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Modulation of Photoswitching Profiles by 10,11-Dialkoxymethyl Substituents in C_2-Symmetric Dibenzosuberane-Based Helicenes

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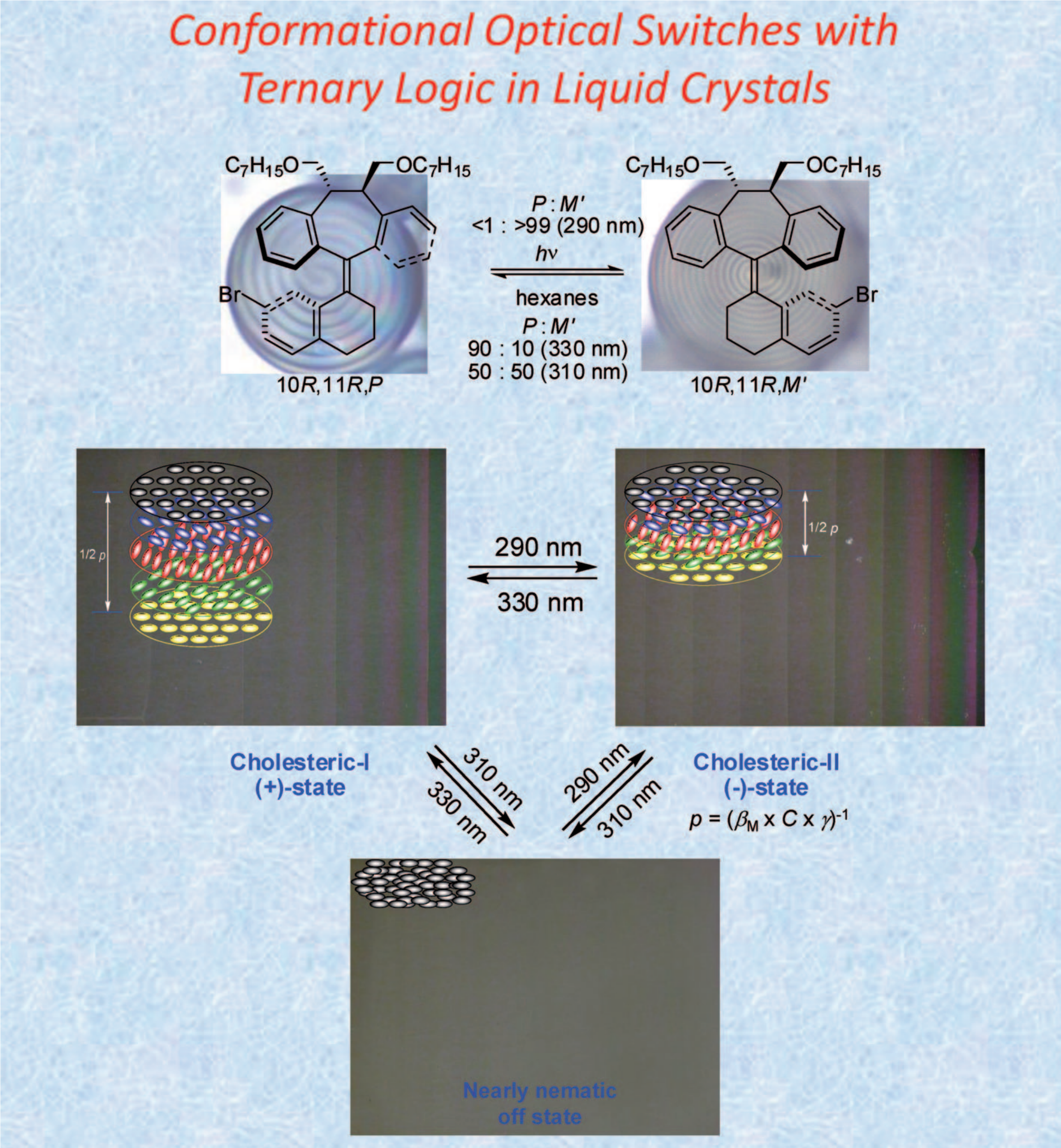


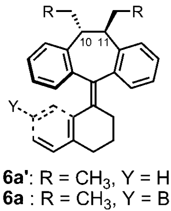
Abstract: A series of C_2-symmetric, 10,11-disubstituted dibenzosuberane (DBS)-based helicenes **6a–c** with a common 7-bromo-α-tetralin-based bottom fragment were synthesized. Their absolute stereochemistry was determined to be 10*R*,11*R*,*P* after reductive desulfurization of the corresponding (10*R*,11*R*,1′*S*)-episulfides with complete stereospecificity. Photoisomerization of the diastereomerically pure (*P*)-**6c** in hexane led to virtually exclusive formation of the opposite *M*-form diastereomer (*P*/*M*′, <1:>99) at 290 nm. The preferential return of (*M*′)-**6c** to (*P*)-**6c** was also achieved with high selectivity (*P*/*M*′, 90:10) at 330 nm. Molecular simulations of (*P*)-**6c** and (*M*′)-**6c** with both DBS conformations suggest that the selectivities of photoswitching are controlled by the conformation of the top DBS template as evidenced by their ^{1}H NMR spectra. Doping **6c** into a nematic liquid crystal (E7) led to a cholesteric mesophase with modulated pitches, reversible helical senses, and with a switch memory of ternary logic.

Keywords: chirality · heavy atom effect · helicenes · liquid crystals · optical switches

Introduction

Bistable molecular switches that can be interchanged by external mediators served as the memory units of binary logic and were especially in focus.[1] Light, temperature, pH, redox potential, and metal ions are some common external mediators with alteration of controllable stimuli. Many well-documented systems include photoswitches,[2] switchable rotaxanes and catenanes,[3] conformational switches,[4] and redox switches.[5] Because light constitutes one type of clean energy, the researches for molecular switches stimulated by light are particularly attractive. So far, representative photoreversible molecular switches include sterically overcrowded olefins,[6] azobenzenes,[7] diarylethenes,[8] spiropyrans,[9] and fulgides.[10] Helically shaped, overcrowded olefins (helicenes) constitute a specific type of chirochromic molecules, the switching profiles of which exhibit a reversible change in helicity. In the past few years, some unique helicene-based architectures of light-driven molecular motors were reported by Feringa and co-workers.[11] The induced rotation around a central olefinic bond (i.e., clockwise or counterclockwise) is governed by the orientation of the substituent at the stereogenic center attached to the conformational, flexible framework of the molecular motor. Namely, the conformational, axial-to-equatorial alternation of substituents in a five-, six-, or even seven-membered ring couples in a dynamic fashion with the helicity transformation of the helicene during the process of photo- or thermal isomerization.

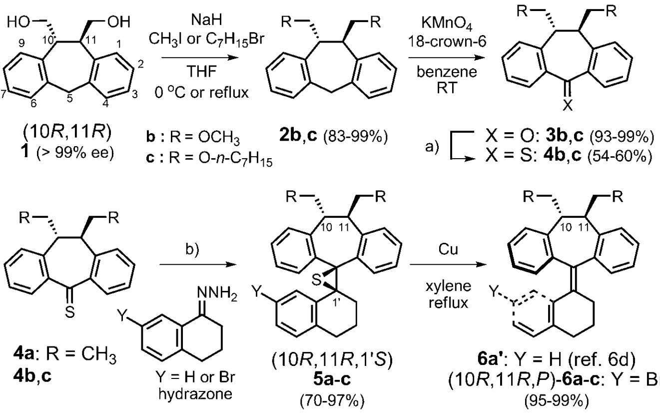
As an extension of our ongoing program on the uses of C_2-symmetric, 10,11-diethyl-dibenzosuberane (DBS)-based helicene **6a′** as chirochromic liquid-crystal (LC) optical switches,[6d–f] we decided to examine helicenes **6b**,**c**, which possess methoxymethyl (MOM) or *n*-heptoxymethyl (HOM) groups at both C10 and C11 positions of the seven-membered DBS template. The preferred conformation of these two substituents (pseudo bisequatorial vs. pseudo bisaxial) in the DBS template may be altered with increasing sterics from ethyl to MOM and HOM. To understand the conformational effects of the C10 and C11 appendages on photoswitching selectivity, helicenes **6b**,**c** with a common 7-bromo-α-tetralin-based bottom fragment were designed and compared with the corresponding 10,11-diethyl analogue **6a**.



6a′: R = CH_3, Y = H
6a : R = CH_3, Y = Br
6b : R = OCH_3, Y = Br
6c : R = O-*n*-C_7H_{15}, Y = Br

Results and Discussion

The synthetic route for helicenes **6a–c** is shown in Scheme 1. Optically pure, C_2-symmetric dihydroxymethyl-substituted DBS (10*R*,11*R*)-**1** was utilized as a precursor for the corresponding (10*R*,11*R*)-dialkoxymethyl-DBS-5-thiones **4b** and **c**. To derivatize the alcohol moieties into two different alkoxy appendages, the diol **1** was subjected to William-



Scheme 1. Synthesis of (10*R*,11*R*,*P*)-helicenes **6a** (R = CH_3) and **6b**,**c** (R = OCH_3 and O-*n*-C_7H_{15}). a) $[CH_3OC_6H4P(S)S]_2$, toluene, reflux; b) hydrazone, $Ag_2O/MgSO_4$, KOH/MeOH, CH_2Cl_2, −20 to 0 °C.

