Structural diversity of ethylzinc derivatives of 3,5-substituted pyrazoles

Szymon Komorski,[†] Michał K. Leszczyński, [†,‡] Iwona Justyniak,[‡] and Janusz Lewiński*,[†,‡]

[†] Warsaw University of Technology, Faculty of Chemistry, Noakowskiego 3, 00-664 Warsaw, Poland
[‡] Polish Academy of Sciences, Institute of Physical Chemistry, Kasprzaka 44/52, 01-224 Warsaw, Poland

Contents: .....Page

X-ray structure determination

The crystals were selected under Paratone-N oil, mounted on the nylon loops and positioned in the cold stream on the diffractometer. The X-ray data for complexes **1,2,3** and **6** were collected at 100(2)K on a SuperNova Agilent diffractometer using graphite monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å). The data were processed with *CrysAlisPro*.[1] The X-ray data for complexes **4** and **5** were collected on a Nonius Kappa CCD diffractometer using graphite monochromated MoKα radiation (λ = 0.71073 Å). The data were processed with *DENZO* and *SCALEPACK* (*HKL2000* package).[2] The structures were solved by direct methods using the SHELXS-97 program and were refined by full matrix least–squares on F^2 using the program SHELXL.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were added to the structure model at geometrically idealized coordinates and refined as riding atoms. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk). CCDC: 2025235 (**1**), 2025236 (**2**), 2025237 (**3**), 2025238 (**4**), 2025239 (**5**) and 2025240 (**6**).

Crystal data and structure refinement for **1**•PhMe

Empirical formula	$C_{49}H_{76}N_{12}O_2Zn_4$	
Formula weight	1126.69	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.1493(2) Å	a = 90°
	b = 17.0654(5) Å	b = 98.620(2)°
	c = 19.1930(4) Å	g = 90°
Volume	2639.04(12) $Å^3$	
Z	2	
Density (calculated)	1.418 Mg/m^3	
Absorption coefficient	1.845 mm^{-1}	
F(000)	1180	
Crystal size	0.26 x 0.18 x 0.09 mm^3	
Theta range for data collection	2.891 to 29.510°.	
Index ranges	-11<=h<=10, -22<=k<=23, -21<=l<=25	
Reflections collected	14293	
Independent reflections	6309 [R(int) = 0.0514]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.847 and 0.678	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6309 / 42 / 329	
Goodness-of-fit on F^2	1.041	
Final R indices [I>2sigma(I)]	R1 = 0.0409, wR2 = 0.0844	
R indices (all data)	R1 = 0.0610, wR2 = 0.0916	
Largest diff. peak and hole	0.547 and -0.542 $e.Å^{-3}$	

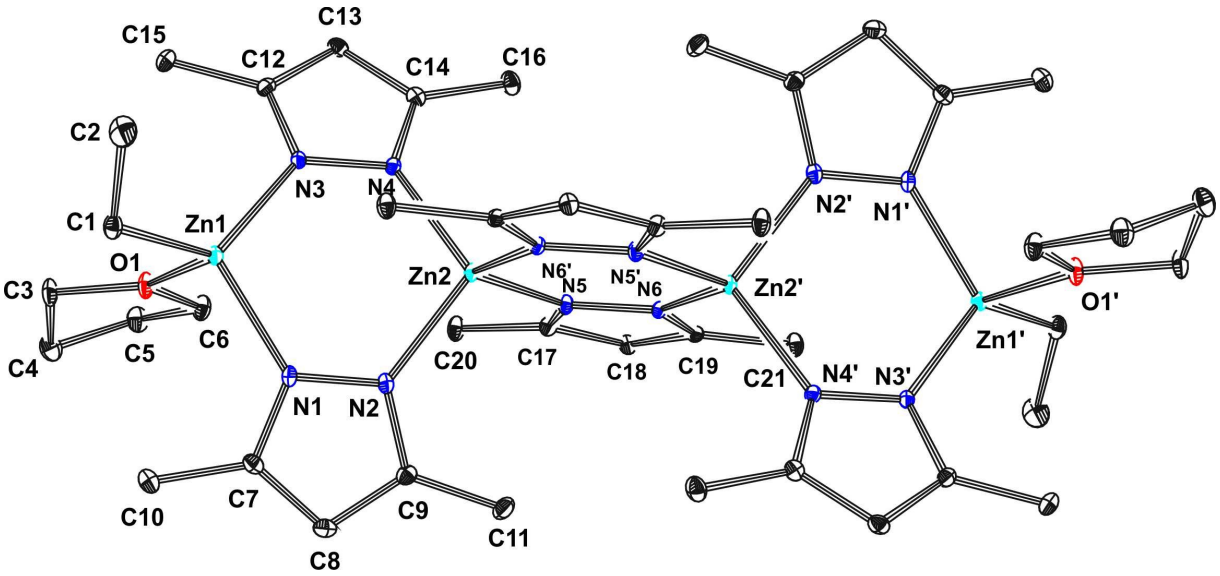

Figure S1. Molecular structure of **1** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: (*-x, -y, -z*).

Table S1. Selected bond lengths [Å] and angles [°] for **1**•PhMe

C1 – Zn1	1.990(3)	O1 – Zn1 – N1	92.20(8)
O1 – Zn1	2.2131(19)	O1 – Zn1 – N3	91.95(8)
N1 – Zn1	2.006(2)	C1 – Zn1 – N1	124.46(10)
N3 – Zn1	2.014(2)	C1 – Zn1 – N3	124.85(11)
N2 – Zn2	2.003(2)	C1 – Zn1 – O1	107.90(10)
N4 – Zn2	2.008(2)	N1 – Zn1 – N3	104.78(9)
N5 – Zn2	1.995(2)	N2 – Zn2 – N5	107.32(9)
N6’ – Zn2	2.002(2)	N2– Zn2 – N4	106.79(9)
N1 – N2	1.382(3)	N2 – Zn2 – N6’	110.58(9)
N3 – N4	1.382(3)	N4 – Zn2 – N6’	113.00(9)
N5 – N6	1.378(3)	N4 – Zn2 – N5	110.74(8)
		N5 – Zn2 – N6’	108.28(8)

Crystal data and structure refinement for **2**

Empirical formula	$C_{32}H_{54}N_8O_2Zn_3$	
Formula weight	778.94	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 7.7664(3) Å	a = 90°
	b = 29.8024(12) Å	b = 102.299(4)°
	c = 16.0219(6) Å	g = 90°
Volume	3623.3(2) Å ^{3}	
Z	4	
Density (calculated)	1.428 Mg/m^3	
Absorption coefficient	2.010 mm^{-1}	
F(000)	1632	
Crystal size	0.27 x 0.22 x 0.09 mm^3	
Theta range for data collection	3.028 to 28.598°.	
Index ranges	-9<=h<=9, -39<=k<=37, -19<=l<=20	
Reflections collected	17361	
Independent reflections	8162 [R(int) = 0.0234]	
Completeness to theta = 26.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.835 and 0.594	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8162 / 0 / 416	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0296, wR2 = 0.0629	
R indices (all data)	R1 = 0.0379, wR2 = 0.0654	
Largest diff. peak and hole	0.483 and -0.366 e. Å $^{-3}$	

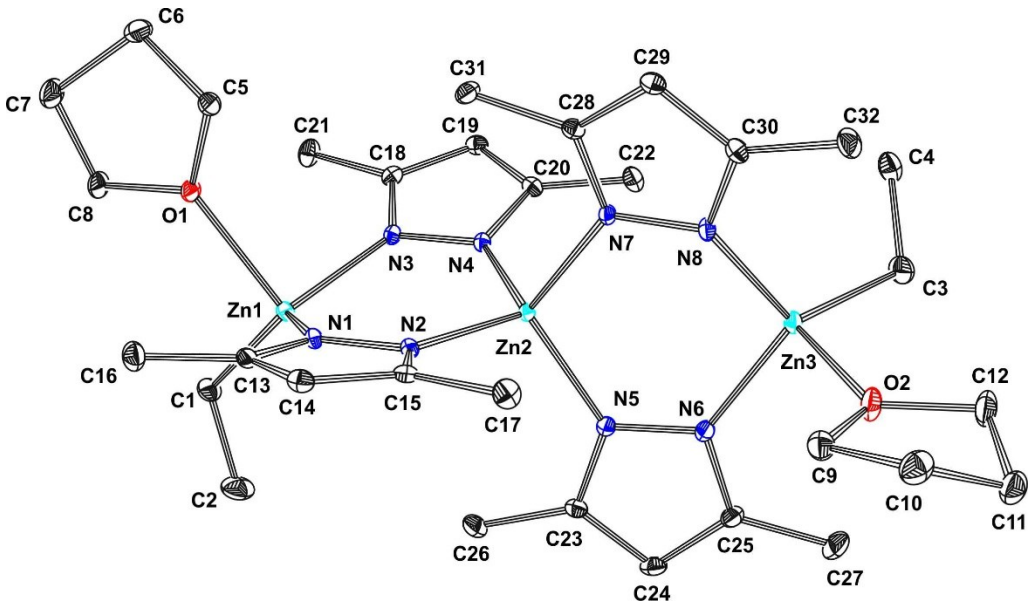

Figure S2. Molecular structure of **2** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Table S2. Selected bond lengths [Å] and angles [°] for **2**

C1 – Zn1	1.991(2)	O1 – Zn1 – N1	96.46(6)
O1 – Zn1	2.1849(14)	O1 – Zn1 – N3	94.73(6)
N1 – Zn1	2.0123(16)	C1 – Zn1 – N1	124.75(8)
N3 – Zn1	2.0185(17)	C1 – Zn1 – N3	124.74(8)
N2 – Zn2	1.9788(16)	C1 – Zn1 – O1	101.59(8)
N4 – Zn2	1.9886(15)	N1 – Zn1 – N3	104.87(6)
N5 – Zn2	1.9793(17)	N2 – Zn2 – N4	108.53(7)
N7 – Zn2	1.9940(16)	N2– Zn2 – N5	110.97(7)
C3 – Zn3	1.991(2)	N2 – Zn2 – N7	106.50(7)
O2 – Zn3	2.1908(14)	N4 – Zn2 – N5	115.52(7)
N6 – Zn3	2.0118(17)	N4 – Zn2 – N7	105.44(7)
N8 – Zn3	2.0196(17)	N5 – Zn2 – N7	109.37(7)
N1 – N2	1.378(2)	O2 – Zn3 – N6	96.69(6)
N3 – N4	1.377(2)	O2 – Zn3 – N8	96.88(6)
N5 – N6	1.377(2)	C3 – Zn3 – N6	126.09(9)
N7 – N8	1.375(2)	C3 – Zn3 – N8	120.29(9)
		C3 – Zn3 – O2	103.88(8)
		N6 – Zn3 – N8	105.56(7)

Crystal data and structure refinement for **3**

Empirical formula	$C_{40}H_{70}N_8Zn_3$	
Formula weight	859.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 14.0604(4) Å	a = 90°
	b = 18.0359(6) Å	b = 92.433(3)°
	c = 17.1111(6) Å	g = 90°
Volume	4335.3(2) $Å^3$	
Z	4	
Density (calculated)	1.316 Mg/m^3	
Absorption coefficient	1.683 mm^{-1}	
F(000)	1824	
Crystal size	0.26 x 0.16 x 0.12 mm^3	
Theta range for data collection	2.960 to 27.000°.	
Index ranges	-17<=h<=17, -23<=k<=22, -21<=l<=21	
Reflections collected	24508	
Independent reflections	9372 [R(int) = 0.0544]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.818 and 0.733	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9372 / 0 / 478	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.1028	
R indices (all data)	R1 = 0.0799, wR2 = 0.1212	
Largest diff. peak and hole	0.951 and -0.756 $e.Å^{-3}$	

