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C_3-Symmetrical Tribenzotriquinacene Derivatives: Optical Resolution through Cryptophane Synthesis and Supramolecular Self-Assembly into Nanotubes

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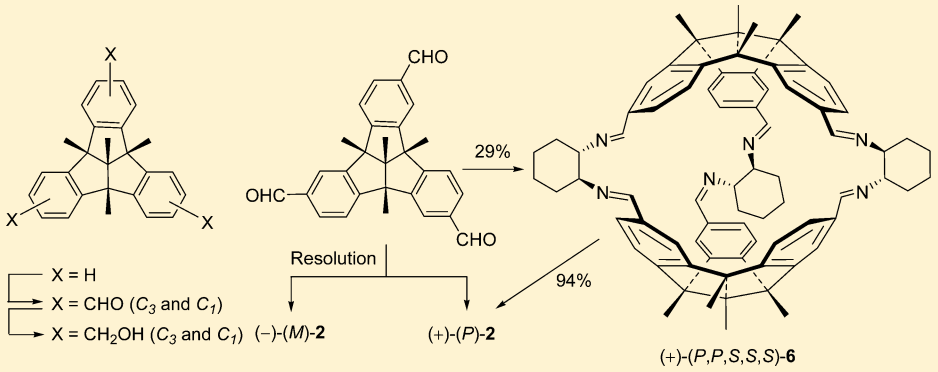
Supporting Information



ABSTRACT: Based on a regioselective tris-formylation of a tribenzotriquinacene (TBTQ) hydrocarbon, the racemic C_3-symmetrical TBTQ-trialdehyde and the corresponding TBTQ-trimethanol were synthesized along with their C_1-isomers. Conversion of the C_3-trialdehyde to three diastereomeric TBTQ-based cryptophanes occurring in high yield enabled the preparation of the optically pure C_3-symmetrical TBTQ-trialdehydes and the determination of their absolute configuration. The racemic C_3-symmetrical TBTQ-trimethanol was found to form several stable nanotubular aggregates in the solid state.

INTRODUCTION

Molecular self-assembly constitutes a facile bottom-up approach toward the synthesis of complex yet ordered molecular architectures through simple operations.[1] The success of this approach relies heavily on the optimal geometry matching of the various building blocks. Hence the design of molecular motifs with new structural parameters is pivotal to the generation of unique self-assembling systems with novel architecture and potentially new functional properties. Self-organized systems with various degrees of complexity have been developed that exhibit many applications in the fields of controlled drug delivery,[2] separation and storage,[3] sensing,[4,5] catalysis,[6,7] and host−guest complexation.[5,8−10] Among the many motifs, trifunctionalized C_3-symmetrical molecules such as cyclotriveratrylenes (CTVs)[11,12] and functionalized trinuclear metallamacrocycles[13] are of special interest. Owing to the nonplanar disposition of the functionalities, they were employed in the construction of three-dimensional molecular objects such as cryptophanes,[14−16] molecular cubes,[17] and molecular spheres[18] with specific and highly selective complexation properties. In this report, we unravel the first use of the molecular scaffold of tribenzotriquinacene (TBTQ)[19] for the construction of cryptophanes. The CTV and TBTQ frameworks are similar in terms of symmetry and shape but differ in conformational rigidity. As has been pointed out recently,[20−22] the rigid, convex−concave framework of TBTQ and its derivatives, such as the tetramethyl analogue **1**, is a promising scaffold for the construction of cryptophane-type systems because of the almost perfect orthogonal orientation of its three indane wings in space.[23,24] This unique motif has started to receive attention in various areas, including host−guest chemistry with fullerenes,[25−27] molecular antennas containing orthogonal chromophores,[28] microporous materials,[29] and curved graphene-type carbon networks.[20−22,30−32] Herein we wish to report some important progress toward such aims based on the supramolecular self-assembly chemistry of two new TBTQ synthons, the C_3-symmetrical TBTQ-trialdehyde

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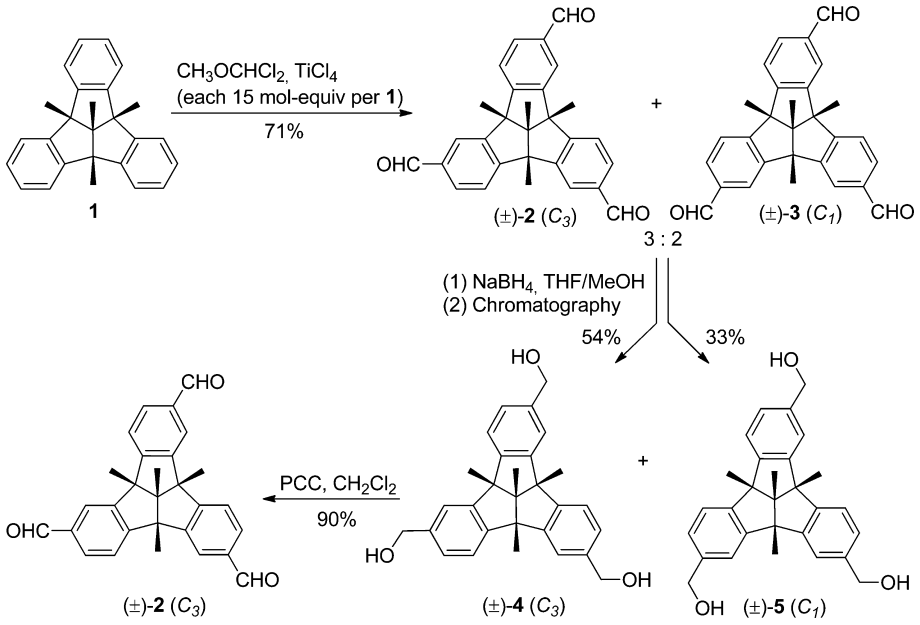
Scheme 1. Formylation of Tetramethyltribenzotriquinacene 1 to the Mixture of the Trialdehydes (±)-2 and (±)-3, Reduction of the Mixture to the TBTQ Triols (±)-4 and (±)-5, and Preparation of the Pure Trialdehyde (±)-2 after Chromatography of the Triol Mixture



