

## Electronic Supplementary Information

### Porous networks based on iron (II) clathrochelate complexes

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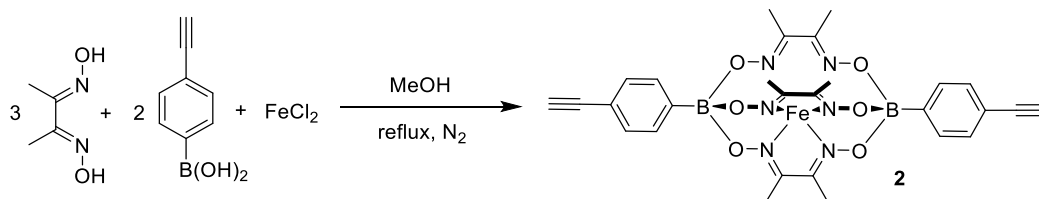
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## 1. General

Complex **1** was prepared as described in the literature.<sup>1</sup> All reagents were obtained from commercial sources and used without further purification unless stated otherwise. Solid state MAS NMR were measured on a Bruker AVIIIHD spectrometers (400 MHz and 800 MHz) equipped with a 2.5 mm H/X/Y CP-MAS (solid) and 1.3 mm <sup>1</sup>H/<sup>13</sup>C/<sup>79</sup>Br/<sup>15</sup>N CP-MAS (solid) probes respectively. Liquid state <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained on a Bruker Avance III spectrometer (<sup>1</sup>H: 400 MHz) equipped with a 5 mm BBFO-Plus<sub>2</sub> probe and a Bruker Avance III HD spectrometer (<sup>1</sup>H: 600MHz) equipped with 5 mm CPTCl<sub>2</sub> probe. The chemical shifts are reported in parts per million  $\delta$  (ppm) referenced to an internal solvent. All spectra were recorded at 298 K. The NMR data was analyzed with the help of MestreNova software. The thermogravimetric analyses were performed with a Perkin Elmer 4000 TGA between 30 °C and 500 °C with an inert nitrogen atmosphere at 20 mLmin<sup>-1</sup> flowrate. The data were analyzed with Perkin Elmer Pyris software. Electrospray-ionisation MS data were acquired on a Q-ToF Ultima mass spectrometer (Waters) operated in the positive ionization mode and data were processed using the MassLynx 4.1 software. Dinitrogen (77 K), carbon dioxide (273 K) and hydrogen (77 K) sorption measurements were performed on a Quantachrome Autosorb iQ analyzer. SEM-EDX measurements were performed on a Zeiss Merlin SEM.

## 2. Experimental procedures

### Synthesis of complex 2

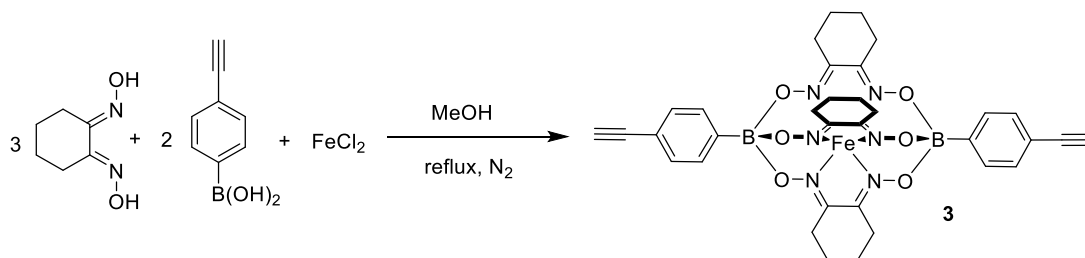


**Scheme S1** – Synthesis of complex 2.

Dimethylglyoxime (59.6 mg, 0.51 mmol), 4-ethynylphenylboronic acid (50 mg, 0.34 mmol), and anhydrous  $\text{FeCl}_2$  (21.7 mg, 0.17 mmol) were dissolved in MeOH (15 mL) and heated under reflux under an inert atmosphere for 3 h. The reaction mixture was allowed to cool to RT, and the resulting precipitates were isolated by filtration, washed with MeOH and diethyl ether, and dried under vacuum to yield a brown powder (63 mg, 60%).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  2.35 (s, 18H,  $\text{CH}_3$ ), 2.99 (s, 2H,  $\text{CH}$ ), 7.43 (d,  $J = 8.0$  Hz, 4H, Ar- $\text{CH}$ ), 7.63 (d,  $J = 8.0$  Hz, 4H, Ar- $\text{CH}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz, TMS)  $\delta$  13.4 ( $\text{CH}_3$ ), 76.5 ( $\text{C}\equiv\text{CH}$ ), 84.7 ( $\text{C}\equiv\text{CH}$ ), 121.3 ( $\text{C}(\text{C}\equiv\text{CH})$ ), 131.2 (Ar- $\text{CH}$ ), 131.6 (Ar- $\text{CH}$ ), 152.2 (N-C), (C-B not detected); **HRMS-ESI** (positive mode):  $m/z$  calculated for  $\text{C}_{28}\text{H}_{28}\text{B}_2\text{FeN}_6\text{O}_6$   $[\text{M}+\text{H}]^+$  622.1605; found: 622.1662.

### Synthesis of complex 3



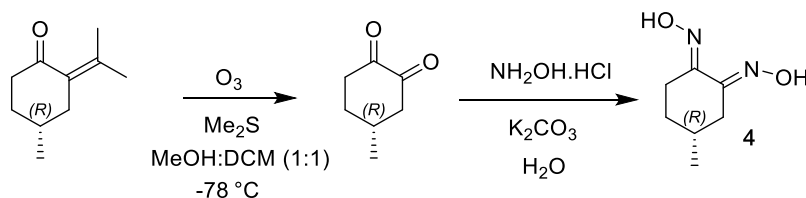
**Scheme S2** – Synthesis of complex 3.

Nioxime (73 mg, 0.51 mmol), 4-ethynylphenylboronic acid (50 mg, 0.34 mmol), and anhydrous  $\text{FeCl}_2$  (21.7 mg, 0.17 mmol) were dissolved in MeOH (15 mL) and heated under reflux under an inert atmosphere for 3 h. The reaction mixture was allowed to cool to RT, and the resulting precipitates were isolated by filtration, washed with MeOH and diethyl ether, and dried under vacuum to yield a brown powder (96 mg, 80%).

$^1\text{H NMR}$  ( $\text{CDCl}_3$ , 400 MHz, TMS)  $\delta$  1.73 (s, 12H,  $\text{CH}_2$ ), 2.86 (s, 12H,  $\text{CH}_2$ ), 2.98 (s, 2H,  $\text{CH}$ ), 7.41 (d,  $J = 8.0$  Hz, 4H, Ar- $\text{CH}$ ), 7.59 (d,  $J = 8.0$  Hz, 4H, Ar- $\text{CH}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz, TMS)  $\delta$  21.6

(CH<sub>2</sub>), 26.3 (CH<sub>2</sub>), 76.4 (CH), 84.7 (C≡CH), 121.2 (C(C≡CH)), 131.1 (Ar-CH), 131.6 (Ar-CH), 151 (N-C), (C-B not detected); **HRMS-APPI** (positive mode): *m/z* calculated for C<sub>34</sub>H<sub>35</sub>B<sub>2</sub>FeN<sub>6</sub>O<sub>6</sub> [M+H]<sup>+</sup> 701.2148; found: 701.2118.

Synthesis of the chiral dioxime 4<sup>2,3,4</sup>



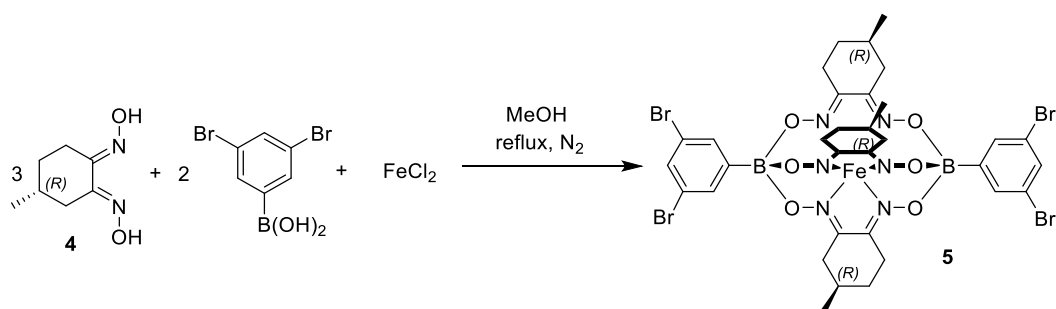
**Scheme S3** – Synthesis of dioxime 4.

(R)-(+)- Pulegone (2.0 g, 0.013 mol) was dissolved in a mixture of MeOH and DCM (1:1, 20 mL) and cooled to –78 °C. Ozone was added, and the mixture was stirred until the solution became blue. The system was purged with N<sub>2</sub> for 5 min until the blue color disappeared. Subsequently, Me<sub>2</sub>S (5 mL) was added slowly at –78 °C. The reaction mixture was left to warm to RT, followed by stirring for additional 3 h. The solvent was removed to dryness, and the product was filtered through a silica pad and the pad was washed with a mixture of hexane and Et<sub>2</sub>O (1:1, 50 mL). The solvent was removed under vacuum and the product was used without further purification.

A mixture of [NH<sub>3</sub>OH]Cl (18.2 g, 0.26 mol) and K<sub>2</sub>CO<sub>3</sub> (26.9 g, 0.19 mol) in distilled water (50 mL) was added to the crude diketone, and the mixture was stirred overnight at RT. The solution was placed in a fridge (4 °C). After 12 h, the resulting precipitates were isolated by filtration, washed with water (300 mL), and dried under vacuum overnight to give a light pink powder (1.31 g, 64 %).

<sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, TMS) δ 1.01 (d, *J* = 6.5 Hz, 3H, CH<sub>3</sub>), 1.28 – 1.13 (m, 1H, CH), 1.80 – 1.62 (m, 2H, CCH<sub>2</sub>CH<sub>2</sub>), 1.92 (dd, *J* = 17.1, 11.0 Hz, 1H, CCH<sub>2</sub>CH<sub>2</sub>), 2.29 (ddd, *J* = 17.8, 11.9, 6.2 Hz, 1H, -CCH<sub>2</sub>CH<sub>2</sub>), 2.85 (dddd, *J* = 23.6, 17.6, 5.3, 2.7 Hz, 2H, CCH<sub>2</sub>), 11.21 (s, 2H, OH); <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 101 MHz, TMS) δ 21.8 (CH<sub>3</sub>), 24.2 (CCH<sub>2</sub>CH<sub>2</sub>), 28.9 (CCH<sub>2</sub>CH<sub>2</sub>), 30.3 (CH), 33.3 (CCH<sub>2</sub>), 152.2 (N-C); **HRMS (ESI TOF)** *m/z* calcd for C<sub>7</sub>H<sub>13</sub>N<sub>2</sub>O<sub>2</sub> [M-H]<sup>+</sup> 157.0972, found 157.0977.

