# Supporting Information (SI)

## Nitrogen-Rich Salts Based on the Combination of 1,2,4-Triazole and 1,2,3-Triazole Rings: A Facile Strategy for Fine Tuning Energetic Properties

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# 1. Computational Details

Calculations were performed by using the Gaussian 09 suite of programs. The geometric optimization of all the structures and frequency analyses for calculation of heats of formation was carried out by using B3-LYP functional[1] with 6-311+G** basis set,[2] All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. The heats of formation (HOF) of the title compounds were computed through appropriate isodesmic reactions (Scheme S1 and S2). The isodesmic reaction processes, i.e., the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds. The isodesmic reactions used to derive the HOF of the title compounds are in Scheme S1. The change of enthalpy for the reactions at 298 K can be expressed as

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

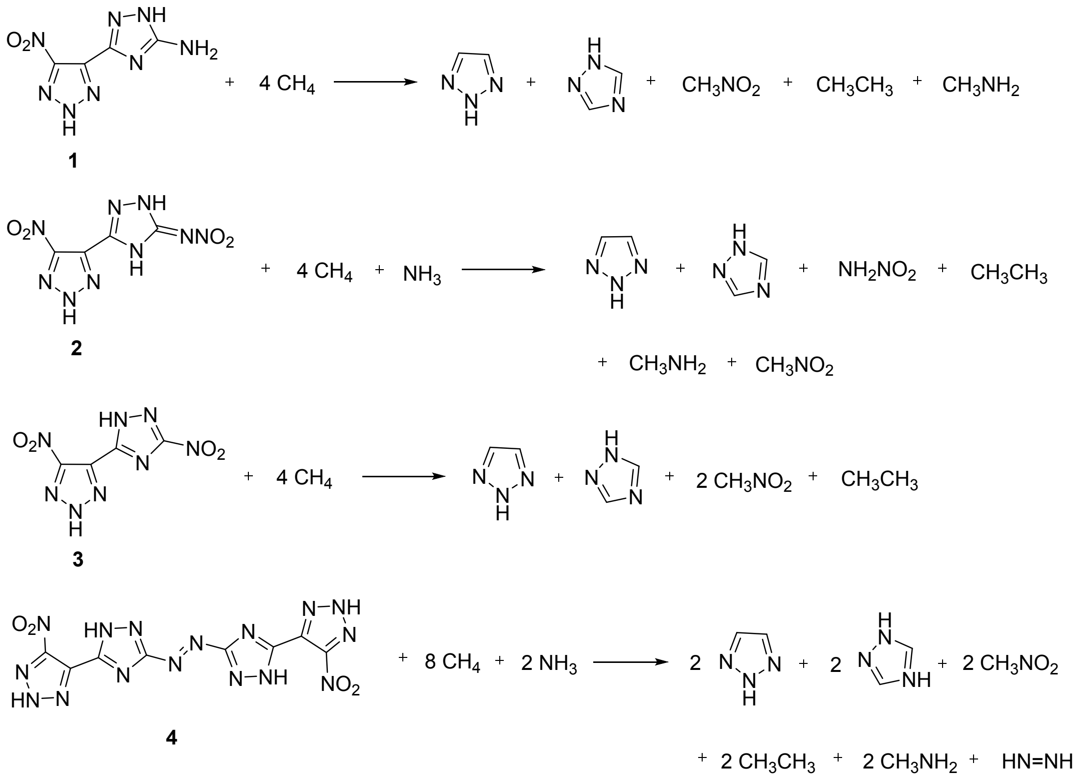
where $\Delta_f H_R$ and $\Delta_f H_P$ are the HOF of reactants and products at 298 K, respectively, and $\Delta H_{298}$ can be calculated using the following expression:

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

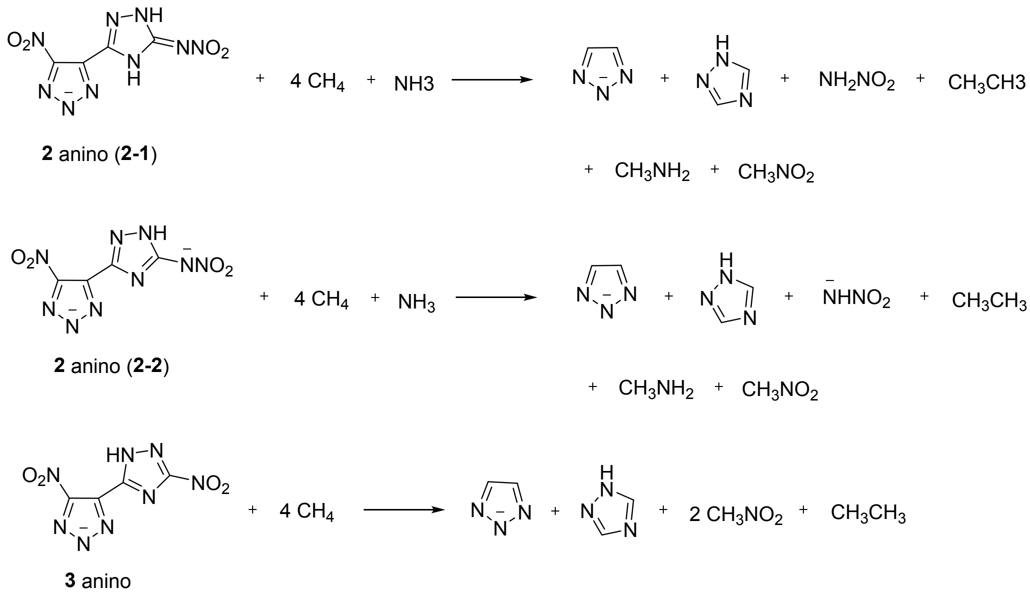
where $E_0$ is the change in total energy between the products and the reactants at 0 K; $\Delta ZPE$ is the difference between the zero-point energies ($ZPE$) of the products and the reactants at 0 K;

ΔHT is thermal correction from 0 to 298 K. The $\Delta(PV)$ value in eq (2) is the $PV$ work term. It equals $\Delta nRT$ for the reactions of ideal gas. For the isodesmic reactions, □n = 0, so $\Delta(PV) = 0$. On the left side of Eq. (1), apart from target compound, all the others are called reference compounds.

The HOF of reference compounds are available either from the experiments[3-5] or from the high level computing like CBS-4M.

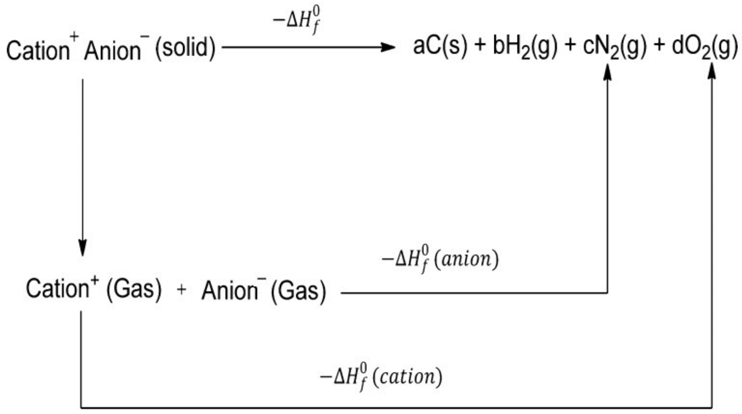


**Scheme S1.** Isodesmic and tautomeric reactions for **1-4** to calculate the HOF.




**Scheme S2.** Isodesmic and tautomeric reactions for 4-nitro-5-(5-nitramino-1,2,4-triazol-3-yl)-1,2,3-triazolate and 4-nitro-5-(5-nitro-1,2,4-triazol-3-yl)-1,2,3-triazolate ions to compute the HOF.

For energetic salts, the solid-phase heat of formation is calculated on the basis of a Born-Haber energy cycle (Scheme S3).[6] The number is simplified by equation 3:




**Scheme S3**. Born−Haber Cycle for the Formation of energetic salts.

$\Delta H_f^\circ$ (salt, 298 K) = $\Delta H_f^\circ$ (cation, 298K) + $\Delta H_f^\circ$ (anion, 298K) – $\Delta H_L$ (3)

in which $\Delta H_L$ can be predicted by using the formula suggested by Jenkins, et al.[7](equation 4):

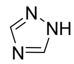
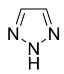
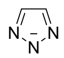
$\Delta H_L = U_{pot} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT$ (4)

In this equation, $n_M$ and $n_X$ depend on the nature of the ions $M$p$^+$ and $X$q$^-$, respectively. The equation for lattice potential energy $U_{pot}$(equation 5) has the form:[6]

$U_{POT}$ [kJ mol$^{-1}$] = $\gamma(\rho_m/M_m)^{1/3} + \delta$ (5)

where $\rho_m$ [gcm$^{-3}$] is the density of the salt, $M_m$ is the chemical formula mass of the ionic material, and values for g and the coefficients γ (kJmol$^{-1}$cm) and δ (kJmol$^{-1}$) are assigned literature values.[7]

**Table S1**. *Ab initio* computational values of small molecules used in isodesmic and tautomeric reactions.

| Compound | $E_0$[a] | ZPE[b] | $H_T$[c] | HOF[d] |
|---|---|---|---|---|
| **1** | -743.3289111 | 299.64 | 32.81 | 520.81 |
| **2** | -947.8585794 | 306.23 | 38.71 | 593.29 |
| **3** | -892.4904784 | 263.3 | 35.43 | 559.59 |
| **4** | -1484.216735 | 487.38 | 61.04 | 1206.92 |
| **2 anino (2-1)** | -947.3712189 | 269.27 | 38.48 | 314.90 |
| **2 anino (2-2)** | -946.773087 | 236.48 | 37.11 | 320.27 |
| **3 anino** | -892.0067566 | 226.07 | 35.25 | 271.42 |
| $NH_2NO_2$ | -261.1248168 | 98.79 | 12.39 | -3.9 |
| $CH_3NO_2$ | -245.0915559 | 124.93 | 11.6 | -80.8 |
| $CH_3NH_2$ | -95.8938402 | 160.78 | 11.64 | -22.5 |
| $NHNO_2^-$ | -259.936099 | 65.95 | 11.23 | -84.00 |
| NH=NH | -110.6795238 | 70.35 | 10.03 | 194.97 |
|  | -242.3203873 | 150.39 | 12.06 | 192.7 |
|  | -242.3001706 | 150.23 | 12.05 | 233.71 |
|  | -241.74 | 113.4 | 11.75 | 146.54 |

[a] Total energy calculated by B3LYP/6-31+G** method (a.u); [b] zero-point correction (kJ mol-1); [c] thermal correction to enthalpy (kJ mol-1); [d] heat of formation (kJ mol-1).

**References:**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[7] H. D. B. Jenkins, D. Tudeal and L. Glasser, *Inorg. Chem.*, **2002**, 41, 2364–236


## 2. Crystallographic data for compounds 2·acetonitrile, 3 and salts 8, 17.

**Table S2.** Crystallographic data for the compounds compounds **2**·acetonitrile, **3** and salts **8** and **17**.

| | **2**·acetonitrile | **3** | **8** | **17** |
|---|---|---|---|---|
| Formula | $C_6H_6N_{10}O_4$ | $C_4H_2N_8O_4$ | $C_5H_8N_{12}O_4$ | $C_6H_{13}N_{15}O_4$ |
| Formula weight | 282.21 | 226.14 | 300.23 | 359.31 |
| Temperature | 172(2) K | 173(2) K | 173(2) K | 173(2) K |
| Crystal system | Triclinic | Orthorhombic | Monoclinic | Orthorhombic |
| Space group | *P*-1 | *Pca2$_1$* | *P2$_1$/n* | *Pca2$_1$* |
| $\rho$/g cm$^{-3}$ | 1.631 | 1.871 | 1.811 | 1.740 |

| | | | | |
|---|---|---|---|---|
| a/Å | 4.5053(5) | 12.9567(12) | 15.6882(15) | 45.902(5) |
| b/Å | 10.4920(13) | 6.4248(8) | 4.8817(5) | 3.5862(4) |
| c/Å | 12.3817(17) | 9.6417(10) | 16.3623(17) | 8.3346(9) |
| $\alpha$/° | 83.323(4) | 90 | 90 | 90 |
| $\beta$/° | 82.161(5) | 90 | 118.492(4) | 90 |
| $\gamma$/° | 85.293(4) | 90 | 90 | 90 |
| Goodness-of-fit on $F^2$ | 1.029 | 1.027 | 1.014 | 1.037 |
| Final R indexes [$I$ >2σ (I)] | $R_1$ = 0.0592, w$R_2$ = 0.0901 | $R_1$ = 0.0498, w$R_2$ = 0.0801 | $R_1$ = 0.0447, w$R_2$ = 0.0804 | $R_1$ = 0.0584, w$R_2$ = 0.0817 |
| Final R indexes (all data) | $R_1$ = 0.1252, w$R_2$ = 0.1064 | $R_1$ = 0.0964, w$R_2$ = 0.0926 | $R_1$ = 0.0940, w$R_2$ = 0.0955 | $R_1$ = 0.1317, w$R_2$ = 0.0981 |
| CCDC | 1540318 | 1559066 | 1544500 | 1572217 |

# 3. X-ray Structural Analysis of compounds 2·acetonitrile, 3 and salts 8, 17.

**Table S3.** Selected bond lengths [Å] and angles [°] for compound **2**·acetonitrile

| | | | |
|---|---|---|---|
| C(1)-N(3) | 1.326(4) | N(6)-C(3)-N(7) | 105.6(3) |
| C(1)-C(2) | 1.389(4) | N(6)-C(3)-N(8) | 135.7(3) |
| C(1)-N(4) | 1.441(4) | N(7)-C(3)-N(8) | 118.7(3) |
| C(2)-N(1) | 1.334(4) | N(5)-C(4)-N(7) | 111.5(3) |
| C(2)-C(4) | 1.463(4) | N(5)-C(4)-C(2) | 126.3(3) |
| C(3)-N(6) | 1.327(4) | N(7)-C(4)-C(2) | 122.1(3) |
| C(3)-N(7) | 1.350(4) | N(10)-C(5)-C(6) | 179.3(5) |
| C(3)-N(8) | 1.352(4) | C(5)-C(6)-H(6A) | 109.5 |
| C(4)-N(5) | 1.299(4) | C(5)-C(6)-H(6B) | 109.5 |
| C(4)-N(7) | 1.367(4) | H(6A)-C(6)-H(6B) | 109.5 |
| C(5)-N(10) | 1.125(4) | C(5)-C(6)-H(6C) | 109.5 |
| C(5)-C(6) | 1.458(5) | H(6A)-C(6)-H(6C) | 109.5 |
| C(6)-H(6A) | 0.9800 | H(6B)-C(6)-H(6C) | 109.5 |
| C(6)-H(6B) | 0.9800 | N(2)-N(1)-C(2) | 103.0(3) |
| C(6)-H(6C) | 0.9800 | N(3)-N(2)-N(1) | 116.9(3) |
| N(1)-N(2) | 1.330(3) | N(3)-N(2)-H(2) | 123(2) |
| N(2)-N(3) | 1.310(4) | N(1)-N(2)-H(2) | 120(2) |
| N(2)-H(2) | 0.87(3) | N(2)-N(3)-C(1) | 102.4(3) |
| N(4)-O(2) | 1.218(3) | O(2)-N(4)-O(1) | 125.6(3) |
| N(4)-O(1) | 1.222(3) | O(2)-N(4)-C(1) | 116.6(3) |
| N(5)-N(6) | 1.384(3) | O(1)-N(4)-C(1) | 117.8(3) |
| N(6)-H(6) | 0.87(3) | C(4)-N(5)-N(6) | 103.8(2) |
| N(7)-H(7) | 0.87(3) | C(3)-N(6)-N(5) | 111.8(2) |
| N(8)-N(9) | 1.343(3) | C(3)-N(6)-H(6) | 131(2) |
| N(9)-O(3) | 1.234(3) | N(5)-N(6)-H(6) | 117(2) |

| | | | |
|---|---|---|---|
| N(9)-O(4) | 1.246(3) | C(3)-N(7)-C(4) | 107.2(3) |
| N(3)-C(1)-C(2) | 110.1(3) | C(3)-N(7)-H(7) | 124.5(19) |
| N(3)-C(1)-N(4) | 120.4(3) | C(4)-N(7)-H(7) | 128.2(19) |
| C(2)-C(1)-N(4) | 129.4(3) | N(9)-N(8)-C(3) | 115.6(2) |
| N(1)-C(2)-C(1) | 107.6(3) | O(3)-N(9)-O(4) | 123.0(3) |
| N(1)-C(2)-C(4) | 120.4(3) | O(3)-N(9)-N(8) | 122.5(3) |
| C(1)-C(2)-C(4) | 131.7(3) | O(4)-N(9)-N(8) | 114.5(3) |

**Table S4.** Selected torsion angles [°] for compound **2**·acetonitrile

| | | | |
|---|---|---|---|
| C2-N1-N2-N3 | 0.8(4) | C4-N7-C3-N6 | 0.7(3) |
| N2-N1-C2-C4 | -175.3(3) | C4-N7-C3-N8 | 179.8(3) |
| N2-N1-C2-C1 | -0.6(3) | C3-N7-C4-N5 | -0.1(3) |
| N1-N2-N3-C1 | -0.7(4) | C3-N7-C4-C2 | 178.8(3) |
| N2-N3-C1-C2 | 0.2(4) | N9-N8-C3-N7 | -179.8(3) |
| N2-N3-C1-N4 | 177.5(3) | C3-N8-N9-O4 | 179.3(3) |
| O1-N4-C1-N3 | -9.2(5) | C3-N8-N9-O3 | 0.8(4) |
| O2-N4-C1-C2 | -10.5(5) | N9-N8-C3-N6 | -1.1(5) |
| O1-N4-C1-C2 | 167.5(3) | N3-C1-C2-N1 | 0.3(4) |
| O2-N4-C1-N3 | 172.8(3) | N3-C1-C2-C4 | 174.1(3) |
| N6-N5-C4-C2 | -179.4(3) | N4-C1-C2-N1 | -176.7(3) |
| C4-N5-N6-C3 | 1.1(3) | N4-C1-C2-C4 | -2.9(6) |
| N6-N5-C4-N7 | -0.6(3) | N1-C2-C4-N5 | -122.4(3) |
| N5-N6-C3-N7 | -1.1(3) | N1-C2-C4-N7 | 58.9(4) |
| N5-N6-C3-N8 | -180.0(3) | C1-C2-C4-N5 | 64.5(5) |
| C1-C2-C4-N7 | -114.3(4) | | |

**Table S5.** Hydrogen bonds present in compound **2**·acetonitrile

| D-H•••A | d(D-H)/ Å | d(H•••A)/ Å | d(D•••A)/ Å | <(DHA)/ ° | comment |
|---|---|---|---|---|---|
| N(2)-H(2)•••O(4)[i] | 0.87(3) | 2.16(3) | 2.911(4) | 145(3) | inter |
| N(2)-H(2)•••N(1)[ii] | 0.87(3) | 2.44(4) | 3.007(4) | 124(3) | inter |
| N(6)-H(6)•••O(3) | 0.87(3) | 2.24(3) | 2.598(3) | 104(3) | intra |
| N(6)-H(6)•••N(10)[iii] | 0.87(3) | 2.02(3) | 2.884(4) | 171(3) | inter |
| N(7)-H(7)•••N(8)[iv] | 0.87(3) | 2.00(3) | 2.840(4) | 163(3) | inter |
| C(6)-H(6A)•••O(2)[v] | 0.98 | 2.48 | 3.077(5) | 119 | inter |

i: -1+x,1+y,z; ii: 1-x,1-y,2-z ; iii: 1+x,-1+y,z; iv: 1-x,-y,2-z; v: 2-x,1-y,1-z.

**Table S6.** Selected bond lengths [Å] and angles [°] for compound **3**

| | | | |
|---|---|---|---|
| C(1)-N(3) | 1.330(6) | C(1)-C(2)-C(4) | 135.6(5) |
| C(1)-C(2) | 1.400(7) | N(6)-C(3)-N(7) | 117.1(4) |
| C(1)-N(4) | 1.435(7) | N(6)-C(3)-N(8) | 121.7(4) |
| C(2)-N(1) | 1.347(6) | N(7)-C(3)-N(8) | 121.2(4) |

| | | | |
|---|---|---|---|
| C(2)-C(4) | 1.456(7) | N(7)-C(4)-N(5) | 109.9(4) |
| C(3)-N(6) | 1.304(6) | N(7)-C(4)-C(2) | 122.5(4) |
| C(3)-N(7) | 1.344(6) | N(5)-C(4)-C(2) | 127.6(4) |
| C(3)-N(8) | 1.451(6) | N(2)-N(1)-C(2) | 103.9(4) |
| C(4)-N(7) | 1.326(6) | N(1)-N(2)-N(3) | 116.8(4) |
| C(4)-N(5) | 1.341(7) | N(1)-N(2)-H(2) | 123(4) |
| N(1)-N(2) | 1.323(6) | N(3)-N(2)-H(2) | 120(4) |
| N(2)-N(3) | 1.329(6) | N(2)-N(3)-C(1) | 101.8(4) |
| N(2)-H(2) | 0.82(5) | O(1)-N(4)-O(2) | 124.8(4) |
| N(4)-O(1) | 1.223(5) | O(1)-N(4)-C(1) | 118.7(4) |
| N(4)-O(2) | 1.231(5) | O(2)-N(4)-C(1) | 116.5(4) |
| N(5)-N(6) | 1.351(5) | C(4)-N(5)-N(6) | 110.2(4) |
| N(5)-H(5) | 0.84(5) | C(4)-N(5)-H(5) | 132(4) |
| N(8)-O(3) | 1.215(6) | N(6)-N(5)-H(5) | 117(4) |
| N(8)-O(4) | 1.224(5) | C(3)-N(6)-N(5) | 101.2(4) |
| N(3)-C(1)-C(2) | 111.0(5) | C(4)-N(7)-C(3) | 101.5(4) |
| N(3)-C(1)-N(4) | 120.0(4) | O(3)-N(8)-O(4) | 125.8(5) |
| C(2)-C(1)-N(4) | 129.1(4) | O(3)-N(8)-C(3) | 117.1(5) |
| N(1)-C(2)-C(1) | 106.5(4) | O(4)-N(8)-C(3) | 117.0(4) |
| N(1)-C(2)-C(4) | 117.8(4) | | |

**Table S7.** Selected torsion angles [°] for compound **3**

| | | | |
|---|---|---|---|
| C2-N1-N2-N3 | 0.2(6) | C4-N7-C3-N8 | -179.2(4) |
| N2-N1-C2-C4 | 178.0(4) | C3-N7-C4-N5 | -0.9(5) |
| N2-N1-C2-C1 | 0.2(5) | C4-N7-C3-N6 | 1.2(6) |
| N1-N2-N3-C1 | -0.5(6) | O4-N8-C3-N6 | 173.7(4) |
| N2-N3-C1-N4 | -177.7(4) | O4-N8-C3-N7 | -5.9(7) |
| N2-N3-C1-C2 | 0.6(5) | O3-N8-C3-N7 | 172.8(5) |
| O1-N4-C1-N3 | 16.7(7) | O3-N8-C3-N6 | -7.7(7) |
| O2-N4-C1-C2 | 18.1(8) | N3-C1-C2-C4 | -177.7(5) |
| O1-N4-C1-C2 | -161.3(5) | N3-C1-C2-N1 | -0.5(6) |
| O2-N4-C1-N3 | -163.9(5) | N4-C1-C2-C4 | 0.4(10) |
| N6-N5-C4-N7 | 0.5(6) | N4-C1-C2-N1 | 177.6(5) |
| C4-N5-N6-C3 | 0.2(5) | C1-C2-C4-N5 | -21.8(10) |
| N6-N5-C4-C2 | -177.5(5) | C1-C2-C4-N7 | 160.5(6) |
| N5-N6-C3-N7 | -0.9(5) | N1-C2-C4-N7 | -16.5(7) |
| N5-N6-C3-N8 | 179.5(4) | N1-C2-C4-N5 | 161.3(5) |
| C3-N7-C4-C2 | 177.2(5) | | |

**Table S8.** Hydrogen bonds present in compound **3**

| D-H•••A | d(D-H)/ Å | d(H•••A)/ Å | d(D•••A)/ Å | <(DHA)/ ° | comment |
|---|---|---|---|---|---|
| N(2)-H(2)•••N(6)i | 0.82(6) | 2.19(5) | 2.966(6) | 157(5) | inter |
| N(5)-H(5)•••O(2) | 0.84(6) | 2.23(5) | 2.776(5) | 123(5) | intra |
| N(5)-H(5)•••N(7)ii | 0.84(6) | 2.04(6) | 2.782(5) | 148(5) | inter |

i: 3/2-x,-1+y,1/2+z; ii: 3/2-x,y,-1/2+z.

**Table S9.** Selected bond lengths [Å] and angles [°] for compound **8**

| | | | |
|---|---|---|---|
| C(1)-N(2) | 1.319(3) | N(8)-C(3)-C(4) | 109.5(2) |
| C(1)-N(3) | 1.350(3) | N(8)-C(3)-N(9) | 119.1(2) |
| C(1)-N(4) | 1.352(3) | C(4)-C(3)-N(9) | 131.5(2) |
| C(2)-N(1) | 1.308(3) | N(6)-C(4)-C(3) | 106.3(2) |
| C(2)-N(3) | 1.362(3) | N(6)-C(4)-C(2) | 118.4(2) |
| C(2)-C(4) | 1.456(3) | C(3)-C(4)-C(2) | 135.3(2) |
| C(3)-N(8) | 1.345(3) | N(10)-C(5)-N(11) | 120.3(3) |
| C(3)-C(4) | 1.384(4) | N(10)-C(5)-N(12) | 119.9(2) |
| C(3)-N(9) | 1.429(3) | N(11)-C(5)-N(12) | 119.9(3) |
| C(4)-N(6) | 1.352(3) | C(2)-N(1)-N(2) | 103.8(2) |
| C(5)-N(10) | 1.317(3) | C(1)-N(2)-N(1) | 112.1(2) |
| C(5)-N(11) | 1.322(3) | C(1)-N(2)-H(2A) | 125.1(18) |
| C(5)-N(12) | 1.327(4) | N(1)-N(2)-H(2A) | 122.8(18) |
| N(1)-N(2) | 1.375(3) | C(1)-N(3)-C(2) | 107.3(2) |
| N(2)-H(2A) | 0.86(3) | C(1)-N(3)-H(3A | 122.6(19) |
| N(3)-H(3A) | 0.84(3) | C(2)-N(3)-H(3A | 130.0(19) |
| N(4)-N(5) | 1.338(3) | N(5)-N(4)-C(1) | 116.9(2) |
| N(5)-O(1) | 1.239(3) | O(1)-N(5)-O(2) | 122.7(2) |
| N(5)-O(2) | 1.245(3) | O(1)-N(5)-N(4) | 114.8(2) |
| N(6)-N(7) | 1.347(3) | O(2)-N(5)-N(4) | 122.5(2) |
| N(7)-N(8) | 1.326(3) | N(7)-N(6)-C(4) | 106.9(2) |
| N(9)-O(3) | 1.234(3) | N(8)-N(7)-N(6) | 111.6(2) |
| N(9)-O(4) | 1.237(3) | N(7)-N(8)-C(3) | 105.8(2) |
| N(10)-H(10A) | 0.879(16) | O(3)-N(9)-O(4) | 123.0(2) |
| N(10)-H(10B) | 0.881(17) | O(3)-N(9)-C(3) | 118.8(2) |
| N(11)-H(11A) | 0.865(17) | O(4)-N(9)-C(3) | 118.2(2) |
| N(11)-H(11B) | 0.883(17) | C(5)-N(10)-H(10A) | 118.5(19) |
| N(12)-H(12A) | 0.878(17) | C(5)-N(10)-H(10B) | 119.5(18) |
| N(12)-H(12B) | 0.878(17) | H(10A)-N(10)-H(10B) | 122(3) |
| N(2)-C(1)-N(3) | 105.7(2) | C(5)-N(11)-H(11A) | 120(2) |
| N(2)-C(1)-N(4) | 120.7(2) | C(5)-N(11)-H(11B) | 121.2(19) |
| N(3)-C(1)-N(4) | 133.7(3) | H(11A)-N(11)-H(11B) | 119(3) |

| | | | |
|---|---|---|---|
| N(1)-C(2)-N(3) | 111.1(2) | C(5)-N(12)-H(12A) | 119.9(19) |
| N(1)-C(2)-C(4) | 123.2(2) | C(5)-N(12)-H(12B) | 121.7(19) |
| N(3)-C(2)-C(4) | 125.7(2) | H(12A)-N(12)-H(12B) | 118(3) |

**Table S10.** Selected torsion angles [°] for compound **8**

| | | | |
|---|---|---|---|
| C2-N1-N2-C1 | -1.0(3) | N6-N7-N8-C3 | -0.7(3) |
| N2-N1-C2-N3 | 0.4(3) | N7-N8-C3-C4 | 0.3(3) |
| N2-N1-C2-C4 | -179.0(2) | N7-N8-C3-N9 | -179.7(2) |
| N1-N2-C1-N4 | 179.9(2) | O3-N9-C3-N8 | 174.0(2) |
| N1-N2-C1-N3 | 1.1(3) | O4-N9-C3-C4 | 174.4(3) |
| C2-N3-C1-N4 | -179.3(3) | O3-N9-C3-C4 | -6.0(4) |
| C1-N3-C2-C4 | 179.6(3) | O4-N9-C3-N8 | -5.7(4) |
| C2-N3-C1-N2 | -0.8(3) | N3-C2-C4-C3 | -1.1(5) |
| C1-N3-C2-N1 | 0.2(3) | N3-C2-C4-N6 | 177.3(3) |
| C1-N4-N5-O2 | -3.5(4) | N1-C2-C4-C3 | 178.2(3) |
| N5-N4-C1-N3 | 2.1(4) | N1-C2-C4-N6 | -3.5(4) |
| C1-N4-N5-O1 | 176.4(2) | N8-C3-C4-N6 | 0.2(3) |
| N5-N4-C1-N2 | -176.3(2) | N9-C3-C4-C2 | -1.4(5) |
| C4-N6-N7-N8 | 0.8(3) | N8-C3-C4-C2 | 178.7(3) |
| N7-N6-C4-C3 | -0.6(3) | N9-C3-C4-N6 | -179.9(3) |
| N7-N6-C4-C2 | -179.4(2) | | |

**Table S11.** Hydrogen bonds present in compound **8**

| D-H•••A | d(D-H)/ Å | d(H•••A)/ Å | d(D•••A)/ Å | <(DHA)/ ° | comment |
|---|---|---|---|---|---|
| N(2)-H(2A)•••N(4)$^{i}$ | 0.86(3) | 1.99(3) | 2.821(4) | 162(3) | inter |
| N(3)-H(3A)•••O(2) | 0.85(3) | 2.11(3) | 2.600(3) | 116(3) | intra |
| N(3)-H(3A)•••O(3) | 0.85(3) | 2.11(3) | 2.752(3) | 132(3) | intra |
| N(10)-H(10A)•••(7)$^{ii}$ | 0.88(3) | 2.08(3) | 2.943(4) | 164(3) | inter |
| N(10)-H(10B)•••N(6) | 0.88(3) | 2.08(3) | 2.959(3) | 174(2) | intra |
| N(11)-H(11A)•••O(1)$^{i}$ | 0.87(3) | 2.39(3) | 3.027(4) | 131(2) | inter |
| N(11)-H(11A)•••O(4)$^{iii}$ | 0.87(3) | 2.58(3) | 3.282(3) | 139(2) | inter |
| N(11)-H(11A)•••N(8)$^{iii}$ | 0.87(3) | 2.62(3) | 3.262(4) | 132(2) | inter |
| N(11)-H(11B)•••N(1) | 0.88(3) | 2.12(3) | 2.989(4) | 169(3) | intra |
| N(12)-H(12A)•••O(4)$^{iii}$ | 0.88(3) | 2.32(3) | 3.106(4) | 150(2) | inter |
| N(12)-H(12B)•••N(7)$^{ii}$ | 0.87(3) | 2.58(3) | 3.286(4) | 139(2) | inter |
| N(12)-H(12B)•••N(8)$^{ii}$ | 0.87(3) | 2.52(3) | 3.376(4) | 168(2) | inter |

i: -x,1-y,1-z; ii: 1-x,-y,1-z; iii: -1/2+x,1/2-y,-1/2+z.

