

Supporting Information (SI)

The first macrocyclic abnormally coordinating tetra-1,2,3-triazole-5-ylidene iron complex: a promising candidate for olefin epoxidation

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1. General considerations

Experimental remarks. Unless otherwise stated, all manipulations were carried out under an argon atmosphere using standard *Schlenk* and glovebox techniques. Dry and degassed solvents were obtained from an Mbraun solvent purification system, degassed *via* freeze-pump-thaw (3 cycles) and stored over molecular sieve (3 or 4 Å) prior to use. Thin-layer chromatography (TLC) was performed on precoated Merck 60 GF254 silica gel plates with a fluorescent indicator. Detection of the individual spots was carried out with UV light at 254 nm and/or by staining with a potassium permanganate solution. Column chromatography is carried out with normal-phase silica gel as stationary phase. $\text{Fe}(\text{btsa})_2(\text{THF})^1$ and thianthrenyl hexafluorophosphate² were synthesised according to literature procedures. Tetrabutylammonium hexafluorophosphate ($[\text{N}(n\text{-Bu})_4]\text{PF}_6$) was recrystallized three times from ethanol³, and ferrocene was sublimed prior to use. All other reagents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Bruker Advanced Ultrashield AV400 (400 MHz) or AV500 (500 MHz) spectrometer at a temperature of 297 K. Chemical shifts (δ) are reported in ppm and referenced to the residual signal of the deuterated solvent⁴. The following abbreviations are used for the signal multiplicities: singlet (s), doublet (d), triplet (t), heptet (hept), multiplet (m), broad singlet (bs). ¹³C-, ¹⁹F-, and ³¹P-NMR spectra were recorded with ¹H-decoupling. Elemental analyses (C/H/N/S) were performed by the microanalytical laboratory at Technische Universität München. Electrospray ionization mass spectrometry (ESI-MS) data were acquired on a Thermo Fisher Ultimate 3000. Cyclic Voltammetry was performed with a BioLogic SP200 potentiostat with EC-Lab software, using 3 mm diameter glassy carbon disk electrodes (PalmSens, Houten Netherlands) as working and counter electrodes. Prior to use, electrodes were polished with 0.05 µm alumina suspensions (CH Instruments Inc., USA). Ag/AgNO_3 (10 mM AgNO_3 and 100 mM $[\text{N}(n\text{-Bu})_4]\text{PF}_6$ in MeCN) was used as the reference electrode, separated *via* a Vycor 3535 frit (Advanced Glass & Ceramics, Holden, MA). CV measurements were conducted in a five-necked glass cell under an argon atmosphere. A scan rate of 100 mV/s was applied. Potentials are reported with reference to an internal standard of ferrocenium/ferrocene (Fc/Fc^+). Tetrabutylammonium hexafluorophosphate $[\text{N}(n\text{-Bu})_4]\text{PF}_6$ (100 mM in dry and degassed MeCN) was used as the electrolyte. The concentration of the complex was about 0.3 mM. UV-Vis spectra were recorded on an Agilent Technologies Cary 60 UV-Vis spectrophotometer at 20 °C. The concentration of the complex was 0.2 mM dissolved in dry and degassed MeCN. GC analysis was performed with an Agilent Technologies 7890B GC-FID system with a 7693A Automatic Liquid Sampler for 150 samples with G4513A Autoinjector using a HP-5 column (30 m × 320 µm × 0.25µm).

2. Single crystal X-ray diffraction

X-ray crystallographic data was collected on a Bruker D8 Venture single crystal X-ray diffractometer with the following setup: A CMOS detector (Bruker Photon-100), a Mo IMS microsource and a Helios optic using the APEX3 software package.⁵ The measurement used MoK α radiation ($\lambda = 0.71073 \text{ \AA}$) and was performed on a single crystal coated with perfluorinated ether. The crystal was fixed on top of a micromount sample holder and frozen under a stream of cold nitrogen at 100 K. A matrix scan was used to determine the initial lattice parameters. Reflections were corrected for Lorentz and polarisation effects, scan speed, and background using SAINT.⁶ Absorption corrections, including odd and even ordered spherical harmonics were performed using SADABS.⁷ Space group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structure was solved by direct methods (SHELXT) with the aid of successive difference Fourier maps, and was refined against all data using SHELXL-2015 in conjunction with SHELXLE.⁸⁻¹⁰ Hydrogen atoms were calculated in ideal positions as follows: Methyl hydrogen atoms were refined as part of rigid rotating groups, with a C–H distance of 0.98 \AA and $U_{iso}(\text{H}) = 1.5 \cdot U_{eq}(\text{C})$. Other H atoms were placed in calculated positions and refined using a riding model, with methylene and aromatic C–H distances of 0.99 \AA and 0.95 \AA , respectively, other C–H distances of 1.00 \AA and $U_{iso}(\text{H}) = 1.2 \cdot U_{eq}(\text{C})$. Non-hydrogen atoms were refined with anisotropic displacement parameters. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o - F_c)^2$ with SHELXL weighting scheme. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.¹¹ The image of the crystal structure was generated with Mercury¹² or Platon¹³. CCDC 2184662 and 2184663 contain the supplementary crystallographic data for this paper. This data can be obtained free of charge *via* www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Single crystals of calix[4]3-methyl-1,2,3-triazolium methyltriflate salt **b** suitable for X-ray diffraction were obtained in acetonitrile at 0 °C. A clear colourless plate-like specimen of C₂₄H₃₀F₁₂N₁₄O₁₂S₄, approximate dimensions 0.089 mm x 0.274 mm x 0.385 mm, was used for the X-ray crystallographic analysis.

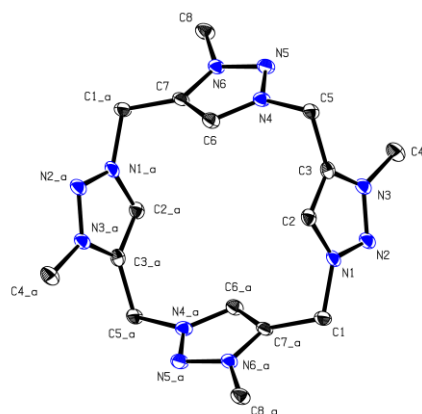


Fig. S1 ORTEP-style representation of the cationic fragment of calix[4]3-methyl-1,2,3-triazolium methyltriflate salt **b**. Hydrogen atoms and OTf⁻ anions, as well as a co-crystallised MeCN molecule are omitted for clarity and thermal ellipsoids are shown at 50% probability level. Symmetry code: $-x+1, -y+1, -z+1$.

Table S1. Crystallographic data and structure refinement parameters of compound **b**.

| Sample and Crystal Data | |
|---|---|
| CCDC number | 2184662 |
| Chemical formula | C ₂₄ H ₃₀ F ₁₂ N ₁₄ O ₁₂ S ₄ |
| Formula weight | 1062.86 g/mol |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal size | 0.089 x 0.274 x 0.385 mm |
| Crystal habit | clear colourless plate |
| Crystal System | monoclinic |
| Space group | P 1 21/c 1 |
| Unit cell dimensions | a = 10.1484(9) Å α = 90 ° b = 19.9082(16) Å β = 97.161(3) ° c = 10.3888(8) Å γ = 90 ° |
| Volume | 2082.5(3) Å ³ |
| Z | 2 |
| Density (calculated) | 1.695 g/cm ³ |
| Absorption coefficient | 0.356 mm ⁻¹ |
| F(000) | 1080 |
| Data Collection and Structure Refinement | |
| Diffractometer | Bruker D8 Venture |
| Radiation Source | IMS microsource, Mo |
| Theta range for data collection | 2.02 to 25.68 ° |
| Index ranges | -12 ≤ h ≤ 12, -24 ≤ k ≤ 24, -12 ≤ l ≤ 12 |
| Reflections collected | 59531 |
| Independent reflections | 3954 [R(int) = 0.0618] |
| Coverage of independent reflections | 99.7% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9690 and 0.8750 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2018/2 (Sheldrick, 2018) |
| Function minimized | Σ w(F _o ² - F _c ²) ² |
| Refinement method | Full-matrix least-squares on F ² |
| Refinement program | SHELXL-2018/3 (Sheldrick, 2018) |
| Data / restraints / parameters | 3954 / 0 / 301 |
| Goodness-of-fit on F ² | 1.138 |
| Final R indices | 3280 data; I > 2σ(I) R1 = 0.0430, wR2 = 0.0793 all data R1 = 0.0559, wR2 = 0.0837 |
| Weighting scheme | w = 1 / [σ ² (F _o ²) + (0.0139P) ² + 3.4897P] where P = (F _o ² + 2F _c ²) / 3 |
| Largest diff. max. min. | 0.502 and -0.490 eÅ ⁻³ |
| R.M.S. deviation from mean | 0.062 eÅ ⁻³ |

A red block-like specimen of complex **2**, approximate dimensions 0.068 mm x 0.076 mm x 0.116 mm, was used for the X-ray crystallographic analysis.

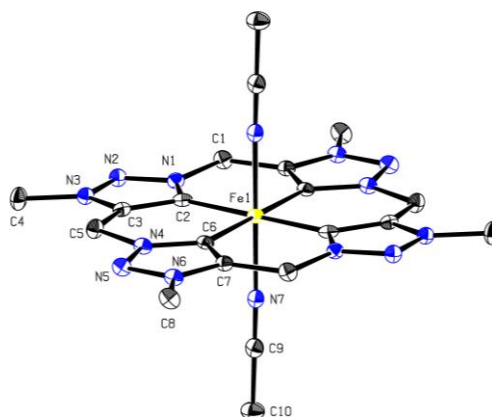


Fig. S2 ORTEP-style representation of the cationic fragment of iron(II) calix[4]3-methyl-1,2,3-triazol-5-ylidene hexafluorophosphate **2**. Hydrogen atoms and PF_6^- anions, as well as a co-crystallised MeCN molecule are omitted for clarity and thermal ellipsoids are shown at 50% probability level. Symmetry code: $-x+1, -y+2, -z+1$.

Table S2. Crystallographic data and structure refinement parameters of complex **2**.

| Sample and Crystal Data | |
|--|--|
| Chemical formula | 2184663 |
| Chemical formula | C ₂₄ H ₃₂ F ₁₂ FeN ₁₆ P ₂ |
| Formula weight | 890.44 g/mol |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal size | 0.068 x 0.076 x 0.116 mm |
| Crystal habit | red block |
| Crystal System | triclinic |
| Space group | P -1 |
| Unit cell dimensions | a = 9.1316(7) Å α = 112.440(3) ° b = 9.4899(9) Å β = 109.710(3) ° c = 11.6931(10) Å γ = 94.233(4) ° |
| Volume | 857.48(13) Å ³ |
| Z | 1 |
| Density (calculated) | 1.724g/cm ³ |
| Absorption coefficient | 0.646 mm ⁻¹ |
| F(000) | 452 |
| Data Collection and Structure Refinement | |
| Diffractometer | Bruker D8 Venture |
| Radiation Source | IMS microsource, Mo |
| Theta range for data collection | 2.02 to 25.68 ° |
| Index ranges | -11<=h<=11, -11<=k<=11, -14<=l<=14 |
| Reflections collected | 31239 |
| Independent reflections | 3267 [R(int) = 0.0677] |
| Coverage of independent reflections | 100.0% |
| Absorption correction | Multi-Scan |
| Max. and min. transmission | 0.9570 and 0.9290 |
| Structure solution technique | direct methods |
| Structure solution program | SHELXT 2018/2 (Sheldrick, 2018) |
| Function minimized | Σ w(Fo ² - Fc ²) ² |
| Refinement method | Full-matrix least-squares on F ² |
| Refinement program | SHELXL-2018/3 (Sheldrick, 2018) |
| Data / restraints / parameters | 3267 / 0 / 254 |
| Goodness-of-fit on F2 | 1.039 |
| Final R indices | 2850 data; I>2σ(I) R1 = 0.0316, wR2 = 0.0652 all data R1 = 0.0389, wR2 = 0.0686 |
| Weighting scheme | w=1/[σ ² (Fo ²)+(0.0186P) ² +0.9044P] where P=(Fo ² +2Fc ²)/3 |
| Largest diff. max. min. | 0.303 and -0.316 eÅ ⁻³ |
| R.M.S. deviation from mean | 0.057 eÅ ⁻³ |

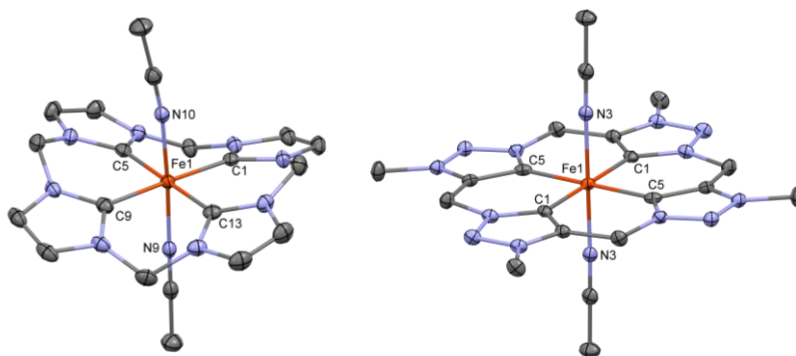


Fig. S3 ORTEP-style representation of the cationic fragment of compound **1**¹⁴ (left) and **2** (right). Hydrogen atoms and PF₆⁻ anions, as well as co-crystallised MeCN molecules are omitted for clarity and thermal ellipsoids are shown at 50% probability level.

Table S3. Comparison of selected crystallographic data of compound **1** and **2**.

| Bond length [Å] | 1 | 2 | Δ [Å] | σ_Δ [Å] |
|--------------------------------------|----------|------------|--------------|--------------------------|
| Fe–C _{NHC} | 1.907(3) | 1.928(2) | 0.021 | 0.0036 |
| Fe–N | 1.932(3) | 1.9247(17) | 0.0073 | 0.0034 |
| Bond Angles [°] | 1 | 2 | Δ [°] | σ_Δ [°] |
| N–Fe–N | 177.1(1) | 180.0(0) | 2.9 | 1 |
| C ₁ –Fe–C _{9/1} | 178.3(1) | 180.0(0) | 1.7 | 1 |
| C ₅ –Fe–C _{13/5} | 179.6(1) | 180.0(0) | 0.4 | 1 |

3. Cyclic voltammetry

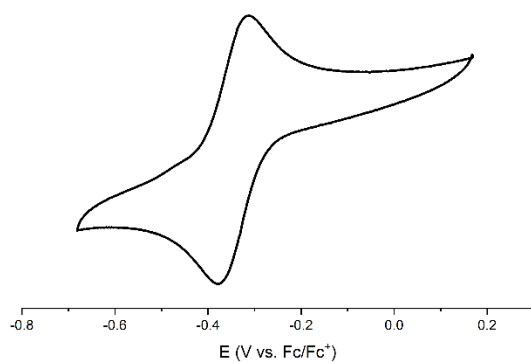


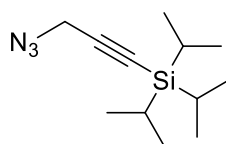
Fig. S4 Cyclic voltammogram of **2** in acetonitrile. Half-cell potential is determined to be $E_{1/2} = -0.34$ V (Fe^{II}/Fe^{III}) and oxidation/reduction potentials are determined to be $E_{ox} = -0.31$ V and $E_{red} = -0.38$ V.

of an aqueous, saturated solution of ammonium chloride are added, whereas a colourless solid participates. The aqueous mixture is extracted with dichloromethane (3 x 300 mL). The organic phases are collected, dried with MgSO₄, filtrated and concentrated under reduced pressure (150 mbar, 60 °C). The crude product is purified *via* column chromatography (SiO₂, *n*-hexane:DCM = 19:1, R_f = 0.75). 15.9 g of the product are obtained as colourless oil (57.9 mmol, 62%).

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 3.94 (s, 2 H, CH₂), 1.09 – 1.06 (m, 21 H, CH(CH₃)₃).

¹³C-NMR (400 MHz, CDCl₃): δ [ppm] = 102.00 (SiCCCH₂), 89.24 (SiCCCH₂), 18.65 (CH₃), 15.03 (CH₂), 11.31 (CH).

(3-Azidoprop-1-yn-1-yl)triisopropylsilane **S3**



S3

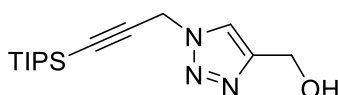
C₁₂H₂₃N₃Si
237.42 g/mol

(3-Azidoprop-1-yn-1-yl)triisopropylsilane **S3** was synthesised according to a literature known procedure.¹⁶ 15.9 g (3-Bromoprop-1-yn-1-yl)triisopropylsilane **S2** (57.9 mmol, 1.00 eq.) and 7.53 g sodium azide (116 mmol, 2.00 eq.) are suspended in 400 mL methanol. The mixture is stirred for 16 h at 75 °C under reflux. The solution is concentrated under reduced pressure (350 mbar, 60 °C), whereas a colourless solid participates. Subsequently, 250 mL water and 200 mL ethyl acetate are added. The water phase is separated and extracted with ethyl acetate (2 x 100 mL). The collected organic layers are washed with 30 mL water and 30 mL brine, dried *via* MgSO₄, filtered and the volatiles are removed under reduced pressure. 12.4 g of the product are obtained as slight yellow oil (52.0 mmol, 90%) and utilised without further purification.

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 3.95 (s, 2 H, CH₂), 1.10 – 1.07 (m, 21 H, CH(CH₃)₃).

¹³C-NMR (400 MHz, CDCl₃): δ [ppm] = 98.65 (SiCCCH₂), 89.37 (SiCCCH₂), 40.84 (CH₂), 18.63 (CH₃), 11.19 (CH).

