Electronic Supplementary Information

Triazole-Induced Planarization of A Twisted Tetrazole-based Molecule towards Energetic Materials With Improved Thermostability and Insensitivity

Zhaoyang Yin, [1a] Lijincao Hu, [1a] Wei Huang, [*a] Yuji Liu and Yongxing Tang [*a]

[a] School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094 (China). E-mail: huang_wei@njust.edu.cn, yongxing@njust.edu.cn.

[1] These authors contributed equally to this work.

Crystal structure analysis

Table S1. Crystallographic data and structure determination details for **3**·DMF and **4**·H_2O.

Parameters	**3**·DMF	**4**·H_2O
CCDC	2241992	2241993
$D_{calc.}$ (g cm^{-3})	1.610	1.729
T (K)	193	193
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	Cc
a (Å)	3.7982(3)	3.66370(10)
b (Å)	25.3702(15)	24.8780(5)
c (Å)	12.2141(7)	12.5043(3)
α (°)	90	90
β (°)	91.171(4)	93.1820(10)
γ (°)	90	90
V (Å^3)	1176.72(13)	1137.95(5)
Z	4	8
2θmin°	6.968	7.106
2θmax°	136.768	136.194
GoF	1.090	1.091
wR_2 (all data)	0.2714	0.0597
wR_2 [$I > 2\sigma(I)$]	0.2577	0.0592
R_1 (all data)	0.1106	0.0248
R_1 [$I > 2\sigma(I)$]	0.0940	0.0243

Table S2. Bond lengths [Å] for **3**·DMF.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(1)	N(11)	1.232(5)	N(5)	C(3)	1.386(5)
O(2)	N(11)	1.217(5)	N(6)	N(9)	1.361(5)
N(1)	N(11)	1.343(5)	N(6)	C(3)	1.332(6)
N(1)	C(1)	1.375(5)	N(7)	N(8)	1.365(5)
N(2)	C(1)	1.369(6)	N(7)	C(3)	1.303(6)
N(2)	C(2)	1.330(5)	N(8)	N(9)	1.294(5)
N(3)	N(5)	1.397(5)	O(3)	C(4)	1.246(6)
N(3)	C(1)	1.308(6)	N(10)	C(4)	1.310(6)
N(4)	C(2)	1.314(6)	N(10)	C(5)	1.457(6)
N(5)	C(2)	1.370(5)	N(10)	C(6)	1.453(6)

Table S3. Bond angles [°] for **3**·DMF.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
N(11)	N(1)	C(1)	126.4(4)	N(2)	C(1)	N(1)	114.8(4)
C(2)	N(2)	C(1)	103.4(3)	N(3)	C(1)	N(1)	128.2(4)
C(1)	N(3)	N(5)	100.5(3)	N(3)	C(1)	N(2)	117.0(4)
C(2)	N(5)	N(3)	110.7(3)	N(2)	C(2)	N(5)	108.4(3)
C(2)	N(5)	C(3)	127.4(4)	N(4)	C(2)	N(2)	126.9(4)
C(3)	N(5)	N(3)	121.7(3)	N(4)	C(2)	N(5)	124.7(4)
C(3)	N(6)	N(9)	106.0(3)	N(6)	C(3)	N(5)	123.5(4)
C(3)	N(7)	N(8)	104.4(4)	N(7)	C(3)	N(5)	124.9(4)
N(9)	N(8)	N(7)	110.9(3)	N(7)	C(3)	N(6)	111.6(4)
N(8)	N(9)	N(6)	107.1(3)	C(4)	N(10)	C(5)	121.0(4)
O(1)	N(11)	N(1)	116.0(4)	C(4)	N(10)	C(6)	120.6(4)
O(2)	N(11)	O(1)	125.5(4)	C(6)	N(10)	C(5)	118.4(4)
O(2)	N(11)	N(1)	118.5(4)	O(3)	C(4)	N(10)	123.6(4)

Table S4. Torsion angles [°] for **3**·DMF.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N(3)	N(5)	C(2)	N(2)	1.1(5)	C(1)	N(2)	C(2)	N(4)	179.6(5)
N(3)	N(5)	C(2)	N(4)	-179.4(4)	C(1)	N(2)	C(2)	N(5)	-0.8(5)
N(3)	N(5)	C(3)	N(6)	-3.2(7)	C(1)	N(3)	N(5)	C(2)	-0.8(5)
N(3)	N(5)	C(3)	N(7)	177.1(4)	C(1)	N(3)	N(5)	C(3)	-176.4(4)
N(5)	N(3)	C(1)	N(1)	-179.2(5)	C(2)	N(2)	C(1)	N(1)	179.9(4)
N(5)	N(3)	C(1)	N(2)	0.3(5)	C(2)	N(2)	C(1)	N(3)	0.4(6)
N(7)	N(8)	N(9)	N(6)	0.3(5)	C(2)	N(5)	C(3)	N(6)	-178.0(4)
N(8)	N(7)	C(3)	N(5)	-180.0(4)	C(2)	N(5)	C(3)	N(7)	2.4(8)
N(8)	N(7)	C(3)	N(6)	0.4(5)	C(3)	N(5)	C(2)	N(2)	176.3(4)
N(9)	N(6)	C(3)	N(5)	-179.9(4)	C(3)	N(5)	C(2)	N(4)	-4.1(8)
N(9)	N(6)	C(3)	N(7)	-0.2(5)	C(3)	N(6)	N(9)	N(8)	0.0(5)
N(11)	N(1)	C(1)	N(2)	178.9(5)	C(3)	N(7)	N(8)	N(9)	-0.4(5)
N(11)	N(1)	C(1)	N(3)	-1.6(9)	C(5)	N(10)	C(4)	O(3)	178.7(5)
C(1)	N(1)	N(11)	O(1)	179.3(5)	C(6)	N(10)	C(4)	O(3)	-0.5(8)
C(1)	N(1)	N(11)	O(2)	-1.7(8)	C6	N7A	N8	O3	

Table S5. Hydrogen bonds for **3**·DMF [Å and °].

D	**H**	**A**	**d(D-H)/Å**	**d(H-A)/Å**	**d(D-A)/Å**	**D-H-A/°**
N4	H4A	N7	0.85(6)	2.25(6)	2.859(6)	129(5)
N6	H6	O3[1]	0.82(6)	1.76(6)	2.558(5)	167(5)
N1	H1	N2[2]	0.92(6)	1.93(6)	2.801(6)	157(5)

[1]-1+X,+Y,+Z; [2]2-X,1-Y,1-Z.

Table S6. Bond lengths [Å] for **4**·H_2O.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N12	1.416(2)	N6	N5	1.404(3)
O3	N9	1.274(2)	N6	C3	1.322(3)
O2	N9	1.244(3)	N10	C3	1.390(3)
O4	N11	1.406(3)	N5	C1	1.393(3)
N7	C3	1.377(3)	N5	C2	1.362(3)
N7	C2	1.330(3)	N1	N2	1.300(3)
N3	N2	1.352(3)	N1	N4	1.356(3)
N3	C1	1.321(3)	N4	C1	1.335(3)
N9	N10	1.301(3)	N8	C2	1.332(3)

Table S7. Bond angles [°] for **4**·H_2O.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	N7	C3	103.64(19)	N1	N2	N3	109.30(19)
C1	N3	N2	104.08(19)	C1	N4	N1	102.8(2)
O3	N9	N10	116.42(18)	N3	C1	N5	124.2(2)
O2	N9	O3	119.0(2)	N3	C1	N4	113.4(2)
O2	N9	N10	124.60(19)	N4	C1	N5	122.4(2)
C3	N6	N5	101.23(19)	N7	C3	N10	113.8(2)
N9	N10	C3	117.8(2)	N6	C3	N7	115.7(2)
C1	N5	N6	120.36(18)	N6	C3	N10	130.4(2)
C2	N5	N6	110.02(18)	N7	C2	N5	109.41(19)
C2	N5	C1	129.04(19)	N7	C2	N8	126.4(2)
N2	N1	N4	110.41(18)	N8	C2	N5	124.1(2)

Table S8. Torsion angles [°] for **4**·H_2O.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O3	N9	N10	C3	-177.2(2)	N2	N1	N4	C1	0.2(2)
O2	N9	N10	C3	2.2(3)	N4	N1	N2	N3	-0.2(2)
N9	N10	C3	N7	177.53(18)	C1	N3	N2	N1	0.1(2)
N9	N10	C3	N6	0.8(4)	C1	N5	C2	N7	172.1(2)
N6	N5	C1	N3	-5.7(3)	C1	N5	C2	N8	-9.3(4)
N6	N5	C1	N4	173.6(2)	C3	N7	C2	N5	-0.6(2)
N6	N5	C2	N7	0.9(3)	C3	N7	C2	N8	-179.1(2)
N6	N5	C2	N8	179.5(2)	C3	N6	N5	C1	-172.87(19)
N5	N6	C3	N7	0.5(3)	C3	N6	N5	C2	-0.8(2)
N5	N6	C3	N10	177.1(2)	C2	N7	C3	N6	0.0(3)
N1	N4	C1	N3	-0.2(2)	C2	N7	C3	N10	-177.16(18)
N1	N4	C1	N5	-179.63(19)	C2	N5	C1	N3	-176.1(2)
N2	N3	C1	N5	179.51(19)	C2	N5	C1	N4	3.2(3)
N2	N3	C1	N4	0.1(3)					

Table S9. Hydrogen bonds for **4**·H_2O [Å and °].