(±)-**2** and the related C_3-TBTQ-trimethanol (±)-**4**. First, [3 + 2] dynamic covalent assembly between the racemic trialdehyde (±)-**2** and optically pure (1*S*,2*S*)-diaminocyclohexane furnished the three diastereomeric multiple-Schiff-base TBTQ-cryptophanes **6**–**8**, separation of which allowed us to prepare and characterize the optically pure C_3-symmetrical TBTQ-trialdehydes (+)-**2** and (−)-**2** as versatile building blocks. Second, the racemic triol (±)-**4** was found to self-assemble by intermolecular H-bonding in the solid state to form stable organic nanotubes[33] that are capable of entrapping guest molecules. The latter finding represents another interesting example for the assembly of large, spatially well-defined, supramolecular networks from conformationally rigid, geometrically highly symmetrical molecular building blocks. In the case of triol (±)-**4**, a self-sorting process involving the aggregation of enantiopure triol (+)-**4** or (−)-**4** in each layer in the crystal lattice was observed. These findings further emphasize that C_3-symmetrical tribenzotriquinacenes bearing three orthogonally oriented, singly functionalized indane wings are versatile targets for the construction of highly organized self-assembled systems.

RESULTS AND DISCUSSION

Starting from the fully bridgehead-methylated tribenzotriquinacene **1**,[23,34,35] three formyl groups were introduced by treating this hydrocarbon with a mixture of dichloromethyl methyl ether and titanium tetrachloride ($[CH_3OCHCl_2]$:$[TiCl_4]$:[**1**] = 15:15:1) in dichloromethane (Scheme 1).[36−39] The two possible triformyl derivatives, namely, the C_3-symmetrical isomer (±)-**2** and the C_1-symmetrical isomer (±)-**3**, were formed in 71% isolated yield and with the former isomer as the major product: [(±)-**2**]:[(±)-**3**] = 1.5:1. It is interesting to note that this isomer ratio is far different from that obtained for the respective 3-fold nitration of **1** giving the statistical ratio, $[C_3]$:$[C_1]$ = 1:3.[40−42] While only one single spot was observed by TLC analysis of the mixture, the ^{13}C NMR spectrum indicated the presence of the two isomers; for example, at least 22 different resonances appeared for the arene carbon atoms. Reduction of the mixture of the triformyl derivatives (±)-**2** and (±)-**3** by sodium borohydride in tetrahydrofuran/methanol (10:1, v/v) gave the corresponding C_3- and C_1-symmetrical benzylic trialcohols (±)-**4** and (±)-**5**, which turned out to be cleanly separable by column chromatography through silica gel. The ^{13}C NMR spectrum of the racemic isomer (±)-**4** confirmed its C_3-symmetry (6 arene resonances only, as expected), whereas the ^{13}C NMR spectrum of the racemic triol (±)-**5** reflected its molecular C_1-symmetry (17 of 18 possible arene resonances). Reoxidation of the racemic C_3-symmetrical triol (±)-**4** with pyridinium chlorochromate in dichloromethane regenerated a sample of the pure C_3-trialdehyde (±)-**2** in 90% yield, as documented by ^1H and ^{13}C NMR spectroscopy (see Supporting Information). The structural identity of the C_3-symmetrical trialdehyde (±)-**2** and of both of the trialcohols (±)-**4** and (±)-**5** was corroborated by X-ray crystallography (see Supporting Information, S3–S5).

When solutions of the C_3-symmetrical trialcohol (±)-**4** in various solvents, such as ethyl acetate/petroleum ether, tetrahydrofuran, or methanol/dichloromethane, were allowed to stand at room temperature for 1 or 2 days, colorless, cubic (or flattened cubic) crystals of sizes in the range of 0.2–1.0 mm were formed. They were found to remain stable under exposure to air for several days. The X-ray structure analyses performed with these various single crystals of triol (±)-**4** were revealing (Figure 1).[43] Apart from the structure of the crystals obtained from acetone, all others showed the presence of regular-hexagonal nanotubes with the same diameter (∼5.2 Å) arranged in parallel series along the crystallographic *c* axis. The molecules of (±)-**4** are packed in alternate layers each of which consists of either the (*P*)- or the (*M*)-enantiomer, similar to the molecular packing of the C_1-symmetrical isomer (±)-**5** (Supporting Information, S-Figure 1d). O–H···O hydrogen bonding between these adjacent layers gives rise to columnar cavities oriented perpendicular to the layers and coated by the

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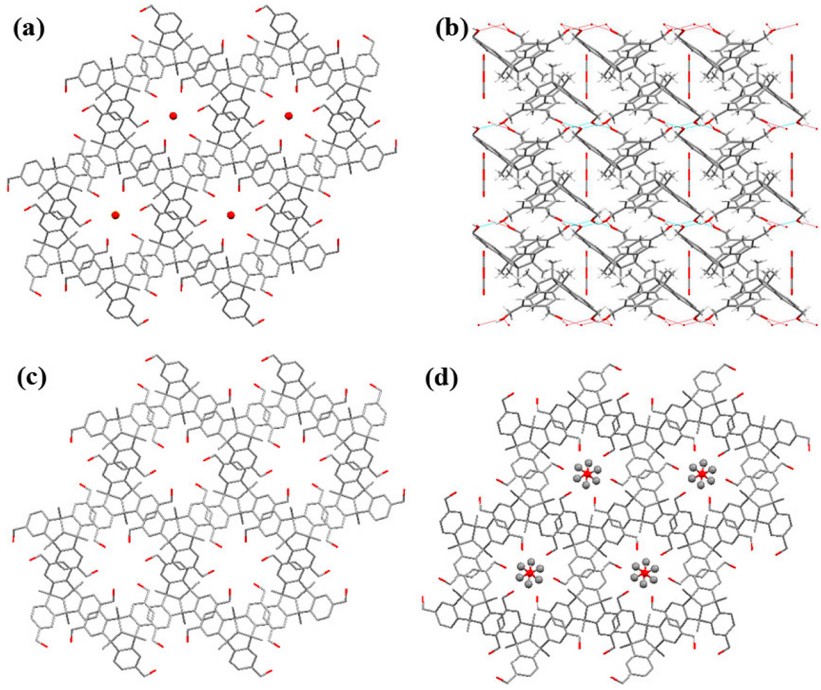

