Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Assembling tetrazole-rings on a fused ring framework: toward energetic materials with enhanced performance

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Supporting Information

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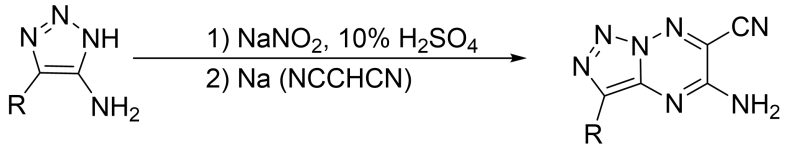
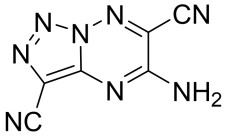
1. Experimental Section



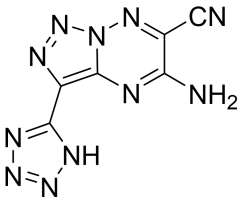
General procedure 1 for synthesis 1-2:

To an ice-cold suspension of **S1-S2** [1] (1.0 mmol) in 10.0 mL 10% H_2SO_4, sodium nitrite (103.5 mg, 1.5 mmol) in distilled water (5.0 mL) was added dropwise. The mixture was warmed up to ~20 °C and stirred 0.5-1 h at this temperature. A mixture of malononitrile (198.0 mg, 3.0 mmol) in distilled water (2.0 mL) was added dropwise into the as-prepared solution of diazonium salt at 0-5 °C. The final reaction was stirred at room temperature for 3 days. The final mixture was filtered, washed by water and dried in vacuum to give **1-2**.



1

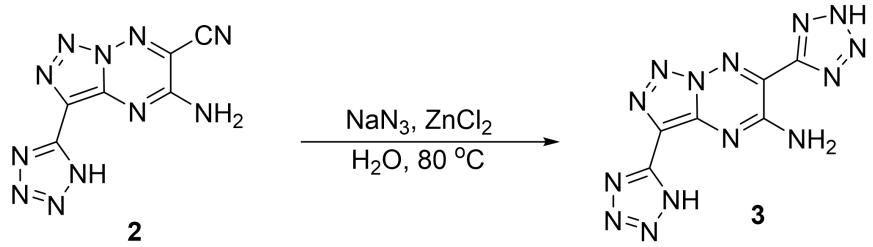
Compound 5-amino-[1,2,3]triazolo[1,5-b][1,2,4]triazine-3,6-dicarbonitrile **1** was obtained as a merdoie solid in 81% yield according to the general procedure 1. **^{1}H NMR** (400 MHz, [D6]DMSO) δ 9.40 (s, 1H), 8.88 (s, 1H). **^{13}C NMR** (101 MHz, [D6]DMSO) δ 152.8, 142.3, 123.6, 112.3, 112.1, 104.7. **IR (KBr pellet)**: υ 3389, 3320, 3194, 2247, 2223, 2207, 1651, 1599, 1541, 1456, 1345, 1320, 1301, 1240, 1223, 1130, 1042, 978, 880, 857, 839, 766, 737, 704, 672, 653, 553, 521, 495, 484, 456, 437 cm^{-1}. **Elemental analysis** (%) calcd for $C_6H_2N_8$ (186.14): C, 38.72; H, 1.08; N, 60.20; found: C, 38.62; H, 1.12; N, 59.88.



2

Compound 5-amino-3-(1H-tetrazol-5-yl)-[1,2,3]triazolo[1,5-b][1,2,4]triazine-6-carbonitrile **2** was obtained as a merdoie solid in 82% yield according to the general procedure 1. **^{1}H NMR** (400 MHz, [D6]DMSO) δ 9.12 (s, 1H), 8.55 (s, 1H). **^{13}C NMR** (101 MHz, [D6]DMSO) δ 151.9, 148.3, 136.8, 122.8, 117.8, 112.4. **IR (KBr pellet)**: υ 3445, 3353, 3271, 3204, 2359, 2341, 2223, 1648, 1601, 1522, 1484, 1456, 1406, 1316, 1303, 1277, 1226, 1122, 1059, 865, 797, 766, 755, 714, 670, 646, 599, 528 cm^{-1}. **Elemental analysis** (%) calcd for $C_6H_3N_{11}$ (229.17): C, 31.45; H, 1.32; N, 67.23; found: C, 31.31; H, 1.38; N, 67.01.

Synthetic procedure of 3



To a solution of **2** (1.0 mmol, 206.0 mg) in 5 mL H_2O was added NaN_3 (1.5 mmol, 98.0 mg) and $ZnCl_2$ (1.2 mmol, 163.0 mg). The reaction mixture was heated to 80 °C and refluxed overnight. Then the resulting mixture was cooled to room temperature and acidified to pH 1-2 with 20% HCl. The precipitate formed was collected and dried in vacuum, giving **3** as a orange solid (45% yield). **^{1}H NMR** (400 MHz, [D6]DMSO) δ 9.25 (s, 1H), 8.59 (s, 1H). **^{13}C NMR** (101 MHz, [D6]DMSO) δ 152.1, 151.1, 148.5, 136.5, 130.8, 117.7. **IR (KBr pellet)**: υ 3374, 3272, 2647, 1606, 1569, 1485, 1444, 1326, 1289, 1261, 1174, 1133, 1078, 1000, 978, 805, 783, 754, 728, 697, 667, 617, 514, 456, 407 cm^{-1}. **Elemental analysis** (%) calcd for $C_6H_4N_{14}$ (272.2): C, 26.48; H, 1.48; N, 72.04; found: C, 26.68; H, 1.53; N, 71.83.

