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Efficient Syntheses and Resolutions of Inherently Chiral Calix[4]quinolines in the Cone and Partial-Cone Conformation

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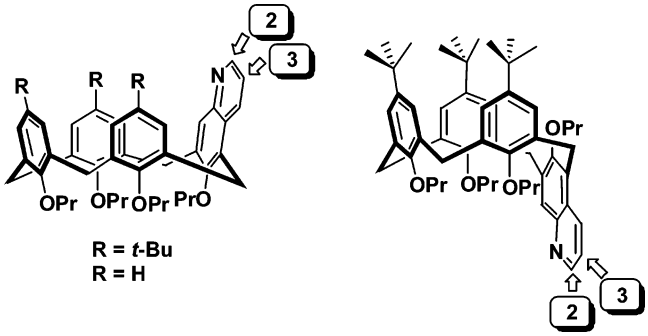
Received May 17, 2005



The syntheses of five pairs of novel inherently chiral calix[4]arenes are described. Two synthetic routes were adopted to generate racemic 3-carboxylic or 2-carboxylic group substituted calix[4]-quinolines in the cone or the partial-cone conformation, respectively. The chiral products were thoroughly characterized by various spectroscopic methods. The optical resolutions of chiral calix-[4]quinolines **5**, **6**, **11**, and **17** were successfully achieved through the separation of their diastereomers using common column chromatography or preparative TLC. The chirality of compound **20** was proven by the splitting of the ^{1}H NMR signals in the presence of Pirkle's reagent. The ^{1}H NMR features of the diastereomers are discussed. The CD spectra of each pair of enantiomers showed excellent mirror images. The experimental results disclose that 3-carboxylic calix[4]-quinolines can be resolved more easily than the 2-carboxylic ones in both the cone conformation and the partial-cone conformation.

Introduction

Calixarenes,[1] easily prepared by base-induced condensation of certain *p*-substituted phenols with formaldehyde, attract considerable interest in the field of supramolecular chemistry due to their unique cavity-shaped architecture and their ability to be functionalized in various ways. Hence, calixarenes have been widely used as three-dimensional building blocks for the design of selective receptors for cations,[2] anions,[3] and neutral molecules.[4] Compared to the achiral receptors, chiral receptors are of particular interest in enzyme mimics, and this has led to the development of chiral calixarenes. Chiral derivatives can be obtained by simply attaching chiral residues at the upper or lower rim of the calixarene skeleton,[5] but recent interest has been focused on the possibility of synthesizing "inherently" chiral calix-

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(2) For recent articles for cation receptors see: (a) Yoon, K.; Kim, K. *J. Org. Chem*. **2005**, *70*, 427−432. (b) He, H.; Mortellaro, M. A.; Leiner, M. J. P.; Fraatz, R. J.; Tusa, J. K. *J. Am. Chem. Soc*. **2003**, *125*, 1468−1469. (c) Kim, J. S.; Noh, K. H.; Lee, S. H.; Kim, S. K.; Kim, S. K.; Yoon, J. *J. Org. Chem*. **2003**, *68*, 597−600. (d) Chen, Q. Y.; Chen, C. F. *Tetrahedron Lett*. **2005**, *46*, 165−168.

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10.1021/jo050980b CCC: $30.25
Published on Web 08/17/2005

[4larenes, which are built up of achiral subunits and consequently owe their chirality to the fact that the calixarene molecule is not planar.

Since No and Gutsche reported the first example of inherently chiral calix[4]arene in 1982,[6] there has been increasing interest focused on the syntheses of inherently chiral calixarenes for their potential application to chiral recognition and asymmetric catalysis. Several strategies have been developed for the preparation of inherently chiral calixarenes. The general synthesis of chiral derivatives involves the chiral arrangement of several achiral units at the upper[7] or lower[8] rim of calixarenes. Another method involves *m*-substitution[9] of the phenol rings of the calixarenes. The versatile conformation of calixarenes can also provide the possibility of chiral derivatives. In this respect, Iwamoto et al. have reported a systematic classification of all possible chiral isomers derivable from calix[4]arene.[10]

The evidence for the existence of inherent chirality in calixarenes can be deduced from their ^{1}H NMR spectra in the absence or presence of a chiral reagent and confirmed by the CD spectra of the enantiomers.[11] Usually, their optical resolutions are achieved through HPLC using suitable chiral-packed columns.[12] Also, a few reports on resolutions of chiral calixarenes through separation of their diastereomers have appeared in the literarure.[13,14b] This is mainly due to the difficulty of the resolution process, so there have been few reports[14] on the application of inherently chiral calixarenes, although they have been studied for more than two decades.

Moreover, despite the extensive synthetic strategies, the generation of inherently chiral calixarenes on the upper rim is still underdeveloped, especially in facile optical resolutions. In 1996, Ikeda et al. synthesized one naphthalene-containing inherently chiral calix[4]arene through intramolecular ring closure on the upper rim and then confirmed the noninterconvertibility between the enantiomers through the ^{1}H NMR spectrum in the presence of Pirkle's reagent without further optical resolution.[15] This report indicates that a naphthalene unit, which is introduced by transformation of an upper-rim-appended formyl group, can create asymmetry which makes a cone-immobilized calix[4]arene. Herein we wish to report (1) the syntheses of novel inherently chiral calix-[4]arenes on the upper rim, which are obtained by the transformation of the upper rim into the quinoline-containing structure through the intramolecular ring closure process and (2) the efficient optical resolutions of inherently chiral calix[4]quinolines, which were successfully achieved through the separation of their diastereomers using common column chromatography or preparative TLC.

Result and Discussion

Syntheses of Inherently Chiral Calix[4]quinoline. As shown in Scheme 1, 2-carboxylic or 3-carboxylic group substituted calix[4]quinolines in the cone conformation have been efficiently synthesized from route A or B. Compound **1** was prepared according to the literature method.[16] In route A,[17] ethyl acetoacetate together with Vilsmeier reagent converted compound **1** to the racemic inherently chiral calix[4]quinoline **3** in 47% yield. Hydrolysis of compound **3** was carried out by a simple treatment with NaOH in EtOH/H_2O (3/1) to form racemic acid **5** with the carboxylic group in the 3-position of the quinoline moiety in 85% yield. In route B,[18] compound **1** reacted with crotonaldehyde at reflux in *n*-BuOH/H_2O to afford racemic calix[4]quinoline **10** in 72% yield. Then compound **11** was obtained by direct oxidation of **10** with SeO_2 in pyridine in 70% yield. The formation of the quinoline ring was established by the ^{1}H NMR spectra, where the characteristic signals of the quinoline part exhibited three singlets at δ 9.17 (1H), 7.35 (1H), and 2.88 (3H) for **5** and two doublets at δ 8.50 (J = 8.8 Hz, 1H) and 7.86 (J = 8.8 Hz, 1H) and one singlet at δ 7.28 (1H) for **11**. Because of the asymmetric structure, four pairs of doublets for the $ArCH_2Ar$ methylene protons (AX

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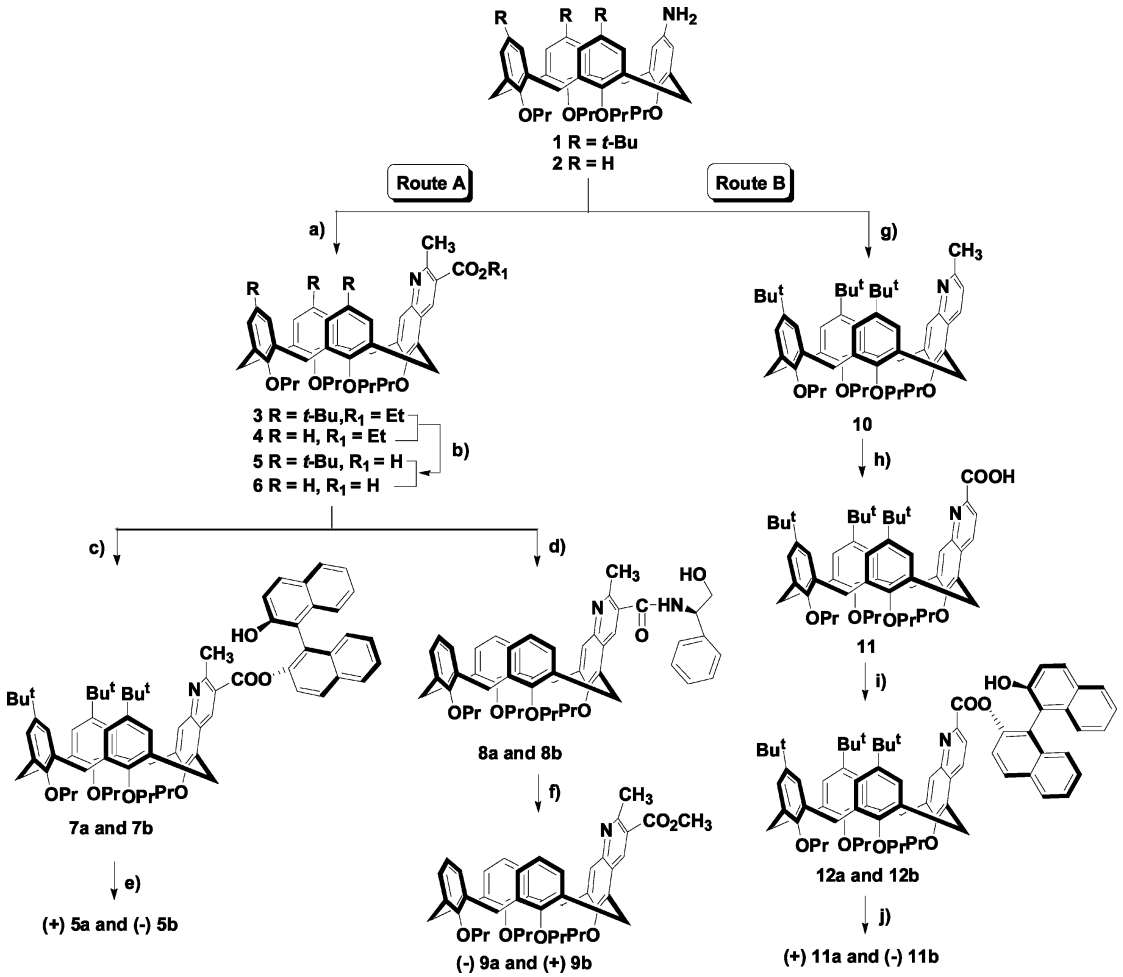
SCHEME 1. Synthesis of Inherently Chiral Calix[4]quinoline in the Cone Conformation[a]



[a] Conditions: (a) $POCl_3$/DMF, CH_3COCH_2COEt, 0−5 °C, 47% **3** and 35% **4**; (b) NaOH, EtOH/H_2O, reflux, 85% **5** and 80% **6**; (c) DCC/DMAP, (*S*)-BINOL, CH_2Cl_2 (anhydrous), rt, 43% **7a** and 40% **7b**; (d) $SOCl_2$, then (*R*)- phenylglycinol, Et_3N, CH_2Cl_2, rt, 42% **8a** and 39% **8b**; (e) NaOH, EtOH/H_2O, reflux, 80% **5a** and 82% **5b**; (f) $NaOCH_3$, DMC, rt, 46% **9a** and 45% **9b**; (g) crotonaldehyde, toluene, *n*-BuOH/H_2O, reflux, 72%; (h) SeO_2, pyridine, reflux, 70%; (i) DCC/DMAP, (*S*)-BINOL, CH_2Cl_2 (anhydrous), rt, 36% **12a** and 33% **12b**; (j) NaOH, EtOH/H_2O, reflux, 85% **11a** and 87% **11b**.

systems) were found in the spectra, one of the equatorial signals being shifted down and hidden by the methylene protons of the OCH_2 group on the lower rim. Such an unusual downfield shift of the equatorial proton is obviously caused by the deshielding effect of the quinoline moiety.

