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An Approach to Optically Pure Bridging Chiral *p-tert*-Butylcalix[4]arenes through a Homologous Anionic Ortho-Fries Rearrangement

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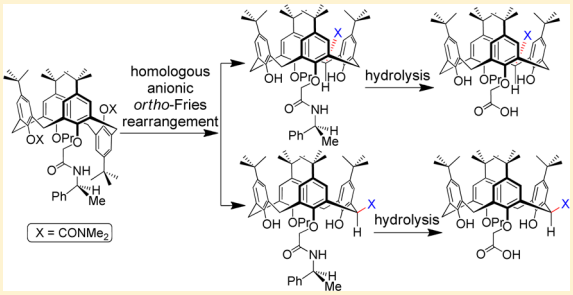
Supporting Information

ABSTRACT: A novel efficient approach to optically pure bridging chiral calix[4]arenes through a homologous anionic ortho-Fries rearrangement of inherently chiral calix[4]arenes was presented for the first time. As a result, two pairs of *N,N′*-dimethylformamidyl-substituted bridging chiral *p-tert*-butylcalix[4]arene enantiomers were facilely obtained. Their absolute configurations were determined through ROESY analysis, ECD comparison, and X-ray crystallographic analysis.

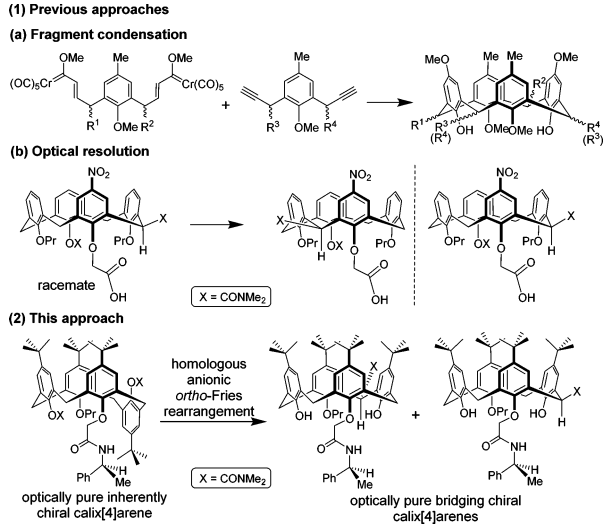


INTRODUCTION

Inherently chiral calixarenes have been diversely prepared and widely applied in chiral recognition and asymmetric catalysis in the past decades. However, their chiral recognition capability and asymmetric catalysis efficiency were generally shown to be unsatisfactory.[1] It is well-known that inherently chiral calixarenes originated from asymmetric substitutions on phenyl rings and (or) oxygen atoms. When calixarene skeletons are asymmetrically substituted on not only phenyl rings and (or) oxygen atoms but also bridging methylenes, a novel type of intrinsically chiral calixarene can be constructed, whose representative characteristic is that point chirality exists on the substituted bridging methylene. The exclusive bridging-point chirality will theoretically provide a platform to construct specific chiral hosts and catalysts. In order to draw high attention to the novel chiral macrocyclic molecules, they were endowed with an exclusive descriptor, "bridging chiral" calixarenes, in our recent pioneering work.[2]

Until now, there have been only two approaches to optically pure bridging chiral calix[4]arenes: fragment condensation from Wulff's work and optical resolution from our recent work (Scheme 1).[2,3] To lay a substantial foundation for their applications in chiral recognition and asymmetric catalysis, more novel approaches to their enantiomers are considerably necessary. A homologous anionic ortho-Fries rearrangement with lithium diisopropylamide (LDA) in THF has been successfully used to construct bridging chiral calix[4]arene racemates from dipropoxycalix[4]arene dimethyl *O*-carbamate in a partial cone conformation in high yields by Reinhoudt.[4] It was envisioned that a novel efficient approach to optically pure bridging chiral calix[4]arenes may be obtained when the homologous anionic ortho-Fries rearrangement can be perfectly combined with the optical isomer preparation of inherently chiral calix[4]arenes (Scheme 1).

Scheme 1. Synthesis Approaches of Optically Pure Bridging Chiral Calix[4]arenes



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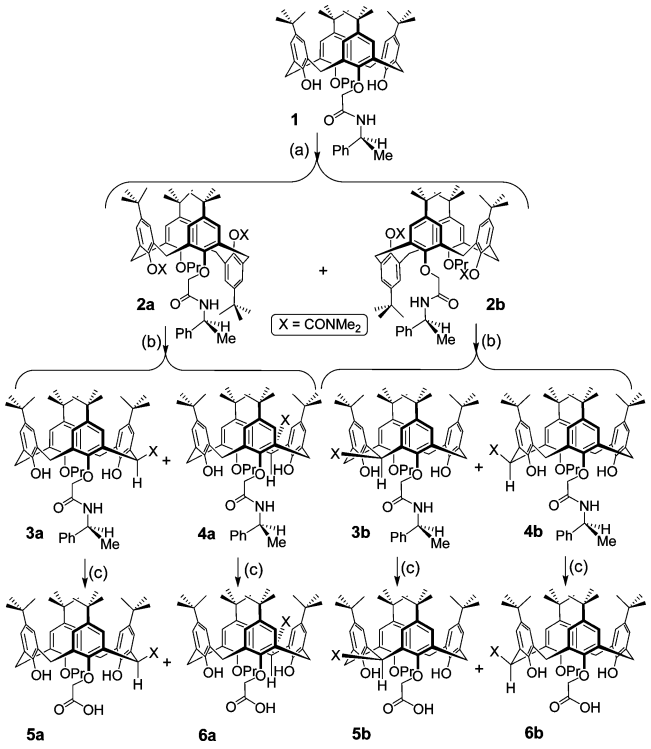
RESULTS AND DISCUSSION

(*S*)-*N*-(α-Phenylethyl)bromoacetamide as a chiral auxiliary has been frequently used to optically resolve inherently chiral calix[4]arene substituted on the lower rim.[1] Therefore, (*S*)-*N*-(α-phenylethyl)carbamoylmethylene was designed to replace one propyl arm in dipropoxycalix[4]arene dimethyl *O*-carbamate. Moreover, *p*-*tert*-butylcalix[4]arene as a more available starting material was designed to replace its macrocyclic skeleton (Scheme 1). As depicted in Scheme 2, **1** can be prepared through distal etherification of mono-*O*-propylated *p*-*tert*-butylcalix[4]arene with (*S*)-*N*-(α-phenylethyl)-bromoacetamide in the presence of K_2CO_3 in CH_3CN.[5] Subsequently, carbamoylation of **1** with dimethylcarbamoyl chloride in the presence of KO-*t*-Bu in 1,4-dioxane at 100 °C can afford the pair of inherently chiral calix[4]arene bis-*O*-carbamate diastereoisomers **2a**,**b** in a partial cone conformation. Fortunately, the diastereomeric mixture can be successfully resolved by column chromatography on silica gel (petroleum ether/ethyl acetate 3/1 v/v) in 90% total isolated yield (**2a**, 48%; **2b**, 42%).

