Supporting Information

Regulation of Stability and Detonation Performance: Preparation of Coordination Compounds by using Isomeric Ligands

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Experimental Section

Caution!

Since the target compound we reported is very dangerous, we should be highly vigilant when synthesizing and using it. Since violent explosion occurred during the characterization of the target compound, it is recommended that all operators should protect the test instrument when repeating our work. If some scholars repeat our work, such as the preparation of ligands and complexes, it is recommended that operators strictly follow our description, because these conditions are obtained after our repeated research. In the preparation, testing and other operations, it must be accompanied by professionals. Non-professionals are advised not to carry out this work because of the potentially dangerous. All operations must be carried out in specially customized equipment, which should have a good protective effect.

Materials and Equipment

During the experiment, the reagents (analytical grade) used were purchased from Aladdin and Azov and used without further purification. Single crystal X-ray diffraction data was collected by using Rigaku supernova single X-ray diffractometer area detector ($Mo_{K\alpha'}$, 0.71073 Å). Powder X-ray diffraction (PXRD) data of the product was tested using a Bruker D8 ADVANCE X-ray powder diffractometer ($Cu_{K\alpha'}$, 1.5418 Å). The thermal behavior of the compound was analyzed by differential scanning calorimeter (TGA/DSC2, METTLER TOLEDO STAR [e] system), with the heating rate was 5 K·min^{-1}, and the gas atmosphere was N_2. Infrared (IR) spectra were measured on

a Nicolet Is10 spectrometer (Equipped with KBr discs) with a measurement range of 4000 - 400 cm $^{-1}$. Elemental analyses (C,H,N or C,H,N,S) were carried out on an elemental analyzer (Vario EL Cube, Germany). The mechanical sensitivities (including impact sensitivity and friction sensitivity) of the material were determined by the standard step method of the drop weight device with a BAM DFH-10 device with a weight drop of 10 kg. The constant pressure reaction heat is measured by High Pressore Oxygen Calorimeter (BCA$^{@}$ 500), with the standard molar combustion enthalpy can be converted by the combustion equation. The experimental density is obtained by the powder densitometer test (Micromeritics AccuPyc II 1340). The laser performance test is measured by Diode Laser (Changchun laser technology co., LTD. LR-ISP-980/1~1000mW. Spectral Line width (nm): < 3, Output Power (mW): 1~1000, Beam Diameter at Aperture (mm): 5.0 x 5.0, Modulating Repetition: 100KHz TTL / 10KHz Analogue. Operating parameters: theoretical maximal output power P_{max} = 30.15 W; theoretical pulse length τ_{max} = 49571 µs. wavelength λ = 915 nm. Frequency F = 1Hz.).

Synthesis of 1H-imidazole-4-carbohydrazide (2, 4-IMCA)

Add methyl 4-imidazolecarboxylate (0.1 mmol) to a reaction flask containing 50 ml of methanol. Then, slowly add hydroxylamine hydrate (0.25 mmol, 80 %) with stirring. Allow the reaction to proceed at room temperature for 3 h, followed by refluxing for 4 h. After the reaction is completed, cool the entire reaction solution to room temperature and store the solution overnight in a refrigerator to obtain a large amount of white target product 4-IMCA. Yield: 79 %. IR (KBr, ν/cm^{-1}): 3290(m), 2840(m), 1683(m), 1540(s),

1346(s), 1110(s), 1086(s), 993(m), 940(m), 626 (s). MS (ESI), m/z: 125.03 [$C_4H_5N_4O^-$].

Elemental analysis (%) for $C_4H_6N_4O$ (Mr = 126.05 g mol^{-1}): calcd. C 38.1, H 4.8, N 44.4; found C 38.3, H 4.6, N 44.8. ^{1}H NMR (400 MHz, DMSO-d_6): δ 4.35 (s, 2H), 7.61 (s, 1H), 7.72 (d, 1H), 9.10 (s, 1H), 12.49 (s, 1H). ^{13}C NMR (400 MHZ, D$_2$O/NaOH-d_6): δ 164.97, 146.09, 133.25,129.83.

