A New Model of Light-Powered Chiral Molecular Motor with Higher Speed of Rotation, Part 1 – Synthesis and Absolute Stereostructure

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To develop a molecular motor with a higher speed of rotation, a new model light-powered chiral molecular motor **2** of five-membered ring type was designed, and the motor rotation isomers (–)-**2a** and (–)-**2c** were directly synthesized in enantiopure forms for the first time from the ketone (+)-**8**. The precursor alcohols **9** and **10** were enantioresolved by the camphorsultam-dichlorophthalic acid (CSDP acid; **3**) method, and their absolute configurations were determined by X-ray crystallographic analysis of the CSDP ester (–)-**11b** and chemical correlations. The enantiopure ketone (*S*)-(+)-**8** formed from (1*S*,2*S*)-(+)-**9** or (1*R*,2*S*)-(–)-**10** was subjected to the McMurry reaction with $TiCl_3/LiAlH_4$, yielding the motor rotation isomers [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** and [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c**. These studies enabled us unambiguously to determine the absolute stereostructure of the motor **2**, which is of critical importance for control over the direction of motor rotation.

Introduction

A "molecular machine" is a molecule or a molecular system capable of converting external energy into mechanical motion and of repeating the process continuously, and among molecular machines, molecular motors have attracted much recent attention. In 1997, H. Noji et al. reported the direct observation of the rotation of a biological motor, F_1-ATPase.[1] In 1999, B. L. Feringa et al. and we first succeeded in the construction of the synthetic molecular motor **1**, which can rotate in one rotational direction through conversion of light energy into motor rotation and can repeat this rotation continuously.[2,3] At the same time, T. R. Kelly et al. reported the one-directional rotation of the triptycene-helicene system, but this rotates by 120° only once and so cannot rotate continuously.[4] In 2003 and 2004, D. A. Leigh et al. reported one-directional rotation in a catenane system and the construction of a reversible molecular motor that can be made to rotate in one direction through sequential application of chemical reactions.[5] For the construction of a molecular motor, there are several key requirements. The first issue is that the system should be able to rotate by 360°, to come back to the starting state, and then to repeat the rotation continuously. The second issue is that the motor should have an engine mechanism capable of converting external energy into mechanical motor rotation. The third issue is that the motor should have a suitable mechanism to control the direction of motor rotation in the absolute sense: clockwise or counterclockwise.

Our light-powered chiral molecular motor **1** is composed of four motor rotation isomers **1a**, **1b**, **1c**, and **1d**, as shown in Figure 1.[2,3] On UV irradiation, the stable *trans*-olefin (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(–)-**1a** is converted into the unstable *cis*-olefin (3*R*,3′*R*)-(*M*,*M*)-(*Z*)-**1b**, which transforms thermally into the stable *cis*-olefin (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-(+)-**1c** at room temperature. Since the conversion **1a** → **1b** is a photochemical *trans*/*cis* isomerization, the reverse reaction **1b** → **1a** occurs naturally. However, the next step **1b**→**1c** is a thermal reaction and proceeds in one direction. Therefore, the total reaction shown in the upper half proceeds in the direction of **1a** → **1b** → **1c**. A similar mechanism applies for the reactions shown in the lower half. The stable *cis*-olefin (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-(+)-**1c** undergoes photochemical isomerization into the unstable *trans*-olefin (3*R*,3′*R*)-(*M*,*M*)-(*E*)-(+)-**1d**, which reverts to the original starting material, the stable *trans*-olefin (3*R*,3′*R*)-(*P*,*P*)-(*E*)-(–)-**1a**, upon heating at around 50–70 °C. The lower half reaction sequence **1c** → **1d** → **1a** also proceeds in one direction. During the reactions **1a** → **1b** → **1c** → **1d** → **1a**, the naphthalene moiety on the left side rotates by 360° counterclockwise relative to the naphthalene moiety on the right, fixed as the static part. The absolute sense of the motor rotation is controlled by the chirality of the motor molecule, so, if the motor is synthesized as the opposite enantiomer (3*S*,3′*S*)-(*M*,*M*)-(*E*)-**1a**, it rotates clockwise. It is thus important to control the chi-

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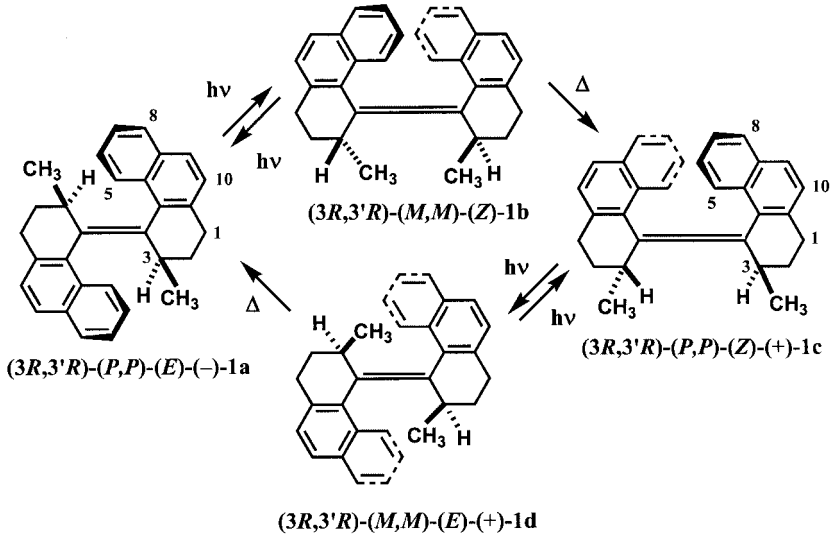
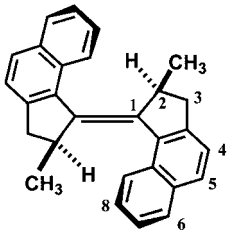


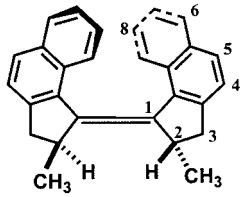
Figure 1. The first light-powered chiral molecular motor of the six-membered ring type, developed jointly by Feringa's group and by our own group, in which the rotational direction of the motor is controlled by the chirality of the molecule.

rality of the motor and to synthesize it in an enantiopure form. Our light-powered chiral molecular motor **1** hence ideally satisfies the requirements described above.

In the molecular motor **1**, the last step of the motor rotation, the thermal isomerization **1d** → **1a**, is relatively slow in relation to the other steps, resulting in slow motor rotation. This is due to the severe steric hindrance in the *trans*-1,1′,2,2′,3,3′,4,4′-octahydro-4,4′-biphenanthrylidene skeleton contained in motor type **1**, with the six-membered ring. To develop a molecular motor with a higher speed of rotation, we have designed a new motor system (**2**) containing five-membered rings (Figure 2). Our idea was that in the *trans* form **2a** of the motor, the naphthalene moiety is relatively remote from the five-membered ring, diminishing the steric hindrance, relative to that in **1a** of six-membered ring type. We expected that the same should be applicable to the unstable *trans* form **2d**, and that the motor **2** should hence rotate more speedily.



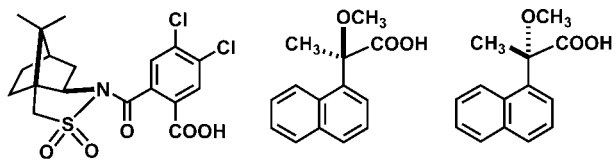
[CD(–)257.8]-(2*S*,2'*S*)-(*M*,*M*)-(*E*)-**2a**



[CD(–)270.0]-(2*S*,2'*S*)-(*M*,*M*)-(*Z*)-**2c**

Figure 2. The new light-powered chiral molecular motor of the five-membered ring type and motor rotational isomers, the absolute stereostructures of which were unambiguously determined as shown; the absolute configurational assignment by Feringa's group needs to be revised.

As described above, it is of critical importance to synthesize the molecular motor **2** in an enantiopure form and to determine its absolute stereochemistry unambiguously, so we adopted a strategy of enantioresolution of the racemic precursors with camphorsultam dichlorophthalic acid [CSDP acid; (1*S*,2*R*,4*R*)-(–)-**3**] and/or 2-methoxy-2-(1-naphthyl)propionic acids [MαNP acids; (*R*)-(–)-**4** and (*S*)-(+)-**4**], previously developed by us as chiral molecular tools useful for preparation of enantiopure alcohols and for simultaneous determination of their absolute configurations (Figure 3).[6,7] In the case of the chiral molecular motor **2**, the CSDP acid method was successful for enantioresolving alcohols and also for determining their absolute configurations by X-ray crystallography. The chiral molecular motor **2** was synthesized in an enantiopure form starting from the obtained enantiopure alcohols as described below. Although Feringa's group has also recently reported the chiral molecular motor **2**,[8] we have studied the same motor independently,[9] and here we report our own data. It should be noted that we have succeeded in the direct synthesis of chiral molecular motor **2** and hence in the unambiguous determination of its absolute stereochemistry, which disagreed with that proposed by the Feringa group, so their absolute configurational assignment needs to be revised.



CSDP acid (1*S*,2*R*,4*R*)-(–)-**3**

MαNP acid (*R*)-(–)-**4**

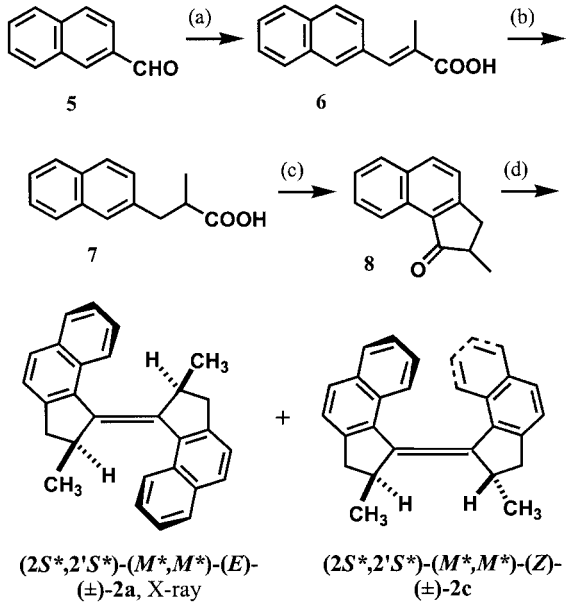
MαNP acid (*S*)-(+)-**4**

Figure 3. Chiral molecular tools **3** and **4**, useful for enantioresolution of alcohols and determination of their absolute configurations.