2. X-ray Crystallography

compound	**1**· CH_3CN
CCDC number	2246333
Empirical formula	$C_9H_5N_8$
Formula weight	225.21
Temperature/K	296(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	5.4523(16)
b/Å	12.972(4)
c/Å	14.974(5)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	1059.1(6)
Z	4
$\rho_{calc}g/cm^3$	1.412
μ/mm^{-1}	0.099
F(000)	460.0
Crystal size/mm^3	0.15 × 0.08 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.154 to 55.572
Index ranges	$-7 \le h \le 6$, $-16 \le k \le 15$, $-18 \le l \le 19$
Reflections collected	6680
Independent reflections	2476 [R_{int} = 0.0362, R_{sigma} = 0.0450]
Data/restraints/parameters	2476/0/155
Goodness-of-fit on F^2	1.011
Final R indexes [I>=2σ (I)]	R_1 = 0.0451, wR_2 = 0.0951
Final R indexes [all data]	R_1 = 0.0615, wR_2 = 0.1028
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.26

compound	**2**·$3H_2O$
CCDC number	2246334
Empirical formula	C6 H9 N11 O3
Formula weight	283.24
Temperature	160(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	a = 5.6133(12) Å, α= 90°.
	b = 13.359(3) Å, β= 90°.
	c = 16.245(4) Å, γ= 90°.
Volume	1218.1(4) $Å^3$
Z	4
Density (calculated)	1.544 Mg/m^3
Absorption coefficient	0.127 mm^{-1}
F(000)	584
Crystal size	0.200 x 0.200 x 0.200 mm^3
Theta range for data collection	2.508 to 26.406°.
Index ranges	-6<=h<=7, -16<=k<=15, -20<=l<=19
Reflections collected	7107
Independent reflections	2474 [R(int) = 0.0738]
Completeness to theta = 25.242°	99.3 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2474 / 9 / 199
Goodness-of-fit on F^2	1.023
Final R indices [I>2sigma(I)]	R1 = 0.0532, wR2 = 0.0894
R indices (all data)	R1 = 0.0970, wR2 = 0.1072
Absolute structure parameter	0.3(10)
Extinction coefficient	n/a
Largest diff. peak and hole	0.243 and -0.248 e.$Å^{-3}$

3. Calculations of the Heats of Formation.

The heats of formation of **1**, **2** and **3** were computed with the method of isodesmic reactions by using the Gaussian 16 program [2].

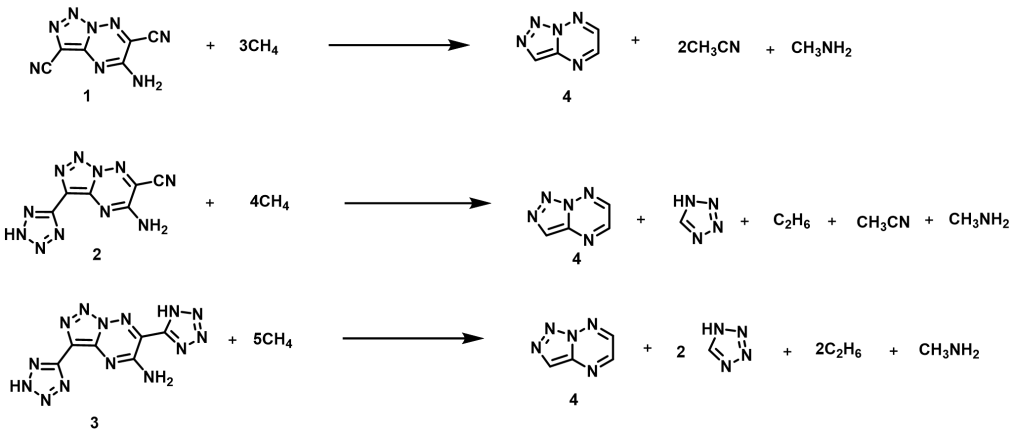


Table S1 Calculated (M052X/6-31+G**// MP2/6-311++G**) total energy(E0), zero-point energy (*ZPE*), values of the correction (Hr), and heats of formation (HOF) of **1**, **2** and **3**.

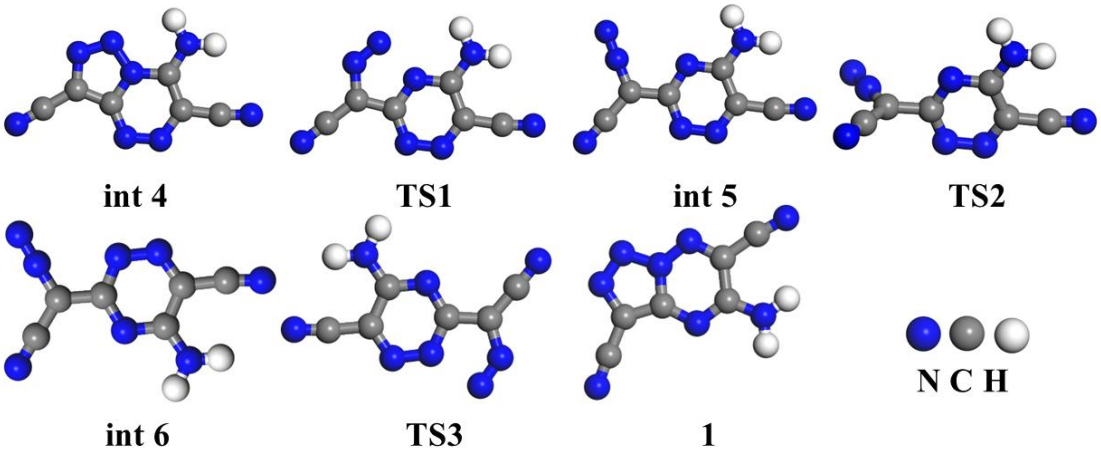
compounds	E_0	*ZPE*	H_r	HOF
CH_4	-40.3796220	0.044793	0.048605	-74.6
CH_3CN	-132.4107856	0.045278	0.049841	74
C_2H_6	-79.5716306	0.074599	0.079027	-84.0
CH_3NH_2	-95.59384	0.06403	0.06840	-23.5
1*H*-tetrazole	-257.65387	0.04686	0.05129	320.0
1	-666.1577495	0.096462	0.108153	755.375515
2	-830.6114171	0.126064	0.139642	938.4574189
3	-995.0806626	0.156527	0.171635	1084.880608
4	-426.8569015	0.083005	0.089449	570.5479602