Figure 1. X-ray crystal structures of single crystals of the C_3-symmetrical triol (±)-**4**: as obtained from (a and b) ethyl acetate/petroleum ether [(a) viewed along the crystallographic *c* axis and (b) along the *a* axis], with one molecule of EtOAc per two molecules of (±)-**4** being enclosed in the nanotubes, (c) from tetrahydrofuran, with THF molecules within the nanotubes being unresolved, and (d) from methanol/dichloromethane (*c* axis), with two molecules of MeOH per two molecules of (±)-**4** being enclosed into the nanotubes.

hydroxyl groups. Three molecules from one layer and three from the next one each contribute one of their hydroxymethyl groups to each section of a single nanotube, and each molecule contributes in this way to three adjacent, parallel nanotubes. Some solvent molecules, such as ethyl acetate (EtOAc:(±)-**4** = 1:2, Figure 1a,b and Supporting Information S-Figure 2a) and methanol (MeOH:(±)-**4** = 1:1, Figure 1d and Supporting Information S-Figure 2b) were found to stably exist within these nanotubes, as corroborated by TG/DTG analysis showing the fractional loss of a molecular species with $\Delta M \approx 88$ in the former case. The same type of molecular packing with parallel nanotubes perpendicular to the alternant layers of (+)-(*P*)-**4** and (−)-(*M*)-**4** was obtained by crystallization from tetrahydrofuran (Figure 1c), but the solvent molecules could not be localized in this case. When acetone was used as a solvent, the crystal packing showed no nanotube formation, possibly because the acetone molecules interact with the hydroxymethyl groups and perturbate the intermolecular hydrogen bonding between the molecules of (±)-**4**. Noteworthily, neither the X-ray crystal structures of the C_1-symmetrical triol (±)-**5** nor the C_3-symmetrical trialdehyde (±)-**2** showed this type of nanotube formation. This emphasizes the role of the hydrogen bonding through the hydroxyl groups and the importance of the molecular C_3-symmetry as a prerequisite for securing the nanotubular architecture (see Supporting Information for details, S3−S5).

Schiff base macrocycles are of great importance in macrocyclic and supramolecular chemistry, and a broad variety of such compounds can be utilized as biological models for metal binding.[44−47] Accordingly, we were interested in the incorporation of Schiff-base functionalities into TBTQ-based cryptophanes. Stirring a mixture of (±)-**2** and 1.78 equiv of (1*S*,2*S*)-diaminocyclohexane (99% ee) in chloroform at room temperature for 12 h gave a mixture of three diastereoisomeric cryptophanes, **6**−**8**, in excellent yield (94%) (Scheme 2). Chromatographic separation through silica gel allowed us to isolate all of the three diastereomers (+)-(*P*,*P*,*S*,*S*,*S*)-**6** (29% yield), (+)-(*P*,*M*,*S*,*S*,*S*)-**7** (40%), and (−)-(*M*,*M*,*S*,*S*,*S*)-**8** (25%) in pure state and to characterize them by nuclear magnetic resonance spectroscopy and ESI mass spectrometry. The ^{1}H and ^{13}C NMR spectral features of cryptophanes **6** and **8** were found to be very similar and to reflect a degeneracy of resonances due to molecular symmetry (e.g., for 1-H and 2-H of the cyclohexane rings). In contrast, the spectra of isomer **7** were significantly more complex, showing no such degeneracy, and clearly distinct from a mixture of isomers **6** and **8** (see Supporting Information, S12−S14). Unfortunately, despite many attempts to grow crystals of cryptophanes **6**−**8**, none of them was found to be suitable for X-ray crystal structure determination. When the individual cryptophanes **6**, **7**, and **8** were hydrolyzed in aqueous trifluoroacetic acid, the corresponding trialdehydes (+)-(*P*)-**2** (97% ee), (±)-**2**, and (−)-(*M*)-**2** (96% ee) were obtained in 88−94% yields. The specific optical rotation for (+)-(*P*)-**2** and (−)-(*M*)-**2** was found to be $[\alpha]^{20}_{D}$ = +18.0 and −18.0, respectively, and their CD spectra displayed a perfect mirror image relationship, confirming their enantiomeric nature and purity (Figure 2). Therefore, condensation of the trialdehyde (±-**2**) with optically pure *trans*-1,2-diaminocyclohexane represents a convenient method for the optical resolution of this type of trifunctionalized C_3-symmetrical TBTQ derivatives, which are promising chiral building blocks for the construction of well-defined large, covalently bound, and supramolecular nanostructures.[21]

The C_3-symmetrical TBTQ-trialdehyde (±)-**2** can be regarded as a derivative of cyclotribenzylene[48−50] and as an analogue of cyclotriveratrylene[8−12] bearing a similar but highly rigidified polycyclic framework. Therefore, we suggest to assign the absolute configuration of the enantiomers (+)-(*P*)-**2** and

