Electronic Supplementary Material (ESI) for RSC Advances

SUPPORTING INFORMATION

Self-assembly and Ring-opening Metathesis Polymerization of a Bifunctional Carbonate Stilbene Macrocycle

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Materials and instruments: All chemicals were purchased from either Sigma-Aldrich or VWR and used without further purification. HPLC grade chloroform was used for ring-opening metathesis polymerization and vacuum distilled prior to use.

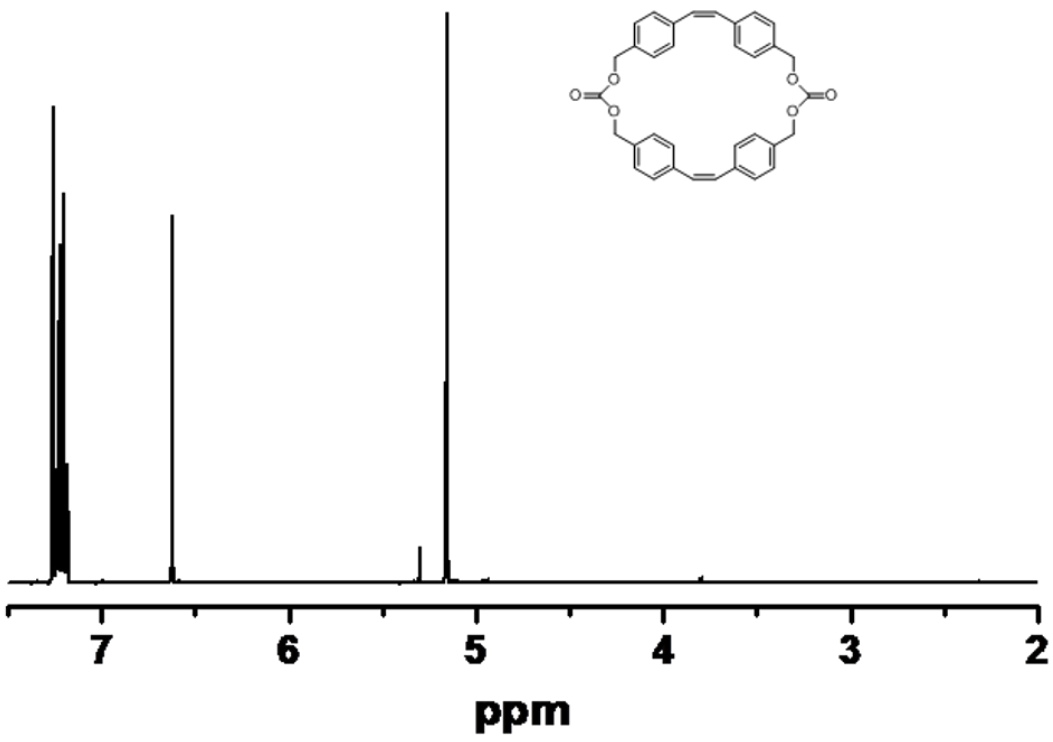


Figure S1. ^{1}H NMR spectrum of macrocycle.