### Synthesis of complex 5

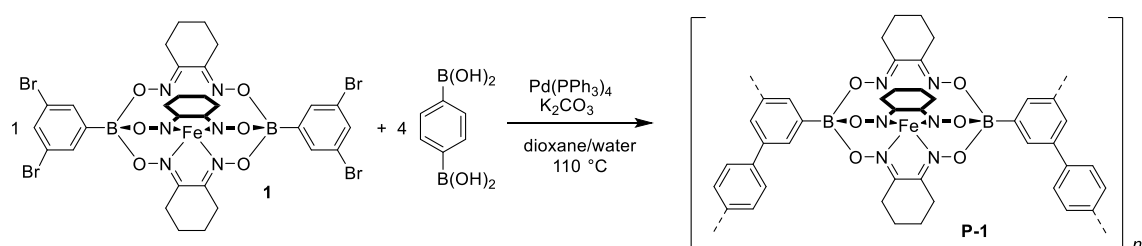


Scheme S4 – Synthesis of complex 5.

Compound **4** (50 mg, 0.32 mmol), 3,5-dibromobenzenboronic acid (61.5 mg, 0.22 mmol), and anhydrous  $\text{FeCl}_2$  (13.4 mg, 0.11 mmol) were dissolved in MeOH (15 mL) and heated under reflux under an inert atmosphere for 3 h. The reaction mixture was allowed to cool to RT, and the resulting precipitates were isolated by filtration, washed with MeOH and diethyl ether, and dried under vacuum to yield a brown powder (107 mg, 61%).

$^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  1.04 (d,  $J = 6.4$  Hz, 9H,  $\text{CH}_3$ ), 1.37 (tq,  $J = 12.5, 5.4$  Hz, 3H,  $\text{CH}$ ), 1.84 (s, 6H,  $\text{CCH}_2\text{CH}_2$ ), 2.27 (dd,  $J = 18.8, 10.7$  Hz, 3H,  $\text{CCH}_2\text{CH}_2$ ), 2.66 (ddd,  $J = 18.7, 11.6, 6.1$  Hz, 3H,  $-\text{CCH}_2\text{CH}_2$ ), 3.18 – 3.04 (m, 4H,  $\text{CCH}_2$ ), 7.54 (q,  $J = 1.9$  Hz, 2H, Ar- $\text{CH}$ ), 7.63 (p,  $J = 1.7$  Hz, 4H, Ar- $\text{CH}$ );  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ , 101 MHz, TMS)  $\delta$  21.1 ( $\text{CH}_3$ ), 25.5 ( $\text{CH}$ ), 28.5 ( $\text{CCH}_2\text{CH}_2$ ), 29.6 ( $\text{CCH}_2\text{CH}_2$ ), 34.1 ( $\text{CCH}_2$ ), 122.6 (C-Br), 133.2 (Ar- $\text{CH}$ ), 152.2 (N-C), 152.5 (N-C), (C-B not detected). All attempts to record a HRMS failed. Elem. anal. calcd for  $\text{C}_{33}\text{H}_{36}\text{B}_2\text{FeBr}_4\text{N}_6\text{O}_6$ : C 39.25; H 3.59; N 8.32. Found: C 39.55; H 3.44; N 7.85.

### Synthesis of polymer P-1

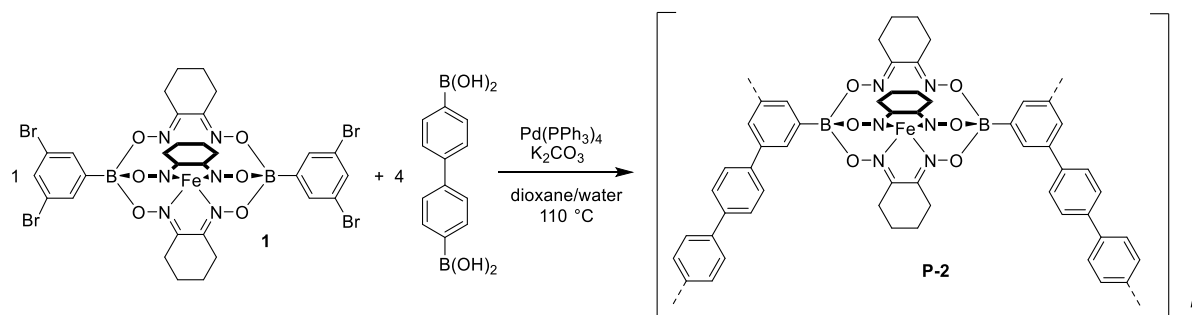


Scheme S5 – Synthesis of polymer P-1.

1,4-Dioxane (15 mL) was purged with  $\text{N}_2$  for 30 min in a Pyrex microwave vial. Subsequently, clathrochelate **1** (50 mg, 0.052 mmol) and 1,4-benzenediboronic acid (34.5 mg, 0.208 mmol) were added, and the mixture was purged again with  $\text{N}_2$  for 10 min. A solution of  $\text{K}_2\text{CO}_3$  (100 mg, 0.723 mmol) in water (2.5 mL) was added, and the solution was purged with  $\text{N}_2$  for another 15 min.  $\text{Pd}(\text{PPh}_3)_4$  (19.4 mg, 0.016 mmol) was added, the vial was

sealed, and the solution was stirred overnight at 110 °C. The precipitates were isolated by filtration and washed with hot solvents (50 mL DMF, 60 mL water, and 60 mL diethyl ether) to yield a brown powder (65 mg).

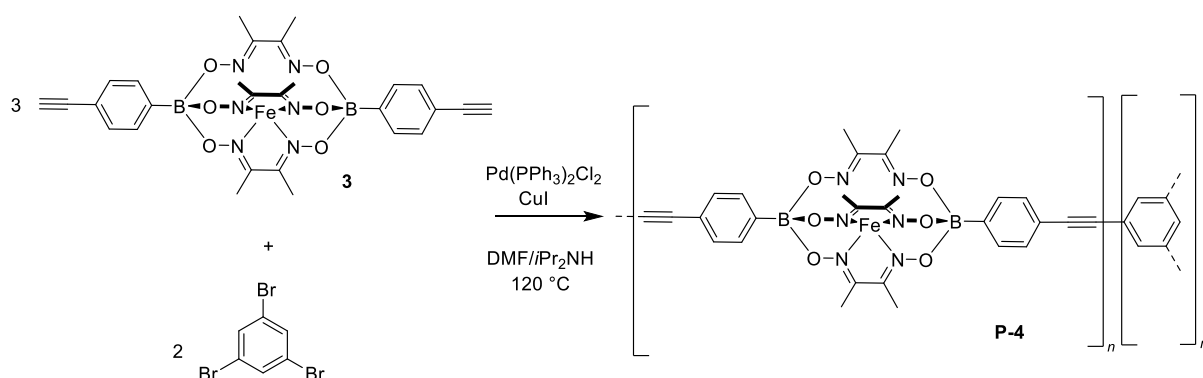
### Synthesis of polymer P-2



**Scheme S6** – Synthesis of polymer P-2.

1,4-Dioxane (15 mL) was purged with nitrogen for 30 min in a Pyrex microwave vial. Subsequently, compound **1** (50 mg, 0.052 mmol) and 4,4'-biphenyldiboric acid (50.3 mg, 0.208 mmol) were added, and the mixture was purged with N<sub>2</sub> for 10 min. A solution of K<sub>2</sub>CO<sub>3</sub> (100 mg, 0.723 mmol) in water (2.5 mL) was added, and the solution was purged with N<sub>2</sub> for another 15 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (19.4 mg, 0.016 mmol) was added, the vial was sealed, and the solution was stirred overnight at 110 °C. The precipitates were isolated by filtration and washed with hot solvents (50 mL DMF, 60 mL water, and 60 mL diethyl ether) to yield a brown powder (106 mg).

### Synthesis of polymer P-3

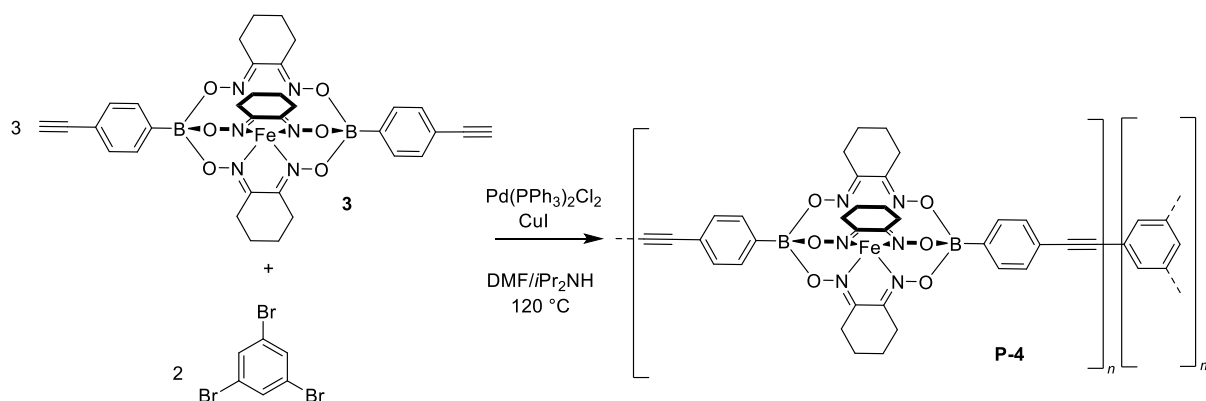


**Scheme S7** – Synthesis of polymer P-3.

A mixture of DMF and *i*PrNH<sub>2</sub> (1:1, 10 mL) was purged with N<sub>2</sub> for 30 min in a Pyrex microwave vial. Subsequently, 1,3,5-tribromobenzene (16.8 mg, 0.053 mmol) and complex **2** (50 mg, 0.080 mmol) were added, and the mixture was purged with N<sub>2</sub> for 10 min. CuI (0.5 mg, 0.004 mmol) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (2.1 mg, 0.004

mmol) were added under  $N_2$ , the reaction mixture was sealed and stirred for 48 h at 120 °C. The precipitates were isolated by filtration while hot and washed with DMF (50 mL), water (50 mL), THF (50 mL), and diethyl ether (50 mL) to yield a brown product (60 mg).

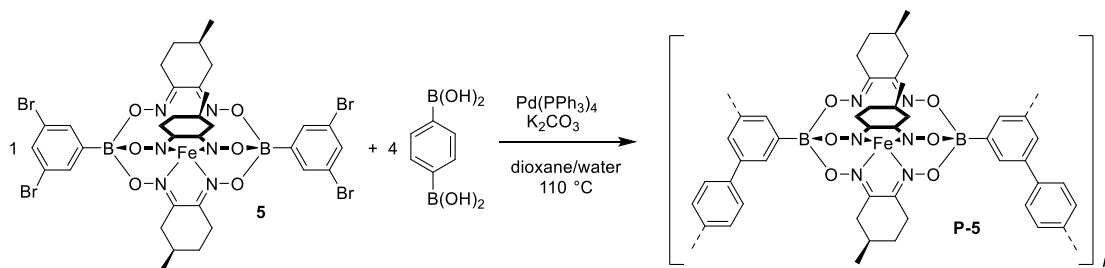
#### Synthesis of polymer P-4



**Scheme S8** – Synthesis of polymer **P-4**.

A mixture of DMF and  $iPr_2NH$  (1:1, 10 mL) was purged with nitrogen for 30 min in a Pyrex microwave vial. Subsequently, the 1,3,5-tribromobenzene (14.9 mg, 0.048 mmol) and complex **3** (50 mg, 0.071 mmol) were added, and the mixture was purged with  $N_2$  for 10 min.  $CuI$  (0.7 mg, 0.004 mmol) and  $Pd(PPh_3)_2Cl_2$  (2.8 mg, 0.004 mmol) were added under  $N_2$ , the reaction mixture was sealed and stirred for 48 h at 120 °C. The precipitates were isolated by filtration while hot and washed with DMF (50 mL), water (50 mL), THF (50 mL), and diethyl ether (50 mL) to yield a brown product (58 mg).