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son's ether synthesis in 83–99 % yields by treatment with methyl iodide or *n*-heptyl bromide in THF in the presence of NaH. The C5-methylene unit in the DBS template in **2b** and **c** was readily oxidized at ambient temperature to the corresponding ketones **3b** and **c** in 93–99 % yields by $KMnO_4$ solvated in benzene by using [18]crown-6 as a phase-transfer reagent. (10*R*,11*R*)-Dialkoxymethyl-DBS-5-thiones **4b** and **c** were generated by thiation of the corresponding ketones **3b** and **c** with Lawesson's reagent. Treatment of in situ generated diazo compounds arising from 7-bromo-α-tetralone-derived hydrazone with respective thioketones **4b** and **c** in a 1,3-dipolar cycloaddition fashion and subsequent extrusion of molecular nitrogen led to the corresponding episulfides **5b** and **c** in 70–97 % yields. The corresponding (10*R*,11*R*)-diethyl analogue **5a** was made similarly from thione **4a**.[6d] Their reductive desulfurization by Cu powder in xylene at reflux led to the respective, axially dissymmetric helicenes **6a–c** in 95–99 % yields.

The absolute stereochemistry at C1′ for optically pure (10*R*,11*R*)-MOM-DBS-based episulfide **5b** was found to be *S*, as determined by X-ray crystallographic analysis (Figure 1 a). On the other hand, single crystals from racemic (10*S**,11*S**,1′*R**)-**5b** and the corresponding (10*S**,11*S**,*M**)-MOM-DBS-based helicene **6b** were found to be suitable for X-ray diffraction analyses. In accordance with our expectation, the relative stereochemistry at C1′ for episulfide (10*S**,11*S**)-**5b** was found to be *R** (Figure 1 b), which can lead to the corresponding helicene (10*S**,11*S**)-**6b** of relative *M** helicity (Figure 1 c) after reductive desulfurization of **5b** with complete chirality transfer. Consequently, the absolute helical chirality of optically pure (10*R*,11*R*)-MOM-DBS-based helicene **6b** should be *P*, which results from stereospecific chirality transfer from optically pure (10*R*,11*R*,1′*S*)-episulfide **5b**. Since optically pure helicenes (10*R*,11*R*)-**6a** and **6c** show the same exciton chirality in their CD spectra, we conclude that **6a–c** share the same (*P*)-helical chirality.[12]

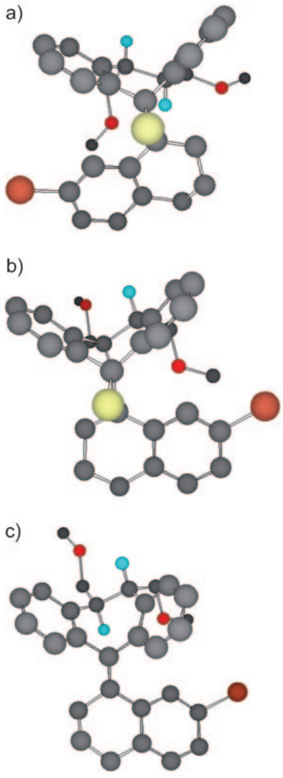


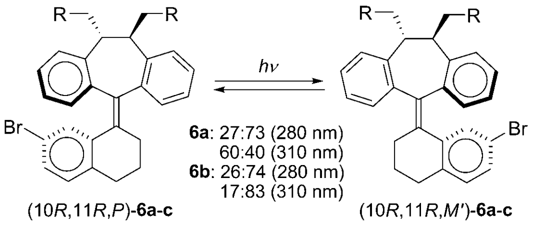
Figure 1. Chem 3D presentation for the X-ray crystal structures of a) (10*R*,11*R*,1′*S*)-**5b**; b) (10*S**,11*S**,1′*R**)-**5b**, and c) (10*S**,11*S**,*M**)-**6b**. Only axial hydrogen atoms in the DBS template are shown for clarity.

To judiciously choose two different irradiation wavelengths to achieve photochemical switching between two diastereomeric helicenes of complementary helicity, the individual UV/Vis and difference spectra with discernible extinction coefficient changes ($\Delta\varepsilon$) need to be identified. This information allows the relative abundance of the photostationary state (pss) of a given irradiation wavelength to be assessed. The diastereomeric excess (*de*) of the pss at a given irradiation wavelength is given by $[de]_{\mathrm{pss}}=(P-M')/(P+M')=[(\varepsilon_{M'}\Phi_{M'\rightarrow P}-\varepsilon_{P}\Phi_{P\rightarrow M'})/(\varepsilon_{M'}\Phi_{M'\rightarrow P}+\varepsilon_{P}\Phi_{P\rightarrow M'})]$. The $[de]_{\mathrm{pss}}$ at a given wavelength can often be directly determined by the extinction coefficient difference under the conditions at which the photoisomerization quantum yields ($\Phi_{M'\rightarrow P}$ and $\Phi_{P\rightarrow M'}$) for both processes remain similar. Therefore, to effect efficient switching in a highly selective manner, irradiation is better targeted at regions with significant changes in the extinction coefficients.

Due to lack of any UV/Vis spectral information for the corresponding (10*R*,11*R*,*M*′) diastereomers, photoisomerizations by irradiation at 280 and 310 nm were first selected for (10*R*,11*R*,*P*)-helicenes **6a–c** based on our previous experience on the diethyl system, (10*R*,11*R*,*P*)-**6a′**.[6d] Unfortunately, helicene (10*R*,11*R*,*P*)-**6a** shows only moderate switching selectivities at 280 (*P*/*M*′, 27:73) and 310 nm (*P*/*M*′, 60:40) in hexane (Table 1). Notably, the pss compositions at both wavelengths can also be reached by starting from pure (10*R*,11*R*,*M*′)-**6a**. In marked contrast, the pss composition (*P*/*M*′, 70:30) upon irradiation of (10*R*,11*R*,*P*)-**6a′** at 310 nm in hexane could not be attained by starting from pure (10*R*,11*R*,*M*′)-**6a′** due to its low phtoisomerization efficiency.[6d] The results suggest the potential heavy atom effect of the C7-bromo substituent in **6a** on photoisomerization efficiency by enhanced spin–orbit perturbation.[13]

On the other hand, heliecenes (10*R*,11*R*,*P*)-**6b** and **c** were found to be photoswitchable, but only in favor of the (10*R*,11*R*,*M*)-**6b** and **c** isomers (*P*/*M*′, 26:74–17:83 and 50:50–5:95, respectively) in hexane at both irradiation wavelengths (Table 1, entries 1 and 3). Notably, the photoisomerization diastereoselectivities at 280 nm were increased significantly by increasing the sterics of the C10 and C11 substituents from MOM to HOM presumably due to conformational flip of the substituents from the pseudo-bisequatorial to the pseudo-bisaxial position. The conformational flips of the substituents in **6b** and **c** were found to be facile on the NMR timescale in solution in ^{1}H NMR spectrometry measurements.[12] Diastereomer (*M*′)-**6c** thus obtained by photoisomerization of (*P*)-**6c** at 280 nm in hexane was separated in a pure form by column chromatography.

Table 1. Diastereoselective photoisomerization by irradiation of (10*R*,11*R*,*P*)-**6a**–**c** in different solvents with varying wavelengths.



Entry	Solvent	λ [nm][a]	d.r. (P:M'-**6c**)[b] [%]	*de*[c] [%]
1	hexane	280	5:95	−90
2	hexane	290	≤1:≥99	−98
3	hexane	310	50:50	0
4	hexane	330[d]	90:10	+80
5	CH_2Cl_2	290	10:90	−80
6	CH_2Cl_2	330	82:18	+64
7	cyclohexane	290	8:92	−84
8	cyclohexane	330	85:15	+70
9	toluene	290	12:88	−76
10	toluene	330	80:20	+60

[a] Irradiation time is 1 h unless otherwise stated. [b] Determined by HPLC analysis on Chiralpak OT(+) column at 249 nm (which shows an isosbestic point of these two diastereomers) detection wavelength. [c] Defined as (P-M'-**6c**)/(P+M'-**6c**). [d] Irradiation time is 40 min.

