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A Convenient Synthetic Route to Partial-Cone *p*-Carboxylatocalix[4]arenes

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Abstract: *p*-Carboxylatocalix[*n*]arenes have emerged as useful building blocks for the construction of a diverse range of supramolecular assemblies. A convenient route to a *p*-carboxylatocalix[4]arene that is locked in a partial-cone conformation is presented. The conformation gives the molecule markedly different topological directionality relative to those previously used in self- and metal-directed assembly studies.

Keywords: *p*-Carboxylatocalix[4]arene · Supramolecular assemblies

The calix[4]arene framework (C[4], Fig. 1A) represents one of the most widely modifiable synthetic platforms in supramolecular chemistry.[1] In this regard significant effort has been invested in controlling the conformation of these molecules for a variety of reasons.[2] A good example of this can be seen when considering OH (or pairs of distal OH/alkoxy) groups at the lower-rim, with the molecules adopting a cone conformation as shown in Fig. 1A. In this conformation, C[4]s with varying upper-rim functionality (*e.g.* sulfonate,[3] phosphonate[4] and carboxylate[5,6]) possess molecular clefts that are perfectly suited to act as hosts towards a wide range of both organic and inorganic guests. Changes in lower-rim functionalisation, for example tetra-*O*-alkylation in the presence of different bases, provide access to the entire range of C[4] conformations shown in Fig. 1. Through synthetic control one can thus a) control the topological directionality of this platform and b) tune the nature of any resulting molecular cleft by careful selection of the group to be introduced at the C[4] lower-rim.

p-Carboxylatocalix[4]arenes (*p*CO_2[4]s) have emerged as versatile building blocks for a) the template-directed assembly of non-covalent nanotubes and bi-layers,[5] and b) the metal-directed assembly of coordination polymers and nanometre-scale capsules.[6] The positioning and number of CO_2H groups around the upper-rim of the C[4] framework is important in controlling assembly properties and, although they appear simple from a synthetic perspective, isolation of these molecules can be challenging at times. As shown in Scheme 1, *p*-carboxylatocalix[4]arene (**1**) is accessed through an upper-rim two-step formylation *via* a bromomethyl intermediate, followed by oxidation.[7,8] Calix[4]arene lower-rim tetra-*O*-alkylation (with alkyl chains greater or equal in length to propyl) is known to lock the C[4] framework in a pinched-cone conformation, preventing rotation through the annulus. Compound **2** (Scheme 1) is accessed *via* lower-rim tetra-*O*-alkylation, upper-rim formylation and subsequent oxidation to afford the corresponding carboxylic acid.[8]

Given our interest in *p*-CO_2[4]-based self- and metal-directed assembly we recently began to investigate the introduction of a variety of groups to the lower-rim of the general *p*-CO_2[4] framework. As many of the groups we wished to introduce would not survive the conditions required for C[4] upper-rim functionalisation, it was necessary to find an alternative synthetic strategy to these new building blocks. As a starting point we explored esterification of compound **1** prior to lower-rim modification, the results of which are presented in this contribution.

Esterification of compound **1** was carried out by acid catalysis in ethanol to afford *p*-carboxyethylcalix[4]arene (**3**) as a brown solid in 72% yield (Scheme 2).[10] Analysis by ^{1}H NMR spectroscopy confirmed that **3** was in a cone conformation as expected, which is driven by the presence of lower-rim OH groups, all of which hydrogen bond in concert to stabilise the

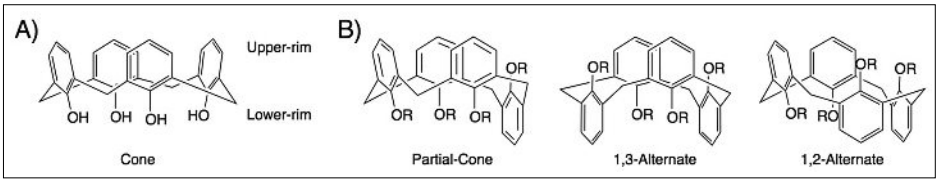
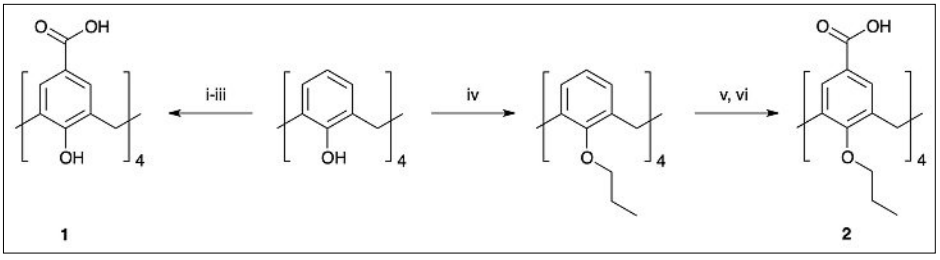


