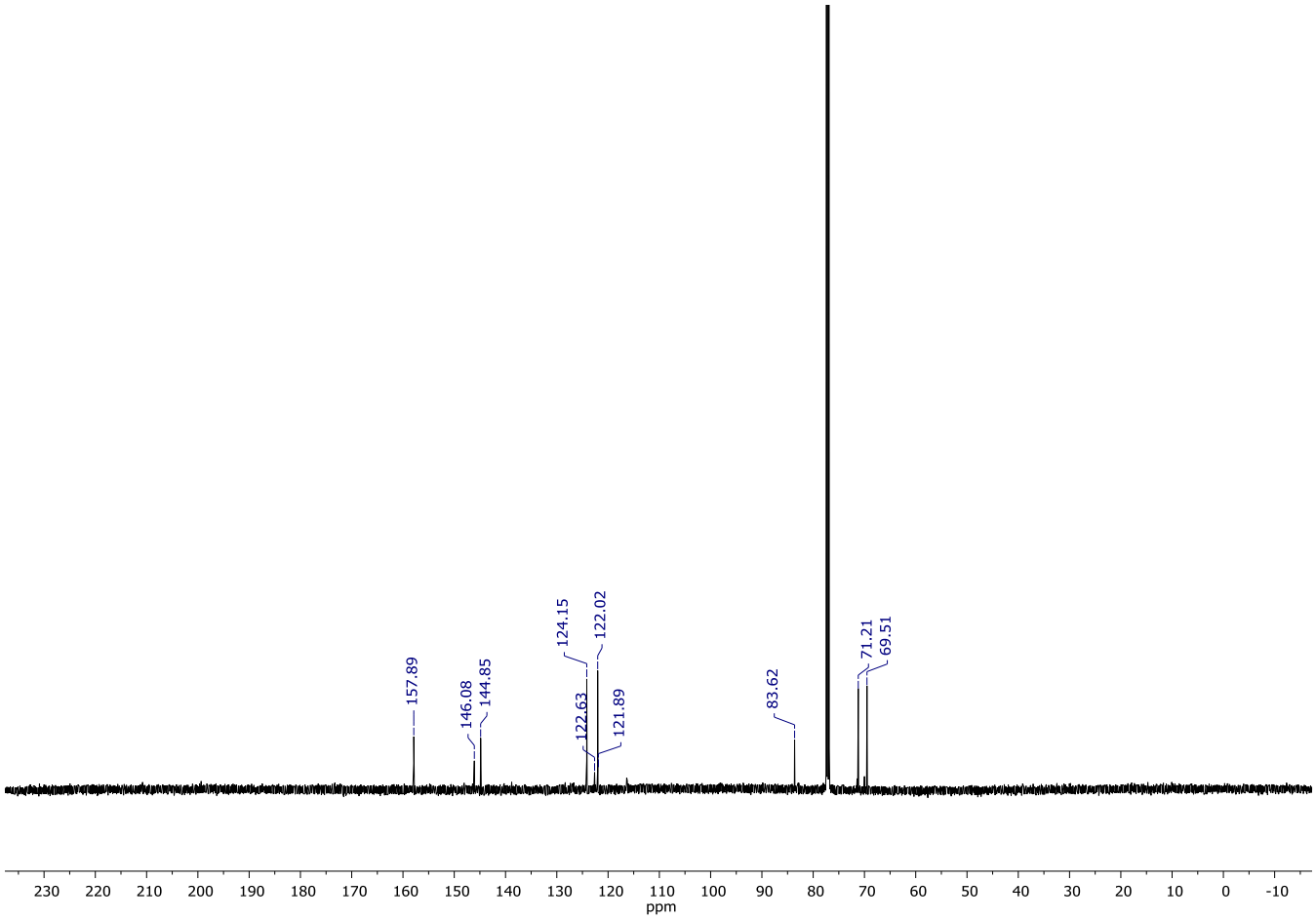


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of **FcC2** in $CDCl_3$ (500 MHz).

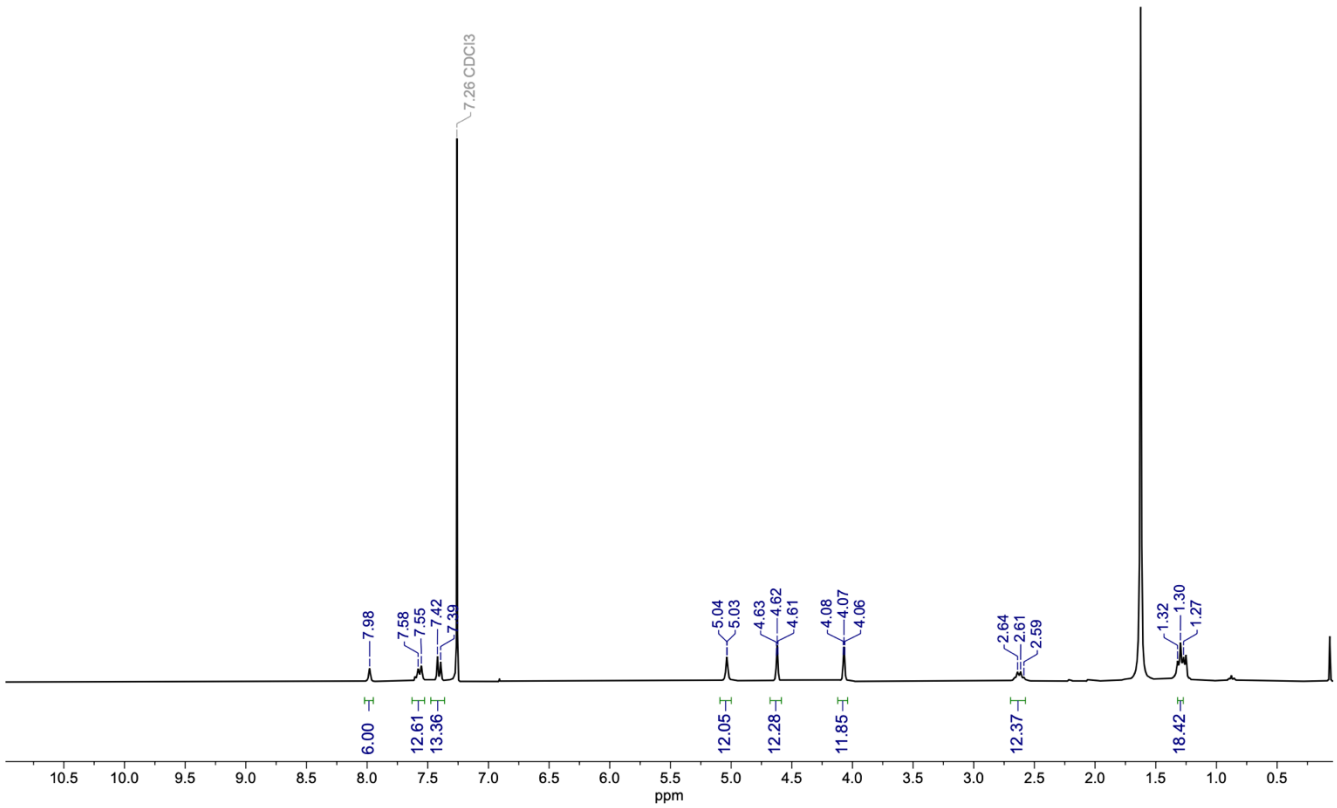


Figure S16: ^{1}H NMR spectrum of **FcC3** in $CDCl_3$ (300 MHz).

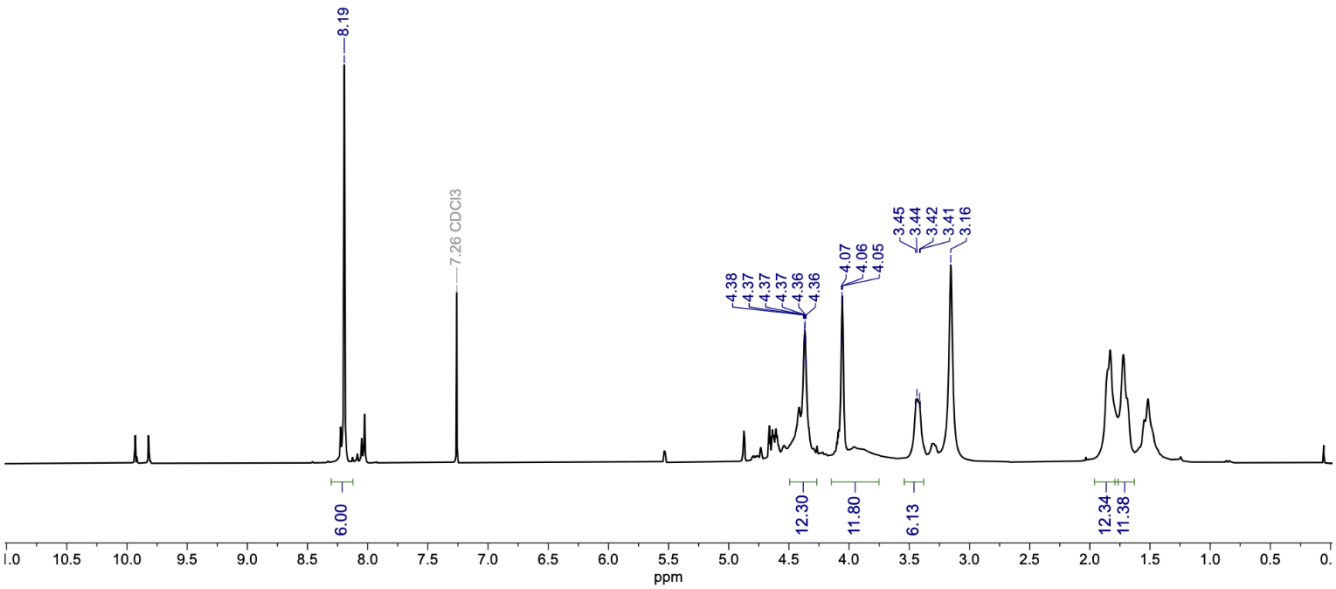


Figure S17: ^{1}H NMR spectrum of the crude reaction product for **FcM1** in $CDCl_3$ (300 MHz).

