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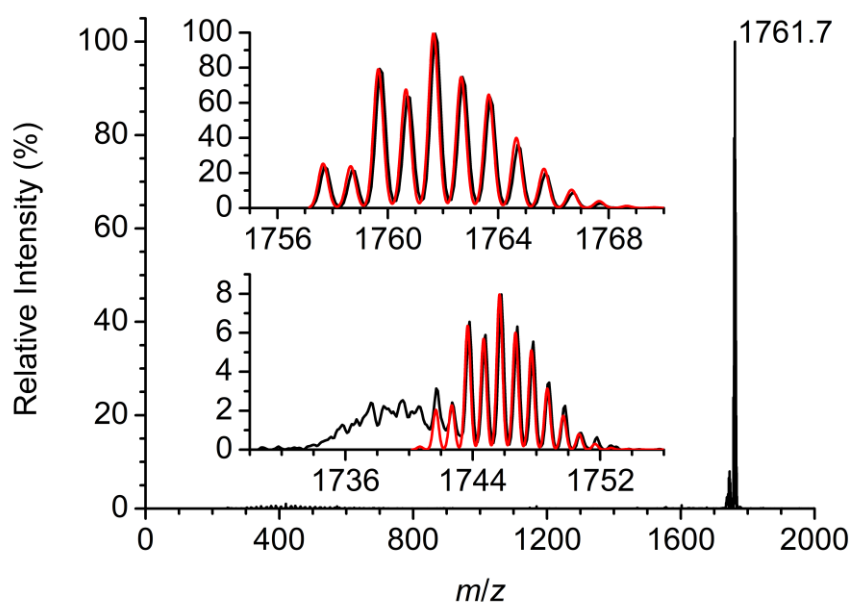


Figure S1. ESI-MS spectrum of $1^4\text{-Py}\cdot\text{EtOH}$ (direct infusion, $i\text{PrOH} : \text{CH}_2\text{Cl}_2$ 3:1 v/v, positive ion mode). The inset shows the experimental (black line) and simulated (red line) isotopic patterns of the peaks at $m/z = 1761.7$ ($[1^4\text{-Py}+\text{Na}]^+$) and 1745.8 ($[1^4\text{-Py}+\text{Li}]^+$).

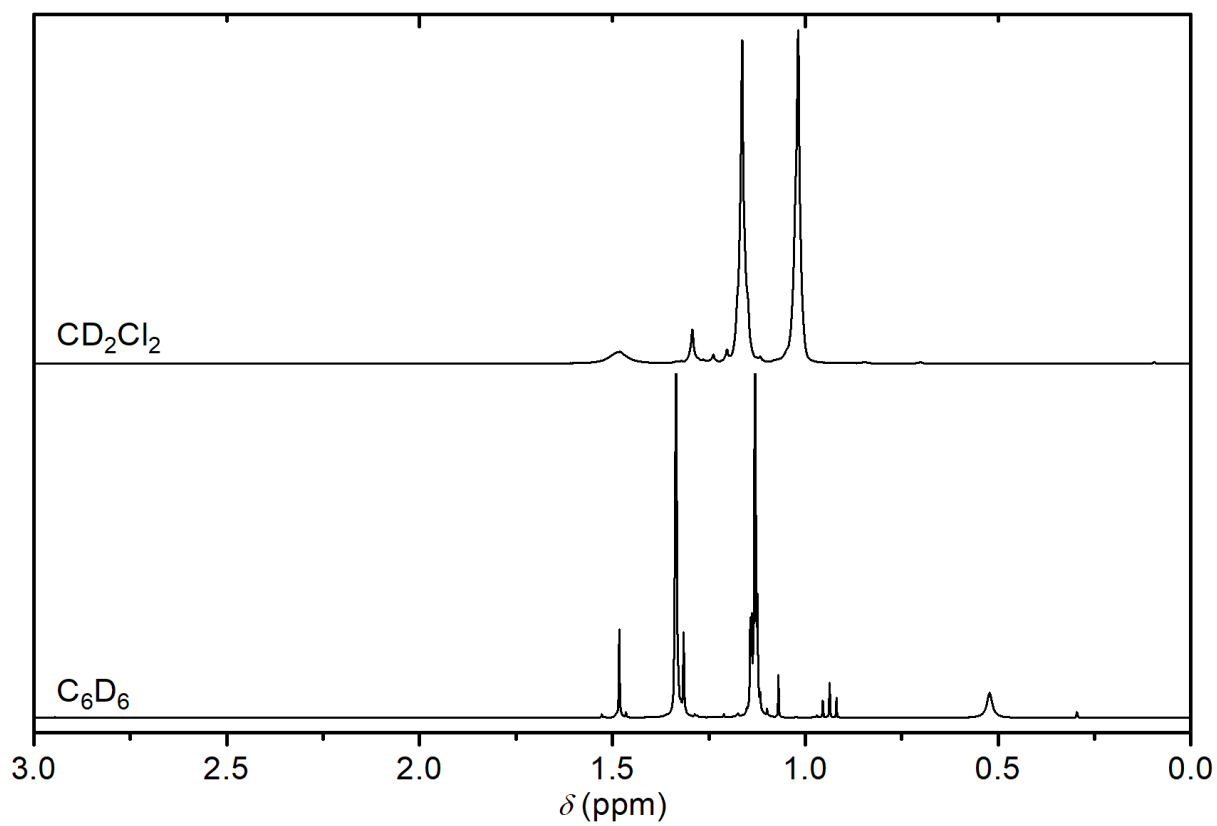
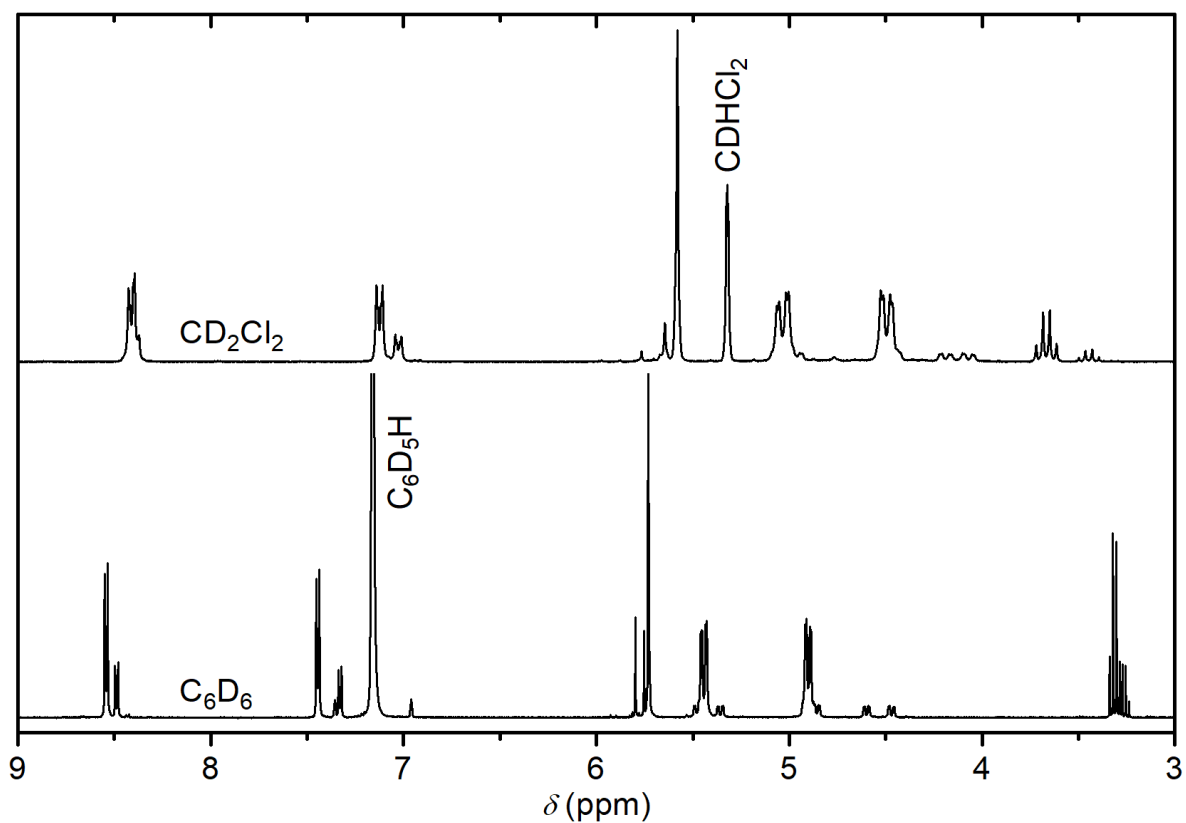