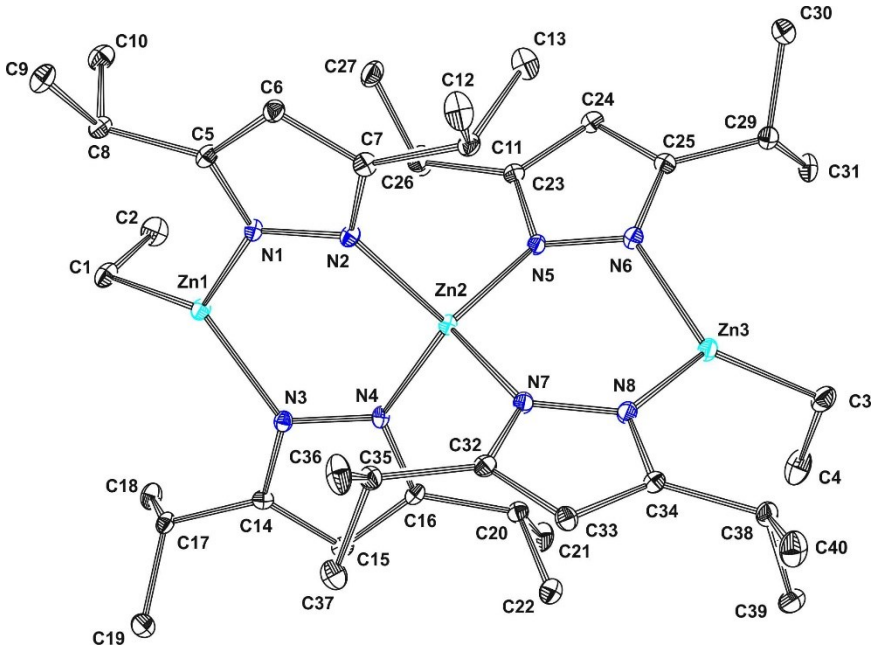

Figure S3. Molecular structure of **3** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Table S3. Selected bond lengths [Å] and angles [°] for **3**

C1 – Zn1	1.969(3)	C1 – Zn1 – N1	128.35(13)
N1 – Zn1	1.973(3)	C1 – Zn1 – N3	122.99(13)
N3 – Zn1	1.991(2)	N1 – Zn1 – N3	107.59(10)
N2 – Zn2	2.001(2)	N2 – Zn2 – N4	109.68(10)
N4 – Zn2	1.982(3)	N2– Zn2 – N5	107.94(11)
N5 – Zn2	1.978(3)	N2 – Zn2 – N7	109.80(11)
N7 – Zn2	1.989(3)	N4 – Zn2 – N5	113.14(11)
C3 – Zn3	1.965(3)	N4 – Zn2 – N7	106.91(11)
N6 – Zn3	2.000(2)	N5 – Zn2 – N7	109.36(10)
N8 – Zn3	1.980(3)	C3 – Zn3 – N6	124.19(13)
N1 – N2	1.381(3)	C3 – Zn3 – N8	128.10(13)
N3 – N4	1.391(3)	N6 – Zn3 – N8	106.99(10)
N5 – N6	1.390(3)		
N7 – N8	1.390(3)		

*Crystal data and structure refinement for **4***

Empirical formula	$C_{26}H_{46\cdot24}N_4Zn_2$	
Formula weight	545.69	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.9820(15) Å	a = 90°
	b = 18.677(3) Å	b = 109.536(8)°
	c = 14.857(2) Å	g = 90°
Volume	2871.9(7) $Å^3$	
Z	4	
Density (calculated)	1.262 Mg/m^3	
Absorption coefficient	1.689 mm^{-1}	
F(000)	1161	
Crystal size	0.22 x 0.16 x 0.10 mm^3	
Theta range for data collection	2.250 to 25.414°.	
Index ranges	-12<=h<=12, -22<=k<=22, -9<=l<=17	
Reflections collected	4642	
Independent reflections	4642 [R(int) = 0.0563]	
Completeness to theta = 25.414°	88.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.845 and 0.730	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4642 / 202 / 340	
Goodness-of-fit on F^2	1.141	
Final R indices [I>2sigma(I)]	R1 = 0.1877, wR2 = 0.4182	
R indices (all data)	R1 = 0.2046, wR2 = 0.4252	
Largest diff. peak and hole	1.268 and - -1.423 $e.Å^{-3}$	

This compound crystallizes as twins. The ratio of the twin components being 0.721(11) : 0.279(11).

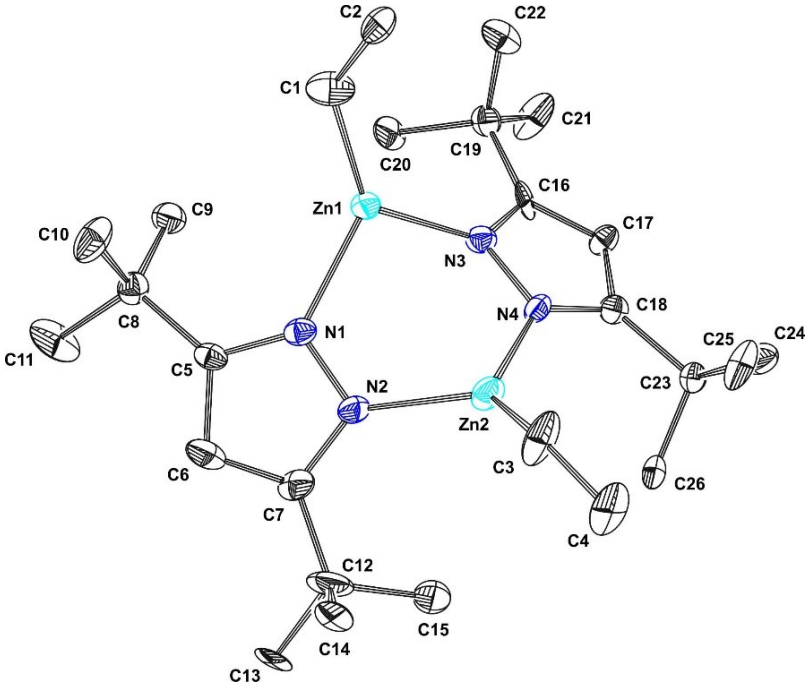

Figure S4. Molecular structure of **4** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Due to the poor quality of the data bond lengths and angle parameters are not analyzed.

Crystal data and structure refinement for ***5***

Empirical formula	$C_{64}H_{120}N_8O_3Zn_4$	
Formula weight	1311.15	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P 1	
Unit cell dimensions	a = 11.89(2) Å	a = 72.50(6)°
	b = 15.35(2) Å	b = 88.38(8)°
	c = 22.38(5) Å	g = 69.64(3)°
Volume	3639(11) $Å^3$	
Z	2	
Density (calculated)	1.197 Mg/m^3	
Absorption coefficient	1.347 mm^{-1}	
F(000)	1408	
Crystal size	0.19 x 0.17 x 0.09 mm^3	
Theta range for data collection	1.49 to 25.698°.	
Index ranges	-13<=h<=13, -17<=k<=17, -26<=l<=26	
Reflections collected	14273	
Independent reflections	12182 [R(int) = 0.0691]	
Completeness to theta = 24.699°	98.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.886 and 0.774	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12182 / 6 / 741	
Goodness-of-fit on F^2	1.088	
Final R indices [I>2sigma(I)]	R1 = 0.1088, wR2 = 0.3109	
R indices (all data)	R1 = 0.1387, wR2 = 0.3274	
Largest diff. peak and hole	2.718 and -1.560 $e.Å^{-3}$	

This compound crystallizes as twins. The ratio of the twin components being 0.558(7) : 0.442(7).

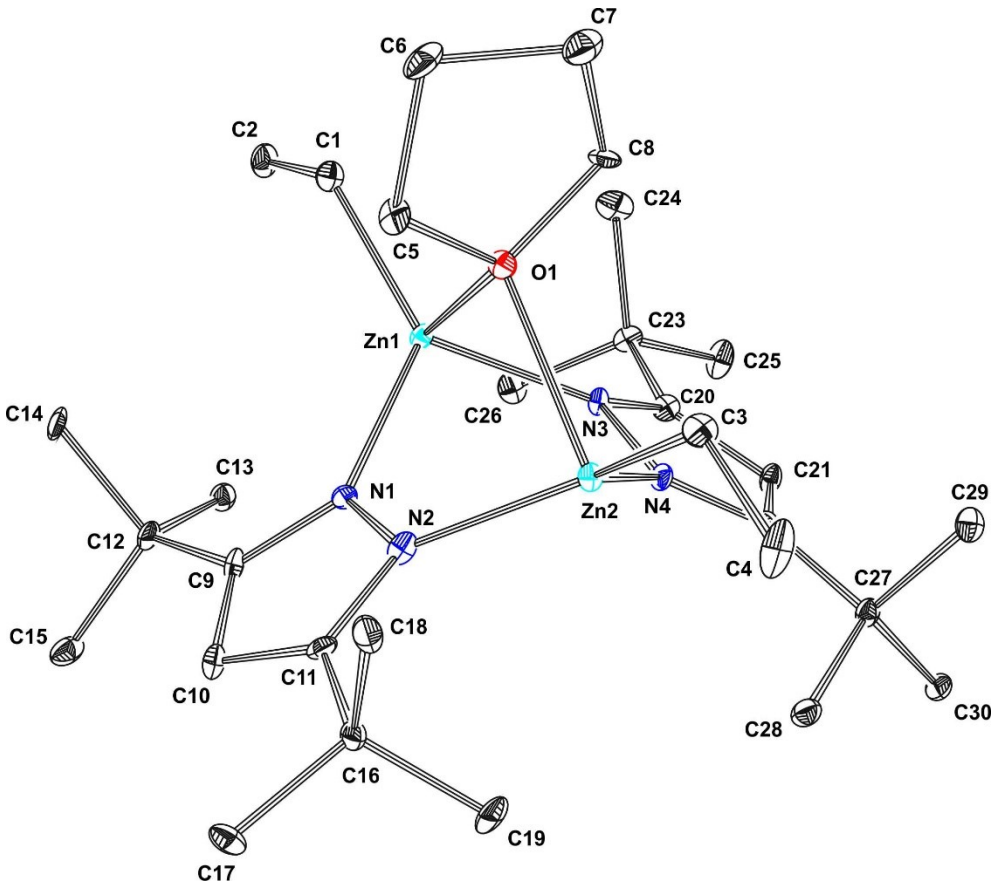

Figure S5. Molecular structure of **5** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity.

