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Synthesis and Stereochemical Analysis of Planar-Chiral (*E*)-4-[7]Orthocyclophene

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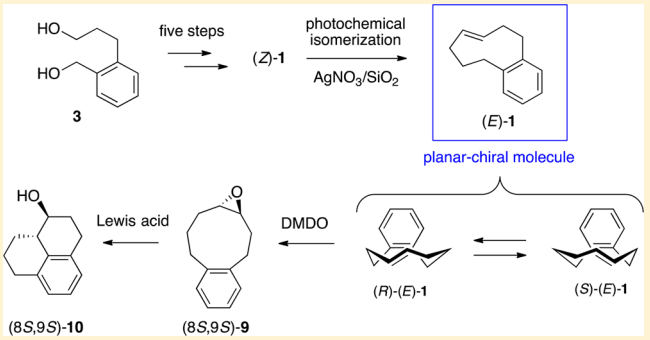
Supporting Information

ABSTRACT: An efficient synthesis of (*E*)-4-[7]-orthocyclophene (*E*)-**1** via photochemical isomerization of (*Z*)-**1** has been achieved. The key intermediate (*Z*)-**1** was synthesized from commercially available 2-(hydroxymethyl)-benzenepropanol (**3**) in five steps: (i) group-selective Mitsunobu reaction with $CH_2{=}CHCH_2CH(SO_2Ph)_2$, (ii) oxidation of alcohol, (iii) olefination, (iv) RCM, and (v) removal of sulfones in an overall yield of 73%. The photochemical isomerization of (*Z*)-**1** was efficiently performed in the presence of $AgNO_3$-impregnated silica gel ($AgNO_3/SiO_2$). The resulting (*E*)-**1** shows dynamic planar chirality at rt. Enantioenriched (*E*)-**1** was prepared by the HPLC separation of enantiomers using a chiral stationary phase, and the absolute stereochemistry was determined by X-ray diffraction analysis of the Pt-coordinated crystalline derivative. The planar chirality of (*E*)-**1** can be converted into the central chirality of carbon; e.g., the oxidation of (*R*)-(*E*)-**1** using DMDO provided epoxide (8*S*,9*S*)-**9** in a stereospecific manner. Furthermore, the Lewis acid-promoted reaction of (8*S*,9*S*)-**9** afforded a unique tricyclic compound (8*S*,9*S*)-**10** in an excellent yield and in a stereospecific manner.



INTRODUCTION

Medium-sized (*E*)-cycloalkenes have attracted much interest in structural and synthetic chemistry, because of the unique stereochemical property and reactivity of the alkene moiety.[1−3] In particular, certain medium-sized (*E*)-cycloalkenes possess planar chirality, and their stereochemical stabilities are highly dependent on ring size. For example, in the early 1960s, Cope and colleagues reported that (*E*)-cyclooctene has remarkably stable planar chirality,[1f] whereas its one-carbon homologue, (*E*)-cyclononene, has only transient chirality (Figure 1).[1e]

On the other hand, the presence of an additional trigonal carbon in the ring may also affect the stereochemical stability because of the decrease in conformational flexibility. In this context, Cope and Fordice reported the synthesis of (*E*)-4-[7]orthocyclophene [(*E*)-**1**], the aromatic ring-containing congener of (*E*)-cyclononene, in 1967.[4] Their synthesis started from diester **i** prepared from 2-hydroxy-3-naphthoic acid in five steps based on Fry and Fieser's protocol (Scheme 1).[5] The intramolecular condensation of **i** afforded the regioisomers of acyloin **iia** and **iib**. The oxidation to diketone **iii**, its transformation into bishydrazone, and oxidation with mercuric oxide provided a mixture of (*Z*)-**1** and alkyne **iv**.

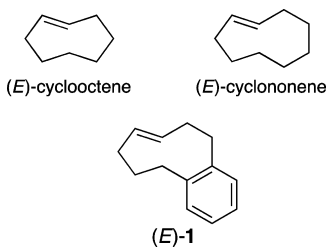


Figure 1. Medium-sized (*E*)-cycloalkenes.