Figure S2. ^1H NMR spectrum of $1^4\text{-Py}\cdot\text{EtOH}$ in CD_2Cl_2 (200.13 MHz) and C_6D_6 (400.13 MHz) at 298 K.

SpinWorks 4: Ga4pPy2dpm6*EtOH ib C6D6
T=298K

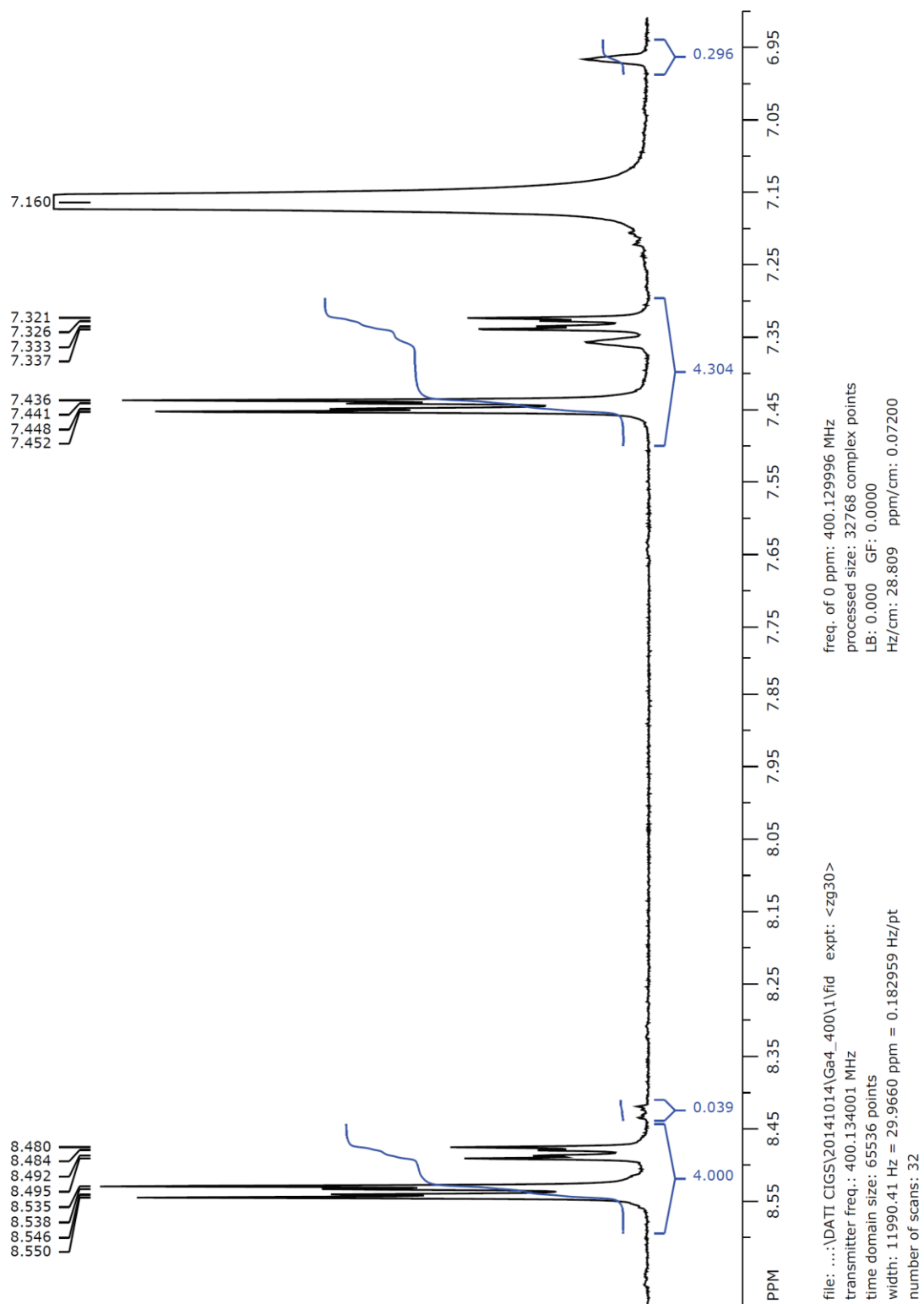


Figure S3. ^1H NMR spectrum of $1^4\text{Py}\cdot\text{EtOH}$ (400.13 MHz, C_6D_6 , 298 K).

