Synthesis, structural characterization and NMR studies of group 10 metal complexes with macrocyclic amine *N*-heterocyclic carbene ligands

Taotao Lu,[a] Zhiming Liu,[b] Carlos A. Steren,[b] Fan Fei,[a] Tabitha M. Cook,[b] Xue-Tai Chen[a] and Zi-Ling Xue*[b]*

[a] State Key Laboratory of Coordination Chemistry, Nanjing National Laboratory of Microstructures, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China.

E-mail: xtchen@nju.edu.cn; Fax: +86 25 89682309

[b] Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, USA.

E-mail: xue@utk.edu

Electronic Supplementary Information

Table of Contents

Table S1 Crystallographic data for **1**·CH_3CN, **2** and **3**.

	1·CH_3CN	**2**	**3**
CCDC	1561213	1561968	1561218
Formula	$C_{27}H_{27}F_{12}N_7P_2Ni$	$C_{25}H_{24}F_{12}N_6P_2Pd$	$C_{25}H_{24}F_{12}N_6P_2Pt$
M	798.20	804.84	893.53
T [K]	296(2)	150(2)	150(2)
Crystal system	monoclinic	triclinic	triclinic
Space group	$C2/c$	P-1	P-1
a [Å]	22.859(3)	10.9687(9)	10.8761(9)
b [Å]	17.982(2)	11.3949(9)	11.3704(10)
c [Å]	17.138(2)	12.2882(9)	12.1822(11)
α [°]	90	99.532(2)	99.4000(10)
β [°]	113.277(2)	91.502(2)	91.5800(10)
γ [°]	90	104.897(2)	104.1730(10)
V [Å^3]	6471.2(13)	1459.9(2)	1437.4(2)
Z	8	2	2
D_{calc} [g cm^{-3}]	1.639	1.831	2.064
μ (mm^{-1})	0.800	0.852	5.100
F (000)	3232	800	864
θ range [°]	1.491/25.018	2.290/27.435	1.699/27.115
Reflns collected	18073	13143	12592
R_{int}	0.0634	0.0535	0.0215
Indep. reflns	5722	6621	6236
Refns obs. [$I > 2\sigma(I)$]	3130	4649	5866
Data/restr./paras	5722/404/487	6621/2364/546	6236/732/444
GoF	1.053	1.026	1.045
R_1, wR_2 [all data]	0.1372/0.2486	0.0993/0.1231	0.0260/0.0685
R_1, wR_2 [I $>2\sigma(I)$]	0.0779/0.2139	0.0578/0.1090	0.0238/0.0674
Larg. peak/hole (e. Å)	0.766/-0.526	0.873/-0.481	1.160/-0.979

Table S2 Crystallographic data for **4a-6a**

	4a	**5a**	**6a**
CCDC	1561967	1561969	1561970
Formula	$C_{22}H_{26}F_{12}N_6P_2Ni$	$C_{22}H_{26}F_{12}N_6P_2Pd$	$C_{22}H_{26}F_{12}N_6P_2Pt$
M	723.14	770.83	859.52
T/[K]	150(2)	293(2)	293(2)
Crystal system	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1
a [Å]	8.8606(18)	8.919(2)	8.878(2)
b [Å]	8.999(2)	9.073(2)	9.179(2)
c [Å]	9.611(2)	9.755(3)	9.616(2)
α [°]	87.532(5)	85.179(4)	82.780(4)
β [°]	64.664(4)	63.814(3)	64.264(4)
γ [°]	74.006(5)	74.460(3)	74.900(4)
V [Å^3]	663.3(2)	681.9(3)	681.4(3)
Z	1	1	1
D_{calc} [g cm^{-3}]	1.810	1.877	2.095
μ (mm^{-1})	0.964	0.907	5.375
F (000)	366	384	416
θ range [°]	2.353/ 27.584	2.328/ 27.384	2.298/ 27.848
Reflns collected	5223	4329	4729
R_{int}	0.0658	0.0196	0.0225
Indep. reflns	3042	3045	3188
Refns obs. [$I > 2\sigma(I)$]	1904	2795	3170
Data/restr./paras	3042/155/245	3045/153/242	3188/1022/276
GoF	1.050	1.110	1.050
R_1, wR_2 [all data]	0.1503/0.1870	0.0485/0.1182	0.0298/0.0714
R_1, wR_2 [I > $2\sigma(I)$]	0.0916/0.1660	0.0429/0.1137	0.0296/0.0713
Larg. peak/hole (e. Å)	1.040/-0.630	0.652/-0.414	1.300/-1.452

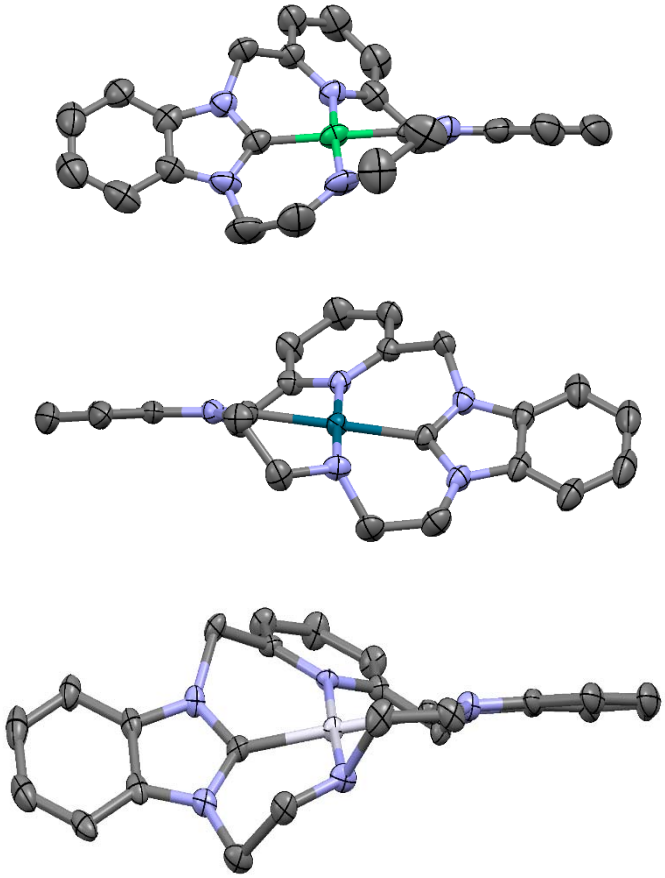

Fig. S1 Structures of **1** (top), **2** (middle) and **3** (bottom). Thermal ellipsoids are drawn at 30% probability.

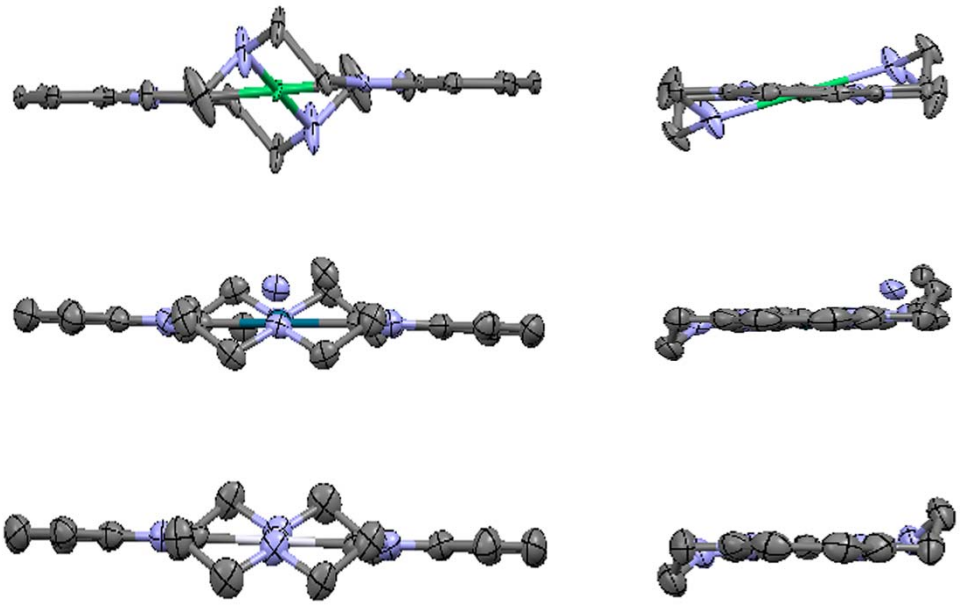

Fig. S2 Structures of **4a** (top), **5a** (middle) and **6a** (bottom). Thermal ellipsoids are drawn at 30% probability.

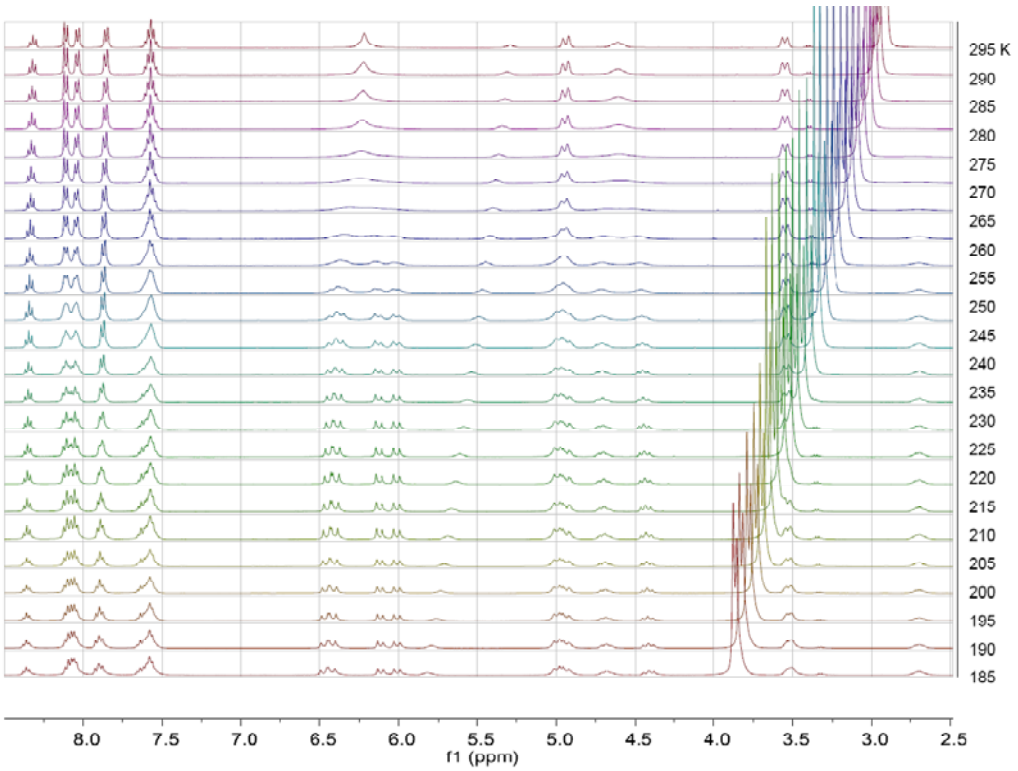

Fig. S3 VT ^{1}H NMR spectra of **1** in acetone-d_6 (400 MHz).

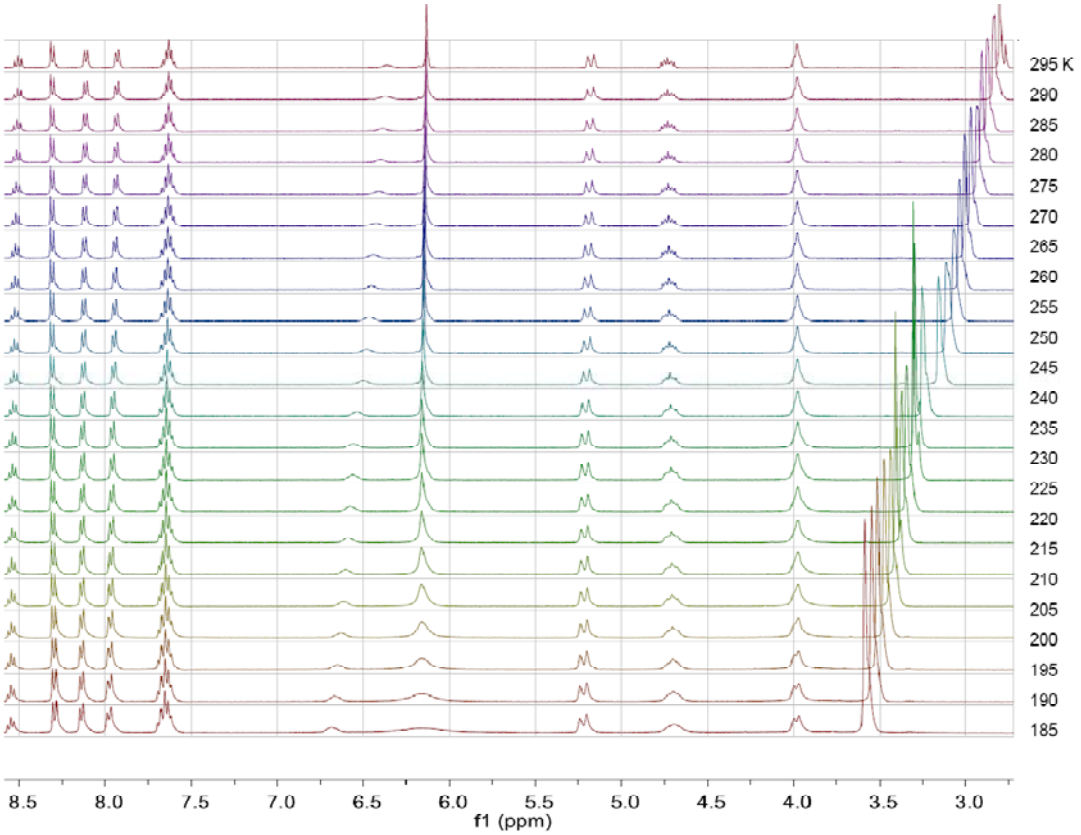

Fig. S4 VT ^{1}H NMR spectra of **2** in acetone-d_6 (400 MHz).

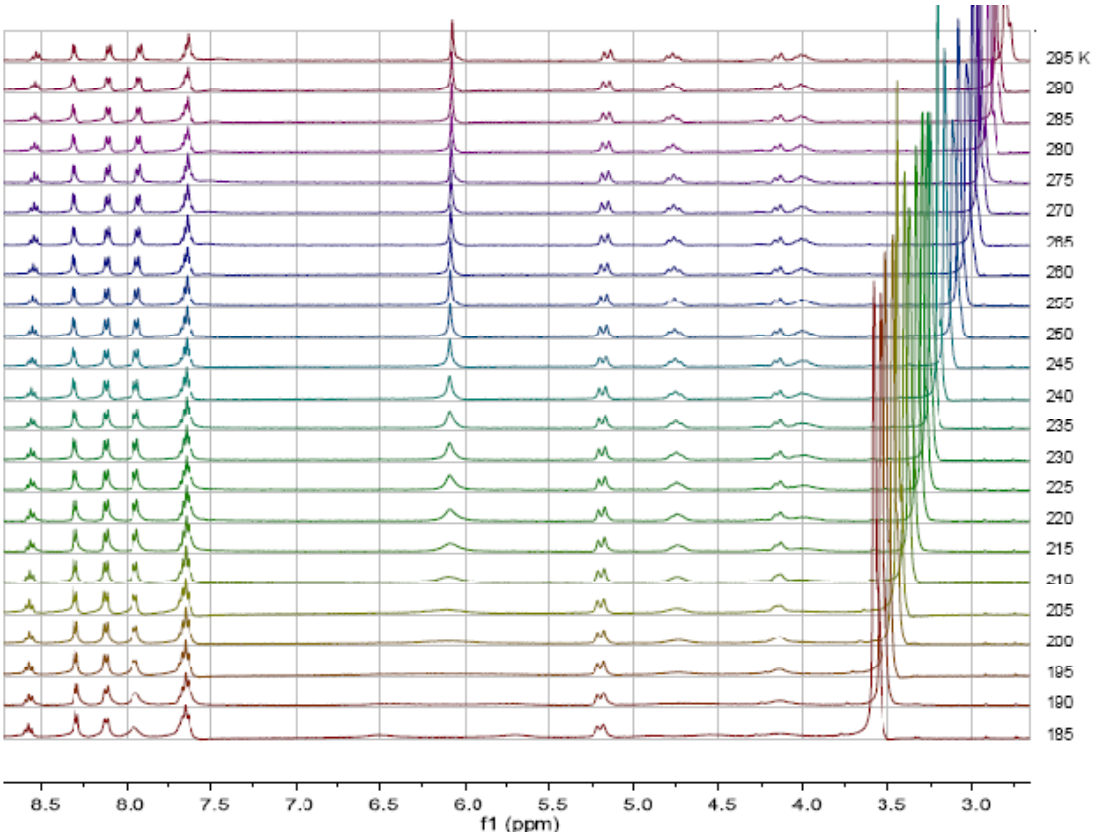

Fig. S5 VT ^{1}H NMR spectra of **3** in acetone-d_6 (400 MHz).

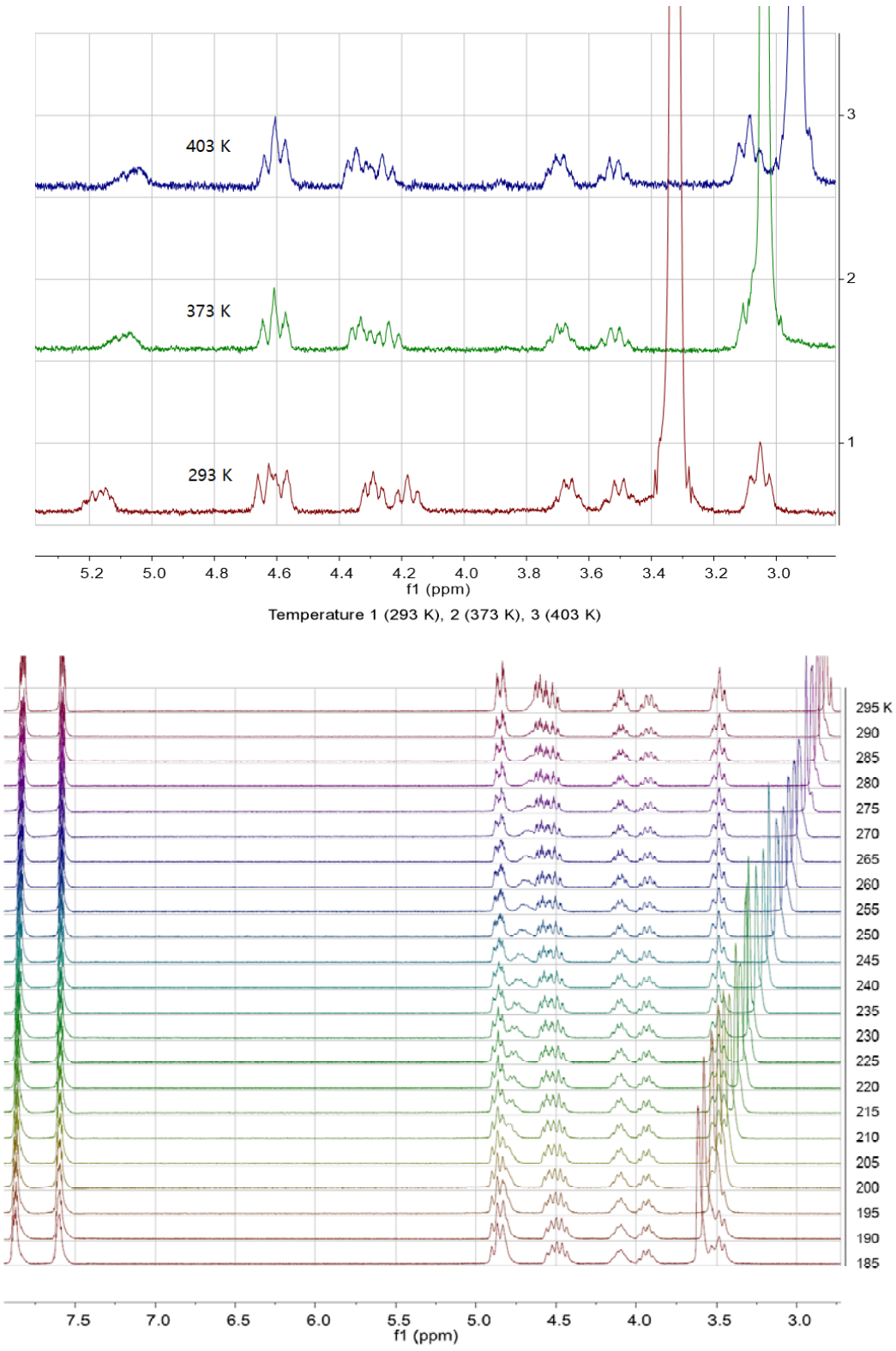

Fig. S6 VT ^{1}H NMR spectra of **4**: (Top) 293-403 K (DMSO-d_6, 400 MHz); (Bottom) at 185-295 K (acetone-d_6, 400 MHz).

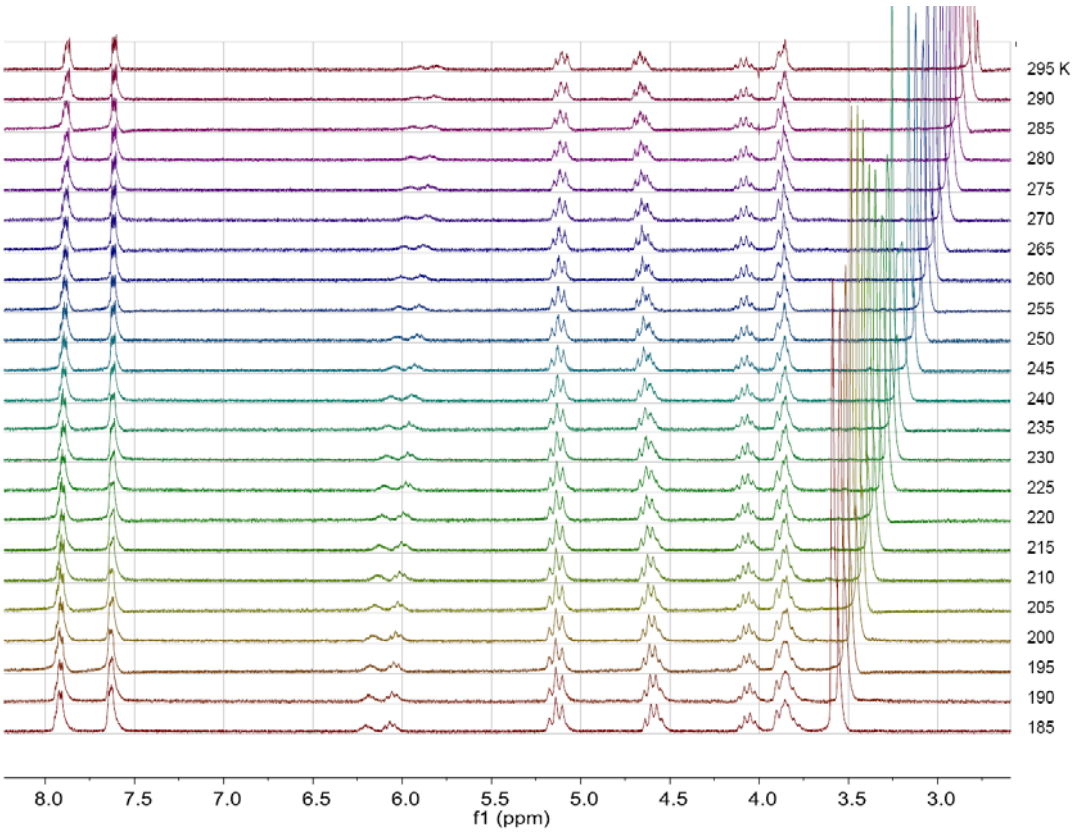

Fig. S7 VT ^{1}H NMR spectra of **5** (acetone-d_6, 400 MHz).

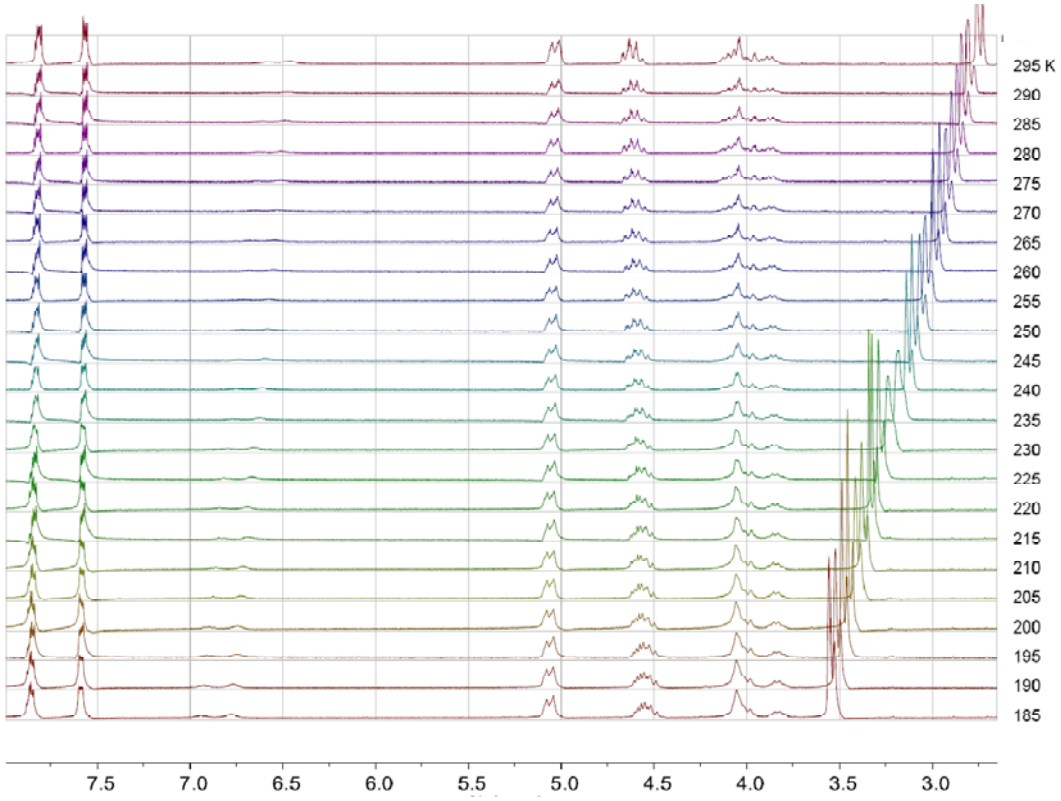

Fig. S8 VT ^{1}H NMR spectra of **6** (acetone-d_6, 400 MHz).

