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Serendipitous one-pot formation of an unusual calix[5]arene-bis-crown-3 receptor

Giuseppe Gattuso [a], Claudia Liotta [a], Anna Notti [a], Sebastiano Pappalardo [b,*], Melchiorre F. Parisi [a,*]

[a] Dipartimento di Chimica Organica e Biologica, Università di Messina, Salita Sperone 31, 98166 Messina, Italy
[b] Dipartimento di Scienze Chimiche, Università di Catania, Viale A. Doria 6, 95125 Catania, Italy

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ABSTRACT

Alkylation of *p-tert*-butylcalix[5]arene **1c** with an excess of 2-(2-chloroethoxy)ethyl tosylate **2** and anhydrous K_2CO_3, has led to the serendipitous regioselective formation of *cone-in* (1,2–3,5)-calix[5]arene bis-crown-3 derivative **4** possessing a reactive 2-(2-chloroethoxy)ethoxy pendant functionality at the lower rim. The structure and conformation of **4** have firmly been assigned by a combination of NMR analysis and HF/6-31G* ab initio calculations, as well as by an independent stepwise synthesis. A preliminary ESI-MS screening of the binding properties of **4** toward alkali metal ions has shown a clear preference for the larger cations.

The three-dimensional concave framework of calixarenes,[1] their ready availability, tunable size, and versatility of derivatization, both at the upper and lower rims, have rendered this class of compounds one of the prime molecular platforms for the design of ion-selective ionophores and for the study of molecular encapsulation. The ease of adding crown ether loops[2] onto the calixarene lower rim has been extensively harnessed over the past years for the production of the most diverse calix-crown derivatives, which have shown a wide and varied range of complexation properties toward metal and organic ions.[3]

Among molecular architectures derived from calixcrowns, tubular calixarenes[4] have attracted considerable attention for their potential to act as synthetic channels for ion-transport through cell membranes.[5] These molecules, however, posed a considerable synthetic challenge until Beer and co-workers reported the preparation of a series of calix[4]tubes composed of two calix[4]arene residues linked together, at their lower rims, by four ethylene bridges.[6]

In our pursuit of structurally related calix[5]tubes, a few years ago, we obtained a mixed-cavity calix[4][5]tube.[7] Similar studies, by Raston and co-workers, also showed that a direct attempt to obtain a calix[5]tube by reacting *p-tert*-butylcalix[5]arene **1c**[8] with 2-chloroethyl tosylate and K_2CO_3 afforded a doubly intrabridged bis-ethylene calix[5]arene derivative, presumably as a result of the *intramolecular* reaction of a tri-O-alkylated intermediate.[9] We, therefore, decided to explore the K_2CO_3-promoted per-O-alkylation of a series of calix[5]arenes **1** with the longer 2-(2-chloroethoxy)ethyl tosylate **2**,[10] reasoning that the presence of an additional oxygen atom in the bridge might help—via possible template effects from K^+ ions—in the formation of the desired calix[5]arene precursors.

Reaction of *p*-H-calix[5]arene **1a**[11] and *p*-methylcalix[5]arene **1b**[12] with an excess of **2** and K_2CO_3 (10 equiv each) in refluxing CH_3CN gave (1,3)-bridged 2,4,5-tris[2-(2-chloroethoxy)ethoxy]-calix[5]arene-crown-3 derivatives **3a** (41%) and **3b** (53%) as shown in Scheme 1.[13] ESI-MS analysis of **3a** and **3b** showed molecular ion peaks at *m/z* 919.1 and 989.1, respectively, featuring a three-chlorine isotopic pattern, along with ion peaks at higher masses corresponding to $[M{\cdot}NH_4]^+$, $[M{\cdot}Na]^+$, and $[M{\cdot}K]^+$ ions. Their ^1H and ^{13}C NMR spectra indicate the formation of 1,3-bridged mono-crown derivatives (vide infra) fixed[14,15] in a *cone-in* conformation on the basis of the following features: (i) three diagnostically important AX systems (ratio 2:1:2) for the bridging methylene groups and resonances of relevant carbons in the range 28–31 ppm[16] and (ii) high field resonances for the hydrogens of the isolated *p*-H- or *p*-Me-phenyl moieties ($\delta = 6.43$ (1H) and 1.57 (3H) ppm, respectively), consistent with their leaning toward the interior of the cavity (self-filling).[17]

