

Supporting information

Carbon skeleton: route to investigate high-density insensitive energetic materials

Qian Wang, and Ming Lu*

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Experimental section

General Methods

All reagents were of analytical grade and were used without further purification. Elemental analyses were performed on a vario EL III CHNOS elemental analyzer. ^1H , ^{13}C NMR spectra were recorded on nuclear magnetic resonance spectrometer operating at 500 and 50.69 MHz, respectively. Chemical shifts in the ^1H and ^{13}C spectra were reported in ppm relative to TMS. The DSC spectra were obtained on a differential scanning calorimeter (Mettler Toledo DSC823e) at a heating rate of $5\text{ }^\circ\text{C min}^{-1}$. FT-IR spectra were obtained on a Thermo Nicolet iS10 spectrometer. Powder X-ray diffraction (PXRD) measurements were performed on a Bruker D8 Advance X-ray diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.5406\text{ \AA}$) radiation. The constant-volume energies of combustion of the samples were obtained from combustion calorimetry with an oxygen-bomb calorimeter (Parr 6200 CALORIMETER).

X-ray crystallography

The data for **3**, **4**, and **6** was collected with a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda=0.071073\text{ nm}$) at 172-173 K. 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). Empirical absorption corrections were applied by using the SADABS (v2008/1) program. The structures were solved by direct methods and refined by the full matrix least-squares based on F2 using SHELXTL--2014/7 (Sheldrick, 2014) programme package. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to ligands were generated geometrically and refined using a riding model.

Syntheses

Caution! Although all the fused compounds obtained here have a good sensitivity, they should be handled carefully. Some safety practices must be provided, such as face shield, leather gloves.

Sodium 2,5-dinitro-3,6-dioxocyclohexa-1,4-diene-1,4-bis(olate) (**2**)¹ was synthesized based on the reported method.

4-Amino-3,5-dinitrocyclopent-3-ene-1,2-dione (3): Compound **2** (0.274 g, 1.00 mmol) and hydroxylamine hydrochloride (0.209 g, 3.00 mmol) were suspended in 10mL water. The reaction system was heated to reflux and refluxed for 2 h. Then the resulting mixture was cooled to room temperature and filtered off. The filter cake was added to 5mL 50% HClO_4 and heated to $60\text{ }^\circ\text{C}$. The resulting solution was cooled and the crystals of **3** was formed. The precipitate was filtered off, washed with water and dried in air afford compound **3** (0.443 g, 0.61 mmol) in a yield of 61%. T_d : $130\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 4.96 (s, 1H), 9.61 (s, 2H) ppm. ^{13}C NMR (500 MHz, $\text{DMSO-}d_6$): δ 114.36, 163.25, 173.48 ppm. IR (KBr): $\tilde{\nu}$ 3544, 3554, 3388, 3258, 1702, 1631, 1405, 1267, 1231, 996, 683 cm^{-1} . Elemental analysis for $\text{C}_5\text{H}_3\text{N}_3\text{O}$ (201.09): calcd C 29.86, H 1.50, N 20.90%. Found: C 29.87, H 1.51, N 20.89%.

General procedure for the preparation of salts **4** to **6**

A solution of 28% aqueous ammonia (0.024 g, 1.37 mmol), 98% hydrazine monohydrate (0.511 g, 1.00 mmol), 50% aqueous hydroxylamine (0.661 mg, 1 mmol) in ethanol (2 mL) were slowly added under stirring to a solution of **3** (0.201 g, 1.00 mmol) in acetonitrile (5 mL) at $25\text{ }^\circ\text{C}$. After stirring for 2h, the precipitate was collected, washed with acetonitrile, and dried in air.

Ammonium 2-amino-1,3-dinitro-4,5-dioxocyclopent-2-en-1-ide (4): Yield: 0.203 g, 0.93 mmol, 93%. Yellow solid. T_d : $275\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 7.16 (s, 1H), 9.62 (s, 2H) ppm. ^{13}C NMR (500 MHz, $\text{DMSO-}d_6$): δ 114.34, 163.29, 173.52 ppm. IR (KBr): $\tilde{\nu}$ 3252, 1644, 1610, 1571, 1411, 1263, 1231, 1187, 995, 785, 769 cm^{-1} . Elemental analysis for $\text{C}_5\text{H}_6\text{N}_4\text{O}_6$ (218.13): calcd C 27.53, H 2.77, N 25.69%. Found: C 27.52, H 2.78, N 25.71%.

