Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

C-C bonded bis-5,6 fused triazole-triazine compound: An advanced heat-resistant explosive with high energy and low sensitivity

Chengchuang Li, Caijin Lei, Jie Tang, Teng Zhu, Guangbin Cheng* and Hongwei Yang*

School of Chemistry and Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China

* Corresponding author. E-mail addresses: gcheng@mail.njust.edu.cn; hyang@mail.njust.edu.cn

Table of Contents

1. Experimental Section

Reagents were purchased from Aldrich and Acros Organics and were used as received. ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz (Bruker AVANCE 500) NMR spectrometer operating at 500 and 125 MHz, respectively. The decomposition points were obtained on a differential scanning calorimeter at a heating rate of 5°C min^{-1}. IR spectra were recorded on a FT-IR spectrometer (Thermo Nicolet AVATAR 370) as thin films by using KBr plates. Densities were determined at 25 °C by employing a Micromeritics AccuPyc II 1340 gas pycnometer. Elemental analyses were carried out by using a Vario Micro cube Elementar Analyser. Impact and friction sensitivity measurements were made by using a standard BAM Fall hammer and a BAM friction tester. Detonation velocity and detonation pressure data were calculated by program package EXPLO5 (version 6.01).

Synthesis of 3,3'-dinitro- [7,7'-bi [1,2,4] triazolo[5,1-c] [1,2,4] triazine]-4,4'-diamine (2)

Compound **1** (1.66 g, 10.0 mmol) was added to the mixture of 10 ml of concentrated hydrochloric acid in 24 ml of water. Then, a solution of sodium nitrite (1.60 g, 23.0 mmol) in 10 ml of water was added slowly at 0 ◦C. After stirring 0.5 h at 0 ℃, a solution of sodium nitroacetonitrile (nitroacetonitrile (3.44 g, 40.0 mmol) and sodium hydroxide (1.60 g, 40.0 mmol) in 24 ml water) prepared in advance was added dropwise. The mixture was allowed to warm to room temperature and stirred for 24 h. After that, the 50 ml of water was added to reaction mixture and acidified with 37% hydrochloric acid to pH = 6-7 and stirring for 30 minutes. The precipitate was collected by filtered, washed with water and methanol to give yellow solid of compound **2**. (3.27 g, yield: 91.1%). IR (KBr): 3440, 3315, 3299, 3300, 3149,1649, 1560, 1476, 1455, 1488, 1407, 1302, 1297, 1217, 1187,1090, 1001, 827, 770, 755, 705, 661, 600, 585 cm^{-1}.^{1}H NMR (500 MHz, DMSO-d_6): 10.70 (s), 10.08 (s) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 141.2, 141.6, 157.3, 157.5 ppm. Elemental analysis for $C_8H_4N_{14}O_4$ (360.05): calcd. C 35.30, H 1.48, N 51.46 %. Found: C 35.35, H 1.49, N 51.40 %.

Synthesis of 4,4'-diamino- [7,7'-bi [1,2,4] triazolo[5,1-c] [1,2,4] triazine]-3,3'-dicarbonitrile (3)

Compound **1** (1.66 g, 10.0 mmol) was added to the mixture of 10 ml of concentrated hydrochloric acid in 24 ml of water. Then, a solution of sodium nitrite (1.60 g, 23.0 mmol) in 10 ml of water was added slowly at 0 ◦C. After stirring 0.5 h at 0 ℃, a solution of malononitrile (1.00 g, 20.0 mmol) and sodium acetate (8.00 g, 24

mmol) in 20 ml of water was added dropwise. The reaction system was stirred at this temperature for 1 h, and then reacted at room temperature for 36 h. The precipitate was obtained by filtered, washed with cold water and dried in air to give yellow solid (2.81 g, 87.2%). IR (KBr): 3621, 3517, 3489, 3358, 2849, 2211, 1625, 1585, 1433, 1302, 1207, 820, 776, 728 cm^{-1}.^{1}H NMR (500 MHz, DMSO-d_6): 10.23 (s) ppm. ^{13}C NMR (125 MHz, DMSO-d_6) δ 111.2, 115.0, 144.5, 155.6, 156.2 ppm. Elemental analysis for $C_{10}H_4N_{14}$ (320.07): calcd. C 29.56, H 1.49, N 68.95 %. Found: C 29.66, H 1.48, N 68.86 %.

Synthesis of 3,3'-di(1H-tetrazol-5-yl)-[7,7'-bi[1,2,4]triazolo[5,1-c][1,2,4]triazine]-4,4'-diamine (4)

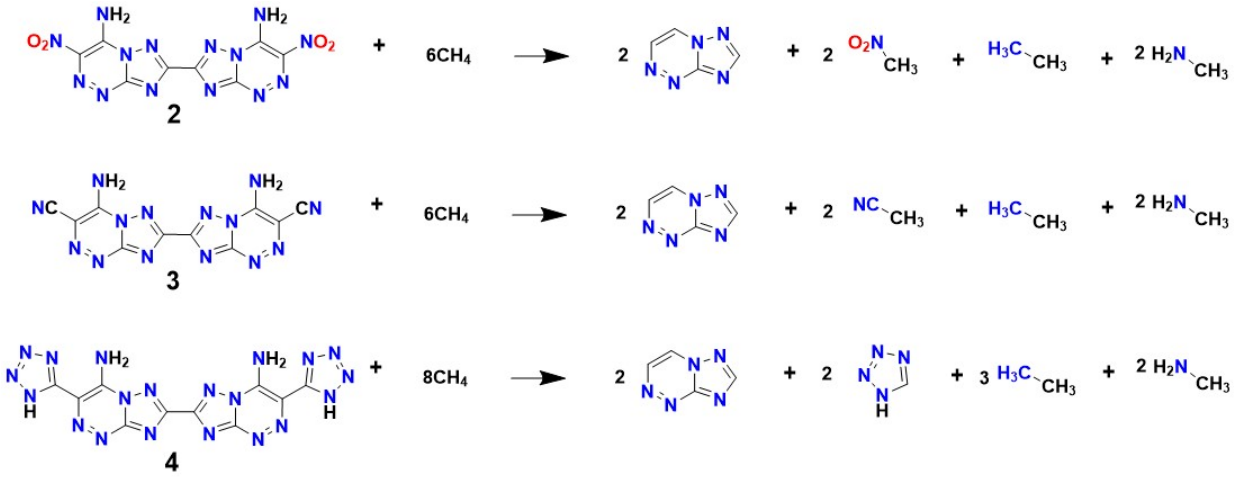
Sodium azide (2.93 g, 45.1 mmol) and zinc chloride (3.46 g, 25.4 mmol) were added into a solution of of compound **3** (5.9 g, 18.7 mmol) in water (100 mL). The solution was allowed to heat slowly to 100 °C and stirred for 24 hours. The precipitate was obtained by filtered, washed with water and dried in air to give brown black solid (6.1 g, 78.8%). ^{1}H NMR (500 MHz, DMSO-d_6): 5.90 (s), 9.96 (s) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 140.9, 142.6, 155.9, 156.2, 165.3 ppm. IR (KBr): 3681, 3522, 3156, 2625, 2144, 1647, 1594, 1556, 1450, 1399, 1264, 1254, 1160, 1101, 823, 763 cm^{-1}. Elemental analysis for $C_{10}H_6N_{20}$ (406.11): calcd. C 37.51, H 1.26, N 61.23 %. Found: C 37.55, H 1.28, N 61.18 %.

