

Supporting Information

Synthesis, structure and properties of neutral energetic materials based on N-functionalization of 3,6-dinitropyrazolo[4,3-c]pyrazole

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1. X-ray crystallography

Single crystals suitable for X-ray measurement were obtained by slow evaporation of aqueous solution of DNPP, **4**, dimethyl formamide solution of **12**, and methanol solution of **15** at room temperature, respectively. Bond lengths, bond angles and torsion angles of the data collection and refinement are given in Table S1–S6. The CIF files of **4**·2H₂O, **12** and **15** have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication 1487948, 1434787, and 1410323.

Table S1. Bond lengths [Å] for the structure of **4**·2H₂O.

O(6)-H(6A)	0.807(18)	N(6)-C(14)	1.361(3)
O(6)-H(6B)	0.811(18)	N(6)-H(6)	0.8600
N(5)-C(15)	1.331(3)	N(1)-O(2)	1.219(2)
N(5)-N(6)	1.346(2)	N(1)-C(15)	1.426(3)
O(3)-N(2)	1.225(2)	N(3)-C(16)	1.361(3)
O(1)-N(1)	1.229(2)	N(3)-H(3)	0.8600
O(4)-N(2)	1.219(2)	C(13)-C(16)#1	1.404(3)
N(4)-C(13)	1.329(3)	C(14)-C(14)#2	1.380(4)
N(4)-N(3)	1.350(2)	C(14)-C(15)#2	1.409(3)
O(5)-H(5A)	0.821(18)	C(15)-C(14)#2	1.409(3)
O(5)-H(5B)	0.825(18)	C(16)-C(16)#1	1.379(4)
N(2)-C(13)	1.436(3)	C(16)-C(13)#1	1.404(3)

Table S2. Bond angles [deg] and torsion angles [deg] for the structure of **4**·2H₂O.

H(6A)-O(6)-H(6B)	109(3)	C(15)-N(5)-N(6)-C(14)	0.0(2)
C(15)-N(5)-N(6)	105.91(17)	C(13)-N(4)-N(3)-C(16)	0.3(2)
C(13)-N(4)-N(3)	105.67(17)	N(3)-N(4)-C(13)-C(16)#1	-0.1(2)
H(5A)-O(5)-H(5B)	103(3)	N(3)-N(4)-C(13)-N(2)	-179.53(18)
O(4)-N(2)-O(3)	124.09(18)	O(4)-N(2)-C(13)-N(4)	2.4(3)
O(4)-N(2)-C(13)	119.59(18)	O(3)-N(2)-C(13)-N(4)	-178.0(2)
O(3)-N(2)-C(13)	116.32(18)	O(4)-N(2)-C(13)-C(16)#1	-177.0(2)
N(5)-N(6)-C(14)	111.01(16)	O(3)-N(2)-C(13)-C(16)#1	2.7(3)
N(5)-N(6)-H(6)	124.5	N(5)-N(6)-C(14)-C(14)#2	0.0(3)
C(14)-N(6)-H(6)	124.5	N(5)-N(6)-C(14)-C(15)#2	179.9(3)
O(2)-N(1)-O(1)	123.94(19)	N(6)-N(5)-C(15)-C(14)#2	-0.1(3)
O(2)-N(1)-C(15)	119.38(18)	N(6)-N(5)-C(15)-N(1)	-179.7(2)
O(1)-N(1)-C(15)	116.68(18)	O(2)-N(1)-C(15)-N(5)	1.1(3)
N(4)-N(3)-C(16)	110.73(16)	O(1)-N(1)-C(15)-N(5)	-179.2(2)
N(4)-N(3)-H(3)	124.6	O(2)-N(1)-C(15)-C(14)#2	-178.4(2)
C(16)-N(3)-H(3)	124.6	O(1)-N(1)-C(15)-C(14)#2	1.3(4)
N(4)-C(13)-C(16)#1	111.81(18)	N(4)-N(3)-C(16)-C(16)#1	-0.4(3)
N(4)-C(13)-N(2)	120.11(18)	N(4)-N(3)-C(16)-C(13)#1	-179.8(3)
C(16)#1-C(13)-N(2)	128.08(19)		
N(6)-C(14)-C(14)#2	107.7(2)		

N(6)-C(14)-C(15)#2	148.24(19)
C(14)#2-C(14)-C(15)#2	104.1(2)
N(5)-C(15)-C(14)#2	111.31(18)
N(5)-C(15)-N(1)	120.81(19)
C(14)#2-C(15)-N(1)	127.88(19)
N(3)-C(16)-C(16)#1	107.9(2)
N(3)-C(16)-C(13)#1	148.21(19)
C(16)#1-C(16)-C(13)#1	103.9(2)

Symmetry transformations used to generate equivalent atoms: #1 -x, -y+2, -z+1; #2 -x, -y+1, -z+2

Table S3. Bond lengths [\AA] for the structure of **12**.

N(1)-O(1)	1.215(3)	N(3)-N(4)	1.396(3)
N(1)-O(2)	1.227(3)	N(4)-H(4A)	0.8600
N(1)-C(1)	1.425(3)	N(4)-H(4B)	0.8600
N(2)-C(1)	1.330(3)	C(1)-C(2)#1	1.403(3)
N(2)-N(3)	1.339(3)	C(2)-C(2)#1	1.380(5)
N(3)-C(2)	1.365(3)	C(2)-C(1)#1	1.403(3)

Table S4. Bond angles [deg] and torsion angles [deg] for the structure of **12**.

O(1)-N(1)-O(2)	124.2(2)	C(1)-N(2)-N(3)-C(2)	-0.4(3)
O(1)-N(1)-C(1)	120.1(2)	C(1)-N(2)-N(3)-N(4)	-176.9(2)
O(2)-N(1)-C(1)	115.7(2)	N(3)-N(2)-C(1)-C(2)#1	0.2(3)
C(1)-N(2)-N(3)	105.8(2)	N(3)-N(2)-C(1)-N(1)	-179.9(2)
N(2)-N(3)-C(2)	111.48(19)	O(1)-N(1)-C(1)-N(2)	2.7(4)
)		
N(2)-N(3)-N(4)	118.6(2)	O(2)-N(1)-C(1)-N(2)	-177.9(2)
C(2)-N(3)-N(4)	129.8(2)	O(1)-N(1)-C(1)-C(2)#1	-177.4(2)
N(3)-N(4)-H(4A)	120.0	O(2)-N(1)-C(1)-C(2)#1	2.0(4)
N(3)-N(4)-H(4B)	120.0	N(2)-N(3)-C(2)-C(2)#1	0.4(3)
H(4A)-N(4)-H(4B)	120.0	N(4)-N(3)-C(2)-C(2)#1	176.4(3)
N(2)-C(1)-C(2)#1	111.3(2)	N(2)-N(3)-C(2)-C(1)#1	180.0(3)
N(2)-C(1)-N(1)	121.1(2)	N(4)-N(3)-C(2)-C(1)#1	-4.0(6)
C(2)#1-C(1)-N(1)	127.6(2)		
N(3)-C(2)-C(2)#1	106.9(3)		
N(3)-C(2)-C(1)#1	148.6(2)		
C(2)#1-C(2)-C(1)#1	104.5(3)		

Symmetry transformations used to generate equivalent atoms: #1 -x+2, -y, -z+1

Table S5. Bond lengths [\AA] for the structure of **15**.