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O1	H1	N3	0.84	1.83	2.645(3)	164.2
N8	H8A	O2[1]	0.88	2.10	2.934(3)	156.9
N8	H8B	N4	0.88	2.24	2.859(3)	126.9
N12	H12A	N7[2]	0.88	2.01	2.877(3)	165.3
N12	H12B	O1[3]	0.88	2.29	2.995(3)	136.9
N12	H12C	O2	0.94(2)	2.10(3)	2.696(3)	120(2)
N12	H12C	N6	0.94(2)	1.99(2)	2.890(3)	161(3)
O4	H4	O5	0.84	1.77	2.596(3)	169.7
N11	H11A	N1[4]	0.89	1.99	2.847(3)	163.0
N11	H11B	O3	0.89	1.88	2.733(3)	159.9
N11	H11C	O1[1]	0.95(3)	2.18(3)	2.940(3)	136(2)
O5	H5A	N2[1]	0.87	2.01	2.872(3)	168.8
O5	H5B	N4[4]	0.87	2.10	2.902(3)	152.7

[1]-1+X,1-Y,-1/2+Z; [2]1+X,1-Y,1/2+Z; [3]-1+X,+Y,+Z; [4]-1/2+X,-1/2+Y,+Z.

General methods

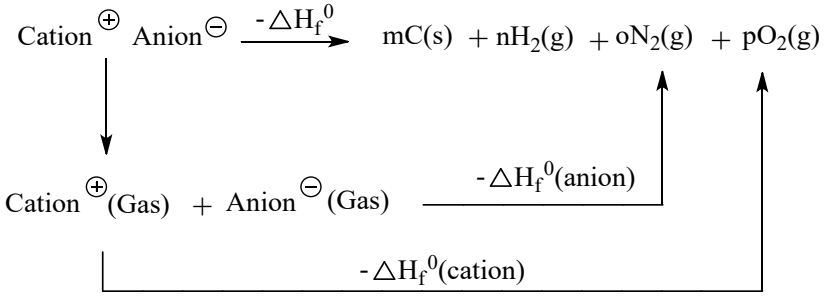
All the reagents used in this work were purchased in analytical grade and were used without further purification. ^{1}H and ^{13}C signals are recorded on a Bruker 500 MHz nuclear magnetic resonance (NMR) spectrometer by using DMSO-d_6. The onset decomposition temperature was measured by using a differential scanning calorimeter (DSC25) at a heat rating of 5 °C min^{-1}. Infrared (IR) spectra was recorded on a PerkinElmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Analyses of C/H/N were performed with a Vario EL III Analyzer. The impact sensitivity and friction sensitivity were measured by using a BAM Fallhammer and a BAM friction tester, respectively.

Computational methods

The gas phase enthalpies of formation were calculated based on the G2 method. The solid-state heat of formation (for **3**) was calculated based on Trouton's rule according to eq 1 (*T* represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition). The gas phase enthalpy of formation and heat of sublimation of **3** are 588.62 kJ mol^{-1} and 78.58 kJ mol^{-1}, respectively.

$$\Delta H_{sub} = 188/Jmol^{-1}K^{-1} \times T \qquad (1)$$

For energetic salts (**4**−**11**), the solid-phase enthalpy of formation is obtained using a Born−Haber energy cycle (eq 2) and the relevant calculation formulas are shown below.



(2)

$$\Delta H_f(\text{salt},298\text{K}) = \Delta H_f(\text{cation},298\text{K}) + \Delta H_f(\text{anion},298\text{K}) - \Delta H_L$$

$$\Delta H_L = U_{POT} + [\, p(n_M/2 - 2) + q(n_X/2 - 2)]RT$$

$$U_{POT}\ (\text{kJ}\cdot\text{mol}^{-1}) = \gamma\,(\rho_m/M_m)^{1/3} + \delta$$

Crystal detection methods

A suitable yellow block crystal (**3**·DMF) with dimensions 0.22 × 0.15× 0.07 mm^3 or a suitable yellow needle crystal (**4**·H_2O) with dimensions 0.37 × 0.14 × 0.26 mm^3 was selected and mounted on a nylon loop with paratone oil on a Bruker D8 VENTURE diffractometer. The crystals were kept at a steady T = 193 K during data collection. The structures were solved with the olex2.solve structure solution program using Charge Flipping and refined with the SHELXL refinement package using Least Squares minimization.

Calculation details for heats of formation

Table S10. Lattice energy for heat of formation.

Compounds	ΔH_L (kJ/mol)	ΔH_f^{Cation} (kJ/mol)	ΔH_f^{anion} (kJ/mol)	ΔH_f^{298} (kJ/mol)
4	1374.8	669.5	486.1	450.4
5	1363.5	770.0	486.1	662.6
6	1407.8	626.4	486.1	331.2
7	1594.7	501.1	486.1	-106.4
8	1230.9	575.9	486.1	407.0
9	1238.9	667.4	486.1	582.0
10	1171.2	774.8	486.1	864.5
11	1191.9	806.3	486.1	906.8

NMR plots

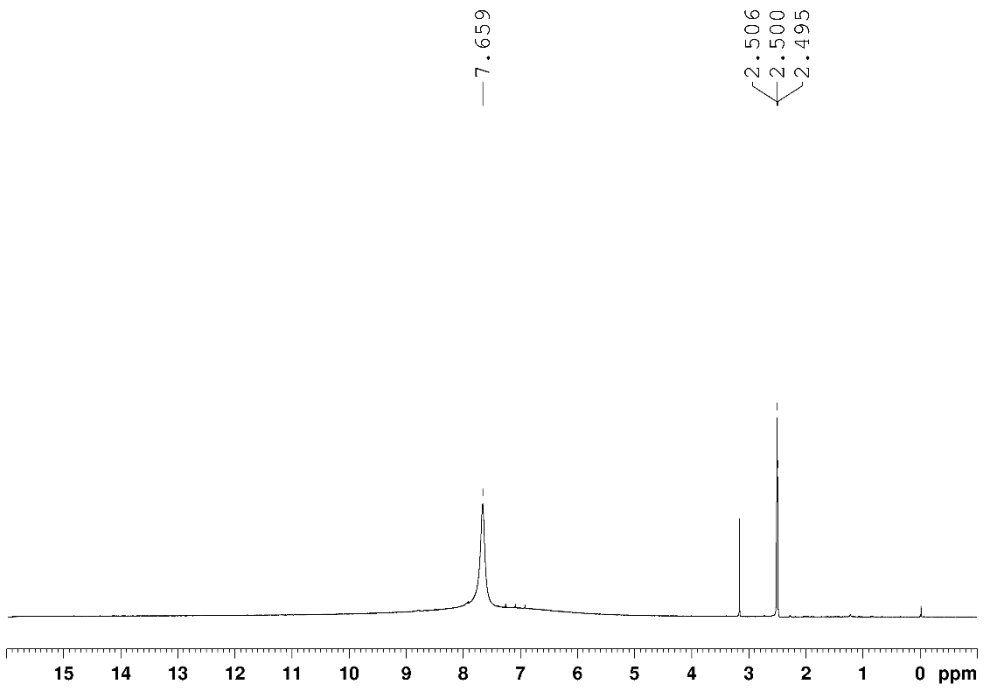


Figure S1. ^{1}H NMR spectrum of **3**.

