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Supporting Information for:

Multi-responsive coordination polymers utilising metal-stabilised, dynamic covalent imine bonds

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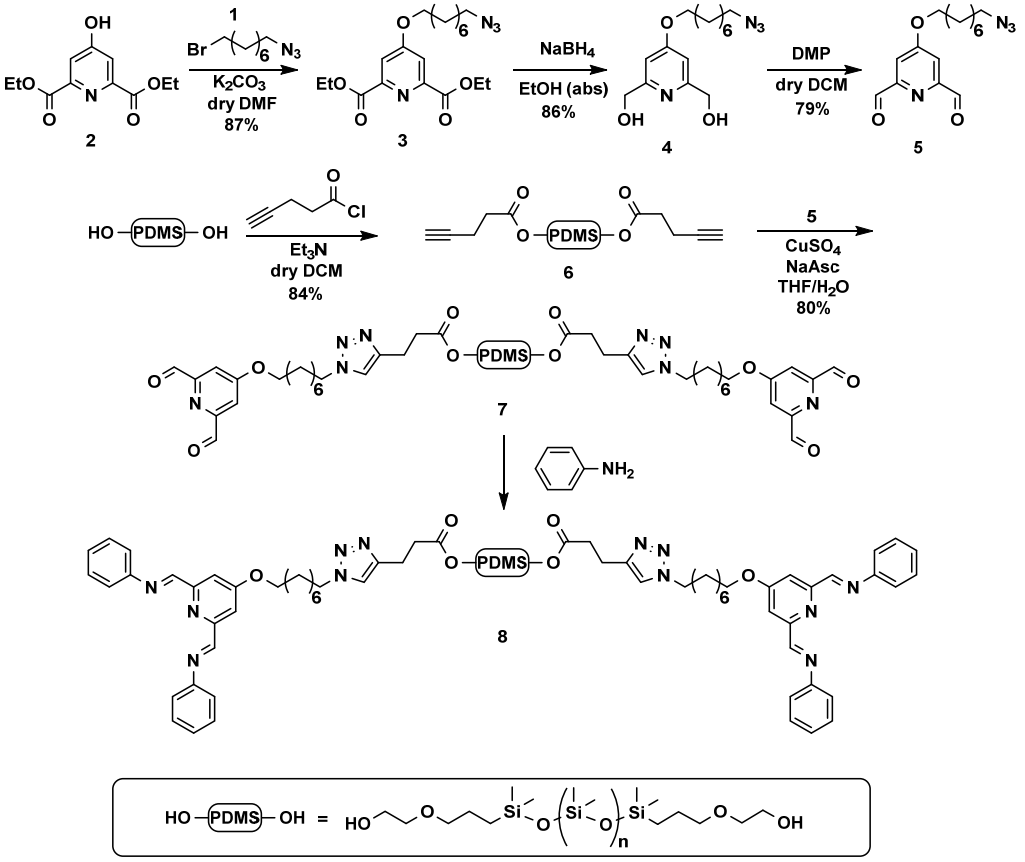
1 General experimental conditions

1.1 Materials & Methods

All solvents (DMF, ethylacetate, heptane, DCM, methanol, ethanol, THF and chloroform, DMSO, acetone, acetonitrile, diisopropyl ether) as well as standard lab chemicals ($NaBH_4$, triethylamine, K_2CO_3, $MgSO_4$, $NaHCO_3$) were obtained from Sigma-Aldrich, VWR or Alfa Aesar. Solvents were dried using a Pure Solv 400 solvent purification system (Innovative Technology, Amesbury, USA). Deuterated solvents were purchased from Sigma-Aldrich or Acros.
Dess-Martin periodinane was obtained from TCI, 4-pentynoic acid from Sigma-Aldrich, oxalyl chloride from Sigma-Aldrich, copper(II) sulfate from Sigma-Aldrich, sodium ascorbate from Sigma-Aldrich, EDTA sodium salt from Sigma-Aldrich, aniline from Sigma-Aldrich, 1-bromooctane from Sigma-Aldrich, zinc trifluoromethanesulfonate from Strem Chemicals, iron(II) trifluoromethanesulfonate from Sigma-Aldrich, cobalt tetrafluoroborate from Alfa Aesar, copper(II) acetate from Fisher Scientific, europium trifluoromethanesulfonate from Sigma-Aldrich Sigma-Aldrich. The starting linear dihydroxy terminated PDMS was purchased from Sigma Aldrich (average M_n ~5,600, CAS Number 156327-07-0).
^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 spectrometer (observation of ^1H nucleus 400 MHz, and of ^{13}C nucleus 100 MHz). Chemical shifts are reported in parts per million (ppm), calibrated on the residual peak of the solvent, whose values are referred to tetramethylsilane (TMS, δ_{TMS} = 0 ppm), as the internal standard. ^{13}C NMR spectra were performed with proton decoupling. ^1H DOSY experiments were carried out at 293 K on a Bruker Avance III 400 spectrometer. The diffusion gradients were incremented from 2% to 95% of maximum gradient strength in 32 linear steps. Signal averaging ranged from 16 to 128 scans per increment as required for adequate signal-to noise ratio. The data obtained were evaluated with the TopSpin T_1/T_2 package and the fitting of the diffusion decays were performed by the SimFit algorithm. The 2D projections were obtained using the automated Bayesian DOSY Transform method provided by MNova. The D_{coeff} was calculated from the average of all the signals corresponding to the polymers with exception for the cross-linked systems, for which the D_{coeff} was calculated from the signal at 4.22 ppm, which was the one that fitted best to the decay curve.
Electrospray ionisation (ESI) mass analyses were performed on a Finnigan LXQ, while high resolution ESI mass analyses were recorded on a Thermo Scientific Q Exactive High-Resolution mass spectrometer. Infra-red analyses were performed on a Bruker FT-IR spectrometer equipped with a Platinum ATR. UV-vis spectra were recorded on a Varian Cary 50 spectrophotometer. Viscometry data were recorded using a Ubbelohde capillary viscometer immersed in a water bath. The temperature was checked for each measurement and in the range 20.3 – 21.6°C. For each sample the elution time was recorded 3-fold and the mean average was used for calculating the specific viscosity.

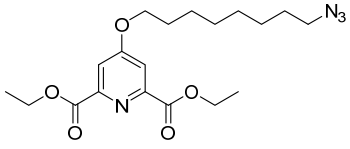
2 Synthesis

Reaction Scheme



1-Azido-8-bromooctane (**1**) and diethyl 4-hydroxypyridine-2,6-dicarboxylate (**2**) were prepared and characterised according to a reported procedure.[S1]

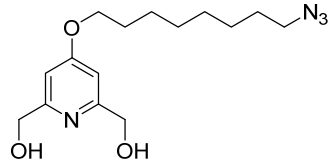
Diethyl 4-((8-azidooctyl)oxy)pyridine-2,6-dicarboxylate (3)



3
Chemical Formula: $C_{19}H_{28}N_4O_5$
Molecular Weight: 392.46

Pyridine diester (**2**) (5.12 mmol, 1.22 g) was dissolved in dry DMF (50 mL) under Ar atm. To this solution, dry K_2CO_3 (12.81 mmol, 1.77 g) is added and stirred until a white precipitate was formed. Then, the 1-azido-6-bromoctane (**1**) (4.27 mmol, 1.0 g) is added and the reaction mixture stirred at 100 °C overnight. Then, the reaction mixture is cooled to room temperature, diluted with water (100 mL) and extracted with ethyl acetate (2×150 mL). The organic layer was washed with ice-water (150 mL) and brine (150 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude was purified by column chromatography (silica gel, heptane/ethyl acetate 2/1, R_f = 0.53) to yield compound **3** as a light yellow oil. Yield: 87%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (s, 2H), 4.46 (q, J = 7.2, 1.1 Hz, 4H), 4.12 (t, J = 6.4 Hz, 2H), 3.26 (t, J = 6.9 Hz, 2H), 1.89 – 1.77 (m, 2H), 1.60 (t, J = 7.0 Hz, 2H), 1.53 – 1.29 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 164.8, 150.1, 114.3, 68.9, 62.3, 51.4, 33.6, 29.0, 29.0, 28.9, 28.7, 28.6, 26.6, 25.7, 14.1. FTIR (ATR) 558, 589, 635, 705, 728, 786, 827, 863, 882, 944, 990, 1028, 1101, 1155, 1172, 1227, 1243, 1299, 1340, 1372, 1391, 1406, 1445, 1465, 1567, 1593, 1717, 1746, 2094, 2858, 2633, 2981 cm^{-1}. HRMS (ESI): calculated for $C_{19}H_{29}N_4O_5$ $[M+H]^+$, 393.2138; found, 393.2121.

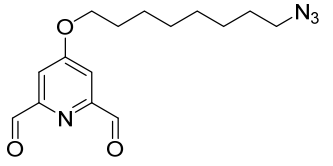
(4-((8-azidooctyl)oxy)pyridine-2,6-diyl)dimethanol (4)



4
Chemical Formula: $C_{15}H_{24}N_4O_3$
Molecular Weight: 308.38

Diester **3** (0.49 g, 1.26 mmol) was dissolved in absolute ethanol (40 mL). To this solution $NaBH_4$ (0.29 g, 7.55 mmol) was added carefully. The reaction mixture was heated at 40 °C overnight. Then, it was cooled down to 0 °C and the reaction was carefully quenched with water. Then, the ethanol was evaporated, extracted with DCM (3×15 mL) and the organic layer washed with brine (10 mL). The organic layer was dried over $MgSO_4$, filtered and the solvent evaporated under reduced pressure. The diol **4** is obtained as an oil without need of any further purification. Yield 86%. R_f = 0.12 (ethyl acetate). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.69 (s, 2H), 4.64 (s, 4H), 3.99 (t, J = 6.5 Hz, 2H), 3.25 (t, J = 6.9 Hz, 2H), 1.85 – 1.68 (m, 2H), 1.65 – 1.52 (m, 2H), 1.51 – 1.40 (m, 2H), 1.40 – 1.28 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 160.5, 105.6, 68.0, 64.4, 51.4, 29.0, 28.9, 28.8, 28.7, 26.5, 25.7. HRMS (ESI): calculated for $C_{15}H_{25}N_4O_3$ $[M+H]^+$, 309.1927; found, 309.1915.

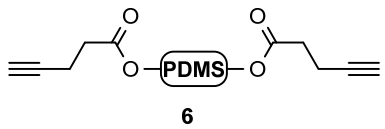
4-((8-azidooctyl)oxy)pyridine-2,6-dicarbaldehyde (5)



5
Chemical Formula: $C_{15}H_{20}N_4O_3$
Molecular Weight: 304.35

Compound **4** (0.75 g, 2.43 mmol) was dissolved in dry DCM (40 mL) and to this solution, Dess-Martin periodinane (2.43 g, 5.83 mmol) was added and the reaction mixture stirred at room temperature for four hours. After that, 25 mL of 1M NaOH solution were added and stirred for additional 15 minutes. Then, the reaction mixture was diluted with DCM (50 mL), the organic layer was separated and washed it with saturate solution of $NaHCO_3$ (100 mL) and brine. The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude was purified by chromatographic column (silica gel, heptane : ethyl acetate 2:1) to obtain **5** as an oil. Yield 79%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.06 (s, 2H), 7.58 (s, 2H), 4.11 (t, J = 6.5 Hz, 2H), 3.23 (t, J = 6.9 Hz, 2H), 1.90 – 1.72 (m, 2H), 1.56 (q, J = 7.1 Hz, 2H), 1.51 – 1.40 (m, 2H), 1.42 – 1.26 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 167.1, 154.7, 111.45, 6.25, 51.4, 29.0, 29.0, 28.8, 28.6, 26.61, 25.7. FTIR (ATR) 715, 873, 942, 1038, 1159, 1313, 1361, 1450, 1593, 1711, 2093, 2856, 2831 cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{20}N_4O_3Na$ $[M+Na]^+$, 327.1428; found, 327.1420.

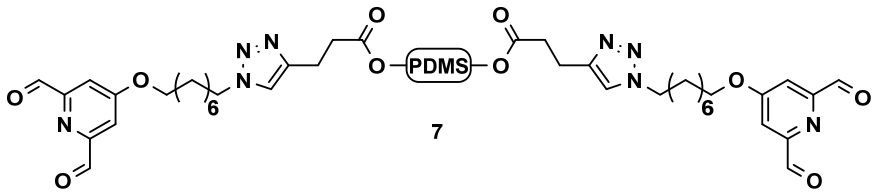
PDMS-dialkyne (6)



6

4-Pentynoic acid (0.949 mg, 9.67 mmol, 10 eq.) was dissolved in dry DCM (25 mL) and a drop of dry DMF and oxalyl chloride (0.83 mL, 9.67 mmol, 10 eq.) were added. The reaction mixture was stirred at room temperature for 1.5 h until no more gas formed. 4-Pentynoic acid chloride was obtained after evaporating the solvent under reduced pressure. Dihydroxy-terminated PDMS (5.00 g, 0.967 mmol, 1 eq.) was dissolved in dry DCM (100 mL) and the 4-pentynoic acid chloride was added as a solution in dry DCM. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with DCM to 200 mL and washed with water (150 mL), 1M NaOH solution (100 mL), saturated $NaHCO_3$ solution (150 mL) and brine (150 mL). The organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The mixture was purified by column chromatography (silica gel; ethyl acetate : heptane = 4:1) to give PDMS-dialkyne (**6**). Yield 84%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.25 (t, J = 4.8 Hz, 4H), 3.63 (t, J = 4.8 Hz, 4H), 3.42 (t, J = 7.0 Hz, 4H), 2.62 – 2.55 (m, 4H), 2.54 – 2.47 (m, 4H), 1.96 (t, J = 2.3 Hz, 2H), 1.66 – 1.56 (m, 4H), 0.57 – 0.48 (m, 4H), 0.24 – -0.11 (m, 430H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9, 82.6, 74.3, 69.2, 68.6, 64.1, 33.5, 23.6, 14.5, 14.3, 1.2, 0.3.

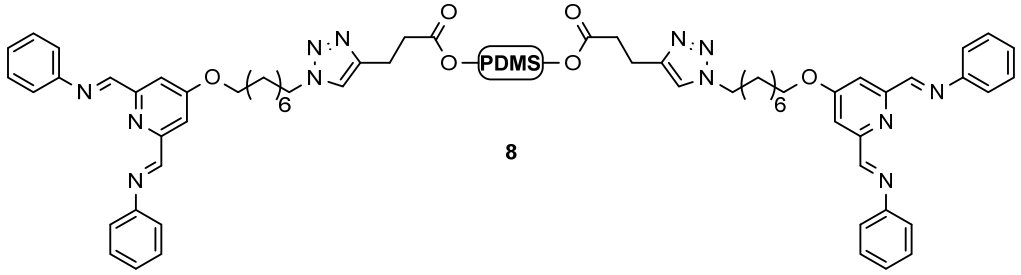
PDMS-pincer bis(dialdehyde) (7)



7

Compund **5** (0.719 g, 2.364 mmol, 3 eq.) and PDMS-dialkyne **6** (4.20 g, 0.788 mmol, 1 eq..) were dissolved in a mixture of THF (80 mL) and water (60 mL). Copper(II) sulfate (78.6 mg, 0.315 mmol, 0.4 eq) and sodium ascorbate (124.9 mg, 0.630 mmol, 0.8 eq.) were added and the reaction mixture was stirred for 18 h at room temperature, while bubbling argon through the mixture. 300 mg of EDTA sodium salt was added and the mixture was stirred for 2 h at room temperature. Reaction mixture was diluted with water to 200 mL and 50 mL of brine was added and the mixture was extracted with DCM (4×100 mL). Combined organic layers were washed with brine (250 mL) and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The mixture was purified by size exclusion chromatography (Biobeads SX-1, DCM) to obtain PDMS-pincer bis(dialdehyde) **7** as a yellow oil. Yield 80%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.10 (s, 4H), 7.62 (s, 4H), 7.34 (s, 2H), 4.30 (t, J = 7.2 Hz, 4H), 4.24 – 4.20 (m, 4H), 4.13 (t, J = 6.5 Hz, 4H), 3.65 – 3.56 (m, 4H), 3.42 (t, J = 7.1 Hz, 4H), 3.04 (t, J = 7.3 Hz, 4H), 2.76 (t, J = 7.2 Hz, 4H), 1.95 – 1.77 (m, 8H), 1.66 – 1.54 (m, 4H), 1.51 – 1.27 (m, 4H), 0.58 – 0.45 (m, 4H), 0.28 – –0.17 (m, PDMS backbone). ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.6, 173.0, 167.3, 154.9, 146.6, 121.2, 111.6, 74.4, 69.4, 68.6, 63.9, 50.3, 33.8, 30.5, 29.2, 29.1, 28.8, 26.6, 25.9, 23.5, 21.2, 14.2, 1.58, 1.35, 1.21, 0.84, 0.29.

PDMS-imine macromonomer (8)



8

PDMS-pincer bis(dialdehyde) **7** (675 mg, 0.098 mmol) was dissolved in chloroform (10 mL) and activated molecular sieves (3 Å) were added. Aniline (405 µL, 0.390 mmol) was then added as a solution in chloroform. The reaction mixture was stirred at 50 °C for 2 h and then cooled to room temperature. The molecular sieves were filtered off and the solvent was evaporated under reduced pressure to obtain macromonomer **8** that was further reacted with the appropriate metal without further purification. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 4H), 7.43 (t, J = 7.5 Hz, 8H), 7.36 – 7.27 (m, 14H), 4.30 (t, J = 7.3 Hz, 4H), 4.21 (m, 8H), 3.61 (t, J = 4.9 Hz, 4H), 3.42 (t, J = 7.1 Hz, 4H), 3.04 (t, J = 7.4 Hz, 4H), 2.76 (t, J = 7.3 Hz, 4H), 1.98 – 1.79 (m, 8H), 1.61 – 1.37 (br, 20H), 0.59 – 0.46 (m, 4H), 0.07 (s, 457H).

3 End group functionalisation

^{1}H NMR was used to confirm that both chain ends of the PDMS macromonomer had reacted in the synthesis of intermediates **6** and **7**. Firstly, the complete disappearance of the protons in α and β positions relative to the hydroxyl group of the dihydroxy-terminated PDMS was observed (signals between 3.8 – 3.5 ppm) in the ^{1}H spectrum of in the dialkyne-PDMS **6**. In the next step the complete disappearance of the alkyne proton at 2.0 ppm, originating from dialkyne-PDMS **6**, indicated full conversion towards the PDMS-pincer bis(dialdehyde) **7**. These relevant ^{1}H signals are highlighted in the spectra below.

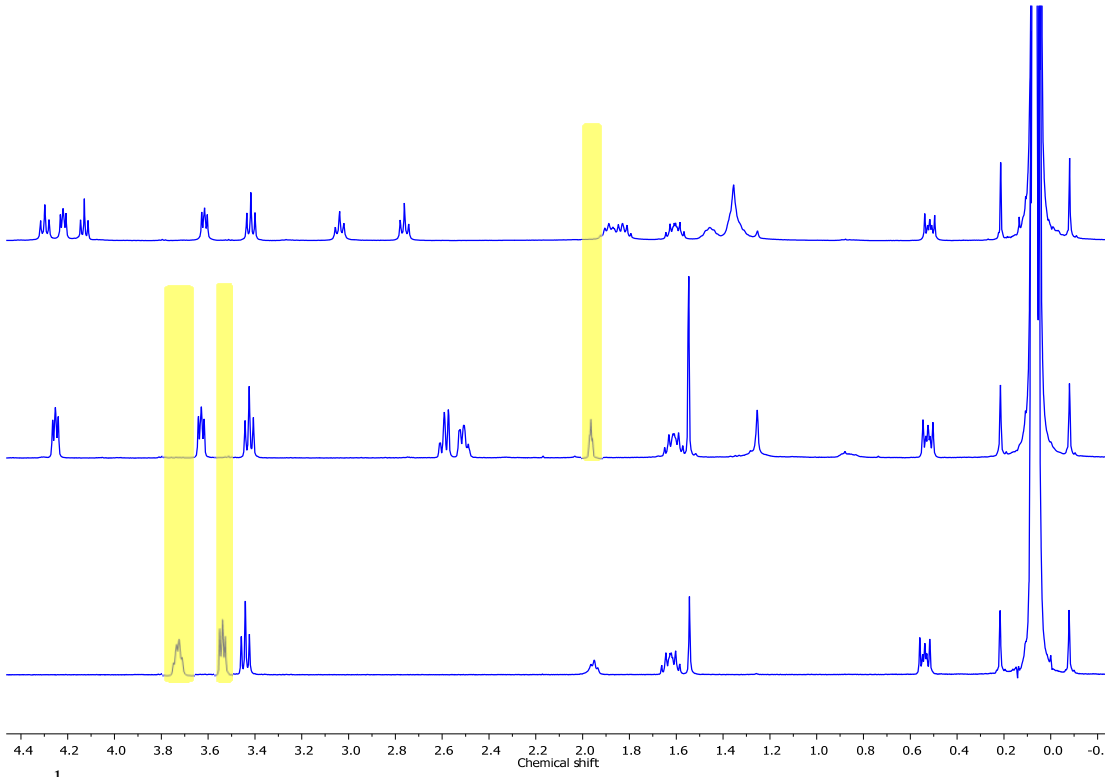


Fig S1. a) ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of starting dihydroxy-terminated PDMS (bottom); dialkyne-PDMS **6** (middle) and PDMS-bis(dialdehyde pincer) **7** (top). For full assignment of the spectrum, please refer to Section 10.

Successful conversion of both chain ends of the dihydroxy-terminated PDMS was further provided by the ^{13}C and DEPT 135 NMR spectra. In the ^{13}C spectrum from the dialkyne-PDMS **6** no signal at 62 ppm was observed (which corresponds to the C attached to the hydroxy groups in the starting dihydroxy-terminated PDMS). This signal is highlighted in the spectra below.

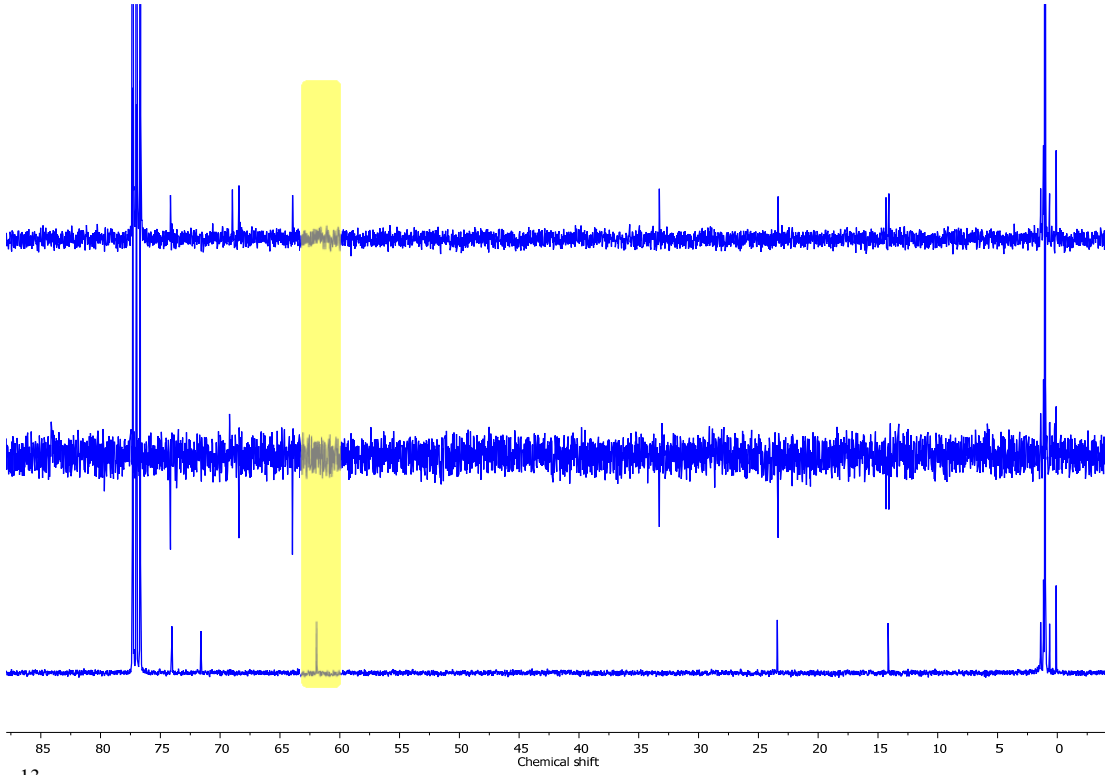
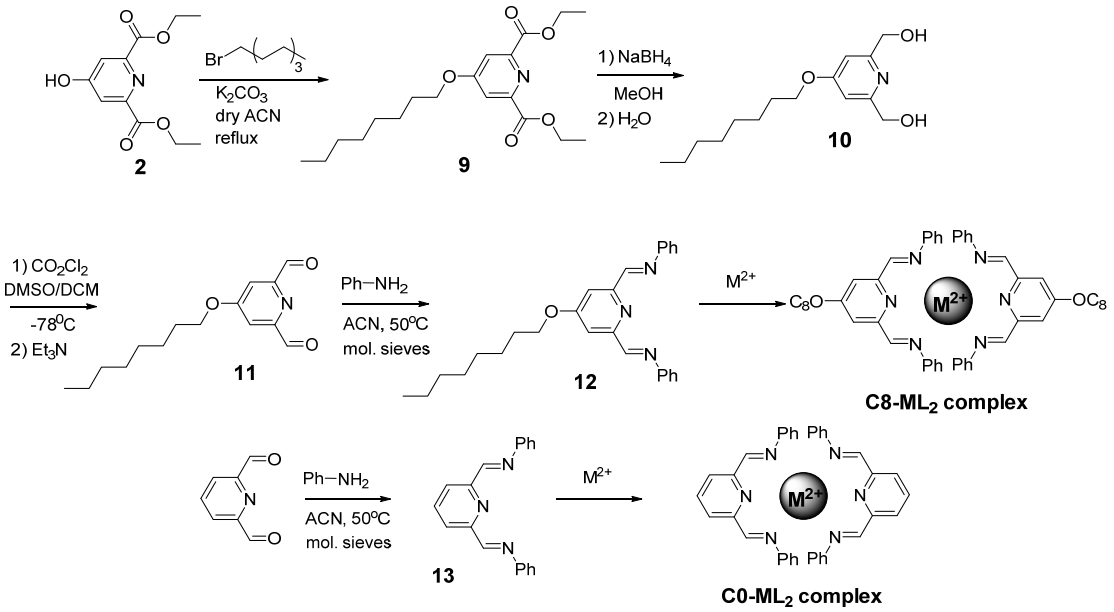


Fig S1. ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 293 K) of starting dihydroxy-terminated PDMS (bottom); DEPT135 (100 MHz, $CDCl_3$, 293 K) of dialkyne-PDMS **6** (middle); ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) of PDMS-pincer bis(dialdehyde) **7** (top).