Results and Discussion

Synthesis of the Racemic Molecular Motor 2 of Five-Membered Ring Type and its Relative Stereochemistry

The precursor to the racemic ketone **8** was easily prepared as shown in Scheme 1; unlike in the case of the previous molecular motor of the six-membered ring type, the synthetic route was much shortened by use of the Perkin reaction.[10] The obtained carboxylic acid **6** adopted the (*E*) configuration, as was confirmed by the NOE correlation between Me2 and aromatic H1′ and H3′, although the double bond configuration was abolished in the next hydrogenation reaction. The cyclization of carboxylic acid **7** proceeded well, yielding ketone **8** with a five-membered ring, and this was next subjected to the McMurry reaction.[11] Out of the many preparation methods for the low-valent titanium McMurry reagent, we have adopted the combination of $TiCl_3$ and $LiAlH_4$; $LiAlH_4$ in THF was added to a suspension of $TiCl_3$ in dry THF cooled to 0 °C. After the mixture had been stirred at 0 °C for 0.5 h and had then been heated gently at reflux for 1.5 h, a solution of ketone **8** in dry THF was added, and the mixture was heated gently at reflux for 96 h. The crude product obtained was purified by column chromatography on silica gel (hexane/AcOEt, 20:1), by HPLC (silica gel, hexane), and finally by HPLC (ODS, MeOH). The *cis*-olefin (2*S**,2′*S**)-(*M**,*M**)-(*Z*)-(±)-**2c** was obtained as faintly yellow needles from the first fraction eluted (6%), whilst the *trans*-olefin (2*S**,2′*S**)-(*M**,*M**)-(*E*)-(±)-**2a** was obtained as colorless prisms (14%) from the second fraction.



Scheme 1. Synthesis of racemic molecular motor **2**. a) $(EtCO)_2O$, EtCOONa, 180 °C, 83%. b) H_2/Pd-C, EtOH, 87%. c) i) PCl_5, toluene. ii) $SnCl_4$, toluene, 98%. d) $TiCl_3$, $LiAlH_4$/THF, 80 °C, 96 h, (*E*)-**2a**, 14% and (*Z*)-**2c**, 6%.

The relative stereochemistries of these olefins were determined with the aid of the NMR spectroscopic data listed in Table 1 and Table 2 (and Supporting Information, figures S01 and S02); all NMR peaks including ^{13}C NMR peaks were fully assigned by the ^1H-^1H COSY, HMQC, HMBC, and NOESY spectra as shown. The olefins **2a** and **2c** each showed ^1H and ^{13}C NMR spectral peaks corresponding to half of the molecule, indicating their C_2-symmetrical structures. Namely, both olefins **2a** and **2c** were composed of homochiral halves. Since racemic ketone **8** had been used as the starting material, there had been the possibility of forming *trans* and *cis*-olefins composed of heterochiral halves, and compounds corresponding to such heterodimers without C_2-symmetrical structures were indeed isolated in 5% yield, although no further characterization studies were carried out.

The aromatic protons in the olefin **2c**, especially those at the 6-, 7-, 8-, and 9-positions, appeared at higher magnetic fields than those in the other olefin **2a**, indicating the dia-

Table 1. NMR spectroscopic data for the stable *trans*-olefin (±)-**2a** in $CDCl_3$.[a]

C/No.	H/No.	^1H [ppm]	^{13}C [ppm]	^1H–^1H COSY	HMBC	NOESY
C1			141.5			
C2	H2eq	3.06 (dq, *J* = 6.4, 6.4 Hz, 2 H)	43.1	Me2ax, H3ax	C3a, C9b	Me2ax
Me2ax	Me2ax	1.30 (d, *J* = 6.4 Hz, 6 H)	19.3	H2eq	C1, C2, C3	H2eq, H3eq, H9′
C3	H3eq	2.33 (d, *J* = 14.6 Hz, 2 H)	41.3	H3ax	C1, C2, Me2ax, C3a, C4, C9b	H2eq, H3ax, Me2ax
	H3ax	2.96 (dd, *J* = 14.6, 6.4 Hz, 2 H)		H2eq, H3eq	Me2ax, C3a	H3eq
C3a			141.9			
C4	H4	7.30 (d, *J* = 8.0 Hz, 2 H)	124.1	H5	C3, C5a, C9b	H3eq, H5
C5	H5	7.75 (d, *J* = 8.0 Hz, 2 H)	127.8	H4	C3a, C6, C9a	H4, H6
C5a			133.0			
C6	H6	7.90 (d, *J* = 8.3 Hz, 2 H)	128.5	H7	C5,C8, C9a	H5, H7
C7	H7	7.46 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2 H)	124.7	H6, H8, H9	C5a, C9	H6, H8
C8	H8	7.53 (ddd, *J* = 8.3, 6.8, 1.3 Hz, 2 H)	125.0	H6, H7, H9	C6, C9a	H7, H9
C9	H9	8.25 (d, *J* = 8.3 Hz, 2 H)	126.7	H8	C5a, C7, C9	Me2′ax, H8
C9a			130.3			
C9b			138.6			

[a] ^1H NMR (600 MHz) and ^{13}C NMR (150 MHz).

Table 2. NMR spectroscopic data for the stable *cis*-olefin (±)-**2c** in $CDCl_3$.[a]

C/No.	H/No.	^{1}H [ppm]	^{13}C [ppm]	^{1}H–^{1}H COSY	HMBC	NOESY
C1			139.9			
C2	H2eq	3.62 (dq, *J* = 6.7, 6.7 Hz, 2 H)	42.2	Me2ax,H3ax	C1, C3a, C9b	
Me2ax	Me2ax	1.22 (d, *J* = 6.7 Hz, 6 H)	20.7	H2eq	C1, C2, C3	H2eq, H3eq
C3	H3eq	2.68 (d, *J* = 14.5 Hz, 2 H)	40.6	H3ax	C1, C2, Me2ax, C3a, C4, C9b	
	H3ax	3.59 (dd, *J* = 14.5, 6.7 Hz, 2 H)		H2eq, H3eq	Me2ax, C3a	
C3a			144.0			
C4	H4	7.48 (d, *J* = 8.1 Hz, 2 H)	123.4	H5	C3, C5a, C9b	
C5	H5	7.70 (d, *J* = 8.1 Hz, 2 H)	128.4	H4	C3a, C5a, C6, C9a	
C5a			132.2			
C6	H6	7.64 (d, *J* = 8.1 Hz, 2 H)	127.6	H7	C5,C8, C9a	
C7	H7	6.96 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 2 H)	124.0	H6, H8, H9	C5a, C9	
C8	H8	6.36 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 2 H)	124.0	H6, H7, H9	C6, C9a	
C9	H9	6.58 (dd, *J* = 8.5, 1.3 Hz, 2 H)	126.6	H7, H8	C5a, C7, C9	
C9a			129.8			
C9b			136.9			

[a] ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz).

magnetic anisotropy effect due to the aromatic ring current. The *cis* structure, in which two naphthalene rings overlap each other, was therefore assigned to olefin **2c**, and the *trans* structure to olefin **2a**. The NOE observed between Me2ax and H9′ in olefin **2a** also supported the *trans* geometry of **2a**. In *trans*-olefin **2a** it was found that the methyl group had adopted the axial orientation, because the coupling constant between H2eq and H3eq was nil, indicating a dihedral angle of ca. 90° between them; this was possible only in the case of H2 having an equatorial orientation, dictating the axial orientation of the methyl group. The NOE between Me2ax and H3eq also supported this assignment. If the methyl group at the position 2 were to have the equatorial orientation, the compound would become extremely unstable due to the steric hindrance between methyl and naphthalene groups, as discussed in the following paper. From those studies, the relative stereochemistry of *trans*-olefin **2a** was determined as (2*S**,2′*S**)-(*M**,*M**); namely, if the methyl group is positioned in (*S*) fashion the helicity of naphthalene/double bond/naphthalene is *M*(minus)/*M*(minus), while the (*R*) configuration implies the *P*(plus)/*P*(plus) helicity.

Similar assignments were carried out for *cis*-olefin **2c**; the coupling constant between H2eq and H3eq was zero, implying a right angle between them, so the methyl group had the axial orientation. Other coupling constants and NOE data agreed reasonably with the assigned stereochemistry [(2*S**,2′*S**)-(*M**,*M**)] of *cis*-olefin **2c**. This stereostructure is reasonable for diminishing steric hindrance; if the methyl group at position 2 were to take the equatorial orientation in the *cis*-olefin, two methyl groups would collide with each other, again giving rise to an unstable conformation.

These stereochemical assignments by NMR spectroscopy were confirmed by the X-ray crystallographic analysis of racemic *trans*-olefin **2a** as follows. When (*E*)-(±)-**2a** was recrystallized from MeOH, colorless prisms (m.p. 191–192 °C) suitable for X-ray analysis were obtained, and a single crystal was subjected to X-ray crystallography (orthorhombic; space group *Pbca* (#61); radiation, Cu-K_α (1.54178 Å); unique data $F_o > 3\sigma(F_o)$, 3410). The structure was solved conventionally by direct methods and successive Fourier syntheses (R = 0.0500 and R_w = 0.0581; Table 3). As shown in Figure 4, the methyl group has the axial orientation, and the (2*S**,2′*S**)-(*M**,*M**)-(*E*) relative stereochemistry was determined unambiguously.