#### Synthesis of polymer P-5

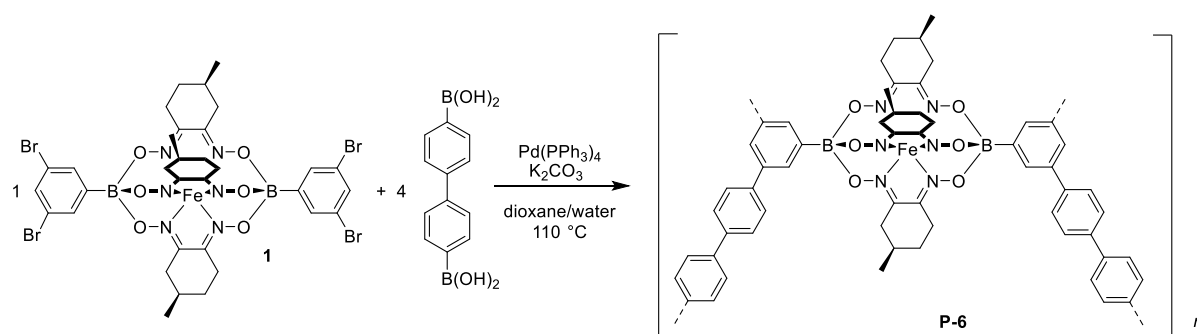


**Scheme S9** – Synthesis of polymer **P-5**.

1,4-Dioxane (10 mL) was purged with  $N_2$  for 30 min in a Pyrex microwave vial. Subsequently, complex **5** (50 mg, 0.05 mmol) and 1,4-benzenediboronic acid (32.5 mg, 0.20 mmol) were added, and the mixture was purged again with  $N_2$  for 10 min. A solution of  $K_2CO_3$  (135 mg, 0.98 mmol) in water (2.5 mL) was added, and the solution

was purged with N<sub>2</sub> for another 15 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (17 mg, 0.015 mmol) was added, the vial was sealed, and the solution was stirred overnight at 110 °C. The precipitates were isolated by filtration and washed with hot solvents (50 mL DMF, 60 mL water, and 60 mL diethyl ether) to yield a brown powder (51 mg).

### Synthesis of polymer P-6



**Scheme S10** – Synthesis of polymer P-6.

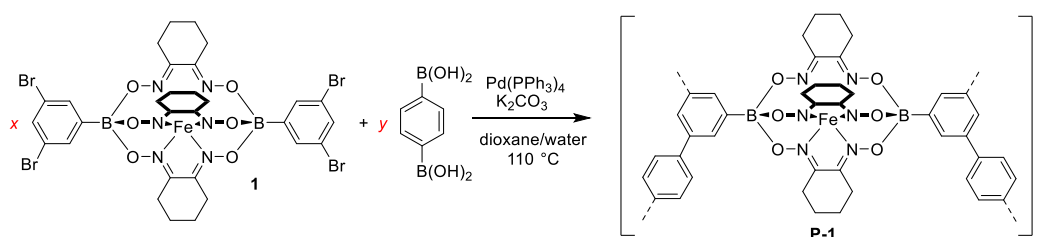
1,4-Dioxane (10 mL) was purged with N<sub>2</sub> for 30 min in a Pyrex microwave vial. Subsequently, complex 5 (50 mg, 0.05 mmol) and 4,4'-biphenyldiboric acid (48.4 mg, 0.20 mmol) were added, and the mixture was purged with N<sub>2</sub> for 10 min. A solution of K<sub>2</sub>CO<sub>3</sub> (135 mg, 0.98 mmol) in water (2.5 mL) was added, and the solution was purged with N<sub>2</sub> for another 15 min. Pd(PPh<sub>3</sub>)<sub>4</sub> (17 mg, 0.015 mmol) was added, the vial was sealed, and the solution was stirred overnight at 110 °C. The precipitates were isolated by filtration and washed with hot solvents (50 mL DMF, 60 mL water, and 60 mL diethyl ether) to yield a brown powder (85 mg).



### 3. Optimizations

#### Part 1: Suzuki-Miyaura cross-coupling reactions

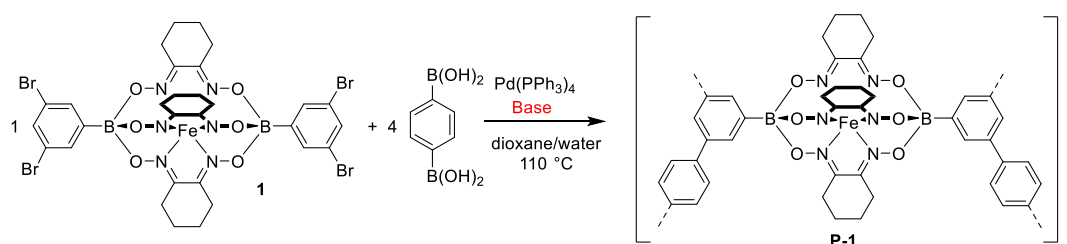
Several conditions for the synthesis of porous clathrochelate polymers were examined. First, the ratio between clathrochelate **1** (*x*) and 1,4-benzene diboronic acid (*y*) was varied. The apparent BET surface areas were determined by 11 point isotherms, and the resulting values are reported in Table S1. Subsequently, we have examined the influence of the base (Table S2) and the solvent (Table S3).



**Scheme S11** – Synthesis of **P-1** using different ratios of starting materials.

**Table S1** – Influence of the ratio of the starting materials on the porosity of the final polymer.

	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>	<b>E</b>
<b>x</b>	1	1	1	1	1
<b>y</b>	1	2	3	4	5
<b>SA<sub>BET</sub> [m<sup>2</sup> g<sup>-1</sup>]</b>	28	126	481	550	432



**Scheme S12** – Synthesis of **P-1** with different bases.

**Table S2** – Influence of the base on the porosity of the final polymer.

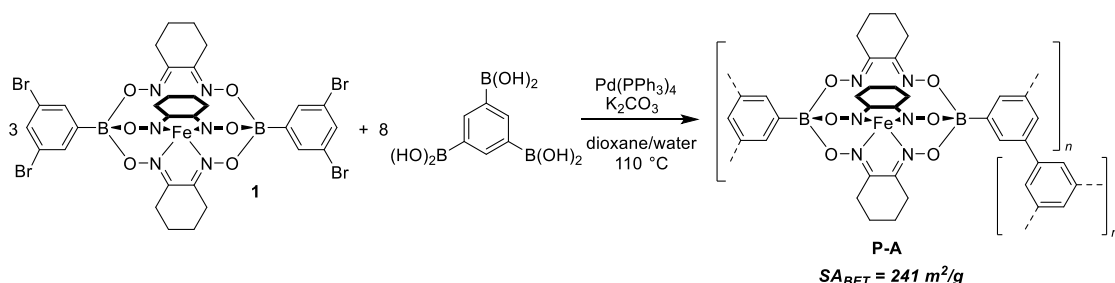
	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
<b>Base</b>	K <sub>2</sub> CO <sub>3</sub>	Na <sub>2</sub> CO <sub>3</sub>	Cs <sub>2</sub> CO <sub>3</sub>	KOtBu
<b>SA<sub>BET</sub> [m<sup>2</sup> g<sup>-1</sup>]</b>	550	461	5	7

**Table S3** - Influence of the solvent on the porosity of the final polymer.

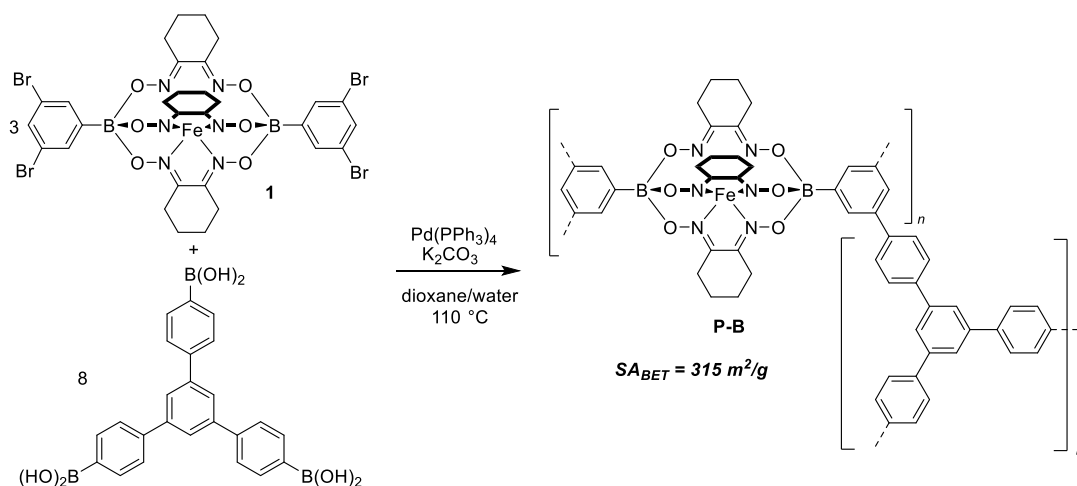
	<b>A</b>	<b>B</b>	<b>C</b>	<b>D</b>
<b>Solvent</b>	Dioxane:H <sub>2</sub> O (6:1)	THF:H <sub>2</sub> O (6:1)	DMF:H <sub>2</sub> O (6:1)	DMF:THF:H <sub>2</sub> O (3:3:1)
<b>SA<sub>BET</sub> [m<sup>2</sup> g<sup>-1</sup>]</b>	550	381	501	456

### Synthesis of the clathrochelate networks P-A and P-B based on triboronic acids

The optimized reactions conditions were used to perform polycross-coupling reactions between clathrochelate **1** and triboronic acids. The resulting polymers **P-A** and **P-B** did show a lower apparent surface area compared to the polymers based on diboronic acids (**P-1** and **P-2**), and more detailed investigations were not undertaken.



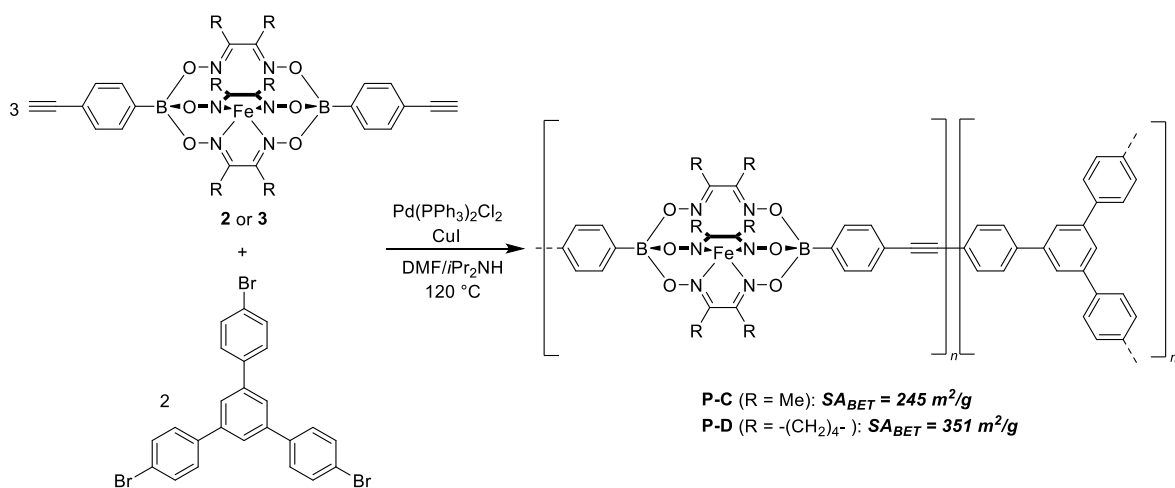
**Scheme S13** – Synthesis of polymer P-A.