**Table S12.** Selected bond lengths [Å] and angles [°] for compound **17**

| | | | |
|---|---|---|---|
| C(1)-N(3) | 1.341(7) | N(7)-C(3)-N(8) | 119.0(5) |
| C(1)-C(2) | 1.383(7) | N(6)-C(3)-N(8) | 131.3(5) |

| | | | |
|---|---|---|---|
| C(1)-N(4) | 1.441(7) | N(5)-C(4)-N(7) | 115.1(5) |
| C(2)-N(1) | 1.353(6) | N(5)-C(4)-C(2) | 120.2(5) |
| C(2)-C(4) | 1.467(8) | N(7)-C(4)-C(2) | 124.6(5) |
| C(3)-N(7) | 1.339(7) | N(11)-C(5)-N(12) | 121.0(5) |
| C(3)-N(6) | 1.338(7) | N(11)-C(5)-N(10) | 120.4(5) |
| C(3)-N(8) | 1.380(6) | N(12)-C(5)-N(10) | 118.7(5) |
| C(4)-N(5) | 1.314(7) | N(15)-C(6)-N(13) | 120.8(5) |
| C(4)-N(7) | 1.368(6) | N(15)-C(6)-N(14) | 120.0(5) |
| C(5)-N(11) | 1.310(7) | N(13)-C(6)-N(14) | 119.2(5) |
| C(5)-N(12) | 1.320(7) | C(2)-N(1)-N(2) | 107.8(5) |
| C(5)-N(10) | 1.329(7) | N(3)-N(2)-N(1) | 110.9(4) |
| C(6)-N(15) | 1.307(7) | N(2)-N(3)-C(1) | 105.1(4) |
| C(6)-N(13) | 1.315(7) | O(2)-N(4)-O(1) | 124.5(5) |
| C(6)-N(14) | 1.339(7) | O(2)-N(4)-C(1) | 117.5(5) |
| N(1)-N(2) | 1.355(6) | O(1)-N(4)-C(1) | 117.9(5) |
| N(2)-N(3) | 1.341(6) | C(4)-N(5)-N(6) | 102.4(4) |
| N(4)-O(2) | 1.217(6) | C(3)-N(6)-N(5) | 110.4(5) |
| N(4)-O(1) | 1.220(6) | C(3)-N(6)-H(6A) | 124(4) |
| N(5)-N(6) | 1.364(6) | N(5)-N(6)-H(6A) | 125(4) |
| N(6)-H(6A) | 0.86(6) | C(3)-N(7)-C(4) | 102.4(5) |
| N(8)-N(9) | 1.314(6) | N(9)-N(8)-C(3) | 116.1(5) |
| N(9)-O(4) | 1.258(6) | O(4)-N(9)-O(3) | 119.7(5) |
| N(9)-O(3) | 1.272(5) | O(4)-N(9)-N(8) | 124.2(5) |
| N(10)-H(10A) | 0.91(2) | O(3)-N(9)-N(8) | 116.0(5) |
| N(10)-H(10B) | 0.92(2) | C(5)-N(10)-H(10A) | 122(3) |
| N(11)-H(11A) | 0.90(2) | C(5)-N(10)-H(10B) | 116(3) |
| N(11)-H(11B) | 0.91(2) | H(10A)-N(10)-H(10B) | 119(4) |
| N(12)-H(12A) | 0.92(2) | C(5)-N(11)-H(11A) | 118(3) |
| N(12)-H(12B) | 0.90(2) | C(5)-N(11)-H(11B) | 118(3) |
| N(13)-H(13A) | 0.89(2) | H(11A)-N(11)-H(11B) | 121(4) |
| N(13)-H(13B) | 0.89(2) | C(5)-N(12)-H(12A) | 120(3) |
| N(14)-H(14A) | 0.90(2) | C(5)-N(12)-H(12B) | 121(3) |
| N(14)-H(14B) | 0.89(3) | H(12A)-N(12)-H(12B) | 119(4) |
| N(15)-H(15A) | 0.89(2) | C(6)-N(13)-H(13A) | 118(3) |
| N(15)-H(15B) | 0.89(2) | C(6)-N(13)-H(13B) | 117(3) |
| N(3)-C(1)-C(2) | 111.1(5) | H(13A)-N(13)-H(13B) | 123(4) |
| N(3)-C(1)-N(4) | 119.1(5) | C(6)-N(14)-H(14A) | 116(4) |
| C(2)-C(1)-N(4) | 129.8(5) | C(6)-N(14)-H(14B) | 116(3) |
| N(1)-C(2)-C(1) | 105.2(5) | H(14A)-N(14)-H(14B) | 123(4) |
| N(1)-C(2)-C(4) | 121.3(5) | C(6)-N(15)-H(15A) | 116(3) |
| C(1)-C(2)-C(4) | 133.5(5) | C(6)-N(15)-H(15B) | 118(3) |

| | | | |
|---|---|---|---|
| N(7)-C(3)-N(6) | 109.7(5) | H(15A)-N(15)-H(15B) | 125(4) |

**Table S13.** Selected torsion angles [°] for compound **17**

| | | | |
|---|---|---|---|
| C2-N1-N2-N3 | -0.1(6) | C4-N7-C3-N8 | -179.0(5) |
| N2-N1-C2-C4 | 177.2(5) | C3-N7-C4-N5 | 0.3(7) |
| N2-N1-C2-C1 | -0.6(6) | C3-N7-C4-C2 | 177.6(5) |
| N1-N2-N3-C1 | 0.8(6) | N9-N8-C3-N7 | 179.2(5) |
| N2-N3-C1-C2 | -1.2(6) | C3-N8-N9-O4 | 0.2(8) |
| N2-N3-C1-N4 | 176.5(5) | C3-N8-N9-O3 | 179.6(5) |
| O1-N4-C1-N3 | 20.7(8) | N9-N8-C3-N6 | 1.2(9) |
| O2-N4-C1-C2 | 19.5(9) | N3-C1-C2-N1 | 1.1(6) |
| O1-N4-C1-C2 | -162.1(6) | N3-C1-C2-C4 | -176.3(6) |
| O2-N4-C1-N3 | -157.7(5) | N4-C1-C2-N1 | -176.3(5) |
| N6-N5-C4-C2 | -177.3(5) | N4-C1-C2-C4 | 6.3(10) |
| C4-N5-N6-C3 | -0.4(6) | N1-C2-C4-N5 | 23.8(8) |
| N6-N5-C4-N7 | 0.1(7) | N1-C2-C4-N7 | -153.4(5) |
| N5-N6-C3-N7 | 0.6(7) | C1-C2-C4-N5 | -159.1(6) |
| N5-N6-C3-N8 | 178.8(6) | C1-C2-C4-N7 | 23.7(10) |
| C4-N7-C3-N6 | -0.5(6) | | |

**Table S14.** Hydrogen bonds present in compound **17**

| D-H···A | d(D-H)/ Å | d(H···A)/ Å | d(D···A)/ Å | <(DHA)/ ° | comment |
|---|---|---|---|---|---|
| N(6)-H(6A)···O(1)$^{i}$ | 0.86(6) | 2.50(6) | 3.149(7) | 134(4) | inter |
| N(6)-H(6A)···O(4) | 0.86(6) | 2.05(5) | 2.555(6) | 117(4)' | intra |
| N(10)-H(10A)···O(3) | 0.91(5) | 2.30(4) | 3.135(6) | 153(4) | intra |
| N(10)-H(10A)···O(4) | 0.91(5) | 2.29(4) | 3.096(6) | 147(4)' | intra |
| N(10)-H(10B)···O(3)$^{ii}$ | 0.92(3) | 2.10(4) | 2.929(6) | 150(4) | inter |
| N(11)-H(11A)···O(3)$^{iii}$ | 0.90(2) | 2.23(4) | 3.039(6) | 150(4) | inter |
| N(11)-H(11B)···N(8)$^{i}$ | 0.91(4) | 2.07(4) | 2.975(7) | 179(6) | inter |
| N(12)-H(12A)···N(7)$^{i}$ | 0.92(4) | 2.13(4) | 3.045(7) | 172(4) | inter |
| N(12)-H(12B)···O(2)$^{iv}$ | 0.90(4) | 2.42(5) | 3.058(6) | 128(3) | inter |
| N(12)-H(12B)···O(4) | 0.90(4) | 2.34(4) | 3.128(6) | 145(4)' | intra |
| N(13)-H(13A)···N(1) | 0.89(4) | 2.08(4) | 2.954(7) | 168(4) | intra |
| N(13)-H(13B)···N(2)$^{v}$ | 0.89(3) | 2.44(4) | 3.221(7) | 147(5) | inter |
| N(14)-H(14A)···N(2)$^{v}$ | 0.90(4) | 2.13(4) | 2.997(7) | 163(4) | inter |
| N(14)-H(14B)···N(3)$^{i}$ | 0.89(5) | 2.52(5) | 3.294(7) | 146(4) | inter |
| N(15)-H(15A)···O(1)$^{i}$ | 0.89(4) | 2.23(5) | 2.837(7) | 125(4) | inter |
| N(15)-H(15A)···N(3)$^{i}$ | 0.89(4) | 2.28(4) | 3.134(7) | 161(4)' | inter |
| N(15)-H(15B)···N(5) | 0.89(4) | 2.00(4) | 2.858(7) | 161(4) | intra |

i: x,-1+y,-1+z; ii: 3/2-x,y,-1/2+z; iii: 3/2-x,-1+y,-1/2+z; iv: x,y,-1+z; v: 2-x,2-y,-1/2+z.