(1-(3-(Triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methanol **S4**



S4

$C_{15}H_{27}N_3OSi$
293.49 g/mol

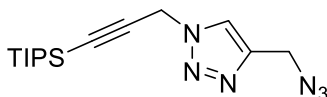
(1-(3-(Triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methanol **S4** was synthesised according to a modified literature known procedure.¹⁷ 12.4 g (3-Azidoprop-1-yn-1-yl)triisopropylsilane **S3** (52.0 mmol, 1.00 eq.) are dissolved in 300 mL *t*BuOH and water (1 : 1). 4.54 mL Propargyl alcohol (78.0 mmol, 1.50 eq.), copper(II)sulfate pentahydrate (10.4 mmol, 0.20 eq.) and sodium ascorbate (20.8 mmol, 0.40 eq.) are added subsequently. The orange suspension is stirred at 60 °C for 21 h. After cooling to r.t. the mixture is extracted with dichloromethane (4 x 200 mL). The united organic layers are washed with 60 mL water and 180 mL brine, dried *via* MgSO₄, filtered and the volatiles are removed under reduced pressure. The brownish solid is washed with cold pentane (3 x 25 mL). After drying under vacuum, 9.14 g of the product are obtained as colourless solid (31.1 mmol, 60%).

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.77 (s, 1 H, *H*_{trz}), 5.22 (s, 2 H, CCH₂N), 4.81 (s, 2 H, CCH₂OH), 1.09 – 1.06 (m, 21 H, CH(CH₃)₃).

¹³C-NMR (400 MHz, CDCl₃): δ [ppm] = 142.94 (*C*_{trz}CH₂OH), 121.85 (*C*_{trz}NCH₂), 97.46 (SiCCCH₂), 90.53 (SiCCCH₂), 45.83 (CH₂OH), 41.22 (NCH₂C), 18.66 (CH₃), 11.17 (CH₃CH).

ESI-MS (*m/z*): calcd [M–H]⁺: 294.20; found: 294.09 [M–H]⁺.

4-(Azidomethyl)-1-(3-(triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazole **S5**



S5

$C_{15}H_{26}N_6Si$
318.50 g/mol

4-(Azidomethyl)-1-(3-(triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazole **S5** was synthesised according to a modified literature known procedure.¹⁷ Under *Schlenk*-conditions 9.14 g (1-(3-(Triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methanol **S4** (31.1 mmol, 1.00 eq.) are dissolved in 200 mL degassed dimethylformamide in a flame dried *Schlenk*-flask and cooled to 0 °C. Under stirring, 16.8 g PPh₃ (63.8 mmol, 2.05 eq.) are added portionwise at this temperature, whereby the solution turns brown. The mixture is stirred for further 5 min at 0 °C. Subsequently, 22.7 g carbon tetrabromide (68.5 mmol,

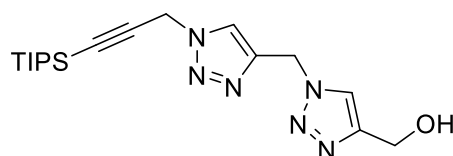
2.20 eq.) is added portionwise at 0 °C, whereby the solution decolours briefly and then turns brown again. The mixture is stirred for further 15 min at 0 °C. Subsequently, 6.07 g sodium azide (93.4 mmol, 3.00 eq.) is added at 0 °C, whereby the solution turns red brownish. The mixture is again stirred for further 10 min at 0 °C and allowed to warm up to room temperature. The mixture is stirred at r.t. for 1 h. At atmospheric conditions, the reaction is quenched by the addition of 200 mL water. The mixture is extracted with ethyl acetate (4 x 200 mL). The collected organic layers are washed with 130 mL brine, dried *via* MgSO₄, filtered and the volatiles are removed under reduced pressure (16 mbar, 60 °C). The crude product is obtained as brown solid and purified *via* column chromatography (SiO₂, *n*-hexane:EtOAc = 3:1 to 2:1, R_f = 0.32). 8.99 g of the product are obtained as slight yellow oil (28.2 mmol, 91%).

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.80 (s, 1 H, H_{trz}), 5.24 (s, 2 H, CCH₂N), 4.50 (s, 2 H, CCH₂N₃), 1.09 – 1.07 (m, 21 H, CH(CH₃)₃).

¹³C-NMR (400 MHz, CDCl₃): δ [ppm] = 142.94 (C_{trz}CH₂OH), 121.84 (C_{trz}NCH₂), 97.48 (SiCCCH₂), 90.53 (SiCCCH₂), 45.83 (CH₂OH), 41.21 (NCH₂C), 18.66 (CH₃), 11.18 (CH₃CH).

ESI-MS (*m/z*): calcd [M]⁺: 318.20, found: 318.96.

(1-((1-(3-(Triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methanol **S6**



S6

C₁₈H₃₀N₆OSi
374.56 g/mol

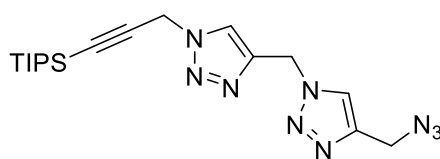
(1-((1-(3-(Triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methanol **S6** was synthesised according to a modified literature known procedure.¹⁷ 8.99 g 4-(Azidomethyl)-1-(3-(triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazole **S5** (28.3 mmol, 1.00 eq.) are dissolved in 250 mL *t*BuOH and water (1 : 1). 2.46 mL Propargyl alcohol (42.3 mmol, 1.50 eq.), copper(II)sulfate pentahydrate (5.65 mmol, 0.20 eq.) and sodium ascorbate (11.3 mmol, 0.40 eq.) are added subsequently. The orange suspension is stirred at 60 °C for 20 h. After cooling to r.t., the mixture is extracted with dichloromethane (1 x 300 mL and 2 x 200 mL). The united organic layers are washed with 180 mL brine, dried *via* MgSO₄, filtered and the volatiles are removed under reduced pressure. After drying under vacuum, 9.14 g of the product are obtained as brownish solid (24.4 mmol, 86%). The product is used without further purification.

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.83 (s, 1 H, *H*_{trz}), 7.69 (s, 1 H, *H*_{trz}), 5.66 (s, 2 H, CCH₂N), 5.21 (s, 2 H, CCH₂N), 4.75 (s, 2 H, CCH₂OH), 3.07 (bs, 1 H, OH), 1.07 – 1.02 (m, 21 H, CH(CH₃)₃).

¹³C-NMR (400 MHz, CDCl₃): δ [ppm] = 148.38 (C_{trz}CH₂OH), 141.91 (C_{trz}CH₂N), 122.76 (C_{trz}C_{trz}CH₂N), 122.11 (C_{trz}C_{trz}CH₂OH), 97.15 (SiCCCH₂), 90.77 (SiCCCH₂), 56.48 (CH₂OH), 45.43 (C_{trz}CH₂N), 41.29 (NCH₂C), 18.62 (CH₃), 11.11 (CH₃CH).

ESI-MS (*m/z*): calcd [M–H]⁺: 375.23, found: 375.04.

4-(Azidomethyl)-1-((1-(3-(triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazole **S7**



S7

C₁₈H₂₉N₉Si
399.58 g/mol

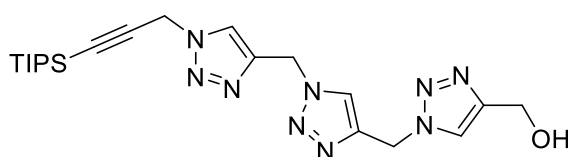
4-(Azidomethyl)-1-((1-(3-(triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazole **S7** was synthesised according to a modified literature known procedure.¹⁷ Under *Schlenk*-conditions, 9.46 g (1-((1-(3-(Triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methanol **S6** (25.3 mmol, 1.00 eq.) are dissolved in 200 mL degassed dimethylformamide in a flame dried *Schlenk*-flask and cooled to 0 °C. Under stirring 13.6 g PPh₃ (51.8 mmol, 2.05 eq.) are added portion wise at this temperature, whereby the solution turns brown. The mixture is stirred for further 5 min at 0 °C. Subsequently, 18.4 g carbon tetrabromide (55.6 mmol, 2.20 eq.) is added portionwise at 0 °C, whereby the solution decolours briefly and then turns brown again. The mixture is stirred for further 15 min at 0 °C. Subsequently, 4.93 g sodium azide (75.8 mmol, 3.00 eq.) is added at 0 °C, whereby the solution turns red brownish. The mixture is again stirred for further 10 min at 0 °C and allowed to warm up to room temperature. The mixture is stirred at r.t. for another 3 h. At atmospheric conditions, the reaction is quenched by the addition of 200 mL water. The mixture is extracted with ethyl acetate (5 x 200 mL). The collected organic layers are dried *via* MgSO₄, filtered and the volatiles are removed under reduced pressure (10 mbar, 60 °C). The crude product is obtained as brown solid and purified *via* column chromatography (SiO₂, EtOAc: *n*-hexane = 2:1, R_f = 0.5). 8.48 g of the product are obtained as yellow crystalline solid (22.2 mmol, 84%).

¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.84 (s, 1 H, *H*_{trz}), 7.72 (s, 1 H, *H*_{trz}), 5.69 (s, 2 H, CCH₂N), 5.21 (s, 2 H, CCH₂N), 4.45 (s, 2 H, CCH₂N₃), 1.07 – 1.02 (m, 21 H, CH(CH₃)₃).

¹³C-NMR (400 MHz, CDCl₃): δ [ppm] = 143.19 (C_{trz}CH₂N₃), 141.70 (C_{trz}CH₂N), 122.70 (C_{trz}C_{trz}CH₂N), 122.57 (C_{trz}C_{trz}CH₂N₃), 97.08 (SiCCCH₂), 90.83 (SiCCCH₂), 45.70 (CH₂N₃), 45.56 (C_{trz}CH₂N), 41.29 (NCH₂C), 18.60 (CH₃), 11.09 (CH₃CH).

ESI-MS (*m/z*): calcd [M-H]⁺: 400.24, found: 400.05.

(1-((1-((1-(3-(Triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methanol S8



S8

C₂₁H₃₃N₉OSi
455.64 g/mol

8.48 g 4-(Azidomethyl)-1-((1-(3-(triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazole **S7** (21.2 mmol, 1.00 eq.) are dissolved in 250 mL *t*BuOH and water (1 : 1). 1.85 mL propargyl alcohol (31.8 mmol, 1.50 eq.), 1.06 g copper(II)sulfate pentahydrate (4.24 mmol, 0.20 eq.) and 1.68 g sodium ascorbate (8.49 mmol, 0.40 eq.) are added subsequently. The yellow suspension is stirred at 60 °C for 15 h. After cooling to r.t., the orange mixture is diluted with 85 mL water and extracted with dichloromethane (3 x 200 mL and 1 x 100 mL). The united organic layers are washed with 60 mL brine, dried *via* MgSO₄, filtered and the volatiles are removed under reduced pressure. The brown oil is washed with pentane 3 x 20 mL, which forms a colourless solid. After drying under vacuum, 9.24 g of the product are obtained as off-white solid (20.3 mmol, 96%).

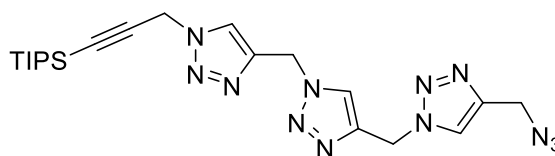
¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.87 (s, 1 H, H_{trz}), 7.81 (s, 1 H, H_{trz}), 7.70 (s, 1 H, H_{trz}), 5.67 (s, 2 H, CCH₂N), 5.63 (s, 2 H, CCH₂N), 5.22 (s, 2 H, CCH₂N), 4.74 (s, 2 H, CCH₂OH), 1.08 – 1.03 (m, 21 H, CH(CH₃)₃).

¹H-NMR (400 MHz, DMSO-*d*₆): δ [ppm] = 8.19 (s, 2 H, H_{trz}), 7.97 (s, 1 H, H_{trz}), 5.71 (s, 2 H, CCH₂N), 5.64 (s, 2 H, CCH₂N), 5.42 (s, 2 H, CCH₂N), 5.18 (t, ³J = 5.5 Hz, 1 H, OH) 4.47 (d, ³J = 5.5 Hz, 2 H, CCH₂OH), 1.02 – 0.99 (m, 21H, CH(CH₃)₃).

¹³C-NMR (400 MHz, DMSO-*d*₆): δ [ppm] = 148.37 (C_{trz}CH₂OH), 141.98 (C_{trz}CH₂N), 141.73 (C_{trz}CH₂N), 124.18 (C_{trz}C_{trz}CH₂N), 124.01 (C_{trz}C_{trz}CH₂N), 122.79 (C_{trz}C_{trz}CH₂OH), 100.67 (SiCCCH₂), 86.90 (SiCCCH₂), 55.05 (C_{trz}CH₂N) 54.92 (CH₂OH), 44.53 (CCH₂N), 44.38 (C_{trz}CH₂N), 18.38 (CH₃), 10.55 (CH₃CH).

ESI-MS (*m/z*): calcd [M-H]⁺: 456.27, found: 456.07.

4-(Azidomethyl)-1-((1-((1-(3-(triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazole S9



S9

C₂₁H₃₂N₁₂Si
480.66 g/mol

Under *Schlenk*-conditions 9.24 g (1-((1-((1-(3-(Triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methanol **S8** (20.3 mmol, 1.00 eq.) are dissolved in 250 mL degassed dimethylformamide in a flame dried *Schlenk*-flask and cooled to 0 °C. Under stirring, 10.9 g PPh₃ (41.6 mmol, 2.05 eq.) are added portionwise at this temperature, whereby the solution turns brown. The mixture is stirred for further 5 min at 0 °C. Subsequently, 14.8 g carbon tetrabromide (44.6 mmol, 2.20 eq.) is added portionwise at 0 °C, whereby the solution decolours briefly and then turns brown again. The mixture is stirred for further 15 min at 0 °C. Subsequently, 3.96 g sodium azide (60.8 mmol, 3.00 eq.) is added at 0 °C, whereby the solution turns red brownish. The mixture is again stirred for further 10 min at 0 °C and allowed to warm up to room temperature. The mixture is stirred at r.t. for 3 h. At atmospheric conditions, the reaction is quenched by the addition of 250 mL water. The mixture is extracted with ethyl acetate (1 x 400 mL and 2 x 200 mL). The collected organic layers are washed with 150 mL brine, dried *via* MgSO₄, filtered and the volatiles are removed under reduced pressure. The crude product is obtained as brown solid and purified *via* column chromatography (SiO₂, Acetone: *n*-hexane = 2:1, R_f = 0.81). Subsequent washing with 80 mL cold ethyl acetate obtains 4.55 g of the product as white solid (9.46 mmol, 46%).

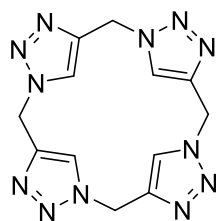
¹H-NMR (400 MHz, CDCl₃): δ [ppm] = 7.85 (s, 1 H, H_{trz}), 7.77 (s, 1H, H_{trz}), 7.71 (s, 1 H, H_{trz}), 5.67 (s, 2 H, CCH₂N), 5.65 (s, 2 H, CCH₂N), 5.22 (s, 2 H, CCH₂N), 4.46 (s, 2 H, CCH₂OH), 1.09 – 1.04 (m, 21 H, CH(CH₃)₃).

¹H-NMR (400 MHz, CD₃CN): δ [ppm] = 7.94 (s, 1 H, H_{trz}), 7.90 (s, 1 H, H_{trz}), 7.85 (s, 1 H, H_{trz}), 5.64 (s, 2 H, CCH₂N), 5.62 (s, 2 H, CCH₂N), 5.21 (s, 2 H, CCH₂N), 4.42 (s, 2 H, CCH₂OH), 1.08 – 1.02 (m, 21 H, CH(CH₃)₃).

¹³C-NMR (400 MHz, CD₃CN): δ [ppm] = 143.45 (C_{trz}CH₂N₃), 142.88 (C_{trz}CH₂N), 142.85 (C_{trz}CH₂N), 124.68 (C_{trz}C_{trz}CH₂N), 124.41 (C_{trz}C_{trz}CH₂N), 124.38 (C_{trz}C_{trz}CH₂N₃), 100.41 (SiCCCH₂), 89.05 (SiCCCH₂), 46.02 (SiCCCH₂) 45.97 (C_{trz}CH₂N), 45.96 (C_{trz}CH₂N), 41.53 (CH₂N₃), 18.82 (CH₃), 11.82 (CH₃CH).

ESI-MS (*m/z*): calcd [M-H]⁺: 481.27, found: 481.04.

Calix[4]1,2,3-triazole a



a

$C_{12}H_{12}N_{12}$
324.31 g/mol

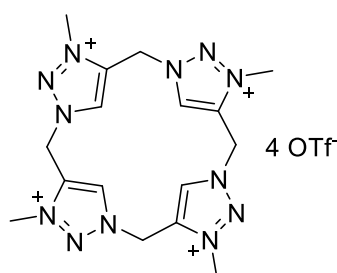
Calix[4]1,2,3-triazole **a** was synthesised according to a modified literature known procedure.¹⁷ Under *Schlenk*-conditions, 500 mg 4-(azidomethyl)-1-((1-((1-(3-(triisopropylsilyl)prop-2-yn-1-yl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazol-4-yl)methyl)-1,2,3-triazole **S9** (1.54 mmol, 1.00 eq.) are dissolved in 1070 mL degassed DMF. 604 mg potassium fluoride (10.4 mmol, 10.0 eq.), 353 μ L of an 48% hydrogen bromide solution in water (3.12 mmol, 3.00 eq.) and 119 mg copper(I) iodide (624 μ mol, 0.60 eq.) are added. The mixture is stirred for 4 d at r.t. until a colourless solid precipitates. All volatiles are removed under reduced pressure. The solid is washed with 60 mL methanol, 60 mL of a semi-concentrated aqueous ammonia solution, 2 x 30 mL water, 60 mL methanol and 60 mL diethyl ether. Residual solvent was removed *via* high vacuum. 308 mg of the product are obtained as white solid (0.96 mmol, 93%). Due to the low solubility of the product in any solvents, only $^1\text{H-NMR}$ spectrometry was applied.

