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Regioselective Friedel–Crafts acylation of calix[4]arenes

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ABSTRACT

Friedel–Crafts acylation of 25,27-dialkoxycalix[4]arenes has been studied. Direct acylation of de-*tert*-butylated calixarene using acyl chlorides and $AlCl_3$ in 1,2-dichloroethane provided the corresponding diacyl derivatives regioselectively in high yields. Furthermore, *ipso*-substitution in the *tert*-butylated series under the same reaction conditions is possible, albeit in lower yields. As indicated by the unsuccessful application of this chemistry to *O*-acyl derivatives, the *ipso*-acylation reaction of calix[4]arenes proceeds by direct attack at the upper rim and not by a Fries rearrangement mechanism.

1. Introduction

Calix[*n*]arenes[1] are macrocyclic oligophenols and very popular in supramolecular chemistry, as they offer variably sized cavities combined with well-established chemistry allowing for easy derivatization. Moreover, in the case of calix[4]arene, it is possible to tune the three-dimensional shape of the cavity to form four basic conformations (atropisomers)—*cone*, *partial cone*, *1,3-alternate*, and *1,2-alternate*.[1] These precisely shaped cavities can then serve as molecular scaffolds in the design of novel receptors[2] as one can introduce various functional groups, necessary for supramolecular action, into exactly defined mutual positions in space.

Electrophilic aromatic substitution represents the most straightforward strategy for the derivatization of the upper rim (aromatic part of molecule) of calixarenes. For instance, nitration of calix[4]arenes is a well-established and frequently employed method, which can be carried out directly,[3] or via *ipso*-substitution[4] of the *tert*-butyl groups. Moreover, it can be used not only for per-substitution, but also for regioselective substitution[5] of the basic skeleton depending on the reaction conditions used.

Interestingly, despite its possible usefulness in the preparation of reactive intermediates, the Friedel–Crafts acylation[6] of calix[4]arene has been largely unexplored, being used primarily for the introduction of four acyl groups onto the unsubstituted upper rim of calix[4]arenes, via a direct mechanism. There are only a handful of papers[6a,7] some of them published more than two decades ago, dealing with the regioselective Friedel–Crafts acylations of distally dialkylated calix[4]arenes. Furthermore, the results of these reactions remain rather controversial (Fig. 1). While No et al. described[7a] the introduction of the acetyl group into the *para*-position of the anisole subunits, Huang et al.[7b] claimed the same reaction led to *para* substitution of the free phenolic units. It is well known in calix[4]arene chemistry that the introduction of alkoxy groups into distal positions render these aromatic subunits less reactive compared with the remaining free phenolic units. Consequently, electrophilic substitution like nitration, bromination, and formylation occur preferentially on the phenolic subunits. In order to resolve

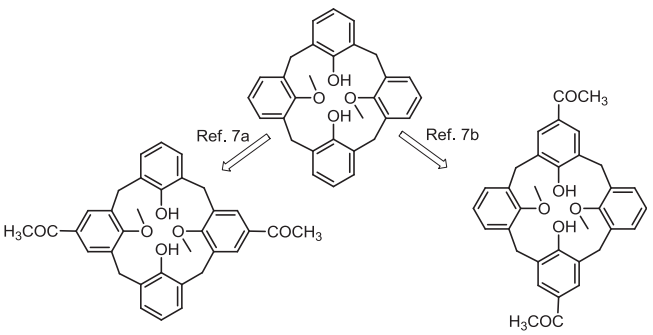

Fig. 1. Conflicting accounts over the regioselectivity of the Friedel–Crafts acetylation of calixarenes (AcCl+$AlCl_3$ used).

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this controversy, we report on the systematic study of the regioselective Friedel–Crafts acylation of dialkylated calix[4]arenes, which can be done either directly or via *ipso*-substitution in the *tert*-butylated series.