Scheme 2. Synthesis of Bridging Chiral Calix[4]arenes[a]



[a]Conditions: (a) (i) $ClCONMe_2$, KO-*t*-Bu, dioxane, reflux; (ii) separation by silica gel column chromatography; (b) LDA, THF, 0 °C to room temperature, 4 h; (c) $Ba(OH)_2$, DMSO/*n*-butanol, 130 °C.

Then, the ortho-Fries rearrangement of inherently chiral calix[4]arene bis-*O*-carbamate diastereoisomers was carried out under the reaction conditions reported in Reinhoudt's work.[4] Expectedly, two rearrangement products from **2a** in 68% total isolated yield (**3a**, 33%; **4a**, 35%), and another two from **2b** in 66% total isolated yield (**3b**, 34%; **4b**, 32%) can be produced under the optimal reaction conditions (a large excess of LDA in THF at 0 °C, subsequently room temperature for 4 h). Finally, removal of chiral auxiliaries in the separated rearrangement products resulted in two pairs of bridging chiral calix[4]arene carboxylic acid enantiomers **5a** ($[\alpha]_D^{25}$ = −81.0) and **5b** ($[\alpha]_D^{25}$ = +81.4), and **6a** ($[\alpha]_D^{25}$ = −61.3) and **6b** ($[\alpha]_D^{25}$ = +62.5), respectively.

In the ^{1}H NMR spectrum of **2a**, three *N*-CH_3 groups of *O*-carbamate groups characteristically resonate at 2.58, 2.48, and 2.32 ppm, respectively, and another group is seriously shielded by the calix[4]arene cavity and moves upfield to 0.15 ppm. A similar case occurs for **2b**, and its four methyl *O*-carbamate groups resonate at 2.98, 2.57, 2.43, and 0.13 ppm, respectively. They are confirmed to adopt a partial cone conformation, since the signals of their bridging methylenes (36.8 and 36.7 ppm for **2a**, 37.2 and 36.8 ppm for **2b**) appear at about 37 ppm in their ^{13}C NMR spectra.[6] It has been concluded by Reinhoudt that, in the ^{1}H NMR spectra of the rearrangement compounds, the axially and equatorially *N*,*N*′-dimethylformamidyl-substituted bridging methines resonate at 4.71−4.99 and 5.75−6.23 ppm, respectively.[4] Therefore, the bridging methine signals of four rearrangement products (5.82 ppm for **3a**, 6.11 ppm for **4a**, 5.89 ppm for **3b**, and 6.09 ppm for **4b**) confirm they are all equatorially *N*,*N*′-dimethylformamidyl substituted on their bridging methines. From their heteronuclear multiple-bond correlation (HMBC) and heteronuclear single quantum coherence (HSQC) spectra, the signals of their hydroxylic phenolic protons can be easily assigned (6.38 and 7.03 ppm for **3a**, 6.92 and 7.22 ppm for **4a**, 6.51 and 7.22 ppm for **3b**, and 6.76 and 7.14 ppm for **4b**, respectively) (see Figure S21 and S22, S29 and S30, S25 and S26, and S33 and S34 in the Supporting Information). No bridging methylene signal at about 37 ppm in their ^{13}C NMR spectra shows that the calix[4]arene skeleton conformation has been inverted from a partial cone to a cone in the rearrangement process. In the ^{1}H NMR spectra of four bridging chiral calix[4]arene carboxylic acids, the downfield signals (13.09 ppm for **5a**,**b**, 13.13 ppm for **6a**,**b**) prove that the carboxyl groups indeed exist. Their experimental electronic circular dichroism (ECD) spectra show two pairs of excellent mirror images (Figure 1), which proves they are two pairs of enantiomers.

The absolute configurations of bridging chiral calix[4]arenes were determined through rotating frame Overhauser effect spectroscopy (ROESY) analysis, ECD comparison, and X-ray crystallographic analysis. The ^{1}H NMR signals of methine, carbamoylmethylene, and propyl groups in **3a**,**b** and **4a**,**b** can be undoubtedly assigned by their HMBC and HSQC spectra (see Figures S21 and S22, S27 and S28, S24 and S25, and S30 and S31 in the Supporting Information, respectively). The significant ROESY correlations of bridging methine (5.82 ppm)/carbamoylmethylene (4.29 and 4.27 ppm) in **3a** and bridging methine (5.89 ppm)/carbamoylmethylene (4.41 and 4.36 ppm) in **3b** were observed (Figure 2) (see Figures S23 and S24 and S31 and S32 in the Supporting Information), which indicate bridging methine and carbamoylmethylene are all spatially proximal in **3a**,**b**. The significant ROESY correlations of bridging methine (6.11 ppm)/propyl (3.79, 3.67, 1.64, and 0.87 ppm) in **4a** and bridging methine (6.09 ppm)/carbamoylmethylene (3.93, 3.72, 1.86, and 1.13 ppm) in **4b** were observed (Figure 2) (see Figures S27 and S28 and S35 and S36 in the Supporting Information), which indicate that bridging methine and propyl are all spatially proximal in **4a**,**b**. Therefore, it can clearly be deduced that bridging methine and carboxylmethylene are spatially proximal in **5a**,**b** and bridging methine and propyl are spatially proximal in **6a**,**b** on the basis of the above ROESY analysis.

