Separation of Cyclohexanol from Cyclohexanol/Cyclohexene Mixtures by Crystals of Pillar[6]arene Containing Three Benzoquinone Units

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Electronic Supplementary Information (12 pages)

1. Materials

All reagents were commercially available and used as supplied without further purification. Solvents were either employed as purchased or dried according to procedures described in the literature. Compounds **P3QA** were prepared according to published literature procedures.[S1] Activated crystal **P3QA** was dried under vacuum at 100 °C overnight. All **CHA-ol/CHA-ene** mixtures were 50:50 (*v/v*).

2. Methods

2.1 Solution ^{1}H NMR Spectroscopy

^{1}H NMR spectra were recorded using a Bruker Avance DMX 400 spectrometer and a Bruker Avance DMX 500 spectrometer.

2.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out on a DSCQ1000 Thermal Gravimetric Analyzer with an automated vertical overhead thermobalance. The samples were heated at the rate of 10 °C/min using N_2 as the protective gas.

2.3 Powder X-Ray Diffraction

PXRD data were collected on a Rigaku Ultimate-IV X-Ray diffractometer operating at 40 kV/30 mA using the Cu K_α line (λ= 1.5418 Å). Data were measured over the range of 5–45° in 5°/min steps over 8 min.

2.4 Single Crystal Growth

Single crystals of **CHA-ol** loaded **P3QA** were grown by slow evaporation: 5 mg of dry **P3QA** powder were put in a small vial where 1 mL of **CHA-ol** was added. Then CH_2Cl_2 was added dropwise until all the powder was dissolved. The small vial was then placed inside a larger bottle containing methanol as a poor solvent. The methanol slowly diffused into the small vial, resulting in the formation of orange crystals in 2 to 3 days.

2.5 Single Crystal X-ray Diffraction

Suitable crystals were selected and measured on a Bruker D8 Ventune diffractometer with Mo-K_α radiation (λ= 0.71073 Å) for cell determination. Supplementary CIFs, which include structure factors, are available free of charge from the Cambridge

Crystallographic Data Centre (CCDC) via https://www.ccdc.cam.ac.uk/structures/.

2.6 Gas Chromatography

Gas chromatographic (GC) analysis: GC measurements were carried out using an Agilent 7890B instrument configured with an FID detector and a DB-624 column (30 m $\times$ 0.53 mm $\times$ 3.0 μm).

2.7 Computational Method

All-electron DFT calculations have been carried out by Gaussian 16 software. The B3LYP functional was adopted for all calculations. For geometry optimization and frequency calculations, the def2-SVP basis set was used, and the optimal geometry for each compound was determined. The singlet point energy calculations were performed with a larger basis set def2-TZVP basis set. The DFT-D3 dispersion correction with BJ-damping was applied to correct the weak interaction to improve the calculation accuracy. Electrostatic potential analysis was performed by Multiwfn package. The visualization of the ESP analysis was achieved using GaussView software.[S2–S5]

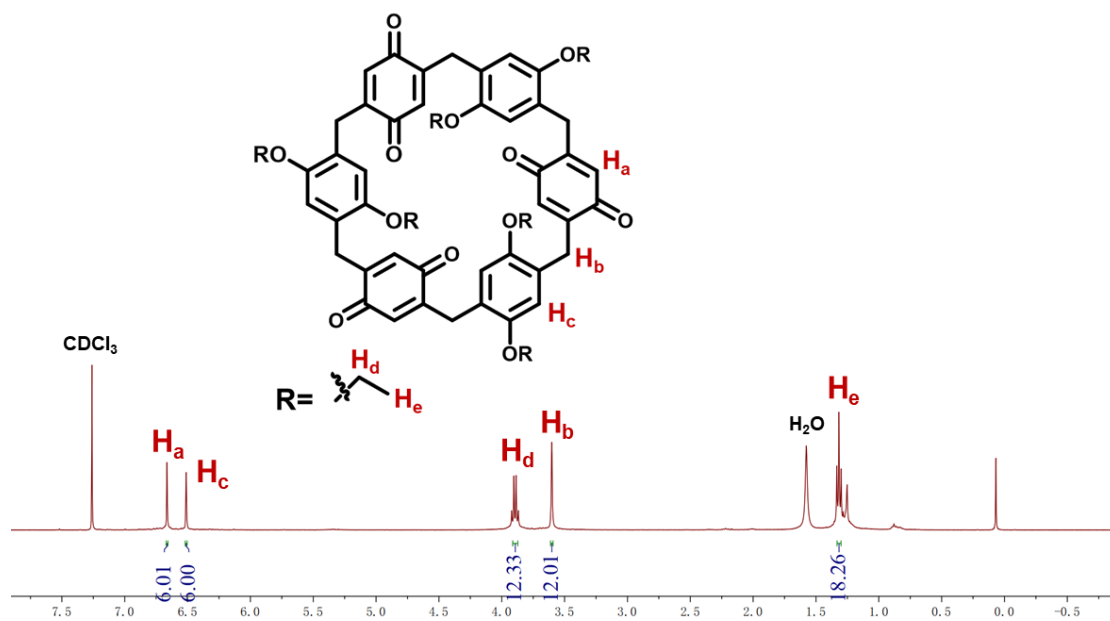## 3. Characterization of Activated P3QA Crystals

