

Supporting Information

Synthesis and Characteristics of High-Nitrogen 1,2,4-Oxadiazoles

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General.....	S1
AOG, AOG ₂ Tz.....	S2
MOPAC calculation of AOG, AOG ₂ Tz.....	S2
Spectra of AOG, AOG ₂ Tz.....	S4

General

¹H and ¹³C NMR spectra are recorded on Bruker Advance 400 spectrometer at 400 and 100 MHz, respectively. Chemical shifts are reported in ppm relative to TMS. The solvent is [D₆]dimethyl sulfoxide (DMSO-*d*₆) unless otherwise specified. The melting, decomposition points is recorded with the peak value on a METTLER TOLEDO differential scanning calorimeter at a scan rate of 10 °C min⁻¹, IR spectra is recorded on IR-408 using KBr pellets. ESI-MS is recorded and analyzed on Agilent 500-MS, Bruker Apex IV FTMS and Bruker Compass Data Analysis 4.0. NOG and BT are prepared refereeing to reported methods. Other materials are purchased from from Alfa Aesar. The crystal density is calculated by a patented method.¹

3-azido-5-guanidino-1,2,4-oxadiazole (AOG)

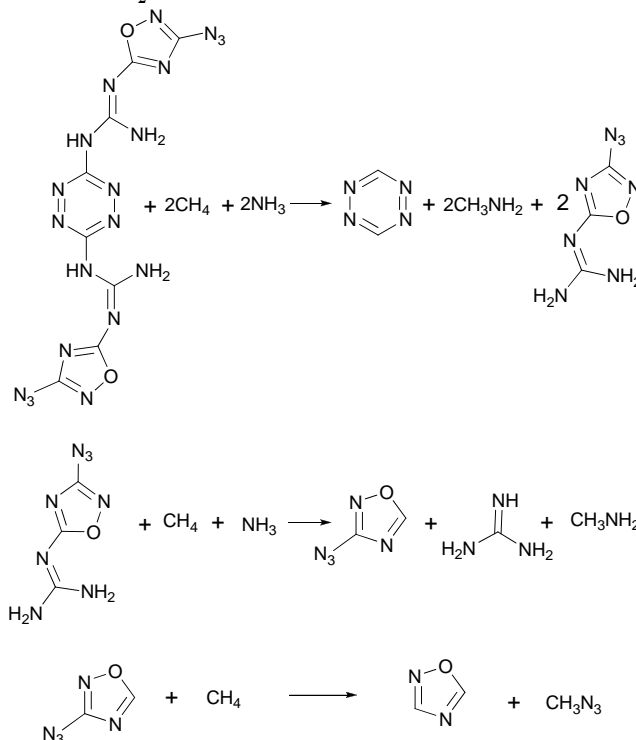
To a solution of DMSO (4 mL), H₂O (1 mL) and NaN₃ (195 mg, 3 mmol) is added NOG (344 mg, 2 mmol). The mixture is stirred with an overhead stirrer, heated to 50 °C for 5 h. The reaction is then poured into ice water (10 mL), the pale yellow precipitate is filtered, washed thoroughly with water and dried to give the product solid (120 mg, 36%). *T*_{dec.}: 196 °C. ¹H NMR (400 MHz, DMSO-*d*₆, TMS): δ_H 7.14(NH₂). ¹³C NMR (100 MHz, DMSO-*d*₆, TMS): δ_C 174.6, 163.5, 159.8. IR (KBr): 3433, 3391, 3230, 3103, 2160, 1673, 1580, 1537, 1420, 1214, 974, 766, cm⁻¹. Anal. Calcd for C₃H₄N₈O, 168: C, 21.43; H, 2.37; N, 66.65; Found: C, 21.60; H, 2.37; N, 66.52.