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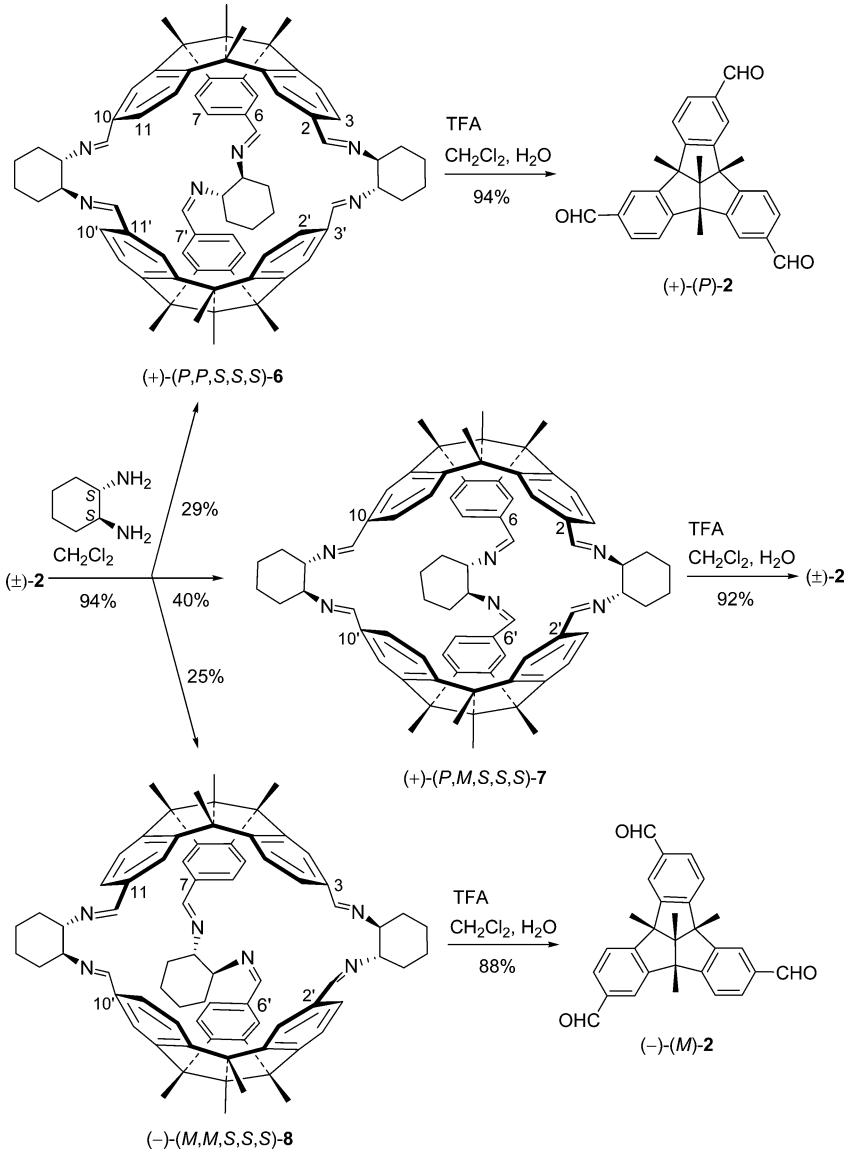
Scheme 2. Synthesis of Diastereomeric Cryptophanes (+)-(*P,P,S,S,S*)-6, (+)-(*P,M,S,S,S*)-7, and (−)-(*M,M,S,S,S*)-8 and Hydrolysis Affording Optically Pure TBTQ-Trialdehydes (+)-(*P*)-2 and (−)-(*M*)-2



(−)-(*M*)-**2** on the basis of their ECD spectra (Figure 2) by use of the Kuhn-Kirkwood model.[51−54] It was demonstrated that the excitonic coupling between the three aromatic rings could be used to predict the sign of the Cotton effect of the two forbidden transitions, B_{1u} (^{1}La) and B_{2u} (^{1}Lb), of the benzene chromophores and that the sign of the ECD signals for the B_{1u} and B_{2u} transitions is strongly dependent on the relative intensity of the spectroscopic moments of the two different groups, R^1 and R^2, attached to a benzene ring. In the case of trialdehyde **2**, the spectroscopic moment of the formyl group (R^1 = CHO) is much larger than that of the hydrogen atom (R^2 = H), and as a consequence, the ECD spectrum presented by the solid line in Figure 2 is attributed to the enantiomer (+)-(*P*)-**2**, showing two positive exciton patterns centered at ca. 300 and 264 nm connected to the benzene B_{2u} and B_{1u} transitions, respectively. Conversely, the ECD spectrum presented by the dotted line is attributed to the (−)-(*M*)-**2** enantiomer. The absolute configuration assignments of the three cryptophane precursors of trialdehydes (+)-(*P*)-**2** and (−)-(*M*)-**2** are therefore assigned as (+)-(*P,P,S,S,S*)-**6**, (+)-(*P,M,S,S,S*)-**7**, and (−)-(*M,M,S,S,S*)-**8** (Scheme 2).

An estimation of the relative thermochemical stabilities of the three diastereomers **6**−**8** was carried out by the DFT approach at the SIESTA and L-BFGS level (Figure 3).[55−58] The results suggest that all three cryptophanes have very similar heats of formation (within ±0.1 eV = 10.3 kJ mol^{-1}).[59] This finding is in agreement with the observation that, under all reaction conditions used in our experiments, the isolated yields of the three diastereomers are close to the statistical ratio, [**6**]:[**7**]:[**8**] = 1:2:1, expected for the thermodynamically controlled Schiff base formation.

■ CONCLUSION

A convenient synthesis of two new C_3-symmetrical TBTQ derivatives, trialdehyde (±)-**2** and the corresponding 3-fold benzylic alcohol (±)-**4**, has been described. One of them, trialcohol (±)-**4**, was found to form supramolecular nanotubes that can host various organic solvents such as ethyl acetate and methanol in the crystalline state. The other derivative,

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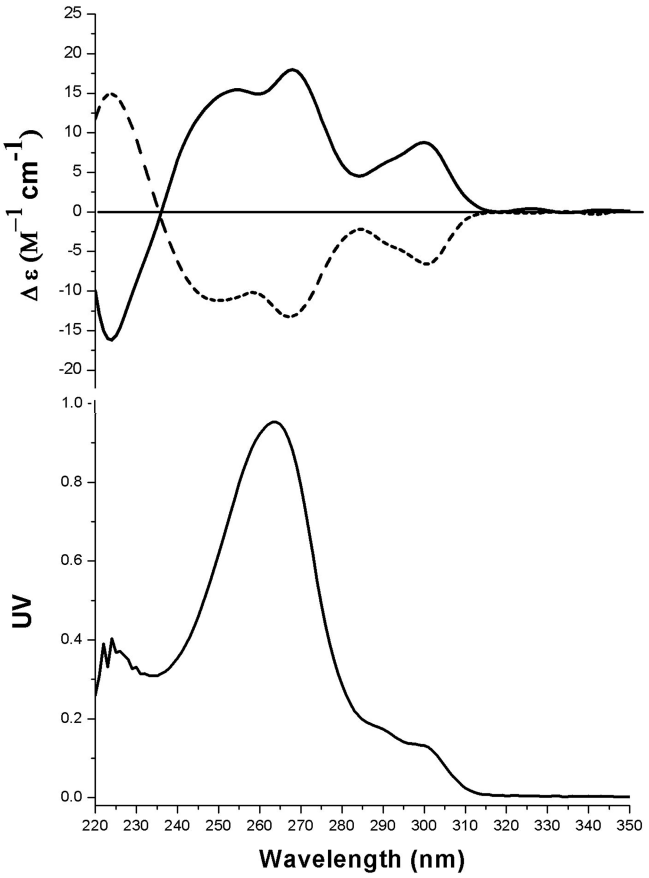