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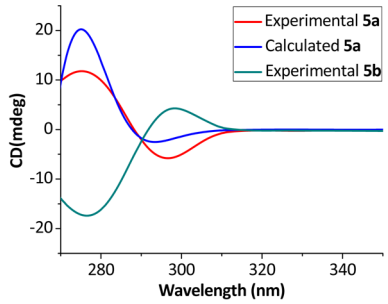
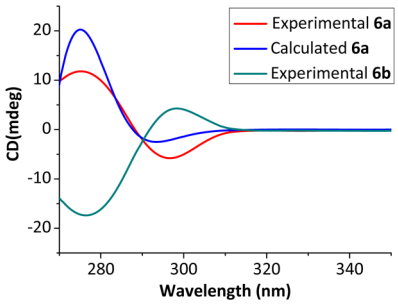


(a)



(b)

Figure 1. Experimental ECD spectra of **5a,b** (a) and **6a,b** (b) in methanol and ECD spectra of **5a** (a) and **6a** (b) calculated at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level.

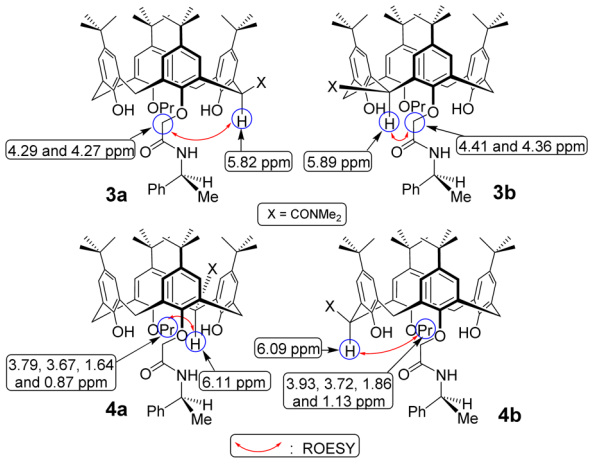


Figure 2. Key ROESY correlations in **3a,b** and **4a,b**.

On the basis of the relative spatial relation between bridging methine and carboxylmethylene and propyl in **5a** and **6a**, their theoretical ECD spectra can be calculated using quantum chemical methods and compared to those measured in methanol. As illustrated in Figure 1, their calculated ECD spectra at the TD-B3LYP/6-31G(d)//B3LYP/6-31G(d) level show an acceptable fit with their experimental spectra in terms of form and sign of the bands with respect to wavelength. From an ECD comparison in Figure 1, the absolute configurations of bridging methines in **5a** and **6a** can be assigned as *R* and *S*, respectively. Therefore, the absolute configurations of bridging methines in **5b** and **6b** can be deduced as *S* and *R*, respectively. Moreover, the absolute configurations of bridging methines in **3a,b** and **4a,b** can be deduced as *R*, *S*, *S*, and *R* on the basis of these analysis results of **5a,b** and **6a,b**, respectively. It is very fortunate that **3a** could be crystallized from dichloromethane, and its X-ray crystal structure was determined (see Figure S39 in the Supporting Information). On the basis of an X-ray crystallographic analysis, the absolute configuration of bridging methine in **3a** can be assigned as *R*. Therefore, the absolute configurations of bridging methines in **3b** and **5a,b** can be deductively assigned as *S*, *R*, and *S*, respectively, which are consistent with those from an ECD comparison.

CONCLUSIONS

In conclusion, for the first time, a novel approach to optically pure bridging chiral calix[4]arenes was obtained through the combination of a homologous anionic ortho-Fries rearrangement and the optical isomer preparation of inherently chiral calix[4]arenes. Moreover, two pairs of optically pure *N,N′*-dimethylformamidyl-substituted bridging chiral *p-tert*-butylcalix[4]arenes were facilely prepared from a homologous anionic ortho-Fries rearrangement of one pair of optically pure inherently chiral *p-tert*-butylcalix[4]arene bis-*O*-carbamate diastereoisomers and subsequent removal of chiral auxiliaries. The absolute configurations of bridging chiral calix[4]arenes were determined through ROESY analysis, ECD comparison, and X-ray crystallographic analysis. The synthesis approach can be treated as a common strategy to prepare optically pure bridging chiral calix[4]arenes.

EXPERIMENTAL SECTION

General Information. All reactions were conducted under atmosphere. All chemicals were purchased from commercial sources and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz (^{1}H) and at 75.5 MHz (^{13}C). $CDCl_3$ (δ 7.26 ppm), d_6-DMSO (δ 2.50 and 3.33 ppm), and TMS (δ 0.00 ppm) were used as internal standards for ^{1}H NMR spectra; $CDCl_3$ (δ 77.00 ppm), d_6-DMSO (δ 39.58 ppm), and TMS (δ 0.00 ppm) were used as internal standards for ^{13}C NMR spectra. The following abbreviations are used to indicate the multiplicity in NMR spectra: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. *J* indicates the NMR coupling constant measured in hertz. The courses of the reactions were monitored by TLC using TLC aluminum sheets with silica gel 60 GF254. Column chromatography was performed using silica gel 60. Optical rotations were measured using a polarimeter with a 1 dm path length. Experimental circular dichroism (CD) spectra were recorded in a quartz cuvette of 1 mm optical path length. High-resolution mass spectra (HRMS) were measured on a mass spectrometer equipped with a TOF system and an electrospray ionization (ESI) ion source. X-ray data for the crystals were collected on a charge-coupled device diffractometer using graphite-monochromated Cu Kα (λ = 1.54178 Å) radiation.