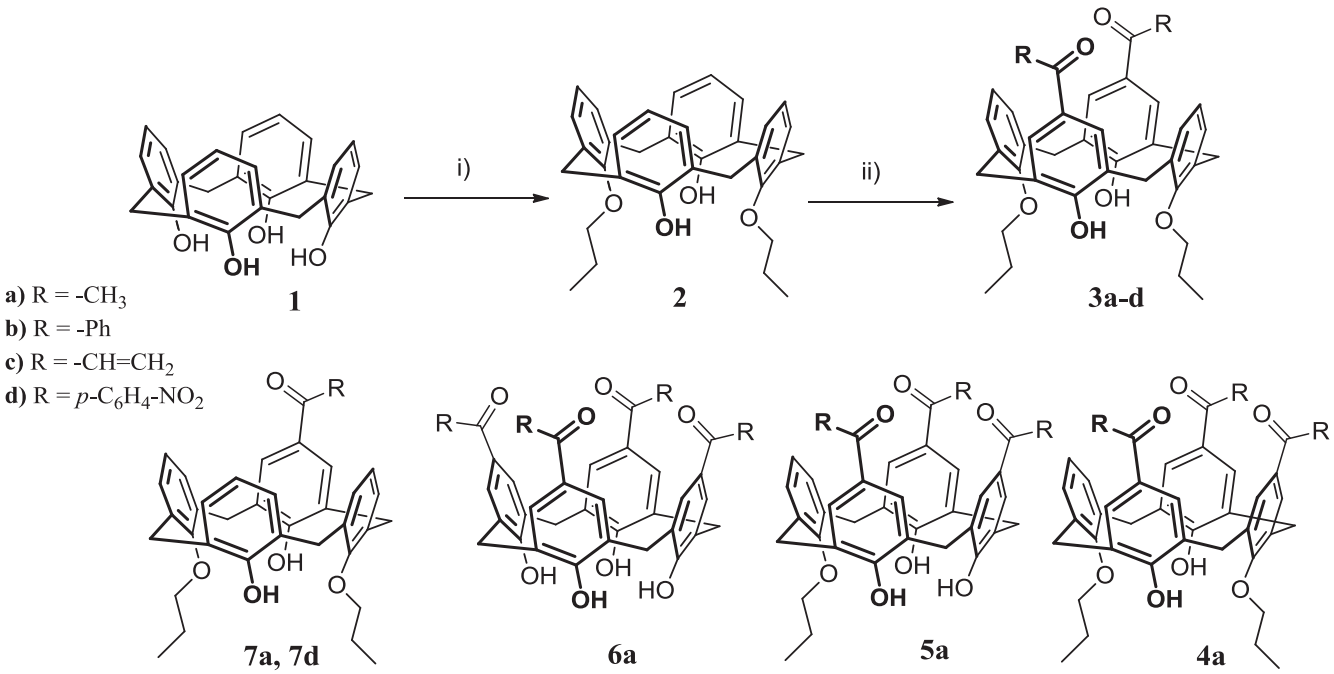
2. Results and discussion

The alkylation of parent calix[4]arene **1** with propyl iodide in the presence of K_2CO_3 gave distally dialkylated derivative **2**[8] (Scheme 1), which was used for the acylation study. The reaction conditions used by Huang[7b] ($AcCl/AlCl_3$, nitrobenzene as solvent, 1 week, room temperature) gave only 34% yield of the expected diacetylated compound **3a** accompanied by 4% of triacetyl derivative **4a**. Heating (50 °C) under otherwise identical reaction conditions provided complex reaction mixtures where compounds **3a** and **4a** represented only minor products, while monodealkylated compound **5a** was isolated in 41% yield. Unfortunately, these reactions were found to be reproducible only on a small scale (100–200 mg), all attempts to increase the scale of the reaction resulted in very complicated reaction mixtures. Moreover, nitrobenzene is not a suitable solvent for large-scale preparation, anyway, as it has to be removed from the reaction mixture using time consuming procedures (i.e., vacuum or steam distillation).

monoacylated isomer **7d** after preparative TLC. Surprisingly, our attempts to improve the yield using longer reaction times or a greater excess of acylating agent did not provide better results. The isolation of monoacylated calixarene **7d** allowed us to focus our attention on deliberate monoacetylation of **2**. Indeed, the optimized reaction conditions using just 1 equiv of AcCl led smoothly to monoacylated derivative **7a** in 80% yield.

The structures of **3a**–**3d** were confirmed using ^1H NMR spectroscopy. The splitting pattern and multiplicity of the signals perfectly corresponded to the expected C_{2v} symmetry of the products. Thus, one triplet of the terminal CH_3 groups (at 1.32 ppm in $CDCl_3$) and one singlet of the $-COCH_3$ groups (at 2.54 ppm) indicated the presence of two perpendicular symmetry planes in **3a**. Two doublets at 4.30 and 3.47 ppm, with typical geminal interaction constants of J=13.2 Hz originating from the equatorial and axial protons of CH_2 bridging moieties, supported the presence of the *cone* conformation.

The final unambiguous structural evidence was obtained by X-ray crystallography. Single crystals were obtained by slow evaporation of solutions of **3a**–**3d** in acetone. The resultant crystals possessed some characteristic general features: (i) All structures were substituted at the *para*-positions of the free phenolic subunits. (ii) The *cone* conformation was held by a circular hydrogen bond array



Scheme 1. Direct Friedel–Crafts acylation of dipropoxycalix[4]arene: (i) PrI/K_2CO_3/MeCN, reflux (83%); (ii) R–$COCl/AlCl_3$/DCE, rt (**3a**, 82%, **3b** 81%, **3c**, 86%, **3d**, 45%).

As a result, we sought improved reaction conditions. By changing the solvent to 1,2-dichloroethane, the Friedel–Crafts acylation proceeded much faster and in superior yield. Stirring the reaction mixture at room temperature for 10 min resulted in >80% (NMR yield) conversion to **3a**, and after 60 min 80% of **4a**. The longer reaction times induced full dealkylation of the propoxy groups, finally providing **6a** as the major product. The optimized reaction conditions (2 equiv of R–COCl and 4 equiv of $AlCl_3$ for calixarene, 10–15 min at room temperature) were then applied to selected acyl chlorides to demonstrate the scope of this procedure. The Friedel–Crafts diacylation using acetyl, benzoyl, and acryloyl chlorides furnished the corresponding products **3a**, **3b**, and **3c** in 82%, 81%, and 86% yields (isolated by crystallization), respectively, without issue. The same reaction with *p*-nitrobenzoyl chloride gave the expected product **3d** in 45% yield accompanied by 40% of

on the lower rim of the calixarenes (see Fig. 2a) with typical O–H···O distances ranging from 1.801 Å (**3b**) to 1.973 Å (**3d**). (iii) The calix[4]arenes adopted the *pinched cone* conformation with two opposite phenolic units being almost coplanar and the two remaining *para*-substituted rings pointing outwards from the cavity. (iv) Every calixarene molecule included a molecule of solvent (acetone) located in the cavity and held by CH–π interactions from the aromatic subunits. As shown in Fig. 2b–d, there are several bonding geometries differing by mutual positions of the acetone molecule and the cavity. Moreover, some structures displayed interesting crystal packing. For instance, as shown in Fig. 2e, the allyl derivative **3c** created a dimeric arrangement held together by π–π interactions of the coplanar aromatic units (interannular distance 3.393 Å).

The *ipso*-Friedel–Crafts reaction has been used previously in calixarene chemistry for the per-substitution of *tert*-butyl groups