Figure 2. ECD spectra (CH_2Cl_2) of the trialdehydes (+)-(*P*)-**2** and (−)-(*M*)-**2** (top) and UV spectrum of (+)-(*P*)-**2** (bottom).

trialdehyde (±)-**2**, could be transformed into three multiple Schiff-base cryptophanes **6**−**8** via a condensation reaction with (1*S*,2*S*)-diaminocyclohexane. After separation, hydrolysis of the individual diastereomers (+)-(*P*,*P*,*S*,*S*,*S*)-**6** and (−)-(*M*,*M*,*S*,*S*,*S*)-**8** allowed us to prepare, for the first time, optically pure C_3-symmetrically 2,6,10-trifunctionalized tribenzotriquinacenes, which represent promising building blocks for the construction of highly condensed concave or even globular architectures, such as nanotetrahedra and nanocubes. The chemistry described here further extends the structural diversity of the cryptophanes and opens an access to novel cryptophane-based structures and devices. The unexpected formation of the supramolecular nanotubes reported here represents a fortunate outgrowth of the particular solid-state interaction of C_3-symmetrical TBTQ molecules through intermolecular hydrogen bonds. More detailed understanding of the interplay of geometrical fitting and thermodynamic stabilization of such wholly organic C_3-symmetrical molecular entities in the formation of nanometer-sized tubes and cubic crystal architecture is needed.

EXPERIMENTAL SECTION

General Information. All reactions that required anhydrous conditions were carried by standard procedures under argon. Commercially available reagents were used as received. The solvents were dried by distillation over the appropriate drying reagents. Petroleum ether (PE) used had a boiling range of 60−90 °C. Reactions were monitored by TLC on silica gel GF 254 plates. Column chromatography was generally performed through silica gel (200−300 mesh). IR spectra were recorded on a FT-IR spectrophotometer and reported in wavenumbers (cm^{-1}). Melting points were determined by use of a microscope apparatus and are uncorrected. ^1H NMR and ^{13}C NMR spectra were recorded on a 400 or 600 MHz spectrometer, as were the DEPT 135 experiments. Chemical shift values are given in ppm and coupling constants (*J*) in Hertz. Residual solvent signals in the ^1H NMR and ^{13}C NMR spectra were used as an internal reference ($CDCl_3$: δ_H = 7.26, δ_C = 77.0 ppm; acetone-d_6: δ_H = 2.04, δ_C = 29.8 ppm). Accurate mass measurements were obtained on a 7.0 T FT-ICR or 4G mass spectrometer or on a double focusing sector-field instrument. X-ray data were collected with graphite monochromated Mo Kα radiation. The ee values were determined by chiral HPLC separation. CD spectra were recorded with a DSM 1000 spectrometer.

Tris-Formylation of Tetramethyltribenzotriquinacene 1. Titanium tetrachloride (0.49 mL, 4.50 mmol) was added to a stirred solution of tribenzotriquinacene **1** (100 mg, 0.30 mmol) in anhydrous dichloromethane (5 mL) at 0 °C. Then dichloromethyl methyl ether (0.39 mL, 4.50 mmol) was added dropwise over a period of 1 min. The mixture was stirred at room temperature for 20 h and then quenched with ice/water. The mixture was extracted with dichloromethane (3 × 15 mL), and the combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was then purified by silica gel chromatography (hexane/EtOAc, 5:1, R_f = 0.3) to afford a mixture of the trialdehydes (±)-**2** and (±)-**3** (ratio 3:2 by ^1H NMR spectroscopy) as a pale yellow solid (89 mg, 71%), mp range 239−248 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 9.96−9.94 (m, 3H), 7.94−7.91 (m, 3H), 7.75−7.71 (m, 3H), 7.62−7.54 (m, 3H), 1.75−1.73 (m, 9H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (t), 155.2 (q), 154.9 (q), 154.8 (q), 154.5 (q), 149.4 (q), 149.14 (q), 149.11 (q), 148.9 (q), 136.94 (q), 136.88 (q), 136.84 (q), 136.79 (q), 131.2 (t), 130.8 (t), 130.5 (t), 130.1 (t), 124.5 (t), 124.2 (t), 123.9 (t), 123.8 (t), 123.7 (t), 123.6 (t), 70.62 (q), 70.58 (q), 63.2 (q), 62.8 (q), 62.7 (q), 62.4 (q), 25.9 (p), 25.6 (p), 25.3 (p), 15.9 (p); IR (KBr) $\tilde{\nu}$ 3368, 2968, 2927, 1693, 1602, 1166, 828, 807 cm^{-1}; EI-MS (70 eV) *m*/*z* (%) 420 (25, $M^{\bullet+}$), 405 (100, $[M - CH_3]^+$), 303 (4), 302 (4), 291 (3), 290 (4), 289 (8), 202 (5); accurate mass (ESI-MS) *m*/*z* calcd for $C_{29}H_{25}O_3$ ($[M + H]^+$) 421.1798, found 421.1796.