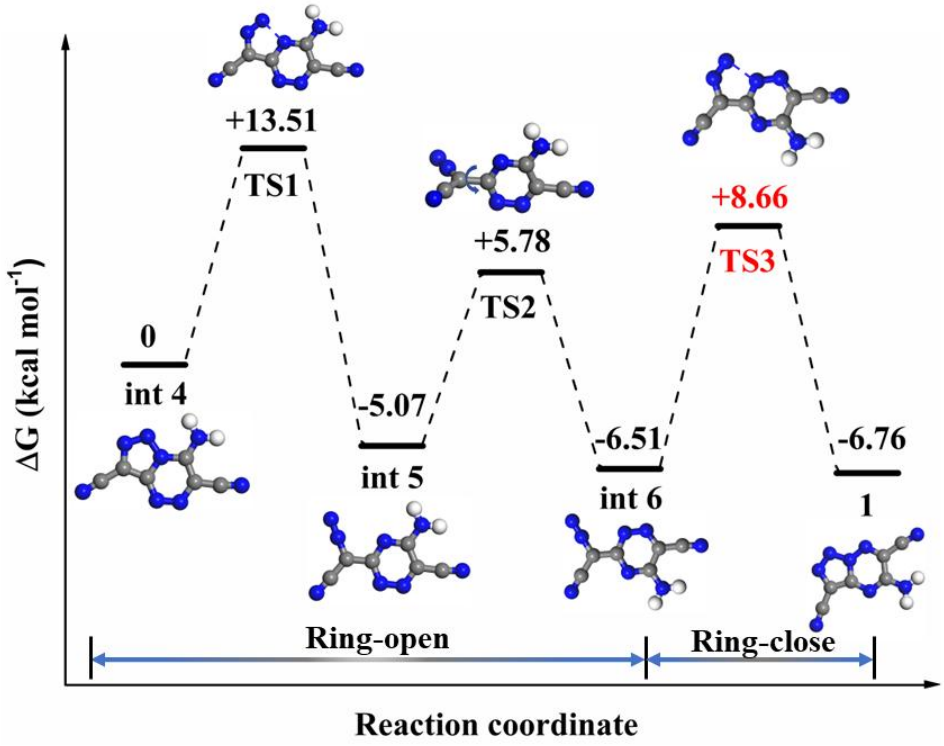
[a] The values of total energy(E0), zero-point energy (*ZPE*), values of the correction (Hr) were calculated with the MP2 method by using the Gaussian 16 program, the value of HOF was calculated with the G2 method by using the Gaussian 16 program.

4. DFT Calculations of Mechanism for DR Reaction.

The geometry optimization and frequency calculations of all species in this study were performed using M062X-D3/def2-TZVP by Gaussian 16 package. The intrinsic reaction coordinate (IRC) was conducted to confirm the connection between the transition state and the right reactant/product. All single-point calculations with the level of wB97X-2-D3/def2-TZVPP were performed by ORCA 5.0.0. [3] Based on high-precision single-point energy and frequency analysis the Gibbs free energy and thermodynamic corrections to Gibbs free energy of all species in the gas-phase of 298.15 K, 1atm were performed by Shermo 2.3.4 package.[4]

Species	E(M062X-D3/def2-TZVPP)(a.u.)	TCG(a.u.)	G(a.u.)	del-G(kcal/mol)
int 4	-666.595488	0.057364	-666.538124	0
TS1	-666.570882	0.054295	-666.516587	13.51
int 5	-666.599762	0.053555	-666.546207	-5.07
TS2	-666.582870	0.053953	-666.528918	5.78
int 6	-666.602164	0.053666	-666.548498	-6.51
TS3	-666.578877	0.054556	-666.524321	8.66
1	-666.606398	0.057498	-666.5489004	-6.76





5. The Electrostatic Potentials (ESP) Analysis of 1, 2 and 3.

Table S2 The detail values of electropositive and electronegative areas of **1**.

The number of surface minima: 8						
number	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	-0.02608729	-0.709871	-16.370033	-6.200722	-0.766771	0.022017
2	0.02835275	0.771517	17.791632	-1.990558	2.398199	1.969828
3	0.02855208	0.776942	17.916717	-1.947224	2.409411	-1.964891
4	-0.01727751	-0.470145	-10.841811	-1.159026	-3.260740	0.033956
5	-0.03994699	-1.087013	-25.067139	1.043038	-4.006705	0.020256
6	-0.01791453	-0.487479	-11.241546	1.265945	2.802968	0.049556
7	-0.04644782	-1.263909	-29.146470	3.921664	-2.621099	-0.011180
8*	-0.05575471	-1.517163	-34.986635	5.644928	2.661317	-0.017735

The number of surface maxima: 6						
number	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	0.10250319	2.789254	64.321777	-4.168623	2.406085	0.045359
2	0.06626631	1.803198	41.582772	-2.523385	0.686259	-1.624892
3	0.06604795	1.797256	41.445748	-2.612347	0.681219	1.603320

4*	0.10465363	2.847770	65.671201	-1.469699	4.206911	0.007103
5	0.07190994	1.956769	45.124207	-0.470394	-0.072570	-1.642662
6	0.07208645	1.961572	45.234968	-0.488230	-0.085533	1.642546

Table S3 The detail values of electropositive and electronegative areas of **2**.

