

## Supporting Information

# **Nitropyrazole-triazole backbone: a promising energetic skeleton to advanced energetic materials**

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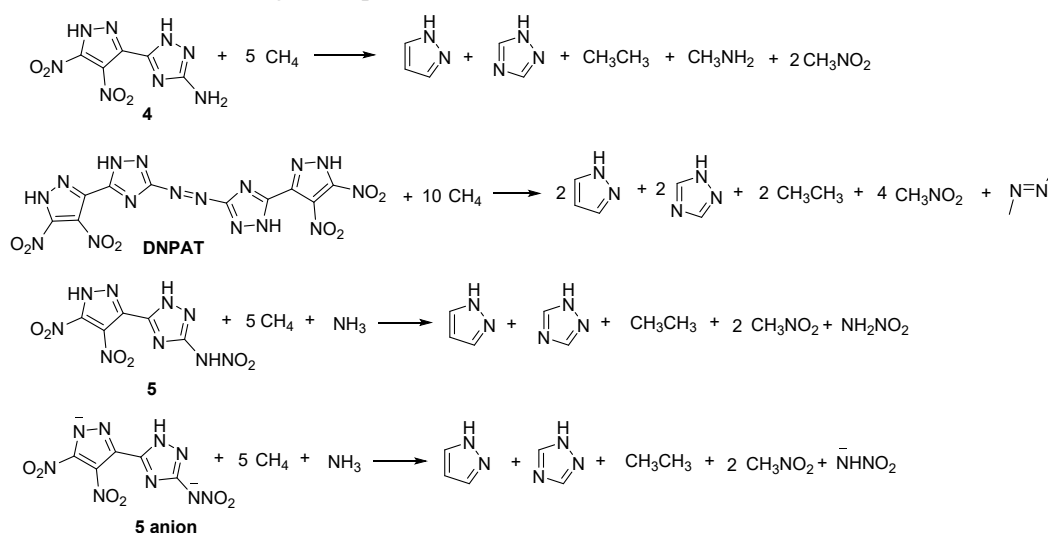
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## 1. Computational details

Computations were performed by using the Gaussian09 suite of programs.<sup>1</sup> The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)<sup>2</sup> functional with the 6-311+G\*\* basis set.<sup>3</sup> 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.<sup>4</sup> All the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies. The lattice energy of the trinitroethyl derivatives were predicted by using the formula suggested by Jenkins et al.

The predictions of heats of formation (HOF) 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 of target compounds are shown in Scheme S1.



**Scheme S1.** The isodesmic reactions for calculating heat of formation for synthesized compounds.

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

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

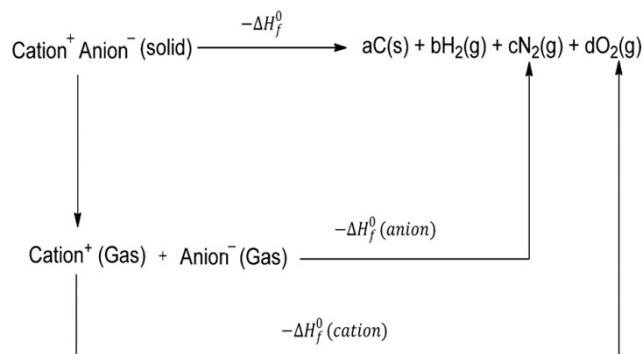
Where  $\Sigma \Delta_f H_P$  and  $\Sigma \Delta_f H_R$  are the HOF of the reactants and products at 298 K, respectively, and  $\Delta H_{298}$  can be calculated from the following expression in Equation (2):

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

where  $\Delta E_0$  is the change in total energy between the products and the reactants at 0 K;  $\Delta ZPE$  is the difference between the zero-point energies (ZPE) of the products and the reactants at 0 K;  $\Delta H_T$  is the thermal correction from 0 to 298 K. The  $\Delta(PV)$  value in Equation(2) is the  $PV$  work term. It equals  $\Delta nRT$  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.

Based on a Born-Haber energy cycle (Scheme S2, the heat of formation of a salt can be simplified by Equation (3):

$$\Delta H_f^\circ(\text{ionic salt}, 298 \text{ K}) = \Delta H_f^\circ(\text{cation}, 298 \text{ K}) + \Delta H_f^\circ(\text{anion}, 298 \text{ K}) - \Delta H_L \quad (3)$$



**Scheme S2** Born–Haber cycle for the formation of energetic salts

where  $\Delta H_L$  is the lattice energy of the salt which could be predicted by the formula suggested by Jenkins et al.<sup>4</sup> as given in Equation (4):


$$\Delta HL = UPOT + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (4)$$

where  $n_M$  and  $n_X$  depend on the nature of the ions  $Mp^+$  and  $Xq^-$ , respectively, and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy  $UPOT$  takes the form of equation (5):

$$UPOT (\text{kJ} \cdot \text{mol}^{-1}) = \gamma(\rho_m/M_m)^{1/3 + \delta} \quad (5)$$

where  $\rho_m$  is the density ( $\text{g} \cdot \text{cm}^{-3}$ ),  $M_m$  is the chemical formula mass of the ionic material and the coefficients  $\gamma$  ( $\text{kJ} \cdot \text{mol}^{-1} \text{cm}$ ) and  $\delta$  ( $\text{kJ} \cdot \text{mol}^{-1}$ ) are 8375.6 and -178.8, respectively.

Total energy and heat of formation for the title compounds at B3LYP/6-311+G\*\* level are provide as follows:

Compound	$E_0^a/\text{a.u.}$	ZPE <sup>b</sup> /kJ mol <sup>-1</sup>	$H_T^c/\text{kJ mol}^{-1}$	HOF <sup>d</sup> /kJ mol <sup>-1</sup>
CH <sub>4</sub>	-40.5339263	112.26	10.04	-74.6 <sup>e</sup>
NH <sub>3</sub>	-56.5826356	86.27	10.05	-45.9 <sup>e</sup>
CH <sub>3</sub> CH <sub>3</sub>	-79.8565413	187.31	11.79	-84 <sup>e</sup>
CH <sub>3</sub> NH <sub>2</sub>	-95.8938402	160.78	11.64	-22.5 <sup>e</sup>
NH <sub>2</sub> NO <sub>2</sub>	-261.124816	98.79	12.39	-3.9 <sup>e</sup>
CH <sub>3</sub> NO <sub>2</sub>	-245.091555	124.93	11.6	-80.8 <sup>e</sup>
CH <sub>3</sub> NNCH <sub>3</sub>	-189.333735	211.85	16.32	147.85
NHNO <sub>2</sub> <sup>-</sup>	-250.573074	65.76	11.37	-120.22 <sup>f</sup>
NH <sub>2</sub> NH <sub>2</sub>	-	134.28	11.16	95.4
Pyrazole anion	-225.669742	141.88	12.21	163.53
Pyrazole	-226.260331	179.2	12.57	177.4
triazole	-242.320387	150.39	12.06	192.7
	-242.669331	184.02	12.27	831.72

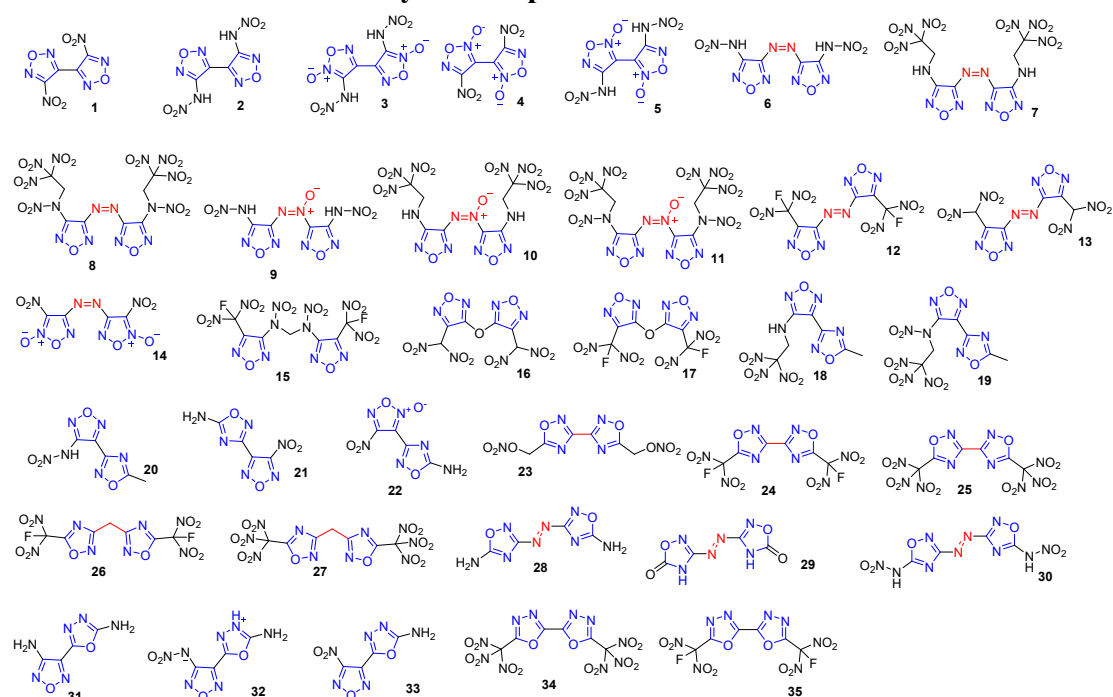
## 2. Experimental Methods

**General:** Although we have not encountered any difficulties in preparing the new energetic material, manipulations must be carried out by using standard safety precautions. Leather coat, ear protection, latex gloves, and face shield are strongly recommended for the experimental operation. All compounds should be handled with extreme care.

**General methods:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 500 and 125 MHz, respectively, by using either DMSO- $d_6$  or acetone- $d_6$  as the solvent and locking solvent unless otherwise stated. Chemical shifts in  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are reported relative to DMSO. DSC was performed at a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in closed Al containers with a nitrogen flow of  $30\text{ mL min}^{-1}$  on an STD-Q600 instrument. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR equipped with an ATR unit at  $25\text{ }^\circ\text{C}$ . Impact sensitivity, friction sensitivity and electrostatic discharge sensitivity of samples are measured by using the standard BAM methods.