N(1)-O(1)	1.219(7)	N(7)-C(6)	1.331(7)
N(1)-O(2)	1.230(7)	N(8)-O(9)	1.212(7)
N(1)-C(1)	1.434(8)	N(8)-O(10)	1.225(7)
N(2)-C(1)	1.315(7)	N(8)-C(6)	1.441(8)

N(2)-N(3)	1.346(6)	O(3)-C(3)	1.435(8)
N(3)-C(2)	1.375(7)	O(8)-C(4)	1.430(7)
N(3)-C(3)	1.436(7)	C(1)-C(2)#1	1.397(8)
N(4)-O(4)	1.091(9)	C(2)-C(2)#1	1.375(11)
)	
N(4)-O(5)	1.163(10)	C(2)-C(1)#1	1.397(8)
N(4)-O(3)	1.414(9)	C(3)-H(3A)	0.9700
N(5)-O(6)	1.175(8)	C(3)-H(3B)	0.9700
N(5)-O(7)	1.198(8)	C(4)-H(4A)	0.9700
N(5)-O(8)	1.405(8)	C(4)-H(4B)	0.9700
N(6)-N(7)	1.338(7)	C(5)-C(5)#2	1.365(11)
)	
N(6)-C(5)	1.369(7)	C(5)-C(6)#2	1.398(8)
N(6)-C(4)	1.430(7)	C(6)-C(5)#2	1.398(8)

Table S6. Bond angles [deg] and torsion angles [deg] for the structure of **15**.

O(1)-N(1)-O(2)	124.3(5)	C(1)-N(2)-N(3)-C(2)	-1.7(7)
O(1)-N(1)-C(1)	120.0(6)	C(1)-N(2)-N(3)-C(3)	-173.9(5)
O(2)-N(1)-C(1)	115.6(5)	C(5)-N(6)-N(7)-C(6)	-0.9(6)
C(1)-N(2)-N(3)	107.0(5)	C(4)-N(6)-N(7)-C(6)	-174.3(5)
N(2)-N(3)-C(2)	109.7(4)	O(4)-N(4)-O(3)-C(3)	178.9(8)
N(2)-N(3)-C(3)	119.8(5)	O(5)-N(4)-O(3)-C(3)	-3.4(10)
C(2)-N(3)-C(3)	130.0(5)	O(6)-N(5)-O(8)-C(4)	-5.0(8)
O(4)-N(4)-O(5)	131.8(12)	O(7)-N(5)-O(8)-C(4)	176.1(6)
O(4)-N(4)-O(3)	119.2(10)	N(3)-N(2)-C(1)-C(2)#1	1.0(7)
O(5)-N(4)-O(3)	109.0(9)	N(3)-N(2)-C(1)-N(1)	177.7(6)
O(6)-N(5)-O(7)	130.6(8)	O(1)-N(1)-C(1)-N(2)	-2.9(11)
O(6)-N(5)-O(8)	119.4(6)	O(2)-N(1)-C(1)-N(2)	177.3(7)
O(7)-N(5)-O(8)	110.0(7)	O(1)-N(1)-C(1)-C(2)#1	173.1(7)
N(7)-N(6)-C(5)	110.6(5)	O(2)-N(1)-C(1)-C(2)#1	-6.7(11)
N(7)-N(6)-C(4)	118.5(4)	N(2)-N(3)-C(2)-C(2)#1	1.7(8)
C(5)-N(6)-C(4)	130.5(5)	C(3)-N(3)-C(2)-C(2)#1	172.9(6)
C(6)-N(7)-N(6)	106.2(4)	N(2)-N(3)-C(2)-C(1)#1	179.8(9)
O(9)-N(8)-O(10)	124.7(6)	C(3)-N(3)-C(2)-C(1)#1	-9.0(14)
O(9)-N(8)-C(6)	120.8(6)	N(2)-N(3)-C(3)-O(3)	-124.3(6)
O(10)-N(8)-C(6)	114.5(6)	C(2)-N(3)-C(3)-O(3)	65.2(9)
N(4)-O(3)-C(3)	114.5(6)	N(4)-O(3)-C(3)-N(3)	89.6(7)
N(5)-O(8)-C(4)	113.1(5)	N(7)-N(6)-C(4)-O(8)	-117.9(6)
N(2)-C(1)-C(2)#1	111.3(5)	C(5)-N(6)-C(4)-O(8)	70.2(7)
N(2)-C(1)-N(1)	119.9(5)	N(5)-O(8)-C(4)-N(6)	78.1(6)
C(2)#1-C(1)-N(1)	128.7(6)	N(7)-N(6)-C(5)-C(5)#2	1.4(7)
C(2)#1-C(2)-N(3)	107.4(6)	C(4)-N(6)-C(5)-C(5)#2	173.8(6)
C(2)#1-C(2)-C(1)#1	104.7(6)	N(7)-N(6)-C(5)-C(6)#2	179.1(8)
N(3)-C(2)-C(1)#1	148.0(5)	C(4)-N(6)-C(5)-C(6)#2	-8.5(13)

N(3)-C(3)-O(3)	113.9(5)	N(6)-N(7)-C(6)-C(5)#2	0.1(6)
N(3)-C(3)-H(3A)	108.8	N(6)-N(7)-C(6)-N(8)	178.1(5)
O(3)-C(3)-H(3A)	108.8	O(9)-N(8)-C(6)-N(7)	-7.7(9)
N(3)-C(3)-H(3B)	108.8	O(10)-N(8)-C(6)-N(7)	174.0(6)
O(3)-C(3)-H(3B)	108.8	O(9)-N(8)-C(6)-C(5)#2	169.9(6)
H(3A)-C(3)-H(3B)	107.7	O(10)-N(8)-C(6)-C(5)#2	-8.4(10)
N(6)-C(4)-O(8)	112.4(4)		
N(6)-C(4)-H(4A)	109.1		
O(8)-C(4)-H(4A)	109.1		
N(6)-C(4)-H(4B)	109.1		
O(8)-C(4)-H(4B)	109.1		
H(4A)-C(4)-H(4B)	107.9		
C(5)#2-C(5)-N(6)	107.4(6)		
C(5)#2-C(5)-C(6)#2	104.9(6)		
N(6)-C(5)-C(6)#2	147.7(6)		
N(7)-C(6)-C(5)#2	110.9(5)		
N(7)-C(6)-N(8)	119.2(5)		
C(5)#2-C(6)-N(8)	129.9(6)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1; #2 -x, -y, -z