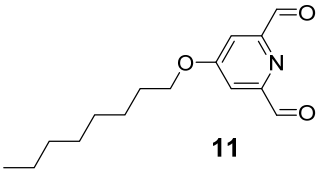
4 Model compounds characterisation

4.1 Synthesis



The synthesis of model compound **11** followed the same procedure as for the synthesis of compound **5**, with the only exception that instead of 1-azido-8-bromooctane (**1**), 1-bromooctane was used. C_0-diiminepincer **13** was prepared and characterised according to a reported procedure.[S2]

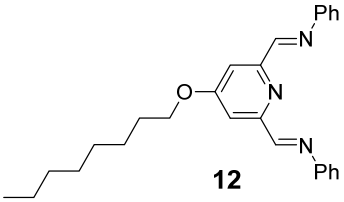
C_8-dicarbaldehydepincer (11)



Chemical Formula: $C_{15}H_{21}NO_3$
Exact Mass: 263.1521

Oxalyl chloride (1.65 mL, 18.59 mmol) was dissolved in dry DCM (40 mL) under Ar atmosphere. The solution was immersed in a N_2 liq./acetone bath and the temperature was set at –78 °C. Then, a mixture of DMSO (2.2 mL, 31.46 mmol) in dry DCM (10 mL) was added dropwise. The mixture was stirred for 15 min and then, a solution of diol **10** (1.91 g, 7.15 mmol) dissolved in dry DCM (150 mL) was added dropwise. The reaction mixture was stirred at T < –78 °C for one hour. After that, triethylamine (9.9 mL, 71.5 mmol) was added and let it warm up to room temperature. The organic layer was washed 7× with a bleach solution and then, the solvent was removed under reduced pressure to yield **11** without no need of further purification. Yield: 99%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 10.11 (s, 2H), 7.62 (s, 2H), 4.14 (t, J = 6.5 Hz, 2H), 1.90 – 1.78 (m, 2H), 1.47 (t, J = 7.6 Hz, 2H), 1.39 – 1.23 (m, 8H), 0.94 – 0.85 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 165.6, 153.2, 109.8, 67.8, 30.2, 27.6, 27.6, 27.1, 24.2, 21.0, 12.4. FTIR (ATR) 703, 725, 877, 906, 942, 974, 989, 1041, 1062, 1081, 1129, 1155, 1199, 1276, 1316, 1364, 1435, 1562, 1591, 1596, 1661, 1699, 1710, 2854, 2871, 2917, 2955, 3080 cm^{-1}.

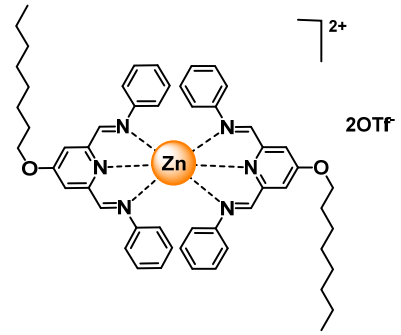
C_8-diiminepincer (12)



Chemical Formula: $C_{27}H_{31}N_3O$
Exact Mass: 413.2467

Model C_8-dicarbaldehydepincer (**11**) (0.61 g, 2.31 mmol) was dissolved in dry methanol with activated molecular sieves (3Å) and then, aniline was added (425 µL, 4.62 mmol). The reaction mixture was heated at 60 °C for two hours. Then, the solvent was evaporate under reduced pressure. The excess of aniline was washed off with methanol. Yield: 69%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (s, 1H), 7.81 (s, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.29 (dd, J = 17.2, 8.0 Hz, 3H), 4.19 (t, J = 6.6 Hz, 1H), 1.86 (t, J = 7.3 Hz, 1H), 1.56 – 1.45 (m, 1H), 1.33 (q, J = 17.4, 13.7 Hz, 6H), 0.91 (t, J = 6.7 Hz, 2H). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 8.57 (s, 2H), 7.74 (s, 2H), 4.19 (t, J = 6.5 Hz, 2H), 1.81 (dq, J = 13.3, 6.0, 5.4 Hz, 2H), 1.48 (td, J = 9.2, 8.3, 4.5 Hz, 2H), 1.44 – 1.24 (m, 11H), 0.95 – 0.84 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 158.9, 154.9, 149.5, 127.9, 125.5, 119.8, 108.2, 67.3, 30.4, 27.9, 27.9, 27.6, 24.6, 21.3, 12.8. FTIR (ATR) 666, 692, 731,752, 766, 802, 846, 867, 907, 950, 969, 990, 1024, 1042, 1074, 1164, 1207, 1261, 1299, 1365, 1398, 1431, 1443, 1485, 1502, 1558, 1590, 1627 (imine C=N st), 2854, 2925, 2958, 3064 cm^{-1}. HRMS (ESI): m/z for $C_{27}H_{32}ON_3$ $(M+1)^+$ obs. 414.2542, calculated 414.2540.

C_8-Zn model complex



C_8-diiminepincer **12** (0.18 g, 0.44 mmol) was dissolved in dry acetonitrile (5 mL) with molecular sieves (3Å) and to this solution zinc (II) triflate (79 mg, 0.22 mmol) was added. The solution was stirred at room temperature for 4 hours and then the solvent was evaporated. The product was purified by size exclusion chromatography (SX3, DCM) followed by precipitation in diisopropyl ether, yielding 110 mg of an orange powder. Yield: 42%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.67 (s, 2H), 7.65 (s, 2H), 7.30 (m, 6H), 6.80 (d, J = 8.5 Hz, 4H), 4.33 (t, J = 4.3 Hz, 2H), 1.89 (m, 2H), 1.52 (m, 2H), 1.40 – 1.34 (br, 10H), 0.91 (m, 3H). ^{13}C NMR (101 MHz, CD_3CN) δ 172.7, 160.1, 148.8, 146.3, 130.8, 130.1, 122.0, 118.0, 72.0, 32.5, 29.9, 29.8, 29.0, 26.3, 23.3, 23.1, 14.3. HRMS (ESI): m/z for $C_{54}H_{62}O_2N_6Zn$ $(M)^{2+}$ obs. 445.2109, calculated 445.2107 (Fig S4).

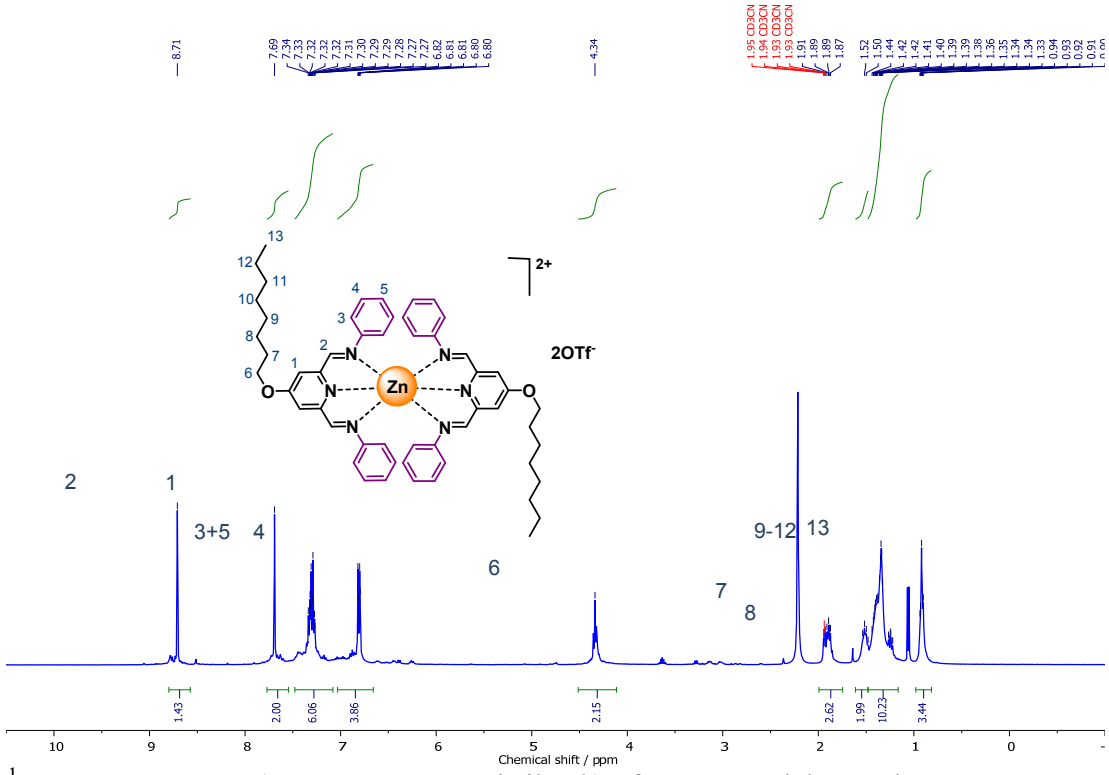


Fig S3. ^{1}H NMR spectrum (400 MHz, Acetonitrile-d_3) of C_8-Zn model complex.

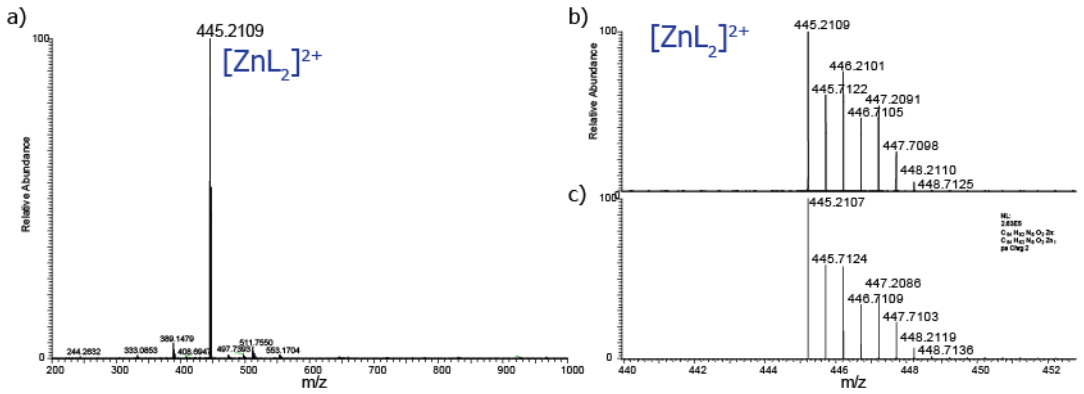
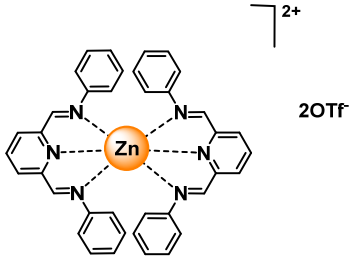


Fig S4. HRMS spectrum (ESI, positive mode) of the C_8-Zn model complex. The full range spectrum (a) and a zoom showing the experimental (b) and simulated (c) isotopic distribution for the 2+ species.

C_0-Zn model complex



C_0-diiminepincer **13** (87 mg, 0.31 mmol) was dissolved in acetonitrile (2 mL) with molecular sieves (3Å) and to this solution zinc (II) triflate (56 mg, 0.15 mmol) was added. The solution was stirred at 60 °C for 3 hours and then the solvent was evaporated. The crude was redissolved in a small amount of acetonitrile and precipitated in diethylether. The precipitate was filtered affording 103 mg of an orange powder. Yield: 71%. ^{1}H NMR (400 MHz, CD_3CN) δ 8.82 (s, 2H), 8.57 (t, J = 8.2 Hz, 1H), 8.26 (d, J = 8.2 Hz, 2H), 7.34 (m, 2H), 7.27 (m, 4H), 6.80 (d, J = 6.8 Hz, 4H). ^{13}C NMR (100 MHz, CD_3CN) δ 159.1, 146.0, 145.1, 131.1, 129.6, 129.1, 121.2, 120.8. HRMS (ESI): m/z for $C_{38}H_{30}N_6Zn$ $(ZnL_2)^{2+}$ obs. 317.0906, calculated 317.0913.

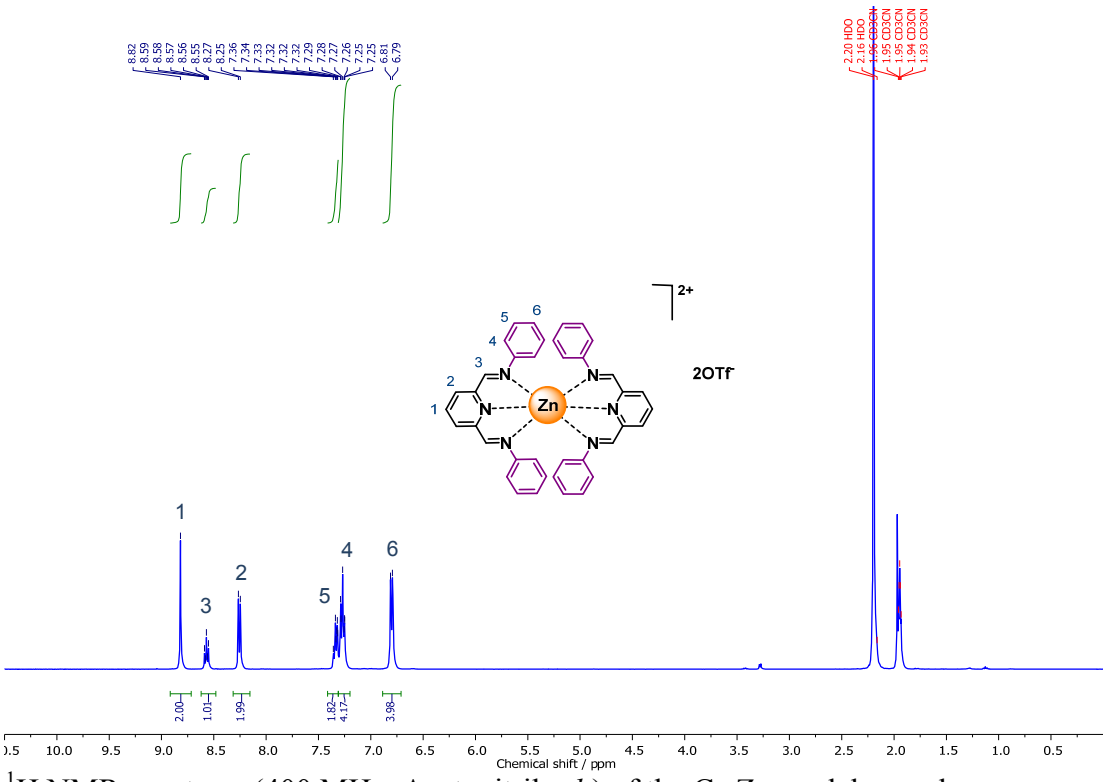


Fig S5. ^{1}H NMR spectrum (400 MHz, Acetonitrile-d_3) of the C_0-Zn model complex.

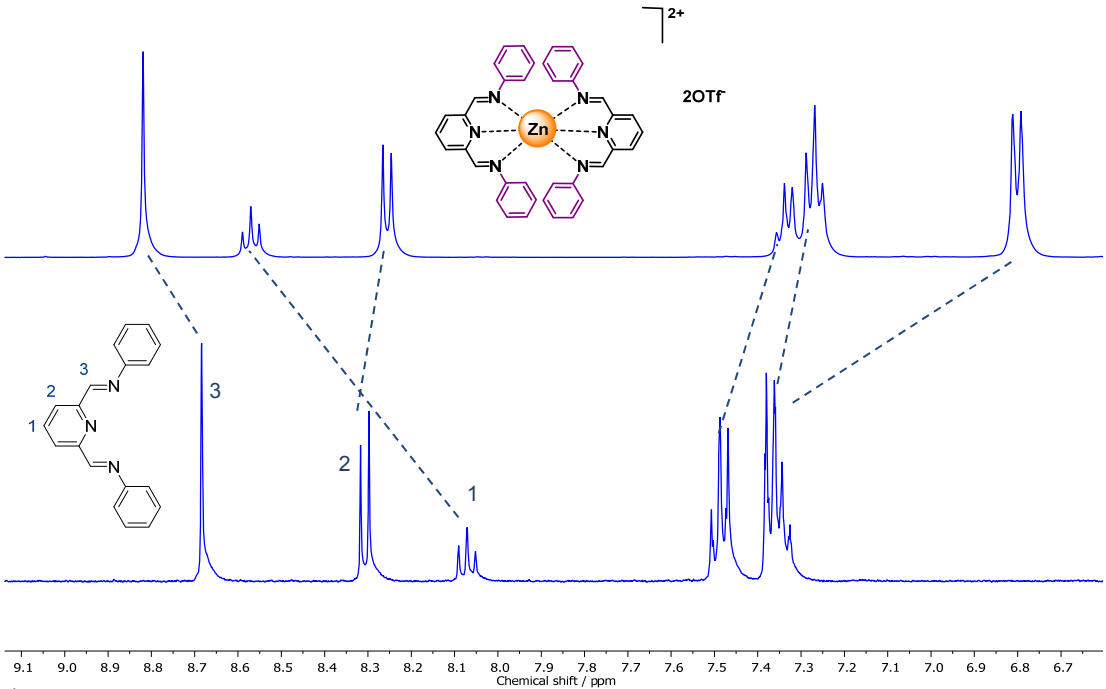
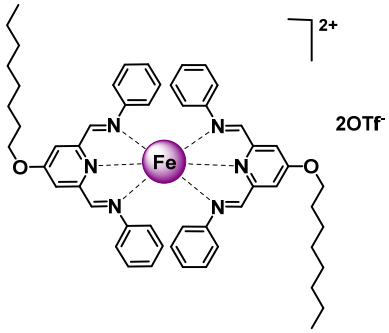


Fig S6. ^{1}H NMR spectrum (400 MHz, Acetonitrile-d_3) of C_0-diiminepincer **13** (bottom) and the C_0-Zn model complex (top) showing the shift of all the resonances and specially, the characteristic downfield shift of the imine resonance (labelled as 3) upon formation of the ZnL_2 complex.

C_8-Fe model complex



C_8-diiminepincer **12** (0.24 g, 0.89 mmol) was dissolved in dry acetonitrile (10 mL) with molecular sieves (3Å) and to this solution iron (II) triflate (186 mg, 0.45 mmol) was added. The solution turned immediately blue and was stirred at 50 °C for 2 hours. Then, the solvent was evaporated and purified by size exclusion chromatography (SX3, DCM) yielding 311 mg of an blue solid. Yield: 30%. ^{1}H NMR (400 MHz, CD_3CN) 11.8 (br, 1H), 9.34 (br, 2H), 7.46 (br, 4H), 7.15 (m, 2H), 6.20 (br, 4H), 4.44 (br, 2H), 1.86 (m, 2H), 1.50 (m, 2H), 1.27 – 1.21 (br, 10H), 0.90 (t, 3H) (Fig S7); ^{13}C NMR (100 MHz, CD_3CN) δ 199.4, 160.3, 131.5, 129.9, 126.9, 123.5, 120.3, 71.2, 32.4, 29.8, 29.8, 29.1, 26.2, 23.2, 14.3. HRMS (ESI): m/z for $C_{54}H_{62}O_2N_6Fe$ $(M)^{2+}$ obs. 441.2125, calculated 441.2136 (Fig S8).

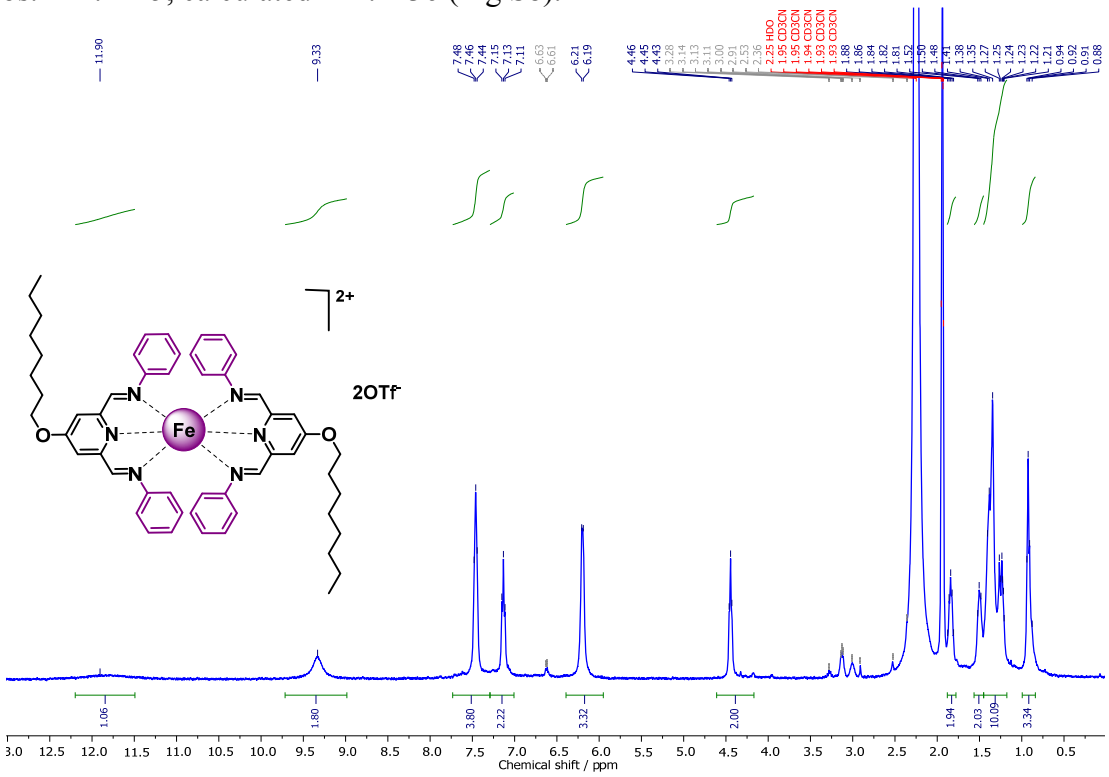


Fig S7. ^{1}H NMR spectrum (400 MHz, Acetonitrile-d_3) of C_8-Fe model complex. The broad signals are attributed to paramagnetic nature of the (partial) high spin Fe^{2+}, which prevented an accurate assignment of the peaks.

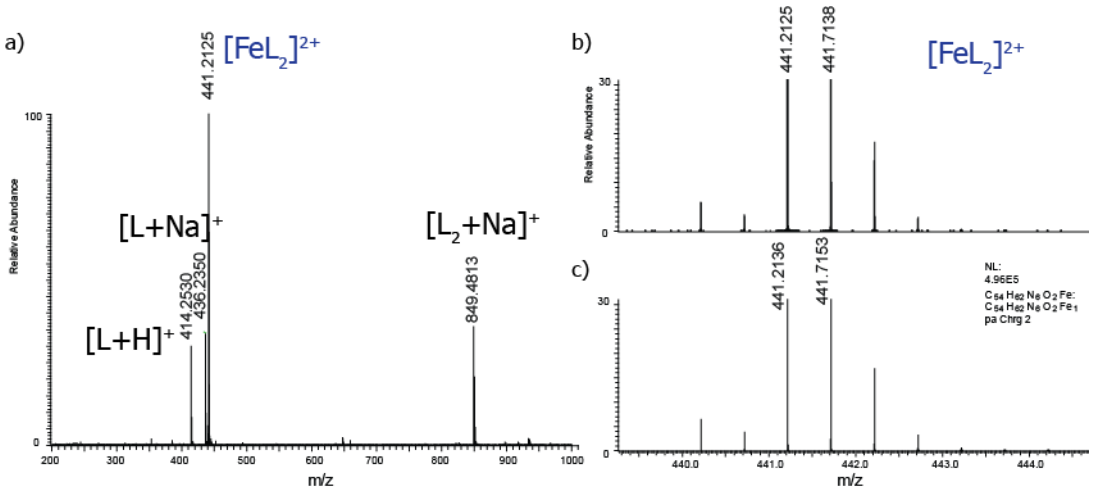


Fig S8. HRMS spectrum (ESI, positive mode) of the C_8-Fe model complex. The full range spectrum (a) and a zoom showing the experimental (b) and simulated (c) isotopic distribution for the 2+ species.

4.2 UV-vis titrations

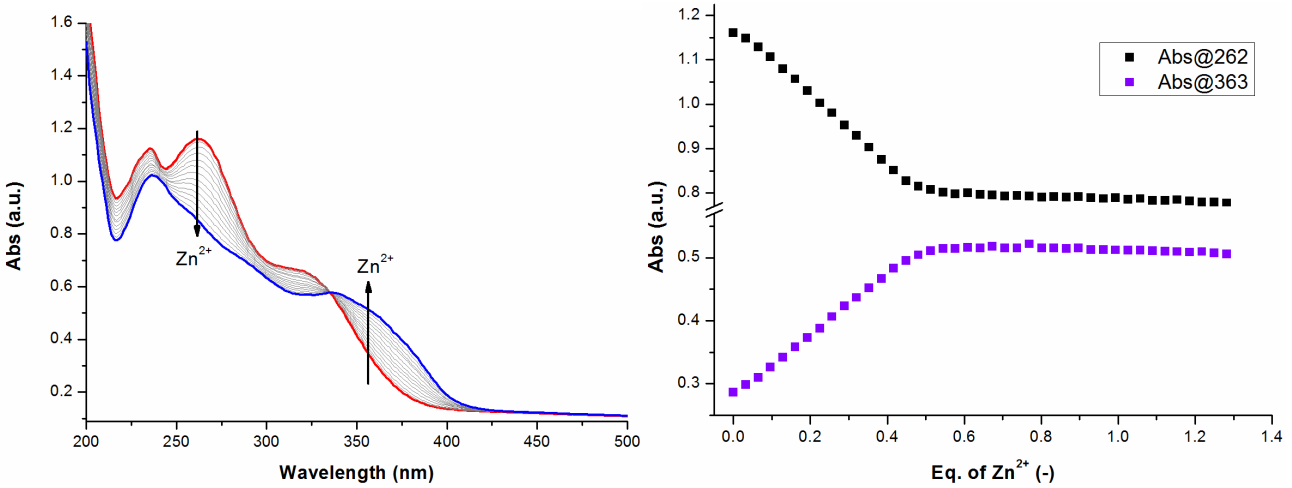


Fig S9. UV-vis titration of C_8-diiminepincer (**12**) with $Zn(OTf)_2$ (left). The starting (red trace) and the final state (blue trace) are coloured for clarity purposes. Corresponding change in the absorbance against the eq. of metal added (right). Acetonitrile, $l = 1$ cm, $[\mathbf{12}]_0 = 4.3 \cdot 10^{-5}$ M.

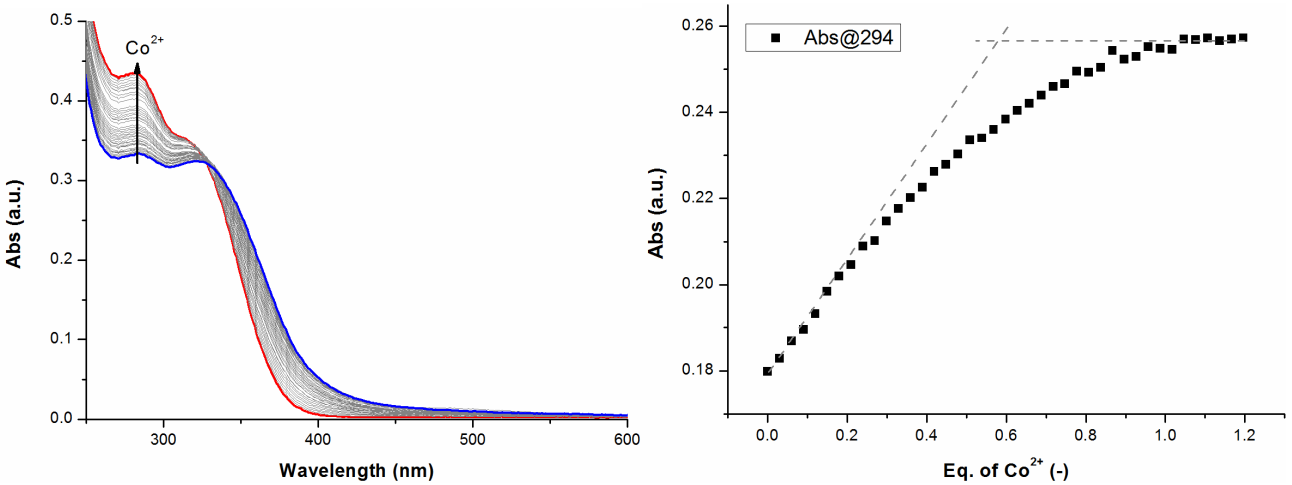


Fig S10. UV-vis titration of C_0-diiminepincer (**13**) with $Co(BF_4)_2$ (left). The starting (blue trace) and the final state (red trace) are coloured for clarity purposes. Corresponding change in the absorbance against the eq. of metal added (right). Methanol, $l = 1$ cm, $[\mathbf{13}]_0 = 3.9 \cdot 10^{-5}$ M.