$^1\text{H-NMR}$ (400 MHz, $\text{DMSO-}d_6$): δ [ppm] = 7.71 (s, 4 H, H_{trz}), 5.67 (s, 8 H, CH_2).

Analytical calculation (%) for $C_{12}H_{12}N_{12}$: C 44.44; H 3.73; N 51.83. Found: C 44.45; H 3.70; N 50.52.

4.2 Synthesis of calix[4]3-methyl-1,2,3-triazolium salts b and c

Calix[4]3-methyl-1,2,3-triazolium triflate b



b

$C_{20}H_{24}F_{12}N_{12}O_{12}S_4$
980.70 g/mol

Under *Schlenk*-conditions, 500 mg calix[4]1,2,3-triazole **a** (1.54 mmol, 1.00 eq.) are suspended in 10 mL dry and degassed acetonitrile. 3.49 mL of trifluoromethanesulfonate (30.8 mmol, 20.0 eq.) are added and the reaction mixture is stirred at room temperature. After 5 min the solid is solved and after

another 5 min a colourless solid participates again. The mixture is heated to 60 °C until everything is dissolved. After subsequent cooling to 40 °C the mixture is stirred for another 3 d at 40 °C. After cooling to room temperature, the colourless solid is separated from the orange solution by centrifugation at atmospheric conditions and washed with acetonitrile (3 x 2 mL) and diethyl ether (1 x 10 mL). After drying under high vacuum, 1.09 g of the product are obtained as colourless solid (1.11 mmol, 72%).

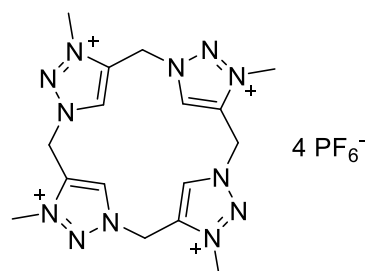
$^1\text{H-NMR}$ (400 MHz, CD_3CN): δ [ppm] = 8.73 (s, 4 H, H_{trz}), 6.21 (s, 8 H, CH_2), 4.37 (s, 12 H, CH_3).

$^{13}\text{C-NMR}$ (400 MHz, CD_3CN): δ [ppm] = 139.60 ($\text{C}_{\text{trzCH}_2\text{N}}$), 131.80 ($\text{NC}_{\text{trz}}\text{HC}_{\text{trz}}\text{CH}_2$), 46.95 (CH_2), 40.61 (CH_3).

$^{19}\text{F-NMR}$ (400 MHz, CD_3CN): δ [ppm] = -79.23 (s, 12 F).

ESI-MS (m/z): calcd [$\text{M-H}_4^{4+}\text{OTf}^-$] $^{3+}$: 179.07, found: 179.03; calcd [$\text{M-H}_4^{4+}2\text{OTf}^-$] $^{2+}$: 343.08, found: 344.02; calcd [$\text{M-H}_4^{6+}4\text{OTf}^-$] $^{2+}$: 492.03 found: 493.89; calcd [$\text{M}^{4+}3\text{OTf}^-$] $^{1+}$: 831.08, found: 830.56.

Calix[4]3-methyl-1,2,3-triazolium hexafluorophosphate **c**



c

$\text{C}_{16}\text{H}_{24}\text{F}_{24}\text{N}_{12}\text{P}_4$
964.31 g/mol

1.09 g Calix[4]3-methyl-1,2,3-triazolium triflate **b** (1.11 mmol, 1.00 eq.) are dissolved in 50 mL water and dropwise added to a solution of 2.71 g Ammonium hexafluorophosphate (16.6 mmol, 15.0 eq.) in 20 mL water. The precipitated colourless solid is separated *via* centrifugation of the reaction mixture and washed with H_2O (2 x 5 mL), cold MeOH (10 mL) and Et_2O (10 mL). After drying under vacuum, 1.07 g of the product (1.11 mmol, 100%) are obtained as colourless solid.

$^1\text{H-NMR}$ (400 MHz, CD_3CN): δ [ppm] = 8.36 (s, 4 H, H_{trz}), 6.23 (s, 8 H, CH_2), 4.38 (s, 12 H, CH_3).

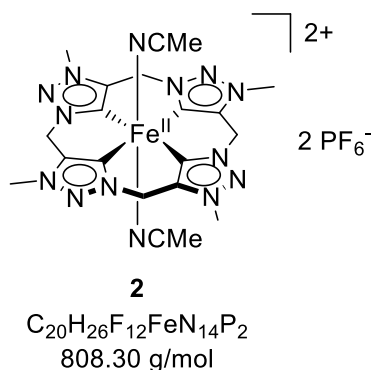
$^{13}\text{C-NMR}$ (400 MHz, CD_3CN): δ [ppm] = 139.45 ($\text{C}_{\text{trzCH}_2\text{N}}$), 131.41 ($\text{NC}_{\text{trz}}\text{HC}_{\text{trz}}\text{CH}_2$), 46.43 (CH_2), 40.50 (CH_3).

$^{19}\text{F-NMR}$ (400 MHz, CD_3CN): δ [ppm] = -73.01 (d, $^2J = 707.28$, 24 F).

$^{31}\text{P-NMR}$ (400 MHz, CD_3CN): δ [ppm] = -144.88 (hept, $^2J = 707.91$, 4 P).

Analytical calculation (%) for $C_{16}H_{24}N_{12}P_4$: C 19.69; H 2.51; N 17.43. Found: C 19.80; H 2.54; N 16.44.

4.3 Synthesis of iron(II) calix[4]3-methyl-1,2,3-triazol-5-ylidene hexafluorophosphate 2



Under *Schlenk*-conditions 93.1 mg $Fe(btsa)_2(THF)$ (207 μ mol, 2.00 eq.) are dissolved in 3 mL dry and degassed acetonitrile and cooled to -40 °C. In another *Schlenk*-tube, 100 mg calix[4]3-methyl-1,2,3-triazolium hexafluorophosphate **c** (104 μ mol, 1.00 eq.) are dissolved in 4 mL dry and degassed acetonitrile and also cooled to -40 °C. Under stirring, the cold ligand solution was added to the cold iron precursor solution *via* transfer cannula. The mixture is slowly allowed to warm up to room temperature, while the solution turns from light yellowish over orange to orange-brownish within minutes. After 3 h of stirring, an orange solid begins to precipitate. The mixture is stirred for further 16 h at room temperature. Subsequently, the orange solid is separated from the brown solution *via* *Whatman*-filtration and washed first with dry and degassed acetonitrile (1 x 0.5 mL) and dry and degassed diethyl ether (3 x 1 mL). After drying under vacuum, 74.4 mg of the product (92.2 μ mol, 78%) are obtained as orange solid.

1H -NMR (400 MHz, CD_3CN): δ [ppm] = 6.12 (s, 8 H, CH_2), 4.21 (s, 12 H, CH_3), 1.96 (s, 6 H, CH_3CN).

^{13}C -NMR (400 MHz, CD_3CN): δ [ppm] = 190.35 (C_{carbene}), 138.88 ($C_{\text{trz-}CH_2N}$), 49.05 (CH_2), 37.08 (CH_3).

^{31}P -NMR (400 MHz, CD_3CN): δ [ppm] = -144.62 (hept, $^2J = 707.91$, 4 P).

ESI-MS (m/z): calcd $[M]^{2+}$: 218.06; found: 217.64 $[M]^{2+}$; calcd $[M^{2+}PF_6^-]^+$: 581.09; found: 580.68 $[M^{2+}PF_6^-]^+$; calcd $[M-H_3^{2+}PF_6^-MeCN]^+$: 625.14; found: 625.57 $[M-H_3^{2+}PF_6^-MeCN]^+$.

Analytical calculation (%) for $C_{20}H_{26}F_{12}FeN_{14}P_2 \cdot 0.45C_4H_{10}O$: C 31.11; H 3.65; N 23.30. Found: C 30.87; H 3.40; N 23.12.

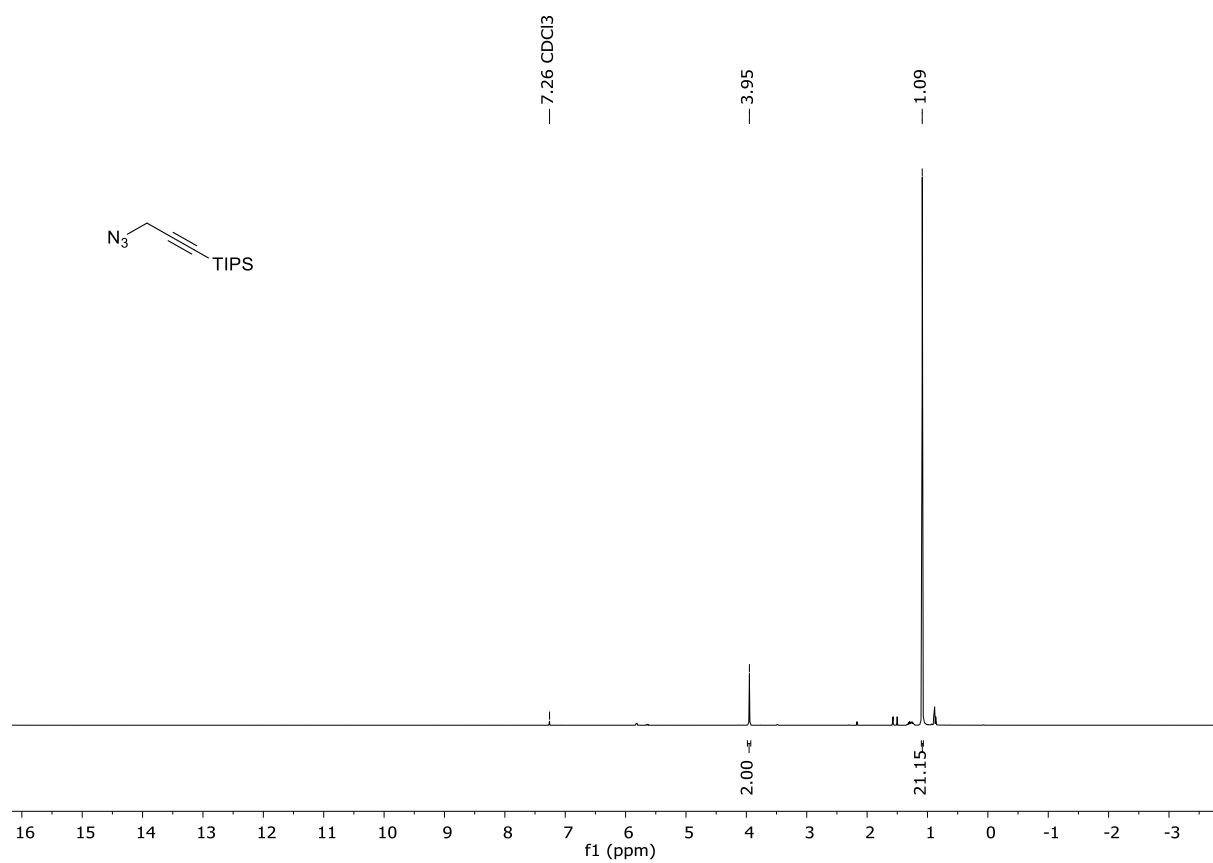


Fig. S7 $^1\text{H-NMR}$ spectrum of **S3** in CDCl_3 .

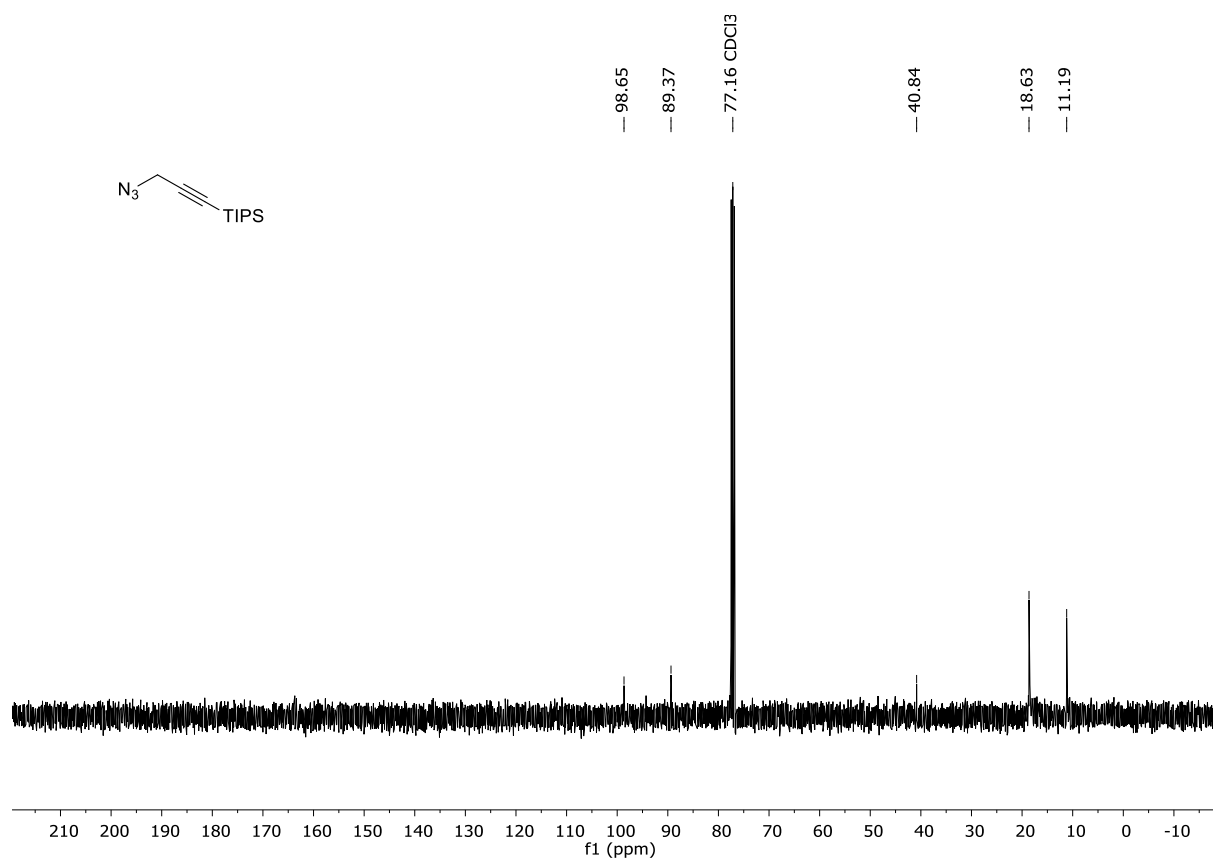


Fig. S8 $^{13}\text{C-NMR}$ spectrum of **S3** in CDCl_3 .

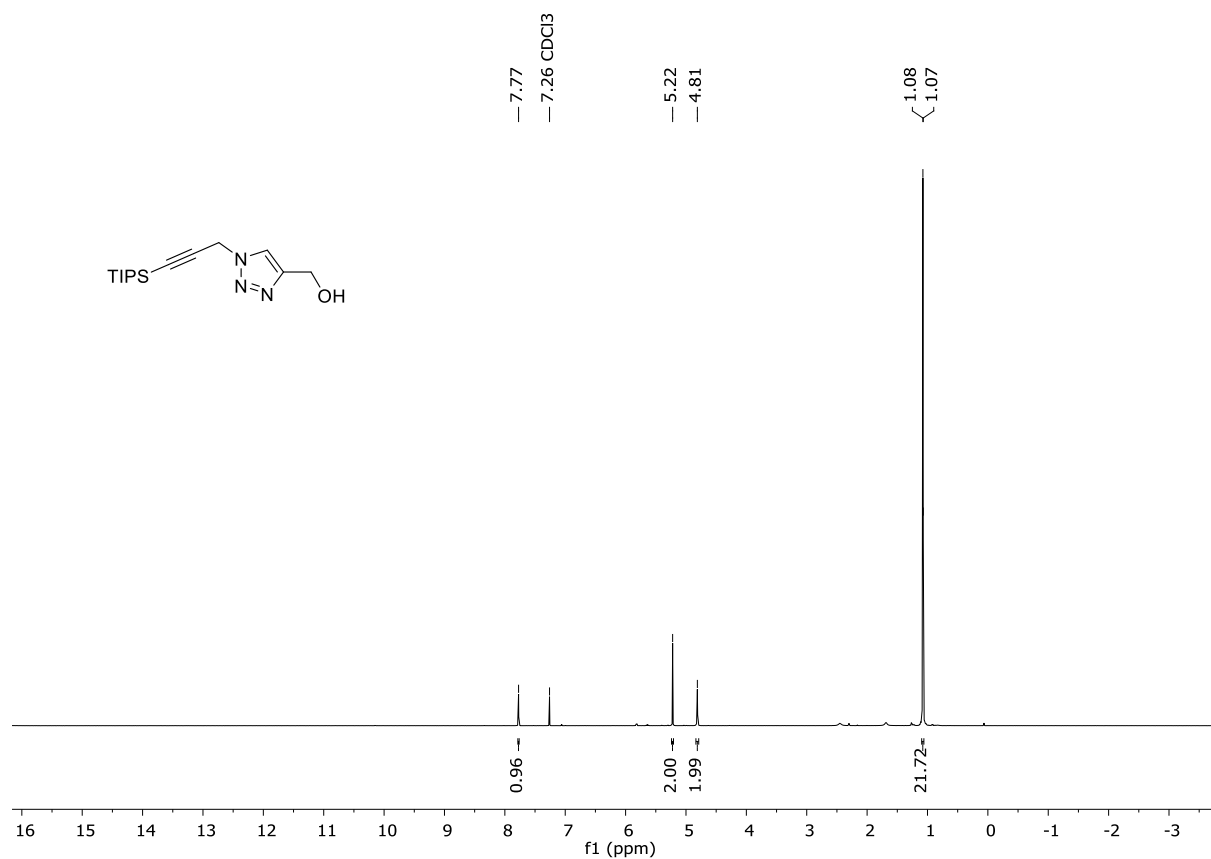


Fig. S9 ¹H-NMR spectrum of **S4** in CDCl₃.