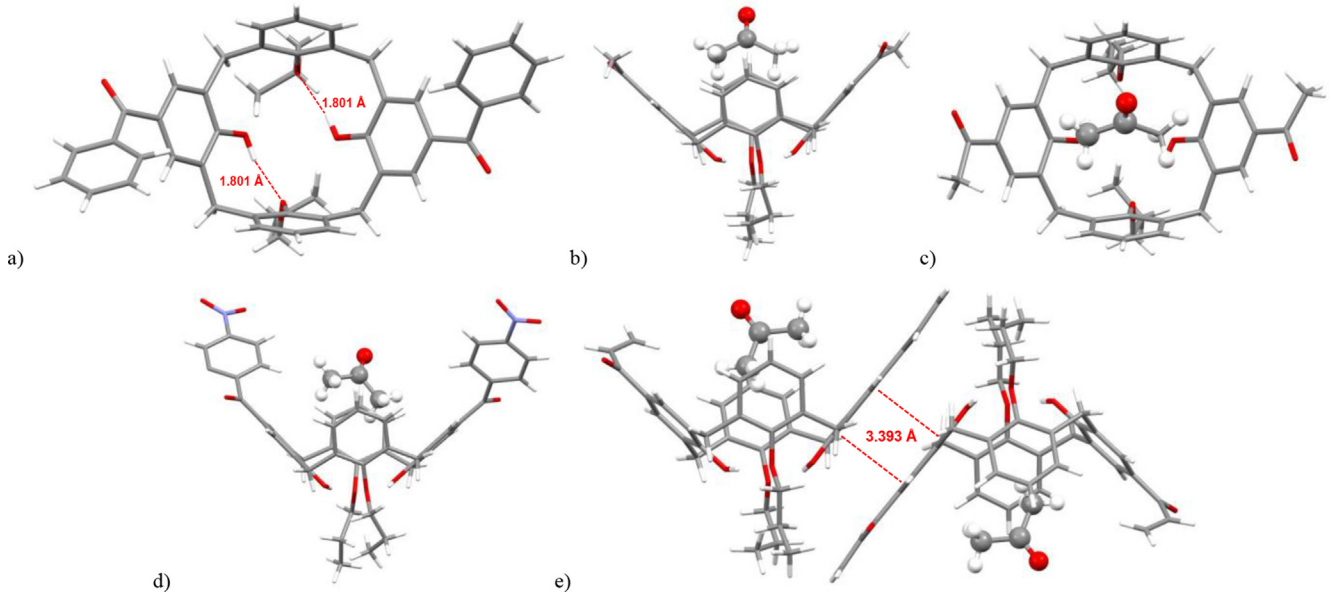
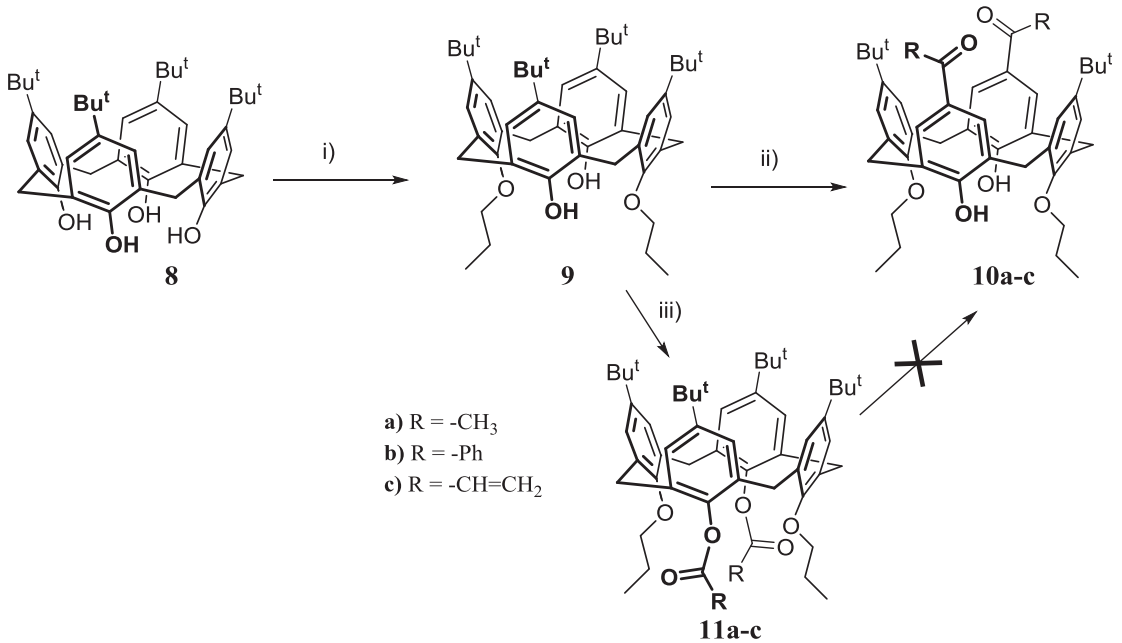


Fig. 2. X-ray structures of derivatives **3a**–**3d**: (a) The circular hydrogen bond array on the lower rim of **3b** with interatomic O–H···O distances; (b) side view of the **3a**·acetone complex; (c) top-down view of the same complex; (d) side view of the **3d**·acetone complex; (e) side view of the **3c**·acetone complex with intermolecular π–π interactions between two coplanar aromatic subunits.

by the acyl moiety in the parent (lower rim-unsubstituted) calix[4]-[8]arenes.[6b] To show the potential utility of this reaction for regioselective substitution of partly alkylated calix[4]arenes, propoxy derivative **9**[9] was prepared by reacting starting compound **8** with propyl iodide in the presence of K_2CO_3 as a base (Scheme 2). This compound was then subjected to the same reaction conditions that were used for the direct substitution. Acylation with benzoyl chloride gave the expected *ipso*-disubstituted product **10b** in 91% yield. On the other hand, the same reaction with acetyl chloride and acryloyl chloride led to complicated reaction mixtures from which products **10a** and **10c** were isolated only in 31% and 26% yields, respectively. In both cases, the reaction mixtures contained *O*-acylated by-products (esters **11a** and **11c**), which were proven by a combination of NMR and MS techniques.

These data presented an interesting mechanistic quandary about the nature of the *ipso*-acylation. The reaction could either proceed directly or via a two-step mechanism—O-acylation followed by Fries rearrangement[10] to the *para*-position—as has been suggested previously. In order to elucidate the mechanism, we prepared the corresponding *O*-acylated compounds **11a**–**c** and subjected them to Fries rearrangement under the identical reaction conditions (Scheme 2). To our surprise no reaction was observed after addition of $AlCl_3$ to **11a**–**c** in DCE solution, hence, these *O*-acylated intermediates cannot be transformed into *C*-acylated products **10a**–**c** under the reaction conditions used for *ipso*-substitution. This indicated that the *ipso*-acylation occurred by direct attack of the acylation agent to the upper rim (carbon carrying the *tert*-butyl groups) of the calixarenes. For less reactive benzoyl



Scheme 2. *ipso*-Friedel–Crafts acylation of dipropoxycalix[4]arene: (i) PrI/K_2CO_3/MeCN, reflux (74%); (ii) R–COCl/$AlCl_3$/DCE, rt (**10a**, 33%, **10b**, 91%, **10c**, 26%); (iii) (1) NaH/DMF, (2) R–COCl, rt (**11a**, 77%, **11b**, 84%, **11c**, 89%).