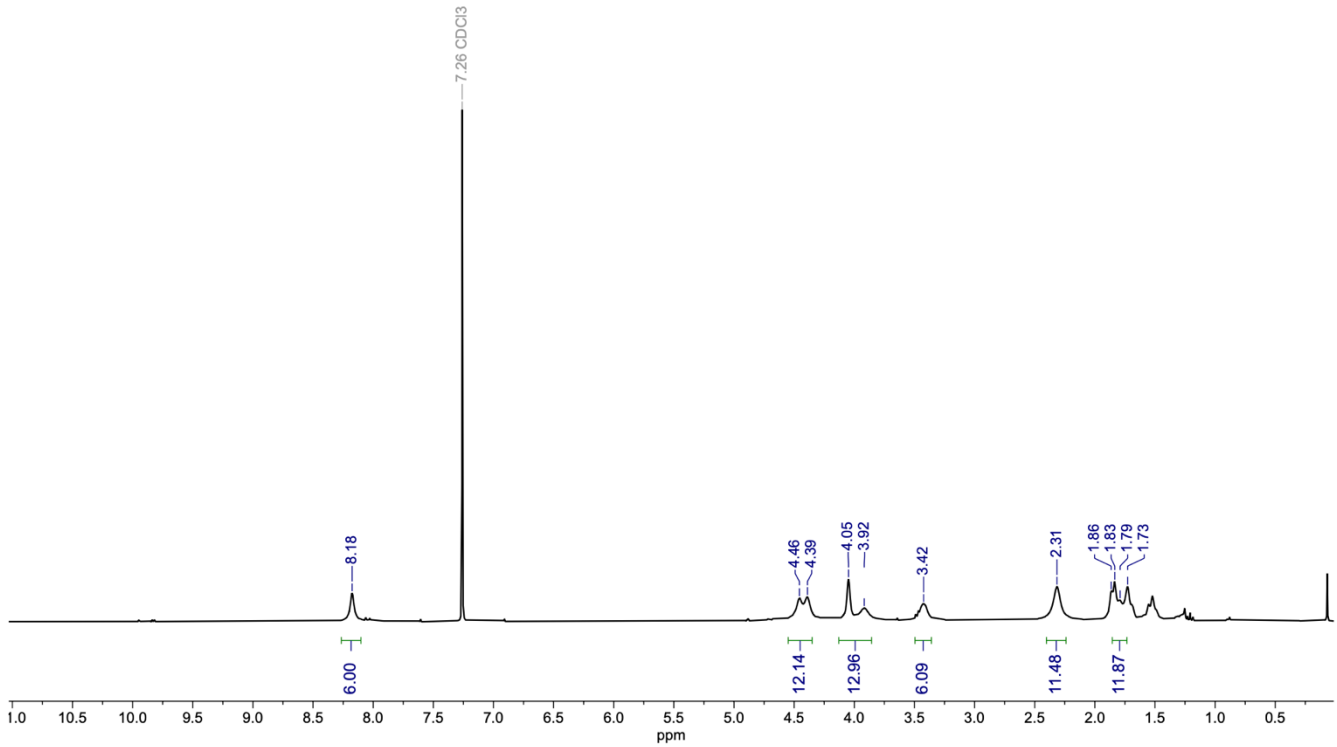


Figure S18: ^{1}H NMR spectrum of **FcM1** in $CDCl_3$ (300 MHz).

NMR kinetics of FcC1-3

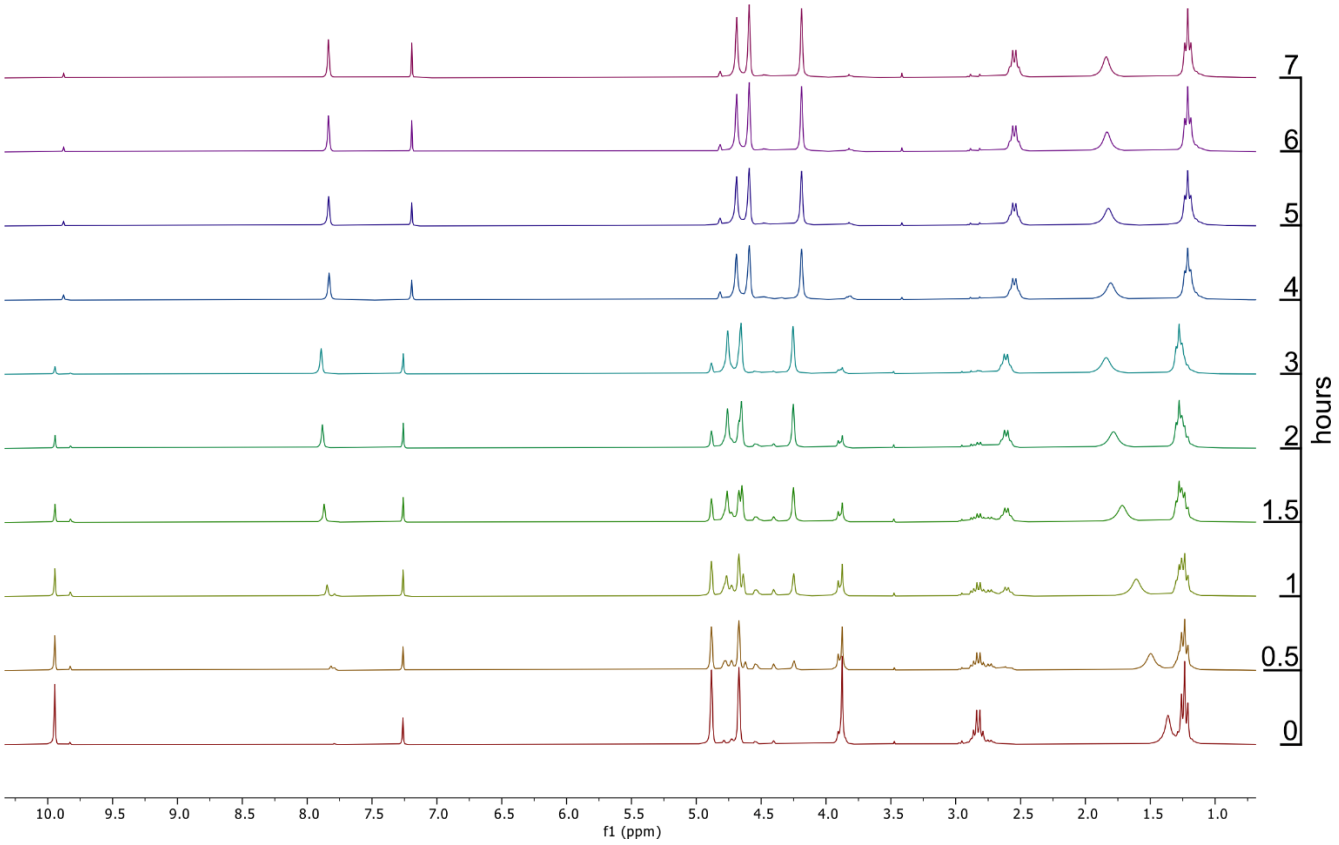


Figure S19: Overlay of ^{1}H NMR spectra after mixing **1** and **3** in $CDCl_3$ at rt in a concentration of ~25 mM after 0-7 hours (from bottom to top) for the attempted formation of **FcC1** under typical dilution conditions commonly employed in dynamic covalent imine chemistry (300 MHz).