Synthesis of Cu(4-IMCA)$_2$(ClO$_4$)$_2$ (3, ECCs-1)

Add **4-IMCA** to 10 mL of water and heat to 45 °C slowly with stirring. While stirring, gradually add HClO$_4$ until the solution becomes clear. Then add 20 ml of methanol and stir for an additional 5 minutes. Add Cu(ClO$_4$)$_2$ solid and continue stirring until it is dissolved. Stirred at a constant temperature for about 30 min and a large amount of blue precipitate appeared. Filter while hot, slowly evaporate the filtrate, and after 1-2 days, blue crystals can be obtained. Yield: 63 %. IR (KBr, ν/cm-1): 3134(m), 1617(s), 1558(s), 1507(s), 1082(s), 900(s), 755(s), 626(s). Elemental analysis (%) for $C_8H_{12}N_8O_{10}Cl_2Cu$ (Mr = 514.68 g mol^{-1}): calcd. C 18.7, H 2.4, N 21.8; found C 18.4, H 2.6, N 21.9.
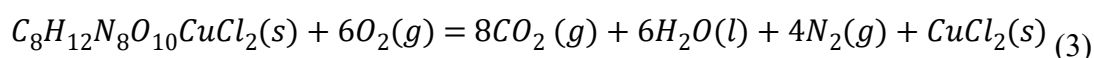
Oxygen bomb calorimetry

The constant pressure reaction heat ($\Delta_C U$) of **ECCs-1** was measured by an oxygen bomb calorimeter, and the average value was obtained by three measurements independently. The standard molar combustion enthalpy ($\Delta_C H^\theta_m$) can be obtained from the constant pressure reaction heat ($\Delta_C U$) according to the equation 1. According to the

principle of Hess' law, the complete combustion reaction equations were shown in equation **1** to **3**, and the standard molar generation enthalpy ($\Delta_f H^\theta_m$) can be obtained based on the formulas **2** and **3** [$CO_2(g)$: -393.51 kJ mol^{-1}; $CuCl_2(s)$: -220.1 kJ mol^{-1}; $HCl(g)$: -92.31 kJ mol^{-1}; $H_2O(l)$: -285.85 kJ mol^{-1}]. The final experimental results showed that he standard molar enthalpy of formation ($\Delta_f H^\theta_m$) of **ECCs-1** is -210 kJ mol^{-1}.

$$\Delta c H^\theta m = \Delta c U + \Delta n R T \tag{1}$$

$\Delta_n = n_g$(products)-n_g(reactants), (n_g is the sum of the total moles of gas in the product or reactant, R = 8.314 J mol^{-1} K^{-1}, T = 298.15 K)

$$\Delta_f H^\theta m(compound) = \sum \Delta_f H^\theta m(products) - \Delta_c H^\theta m(compound) \tag{2}$$

$$C_8H_{12}N_8O_{10}CuCl_2(s) + 6O_2(g) = 8CO_2(g) + 6H_2O(l) + 4N_2(g) + CuCl_2(s) \tag{3}$$

Theoretical simulation based on K-J equations

   The constant pressure reaction heat ($\Delta_C U$) of ECCs-1 was measured by an oxygen bomb calorimeter, Detonation speed (D) and explosion pressure (P) are the main indicators for measuring energetic materials. The various detonation characteristics of the ECCs were predicted using the modified Kamlet-Jacbos (K-J) equations (eq 4-7) which is a commonly used equation for predicting the detonation velocity and pressure of high energy materials.

$$C_8H_{12}N_8O_{10}CuCl_2(s) = 4CO(g) + 6H_2O(g) + 4N_2(g) + CuCl_2(s) + 4C(s) \tag{4}$$
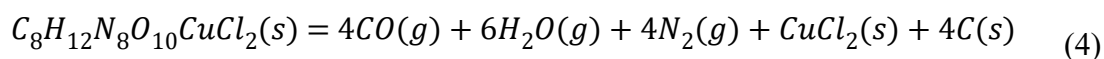
$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho)$$ (5)

$$P = 1.55\rho^2 NM^{1/2}Q^{1/2}$$ (6)

$$Q = \frac{-[\Delta H_f(\text{detonation production}) - \Delta H_f(\text{explosive})]}{\text{formulaweightof explosive}}$$

(7)

D: detonation velocity, km s-1); P: detonation pressure, GPa; ρ: density, g cm^{-3}; ΔHf: heat of formation, kJ mol^{-1}); Q: heat of detonation, J g^{-1}); N: moles of detonation gases per gram of explosive, mol g^{-1}); M: average molecular weight of gases, g mol^{-1})

Hot-ignition tests

Approximately 4-5 mg of the compound was dispersed on the filter paper in a powdered state. Light the filter paper, and then slowly ignite compound, while recording the deflagration process of the compound with a high-speed camera.

