Supplementary Information (SI) for CrystEngComm.

Electronic Supporting Information

Spin-crossover iron(II) complexes featuring boronic acid and boronic ester groups: synthesis and magnetic properties

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Contents

1. Crystallography

Crystallographic information: CCDC-2494923 (for **1a**), CCDC-2494924 (for **1b**), CCDC-2494925 (for **1c**), and CCDC-2494926 (for **2b**) contain the supplementary crystallographic data for compounds **1** in this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures.

Suitable single crystals of the investigated compounds were embedded in protective perfluoropolyalkyether oil on a microscope slide and a single specimen was selected and subsequently transferred to the diffractometer. Intensity data were collected at 100 K on a Bruker Kappa Photon2 *IμS* Duo diffractometer equipped with QUAZAR focusing Montel optics using Mo*Kα* radiation (λ = 0.71073 Å). Data were corrected for Lorentz and polarization effects, semi-empirical absorption corrections were performed on the basis of multiple scans using *SADABS*.[1] The structures were solved by direct methods (SHELX XT 2014/5)[2] and refined by full-matrix least-squares procedures on F^2 using SHELXL 2019/3.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of the oxygen bound hydrogen atoms were taken from a difference Fourier map and their positional parameters were either refined (for **1a**, **1b**, and **1c**) or allowed to ride on their oxygen carrier atom ((**2b**). All other hydrogen atoms were placed in positions of optimized geometry. The isotropic displacement parameters of all H atoms were tied to those of the corresponding carrier atoms by a factor of either 1.2 or 1.5. *Olex2*[4] was used to prepare materials for publication. Crystallographic data, data collection, and structure refinement details are given in Table S1.

In the crystal structures of **1a**, **1b**, and **1c** the iron complex molecule was located on a crystallographic twofold rotation axis and, consequently, these three iron complexes exhibited crystallographically imposed C_2 molecular symmetry. The asymmetric unit of the crystal structure of **1a** contained additionally a partially occupied water molecule (27%) that was found to be situated also on a crystallographic twofold axis.

In the crystal structure of **2b** two of the *t*Bu groups in one of the two ligands were disordered. Two alternative orientations were refined and resulted in site occupancies of 50.0(7) % each for the atoms C12 – C15 and C12A – C15A.
Compound **2b** crystallized with two molecules of diethyl ether per fomula unit. Both of these solvent molecules were disordered. Two alternative orientations were refined for the first Et_2O molecule and resulted in site occupancies of 68.6(7) and 31.4(7) % for the atoms C101 – C105 and C111 – C115. For the second Et_2O molecule three alternative orientation were refined with the following site occupancies obtained: 40.7(5) % for the atoms C201 – C205, 26.7(5) % for the atoms C211 – C215, and 32.8(5) % for the atoms C221 – C225, respectively.
Similarity and in part pseudo-isotropic restraints were applied in the refinement of the anisotropic displacement parameters of the disordered atoms.

Table S1. Crystallographic data, data collection and structure refinement details

	1a	1b	1c	2b
CCDC number	CCDC-2494923	CCDC-2494924	CCDC-2494925	CCDC-2494926
temperature K	100	100	100	100
chemical Formula	$C_{22}H_{20}B_2Cl_2FeN_{10}O_{12}$, 0.27 H_2O	$C_{24}H_{24}B_2Cl_2FeN_{10}O_{12}$	$C_{26}H_{28}B_2Cl_2FeN_{10}O_{12}$	$C_{40}H_{56}B_2FeCl_2FeN10O_{12}$· $2(C_4H_{10}O)$
fw	769.80	792.90	820.95	1165.55
crystal size, mm	0.18×0.12×0.12	0.17×0.14×0.09	0.20×0.06×0.06	0.24 × 0.22 × 0.18
Crystal shape / color	block / orange	block / yellow	block / orange	block / orange
crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	*C*2/*c*	*C*2/*c*	*C*2/*c*	$P2_1/n$
a(Å)	22.6294(15)	23.6479(17)	25.4259(15)	16.4968(12)
b(Å)	9.8872(6)	10.1118(6)	10.0950(5)	18.4483(13)
c(Å)	15.7450(12)	16.0253(11)	16.2659(11)	20.7114(16)
α(°)	90	90	90	90
β(°)	125.515(4)	126.737(4)	126.226(3)	91.181(3)
γ(°)	90	90	90	90
V(Å^3)	2867.4(4)	3070.9(4)	3368.0(4)	6301.9(8)
Z	4	4	4	4
D_{ber} (g·cm^{-3})	1.783	1.715	1.619	1.228
reflns collected/2θmax, deg	61204/61.1	44492/59.3	68150/61.1	281194/54.2
unique reflns	4385	4329	5152	13889
obs reflns (I > 2σ(I))	3917	3624	4553	11553
no.of param/restraints	234/0	235/0	244/0	927/695
μ(Mo*K*α), mm^{-1}	0.798	/0.747	0.684	0.388
R_1 [I > 2σ(I)]	0.0289	0.0432	0.0314	0.0573
wR_2 (all data)	0.0735	0.1042	0.0803	0.1648
goodness of fit	1.057	1.073	1.054	1.120
residual density e·Å^{-3}	+0.894/-0.426	+0.766/-0.562	+0.484/-0.548	+0.859/-0.641

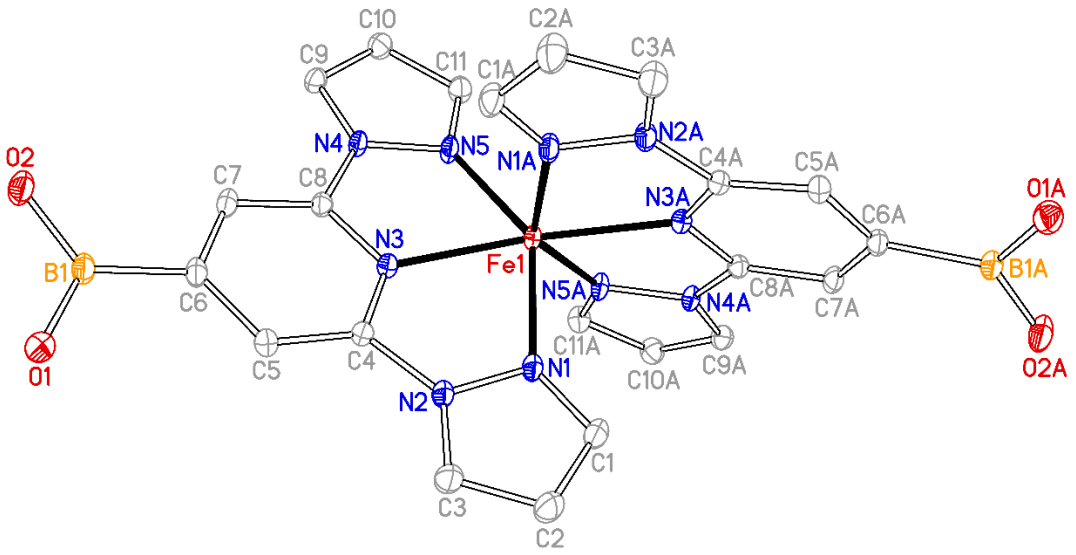


Figure S1. Thermal ellipsoid representation of the molecular structure of **1a** with the applied numbering scheme (50% probability level, ClO_4 anions, hydrogen atoms and solvent molecules omitted for clarity).