SpinWorks 4: Ga4Py2dpm6*EtOH ib C6D6
T=298K

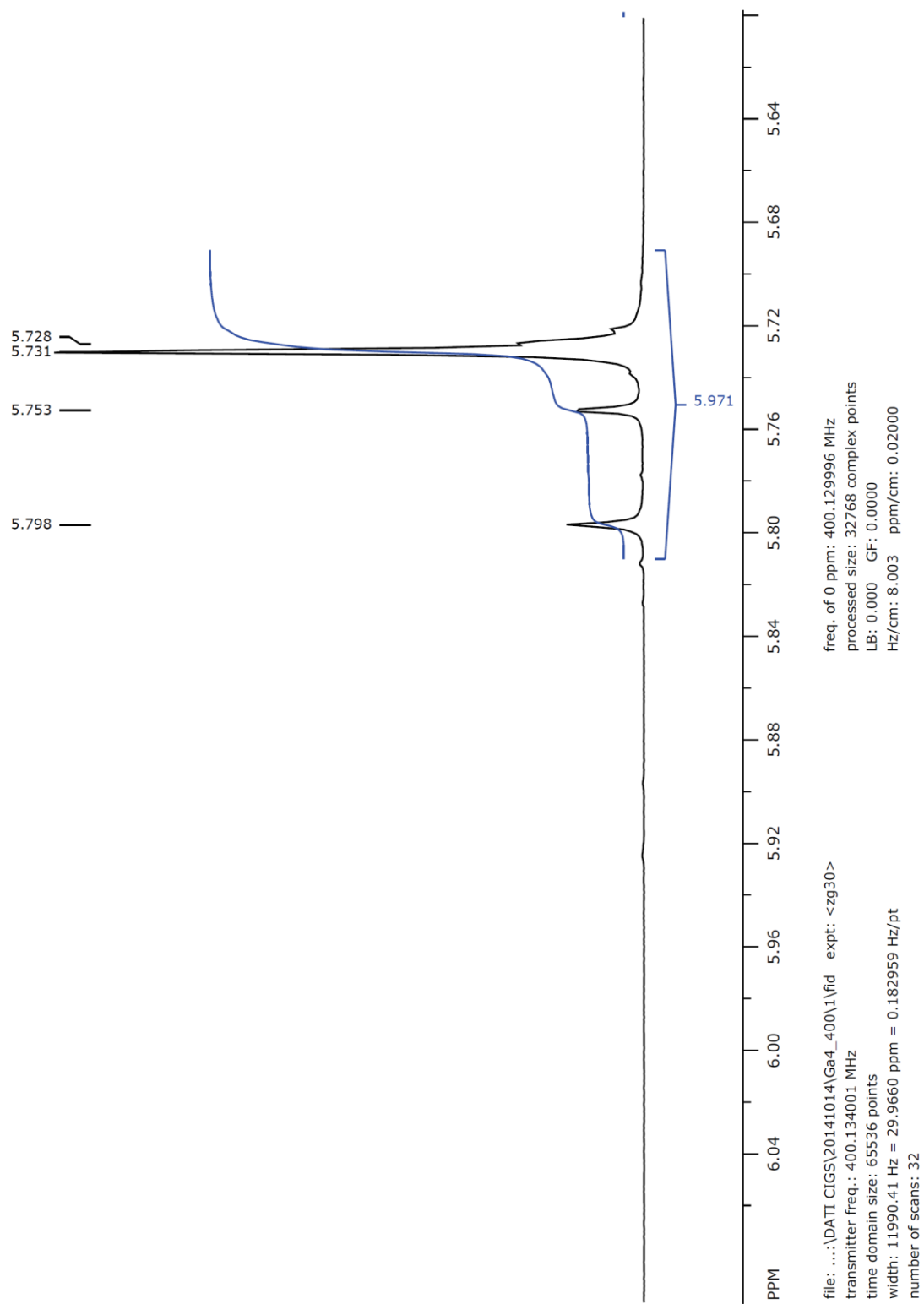


Figure S4. ^1H NMR spectrum of $1^4\text{-Py}\cdot\text{EtOH}$ (400.13 MHz, C_6D_6 , 298 K).

