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Synthesis and structures of *O*-anthrylmethyl-substituted hexahomotrioxacalix[3]arenes

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Abstract: *O*-Alkylation of 7,15,23-tri-*tert*-butyl-25,26,27-trihydroxy-2,3,10,11,18,19-hexahomo-3,11,19-trioxacalix[3]arene (**1**H_3) with 9-chloromethylanthracene **5** was carried out under different reaction conditions. Variation of the number of anthrylmethyl group introduced at the phenolic rim of hexahomotrioxacalix[3]arene **1**H_3 was achieved through selective *O*-alkylation using stoichiometric amounts of 9-chloromethylanthracene **5** in acetone to afford the mono-*O*-alkylated product **2**H_2An, the di-*O*-alkylated product **3**HAn_2 and the *tri*-*O*-alkylated product *partial*-*cone*-**4**An_3, respectively. Interestingly, by using an acetone/benzene (1:1 v/v) mixed solvent system, the *cone*-**4**An_3 was successfully synthesized. These results suggest that the solvent can also control the conformation of the *O*-alkylation products. The possible reaction routes of the *cone*-**4**An_3 and *partial*-*cone*-**4**An_3 are also discussed.

Keyword: Homotrioxacalix[3]arenes/ Selective *O*-alkylation/ Solvent effects/ Conformation.

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HIGHLIGHTS

♦ *O*-Alkylation of compound **1**H_3 with 9-chloromethylanthracene **5** was carried out under the different reaction conditions.

♦ The solvent can control the conformation of the *O*-alkylation products.

♦ The possible reaction routes of the final products were described in detail.

1. Introduction

In the field of supramolecular chemistry, calixarenes and related macrocycles have been receiving considerable attention as useful hosts for cations, anions and neutral molecules [1–7]. The increased interest in these compounds is stimulated by the availability of simple large-scale syntheses and the different ways in which they can be selectively functionalized either at the narrow (phenolic, lower) rim or at the wide (upper) rim. Molecular recognition is a fundamental phenomenon in biology, and tuning the affinity of a receptor for a ligand by the environment is key to the regulation of biological processes. This has inspired many chemists to design artificial receptors [8–11].

Hexahomotrioxacalixarenes are a class of synthetic macrocycles having phenolic units linked by CH_2OCH_2 bridges, and their trimer has been widely used as a platform to generate versatile hosts for metal cations [12–19], ammonium cations [20–22], and fullerene derivatives [23–25]. In most cases, the functionalization of hexahomotrioxacalix[3]arene has been achieved by *O*-alkylation of the OH groups at the lower rim. Recently, we reported in detail on the influence of *O*-substituents on the conformational isomerism of hexahomotrioxacalix[3]arenes, which selectively recognize primary ammonium ions and heavy metal ions [26–30].

Introduction of larger alkyl groups on the phenolic oxygens of calix[4]arenes led to a situation where the OR groups within a cyclophane ring cannot pass each other by oxygen-through-the-annulus rotation [3]. Although there exists four possible conformational isomers in calix[4]arenes; i.e. *cone*, *partial-cone*, 1,2-*alternate* and 1,3-*alternate*, only two different conformational isomers, "*cone*" and "*partial-cone*" can be clearly obtained in hexahomotrioxacalix[3]arene chemistry.

Shinkai and co-workers have reported the influence of *O*-substituents on the conformational isomerism of hexahomotrioxacalix[3]arenes in detail [22,31,32]. They have established that interconversion between conformers occurred via oxygen-through-the-annulus rotation and it is sterically allowed for methyl, ethyl, and propyl

groups, whereas butyl groups inhibited the process. More recently, we found that the interconversion is also facile for the propargyl moiety [30].

Insert Figure 1 in here

In their studies on the conformer distribution of hexahomotrioxacalix[3]arenes, Shinkai and co-workers reported that the partial-cone is sterically less crowded than the cone and therefore formed preferentially, regardless of the *O*-alkylation conditions. On the other hand, the cone results only when a template metal is present in the reaction system [32,33]; the metal ion interacts strongly with phenolic oxygen atoms which are functionalized with groups such as ethoxycarbonylmethyl or *N*,*N*-diethylaminocarbonylmethyl groups. However, the selective introduction of alkyl groups on the lower-rim has not yet been reported.

In this paper, we describe the selective synthesis of tris(anthrylmethyloxy)hexahomo-trioxacalix[3]arenes **4**An_3, with cone and partial-cone conformations, by *O*-alkylation of hexahomotrioxacalix[3]arene **1**H_3 in different solvent systems and the possible reaction routes to the final products, *cone*-**4**An_3 and *partial-cone*-**4**An_3 is discussed.

2. Experimental

General procedures

All melting points (Yanagimoto MP-S1) are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Nippon Denshi JEOL FT-300 NMR spectrometer and Varian-400MR-vnmrs400 with $SiMe_4$ as an internal reference: J-values are given in Hz. IR spectra were measured for samples as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrophotometer. Mass spectra were obtained with a Nippon Denshi JMS-HX110A Ultrahigh Performance mass spectrometer at 75 eV by using a direct-inlet system. UV-vis spectra were recorded using a Shimadzu UV- 3150UV-vis-NIR spectrophotometer. Elemental analyses were performed by a Yanaco MT-5.

Materials: The synthesis of 7,15,23-tri-*tert*-butyl-2,4,10,12,18,20-hexahomo-3,11,19-trioxa-calix[3]arene (**1**H_3) was carried out according to the reported procedure [34].

*2.1. Synthesis of mono-substituted hexahomotrioxacalix[3]arenes (**2**H_2An)*

A mixture of **1**H_3 (700 mg, 1.22 mmol) and potassium carbonate (3.55 g, 10.9 mmol) in dry acetone (20 mL) was heated at reflux for 1 h under N_2. Then 9-chloromethylanthracene **5** (310 mg, 1.35 mmol) was added and the mixture was heated at reflux for an additional 17 h. After cooling to room temperature, the mixture was filtered. The filtrate was concentrated to give a yellow oil, which was chromatographed over silica gel (Wako, C-300; 100 g) with hexane as eluent to give a colourless solid for which ^{1}H NMR spectroscopic analysis was in accord with it being the compound **2**H_2An. This solid was washed with methanol (20 mL) to give 845 mg (66 %) of **2**H_2An as a pale yellow solid. M.p. 208–210 °C. IR: ν_{max} (KBr)/cm^{-1}: 3415, 2951, 2904, 2865, 1481, 1362, 1195, 1070, 883. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.22 (18H, s, *t*-Bu), 1.31 (9H, s, *t*-Bu), 4.08 (2H, d, *J* = 10.5 Hz, Ar*C*H_2O*C*H_2Ar), 4.21 (2H, d, *J* = 10.5 Hz, Ar*C*H_2O*C*H_2Ar), 4.38 (2H, d, *J* =10.5 Hz, Ar*C*H_2O*C*H_2Ar), 4.50 (2H, d, *J* = 10.5 Hz, Ar*C*H_2O*C*H_2Ar), 4.61 (2H, d, *J* = 10.5 Hz, ArCH_2OCH_2Ar), 4.82 (2H, d, *J* = 10.5 Hz, Ar*C*H_2O*C*H_2Ar), 6.00 (2H, s, ArO*C*H_2An), 7.04 (2H, d, *J* = 2.4 Hz, Ar-*H*), 7.06 (2H, d, *J* =2. 4 Hz, Ar-*H*), 7.24–7.43 (4H, m, An-*H*), 7.81(2H, s, *OH*), 7.97 (2H, d, *J* = 10.0 Hz, Ar-*H*), 8.26 (2H, d, *J* = 9.0 Hz, An-*H*), 8.45 (1H, s, An-H). ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 31.48 ($C(CH_3)_3$), 31.52 ($C(CH_3)_3$), 33.88 ($C(CH_3)_3$), 34.29 ($C(CH_3)_3$), 68.24 (OCH_2), 68.83 (OCH_2), 69.20 (OCH_2), 71.53 (OCH_2), 123.49 (ArC), 123.67 (ArC), 124.62 (ArC), 124.91 (ArC), 126.15 (ArC), 126.50 (ArC), 126.90 (ArC), 127.75 (ArC), 128.82 (ArC), 130.24 (ArC), 131.10 (ArC), 141.48 (ArC), 146.33 (ArC), 153.69 (ArC), 155.78 (ArC) ppm. FABMS: *m/z*: = 766.28 [M^+]. $C_{51}H_{58}O_6$ (956.27): calcd. C 79.86, H 7.62. Found: C 79.63, H 7.42.

*2. 2 Synthesis of di-anthrylmethyl substituted hexahomotrioxacalix[3]arenes (**3**HAn_2)*

A mixture of **1**H_3 (700 mg, 1.22 mmol) and potassium carbonate (3.55 g, 10.9 mmol) in dry acetone (70 mL) was heated at reflux for 1 h under N_2. Then 9-chloromethylanthracene **5** (690 mg, 2.55 mmol) was added and the mixture was heated at reflux for an additional 17 h.

After cooling to room temperature, the mixture was filtered. The filtrate was concentrated to give a yellow oil, which was chromatographed over silica gel (Wako, C-300; 100 g) with hexane as eluent to give a colourless solid for which ^{1}H NMR spectroscopic analysis was in accord with it being a mixture of the starting compound **1**H_3 and *partial-cone*-**3**HAn_2 in the ratio of 5:95. This solid was washed with methanol (20 ml) to give 845 mg (71 %) of *partial-cone*-**3**HAn_2 as a pale yellow solid. M.p. 126–127 °C. IR: ν_{max} (KBr)/cm^{-1}: 3415, 2951, 2904, 2865, 1481, 1362, 1195, 1070, 883. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (18H, s, t-Bu), 1.22 (9H, s, t-Bu), 3.71 (2H, d, *J* = 11.7 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 3.90 (2H, d, *J* = 10.5 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 4.24 (2H, d, *J* =11.5 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 4.40 (2H, d, *J* = 9.2 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 4.44 (2H, d, *J* = 10.5 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 5.14 (2H, d, *J* = 11.7 Hz, ArC*H*$_2$OC*H*$_2$Ar), 5.54 (2 H, d, *J* = 11.7 Hz, ArO*CH*$_2$An), 5.77 (2 H, d, *J* = 11.7 Hz, ArO*CH*$_2$An), 7.01 (4 H, s, Ar-*H*), 7.10 (2 H, d, *J* =2. 4 Hz, Ar-*H*), 7.15–7.32 (8 H, m, An-*H*), 7.48 (1 H, s, *OH*), 7.88 (4 H, d, *J* = 8.25 Hz, Ar-*H*), 8.09 (4H, d, *J* = 9.0 Hz, An-*H*), 8.35 (1H, s, An-H). ^{13}C NMR (400 MHz, CDCl3, 25 °C): δ = 31.36 (C(CH_3)$_3$), 31.56 (C(CH_3)$_3$), 33.84 (C(CH_3)$_3$), 34.14 (C(CH_3)$_3$), 65.58 (OCH_2), 67.29 (OCH_2), 68.24 (OCH_2), 68.85 (OCH_2), 123.54 (ArC), 124.72 (ArC), 124.88 (ArC), 125.73 (ArC), 126.68 (ArC), 127.62 (ArC), 128.47 (ArC), 128.64 (ArC), 130.43 (ArC), 130.74 (ArC), 131.21 (ArC), 140.99 (ArC), 146.10 (ArC), 153.77 (ArC) and 155.36 (ArC) ppm. FABMS: *m/z*: = 955.28 [M$^+$]. $C_{66}H_{68}O_6$ (956.27): calcd. C 82.81, H 7.16. Found: C 82.75, H 7.13.