Fig. 1. A) calix[4]arene (C[4]) in the cone conformation. B) Lower-rim altered C[4]s in the other three general conformations found for this molecular framework (R = alkyl).



Scheme 1. Synthetic routes to *p*-carboxylatocalix[4]arene (**1**) and the related tetra-*O*-propyl analogue (**2**). Conditions as follows: i) paraformaldehyde / HBr / acetic acid; ii) HMTA / glacial acetic acid; iii) $NaClO_2$ / NaH_2PO_4 / dmso; iv) NaH / iodopropane / dmf; v) HMTA / trifluoroacetic acid; vi) $NaClO_2$ / sulfamic acid.[7–9]

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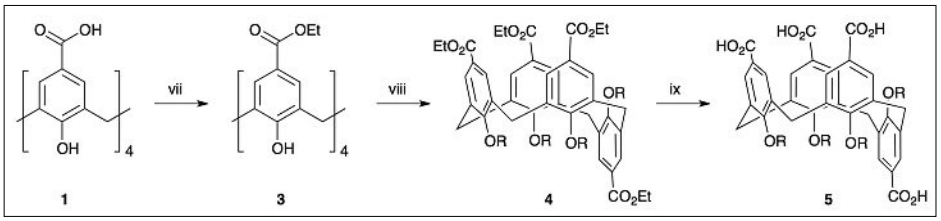
arrangement. Compound **3** was recrystallised from a number of solvents in order to obtain supporting structural data. Slow evaporation of a pyridine solution of **3** afforded colourless single crystals that were suitable for diffraction studies.

Structure analysis showed the crystals to be in a monoclinic cell and structure solution was performed in the space group $P2_1/n$. The asymmetric unit revealed formation of a pyridinium complex as shown in Fig. 2, with corresponding formula of [**PyH**][**3-H**]. Protonation of the pyridine occurs with simultaneous deprotonation of the lower-rim O(1) hydroxyl group in **3**. The pyridinium cation is found to reside in the C[4] cavity, which is stabilised by concerted hydrogen bonding interactions; this occurs with three OH···O distances lying in the range of 1.667–1.994 Å. There are two CH···π interactions observed between the *ortho* and *para* H atoms on the [**PyH**]$^+$ guest and the aromatic rings of [**3-H**]$^-$, and these occur with H[43]···centroid and H[45]···centroid distances of 2.901 and 2.494 Å respectively (Fig. 2). In addition to this, the pyridinium cation forms one NH···OCOH and one CH···OCOH hydrogen bonding interaction with symmetry equivalent (s.e.) [**3-H**]$^-$ anions to build up an extended H-bonded array; this occurs with respective H[1N]···O[12] s.e. and H[42]···O[8] s.e. distances of 1.864 and 2.307 Å (Fig. 3).

Following successful esterification of **1** (to give **3**) we attempted lower-rim alkylation under analogous conditions to those used to alkylate C[4] in the synthetic pathway to compound **2** (Scheme 1).[8] Reaction of **3** with iodopropane in the presence of NaH as a base in dmf, followed by recrystallisation from acetone, afforded colourless single crystals in 68% yield. It was immediately obvious from ^{1}H NMR spectroscopy that the product was not in a cone conformation as desired, but rather that it had reacted in an alternative manner and become locked in a partial-cone arrangement. Structural analysis confirming this found single crystals of tetra-*O*-propoxy-*p*-carboxyethylcalix[4]arene (**4**) to be in an orthorhombic cell and structure solution was performed in the space group *Pnma*. The asymmetric unit comprises one half of the molecule and symmetry expansion reveals the partial-cone conformation in **4** as shown in Fig. 4. Following this observation we attempted to isolate a sodium complex of **3** but were unsuccessful. We can only therefore conclude that there is an influencing interaction between the sodium ion and the upper-rim CO_2Et group rotated out of the cone prior to *O*-alkylation.