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chloride this was the only reaction pathway, leading finally to a very good yield of *ipso*-substituted product **10b**. The more reactive acetyl or acryloyl chloride attacked also the lower rim of the calixarenes (free OH groups), which substantially lowered overall yield of C-acylation.

3. Conclusions

Friedel–Crafts acylation of 25,27-dialkoxycalix[4]arenes was studied. Direct acylation of de-*tert*-butylated calixarene using acyl chlorides and $AlCl_3$ in 1,2-dichloroethane gave the corresponding diacyl derivatives regioselectively and in high yield. The same reaction can deliver *ipso*-substituted calixarenes in the *tert*-butylated series, albeit in lower yield. Furthermore, due to the inability of the *O*-acyl derivatives to undergo Fries rearrangement, the *ipso*-Friedel–Crafts reaction of calix[4]arenes proceeds by direct attack at the upper rim and not by a two-step O-acylation/Fries rearrangement mechanism. All acylated derivatives represent useful intermediates in the chemistry of calixarenes with potential applications in the design and synthesis of novel receptors.

4. Experimental

4.1. General

All chemicals were purchased from commercial sources and used without further purification. 1,2-Dichloroethane and *N*,*N*′-dimethylformamide used for the reactions were dried with CaH_2 and stored over molecular sieves. Melting points were measured on Heiztisch Mikroskop-Polytherm A (Wagner & Munz, Germany) and were not corrected. The IR spectra were measured on an FT-IR spectrometer Nicolet 740 in $CHCl_3$ and/or in KBr. NMR spectra were recorded on spectrometers Varian Gemini 300 (^{1}H: 300 MHz, ^{13}C: 75 MHz) and Agilent 400-MR DDR2 (^{1}H: 400 MHz, ^{13}C: 100 MHz). Chemical shifts (δ) are expressed in parts per million (ppm) and are referenced to the residual peak of solvent or TMS as an internal standard, coupling constants (J) are in hertz (Hz). The mass analyses were performed using ESI technique on an FT-MS (LTQ Orbitrap Velos) spectrometer. Purity of the substances and courses of the reactions were monitored by TLC using TLC aluminum sheets with Silica gel 60 F_{254} (Merck) and analyzed at 254 or 365 nm. Preparative TLC chromatography was carried out on a Chromatotron (Harrison Research) with plates covered by Silica gel 60 GF_{254} (Merck). Starting compounds **2** (25,27-dipropoxycalix[4]arene)[11] and **8** (5,11,17,23-tetra-*tert*-butyl-25,27-dipropoxycalix[4]arene)[12] were prepared according to known procedures.

4.2. General procedure for Friedel–Crafts acylation of 2

Calixarene **2** (1 equiv) was dissolved in dry 1,2-dichloroethane (c=6–9 mmol l^{-1}), then $AlCl_3$ (4 equiv) was added and the mixture was vigorously stirred for 5 min at room temperature. The corresponding acyl chloride (2 equiv) was added quickly (directly with Hamilton syringe for liquid agents or as a solution in 1,2-dichloroethane for solids). The reaction was monitored by TLC and after completion it was quenched by addition of 1 M HCl (aq). The layers were separated and water layer was extracted with CH_2Cl_2 (3×). Organic layers were collected and washed with $NaHCO_3$ (1×), water (2×) and dried over $MgSO_4$. The $MgSO_4$ was filtered off and the solvent was removed under reduced pressure. The crude product was purified by recrystallization from hot MeCN or precipitated from CH_2Cl_2/MeOH, as indicated, to obtain the highly pure product.

*4.2.1. Synthesis of 5,17-diacetyl-25,27-dipropoxycalix[4]arene (**3a**).* The general procedure was applied to compound **2** (100 mg, 0.2 mmol) and acetyl chloride. Product was isolated as white needle-shaped crystals after recrystallization from MeCN (97 mg, 82%), mp: 275–278 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ (ppm): 9.04 (s, 2H, Ar–*OH*), 7.74 (s, 4H, Ar–*H*), 6.96 (d, 4H, J=7.3 Hz, Ar–*H*), 6.78 (t, 2H, J=7.5 Hz, Ar–*H*), 4.30 (d, 4H, J=13.2 Hz, Ar–*CH*$_2$–Ar), 4.01 (t, 4H, J=6.3 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.47 (d, 4H, J=13.2 Hz, Ar–*CH*$_2$–Ar), 2.54 (s, 6H, ArCO–*CH*$_3$), 2.08 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.32 (t, 6H, J=7.5 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 293 K) δ (ppm): 196.38, 157.93, 151.36, 132.36, 129.23, 128.93, 128.59, 127.56, 125.24, 78.14, 31.01, 25.90, 23.12, 10.58. IR (KBr) ν (cm^{-1}): 3282.9, 3049.6, 2965.9, 2935.0, 2877.4, 2358.9, 1665.3, 1595.4, 1481.8, 1457.4, 1428.0, 1356.8, 1313.0, 1283.4, 1220.3, 1190.3, 994.1, 959.2, 770.7, 732.1. HRMS-ESI ($C_{38}H_{40}O_6$) m/z (% int.) calcd: 615.2717 [M+Na]$^+$, found: 615.2719 [M+Na]$^+$ (100%).

*4.2.2. Synthesis of 5,17-dibenzoyl-25,27-dipropoxycalix[4]arene (**3b**).* The general procedure was applied to compound **2** (100 mg, 0.2 mmol) and benzoyl chloride. Product was obtained as a white solid after recrystallization from MeCN (116 mg, 81%), mp: 279–281 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ (ppm): 9.14 (s, 2H, Ar–*OH*), 7.73 (d, 4H, J=7.9 Hz, Ar–*H*), 7.63 (s, 4H, Ar–*H*), 7.56 (d, 2H, J=7.0 Hz, Ar–*H*), 7.48 (t, 4H, J=7.3 Hz, Ar–*H*), 6.97 (d, 4H, J=7.3 Hz, Ar–*H*), 6.83 (t, 2H, J=7.3 Hz, Ar–*H*), 4.32 (d, 4H, J=13.2 Hz, Ar–*CH*$_2$–Ar), 4.01 (t, 4H, J=6.2 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.46 (d, 4H, J=13.2 Hz, Ar–*CH*$_2$–Ar), 2.10 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.34 (t, 6H, J=7.3 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 293 K) δ (ppm): 10.82, 23.37, 31.22, 78.45, 125.51, 127.71, 127.97, 128.49, 129.19, 129.58, 131.50, 132.74, 138.66, 151.66, 157.95, 195.53. IR (KBr) ν (cm^{-1}): 3380.6, 2925.8, 2875.2, 1645.8, 1597.5, 1479.0, 1456.5, 1319.1, 1282.6, 1215.3, 1160.6, 1122.4, 956.3, 765.1, 722.4, 696.5. HRMS-ESI ($C_{48}H_{44}O_6$) m/z (% int.) calcd: 739.3030 [M+Na]$^+$, found: 739.3031 [M+Na]$^+$ (100%).