Compounds 2a,b. A suspension of calix[4]arene **1** (2 g, 2.34 mmol) and KO-*t*-Bu (2.63 g, 23.4 mmol) in dioxane (30 mL) was stirred for 30 min at room temperature, whereupon dimethylcarbamoyl chloride (2.52 g, 23.4 mmol) was added and the reaction mixture was heated under reflux for 20 h. The reaction mixture was evaporated to dryness and redissolved in 10% HCl (30 mL) and CH_2Cl_2 (30 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic layers were washed with brine, dried with Na_2SO_4, and evaporated to dryness. The diastereomeric mixture was further purified by silica gel column chromatography (eluent petroleum ether/ethyl acetate, 3/1 v/v) to produce **2a** (1.12 g, 48%) and **2b** (0.98 g, 42%). **2a**: mp 173.8−175.3 °C; $[\alpha]_D^{25}$= 20.7 (*c* = 1.16, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.25 (m, 5H, CH_3(*Ph*)CHNH), 7.21−7.14 (m, 4H, Ar-*H*), 7.13 (d, *J* = 2.3 Hz, 1H, Ar-*H*), 7.11 (d, *J* = 2.3 Hz, 1H, Ar-*H*), 6.82 (d, *J* = 2.2 Hz, 1H, Ar-*H*), 6.76 (d, *J* = 2.2 Hz, 1H, Ar-*H*), 6.62 (d, *J* = 8.2 Hz, 1H, CH_3(Ph)CHN*H*), 5.20 (m, 1H, CH_3 (Ph) C*H*NH), 4.62 (d, *J* = 15.2 Hz, 1H, NHC(O)CH_2), 4.21 (d, *J* = 15.2 Hz, 1H, NHC(O)CH_2), 4.15 (d, *J* = 12.4 Hz, 1H, Ar-CH_2-Ar), 4.01 (d, *J* = 12.4 Hz, 1H, Ar-CH_2-Ar), 3.93 (d, *J* = 12.0 Hz, 1H, Ar-CH_2-Ar), 3.89 (d, *J* = 12.0 Hz, 1H, Ar-CH_2-Ar), 3.48−3.81 (m, 4H,

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Ar-CH_2-Ar, O-CH_2-CH_2-CH_3), 3.35 (d, J = 12.4 Hz, 1H, Ar-CH_2-Ar), 3.27 (d, J = 12.4 Hz, 1H, Ar-CH_2-Ar), 2.58 (s, 3H, N-CH_3), 2.48 (s, 3H, N-CH_3), 2.32 (s, 3H, N-CH_3), 1.57 (m, 2H, O-CH_2-CH_2CH$_3$), 1.49 (d, J = 6.9 Hz, 3H, CH_3(Ph)CHNH), 1.37 (s, 9H, *t-Bu*), 1.27 (s, 9H, *t-Bu*), 1.19 (s, 9H, *t-Bu*), 1.17 (s, 9H, *t-Bu*), 0.84 (t, J = 7.4 Hz, 3H, O−CH_2−CH_2−CH_3), 0.15 (s, 3H, N-CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.9, 155.4, 153.7, 153.6, 152.7, 147.8, 146.9, 146.7, 145.5, 144.9, 144.4, 142.4, 135.6, 134.2, 134.0, 133.0, 132.5, 132.2, 131.5, 131.1, 128.8, 127.5, 126.8, 126.3 (2C), 125.9, 125.8, 125.7, 125.3, 124.8 (2C), 76.2, 73.2, 48.3, 39.2, 39.1, 36.8, 36.7 (2C), 34.2, 34.0, 33.9, 33.8, 31.7, 31.6, 31.5 (2C), 23.2, 21.4, 10.2 ppm; HRMS (ESI) m/z calcd for $C_{63}H_{85}N_3O_7$ [(M + H)$^+$] 995.6388, found 995.6292. **2b**: mp 166.8−170.5 °C; $[\alpha]_D^{25}$ = −20.5 (c = 1.17, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (m, 2H, CH$_3$(*Ph*)CHNH), 7.25−7.16 (m, 6H, CH$_3$(*Ph*)CHNH, Ar-*H*), 7.12 (d, J = 2.4 Hz, 1H, Ar-*H*), 7.10 (d, J = 2.3 Hz, 1H, Ar-*H*), 7.07 (d, J = 2.4 Hz, 1H, Ar-*H*), 6.79 (d, J = 2.3 Hz, 1H, Ar-*H*), 6.77 (d, J = 2.2 Hz, 1H, Ar-*H*), 6.61 (d, J = 7.9 Hz, 1H, CH$_3$(Ph)CHN*H*), 5.12 (m, 1H, CH$_3$ (Ph) C*H*NH), 4.61 (d, J = 15.2 Hz, 1H, NHC(O)CH_2), 4.20 (d, J = 15.2 Hz, 1H, NHC(O)CH_2), 4.06 (d, J = 12.8 Hz, 1H, Ar-CH_2-Ar), 4.03 (d, J = 12.4 Hz, 1H, Ar-CH_2-Ar), 3.57−3.92 (m, 6H, Ar-CH_2-Ar, O-CH_2-CH_2−CH$_3$), 3.29 (d, J = 12.6 Hz, 1H, Ar-CH_2-Ar), 3.13 (d, J = 12.6 Hz, 1H, Ar-CH_2-Ar), 2.98 (s, 3H, N-CH_3), 2.57 (s, 3H, N-CH_3), 2.43 (s, 3H, N-CH_3), 1.69 (m, 2H, O−CH_2−CH_2CH$_3$), 1.52 (d, 3H, J = 7.0 Hz, CH_3(Ph)CHNH), 1.38 (s, 9H, *t-Bu*), 1.26 (s, 9H, *t-Bu*), 1.18 (s, 9H, *t-Bu*), 1.17 (s,9H, *t-Bu*), 0.88 (t, 3H, J = 7.4 Hz, O−CH$_2$−CH$_2$−CH_3), 0.13 (s, 3H, N-CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 155.4, 153.7, 153.4, 152.7, 147.8, 146.9, 146.8, 145.4, 144.9, 144.3, 142.6, 135.6, 134.1, 133.9, 133.1, 132.3, 132.2, 131.3, 130.8, 128.7, 127.5, 126.9, 126.4, 126.3, 126.1, 125.8, 125.7, 125.4, 124.8, 124.7, 76.1, 72.9, 68.9, 66.5, 64.6, 48.9, 39.2, 39.1, 37.2, 36.8, 34.2 (2C), 33.9, 33.8, 31.7, 31.6, 31.5 (2C), 31.4, 23.2, 22.1, 10.2 ppm; HRMS (ESI) m/z calcd for $C_{63}H_{85}N_3O_7$ [(M + H)$^+$] 995.6388, found 995.6292.