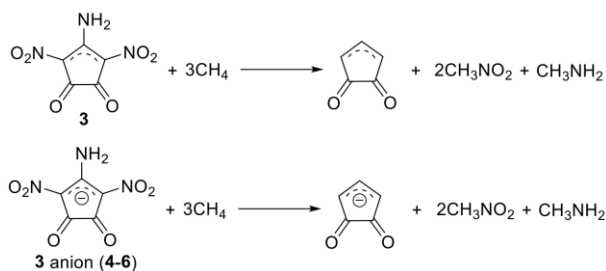
Hydrazinium 2-amino-1,3-dinitro-4,5-dioxocyclopent-2-en-1-ide (5): Yield: 0.214 g, 0.92 mmol, 92%. Yellow solid. T_d : $215\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 9.62 (s, 2H) ppm. ^{13}C NMR (500 MHz, $\text{DMSO-}d_6$): δ 114.73, 158.22, 171.52 ppm. IR (KBr): $\tilde{\nu}$ 3328, 3256, 3119, 1702, 1587, 1541, 1362, 1187, 1100, 990, 952, 767, 740, 679 cm^{-1} . Elemental analysis for $\text{C}_5\text{H}_7\text{N}_5\text{O}_6$ (233.13): calcd C 25.76, H 3.03, N 30.04%. Found: C 25.77, H 3.04, N 30.05%.

Hydroxylammonium 2-amino-1,3-dinitro-4,5-dioxocyclopent-2-en-1-ide (6): Yield: 0.208 g, 0.89 mmol, 89%. Yellow solid. T_d : $191\text{ }^\circ\text{C}$. ^1H NMR (500 MHz, $\text{DMSO-}d_6$): δ 9.62 (s, 2H), 10.13 (s, 4H) ppm. ^{13}C NMR (500 MHz, $\text{DMSO-}d_6$): δ 114.33, 163.28, 173.51 ppm. IR (KBr): $\tilde{\nu}$ 3367, 3244, 3208, 3073, 1568, 1421, 1351, 1235, 1189, 1013, 988, 916, 804, 768, 682 cm^{-1} . Elemental analysis for $\text{C}_5\text{H}_6\text{N}_4\text{O}_7$ (234.12): calcd C 25.65, H 2.58, N 23.93%. Found: C 25.64, H 2.59, N 23.94%.

Computational Details

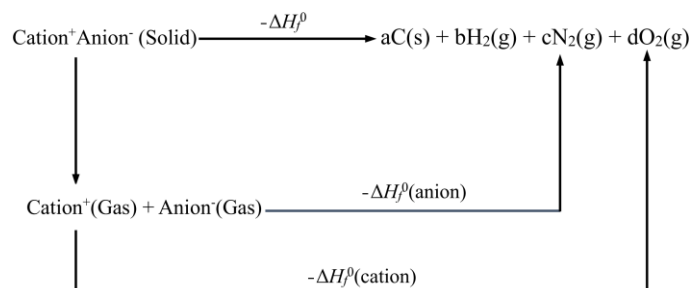
Computations were performed by using the Gaussian09 suite of programs.¹ The elementary geometric optimization and the frequency analysis were performed at the level of the Becke three parameter, Lee-Yan-Parr (B3LYP)² functional with the 6-311++G** basis set.³ All of the optimized structures were characterized to be local energy minima on the potential surface without any imaginary frequencies. Atomization energies were calculated by the CBS-4M.⁴ 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 of compounds **3-6** are shown in Scheme S1.



Scheme S1. Isodesmic reactions for calculating heats of formation for **3-6**.

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Scheme S2).⁵ The number is simplified by equation 1:



Scheme S2. Born-Haber Cycle for the formation of energetic salts.

$$\Delta H_f^\circ (\text{salt}, 298 \text{ K}) = \Delta H_f^\circ (\text{cation}, 298 \text{ K}) + \Delta H_f^\circ (\text{anion}, 298 \text{ K}) - \Delta H_L \quad (1)$$

where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al. [Eq. (2)]

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

where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-} , 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 U_{POT} [Eq. (3)] has the form:

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

where ρ_m [g cm^{-3}] is the density of the salt, M_m is the chemical formula mass of the ionic material, and values for γ and δ (kJ mol^{-1}) are assigned literature values.⁵

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

Compound	ZPE/au	H _T /au	E ₀ /au	HOF/kJ mol ⁻¹
3	0.099288	0.013226	-807.748	-172.182
3 anion	0.087172	0.012695	-807.283	-161.881
CH ₄	0.043894	0.003821	-40.5262	-74.6
cyclopent-3-ene-1,2-dione	0.077115	0.006864	-343.3688494	-141.1
4,5-dioxocyclopent-2-en-1-ide	0.063677	0.006698	-342.8152746	100
CH ₃ NH ₂	0.062724	0.004419	-95.872	-23
CH ₃ NO ₂	0.048858	0.00534	-245.029	-74.3

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature,⁶ the heat of sublimation can be estimated with Trouton's rule according to supplementary equation 1, where T represents either the melting point or the decomposition temperature when no melting occurs prior to decomposition:

$$\Delta H_{\text{sub}} = 188 \text{ J mol}^{-1} \text{ K}^{-1} \times T$$

Crystallographic data for **3**, **4** and **6**

Table S2 Crystallographic data of **3**, **4** and **6**.