Fig. S1 ^{1}H NMR spectrum (400 MHz, CDCl$_3$, room temperature) of activated **P3QA** crystals.
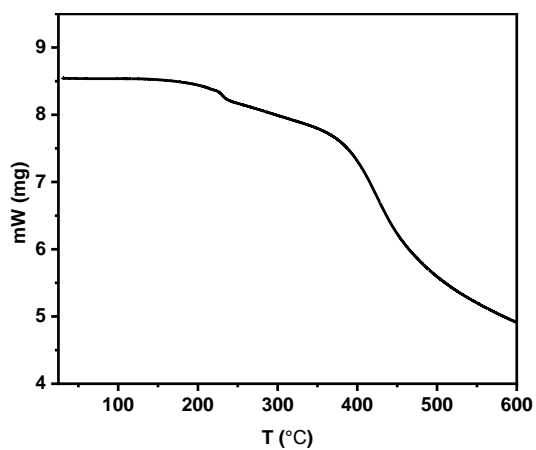

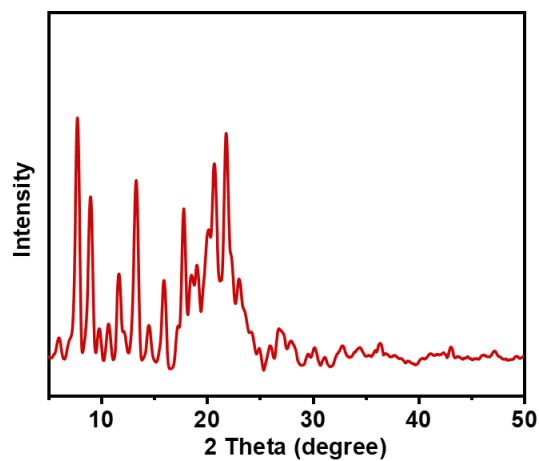***Fig. S2*** Thermogravimetric analysis of activated **P3QA** crystals.

Fig. S3 PXRD pattern of activated **P3QA** crystals.
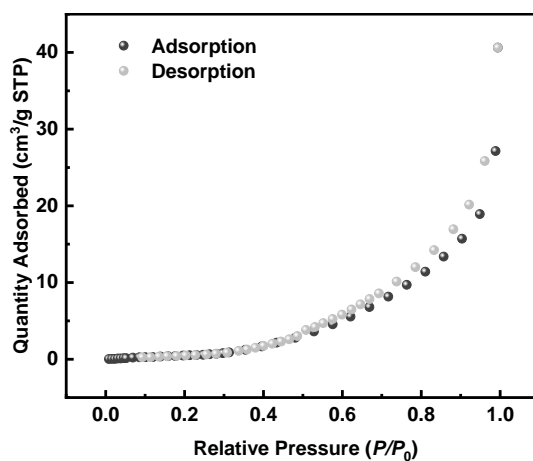

Fig. S4 N$_2$ adsorption and desorption isotherms of activated **P3QA** crystals. Adsorption, black symbols; desorption, light grey symbols.
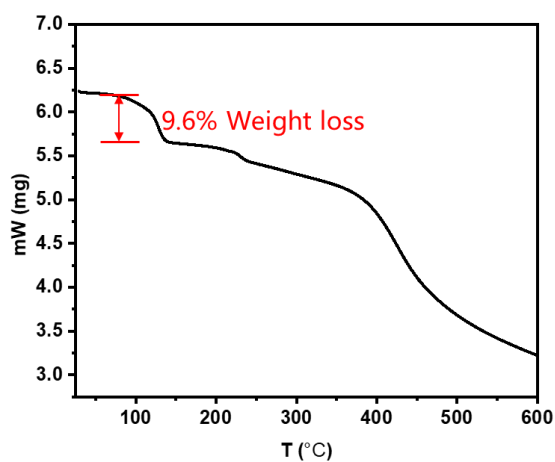

Fig. S5 Thermogravimetric analysis of **P3QA** after exposure to **CHA-ol** vapor. The weight loss below 160 °C can be calculated as one **CHA-ol** molecule per **P3QA** molecule.