Compounds 3a and 4a. A solution of calix[4]arene **2a** (0.996 g, 1.0 mmol) in THF (5 mL) was added via a cannula to a large excess of LDA solution at 0 °C. Subsequently, the reaction mixture was warmed to room temperature over 4 h. The reaction mixtures were quenched by the addition of 30 mL of a concentrated NH_4Cl solution in water. Workup refers to the subsequent extracting with CH_2Cl_2 (2 × 30 mL), washing the organic phase with brine (20 mL), drying the organic phase with Na_2SO_4, and evaporating the solvent. The product was further purified by silica gel column chromatography (eluent petroleum ether/ethyl acetate, 3/2, v/v) to produce 0.31 g (31% yield) of **3a** and 0.35 g (35% yield) of **4a** as a white solid. **3a**: mp 127.8−130.2 °C; $[\alpha]_D^{25}$ = +24.7 (c = 1.46, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, J = 8.6 Hz, 1H, CH$_3$(Ph)CHN*H*), 7.54−7.21 (m, 5H, CH$_3$(*Ph*)CHNH), 7.10 (m, 4H, Ar-*H*), 7.03 (s, 1H, O-*H*), 6.90 (d, J = 2.4 Hz, 1H, Ar-*H*), 6.80 (d, J = 2.4 Hz, 1H, Ar-*H*), 6.77 (d, J = 2.3 Hz, 1H, Ar-*H*), 6.62 (d, J = 2.3 Hz, 1H, Ar-*H*), 6.38 (s, 1H, O-*H*), 5.82 (s, 1H, Ar-C*H*-Ar), 5.36 (m, 1H, CH$_3$(Ph)C*H*NH), 4.29 (d, J = 15.0 Hz, 1H, NHC(O)CH_2), 4.27 (d, J = 15.0 Hz, 1H, NHC(O)CH_2), 4.21 (d, J = 7.2 Hz, 1H, Ar-CH_2-Ar), 4.17 (d, J = 7.3 Hz, 1H, Ar-CH_2-Ar), 4.13−3.27 (m, 6H, Ar-CH_2-Ar, O-CH_2-CH_2CH$_3$), 2.94 (s, 3H, N-CH_3), 2.61 (s, 3H, N-CH_3), 1.86 (m, 2H, O-CH$_2$-CH_2CH$_3$), 1.65 (d, J = 7.0 Hz, 3H, CH_3(Ph)CHNH), 1.33 (s, 9H, *t-Bu*), 1.27 (s, 9H, *t-Bu*), 1.04 (t, J = 7.4 Hz, 3H, O-CH$_2$-CH$_2$-CH_3), 0.93 (s, 9H, *t-Bu*), 0.81 (s, 9H, *t-Bu*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 167.6, 149.9, 149.6, 149.3, 148.4, 148.2, 146.5, 144.1, 142.8, 142.5, 132.4, 131.5, 131.0, 129.7, 129.3, 128.4, 127.9, 127.9, 127.7, 126.9, 126.6, 126.1, 125.6, 125.4, 125.1, 125.1, 125.0, 122.1, 78.7, 74.4, 48.8, 41.0, 37.4, 36.0, 34.1, 34.0, 33.9, 33.9, 32.2, 31.8, 31.7, 31.2, 30.9, 30.9, 22.9, 10.6 ppm; HRMS (ESI) m/z calcd for $C_{60}H_{78}N_2O_6$ [(M + H)$^+$] 922.5860, found 922.5889. **4a**: mp 135.5−137.6 °C; $[\alpha]_D^{25}$ = −51.6 (c = 1.24, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 7.9 Hz, 1H, CH$_3$(Ph)CHN*H*), 7.57−7.21 (m, 5H, CH$_3$(*Ph*)CHNH), 7.22 (s, 1H, O-*H*), 7.15 (d, J = 2.3 Hz, 1H, Ar-*H*), 7.12 (d, J = 2.3 Hz, 1H, Ar-*H*), 7.08 (d, J = 2.4 Hz, 1H, Ar-*H*), 7.05 (d, J = 2.3 Hz, 1H, Ar-*H*), 7.01 (d, J = 2.4 Hz, 1H, Ar-*H*), 6.92 (s, 1H, O-*H*), 6.85 (d, J = 2.3 Hz, 1H, Ar-*H*), 6.75 (d, J = 2.3 Hz, 1H, Ar-*H*), 6.67 (d, J = 2.3 Hz, 1H, Ar-*H*), 6.11 (s, 1H, Ar-C*H*-Ar), 5.30 (m, 1H, CH$_3$ (Ph) C*H*NH), 4.75 (d, J = 14.9 Hz, 1H, NHC(O)CH_2), 4.35 (d, J = 14.9 Hz, 1H, NHC(O)CH_2), 4.29 (d, J = 12.8 Hz, 1H, Ar-CH_2-Ar), 4.07 (d, J = 13.8 Hz, 1H, Ar-CH_2-Ar), 4.01 (d, J = 13.8 Hz, 1H, Ar-CH_2-Ar), 3.79 (m, 1H, O-CH_2-CH$_2$-CH$_3$), 3.67 (m, 1H, O-CH_2-CH$_2$-CH$_3$), 3.44 (d, J = 11.9 Hz, 1H, Ar-CH_2-Ar), 3.41 (d, J = 11.9 Hz, 1H, Ar-CH_2-Ar), 3.33 (d, J = 12.8 Hz, 1H, Ar-CH_2-Ar), 3.07 (s, 3H, N-CH_3), 3.01 (s, 3H, N-CH_3), 1.64 (m, 5H, O−CH$_2$−CH_2CH$_3$, CH_3(Ph)CHNH), 1.32 (s, 9H, *t-Bu*), 1.28 (s, 9H, *t-Bu*), 0.94 (s, 9H, *t-Bu*), 0.87 (m, 12H, *t-Bu*, O-CH$_2$-CH$_2$-CH_3) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 168.1, 150.1, 149.3, 148.9, 148.7, 147.9, 146.5, 143.5, 142.8, 142.3, 132.5, 131.3, 130.2, 130.2, 128.9, 128.5, 128.3, 127.7, 127.5, 127.2, 126.9, 126.3, 126.2, 126.0, 125.8, 125.4, 125.3, 124.9, 122.1, 79.2, 73.7, 48.4, 40.9, 37.3, 36.0, 34.0, 33.9, 33.9, 33.9, 31.7, 31.6, 31.4, 31.1, 30.9, 30.9, 23.3, 22.9, 10.8 ppm; HRMS (ESI) m/z calcd for $C_{60}H_{78}N_2O_6$ [(M + H)$^+$] 922.5860, found 922.5889.