Compd.	3	4	6
CCDC number	1945173	1945174	1945175
formula	C ₅ H ₅ N ₃ O ₇	C ₅ H ₅ N ₄ O ₇	C ₅ H ₆ N ₄ O ₇

Mw	219.12	236.15	234.14
crystal system	Monoclinic	orthorhombic	monoclinic
space group	<i>C</i> 2	<i>P</i> ca21	<i>P</i> 21
a [Å]	7.259(4)	14.319(2)	7.2036(5)
b [Å]	7.067(4)	9.3621(14)	7.0213(5)
c [Å]	8.126(4)	6.8195(9)	8.3381(5)
α [°]	90	90	90
β [°]	101.221(15)	90	104.364(2)
γ [°]	90	90	90
V [Å ³]	408.9(4)	914.2(2)	408.55(5)
Z	2	4	2
T [K]	296(2)	296(2)	296(2)
λ [Å]	0.71073	0.71073	0.71073
ρ_{calcd} [g cm ⁻³]	1.780	1.716	1.903
μ [mm ⁻¹]	0.170	0.161	0.180
<i>F</i> (000)	224	488	240
θ range [°]	2.555–27.473	2.599–27.567	2.919–27.402
Data/restraints/parameter	864/5/74	2059/1/145	1794/1/149
S	1.063	1.061	1.081
R ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0609(628)	0.0382(1622)	0.0300(1652)
wR ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.1395(864)	0.0907(2059)	0.0799(1794)

Table S3 Selected bond lengths [Å] and angles [°] for compound **3**.

C1-N1	1.399(7)	N1-C1-C3	124.6(5)
C1-C3	1.419(8)	N1-C1-C2	124.8(4)
C1-C2	1.430(7)	C3-C1-C2	110.6(5)
C2-N2	1.308(10)	N2-C2-C1	126.0(3)
C3-O3	1.223(6)	N2-C2-C1	126.0(3)
C3-C3	1.557(8)	C1-C2-C1	108.0(6)
N1-O2	1.232(7)	O3-C3-C1	132.7(4)
N1-O1	1.248(6)	O3-C3-C3	121.8(3)
N2-H2A	0.8600	C1-C3-C3	105.4(3)
N2-H2B	0.8600	O2-N1-O1	122.1(5)
O4-H4A	0.88(2)	O2-N1-C1	118.9(5)
O4-H4B	0.85(3)	O1-N1-C1	119.0(5)
O4-H4A	0.88(2)	C2-N2-H2A	120.0
H4A-O4-H4B	110(4)	C2-N2-H2B	120.0
H4A-O4-H4A	140(8)	H2A-N2-H2B	120.0
H4B-O4-H4A	110(4)		

Table S4 Hydrogen bonds present in compound **3**.

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°
N2-H2B...O1	0.86	2.14	2.731(5)	125.4
N2-H2B...O3	0.86	2.19	2.887(7)	138.1
N2-H2A...O1	0.86	2.14	2.731(5)	125.4
N2-H2A...O3	0.86	2.19	2.887(7)	138.1
O4-H4A...O2	0.88(2)	2.57(6)	3.021(8)	113(5)
O4-H4A...O3	0.88(2)	1.97(3)	2.832(4)	167(6)
O4-H4B...O1	0.85(3)	2.420(18)	3.038(7)	130.3(5)
O4-H4B...O1	0.85(3)	2.420(18)	3.038(7)	130.3(5)

Table S5 Selected bond lengths [Å] and angles [°] for compound **4**.

C1-N1	1.387(3)	N1-C1-C5	125.2(2)
C1-C5	1.421(3)	N1-C1-C2	124.2(2)
C1-C2	1.432(4)	C5-C1-C2	110.6(2)
C2-N3	1.308(3)	N3-C2-C3	126.6(3)
C2-C3	1.428(4)	N3-C2-C1	125.1(3)
C3-N2	1.389(3)	C3-C2-C1	108.3(2)
C3-C4	1.430(4)	N2-C3-C2	124.6(2)
C4-O5	1.219(3)	N2-C3-C4	125.2(3)
C4-C5	1.557(4)	C2-C3-C4	110.1(2)
C5-O6	1.224(3)	O5-C4-C3	132.8(2)
N1-O2	1.248(3)	O5-C4-C5	121.6(2)
N1-O1	1.248(3)	C3-C4-C5	105.6(2)
N2-O4	1.238(3)	O6-C5-C1	132.7(3)
N2-O3	1.252(3)	O6-C5-C4	121.9(2)
N3-H3A	0.8600	C1-C5-C4	105.4(2)
N3-H3B	0.8600	O2-N1-O1	121.1(2)
N4-H4A	0.8968	O2-N1-C1	119.5(2)
N4-H4B	0.9454	O1-N1-C1	119.4(2)
N4-H4C	0.9567	O4-N2-O3	121.3(2)
N4-H4D	0.9249	O4-N2-C3	119.7(2)
O7-H7A	0.8940	O3-N2-C3	119.0(2)
O7-H7B	0.8842	C2-N3-H3A	120.0

Table S6 Hydrogen bonds present in compound 4.