Table S4. Selected bond lengths [Å] and angles [°] for **5**

C1 – Zn1	2.011(12)	O1 – Zn1 – N1	89.8(3)
O1 – Zn1	2.297(8)	O1 – Zn1 – N3	87.0(3)
N1 – Zn1	2.039(9)	C1 – Zn1 – N1	126.4(4)
N3 – Zn1	2.037(9)	C1 – Zn1 – N3	133.8(4)
C3 – Zn2	2.000(11)	C1 – Zn1 – O1	96.1(4)
O1 – Zn2	2.307(8)	N1 – Zn1 – N3	99.5(4)
N2 – Zn2	2.027(10)	O1 – Zn2 – N2	86.7(3)
N4 – Zn2	2.042(9)	O1– Zn2 – N4	90.0(3)
N1 – N2	1.406(12)	C3 – Zn2 – N2	133.9(4)
N3 – N4	1.402(12)	C3 – Zn2 – N4	126.0(4)
		C3 – Zn2 – O1	96.7(4)
		N2 – Zn2 – N4	99.9(4)

Crystal data and structure refinement for ***6***

Empirical formula	$C_{26}H_{36}N_4O_2Zn_2$	
Formula weight	567.39	
Temperature	100.01(10) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 1 2/c 1	
Unit cell dimensions	a = 12.2907(9) Å	a= 90°
	b = 16.3872(10) Å	b= 109.417(8)°
	c = 13.4133(11) Å	g = 90°
Volume	2547.9(3) $Å^3$	
Z	4	
Density (calculated)	1.4790 Mg/m^3	
Absorption coefficient	1.913 mm^{-1}	
F(000)	1186.8169	
Crystal size	0.32 x 0.24 x 0.12 mm^3	
Theta range for data collection	3.22 to 27.00°.	
Index ranges	-15<=h<=15, -21<=k<=11, -14<=l<=16	
Reflections collected	5259	
Independent reflections	2737 [R(int) = 0.0454]	
Completeness to theta = 26.9978°	98.35 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.795 and 0.582	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2737 / 0 / 155	
Goodness-of-fit on F^2	1.0447	
Final R indices [I>2sigma(I)]	R1 = 0.0564, wR2 = 0.1447	
R indices (all data)	R1 = 0.0653, wR2 = 0.1602	
Largest diff. peak and hole	1.5187 and -0.8272 $e.Å^{-3}$	

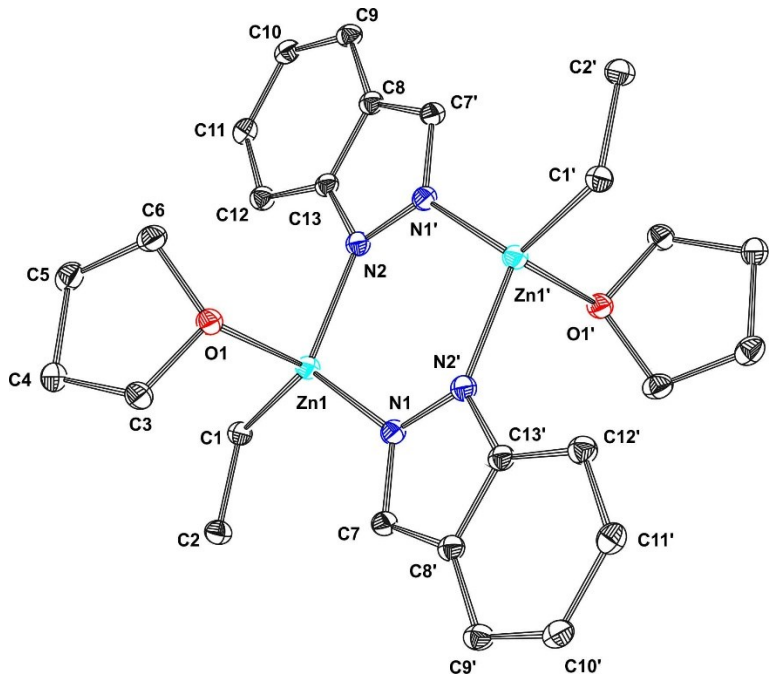

Figure S6. Molecular structure of **6** with thermal ellipsoids set at 35% probability. Hydrogen atoms have been omitted for clarity. Symmetry transformations used to generate equivalent atoms: (*-x+3/2, -y+1/2, -z*).

Table S5. Selected bond lengths [Å] and angles [°] for **6**

C1 – Zn1	1.981(3)	O1 – Zn1 – N1	90.69(10)
O1 – Zn1	2.220(2)	O1 – Zn1 – N2	94.28(10)
N1 – Zn1	2.025(3)	C1 – Zn1 – N1	122.90(13)
N2 – Zn1	1.996(3)	C1 – Zn1 – N2	123.34(13)
N1 – N2’	1.373(4)	C1 – Zn1 – O1	109.31(12)
		N1 – Zn1 – N2	106.86(11)

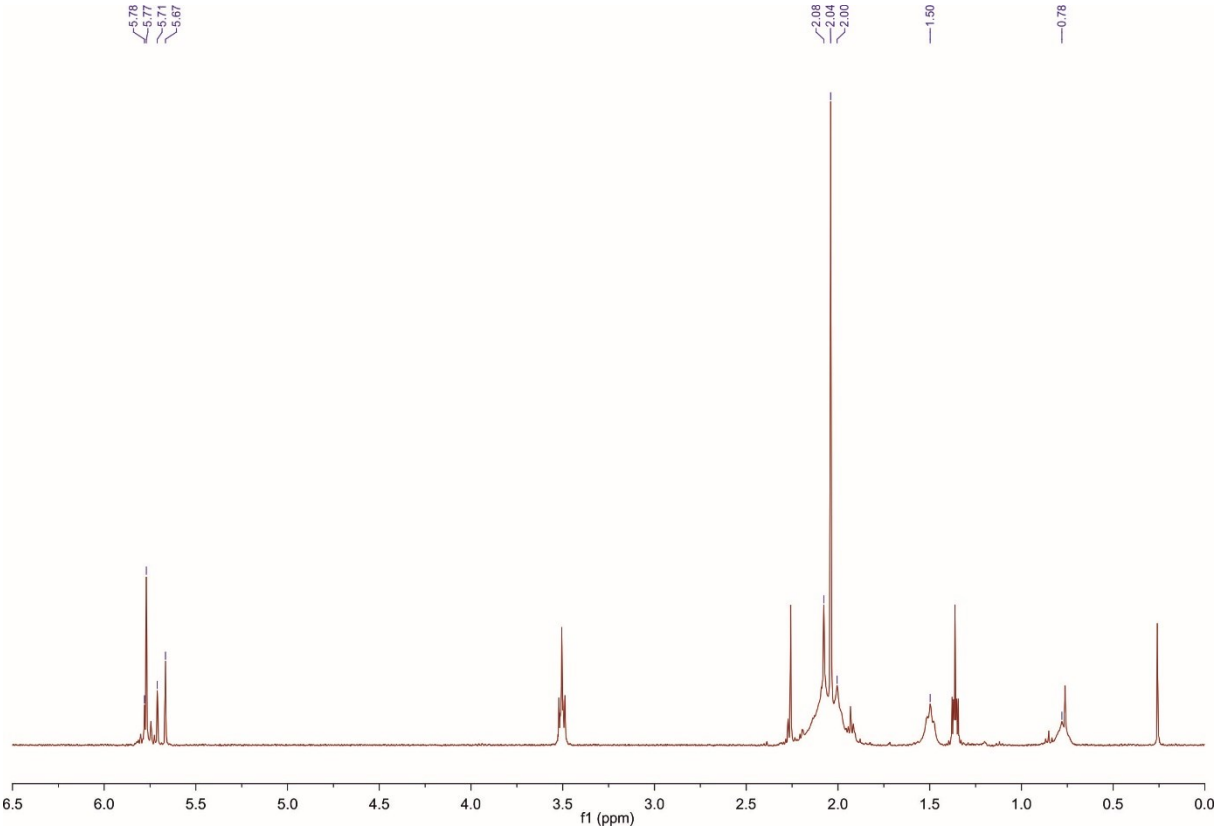

Figure S7. ^{1}H NMR spectrum of compound **1** (C_6D_6).

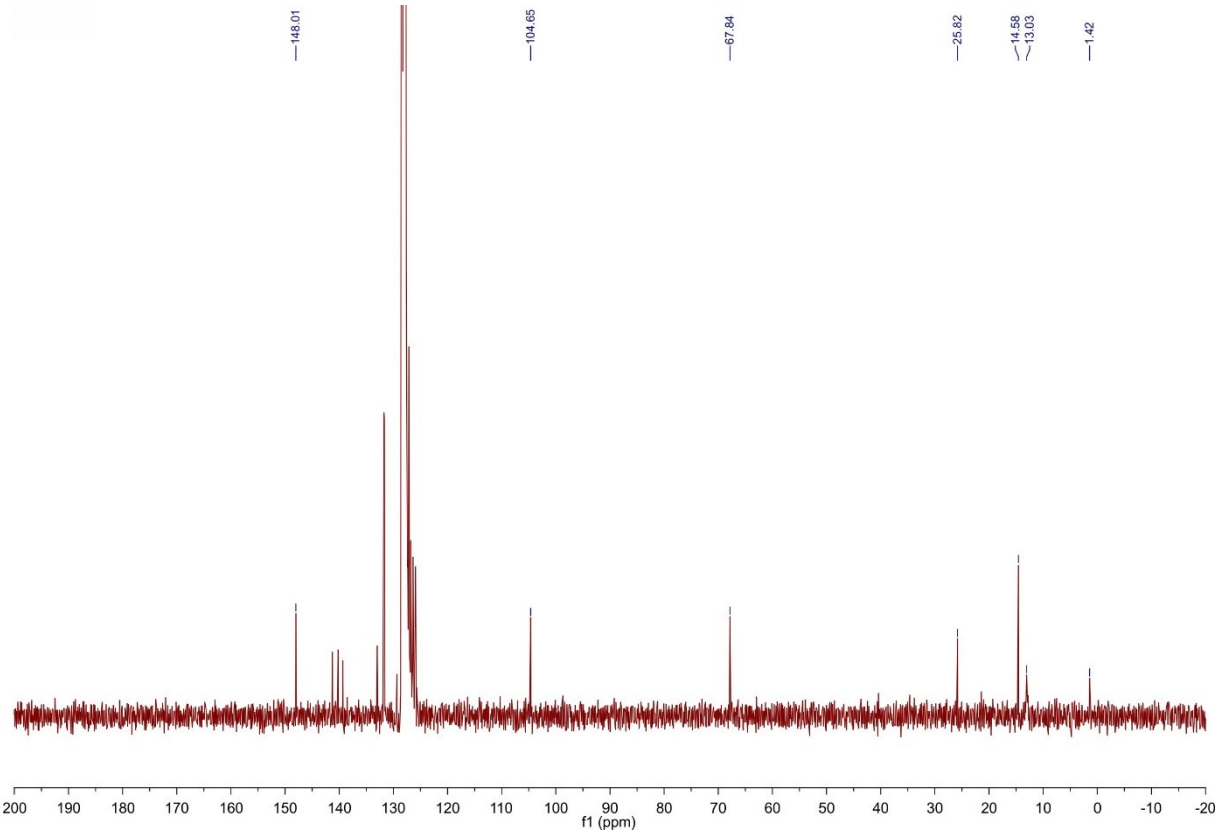

Figure S8. ^{13}C NMR spectrum of compound **1** (C_6D_6).