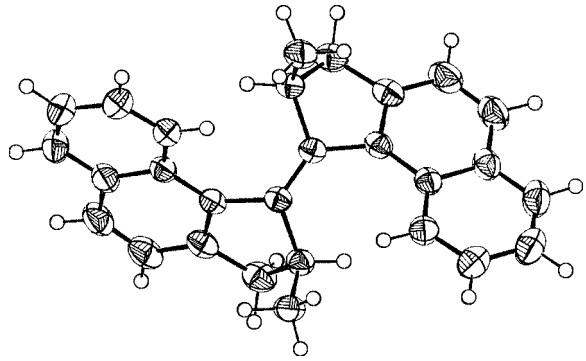
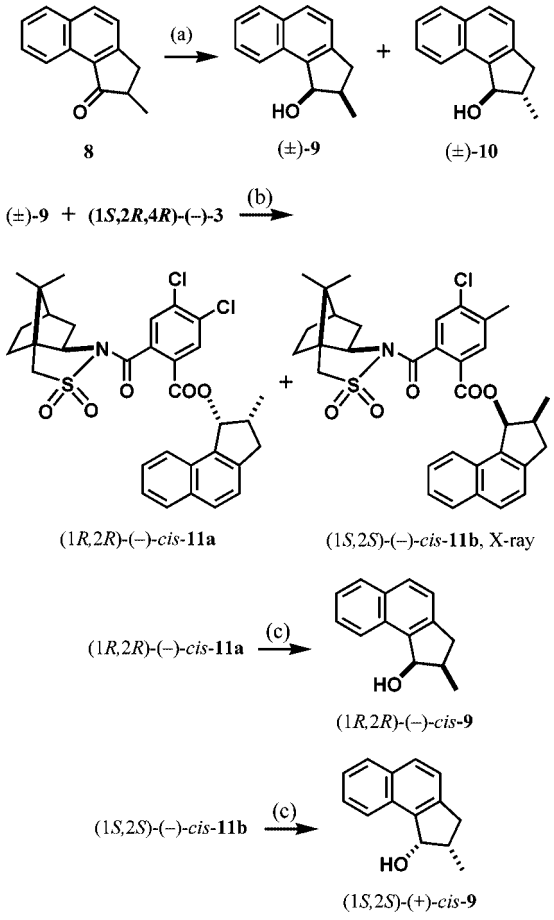


Figure 4. ORTEP drawing of *trans*-olefin (±)-**2a**. The atoms are drawn as 50% probability ellipsoids.

Enantioresolution of Precursory Alcohols by the CSDP Acid Method and Determination of Their Absolute Configurations

For the construction of the chiral molecular motor **2** of five-membered ring type, the precursory ketone **8** as a chiral half has to be synthesized in an enantiopure form and its absolute configuration also has to be determined unambiguously. To obtain enantiopure ketone **8**, we adopted the camphorsultam dichlorophthalic acid [(1*S*,2*R*,4*R*)-(–)-CSDP acid, **3**, Figure 3][6] method as follows. Racemic ketone (±)-**8** was reduced with $LiAlH_4$, yielding *cis* alcohol (±)-**9** and *trans* alcohol (±)-**10**, with no stereoselectivity in the reduction reaction (Scheme 2). However, both alcohols

were enantioresolved well by the CSDP acid method as shown below, so no further efforts to improve the stereoselectivity have been performed.



Scheme 2. Preparation of enantiopure *cis* alcohol **9** by the CSDP acid method. a) $LiAlH_4$/THF, r.t., **9**, 47% and **10**, 51%. b) DCC, DMAP/CH_2Cl_2, r.t., **11a**, 50% and **11b**, 49%. c) KOH, CH_3OH, 94–96%.

Racemic *cis* alcohol (±)-**9** was esterified with CSDP acid (1*S*,2*R*,4*R*)-(–)-**3** (Scheme 2); a mixture of alcohol (±)-**9**, CSDP acid (–)-**3**, 4-dimethylaminopyridine (DMAP), and 1,3-dicyclohexylcarbodiimide (DCC) in CH_2Cl_2 was stirred at room temperature overnight, yielding a diastereomeric mixture of esters **11a** and **11b**, which was easily separated by HPLC on silica gel (hexane/EtOAc, 10:1; separation factor α = 1.17; resolution factor *R*s = 1.79). The first eluted ester obtained was (–)-**11a** (50%) and the second one (–)-**11b** (49%).

One of the advantages of the CSDP acid method is that CSDP esters tend to give single crystals suitable for X-ray analysis with high probability. In the case of esters **11a** and **11b**, good single crystals (m.p. 245 °C) of the second ester to be eluted – (–)-**11b** – were obtained by recrystallization from hexane/EtOAc. One single crystal was subjected to X-ray crystallography [orthorhombic; space group $P2_12_12_1$ (#19); radiation, Cu-K_α (1.54178 Å); unique data $F_o > 3\sigma(F_o)$, 2871; Table 3]. The structure was solved conventionally by direct methods and successive Fourier syntheses: R = 0.0310 and R_w = 0.0410 (R = 0.0501 and R_w = 0.0665 for the mirror image structure). As shown in the ORTEP drawing in Figure 5, the alcohol part has the *cis* structure, and its absolute stereochemistry was clearly determined as (1*S*,2*S*) by internal reference, from the (1*S*,2*R*,4*R*) absolute configuration of the camphor part, and also by the heavy atom effect. The absolute configurations of the first ester to be eluted – (–)-**11a** – were naturally assigned as (1*R*,2*R*).

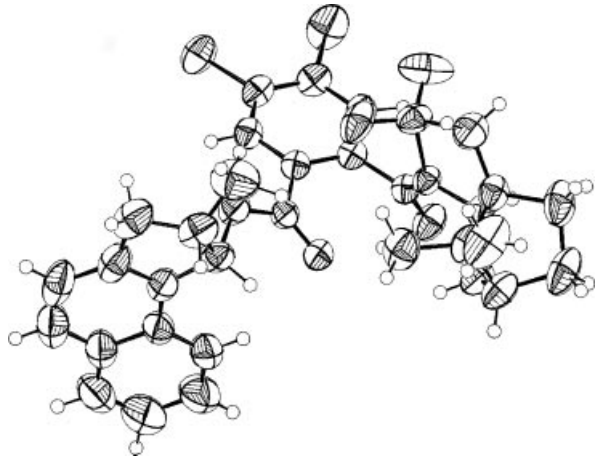
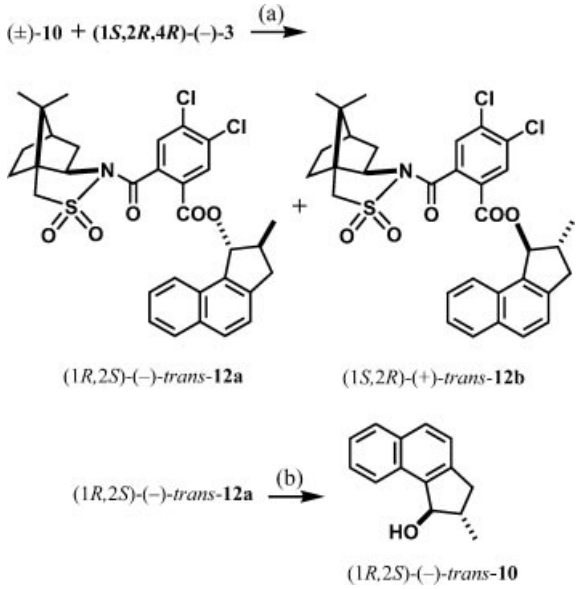


Figure 5. ORTEP drawing of the CSDP ester of *cis* alcohol (1*S*,2*S*)-(–)-**11b**. The atoms are drawn as 50% probability ellipsoids.

To recover the chiral alcohol, the first-eluted CSDP ester (1*R*,2*R*)-(–)-*cis*-**11a** was treated with KOH in MeOH, yielding enantiopure alcohol (1*R*,2*R*)-(–)-*cis*-**9** [96%, $[\alpha]_D^{25}$ –170.2 (c = 1.13, $CHCl_3$), Scheme 2]. From the ester eluted second, (1*S*,2*S*)-(–)-*cis*-**11b**, the opposite enantiomer (1*S*,2*S*)-(+)-*cis*-**9** (94%) was obtained: $[\alpha]_D^{25}$ = +170.1 (c = 0.99, $CHCl_3$).

The racemic *trans* alcohol (±)-**10** was similarly enantioresolved by the CSDP acid method (Scheme 3). The CSDP



Scheme 3. Preparation of enantiopure *trans* alcohol **10** by the CSDP acid method. a) DCC, DMAP/CH_2Cl_2, r.t., **12a**, 49% and **12b**, 50%. b) KOH, CH_3OH, 99%.