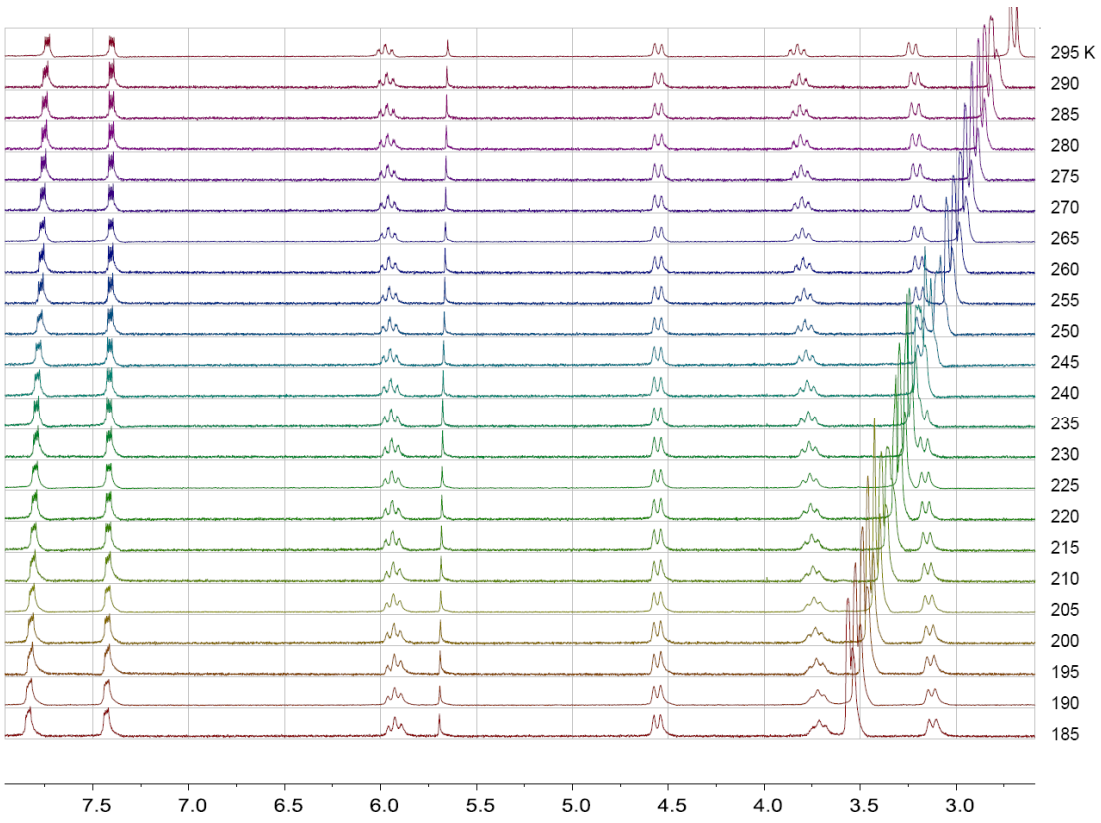

Fig. S9 VT ^{1}H NMR spectra of **7** (acetone-d_6, 400 MHz).

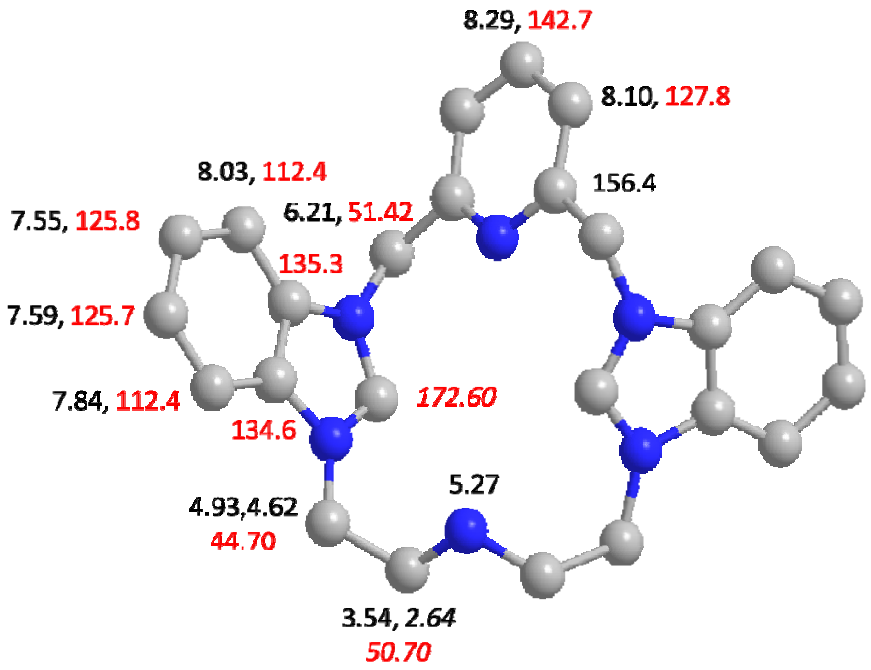

Fig. S10 Chemical shifts assignments for **1**. ^{1}H and ^{13}C shifts are in black and red colors, respectively. The metal atom not shown. Temperature: 298 K except those in italic which were measured at 318 K.

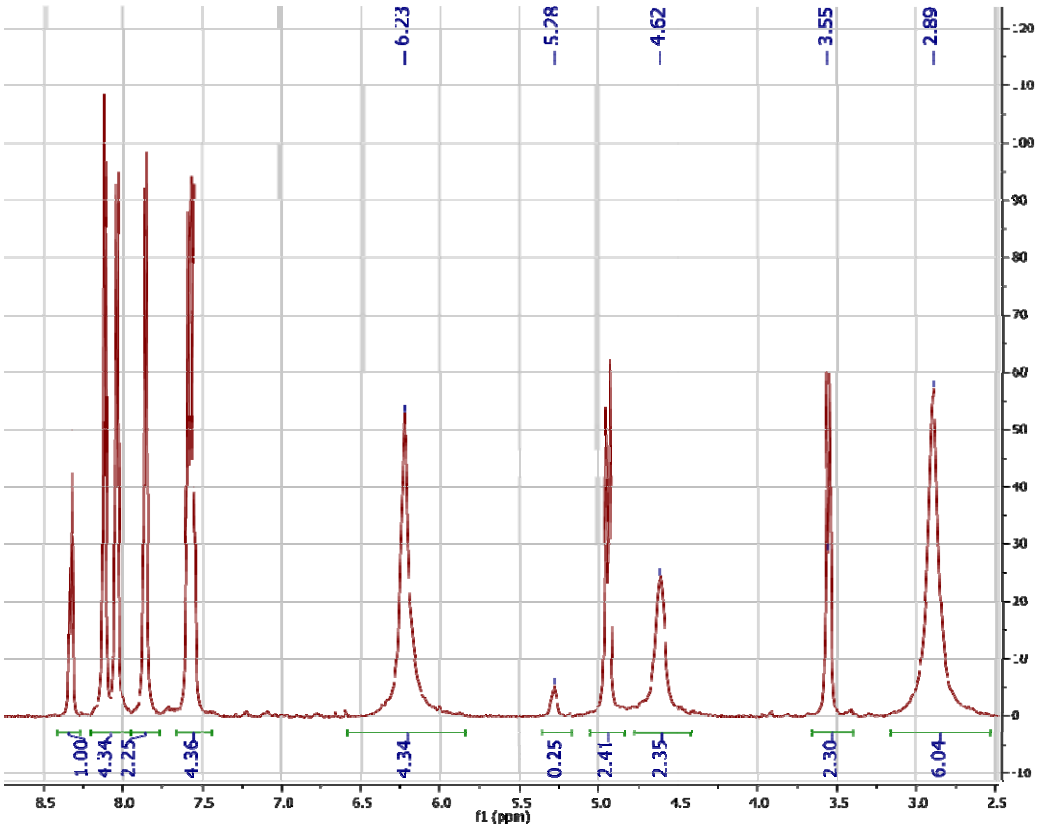

Fig. S11 ^{1}H NMR spectrum of **1** (acetone-d_6, 600 MHz, 298 K).

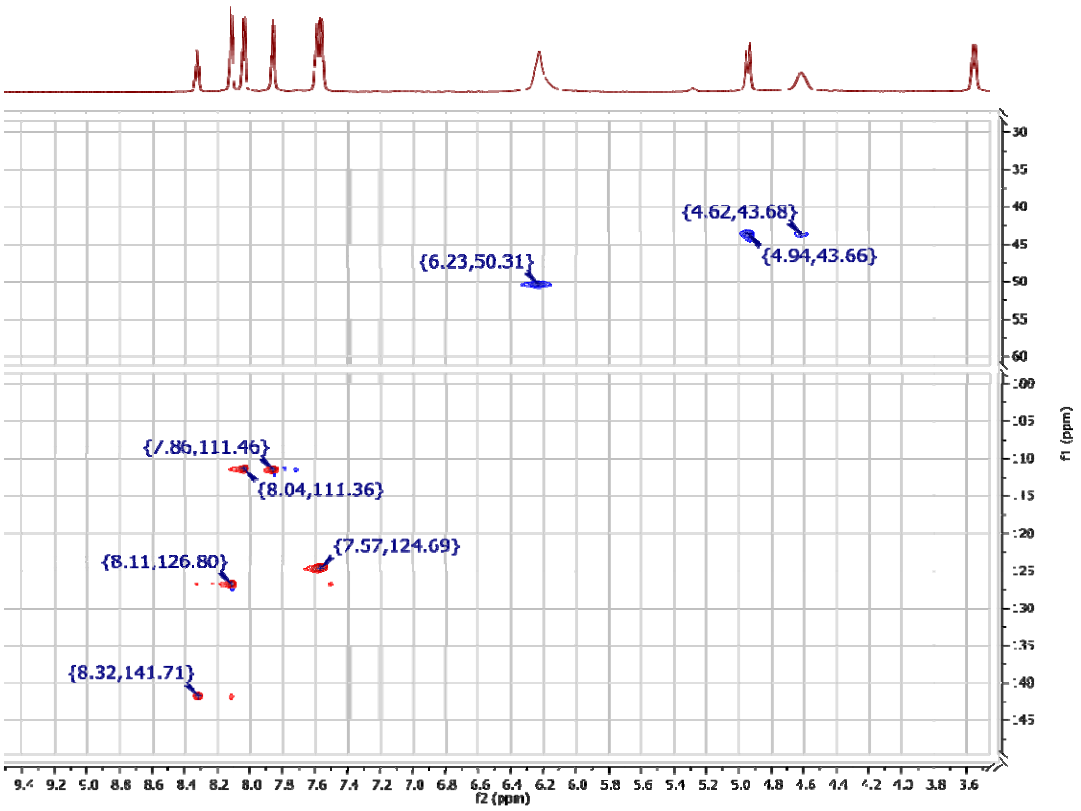

Fig. S12 ^{13}C gHSQCAD spectrum of **1** (acetone-d_6, 600 MHz, 298 K).

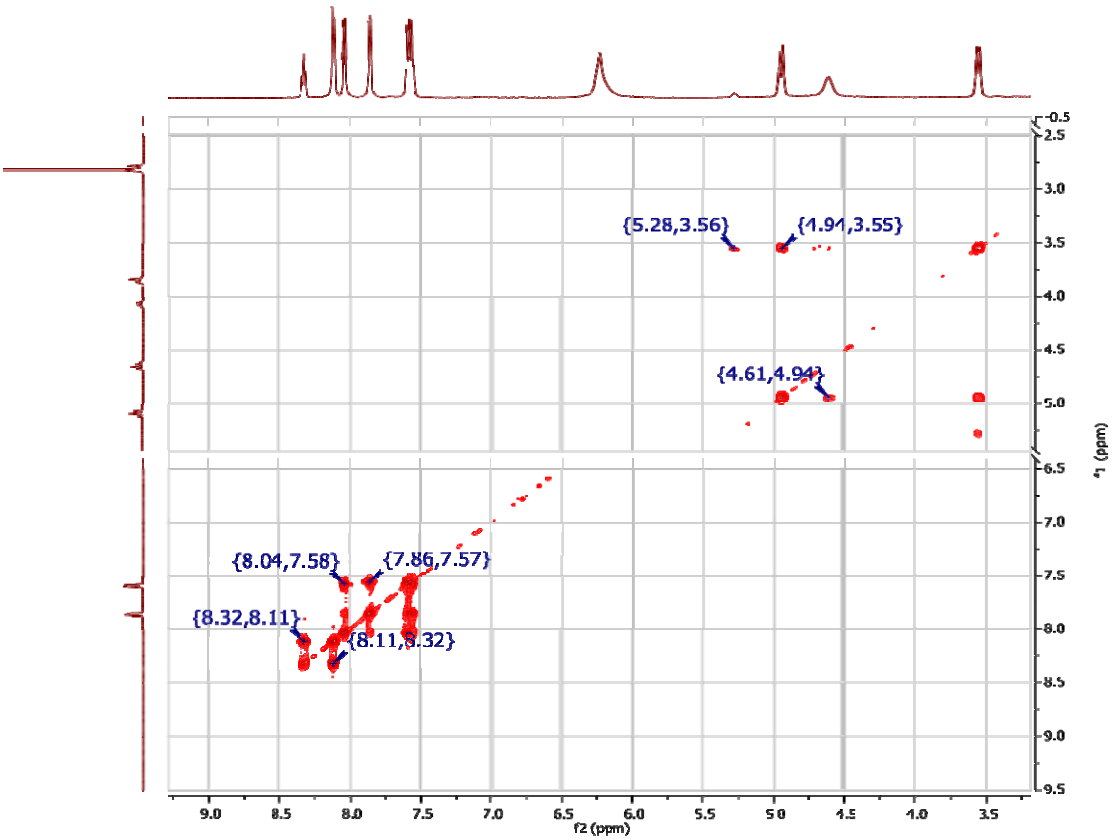

Fig. S13 gCOSY spectrum of **1** (acetone-d_6, 600 MHz, 298 K).

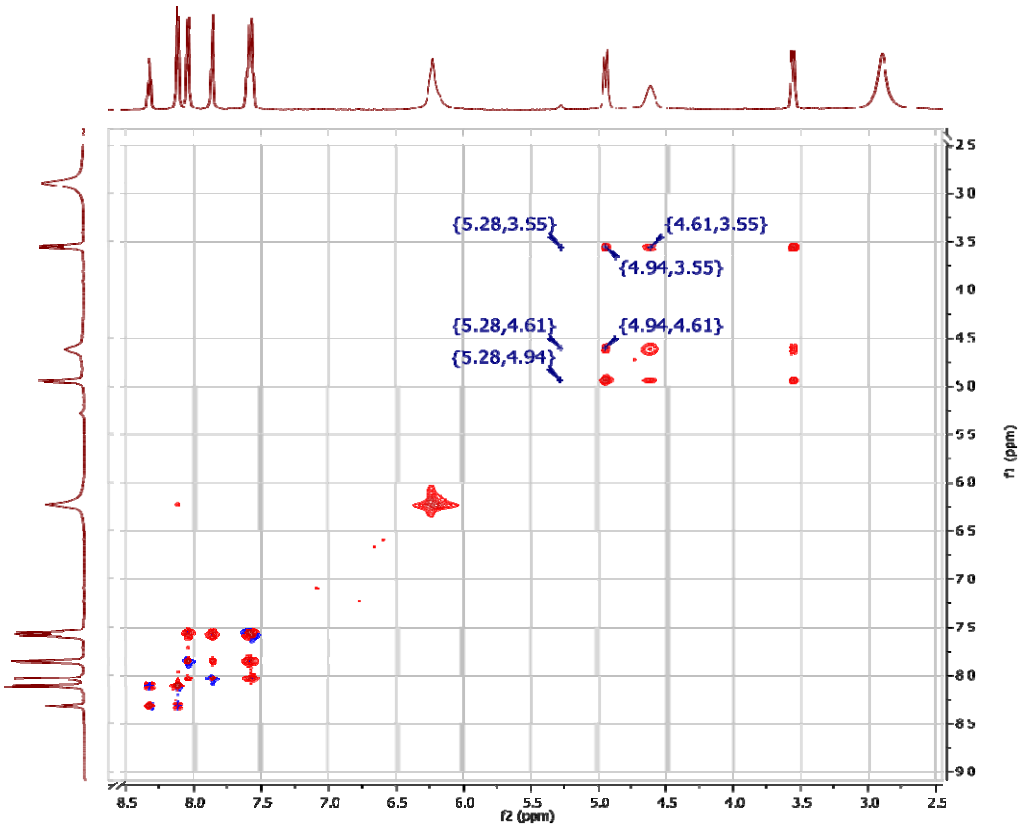

Fig. S14 TOCSY spectrum of **1** (acetone-d_6, 600 MHz, 298 K).

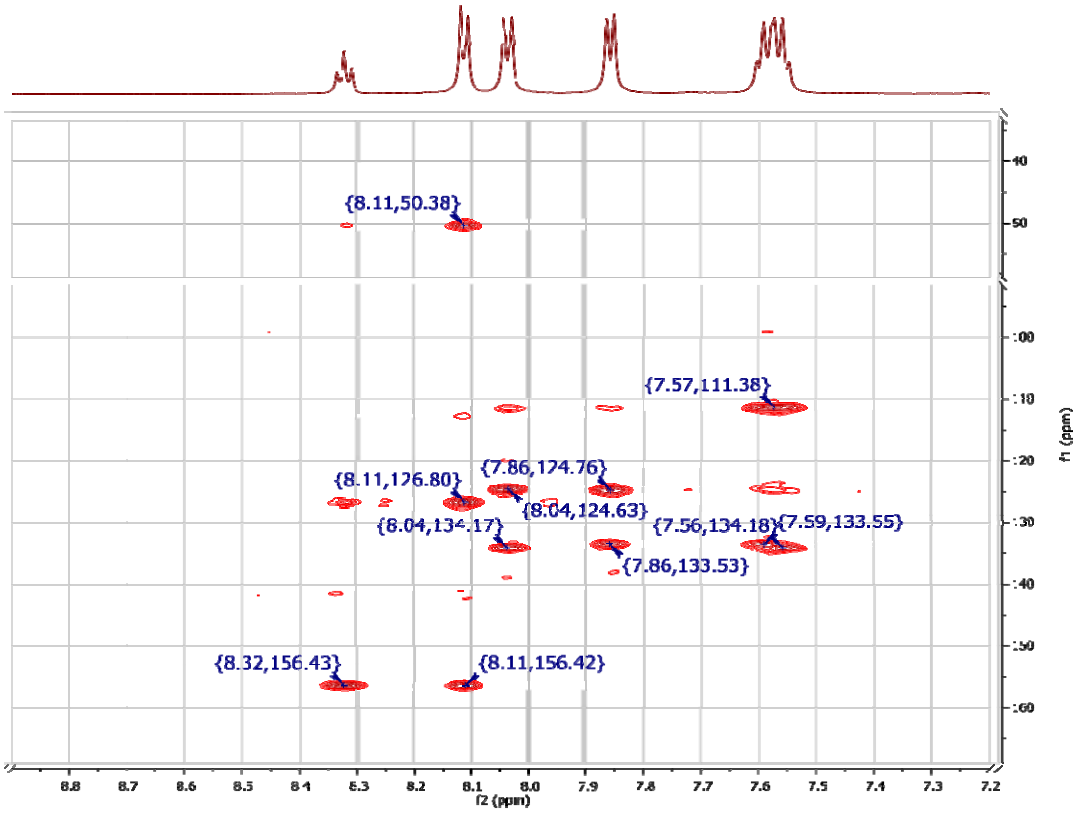

Fig. S15 ^{13}C gHMBCAD spectrum of **1** (acetone-d_6, 600 MHz, 298 K).

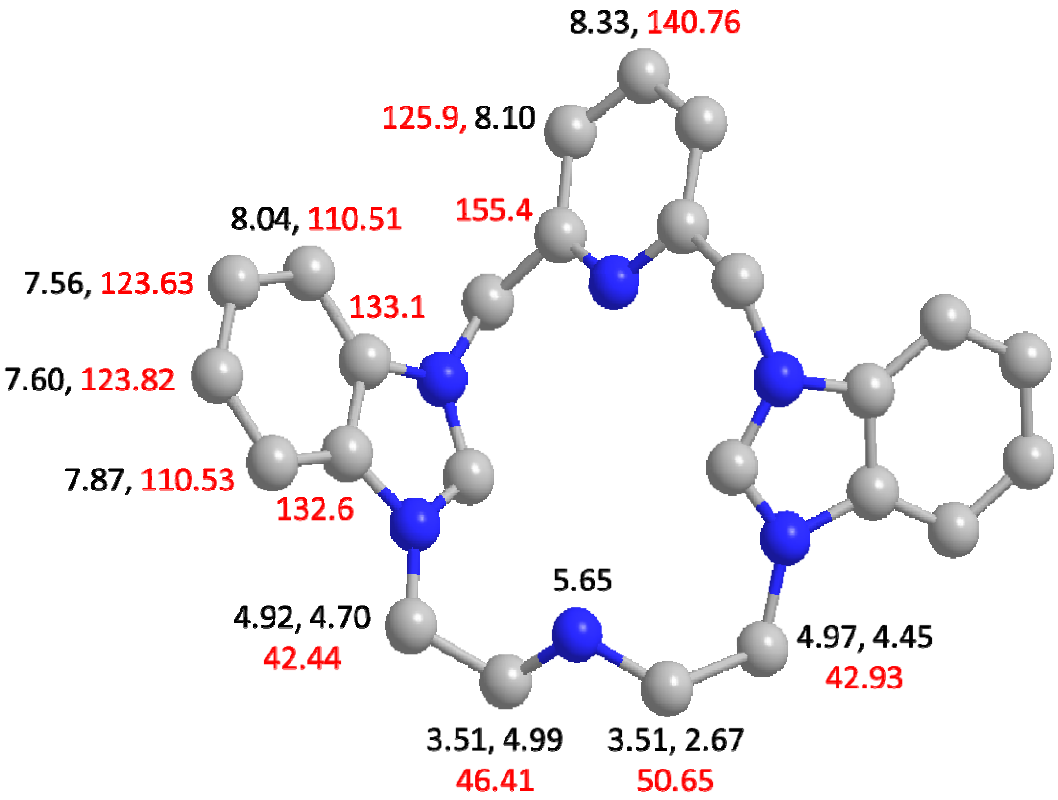

Fig. S16 Chemical shifts assignments for **1** at 253 K. ^{1}H and ^{13}C shifts are in black and red colors, respectively. The metal atom not shown.

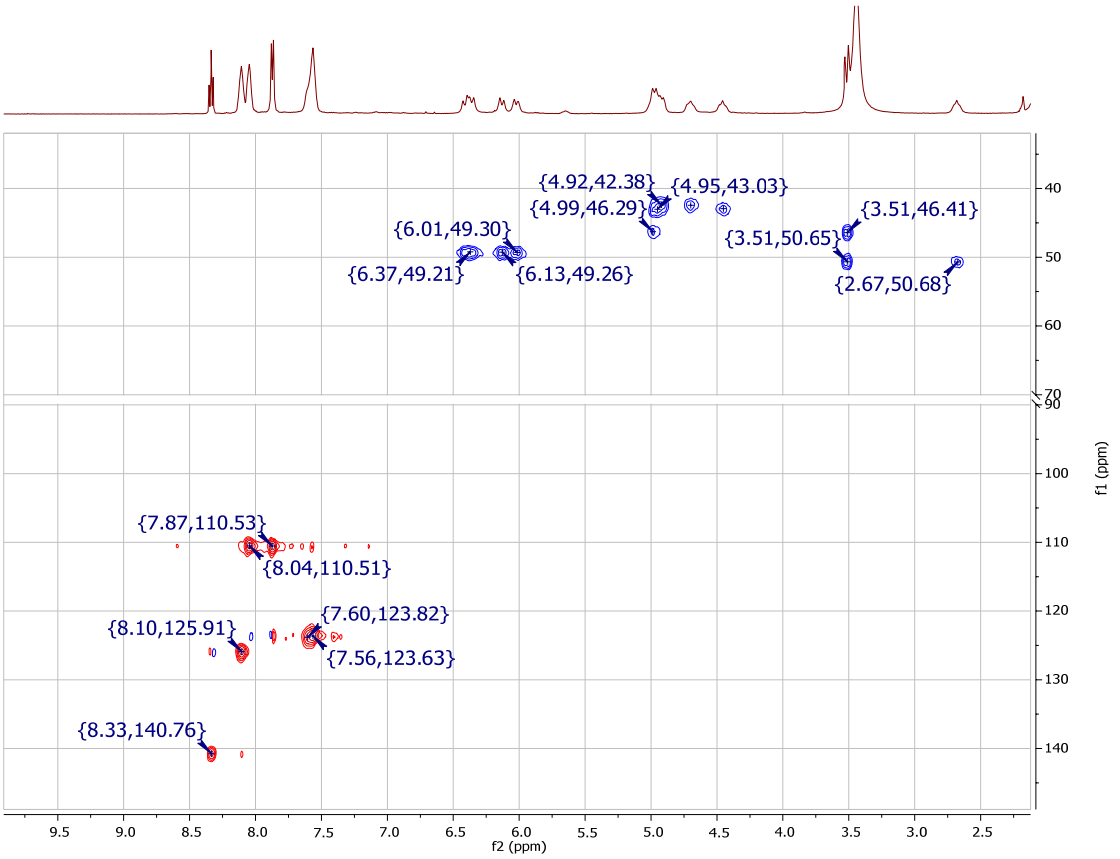

Fig. S17 ^{13}C gHSQCAD spectrum of **1** (acetone-d_6, 500 MHz, 253 K).

