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Bis- and tetracalix[4]arenes in the partial cone conformation: synthesis, structure and RCM reactions

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Abstract—The synthesis, structure and ring-closing metathesis (RCM) reactions of polyether bridged biscalix[4]arenes **6** in the partial cone conformation with upper rim allyl substituents are reported. The RCM reaction modes depend on the length of polyether chain. Diethylene glycolic chain produced the dimer **7a** and linear oligomer **7a′** with multi-cavities, whereas triethylene and tetraethylene glycolic chains allowed direct cyclization through intramolecular head-to-tail pattern to yield novel bridged biscalix[4]arenes **7b–c**.

1. Introduction

Calixarenes[1] are a class of well defined macrocyclic oligomers of phenols bridged by methylene groups. Owing to their (1) convenient preparation in large quantities; (2) easy chemical modification on both lower and upper rims; (3) versatile complexation towards ions and molecules and (4) unique structural properties, they have been one of the most extensively studied synthetic receptors in recent years.

A permanent and challenging topic in supramolecular chemistry is the design and construction of sophisticated artificial receptors with defined multi-cavities which would show various supramolecular function.[2] Suitable calixarene derivatives have been used as building blocks for this purpose. One of particular interest in this regard are the construction of double- and multi-calixarenes,[3,4] consisting of more than two calixarene subunits, for their peculiar multi-cavity structures and molecular recognition abilities. Covalently linked double calixarenes could be constructed by intermolecular bridges in a head-to-head, tail-to-tail, or head-to-tail arrangement, in which the calixarene subunits adopt the cone or the 1,3-alternate conformation.[4] Similar cases occurred to covalently linked multi-calixarenes. To our knowledge, no double- and multi-calixarenes bridged by intramolecular head-to-tail arrangement of calixarenes in the partial cone conformation were reported so far,[5] although they could provide novel and efficient receptors with potential complexation towards complicated guests.[4a,c]

Ring-closing metathesis (RCM)[6] has been established as an efficient approach to macrocyclic systems and also found powerful applications in supramolecular chemistry.[7] In this regard, Grubbs' ruthenium catalyst ($RuCl_2(CHPh)(PCy_3)_2$, **1**) is particularly attractive due to its remarkable functional group tolerance, operational simplicity, high stability and commercial availability. Herein, we report the synthesis, structure and RCM reactions of polyether bridged biscalix[4]arenes **6** in the partial cone conformation with upper rim allyl substituents. Through different RCM reaction modes in the presence of Grubbs' catalyst **1**, novel bridged double- and tetra-calix[4]arenes with multi-cavities were obtained.

2. Results and discussion

As shown in Scheme 1. Tri(*n*-propoxy)calix[4]arene **3**,[8] prepared according to the reference, reacted with excess 3-bromopropene in dry THF in the presence of NaH to give allyloxy-substituted calix[4]arene **4** in 65% yield. **4** then underwent Claisen rearrangement in refluxing *N*,*N*-diethylaniline to yield calix[4]arene **5** in 85% yield with monoallyl substituent on the upper rim. The ^{1}H NMR spectrum of **5** showed two doublets at 4.44 and 4.38 ppm, and a AB signal at 3.26 ppm for the bridging methylene protons. Two signals at 30.7 and 30.5 ppm for the bridging methylene carbons in its ^{13}C NMR spectrum indicated that **5** adopts the cone conformation. This conformation was further confirmed by its crystal structure (Fig. 1).

Keywords: Multi-calix[4]arene; Partial cone conformation; RCM reaction; Synthesis; Structure.
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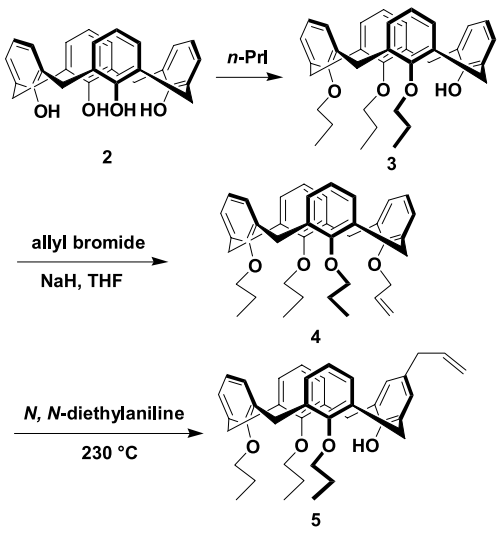


Scheme 1.