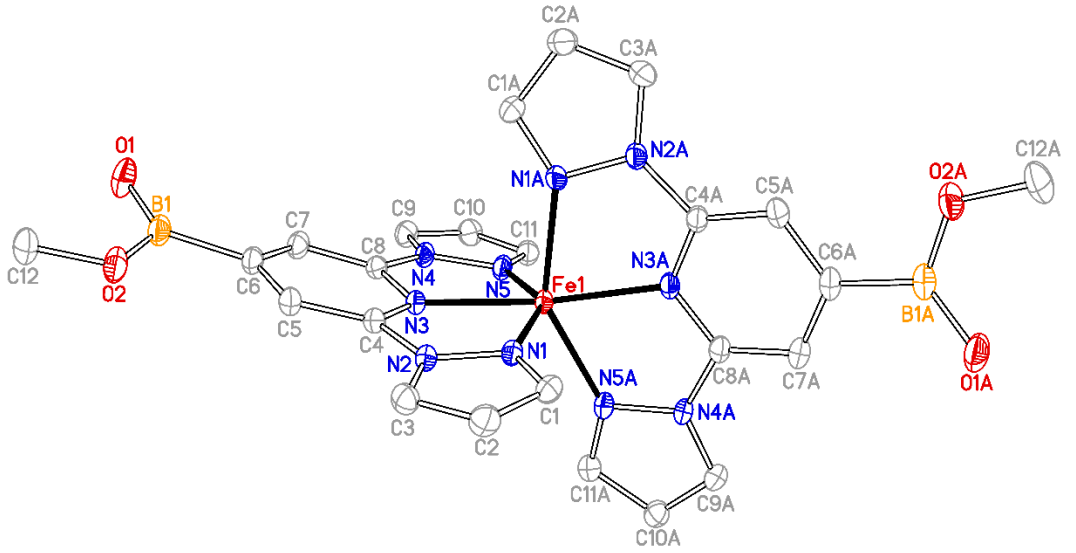


Figure S2. Thermal ellipsoid representation of the molecular structure of **1b** with the applied numbering scheme (50% probability level, ClO_4 anions and hydrogen atoms omitted for clarity).

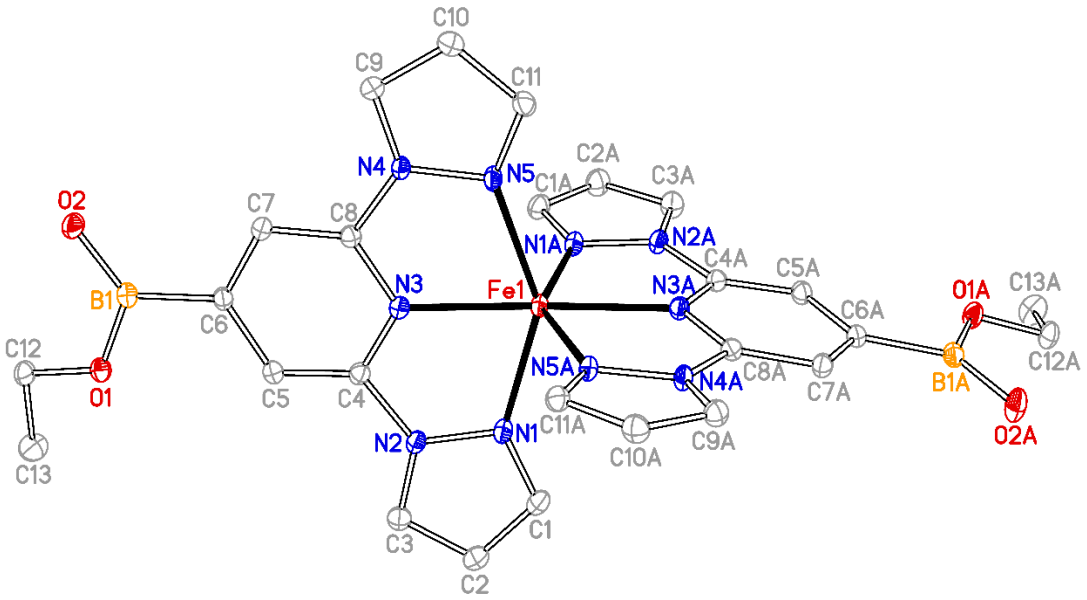


Figure S3. Thermal ellipsoid representation of the molecular structure of **1c** with the applied numbering scheme (50% probability level, ClO_4 anions and hydrogen atoms omitted for clarity).

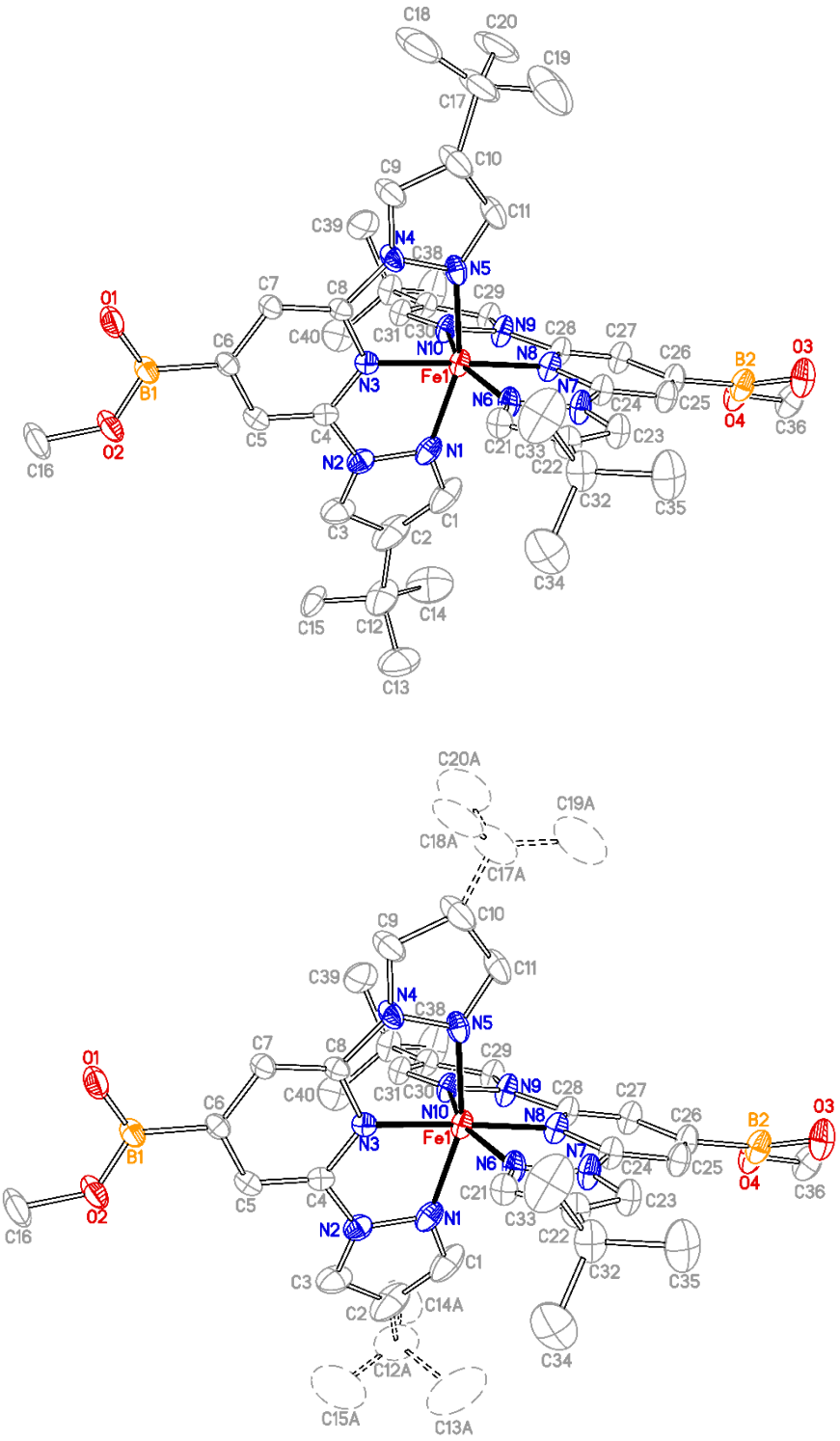


Figure S4. Thermal ellipsoid representation of the molecular structure of **2b** with the applied numbering scheme (50% probability level, ClO_4 anions, hydrogen atoms, and solvent molecules omitted for clarity). Top: major fraction of the disordered ligand is displayed, bottom: minor fraction of the disordered ligand is displayed with dotted ellipsoids and bonds.