## 4. $^{1}H$ and $^{13}C$ NMR spectra of the title compounds:

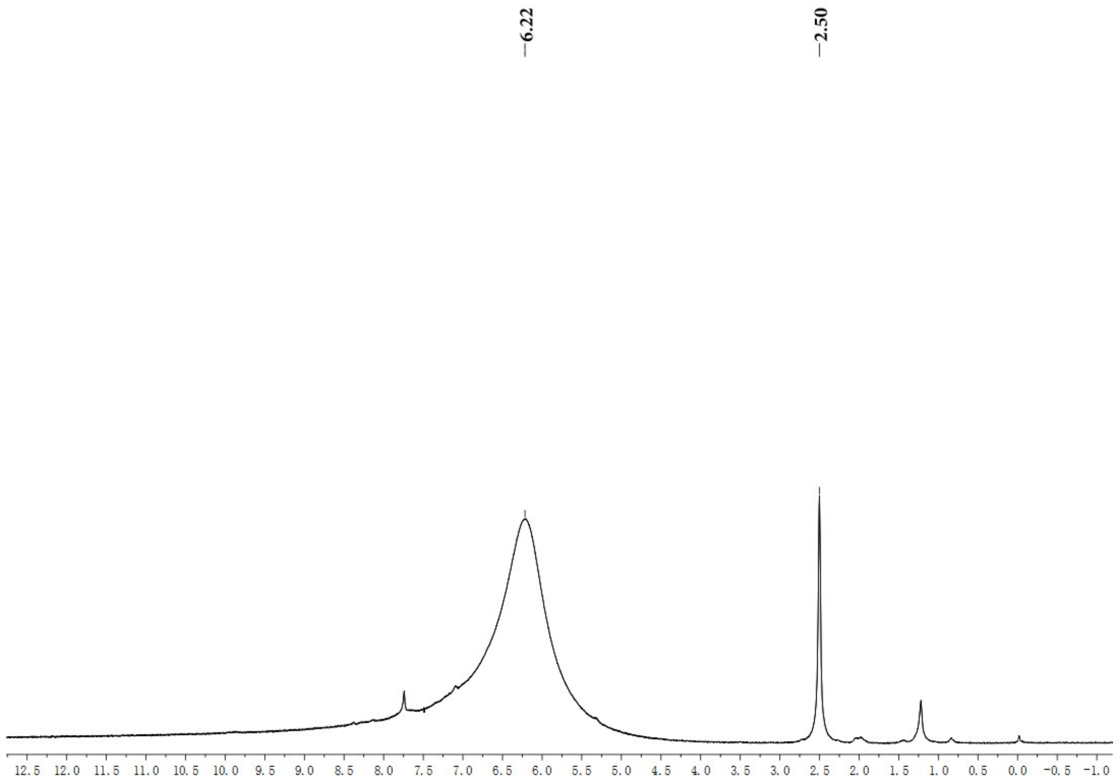


**Figure S1** $^{1}H$ NMR spectra (300 MHz) of **1** in DMSO-$d_6$ at 25 °C

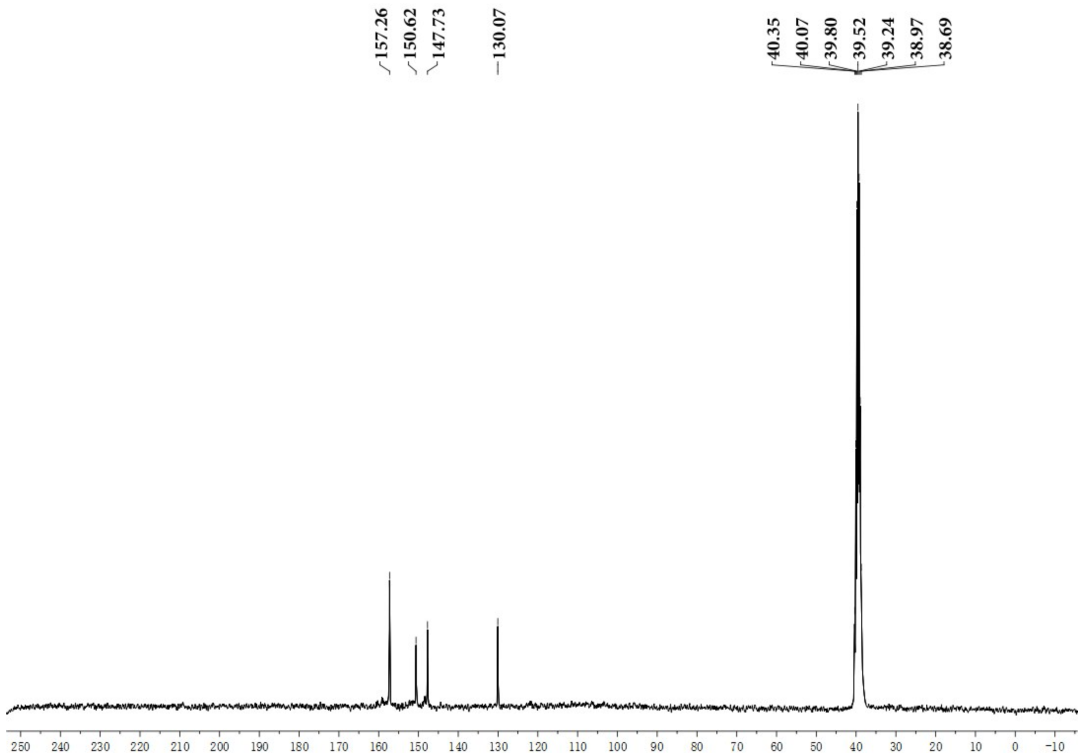


**Figure S2** $^{13}C$ NMR specta (75 MHz) of **1** in DMSO-$d_6$ at 25 °C

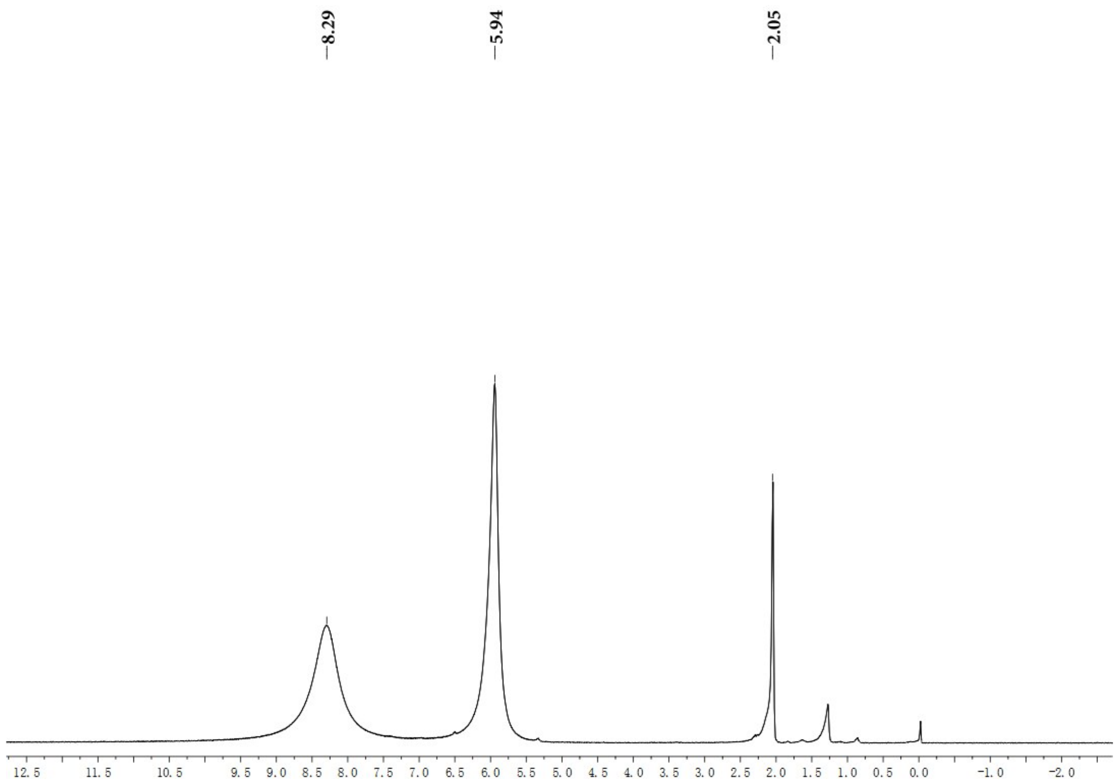


**Figure S3** [1]H NMR spectra (300 MHz) of **2** in acetone-$d_6$ at 25 °C

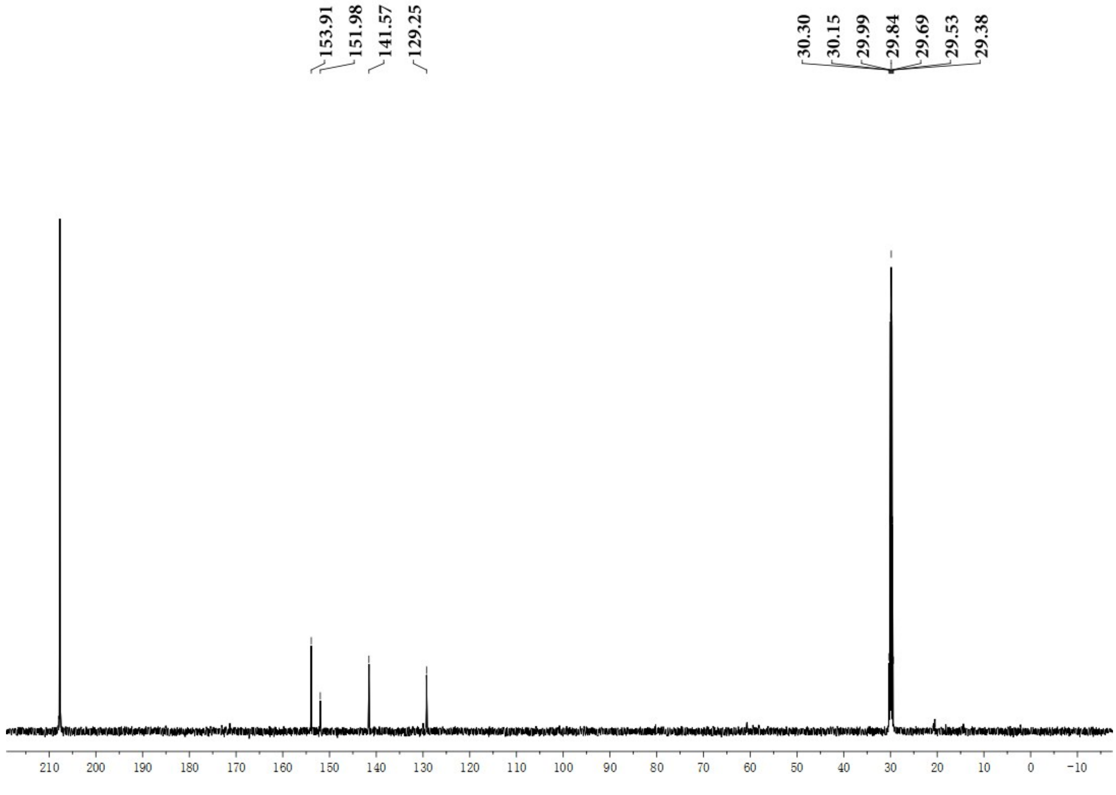


**Figure S4** [13]C NMR specta (75 MHz) of **2** in acetone-$d_6$ at 25 °C

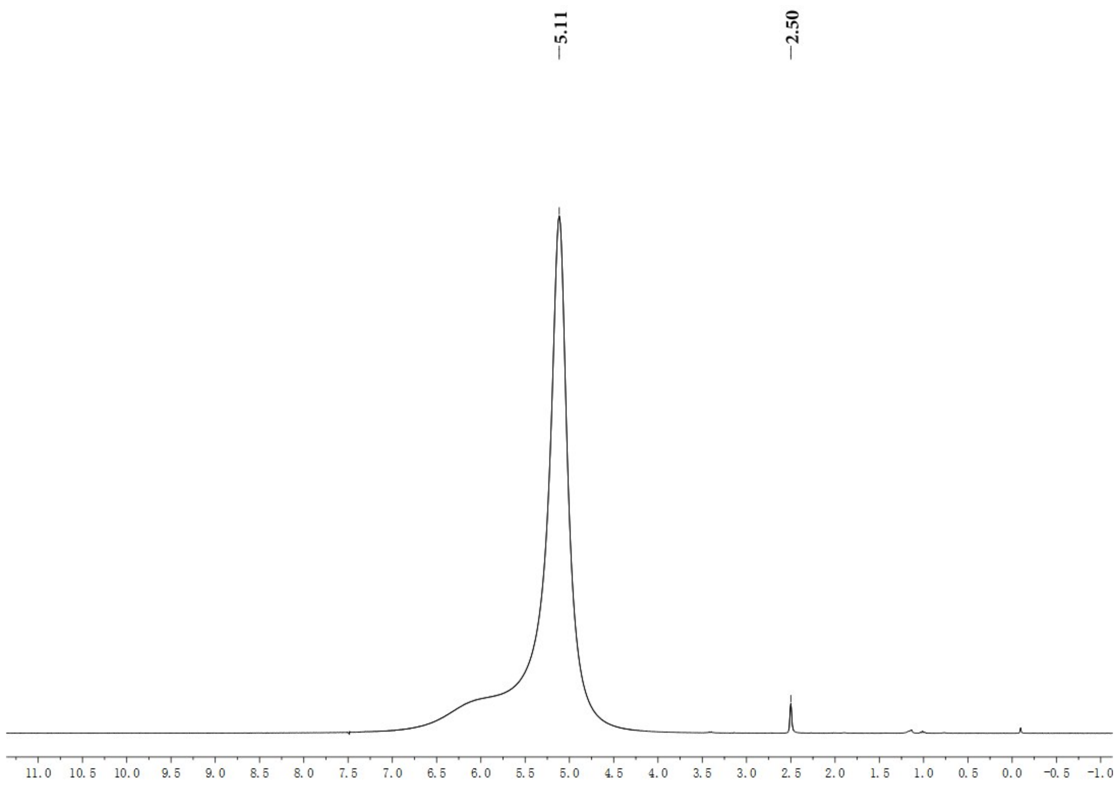


**Figure S5** $^{1}H$ NMR spectra (300 MHz) of **1** in DMSO-$d_6$ at 25 °C

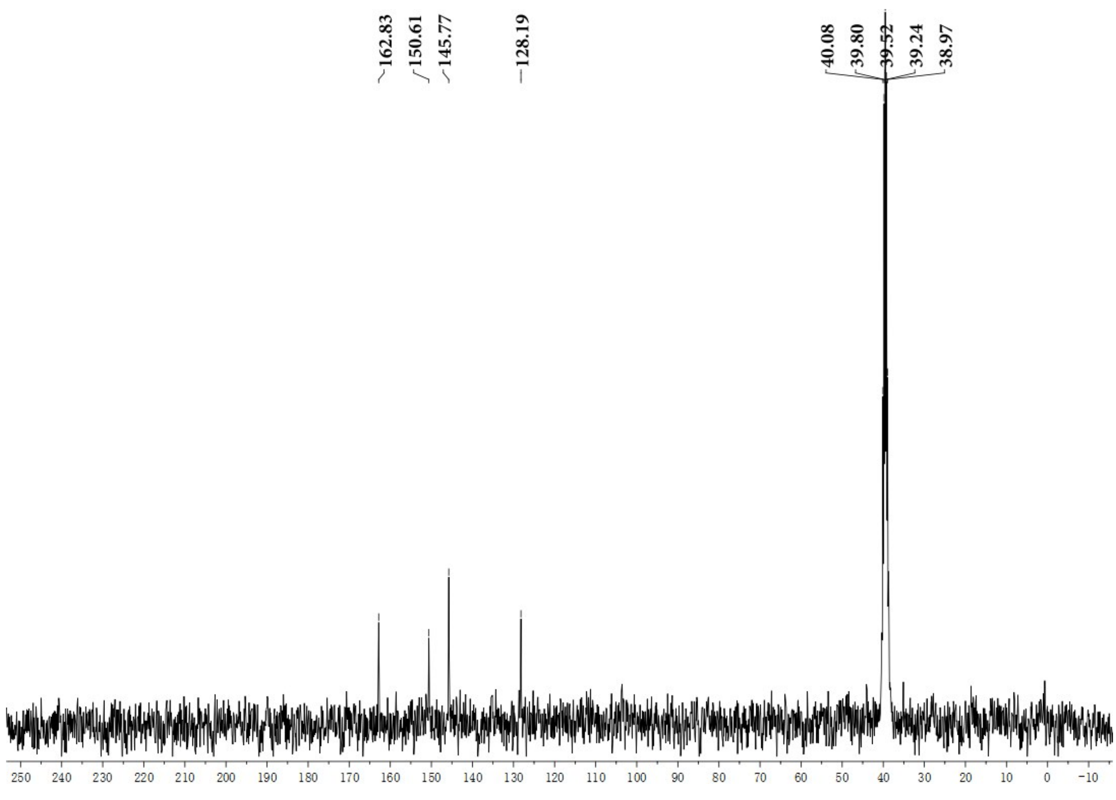


**Figure S6** $^{13}C$ NMR specta (75 MHz) of **3** in DMSO-$d_6$ at 25 °C

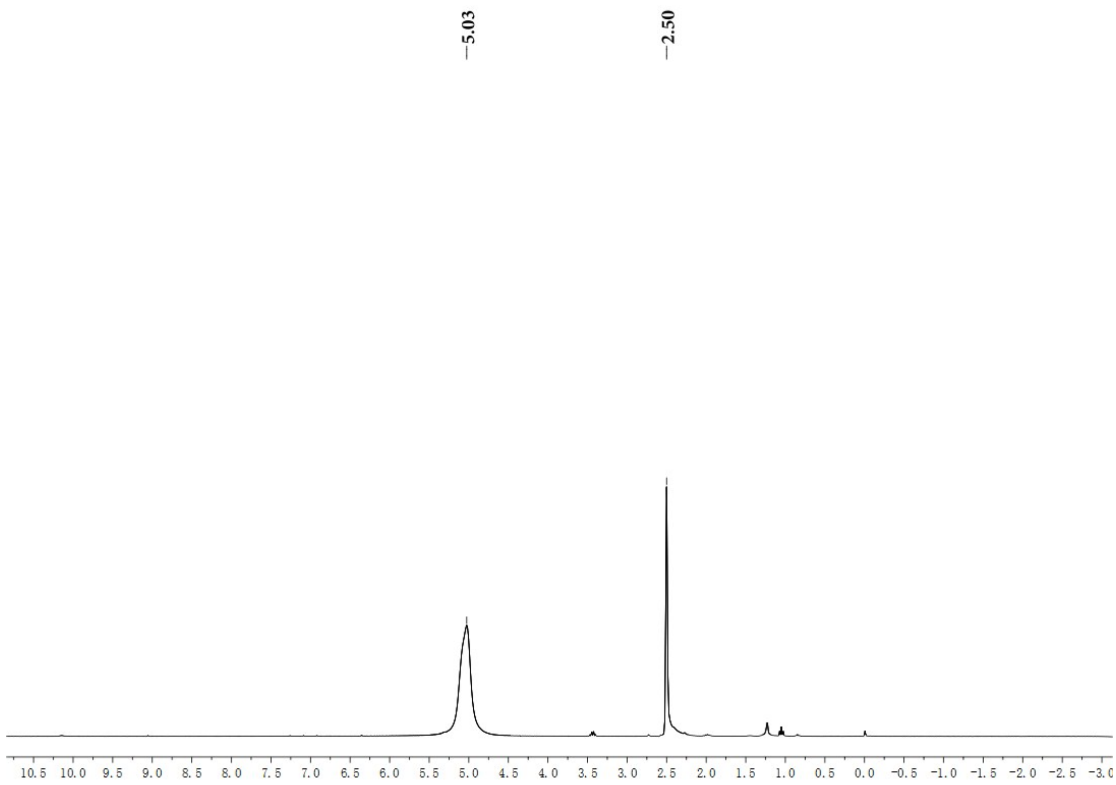


**Figure S7** $^{1}$H NMR spectra (300 MHz) of **4** in DMSO-$d_6$ at 25 °C

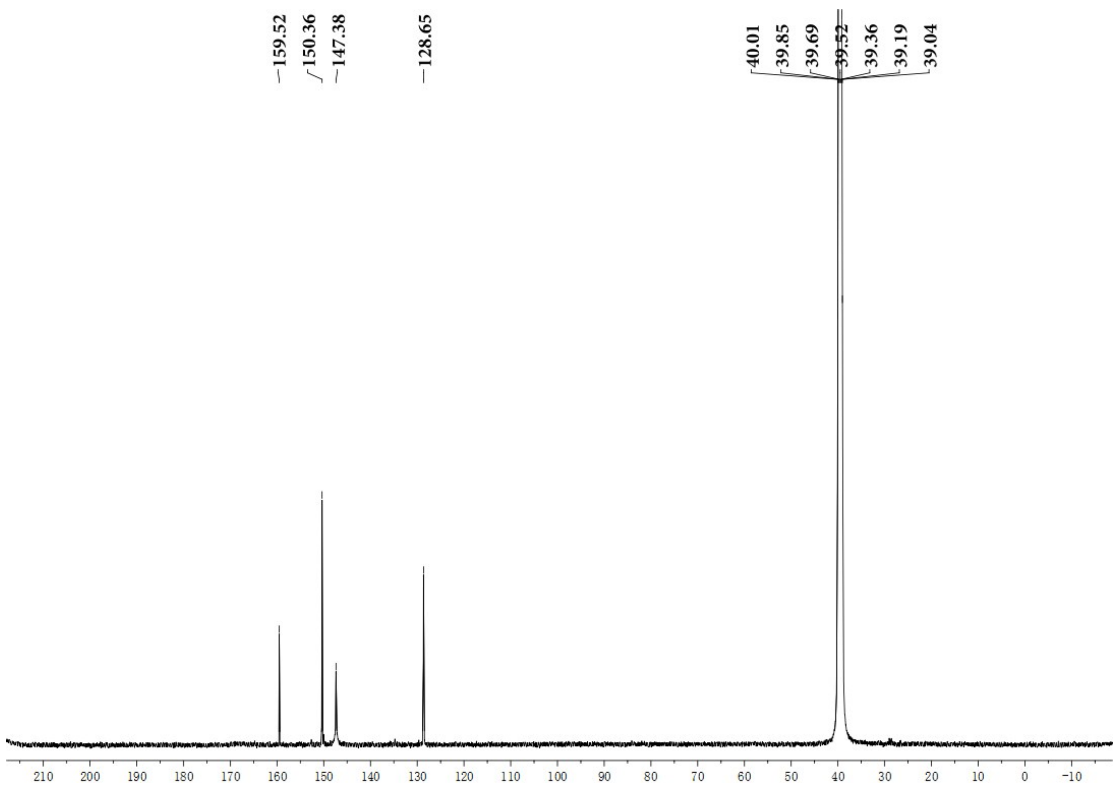


**Figure S8** $^{13}$C NMR specta (75 MHz) of **4** in DMSO-$d_6$ at 25 °C

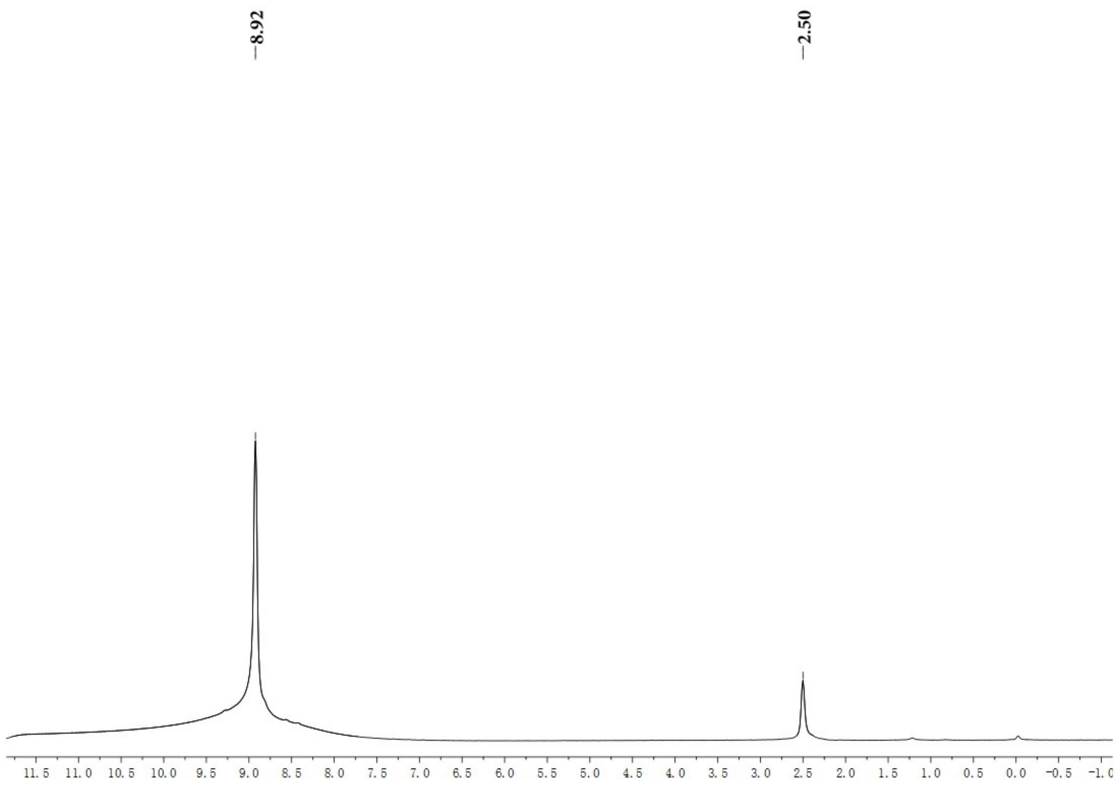


**Figure S9** [1]H NMR spectra (300 MHz) of **5** in DMSO-$d_6$ at 25 °C

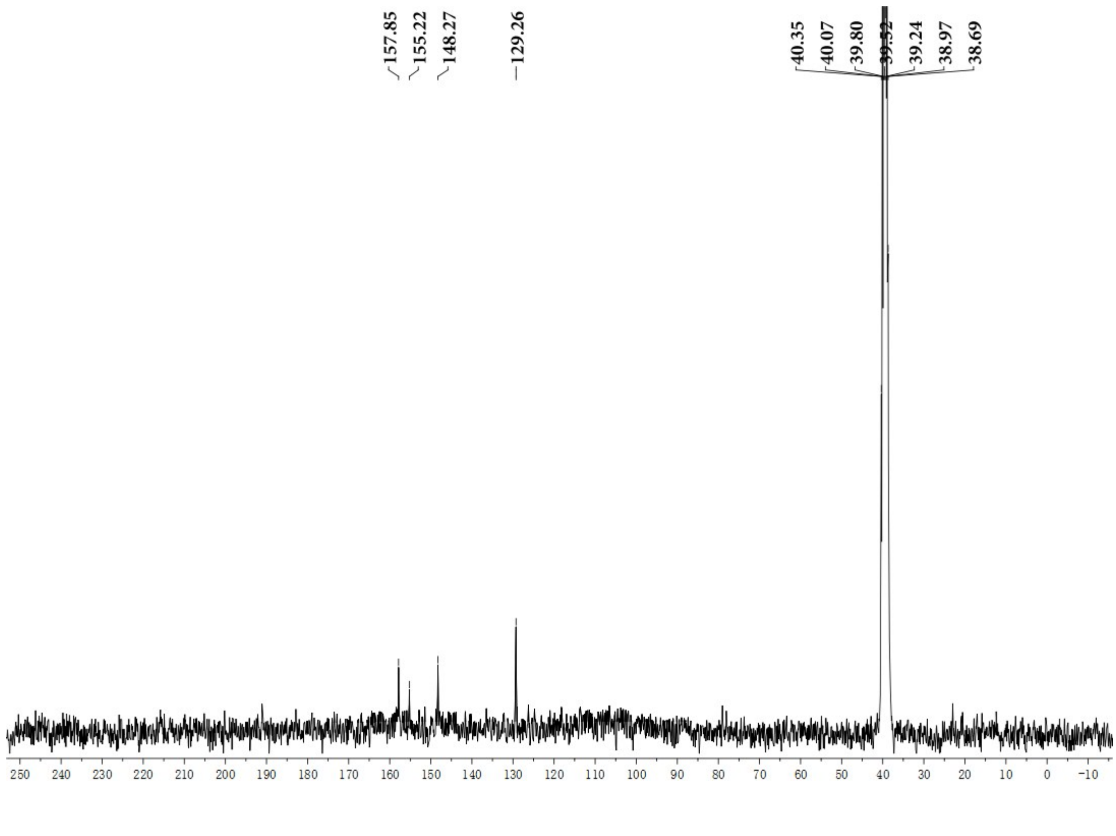


**Figure S10** [13]C NMR specta (75 MHz) of **5** in DMSO-$d_6$ at 25 °C

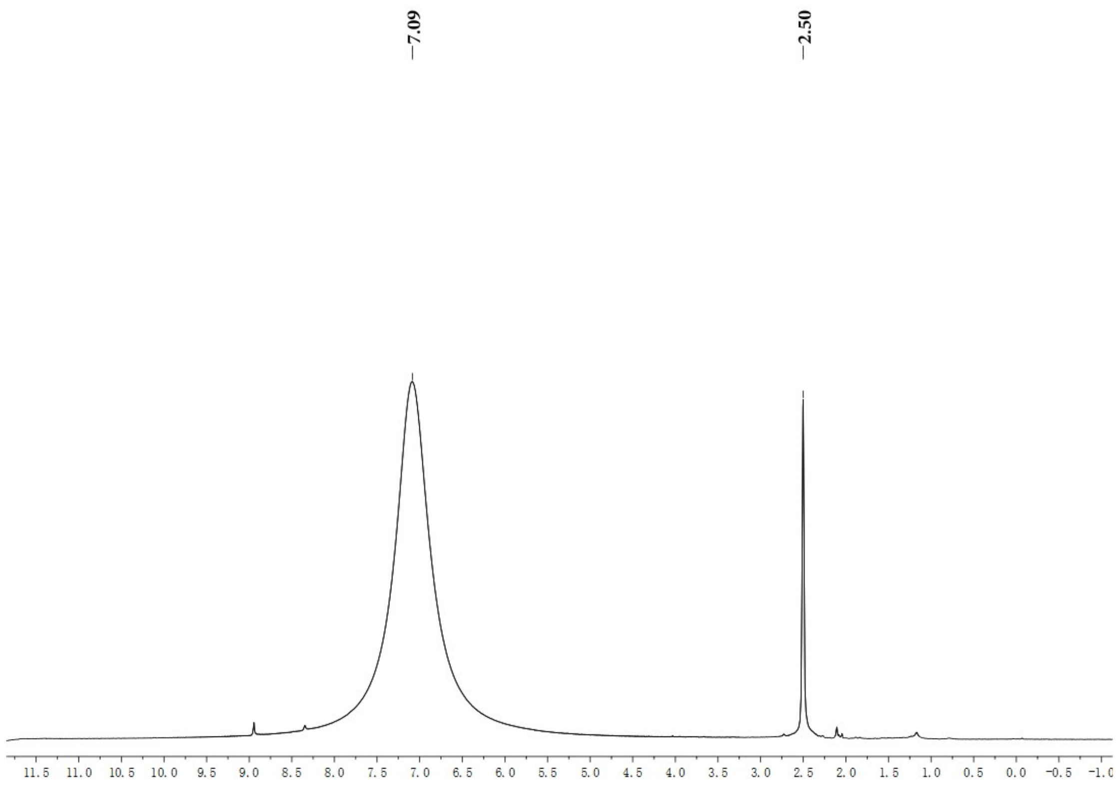


**Figure S11** $^{1}$H NMR spectra (300 MHz) of **6** in DMSO-$d_6$ at 25 °C

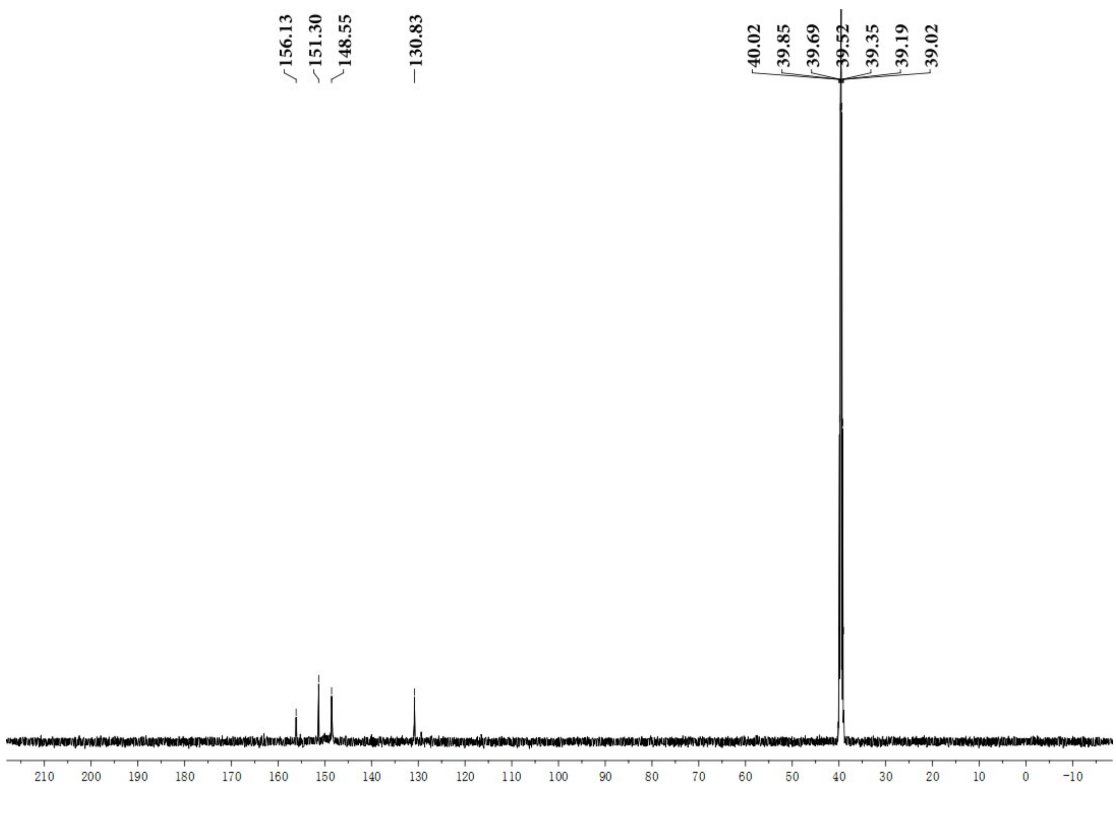