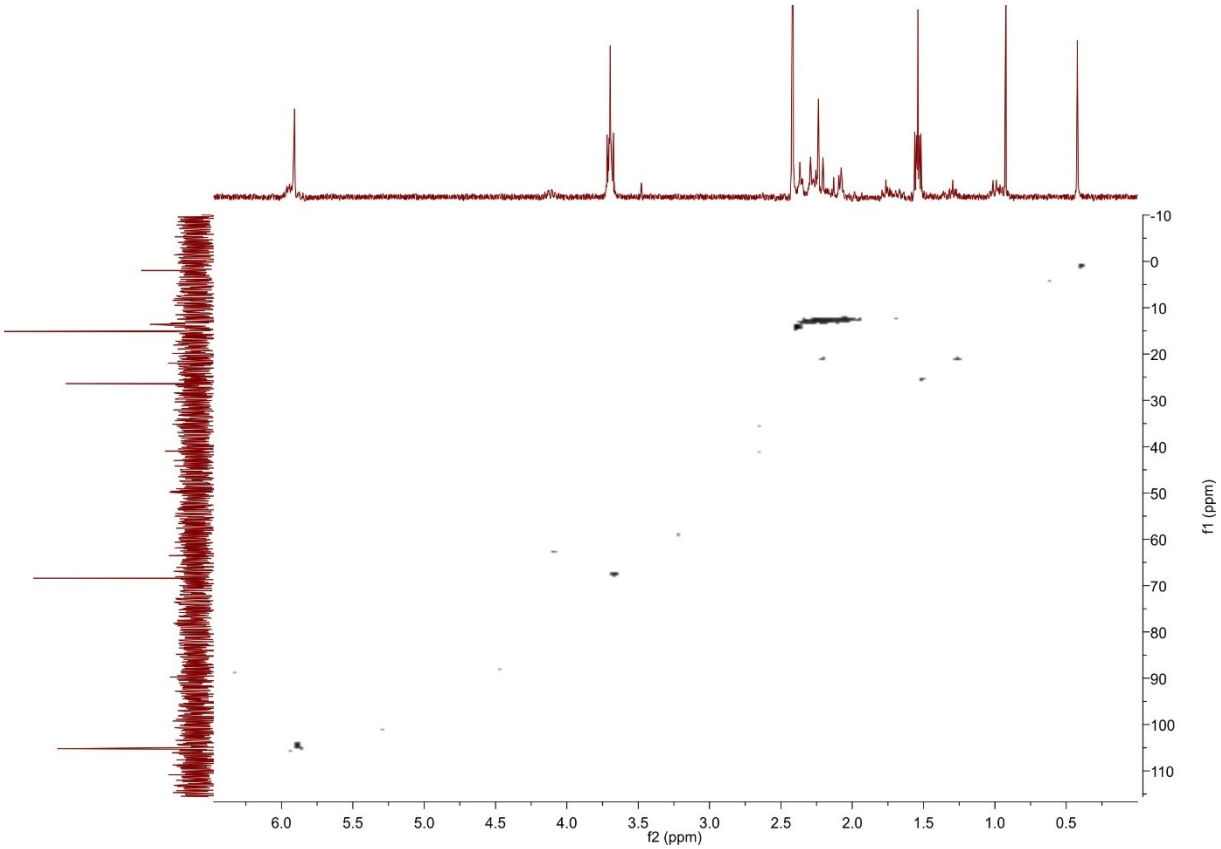

Figure S9. HMQC NMR spectrum of **1** (C_6D_6.)

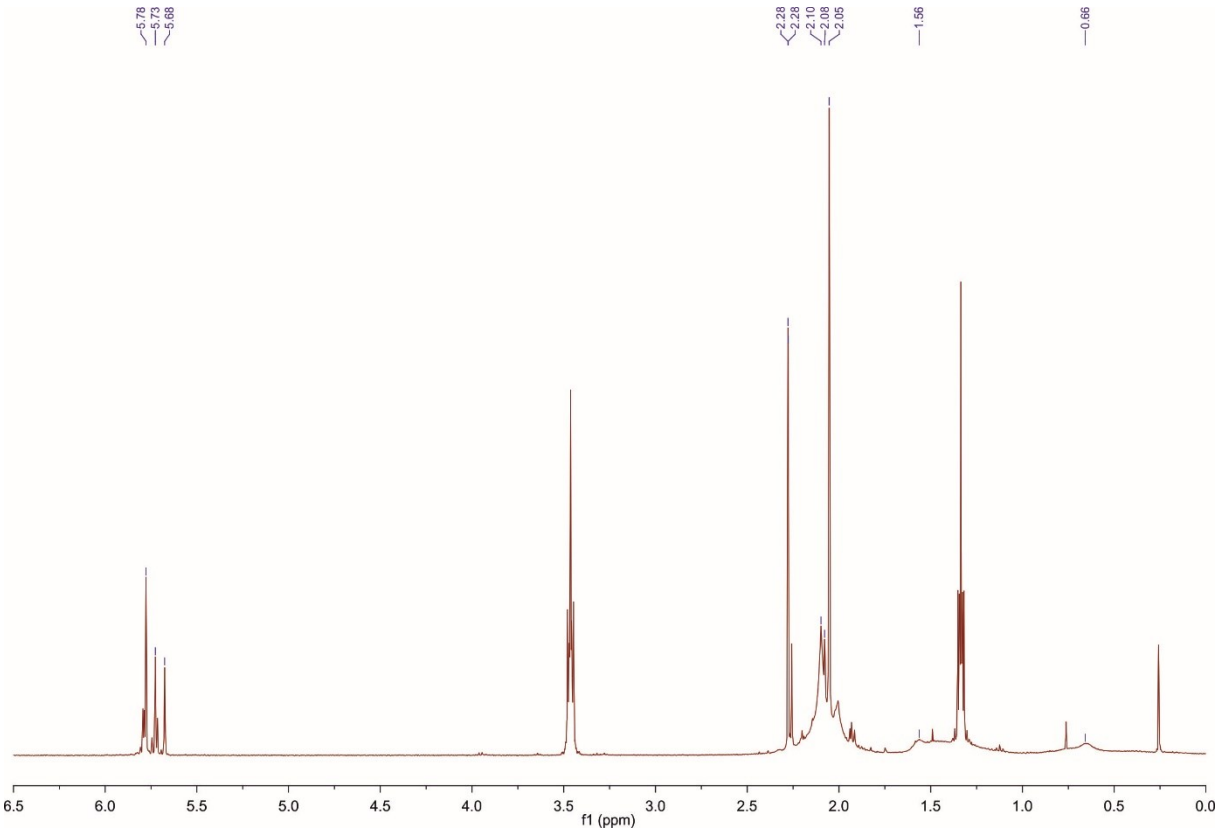

Figure S10. ^{1}H NMR spectrum of compound **2** (C_6D_6).

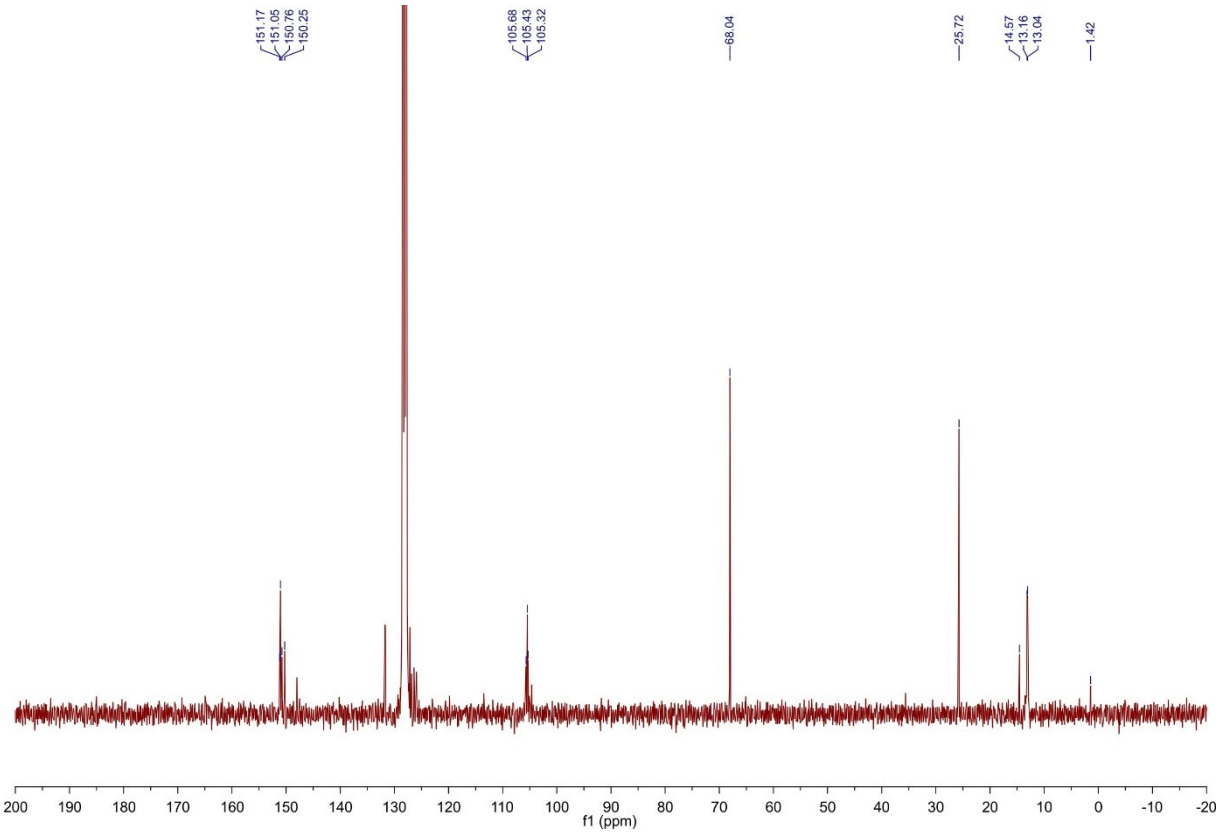

Figure S11. ^{13}C NMR spectrum of compound **2** (C_6D_6).