3,6-bis(3'-azido-1',2',4'-oxadiazole-5'-guanyl)- 1,2,4,5-tetrazine (AOG₂Tz)

AOG (252 mg, 1.5 mmol) is placed in an oven dried round-bottomed flask (50 mL) with a stir bar and dissolved in anhydrous dimethylformamide (20 mL). The solution is cooled to 0 °C and NaH (60% dispersion in oil, 92 mg, 3.3 mmol) is added portionwise over 5 min. The reaction is stirred for 30 min at 0 °C and BT (162 mg, 0.6 mmol) is added in one portion. The reaction is stirred at 0 °C for 1 h and then allowed to warm to room temperature for 4 h. The reaction is then poured into ice water (20 mL) and acidified to pH=1 by the addition of 3 N HCl. The brown-red precipitate is filtered, washed thoroughly with water and dried to give AOG₂Tz (240 mg, 96.7%). *T*_{dec.}: 210 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ_H 12.14 (bs, 2H), 9.05 (bs, 2H), 8.80(bs, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ_C 154.9, 158.6, 164.0, 174.0. IR (KBr): 3372, 3262, 3212, 2153, 1635, 1538, 1367, 1294, 1194, 1050, 774, 610, cm⁻¹. HRMS-ESI (414.1055): *m/z* positive mode, 415.1058 [M+H]⁺.

Calculated total energy (E0), zero-point energy (ZPE), enthalpy of formation (HOF) of compound AOG and AOG₂Tz

Isodesmic reactions for compound AOG and AOG₂Tz



First, we calculated the heat of formation of each molecule according to following formulation:

heat of formation of each molecule at 0K:

$$\Delta_f H^0(M, 0K) = \sum_{atoms} x \Delta_f(X, 0K) - \sum D_0(M)$$
$$= \sum_{atoms} x \Delta_f(X, 0K) - \left(\sum_{atoms} x \varepsilon_0(X) - \varepsilon_0(M) - \varepsilon_{zpe}(M) \right)$$

Here, M represents the molecule, X represents atom.

Here, except the enthalpy of atom, other energy all are calculated by first-principle. The Experimental enthalpy values of atom are taken from J. Chem. Phys. **106**, 1063 (1997).

Heat of formation of each molecule at 298K:

$$\Delta_f H^0(M, 298K) = \Delta_f H^0(M, 0K) + (H_M^0(298K) - H_M^0(0K))$$
$$- \sum_{atoms} x (H_X^0(298K) - H_X^0(0K))$$

Here, (H(298K)-H(0)) are thermal correction of the heat of formation for molecule or atom, respectively.

Second, we calculated the reaction enthalpy of isodesmic reactions. It equals to the enthalpy difference between the substrate and product.

We also calculated heat of formation for some small molecule, such as CH₄. Our calculated formation of heat also is agreement well with experiment.

For more information on the calculation formulation, you can refer the webpage:
http://www.gaussian.com/g_whitepap/thermo.htm#SECTION00053000000000000000

All the calculations are done at the semi-empirical level using the PM6 method² implemented in the MOPAC package³. The heat of formation is obtained at the room temperature (298.15K) through the atomization reaction.

Table S1 Calculated heats of formation by MOPAC

Compd.	E ₀ /ev	ZPE/ev	HOF/(KJ mol ⁻¹)
AOG	-2367.64277	2.60549941449	235.07941
AOG₂Tz	-5667.81698	5.60450188663	957.34882

References

1. Y.-K. Wu, D.-Y. Chen, H.-S. Dong, *Chinese Patent*, 2011, CN101957300A.
2. J. J. P. Stewart, *J. Mol. Modeling*, 2007, **13**, 1173-1213.
3. MOPAC2009, J. J. P. Stewart, *Stewart Computational Chemistry*, Colorado Springs: CO, USA, [HTTP://OpenMOPAC.net](http://OpenMOPAC.net) (2008).