**Figure S12** $^{13}$C NMR specta (75 MHz) of **6** in DMSO-$d_6$ at 25 °C

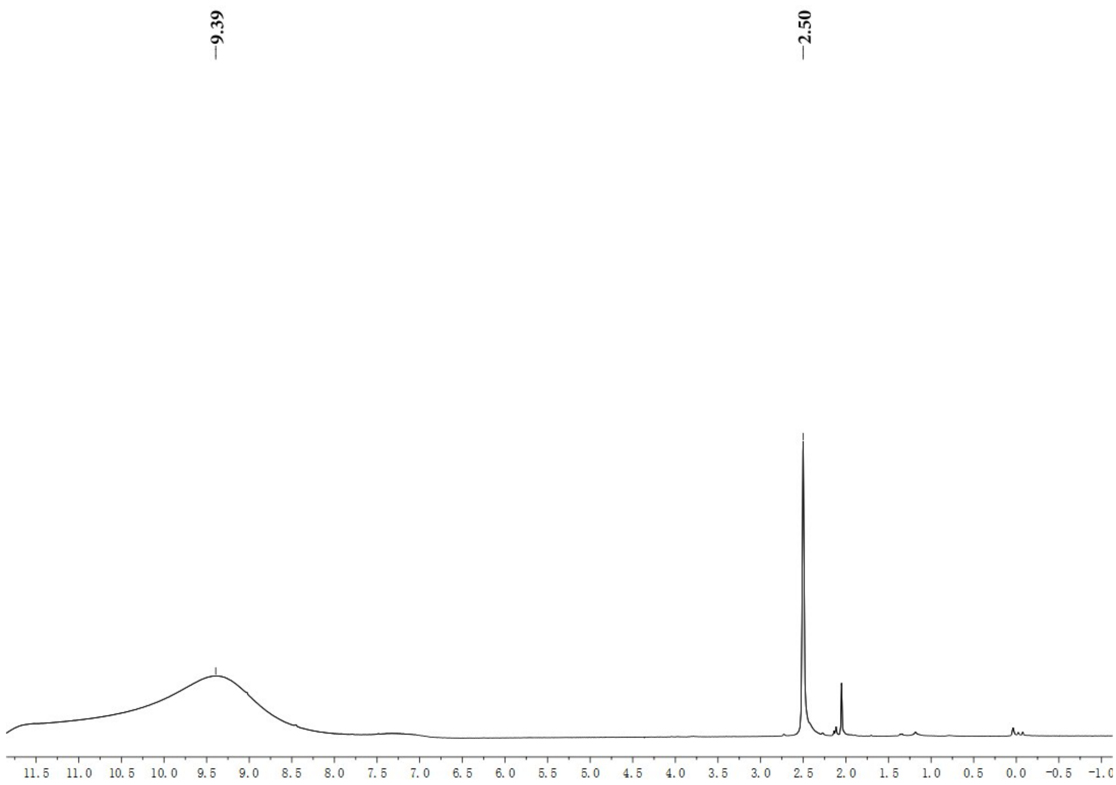


**Figure S13** $^{1}H$ NMR spectra (300 MHz) of **7** in DMSO-$d_6$ at 25 °C

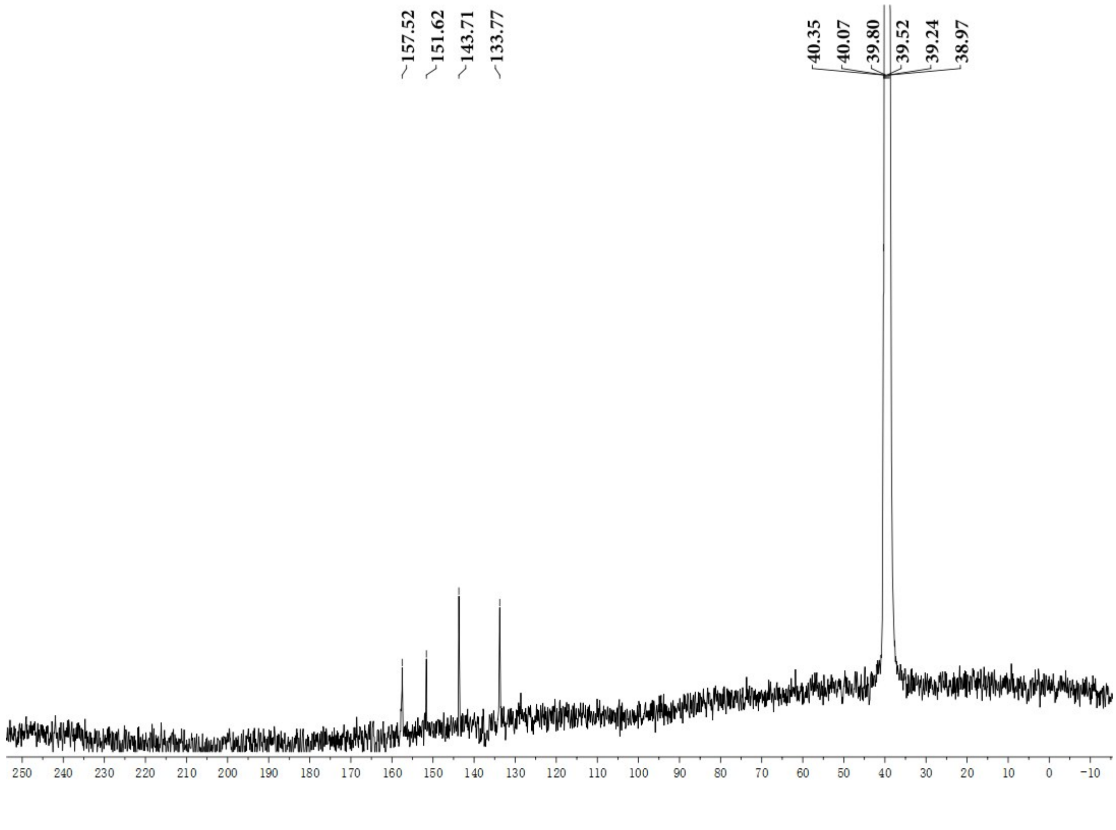


**Figure S14** $^{13}C$ NMR specta (75 MHz) of **7** in DMSO-$d_6$ at 25 °C

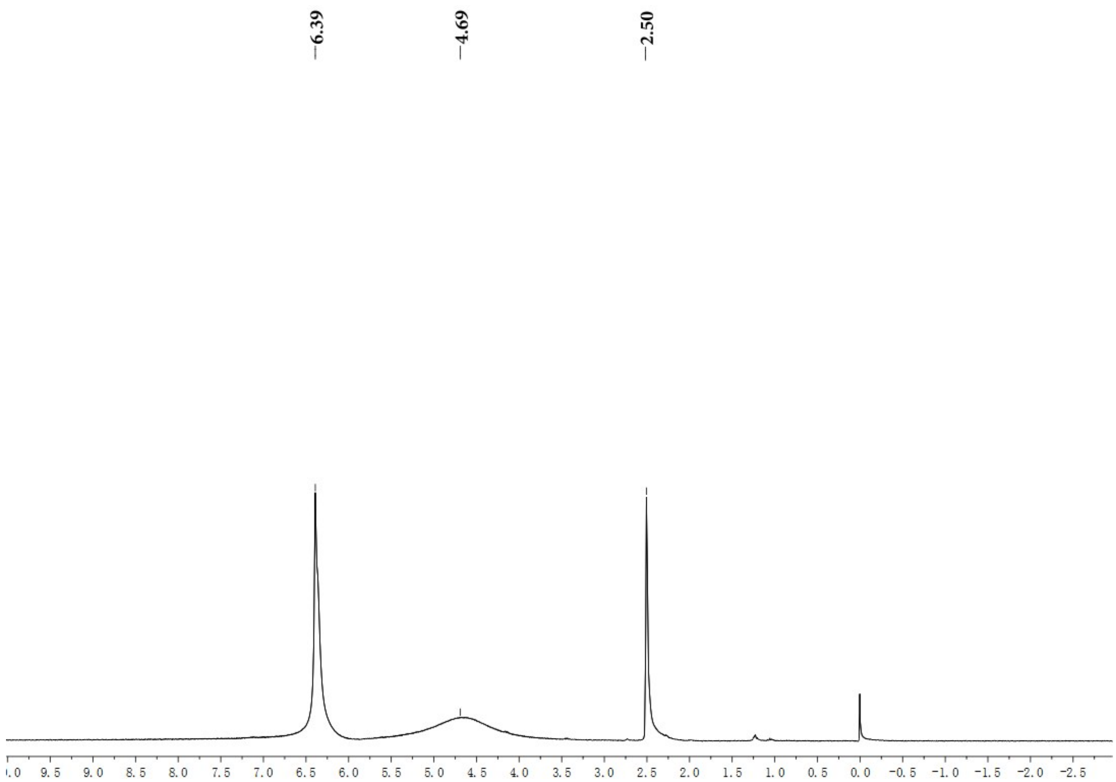


**Figure S15** $^{1}H$ NMR spectra (300 MHz) of **8** in DMSO-$d_6$ at 25 °C

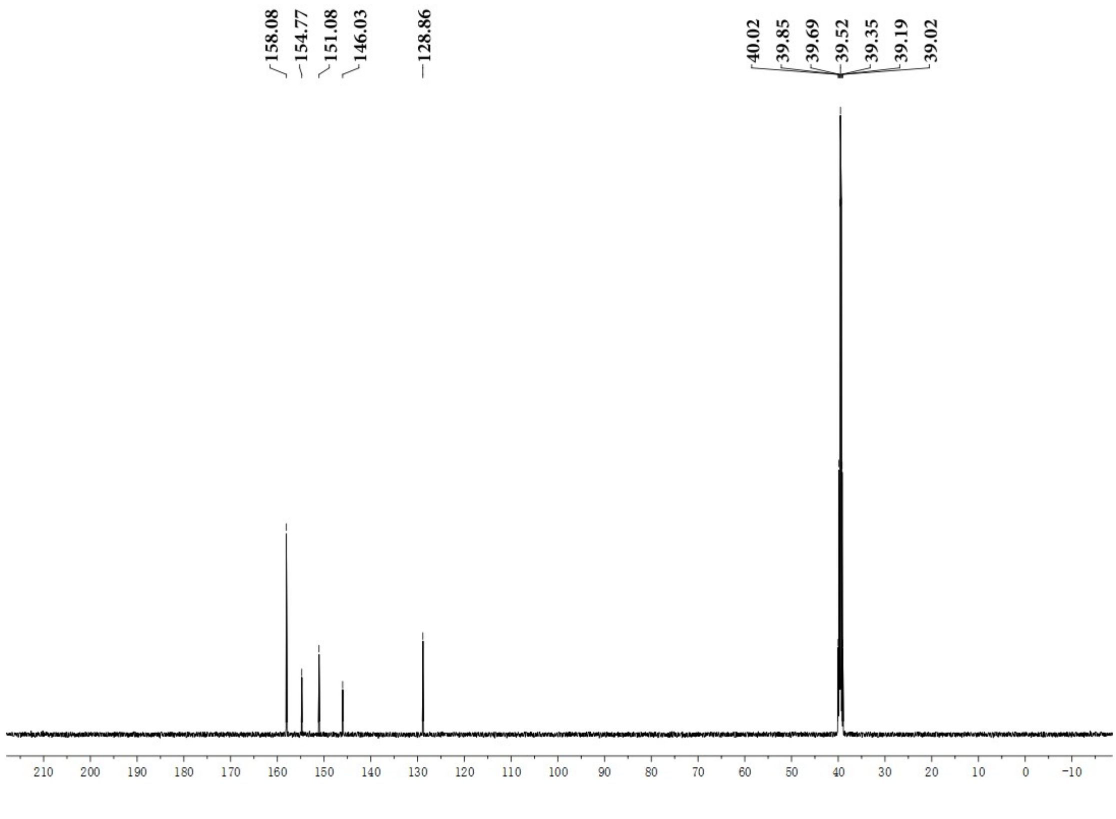


**Figure S16** $^{13}C$ NMR specta (75 MHz) of **8** in DMSO-$d_6$ at 25 °C

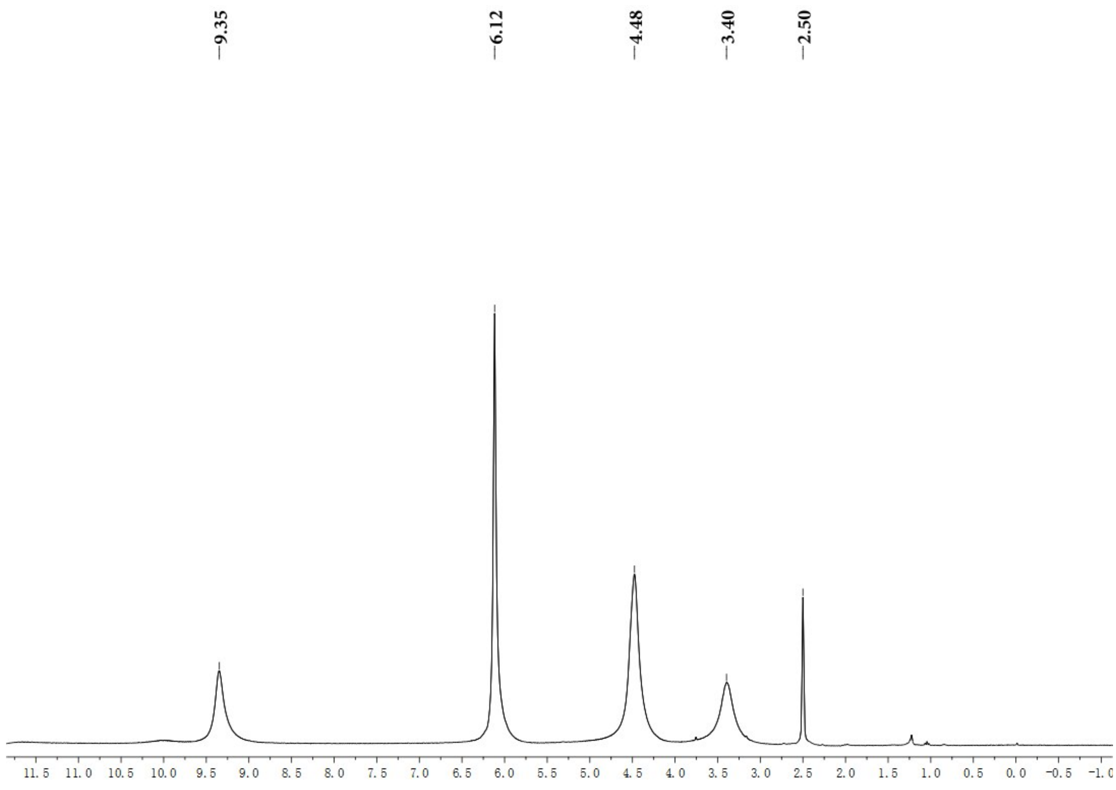


**Figure S17** $^{1}H$ NMR spectra (300 MHz) of **9** in DMSO-$d_6$ at 25 °C

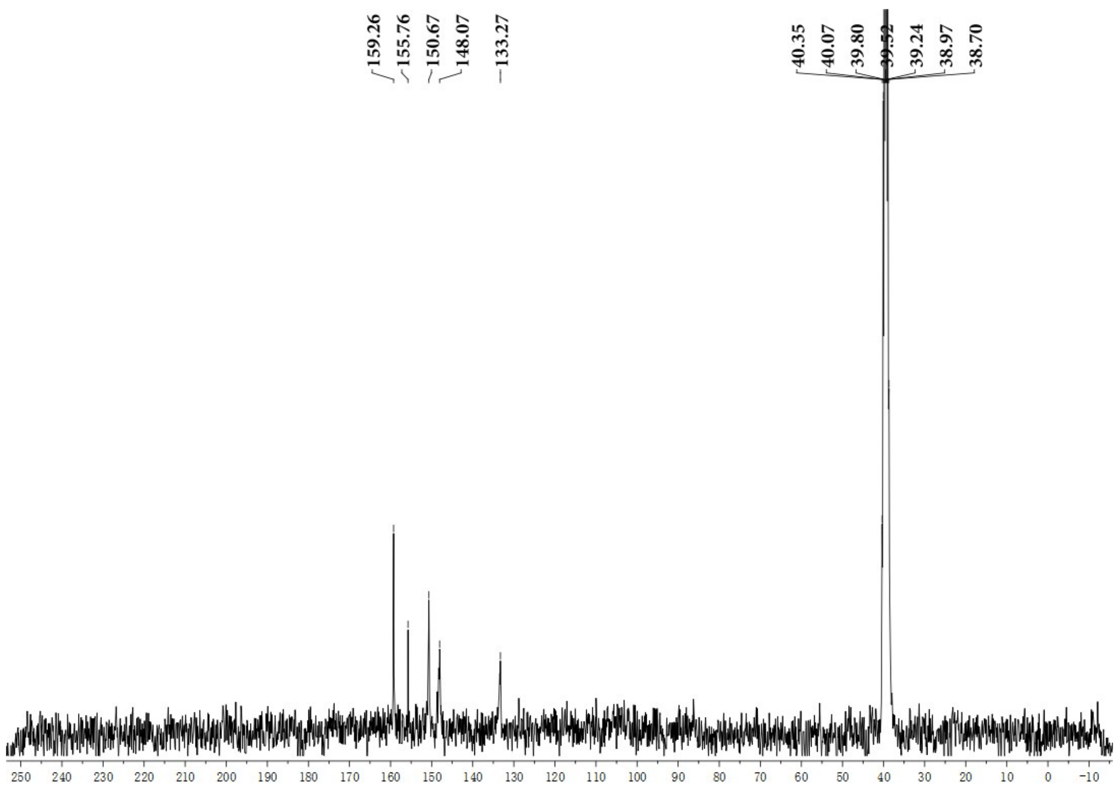


**Figure S18** $^{13}C$ NMR specta (75 MHz) of **9** in DMSO-$d_6$ at 25 °C

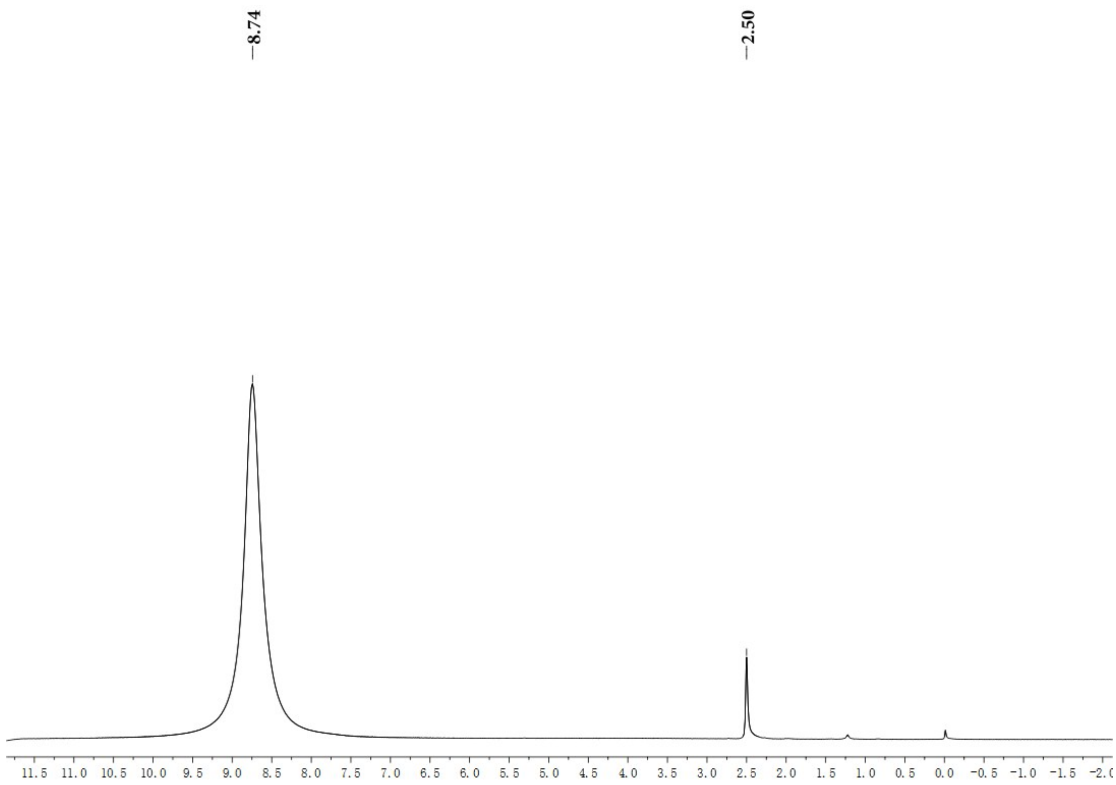


**Figure S19** $^{1}H$ NMR spectra (300 MHz) of **10** in DMSO-$d_6$ at 25 °C

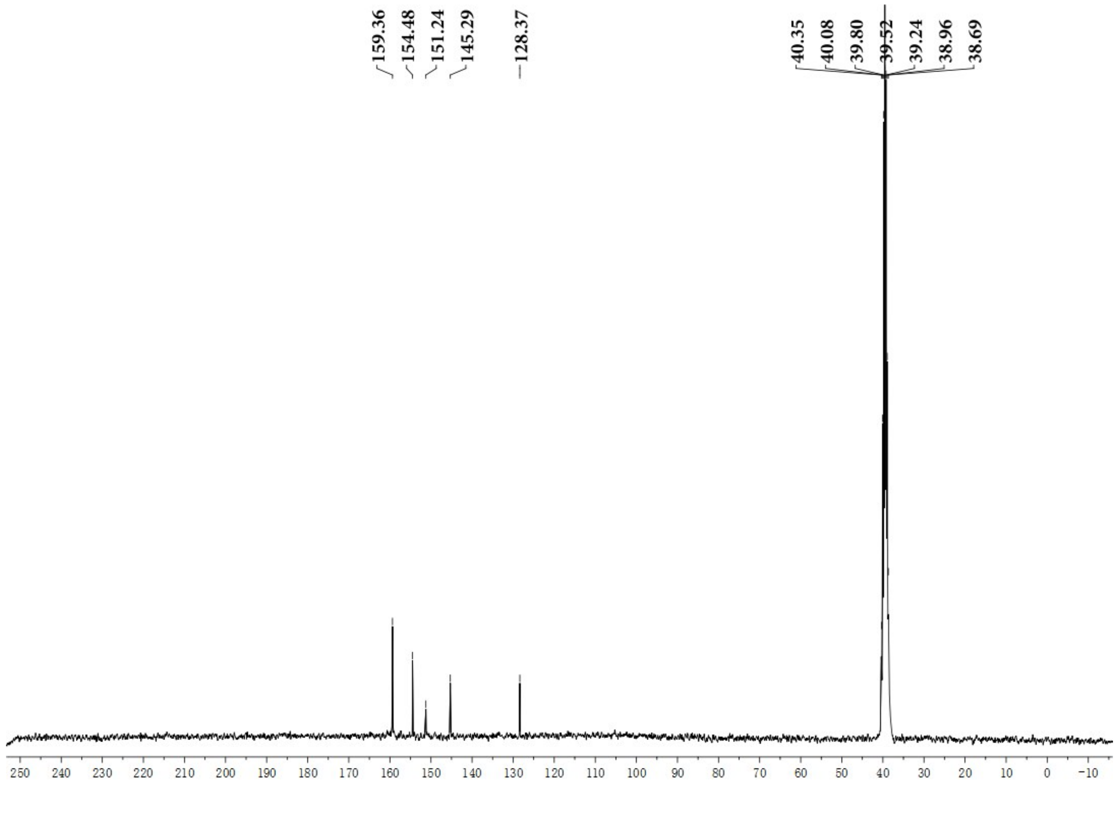


**Figure S20** $^{13}C$ NMR specta (75 MHz) of **10** in DMSO-$d_6$ at 25 °C

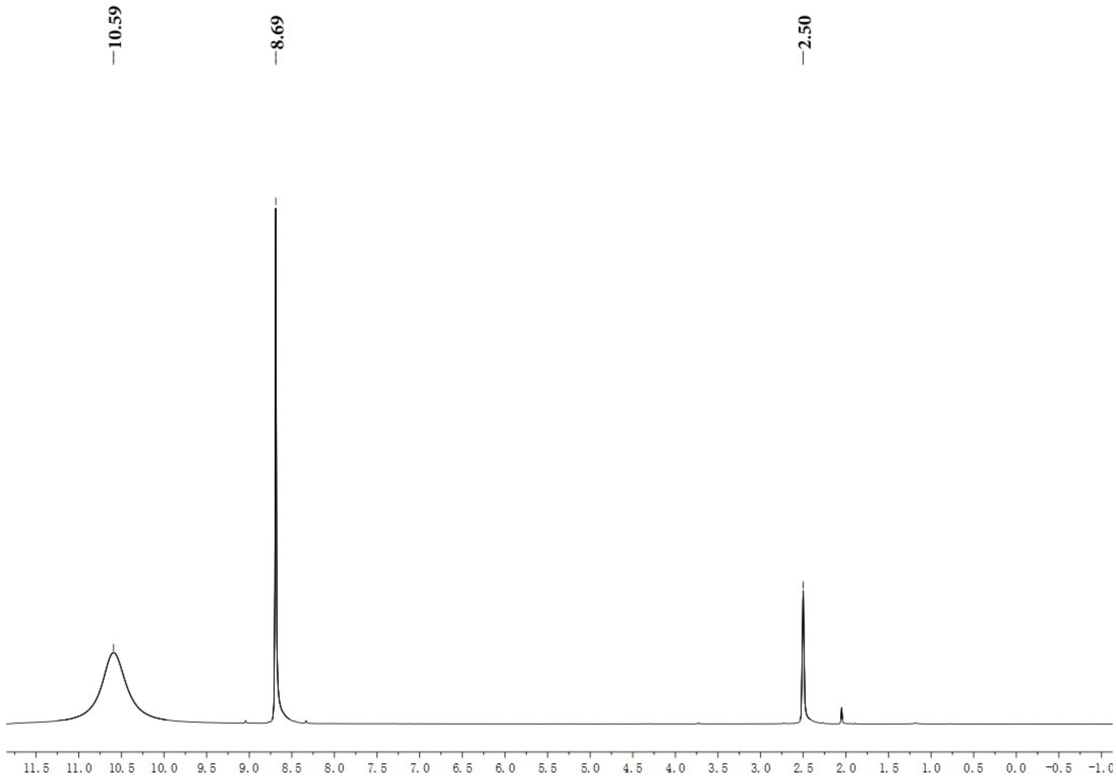


**Figure S21** $^{1}$H NMR spectra (300 MHz) of **11** in DMSO-$d_6$ at 25 °C

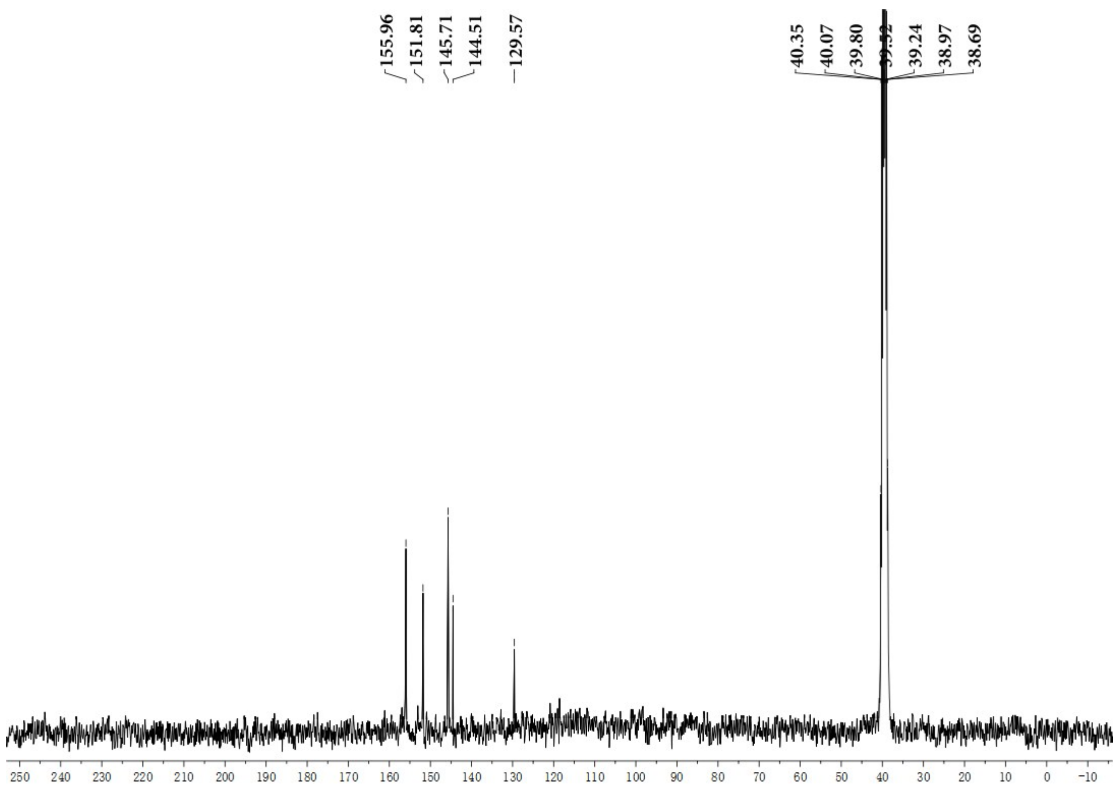


**Figure S22** $^{13}$C NMR specta (75 MHz) of **11** in DMSO-$d_6$ at 25 °C

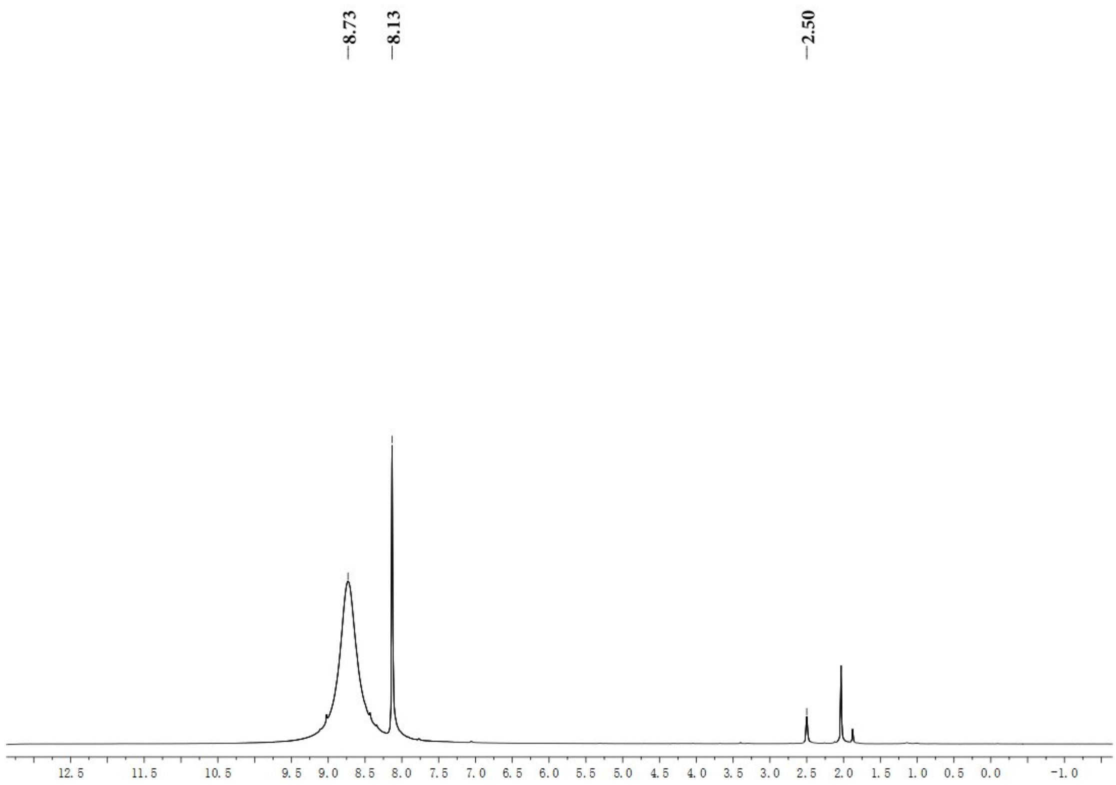