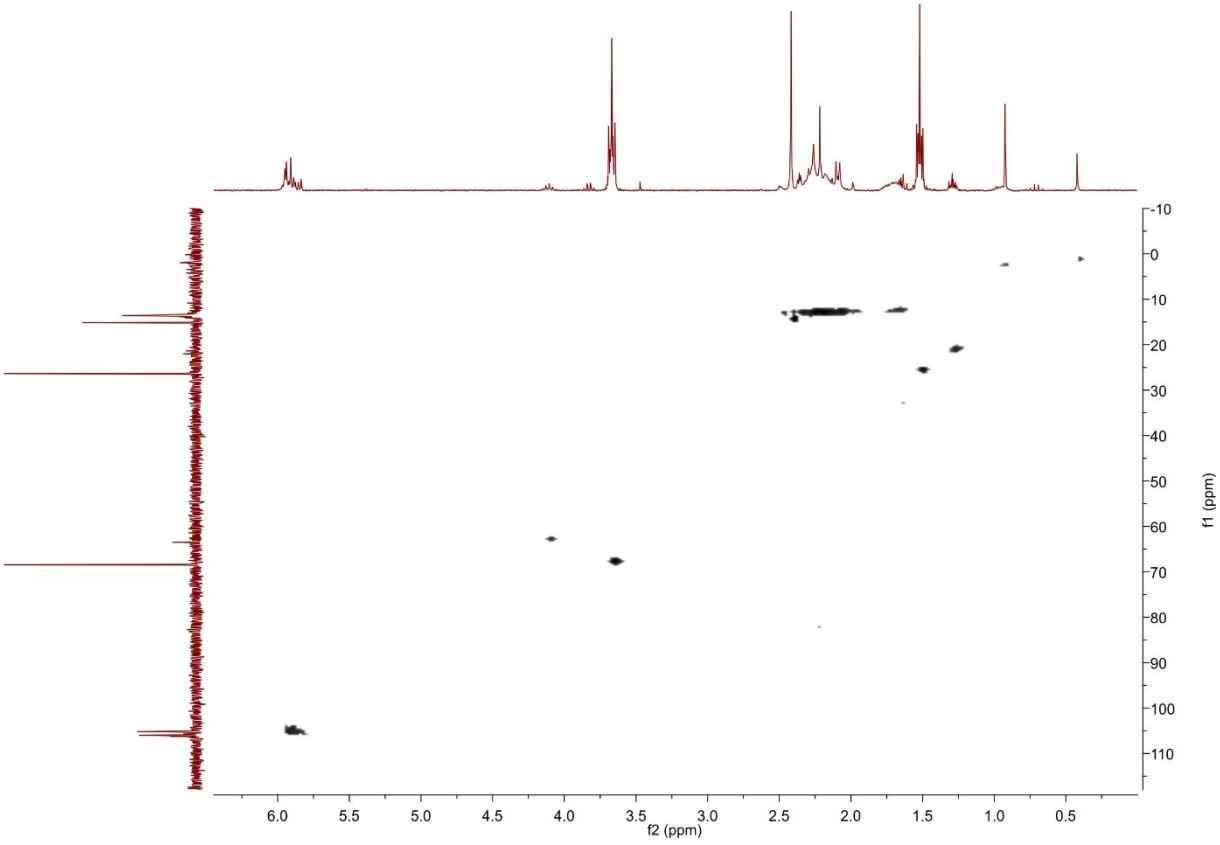

Figure S12. HMQC NMR spectrum of **2** (C_6D_6.)

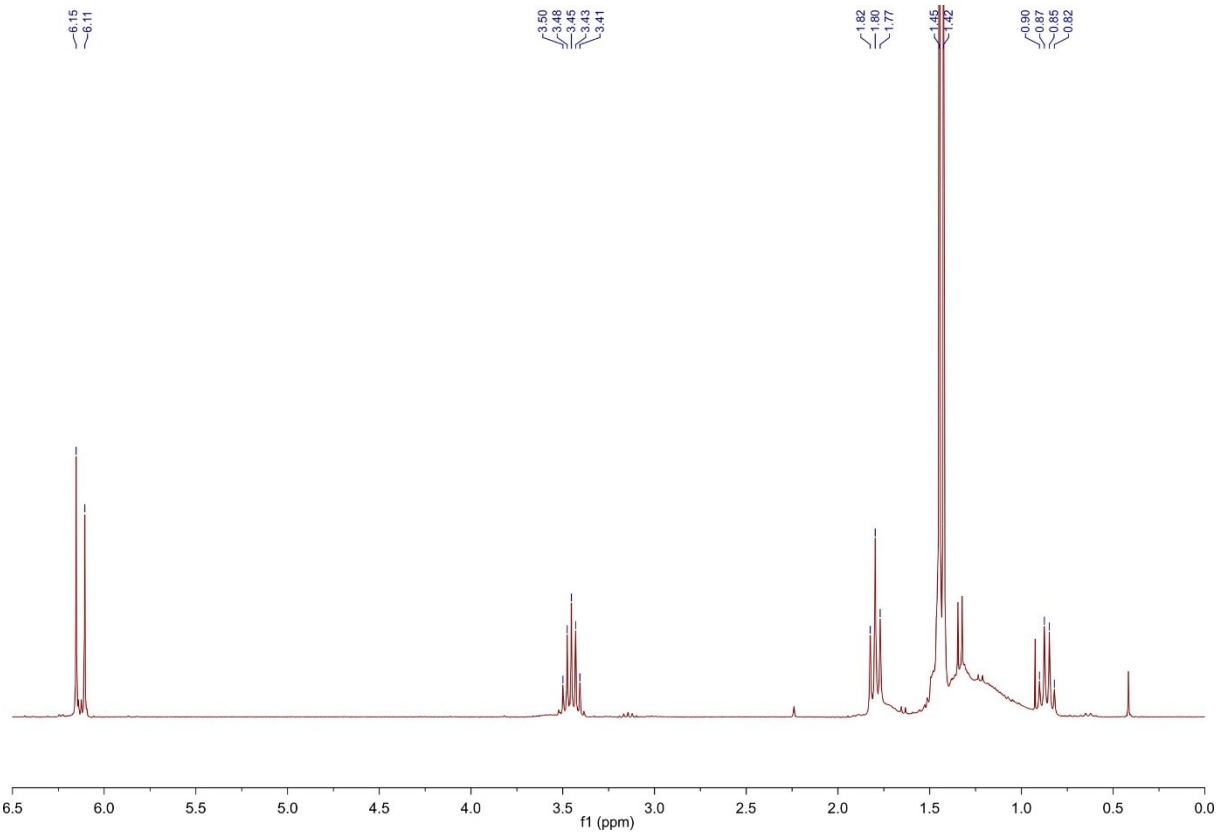

Figure S13. ^{1}H NMR spectrum of compound **3** (C_6D_6).

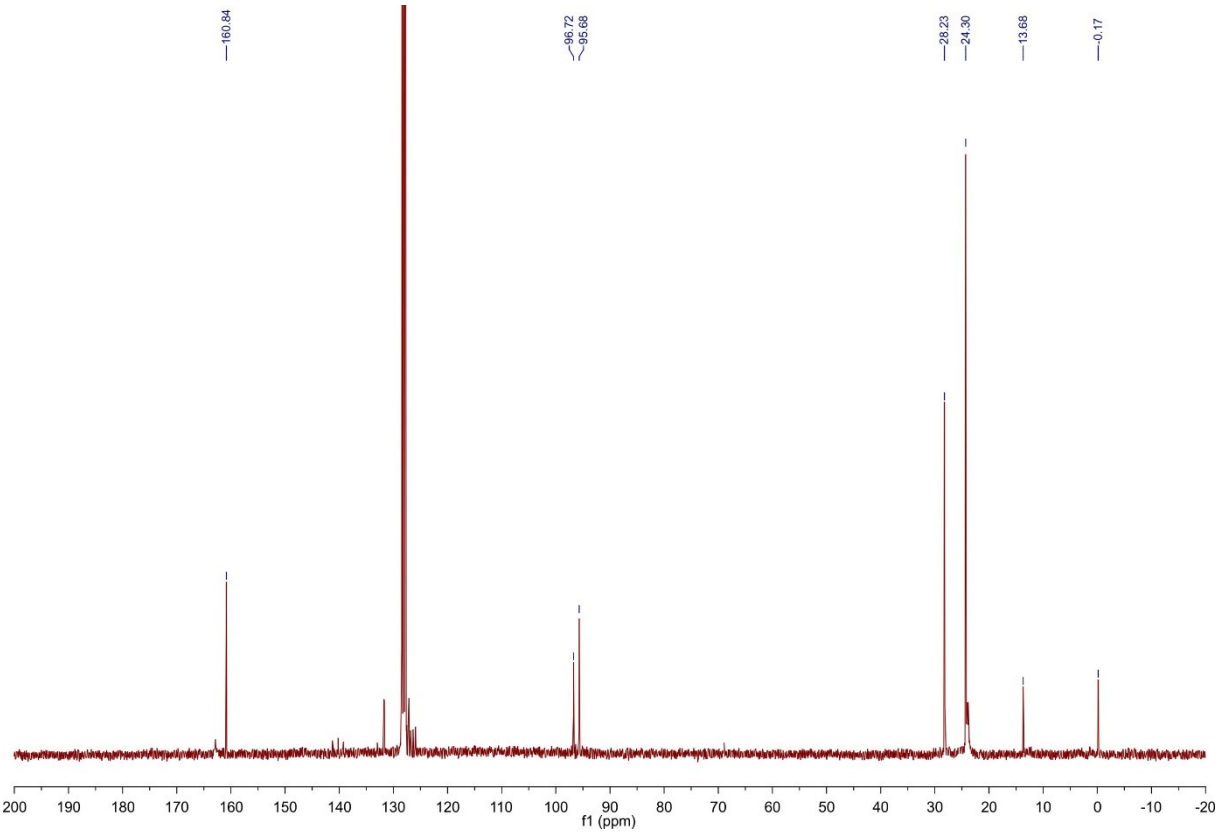

Figure S14. ^{13}C NMR spectrum of compound **3** (C_6D_6).

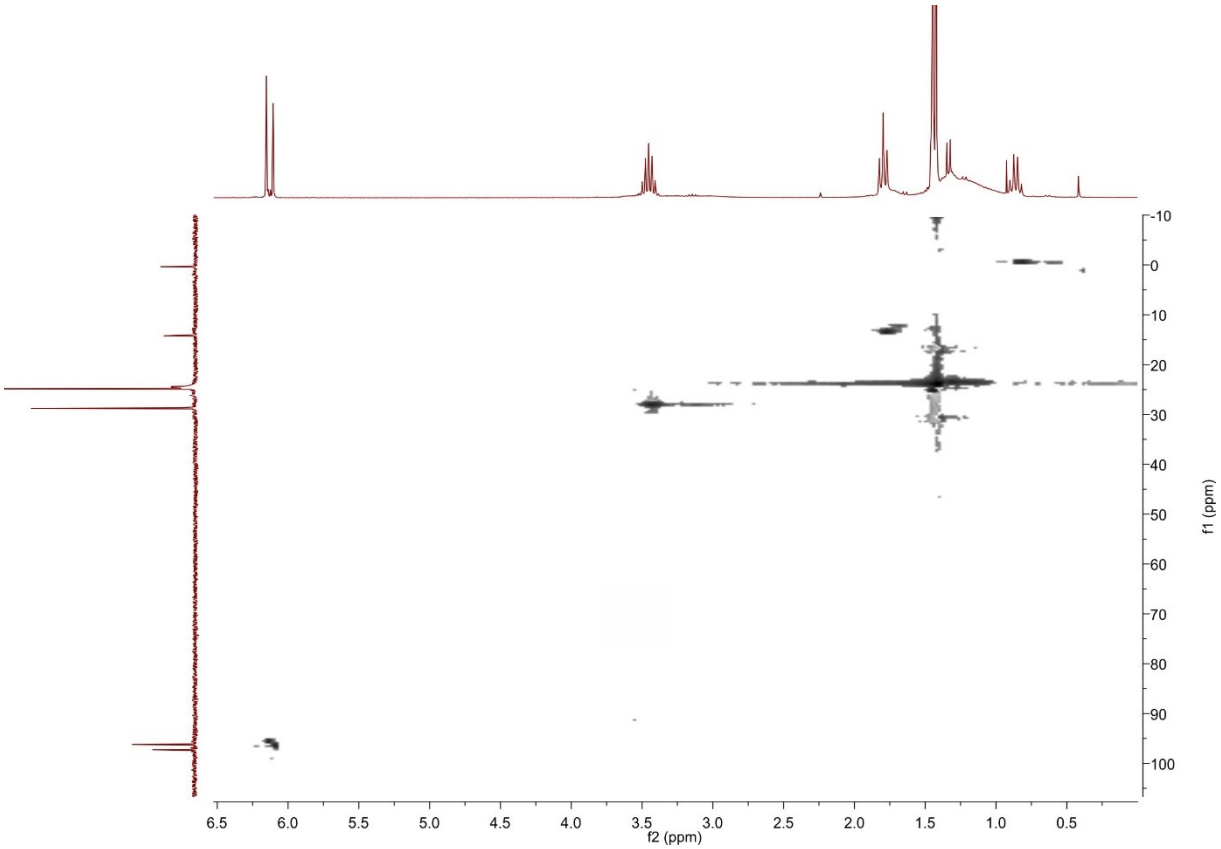

Figure S15. HMQC NMR spectrum of **3** (C_6D_6)