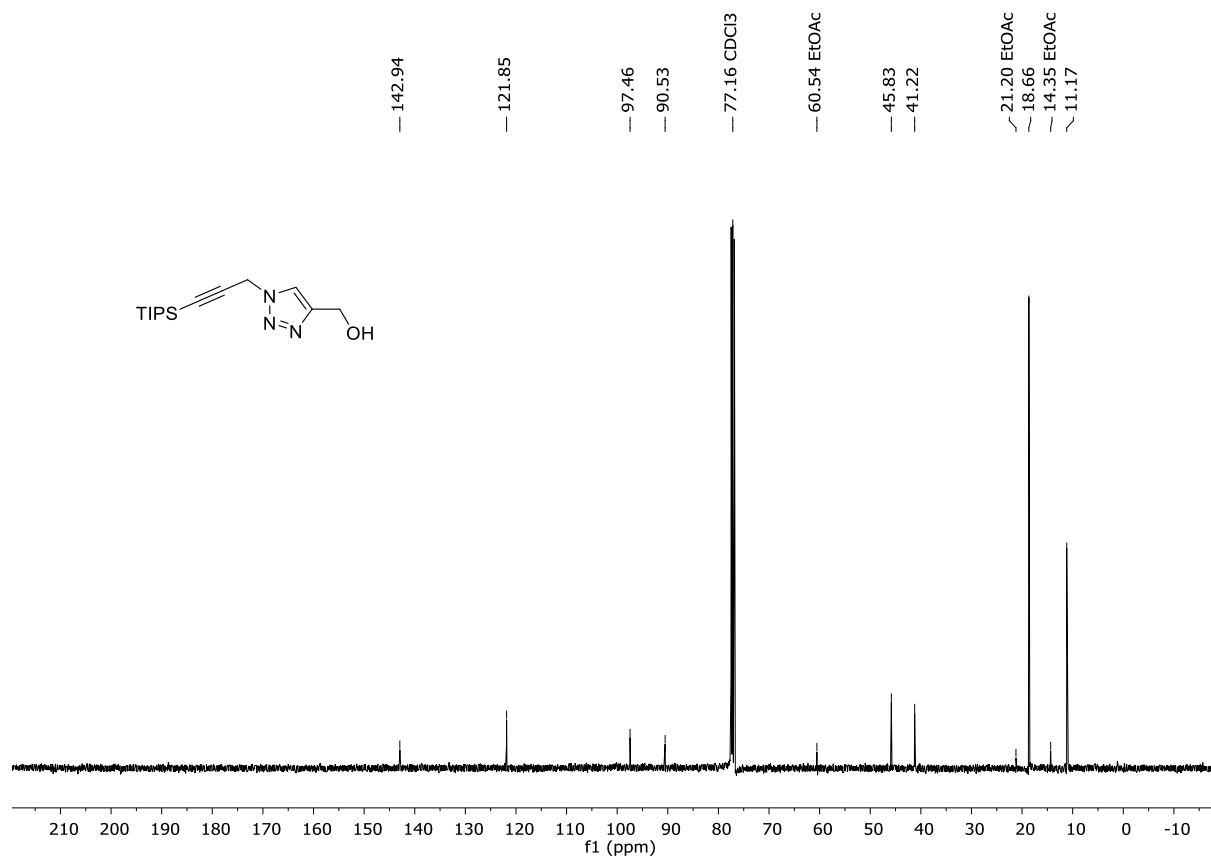


Fig. S10 ¹³C-NMR spectrum of **S4** in CDCl₃.

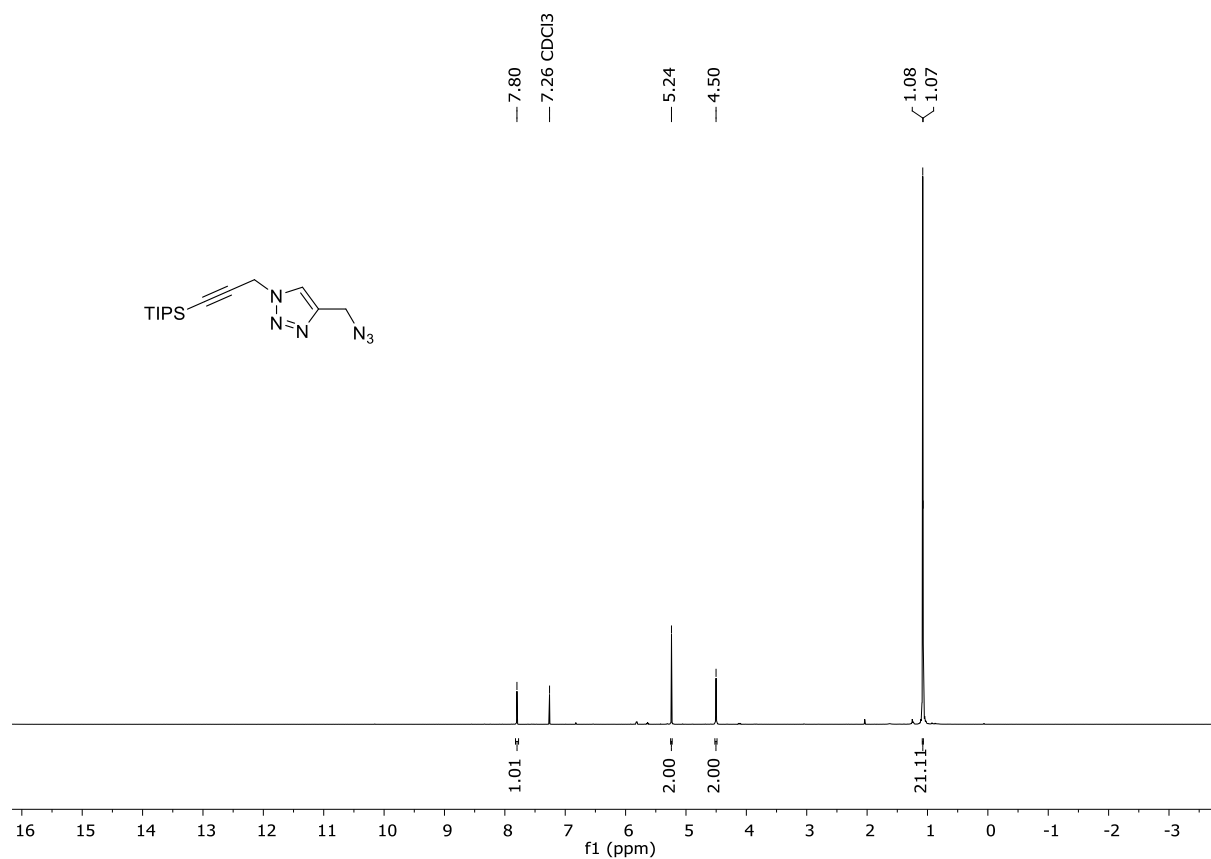


Fig. S11 ¹H-NMR spectrum of **S5** in CDCl₃.

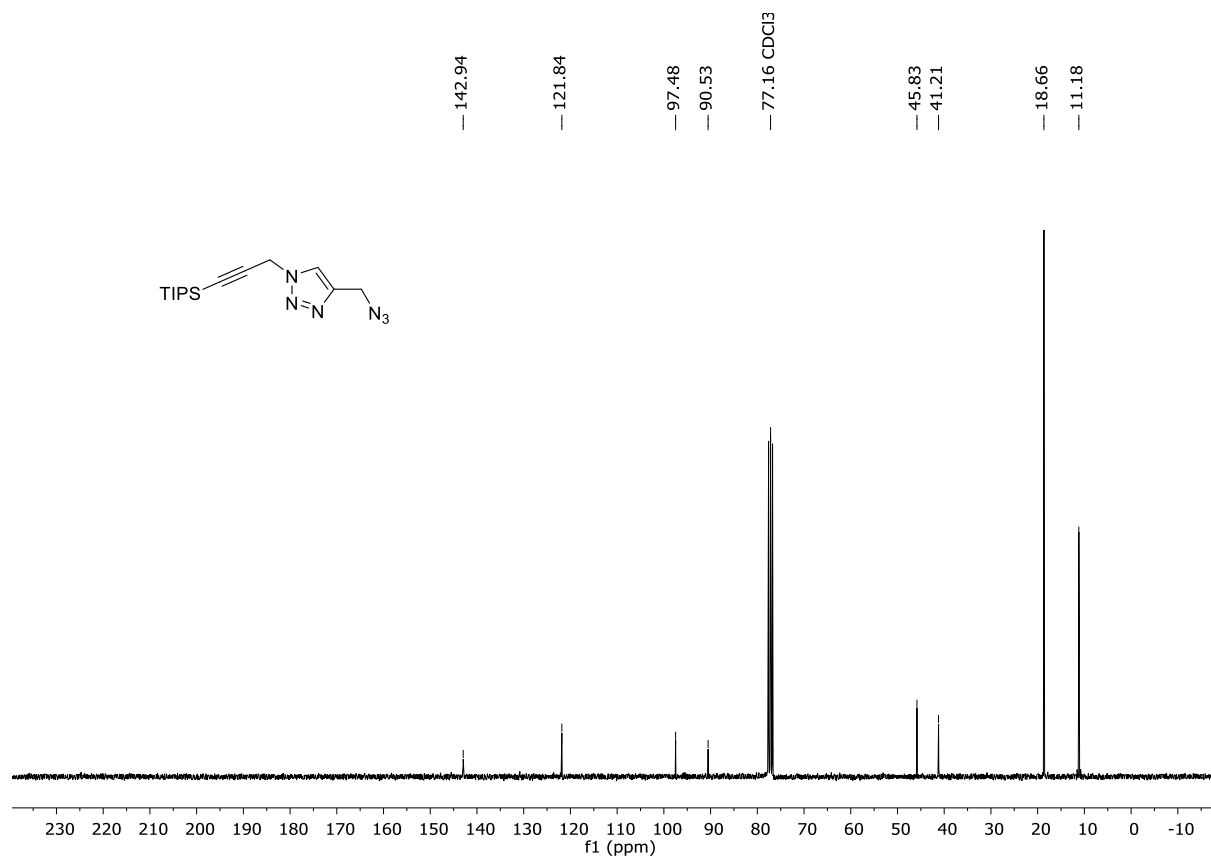


Fig. S12 ¹³C-NMR spectrum of **S5** in CDCl₃.

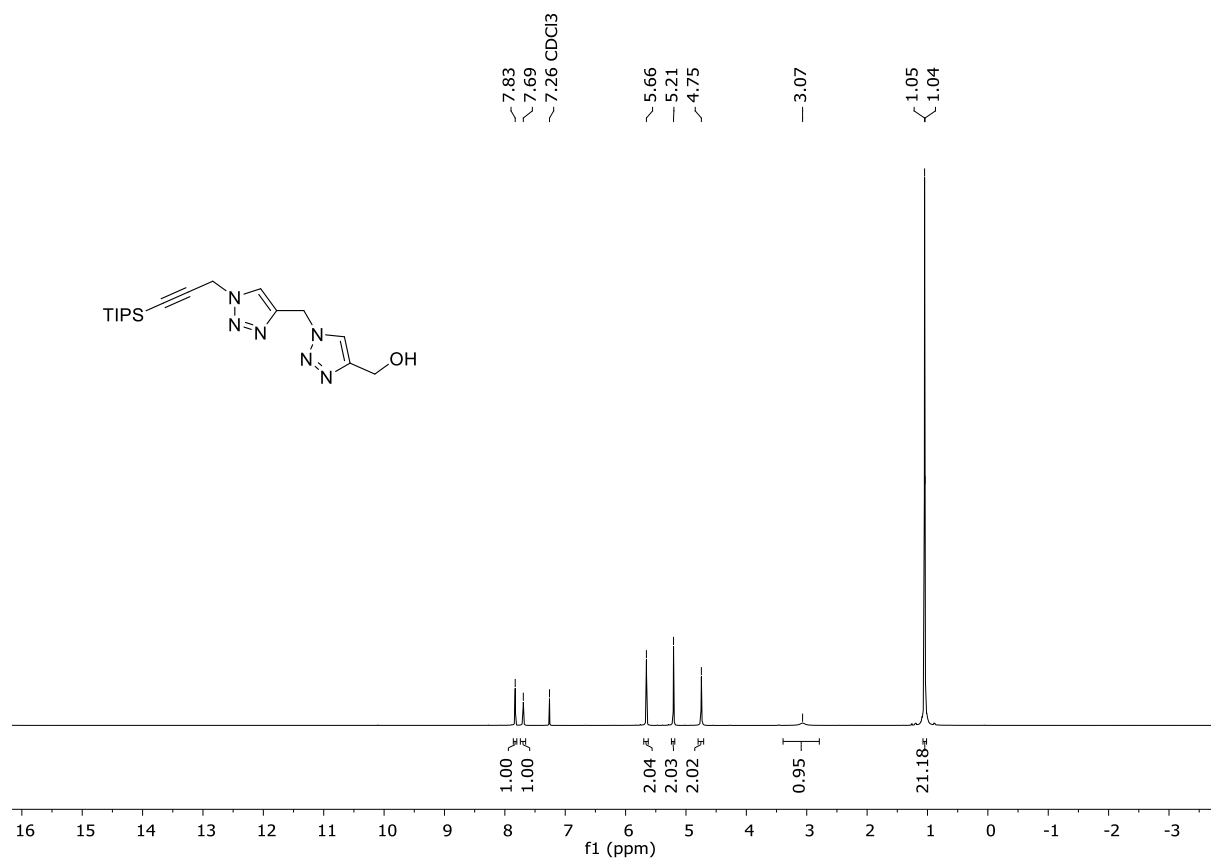


Fig. S13 ¹H-NMR spectrum of **S6** in CDCl₃.

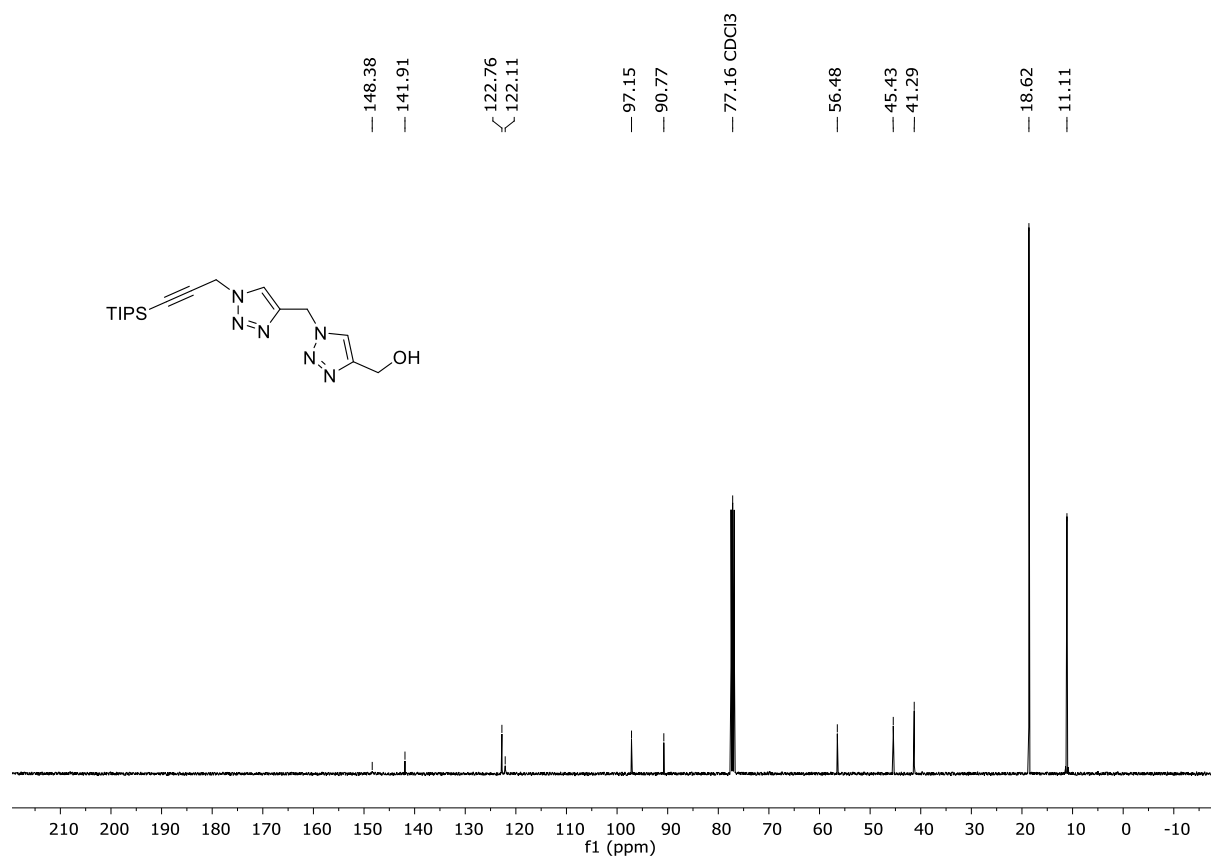


Fig. S14 ¹³C-NMR spectrum of **S6** in CDCl₃.

