Electronic Supplementary Information

for
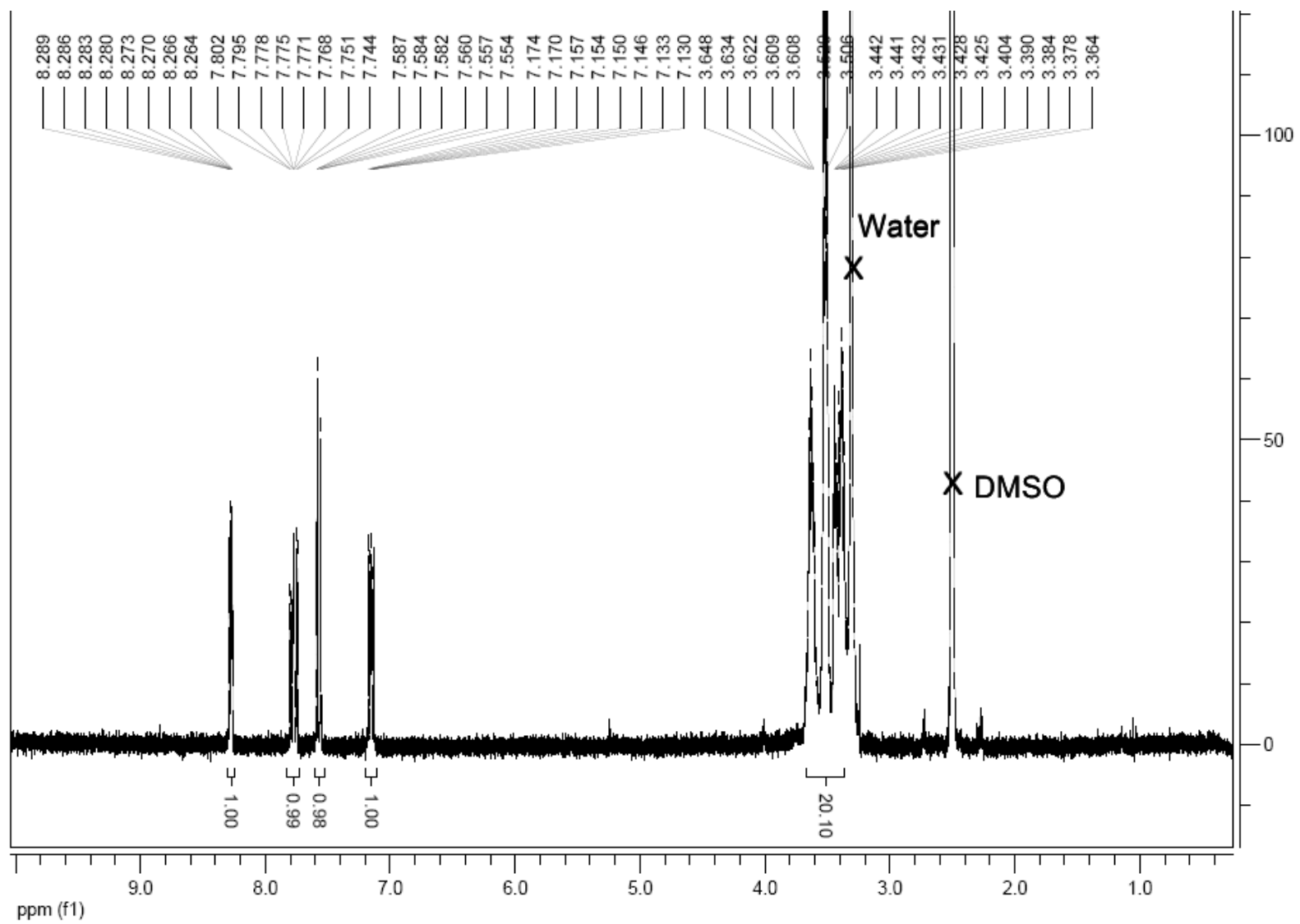
Spin crossover in polymeric and heterometallic Fe^{II} species containing polytopic dipyridylamino-substituted-triazine ligands

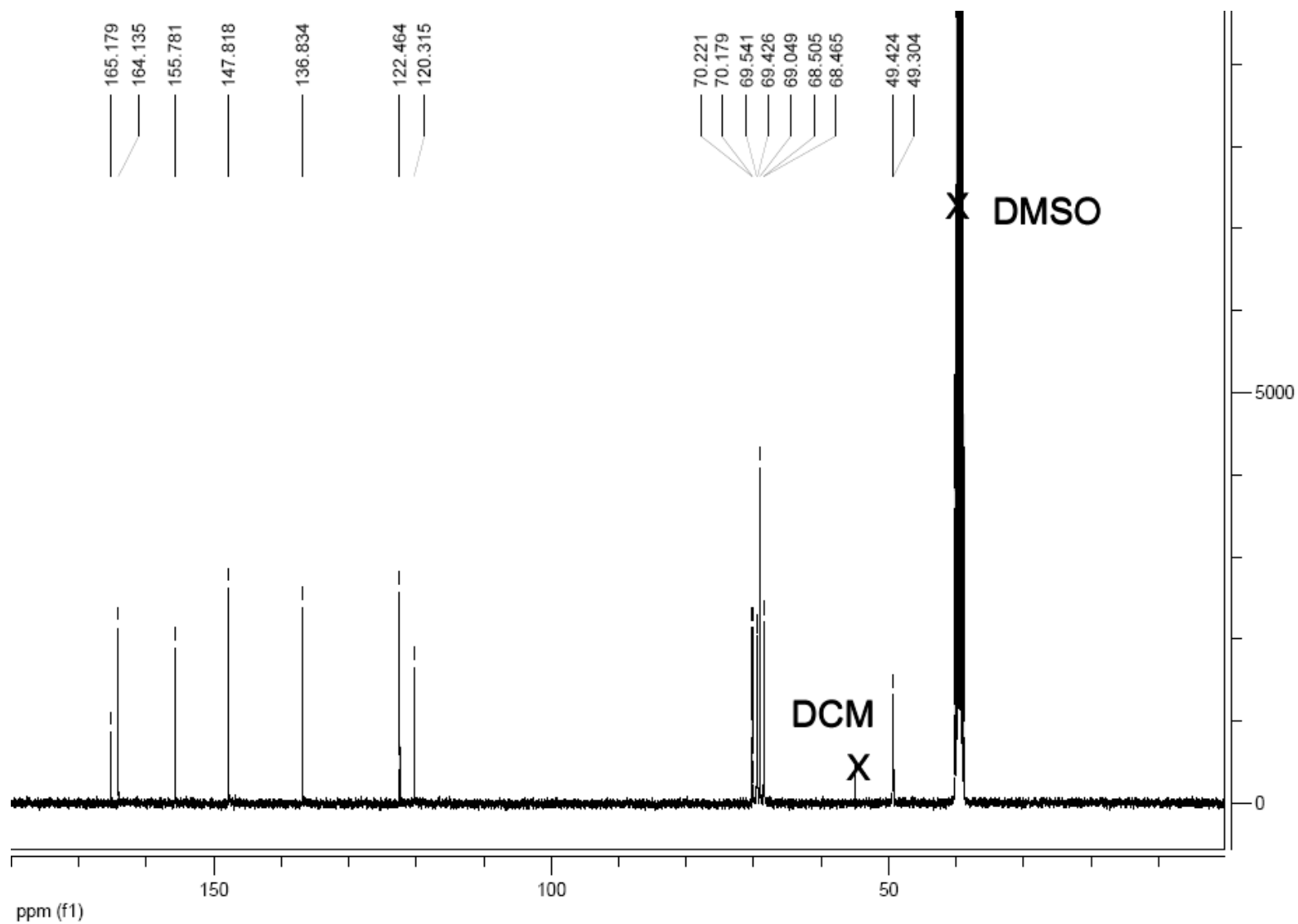Tamsyn M. Ross,[a] Boujemaa Moubaraki,[a] Stuart R. Batten[a] and Keith S. Murray[*a]