2. Computational Details

Computations were performed by using the Gaussian09 suite of programs [1]. The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP) functional with the 6-311+G** basis set [2-4]. All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M [5]. All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

The predictions of heats of formation (HOF) of compounds used the hybrid DFTB3LYP methods with the 6-311+G** basis set through designed isodesmic reactions. The isodesmic reaction processes, that is, the number of each kind of formal bond is conserved, were used with the application of the bond separation reaction (BSR) rules. The molecule was broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF

shown in Scheme S1.



Scheme S1. The isodesmic reactions for calculating heat of formation for **2**, **3** and **4**.

The change of enthalpy for the reactions at 298K can be expressed by Equation (1):

$$\Delta H_{298} = \Sigma\Delta_f H_P - \Sigma\Delta_f H_R \qquad (1)$$

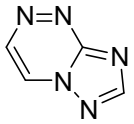
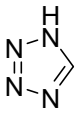
Where $\Sigma\Delta_f H_P$ and $\Sigma\Delta_f H_R$ are the *HOF* of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression in Equation (2):

$$\Delta H_{298} = \Delta E_{298} + \Delta(PV) = \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \qquad (2)$$

where ΔE_0 is the change in total energy between the products and the reactants at 0 K; ΔZPE is the difference between the zero-point energies (*ZPE*) of the products and the reactants at 0 K; ΔH_T is the thermal correction from 0 to 298 K. The $\Delta(PV)$ value in Equation (2) is the *PV* work term. It equals ΔnRT for the reactions of an ideal gas. For the isodesmic reactions $\Delta n = 0$, so $\Delta(PV) = 0$. On the left side of Equation (2), apart from target compound all the others are called reference compounds. The HOF of reference compounds are available either from experiments or from the high level computing such as CBS-4M.

Table S1. Calculated zero-point energy (ZPE), thermal correction to enthalpy (HT), total energy (E0) and heats of formation (HOF)

Compound	E_0 / a. u	ZPE / kJ mol^{-1}	ΔH_T / kJ mol^{-1}	HOF/kJ mol^{-1}
2	-1374.6733277	457.15	54.82	1076.817875
3	-1150.1292465	436.49	52.04	1234.136674
4	-1479.8892761	586.37	60.18	1606.346031

	-428.0233407	221.57	16.25	487.1305385
	-258.3241779	117.69	11.84	334.3
CH_4	-40.5339263	112.26	22.92	-74.60
CH_3NO_2	-245.0915559	124.93	11.6	-80.8
CH_3CH_3	-79.8565413	187.31	11.79	-84
CH_3NH_2	-95.8938402	160.78	11.64	-22.5
CH_3CN	-132.793	113.98	12.07	67.8

3. Crystallographic Data for 2, 3

Table S2 Crystallographic Data for **2**·NaOH·5H_2O·2DMF, **2**·4 CH_3OH and **3**·4 DMSO.

	2·NaOH·5H_2O·2DMF	**2**·4 CH_3OH	**3**·4 DMSO
Empirical formula	C14 H29 N16 Na O12	C12 H20 N14 O8	C18 H28 N14 O4S4
Formula weight	636.52	488.42	632.78
Temperature/K	193	193	193
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/c$	P-1
a/Å	5.0210(3)	13.6503(13)	5.9008(6)
b/Å	26.654(2)	11.5914(17)	11.3741(9)
c/Å	10.3060(7)	6.6234(7)	11.9467(11)
α/°	90	90	68.425(3)
β/°	98.410(5)	99.337(4)	88.011(4)
γ/°	90	90	76.253(3)
Volume/Å^3	1364.40(14)	1034.1(2)	723.05(12)
Z	2	2	1
ρ_{calc} g/cm^3	1.549	1.569	1.453
μ/mm^{-1}	1.295	0.132	0.381
F(000)	664.0	508.0	330.0
Crystal size/mm^3	0.16×0.13×0.08	0.15×0.14×0.1	0.16×0.15×0.12
Radiation	CuKα (λ=1.54178)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2Θ range for data collection/°	9.288 to136.642	4.636 to 54.974	4.294 to 54.914
Index ranges	-6≤h≤6, -31≤k≤32, -11≤l≤ 12	-16≤ h ≤ 17, -104≤ k ≤ 15, -6 ≤ l ≤ 8	-7≤ h ≤7, -14≤ k ≤ 14, -15 ≤ l ≤ 15

Reflections collected	10182	8748	15150
Independent reflections	2478	2381	3306
Data/restraints/parameters	2478/4/210	2381/0/194	3306/0/224
Goodness-of-fit on F^2	1.018	1.047	1.037
Final R indexes [I>=2σ (I)]	R_1 = 0.0645, wR_2 = 0.1699	R1 = 0.0512, wR2 =0.1170	R1 = 0.0554, wR2 =0.1186
Final R indexes [all data]	R_1 = 0.0845, wR_2 = 0.1912	R1 = 0.0823, wR2 = 0.1382	R1 = 0.0995, wR2 = 0.1436
Largest diff. peak/hole / e $Å^{-3}$	0.82/-0.35	0.27/-0.27	0.33/-0.40
CCDC	2176161	2176159	2176160