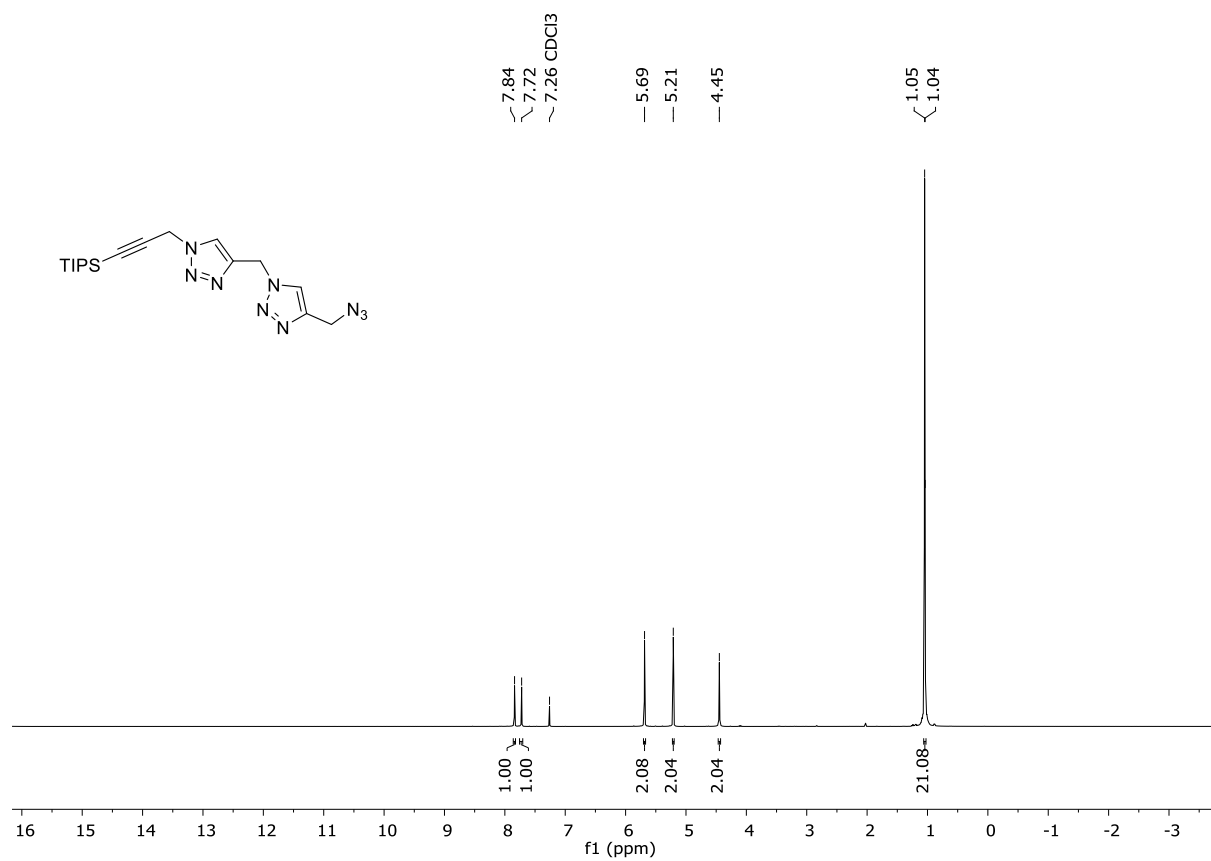


Fig. S15 ¹H-NMR spectrum of **S7** in CDCl₃.

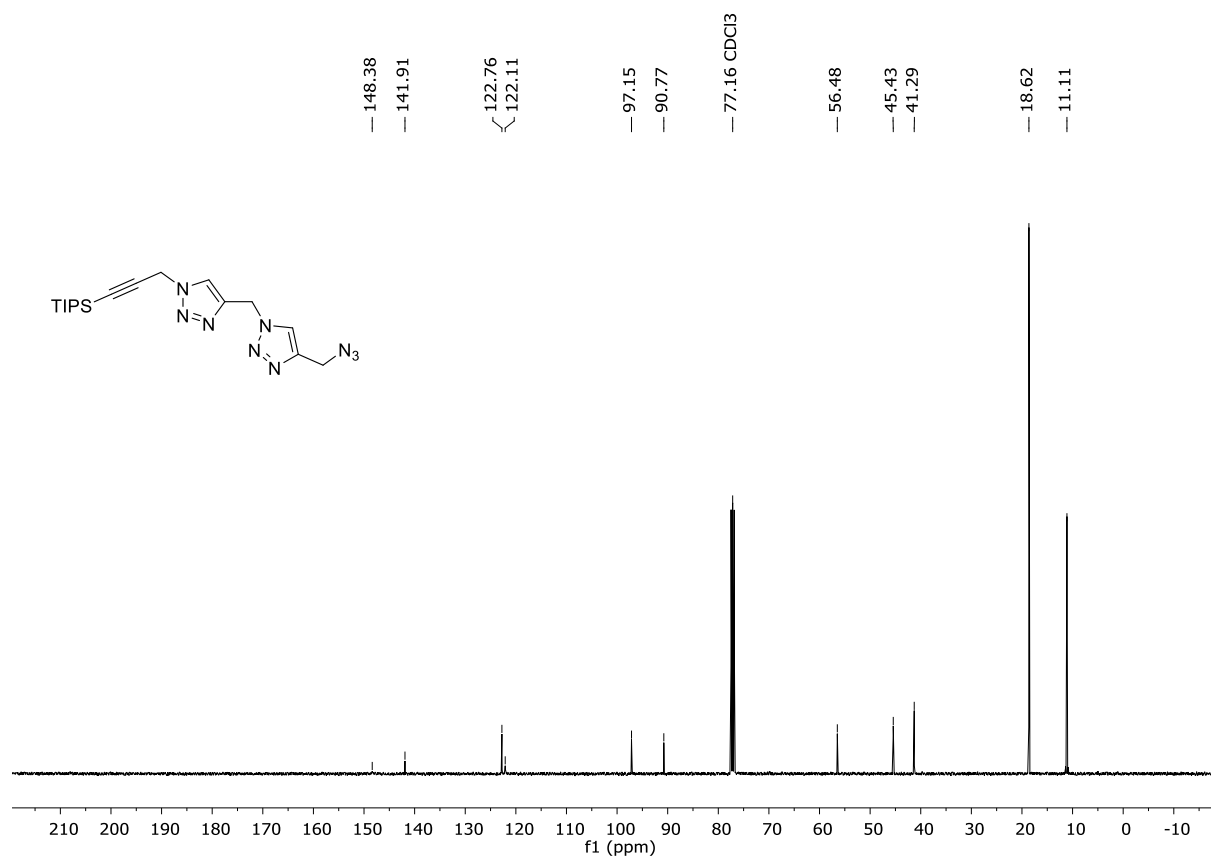


Fig. S16 ¹³C-NMR spectrum of **S7** in CDCl₃.

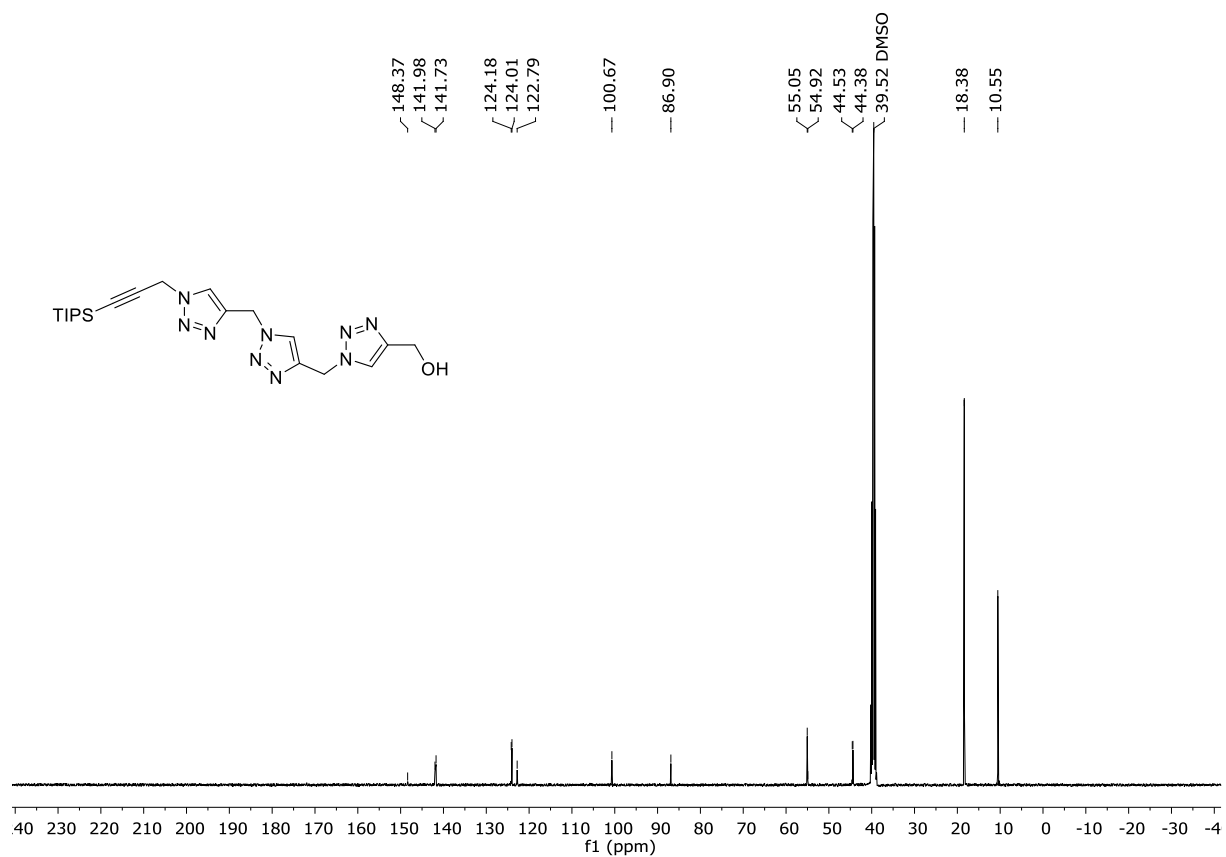


Fig. S19 ¹³C-NMR spectrum of **8** in DMSO-*d*₆.

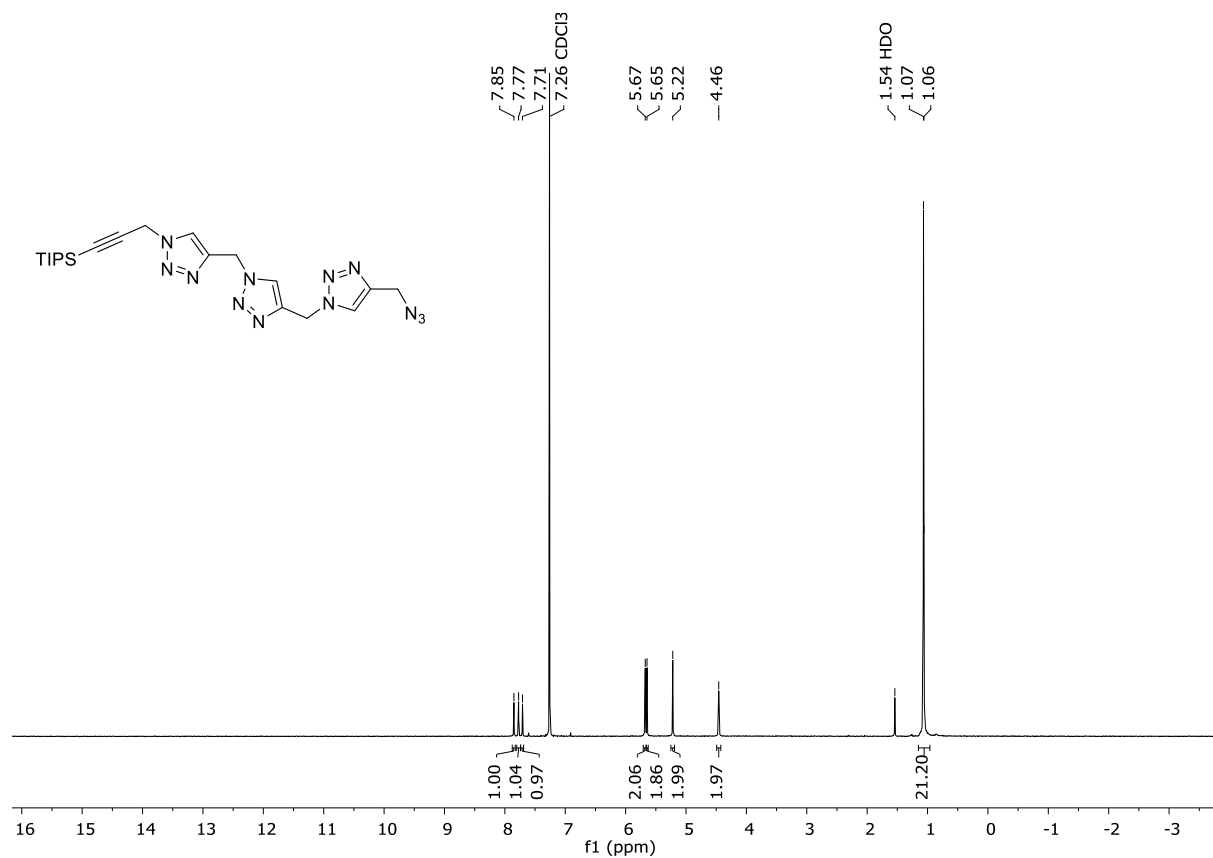


Fig. S20 ¹H-NMR spectrum of **9** in CDCl₃.

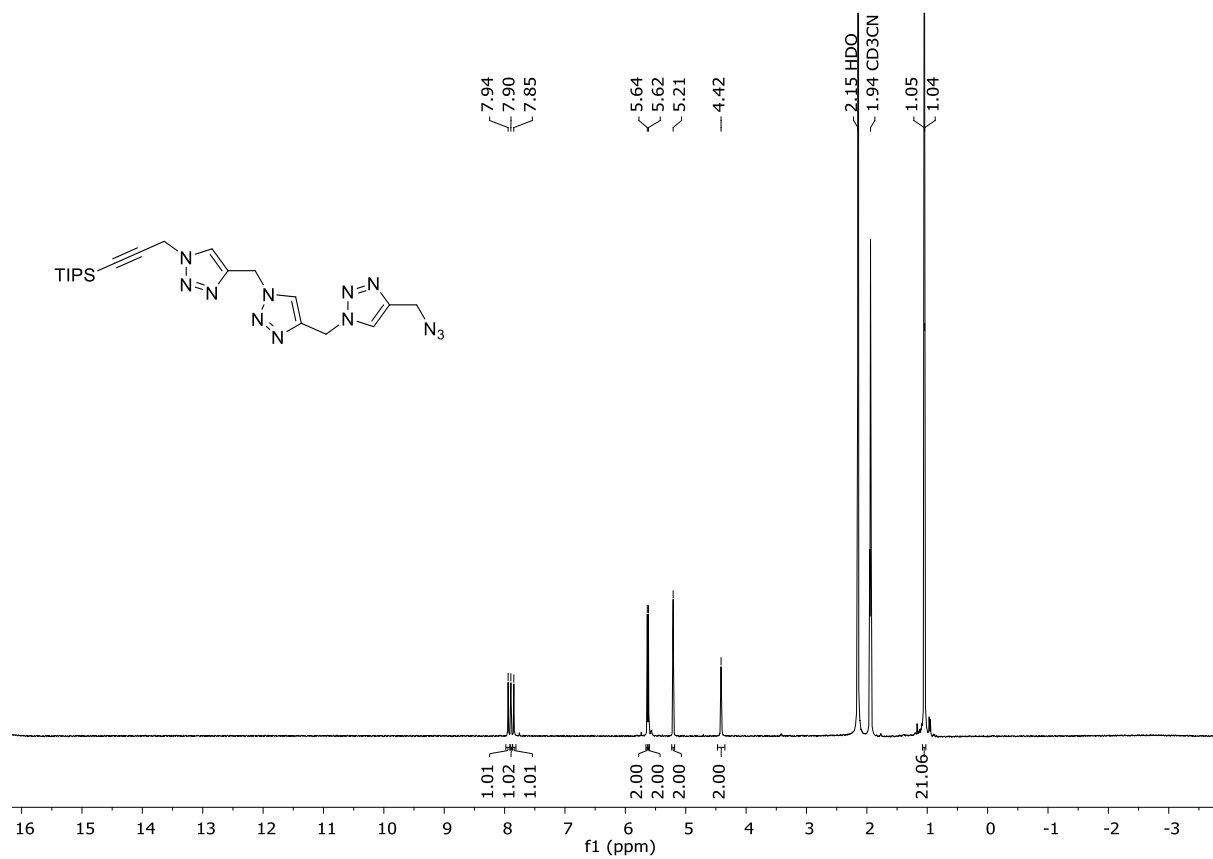


Fig. S21 ¹H-NMR spectrum of S9 in CD₃CN.