On the other hand, we still hope to check the importance of the *tert*-butyl substitution on the upper rim of the calix[4]arene core, so 3-carboxylic group substituted calix[4]quinoline **6** has been prepared from aminocalix[4]arene **2**[19] in route A (Scheme 1). Similarly, the formation of **6** was confirmed by the ^1H and ^{13}C NMR spectra.

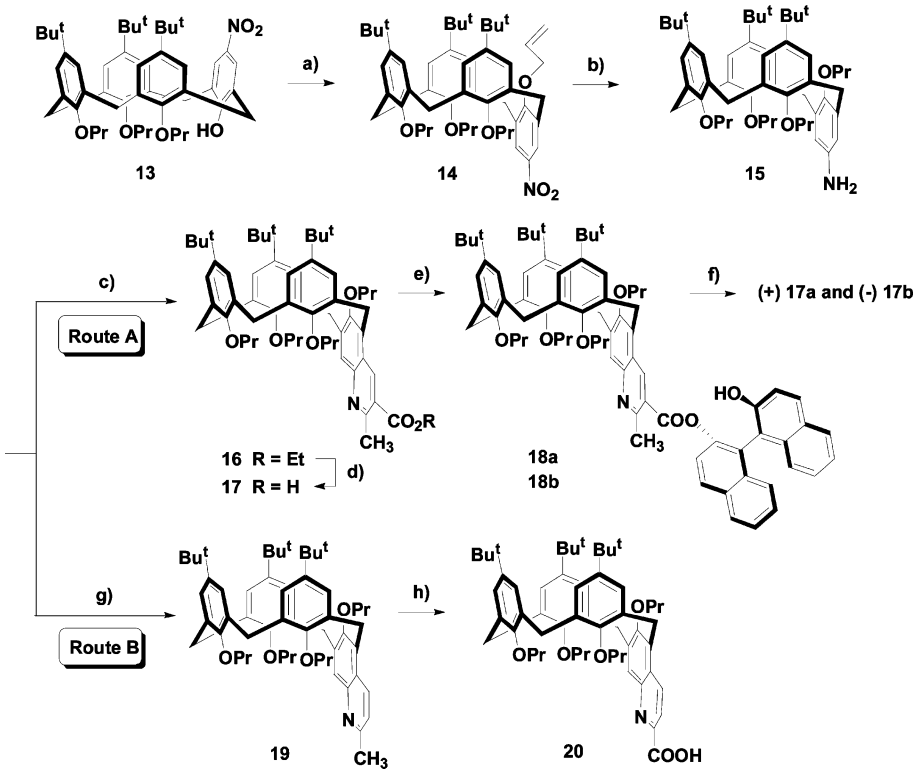
For further comparison of the difference of the conformation effect of calix[4]arenes, inherently chiral calix[4]quinolines **17** and **20** in the partial-cone conformation were synthesized in routes A and B, respectively (Scheme 2). In the alkylation step, because Cs^+ could induce the inversion of the residual phenol ring, Cs_2CO_3 was used to furnish the partial-cone conformer **14** through the allylation of **13** with allyl bromide in DMF in 50% yield.[20] Then, under H_2 atmosphere, compound **14** was hydrogenized to compound **15** at room temperature in 98% yield. Subsequently, the racemic compounds **17** and **20** were prepared efficiently according to routes A and B, respectively. Because the ^1H NMR spectra of **17** and **20** were complex, the structural assignment was conducted with the aid of the 2D correlation spectroscopy ($^1H-^1H$ COSY) experiment. The ^1H NMR spectra exhibited three singlets at δ 9.56 (1H), 8.34 (1H), and 3.19 (3H) for the quinoline part of **17** and two doublets at δ 8.91 (J = 8.8 Hz, 1H) and 8.26 (J = 8.8 Hz, 1H) and one singlet at δ 8.14 (1H) for the quinoline part of **20**, respectively. The diagnostically important $ArCH_2Ar$ methylene protons of **17** and **20** gave rise to three AX systems and an AB system of relative intensities of 1:1:1:1 (see the Supporting Information).[21] These patterns are compatible with the structures of inherently chiral calix[4]quinolines **17** and **20**.

The confirmations of their stereochemistry have been made on the basis of the distinctive ^1H NMR and ^{13}C

(19) Zeng, C. C.; Zheng, Q. Y.; Tang, Y. L.; Huang, Z. T. *Tetrahedron* **2003**, *59*, 2539−2548.

(20) The partial-cone conformation of **14** was established by its ^{13}C NMR spectroscopy, which showed two resonances for the $ArCH_2Ar$ groups at δ 37.1 and 30.5, in agreement with the de Mendoza rule for the determination of calix[4]arene conformations.

SCHEME 2. Synthesis of Inherently Chiral Calix[4]quinoline in the Partial-Cone Conformation[a]



[a] Conditions: (a) allyl bromide, Cs_2CO_3, DMF, rt, 65%; (b) H_2, Pd/C (10%), rt, 98%; (c) $POCl_3$/DMF, CH_3COCH_2COEt, 0−5 °C, 43%; (d) NaOH, EtOH/H_2O, reflux, 78%; (e) DCC/DMAP, (*S*)-BINOL, CH_2Cl_2 (anhydrous), rt, 43% **18a** and 40% **18b**; (f) NaOH, EtOH/H_2O, reflux, 73% **17a** and 74% **17b**; (g) crotonaldehyde, toluene, *n*-BuOH/H_2O, reflux, 70%; (h) SeO_2, pyridine, reflux, 73%.

NMR spectral patterns. Jaime et al. have reported that the resonance arising from the bridge methylene carbon is near δ 31 when two adjacent aryl groups are in the syn orientation and near δ 37 when they are in the anti orientation.[22] Indeed, the resonances for the bridge methylene carbon are observed at δ 31.4, 31.2, and 28.8 for **5**, δ 30.9, 30.0, 29.9, and 23.6 for **6**, δ 31.4, 30.8, and 29.1 for **11**, δ 38.3, 30.7, 30.6, and 29.7 for **17**, and δ 38.1, 30.7, 30.6, and 29.6 for **20**. These findings are in full agreement with the expected conformation.[23]

Optical Resolutions of Inherently Chiral Calix[4]quinolines. With all of these racemic calix[4]quinoline derivatives in hand, we attempted to resolve them by the convenient diastereomers media method rather than by the HPLC method. To take advantage of the carboxylic group in these calix[4]quinolines, we chose (*R*)-phenylglycinol, (*R*)-4-phenyloxazolidinone[24] and (*S*)-BINOL as chiral auxiliaries for the compound **5**, **6**, **11**, **17**, or **20**. The experimental results showed that (*S*)-BINOL was an excellent chiral auxiliary for **5**, **11**, and **17**, and (*R*)-phenylglycinol was an excellent chiral auxiliary for **6**.

Compound **5** or **17** condensing with (*S*)-BINOL in the presence of DCC and DMAP afforded the diastereomers **7a** and **7b** or **18a** and **18b**. Fortunately, we found that they could be separated easily just using common silica column chromatography. Then hydrolysis of these diastereomers in EtOH/H_2O (3/1) under alkaline condition allowed the clean removal of the chiral auxiliary to give the corresponding optically active calix[4]quinolines (+)-5a and **(−)-5b** in the cone conformation (Scheme 1) or **(+)-17a** and **(−)-17b** in the partial-cone conformation (Scheme 2). To the best of our knowledge, until now these are the first two examples in the study of inherently chiral calix[4]arenes in the upper rim which can be resolved through the separation of their diastereomers using column chromatography without using HPLC through suitable chiral-packed columns. This allows the gram-scale preparation of these enantiopure inherently chiral calix[4]quinoline derivatives and further research on their potential applications.

Under the same conditions, compound **11** reacted with (*S*)-BINOL to yield diastereomers **12a** and **12b**. However, they cannot be separated using common silica column chromatography other than preparative TLC. Subsequently, hydrolysis of **12a** and **12b** with NaOH afforded the optical active calix[4]quinolines **(+)-11a** and **(−)-11b** in 85% and 88% yield, respectively (Scheme 1).

In the case of compound **6**, facile optical resolution was achieved by use of (*R*)-phenylglycinol as the auxiliary. Through reactions with $SOCl_2$ and then (*R*)-phenylglycinol, the racemic acid **6** was converted to the diastereomers **8a** and **8b** in the cone conformation, which were

(21) On the basis of the ^1H and ^{13}C NMR spectra of compounds **17** and **20**, it was presumed that the introduction of the quinoline part led to one distorted partial-cone conformation. So, the signals of the $ArCH_2Ar$ groups exhibited three AX systems and an AB system in the ^1H NMR spectra and one around 38 ppm and three around 30 ppm in the ^{13}C NMR spectra.