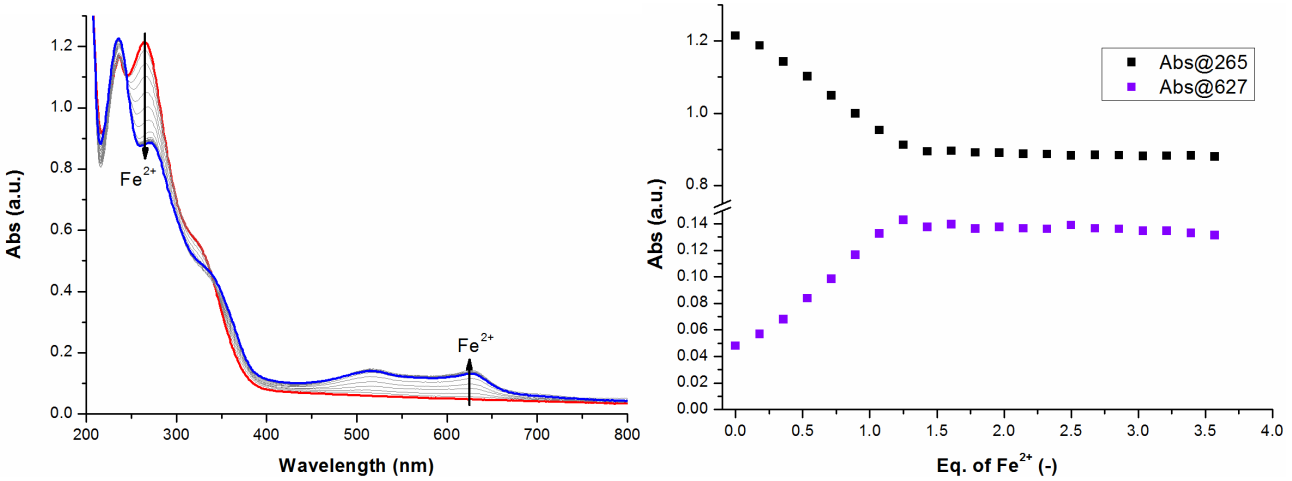


Fig S11. UV-vis titration of C_8-diiminepincer (**12**) with $Fe(OTf)_2$ (left). The starting (red trace) and the final state (blue trace) are coloured for clarity purposes. Corresponding change in the absorbance against the eq. of metal added (right). Acetonitrile, $l = 1$ cm, $[\mathbf{12}]_0 = 4.3 \cdot 10^{-5}$ M.

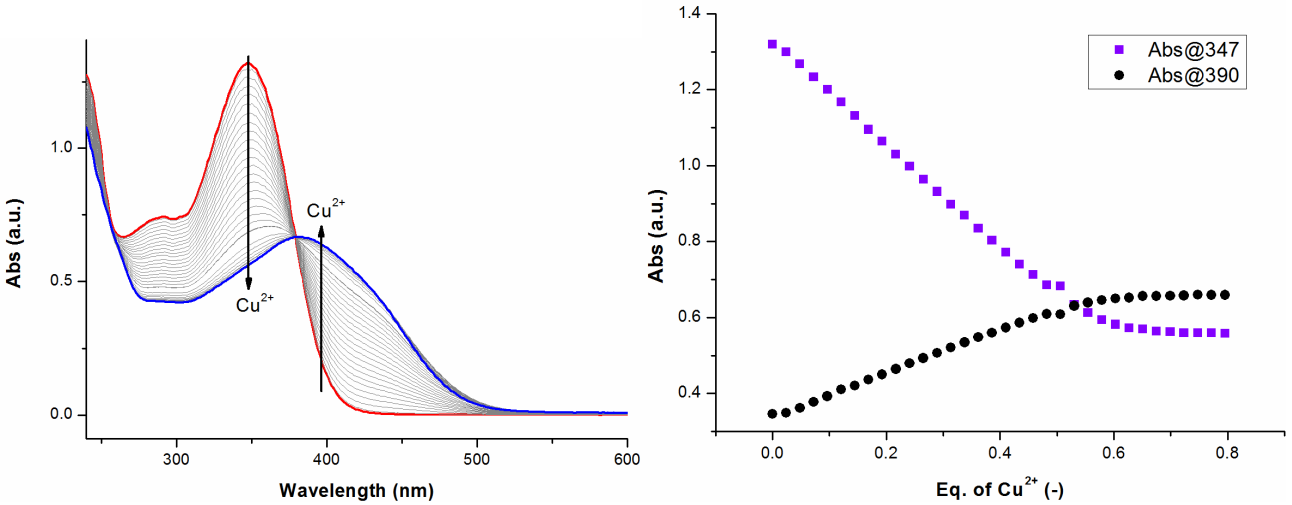


Fig S12. UV-vis titration of C_0-diiminepincer (**13**) with $Cu(OAc)_2$ (left). The starting (red trace) and the final state (blue trace) are coloured for clarity purposes. Corresponding change in the absorbance against the eq. of metal added (right). Methanol, $l = 1$ cm, $[\mathbf{13}]_0 = 4.9 \cdot 10^{-5}$ M.

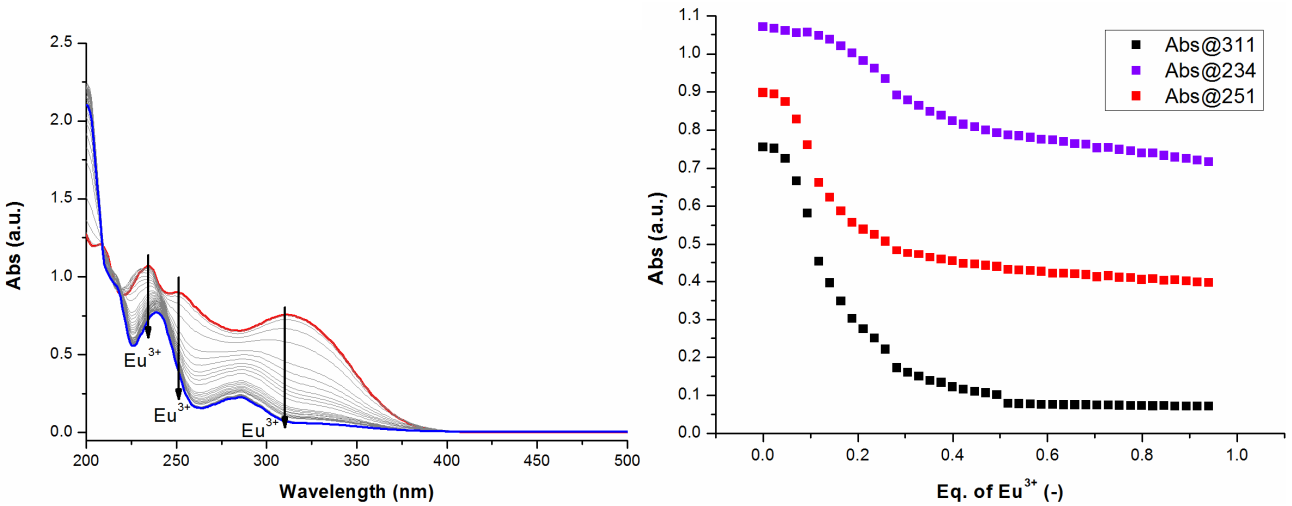


Fig S13. UV-vis titration of C_0-diiminepincer (**13**) with Eu(OTf)$_3$ (left). The starting (red trace) and the final state (blue trace) are coloured for clarity purposes. Corresponding change in the absorbance against the eq. of metal added (right). Acetonitrile, $l = 1$ cm, $[\mathbf{13}]_0 = 4.3 \cdot 10^{-5}$ M.

4.3 Transimination model compounds

4.3.1 Exchange with a more nucleophilic aromatic amine

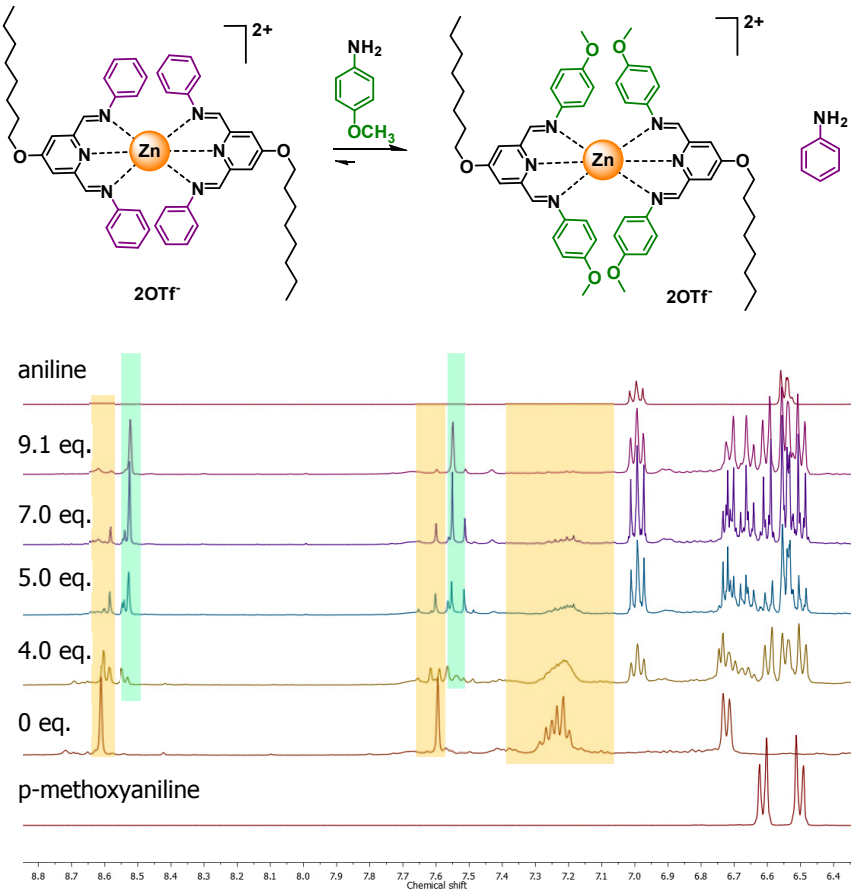


Fig S14. Partial ^{1}H NMR spectrum (400 MHz, CD_3CN, 293 K) titration of the C_8-Zn model complex (10 mM) with *p*-methoxyaniline, with the number of equivalents of *p*-methoxyaniline indicated in the figure. The signals corresponding to the starting complex are highlighted in yellow and the ones corresponding to the transimination complex in green. The release of aniline is observed upon transimination, for comparison the spectra for aniline and *p*-methoxyaniline are also shown.

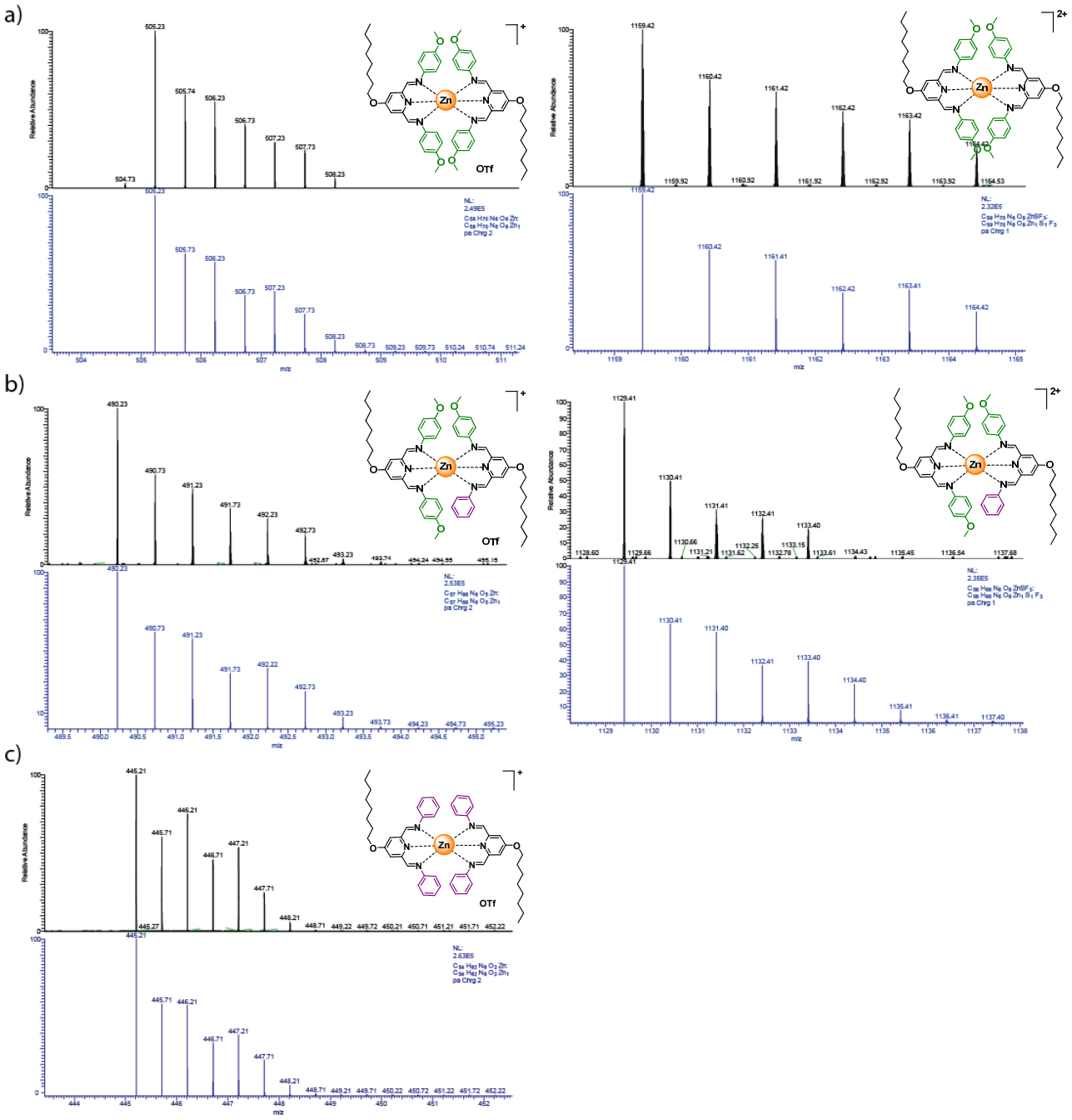


Fig S15. HRMS spectrum (ESI, positive mode) for the titration experiment for which the corresponding NMR data are presented above (Fig S14), showing the final transimination complex (a), an intermediate in which only three anilines have been replaced (b) and the starting complex (c). In blue is depicted the corresponding calculated isotopic distribution for each species.

4.3.2 Exchange kinetics

Procedure: 0.5 mL of a solution of C_8-Zn model complex (19 mM) was placed in an NMR tube. To this solution TMS was added as internal standard and to this 13 µL of a 1M solution of *p*-methoxyaniline was added, after which the measurement was started directly. The amount of *p*-methoxyaniline (40 eq., 10× excess) was chosen that high that its concentration does not change more than a 10% during the reaction. The integrals were normalised with respect to the integral of the TMS.

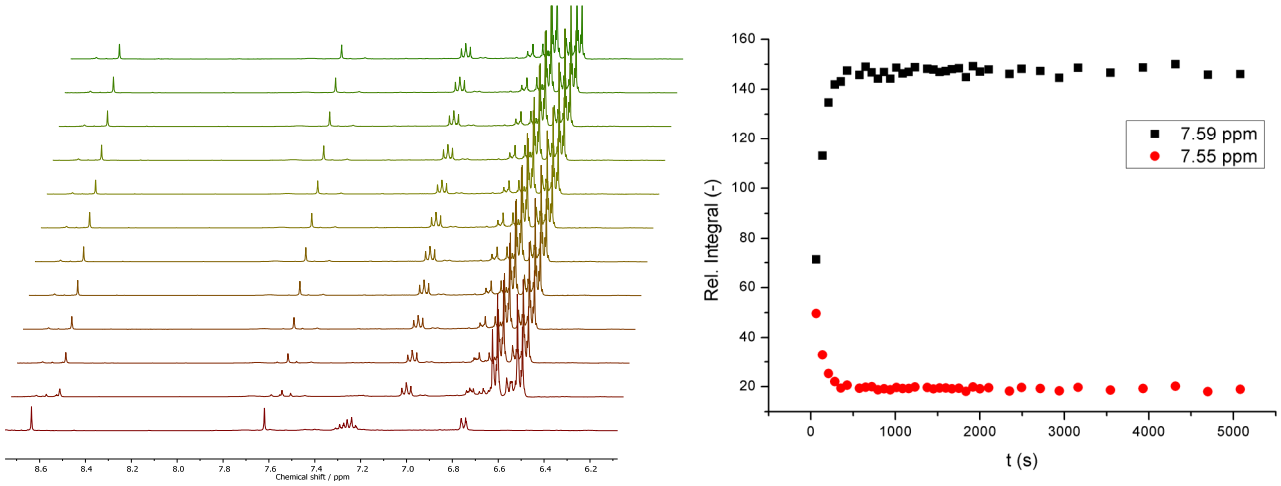
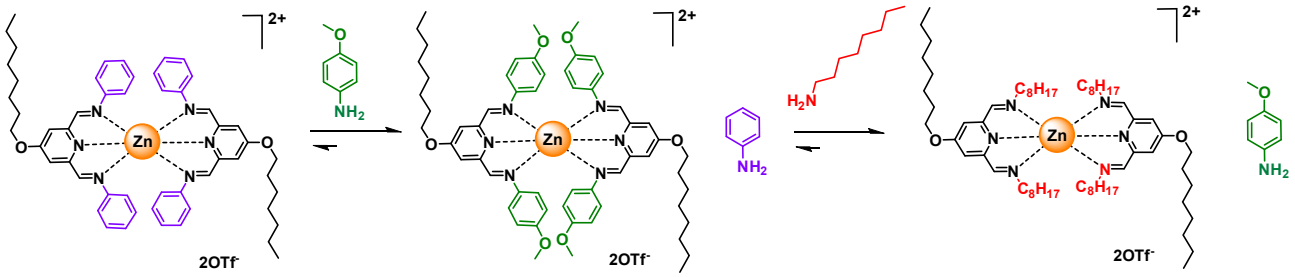


Fig S16. Partial ^{1}H NMR spectrum (400 MHz, CD_3CN, 300 K) for the kinetic experiment with *p*-methoxyaniline (left), and the kinetic profiles of the relative integrals corresponding to the pyridine and the imine protons (right), revealing that the exchange reaction is completed within 500 s.

4.3.3 Three-step exchange with two amines



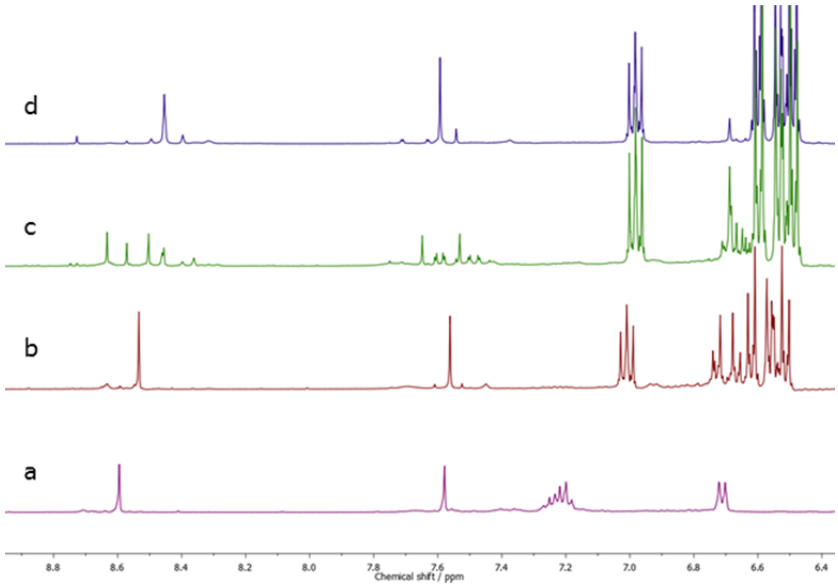


Fig S17. Partial ^{1}H NMR spectrum (400 MHz, CD_3CN, 293 K) showing the C_8-Zn model complex (19 mM) (a), after exchange reaction with *p*-methoxyaniline (b), and the exchange complex shown in (b) after subsequent addition of 4 eq. (c) and 8 eq. (d) of 1-octylamine.

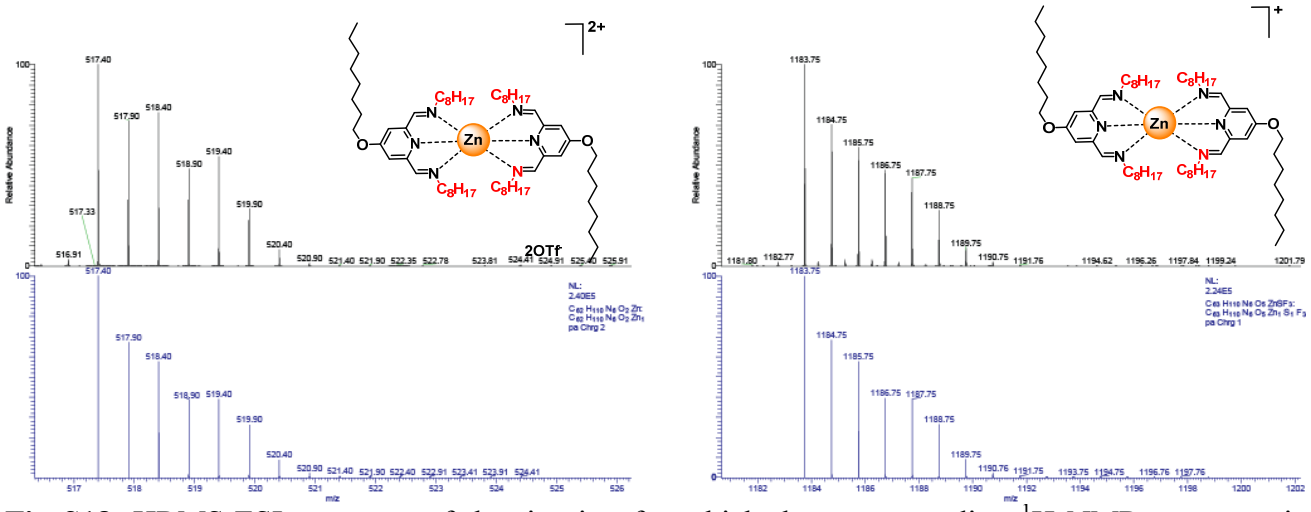


Fig S18. HRMS-ESI spectrum of the titration for which the corresponding ^{1}H NMR spectrum is shown above (Fig S17) showing the final transimination complex. On the left is depicted the 2+ species and on the right the 1+. In blue are depicted the calculated isotopic distribution for each species.

5 Zn^{2+}-polymer

5.1 Synthesis

PDMS-pincer bis(dialdehyde) **7** (516 mg, 0.0738 mmol, 1 eq.) was dissolved in chloroform (10 mL). Aniline (27.5 mg, 0.295 mmol, 4 eq.) as a solution in chloroform, and molecular sieves were added and the reaction mixture was stirred at 60 °C for 1.5 h. $Zn(OTf)_2$ (26.8 mg, 0.0738 mmol, 1 eq.) was added as a solution in MeOH and the mixture was stirred at 60 °C for 1 h. Molecular sieves were filtered off and the solvent was evaporated under reduced pressure to obtain the Zn^{2+}-polymer. Below the characterisation results of the polymer are reported.

5.2 UV/vis spectroscopy

Due to the polydispersity of the PDMS polymer it was needed to carefully determine the amount of Zn^{2+} needed to obtain the exact 1:1 stoichiometry with the macromonomer to avoid the formation of small oligomers. For that purpose we performed a UV-vis titration to determine the equivalence point and with this data extrapolate the amount of Zn salt that is needed for the reaction. From this, 175 µL of $1.38 \cdot 10^{-4}$ M solution of $Zn(OTf)_2$ is needed to titrate 2.0 mL of a solution of [**8**] = $8.3 \cdot 10^{-2}$ mg/mL, which corresponds to a M_w of the polymer of $6.93 \cdot 10^3$ g/mol. This value was used during the Zn^{2+}-polymer preparation.

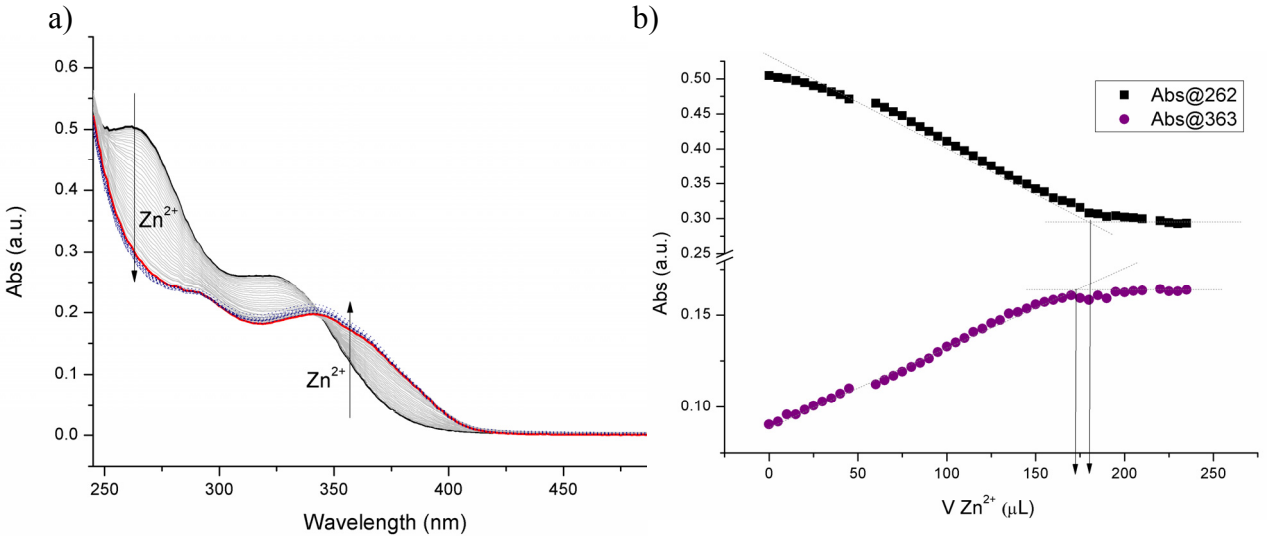


Fig S19. a) UV-vis titration of PDMS-pincer bis(diimine) (**8**) with $Zn(OTf)_2$. The starting (black trace) and at the equivalence point (red trace) are coloured for clarity purposes. The intermediate spectra are depicted in grey and the ones after the equivalence point are depicted in dotted blue. b) Corresponding change in the absorbance against the volume of $Zn(OTf)_2$. Chloroform, l = 1 cm, additions of 5 µL.