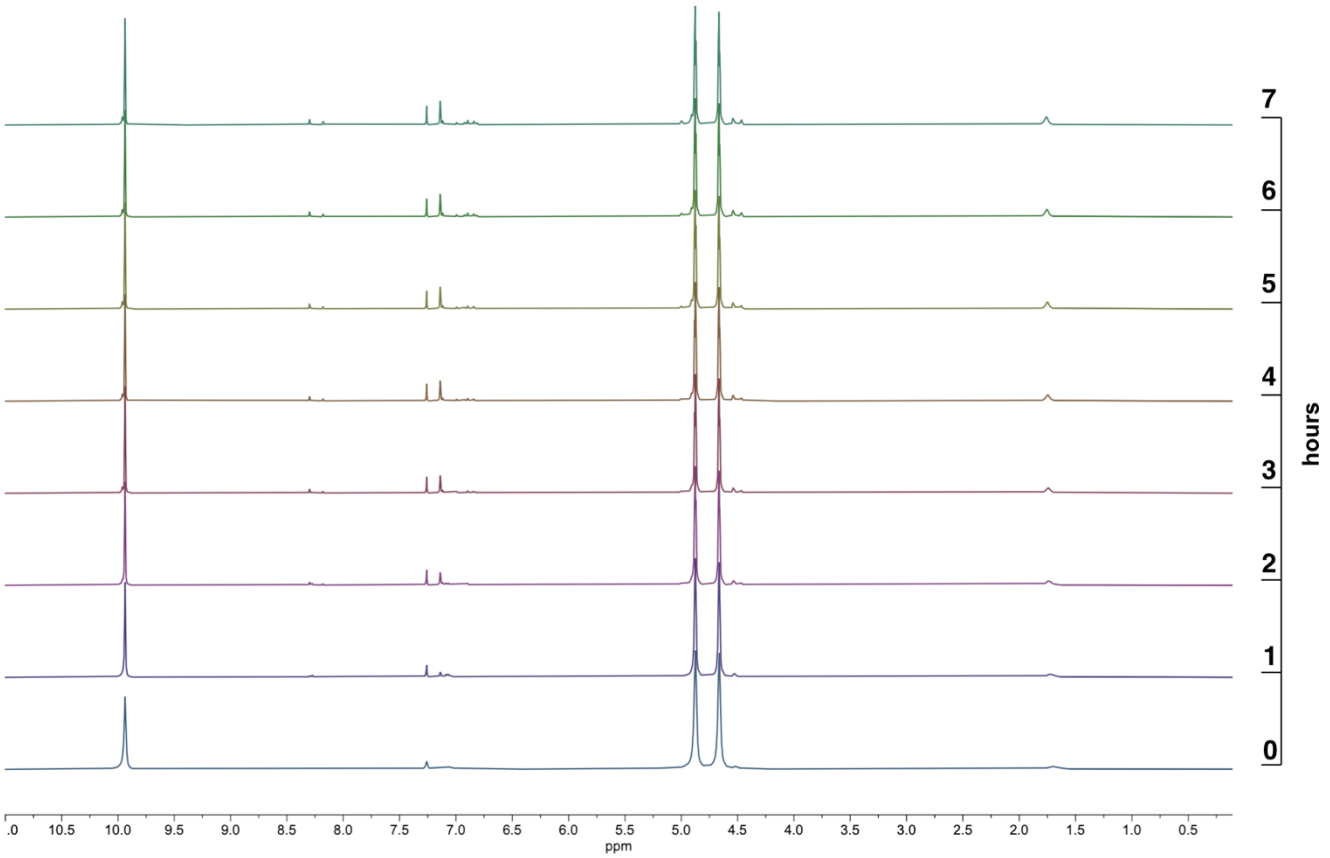


Figure S20: Overlay of ^{1}H NMR spectra of mixing **1** and **4** in $CDCl_3$ at rt in a concentration of 71 mM after 0-7 hours (from bottom to top) for the attempted formation of **FcC2** (300 MHz).

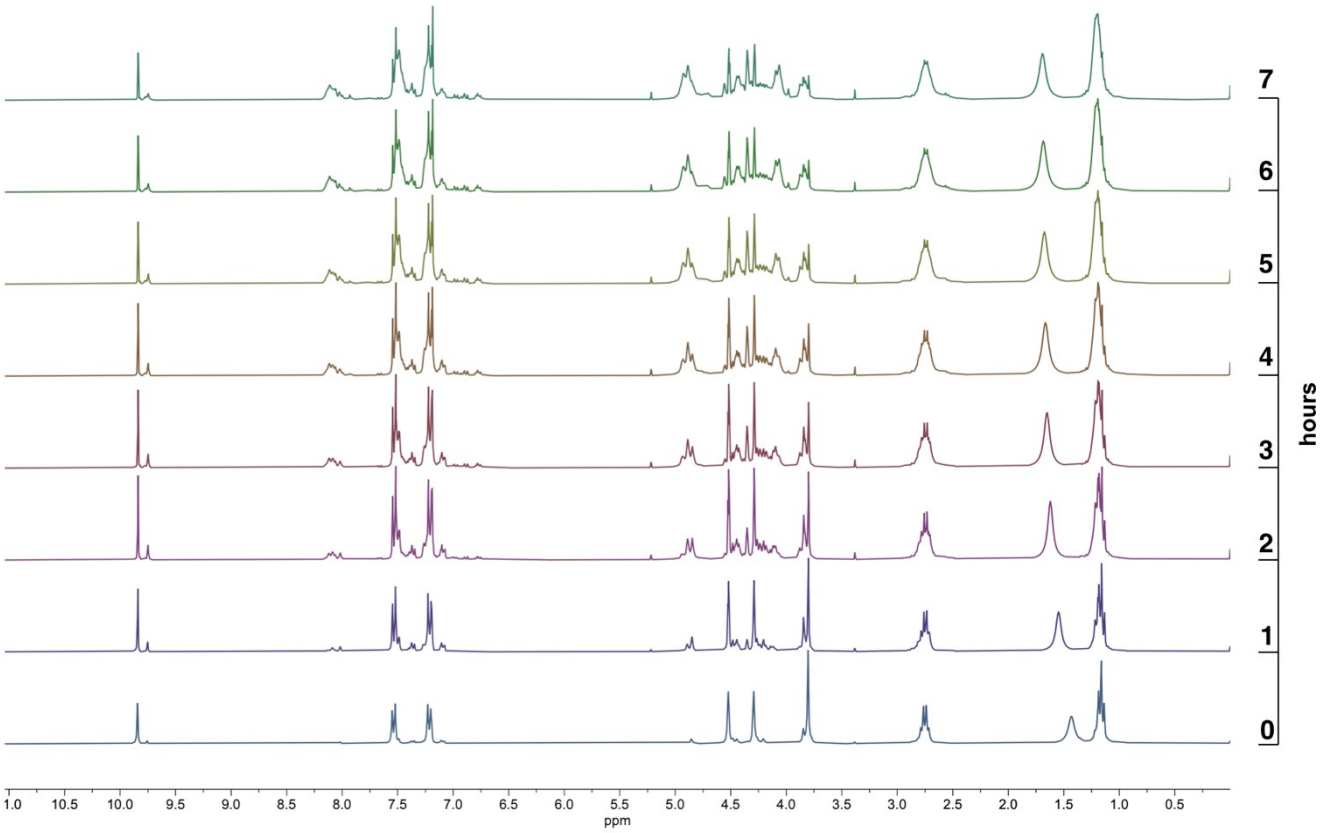


Figure S21: Overlay of ^{1}H NMR spectra of mixing **2** and **3** in $CDCl_3$ at rt in a concentration of 71 mM after 0-7 hours (from bottom to top) for the attempted synthesis of **FcC3** (300 MHz).

NMR spectra of failed grinding experiments using non-Fc containing building blocks

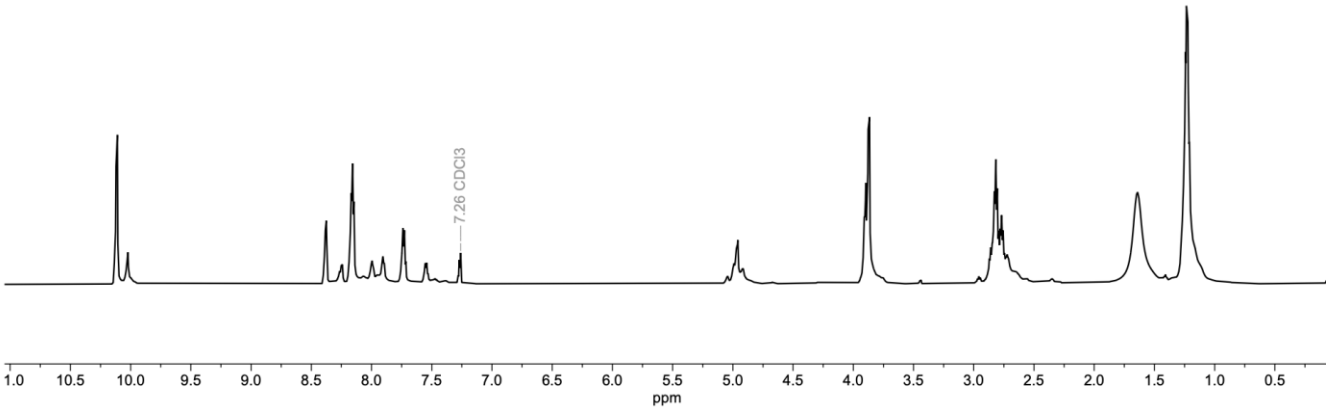


Figure S22: ^{1}H NMR spectrum of mixing isophthalaldehyde and **3** in a reaction tube and grinding for 30 minutes (< 10 minutes from dissolving the compounds to NMR experiment), solvent $CDCl_3$ (300 MHz).