Laser performance test

Weigh 2 mg testing samples, a total of 5 parts, and place them in sample tubes. Use a semiconductor laser to trigger the sample. Determine the minimum trigger energy by adjusting the action time and power. Take the average value as the final test value.

Detonation initiation

The test device used to breakdown of the lead plate, the material inside can be divided into two parts: the first part is filled with **ECCs-1** (40 mg, pressure of fixation is 25

MPa); the second component is RDX or **ECCs-1** (500 mg, charge pressure is 40 MPa).
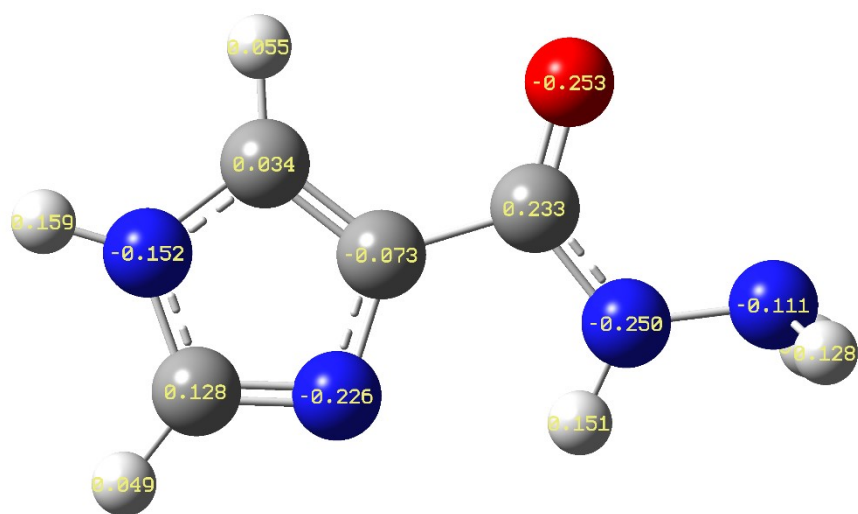
Supplementary Figures S1-S7
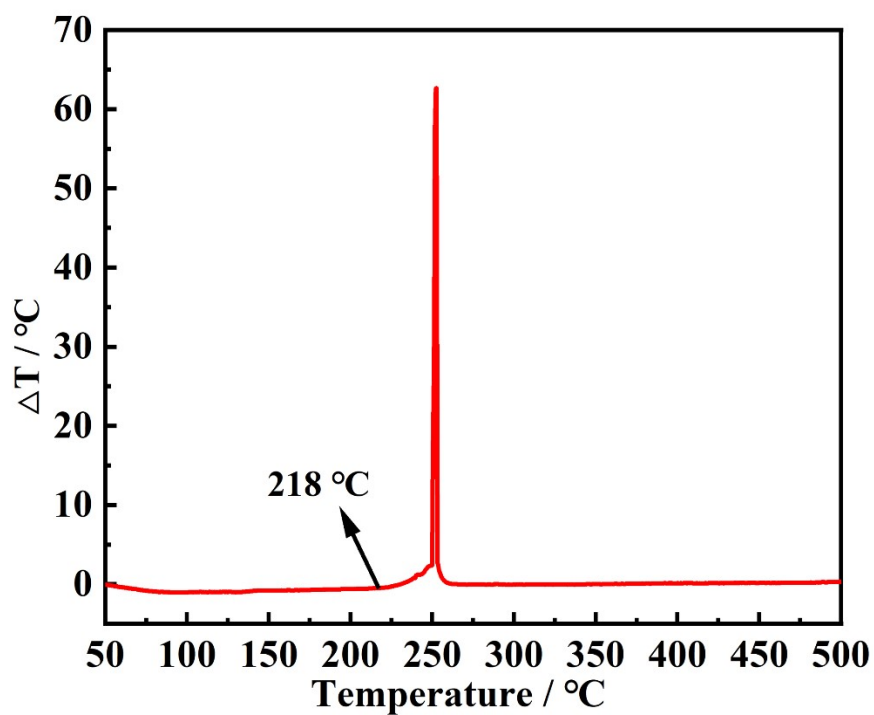