Table S3. Bond lengths for **2**·NaOH·5H_2O·2DMF

Parameter		Bond length (Å)	Parameter		Bond length (Å)
Na1	-O6_b	2.068(2)	N3	-C4	1.364(4)
Na1	-O6	2.068(2)	N4	-C3	1.360(4)
Na1	-O4	2.073(2)	N4	-C4	1.336(4)
Na1	-O5	2.140(2)	N5	-N6	1.371(3)
Na1	-O4_b	2.073(2)	N5	-C3	1.329(4)
Na1	-O5_b	2.140(2)	N6	-C2	1.399(4)
Na1	-H5E	1.50(19)	N6	-C4	1.353(4)
Na1	-H5E_b	1.50(19)	N	-HB	0.8800
O1	-N1	1.232(4)	N	-HA	0.8800
O2	-N1	1.224(4)	N8	-C5	1.457(5)
O4	-H4A	0.8700	N8	-C7	1.323(4)
O4	-H4B	0.8700	N8	-C6	1.452(5)
O5	-H5D	0.8700	C1	-C2	1.462(4)
O5	-H5E	0.89(16)	C3	-C3_a	1.466(4)
O6	-H6D	0.8700	C5	-H5A	0.9800
O6	-H6E	0.8700	C5	-H5B	0.9800
O3	-C7	1.230(5)	C5	-H5C	0.9800
N	-C2	1.271(4)	C6	-H6A	0.9800

Table S4 Torsion angles of **2**·NaOH·5H_2O·2DMF

Parameter			Bond angle (°)	Parameter			Bond angle (°)
O1	-N1	-C1 -N2	179.6(3)	C4	-N6	-C2 -N	-178.1(3)
O1	-N1	-C1 -C2	-1.0(4)	C4	-N6	-C2 -C1	2.1(4)
O2	-N1	-C1 -N2	0.6(4)	N5	-N6	-C4 -N3	-179.4(3)
O2	-N1	-C1 -C2	179.9(3)	N5	-N6	-C4 -N4	0.2(3)
C1	-N2	-N3	0.9(4)	C2	-N6	-C4	-1.0(4)

	-C4				-N3		
N3	-N2	-C1	180.0(2)	C2	-N6	-C4	178.6(2)
	-N1				-N4		
N3	-N2	-C1	0.6(5)	C5	-N8	-C7	179.9(3)
	-C2				-O3		
N2	-N3	-C4	179.8(3)	C6	-N8	-C7	-0.6(5)
	-N4				-O3		
N2	-N3	-C4	-0.8(4)	N1	-C1	-C2	-1.1(5)
	-N6				-N		
C4	-N4	-C3	-0.2(3)	N2	-C1	-C2	-2.1(4)
	-N5				-N6		
C4	-N4	-C3	179.4(3)	N1	-C1	-C2	178.7(2)
	-C3_a				-N6		
C3	-N4	-C4	179.5(3)	N2	-C1	-C2	178.2(3)
	-N3				-N		
C3	-N4	-C4	0.0(3)	N4	-C3	-	-180.0(3)
	-N6			C3_a	-N4_a		
C3	-N5	-N6	-178.7(3)	N5	-C3	-	180.0(3)
	-C2			C3_a	-N5_a		
C3	-N5	-N6	-0.3(3)	N4	-C3	-	0.4(4)
	-C4			C3_a	-N5_a		
N6	-N5	-C3	0.3(3)	N5	-C3	-	-0.4(4)
	-N4			C3_a	-N4_a		
N6	-N5	-C3	-179.3(2)				
	-C3_a						
N5	-N6	-	0.1(4)				
C2	-N						
N5	-N6	-C2	-179.7(2)				
	-C1						

Table S5 Hydrogen bonds of **2**·NaOH·5H_2O·2DMF

D-H···A			**d(D-H)/ Å**	**d(H...A)/ Å**	**d(D...A)/ Å**	**<(DHA)/ °**
N	-- HA	.. O5	0.8800	1.9800	2.771(3)	149.00
N	-- HA	.. N5	0.8800	2.4700	2.809(4)	104.00
N	-- HB	.. O1	0.8800	2.2300	2.774(4)	120.00
O4	-- H4A	.. O5	0.8700	1.8900	2.752(3)	174.00
O4	-- H4B	.. N4	0.8700	2.0100	2.883(4)	176.00
O5	-- H5D	.. O3	0.8700	1.8600	2.715(4)	166.00
O6	-- H6D	.. O3	0.8700	1.8600	2.713(3)	166.00
O6	-- H6E	.. N3	0.8700	1.9400	2.810(4)	175.00
C5	-- H5B	.. O2	0.9800	2.4900	3.470(5)	177.00

Table S6. Bond lengths for **2**·4 CH_3OH

Parameter		Bond length (Å)	Parameter		Bond length (Å)
O1	-N6	1.213(3)	N5	-C3	1.332(3)
O2	-N6	1.240(3)	N6	-C3	1.453(3)
O3	-C6	1.421(4)	N7	-C4	1.305(3)
O3	-H3	0.84(4)	N7	-H7A	0.85(3)
O4	-C5	1.409(4)	N7	-H7B	0.92(3)
O4	-H4	0.90(4)	C1	-C1_a	1.466(3)
N1	-C2	1.327(3)	C3	-C4	1.412(3)
N1	-C1	1.355(3)	C6	-H6C	0.92(5)
N2	-C1	1.332(3)	C6	-H6A	0.98(4)
N2	-N3	1.362(3)	C6	-H6B	1.03(4)
N3	-C2	1.367(3)	C5	-H5A	0.94(4)
N3	-C4	1.374(3)	C5	-H5B	0.97(4)
N4	-C2	1.357(3)	C5	-H5C	0.97(5)
N4	-N5	1.313(3)			