The photoisomerization quantum yields, $\Phi_{P\rightarrow M'}$ and $\Phi_{M'\rightarrow P}$, for **6c** are 0.33 and 0.35, respectively. These two values are somewhat larger than those of **6a**,**b** ($\Phi_{P\rightarrow M}$ and $\Phi_{M\rightarrow P} \leq 0.30$). Since the photoisomerization quantum yields ($\Phi_{M'\rightarrow P}$ and $\Phi_{P\rightarrow M'}$) stay similar in all cases, the differences in extinction coefficients between the *P* and *M′* isomers (i.e., $\Delta\varepsilon$) govern the *de* values of the photoisomerization events. Apparently, the steric effect of the C10 and C11 substituents affected the preferred conformations of the DBS templates in **6a**–**c** and thus the extinction coefficient differences of the diastereomeric helicenes. In the case of **6b**, the UV/Vis difference ($\varepsilon_{M'}-\varepsilon_{P}$) spectrum showed only a positive difference with two maximum values of around 275 and 330 nm, respectively.[12] Therefore, no complementary photoswitching events could be accessed. Conversely, by subtracting the UV/Vis spectrum of (*M′*)-**6c** from that of (*P*)-**6c**, we were able to locate a couple of wavelengths (290 and 330 nm) with opposite difference in extinction coefficients and a couple of isosbestic points (249 and 307 nm) (Figure 2a). Notably, the pss compositions upon irradiation at 280 and 310 nm could also be reached by starting from pure (*M′*)-**6c** within a similar timeframe; these are consistent with the similar photoisomerization efficiencies observed for both diastereomers.

Upon irradiation of a solution of (*P*)-**6c** in degassed hexane at 290 nm led to almost exclusive formation of the opposite diastereomer (*M′*)-**6c**, as evidenced by HPLC analysis on a Chiralpak OT(+) column at 249 nm (an isosbestic point) detection wavelength (Table 1, entry 2). In CD stacked plots, the exciton chirality couplet at 193 and 208 nm is inverted from negative to positive, indicating a reversal of helical chirality (Figure 2b).[14] As revealed in the stacked plots, there are two isodichroic points at 199 and 257 nm, respectively. Their presence strongly implies that the newly generated product (i.e., (*M′*)-**6c**) is the only homogeneous species in solution and has similar photochromic properties as in (*P*)-**6c**.

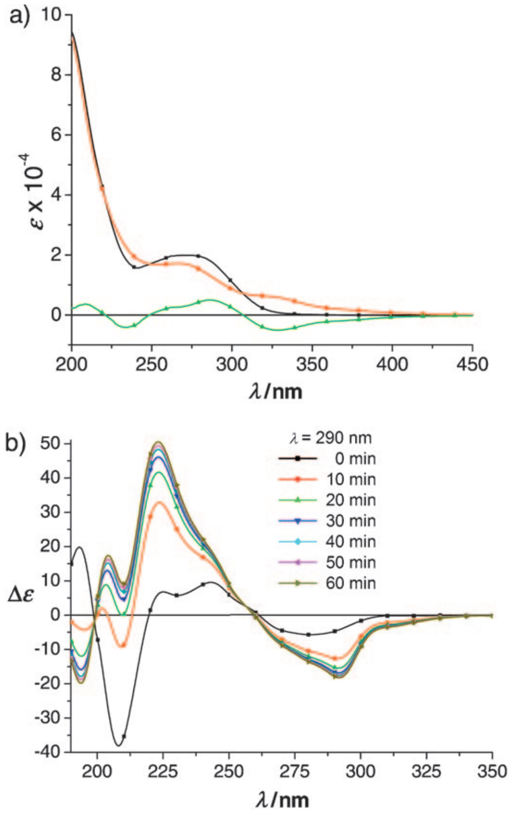


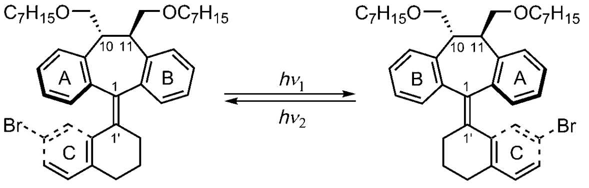
Figure 2. a) UV spectra of (10*R*,11*R*,*P*)-**6c** (black) and (10*R*,11*R*,*M′*)-**6c** (red), and the UV difference spectrum (green) in hexane; b) CD stacked plots of (10*R*,11*R*,*P*)-**6c** (10 μM) in hexane at 25 °C under UV irradiation (290 nm at 0, 10, 20, 30, 40, 50, 60 min).

Preferential return of (*M′*)-**6c** to (*P*)-**6c** can be effected upon irradiation of (*M′*)-**6c** at 330 nm. A pss consisting of 90 % (*P*)-**6c** was reached after 40 min, as evidenced by HPLC analysis (Table 1, entry 4). The photoinduced switching processes at 290 and 330 nm, respectively, amount to a 178 % difference in *de* (from ≥−98 to +80 %). The extinction coefficients at 307 nm for (*P*)-**6c** and (*M′*)-**6c** are nearly identical; irradiation of either diastereomers of **6c** at 310 nm in degassed hexane has led to a pss with an almost equal composition of (*P*)-**6c** and (*M′*)-**6c** (Table 1, entry 3). The results of several photoisomerization experiments for either diastereomers of **6c** in various solvents are compiled in Table 1. Similar switching profiles with selectivities in the range of 12:88–8:92 (*P*/*M′*) at 290 nm and 80:20–85:15 (*P*/*M′*) at 330 nm were observed in CH_2Cl_2, cyclohexane, and toluene (Table 1, entries 5–10).

To gain insights into the origin of the highly diastereoselective photoswitching efficiency of **6c**, molecular simulations of (*P*)-**6c** and (*M′*)-**6c** with conformational permutations of the DBS were carried out by using the QuantumCache program on MOPAC2000-AM1. The minimized energies and three appropriate phenyl torsional angels for (*P*)-

6c and (*M*′)-**6c** are compiled in Table 2. Notably, the DBS with the pseudoequatorially and pseudoaxially oriented *n*-heptoxymethyl groups constitute the more stable conformations for (*P*)-**6c** and (*M*′)-**6c**, respectively (Table 2 and Scheme 2). In addition, the relative stability for either conformations of (*P*)-**6c** or (*M*′)-**6c** seems to correlate with the phenyl torsion ($|\phi_1+\phi_3|$) between ring A and ring C. Namely, the larger torsional angle between the upper and lower phenyl rings, the higher the energy.

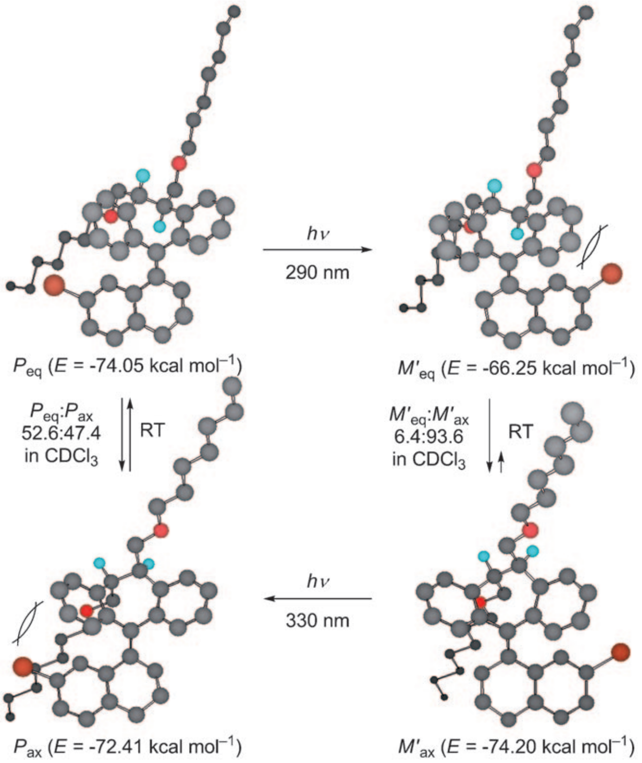
Table 2. Minimized energies and three appropriate phenyl torsional angles for (*P*)-**6c** and (*M*′)-**6c**.



(10*R*,11*R*,*P*)-**6c** **diastereomeric** (10*R*,11*R*,*M*′)-**6c**

	E [kcal mol^{-1}]	ϕ_1 (A and C1=C1′)[a]	ϕ_2 (B and C1=C1′)[b]	ϕ_3 (C and C1′=C1)[c]	$\|\phi_1+\phi_3\|$
P_{eq}	−74.1	58.3	−67.8	31.6	89.9
P_{ax}	−72.4	64.2	−54.4	36.6	100.8
M'_{eq}	−66.3	−68.0	66.8	−36.1	104.1
M'_{ax}	−74.2	−51.1	69.8	−33.3	84.4

[a] ϕ_1 means the phenyl torsion between ring A and the central double bond. [b] ϕ_2 means the phenyl torsion between ring B and the central double bond. [c] ϕ_3 means the phenyl torsion between ring C and the central double bond.



Scheme 2. Proposed photoswitching cycle between (*P*)-**6c** and (*M*′)-**6c**.