**X-ray crystallography:** The data were collected with a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. A Kryoflex low-temperature device was used to keep the crystals at a constant 100 K during the data collection. The data collection and the initial unit cell refinement were performed by using APEX2 (v2010.3-0). Data reduction was performed by using SAINT (v7.68A) and XPREP (v2008/2). Corrections were applied for Lorentz, polarization, and absorption effects by using SADABS (v2008/1). The structure was solved and refined with the aid of the programs in the SHELXTL-plus (v2008/4) system of programs. The full-matrix least-squares refinement on F2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included in a riding model. The structure was solved by direct methods with SHELXS-97 and expanded by using the Fourier technique. The nonhydrogen atoms were refined anisotropically. The hydrogen atoms were located and refined.

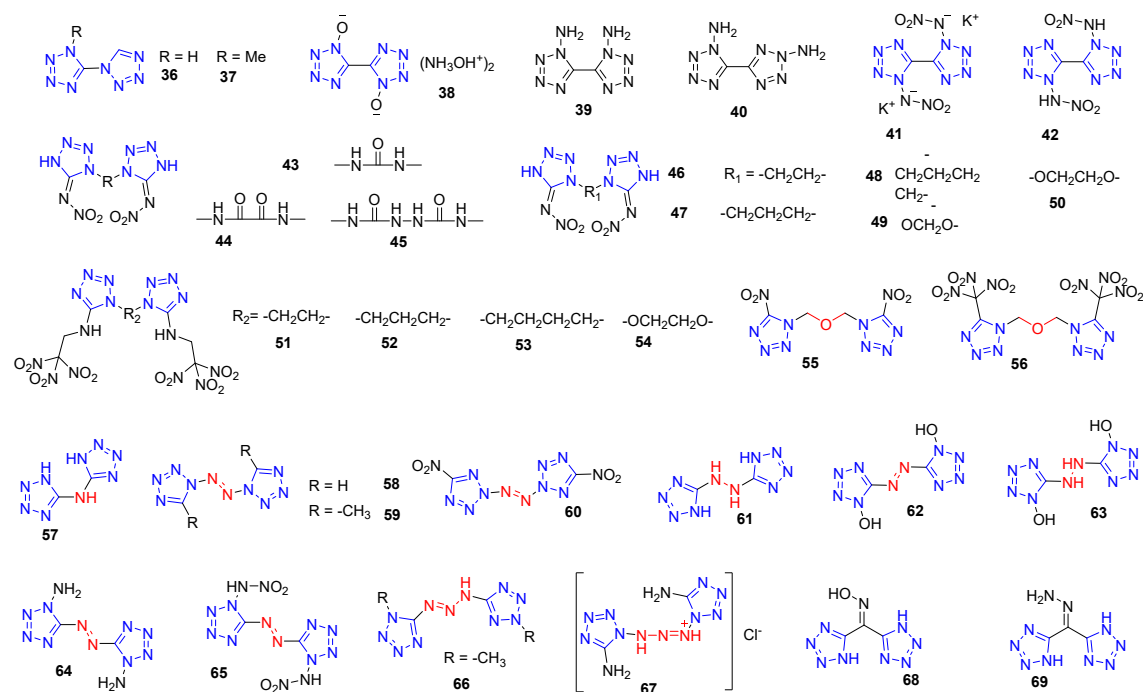
### 3. Database of N-hetero-bicyclic compounds



**Table S1.** Energetic properties of bicyclic oxadiazole-based energetic compound

Compd	$T_d^a$ [°C]	$\Delta_f H^b$ [kJ mol <sup>-1</sup> ]	$D^c$ [m s <sup>-1</sup> ]	$P^d$ [GPa]	$d^e$ [g cm <sup>-3</sup> ]	$IS^f$ [J]	$FS^g$ [N]
<b>1</b>	85	414	9227	35.7	1.85	3.5	/
<b>2</b>	80	526	9477	41.5	1.94	1.5	48
<b>3</b>	74.5	462	9381	40.8	1.91	3.0	20
<b>4</b>	140	449	9525	34.7	2.01	/	/
<b>5</b>	91.3	431	9472	41.7	1.94	2	20
<b>6</b>	122	824	9255	41.4	1.91	3.0	20
<b>7</b>	230	781	8900	36.3	1.82	7.4	111
<b>8</b>	159	1259	9486	40.8	1.87	3.5	70
<b>9</b>	90	772	9131	44.1	1.88	1.0	2
<b>10</b>	190	759	9041	36.7	1.84	7.9	130
<b>11</b>	145	961	9458	41.2	1.92	1.2	80
<b>12</b>	166	176	8492	30.5	1.87	5	120
<b>13</b>	140	526	8936	34.6	1.81	2	40
<b>14</b>	119	667	10000	/	2.00	< 1	/
<b>15</b>	128	299	8885	37.8	1.87	2	80
<b>16</b>	196	167	8715	34.8	1.83	2	/
<b>17</b>	> 270	/	8497	/	1.91	14	64
<b>18</b>	200	295	8118	27.7	1.71	> 60	> 360
<b>19</b>	172	413	8602	32.8	1.78	/	/

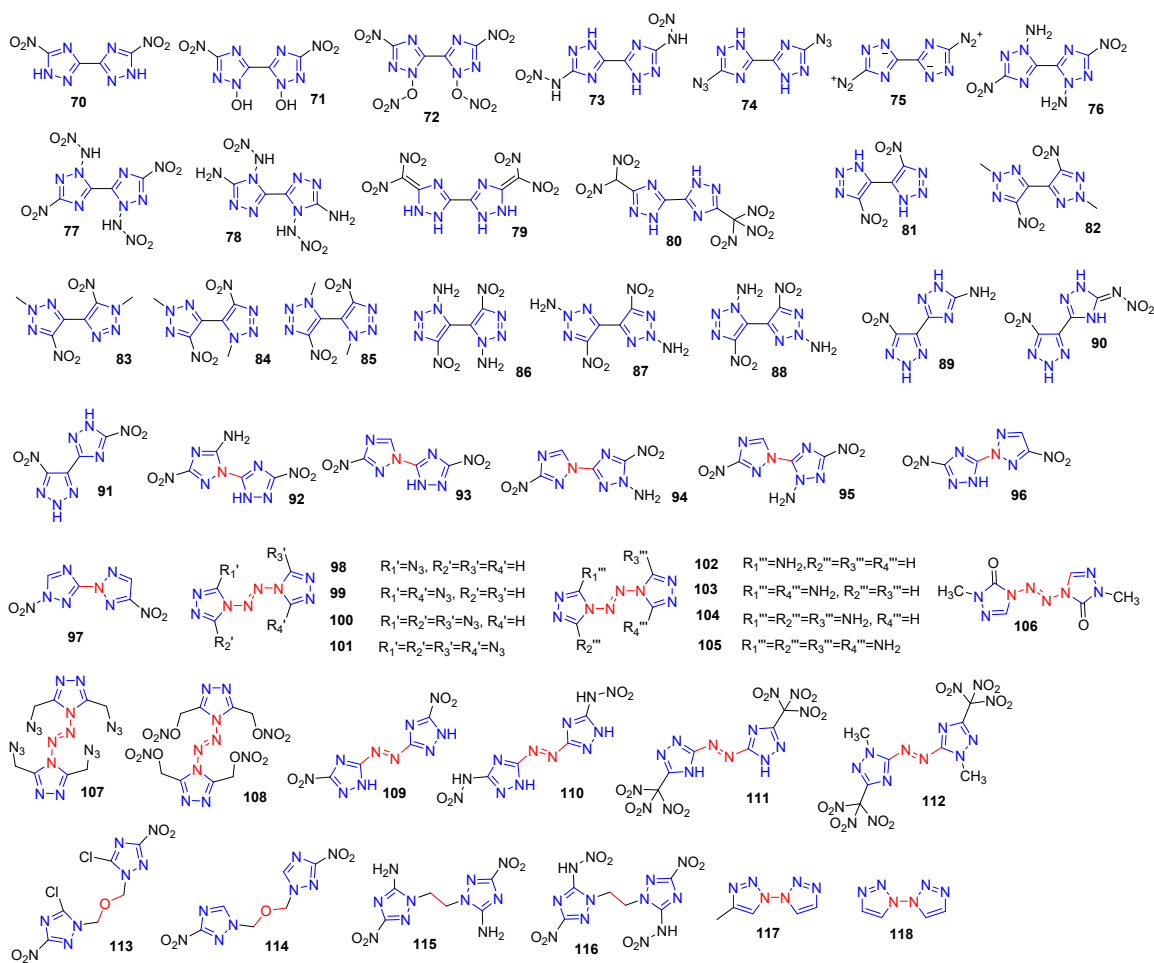
<b>20</b>	159	356	7810	24.1	1.65	37.8	360
<b>21</b>	89	270	8155	27.3	1.74	35	360
<b>22</b>	176	412	8651	33.7	1.85	20	240
<b>23</b>	183	-79	8180	29.4	1.83	8.7	282
<b>24</b>	151	-362	8367	30.1	1.96	10	192
<b>25</b>	124	62	8814	34.5	1.94	10	80
<b>26</b>	166	-273	8580	32.6	1.88	/	/
<b>27</b>	117	174	<b>9053</b>	37.4	1.91	13	72
<b>28</b>	355	334	7980	23.4	1.73	> 40	/
<b>29</b>	123	-81	7363	20.7	1.70	> 40	/
<b>30</b>	140	487	<b>9190</b>	37.5	1.90	2	10
<b>31</b>	246	185	7493	20.4	1.68	40	360
<b>32</b>	132	238	8227	28	1.77	15	120
<b>33</b>	155	219	8102	26.9	1.75	35	360
<b>34</b>	99	231	8764	33.2	1.90	10	160
<b>35</b>	/	-212	8440	29.7	1.90	/	/
<b>RDX</b>	204	70.3	8795	34.9	1.80	7.4	120
<b>HMX</b>	287	74.8	<b>9144</b>	39.2	1.91	7.4	120