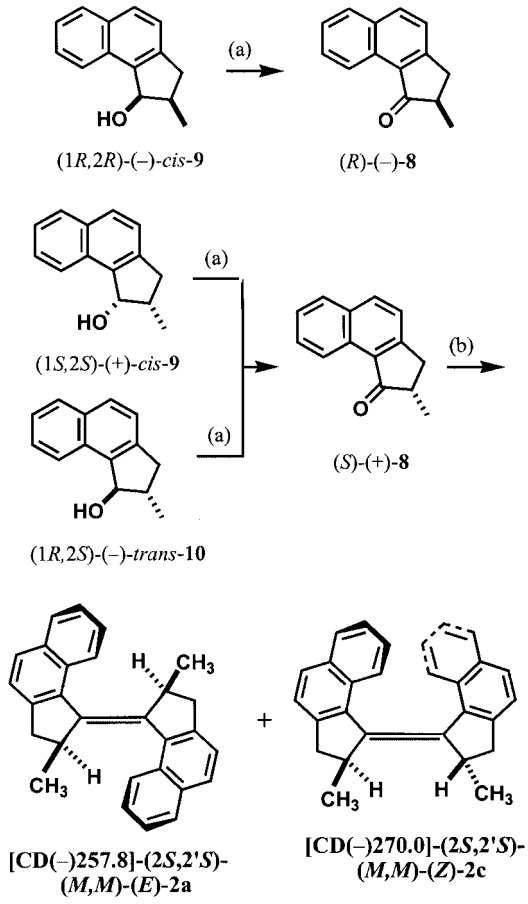
esters **12a** and **12b** formed were readily separated by HPLC on silica gel (hexane/EtOAc, 8:1; separation factor α = 1.17; resolution factor *R*s = 1.50) to provide first the ester (–)-**12a** (49%) and then the second one (+)-**12b** (50%). To determine the absolute configuration of the esters by X-ray crystallography, we tried recrystallization of the products many times, but all attempts were unsuccessful, so the absolute configurations of esters (–)-**12a** and (+)-**12b** remained undetermined. To recover enantiopure *trans* alcohol, the first-eluted CSDP ester (–)-*trans*-**12a** was treated with KOH in MeOH, yielding enantiopure alcohol (–)-*trans*-**10** [99%; $[\alpha]_D^{30}$ –67.9 (*c* = 1.00, $CHCl_3$)].

We have also previously developed 2-methoxy-2-(1-naphthyl)propionic acid (MαNP acid, **4**; Figure 3) as a chiral molecular tool both for enantioresolution of alcohols and also for simultaneous determination of their absolute configurations by ^{1}H-NMR anisotropy, and so the MαNP acid method was applied to racemic alcohols **9** and **10**. However, the diastereomeric MαNP esters prepared were not separable by HPLC on silica gel.

Synthesis of the Chiral Molecular Motor 2 and its Absolute Configuration

To prepare the enantiopure ketone **8**, useful as the chiral half of the molecular motor **2**, the *cis* alcohol (1*R*,2*R*)-(–)-**9** was oxidized with pyridinium chlorochromate (PCC), yielding enantiopure ketone (*R*)-(–)-**8** {94%; $[\alpha]_D^{24}$ –100.2 (*c* = 1.23, $CHCl_3$); Scheme 4}. Another *cis* alcohol (1*S*,2*S*)-(+)-**9** was similarly converted into enantiopure ketone (*S*)-(+)-**8** {88%; $[\alpha]_D^{27}$ = +100.3 (*c* = 0.97, $CHCl_3$)}. The *trans* alcohol (–)-**10**, the absolute configuration of which had remained undetermined, was similarly oxidized, affording enantiopure ketone (+)-**8** {96%, $[\alpha]_D^{26}$ = +101.1 (*c* = 1.85, $CHCl_3$)}, which was identical with the authentic sample (*S*)-(+)-**8** prepared from *cis* alcohol (1*S*,2*S*)-(+)-**9**. The absolute configurations of the *trans* alcohol (–)-**10** and its precursor CSDP ester **12a** were therefore determined as follows: CSDP ester (1*R*,2*S*)-(–)-*trans*-**12a** and alcohol (1*R*,2*S*)-(–)-*trans*-**10** (Scheme 3 and Scheme 4).

To synthesize the chiral molecular motor **2**, enantiopure ketone (*S*)-(+)-**8** was subjected to the McMurry reaction, $LiAlH_4$ being added to a suspension of $TiCl_3$ in dry THF cooled to 0 °C. This mixture was stirred at 0 °C for 0.5 h and was then heated gently at reflux for 4 h. After a solution of enantiopure ketone (*S*)-(+)-**8** in dry THF had been added, the reaction mixture was heated gently at reflux for a further 3 h. The reaction mixture was subjected to short column chromatography on silica gel (EtOAc), and the crude products obtained were separated and purified by HPLC on silica gel (hexane) and finally by HPLC on ODS (MeOH). The *cis*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** was obtained as pale yellow prisms {5%, m.p. 179 °C, $[\alpha]_D^{24}$ –957 (*c* = 0.465, $ClCH_2CH_2Cl$)} from the first fraction eluted, whilst the *trans*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** was obtained as colorless prisms {21%, m.p. 177 °C, $[\alpha]_D^{24}$ –350.8 (*c* = 1.00, $ClCH_2CH_2Cl$)} from the second fraction. The ^{1}H and ^{13}C NMR spectroscopic data of these chiral olefins (–)-**2a** and (–)-**2c** completely agreed with those of the racemic olefins (±)-**2a** and (±)-**2c**. Both chiral olefins showed very large $[\alpha]_D$ values due to the strongly twisted π-electron systems. It should be noted that the chiral configuration of the methyl group was preserved in olefins **2a** and **2c**, indicating that no racemization occurred during the McMurry reaction. This is the great advantage of the McMurry reaction conditions we have used, in comparison with those employed by Feringa's group, who reported that the olefins obtained under their reaction conditions were racemates, although chiral ketone had been used as the starting material.[8]



Scheme 4. Synthesis of enantiopure molecular motor **2**. (a) PCC, MS 4 A, CH_2Cl_2, 88~96%. (b) $TiCl_3$, $LiAlH_4$/THF, reflux, 4 h, [CD(–)257.8]-(*E*)-**2a**, 21% and [CD(–)270.0]-(*Z*)-**2c**, 5%.

To check the enantiopurity of the synthesized chiral motor (2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** of five-membered ring type, we studied the enantioseparation of racemic motor (±)-**2a** by HPLC on a chiral stationary phase column. Among chiral HPLC columns, we found that the column of CHIRALCEL OD-H® was good for enantioseparation when used under reversed-phase conditions [mobile phase, MeOH; CD detector (375 nm); separation factor α = 1.43; resolution factor *R*s = 1.85; Figure 6 (a)]. By comparison of the CD spectrum with that of the authentic sample synthesized above (see Figure 7), it was determined that the

peak eluted first corresponded to the motor (2*R*,2′*R*)-(*P*,*P*)-(*E*)-**2a** and the second one to (2*S*,2′*S*)-(*M*,*M*)-(*E*)-**2a**. The synthesized chiral motor (2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** was injected under the same HPLC conditions. As shown in Figure 6 (b), only a peak for (2*S*,2′*S*)-(*M*,*M*)-(*E*)-**2a** was observed, and no peak of (2*R*,2′*R*)-(*P*,*P*)-(*E*)-**2a** was ever detected, indicating that our synthesized chiral molecular motor was enantiopure.

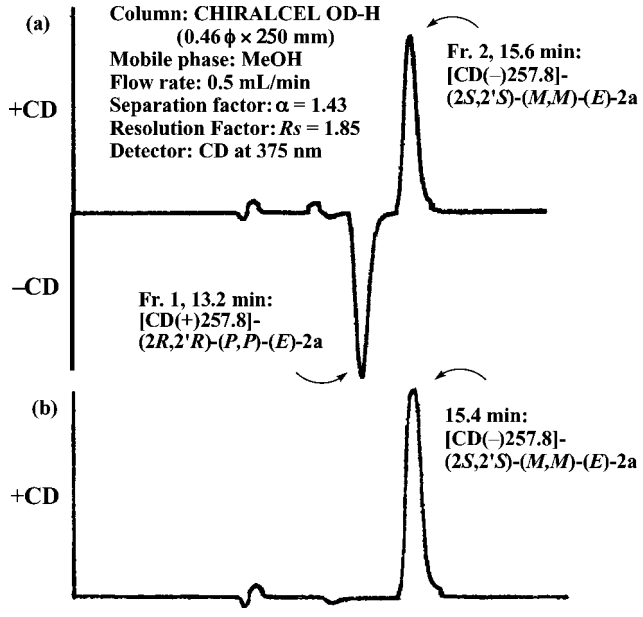


Figure 6. a) Enantioseparation of racemic molecular motor (*E*)-**2a** by chiral HPLC. b) HPLC check of the enantiopurity of synthetic chiral molecular motor [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-**2a**.

The CD and UV spectra of the synthesized chiral molecular motor (2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** are shown in Figure 7; unlike in the case of the motor **1a**, of six-membered ring type, the UV spectrum shows three major bands around 380–330 nm, 260–230 nm, and 230–200 nm. In the corresponding regions, the CD spectrum shows a positive Cotton effect of middle intensity (380–310 nm), an intense negative Cotton effect (260–230 nm), and two intense negative Cotton effects (230–200 nm), indicating the strongly twisted π-electron system of **2a**; the CD spectral pattern is very different from that of the six-membered ring type motor **1a**. Since an intense negative Cotton effect is observed at 257.8 nm, the absolute stereochemistry of the molecular motor **2a** is fully designated as [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–).

The CD and UV spectra of the synthesized chiral molecular motor (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** are also shown, in Figure 8. The UV spectrum shows a pattern similar to that of **2a**: three major bands around 400–340 nm, 280–230 nm, and 230–200 nm. The CD spectrum shows a weak negative Cotton effect (400–340 nm), an intense negative Cotton effect (280–250 nm), and an intense positive Cotton effect (250–220 nm). Since an intense negative Cotton effect is observed at 270.0 nm, the absolute stereochemistry of the molecular motor **2c** is designated as [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–).