Finally, the Birch reduction of **iv** afforded a mixture of (*E*)-**1** and (*Z*)-**1** in an ∼1:1 mixture, and the pure (*E*) isomer was isolated in 39% yield via $AgNO_3$ extraction. Cope and Fordice conducted a detailed stereochemical study of (*E*)-**1**, including the preparation of a Pt complex derivative having a chiral ligand, recrystallization, and liberation of the Pt moiety. However, the optically active form of (*E*)-**1** could not be isolated, and hence, they concluded that (*E*)-**1** might not possess significant planar chirality at ambient temperature.

Recently, we revisited the historical compound (*E*)-**1** during the course of our study in planar-chiral orthocyclophene chemistry and found that it possesses labile planar chirality at ambient temperature.[6] However, the detailed stereochemical behavior and absolute stereochemistry of (*E*)-**1** have yet to be determined. Herein, we wish to report the details of our synthesis of (*E*)-**1** and clarify the long-standing stereochemical problems thereof.

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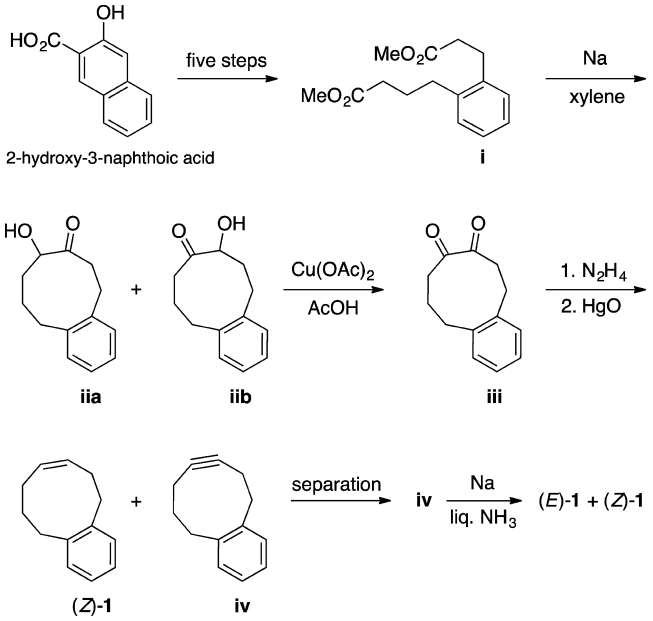
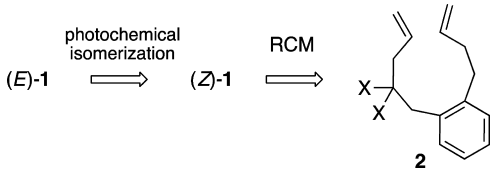
Scheme 1. Synthesis of (*E*)-1 Reported by Cope and Fordice



RESULTS AND DISCUSSION

Synthesis of (*E*)-1. To conduct the various studies of (*E*)-**1**, we faced some difficulties because of the substantial amount synthesized by Cope's original procedure, which suffers from many steps (*vide ante*), along with instability and/or high volatility of intermediates. Hence, an alternative concise approach to (*E*)-**1** was needed. Scheme 2 shows our

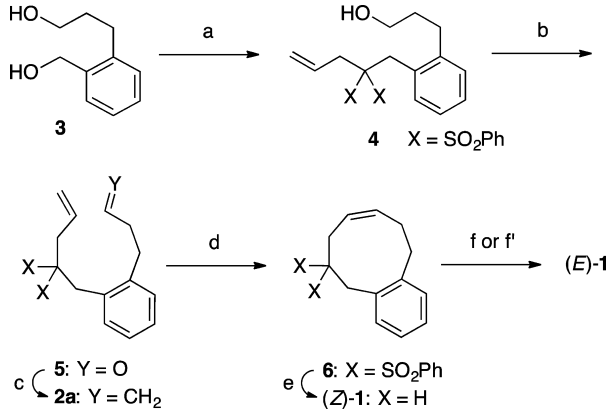
Scheme 2



retrosynthetic analysis. The *trans*-alkene moiety of (*E*)-**1** can be constructed through the photochemical isomerization of (*Z*)-**1**. Key intermediate (*Z*)-**1** can be synthesized from acyclic diene **2** via RCM.