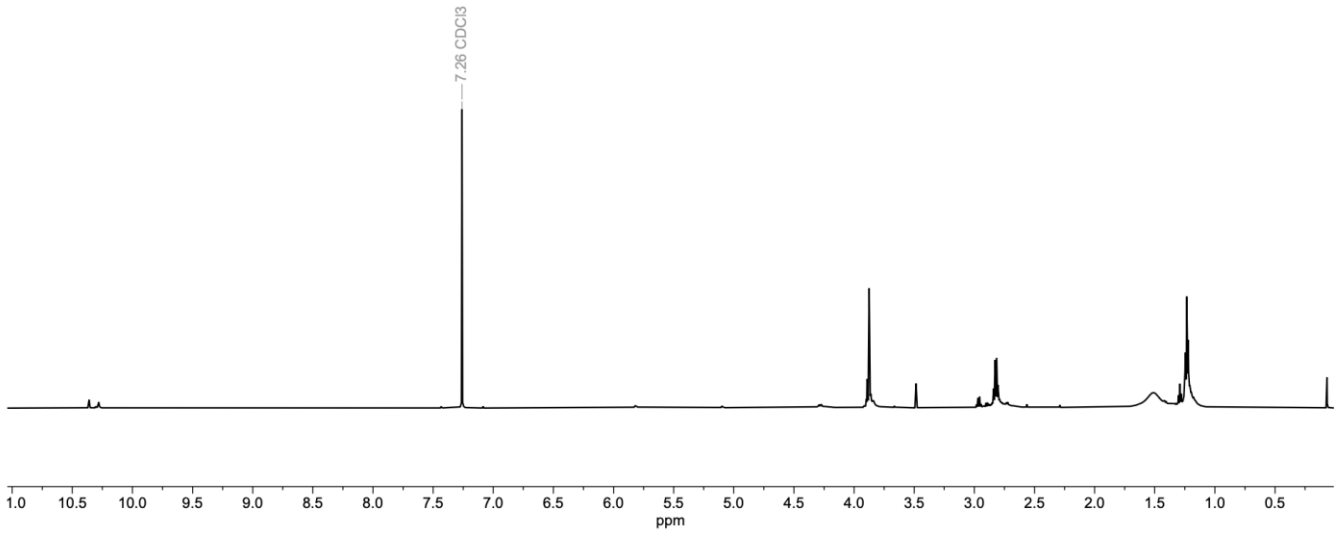


Figure S23: ^{1}H NMR spectrum of mixing tetrafluoroterephthalaldehyde and **3** in a reaction tube and grinding for 30 minutes (< 10 minutes from dissolving the compounds to NMR experiment), solvent $CDCl_3$ (300 MHz).

VI. MS spectra

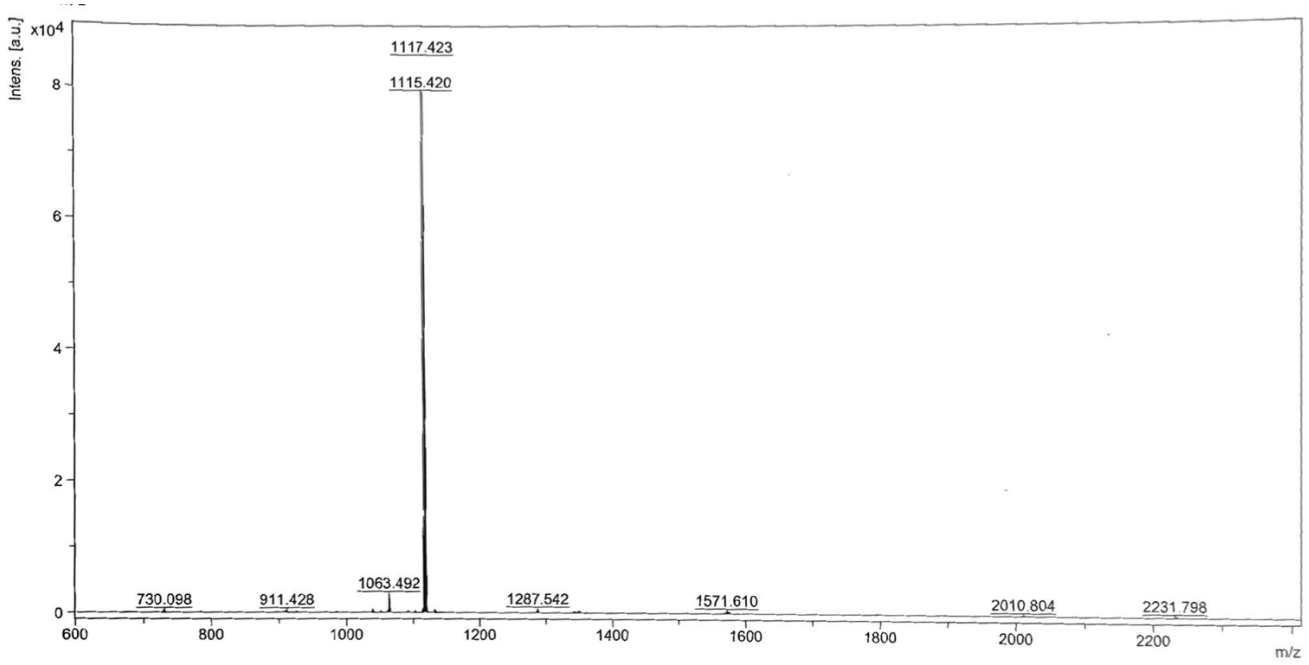


Figure S24: MALDI MS spectrum of a solid sample of **FcC1** taken directly from the solid mixing after 10 min.

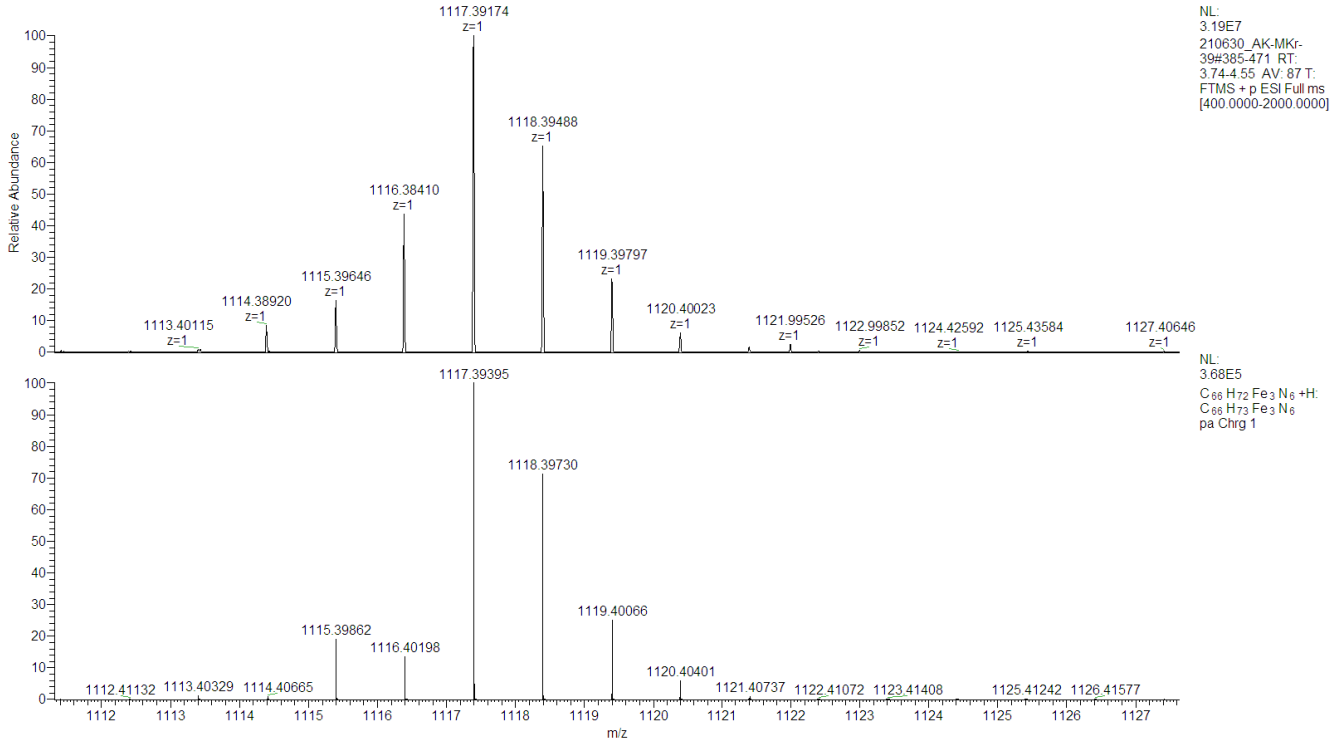


Figure S25: TOF-HRMS(ESI) spectrum of **FcC1**.