Reaction of **1c** and **2**, under the very same conditions, also produced a single product (56%),[13] whose ^1H NMR spectrum suggested once again a C_s symmetric *cone-in* conformation of the molecule (three AX systems for the $ArCH_2Ar$ hydrogens, and singlets at $\delta = 5.90$ (2H) and 0.04 (9H) ppm for the self-filling *p-tert*-butylphenyl moiety). Unexpectedly, though, its ESI-MS spectrum displayed molecular ion peaks at *m/z* 1057.4 ($[M{\cdot}H]^+$), 1074.4 ($[M{\cdot}NH_4]^+$), 1079.4 ($[M{\cdot}Na]^+$), and 1095.3 ($[M{\cdot}K]^+$, base peak), all of them exhibiting a monochlorinated isotopic pattern, compatible

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* Corresponding authors. Tel.: +39 095 7385018; fax: +39 095 580138 (S.P.); tel.: +39 090 6765170; fax: +39 090 393895 (M.F.P.).
E-mail addresses: spappalardo@unict.it (S. Pappalardo), mparisi@unime.it (M. F. Parisi).

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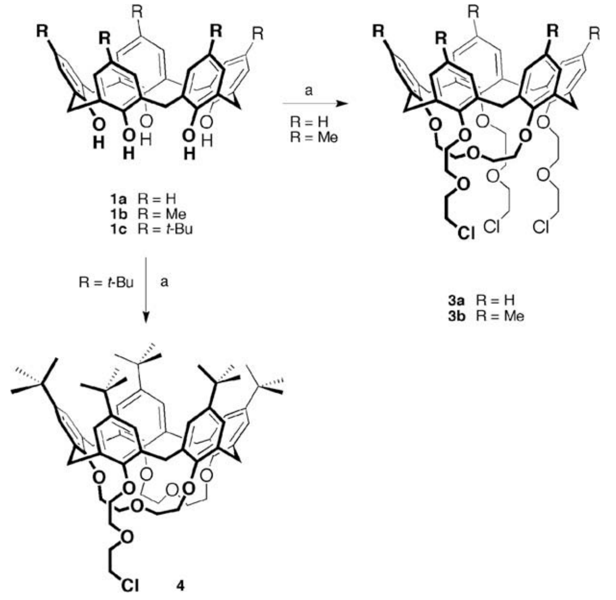
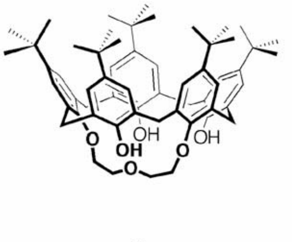


Scheme 1. Synthesis of calix[5]arene-crown-3 **3a**,**b** and calix[5]arene-biscrown-3 **4**. Reagents and conditions: (a) $Ts(OCH_2CH_2)_2Cl$ **2**, K_2CO_3, CH_3CN, (**3a**, 41%; **3b**, 53%; **4**, 56%).

with the formation of a calix[5]arene-bis-crown-3 derivative **4**, possessing a reactive 2-(2-chloroethoxy)ethoxy pendant functionality at the lower rim. This is, to our knowledge, the first example of a calix[5]arene adorned with two crown ether loops at the narrow rim.[18]

In principle, two possible intramolecular bridging products (i.e., 1,2–3,4- and 1,2–3,5-isomer) were envisioned for this reaction, according to the identity of the first-formed (1,2- or 1,3-) polyether linkage. NMR analysis of **4**, however, did not allow us to determine which one had been formed, because of their similar C_s-symmetry point group. Assuming the well-established stepwise mechanism of calixarene alkylation with weak bases, the formation of **4** could have resulted from either a 1,2- or a 1,3-bridged intermediate. While the former can statistically evolve toward both calix[5]-arene-bis-crowns, the latter can only afford the 1,2–3,5-regioisomer. The regioselective outcome of the reaction could therefore be explained by assuming (1,3)-*p-tert*-butylcalix[5]arene-crown-3 **5** as the eligible intermediate. To shed light on this matter, calix[5]-arene crown ether **5**, synthesized on purpose from **1c** and diethyleneglycol ditosylate under Böhmer's conditions,[3b,19,20] was subjected to an excess of **2** and K_2CO_3 in refluxing CH_3CN, to yield a product identical in all respects to **4**, obtained by the one-pot reaction described above. Furthermore, crown ethers **4** and **5**, as well as O-alkylated mono-crown intermediate **6**, were isolated and characterized (NMR) as the products of the K_2CO_3-promoted reaction of **1c** with a defect of **2** (1 equiv) in refluxing CH_3CN (3 days).