*4.2.3. Synthesis of 5,17-diacryoyl-25,27-dipropoxycalix[4]arene (**3c**).* The general procedure was applied to compound **2** (100 mg, 0.2 mmol) and acryloyl chloride. Product was obtained as a white solid after recrystallization from MeCN (106 mg, 86%), mp: 138–142 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ (ppm): 9.13 (s, 2H, Ar–*OH*), 7.78 (s, 4H, Ar–*H*), 7.20 (dd, 2H, J=17.3 Hz, 10.5, CO–*CH*–CH$_2$), 6.97 (d, 4H, J=7.6 Hz, Ar–*H*), 6.79 (t, 2H, J=5 Hz, Ar–*H*), 6.38 (dd, 2H, J=17.0 Hz, 1.8, CO–CH–*CH*$_2$), 5.84 (dd, 2H, J=10.3, 1.8 Hz, CO–CH–*CH*$_2$), 4.31 (d, 4H, J=13.2 Hz, Ar–*CH*$_2$–Ar), 4.01 (t, 4H, J=6.3 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.49 (d, 4H, J=13.2 Hz, Ar–*CH*$_2$–Ar), 2.08 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.33 (t, 6H, J=7.5 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 293 K) δ (ppm): 189.16, 158.46, 151.60, 132.53, 132.28, 129.96, 129.23, 128.57, 128.01, 125.52, 78.44, 31.32, 30.83, 23.41, 10.86. IR (KBr) ν (cm^{-1}): 3255.1, 2930.6, 1659.4, 1583.6, 1458.3, 1428.7, 1400.1, 1316.1, 1273.8, 1171.4, 1058.9, 960.0, 911.1, 766.8, 732.4. HRMS-ESI ($C_{40}H_{40}O_6$) m/z (% int.) calcd: 639.2717 [M+Na]$^+$, found: 639.2723 [M+Na]$^+$ (100%).

*4.2.4. Synthesis of 5,17-bis(4-nitrobenzoyl)-25,27-dipropoxycalix[4]arene (**3d**).* The general procedure was applied to compound **2** (100 mg, 0.2 mmol) and 4-nitrobenzoyl chloride. The crude product was purified by preparative TLC on silica gel. Title compound was obtained as a green solid (73 mg, 45%), mp: 273–275 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 293 K) δ (ppm): 9.37 (s, 2H, Ar–*OH*), 8.35 (d, 4H, J=8.5 Hz, Ar–*H*), 7.84 (d, 4H, J=8.8 Hz, Ar–*H*), 7.60 (s, 4H, Ar–*H*), 6.96 (d, 4H, J=7.3 Hz, Ar–*H*), 6.86 (t, 2H, J=7.5 Hz, Ar–*H*), 4.32 (d, 4H, J=13.2 Hz, Ar–*CH*$_2$–Ar), 4.02 (t, 4H, J=6.2 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.44 (d, 4H, J=13.2 Hz, Ar–*CH*$_2$–Ar), 2.10 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.35 (t, 6H, J=7.5 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$). ^{13}C NMR (75 MHz, $CDCl_3$, 293 K) δ (ppm): 193.43, 158.92, 151.63, 149.25, 144.25, 132.55, 131.55, 130.15, 129.26, 128.19, 127.34, 125.60, 123.30, 78.61, 31.24, 23.40, 10.86. IR (KBr) ν

(cm^{-1}): 3238.7, 2964.9, 2933.8, 2876.4, 1649.5, 1590.2, 1521.9, 1480.9, 1458.7, 1430.8, 1348.4, 1315.9, 1286.0, 1214.3, 1161.4, 1123.8, 1077.1, 1059.6, 957.9, 909.9, 864.4, 842.8, 768.4, 730.9. HRMS-ESI ($C_{48}H_{42}O_{10}N_2$) *m/z* (% int.) calcd: 829.2732 $[M+Na]^+$, found: 829.2730 $[M+Na]^+$ (73%).

4.3. General procedure for Friedel–Crafts *ipso*-acylation of 8

Calixarene **9** (1 equiv) was dissolved in dry 1,2-dichloroethane (c=6–9 mmol l^{-1}), then $AlCl_3$ (4 equiv) was added and the mixture was vigorously stirred for 5 min. During this time the reaction mixture turned yellow and the corresponding acyl chloride (2 equiv) was quickly added (directly by Hamilton syringe for liquids or as solution in 1,2-dichloroethane for solids). The reaction was monitored by TLC and after completion it was quenched by addition of 1 M HCl (aq). The layers were separated and water layer was extracted with CH_2Cl_2 (3×). The combined organic layers were washed with $NaHCO_3$ (1×), water (2×) and dried over $MgSO_4$. The $MgSO_4$ was filtered off and the solvent was evaporated under reduced pressure. The crude product was purified by precipitation from CH_2Cl_2/MeOH or by preparative TLC.