5.3 ^{1}H NMR spectroscopy

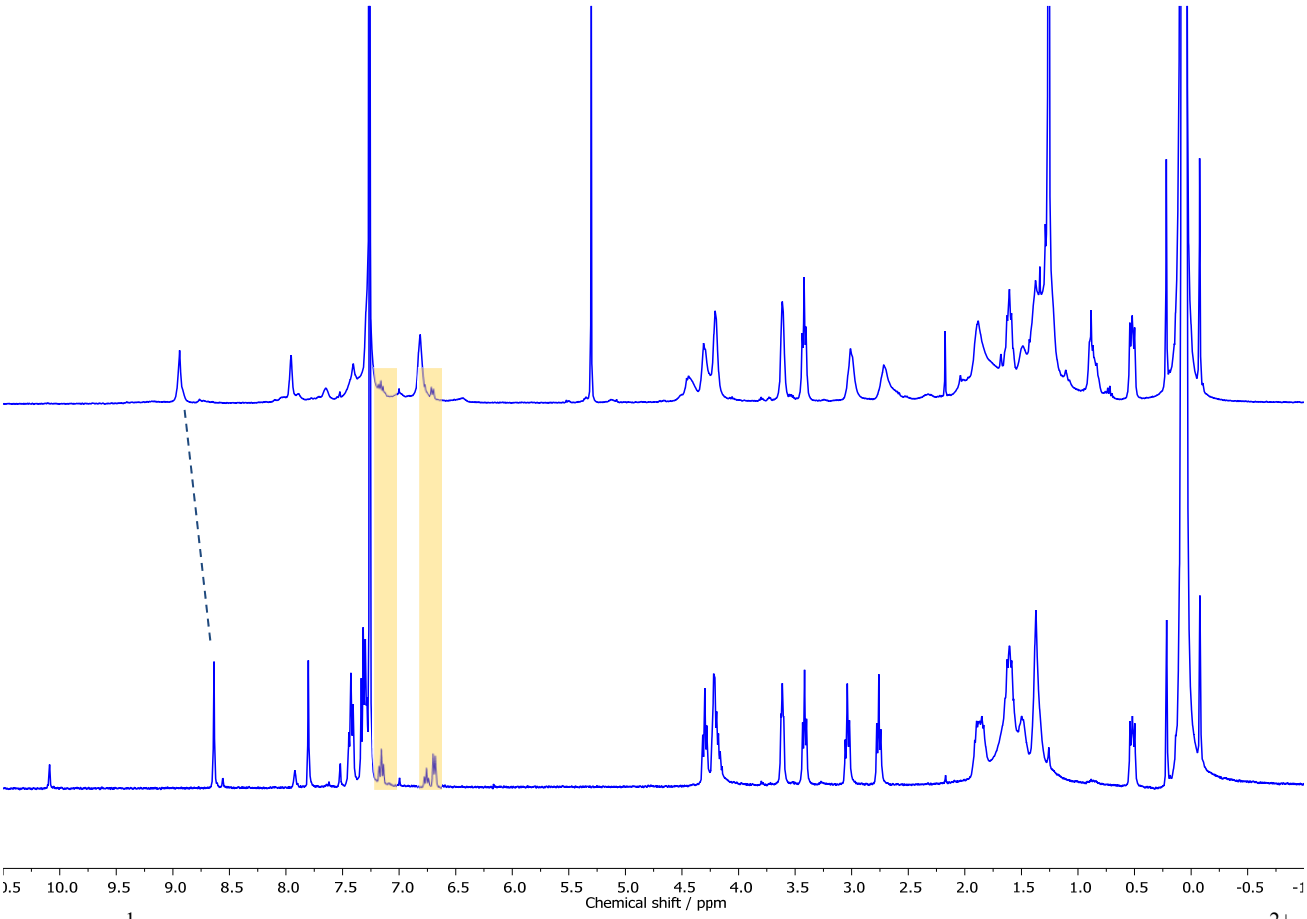


Fig S20. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) of the PDMS-pincerdiimine **8** (bottom) and the Zn^{2+}-PDMS polymer (top). It is noteworthy the broadening on the signals on the top spectrum suggesting the polymer formation. The dashed line highlights the characteristic downfield shift in the imine proton upon complexation. Highlighted in yellow is the decrease of the intensity of the free aniline resonances upon complexation.

5.4 DOSY calibration

The polystyrene standards (2000, 25000, 123000) solutions were prepared in deuterated chloroform with concentration of 5 mg/mL and then 0.5 mL were taken to an NMR tube. For the calibration curve the signal from the chloroform (M_w = 120.38, $D_{coeff} = 2.18 \cdot 10^{-9}$ m^2/s) was also used.
The M_w calculated with the calibration curve for the PDMS-pincer bis(dialdehyde) **7** (macromonomer) was $8.0 \cdot 10^3$ g/mol ($D_{coeff} = 1.8 \cdot 10^{-10}$ m^2/s) in good agreement with the M_w obtained by the UV-vis titration with Zn^{2+} (section 5.2). For a concentrated sample of the Zn^{2+}-PDMS polymer, a M_w of $7.3 \cdot 10^5$ g/mol was obtained ($D_{coeff} = 1.3 \cdot 10^{-11}$ m^2/s).

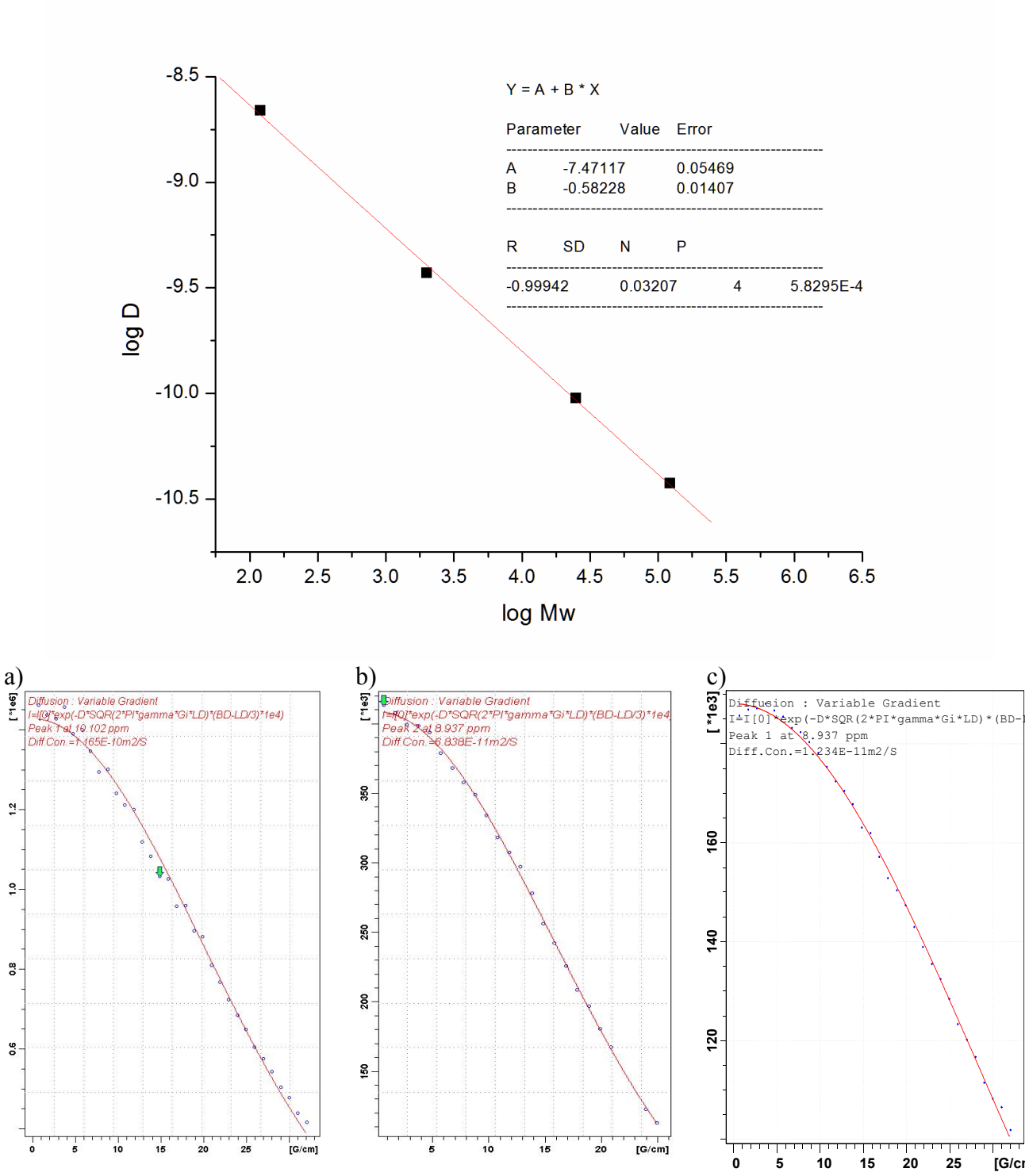


Fig S21. Top: Calibration curve of the log(D_{coeff}) vs the log(M_w) for the DOSY spectra. Bottom: Fitting of the decay representative protons for a) macromonomer **7**; b) Zn^{2+}-polymer at 50 mg/mL; c) Zn^{2+}-polymer at 65 mg/mL. One representative decay fitting curve is shown, the D_{coeff} was determined by taking the average from all the peaks corresponding to the polymer, resulting in value of $1.8 \cdot 10^{-10}$ m^2/s for macromonomer **7**, $6.8 \cdot 10^{-11}$ m^2/s for the Zn^{2+}-polymer at 50 mg/mL and $1.3 \cdot 10^{-11}$ m^2/s for the Zn^{2+}-polymer at 65 mg/mL.

5.5 Viscometry

Table S1. Viscometry data for bis(dialdehyde) PDMS polymer **7**.

Concentration (mg/mL)	Time (s)	η_{sp} (-)
25.7	66	0.66
22.0	68	0.42
19.3	66	0.42
17.1	66	0.32
11.0	58	0.19
0 (i.e. pure solvent)	46	0

Table S2. Viscometry data for the Zn^{2+}-polymer.

Concentration (mg/mL)	Time (s)	η_{sp} (-)
24.5	115	1.48
21.0	93	1.01
18.4	85	0.84
16.3	75	0.61
14.7	69	0.49
13.4	66	0.42
12.2	64	0.38
11.3	62	0.34
10.5	59	0.27
0 (i.e. pure solvent)	46	0

Table S3. Viscometry data for the Zn^{2+}-polymer in the presence of 0.6 eq. 1,12-dodecyldiamine.

Concentration (mg/mL)	Time (s)	η_{sp} (-)
24.5	182	2.93
21.0	120	1.59
18.4	98	1.12
16.3	80	0.73
14.7	72	0.54
13.4	68	0.48
12.2	64	0.38
11.3	62	0.33
10.5	59	0.27
0 (i.e. pure solvent)	46	0

5.6 Addition of EDTA

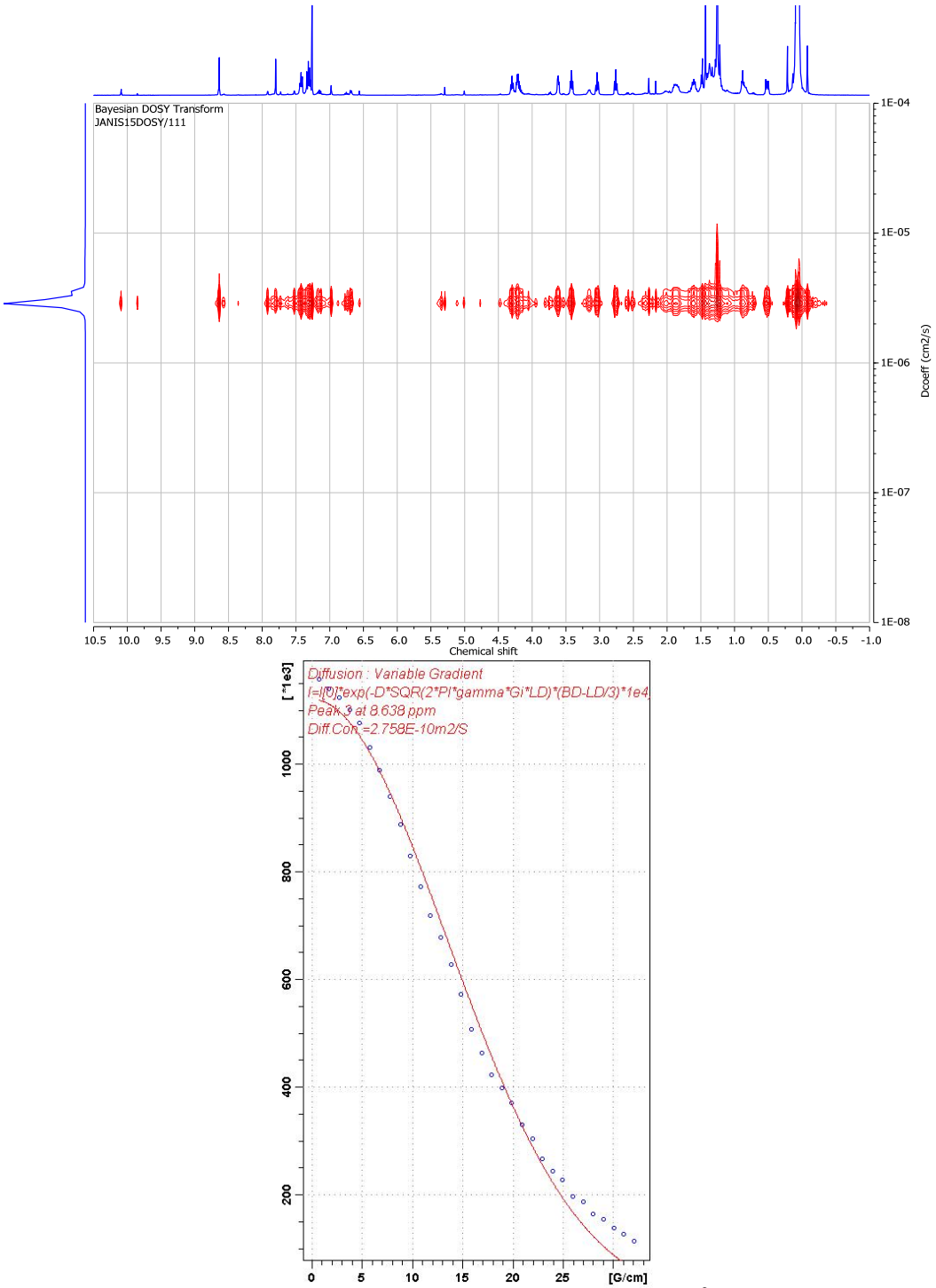


Fig S23. Top: DOSY spectrum (400 MHz, $CDCl_3$, 293 K) of the Zn^{2+}-polymer after stirring with excess of sodium EDTA and after extraction of the organic layer. Bottom: Representative example of the fitting of the decay curve for the imine proton is shown, yielding a value of $2.7 \cdot 10^{-10}$ m^2/s for the diffusion coefficient.

6 Fe^{2+}-polymer

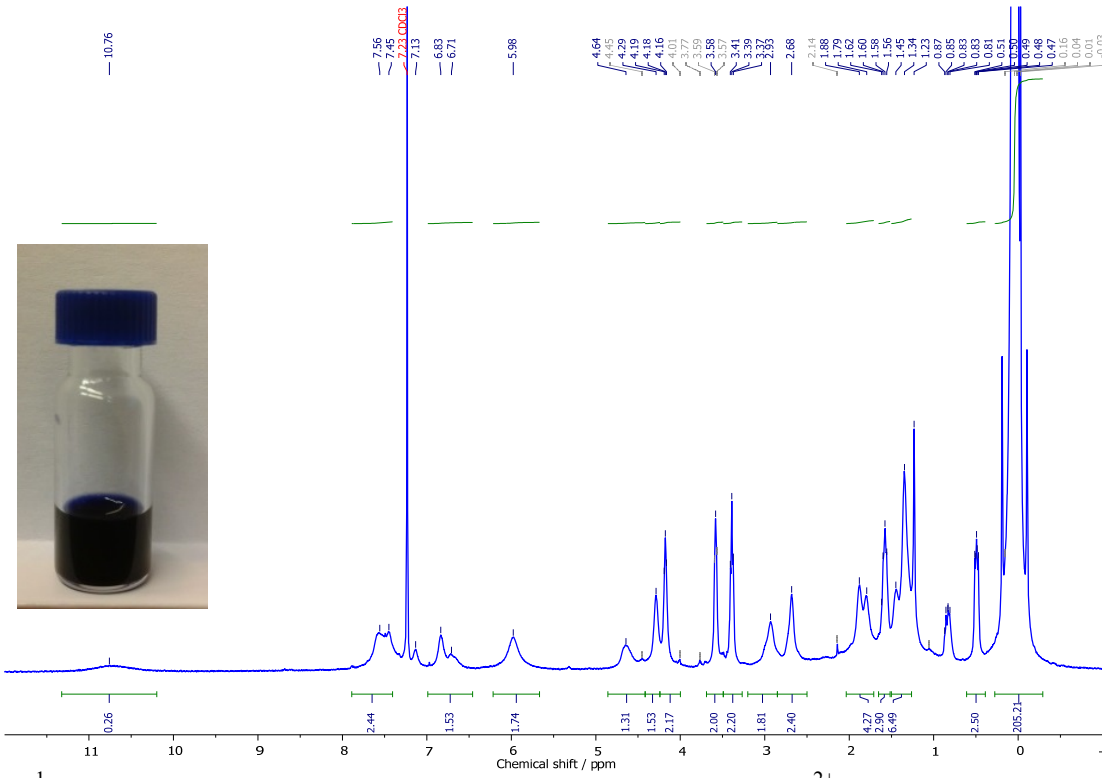


Fig S23. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K) of the Fe^{2+}-polymer (50 mg/mL). The spectrum contains broad peaks like the one of the C_8-Fe model complex (Fig. S7) due to the paramagnetic nature of Fe^{2+}, while in this case it can also be indicative of the polymer formation. Inset: Picture of the dark blue-coloured Fe^{2+}-polymer solution.

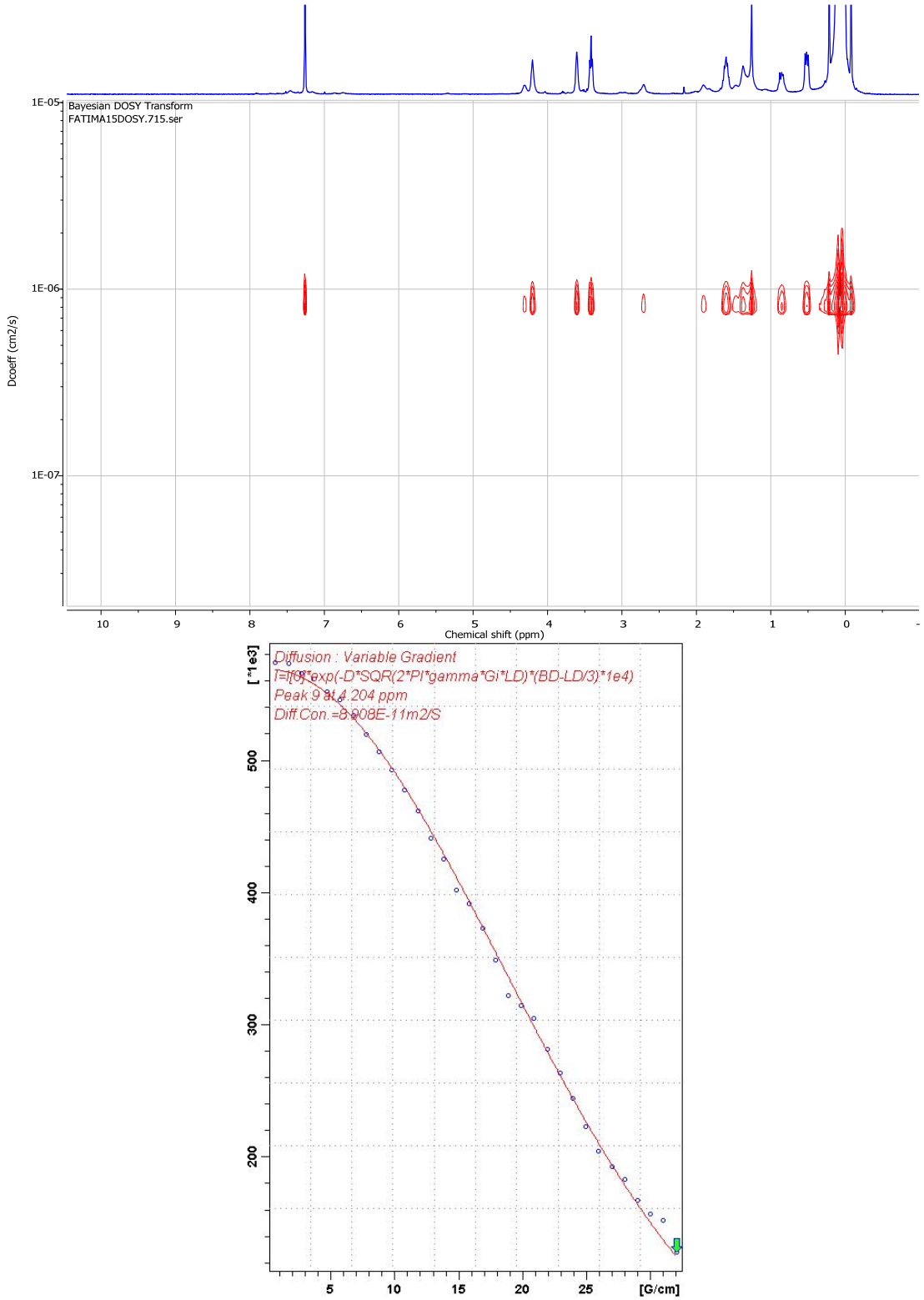


Fig S24. Top: DOSY spectrum (400 MHz, $CDCl_3$, 293 K) of the Fe^{2+}-polymer (50 mg/mL). Bottom: Fitting of the decay for the imine proton, yielding $D_{coeff} = 8.9 \cdot 10^{-11}$ m^2/s.

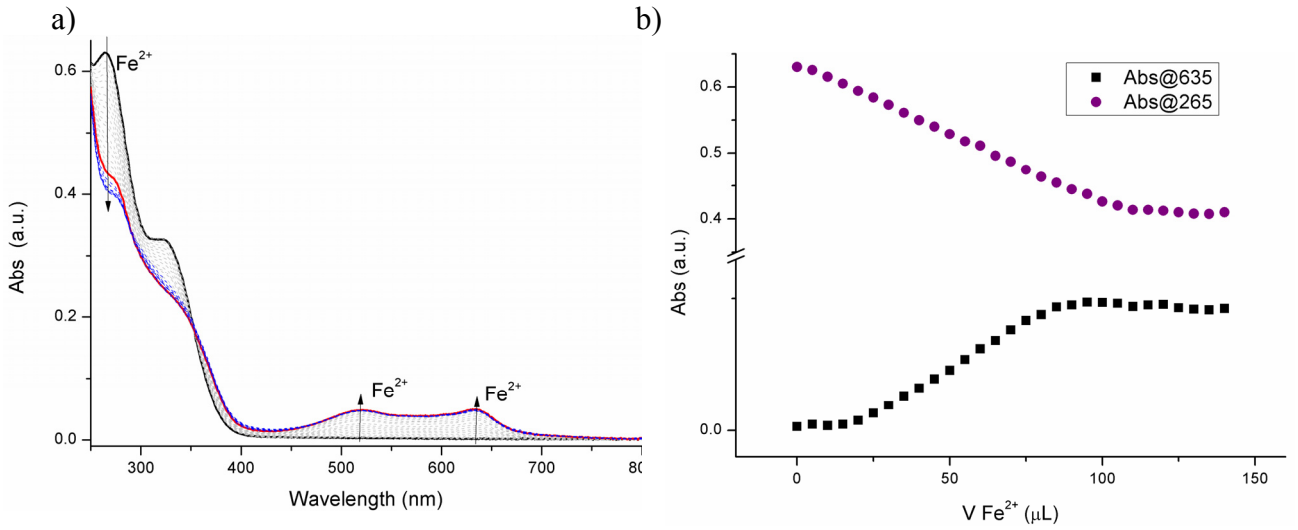


Fig S25. a) UV-vis titration of PDMS-pincer bis(diimine) (**8**) (V_0 = 2 mL, c = $1.30 \cdot 10^{-5}$ M) with $Fe(OTf)_2$ ($2.27 \cdot 10^{-4}$ M). The starting (black trace) and at the equivalence point (red trace) are coloured for clarity purposes. The intermediate spectra are depicted in dashed grey and the ones after the equivalence point are depicted in dashed blue. b) Corresponding change in the absorbance against the volume of $Fe(OTf)_2$. Chloroform, l = 1 cm, additions of 5 µL.

7 Crosslinking experiments

7.1 Addition of Europium

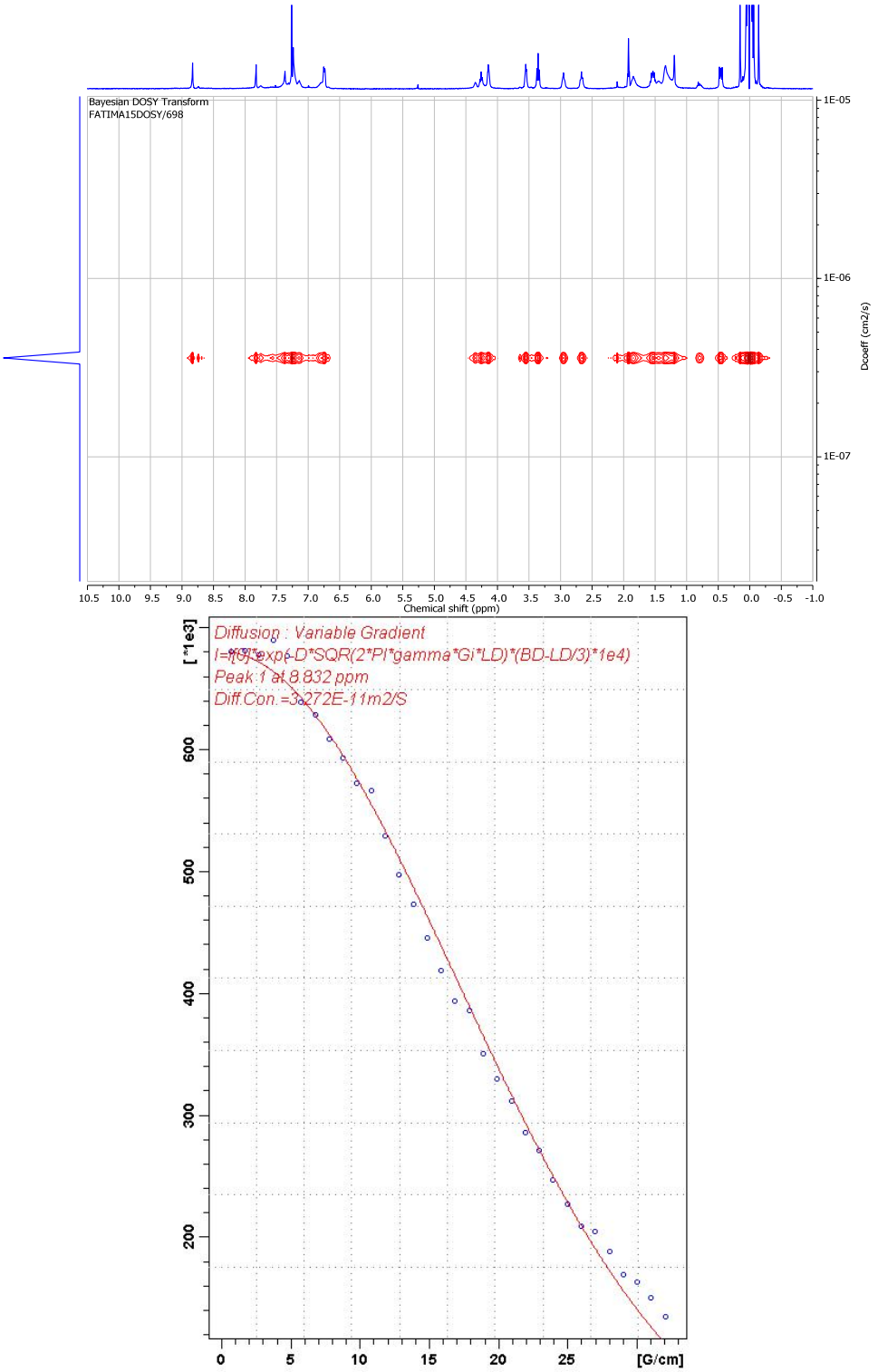


Fig S26. Top: DOSY spectrum (400 MHz, $CDCl_3$, 293 K) of the Zn^{2+}-polymer after the addition of 7% of $Eu(OTf)_3$ to a 35 mg/mL solution of the Zn^{2+}-polymer. Bottom: Fitting of decay curve for the imine proton, resulting in $D_{coeff} = 3.3 \cdot 10^{-11}$ m^2/s.