Synthesis of the Tris(hydroxymethyl)-Substituted Tribenzotriquinacenes (±)-4 and (±)-5. A solution of the mixture containing the trialdehydes (±)-**2** and (±)-**3** (100 mg, 0.24 mmol) in THF/MeOH (10:1, 8 mL) was stirred while sodium borohydride (90 mg,

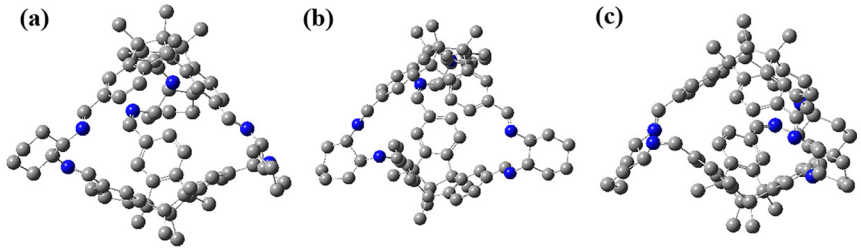

Figure 3. Optimized geometries of cryptophanes (a) (+)-(*P*,*P*,*S*,*S*,*S*)-**6**, (b) (+)-(*M*,*P*,*S*,*S*,*S*)-**7**, and (c) (−)-(*M*,*M*,*S*,*S*,*S*)-**8**, as calculated by use of the SIESTA package with numerical atomic orbital basis sets and Troullier-Martins norm-conserving pseudopotentials.

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2.38 mmol) was added in one portion at 0 °C under argon. The solution was stirred for 4 h at this temperature and then quenched with ice−water. The mixture was concentrated, and the residue was dissolved in EtOAc (10 mL) and washed with brine (3 × 10 mL). The organic layers were dried over sodium sulfate, filtered, and then concentrated under reduced pressure. Flash chromatography of the residue through silica gel (PE/EtOAc 1:1) afforded the triols (±)-**4** (55 mg, 54%, R_f = 0.38) and (±)-**5** (34 mg, 33%, R_f = 0.34).

2,6,10-Tris(hydroxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(±)-4]. Colorless solid, mp >350 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.46 (s, 3H), 7.43 (d, J_{H-H} = 8.0 Hz, 3H), 7.14 (d, J_{H-H} = 8.0 Hz, 3H), 4.54 (d, J_{H-H} = 6.0 Hz, 6H), 4.03 (t, J_{H-H} = 6.0 Hz, 3H), 1.66 (s, 9H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 150.0 (q), 148.7 (q), 142.9 (q), 127.2 (t), 123.7 (t), 122.2 (t), 71.1 (q), 65.0 (s), 63.3 (q), 26.3 (p), 16.4 (p); IR (KBr) $\tilde{\nu}$ 3349, 2961, 2922, 2860, 1700, 1421, 1031, 882, 815 cm^{-1}; EI-MS (70 eV) m/z (%) 426 (19, M$^{\bullet+}$), 411 (100, [M − CH_3]$^+$), 409 (14, [M − OH]$^+$), 395 (6), 393 (4), 303 (6), 302 (5), 289 (6); accurate mass (ESI-MS) m/z calcd for $C_{29}H_{34}NO_3$ ([M + NH_4]$^+$) 444.2533, found 444.2539.

2,6,11-Tris(hydroxymethyl)-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(±)-5]. Colorless solid, mp 259−261 °C; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.50−7.42 (m, 6H), 7.16−7.13 (m, 3H), 4.55−4.54 (m, 6H), 3.70−2.90 (brs, 3H), 1.66−1.65 (m, 9H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, acetone-d_6) δ 149.9 (q), 149.8 (q), 149.7 (q), 148.9 (q), 148.8 (q), 148.7 (q), 142.63 (q), 142.60 (q), 127.2 (t), 127.14 (t), 127.09 (t), 123.60 (t), 123.55 (t), 123.54 (t), 122.17 (t), 122.15 (t), 122.1 (t), 71.0 (q), 64.8 (s), 63.4 (q), 63.2 (q), 63.0 (q), 26.4 (p), 26.2 (p), 26.1 (p), 16.4 (p) [overlapping signals: 1 aromatic C (q) and 2 aliphatic C (s)]; IR (KBr): $\tilde{\nu}$ = 3347, 2960, 2922, 2868, 1700, 1420, 1031, 882, 815 cm^{-1}; EI-MS (70 eV) m/z (%) 426 (19, M$^{\bullet+}$), 411 (100, [M − CH_3]$^+$), 409 (13, [M − OH]$^+$), 395 (4), 393 (2), 303 (6), 302 (4), 289 (5); accurate mass (ESI-MS) m/z calcd for $C_{29}H_{34}NO_3$ ([M + NH_4]$^+$) 444.2533, found 444.2529.

2,6,10-Triformyl-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(±)-2]. A solution of the triol (±)-**4** (60 mg, 0.14 mmol) and pyridinium chlorochromate (900 mg) in anhydrous dichloromethane (20 mL) was stirred for 4 h at ambient temperature. The reaction mixture was diluted with water (20 mL) and extracted with dichloromethane (3 × 20 mL). The combined organic layers were washed with brine, dried over sodium sulfate, filtered, and then concentrated under reduced pressure. Flash chromatography of the residue through silica gel (PE/EtOAc, 2:1, R_f = 0.54) afforded trialdehyde (±)-**2** as a colorless solid (53 mg, 90%), mp 311−313 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 3H), 7.91 (d, J_{H-H} = 1.0 Hz, 3H), 7.73 (dd, J_{H-H} = 8.0, 1.6 Hz, 3H), 7.61 (d, J_{H-H} = 8.0 Hz, 3H), 1.75 (s, 9H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (t), 155.2 (q), 148.9 (q), 136.8 (q), 131.2 (t), 123.9 (t), 123.5 (t), 70.6 (q), 62.8 (q), 25.6 (p), 16.0 (p); IR (KBr) $\tilde{\nu}$ 3368, 2968, 2927, 1693, 1602, 1166, 807 cm^{-1}; EI-MS (70 eV) m/z (%) 420 (26, M$^{\bullet+}$), 405 (100, [M − CH_3]$^+$), 303 (4), 302 (4), 291 (3), 290 (4), 289 (9), 202 (5); accurate mass (ESI) m/z calcd for $C_{29}H_{24}NaO_3$ ([M + Na]$^+$) 443.1618, found 443.1611.

