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Supporting Information (SI)

Construction of *p*-nitropyrazole-1,3,4-triazole framework energetic compounds: towards a series of high-performance heat-resistant explosives

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1. Experimental sections

General methods

¹H and ¹³C NMR spectra were recorded on 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometers operating at 500 and 126 MHz, respectively, by using DMSO-d₆ as the solvent and locking solvent unless otherwise stated. Chemical shifts in ¹H and ¹³C NMR spectra are reported relative to DMSO. DSC was performed in closed Al containers with a nitrogen flow of 30 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 °C. Impact sensitivity and friction sensitivity of samples are measured by using the standard BAM methods.

Synthesis

5-(3-(1H-pyrazol-4-yl)-1H-1,2,4-triazol-1-yl)-1H-tetrazole (**A3**)

To a mixture of ethyl 1H-pyrazole-4-carbimidate (**1**) (1.39 g, 10 mmol) and ethanol (15 mL), 5-hydrazineyl-1H-tetrazole (**A1**) (1 g, 10 mmol) and TEA (2.02 g, 20 mmol) were added in sequence at ambient temperature. Heat the mixed solution to 35 °C and stirred continuously for 3 h. The solid was dispersed in 15 mL formic acid and heat to reflux for 12 h. After the solution temperature was restored to room temperature, the solution was filtered to obtain solid **A3** (1.69 g, 83 %). ¹H NMR (500 MHz, DMSO-d₆): δ = 6.24 (br), 8.17 (s), 9.34 (s) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 112.28, 133.24, 145.89, 155.49, 159.34 ppm. IR (KBr): $\tilde{\nu}$ 3436.2, 1603.4, 1573.4, 1531.4, 1486.5, 1433.9, 1208.5, 1085.6, 1002.8, 696.3 cm⁻¹. Elemental analysis for C₆H₅N₉ (203.17): calcd C, 35.47; H, 2.48; N, 62.05%. Found: C 33.44, H 2.50, N 64.06%.

3-(3,5-dinitro-1H-pyrazol-4-yl)-1H-1,2,4-triazole (**DPT**)

A3 (1.27 g, 6.60 mmol) was added to the mixture of 98 % sulfuric acid (24 mL) and 98 % nitric acid (4 mL) at 0 °C. The mixture was warmed up to room temperature slowly. The final reaction was stirred at 30 °C for 2 h. After pouring into ice-water under vigorous stirring, the final mixture was filtered, washed with ice-water and dried in air, giving **DPT** as a white solid (1.16 g, 78 %). ¹H NMR (500 MHz, DMSO-d₆): δ = 6.15 (s), 9.01 (s) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 100.01, 145.63, 147.29, 152.44 ppm. IR (KBr): $\tilde{\nu}$ 3417.2, 2633.4, 1659.1, 1599.9, 1593.5, 1333.7, 1014.9, 868, 820.7 cm⁻¹. Elemental analysis for C₅H₃N₇O₄ (225.12): calcd C, 26.68; H, 1.34; N, 43.55%. Found: C 26.67, H 1.36, N 43.53%.

4-(3-(1H-pyrazol-4-yl)-1H-1,2,4-triazol-5-yl)-1,2,5-oxadiazol-3-amine (**B2**)

To a solution of **1** (0.69 g, 5 mmol) in 30 mL absolute methanol, 4-amino-1,2,5-oxadiazole-3-carbohydrazide (**B1**) (0.72 g, 5 mmol) and TEA (1.01 g, 10 mmol) were added in portions. The resulted mixture was refluxed for 12 h. The precipitate was collected through filtration. Dissolve the sediment in 50 mL water, slowly add 0.5 g KOH, and reflux the reaction system for 12h. After cooled to room temperature, concentrated hydrochloric acid was added dropwise to adjust the pH value to 1. The precipitate was collected through filtration, washed with water and dried at 40 °C. ¹H NMR (500 MHz, DMSO-d₆): δ = 6.53 (s), 8.30 (s) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 108.91, 133.40, 143.11, 148.03, 151.89, 159.38 ppm. IR (KBr): $\tilde{\nu}$ 3415.1, 1664.8, 1617.4, 1595.3, 1471.6, 1392.6, 1230.3, 1068.4, 1031.4, 978.8, 915.6 cm⁻¹. Elemental analysis for C₇H₆N₈O (218.18): calcd C, 38.54; H, 2.77; N, 51.36%. Found: C 38.56, H 2.75, N 51.37%.

3-(3-(1H-pyrazol-4-yl)-1H-1,2,4-triazol-5-yl)-4-nitro-1,2,5-oxadiazole (**B3**)

10 mL hydrogen peroxide (H₂O₂, 30%) was added 20 mL sulfuric acid (H₂SO₄, 98%) at 0 °C. Then **B2** (1.30 g, 6 mmol) was slowly added. The resulted solution was maintained at room temperature for 12 h. Then the acidic solution was quenched with the ice. The formed solid was filtrated to give the white powder **B3** (1.01 g, 68 %). ¹H NMR (500 MHz, DMSO-d₆): δ = 8.23 (s) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 109.24, 137.35, 139.59, 151.45, 155.83, 159.76 ppm. IR (KBr): $\tilde{\nu}$ 3445.3, 1726.4, 1614.3, 1598.7, 1448.0, 1391.6, 1340.8, 1237.5, 1146.2, 1060.6, 980.5, 864.4 cm⁻¹. Elemental analysis for C₇H₄N₈O₃ (248.16): calcd C, 33.88; H, 1.62; N, 45.15%. Found: C 33.87, H 1.64, N 45.14%.

3-nitro-4-(3-(3-nitro-1H-pyrazol-4-yl)-1H-1,2,4-triazol-5-yl)-1,2,5-oxadiazole (**B4**)

15 mL concentrated H₂SO₄ (98%) was cooled to 0 °C, then compound **B3** (1.48 g, 6 mmol) was added slowly. After complete dissolution, 5 mL fuming HNO₃ was added dropwise. The resulted mixture was heated at 100 °C for 12 h. Finally, the acidic mixture was quenched with crushed ice and the precipitate was filtrated to obtained the final product as white powder. **B4** (1.71 g, 97 %). ¹H NMR (500 MHz, DMSO-d₆): δ = 8.21 (s) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 97.78, 125.20, 144.71, 148.11, 148.66, 149.71, 155.38 ppm. IR (KBr): $\tilde{\nu}$ 3462.6, 1662.8, 1456.2, 1348.1, 1285.5, 1263.7, 1254.8, 1194.7, 1084.2, 1077.4, 1069.2, 734.2, 525.2 cm⁻¹. Elemental analysis for C₇H₃N₉O₅ (293.16): calcd C, 28.68; H, 1.03; N, 43.00%. Found: C 28.70, H 1.01, N 43.01%.

3-(3-(3,5-dinitro-1H-pyrazol-4-yl)-1H-1,2,4-triazol-5-yl)-4-nitro-1,2,5-oxadiazole

(DPTO)

15 mL concentrated fuming H₂SO₄ (20%) was cooled to 0 °C, then compound **B3** (1.48 g, 6 mmol) was added slowly. After complete dissolution, 5 mL fuming HNO₃ was added dropwise. The resulted mixture was heated at 120 °C for 12 h. Finally, the acidic mixture was quenched with crushed ice and the precipitate was filtrated to obtained the final product as white powder. **DPTO** (1.91 g, 94 %). ¹³C NMR (126 MHz, DMSO-d₆): δ = 100.14, 143.01, 147.25, 148.08, 152.19, 159.52 ppm. IR (KBr): $\tilde{\nu}$ 3436.9, 3380.5, 1727.7, 1692.9, 1678.0, 1375.6, 1338.8, 1336.1, 1067.8, 813.4, 796.8, 696.1 cm⁻¹. Elemental analysis for C₇H₂N₁₀O₇ (338.16): calcd C, 24.86; H, 0.60; N, 41.42%. Found: C 24.86, H 0.62, N 41.39%.

5-(4,5-dinitro-1H-pyrazol-3-yl)-3-(1H-pyrazol-4-yl)-1H-1,2,4-triazole (**C2**)

The synthetic procedure for **C2** was similar to that of **B2**, only 4,5-dinitro-1H-pyrazole-3-carbohydrazide (**C1**) (0.54 g, 2.5 mmol) was used instead of **B1**. **C2** (0.54 g, 79 %). ¹H NMR (500 MHz, DMSO-d₆): δ = 8.18 (s) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 114.35, 136.16, 138.48, 144.79, 148.51, 156.23, 157.62 ppm. IR (KBr): $\tilde{\nu}$ 3394.1, 1724.8, 1680.6, 1605.1, 1343.1, 1335.8, 1329.5, 1315.4, 1252.9, 1236.7, 817.7, 778, 730.6 cm⁻¹. Elemental analysis for C₈H₅N₉O₄ (291.19): calcd C, 33.00; H, 1.73; N, 43.29%. Found: C 33.01, H 1.71, N 43.31%.

5-(4,5-dinitro-1H-pyrazol-3-yl)-3-(3,5-dinitro-1H-pyrazol-4-yl)-1H-1,2,4-triazole (**DPPT**)

The synthetic procedure for **DPPT** was similar to that of **B4**, only **C2** (0.72 g, 2.5 mmol) was used instead of **B3**. **DPPT** (0.36 g, 38 %). ¹³C NMR (126 MHz, DMSO-d₆): δ = 104.48, 138.46, 140.10, 144.19, 148.69, 157.34, 162.80 ppm. IR (KBr): $\tilde{\nu}$ 3389.3, 3381.3, 1728.8, 1690.9, 1688.0, 1681.0, 1341.5, 1336.0, 1314.5, 817.5, 813.3 cm⁻¹. Elemental analysis for C₈H₃N₁₁O₈ (381.18): calcd C, 25.21; H, 0.79; N, 40.42%. Found: C 25.22, H 0.77, N 40.44%.

5'-(1H-pyrazol-4-yl)-1H,2'H-[3,3'-bi(1,2,4-triazol)]-5-amine (**D2**)

The synthetic procedure for **D2** was similar to that of **B2**, only 4,5-dinitro-1H-pyrazole-3-carbohydrazide (**D1**) (0.35 g, 2.5 mmol) was used instead of **B1**. **D2** (0.46 g, 85 %). ¹H NMR (500 MHz, DMSO-d₆): δ = 5.15 (br), 8.22 (s) ppm. ¹³C NMR (126 M, DMSO-d₆): δ = 110.20, 133.24, 147.01, 151.54, 156.96, 161.08 ppm. IR (KBr): $\tilde{\nu}$ 1627.6, 1607.6, 1422.4, 1402.2, 1383.5, 1318.2, 1201.1, 1135.4, 1035.2, 725.6, 632.4, 608.3, 579.8 cm⁻¹. Elemental analysis for C₇H₇N₉ (217.20): calcd C, 38.71; H, 3.25; N,

58.04%. Found: C 38.72, H 3.23, N 58.05%.

5-nitro-5'-(1H-pyrazol-4-yl)-1H,2'H-3,3'-bi(1,2,4-triazole) (**D3**)

D2 (2.17 g, 10 mmol) in 20% sulfuric acid (6 ml) was added dropwise to a solution of sodium nitrite (6.8 g, 98 mmol) in water (10 ml) at 40°C. The resulted solution was maintained at 50 °C for 12 h. Then the acidic solution was quenched with the ice. The formed solid was filtrated to give the white powder **D3** (1.63 g, 68%). ¹H NMR (500 MHz, DMSO-d₆): δ = 8.92 (s) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 109.23, 137.24, 139.78, 147.46, 157.20, 159.77 ppm. IR (KBr): $\tilde{\nu}$ 3407.6, 1677.7, 1606.8, 1508.7, 1439.5, 1410.1, 1338.0, 1323.7, 1212.8, 1195.9, 796.9, 733.2, 637.7 cm⁻¹. Elemental analysis for C₇H₅N₉O₂ (247.18): calcd C, 34.01; H, 2.04; N, 51.00%. Found: C 34.02, H 2.02, N 51.02%.

(Z)-1,2-bis(5'-(3,5-dinitro-1H-pyrazol-4-yl)-1H,2'H-[3,3'-bi(1,2,4-triazol)]-5-yl)diazene (**D4**)

The synthetic procedure for **D4** was similar to that of **B4**, only **D2** (0.78 g, 0.25 mmol) was used instead of **B3**. **D4** (0.59 g, 39 %). ¹³C NMR (126 MHz, DMSO-d₆): δ = 102.09, 139.70, 155.93, 157.29, 157.66, 159.77 ppm. IR (KBr): $\tilde{\nu}$ 3386.5, 1693.8, 1671.7, 1430.6, 1334.3, 1331.3, 1315.3, 1240.5, 1233.4, 1103.7, 814.3, 731.6, 672.1 cm⁻¹. Elemental analysis for C₁₄H₆N₂₂O₈ (610.35): calcd C, 27.55; H, 0.99; N, 50.49%. Found: C 27.54, H 1.01, N 50.47%.

5'-(3,5-dinitro-1H-pyrazol-4-yl)-5-nitro-1H,2'H-3,3'-bi(1,2,4-triazole) (**DPBT**)

The synthetic procedure for **DPBT** was similar to that of **B4**, only **D3** (0.62 g, 2.5 mmol) was used instead of **B3**. **DPBT** (0.29 g, 35 %). ¹³C NMR (126 MHz, DMSO-d₆): δ = 102.18, 139.56, 149.46, 157.51, 158.35, 159.74 ppm. IR (KBr): $\tilde{\nu}$ 3401.9, 3383.3, 1692.0, 1684.5, 1676.7, 1438.6, 1337.2, 1326.0, 1316.9, 1222.2, 813.8, 797.2, 733.6 cm⁻¹. Elemental analysis for C₇H₃N₁₁O₆ (337.03): calcd C, 24.94; H, 0.90; N, 45.70%. Found: C 24.95, H 0.88, N 45.71%.

3,3'-(4-nitro-1H-pyrazole-3,5-diyl)bis(5-(1H-pyrazol-4-yl)-1H-1,2,4-triazole) (**E2**)

The synthetic procedure for **E2** was similar to that of **B2**, only 4-nitro-1H-pyrazole-3,5-dicarbohydrazide (**E1**) (0.27 g, 1.2 mmol) was used instead of **B1**. **E2**: (0.35 g, 77 %). ¹H NMR (500 MHz, DMSO-d₆): δ = 8.04 (s) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 99.99, 117.89, 134.99, 135.52, 136.74, 164.84 ppm. IR (KBr): $\tilde{\nu}$ 3443.4, 1682.8, 1619.8, 1612.8, 1593.4, 1439.6, 1436.3, 1341.0, 1237.5, 1203.8, 1050.5, 667.5, 595.8

cm⁻¹. Elemental analysis for C₁₃H₉N₁₃O₂ (379.30): calcd C, 41.17; H, 2.39; N, 48.01%. Found: C 41.18, H 2.37, N 48.02%.