2. Magnetic data.

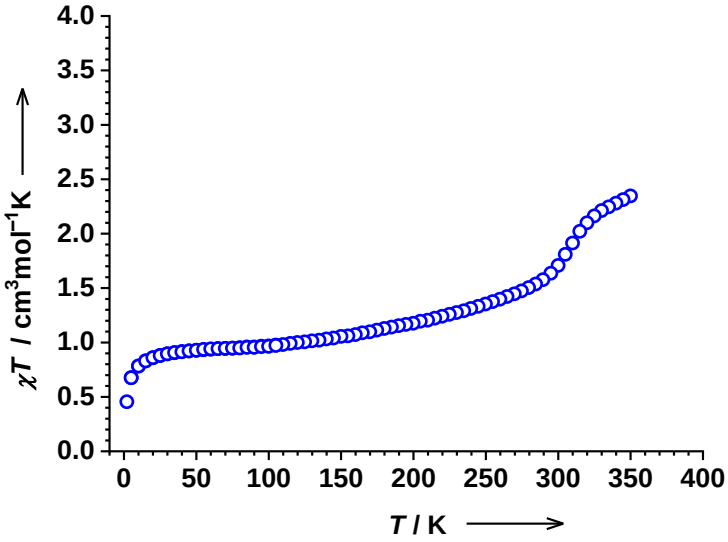


Figure S5. Variable-temperature χT products of **1a** measured from 300K to 2K to 350 K

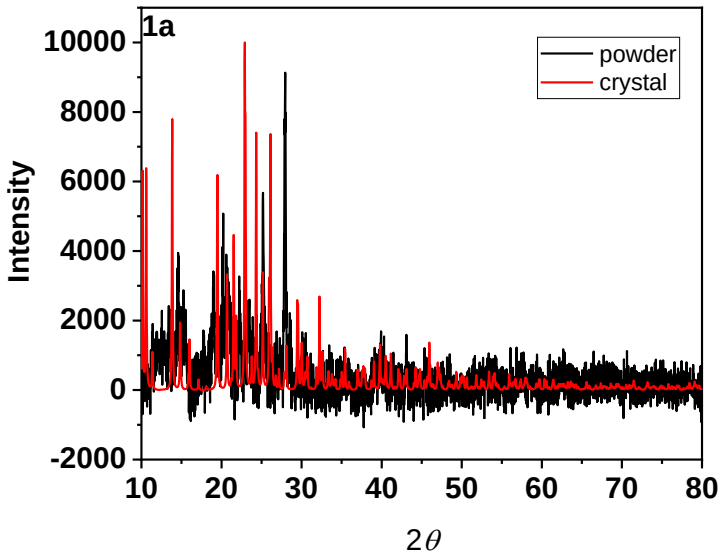
3. Powder X-ray

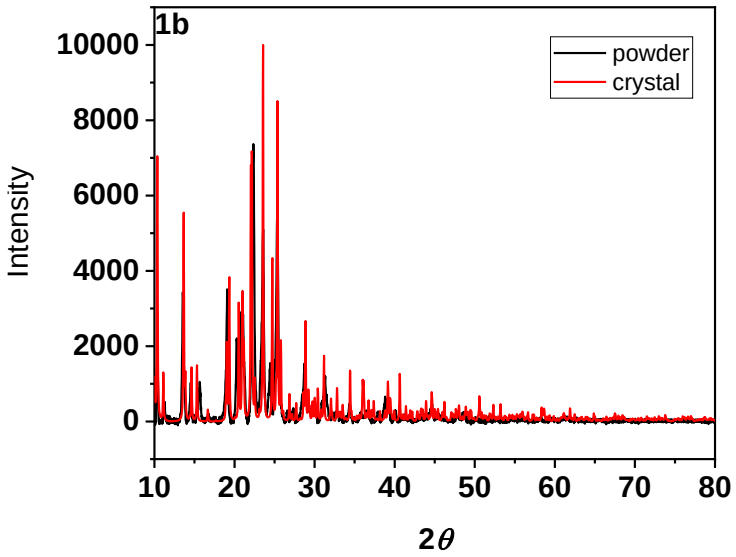
Powder X-ray measurements were performed on all four samples.

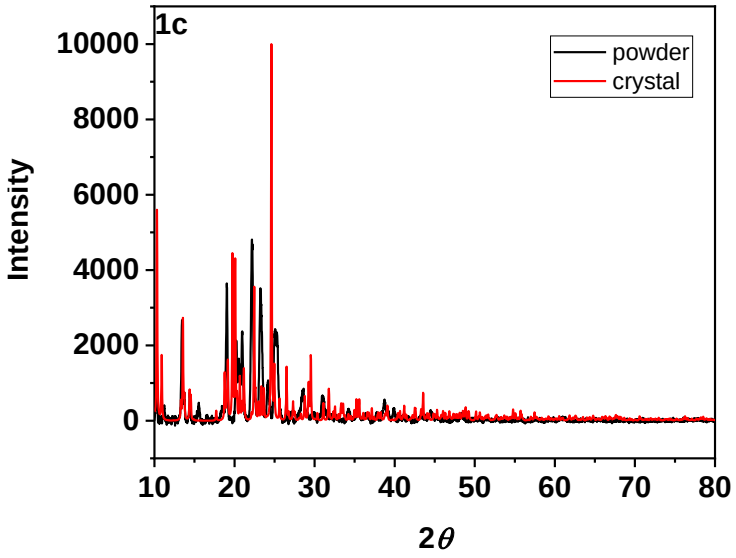
For **1a**, the powder diffraction pattern measured on a powder sample does not match with the one calculated from a single crystal data, which reveals that the two phases, powder and crystalline material, are very different. This further explains the differing spin-state situations observed in magnetic measurements (powder sample) and crystal structure (crystalline material).

The measured XRD pattern of **1b** is fully consistent with the calculated on a single crystal data, thus revealing the phase purity of the bulk sample. For **1c**, the measured XRD pattern is very similar but not identical to the calculated one. We attribute those small discrepancies to slowly decomposition of monoethyl ester group, which is in line with the magnetic measurements and Mössbauer spectroscopy.

The major absence of sharp reflections in XRD pattern of **2b** arises from the loss of crystallinity of the sample.




1b
powder
crystal
Intensity
10000
8000
6000
4000
2000
0
10
20
30
40
50
60
70
80
2θ


1c
powder
crystal
Intensity
10000
8000
6000
4000
2000
0
10
20
30
40
50
60
70
80
2θ

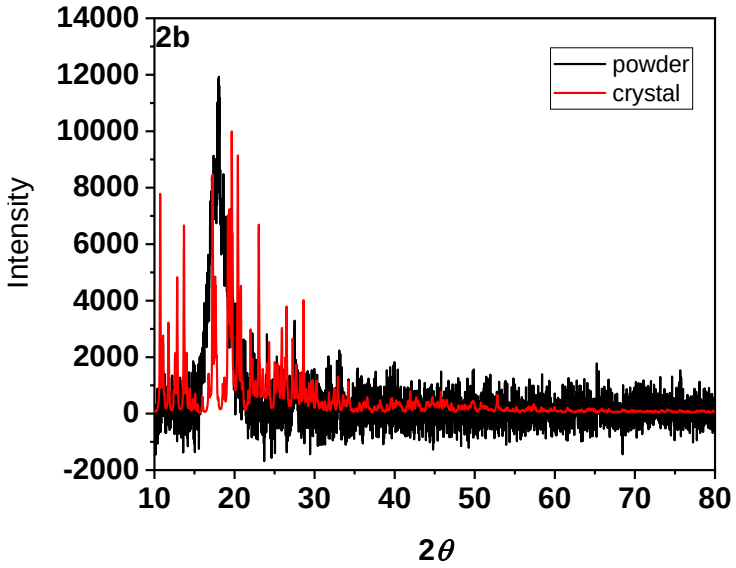


Figure S6. XRD patterns measured on a powder sample (black) and simulated from the X-ray structure (red) for **1a**, **1b**, **1c and 2b**.