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°
N3-H3A...O3	0.86	2.14	2.728(3)	124.8
N3-H3A...O6	0.86	2.31	3.025(3)	141.1
N3-H3B...O2	0.86	2.11	2.702(3)	125.6
N3-H3B...O5	0.86	2.43	2.941(3)	118.8
N4-H4A...O7	0.90	1.93	2.822(3)	175.1
N4-H4B...O7	0.95	1.89	2.826(4)	170.4
N4-H4C...O1	0.96	2.34	2.899(3)	116.4
N4-H4C...O6	0.96	2.04	2.943(3)	156.2
N4-H4D...O4	0.92	2.18	3.061(3)	158.3
O7-H7A...O5	0.89	1.88	2.751(3)	163.2
O7-H7B...N1	0.88	2.61	3.396(3)	149.4
O7-H7B...O1	0.88	2.05	2.933(3)	175.2

Table S7 Selected bond lengths [Å] and angles [°] for compound 6.

C1-N1	1.297(3)	C3-C2-C1	110.11(18)
C1-C5	1.430(3)	O1-C3-C2	131.73(18)
C1-C2	1.436(3)	O1-C3-C4	122.63(19)
C2-N2	1.369(3)	C2-C3-C4	105.64(17)
C2-C3	1.427(3)	O2-C4-C5	131.68(18)
C3-O1	1.224(3)	O2-C4-C3	122.85(18)
C3-C4	1.558(3)	C5-C4-C3	105.47(17)
C4-O2	1.216(3)	N3-C5-C4	125.1(2)
C4-C5	1.427(3)	N3-C5-C1	124.47(19)
C5-N3	1.382(3)	C4-C5-C1	110.43(18)
N1-H1A	0.8600	C1-N1-H1A	120.0
N1-H1B	0.8600	C1-N1-H1B	120.0
N2-O4	1.249(3)	H1A-N1-H1B	120.0
N2-O3	1.256(3)	O4-N2-O3	120.7(2)
N3-O5	1.239(3)	O4-N2-C2	119.0(2)
N3-O6	1.250(3)	O3-N2-C2	120.3(2)
N4-O7	1.401(2)	O5-N3-O6	121.5(2)
N4-H4B	0.8900	O5-N3-C5	119.1(2)
N4-H4A	0.8900	O6-N3-C5	119.4(2)
N4-H4C	0.8900	O7-N4-H4B	109.5
O7-H7	1.06(4)	O7-N4-H4A	109.5
N1-C1-C5	126.05(18)	H4B-N4-H4A	109.5
N1-C1-C2	125.65(19)	O7-N4-H4C	109.5
C5-C1-C2	108.30(19)	H4B-N4-H4C	109.5
N2-C2-C3	125.5(2)	H4A-N4-H4C	109.5
N2-C2-C1	124.39(19)	N4-O7-H7	104.6(19)

Table S8 Hydrogen bonds present in compound 6.

D-H...A	D-H/Å	H...A/Å	D...A/Å	D-H...A/°
O7-H7...4	1.06(4)	1.72(4)	2.695(2)	150(3)
O7-H7...N2	1.06(4)	2.53(3)	3.425(3)	142(3)
N4-H4C...O6	0.89	2.39	3.090(3)	135.4
N4-H4C...O3	0.89	2.43	3.012(3)	123.6
N4-H4A...O5	0.89	2.32	3.038(3)	137.7
N4-H4A...O2	0.89	2.12	2.823(2)	135.5
N4-H4B...O4	0.89	2.43	2.911(3)	114.5
N4-H4B...O1	0.89	2.08	2.918(2)	157.3

IR and NMR spectra

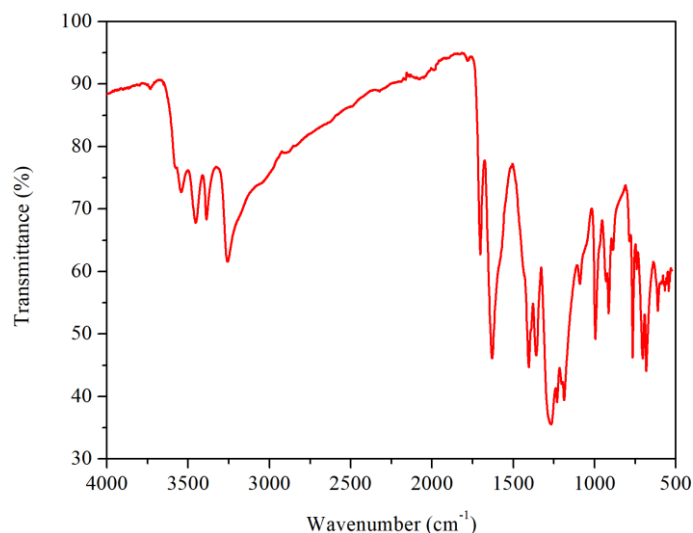


Fig. S1 IR spectra for 3.