As shown in Scheme 2, compound (*P*)-**6c** preferentially adopts a DBS conformation (P_{eq}, $E=-74.1$ kcal mol^{-1}) with pseudoequatorially disposed *n*-heptoxymethyl groups. The conformation (P_{ax}, $E=-72.4$ kcal mol^{-1}) with the flipped DBS ring is clearly less favored (by 1.6 kcal mol^{-1}) in view of the larger $|\phi_1+\phi_3|$ (increased by 10.9°) and the increased steric repulsion between the C ring and the proximal pseudoaxial *n*-heptoxymethyl group. On the other hand, adoption of the same DBS conformation for (*M*′)-**6c** (M'_{eq}, $E=-66.3$ kcal mol^{-1}) would impose a larger phenyl distortion for $|\phi_1+\phi_3|$ (104.1°) by 14.2° beside the steric interaction between ring C and the proximal pesudoaxial hydrogen. The unfavorable phenyl and steric strains can be relieved in M'_{eq} by a conformational inversion leading to M'_{ax} ($E=-74.2$ kcal mol^{-1}) in which the $|\phi_1+\phi_3|$ is reduced by almost 20° and the ring C is now *anti* to the proximal, axial *n*-heptoxymethyl group. Therefore, we surmise that P_{eq} and M'_{ax} are the predominant species in solution (i.e., hexane[15]) for (*P*)-**6c** and (*M*′)-**6c**, respectively. On the basis of this presumption, photoisomerization of P_{eq} would involve its initial double-bond rotation in a counterclockwise fashion leading to M'_{eq} followed by a facile conformational flip leading to M'_{ax}. Inverse photoisomerization of M'_{ax} would involve an initial double-bond rotation in a clockwise fashion leading to P_{ax} followed by a facile conformational flip leading to the thermal equilibrium of P_{ax} and P_{eq}. Consequently, the helical shape of **6c** can be controlled by the conformation of DBS and the thermal conversion from the less stable to the more stable conformer might be expected.

Doping a reasonable amount (1–10 wt %) of chiral dopant (10*R*,11*R*,*P*)-**6b** into a nematic LC host did not lead to an observable cholesteric LC phase due to its poor solubility in the nematic LC. Subsequently, we tried to utilize (10*R*,11*R*,*P*)-**6c**, which possesses two *n*-heptoxymethyl chains, as a chiral dopant. As expected, doping (10*R*,11*R*,*P*)-**6c** (1 wt %) into a nematic LC host (E7 mixture[12]) led to a phase change to a cholesteric LC phase. The reciprocal of the helical pitch (*p*) of a cholesteric mesophase is proportional to the product of optical purity γ, helical twisting power β_M, and concentration *C* of the chiral dopant (i.e., (10*R*,11*R*,*P*)-**6c**) according to the Equation (1):

$$p^{-1}=\beta_M C\gamma \qquad (1)$$

The helical sense of the induced cholesteric mesophase in (10*R*,11*R*,*P*)-**6c** was found to be positive by means of the contact method.[16] The homogeneous mixture was capillary filled into a Cano's wedge cell. The resulting, induced Cano's lines were observed at 25 °C under a polarized optical microscope. The helical pitch, *p*, of the induced cholesteric mesophase is 13.9 μm, as calculated by Cano's wedge method,[17] and the β_M is +7.2 μm^{-1}, as calculated by Equation (1). To gain insights into the photoswitching efficiency of **6c** directly in the LC mesophase, the wedge cell containing 1 wt % of (10*R*,11*R*,*P*)-**6c** in E7 was irradiated at 290 nm for 3 h. A distinct decrease in *p* value from 13.9 to 8.2 μm (corresponds to a β_M value of −12.1 μm^{-1}) resulted, as evidenced by a variation in the distance between two consecutive Cano's lines (panel **A** to **B**, Figure 3). Upon irradiation of the same cell at 330 nm for 2 h, the *p* value reverts back to 16.3 μm (panel **B** to **C**) and the corresponding β_M was +6.1 μm^{-1}. Irradiation of either cell at 310 nm for 3 h led to a nearly nematic phase (panel **D**). Alternate irradiation with these three different wavelengths resulted in photomodulation of the pitch, reversal, and turn off of the helical handedness in the induced mesophase.

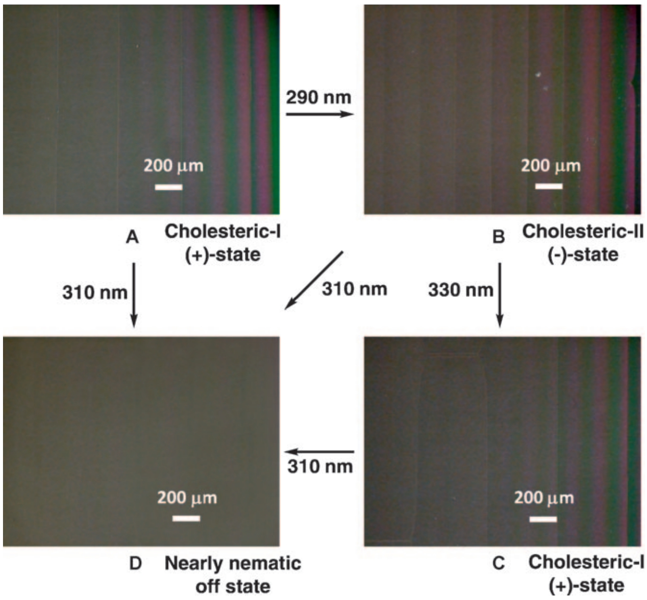


Figure 3. Polarized optical photomicrographs (40× magnification) of 1 wt% (10*R*,11*R*,*P*)-**6c** dissolved in E7 at 25 °C in a wedge cell (**A**: the initial state; **B**: after irradiation at 290 nm of **A** for 3 h; **C**: after irradiation of **B** at 330 nm for 2 h; **D**: after irradiation at 310 nm for 3 h).

Conclusion

We have documented a series of helicenes with C_2-symmetric, 10,11-disubstituted-DBS templates and a common 7-bromo-α-tetralin-based bottom fragment. The absolute stereochemistry was determined to be 10*R*,11*R*,*P* after retentive chirality transfer from the corresponding (10*R*,11*R*,1′*S*)-episulfides. Highly diastereoselective, chirochromic photoswitchings can be effected in a reversible manner by increasing the sterics of the pendant C10, C11 substituents from ethyl, MOM, to HOM with concomitant conformational flips, as evidenced by CD and HPLC trace experiments. Nematic LC E7 doped with **6c** led to cholesteric mesophases with modulated pitches (i.e., modulated colors of a refractive light), complementary handedness, and with a memory of ternary logic. Molecular simulations of (*P*)-**6c** and (*M*′)-**6c** with both DBS conformations suggest that the selectivities of photoswitching are controlled by the conformation of the top DBS template, as evidenced by their ^{1}H NMR spectra.

Experimental Section

General: ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance 500 (500 MHz ^{1}H, 125 MHz ^{13}C), Bruker Avance 400 (400 MHz ^{1}H, 100 MHz ^{13}C), and Varian Gemini-2000 (200 MHz ^{1}H, 50 MHz ^{13}C) spectrometers in deuterochloroform with chloroform as an internal reference unless otherwise stated. Infrared spectra were recorded on a Perkin–Elmer Paragon-500 FTIR spectrometer. Mass spectra were recorded on a Finnigan TSQ-700 spectrometer with an ionization voltage of 70 or 20 eV. High-resolution mass spectra were recorded on a Finnigan MAT 95S spectrometer. X-ray structures were measured on Nonius CAD4 or Bruker Nonius Kappa CCD instrument. Combustion analyses were performed on a Heraeus VarioEL III-NCSH analyzer by the Northern Instrument Center of Taiwan. Melting points were determined on a Hargo MP-2D melting point apparatus and are uncorrected. Analytical TLC was performed on Merck silica gel plates with QF-254 indicator. Visualization was accomplished with UV light, phosphomolybdic acid (PMA), and $KMnO_4$. Column (flash) chromatography was performed by using 32–63 μm silica gel. Absorption spectra (hexane) were measured on a HP-8453 Diode Array spectrometer by using spectrophotometric grade solvents. Solvents used for recrystallization were of spectral grade unless otherwise indicated. Solvents used for extraction and chromatography were reagent grade. Analytical high-pressure liquid chromatography (HPLC) was performed on a Jasco Liquid Chromatograph equipped with PU-980 pumps, UV-975 detector, and 807-IT integrator. The columns used were Daicel Chiralpak OT(+) and OJ columns. The flow rate, solvent systems, and detector wavelength were as denoted. Optical rotation were obtained on a Jasco DIP-1000 Digital Polarimeter at room temperature and reported as follows: $[\alpha]_D$, concentration (c = g/100 mL), and solvent. UV/Vis spectra were recorded on a HP-8453 Diode Array UV/Vis spectrometer in hexane unless otherwise noted. CD spectra were recorded on a Jasco model J-715 spectropolarimeter. All reagents were purchased from Acros, Aldrich, and TCI with purification in advance before use. Solvents for extraction and chromatography were reagent grade. Dichloromethane, MeOH, and xylene were dried over CaH_2 before use. Benzene, THF, and toluene were dried over Na with benzophenone-ketyl intermediate as indicator. Photoirradiation in solution was performed by irradiation of a sample (10 μM in solvent) in a sealed 1 cm pathlength quartz cuvette with an 300 W Oriel 66901 Xe-lamp attached to an Oriel 74100 Cornerstone 260 1/4 M monochromator. Photostationary states (pss) were ensured by monitoring composition changes in time by taking CD spectra at distinct intervals until no changes were observed. Ratios of the different isomers of the optical switches were determined by HPLC with the detector wavelength at a given isosbestic point. Photoisomerization in liquid crystal E7 was performed with the same light source. Cano's lines were observed by using Cano wedge-type cells (EHC, KCRK-07, $\tan\theta = 0.0183$), an Olympus BX 50-P polarized optical microscope equipped with a Toshiba CCD color video camera, and a Mettler FP82HT hot stage attached to a Mettler FP90 central processor.