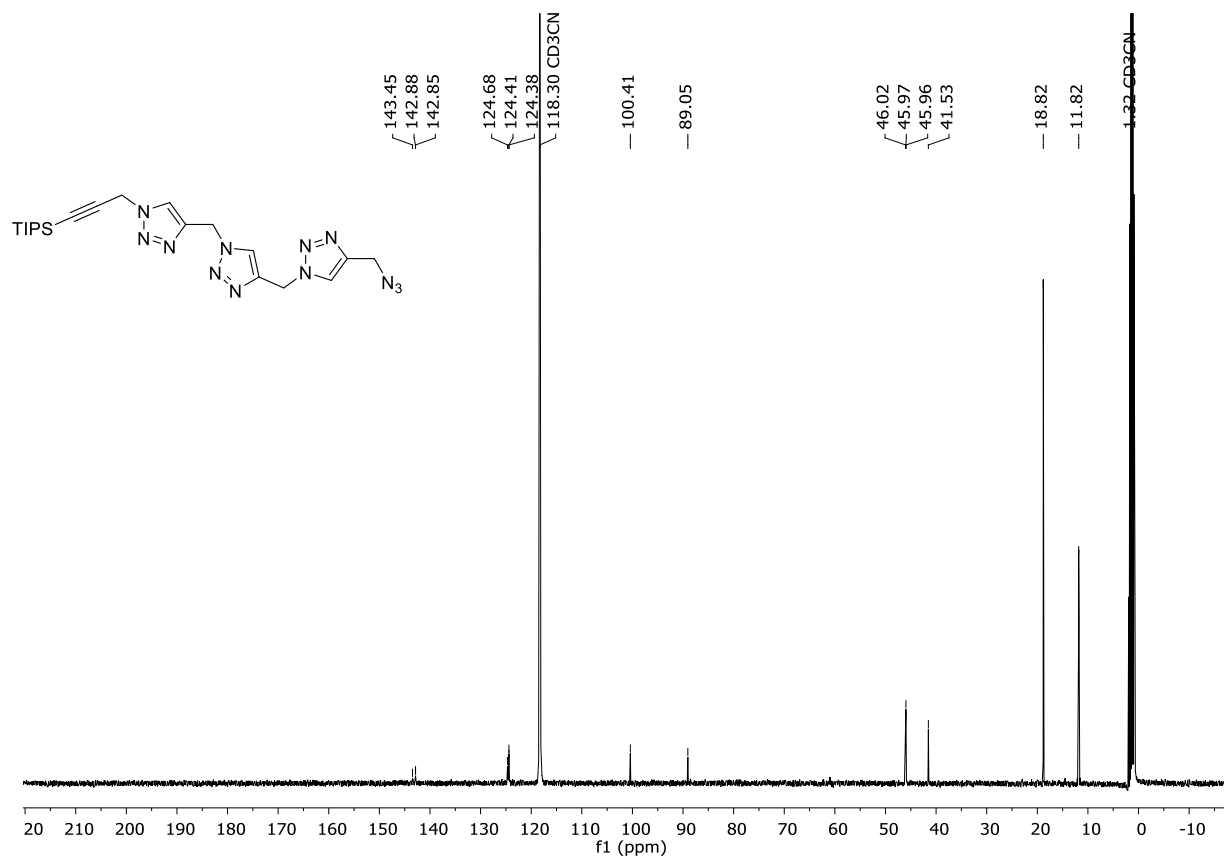


Fig. S22 ¹³C-NMR spectrum of S9 in CD₃CN.

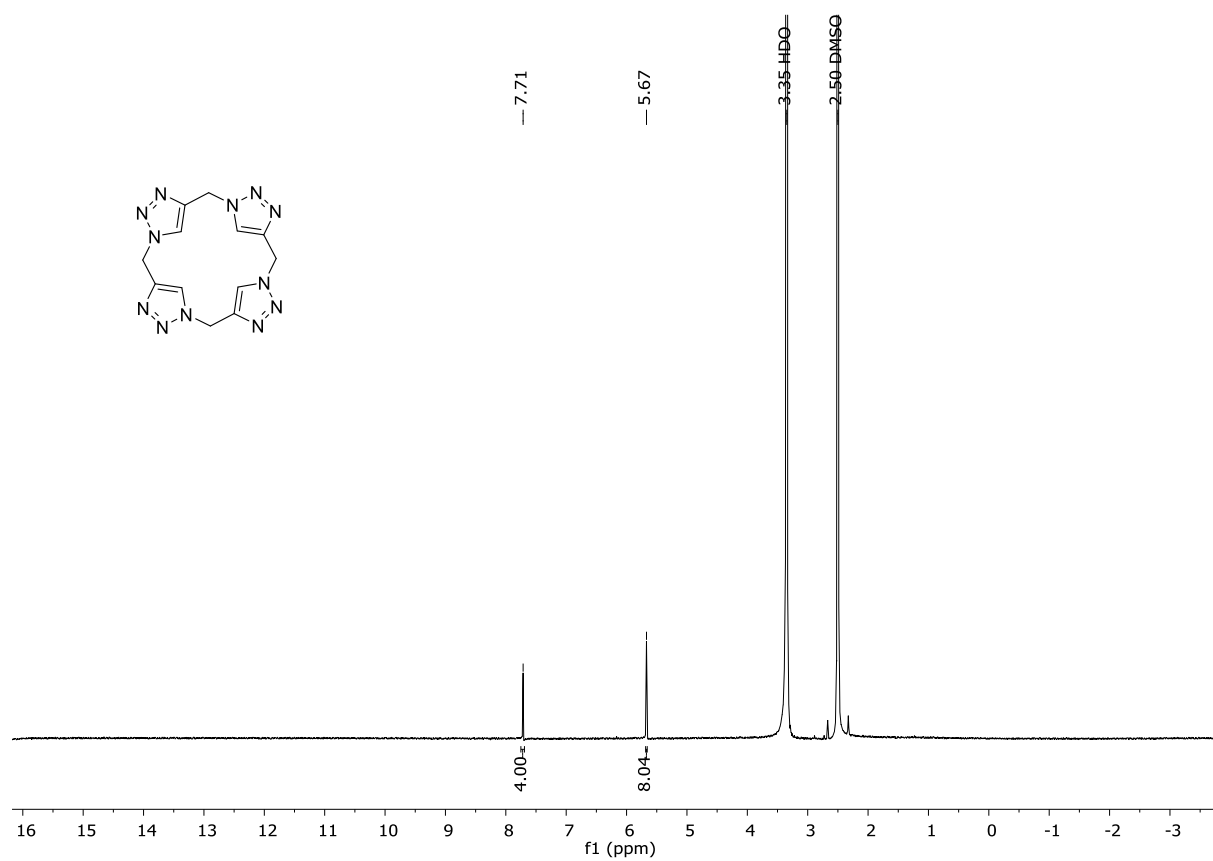


Fig. S23 $^1\text{H-NMR}$ spectrum of **a** in $\text{DMSO-}d_6$.

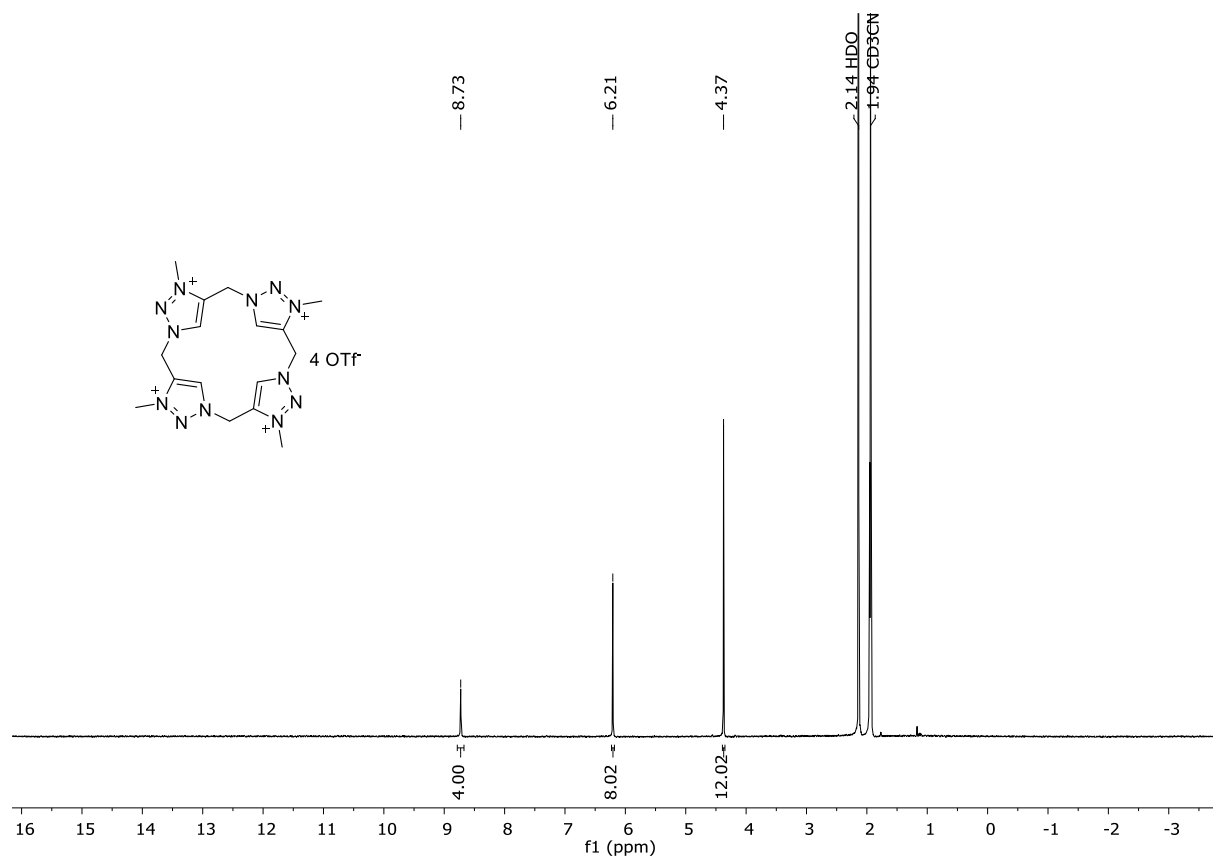


Fig. S24 $^1\text{H-NMR}$ spectrum of **b** in CD_3CN .

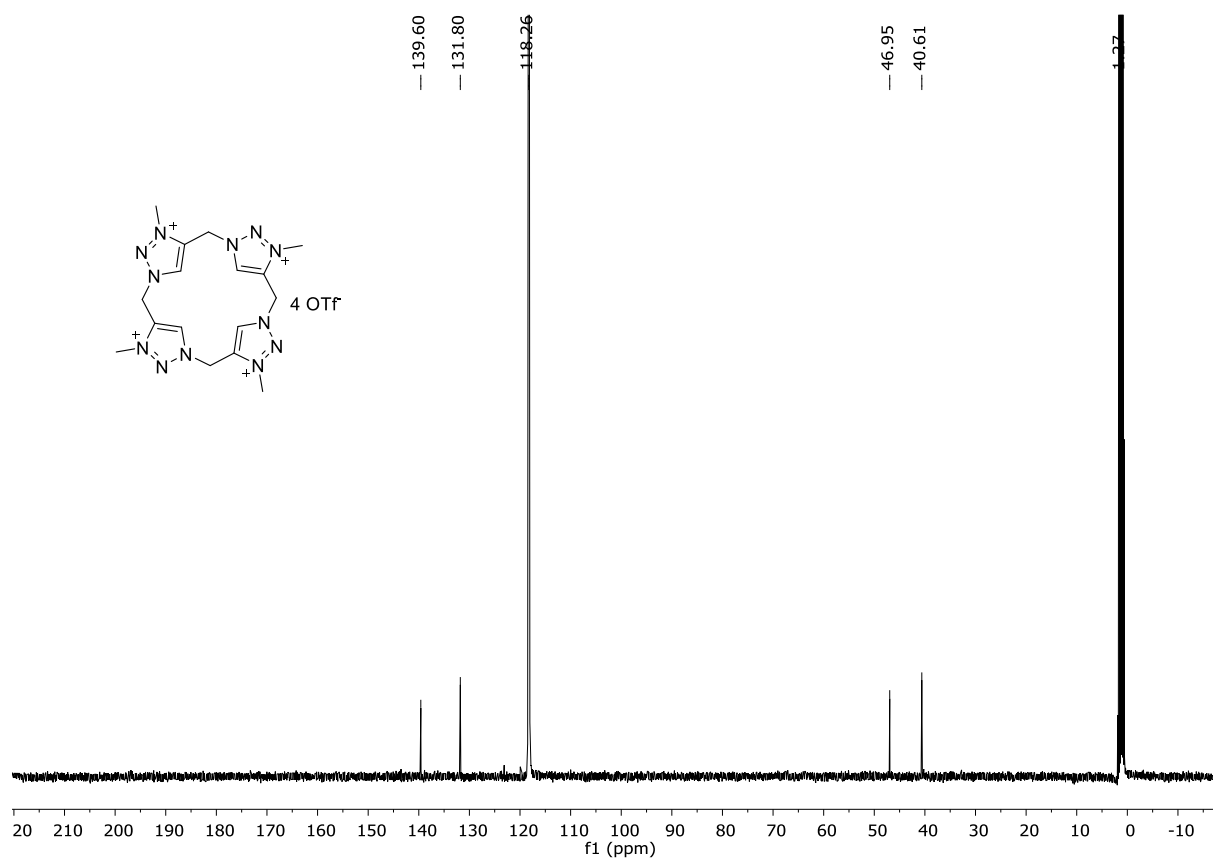


Fig. S25 ^{13}C -NMR spectrum of **b** in CD_3CN .

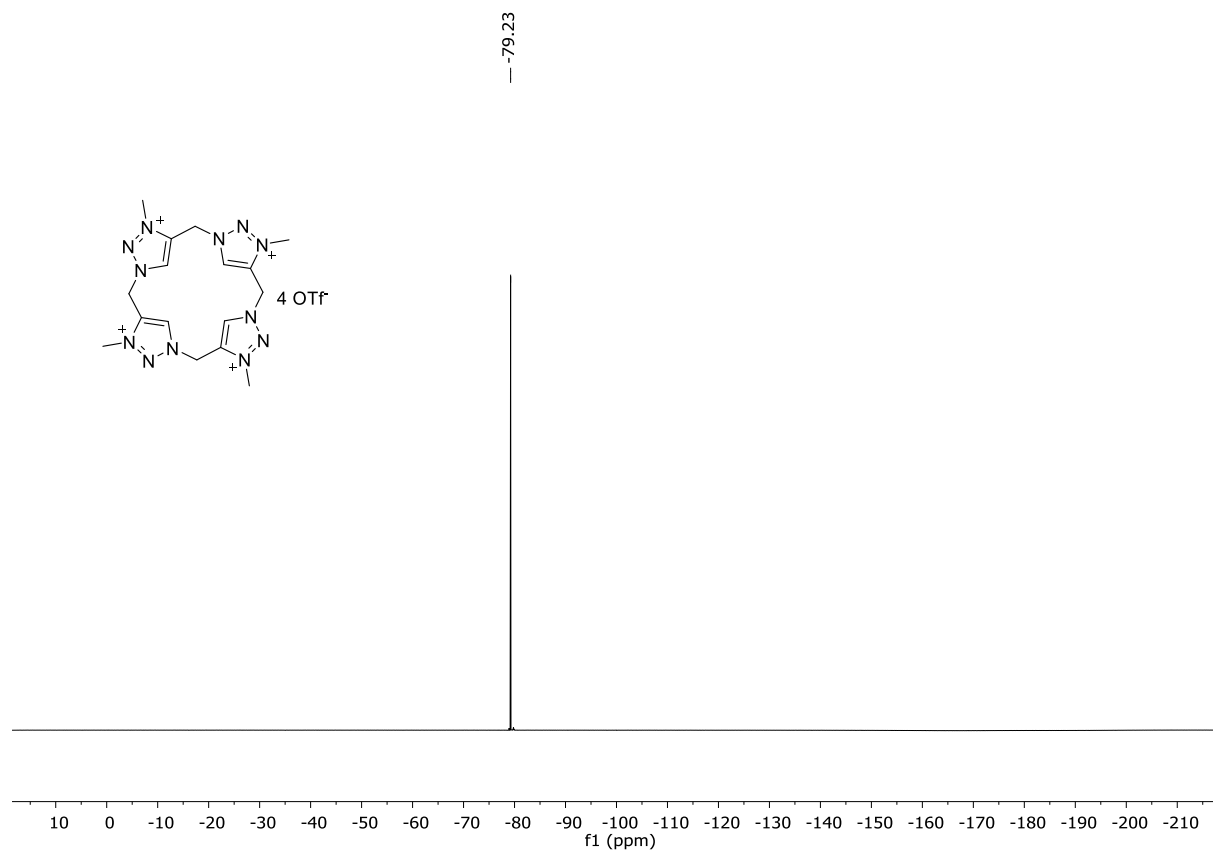


Fig. S26 ^{19}F -NMR spectrum of **b** in CD_3CN .