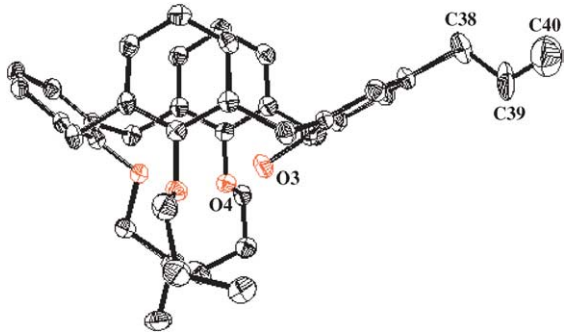
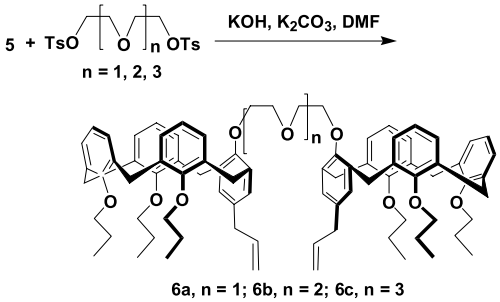


Figure 1. The crystal structure of **5**, hydrogen atoms are omitted for clarity. Selective bond lengths: C39–C40, 1.39 Å; C38–C39, 1.55 Å; O3–H…O4, 2.46 Å.

Treatment of compound **5** with diethylene glycol ditosylate in the presence of KOH and K_2CO_3 mixture in DMF, we exclusively isolated a single bridged biscalix[4]arene **6a** (56%) in which the two calix[4]arene subunits are in the partial cone conformation. The ^{1}H NMR spectrum of **6a** showed two doublets at δ 4.13 and 3.11 ppm and one AB signal at δ 3.69 ppm for the bridging methylene protons. Meanwhile, its ^{13}C NMR spectrum exhibited two signals at δ 35.6 and 30.4 ppm for the bridging methylene carbons, which demonstrated its partial cone conformer.[9] Under the same conditions as above, biscalix[4]arenes **6b** and **6c** in the partial cone conformation were synthesized by the reactions of compound **5** with triethylene or tetraethylene glycol ditosylate, respectively. In each case, the partial cone conformation of calix[4]arene skeleton in solution was determined by the NMR spectra (Scheme 2).



Scheme 2.

To determine the structure of the polyether bridged biscalix[4]arenes in the solid state, the single crystal X-ray analyses of **6a** and **6c** were undertaken. Crystals of compound **6a** were obtained by slow evaporation of a dichloromethane and *n*-hexane solution. As seen in Figure 2, the rings bearing allyl group are inverted relative to the other rings. Consequently, the calix[4]arenes in **6a** adopt the partial cone conformation, all of the propoxy groups point outwards from the center of the molecule and the two allyl groups are in opposite position. Moreover, the molecule **6a** resides on a crystallographic two-fold axis, and its two calix[4]arene subunits are related by symmetry in the crystal structure. For the subunits, the four linking methylene carbons are all coplanar to within 0.02 Å, and the interplanar angle between the two planes is 34.5°. The inclinations of rings A–D to the reference plane are 92.4, 98.4, 35.3 and 80.5°, respectively. The opposite aromatic rings A and C have an interplanar angle of 57.1°, while the rings B and D have an interplanar angle of 17.9°.

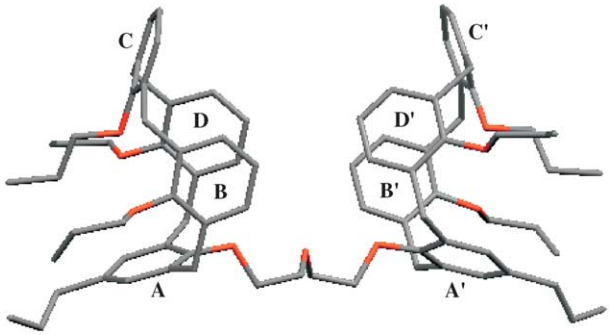


Figure 2. The crystal structure of **6a**, hydrogen atoms are omitted for clarity.

Crystals of **6c** were obtained by slow evaporation of a CH_2Cl_2/CH_3CN solution, and its X-ray structure is shown in Figure 3. Similar to **6a**, the two calix[4]arene subunits in **6c** all adopt the partial cone conformation, and the four linking methylene carbons are coplanar to within 0.01 Å for the two subunits. The interplanar angle between the two reference planes is 13.1°, which is obviously smaller than that of **6a** due to the long flexible chain in **6c**. The phenyl rings in **6c** are inclined by between 30.6 and 97.8°, to the reference planes. The interplanar angles between the opposite

