

Supporting Information

**Linear and macrocyclic oligo(*p*-phenylene iminoboranes) with ferrocenyl side groups –
observation of selective, non-templated macrocyclization**

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1. Experimental Section

General procedures. All manipulations were performed under an atmosphere of dry argon using standard Schlenk techniques or in an MBraun glove box. Solvents (toluene, dichloromethane, *n*-pentane and *n*-hexane) were dried and degassed by means of an Innovative Technology solvent purification system (SPS).

Deuterated solvents for NMR spectroscopy were dried and degassed at reflux over CaH_2 (CDCl_3) or Na (C_6D_6) and freshly distilled prior to use. Anilin-TMS^[1], *p*-PDA(TMS)₂^[2], (dibromoboryl)ferrocene^[3], trimethylstannylferrocene^[4], dibromo(phenyl)borane^[5] and 1,4-bis(dibromo-borane)benzene^[5] were prepared according to procedures described in the literature.

Unless otherwise stated, NMR spectra were recorded at 25 °C on a Bruker Avance III HD spectrometer operating at 300 MHz, on a Bruker Avance Neo I 500 spectrometer operating at 500 MHz or on a Bruker Avance Neo I 600 spectrometer operating at 600 MHz. Chemical shifts were referenced to residual protic impurities in the solvent (^1H) or the deuterated solvent itself (^{13}C) and reported relative to external SiMe_4 (^1H , ^{13}C) or $\text{BF}_3 \cdot \text{OEt}_2$ (^{11}B) standards.

Mass spectra were obtained with the use of a Thermo Scientific Exactive Plus Orbitrap MS system employing liquid injection field desorption ionization (LIFDI) and showed excellent congruence with the calculated isotopic distribution patterns.

Cyclic voltammetry experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a Vycor tip, serving as the reference electrode. Tetra-*n*-butylammonium hexafluorophosphate ($[\text{n-Bu}_4\text{N}][\text{PF}_6]$) was employed as the supporting electrolyte. Compensation for resistive losses (*iR* drop) was employed for all measurements. Cyclic voltammetry scans were conducted with a scan rate of 250 mV/s. The scans were referenced after the addition of a small amount of decamethylferrocene (bis(pentamethylcyclopentadienyl)iron(II)) as internal standard. The potentials are reported relative to the ferrocene/ferrocenium couple.

UV–vis spectra were obtained using a Jasco V-630 spectrophotometer. Emission spectra were recorded using an Edinburgh Instruments FLSP920 spectrometer equipped with a double monochromator for both excitation and emission, operating in right-angle geometry mode, and all spectra were fully corrected for the spectral response of the instrument.

Synthesis

Synthesis of FcB(Ph)Br (1).

FcSnMe₃^[4] (3.42 g, 9.8 mmol) was dissolved in *n*-hexane 20 mL and added dropwise to a solution of PhBBr₂^[5] (2.43 g, 9.8 mmol) in *n*-hexane (13 mL) at -78 °C. The reaction mixture was warmed to room temperature and stirred overnight. All volatiles were removed and the crude product was sublimated (50 °C, HV) and obtained as a dark red solid (2.88 g, 8.2 mmol, 84%).

¹H NMR (600 MHz, CDCl₃): δ = 8.01 (m, 2H, *H*_{ortho}-Ph), 7.53 (m, 1H, *H*_{para}-Ph), 7.45 (m, 2H, *H*_{meta}-Ph), 4.89 (t, 2H, *H*-Cp_{substit.}), 4.67 (t, 2H, *H*-Cp_{substit.}), 4.16 (s, 5H, *H*-Cp_{unsubstit.}) ppm; ¹¹B NMR (192 MHz, CDCl₃): δ = 57.5 ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 140.6 (br s, *C*_{ipso}-Ph), 134.7 (s, *C*_{ortho}-Ph), 131.3 (s, *C*_{para}-Ph), 127.8 (s, *C*_{meta}-Ph), 77.8 (s, C-Cp_{substit.}), 77.2 (s, C-Cp_{substit.}), 72.7 (s, *C*_{ipso}-Cp), 70.6 (s, C-Cp_{unsubstit.}) ppm.

Synthesis of *p*-C₆H₄-[B(Fc)Br]₂ (2).

FcSnMe₃^[4] (1.8 g, 5.2 mmol) was dissolved in dichloromethane (40 mL) and added dropwise to a solution of *p*-C₆H₄-[BBr₂]₂^[5] (1.08 g, 2.6 mmol) in dichloromethane (20 mL) at -78 °C. The reaction mixture was warmed to room temperature and stirred overnight. All volatiles were removed and the crude product was sublimated (50 °C, HV) and obtained as a red solid (1.3 g, 2.0 mmol, 77%).

¹H NMR (600 MHz, CDCl₃): δ = 8.04 (s, 4H, *H*-phenylene), 4.93 (t, 4H, *H*-Cp_{substit.}), 4.69 (t, 4H, *H*-Cp_{substit.}), 4.20 (s, 10H, *H*-Cp_{unsubstit.}) ppm; ¹¹B NMR (192 MHz, CDCl₃): δ = 56.7 ppm; ¹³C NMR (150 MHz, CDCl₃): δ = 133.8 (s, C-phenylene), 78.0 (s, C-Cp_{substit.}), 77.6 (s, C-Cp_{substit.}), 70.9 (s, C-Cp_{unsubstit.}), not observed (*C*_{ipso}-Ph), (*C*_{ipso}-Cp) ppm.

Synthesis of FcB(Ph)NHP (3).

To a stirred solution of FcB(Ph)Br (1) (356.1 mg, 1.0 mmol) in dichloromethane (10 mL) was added PhNHTMS (167.1 mg, 1.01 mmol) dropwise at room temperature. The solution was stirred overnight and all volatiles were removed in *vacuo*. Crystallization of the crude product from *n*-hexane/DCM at -35 °C yielded in **3** as orange solid (206 mg, 56.4 mmol, 56%).

¹H NMR (600 MHz, CDCl₃): δ = 7.56 (s, 2H, *H*_{ortho}-BPh), 7.36 (s, 3H, *H*_{para}-BPh, *H*_{meta}-BPh), 7.13 (s, 2H, *H*_{meta}-NPh), 6.96 (s, 1H, *H*_{para}-NPh), 6.86 (s, 2H, *H*_{ortho}-BPh), 6.38 (s, 1H, NH), 4.50 (s, 2H, *H*-Cp_{substit.}), 4.34 (s, 2H, *H*-Cp_{substit.}), 4.20 (s, 5H, *H*-Cp_{unsubstit.}) ppm; ¹¹B NMR (192 MHz, CDCl₃): δ = 42.3 ppm; (**E**)-**isomer of 3**: ¹H NMR (500 MHz, -10 °C, CDCl₃): δ = 7.58 - 7.55 (m, 2H, *H*_{ortho}-BPh), 7.39 - 7.34 (m, 3H, *H*_{para}-BPh, *H*_{meta}-BPh), 7.14 (t, 2H, 2H, *H*_{meta}-NPh), 6.96 (t, 1H, *H*_{para}-NPh), 6.86 (d, 2H, *H*_{ortho}-BPh), 6.39 (br s, 1H, NH), 4.51 (t, 2H, *H*-Cp_{substit.}), 4.35 (t, 2H, *H*-Cp_{substit.}), 4.21 (s, 5H, *H*-Cp_{unsubstit.}) ppm; ¹³C NMR (150 MHz, 25 °C, CDCl₃): δ = 143.5 (s, *C*_{ipso}-NPh), 140.0 (s, *C*_{ipso}-BPh), 132.8 (s, *C*_{ortho}-BPh), 128.8 (s, *C*_{meta}-NPh), 128.3 (s, *C*_{para}-BPh), 127.7 (s, *C*_{meta}-BPh), 122.6 (s, *C*_{para}-NPh), 122.2 (s, *C*_{ortho}-NPh), 76.4

(br s, C_{ipso} -Cp), 73.8 (s, C-Cp_{substit.}), 72.6 (s, C-Cp_{substit.}), 68.8 (s, C-Cp_{unsubstit.}) ppm; **(Z)-isomer of 3**: ^1H NMR (500 MHz, -10°C , CDCl_3): δ = 8.12-8.10 (m, 1H, H -Ph), 7.89-7.86 (m, 2H, H -Ph), 7.48-7.46 (m, 3H, H -Ph), 7.31-7.29 (m, 2H, H -Ph), 7.23-7.22 (m, 1H, H -Ph), 6.15 (br s, 1H, NH), 4.57-4.56 (m, 2H, H -Cp_{substit.}), 4.09 (s, 5H, H -Cp_{unsubstit.}), 4.01 (m, 2H, H -Cp_{substit.}) ppm; ^{13}C NMR (150 MHz, 25°C , CDCl_3): δ = 134.5 (s, C-Ph), 132.8 (s, C-Ph), 128.0 (s, C-Ph), 127.7 (s, C-Ph), 122.5 (s, C-Ph), 75.6 (s, C-Cp_{substit.}), 69.0 (s, C-Cp_{unsubstit.}), 68.1 (s, C-Cp_{substit.}) ppm. HRMS (LIFDI) [M^+]: m/z calcd. 365.1033, found 365.1029.

Synthesis of $p\text{-C}_6\text{H}_4\text{-[NHB(Ph)Fc]}_2$ (**4**).

To a stirred solution of **FcB(Ph)Br** (**1**) (704.7 mg, 2.0 mmol) in dichloromethane (7 mL) was added $p\text{-C}_6\text{H}_4\text{-[NHTMS]}_2$ (252.6 mg, 1.0 mmol) in dichloromethane (3 mL) at room temperature. The solution was stirred overnight and all volatiles were removed *in vacuo*. Crystallization of the crude product from *n*-hexane/DCM at -35°C yielded in **4** as orange solid (440.0 mg, 0.67 mmol, 67%).

^1H NMR (500 MHz, CDCl_3): δ = 7.50 (s, 4H, H -Ph), 7.32 (s, 6H, H -Ph), 6.61 (s, 4H, H -phenylene), 6.25 (s, 2H, NH), 4.46 (s, 4H, H -Cp_{substit.}), 4.30 (s, 4H, H -Cp_{substit.}), 4.17 (s, 10H, H -Cp_{unsubstit.}) ppm; ^{11}B NMR (160 MHz, CDCl_3): δ = 41.5 ppm; **(E,E)-isomer of 4**: ^1H NMR (500 MHz, -10°C , CDCl_3): δ = 7.53-7.51 (m, 4H, H -Ph), 7.37-7.31 (m, 6H, 2H of the (E,Z)-isomer included in multiplet, H -Ph), 6.60 (s, 4H, H -phenylene), 6.26 (s, 2H, NH), 4.47 (t, 4H, H -Cp_{substit.}), 4.31 (t, 4H, H -Cp_{substit.}), 4.18 (s, 10H, H -Cp_{unsubstit.}) ppm; ^{13}C NMR (125 MHz, 25°C , CDCl_3): δ = 140.0 (br s, C_{ipso} -BPh), 138.4 (s, C_{ipso} -NPh), 133.0 (s, C-Ph), 132.3 (s, C-Ph), 128.2 (s, C-Ph), 127.8 (s, C-Ph), 127.6 (s, C-Ph), 122.8 (s, C_{ortho} -phenylene), 76.4 (s, C_{ipso} -Cp), 73.7 (s, C-Cp_{substit.}), 72.4 (s, C-Cp_{substit.}), 68.8 (s, C-Cp_{unsubstit.}) ppm; **(E,Z)-isomer of 4**: ^1H NMR (500 MHz, -10°C , CDCl_3): δ = 7.82-7.80 (m, 2H, H -Ph), 7.58-7.56 (m, 2H, H -Ph), 7.48-7.47 (m, 1H, H -Ph), 7.44-7.43 (m, 3H, H -Ph), 7.37-7.31 (m, 2H, included in multiplet of the main isomer, H -Ph), 7.03 (d, 2H, H -phenylene), 6.83 (d, 2H, H -phenylene), 6.41 (br s, 1H, NH), 5.98 (br s, 1H, NH), 4.52 (t, 2H, H -Cp_{substit.}), 4.38 (t, 2H, H -Cp_{substit.}), 4.36 (t, 2H, H -Cp_{substit.}), 4.23 (s, 5H, H -Cp_{unsubstit.}), 4.06 (s, 5H, H -Cp_{unsubstit.}), 3.94 (t, 2H, H -Cp_{substit.}) ppm; ^{13}C NMR (125 MHz, 25°C , CDCl_3): δ = 133.1 (s, C-Ph), 132.2 (s, C-Ph), 128.3 (s, C-Ph), 128.0 (s, C-Ph), 127.8 (s, C-Ph), 127.1 (s, C_{ortho} -phenylene), 123.2 (s, C_{ortho} -phenylene), 73.4 (s, C-Cp_{substit.}), 73.6 (s, C-Cp_{substit.}), 72.3 (s, C-Cp_{substit.}), 72.2 (s, C-Cp_{substit.}), 68.6 (s, C-Cp_{unsubstit.}) ppm; signals of **(Z,Z)-isomer of 4** are superimposed by the signals of the other, more dominant isomers. HRMS (LIFDI) [M^+]: m/z calcd. 652.1601, found 652.1595.

Synthesis of $p\text{-C}_6\text{H}_4\text{-[B(Fc)NHP]}_2$ (**5**).

To a stirred solution of $p\text{-C}_6\text{H}_4\text{-[FcB(Fc)Br]}_2$ (**2**) (628.7 mg, 1.0 mmol) in dichloromethane (7 mL) was added PhNHTMS (333.3 mg, 1.01 mmol) in dichloromethane (5 mL) at room temperature. The solution was stirred overnight and all volatiles were removed *in vacuo*. Crystallization of the crude product in *n*-hexane/DCM at -35°C yielded in **5** as an orange solid (536.0 mg, 0.82 mmol, 82%). ^1H NMR (500 MHz, CDCl_3): δ = 7.52 (s, 4H, H_{ortho} -phenylene), 7.15 (s, 4H, H_{meta} -NPh), 6.94 (m, 6H, H_{para} -NPh, H_{ortho} -NPh), 6.38 (s, 2H, NH), 4.51 (s, 4H, H -Cp_{substit.}), 4.39 (s, 4H, H -Cp_{substit.}), 4.21 (s, 10H, H -Cp_{unsubstit.}) ppm; ^{11}B NMR (160 MHz, CDCl_3): δ = 41.6 ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 143.7 (s, C_{ipso} -NPh), 139.9

(br s, C_{ipso} -BPh), 131.7 (s, C_{ortho} -phenylene), 128.7 (s, C_{meta} -NPh), 122.5 (s, C_{para} -NPh), 122.1 (s, C_{ortho} -NPh), 76.3 (s, C_{ipso} -Cp), 73.7 (s, C-Cp_{substit.}), 72.6 (s, C-Cp_{substit.}), 68.8 (s, C-Cp_{unsubstit.}) ppm. HRMS (LIFDI) [M^+]: m/z calcd. 652.1601; found 652.1585.

Synthesis of macrocycle *cyclo*-[B(Fc)NH-*p*-C₆H₄-NHB(Fc)-*p*-C₆H₄]₂ (**6**)

To a stirred solution of *p*-C₆H₄-[FcB(Fc)Br]₂ (**2**) (314.6 mg, 0.5 mmol) in dichloromethane (0.2 mL) was added *p*-C₆H₄-[NHTMS]₂ (126.6 mg, 0.5 mmol) in dichloromethane (0.8 mL) at room temperature. During addition the solid dissolved. The red orange-red mixture was stirred for 24 h. Subsequently, the mixture was precipitated into cooled (−78 °C) pentane (30 mL). The supernatant liquid was removed by filtration and the product was dried *in vacuo* to give **6** as an orange solid (276.6 mg, 0.24 mmol, 48%). ¹H NMR (300 MHz, CDCl₃): δ = 7.49 (s, 8H, H_{ortho} -phenylene-B), 6.57 (s, 8H, H_{ortho} -phenylene-NH), 6.27 (s, 4H, NH), 4.47 (t, 8H, H -Cp_{substit.}), 4.34 (t, 8H, H -Cp_{substit.}), 4.19 (s, 20H, H -Cp_{unsubstit.}) ppm; ¹¹B NMR (160 MHz, CDCl₃): δ = 42.4 ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 140.3 (br s, C_{ipso} -BPh), 138.1 (s, C_{ipso} -NPh), 131.2 (s, C-phenylene), 120.9 (s, C-phenylene), 73.5 (s, C-Cp_{substit.}), 72.4 (s, C-Cp_{substit.}), 68.8 (s, C-Cp_{unsubstit.}) ppm. HRMS (LIFDI) [M^+]: m/z calcd. 1148.2269; found 1148.2285.

