

Electronic Supplementary Information

Strapping a benzaldehyde-appended 2,2'-bis-dipyrrin Zn(II) double-stranded helicate using imine bond formation

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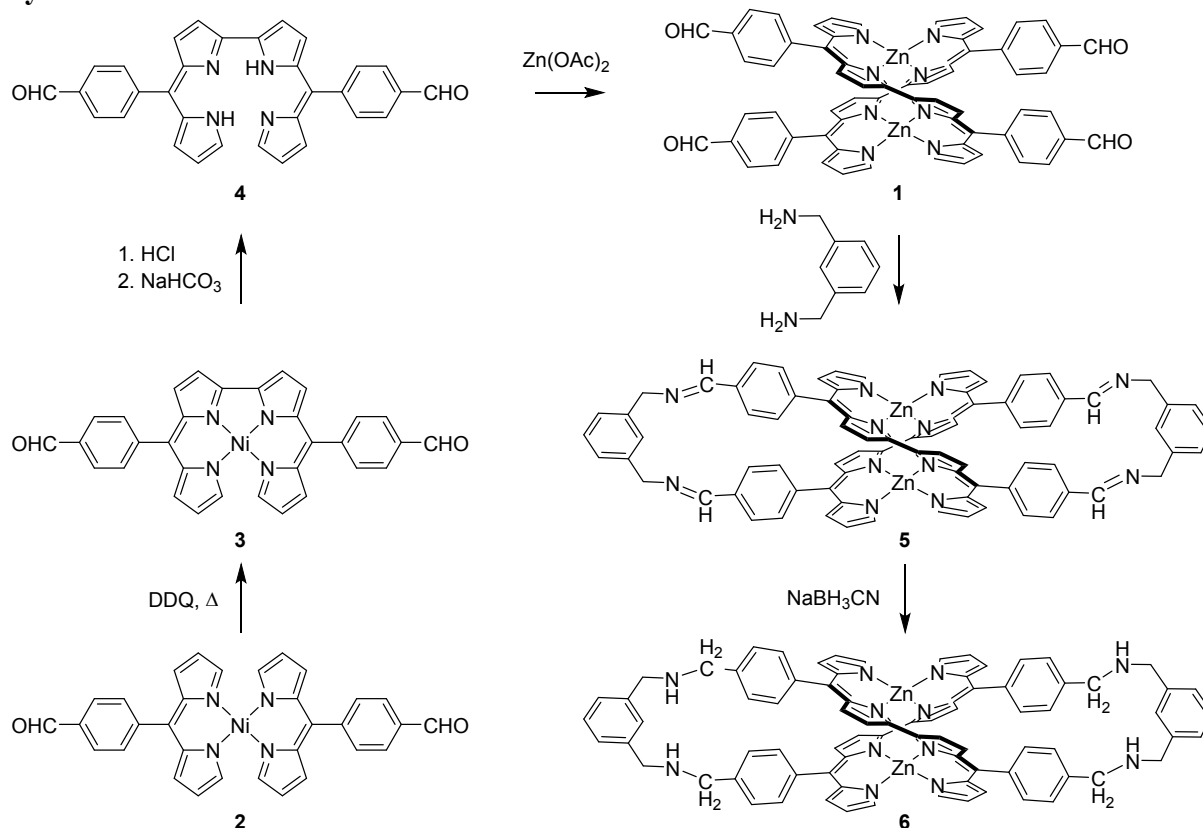
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Synthesis



5-(4-formylphenyl)dipyrrin was synthesized as described.¹ ¹H and ¹³C NMR spectra were recorded at 25 °C on a Bruker AV500 (500 MHz) or AV400 (400 MHz) with the deuterated solvent as the internal reference. NMR chemical shifts and *J* values are given in parts per million (ppm) and in Hertz, respectively. Mass spectrometry was performed by the Service commun d'analyse (University of Strasbourg).

Complex 2: To a CHCl_3 (50 mL) solution of 5-(4-formylphenyl)dipyrin (0.83 g; 3.34 mmol), a MeOH (50 mL) solution of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ (0.42 g; 1.67 mmol) was added. The mixture was stirred at room temperature overnight. It was then evaporated under reduced pressure and the residue was washed with MeOH affording complex **2** as a dark red solid (0.76 g, 82%). δ_{H} (400 MHz, CDCl_3) 10.96 (s, 4H, pyrroleH), 10.10 (s, 2H, CHO), 8.30 (d, $J = 2.5$ Hz, 4H, pyrroleH), 7.91 (d, 4H, $J = 7.8$ Hz, PhH), 7.52 (d, 4H, $J = 7.9$ Hz, PhH), 6.67 (s, $J = 3.8$ Hz, 4H, pyrroleH). δ_{C} (125 MHz, CDCl_3) 191.8, 175.7, 149.2, 142.8, 141.6, 139.4, 136.9, 136.6, 131.2, 128.8. Single crystals were obtained by *n*-pentane vapor diffusion into a THF solution of the complex.

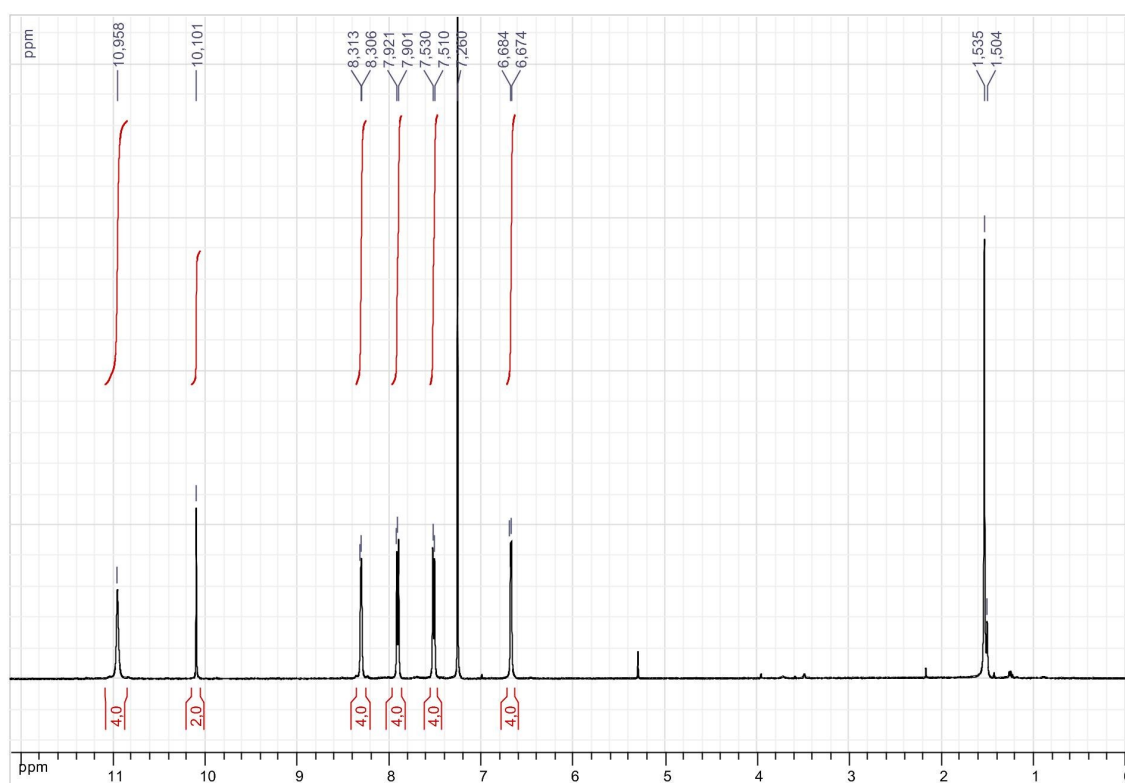


Fig. ESI1 $^1\text{H-NMR}$ spectrum of complex **2** in CDCl_3 .



Fig. ESI2 ^{13}C -NMR spectrum of complex **2** in CDCl_3 .