*4.3.1. Synthesis of 5,17-diacetyl-11,23-di-tert-butyl-25,27-dipropoxycalix[4]arene (**10a**).* The general procedure was applied to compound **9** (200 mg, 0.273 mmol) and acetyl chloride. Pure product was obtained after preparative TLC on silica gel as a white solid (63 mg, 33%), mp: 266–272 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ (ppm): 9.03 (s, 2H, Ar–*OH*), 7.73 (s, 4H, Ar–*H*), 6.95 (s, 4H, Ar–*H*), 4.30 (d, 4H, *J*=13.3 Hz, Ar–*CH*$_2$–Ar), 3.99 (t, 4H, *J*=6.5 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.45 (d, 4H, *J*=12.9 Hz, Ar–*CH*$_2$–Ar), 2.53 (s, 6H, ArCO–*CH*$_3$), 2.06 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.29 (t, 6H, *J*=7.4 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$), 1.06 (s, 18H, Ar–C–(*CH*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ (ppm): 196.86, 158.19, 149.73, 147.78, 132.07, 129.35, 128.80, 128.22, 125.85, 78.34, 34.11, 31.58, 31.13, 26.23, 23.38, 10.81. IR (KBr) ν (cm^{-1}): 3255.0, 2962.3, 2934.9, 2874.7, 1670.7, 1593.9, 1481.0, 1481.0, 1428.8, 1387.0, 1357.6, 1313.5, 1296.8, 1283.1, 1190.2, 1109.0, 1089.5, 1061.0, 997.2, 962.7, 942.1, 910.9, 942.1, 910.9, 876.2, 732.6. HRMS-ESI ($C_{46}H_{56}O_6$) *m/z* (% int.) calcd: 727.3969 $[M+Na]^+$, found: 727.3977 $[M+Na]^+$ (100%).

*4.3.2. Synthesis of 5,17-dibenzoyl-11,23-di-tert-butyl-25,27-dipropoxycalix[4]arene (**10b**).* The general procedure was applied to compound **9** (200 mg, 0.273 mmol) and benzoyl chloride. Pure product was obtained by precipitation as a white solid (206 mg, 91%), mp: 273–275 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ (ppm): 9.29 (s, 2H, Ar–*OH*), 7.74 (d, 4H, *J*=7.4 Hz, Ar–*H*), 7.65 (s, 4H, Ar–*H*), 7.57 (t, 2H, *J*=7.4 Hz, Ar–*H*), 7.46 (t, 4H, *J*=7.8 Hz, Ar–*H*), 7.02 (s, 4H, Ar–*H*), 4.32 (d, 4H, *J*=12.9 Hz, Ar–*CH*$_2$–Ar), 4.00 (t, 4H, *J*=6.3 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.45 (d, 4H, *J*=12.9 Hz, Ar–*CH*$_2$–Ar), 2.10 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.32 (t, 6H, *J*=7.2 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$), 1.16 (s, 18H, Ar–C–(*CH*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ (ppm): 195.77, 158.28, 149.88, 147.84, 138.88, 132.35, 131.61, 129.75, 128.52, 128.03, 126.01, 78.50, 34.27, 31.78, 31.28, 23.45, 10.93. IR (KBr) ν (cm^{-1}): 3281.7, 3060.4, 2957.9, 2932.4, 2876.0, 2360.5, 2339.5, 1958.3, 1725.7, 1649.1, 1598.4, 1480.9, 1446.8, 1429.0, 1389.0, 1362.3, 1322.0, 1216.4, 1175.0, 1126.5, 1101.8, 1061.4, 1007.9, 962.1, 942.1, 906.1, 877.9, 717.9, 693.3, 632.5, 585.3, 564.7. HRMS-ESI ($C_{56}H_{60}O_6$) *m/z* (% int.) calcd: 851.4282 $[M+Na]^+$, found: 851.4287 $[M+Na]^+$ (100%).

*4.3.3. Synthesis of 5,17-diacryloyl-11,23-di-tert-butyl-25,27-dipropoxycalix[4]arene (**10c**).* The general procedure was applied to compound **9** (200 mg, 0.273 mmol) and acroyl chloride. Pure product was obtained by preparative TLC on silica gel as a white solid (52 mg, 26%), mp: 235–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ (ppm): 9.07 (s, 2H, Ar–*OH*), 7.76 (s, 4H, Ar–*H*), 7.14 (dd, 2H, *J*=16.8, 10.6 Hz, CO–*CH*–CH$_2$), 6.94 (s, 4H, Ar–*H*), 6.35 (dd, 2H, *J*=17.2, 2.0 Hz, CO–CH–*CH*$_2$), 5.84 (dd, 2H, *J*=10.6, 2.0 Hz, CO–CH–*CH*$_2$), 4.30 (d, 4H, *J*=13.3 Hz, Ar–*CH*$_2$–Ar), 3.99 (t, 4H, *J*=6.5 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.45 (d, 4H, *J*=13.3 Hz, Ar–*CH*$_2$–Ar), 2.07 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.29 (t, 6H, *J*=7.4 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$), 1.04 (s, 18H, Ar–C–(*CH*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ (ppm): 189.62, 158.46, 149.77, 147.89, 132.60, 132.06, 129.95, 128.67, 128.56, 128.41, 125.93, 77.20, 34.17, 31.69, 31.18, 23.43, 10.86. IR (KBr) ν (cm^{-1}): 3251.3, 3048.2, 2962.0, 2874.9, 2355.8, 1732.7, 1662.9, 1589.8, 1480.8, 1428.6, 1399.9, 1362.8, 1316.6, 1293.6, 1272.6, 1197.2, 1172.3, 1105.2, 1060.2, 962.8, 942.1, 909.8, 878.5, 792.1, 733.1, 698.8, 635.0, 586.5. HRMS-ESI ($C_{48}H_{56}O_6$) *m/z* (% int.) calcd: 751.3969 $[M+Na]^+$, found: 751.3978 $[M+Na]^+$ (100%).

4.4. General procedure for O-acylation of 9

Calixarene **9** (1 equiv) was dissolved in dry DMF (c=25–27 mmol l^{-1}) and the mixture was cooled down to −5 °C in an ice/salt bath. Then, NaH (2.1 equiv) was added and the mixture was stirred for 30 min. Upon reaction completion (as determined by cessation of H_2 release), the corresponding acyl chloride (4 equiv) was added slowly with a syringe. The reaction was monitored with TLC and after completion (~2 d) it was quenched by addition of 1 M HCl (aq), and diluted with CH_2Cl_2. The layers were separated and water layer was extracted with CH_2Cl_2 (3×). Organic layers were collected and washed with $NaHCO_3$ (1×), water (2×) and dried over $MgSO_4$. The $MgSO_4$ was filtered off and the solvent was evaporated under reduced pressure. The crude product was purified by precipitation from CH_2Cl_2/MeOH or by crystallization from acetone/MeOH.