Table S7 Torsion angles of **2**·4 CH_3OH

Parameter			Bond angle (°)	Parameter			Bond angle (°)
C2	-N1 -N2	-C1	0.4(3)	N4	-N5 -N6	-C3	-177.42(19)
C2	-N1 -C1_a	-C1	179.1(2)	N4	-N5 -C4	-C3	3.7(4)
C1	-N1 -N3	-C2	-0.5(2)	O1	-N6 -N5	-C3	-5.9(3)
C1	-N1 -N4	-C2	-179.3(2)	O1	-N6 -C4	-C3	173.1(2))
C1	-N2 -C2	-N3	-0.3(2)	O2	-N6 -N5	-C3	173.6(2)
C1	-N2 -C4	-N3	173.0(2)	O2	-N6 -C4	-C3	-7.4(3)
N3	-N2 -N1	-C1	-0.1(3)	N1	-C1 C1_a -N2_a	-	-180.0(2)
N3	-N2 -C1_a	-C1	-178.76(19)	N1	-C1 C1_a -N2_a	-	1.4(3)
N2	-N3 -N1	-C2	0.5(3)	N2	-C1 C1_a -N1_a	-	-1.4(3)
N2	-N3 -N4	-C2	179.4(2)	N2	-C1 C1_a -N2_a	-	180.0(2)
C4	-N3 -N1	-C2	-173.01(19)	N5	-C3 -N3	-C4	-1.6(3)
C4	-N3 -N4	-C2	5.8(3)	N5	-C3 -N7	-C4	179.6(2)
N2	-N3 -N7	-C4	3.5(3)	N6	-C3 -N3	-C4	179.56(18)

N2 -N3 -C3	-C4	-175.50(19)		N6 -C3 -N7	-C4	0.8(4)	
C2 -N3 -N7	-C4	176.0(2)		N5 -N4 -N3	-C2	-3.6(3)	
C2 -N3 -C3	-C4	-2.9(3)		N5 -N4 -N1	-C2	175.0(2)	
C2 -N4 -C3	-N5	-0.9(3)					

Table S8 Hydrogen bonds of **2**·4 CH_3OH

D-H···A			d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
O3	-- H3	.. N1	0.84(4)	1.96(4)	2.797(3)	173(4)
O4	-- H4	.. O3	0.90(4)	1.77(4)	2.671(3)	175(4)
N7	-- H7A	.. O2	0.85(3)	2.06(3)	2.675(3)	128(2)
N7	-- H7A	.. O2	0.85(3)	2.43(3)	3.186(3)	148(2)
N7	-- H7B	.. O4	0.92(3)	1.82(3)	2.718(3)	167(3)

Table S9. Bond lengths for **3**·4 DMSO

Parameter		Bond length (Å)	Parameter		Bond length (Å)
N1	-C1	1.353(4)	C1	-C1_a	1.461(5)
N1	-C2	1.329(4)	C3	-C5	1.433(5)
N2	-C1	1.337(4)	C3	-C4	1.417(5)
N2	-N3	1.362(3)	C6	-H6C	0.9800
N3	-C2	1.379(4)	C6	-H6B	0.9800
N3	-C4	1.360(4)	C6	-H6A	0.9800
N4	-N5	1.318(4)	C7	-H7D	0.9800
N4	-C2	1.351(4)	C7	-H7E	0.9800
N5	-C3	1.354(4)	C7	-H7C	0.9800
N6	-C5	1.139(5)	C8	-H8C	0.9800
N7	-C4	1.306(4)	C8	-H8A	0.9800
N7	-H7B	0.8800	C8	-H8B	0.9800
N7	-H7A	0.8800	C9	-H9A	0.9800
C9A	-H9AC	0.9800			

Table S10 Torsion angles of **3**·4 DMSO

Parameter			Bond angle (°)	Parameter			Bond angle (°)
C2 -N2	-N1	-C1	-0.2(4)	C4 -N1	-N3	-C2	177.2(2)
C2 -C1_a	-N1	-C1	179.2(3)	C4 -N4	-N3	-C2	-3.1(5)
C1 -N3	-N1	-C2	0.2(3)	N2 -N7	-N3	-C4	-1.1(4)
C1	-N1	-C2	-179.5(3)	N2	-N3	-C2	179.6(3)

	-N4				-N4		
C1	-N2	-N3	0.0(3)	N2	-N3	-C2	-0.1(3)
	-C2				-N1		
C1	-N2	-N3	-177.2(3)	C2	-N3	-C4	2.0(4)
	-C4				-C3		
N3	-N2	-C1	0.1(3)	C2	-N3	-C4	-178.0(3)
	-N1				-N7		
N3	-N2	-C1	-179.3(3)	N2	-N3	-C4	178.8(3)
	-C1_a				-C3		
N2	-C1	-	180.0(3)	C2	-N4	-N5	-0.4(4)
C1_a	-N2_a				-C3		
N1	-C1	-	-180.0(3)	N5	-N4	-C2	2.1(4)
C1_a	-N1_a				-N3		
N5	-C3	-C4	179.7(3)	N5	-N4	-C2	-178.2(3)
	-N7				-N1		
C5	-C3	-C4	-180.0(3)	N4	-N5	-C3	179.2(3)
	-N3				-C5		
C5	-C3	-C4	0.0(5)	N4	-N5	-C3	-0.5(5)
	-N7				-C4		

Table S11 Hydrogen bonds of **3**·4 DMSO

D-H···A			**d(D-H)/ Å**	**d(H...A)/ Å**	**d(D...A)/ Å**	**<(DHA)/ °**
N7	-- H7A	.. N2	0.8800	2.5500	2.846(3)	101.00
N7	-- H7A	.. O1	0.8800	1.8900	2.738(3)	161.00
N7	-- H7B	.. O2	0.8800	1.9700	2.783(5)	152.00
C8	-- H8A	.. N6	0.9800	2.5300	3.473(10)	161.00