**Figure S23** $^{1}H$ NMR spectra (300 MHz) of **12** in DMSO-$d_6$ at 25 °C

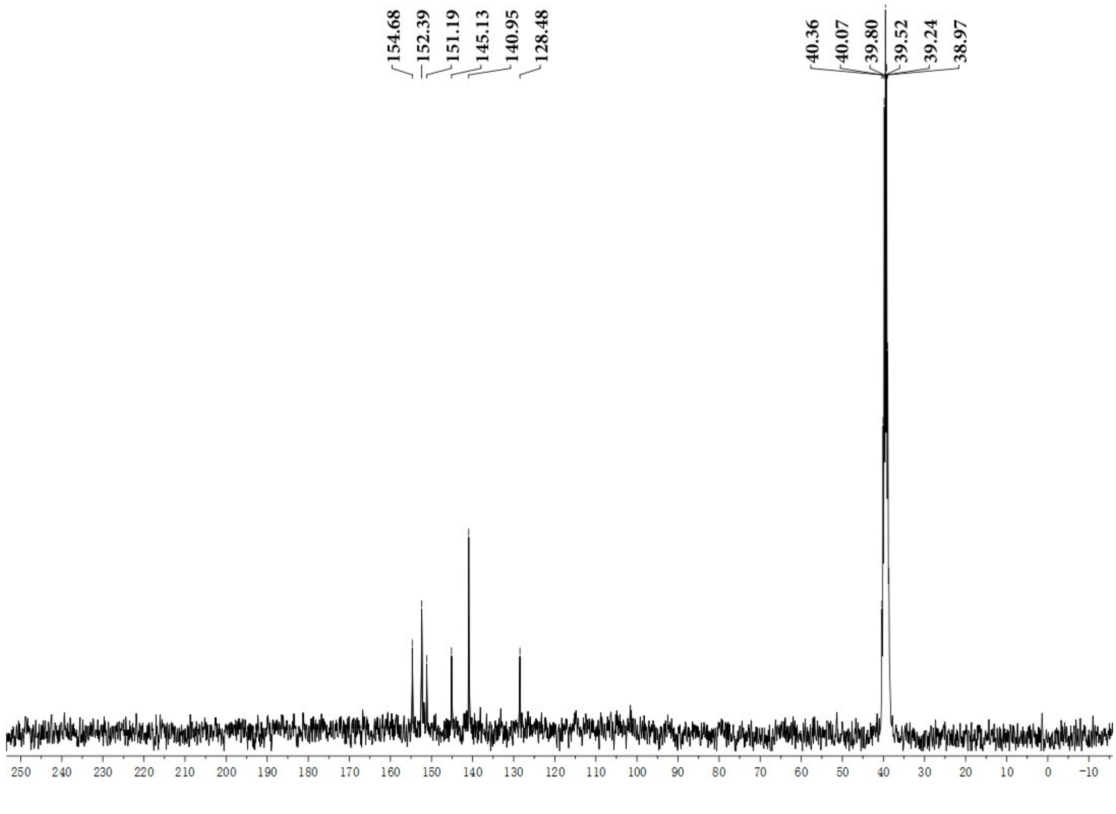


**Figure S24** $^{13}C$ NMR specta (75 MHz) of **12** in DMSO-$d_6$ at 25 °C

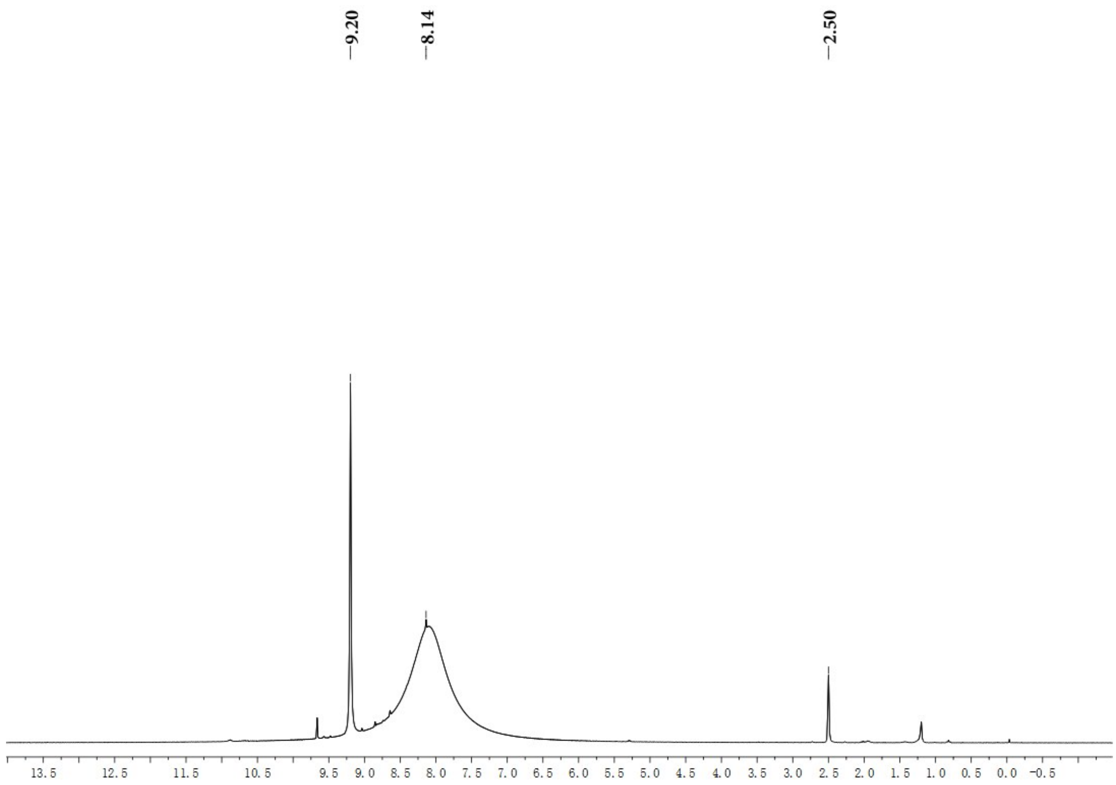


**Figure S25** ¹H NMR spectra (300 MHz) of **13** in DMSO-$d_6$ at 25 °C

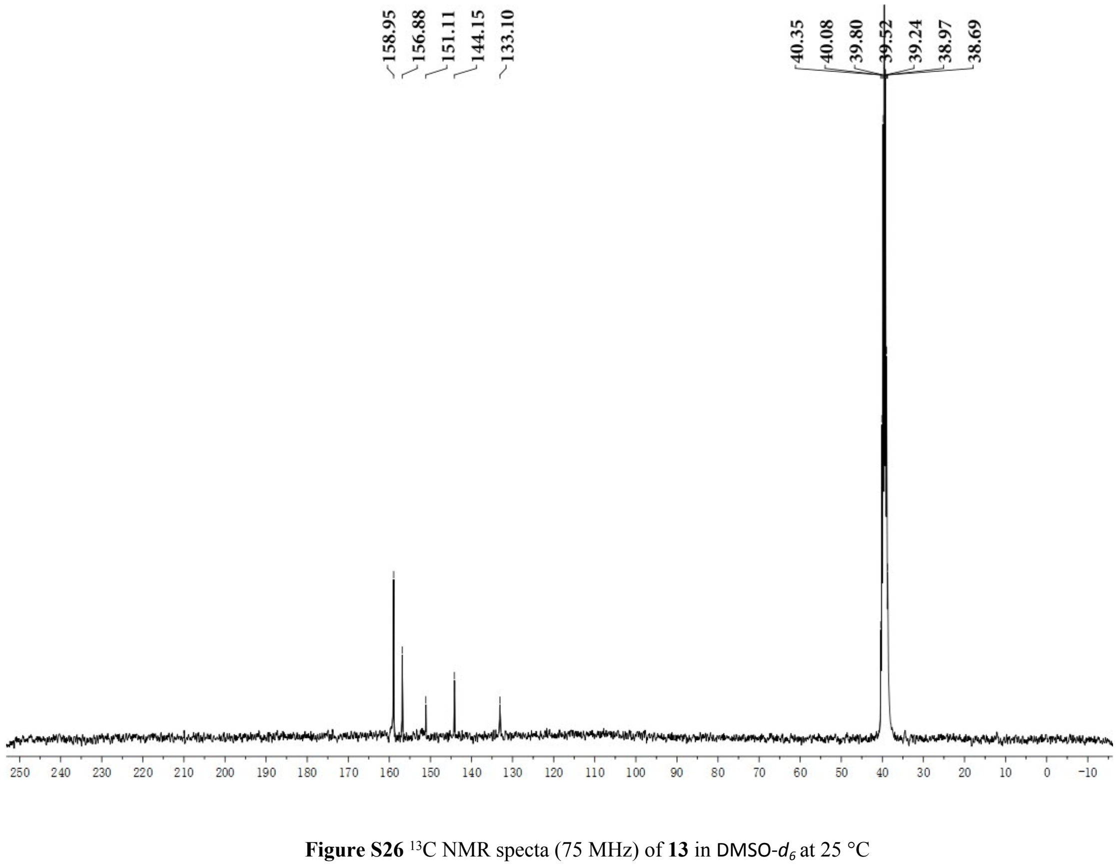


**Figure S26** ¹³C NMR specta (75 MHz) of **13** in DMSO-$d_6$ at 25 °C

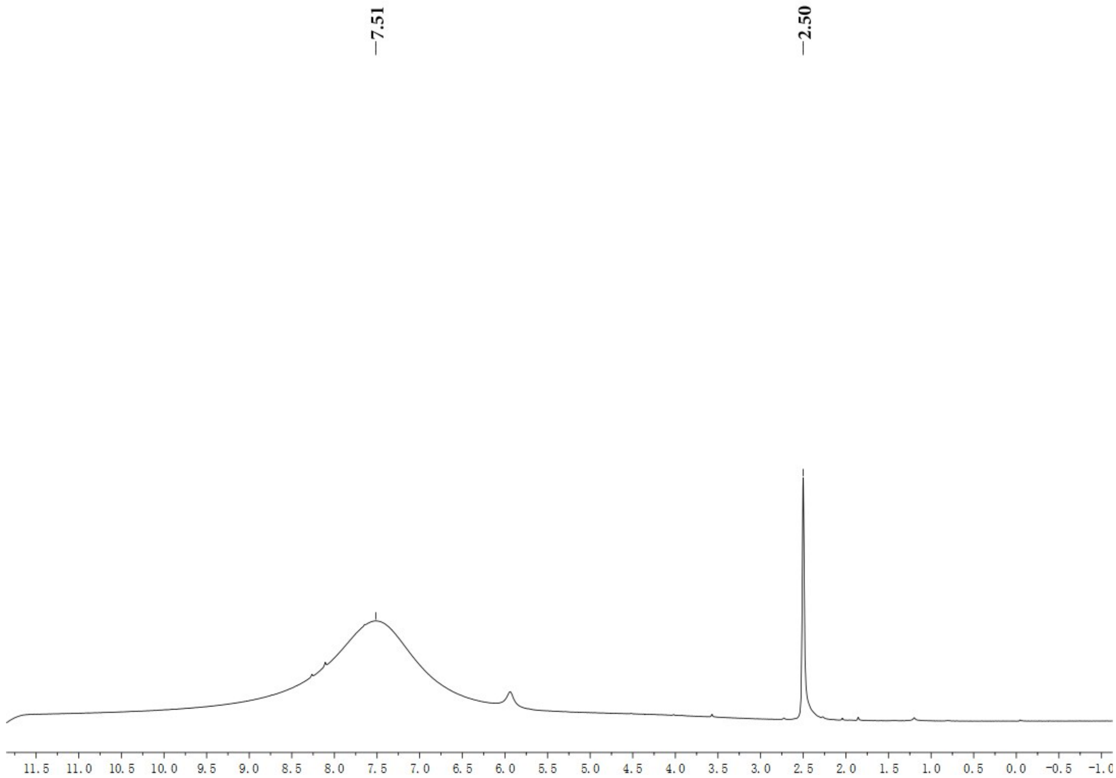


**Figure S27** $^{1}H$ NMR spectra (300 MHz) of **14** in DMSO-$d_6$ at 25 °C

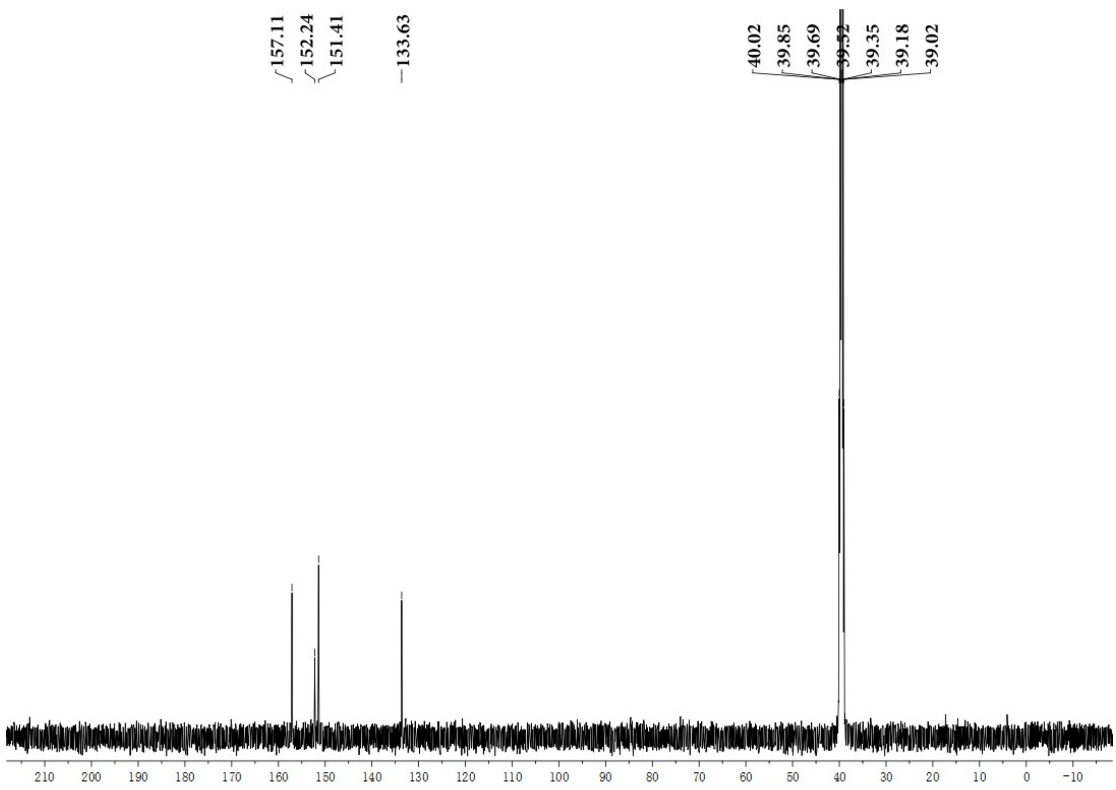


**Figure S28** $^{13}C$ NMR specta (75 MHz) of **14** in DMSO-$d_6$ at 25 °C

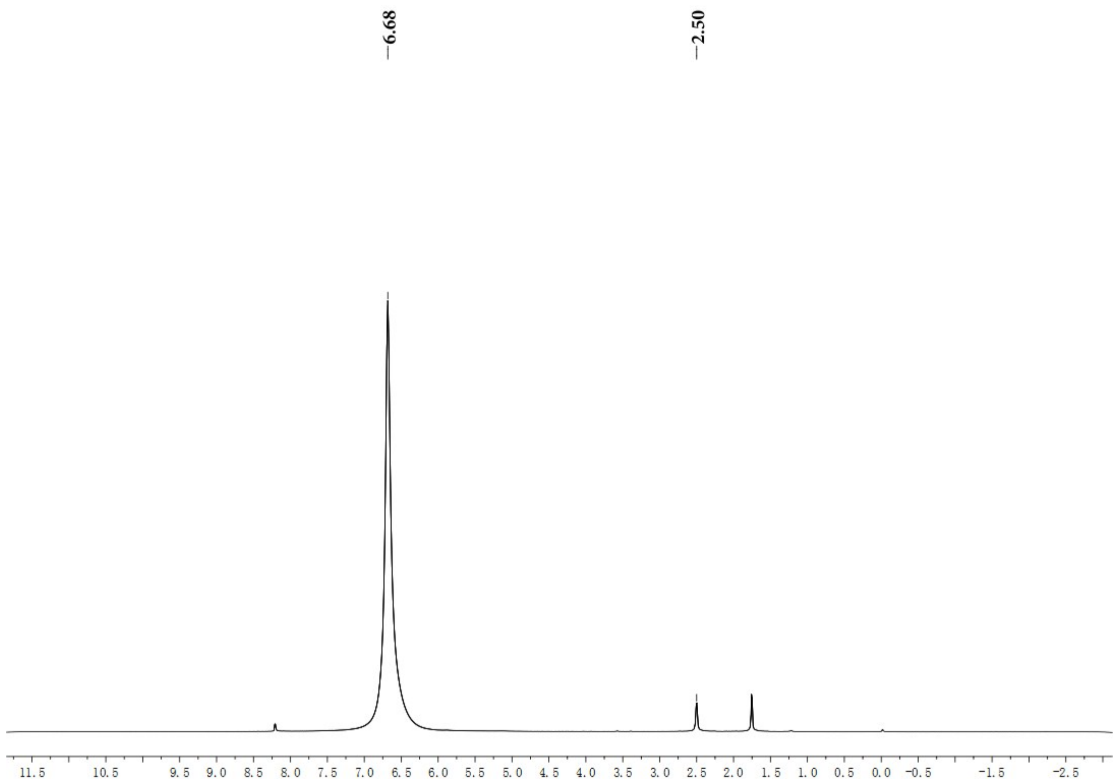


**Figure S29** [1]H NMR spectra (300 MHz) of **15** in DMSO-$d_6$ at 25 °C

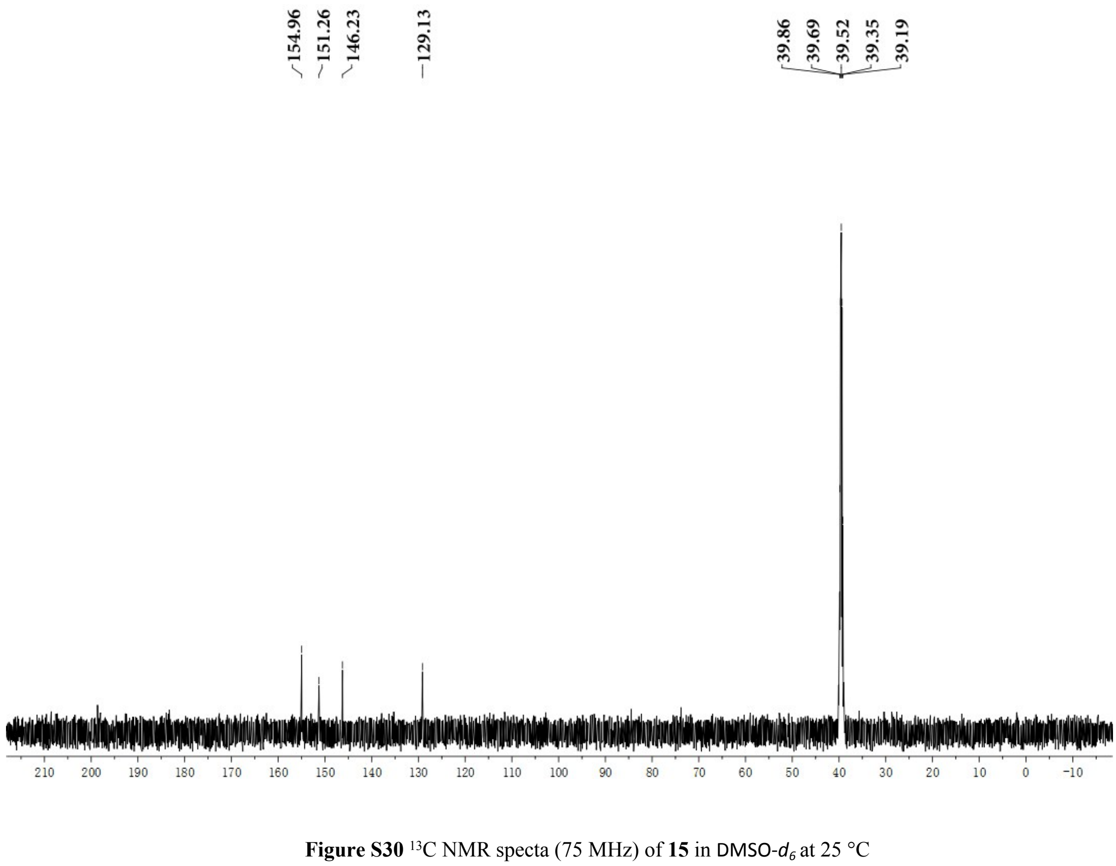


**Figure S30** [13]C NMR specta (75 MHz) of **15** in DMSO-$d_6$ at 25 °C

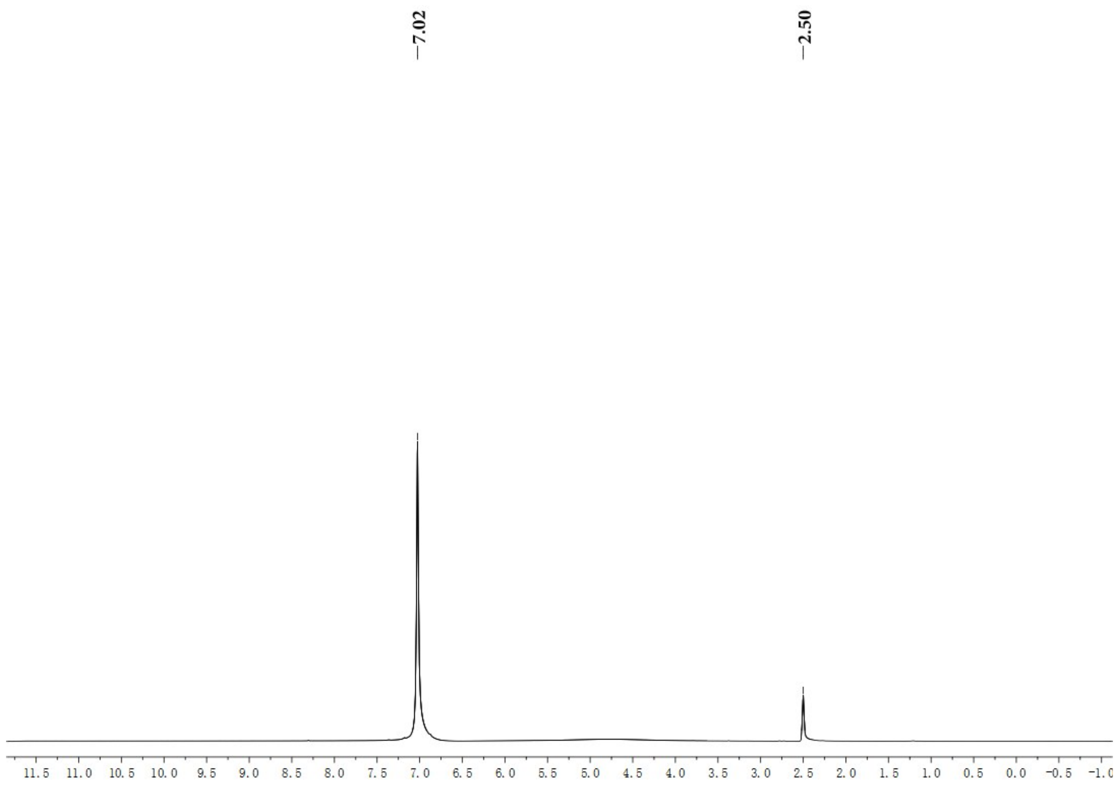


**Figure S31** $^{1}H$ NMR spectra (300 MHz) of **16** in DMSO-$d_6$ at 25 °C

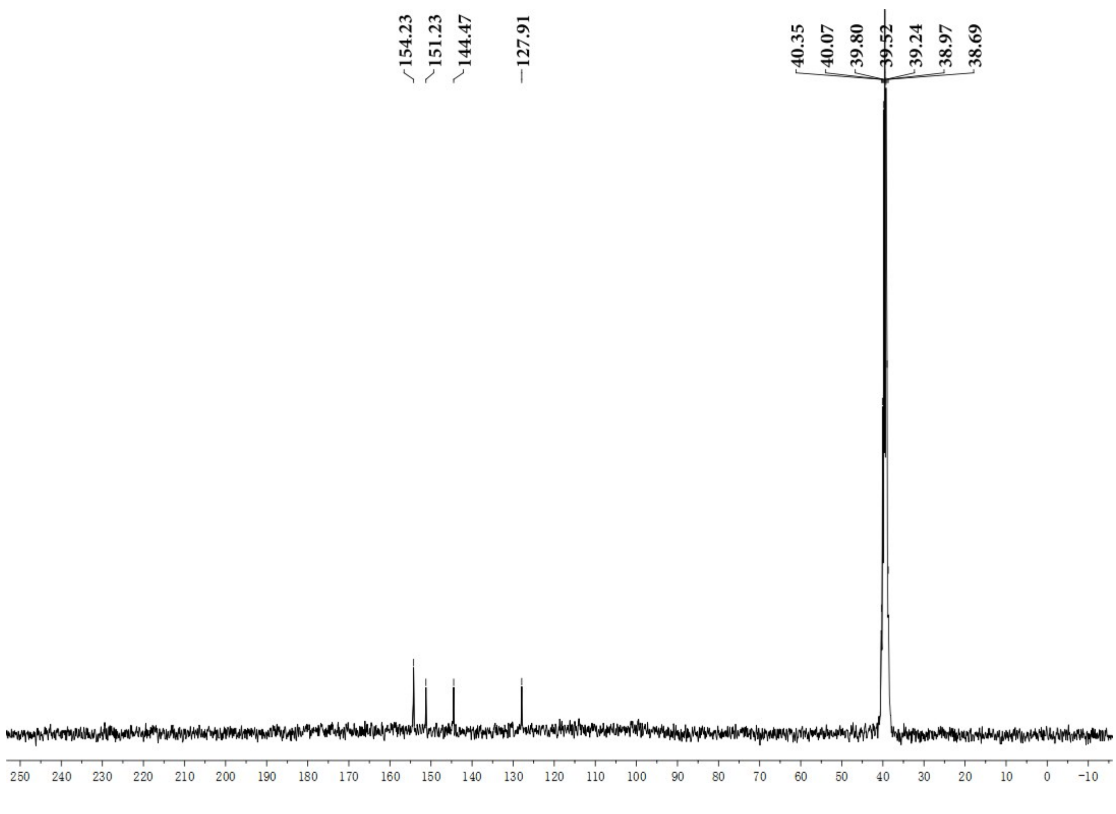


**Figure S32** $^{13}C$ NMR specta (75 MHz) of **16** in DMSO-$d_6$ at 25 °C

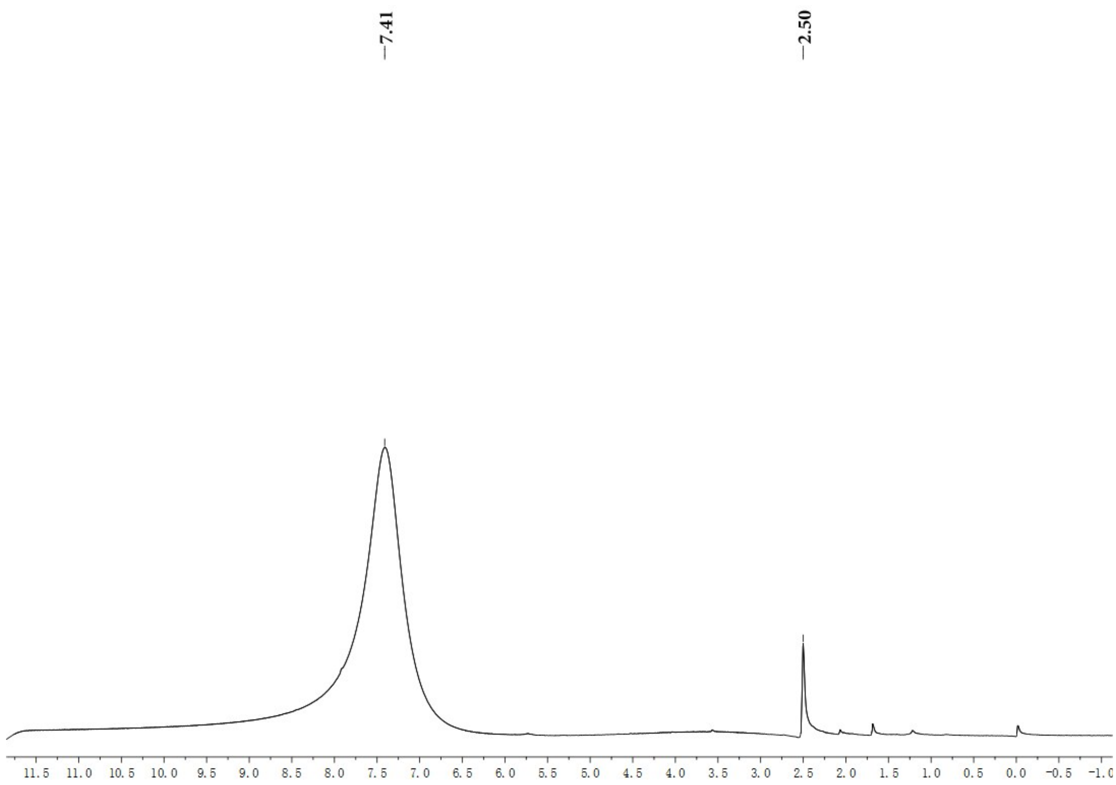


**Figure S33** $^{1}H$ NMR spectra (300 MHz) of **17** in DMSO-$d_6$ at 25 °C

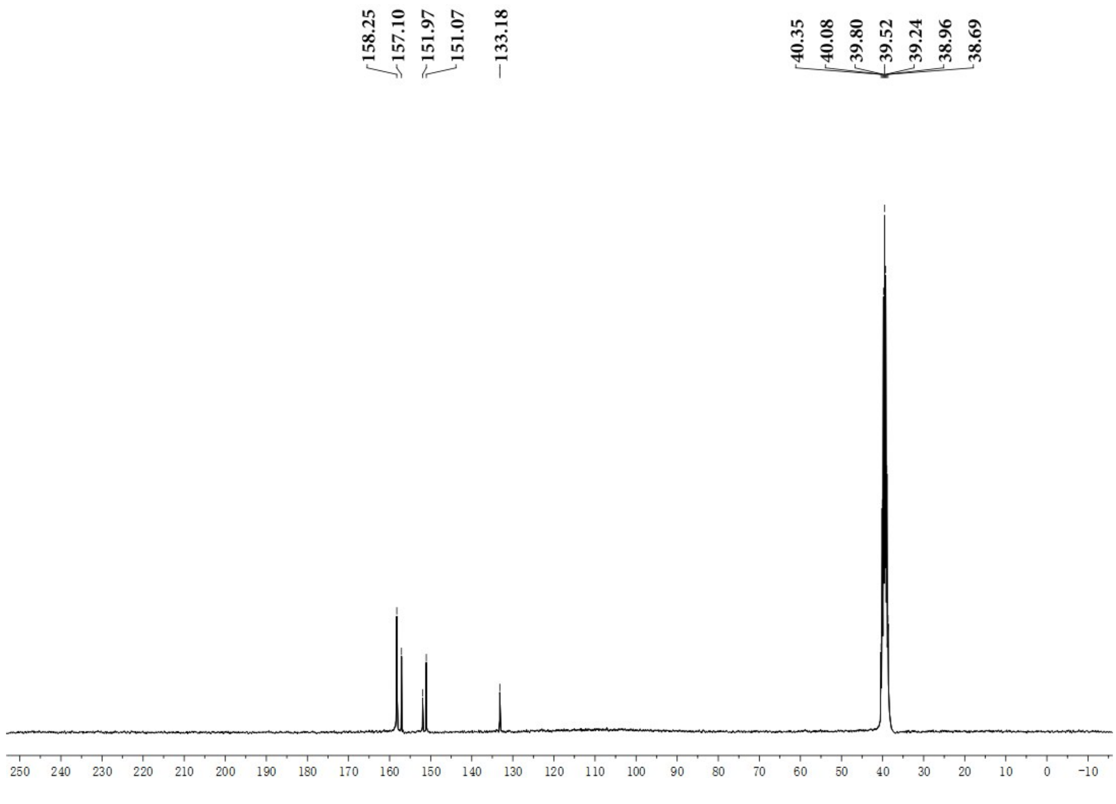


**Figure S34** $^{13}C$ NMR specta (75 MHz) of **17** in DMSO-$d_6$ at 25 °C

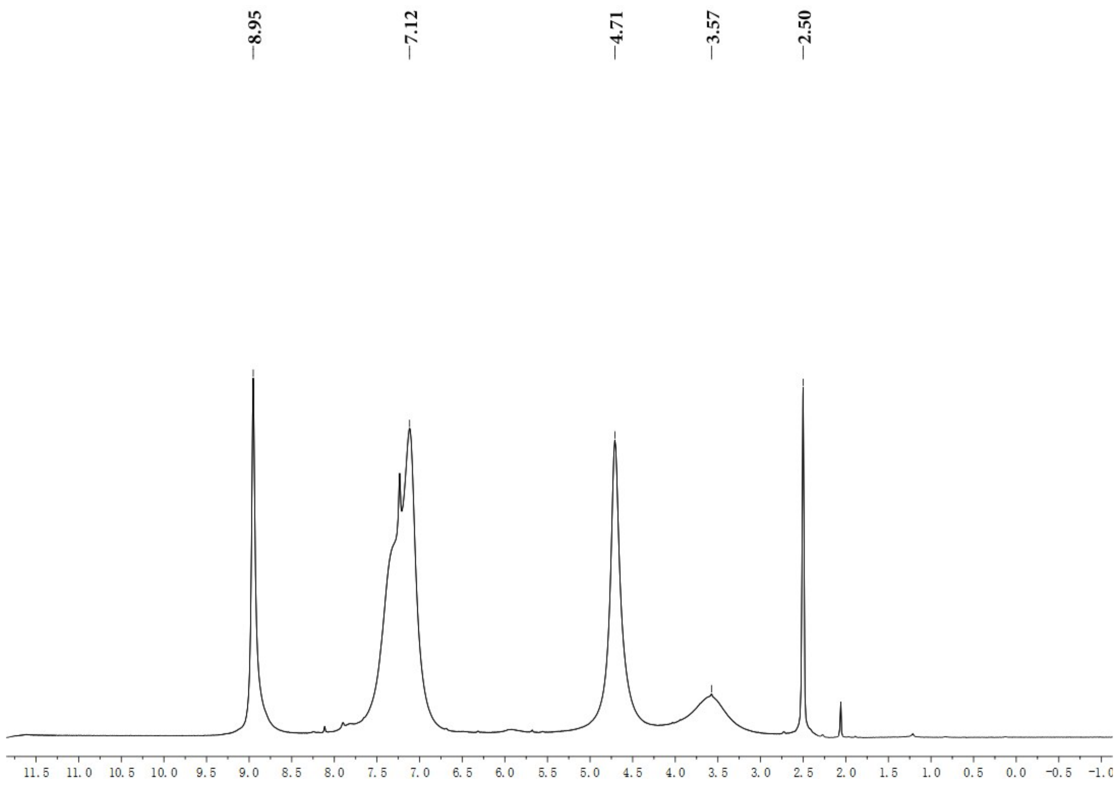