**Table S2.** Energetic properties of tetrazole derivatives

Compd	T <sub>dec</sub> [°C]	D [m s <sup>-1</sup> ]	P [GPa]	Δ <sub>f</sub> H [kJ mol <sup>-1</sup> ]	IS [J]	d [g cm <sup>-3</sup> ]
<b>36</b>	145	8355	28.2	622	< 1	1.73
<b>37</b>	135	7593	21.3	592	9	1.57
<b>38</b>	221	9698	42.4	447	20	1.88
<b>39</b>	185	8898	32.6	798	3	1.76
<b>40</b>	175	8934	32.9	809	3	1.76
<b>41</b>	200	8330	31.7	326	1	2.11
<b>42</b>	107	10142	45.6	932	<1	1.93
<b>43</b>	223	8255	24.1	639	25	1.65
<b>44</b>	232	7767	21.2	498	25	1.65
<b>45</b>	215	7886	21.5	523	25	1.63
<b>46</b>	194	9329	38.2	1038	10	1.86
<b>47</b>	173	8374	28.1	1032	10	1.66
<b>48</b>	145	7963	24.7	989	15	1.58
<b>49</b>	157	9897	46.7	1088	1	1.90
<b>50</b>	134	9200	38.4	1103	1.5	1.81
<b>51</b>	183	8460	32.1	420	23	1.79
<b>52</b>	143	8256	29.3	414	36	1.73
<b>53</b>	166	7996	26.3	382	>40	1.66
<b>54</b>	147	8734	35.7	498	11	1.84
<b>55</b>	203	8892	34.6	487	4	1.85
<b>56</b>	130	8909	35.1	435	<2	1.83
<b>57</b>	250	9120	34.3	633	>30	1.86
<b>58</b>	80	9185	/	1030	<1	1.74
<b>59</b>	127	7320	21.0	986	/	1.48
<b>60</b>	/	9184	39.0	1092	<<<1	1.80
<b>61</b>	208	8523	27.7	2463	>30	1.84
<b>62</b>	170	9548	42.4	883	<1	1.90
<b>63</b>	120	8711	31.2	390	1	1.71
<b>64</b>	179	8723	/	429	H <sub>50</sub> < 4 cm	1.66
<b>65</b>	/	9330	40.0	1058	/	/
<b>66</b>	182	7825	20.9	514	3	1.53
<b>67</b>	201	7220	/	1499	10	1.56
<b>68</b>	288	8226		590	>40	1.74
<b>69</b>	247	8307		646	25	1.71

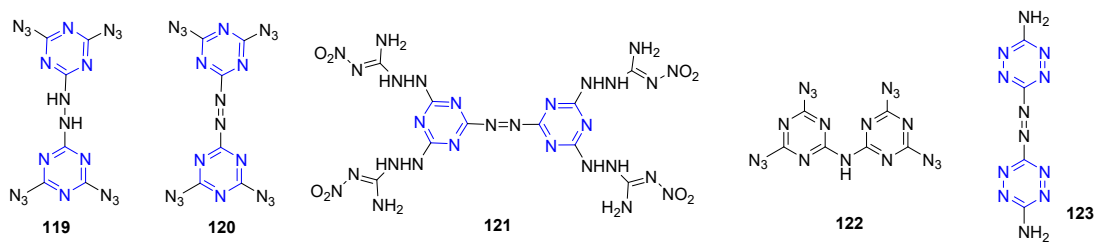




**Table S3.** Energetic properties of bicyclic triazole-based derivatives.

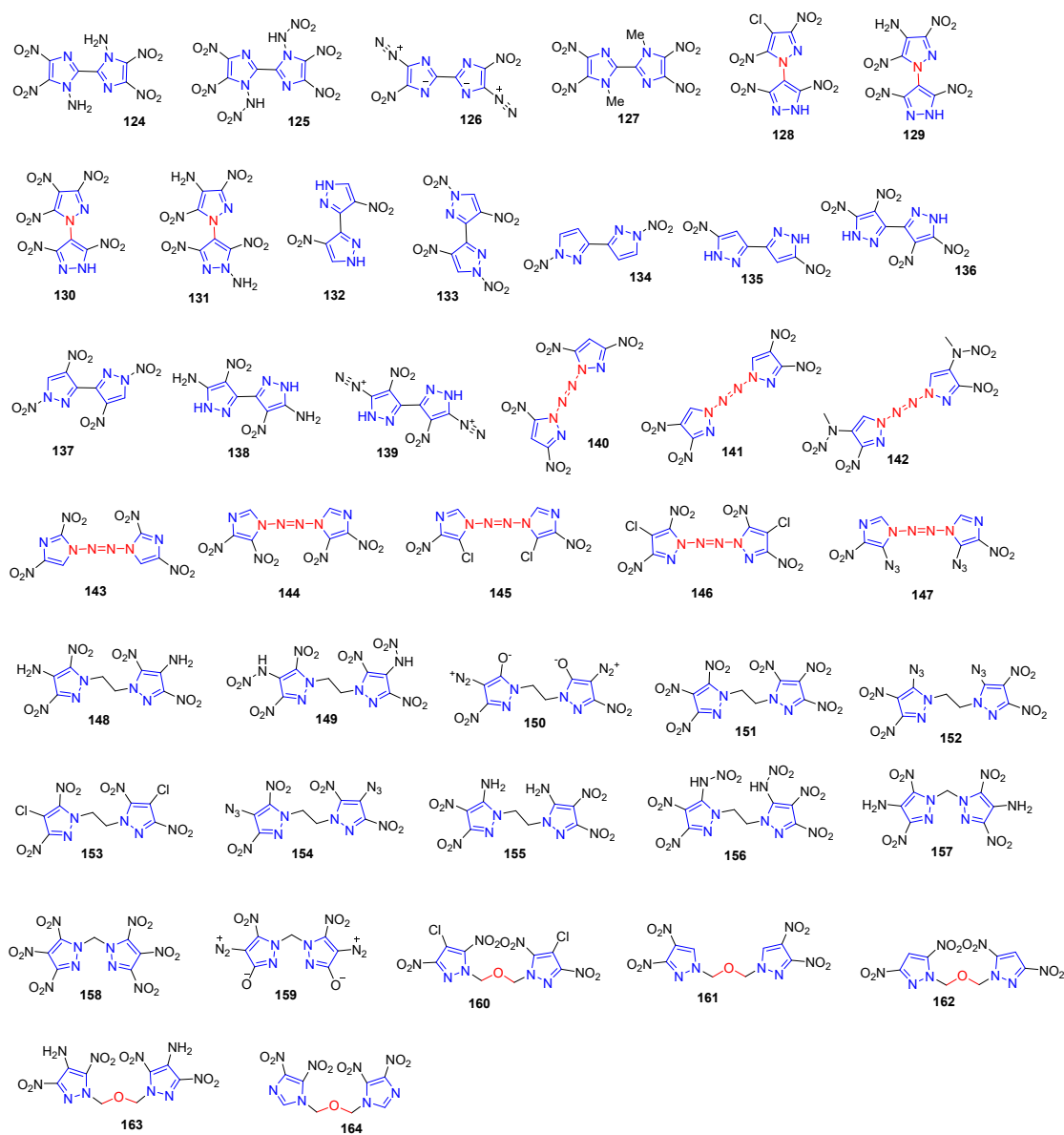
compd	$T_{\text{dec}}$ [°C]	$D$ [m s <sup>-1</sup> ]	$P$ [GPa]	$\Delta_f H$ [kJ mol <sup>-1</sup> ]	$IS$ [J]	$FS$ [N]	$d$ [g cm <sup>-3</sup> ]
70	251	8413	32.0	285	10	360	1.90
71	191	8729	36.2	290	10	360	1.91
72	176	8639	32.7	114	6	60	1.83
73	194	8355	30.0	405	3	108	1.80
74	201	7944	25.0	971	3	48	1.70
75	120	7780	26.7	1256	/	/	1.73
76	271	8677	31.8	440	40	360	1.83
77	121	9234	38.2	592	3	40	1.88
78	259	8846	31.2	692	9	120	1.76
79	121	8499	34.1	298	20	360	1.80
80	148	9073	36.2	332	23	252	1.89
81	155	/	/	439	/	/	/
82	227	7563	21.3	373	>40	/	1.62
83	275	7642	22.0	403	>40	/	1.63
84	229	/	/	397	/	/	/

85	237	7626	21.9	391	>40	/	1.63
86	198	8930	34.5	581	9	/	1.85
87	235	8884	33.9	576	10	/	1.85
88	191	8887	34.0	579	9	/	1.84
89	263	8384	27.4	521	>40	>360	1.76
90	168	9067	36.2	593	16	180	1.88
91	211	8961	35.2	560	24	360	1.86
92	252	7867	24.3	86.2	>40	>360	1.68
93	250	8364	29.0	361.8	22	160	1.78
94	167	8630	31.5	476	25	240	1.81
95	242	8577	30.9	465	28	240	1.80
96	250	8980	28.9	190	4	>36 (kp)	1.89
97	164	8980	30.8	516	2	8.1 (kp)	1.82
98	190	8280	27.0	1205	12	/	1.63
99	186	8540	30.0	1549	8	/	1.66
100	136	8950	34.0	1889	<3	/	1.74
101	136	9370	38.0	2245	<3	/	1.76
102	248	7640	22.0	830	>40	/	1.53
103	245	7840	23.0	799	>40	/	1.59
104	246	7730	22.0	774	>40	/	1.57
105	290	7700	22.0	779	>40	/	1.57
106	258	7470	19.2	344	>40	>360	1.62
107	136	7693	20.9	1940	<2	<5	1.53
108	146	8194	28.5	247	6	80	1.70
109	/	8500	/	407	12.5	250-360	1.88
110	209	8784	33.7	647.7	2	20	1.85
111	150	8964	36.7	555	1.5	/	1.83
112	165	8742	33.8	506	5.5	/	1.78
113	280	7401	22.9	119	28	240	1.86
114	320	7543	21.5	167	20	240	1.64
115	307	8069	24.5	315	>40	360	1.72
116	107	8816	34.3	516	10	160	1.84
117	202	6850	15.2	628	18	260	1.41
118	185	7208	17.5	664	17	290	1.51



**Table S4.** Energetic properties of triazine and tetrazine derivatives

compd	$T_{\text{dec}} [^{\circ}\text{C}]$	$D [\text{m s}^{-1}]$	$P [\text{GPa}]$	$\Delta_f H [\text{kJ mol}^{-1}]$	IS [J]	FS [N]	$d [\text{g cm}^{-3}]$
119	202	/	/	1753	18.3 cm ( $H_{50}$ )	29	1.65
120	200	/	/	2171	6.2 cm ( $H_{50}$ )	24	1.72
121	201	7812	23.9	598	>40	360	1.71
122	/	7190	22.2	1941	/	/	1.71
123	252	/	/	862	70 cm ( $H_{50}$ )	360	1.84