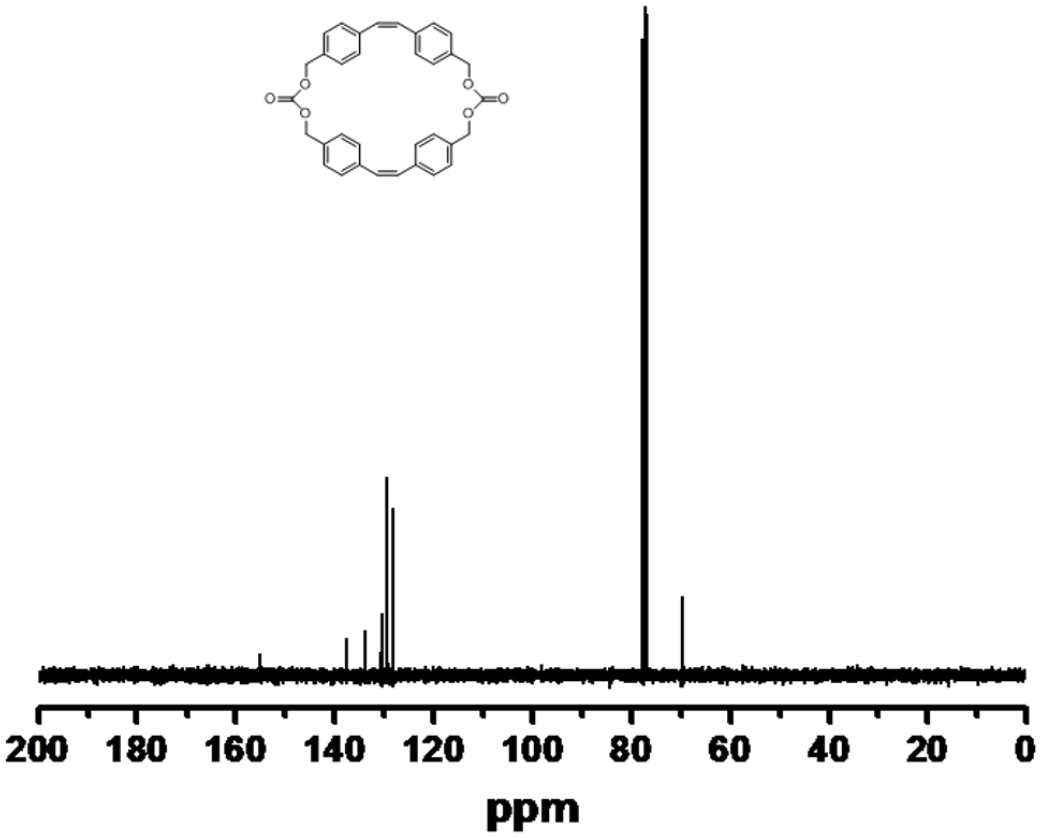


Figure S2. ^{13}C NMR spectrum of macrocycle.