[a] School of Chemistry, Building 23, Monash University, Clayton, Victoria 3800, Australia,
   Fax: +61-3-99054597 E-mail: keith.murray@monash.edu

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Figure S1 ^{1}H NMR of ddta (DMSO = dimethylsulfoxide).

Figure S2 ^{13}C NMR of ddta (DCM = dichloromethane).

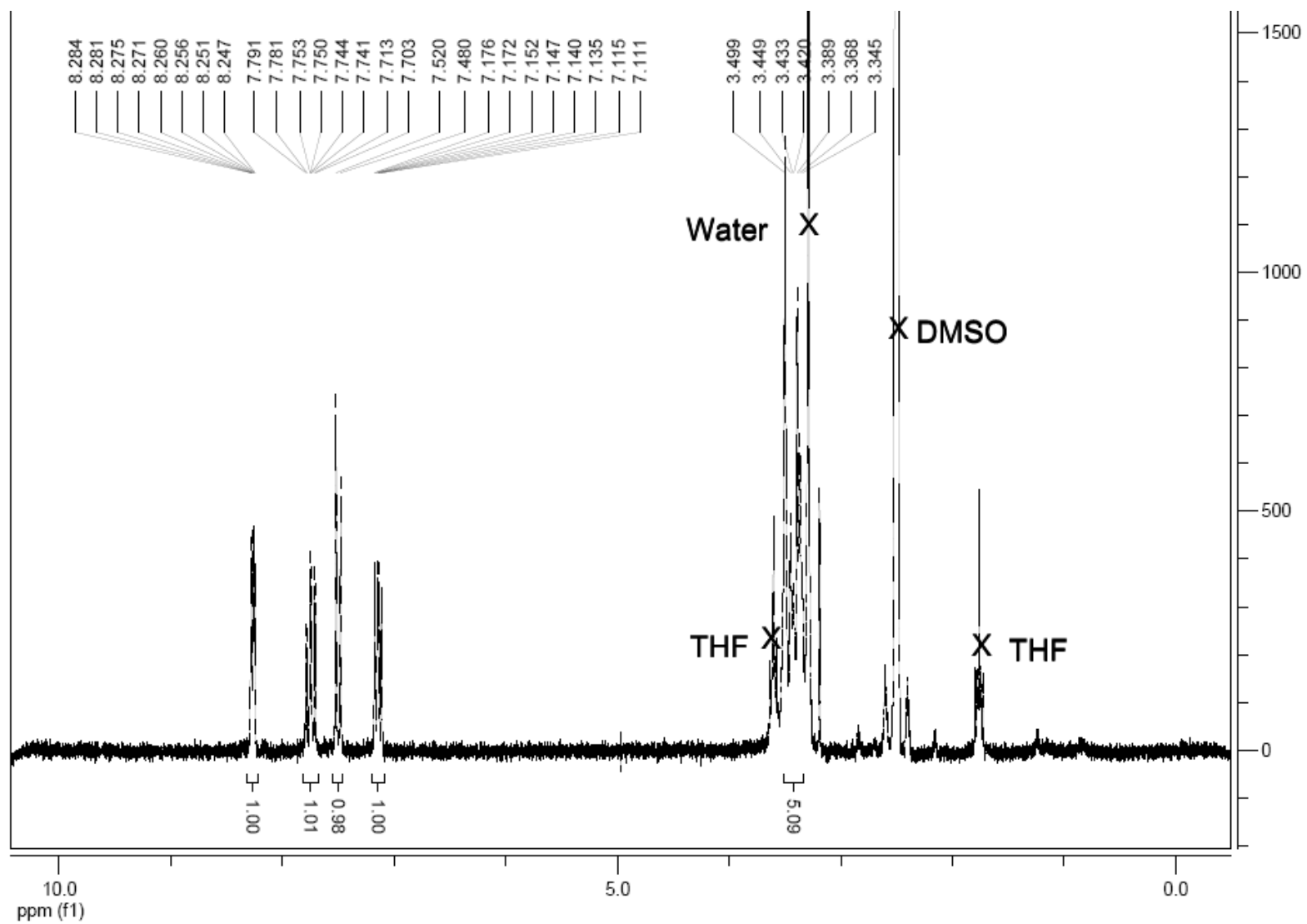**Figure S3** ^{1}H NMR of tptd (THF = tetrahydrofuran).
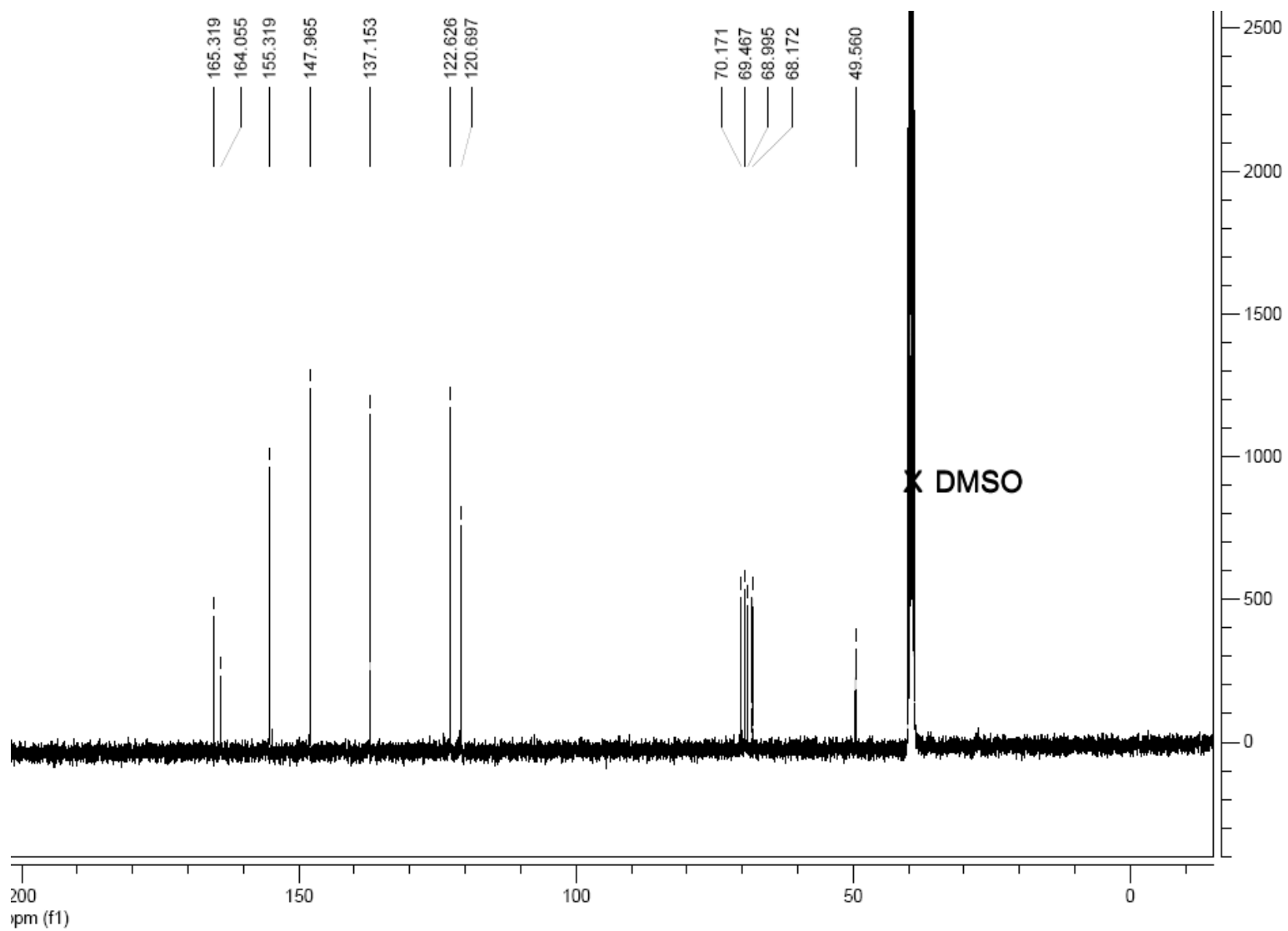
Figure S4 ^{13}C NMR of tptd.