Synthesis of Cryptophanes (+)-(*P,P,S,S,S*)-6, (+)-(*P,M,S,S,S*)-7, and (−)-(*M,M,S,S,S*)-8. A solution of trialdehyde (±)-**2** (59 mg, 0.14 mmol) and (1*S*,2*S*)-(−)-1,2-diaminocyclohexane (28 mg, 0.25 mmol, 99% ee) in anhydrous dichloromethane (10 mL) was stirred for 12 h at 30 °C. The reaction mixture was then concentrated under reduced pressure. Flash chromatography of the residue through silica gel [PE (or cyclohexane)/EtOAc/Et_3N, 100:25:1] afforded the diastereomers **6** (22 mg, 29%), **7** (30 mg, 40%), and **8** (19 mg, 25%), respectively.

Bis-TBTQ-cryptophane (+)-(*P,P,S,S,S*)-6. Colorless solid, mp >350 °C; $[\alpha]^{20}_D$ = +21 (*c* 1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 6H), 7.69 (dd, J_{H-H} = 8.0, 0.8 Hz, 6H), 7.16 (d, J_{H-H} = 8.0 Hz, 6H), 7.14 (d, J_{H-H} = 0.8 Hz, 6H), 3.34 (t, J_{H-H} = 5.0 Hz, 6H), 1.85−1.83 (m, 6H), 1.75−1.72 (m, 12H), 1.53 (s, 18H), 1.52−1.46 (m, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0 (t), 150.7 (q), 148.0 (q), 136.1 (q), 125.5 (t), 125.3 (t), 123.0 (t), 74.7 (t), 70.4 (q), 62.3 (q), 33.1 (s), 25.7 (p), 24.5 (s), 16.0 (p); IR (KBr) $\tilde{\nu}$ 3431, 2924, 2853, 1644, 1450, 938, 830 cm^{-1}; ESI-MS ($CHCl_3$/MeOH): m/z (%) 1075.7 (100, [M + H]$^+$), 1076.7 (83, {[$^{13}C_1$]-M + H]$^+$}), 1077.7 (40, {[$^{13}C_2$]-M + H]$^+$}), 1078.7 (14, {[$^{13}C_3$]-M + H]$^+$}); accurate mass (ESI) m/z calcd for $C_{76}H_{79}N_6$ ([M + H]$^+$) 1075.6361, found 1075.6349.

Bis-TBTQ-cryptophane (+)-(*P,M,S,S,S*)-7. Colorless solid, mp >350 °C; $[\alpha]^{20}_D$ = +16 (*c* 1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 3H), 8.04 (s, 3H), 7.77 (s, 3H), 7.59 (d, J_{H-H} = 8.0 Hz, 3H), 7.36 (d, J_{H-H} = 8.0 Hz, 3H), 7.17 (d, J_{H-H} = 8.0 Hz, 3H), 7.10 (s, 3H), 7.04 (d, J_{H-H} = 8.0 Hz, 3H), 3.41−3.37 (m, 3H), 3.30−3.24 (m, 3H), 1.95−1.80 (m, 12H), 1.78−1.68 (m, 6H), 1.56 and 1.55 (each s, 18H), 1.51−1.43 (m, 6H), 1.28−1.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (t), 160.3 (t), 151.3 (q), 150.3 (q), 148.5 (q), 148.0 (q), 136.3 (q), 135.7 (q), 131.8 (t), 125.3 (t), 125.1 (t), 123.5 (t), 122.8 (t), 119.2 (t), 75.7 (t), 73.3 (t), 70.4 (q), 70.1 (q), 62.3 (q), 33.4 (s), 32.6 (s), 26.3 (p), 25.5 (p), 24.6 (s), 14.2 (p), 14.1 (p) (overlapping signals: 1 aliphatic C (q) and 1 aliphatic C (s); IR (KBr) $\tilde{\nu}$ 3363, 2920, 2851, 1690, 1450, 938, 827 cm^{-1}; ESI-MS ($CHCl_3$/MeOH): m/z (%) 1075.7 (100, [M + H]$^+$), 1076.7 (90, {[$^{13}C_1$]-M + H]$^+$}), 1077.7 (37, {[$^{13}C_2$]-M + H]$^+$}), 1078.7 (10, {[$^{13}C_3$]-M + H]$^+$}); accurate mass (ESI) m/z calcd for $C_{76}H_{79}N_6$ ([M + H]$^+$) 1075.6361, found 1075.6394.

Bis-TBTQ-cryptophane (−)-(*M,M,S,S,S*)-8. Colorless solid, mp >350 °C; $[\alpha]^{20}_D$ = −7 (*c* 1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (s, 6H), 7.75 (s, 6H), 7.31 (d, J_{H-H} = 7.6 Hz, 6H), 6.92 (d, J_{H-H} = 7.6 Hz, 6H), 3.39−3.38 (m, 6H), 1.87−1.85 (m, 6H), 1.82−1.70 (m, 12H), 1.57 (s, 18H), 1.52−1.47 (m, 6H), 1.24 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6 (t), 151.3 (q), 148.6 (q), 136.1 (q), 131.3 (t), 123.2 (t), 119.6 (t), 75.4 (t), 69.9 (q), 62.4 (q), 33.3 (s), 25.9 (p), 24.6 (s), 16.1 (p); IR (KBr) $\tilde{\nu}$ 3411, 2927, 2855, 1643, 1450, 934, 824 cm^{-1}; ESI-MS ($CHCl_3$/MeOH): m/z (%) 1075.8 (100, [M + H]$^+$), 1076.8 (78, {[$^{13}C_1$]-M + H]$^+$}), 1077.8 (32, {[$^{13}C_2$]-M + H]$^+$}), 1078.8 (8, {[$^{13}C_3$]-M + H]$^+$}); accurate mass; (ESI) m/z calcd for $C_{76}H_{79}N_6$ ([M + H]$^+$) 1075.6361, found 1075.6384.