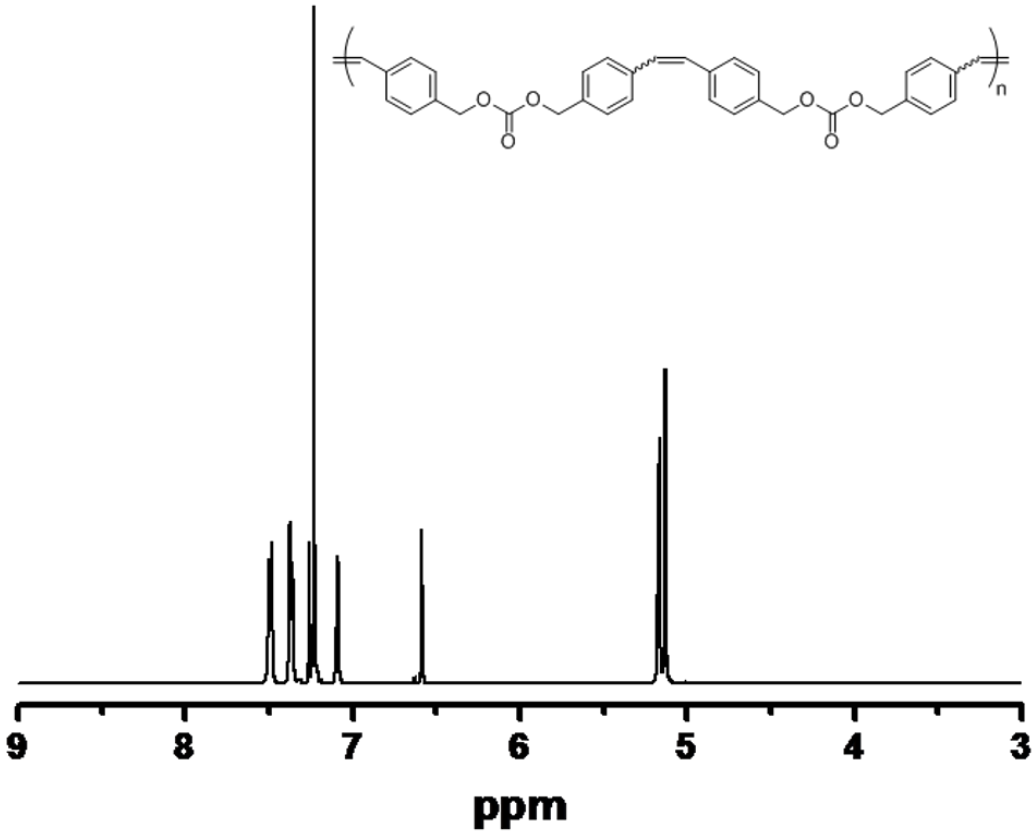


Figure S3. ^{1}H NMR spectrum of polymer 4.

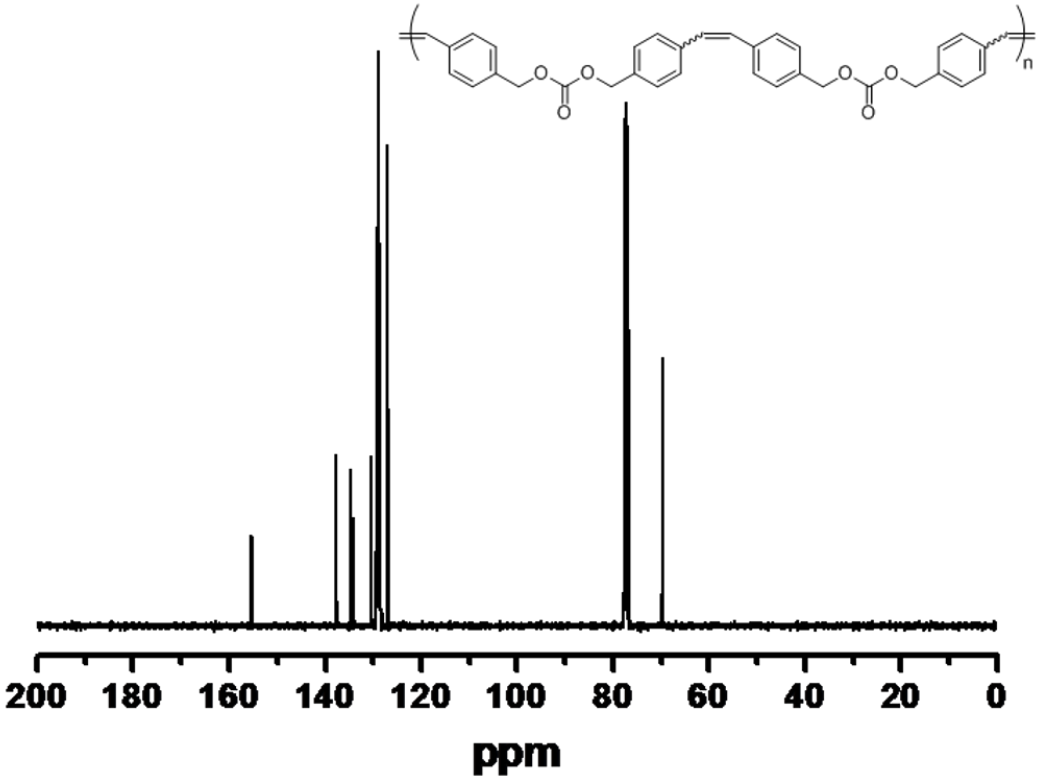


Figure S4. ^{13}C NMR spectrum of polymer 4.

Gas adsorption measurements:

N_2 gas adsorption isotherm was obtained by using Micomeritics ASAP 2020 instrument. Before experiment was run, the macrocycle 1 sample was heated up to 100 ^oC for overnight at high vacuum to remove solvent molecules. Gas adsorption experiment was run at 77 K. The BET surface area, pore volume and pore size of the sample were calculated using the Micomeritics software package associated with the instrument.

BET Surface Area Report

BET Surface Area: 314.1270 ± 3.7693 m^2/g

Slope: 0.181297 ± 0.003694 g/mmol

Y-Intercept: 0.129319 ± 0.000495 g/mmol

C: 2.401939

Qm: 3.21940 mmol/g

Correlation Coefficient: 0.9993778

Molecular Cross-Sectional Area: 0.1620 nm^2

Table S1. BET analysis of macrocycle 1.