The requisite precursor **2a** (X = SO_2Ph) was readily synthesized from the known diol **3**[6] in three steps as shown in Scheme 3. The Mitsunobu reaction of diol **3** and CH_2=$CHCH_2CH(SO_2Ph)_2$ using *N*,*N*,*N*′,*N*′-tetramethylazodicarboxamide (TMAD) proceeded with high group selectivity and provided alcohol **4** as the sole product quantitatively.[7] The PCC oxidation of the alcohol moiety of **4** followed by the Wittig olefination reaction afforded key intermediate **2a** in 73% yield (two steps). The RCM reaction of **2a** with Grubbs' first-generation catalyst, followed by the removal of sulfones by reduction using Mg, provided (*Z*)-**1** in 92% yield (two steps).[8] Initially, the photochemical isomerization of (*Z*)-**1** was performed according to Inoue's procedure (Scheme 3, step f).[9] The irradiation of (*Z*)-**1** with 280 nm UV light in the presence of a sensitizer, dimethyl isophthalate (DMIP), in CH_3CN at rt for 12 h quantitatively afforded a 22:78 (*E*)-**1**/(*Z*)-**1** mixture. Pure (*E*)-**1** was isolated in 22% yield using $AgNO_3$-impregnated silica gel ($AgNO_3/SiO_2$) chromatography;[10] subsequent photochemical isomerization of the recovered (*Z*)-**1** produced a reasonable amount of (*E*)-**1**. While we accomplished a short step synthesis of (*E*)-**1** from **3**, the photochemical isomerization step suffered from a low (*E*) selectivity. To overcome this problem, we envisaged the photochemical isomerization of (*Z*)-**1** in the presence of $AgNO_3/SiO_2$; the generated (*E*) isomer should be selectively adsorbed on the $AgNO_3/SiO_2$ and can be removed from the isomerization process as shown in Figure 2.[11] In addition, the resulting (*E*) isomer would be liberated from the $AgNO_3/SiO_2$ by being treated with argyrophilic amine base.

Scheme 3[a]



[a]Reagents and conditions: (a) CH_2=$CHCH_2CH(SO_2Ph)_2$, TMAD, *n*-Bu_3P, Et_3N, benzene, 0 °C to rt, quant.; (b) PCC, CH_2Cl_2, rt, 83%; (c) Ph_3PMeI, *n*-BuLi, THF, 0 °C to rt, 88%; (d) Grubbs' first-generation catalyst, CH_2Cl_2, reflux, quant.; (e) Mg, MeOH, rt, 92%; (f) DMIP, 280 nm UV light, CH_3CN, rt, 22% (*E*)-**1**, 78% (*Z*)-**1**; (f′) DEIP, $AgNO_3/SiO_2$, 280 nm UV light, pentane, rt, 76% (*E*)-**1**.

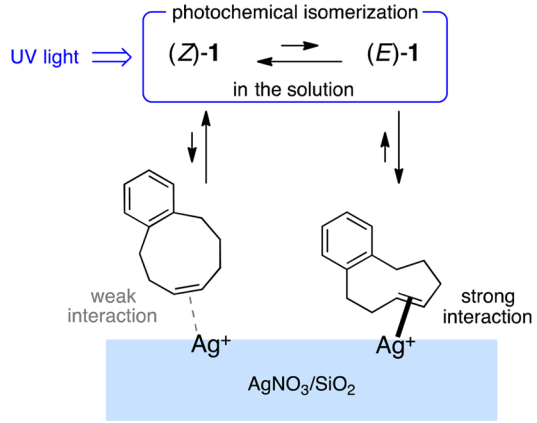


Figure 2. Concept of photochemical isomerization in the presence of $AgNO_3/SiO_2$.

The reaction was performed in a three-neck round-bottom Pyrex flask equipped with a cylindrical Teflon-coated magnetic stir bar (Figure 3). The left neck was capped with a rubber septum, the center neck fitted with a Teflon connecter holding a quartz photoinlet adapter, and the right neck fitted with a three-direction cock connected to an argon balloon.