NMR Spectra

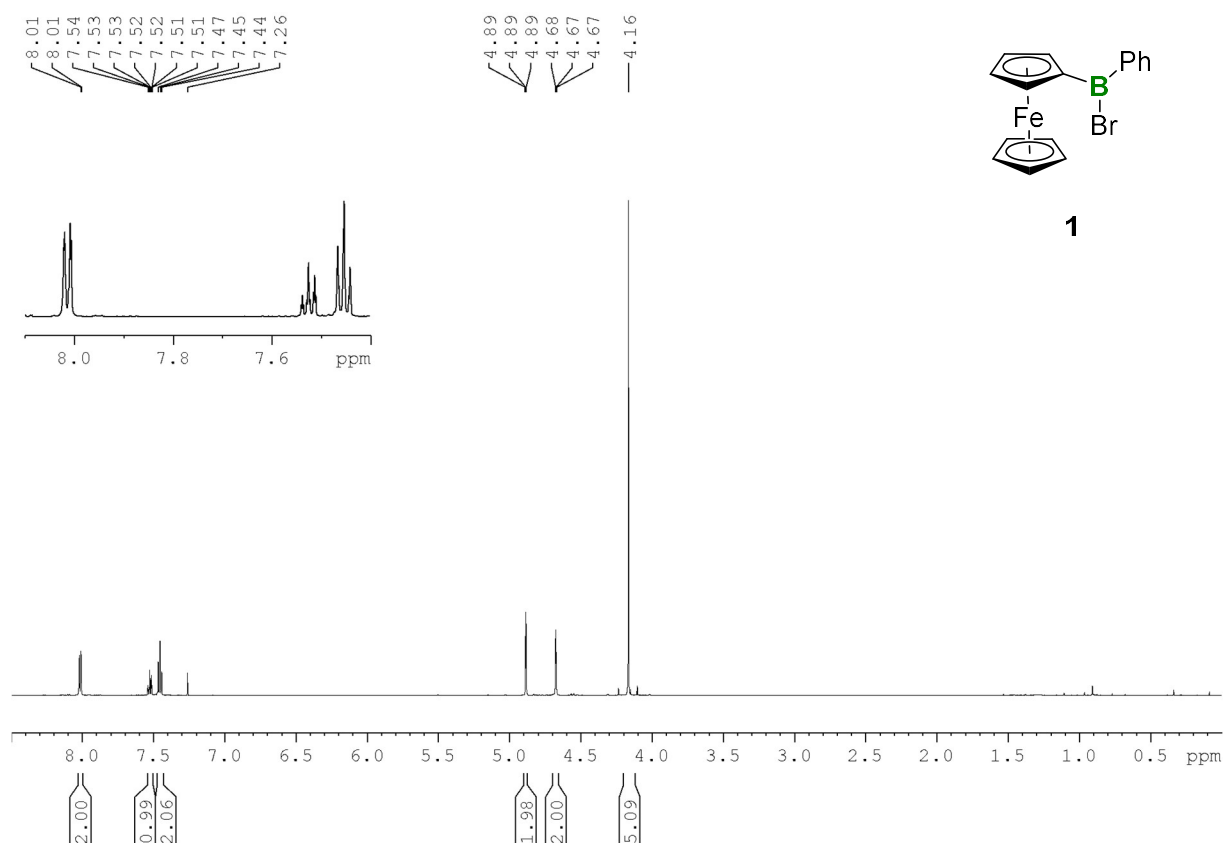


Figure S1. ¹H NMR spectrum of **FcB(Ph)Br (1)** (600 MHz, in CDCl₃).

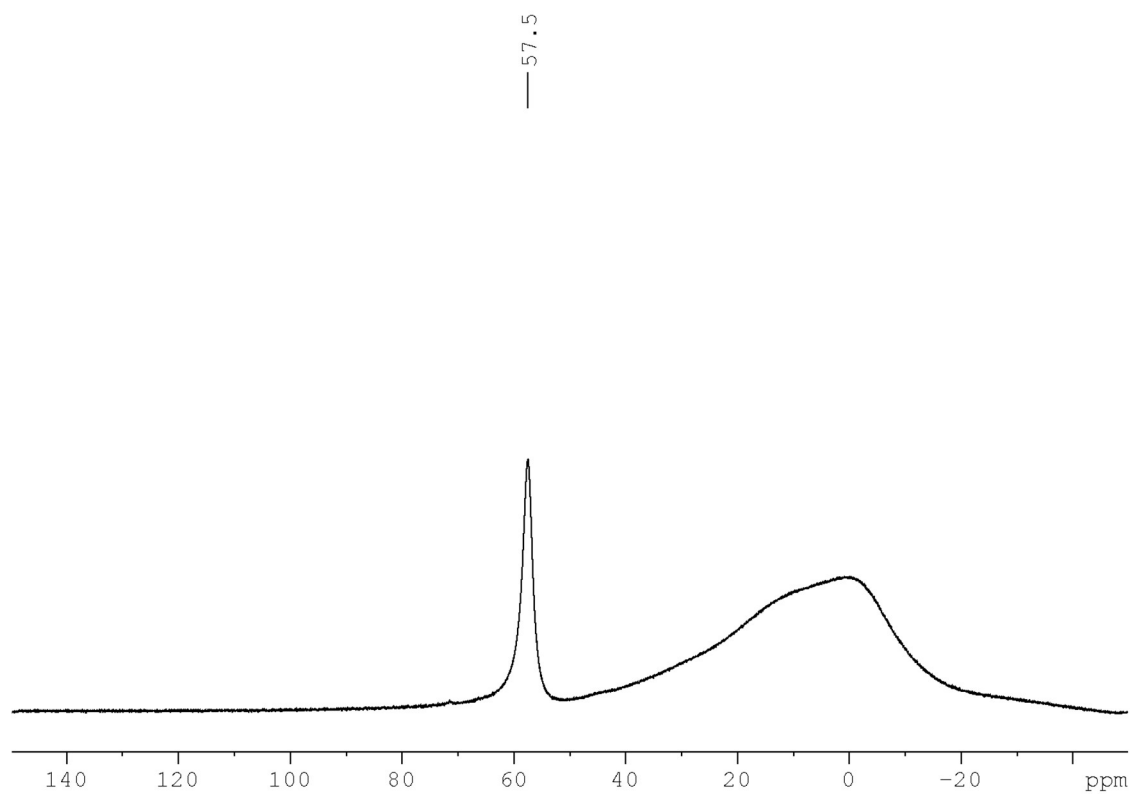


Figure S2. ¹¹B{¹H} NMR spectrum of **FcB(Ph)Br (1)** (192 MHz, in CDCl₃).

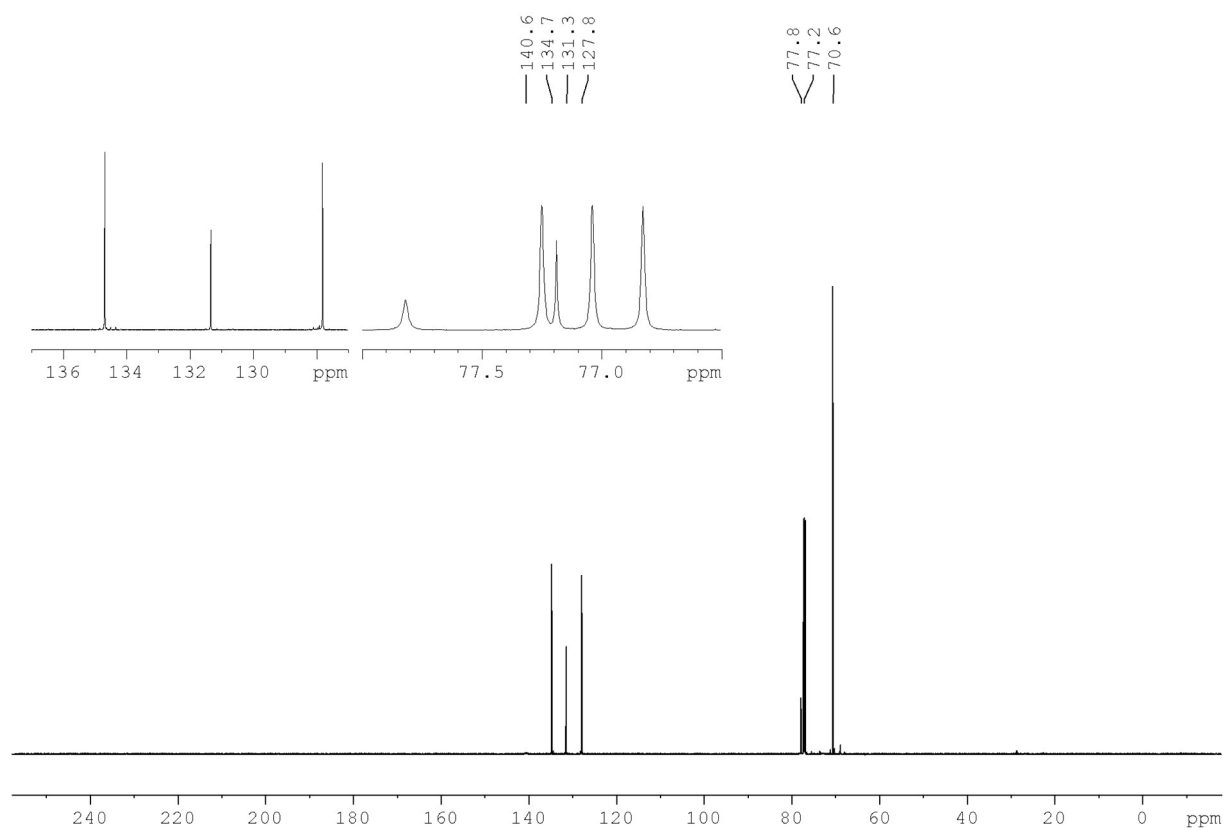


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **FcB(Ph)Br (1)** (150 MHz, in CDCl_3).

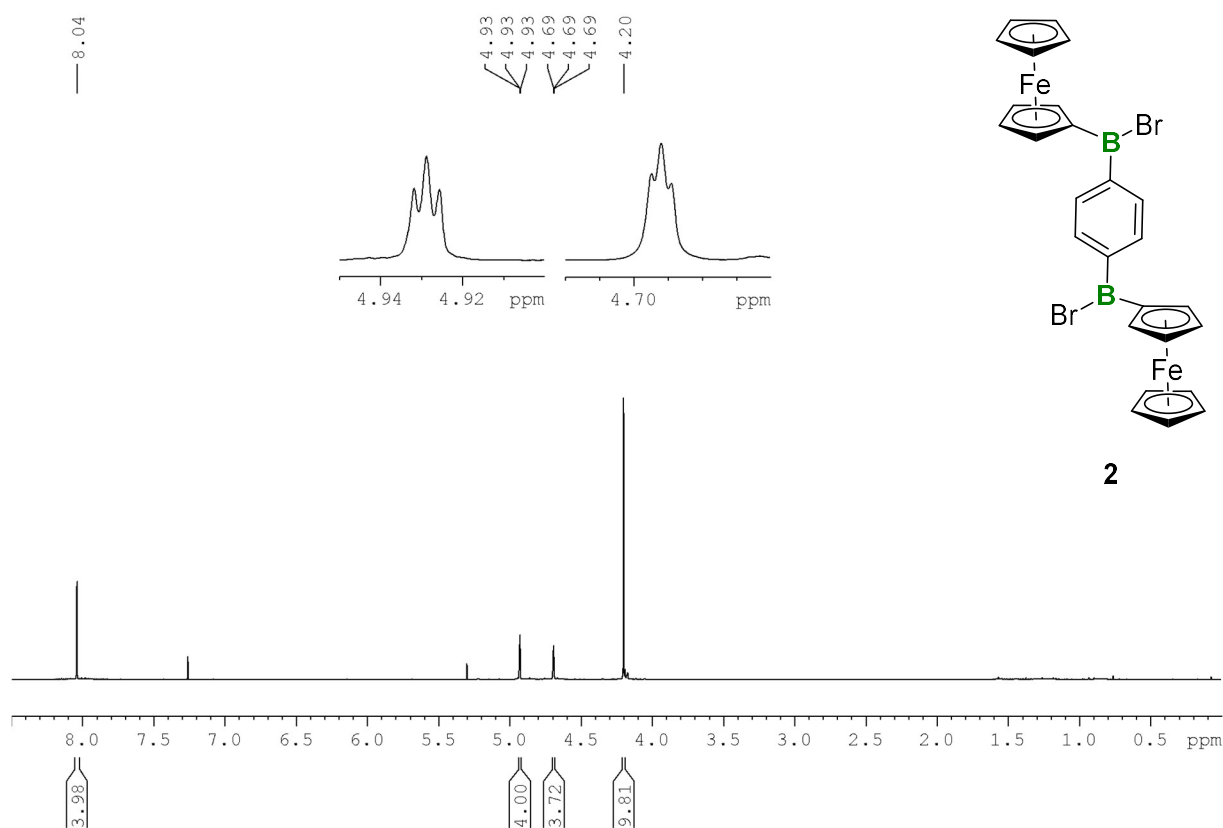


Figure S4. ^1H NMR spectrum of ***p*-C₆H₄-[B(Fc)Br]₂ (2)** (600 MHz, in CDCl_3).

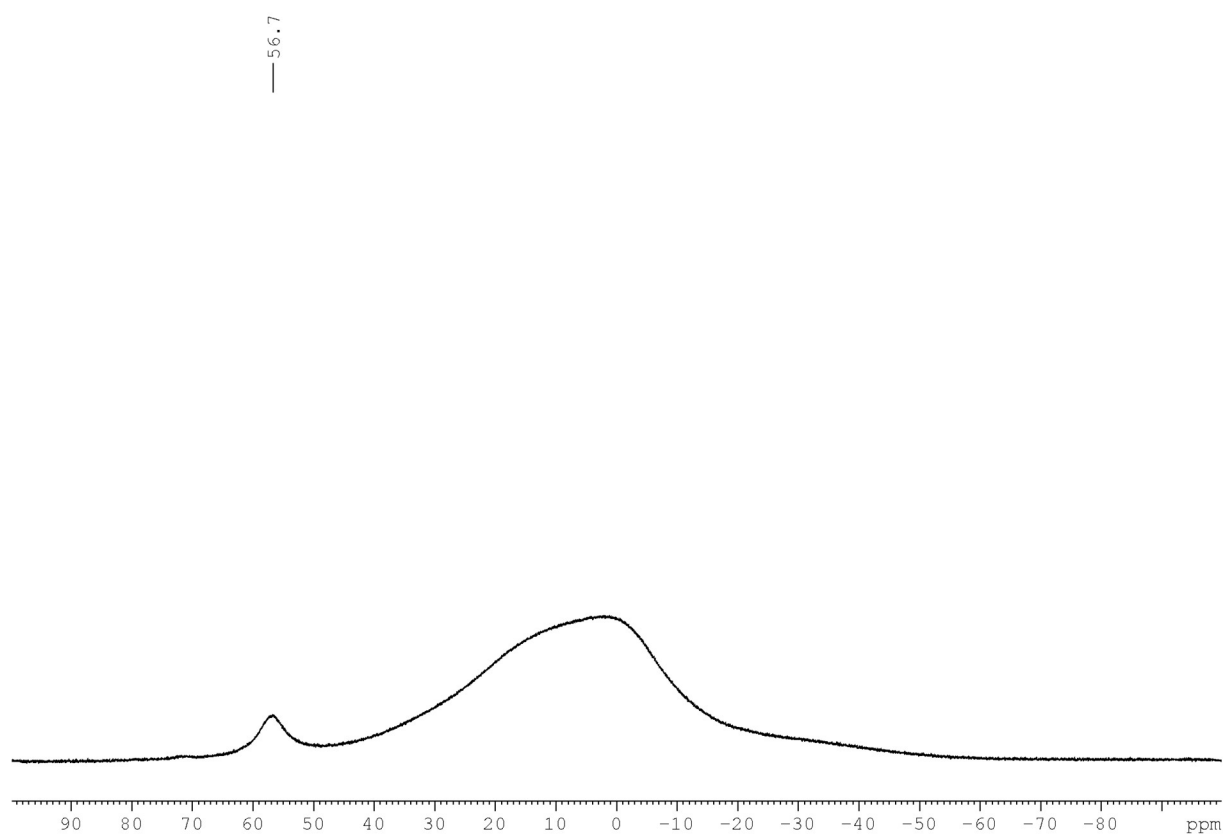


Figure S5. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of $p\text{-C}_6\text{H}_4\text{-[B(Fc)Br]}_2$ (**2**) (192 MHz, in CDCl_3).