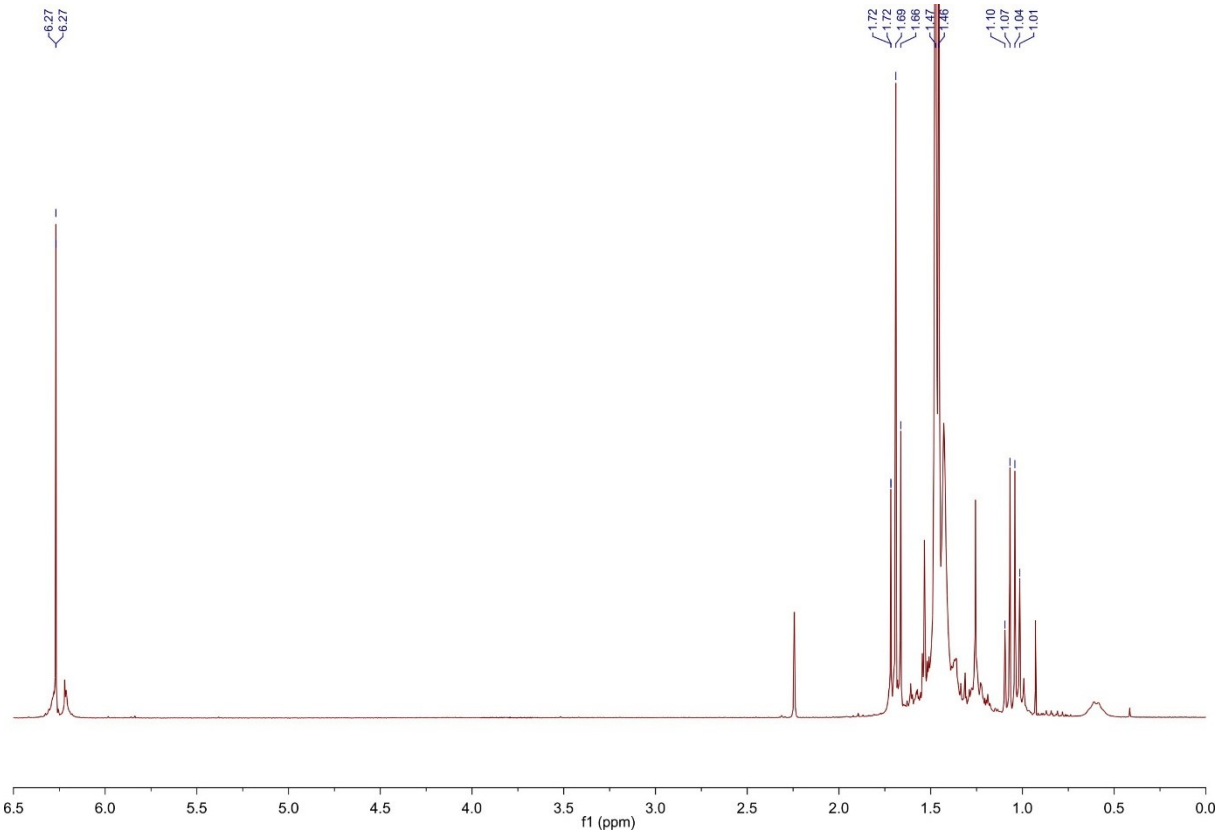

Figure S16. ^{1}H NMR spectrum of compound **4** (C_6D_6).

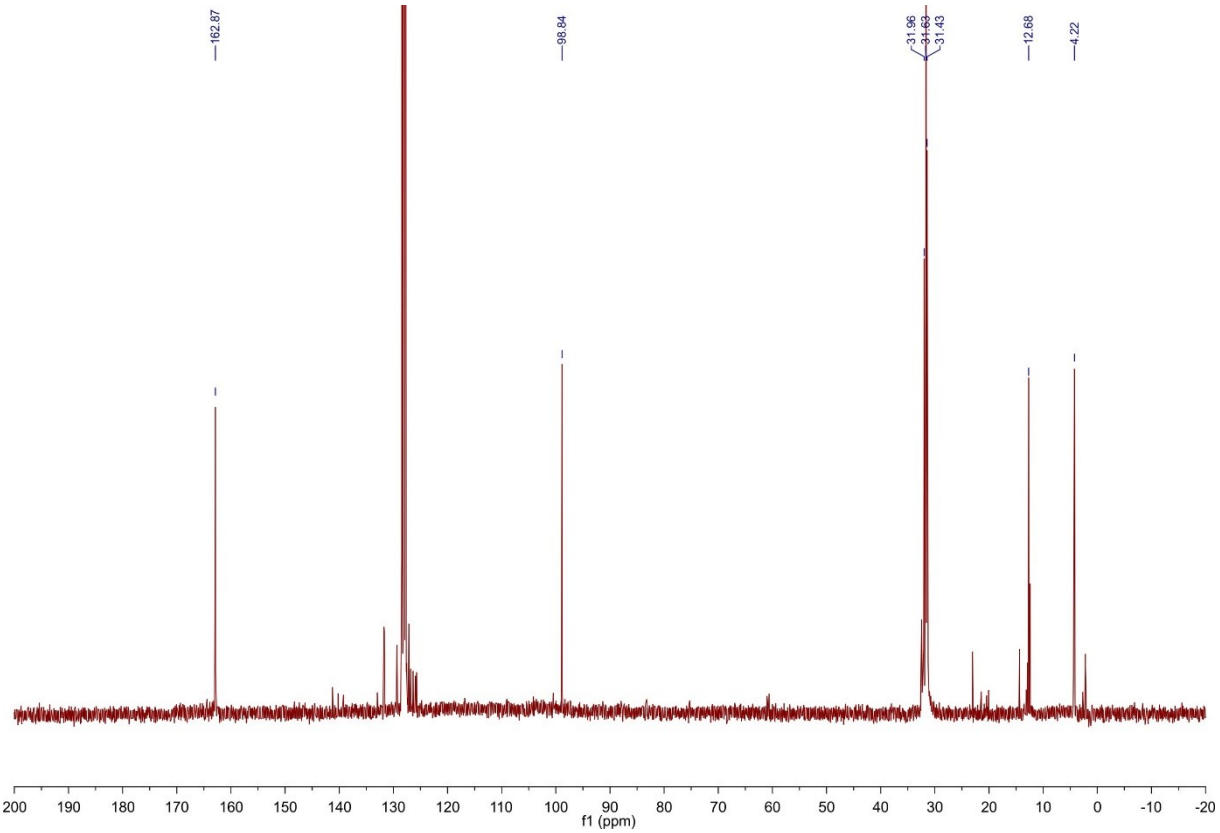

Figure S17. ^{13}C NMR spectrum of compound **4** (C_6D_6).

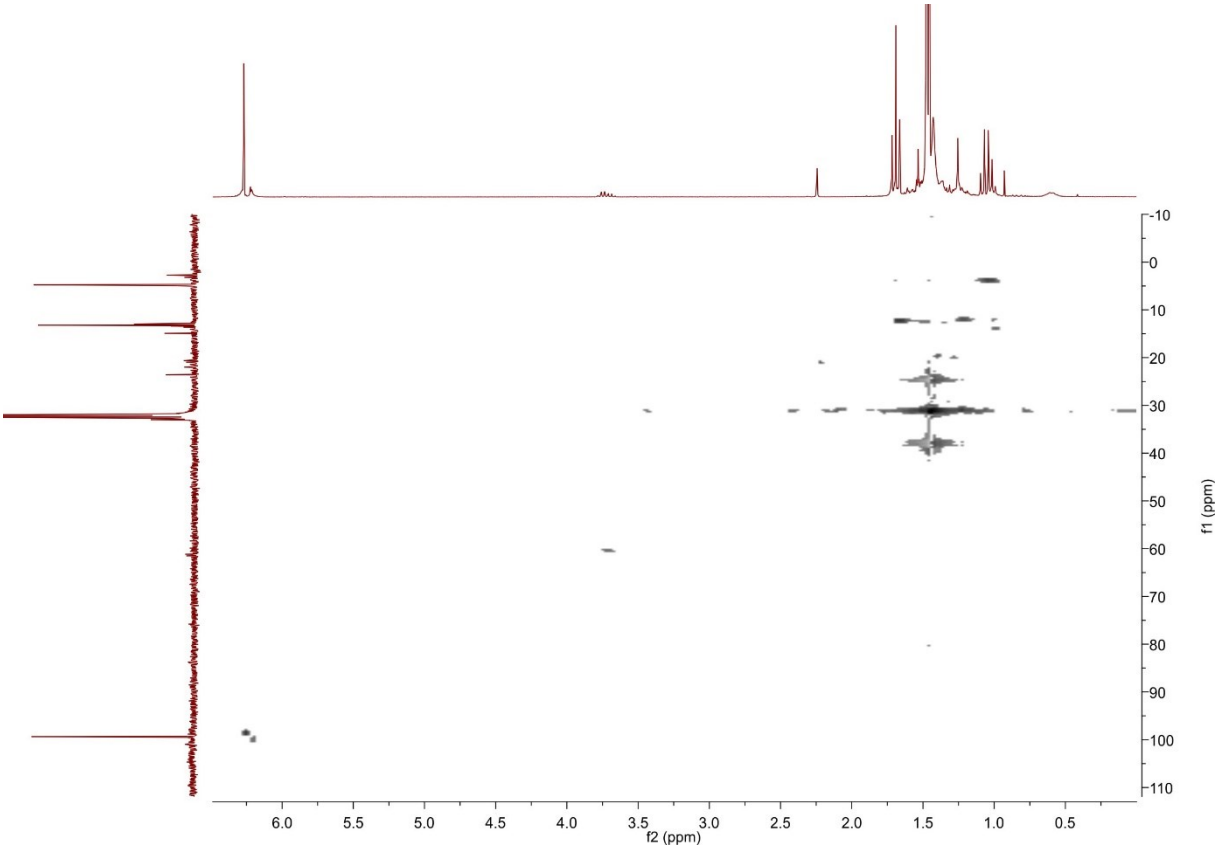

Figure S18. HMQC NMR spectrum of **4** (C_6D_6)