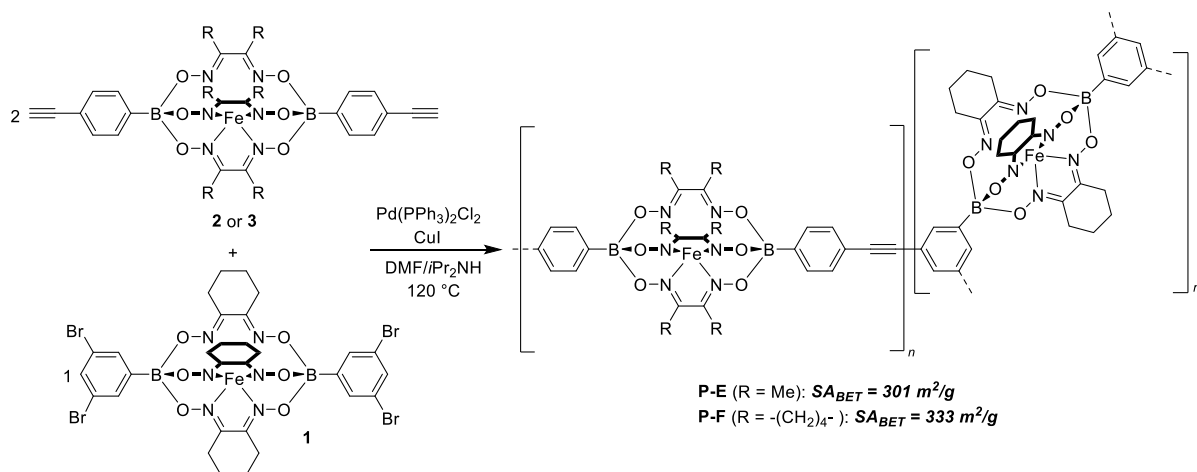
**Scheme S14** – Synthesis of polymer P-B.

## Part 2: Sonogashira-Hagihara cross-coupling reactions

The reaction conditions for the synthesis of **P-3** and **P-4** were used to perform polycross-coupling of clathrochelate **2** or **3** with 1,3,5-tris (4-bromophenyl) benzene or the bromo substituted clathrochelate **1**. The resulting polymers did not show a significant change in apparent *BET* surface areas compared to **P-3** and **P-4**. Hence further investigations were not performed.



Scheme S15 – Synthesis of the polymers **P-C** and **P-D**.



Scheme S16 – Synthesis of the polymers **P-E** and **P-F**.

#### 4. Solution NMR spectra

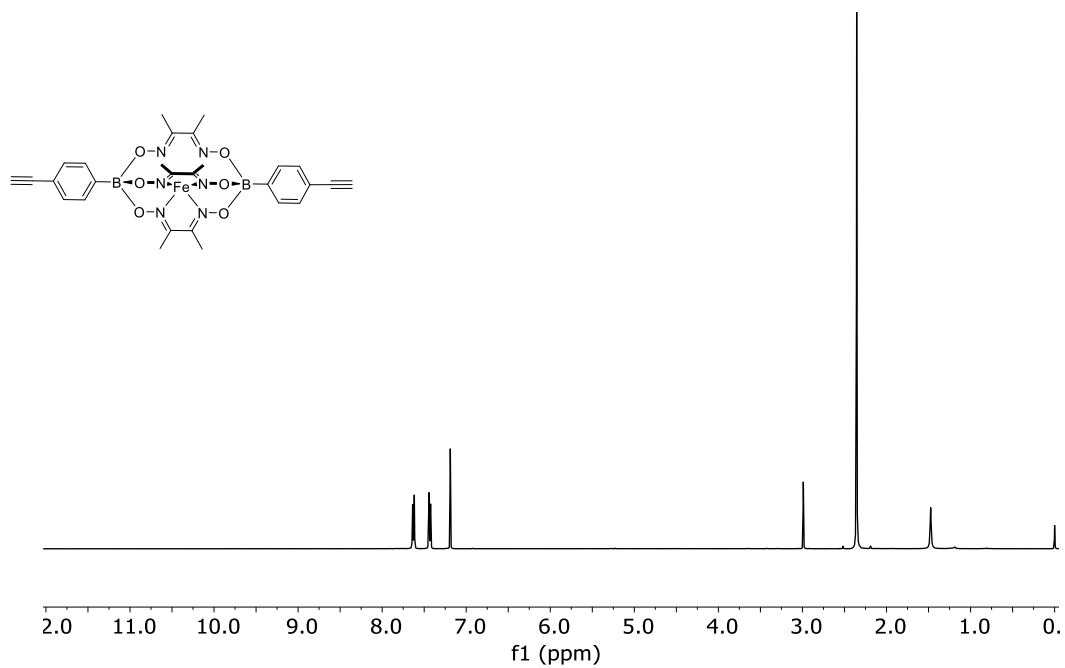


Figure S1 – <sup>1</sup>H NMR spectrum of complex 2 in CDCl<sub>3</sub>.

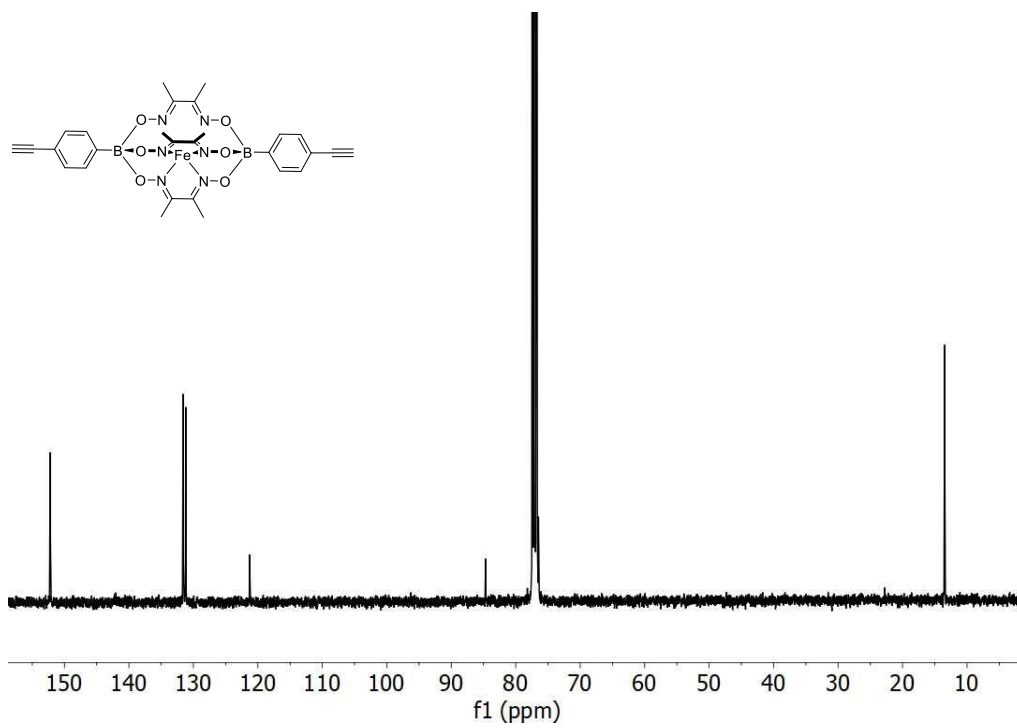
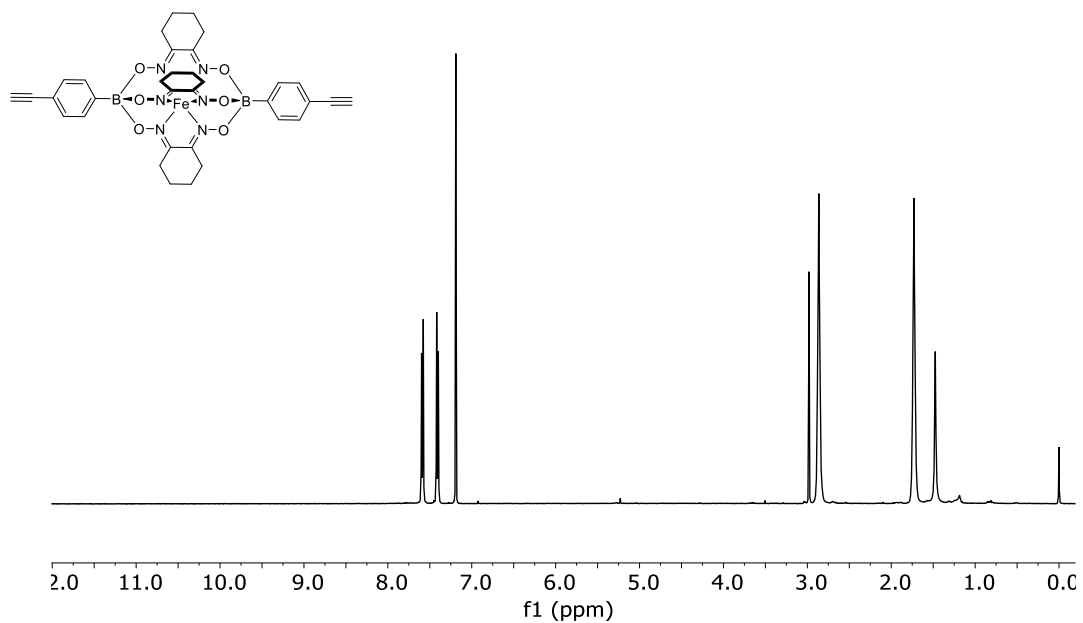
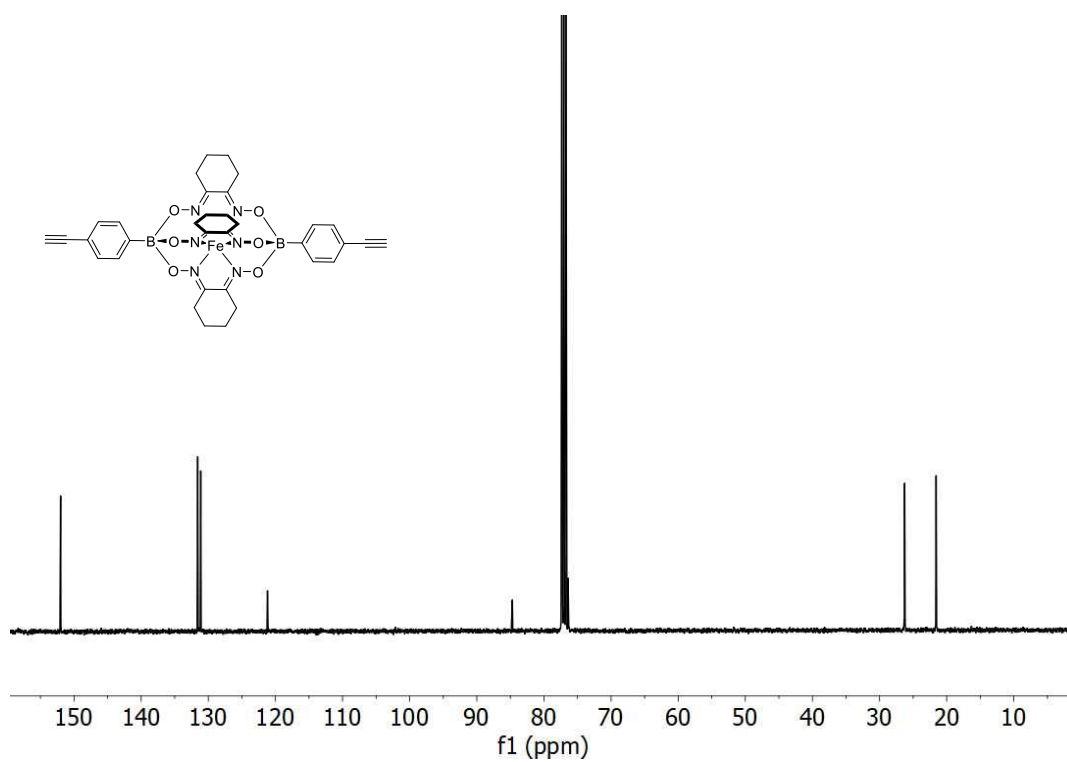