Compound 2b:[18] 60% NaH (0.16 g, 6.8 mmol) was added to a 25 mL, two-necked, round-bottomed flask equipped with an N_2 inlet and septum. The NaH was washed with anhydrous hexane (3×6 mL) and dried under vacuum and then suspended in anhydrous THF (10 mL). The suspended solution was cooled to 0 °C and then treated with a solution of diol (10*R*,11*R*)-**1**[19] (0.22 g, 0.9 mmol) in anhydrous THF (6 mL) through a cannula. After having been stirred for 4 h at 0 °C, the reaction mixture was treated with freshly distilled CH_3I (1.92 g, 13.5 mmol) through a microsyringe. The resulting reaction mixture was stirred at ambient temperature for 12 h and then quenched by the addition of a saturated aqueous solution of NH_4Cl (30 mL). The aqueous layer was separated and extracted with diethyl ether (3×25 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude oil was purified by column chromatography (EtOAc/hexane, 1:7) to give **2b** as a yellowish oil(0.24 g, 99%). $R_f = 0.45$ (EtOAc/hexane, 1:7); $[\alpha]_D^{25} = +10$ ($c = 0.1$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.25$–7.15 (m, 8H), 4.20 (s, 2H), 3.68 (dd, $J = 5.2$, 1.4 Hz, 2H), 3.58–3.47 (m, 4H), 3.31 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.6$, 138.1, 131.5, 129.4, 126.5, 126.4, 75.4, 58.7, 45.4, 42.2 ppm; IR ($CDCl_3$): $\tilde{\nu} = 3066$, 3020, 2924, 2358, 2335, 2245, 1486, 1458, 1385, 1193, 1113 cm^{-1}; MS (70 eV): *m/z* (%): 282 (6) [M^+], 250 (43), 205 (100), 191 (55), 178 (32); elemental analysis calcd (%) for $C_{19}H_{22}O_2$: C 80.82, H 7.85; found: C 80.77, H 7.85.

Compound 3b:[20] $KMnO_4$ (0.30 g, 1.9 mmol) in benzene (3 mL) was added to a 25 mL, two-necked, round-bottomed flask equipped with an N_2 inlet and septum. A solution of dicyclohexano[18]crown-6 (0.50 g, 1.9 mmol) in benzene (2 mL) was added. The solution became homogeneous and purple. A solution of **2b** (0.22 g, 0.76 mmol) in benzene (3 mL) was added to this mixture. The resulting mixture was stirred at ambient temperature for 3 h and then passed through a short pad of Celite with diethyl ether/hexane (1:3) as eluent. The filtrate was concentrated to give **3b** as a transparent oil (0.21 g, 93 %). $R_f = 0.25$ (EtOAc/hexane, 1:7); $[\alpha]_D^{25} = +175$ ($c = 0.1$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.07$ (dd, $J = 7.9$, 1.4 Hz, 2H), 7.47 (td, $J = 7.4$, 1.5 Hz, 2H), 7.37 (td, $J = 7.8$, 1.3 Hz, 2H), 7.31 (dd, $J = 7.5$, 1.1 Hz, 2H), 3.69–3.64 (m, 2H), 3.41 (dd, $J = 9.5$, 5.7 Hz, 2H), 3.28 (t, $J = 9.2$ Hz, 2H), 3.15 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 193.8$, 138.7, 137.9, 132.6, 131.7, 130.8, 127.2, 75.5, 58.6, 46.6 ppm; IR($CDCl_3$): $\tilde{\nu} = 3066$ (w), 2975 (s), 2930 (s), 2874 (s), 1650 (s), 1639 (s), 1605 (m), 1453 (m), 1385 (m), 1294 (s), 1243 (m), 1193 (m), 1107 (s); MS (70 eV): *m/z* (%): 296 (7) [M^+], 268 (48), 220 (81), 178 (100), 165 (33), 152 (20); HRMS: *m/z* calcd for $C_{19}H_{20}O_3$: 296.1407; found: 296.1424.

Compound 4b:[21] $[CH_3OC_6H_4P(S)S]_2$ (1.30 g, 3.2 mmol) in anhydrous toluene (5.0 mL) was added to a 50 mL, two-necked, round-bottomed flask fitted with a condenser topped with an N_2 inlet and septum. A solution of **3b** (0.64 g, 2.2 mmol) in anhydrous toluene (20 mL) was added through a cannula. The reaction mixture was heated at reflux for 15 h and then passed through a short column of neutral alumina (40 mm × 5 cm) by using EtOAc/hexane (1:5) as eluent. The filtrate was collected and concentrated. The crude product was recrystallized from hexane to give **4b** as a blue solid (0.40 g, 60 %). $R_f = 0.3$ (EtOAc/hexane, 1:7) $[\alpha]_D^{25} = -120$ ($c = 0.1$ in hexane); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.90$ (dd, $J = 7.8$, 1.3 Hz, 2H), 7.40 (td, $J = 7.5$, 1.4 Hz, 2H), 7.24 (dd, $J = 7.9$, 1.3 Hz, 2H), 7.19 (td, $J = 7.7$, 1.1 Hz, 2H), 3.65–3.59 (m, 2H), 3.51 (dd, $J = 9.6$, 5.7 Hz, 2H), 3.36 (t, $J = 9.2$ Hz, 2H), 3.22 ppm (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 148.1$, 134.1, 131.4, 131.2, 131.0, 126.8, 74.6, 58.7, 46.1 ppm; IR ($CDCl_3$): $\tilde{\nu} = 3688$, 3598, 3067, 2988, 2925, 2898, 2824, 1599, 1480, 1446, 1378, 1299, 1277, 1192, 1113, 1028 cm^{-1}; MS (70 eV): *m/z* (%): 312 (84) [M^+], 279 (20), 267 (88), 235 (100), 209 (87), 202 (56), 165(39).

Compound 7: 7-Bromo-α-tetralone (0.23 g, 1.0 mmol) in anhydrous ethanol (14 mL) was added to a 25 mL, two-necked, round-bottomed flask fitted with a Dean–Stark trap. Hydrazine monohydrate (0.9 mL, 18.0 mmol) was added and the whole mixture was heated at reflux for 2 h. After cooling, the mixture was concentrated under reduced pressure to yield hydrazone **7** quantitatively a as pale yellow solid. $R_f = 0.35$ (EtOAc/hexane, 1:2); M.p. 60–62 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 8.07$ (d, $J = 2.2$ Hz, 1H), 7.27 (dd, $J = 8.2$, 2.1 Hz, 1H), 6.95 (d, $J = 8.1$ Hz, 1H), 5.36 (br, 2H), 2.65 (t, $J = 5.9$ Hz, 2H), 2.42 (t, $J = 6.6$ Hz, 2H), 1.91–1.86 ppm (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 145.4$, 137.0, 135.3, 130.3, 129.8, 126.6, 120.2, 29.0, 23.3, 21.1 ppm; MS (20 eV): *m/z* (%): 240 (29), 238 (30) [M^+], 228 (19), 226 (100), 224 (86), 211 (18), 210 (36), 208 (38), 199 (19), 198 (59), 196 (58), 171 (12), 170 (34), 168 (34), 160 (16), 147 (23), 145 (21), 142 (17); HRMS: *m/z* calcd for $C_{10}H_{11}BrN_2$: 238.0100; found: 238.0113.