2. NMR spectra of all compounds

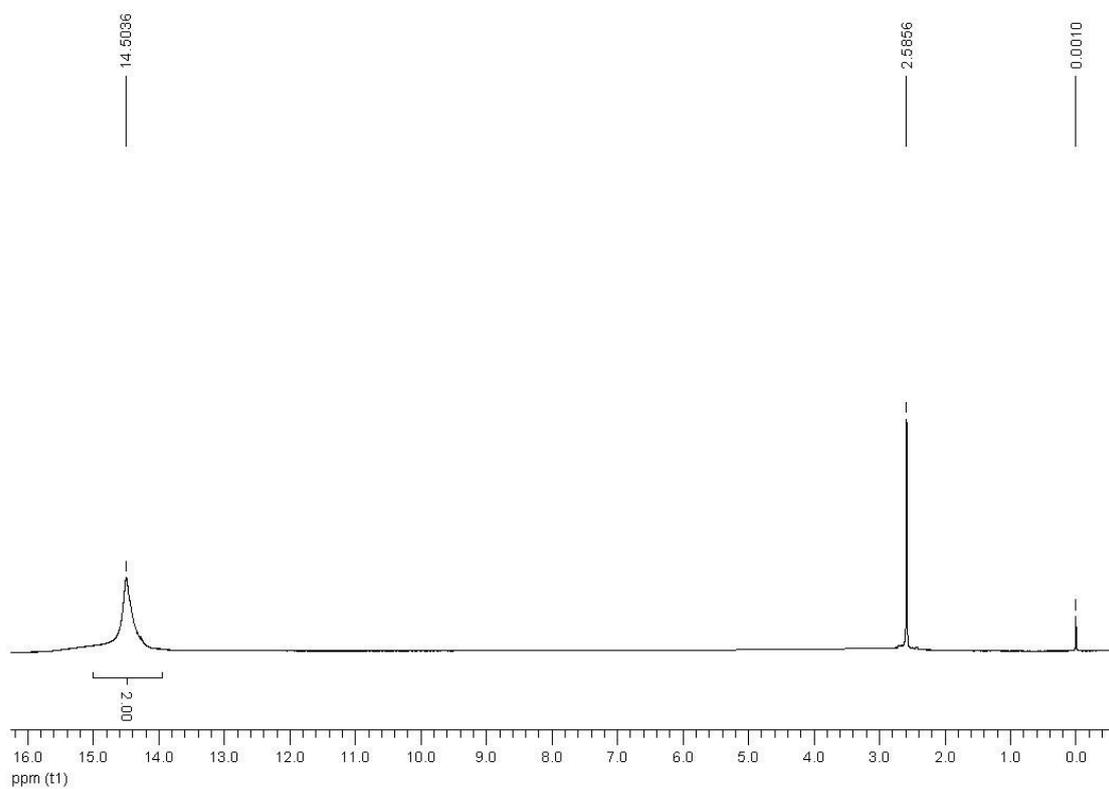


Fig. S1 ^1H NMR spectrum of **4** in $\text{DMSO-}d_6$

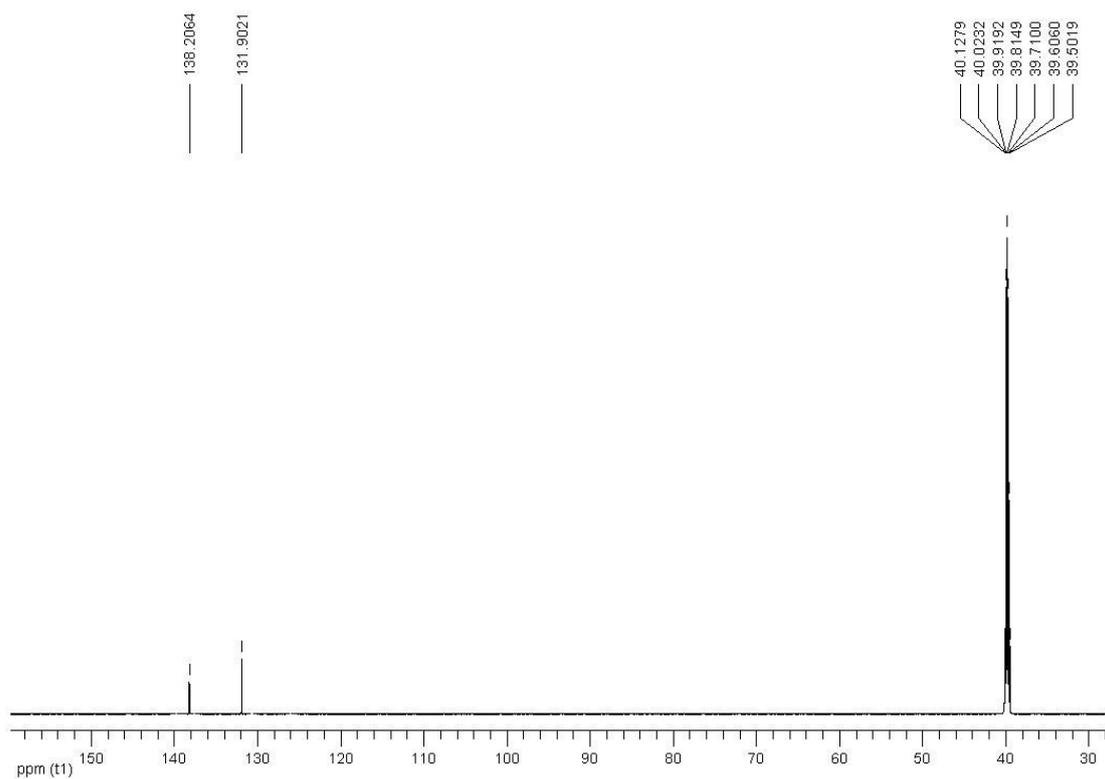


Fig. S2 ^{13}C NMR spectrum of **4** in $\text{DMSO-}d_6$

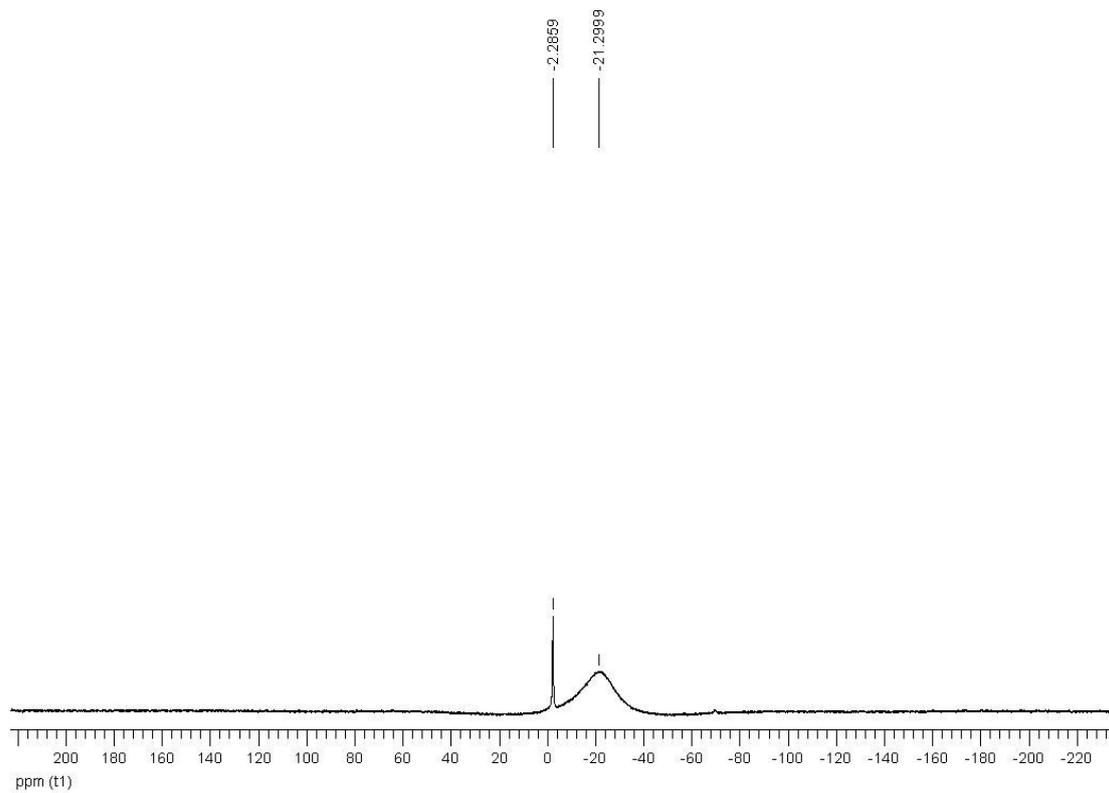


Fig. S3 ^{14}N NMR spectrum of **4** in $\text{DMSO-}d_6$

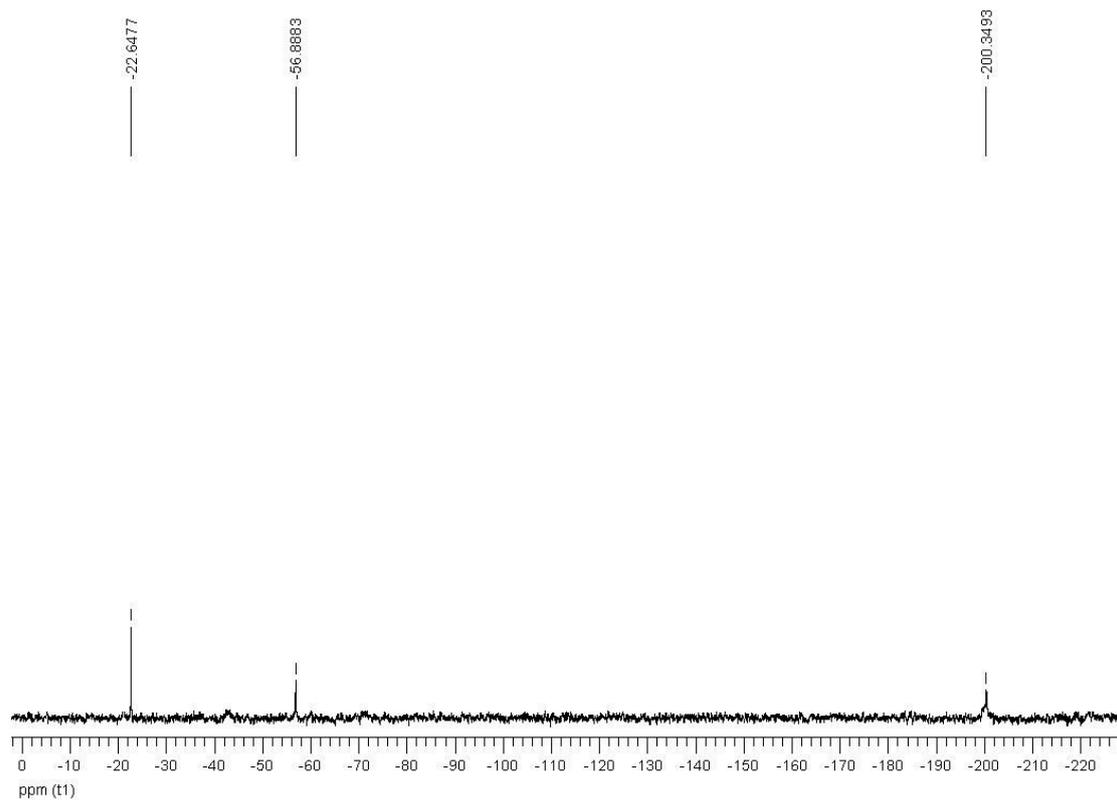


Fig. S4 ¹⁵N NMR spectrum of **4** in DMSO-*d*₆

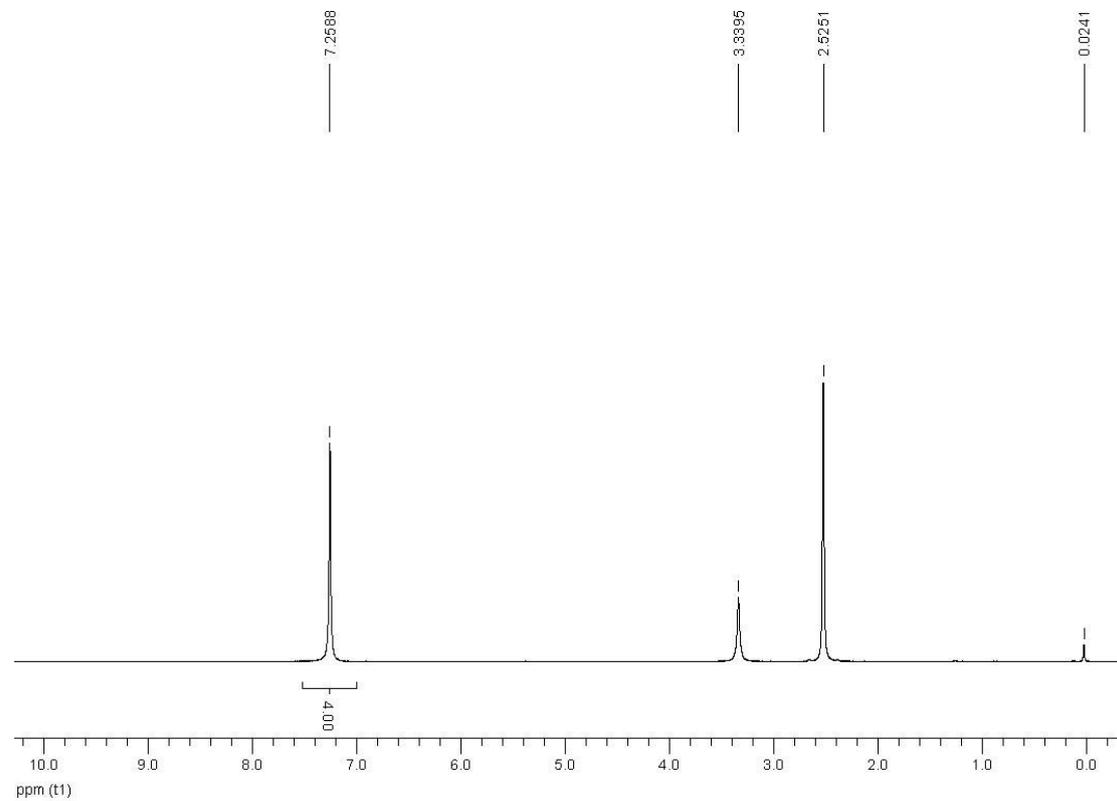


Fig. S5 ¹H NMR spectrum of **12** in DMSO-*d*₆

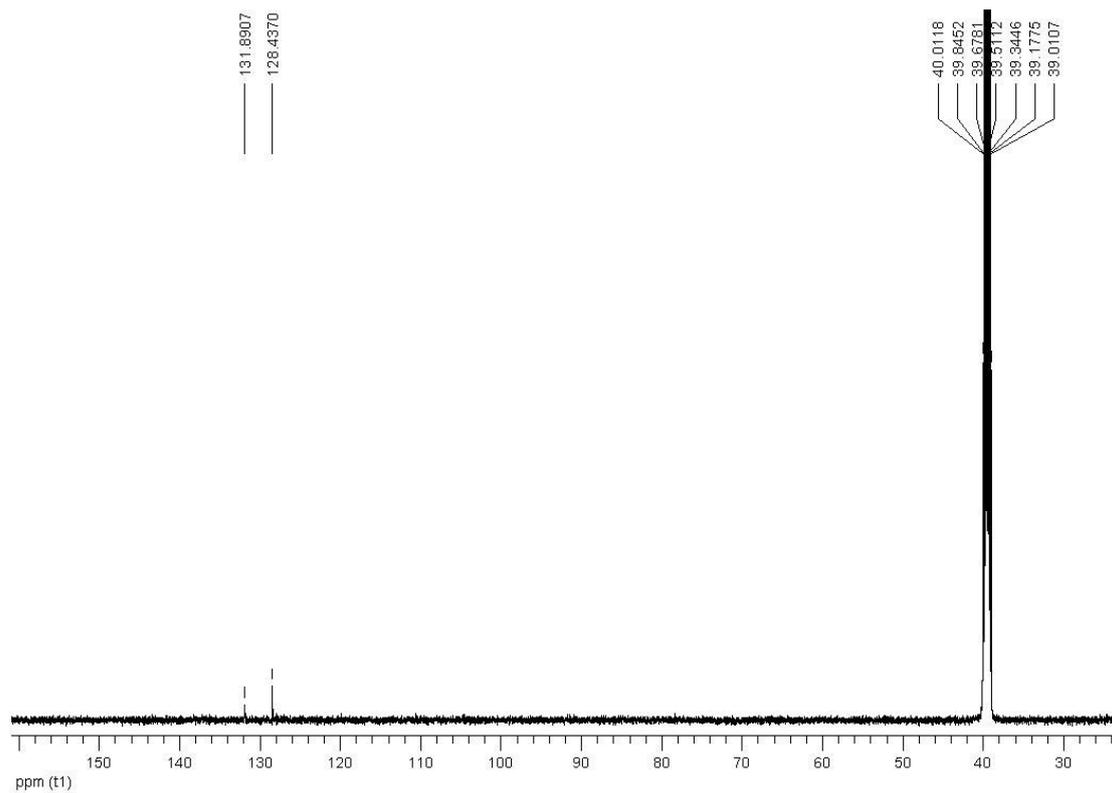


Fig. S6 ^{13}C NMR spectrum of **12** in $\text{DMSO-}d_6$