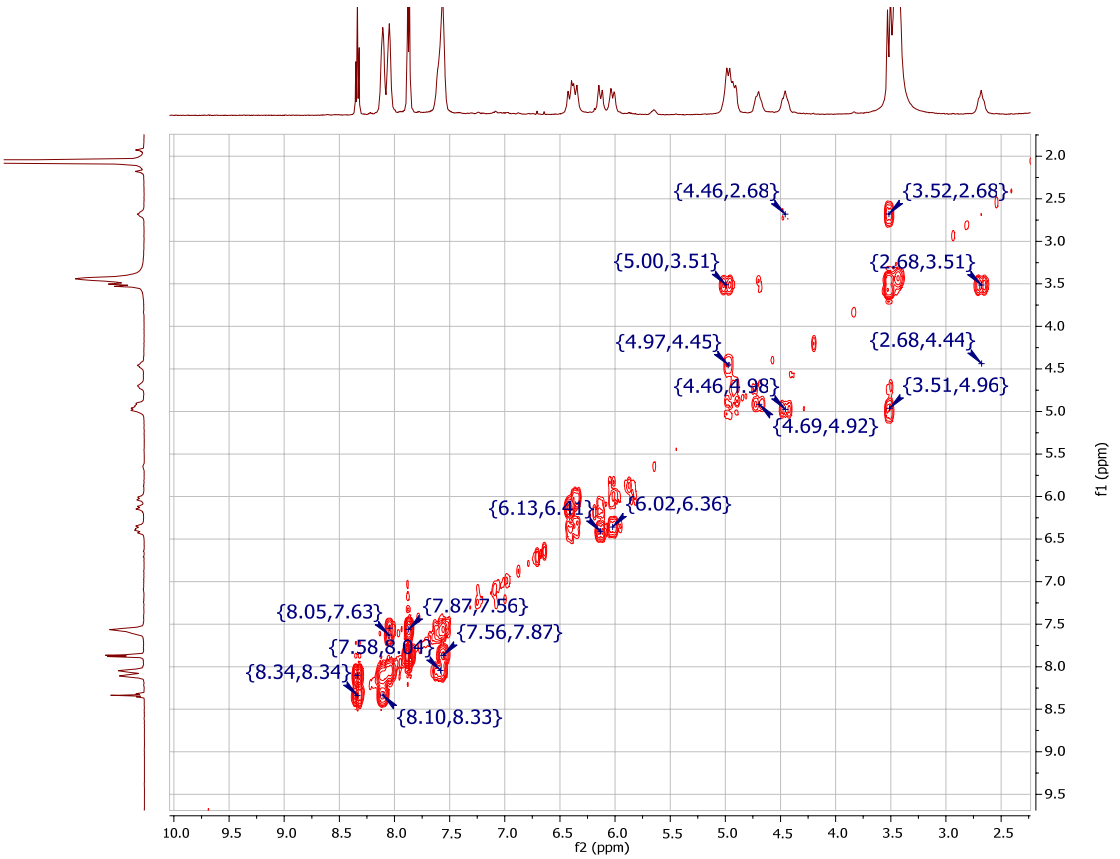

Fig. S18 ^{13}C gCOSY spectrum of **1** (acetone-d_6, 500 MHz, 253 K).

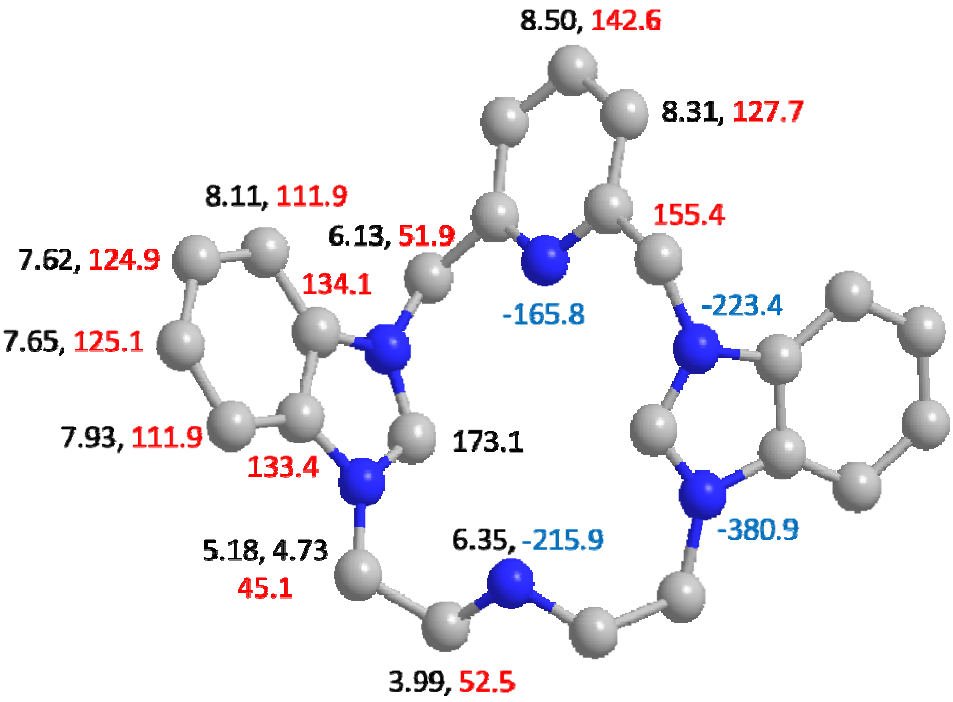

Fig. S19 Chemical shift assignments for **2** at 298 K. ^{1}H, ^{13}C and ^{15}N shifts in black, red and blue colors, respectively. The metal atom not shown.

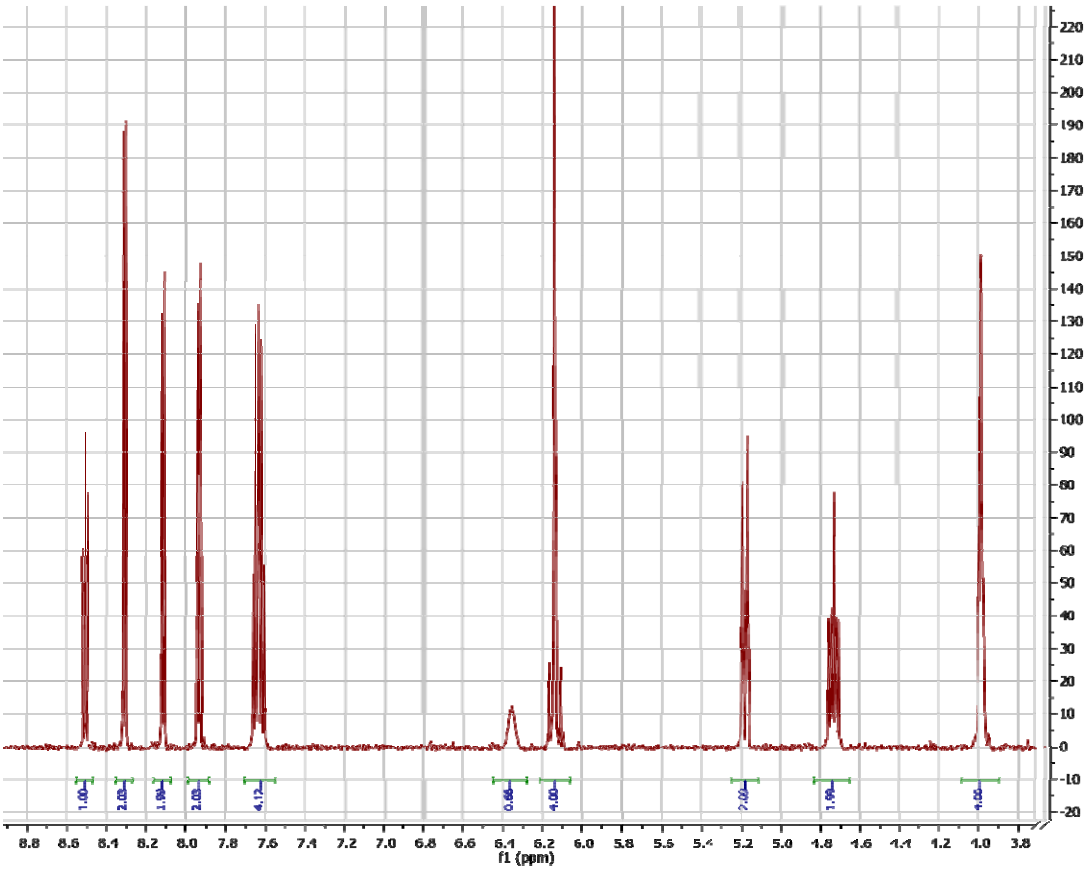

Fig. S20 ^{1}H NMR spectrum of **2** (acetone-d_6, 600 MHz, 298 K).

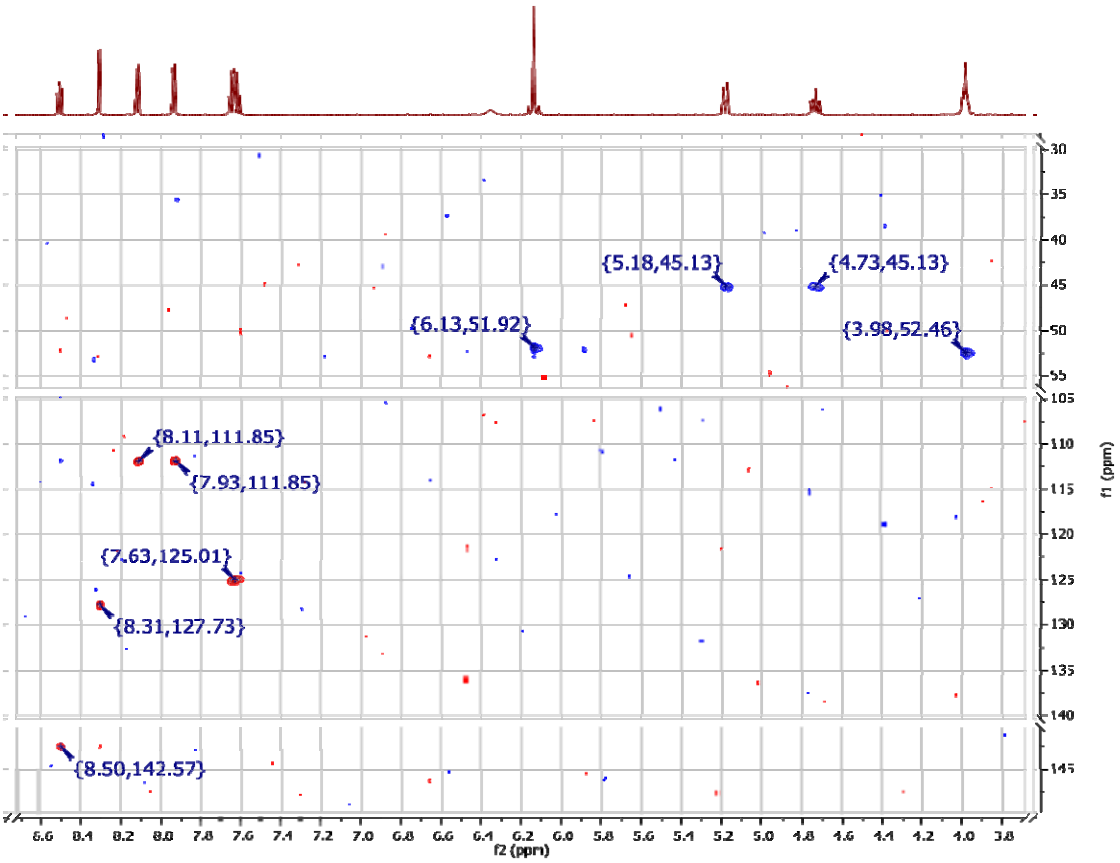

Fig. S21 ^{13}C gHSQCAD spectrum of **2** (acetone-d_6, 600 MHz, 298 K).

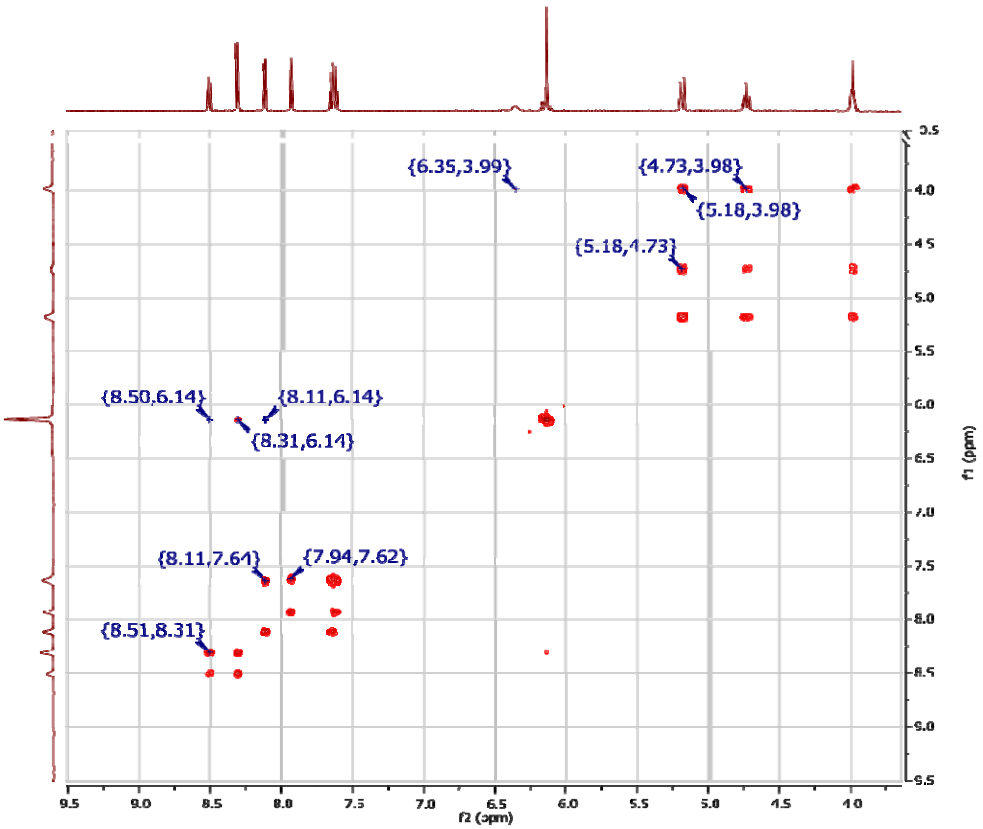

Fig. S22 gCOSY spectrum of **2** (acetone-d_6, 600 MHz, 298 K).

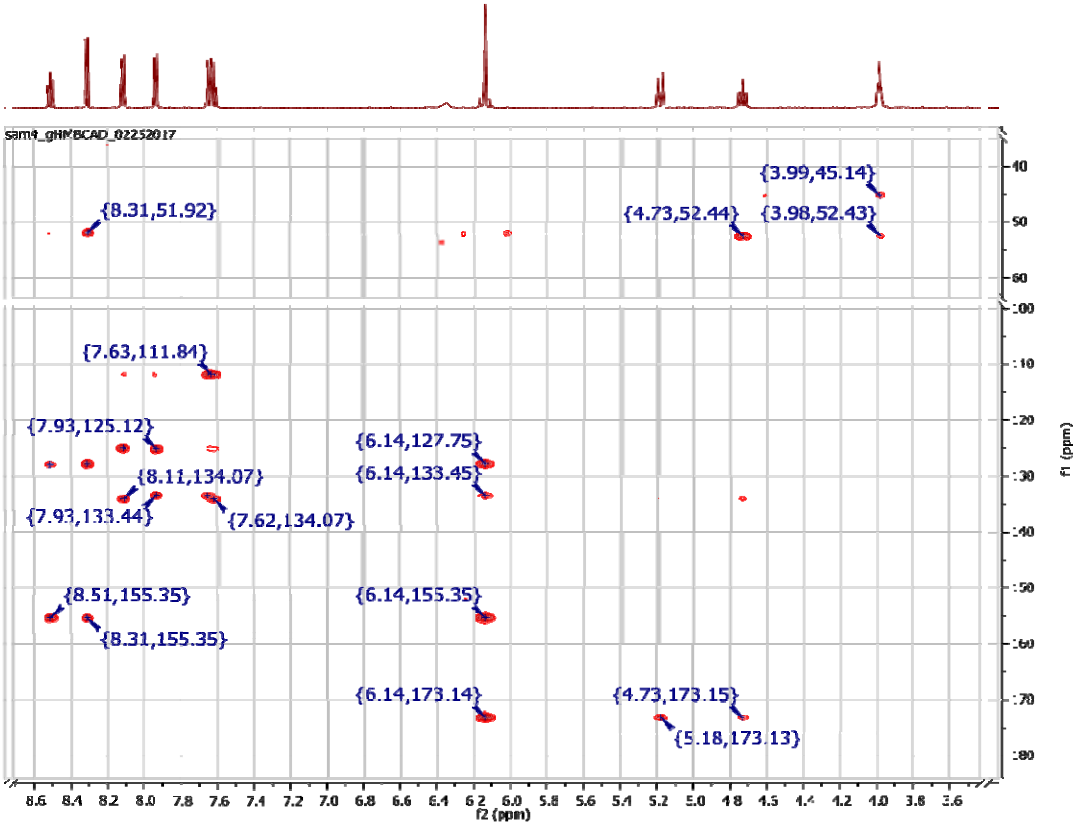

Fig. S23 ^{13}C gHMBCAD spectrum of **2** (acetone-d_6, 600 MHz, 298 K).

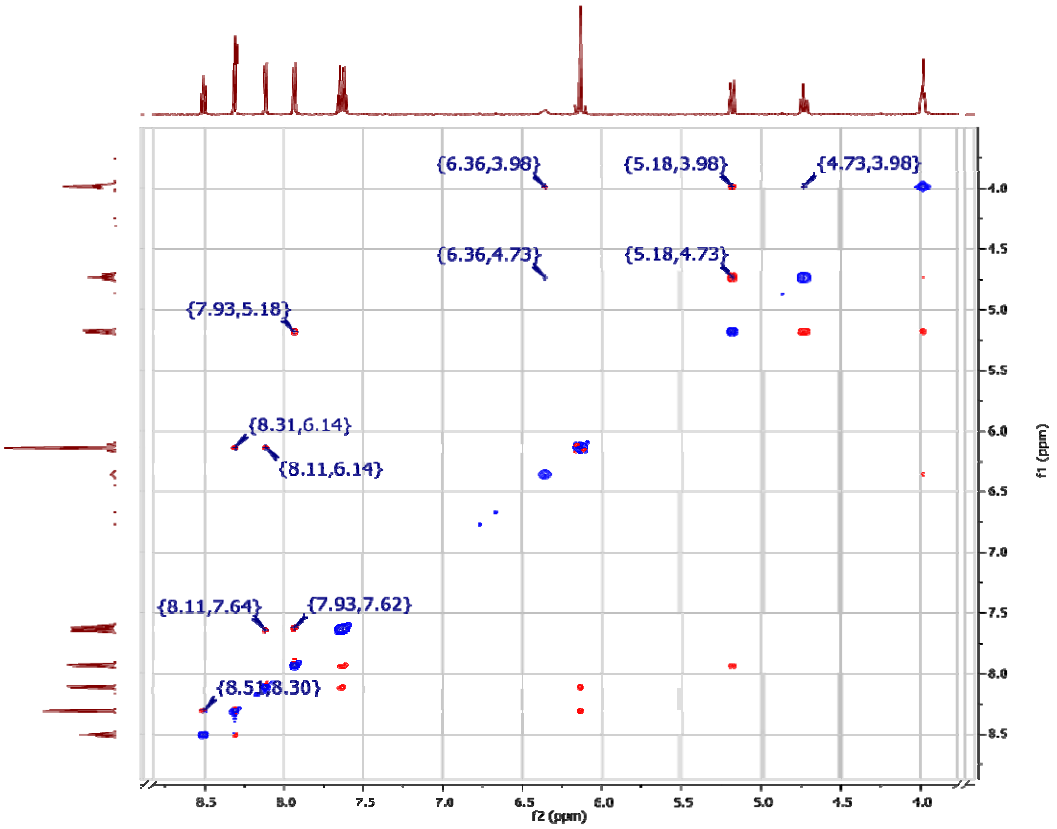

Fig. S24 NOESY spectrum of **2** (acetone-d_6, 600 MHz, 298 K).

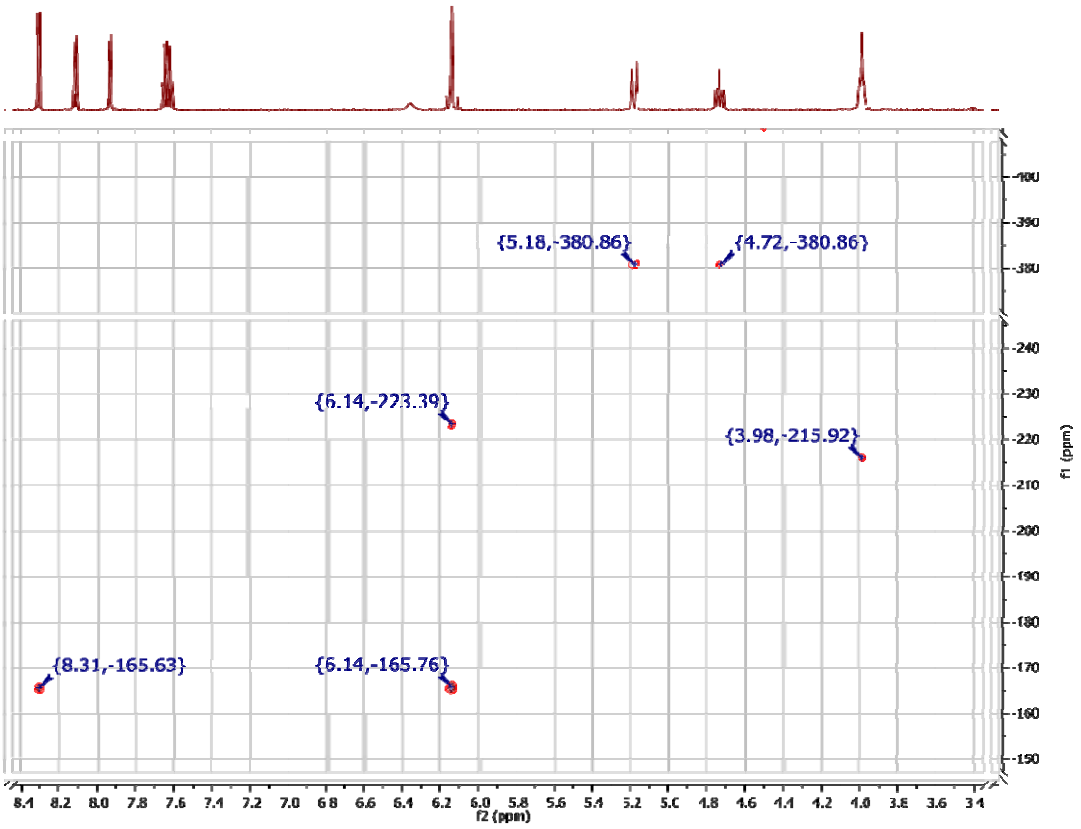

Fig. S25 ^{15}N gHMBCAD spectrum of **2** (acetone-d_6, 600 MHz, 298 K).