4. Electronic absorption

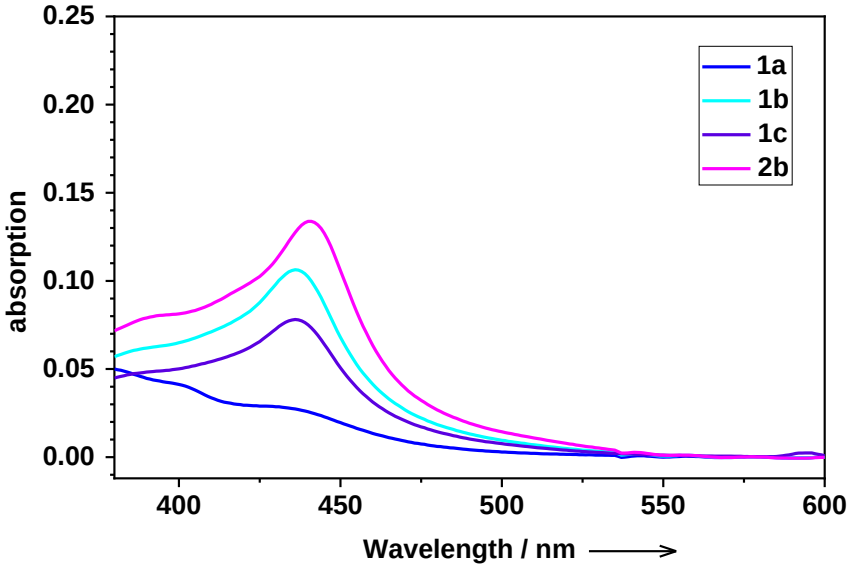
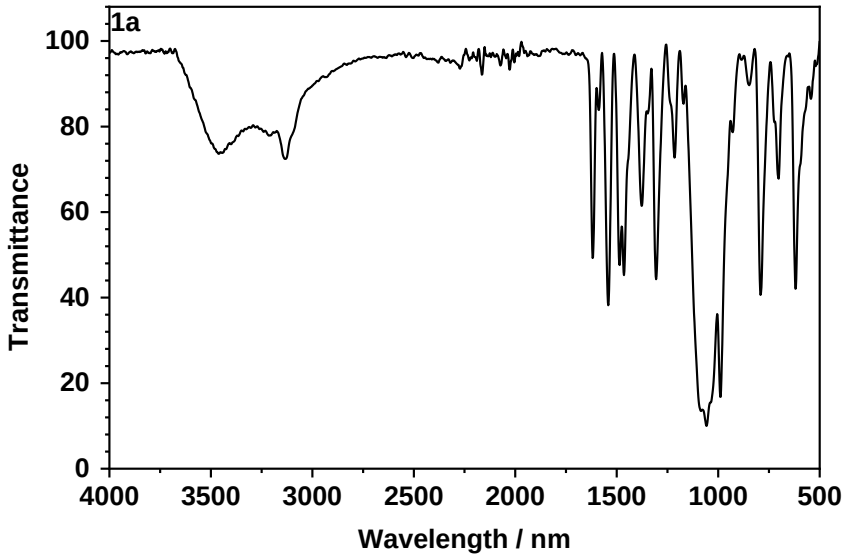
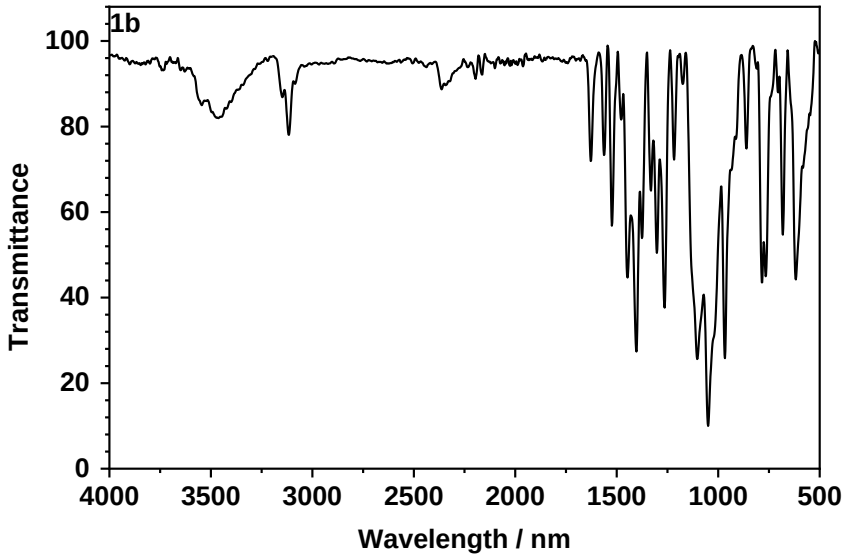


Figure S7. UV-vis spectra of **1a**, **1b**. **1c and 2b** (2.5 X 10^{-4} M) in acetonitrile. Note that the concentration of **1a** is not accurate because of its poor solubility.

5. IR spectra


1a
Transmittance
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength / nm


1b
Transmittance
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavelength / nm