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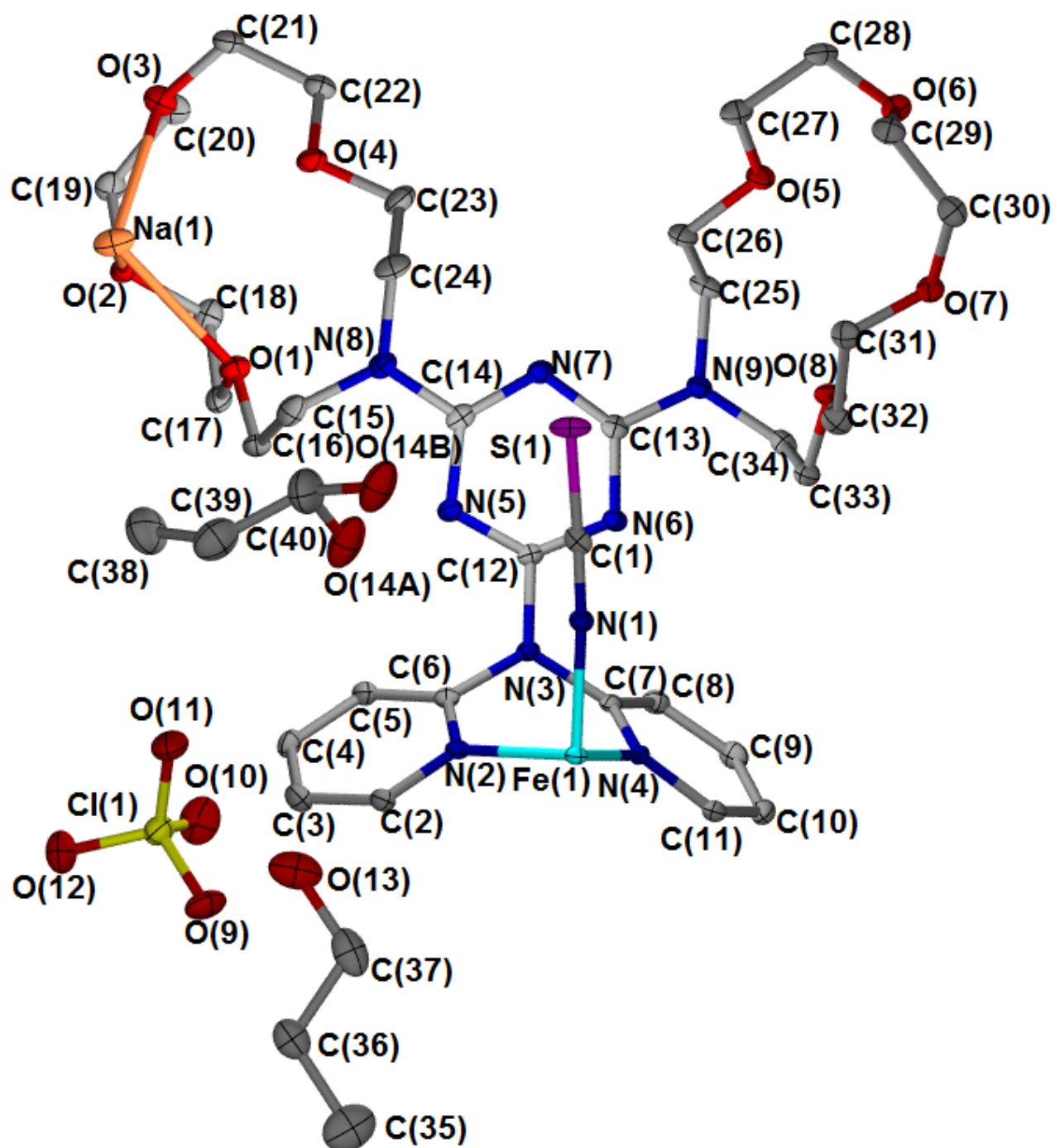
Figure S5 Labelled asymmetric unit of **1a**, with ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity.
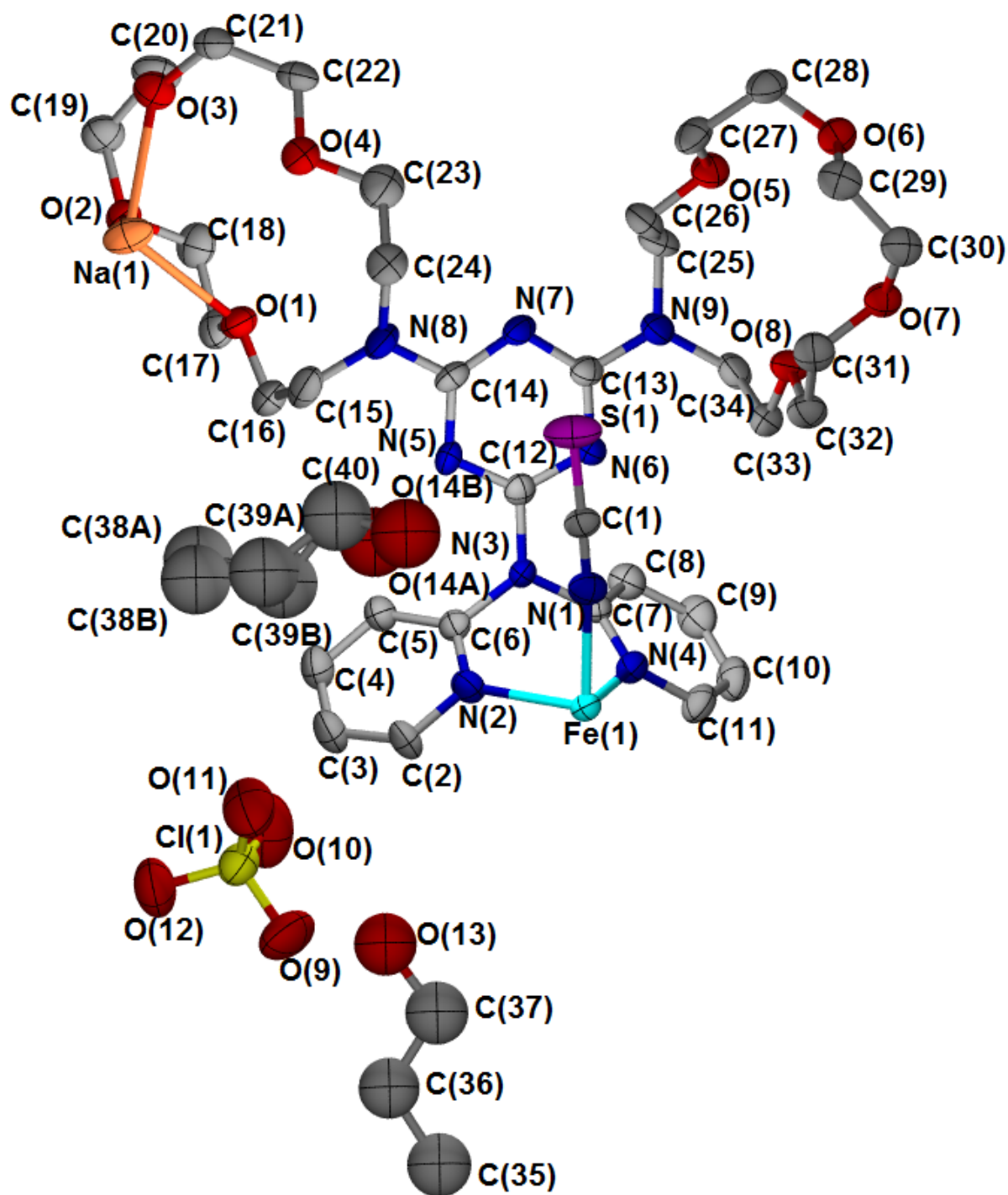