Compounds 3b and 4b. The same procedure as described for compounds **3a** and **4a** was used. The products were further purified by silica gel column chromatography (eluent petroleum ether/ethyl acetate, 3/2 v/v) to produce 0.34 g (34% yield) of **3b** and 0.32 g (32% yield) of **4b** as a white solid. **3b**: mp 130.8−133.6 °C; $[\alpha]_D^{25}$ = −43.1 (c = 1.21, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.3 Hz, 1H, CH$_3$(Ph)CHN*H*), 7.45 (d, J = 8.0 Hz, 2H, CH$_3$(*Ph*)CHNH), 7.09−7.32 (m, 7H, CH$_3$(*Ph*)CHNH, Ar-*H*), 7.22 (s, 1H, O-*H*), 6.64−6.96 (m, 4H, Ar-*H*), 6.51 (s, 1H, O-*H*), 5.89 (s, 1H, Ar-C*H*-Ar), 5.33 (m, 1H, CH$_3$ (Ph) C*H*NH), 4.41 (d, J = 15.0 Hz, 1H, NHC(O)CH_2), 4.36 (d, J = 15.0 Hz, 1H, NHC(O)CH_2), 4.23 (d, J = 13.2 Hz, 1H, Ar-CH_2-Ar), 4.12 (d, J = 13.4 Hz, 1H, Ar-CH_2-Ar), 4.07 (d, J = 13.7 Hz, 1H, Ar-CH_2-Ar), 3.99−3.86 (m, 2H, O-CH_2-CH$_2$−CH$_3$), 3.45 (d, J = 13.7 Hz, 1H, Ar-CH_2-Ar), 3.36 (d, J = 13.2 Hz, 1H, Ar-CH_2-Ar), 3.29 (d, J = 13.4 Hz, 1H, Ar-CH_2-Ar), 3.05 (s, 3H, N-CH_3), 2.99 (s, 3H, N-CH_3), 1.79 (m, 2H, O-CH$_2$-CH_2CH$_3$), 1.64 (d, 3H, J = 7.0 Hz, CH_3(Ph)CHNH), 1.33 (s, 9H, *t-Bu*), 1.28 (s, 9H, *t-Bu*), 0.99 (t, 3H, J = 7.4 Hz, O-CH$_2$-CH$_2$-CH_3), 0.93 (s, 9H, *t-Bu*), 0.84 (s, 9H, *t-Bu*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 168.1, 150.2, 149.4, 149.0, 148.8, 147.7, 146.6, 143.6, 142.9, 142.2, 132.6, 131.3, 130.4, 130.1, 128.9, 128.6, 128.2, 127.6, 127.6, 127.0, 126.2, 125.9, 125.9, 125.3, 125.1, 124.9, 122.1, 79.1, 73.8, 48.5, 41.2, 37.6, 36.1, 34.0, 33.9, 33.9, 33.9, 32.0, 31.7, 31.7, 31.6, 31.1, 30.9, 30.9, 23.2, 23.1, 10.7 ppm; HRMS (ESI) m/z calcd for $C_{60}H_{78}N_2O_6$ [(M + H)$^+$] 922.5860, found 922.5889. **4b**: mp 127.9−130.3 °C; $[\alpha]_D^{25}$ = +45.2 (c = 1.35, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (d, 1H, J = 8.1 Hz, CH$_3$(Ph)CHN*H*), 7.42−7.35 (m, 2H, CH$_3$(*Ph*)CHNH), 7.22−7.10 (m, 6H, CH$_3$(*Ph*)CHNH, Ar-*H*),7.14 (s, 1H, O-*H*), 7.06 (d, 1H, J = 2.2 Hz, Ar-*H*), 6.98 (d, 1H, J = 2.3 Hz, Ar-*H*), 6.80 (d, 1H, J = 2.2 Hz, Ar-*H*), 6.76 (s, 1H, O-*H*), 6.74 (d, 1H, J = 2.2 Hz, Ar-*H*), 6.67 (d, 1H, J = 2.3 Hz, Ar-*H*), 6.09 (s, 1H, Ar-C*H*-Ar), 5.29 (m, 1H, CH$_3$ (Ph) C*H*NH), 4.77 (d, 1H, J = 14.9 Hz, NHC(O)CH_2), 4.25 (d, 1H, J = 14.9 Hz, NHC(O)CH_2), 4.17 (d, 1H, J = 12.9 Hz, Ar-CH_2-Ar), 4.09 (d, 1H, J = 13.8 Hz, Ar-CH_2-Ar), 4.02 (d, 1H, J = 13.8 Hz, Ar-CH_2-Ar), 3.93 and 3.72 (m, 2H, O-CH_2-CH$_2$-CH$_3$), 3.46 (d, 1H, J = 9.8 Hz, Ar-CH_2-Ar), 3.42 (d, 1H, J = 9.8 Hz, Ar-CH_2-Ar), 3.19 (d, 1H, J = 12.9 Hz, Ar-CH_2-Ar), 3.06 (s, 3H, N-CH_3), 2.97 (s, 3H, N-CH_3), 1.86 (m, 2H, O-CH$_2$-CH_2CH$_3$), 1.72 (d, 3H, J = 7.0 Hz, CH_3(Ph)CHNH), 1.33 (s, 9H, *t-Bu*), 1.27 (s, 9H, *t-Bu*), 1.13 (t, 3H, J = 7.4 Hz, O-CH$_2$-CH$_2$-CH_3), 0.92 (s, 9H, *t-Bu*), 0.86 (s, 9H, *t-Bu*) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 167.5, 149.8, 149.7, 149.3, 148.5, 148.1, 146.5, 143.5, 142.8, 142.6, 132.4, 131.5, 130.9, 129.8, 129.3, 128.5, 127.9, 127.7, 127.0, 126.6, 126.6, 126.2, 125.6, 125.4, 125.1, 125.0, 124.9, 122.0, 78.7, 74.5, 48.9, 41.1, 37.5, 36.0, 33.9, 32.1, 31.7, 31.7, 31.6, 31.5, 31.4, 31.3, 31.2, 30.9, 30.9, 23.3, 22.5, 11.1 ppm; HRMS (ESI) m/z calcd for $C_{60}H_{78}N_2O_6$ [(M + H)$^+$] 922.5860, found 922.5889.