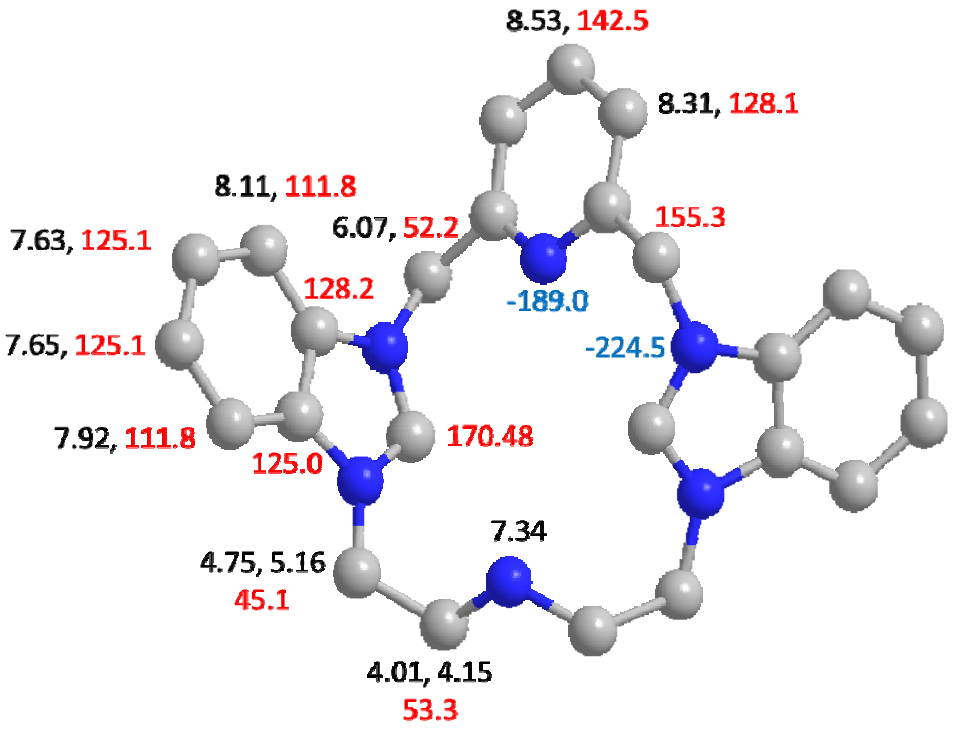

Fig. S26 Chemical shift assignments for **3** at 298 K. ^{1}H, ^{13}C and ^{15}N shifts in black, red and blue colors, respectively. The metal atom not shown.

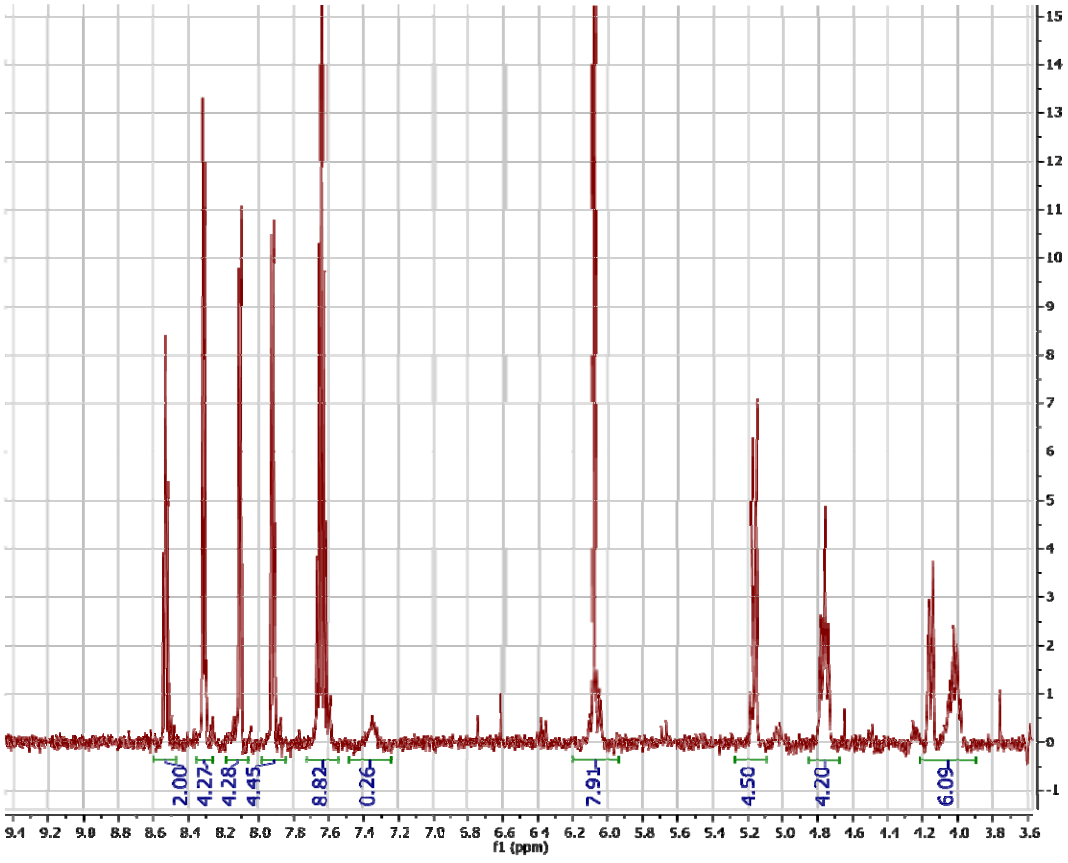

Fig. S27 ^{1}H NMR spectrum of **3** (acetone-d_6, 600 MHz, 298 K).

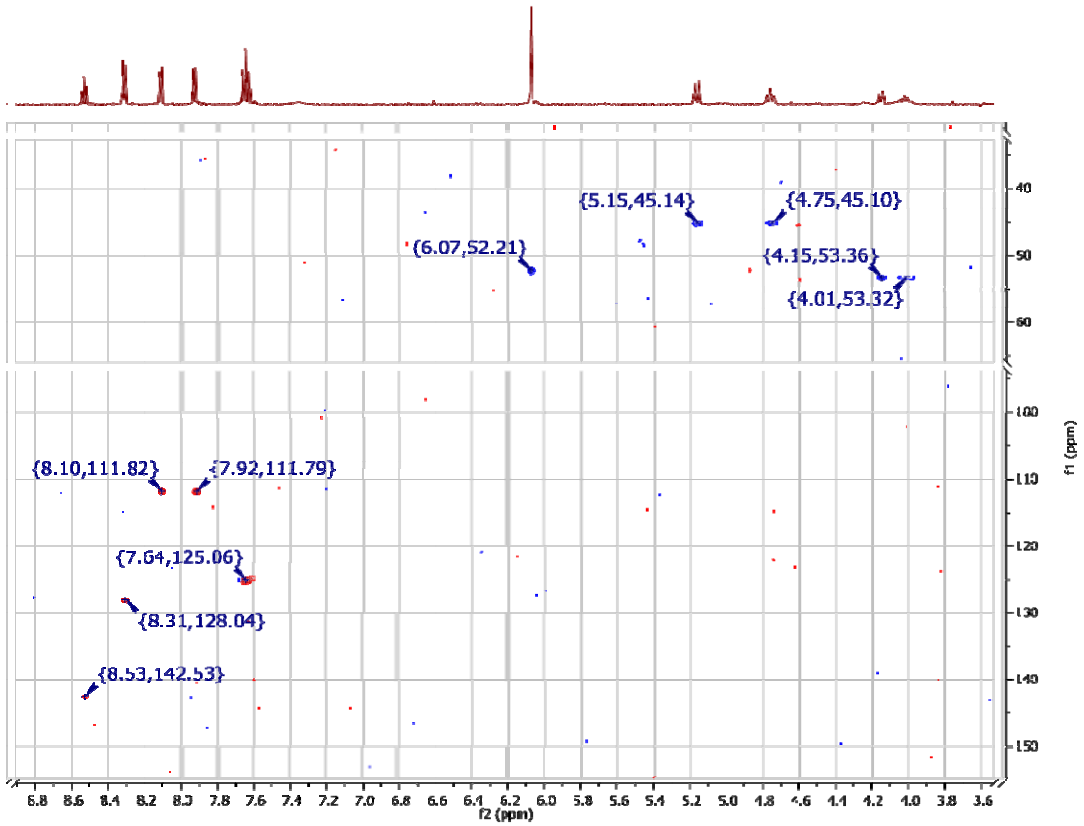

Fig. S28 ^{13}C gHSQCAD spectrum of **3** (acetone-d_6, 600 MHz, 298 K).

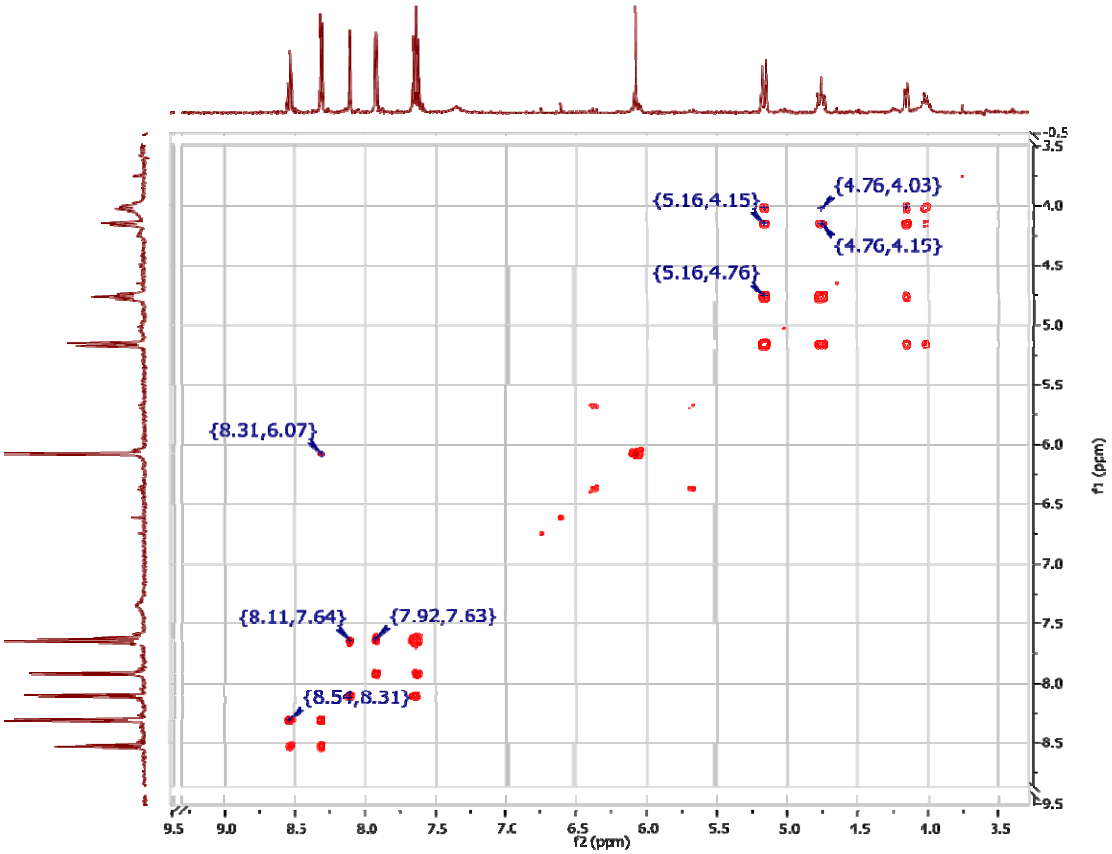

Fig. S29 gCOSY NMR spectrum of **3** (acetone-d_6, 600 MHz, 298 K).

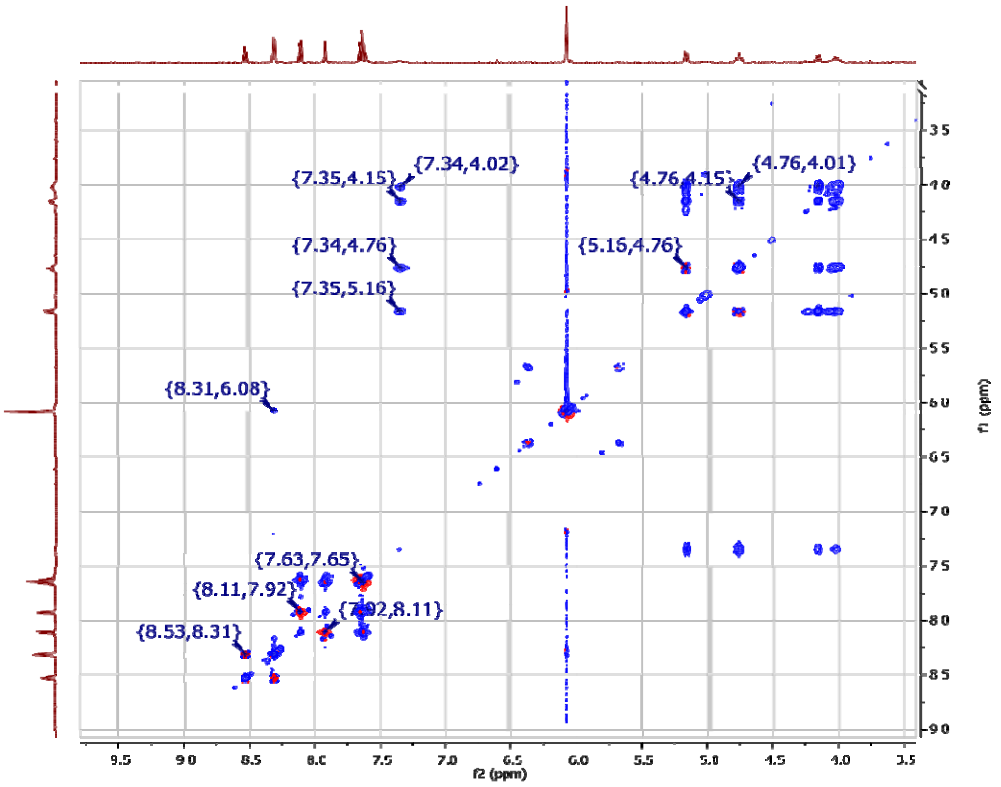

Fig. S30 TOCSY spectrum of **3** (acetone-d_6, 600 MHz, 298 K).

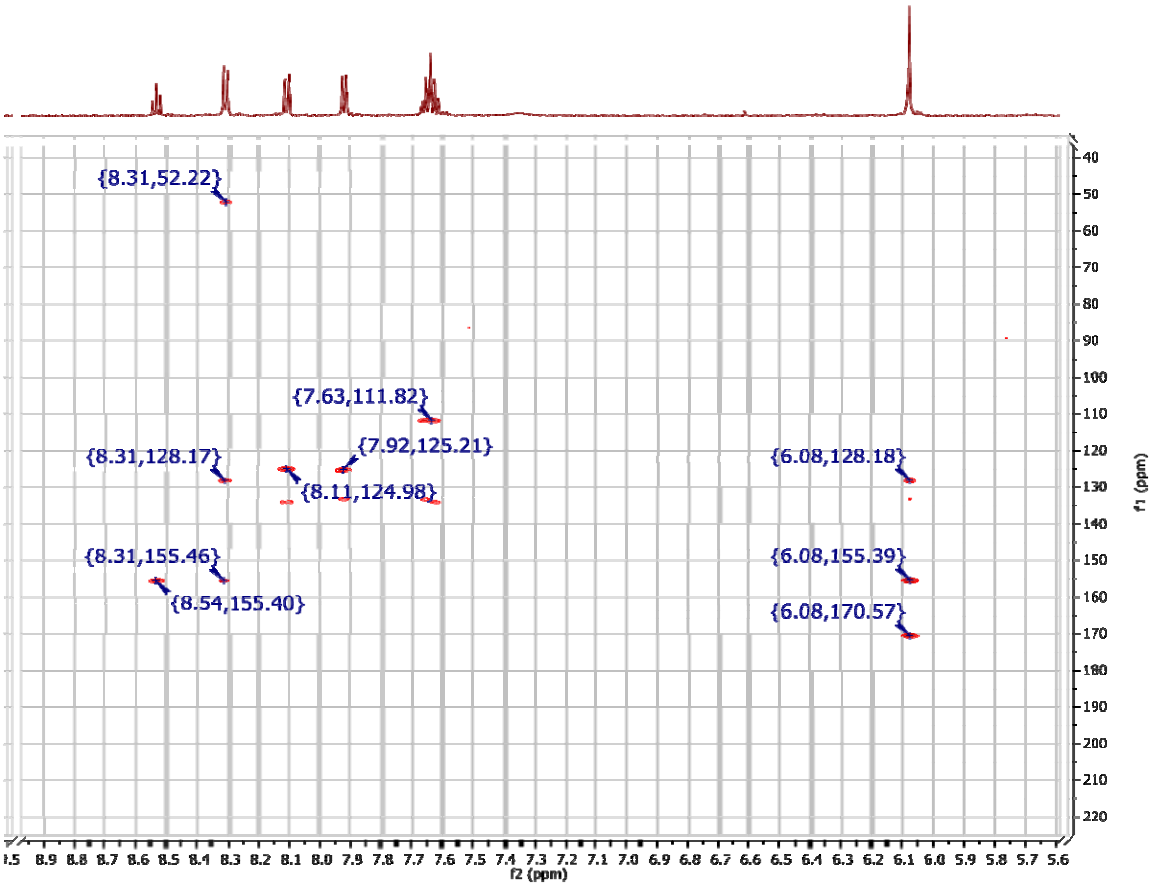

Fig. S31 ^{13}C gHMBCAD spectrum of **3** (acetone-d_6, 600 MHz, 298 K).

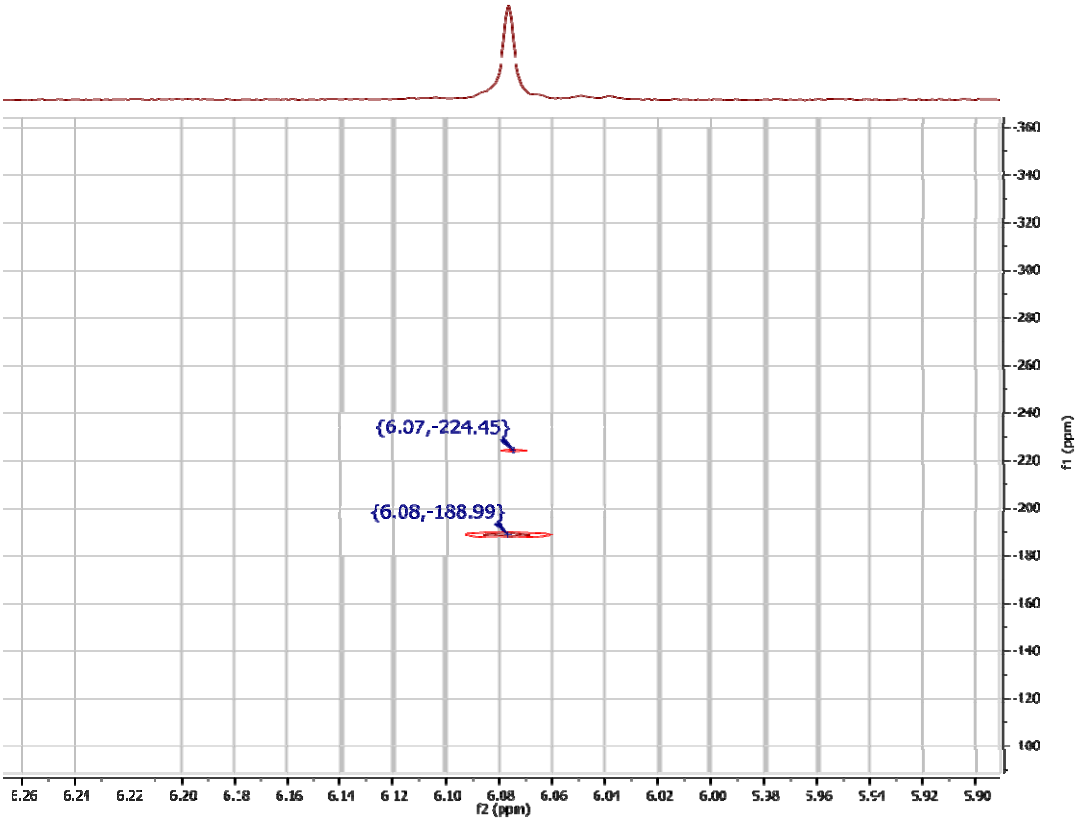

Fig. S32 ^{15}N gHMBCAD spectrum of **3** (acetone-d_6, 600 MHz, 298 K).

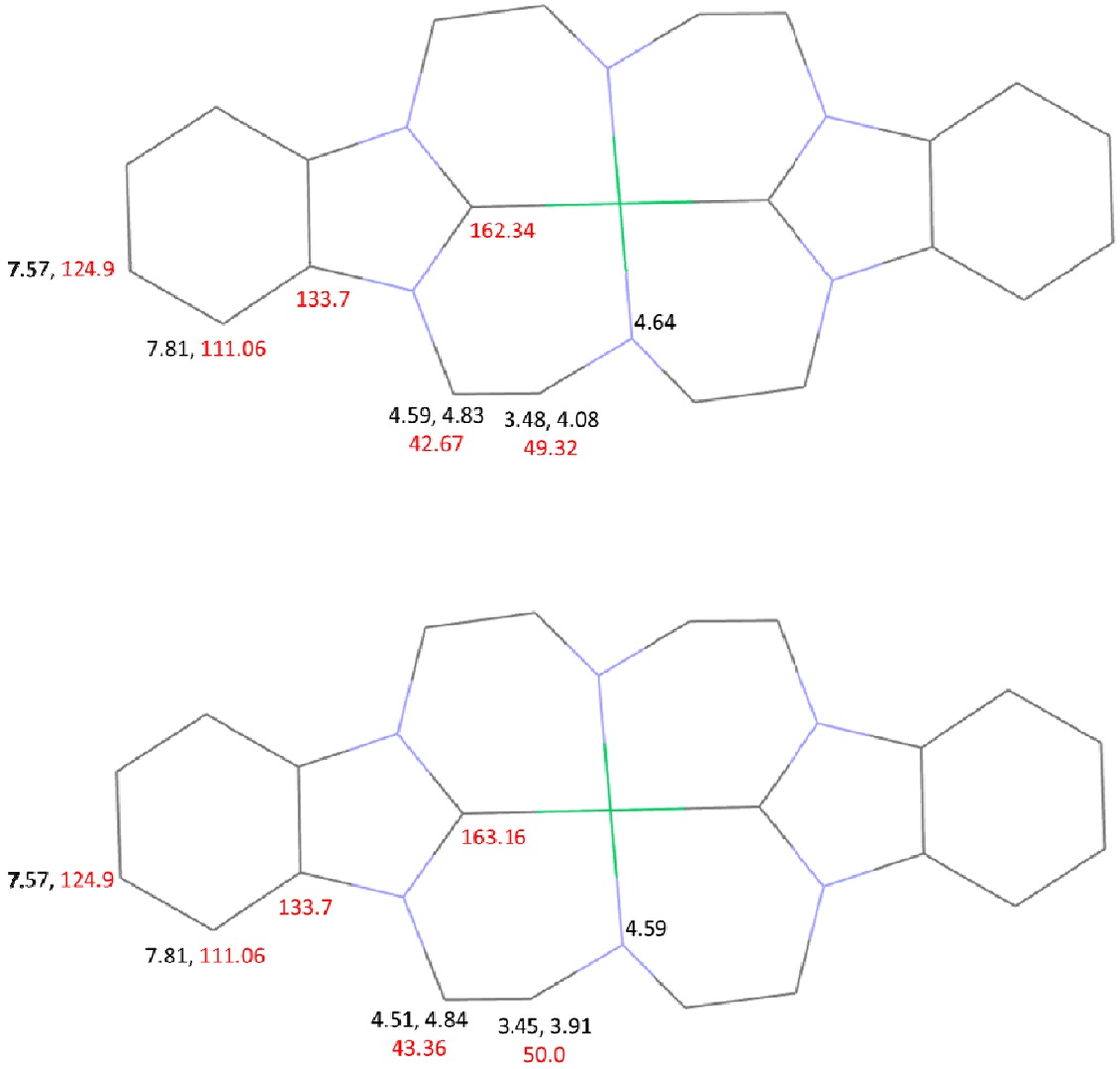

Fig. S33 Chemical shift assignments for conformer **4a** (top) and **4b** (bottom). ^{1}H and ^{13}C shifts are in black and red colors, respectively. The four ethylene linkers are magnetic equivalent.

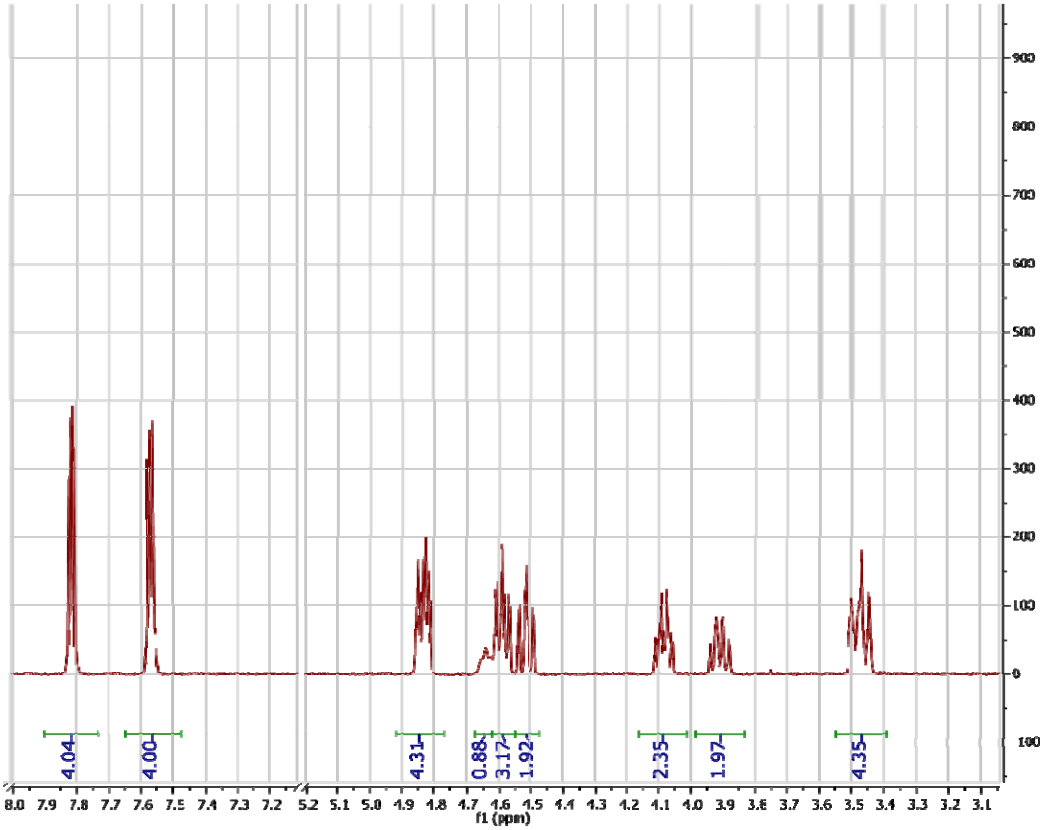

Fig. S34 ^{1}H NMR spectrum of **4** (acetone-d_6, 600 MHz, 298 K).