SpinWorks 4: Ga4pPy2dpm6*EtOH ib C6D6
T=298K

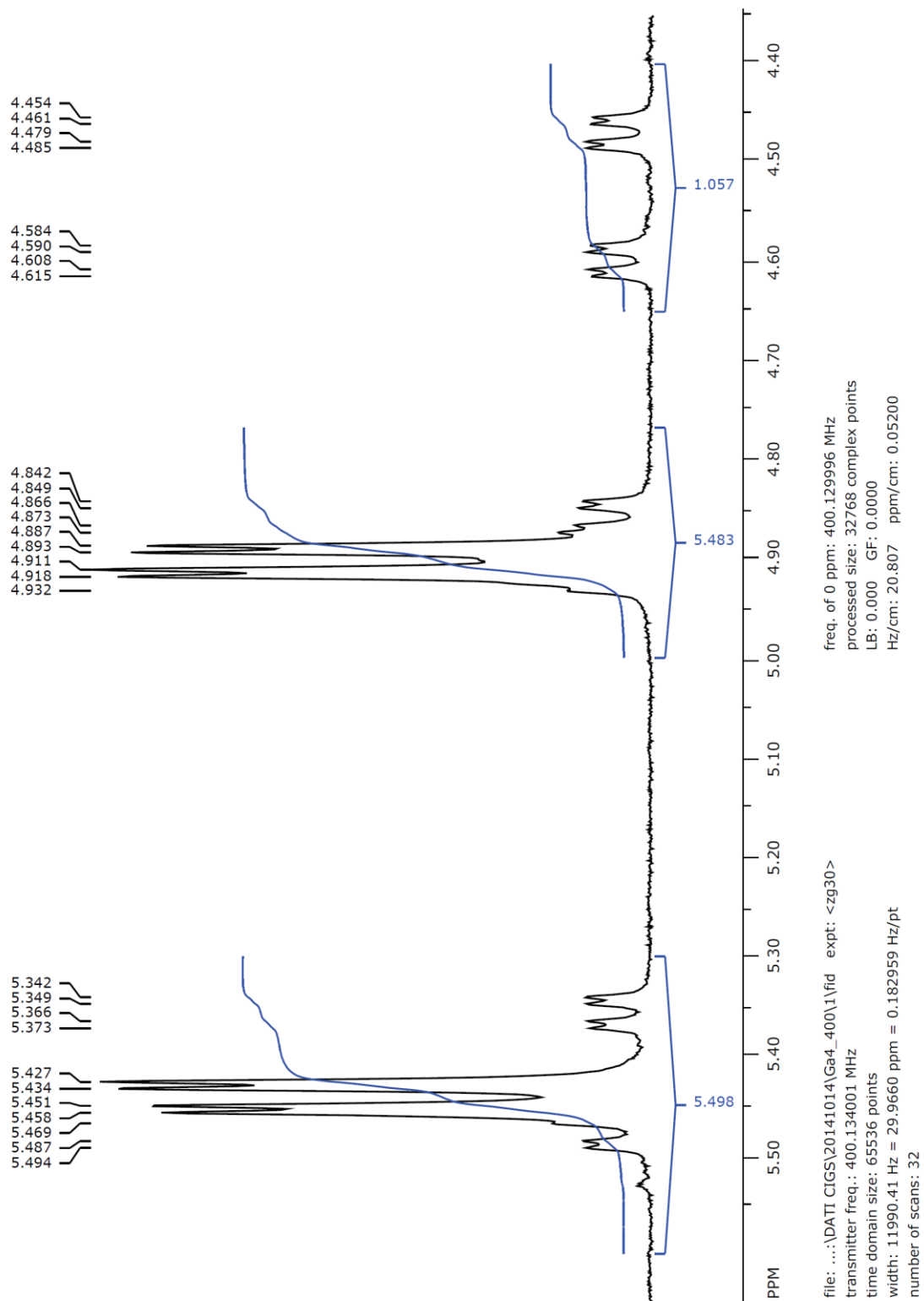


Figure S5. ^1H NMR spectrum of $1^4\text{-Py}\cdot\text{EtOH}$ (400.13 MHz, C_6D_6 , 298 K).

SpinWorks 4: Ga4pPy2dpm6*EtOH ib C6D6
T=298K

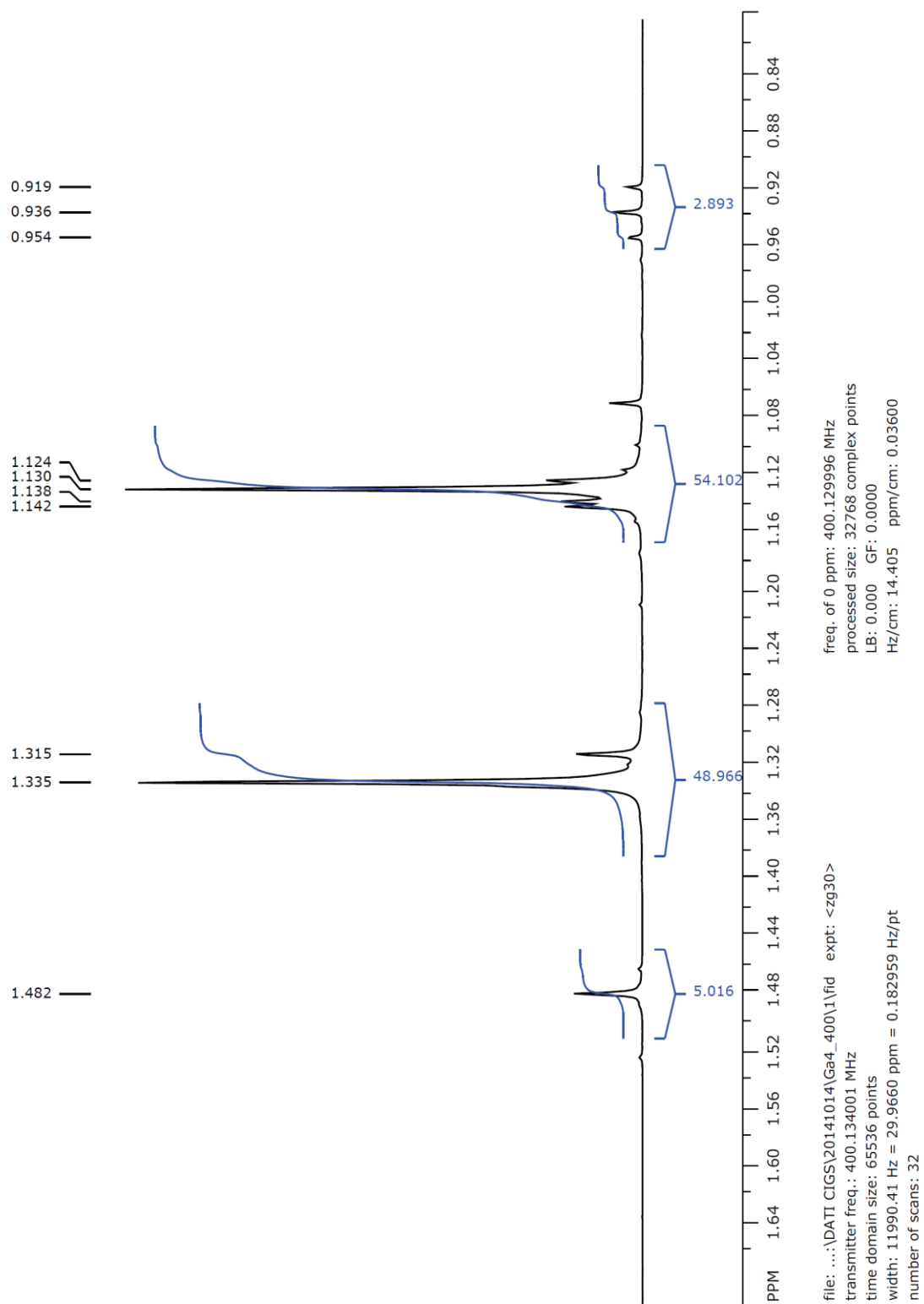


Figure S6. ^1H NMR spectrum of $1^{4\text{-Py}}$.EtOH (400.13 MHz, C_6D_6 , 298 K).