8 Polyimine formation

Procedure

300 mg of PDMS-imine macromonomer (**8**) was dissolved in deuterated chloroform (6 mL). An aliquot of 500 µL was transferred to a vial and different amounts (0–200 µL) of a solution of 1,12-dodecyldiamine (34.6 mM) were added. The vials were heated at 60 °C for 1 h, resulting in an increase of the viscosity upon increasing the amount of 1,12-DA but without gel formation.

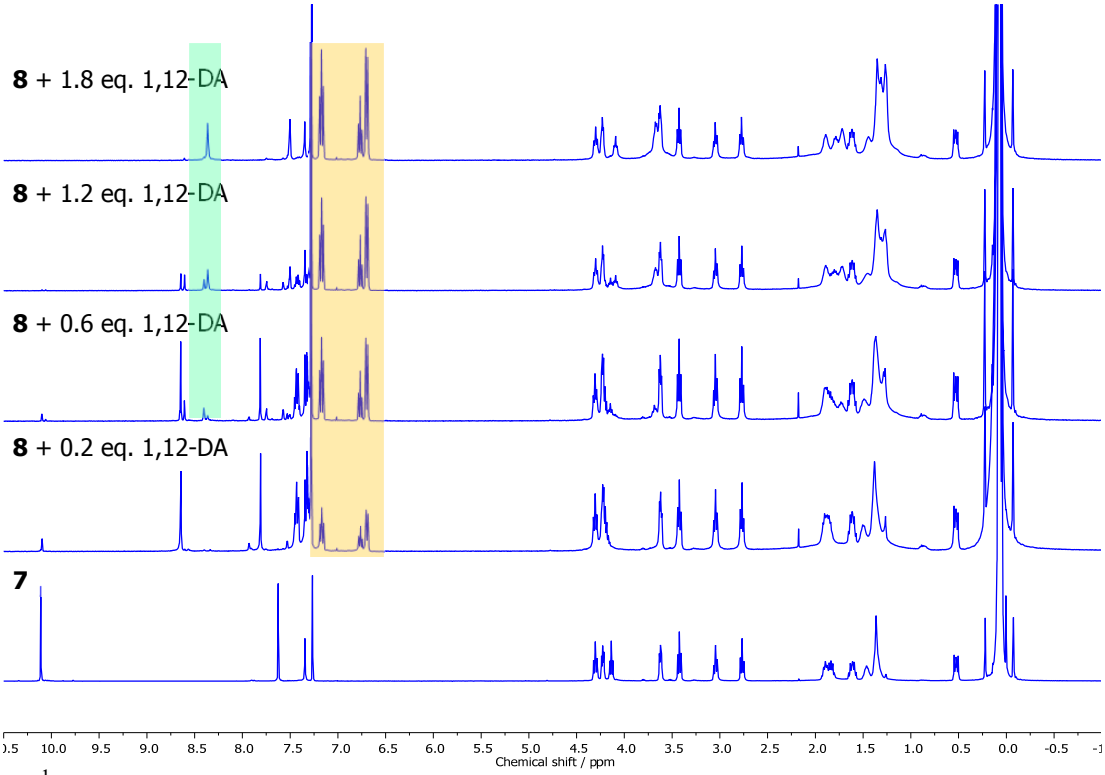


Fig S27. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 293 K, 50 mg/mL) of the PDMS-pincer bis(dialdehyde) (**7**) and PDMS-imine macromonomer (**8**) with increasing amounts of 1,12-dodecyldiamine (1,12-DA). The release of aniline during the exchange reaction is observed (yellow). Also indicated is the new imine proton from the transimination reaction (green).

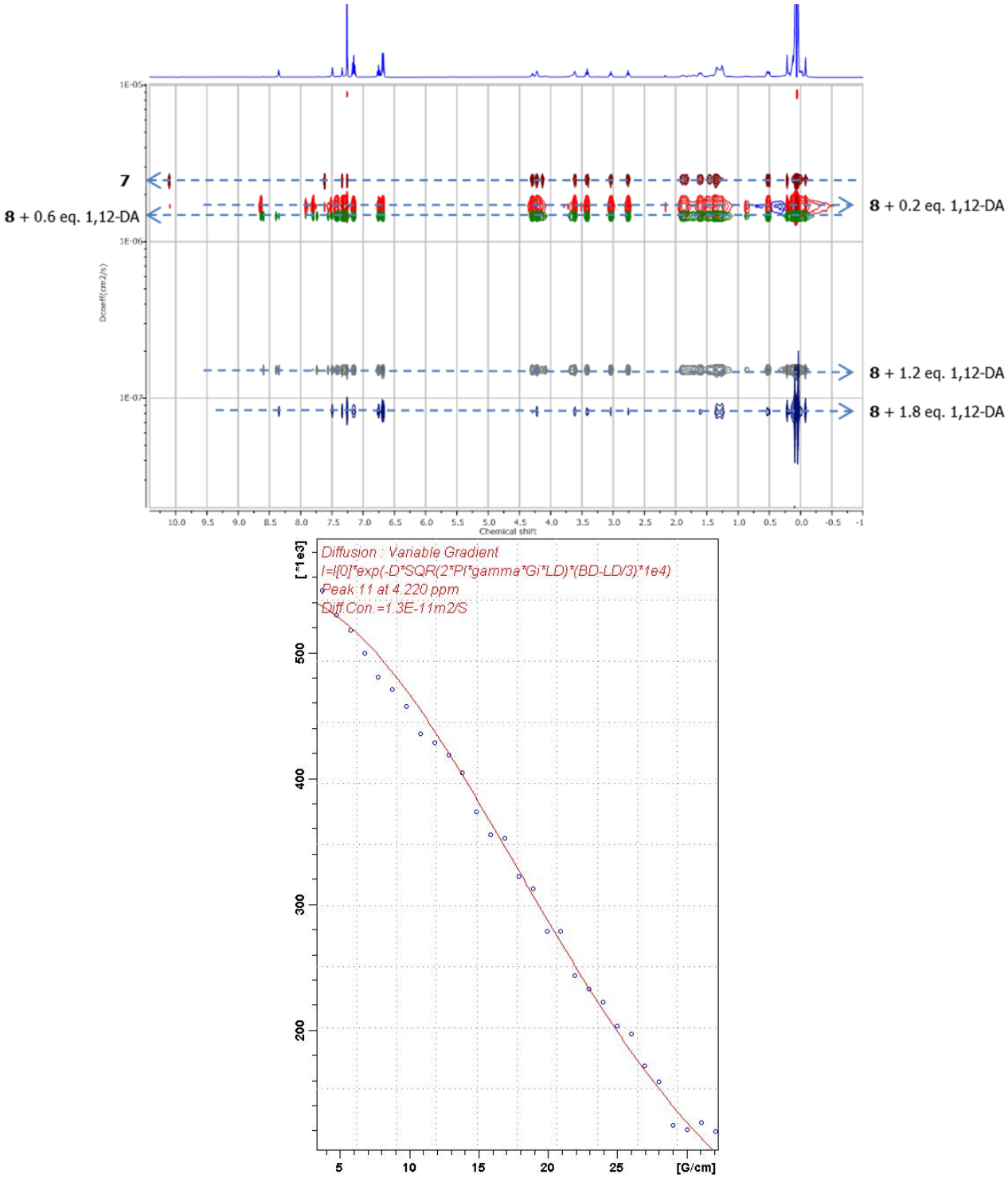


Fig S28. Top: Overlaid DOSY spectra (400 MHz, $CDCl_3$, 293 K, 50 mg/mL) of the PDMS-pincer bis(dialdehyde) (**7**) and PDMS-imine macromonomer (**8**) with increasing amounts of 1,12-dodecyldiamine (1,12-DA). A decrease in the D_{coeff} is observed due to the cross-linking of the macromonomer by the transamination reaction with 1,12-DA. The ^{1}H NMR of macromonomer **8** in the presence of 1,12-DA is shown for clarity purposes. Bottom: Fitting of the decay of the proton at 4.22 ppm for the sample to which 1.8 eq of 1,12-DA was added, yielding a value of $1.3 \cdot 10^{-11}$ m^2/s for the diffusion coefficient.

9 Transimination of the Zn^{2+}-polymer

Preparation of gels

300 mg of PDMS Zn^{2+}-polymer was dissolved in deuterated chloroform (6 mL). An aliquot of 500 µL was transferred to a vial and different amounts (0–200 µL) of a solution of 1,12-dodecyldiamine (34.6 mM) were added. The vials were heated at 60 °C for 1 h, resulting in the transformation of the ones containing more than 0.8 eq. of 1,12 DA into a gel.

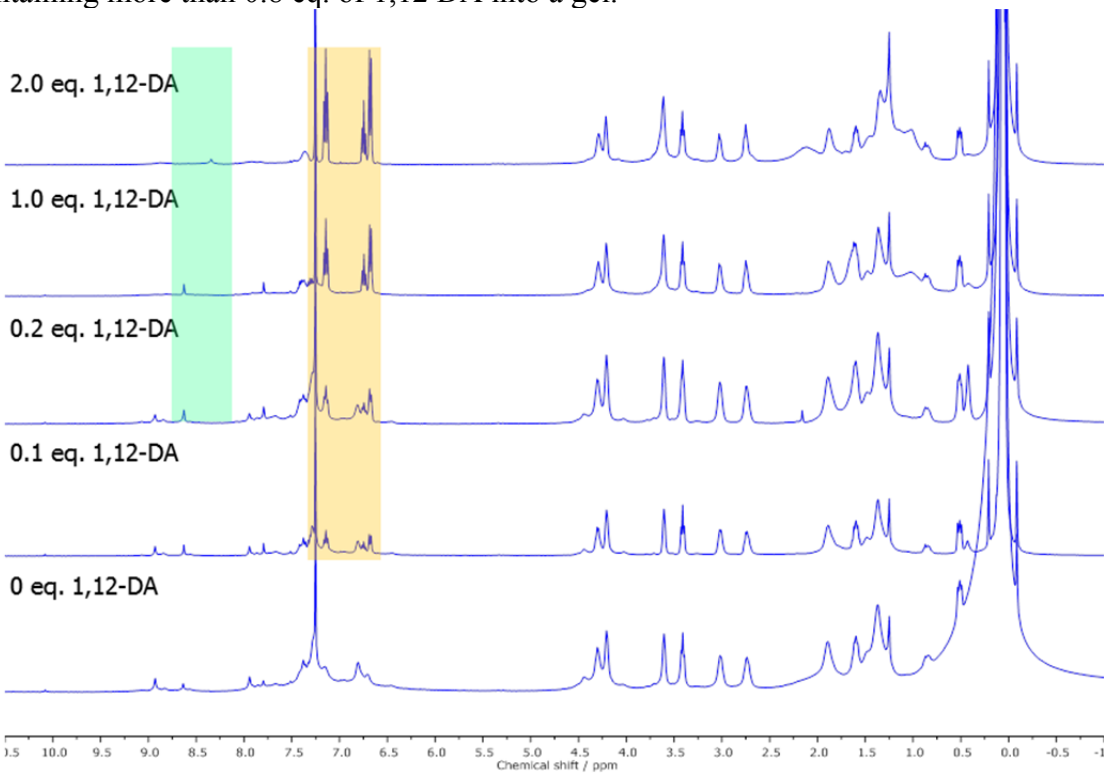


Fig S29. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 293 K, 50 mg/mL) of the Zn^{2+}-polymer after the addition of increasing amounts of 1,12-dodecyldiamine. Upon addition of the diamine, the original imine peak decreases with concomitant increase in the peaks corresponding to the free aniline. Also, (broad) peaks corresponding to the newly formed imine are visible.

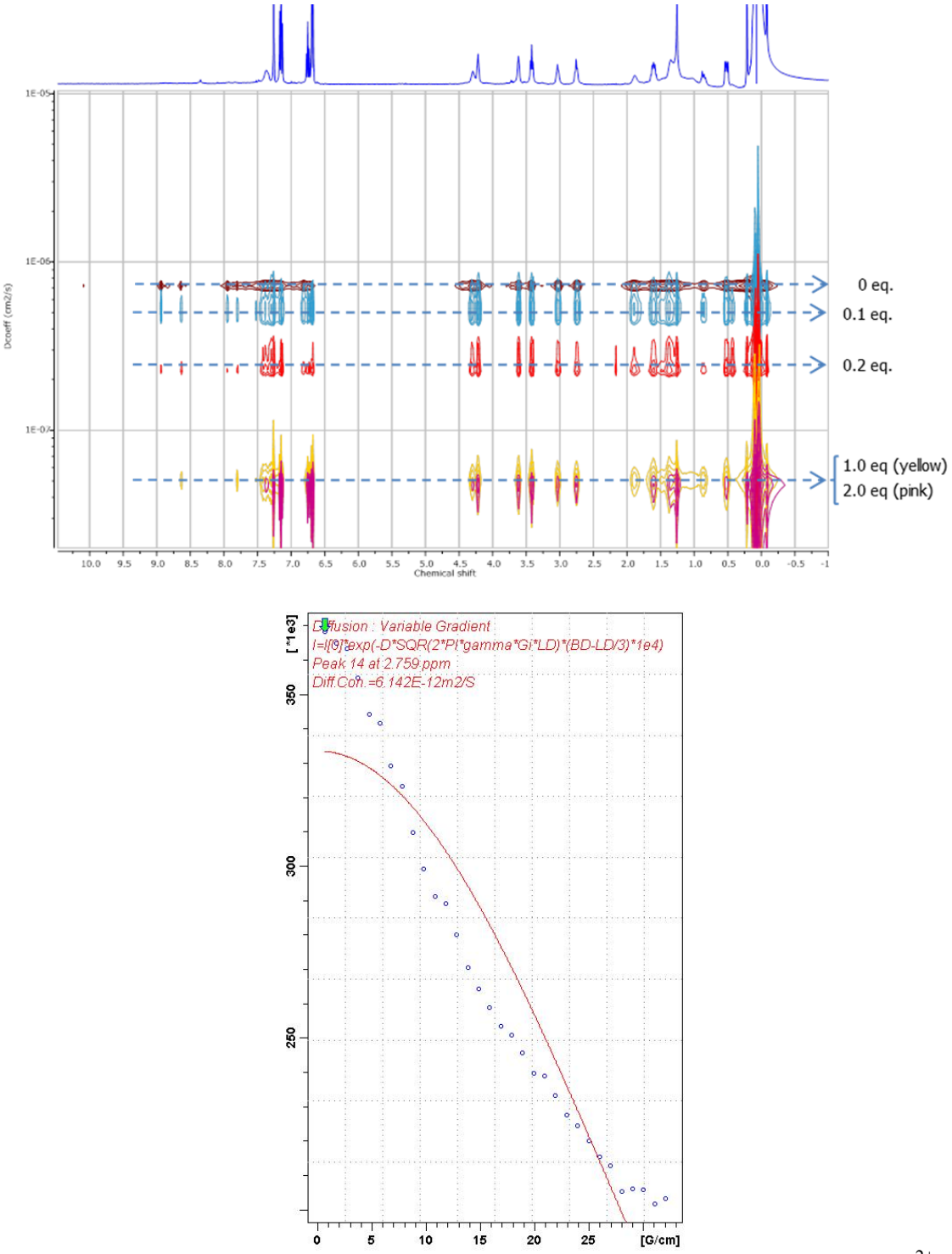


Fig S30. Top: Overlaid DOSY spectra (400 MHz, $CDCl_3$, 293 K, 50 mg/mL) of the Zn^{2+}-polymer with increasing amounts of 1,12-dodecyldiamine (1,12-DA). A decrease in the D_{coeff} is observed due to the cross-linking of the Zn^{2+}-polymer by the transamination reaction with 1,12-DA. The ^1H NMR of Zn^{2+}-polymer in the presence of 2.0 eq. of 1,12-DA is shown for clarity purposes. Bottom: Fitting of the decay curve for the proton at 2.76 ppm for Zn^{2+}-polymer + 1.0 eq. of 1,12-DA, yielding a value of $5.3 \cdot 10^{-12}$ m^2/s for the D_{coeff}. As a result of gel formation, only a moderate fit of the data was obtained, implying that the determined diffusion coefficient should be considered as an upper limit.

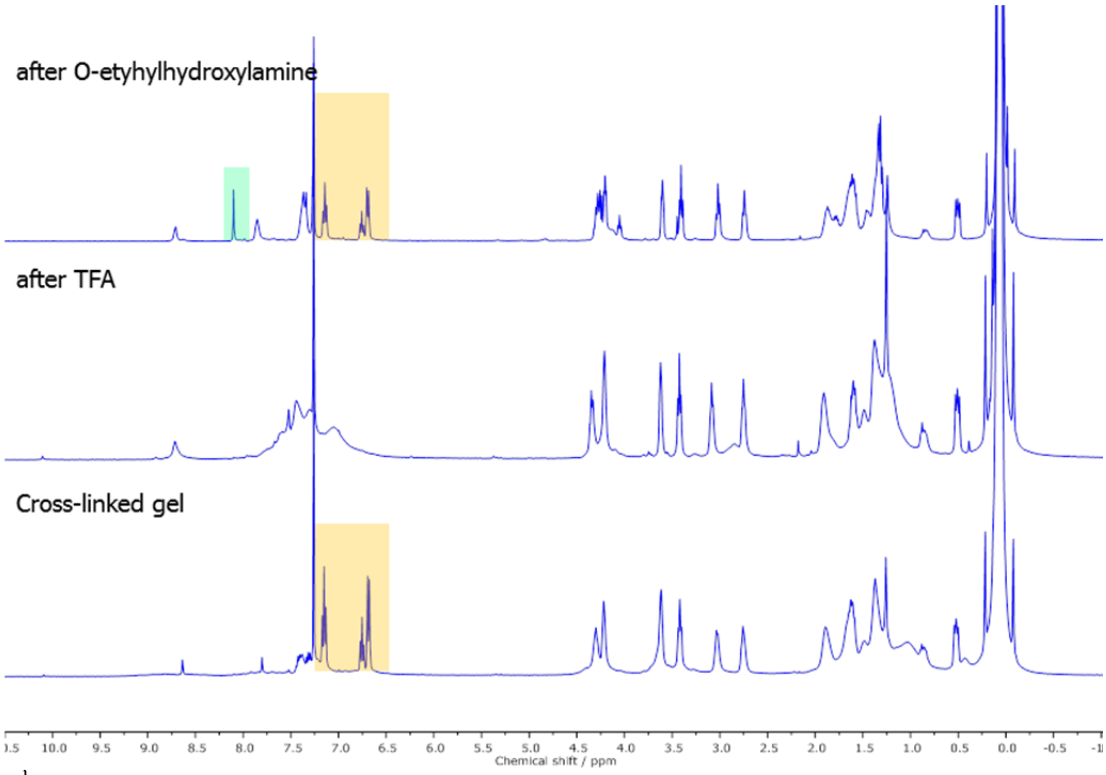


Fig S31. ^{1}H NMR spectra (400 MHz, $CDCl_3$, 293 K, 50 mg/mL) of the cross-linked (1.0 eq of 1,12-DA) Zn^{2+}-polymer gel (bottom). Middle: After the disruption of the gel with 2.0 eq of TFA (middle). It is noteworthy that after the addition of TFA the signals from the free aniline (highlighted in orange) are lost, suggesting the aniline is reincorporated into the imine, inducing the reformation of the linear Zn^{2+}-polymer. Top: after the exchange reaction with 2.0 eq. *O*-ethylhydroxylamine. Highlighted in orange is the free aniline that is still present, suggesting that the *O*-ethylhydroxylamine is incorporated into the Zn^{2+}-polymer rather than the aniline. Also the appearance of a new imine signal is highlighted in green, which can be attributed to the newly formed oxime.

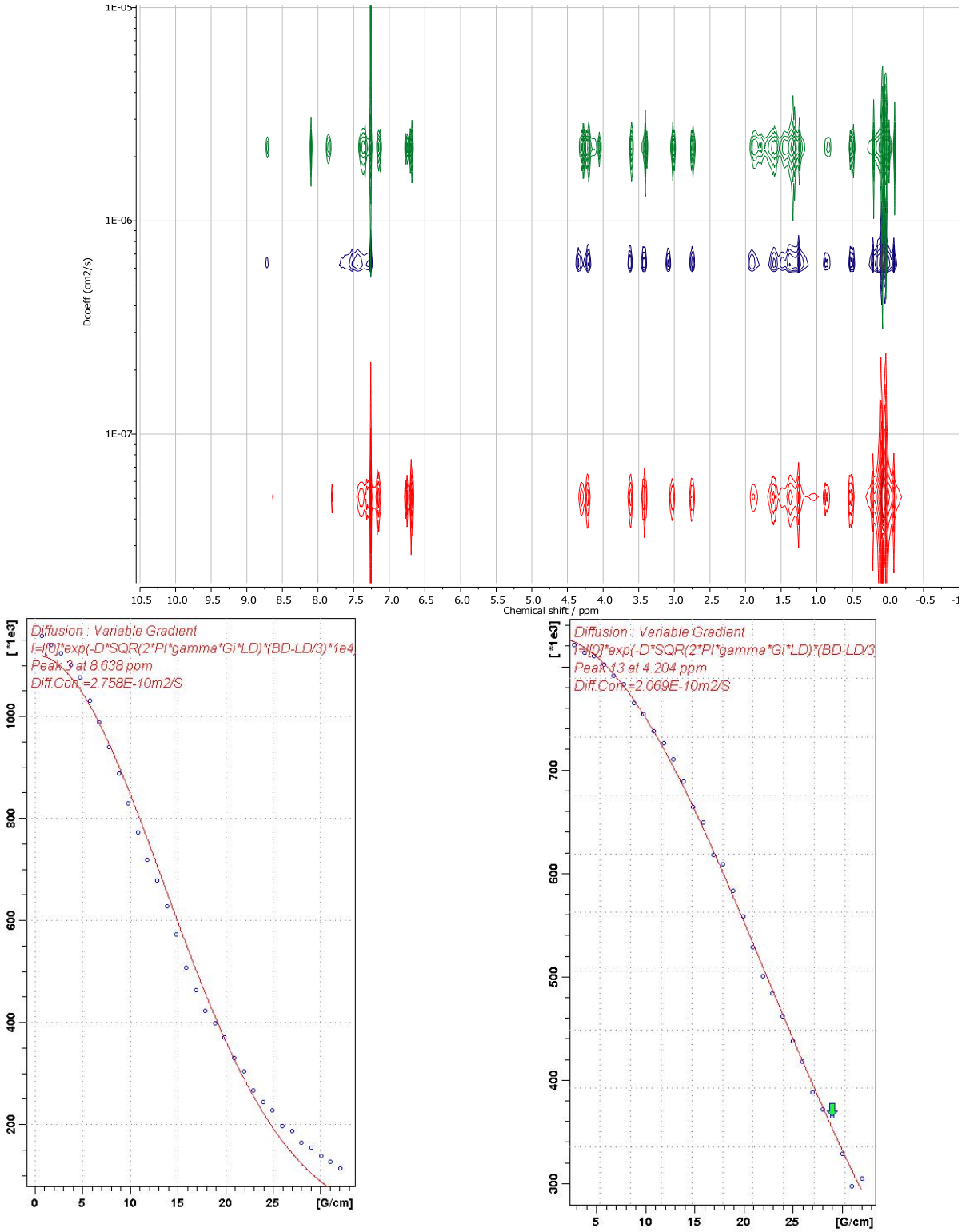
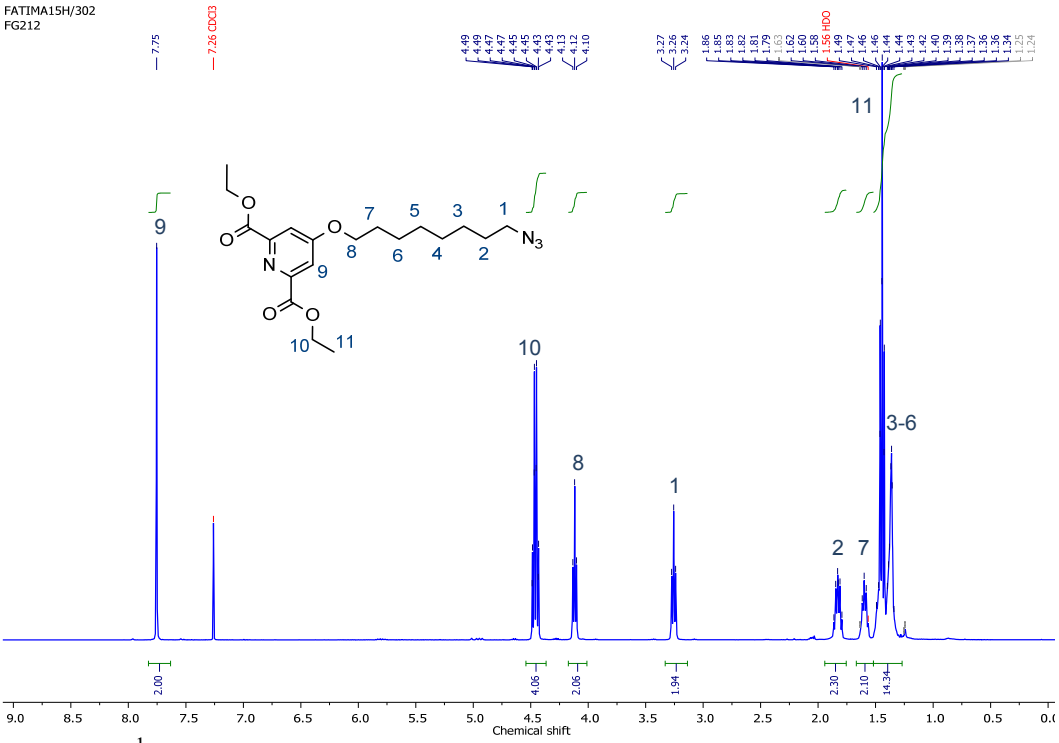
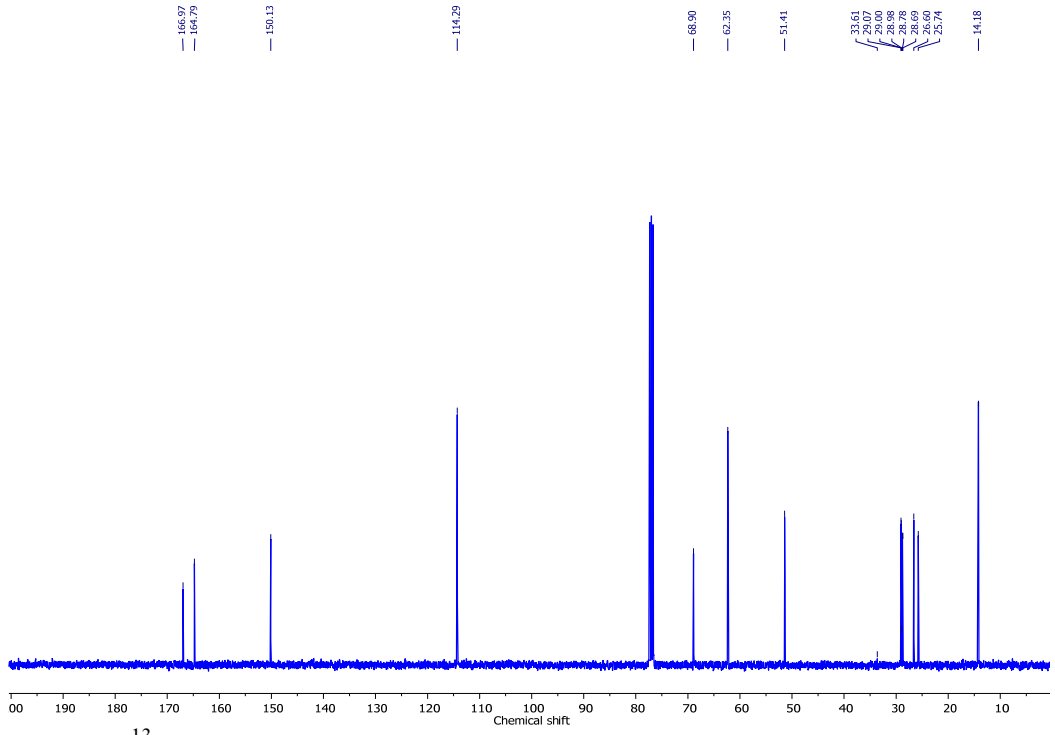


Fig S32. Top: Overlaid DOSY spectra (400 MHz, $CDCl_3$, 293 K, 50 mg/mL) of the cross-linked Zn^{2+}-polymer gel (1.0 eq. of 1,12-DA) (red trace), after addition of 2.0 eq. of TFA (green trace), and after the addition of 2.0 eq. *O*-ethylhydroxylamine (blue trace). Bottom: fitting results for the imine proton for the TFA disruption of the gel, yielding $D_{coeff} = 2.76 \cdot 10^{-10}$ m^2/s (left), and for the signal at 4.22 ppm for the *O*-ethylhydroxylamine disruption, yielding $D_{coeff} = 2.07 \cdot 10^{-10}$ m^2/s (right).