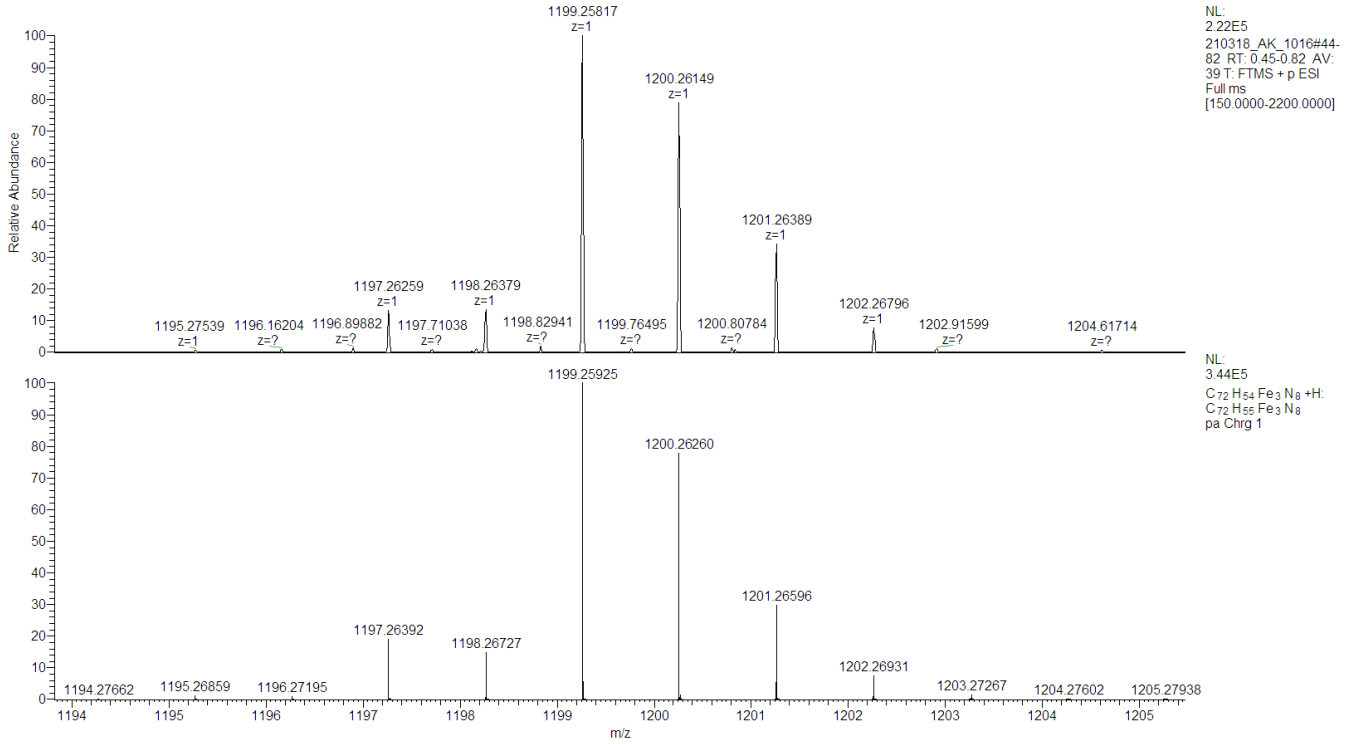


Figure S26: TOF-HRMS(ESI) spectrum of **FcC2**.

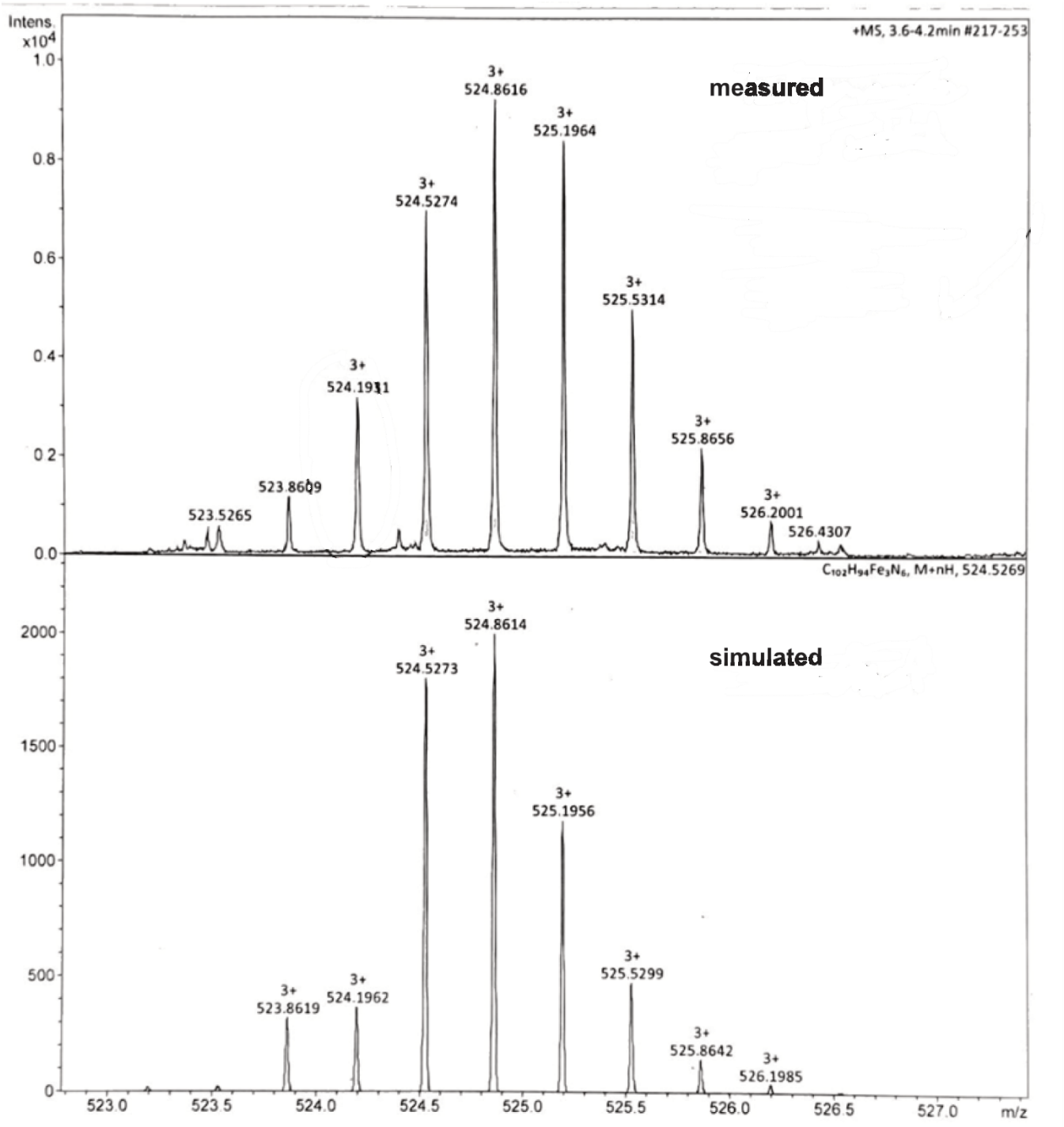


Figure S27: HRMS(ESI) spectrum of **FcC3** crystals dissolved in MeOH/$CHCl_3$ 9:1.

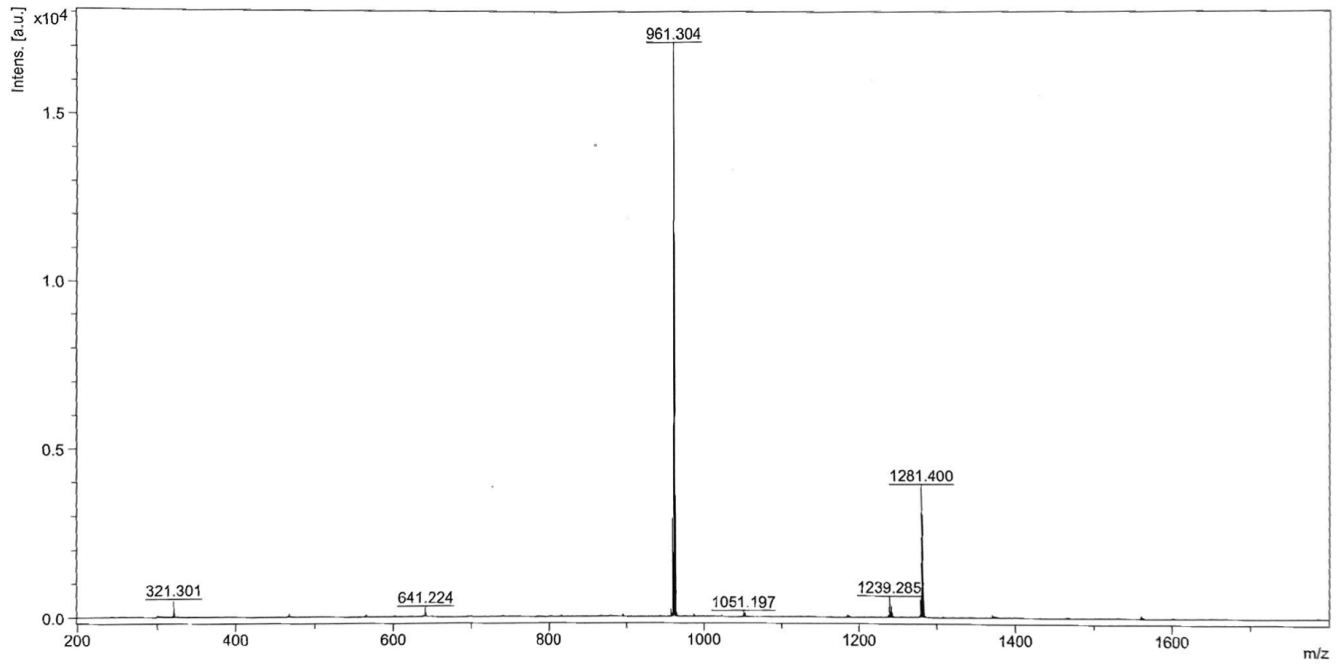


Figure S28: MALDI MS spectrum of **FcM1**, solid sample taken directly from the solid mixture experiments.