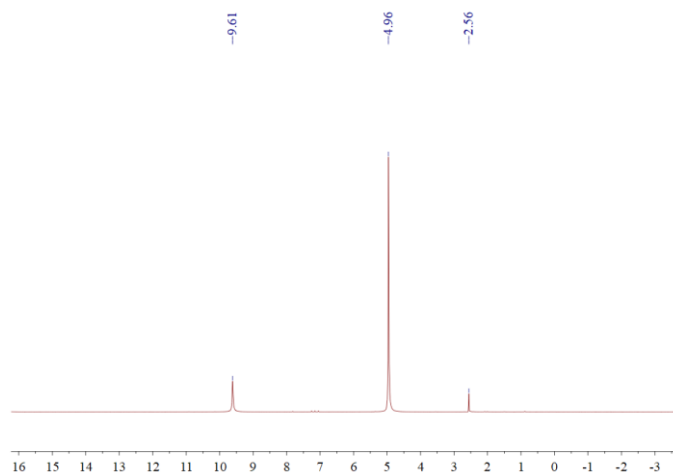


Fig. S2 ¹H NMR spectra in DMSO-*d*₆ for 3.

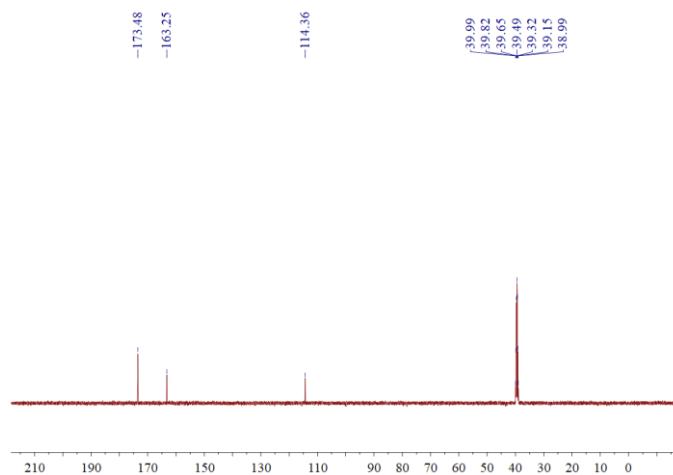


Fig. S3 ¹³C NMR spectra in DMSO-*d*₆ for 3.

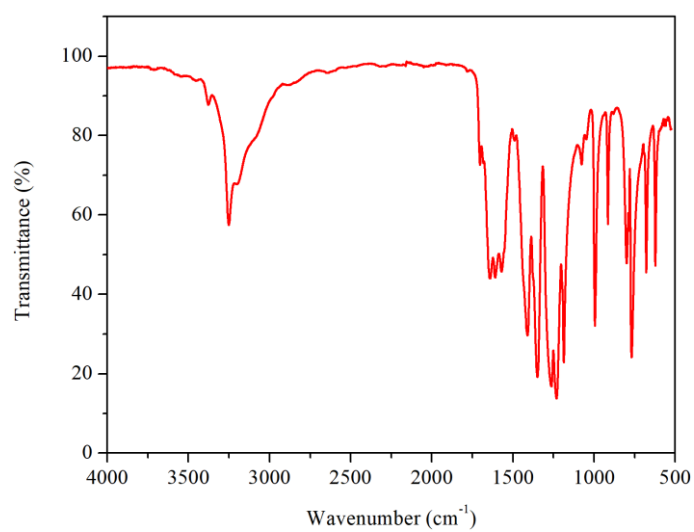


Fig. S4 IR spectra for 4.

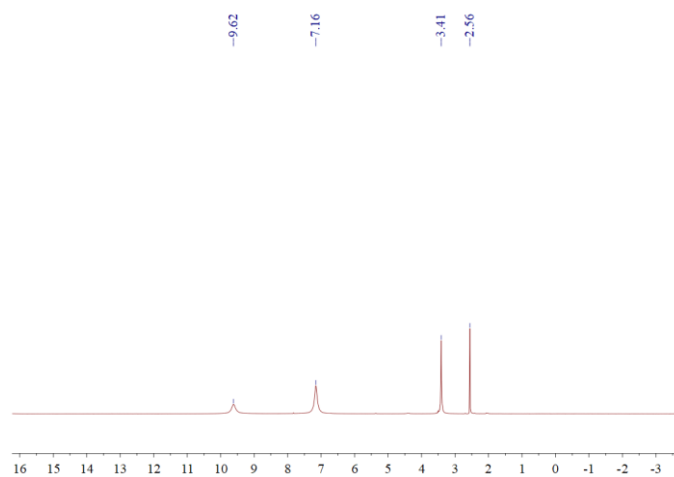


Fig. S5 ^1H NMR spectra in $\text{DMSO-}d_6$ for **4**.