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(24) Nicolás, E.; Russell, K. C.; Hruby, V. J. *J. Org. Chem.* **1993**, *58*, 766−770

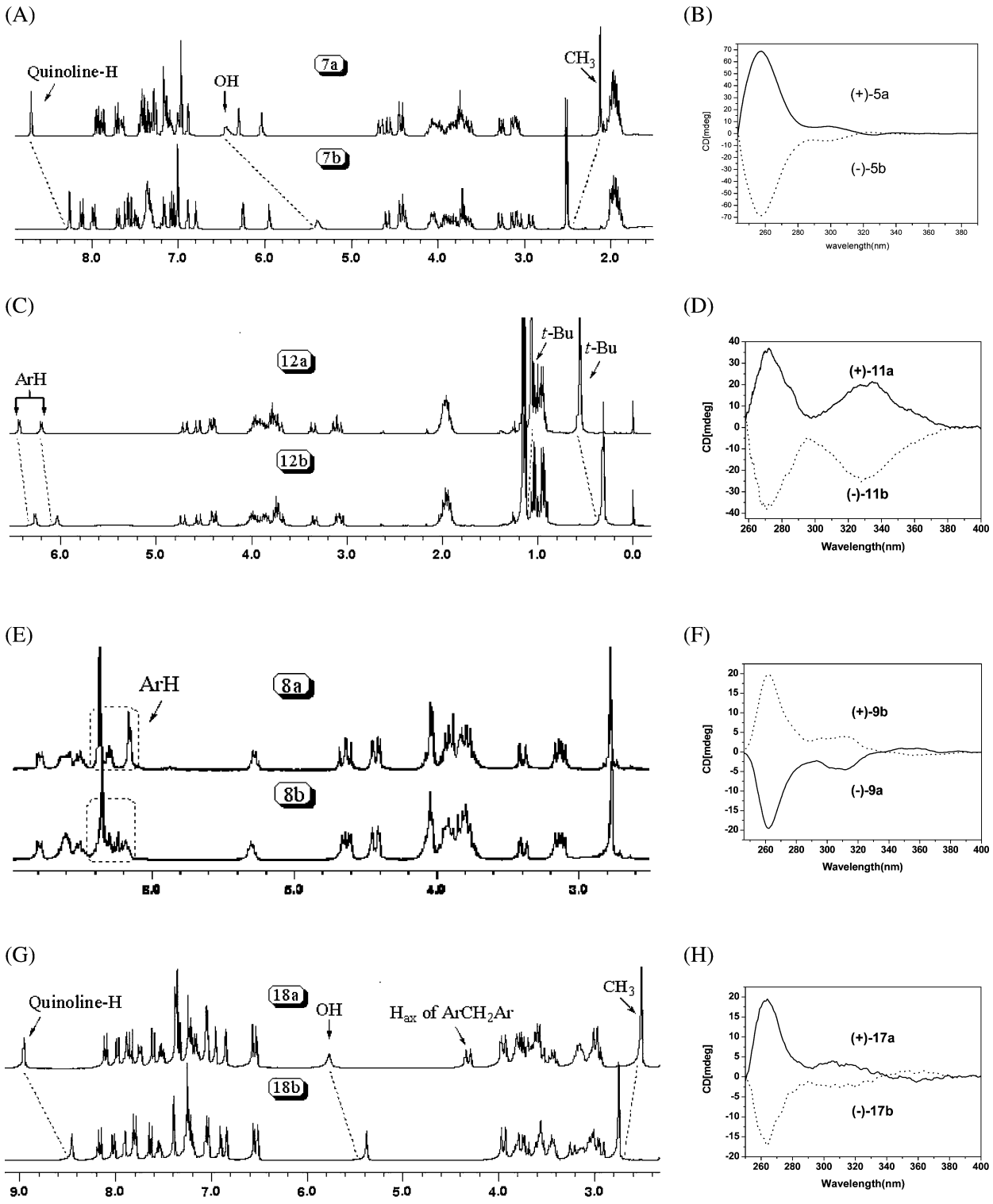

FIGURE 1. Partial ^{1}H NMR spectra of diasteromers and CD spectra of isomers. (A) Partial ^{1}H NMR spectra of diasteromers **7a** and **7b**; (B) CD spectra of isomers **5a** and **5b**; (C) Partial ^{1}H NMR spectra of diasteromers **12a** and **12b**; (D) CD spectra of isomers **11a** and **11b**; (E) Partial ^{1}H NMR spectra of diasteromers **8a** and **8b**; (F) CD spectra of isomers **9a** and **9b**; (G) Partial ^{1}H NMR spectra of diasteromers **18a** and **18b**; (H) CD spectra of isomers **17a** and **17b**.

separated using preparative TLC. Subsequently, **8a** and **8b** treated with NaOMe in the presence of DMC (dimethyl carbonate) at room temperature afforded **(−)-9a** and **(+)-9b** in 45−47% yield (Scheme 1).[25] As for compound **20**, it seemed inseparable using these chiral auxiliaries by column chromatography or preparative TLC.

Study of ^{1}H NMR Spectra of Diasteromers and CD Spectra of Enantiomers. As illustrated in Figure 1 (parts B, D, F, H), circular dichroism (CD) spectroscopy shows an excellent mirror image between (+)-**5a** ($[\alpha]_D$ +50.4°) and (−)-**5b** ($[\alpha]_D$ −49.6°), (+)-**11a** ($[\alpha]_D$ +156°) and (−)-**11b** ($[\alpha]_D$ −156°), (−)-**9a** ($[\alpha]_D$ −51.2°) and (+)-

9b ($[\alpha]_D$ +52°), and (+)-**17a** ($[\alpha]_D$ +8°) and (−)-**17b** ($[\alpha]_D$ −8°), indicating the inherent chirality of each pair clearly.

Diastereomers **7a** and **7b** and **12a** and **12b** are both in the cone conformation, but the same auxiliary ((*S*)-BINOL) is located at the 3- and 2-position of the quinoline moiety. Diastereomers **7a** and **7b** show remarkable differences in the ^{1}H NMR spectra (Figure 1A). The proton of the hydroxy group of the BINOL moiety resonates at δ 6.44 and 5.39, respectively. The proton at 4-position of the quinoline moiety resonates at δ 8.70 and 8.26, and the methyl group of the quinoline resonates at δ 2.12 and 2.56, respectively. In the case of **12a** and **12b** (Figure 1C), the two protons of the phenyl moiety of calix[4]arene resonate at δ 6.43/6.20 and 6.27/6.04 and the protons of the two *tert*-butyl groups of calix[4]arene are at δ 1.07/0.56 and 1.13/0.30, respectively. These results indicate clearly that the structural difference between **7a** and **7b** are more obvious than that between **12a** and **12b**, which could be one possible reason for the easier separation of diastereomers **7a** and **7b** than that of **12a** and **12b**. This suggests that in the cone conformation the auxiliary located at the 3-position is more effective than that located at 2-position of the quinoline moiety.

Compared to **7a** and **7b**, the ^{1}H NMR spectra of the amide diastereomers of **8a** and **8b** appeared almost the same except for a small difference of ArH, which means that the structural differences between **8a** and **8b** are less and their separation is possibly more difficult than that of **7a** and **7b**. In fact, **8a** and **8b** can only be separated by preparative TLC (Figure 1E). More comparably, when using (*S*)-BINOL as the auxiliary we only got the inseparable diastereomers. Compared with the result of **7a** and **7b**, this suggests that the *tert*-butyl groups on the upper rim play a very important role in the interaction between the chiral auxiliary moiety and the core of calix[4]arene in the cone conformation.

Compared with above diastereomers in the cone conformation, owing to the partial-cone conformation character, the ^{1}H NMR spectral patterns of **18a** and **18b** are more complex in the high field. But the evident differences in the ^{1}H NMR spectra are the protons of the 4-position and methyl group at the quinoline moiety. As shown in Figure 1G, they are at δ 8.95 and 8.45 and at 2.51 and 2.75, respectively. In addition, one of the methylene protons of $ArCH_2Ar$ is at δ 4.32 in the spectra of **18a**, while the proton signals of $ArCH_2Ar$ in **18b** are hidden by those of the protons of the propoxy group. This phenomenon coincides with the experimental results that this pair of diastereomers can be resolved easily using column chromatography. However, for compound **20**, we could not find an appropriate method to separate the enantiomers.

To ascertain that **19** is an enantiomeric mixture, we measured the ^{1}H NMR spectra in the absence and presence of Pirkle's reagent [(*s*)-2,2,2-trifluoro-1-(9-anthryl)ethanol]. As shown in Figure 2, the signals assignable to the methylene of $ArCH_2Ar$ and *tert*-butyl group split into pairs, indicating that **19** is consistent with an inherently chiral calixarene.

The experimental results showed that for the calix[4]-quinolines in the cone conformation, the *tert*-butyl group contributed to the separation of the diastereomers. Due to the steric effect of calix[4]arenes in the three-dimensional structure, the auxiliary located at the 3-position is more effective than that located at the 2-position of the quinoline moiety in both the cone and partial-cone conformations.

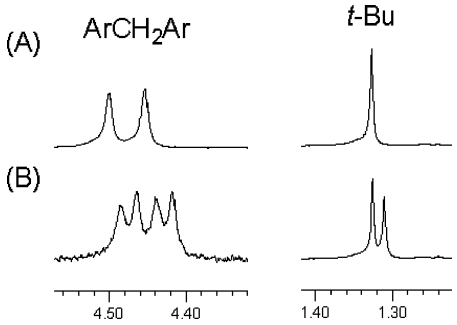

FIGURE 2. Partial ^{1}H NMR spectrum for the *tert*-butyl and bridging methylene group of **19** in $CDCl_3$. (A) Racemic **19**, (B) Racemic **19** + Pirkle's reagent (1.2 times **19**).

Conclusion

In summary, we have presented the facile synthesis of a series of inherently chiral calix[4]quinolines on the upper rim in two different routes (A and B) and found that their optical resolutions could be conveniently achieved through the separation of their diastereomers derived from (*S*)-BINOL or (*R*)-phenylglycinol by common column chromatography or preparative TLC. Moreover, it has also been found that the diastereomers derived from the 3-position of calix[4]quinolines were more easily separated than those of the 2-position of calix[4]quinolines. The current investigation provides a basis for the study of the application of these chiral calix[4]quinolines to chiral recognition and asymmetric catalysis. These works are now in process in our laboratory.

Experimental Section

Calix[4]quinoline 3 (Racemic Mixture). To DMF (0.31 mL, 4.0 mmol) was added $POCl_3$ (0.45 mL, 4.8 mmol) dropwise at 0−5 °C, and the resultant solution was stirred for 30 min at room temperature and then cooled to 0−5 °C. Ethyl acetoacetate (0.51 mL, 4.0 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 2.5 h. After the reaction mixture was cooled to 0−5 °C, compound **1** (3.12 g, 4.0 mmol) in DMF (3 mL) was added, and after warming to room temperature the resultant mixture was heated at 90 °C for 4.5 h. The mixture was then cooled, dissolved in CH_2Cl_2 (30 mL), and added slowly to ice-cold aqueous ammonia (10%, 50 mL). The organic phase was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic phase was washed successively with water and brine and was dried over anhydrous Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 15/1) to afford **3** (1.70 g, yield 47%) as a white solid. Mp: 99−100 °C. MALDI-TOF MS: m/z = 898.6 $(M + H)^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.90 (s, 1H), 7.28 (s, 1H), 7.14 (d, J = 2.0 Hz, 1H), 7.06 (d, J = 2.0 Hz, 1H), 7.01 (d, J = 2.2 Hz, 1H), 6.91 (d, J = 2.2 Hz, 1H), 6.29 (d, J = 2.2 Hz, 1H), 6.01 (s, 1H), 4.77 (d, J = 13.6 Hz, 1H), 4.62 (d, J = 12.8 Hz, 1H), 4.35−4.48 (m, 4H), 3.69−4.10 (m, 9H), 3.35 (d, J = 12.8 Hz, 1H), 3.13 (d, J = 13.6 Hz, 1H), 3.08 (d, J = 13.6 Hz, 1H), 2.75 (s, 3H), 1.97−2.03 (m, 8H), 1.42 (t, J = 7.2 Hz, 3H), 1.27 (s, 9H),

(25) Kanomata, N.; Maruyama, S.; Tomono, K.; Anada, S. *Tetrahedron Lett*. **2003**, *44*, 3599−3603.