With formation of partial-cone **4** confirmed, subsequent saponification afforded the carboxylic acid derivative **5** (Scheme 2)



Scheme 2. Synthetic routes to *p*-carboxyethylcalix[4]arene (**3**) and related partial-cone tetra-*O*-propyl derivatives **4** and **5**. Conditions as follows: vii) TsOH / EtOH; viii) NaH / iodopropane / dmf; ix) NaOH / THF / MeOH / H_2O.[10]

as a yellow solid in 24% yield. Attempts were made to recrystallise **5** from a number of different solvents, and slow evaporation of a dmf solution did afford colourless single crystals that were suitable for diffraction studies. Structural analysis found the crystals to be in a monoclinic cell and structure solution was performed in space group *C*2/*c*. The asymmetric unit comprises one molecule of **5** and two dmf of crystallisation as shown in Fig. 5A. One dmf forms hydrogen bonding interactions with the CO_2H group of the rotated aromatic ring with O[14]···H[10O] and O[9]···H[48] distances of 1.777 and 2.423 Å respectively. Symmetry expansion results in the formation of a hydrogen-bonded head-to-head dimer, a motif seen for other pCO$_2$[4]s[5] in the absence of a solvent/species capable of interrupting the common CO_2H···CO_2H homosynthon (Fig. 5B); this occurs through two crystallographically unique OCOH···OCOH hydrogen bonding interactions with respective H[8O]···O[12] and H[11O]···O[7] distances of 1.820 and 1.805 Å. The second dmf is disordered over two positions and was modelled in each at 50% occupancy. This also forms hydrogen bonding interactions with the CO_2H group of the splayed aromatic ring with O[13]···H[5O] and O[6]···H[45] distances of 1.787 and 3.230 Å respectively. Examination of the extended structure reveals that molecules/dimers pack in an anti-parallel bi-layer array as is often observed for such systems (Fig. 5C).[5]

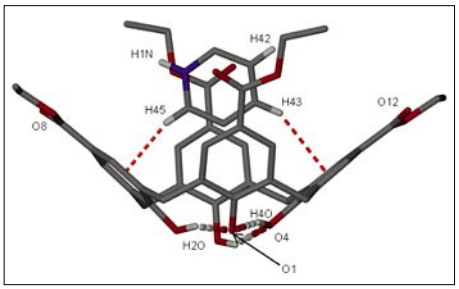


Fig. 2. Selectively labelled asymmetric unit in the single crystal X-ray structure of [**PyH**][**3-H**]. Hydrogen bonding interactions are shown as split-colour dashed lines and CH···π interactions are shown as red dashed lines. Hydrogen atoms (apart from those involved in hydrogen bonding and CH···π interactions) omitted for clarity.

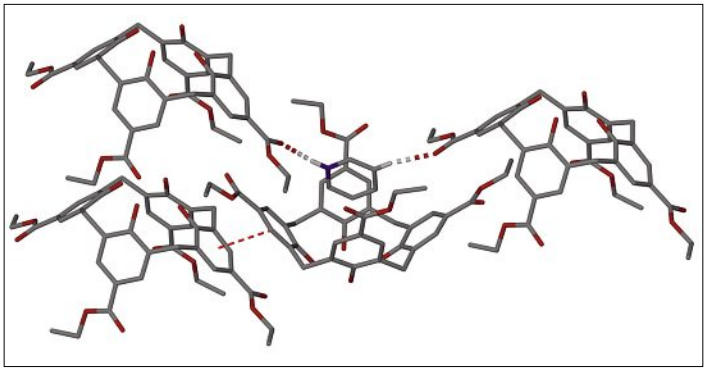


Fig. 3. Extended structure in [**PyH**][**3-H**] showing H-bonding and π···π interactions as split-colour and red-dashed lines respectively. Hydrogen atoms (apart from those involved in hydrogen bonding and π···π interactions) have been omitted for clarity.