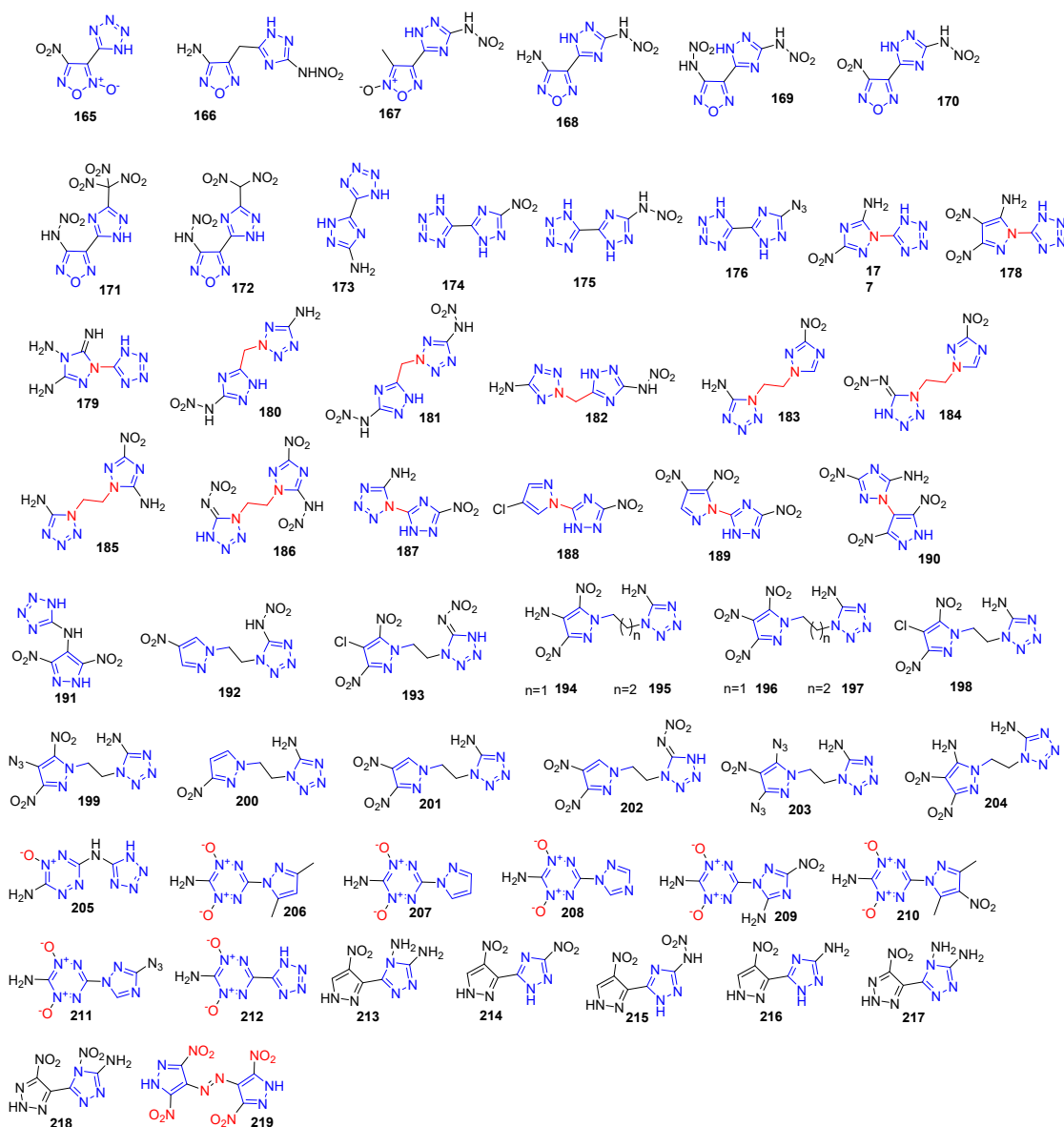


**Table S5.** Energetic properties of bicyclic pyrazole and imidazole derivatives

Compd	T <sub>dec</sub> [°C]	D [m s <sup>-1</sup> ]	P [GPa]	Δ <sub>f</sub> H [kJ mol <sup>-1</sup> ]	IS [J]	FS [N]	d [g cm <sup>-3</sup> ]
<b>124</b>	217	<b>9012</b>	36.6	309	<b>15</b>	160	1.93
<b>125</b>	116	<b>9350</b>	40.1	476	3	20	1.94
<b>126</b>	199	8653	31.1	820	1	20-40	1.83
<b>127</b>	258	7604	24.2	145	>40	>292	1.70
<b>128</b>	308	8724	36.0	185	>40	/	1.96
<b>129</b>	242	8600, 8789, 8626 <sup>a</sup>	35.0, 35.9, 36.0 <sup>a</sup>	388	>40	/	1.89
<b>130</b>	297	8814, 8760, 8981 <sup>a</sup>	37.0, 35.0, 36.0 <sup>a</sup>	824	28	/	1.82
<b>131</b>	284	8648, 8760, 8653 <sup>a</sup>	35.1, 35.4, 33.9 <sup>a</sup>	478	>40	/	1.87
<b>132</b>	365	8120	26.9	221	>40	>360	1.83
<b>133</b>	206	8869	34.5	407	2	40	1.85
<b>134</b>	183	8301	28.8	414	20	240	1.81
<b>135</b>	376	8026	26.2	229	>40	>360	1.81
<b>136</b>	243	8556	32.3	42.7	30	360	1.84
<b>137</b>	152	8926	35.4	444	2	60	1.86
<b>138</b>	228	7779	23.0	212	>60	>360	1.72
<b>139</b>	150	8943	34.0	987	1	20	1.85
<b>140</b>	240	8928	34.8	687	5	60	1.81
<b>141</b>	223	8964	35.1	687	5	80	1.82
<b>142</b>	195	8834	34.6	644	2	40	1.80
<b>143</b>	258	8979	35.1	592	15	160	1.85
<b>144</b>	232	8932	35.1	612	10	120	1.83
<b>145</b>	271	7632	24.9	578	25	360	1.86
<b>146</b>	251	8255	30.6	666	4	40	1.92
<b>147</b>	154	8702	31.4	1259	2	40	1.77
<b>148</b>	311	8189	27.9	219	>40	>360	1.77
<b>149</b>	80	8753	34.3	381	7	80	1.84
<b>150</b>	247	7803	24.2	442	20	80	1.72
<b>151</b>	250	8759	34.1	307	25	160	1.84
<b>152</b>	112	8797	33.4	1234	4	60	1.78

<b>153</b>	319	7877	27.0	230	>40	>360	1.88
<b>154</b>	135	8558	31.0	1014	3	60	1.76
<b>155</b>	256	8127	27.3	238	>40	>360	1.75
<b>156</b>	81	8710	33.7	368	6	60	1.83
<b>157</b>	310	8332	29.6	205	11	>360	1.80
<b>158</b>	205	9304	39.1	379	4	144	1.93
<b>159</b>	226	8016	26.0	497	1.5	40	1.73
<b>160</b>	284	7813	26.2	129	30	>360	1.84
<b>161</b>	298	7904	26.0	163	>40	>360	1.69
<b>162</b>	299	7874	25.7	141	10	240	1.69
<b>163</b>	203	8068	27.1	127	25	>360	1.74
<b>164</b>	270	8067	27.8	75	>40	>360	1.76

a. Detonation velocity calculated by the EXPLO5 program, modified nitrogen equivalent method, and Kamlet-Jacobs equations.



**Table S6.** Energetic properties of mixed heterocyclic-based energetic compound

Compd	T <sub>dec</sub> [°C] <sup>a</sup>	D [m s <sup>-1</sup> ] <sup>b</sup>	P [GPa] <sup>c</sup>	Δ <sub>r</sub> H [kJ mol <sup>-1</sup> ] <sup>d</sup>	IS [J] <sup>e</sup>	FS [N] <sup>f</sup>	d [g cm <sup>-3</sup> ] <sup>g</sup>
<b>165</b>	169	8681	34.3	500	<2	/	1.81
<b>166</b>	197	8079	24.9	449	>40	>360	1.70
<b>167</b>	181	8236	28.2	444	>40	>360	1.74
<b>168</b>	196	8332	27.7	468	35	360	1.74
<b>169</b>	128	<b>9258</b>	39.1	549	<b>18</b>	250	1.92
<b>170</b>	163	<b>9025</b>	36.0	525	<b>20</b>	280	1.85
<b>171</b>	67	<b>9278</b>	39.0	549	4	60	1.89
<b>172</b>	91	<b>9005</b>	36.3	537	9	100	1.85
<b>173</b>	347	7193	18.7	511	>40	>360	1.61
<b>174</b>	211	8020	26.5	519	25	288	1.73

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<b>175</b>	215	8097	26.6	577	<1	18	1.71
<b>176</b>	164	7874	24.1	859	<1	20	1.66
<b>177</b>	246	8316	28.8	487	>40	>360	1.77
<b>178</b>	324	8423	24.2	440	>60	/	1.69
<b>179</b>	239	7852	23.0	223	>40	>360	1.65
<b>180</b>	204	8187	24.9	476	15	240	1.71
<b>181</b>	159	8750	31.8	285	10	160	1.81
<b>182</b>	218	8213	25.2	462	18	360	1.72
<b>183</b>	255	7395	18.8	383	>40	>360	1.58
<b>184</b>	181	8113	25.6	477	38	>360	1.69
<b>185</b>	277	7807	21.6	359	>40	>360	1.66
<b>186</b>	96	8690	32.2	512	12	240	1.80
<b>187</b>	200 (melt)	6662	16.8	328	>40	>360	1.66
<b>188</b>	330	8262	29.0	140	>40	>360	1.75
<b>189</b>	270	9167	37.8	833	9	240	1.84
<b>190</b>	222	9261	38.3	848	25	168	1.85
<b>191</b>	279	9289	38.6	856	35	240	1.86
<b>192</b>	136	7824	23.1	463	39	360	1.65
<b>193</b>	130	7890	25.9	242	24	360	1.75
<b>194</b>	257	7889	23.2	334	>40	360	1.67
<b>195</b>	265	7768	21.8	356	>40	360	1.65
<b>196</b>	135	8172	27.1	431	30	240	1.71
<b>197</b>	134	7959	24.7	437	>40	360	1.67
<b>198</b>	221	7448	21.7	393	>40	>360	1.71
<b>199</b>	159	8185	26.1	785	10	120	1.66
<b>200</b>	254	7072	16.8	356	>40	>360	1.53
<b>201</b>	232	7516	20.6	395	>40	>360	1.59
<b>202</b>	157	8114	26.7	486	34	240	1.69
<b>203</b>	127	7917	23.1	1058	3	80	1.63
<b>204</b>	239	7883	23.0	369	>40	>360	1.68
<b>205</b>	192	8429	27.3	352	35	360	1.76
<b>206</b>	252	8180	23.6	348	35	360	1.76
<b>207</b>	237	8304	26.4	427	27	360	1.79
<b>208</b>	221	8438	27.7	449	24	360	1.80

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<b>209</b>	168	8707	32.0	431	17	240	1.84
<b>210</b>	211	8413	27.5	328	19	360	1.82
<b>211</b>	161	8731	30.9	781	8	60	1.82
<b>212</b>	181	8884	32.4	539	14	120	1.85
<b>213</b>	331	9075	30.7	475	>80	>360	1.87
<b>214</b>	278	8182	27.0	366	50	324	1.79
<b>215</b>	205	8336	27.8	390	20	240	1.80
<b>216</b>	281	8255	24.6	389	>80	>360	1.79
<b>217</b>	263	8194	25.2	663	18	200	1.70
<b>218</b>	221	8733	31.6	730	16	180	1.78
<b>219</b>	221	9083	36.6	699.8	>40	240	1.85

[a] Decomposition temperature. [b] Detonation velocity. [c] Detonation pressure. [d] Calculated heat of formation. [e] Impact sensitivity. [f] Friction sensitivity [g] Density.