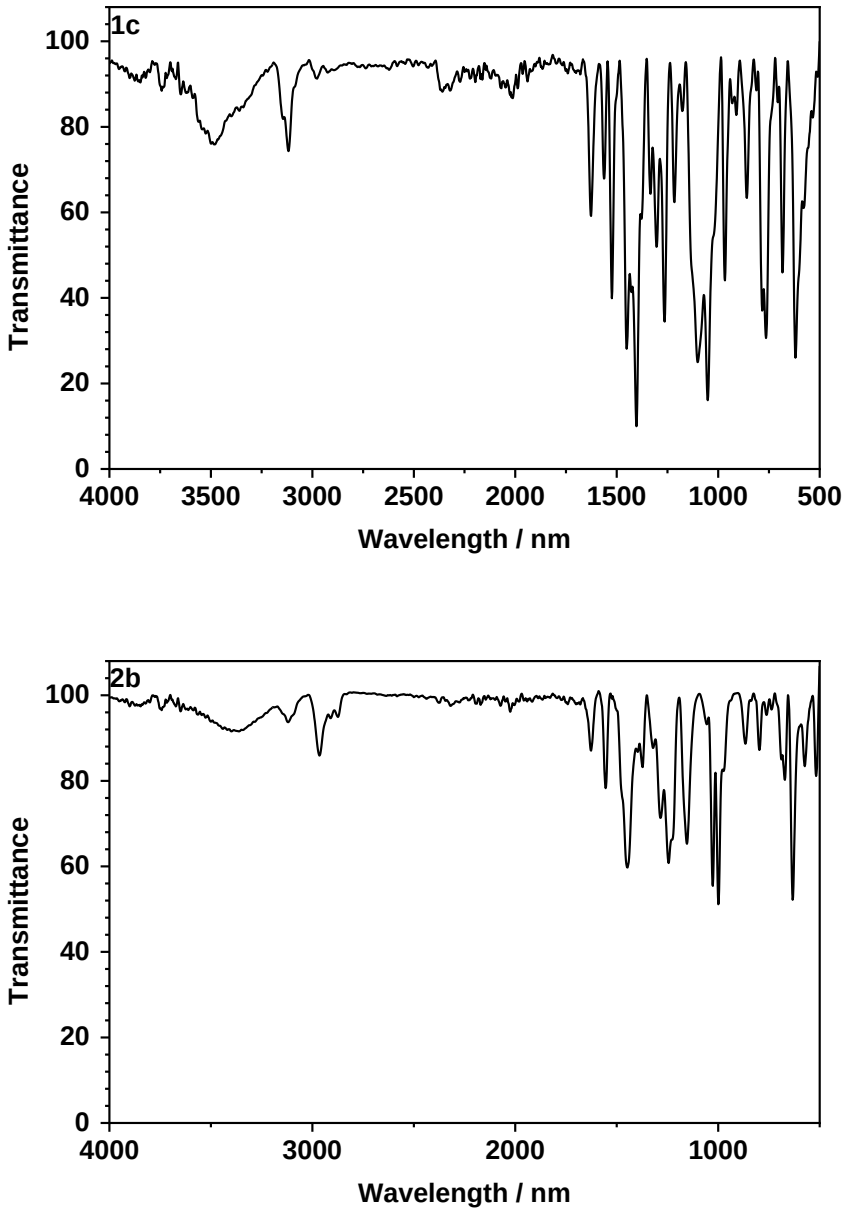
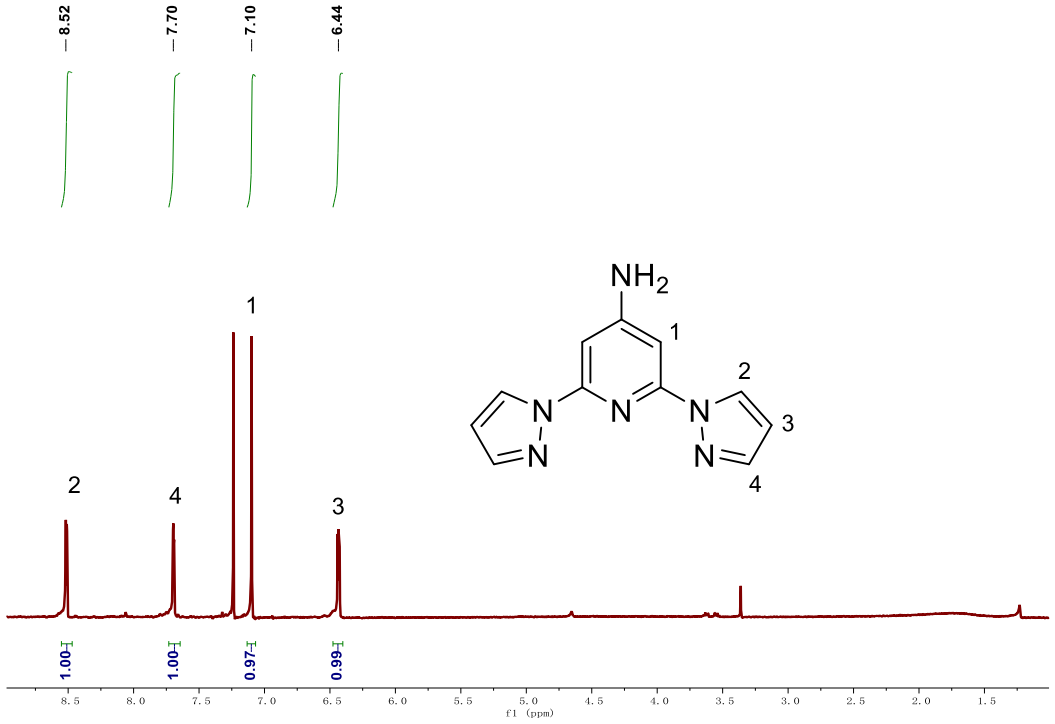
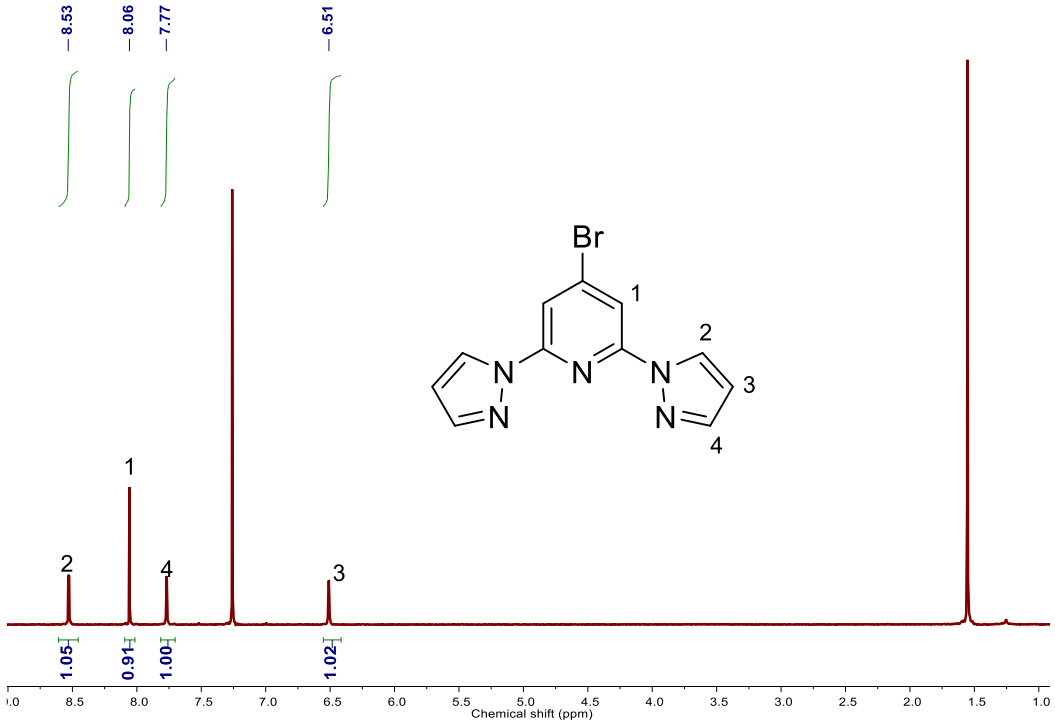
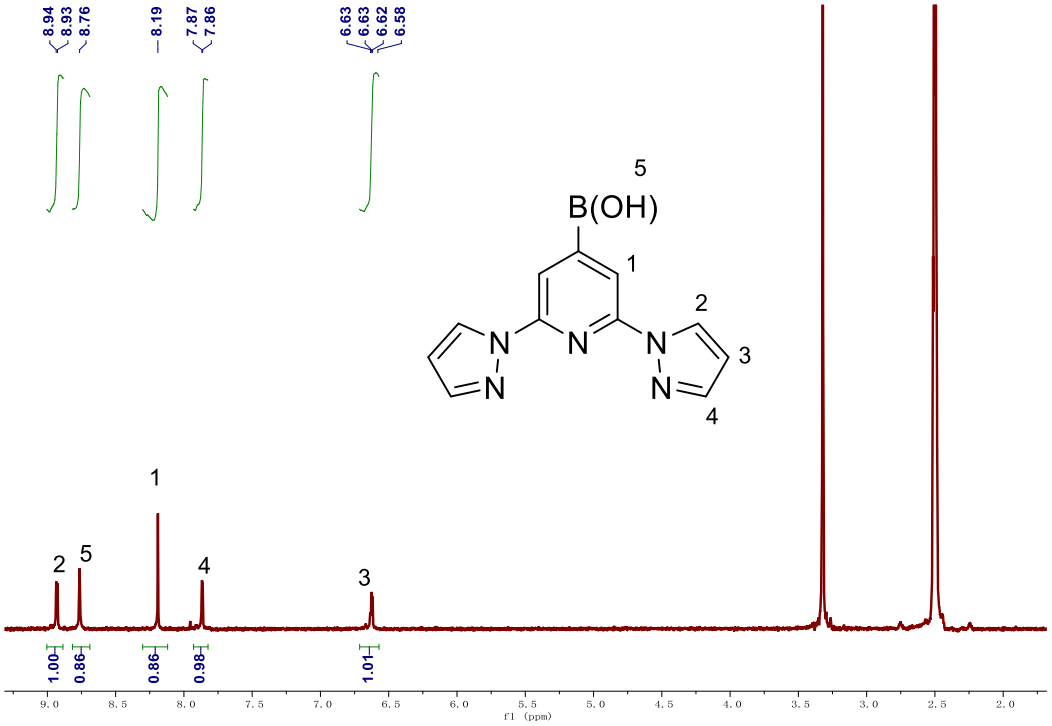