The number of surface minima: 11						
number	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	-0.02398382	-0.652633	-15.050089	-7.079017	-0.281843	0.005142
2	-0.01606853	-0.437247	-10.083166	-2.704876	3.141705	0.014812
3	0.03599302	0.979420	22.585982	-2.431931	-2.527477	-1.975575
4	0.03465223	0.942935	21.744620	-2.440307	-2.531846	1.979592
5	-0.04142160	-1.127139	-25.992469	-0.572820	4.357305	0.020753
6	0.02418129	0.658006	15.173999	0.112504	-1.838338	1.642570
7	0.02425255	0.659945	15.218718	0.115836	-1.815912	-1.652219
8	-0.06064792	-1.650314	-38.057178	2.836162	3.022500	0.001051
9*	-0.07026192	-1.911924	-44.090056	4.346811	2.405596	0.041852
10	-0.04585189	-1.247693	-28.772520	5.179148	-2.990854	0.083313
11	-0.06616345	-1.800399	-41.518224	6.470313	-0.253196	0.039462

The number of surface maxima: 7						
number	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	0.10683448	2.907114	67.039707	-4.414077	-3.055484	0.016840
2	0.07049157	1.918173	44.234168	-3.150888	-1.001934	-1.632007
3	0.06976543	1.898414	43.778505	-3.086331	-0.937378	1.664936
4*	0.11560531	3.145780	72.543485	-1.366505	-4.193896	0.045991
5	0.07549187	2.054238	47.371904	-1.323261	0.157961	-1.642989
6	0.07549581	2.054345	47.374376	-1.341751	0.274505	1.640999
7	0.09814239	2.670590	61.585333	1.330428	-3.003040	0.045909

Table S4 The detail values of electropositive and electronegative areas of **3**.

The number of surface minima: 11						
number	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	-0.06821077	-1.856109	-42.802937	-7.369816	-0.159871	0.056004
2	-0.04841078	-1.317324	-30.378247	-6.075708	-2.969347	0.037928

3*	-0.07218068	-1.964136	-45.294098	-5.300280	2.434318	0.025894
4	-0.06262892	-1.704219	-39.300272	-3.711509	2.977786	0.021867
5	0.01860232	0.506195	11.673139	-1.024641	-1.872517	-1.648439
6	0.01865975	0.507758	11.709178	-0.966357	-1.805123	1.695634
7	-0.03820174	-1.039522	-23.971973	-0.481567	4.359212	0.020155
8	0.02575255	0.700762	16.159980	1.573109	-2.689680	-1.960161
9	0.02573730	0.700348	16.150416	1.678351	-2.596503	1.964161
10	-0.03503384	-0.953319	-21.984087	6.859749	-1.790345	0.020058
11	-0.02215687	-0.602919	-13.903657	7.087440	1.243473	-0.004497

The number of surface maxima: 14						
number	a.u.	eV	kcal/mol	X/Y/Z coordinate(Angstrom)		
1	0.01254196	0.341284	7.870206	-4.061539	-0.571899	-1.774862
2	0.01257158	0.342090	7.888789	-4.113871	-0.590646	1.758699
3	0.09323484	2.537049	58.505795	-2.264262	-2.986097	0.021787
4	0.10534851	2.866679	66.107246	0.205266	-4.179012	-0.007188
5	0.07181579	1.954207	45.065125	0.544735	0.221085	-1.653623
6	0.07178038	1.953243	45.042906	0.548161	0.222777	1.654055
7	0.06322570	1.720459	39.674761	2.073867	-0.872470	-1.736805
8	0.06321526	1.720175	39.668206	2.103453	-0.851795	1.737860
9	0.06042013	1.644115	37.914235	2.741649	0.848832	1.710937
10	0.06037703	1.642942	37.887189	2.770303	0.873346	-1.705606
11	0.07822570	2.128630	49.087411	3.013563	-3.618778	0.030989
12*	0.11984336	3.261104	75.202906	3.843863	3.136443	0.040592
13	0.05243500	1.426829	32.903487	4.184944	0.050853	-1.744225
14	0.05247304	1.427864	32.927360	4.212384	0.070122	1.739196

Reference

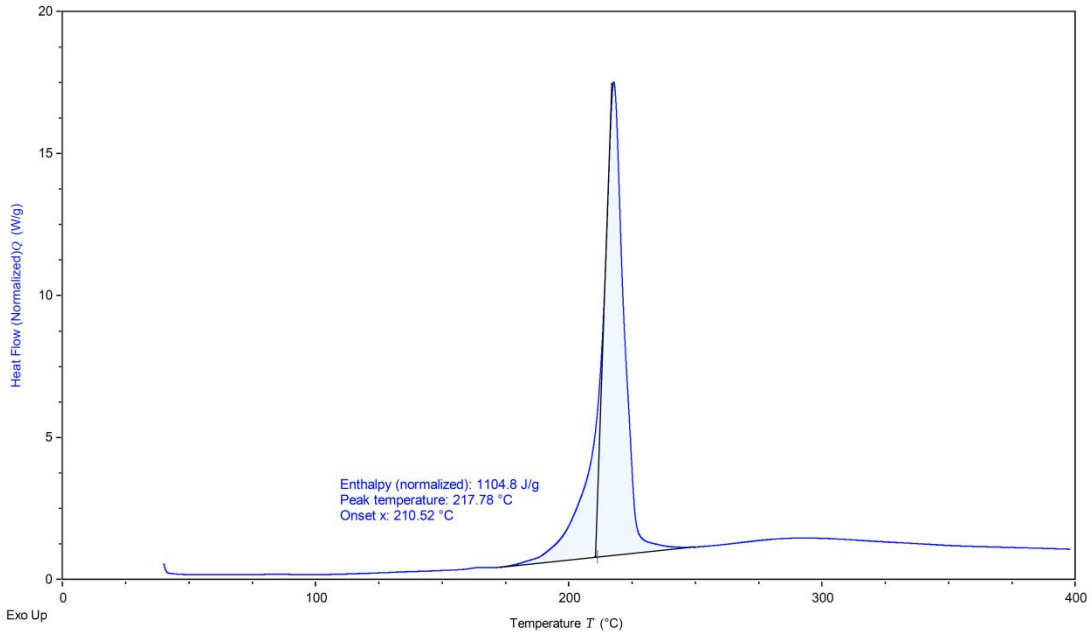
[1] D. Izsak, T. M. Klapötke and C. Pfluger, Dalton Trans., 2015, 44, 17054–17063.