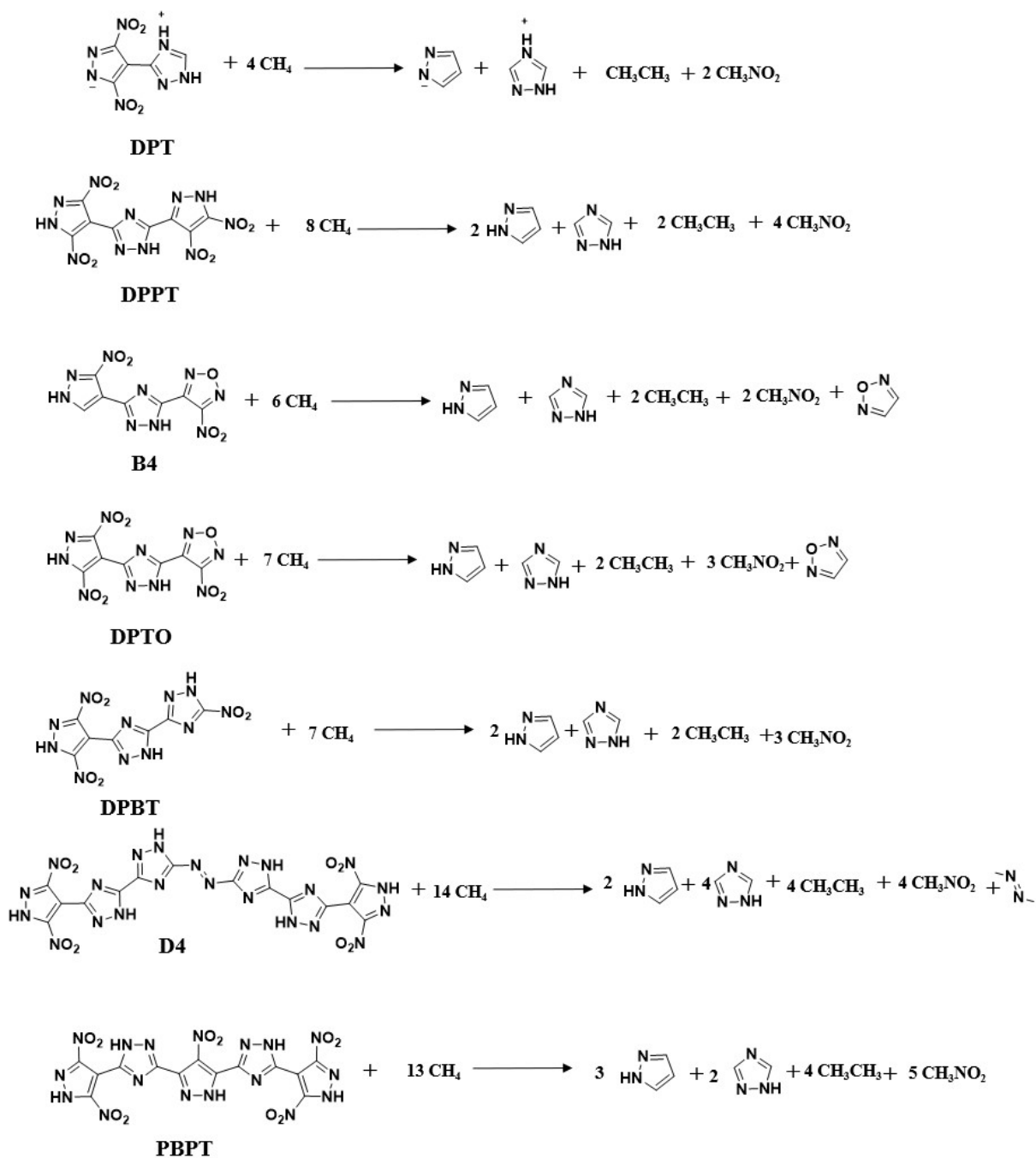
3,3'-(4-nitro-1H-pyrazole-3,5-diyl)bis(5-(3,5-dinitro-1H-pyrazol-4-yl)-1H-1,2,4-triazole) (**PBPT**)

The synthetic procedure for **PBPT** was similar to that of **B4**, only **E2** (0.47 g, 0.12 mmol) was used instead of **B3**. **PBPT** (0.24 g, 36 %). ¹H NMR (500 MHz, DMSO-d₆): δ = 6.44 (br) ppm. ¹³C NMR (126 MHz, DMSO-d₆): δ = 101.53, 130.71, 133.78, 147.31, 150.58, 151.60 ppm. IR (KBr): $\tilde{\nu}$ 3393.4, 3372.5, 3371.8, 1712.5, 1702.0, 11674.1, 1665.2, 1650.2, 1339.3, 1336.4, 1312.2, 1306.3, 815 cm⁻¹. Elemental analysis for C₁₃H₅N₁₇O₁₀ (559.29): calcd C, 27.92; H, 0.90; N, 42.58%. Found: C 27.93, H 0.88, N 42.59%.

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.

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

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

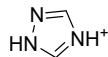



Where $\Sigma \Delta_f H_P$ and $\Sigma \Delta_f H_R$ are the *HOF* of the reactants and products at 298 K, respectively, and ΔH_{298} can be calculated from the following expression in Equation (2):

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

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	$E_0 / \text{a. u.}$	$ZPE / \text{kJ mol}^{-1}$	$\Delta H_T / \text{kJ mol}^{-1}$	$HOF / \text{kJ mol}^{-1}$
DPT	-876.463487	292.68	36.14	470.14
B4	-1137.369522	358.14	46.29	748.38
DPTO	-1341.913565	363.40	53.49	788.49
DPPT	-1510.616356	434.52	60.49	737.21
D4	-2343.448562	760.40	96.68	1626.60
DPBT	-1322.133698	399.20	53.22	723.01
PBPT	-2181.352722	672.35	88.11	1149.88
CH_4	-40.5339263	112.26	22.92	-74.60
CH_3NO_2	-245.0915559	124.93	11.60	-80.80
CH_3CH_3	-79.8565413	187.31	11.79	-84.00
Pyrazole anion	-225.669742	141.88	12.21	163.33
	-242.669331	184.02	12.27	831.72
	-242.320387	150.39	12.06	192.70
	-226.260331	179.20	12.57	177.40
	-262.1183629	114.62	11.84	215.70

Reference

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3. Crystallographic data

Table S2. Crystallographic data for **DPT**, **DPTO**, **PPBTBT** and **PBPT**.

Crystal	DPT·H ₂ O	DPTO·DMSO	D4·4DMSO	PBPT·6.375H ₂ O
CCDC number	2240058	2240059	2240060	2157697
Empirical Formula	C ₅ H ₃ N ₇ O ₄	C ₉ H ₈ N ₁₀ O ₈ S	C ₂₂ H ₃₀ N ₂₂ O ₁₂ S ₄	C ₂₆ H _{35.5} N ₃₄ O _{32.75}
Formula weight	243.16	416.31	922.92	1348.38
Temperature [K]	150.0	193.0	193.0	193.0
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	P2 ₁ /c	C2/c	P2 ₁ /n	P-1
<i>a</i> /Å	8.0502(9)	14.8387(6)	13.3925(10)	12.8475(2)
<i>b</i> /Å	7.1414(11)	10.0023(6)	9.5809(8)	13.8913(3)
<i>c</i> /Å	16.024(3)	22.8813 (11)	15.0000 (11)	15.5935(3)
α /°	90	90	90	94.3860 (10)
β /°	98.172(8)	104.593(5)	99.347(8)	104.9360(10)
γ /°	90	90	90	99.5510(10)
Cell volume (Å ³)	911.8(2)	3286.3(9)	1899.1(3)	2630.80(9)
Crystal	DPT·H ₂ O	DPTO·DMSO	D4·4DMSO	PBPT·6.375H ₂ O
Density (g cm ⁻³)	1.771	1.683	1.614	1.702
μ (mm ⁻¹)	0.158	2.421	0.214	1.384
F (000)	496.0	1696.0	750.0	1383.0
Crystal Size (mm ³)	0.11×0.06×0.04	0.13×0.12×0.1 1	0.13×0.12×0.10	0.12×0.1×0.1
2 θ range for data collection (°)	5.136 to 52.798	7.986 to 136.994	2.532 to 27.507	5.912 to 136.688
Index ranges	-10 ≤ <i>h</i> ≤ 8, -8 ≤ <i>k</i> ≤ 8, -20 ≤ <i>l</i> ≤ 19	-13 ≤ <i>h</i> ≤ 17, -12 ≤ <i>k</i> ≤ 11, -27 ≤ <i>l</i> ≤ 26	-17 ≤ <i>h</i> ≤ 17, -12 ≤ <i>k</i> ≤ 12, -19 ≤ <i>l</i> ≤ 18	-14 ≤ <i>h</i> ≤ 15, -16 ≤ <i>k</i> ≤ 16, -18 ≤ <i>l</i> ≤ 18
Reflections collected	8280	12557	20190	35906
Independent reflections	1848 [R _{int} = 0.0431, R _{sigma} = 0.0362]	3006 [R _{int} = 0.0501, R _{sigma} = 0.0367]	4350 [R _{int} = 0.0772, R _{sigma} = 0.0545]	9610 [R _{int} = 0.0592, R _{sigma} = 0.0492]
Data/restraints/parameters	1848/0/161	3006/0/263	4350/24/254	9610/0/881
Goodness-of-fit on F ²	1.080	1.056	1.064	1.024
Final R indexes [I ≥ 2 σ (I)]	R ₁ = 0.0403,	R ₁ = 0.0364,	R ₁ = 0.0886,	R ₁ = 0.0501,

	$wR_2 = 0.0950$	$wR_2 = 0.1001$	$wR_2 = 0.2532$	$wR_2 = 0.1280$
Final R indexes [all data]	$R_1 = 0.0563,$ $wR_2 = 0.1049$	$R_1 = 0.0400,$ $wR_2 = 0.1015$	$R_1 = 0.1373$ $wR_2 = 0.2953$	$R_1 = 0.0609,$ $wR_2 = 0.1354$

Table S3. Bond angles for DPT.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
H5A	-O5	-H5B	109.00	N3	-C1	-C2	106.3(3)
N2	-N1	-C3	107.8(1)	N2	-C1	-N3	122.3(3)
N1	-N2	-C1	106.6(1)	N2	-C1	-C2	131.1(2)
O3	-N3	-C1	117.4(2)	C3	-C2	-C4	106.5(2)
O4	-N3	-C1	118.7(2)	C1	-C2	-C3	133.3(2)
O3	-N3	-C4	123.8(2)	C1	-C2	-C4	109.4(2)
O1	-N4	-C3	118.1(1)	N1	-C3	-N4	117.2(3)
O2	-N4	-C3	128.9(2)	N1	-C3	-C2	116.1(2)
O1	-N4	-O2	124.9(2)	N4	-C3	-C2	120.6(2)
N6	-N5	-C5	123.7(2)	N5	-C4	-C2	123.3(3)
N5	-N6	-C5	111.2(2)	N7	-C4	-C2	109.9(3)
C4	-N7	-H6	106.4(2)	N5	-C4	-N7	122.2(2)
C5	-N6	-H6	128.2(2)	N6	-C5	-N7	127.9(3)
N5	-N6	-H7	120.3(2)	N6	-C5	-H5	109.5(2)
C5	-N7	-H7	127.00	N7	-C5	-H5	119.5(3)

Table S4. Hydrogen bonds for DPT.

D-H...A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
O5-H5A...O3	0.8700	2.0800	2.941(2)	173.00
O5-H5B...N2	0.8700	2.0900	2.954(2)	172.00
N6-H6...O1	1.08(3)	2.45(3)	3.063(2)	115.2(17)
N6-H6...N1	1.08(3)	1.65(3)	2.706(2)	165(2)
N7-H7...O5	0.8800	1.8500	2.688(2)	159.00
C5-H5...O1	0.9500	2.5000	3.409(2)	159.00

D-H...A	d(D-H)/ Å	d(H...A)/ Å	d(D...A)/ Å	<(DHA)/ °
C5-H5...O2	0.9500	2.5000	3.149(2)	125.00

Table S5. Torsion angles for **DPTO**.

Parameter	Bond angles (Å)	Parameter	Bond angles (Å)
N3-O1-N2-C1	1.00(19)	C4-C5-C6-N7	-2.9(3)
N2-O1-N3-C2	-1.05(18)	C4-C5-C6-N8	176.8(16)
O2-N1-C1-N2	47.0(3)	C7-C5-C6-N7	-179.4(17)
O2-N1-C1-C2	-134.6(3)	C7-C5-C6-N8	0.29(19)
O3-N1-C1-N2	-131.2(2)	C4-C5-C7-N9	-177.4(17)
O3-N1-C1-C2	47.1(3)	C4-C5-C7-N10	-1.7(3)
N6-C4-C5-C6	120.1(2)	C6-C5-C7-N9	-1.15(18)
N6-C4-C5-C7	-64.4(3)	C6-C5-C7-N10	174.6(17)

Table S6. Torsion angles for **D4**.

Parameter	Bond angles (Å)	Parameter	Bond angles (Å)
O1-N4-C11-C12	-176.0(7)	N2-N3-C11-N4	-179.6(4)
O1-N4-C11-N3	3.6(7)	N2-N3-C11-C12	0.0(5)
O2-N4-C11-N3	-177.5(4)	C15-N7-C8-N10	-1.0 (4)
O2-N4-C11-C12	3.0(7)	C15- N7-C8-C14	175.2(4)
O5-N1-C10-N2	-173.5(4)	C8- N7-C15-N11	0.9(4)
O5-N1-C10-C12	7.0(7)	C8- N7-C15-N1012	-177.7(4)
N3-N2-C10-N1	177.2(4)	C14- N9-C13-N6	-0.7(4)
N3-N2-C10-C12	-0.8(5)	C14- N9-C13-C12	175.6(4)

Table S7. Torsion angles for **PBPT**.

Parameter	Bond angles (Å)	Parameter	Bond angles (Å)
N2-N1-C3-N3	176.4(19)	O3-N4-C1-N2	23.6(3)
N2-N1-C3-C2	0.2(3)	O3-N4-C1-C2	-159.2(2)
N1-N2-C1-N4	177.1(19)	O4-N4-C1-N2	-156.2(2)

N1-N2-C1-C2	-0.5(3)	O4-N4-C1-C2	21.1(2)
O1-N3-C3-N1	8.9(3)	C5-N7-C4-N5	0.5(3)
O1-N3-C3-C2	-175.8(2)	C5-N7-C4-C2	-177.9(2)
O2-N3-C3-N1	-170.4(2)	C4-N7-C5-N6	-0.4(2)
O2-N3-C3-C2	5.0(4)	C4-N7-C5-C6	-179.2 (2)

Table S8. Hydrogen bonds for PBPT.