Compound 5a:[22] Hydrazone **7** (478.2 mg, 2 mmol) in anhydrous CH_2Cl_2 (20 mL) was added to a 50 mL, two- necked, round-bottomed flask fitted with a Schlenk filtration tube and septum. The solution was cooled to −30 °C, whereupon $MgSO_4$ (1.31 g, 10.9 mmol), Ag_2O (0.69 g, 3 mmol), and a saturated solution of KOH in methanol (1.57 mL) were successively added. After having been stirred for 40 min, the resulting deep red solution was filtered into another ice-cooled flask, and the remaining residue was washed with CH_2Cl_2 (3 mL). A solution of thioketone **4a**[6d] (201.7 mg, 0.72 mmol, 0.1 M in CH_2Cl_2) was added dropwise by a syringe to the collected solution. Evolution of nitrogen was observed, and the deep red solution slowly decolored. After having been stirred for 9 h, the resulting reaction mixture was quenched by adding a saturated aqueous solution of $NaHCO_3$ (15 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography (hexane) to give **5a** as a white solid (341.5 mg, 97 %). $R_f = 0.3$ (hexane); $[\alpha]_D^{25} = -1080$ ($c = 0.03$ in *i*PrOH); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.03$ (dd, $J = 9.2$, 2.6 Hz, 1H), 7.51 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.29–7.11 (m, 7H, Ar), 6.96–6.89 (m, 2H, Ar), 3.11 (td, $J = 11.0$, 4.0 Hz, 1H), 2.89–2.82 (m, 2H), 2.50–2.25 (m, 3H), 2.10–1.86 (m, 4H), 1.75–1.56 (m. 1H), 1.08 (t, $J = 7.4$ Hz, 3H), 0.82–0.59 (m, 1H), 0.45 ppm (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (50 MHz, $CDCl_3$): $\delta = 145.5$, 140.5 139.1, 138.4, 137.8, 137.1, 132.2, 131.9, 130.3, 129.7, 128.0, 127.54, 127.46, 126.11, 126.07, 125.8, 119.2, 71.5, 57.3, 51.5, 44.1, 38.9 30.7, 29.5, 22.9, 22.0, 12.5, 11.3 ppm; IR (CCl_4): $\tilde{\nu} = 3064$, 2935, 2875, 2360, 2340, 1741, 1478, 1087, 1047, 1020, 921 cm^{-1}; MS (70 eV): *m/z* (%): 490 (26), 489 (19) [M^+], 488 (23), 456 (86), 429 (62), 427 (71), 348 (34), 319 (19), 308 (35), 303 (41), 289 (31), 258 (40), 256 (94), 247 (85), 226 (69), 219 (100), 203 (61), 192 (93), 178 (58), 160 (63); HRMS: *m/z* calcd for $C_{29}H_{29}BrS$: 488.1173; found: 488.1186.

Compound 6a: A solution of episulfide **5a** (200 mg, 0.41 mmol) and copper powder (262 mg, 4.1 mmol) in anhydrous xylene (5 mL) was added to a 25 mL, two-necked, round-bottomed flask fitted with a condenser topped with an N_2 inlet and septum. The resulting reaction mixture was heated at reflux for 2 h, then passed through a filter, and concentrated. The crude product was purified by column chromatography (hexane) to give **6a** as a white solid (187 mg, 100 %). $R_f = 0.35$ (hexane); $[\alpha]_D^{25} = +137$ ($c = 0.02$ in *i*PrOH); ^{1}H NMR (400 MHz, $CDCl_3$): major conformer: $\delta = 7.19$–6.68 (m, 11H, Ar), 3.19–3.12 (m, 1H), 2.87–2.64 (m, 3H), 2.23–1.68 (m, 8H), 0.99 (t, $J = 8.0$ Hz, 3H), 0.69 ppm (t, $J = 8.0$ Hz, 3H); minor conformer: $\delta = 7.19$–6.68 (m, 11H, Ar), 3.01–2.96 (m, 2H), 2.56–2.43 (m, 2H), 2.23–1.68 (m, 8H), 0.91 (t, $J = 8.0$ Hz, 3H), 0.86 ppm (t, $J = 8.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): major conformer: $\delta = 145.4$, 142.7, 141.6, 139.5, 139.3, 138.8, 138.3, 133.3, 132.5, 132.2, 130.7, 129.9, 128.14, 128.12, 127.4, 127.2, 126.74, 126.70, 126.0, 118.8, 50.2, 45.4, 28.8, 28.4, 27.8, 24.3, 23.0, 12.1, 9.2 ppm; minor conformer: $\delta = 147.1$, 142.1, 141.2, 139.4, 139.4, 138.7, 138.4, 133.3, 132.5, 130.9, 130.4, 130.0, 129.3, 127.4, 127.2, 127.1, 126.64, 126.61, 126.1, 118.6, 51.0, 45.1, 29.2, 28.8, 28.5, 24.3, 22.9, 12.2, 10.2 ppm; IR (CCl_4): $\tilde{\nu} = 3063$, 2962, 2932, 2867, 1942, 1911, 1597, 1558, 1507, 1481, 1437, 1260, 1109, 1074 cm^{-1}; MS (70 eV): *m/z* (%): 459 (19), 458 (74), 457 (23) [M^+], 456 (75), 427 (54), 349 (12), 348 (44), 303 (28), 289 (38), 247 (100), 219 (87), 191 (70), 178 (34), 129 (19), 128 (31), 91 (23); HRMS: *m/z* calcd for $C_{29}H_{29}Br$: 456.1453; found: 456.1439; HPLC: $t_R = 10.83$ min (Chiralpak AD, hexane, 0.5 mL min^{-1}, $\lambda = 254$ nm).

Compound 5b: Hydrazone **7** (80 mg, 0.3 mmol) in anhydrous CH_2Cl_2 (10 mL) was added to a 50 mL, two- necked, round-bottomed flask fitted with a Schlenk filtration tube and septum. The solution was cooled to −20 °C, whereupon $MgSO_4$ (220 mg, 1.8 mmol), Ag_2O (0.12 g, 0.5 mmol), and a saturated solution of KOH in methanol (0.3 mL) were successively added. After having been stirred for 12 h, the resulting deep red solution was filtered into another ice-cooled flask, and the remaining residue was washed with CH_2Cl_2 (5 mL). A solution of thioketone **4b** (102 mg, 0.3 mmol, 0.1 M in CH_2Cl_2) was added dropwise by a syringe to the collected solution. Evolution of nitrogen was observed, and the deep red solution slowly decolored. After having been stirred for 16 h, the resulting reaction mixture was quenched by adding a saturated aqueous solution of $NaHCO_3$ (15 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography (EtOAc/hexane, 1:10) to give **5b** as a white solid (132 mg, 74 %). $R_f = 0.33$ (EtOAc/hexane, 1:10); $[\alpha]_D^{25} = -175$ ($c = 0.1$ in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.94$–7.90 (m, 1H), 7.42 (dd, $J = 7.6$, 1.3 Hz, 1H), 7.39 (d, $J = 7.6$ Hz, 1H), 7.23 (td, $J = 7.6$, 1.3 Hz, 1H), 7.21–7.17 (m, 2H), 7.16–7.09 (m, 2H), 7.06–7.04 (m, 1H), 7.02 (d, $J = 1.9$ Hz, 1H), 6.94 (d, $J = 8.2$ Hz, 1H), 4.00–3.92 (m, 2H), 3.50 (td, $J = 8.7$, 3.1 Hz, 1H), 3.43 (s, 3H), 3.06–2.97 (m, 2H), 2.94 (s, 3H), 2.87–2.81 (m, 1H), 2.79–2.71 (m, 2H), 2.24 (ddd, $J = 15.8$, 12.2 Hz, 4.0, 1H), 1.98–1.80 ppm (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 144.4$, 139.0, 138.6, 138.5, 138.0, 136.8, 132.5, 131.8, 131.6, 130.3, 129.7, 128.0, 127.8, 127.6, 126.57, 126.56, 126.4, 119.0, 79.4, 72.5, 70.7, 58.9, 58.5, 57.1, 45.8, 41.5, 38.6, 30.6, 22.0 ppm; IR ($CDCl_3$): $\tilde{\nu} = 3063$, 2982, 2926, 2890, 2834, 1479, 1448, 1290, 1194, 1107 cm^{-1}; MS (70 eV): *m*/*z* (%): 520 (13) [M^+], 490 (26), 457 (100), 423 (80), 418 (52), 344 (48), 315 (26), 289 (17), 234 (54), 202 (97), 189 (95), 178 (24), 128 (20), 57 (22); HRMS: *m*/*z* calcd for $C_{29}H_{29}BrO_2S$: 520.1066; found: 520.1067.