4. Spectrums of Compounds 2-4

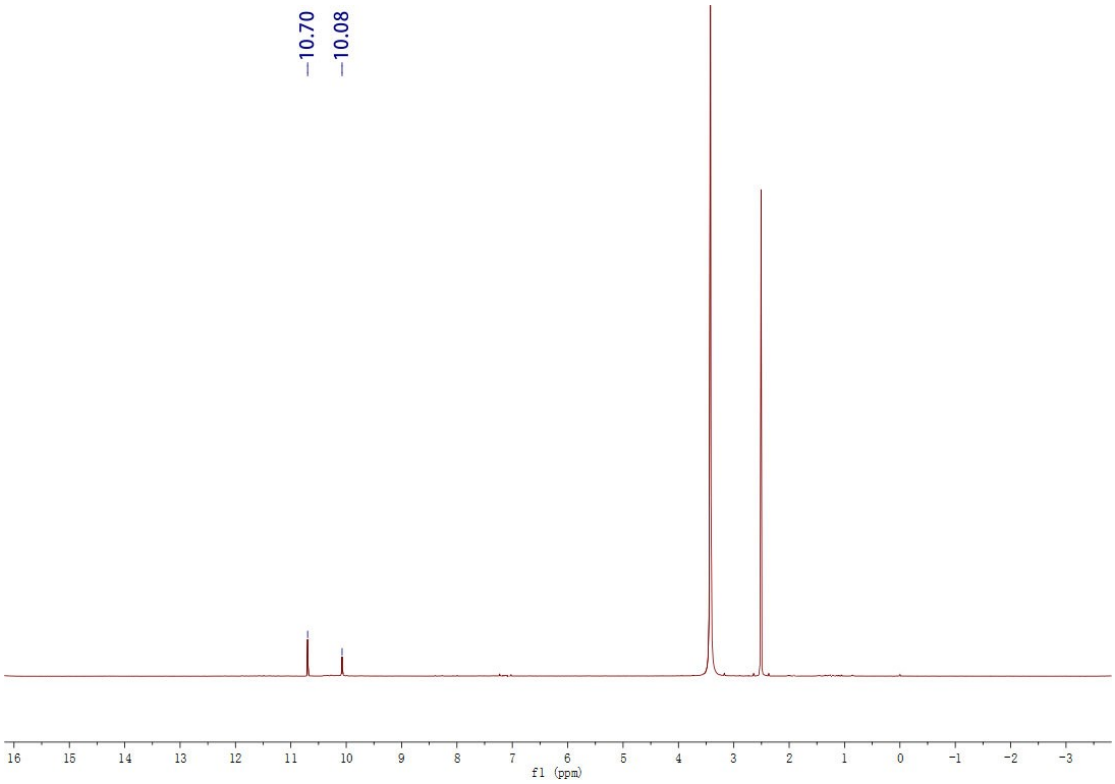


Figure S1. ^{1}H NMR spectra in DMSO-d6 for compound **2**.

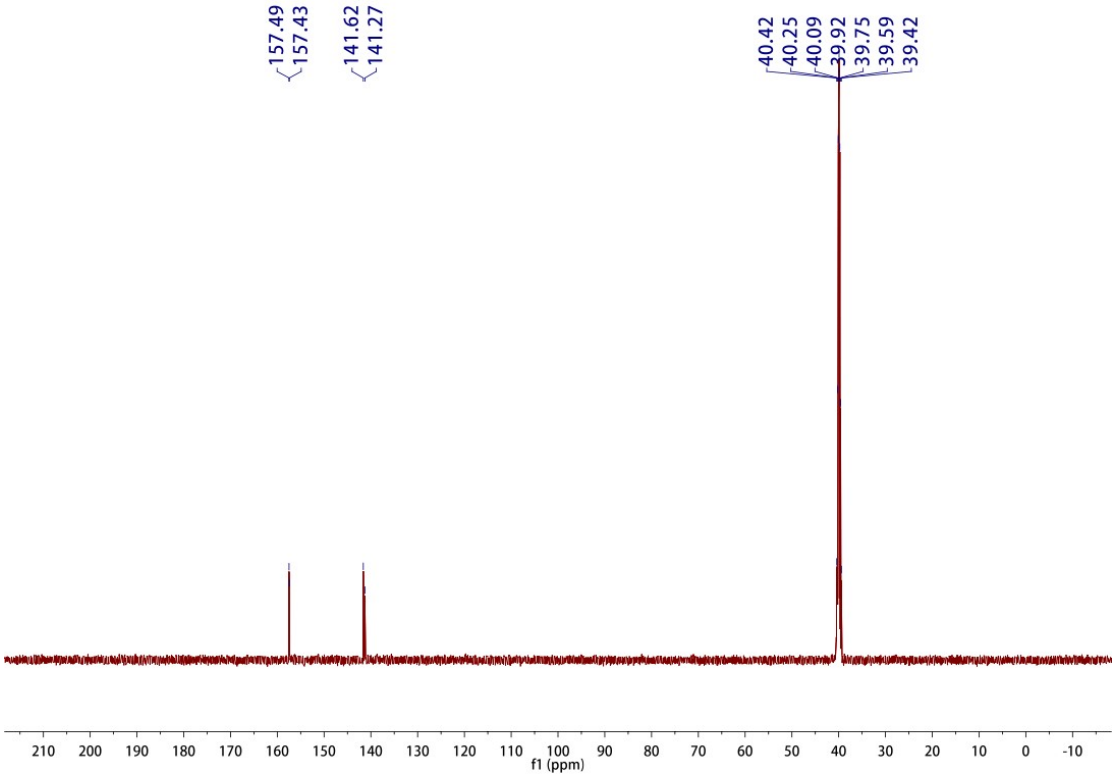


Figure S2. ^{13}C NMR spectra in DMSO-d6 for compound **2**.