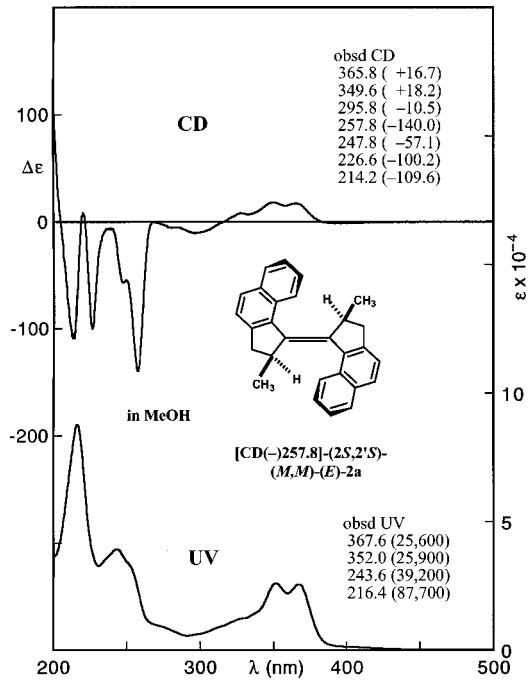


Figure 7. CD and UV spectra of chiral molecular motor [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-**2a** in MeOH.

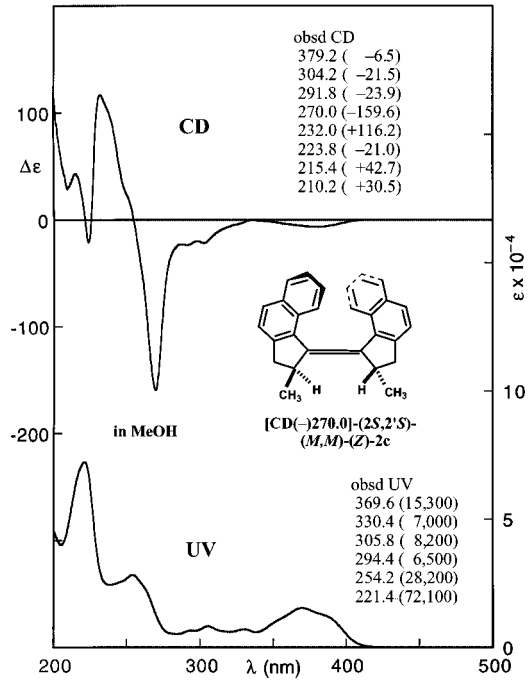


Figure 8. CD and UV spectra of chiral molecular motor [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-**2c** in MeOH.

It should be noted that these absolute configurational assignments – [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** and [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** – disagree with those reported by the Feringa group,[8] who assigned the (2*R*,2′*R*)-(*P*,*P*)-(*Z*) configuration to the *cis*-olefin showing a negative Cotton effect at 269.8 nm by comparison of the

CD data with those for (3*R*,3′*R*)-(*P*,*P*)-(*Z*)-**1c**. Similarly, they also assigned the (2*R*,2′*R*)-(*P*,*P*)-(*E*) configuration to the *trans*-olefin showing a negative Cotton effect at 258.0 nm. It is therefore obvious that such comparison of CD data results in erroneous absolute configurational assignment, and that their assignments should be revised.

Conclusions

A new model light-powered chiral molecular motor of five-membered ring type was designed for the purpose of higher speed of rotation, and the motor rotation isomers (–)-**2a** and (–)-**2c** have been directly synthesized in enantiopure forms for the first time from the precursor ketone (+)-**8**, the absolute configuration of which was determined by X-ray crystallographic analysis of CSDP ester (–)-**11b** and chemical conversion. These studies enabled us to determine the absolute stereostructures of motor rotation isomers unambiguously as [CD(–)257.8]-(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** and [CD(–)270.0]-(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c**, which is of critical importance for control of the direction of motor rotation. The mechanism and dynamics of the motor rotation are discussed in the following paper.[12]

Experimental Section

General Methods: Melting points were uncorrected. IR spectra were obtained neat, as films on KBr, or as KBr disks on a Jasco FT/IR-410 spectrophotometer. ^{1}H-NMR spectra were recorded on Jeol JNM-LA400 (400 MHz) and/or Jeol JNM-LA600 (600 MHz) spectrometers. ^{13}C NMR spectra were obtained on Jeol JNM-LA400 (100 MHz) and/or Jeol JNM-LA600 (150 MHz) spectrometers. All NMR spectroscopic data of $CDCl_3$ solutions are reported in ppm (δ) downfield from TMS. In CD_2Cl_2 solutions, the signal of $CHDCl_2$ was used as the internal chemical shift standard. Optical rotations $[\alpha]_D$ were measured on a Jasco DIP-1000 spectropolarimeter. Silica gel 60 F_{254} precoated plates on glass from Merck Ltd. were used for thin layer chromatography (TLC). HPLC separation and purification were performed with a prepacked glass column (22 φ × 300 mm, or 25 φ × 400 mm) of silica gel (particle size 5–10 μm) and/or a prepacked glass column (15 φ × 300 mm) of ODS from Kusano Co., Ltd., and a UV/RI detector, Shimamura YRU-880. Enantiopurity was checked by HPLC with a column of CHIRALCEL OD-H® from Daicel Co., Ltd and a Jasco CD-1595 CD detector. The purities of the title compounds were shown to be ≥ 99% by ^{1}H NMR, TLC, HPLC, and/or elemental analysis.

X-ray Crystallography: A single crystal was selected for data collection and mounted on a Mac Science MXC18 automated four-circle diffractometer: radiation, Cu-K_α (1.54178 Å); monochromator, graphite crystal. The crystal system, space group, unit cell parameters, and orientation matrix were determined. Data collection was carried out by use of a 2θ–θ scan: temperature 20 °C; scan speed 14° min^{-1}; scan range 1.75–1.87° + 0.2°tan θ; 2θ scan limits, 2°–130°; standard reflections, 3 per 100 reflections; crystal stability, no indication of standard reflection decay during data collection. The density of crystals was measured by flotation with a CCl_4/hexane solution; see Table 3 for data.

Table 3. X-ray crystallographic data for *trans*-olefin (±)-**2a** and CSDP acid ester (–)-*cis*-**11b**.[a]

Compound	(±)-**2a**	(–)-**11b**
formula	$C_{28}H_{24}$	$C_{32}H_{31}Cl_2NO_5S$
formula mass [amu]	360.50	612.57
m.p. [°C], solvent	191–192, MeOH	245, hexane/EtOAc
crystal dimension [mm]	0.33 × 0.32 × 0.22	0.34 × 0.30 × 0.29
crystal system	orthorhombic	orthorhombic
space group	*Pbca* (#61)	$P2_12_12_1$ (#19)
a [Å]	19.111 (4)	15.892 (4)
b [Å]	22.170 (4)	15.897 (3)
c [Å]	9.478 (2)	11.836 (2)
V [Å^3]	4016 (1)	2990 (1)
Z	8	4
D_x [g cm^{-3}]	1.193	1.361
D_m [g cm^{-3}][b]	1.188	1.353
no. of independent reflections with $F_o > 3.0\ \sigma(F_o)$	3410	2871
absolute configuration	–	1*S*,2*S*,(1′*S*,2′*R*,4′*R*)
final *R* and (R_w)	0.0500 (0.0581)	0.0310 (0.0410)
final *R* and (R_w) for the mirror image	–	0.0501 (0.0665)

[a] CCDC-261704 [for (±)-**2a**] and -261705 [for (–)-**11b**] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. [b] By flotation by use of a CCl_4/hexane solution.

(*E*)-2-Methyl-3-(2-naphthyl)propenoic Acid (6): A mixture of naphthalene-2-carbaldehyde (**5**, 2.24 g, 14.4 mmol), propionic anhydride (3.74 g, 28.7 mmol), and sodium propionate (2.07 g, 21.5 mmol) was heated at 180 °C for 15 h. After having been cooled to room temperature, the mixture was poured into water and extracted three times with EtOAc. The combined organic layers were washed with saturated aqueous $NaHCO_3$, and the separated aqueous layer was acidified with aqueous HCl (2 M). The obtained precipitate was filtered, washed with water, dried, and recrystallized from EtOAc, yielding carboxylic acid **6** (2.53 g, 83%) as colorless needles with m.p. 144–145 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.25 (d, *J* = 1.5 Hz, 3 H), 7.51 (ddd, *J* = 6.8, 6.8, 1.7 Hz, 1 H), 7.52 (ddd, *J* = 6.8, 6.8, 1.7 Hz, 1 H), 7.55 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.84–7.88 (m, 3 H), 7.92 (br. s, 1 H), 8.00 (br. s, 1 H) ppm. difference NOE, irradiation of 2-Me -> aromatic 1′-H (+1.4%) and 3′-H (+1.1%). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 126.5, 126.9, 127.0, 127.67, 127.73, 128.0, 128.4, 129.8, 133.07, 133.09, 133.11, 141.2, 174.0 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3047, 2979, 1712, 1621, 1417, 1337, 1254, 1127, 998, 950, 900, 863, 828, 813, 735, 679, 636, 607, 559 cm^{-1}. $C_{14}H_{12}O_2$ (212.25): calcd. C 79.22, H 5.70; found C 78.98, H 5.78.

2-Methyl-3-(2-naphthyl)propionic Acid (7): A mixture of propenoic acid **6** (1.55 g, 7.30 mmol) and Pd-C (5%, 0.310 g) in EtOH (50 mL) was stirred under hydrogen at room temperature for 14 h. Removal of the catalyst by filtration and evaporation of the solvent afforded propionic acid **7** as colorless prisms (1.47 g, 94%), m.p. 89–91 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.21 (d, *J* = 6.6 Hz, 3 H), 2.82 (dd, *J* = 12.7, 8.0 Hz, 1 H), 2.87 (ddq, *J* = 8.0, 6.6, 5.5 Hz, 1 H), 3.24 (dd, *J* = 12.7, 5.5 Hz, 1 H), 7.32 (dd, *J* = 8.5, 1.7 Hz, 1 H), 7.43 (ddd, *J* = 6.8, 6.8, 1.7 Hz, 1 H), 7.46 (ddd, *J* = 6.8, 6.8, 1.7 Hz, 1 H), 7.63 (br. s, 1 H), 7.76–7.82 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.5, 39.4, 41.1, 125.4, 126.0, 127.3, 127.47, 127.53, 127.6, 128.1, 132.2, 133.5, 136.5, 182.1 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3054, 2976, 1704, 1601, 1509, 1463, 1416, 1293, 1238, 1112, 942,

897, 857, 811, 747, 659, 643, 620, 560, 512, 481 cm^{-1}. $C_{14}H_{14}O_2$ (214.26): calcd. C 78.48, H 6.59; found C 78.55, H 6.68.