Compound 6b: A solution of episulfide **5b** (132 mg, 0.24 mmol) and copper powder (153 mg, 2.4 mmol) in anhydrous xylene (3 mL) was added to a 25 mL, two-necked, round-bottomed flask fitted with a condenser topped with an N_2 inlet and septum. The resulting reaction mixture was heated at reflux for 2 h, filtered, and concentrated. The crude product was purified by column chromatography (EtOAc/hexane, 1:15) to give **6b** as a white solid (124 mg, 100 %). $[\alpha]_D^{25}=-113$ ($c=0.1$ in hexane); $R_f=0.28$ (EtOAc/hexane, 1:15); ^{1}H NMR (400 MHz, $CDCl_3$): major conformer: $\delta=7.57$ (d, $J=1.8$ Hz, 1 H), 7.50 (d, $J=7.7$ Hz, 1 H), 7.23–7.12 (m, 5 H), 7.11–7.06 (m, 1 H), 6.96 (d, $J=8.2$ Hz, 1 H), 6.89 (t, $J=7.6$ Hz, 1 H), 6.76 (d, $J=7.7$ Hz, 1 H), 4.01 (dd, $J=9.0$, 3.8 Hz, 1 H), 3.95–3.91 (m, 1 H), 3.89–3.87 (m, 2 H), 3.83 (dd, $J=9.0$, 3.1 Hz, 1 H), 3.48 (s, 3 H), 3.36 (s, 3 H), 3.30–3.27 (m, 1 H), 2.96–2.72 (m, 3 H), 2.07–1.96 ppm (m, 3 H); minor conformer: $\delta=7.36$ (d, $J=7.8$ Hz, 1 H), 7.23–7.12 (m, 6 H), 7.11–7.06 (m, 1 H), 6.98 (d, $J=8.2$ Hz, 1 H), 6.86 (t, $J=7.6$ Hz, 1 H), 6.65 (d, $J=1.8$ Hz, 1 H), 3.88–3.86 (m, 2 H), 3.70–3.65 (m, 1 H), 3.59 (dd, $J=9.6$, 5.2 Hz, 1 H), 3.51–3.48 (m, 1 H), 3.37–3.34 (m, 1 H), 3.38 (s, 3 H), 3.25 (s, 3 H), 2.96–2.72 (m, 3 H), 2.07–1.96 ppm (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): major conformer: $\delta=144.8$, 141.6, 139.7, 139.3, 138.2, 137.7, 133.4, 131.8, 131.4, 131.2, 129.4, 129.4, 129.1, 127.0, 126.9, 126.8, 125.87, 125.85, 118.1, 77.6, 73.3, 59.4, 58.8, 46.3, 39.6, 29.5, 28.7, 23.7 ppm; minor conformer: $\delta=142.1$, 141.1, 140.7, 138.4, 137.9, 137.7, 137.2, 131.8, 131.6, 131.0, 129.7, 129.4, 127.6, 127.3, 126.4, 126.2, 126.0, 118.1, 76.2, 75.3, 59.0, 58.4, 45.9, 43.0, 29.4, 28.8, 23.4 ppm; IR ($CDCl_3$): $\tilde{\nu}=3060$, 2987, 2925, 2891, 2828, 1583, 1481, 1422, 1402, 1385, 1266, 1186, 1107 cm^{-1}; MS (70 eV): *m*/*z* (%): 488 (23) [M^+], 424 (29), 411 (45), 397 (12), 332 (46), 302 (29), 289 (19), 247 (100), 191 (42), 178 (12); elemental analysis calcd (%) for $C_{29}H_{29}BrO_2$: C 71.16, H 5.97; found: C 71.15, H 5.96.

Compound 2c: 60 % NaH (103 mg, 4.0 mmol) was added to a 25 mL, two-necked, round-bottomed flask fitted with a condenser topped with an N_2 inlet and septum. The NaH was washed with anhydrous hexane (3×5 mL) and dried under vacuum and then suspended in anhydrous THF (2 mL). The suspended solution was cooled to 0 °C and then treated with a solution of diol (10*R*,11*R*)-**1** (132 mg, 0.5 mmol) in anhydrous THF (3.7 mL) through a cannula. After having been stirred for 4 h at 0 °C, the reaction mixture was treated with freshly distilled *n*-$C_7H_{15}Br$ (1.43 g, 8.0 mmol) through a microsyringe. The resulting reaction mixture was stirred at ambient temperature for 18 h and then quenched by adding a saturated aqueous solution of NH_4Cl (40 mL). The aqueous layer was separated and extracted with diethyl ether (3×20 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude oil was purified by column chromatography (EtOAc/hexane, 1:50) to give **2c** as a yellowish oil (194 mg, 83 %). $R_f=0.31$ (EtOAc/hexane, 1:50); $[\alpha]_D^{25}=+14$ ($c=1.0$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.24$–7.13 (m, 8 H), 4.18 (s, 2 H), 3.70 (dd, $J=8.5$, 3.9 Hz, 2 H), 3.58–3.50 (m, 4 H), 3.40–3.27 (m, 4 H), 1.55–1.50 (m, 4 H), 1.33–1.29 (m, 16 H), 0.91 ppm (t, $J=6.6$ Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=138.8$, 138.4, 131.6, 129.2, 126.4, 126.2, 73.4, 71.1, 45.6, 42.2, 31.8, 29.7, 29.1, 26.1, 22.6, 14.1 ppm; IR (CH_2Cl_2): $\tilde{\nu}=3061$, 2924, 2856, 1600, 1489, 1466, 1454, 1373, 1300, 1219, 1109 cm^{-1}; MS (20 eV): *m*/*z* (%): 451 (5) [M$^+$], 334 (74), 218 (70), 205 (100), 192 (51), 178 (21), 57 (15); HRMS: *m*/*z* calcd for $C_{31}H_{46}O_2$: 450.3492; found: 450.3476; elemental analysis calcd (%) for $C_{31}H_{44}O_3$: C 82.61, H 10.29; found: C 82.70, H 10.22.

Compound 3c: $KMnO_4$ (1.19 g, 7.5 mmol) in benzene (12 mL) was added to a 25 mL, two-necked, round-bottomed flask equipped with an N_2 inlet and septum. A solution of [18]crown-6 (1.98 g, 7.5 mmol) in benzene (12 mL) was added. The solution became homogeneous and purple. A solution of **2c** (1.35, 3.0 mmol) in benzene (16 mL) was added to this mixture. The resulting mixture was stirred at ambient temperature for 20 h and then passed through a short pad of Celite with ether/hexane (1:3) as eluent. The filtrate was concentrated to give **3c** as a transparent oil (1.39 g, 99 %). $R_f=0.35$ (EtOAc/hexane, 1:25); $[\alpha]_D^{25}=+226$ ($c=1.0$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=8.08$ (d, $J=7.8$ Hz, 2 H), 7.46 (t, $J=7.4$ Hz, 2 H), 7.35 (t, $J=7.6$ Hz, 2 H), 7.31 (d, $J=7.6$ Hz, 2 H), 3.72–3.69 (m, 2 H), 3.46 (dd, $J=9.4$, 5.2 Hz, 2 H), 3.29 (t, $J=9.2$ Hz, 2 H), 3.26–3.04 (m, 4 H), 1.40–1.38 (m, 4 H), 1.28–1.21 (m, 16 H), 0.88 ppm (t, $J=6.6$ Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=193.8$, 139.0, 138.0, 132.5, 131.8, 130.8, 127.1, 73.4, 71.0, 46.8, 31.8, 29.5, 29.0, 26.0, 22.6, 14.0 ppm; IR (CH_2Cl_2): $\tilde{\nu}=3066$, 2930, 2857, 1647, 1600, 1483, 1466, 1454, 1360, 1292, 1244, 1185, 1110 cm^{-1}; MS (20 eV): *m*/*z* (%): 464 (30) [M^+], 384 (15), 220 (100), 206 (49), 178 (24), 57 (27); HRMS: *m*/*z* calcd for $C_{31}H_{44}O_3$: 464.3285; found: 464.3300; elemental analysis calcd (%) for $C_{31}H_{44}O_3$: C 80.13, H 9.54; found: C 80.34, H 9.81.

Compound 4c: $[CH_3OC_6H_4P(S)S]_2$.(1.21 g, 3.0 mmol) in anhydrous toluene (5.0 mL) was placed to a 25 mL, two-necked, round-bottomed flask fitted with a condenser topped with an N_2 inlet and septum. A solution of **3c** (0.70 g, 1.5 mmol) in anhydrous toluene (15 mL) was added through a cannula. The reaction mixture was heated at reflux for 19 h and then passed through a short column of neutral alumina (40 mm×5 cm) by using EtOAc/hexane (1:30) as eluent. The filtrate was collected and concentrated. The crude product was purified by column chromatography (EtOAc/hexane, 1:30) to give **4c** as a blue oil 0.61 g (54 %). $R_f=0.33$ (EtOAc/hexane, 1:30); $[\alpha]_D^{25}=-145$ ($c=1.0$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.91$ (d, $J=7.6$ Hz, 2 H), 7.39 (td, $J=7.3$, 0.8 Hz, 2 H), 7.24–7.19 (m, 4 H), 3.67–3.63 (m, 2 H), 3.54 (dd, $J=9.4$, 5.4 Hz, 2 H), 3.39 (t, $J=9.3$ Hz, 2 H), 3.30–3.16 (m, 4 H), 1.48–1.45 (m, 4 H), 1.30–1.25 (m, 16 H), 0.89 ppm (t, $J=6.6$ Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=148.0$, 134.4, 131.5, 131.1, 131.0, 126.6, 72.6, 71.1, 46.2, 31.8, 29.6, 29.1, 26.1, 22.6, 14.1 ppm.