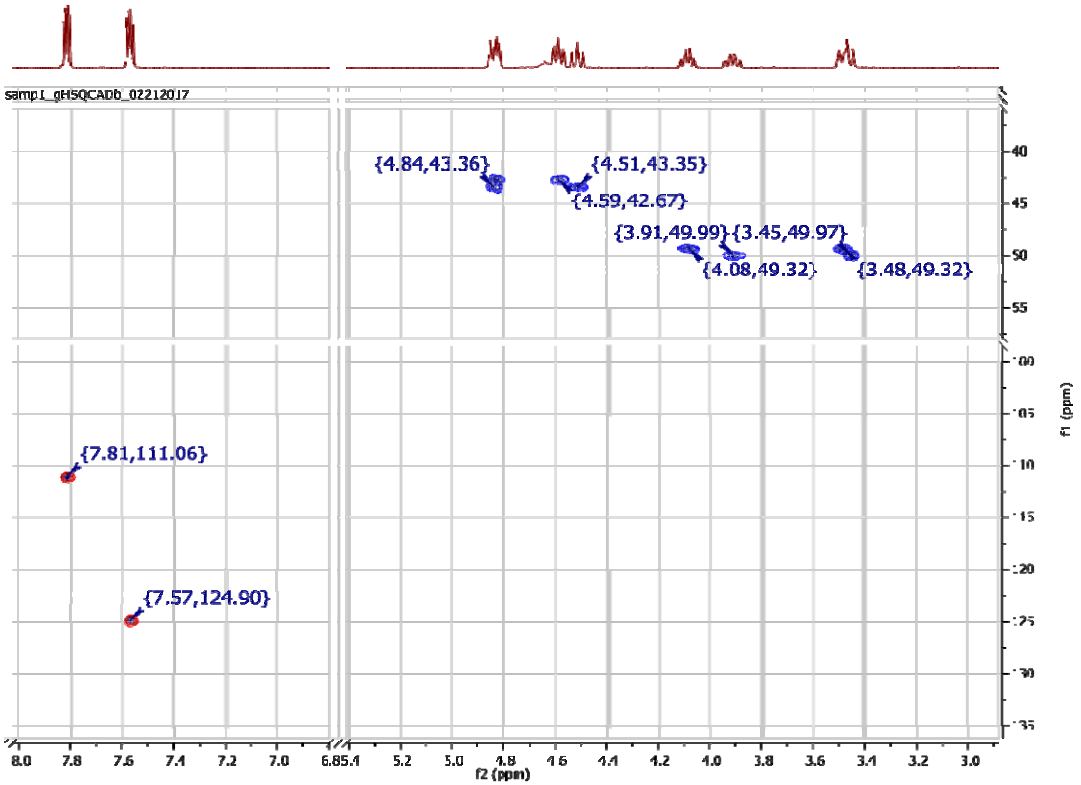

Fig. S35 ^{13}C gHSQCAD spectrum of **4** (acetone-d_6, 600 MHz, 298 K).

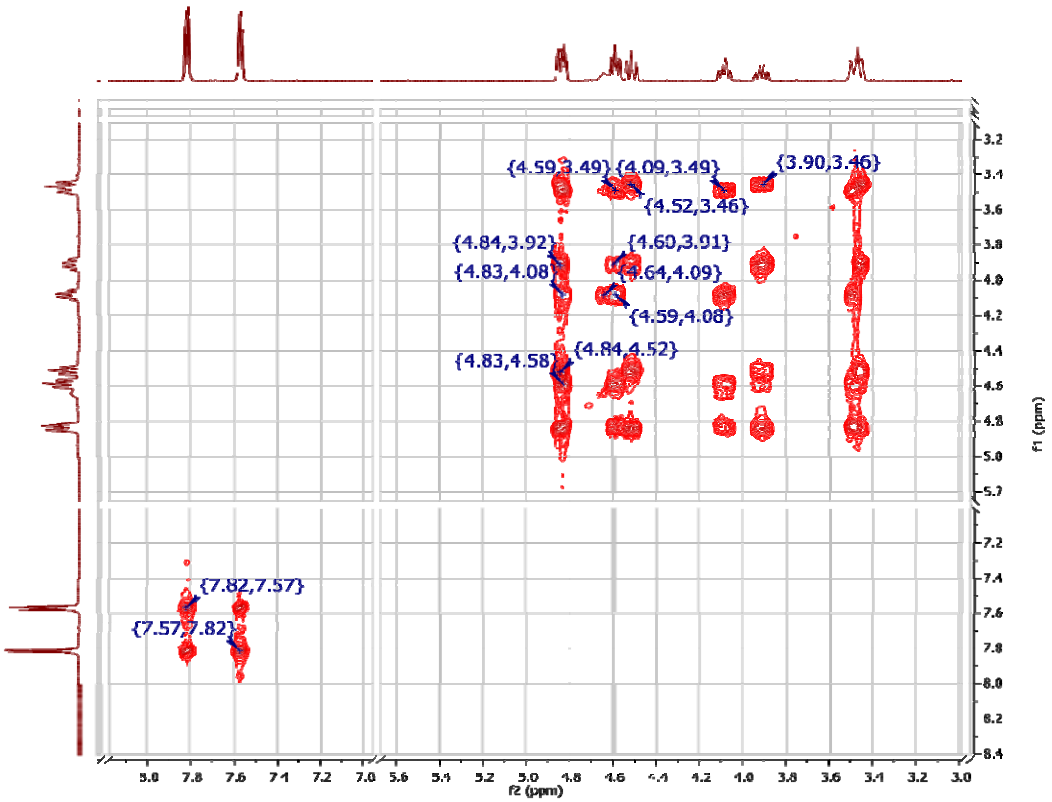

Fig. S36 gCOSY spectrum of **4** (acetone-d_6, 600 MHz, 298 K).

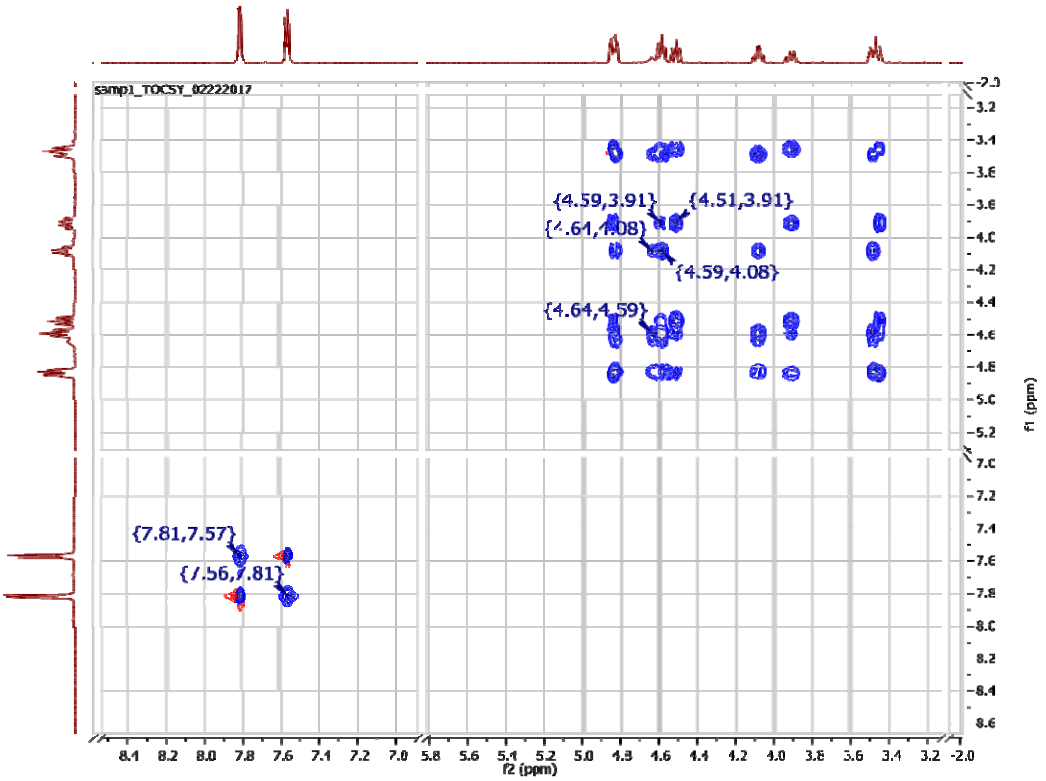

Fig. S37 TOCSY spectrum of **4** (acetone-d_6, 600 MHz, 298 K).

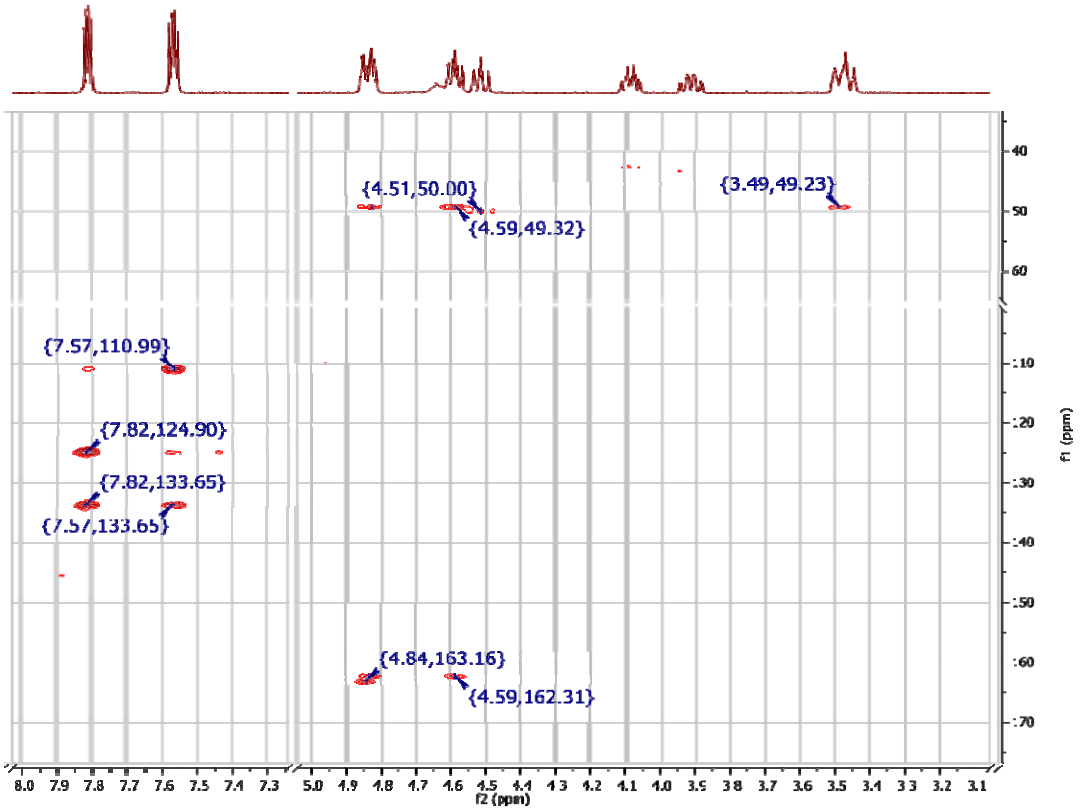

Fig. S38 ^{13}C gHMBCAD spectrum of **4** (acetone-d_6, 600 MHz, 298 K).

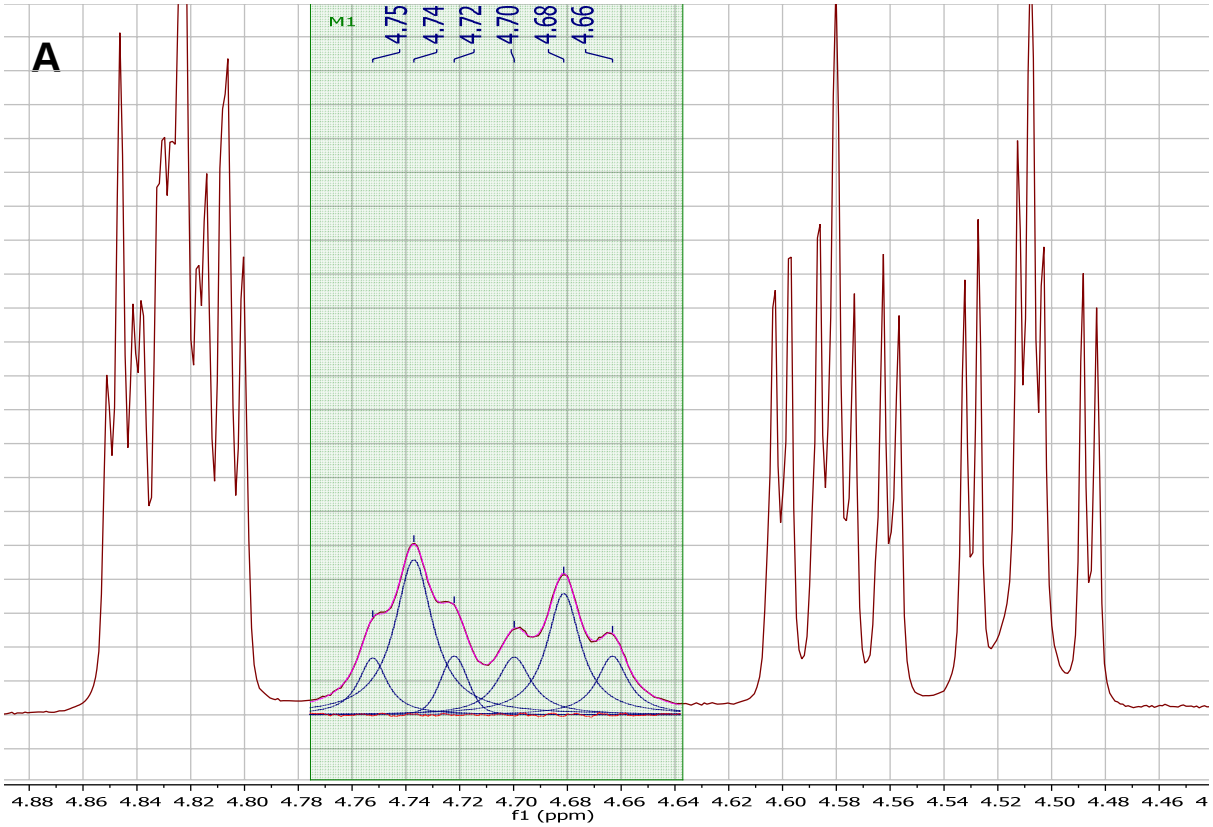

Fig. S39A $^{3}J_{\text{H-H}}$ couplings between N-*H* and two *H*-C atoms (–C*H*-N*H*-C*H*-) are calculated from the fittings shown here: (a) For N-*H* at 4.68 ppm, $^{3}J_{\text{H-H}}$ = 11 Hz; (b) For N-*H* at 4.74 ppm, $^{3}J_{\text{H-H}}$ = 9 Hz.

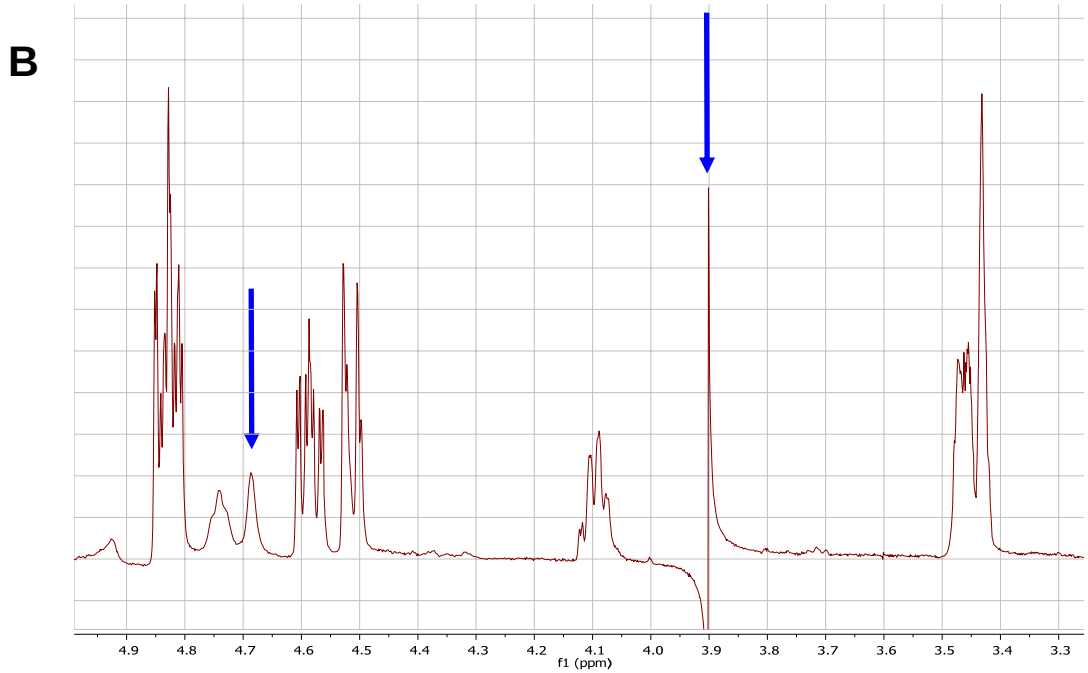

Fig. S39B For conformer **4a**, saturating the C-H_{A} peak at 3.90 ppm leads to the decoupling and, thus, sharpening of the H-N peak for this conformer.

C

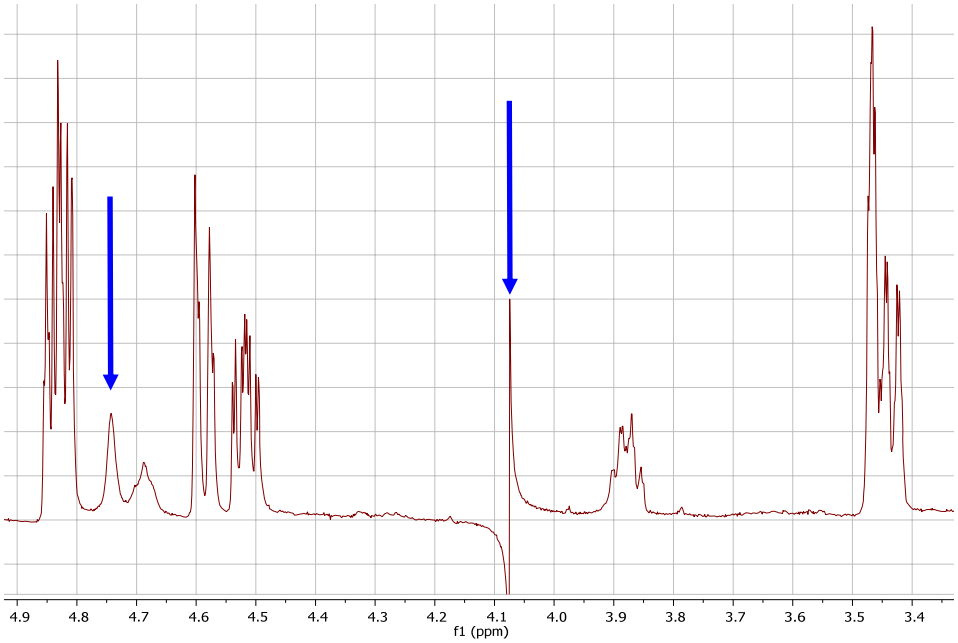

Fig. S39C For conformer **4b**, saturating the C-H_A peak at 4.07 ppm leads to the decoupling and, thus, sharpening of the H-N peak for this conformer.

D

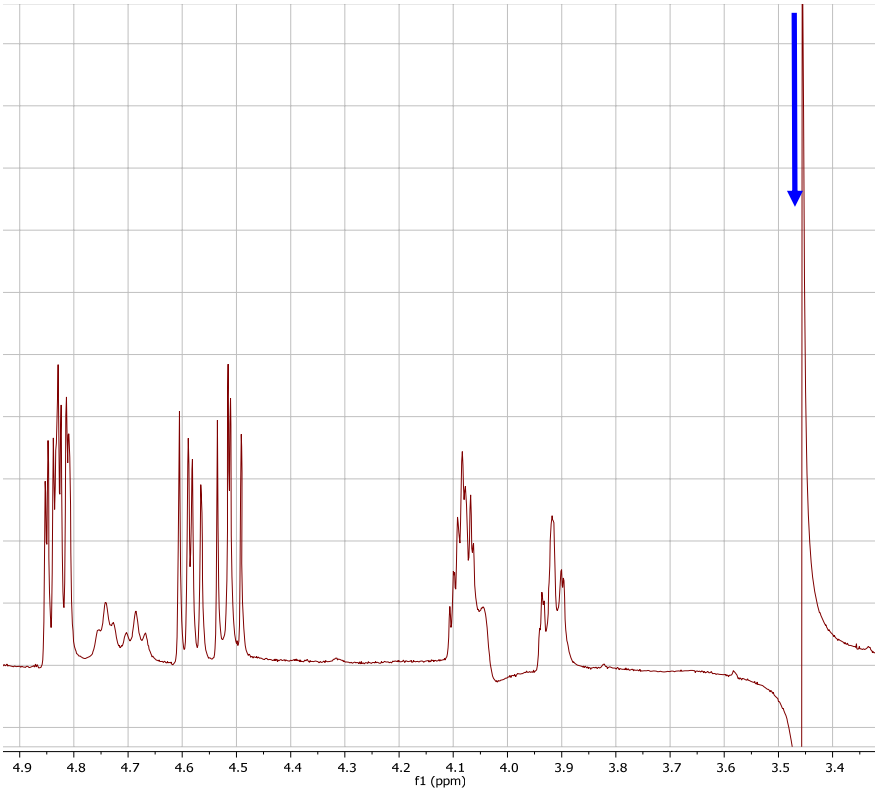

Fig. S39D For both conformers **4a** and **4b**, decoupling the C-H_B peak at 3.45-3.48 ppm does not affect the N-H peaks, indicating these atoms do not couple to H-N.

Fig. S39A-D ^{1}H decoupling NMR studies showing that N-*H* is coupled to the two H_A-C atoms (–CH_AH$_B$-N*H*-CH_AH$_B$-), but is not coupled to the other two H_B atoms.