Figure S1. Atomic charge analysis of **4-IMCA**.
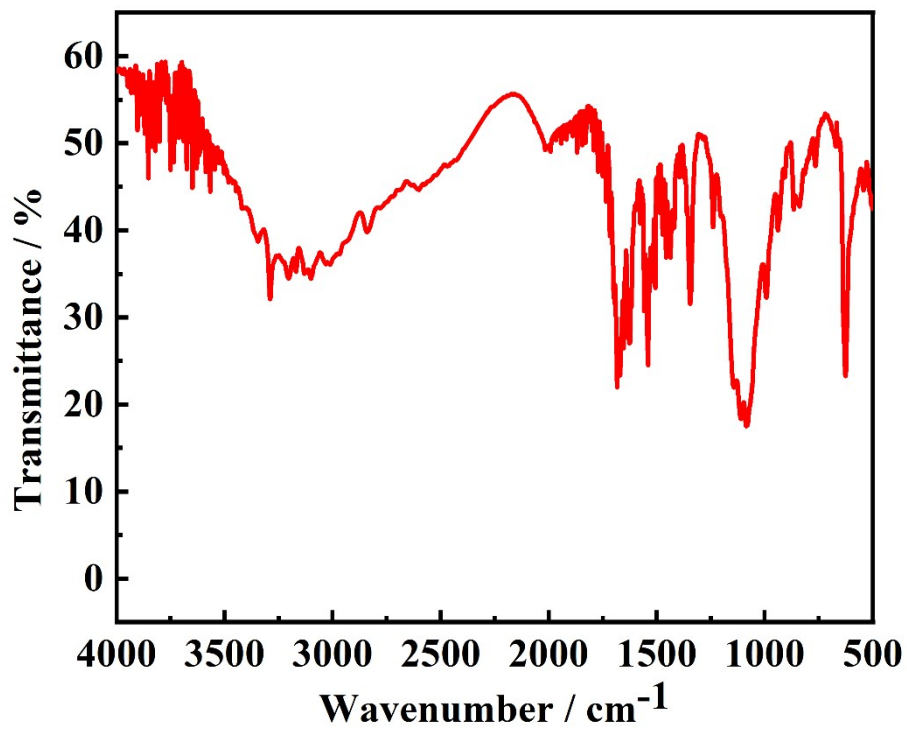

Figure S2. DTA curves of **ECCs-1**.

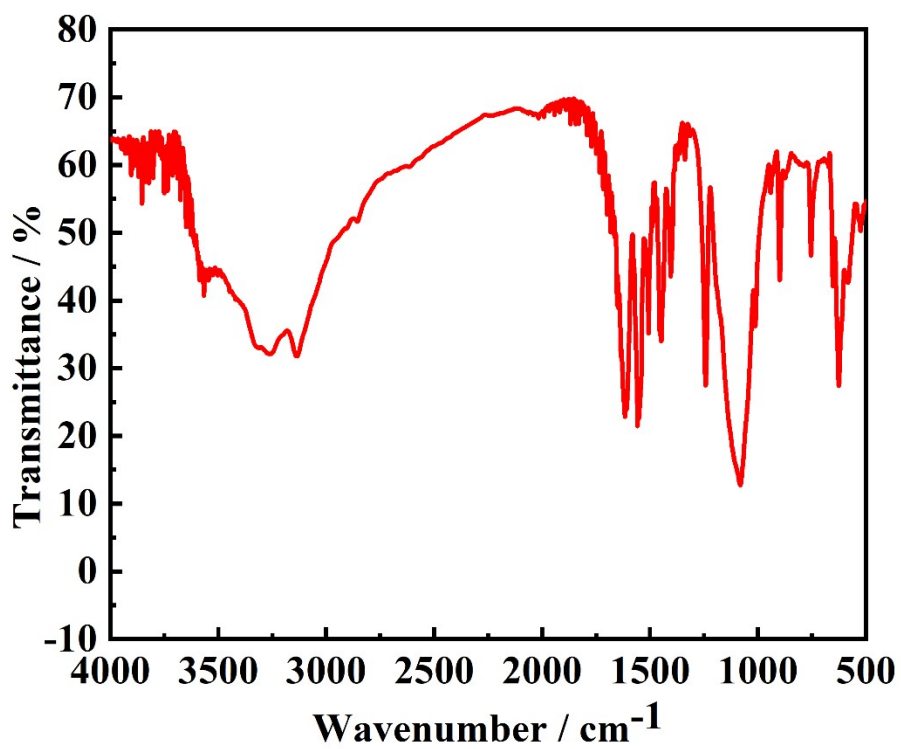**Figure S3.** Infrared spectra of **4-IMCA.**