4. Studies of the Host–Guest Interactions between P3QA and CHA-ol

To determine the stoichiometry and association constant for the complexation of **P3QA** with **CHA-ol**, ^{1}H NMR titrations were conducted with solutions which had a constant concentration of **P3QA** (5.00 mM) and varying concentrations of **CHA-ol**. The results indicated that the binding stoichiometry is 1:1 for **P3QA** and **CHA-ol** in CDCl$_3$ (*Fig. S9*). The association constant between **P3QA** and **CHA-ol** was determined using the curve-fitting analysis method in *Fig. S8*, yielding a value of (9.49 ± 0.26) M^{-1} in CDCl$_3$.
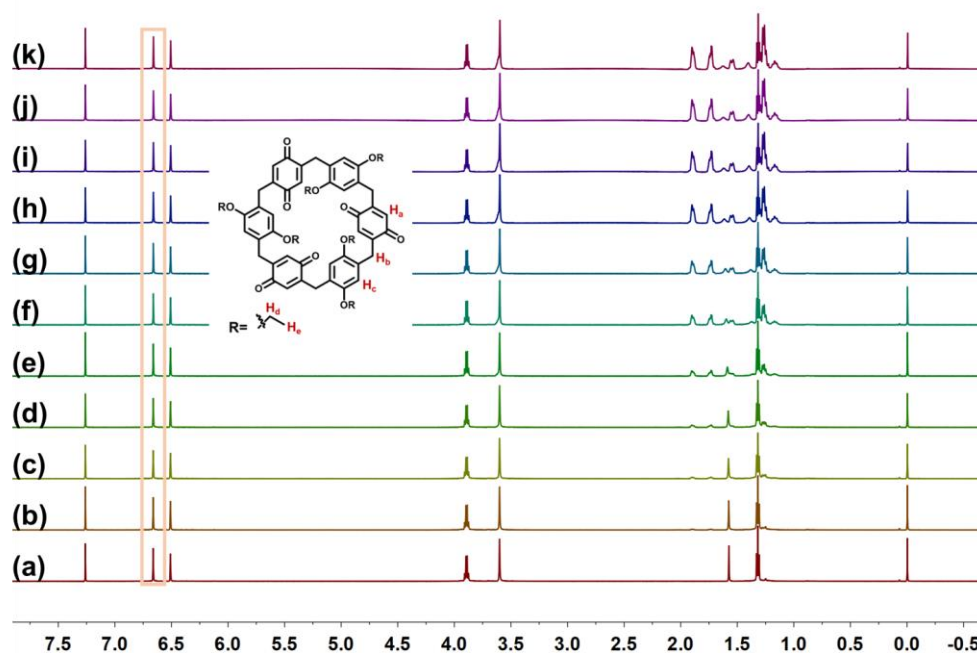

Fig. S6 Partial ^{1}H NMR spectra (600 MHz, CDCl$_3$, room temperature) of **P3QA** at a constant concentration of 5.00 mM upon gradually addition of **CHA-ol**, the ratio of host and guest molecules is (a) **P3QA** only; (b) 1.00:0.20; (c) 1.00:0.40; (d) 1.00:0.60; (e) 1.00:0.80; (f) 1.00:1.00; (g) 1.00:1.20; (h) 1.00:1.60; (i) 1.00:2.00; (j) 1.00:3.00; (k) 1.00:4.00.
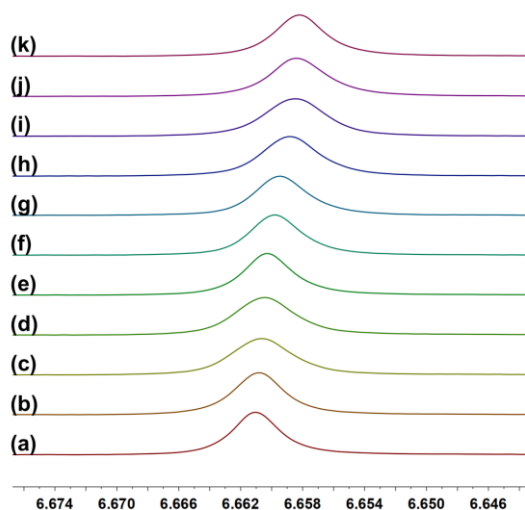
Fig. S7 The marked region (6.674 ppm to 6.646 ppm) of **Fig. S6**.