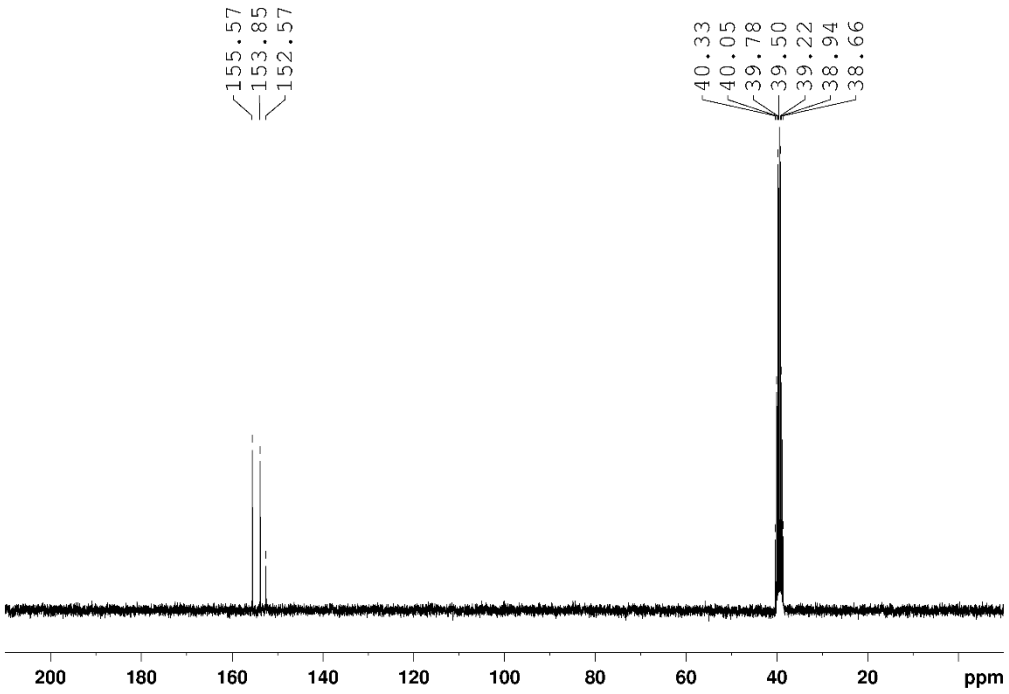


Figure S2. ^{13}C NMR spectrum of **3**.

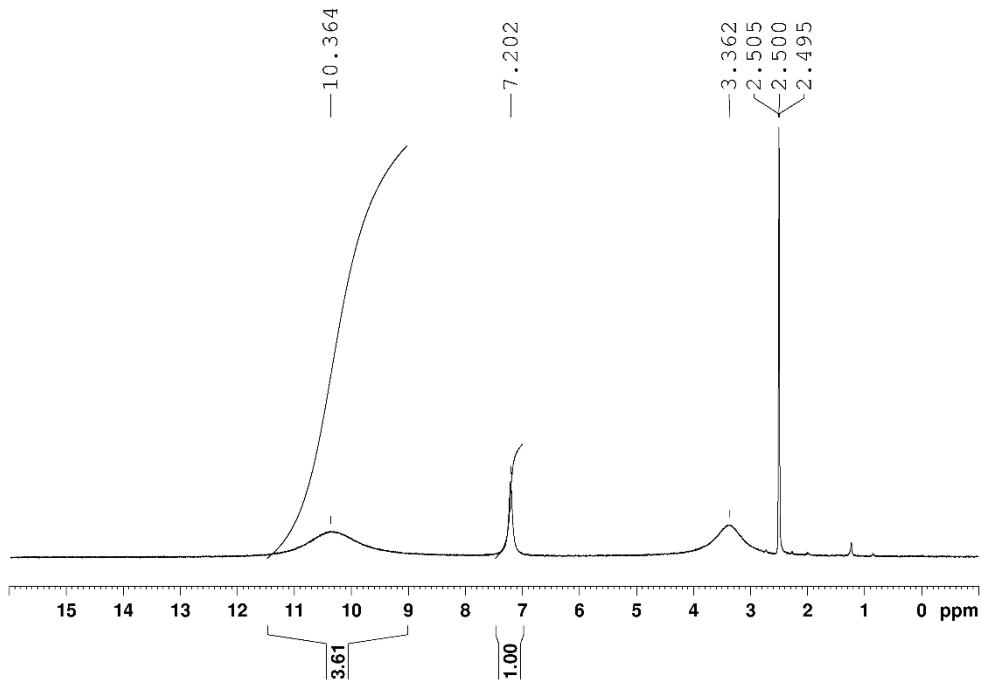


Figure S3. ^{1}H NMR spectrum of **4**.

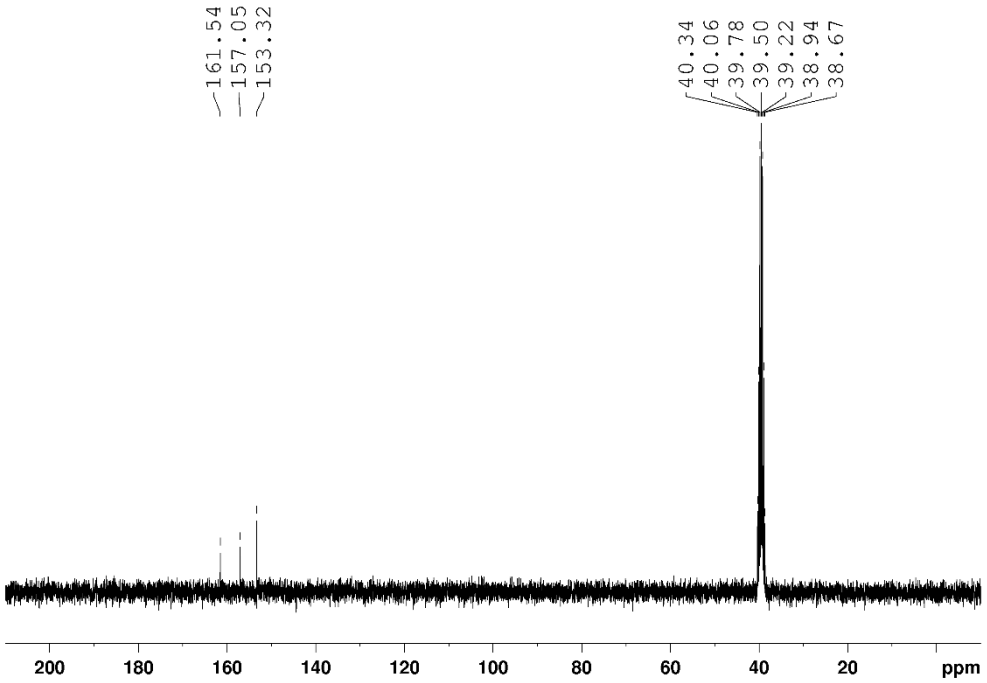


Figure S4. ^{13}C NMR spectrum of **4**.

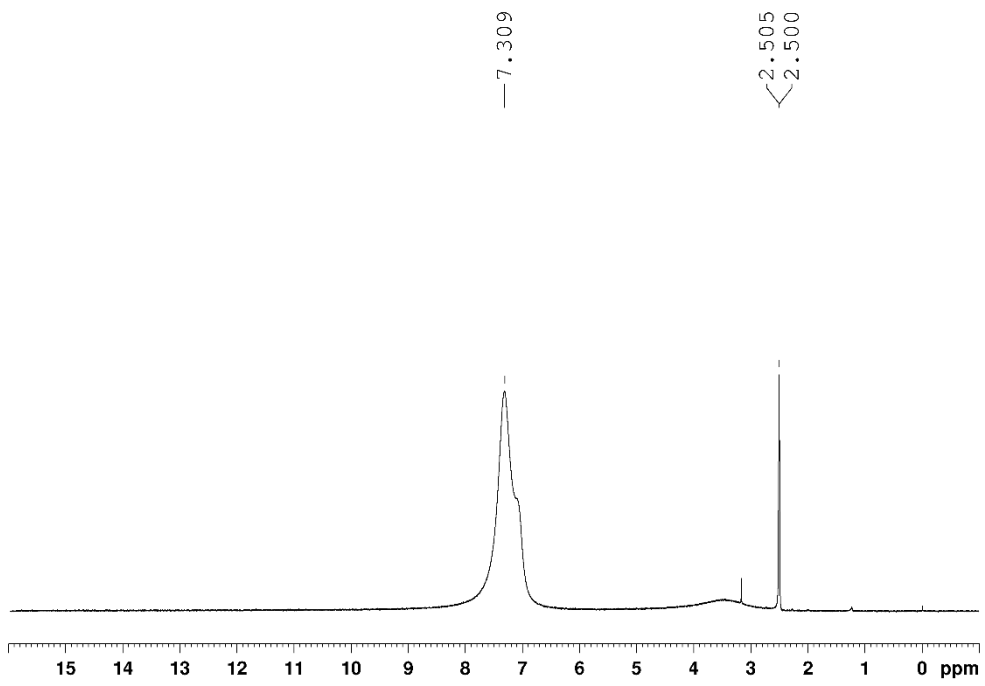


Figure S5. ^{1}H NMR spectrum of **5**.