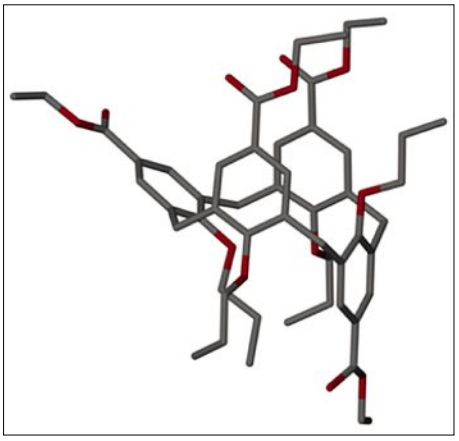


Fig. 4. Symmetry expanded single crystal X-ray crystal structure of compound **4** in the partial-cone conformation.

To conclude, we have presented the synthesis of an unexpected partial-cone pCO$_2$[4] and have confirmed structural changes throughout the synthetic pathway *via* single crystal *X*-ray studies. Through comparison with the synthetic route for

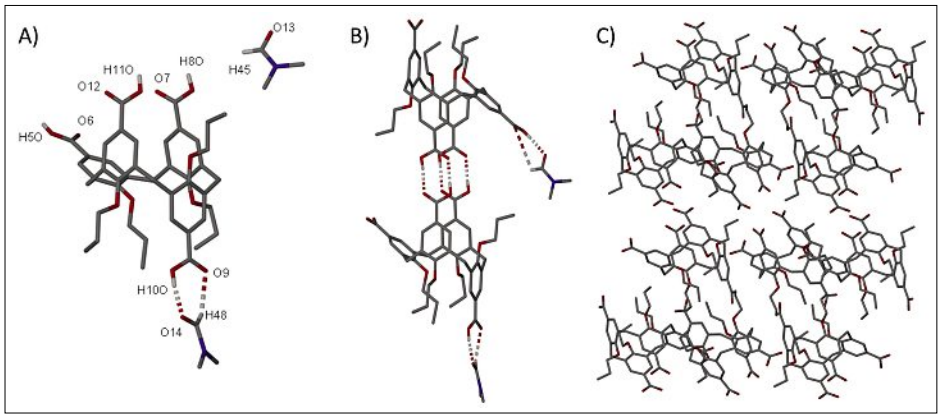


Fig. 5. A) Selectively labelled asymmetric unit found in the single crystal X-ray structure of **5**. B) Symmetry expanded structure showing a hydrogen-bonded head-to-head dimer. C) Extended structure showing the bilayer array. Hydrogen bonding interactions are shown as split-colour lines. Hydrogen atoms (apart from those involved in hydrogen bonding) have been omitted for clarity. DMF of crystallisation omitted for clarity in C.

cone-shaped tetra-*O*-propyl-*p*-carboxylatocalix[4]arene, it is clear that the presence of upper-rim ester functionality has a dramatic effect on the prevailing conformation. Future work will focus on the use of partial-cone pCO_2[4]s in the formation of both non-covalent and metal-directed assemblies with a view to exploring the effects of this unusual conformation coupled with topological directionality. These results will be reported in due course.

Experimental

p-Carboxylatocalix[4]arene (**1**) was synthesised according to literature procedures.[7] CCDC 1404296 – 1404298 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via www.ccdc.cam.ac.uk/data_request/cif*.