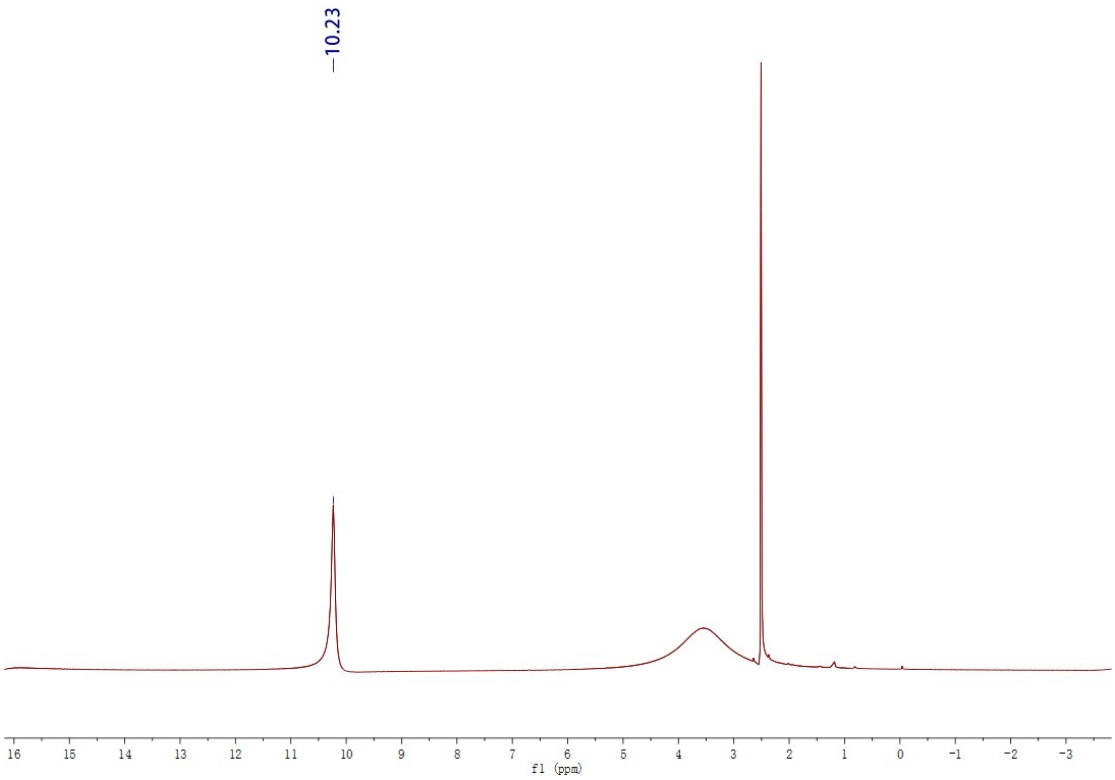


Figure S3. ^{1}H NMR spectra in DMSO-d6 for compound **3**.

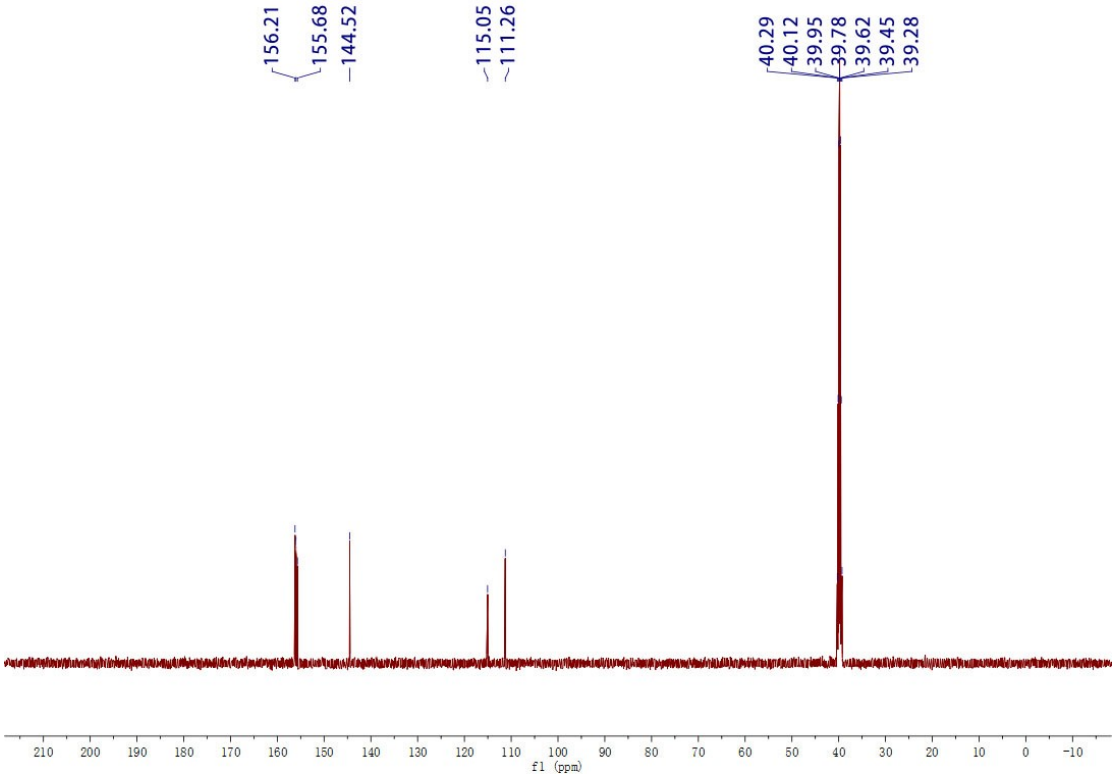


Figure S4. ^{13}C NMR spectra in DMSO-d6 for compound **3**.