Complex 3: A toluene (150 mL) solution of DDQ (0.34 g; 1.49 mmol) was added dropwise to a toluene (200 mL) solution of complex **2** (0.75 g; 1.36mmol). The color of the mixture turned from red to brown, upon heating at reflux for 24 hours. After evaporation under reduced pressure, the residue was purified by column chromatography (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{Cyclohexane}$: 9/1) affording the desired compound **3** as a red solid (0.6 g, 80%). δ_{H} (500 MHz, CDCl_3) 10.14 (s, 2H, CHO), 8.00 (d, 4H, $J = 8.2$ Hz, PhH), 7.73 (d, 4H, $J = 8.2$ Hz, PhH), 6.73 (d, 2H, $J = 4.7$ Hz, pyrroleH), 6.68 (d, 2H, $J = 4.4$ Hz, pyrroleH), 6.65 (d, 2H, $J = 4.4$ Hz, pyrroleH), 6.46 (d, 2H, $J = 4.7$ Hz, pyrroleH), 5.94 (s, 2H, pyrroleH). δ_{C} (125 MHz, CDCl_3) 191.9, 161.9, 154.1, 142.9, 141.7, 138.6, 136.7, 135.5, 134.7, 131.6, 130.0, 129.1, 117.8, 116.0. $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ ($\epsilon/\text{mol}^{-1}\cdot\text{L}\cdot\text{cm}^{-1}$) 302 (22700), 355 (24200), 418 (35400), 573 (12900), 775 (5600).: HRMS (ESI), m/z : $[\text{M}]^+$ calcd. for $\text{C}_{32}\text{H}_{20}\text{N}_4\text{NiO}_2$: 550.0934, Found 550.0947.

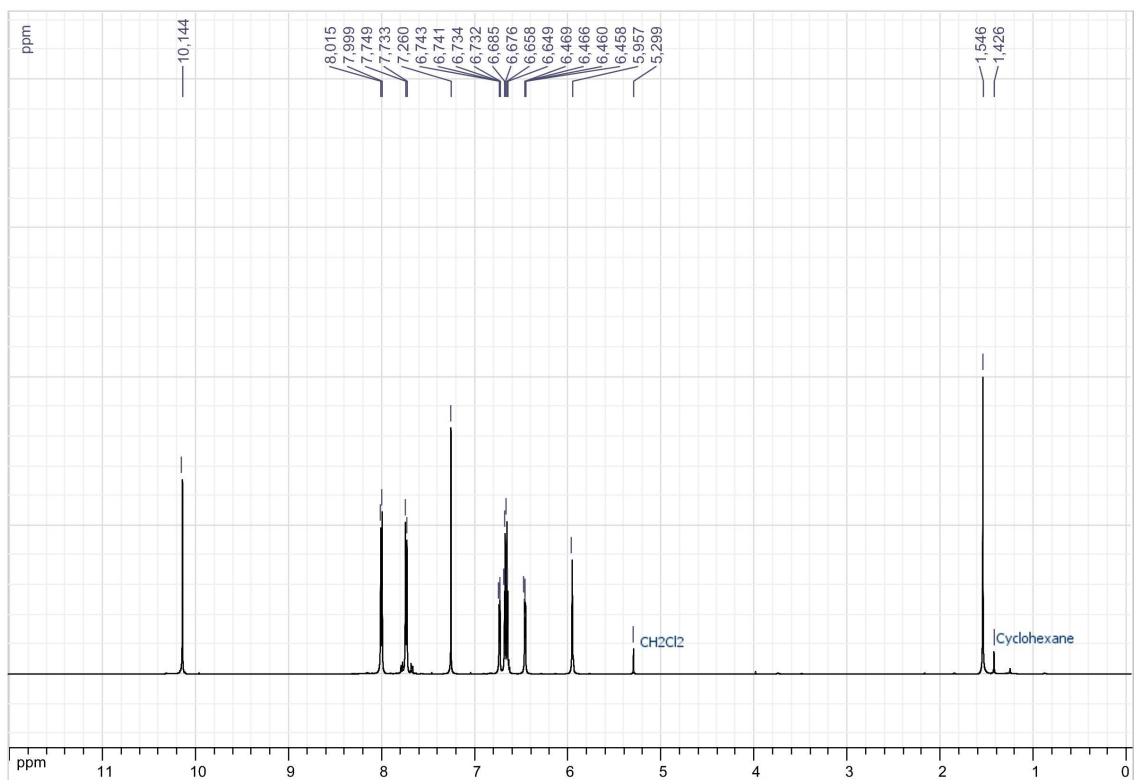


Fig. ESI3 $^1\text{H-NMR}$ spectrum of complex **3** in CDCl_3 .

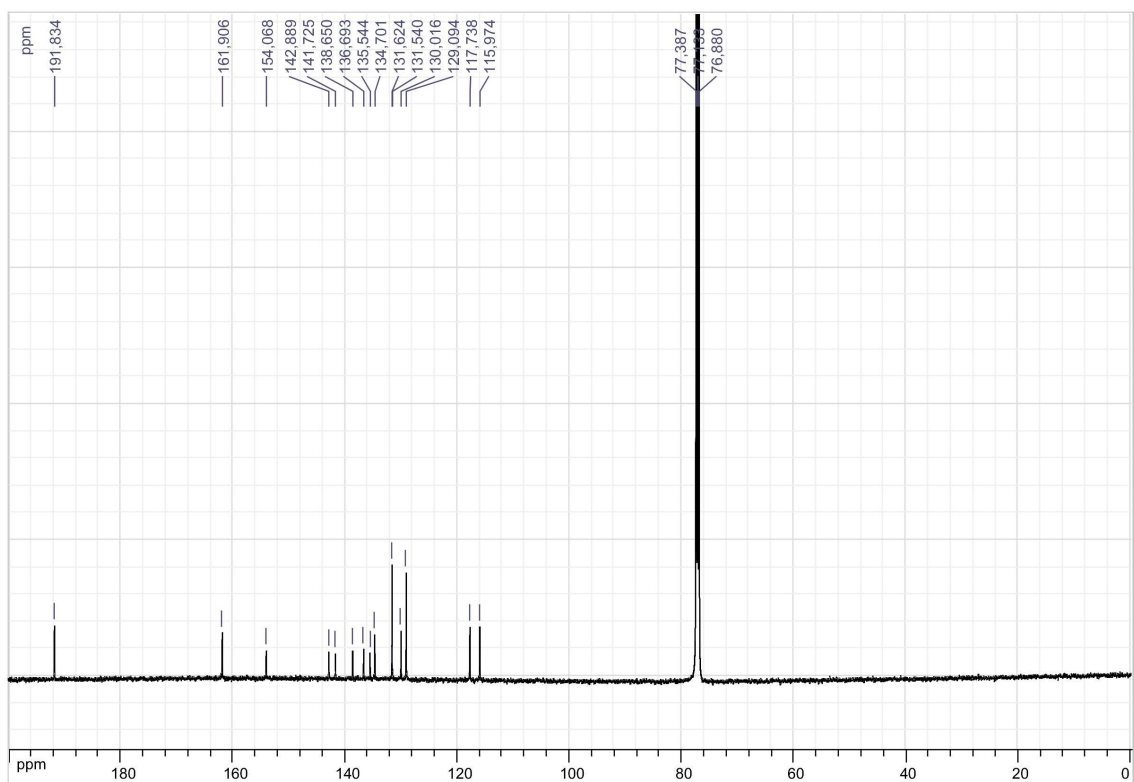


Fig. ESI4 $^{13}\text{C-NMR}$ spectrum of complex **3** in CDCl_3 .