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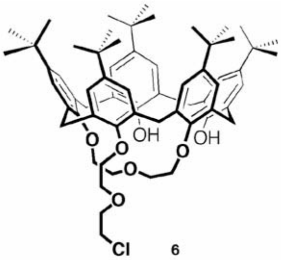

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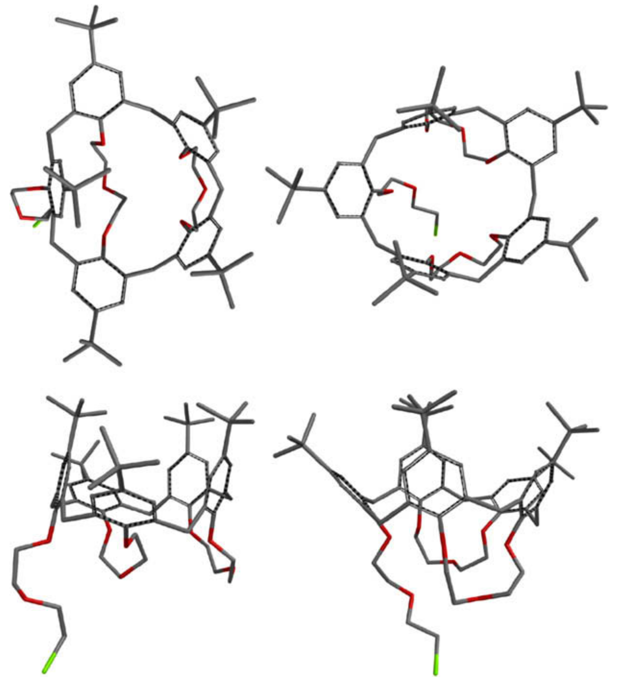

Figure 1. Top and side views of the equilibrium geometries of calix[5]arene-bis-crown-3 **4** (left) and its 1,2–3,4-regioisomer (right), based on HF/6-31G* geometry optimizations.

Further, evidence on the structural assignment of **4** was provided by calculations[21] of equilibrium geometries of **4** and its (1,2–3,4)-regioisomer, by using the Hartree–Fock method with the 6-31G* basis set (Fig. 1).[22]

The calculated structures show that, as predicted, **4** possesses a *cone-in* conformation, whereas its regioisomer has a regular *cone* conformation.[23] These findings are in excellent agreement with the NMR data of **4**, confirming that the aryl moiety bearing the pendant group is indeed in a tilted self-filling position. Furthermore, the 2-(2-chloroethoxy)ethoxy pendant and flanking crown-3 subunit at the narrow rim of calix[5]arene **4** generate an ionophoric pocket lined by ethereal oxygen atoms that could be harnessed for the complexation of alkali metal cations.

The binding affinities and selectivities of bis-crown derivative **4** toward alkali metal ions were preliminarily estimated in competitive complexation experiments by the ESI-MS technique.[24] The ESI spectrum of **4** in the presence of an equimolar mixture of alkali metal ion picrate salts (Fig. 2) evidences a clear preference of the bis-crown derivative for the larger alkali metal ions—prominent ion peaks corresponding to $[M{\cdot}Cs]^+$ (base peak), $[M{\cdot}Rb]^+$ (68%), and $[M{\cdot}K]^+$ (60%) 1:1 complexes—whereas ion peaks relative to