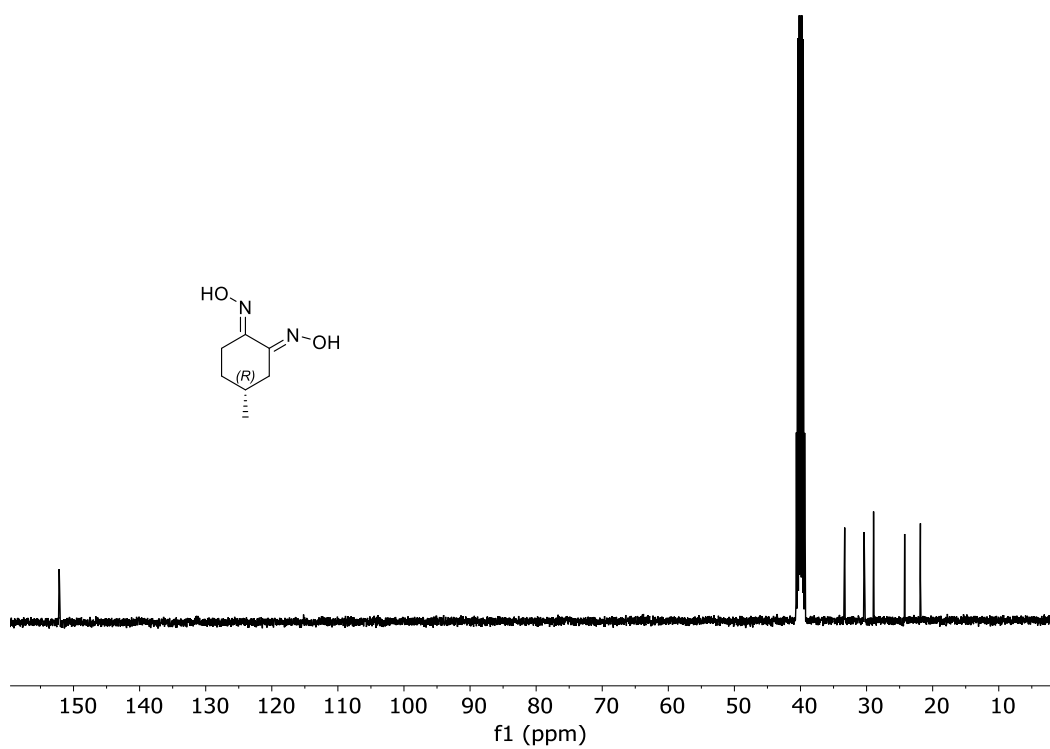
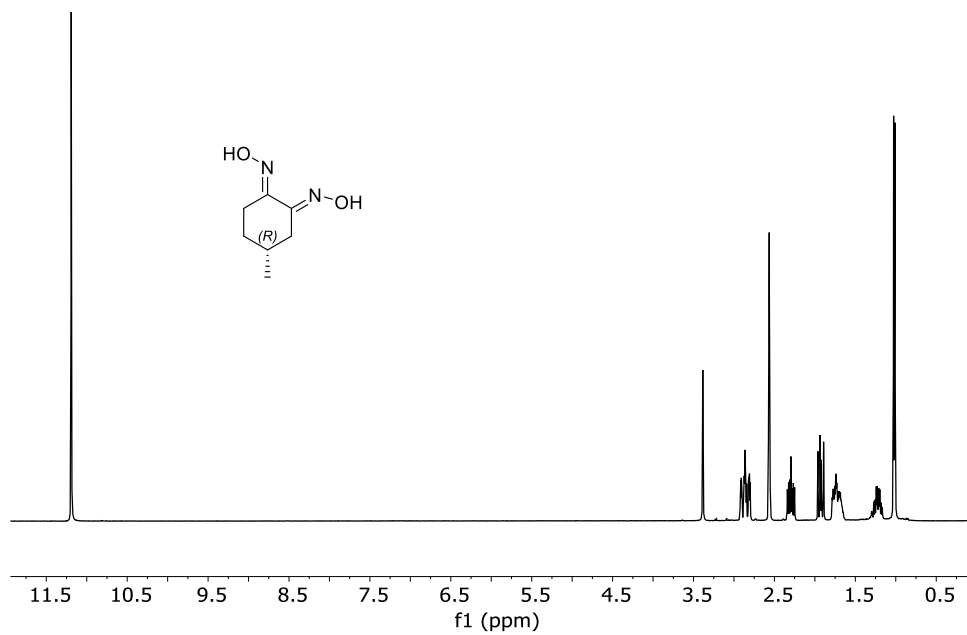
Figure S2 – <sup>13</sup>C NMR spectrum of complex 2 in CDCl<sub>3</sub>.



**Figure S3** –  $^1\text{H}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$ .



**Figure S4** –  $^{13}\text{C}$  NMR spectrum of complex **3** in  $\text{CDCl}_3$ .



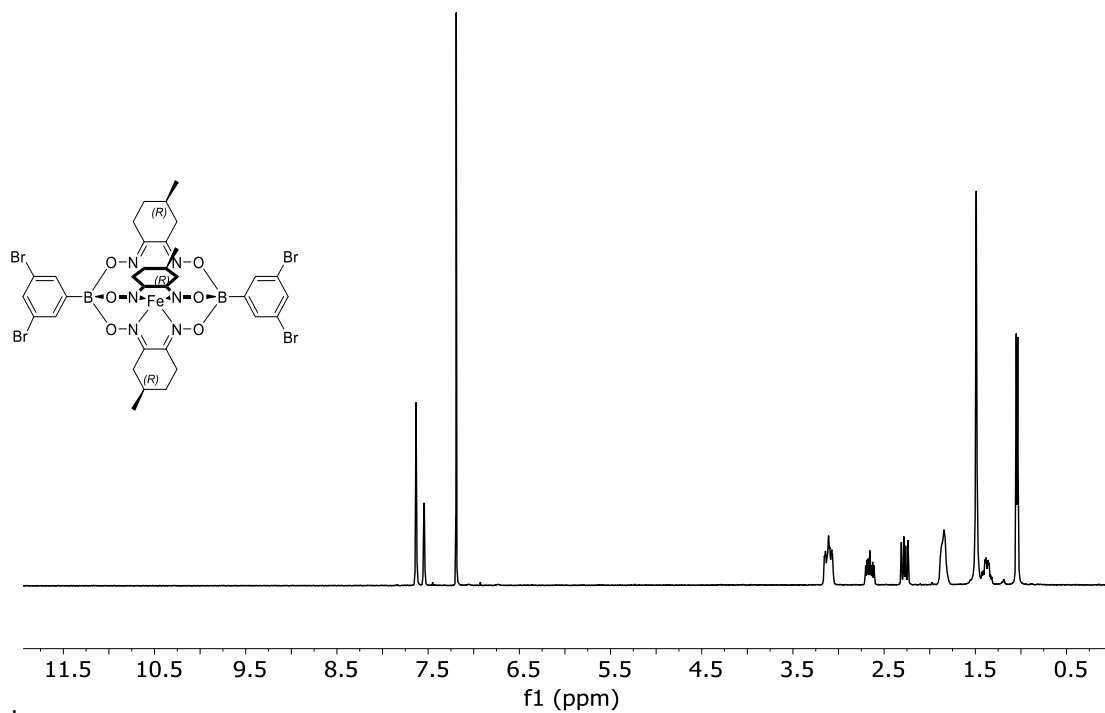


Figure S7 –  $^1\text{H}$  NMR spectrum of complex 5 in  $\text{CDCl}_3$ .

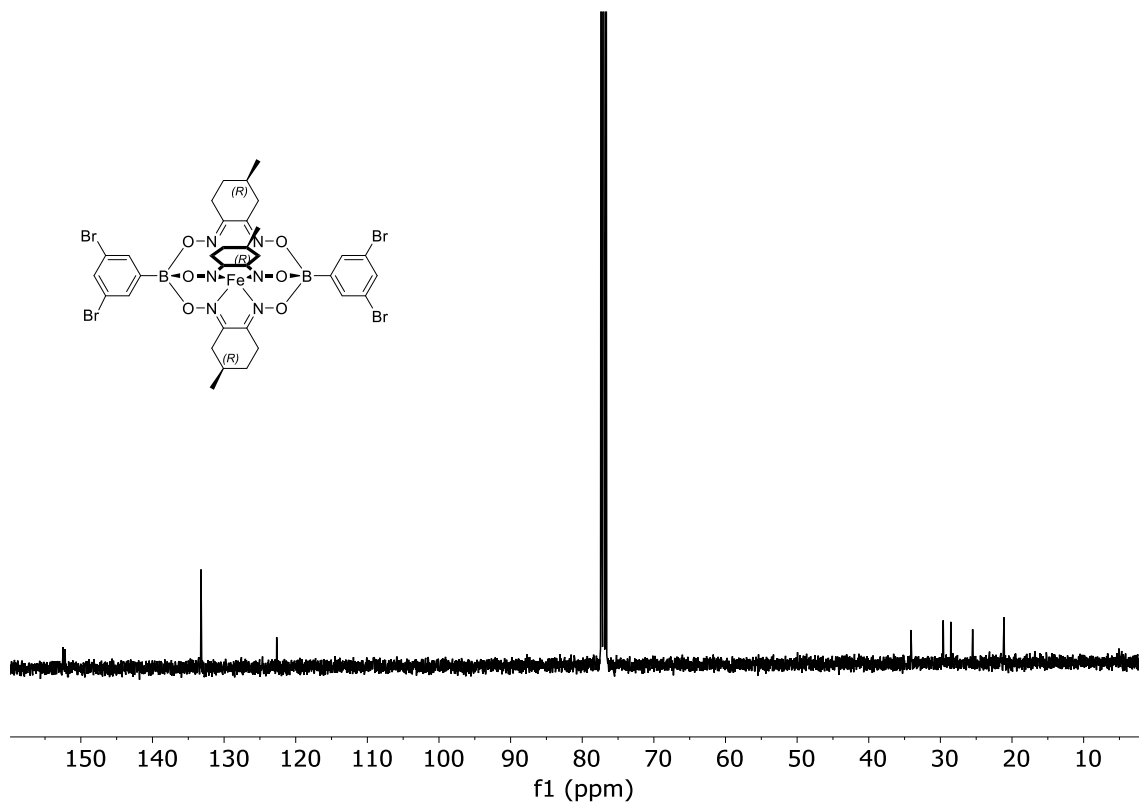


Figure S8 –  $^{13}\text{C}$  NMR spectrum of complex 5 in  $\text{CDCl}_3$ .