*2. 3 Synthesis of tri-anthrylmethyl substituted hexahomotrioxacalix[3]arenes (**4**An$_3$)*

*2.3.1 Synthesis of cone-**4**An$_3$*

A mixture of **1**H_3 (200 mg, 0.347 mmol) and caesium carbonate (2.27 g, 6.94 mmol) in dry acetone/benzene (1:1) (15 ml) was heated at reflux for 1 h under N_2. Then 9-chloromethylanthracene **5** (310 mg, 1.15 mmol) was added and the mixture was heated at reflux for an additional 40 h. After cooling to room temperature, the mixture was filtered. The filtrate was concentrated to give a yellow oil, for which the ^{1}H NMR spectrum was

consistent with it being *cone*-**4**An_3. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with hexane as eluent to give a yellow solid. This solid was washed with hexane to give 108 mg (69 %) of *cone*-**4**An_3 as a pale yellow solid. M.p. 257–258 °C. IR: ν_{max} (KBr)/cm^{-1}: 3410, 3058, 2988, 2920, 2897, 1760, 1480, 1455, 1377, 1200, 1199, 1094, 1058. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.02 (s, 27 H, *t*Bu), 4.21 (6H, d, *J* = 13.4 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 4.30 (6H, d, *J* = 13.4 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 5.43 (6H, s, ArO*CH*$_2$An), 6.83 (6H, s, Ar-*H*), 7.10–7.15 (6H, m, An-*H*), 7.20–7.28 (6H, m, Ar-*H*), 7.85 (6H, d, *J* = 8.3 Hz, An-*H*), 7.89 (6H, d, *J* = 8.3 Hz, An-*H*), 8.34 (3H, s, An-*H*) ppm. ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 28.98 ($C(CH_3)_3$), 30.14 ($C(CH_3)_3$), 64.79 (OCH_3), 67.05 (OCH_3), 68.48 (OCH_3), 122.40 (ArC), 123.47 (ArC), 124.00 (ArC), 125.06 (ArC), 126.28 (ArC), 126.73 (ArC), 127.82 (ArC), 128.26 (ArC), 129.57 (ArC), 144.34 (ArC) and 152.54 (ArC) ppm. FABMS: *m/z*: 1146.65 [M^+]. $C_{81}H_{78}O_6$ (1147.52): calcd. C 84.78, H 6.85. Found: C 84.92, H 7.05.

*2.3.2 Synthesis of partial-cone-**4**An$_3$*

A mixture of **1**H_3 (200 mg, 0.347 mmol) and caesium carbonate (2.63 g, 6.94 mmol) in dry acetone (20 ml) was heated at reflux for 1 h under N_2. Then 9-chloromethylanthracene **5** (310 mg, 1.15 mmol) was added and the mixture was heated at reflux for an additional 17 h. After cooling to room temperature, the mixture was filtered. The filtrate was concentrated to give a yellow oil, for which the ^{1}H NMR spectrum was consistent with it being only *partial-cone*-**4**An_3. The residue was chromatographed over silica gel (Wako, C-300; 100 g) with hexane as eluent to give a yellow solid. This solid was washed with hexane to give 126 mg (75 %) of *partial-cone*-**4**An_3 as a pale yellow solid. M.p. 257–258 °C. IR: ν_{max} (KBr)/cm^{-1}: 3400, 2975, 2915, 2867, 1758, 1483, 1456, 1363, 1234, 1199, 1094, 1058. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.85 (18H, s, *t*Bu), 1.05 (9H, s, *t*Bu), 3.87 (2H, d, *J* = 11.7 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 3.89 (2H, d, *J* = 11.2 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 3.99 (2H, d, *J* = 11.7 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 4.00 (2H, d, *J* = 11.2 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 4.23 (2H, d, *J* = 11.7 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 4.31 (2H, d, *J* = 11.2 Hz, Ar*CH*$_2$O*CH*$_2$Ar), 5.25 (2H, s, ArO*CH*$_2$An), 5.36 (2H, d, *J* = 12.7 Hz, ArO*CH*$_2$An), 5.54 (2H, d, *J* = 12.7 Hz, ArO*CH*$_2$An), 6.86 (2H, d, *J* =

2.4 Hz, Ar-*H*), 6.99 (2H, d, *J* = 2.4 Hz, Ar-*H*), 7.10 (2H, s, Ar-*H*), 7.14–7.40 (12H, m, Ar-*H*), 7.82 (2H, d, *J* = 8.3 Hz, An-*H*), 7.89 (4H, d, *J* = 8.3 Hz, An-*H*), 7.91 (6H, m, An-*H*), 8.35 (1 H, s, An-*H*), 8.37 (2H, s, An-*H*) ppm; ^{13}C NMR (400 MHz, $CDCl_3$, 25 °C): δ = 31.12 ($C(CH_3)_3$), 31.33 ($C(CH_3)_3$), 33.88 ($C(CH_3)_3$), 33.97 ($C(CH_3)_3$), 64.71 (OCH_2), 66.59 (OCH_2), 67.97 (OCH_2), 68.48 (OCH_2), 69.63 (OCH_2), 68.81 (OCH_2), 124.46 (ArC), 124.69 (ArC), 124.72 (ArC), 124.76 (ArC), 125.78 (ArC), 125.84 (ArC), 125.91 (ArC), 128.30 (ArC), 128.38 (ArC), 128.41 (ArC), 128.57 (ArC), 128.86 (ArC), 129.68 (ArC), 129.84 (ArC), 130.90 (ArC), 131.00 (ArC), 131.15 (ArC), 145.86 (ArC), 152.96 (ArC), 154.14 (ArC) and 157.34 (ArC) ppm. FABMS: *m/z*: 1146.72 [M^+]. $C_{81}H_{78}O_6$ (1147.52): calcd. C 84.78, H 6.96. Found: C 84.99, H 7.06.

3. Results and discussion

Synthesis

Hexahomotrioxacalix[3]arene **1**H_3 was *O*-alkylated with 9-chloromethylanthracene **5** (3.3 equiv.) using acetone as solvent in the presence of either Cs_2CO_3 or K_2CO_3 as base, exclusively affording the conformational isomer, *partial-cone*-**4**An_3 in 95 % yield, while the other possible isomer *cone*-**4**An_3 was not observed. On the other hand, when Na_2CO_3 or NaH are employed, only the hexahomotrioxacalix[3]arene **1**H_3 was recovered in 92 %, even when a large excess of Na_2CO_3 or NaH were used. Interestingly, hexahomotrioxacalix[3]arene **1**H_3 when using a acetone/benzene (1:1 v/v) mixed solvent system in the presence of Cs_2CO_3, afforded one pure conformational isomer, *cone*-**4**An_3 as the major product (Scheme 1). The conformer distribution for the reaction of **1**H_3 and 9-chloromethyl-anthracene **5** are summarized in Table 1.

Insert Scheme 1 in here

Insert Table 1 in here

Interestingly, we have succeeded in synthesizing both mono-*O*-alkylated product **2**H_2An

and di-*O*-alkylated product **3**HAn_2. The synthetic pathway of compounds **2**H_2An and **3**HAn_2 are shown in Scheme 2. The selective *O*-alkylation reaction of hexahomotrioxaocalix[3]arene **1**H_3 with 1 equiv. of 9-chloromethylanthracene **5** was carried out in presence of K_2CO_3 to afford calixarene **2**H_2An in 66 % yield. When 2.1 equiv. of 9-chloromethylanthracene **5** was used, the desired di-substituted product *partial-cone*-**3**HAn_2 was obtained in 71 % yield.

Insert Scheme 2 in here

Structure assignments

In the ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **2**H_2An, the signals for the aromatic protons are supposed to appear as two pairs of singlet at δ 7.04 and 7.06 ppm and those for the *tert*-butyl groups as two singlets at δ 1.31, 1.22 ppm. The ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **3**H_2An exhibits four peaks for the *tert*-butyl carbon at δ 31.48, 31.52, 33.88 and 34.29 ppm. On the other hand, there are six pairs of doublets for the bridge protons (ArO*C*H_2O) which indicates the existence of intramolecular hydrogen bonding between the hydroxyl groups and the 9-anthryl groups of the cyclic structure, which may fix the "*cone*" conformation. Compound **2**H_2An is expected to have a plane of chirality, because it has two types of substituents which are fixed and the C_1 symmetrical conformer does not show conformational change at room temperature. The ^{1}H NMR spectra in the presence of chiral shift reagents was measured to confirm that the compound **2**H_2An consists of one pair of enantiomers [35]. The ^{1}H NMR spectra of the compound **2**H_2An in the presence of Pirkle's reagent [(*S*)-2,2,2-trifluoro-1-(9-anthryl)ethanol] are shown in Figure 2. It is reported [21] that hydroxyl groups which do not participate in the intramolecular hydrogen bonding are necessary for an effective interaction between chiral calix[4]arenes and Pirkle's reagent. In the spectrum of compound **2**H_2An, all peaks of the bridged protons are split on addition of Pirkle's reagent due to the formation of two diastereomeric complexes (Figure 2). These findings suggest that one methoxy and a hydroxyl group of **2**H_2An play an important role to

coordinate with Pirkle's reagent.

Insert Figure 2 in here

The ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of compound **3**HAn_2 presents two singlets for the *tert*-butyl protons at δ 1.15 and 1.21 ppm (relative intensity 2:1). Furthermore, the resonance for the ArO*CH*$_2$Ph methylene protons appeared as a pair of doublets at δ 5.54 and 5.77 (J_{AB} = 11.7 Hz) ppm. The rotation of the unmodified OH group is still allowed, so that the two 9-anthryl groups are regarded to be equivalent both in a *cone* and a *partial-cone* conformation. Therefore, we cannot specify the conformation from ^{1}H NMR spectroscopy alone. The ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **3**HAn_2 exhibits four peaks for the *tert*-butyl carbons at δ 31.36, 31.56, 33.84 and 34.14 ppm. Fortunately, we were also able to obtain the crystal structure of *partial-cone*-**3**HAn_2 (Figure 3). Thus, the two 9-anthryl groups in the compound point up and down between the calixarene ring. Single crystals of **3**HAn_2 were grown from a mixture of hexane and chloroform (1:10), and the structure was investigated by X-ray crystallography to verify the conformation. The crystal structure was found to belong to the monoclinic crystal system with the space group l 2/a. The crystal structure of **3**HAn_2 is shown in Figure 3. The X-ray structure also supports the ^{1}H NMR spectrum. It is clear that one 9-anthryl group is present on the upper side of the calixarene ring and the other 9-anthryl group is on the lower side. Both the ^{1}H NMR spectrum and the single crystal analysis confirmed the *partial-cone* conformation of **3**HAn_2.