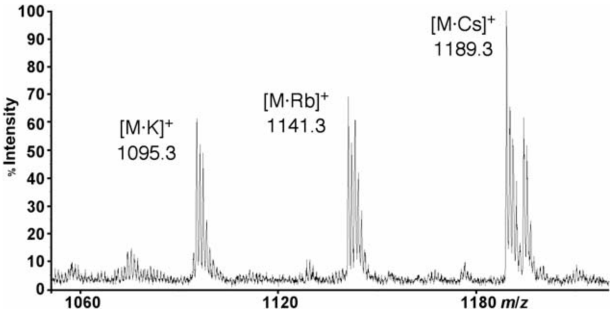

Figure 2. Positive ESI-MS spectrum of a mixture of $[\mathbf{4}] = [Li^+] = [Na^+] = [K^+] = [Rb^+] = [Cs^+] = 10\ \mu M$ (as picrate salts) in $CHCl_3/MeOH$ 4:1.

complexes with the smaller Li$^+$ and Na$^+$ ions are negligible or even absent.

In conclusion, we have described the one-pot synthesis of novel calix[5]arene mono- and bis-crown ether building blocks **3** and **4** endowed with modifiable ponytail(s) at the lower rim. Further investigations into the binding properties of **3** and **4**, and the design and synthesis of new receptors by exploiting the potential offered by their reactive pendant functionalities are underway.