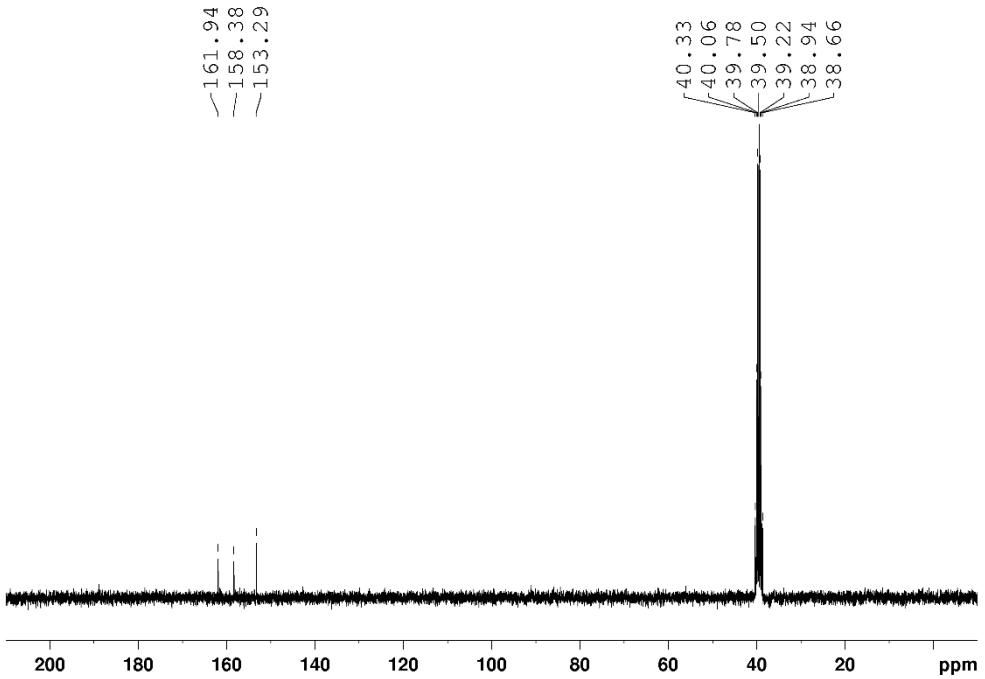


Figure S6. ^{13}C NMR spectrum of **5**.

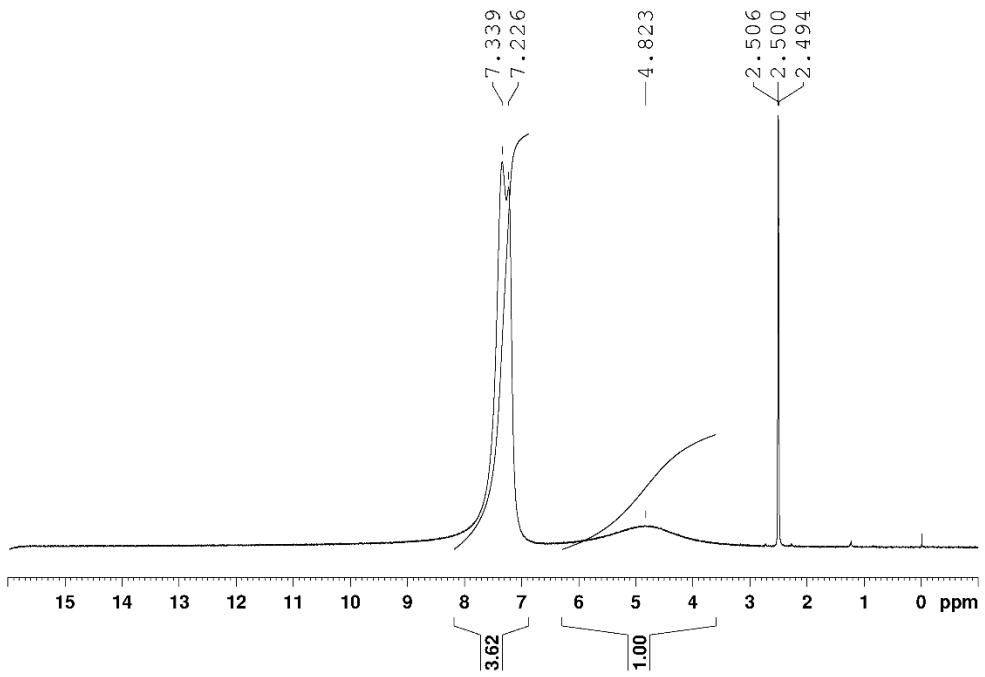


Figure S7. ^{1}H NMR spectrum of **6**.

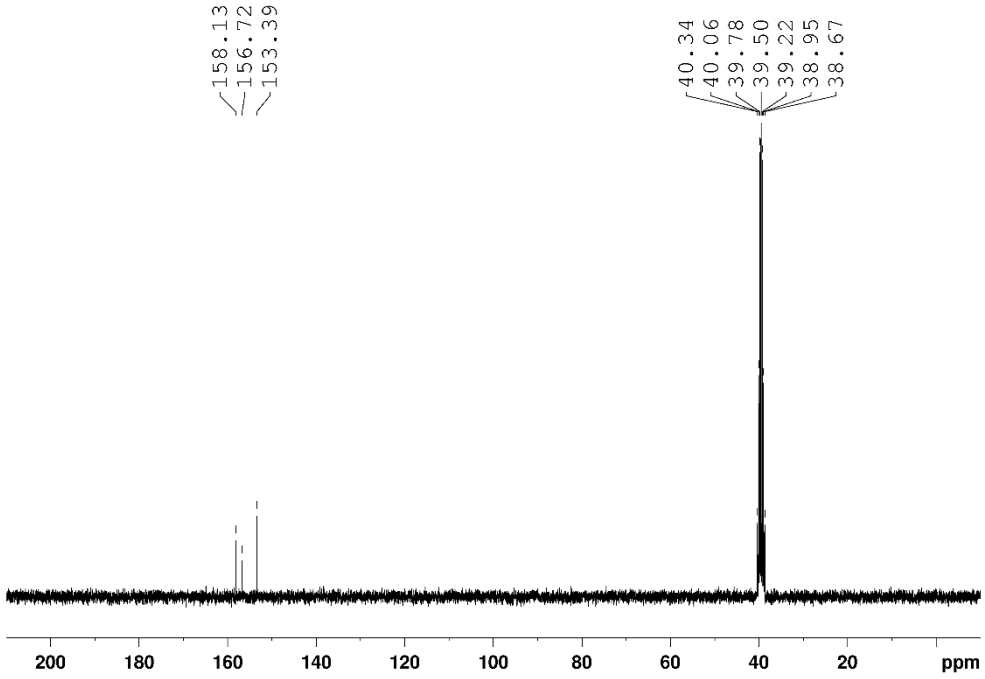


Figure S8. ^{13}C NMR spectrum of **6**.

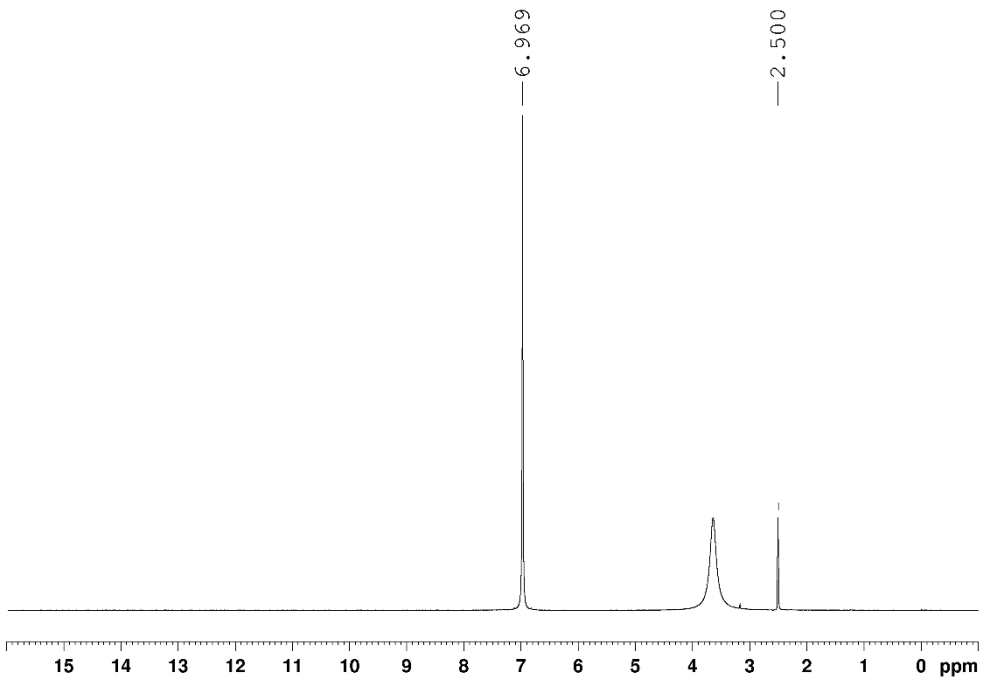


Figure S9. ^{1}H NMR spectrum of **7**.