Relative Pressure (P/Po)	Quantity Adsorbed (mmol/g)	1/[Q(Po/P - 1)]
0.061000865	0.46174	0.14069
0.076877574	0.58124	0.14328
0.120241422	0.90696	0.15070
0.160068946	1.20601	0.15802
0.199968358	1.50593	0.16598

Ring strain calculation of macrocycle 1:

The atomic coordinates of macrocycle **1** was generated by inputting the .cif file obtained from single crystal X-ray analysis into *Mercury 2.3* and exported it as .xyz file, then opened the .xyz file of macrocycle **1** in *Spartan 10* to generate the corresponding simulation model. After model of macrocycle **1** was built, the Monte Carlo conformer distribution search, with Molecular Mechanics (MMFF) force field, was run to find the lowest energy conformer of macrocycle **1**. During the search, 100,000 conformers were examined and 100 conformers were kept. Then the equilibrium geometry calculation was run for the lowest energy conformer of macrocycle **1** (figure Xa)**,** the calculation was done at B3LYP level and using the 6-31+G* basis set. The energy of macrocycle **1** E_1 was -1763.89456 a.u.

In order to study the strain energy of the macrocycle, we broken macrocycle **1** from C2-C3 and C19-C20 bonds to form two identical open chains and named it as fragment **5**. Two hydrogen atoms were automatically added to C3' (C3'= C3 or C20) and C2' (C2'= C2 or C19) by *Spartan 10* while breaking the C-C bonds. We also did Monte Carlo search for fragment **5** under MMFF force field to find the lowest energy conformer of **5** (figure Xb). Then the same equilibrium geometry calculation was run for the lowest energy conformer of fragment **5** and gave the energy E_5 of -883.146979 a.u.

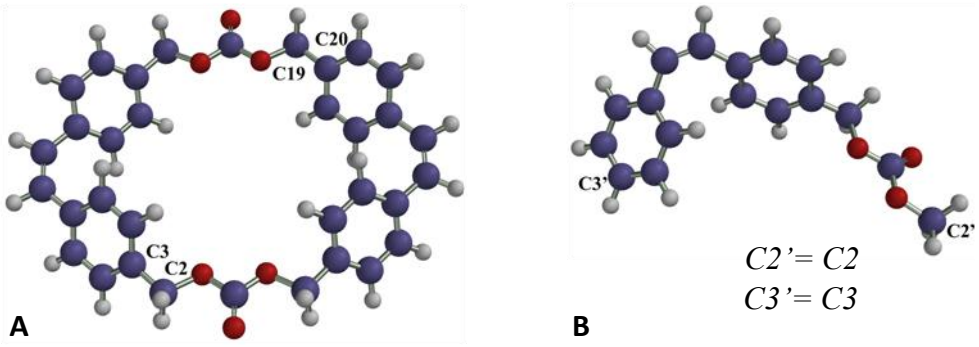


Figure S5. Molecular models simulated by Spartan: (a) geometry optimized model of macrocycle **1**; (b) the lowest energy conformer of fragment **5** generated by Monte Carlo conformer distribution search.

Since the energy comes from the formation of two C-H bonds ($E_{C2'\text{-}H}$ and $E_{C3'\text{-}H}$) and breaking of C-C bonds ($E_{C\text{-}C}$) needs to be taken account into the ring strain calculation, the strain energy E_{RS} of macrocycle **1** could be calculated by equation:

$$E_{RS} = E_{\mathbf{1}} - 2E_{\mathbf{5}} + 2\Delta E \qquad (1)$$

Where

$$\Delta E = E_{C2'\text{-}H)} + E_{C3'\text{-}H} - E_{C\text{-}C}. \qquad (2)$$

The C-C bond energy was estimated by breaking fragment **5** into radical **6** and radical **7** (Table S2.), the energy calculation of these two radicals were performed by DFT at B3LYP level with 6-31+G* basis set, the bond energy $E_{C\text{-}C}$ can calculated by:

$$E_{C\text{-}C} = E_5 - E_6 - E_7 \qquad (3)$$

and $E_{C\text{-}C}$ was -0.157355 a.u.