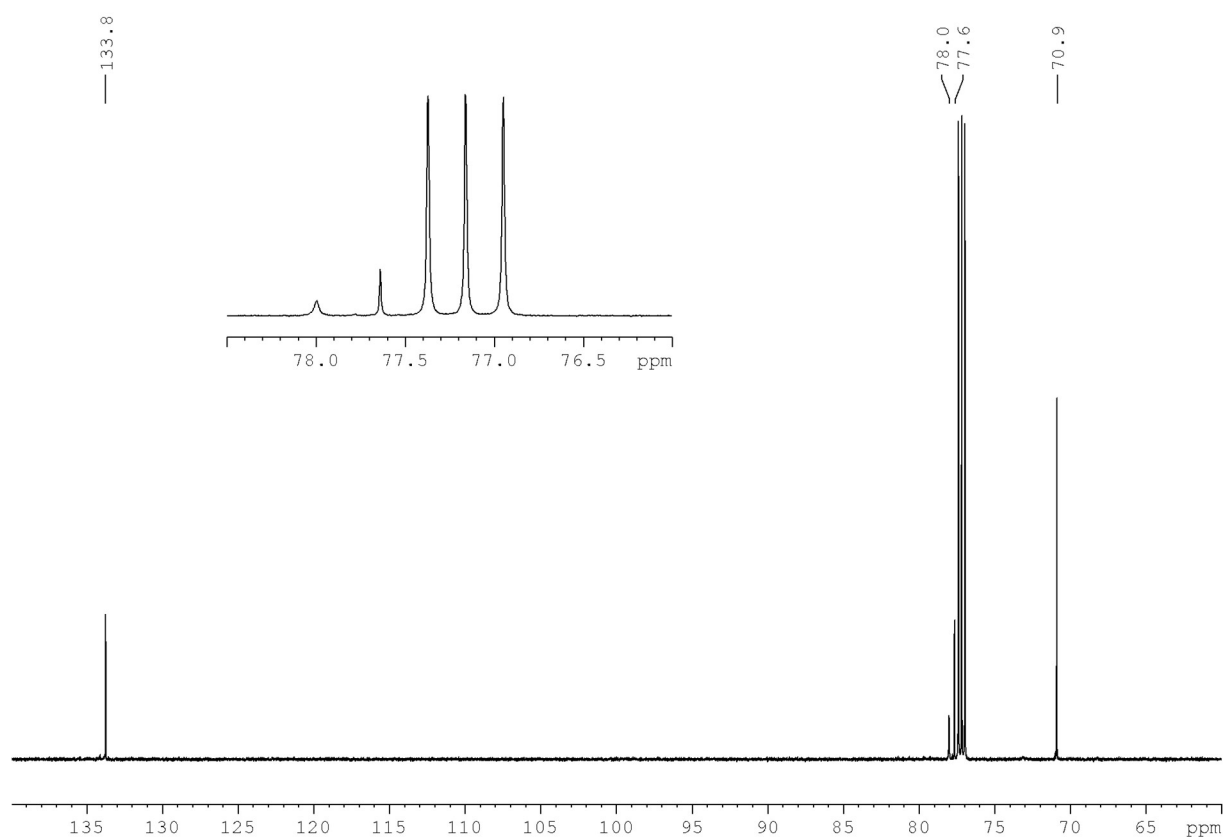


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $p\text{-C}_6\text{H}_4\text{-[B(Fc)Br]}_2$ (**2**) (150 MHz, in CDCl_3).

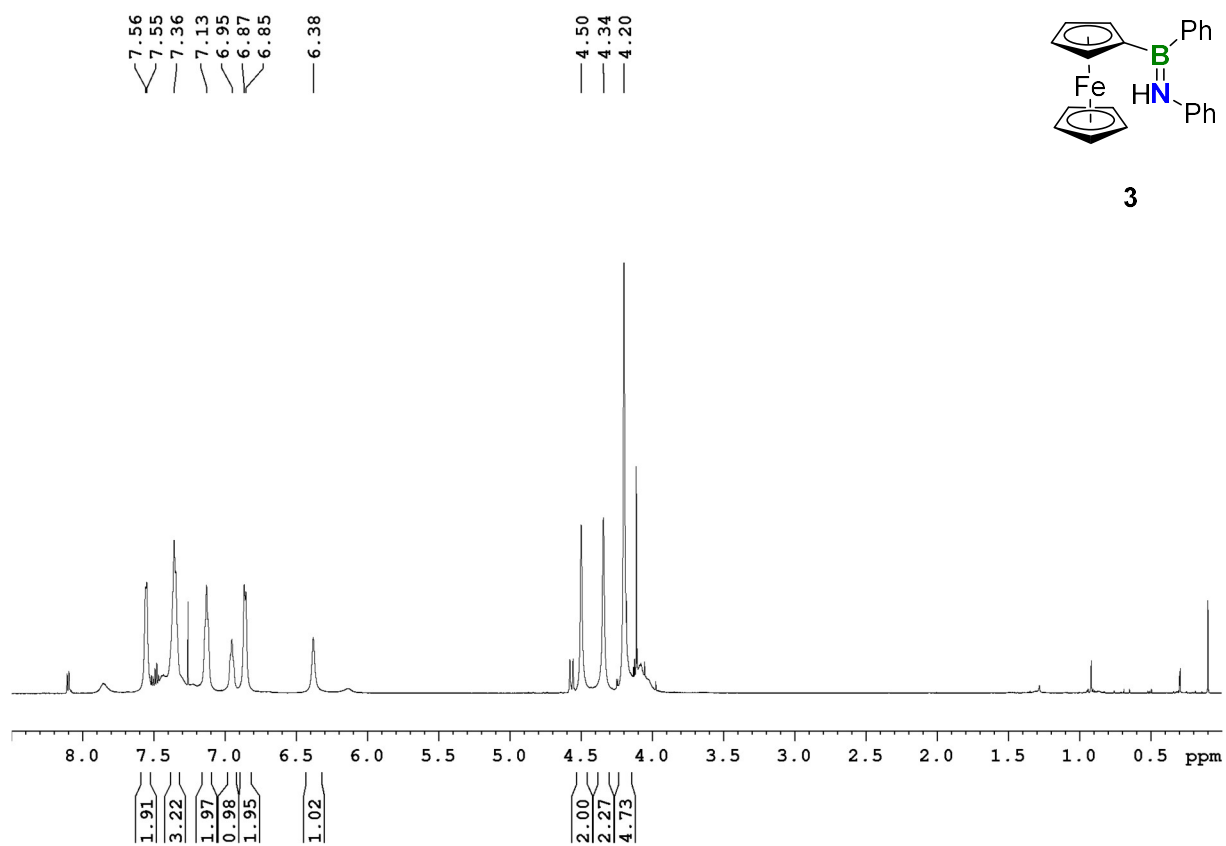


Figure S7. ¹H NMR spectrum of **3** (600 MHz, in CDCl₃).

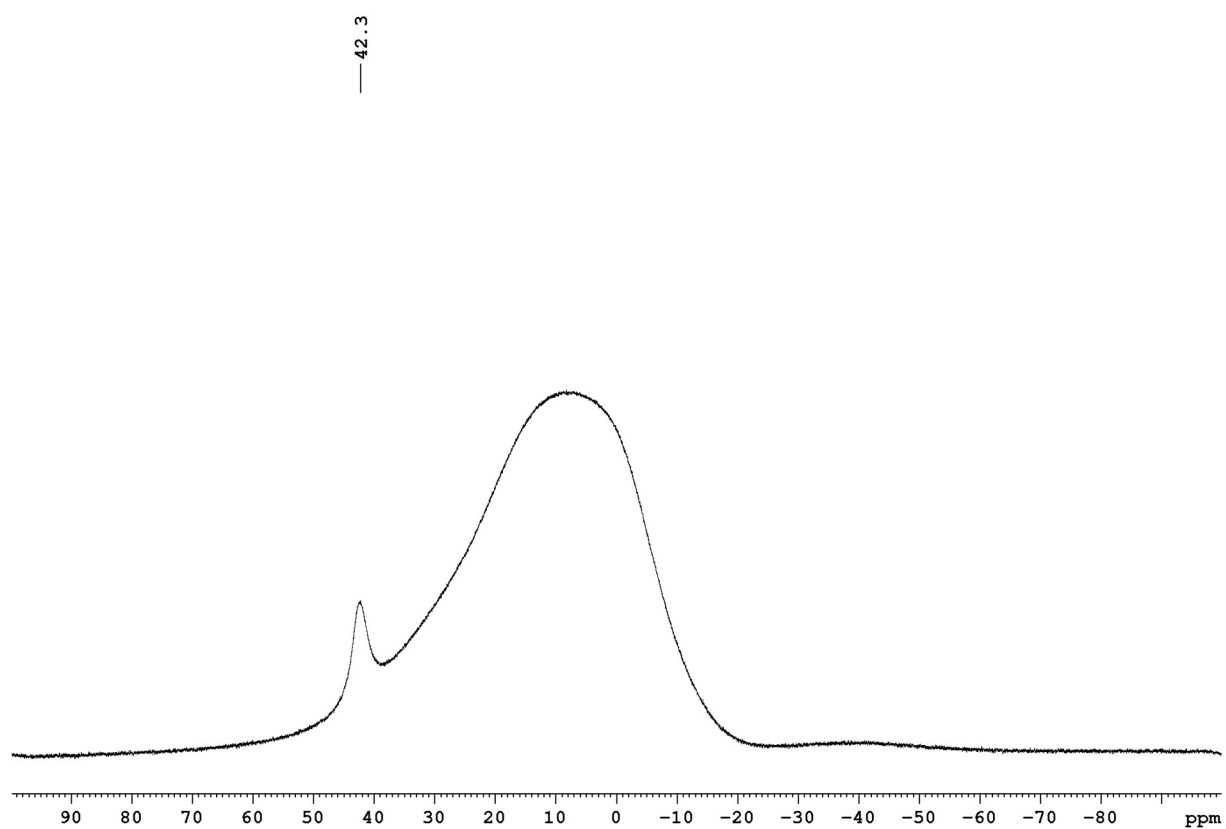


Figure S8. ¹¹B{¹H} NMR spectrum of **3** (192 MHz, in CDCl₃).

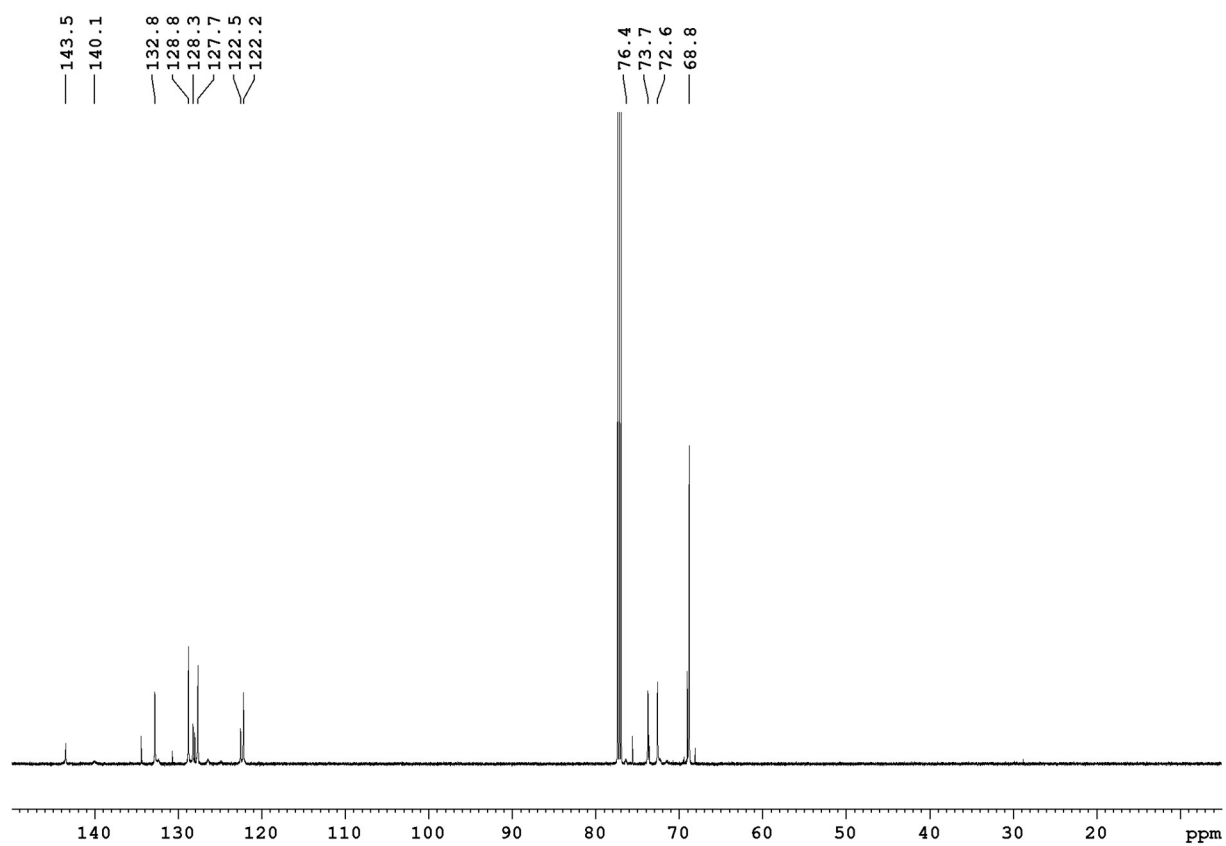


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **3** (150 MHz, in CDCl_3).

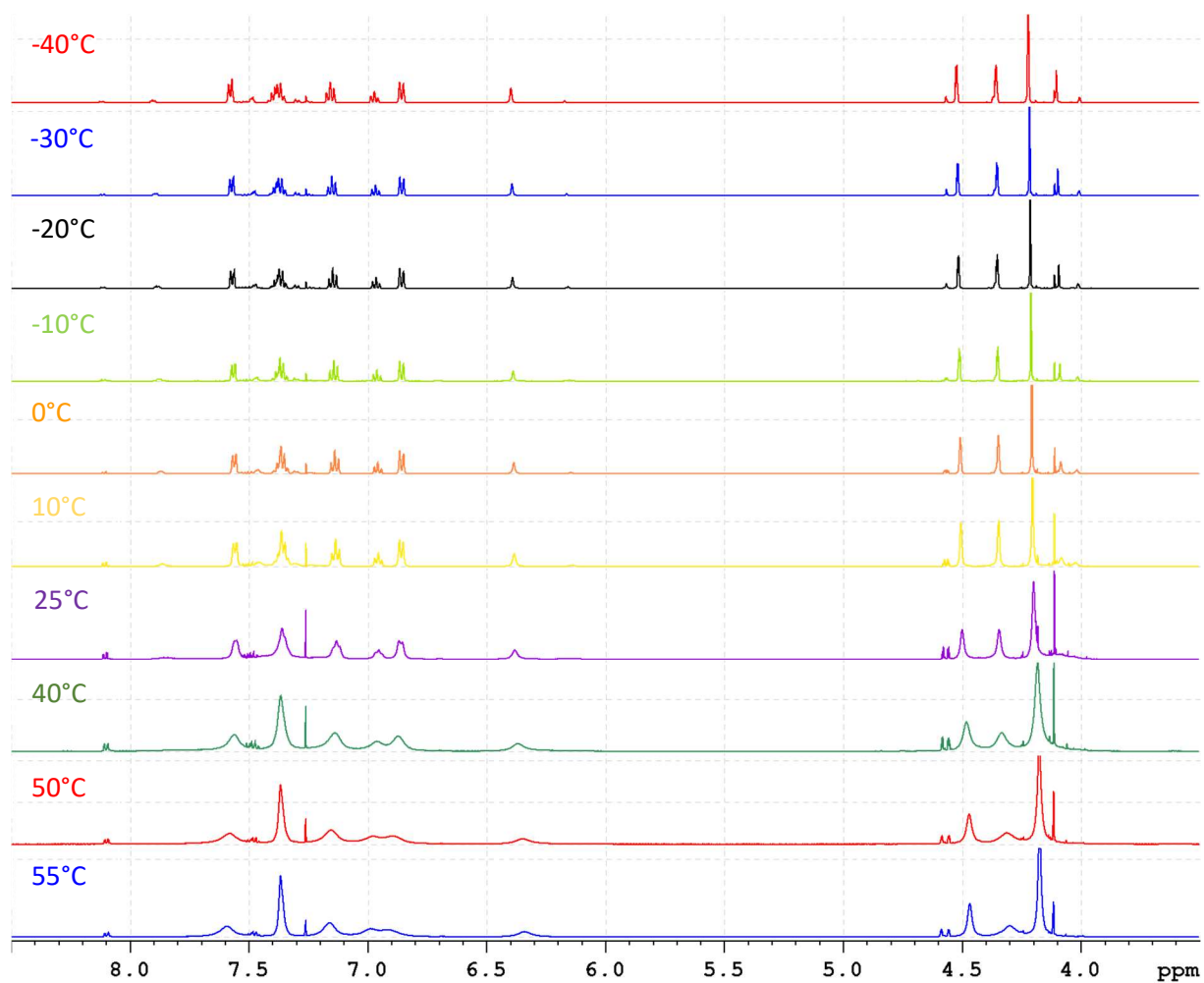


Figure S10. VT-¹H NMR spectra of **3** (500 MHz, in CDCl₃).