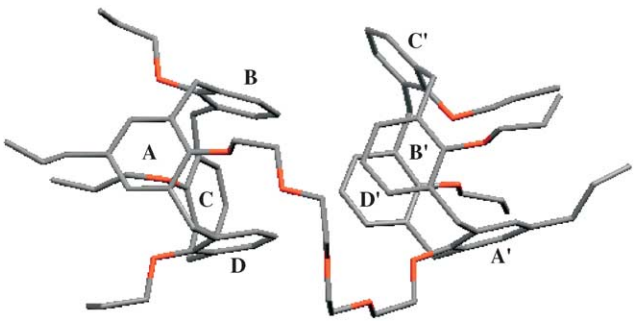
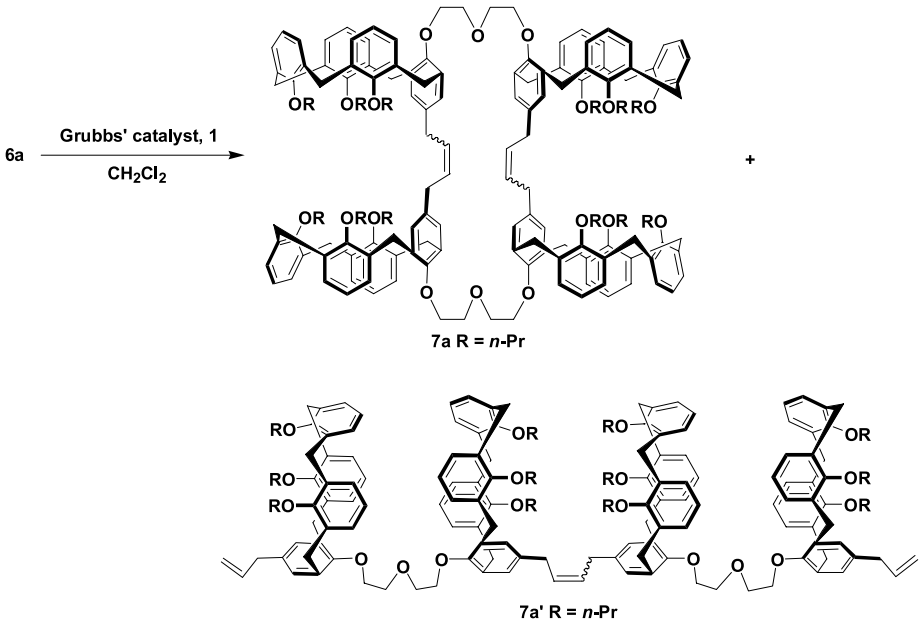


Figure 3. The crystal structure of **6c**, hydrogen atoms are omitted for clarity.

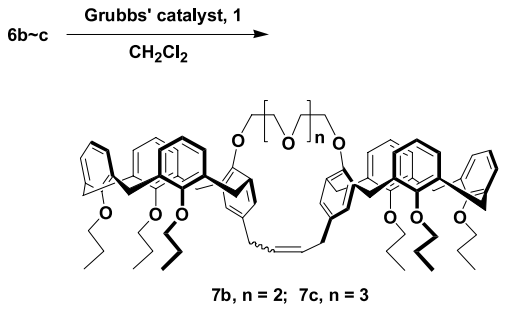


Scheme 3.

aromatic rings of A and C, B and D, A′ and C′ and B′ and D′ are 109.4, 154.5, 118.5 and 16.3°, respectively.

RCM reactions were carried out with 5 mol% Grubbs' catalyst **1** in dry CH_2Cl_2 under argon at room temperature. The biscalix[4]arene **6a** has shorter polyether chain and the direct cyclic reaction may suffer greater steric strain. So it should be possible that intermolecular metathesis competed with intramolecular bridging. In fact, only two intermolecular reaction products, dimer **7a** and linear oligomer **7a′** with multi-cavities were isolated from the metathesis reactions of compound **6a**. The structures of **7a** and **7a′** were demonstrated by their NMR and mass spectra. Compound **7a** showed similar NMR spectral features of calix[4]arene skeleton with those of its precursor **6a**, which suggested that it may be a single isomer of *E*,*Z* geometry, and the calix[4]arenes in **7a** all retained the partial cone conformation. The NMR spectra of **7a′** displayed the signals for one symmetric disubstituted alkene and two terminal vinyl groups, and also confirmed that the calix[4]arene units all kept the partial cone conformation. The MAIDL-TOF mass spectrum of **7a′** was also fully consistent with its oligomer structure (Scheme 3).

Under the same reaction conditions as **6a**, RCM reaction of compound **6b** with longer chain only produced a single cyclization product **7b** in 52% yield through intramolecular head-to-tail pattern of calix[4]arene. Same case occurred to compound **6c**, as a result, biscalix[4]arene **7c** was obtained in 66% yield. The NMR spectra of **7b** and **7c** showed that the signals for the terminal vinyl groups of **6b** and **6c** were replaced by those of a single disubstituted alkene, and the calix[4]arenes retained the partial cone conformation in solution. Their MAIDL-TOF MS confirmed the loss of two methylene groups and the formation of intramolecular RCM products (Scheme 4).



Scheme 4.