#### 4. Crystallographic datas

The crystal of **DNPAT** and **5** were performed on a Bruker Smart Apex II diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), respectively. Integration and scaling of intensity data were accomplished using the SAINT program2. The structures were solved by intrinsic using SHELXT2014 and refinement was carried out by a full- matrix least-squares technique using SHELXT2014. The hydrogen atoms were refined isotropically, and the heavy atoms were refined anisotropically. N-H and O-H hydrogens were located from different electron density maps, and C-H hydrogens were placed in calculated positions and refined with a riding model. Data were corrected for the effects of absorption using SADABS4 Relevant crystal data and refinement results are summarized in Table S7.

**Table S7** Crystallographic datas for compounds **DNPAT** and **5**

Compound	<b>DNPAT</b>	<b>5</b>
Empirical formula	C <sub>10</sub> H <sub>4</sub> N <sub>16</sub> O <sub>8</sub>	C <sub>5</sub> H <sub>3</sub> N <sub>9</sub> O <sub>6</sub> 1.5(C <sub>4</sub> H <sub>8</sub> O <sub>2</sub> )
Formula weight	476.29	417.32
Temperature/K	173	173
Crystal system	orthorhombic	triclinic
Space group	Pbca	P-1
a/Å	10.7356(16)	8.7665(19)
b/Å	10.1583(16)	10.158(2)
c/Å	15.310(2)	10.814(2)
$\alpha$ /°	90	114.184(3)
$\beta$ /°	90	98.141(3)
$\gamma$ /°	90	99.022(3)
Volume/Å <sup>3</sup>	1669.6(4)	844.7(3)
Z	4	2
$\rho$ (calc) mg/mm <sup>3</sup>	1.895	1.641
Absorption coefficient m/mm <sup>-1</sup>	0.166	0.143
F(000)	960.0	432
Crystal size/mm <sup>3</sup>	0.19 × 0.12 × 0.08	0.05 × 0.11 × 0.23
2 $\theta$ range for data collection	5.322 to 52.918	4.242 to 50.036°
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 12, -19 ≤ l ≤ 18	-10 ≤ h ≤ 10, -12 ≤ k ≤ 12, -12 ≤ l ≤ 12
Reflections collected	12929	9753
Independent reflections	1726[R <sub>int</sub> = 0.0696, R <sub>sigma</sub> = 0.0408]	2948[R(int) = 0.0518]
Data/restraints/parameters	1726/176/180	2948/3/271
Goodness-of-fit on F <sup>2</sup>	1.062	1.051
Final R indexes [I ≥ 2 $\sigma$ (I)]	0.0560, 0.1508	0.0440, 0.0809
Final R indexes [all data]	0.0753, 0.1650	0.0741, 0.0916

**Table S8** Hydrogen bonds for [ $\text{\AA}$  and  $^\circ$ ] compound **DNPAT**

D—H $\cdots$ A	d(D-H)/ $\text{\AA}$	d(H $\cdots$ A)/ $\text{\AA}$	d(D $\cdots$ A)/ $\text{\AA}$	$\angle$ (DHA)/ $^\circ$
N4—H4 $\cdots$ N6 <sup>i</sup>	0.90(4)	1.94(4)	2.803(3)	161(3)
N5—H5 $\cdots$ O1	0.85(4)	2.34(3)	2.819(3)	116(3)
N5—H5 $\cdots$ N7 <sup>ii</sup>	0.85(4)	2.21(4)	2.961(3)	148(3)

Symmetry Code i: 3/2-x, -1/2+y, z ii: 3/2-x, 1/2+y, z

**Table S9** Hydrogen bonds for [ $\text{\AA}$  and  $^\circ$ ] compound **5**

D—H $\cdots$ A	d(D-H)/ $\text{\AA}$	d(H $\cdots$ A)/ $\text{\AA}$	d(D $\cdots$ A)/ $\text{\AA}$	$\angle$ (DHA)/ $^\circ$
N2-H2 $\cdots$ O2	0.91(3)	2.23(3)	2.650(3)	107(2)
N2-H2 $\cdots$ O9	0.91(3)	1.84(3)	2.706(3)	157(3)
N4-H4 $\cdots$ O7	0.906(19)	1.796(19)	2.701(3)	178(3)
N6-H6 $\cdots$ O8 <sup>i</sup>	0.905(19)	1.920(19)	2.784(3)	159(2)
C7-H7A $\cdots$ O4 <sup>ii</sup>	0.9900	2.5800	3.559(3)	168.00
C8-H8A $\cdots$ O6 <sup>iii</sup>	0.9900	2.5600	3.491(3)	157.00

Symmetry Code: i: 2-x, 2-y, 1-z, ii: x, -1+y, z, iii: 1+x, y, 1+z

**5.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of target compounds**

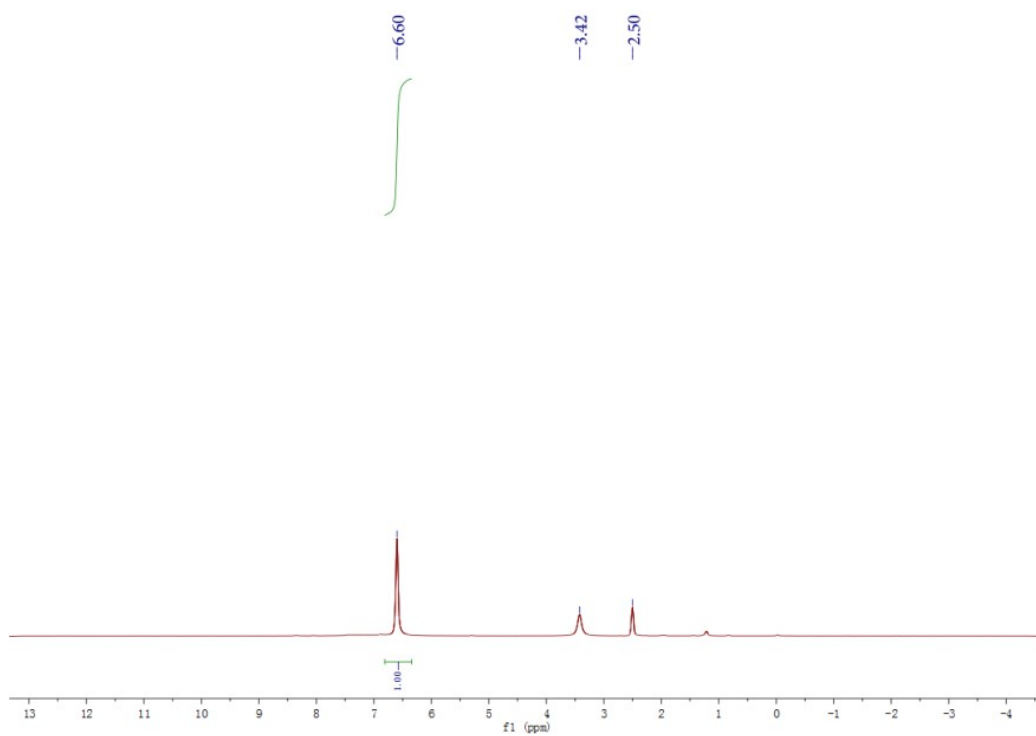


Figure S1.  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  for compound 4

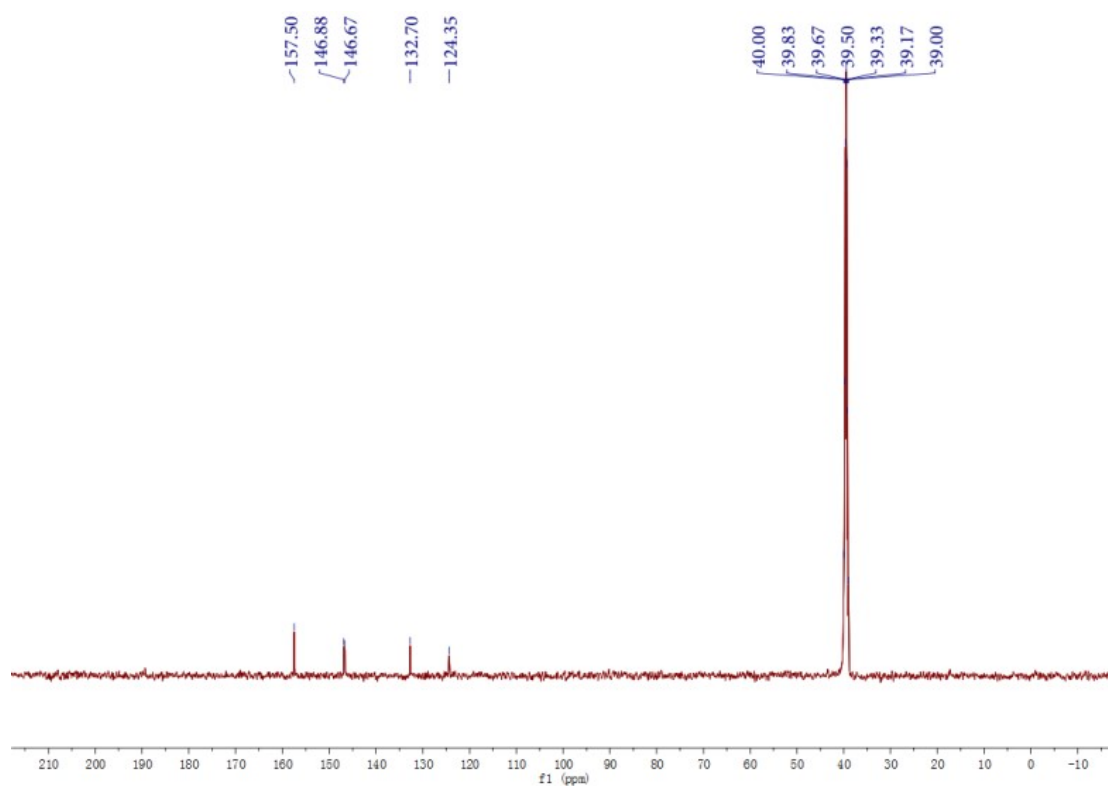


Figure S2.  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  for compound 4