SpinWorks 4: Ga4pPy2dpm6*EtOH ib C6D6
T=298K

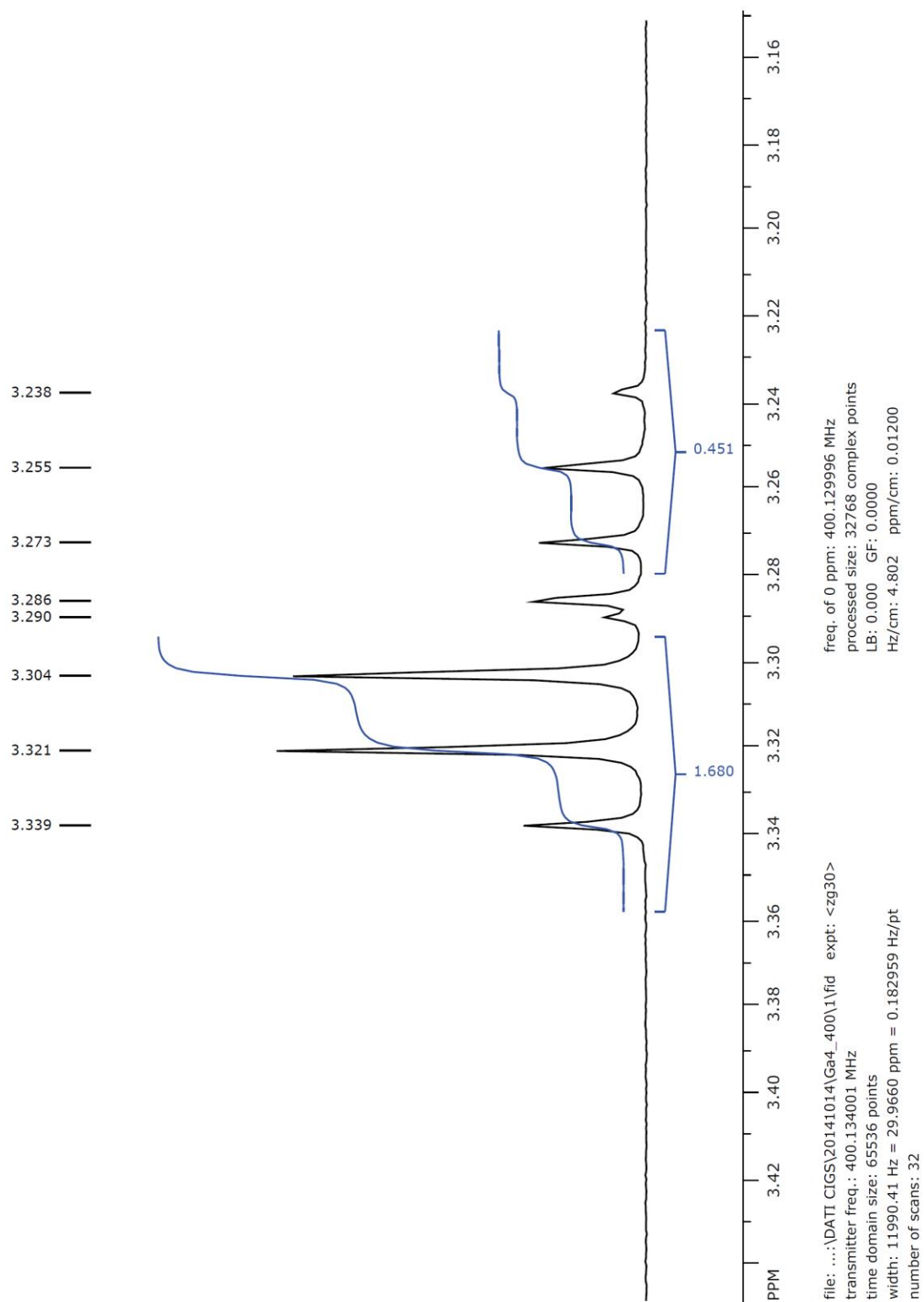