Insert Figure 3 in here

The ^{1}H NMR spectrum of *cone*-**4**An_3 shows a singlet for the *tert*-butyl protons at δ 1.01 ppm and a singlet for ArO*CH*$_2$Ph and the aromatic protons at δ 5.45 and 6.85 ppm, respectively indicating a C_3-symmetric structure of *cone*-**4**An_3. The X-ray structure of *cone*-**2**An_3 is shown in Figure 4. Within each calixarene is present H-bonding between the

chloroform molecules and the bridging oxygen atom, and another H-bond between the chloroform molecules and *t*-Bu-H. The calixarene molecule adopts a collapsed, or squashed conformation to facilitate this H-bonding and a π···π interaction between the arene rings. In the lower rim, the three anthryl rings are close to parallel and overlapping. This is achieved by considerable distortion from the potential C_3 symmetry and formation of a very irregular 18-membered ring, through O, around the center of the calixarene system. The ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of *cone*-**4**An_3 exhibits two peaks for the *tert*-butyl carbons at δ 28.98 and 30.14 ppm. Both the NMR spectrum and single crystal analysis confirmed the *cone* conformation of *cone*-**4**An_3.

Insert Figure 4 in here

The ^{1}H NMR spectrum ($CDCl_3$, 300 MHz) of *partial-cone*-**4**An_3 exhibits two groups of peaks for the anthryl protons at δ 8.37, 7.91 and 8.35, 7.89 ppm (relative intensity 2:1), and two singlets for the *tert*-butyl protons at δ 0.83, 1.05 ppm (relative intensity 2:1). Furthermore, the resonance for the ArO*CH*$_2$Ph methylene protons appeared as a singlet at δ 5.25 ppm and a pair of doublets at δ 5.36, 5.54 ppm (J_{AB} = 12.7 Hz). Upfield shifts for the inverted 9-anthryl ring protons were observed. The ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of *partial-cone*-**4**An_3 exhibits four peaks for the *tert*-butyl carbons at δ 31.12, 31.33, 33.88 and 33.97 ppm. These signals correspond to a C_S-symmetric structure.

Partial-cone and cone conformation

Shinkai and co-workers reported that the conformer distribution of a calixarene can be affected by the metal cation employed as the base [22]. It was shown that template metal cations such as Na^+ which strongly interacts with calix[4]arenes, suppress the rotation of the phenyl units and give rise to less-rotated conformers (such as *cone* and *partial-cone*), whereas non-template metal cations such as Cs^+ which scarcely interact with calix[4]arenes cannot suppress the rotation of the phenyl units, and give rise to rotated conformers (such as

1,2- and 1,3-*alternate*). Here, we can use this result by changing the base employed and then observe the effect on the conformer distribution of *partial-cone*-**4**An_3.

Insert Figure 5 in here

Insert Table 2 in here

On the other hand, the synthetic process for the *cone*-**4**An_3 is described in Table 2. In the presence of acetone, only *partial-cone*-**4**An_3 was produced but when a benzene/acetone mixture was used, the *cone*-**4**An_3 was also observed. Interestingly, on increasing the ratio of benzene in the solvent system, the possibility of forming *cone*-**4**An_3 was much greater than for *partial-cone*-**4**An_3 and in an acetone/benzene (1: 1 v/ v) system, a 90% yield of *cone*-**4**An_3 was observed. These results suggest that the solvent can also control the conformation of the *O*-alkylation products. Gholami and co-workers reported that solvents can considerably change both the rate and the mechanism of a chemical reaction. Solvent effects are closely related to the nature and extent of solute–solvent interactions [31]. The study of the solvent effects on this reaction in aprotic solvents has revealed a relationship to hydrogen bond donor and acceptor abilities and the polarity of solvent. At the most simplistic level, hydrogen bonding is favored in nonpolar organic solvents, while polar solvents lead to attractive interactions between nonpolar groups [36]. Therefore, in the presence of the polar solvent acetone, a hydrogen bond is formed between the solvent and hexahomotrioxacalix[3]arene. Here, intermolecular H-bonding is stronger than intramolecular hydrogen bonding. This time, rotation of the unmodified OH group is still allowed, and the reaction exclusively afforded the conformational isomer *partial-cone*-**4**An_3 rather than *cone*-**4**An_3. On the other hand, when the nonpolar solvent benzene is used, strong hydrogen bonding favorably forms between the three phenolic oxygens and they are arranged on the same side. The possible reaction route from **l**H_3 to *cone*-**4**An_3 is illustrated in Figure 5.

To confirm the reaction pathway of *cone*-**4**An_3, mono-*O*-alkylated compound **2**H_2An was *O*-alkylated with 9-chloromethylanthracene **5** (2.3 equiv.) in an acetone/benzene (1:1 v/v)

mixed solvent system (Scheme 3) in the presence of Cs_2CO_3. The product was separated by column chromatography; ^{1}H NMR spectroscopy established that *cone*-**4**An_3 derivatives are present. Retrospectively, it can be used to prove the reaction path of *cone*-**4**An_3 from compound **2**H_2An to *cone*-**4**An_3.

Insert Scheme 3 in here

The reaction route for **4**An_3 from **l**H_3 is illustrated in Figure 6. As already mentioned, the selective *O*-alkylation of compound **1**H_3 gradually formed compound, **2**H_2An, **3**HAn_2 and **4**An_3. **3**HAn_2 and **4**An_3 both possess the *cone*- and *partial-cone*-conformation. In the case of the *partial- cone* conformation, *partial-cone*-**4**HAn_3 could be produced from both *cone*-**3**HAn_2 and *partial-cone*-**3**HAn_2. Whereas, in the acetone solvent system, *partial-cone*-**3**HAn_2 was produced from **2**H_2An, which was confirmed by ^{1}H NMR spectroscopic analysis of **3**HAn_2. As a result, *partial-cone*-**4**An_3 was easily synthesized from *partial-cone*-**3**HAn_2 and the second 9-anthryl group which was introduced into *partial-cone*-**3**HAn_2 has a contribution to the formation of *partial-cone*-**4**An_3. However, in the case of the *cone* conformation, *cone*-**3**HAn_2 was obtained in an acetone/benzene (1:1 v/v) mixed solvent system as an intermediate compound and a small peak in the ^{1}H NMR spectrum was observed attributed to *cone*-**3**HAn_2. As a result, *cone*-**4**An_3, was only synthesized from *cone*-**3**HAn_2 in the presence of the acetone/benzene (1:1 v/v) solvent system. This strongly indicates that benzene plays a vital role in the step from compound **2**H_2An to *cone*-**3**HAn_2, and finally, to afford the desired compound *cone*-**4**An_3.

Insert Figure 6 in here

Conclusions

In conclusion, we have succeeded in the synthesis of the lower rim functionalized hexahomotrioxacalix[3]arenes, mono-*O*-alkylated **2**H_2An, di-*O*-alkylated **3**HAn_2,

tri-*O*-alkylated *cone*-**4**An_3 and *partial-cone*-**4**An_3, respectively and their structures were confirmed by ^1H NMR, ^{13}C NMR, IR, MS spectroscopy and by X-ray diffraction. Interestingly, **2**H_2An, **3**HAn_2, and *partial-cone*-**4**An_3 were synthesized from compound **1**H_3 through selective alkylation in acetone, whereas by using an acetone/benzene (1: 1 v /v) mixed solvent system, the *cone*-**4**An_3 was produced. These results suggest that the solvent can also control the conformation of the *O*-alkylation products. The solvent effects in this reaction when using aprotic solvents, has revealed a dependence on hydrogen bond donor and acceptor abilities and polarity of solvent. The possible reaction routes of the *cone*-**4**An_3 and *partial-cone*-**4**An_3 were also discussed herein.

Acknowledgements

This work was performed under the Cooperative Research Program of "Network Joint Research Center for Materials and Devices (Institute for Materials Chemistry and Engineering, Kyushu University)". We would like to thank the OTEC at Saga University and the International Collaborative Project Fund of Guizhou province at Guizhou University for financial support. We also would like to thank the EPSRC (overseas travel grant to CR.).

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HIGHLIGHTS

Hexahomotrioxacalixarenes, a class of synthetic macrocycles having phenolic units linked by CH_2OCH_2 bridges and their trimer, have been widely used as a platform to generate versatile hosts for metal cations, ammonium cations, and fullerene derivatives. In most cases, the functionalization of hexahomotrioxacalix[3]arene has been achieved by *O*-alkylation of the OH groups at the lower rim. There exists two possible conformational isomers for the hexahomotrioxacalix[3]arene, namely "*cone*" and "*partial-cone*". The influence of *O*-substituents on the conformational isomerism of hexahomotrioxacalix[3]arenes, which selectively recognize primary ammonium ions and heavy metal ions, has been recognised.

In this paper, the lower rim functionalized hexahomotrioxacalix[3]arenes (**2**H_2An, **3**HAn_2, *cone*-**4**An_3 and *partial-cone*-**4**An_3.) were synthesized. These structures were confirmed by ^{1}H NMR, ^{13}C NMR, IR, MS spectroscopy and X-ray analysis. Variation of the number of anthrylmethyl groups introduced at the phenolic rim of hexahomotrioxacalix[3]arene **1**H_3 was achieved through selective *O*-alkylation using stoichiometric amounts of 9-chloromethylanthracene **5** in acetone to afford the mono-*O*-alkylated product **2**H_2An, the di-*O*-alkylated product **3**HAn_2 and the *tri*-*O*-alkylated product *partial-cone*-**4**An_3, respectively. Interestingly, in an acetone/benzene (1:1 v/v) mixed solvent system, we successfully synthesized the *cone*-**4**An_3. These results suggest that the solvent can also control the conformation of the *O*-alkylation products via hydrogen bonding with the hydroxyl of the calixarene. The possible reaction routes of the *cone*-**4**An_3 and *partial-cone*-**4**An_3 were also discussed in detail.