$R^2=0.99$
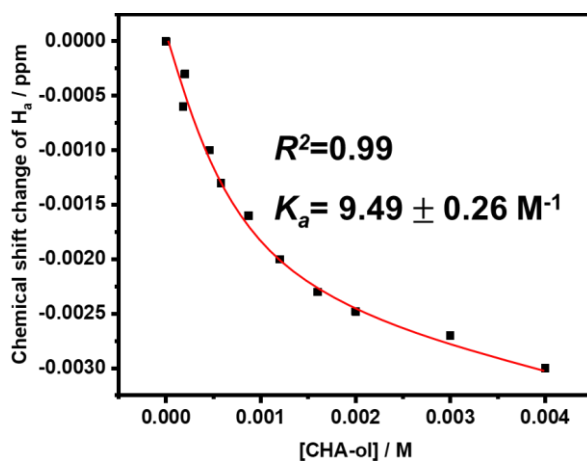
$K_a= 9.49 \pm 0.26$ M^{-1}

Fig. S8 The chemical shift changes of H$_a$ on **P3QA** upon addition of **CHA-ol**. The red solid line was obtained from the non-linear curve-fitting using the above equation.
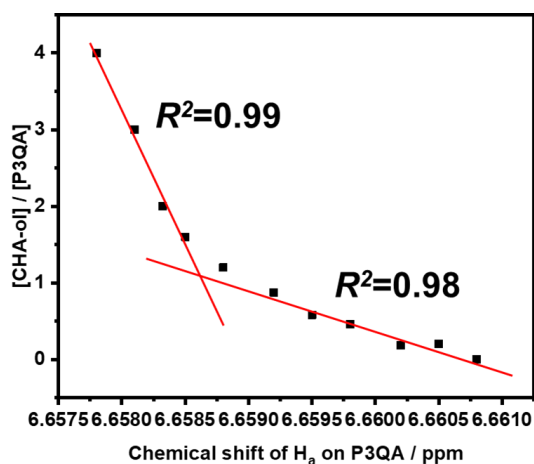

$R^2=0.99$

$R^2=0.98$

Fig. S9 Molar ratio plot for the complexation between **P3QA** and **CHA-ol** in CDCl$_3$, indicating a 1:1 binding stoichiometry.

5. Vapor-Phase Adsorption Measurements

In the solid−gas adsorption experiment, 10 mg of activated **P3QA** crystals were introduced into an open 1.5 mL vial, which was then placed within a sealed 8 mL vial pre-filled with 1 mL of an equal-volume mixture of **CHA-ol** and **CHA-ene**. The temporal uptake of guest molecules by the **P3QA** crystals were ascertained by fully dissolving the crystals in CDCl$_3$ and subsequently determining the molar ratios of **CHA-ol** and **CHA-ene** on **P3QA** crystals through ^{1}H NMR spectroscopy.
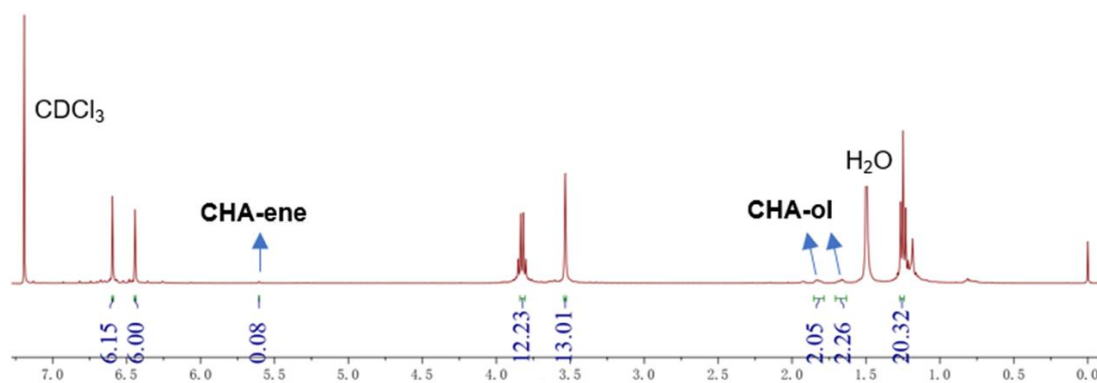