We also obtained the crystals of **7b** from a mixture of dichloromethane and *n*-hexane. Its X-ray structure analysis revealed that both of the calix[4]arene subunits retained the partial cone conformation, the double bond (C73 and C74) adopted the *E* conformation and all the propoxy groups are in the same direction (Fig. 4(a)). The four linking methylene carbon atoms for the two calix[4]arene subunits are coplanar to 0.01 and 0.02 Å, respectively, and the phenyl rings A–D (A′–D′) are inclined by 91.6, 97.5, 140.8, 84.8° (88.9, 95.8, 37.7, 86.6°), respectively, to the reference planes. The interplanar angle between the two reference planes is 44.4°, and the interplanar angle between phenyl rings A and A′ is 106.8°. Interestingly, we found that four molecules of biscalix[4]arene **7b** composed of an italics capital letter *N* along the *a* axis in its crystal cell, and their packing further formed a wave type structure with polychannels in the solid state (Fig. 4(b)).

In summary, polyether bridged bis-calix[4]arenes in the partial cone conformation with allyl substituents on the upper rim were synthesized, and their structures in solution and in the solid state were characterized. The RCM reaction modes were found to depend on the length of polyether chain. Diethylene glycolic chain produced the dimer and linear oligomer with multi-cavities, whereas the longer chains allowed direct cyclization through intramolecular head-to-tail pattern to yield novel bridged biscalix[4]arenes.

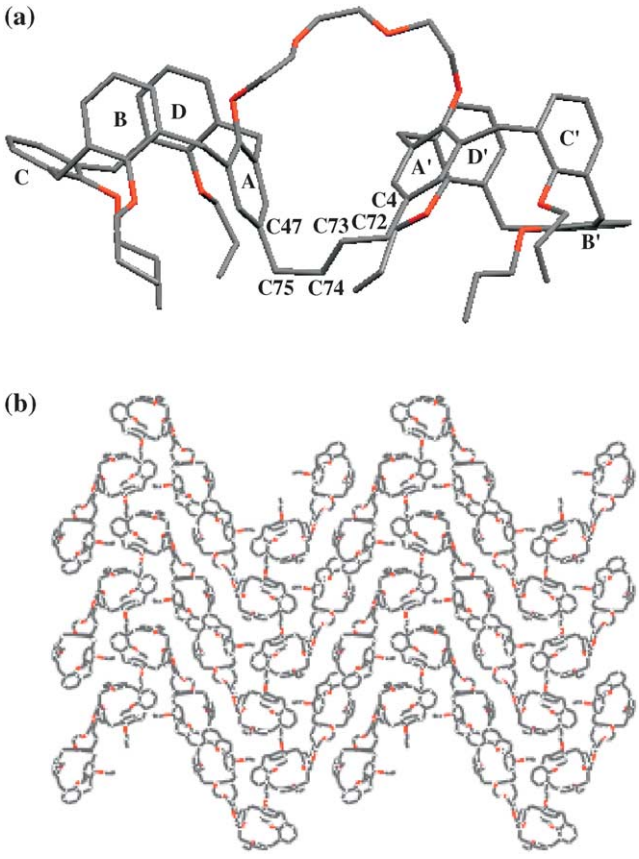


Figure 4. The crystal structure (a) and perspective view of the crystal lattice along the *a* axis of the cell (b) of **7b**, hydrogen atoms are omitted for clarity. Selective bond lengths: C4–C72, 1.51 Å; C72–C73, 1.48 Å; C73–C74, 1.38 Å; C74–C75, 1.51 Å; C75–C47, 1.51 Å.

3. Experimental

3.1. General

Melting points were determined on an electrothermal melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained at 300 MHz ($CDCl_3$, TMS as internal standard) on a Bruker DMX 300 NMR. MALDI-TOF MS were recorded on a Bruker BIFLEXIII mass spectrometer with CCA (2-cyano-4′-hydroxycinnamic acid) as the matrix. Elemental analyses were performed by the Analytical Laboratory of the Institute. IR Spectra were recorded on JASCO 480 spectrometer. NaH (60% dispersed in mineral oil, ACROS) was washed twice with petroleum ether (30–60 °C) and stored in a desiccator. Dichloromethane used in the RCM reactions was distilled from calcium hydride. DMF was dried over 4 Å molecular sieve. All other chemicals were reagent grade and were used without further purification. Column chromatography was performed with silica gel (200–300 mesh). Petroleum ether for column chromatography refers to that of 30–60 °C boiling range.