Synthesis of Trialdehydes (+)-(*P*)-2, (±)-2, and (−)-(*M*)-2 by Hydrolysis of the Respective Cryptophanes (+)-(*P,P,S,S,S*)-6, (+)-(*P,M,S,S,S*)-7, and (−)-(*M,M,S,S,S*)-8. (+)-(*P*)-2,6,10-Triformyl-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(+)-(*P*)-2]. A solution of cryptophane (+)-(*P,P,S,S,S*)-**6** (22 mg, 20 μmol) in anhydrous dichloromethane (10 mL) was stirred while trifluoroacetic acid (200 μL) was added dropwise under argon. The mixture was stirred for another 12 h at ambient temperature and then quenched with ice/water (10 mL). The mixture was extracted with dichloromethane (3 × 15 mL), and the combined organic layers were washed with brine, dried over sodium sulfate, filtered, and concentrated under reduced pressure. Flash chromatography of the residue through silica gel (PE/EtOAc, 2:1, R_f = 0.54) afforded the enantiomerically pure trialdehyde (+)-(*P*)-**2** as a pale yellow solid (16 mg, 94%). mp 311−313 °C; $[\alpha]^{20}_D$ = +18 (*c* 1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.94 (s, 3H), 7.91 (d, J_{H-H} = 1.2 Hz, 3H), 7.72 (dd, J_{H-H} = 8.0, 1.2 Hz, 3H), 7.61 (d, J_{H-H} = 8.0 Hz, 3H), 1.75 (s, 9H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.6 (t), 155.2 (q), 148.9 (q), 136.9 (q), 131.2 (t), 123.9 (t), 123.6 (t), 70.6 (q), 62.8 (q), 25.6 (p), 16.0 (p); IR (KBr) $\tilde{\nu}$ 3370, 2923, 2853, 1691, 1026, 802 cm^{-1}; EI-MS (70 eV) m/z (%) 420 (25, M$^{\bullet+}$), 405 (100, [M − CH_3]$^+$), 303 (4), 302 (4), 291 (3), 290 (4), 289 (9), 202 (5); accurate mass (ESI) m/z calcd for $C_{29}H_{24}NaO_3$ ([M + Na]$^+$) 443.1618, found 443.1619.

Racemic Trialdehyde (±)-2. According to the procedure given above for trialdehyde (+)-(*P*)-**2**, hydrolysis of cryptophane (+)-(*P,M,S,S,S*)-7 (15 mg, 14 μmol) afforded trialdehyde (±)-**2** (11 mg, 92%) as a colorless solid $[\alpha]^{20}_D$ = 0 (*c* 1, CH_2Cl_2); mp 311−313 °C. The ^{1}H and ^{13}C NMR data of this product (±)-**2** obtained from (+)-(*P,M,S,S,S*)-7 are identical to those of the product (±)-**2** synthesized from (±)-**4**.

(−)-(*M*)-2,6,10-Triformyl-4b,8b,12b,12d-tetramethyl-4b,8b,12b,12d-tetrahydrodibenzo[2,3:4,5]pentaleno[1,6-*ab*]indene [(−)-(*M*)-2]. Similar to the procedure given above for trialdehyde (+)-(*P*)-**2**, hydrolysis of cryptophane (−)-(*M,M,S,S,S*)-**8** (22 mg, 20 μmol) afforded enantiomerically pure trialdehyde

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(−)-(*M*)-**2** as a colorless solid (15 mg, 88%), $[\alpha]^{20}_{D}$ = −18 (*c* 1, CH_2Cl_2); mp 310−313 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.95 (s, 3H), 7.91 (s, 3H), 7.73 (d, J_{H-H} = 8.0 Hz, 3H), 7.61 (d, J_{H-H} = 8.0 Hz, 3H), 1.75 (s, 9H), 1.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.5 (t), 155.2 (q), 148.9 (q), 136.9 (q), 131.2 (t), 123.9 (t), 123.6 (t), 70.7 (q), 62.8 (q), 25.7 (p), 16.0 (p); IR (KBr) $\tilde{\nu}$ 3365, 2920, 2851, 1690, 1025, 802 cm^{-1}; EI-MS (70 eV) *m*/*z* (%) 420 (25, $M^{\bullet+}$), 405 (100, $[M - CH_3]^+$), 303 (4), 302 (4), 291 (3), 290 (4), 289 (9), 202 (5); accurate mass (ESI) *m*/*z* calcd for $C_{29}H_{24}NaO_3$ ($[M + Na]^+$) 443.1618, found 443.1622.

■ ASSOCIATED CONTENT

Supporting Information

Crystal packing of (±)-**2**, (±)-**4**, and (±)-**5**; TG/DTG data of a crystal (±)-**4**; chiral HPLC data and figure of compounds (+)-(*P*)-**2**, (±)-**2**, and (−)-(*M*)-**2**; ^{1}H, ^{13}C NMR (DEPT 135) spectra of a mixture of (±)-**2** and (±)-**3**, compounds (±)-**4**, (±)-**5**, (±)-**2**, (+)-(*P*,*P*,*S*,*S*,*S*)-**6**, (+)-(*P*,*M*,*S*,*S*,*S*)-**7**, (−)-(*M*,*M*,*S*,*S*,*S*)-**8**, (+)-(*P*)-**2**, and (−)-(*M*)-**2**; CIF files of compounds (±)-**2**, (±)-**4**, and (±)-**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(43) X-ray crystal data for (±)-**4** from ethyl acetate/petroleum ether: $C_{31}H_{34}O_4$; *M* = 470.25; triclinic; *a* = 11.9712(12), *b* = 11.9712(12), *c* = 9.9653(13) Å; α = 90.00°, β = 90.00°, γ = 120.00°; *V* = 1236.8(2) Å^3; space group *P*-3; Z = 2; ρ_{calcd} = 1.242 Mg m^{-3}; T = 296(2)K; λ (Mo Kα) = 0.71073 Å; 6961 reflections collected; R_{int} = 0.0455; 1613 parameters refined on F^2; R_1 = 0.0619, $wR_2[F^2]$ = 0.1715 (all data); GOF on F^2 = 0.1960. CCDC-854242 contains the supplementary

crystallographic data for (±)-**4**; CCDC-854243 and CCDC-854244 contains the supplementary crystallographic data for (±)-**4** from methanol/dichloromethane and tetrahydrofuran, respectively.
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