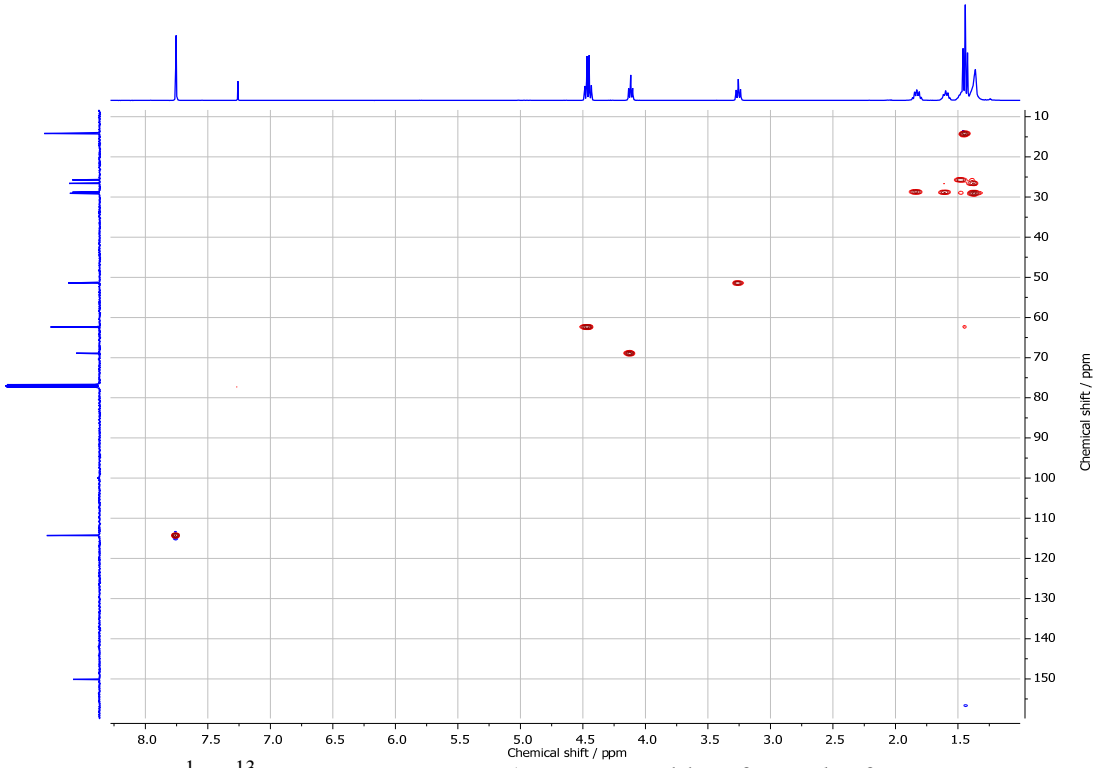
10 Additional spectra



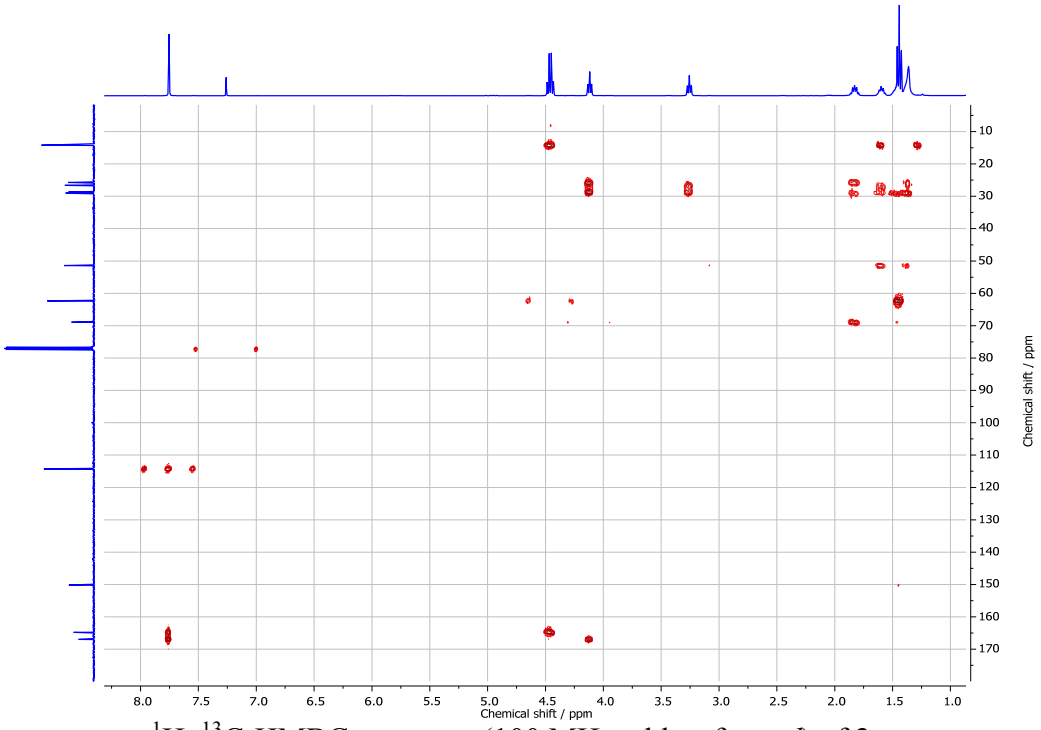
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of compound **3**.



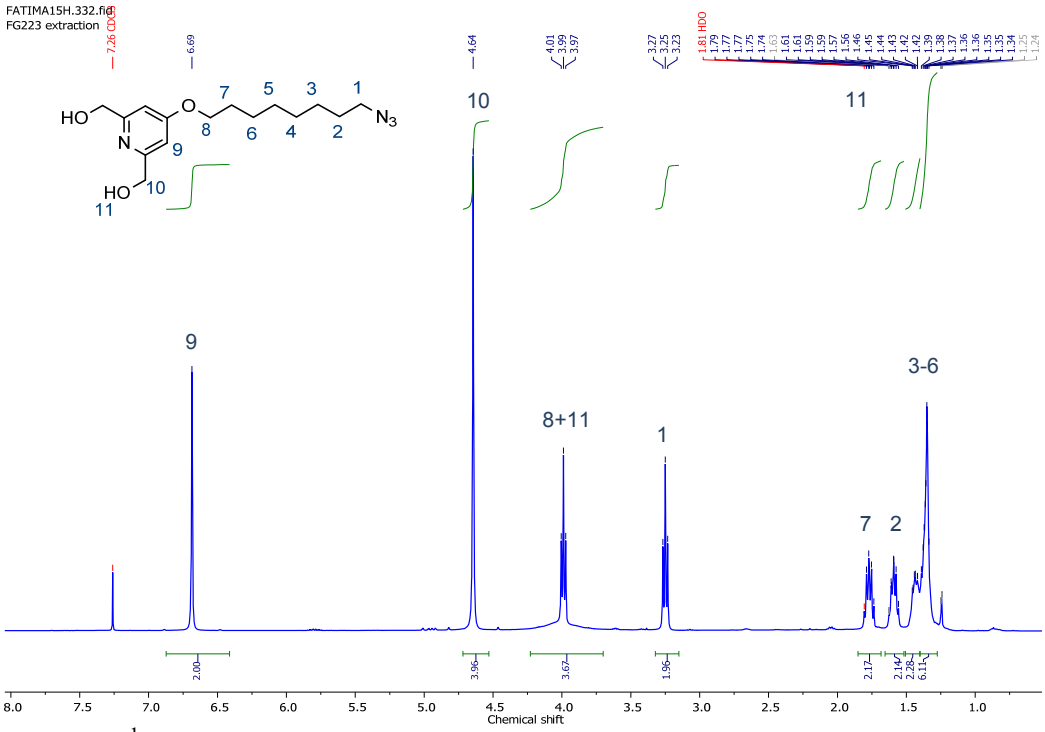
^{13}C NMR spectrum (100 MHz, chloroform-*d*) of compound **3**.



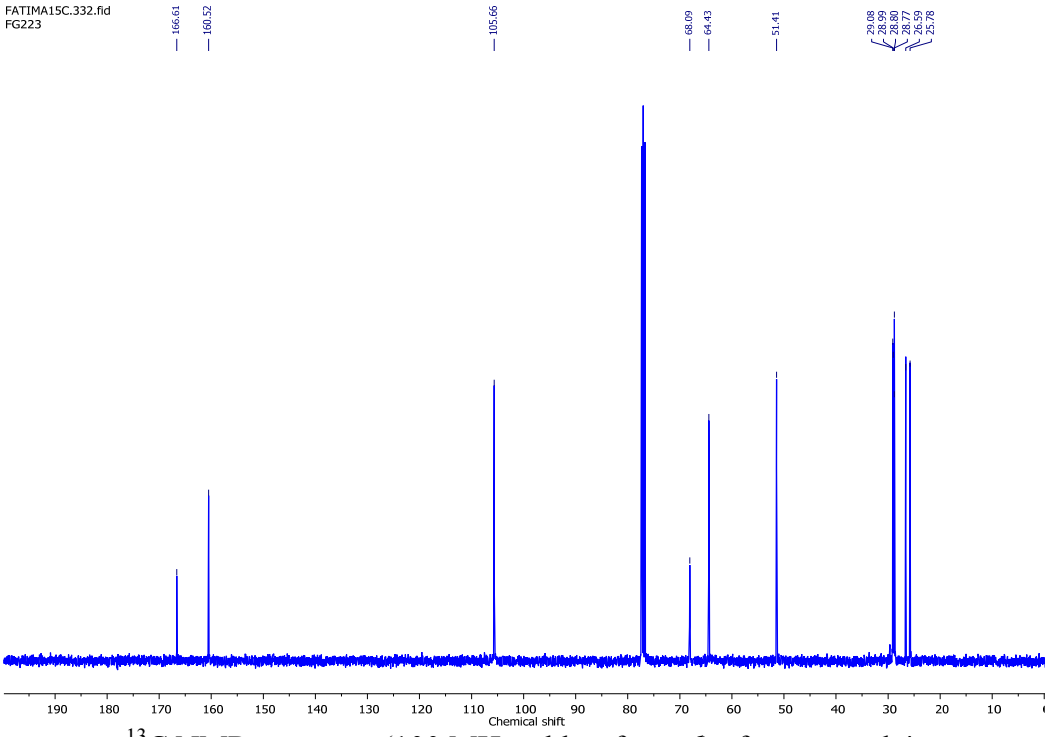
^{1}H, ^{13}C-HSQC spectrum (100 MHz, chloroform-*d*) of **3**.



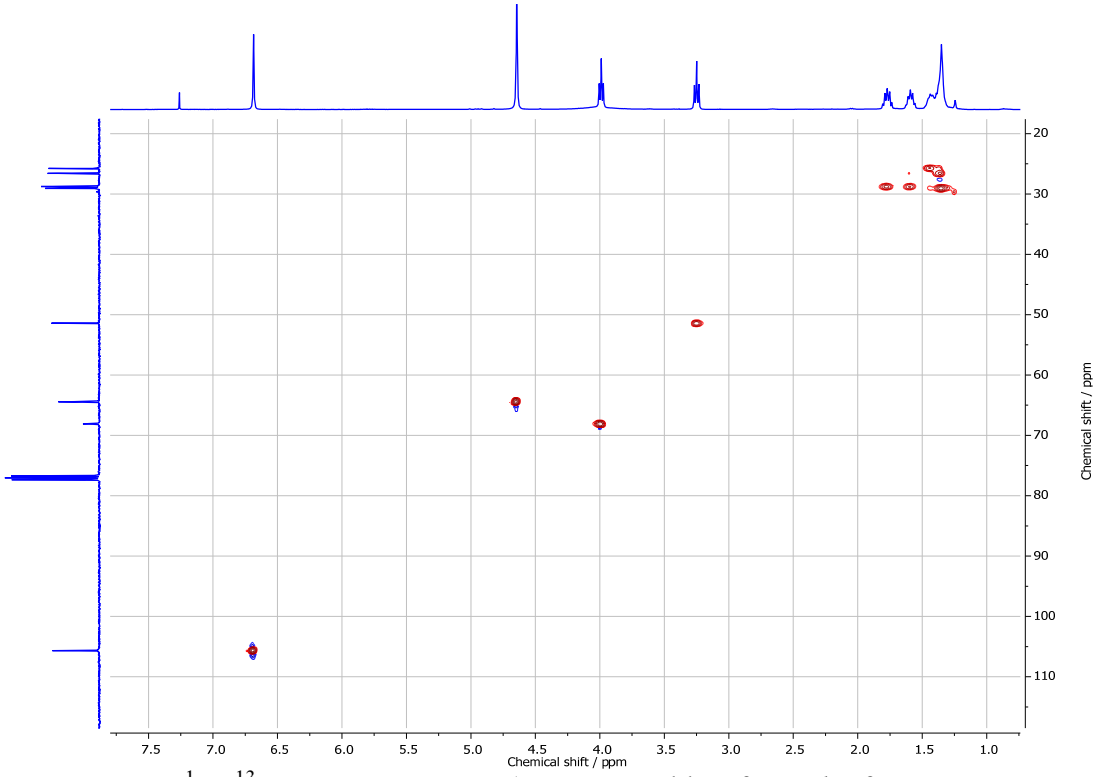
^{1}H, ^{13}C-HMBC spectrum (100 MHz, chloroform-*d*) of **3**.



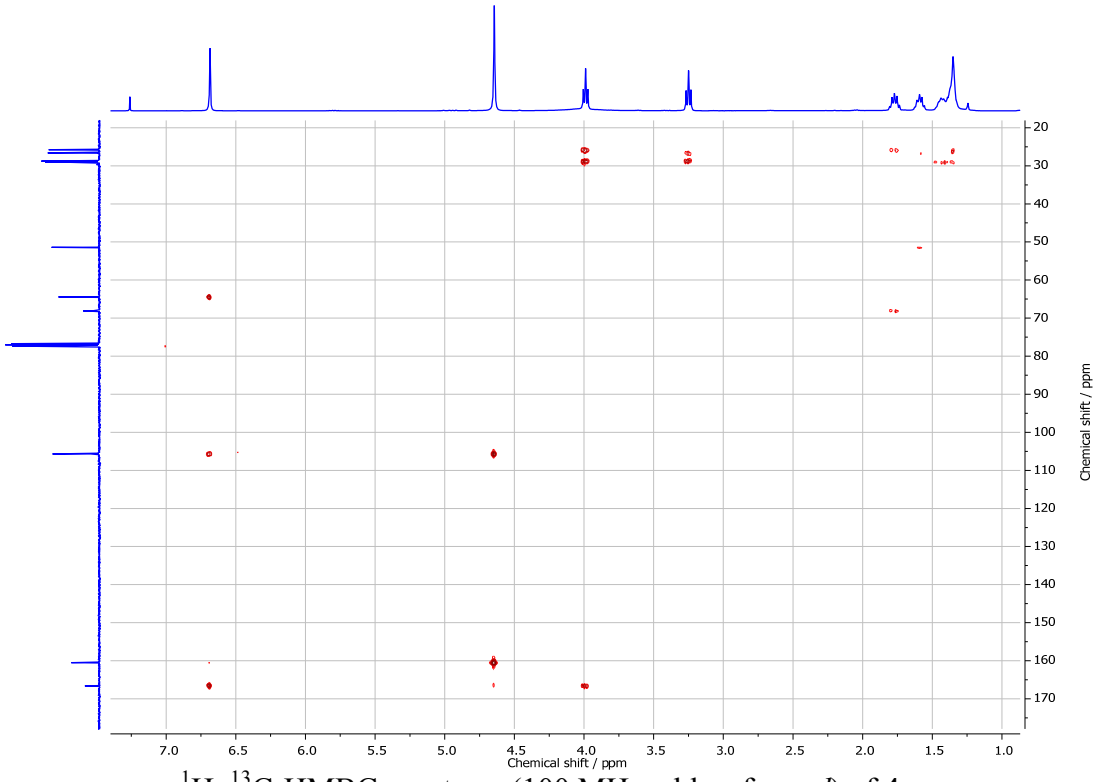
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of compound **4**.



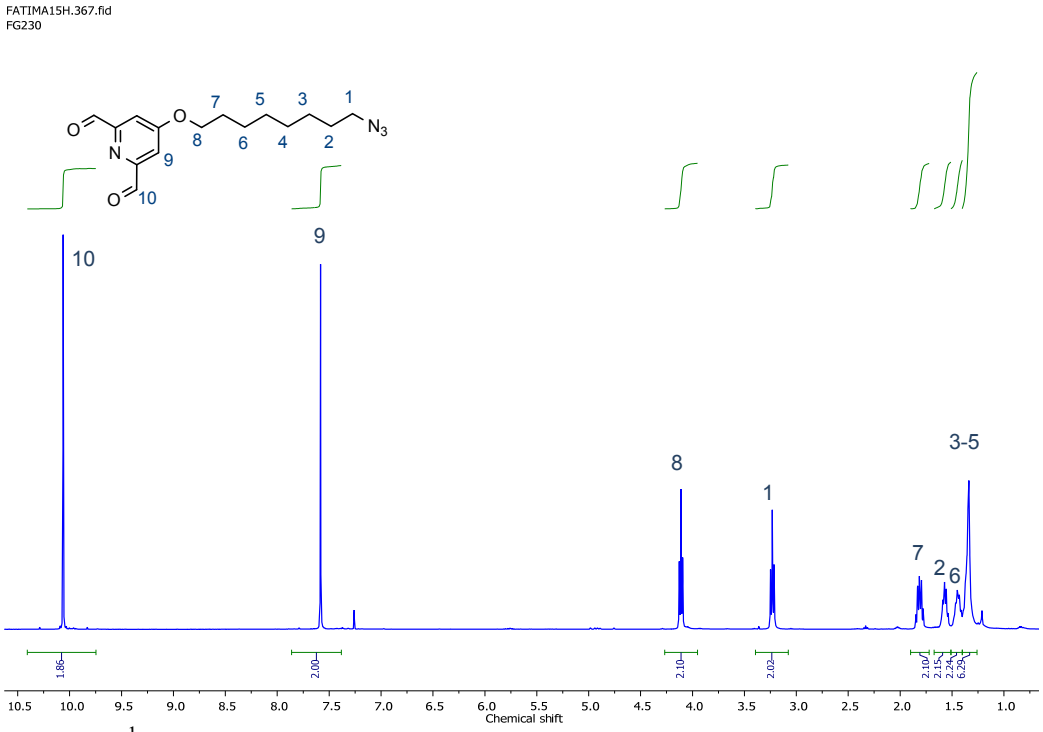
^{13}C NMR spectrum (100 MHz, chloroform-*d*) of compound **4**.



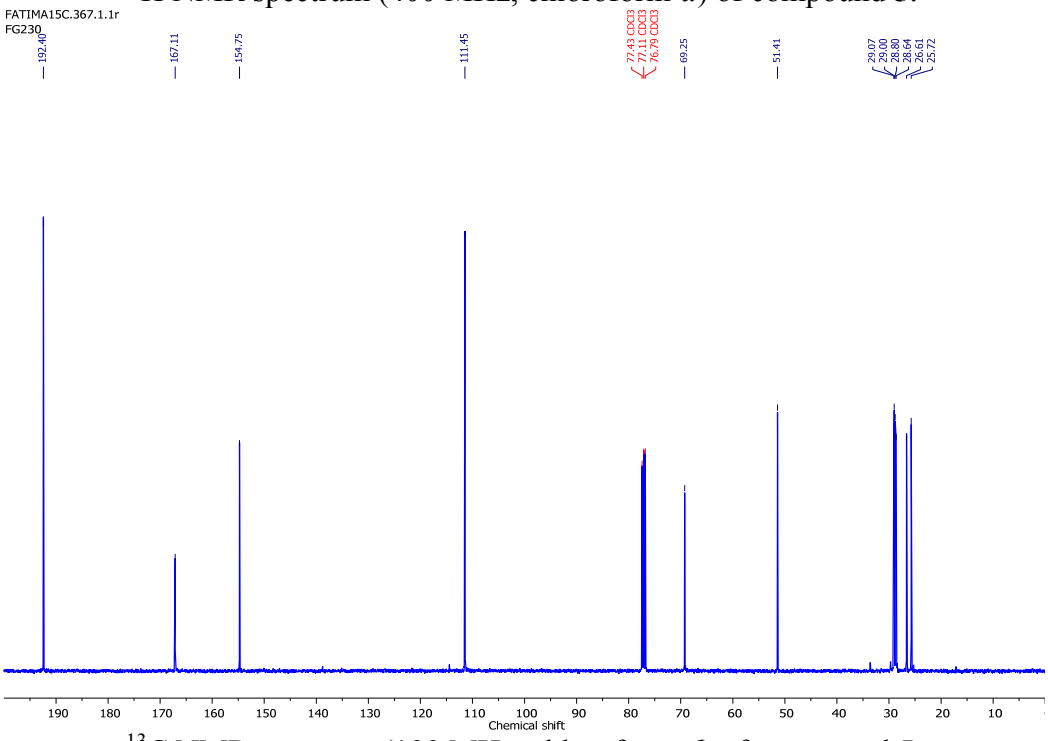
^{1}H, ^{13}C-HSQC spectrum (100 MHz, chloroform-*d*) of **4**.



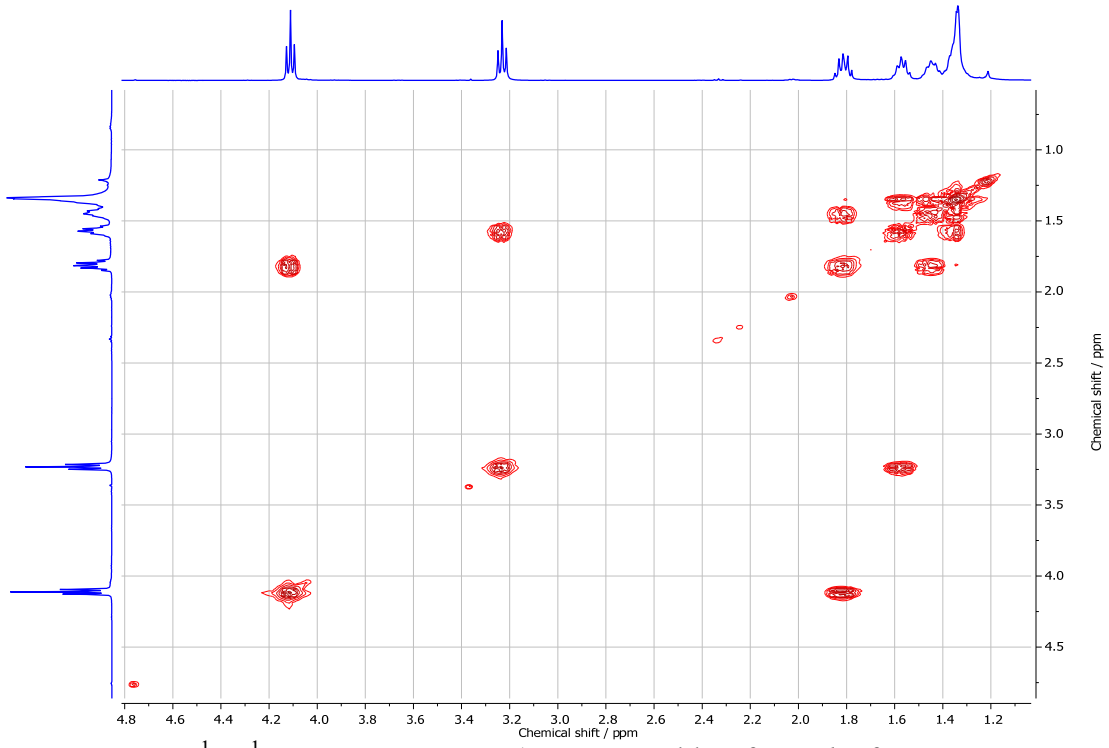
^{1}H, ^{13}C-HMBC spectrum (100 MHz, chloroform-*d*) of **4**.