**Figure S35** [1]H NMR spectra (300 MHz) of **18** in DMSO-$d_6$ at 25 °C

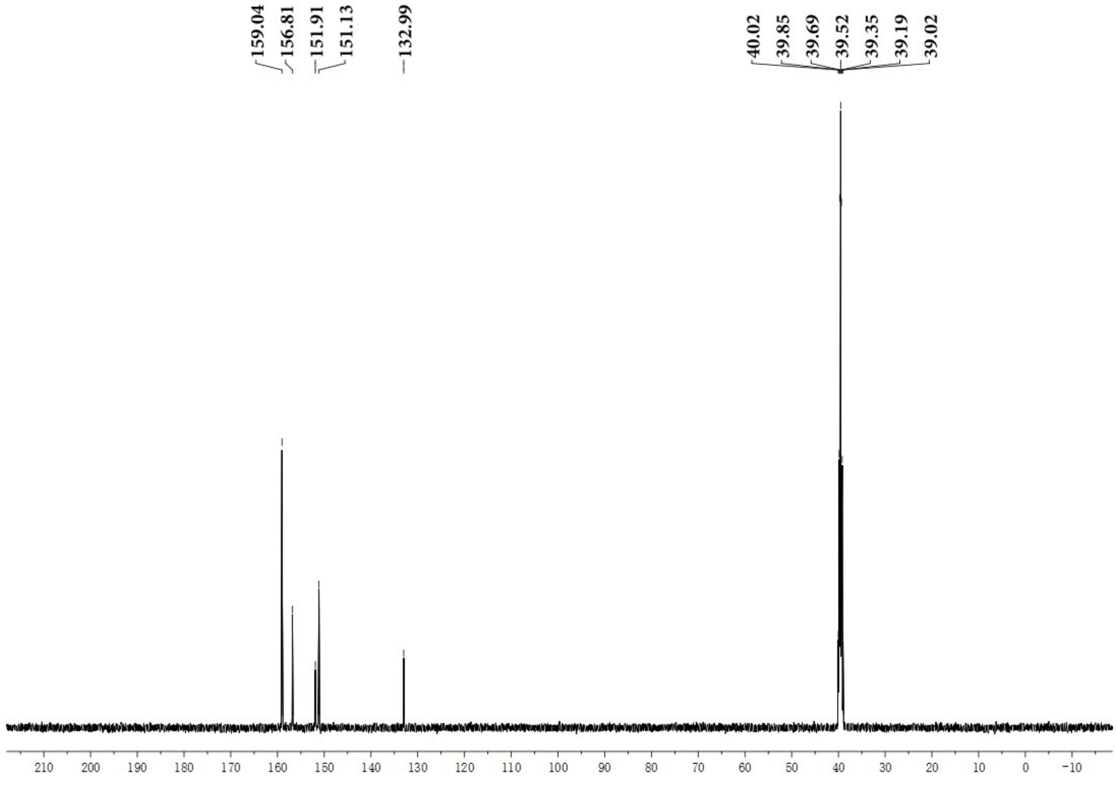


**Figure S36** [13]C NMR specta (75 MHz) of **18** in DMSO-$d_6$ at 25 °C

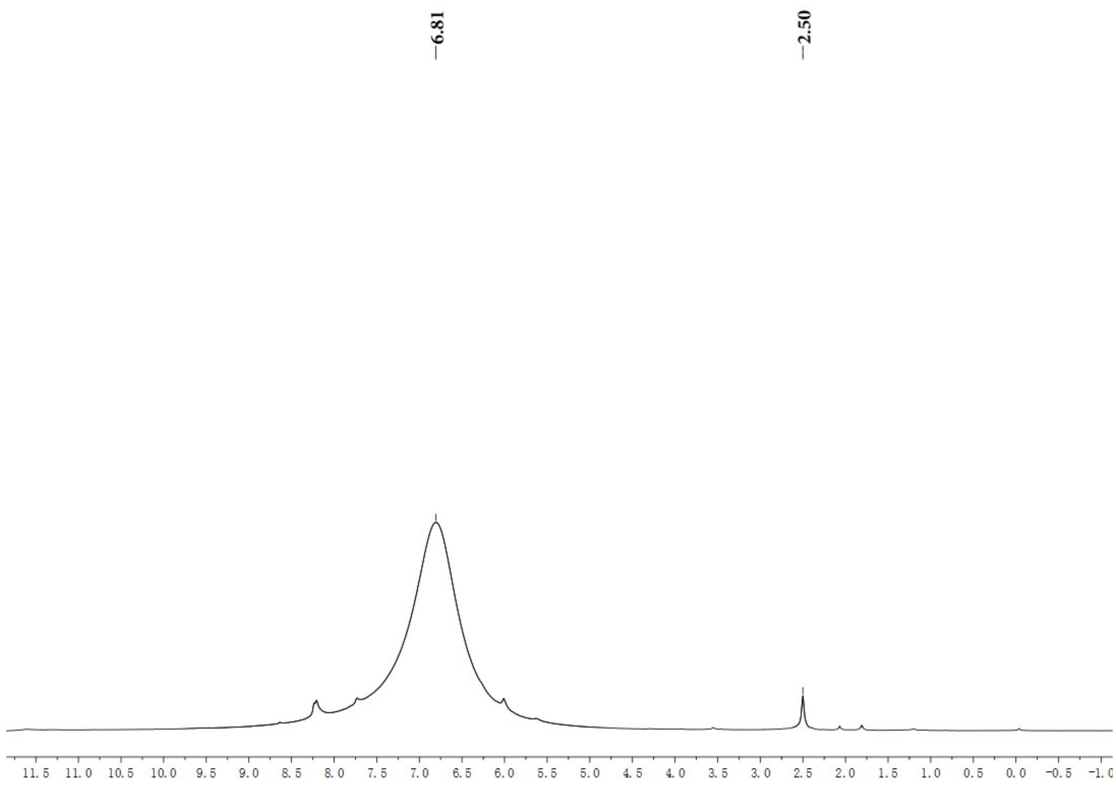


**Figure S37** $^{1}H$ NMR spectra (300 MHz) of **19** in DMSO-$d_6$ at 25 °C

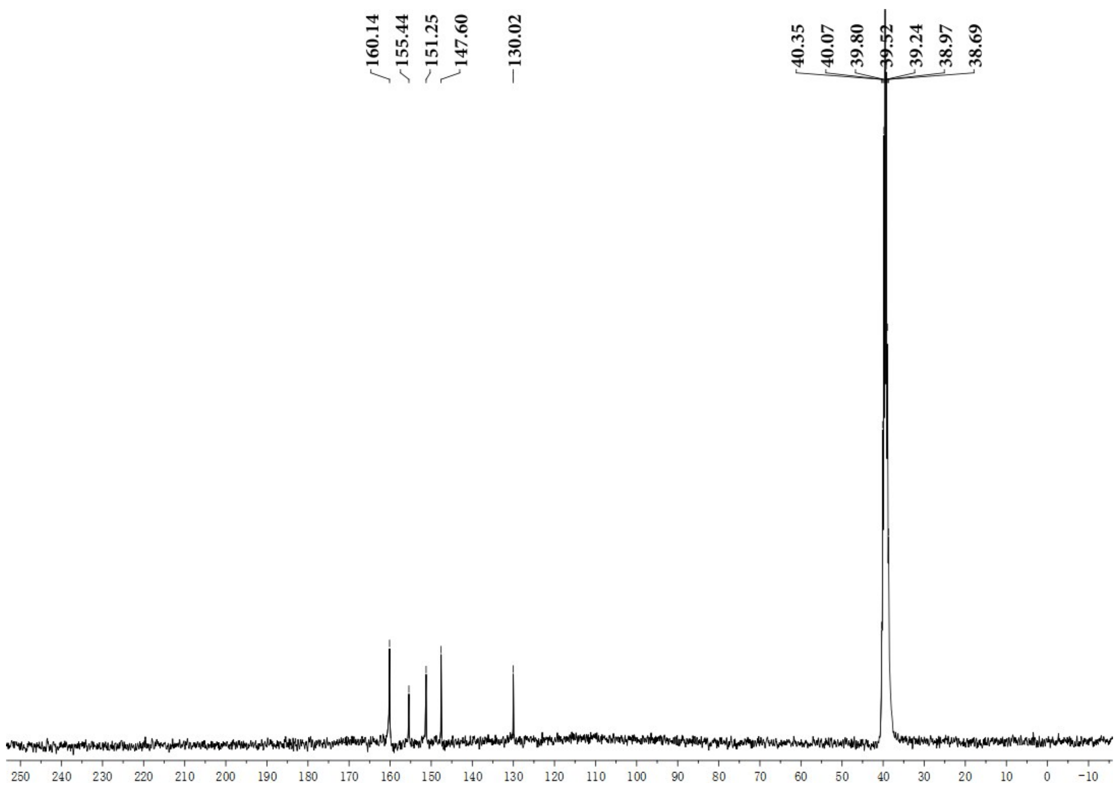


**Figure S38** $^{13}C$ NMR specta (75 MHz) of **19** in DMSO-$d_6$ at 25 °C

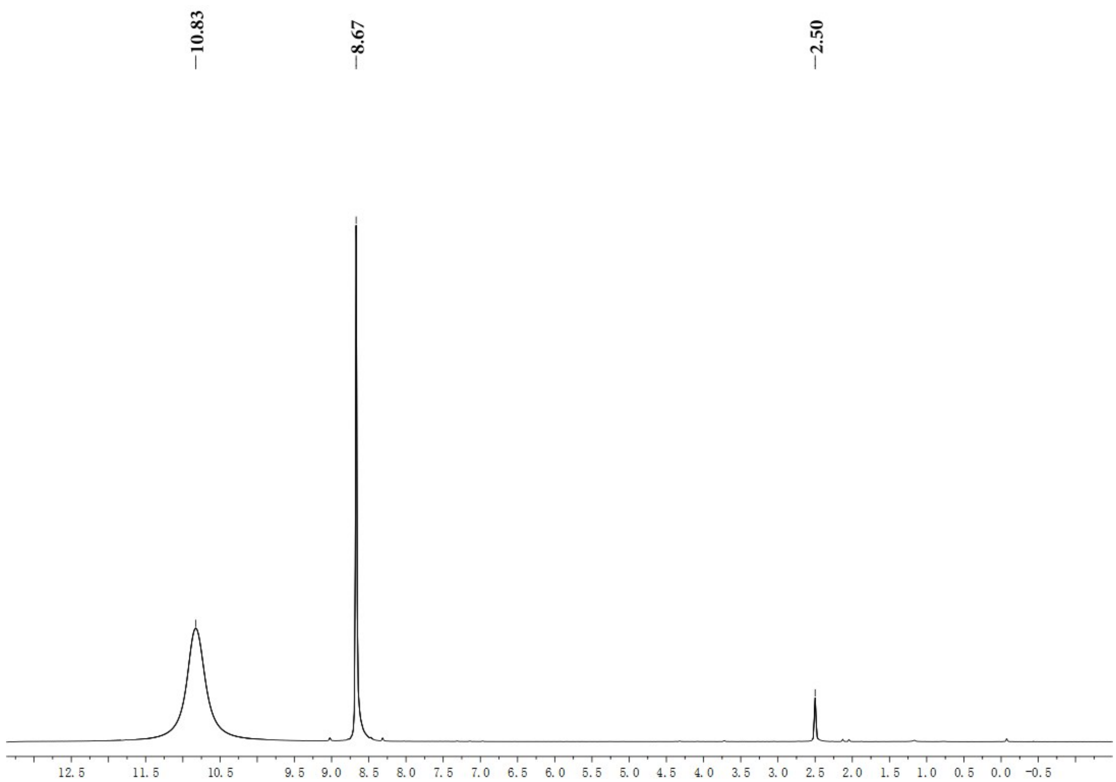


**Figure S39** [1]H NMR spectra (300 MHz) of **20** in DMSO-$d_6$ at 25 °C

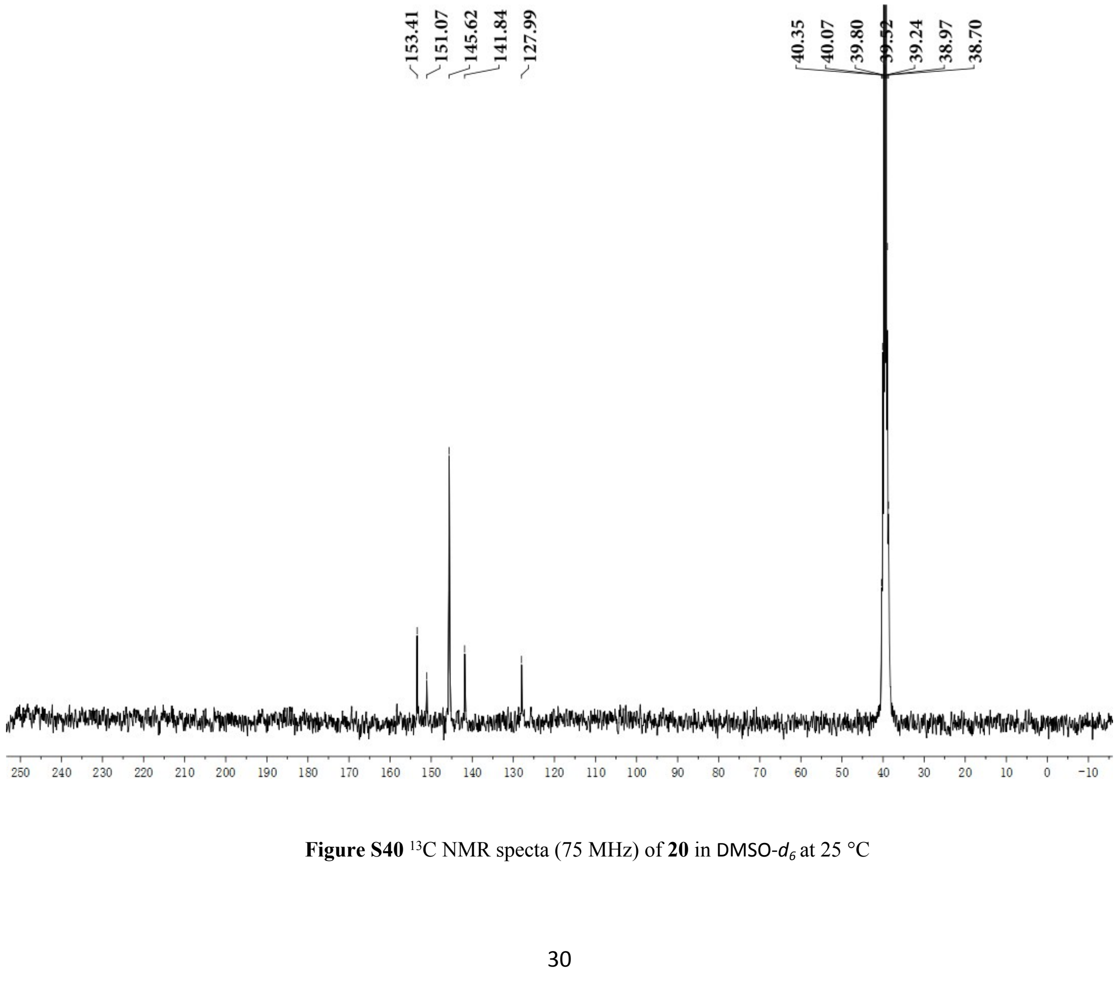


**Figure S40** [13]C NMR specta (75 MHz) of **20** in DMSO-$d_6$ at 25 °C

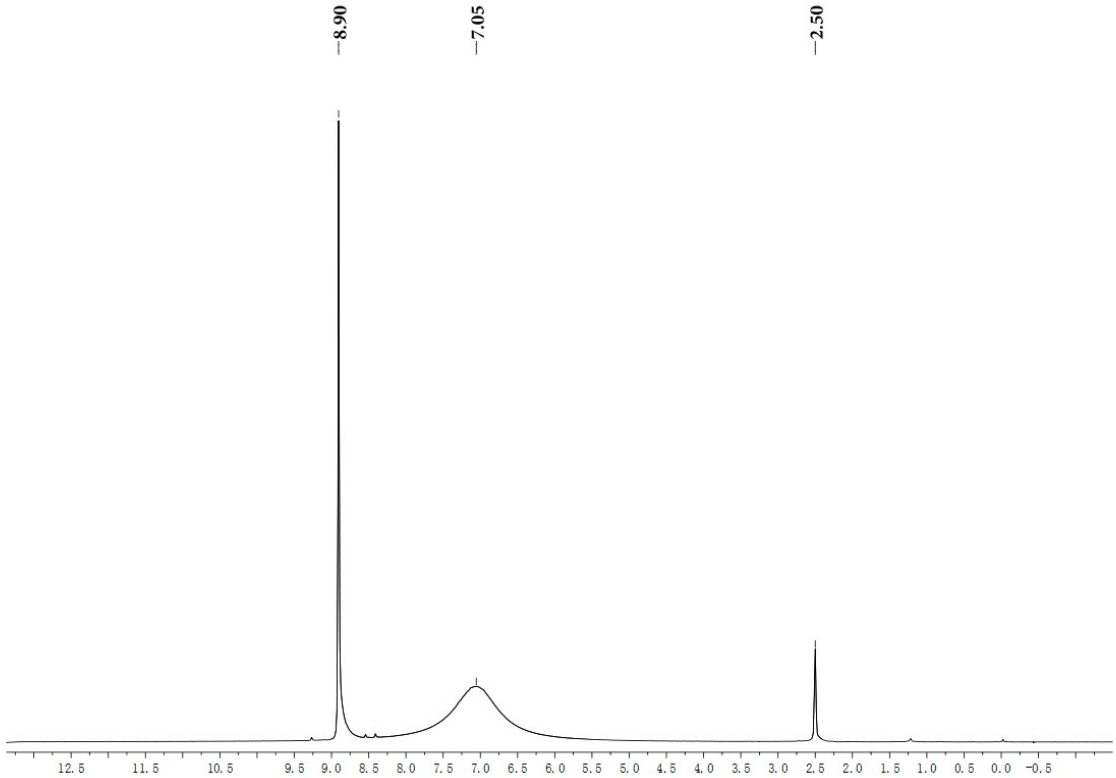


**Figure S41** $^{1}$H NMR spectra (300 MHz) of **21** in DMSO-$d_6$ at 25 °C

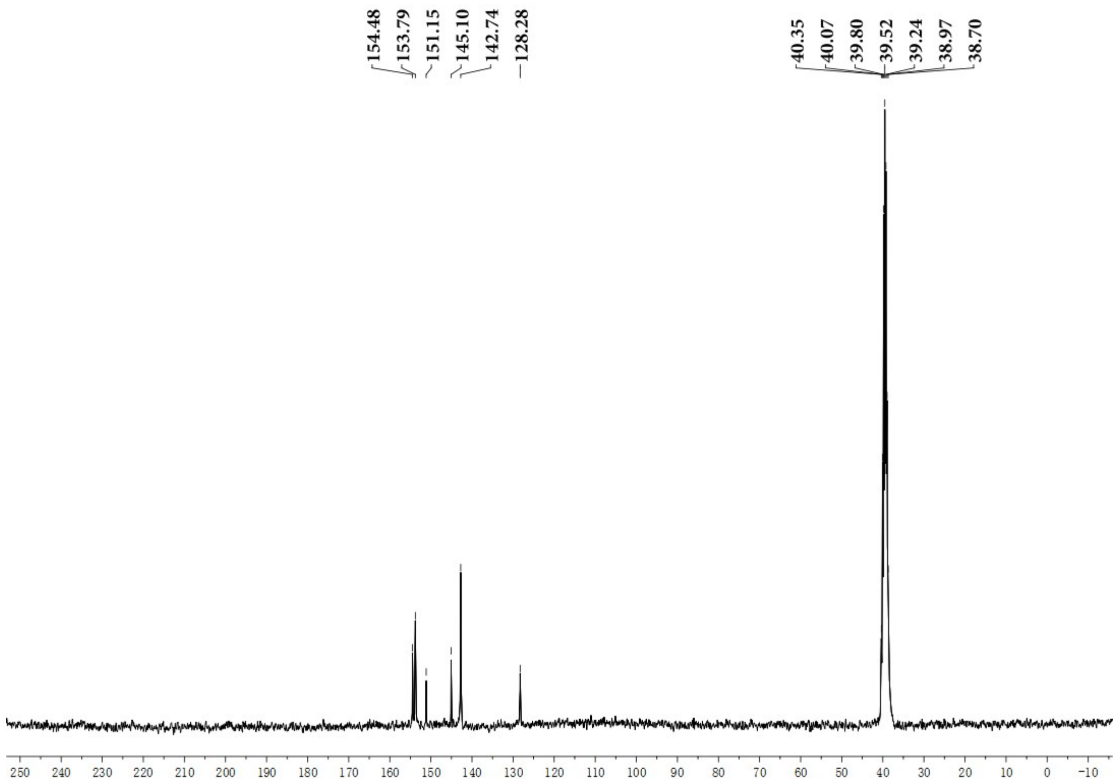


**Figure S42** $^{13}$C NMR specta (75 MHz) of **21** in DMSO-$d_6$ at 25 °C

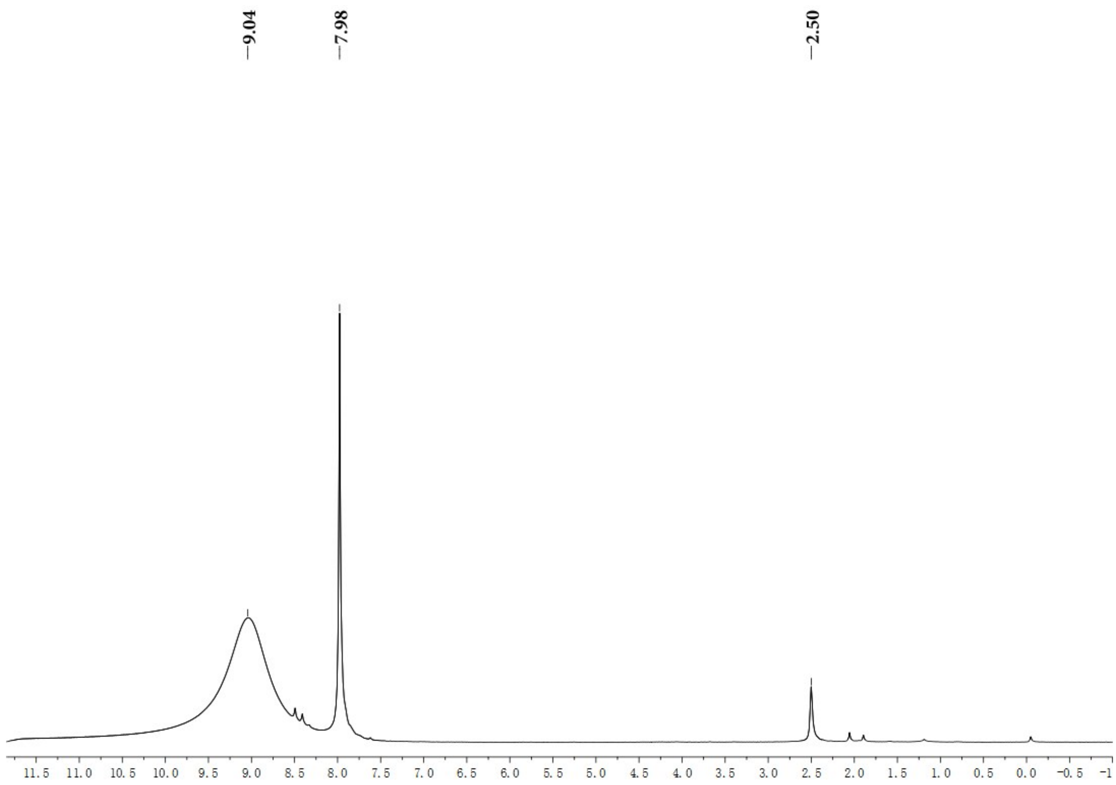


**Figure S43** [1]H NMR spectra (300 MHz) of **22** in DMSO-$d_6$ at 25 °C

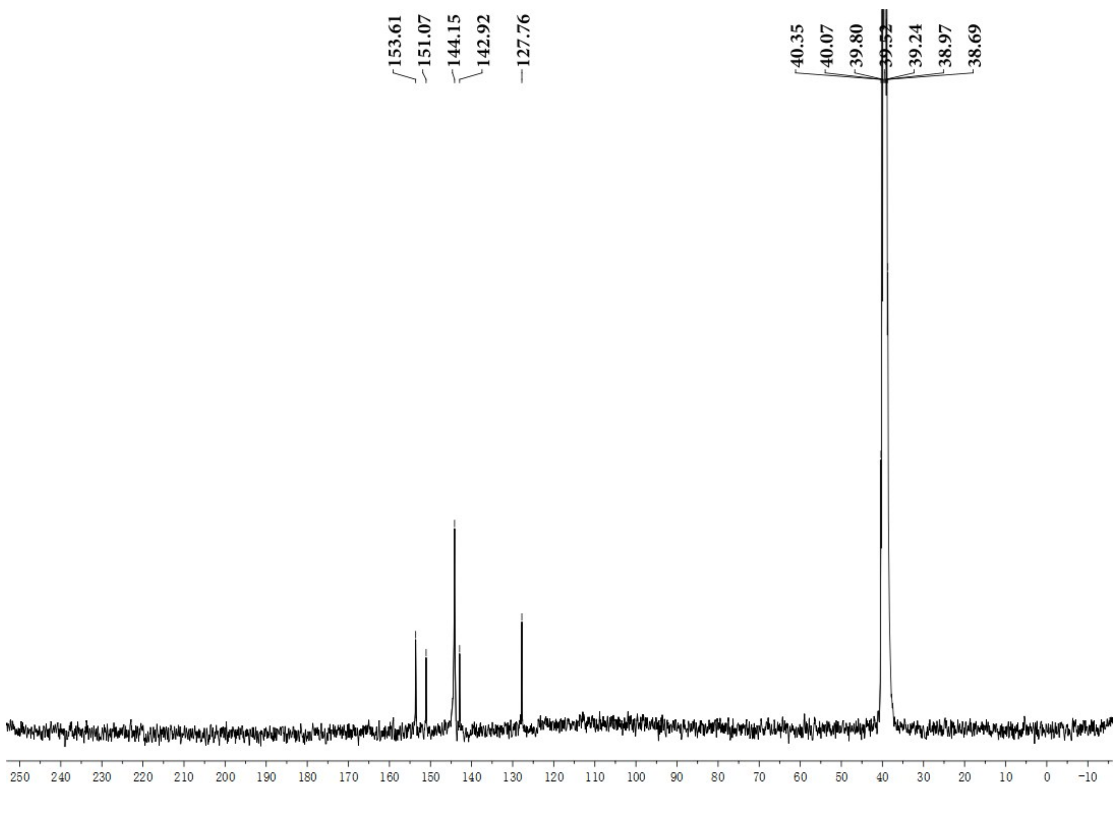


**Figure S44** [13]C NMR specta (75 MHz) of **22** in DMSO-$d_6$ at 25 °C

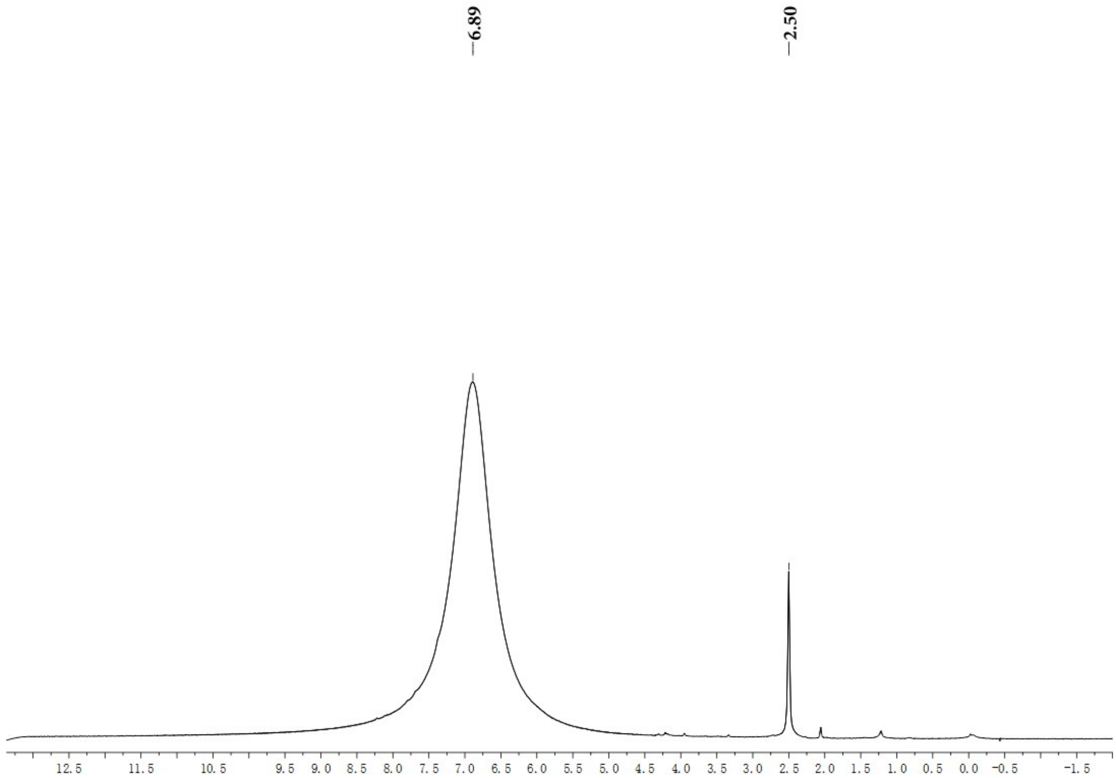


**Figure S45** $^{1}$H NMR spectra (300 MHz) of **23** in DMSO-$d_6$ at 25 °C

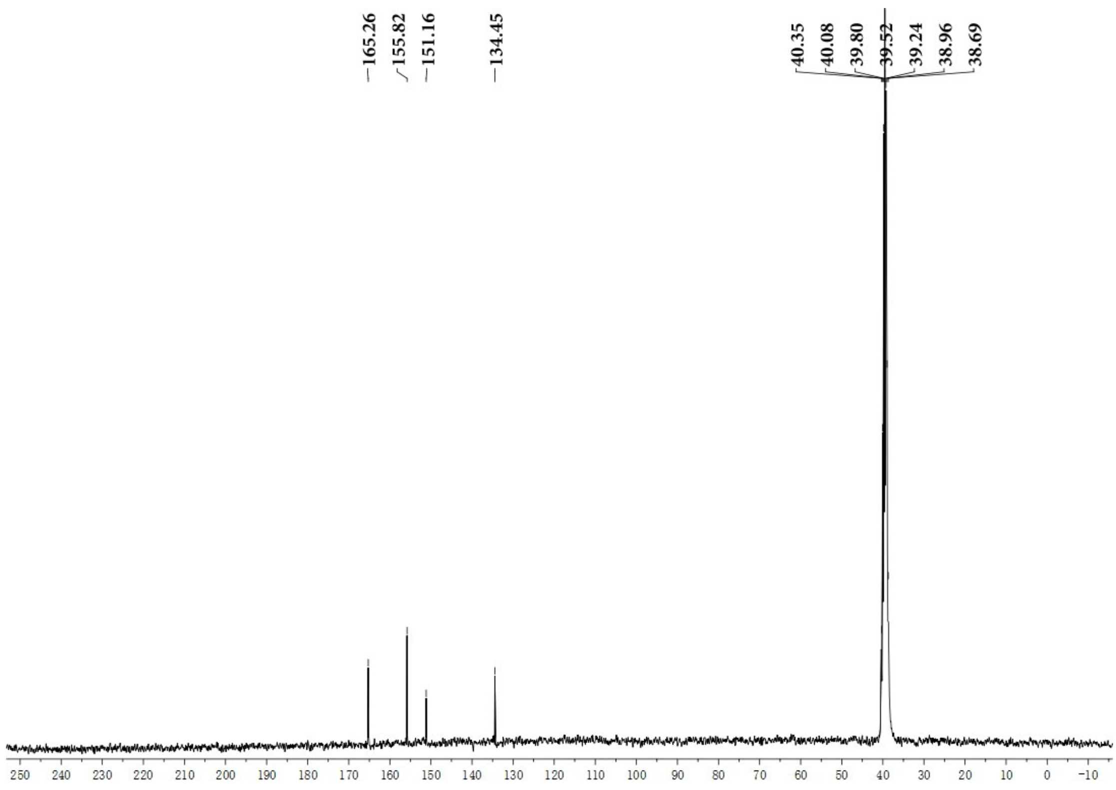