Figure(s)

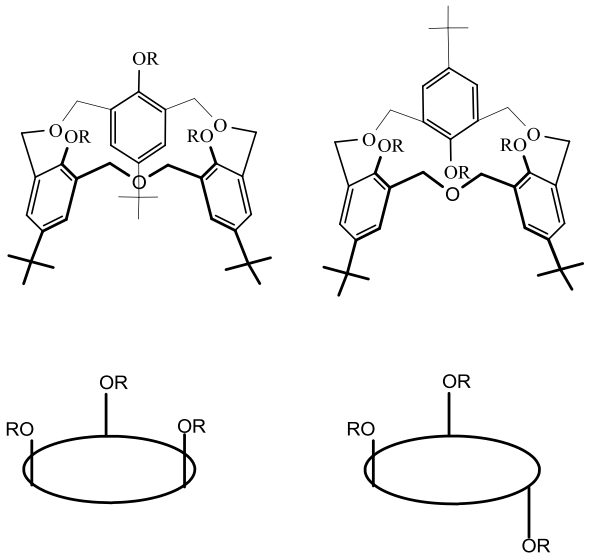


Fig. 1. Two possible conformers of *O*-alkylated hexahomotrioxacalix[3]arenes

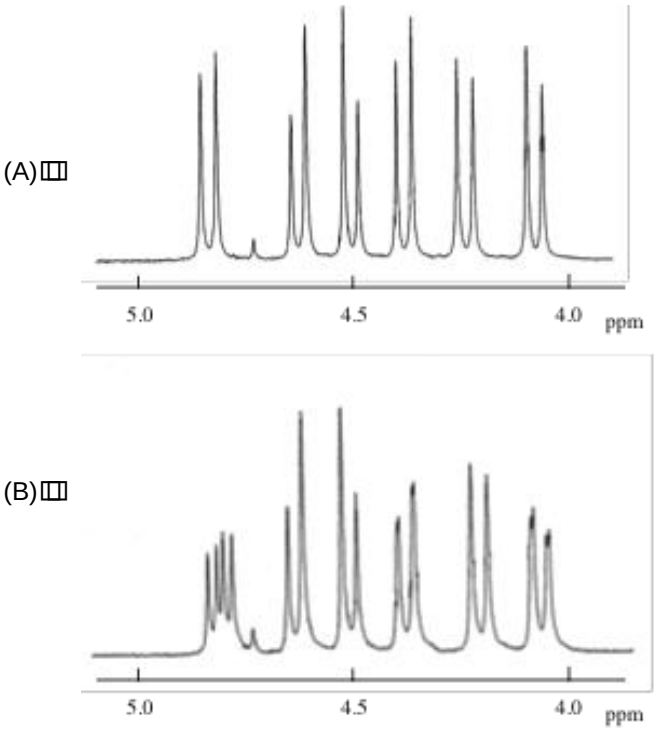
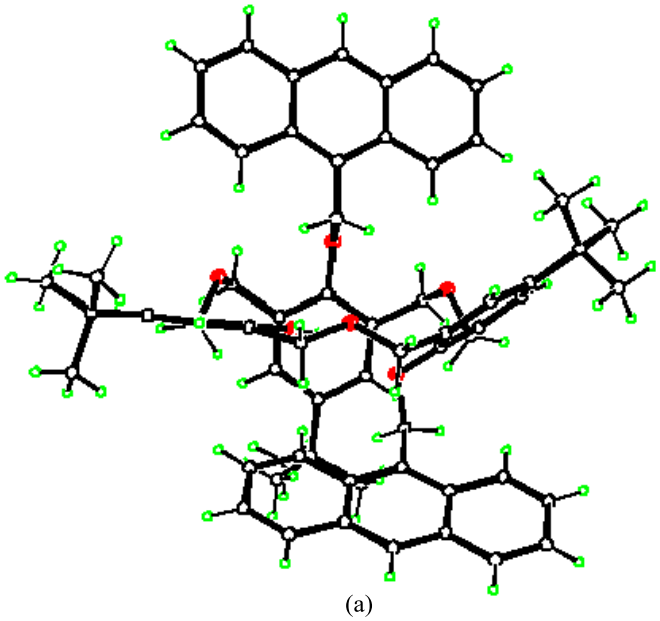
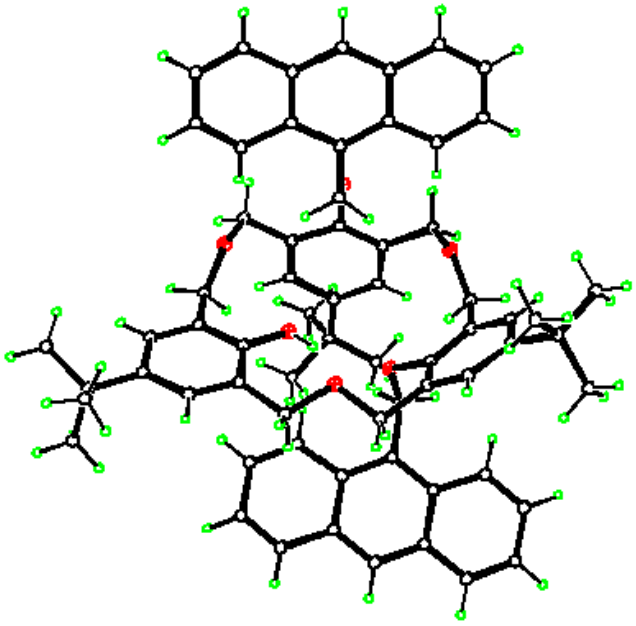


Fig. 2. Partial ^{1}H NMR spectra for bridged protons ($CDCl_3$, 300 MHz); (A) **2**H_2An (5 10^{-3} M), (B) **2**H_2An + Pirkle's reagent (1.2 times of [**2**H_2An]).



(a)



(b)

Fig. 3. ORTEP drawing of *partial-cone*-**3**HAn_2 with top (a) and side (b) views. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms except one are omitted for clarity.

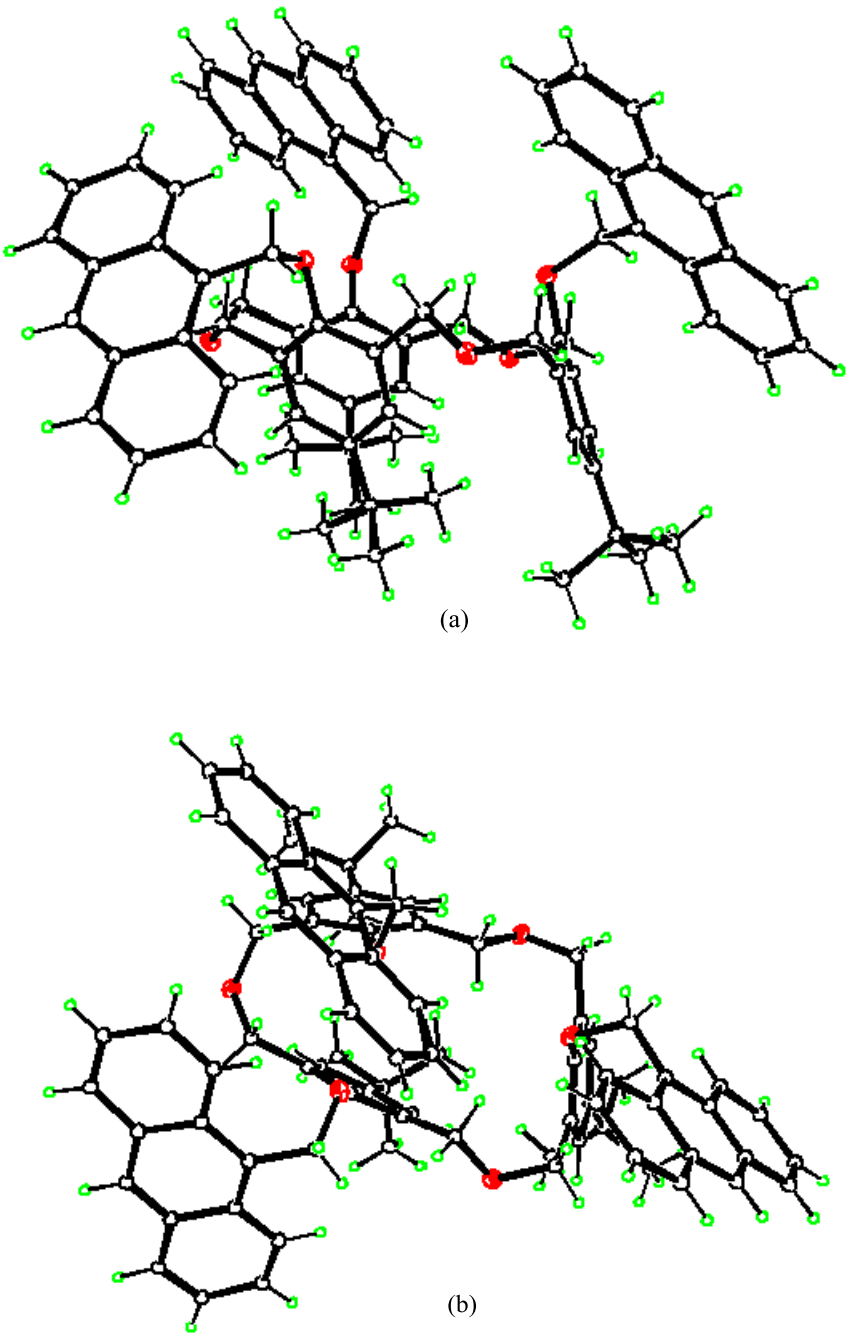


Fig. 4. ORTEP drawing of *cone*-**4**An_3 with top (a) and side (b) views. Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms except one are omitted for clarity.

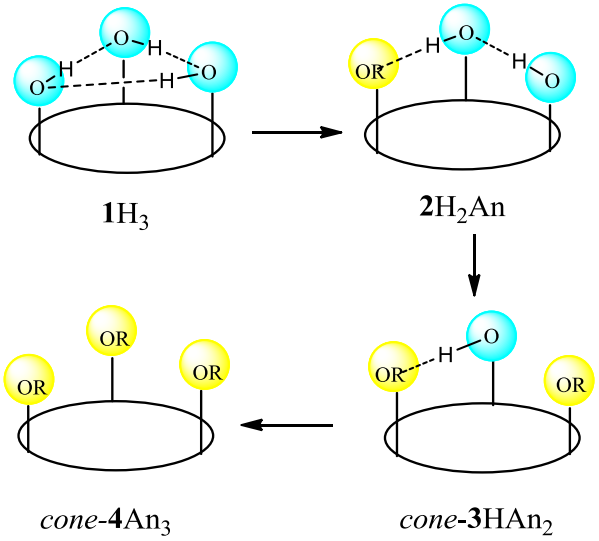


Fig. 5. Possible reaction pathway of *cone*-**4**An_3.

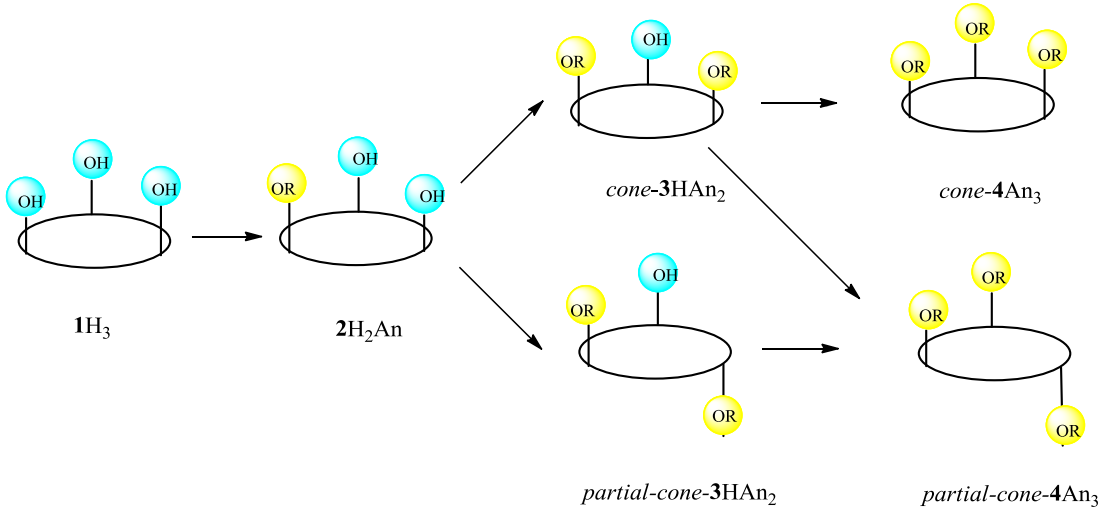


Fig. 6. Reaction pathways from compound **1**H_3 to compound **4**An_3**.**

Table 1 *O*-Alkylation reaction of hexahomotrioxaocalix[3]arene **1**H_3 with 9-chloromethylanthracene **5** (3.3 equiv.).