[2] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian, Inc., Wallingford CT, 2019.

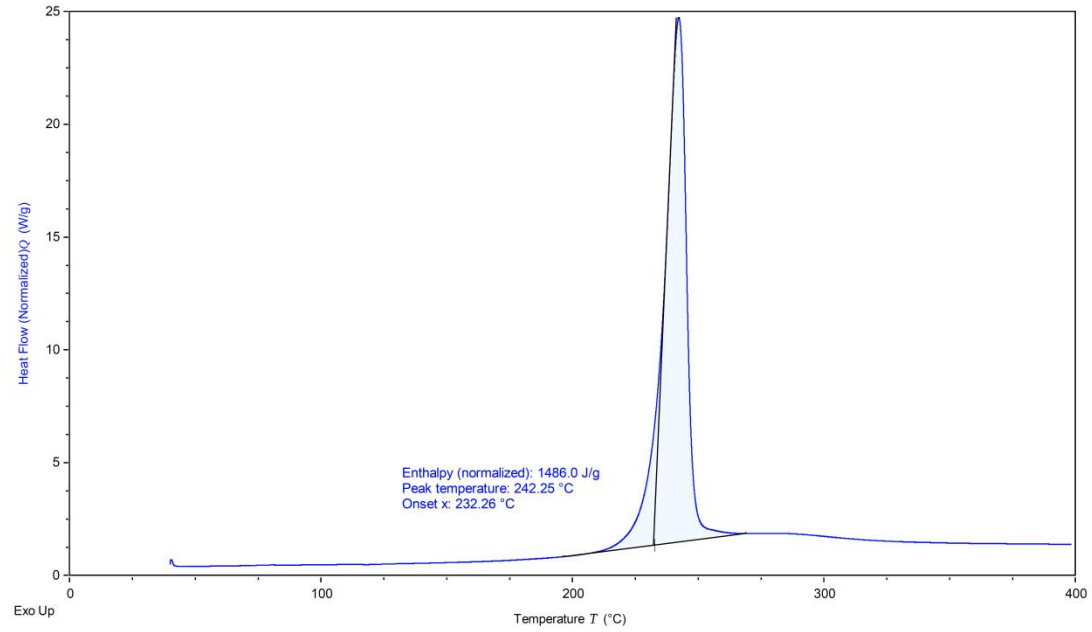
[3] Neese, F. Software update: The ORCA program system—Version 5.0. WIREs Comput Mol Sci., 2022, 12:e1606. DOI: 10.1002/wcms.1606

[4] Tian Lu, Qinxue Chen. Shermo: A general code for calculating molecular thermochemistry properties, Comput. Theor. Chem., 2021, 1200, 113249.

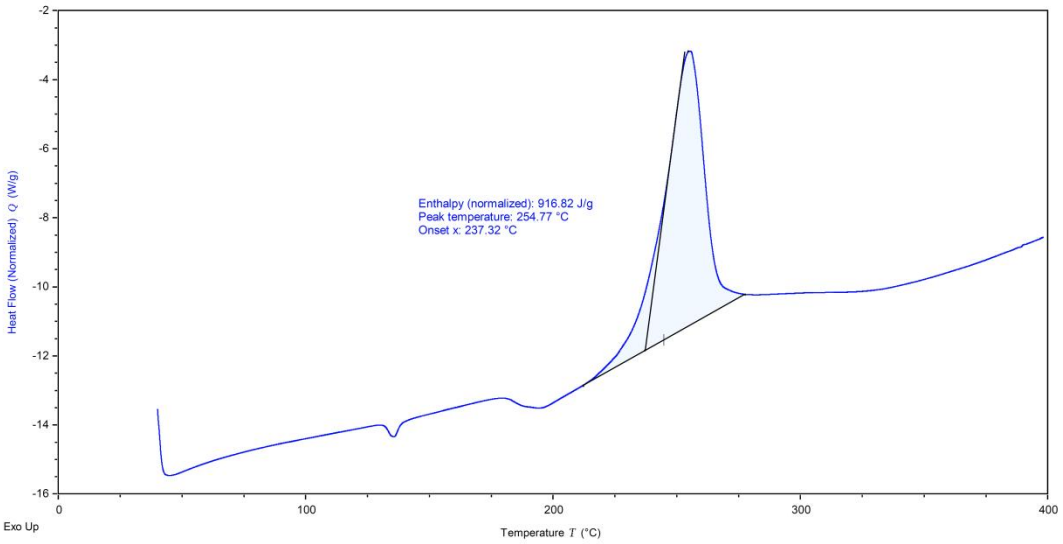
6. DSC Plot of All Products.