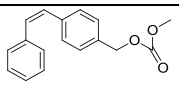
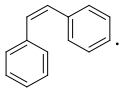
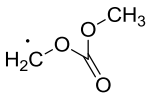
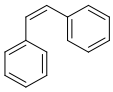
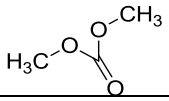
Similarly, the energy of two C-H bonds $E_{C2'\text{-}H}$ and $E_{C3'\text{-}H}$ could be evaluated by designing model **8** and **9** (Table S2.),

$$E_{C2'\text{-}H} = E_9 - E_7 \qquad (4)$$

$$E_{C3'\text{-}H} = E_8 - E_6 \qquad (5)$$

$E_{C2'\text{-}H}$ was -0.668356 a.u. and $E_{C3'\text{-}H}$ was -0.687446 a.u.

Table S2. Models simulated by *Spartan 10*.

	Model	E (Hartrees)
5		-883.146979
6		-540.0346
7		-342.9955024
8		-540.772046
9		-343.623380

By Taking the energy of $E_{C\text{-}C}$, $E_{C2'\text{-}H}$ and $E_{C3'\text{-}H}$ together, ΔE was calculated to -1.198447 a.u. based on eq. **2**, and the strain energy E_{RS} of macrocycle **1** was estimated by inputting ΔE , E_3 and E_5 into eq. **1,** and calculated around 1.57 kcal/mol.

X-Ray Structure Determination, $C_{34}H_{28}O_6 \cdot CH_2Cl_2$ (yx-01-033)

X-ray intensity data from a colorless parallelogram-shaped plate crystal were measured at 150(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] Raw area detector data frame integration was performed with SAINT+.[1] Final unit cell parameters were determined by least-squares refinement of 7850 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[2]

The compound crystallizes in the triclinic system. The space group P $\bar{1}$ was confirmed by the successful solution and refinement of the structure. The asymmetric unit consists of one $C_{34}H_{28}O_6$ molecule and one CH_2Cl_2 molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms.

(1) SMART Version 5.630, SAINT+ Version 6.45. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.
(2) Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

Table 1. Crystal data and structure refinement for yx01033.

Identification code	yx01033m	
Empirical formula	C35 H30 Cl2 O6	
Formula weight	617.49	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 10.9128(8) Å	α = 97.0810(10) °
	b = 11.6446(8) Å	β = 100.5130(10) °
	c = 12.4210(9) Å	γ = 98.8060(10) °
Volume	1514.93(19) $Å^3$	
Z	2	
Density (calculated)	1.354 Mg/m^3	
Absorption coefficient	0.260 mm^{-1}	
F(000)	644	
Crystal size	0.52 x 0.22 x 0.10 mm^3	
Theta range for data collection	1.69 to 25.02 °.	
Index ranges	-12<=h<=12, -13<=k<=13, -14<=l<=14	
Reflections collected	21031	
Independent reflections	5346 [R(int) = 0.0433]	
Completeness to theta = 25.02 °	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5346 / 0 / 388	
Goodness-of-fit on F^2	1.065	
Final R indices [I>2sigma(I)]	R1 = 0.0492, wR2 = 0.1362	
R indices (all data)	R1 = 0.0603, wR2 = 0.1449	
Largest diff. peak and hole	0.588 and -0.458 e.$Å^{-3}$	

X-Ray Structure Determination, $C_{34}H_{28}O_6 \cdot C_4H_8O$ (YX01-02-06)

X-ray intensity data from a colorless needle crystal were collected at 100(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] The raw area detector data frames were reduced and corrected for absorption effects with the SAINT+ and SADABS programs.[1] Final unit cell parameters were determined by least-squares refinement of 2790 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXS/L[2] within OLEX2.[3]

The compound crystallizes in the monoclinic space group $P2_1/n$ as determined uniquely by the pattern of systematic absences in the intensity data. The asymmetric unit consists of half of one $C_{34}H_{28}O_6$ cycle molecule, which is located on a crystallographic inversion center, and a tetrahydrofuran molecule. The THF molecule is disordered across the inversion center, and only half is present per asymmetric unit. The THF atoms were refined with site occupation factors of 0.5. C-O and C-C "same-distance" restraints were applied to chemically equivalent bonds in the THF molecule, using the SADI instruction in SHELX. The C22-C23 bond distance was restrained to 1.54(2) Å. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms bonded to carbon were placed in geometrically idealized positions and included as riding atoms.