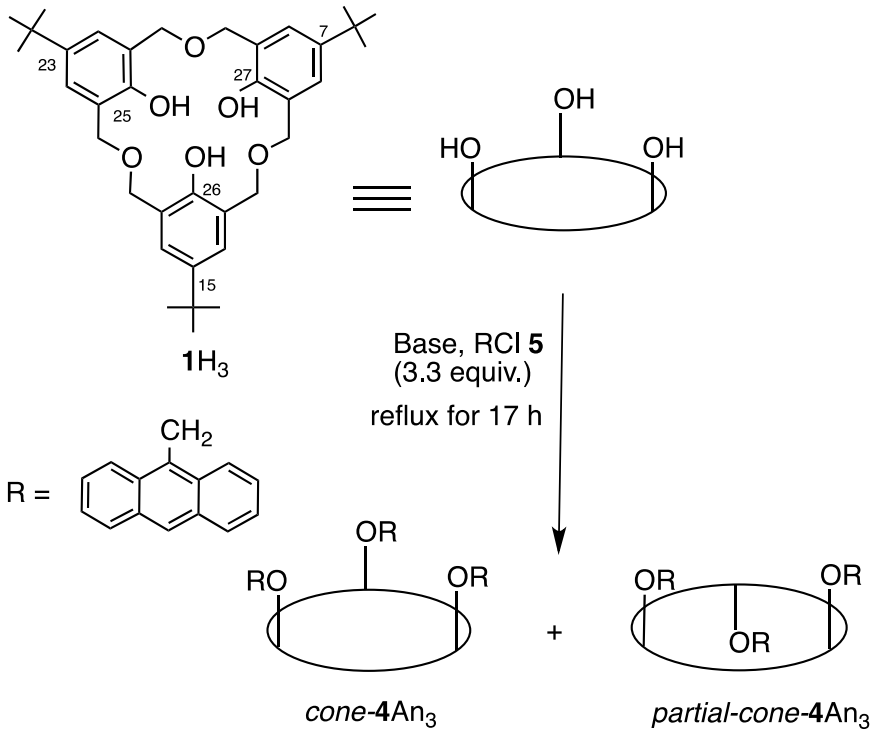
Run	Base	Solvemt	Distribution(%) [a, b]	
			cone-**4**An_3	*partial-cone*-**4**An_3
1	NaH	THF	0	0
2	Na_2CO_3	Acetone	0	0
3	K_2CO_3	Acetone	0	95 (75)
4	Cs_2CO_3	Acetone	0	95(72)
5	Cs_2CO_3	Acetone/ Benzene (1:1)	90 (69)	5

[a] Relative yields determined by ^{1}H NMR spectroscopy. [b] Isolated yields are shown in parentheses. [c] Starting compound **1**H_3 was recovered in quantitative yield.

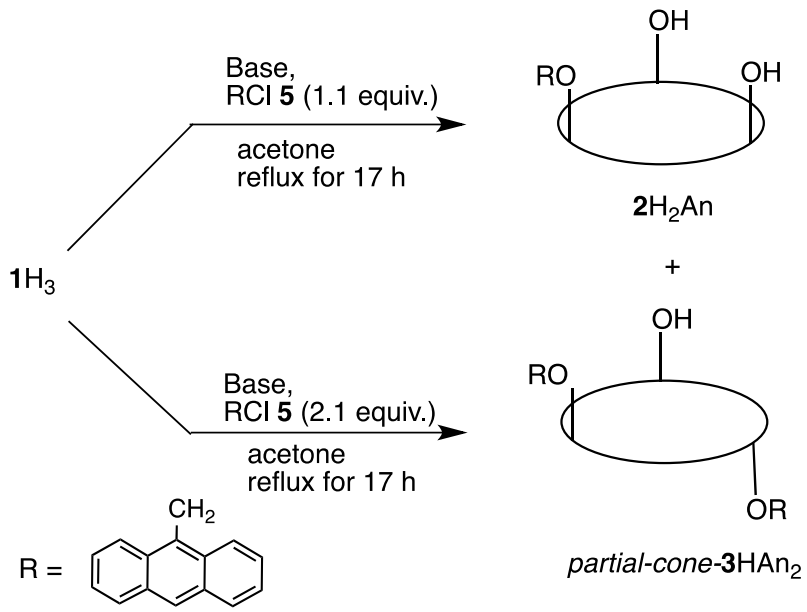
Table 2 *O*-Substitution reaction of hexahomotrioxaocalix[3]arene **1**H_3 with 9-chloromethylanthracene **5** (3.3 equiv.) in different ratio of acetone and benzene.

Run	Ratio (acetone: benzene)	Reaction time (h)	Distribution(%) [a, b]	
			cone-**4**An_3	*partial-cone*-**4**An_3
1	100:0	17	0	95 (72)
2	90:10	30	16	79 (52)
3	80:20	35	33 (14)	62 (38)
4	70:30	35	47 (23)	48 (31)
5	60:40	35	64 (42)	31 (12)
6	50:50	40	90 (69)	5

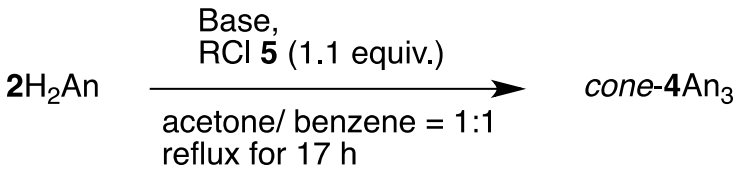
[a] Relative yields determined by ^{1}H NMR spectroscopy. [b] Isolated yields are shown in parentheses. [c] Starting compound **1**H_3 was recovered in quantitative yield.



Scheme 1. *O*-Substitution reaction of hexahomotrioxaocalix[3]arene **1**H_3 with 9-chloromethylanthracene **5** (3.3 equiv.).

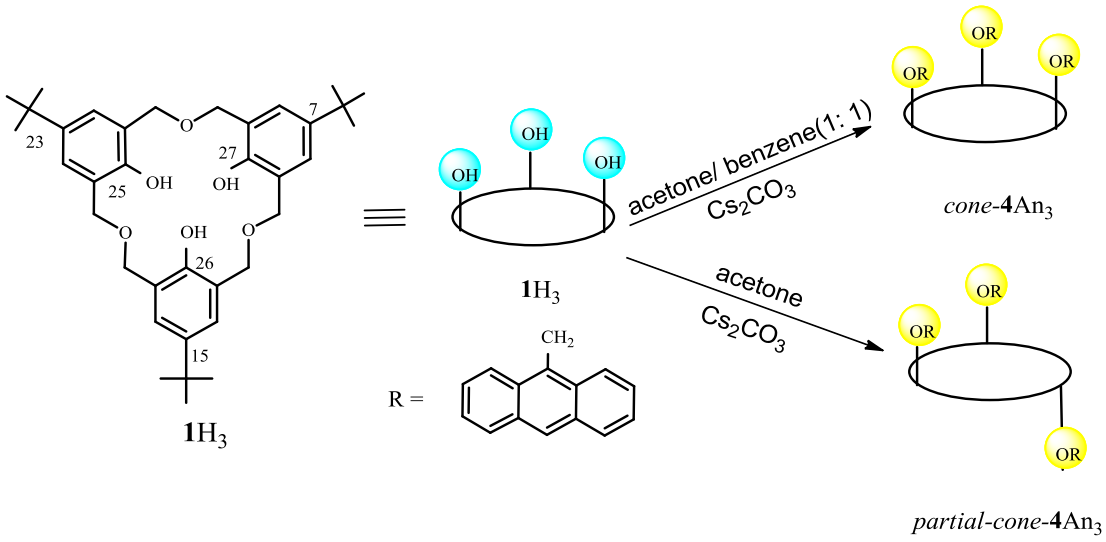


Scheme 2. *O*-Substitution reaction of hexahomotrioxaocalix[3]arene **1** with different amount of 9-chloromethylanthracene **5** (1.1 equiv. and 2.1 equiv.) in the presence of K_2CO_3.



Scheme 3. *O*-Alkylation reaction of compound **2**H_2An with 9-chloromethyl anthracene **5** in the presence of Cs_2CO_3.

Graphical abstract



Synthesis and structures of *O*-anthrylmethyl-substituted hexahomotrioxacalix[3]arenes

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Supplementary Information

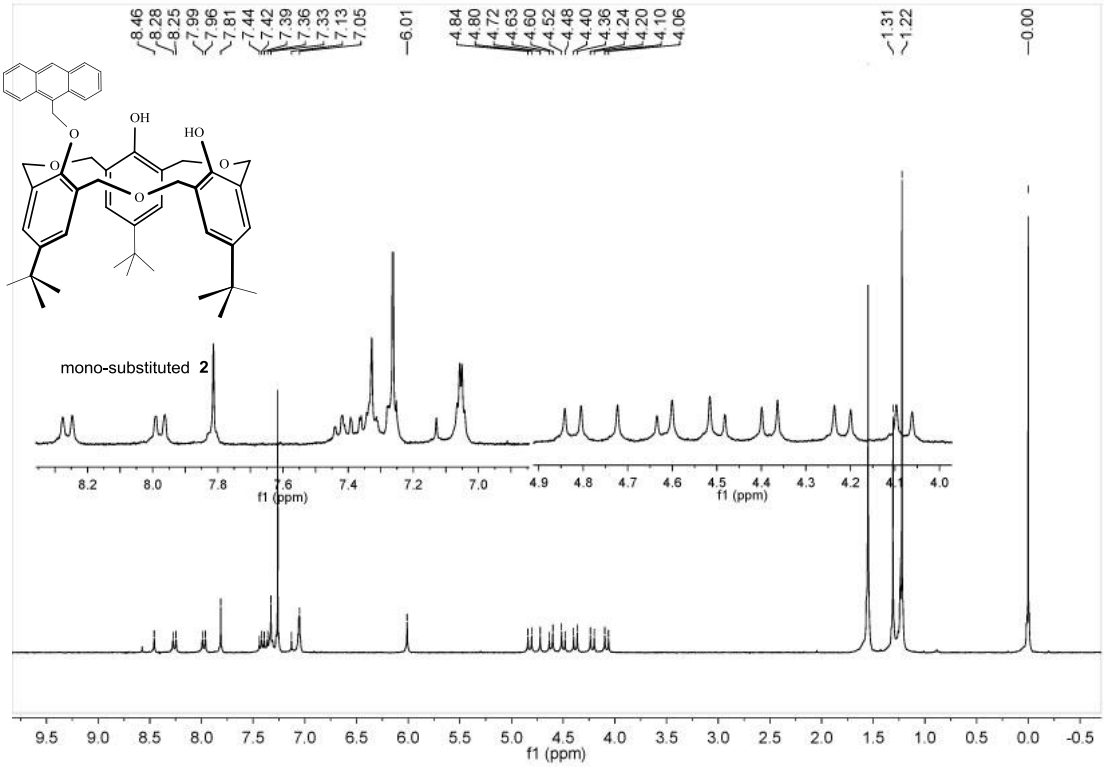
Fig S1: ^{1}H and ^{13}C NMR spectra of compound **2**H_2An.