3.1.1. Synthesis of compound 4. To the solution of **3**[8] (550 mg, 1.0 mmol) in dry THF (30 mL) under argon atmosphere was added NaH (160 mg, 4.0 mmol). The mixture was stirred for 30 min at room temperature and then added dropwise allyl bromide (726 mg, 6.0 mmol) in dry THF (10 mL). The mixture was refluxed for 4 h, quenched by methanol (10 mL) and then concentrated. The residue was dissolved in CH_2Cl_2 (50 mL), washed with water (2×20 mL) and saturated NaCl (2×20 mL), respectively. The organic layer was dried over anhydrous $MgSO_4$. The solvent was removed in vacuo and the crude product was recrystallized from MeOH–CH_2Cl_2 to give **4** (384 mg, 65%) as a white power. Mp: 176–178 °C; ^{1}H NMR ($CDCl_3$): δ 6.86 (d, J=7.4 Hz, 4H), 6.78–6.72 (m, 2H), 6.64–6.60 (m, 2H), 6.45–6.44 (m, 4H), 6.27–6.34 (m, 1H), 5.17–5.25 (m, 2H), 4.56 (d, J=6.4 Hz, 2H), 4.48 (ABq, J=12.8 Hz, 4H), 3.98 (t, J=7.7 Hz, 2H), 3.82 (t, J=7.1 Hz, 4H), 3.19 (d, J=13.4 Hz, 4H), 2.02–1.91 (m, 6H), 1.05 (t, J=7.4 Hz, 6H), 0.96 (t, J=7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$): δ 157.2, 156.7, 156.5, 156.1, 136.2, 136.1, 135.2, 134.4, 129.4, 129.0, 128.5, 127.8, 122.3, 122.0, 116.5, 77.6, 76.7, 75.8, 31.3, 31.1, 23.5, 23.4, 10.5, 10.3. MALDI-TOF MS *m/z*: 613.6 ($M+Na^+$), 629.6 ($M+K^+$). Anal. Calcd for $C_{40}H_{46}O_4$: C, 81.32; H, 7.85. Found: C, 81.35; H, 7.91.

3.1.2. Synthesis of compound 5. A solution of compound **4** (500 mg, 0.85 mmol) in *N*,*N*-diethylaniline (10 mL) was refluxed for 3 h in an atmosphere of N_2. After cooling to rt, the mixture was poured into 2 N HCl (20 mL), and then filtrated. The crude product was recrystallized from MeOH–$CHCl_3$ to give **5** (425 mg, 85%) as a white solid. Mp: 112–113 °C; ^{1}H NMR ($CDCl_3$): δ 7.20 (d, J=7.4 Hz, 2H), 6.99 (t, J=7.4 Hz, 1H), 6.93 (s, 2H), 6.43–6.36 (m, 6H), 6.12–5.99 (m, 1H), 5.12 (d, J=4.6 Hz, 1H), 5.07 (s, 1H), 4.49 (s, 1H), 4.44 (d, J=13.3 Hz, 2H), 4.38 (d, J=13.7 Hz, 2H), 3.86 (t, J=8.4 Hz, 2H), 3.75 (t, J=6.7 Hz, 4H), 3.38 (d, J=6.5 Hz, 2H), 3.26 (ABq, J=12.8 Hz, 4H), 2.36–2.23 (m, 2H), 2.00–1.83 (m, 4H), 1.14 (t, J=7.3 Hz, 6H), 0.95 (t, J=7.5 Hz, 3H). ^{13}C NMR ($CDCl_3$): δ 156.8, 154.4, 151.5, 138.5, 137.2, 133.3, 132.7, 131.2, 130.4, 129.3, 129.0, 128.4, 128.3, 127.7, 122.9, 115.0, 77.4, 76.5, 39.5, 30.7, 30.5, 23.4, 22.3, 10.8, 9.5. MALDI-TOF MS *m/z*: 613.3 ($M+Na^+$). Anal. Calcd for $C_{40}H_{46}O_4$: C: 81.32, H 7.85. Found: C: 81.27; H 7.97.

3.2. General procedure for synthesis of 6

To the mixture of compound **5** (590 mg, 1 mmol), KOH (72 mg, 1.29 mmol) and K_2CO_3 (72 mg, 0.52 mmol) in dry DMF (15 mL) under N_2 was added dropwise *p*-toluenesulfonate derivative (0.4 mmol) in dry DMF (10 mL). The reaction mixture was stirred at rt for 24 h. The solvent was then removed in vacuo and the residue was dissolved in CH_2Cl_2 (100 mL). The organic phase was washed with brine (2×30 mL) and water (2×30 mL), dried over anhydrous $MgSO_4$ and then concentrated to give a residue, which was separated by column chromatography with ethyl acetate and petroleum ether (1:4, v/v) as eluent to provide **6** as a white solid.

3.2.1. Compound 6a. Yield 56%; mp 197–199 °C; ^{1}H NMR ($CDCl_3$): δ 7.11–7.05 (m, 12H), 6.91 (t, J=7.6 Hz, 2H), 6.43 (t, J=7.5 Hz, 4H), 6.28 (d, J=7.5 Hz, 4H), 6.13–5.97 (m, 2H), 5.16 (d, J=16.1 Hz, 2H), 5.12 (d, J=9.0 Hz, 2H), 4.08 (d, J=13.1 Hz, 4H), 4.04–4.02 (m, 4H), 3.90 (t, J=4.7 Hz, 4H), 3.78–3.73 (m, 4H), 3.66 (ABq, J=12.8 Hz, 8H), 3.64–3.52 (m, 4H), 3.40 (d, J=6.9 Hz, 4H), 3.35 (t, J=8.4 Hz, 4H), 3.06 (d, J=13.3 Hz, 4H), 1.91–1.86 (m,