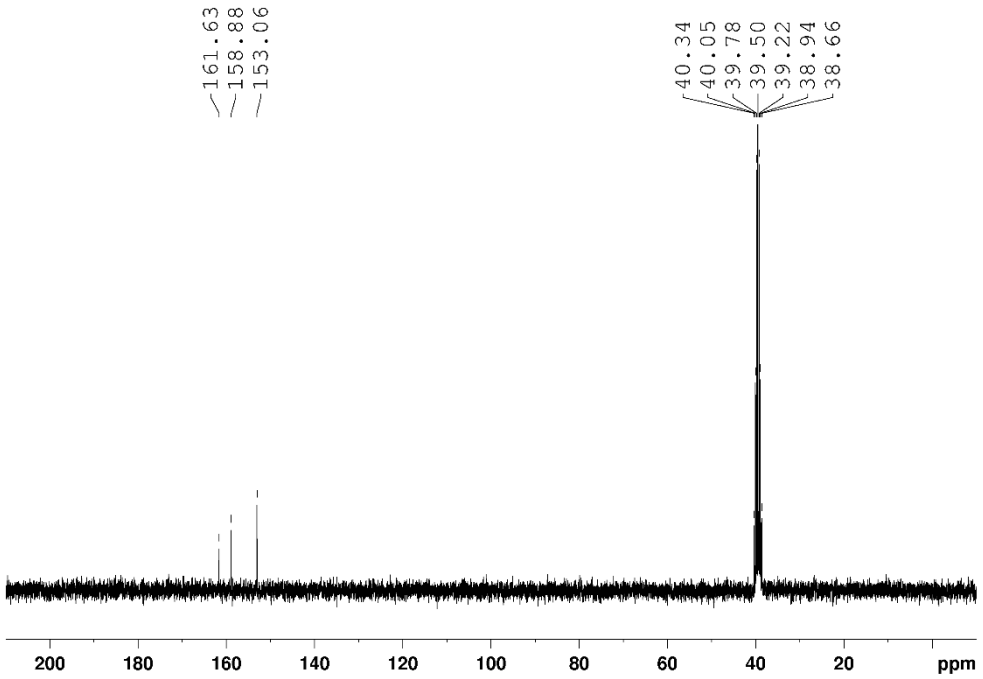


Figure S10. ^{13}C NMR spectrum of **7**.

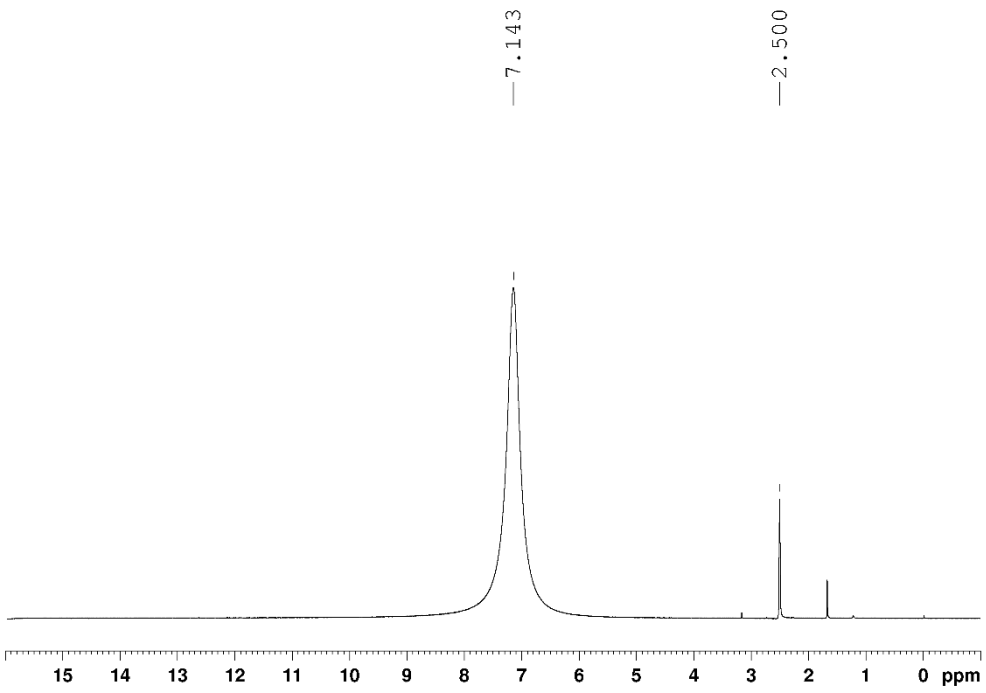


Figure S11. ^{1}H NMR spectrum of **8**.

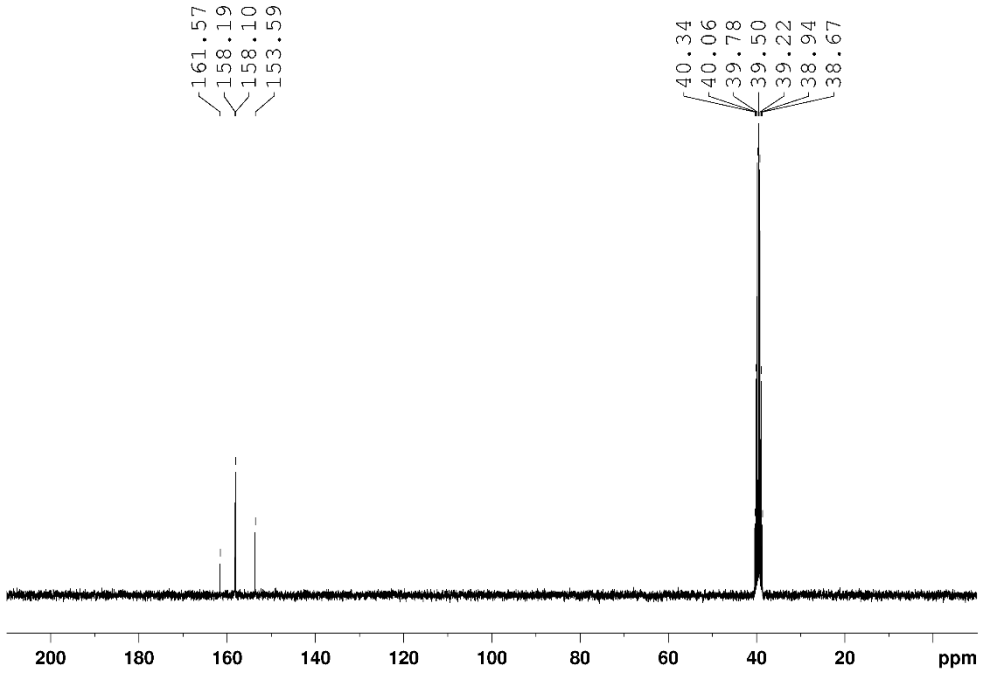


Figure S12. ^{13}C NMR spectrum of **8**.

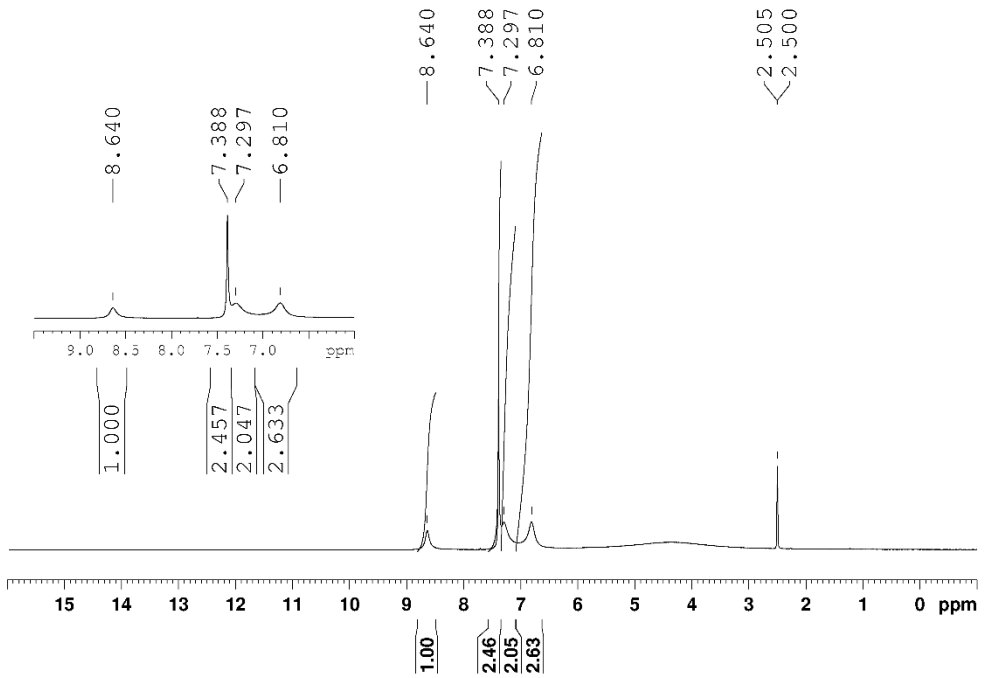


Figure S13. ^{1}H NMR spectrum of **9**.