2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-one (8): A mixture of propionic acid **7** (0.423 g, 1.98 mmol) and PCl_5 (0.535 g, 2.57 mmol) in toluene (10 mL) was stirred at room temperature for 1 h, and $SnCl_4$ (0.46 mL, 3.95 mmol) was then added at 0 °C. After having been stirred at room temperature for 13 h, the reaction mixture was treated at 0 °C with HCl (2 M, 5 mL) and extracted three times with toluene. The combined organic layers were washed with aqueous $NaHCO_3$, water, and brine and dried over anhydrous $MgSO_4$, and the solvents were evaporated to dryness. The crude product was purified by short column chromatography on silica gel (hexane/EtOAc, 5:1), yielding ketone **8** as a colorless oil (0.380 g, 98%). ^1H NMR (600 MHz, $CDCl_3$): δ = 1.38 (d, J = 7.3 Hz, 3 H), 2.79–2.85 (m, 2 H), 3.48 (dd, J = 17.9, 8.0 Hz, 1 H), 7.50 (d, J = 8.2 Hz, 1 H), 7.55 (ddd, J = 8.1, 6.9, 1.0 Hz, 1 H), 7.67 (ddd, J = 8.2, 6.9, 1.3 Hz, 1 H), 7.88 (d, J = 8.1 Hz, 1 H), 8.04 (d, J = 8.2 Hz, 1 H), 9.15 (dd, J = 8.2, 1.0 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 16.6, 35.4, 42.4, 123.9, 124.0, 126.5, 128.1, 128.8, 129.6, 130.2, 132.7, 135.7, 156.6, 210.0 ppm. IR (neat): $\tilde{\nu}_{max}$ = 3055, 2963, 2929, 2871, 1694, 1628, 1593, 1573, 1517, 1456, 1439, 1372, 1312, 1202, 1171, 1152, 1116, 1073, 1024, 920, 881, 821, 789, 747, 631, 564, 512, 494 cm^{-1}. $C_{14}H_{12}O$ (196.25): calcd. C 85.68, H 6.16; found C 85.51, H 6.31.

Synthesis of the Racemic Molecular Motors (2*S,2′*S**)-(*M**,*M**)-(*E*)-(±)-2,2′-Dimethyl-2,2′,3,3′-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene] (2a) and (2*S**,2′*S**)-(*M**,*M**)-(*Z*)-(±)-2,2′-Dimethyl-2,2′,3,3′-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene] (2c):** A mixture of $LiAlH_4$ (0.0944 g, 2.49 mmol) and dry THF (10 mL) was added dropwise to a suspension of $TiCl_3$ (0.768 g, 4.98 mmol) in dry THF (20 mL), cooled to 0 °C. The mixture was stirred at 0 °C for 0.5 h and was then heated gently at reflux for 1.5 h. After a solution of ketone **8** (0.326 g, 1.66 mmol) in dry THF (20 mL) had been added, the reaction mixture was heated gently at reflux for 96 h. The reaction mixture was filtered with Celite, and the filtrate was treated with dilute aqueous HCl and extracted three times with $CHCl_3$. The combined organic layers were washed with brine and dried over anhydrous $MgSO_4$, and the solvents were evaporated to dryness. The crude product was purified by short column chromatography on silica gel (hexane/AcOEt, 20:1), by HPLC (silica gel, hexane), and finally by HPLC (ODS, MeOH). The (±)-*cis*-olefin (2*S**,2′*S**)-(*M**,*M**)-(*Z*)-(±)-**2c** was obtained as faint yellow needles (0.0167 g, 6%) from the first fraction eluted, whilst the *trans*-olefin (2*S**,2′*S**)-(*M**,*M**)-(*E*)-(±)-**2a** was obtained as colorless prisms (0.0407 mg, 14%) from the second fraction eluted.

(2*S,2′*S**)-(*M**,*M**)-(*E*)-(±)-2,2′-Dimethyl-2,2′,3,3′-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene] (2a):** m.p. 191–192 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.29 (d, J = 6.4 Hz, 6 H, 2ax-Me), 2.35 (d, J = 14.6 Hz, 1 H, 3eq-H), 2.95 (dd, J = 14.6, 5.6 Hz, 2 H, 3ax-H), 3.03 (dq, J = 6.4, 5.6 Hz, 2 H, 2eq-H), 7.41 (d, J = 8.3 Hz, 2 H, 4-H), 7.47 (ddd, J = 8.1, 6.8, 1.2 Hz, 2 H, 7-H), 7.55 (ddd, J = 8.3, 6.8, 1.4 Hz, 2 H, 8-H), 7.76 (d, J = 8.3 Hz, 2 H, 5-H), 7.90 (d, J = 8.1 Hz, 2 H, 6-H), 8.24 (d, J = 8.3 Hz, 2 H, 9-H) ppm; for other NMR spectroscopic data, see Table 1. IR (KBr): $\tilde{\nu}_{max}$ = 3048, 2968, 2926, 2868, 2840, 1559, 1542, 1515, 1456, 1435, 1364, 1300, 1252, 1215, 1154, 1020, 966, 868, 845, 810, 782, 754, 711, 665, 598, 555, 526 cm^{-1}. High-resolution mass spectrum (HRMS): calcd. for $C_{28}H_{24}$ m/z 360.1878; found 360.1881. $C_{28}H_{24}$ (360.50): calcd. C 93.29, H 6.71; found C 93.16, H 6.74.

(2*S,2′*S**)-(*M**,*M**)-(*Z*)-(±)-2,2′-Dimethyl-2,2′,3,3′-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene] (2c):** m.p. 174–175 °C. ^1H NMR (400 MHz, CD_2Cl_2): δ = 1.21 (d, J = 6.8 Hz, 6 H, 2ax-Me), 2.70 (d, J = 14.6 Hz, 2 H, 3eq-H), 3.59 (dd, J = 14.6, 6.8 Hz, 2 H, 3ax-H), 3.64 (dq, J = 6.8, 6.8 Hz, 2 H, 2eq-H), 6.35 (ddd, J = 8.3, 6.8, 1.2 Hz, 2 H, 8-H), 6.60 (dd, J = 8.3, 1.2 Hz, 2 H, 9-H), 6.96 (ddd, J = 8.0, 6.8, 1.2 Hz, 2 H, 7-H), 7.51 (d, J = 8.0 Hz, 2 H, 4-H), 7.65 (d, J = 8.0 Hz, 2 H, 6-H), 7.71 (d, J = 8.0 Hz, 2 H, 5-H) ppm; for other NMR spectroscopic data, see Table 2. IR (KBr): $\tilde{\nu}_{max}$ = 3049, 2958, 2924, 2863, 2842, 1621, 1585, 1515, 1452, 1434, 1367, 1304, 1212, 1163, 1054, 1025, 955, 906, 863, 809, 783, 741, 687, 658, 614, 579, 533, 515 cm^{-1}. HRMS: calcd. for $C_{28}H_{24}$ m/z 360.1878; found 360.1862. $C_{28}H_{24}$ (360.50): calcd. C 93.29, H 6.71; found C 93.50, H 6.93.

Preparation of *trans*- and *cis*-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-ols: $LiAlH_4$ (0.011 g, 0.28 mmol) was added at 0 °C to a solution of ketone (±)-**8** (0.055 g, 0.28 mmol) in dry THF (5 mL), and the reaction mixture was stirred at room temperature for 1 h. The mixture was treated with a small amount of aqueous NH_4Cl, and the organic layer was dried over anhydrous $MgSO_4$ and evaporated under reduced pressure. The residue was subjected to short column chromatography on silica gel, and the obtained epimeric alcohols were separated by HPLC on silica gel (hexane/EtOAc, 10:1), yielding (±)-*cis*-**9** (0.026 g, 47%) as the alcohol eluted first and (±)-*trans*-**10** (0.029 g, 51%) as the alcohol eluted second.

(±)-*cis*-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-ol (9): Colorless prisms with m.p. 121 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 1.31 (d, J = 7.1 Hz, 3 H), 1.49 (br. s, 1 H), 2.64 (dddq, J = 8.7, 7.7, 6.1, 7.0 Hz, 1 H), 2.86 (dd, J = 15.8, 8.7 Hz, 1 H), 3.09 (dd, J = 15.8, 7.7 Hz, 1 H), 5.49 (d, J = 6.1 Hz, 1 H), 7.37 (d, J = 8.4 Hz, 1 H), 7.44 (ddd, J = 8.2, 6.9, 1.1 Hz, 1 H), 7.53 (ddd, J = 8.3, 6.9, 1.3 Hz, 1 H), 7.77 (d, J = 8.4 Hz, 1 H), 7.85 (d, J = 8.2 Hz, 1 H), 8.08 (dd, J = 8.3, 1.1 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 13.89, 39.12, 39.32, 76.27, 123.33, 123.81, 125.03, 126.59, 128.49, 129.27, 130.24, 132.93, 139.72, 141.80 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3204, 3050, 2966, 2935, 2909, 2876, 2844, 1593, 1513, 1438, 1377, 1317, 1241, 1169, 1135, 918, 807, 747, 672 cm^{-1}. $C_{14}H_{14}O$ (198.26): calcd. C 84.81, H 7.12; found C 84.84, H 7.25.