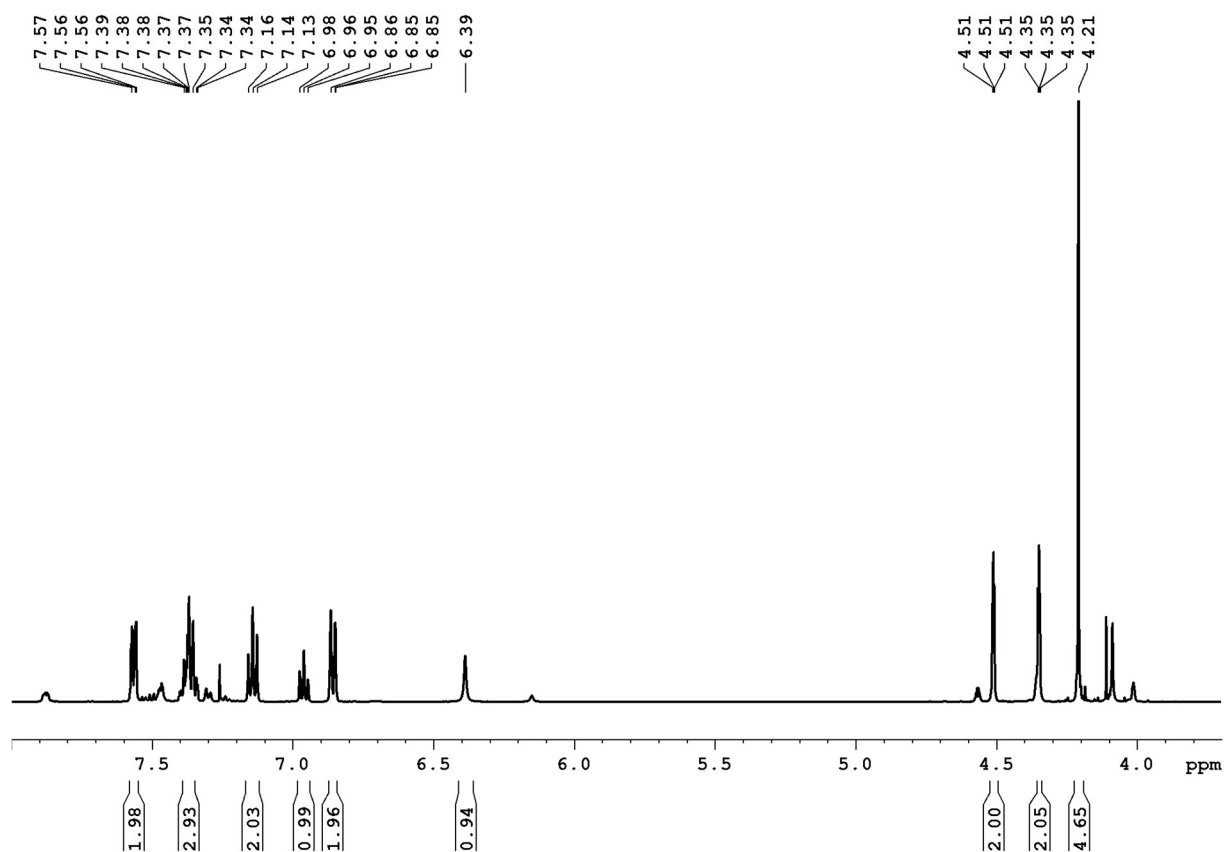


Figure S11. ¹H spectrum of the (*E*)-Isomer of **3** (at -10°C, 500 MHz, in CDCl₃).

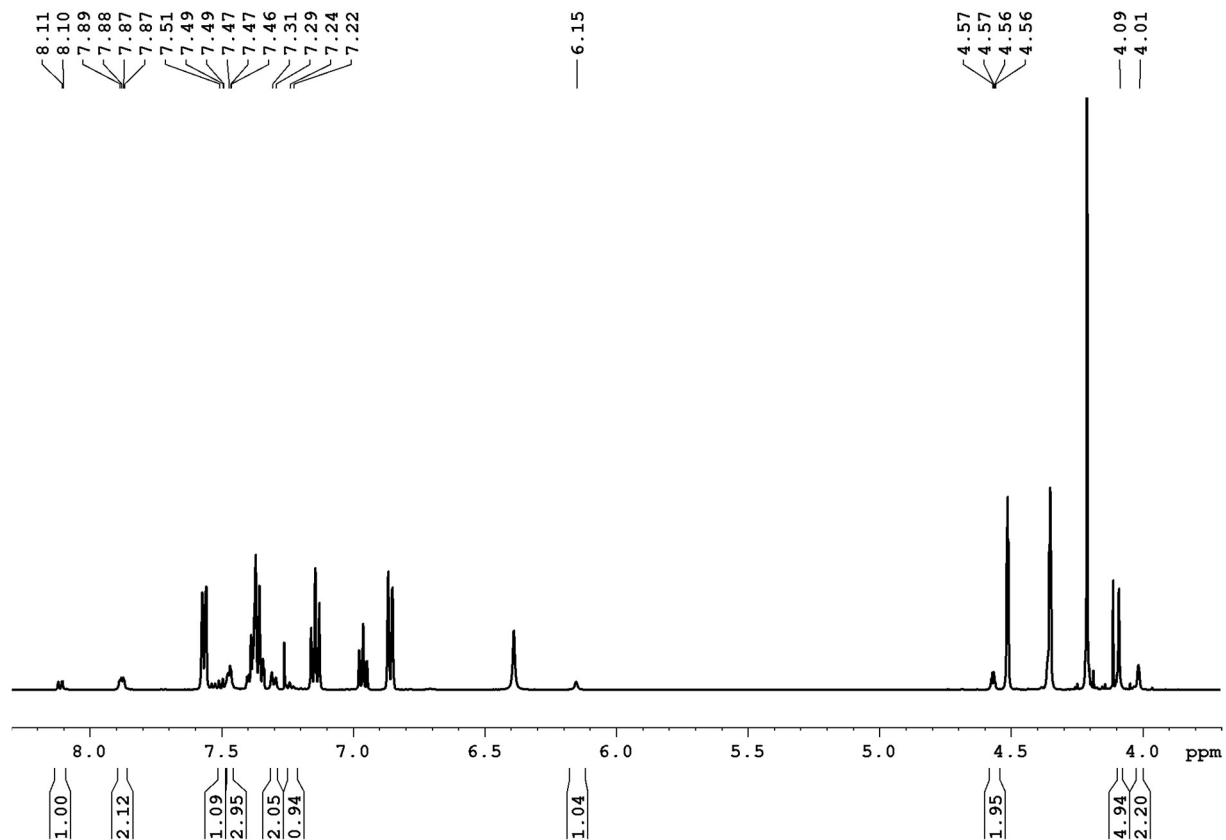


Figure S12. ¹H spectrum of the (*Z*)-Isomer of **3** (at -10°C, 500 MHz, in CDCl₃).

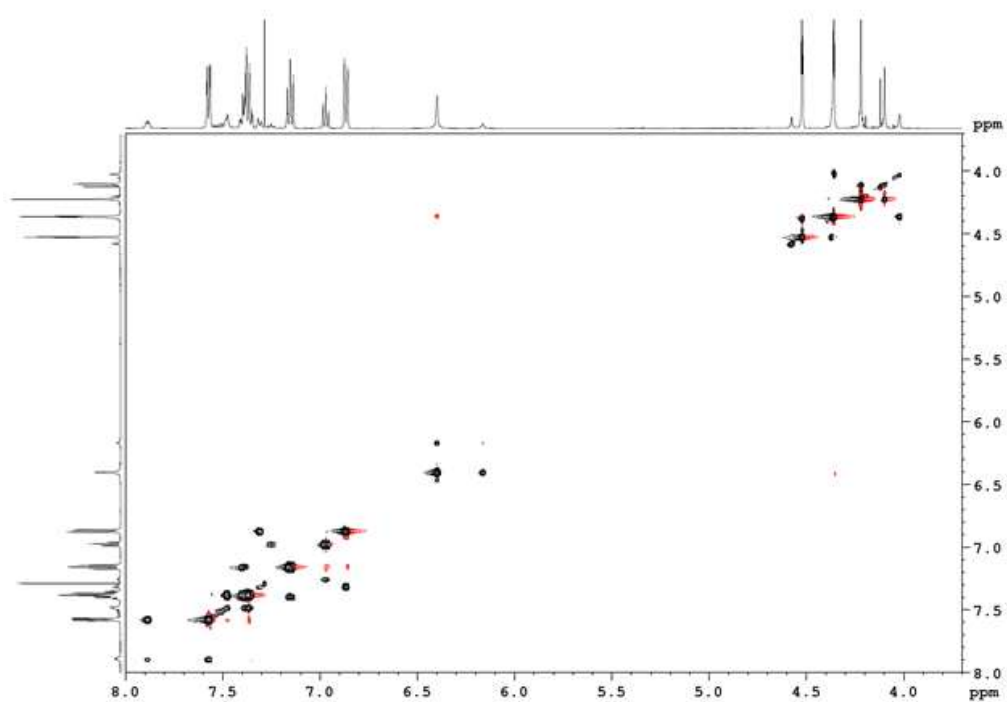


Figure S13. Detail of ^1H , ^1H NOESY spectrum of **3** (at -10°C , 500 MHz, in CDCl_3).

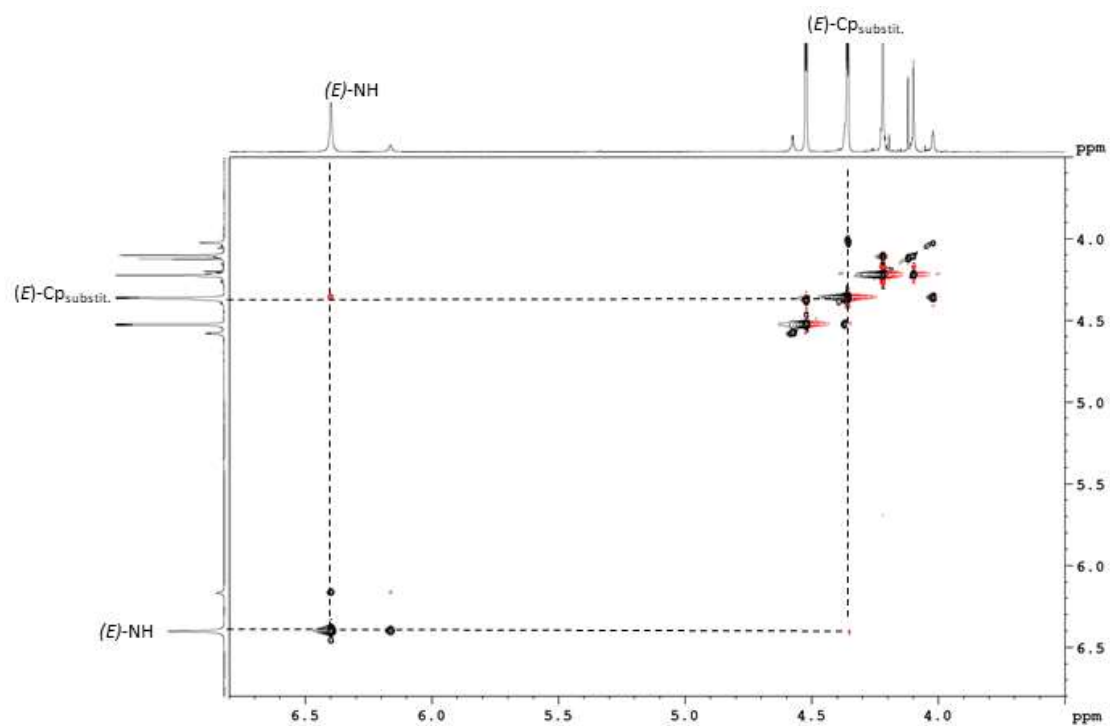


Figure S14. Detail of ^1H , ^1H NOESY spectrum of **3** (at -10°C , 500 MHz, in CDCl_3).

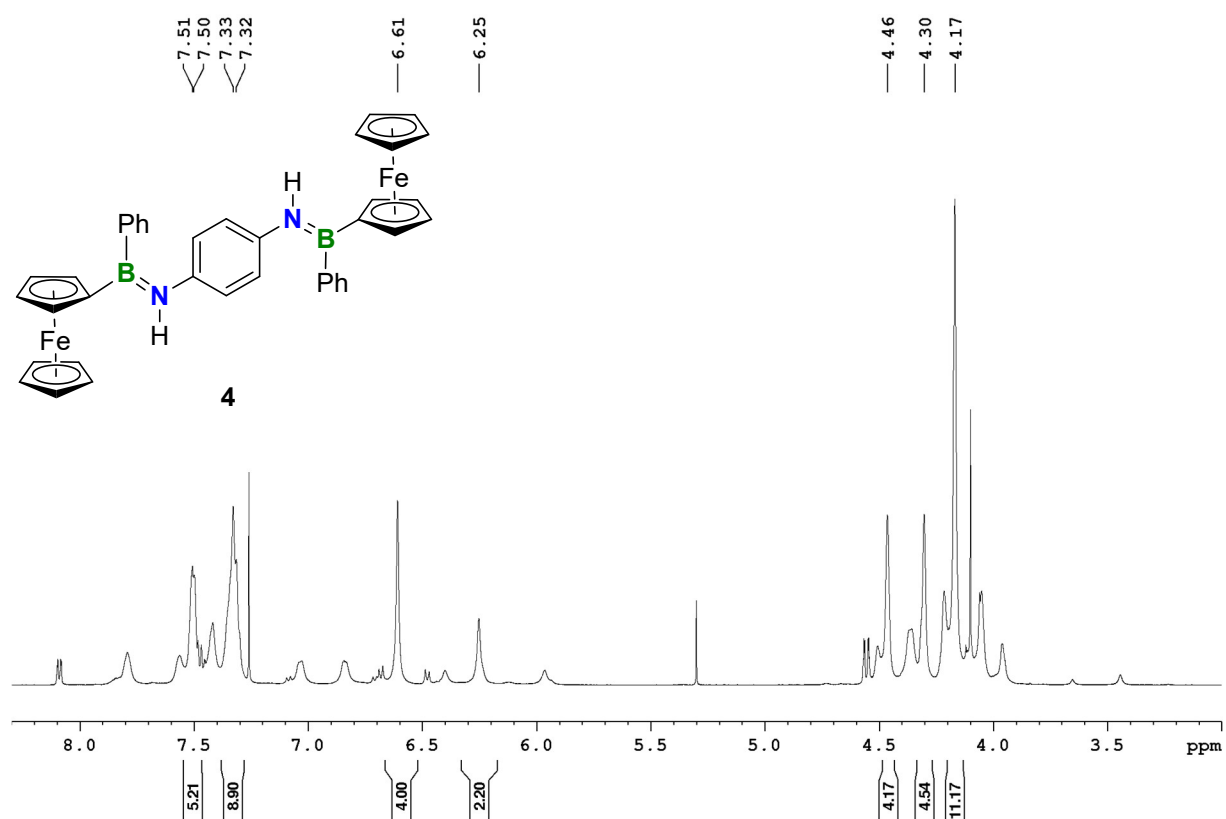


Figure S15. ¹H NMR spectrum of **4** (500 MHz, in CDCl₃).