DSC Plot of Compound **1**

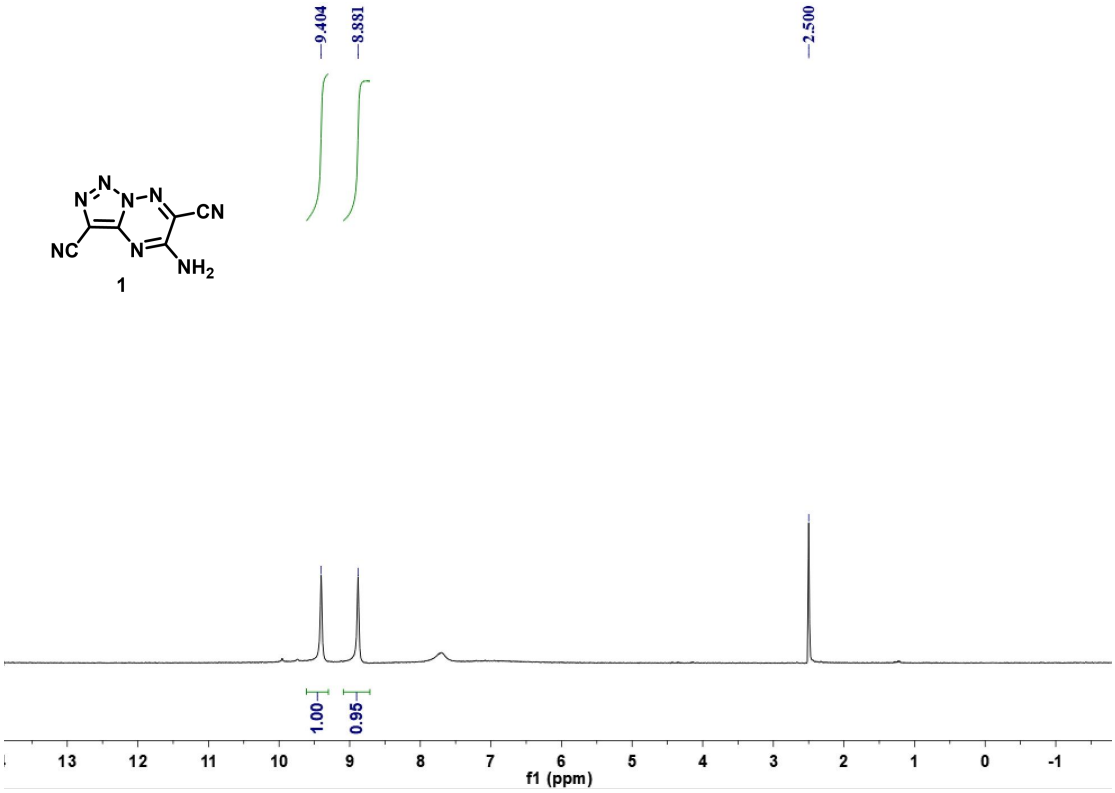


DSC Plot of Compound **2**

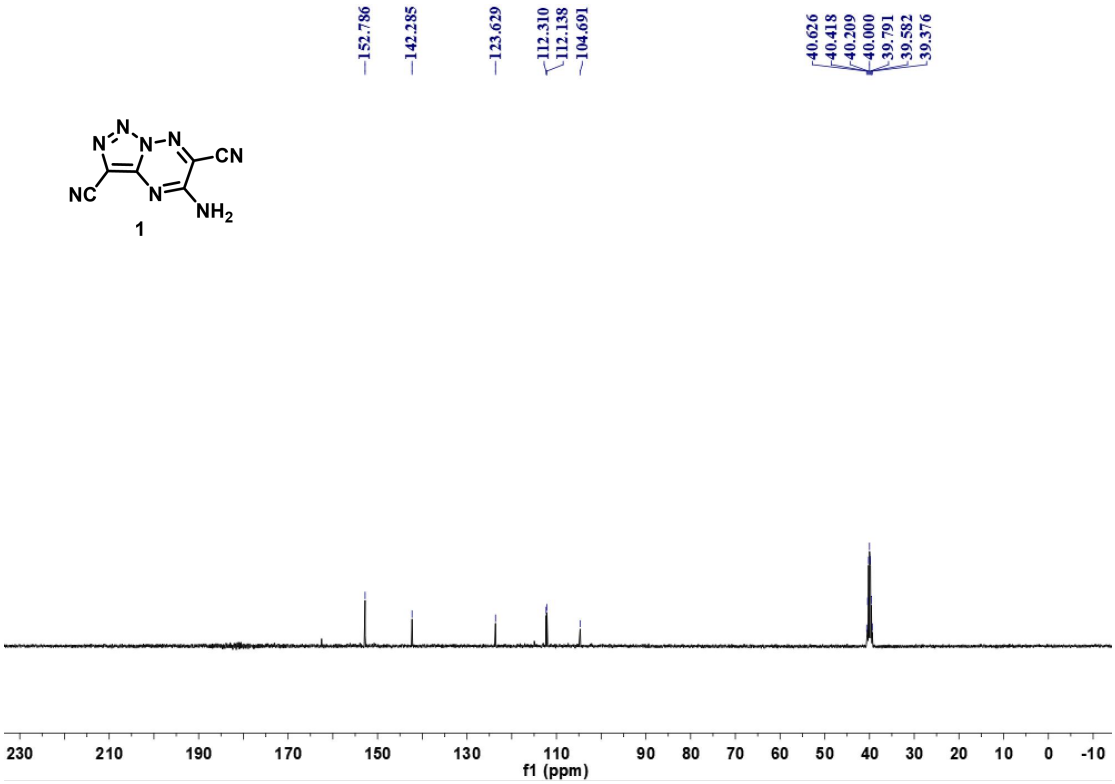


DSC Plot of Compound **3**