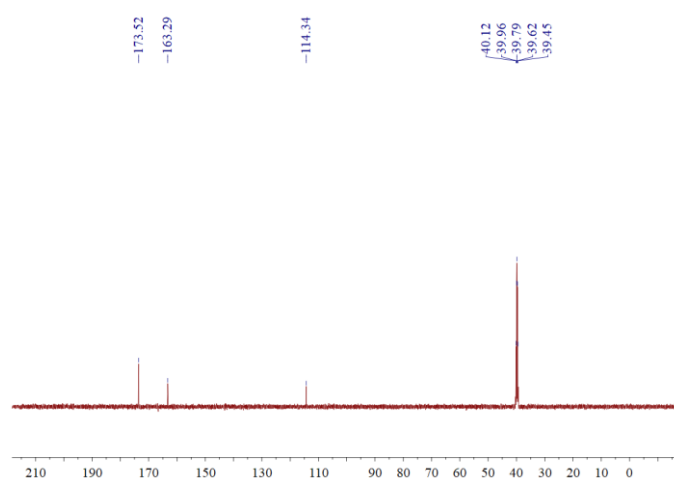


Fig. S6 ^{13}C NMR spectra in $\text{DMSO-}d_6$ for **4**.

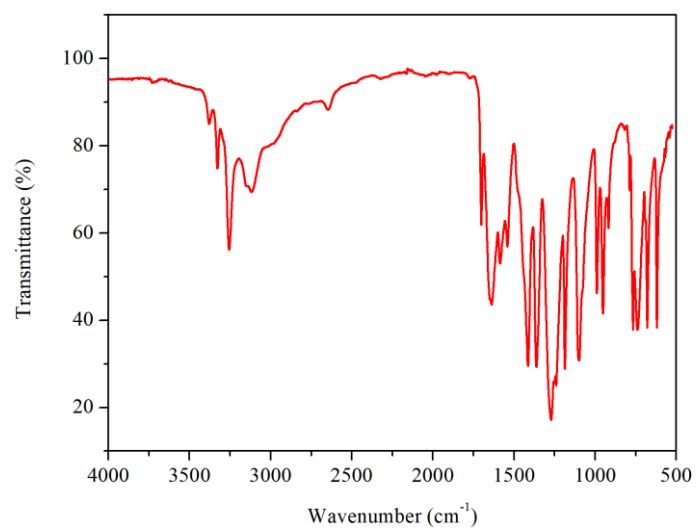


Fig. S7 IR spectra for **5**.

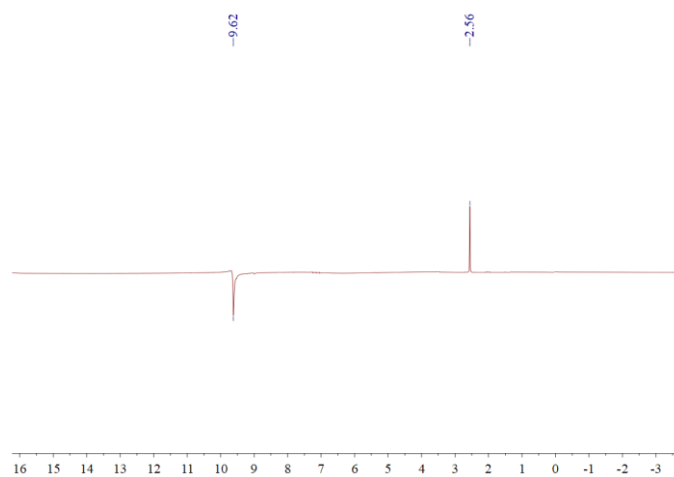


Fig. S8 ^1H NMR spectra in $\text{DMSO-}d_6$ for **5**.

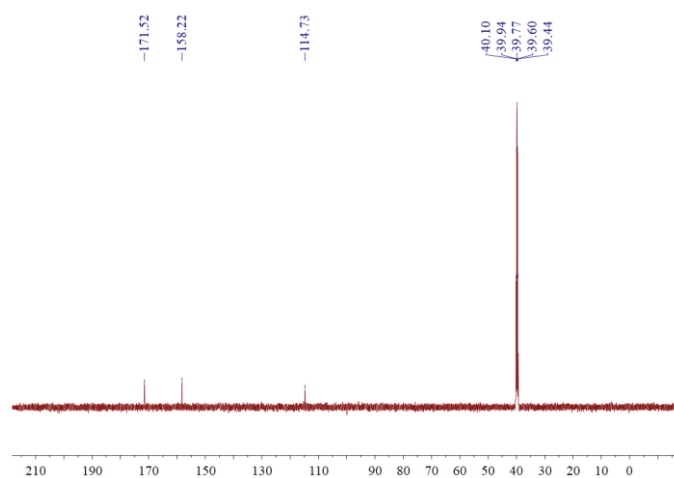


Fig. S9 ^{13}C NMR spectra in $\text{DMSO-}d_6$ for **5**.