1.19 (s, 9H), 1.08 (t, J = 6.3 Hz, 3H), 1.05 (t, J = 6.2 Hz, 3H), 0.95 (t, J = 7.3 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H), 0.49 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.3, 154.9, 154.8, 154.6, 154.5, 153.3, 145.7, 144.8, 144.3, 144.1, 141.7, 136.3, 135.7, 135.5, 133.7, 132.9, 132.8, 132.6, 128.3, 128.0, 126.2, 126.1, 125.7, 125.2, 124.6, 124.1, 123.9, 121.7, 77.5, 77.0, 76.8, 76.4, 61.1, 34.1, 33.9, 33.2, 31.6, 31.5, 31.4, 31.3, 31.2, 30.6, 28.2, 25.1, 23.5, 23.3, 23.1, 22.8, 14.4, 10.7, 10.5, 10.1, 9.9. Anal. Calcd for $C_{59}H_{79}O_6N$: C, 78.89; H, 8.86; N, 1.56. Found: C, 78.52; H, 8.97; N, 1.44.

Calix[4]quinoline 4 (Racemic Mixture). Aminocalix[4]-arene **2** (3.40 g, 5.6 mmol) was reacted in the same manner as **1** in the case of the preparation of **3**. The crude compound was purified by column chromatography on silica gel (petroleum ether/ethyl acetate, 15/1) to give **4** (1.43 g, yield 35%) as a white solid. Mp: 65−66 °C. MALDI-TOF MS: m/z = 730.8 $(M + H)^+$, 752.8 $(M + Na)^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.00 (s, 1H), 7.70 (s, 1H), 6.92 (d, J = 7.2 Hz, 1H), 6.81 (d, J = 7.2 Hz, 1H), 6.66 (t, J = 7.2 Hz, 1H), 6.22−6.26 (m, 5H), 6.05 (d, J = 6.7 Hz, 1H), 4.65 (d, J = 14.40 Hz, 2H), 4.39−4.48 (m, 4H), 3.73−4.13 (m, 9H), 3.43 (d, J = 13.3 Hz, 1H), 3.15 (d, J = 13.5 Hz, 2H), 2.97 (s, 3H), 1.91−1.94 (m, 8H), 1.45 (t, J = 7.1 Hz, 3H), 1.06−1.12 (m, 6H), 0.92−0.98 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.0, 157.5, 155.9, 155.8, 155.7, 145.9, 143.6, 136.5, 136.4, 136.2, 134.1, 133.1, 132.3, 131.0, 128.8, 128.5, 128.1, 128.0, 127.9, 127.7, 127.2, 125.1, 122.6, 122.3, 122.1, 121.8, 77.1, 77.0, 76.9, 76.5, 61.2, 31.9, 31.1, 31.0, 25.4, 24.8, 23.5, 23.4, 23.2, 23.1, 14.5, 10.7, 10.1, 10.0. Anal. Calcd for $C_{47}H_{55}O_6N$: C, 77.34; H, 7.59; N, 1.92. Found: C, 77.53; H, 7.63; N, 1.79.

Calix[4]quinoline 5 (Racemic Mixture). To a solution of NaOH (0.535 g, 13.4 mmol) in EtOH/H_2O (30 mL/10 mL) was added compound **3** (1.2 g, 1.34 mmol), and the reaction mixture was refluxed for 6 h. After removal of the solvent under reduced pressure, the residue was neutralized to pH = 7 with 2 N hydrochloric acid; then, the mixture was extracted with CH_2Cl_2. The combined organic phase was washed with H_2O and dried over anhydrous Na_2SO_4 and concentrated. Compound **5** was isolated by column chromatography (silica gel; petroleum ether/ethyl acetate, 2/1) as a white solid (0.988 g, yield 85%). Mp: 180−181 °C. MALDI-TOF MS: m/z = 870.7 $(M + H^+)$, 892.6 $(M + Na^+)$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 11.60 (br, 1H), 9.17 (s, 1H), 7.35 (s, 1H), 7.30(s, 1H), 7.13 (d, J = 2.1 Hz, 1H), 7.08 (d, J = 2.1 Hz, 1H), 6.96 (d, J = 1.9 Hz, 1H), 6.23 (d, J = 1.9 Hz, 1H), 5.94 (s, 1H), 4.83 (d, J = 13.5 Hz, 1H), 4.66 (d, J = 12.8 Hz, 1H), 4.45 (d, J = 12.8 Hz, 1H), 4.43 (d, J = 13.2 Hz, 1H), 3.67−4.17 (m, 9H), 3.39 (d, J = 12.8 Hz, 1H), 3.14 (d, J = 13.5 Hz, 1H), 3.09 (d, J = 12.8 Hz, 1H), 2.88 (s, 3H), 1.97−2.02 (m, 8H), 1.30 (s, 9H), 1.23 (s, 9H), 1.06−1.11 (m, 6H), 0.86−0.95 (m, 6H), 0.16 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.8, 155.8, 155.0, 154.7, 154.6, 153.2, 145.6, 145.0, 144.4, 144.2, 142.4, 138.5, 136.1, 135.8, 134.0, 132.9, 132.6, 132.2, 128.1, 127.8, 126.6, 126.3, 125.9, 125.3, 124.5, 124.0, 120.5, 77.6, 77.0, 76.9, 76.2, 34.1, 34.0, 33.2, 31.7, 31.5, 31.4, 31.2, 30.6, 28.8, 24.8, 23.6, 23.3, 23.2, 22.6, 10.8, 10.6, 10.0, 9.9. Anal. Calcd for $C_{57}H_{75}O_6N$: C, 78.67; H, 8.69; N, 1.61. Found: C, 78.51; H, 8.79; N, 1.58.

Calix[4]quinoline 6 (Racemic Mixture). Calix[4]quinoline **4** (1.80 g, 2.5 mmol) was hydrolyzed according to the method for the preparation of **5**. Compound **6** was isolated by column chromatography (silica gel; petroleum ether/ethyl acetate, 1/1) as a white solid (1.38 g, yield 80%). Mp: 149−150 °C. MALDI-TOF MS: m/z = 702.7 $(M + H^+)$, 724.7 $(M + Na^+)$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 13.66 (br, 1H), 9.33 (s, 1H), 8.05 (s, 1H), 6.87 (d, J = 7.1 Hz, 1H), 6.78 (d, J = 7.1 Hz, 1H), 6.64 (t, J = 7.1 Hz, 1H), 6.03−6.12 (m, 5H), 5.90 (d, J = 6.4 Hz, 1H), 4.55 (d, J = 13.1 Hz, 2H), 4.34 (d, J = 13.3 Hz, 2H), 3.54−4.08 (m, 9H), 3.40 (d, J = 13.4 Hz, 1H), 3.15 (s, 3H), 3.04 (d, J = 13.4 Hz, 2H), 1.91−1.94 (m, 8H), 0.98 (t, J = 7.2 Hz, 6H), 0.84 (t, J = 7.2 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9, 156.6, 155.7, 154.9, 154.5, 154.4, 144.1, 140.4, 138.1, 135.6, 135.5, 132.9, 132.8, 131.6, 130.8, 130.7, 127.8, 127.5, 127.0, 126.9, 126.6, 126.1, 125.6, 125.0, 123.3, 121.2, 120.7, 76.0, 75.91, 75.8, 75.5, 30.9, 30.0, 29.9, 23.6, 22.4, 22.3, 22.1, 22.0, 21.9, 9.7, 8.9. Anal. Calcd for $C_{45}H_{51}O_6N$: C, 77.00; H, 7.32; N, 2.00. Found: C, 76.85; H, 7.51; N, 1.81.

Calix[4]quinolines 7a and 7b (Diastereomers). A solution of **5** (1.2 g, 1.38 mmol), (*S*)-BINOL (0.434 g, 1.52 mmol), DCC (0.427 g, 2.07 mmol), and DMAP (0.084 g, 0.69 mmol) in dry CH_2Cl_2 (10 mL) was stirred at room temperature for 10 h. During this period, a large amount of insoluble DCU was formed which was removed by filtration. After removal of the solvent, the residue was purified by column chromatography (silica gel; petroleum ether/CH_2Cl_2/ethyl acetate, 10/10/1) to afford **7a** (0.675 g, yield 43%) and **7b** (0.628 g, yield 40%) as pure enantiomers, respectively.

7a: Mp: 146−147 °C. $[\alpha]^{25}_D$ −100° (c 2, acetone). MALDI-TOF MS: m/z = 1138.9 $(M + H)^+$, 1160.8 $(M + Na)^+$, 1176.8 $(M + K^+)$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.70 (s, 1H), 7.94 (d, J = 8.9 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.71 (d, J = 8.9 Hz, 1H), 7.63−7.67 (m, 1H), 7.26−7.43 (m, 5H), 6.88−7.17 (m, 8H), 6.44 (s, 1H), 6.30 (s, 1H), 6.04 (s, 1H), 4.66 (d, J = 13.3 Hz, 1H), 4.57 (d, J = 12.8 Hz, 1H), 4.43 (d, J = 13.3 Hz, 2H), 3.68−4.12 (m, 8H), 3.64 (d, J = 13.3 Hz, 1H), 3.27 (d, J = 13.3 Hz, 1H), 3.12 (d, J = 12.8 Hz, 1H), 3.09 (d, J = 13.3 Hz, 1H), 2.12 (s, 3H), 1.91−2.00 (m, 8H), 1.20 (s, 9H), 1.14 (s, 9H), 1.02−1.08 (m, 6H), 0.92−0.98 (m, 6H), 0.46 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.3, 155.0, 154.8, 154.6, 154.5, 153.5, 152.2, 148.1, 145.7, 144.9, 144.4, 144.3, 142.5, 137.8, 135.5, 135.4, 133.9, 133.8, 133.6, 133.0, 132.8, 132.7, 132.3, 130.4, 130.3, 129.0, 128.5, 128.3, 128.0, 127.2, 126.8, 126.4, 126.2, 126.1, 125.7, 125.3, 124.8, 124.6, 124.4, 123.8, 123.7, 123.6, 122.3, 120.3, 118.4, 114.4, 77.4, 77.1, 76.9, 76.4, 34.1, 34.0, 33.3, 31.7, 31.6, 31.3, 30.9, 30.7, 28.0, 24.6, 23.6, 23.3, 22.9, 10.8, 10.6, 10.2, 10.1. Anal. Calcd for $C_{77}H_{87}O_7N{\cdot}0.5H_2O$: C, 80.59; H, 7.73; N, 1.22. Found: C, 80.27; H, 7.95; N, 1.20.