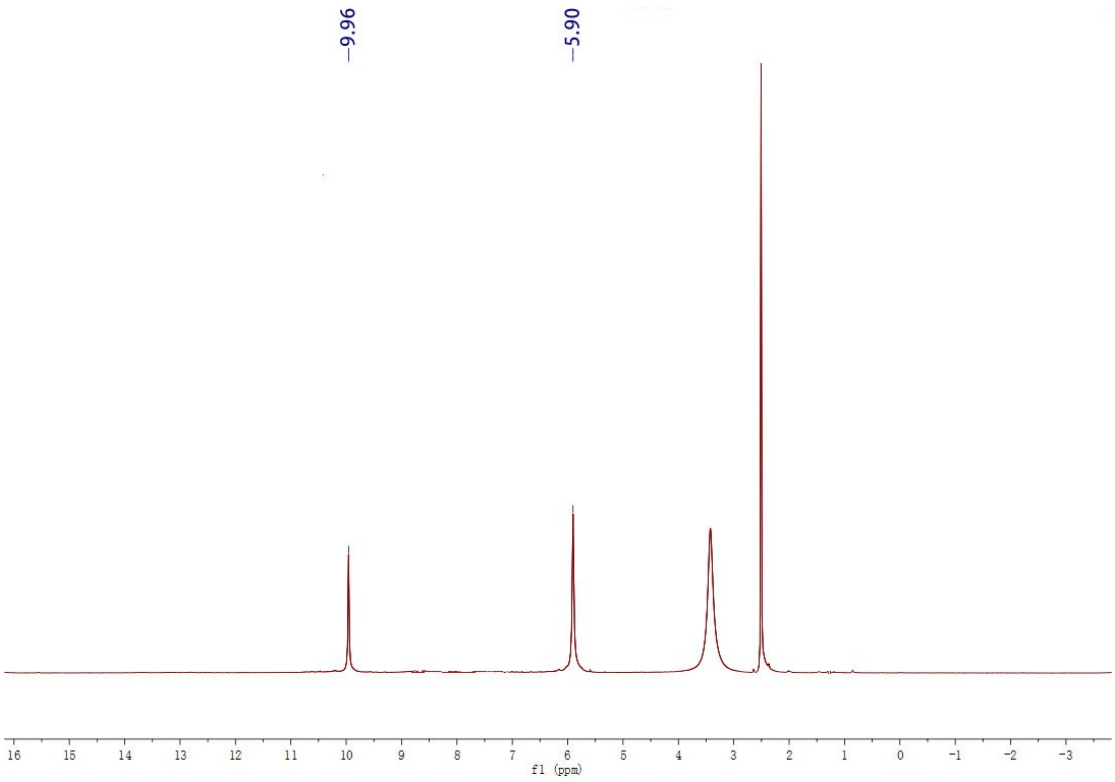


Figure S5. ^{1}H NMR spectra in DMSO-d6 for compound **4**.

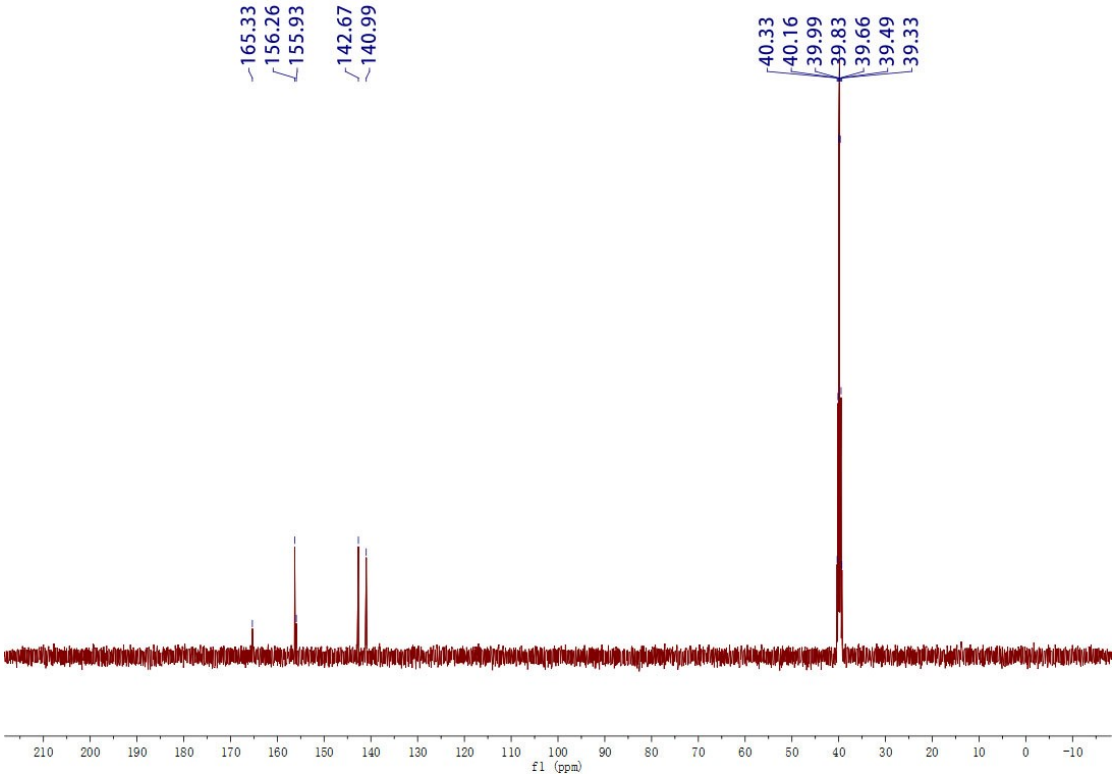


Figure S6. ^{13}C NMR spectra in DMSO-d6 for compound **4**

.