2,2'-bisdipyrrin **4**: A 12 M solution of HCl (20 mL) was added to a CHCl₃ (80 mL) solution of complex **3** (0.56 g; 1.02 mmol) and the mixture was stirred at room temperature overnight. Upon addition of a saturated Na₂CO₃ solution, the organic layer turned from green to dark blue. The mixture was extracted with CHCl₃ (3 × 100 mL) and the combined organic layers were dried over Na₂SO₄, filtered and evaporated affording 2,2'-bisdipyrrin **4** as a dark blue solid (0.5 g, 99%). Single crystals were obtained by slow evaporation of a solution of the complex in CHCl₃. δ_{H} (500 MHz, CDCl₃) 10.14 (s, 2H, CHO), 8.01(d, $J = 8.2$ Hz, 4H, PhH), 7.72 (d, $J = 8.2$ Hz, 4H, PhH), 7.64 (s, 2H, pyrroleH), 7.02(d, $J = 4.4$ Hz, 2H, pyrroleH), 6.68 (d, $J = 4.4$ Hz, 2H, pyrroleH), 6.52 (d, $J = 4.1$ Hz, 2H, pyrroleH), 6.44 (d, $J = 4.1$ Hz, 2H, pyrroleH). δ_{C} (125 MHz, CDCl₃) 191.9, 153.1, 145.2, 143.5, 139.6, 139.0, 138.8, 136.6, 131.8, 131.7, 129.2, 126.5, 120.8, 116.7. λ_{max} (CH₂Cl₂)/nm (ϵ /mol⁻¹.L.cm⁻¹): 258 (31300), 280 (26000), 332 (24300), 413 (22700), 591 (37600). HRMS (ESI), m/z : [M]⁺ calcd. for C₃₂H₂₃N₄O₂: 495.1816, Found 495.1775.

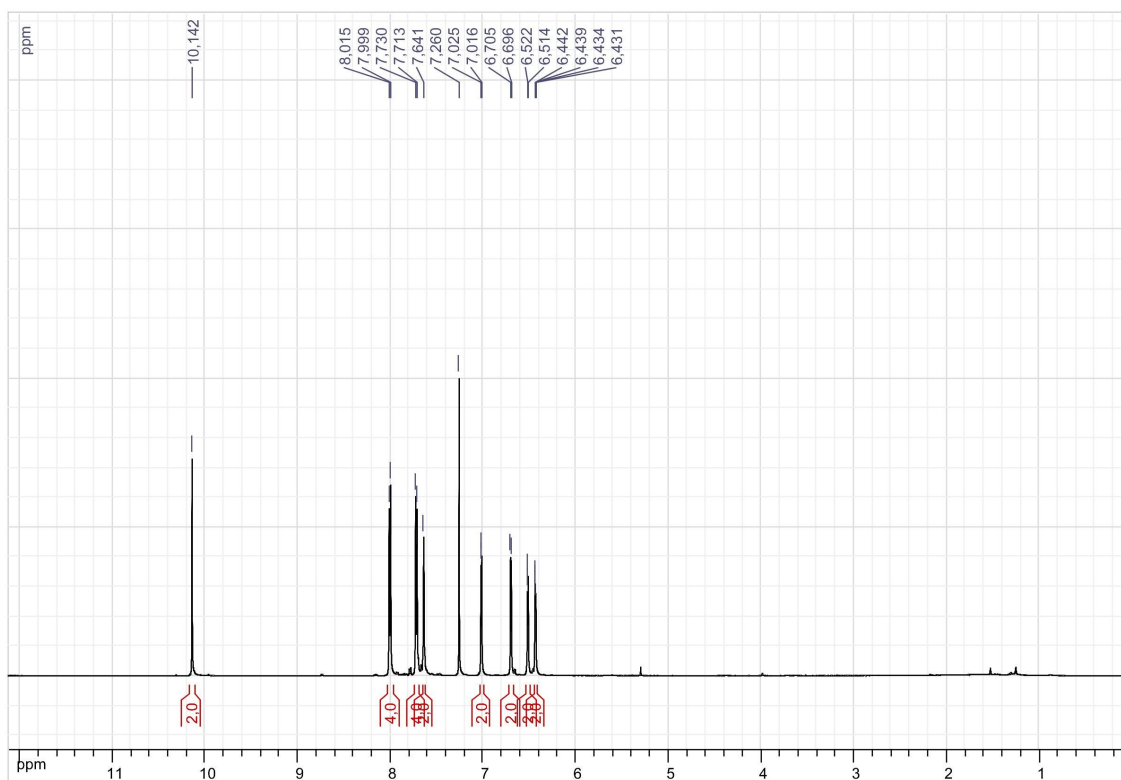


Fig. ESI5 ¹H-NMR spectrum of 2,2'-bis-dipyrrin **4** in CDCl₃.

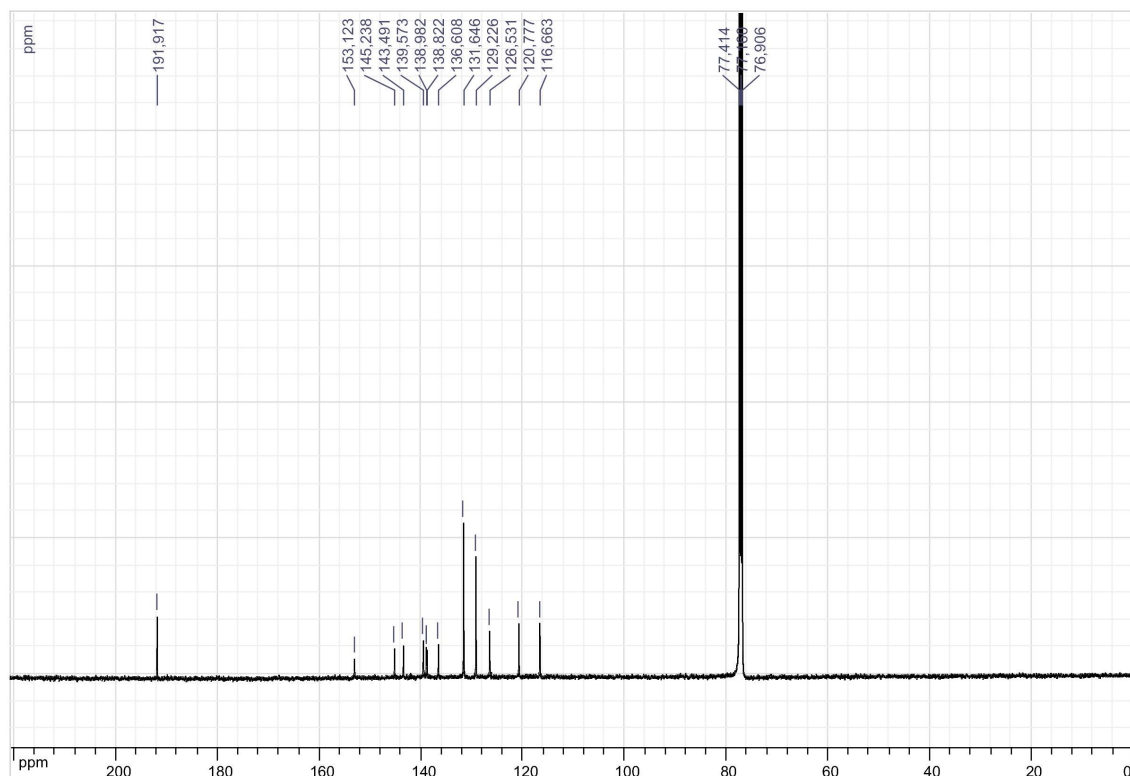


Fig. ESI6 ^{13}C -NMR spectrum of 2,2'-bis-dipyrin **4** in CDCl_3 .

Helicate 1: A MeOH (60 mL) solution of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (78 mg; 0.36 mmol) was added to a CHCl_3 (60 mL) solution of ligand **4** (0.16 g; 0.32 mmol). Upon stirring for 24 hours at room temperature, the solution turned from dark blue to dark green. After evaporation under reduced pressure, the residue was washed with MeOH (3×50 mL) affording **helicate 1** (0.17 g, 94%). δ_{H} (500 MHz, CDCl_3) 10.13 (s, 4H, CHO), 7.95 (d, 4H, $J = 7.8$ Hz, PhH), 7.75 (d, 4H, $J = 7.8$ Hz, PhH), 7.66 (d, 4H, $J = 7.8$ Hz, PhH), 7.22 (d, 4H, $J = 7.8$ Hz, PhH), 6.98 (s, 4H, pyrroleH), 6.51 (d, $J = 4.3$ Hz, 4H, pyrroleH), 6.44 (d, $J = 4.1$ Hz, 4H, pyrroleH), 6.35 (d, $J = 4.1$ Hz, 4H, pyrroleH), 6.31 (d, $J = 4.3$ Hz, 4H, pyrroleH). δ_{C} (125 MHz, CDCl_3) 191.9, 154.9, 150.4, 145.4, 144.8, 141.6, 140.9, 136.5, 132.9, 132.2, 132.2, 131.7, 128.7, 128.4, 118.4, 117.3. $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{L cm}^{-1}$): 257 (71700), 284 (60800), 345 (60000), 432 (110200), 646 (66000). HRMS (ESI), m/z : $[\text{M}]^+$ calcd. for $\text{C}_{64}\text{H}_{40}\text{N}_8\text{O}_4\text{Zn}_2$: 1112.1750, Found 1112.1804.