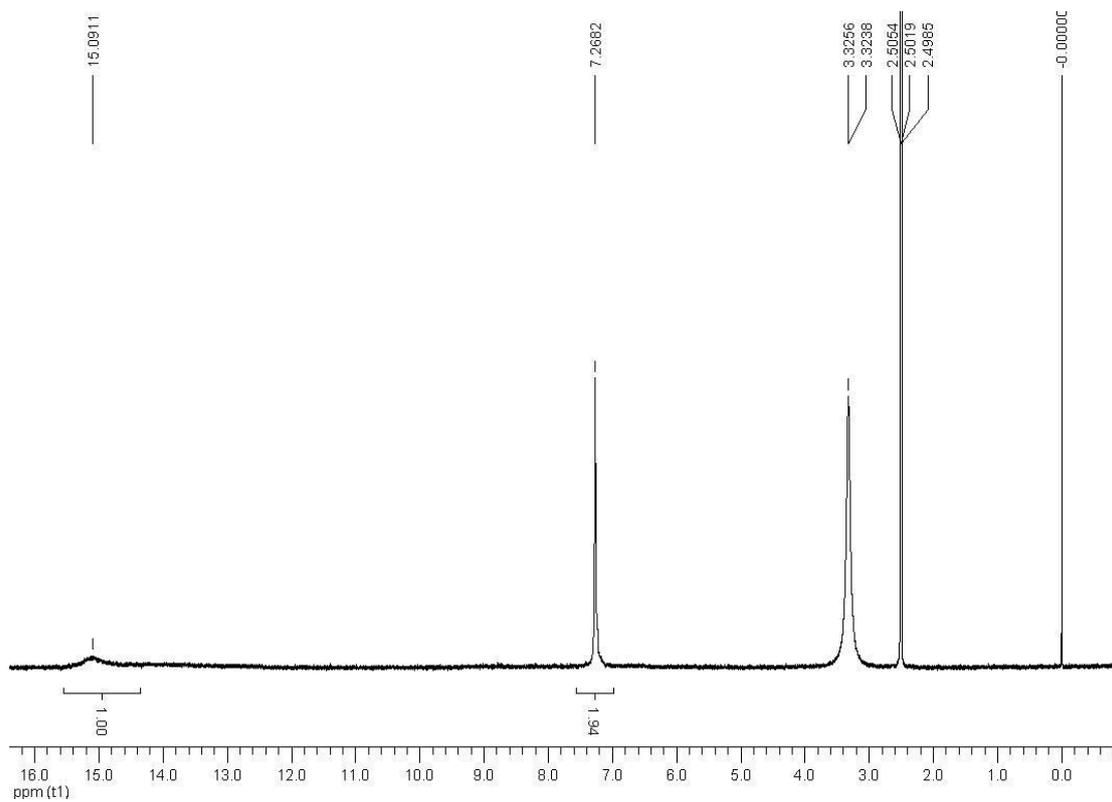


Fig. S7 ^1H NMR spectrum of **13** in $\text{DMSO-}d_6$

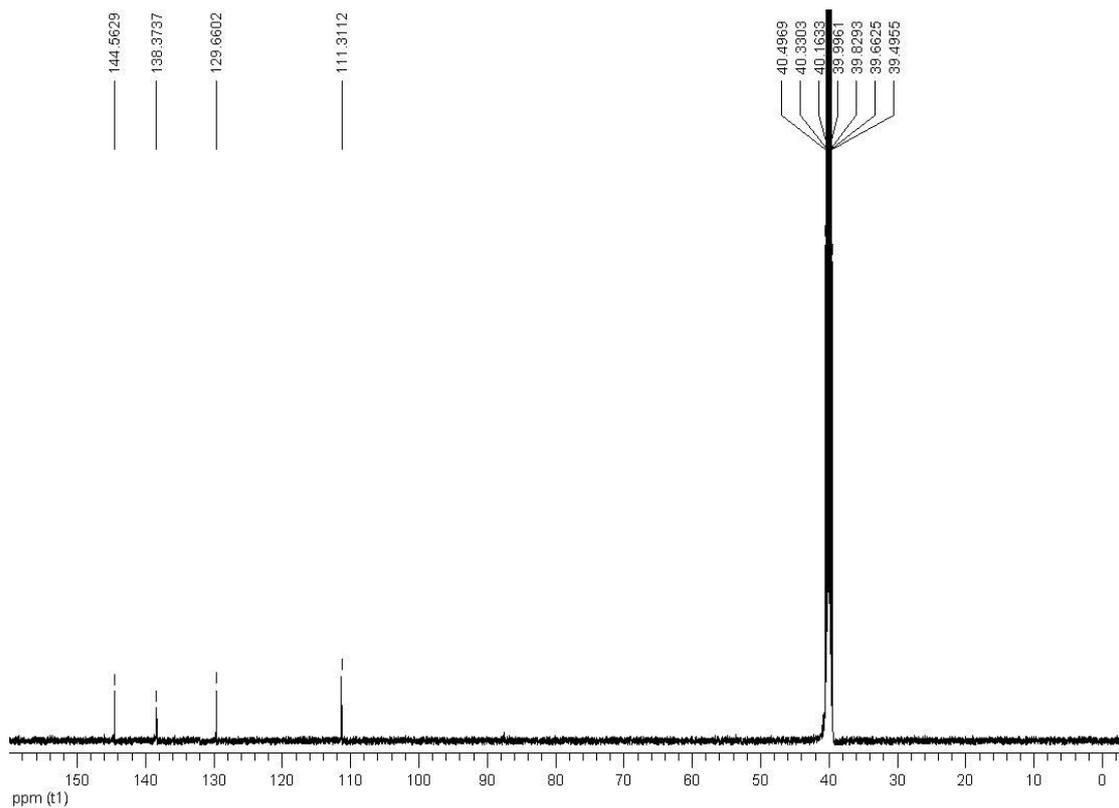


Fig. S8 ^{13}C NMR spectrum of **13** in $\text{DMSO-}d_6$

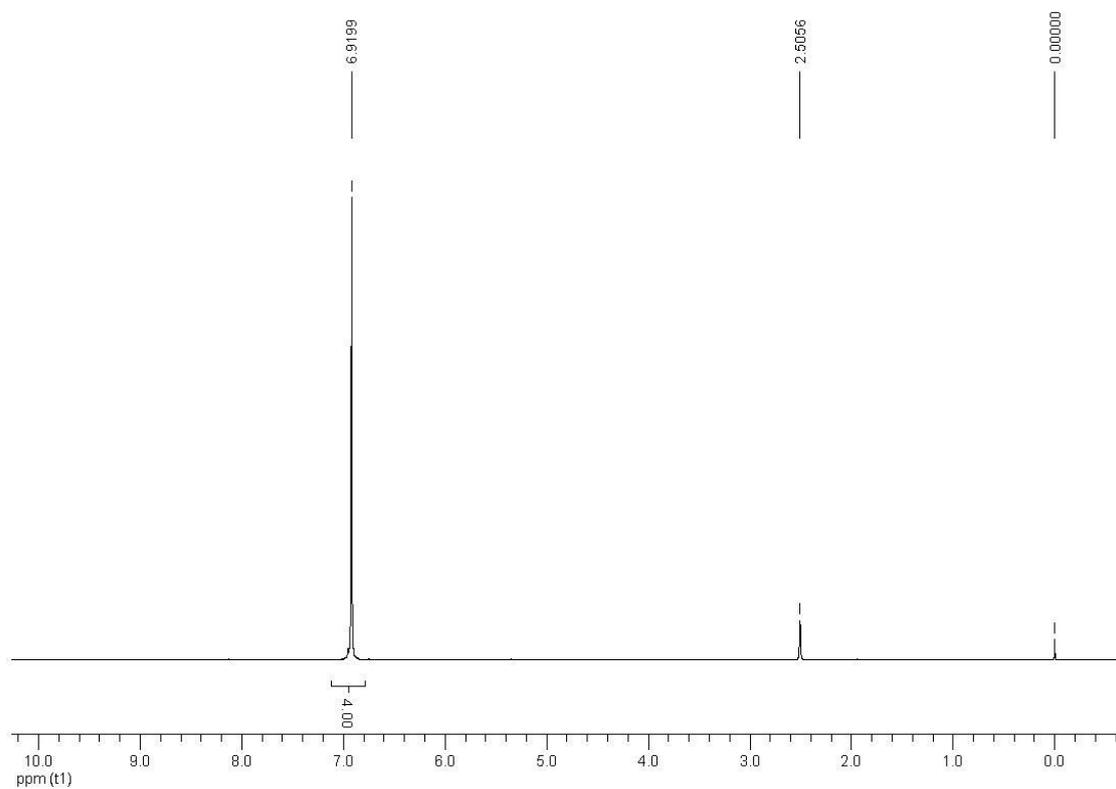


Fig. S9 ^1H NMR spectrum of **15** in $\text{DMSO-}d_6$

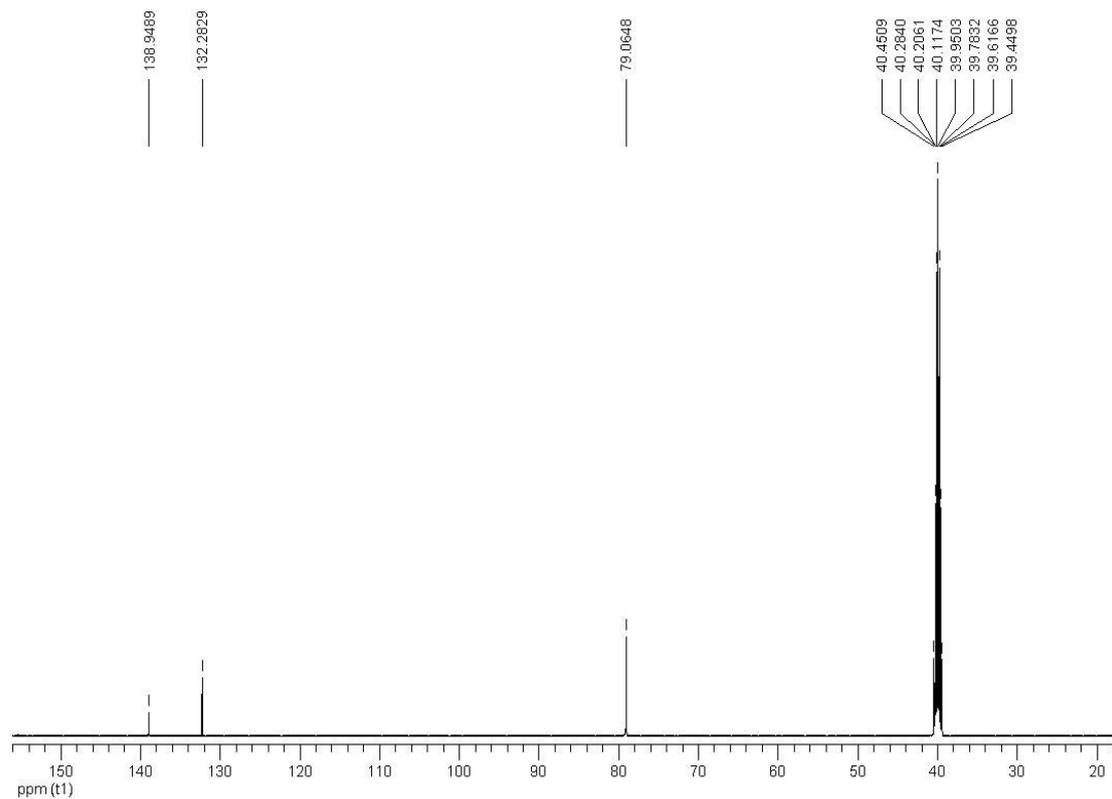


Fig. S10 ^{13}C NMR spectrum of **15** in $\text{DMSO-}d_6$

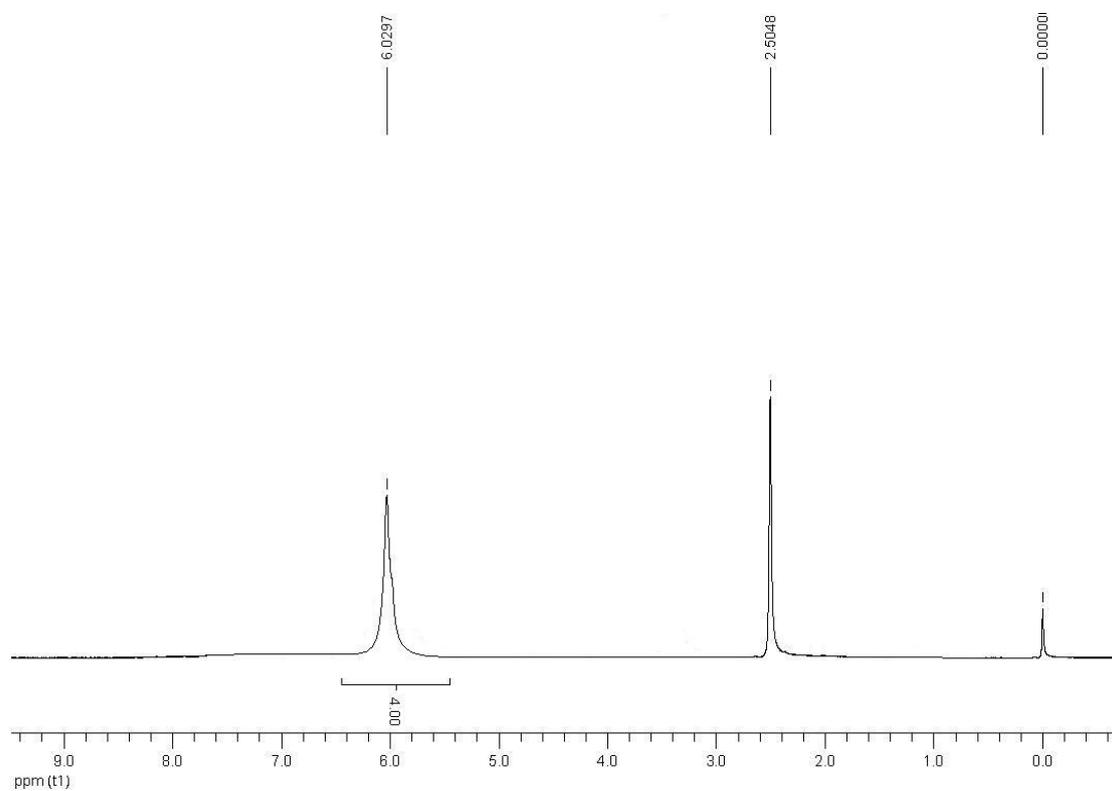


Fig. S11 ^1H NMR spectrum of **17** in $\text{DMSO-}d_6$

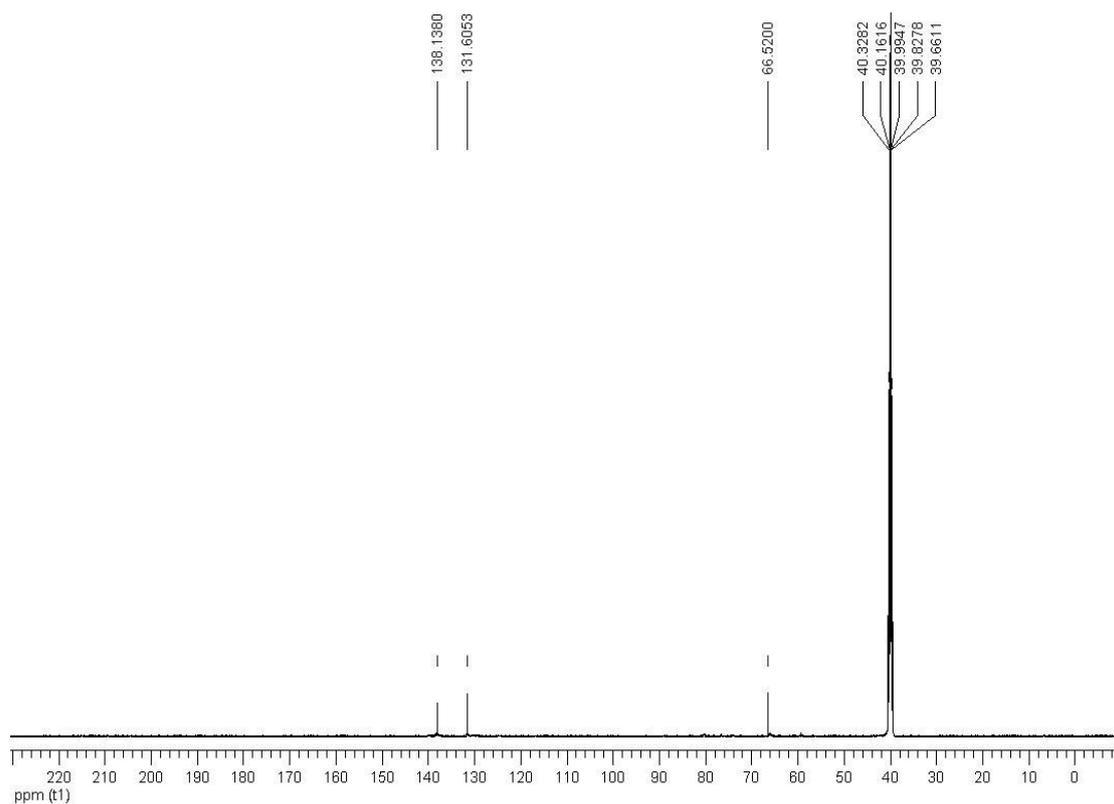


Fig. S12 ^{13}C NMR spectrum of **17** in $\text{DMSO-}d_6$

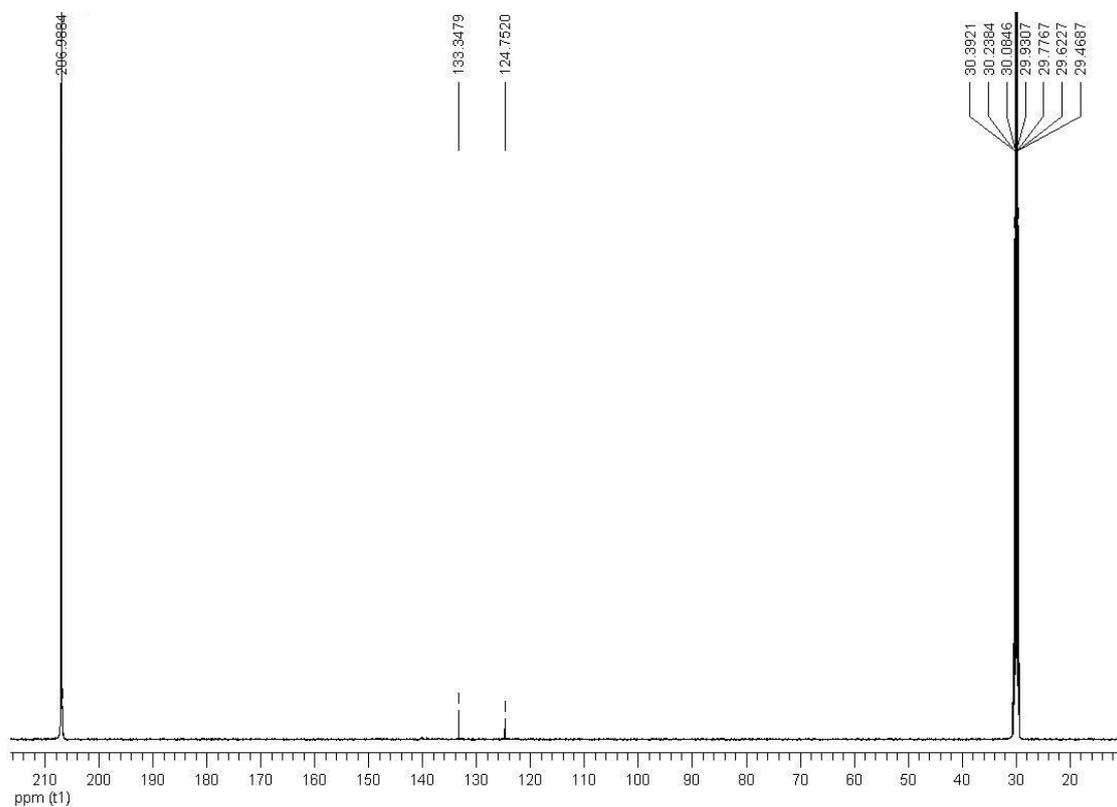