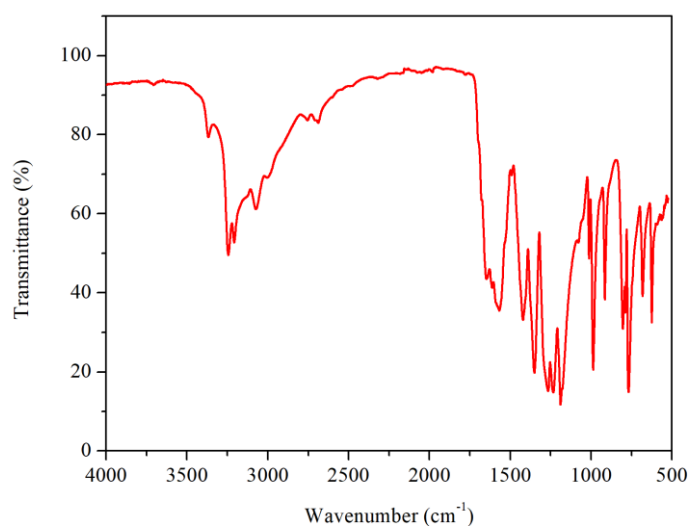


Fig. S10 IR spectra for **6**.

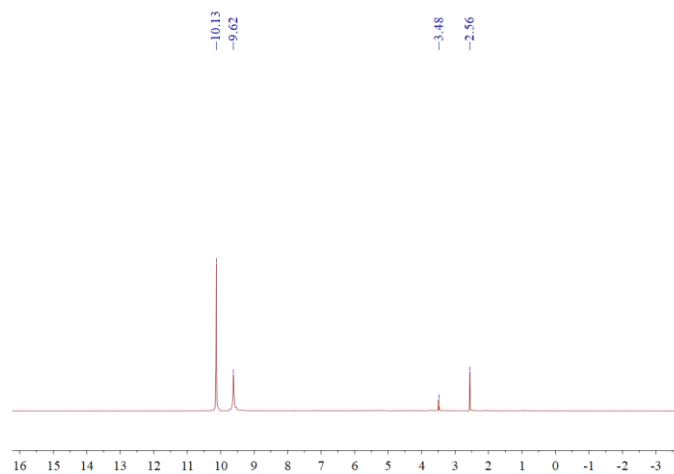


Fig. S11 ^1H NMR spectra in $\text{DMSO-}d_6$ for **6**.

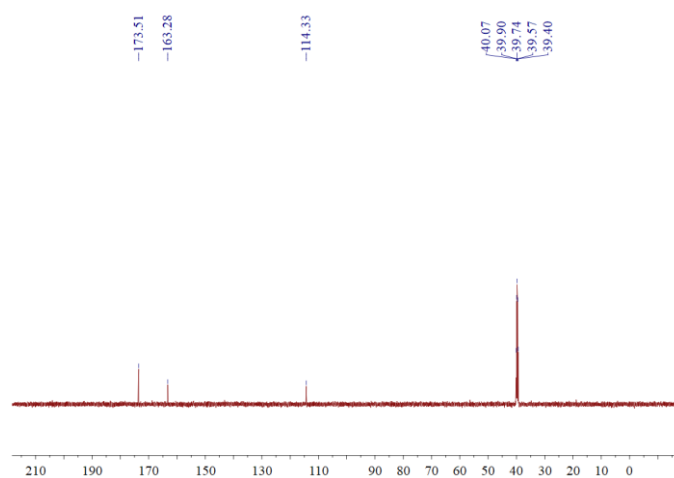


Fig. S12 ^{13}C NMR spectra in $\text{DMSO-}d_6$ for **6**.

DSC curves

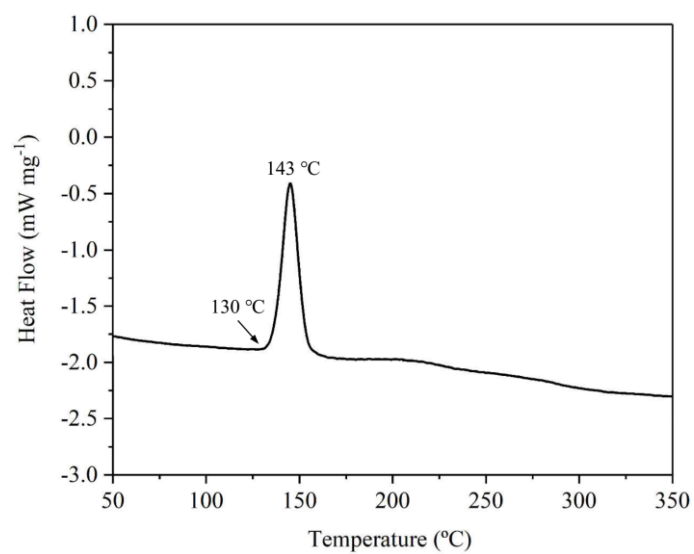


Fig. S13 DSC plot of **3** measured at a heating rate of $5\text{ }^{\circ}\text{C min}^{-1}$ (exo up).