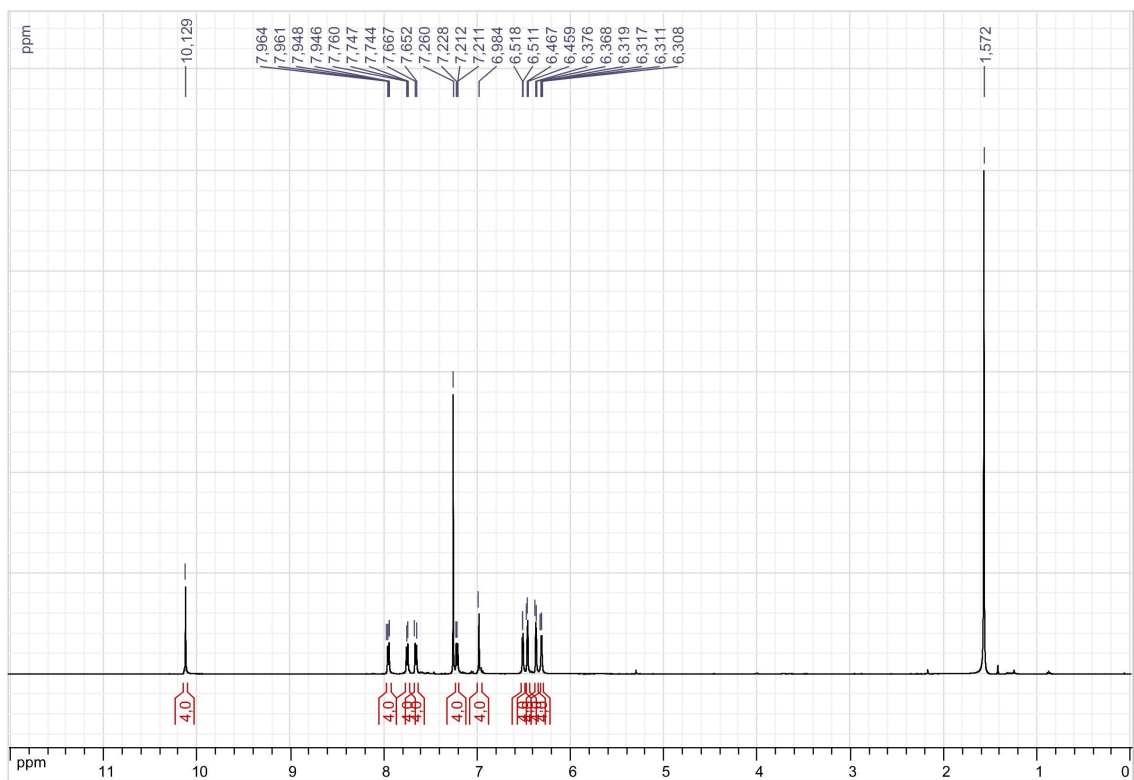


Fig. ESI7 ^1H -NMR spectrum of helicate **1** in CDCl_3 .

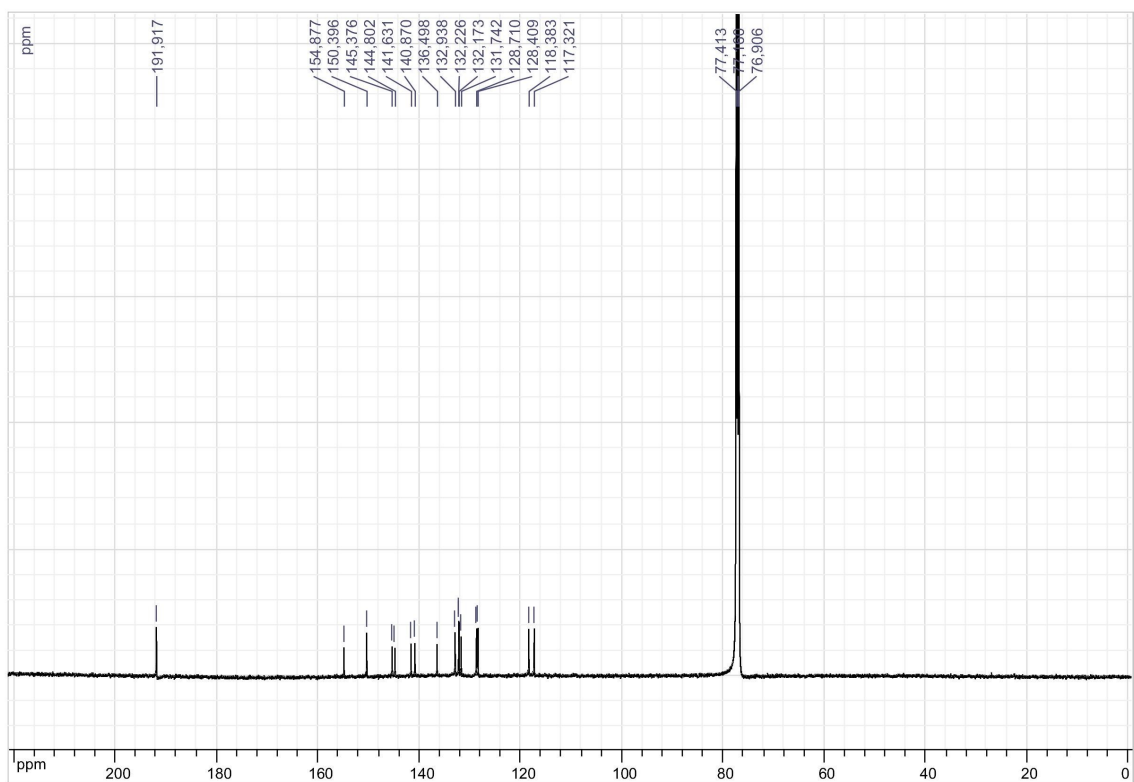


Fig. ESI8 ^{13}C -NMR spectrum of helicate **1** in CDCl_3 .

