

## Supplementary Material

### Solid state aggregation of cyclic iodonium ylides

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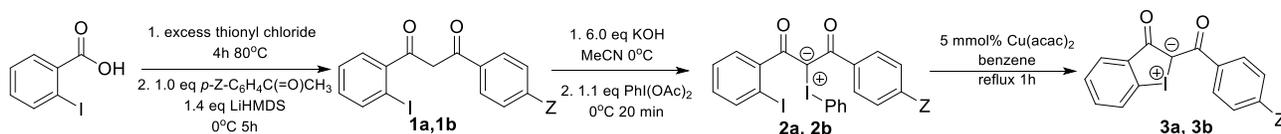
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#### Table of Contents

Experimental Procedures.....	S2
NMR Spectra .....	S4
Crystallographic Analysis .....	S7
References .....	S11

## Experimental Procedures

**General Information.** All starting materials, reagents, and solvents were purchased from commercial sources and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra were obtained on Bruker Avance III HD 500 MHz NMR Spectrometer. Chemical shifts ( $\delta$ ) are reported in parts per million (ppm) and referenced to residue solvent signals. Melting points were determined with Mel-Temp apparatus and are uncorrected. Compounds **1a-3a** and **1b-2b** were prepared as previously described and found to have matching NMR properties with those as reported.<sup>1-5</sup> The synthesis and handling of HVI compounds in general should be done carefully and on small scales, owing to reports of explosive decomposition under heating and/or extensive drying.<sup>6-7</sup>



**Scheme S1.** Synthesis of cyclic iodonium ylide compounds. (a: Z=H, b: Z=NO<sub>2</sub>).

**Compound 1a**, 1-(2-Iodophenyl)-3-phenyl-1,3-propanedione<sup>3</sup>: 2-iodobenzoic acid (2.0 g, 8.08 mmol) was added into a 100 mL flame-dried Schlenk flask and was flushed with nitrogen. Thionyl chloride (30 mL) was injected via a syringe. The mixture was refluxed for 4h and then cooled down to r.t. and concentrated to obtain the yellow solid. LiHMDS (1.0 M in THF, 11.2 mL, 1.4 eq) was injected to a toluene solution of 10 mL acetophenone (0.96 g, 1.0 eq) under nitrogen at 0 °C and stirred at 0 °C for 3h. The resulting yellow solid was all added and the mixture was stirred at 0 °C for 5h. Hydrochloric acid (1.0 M, 20 mL) was added to quench the reaction. The mixture was extracted with ethyl acetate and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purified by column chromatography (DCM: Hexanes= 1:1) to obtain yellow oil. Yield: 1.29 g, 59.7%.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$ = 8.02 – 7.96 (m, 4H), 7.64 – 7.54 (m, 2H), 7.56 – 7.43 (m, 5H), 7.17 (td, *J* = 7.7, 1.7 Hz, 1H), 6.60 (s, 1H), 2.64 (s, 2H).

**Compound 2a**, I-phenyl-I-(4'-benzoyl-2-iodobenzoyl)iodonium ylide<sup>4</sup>: KOH (0.35 g, 6.0 eq) and compound **1a** (0.35 g, 1.0 mmol) were added into a 50 mL Schlenk flask and was flushed with nitrogen. MeOH (10 mL) was injected via a syringe and stirred at 0 °C for 5 min. (Diacetoxyiodo)benzene (0.35 g, 1.1 eq) was added countering nitrogen flow and stirred at 0 °C for another 1h. Water (30 mL) was added and filtered to get the solid. The solid was washed with water and diethyl ether and dried. Yield: 0.48 g, 86.7%.  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$  8.15 (s, 2H), 7.61 (d, *J* = 17.3 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 3H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.99 (s, 2H), 6.90 (s, 2H), 6.68 – 6.60 (m, 1H). Melting point: 115-117 °C.