The flask was charged with a 0.02 M solution of (*Z*)-**1** (34.8 mg, 0.202 mmol) and diethyl isophthalate (DEIP) (91.7 mg, 0.412 mmol) in pentane and 500 mg of $AgNO_3/SiO_2$.[12] A 280 nm UV light was introduced into the flask through the glass

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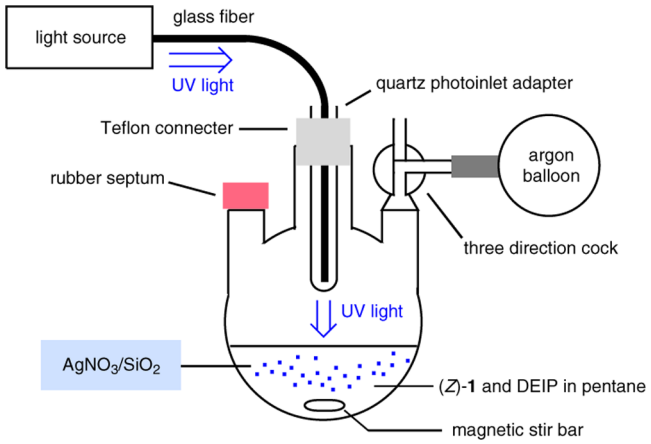

Figure 3. Reaction apparatus for photochemical isomerization in the presence of $AgNO_3/SiO_2$.

fiber inserted into the photoinlet adapter. The reaction mixture was gently stirred at ambient temperature for 42 h. For the liberation of (*E*)-**1** from $AgNO_3/SiO_2$, aqueous ammonia was added to the reaction mixture, and the resulting reaction mixture was extracted with Et_2O. The organic layer was dried over Na_2SO_4, filtered, concentrated, and purified by short-path silica gel column chromatography (pentane), affording a 89:11 (*E*)-**1**/(*Z*)-**1** mixture. The (*E*) isomer was isolated by $AgNO_3/SiO_2$ column chromatography (pentane/Et_2O) in 76% yield (Scheme 3, step f′). Thus, a significant improvement of (*E*) selectivity of photochemical isomerization was realized because of the presence of $AgNO_3/SiO_2$.

Stereochemical Behavior of (*E*)-1. The existence of isolable enantiomers of (*E*)-**1** was revealed by HPLC analysis using a chiral stationary phase equipped with a CD and a UV detector. As shown in Figure 4, both enantiomers of (*E*)-**1** were successfully separated using a CHIRALCEL OD-H column (analytical column, 4.6 mm × 250 mm; preparative column, 20 mm × 250 mm) at rt; the CD signs of the first and second eluates were − and +, respectively at 254 nm.

The rate constants of racemization were obtained by the HPLC measurements of enantiopurity at proper time intervals in hexane. The plot of ln *a* [$a = |S - R|/(S + R)$] versus time furnished a straight line, affording rate constants *k*, and the half-lives of the optical activity of (*E*)-**1** at 5, 15, 25, and 40 °C are 67.5, 15.2, 4.35, and 0.583 h, respectively (Figure 5 and Table 1).

The Eyring plot of $\ln(k'T^{-1}; k' = k/2)$ versus T^{-1} showed an excellent straight line (Figure 6). Activation enthalpy $\Delta H^{\ddagger}$ for the racemization is 22.8 kcal mol^{-1}, and activation entropy $\Delta S^{\ddagger}$ for the racemization is −3.31 cal mol^{-1} K^{-1}.

This result indicates that the planar chirality of (*E*)-**1** is more stable than that of (*E*)-cyclononene (for racemization energy, $\Delta H^{\ddagger}$ = 18.1 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −5.51 cal mol^{-1} K^{-1}).[1e,13]

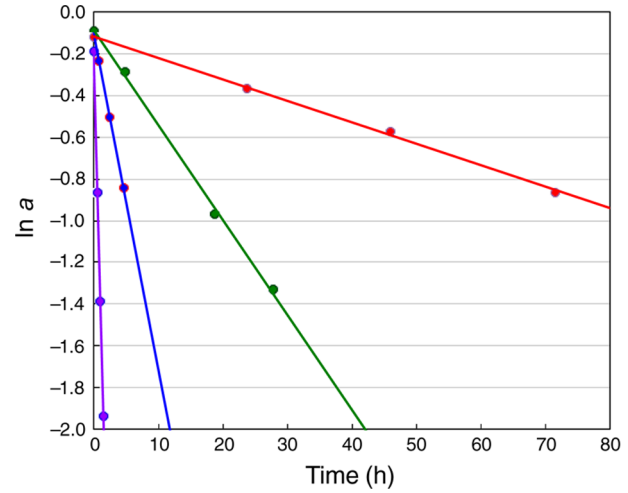

Figure 5. Kinetic measurement of the racemization of (*E*)-**1**.