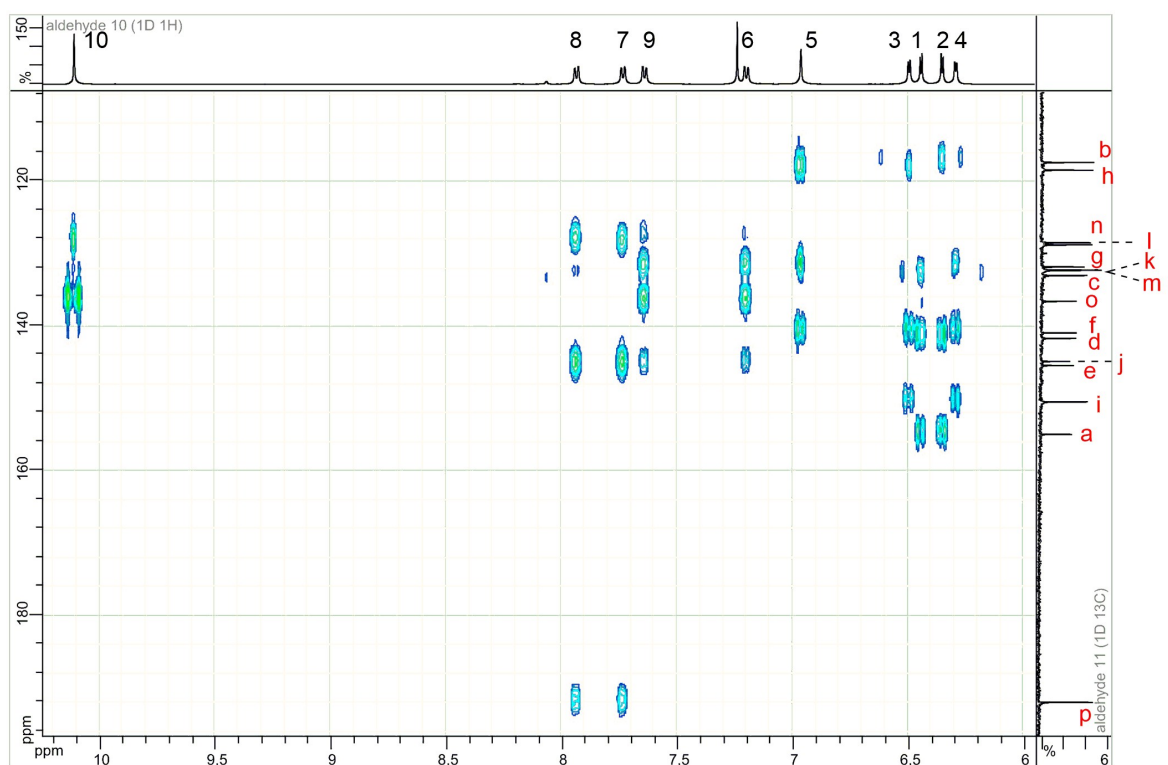
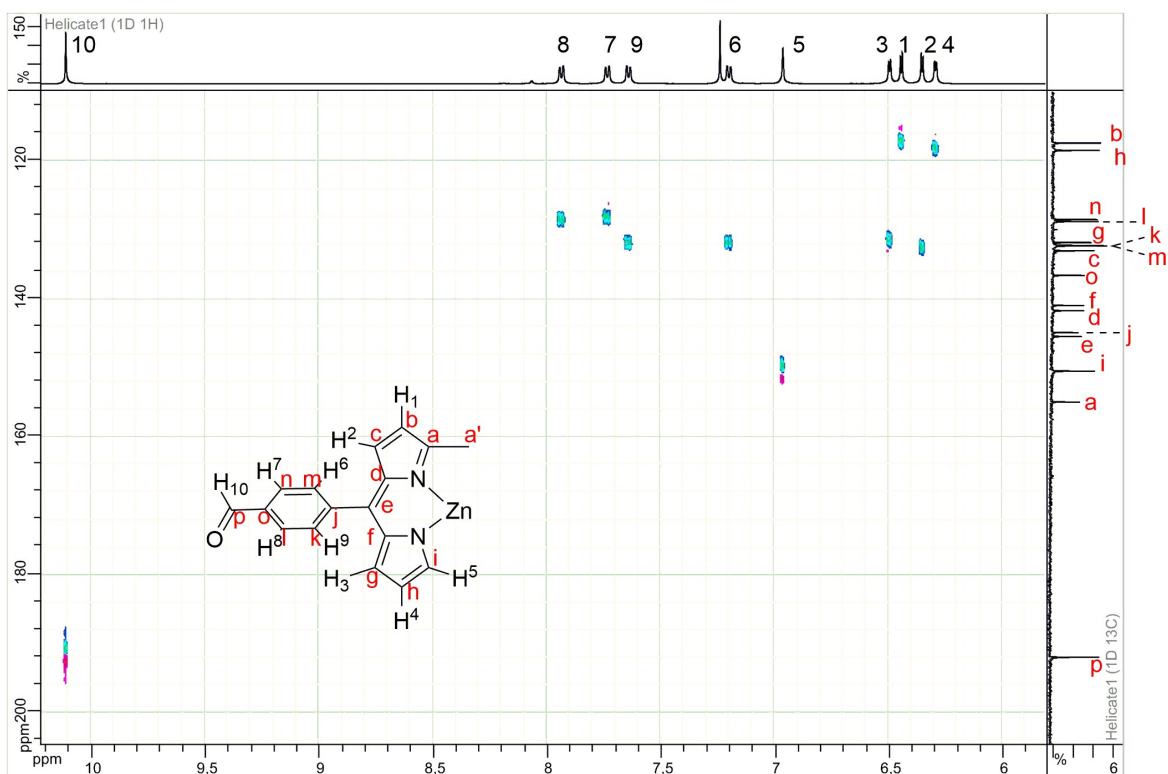


Fig. ESI 9 HSQC (top) and HMBC (bottom) correlation experiments of helicate **1** in CDCl₃ (500 MHz). The numbering scheme used for the assignment of the proton and carbon atoms of a quarter of the helicate is shown as an insert.

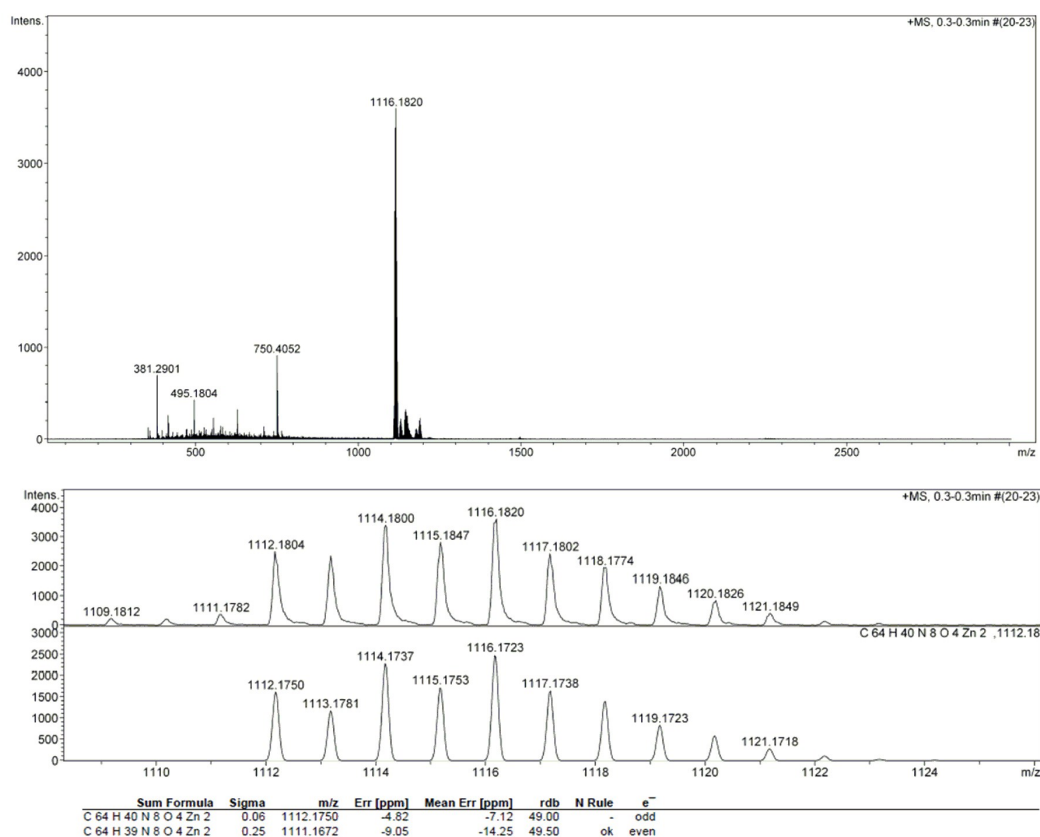


Fig. ESI10 HRMS spectrum of helicate **1**.

Helicate **5**: To a dry CHCl_3 (250 mL) solution of helicate **1** (50 mg; 4.48×10^{-2} mmol), a dry CHCl_3 (250 mL) solution of *m*-xylylenediamine (12.4 μL ; 9.41×10^{-2} mmol, 2 equiv.) and TFA (0.01 equiv) were added under argon. The mixture was stirred at room temperature for 24 hours. It was then evaporated under reduced pressure affording **5** as a dark solid (58 mg, 98%). δ_{H} (500 MHz, CDCl_3) 8.53 (s, 4H, CH=N), 7.92 (d, $J = 7.5$ Hz, 4H, PhH), 7.59 (d, $J = 7.5$ Hz, 4H, PhH), 7.54 (d, $J = 7.5$ Hz, 4H, PhH), 7.44 (s, 2H, PhH), 7.39-7.35 (m, 6H, PhH/pyrroleH), 7.23 (d, $J = 7.5$ Hz, 4H, PhH), 7.1 (d, $J = 7.5$ Hz, 4H, PhH), 6.61 (d, $J = 4.3$ Hz, 4H, pyrroleH), 6.47 (d, $J = 4.3$ Hz, 4H, pyrroleH), 6.38 (d, $J = 4.3$ Hz, 4H, pyrroleH), 6.31 (d, $J = 4.3$ Hz, 4H, pyrroleH), 5.08 (d, $J = 15.2$ Hz, 4H, CH_2), 4.92 (d, $J = 15.2$ Hz, 4H, CH_2). δ_{C} (125 MHz, CDCl_3) 162.1, 155.5, 150.1, 146.3, 142.0, 141.7, 141.0, 140.5, 136.7, 133.8, 132.9, 132.4, 131.1, 129.1, 128.2, 125.2, 124.7, 117.7, 117.3, 63.6. $\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2)/\text{nm}$ ($\epsilon/\text{mol}^{-1} \text{L cm}^{-1}$): 257 (43600), 349 (44400), 431 (56300), 473 (22500), 577 (50200). HRMS (ESI), m/z : $[\text{M}]^+$ calcd. for $\text{C}_{80}\text{H}_{56}\text{N}_{12}\text{Zn}_2$: 1312.3328, Found 1312.3338.