7b: Mp: 159−160 °C. $[\alpha]^{25}_D$ +72° (c 2, acetone). MALDI-TOF MS: m/z = 1138.7 $(M + H^+)$, 1160.6 $(M + Na^+)$, 1176.6 $(M + K^+)$, ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26 (s, 1H), 8.12 (d, J = 8.9 Hz, 1H), 7.98 (d, J = 8.20 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 7.61 (d, J = 8.9 Hz, 1H), 7.56 (d, J = 8.9 Hz, 1H), 7.46−7.49 (m, 1H), 7.31−7.40 (m, 5H), 7.16 (s, 1H), 7.07 (d, J = 8.90 Hz, 1H), 7.01 (s, 2H), 6.89 (d, J = 1.8 Hz, 1H), 6.80 (s, 1H), 6.25 (d, J = 1.8 Hz, 1H), 5.95 (s, 1H), 5.39 (s, 1H), 4.58 (d, J = 13.0 Hz, 1H), 4.43 (d, J = 13.0 Hz, 2H), 4.40 (d, J = 13.0 Hz, 1H), 3.60−4.11 (m, 8H), 3.27 (d, J = 13.0 Hz, 1H), 3.12 (d, J = 13.0 Hz, 1H), 3.06 (d, J = 13.6 Hz, 1H), 2.93 (d, J = 13.6 Hz, 1H), 2.51 (s, 3H), 1.92−2.00 (m, 8H), 1.24 (s, 9H), 1.18 (s, 9H), 1.02−1.08 (m, 6H), 0.90−0.98 (m, 6H), 0.44 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 155.7, 154.8, 154.6, 154.4, 153.3, 152.1, 148.7, 145.9, 144.9, 144.3, 144.2, 142.5, 137.4, 135.6, 135.5, 133.8, 133.6, 132.8, 132.5, 132.4, 130.7, 130.4, 129.0, 128.5, 128.4, 128.0, 127.6, 127.1, 126.4, 126.2, 125.8, 125.4, 125.3, 124.6, 124.5, 124.2, 123.7, 123.6, 123.5, 122.5, 118.9, 118.6, 114.3, 77.4, 77.0, 76.9, 76.3, 34.1, 33.2, 31.7, 31.6, 31.2, 30.6, 27.6, 24.8, 23.6, 23.3, 23.2, 22.8, 10.8, 10.7, 10.1, 10.0. Anal. Calcd for $C_{77}H_{87}O_7N$: C, 81.23; H, 7.70; N, 1.23. Found: C, 80.88; H, 8.06; N, 1.54.

Calix[4]quinolines (+)-5a and (−)-5b (Enantiomerically Pure). Hydrolyzing **7a** (0.675 g, 0.77 mmol) and **7b** (0.628 g, 0.72 mmol) according to the method for preparing **5** afforded (+)-**5a** (0.413 g, yield 80%) and (−)-**5b** (0.480 g, yield 82%), respectively, as white solids with enantiomeric purity.

(+)-5a: Mp: 179−181 °C. $[\alpha]^{25}_D$ +50.4° (c 2, acetone).

(−)-5b: Mp: 180−181 °C. $[\alpha]^{25}_D$ −49.6° (c 2, acetone).

Calix[4]quinolines 8a and 8b (Diastereomers). A solution of **6** (0.58 g, 0.83 mmol) and $SOCl_2$ (0.5 mL) in CH_2Cl_2 (3 mL) was refluxed for 4 h. The reaction mixture was concentrated in vacuo, and the resultant acid chloride was dissolved in CH_2Cl_2 (3 mL) and added to the solution of (*R*)-phenylglycinol (0.17 g, 1.24 mmol) and Et_3N (0.17 mL, 1.24 mmol) in CH_2Cl_2 (5 mL) at room temperature. The mixture was stirred at room temperature for 8 h, and the reaction was stopped by adding water. The organic layer was washed with a small

portion of water and brine and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was purified by column chromatography (petroleum ether/ethyl acetate, 1/1 v/v) to afford **8a** and **8b** as a white solid of diastereomeric mixture (0.487 g, yield 86%), which was then subjected to preparative TLC using petroleum ether/ethyl acetate (1:1, v/v) as eluent. The two dispatched bands (UV−vis) were collected and soaked in ethyl acetate for several hours (decomposed slightly). Then, each was eluted with ethyl acetate through short column chromatography to give **8a** (0.238 g, yield 42%) and **8b** (0.221 g, yield 39%) as pure enantiomers, respectively.

8a: Mp: 117−118 °C. $[\alpha]^{25}_D$ +16° (*c* 2, acetone). MALDI-TOF MS: *m/z* = 821.4 (M + H)$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1H), 7.56 (s, 1H), 7.39−7.41 (m, 4H), 7.31−7.36 (m, 1H), 6.78 (d, *J* = 6.6 Hz, 1H), 6.48−6.64 (m, 3H), 6.35−6.37 (m, 2H), 6.28−6.32 (m, 1H), 6.15−6.18 (m, 2H), 5.25−5.31 (m, 1H), 4.66 (d, *J* = 14.0 Hz, 1H), 4.62 (d, *J* = 13.5 Hz, 1H), 4.43 (d, *J* = 13.4 Hz, 1H), 4.41 (d, *J* = 13.5 Hz, 1H), 3.73−4.07 (m, 12H), 3.39 (d, *J* = 13.5 Hz, 1H), 3.15 (d, *J* = 13.4 Hz, 1H), 3.11 (d, *J* = 13.4 Hz, 1H), 2.78 (s, 3H), 1.88−1.96 (m, 8H), 1.02−1.08 (m, 6H), 0.92−0.97 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.4, 157.2, 156.2, 156.0, 155.9, 153.3, 142.5, 138.8, 136.0, 134.8, 134.6, 133.4, 133.0, 131.5, 129.8, 129.0, 128.6, 128.3, 128.2, 128.1, 128.0, 127.8, 127.4, 126.8, 124.6, 122.3, 121.9, 121.7, 77.0, 76.9, 76.8, 76.5, 66.4, 56.4, 31.7, 31.1, 31.0, 25.5, 23.4, 23.2, 23.17, 23.1, 10.6, 10.5, 10.2, 10.1. Anal. Calcd for $C_{53}H_{60}O_6N_2$: C, 77.53; H, 7.37; N, 3.41. Found: C, 77.04; H, 7.43; N, 3.71.

8b: Mp: 120−121 °C. $[\alpha]^{25}_D$ +88° (*c* 2, acetone). MALDI-TOF MS: *m/z* = 821.4 (M + H)$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.36 (s, 1H), 7.54 (s, 1H), 7.26−7.41 (m, 5H), 6.78 (d, *J* = 6.6 Hz, 1H), 6.46−6.62 (m, 3H), 6.16−6.35 (m, 5H), 5.27−5.32 (m, 1H), 4.64 (d, *J* = 14.3 Hz, 1H), 4.61 (d, *J* = 13.5 Hz, 1H), 4.43 (d, *J* = 13.4 Hz, 1H), 4.42 (d, *J* = 13.5 Hz, 1H), 3.73−4.09 (m, 12H), 3.39 (d, *J* = 13.5 Hz, 1H), 3.14 (d, *J* = 13.4 Hz, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 2.77 (s, 3H), 1.86−1.99 (m, 8H), 1.01−1.08 (m, 6H), 0.92−1.00 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.4, 157.2, 156.2, 156.0, 155.9, 153.3, 145.0, 142.4, 138.8, 136.1, 134.7, 134.6, 133.5, 132.9, 131.3, 129.9, 129.0, 128.6, 128.2, 128.1, 128.0, 127.9, 127.8, 127.4, 126.8, 124.6, 122.3, 122.0, 121.7, 77.1, 76.9, 76.8, 76.5, 66.4, 56.4, 31.7, 31.1, 31.0, 25.5, 23.6, 23.4, 23.2, 23.1, 10.6, 10.5, 10.2, 10.1. Anal. Calcd for $C_{53}H_{60}O_6N_2{\cdot}0.5H_2O$: C, 76.68; H, 7.41; N, 3.37. Found: C, 77.00; H, 7.48; N, 3.59.

General Procedure for the Synthesis of 9a and 9b. A solution of **8a** (0.10 g, 0.12 mmol), sodium methoxide (0.033 g, 0.61 mmol), and dimethyl carbonate (0.055 g, 0.61 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature for 48 h. After the reaction was completed, water was added and the organic layer was separated. The aqueous layer was acidified to ca. pH = 7 with HCl and was extracted with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtered, and concentrated in vacuo. The mixture was chromatographed on silica gel by petroleum ether/ethyl acetate (1:1, v/v) to give **9a** (0.040 g, yield 46%) as a white solid.

9a: Mp: 64−65 °C. $[\alpha]^{25}_D$ −51.2° (*c* 2, CH_2Cl_2). MALDI-TOF MS: *m/z* = 716.5 (M + H)$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.04 (s, 1H), 7.76 (s, 1H), 6.96 (d, *J* = 7.3 Hz, 1H), 6.86 (d, *J* = 7.3 Hz, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.19−6.23 (m, 5H), 5.90−5.98 (m, 1H), 4.64 (d, *J* = 13.7 Hz, 2H), 4.45 (d, *J* = 13.4 Hz, 1H), 4.44 (d, *J* = 13.3 Hz, 1H), 3.95−4.16 (m, 8H), 3.70−3.83 (m, 4H), 3.43 (d, *J* = 13.3 Hz, 1H), 3.15 (d, *J* = 13.4 Hz, 2H), 3.00 (s, 3H), 1.89−1.96 (m, 8H), 1.07−1.12 (m, 6H), 0.90−0.96 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 157.6, 156.0, 155.6, 155.5, 136.6, 136.5, 134.0, 132.9, 132.0, 131.2, 128.8, 128.5, 128.0, 127.9, 127.6, 127.0, 125.1, 122.2, 122.16, 122.1, 121.8, 77.1, 76.9, 76.8, 76.5, 52.5, 31.9, 31.1, 31.0, 25.2, 24.5, 23.5, 23.4, 23.1, 23.0, 10.7, 10.0, 9.96. Anal. Calcd for $C_{46}H_{53}O_6N{\cdot}0.5H_2O$: C, 76.21; H, 7.51; N, 1.93. Found: C, 75.77; H, 7.64; N, 2.13.