5. DSC Plots of Compounds 2, 3 and 4.

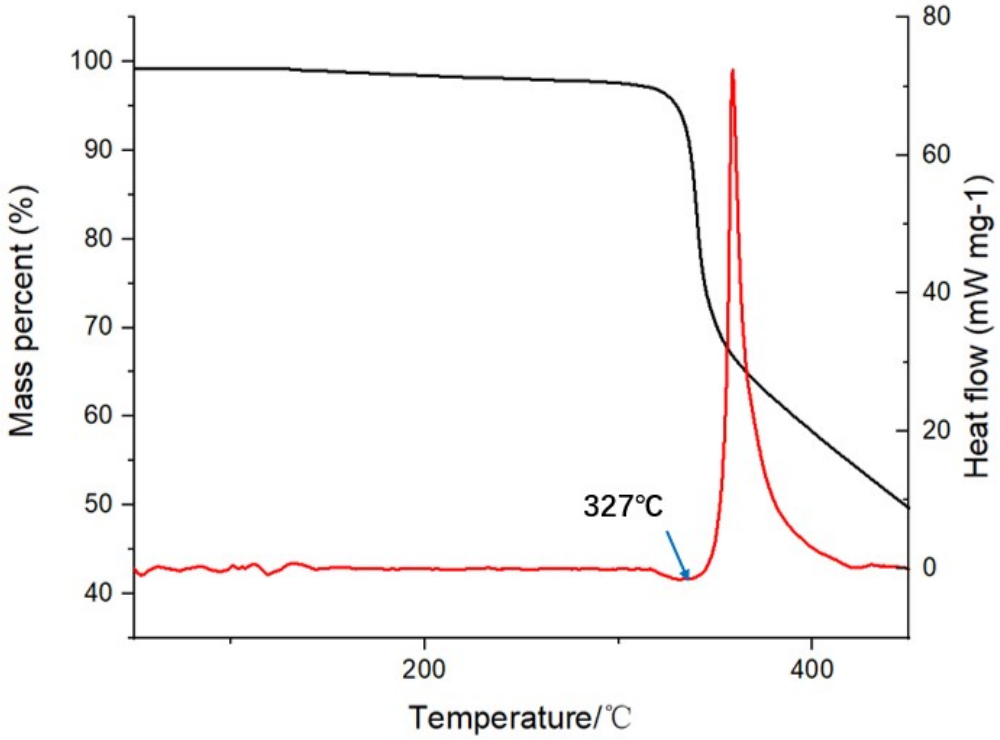


Figure S7 TG and DSC of **2**

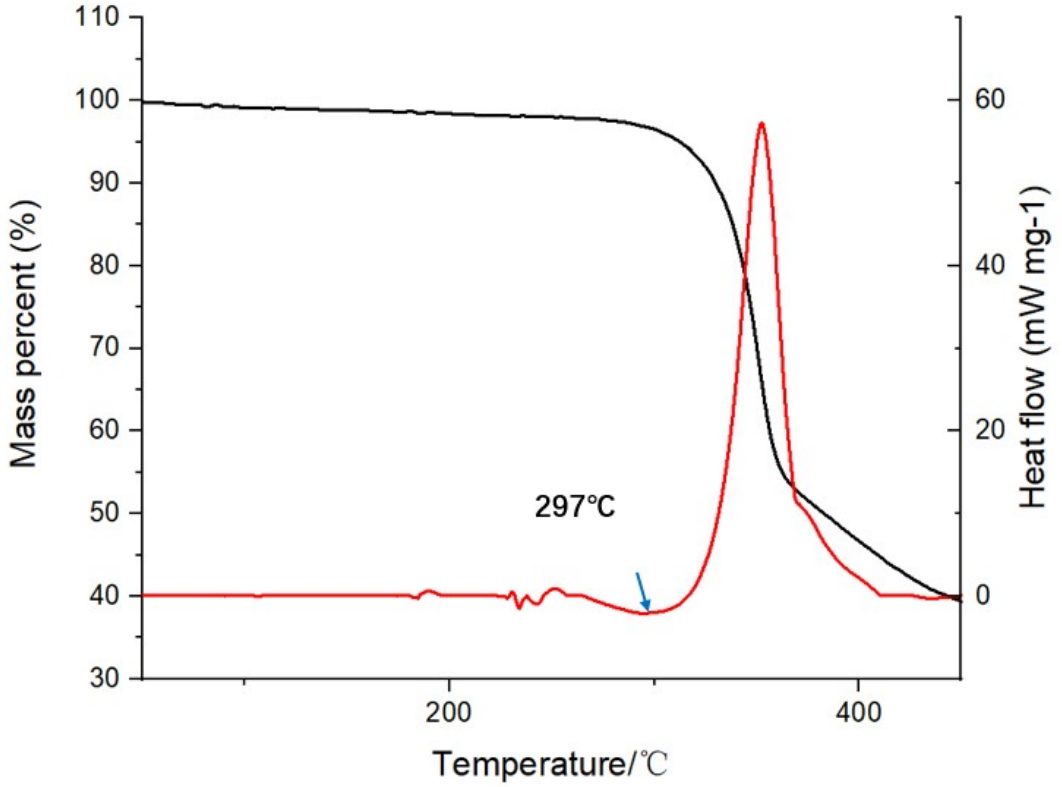


Figure S8 TG and DSC of **3**

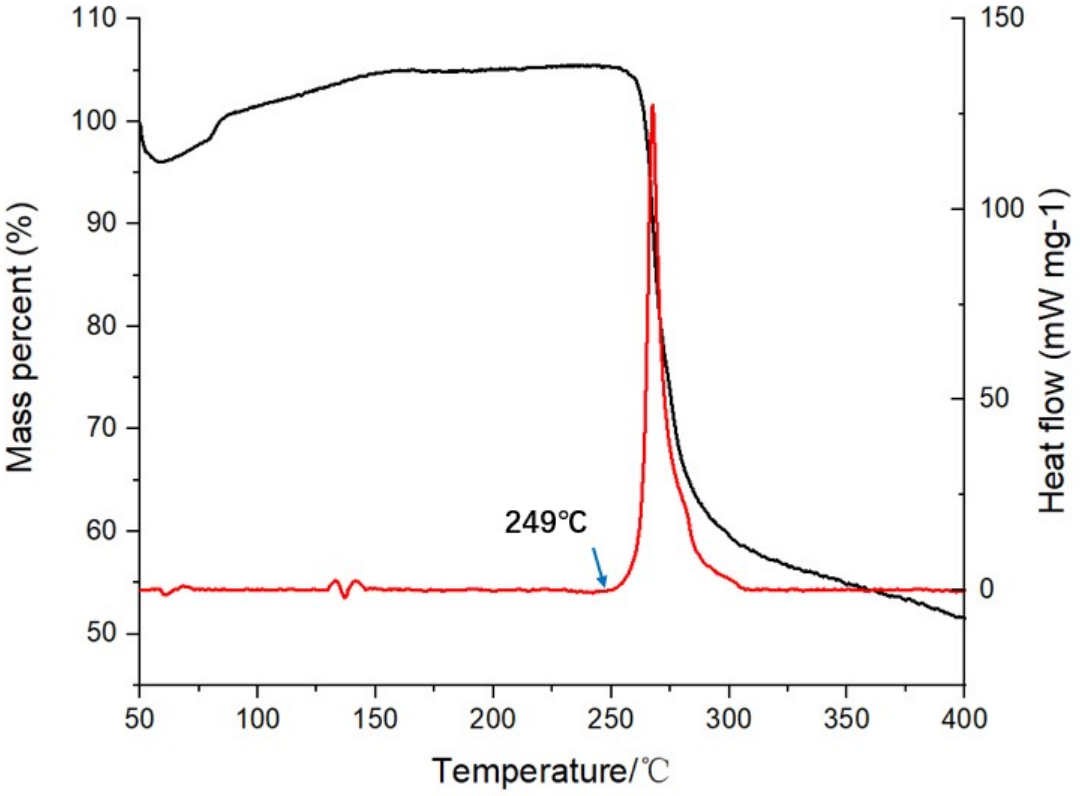


Figure S9 TG and DSC of **4**

6. References

[1] M. J. Frisch. Gaussian 09, Revision D. 01 (Gaussian Inc., 2009).

[2] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652

[3] P. J. Stephens; F. J. Devlin; C. F. Chabalowski; M. J. Frisch. J. Phys. Chem. 1994, 98, 11623-11627.

[4] P. C. Hariharan; J. A. Pople, Theor. Chim. Acta. 1973, 28, 213-222.

[5] J. W. Ochterski; G. A. Petersson ; J. A . Montgomery, J. Chem. Phys. 1996, 104, 2598-2619.