D-H \cdots A	d(D-H)/ Å	d(H \cdots A)/ Å	d(D \cdots A)/ Å	\angle (DHA)/ °
N1-H1 \cdots O31	0.8800	1.7600	2.640(3)	173.00
N6-H6 \cdots O5	0.8800	2.1600	2.783(3)	128.00
N6-H6 \cdots O28	0.8800	2.1100	2.849(3)	141.00
N9-H9 \cdots O27	0.8800	1.8100	2.654(3)	161.00
N13-H13 \cdots O24	0.8800	1.9100	2.762(3)	162.00
N15-H15 \cdots O26	0.8800	1.7000	2.526(3)	156.00

4. Spectrums of compounds.

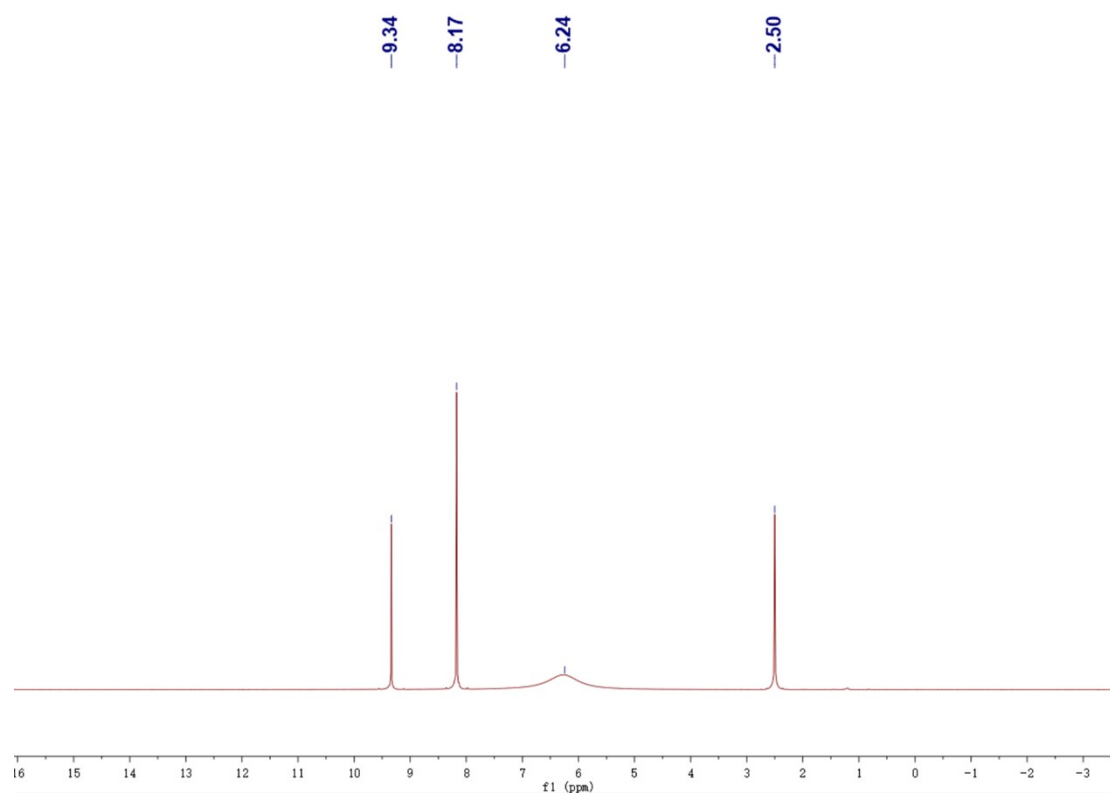


Figure S1. ^1H NMR spectra in DMSO-d6 for **A3**.

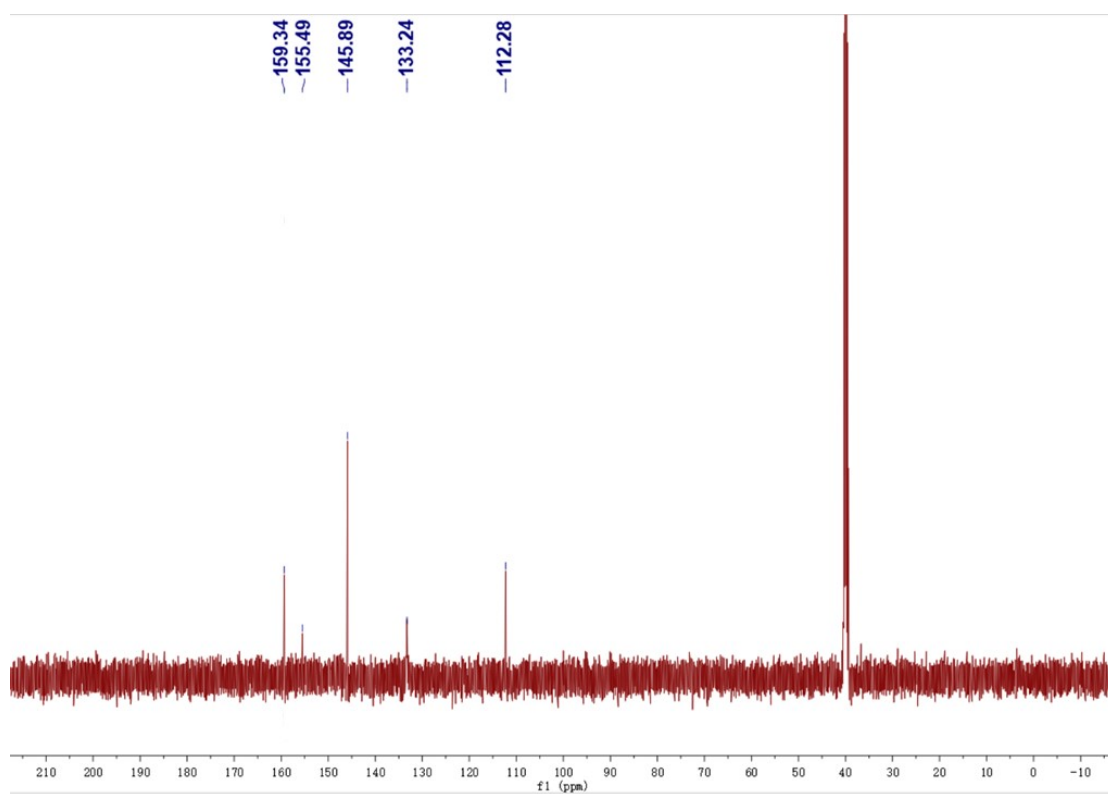


Figure S2. ^{13}C NMR spectra in DMSO-d6 for **A3**.

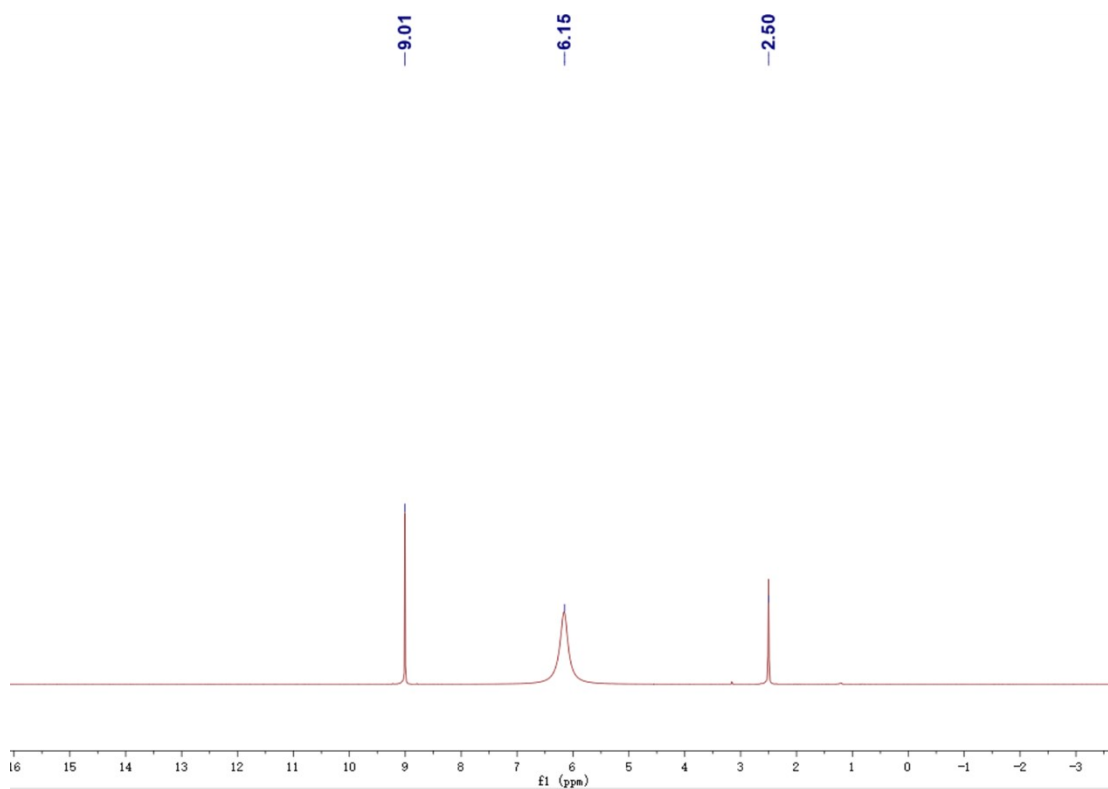


Figure S3. ^1H NMR spectra in DMSO-d6 for **DPT**.

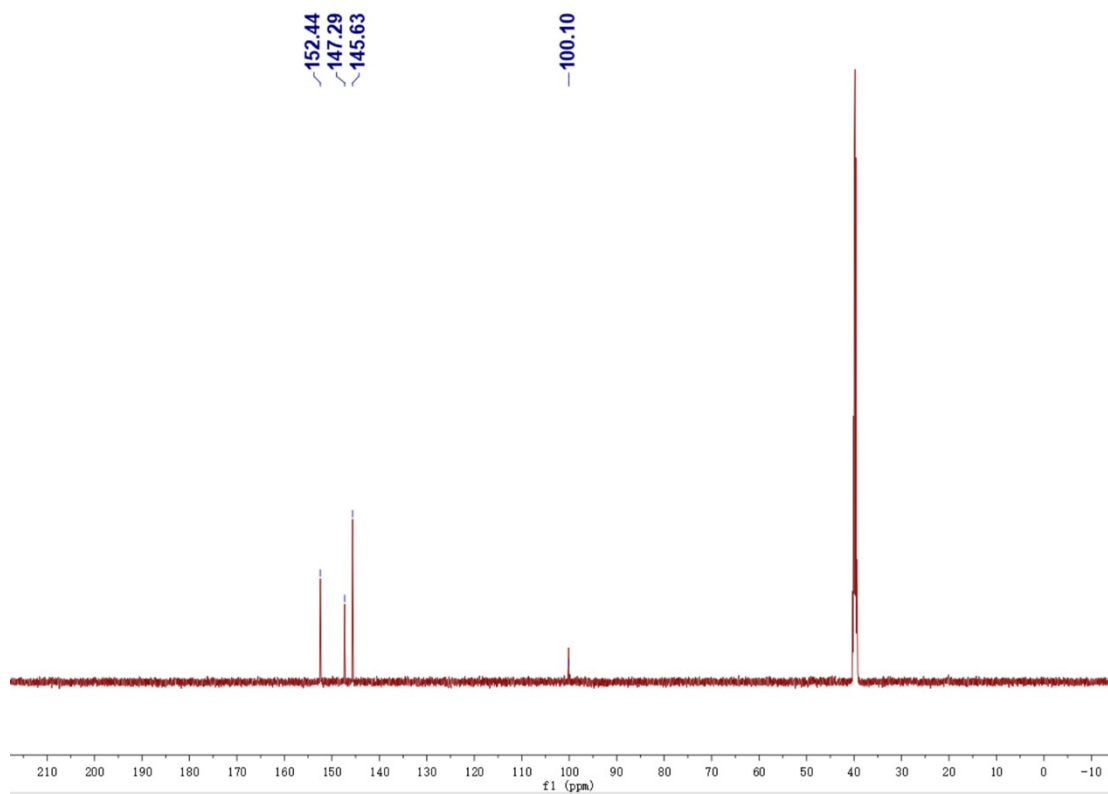


Figure S4. ^{13}C NMR spectra in DMSO-d₆ for **DPT**.

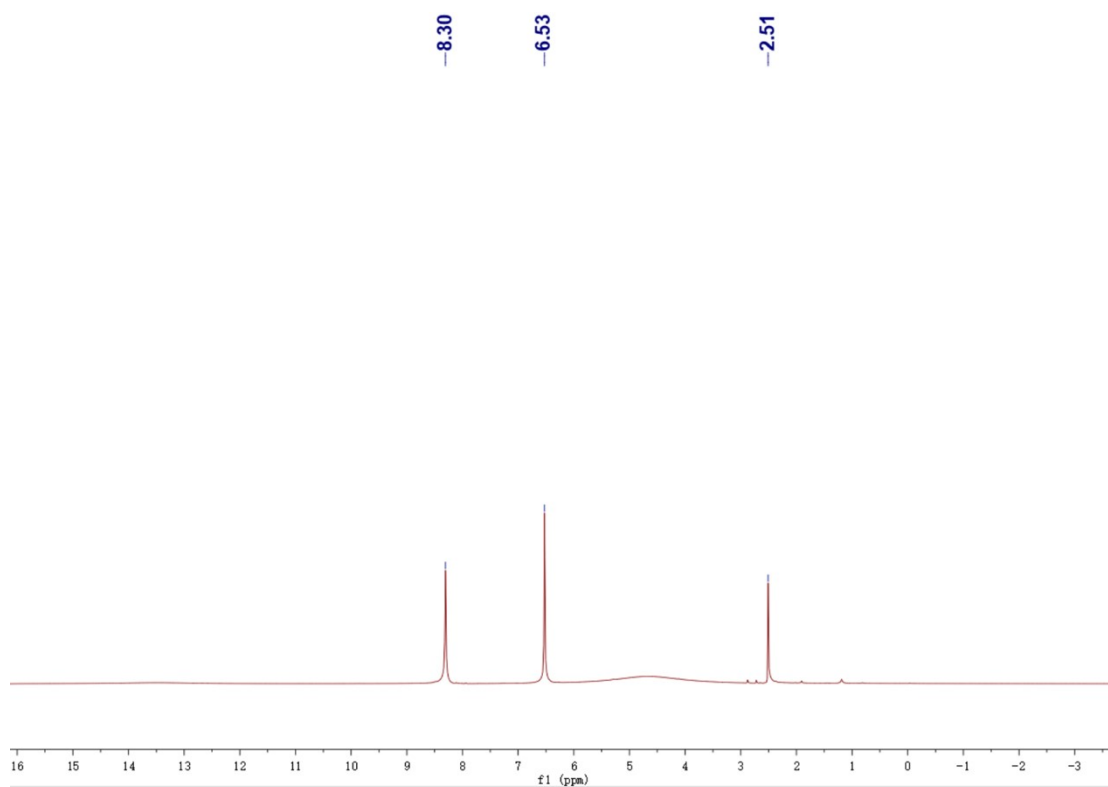


Figure S5. ^1H NMR spectra in DMSO-d₆ for **B2**.

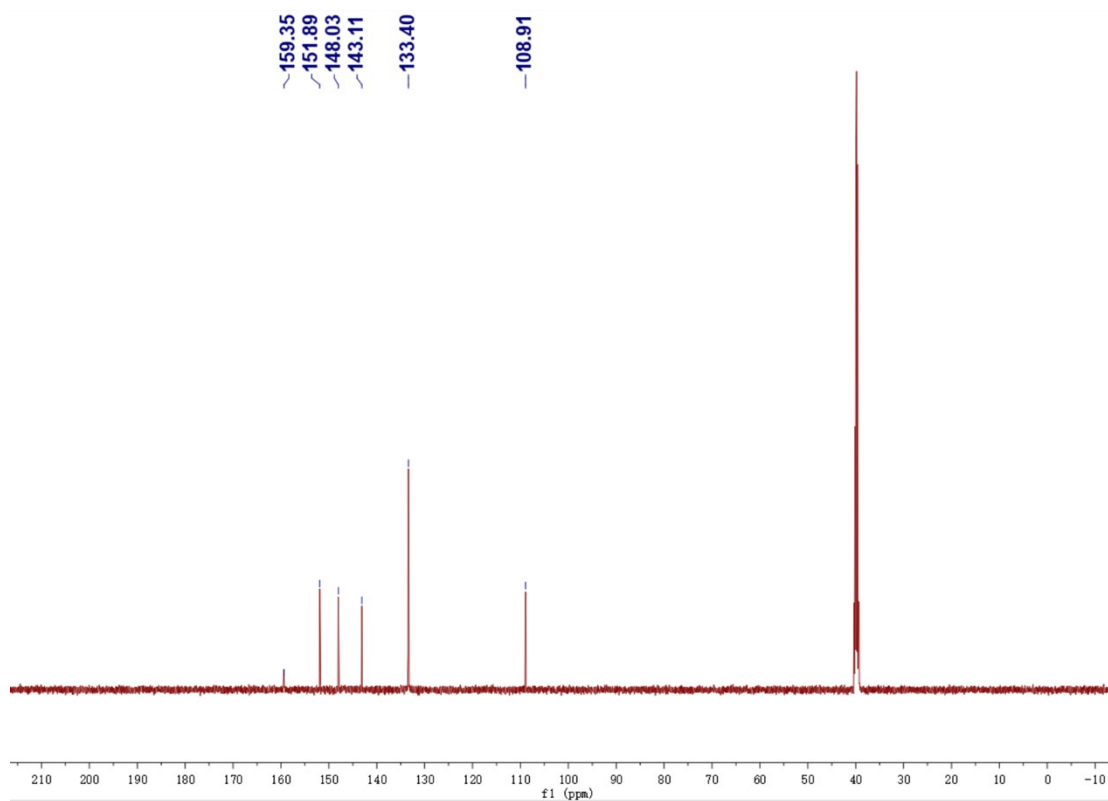


Figure S6. ^{13}C NMR spectra in DMSO-d₆ for **B2**.