Compounds 5a and 6a. A mixture of amide **3a** or **4a** (2 g, 2.168 mmol) and Ba(OH)$_2$ (5.57 g, 32.52 mmol) in *n*-butanol (50 mL)/DMSO (2 mL) was stirred at 130 °C for 24 h. The reaction mixture was evaporated to dryness and redissolved in 10% HCl (30 mL) and CH_2Cl_2 (30 mL). The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL), and the combined organic layers were washed with brine, dried with Na_2SO_4, and evaporated to dryness. The product was further purified by silica gel column chromatography (eluent

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petroleum ether/ethyl acetate/formic acid, 1/2/0.005 v/v/v) to produce 1.65 g (93% yield) of **5a** or 1.69 g (95% yield) of **6a** as a white solid. **5a**: mp 142.3−144.5 °C; $[\alpha]_D^{25}$ = +62.5 (*c* = 1.20, CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO) δ13.09 (s, 1H, COO-*H*), 8.31 (s, 1H, O-*H*), 7.59 (s, 1H, O-*H*), 7.33 (d, 1H, *J* = 2.4 Hz, Ar-*H*), 7.16 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.14 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.10 (d, 1H, *J* = 2.0 Hz, Ar-*H*), 7.06 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.03 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.02 (d, 1H, *J* = 2.0 Hz, Ar-*H*), 6.88 (d, 1H, *J* = 2.4 Hz, Ar-*H*), 6.24 (s, 1H, Ar-C*H*-Ar), 4.59 (d, 1H, *J* = 15.6 Hz, O-CH_2-CO_2), 4.39 (d, 1H, *J* = 15.6 Hz, O-CH_2-CO_2), 4.24 (d, 1H, *J* = 12.4 Hz, Ar-CH_2-Ar), 4.16 (d, 1H, *J* = 12.4 Hz, Ar-CH_2-Ar), 4.04−3.95 (m, 2H, O-CH_2-CH_2-CH_3), 3.51 (d, 1H, *J* = 13.5 Hz, Ar-CH_2-Ar), 3.43 (d, 1H, *J* = 13.5 Hz, Ar-CH_2-Ar), 3.35 (m, 2H, Ar-CH_2-Ar), 2.89 (s, 6H, N-CH_3), 1.88 (m, 2H, O-CH_2-C$H_2$$CH_3$), 1.21 (m, 12H, *t-Bu*, O-CH_2-CH_2-CH_3), 1.20 (t, 3H, *J* = 7.6 Hz, O-CH_2-CH_2CH_3), 1.16 (s, 9H, *t-Bu*), 1.07 (s, 9H, *t-Bu*), 0.97 (s, 9H, *t-Bu*) ppm; ^{13}C NMR (101 MHz, DMSO) δ 171.2, 170.1, 150.7, 150.3, 150.1, 149.8, 149.4, 149.3, 146.8, 145.6, 145.4, 141.5, 141.3, 140.9, 133.1, 132.3, 131.5, 130.7, 127.8, 127.4, 127.3, 127.1, 126.9, 125.9, 125.4, 125.2, 125.1, 122.5, 121.4, 78.1, 72.3, 59.7, 36.7, 35.6, 33.8, 33.8, 33.6, 33.5, 31.4, 31.3, 30.8, 30.7, 22.8, 10.6 ppm; HRMS (ESI) *m*/*z* calcd for $C_{52}H_{70}NO_7$ $[(M + H)^+]$ 820.5152, found 820.5150. **6a**: mp 159.8−162.9 °C; $[\alpha]_D^{25}$ = −81.0 (*c* = 1.31, CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO) δ 13.13 (s, 1H, COO-*H*), 8.25 (s, 1H, O-*H*), 8.01 (s, 1H, O-*H*), 7.55 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.18 (d, 1H, *J* = 2.2 Hz, Ar-*H*), 7.13 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.05−7.09 (m, 5H, Ar-*H*), 6.18 (s, 1H, Ar-C*H*-Ar), 4.77 (d, 1H, *J* = 15.6 Hz, O-CH_2-CO_2), 4.49 (d, 1H, *J* = 15.6 Hz, O-CH_2-CO_2), 4.30 (d, 1H, *J* = 11.2 Hz, Ar-CH_2-Ar), 4.27 (d, 1H, *J* = 11.2 Hz, Ar-CH_2-Ar), 4.01−3.85 (m, 2H, O-CH_2-CH_2-CH_3), 3.49 (d, 1H, *J* = 3.4 Hz, Ar-CH_2-Ar), 3.46 (d, 1H, *J* = 3.5 Hz, Ar-CH_2-Ar), 3.34 (m, 2H, Ar-CH_2-Ar), 2.95 (s, 3H, N-CH_3), 2.89 (s, 3H, N-CH_3), 1.86 (m, 2H, O-CH_2-C$H_2$$CH_3$), 1.24 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-CH_3), 1.21 (s, 9H, *t-Bu*), 1.15 (s, 9H, *t-Bu*), 1.06 (s, 9H, *t-Bu*), 1.04 (s, 9H, *t-Bu*) ppm; ^{13}C NMR (101 MHz, DMSO) δ 171.1, 170.1, 150.3, 150.0, 149.9, 149.2, 146.9, 145.6, 141.5, 140.9, 132.7, 132.3, 132.1, 130.8, 127.9, 127.8, 127.4, 126.9, 126.4, 126.2, 125.5, 125.4, 125.1, 124.8, 121.4, 78.0, 72.3, 36.6, 35.5, 33.9, 33.8, 33.6, 33.5, 31.9, 31.7, 31.4, 31.3, 30.8, 30.8, 22.8, 10.8 ppm; HRMS (ESI) *m*/*z* calcd for $C_{52}H_{70}NO_7$ $[(M + H)^+]$ 820.5152, found 820.5150.