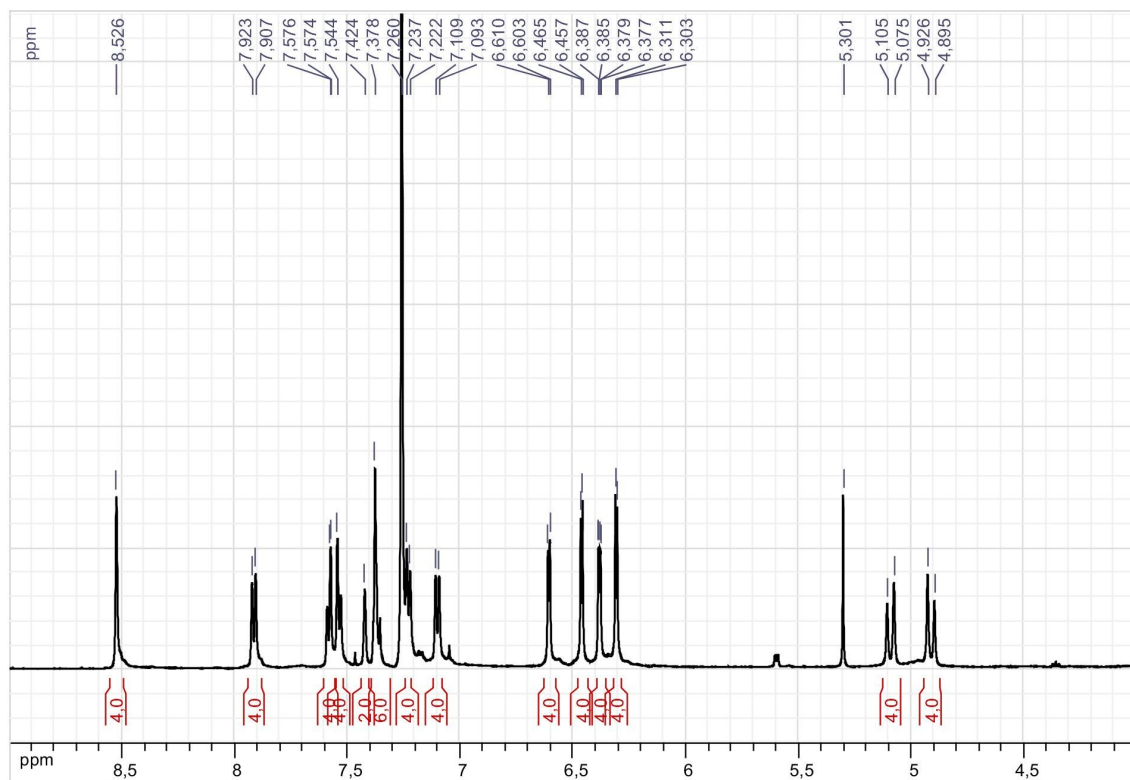


Fig. ESI11 ^1H -NMR spectrum of helicite **5** in CDCl_3 .

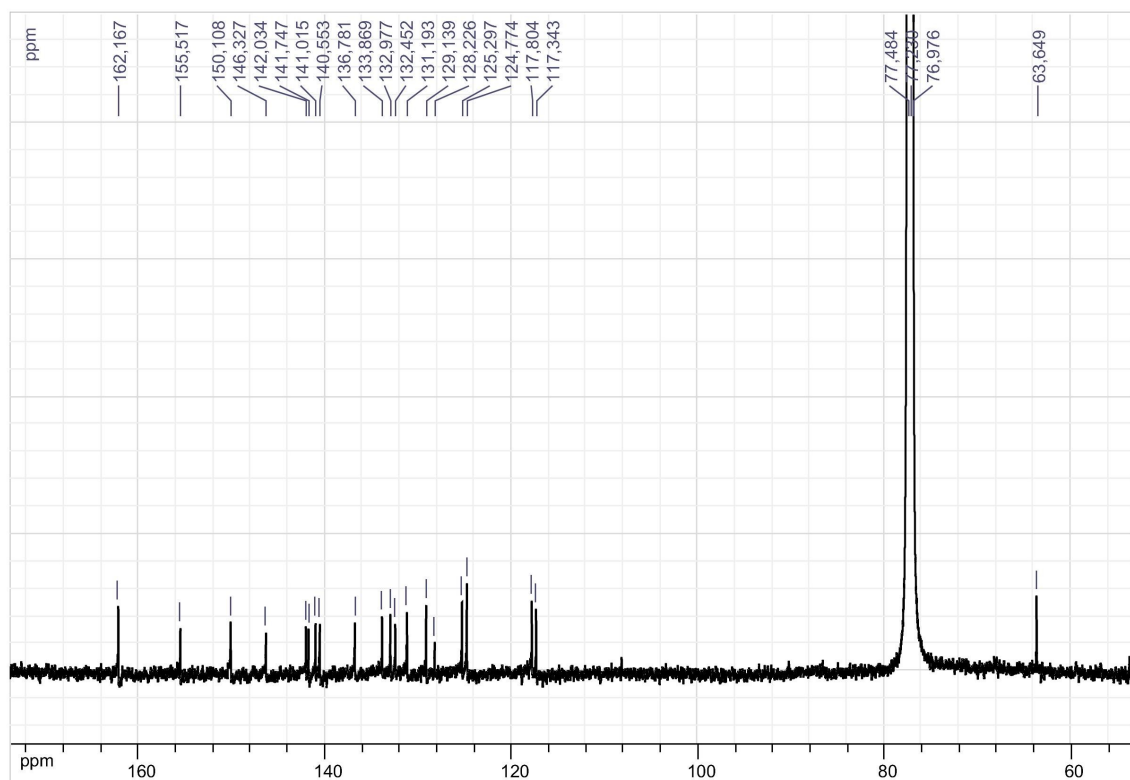


Fig. ESI12 ^{13}C -NMR spectrum of helicite **5** in CDCl_3 .