8H), 1.57–1.31 (m, 4H), 1.10 (t, J=7.3 Hz, 12H), 0.75 (t, J=7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.7, 155.3, 155.0, 137.8, 136.9, 133.5, 133.0, 132.5, 131.8, 130.1, 129.2, 128.6, 128.1, 121.9, 121.2, 115.1, 75.7, 75.2, 71.1, 70.2, 39.6, 35.5, 30.2, 23.6, 21.6, 10.7, 9.5. MALDI-TOF MS *m/z*: 1273.8 ($M+Na^+$), 1289.8 ($M+K^+$). Anal. Calcd for $C_{84}H_{98}O_9\cdot 0.5H_2O$: C, 80.03; H, 7.92. Found: C, 80.01; H, 7.90.

3.2.2. Compound 6b. Yield 62%; mp 64–66 °C; ^{1}H NMR ($CDCl_3$): δ 7.11 (d, J=7.4 Hz, 4H), 7.05 (s, 4H), 7.04 (d, J=7.8 Hz, 4H), 6.92 (t, J=7.4 Hz, 2H), 6.42 (t, J=7.5 Hz, 4H), 6.28 (d, J=7.5 Hz, 4H), 6.15–6.01 (m, 2H), 5.17 (d, J=16.1 Hz, 2H), 5.13 (d, J=8.9 Hz, 2H), 4.08 (d, J=13.1 Hz, 4H), 3.99 (t, J=4.6 Hz, 4H), 3.85 (t, J=4.9 Hz, 4H), 3.84 (s, 4H), 3.79–3.72 (m, 4H), 3.68 (ABq, J=13.0 Hz, 8H), 3.53 (t, J=8.0 Hz, 4H), 3.41 (d, J=6.9 Hz, 4H), 3.35 (t, J=8.4 Hz, 4H), 3.06 (d, J=13.2 Hz, 4H), 1.94–1.82 (m, 8H), 1.50–1.42 (m, 4H), 1.12 (t, J=7.4 Hz, 12H), 0.75 (t, J=7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.9, 155.5, 155.0, 138.0, 137.1, 133.7, 133.2, 132.7, 132.0, 130.4, 129.5, 128.9, 128.3, 122.2, 121.4, 115.4, 76.6, 76.0, 75.4, 71.5, 70.7, 39.9, 35.7, 30.5, 23.8, 21.8, 11.0, 9.8. MALDI-TOF MS *m/z*: 1318.4 ($M+Na^+$), 1334.3 ($M+K^+$). Anal. Calcd for $C_{86}H_{102}O_{10}$: C, 79.72; H, 7.93. Found: C, 79.76; H, 7.97.

3.2.3. Compound 6c. Yield 64%; mp 60–62 °C; ^{1}H NMR ($CDCl_3$): δ 7.15 (d, J=7.4 Hz, 4H), 7.11 (s, 4H), 7.08 (d, J=7.2 Hz, 4H), 6.96 (t, J=7.4 Hz, 2H), 6.48 (t, J=7.4 Hz, 4H), 6.33 (d, J=7.5 Hz, 4H), 6.17–6.08 (m, 2H), 5.22 (d, J=16.1 Hz, 2H), 5.18 (d, J=9.1 Hz, 2H), 4.13 (d, J=13.1 Hz, 4H), 4.01 (t, J=4.5 Hz, 4H), 3.86–3.77 (m, 16H), 3.69 (ABq, J=13.1 Hz, 8H), 3.57 (m, 4H), 3.47 (d, J=6.8 Hz, 4H), 3.40 (t, J=8.4 Hz, 4H), 3.11 (d, J=13.2 Hz, 4H), 1.99–1.88 (m, 8H), 1.56–1.45 (m, 4H), 1.17 (t, J=7.4 Hz, 12H), 0.82 (t, J=7.4 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 156.9, 155.5, 155.3, 138.0, 137.1, 133.7, 133.2, 132.7, 132.0, 130.4, 129.5, 128.8, 128.3, 122.2, 121.4, 115.4, 76.0, 75.4, 71.5, 70.8, 70.6, 39.8, 35.7, 30.5, 23.8, 21.8, 11.0, 9.8. MALDI-TOF MS *m/z*: 1362.2 ($M+Na^+$), 1378.2 ($M+K^+$). Anal. Calcd for $C_{88}H_{106}O_{11}$: C, 78.89; H, 7.97. Found: C, 78.89; H, 7.94.

3.3. General procedure for RCM reactions

To the solution of a calix[4]arene derivative **6** (0.05 mmol) in dry CH_2Cl_2 (10 mL) under argon was added the Grubbs' catalyst **1** (2.1 mg, 5 mol%). The mixture was stirred at room temperature and the reaction process was monitored by TLC. When the reaction was completed, the reaction mixture was quenched by exposure to air for 6 h. The solution was concentrated in vacuo and separated by column chromatography using ethyl acetate: petroleum ether (1:4, v/v) as the eluent to provide the product **7**.