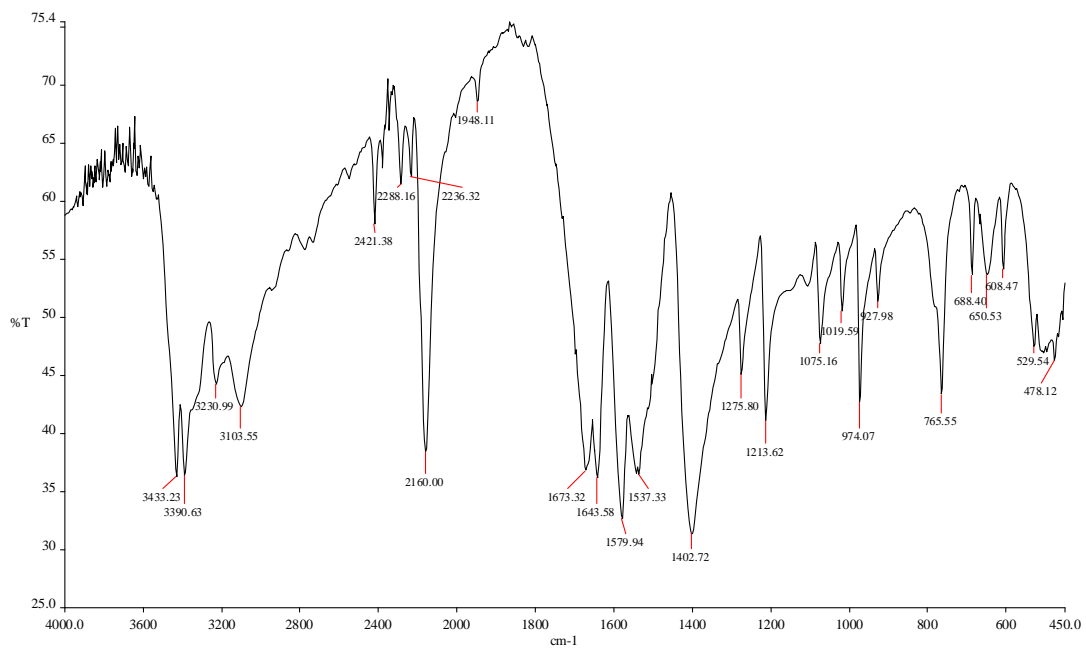


Figure S1 IR spectra of of AOG

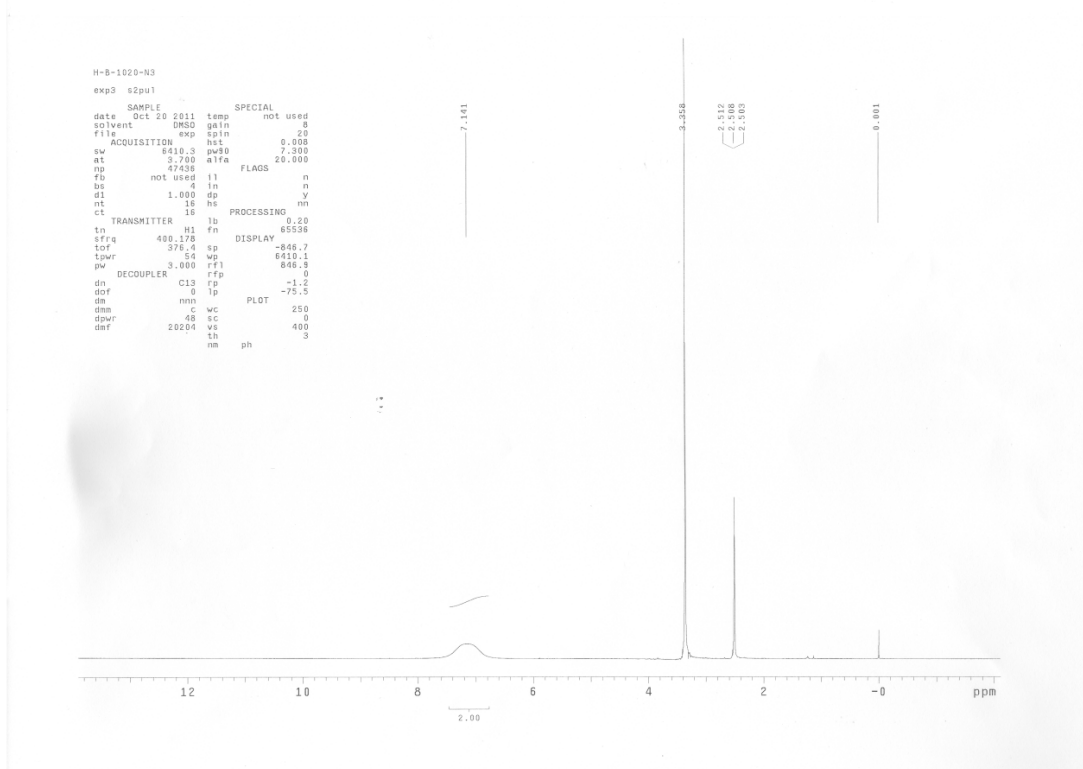


Figure S2 ¹H NMR of AOG

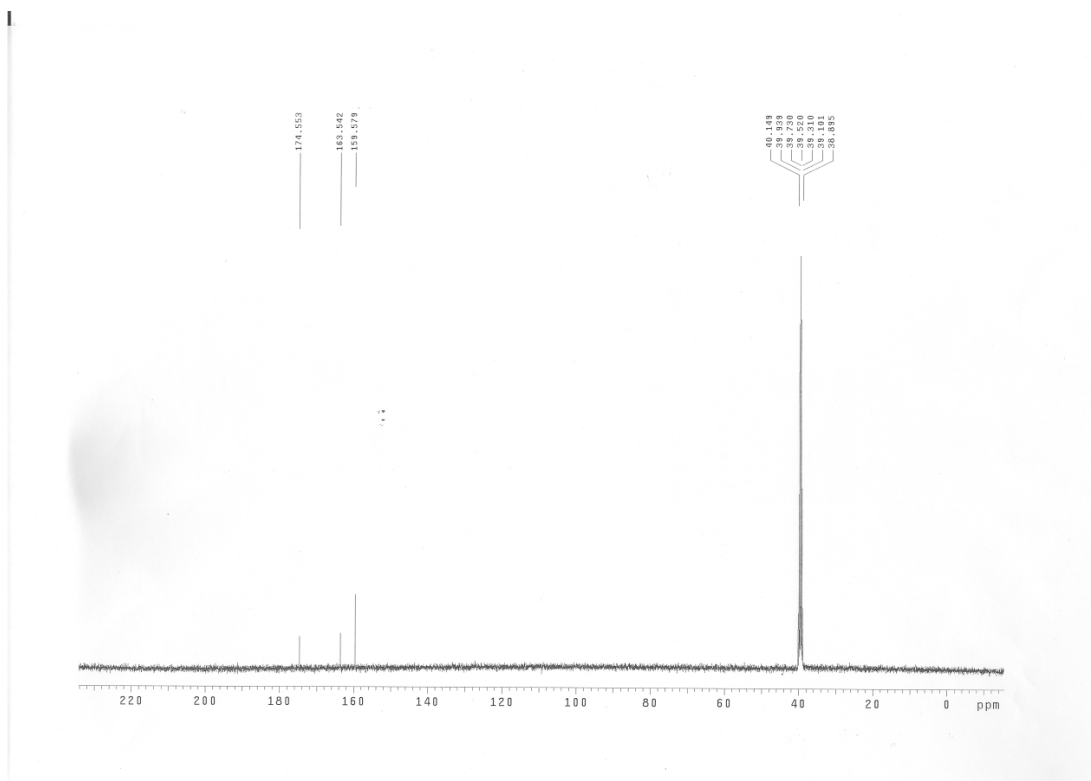