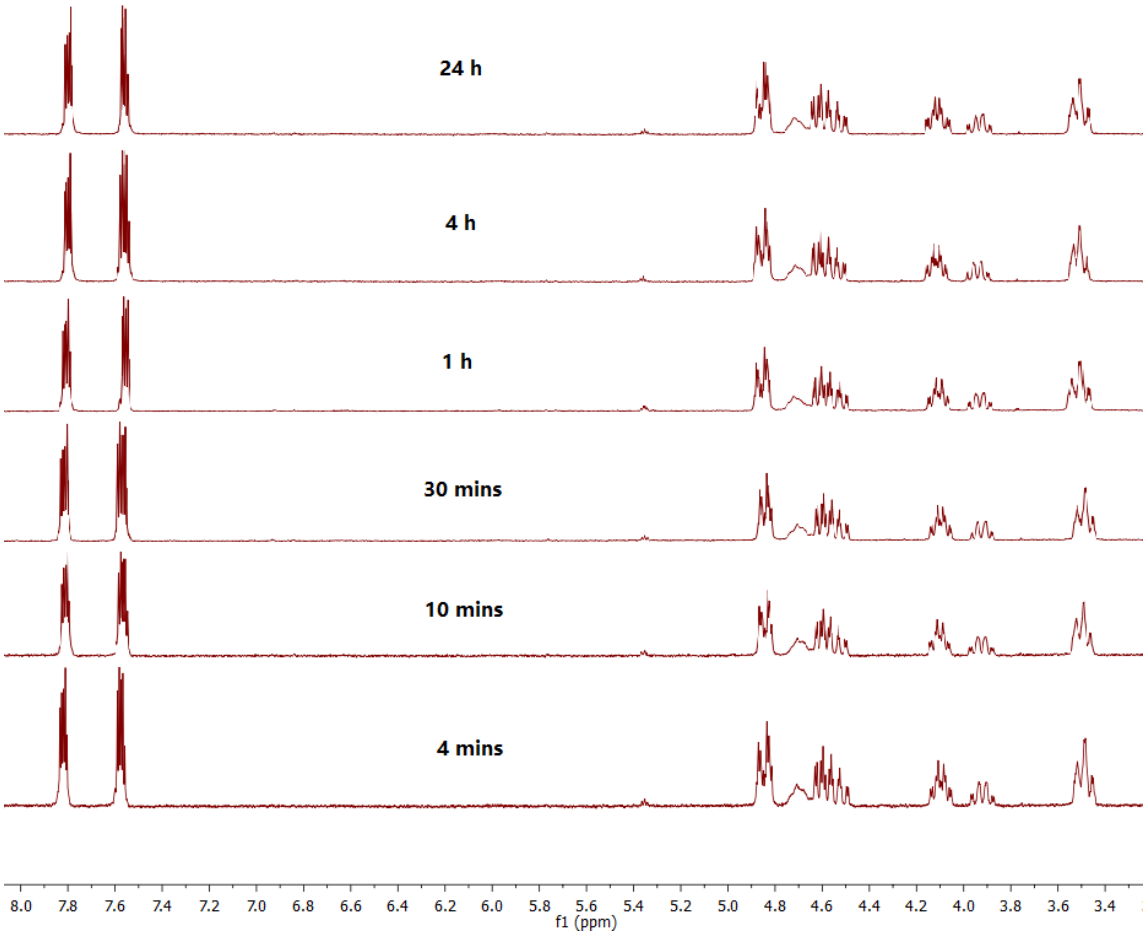

Fig. S40 Time-dependent ^{1}H NMR spectra of **4** (acetone-d_6, 400 MHz, 298 K)

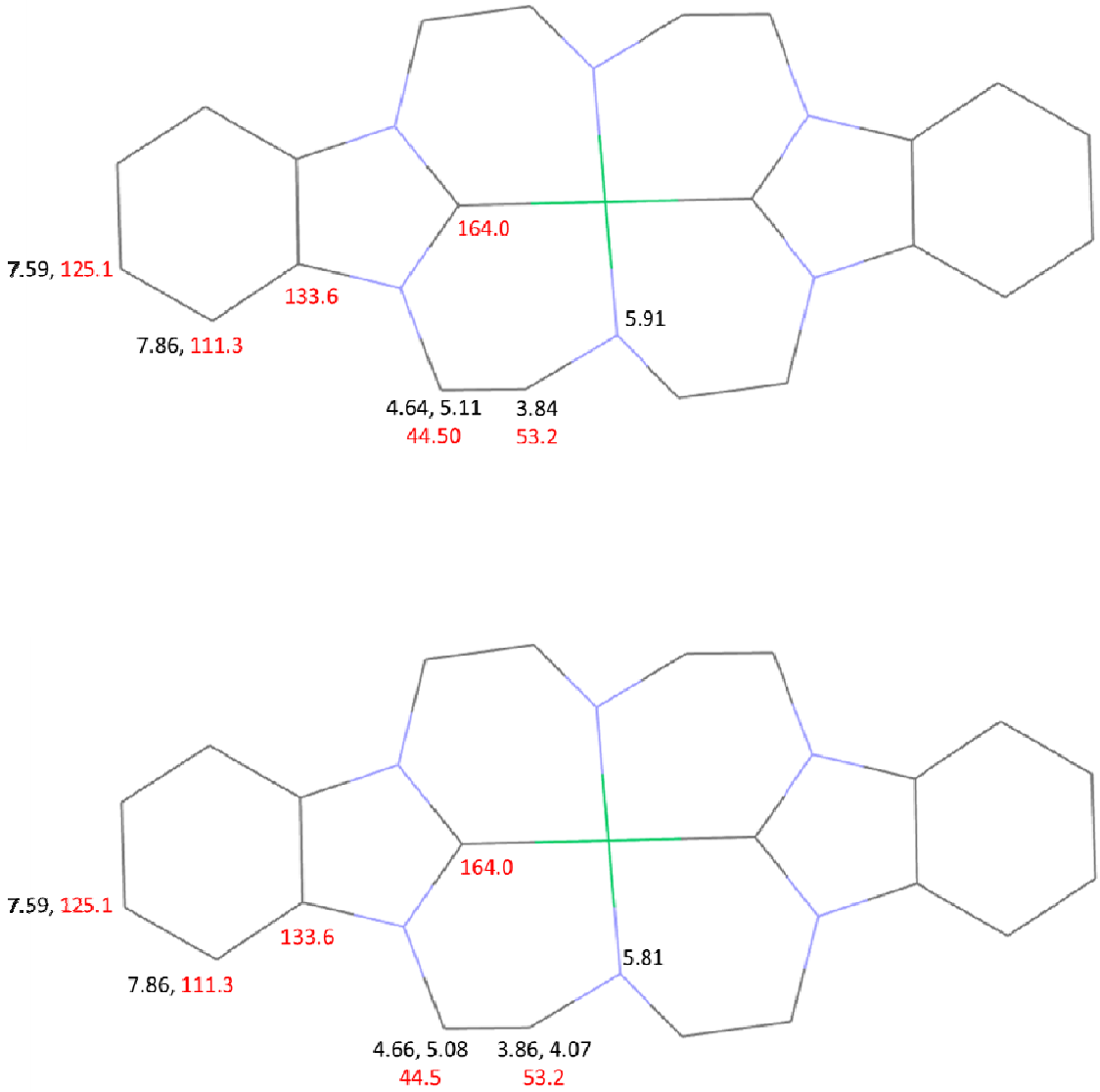

Fig. S41 Chemical shift assignments for conformer **5a** (top) and **5b** (bottom). ^{1}H and ^{13}C shifts are in black and red colors, respectively.

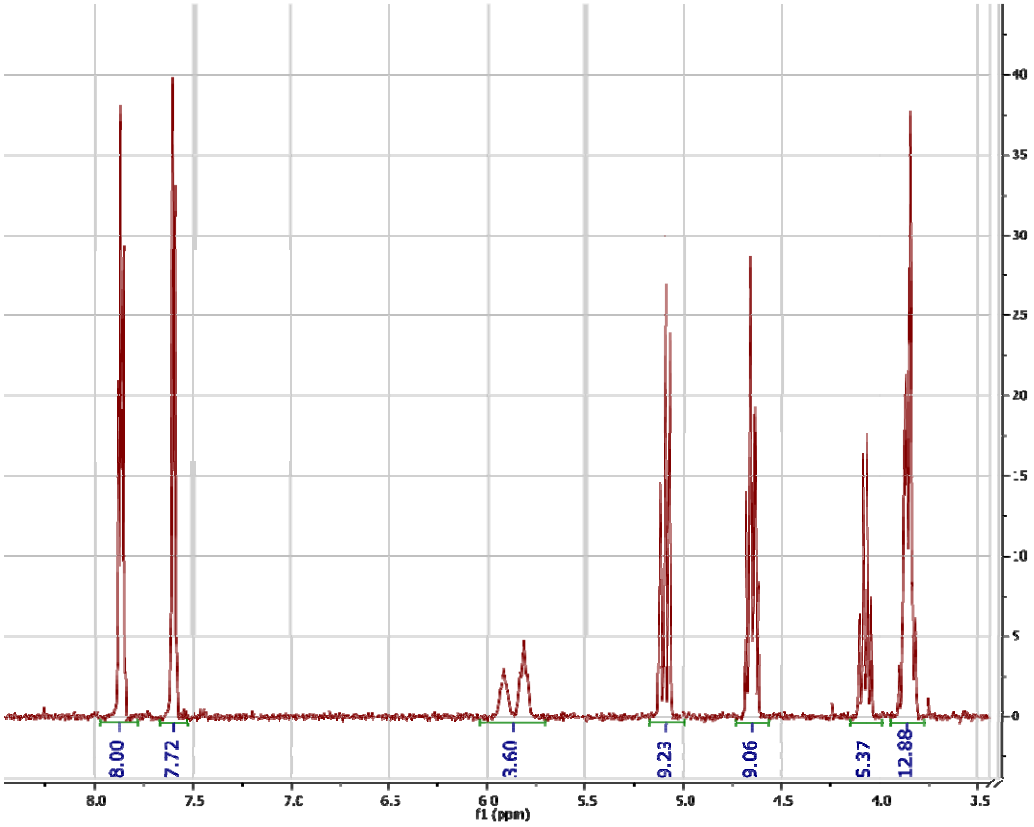

Fig. S42 ^{1}H NMR spectrum of **5** (acetone-d_6, 600 MHz, 298 K).

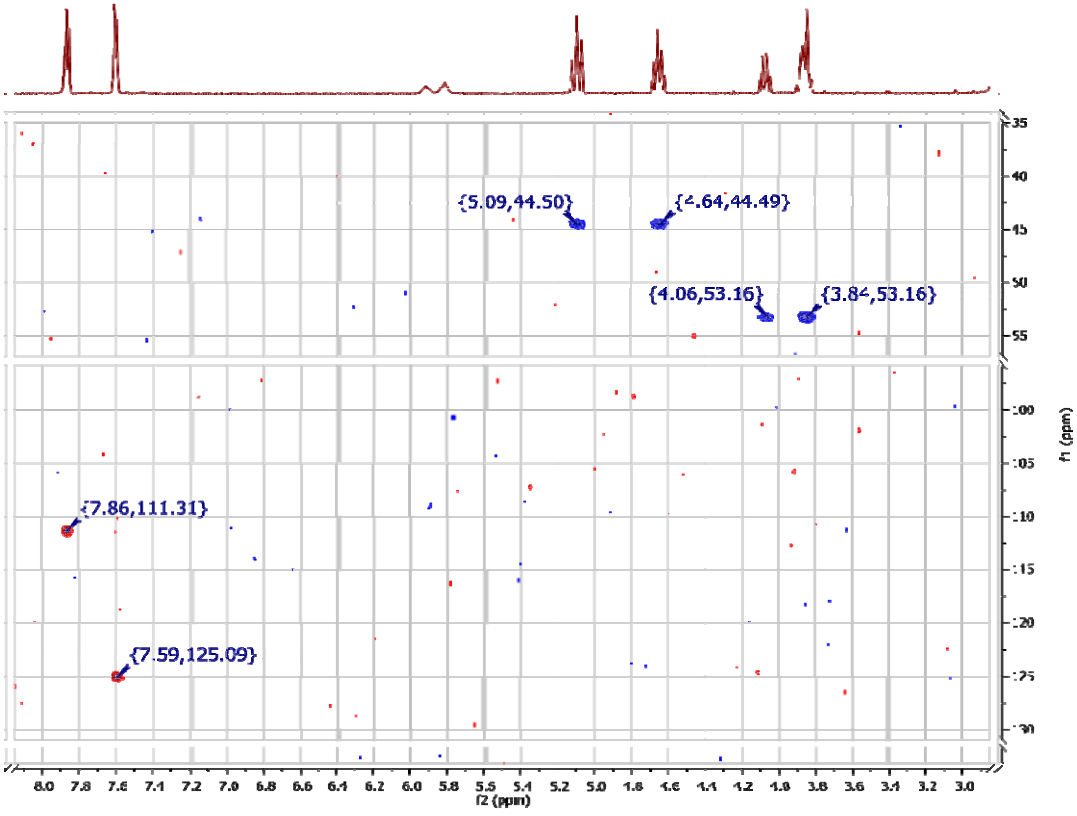

Fig. S43 ^{13}C gHSQCAD spectrum of **5** (acetone-d_6, 600 MHz, 298 K).

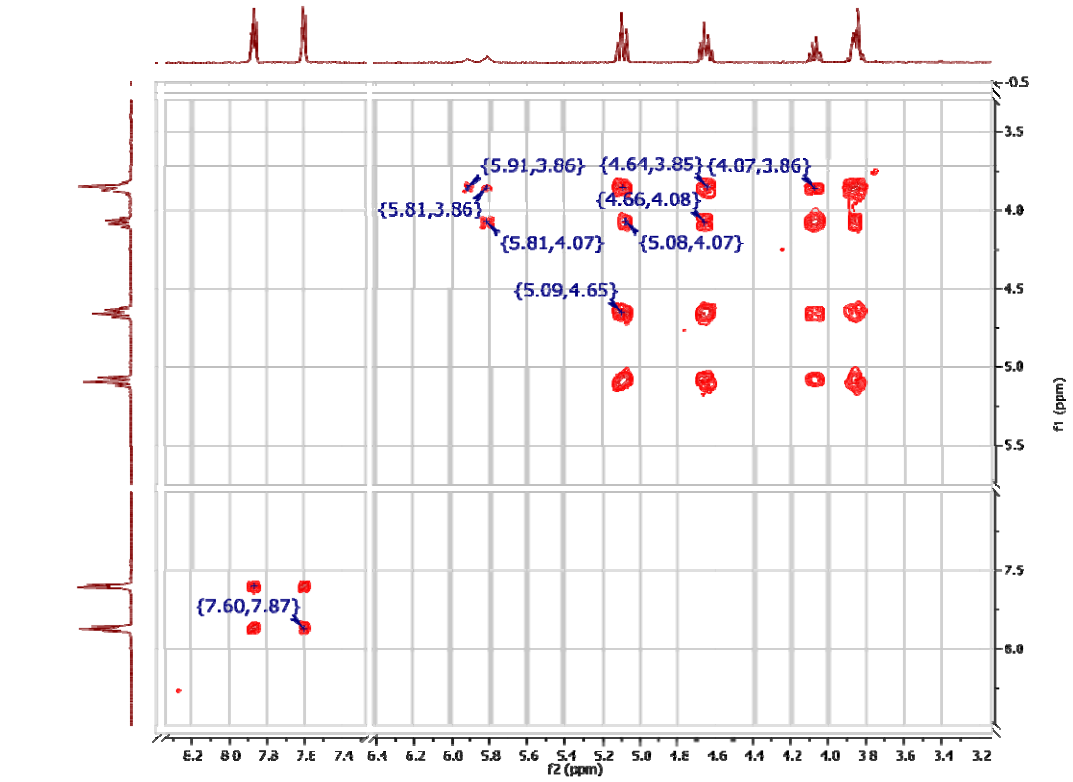

Fig. S44 gCOSY spectrum of **5** (acetone-d_6, 600 MHz, 298 K).

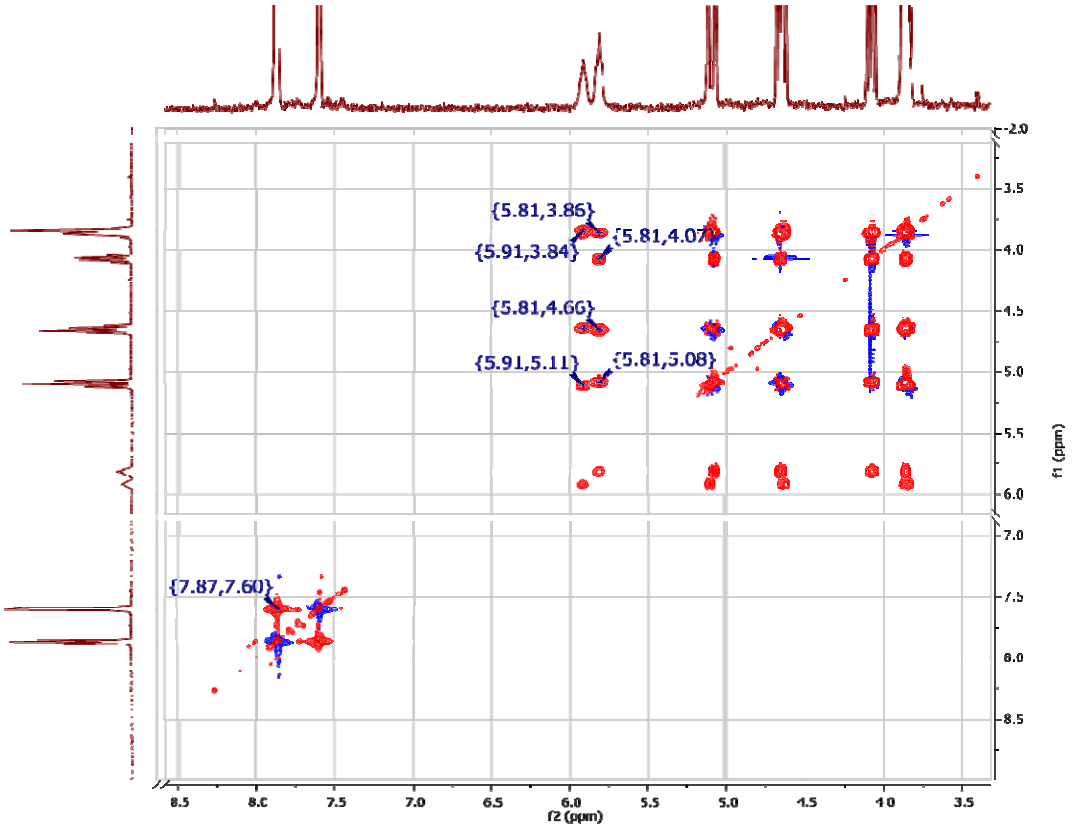

Fig. S45 TOCSY spectrum of **5** (acetone-d_6, 600 MHz, 298 K).

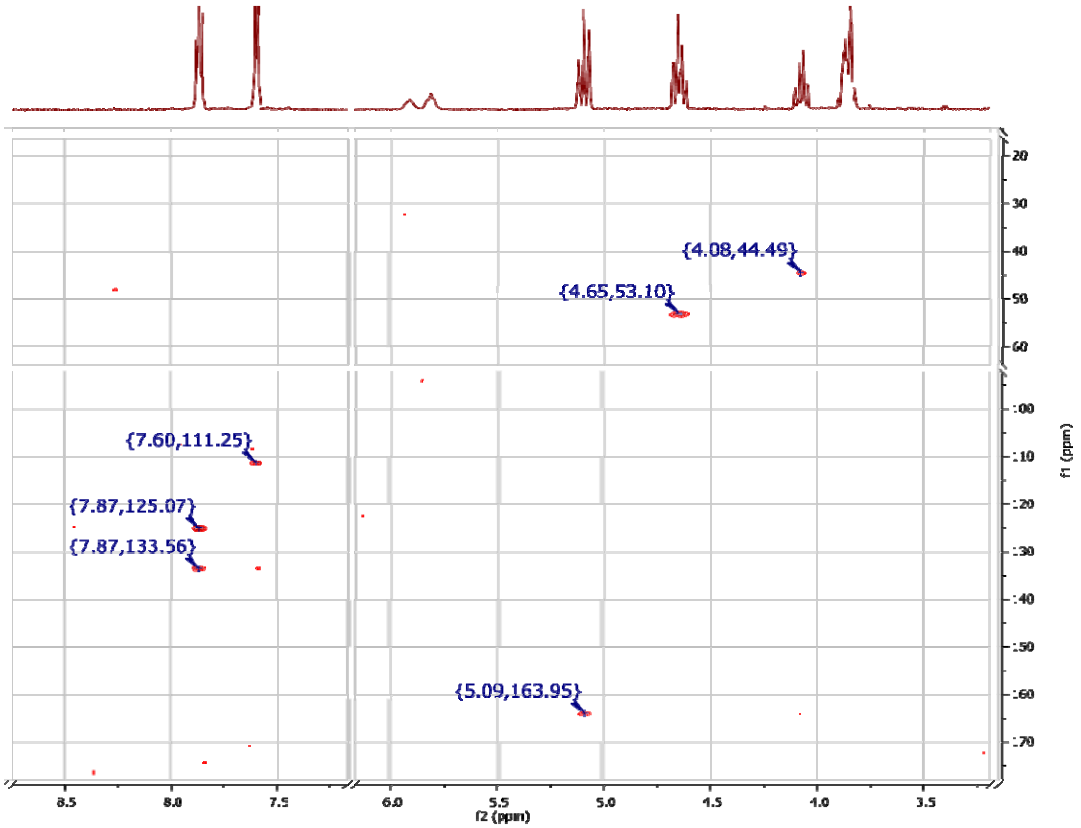

Fig. S46 ^{13}C gHMBCAD spectrum of **5** (acetone-d_6, 600 MHz, 298 K).

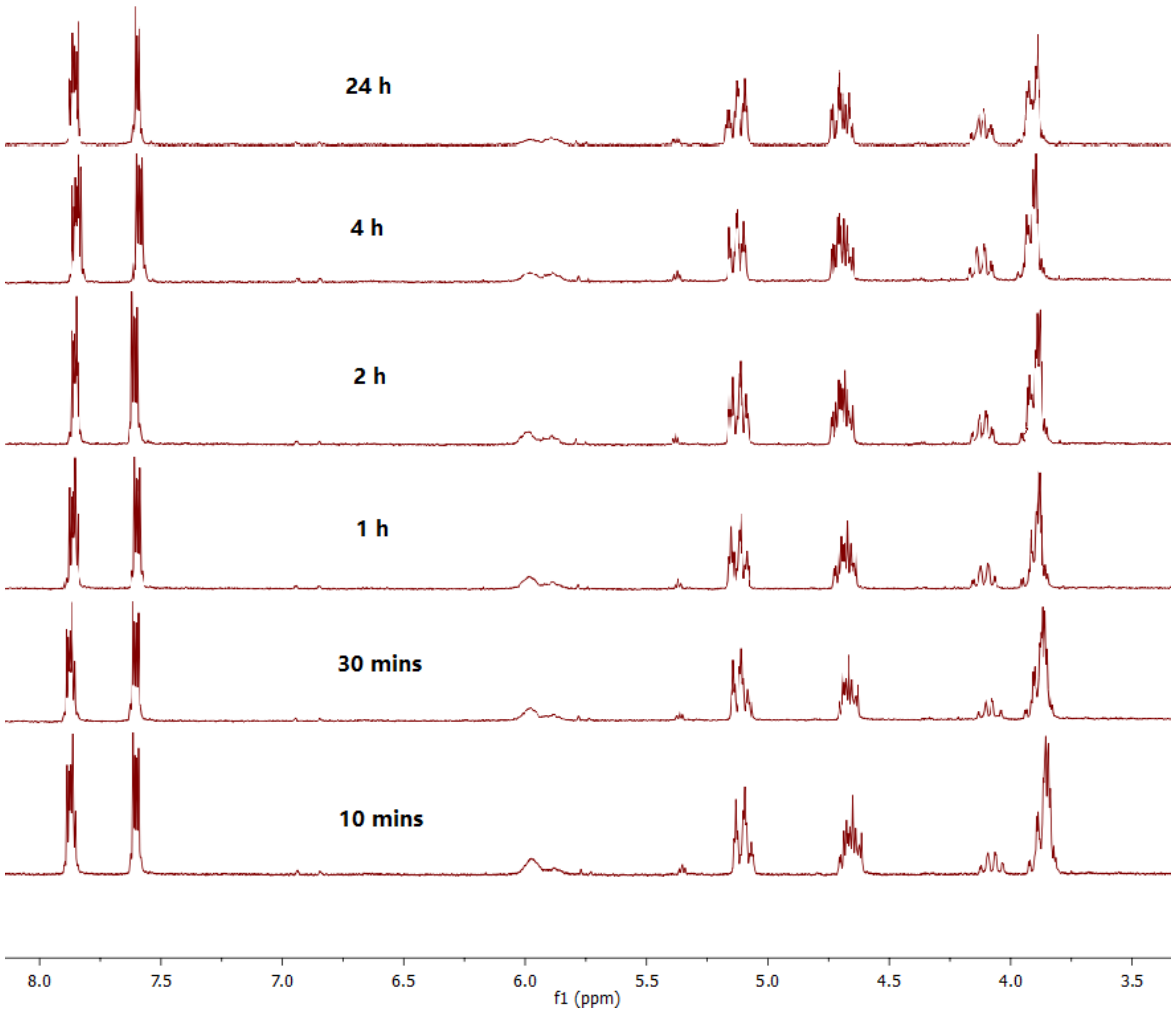

Fig. S47 Time-dependent ^{1}H NMR spectra of **5** (acetone-d_6, 400 MHz, 298 K)

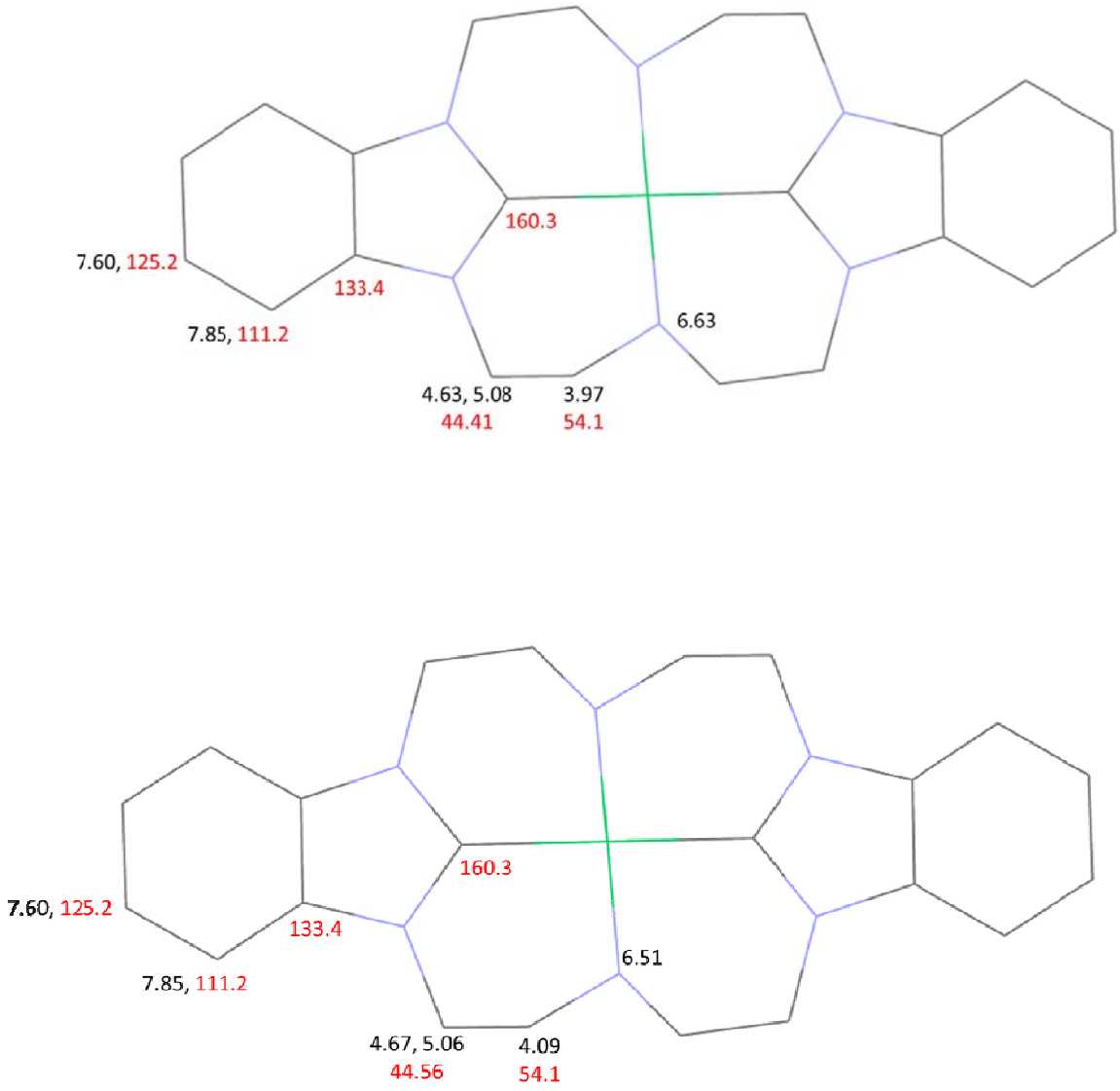

Fig. S48 Chemical shift assignments for conformer **6a** (top) and **6b** (bottom). ^{1}H and ^{13}C shifts are in black and red colors, respectively.