*4.4.1. Synthesis of 5,11,17,23-tetra-tert-butyl-26,28-diacetyloxy-25,27-dipropoxycalix[4]arene (**11a**).* The general procedure was applied to compound **9** (200 mg, 0.273 mmol) and acetyl chloride. Pure product was obtained after crystallization in the form of white crystals (172 mg, 77%), mp: 211–215 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ (ppm): 7.18 (s, 4H, Ar–*H*), 6.71 (s, 4H, Ar–*H*), 4.11 (d, 4H, *J*=12.9 Hz, Ar–*CH*$_2$–Ar), 3.69 (t, 4H, *J*=7.4 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.26 (d, 4H, *J*=12.9 Hz, Ar–*CH*$_2$–Ar), 2.68 (s, 6H, ArCO–*CH*$_3$), 1.91 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.32 (s, 18H, Ar–C-(*CH*$_3$)$_3$), 1.02 (t, 6H, *J*=7.4 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$), 0.91 (s, 18H, Ar–C–(*CH*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ (ppm): 171.29, 151.46, 147.57, 144.80, 144.20, 134.44, 132.11, 125.25, 125.04, 77.98, 34.19, 33.68, 31.56, 31.06, 30.99, 30.42, 23.50, 22.72, 10.42. IR (KBr) ν (cm^{-1}): 2961.6, 2872.7, 2253.0, 1752.8, 1597.8, 1479.5, 1415.0, 1388.8, 1364.9, 1299.1, 1277.0, 1237.5, 1222.6, 1181.8, 1121.8, 1065.1, 1042.6, 1007.1, 964.9, 911.7, 871.0, 821.3, 799.5, 733.2, 648.3, 635.8, 572.8, 551.1. HRMS-ESI ($C_{54}H_{72}O_6$) *m/z* (% int.) calcd: 839.5221 $[M+Na]^+$, found: 839.5228 $[M+Na]^+$ (100%).

*4.4.2. Synthesis of 5,11,17,23-tetra-tert-butyl-26,28-dibenzoyloxy-25,27-dipropoxycalix[4]arene (**11b**).* The general procedure was applied to compound **9** (200 mg, 0.273 mmol) and acetyl chloride. Pure product was obtained after precipitation in the form of white crystals (215 mg, 84%), mp: 332–335 °C. ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ (ppm): 8.61 (d, 4H, *J*=7.4 Hz, Ar–*H*), 7.75 (t, 2H, *J*=7.4 Hz, Ar–*H*), 7.64 (t, 4H, *J*=7.0 Hz, Ar–*H*), 7.16 (s, 4H, Ar–*H*), 6.64 (s, 4H, Ar–*H*), 4.19 (d, 4H, *J*=12.9 Hz, Ar–*CH*$_2$–Ar), 4.12 (t, 4H, *J*=8.2 Hz, ArO–*CH*$_2$–CH$_2$–CH$_3$), 3.24 (d, 4H, *J*=13.3 Hz, Ar–*CH*$_2$–Ar), 1.62 (m, 4H, ArO–CH$_2$–*CH*$_2$–CH$_3$), 1.36 (s, 18H, Ar–C–(*CH*$_3$)$_3$), 0.91 (s, 18H, Ar–C–(*CH*$_3$)$_3$), 0.53 (t, 6H, *J*=7.2 Hz, ArO–CH$_2$–CH$_2$–*CH*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ (ppm): 166.20, 152.97, 146.54, 145.36, 142.74, 135.29, 133.39, 131.51, 130.46, 130.28, 128.17, 125.76, 124.78, 76.18, 34.07, 33.78, 31.70, 31.61, 31.07, 22.11, 9.20. IR (KBr) ν (cm^{-1}): 2960.6, 2872.4, 1958.4, 1730.8, 1600.8, 1479.7, 1385.3, 1361.9, 1302.5,

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1266.3, 1198.4, 1171.3, 1121.5, 1062.4, 1025.8, 1002.9, 947.1, 909.1, 873.1, 709.2. HRMS-ESI ($C_{64}H_{76}O_6$) *m*/*z* (% int.) calcd: 963.5534 $[M+Na]^+$, found: 963.5542 $[M+Na]^+$ (100%).

*4.4.3. Synthesis of 5,11,17,23-tetra-tert-butyl-26,28-diacryloyloxy-25,27-dipropoxycalix[4]arene (**11c**).* The general procedure was applied to compound **9** (200 mg, 0.273 mmol) and acetyl chloride. Pure product was obtained after crystallization 204 mg (89%) of white crystals (mp: 280–285 °C). ^{1}H NMR (400 MHz, $CDCl_3$, 293 K) δ (ppm): 7.22 (s, 4H, Ar–*H*), 7.22 (dd, 2H, *J*=17.2 Hz, 10.6, CO–*CH*–CH_2), 6.71 (s, 4H, Ar–*H*), 6.70 (dd, 2H, *J*=17.6, 1.4 Hz, CO–CH–*CH*$_2$), 6.00 (dd, 2H, *J*=10.4 Hz, *J*=1.4 Hz, CO–CH–*CH*$_2$), 4.14 (d, 4H, *J*=12.9 Hz, Ar–*CH*$_2$–Ar), 3.62 (t, 4H, *J*=7.2 Hz, ArO–*CH*$_2$–CH_2–CH_3), 3.27 (d, 4H, *J*=12.9 Hz, Ar–*CH*$_2$–Ar), 1.78 (m, 4H, ArO–CH_2–*CH*$_2$–CH_3), 1.35 (s, 18H, Ar–C–(*CH*$_3$)$_3$), 0.96 (t, 6H, *J*=7.4 Hz, ArO–CH_2–CH_2–*CH*$_3$), 0.91 (s, 18H, Ar–C–(*CH*$_3$)$_3$). ^{13}C NMR (100 MHz, $CDCl_3$, 293 K) δ (ppm): 166.38, 151.40, 147.74, 144.71, 144.17, 134.68, 132.10, 130.94, 130.35, 125.20, 124.99, 77.98, 34.20, 33.65, 31.55, 31.03, 30.58, 23.16, 10.55. IR (KBr) ν (cm^{-1}): 3044.7, 2961.5, 2873.1, 2254.0, 1735.3, 1635.8, 1597.7, 1479.5, 1404.6, 1362.3, 1296.4, 1237.8, 1196.8, 1160.2, 1121.8, 1066.8, 1041.9, 1005.5, 964.7, 910.7, 871.2, 822.4, 805.5, 733.4, 677.8, 647.6, 635.8, 555.5. HRMS-ESI ($C_{52}H_{72}O_6$) *m*/*z* (% int.) calcd: 863.5221 $[M+Na]^+$, found: 863.5226 $[M+Na]^+$ (100%).