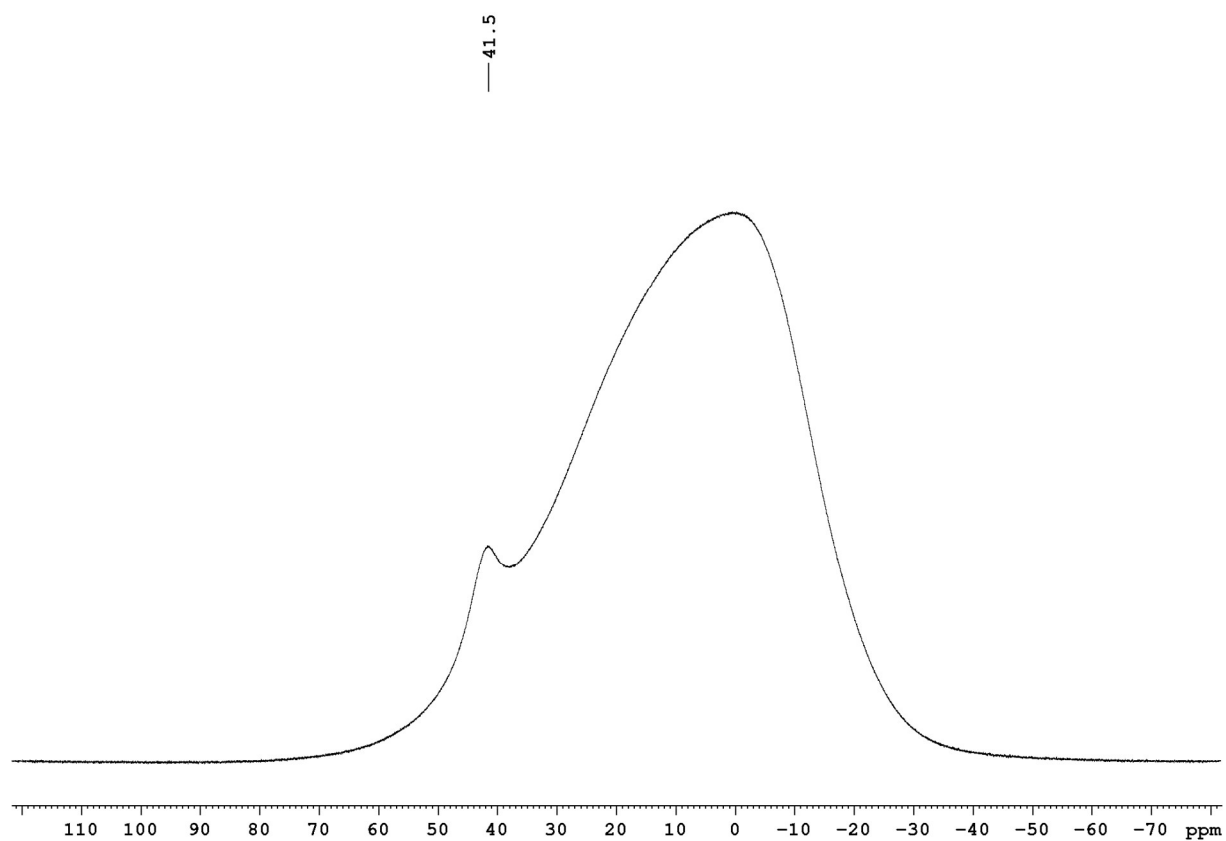


Figure S16. ¹¹B{¹H} NMR spectrum of **4** (160 MHz, in CDCl₃).

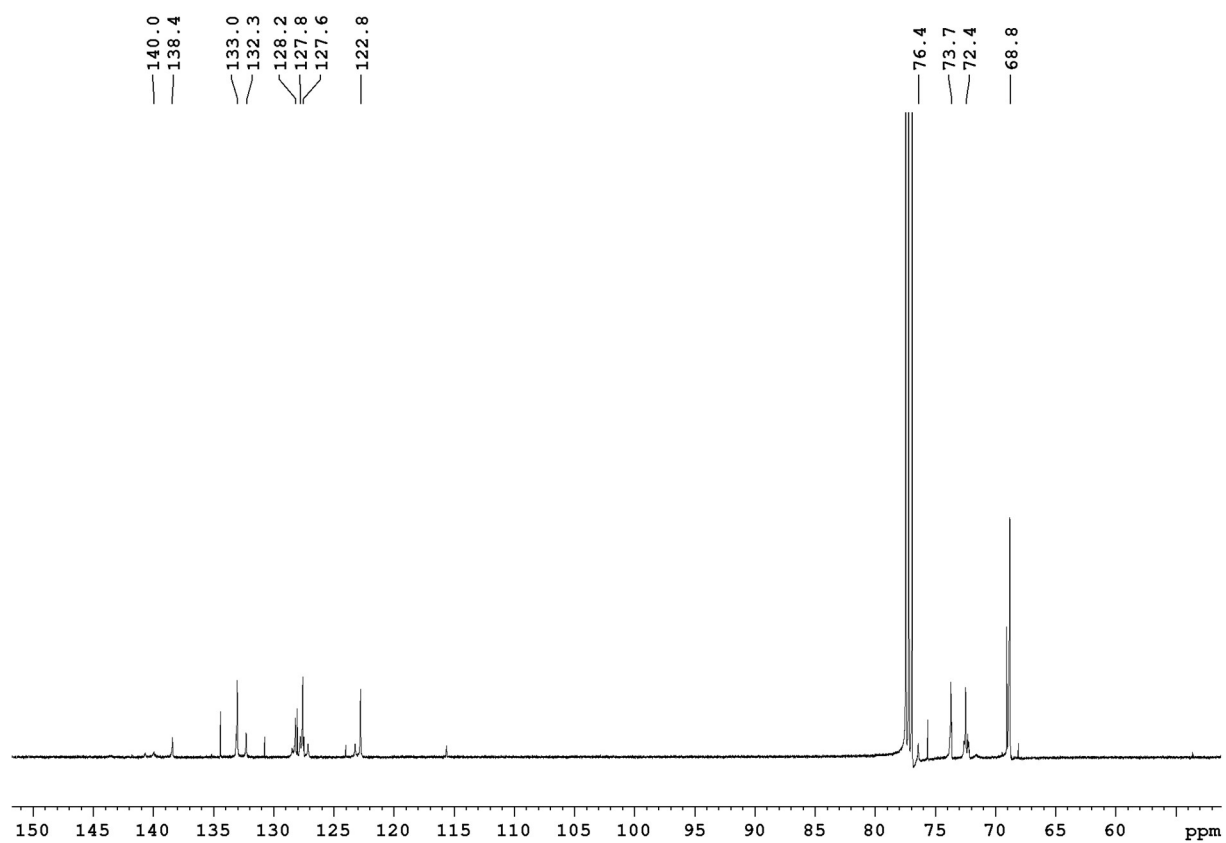


Figure S17. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **4** (125 MHz, in CDCl_3).



Figure S18. VT-¹H NMR spectra of **4** (500 MHz, in CDCl₃).

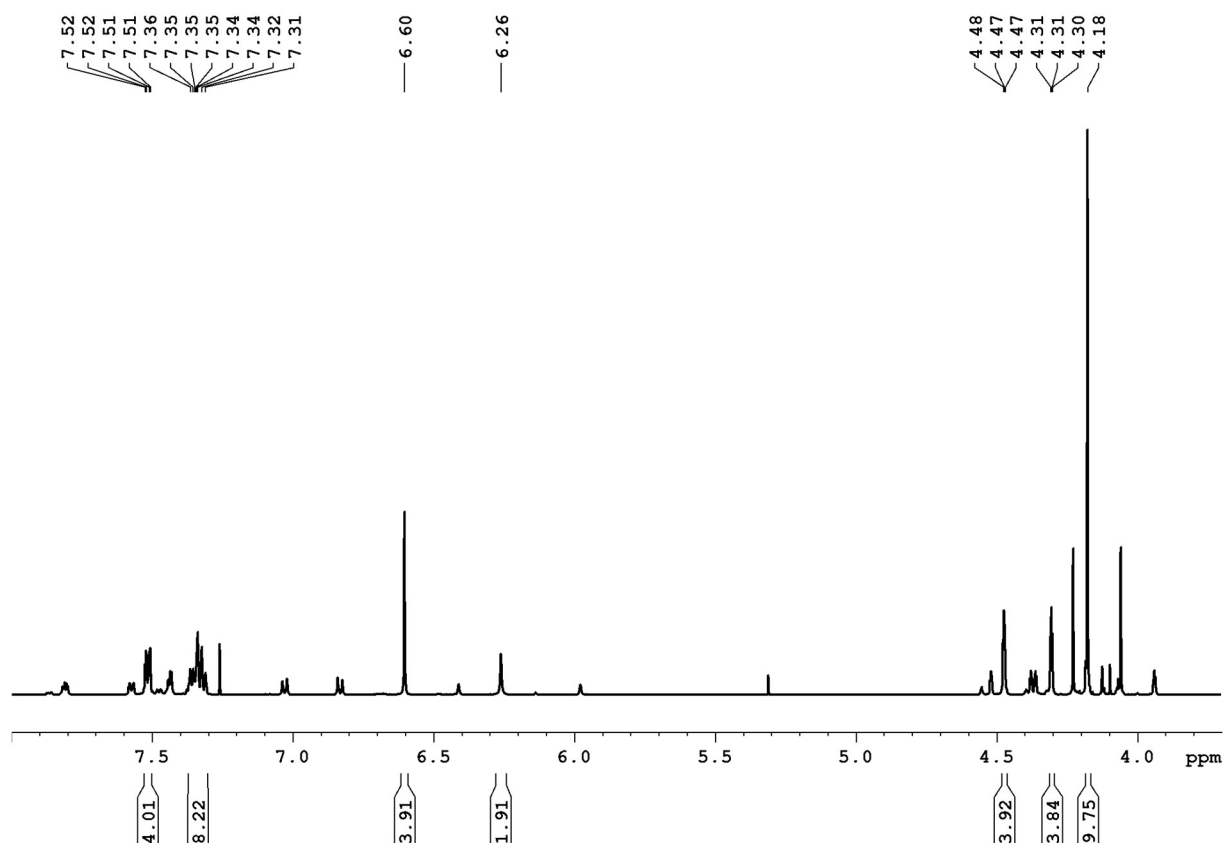


Figure S19. ¹H spectrum of the (E,E)-Isomer of **4** (at -10°C, 500 MHz, in CDCl₃).

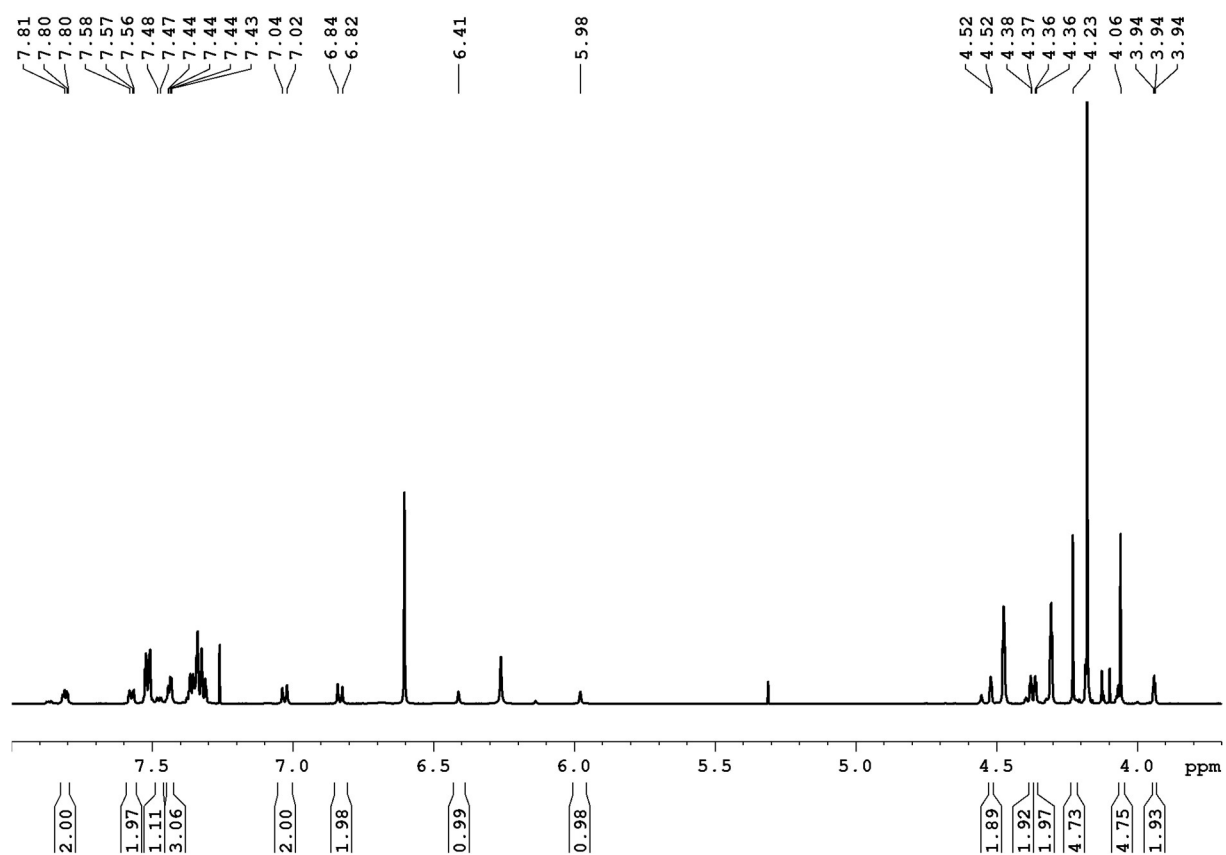


Figure S20. ¹H spectrum of the (E,Z)-Isomer of **4** (at -10°C, 500 MHz, in CDCl₃).

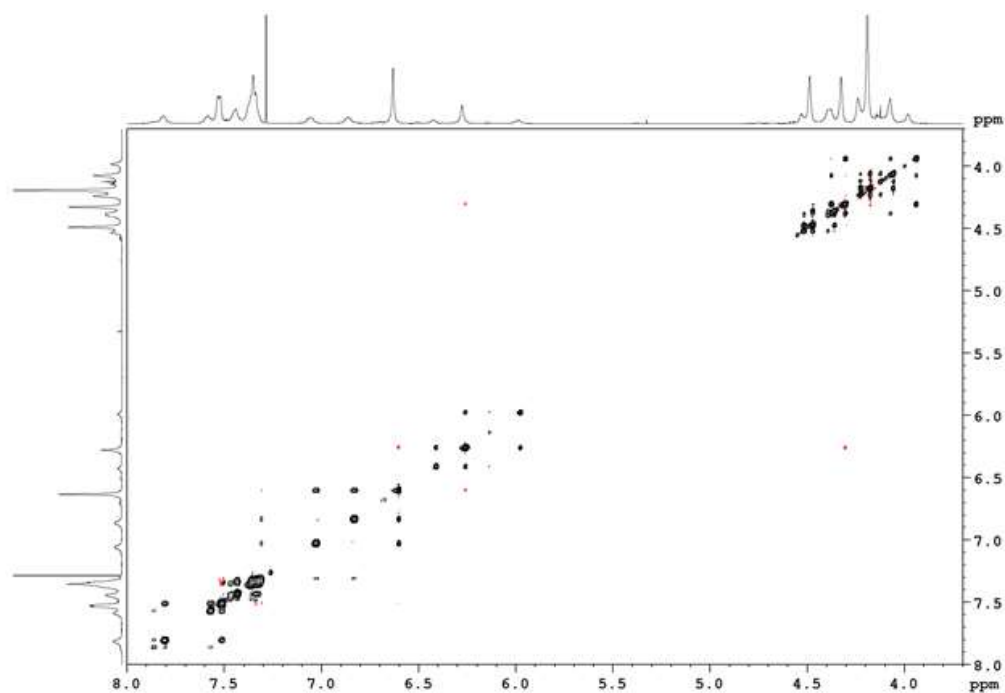


Figure S21. Detail of ^1H , ^1H NOESY spectrum of **4** (at -10°C , 500 MHz, in CDCl_3).

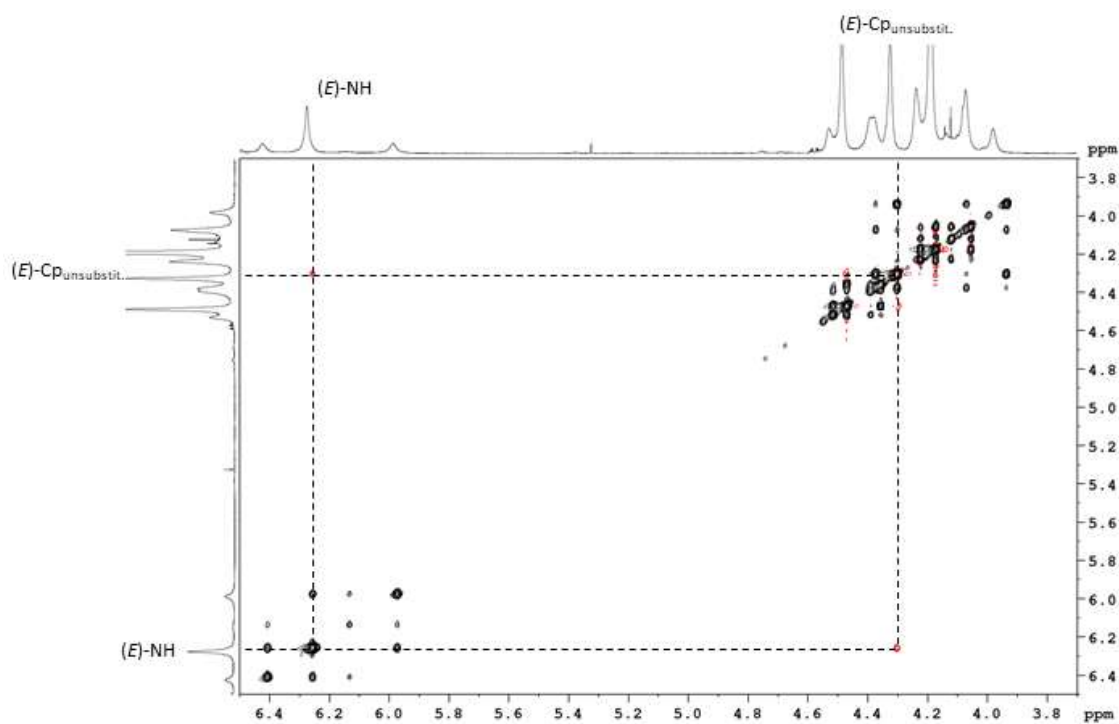


Figure S22. Detail of ^1H , ^1H NOESY spectrum of **4** (at -10°C , 500 MHz, in CDCl_3).