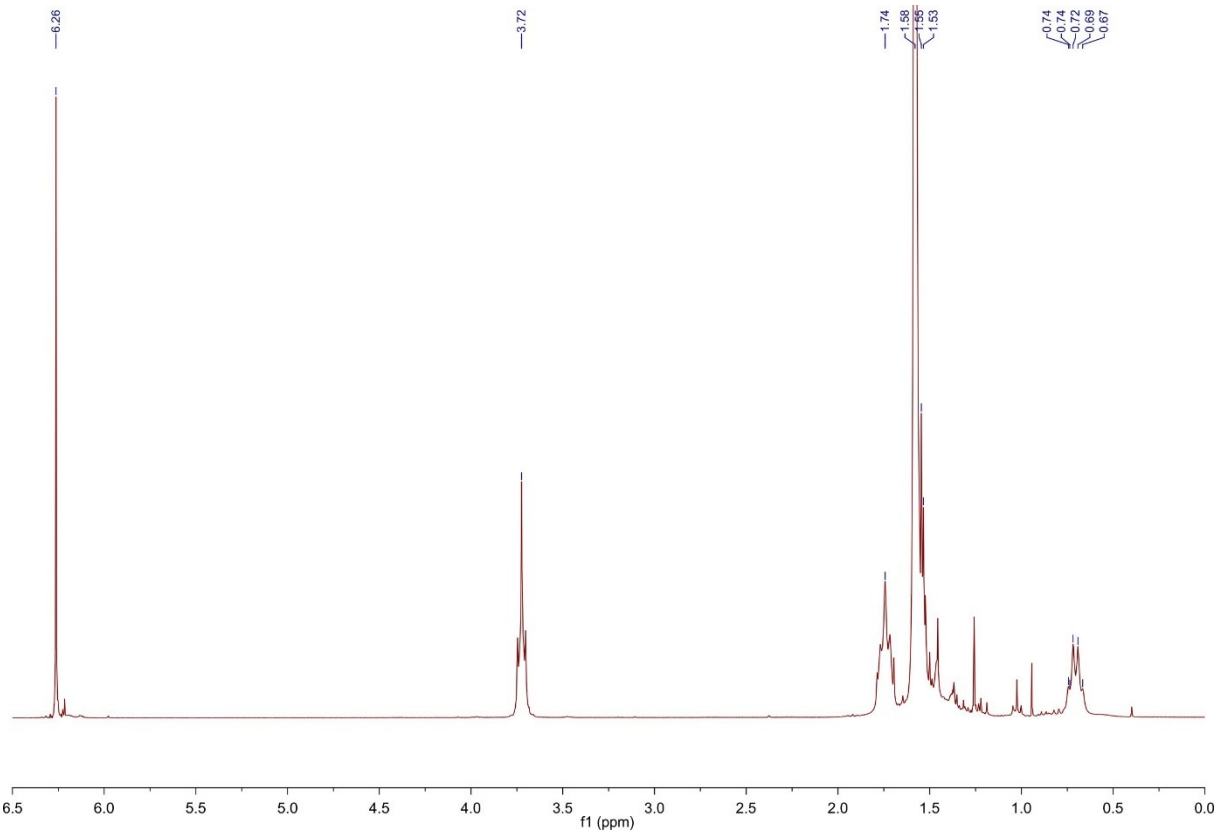

Figure S19. ^{1}H NMR spectrum of compound **5** (C_6D_6).

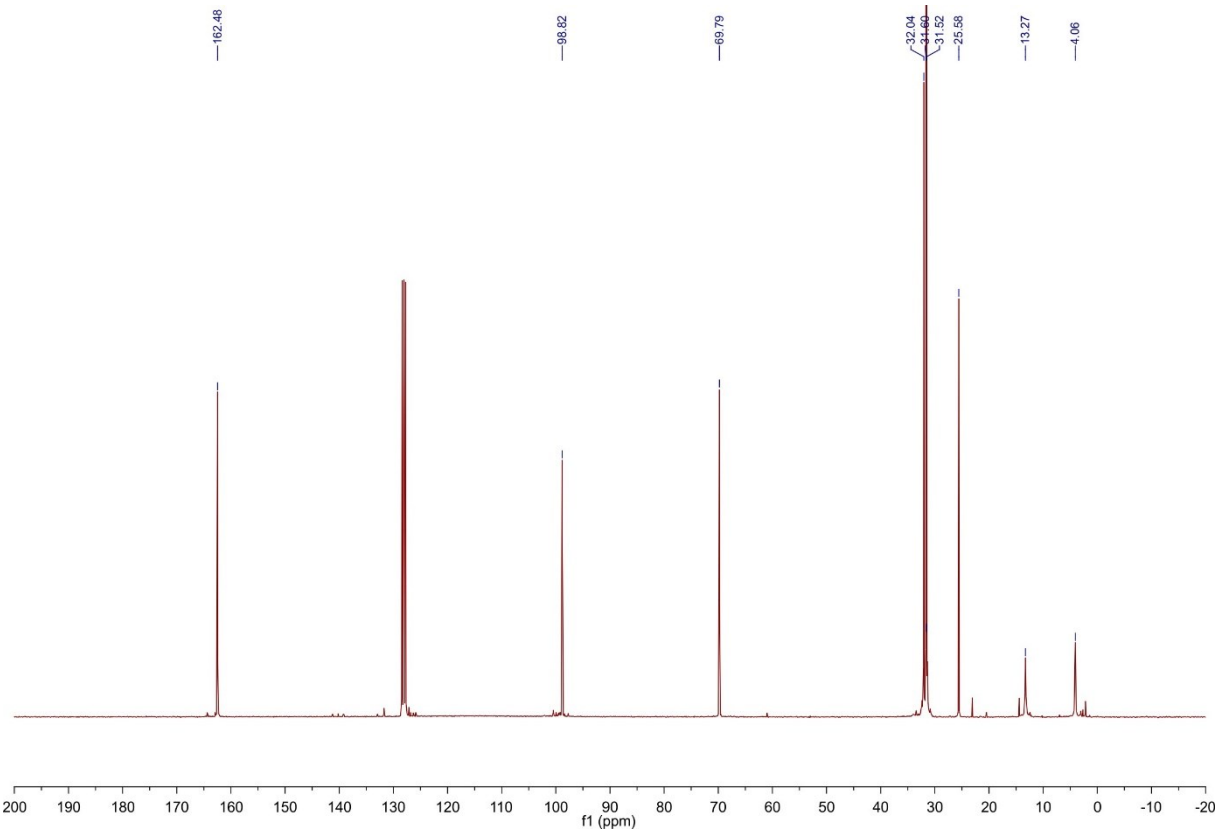

Figure S20. ^{13}C NMR spectrum of compound **5** (C_6D_6).

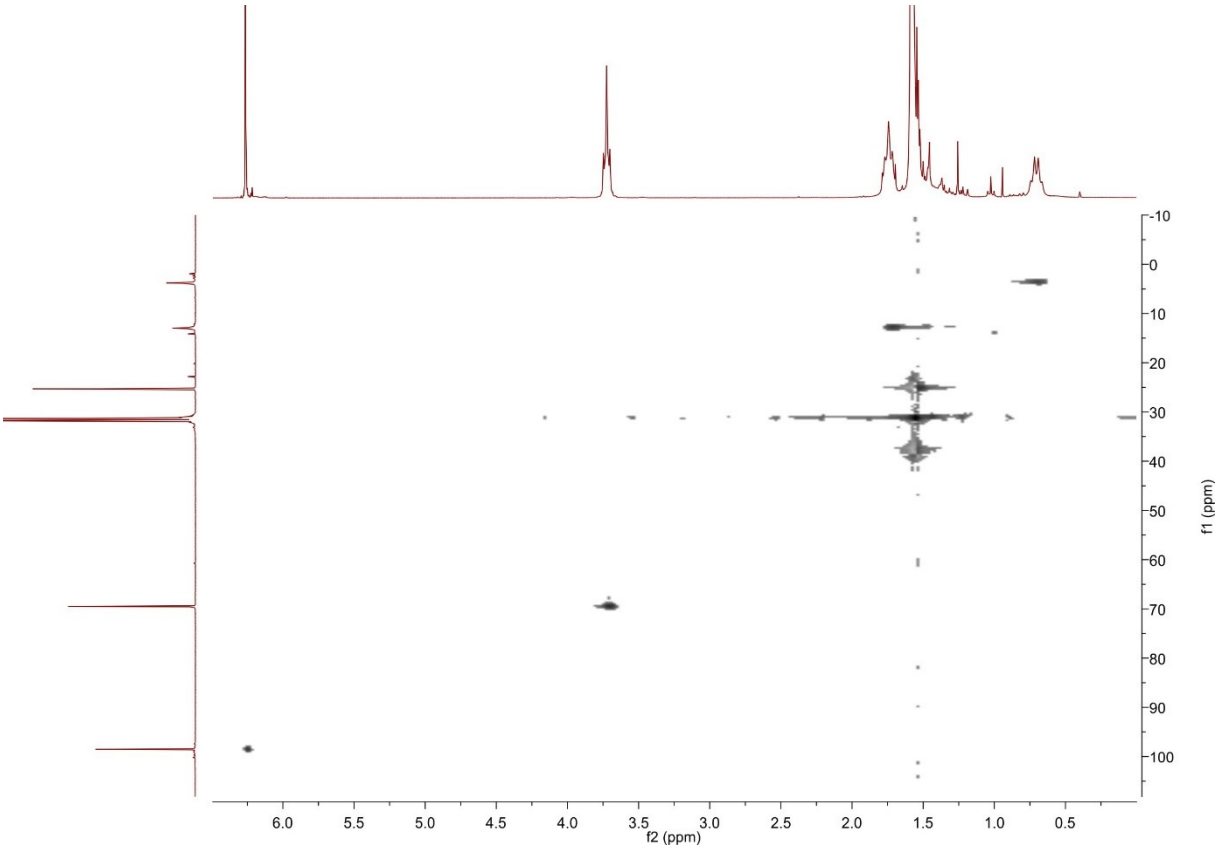

Figure S21. HMQC NMR spectrum of **5** (C_6D_6)