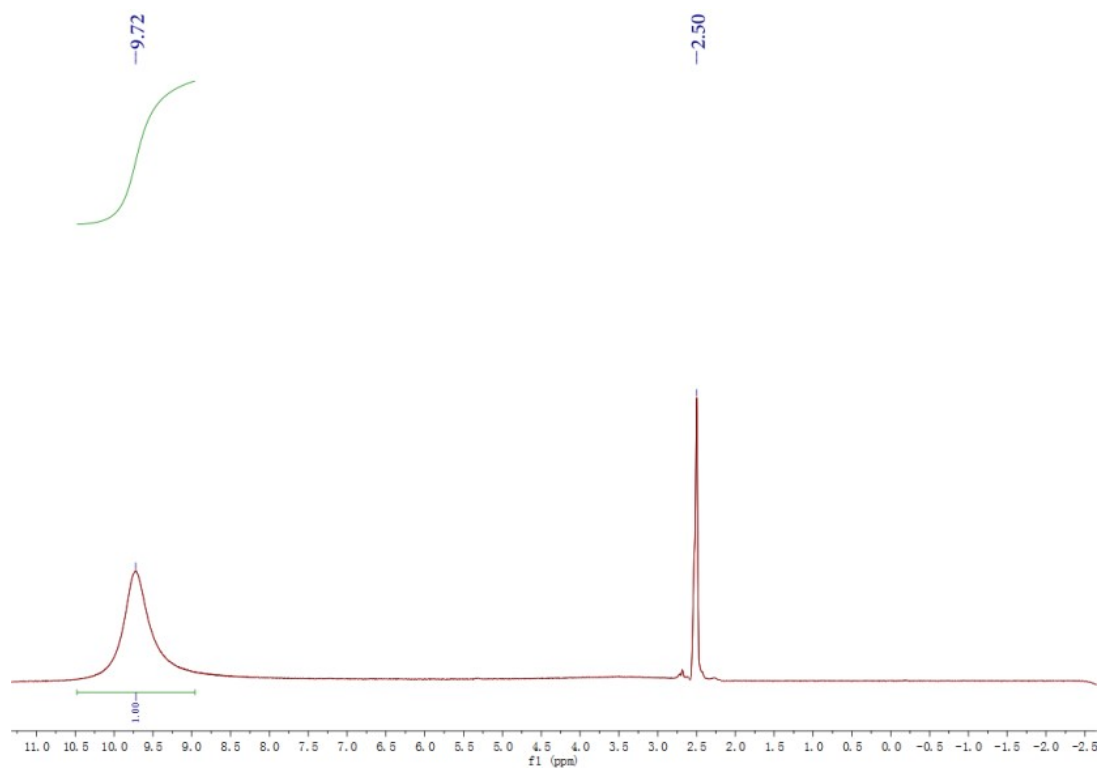


Figure S3.  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  for compound DNPAT

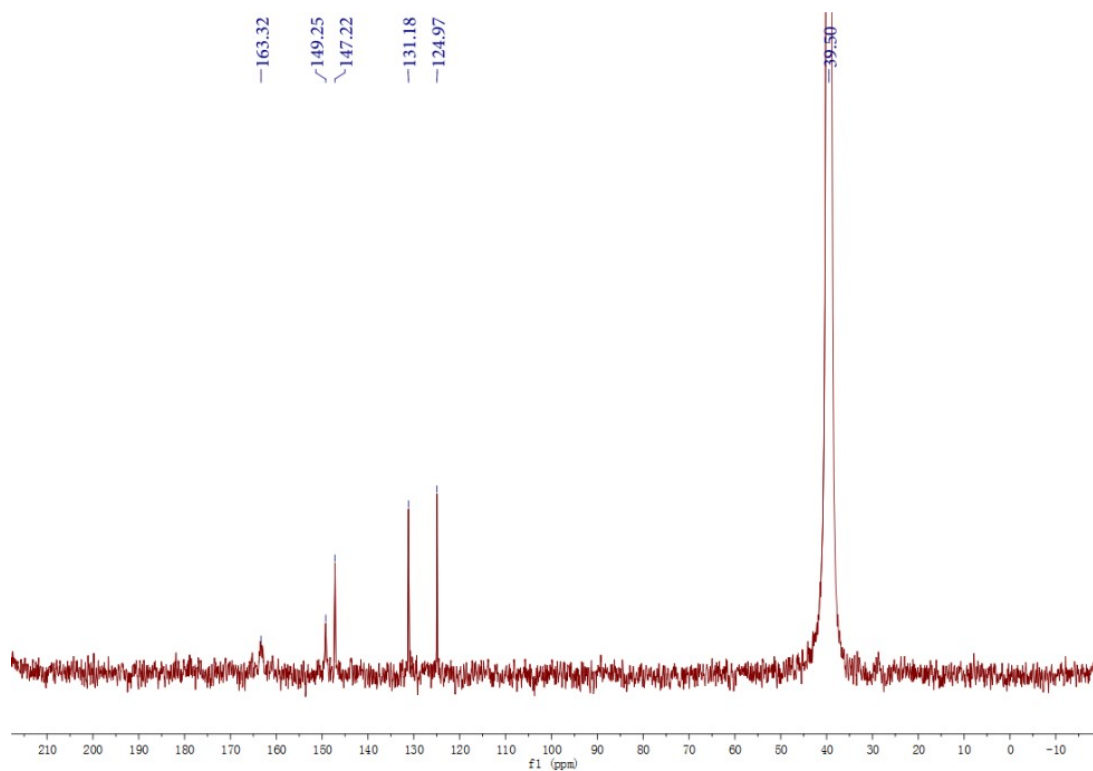
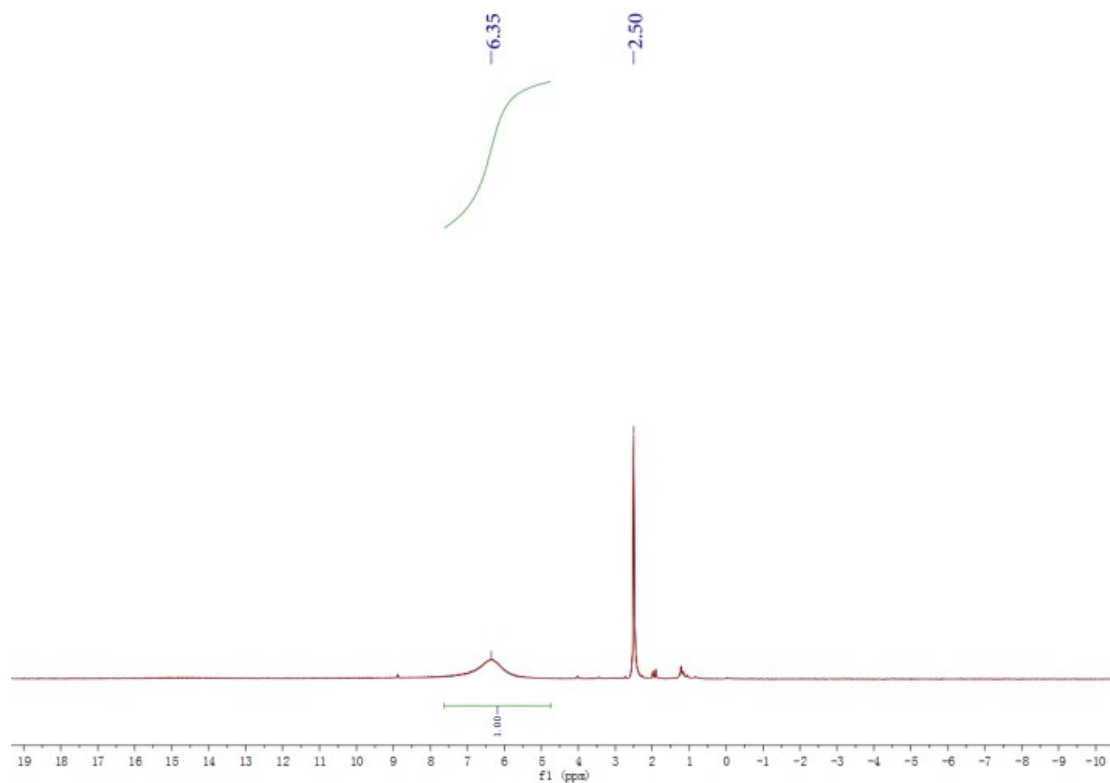
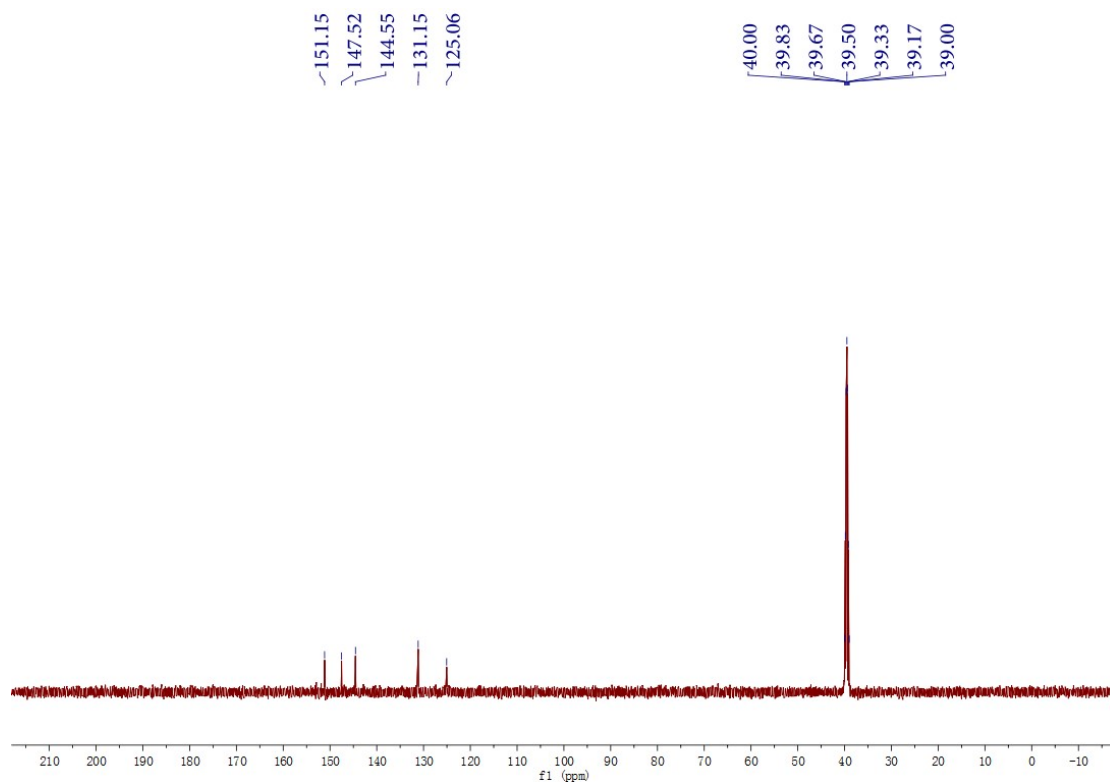