Figure S6 Labelled asymmetric unit of **1b**, with ellipsoids shown at 50% probability.
Hydrogen atoms have been omitted for clarity.
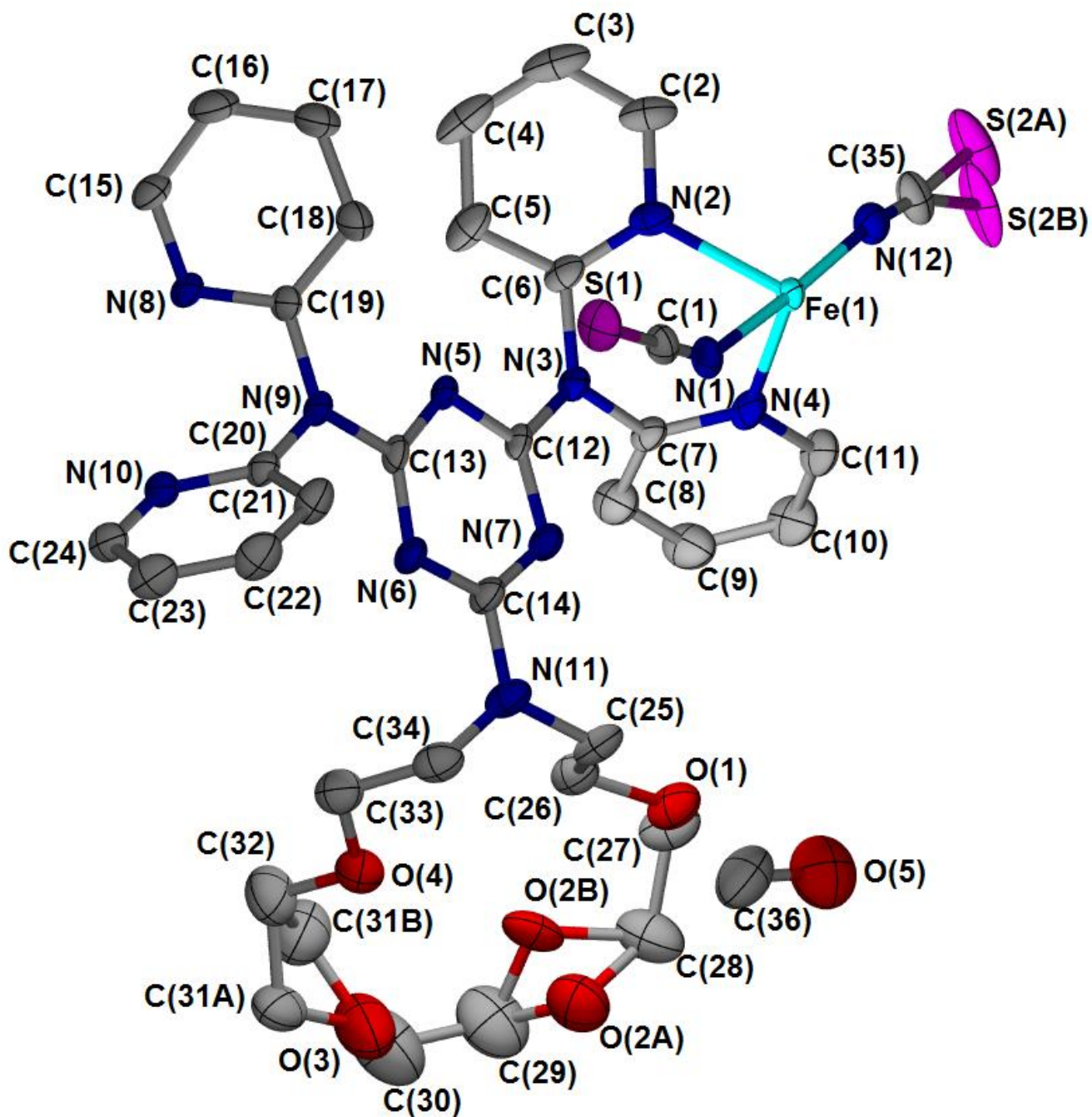
Figure S7 Labelled asymmetric unit of **2**, with ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity.