Fig. S10 The ^{1}H NMR spectrum (400 MHz, CDCl$_3$, room temperature) of activated **P3QA** crystals following a 20 h exposure to the vapor of an equal-volume **CHA-ol/CHA-ene** mixture.

The relative uptake amounts of **CHA-ol** and **CHA-ene** on **P3QA** crystals were also measured by gas chromatography. The **P3QA** samples were using headspace injections and were performed by incubating the sample at 120 °C for 20 min followed by sampling 1.00 mL of the headspace, for ensuring sufficient thermal equilibrium and complete desorption of the volatile compounds. The total volume of the container was 10 mL; the mass of the solid in the container was 10 mg; the total volume of the headspace was 1 mL. The following GC method was used: the oven was programmed from 50 °C, and ramped in 10 °C min^{-1} increments to 150 °C with 15 min hold; the total run time was 25 min; the injection temperature was 250 °C; the detector temperature was 280 °C with nitrogen, air, and make-up flow-rates of 35, 350, and 35 mL min^{-1}, respectively; helium (carrier gas) flow-rate was 3.0 mL min^{-1}. The samples were injected in the split mode (30:1).
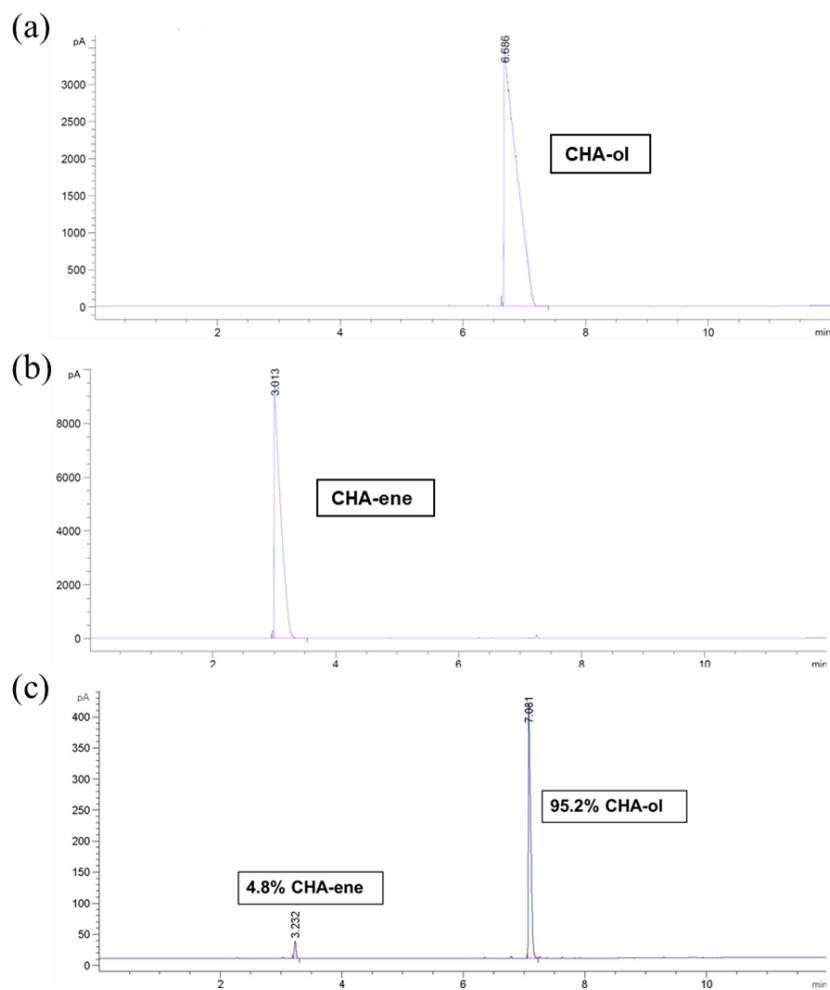
Fig. S11 The GC spectra of (a) **CHA-ol** and (b) **CHA-ene**. (c) Relative uptake of **CHA-ol** and **CHA-ene** adsorbed in **P3QA** crystals over 20 h using GC.
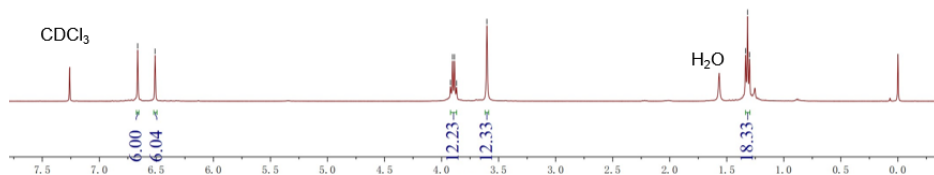
6. Recyclability of P3QA