## 5. Solid state NMR spectra

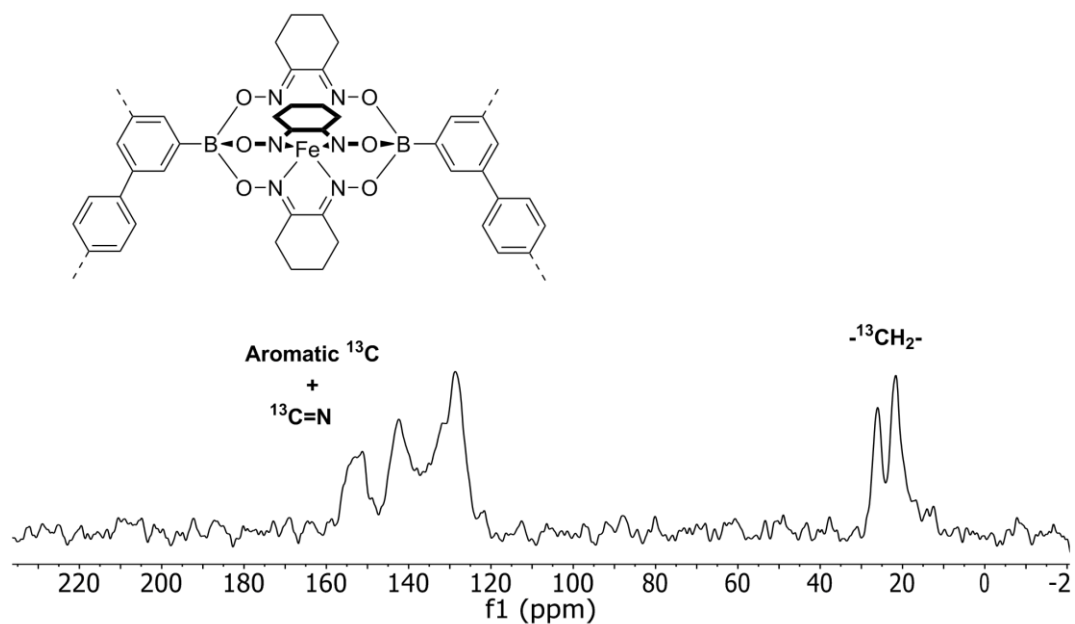


Figure S9 –  $^{13}\text{C}$  Solid-state MAS NMR spectrum of P-1.

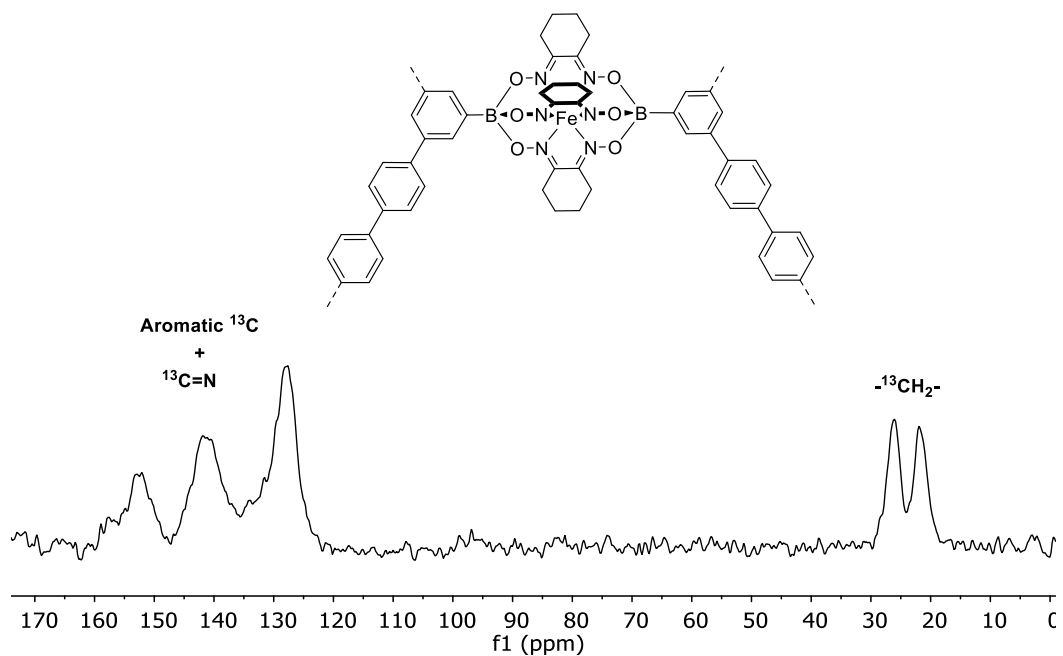


Figure S10 –  $^{13}\text{C}$  Solid-state MAS NMR spectrum of P-2.



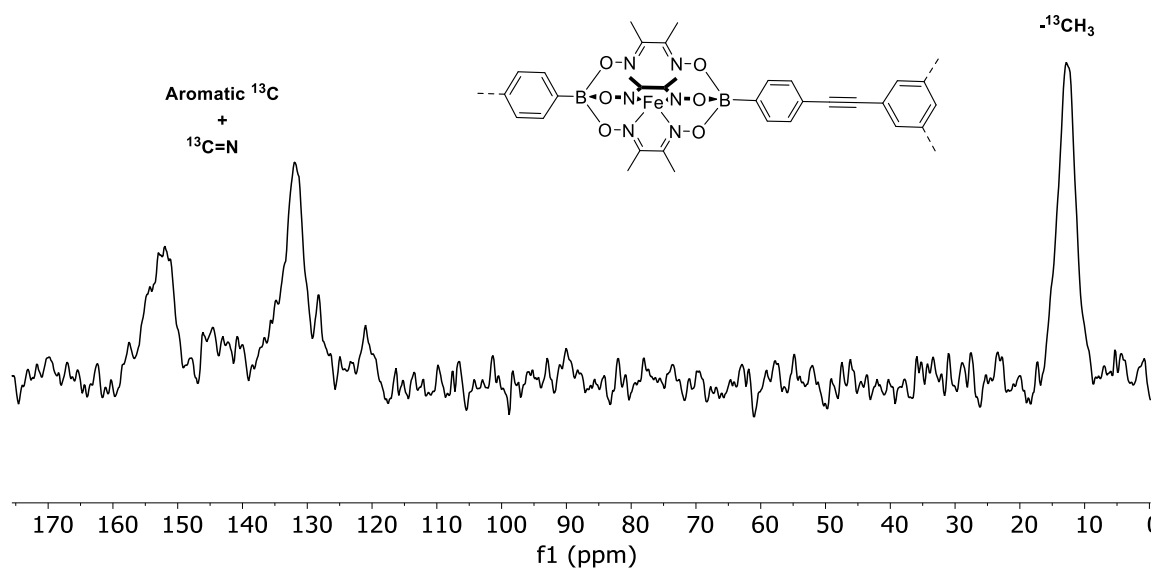


Figure S11 –  $^{13}\text{C}$  Solid-state MAS NMR spectrum of P-3.

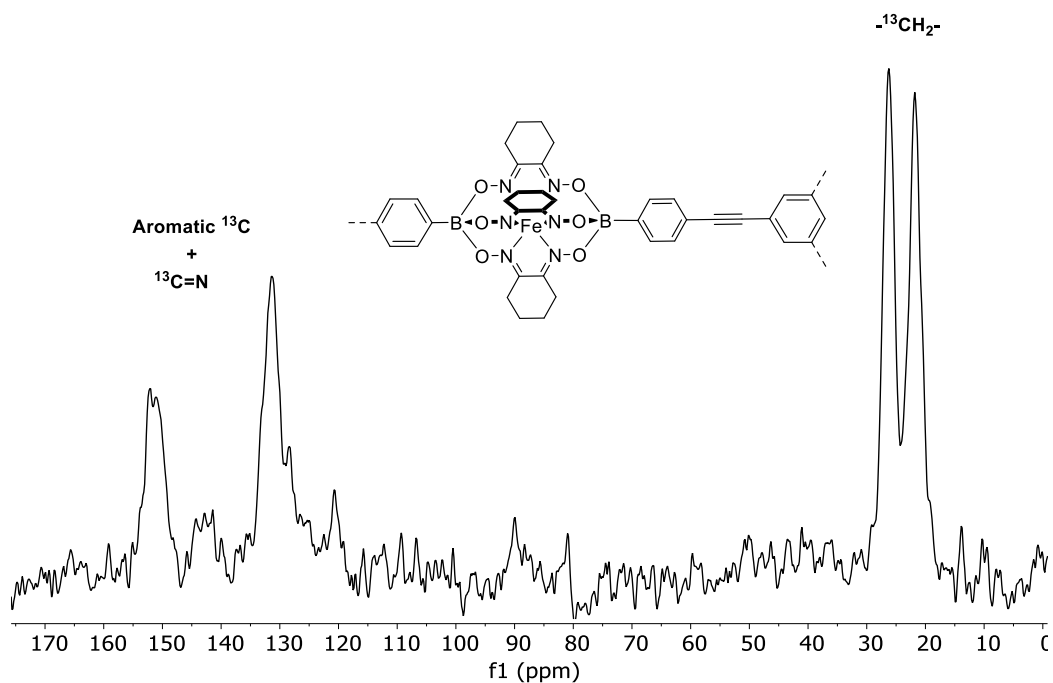


Figure S12 –  $^{13}\text{C}$  Solid-state MAS NMR spectrum of P-4.

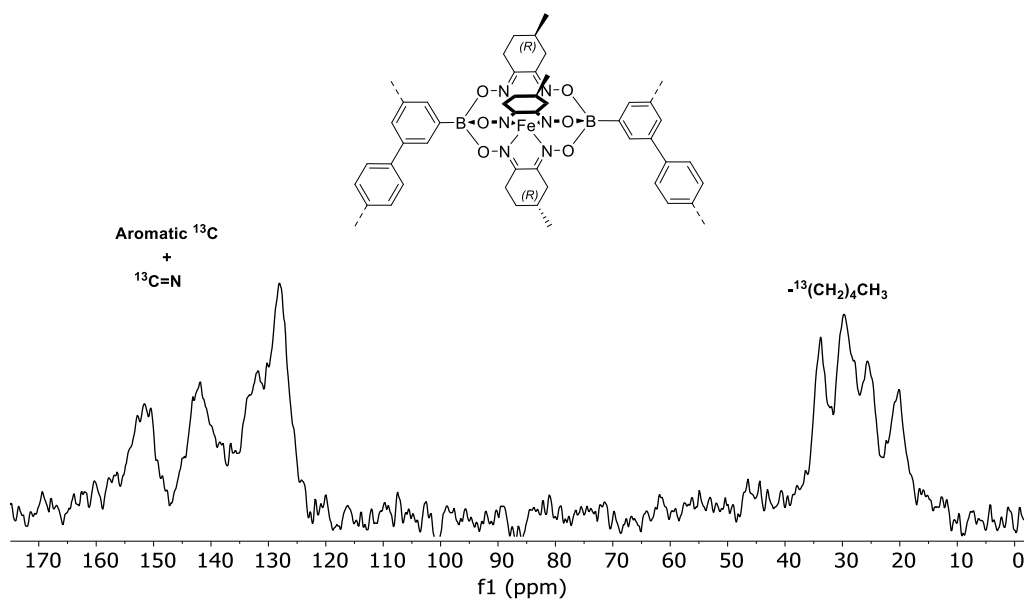


Figure S13 –  $^{13}\text{C}$  Solid-state MAS NMR spectrum of P-5.