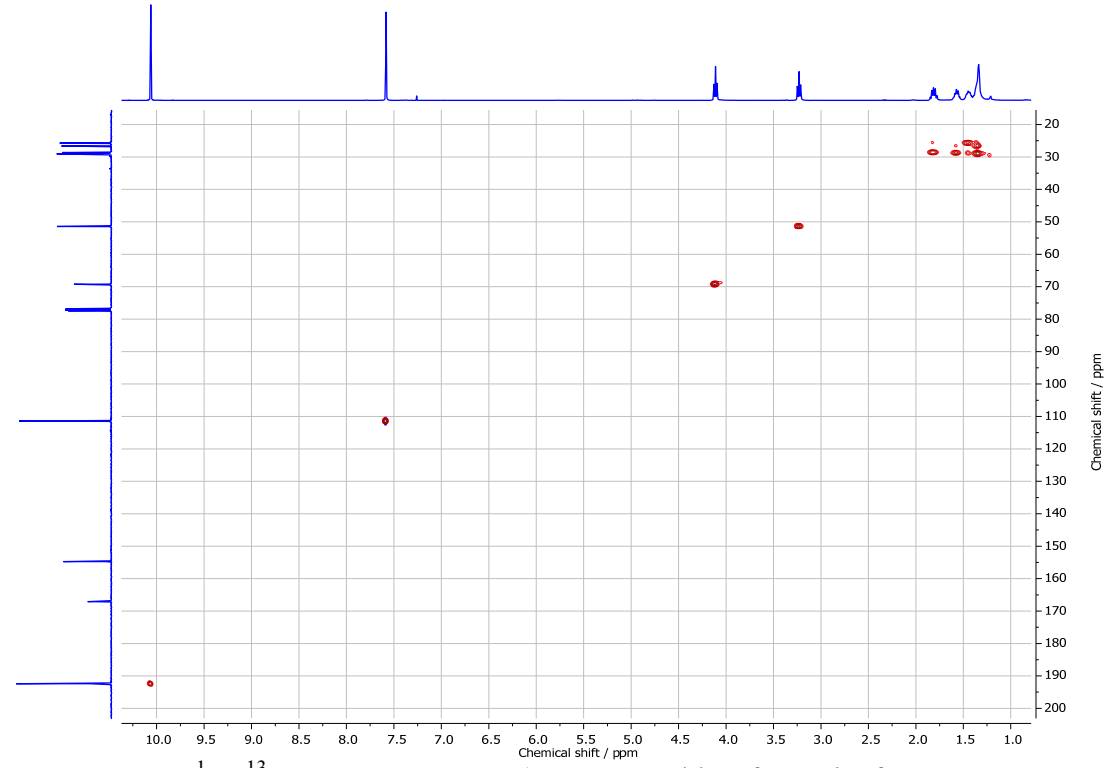
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of compound **5**.



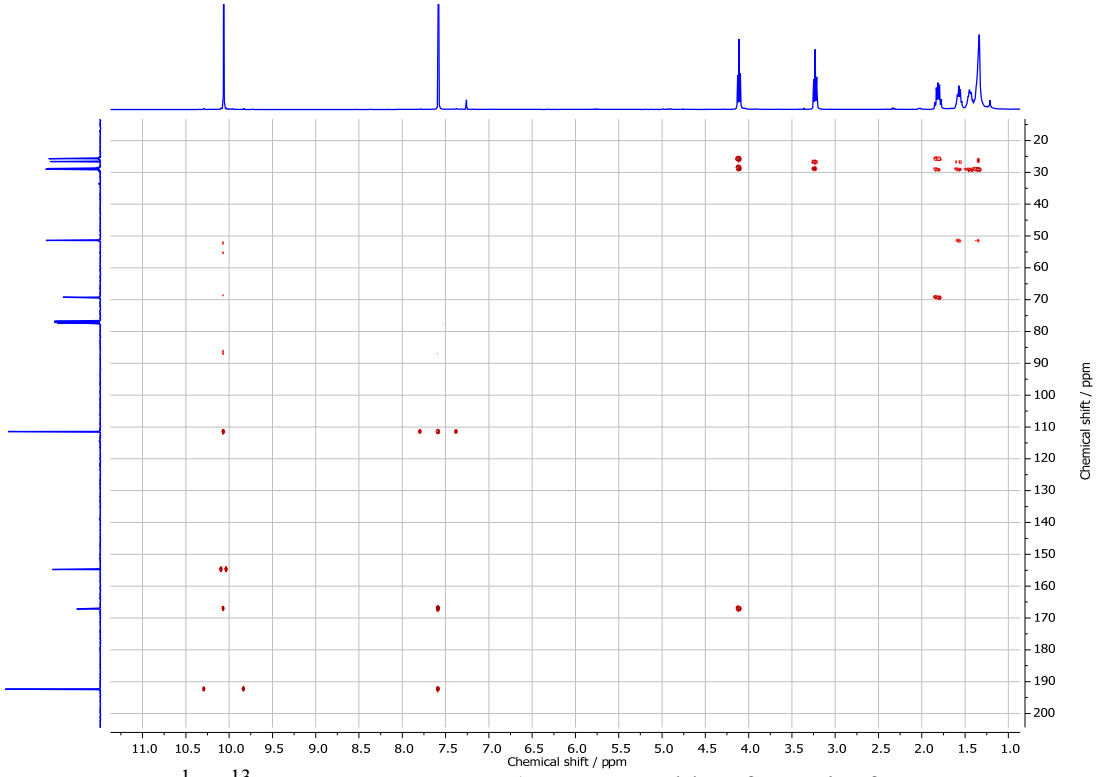
^{13}C NMR spectrum (100 MHz, chloroform-*d*) of compound **5**.



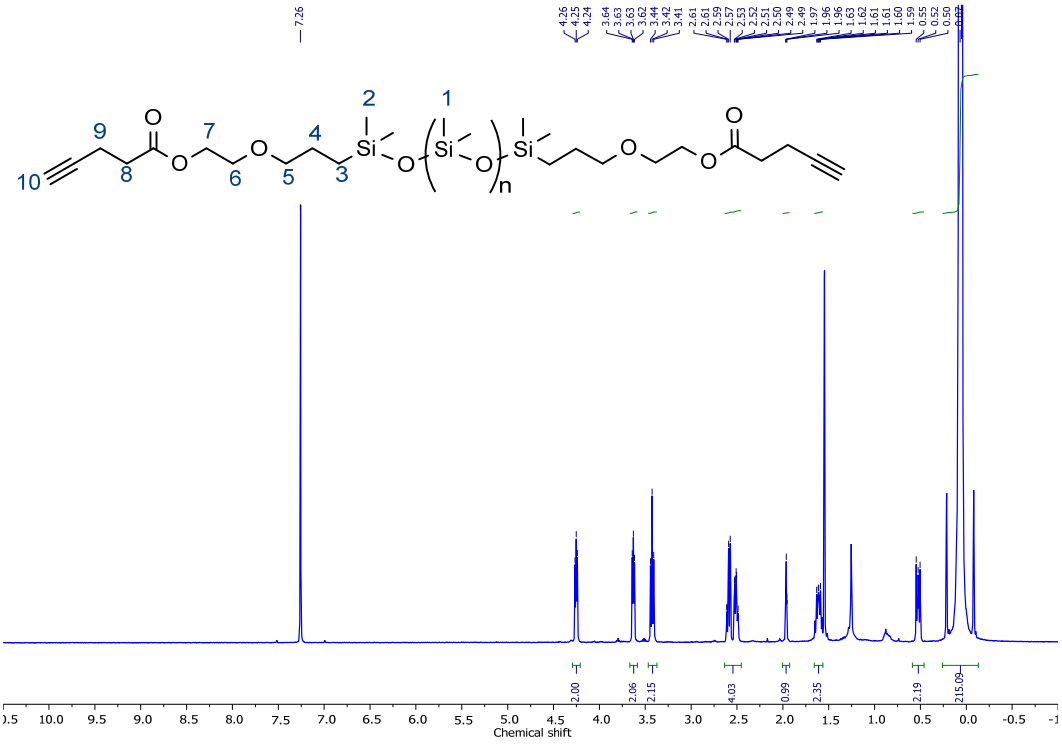
^{1}H, ^{1}H-COSY spectrum (400 MHz, chloroform-*d*) of **5**.



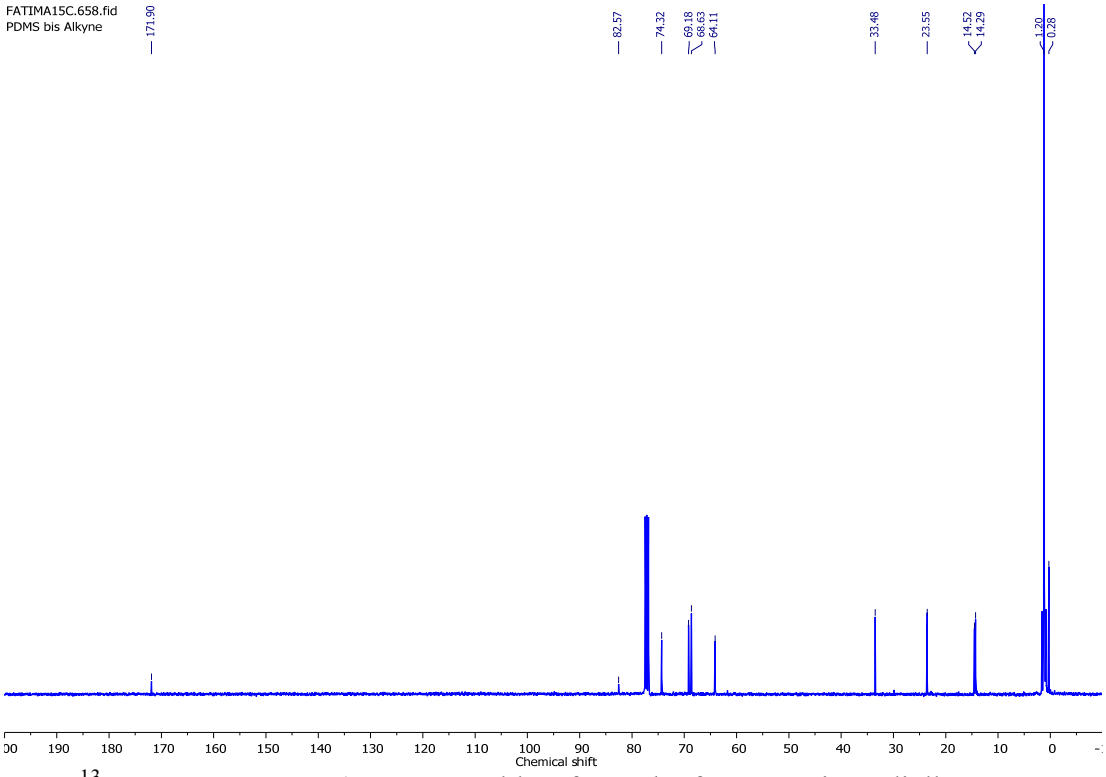
^{1}H, ^{13}C-HSQC spectrum (100 MHz, chloroform-*d*) of **5**.



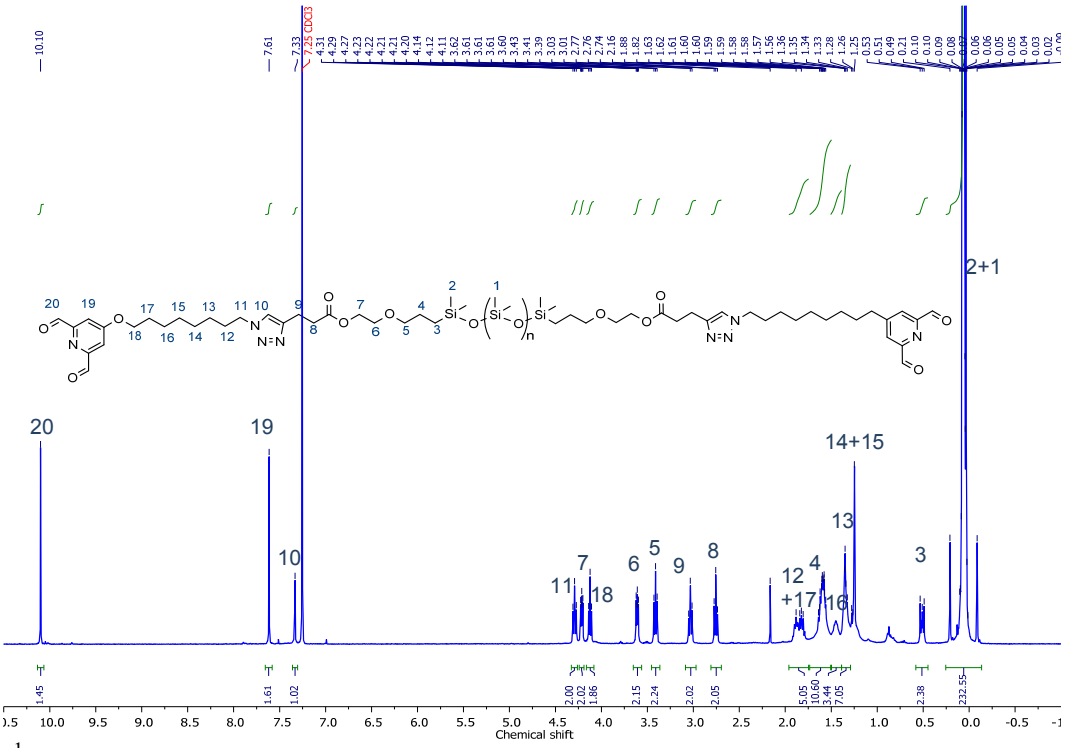
^{1}H, ^{13}C-HMBC spectrum (100 MHz, chloroform-*d*) of **5**.



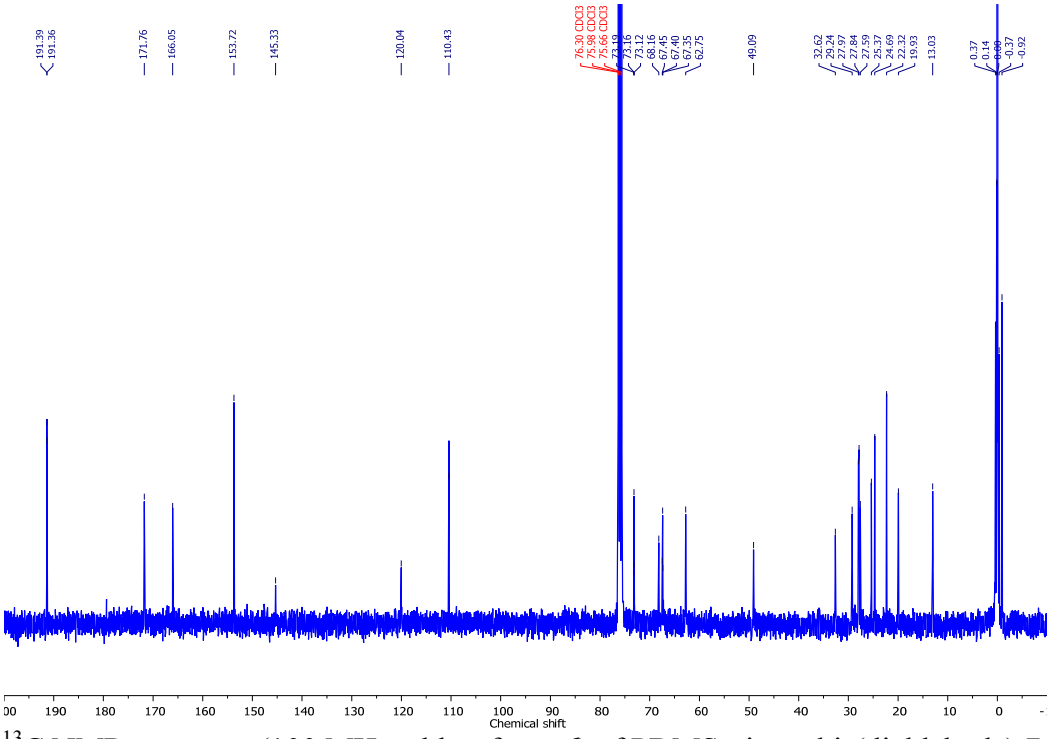
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of PDMS dialkyne **6**.



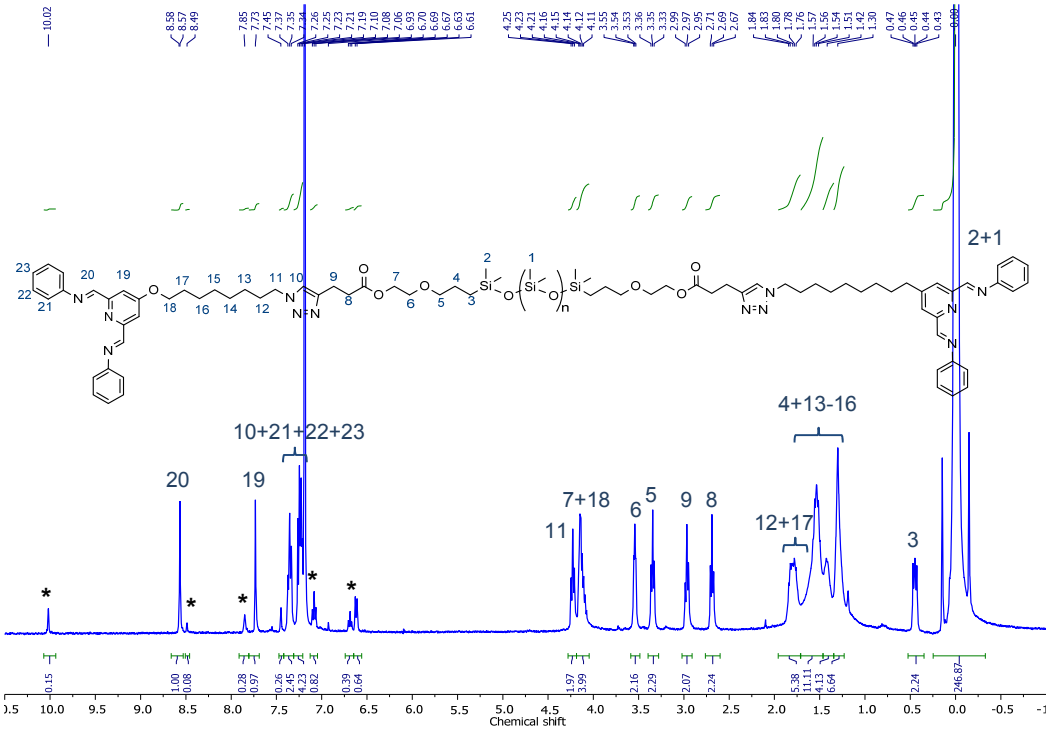
^{13}C NMR spectrum (100 MHz, chloroform-*d*) of PDMS pincerdialkyne **6**.



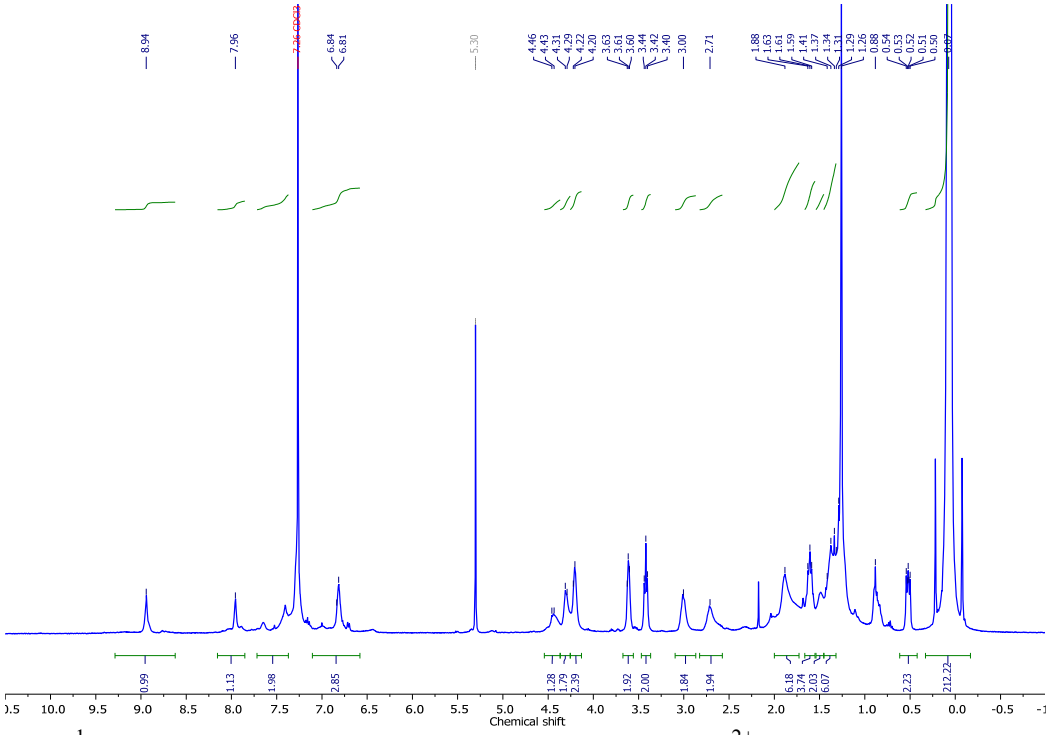
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of PDMS-pincer bis(dialdehyde) **7**.



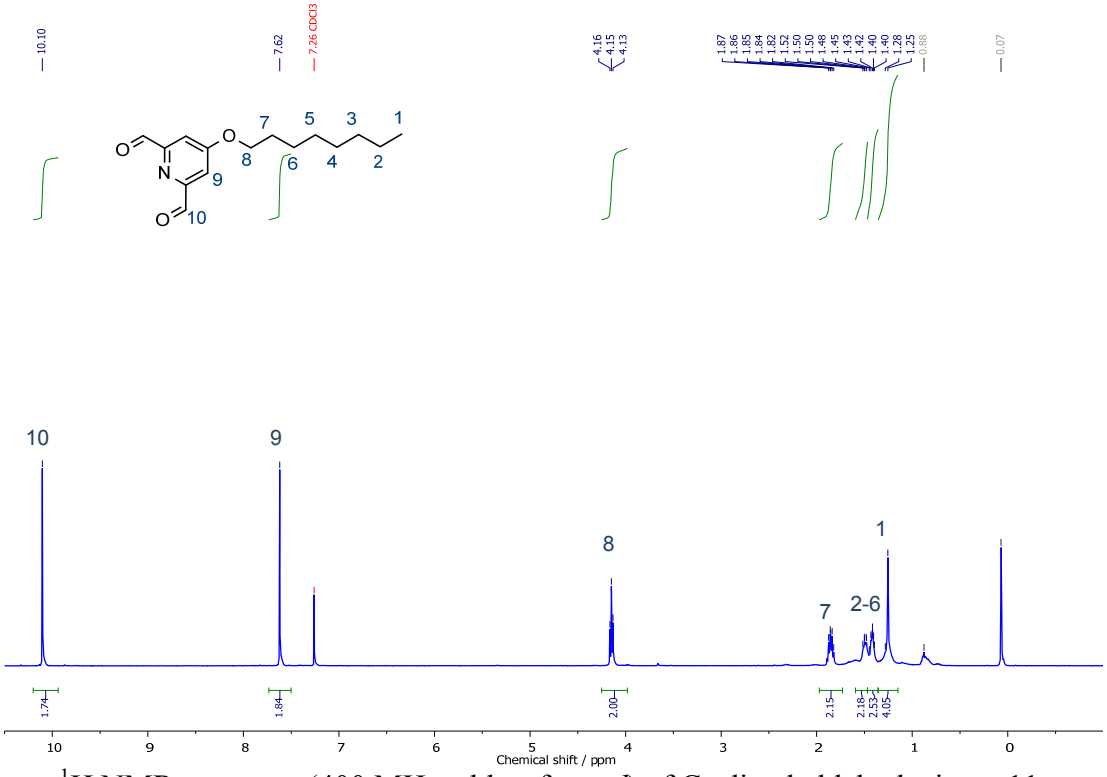
^{13}C NMR spectrum (100 MHz, chloroform-*d*) of PDMS-pincer bis(dialdehyde) **7**.



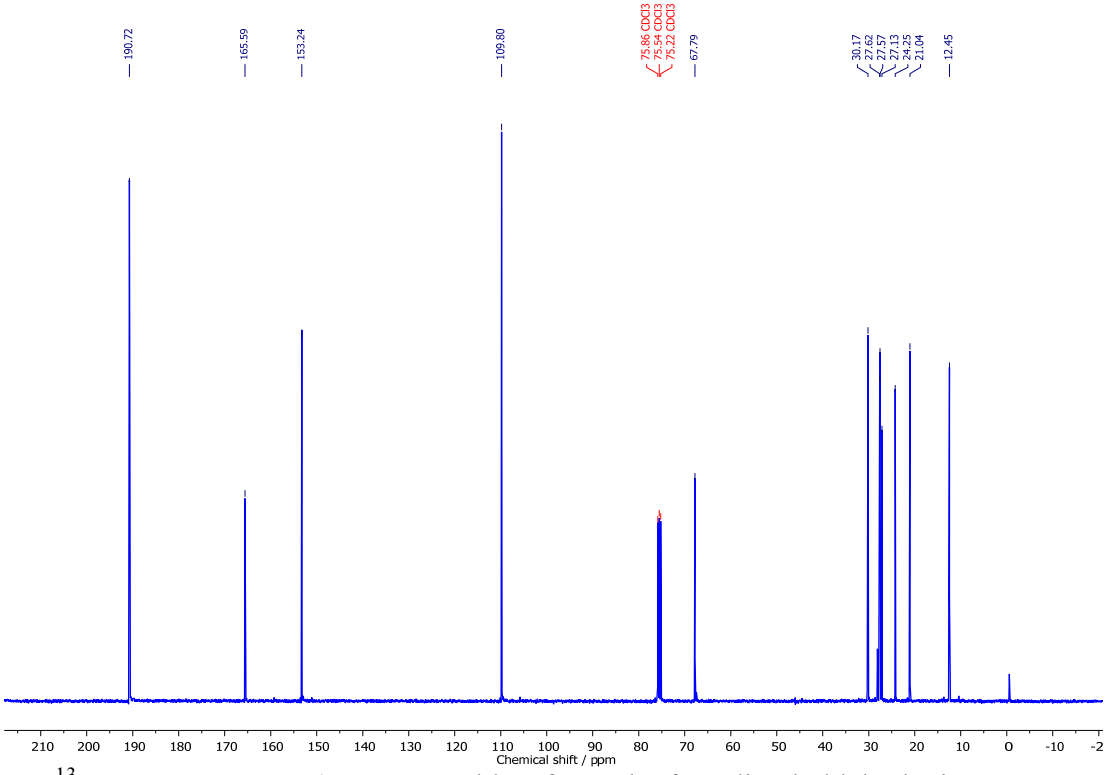
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of PDMS pincerdiimine **8**. The signals corresponding to small degree of hydrolysis of the imine bond are labelled by *.