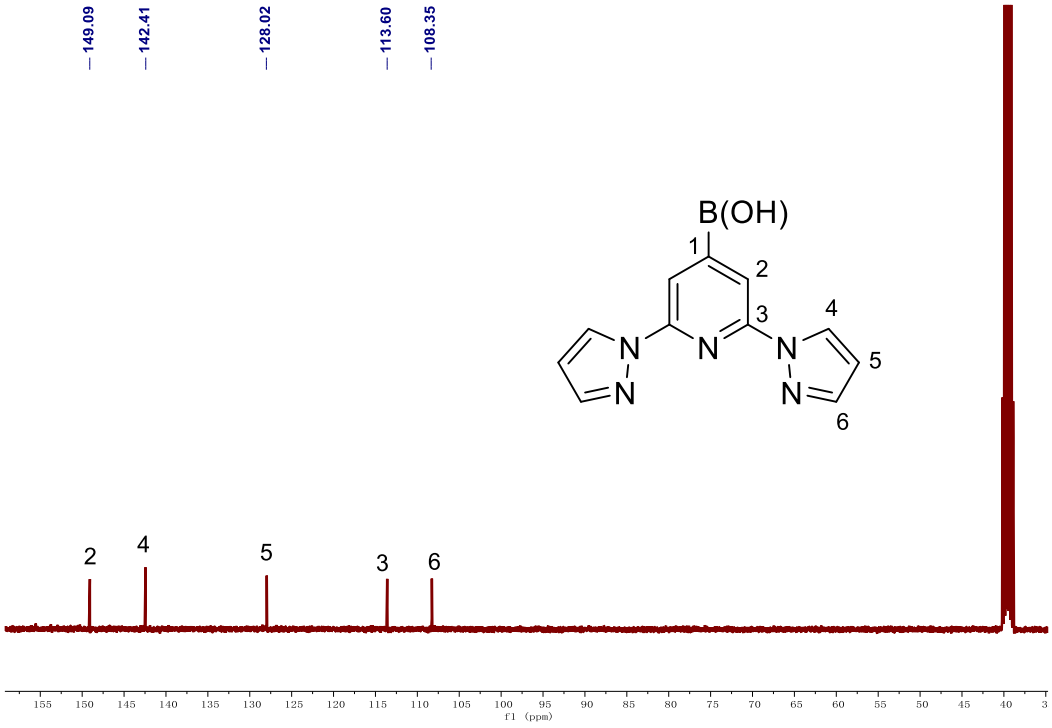
Figure S8. IR spectra of powder sample **1a**, **1b**, **1c** and **2b**.

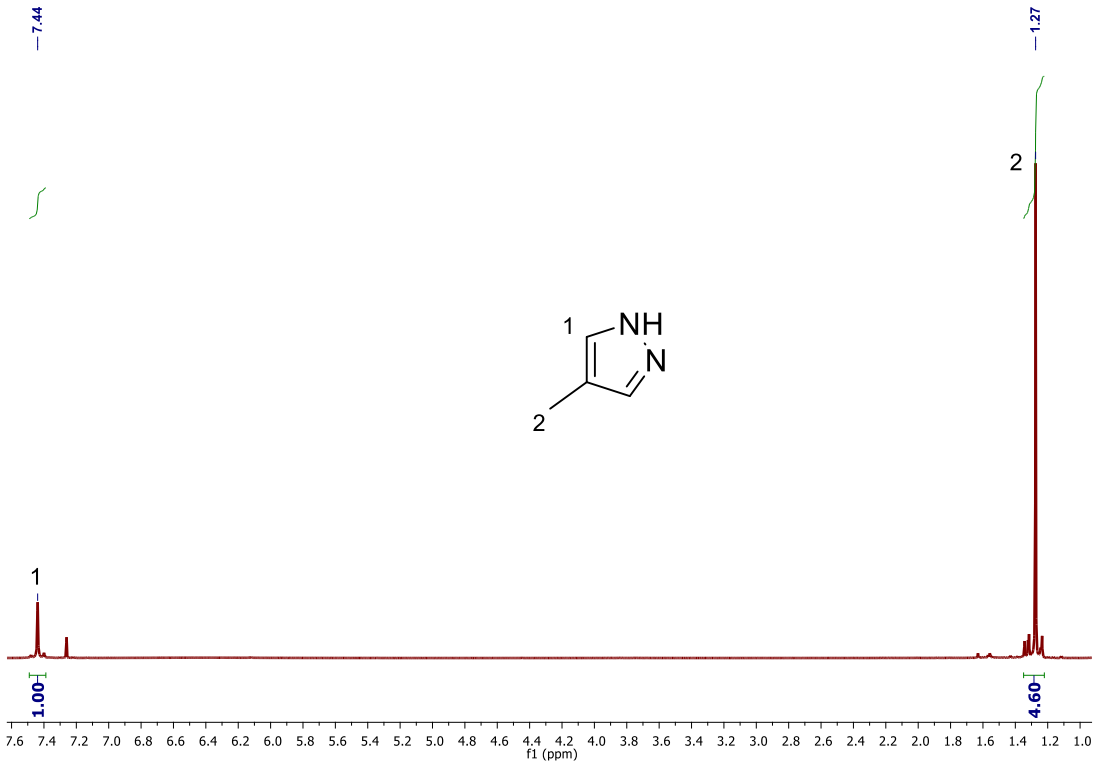
6. NMR data

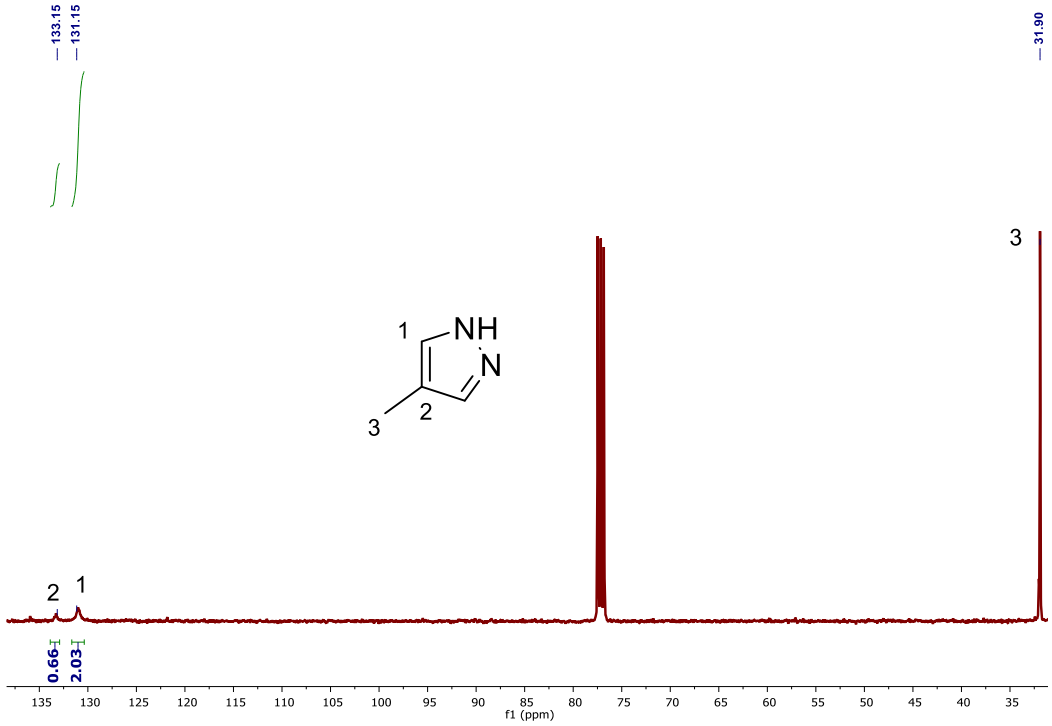

8.52
7.70
7.10
6.44
NH2
1
2
3
4
1.00
1.00
0.97
0.99
f1 (ppm)