Figure S8 Labelled asymmetric unit of **3**, with ellipsoids shown at 50% probability. Hydrogen atoms have been omitted for clarity.

Special Refinement Details for Single Crystal Data

1a: The hydroxyl group of one of the 1-propanol molecules within the structure of **1a** is disordered over two positions, with 65% occupancy for O14A and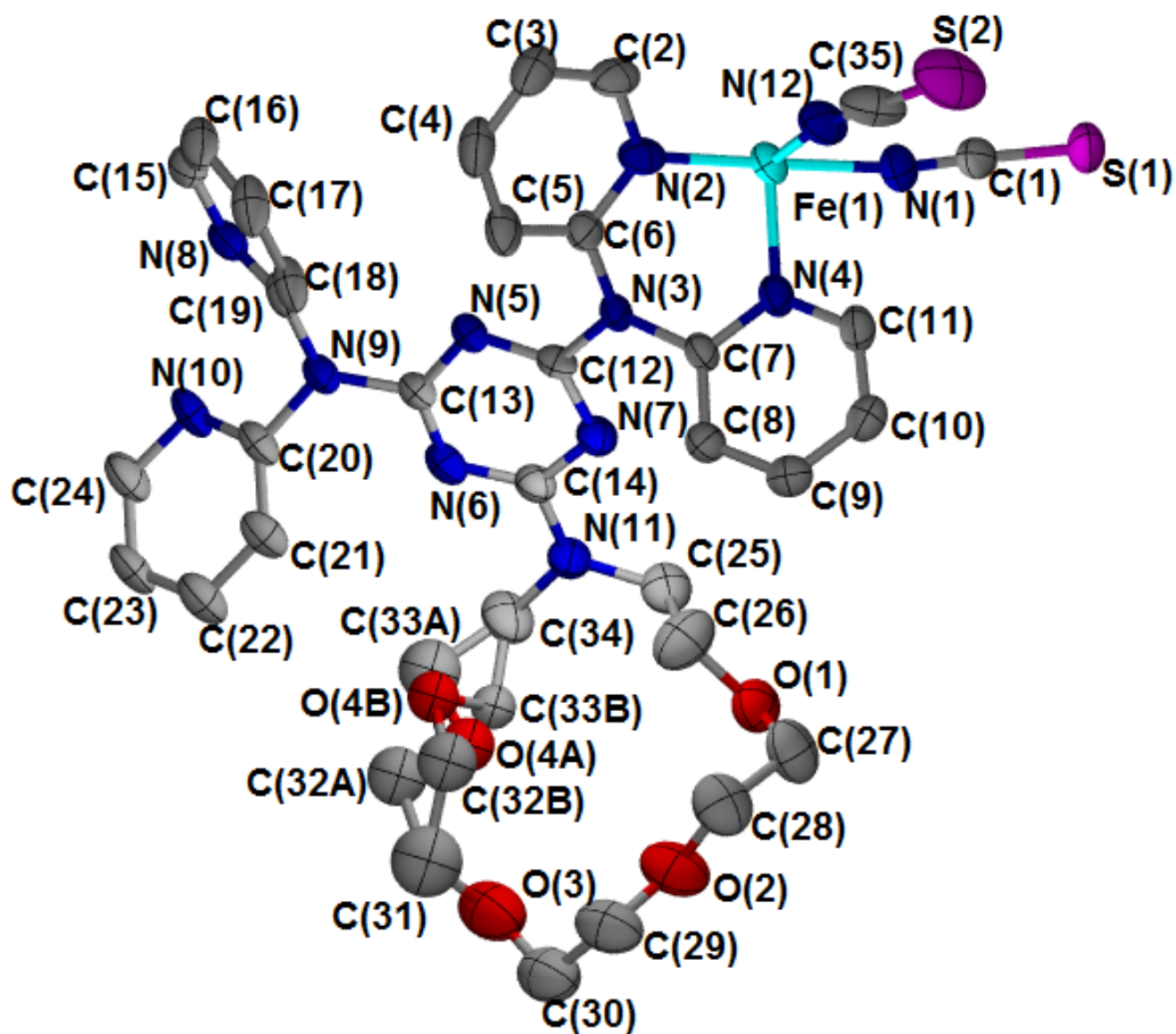 35% occupancy for O14B. O14A and O14B have been restrained to have the same thermal displacement parameters. The distances between C40 and O14A and C40 and O14B have been restrained to 1.430(1) Å. Hydrogen atoms have not been assigned to O14A or O14B.

1b: Within the structure of **1b** the disorder in the 1-propanol molecule that has been described for **1a** has increased. The hydroxyl group of the previously described 1-propanol molecule is disordered over two positions at 50% occupancy each. C38 and C39 of the same 1-propanol molecule are also found to be disordered over two positions, with 50% occupancy at each position for both disordered atoms. The distances between C40 and O14A, and C40 and O14B, have been restrained to be 1.430(1) Å. The distances between C40 and C39A, and C40 and C39B, have been restrained to be 1.50(1) Å. The distances between C39A and C38A, and C39B and C38B, have been restrained to be 1.50(1) Å. The distances between O14A and C39A, and O14B and C39B, have been restrained to be 2.50(1) Å. The distances between C40 and C38A, and C40 and C38B, have been restrained to be 2.50(1) Å. The atoms O14A, O14B, C40, C39A, C39B, C38A and C38B have been restrained to have the same thermal displacement parameters. The distance between C36 and C37 within the second unique 1-propanol molecule has been restrained to be 1.50(1) Å. Hydrogen atoms have not been assigned to O14A, O14B, C40, C39A, C39B, C38A or C38B. The atoms O13, C35, C36, C37, O14A, O14B, C40, C39A, C39B, C38A and C38B have been refined isotropically. ISOR restraints have been applied to C23, C24 and O4.

2: Within one of the two unique NCS⁻ ligands in the structure of **2** the sulfur atom is disordered over two positions. Here, S2A is found to be at 70% occupancy, while S2B is found to be at 30% occupancy. The distances between C35 and S2A, and C35 and S2B, have been restrained to be 1.640(5) Å. The distance between O5 and C36, within the lattice methanol molecule, has been restrained to be 1.40(1) Å. ISOR restraints have also been applied to C36 and O5. Within the monoaza-15-crown-5 moiety of the tptd ligand disorder has been found in O2 and C31, both of which are disordered over two positions. Here, O2A and O2B are each at 50% occupancy, while C31A is at 40% occupancy and C31B is at 60% occupancy. Within the monoaza-15-crown-5 ring the distances between C25 and C26, C27

and C28, C29 and C30, C31A and C32, C31B and C32, and C33 and C34 have been restrained to be the same. Further to this, the distances between C26 and O1, C27 and O1, C28 and O2A, C28 and O2B, C29 and O2A, C29 and O2B, C30 and O3, C31A and O3, C31B and O3, and C32 and O4 have been restrained to be the same. ISOR restraints have been applied to C31A, C31B, C30, C29, O2A, O2B, C36, O5 and C28. Hydrogen atoms have not been assigned to C28, C29, C31A, C31B or C32.