Acknowledgments

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13. *General procedure for the synthesis of calix[5]arene crown ethers* **3a,b** *and* **4**: A stirred mixture of calix[5]arene **1** (0.5 mmol), tosylate **2** (1.39 g, 5 mmol), and anhydrous K_2CO_3 (0.69 g, 5 mmol) in anhydrous CH_3CN (100 mL) was refluxed for 24 h under N_2. The solvent was evaporated under reduced pressure, and the residue was partitioned between chloroform (30 mL) and aqueous HCl (1 M, 30 mL). The organic layer was washed with water (2 × 30 mL), dried ($MgSO_4$), and concentrated. The crude product was purified by column chromatography (SiO_2, petroleum ether/AcOEt 5:2 to 5:4, v/v) to give the appropriate calix[5]crown derivative.
   Crown ether **3a**: (41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.95 (br d, J = 10.5 Hz, 2H), 3.25 and 4.55 (AX, J = 13.5 Hz, ArCH$_2$Ar, 2H), 3.30 (br t, J = 9.0 Hz, 2H), 3.36 and 4.45 (AX, J = 14.5 Hz, ArCH$_2$Ar, 4H), 3.43 (br d, partly buried, 2H), 3.45 and 4.61 (AX, J = 15.5 Hz, ArCH$_2$Ar, 4H), 3.63–3.69 (m, 6H), 3.81–3.87 (m, 8H), 3.91 (t, J = 5 Hz, 4H), 3.99–4.04 (m, 4H), 4.09–4.13 (m, 2H), 4.25 (ddd, J = 13.0, 8.2, 2.5 Hz, 2H), 6.30 (d, J = 7.5 Hz, 2H), 6.43 (overlapping t, J = 7.5 Hz, 3H), 6.62 (t, J = 7.5 Hz, 2H), 6.74 (d, J = 7.5 Hz, 2H), 7.06 (t, J = 7.5 Hz, 2H), 7.20 (dd, J = 7.5, 1.5 Hz, 2H), and 7.27 (dd, J = 7.5, 1.5 Hz, 2H) ppm; ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ 29.3, 29.6, 30.7 (ArCH$_2$Ar), 42.8, 42.9 (CH$_2$Cl), 68.4, 70.38, 70.44, 71.3, 71.4, 71.7, 72.7, 73.0 (OCH$_2$), 123.3, 123.4 (×2), 126.6, 127.3, 128.6, 130.3, 130.9 (*m*- and *p*-Ar), 133.7, 134.0, 134.1, 135.2, 135.3 (*o*-Ar), 153.9, 154.1, and 156.2 (*ipso*-Ar) ppm. ESI-MS *m*/*z* (rel. int.%) 919.1 ([M·H]$^+$, 100), 936.1 ([M·NH$_4$]$^+$, 53), 941.1 ([M·Na]$^+$, 27), 957.0 ([M·K]$^+$, 24). Anal. Calcd for $C_{51}H_{57}Cl_3O_9$: C, 66.56; H, 6.24. Found: C, 66.23; H, 6.27.
   Crown ether **3b**: (53%); mp 193–195 °C (CH_2Cl_2/CH_3OH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.57, 2.05, 2.39 (s, ratio 1:2:2, CH$_3$, 15H), 3.15–3.19 (m, 2H), 3.19 and 4.51 (AX, J = 13.0 Hz, ArCH$_2$Ar, 2H), 3.22 and 4.41 (AX, J = 14.5 Hz, ArCH$_2$Ar, 4H), 3.34 and 4.53 (AX, J = 15.0 Hz, ArCH$_2$Ar, 4H), 3.41 (ddd, J = 10.0, 7.5, 2.7 Hz, 2H), 3.55 (ddd, J = 13.1, 4.6, 3.1 Hz, 2H), 3.62–3.68 (m, 6H), 3.79–3.84 (m, 8H), 3.85–4.00 (m, 8H), 4.03–4.07 (m, 2H), 4.20 (ddd, J = 12.7, 7.5, 3.9 Hz, 2H), 6.04 (s, ArH, 2H), 6.38, 6.78, 6.98, and 7.07 (d, Ar H, 2H each) ppm; ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ 20.3, 20.9, 21.1 (CH$_3$), 28.3, 29.4, 30.8 (ArCH$_2$Ar), 42.8, 42.9 (CH$_2$Cl), 68.9, 70.4, 70.5, 71.3, 71.4, 71.8, 72.6, 73.1 (OCH$_2$), 127.0, 128.0, 129.0, 130.9, 131.4 (*m*-Ar), 132.1, 132.2, 132.4, 133.2, 133,4, 133.8, 134.6, 134.9 (*o*- and *p*-Ar), 151.7, 151.8, and 153.9 (*ipso*-Ar) ppm. ESI-MS *m*/*z* (rel. int.%) 989.1 ([M·H]$^+$, 65), 1006.1 ([M·NH$_4$]$^+$, 100), 1011.1 ([M·Na]$^+$, 36), 1027.1 ([M·K]$^+$, 73). Anal. Calcd for $C_{56}H_{67}Cl_3O_9$: C, 67.91; H, 6.82. Found C, 67.62; H, 6.81.