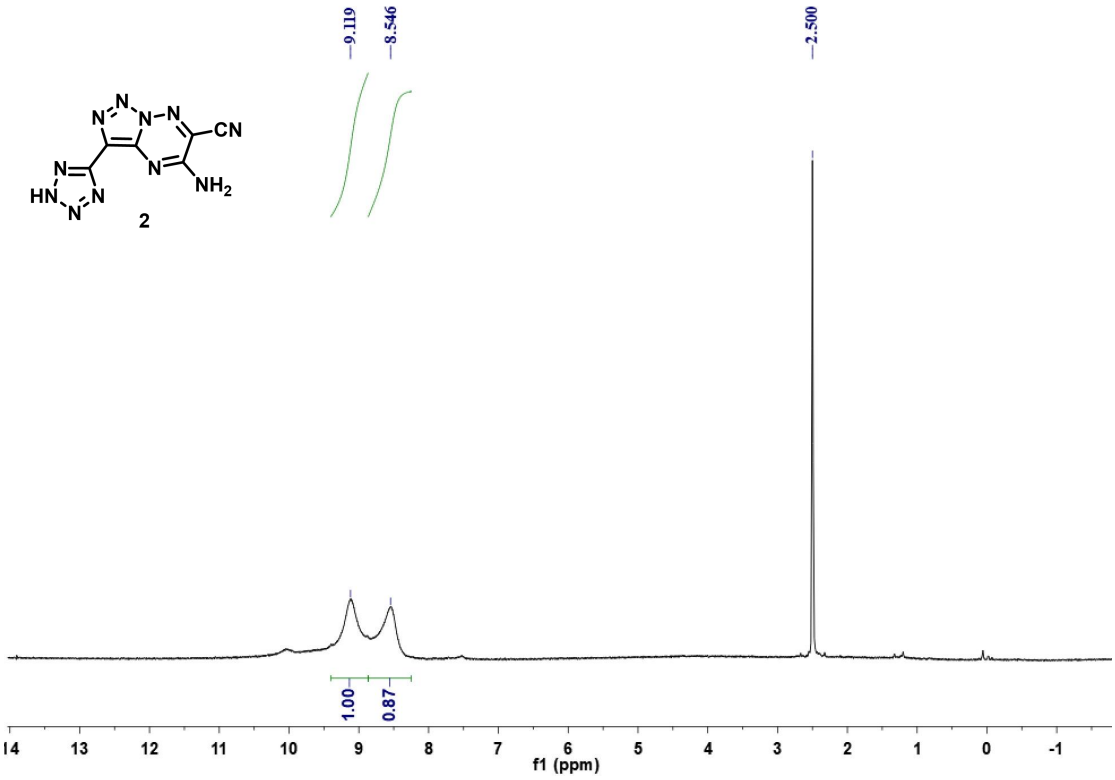
7. NMR Spectra of All Products



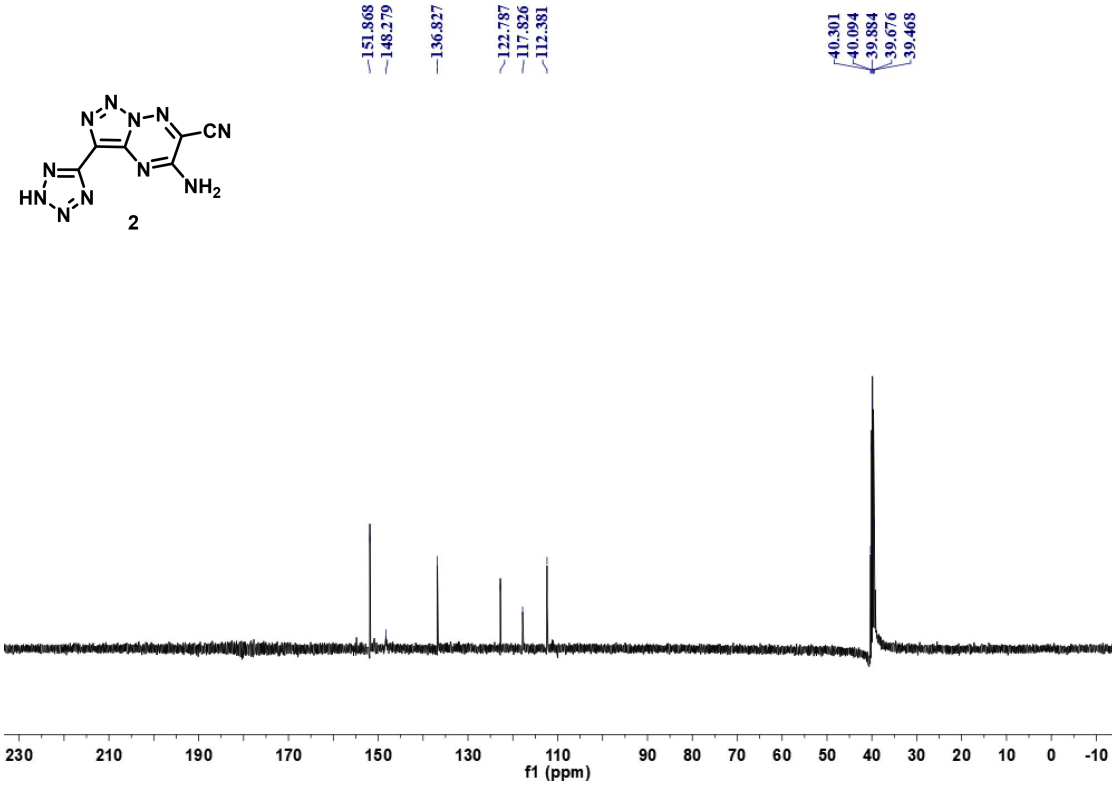
^{1}H NMR of compound **1**



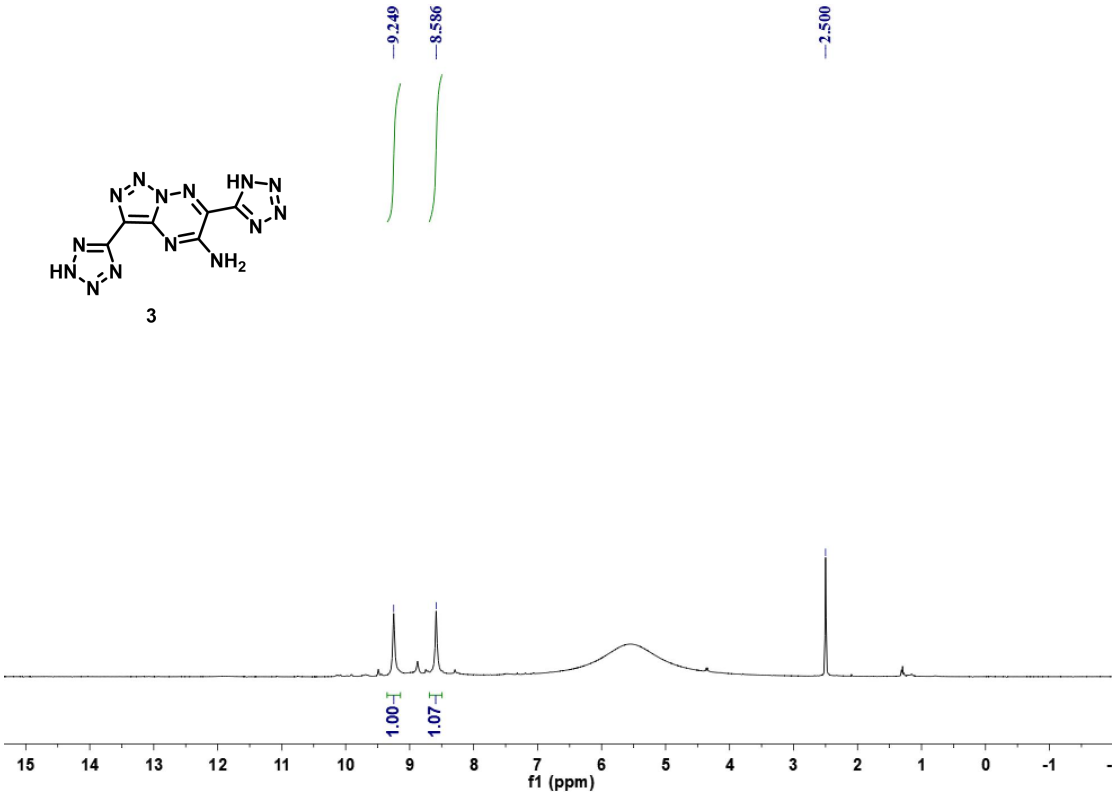