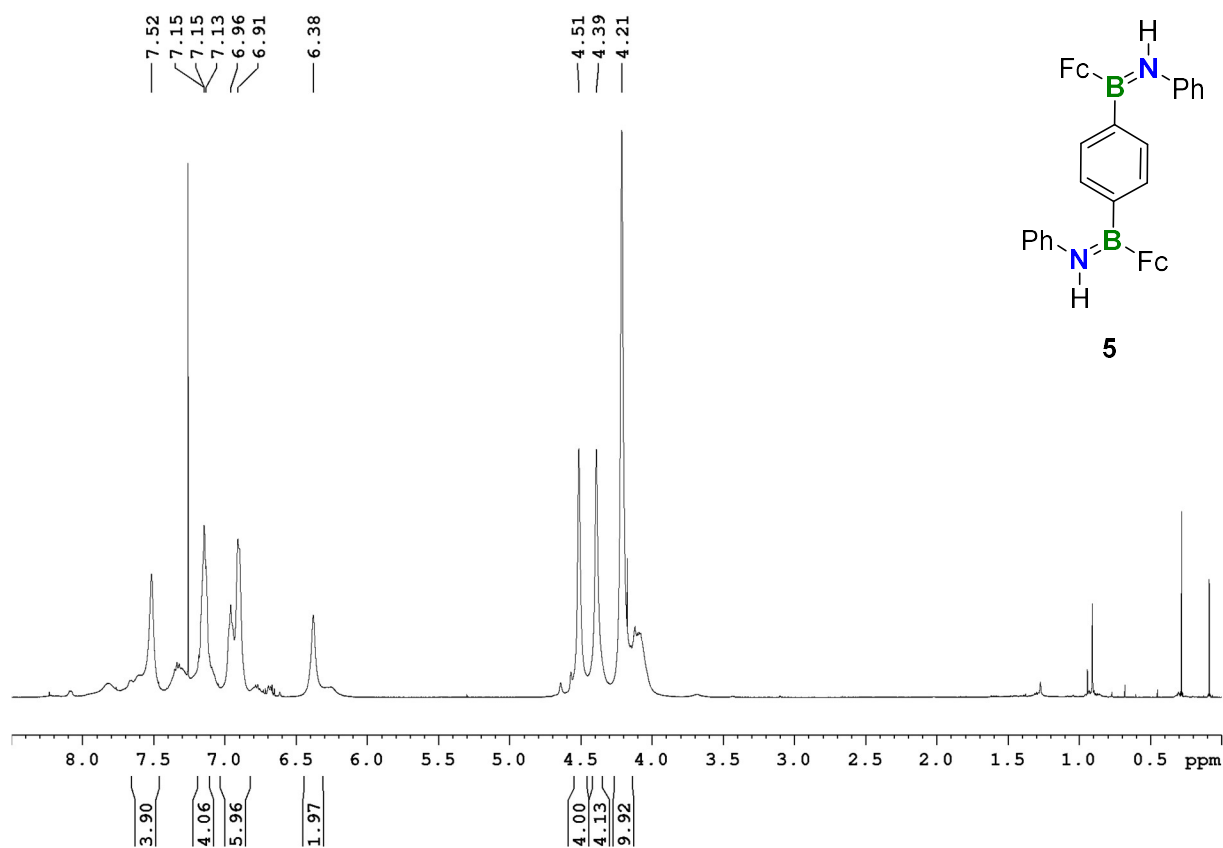


Figure S23. ¹H NMR spectrum of **5** (500 MHz, in CDCl₃).

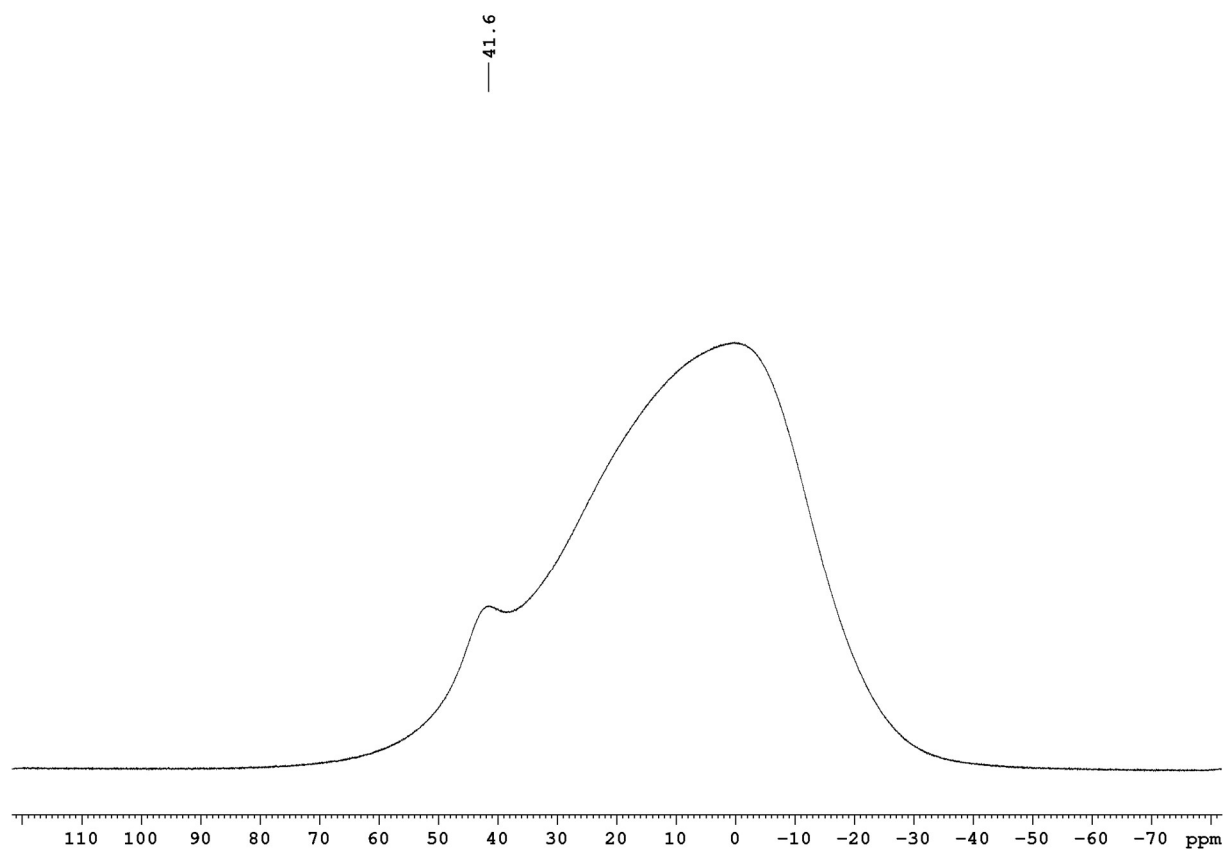


Figure S24. ¹¹B{¹H} NMR spectrum of **5** (160 MHz, in CDCl₃).

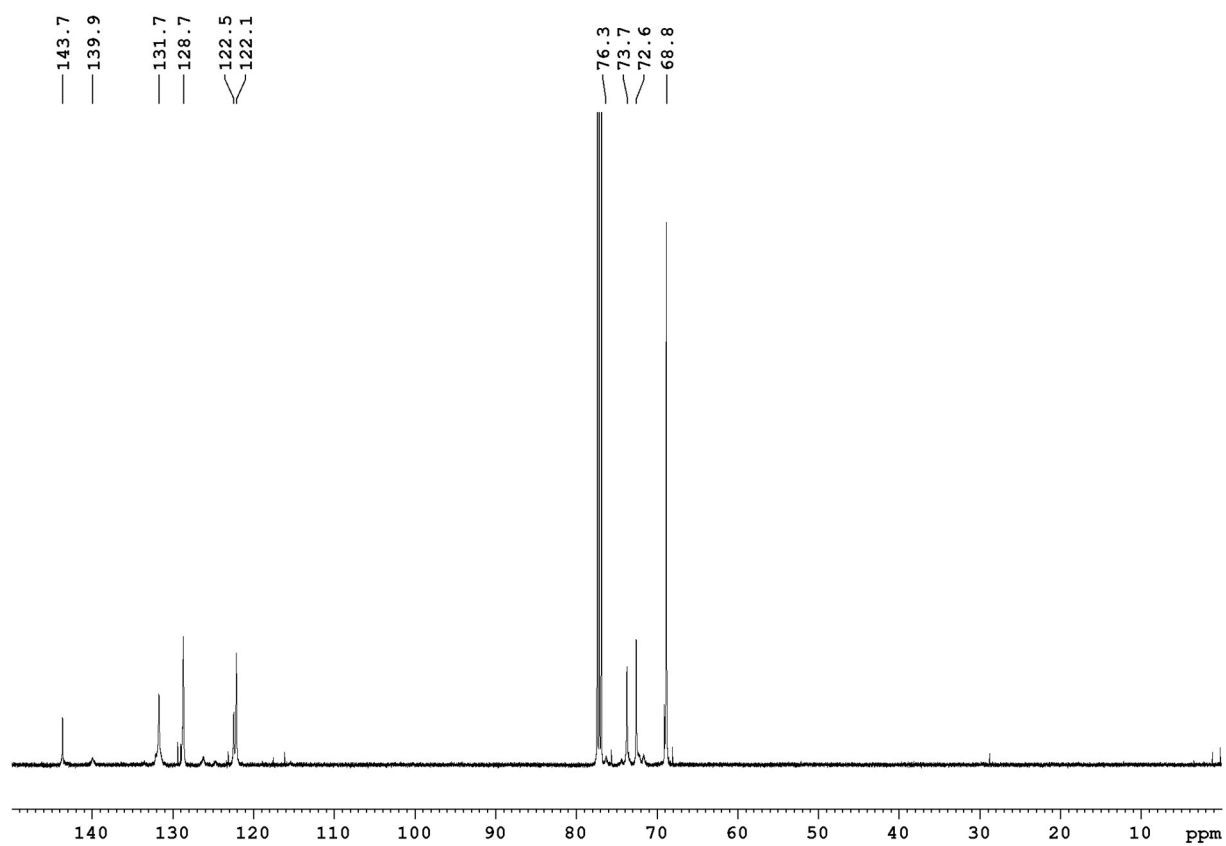


Figure S25. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **5** (125 MHz, in CDCl_3).

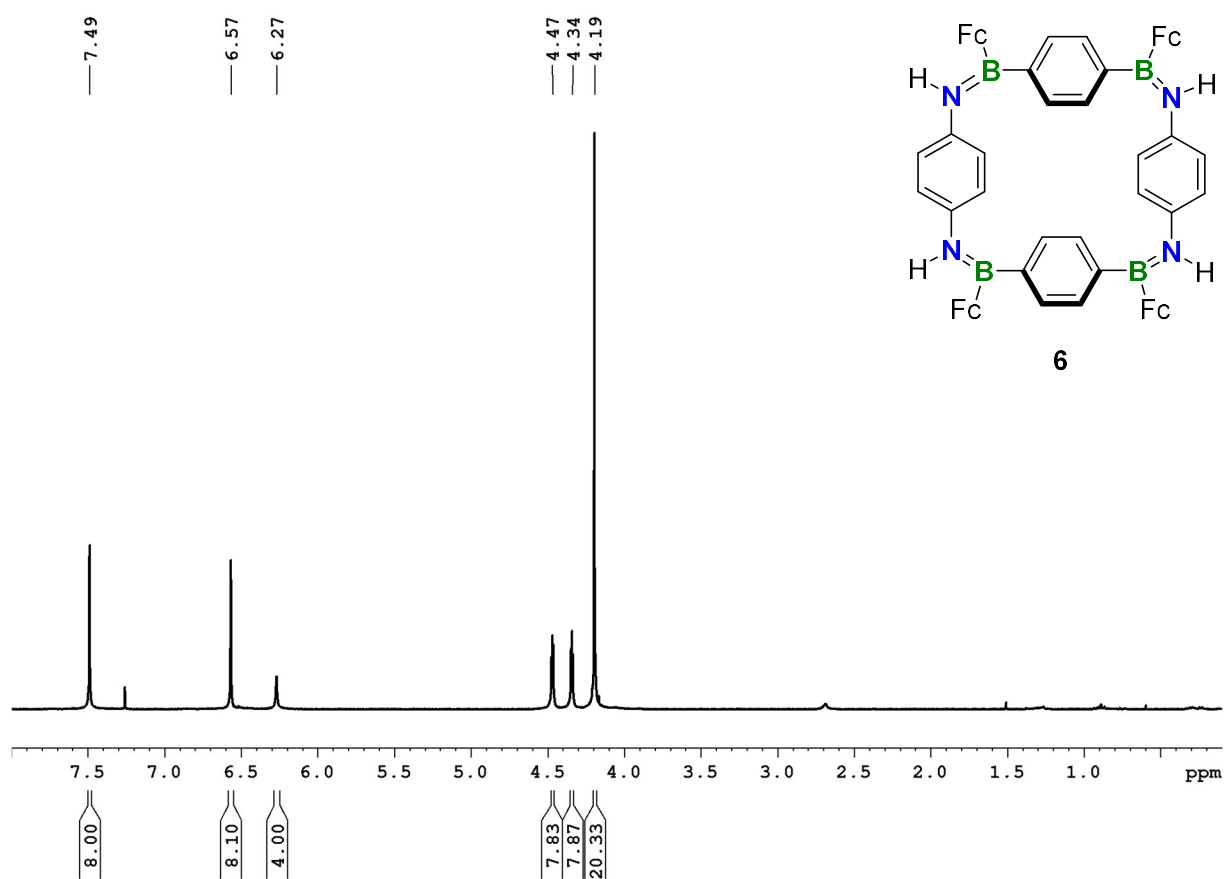


Figure S26. ¹H NMR spectrum of **6** (300 MHz, in CDCl₃).

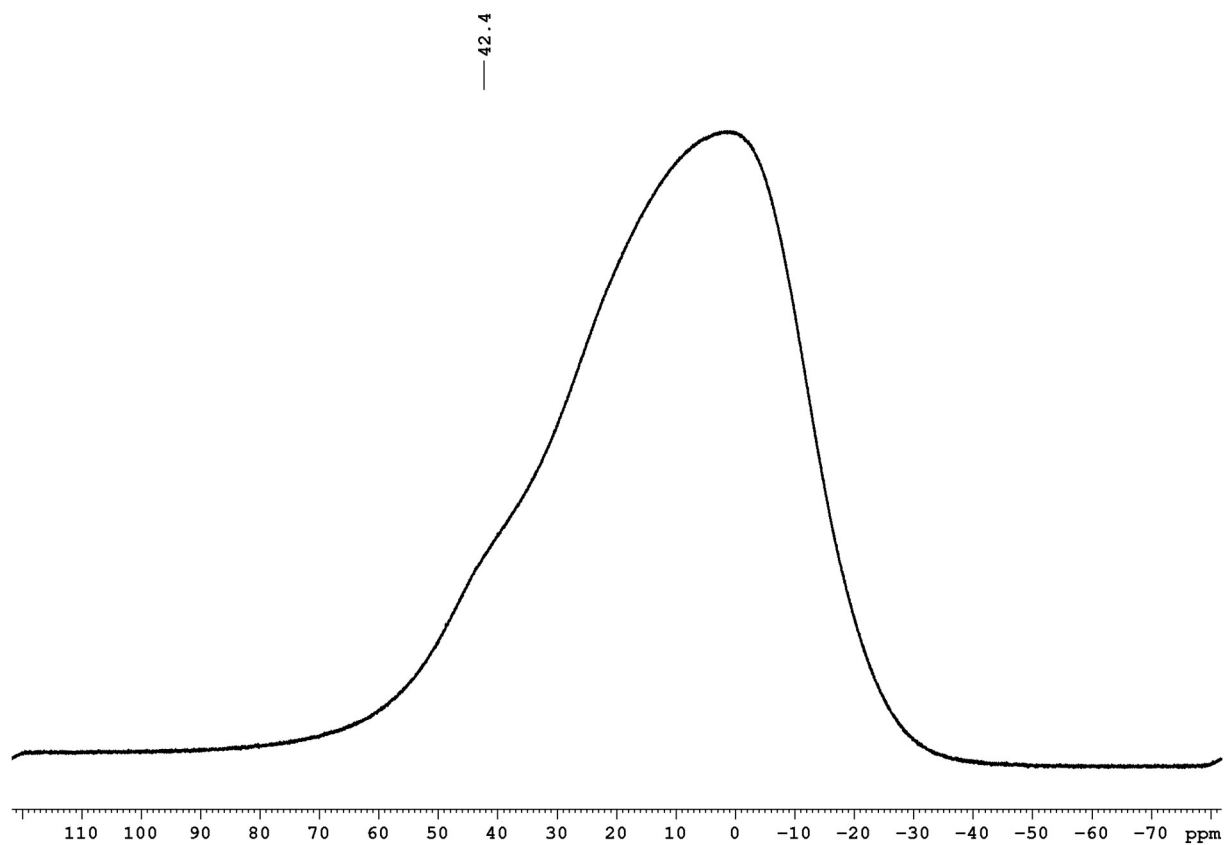


Figure S27. ¹¹B{¹H} NMR spectrum of **6** (160 MHz, in CDCl₃).