**Figure S46** $^{13}$C NMR specta (75 MHz) of **23** in DMSO-$d_6$ at 25 °C

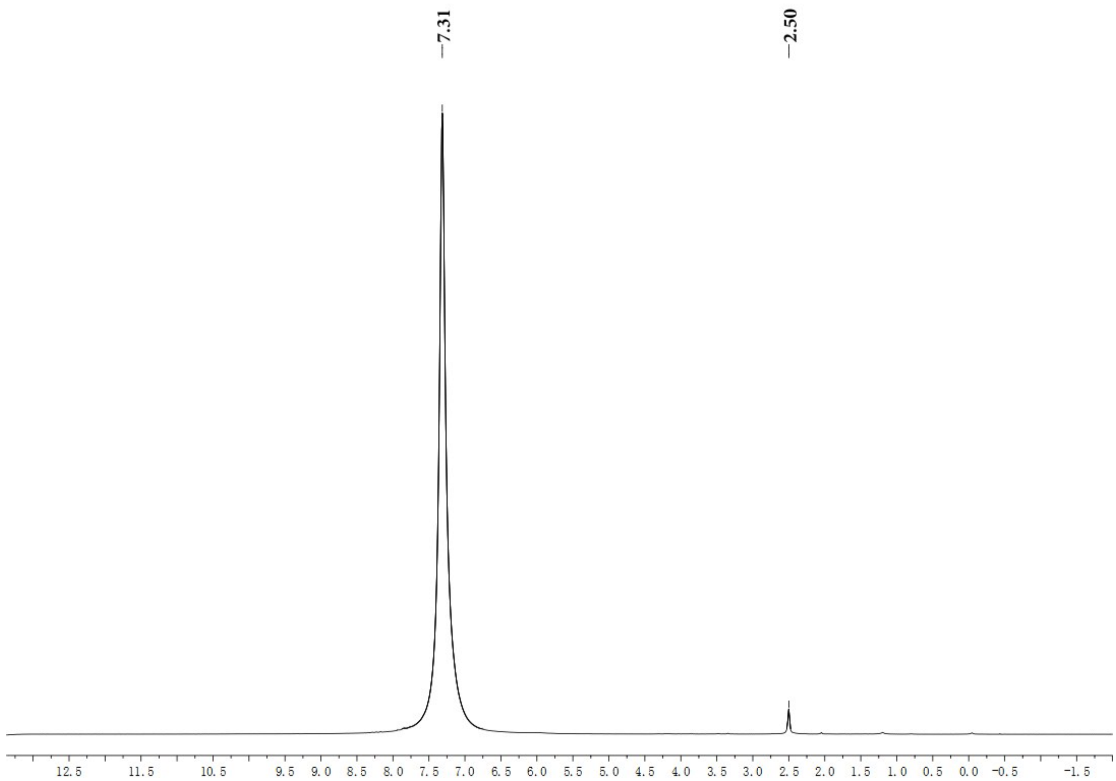


**Figure S47** $^1$H NMR spectra (300 MHz) of **24** in DMSO-$d_6$ at 25 °C

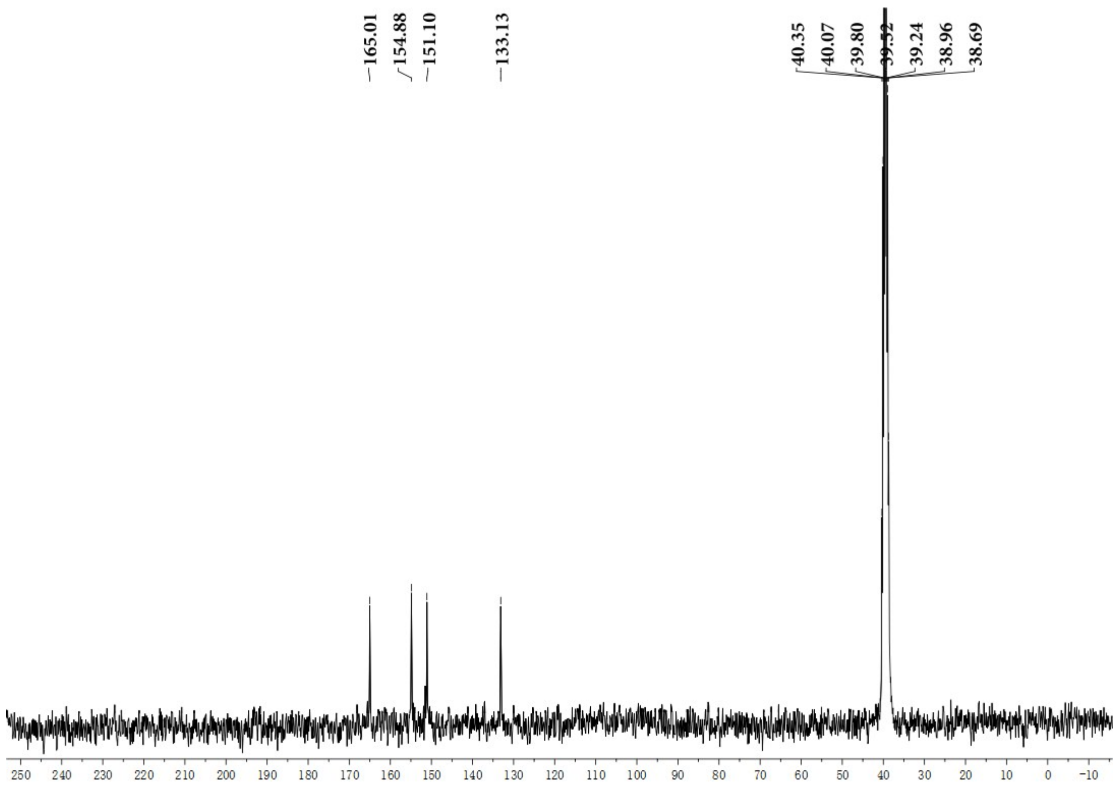

**Figure S48** $^{13}$C NMR specta (75 MHz) of **24** in DMSO-$d_6$ at 25 °C

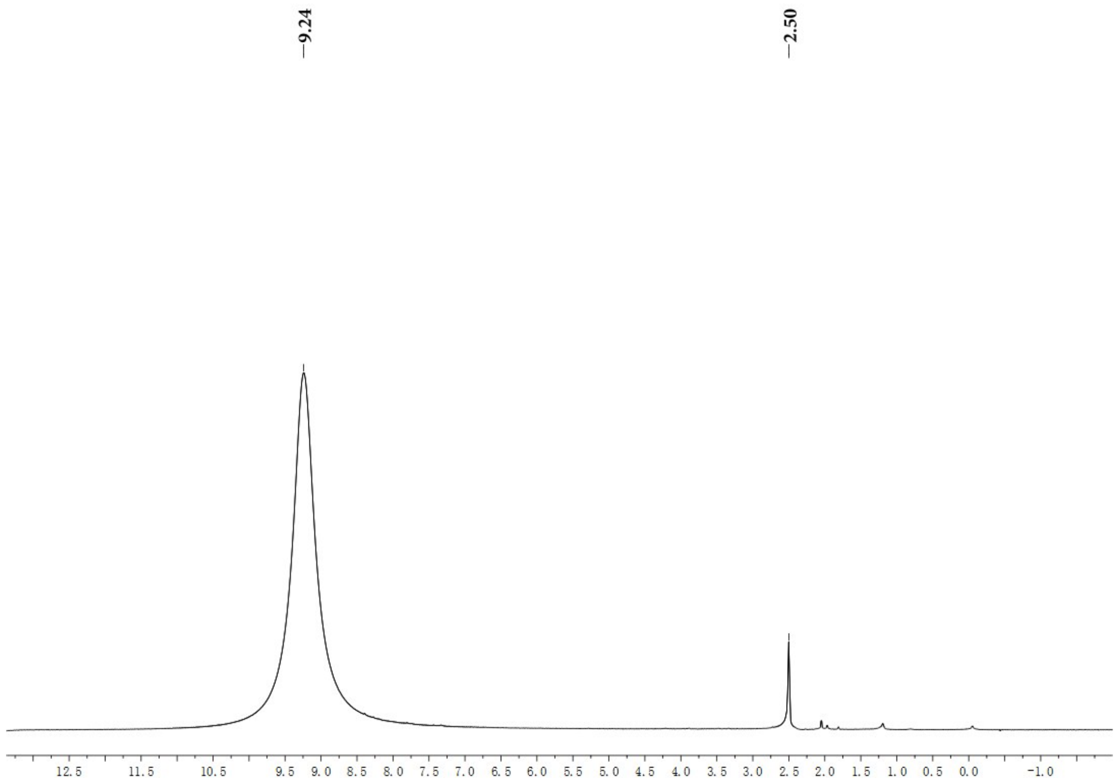


**Figure S49** $^{1}$H NMR spectra (300 MHz) of **25** in DMSO-$d_6$ at 25 °C

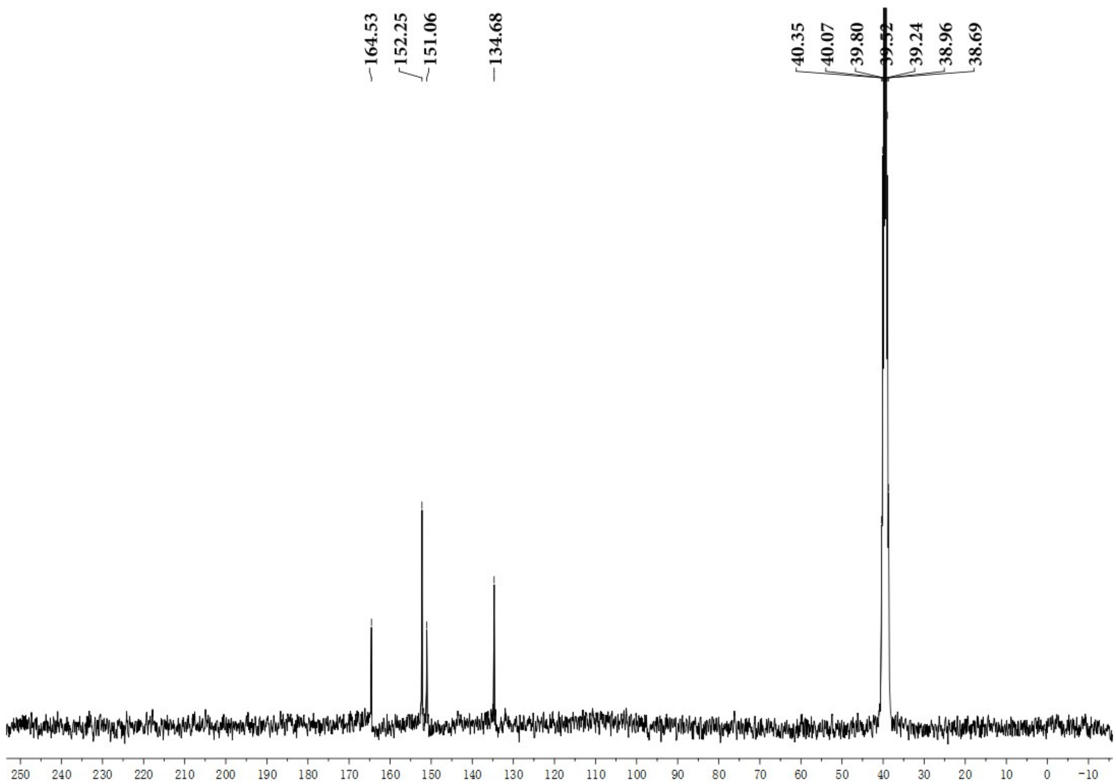

**Figure S50** $^{13}C$ NMR specta (75 MHz) of **25c** in DMSO-$d_6$ at 25 °C

# 5. DSC curves of the title compounds

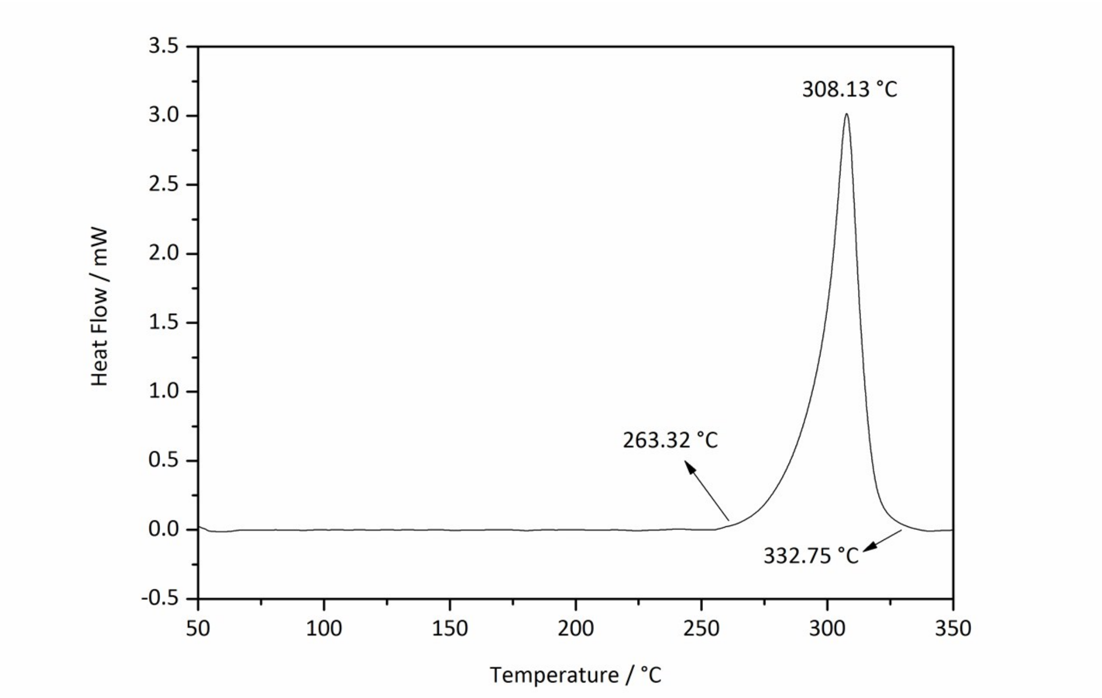


**Figure S51** DSC curve of compound **1**

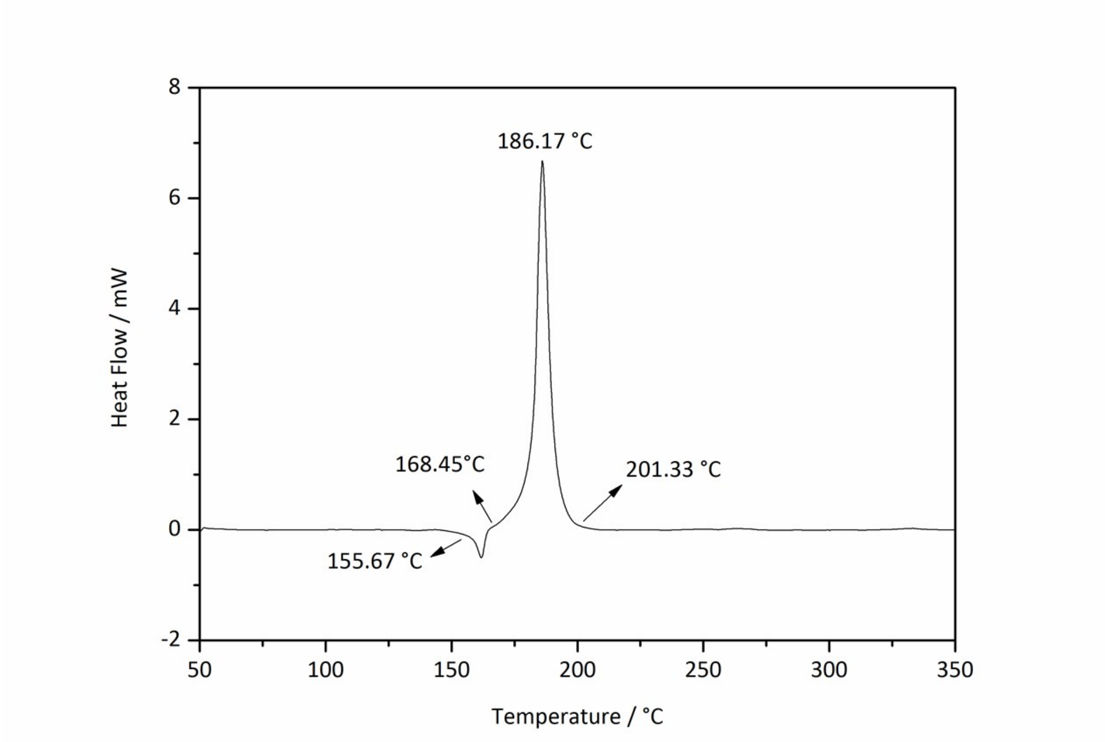


**Figure S52** DSC curve of compound **2**

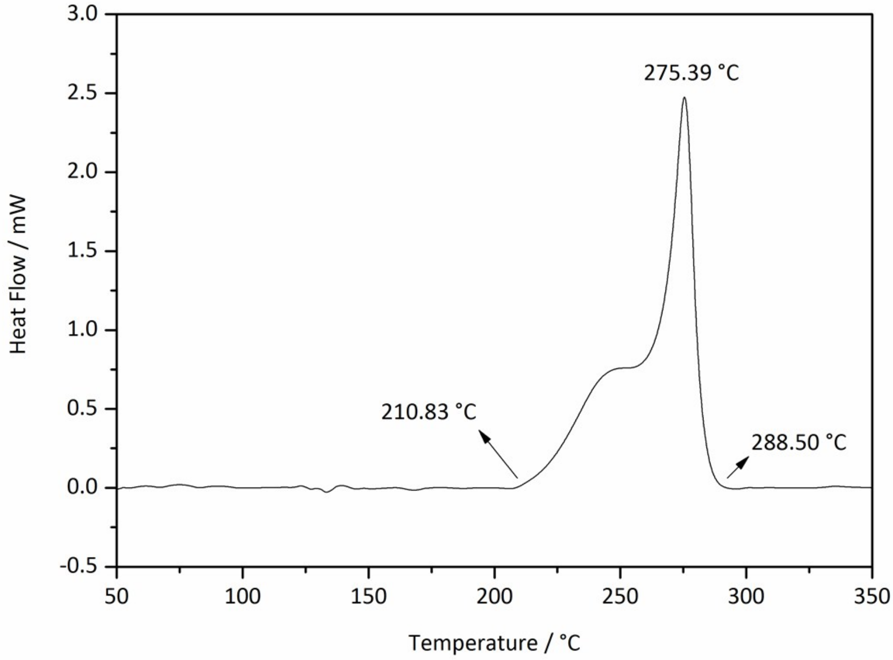


**Figure S53** DSC curve of compound **3**

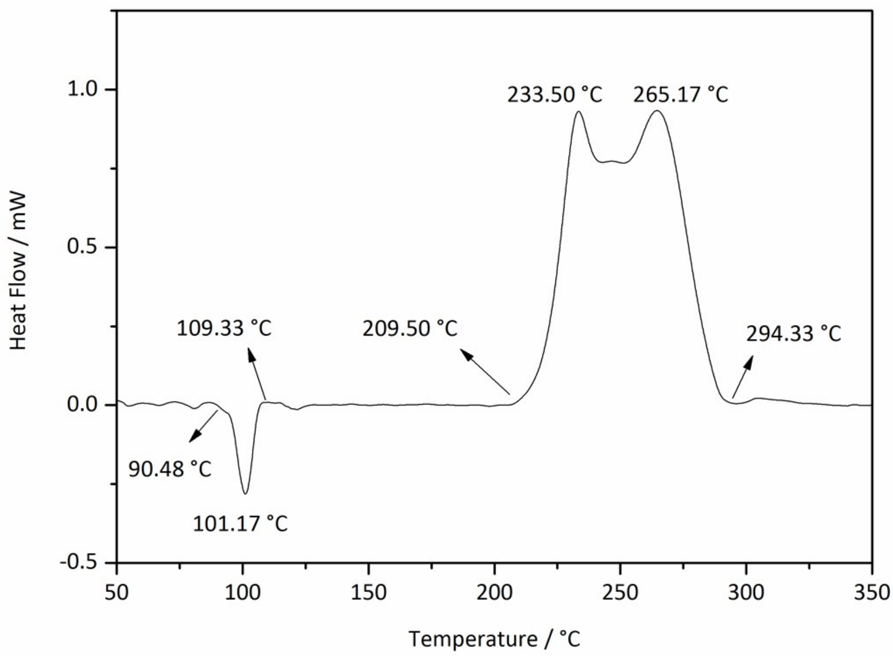


**Figure S54** DSC curve of compound **4**

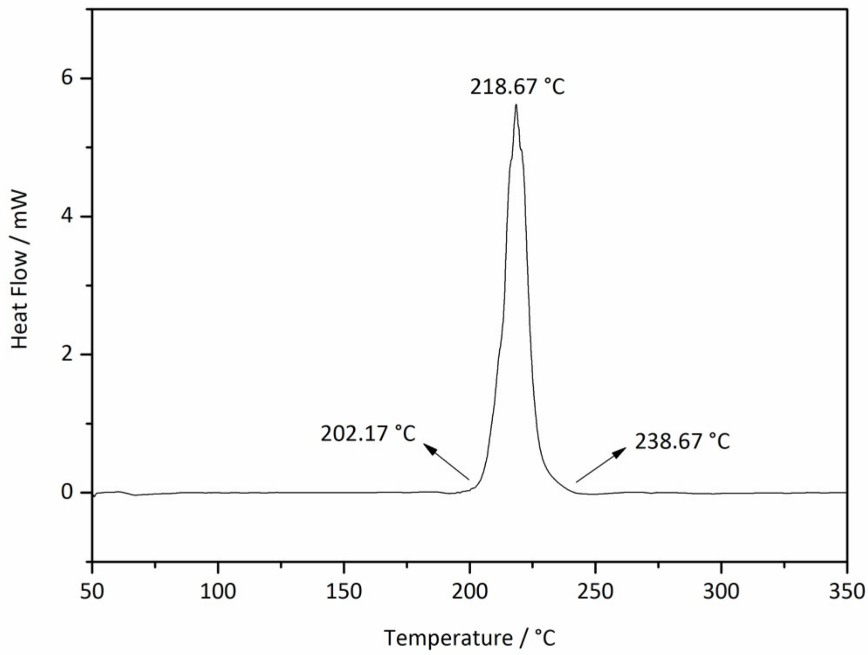


**Figure S55** DSC curve of compound **5**

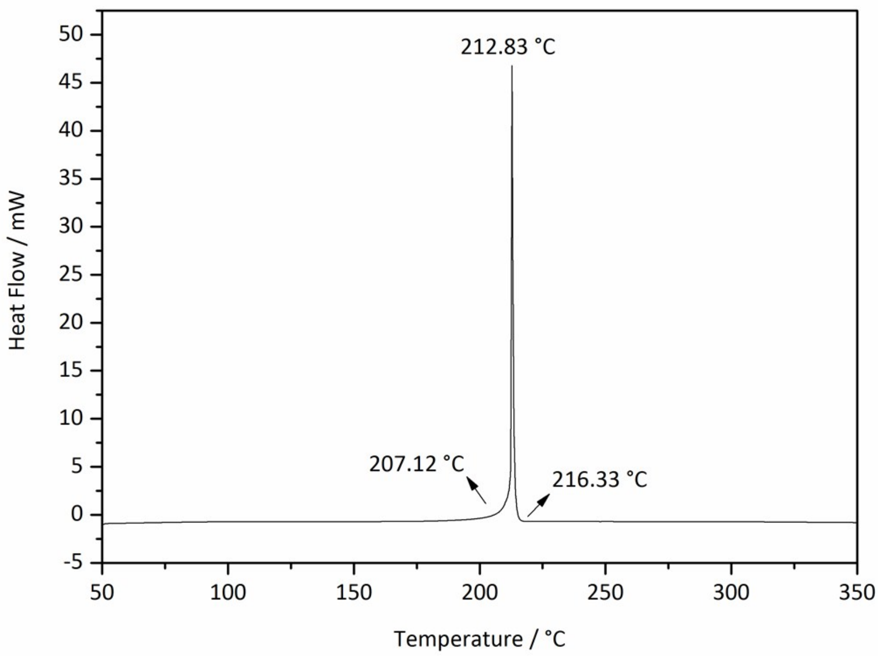


**Figure S56** DSC curve of compound **6**

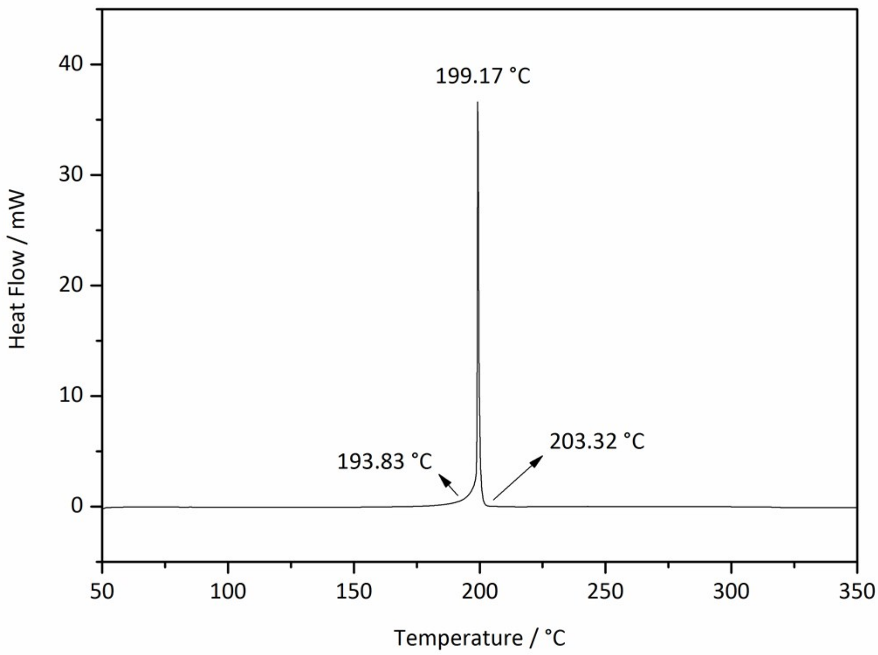


**Figure S57** DSC curve of compound **7**

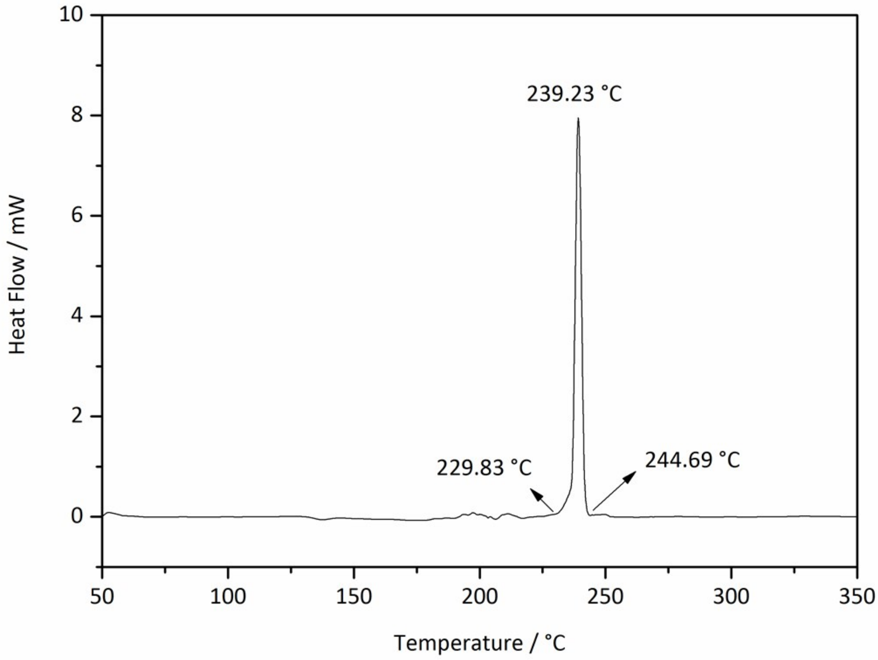


**Figure S58** DSC curve of compound **8**

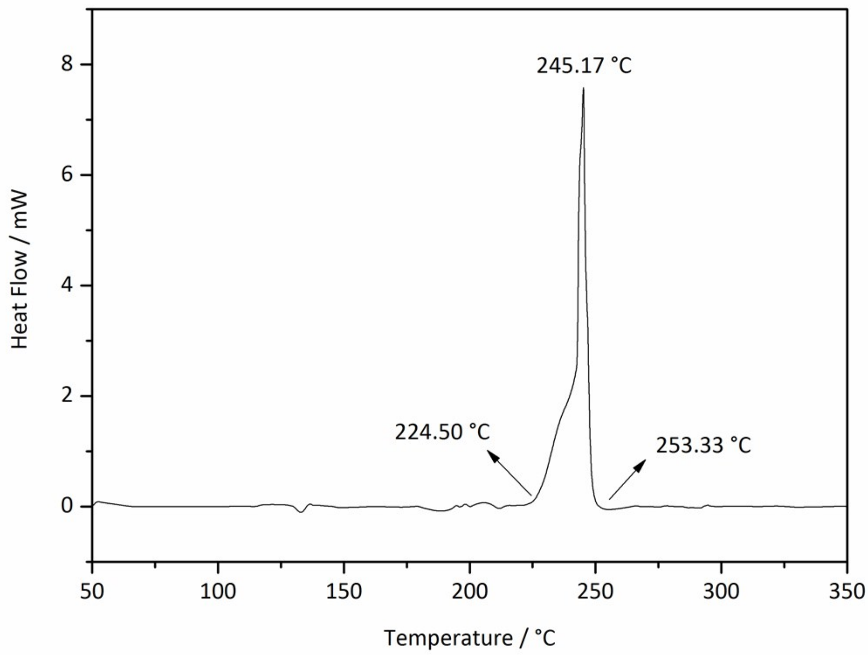


**Figure S59** DSC curve of compound **9**

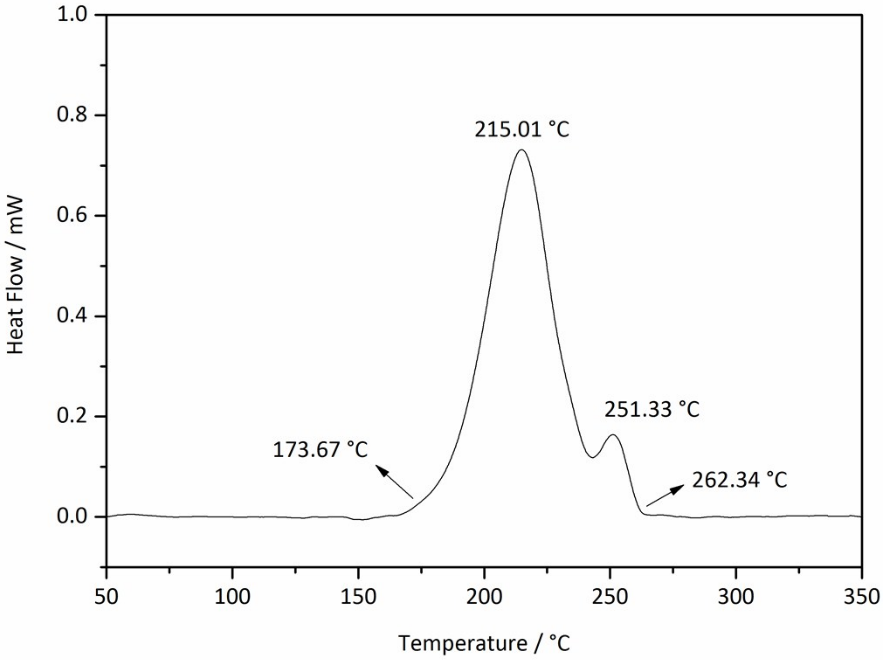