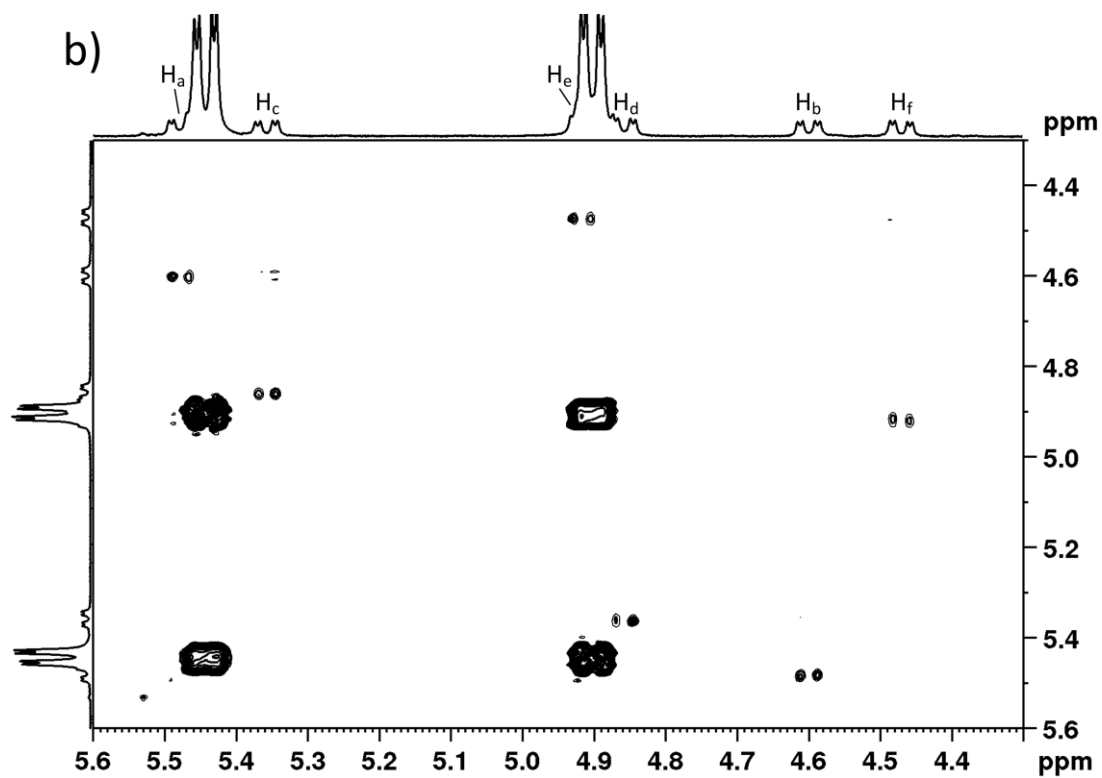
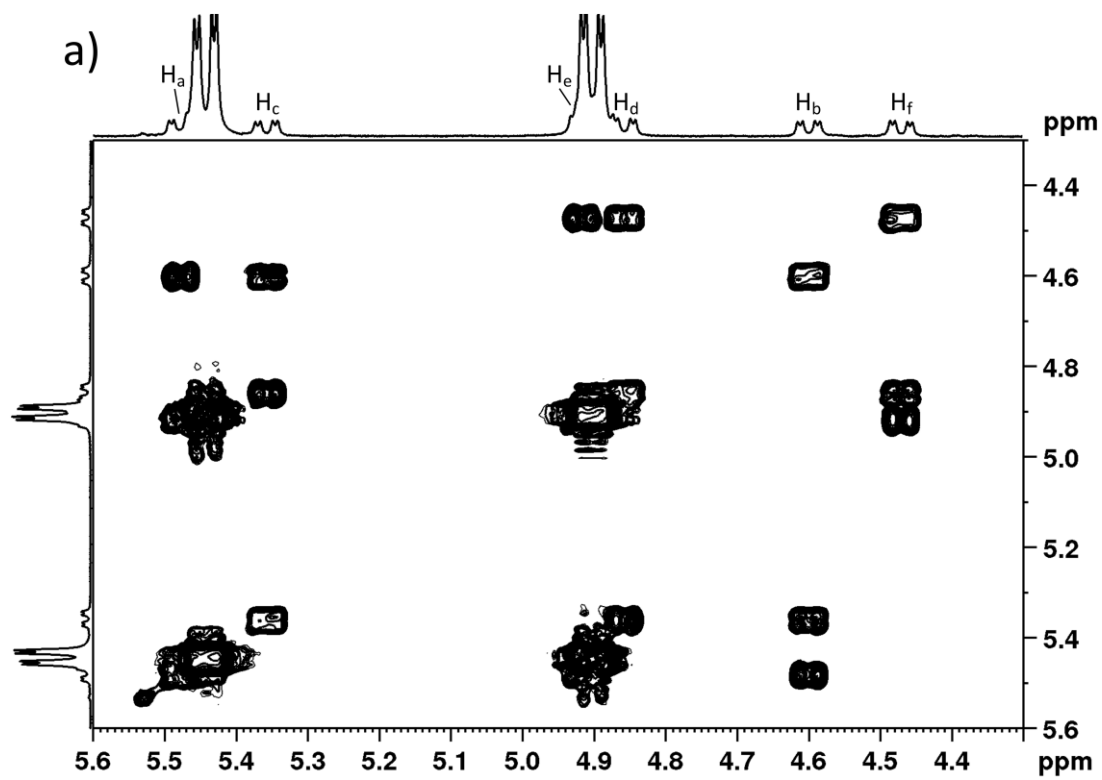