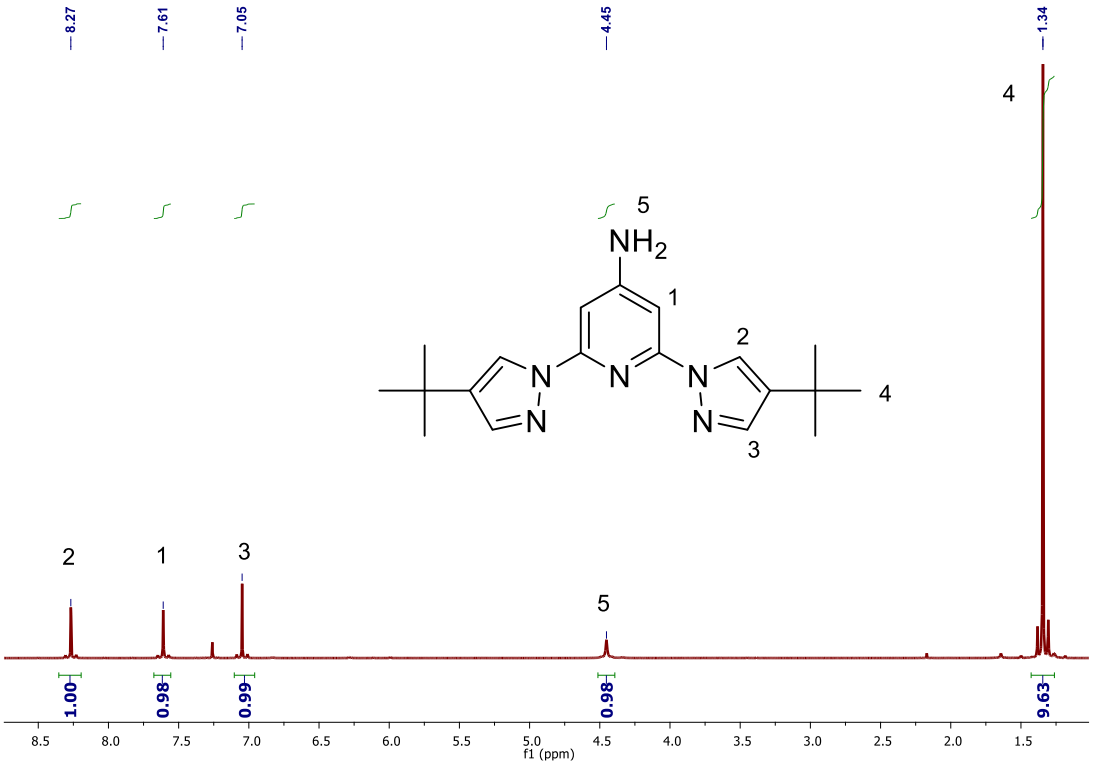

8.53
8.06
7.77
6.51
Br
1
2
3
4
1.05
0.91
1.00
1.02
Chemical shift (ppm)

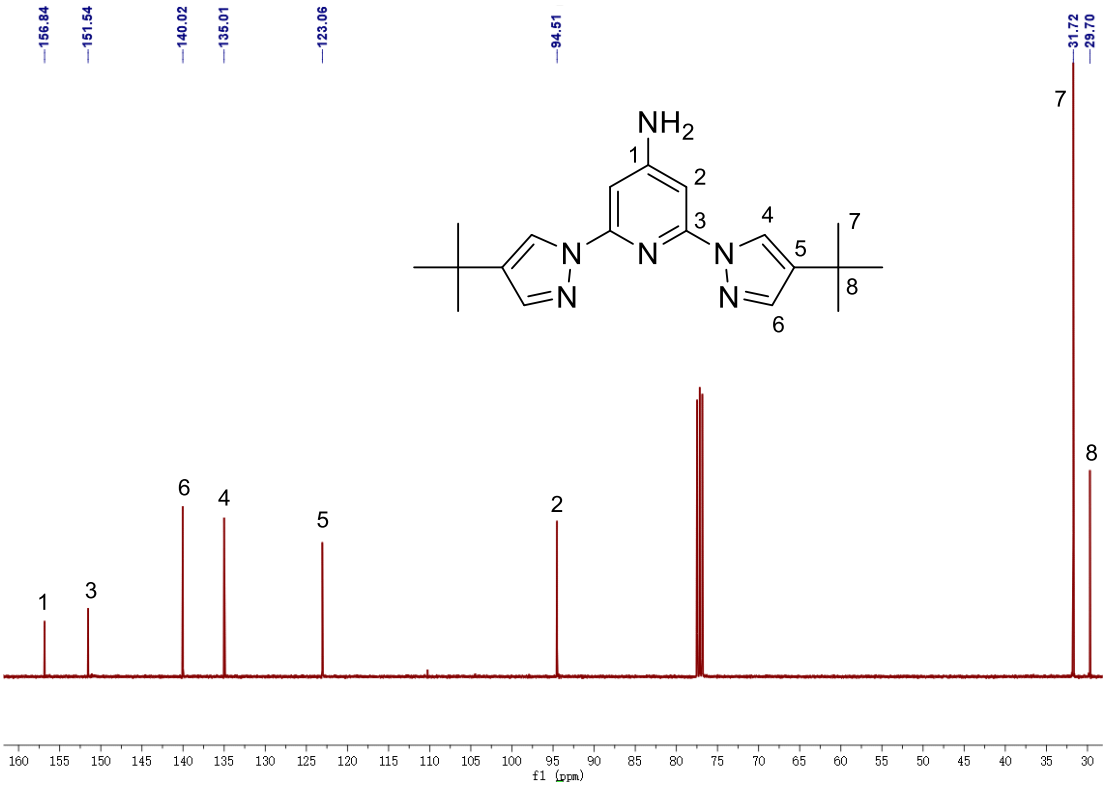

8.94
8.93
8.76
8.19
7.87
7.86
6.63
6.63
6.62
6.58
B(OH)
1
2
3
4
5
1.00
0.86
0.86
0.98
1.01
f1 (ppm)

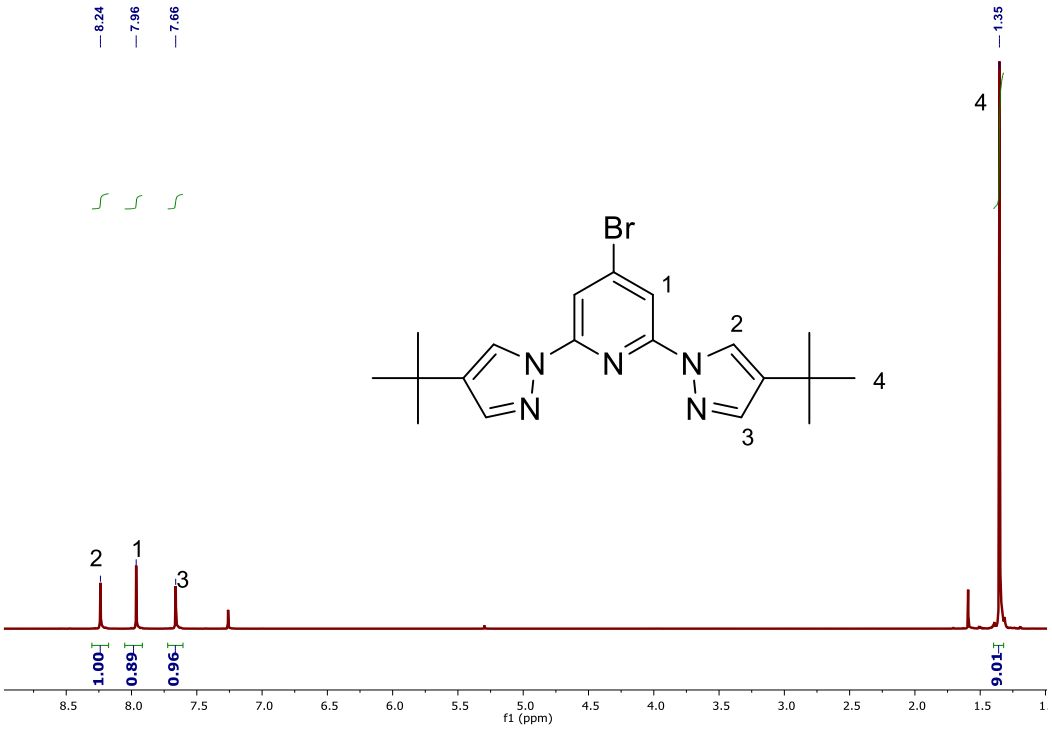

149.09
142.41
128.02
113.60
108.35
B(OH)
1
2
3
4
5
6
f1 (ppm)