(1) SMART Version 5.630, SAINT+ Version 6.45 and SADABS Version 2.10. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.
(2) Sheldrick, G.M. *Acta Cryst*. **2008**, A64, 112-122.
(3) Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard J. A. K. and Puschmann, H. OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Cryst.* **2009**, *42*, 339-341.

Table 2 Crystal data and structure refinement for YX01-02-06

Identification code	YX01-02-06
Empirical formula	$C_{38}H_{36}O_7$
Formula weight	604.67
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	14.555(4)
b/Å	5.6690(16)
c/Å	18.310(5)
α/°	90.00
β/°	96.521(6)
γ/°	90.00
Volume/Å^3	1501.0(7)
Z	2
ρ_{calc}mg/mm^3	1.338
μ/mm^{-1}	0.092
F(000)	640.0
Crystal size/mm^3	0.54 × 0.26 × 0.06
2Θ range for data collection	3.4 to 53.2 °
Index ranges	$-18 \le h \le 18$, $-7 \le k \le 7$, $-23 \le l \le 22$
Reflections collected	16358
Independent reflections	3122[R(int) = 0.0517]
Data/restraints/parameters	3122/4/226
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0416, wR_2 = 0.0942
Final R indexes [all data]	R_1 = 0.0548, wR_2 = 0.1011

Largest diff. peak/hole / e $Å^{-3}$	0.24/-0.21

X-Ray Structure Determination, $C_{34}H_{28}O_6$ (yx-01-033ii)

X-ray intensity data from a colorless plate crystal were measured at 150(2) K using a Bruker SMART APEX diffractometer (Mo Kα radiation, λ = 0.71073 Å).[1] Raw area detector data frame processing was performed with the SAINT+ program.[1] Final unit cell parameters were determined by least-squares refinement of 4511 reflections from the data set. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F^2 were performed with SHELXTL.[2]

The space group $P2_1/c$ was determined by examination of the pattern of systematic absences in the intensity data. The asymmetric unit consists of one molecule. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in geometrically idealized positions and included as riding atoms.

(1) SMART Version 5.630, SAINT+ Version 6.45. Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2003.
(2) Sheldrick, G. M. SHELXTL Version 6.14; Bruker Analytical X-ray Systems, Inc., Madison, Wisconsin, USA, 2000.

Table 3. Crystal data and structure refinement for yx01033ii.

Identification code	yx01033m	
Empirical formula	C34 H28 O6	
Formula weight	532.56	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 11.2731(8) Å	α = 90°
	b = 10.6669(7) Å	β = 91.852(2)°
	c = 22.7178(15) Å	γ = 90°
Volume	2730.4(3) $Å^3$	
Z	4	
Density (calculated)	1.296 Mg/m^3	
Absorption coefficient	0.088 mm^{-1}	
F(000)	1120	
Crystal size	0.22 x 0.16 x 0.08 mm^3	
Theta range for data collection	1.79 to 25.05 °.	
Index ranges	-13<=h<=13, -12<=k<=12, -27<=l<=27	
Reflections collected	30839	
Independent reflections	4848 [R(int) = 0.0662]	
Completeness to theta = 25.05 °	100.0 %	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4848 / 0 / 361	
Goodness-of-fit on F^2	0.912	
Final R indices [I>2sigma(I)]	R1 = 0.0394, wR2 = 0.0755	
R indices (all data)	R1 = 0.0649, wR2 = 0.0840	
Largest diff. peak and hole	0.387 and -0.128 $e.Å^{-3}$	