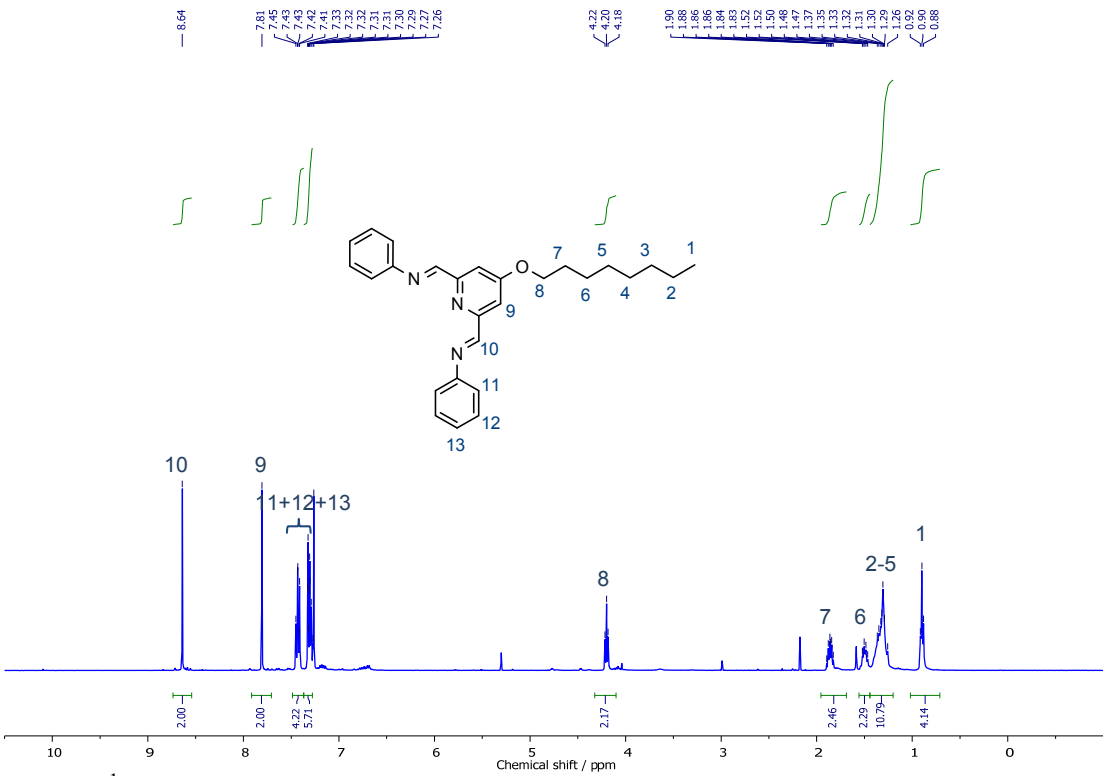
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of Zn^{2+}-PDMS polymer.



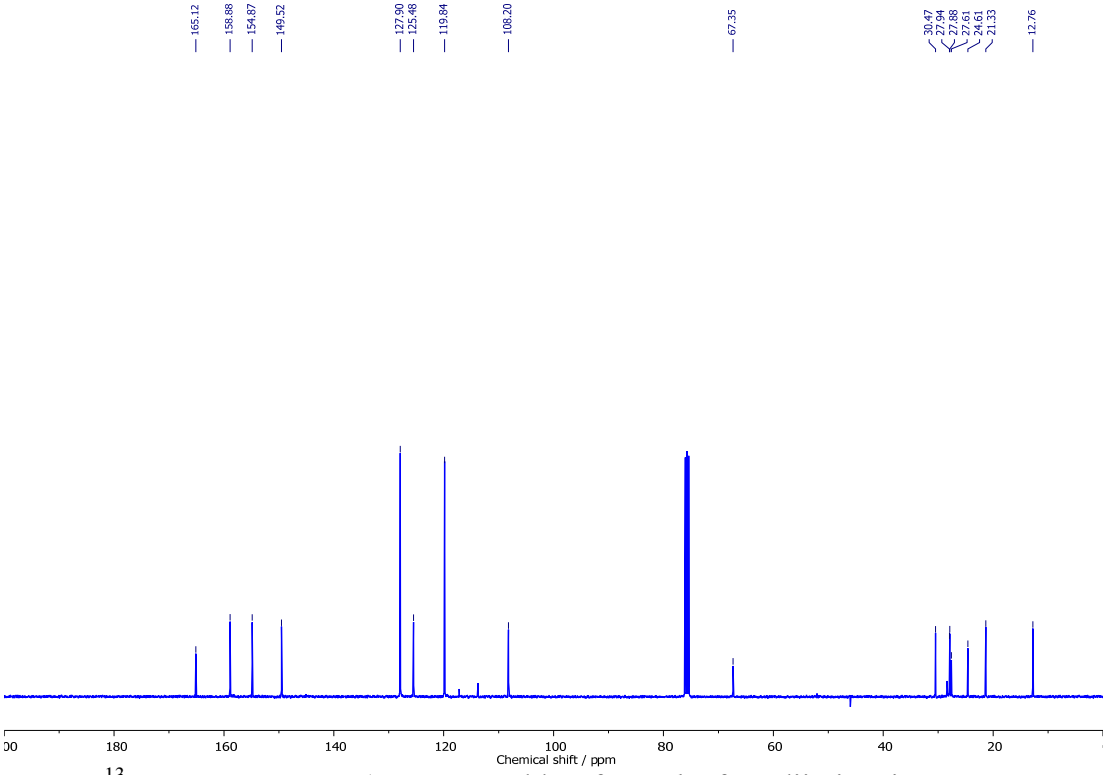
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of C_8-dicarbaldehydepincer **11**.



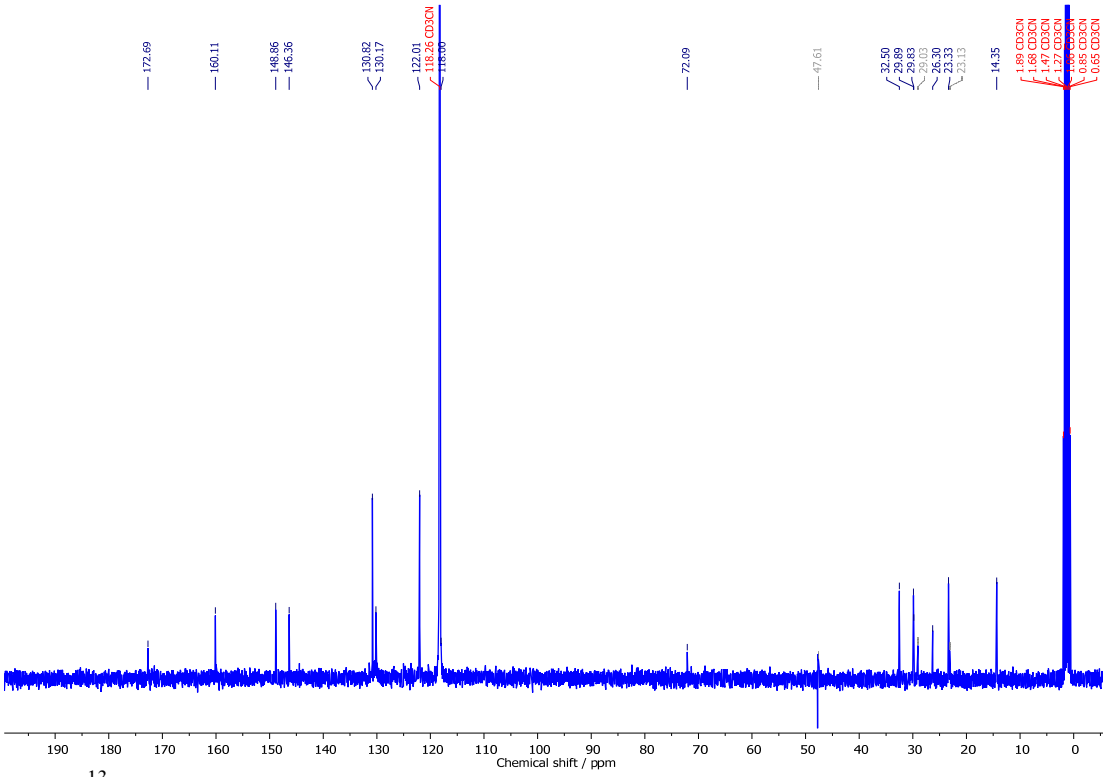
^{13}C NMR spectrum (100 MHz, chloroform-*d*) of C_8-dicarbaldehydepincer **11**.



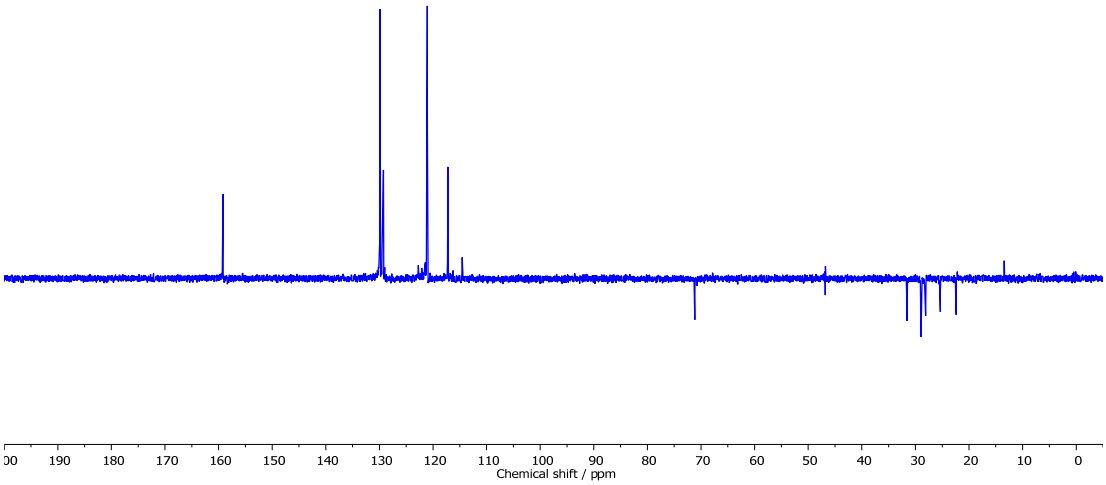
^{1}H NMR spectrum (400 MHz, chloroform-*d*) of C_8-diiminepincer **12**.



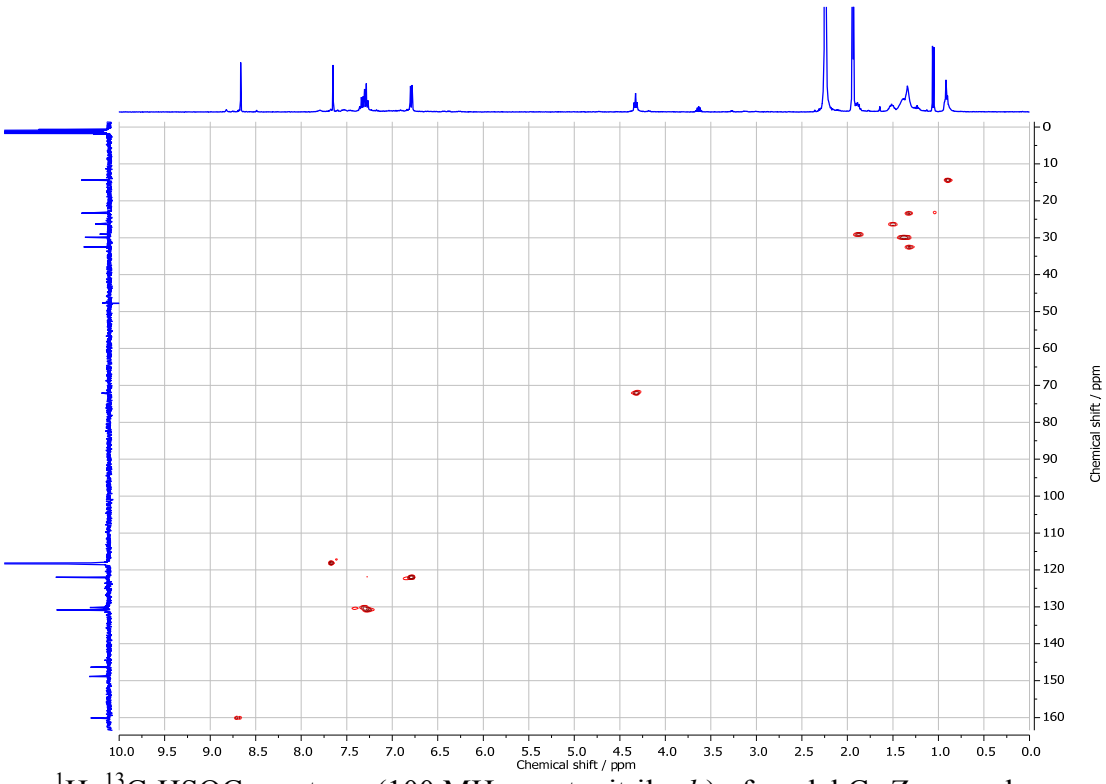
^{13}C NMR spectrum (100 MHz, chloroform-*d*) of C_8-diiminepincer **12**.



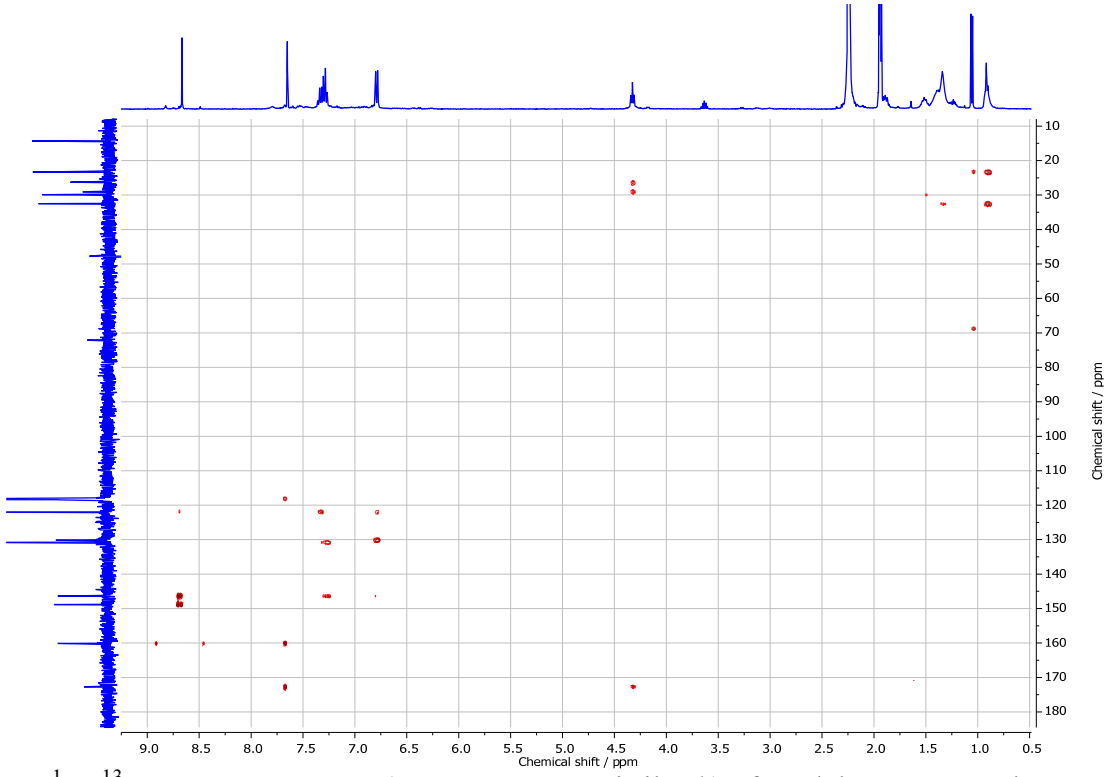
^{13}C NMR spectrum (100 MHz, acetonitrile-d_3) of model C_8-Zn complex.



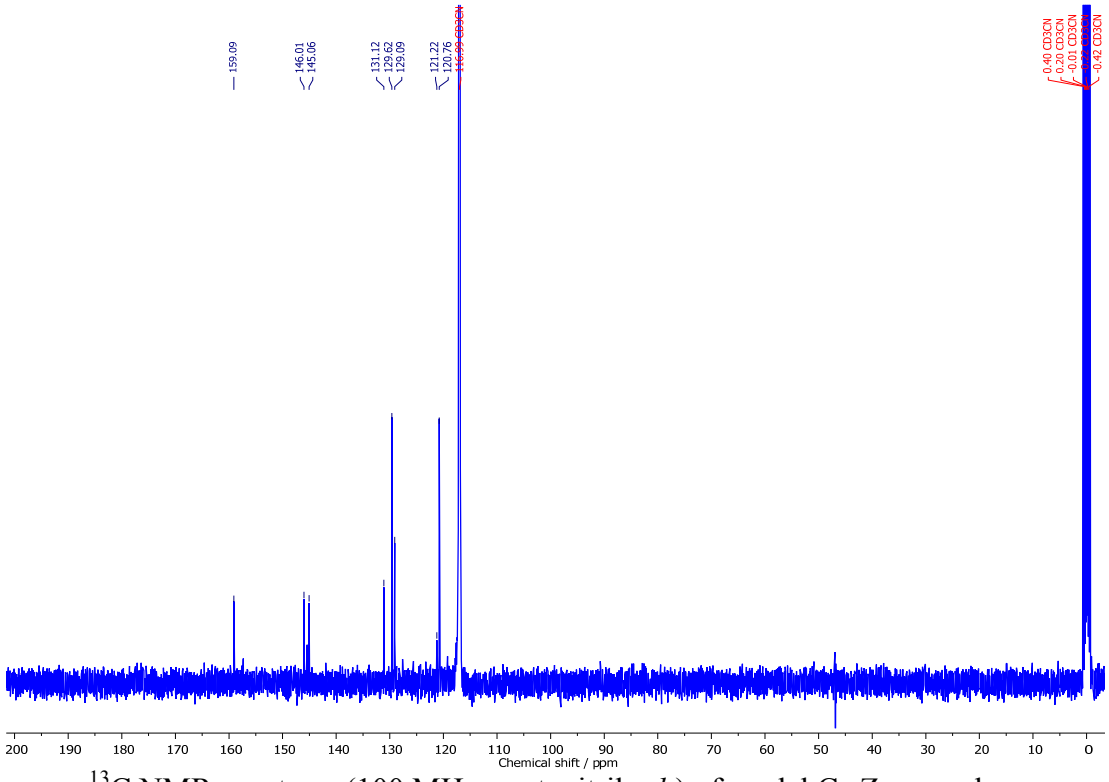
DEPT135 spectrum (100 MHz, acetonitrile-d_3) of model C_8-Zn complex.



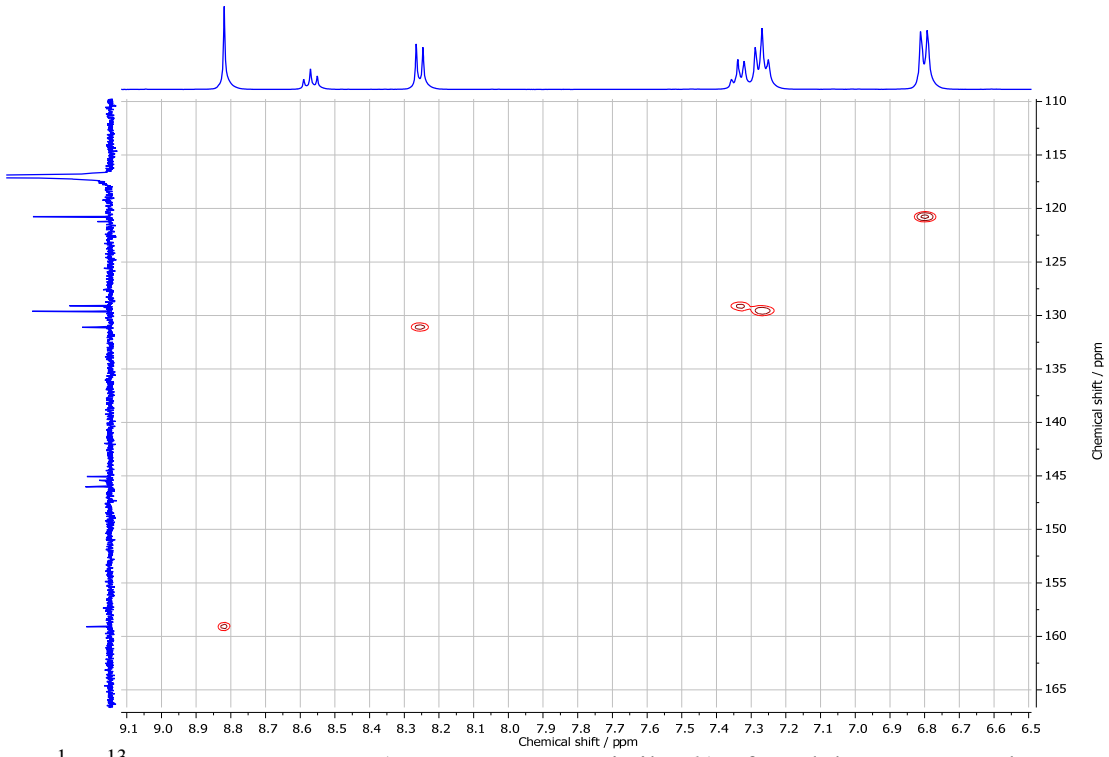
^{1}H, ^{13}C-HSQC spectrum (100 MHz, acetonitrile-d_3) of model C_8-Zn complex.



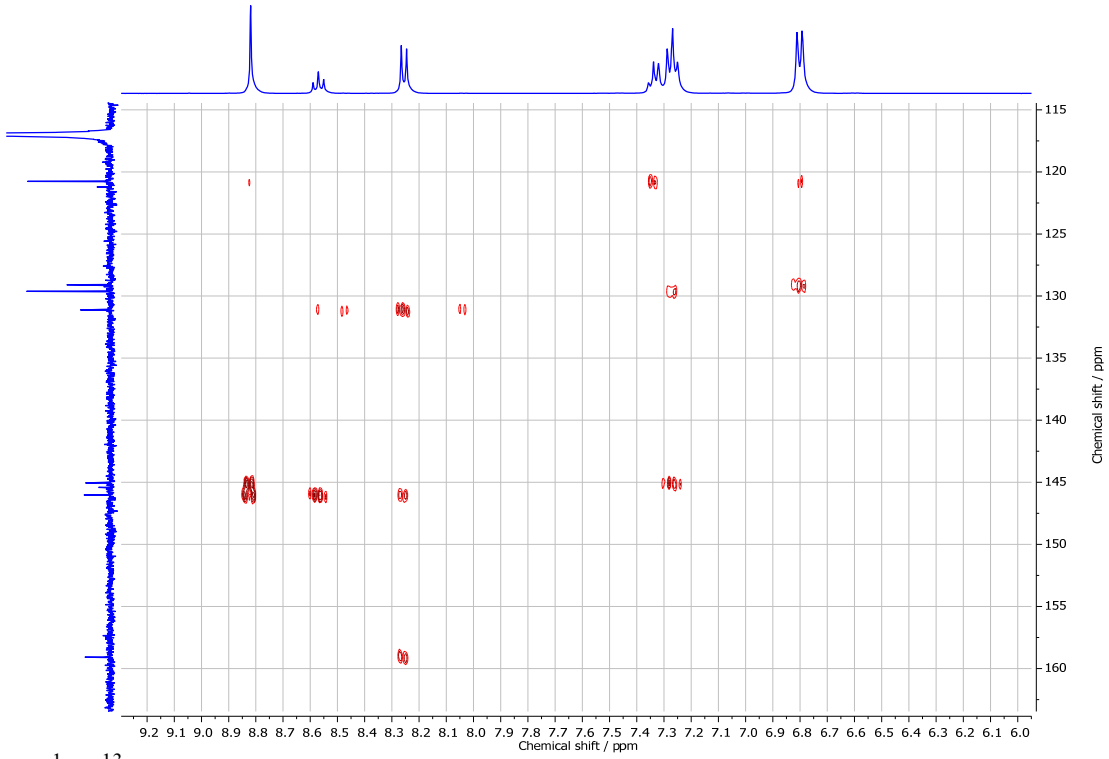
^{1}H, ^{13}C-HMBC spectrum (100 MHz, acetonitrile-d_3) of model C_8-Zn complex.



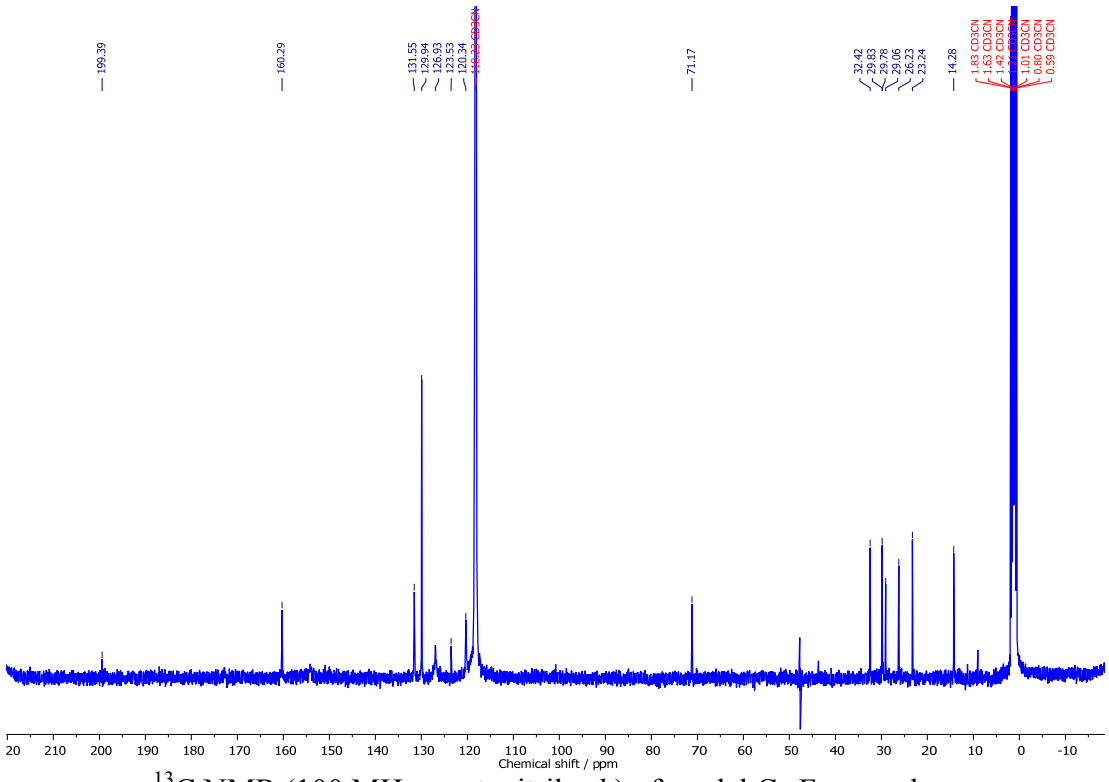
^{13}C NMR spectrum (100 MHz, acetonitrile-d_3) of model C_0-Zn complex.



^{1}H, ^{13}C-HSQC spectrum (100 MHz, acetonitrile-d_3) of model C_0-Zn complex.



^{1}H, ^{13}C-HMBC spectrum (100 MHz, acetonitrile-d_3) of model C_0-Zn complex.



^{13}C NMR (100 MHz, acetonitrile-d_3) of model C_8-Fe complex.

11 References

S1 (a) A. S. Lang and M. Thelakkat, *Polym. Chem.* 2011, **2**, 2213-2221; (b) A.-L. Gassner, C. Duhot, J.-C. G. Bünzli and A.-S. Chauvin, *Inorg. Chem.*, 2008, **47**, 7802-7812.
S2 F. Lions and K. V. Martin, *J. Am. Chem. Soc.*, 1957, **79**, 2733-2738.