Figure S7. ^1H NMR spectrum of $1^4\text{Py}\cdot\text{EtOH}$ (400.13 MHz, C_6D_6 , 298 K).



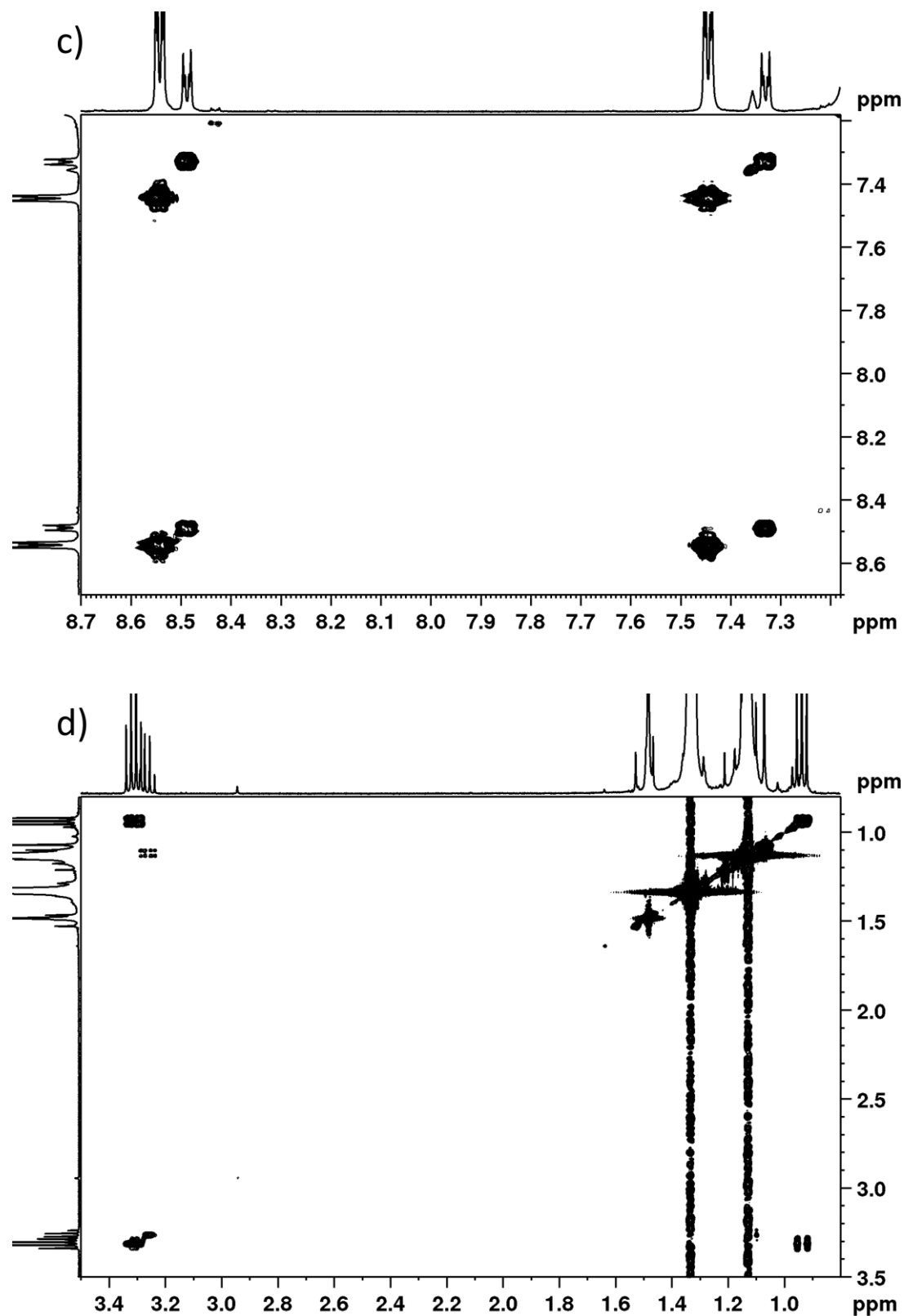


Figure S8. Expanded regions of $^1\text{H}, ^1\text{H}$ -COSY NMR spectrum of $1^4\text{-Py}\cdot\text{EtOH}$ (400.13 MHz, C_6D_6 , 298 K): a) methylene region at lower contour levels showing all couplings (geminal and long-range); b) methylene region at higher contour levels to highlight geminal couplings; c) aromatic region; d) EtOH and Et₂O correlations (CH_3 signal of Et₂O at 1.11 ppm partially hidden under a *t*Bu peak).

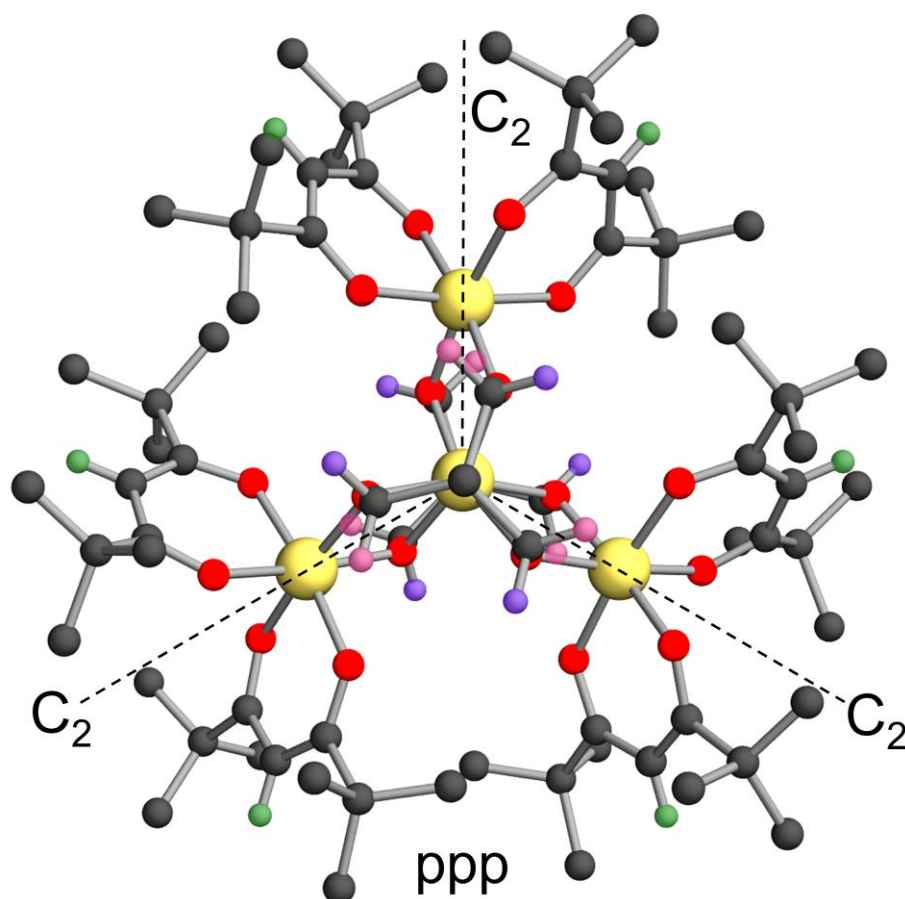


Figure S9. Molecular structure of **14^{-Py}** (ppp isomer), viewed normal to the molecular plane. For clarity, the 4-pyridyl groups and the minority components of disordered *t*Bu substituents, as well as *t*Bu hydrogens, are omitted. The dashed lines are the twofold axes required by idealized D_3 symmetry. The color code for Ga, O and C atoms is the same as in Figure 1, but the color of H atoms indicates equivalence in D_3 symmetry.