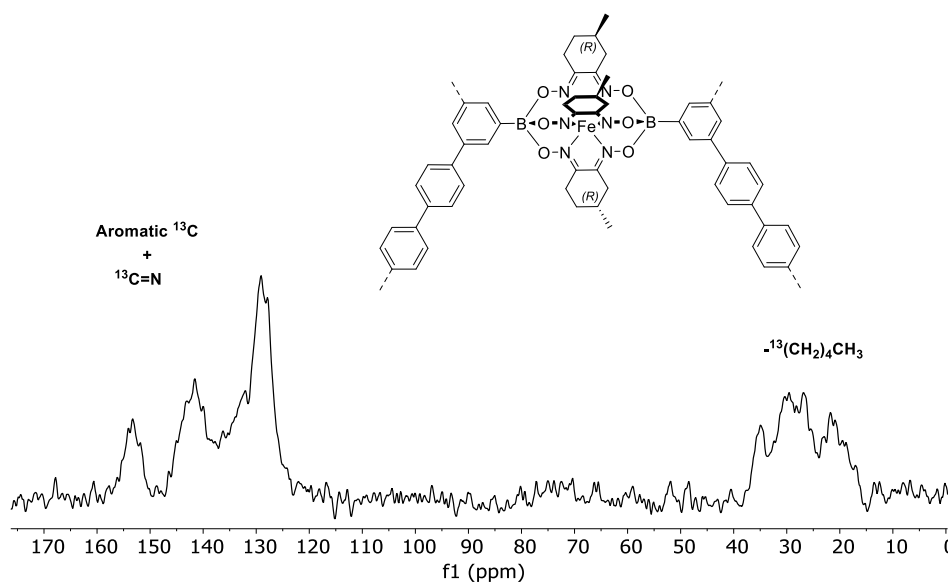


Figure S14 –  $^{13}\text{C}$  Solid-state MAS NMR spectrum of P-6.

## 6. Crystallographic data

Single crystals of complex **2** were obtained by slow diffusion of pentane into a solution of **2** in DCM.

Single crystals of complex **3** were obtained by slow diffusion of isopropyl ether into a solution of **3** in DCM.

Single crystals of complex **5** were obtained by slow diffusion of pentane into a solution of **5** in DCM.

Bragg-intensities of **2**, **3** and **5** were collected at low temperature (see Table S4) using CuK $\alpha$  radiation for compounds **2** and **3**, and MoK $\alpha$  radiation for compound **5**. A Rigaku SuperNova dual system diffractometer with an Atlas S2 CCD detector was used for compounds **2** and **5**, and one equipped with an Atlas CCD detector for compound **3**. The datasets were reduced and corrected for absorption with CrysAlis<sup>Pro</sup>.<sup>5</sup>, by using a set of faces enclosing the crystals as snugly as possible,

The solutions and refinements of the structures were performed by the latest available version of ShelXT<sup>6</sup> and ShelXL.<sup>7</sup> All non-hydrogen atoms were refined anisotropically using full-matrix least-squares based on  $|F|^2$ , but the hydrogen atoms were placed at calculated positions by means of the “riding” model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2  $U_{eq}$  of its parent C-atom (1.5  $U_{eq}$  for the methyl groups). Crystallographic and refinement data are summarized in Table S4. CCDC numbers 1876989-1876991 for compounds **2** (1876989), **3** (1876990), and **5** (1876991), contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/structures](http://www.ccdc.cam.ac.uk/structures).

In the structure of **3**, a solvent mask was calculated with the help of the solvent-masking program in OLEX2<sup>8</sup> and 344.0 electrons were found in a volume of 972.0 Å<sup>3</sup>. This is consistent with the presence of half a dichloromethane solvent molecule per formula unit which account for 336.0 electrons.

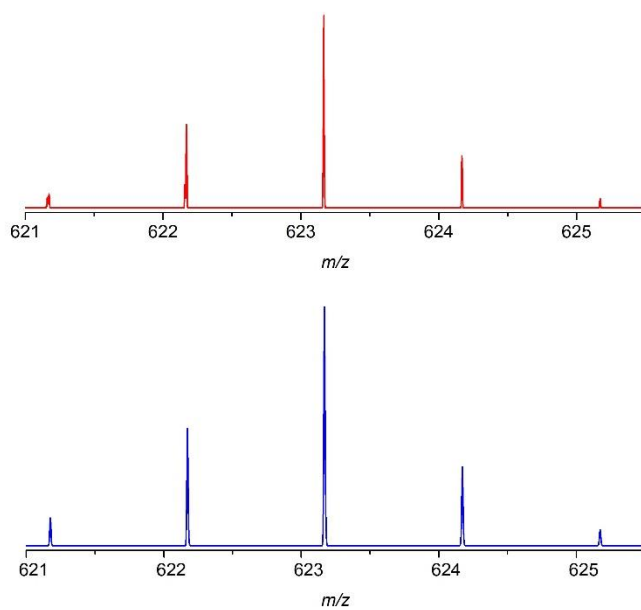
In the case of **5**, the structure was refined as a two-component inversion twin, yielding a BASF parameter of 0.20(2).

A calculated solvent mask found 162.0 electrons in a volume of 558.0 Å<sup>3</sup>. This is consistent with the presence of one dichloromethane solvent molecule per formula unit, which account for 168.0 electrons.

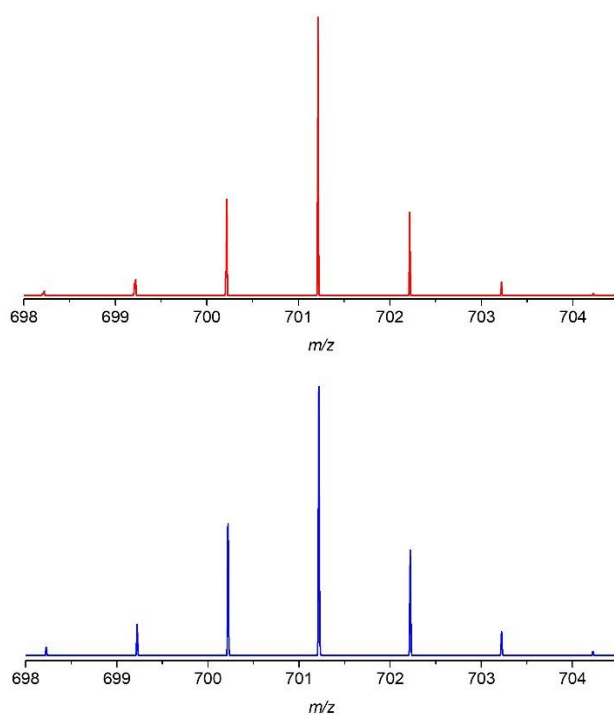
**Table S4** - Crystallographic parameters for complexes **2**, **3** and **5**.

<b>Compound</b>	<b>2</b>	<b>3</b>	<b>5</b>
Formula	C <sub>28</sub> H <sub>28</sub> B <sub>2</sub> FeN <sub>6</sub> O <sub>6</sub>	C <sub>34</sub> H <sub>34</sub> B <sub>2</sub> FeN <sub>6</sub> O <sub>6</sub>	C <sub>33</sub> H <sub>33</sub> B <sub>2</sub> Br <sub>4</sub> FeN <sub>6</sub> O <sub>6</sub>
<i>D</i> <sub>calc.</sub> / g cm <sup>-3</sup>	1.429	1.360	1.572
$\mu$ /mm <sup>-1</sup>	4.631	3.979	4.158
Formula Weight	622.03	700.14	1006.76
Colour	clear intense orange	clear intense red	clear intense red
Shape	plate	prism	plate
Size/mm <sup>3</sup>	0.76×0.60×0.04	0.87×0.12×0.06	0.72×0.52×0.20
<i>T</i> /K	140.00(10)	100.01(10)	140.00(10)
Crystal System	monoclinic	monoclinic	orthorhombic
Space Group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>I</i> 2/ <i>a</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2
<i>a</i> /Å	10.8991(2)	30.5087(8)	14.0642(6)
<i>b</i> /Å	16.1046(3)	9.8259(2)	17.8345(8)
<i>c</i> /Å	16.9882(3)	46.0071(17)	16.9600(8)
$\alpha$ /°	90	90	90
$\beta$ /°	104.090(2)	97.269(3)	90
$\gamma$ /°	90	90	90
<i>V</i> /Å <sup>3</sup>	2892.17(10)	13681.0(7)	4254.1(3)
<i>Z</i>	4	16	4
<i>Z</i> '	1	2	1
Wavelength/Å	1.54184	1.54184	0.71073
Radiation type	CuK $\alpha$	CuK $\alpha$	MoK $\alpha$
$\theta$ <sub>min</sub> /°	3.838	3.704	2.581
$\theta$ <sub>max</sub> /°	76.244	63.685	33.065
Measured Refl.	18388	44155	56046
Independent Refl.	5928	11115	14690
Reflections with <i>I</i> > 2( <i>I</i> )	5407	9347	7740
<i>R</i> <sub>int</sub>	0.0610	0.0443	0.0686
Parameters	394	1000	506
Restraints	0	1384	29
Largest Peak/e Å <sup>-3</sup>	0.834	1.281	0.955
Deepest Hole/e Å <sup>-3</sup>	-0.939	-0.833	-0.999
Goof	1.049	1.067	1.029
<i>wR</i> <sub>2</sub> (all data)	0.1762	0.3377	0.2005
<i>wR</i> <sub>2</sub>	0.1700	0.3284	0.1659
<i>R</i> <sub>1</sub> (all data)	0.0640	0.1281	0.1377
<i>R</i> <sub>1</sub>	0.0603	0.1170	0.0680

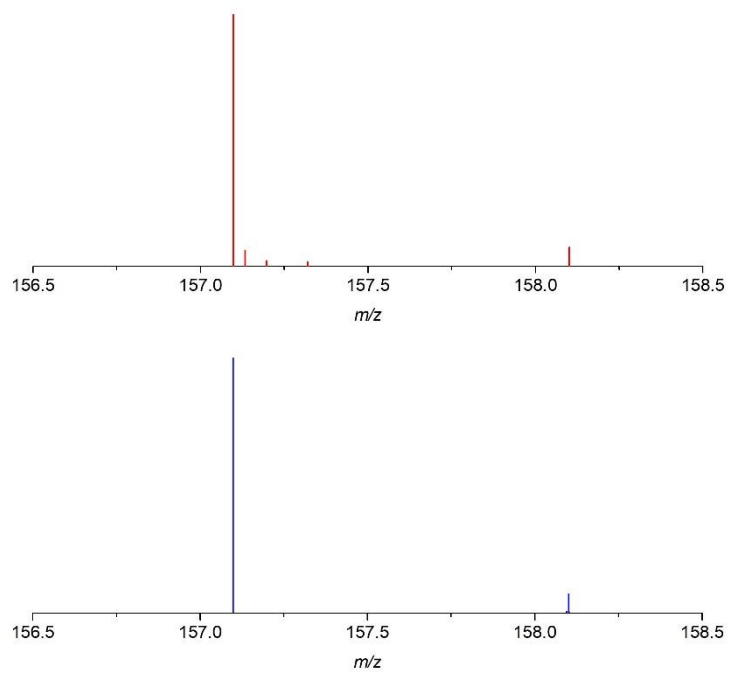
## 7. Mass Spectrometry



**Figure S 15** - HRMS of complex **2**:  $m/z$  calculated for  $C_{28}H_{28}B_2FeN_6O_6 [M+H]^+$  622.1605; found: 622.1662 (red) and simulation (blue)