3: Within the structure of **3** disorder is found in the mono-aza-15-crown-5 moiety of the tptd ligand. Here, C32, O4 and C33 are each disordered over two positions (labelled C32A and C32B, O4A and O4B, C33A and C33B, respectively), where each position was found to be at 50% occupancy for each atom. Atoms C31, C32A, C32B, O4A, O4B, C33A and C33B have been refined isotropically. Within this disordered part of the monoaza-15-crown-5 moiety of the tptd ligand the distances between O3 and C32A, O3 and C32B, C31 and O4A, C31 and O4B, C32A and C33A, C32B and C33B, O4A and C34, and O4B and C34 have been restrained to be 2.40(1) Å. Within the monoaza-15-crown-5 moiety of the tptd ligand the distances between C25 and C26, C27 and C28, C29 and C30, C31 and C32A, C31 and C32B, C33A and C34, and C33B and C34 have been restrained to be 1.50(1) Å. The distances between C26 and O1, C27 and O1, C28 and O2, C29 and O2, C30 and O3, C31 and O3, C32A and O4A, C32B and O4B, C33A and O4A, and C33B and O4B have been restrained to be the same. Hydrogen atoms have not been assigned to C31, C32A, C32B, C33A, C33B or C34. The atoms C32A and C32B have been restrained to have the same thermal displacement parameters.

Table S1 Unit cell and refinement details for variable temperature powder X-Ray diffraction data collected on **1** (*trans*-[$Fe^{II}(NCS)_2(ddta)_2Na_2](ClO_4)_2 \cdot 4CH_3CH_2CH_2OH$)

T/K	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å^3)	χ^2
150	12.2216(1)	13.2399(2)	16.5525(2)	78.3172(7)	89.1164(7)	64.8491(6)	2366.7(8)	4.179
160	12.2257(1)	13.2468(1)	16.5601(2)	78.3528(7)	89.1267(6)	64.8342(6)	2369.8(8)	3.918
170	12.2306(1)	13.2542(1)	16.5689(2)	78.3872(7)	89.1374(6)	64.8189(6)	2373.4(8)	3.958
180	12.2353(1)	13.2636(1)	16.5770(2)	78.4312(6)	89.1388(6)	64.8035(6)	2377.2(8)	3.917
190	12.2418(1)	13.2718(1)	16.5876(1)	78.4830(6)	89.1482(6)	64.7915(6)	2381.8(8)	3.288
200	12.2481(1)	13.2802(1)	16.5986(1)	78.5408(6)	89.1534(5)	64.7789(6)	2386.3(7)	3.220
205	12.2534(1)	13.2857(1)	16.6059(1)	78.5741(6)	89.1532(6)	64.7657(6)	2389.5(7)	3.063
210	12.2570(1)	13.2893(1)	16.6130(1)	78.6097(6)	89.1509(5)	64.7665(5)	2392.3(7)	2.950
215	12.2604(1)	13.2935(1)	16.6208(1)	78.6507(6)	89.1490(5)	64.7699(5)	2395.3(7)	2.920
220	12.2651(1)	13.2976(1)	16.6291(1)	78.6939(6)	89.1442(5)	64.7673(5)	2398.5(7)	2.819
225	12.2687(1)	13.3038(1)	16.6407(1)	78.7410(6)	89.1568(5)	64.7688(5)	2402.5(7)	2.648
230	12.2725(1)	13.3078(2)	16.6500(1)	78.7963(6)	89.1529(6)	64.7741(6)	2406.0(8)	3.582
235	12.2787(1)	13.3125(1)	16.6639(1)	78.8510(6)	89.1470(5)	64.7777(5)	2410.7(7)	2.637
240	12.2825(1)	13.3166(1)	16.6775(2)	78.9112(6)	89.1454(6)	64.7808(6)	2414.8(7)	2.608
245	12.2885(1)	13.3229(1)	16.6922(1)	78.9761(6)	89.1409(6)	64.7847(6)	2420.0(7)	2.588
250	12.2930(1)	13.3278(2)	16.7058(2)	79.0506(7)	89.1339(6)	64.7849(6)	2424.5(8)	3.291
255	12.2986(1)	13.3332(2)	16.7226(2)	79.1289(7)	89.1377(7)	64.7947(7)	2430.0(9)	3.489
260	12.3033(1)	13.3390(2)	16.7382(2)	79.2002(7)	89.1353(7)	64.7976(7)	2435.0(9)	3.409
265	12.3086(1)	13.3453(2)	16.7556(2)	79.2755(7)	89.1368(6)	64.7951(6)	2440.4(8)	3.161
270	12.3126(1)	13.3500(2)	16.7711(2)	79.3510(7)	89.1435(6)	64.8017(6)	2445.1(8)	3.102
275	12.3177(1)	13.3559(2)	16.7862(2)	79.4318(7)	89.1488(7)	64.7907(7)	2450(1)	3.617
280	12.3236(1)	13.3604(2)	16.8012(2)	79.5118(6)	89.1617(7)	64.7896(7)	2454.8(9)	2.812
290	12.3354(2)	13.3740(2)	16.8312(2)	79.6567(7)	89.1746(7)	64.7813(7)	2465.1(9)	3.055
300	12.3412(2)	13.3851(2)	16.8530(2)	79.8110(8)	89.2216(9)	64.7643(8)	2473(1)	3.369
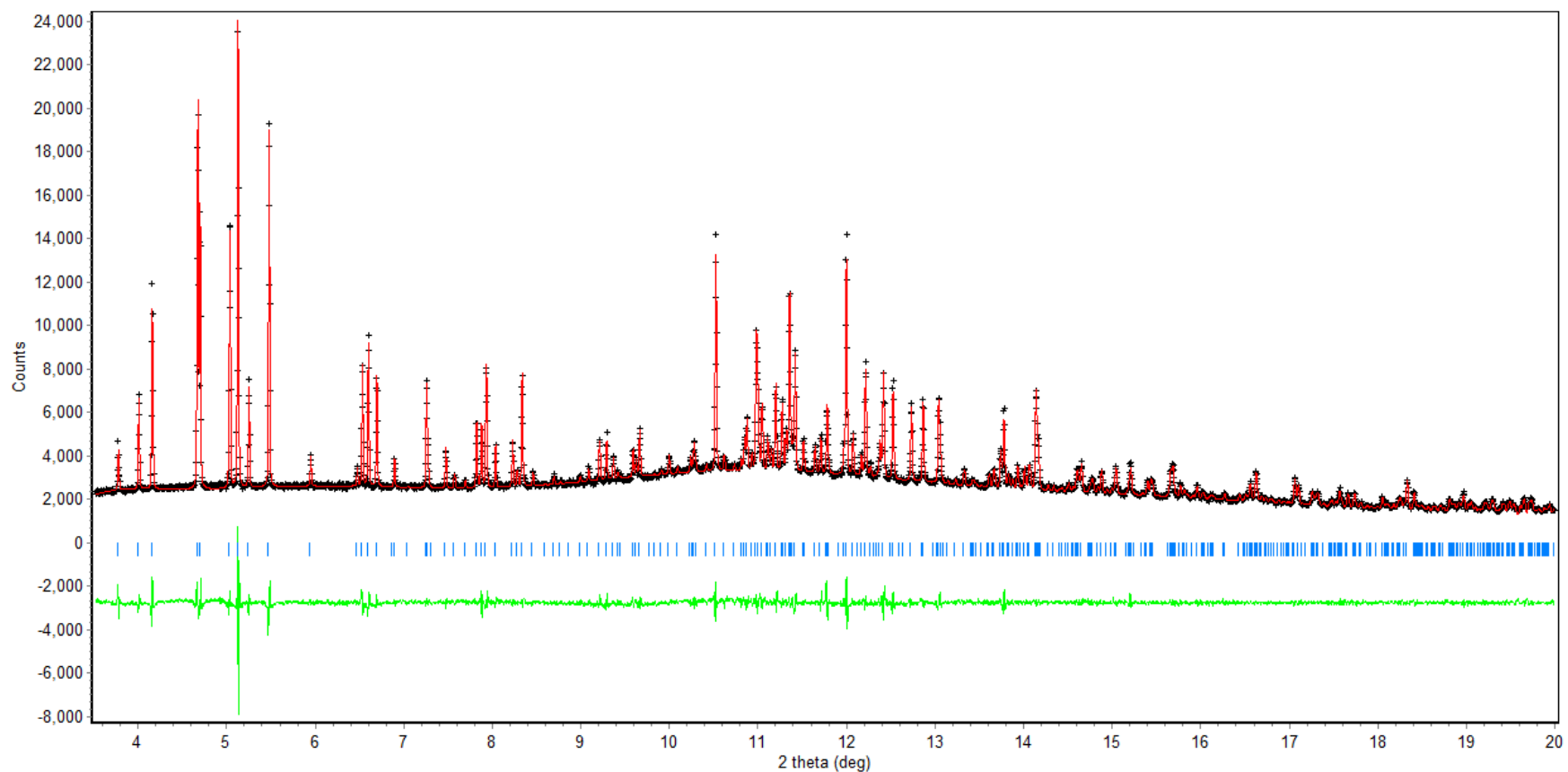
Figure S9 Le Bail fit to synchrotron powder X-Ray data on **1** (*trans*-[Fe^{II}(NCS)$_2$(ddta)$_2$Na$_2$](ClO$_4$)$_2$•4CH$_3$CH$_2$CH$_2$OH) at 150 K. Observed data are shown as black crosses, the calculated data are shown as a red line, the difference between observed and calculated data is shown as a green line, and the predicted, possible location of peaks based on the symmetry of the lattice are shown as vertical blue lines.