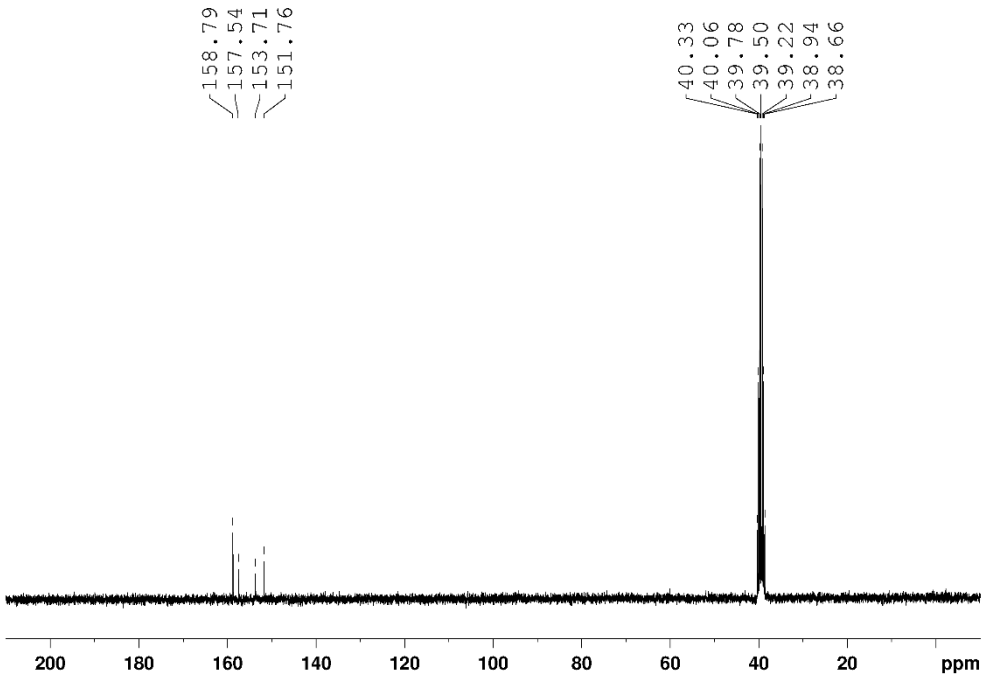


Figure S14. ^{13}C NMR spectrum of **9**.

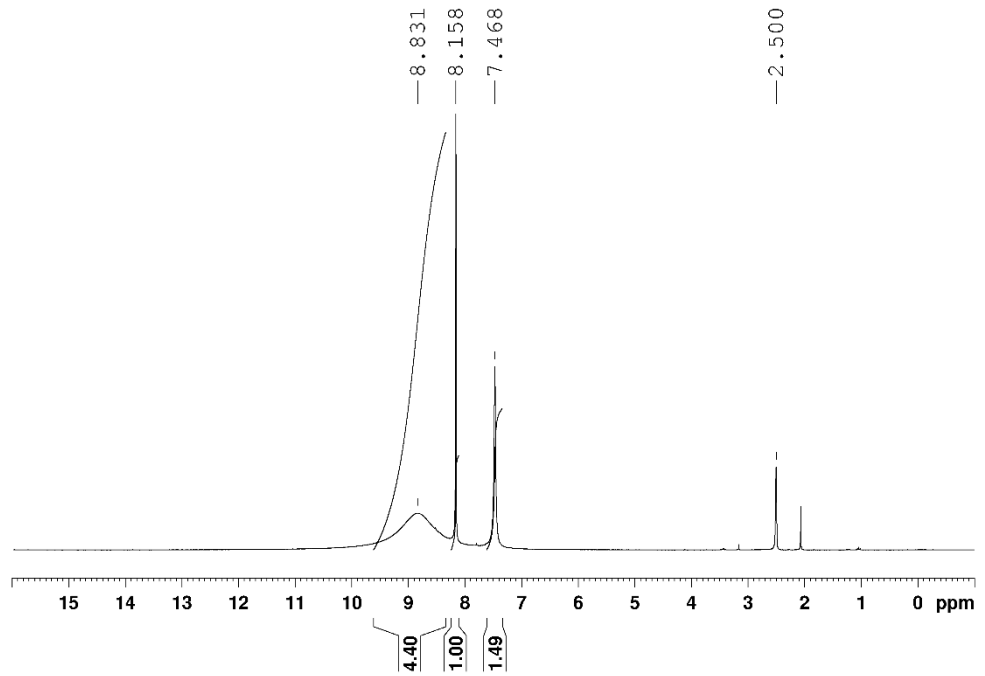


Figure S15. ^{1}H NMR spectrum of **10**.

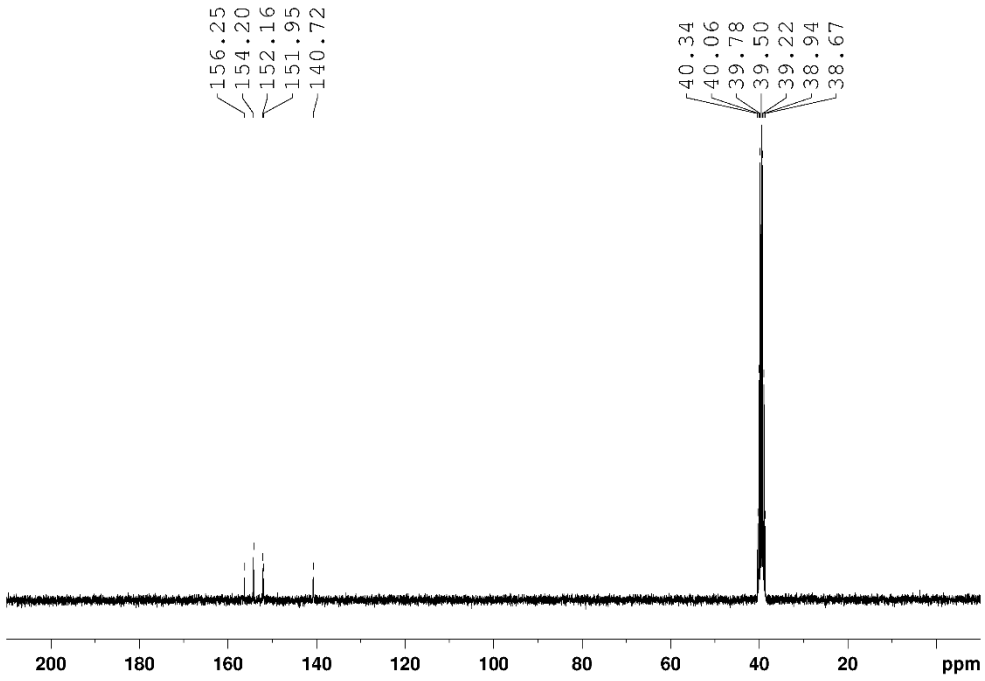


Figure S16. ^{13}C NMR spectrum of **10**.