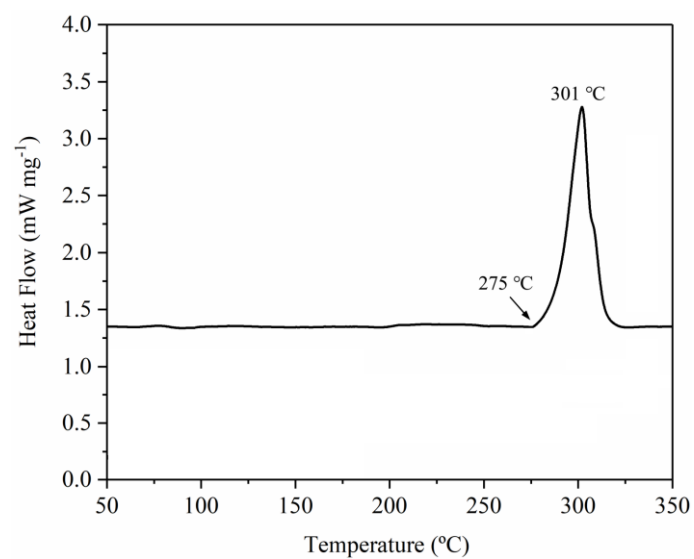


Fig. S14 DSC plot of **4** measured at a heating rate of 5 °C min⁻¹ (exo up).

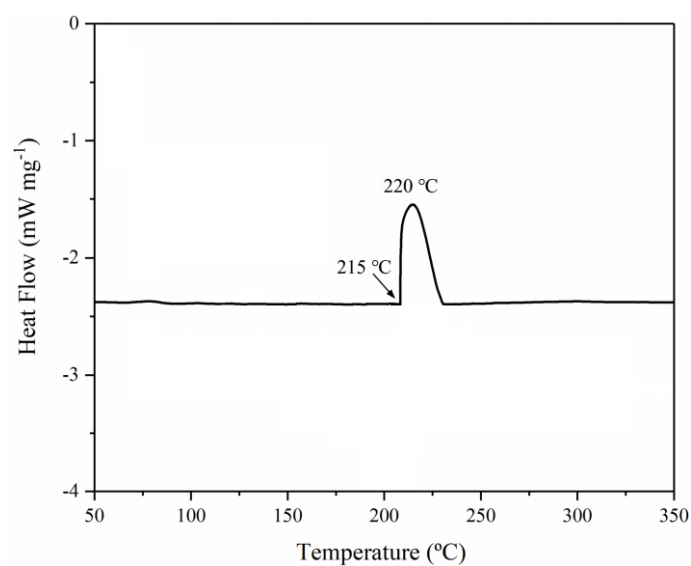


Fig. S15 DSC plot of **5** measured at a heating rate of 5 °C min⁻¹ (exo up).

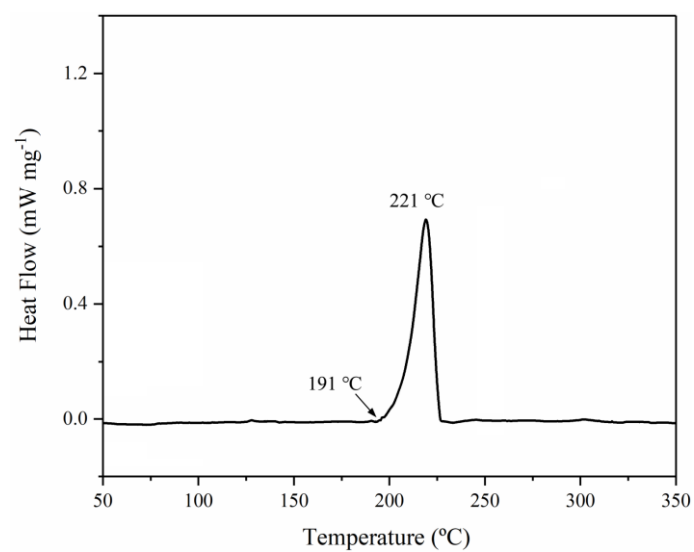


Fig. S16 DSC plot of **6** measured at a heating rate of 5 °C min⁻¹ (exo up).

References

- 1 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle and J. A. Pople, Gaussian 09, revision A. 01; Gaussian, Inc.: Wallingford, CT, 2009.
- 2 (a) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648–5652; (b) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623-11627.
- 3 P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta.*, 1973, **28**, 213-222.
- 4 J. W. Ochterski, G. A. Petersson, J. A. Montgomery, *J. Chem. Phys.*, 1996, **104**, 2598-2619.
- 5 H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.*, 2002, **41**, 2364-2367
- 6 (a) F. Trouton and Philos. Mag. 1884, **18**, 54-57; (b) M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, *J. Am. Chem. Soc.*, 1995, **117**, 5013-5015.