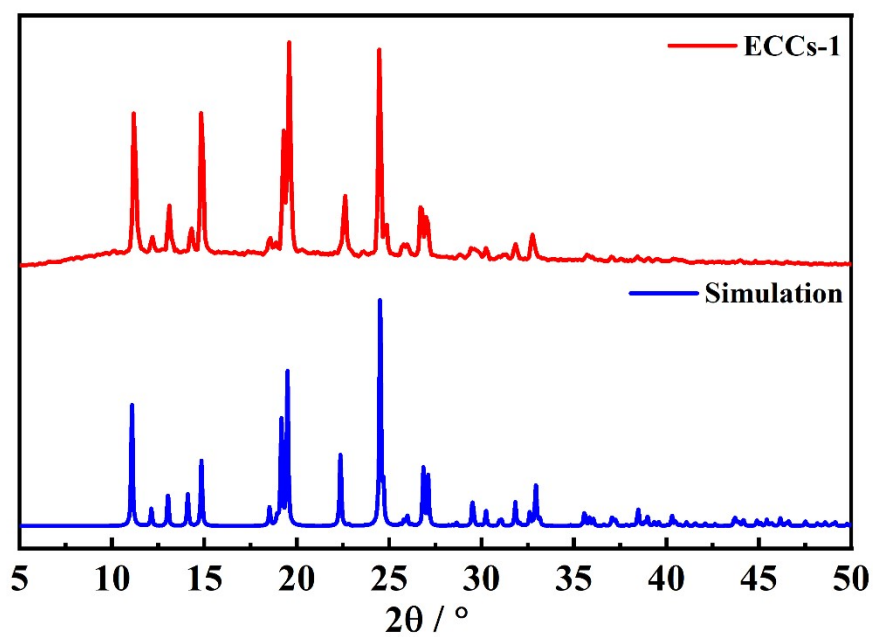**Figure S4.** Infrared spectra of **ECCs-1.**

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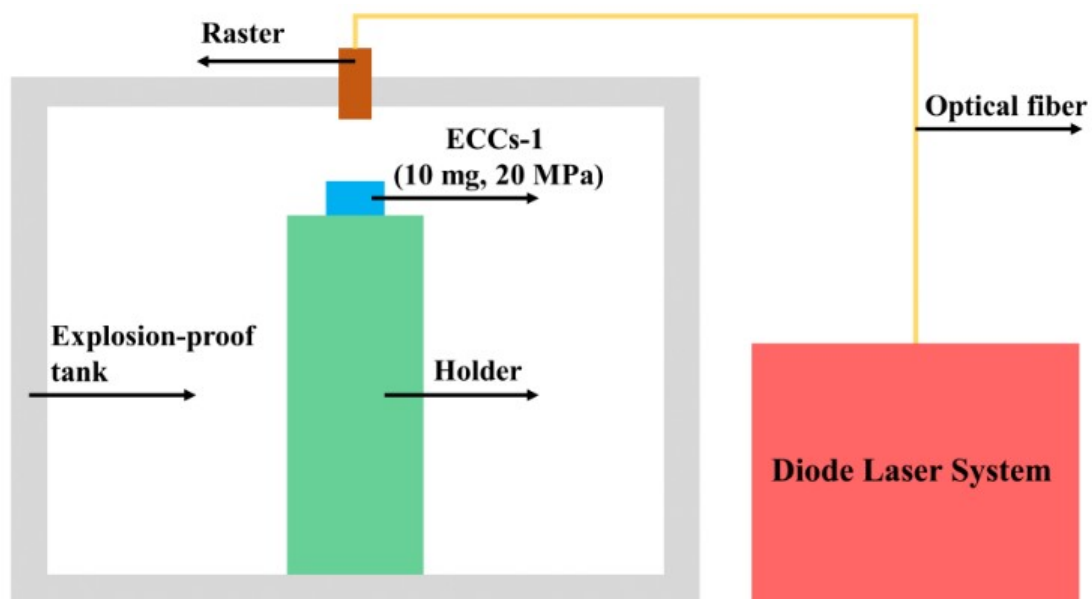**Figure S5.** Comparison of single crystal and powder X-ray diffraction of ECCs-1