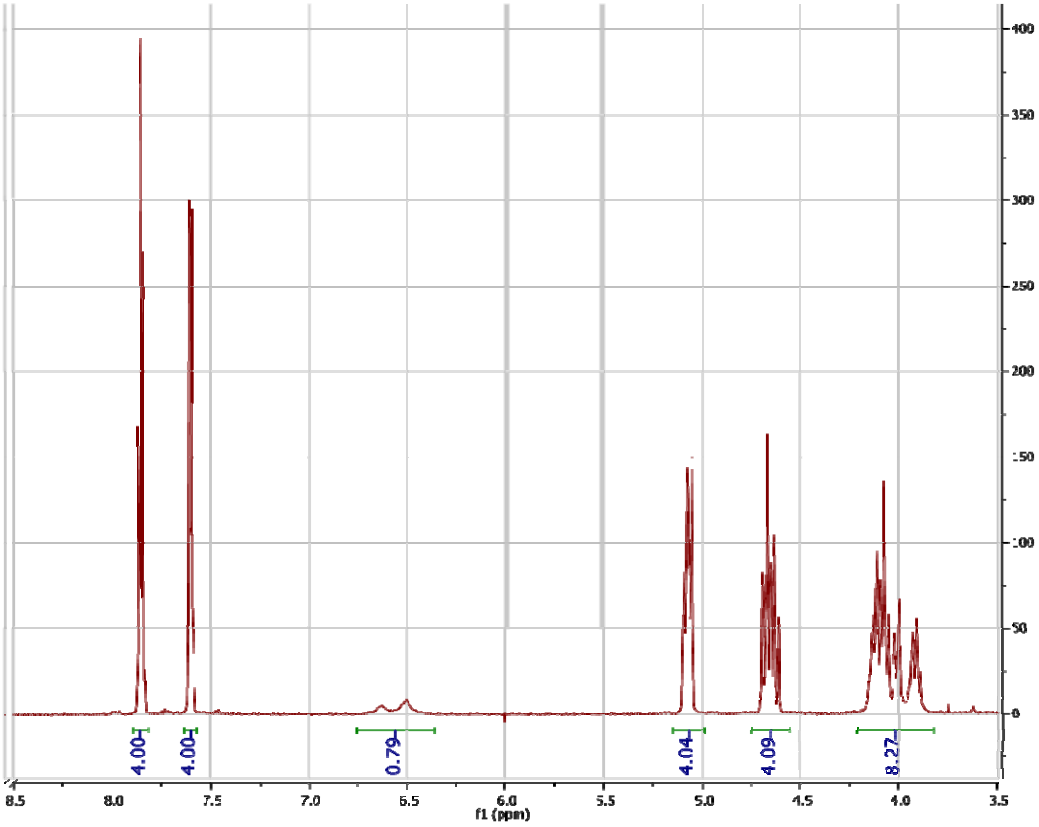

Fig. S49 ^{1}H NMR spectrum of **6** (acetone-d_6, 600 MHz, 298 K).

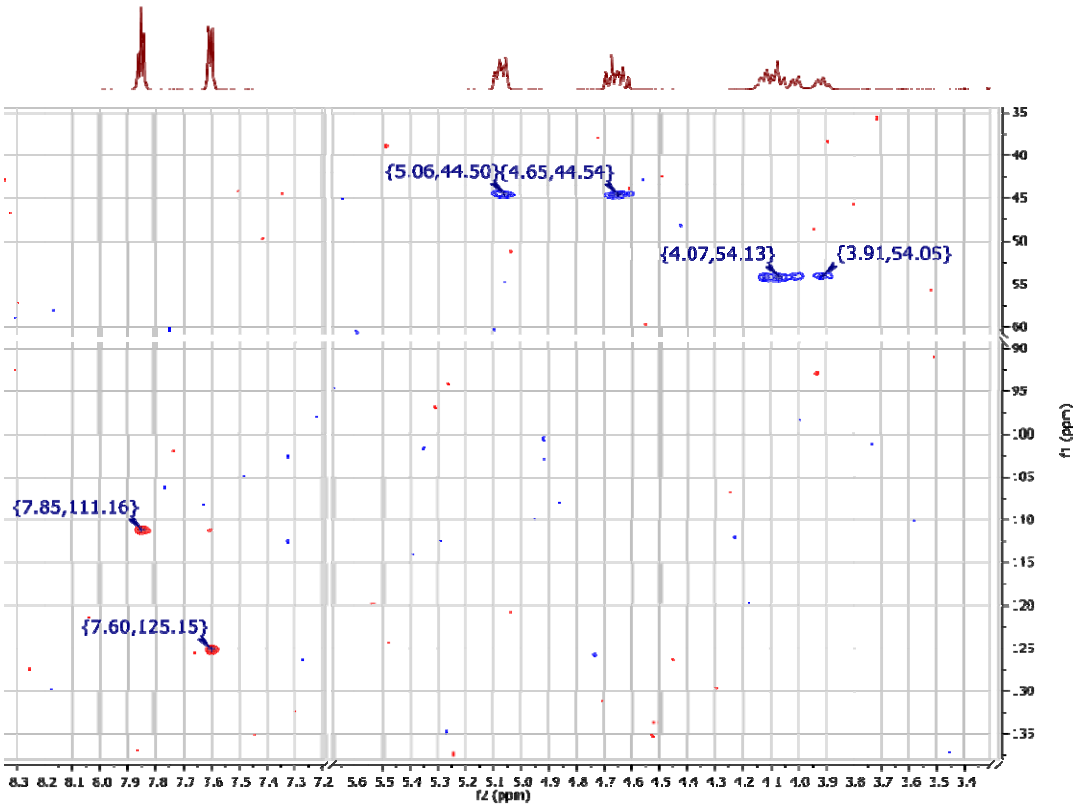

Fig. S50 ^{13}C gHSQCAD spectrum of **6** (acetone-d_6, 600 MHz, 298 K).

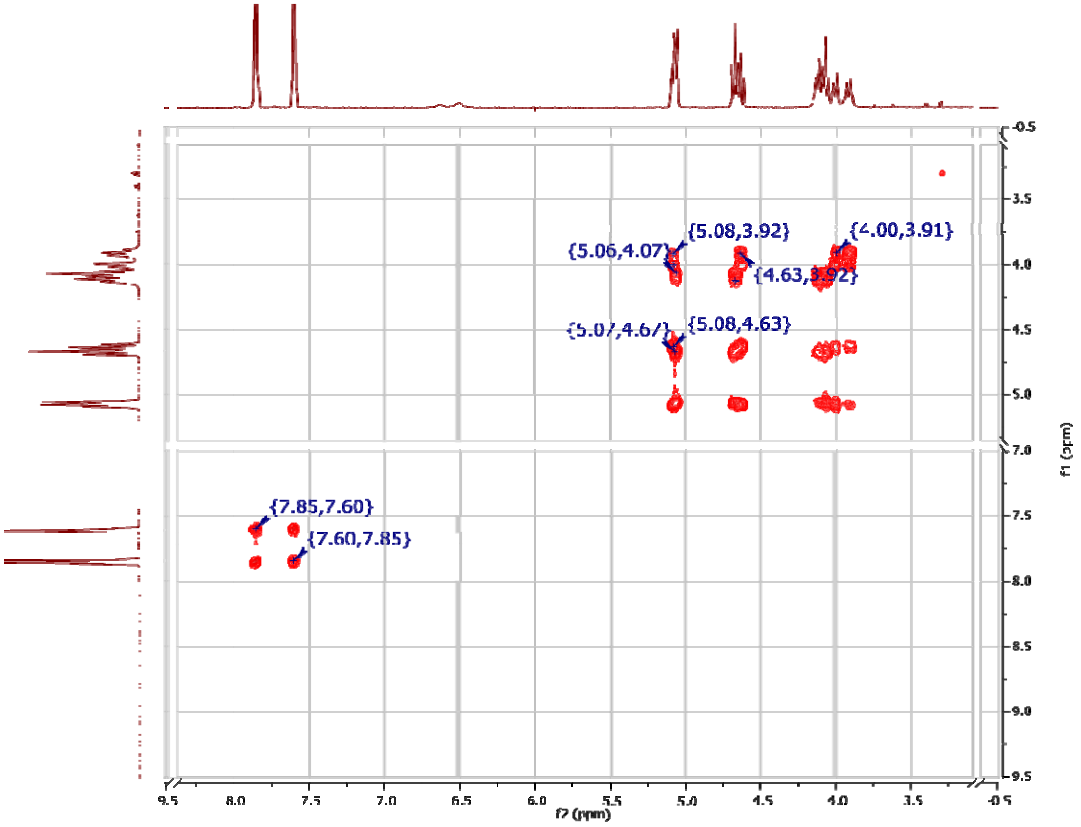

Fig. S51 gCOSY spectrum of **6** (acetone-d_6, 600 MHz, 298 K).

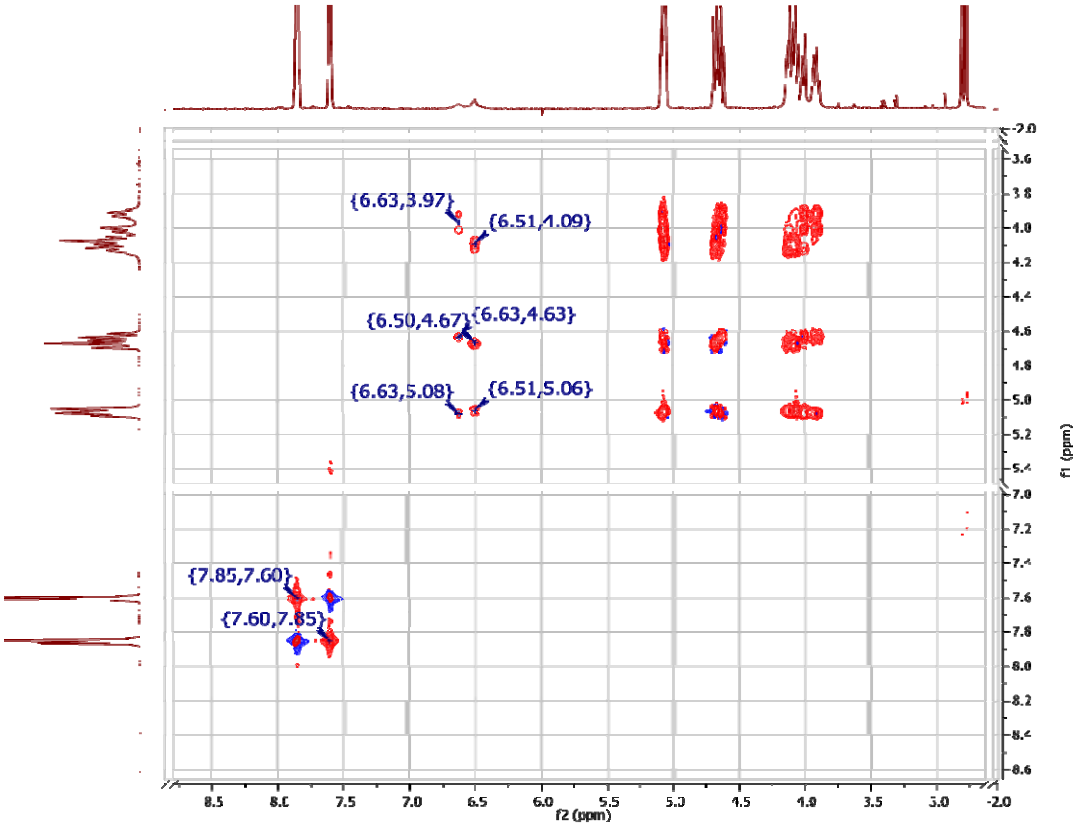

Fig. S52 TOCSY spectrum of **6** (acetone-d_6, 600 MHz, 298 K).

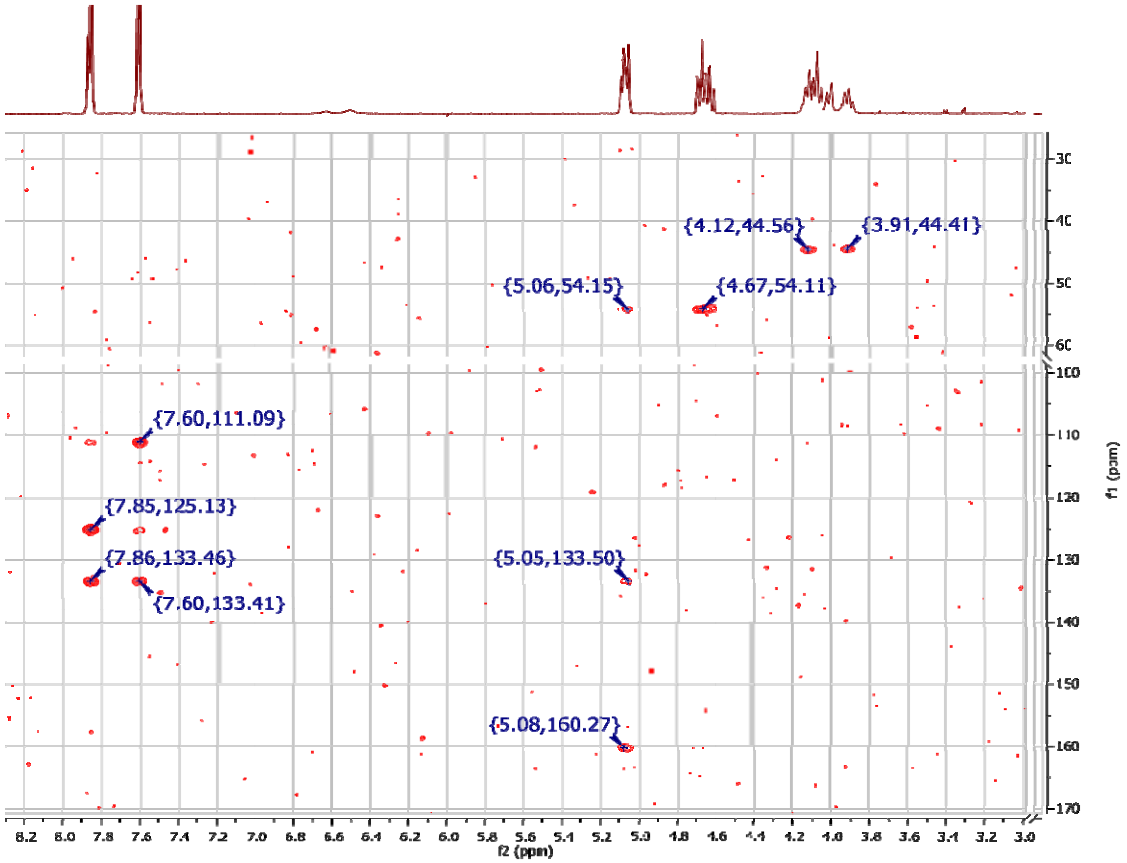

Fig. S53 ^{13}C gHMBCAD spectrum of **6** (acetone-d_6, 600 MHz, 298 K).

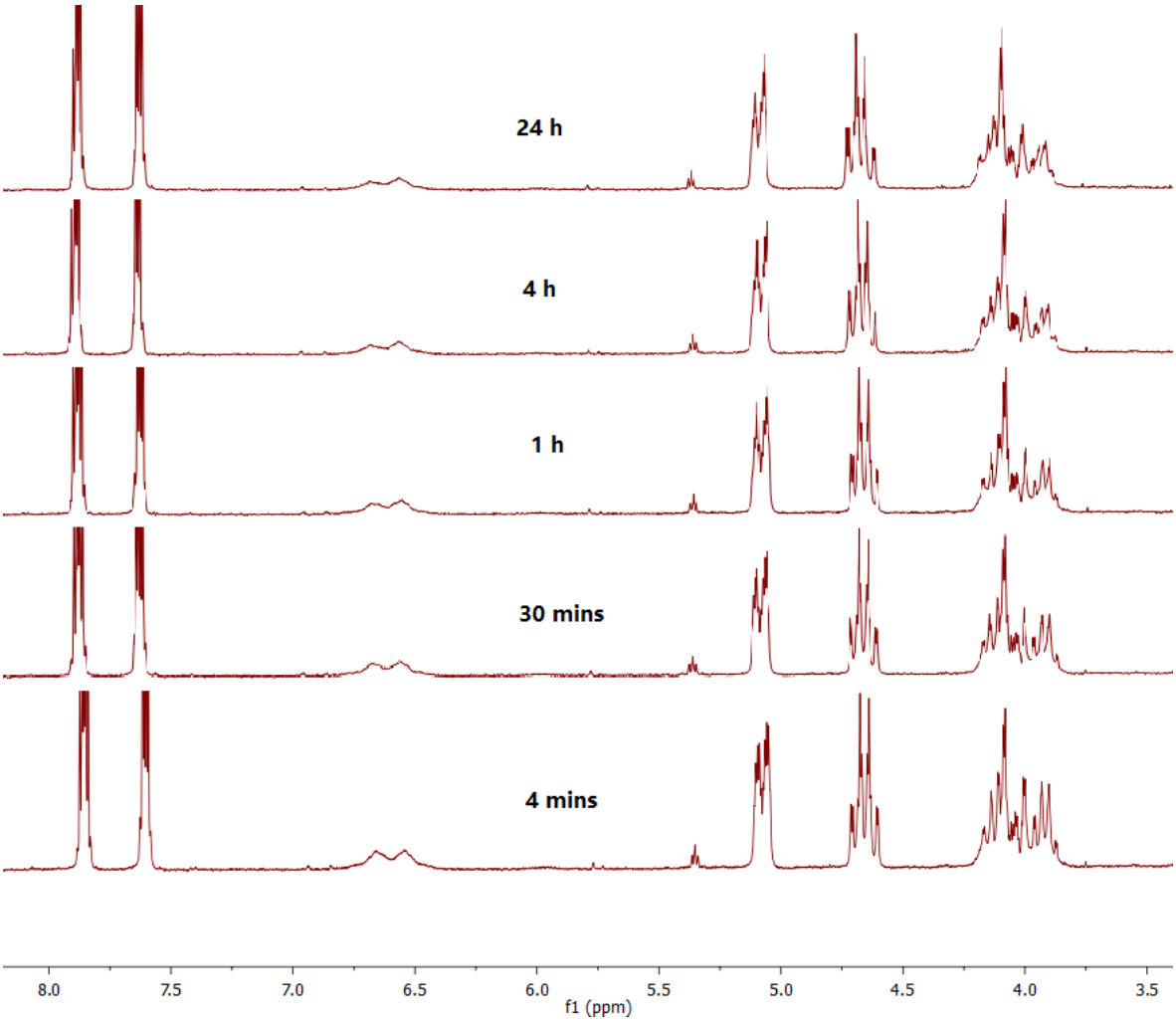

Fig. S54 Time-dependent ^{1}H NMR spectra of **6** (acetone-d_6, 400 MHz, 298 K).

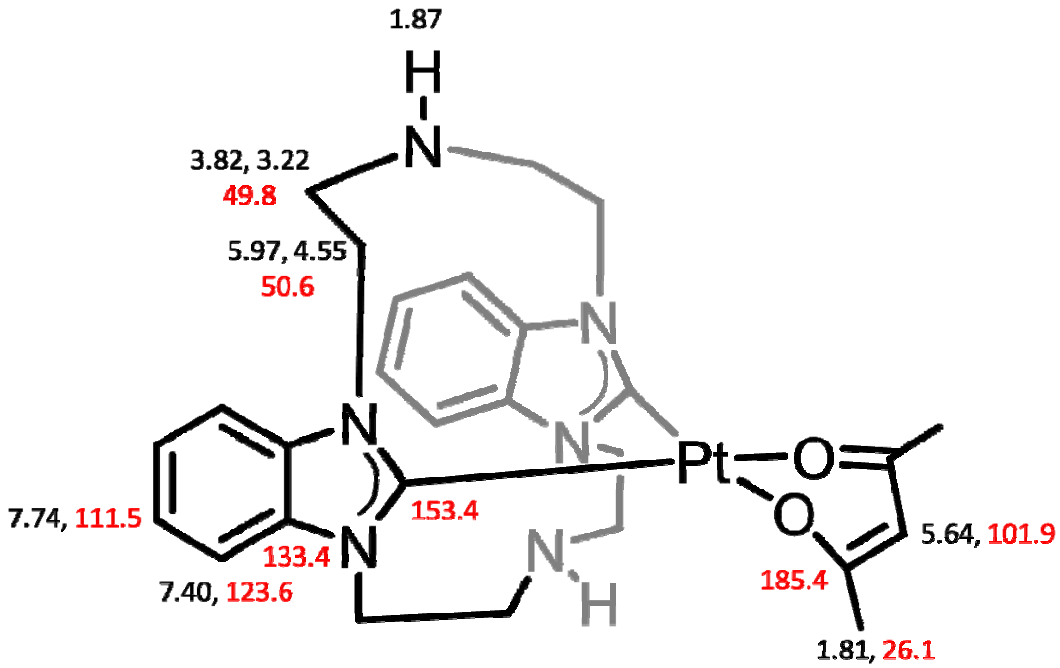

Fig. S55 Chemical shift assignments for **7**. ^{1}H and ^{13}C shifts are in black and red colors, respectively.

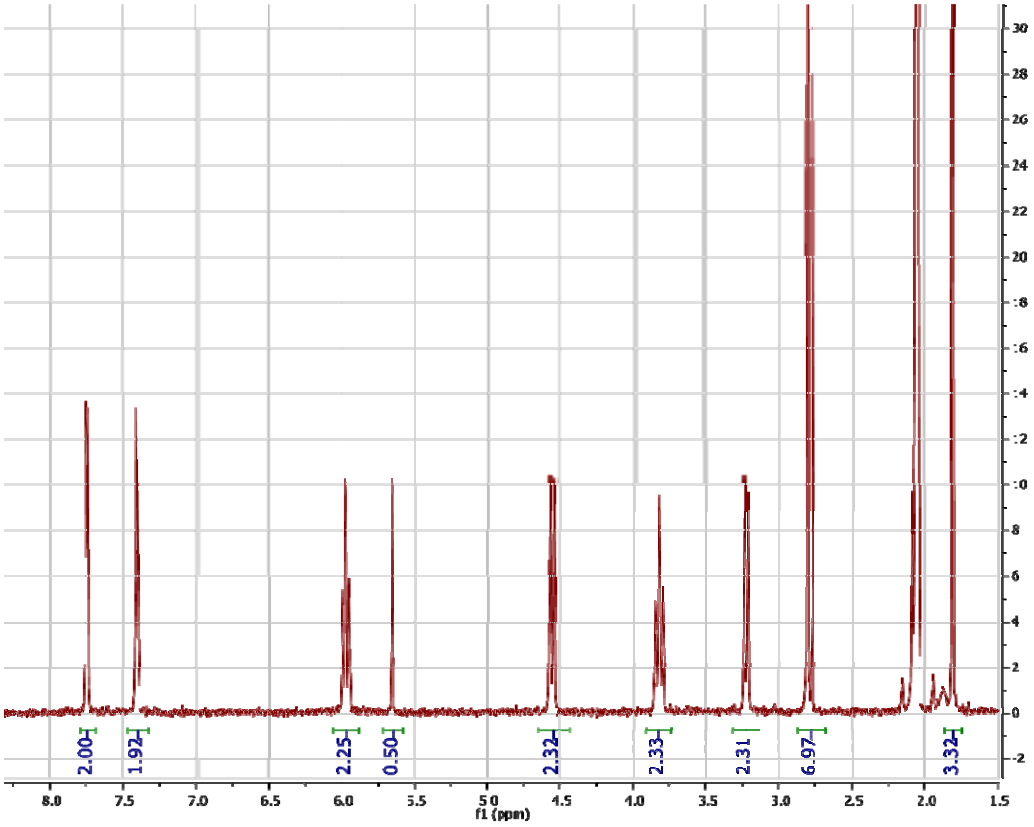

Fig. S56 ^{1}H NMR spectrum of **7** (acetone-d_6, 600 MHz, 298 K).