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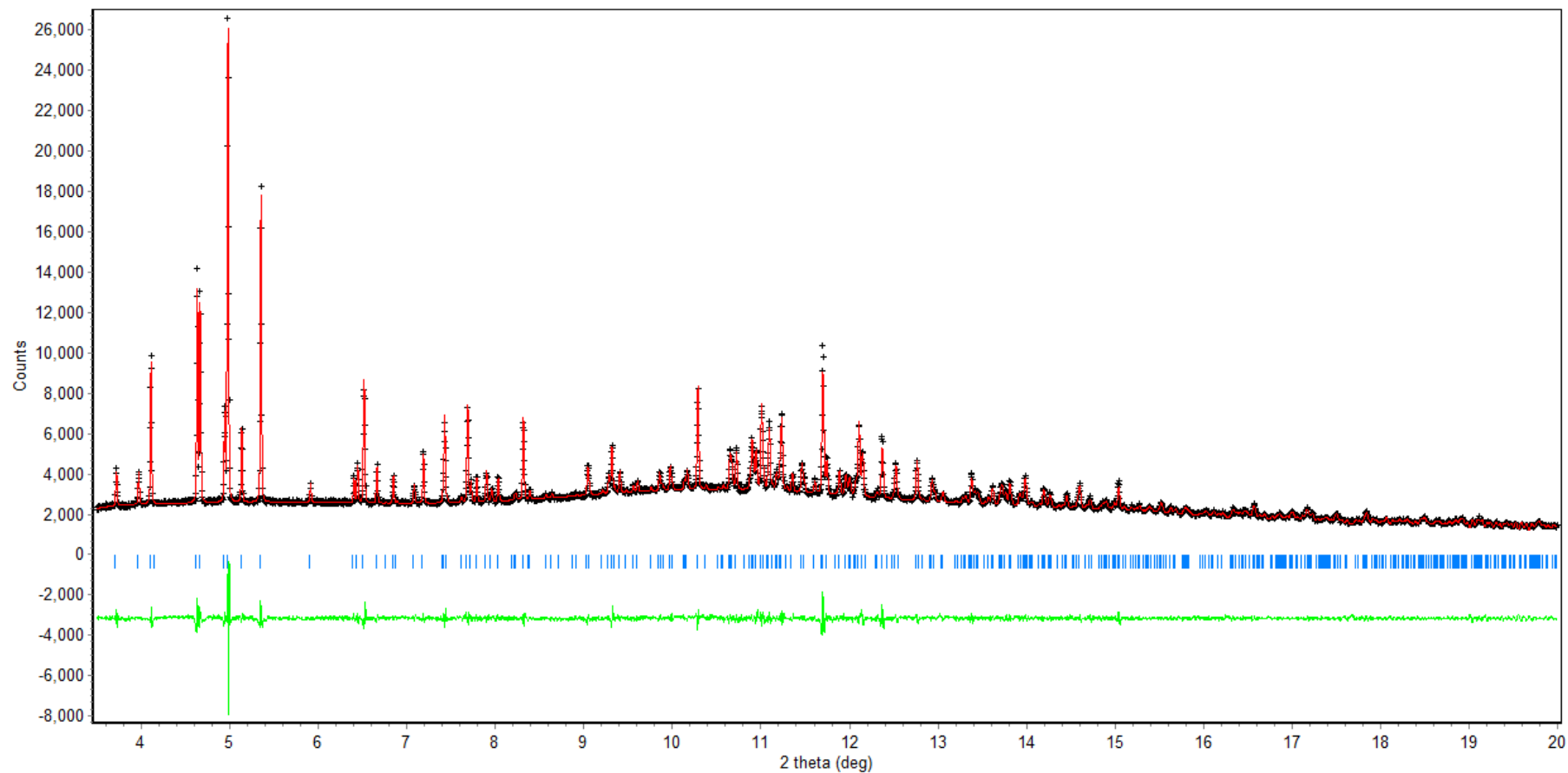
Figure S10 Le Bail fit to synchrotron powder X-Ray data on **1** (*trans*-[Fe^{II}(NCS)$_2$(ddta)$_2$Na$_2$](ClO$_4$)$_2$•4CH$_3$CH$_2$CH$_2$OH) at 300 K. Observed data are shown as black crosses, the calculated data are shown as a red line, the difference between observed and calculated data is shown as a green line, and the predicted, possible location of peaks based on the symmetry of the lattice are shown as vertical blue lines.