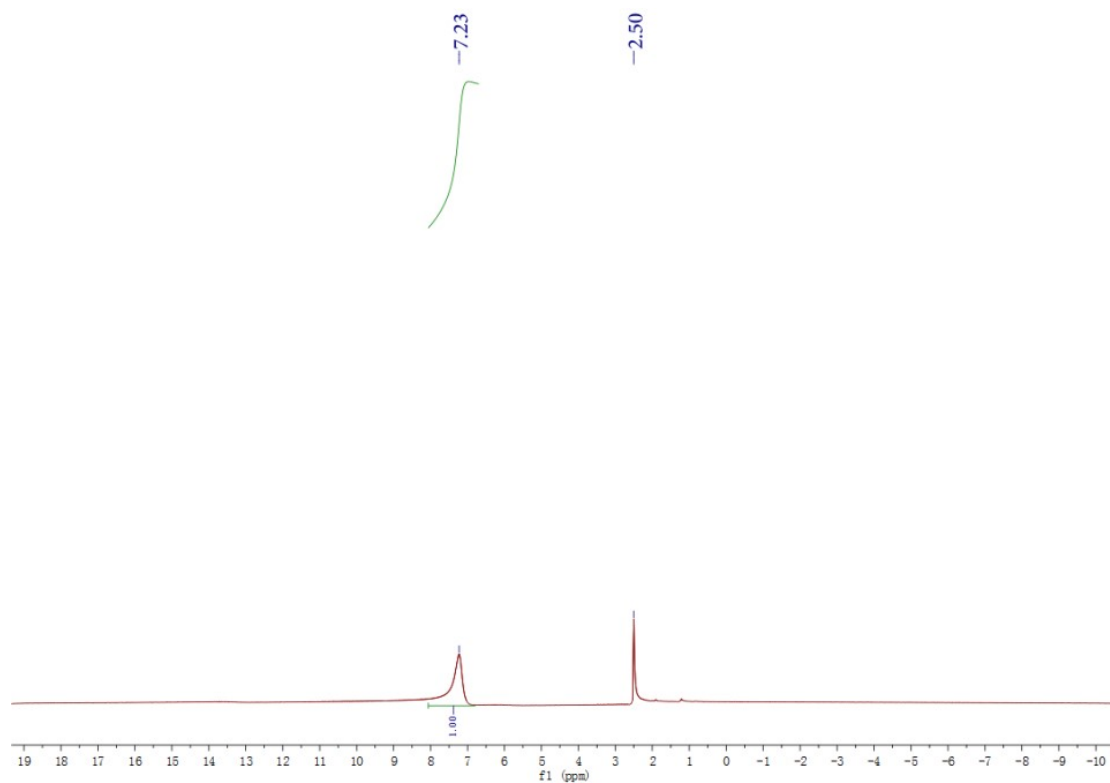
Figure S4.  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  for compound DNPAT



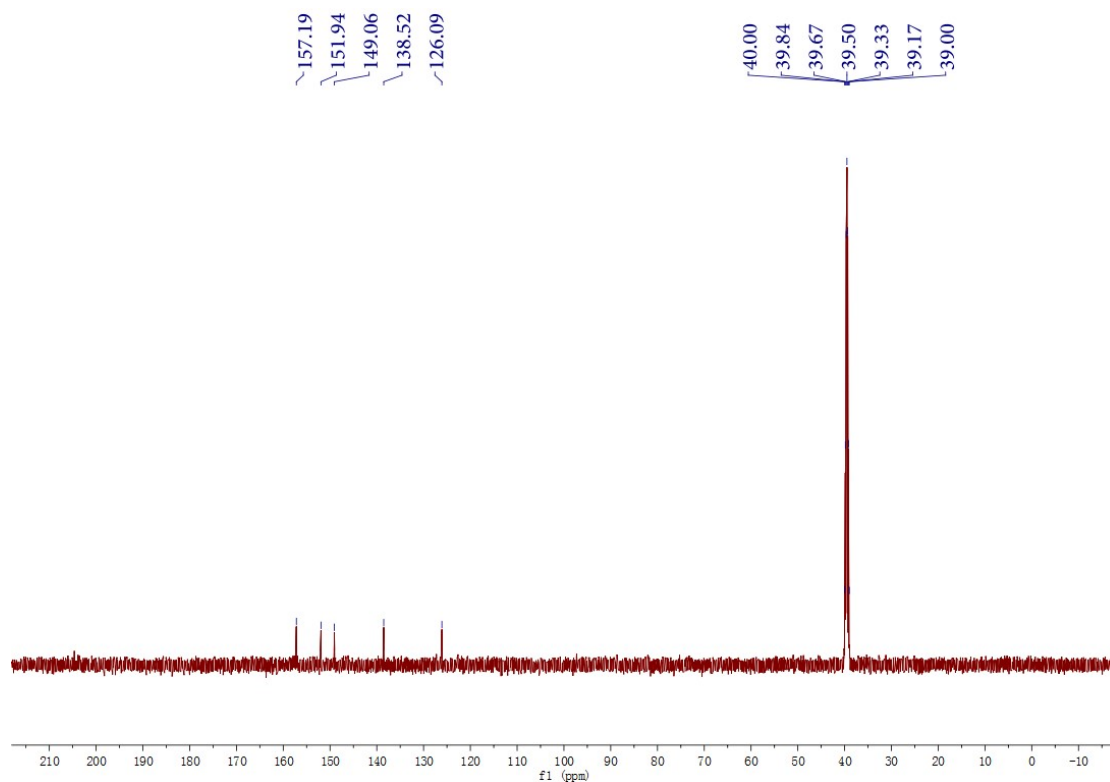
**Figure S5.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  for compound **5**



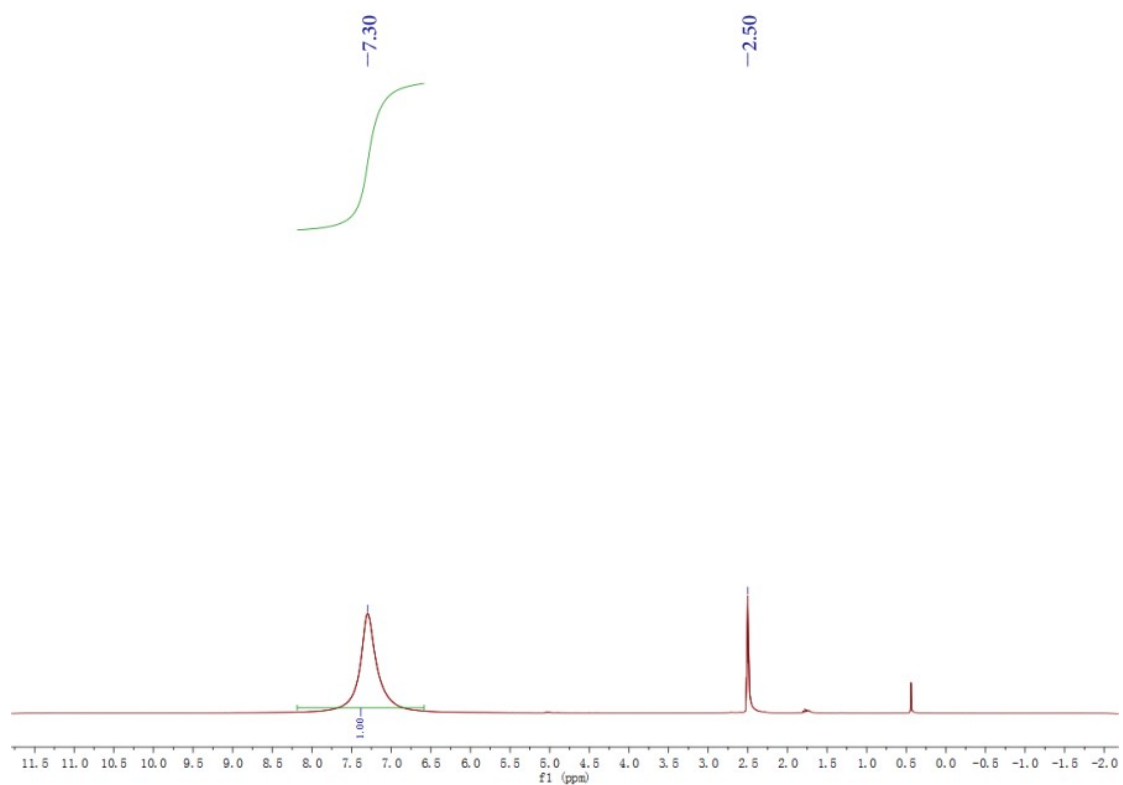
**Figure S6.**  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  for compound **5**