Synthesis of p-Carboxyethyl-25,26,27,28-tetrahydroxycalix[4]arene, 3

A suspension of **1** (4.00 g, 6.66 mmol) and *p*-toluenesulfonic acid (12.70 g, 0.07 mol) in ethanol (250 mL) was added to a 500 mL round-bottomed flask and the mixture was heated at reflux for one week. The solvent was removed under reduced pressure, and the residue dissolved in DCM (300 mL) and washed twice with saturated $NaHCO_3$ (150 mL) and water (150 mL). The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure to afford **3** as a brown solid (3.44 g, 72%). ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ = 10.17 (s, 4H, OH), 7.85 (s, 8H, ArH), 4.34 (q, 8H, OCH_2CH_3), 4.26 (broad s, 4H, $ArCH_2Ar$), 3.75 (broad s, 4H, $ArCH_2Ar$), 1.38 (t, *J* = 4.2 Hz, 12H, OCH_2CH_3). ^{13}C NMR (300 MHz, 25 °C, $CDCl_3$): δ = 165.70, 152.57, 131.16, 127.48, 124.89, 60.88, 31.42, 14.37. MS *m/z* observed 730.2859, theoretical 730.2858 $[M + NH_4]^+$. IR (solid phase, ν cm^{-1}) = 3192m, 2978m, 2928m, 2360w, 1711s, 1607m, 1307s, 1281s, 1187s. Compound **3** was crystallised by slow evaporation from pyridine. Crystal data for [PyH][3-H] (CCDC 1404296): $C_{45}H_{45}N_1O_{12}$, *M* = 791.82, Colourless lath, 0.19 × 0.10 × 0.02 mm^3, monoclinic, space group $P2_1/n$, *a* = 9.3836(3), *b* = 20.4700(7), *c* = 20.3370(7) Å, β = 98.885(2)°, *V* = 3859.5(2) $Å^3$, *Z* = 4, Bruker D8 diffractometer operating with a PHOTON 100 detector, synchrotron radiation, λ = 0.77490 Å, *T* = 100(2)K, $2\theta max$ = 62.3°, 58367 reflections collected, 9613 unique (R_{int} = 0.0490). Final GooF = 1.101, R_1 = 0.0618, wR_2 = 0.1546, R indices based on 7285 reflections with I >2sigma(I) (refinement on F^2).

Synthesis of Partial-cone Tetra-O-propoxy-p-carboxyethylcalix[4]arene, 4

A solution of **3** (1.00 g, 1.40 mmol) dissolved in 50 mL DMF was placed in a 250 mL round-bottom flask. Sodium hydride (60%, 0.48 g, 11.90 mmol) was added and the mixture allowed to stir at RT for 30 minutes. After this time 1-iodopropane (1.16 mL, 0.01 mol) was added and the solution was heated at 80 °C for 1 h. The reaction was quenched by careful addition of MeOH and the solvents removed under reduced pressure to afford a yellow solid. The crude product was washed with water and filtered before being recrystallised from hot acetone to afford colourless single crystals (0.84 g, 68%). ^{1}H NMR (300 MHz, 25 °C, $CDCl_3$): δ = 8.0 (s, 2H, ArH), 7.88 (s, 2H, ArH), 7.67 (s, 2H, ArH), 7.01 (s, 2H, ArH), 4.42 (m, 4H, OCH_2CH_3), 4.23 (m, 6H, OCH_2CH_3), 4.08 (d, *J* = 12.0 Hz, 2H, $ArCH_2Ar$), 3.81 (q, *J* = 6.8 Hz, 4H, $OCH_2CH_2CH_3$), 3.75 (s, 4H, $ArCH_2Ar$), 3.59 (q, *J* = 6.8 Hz, 2H, OCH_2CH_3), 3.24 (q, *J* = 7.0 Hz, 2H, OCH_2CH_3), 3.15 (d, *J* = 12.0 Hz, 2H, $ArCH_2Ar$), 2.12 (q, *J* = 7.0 Hz, 2H, $OCH_2CH_2CH_3$), 1.93 (q, *J* = 6.8 Hz, 2H, $OCH_2CH_2CH_3$), 1.41 (m, 5H, overlap of OCH_2CH_3 and $OCH_2CH_2CH_3$), 1.29 (t, *J* = 7.4 Hz, 6H, $OCH_2CH_2CH_3$), 1.13 (m, 10H, overlap of 3 × $OCH_2CH_2CH_3$ and OCH_2CH_3), 0.64 (t, *J* = 7.4 Hz, 3H, $OCH_2CH_2CH_3$). ^{13}C NMR (300 MHz, 25 °C, $CDCl_3$): δ = 166.78, 166.65, 166.07, 161.56, 160.90, 159.47, 136.34, 133.77, 133.32, 132.37, 131.47, 131.30, 130.91, 130.25, 124.82, 123.97, 123.92, 76.42, 75.72, 74.84, 60.78, 60.49, 60.21, 35.73, 30.93, 30.37, 23.71, 21.86, 14.45, 14.38, 14.20, 10.90, 10.73, 9.05. MS *m/z* observed 898.4740, theoretical 898.4736 $[M + NH_4]^+$. IR (solid phase, ν cm^{-1}) = 3663w, 2969m, 1714s, 1600m, 1283s, 1187s. Crystal data for **4** (CCDC 1404297): $C_{52}H_{64}O_{12}$, *M* = 881.03, Colourless block, 0.40 × 0.25 × 0.20 mm^3, orthorhombic, space group *Pnma*, *a* = 17.0322(13), *b* = 16.7264(11), *c* = 17.3355(13) Å, *V* = 4938.7(6) $Å^3$, *Z* = 4, Bruker X8 Apex II CCD diffractometer, MoKα radiation, λ = 0.71073 Å, *T* = 100(2)K, $2\theta max$ = 49.5°, 26905 reflections collected, 4394 unique (R_{int} = 0.0818). Final GooF = 1.630, R_1 = 0.1277, wR_2 = 0.2703, R indices based on 3429 reflections with I >2sigma(I) (refinement on F^2).