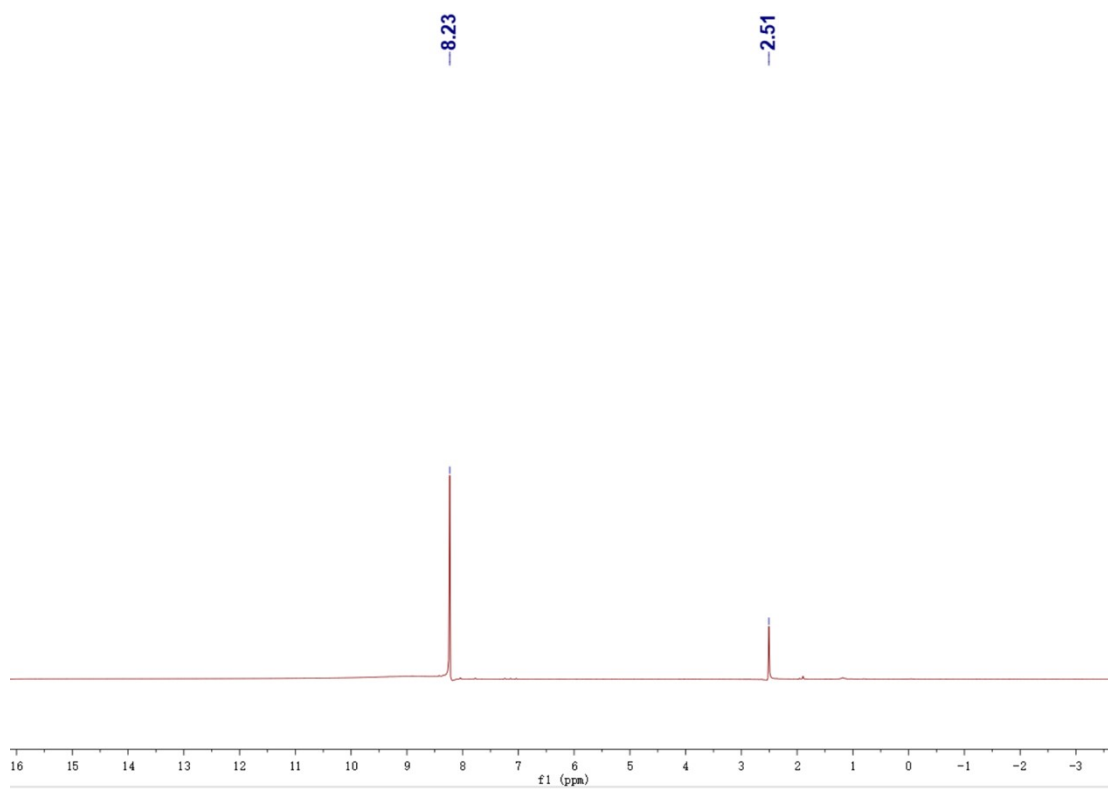


Figure S7. ^1H NMR spectra in DMSO-d₆ for **B3**.

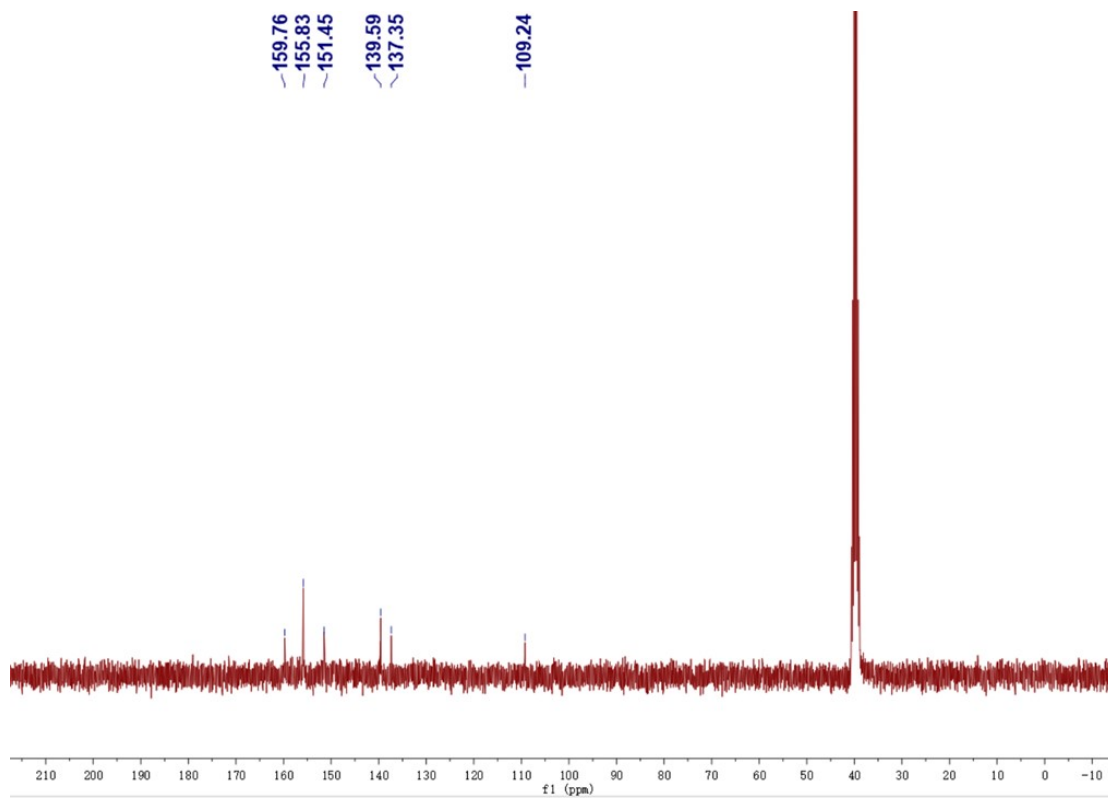


Figure S8. ^{13}C NMR spectra in DMSO-d₆ for **B3**.

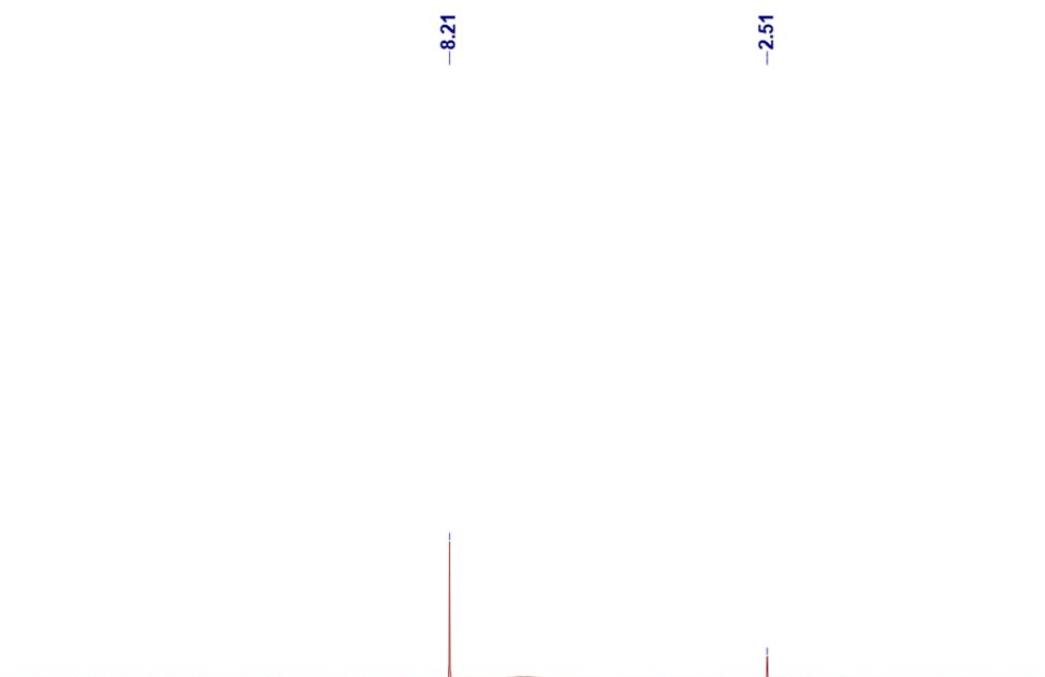


Figure S9. ^1H NMR spectra in DMSO-d₆ for **B4**.

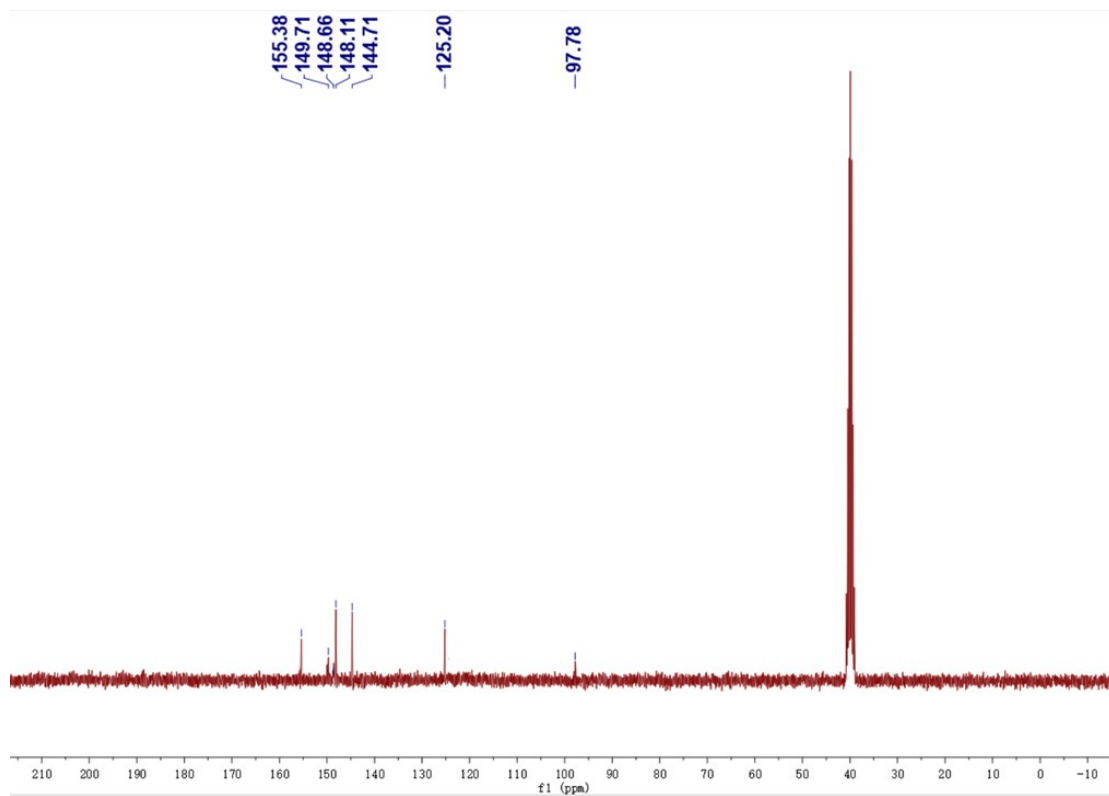


Figure S10. ^{13}C NMR spectra in DMSO- d_6 for **B4**.

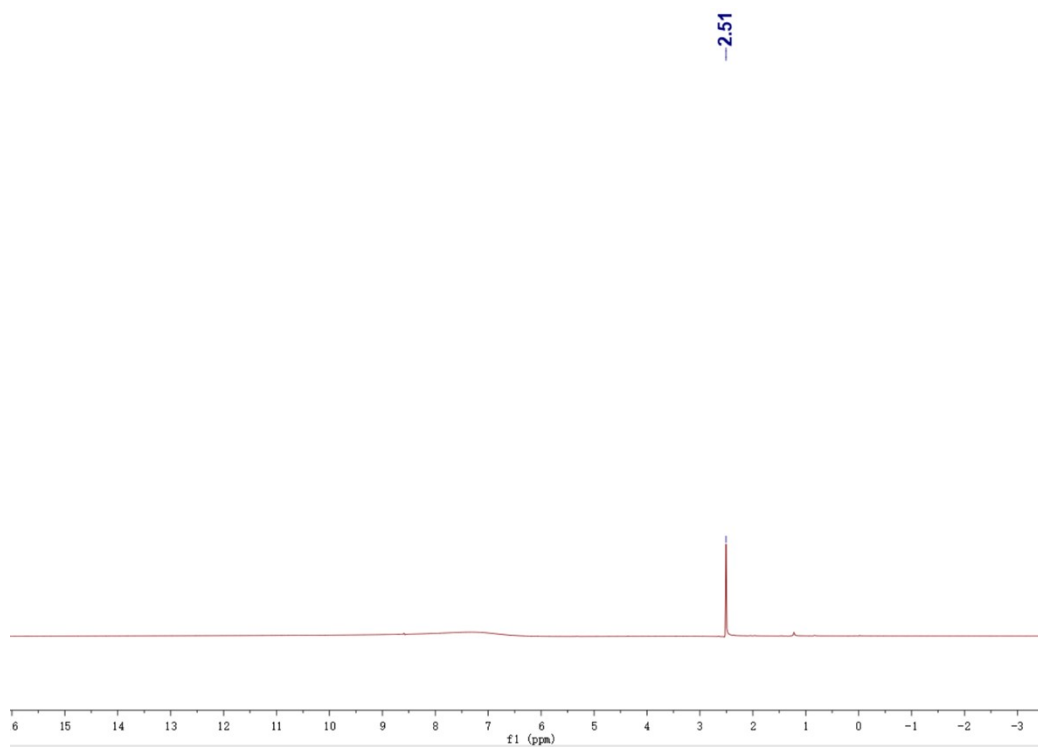


Figure S11. ^1H NMR spectra in DMSO-d6 for DPTO.