Fig S2: ^{1}H and ^{13}C NMR spectra of compound *partial-cone*-**3**HAn$_2$.

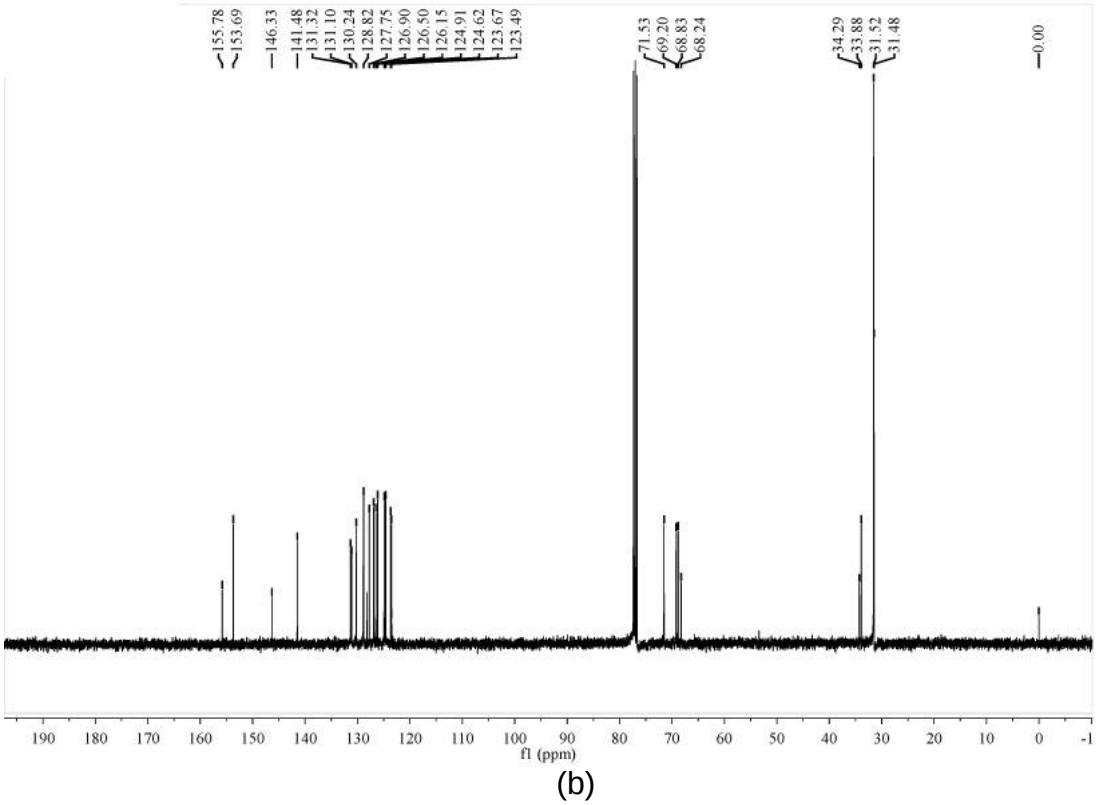
Fig S3: ^{1}H and ^{13}C NMR spectra of compound *cone*-**4**An$_3$.

Fig S4: ^{1}H and ^{13}C NMR spectra of compound *partial-cone*-**4**An$_3$.

Table S1: Summary of crystal data for *partial-cone*-**3**HAn$_2$ and *cone*-**4**An$_3$.

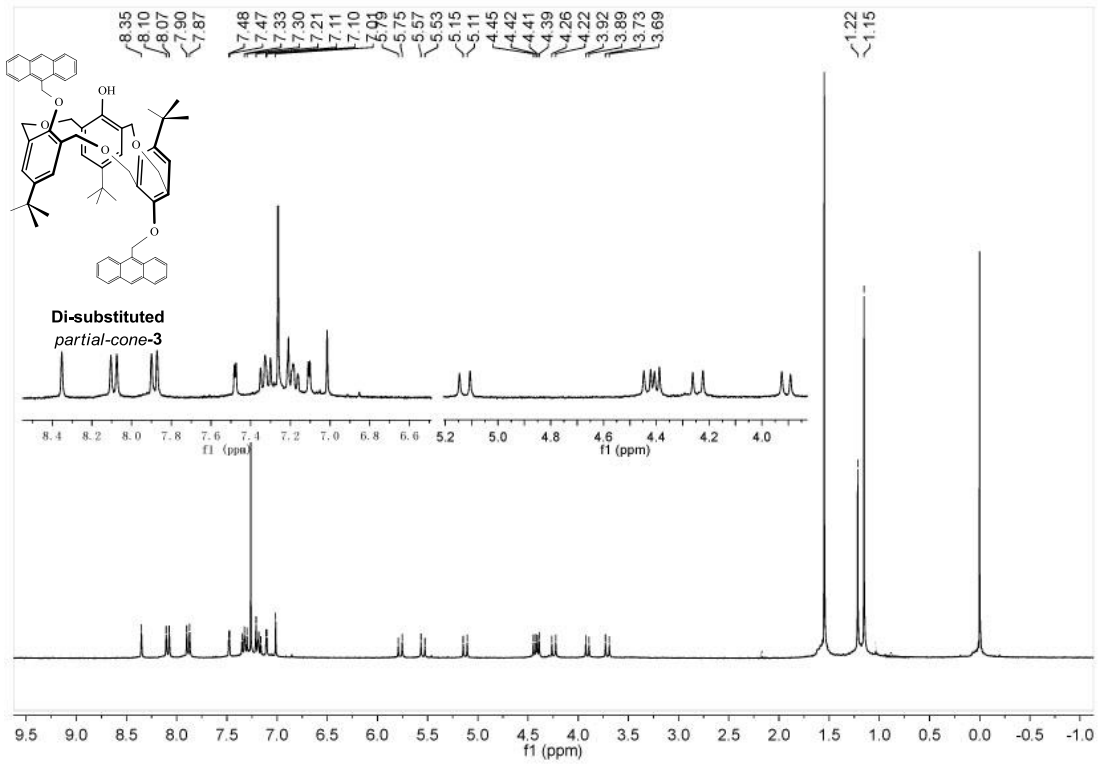


(a)

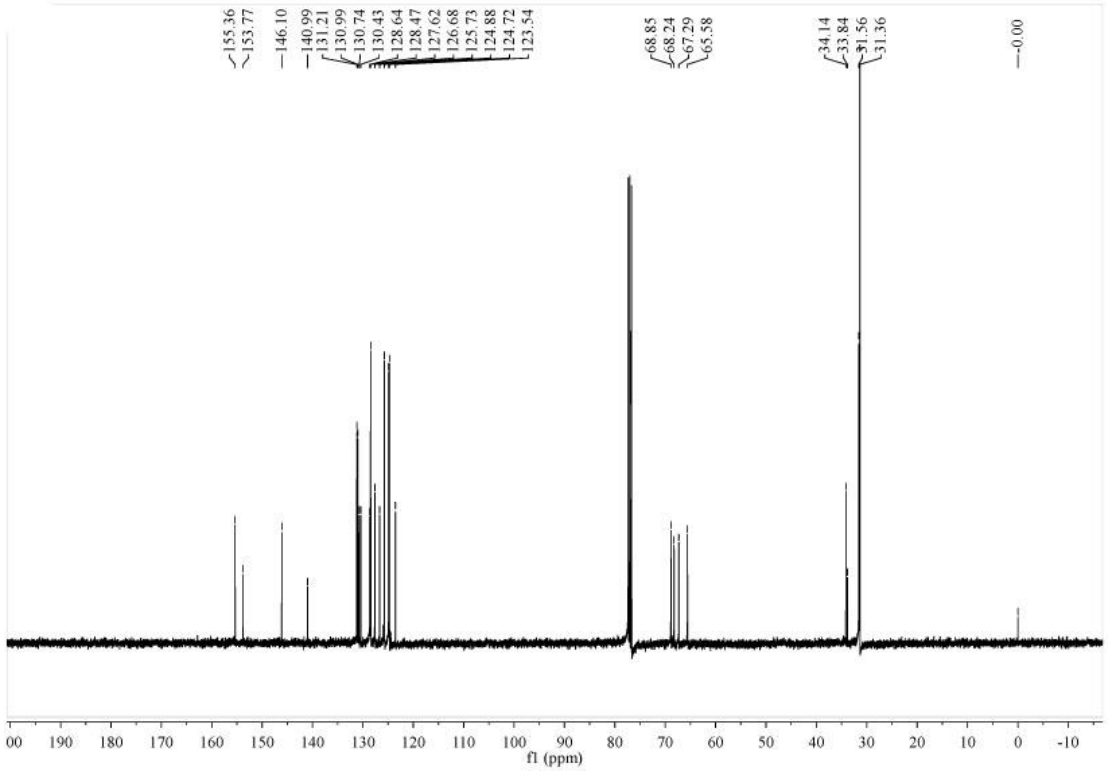


(b)

Fig S1. (a) ^{1}H NMR spectrum of compound **2**H_2An in $CDCl_3$ at 25 ℃, 300 MHz. (b) ^{13}C NMR spectrum of compound **2**H_2An in $CDCl_3$ at 25 ℃, 75 MHz.