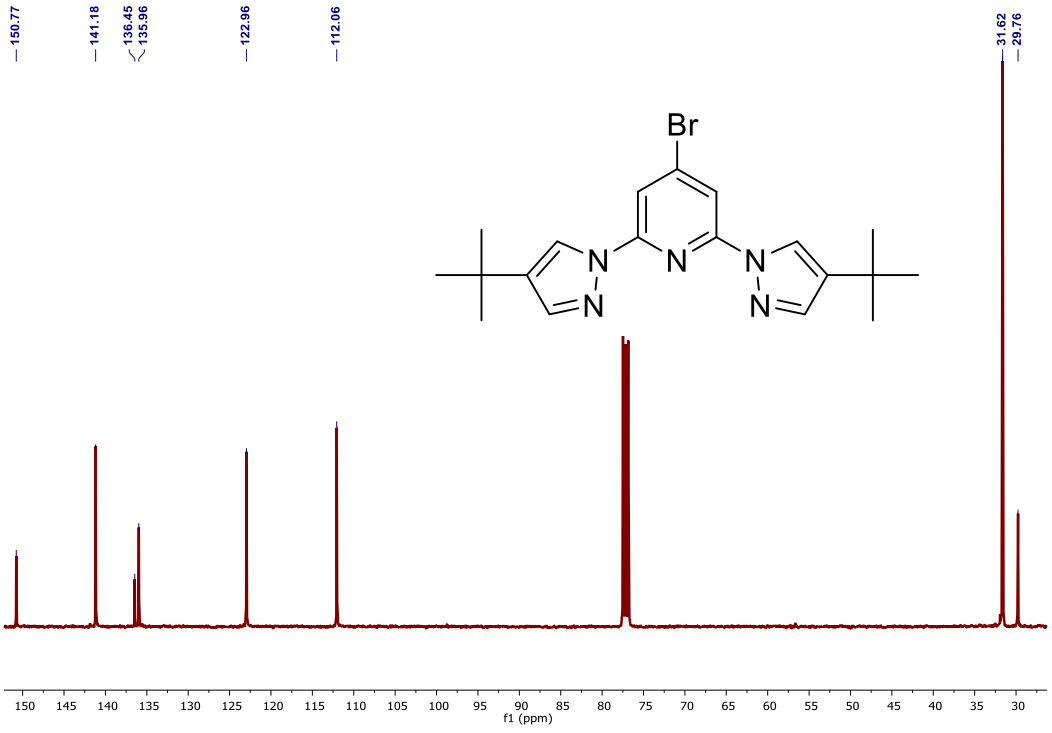

7.44
1.27
1
2
NH
N
1
2
1.00
4.60
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4 1.2 1.0
f1 (ppm)

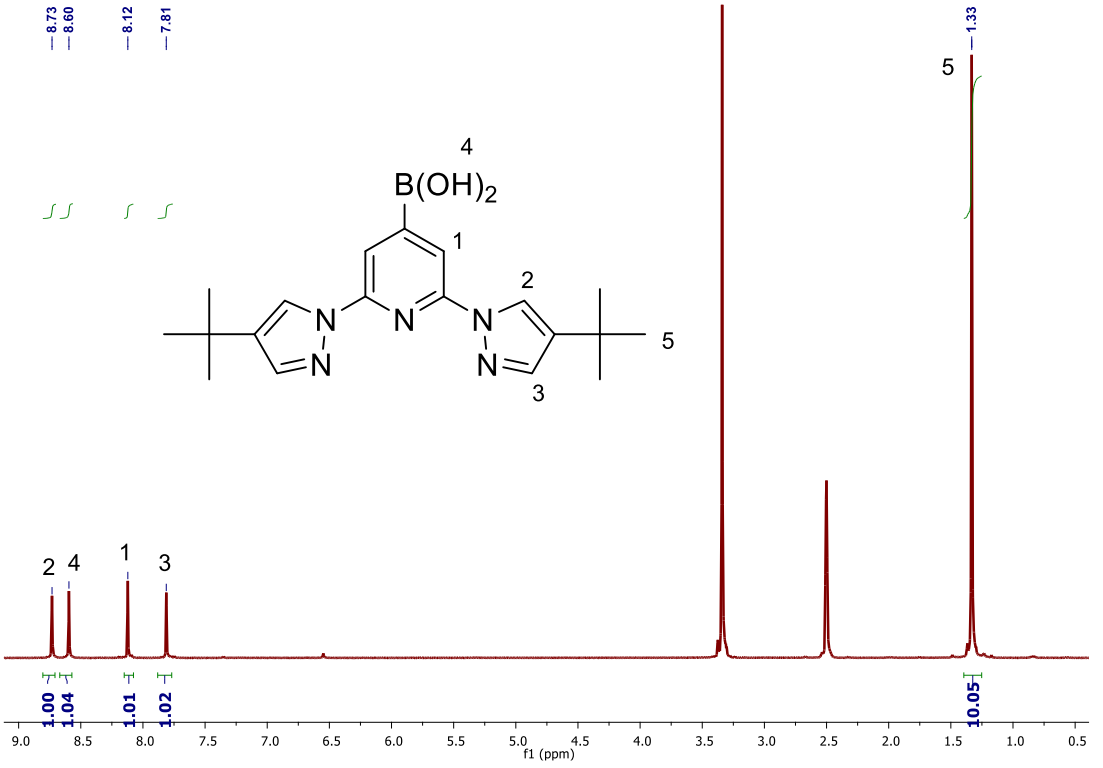

133.15
131.15
31.90
3
NH
N
1
2
3
2
1
0.66
2.03
135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35
f1 (ppm)

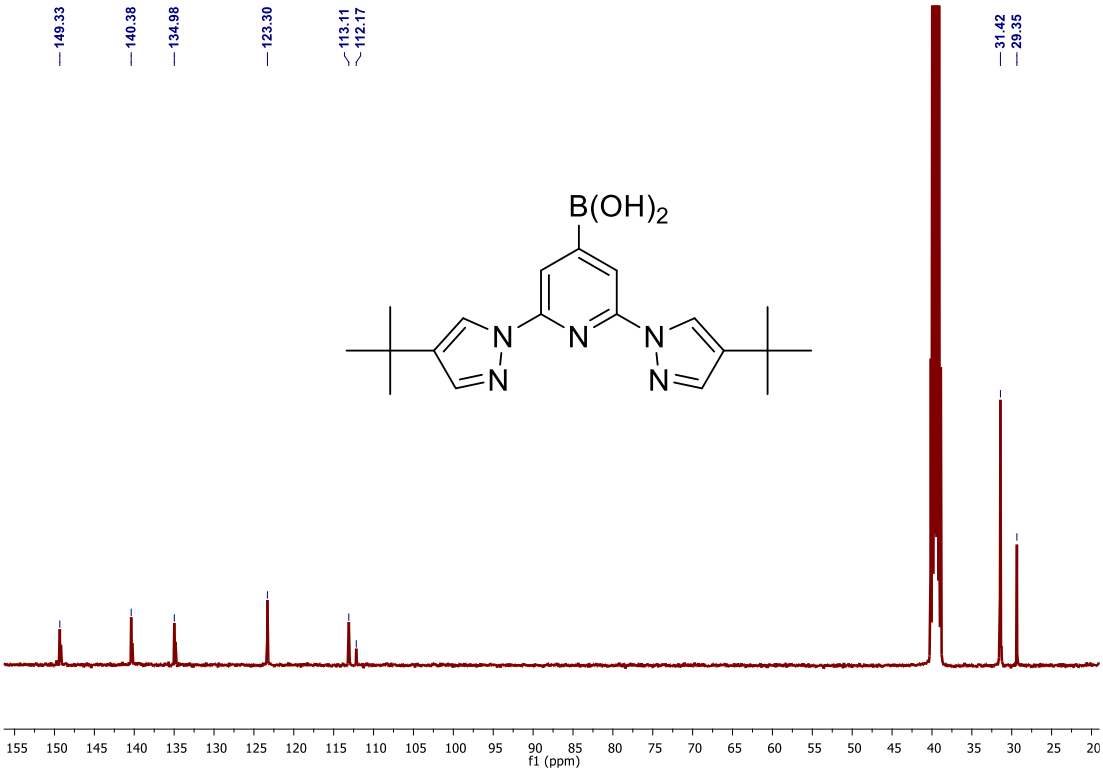

8.27
7.61
7.05
4.45
1.34
NH2
1.00
0.98
0.99
0.98
9.63
f1 (ppm)


156.84
151.54
140.02
135.01
123.06
94.51
31.72
29.70
NH2
f1 (ppm)


8.24
7.96
7.66
1.35
Br
1
2
3
4
N
N
N
N
2
1
3
4
1.00
0.89
0.96
9.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)


150.77
141.18
136.45
135.96
122.96
112.06
31.62
29.76
Br
N
N
N
N
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
f1 (ppm)


8.73
8.60
8.12
7.81
1.33
B(OH)2
1
2
3
4
5
1.00
1.04
1.01
1.02
10.05
f1 (ppm)


149.33
140.38
134.98
123.30
113.11
112.17
31.42
29.35
B(OH)2
f1 (ppm)