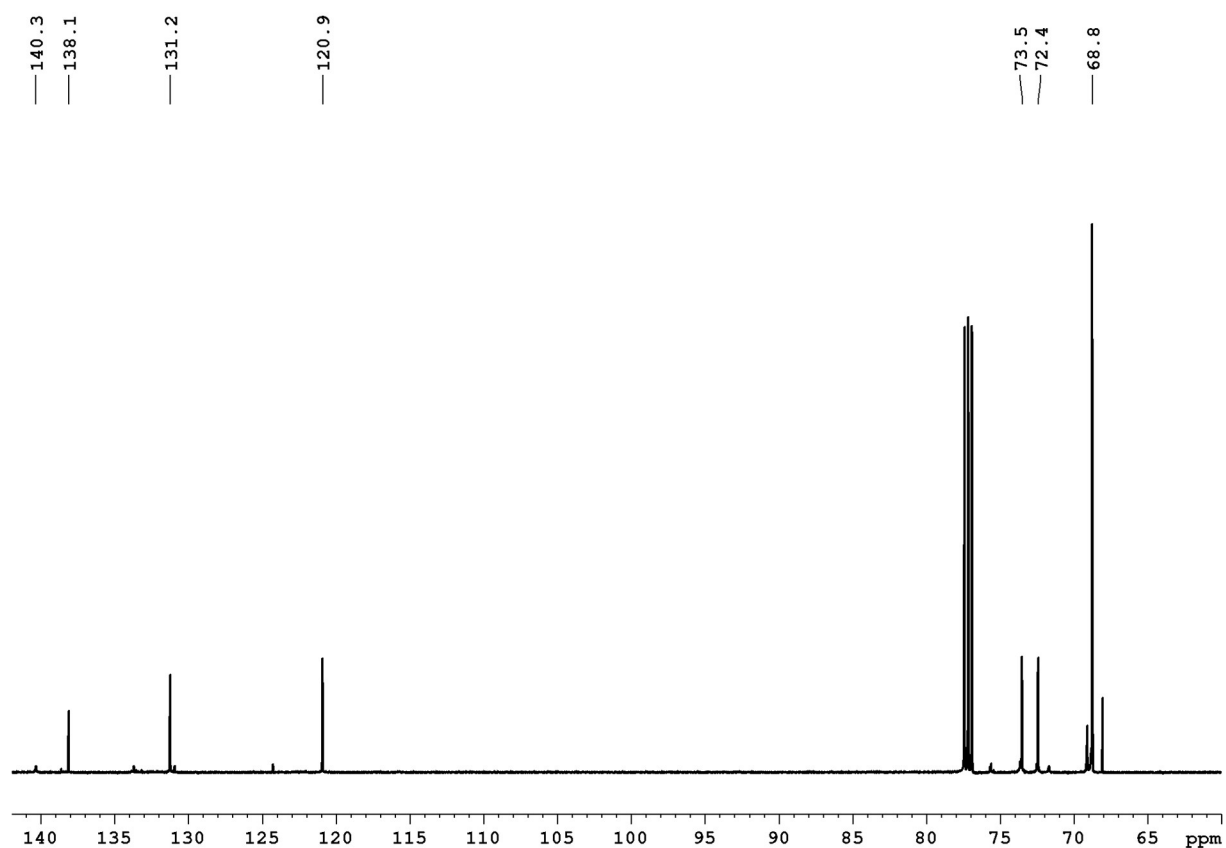


Figure S28. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** (125 MHz, in CDCl_3).

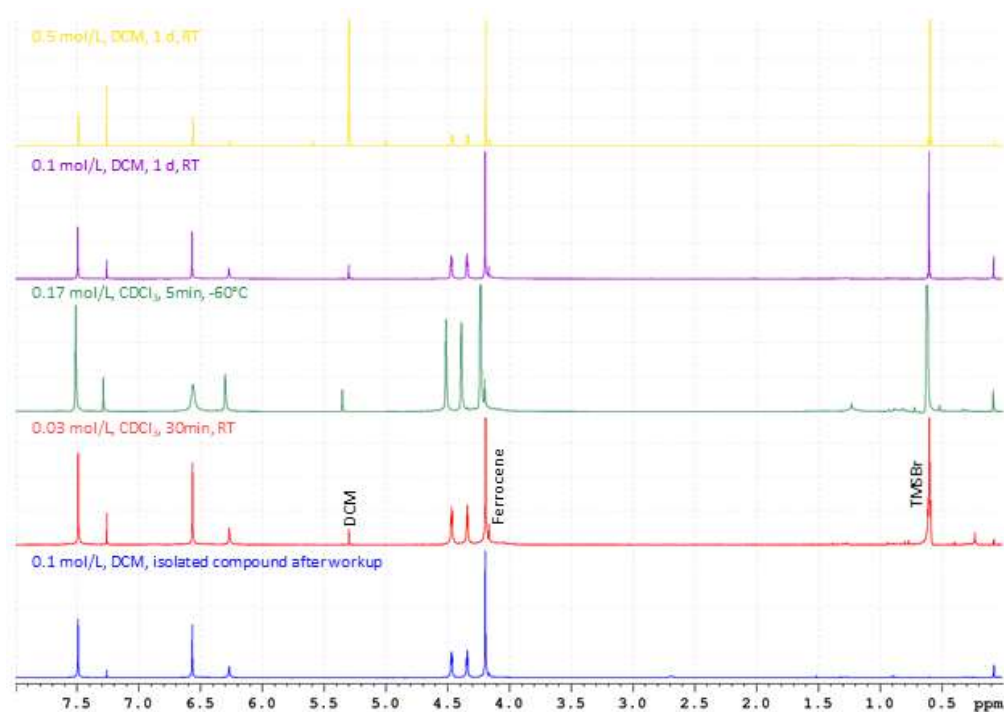


Figure S29. ^1H NMR spectra monitoring the formation of **6** (300 MHz, in CDCl_3 ; green spectrum 600 MHz).

Mass spectra

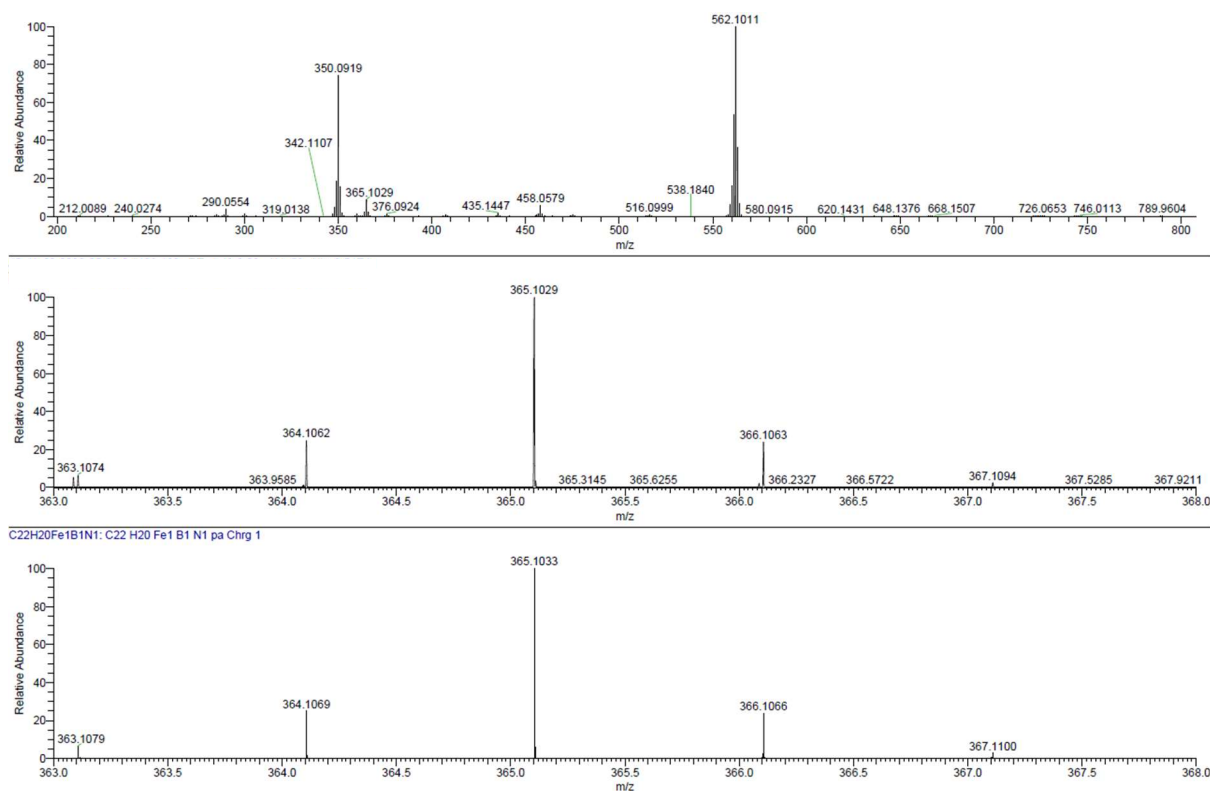


Figure S30. LIFDI spectrum of 3.

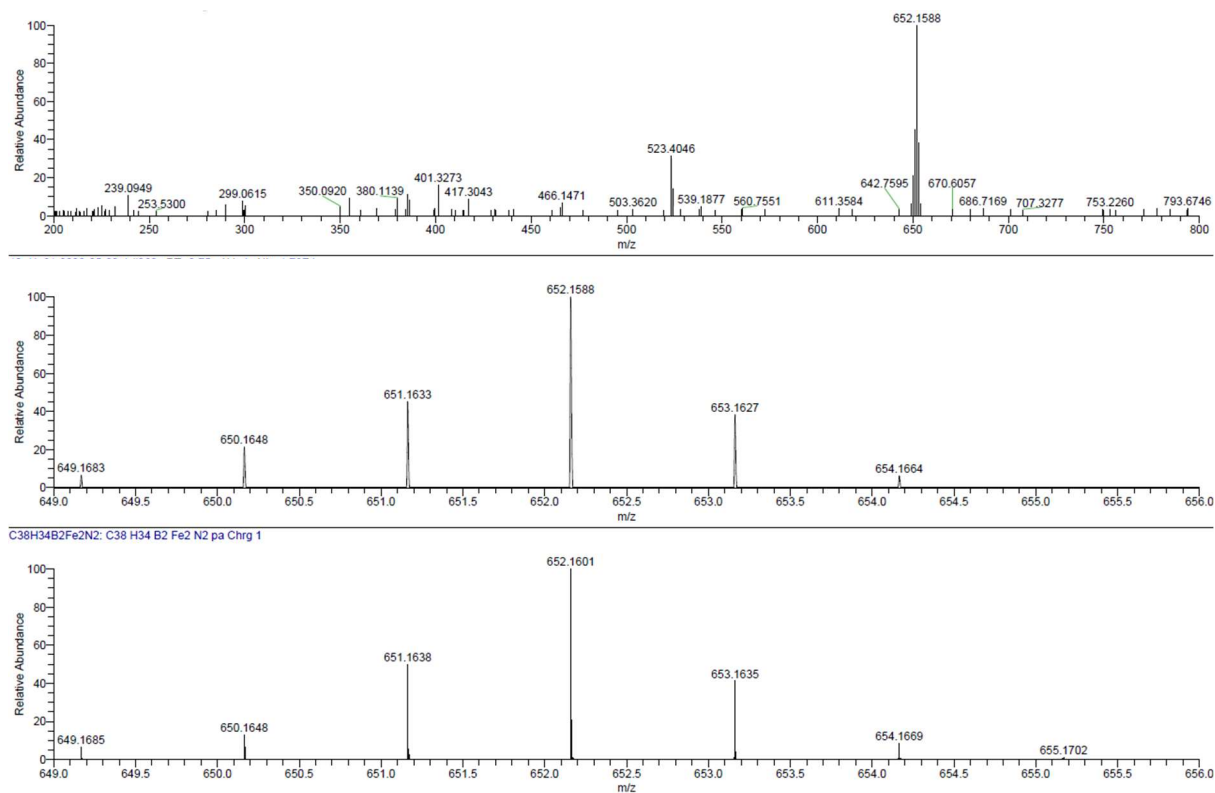


Figure S31. LIFDI spectrum of 4.

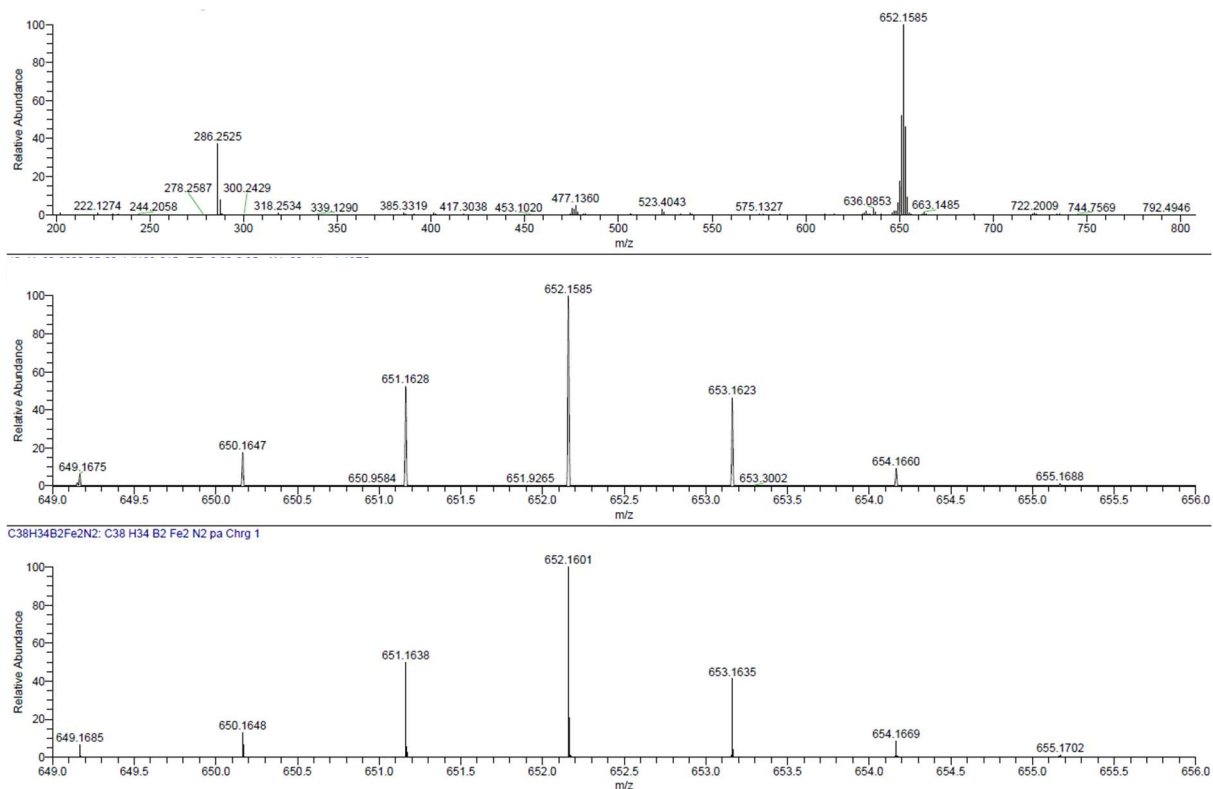


Figure S32. LIFDI spectrum of **5**.