**Compound 3a**, 2-benzoyl-3-oxo-2,3-dihydrobenzo[*b*]iodolyl ylide<sup>5</sup>: Compound **2a** (0.48 g, 0.86 mmol) and benzene (10 mL) were added into a 100 mL flask to make a solution. The solution was then added copper(II) acetylacetonate (11.3 mg, 5 mmol%) and refluxed for 1h. Filtered to get the solid and washed with diethyl ether and dried. Yield: 0.34g, 70.8%. Recrystallized via vapor diffusion (hexanes into a solution of **3a** in DCM).  $^1\text{H}$  NMR (500 MHz, Chloroform-*d*)  $\delta$ = 8.41 (d, *J* = 8.2 Hz, 2H), 8.03 (d, *J* = 7.6 Hz, 1H), 7.72 – 7.59 (m, 3H), 7.58 – 7.43 (m, 3H).  $^{13}\text{C}$  NMR (126 MHz, Chloroform-*d*)  $\delta$ = 186.04, 140.41, 137.11, 132.13, 130.99, 130.68, 130.17, 128.93, 128.56, 127.71, 127.01, 114.38. Melting point: 120 °C dec.

**Compound 1b**, 1-(2-Iodophenyl)-3-(4-nitrophenyl)-1,3-propanedione<sup>3</sup>: 2-iodobenzoic acid (2.0 g, 8.08 mmol) was added into a 100 mL flame-dried Schlenk flask and flushed with nitrogen. Thionyl chloride (30 mL) was injected via a syringe. The mixture was refluxed for 4h and then cooled down to r.t. and concentrated to obtain yellow solid. LiHMDS (1.0 M in THF, 11.2 mL, 1.4 eq) was injected to a toluene solution of 10 mL 4'-Nitroacetophenone (1.3 g, 1.0 eq) under nitrogen at 0 °C and stirred at 0 °C for 3h. The resulting yellow solid was all added

and the mixture was stirred at 0 °C for 5h. Hydrochloric acid (20 mL, 1.0 M) was added to quench the reaction. The mixture was extracted with ethyl acetate and dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated. Purified by column chromatography (DCM: Hexanes= 7:3) to obtain yellow solid. Yield: 1.02 g, 49.8%. <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ= 8.33 (d, J = 8.9 Hz, 2H), 8.11 (d, J = 8.9 Hz, 2H), 7.99 (d, J = 9.1 Hz, 1H), 7.58 – 7.43 (m, 2H), 7.18 (t, J = 8.5 Hz, 1H), 6.65(s, 1H). <sup>13</sup>C NMR (126 MHz, Chloroform-d) δ= 192.92, 179.33, 141.59, 140.16, 132.97, 131.60, 130.10, 128.90, 127.53, 124.78, 123.35, 99.84, 98.52, 92.99, 53.84. Melting point: 145-147 °C.

**Compound 2b**, I-phenyl-I-(2-iodobenzoyl-4'-nitrobenzoyl)iodonium ylide<sup>4</sup>: KOH (0.35 g, 6.0 eq) and compound **2a** (0.84 g, 1.5 mmol) was added into a 100 mL Schlenk flask and flushed with nitrogen. MeOH (30 mL) was injected via a syringe and stirred at 0 °C for 5 min. (Diacetoxy-iodo)benzene (1.77 g, 1.1 eq) was added counter-ing nitrogen flow and stirred at 0 °C for another 1h. Water (30 mL) was added and filtered to get the solid. The solid was washed with water and diethyl ether and dried. Yield: 0.61 g, 68.1%. <sup>1</sup>H NMR (500 MHz, Chloroform-d) δ= 8.14 (d, J = 7.2 Hz, 2H), 7.81 (d, J = 8.2 Hz, 2H), 7.66 – 7.59 (m, 1H), 7.49 – 7.33 (m, 5H), 6.91 (d, J = 15.2 Hz, 2H), 6.66 (s, 1H). <sup>13</sup>C NMR (126 MHz, Chloroform-d) δ= 147.71, 144.59, 139.28, 137.63, 135.88, 132.21, 131.79, 130.39, 130.05, 129.01, 127.61, 122.46. Melting point: 122 °C dec.