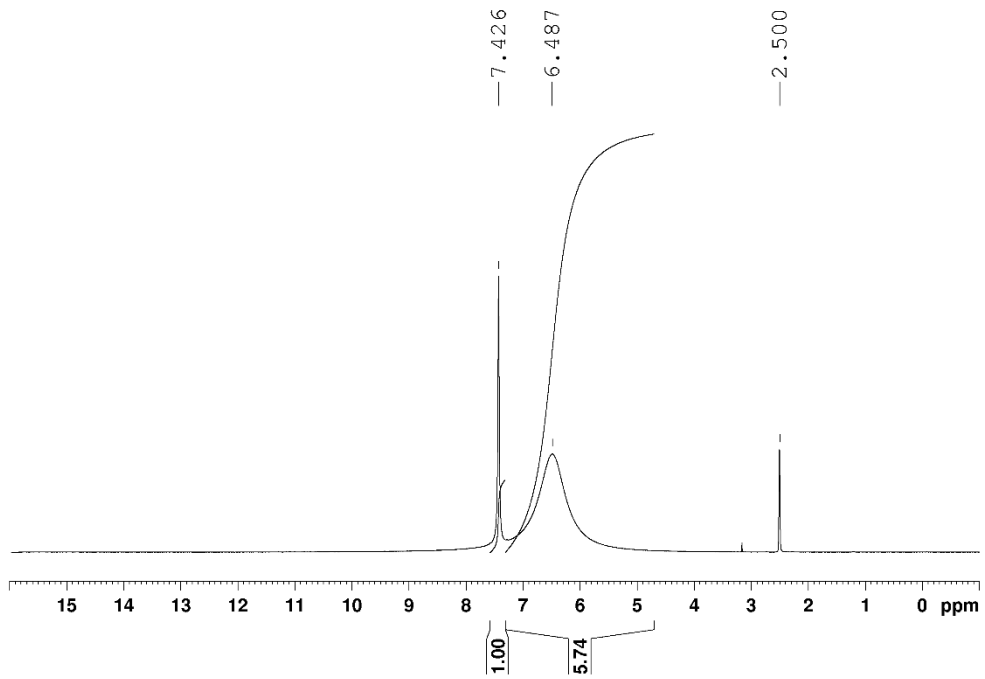


Figure S17. ^{1}H NMR spectrum of **11**.

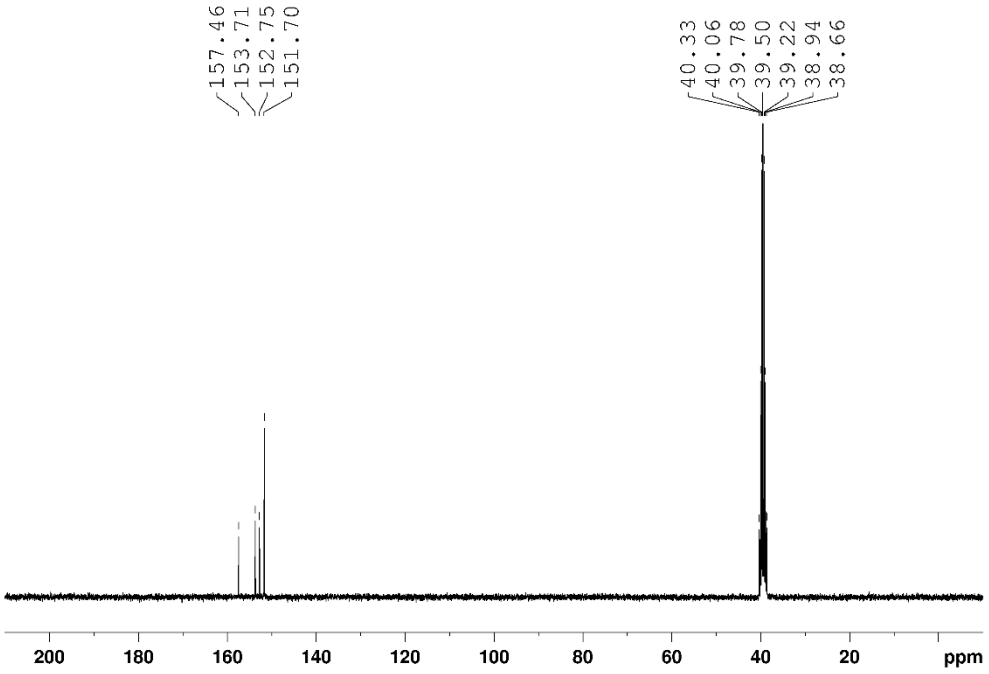


Figure S18. ^{13}C NMR spectrum of **11**.

DSC plots

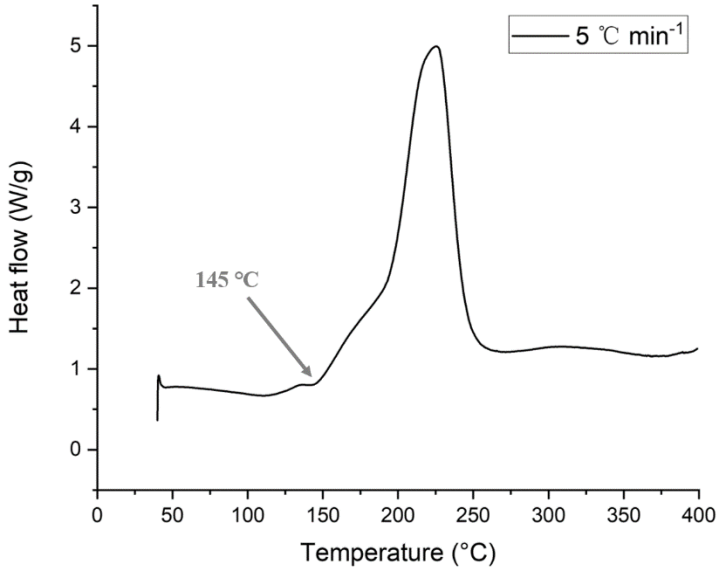


Figure S19. DSC plot of **3**.

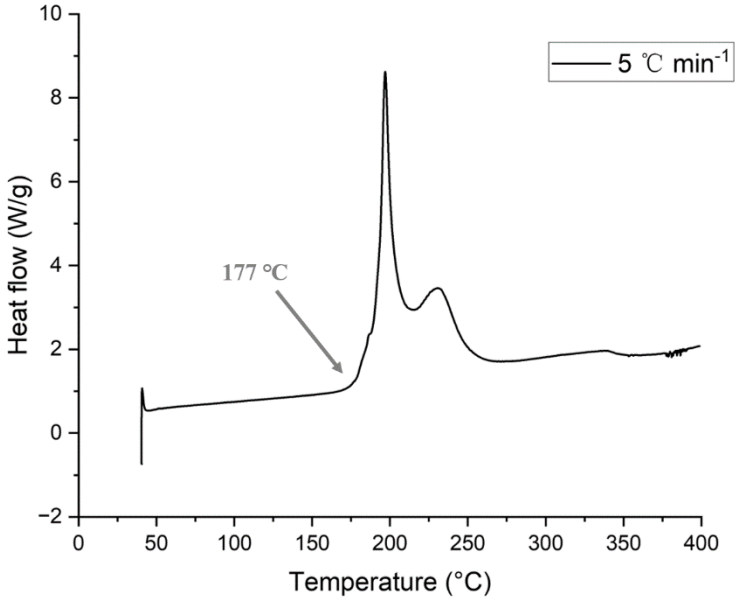


Figure S20. DSC plot of **4**.

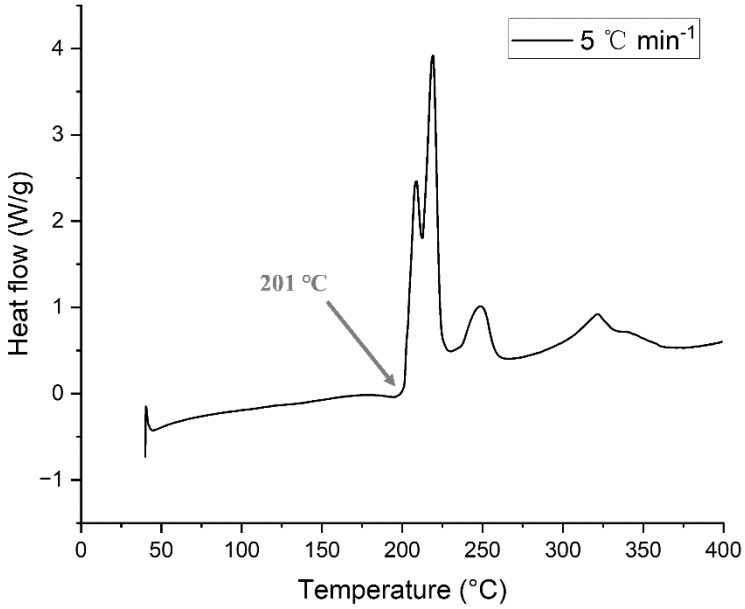


Figure S21. DSC plot of **5**.