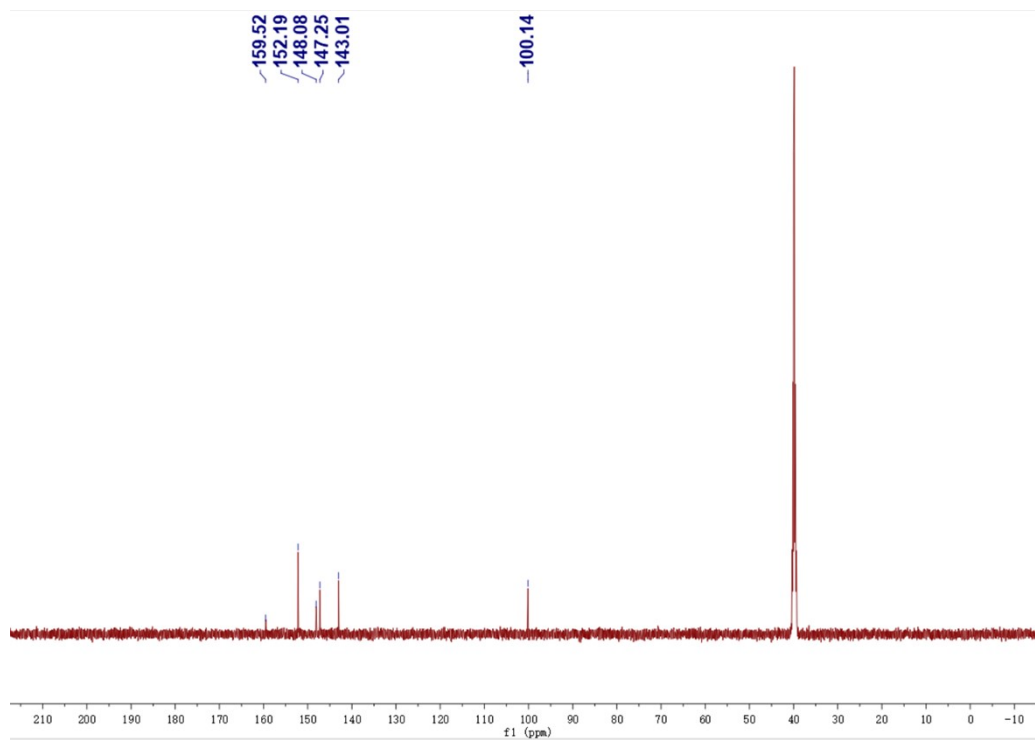


Figure S12. ^1H NMR spectra in DMSO-d6 for DPTO.

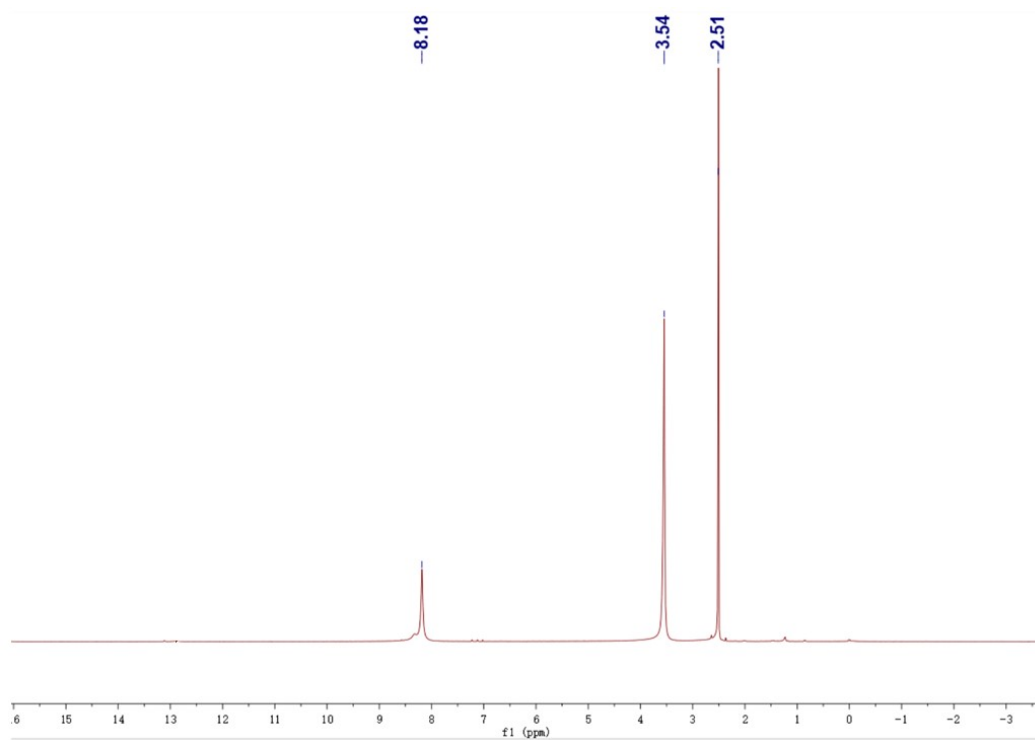


Figure S13. ^1H NMR spectra in DMSO-d₆ for C2.

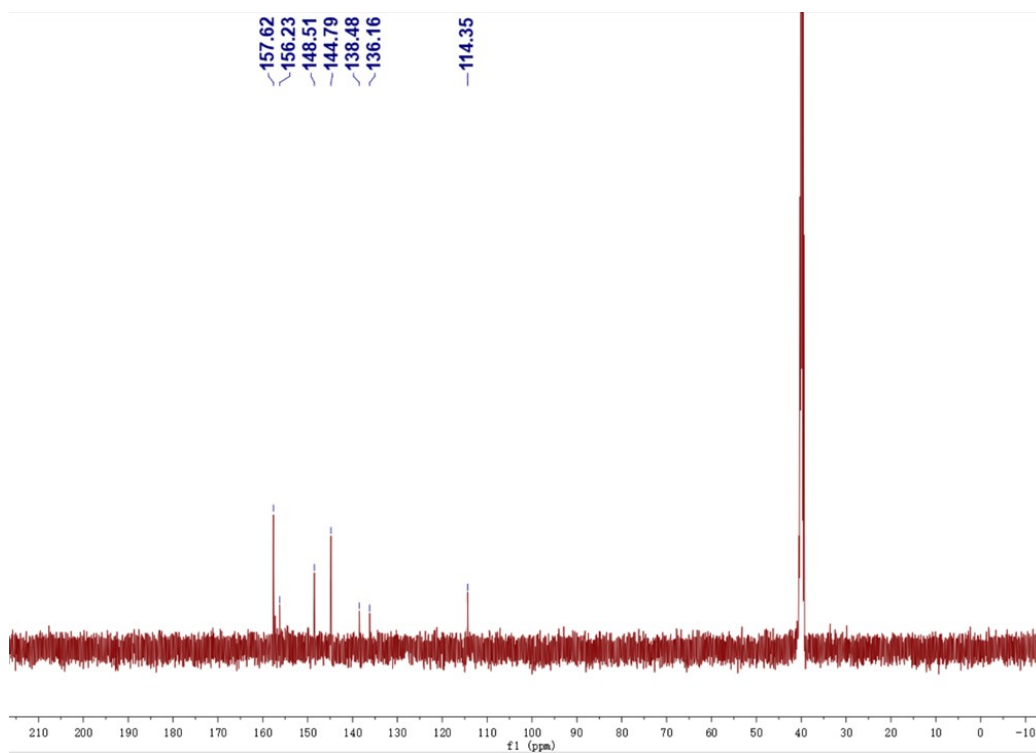


Figure S14. ^1H NMR spectra in DMSO-d₆ for C2.

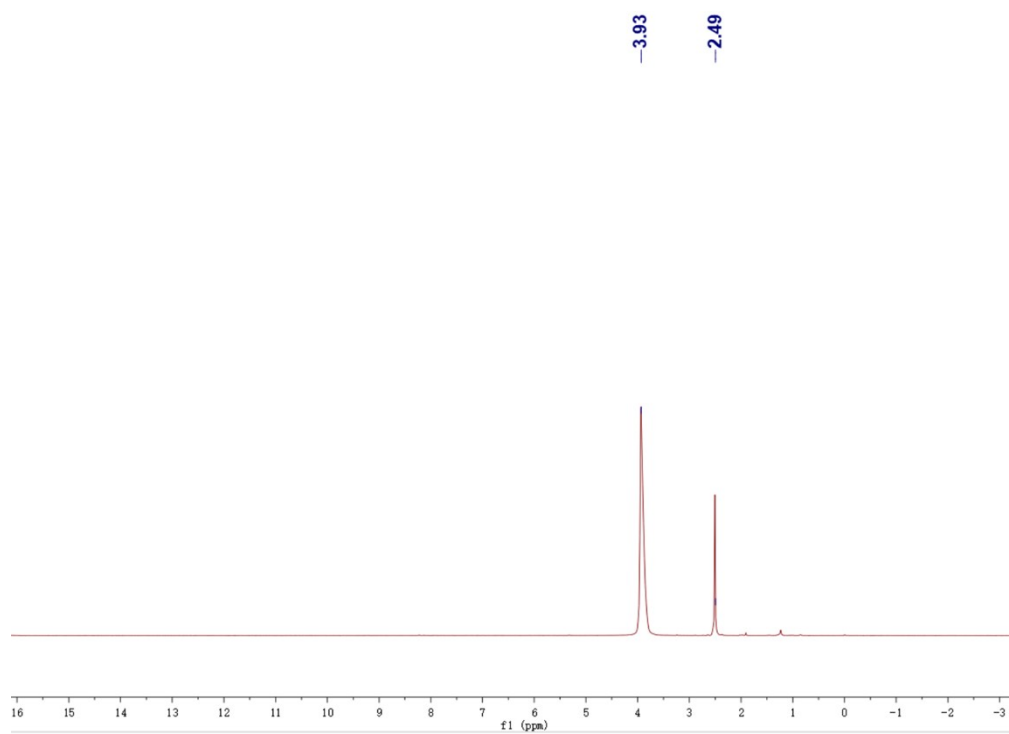


Figure S15. ^1H NMR spectra in DMSO-d6 for DPPT.

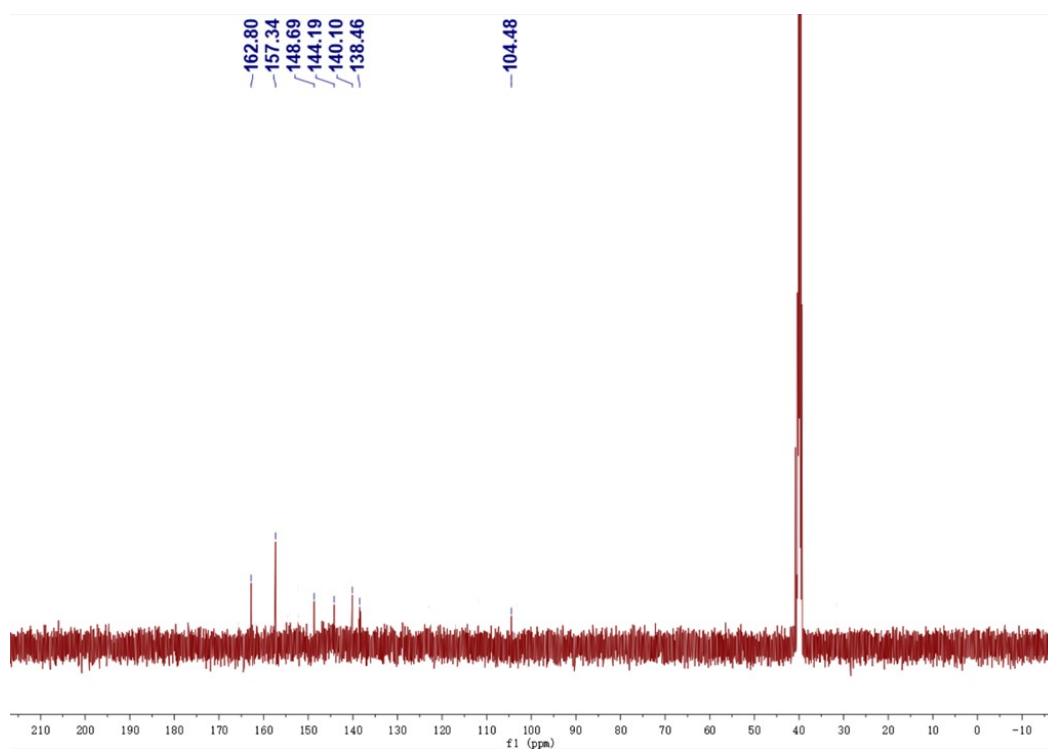


Figure S16. ^1H NMR spectra in DMSO-d6 for DPPT.

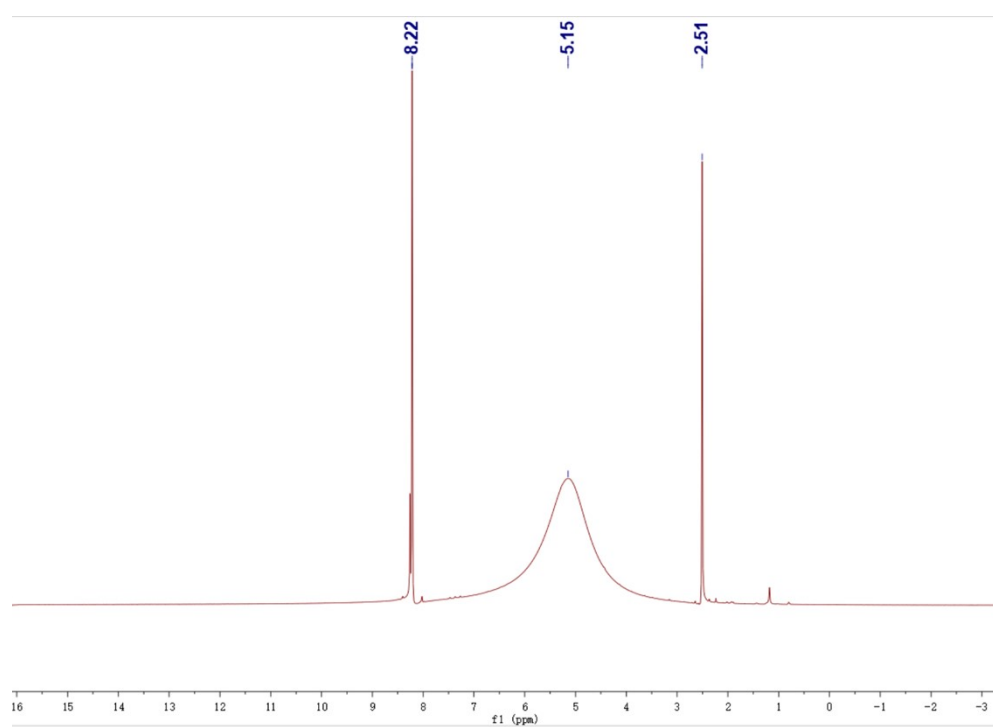


Figure S17. ^1H NMR spectra in DMSO-d₆ for **D2**.