Figure S3 ^{13}C NMR of AOG

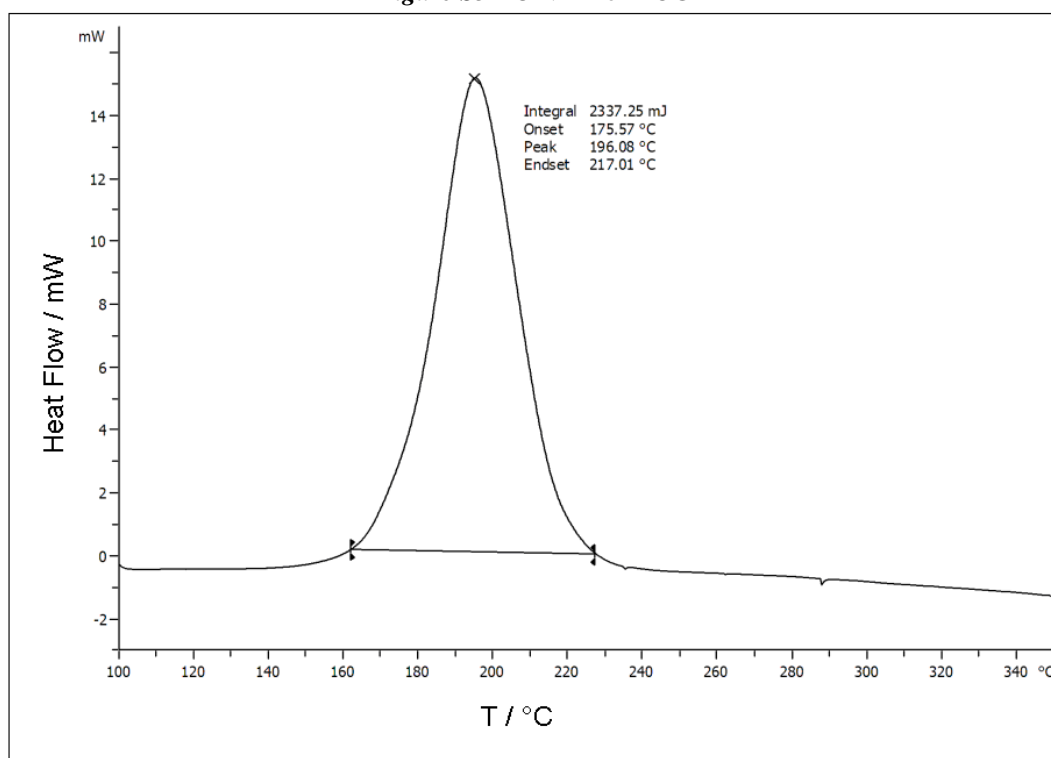


Figure S4 DSC of AOG

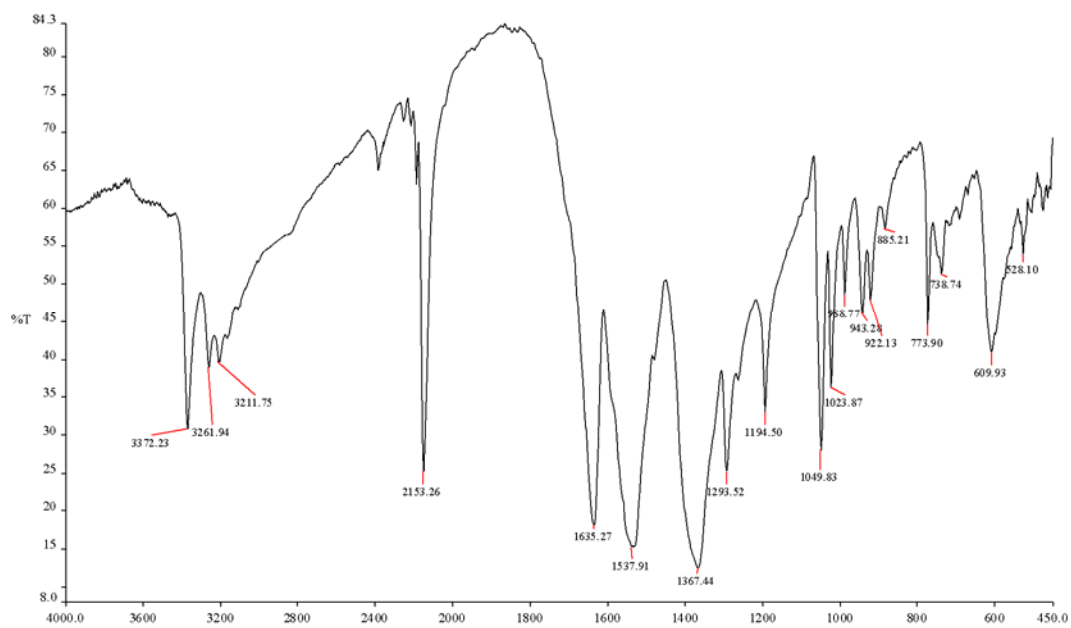


Figure S5 IR spectra of of AOG₂Tz