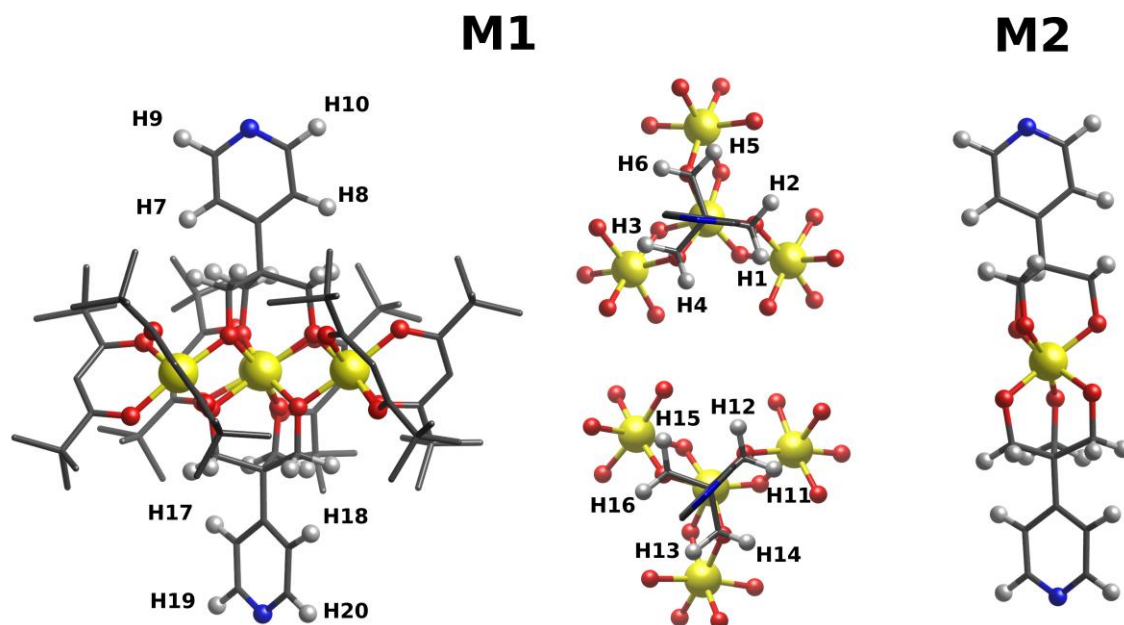


Figure S10. Complete (M1) and truncated (M2) models employed for the DFT calculations. The color code is the same as in Figure 1. Hydrogen atoms of dpm^- ligands are omitted for sake of clarity. The numbering of hydrogens atoms of tripodal ligands is the same in both models.

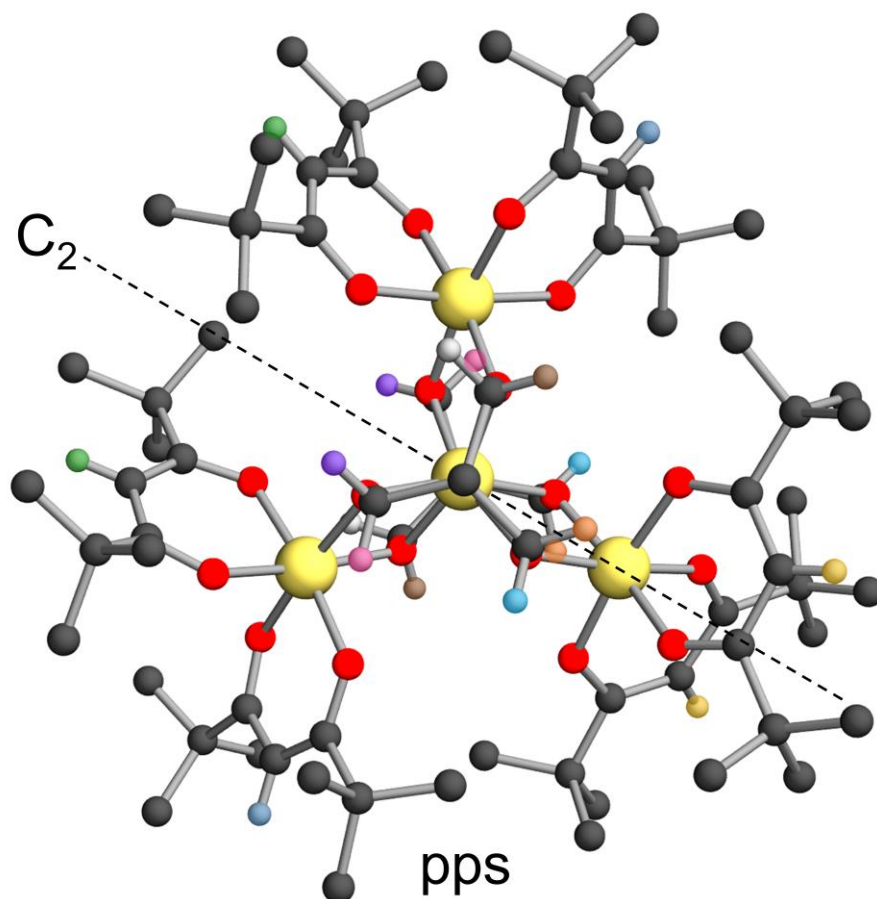


Figure S11. Molecular structure of $1^{4\text{-Py}}$ (pps isomer), viewed normal to the molecular plane. For clarity, the 4-pyridyl groups and the minority components of disordered *t*Bu substituents, as well as *t*Bu hydrogens, are omitted. The dashed line is the twofold axis required by C_2 symmetry. The color code for Ga, O and C atoms is the same as in Figure 1, but the color of H atoms indicates equivalence in C_2 symmetry.

Table S1. Proton chemical shifts δ_{calc} (ppm) computed on complete model M1. The numbering of hydrogens atoms is shown in Figure S10.

<i>alpha</i>		<i>beta</i>		H _A		H _B	
H9	8.610	H7	7.347	H1	5.926	H2	5.295
H10	8.599	H8	7.914	H3	5.790	H4	4.434
H19	8.600	H17	7.353	H5	5.334	H6	5.039
H20	8.603	H18	7.891	H11	5.990	H12	5.307
				H13	5.806	H14	4.531
				H15	5.305	H16	5.002

Table S2. ¹H-¹H scalar couplings *J* (Hz) computed on truncated model M2 and involving methylene protons H1-H6 (interactions among protons H11-H16 of the second, symmetry-related tripodal ligand are identical to those reported here; see Figure S10 for the numbering of hydrogen atoms). Interactions above 1 Hz in magnitude are highlighted in bold.

H1					
H2	-7.159				
H3	0.188	3.454			
H4	0.066	0.104	-8.895		
H5	0.418	0.018	0.123	3.142	
H6	3.736	0.152	0.048	-0.062	-8.293
H_i / H_j	H1	H2	H3	H4	H5

Table S3. Proton chemical shifts δ_{calc} (ppm) computed on truncated model M2. The numbering of hydrogens atoms is shown in Figure S10.

H _A		H _B	
H1	5.291	H2	4.914
H3	5.486	H4	4.319
H5	4.425	H6	4.8
H11	4.404	H12	5.398
H13	5.331	H14	3.901
H15	4.865	H16	5.336