4.5. Crystallographic measurements

*4.5.1. Crystallographic data for $C_{38}H_{40}O_6\cdot C_3H_6O$ (**3a**).* M=650.80 g mol^{-1}, monoclinic system, space group $P2_1/n$, a=14.8747(6) Å, b=15.8030(5) Å, c=15.0103(5) Å, β=99.086 (3)°, Z=4, V=3484.1(2) Å^3, Dc=1.240 g cm^{-3}, μ(Cu Kα)=0.67 mm^{-1}, crystal dimensions of 0.42×0.25×0.16 mm. Data were collected at 120(2) K on a Gemini AtlasCCD diffractometer with mirror collimated Cu Kα radiation. The structure was solved by charge flipping methods[13] using the Jana2006 suite of programs[14,15] and anisotropically refined by full matrix least squares on F squared value to final R=0.039 and R_w=0.093 using 6093 independent reflections (Θ_{max}=67.1°), 446 parameters, and 2 restrains. The positions of disordered solvent were found from the electron density maps and then placed in appropriate positions. The solvent molecule was refined using rigid body refinement, fixing the same geometry for both solvent positions. Site occupancies were refined resulting in full occupation. The hydrogen atoms on carbon atoms were placed in calculated positions. The hydrogen atoms on oxygen were found from electron density maps and refined with restrained bond lengths regularizing their geometry. The structure was deposited into Cambridge Structural Database under number CCDC 1033086.

*4.5.2. Crystallographic data for $C_{48}H_{44}O_6\cdot C_3H_6O$ (**3b**).* M=775.00 g mol^{-1}, tetragonal system, space group $P4_12_12$, a=14.1117(3) Å, c=20.4494(6) Å, Z=4, V=4072.30(17) Å^3, Dc=1.264 g cm^{-3}, μ(Mo Kα)=0.08 mm^{-1}, crystal dimensions of 0.73×0.46×0.35 mm. Data were collected at 120(2) K on a Gemini AtlasCCD diffractometer with graphite monochromated Mo Kα radiation. The structure was solved by charge flipping methods[13] using the Jana2006 suite of programs[14,15] and anisotropically refined by full matrix least squares on F squared value to final R=0.062 and R_w=0.154 using 4991 independent reflections (Θ_{max}=29.3°), 278 parameters, and 2 restrains. The twofold axis lies in vicinity of disordered solvent molecule. Therefore the site occupancies were set to 0.5, resulting in full occupancy of solvent. The proximity of twofold axis to atom C3s (0.364(7) Å) denied us the possibility of harmonic refinement of atom C3s, therefore the atom is refined isotropically. The hydrogen atoms on carbon atoms were placed in calculated positions. The hydrogen atoms on oxygen were found from electron density maps and refined freely. The structure was deposited into Cambridge Structural Database under number CCDC 1033087.

*4.5.3. Crystallographic data for $C_{40}H_{40}O_6\cdot C_3H_6O$ (**3c**).* M=674.80 g mol^{-1}, monoclinic system, space group $P2_1/n$, a=15.3027(7) Å, b=15.6429(8) Å, c=15.3772(7) Å, β=100.394(4)°, Z=4, V=3620.2(3) Å^3, Dc=1.238 g cm^{-3}, μ(Cu Kα)=0.67 mm^{-1}, crystal dimensions of 0.57×0.40×0.25 mm. Data were collected at 180(2) K on an Xcalibur OnyxCCD diffractometer with graphite monochromated Cu Kα radiation. The structure was solved by charge flipping methods[13] using the Jana2006 suite of programs[14,15] and anisotropically refined by full matrix least squares on F squared value to final R=0.052 and R_w=0.141 using 7542 independent reflections (Θ_{max}=77.6°), 464 parameters, and 2 restrains. The positions of disordered solvent were found from the electron density maps and then placed in appropriate positions. The solvent molecule was refined using rigid body refinement, fixing the same geometry for both solvent positions. Site occupancies were refined resulting in full occupation. The hydrogen atoms on carbon atoms were placed in calculated positions. The hydrogen atoms on oxygen were found from electron density maps and refined with restrained bond lengths regularizing their geometry. The structure was deposited into Cambridge Structural Database under number CCDC 1033089.

*4.5.4. Crystallographic data for $C_{48}H_{41}N_2O_{10}\cdot C_3H_6O$ (**3d**).* M=863.90 g mol^{-1}, triclinic system, space group P-1, a=10.1410(2) Å, b=11.3052(2) Å, c=19.1512(3) Å, α=88.6617(14)°, β=88.1548(15)°, γ=83.9483(15)°, Z=2, V=7179.5(4) Å^3, Dc=0.647 g cm^{-3}, μ(Cu Kα)=1.71 mm^{-1}, crystal dimensions of 0.44×0.27×0.18 mm. Data were collected at 180(2) K on an Xcalbur OnyxCCD diffractometer with graphite monochromated Cu Kα radiation. The structure was solved by charge flipping methods[13] using the Jana2006 suite of programs[14,15] and anisotropically refined by full matrix least squares on F squared value to final R=0.052 and R_w=0.143 using 9009 independent reflections (Θ_{max}=77.2°), 590 parameters, and 2 restrains. The positions of disordered solvent were found from the electron density maps and then placed in appropriate positions. The solvent molecule was refined using rigid body refinement, fixing the same geometry for both solvent positions. Site occupancies were refined resulting in full occupation. The hydrogen atoms on carbon atoms were placed in calculated positions. The hydrogen atoms on oxygen were found from electron density maps and refined with restrained bond lengths regularizing their geometry. The structure was deposited into Cambridge Structural Database under number CCDC 1033088.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.02.021.

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