Fig. S13 ^{13}C NMR spectrum of **18** in CD_3CN

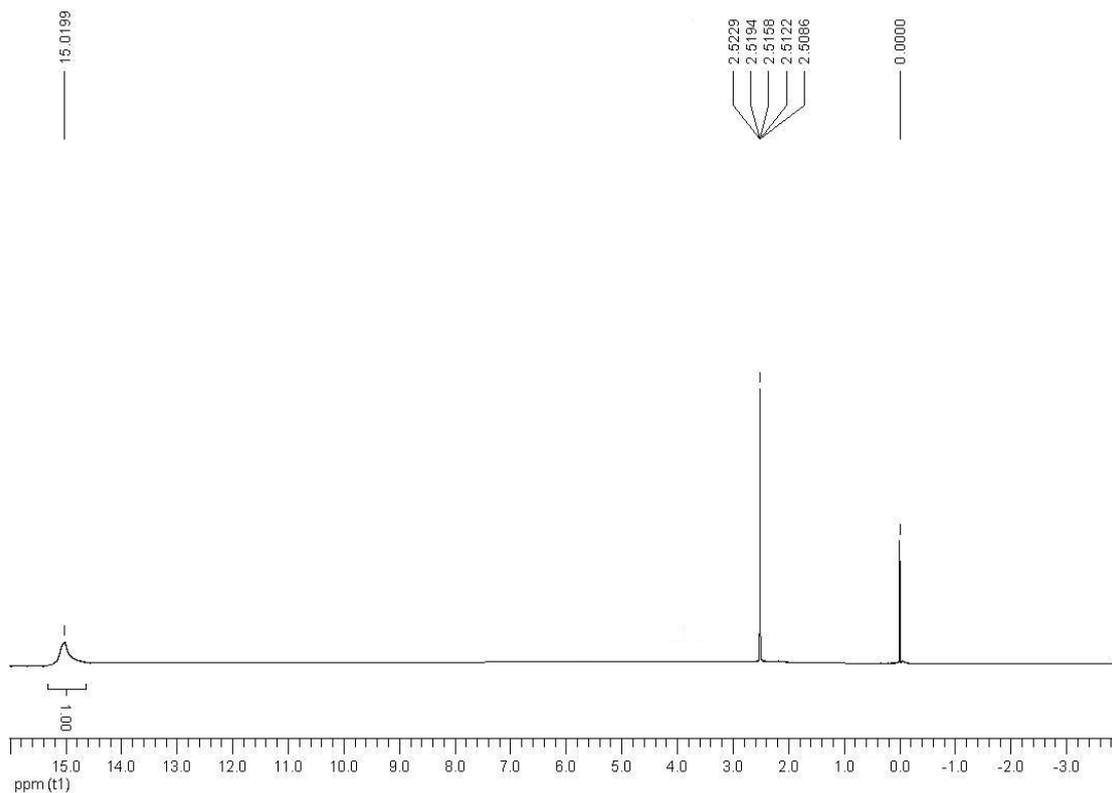


Fig. S14 ^1H NMR spectrum of **20** in $\text{DMSO-}d_6$

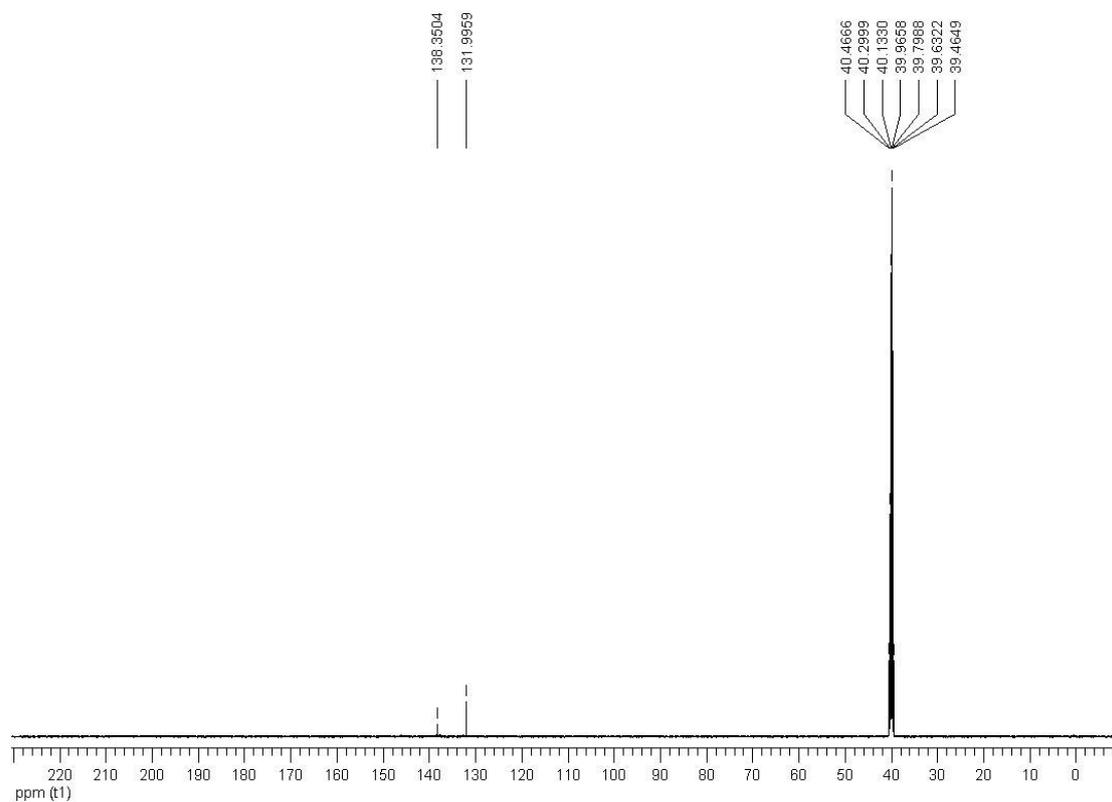


Fig. S15 ^{13}C NMR spectrum of **20** in $\text{DMSO-}d_6$

3. Theoretical study

All quantum chemical calculations were carried out by using the Gaussian 09 (revision A.02) program package and visualized by Gauss View 5.05.^{1,2} The gas phase enthalpies of formation (Table S7) were obtained by the atomization method (equation (1)) based on CBS-4M calculated electronic enthalpies using NIST³ values as standardized values for the standard heats of formation ($\Delta_f H^\circ$) (Table S8).