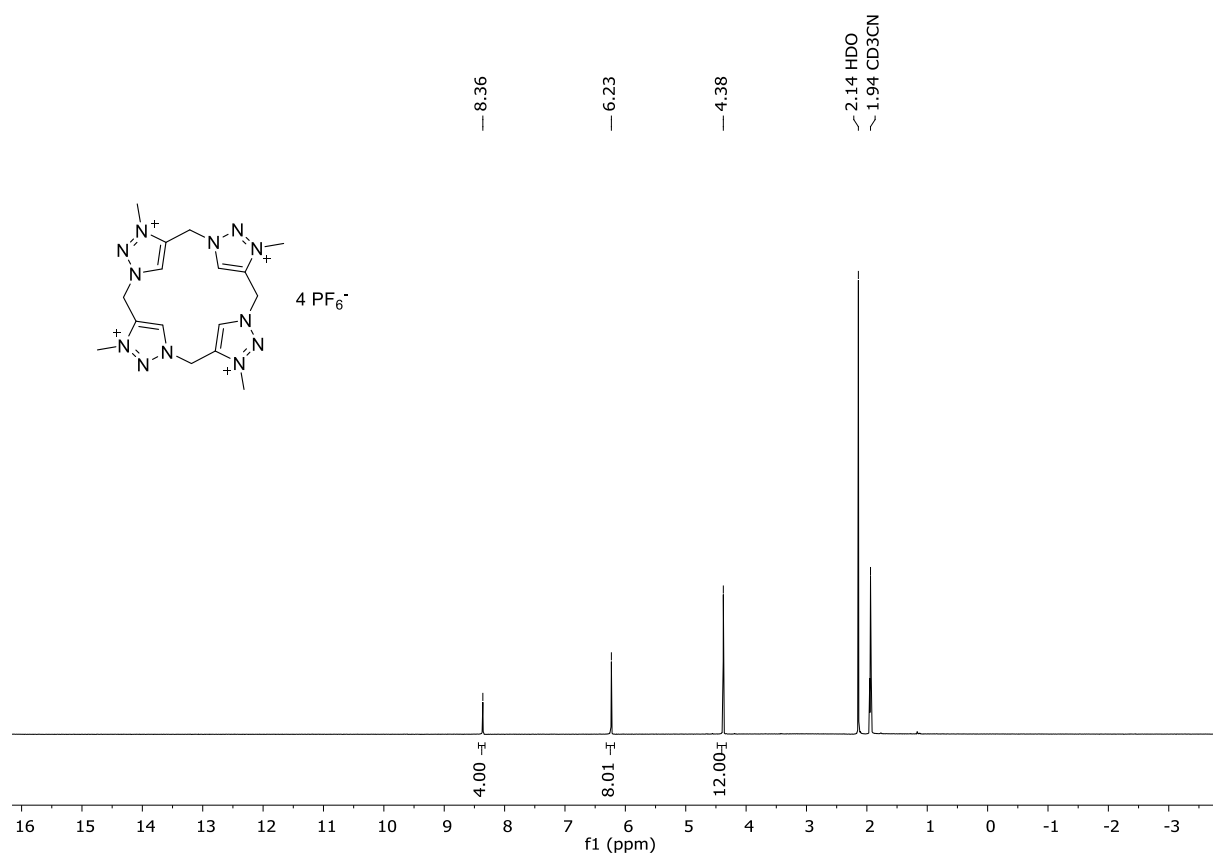


Fig. S27 $^1\text{H-NMR}$ spectrum of **c** in CD_3CN .

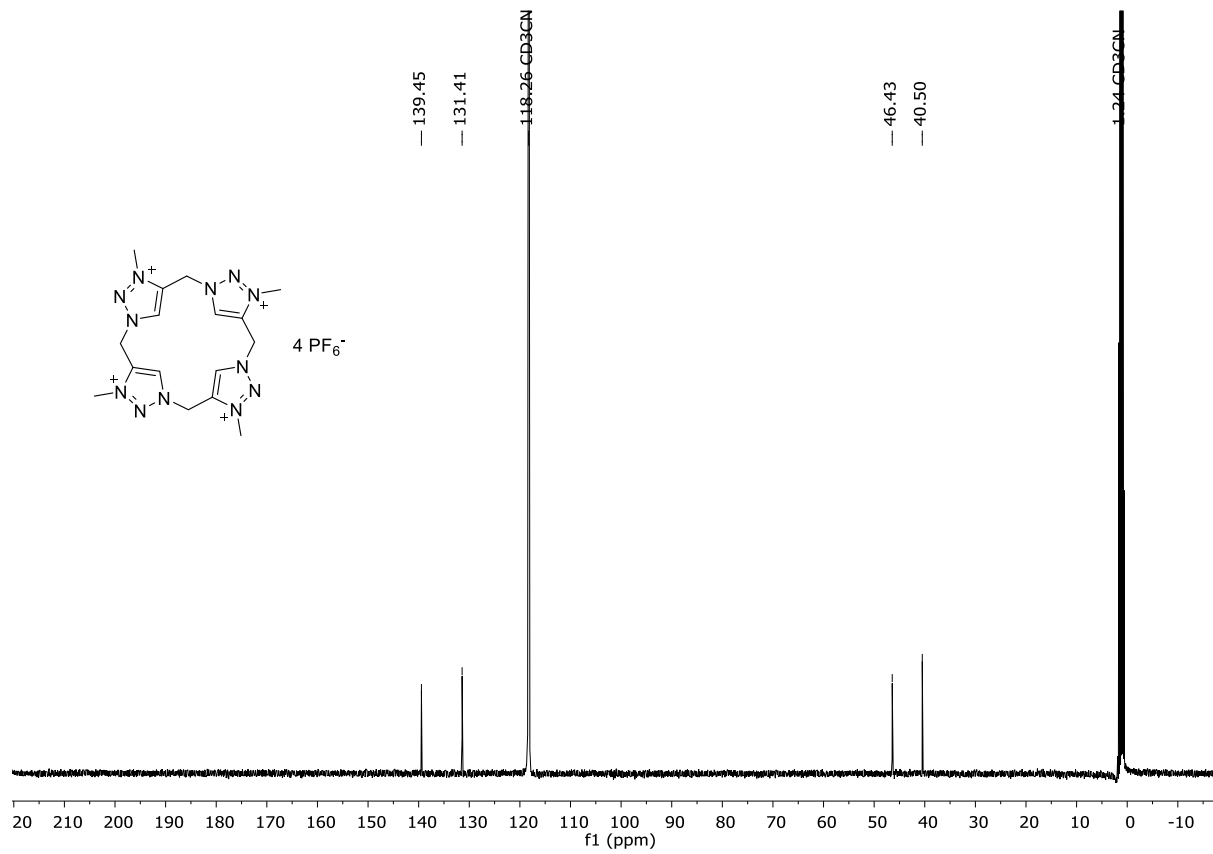


Fig. S28 $^{13}\text{C-NMR}$ spectrum of **c** in CD_3CN .

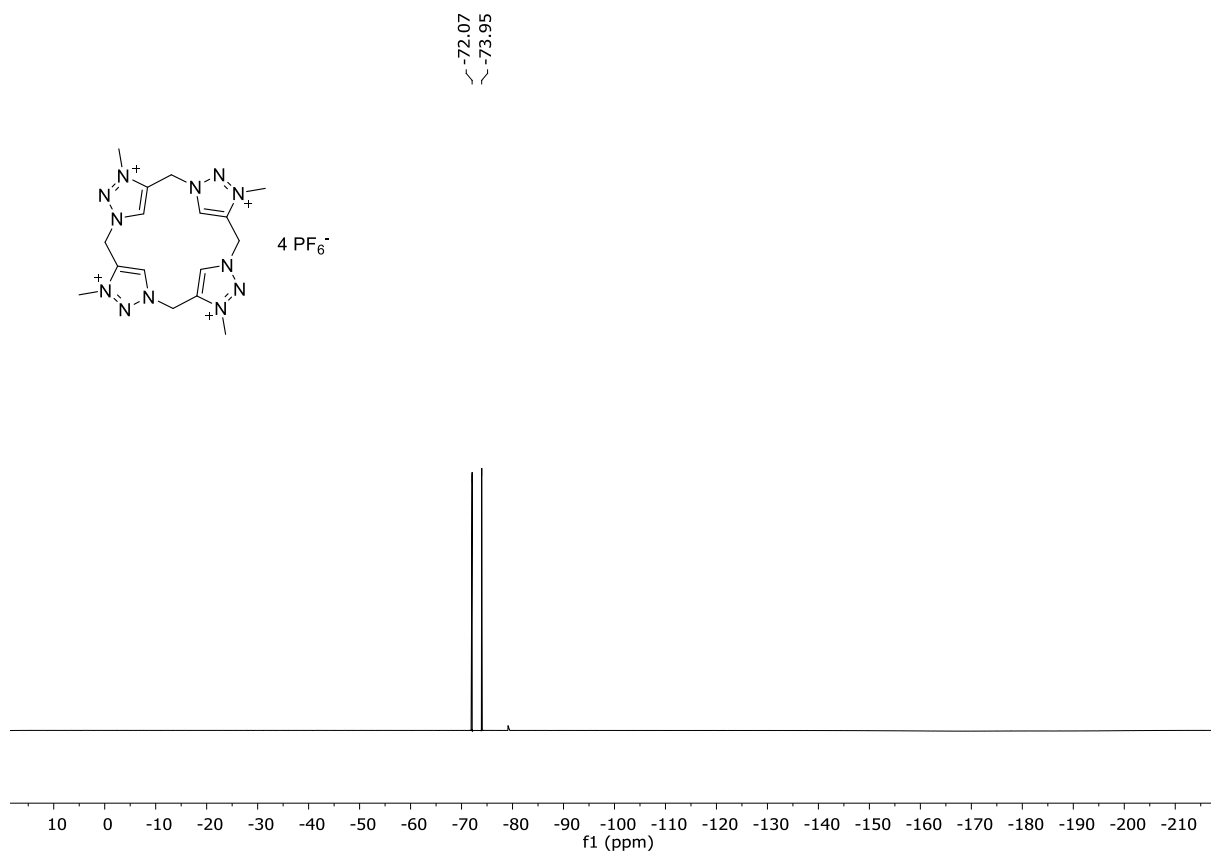


Fig. S29 ¹⁹F-NMR spectrum of **c** in CD₃CN.

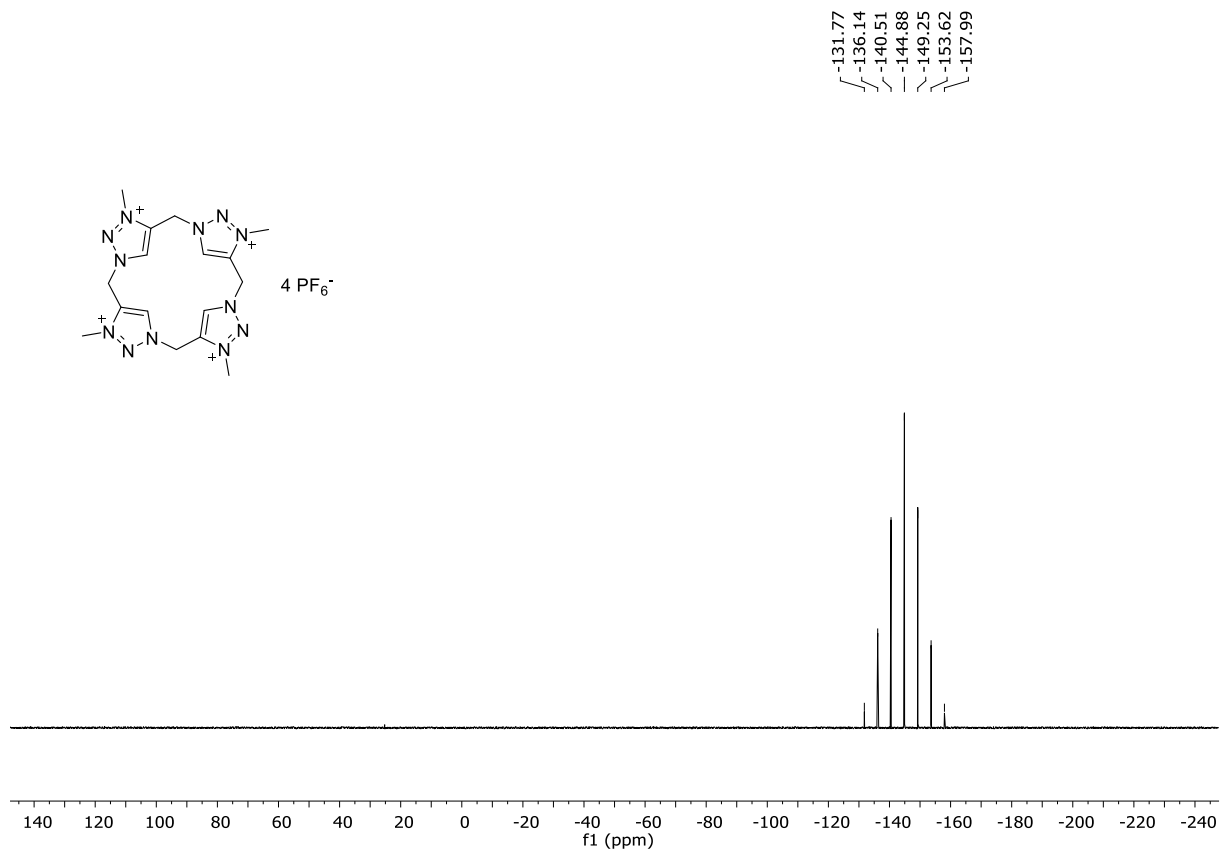


Fig. S30 ³¹P-NMR spectrum of **c** in CD₃CN.

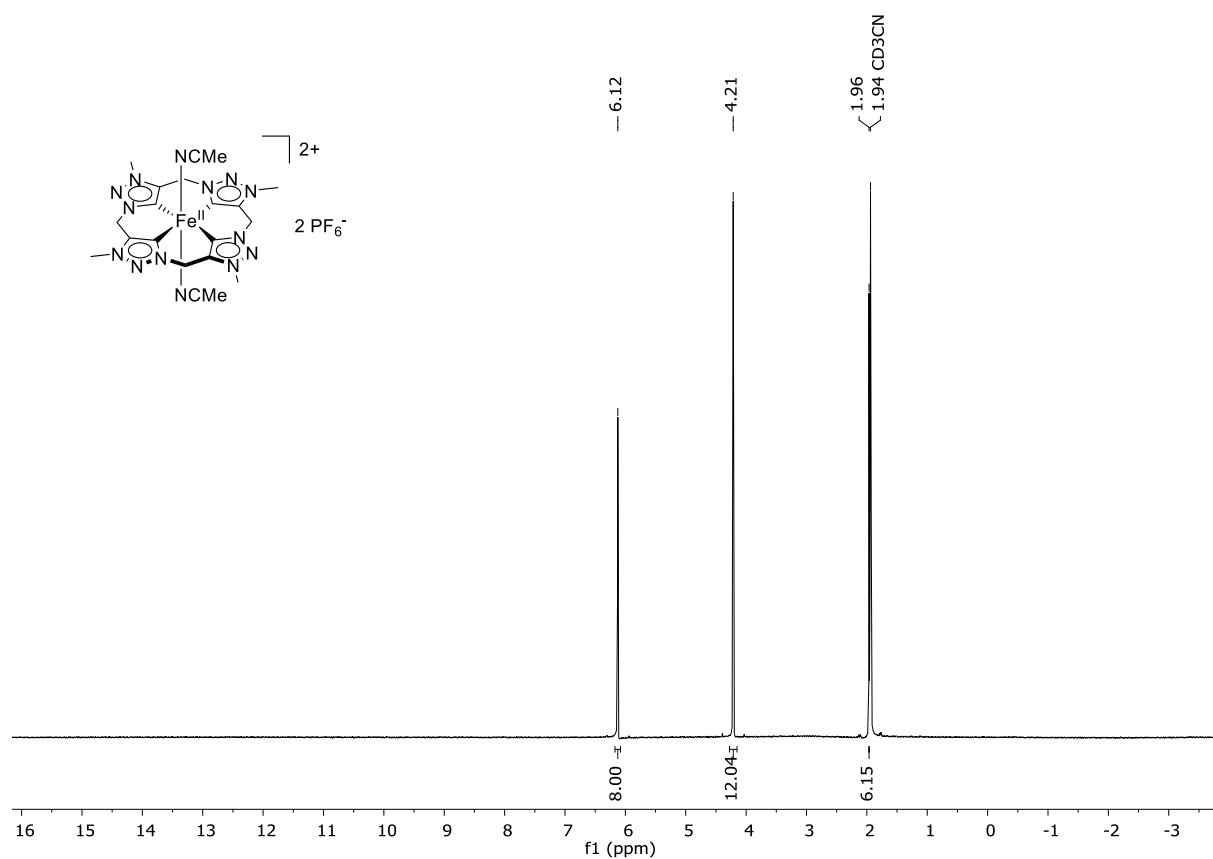


Fig. S31 $^1\text{H-NMR}$ spectrum of **2** in CD_3CN .