**Compound 3b**, 2-(4-nitrobenzoyl)-3-oxo-2,3-dihydrobenzo[b]iodolyl ylide<sup>5</sup>: Compound **2b** (0.60 g, 1.0 mmol) and benzene (30 mL) was added into a 100 mL flask to make a solution. The solution was then added copper(II) acetylacetonate (13.1 mg, 5 mmol%) and refluxed for 1h. Filtered to get the solid and washed with diethyl ether and dried. Recrystallized via vapor diffusion (diethyl ether into a solution of **3b** in DMF). Yield: 0.24 g, 61.5%. <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>) δ= 8.31 (s, 4H), 8.19 (d, J = 7.9 Hz, 1H), 7.82 – 7.71 (m, 3H). <sup>13</sup>C NMR (126 MHz, DMSO-d<sub>6</sub>) δ= 177.58, 172.12, 148.71, 144.28, 142.71, 134.08, 131.30, 130.38, 130.29, 130.10, 122.97, 112.01, 108.96. Melting point: 205 °C dec.

## NMR Spectra

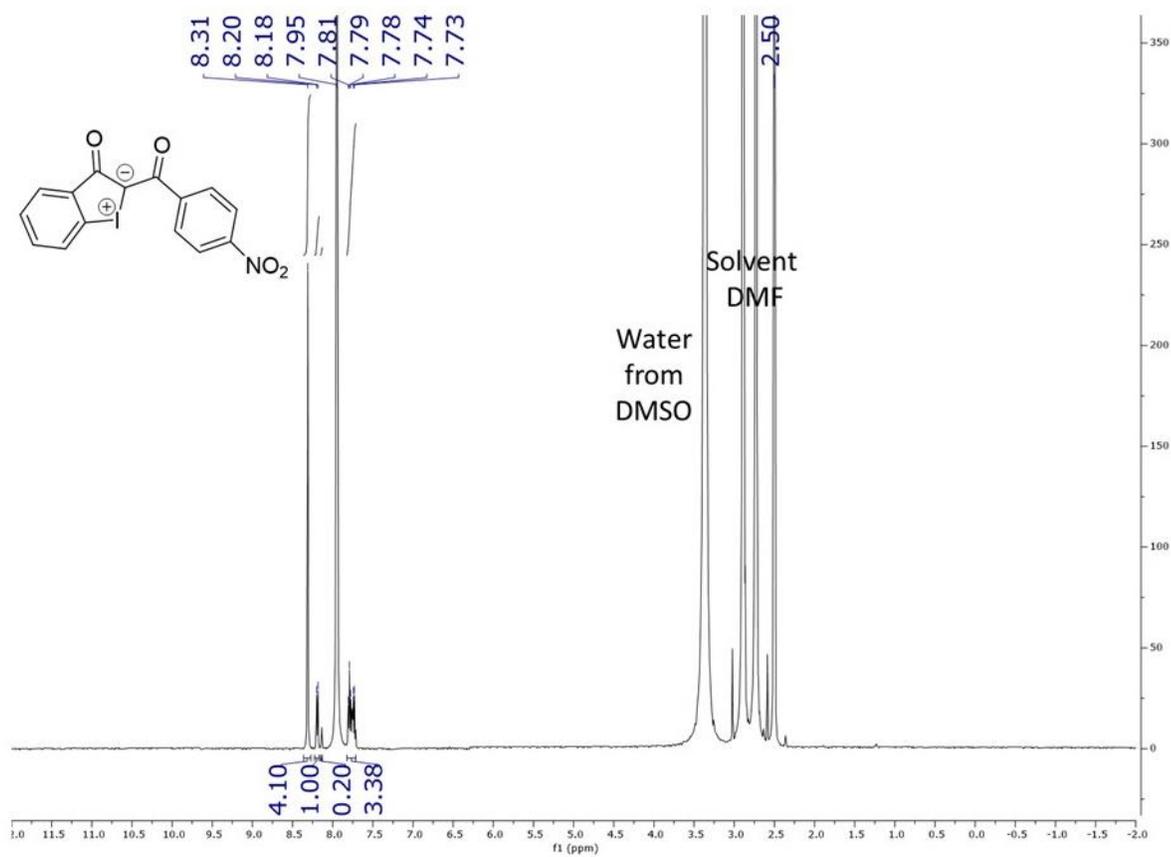
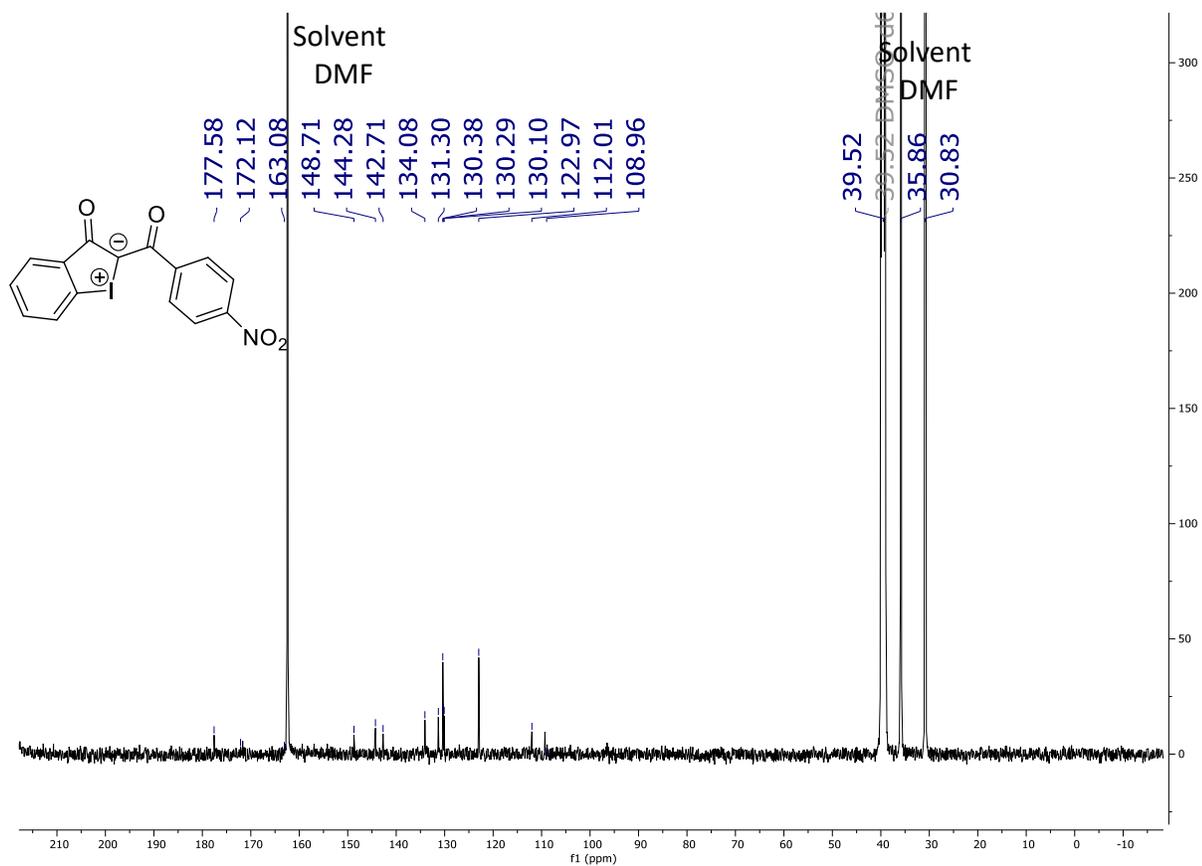
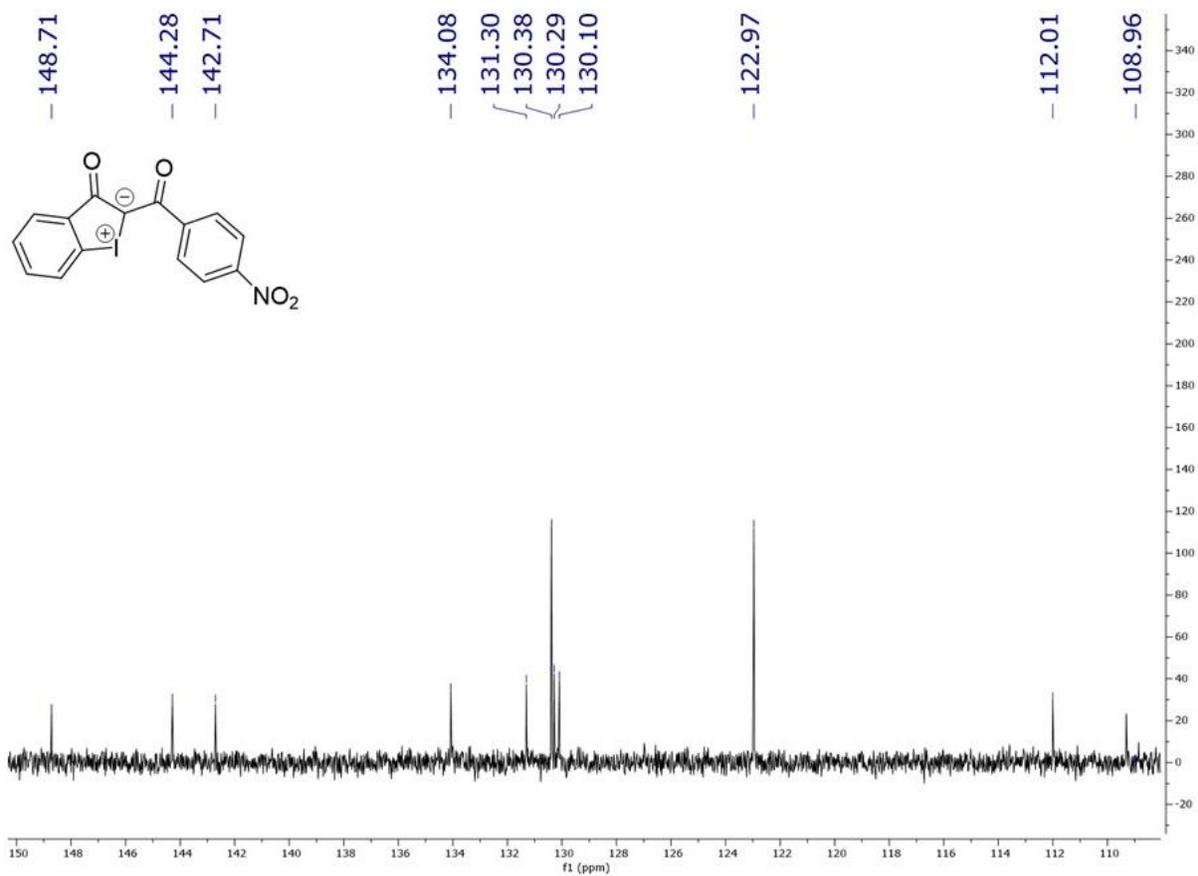