$$\Delta_f H^\circ_{(g, M, 298)} = H_{(Molecule, 298)} - \sum H^\circ_{(Atoms, 298)} + \sum \Delta_f H^\circ_{(Atoms, 298)} \quad (1)$$

The solid state enthalpies of formation (Table S7) can be determined using the gas-phase enthalpy of formation and enthalpy of sublimation phase transition according to the Hess' law of constant heat summation as the equation (2).⁴

$$\Delta H(\text{solid}) = \Delta H(\text{gas}) - \Delta H(\text{sublimation}) \quad (2)$$

Based on the electrostatic potential of a molecule by quantum mechanical prediction, the heat of sublimation can be represented as the equation (3).⁵

$$\Delta H(\text{sublimation}) = a(SA)^2 + b(\sigma_{Tot}^2 \nu)^{1/2} + c \quad (3)$$

Table S7. Heat of formation based on CBS-4M calculations

Compound	$-H_{(M, 298)}^{[a]}$ / a.u.	$\Delta_f H^\circ_{(g)}^{[b]}$ / kJ mol ⁻¹	SA ^[c] / Å ²	$\sigma_{Tot}^2 \nu^{[d]}$ / (kcal mol ⁻¹) ²	$\Delta H^\circ_{(sub)}^{[e]}$ / kJ mol ⁻¹	$\Delta_f H^\circ_{(s)}^{[f]}$ / kJ mol ⁻¹
12	892.312186	591.99	209.44	37.05	131.75	460.25
13	837.067508	482.04	198.20	42.60	126.535	355.51
15	1419.085466	229.89	301.14	20.65	211.115	18.78
17	1187.063864	1056.07	280.96	27.00	193.55	862.52
18	1190.309466	621.85	237.13	20.62	142.61	479.24
20	931.991124	382.77	199.22	24.50	113.36	269.41

[a] CBS-4M electronic enthalpy; [b] gas phase enthalpy of formation; [c] surface area; [d] electrostatic potential of the molecular surface; [e] heat of sublimation based on B3PW91/6-31G(d,p) level; [f] standard solid state enthalpy of formation.

Table S8. CBS-4M values and literature values for atomic $\Delta_f H^\circ$ / kJ mol⁻¹

	$-H^{298}$ / a.u.	NIST ^[5] / $\Delta_f H^\circ_{(298K)}$
H	0.500991	218.2
C	37.786156	717.2
N	54.522462	473.1
O	74.991202	249.5
K	599.187712	89.01

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