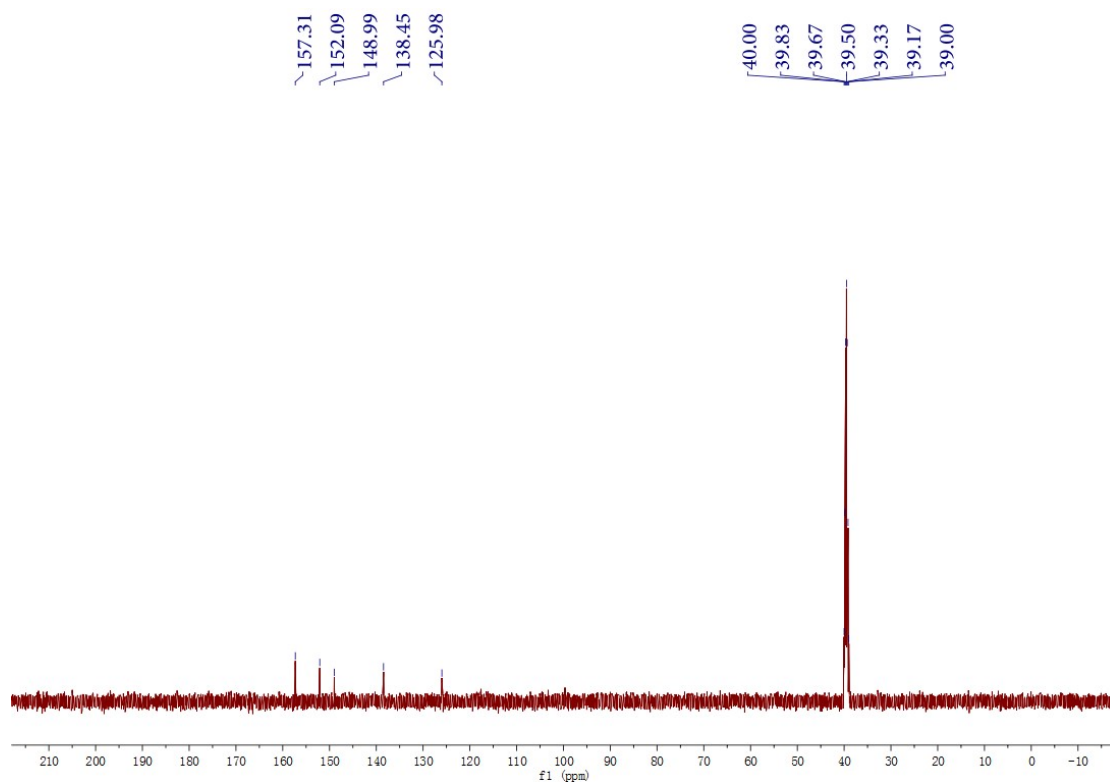
**Figure S7.** <sup>1</sup>H NMR spectra in DMSO-*d*<sub>6</sub> for compound 6



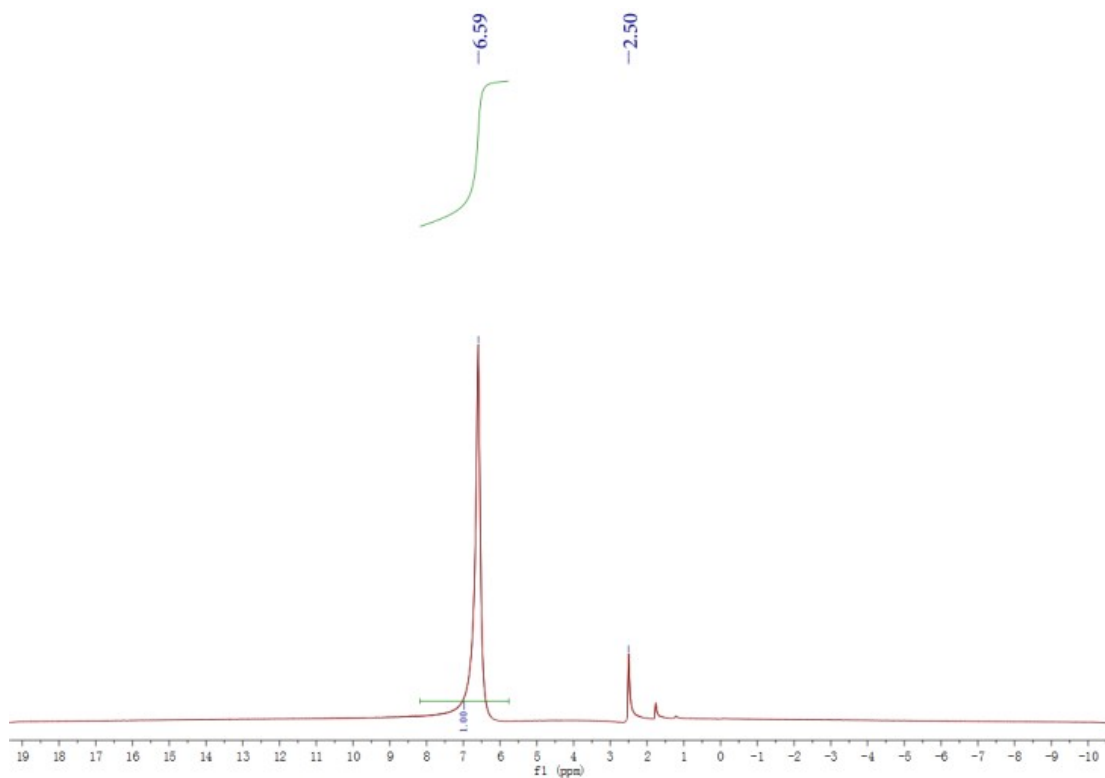
**Figure S8.** <sup>13</sup>C NMR spectra in DMSO-*d*<sub>6</sub> for compound 6



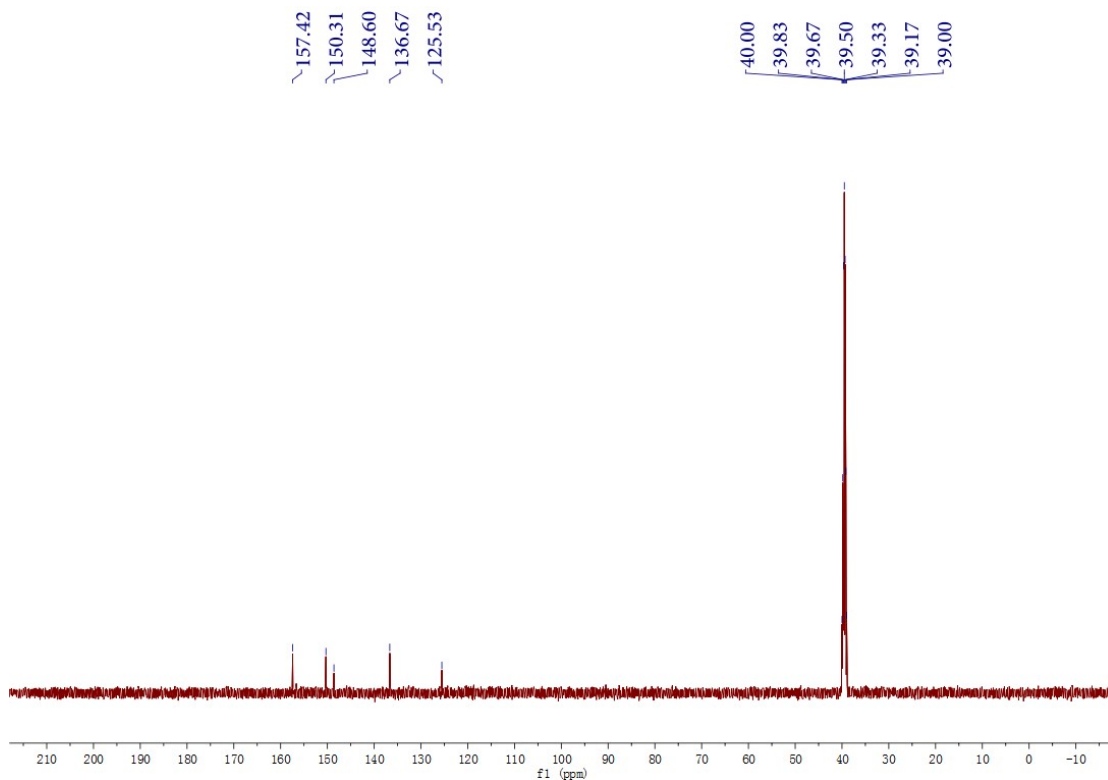
**Figure S9.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  for compound 7



**Figure S10.**  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  for compound 7



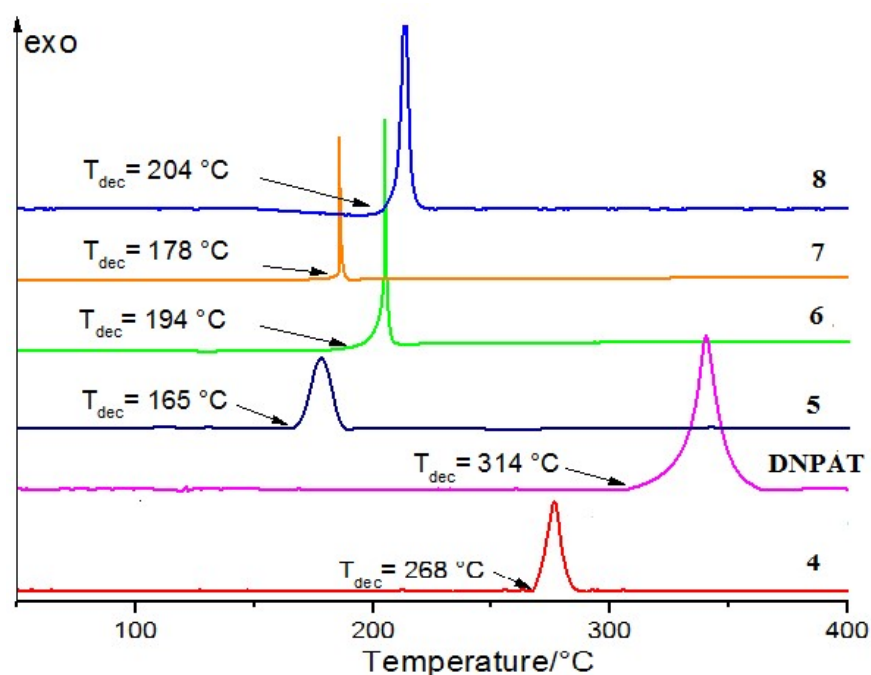
**Figure S11.**  $^1\text{H}$  NMR spectra in  $\text{DMSO-}d_6$  for compound **8**



**Figure S12.**  $^{13}\text{C}$  NMR spectra in  $\text{DMSO-}d_6$  for compound **8**



## 6. The DSC plots of synthesized compounds



**Figure S13.** The DSC plots of compounds **DNPAT**, and **5-8**

## 7. 5s Bursting temperature experiments

**Table S11.** Results of 5s bursting temperature experiments.

Number	1	2	3	4	5	6	7	8	$T_{5s}/$ °C
T/°C	365	370	375	380	385	390	395	400	> 400
$\tau/s$	11.0	10.2	9.4	8.8	8.2	7.5	7.0	6.5	

## 8. Reference

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