Synthesis of Partial-cone Tetra-O-propoxy-p-carboxylatocalix[4]arene, 5

Compound **4** (0.31 g, 0.35 mmol) and NaOH (0.17 g, 4.18 mmol) were dissolved in a mixture of THF, MeOH and water (2:1:1, 5 mL) and the mixture was heated at 50 °C for 3 days. The solution was acidified with 1M HCl, diluted with ethyl acetate and washed with water (2 × 50 mL) followed by brine (2 × 50 mL). The solution was dried over $MgSO_4$ and the solvents evaporated to afford pure **5** as a yellow solid (63.0 mg, 24%). ^{1}H NMR (300 MHz, 25 °C, DMSO-d^6): δ = 12.23 (bs, 4H, COOH), 7.92 (s, 2H, ArH), 7.87 (s, 2H, ArH), 7.59 (s, 2H, ArH), 6.96 (s, 2H, ArH), 4.01 (m, 2H, $OCH_2CH_2CH_3$), 3.94 (d, *J* = 12.0 Hz, 2H, $ArCH_2Ar$), 3.74 (m, 10H, overlap of $OCH_2CH_2CH_3$ and $ArCH_2Ar$), 3.42 (m, 2H, $OCH_2CH_2CH_3$), 3.20 (d, *J* = 12.0 Hz, 2H, $ArCH_2Ar$), 1.91 (m, 2H, $OCH_2CH_2CH_3$), 1.74 (m, 4H, $OCH_2CH_2CH_3$), 1.08 (t, *J* = 7.4 Hz, 6H, $OCH_2CH_2CH_3$), 0.92 (t, *J* = 7.2 Hz, 3H, $OCH_2CH_2CH_3$), 0.55 (t, *J* = 7.2 Hz, 3H, $OCH_2CH_2CH_3$). ^{13}C NMR (300 MHz, 25 °C, DMSO-d^6): δ = 167.46, 166.78, 160.99, 159.09, 136.17, 133.27, 132.81, 132.52, 131.60, 131.16, 130.43, 23.04, 22.88, 10.67, 10.22, 8.90. IR (solid phase, ν cm^{-1}) = 2961m, 2931m, 2875m, 1711s, 1676s, 1599m, 1424m, 1308s, 1283s, 1186s. Compound **5** was crystallised by slow evap-

oration of a dmf solution. MS *m/z* observed 769.8901, theoretical 769.8896 $[M + H]^+$. Crystal data for **5**·2dmf (CCDC 1404298): $C_{50}H_{62}N_2O_{14}$, M = 915.02, Colourless plate, 0.17 × 0.13 × 0.02 mm^3, monoclinic, space group $C2/c$, a = 37.3004(15), b = 14.2873(6), c = 18.2486(8) Å, β = 93.557(2)°, V = 9706.3(7) Å^3, Z = 8, Bruker D8 Diffractometer operating with a PHOTON 100 detector, synchrotron radiation, λ = 0.77490 Å, T = 100(2)K, $2\theta max$ = 52.4°, 54147 reflections collected, 7495 unique (R_{int} = 0.0512). Final GooF = 2.978, R_1 = 0.1240, wR_2 = 0.3633, R indices based on 5993 reflections with I >2sigma(I) (refinement on F^2).

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