(±)-*trans*-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-ol (10): Colorless needles with m.p. 86–87 °C. ^1H NMR (600 MHz, $CDCl_3$): δ = 1.25 (d, J = 7.0 Hz, 3 H), 1.62 (br. s, 1 H), 2.51 (dddq, J = 7.7, 4.9, 3.8, 7.0 Hz, 1 H), 2.59 (dd, J = 16.0, 4.9 Hz, 1 H), 3.43 (dd, J = 16.0, 7.7 Hz, 1 H), 5.29 (d, J = 3.8 Hz, 1 H), 7.36 (d, J = 8.2 Hz, 1 H), 7.45 (ddd, J = 8.1, 6.9, 1.1 Hz, 1 H), 7.53 (ddd, J = 8.3, 6.9, 1.3 Hz, 1 H), 7.78 (d, J = 8.2 Hz, 1 H), 7.86 (br. dd, J = 8.3, 1.1 Hz, 1 H), 8.22 (br. dd, J = 8.1, 1.3 Hz, 1 H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 19.09, 38.95, 43.99, 83.09, 123.55, 123.87, 125.09, 126.47, 128.52, 129.38, 130.53, 133.08, 138.34, 140.64 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3245, 3050, 2958, 2928, 2902, 2850, 1592, 1514, 1453, 1375, 1260, 1159, 1073, 1010, 812, 745, 661 cm^{-1}. $C_{14}H_{14}O$ (198.26): calcd. C 84.81, H 7.12; found C 84.91, H 7.20.

Enantioresolution of Alcohol (±)-*cis*-9 by the CSDP Acid Method: A mixture of alcohol (±)-*cis*-**9** (0.022 g, 0.11 mmol), CSDP acid (1*S*,2*R*,4*R*)-(–)-**3** (0.107 g, 0.25 mmol), DCC (0.051 g, 0.25 mmol), and DMAP (0.003 g, 0.03 mmol) in CH_2Cl_2 (1 mL) was stirred at room temperature overnight. After addition of a small amount of water, the mixture was stirred for 1 h, diluted with EtOAc, and filtered with Celite, which was washed with EtOAc. The organic layer was evaporated under reduced pressure, and the residue was subjected to short column chromatography on silica gel (hexane/EtOAc, 10:1). The diastereomeric esters obtained were separated by HPLC on silica gel (25 × 300 mm column, hexane/EtOAc, 10:1; separation factor α = 1.17; resolution factor Rs = 1.79), giving (1*R*,2*R*)-(–)-*cis*-**11a** (0.034 g, 50%) as the ester eluted first and (1*S*,2*S*)-(–)-*cis*-**11b** (0.033 g, 49%) as the one eluted second.

The First-Eluted CSDP Ester (1*R*,2*R*)-(–)-*cis*-11a: Colorless prisms with m.p. 235–236 °C. $[\alpha]_D^{25}$ –61.5 (*c* = 1.18, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.90 (s, 3 H), 0.97 (m, 1 H), 1.19–1.27 (m, 7 H), 1.69 (m, 1 H), 1.78–1.85 (m, 2 H), 1.99 (m, 1 H), 2.41–2.60 (m, 2 H), 2.87 (m, 1 H), 3.02–3.22 (m, 4 H), 7.01 (d, *J* = 6.1 Hz, 1 H), 7.41–7.50 (m, 4 H), 7.82–7.90 (m, 3 H), 8.12 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.13, 19.92, 21.20, 26.25, 32.57, 37.72, 39.20, 39.81, 44.93, 47.51, 48.12, 52.48, 65.17, 79.41, 122.88, 124.67, 125.38, 126.81, 128.02, 128.09, 130.21, 130.23, 130.75, 132.15, 132.63, 134.60, 134.64, 135.43, 136.70, 143.99, 163.08, 164.91 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2963, 1720, 1687, 1589, 1552, 1517, 1456, 1337, 1299, 1241, 1169, 1141, 1115, 1092, 1063, 973, 909, 814, 731, 648, 539 cm^{-1}. $C_{32}H_{31}Cl_2NO_5S$ (612.57): calcd. C 62.74, H 5.10, Cl 11.58, N 2.29, S 5.23; found C 62.54, H 5.13, Cl 11.72, N 2.26, S 5.13.

The Second-Eluted CSDP Ester (1*S*,2*S*)-(–)-*cis*-11b: Colorless prisms with m.p. 245 °C. $[\alpha]_D^{26}$ –23.0 (*c* = 1.13, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (s, 3 H), 1.20–1.26 (m, 8 H), 1.73–1.85 (m, 3 H), 2.28 (m, 1 H), 2.81–3.40 (m, 6 H), 6.98 (d, *J* = 6.1 Hz, 1 H), 7.42–7.52 (m, 4 H), 7.84–7.88 (m, 3 H), 7.92 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.90, 19.94, 20.82, 26.38, 32.82, 37.56, 38.95, 39.74, 44.70, 47.68, 48.25, 53.00, 65.29, 79.58, 122.98, 124.29, 125.40, 127.01, 128.21, 128.82, 130.11, 130.36, 130.86, 131.87, 132.68, 134.77, 135.44, 136.33, 143.87, 163.56, 164.97 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3055, 1962, 1719, 1686, 1589, 1552, 1517, 1456, 1338, 1299, 1261, 1168, 1141, 1116, 1093, 1062, 909, 814, 758, 731, 647, 536 cm^{-1}. $C_{32}H_{31}Cl_2NO_5S$ (612.57): calcd. C 62.74, H 5.10, Cl 11.58, N 2.29, S 5.23; found C 62.71, H 5.11, Cl 11.85, N 2.30, S 5.13.

Enantioresolution of Alcohol (±)-*trans*-10 by the CSDP Acid Method: Alcohol (±)-*trans*-**10** (0.093 g) was similarly esterified with CSDP acid (1*S*,2*R*,4*R*)-(–)-**3**, and the diastereomeric esters were separated by HPLC on silica gel (25 × 300 mm column, hexane/EtOAc, 8:1; separation factor α = 1.17; resolution factor *R*s = 1.50), giving (1*R*,2*S*)-(–)-*trans*-**12a** (0.141 g, 49%) as the ester eluted first and (1*S*,2*R*)-(–)-*trans*-**12b** (0.143 g, 50%) as the one eluted second .

The First-Eluted CSDP Ester (1*R*,2*S*)-(–)-*trans*-12a: Colorless plates with m.p. 226–227 °C. $[\alpha]_D^{24}$ –110.7 (*c* = 1.05, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.91 (s, 3 H), 0.98 (m, 1 H), 1.23 (br. d, *J* = 7.1 Hz, 3 H), 1.23 (s, 3 H), 1.24 (m, 1 H), 1.70–1.86 (m, 3 H), 2.01 (m, 1 H), 2.43 (m, 1 H), 2.66 (dd, *J* = 16.3, 2.2 Hz, 1 H), 2.74 (br. ddddd, *J* = 7.5, 7.1, 7.1, 7.1, 2.2 Hz, 1 H), 2.80 (m, 1 H), 3.26 (d, *J* = 13.7 Hz, 1 H), 3.33 (m, 1 H), 3.61 (dd, *J* = 16.3, 7.5 Hz, 1 H), 6.45 (br. s, 1 H), 7.27–7.51 (m, 4 H), 7.85–7.88 (m, 3 H), 8.04 (s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.62, 19.98, 21.18, 26.29, 32.79, 37.73, 39.72, 40.23, 44.97, 47.56, 48.15, 52.68, 65.41, 85.67, 123.48, 124.54, 125.38, 126.88, 128.24, 128.65, 130.52, 130.68, 130.75, 132.02, 132.81, 133.49, 134.61, 134.74, 136.60, 143.75, 163.64, 165.18 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 3055, 2961, 2883, 2254, 1719, 1686, 1589, 1553, 1517, 1456, 1373, 1337, 1308, 1298, 1262, 1243, 1167, 1141, 1115, 1093, 1063, 973, 952, 908, 813, 785, 769, 731, 647, 539 cm^{-1}. $C_{32}H_{31}Cl_2NO_5S$ (612.57): calcd. C 62.74, H 5.10, Cl 11.58, N 2.29, S 5.23; found C 62.79, H 5.22, Cl 11.41, N 2.25, S 5.50.

The Second-Eluted CSDP Ester (1*S*,2*R*)-(+)-*trans*-12b: Colorless plates with m.p. 222–223 °C. $[\alpha]_D^{24}$ = +14.8 (*c* = 1.04, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 0.95 (s, 3 H), 1.21 (d, *J* = 7.3 Hz, 3 H), 1.22 (s, 3 H), 1.20–1.28 (m, 2 H), 1.89–1.62 (m, 5 H), 2.37 (m, 1 H), 2.63 (dd, *J* = 16.5, 1.7 Hz, 1 H), 2.74 (br. ddddd, *J* = 7.5, 7.3, 7.3, 7.3, 1.7 Hz, 1 H), 3.24 (d, *J* = 13.9 Hz, 1 H), 3.39 (d, *J* = 13.9 Hz, 1 H), 3.58 (dd, *J* = 16.5, 7.5 Hz, 1 H), 6.49 (br. s, 1 H), 7.43–7.54 (m, 4 H), 7.79 (br. d, *J* = 8.1 Hz, 1 H), 7.87–7.92 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 19.62, 19.98, 20.79, 26.35, 32.93, 37.50, 39.68, 39.74, 44.73, 47.65, 48.24, 52.99, 65.47, 85.46, 123.52, 124.08, 125.40, 127.01, 128.34, 128.63, 130.47, 130.76, 130.92, 131.83, 132.81, 133.41, 134.69, 134.75, 136.55, 143.76, 163.62, 165.06 ppm. IR (KBr): $\tilde{\nu}_{max}$ = 2962, 2353, 2255, 1718, 1686, 1589, 1553, 1517, 1455, 1410, 1375, 1336, 1298, 1263, 1244, 1167, 1141, 1115, 1093, 1063, 1025, 973, 951, 908, 812, 764, 732, 669, 648, 612, 540 cm^{-1}. High-resolution mass spectrum (HRMS, EI): calcd. for $C_{32}H_{31}Cl_2NO_5S$ *m*/*z* 611.1300; found *m*/*z* 611.1314. $C_{32}H_{31}Cl_2NO_5S$ (612.57): calcd. C 62.74, H 5.10, Cl 11.58, N 2.29, S 5.23; found C 61.98, H 5.11, Cl 10.04, N 2.32, S 4.53.