Compound 5c: Hydrazone **7** (292 mg, 1.2 mmol) in anhydrous CH_2Cl_2 (12 mL) was added to a 50 mL,two- necked, round-bottomed flask fitted with a Schlenk filtration tube and septum. The solution was cooled to −20 °C, whereupon $MgSO_4$ (1.49 g, .12.4 mmol), Ag_2O (0.83 g, 3.6 mmol), and a saturated solution of KOH in methanol (1.1 mL) were successively added. After having been stirred for 12 h, the resulting deep red solution was filtered into another ice-cooled flask, and the remaining residue was washed with CH_2Cl_2 (6 mL). A solution of thioketone **4c** (463 mg, 1.0 mmol, 0.1 M in CH_2Cl_2) was added dropwise by a syringe to the collected solution. Evolution of nitrogen was observed, and the deep red solution slowly decolored. After having been stirred for 16 h, the resulting reaction mixture was quenched by adding a saturated aqueous solution of $NaHCO_3$ (15 mL). The aqueous layer was separated and extracted with CH_2Cl_2 (3×15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and evaporated. The crude product was purified by column chromatography (EtOAc/hexane, 1:40) to give **5c** as a transparent oil (481 mg, 70 %). $R_f=0.33$ (EtOAc/hexane, 1:40); $[\alpha]_D^{25}=-158$ ($c=1.0$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): $\delta=7.93$–7.91 (m, 1 H), 7.42 (d, $J=7.7$ Hz, 2 H), 7.22 (t, $J=7.1$ Hz, 1 H), 7.19–7.09 (m, 4 H) , 7.05–7.03 (m, 2 H), 6.93 (d, $J=8.2$ Hz, 1 H), 4.02–3.98 (m, 2 H), 3.50 (t, $J=6.5$ Hz, 2 H), 3.43 (dt, $J=7.2$, 3.8 Hz, 1 H), 3.00–2.94 (m, 4 H), 2.82–2.78 (m, 2 H), 2.59–2.56 (m, 1 H), 2.28–2.25 (m, 1 H), 1.94–1.82 (m, 3 H), 1.60–1.26 (m, 20 H), 0.92–0.87 ppm (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta=144.5$, 139.0, 138.74, 138.67, 137.9, 136.9, 132.8, 131.9, 131.6, 130.3, 129.7, 27.8, 127.6, 127.4, 126.7, 126.5, 126.4, 119.1, 77.7, 71.3, 71.1, 70.9, 70.4, 56.9, 46.2, 42.0, 38.6, 31.9, 30.6, 29.7, 29.6, 29.5, 29.2, 29.1, 26.3, 26.2, 22.64, 22.61, 22.1, 14.1 ppm; MS (70 eV): *m*/*z* (%): 688 (6) [M^+], 541 (10), 457 (13), 443 (26), 430 (48), 422 (34), 398 (19), 331 (100), 319 (16), 203 (15); IR (CH_2Cl_2): $\tilde{\nu}=3062$, 2927, 2856, 1591, 1473, 1454, 1373, 1267, 1178, 1110 cm^{-1}; HRMS: *m*/*z* calcd for $C_{41}H_{53}BrO_2S$: 688.2944; found: 688.2946.

Compound (*P*)-6c: A solution of episulfide **5c** (303 mg, 0.4 mmol) and copper powder (271 mg, 4.3 mmol) in anhydrous xylene (6 mL) was added to a 25 mL, two-necked, round-bottomed flask fitted with a condenser topped with an N_2 inlet and septum. The resulting reaction mixture was heated at reflux for 2 h, filtered, and concentrated. The crude product was purified by column chromatography (ether/hexane, 1:50) to give **6c** as a transparent oil (273 mg, 95 %). $R_f=0.35$ (ether/hexane, 1:50); $[\alpha]_D^{25}=-194$ ($c=1.0$ in CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$): major conformer: $\delta=7.58$ (d, $J=6.1$ Hz, 1 H), 7.46 (d, $J=1.6$ Hz, 1 H), 7.26–7.14 (m, 5 H), 7.13–7.09 (m, 1 H), 6.98 (d, $J=6.5$ Hz, 1 H), 6.94 (td, $J=6.2$, 0.5 Hz, 1 H), 6.79 (dd, $J=6.2$, 1.0 Hz, 1 H), 4.00–3.32 (m, 10 H), 3.00–2.83 (m, 3H), 2.10–1.95 (m, 3H), 1.72–1.15 (m, 20H), 0.94 (t, $J=5.7$ Hz, 3H), 0.86 ppm (t, $J=5.8$, 3H); minor conformer: $\delta=7.42$ (d, $J=6.2$, 1H), 7.26–7.14 (m, 5H), 7.13–7.09 (m, 1H), 6.98 (d, $J=6.5$ Hz, 1H), 6.93 (td, $J=5.8$, 0.8 Hz, 1H), 6.86 (dd, $J=6.1$, 1.0 Hz, 1H), 6.71 (d, $J=1.6$ Hz, 1H), 4.00–3.32 (m, 10H), 3.00–2.83 (m, 3H), 2.10–1.95 (m, 3H), 1.72–1.15 (m, 20H), 0.94 (t, $J=5.7$ Hz, 3H), 0.88 ppm (t, $J=5.6$ Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): major conformer: $\delta=144.6$, 141.5, 139.7, 139.3, 138.28, 138.26, 137.8, 133.4, 131.6, 131.2, 129.6, 129.3, 128.8, 127.3, 126.9, 126.8, 126.7, 126.02, 125.9, 118.1, 75.5, 71.6, 71.4, 71.2, 46.2, 40.2, 31.8, 29.74, 29.67, 29.5, 29.2, 29.1, 28.8, 26.3, 26.1, 23.8, 22.64, 22.57, 14.1 ppm; minor conformer: $\delta=142.1$, 141.2, 138.6, 138.1, 138.0, 137.9, 137.6, 131.9, 131.8, 131.2, 129.9, 129.8, 129.3, 128.6, 127.5, 127.1, 126.3, 125.9, 125.7, 118.2, 74.5, 73.1, 71.3, 70.9, 46.2, 43.0, 31.8, 29.9, 29.6, 29.4, 29.2, 29.1, 28.8, 26.3, 26.1, 23.5, 22.7, 22.6, 14.1 ppm; IR (CH_2Cl_2): $\tilde{\nu}=$ 3059, 2924, 2857, 1587, 1482, 1467, 1373, 1264, 1176, 1121, 1106 cm^{-1}; MS (70 eV): m/z (%): 656 (5) [M^+], 426 (25), 398 (17), 331 (100), 302 (13), 233 (15), 217 (26), 191 (22), 57 (34); HRMS: m/z calcd for $C_{41}H_{53}BrO_2$: 656.3223; found: 656.3224; HPLC: $t_R=4.58$ min (Chiralpak OT(+) column, hexane/*i*PrOH, 99:1, ambient temperature, 1.0 mL min^{-1}, $\lambda=249$ nm); elemental analysis calcd (%) for $C_{41}H_{53}BrO_2$: C 74.87, H 8.12; found: C 74.84, H 8.06.

Compound (*M'*)-6c: A solution of (10*R*,11*R*,*P*)-**6c** (6.6 mg, 10.0 μmol) in degassed *n*-hexane (2.0 mL) was irradiated with a 300 W Xe-lamp equipped with a monochromator. The irradiation wavelength was set at 290 nm with a slit size equivalent to 8 nm bandwidth. The experiment was carried out for 2 days until a constant composition was observed by HPLC analysis on a Chiralpak OT(+) column. The solution was concentrated to give (10*R*,11*R*,*M*)-**6c** quantitatively as a transparent oil. $[\alpha]_D^{25}=+133$ ($c=1.0$ in CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$): Major conformer: $\delta=8.50$ (t, $J=6.2$ Hz, 1H), 7.80 (d, $J=6.1$ Hz, 1H), 7.43–7.33 (m, 3H), 7.29–7.25 (m, 2H), 7.21–7.15 (m, 3H), 6.93 (d, $J=6.1$ Hz, 1H), 3.81–3.74 (m, 2H), 3.61–3.55 (m, 2H), 3.36 (dd, $J=9.3$, 5.3 Hz, 1H), 3.26–3.00 (m, 7H), 2.85–2.65 (m, 3H), 2.09–2.04 (m, 1H), 1.72–1.47 (m, 5H), 1.36–1.33 (m, 15H), 0.91 (t, $J=6.7$ Hz, 3H), 0.83 ppm (t, $J=7.0$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): major conformer: $\delta=139.1$, 138.8, 135.2, 134.5, 134.1, 133.6, 133.3, 132.9, 132.6, 131.0, 130.9, 130.1, 129.2, 127.4, 126.8, 126.1, 126.0, 123.1, 115.8, 74.8, 71.6, 71.3, 70.9, 50.1, 46.6, 31.9, 31.7, 30.8, 29.8, 29.7, 29.5, 29.2, 29.08, 26.3, 25.9, 23.1, 22.7, 22.5, 14.1, 14.0 ppm; MS (70 eV): m/z (%): 656 (5) [M^+], 426 (26), 398 (18), 331 (100), 303 (14), 217 (14), 191 (20); HRMS calcd for $C_{41}H_{53}BrO_2$: 656.3223; found: 656.3229; HPLC: $t_R=7.60$ min (Chiralpak OT(+) column, hexane/*i*PrOH, 99:1, ambient temperature, 1.0 mL min^{-1}, $\lambda=249$ nm).

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