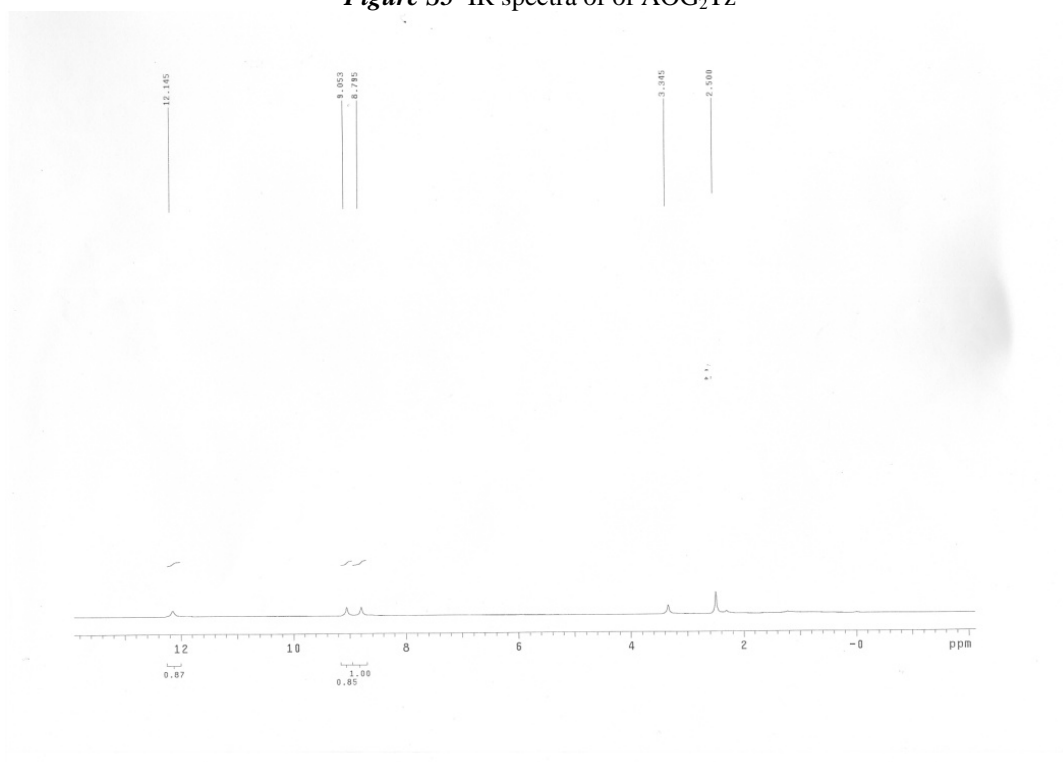


Figure S6 ¹H NMR of AOG₂Tz

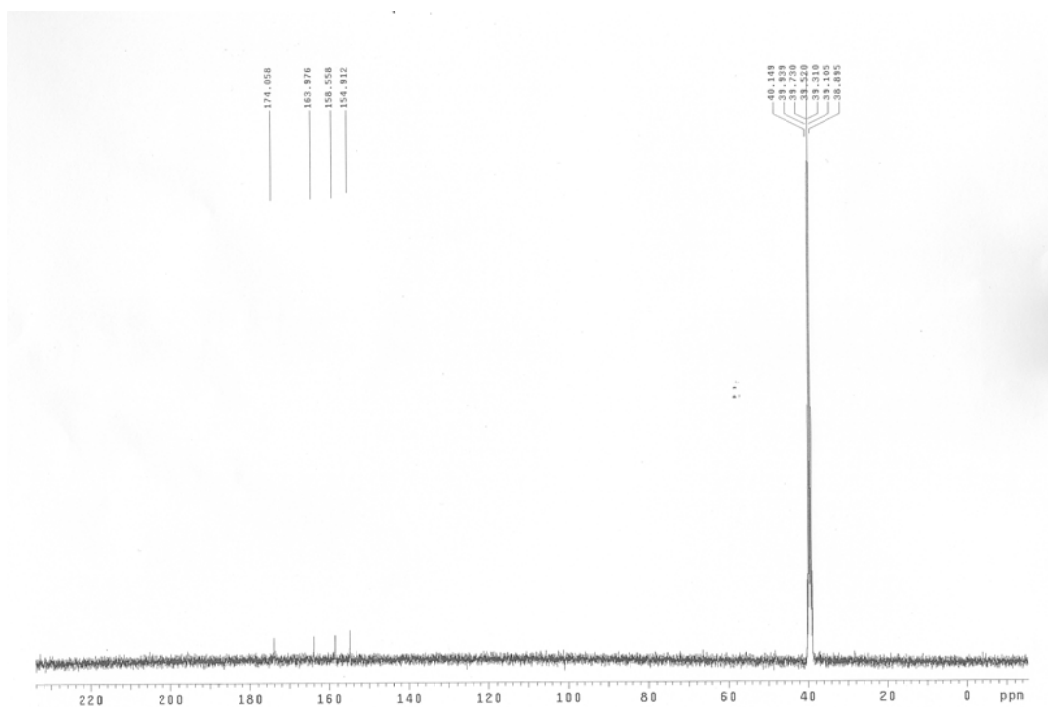


Figure S7 ^1H NMR of AOG₂Tz

Peking University Mass Spectrometry Sample Analysis Report

Analysis Info		Acquisition Date	11/21/2011 4:14:42 PM
Analysis Name	11110869_20111121_000001.d	Instrument	Bruker Apex IV FTMS
Sample	AOG ₂ Tz	Operator	Peking University
Comment	ESI Positive		