9b: Yield: 45%. Mp: 64−65 °C. $[\alpha]^{25}_D$ +52° (*c* 2, CH_2Cl_2). MALDI-TOF MS: *m/z* = 716.5 (M + H)$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.04 (s, 1H), 7.76 (s, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.88 (d, *J* = 7.3 Hz, 1H), 6.73 (t, *J* = 7.3 Hz, 1H), 6.19−6.23 (m, 5H), 5.90−5.98 (m, 1H), 4.64 (d, *J* = 13.6 Hz, 2H), 4.45 (d, *J* = 13.4 Hz, 1H), 4.44 (d, *J* = 13.3 Hz, 1H), 3.95−4.18 (m, 8H), 3.71−3.85 (m, 4H), 3.44 (d, *J* = 13.3 Hz, 1H), 3.16 (d, *J* = 13.4 Hz, 2H), 3.00 (s, 3H), 1.90−2.00 (m, 8H), 1.07−1.12 (m, 6H), 0.90−0.96 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.2, 157.6, 156.0, 155.6, 155.5, 136.6, 136.5, 134.0, 132.9, 132.0, 131.2, 128.8, 128.5, 128.0, 127.9, 127.6, 127.0, 125.1, 122.2, 122.16, 122.1, 121.8, 77.1, 76.9, 76.8, 76.5, 52.3, 31.9, 31.1, 30.9, 25.4, 24.5, 23.5, 23.4, 23.1, 23.0, 10.7, 10.0, 9.95. Anal. Calcd for $C_{46}H_{53}O_6N{\cdot}0.5H_2O$: C, 76.21; H, 7.51; N, 1.93. Found: C, 75.66; H, 7.65; N, 1.85.

Calix[4]quinoline 10 (Racemic Mixture). Compound **1** (1.5 g, 1.94 mmol) was dissolved in 15 mL of HCl (6 N) and 5 mL of 1-butanol. The mixture was stirred and heated to reflux (105 °C) at which point a solution of crotonaldehyde (0.32 mL, 3.88 mmol) in 1-butanol (5 mL) was added to the refluxing solution dropwise over 20 min. After the addition was completed, the mixture was allowed to reflux for another 2 h. After removal of 1-butanol, the aqueous phase was neutralized with 10% NaOH and extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over Na_2SO_4 and evaporated. The crude material was purified by column chromatography through silica gel using petroleum ether/ethyl acetate (6:1, v/v) to yield **10** (1.15 g, yield 72%) as a white solid. Mp: 195−196 °C. MALDI-TOF MS: *m/z* = 826.7 (M + H)$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.4 Hz, 1H), 7.35 (s, 1H), 6.83−6.98 (m, 5H), 6.39 (s, 1H), 6.16 (s, 1H), 4.74 (d, *J* = 13.5 Hz, 1H), 4.59 (d, *J* = 12.7 Hz, 1H,), 4.44 (d, *J* = 13.0 Hz, 1H), 4.42 (d, *J* = 13.0 Hz, 1H), 3.70−4.09 (m, 9H), 3.36 (d, *J* = 12.7 Hz, 1H), 3.13 (d, *J* = 13.0 Hz, 1H), 3.08 (d, *J* = 13.0 Hz, 1H), 2.54 (s, 3H), 1.92−2.05 (m, 8H), 1.20 (s, 9H), 1.14 (s, 9H), 1.01−1.08 (m, 6H), 0.92−0.99 (m, 6H), 0.60 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.4, 154.7, 154.3, 154.0, 153.5, 144.9, 144.6, 144.2, 143.7, 139.1, 135.2, 134.9, 133.7, 133.2, 133.0, 132.6, 128.3, 127.2, 125.9, 125.8, 125.6, 125.0, 124.7, 124.6, 124.2, 119.7, 77.2, 77.0, 76.8, 76.5, 34.0, 33.8, 33.3, 31.6, 31.5, 31.4, 31.3, 31.2, 30.8, 24.7, 23.5, 23.2, 22.8, 10.6, 10.5, 10.1, 10.0. Anal. Calcd for $C_{56}H_{75}O_4N$: C, 81.41; H, 9.16; N, 1.70. Found: C, 81.41; H, 9.41; N, 1.82.

Calix[4]quinoline 11 (Racemic Mixture). A solution of **10** (0.69 g, 0.83 mmol) and SeO_2 (0.212 g, 1.91 mmol) in pyridine (5 mL) was refluxed for 70 min. The reaction mixture was filtered, and the solvent was evaporated to give the residue which was, after addition of a little amount of water, extracted with CH_2Cl_2. The CH_2Cl_2 layer was dried over Na_2SO_4 and concentrated in vacuo. The crude material was purified by column chromatography through silica gel using petroleum ether/ethyl acetate (2:1, v/v) to give **11** (0.501 g, yield 70%) as a white solid. Mp: 129−130 °C. MALDI-TOF MS: *m/z* = 856.7 (M + H)$^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.72 (br, 1H), 8.50 (d, *J* = 8.8 Hz, 1H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.28 (s, 1H), 7.21 (d, *J* = 2.1 Hz, 1H), 7.17 (d, *J* = 2.1 Hz, 1H), 7.10 (d, *J* = 2.3 Hz, 1H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 5.85 (d, *J* = 2.0 Hz, 1H), 4.85 (d, *J* = 13.6 Hz, 1H), 4.67 (d, *J* = 12.9 Hz, 1H,), 4.43 (d, *J* = 12.8 Hz, 1 h), 4.38 (d, *J* = 13.2 Hz, 1H), 3.66−4.19 (m, 9H), 3.39 (d, *J* = 13.2 Hz, 1H), 3.13 (d, *J* = 12.8 Hz, 1H), 3.06 (d, *J* = 13.6 Hz, 1H), 1.88−1.99 (m, 8H), 1.36 (s, 9H), 1.27 (s, 9H), 1.06−1.12 (m, 6H), 0.88−0.98 (m, 6H), 0.34 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.5, 156.6, 155.0, 154.7, 153.1, 145.1, 144.2, 144.1, 142.7, 142.6, 141.4, 136.2, 136.1, 135.2, 134.0, 132.6, 132.4, 132.1, 129.0, 128.4, 127.2, 126.5, 126.4, 126.3, 125.3, 124.5, 123.8, 116.5, 77.7, 77.2, 76.9, 76.2, 34.1, 34.0, 33.0, 31.7, 31.6, 31.5, 30.8, 30.4, 29.1, 23.5, 23.4, 23.2, 22.6, 10.8, 10.6, 10.0, 9.8. Anal. Calcd for $C_{56}H_{73}O_6N$: C, 78.56; H, 7.59; N, 1.64. Found: C, 78.67; H, 8.75; N, 1.57.

Calix[4]quinolines 12a and 12b (Diastereomers). The calix[4]quinolines **12a** and **12b** were synthesized from **11** (0.50 g, 0.59 mmol) as in the case of the preparation of **7a** and **7b**. The crude material was purified by column chromatography

(petroleum ether/ethyl acetate, 5/1) to afford **12a** and **12b** as a white solid of diastereomeric mixture (0.473 g, yield 72%) which was then subjected to preparative TLC using petroleum ether/ethyl acetate (petroleum ether/CH_2Cl_2/ethyl acetate, 10/10/1) as eluent. The two dispatched bands (UV−vis) were collected and soaked in ethyl acetate for several hours (decomposed slightly). Then each was eluted with ethyl acetate through short column chromatography to give **12a** (0.237 g, yield 36%) and **12b** (0.217 g, yield 33%) as pure enantiomers, respectively.

12a: Mp: 160−161 °C. $[\alpha]^{25}_D$ +28° (*c* 2, CH_2Cl_2). MALDI-TOF MS: *m/z* = 1124.8 $(M + H)^+$, 1146.9 $(M + Na)^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.25 (d, *J* = 8.9 Hz, 1H), 8.11 (d, *J* = 8.9 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.75−7.78 (m, 2H), 7.52−7.61 (m, 3H), 7.17−7.35 (m, 7H), 6.88 (s, 2H), 6.78−6.80 (m, 2H), 6.43 (s, 1H), 6.20 (s, 1H), 5.34 (br, 1H), 4.70 (d, *J* = 13.6 Hz, 1H), 4.56 (d, *J* = 12.7 Hz, 1H), 4.42 (d, *J* = 12.8 Hz, 1H), 4.40 (d, *J* = 12.6 Hz, 1H), 3.67−4.09 (m, 9H), 3.35 (d, *J* = 12.8 Hz, 1H), 3.12 (d, *J* = 12.7 Hz, 1H), 3.09 (d, *J* = 12.6 Hz, 1H), 1.94−1.99 (m, 8H), 1.15 (s, 9H), 1.07 (s, 9H), 0.99−1.04 (m, 6H), 0.92−0.98 (m, 6H), 0.56 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.5, 156.9, 154.5, 154.1, 153.6, 151.9, 148.4, 144.8, 144.5, 144.0, 143.8, 141.1, 135.0, 134.6, 133.6, 133.9, 133.4, 133.2, 133.1, 132.9, 132.3, 132.2, 130.8, 130.4, 130.3, 128.9, 128.3, 128.2, 128.0, 127.6, 127.4, 126.7, 126.3, 126.0, 125.9, 125.8, 125.3, 125.0, 124.8, 124.3, 123.4, 123.2, 122.0, 119.0, 118.3, 114.0, 77.3, 77.0, 76.8, 76.6, 34.0, 33.8, 33.3, 31.6, 31.5, 31.4, 31.3, 30.7, 27.3, 23.4, 23.3, 23.2, 22.9, 10.6, 10.3, 10.2, 10.1. Anal. Calcd for $C_{76}H_{85}O_7N{\cdot}0.5H_2O$: C, 80.53; H, 7.65; N, 1.24. Found: C, 80.29; H, 7.61; N, 1.47.