Recovery of Enantiopure Alcohols from CSDP Esters: As an example, a mixture of CSDP ester (1*R*,2*R*)-(–)-*cis*-**11a** (0.481 g, 1.12 mmol) and saturated KOH/MeOH solution (6 mL) was stirred at room temperature overnight. After addition of water, the mixture was extracted with diethyl ether, and the organic layer was filtered and evaporated under reduced pressure. The crude product was purified by HPLC on silica gel (hexane/EtOAc, 8:1–10:1), yielding the enantiopure alcohol (1*R*,2*R*)-(–)-*cis*-**9** (0.184 g, 96%).

(1*R*,2*R*)-(–)-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-ol [*cis*-(9)]: Colorless prisms with m.p. 102–103 °C. $[\alpha]_D^{25}$ –170.2 (*c* = 1.13, $CHCl_3$). CD (EtOH): λ_{ext} = 228.0 nm ($\Delta\varepsilon$ = –22.1). UV (EtOH): λ_{max} = 322.0 nm (ε = 1300), 314.8 (700), 307.8 (900), 279.2 (5500), 227.4 (92900). Other spectroscopic data agreed with those of (±)-*cis*-**9**. $C_{14}H_{14}O$ (198.26): calcd. C 84.81, H 7.12; found C 84.88, H 7.20.

(1*S*,2*S*)-(+)-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-ol [*cis*-(9)]: From CSDP ester (1*S*,2*S*)-(–)-*cis*-**11b**, yield 94%. colorless prisms with m.p. 102–103 °C. $[\alpha]_D^{25}$ = +170.1 (*c* = 0.99, $CHCl_3$). Other spectroscopic data agreed with those of (±)-*cis*-**9**. $C_{14}H_{14}O$ (198.26): calcd. C 84.81, H 7.12; found C 84.46, H 7.19.

(1*R*,2*S*)-(–)-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-ol [*trans*-(10)]: From CSDP ester (1*R*,2*S*)-(–)-*trans*-**12a**, yield 99%. colorless plates with m.p. 110–111 °C. $[\alpha]_D^{30}$ –67.9 (*c* = 1.00, $CHCl_3$). CD (EtOH): λ_{ext} = 320.8 nm ($\Delta\varepsilon$ = +0.4), 290.8 (+0.8), 230.8 (–4.7), 219.6 (–0.8). UV (EtOH): λ_{max} = 322.0 nm (ε = 1300), 278.8 (5500), 227.2 (92900). Other spectroscopic data agreed with those of (±)-*trans*-**10**. $C_{14}H_{14}O$ (198.26): calcd. C 84.81, H 7.12; found C 85.01, H 7.19.

Preparation of Enantiopure Ketones (*R*)-(–)-8 and (*S*)-(+)-8: As an example, a mixture of alcohol (1*R*,2*R*)-(–)-*cis*-**9** (0.032 g, 0.16 mmol), molecular sieves (4 A), and pyridinium chlorochromate (PCC, 0.109 g, 0.51 mmol) in CH_2Cl_2 (2.0 mL) was stirred at room temperature for 1 h, and diethyl ether was then added. After filtration, the organic layer was evaporated to dryness, and the crude product was purified by HPLC on silica gel (hexane/EtOAc, 6:1), yielding enantiopure ketone (*R*)-(–)-**8** (0.030 g, 94%).

(*R*)-(–)-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-one (8): Colorless solid. $[\alpha]_D^{24}$ –100.2 (*c* = 1.23, $CHCl_3$). CD (EtOH): λ_{ext} = 338.4 nm ($\Delta\varepsilon$ = +1.6), 317.4 (–1.6), 246.2 (–4.4). UV (EtOH): λ_{max} = 305.8 nm (ε = 8900), 231.4 (25200), 213.4 (44900). Other spectroscopic data agreed with those of (±)-**8**. $C_{14}H_{12}O$ (196.25): calcd. C 85.68, H 6.16; found C 85.39, H 6.34.

(*S*)-(+)-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-one (8): From (1*S*,2*S*)-(+)-*cis*-**9**, yield 88%. colorless prisms with m.p. 113–114 °C. $[\alpha]_D^{27}$ = +100.3 (*c* = 0.97, $CHCl_3$). CD (EtOH): λ_{ext} = 339.0 nm ($\Delta\varepsilon$ = –1.6), 316.2 (+1.7), 246.8 (+4.5). UV (EtOH): λ_{max} = 305.8 nm (ε = 8900), 231.4 (25200), 213.4 (44700). Other spectroscopic data

agreed with those of (±)-**8**. $C_{14}H_{12}O$ (196.25): calcd. C 85.68, H 6.16; found C 85.86, H 6.35.

(*S*)-(+)-2-Methyl-2,3-dihydro-1*H*-benz[*e*]inden-1-one (8): From (1*R*,2*S*)-(–)-*trans*-**10**, yield 96%. $[\alpha]_D^{26}$ = +101.1 (*c* = 1.85, $CHCl_3$). Other spectroscopic data agreed with those of the authentic sample described above.

Synthesis of Chiral Molecular Motors (2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-2,2'-Dimethyl-2,2',3,3'-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene] (2a) and (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-2,2′-Dimethyl-2,2′,3,3′-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene] (2c): $LiAlH_4$ (0.041 g, 1.08 mmol) was added at 0 °C to a suspension of $TiCl_3$ (0.301 g, 1.95 mmol) and dry THF (3.5 mL). The mixture was stirred at 0 °C for 0.5 h and was then heated gently at reflux for 4 h. After a solution of enantiopure ketone (*S*)-(+)-**8** (0.066 g, 0.33 mmol) in dry THF (2 mL) had been added, the reaction mixture was heated gently at reflux for 3 h. The reaction mixture was subjected to short column chromatography on silica gel (EtOAc), and the crude products obtained were separated and purified by HPLC on silica gel (hexane) and finally by HPLC (ODS-C_{18}, MeOH). The *cis*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-**2c** was obtained as pale yellow prisms (0.0032 g, 5%) from the first fraction eluted, and the *trans*-olefin (2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** was obtained as colorless prisms (0.0126 g, 21%) from the second fraction.

(2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-2,2'-Dimethyl-2,2',3,3'-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene] (2a): m.p. 177 °C. $[\alpha]_D^{24}$ –350.8 (*c* = 1.00, $ClCH_2CH_2Cl$). CD (MeOH): λ_{ext} = 365.8 nm ($\Delta\varepsilon$ = +16.7), 349.6 (+18.2), 295.8 (–10.5), 257.8 (–140.0), 247.8 (–57.1), 226.6 (–100.2), 214.2 (–109.6). UV (MeOH): λ_{max} = 367.6 nm (ε = 25600), 252.0 (25900), 243.6 (39200), 216.4 (87700). HRMS: calcd. for $C_{28}H_{24}$ *m*/*z* 360.1878; found 360.1870. Other spectroscopic data agreed with those of (±)-**2a**.

(2*S*,2′*S*)-(*M*,*M*)-(*Z*)-(–)-2,2'-Dimethyl-2,2',3,3'-tetrahydro-1,1′-bi[1*H*-benz[*e*]indenylidene] (2c): m.p. 179 °C. $[\alpha]_D^{24}$ –957 (*c* = 0.465, $ClCH_2CH_2Cl$). CD (MeOH): λ_{ext} = 379.2 nm ($\Delta\varepsilon$ = –6.5), 304.2 (–21.5), 291.8 (–23.9), 270.0 (–159.6), 232.0 (+116.2), 223.8 (–21.0), 215.4 (+42.7). UV (MeOH): λ_{max} = 369.6 nm (ε = 15300), 330.4 (7000), 305.8 (8200), 294.4 (6500), 254.2 (28200), 221.4 (72100). HRMS: calcd. for $C_{28}H_{24}$ *m*/*z* 360.1878; found 360.1859. Other spectroscopic data agreed with those of (±)-**2c**.

Check of the Enantiopurity of Chiral Motor by HPLC: The racemic motor rotation isomer (±)-**2a** was enantioseparated by HPLC on a column of CHIRALCEL OD-H® (0.46 ϕ × 250 mm), MeOH as eluent, and a CD detector (375 nm): α = 1.43; resolution factor *R*s = 1.85. The compound eluted first was assigned from the CD spectra as (2*R*,2′*R*)-(*P*,*P*)-(+)-*trans*-**2a**, and the second one as (2*S*,2′*S*)-(*M*,*M*)-(–)-*trans*-**2a**. The chiral motor (2*S*,2′*S*)-(*M*,*M*)-(*E*)-(–)-**2a** synthesized above was subjected to the same HPLC treatment, and the other enantiomer (2*R*,2′*R*)-(*P*,*P*)-(*E*)-(+)-**2a** was never detected. Therefore it was concluded that the chiral motor synthesized here was enantiopure.

Supporting Information: Supporting Information for this article is available on the WWW under http://www.eurjoc.org or from the authors: Figure S01, ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2, 22 °C) of molecular motor rotation isomer, stable *trans*-olefin (2*S**,2′*S**)-(*M**,*M**)-(*E*)-**2a**. Figure S02, ^{1}H-NMR spectrum (400 MHz, CD_2Cl_2, 22 °C) of molecular motor rotation isomer, stable *cis*-olefin (2*S**,2′*S**)-(*M**,*M**)-(*Z*)-**2c**.

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