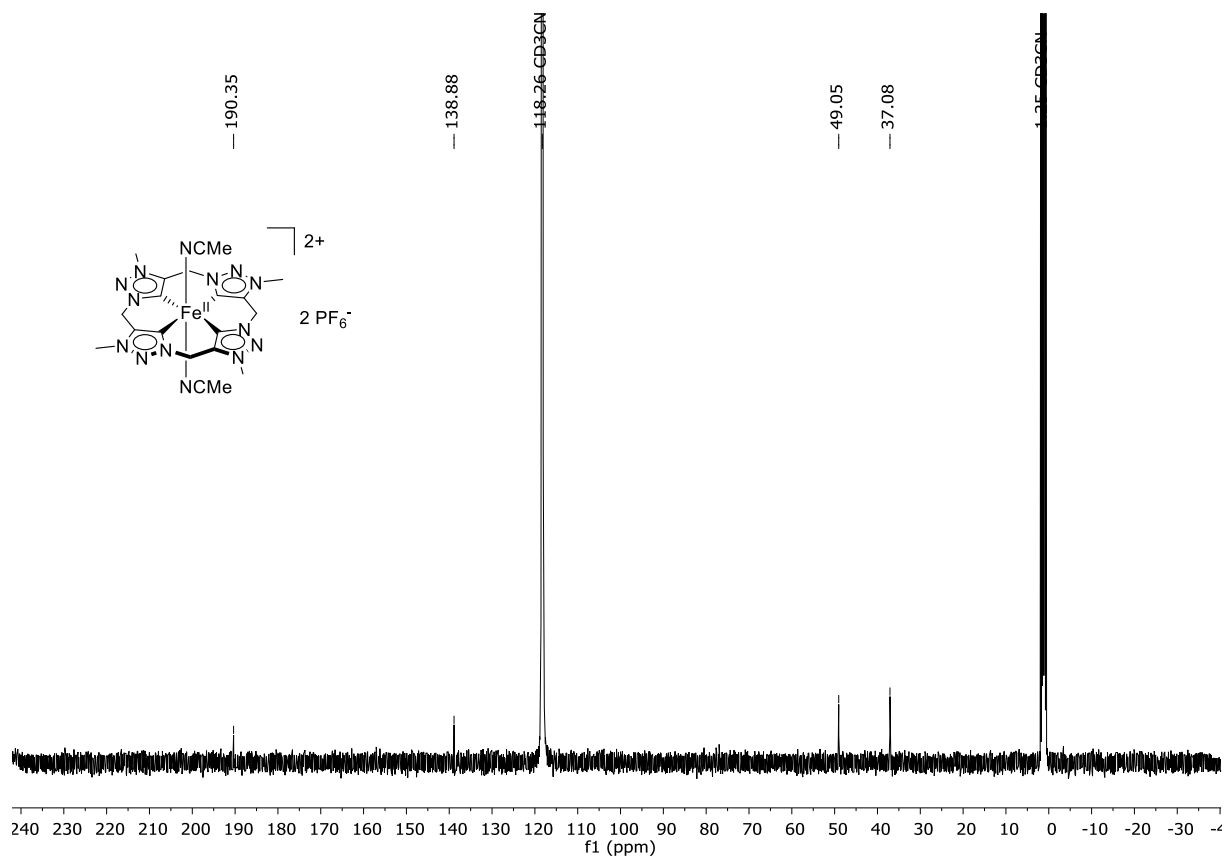


Fig. S32 $^{13}\text{C-NMR}$ spectrum of **2** in CD_3CN .

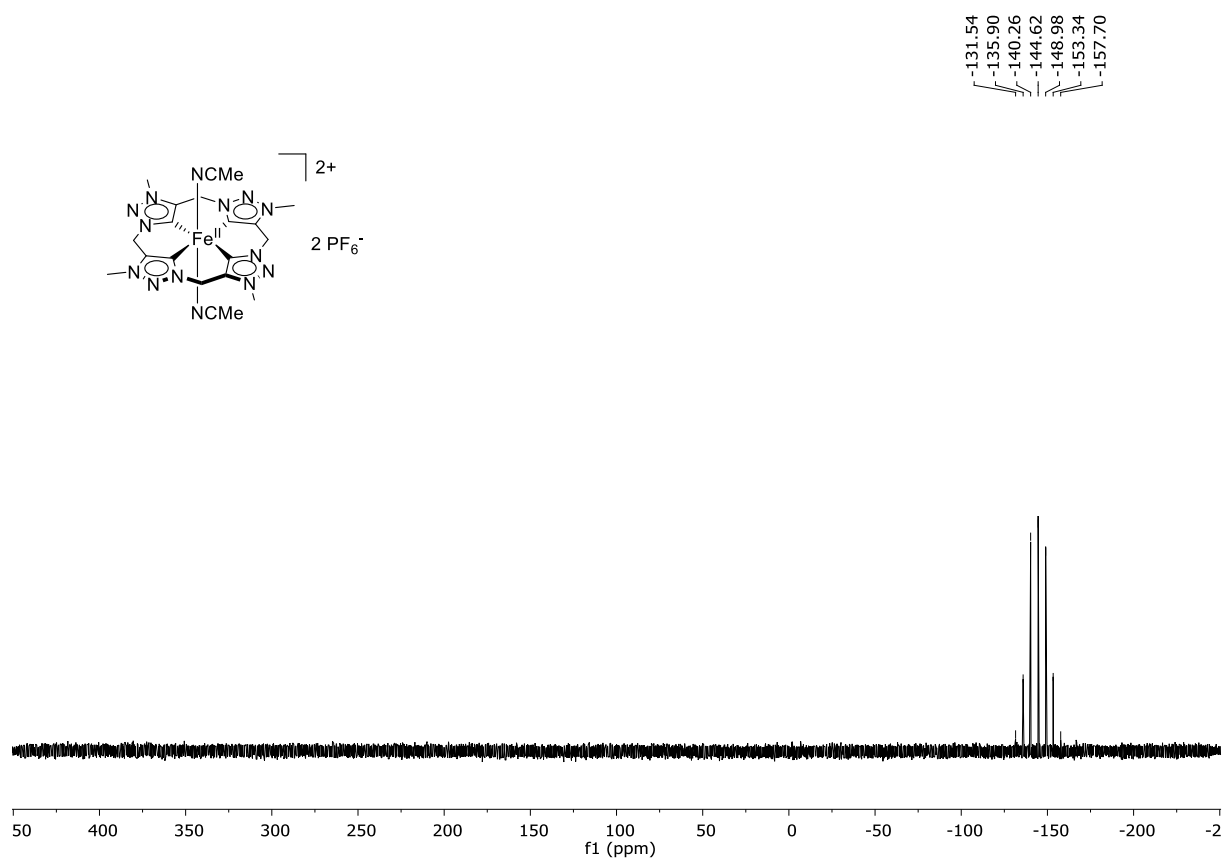


Fig. S33 ^{31}P -NMR spectrum of **2** in CD_3CN .

6. Catalytic procedure

All reactions were conducted at least twice in a cryostat (JulaboFP-50). Acetonitrile (HPLC-grade) as solvent was applied for all experiments. The catalyst (0.50 mol%) was added from a preformed stock solution in dry and degassed acetonitrile corresponding to the appropriate stoichiometry to a solution of *cis*-cyclooctene (1.00 eq., 67.3 $\mu\text{mol/mL}$). Hydrogen peroxide (1.5 eq., 101 $\mu\text{mol/mL}$) was used as oxidising agent and, if required, $\text{Sc}(\text{OTf})_3$ as additive (0.1 eq., 8.41 $\mu\text{mol/mL}$). The reaction was started upon addition of the catalyst stock solution, by adding the catalyst solution all at once. The reaction was terminated by adding electrolytically precipitated activated MnO_2 in order to decompose the excess of H_2O_2 in the reaction solution. After filtration over activated neutral alumina (separation of the catalyst), two GC samples were prepared for each experiment using 200 μL filtrate, diluted with 1300 μL MeCN and *p*-xylene as external standard for each chosen time point. The identification of the product epoxide and by-products, such as 1,2-cyclooctanediol was confirmed *via* GC-FID based on the corresponding retention times. Control experiments without catalyst were performed for all reactions. An additional blank experiment with a simple iron salt, iron(II) chloride in the presence of H_2O_2 was conducted to highlight the importance of iron complexes associated with NHCs due to minimal product and unselective side-product formation. Representative gas chromatograms for the catalytic experiments are shown in Fig. S34 to S37.

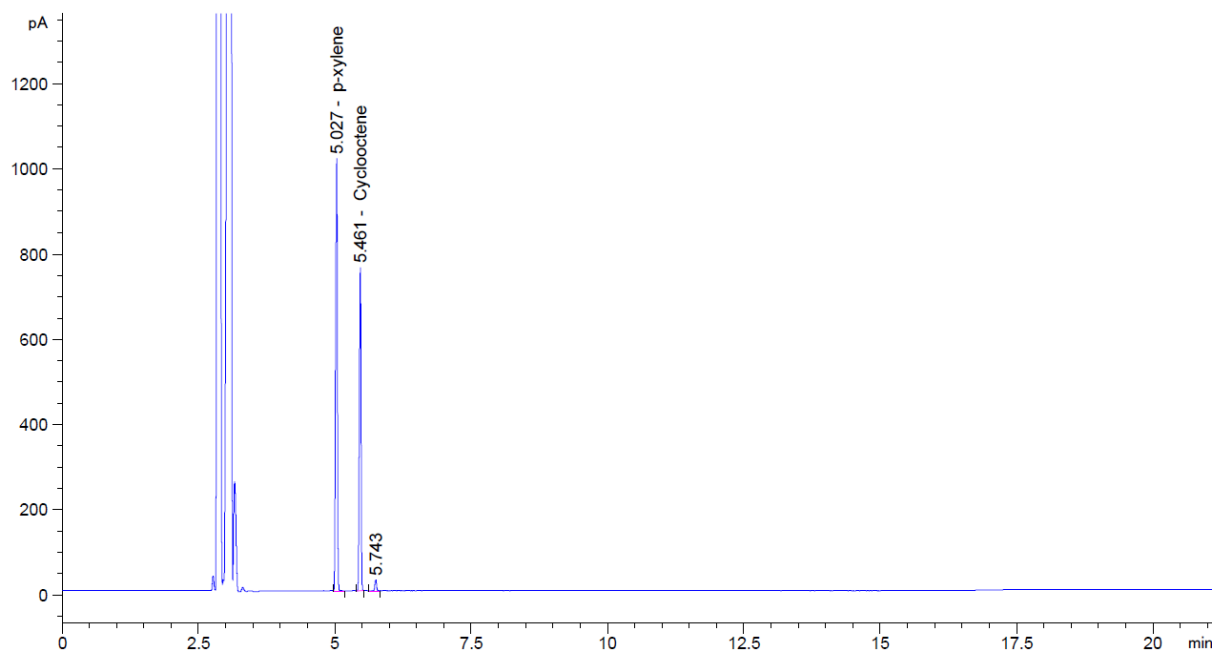


Fig. S34 Representative gas chromatogram for the control experiments without catalyst addition after a reaction time of 10 min at 20 °C.

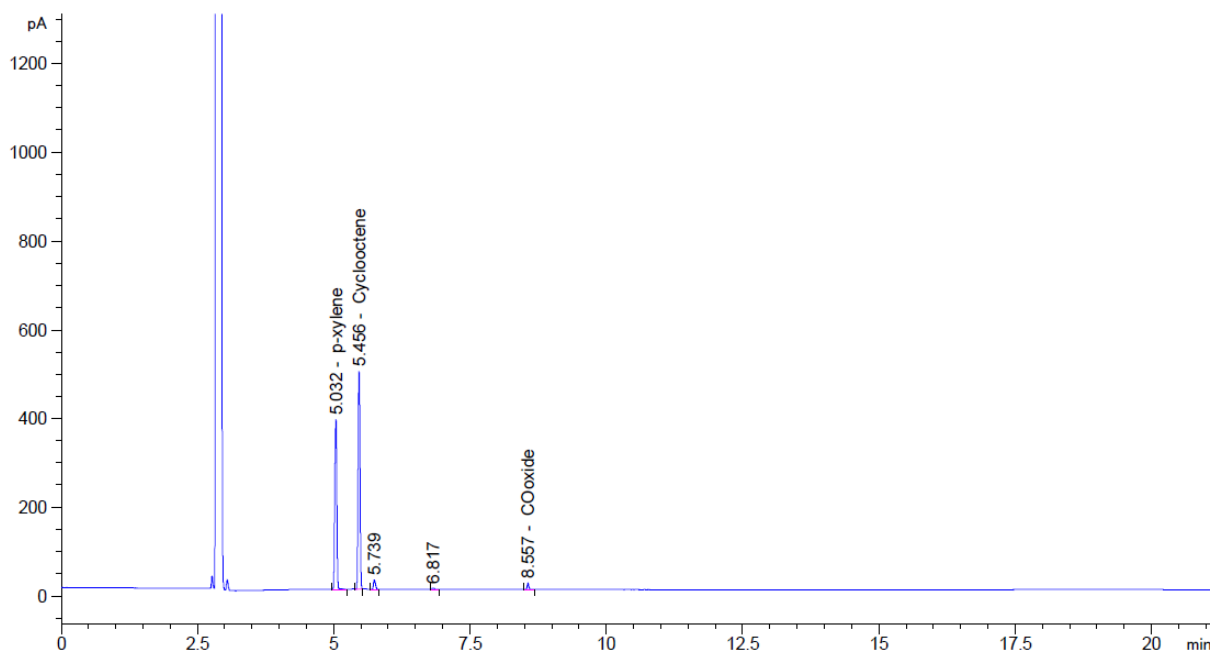


Fig. S35 Representative gas chromatogram for the blank experiments with iron(II) chloride after a reaction time of 10 min at 20 °C.

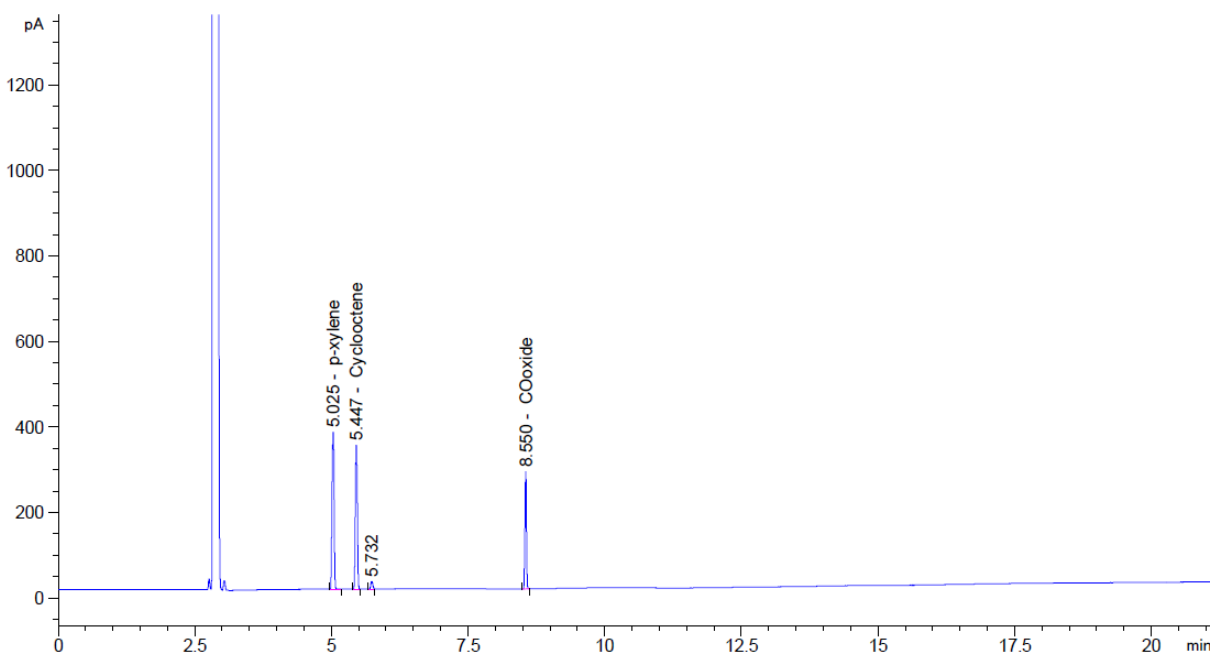


Fig. S36 Representative gas chromatogram for the experiments with **2** after a reaction time of 10 min at 20 °C.

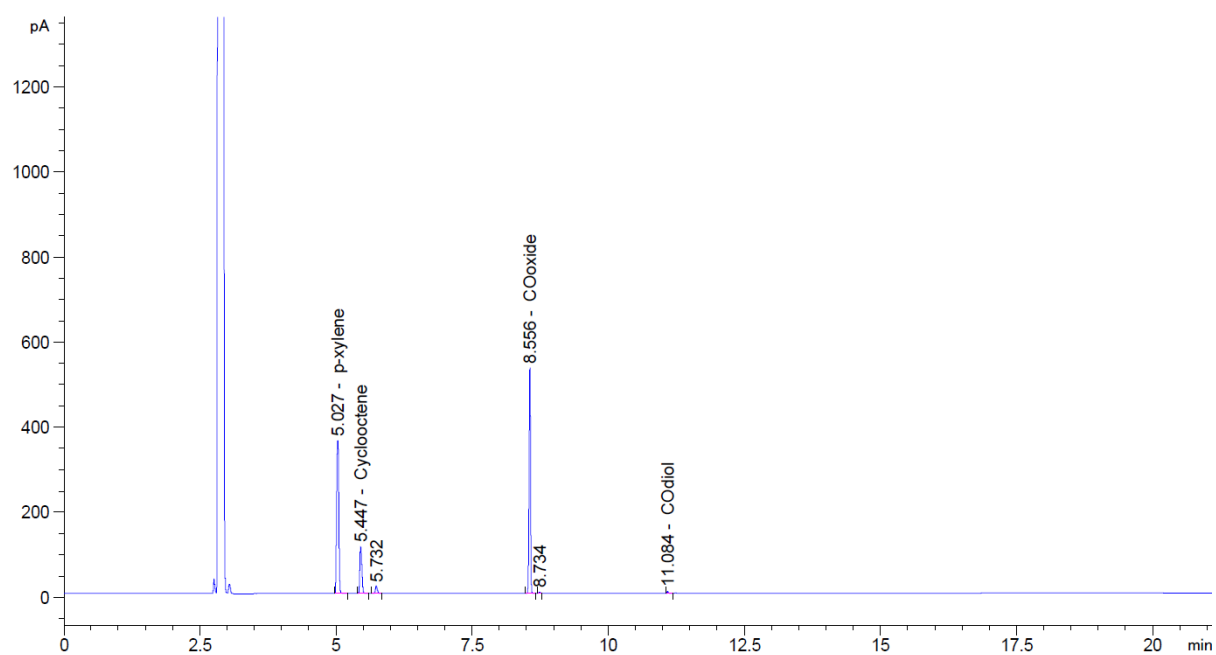


Fig. S37 Representative gas chromatogram for the experiments with **2** with the addition of $\text{Sc}(\text{OTf})_3$ after a reaction time of 5 min at 20 °C.

7. References

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