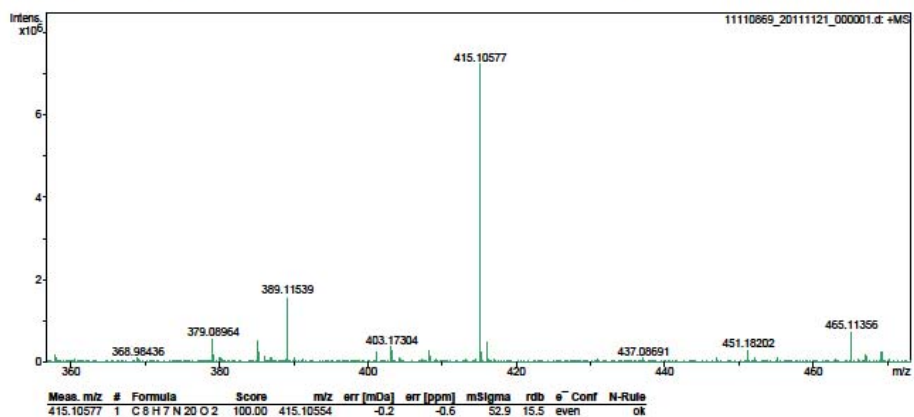


Figure S8 HRMS of AOG₂Tz

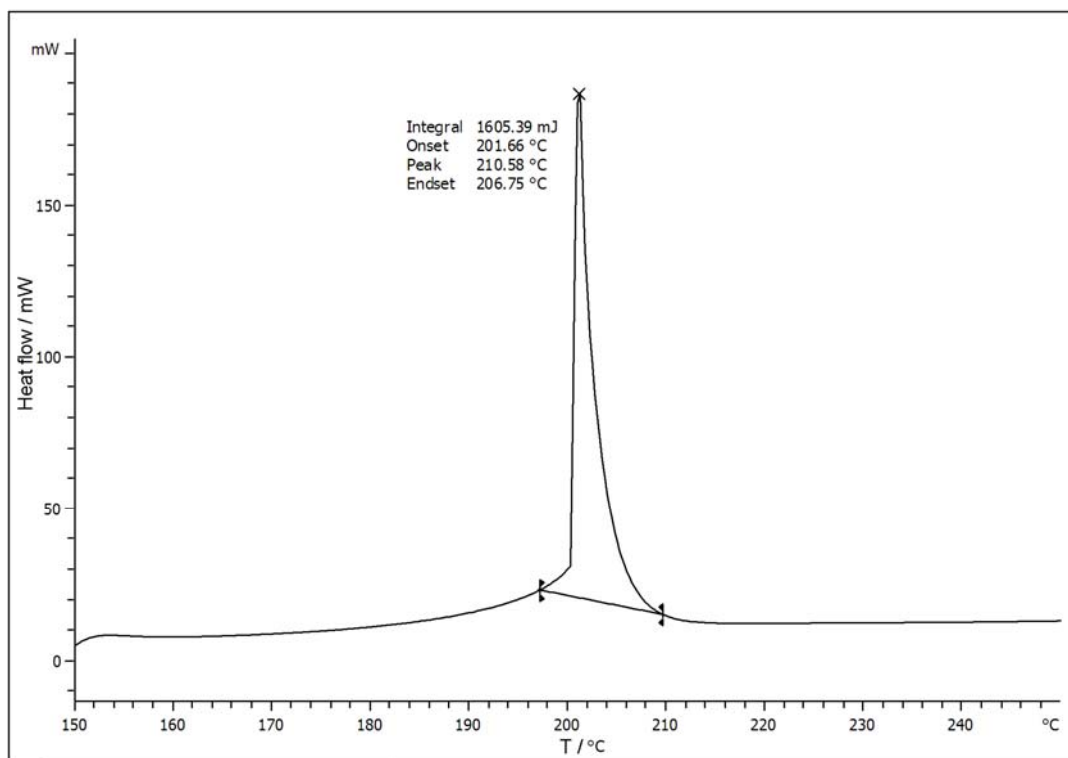


Figure S9 DSC of AOG₂Tz