**Figure S60** DSC curve of compound **10**

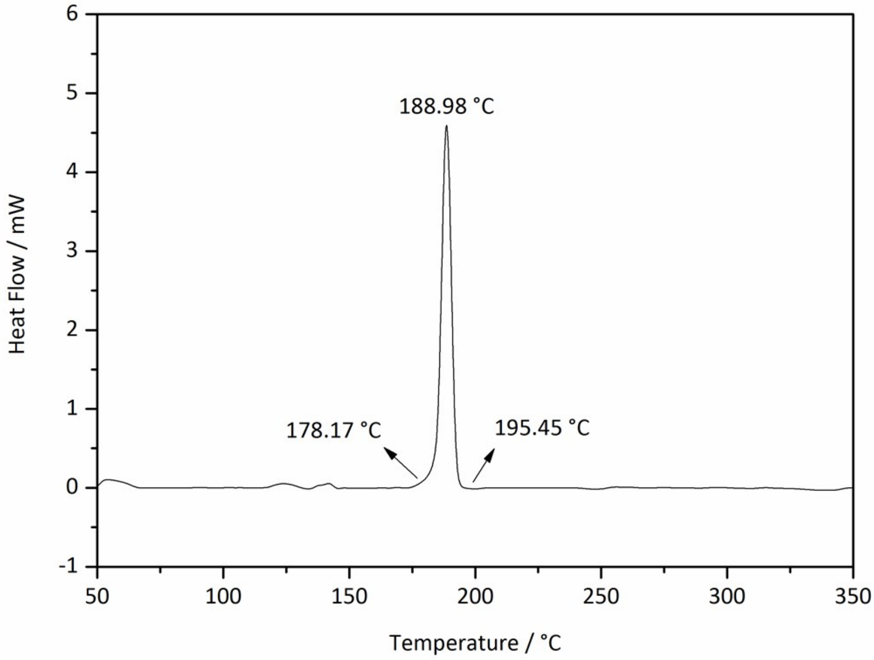


**Figure S61** DSC curve of compound **11**

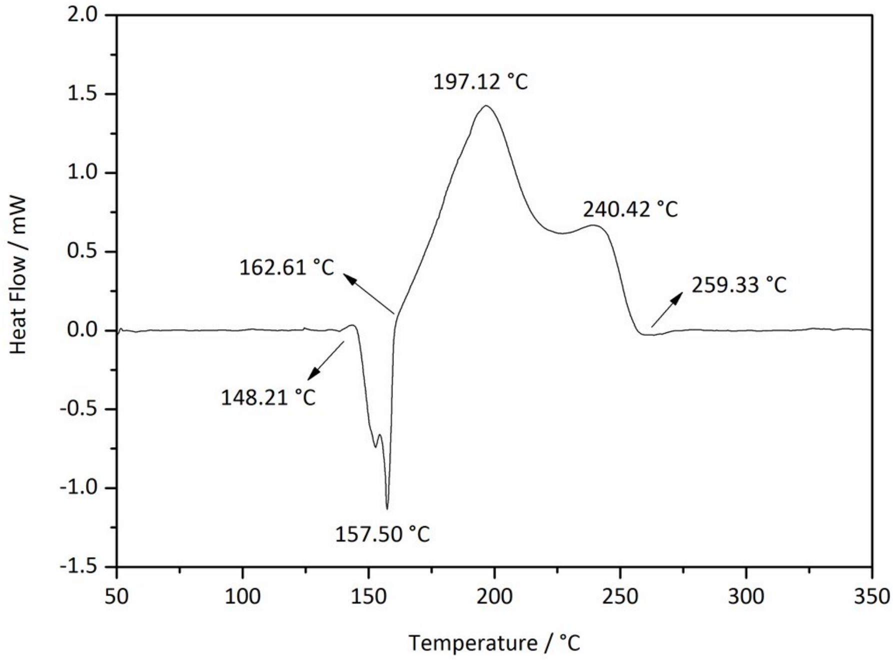


**Figure S62** DSC curve of compound **12**

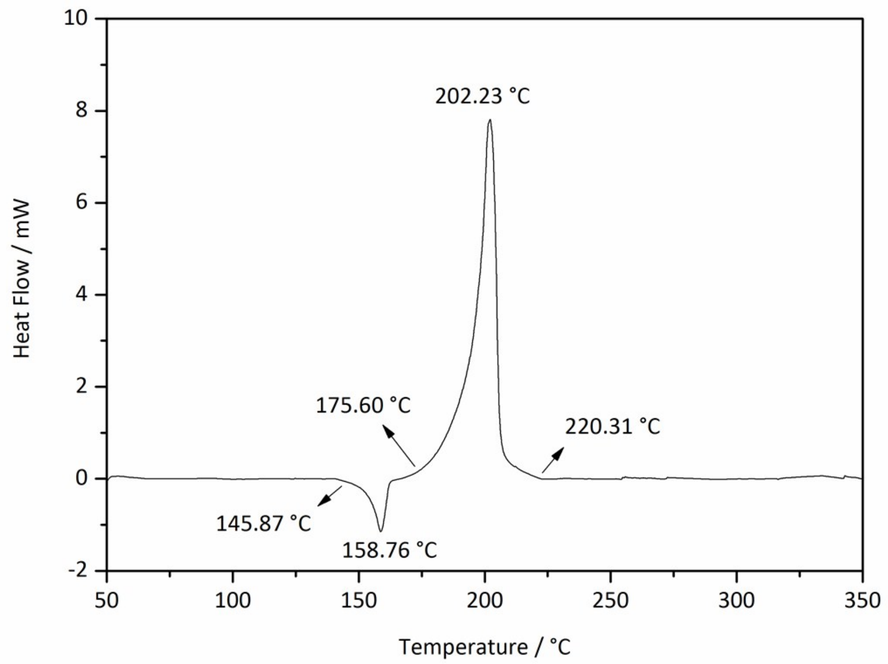


**Figure S63** DSC curve of compound **13**

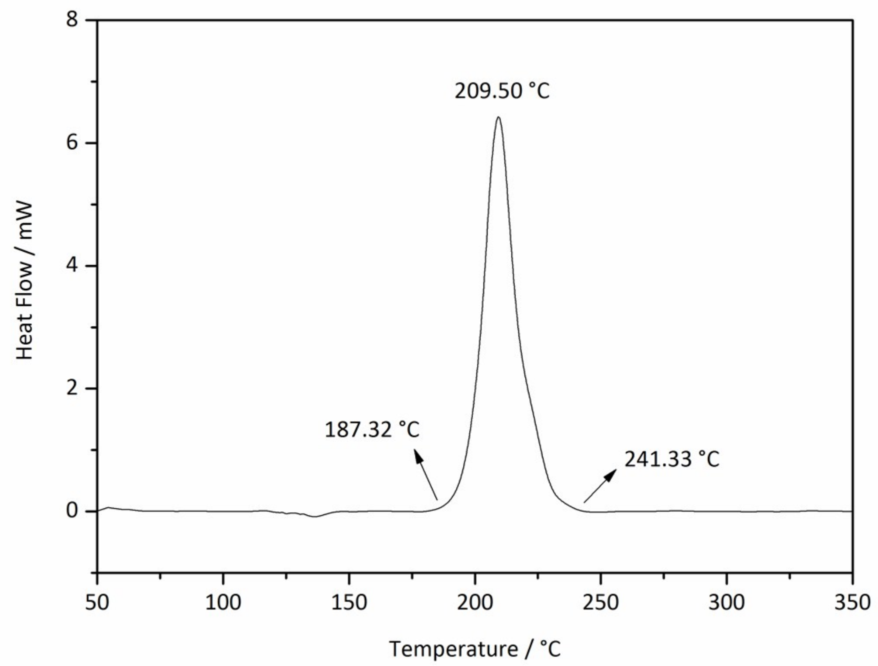


**Figure S64** DSC curve of compound **14**

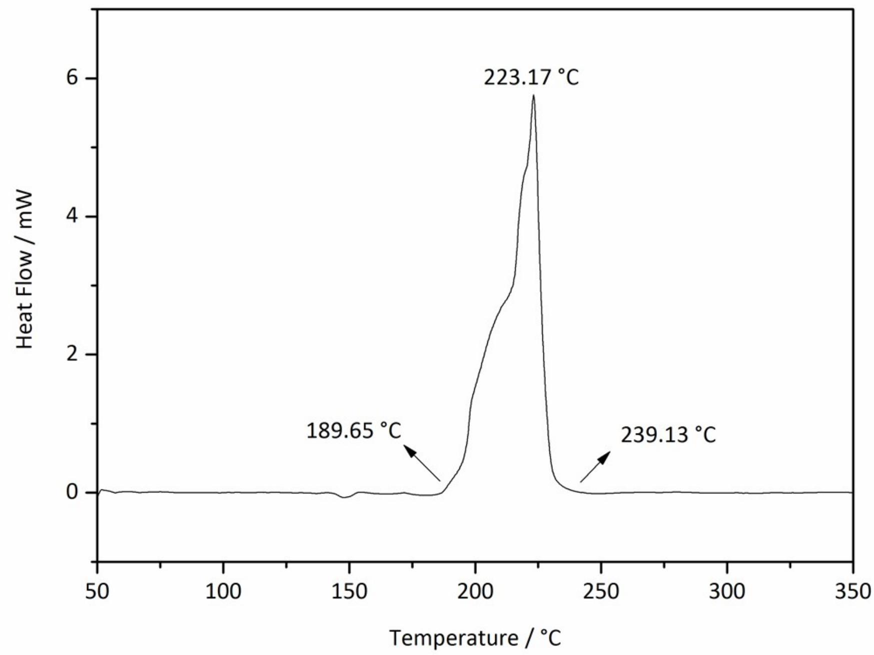


**Figure S65** DSC curve of compound **15**

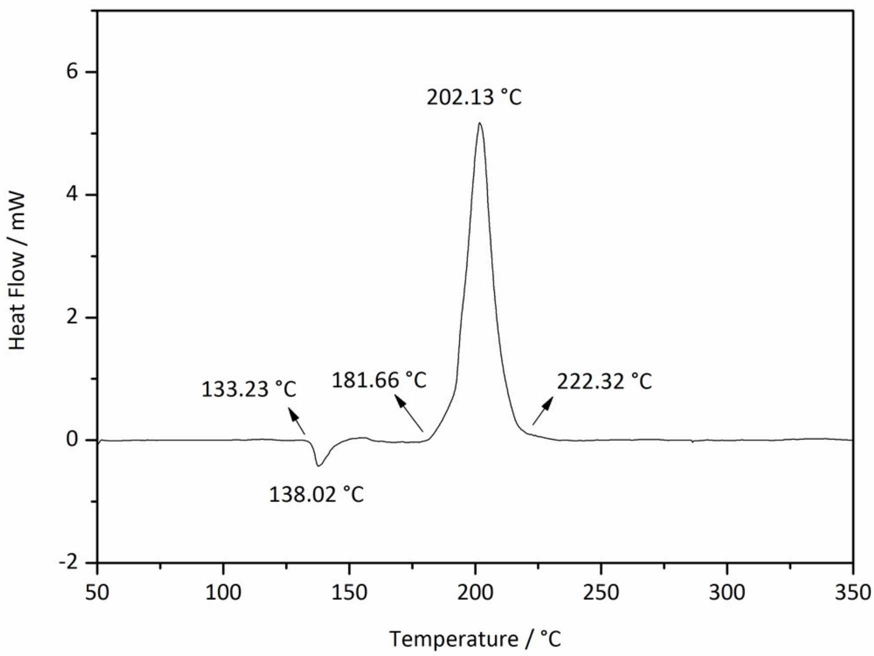


**Figure S66** DSC curve of compound **16**

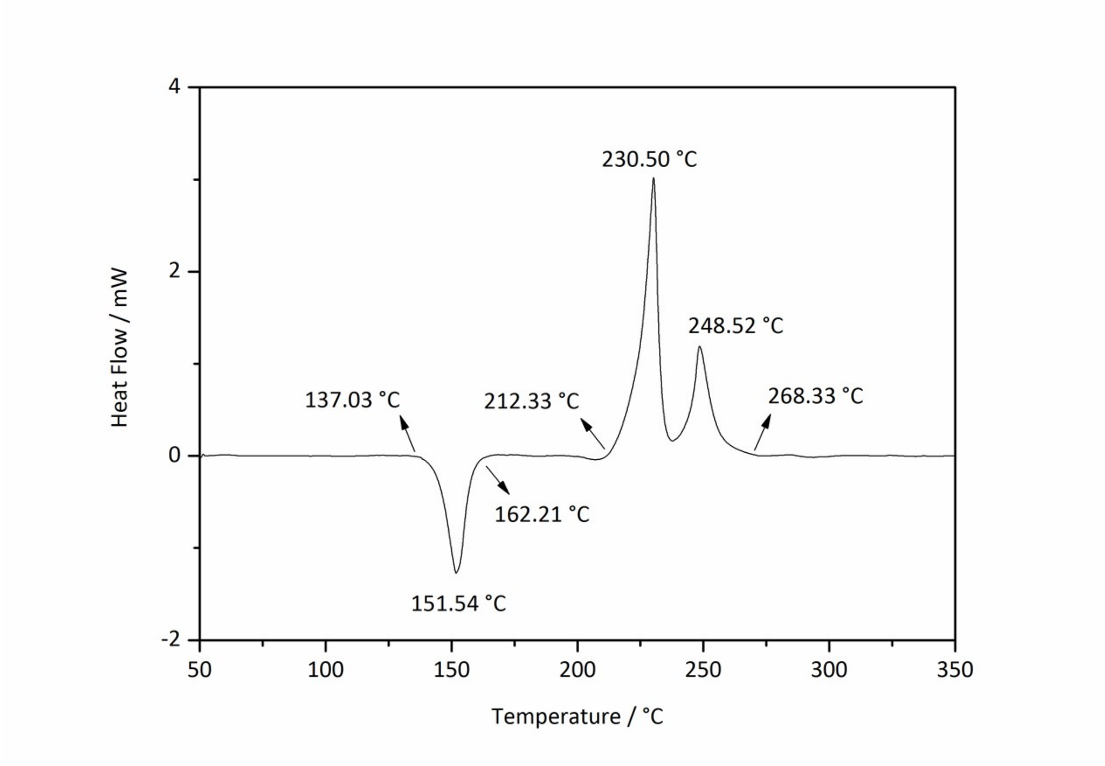


**Figure S67** DSC curve of compound **17**

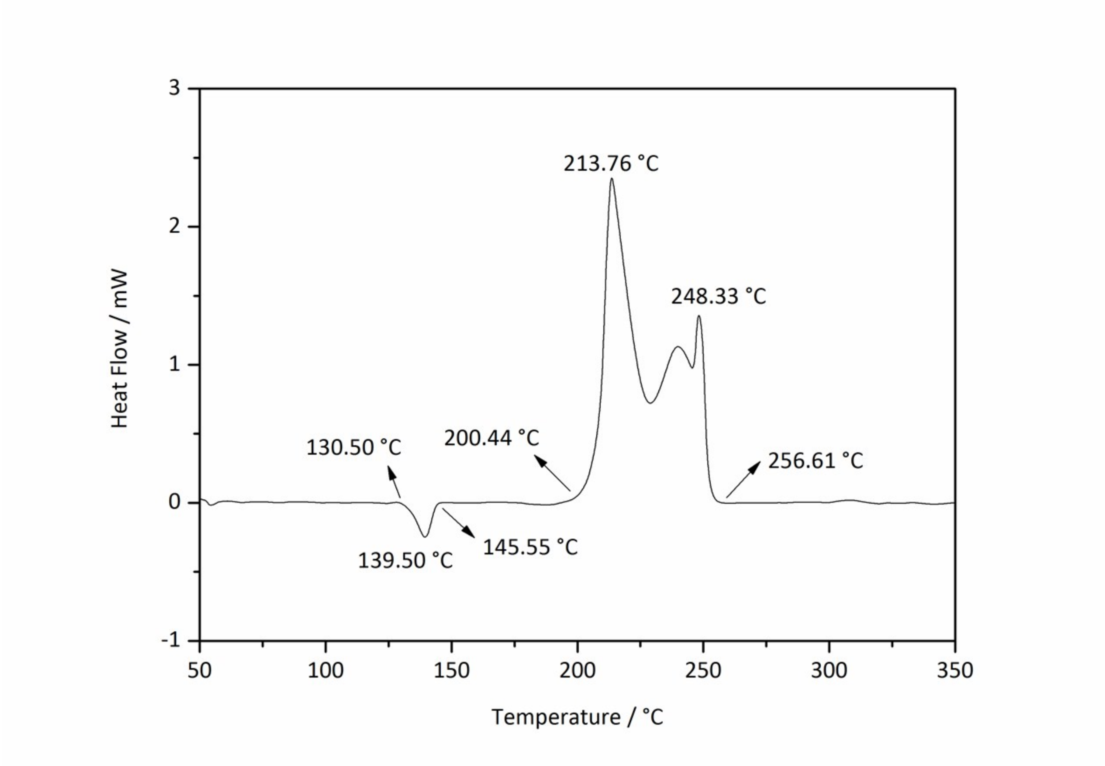


**Figure S68** DSC curve of compound **18**

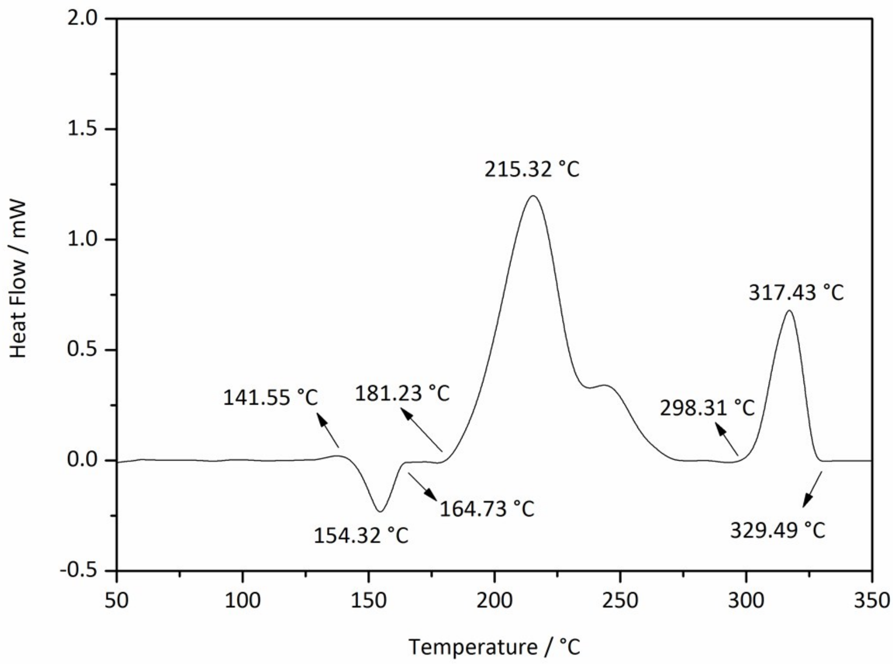


**Figure S69** DSC curve of compound **19**

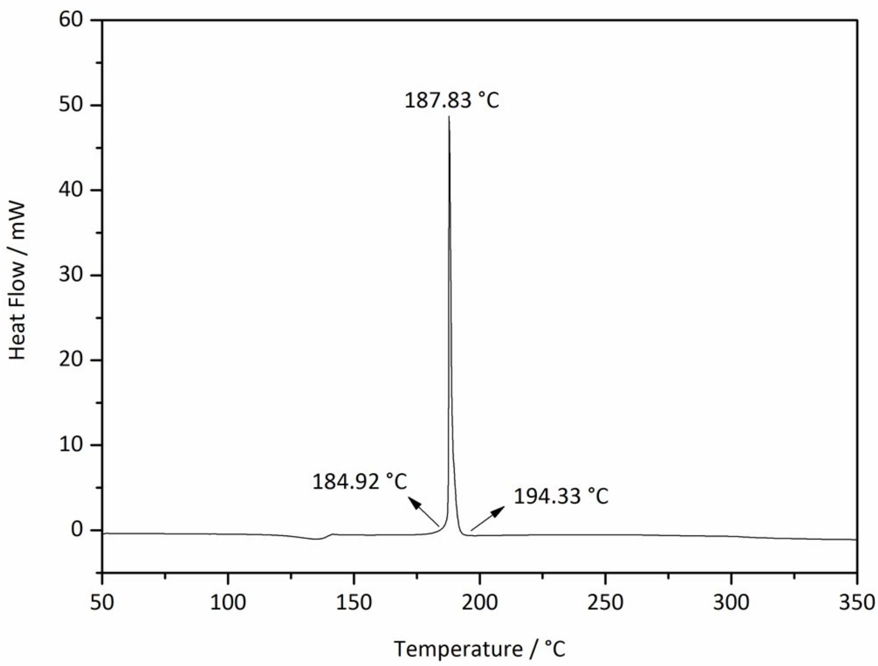


**Figure S70** DSC curve of compound **20**

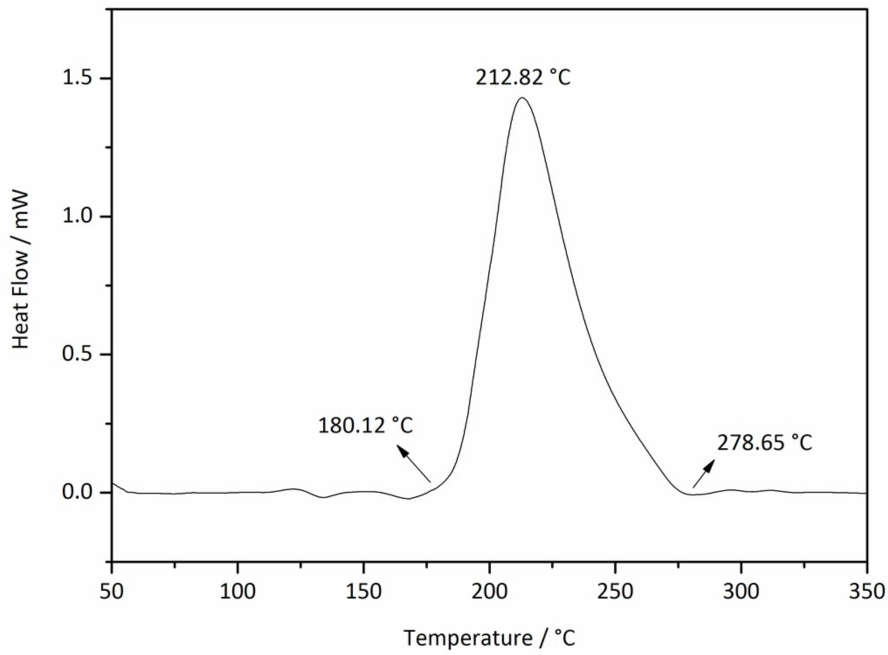


**Figure S71** DSC curve of compound **21**

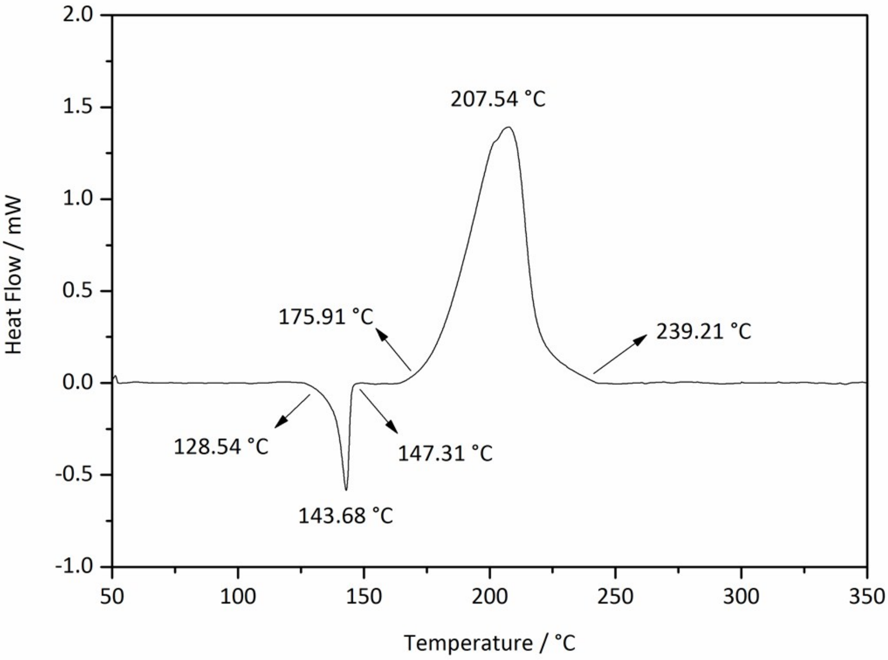


**Figure S72** DSC curve of compound **22**

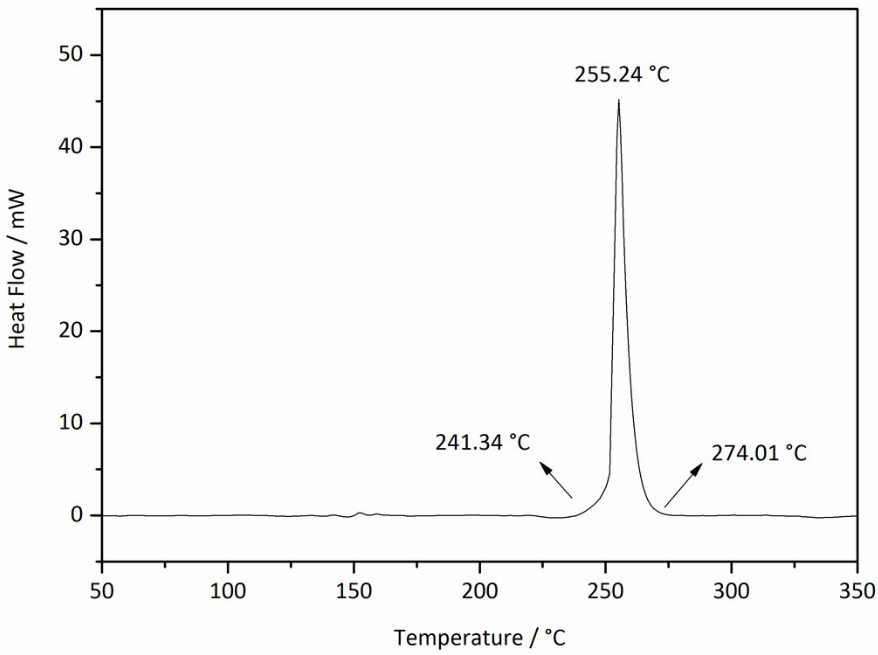


**Figure S73** DSC curve of compound **23**

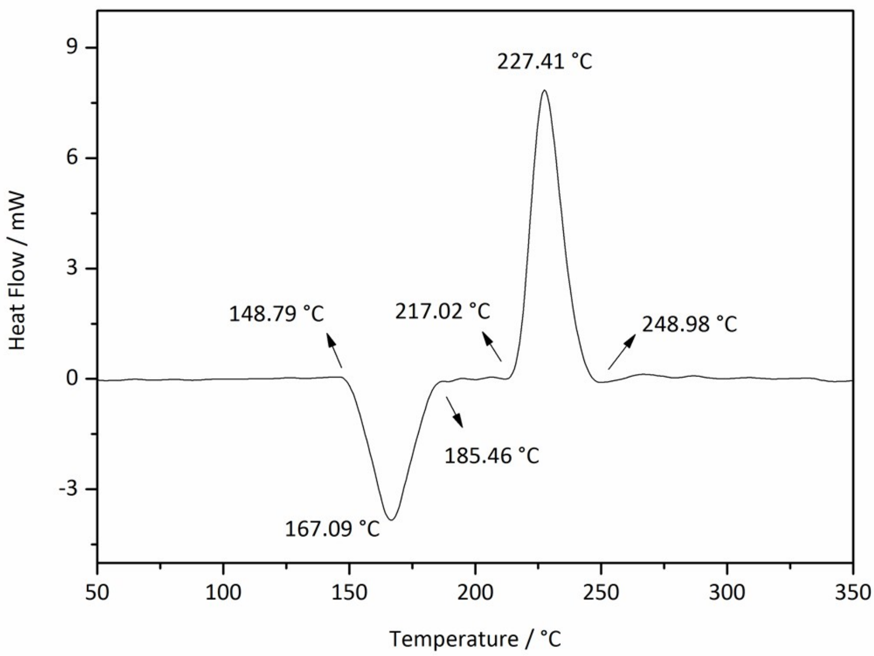


**Figure S74** DSC curve of compound **24**

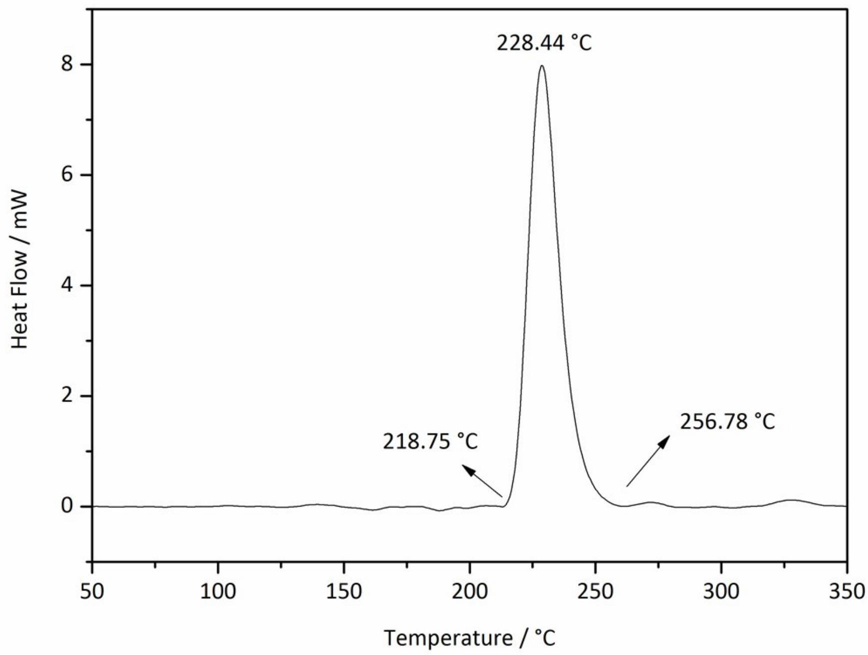


**Figure S75** DSC curve of compound **25**