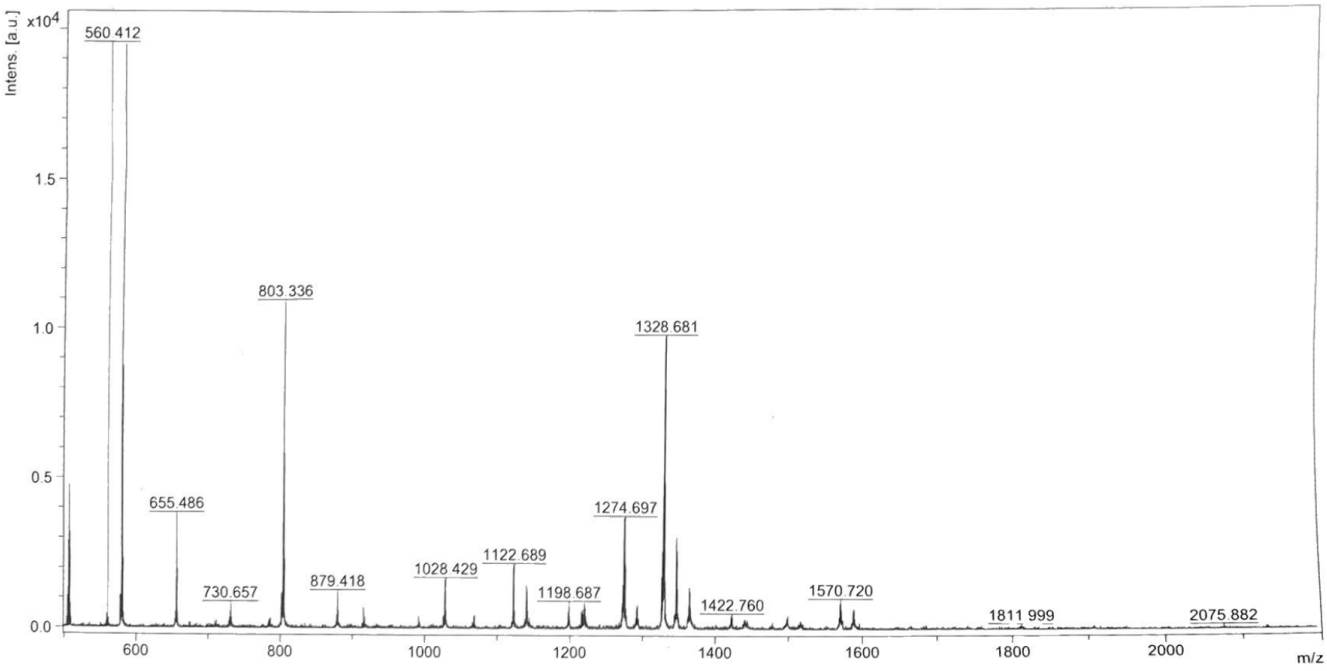


Figure S29: MALDI MS spectrum of **FcC4**, solid sample taken directly from the ball milling experiments.

TOF-HRMS(ESI) studies on the synthesis of FcC1

The reagents (1,1′-diformylferrocene and 1,3,5-triethyl-2,4,6-tris(aminomethyl)benzene) were grinded for 2 mins, 5 mins, 7 mins, or 10 mins. All samples were subjected to immediate ESI-HRMS(ESI) analysis. Intermediate products were identified and labelled as int-A, int-B, int-C, and are presented below.

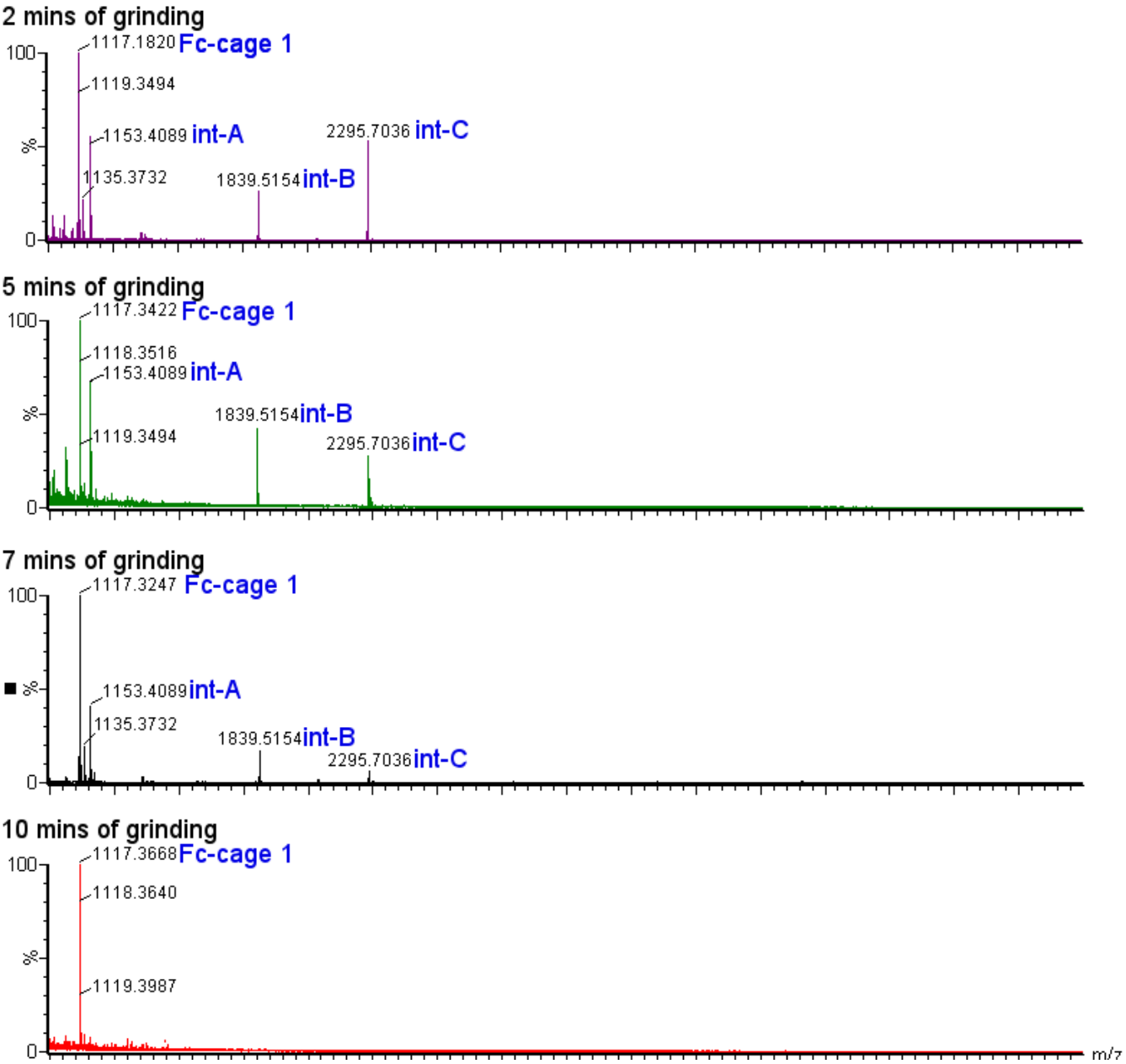


Figure S30: TOF-HRMS(ESI) spectra regarding mechanistic studies with **FcC1**.

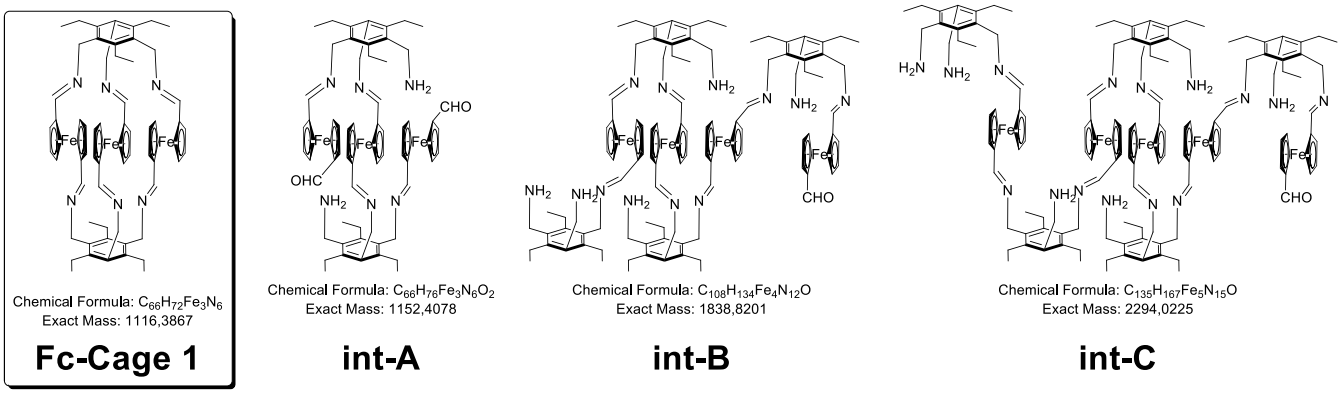


Figure S31: Intermediate products identified with TOF-HRMS(ESI) spectra.