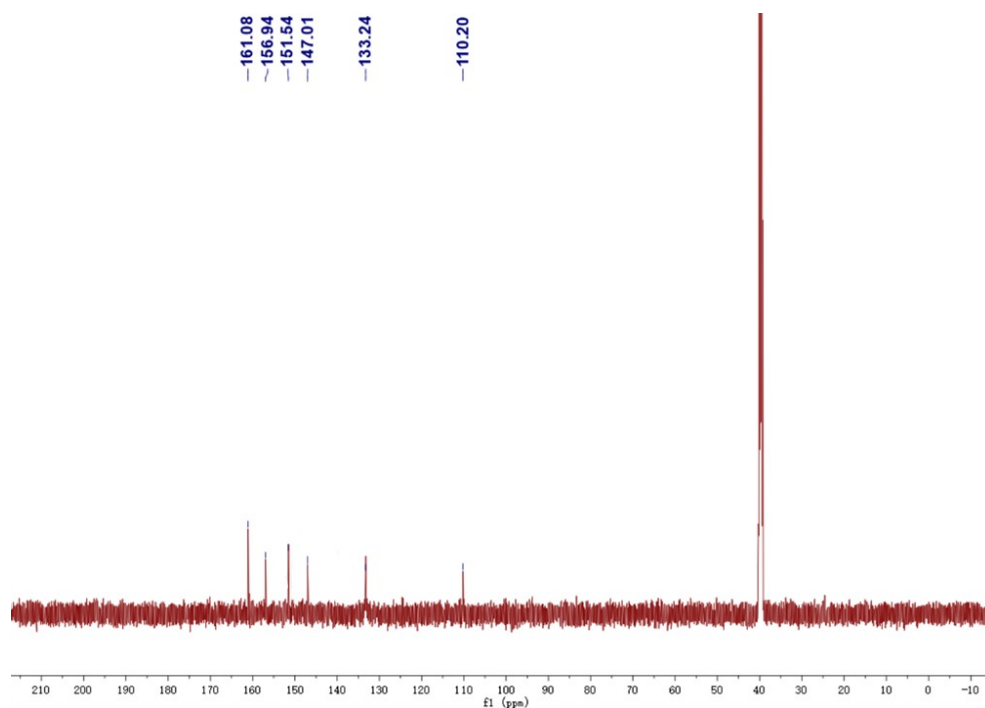


Figure S18. ^{13}C NMR spectra in DMSO-d₆ for **D2**.

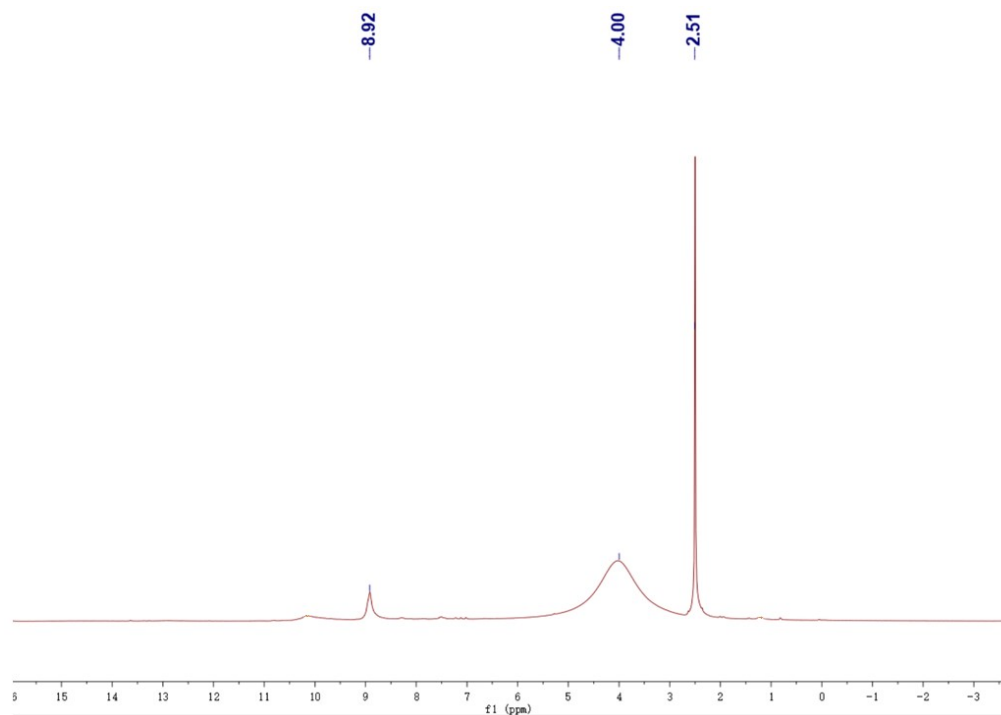


Figure S19. ^1H NMR spectra in DMSO-d₆ for **D3**.

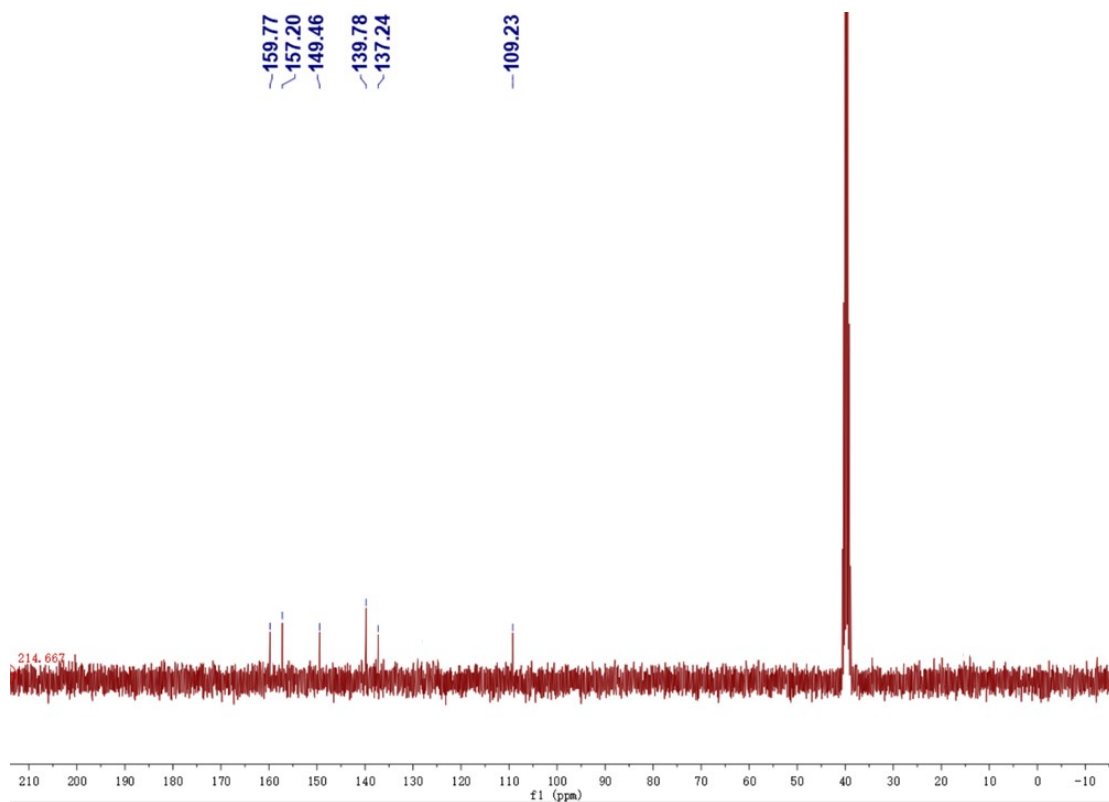


Figure S20. ^{13}C NMR spectra in DMSO- d_6 for D3.

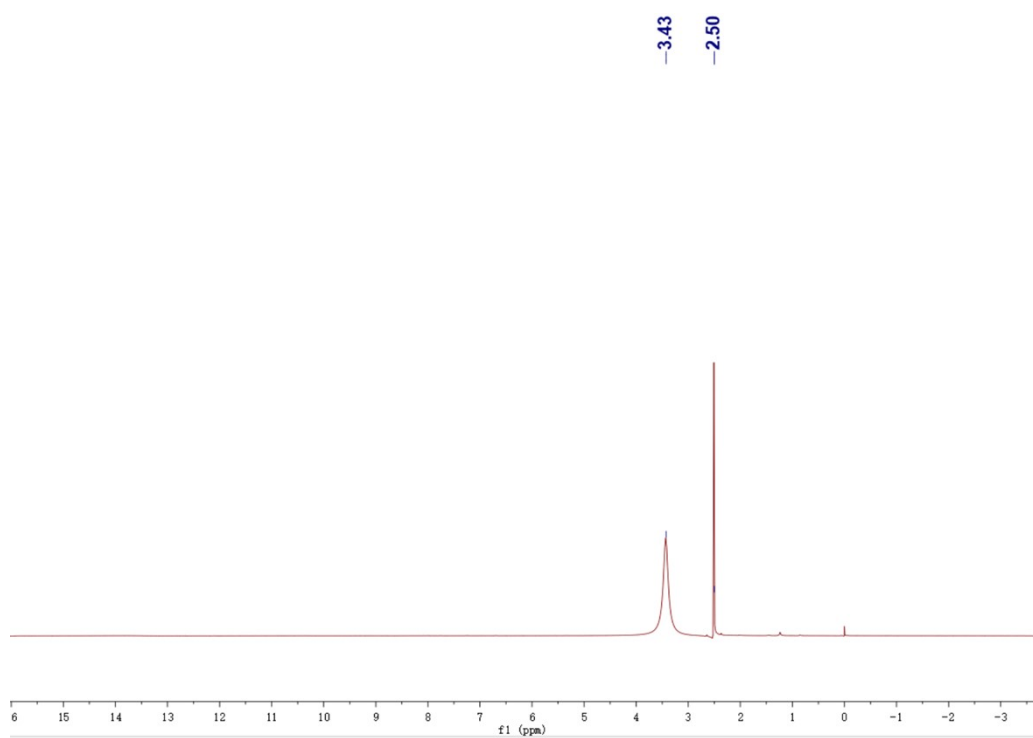


Figure S21. ^1H NMR spectra in DMSO-d₆ for **D4**.

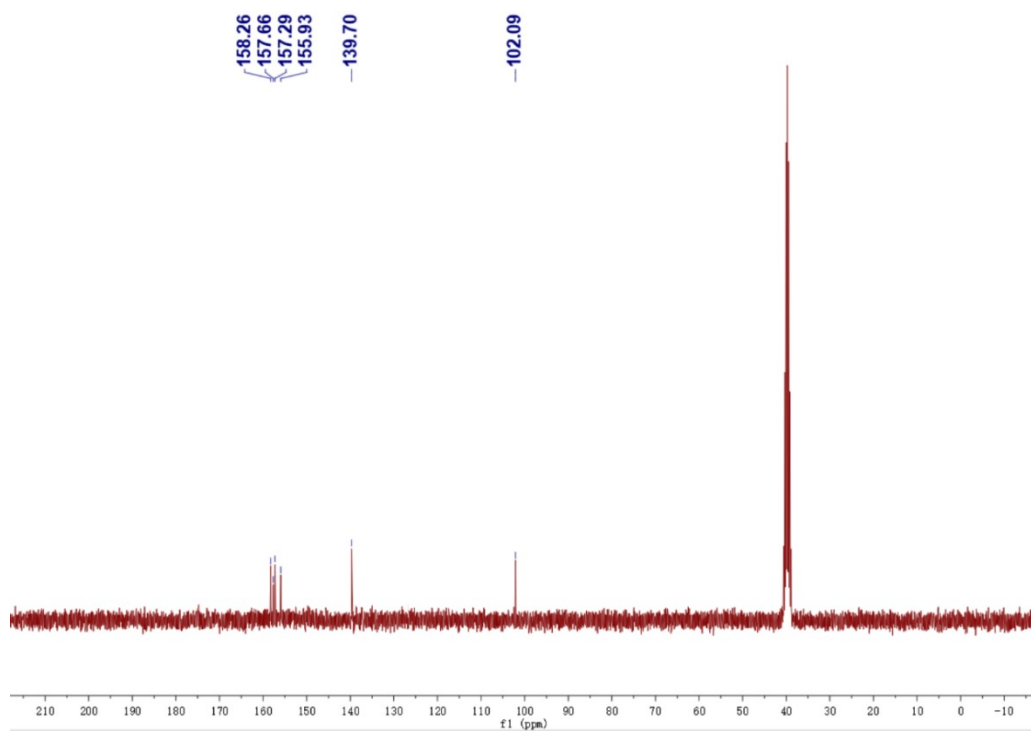


Figure S22. ^{13}C NMR spectra in DMSO-d₆ for **D4**.

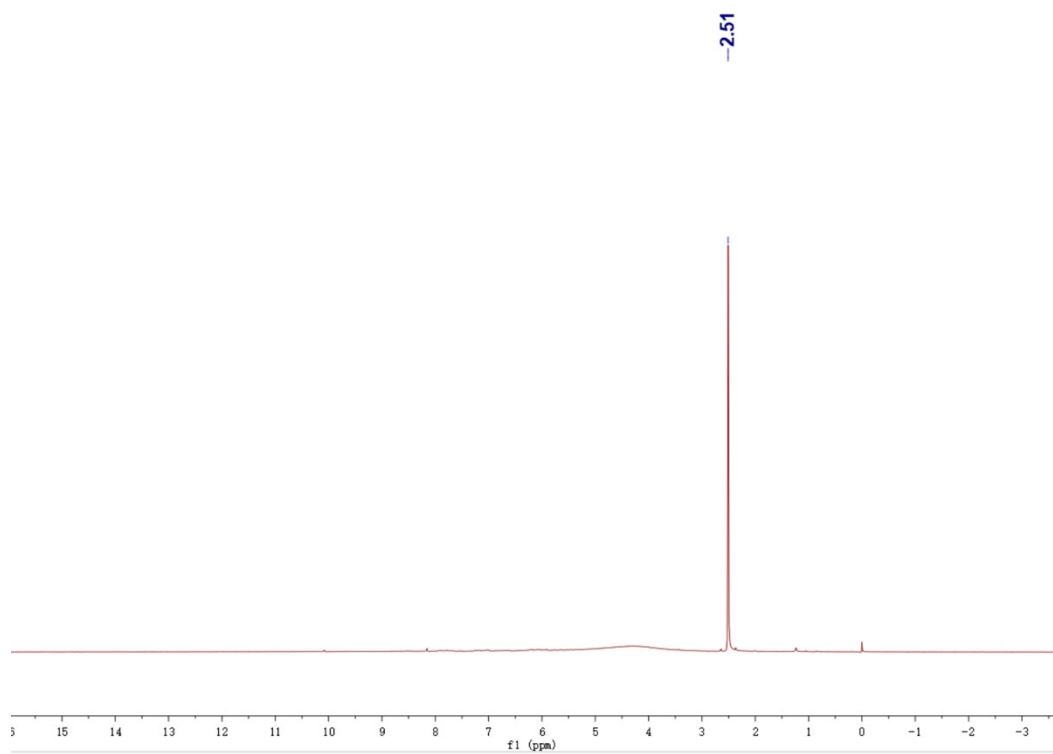


Figure S23. ^1H NMR spectra in DMSO-d6 for DPBT.