Compounds 5b and 6b. The same procedures as described for compounds **5a** and **6a** were used. The products were further purified by silica gel column chromatography (eluent petroleum ether/ethyl acetate/formic acid, 1/2/0.005 v/v/v) to produce 1.62 g (91% yield) of **5b** or 1.63 g (92% yield) of **6b** as a white solid. **5b**: mp 143.7−146.8 °C; $[\alpha]_D^{25}$ = −61.3 (*c* = 1.24, CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO) δ 13.09 (s, 1H, COO-*H*), 8.31 (s, 1H, O-*H*), 7.59 (s, 1H, O-*H*), 7.33 (d, 1H, *J* = 2.4 Hz, Ar-*H*), 7.16 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.14 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.10 (d, 1H, *J* = 2.0 Hz, Ar-*H*), 7.06 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.03 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.02 (d, 1H, *J* = 2.0 Hz, Ar-*H*), 6.88 (d, 1H, *J* = 2.4 Hz, Ar-*H*), 6.24 (s, 1H, Ar-C*H*-Ar), 4.59 (d, 1H, *J* = 15.6 Hz, O-CH_2-CO_2), 4.39 (d, 1H, *J* = 15.6 Hz, O-CH_2-CO_2), 4.24 (d, 1H, *J* = 12.4 Hz, Ar-CH_2-Ar), 4.16 (d, 1H, *J* = 12.4 Hz, Ar-CH_2-Ar), 4.04−3.95 (m, 2H, O-CH_2-CH_2-CH_3), 3.51 (d, 1H, *J* = 13.5 Hz, Ar-CH_2-Ar), 3.43 (d, 1H, *J* = 13.5 Hz, Ar-CH_2-Ar), 3.35 (m, 2H, Ar-CH_2-Ar), 2.89 (s, 6H, N-CH_3), 1.88 (m, 2H, O-CH_2-C$H_2$$CH_3$), 1.21 (m, 12H, *t-Bu*, O-CH_2-CH_2-CH_3), 1.20 (t, 3H, *J* = 7.6 Hz, O-CH_2-CH_2CH_3), 1.16 (s, 9H, *t-Bu*), 1.07 (s, 9H, *t-Bu*), 0.97 (s, 9H, *t-Bu*) ppm; ^{13}C NMR (101 MHz, DMSO) δ 171.2, 170.1, 150.7, 150.3, 150.1, 149.8, 149.4, 149.3, 146.8, 145.6, 145.4, 141.5, 141.3, 140.9, 133.1, 132.3, 131.5, 130.7, 127.8, 127.4, 127.3, 127.1, 126.9, 125.9, 125.4, 125.2, 125.1, 122.5, 121.4, 78.1, 72.3, 59.7, 36.7, 35.6, 33.8, 33.8, 33.6, 33.5, 31.4, 31.3, 30.8, 30.7, 22.8, 10.6 ppm; HRMS (ESI) *m*/*z* calcd for $C_{52}H_{70}NO_7$ $[(M + H)^+]$ 820.5152, found 820.5150. **6b**: mp 159.0−161.7 °C; $[\alpha]_D^{25}$ = +81.4 (*c* = 1.18, CH_2Cl_2); ^{1}H NMR (400 MHz, DMSO) δ 13.13 (s, 1H, COO-*H*), 8.25 (s, 1H, O-*H*), 8.01 (s, 1H, O-*H*), 7.55 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.18 (d, 1H, *J* = 2.2 Hz, Ar-*H*), 7.13 (d, 1H, *J* = 2.3 Hz, Ar-*H*), 7.05−7.09 (m, 5H, Ar-*H*), 6.18 (s, 1H, Ar-C*H*-Ar), 4.77 (d, 1H, *J* = 15.6 Hz, O-CH_2-CO_2), 4.49 (d, 1H, *J* = 15.6 Hz, O-CH_2-CO_2), 4.30 (d, 1H, *J* = 11.2 Hz, Ar-CH_2-Ar), 4.27 (d, 1H, *J* = 11.2 Hz, Ar-CH_2-Ar), 4.01−3.85 (m, 2H, O-CH_2-CH_2-CH_3), 3.49 (d, 1H, *J* = 3.4 Hz, Ar-CH_2-Ar), 3.46 (d, 1H, *J* = 3.5 Hz, Ar-CH_2-Ar), 3.34 (m, 2H, Ar-CH_2-Ar), 2.95 (s, 3H, N-CH_3), 2.89 (s, 3H, N-CH_3), 1.86 (m, 2H, O-CH_2-C$H_2$$CH_3$), 1.24 (t, 3H, *J* = 7.4 Hz, O-CH_2-CH_2-CH_3), 1.21 (s, 9H, *t-Bu*), 1.15 (s, 9H, *t-Bu*), 1.06 (s, 9H, *t-Bu*), 1.04 (s, 9H, *t-Bu*) ppm; ^{13}C NMR (101 MHz, DMSO) δ 171.1, 170.1, 150.3, 150.0, 149.9, 149.2, 146.9, 145.6, 141.5, 140.9, 132.7, 132.3, 132.1, 130.8, 127.9, 127.8, 127.4, 126.9, 126.4, 126.2, 125.5, 125.4, 125.1, 124.8, 121.4, 78.0, 72.3, 36.6, 35.5, 33.9, 33.8, 33.6, 33.5, 31.9, 31.7, 31.4, 31.3, 30.8, 30.8, 22.8, 10.8 ppm; HRMS (ESI) *m*/*z* calcd for $C_{52}H_{70}NO_7$ $[(M + H)^+]$ 820.5152, found 820.5150.

X-ray Data Collection and Structure Refinement. Details of the crystal parameters, data collection, and refinement for compound **3a** are summarized in Table S7 in the Supporting Information. The details of the crystal data have been deposited to the Cambridge Crystallographic Data Centre and are available on request, quoting the deposition number CCDC 1475479.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01682.

NMR spectra of new compounds, ECD computation methods, energies, Boltzmann populations, and atom coordinates of the most stable conformers of **5a** and **6a**, and X-ray molecular structure and crystallographic data for **3a** (PDF)

Crystallographic data for **3a** (CIF)

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Notes

The authors declare no competing financial interest.

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