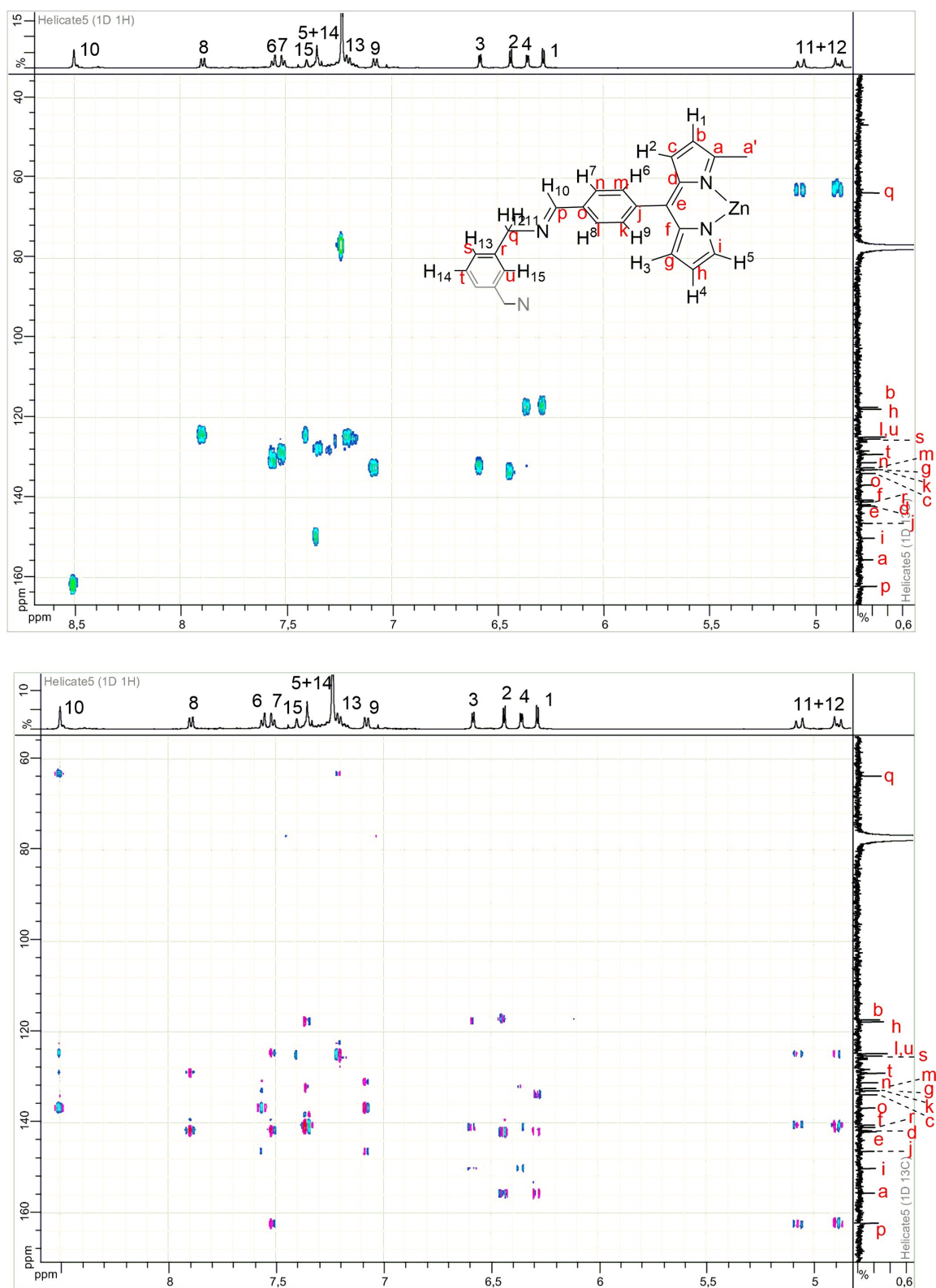


Fig. ESI 13 HSQC (top) and HMBC (bottom) correlation experiments of helicate **5** in CDCl₃ (500 MHz). The numbering scheme used for the assignment of the proton and carbon atoms of a quarter of the helicate is shown as an insert.

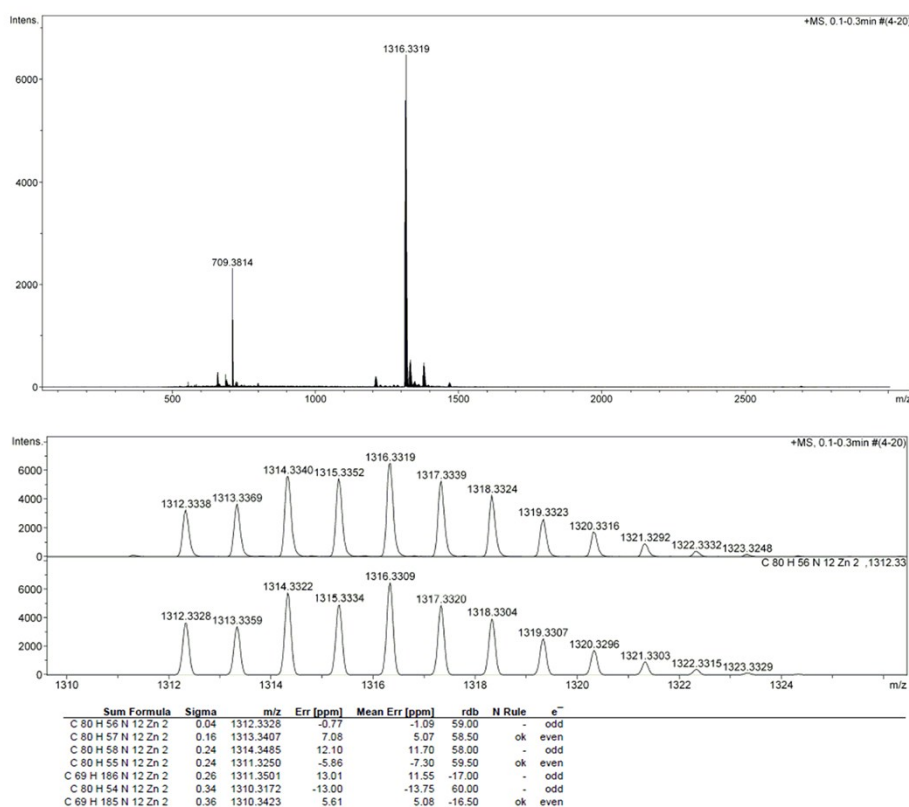


Fig. ESI14 HRMS spectrum of helicite 5.

Helicite 6: A solution of NaBH_3CN (8 mg, 0.12 mmol, 8eq.) in MeOH (4 mL) was added to a solution of **5** (20 mg, 0.015 mmol, 1eq) in CHCl_3 (15ml). Then 0.75ml of TFA solution (1.75 μL in 50 mL CHCl_3) was added and the mixture was stirred at room temperature and monitored by H NMR. After 64 hours, NaBH_3CN (8 mg, 0.12 mmol, 8eq) were added, then after 18 additional hours, 0.75mL of TFA solution (1.75 μL in 50 mL CHCl_3) was added and stirring was continued for 5 days. The reaction mixture was diluted with CHCl_3 and washed with water 3 times. The organic layer was dried on Na_2SO_4 , filtered and evaporated under reduced pressure. The residue was purified by two successive column chromatographies (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{TEA}$: 90/10/4) then (SiO_2 , $\text{CH}_2\text{Cl}_2/\text{MeOH}/\text{TEA}$: 95/5/1) to give 13 mg of **6** as a mixture with TEA. δ_{H} (300 MHz, CD_2Cl_2) 7.62 (s, 2H, PhH), 7.46 (m, 4H, PhH), 7.38 (m, 4H, PhH), 7.33 (m, 6H, PhH), 7.44 (m 4H, PhH), 7.07 (m, 8H, PhH/pyrroleH), 6.66 (dd, $J = 1.0$ and 4.1 Hz, 4H, pyrroleH), 6.35 (d, $J = 4.1$ Hz, 4H, pyrroleH), 6.30 (dd, $J = 1.0$ and 4.1 Hz, 4H, pyrroleH), 3.95 (d, $J = 15.2$ Hz, 4H, CH_2), 3.79 (m, 12H, CH_2). MS (ESI), m/z : $[\text{M}]^{2+}$ calcd. for $\text{C}_{80}\text{H}_{64}\text{N}_{12}\text{Zn}_2$: 660.19, Found 660.20.