   Crown ether **4**: (56%); mp 289–291 °C (CH_3OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.04, 1.14, 1.38 (s, ratio 1:2:2, C(CH$_3$)$_3$, 45H), 3.10–3.18 and 3.20–3.30 (2 × m, 4H), 3.19 and 4.96 (AX, J = 11.9 Hz, ArCH_2Ar, 2H), 3.39 and 4.55 (AX, J = 14.1 Hz, ArCH_2Ar, 4H), 3.42 and 4.32 (AX, J = 13.3 Hz, ArCH_2Ar, 4H), 3.64 (t, J = 5.8 Hz, 2H), 3.76 (br t, J = 9.9 Hz, 2H), 3.86 (t, J = 5.8 Hz, 2H), 3.80–3.88 (m, 2H), 3.96–4.09 (m, OCH$_2$, 8H), 4.22 (d, J = 12.2 Hz, 2H), 4.37–4.45 (m, 2H), 5.90 (s, ArH, 2H), 7.01 and 7.12 (ABq, J = 2.4 Hz, ArH, 4H), 7.16 and 7.36 (ABq, J = 2.4 Hz, ArH, 4H) ppm; ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ 27.6, 29.6, 31.8 (ArCH$_2$Ar), 30.5, 31.4, 31.7 ((CH$_3$)$_3$C), 33.4, 34.2 ((CH$_3$)$_3$C), 42.9 (CH$_2$Cl), 69.0, 70.5, 71.5, 71.6 (×2), 72.8, 75.4, 75.9 (OCH$_2$), 123.5, 123.7, 125.7, 127.4, 127.9 (*m*-Ar), 133.0, 133.9, 134.0, 134.6, 135.0 (*o*-Ar), 145.2, 145.5, 145.7 (*p*-Ar), 150.9, 151.6, and 153.5 (*ipso*-Ar) ppm; ESI-MS *m*/*z* (rel. int.%). 1057.4 ([M·H]$^+$, 8), 1074.4 ([M·NH$_4$]$^+$, 40), 1079.4 ([M·Na]$^+$, 7), and 1095.3 ([M·K]$^+$, 100). Anal. Calcd for $C_{67}H_{89}ClO_8$: C, 76.07; H, 8.48. Found: C, 75.68; H, 8.52.
14. To the best of our knowledge, this is the first case of a *p*-H-calix[5]arene derivative fixed in a *cone* conformation, the 1,3-bridging formed presumably inhibiting the phenyl-through-the-annulus rotation.[15]
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20. Crown ether **5**: mp 172–174 °C (CH_2Cl_2/CH_3OH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10, 1.22, 1.27 (s, ratio 2:1:2, (CH$_3$)$_3$C, 45H), 3.31 and 5.18 (AX, J = 13.7 Hz, ArCH$_2$Ar, 2H), 3.44 and 4.13 (AX, J = 14.0 Hz, ArCH$_2$Ar, 4H), 3.50 and 4.21 (AX, J = 14.5 Hz, ArCH$_2$Ar, 4H), 3.91 (br t, J = 10.5 Hz, OCH$_2$, 2H), 4.10 (t, J = 10.0 Hz, OCH$_2$, 2H), 4.20 (br d, J = 10.5 Hz, OCH$_2$, 2H), 4.52 (br d, J = 10.5 Hz, OCH$_2$, 2H), 7.09 and 7.13 (ABq, J = 2.5 Hz, ArH, 4H), 7.16 (s, ArH, 2H), 7.17 and 7.19 (ABq, J = 2.5 Hz, ArH, 4H), 7.52 and 7.72 (br s, ratio 1:2, OH, 3H) ppm; ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ 28.8, 30.6 (ArCH$_2$Ar), 31.3, 31.4, 31.5 ((CH$_3$)$_3$C), 33.85, 33.87, 34.1 ((CH$_3$)$_3$$C$), 73.6, 76.0 (OCH$_2$), 125.0, 125.6, 125.8, 126.3, 126.49 (*m*-Ar), 126.53, 126.8, 127.3, 132.7, 134.2 (*o*-Ar), 142.8, 143.3, 147.0 (*p*-Ar) 148.0, 148.8, and 150.6 (*ipso*-Ar) ppm. ESI-MS *m*/*z* (rel. int.%) 881.3 ([M·H]$^+$, 3), 898.4 ([M·NH$_4$]$^+$, 100), and 903.3 ([M·Na]$^+$, 20). Anal. Calcd for $C_{59}H_{76}O_6$: C, 80.41; H, 8.69. Found: C, 80.09; H, 8.70.
   Crown ether **6**: mp 100–102 °C (CH_2Cl_2/CH_3OH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.14, 1.18, 1.37 ((CH$_3$)$_3$, ratio 1:2:2, 45H), 3.31 and 4.26 (AX, J = 13.5 Hz, ArCH$_2$Ar, 4H), 3.43 (part of an AX system, J = 14.0 Hz, ArCH$_2$Ar, 1H), 3.53 and 4.52 (AX, J = 15.8 Hz, ArCH$_2$Ar, 4H), 3.65 (br t, J = 5.8 Hz, 2H), 3.78–3.92 (m, 10H), 3.92–4.13 (m, 7H), 5.96 (s, ArH, 2H), 6.97 and 7.02 (ABq, J = 2.3 Hz, ArH, 4H), 7.16 and 7.38 (ABq, J = 2.4 Hz, ArH, 4H) ppm; ^{13}C NMR (APT, 75 MHz, $CDCl_3$) δ 29.7, 30.8, 31.8 (ArCH$_2$Ar), 30.4, 31.4, 31.6 ((CH$_3$)$_3$C), 33.8, 34.3 ((CH$_3$)$_3$$C$), 42.9 (CH$_2$Cl), 68.9, 70.0, 70.6, 71.5, 72.5 (OCH$_2$), 123.1, 124.8, 125.2, 126.4, 127.7 (*m*-Ar), 127.4, 128.3, 132.5, 134.0, 135.1 (*o*-Ar), 142.6, 146.2, 146.7 (*p*-Ar) 148.3, 151.1, and 152.9 (*ipso*-Ar) ppm. Anal. Calcd for $C_{63}H_{83}ClO_7$: C, 76.60; H, 8.47. Found: C, 76.42; H, 8.49.
21. Calculations were performed with Spartan 06 (Wavefunction, Inc.).
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