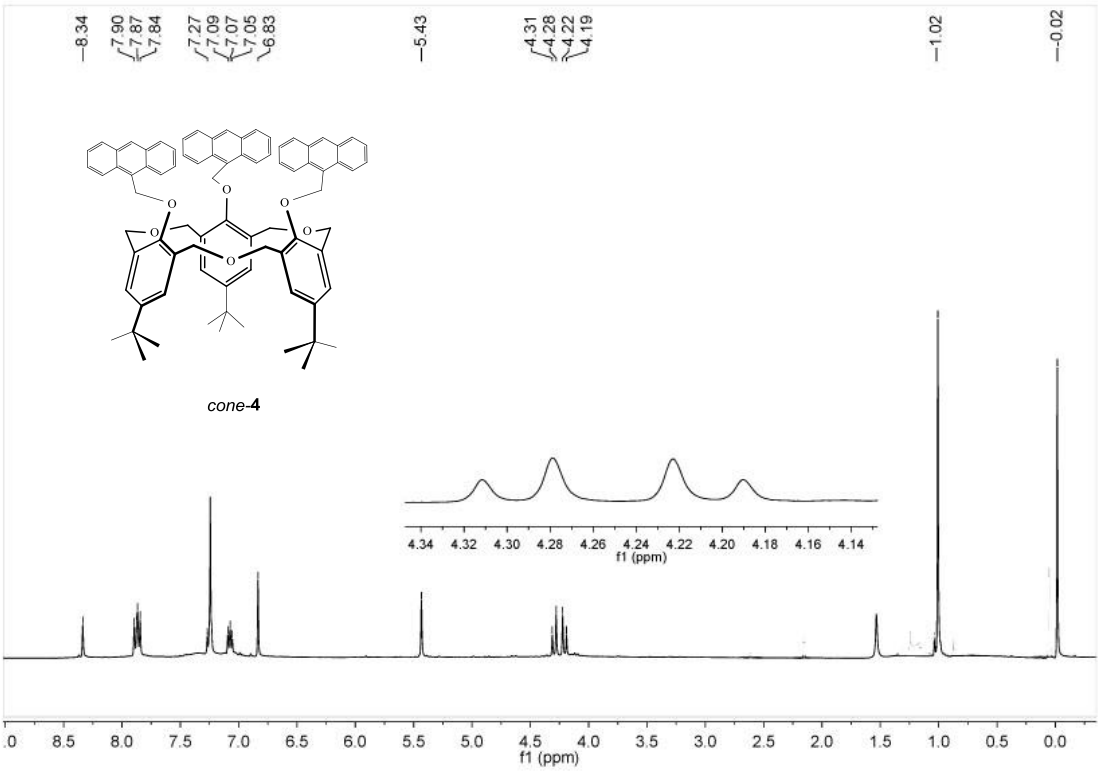


(a)

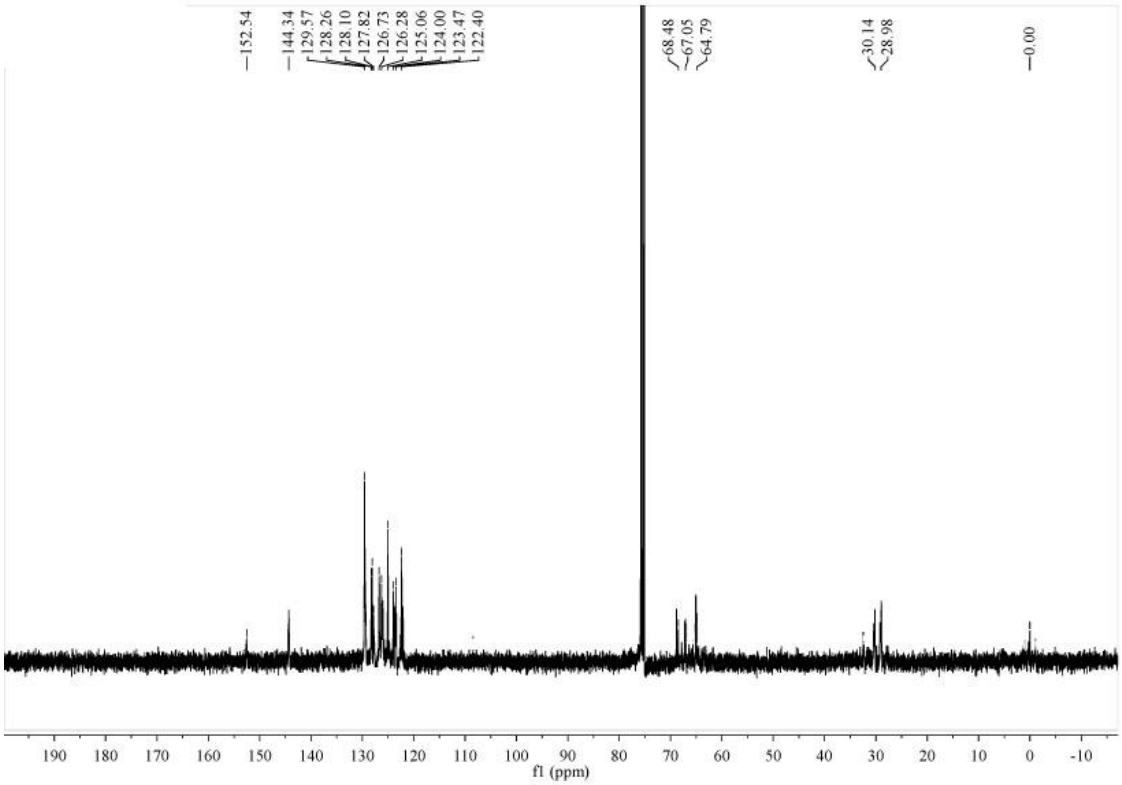


(b)

Fig S2. (a) ^{1}H NMR spectrum of compound *partial-cone*-**3**HAn$_2$ in $CDCl_3$ at 25 ℃, 300 MHz. (b) ^{13}C NMR spectrum of compound *partial-cone*-**3**HAn$_2$ in $CDCl_3$ at 25 ℃, 75 MHz.

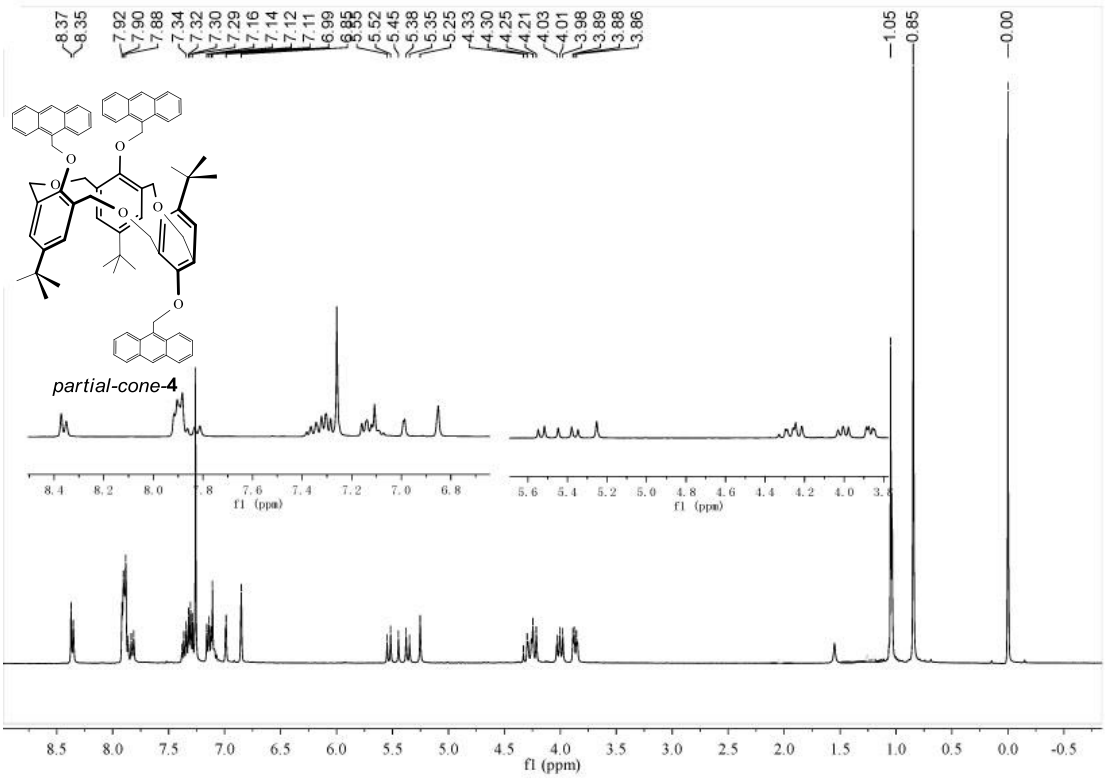


(a)

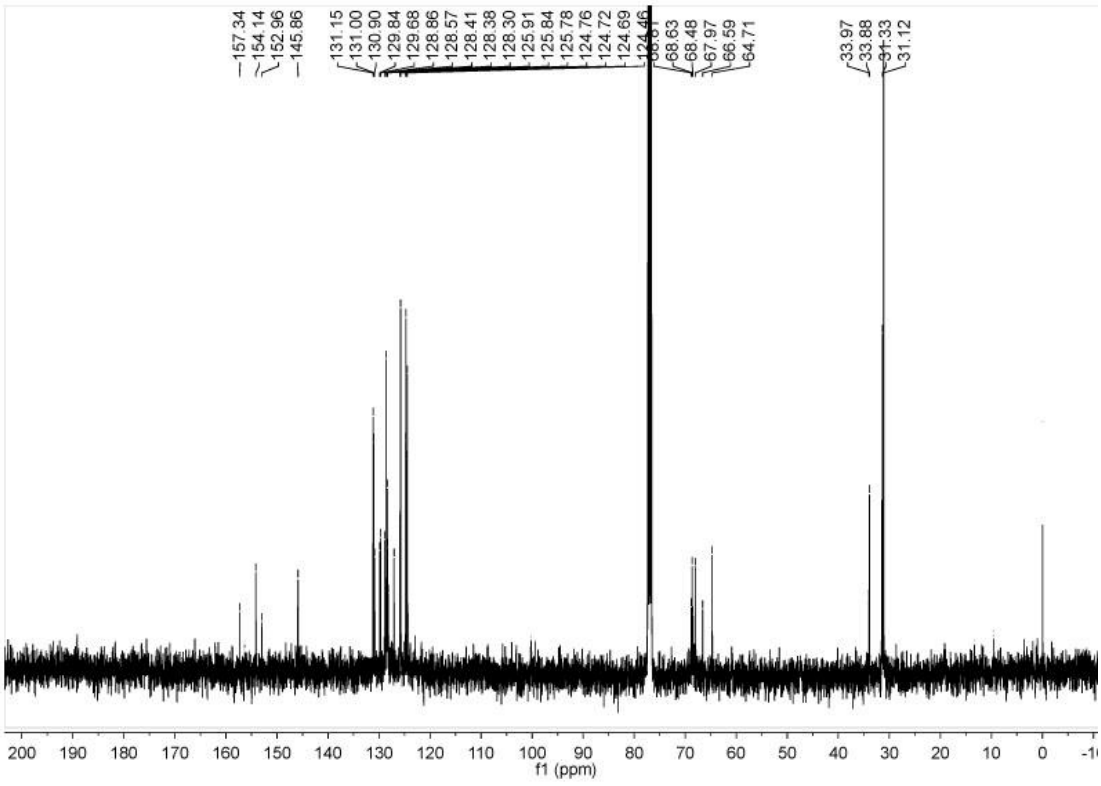


(b)

Fig S3. (a) ^{1}H NMR spectrum of compound *cone*-**4**An$_3$ in $CDCl_3$ at 25 °C, 300 MHz. (b) ^{13}C NMR spectrum of compound *cone*-**4**An$_3$ in $CDCl_3$ at 25 °C, 75 MHz.



(a)



(b)

Fig S4. (a) ^{1}H NMR spectrum of compound *partial-cone*-**4**An$_3$ in $CDCl_3$ at 25 °C, 300 MHz. (b) ^{13}C NMR spectrum of compound *partial-cone*-**4**An$_3$ in $CDCl_3$ at 25 °C, 75 MHz.