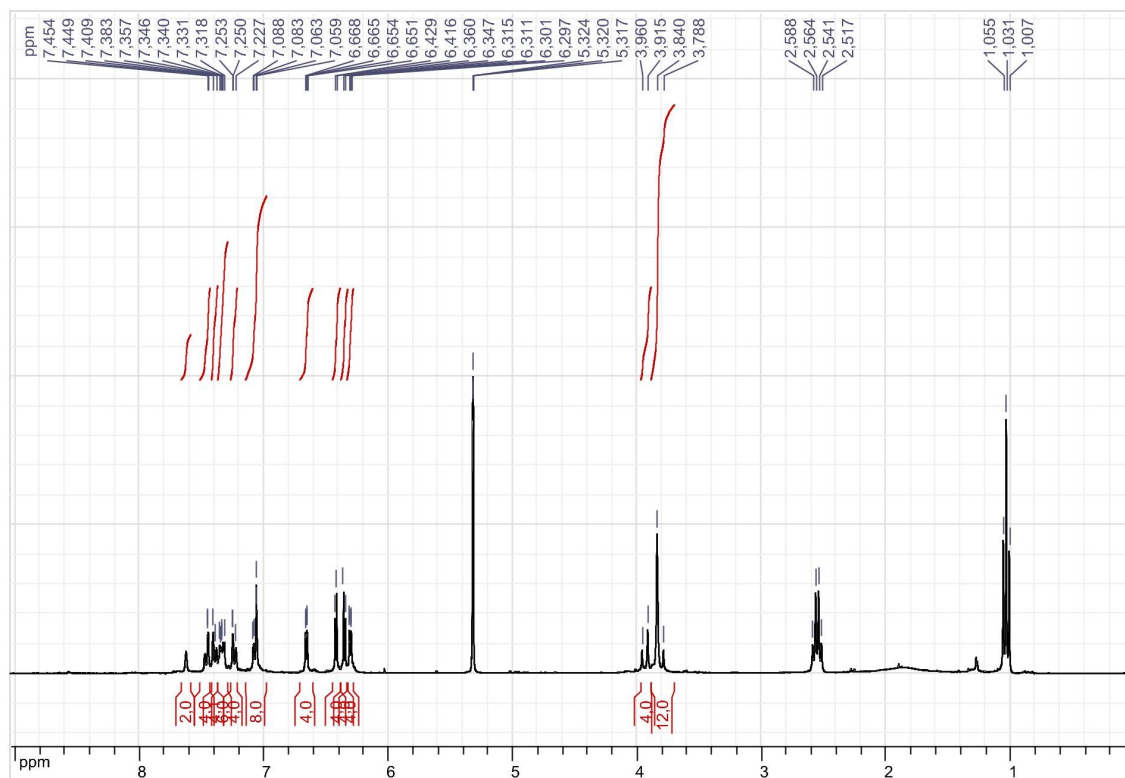


Fig. ESI15 $^1\text{H-NMR}$ spectrum of helicate **6** in CD_2Cl_2 . Traces of NEt_3 are present.

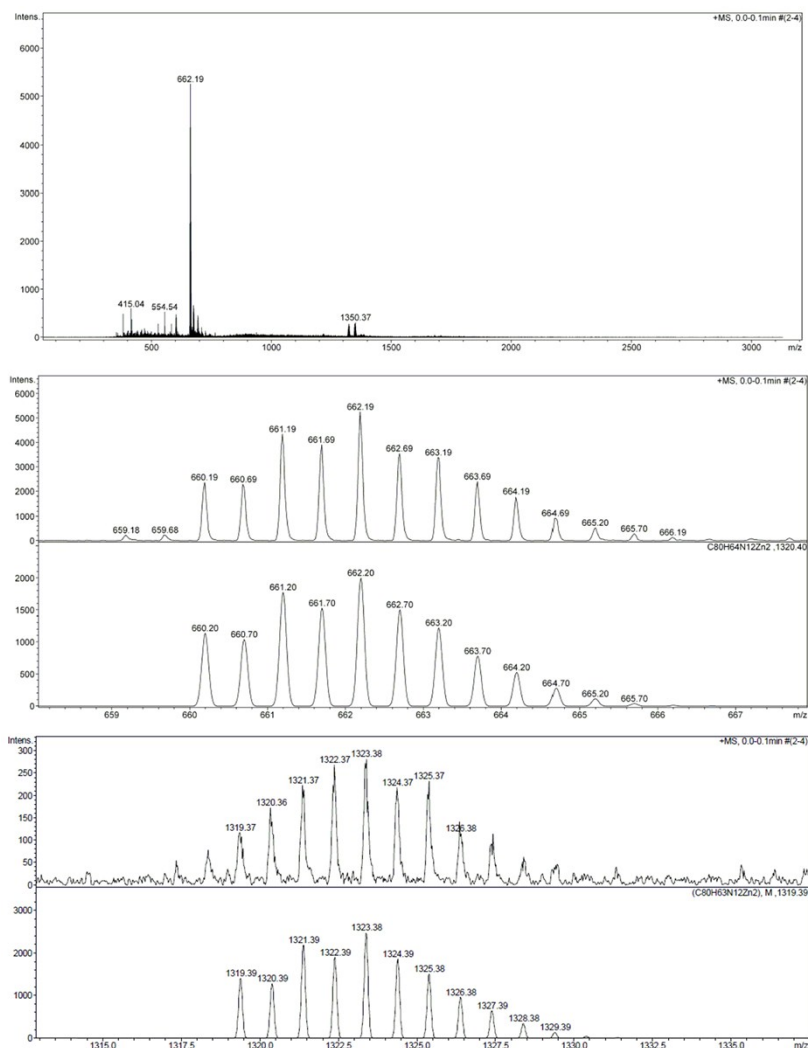


Fig. ESI16 HRMS spectrum of helicate **6**.

X-Ray diffraction

Data (Table ESI1) were collected on a Bruker SMART CCD diffractometer with Mo- $K\alpha$ radiation. The structures were solved using SHELXS-97 and refined by full matrix least-squares on F^2 using SHELXL-2014 with anisotropic thermal parameters for all non-hydrogen atoms.² Hydrogen atoms were introduced at calculated positions and not refined (riding model). In the structure of **4**(CHCl₃), the chloroform molecule is disordered over two positions that have been modelled accordingly.

CCDC 1893175-1893178 contain the supplementary crystallographic data for compounds **1-4**. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Table ESI1. Crystallographic data for compounds **1-4**.

	1	2	3	4 (CHCl₃)
Formula	C ₆₄ H ₄₀ N ₈ O ₄ Zn ₂	C ₃₂ H ₂₂ N ₄ NiO ₂	C ₃₂ H ₂₀ N ₄ NiO ₂	C ₃₃ H ₂₃ Cl ₃ N ₄ O ₂
FW	1115.78	553.24	551.23	613.90
Crystal system	Tetragonal	Triclinic	Triclinic	Monoclinic
Space group	<i>P</i> -4 <i>n</i> 2	<i>P</i> -1	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> / Å	11.9527(3)	9.7819(2)	9.8321(3)	11.4063(4)
<i>b</i> / Å	11.9527(3)	11.6608(3)	10.7832(3)	9.7778(3)
<i>c</i> / Å	17.7035(7)	12.9613(3)	13.3416(3)	13.4576(4)
<i>α</i> / °		110.8970(10)	103.1690(10)	
<i>β</i> / °		98.8930(10)	102.6240(10)	94.7850(10)
<i>γ</i> / °		111.0520(10)	111.8220(10)	
<i>V</i> / Å ³	2529.25(16)	1219.34(5)	1204.51(6)	1495.67(8)
<i>Z</i>	2	2	2	2
<i>T</i> / K	173(2)	173(2)	173(2)	173(2)
<i>μ</i> / mm ⁻¹	1.010	0.836	0.846	0.344
Refls. coll.	40519	24117	23901	28945
Ind. refls. (<i>R</i> _{int})	3750 (0.0574)	6572 (0.0251)	6497 (0.0408)	4084 (0.0233)
<i>R</i> ₁ (<i>I</i> >2σ(<i>I</i>)) ^a	0.0532	0.0326	0.0416	0.0701
<i>wR</i> ₂ (<i>I</i> >2σ(<i>I</i>)) ^a	0.1285	0.0768	0.0946	0.1929
<i>R</i> ₁ (all data) ^a	0.0809	0.0396	0.0628	0.0802
<i>wR</i> ₂ (all data) ^a	0.1443	0.0800	0.1051	0.2026
<i>GOF</i>	1.050	1.053	1.030	1.039

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{1/2}$$

References

- (a) L. Yu, K. Muthukumar, I. V. Sazanovich, C. Kirmaier, E. Hindin, J. R. Diers, P. D. Boyle, D. F. Bocian, D. Holten and J. S. Lindsey, *Inorg. Chem.*, 2003, **42**, 6629. (b) K. Muthukumar, S. H. H. Zaidi, L. Yu, P. Thamyongkit, M. E. Calder, D. S. Sharada and J. S. Lindsey, *J. Porphyrins Phthalocyanines*, 2005, **9**, 745.
- G. M. Sheldrick, *Acta Cryst. C*, 2015, **71**, 3.