12b: Mp: 156−157 °C. $[\alpha]^{25}_D$ −184° (*c* 2, CH_2Cl_2). MALDI-TOF MS: *m/z* = 1124.8 $(M + H)^+$, 1146.9 $(M + Na)^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.24 (d, *J* = 8.9 Hz, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.99 (d, *J* = 8.1 Hz, 1H), 7.74−7.78 (m, 2H), 7.49−7.54 (m, 3H), 7.20−7.34 (m, 7H), 6.90−6.93 (m, 3H), 6.83 (d, *J* = 2.2 Hz, 1H), 6.27 (s, 1H), 6.04 (s, 1H), 5.44 (br, 1H), 4.72 (d, *J* = 13.6 Hz, 1H), 4.56 (d, *J* = 12.8 Hz, 1H), 4.40 (d, *J* = 12.8 Hz, 1H), 4.39 (d, *J* = 13.2 Hz, 1H), 3.67−4.15 (m, 9H), 3.34 (d, *J* = 12.8 Hz, 1H), 3.09 (d, *J* = 12.8 Hz, 1H), 3.06 (d, *J* = 13.2 Hz, 1H), 1.92−1.99 (m, 8H), 1.16 (s, 9H), 1.13 (s, 9H), 0.99−1.07 (m, 6H,), 0.90−0.97 (m, 6H,), 0.31 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.7, 156.7, 154.6, 154.2, 153.4, 151.8, 148.5, 144.8, 144.4, 144.0, 143.5, 140.8, 135.4, 135.0, 133.7, 133.6, 133.2, 133.1, 133.0, 132.8, 132.4, 132.3, 130.8, 130.5, 130.4, 128.9, 128.3, 128.1, 128.0, 127.4, 127.2, 126.7, 126.3, 126.1, 125.8, 125.6, 125.0, 124.8, 123.9, 123.5, 123.4, 122.0, 119.0, 118.3, 114.1, 77.3, 77.0, 76.8, 76.4, 34.0, 33.8, 33.0, 31.6, 31.5, 31.3, 31.2, 30.4, 27.8, 23.5, 23.2, 22.7, 10.6, 10.4, 10.1, 10.0. Anal. Calcd for $C_{76}H_{85}O_7N{\cdot}0.5H_2O$: C, 80.53; H, 7.65; N, 1.24. Found: C, 80.75; H, 7.56; N, 1.57.

(+)-11a and (−)-11b (Enantiomerically Pure). Hydrolyzing **12a** (0.237 g, 0.21 mmol) and **12b** (0.217 g, 0.19 mmol) according to the method for preparing **5** afforded (+)-**11a** (0.153 g, yield 85%) and (−)-**11b** (0.144 g, yield 87%), respectively, as white solids with enantiomeric purity.

11a: Mp: 129−130 °C. $[\alpha]^{25}_D$ +156° (*c* 2, CH_2Cl_2).

11b: Mp: 129−131 °C. $[\alpha]^{25}_D$ −156° (*c* 2, CH_2Cl_2).

Synthetic Procedure for **Compound 14.** A sample of Cs_2CO_3 (10.68 g, 32.8 mmol) was placed in a 250 mL round-bottomed flask followed by DMF (80 mL). To this was added 5,11,17-tri-*tert*-butyl-23-nitro-25-hydroxy-26,27,28-tripropoxycalix[4]arene **13**[26] (2.5 g, 3.3 mmol), and the contents were stirred at rt. A solution of allyl bromide (3.96 g, 32.8 mmol) was added, and the mixture was stirred at room temperature for 24 h. After the reaction was completed, it was neutralized with 2 N hydrochloric acid. Then the organic layer was extracted with CH_2Cl_2. The combined organic layer was washed with water and dried over Na_2SO_4 and concentrated in vacuo. The crude material was purified by column chromatography through silica gel using petroleum ether/CH_2Cl_2 (5:1, v/v) to give **14** (1.72 g, yield 65%) as a white solid. Mp: 226−227 °C. MALDI-TOF MS: *m/z* = 826.7 $(M + Na)^+$, 842.6 $(M + K)^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.22 (s, 2H), 7.10 (s, 2H), 6.80 (d, *J* = 2.1 Hz, 2H), 6.57 (d, *J* = 2.1 Hz, 2H), 6.08−6.18 (m, 1H), 5.29−5.41 (m, 2H), 4.35 (d, *J* = 6.0 Hz, 2H), 4.0 (d, *J* = 12.6 Hz, 2H), 3.64−3.83 (m, 4H), 3.34−3.60 (m, 6H), 3.03 (d, *J* = 12.6 Hz, 2H), 1.89−1.94 (m, 4H), 1.35−1.44 (m, 2H), 1.34 (s, 9H), 1.02−1.08 (m, 6H), 1.01 (s, 18H), 0.64 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.6, 153.8, 153.3, 145.4, 143.9, 142.2, 135.7, 135.2, 134.3, 132.7, 130.0, 126.9, 126.1, 125.7, 125.5, 117.2, 76.5, 75.6, 74.0, 37.1, 34.1, 33.7, 31.7, 31.4, 30.5, 23.6, 21.9, 10.8, 9.2. Anal. Calcd for $C_{52}H_{69}O_6N$: C, 77.67; H, 8.65; N, 1.74. Found: C, 77.32; H, 8.57; N, 1.74.

Synthetic Procedure for **Compound 15.** Compound **14** (3.0 g, 3.74 mmol) was mixed with Pd/C (10%) (0.374 g) in THF/CH_3OH (v/v = 4/1, 50 mL), and the mixture was stirred under a H_2 atmosphere at room temperature. After the reaction was completed, the Pd/C was removed by filtration, and the solvent was evaporated under reduced pressure. The product (2.84 g, yield 98%) was not purified for the next reaction. Mp: 242−243 °C. MALDI-TOF MS: *m/z* = 798.7 $(M + Na)^+$, 814.6 $(M + K)^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.10 (s, 2H), 6.81 (d, *J* = 2.4 Hz, 2H), 6.61 (s, 2H), 6.54 (d, *J* = 2.4 Hz, 2H), 4.07 (d, *J* = 12.6 Hz, 2H), 3.74−3.77 (m, 2H), 3.46−3.56 (m, 10H), 3.30−3.40 (br, 2H), 3.03 (d, *J* = 12.6 Hz, 2H), 1.78−1.89 (m, 8H), 1.35 (s, 9H), 1.06 (t, *J* = 7.5 Hz, 6H), 1.02 (s, 18H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.0, 153.7, 145.1, 143.4, 135.9, 134.1, 132.2, 131.5, 125.9, 125.4, 125.3, 118.9, 76.0, 75.4, 74.8, 37.4, 34.1, 33.7, 31.7, 31.5, 30.7, 24.1, 23.8, 22.2, 10.9, 10.6, 10.0. Anal. Calcd for $C_{52}H_{73}O_4N$: C, 80.47; H, 9.48; N, 1.80. Found: C, 80.66; H, 9.64; N, 1.94.

Calix[4]quinoline 16 (Racemic Mixture). The calix[4]-quinoline **16** was synthesized from **15** (2.84 g, 3.67 mmol) as in the case of the preparation of **3**. The crude compound was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 6/1) to afford **16** (1.414 g, yield 43%) as a white solid. Mp: 217−218 °C. MALDI-TOF MS: *m/z* = 898.6 $(M + H)^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 9.30 (s, 1H), 8.03 (s, 1H), 7.08−7.12 (m, 2H), 6.97 (d, *J* = 2.2 Hz, 1H), 6.89 (d, *J* = 2.2 Hz, 1H), 6.58 (d, *J* = 2.2 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 1H), 4.41−4.60 (m, 3H), 3.64−4.05 (m, 9H), 3.48−3.53 (m, 1H), 2.97−3.47 (m, 5H), 3.04 (s, 3H), 1.91−1.96 (m, 4H), 1.49 (t, *J* = 7.1 Hz, 3H), 1.35 (s, 9H), 1.25−1.6 (m, 2H), 1.09 (s, 18H), 1.02 (t, *J* = 7.4 Hz, 6H), 0.86 (t, *J* = 7.5 Hz, 3H), 0.80−0.90 (m, 1H), 0.25 (t, *J* = 7.5 Hz, 3H), 0.21−0.30 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.5, 156.4,155.4, 153.9, 153.8, 153.6, 146.1, 145.2, 143.7, 143.5, 140.3, 137.0, 135.9, 135.7, 132.6, 132.2, 131.0, 130.8, 130.2, 130.0, 126.2, 125.9, 125.8, 125.7, 125.5, 125.4, 125.3, 121.7, 76.9, 76.1, 75.3, 75.0, 61.1, 38.3, 34.1, 33.7, 31.7, 31.5, 31.4, 30.8, 30.7, 29.6, 25.4, 24.1, 23.6, 23.0, 21.0, 14.4, 10.7, 10.6, 10.2, 8.7. Anal. Calcd for $C_{59}H_{79}O_6N$: C, 78.89; H, 8.86; N, 1.56. Found: C, 78.72; H, 8.94; N, 1.76.

Calix[4]quinoline 17 (Racemic Mixture). The calix[4]-quinoline **17** was synthesized from **16** (1.414 g, 1.58 mmol) as in the case of the preparation of **5**. The crude compound was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 1/1) to give **17** (1.233 g, yield 78%) as a white solid. Mp: 300−301 °C. MALDI-TOF MS: *m/z* = 870.6 $(M + H)^+$, 892.5 $(M + Na)^+$. ^1H NMR (300 MHz, $CDCl_3$): δ = 10.84−10.97 (br, 1H), 9.56 (s, 1H), 8.34 (s, 1H), 7.05−7.26 (m, 2H), 6.96 (d, *J* = 2.1 Hz, 1H), 6.87 (d, *J* = 2.1 Hz, 1H), 6.56 (d, *J* = 2.1 Hz, 1H), 6.53 (d, *J* = 2.1 Hz, 1H), 4.60 (d, *J* = 13.7 Hz, 1H), 3.65−4.14 (m, 9H), 2.96−3.50 (m, 6H), 3.19 (s, 3H), 1.93−1.97 (m, 4H), 1.32 (s, 9H), 1.45−1.6 (m, 2H), 1.05 (s, 18H), 0.98−1.10 (m, 6H), 0.85 (t, *J* = 7.3 Hz, 3H), 0.80−0.90 (m, 1H), 0.29 (t, *J* = 6.0 Hz, 3H), 0.21−0.30 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 171.0, 156.9, 156.0, 153.9, 153.8, 153.6, 145.3, 143.7, 143.6, 141.3, 139.3, 135.9, 135.7, 132.7, 132.3, 130.6, 130.5, 130.0, 128.9, 126.2, 126.0, 125.8, 125.4, 123.2, 77.0, 76.2,

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75.2, 75.0, 38.3, 34.1, 33.8, 31.7, 31.5, 31.4, 30.7, 29.7, 24.1, 23.5, 23.2, 21.1, 10.8, 10.6, 10.2, 8.8. Anal. Calcd for $C_{57}H_{75}O_6N\cdot 0.5H_2O$: C, 77.87; H, 8.71; N, 1.57. Found: C, 78.00; H, 8.80; N, 1.95.