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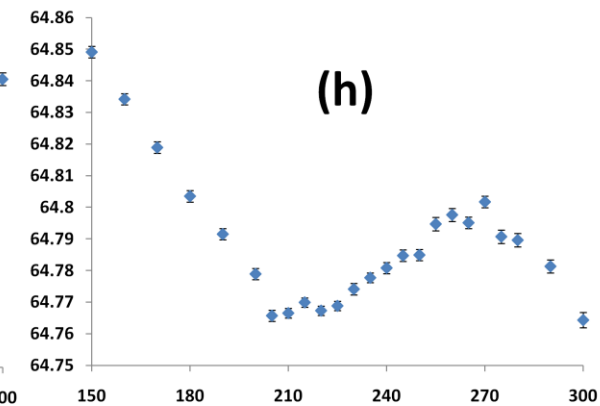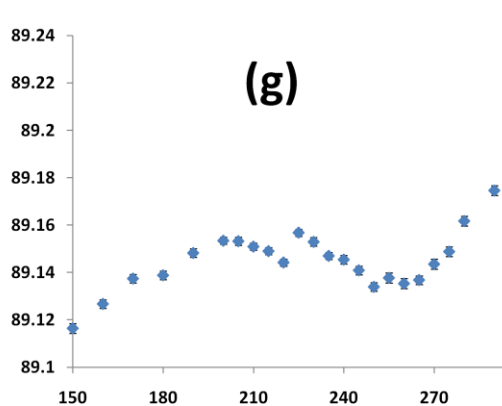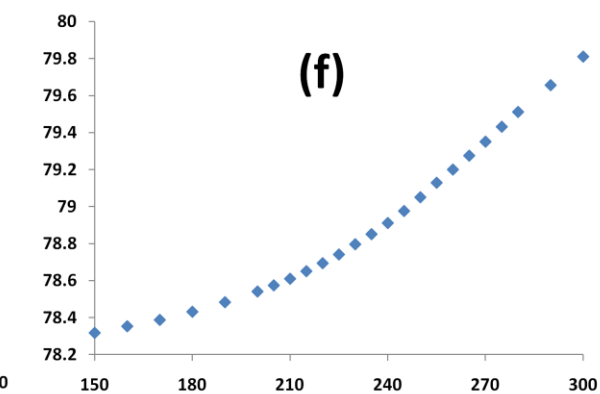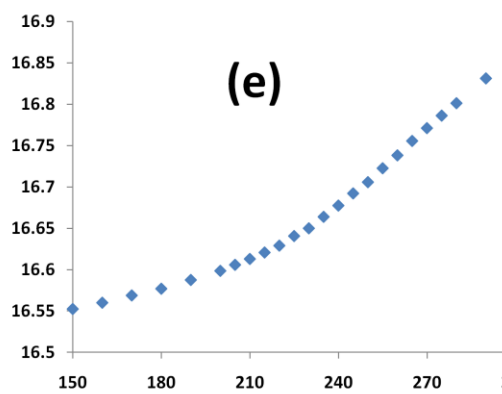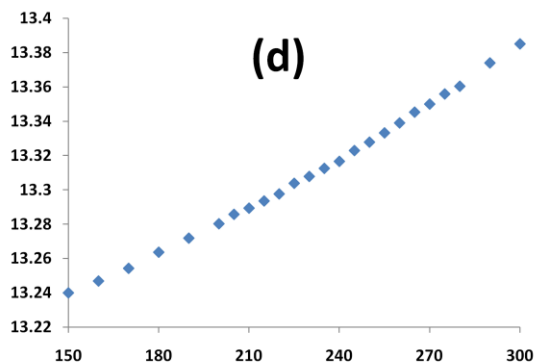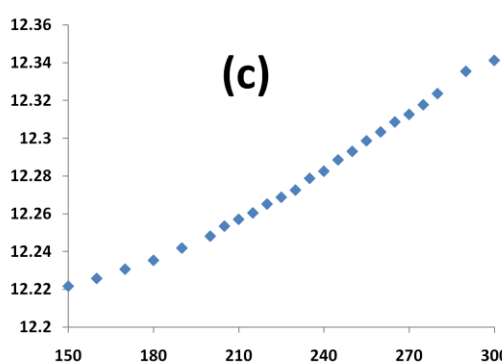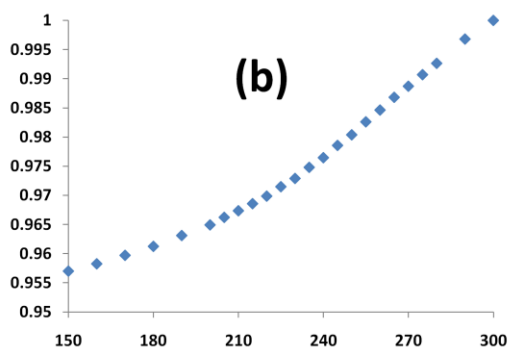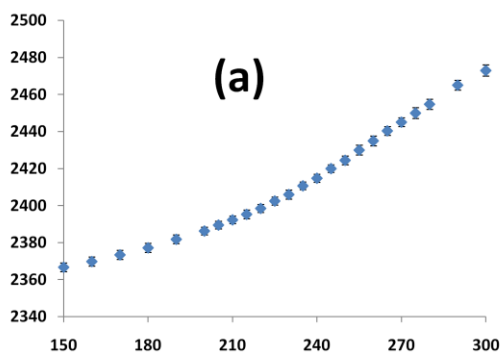
Figure S11 **(a)** Temperature dependent behaviour of the unit cell volume for **1**; **(b)** temperature dependent behaviour of the unit cell volume for **1** given as a proportion of its highest magnitude; **(c)** temperature dependent behaviour of a for **1**; **(d)** temperature dependent behaviour of b for **1**; **(e)** temperature dependent behaviour of c for **1**; **(f)** temperature dependent behaviour of the angle α for **1**; **(g)** temperature dependent behaviour of the angle β for **1**; **(h)** temperature dependent behaviour of the angle γ for **1**. In **(a)** the vertical axis has units of Å^3, in **(b)** the vertical axis is a proportion of the highest value of the unit cell volume, in **(c)** – **(d)** the vertical axis has units of Å, and in **(f)** – **(h)** the vertical axis is given in $^\circ$. In all Figures the horizontal axis is temperature (K). For Figures **(a)** and **(c)** - **(h)** error bars to three times the calculated error are given, but in most cases are eclipsed by the position markers and cannot be seen here; no error bars are given for **(b)**.