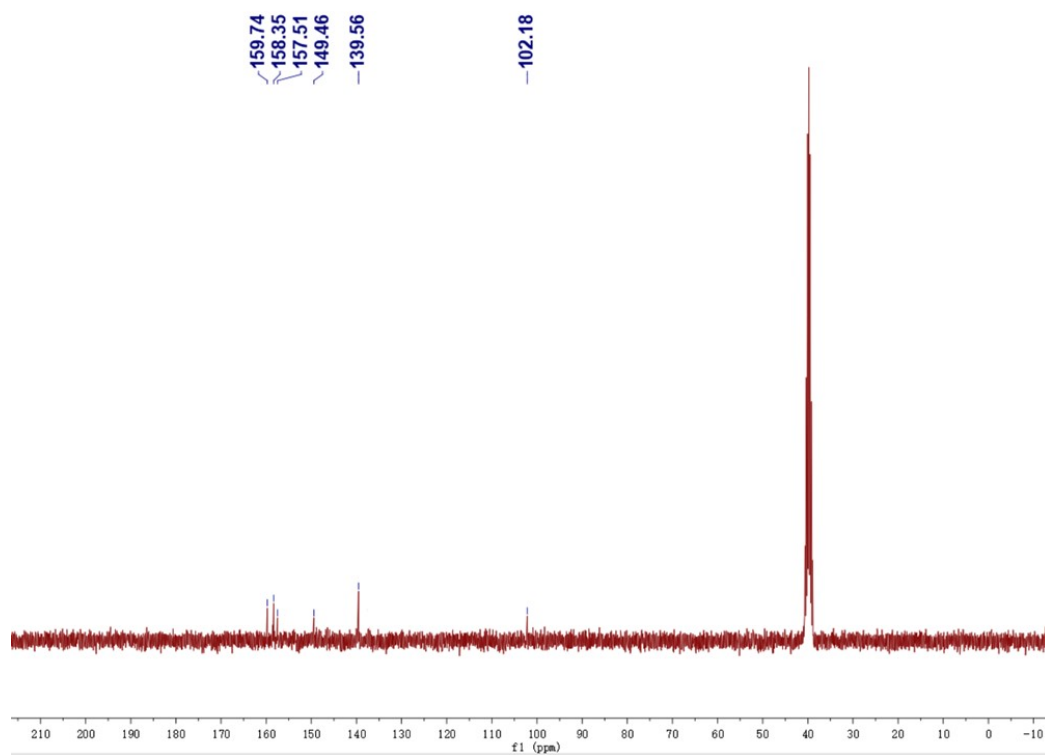


Figure S24. ^1H NMR spectra in DMSO-d6 for DPBT.

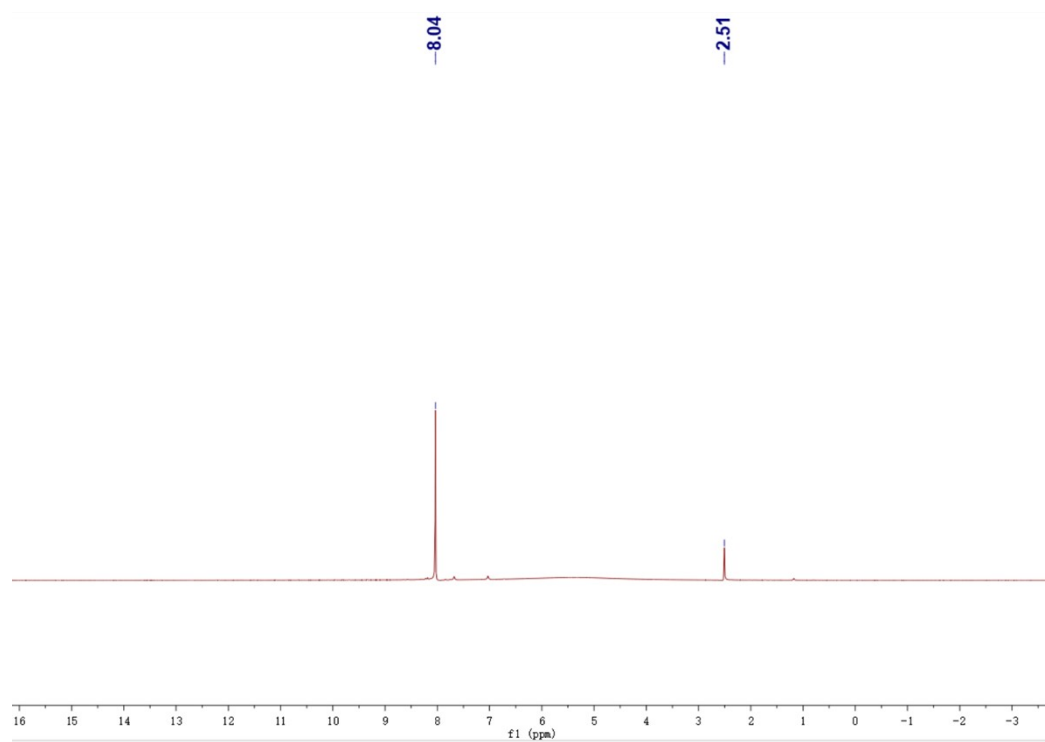


Figure S25. ^1H NMR spectra in DMSO-d₆ for **E3**.

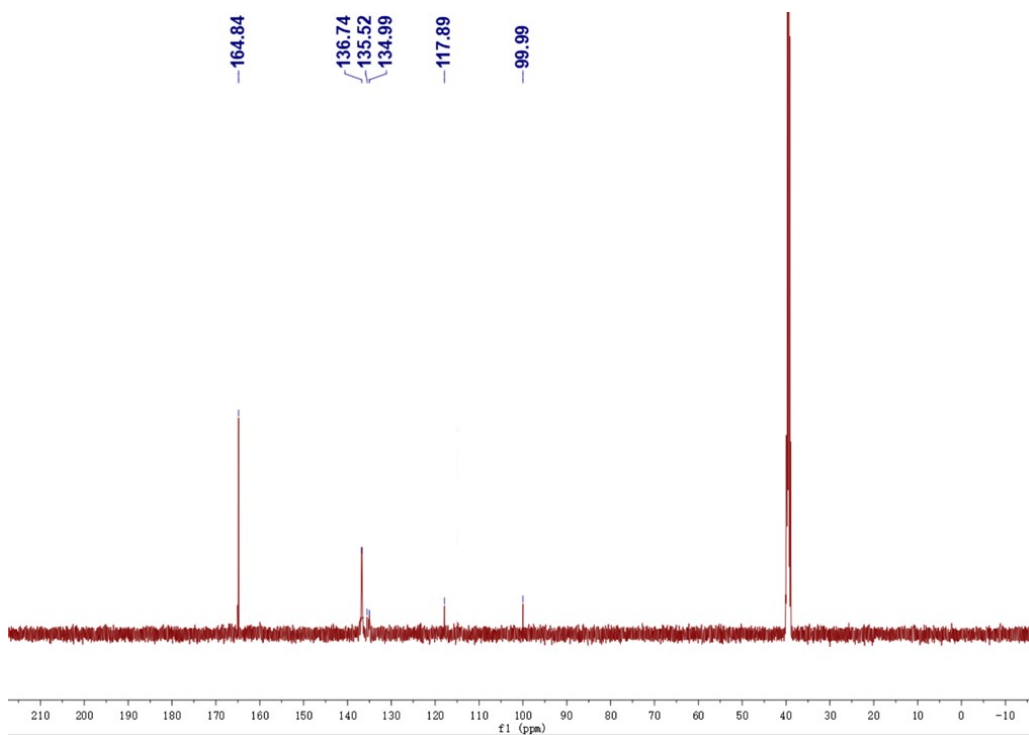


Figure S26. ^{13}C NMR spectra in DMSO-d₆ for **E3**.

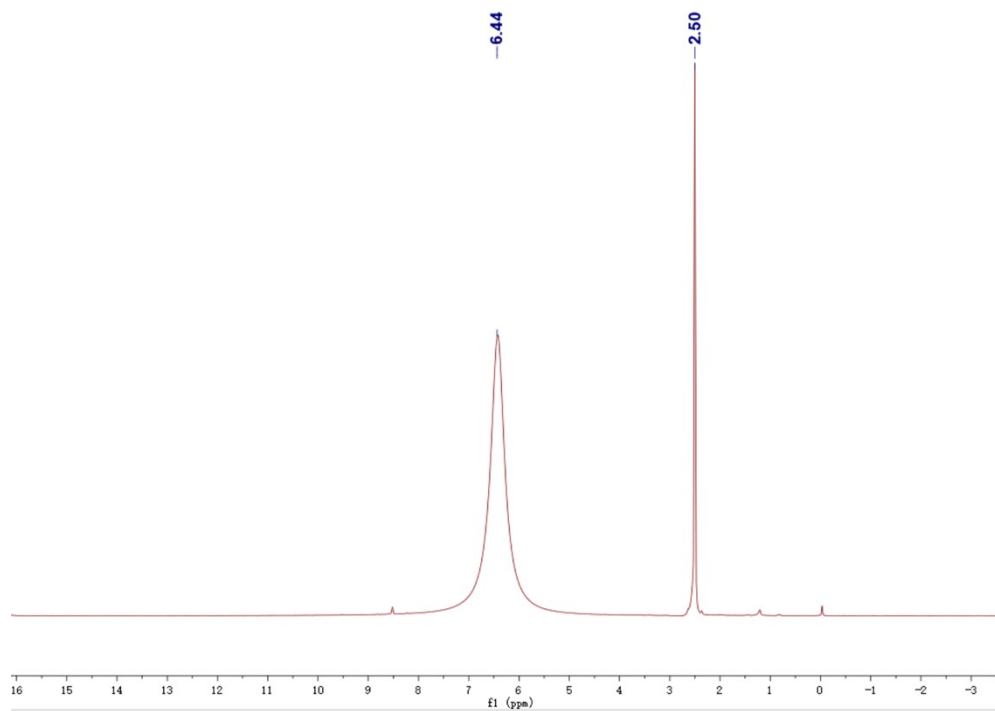


Figure S27. ^1H NMR spectra in DMSO-d₆ for **PBPT**.

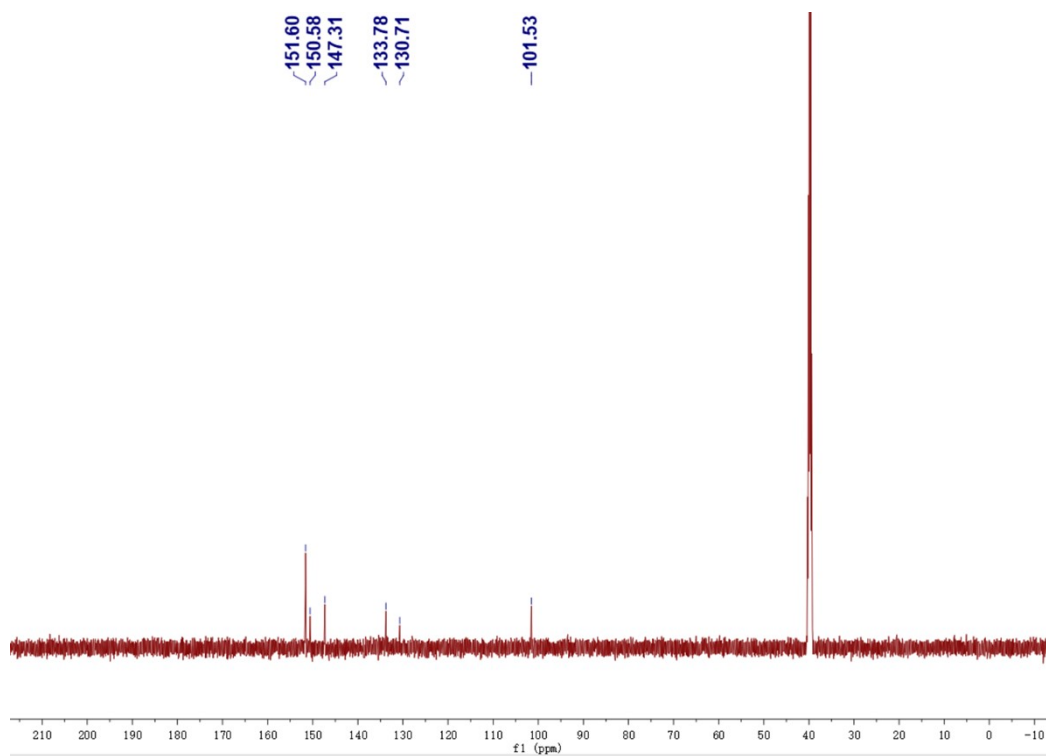


Figure S28. ^{13}C NMR spectra in DMSO- d_6 for PBPT.