Fig. S12 ^{1}H NMR spectrum (400 MHz, CDCl₃, room temperature) of **P3QA** after exposure to **CHA-ol** vapor and heating in vacuum.
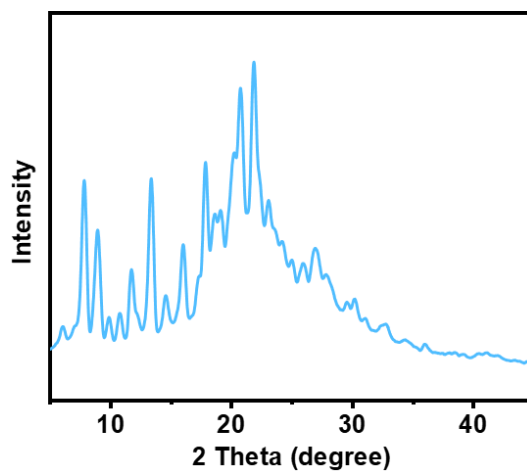

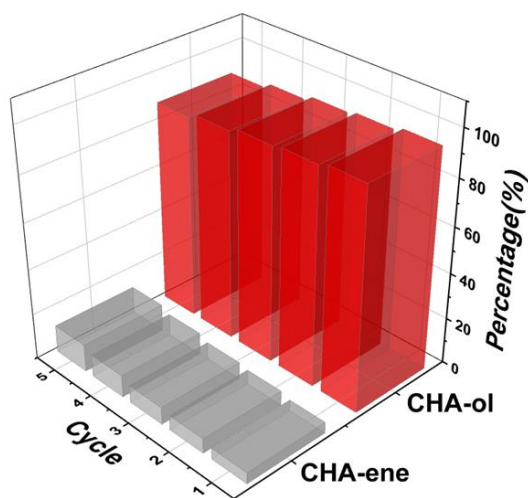*Fig. S13* PXRD pattern of **P3QA** after exposure to **CHA-ol** vapor and heating in vacuum.

Fig. S14 Relative uptake of **CHA-ol** and **CHA-ene** by **P3QA** over 24 h after five cycles.

7. Crystallography Data

Table S1. Experimental crystallographic data for the crystal of **P3QA⊃CHA-ol**.

Parameters	P3QA⊃CHA-ol
Formula	$C_{61}H_{68}Cl_2O_{13}$
Formula weight	1080.05
Temperature (K)	213.00
Crystal system	Trigonal
Space group	$R3c$
a (Å)	13.5991(2)
b (Å)	13.5991(2)
c (Å)	52.4778(8)
α (°)	90
β (°)	90
γ (°)	120
$Volume$ (Å^3)	8404.8(3)
Z	6
ρ_{calc} (g cm^{-3})	1.280
μ (mm^{-1})	1.026
F (000)	3432.0
Goodness-of-fit on F^2	1.057
h, k, l max	16, 16, 63
N_{ref}	3530
T_{min}, T_{max}	0.578, 0.751
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0529$, $wR_2 = 0.1508$
Final R indexes [all data]	$R_1 = 0.0609$, $wR_2 = 0.1593$
CCDC Number	2307418

8. References

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S2. Gaussian 16, Revision C.01,M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Gaussian, Inc., Wallingford CT, 2019.

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S4. S. Grimme, S. Ehrlich and L. Goerigk, *J. Comp. Chem.*, 2011, **32**, 1456–1465.

S5. L. Tian and F. Chen, *J. Comput. Chem.*, 2012, **33**, 580–592.