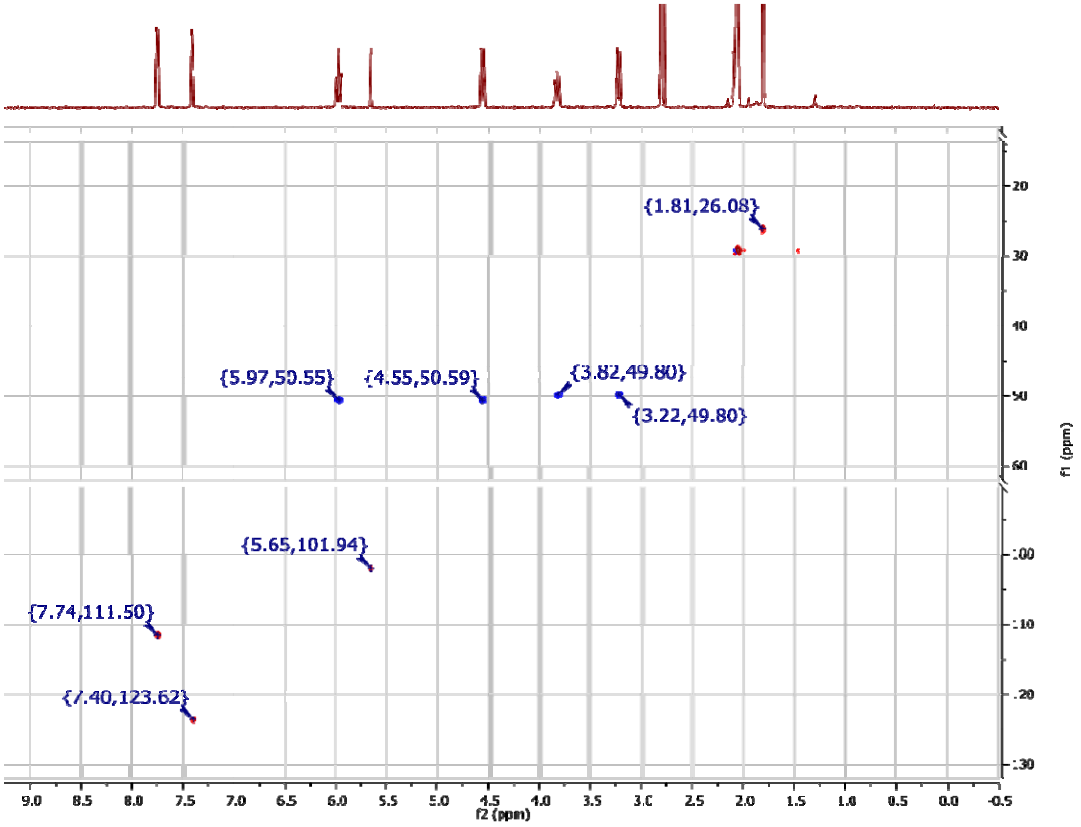

Fig. S57 ^{13}C gHSQCAD spectrum of **7** (acetone-d_6, 600 MHz, 298 K).

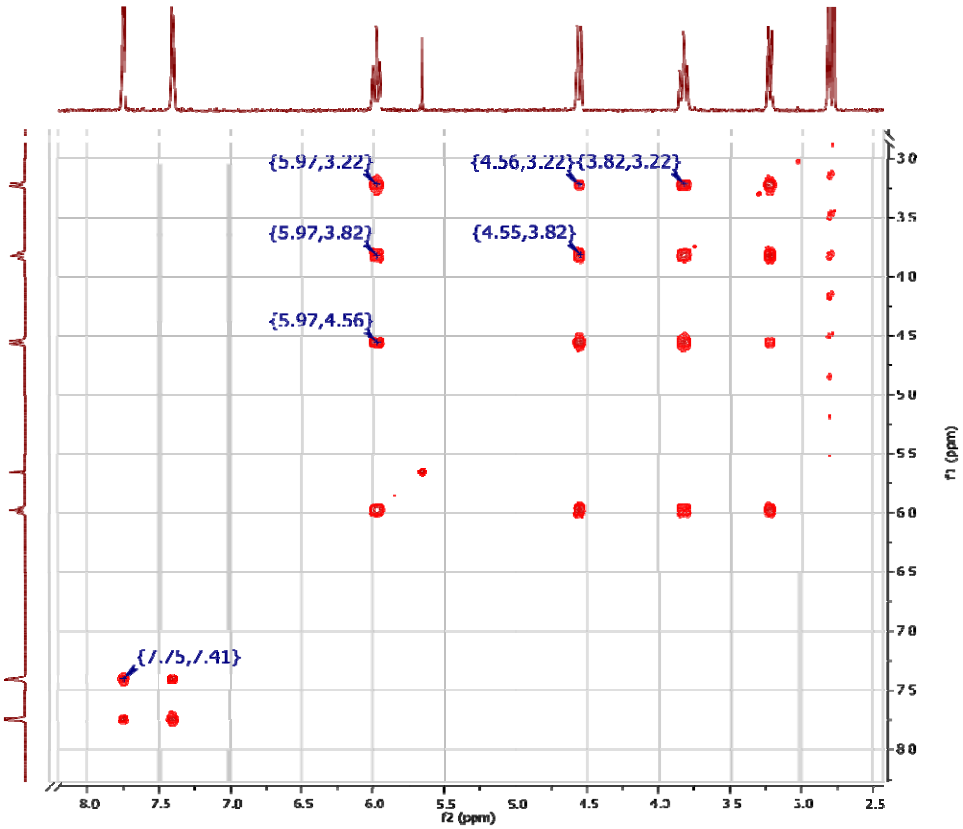

Fig. S58 gCOSY spectrum of **7** (acetone-d_6, 600 MHz, 298 K).

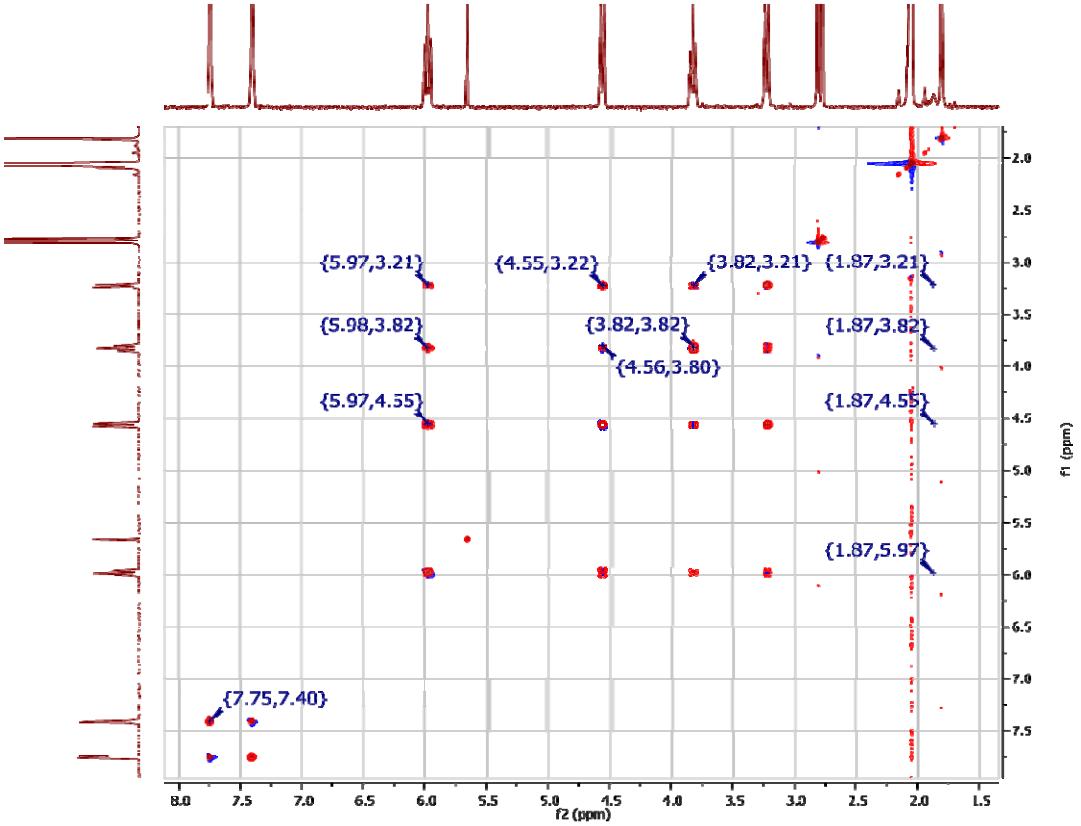

Fig. S59 TOCSY spectrum of **7** (acetone-d_6, 600 MHz, 298 K).

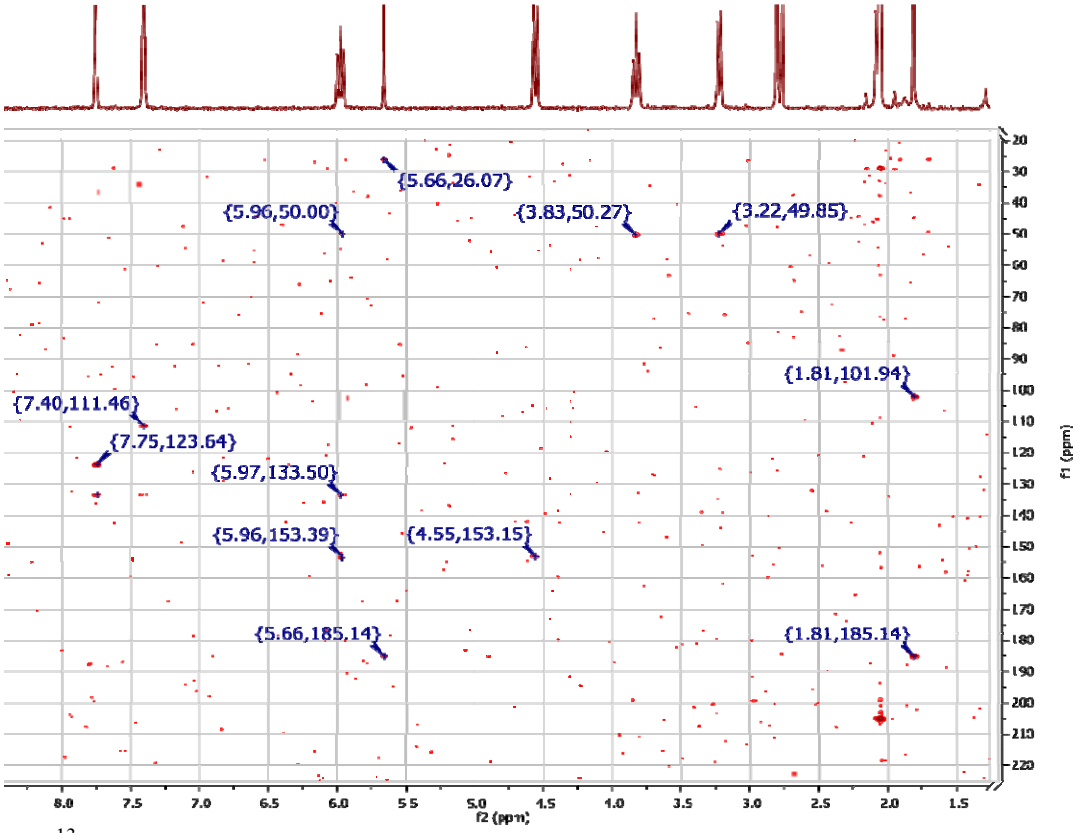

Fig. S60 ^{13}C gHMBCAD spectrum of **7** (acetone-d_6, 600 MHz, 298 K).

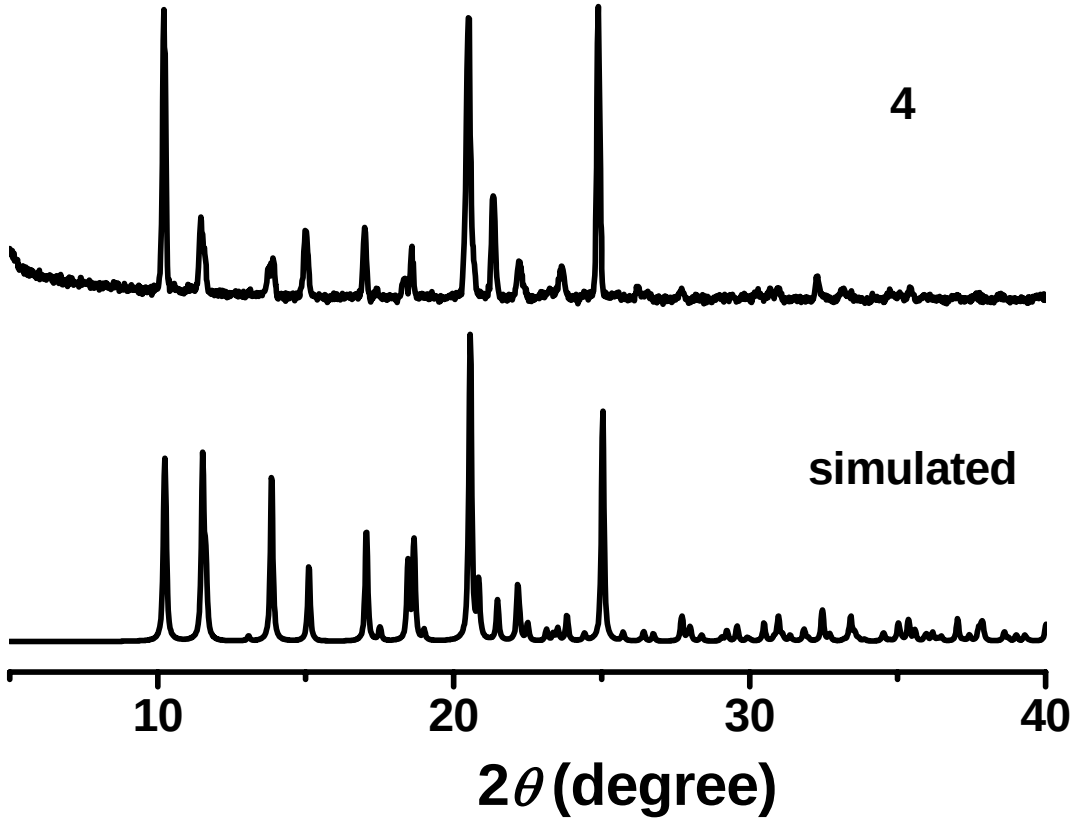

Fig. S61 The PXRD pattern of **4a**.

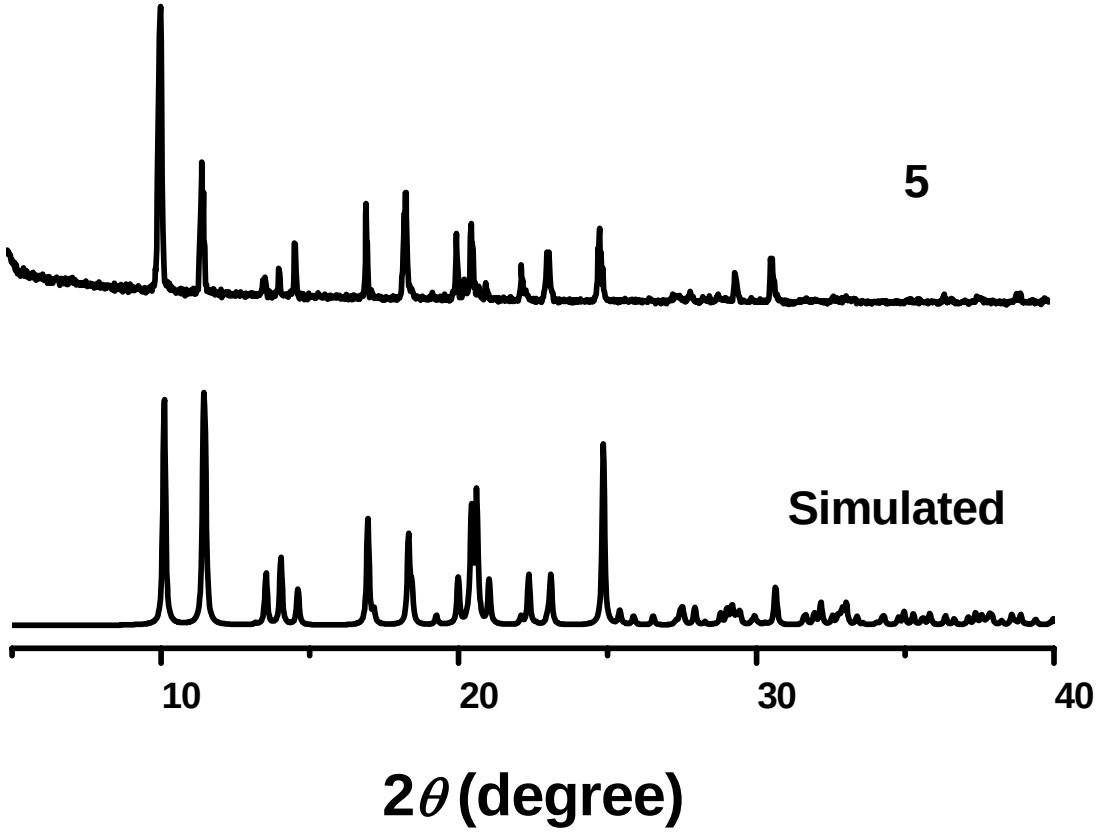

Fig. S62 The PXRD pattern of **5a**.

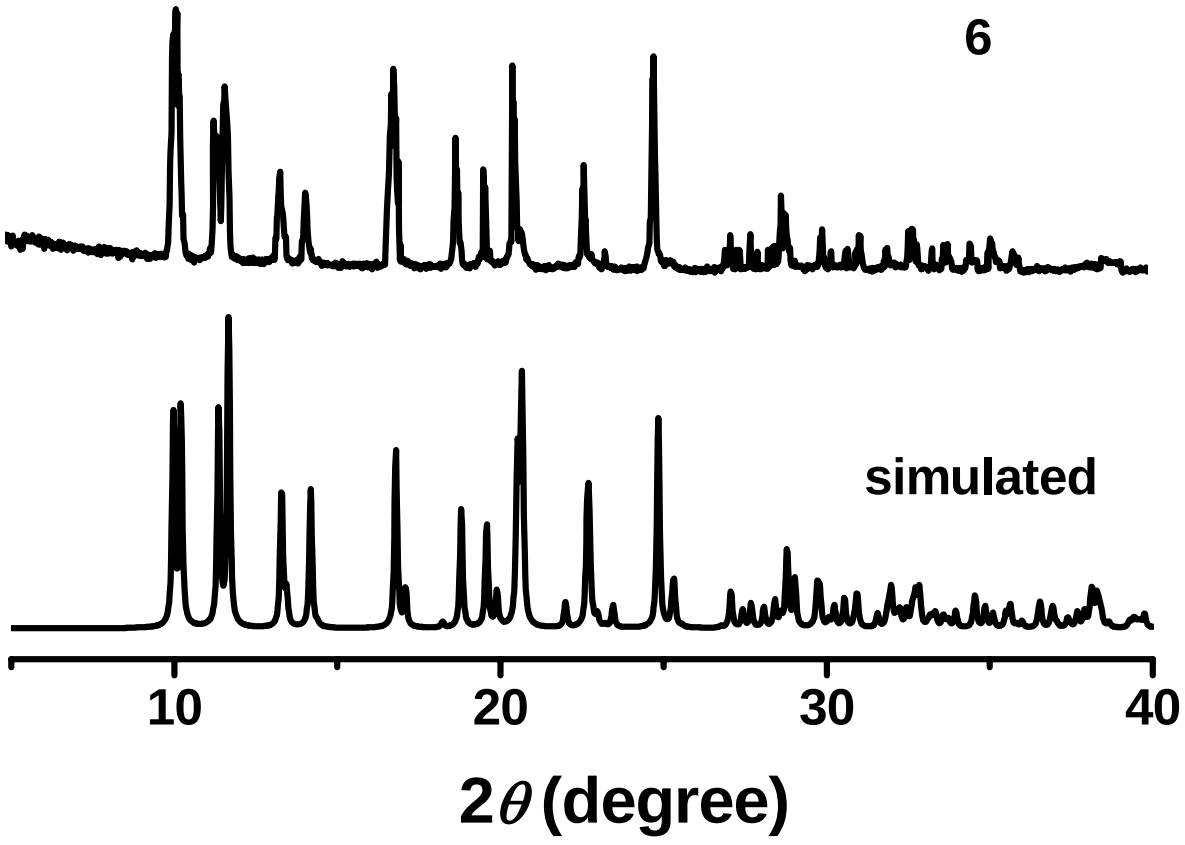

Fig. S63 The PXRD pattern of **6a**.

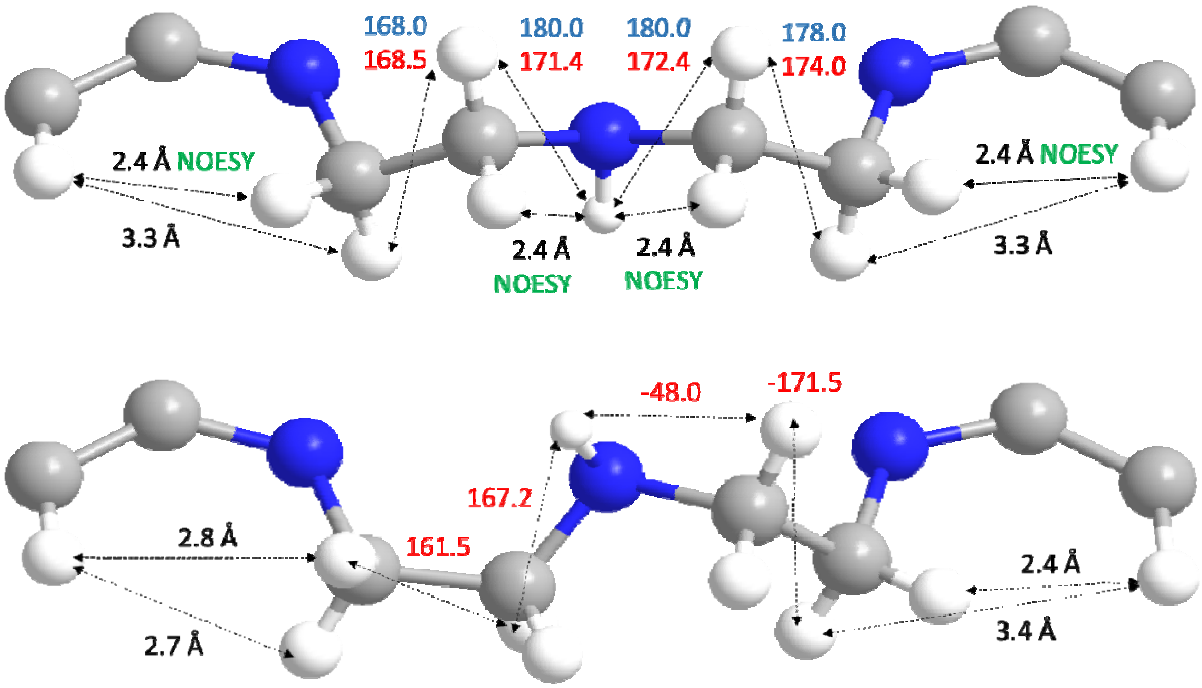

Fig. S64 (Top) X-ray structure of **6a** in comparison with the solution structure of **4** from NMR. (Bottom) X-ray structure of **4a**. Black: Distances from the X-ray structures; Green: H atoms observed by NOESY; Red: Torsion angles (°) from the X-ray structures; Blue: Torsion angles (°) calculated from the $^{3}J_{H\text{-}H}$ coupling constants obtained from solution NMR spectra of **4**.

Structural information obtained from solution NMR data (NOESY and $^{3}J_{H\text{-}H}$ couplings) for **4** was compared with the X-ray structures of **6a** (Fig. S64). The comparison shows that the NMR data are consistent with the X-ray structure of **6a** but not with the X-ray structure of **4a**. The NMR data indicates that in solution, **4** adopts a more square planar conformation similar to the structures of **6a**.

The X-ray structure of **4a** shows that the ethylene groups at both sides of the NH group are not similar. It is possible that the molecule is "forced" to adopt this twisted conformation in the crystal of **4a** in order to minimize the energy and optimize the packing. The volume of the unit cell in the crystal structure of **4a** [663.2(2) Å^{3}] is smaller than the

almost identical volumes [681. 9(3) and 681.4(3) $Å^3$] of **5a** and **6a**.