5. DSC and TG of compounds

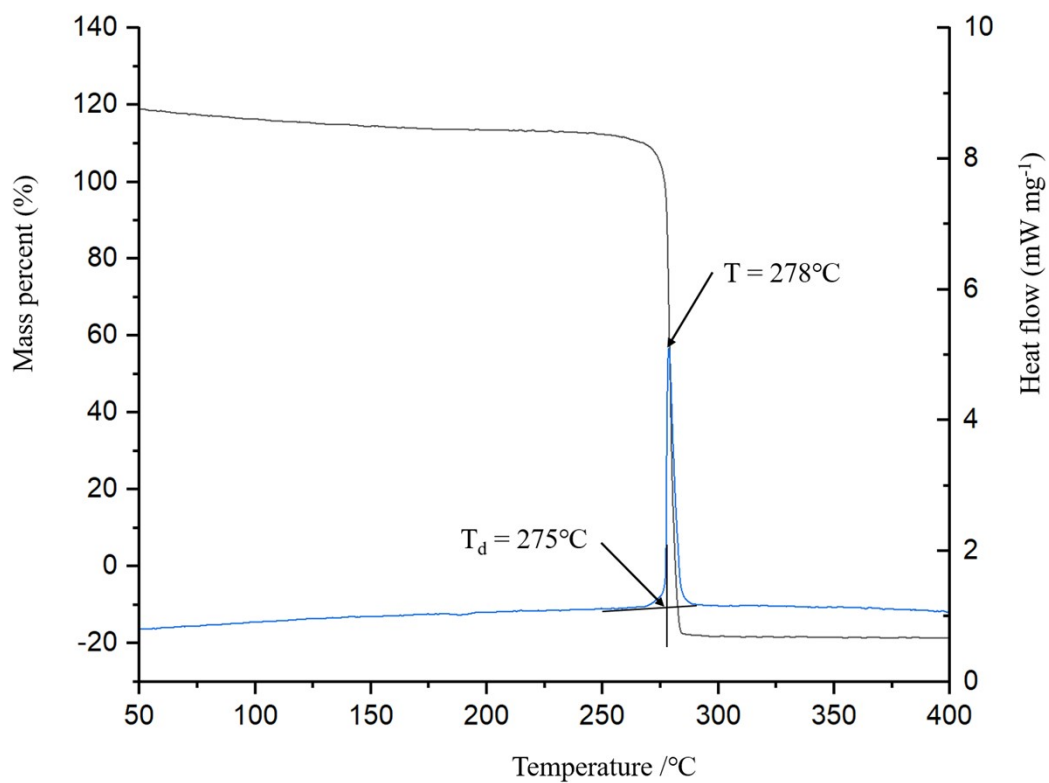


Figure S29 TG and DSC of **DPT**

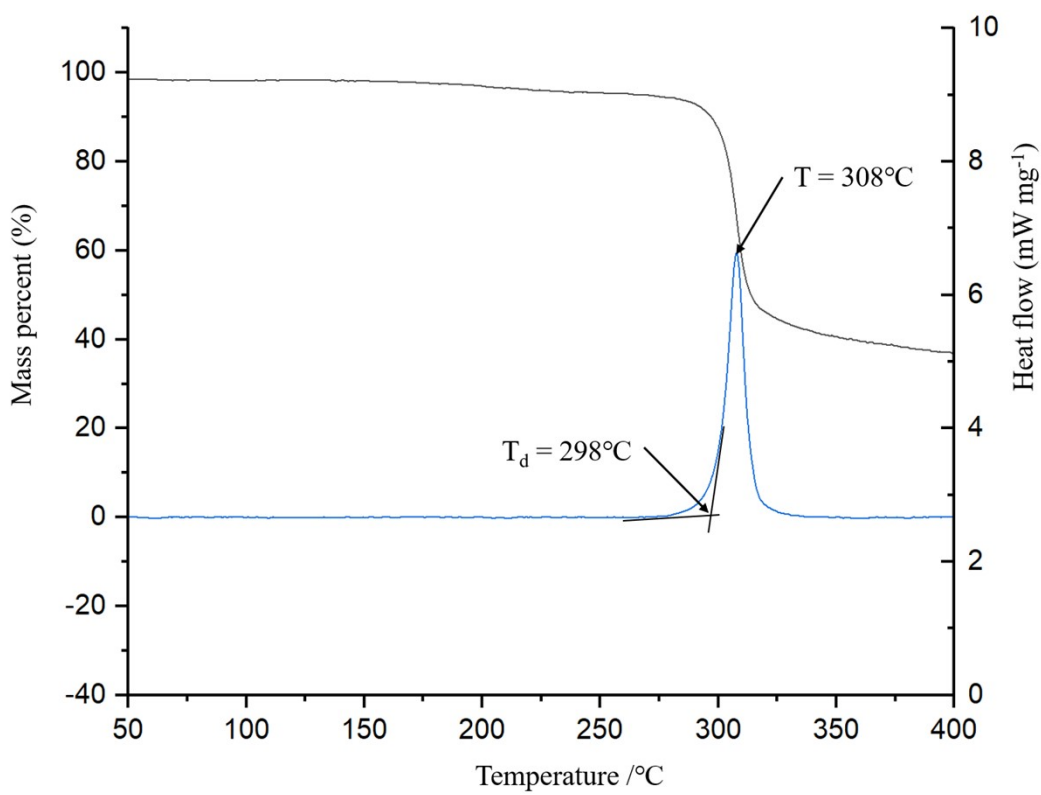


Figure S30 TG and DSC of **B4**

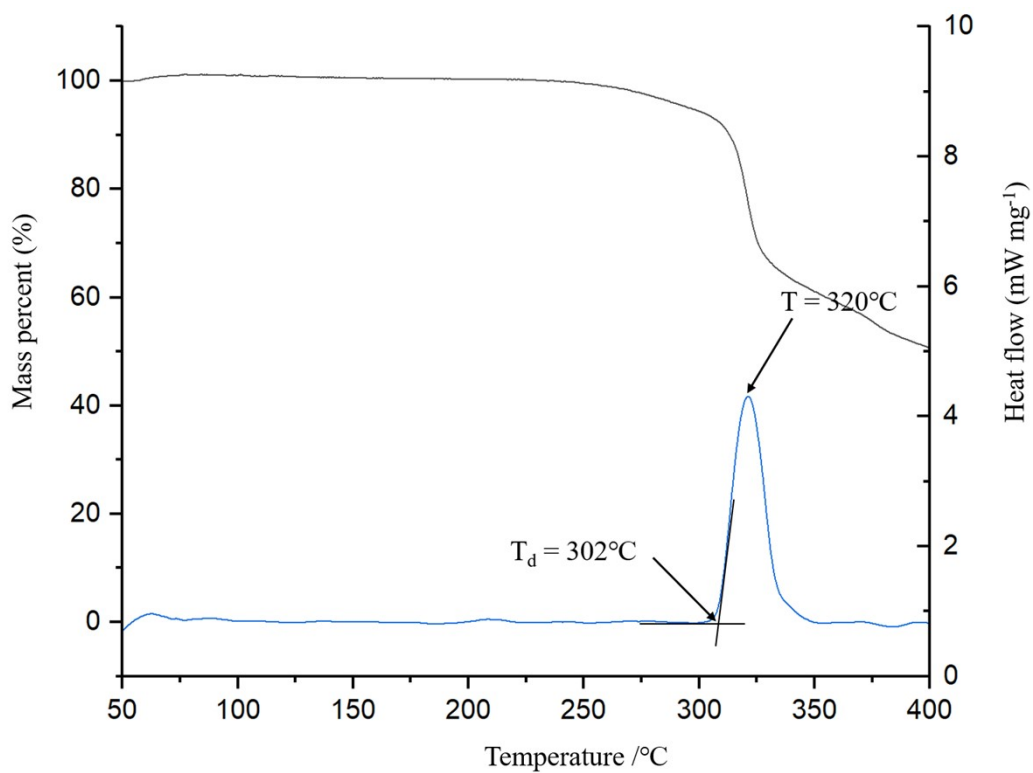


Figure S31 TG and DSC of DPPTO

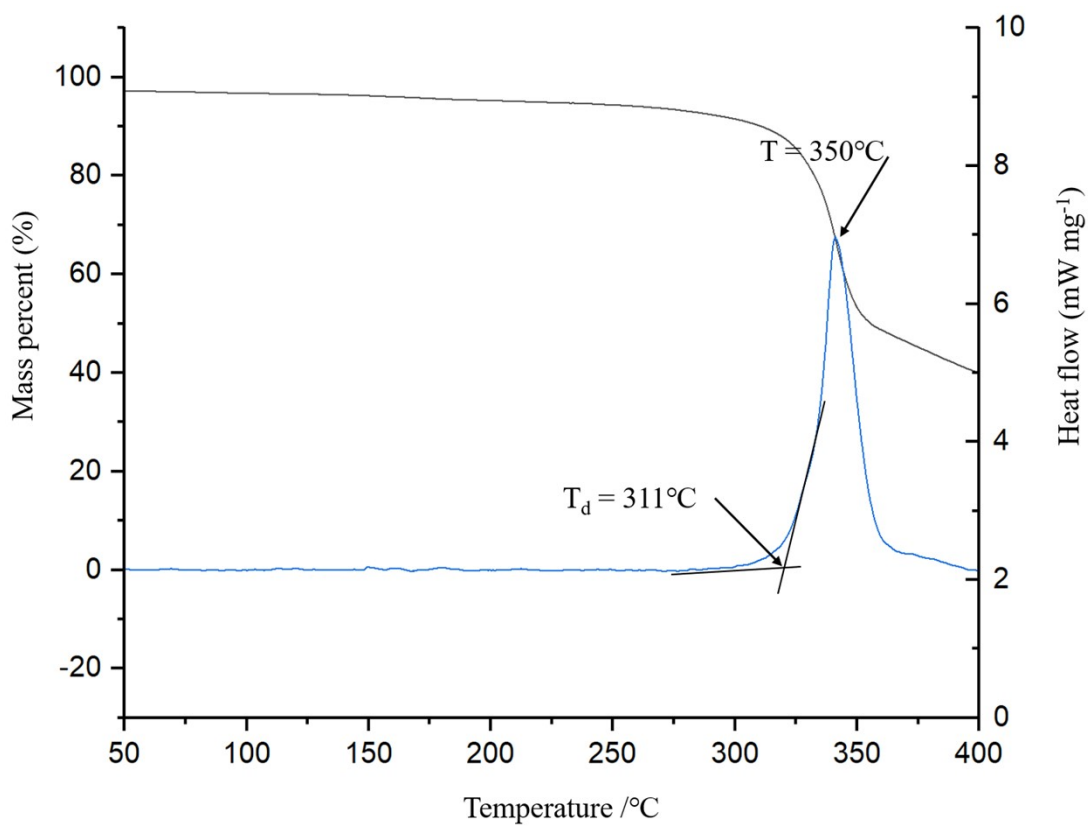


Figure S32 TG and DSC of DPPT

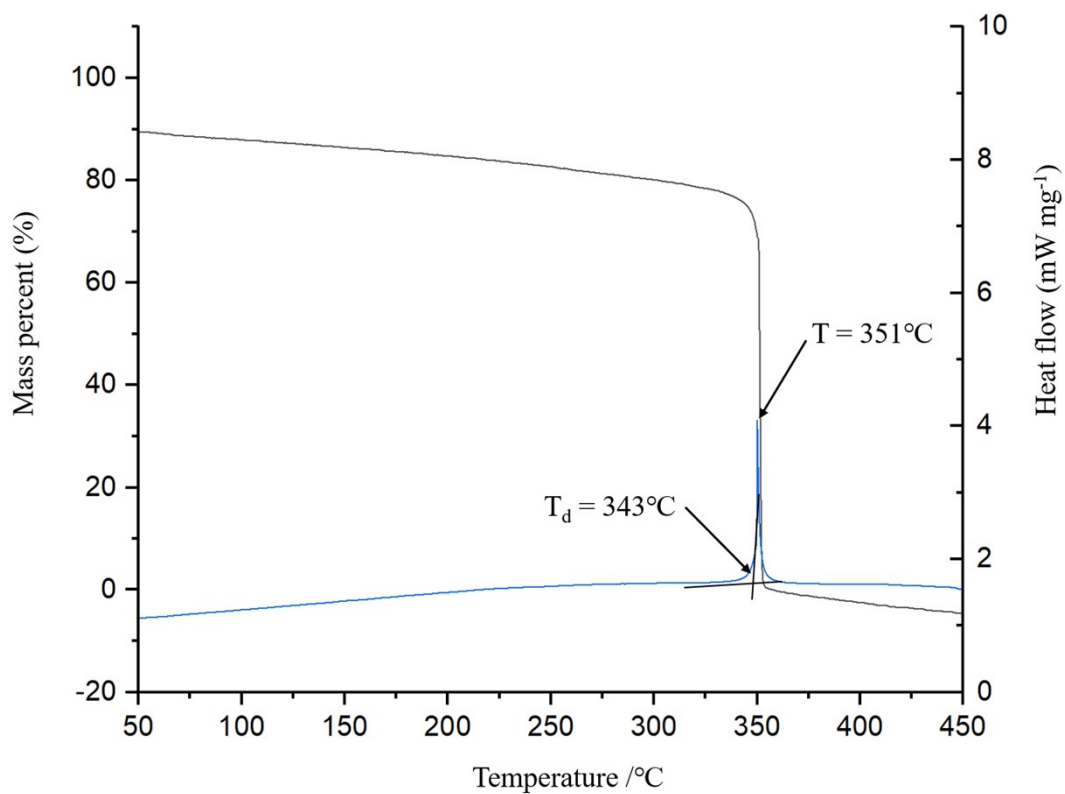


Figure S33 TG and DSC of D4

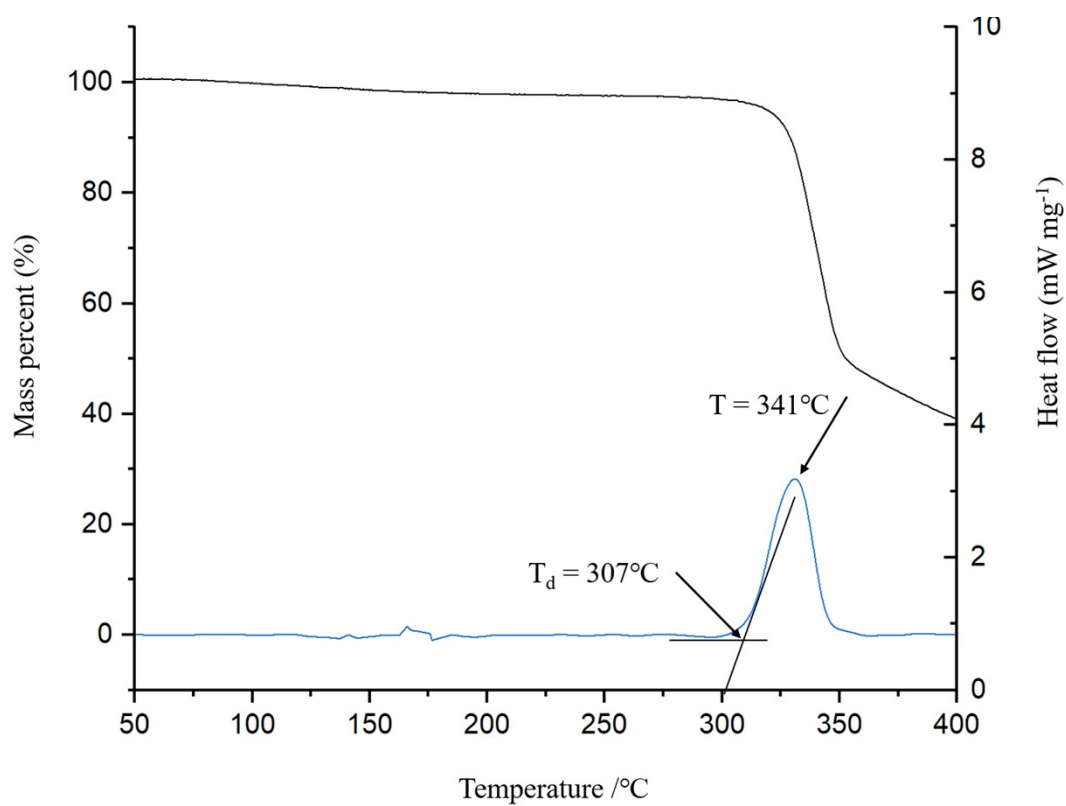


Figure S34 TG and DSC of DPBT

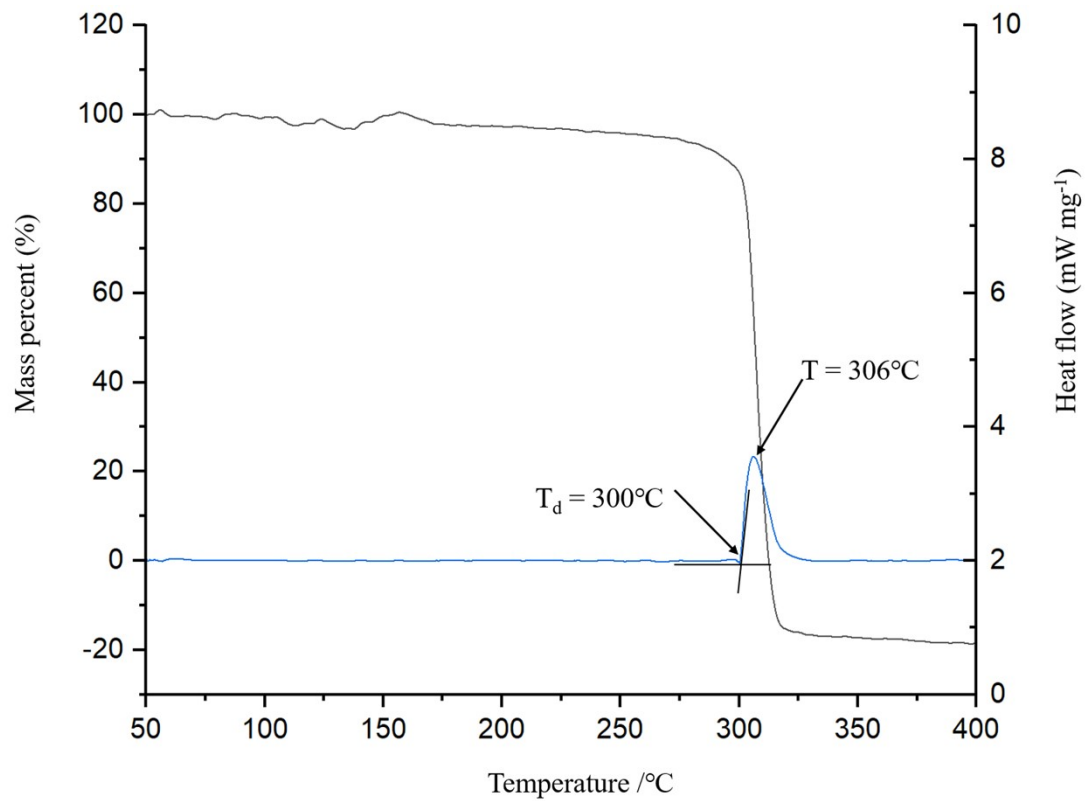


Figure S35 TG and DSC of PBPT