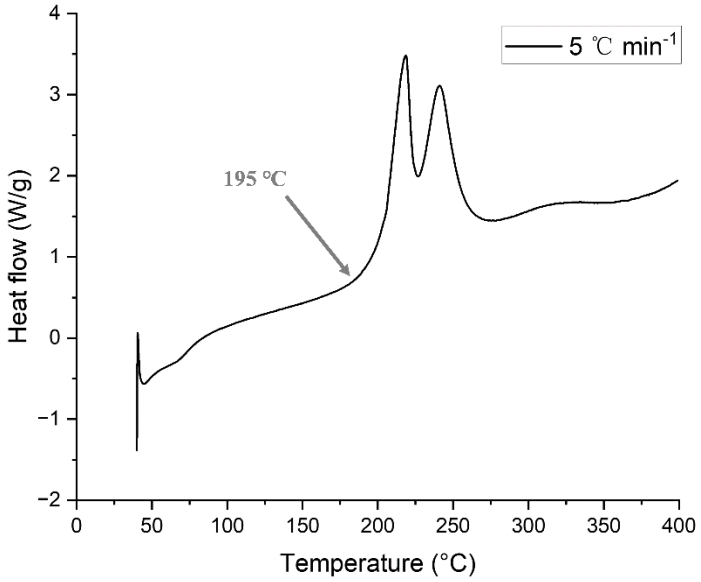


Figure S22. DSC plot of **6**.

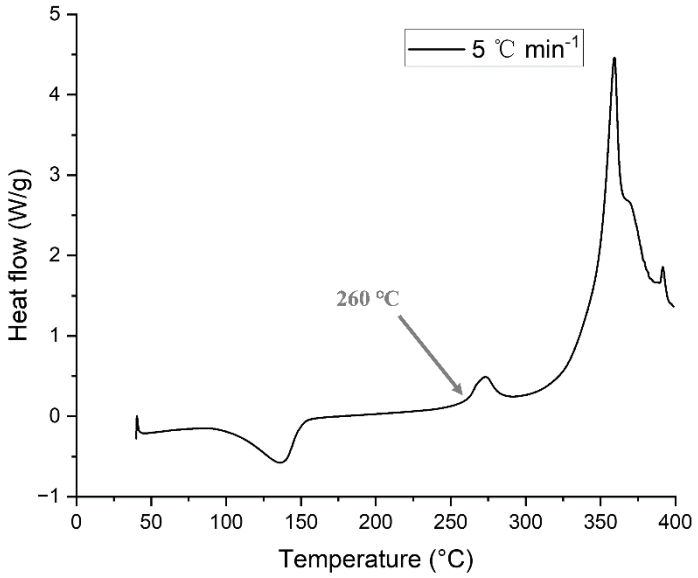


Figure S23. DSC plot of **7**.

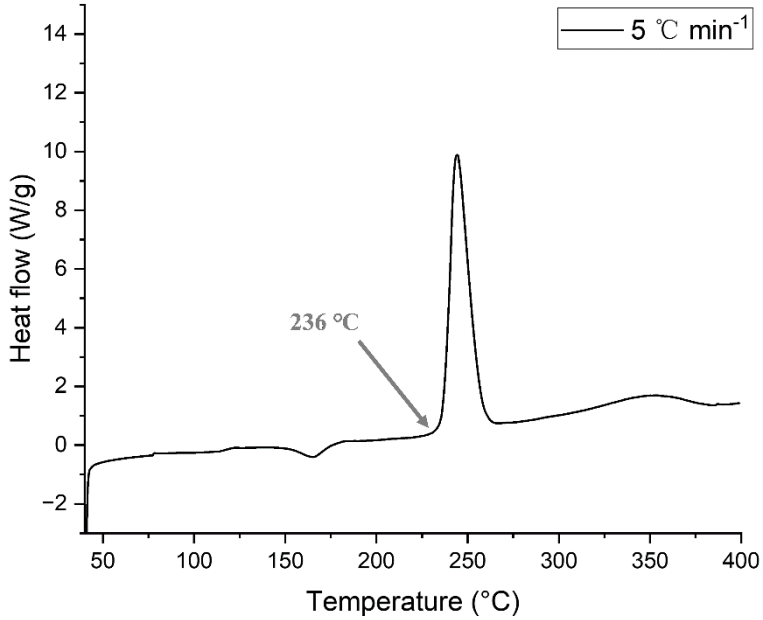


Figure S24. DSC plot of **8**.

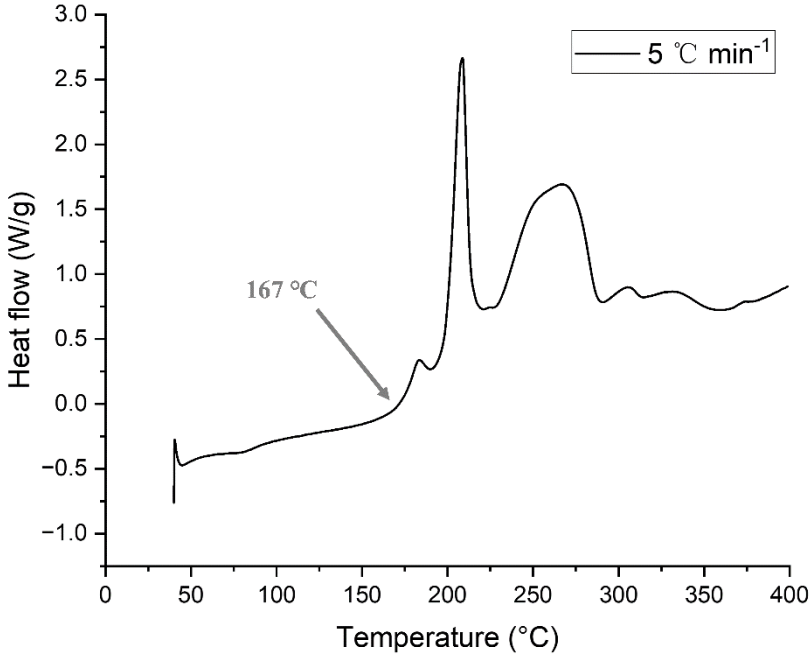


Figure S25. DSC plot of **9**.

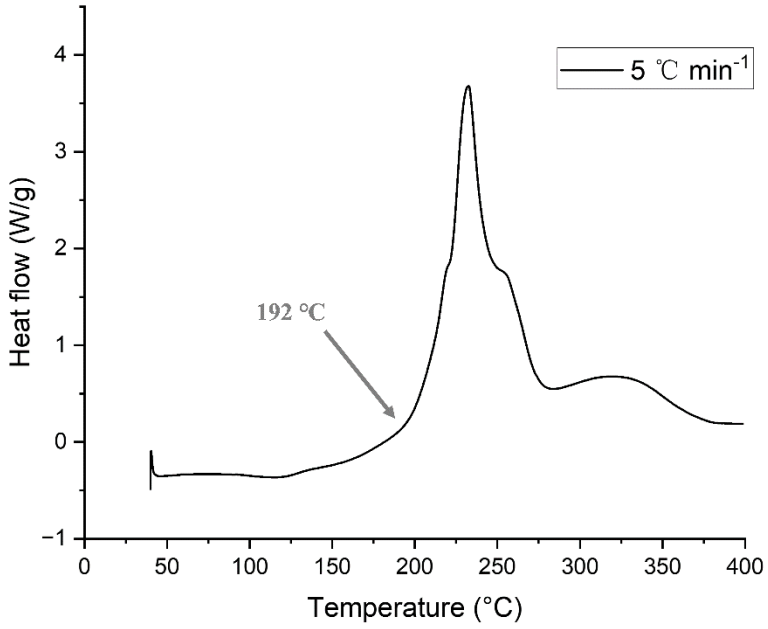


Figure S26. DSC plot of **10**.

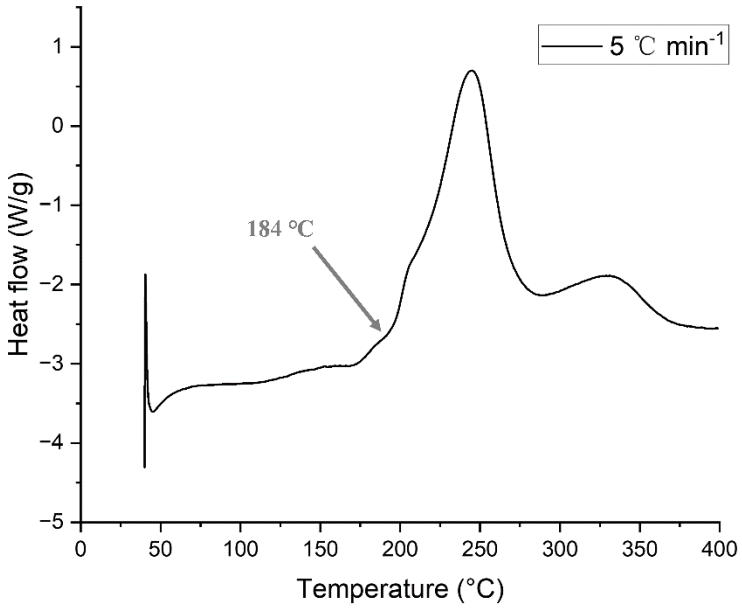


Figure S27. DSC plot of **11**.