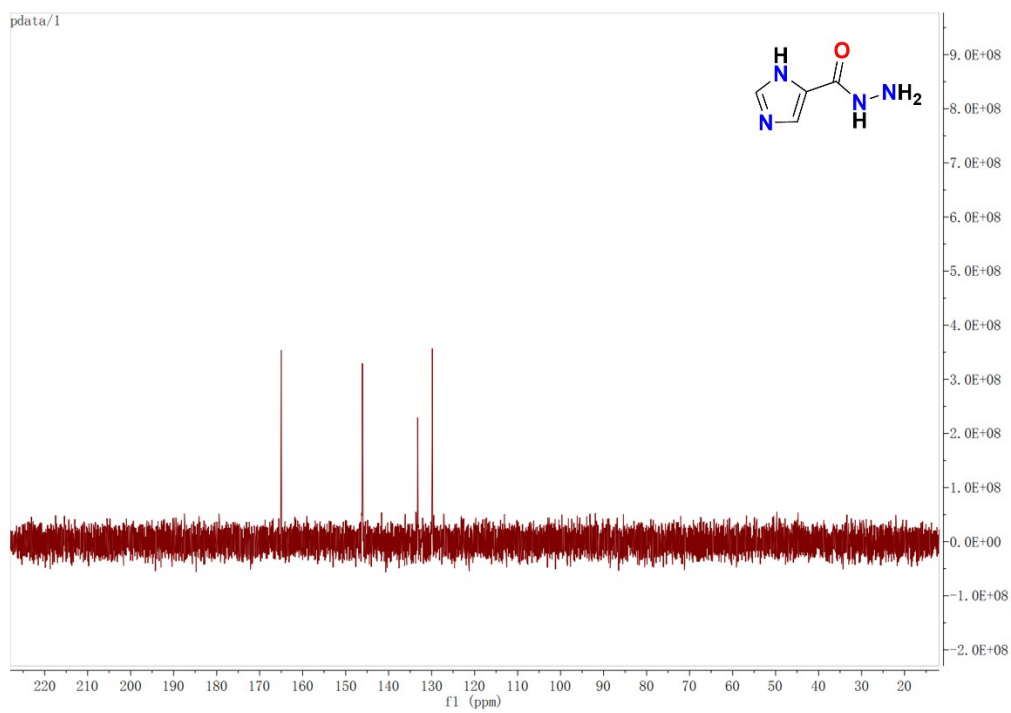**Figure S6**   Illustration of setup of Laser Initiation Tests

Figure S7 ^{13}C NMR of 1*H*-imidazole-4-carbohydrazide

Supplementary Table S1

Table S1. Crystallographic data for **ECCs-1**

Formula	$C_8H_{12}N_8O_{10}Cl_2Cu$
Temperature [K]	298.15
M_w[g mol^{-1}]	809.73
Crystal size [mm^3]	0.1 x 0.1 x 0.1
Crystal system	triclinic
Space group	P-1
unit cell dimensions	a= 7.1701(10) Å, b= 7.7300(11) Å, c[Å]= 8.4411(13) Å
	α[°]= 102.371(12), β[°]= 101.314(12), γ[°]= 101.956(12)
V[[Å^3]	432.67(12)
Z	2
ρ_{calc}[g cm^{-3}]	1.975
μ[mm^{-1}]	5.339
F(000)	258.7
2θ range[°]	11.08 – 155.68
Reflections collected	4102
Index ranges	-9 ≤ h ≤ 8, -9 ≤ k ≤ 9, -9 ≤ l ≤ 10
R_{int}	0.0460
Data/restraints/parameters	1703 / 12 / 133
Final R index [$I > 2\sigma(I)$]	R1 = 0.0603, wR2 = 0.1790
Final R index [all data]	R1 = 0.0705, wR2 = 0.1928
GOF on F^2	1.024
CCDC	2255172