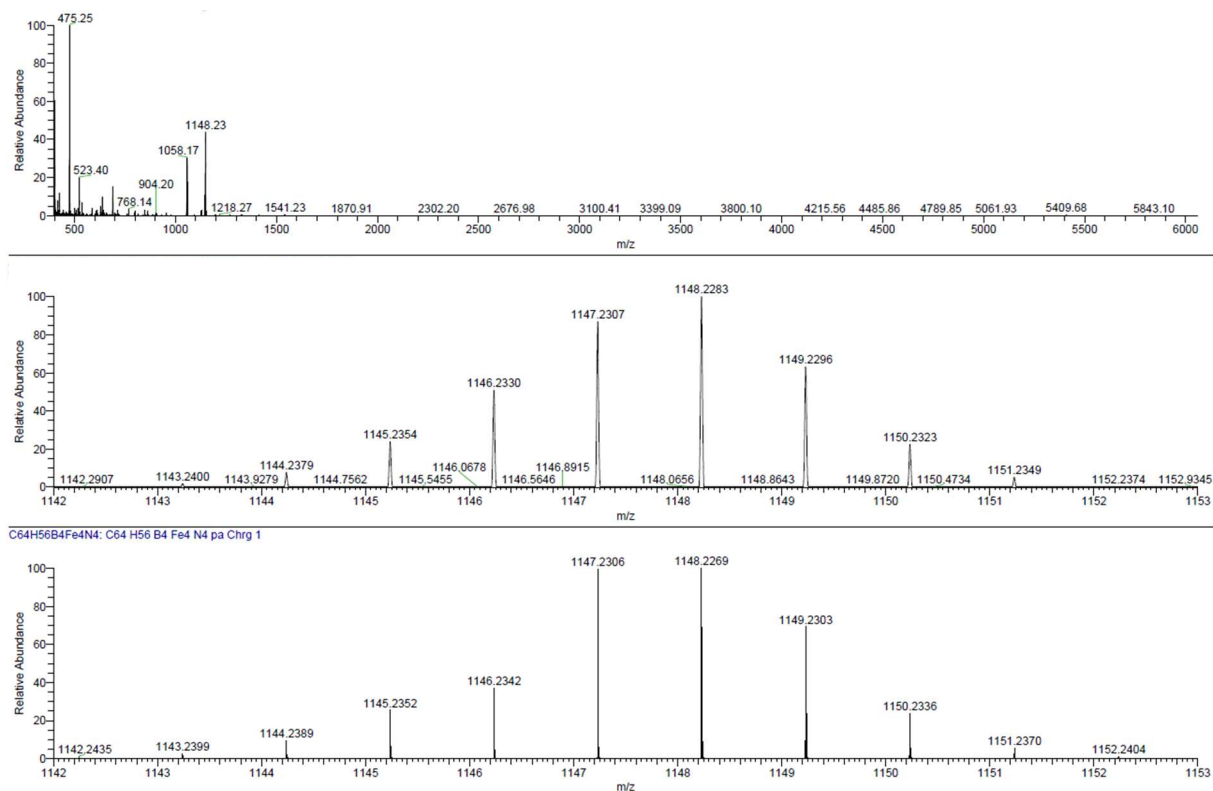


Figure S33. LIFDI spectrum of **6**.

Electrochemical studies

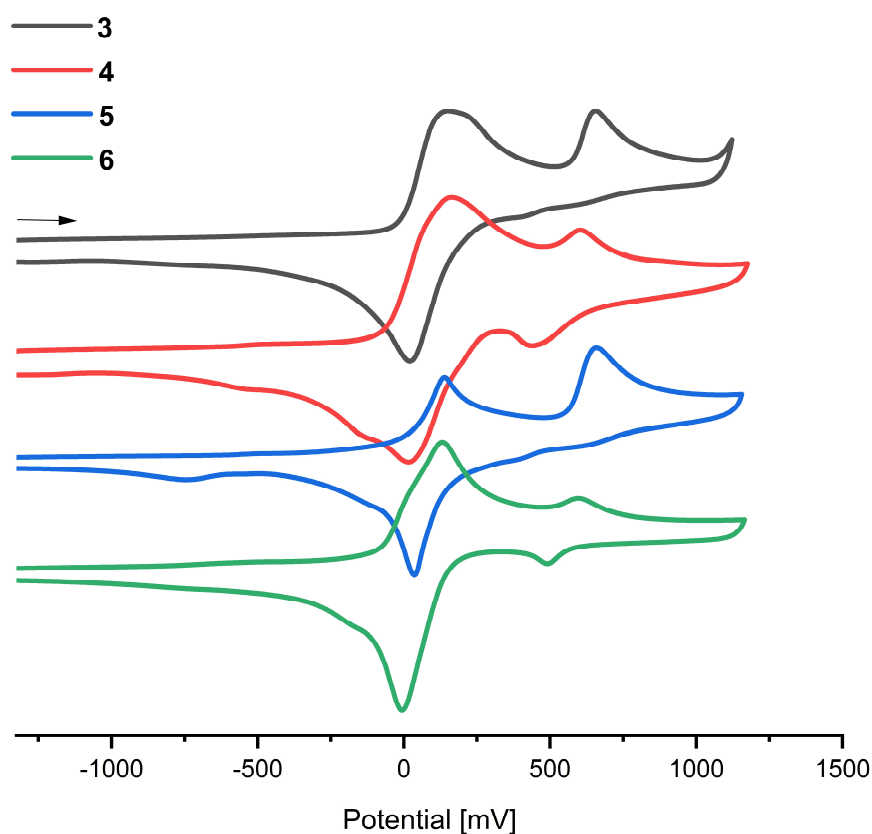


Figure S34. Cyclic voltammograms of **4-6** recorded in DCM containing 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ with a scan rate: 250 mVs^{-1} . Referenced against $[\text{Fc}]^{0/+}$.

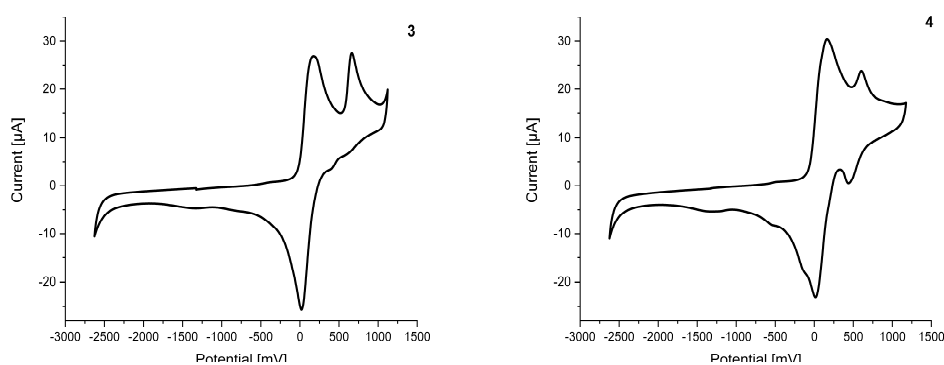


Figure S35. Cyclic voltammogram of **3** (left) and **4** (right) recorded in DCM containing 0.1 M $[n\text{-Bu}_4\text{N}][\text{PF}_6]$ with a scan rate: 250 mVs^{-1} . Referenced against $[\text{Fc}]^{0/+}$.

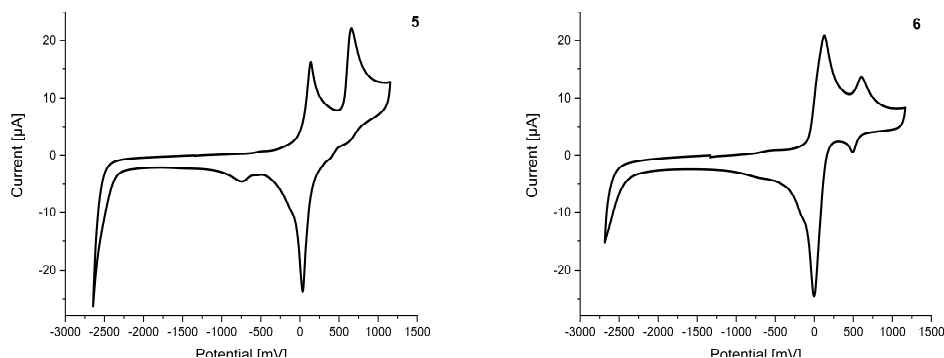


Figure S36. Cyclic voltammogram of **5** (left) and **6** (right) recorded in DCM containing 0.1 M [*n*-Bu₄N][PF₆] with a scan rate: 250 mVs⁻¹. Referenced against [Fc]^{0/+}.

UV-Vis spectra

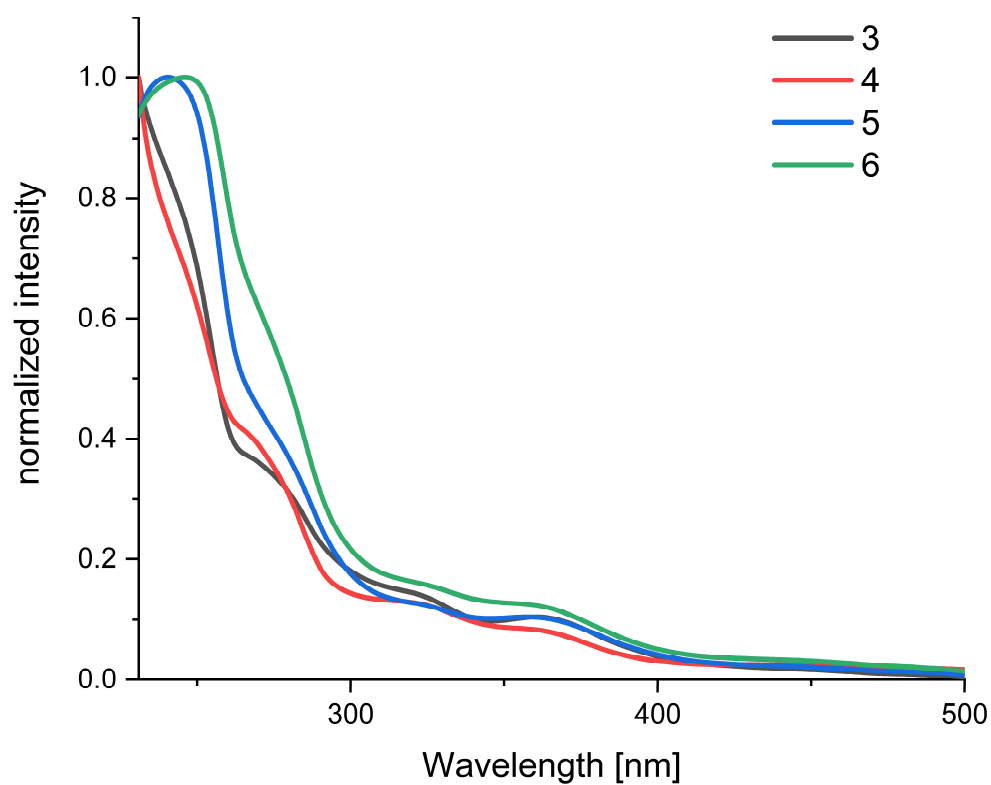


Figure S37. UV-vis spectra of **3-5** and macrocycle **6** in dichloromethane.

X-ray crystallography

Crystals of compounds **1**, **3**, **4**, and **6** suitable for single-crystal X-ray diffraction were obtained by slow crystallization from saturated solutions in DCM with minor amounts of *n*-hexane. The crystals were selected, coated in perfluoropolyether oil, and mounted on MiTeGen sample holders. Diffraction data were collected on Bruker X8 Apex II 4-circle diffractometers with CCD area detectors using Mo-K α radiation. The crystals were cooled using an Oxford Cryostreams low-temperature device. Data were collected at 100 K. The images were processed and corrected for Lorentz-polarization effects and absorption as implemented in the Bruker software packages. The structures were solved using the intrinsic phasing method (SHELXT)^[6] and Fourier expansion technique. All non-hydrogen atoms were refined in anisotropic approximation, with hydrogen atoms 'riding' in idealized positions, by full-matrix least squares against F^2 of all data, using SHELXL^[7] software and the SHELXLE graphical user interface.^[8]

Table S1. X-ray crystallographic information.

No.	1	3	4	6
CCDC number	2252616	2252615	2252618	2252617
Size / mm	0.338 x 0.467 x 0.629	0.214 x 0.428 x 0.488	0.227 x 0.242 x 0.686	0.170 x 0.188 x 0.292
Empiric Formula	C16 H14 B Br Fe	C22 H20 B Fe N	C38 H34 B2 Fe2 N2	C68 H64 B4 Cl8 Fe4 N4
M	352.84	365.05	651.99	1487.47
Crystal system	monoclinic	monoclinic	triclinic	monoclinic
Space group	P 21/c	P 21/c	P -1	C 2/c
<i>a</i> /Å	8.920(4)	13.616(3)	10.3432(19)	22.807(5)
<i>b</i> /Å	11.581(3)	11.0195(13)	12.985(6)	20.081(6)
<i>c</i> /Å	13.820(3)	11.277(2)	13.579(3)	15.326(4)
α /°	90	90	102.62(2)	90
β /°	100.50(3)	91.301(12)	111.269(10))	114.023(10)
γ /°	90	90	107.505(8)	90
<i>V</i> /Å ³	1403.7(8)	1691.6(5)	1506.7(8)	6411(3)
<i>Z</i>	4	4	2	4
μ /mm ⁻¹	3.901	0.894	0.994	1.267
<i>T</i> /K	100(2)	100(2)	100(2)	100(2)
$\theta_{\text{min,max}}$	2.311, 26.471	1.496, 26.405	1.731, 26.419	1.409, 26.421
Completeness	0.995	0.999	0.989	0.998
Reflections: total/independent	2894, 2630	3464, 3208	6109, 5013	6581, 4900
<i>R</i> _{int}	0.0594	0.0642	0.0616	0.0630
Final <i>R</i> 1 and <i>wR</i> 2	0.0294, 0.0762	0.0437, 0.1217	0.0462, 0.1242	0.0713, 0.1981
Largest peak, hole/eÅ ⁻³	0.700, -0.389	0.845, -1.109	0.887, -0.409	2.164, -2.102
ρ_{calc} /g cm ⁻³	1.670	1.433	1.437	1.541

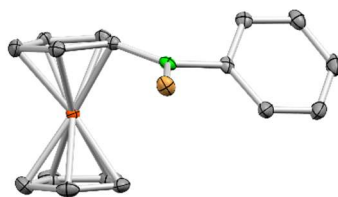


Figure S38. Molecular structure of **1** in the solid state (ellipsoids are shown at the 50% probability level).

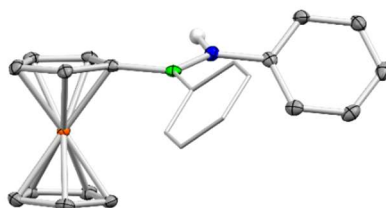


Figure S39. Molecular structure of **4** in the solid state (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bounded H have been omitted for clarity).

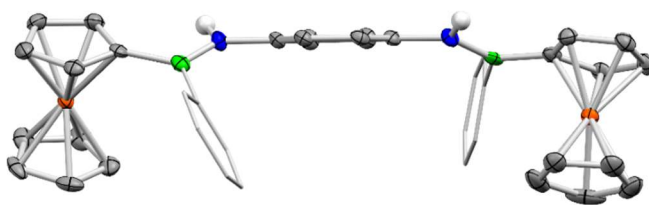


Figure S40. Molecular structure of **5** in the solid state (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bounded H have been omitted for clarity).

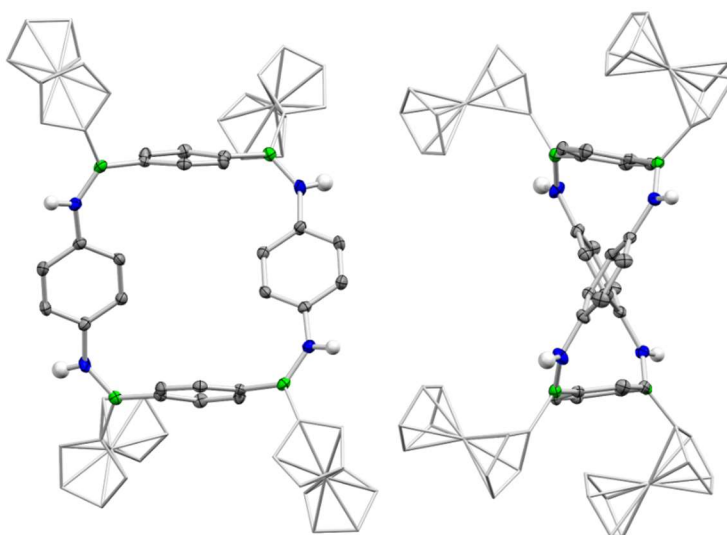


Figure S41. Molecular structure of **6** in the solid state (ellipsoids are shown at the 50% probability level; ellipsoids of the peripheral groups and all hydrogen atoms except for the N-bounded H have been omitted for clarity).

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