X-ray crystallography

Table S1 Summary of crystal data for *partial-cone*-**3**HAn_2 and *cone*-**4**An_3.[a,b]

parameter	*cone*-**4**An_3	*partial-cone*-**3**HAn_2
Formula	$C_{81}\ H_{78}\ O_6$	$C_{70}\ H_{75}\ O_6$
Formula weight	1266.80	957.20
Space group	*P*2(1)/n	*I*2/a
a [Å]	17.8903(4)	30.303(2)
b [Å]	16.8621(4)	14.1499(10)
c [Å]	21.6293(5)	30.774(2)
α [°]	90	90
β [°]	90.561(12)	115.729(2)
γ [°]	90	90
Volume ($Å^3$)	6524.6 (3)	11887.2 (14)
Z	4	8
D(calc) [$g.m^{-3}$]	1.290	1.167
Temperature [K]	120 K	150 K
Unique reflns	11466	10449
Obsd reflns	2680.0	4472.0
Parameters	866	656
R_{int} [mm^{-1}]	0.197	0.075
$R[I>2\sigma(I)]$[a]	0.0845	0.0596
$wR[I>2\sigma(I)]$[b]	0.2216	0.1687
GOF on F^2	1.036	1.085

[a] Conventional *R* on F_{hkl}: $\Sigma\,||Fo| - |Fc||/\sigma|Fo|$.

[b] Weighted *R* on $|F_{hkl}|^2$: $\Sigma\,[w(F_o^2 - F_c^2)^2]/\ \Sigma\,[w(F_o^2)^2]^{1/2}$

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) cr111

No syntax errors found. CIF dictionary Interpreting this report

Datablock: cr111

```
Bond precision:  C-C = 0.0042 A          Wavelength=0.71073

Cell:            a=30.303(2)     b=14.1499(10)        c=30.774(2)
                 alpha=90        beta=115.729(2)      gamma=90
Temperature:     150 K
```

	Calculated	Reported
Volume	11887.2(14)	11887.2(14)
Space group	I 2/a	I2/a
Hall group	-I 2ya	?
Moiety formula	C66 H68 O6	?
Sum formula	C66 H68 O6	C70 H75 O8
Mr	957.20	1044.30
Dx,g cm-3	1.070	1.167
Z	8	8
Mu (mm-1)	0.067	0.075
F000	4096.0	4472.0
F000'	4097.77	
h,k,lmax	36,16,36	36,16,36
Nref	10457	10449
Tmin,Tmax	0.974,0.982	0.966,0.982
Tmin'	0.965	

```
Correction method= MULTI-SCAN

Data completeness= 0.999          Theta(max)= 25.000

R(reflections)= 0.0596( 7381)     wR2(reflections)= 0.1687( 10449)

S = 1.085                 Npar= 656
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level B

PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of . 501 A**3

```
CHEMW03_ALERT_2_B WARNING: The ratio of given/expected molecular weight as
            calculated from the _atom_site* data lies outside
            the range 0.95 <> 1.05
           From the CIF: _cell_formula_units_Z                    8
           From the CIF: _chemical_formula_weight          1044.30
           TEST: Calculate formula weight from _atom_site_*
           atom     mass    num     sum
           C        12.01   66.00  792.73
           H         1.01   68.00   68.54
           O        16.00    6.00   95.99
           Calculated formula weight              957.26
PLAT043_ALERT_1_B Check Reported Molecular Weight ................    1044.30
PLAT201_ALERT_2_B Isotropic non-H Atoms in Main Residue(s) .......          1
```

Alert level C

```
PLAT041_ALERT_1_C Calc. and Reported SumFormula    Strings  Differ          ?
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)...          ?
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C47    --  C48     ..        5.7 su
PLAT340_ALERT_3_C Low Bond Precision on  C-C Bonds ...............     0.0042 Ang
PLAT410_ALERT_2_C Short Intra H...H Contact  H37B   ..  H50     ..       1.99 Ang.
```

Alert level G

```
FORMU01_ALERT_2_G  There is a discrepancy between the atom counts in the
            _chemical_formula_sum and the formula from the _atom_site* data.
            Atom count from _chemical_formula_sum:C70 H75 O8
            Atom count from the _atom_site data:  C66 H68 O6
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G ALERT: Large difference may be due to a
            symmetry error - see SYMMG tests
           From the CIF: _cell_formula_units_Z    8
           From the CIF: _chemical_formula_sum  C70 H75 O8
           TEST: Compare cell contents of formula and atom_site data

           atom    Z*formula  cif sites diff
           C         560.00    528.00   32.00
           H         600.00    544.00   56.00
           O          64.00     48.00   16.00
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF          ?
PLAT007_ALERT_5_G Note: Number of Unrefined D-H Atoms ............          1
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.      14.07
PLAT128_ALERT_4_G Alternate Setting of Space-group C2/c    .......      I2/a
PLAT333_ALERT_2_G Check Large Av C6-Ring C-C Dist. C38    -C51           1.42 Ang.
```

```
   1 ALERT level A = Most likely a serious problem - resolve or explain
   3 ALERT level B = A potentially serious problem, consider carefully
   5 ALERT level C = Check. Ensure it is not caused by an omission or oversight
   8 ALERT level G = General information/check it is not something unexpected

   5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   8 ALERT type 2 Indicator that the structure model may be wrong or deficient
   1 ALERT type 3 Indicator that the structure quality may be low
   1 ALERT type 4 Improvement, methodology, query or suggestion
   2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. In order to resolve some of the more serious problems it may be necessary to carry out additional measurements or structure refinements. However, the purpose of your study may justify the reported deviations and the more serious of these should normally be commented upon in the discussion or experimental section of a paper or in the "special_details" fields of the CIF. checkCIF was carefully designed to identify outliers and unusual parameters, but every test has its limitations and alerts that are not important in a particular case may appear. Conversely, the absence of alerts does not guarantee there are no aspects of the results needing attention. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

Publication of your CIF in IUCr journals

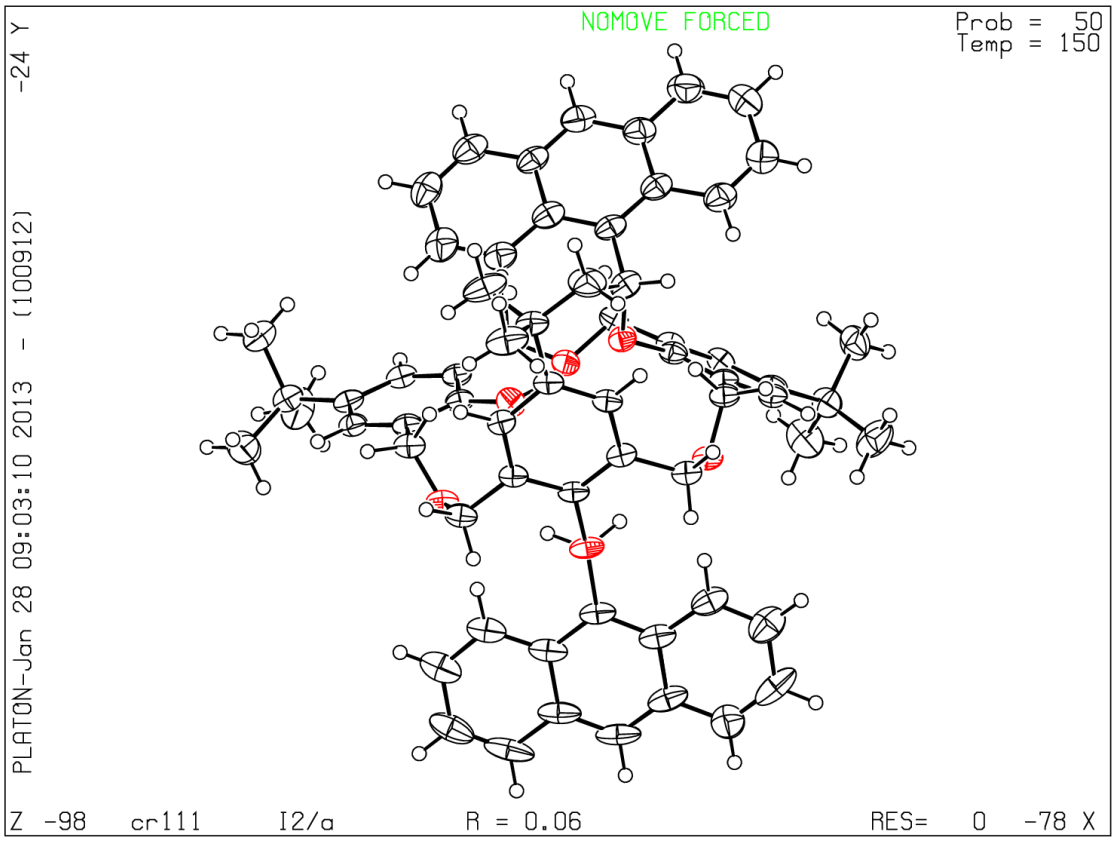
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica, Journal of Applied Crystallography, Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock cr111 - ellipsoid plot



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) cr150

No syntax errors found. CIF dictionary Interpreting this report

Datablock: cr150

```
Bond precision:  C-C = 0.0068 A          Wavelength=0.71073

Cell:            a=17.8903(4)    b=16.8621(4)        c=21.6293(5)
                 alpha=90        beta=90.561(12)     gamma=90
Temperature:     120 K
```

	Calculated	Reported
Volume	6524.6(3)	6524.6(3)
Space group	P 21/n	P2(1)/n
Hall group	-P 2yn	?
Moiety formula	C81 H78 O6, C H Cl3	?
Sum formula	C82 H79 Cl3 O6	C82 H79 Cl3 O6
Mr	1266.81	1266.80
Dx,g cm-3	1.290	1.290
Z	4	4
Mu (mm-1)	0.197	0.197
F000	2680.0	2680.0
F000'	2682.83	
h,k,lmax	21,20,25	21,20,25
Nref	11493	11466
Tmin,Tmax	0.967,0.988	0.950,0.988
Tmin'	0.950	

```
Correction method= MULTI-SCAN

Data completeness= 0.998          Theta(max)= 25.000

R(reflections)= 0.0845( 6821)     wR2(reflections)= 0.2216( 11466)

S = 1.036                 Npar= 866
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds ..... 0.0068 Ang
PLAT410_ALERT_2_C Short Intra H...H Contact H67A .. H70 .. 1.99 Ang.

Alert level G

```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         8
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained Atom Sites ....         8
PLAT005_ALERT_5_G No _iucr_refine_instructions_details  in the CIF         ?
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT Unusually Large.     13.25
PLAT128_ALERT_4_G Alternate Setting of Space-group P21/c   .......     P21/n
PLAT244_ALERT_4_G Low   'Solvent' Ueq as Compared to Neighbors of       C82X
PLAT302_ALERT_4_G Note: Anion/Solvent Disorder ..................       100 Perc.
PLAT860_ALERT_3_G Note: Number of Least-Squares Restraints .......        80
```

```
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  0 ALERT level B = A potentially serious problem, consider carefully
  2 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  8 ALERT level G = General information/check it is not something unexpected

  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  4 ALERT type 2 Indicator that the structure model may be wrong or deficient
  2 ALERT type 3 Indicator that the structure quality may be low
  3 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

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Publication of your CIF in other journals

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PLATON version of 05/11/2012; check.def file version of 05/11/2012

Datablock cr150 - ellipsoid plot