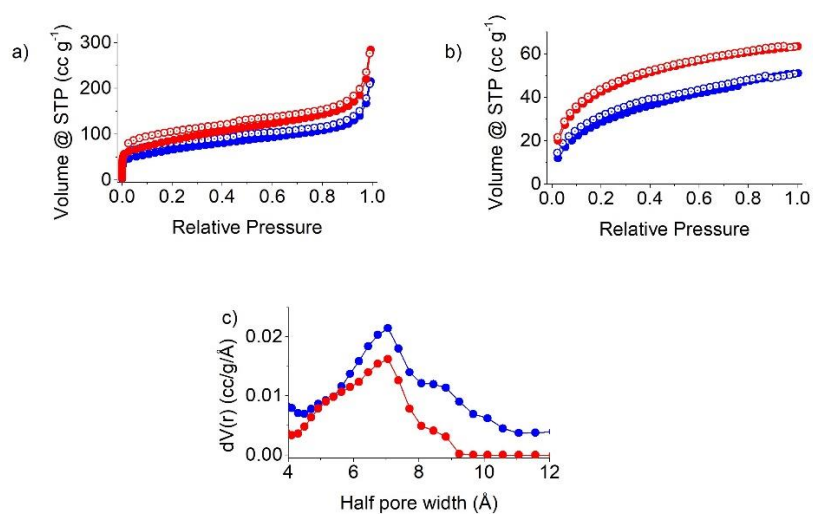


**Figure S 16** - HRMS of complex **2**:  $m/z$  calculated for  $C_{34}H_{35}B_2FeN_6O_6 [M+H]^+$  701.2148; found: 701.2118 (red) and simulation (blue)

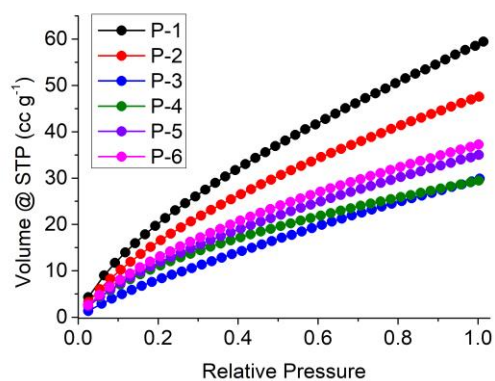


**Figure S 17** - HRMS of complex 4:  $m/z$  calcd for  $C_7H_{13}N_2O_2$   $[M-H]^+$  157.0972, found 157.0977 (red) and simulation (blue)

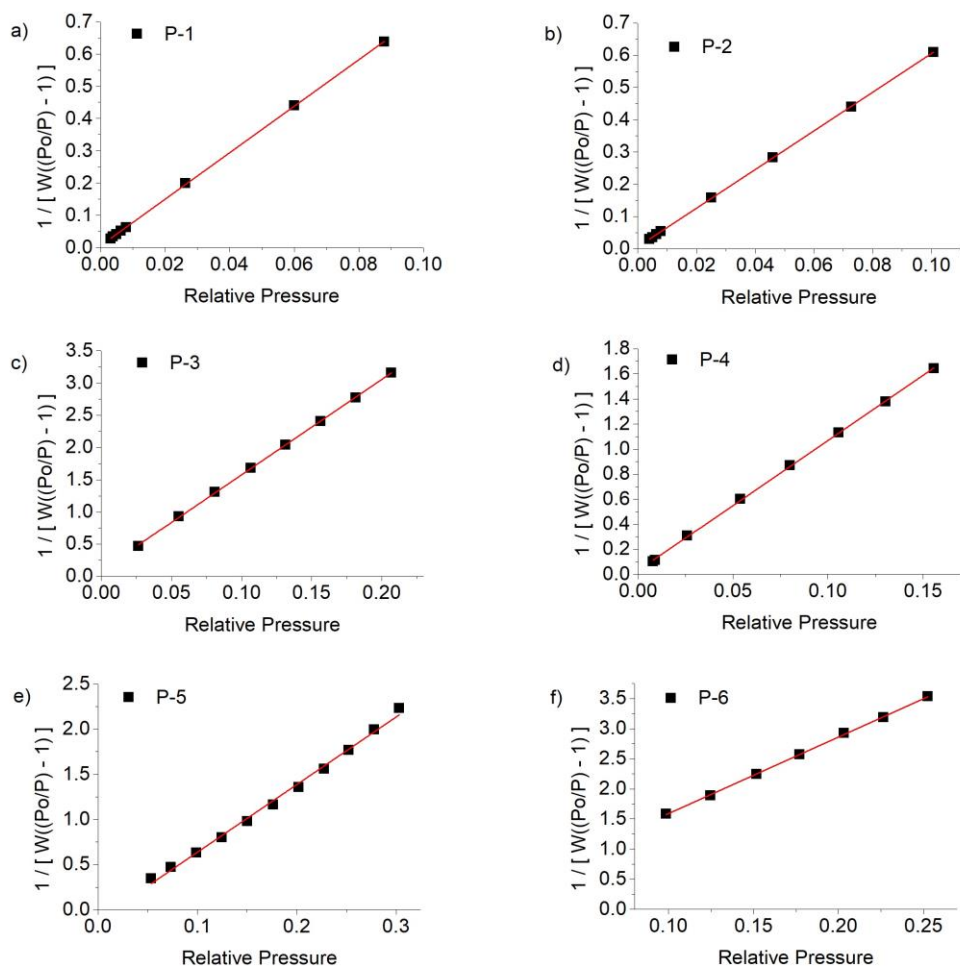
## 8. Adsorption studies



**Figure S18** – Characterization of P-3 (blue symbols) and P-4 (red symbols). a)  $N_2$  adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K; b)  $H_2$  adsorption (filled symbols) and desorption (open symbols) isotherms at 77 K; c) Pore size distribution.



**Figure S19** –  $CO_2$  adsorption studies of P-1 to P-6 at 273.15 K and 1 bar.



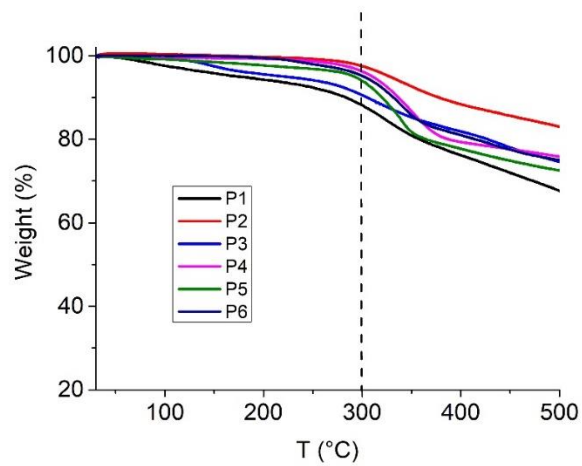
**Figure S20** – BET plots of Porous polymers **P-1** to **P-6** from nitrogen adsorption isotherms at 77 K. The selected points are located in the relative pressure ranges (0.01 and 0.3) determined according to the BET assistant on Quantachrome Autosorb instrument. Linear fit in red.



**Table S5** – CO<sub>2</sub> and H<sub>2</sub> adsorption at 1 bar

<b>Sample</b>	<b>CO<sub>2</sub> adsorption at 1 bar (cm<sup>3</sup>g<sup>-1</sup>)</b>	<b>H<sub>2</sub> adsorption at 1 bar (cm<sup>3</sup>g<sup>-1</sup>)</b>
<b>P-1</b>	58	101
<b>P-2</b>	48	90
<b>P-3</b>	30	51
<b>P-4</b>	30	63
<b>P-5</b>	35	41
<b>P-6</b>	37	96

## 9. Thermogravimetric analysis



**Figure S21** – Thermogravimetric analysis of **P-1** to **P-6** under  $N_2$  atmosphere with  $20 \text{ mL min}^{-1}$  flowrate and  $10 \text{ }^\circ\text{C min}^{-1}$ .

## 10. Adsorption studies with tryptophan

The polymers **P-5** or **P-6** (4 mg) were added to a solution of L- or D-Tryptophan in water (120  $\mu\text{M}$ , 2 mL). After dispersion through sonication and mixing, the suspension was stirred for the desired amount of time and the absorption at 280 nm was recorded. All measurements were performed in triplicates, and the values are reported in Table 5 and 6.

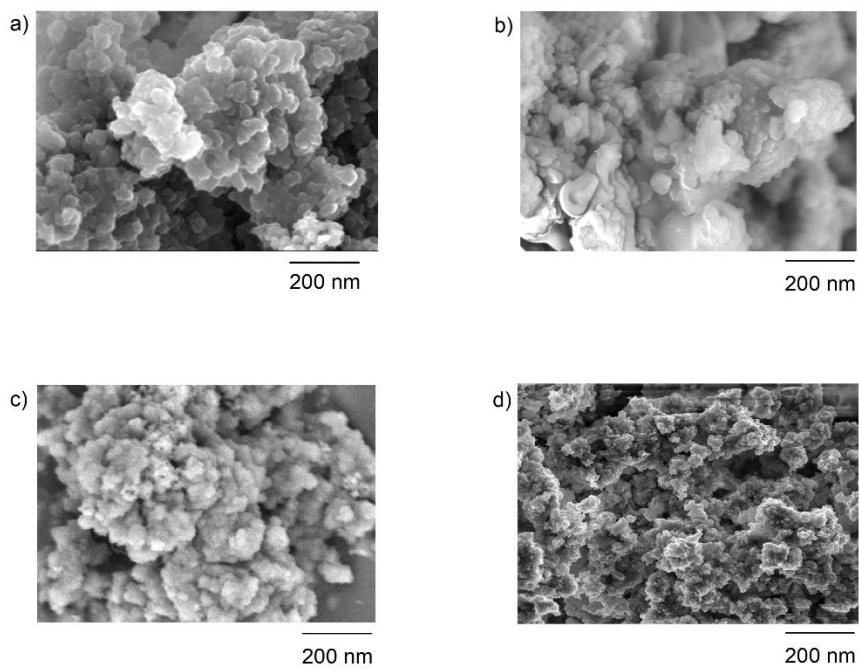
**Table S6** – Tryptophan uptake by **P-5**.

Time	D-Tryptophan Concentration ( $\mu\text{M}$ )				L-Tryptophan Concentration ( $\mu\text{M}$ )			
	1	2	3	Mean	1	2	3	Mean
0	120	120	120	120	120	120	120	120
20	102	103	103	103	109	112	108	110
40	92	96	102	97	106	96	116	106
60	84	88	94	89	101	100	87	96
80	80	73	89	81	90	89	85	88
100	74	81	63	73	81	76	90	82

**Table S7** – Tryptophan uptake by **P-6**.

Time	D-Tryptophan Concentration ( $\mu\text{M}$ )				L-Tryptophan Concentration ( $\mu\text{M}$ )			
	1	2	3	Mean	1	2	3	Mean
0	120	120	120	120	120	120	120	120
20	99	107	88	98	117	105	117	113
40	91	90	106	96	108	103	102	105
60	81	70	83	78	96	116	105	106
80	57	73	87	72	91	89	105	95
100	41	72	59	57	87	91	94	91

## 11. SEM images



**Figure S22** – SEM images of a) P-2 b) P-3 c) P-4 and d) P-6.

## 12. References:

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