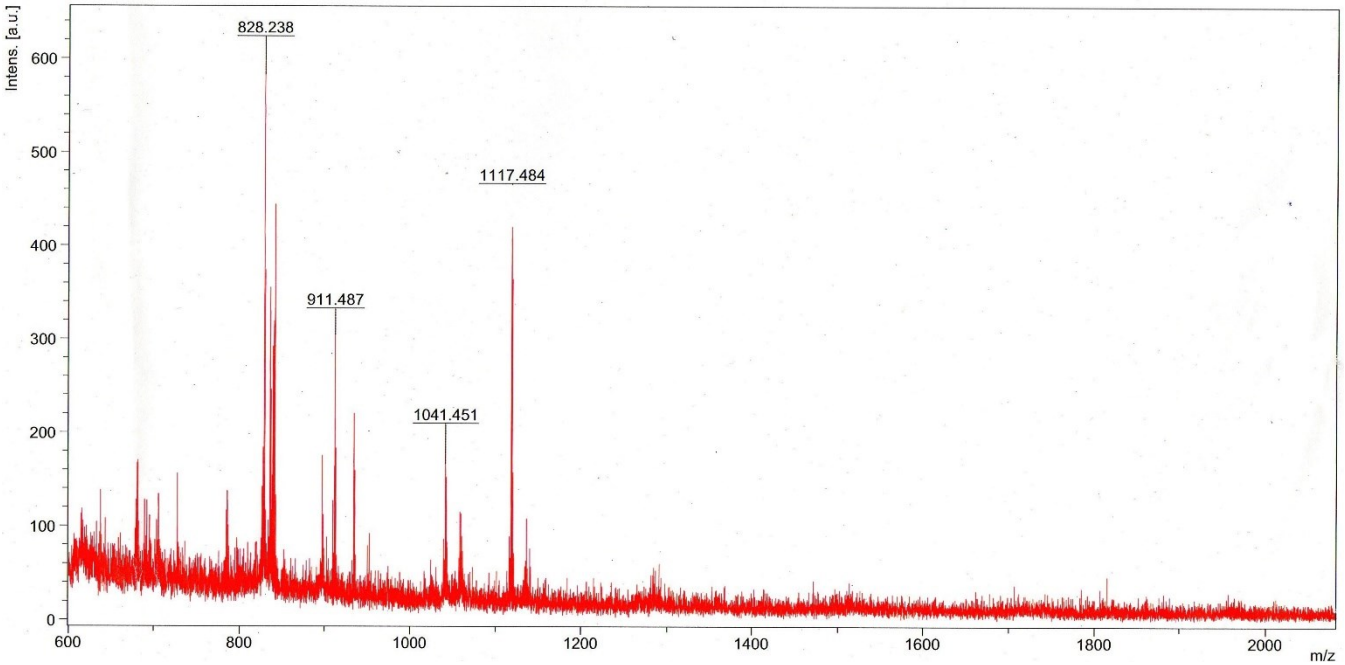


Figure S32: MALDI MS spectrum of a precipitate assumed to be mostly high-mass oligomers, when attempting to prepare **FcC1** in $CDCl_3$ at rt a concentration of >70 mM.

VII. IR spectra

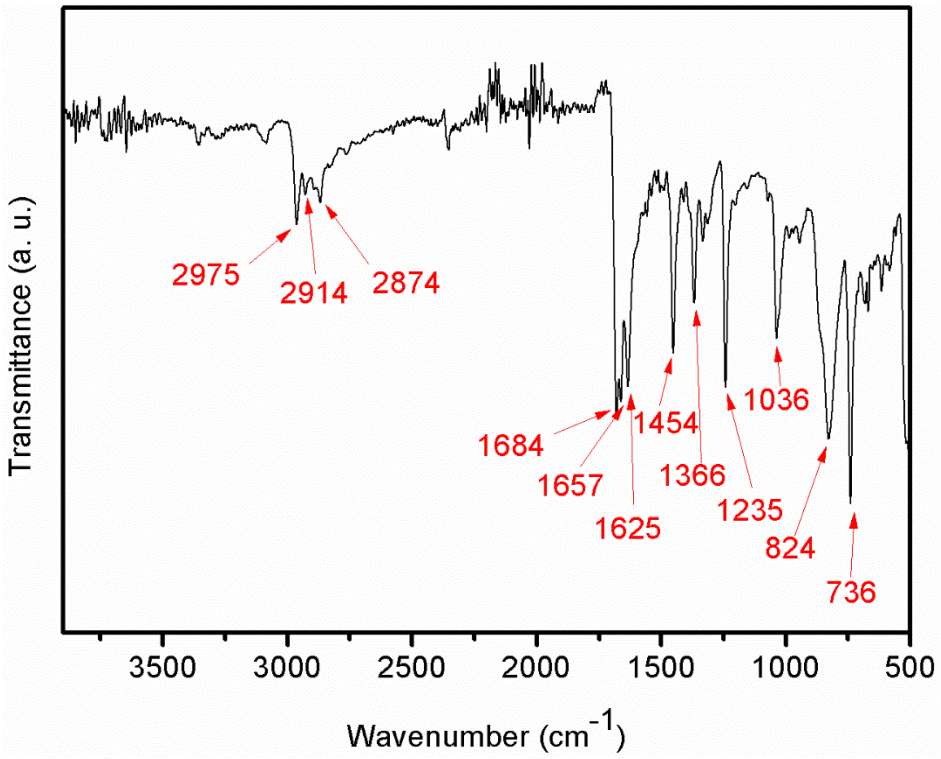


Figure S33: AT-IR spectrum of **FcC1**.

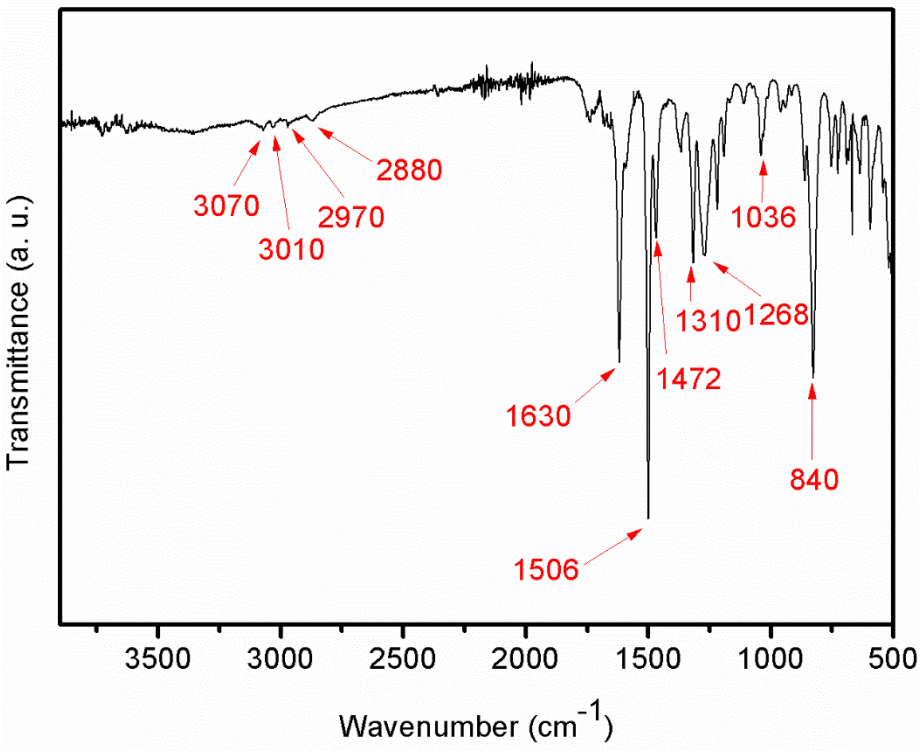


Figure S34: AT-IR spectrum of **FcC2**.

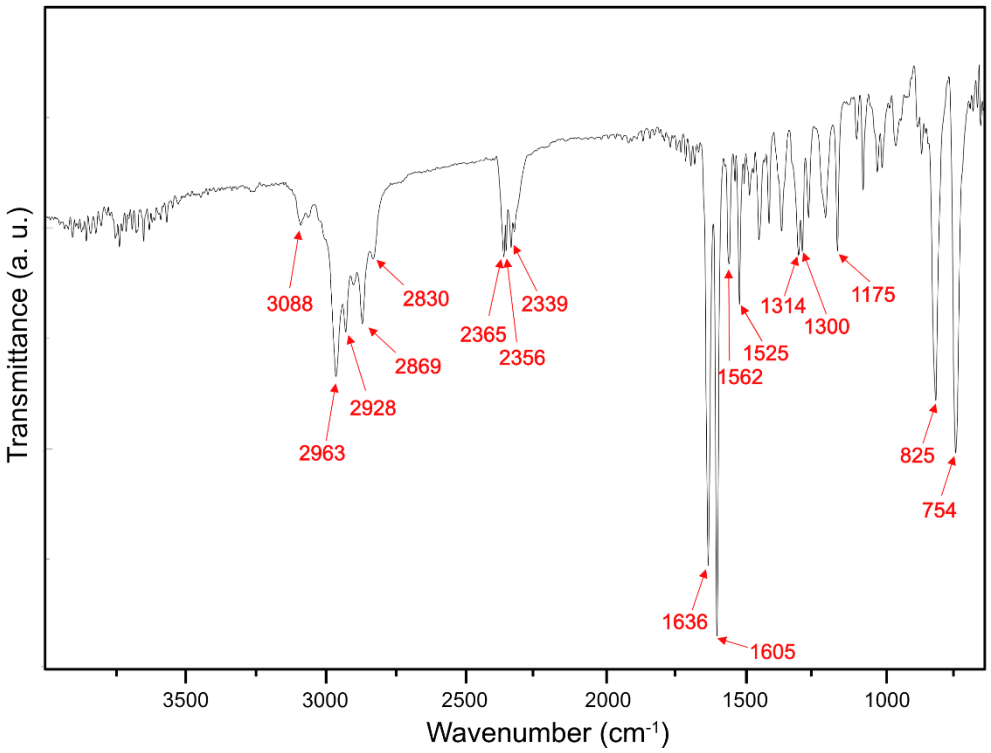


Figure S35: AT-IR spectrum of **FcC3**.