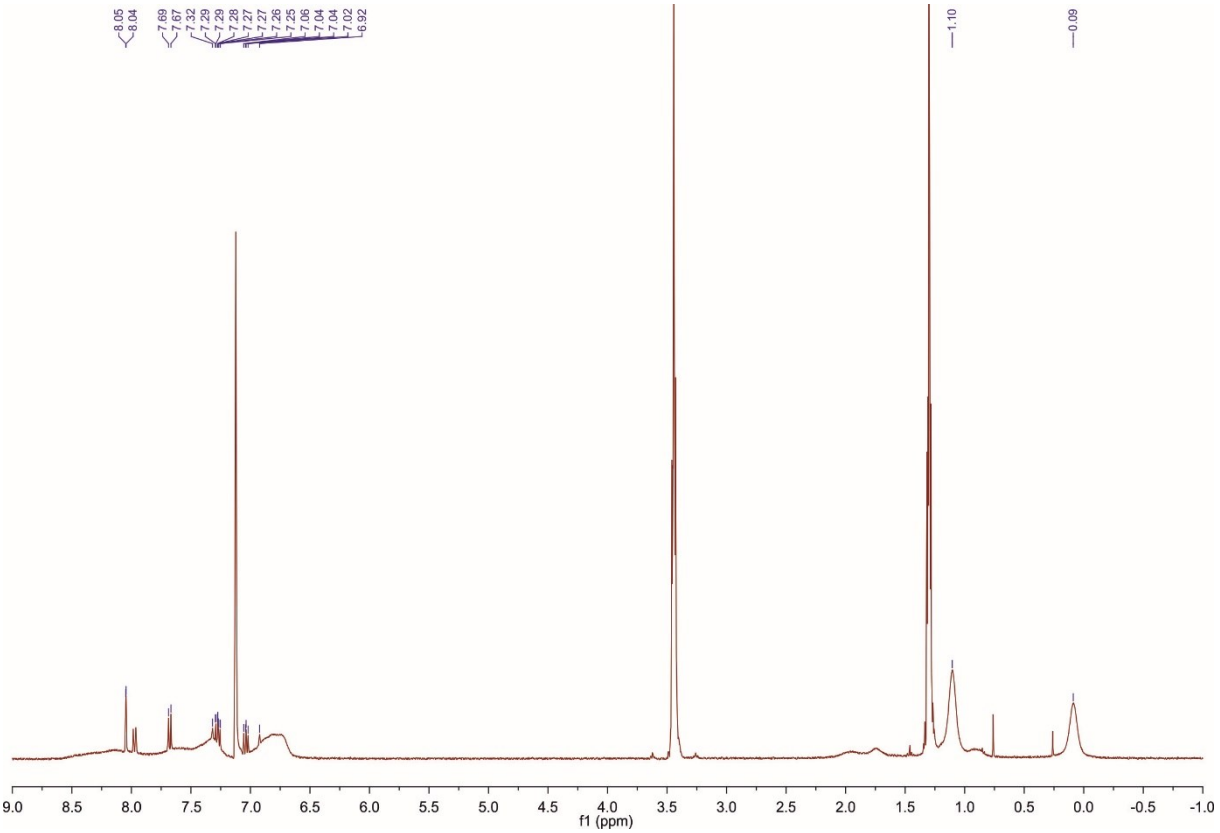

Figure S22. ^{1}H NMR spectrum of compound **6** (C_6D_6).

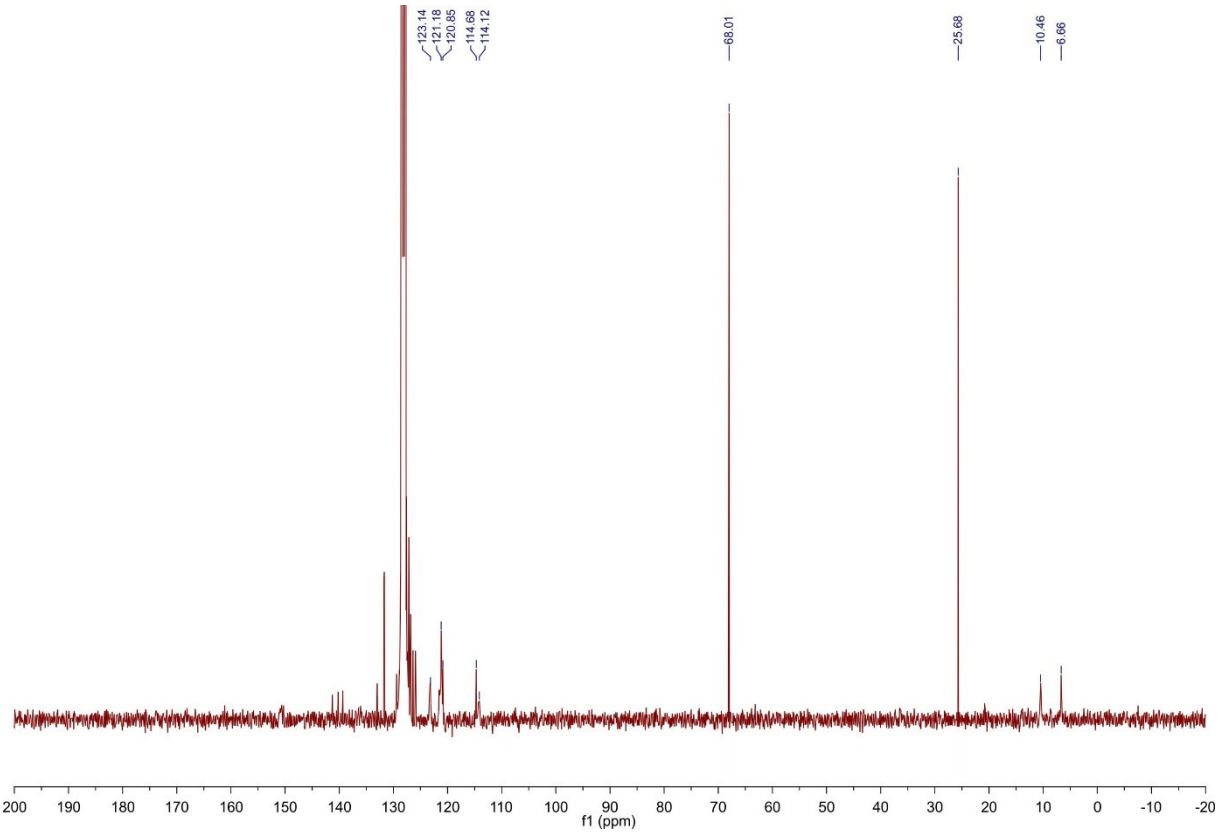

Figure S23. ^{13}C NMR spectrum of compound **6** (C_6D_6).

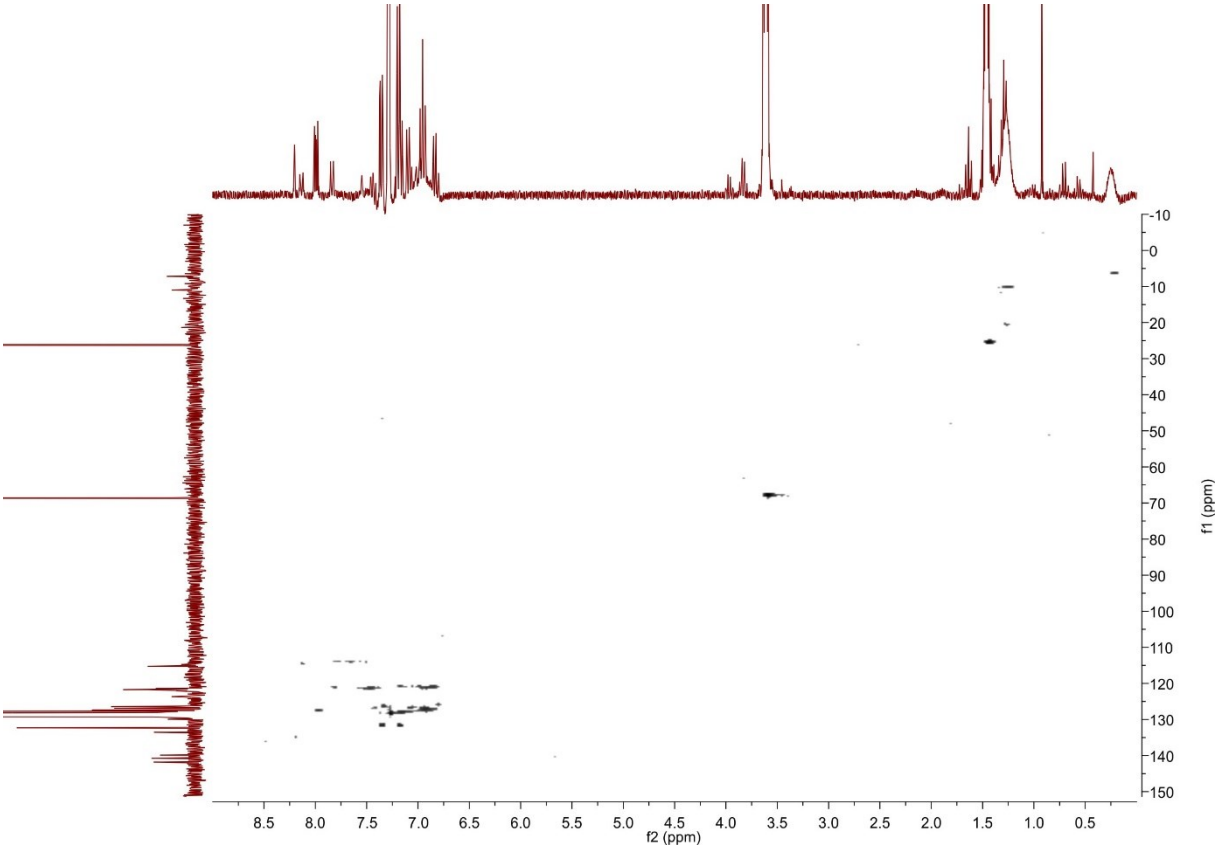

Figure S24. HMQC NMR spectrum of **6** (C_6D_6)

DOSY NMR data processing description

All of the DOSY NMR data processing and analysis was conducted in accordance to the literature reports concerning the usage of the calibration curves of the inert internal standard molecule (1,2,3,4-tetraphenylnaphthalene (TPhN) was selected) in order to accurately determine the molecular weight of the analyte.[4] Moreover, we have applied the van-der-Waals radii-based correction in order to account for the underestimation of MW due to the presence of heavy atoms, according to the literature methods.[5]

Initially the diffusion coefficients (D) of the TPhN reference were identified and averaged. Then for every signal originated from the analyte the normalised diffusion (D_{norm}) coefficient was calculated based on the literature data, followed by the calculation of the molecular weight (MW_{det}) using the external DSE (Dissipated Spheres + Ellipsoids) calibration curve.[4]

The van-der-Waals radii-based correction have been applied to the obtained MW_{det} values following the procedures described in the literature.[5] Initially the potential candidate structures were selected and their Molar van-der-Waals Density MD_W have been calculated. Next the correction factor has been calculated using the calibration curve determined in the previous literature report,[5] which allowed for calculation of the corrected molecular weight values ($MW_{det,corr}$).

The example data illustrating the procedure are provided in Table S1 (for sample DOSY-2).

Table S6. DOSY NMR data processing for sample DOSY-2.

No.	ppm range		D [m^2/s]	log D_{norm}	MW_{det} [g mol^{-1}]	comments
1	7.898	7.825	6.509E-10	-	-	TPhN reference
2	7.277	7.202	6.277E-10	-	-	TPhN reference
3	7.093	7.014	6.398E-10	-	-	TPhN reference
4	7.004	6.930	6.723E-10	-	-	TPhN reference
5	6.879	6.787	6.443E-10	-	-	TPhN reference
6	6.738	6.659	6.478E-10	-	-	TPhN reference
7	3.394	3.251	6.479E-10	-9.166	502	C*H*CH_3 *(pyrazole)*
8	1.739	1.619	6.599E-10	-9.158	487	CH_2CH_3
9	1.338	1.284	6.708E-10	-9.151	474	$CHCH_3$ *(pyrazole)*
10	0.807	0.669	6.688E-10	-9.153	476	CH_2CH_3

References

1 Agilent Technologies, *CrysAlisPro*, Version 1.171.35.21b
2 Z. Otwinowski, W. Minor, *Methods Enzymol*. 1997, **276**, 307-326.
3 Sheldrick, G. M., *Acta Cryst.* 2008, **64A**, 112-122.
4 R. Neufeld and D. Stalke, *Chem. Sci.*, 2015, **6**, 3354–3364.
5 A. K. Kreyenschmidt, S. Bachmann, T. Niklas and D. Stalke, *ChemistrySelect*, 2017, **2**, 6957–6960.