3.3.1. Compound 7a. Yield 20%; mp>300 °C; ^{1}H NMR ($CDCl_3$): δ 7.11–7.01 (m, 24H), 6.92 (t, J=7.4 Hz, 4H), 6.45–6.38 (m, 8H), 6.27 (t, J=6.7 Hz, 8H), 5.76–5.72 (m, 4H), 4.09 (d, J=12.4 Hz, 16H), 3.89–3.83 (m, 8H), 3.75–3.51 (m, 32H), 3.40–3.29 (m, 16H), 3.07 (d, J=12.9, 4H), 3.05 (d, J=12.9, 4H), 1.92–1.70 (m, 16H), 1.57–1.43 (m, 8H), 1.04–1.01 (m, 24H), 0.75 (t, J=7.5 Hz, 12H). ^{13}C NMR ($CDCl_3$): δ 156.0, 154.7, 142.2, 137.2, 133.5, 133.2, 132.1, 130.6, 130.4, 129.8, 129.4, 128.8, 128.2, 122.1, 121.3, 75.9, 75.4, 71.3, 70.5, 38.8, 35.7, 30.5, 22.9, 21.8, 11.0, 9.8. MALDI-TOF MS *m/z*: 2467.3 ($M+Na^+$), 2483.3 ($M+K^+$). Anal. Calcd for $C_{164}H_{188}O_{18}$: C, 80.49; H, 7.74. Found: C, 80.32; H, 7.87.

3.3.2. Compound 7a′. Yield 32%; mp 124–126 °C; ^{1}H NMR ($CDCl_3$): δ 7.13–7.06 (m, 24H), 6.93 (t, J=7.4 Hz, 2H), 6.92 (t, J=7.4 Hz, 2H), 6.48–6.41 (m, 8H), 6.31 (t, J=6.1 Hz, 8H), 6.14–6.01 (m, 2H), 5.84 (t, J=4.8 Hz, 2H), 5.17 (d, J=17.1 Hz, 1H), 5.16 (d, J=17.1, 1H), 5.13 (d, J=9.1 Hz, 1H), 5.12 (d, J=9.1 Hz, 1H), 4.11–3.93 (m, 16H), 3.91 (t, J=4.7 Hz, 8H), 3.80–3.74 (m, 8H), 3.72–3.66 (m, 16H), 3.59–3.47 (m, 16H), 3.41 (d, J=6.8 Hz, 4H), 3.38–3.33 (m, 4H), 3.08 (d, J=13.1 Hz, 4H), 3.07 (d, J=13.3 Hz, 4H), 1.96–1.84 (m, 16H), 1.52–1.45 (m, 8H), 1.13 (t, J=7.4 Hz, 12H), 1.12 (t, J=7.4 Hz, 12H), 0.79–0.74 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 156.9, 155.6, 155.2, 138.0, 137.1, 133.8, 133.3, 132.8, 132.1, 130.4, 129.5, 128.9, 128.3, 122.2, 121.5, 115.4, 76.0, 75.4, 71.4, 70.5, 39.9, 35.8, 30.5, 23.88, 23.84, 21.8, 10.2, 9.8. MALDI-TOF MS *m/z*: 2495.1 ($M+Na^+$), 2511.1 ($M+K^+$). Anal. Calcd for $C_{166}H_{192}O_{18}$: C, 80.55; H, 7.82. Found: C, 80.41; H, 7.86.

3.3.3. Compound 7b. Yield 52%; mp 133–134 °C; ^{1}H NMR ($CDCl_3$): δ 7.12 (d, J=7.3 Hz, 6H), 6.95 (s, 4H), 6.95–6.92 (m, 4H), 6.43 (t, J=7.5 Hz, 4 H), 6.28 (d, J=7.5 Hz, 4H), 5.72 (t, J=6.1 Hz, 2H), 4.09 (d, J=13.1 Hz, 4H), 4.06–4.01 (m, 4H), 3.82–3.75 (m, 12H), 3.70 (s, 4H), 3.59–3.49 (m, 8H), 3.41–3.32 (m, 8H), 3.08 (d, J=13.2 Hz, 4H), 1.96–1.89 (m, 8H), 1.48–1.45 (m, 4H), 1.16 (t, J=6.3 Hz, 12H), 0.79 (t, J=7.5 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 157.1, 155.6, 137.1, 133.9, 133.3, 132.1, 131.4, 130.6, 129.0, 128.8, 128.2, 122.2, 121.4, 75.9, 75.6, 71.5, 70.8, 70.3, 37.6, 35.7, 30.4, 23.9, 21.9, 11.0, 9.7. MALDI-TOF MS *m/z*: 1290.6 ($M+Na^+$). Anal. Calcd for $C_{84}H_{98}O_{10}$: C, 79.59; H, 7.79. Found: C, 79.36; H, 7.91.