VIII. PXRD comparisons

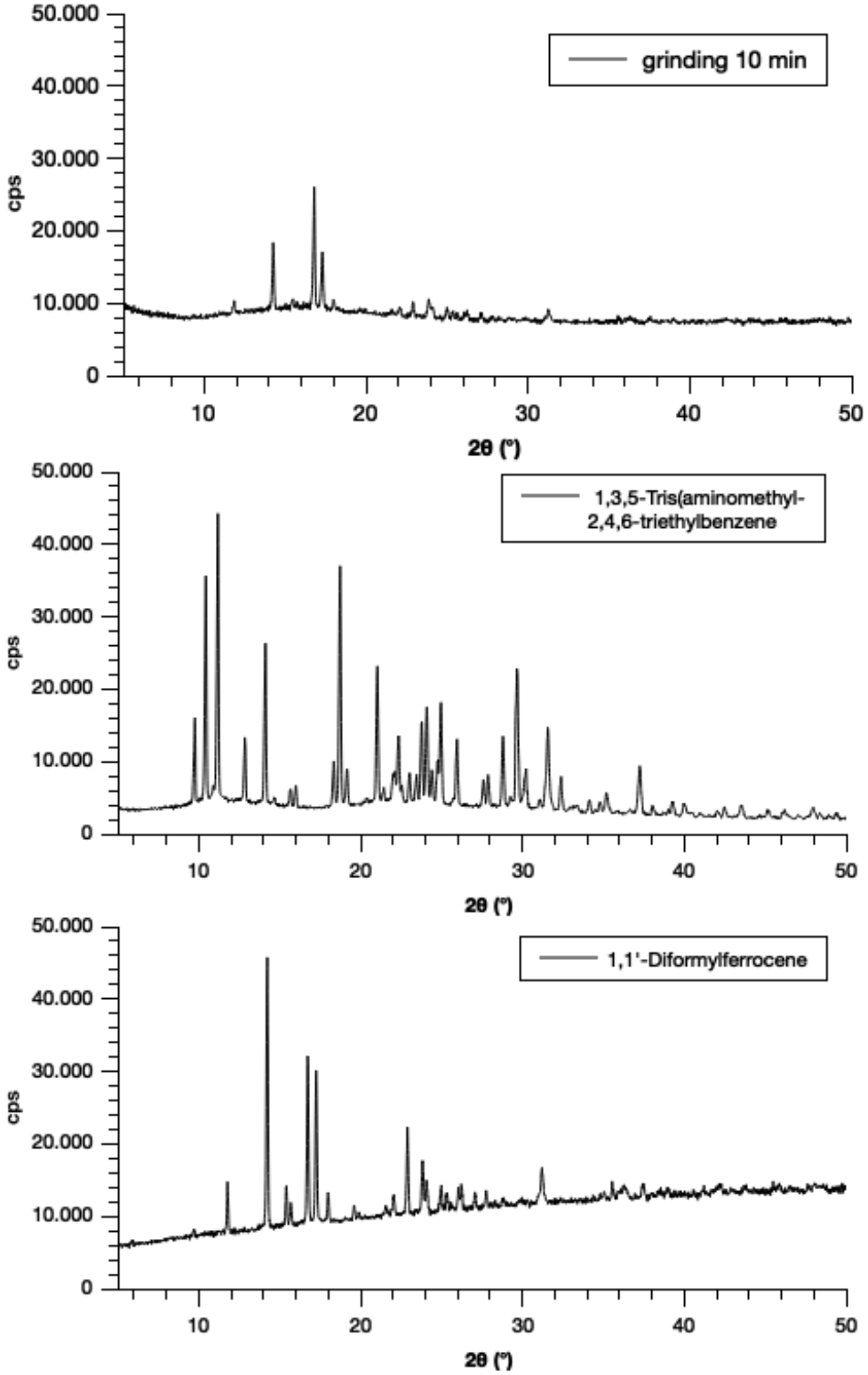


Figure S36: Comparison of PXRD patterns of the starting materials (bottom) and **FcC1** directly from the reaction vial (top).

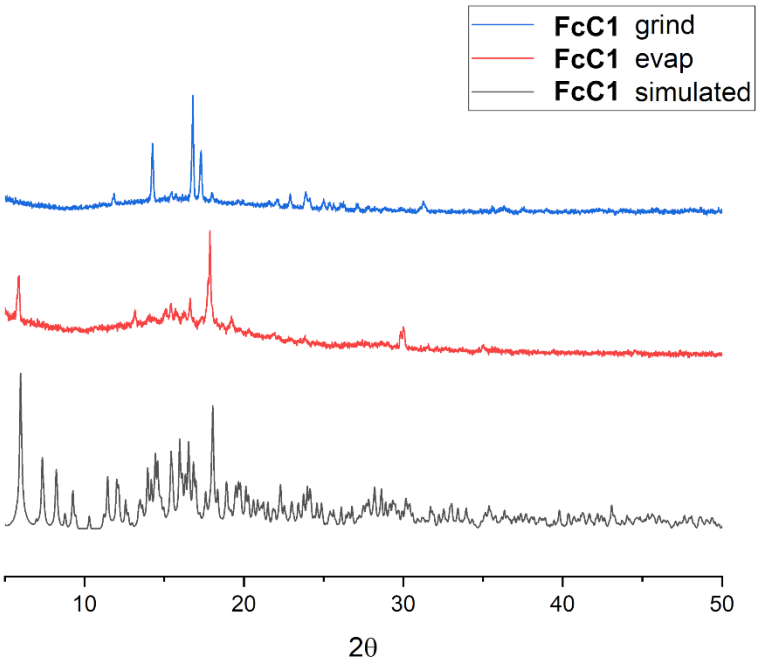


Figure S37: Comparison of PXRD patterns for **FcC1**. Blue PXRD pattern of the sample directly after mechanochemical grinding (top), red PXRD pattern of the sample dissolved in $CHCl_3$ and evaporated again (middle) and black PXRD pattern calculated from SC-XRD data of **FcC1** (bottom).

IX. References

[S1] J. C. Lauer, W.-S. Zhang, F. Rominger, R. R. Schröder and M. Mastalerz, *Chem. Eur. J.*, 2018, **24**, 1816–1820.

[S2] H. Liang, L. Vasamsetty, T. Li, J. Jiang, X. Pang and J. Wang, *Chem. Eur. J.*, 2020, **26**, 14546–14550.

[S3] G. Gattuso, G. Grasso, N. Marino, A. Notti, A. Pappalardo, S. Pappalardo and M. F. Parisi, *Eur. J. Org. Chem.*, 2011, 5696–5703.

[S4] C. F. R. A. C. Lima, A. M. Fernandes, A. Melo, L. M. Gonçalves, A. M. S. Silva and L. M. N. B. F. Santos, *Phys. Chem. Chem. Phys.*, 2015, **17**, 23917–23923.

[S5] B. K. Hong, I. S. Lee, D. M. Shin and Y. K. Chung, *Chem. Commun.*, 2004, 936–937.

[S6] A. I. Kosińska, M. K. Nisiewicz, A. M. Nowicka and A. Kasprzak, *Chempluschem*, 2021, **86**, 820–826.

[S7] S. Viel, F. Ziarelli, G. Pages, C. Carrara and S. Caldarelli, *J. Magn. Reson.*, 2008, **190**, 113–123.

[S8] R. H. Stokes, P. J. Dunlop, J. R. Hall, *Trans. Faraday Soc.* **1953**, *49*, 886–890.

[S9] G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3–8.

[S10] A. L. Spek, *Acta Crystallogr. Sect. C*, 2015, **71**, 9–18.

[S11] S. C. Capelli, H.-B. Bürgi, B. Dittrich, S. Grabowsky and D. Jayatilaka, *IUCrJ*, 2014, **1**, 361–379.

[S12] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.

[S13] F. Kleemiss, O. V. Dolomanov, M. Bodensteiner, N. Peyerimhoff, L. Midgley, L. J. Bourhis, A. Genoni, L. A. Malaspina, D. Jayatilaka, J. L. Spencer, F. White, B. Grundkötter-Stock, S. Steinhauer, D. Lentz, H. Puschmann and S. Grabowsky, *Chem. Sci.*, 2021, **12**, 1675–1692.