Figure S1.  $^1\text{H}$  NMR spectrum of compound 3b ( $\text{CDCl}_3$ , 500 MHz, 298K).

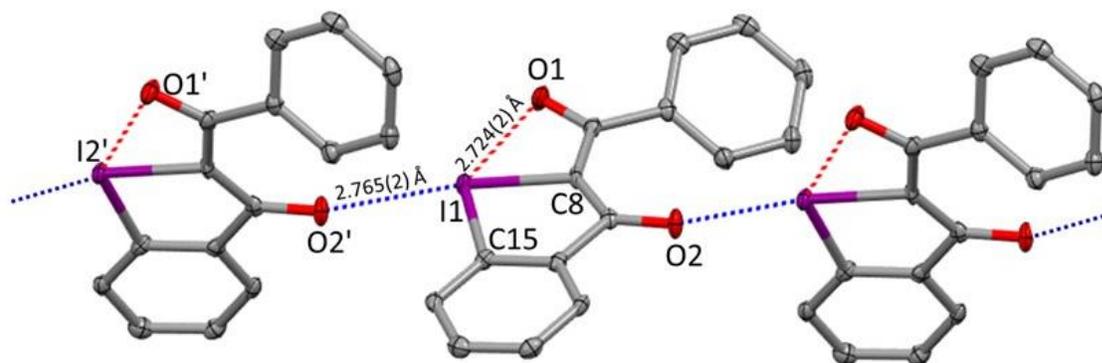


**Figure S2.**  $^{13}\text{C}$  NMR spectrum of compound 3b ( $\text{CDCl}_3$ , 126 MHz, 298K).



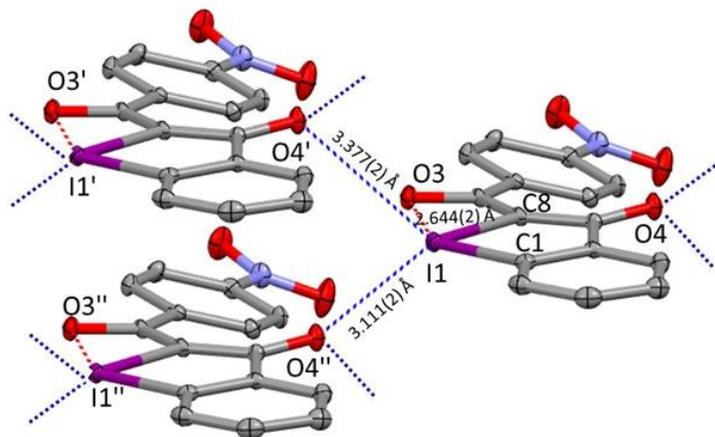
**Figure S3.** <sup>13</sup>C NMR spectrum (zoom in for aromatic rings) of compound 3b (CDCl<sub>3</sub>, 126 MHz, 298K).

## Crystallographic Analysis



**Figure S4.** ORTEP representation of 3a (ellipsoids drawn at 50% probability). Selected bond lengths (Å) and angles I1—C8, 2.090(3); I1—C15 2.099(3); O2'—I1—C8, 166.3(2)°.

Identification code	Compound <b>3a</b>	
Empirical formula	C <sub>15</sub> H <sub>9</sub> IO <sub>2</sub>	
Formula weight	348.12	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	Pna2 <sub>1</sub>	
Unit cell dimensions	a = 18.3859(12) Å	a = 90°.
	b = 5.3759(4) Å	b = 90°.
	c = 12.0862(9) Å	g = 90°.
Volume	1194.61(15) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.936 Mg/m <sup>3</sup>	
Absorption coefficient	2.670 mm <sup>-1</sup>	
F(000)	672	
Crystal size	0.29 x 0.2 x 0.15 mm <sup>3</sup>	
Theta range for data collection	2.215 to 26.744°.	
Index ranges	-17<=h<=23, -6<=k<=6, -14<=l<=15	
Reflections collected	13671	
Independent reflections	2509 [R(int) = 0.0275]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.2607 and 0.1957	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2509 / 1 / 163	
Goodness-of-fit on F <sup>2</sup>	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0147, wR2 = 0.0358	
R indices (all data)	R1 = 0.0157, wR2 = 0.0363	
Absolute structure parameter	-0.015(11)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.393 and -0.284 e.Å <sup>-3</sup>	



**Figure S5.** ORTEP representation of 3b (ellipsoids drawn at 50% probability). Selected bond lengths (Å) and angles (°): I1—C1, 2.103(3); I1—C8, 2.101(3); O4'—I1—C1, 119.5(2)°; O4''—I1—C8, 158.8(9)°.

Identification code	Compound <b>3b</b>	
Empirical formula	C <sub>15</sub> H <sub>8</sub> INO <sub>4</sub>	
Formula weight	393.12	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P1	
Unit cell dimensions	a = 3.9123(4) Å	a = 86.478(5)°.
	b = 6.9163(7) Å	b = 86.434(5)°.
	c = 12.0794(12) Å	g = 75.993(5)°.
Volume	316.16(6) Å <sup>3</sup>	
Z	1	
Density (calculated)	2.065 Mg/m <sup>3</sup>	
Absorption coefficient	2.548 mm <sup>-1</sup>	
F(000)	190	
Crystal size	0.29 x 0.25 x 0.08 mm <sup>3</sup>	
Theta range for data collection	1.691 to 27.158°.	
Index ranges	-5<=h<=5, -8<=k<=8, -15<=l<=15	
Reflections collected	8582	
Independent reflections	2624 [R(int) = 0.0205]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.6338	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	2624 / 3 / 184	
Goodness-of-fit on F <sup>2</sup>	1.073	
Final R indices [I>2sigma(I)]	R1 = 0.0112, wR2 = 0.0271	
R indices (all data)	R1 = 0.0112, wR2 = 0.0271	
Absolute structure parameter	0.015(8)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.359 and -0.309 e.Å <sup>-3</sup>	

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