^{13}C NMR of compound **1**



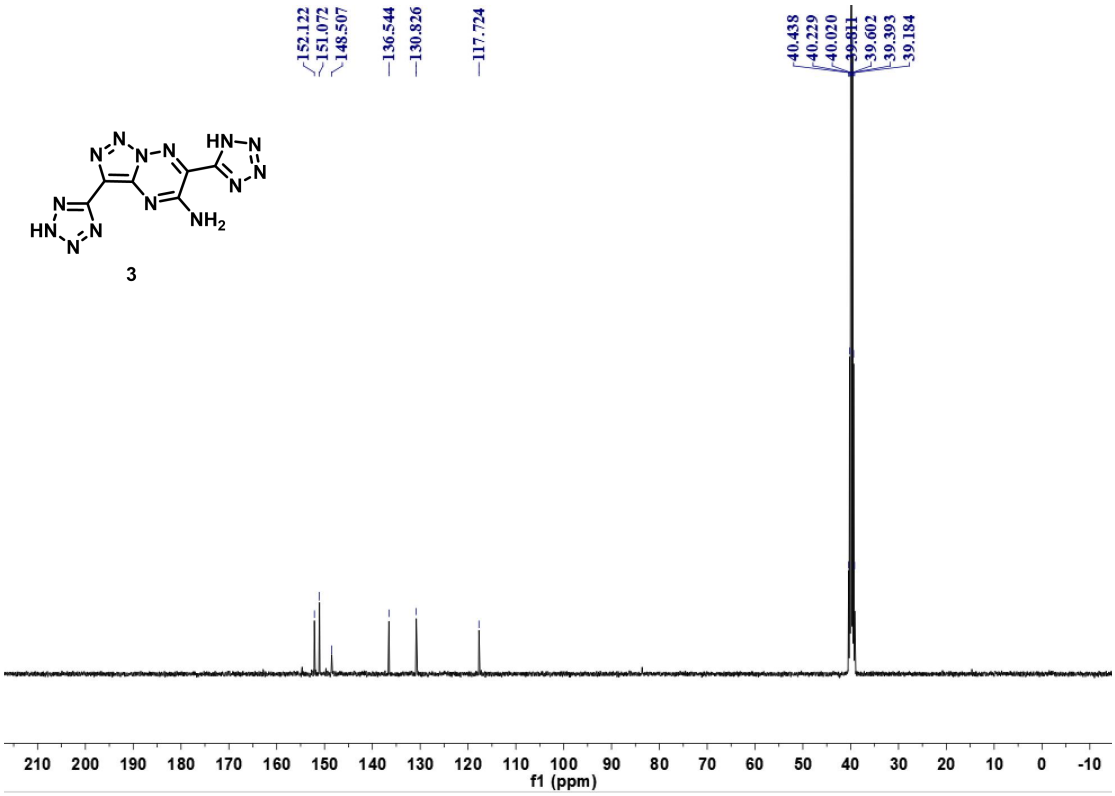
^{1}H NMR of compound **2**



^{13}C NMR of compound **2**



^{1}H NMR of compound **3**



^{13}C NMR of compound **3**