3.3.4. Compound 7c. Yield 66%; mp 128–130 °C; ^{1}H NMR ($CDCl_3$): δ 7.11–7.00 (m, 12H), 6.90 (t, J=7.5 Hz, 2H), 6.41 (t, J=7.5, 4H), 6.24 (d, J=7.4 Hz, 4H), 5.79 (t, J=6.1 Hz, 2H), 4.05 (d, J=13.1 Hz, 4H), 4.02–3.98 (m, 4H), 3.84 (d, J=13.0 Hz, 4H), 3.72–3.64 (m, 12H), 3.59–3.46 (m, 12H), 3.37 (d, J=6.1 Hz, 4H,), 3.32 (t, J=8.5 Hz, 4H,), 3.03 (d, J=13.2 Hz, 4H), 1.82–1.77 (m, 8H), 1.08–1.04 (m, 4H), 1.06 (t, J=7.3 Hz, 12H), 0.76 (t, J=7.3 Hz, 6H). ^{13}C NMR ($CDCl_3$): δ 157.1, 155.6, 154.8, 137.2, 133.7, 133.2, 132.3, 131.1, 130.9, 129.5, 128.9, 128.2, 122.2, 121.5, 76.0, 75.6, 71.4, 70.7, 70.4, 69.9, 38.1, 35.7, 30.5, 23.9, 21.9, 11.0, 9.9. MALDI-TOF MS *m/z*: 1333.6 ($M+Na^+$), 1349.5 ($M+K^+$). Anal. Calcd for $C_{86}H_{102}O_{11}$: C, 78.75; H, 7.84. Found: C, 78.89; H, 7.93.

3.4. X-ray crystallographic study

Crystals suitable for X-ray diffraction were grown from a mixture of dichloromethane and *n*-hexane for compounds **5**, **6a** and **7b**, or a mixture of dichloromethane and acetonitrile for compound **6c**. Data collection was performed at 293 K using a Rigaku R-AXIS RAPID IP detector, and SHELXS-97 and SHELXL-97 programs were used for structure solution and refinement. Crystallographic data for structures

reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-258734 (for compound **5**), CCDC-CCDC 258735 (for compound **6a**), CCDC-258736 (for compound **6c**), and CCDC-258737 (for compound **7b**). These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

3.4.1. Compound 5. $C_{40}H_{46}O_4$, MZ 590.77, crystal dimensions $0.79\times0.75\times0.08$ mm^3, orthorhombic, space group *Pna*21, $a=19.6494(7)$ Å, $b=18.1277(14)$ Å, $c=9.5362(12)$ Å, $U=3396.8(5)$ Å^3, $D_c=1.112$ Mg m^{-3}, $Z=4$, 4110 reflections collected, 2593 independent [R(int)=0.0000], giving $R_1=0.0527$ for observed unique reflection [$F^2>2$ s (F^2)] and $wR_2=0.1447$ for all data.

3.4.2. Compound 6a. $C_{84}H_{98}O_9$, MZ 1251.62, crystal dimensions $0.79\times0.44\times0.04$ mm^3, monoclinic, space group *P*2/*c*, $a=18.311(2)$ Å, $b=11.6641(12)$ Å, $c=18.060(2)$ Å, $\beta=104.258(5)°$, $U=3738.4(7)$ Å^3, $D_c=1.112$ Mg m^{-3}, $Z=2$, 8410 reflections collected, 2384 independent [R(int)=0.0000], giving $R_1=0.0947$ for observed unique reflection [$F^2>2$ s (F^2)] and $wR_2=0.3091$ for all data.

3.4.3. Compound 6b. $C_{88}H_{106}O_{11}\cdot H_2O$, MZ 1357.74, crystal dimensions $0.27\times0.81\times0.29$ mm^3, monoclinic, space group *P*2(*1*)/*c*, $a=14.109$ (3) Å, $b=34.077$ (7) Å, $c=16.963$ (3) Å, $\beta=102.25$ (3)°, $U=7970$ (3) Å^3, $D_c=1.132$ Mg m^{-3}, $Z=4$, 13011 reflections collected, 6086 independent [R(int)=0.0000], giving $R_1=0.0936$ for observed unique reflection [$F^2>2$ s (F^2)] and $wR_2=0.3125$ for all data.

3.4.4. Compound 7c. $C_{84}H_{98}O_{10}$, MZ 1267.62, crystal dimensions $0.672\times0.393\times0.288$ mm^3, monoclinic, space group *P*2(*1*)/*N*, $a=11.560$ (2) Å, $b=39.600$ (8) Å, $c=16.380$ (3) Å, $\beta=97.42$ (3)°, $U=7436$ (3) Å^3, $D_c=1.132$ Mg m^{-3}, $Z=4$, 47393 reflections collected, 3940 independent [R(int)=0.0652], giving $R_1=0.0769$ for observed unique reflection [$F^2>2$ s (F^2)] and $wR_2=0.2259$ for all data.

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