Calix[4]quinolines 18a and 18b (Diastereomers). The calix[4]quinolines **18a** and **18b** were synthesized from **17** (1.233 g, 1.42 mmol) as in the case of the preparation of **7a** and **7b**. The crude compound was purified by column chromatography (silica gel; petroleum ether/acetone, 8/1) to afford **18a** (0.677 g, yield 43%) and **18b** (0.645 g, yield 40%) as pure enantiomers, respectively.

18a: Mp: 162−163 °C. $[\alpha]^{25}_D$ −156° (*c* 2, $CHCl_3$). MALDI-TOF MS: *m/z* = 1138.7 $(M + H)^+$, 1160.7 $(M + Na)^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.95 (s, 1H), 8.10 (d, *J* = 8.9 Hz, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 7.89 (s, 1H), 7.84 (d, *J* = 8.9 Hz, 1H), 7.73−7.76 (m, 1H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.51−7.55 (m, 1H), 7.33−7.37 (m, 2H), 7.13−7.24 (m, 4H), 7.04−7.10 (m, 2H), 6.95 (d, *J* = 2.2 Hz, 1H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.56 (d, *J* = 2.2 Hz, 1H), 6.53 (d, *J* = 2.2 Hz, 1H), 5.76 (s, 1H), 4.32 (d, *J* = 14.0 Hz, 1H), 3.39−3.97 (m, 10H), 2.93−3.18 (m, 5H), 2.51 (s, 3H), 1.80−1.89 (m, 4H), 1.30−1.75 (m, 2H), 1.32 (s, 9H), 1.06 (s, 9H), 1.04 (s, 9H), 0.93−1.02 (m, 6H), 0.67−0.70 (m, 4H), 0.11−0.25 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.5, 156.4, 155.2, 153.9, 153.7, 153.5, 151.8, 148.2, 146.1, 145.2, 143.7, 143.5, 140.8, 137.8, 135.8, 135.6, 133.7, 133.6, 132.7, 132.3, 132.2, 130.9, 130.7, 130.6, 130.2, 130.1, 129.0, 128.4, 128.0, 127.5, 126.8, 126.4, 126.2, 125.9, 125.8, 125.7, 125.3, 124.7, 123.6, 123.3, 122.1, 120.2, 118.0, 114.0, 76.6, 76.1, 75.3, 74.9, 38.3, 34.1, 33.8, 31.7, 31.5, 31.4, 30.7, 29.7, 24.7, 24.1, 23.5, 22.9, 21.0, 10.7, 10.6, 10.5, 8.7. Anal. Calcd for $C_{77}H_{87}O_7N$: C, 81.23; H, 7.70; N, 1.23. Found: C, 80.86; H, 7.75; N, 1.46.

18b: Mp: 159−160 °C. $[\alpha]^{25}_D$ +52° (*c* 2, $CHCl_3$). MALDI-TOF MS: *m/z* = 1138.7 $(M + H)^+$, 1160.6 $(M + Na)^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 8.16 (d, *J* = 8.9 Hz, 1H), 8.02 (d, *J* = 8.1 Hz, 1H), 7.90 (s, 1H), 7.80 (d, *J* = 8.9 Hz, 2H), 7.63 (d, *J* = 8.9 Hz, 1H), 7.51−7.58 (m, 1H), 7.35−7.39 (m, 2H), 7.17−7.25 (m, 4H), 7.02−7.10 (m, 2H), 6.90 (d, *J* = 2.2 Hz, 1H), 6.84 (d, *J* = 2.2 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 1H), 6.51 (d, *J* = 2.2 Hz, 1H), 5.38 (s, 1H), 3.95 (d, *J* = 12.6 Hz, 2H), 3.39−3.85 (m, 8 H), 2.90−3.25 (m, 6H), 2.75 (s, 3H), 1.83−1.89 (m, 4H), 1.08−1.38 (m, 2H), 1.31 (s, 9H), 1.08 (s, 9H), 1.03 (s, 9H), 0.95−1.00(m, 6H), 0.71−0.77 (m, 4H), 0.15−0.20 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 156.3, 155.5, 153.8, 153.7, 153.4, 151.9, 148.4, 146.1, 145.2, 143.7, 143.4, 140.9, 137.2, 135.9, 135.6, 133.6, 132.7, 132.3, 132.1, 130.9, 130.8, 130.7, 130.5, 130.3, 130.0, 129.0, 128.4, 128.2, 127.6, 127.0, 126.4, 126.2, 126.0, 125.7, 125.3, 124.5, 123.6, 123.2, 122.1, 119.6, 118.4, 114.0, 76.6, 76.1, 75.2, 74.8, 38.2, 34.1, 33.8, 31.7, 31.5, 31.4, 30.7, 29.7, 24.6, 24.0, 23.5, 23.0, 21.0, 10.7, 10.6, 10.4, 8.7. Anal. Calcd for $C_{77}H_{87}O_7N\cdot 0.5H_2O$: C, 80.59; H, 7.73; N, 1.22. Found: C, 80.35; H, 7.71; N, 1.36.

(+)-17a and (−)-17b (Enantiomerically Pure). Hydrolyzing **18a** (0.677 g, 0.60 mmol) and **18b** (0.645 g, 0.57 mmol) according to the method for preparing **5** afforded (+)-**17a** (0.378 g, yield 73%) and (−)-**17b** (0.365 g, yield 74%), respectively, as white solids with enantiomeric purity.

17a: Mp: 300−302 °C. $[\alpha]^{25}_D$ +8° (*c* 1, $CHCl_3$).

17b: Mp: 300−301 °C. $[\alpha]^{25}_D$ −8° (*c* 1, $CHCl_3$).

Calix[4]quinoline 19 (Racemic Mixture). Calix[4]-quinoline **19** was synthesized from **15** (1.30 g, 1.68 mmol) as in the case of the preparation of **10**. The crude compound was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 5/1) to give **19** (0.969 g, yield 70%) as a white solid. Mp: 232−234 °C. MALDI-TOF MS: *m/z* = 826.5 $(M + H)^+$, 848.5 $(M + Na)^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.53 (d, *J* = 8.0 Hz, 1H), 7.98 (s, 1H), 7.24 (d, *J* = 8.0 Hz, 1H), 7.04−7.08 (m, 2H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.56 (d, *J* = 2.4 Hz, 1H), 6.51 (d, *J* = 2.4 Hz, 1H), 4.47 (d, *J* = 14.0 Hz, 1H), 3.98 (d, *J* = 12.6 Hz, 2H), 3.29−3.89 (m, 9H), 2.96−3.17 (m, 4H), 2.76 (s, 3H), 1.61−1.96 (m, 6H), 1.33 (s, 9H), 1.05 (s, 9H), 1.04 (s, 9H), 0.96−1.02 (m, 6H), 0.89 (t, *J* = 7.4 Hz, 3H), 0.84−0.88 (m, 1H), 0.22 (t, *J* = 7.0 Hz, 3H), 0.21−0.25 (m,1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 155.8, 155.7, 153.9, 153.8, 153.6, 145.1, 143.5, 143.4, 137.4, 135.9, 135.7, 133.1, 132.6, 132.2, 131.1, 130.7, 128.6, 126.3, 126.0, 125.8, 125.6, 125.4, 125.2, 119.9, 77.0, 76.0, 75.3, 74.8, 38.3, 34.1, 33.7, 31.7, 31.5, 31.4, 30.7, 30.6, 29.4, 25.0, 24.1, 23.6, 23.2, 20.8, 10.7, 10.5, 10.4, 8.7. Anal. Calcd for $C_{56}H_{75}O_4N\cdot 0.5H_2O$: C, 80.53; H, 9.17; N, 1.68. Found: C, 80.57; H, 9.16; N, 1.77.

Calix[4]quinoline 20 (Racemic Mixture). Calix[4]-quinoline **20** was synthesized from **19** (0.969 g, 1.17 mmol) as in the case of the preparation of **11**. The crude compound was purified by column chromatography (silica gel; petroleum ether/ethyl acetate, 1/1) to afford **20** (0.713 g, yield 71%) as a white solid. Mp: 238−239 °C. MALDI-TOF MS: *m/z* = 856.6 $(M + H)^+$. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.94 (br, 1H), 8.91 (d, *J* = 8.8 Hz, 1H), 8.26 (d, *J* = 8.8 Hz, 1H), 8.14 (s, 1H), 7.04−7.07 (m, 2H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.88 (d, *J* = 2.4 Hz, 1H), 6.58 (d, *J* = 2.3 Hz, 1H), 6.53 (d, *J* = 2.3 Hz, 1H), 4.53 (d, *J* = 14.0 Hz, 1H), 3.66−4.08 (m, 9H), 3.49−3.54 (m, 1H), 3.29−3.33 (m, 1H), 2.96−3.15 (m, 4H), 1.93−1.99 (m, 4H), 1.60−1.70 (m, 2H), 1.33 (s, 9H), 1.00−1.11 (m, 6H), 1.05 (s, 18H), 0.87 (t, *J* = 7.4 Hz, 3H), 0.70−0.90 (m, 1H), 0.14 (t, *J* = 6.8 Hz, 3H), 0.11−0.14 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8, 158.9, 153.8, 153.7, 153.5, 145.4, 143.9, 143.7, 143.3, 142.9, 140.0, 135.8, 135.7, 135.6, 132.7, 132.3, 131.5, 130.3, 130.2, 129.6, 126.3, 126.2, 126.0, 125.7, 125.5, 125.4, 117.0, 77.2, 76.2, 75.2, 75.1, 38.1, 34.1, 33.8, 31.7, 31.5, 31.4, 30.7, 30.6, 29.7, 29.6, 24.2, 23.7, 23.3, 20.9, 10.9, 10.5, 10.3, 8.9. Anal. Calcd for $C_{56}H_{73}O_6N$: C, 78.56; H, 8.59; N, 1.64. Found: C, 78.29; H, 8.78; N, 1.75.

Acknowledgment. We thank the National Science Foundation of China, the Major State Basic Research Development Program of China (Grant No. G2000078100, MOST 2002 CCA 03100), and the Chinese Academy of Sciences for financial support.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **3**−**6**, **7a**, **7b**, **8a**, **8b**, **9a**, **9b**, **10**, **11**, **12a**, **12b**, **16**, **17**, **18a**, **18b**, **19**, and **20**; ^{1}H NMR spectrum of **19** in the presence of Pirkle's reagent; 2D ^{1}H−^{1}H COSY spectra for compounds **17** and **20**. This material is available free of charge via the Internet at http://pubs.acs.org

JO050980B