Table 1. Rate Constants and Half-Lives of (*E*)-1

T (°C)	*k* (×10^{-4} s^{-1})	$t_{1/2}$ (h)
5	0.0285	67.5
15	0.1263	15.2
25	0.4422	4.35
40	3.301	0.583

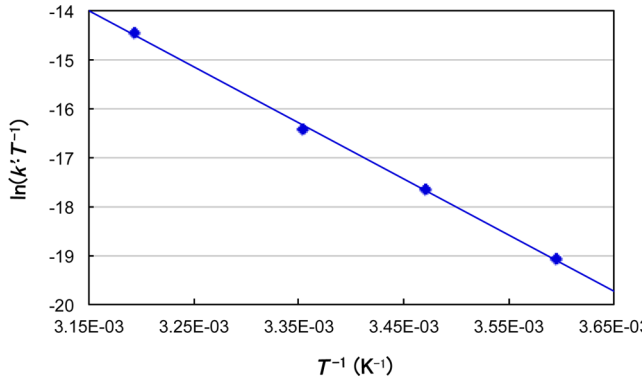

Figure 6. Eyring plot of the racemization of (*E*)-**1**.

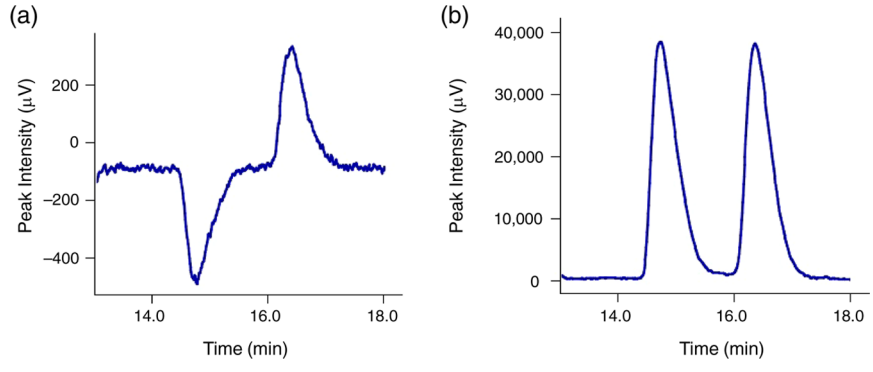

Figure 4. HPLC analysis of (*E*)-**1**: (a) chromatogram with a CD detector and (b) chromatogram with a UV detector.

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On the other hand, Hoppe and colleagues estimated the activation parameters for the racemization of 1,5-(*E*,*Z*)-cyclononadiene as $\Delta H^{\ddagger}$ = 25.9 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −2.01 cal mol^{-1} K^{-1}.[14] Thus, the order of stereochemical stability is as follows: (*E*)-cyclononene < (*E*)-**1** < 1,5-(*E*,*Z*)-cyclononadiene (Figure 7). This trend is reasonably explained by a decrease in

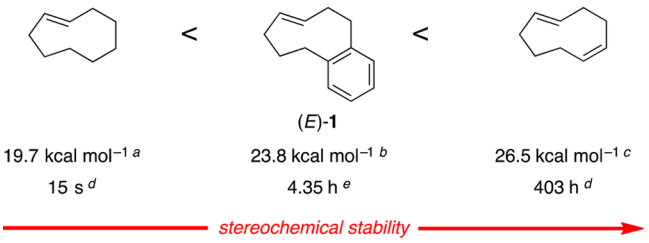


Figure 7. Order of stereochemical stability of (*E*)-cyclononene derivatives: free energies of racemization and half-lives of the optical activity of (*E*)-cyclononenes at 298 K. [a]Reanalyzed $\Delta G^{\ddagger}_{(298\ K)}$ value from reported experimental data from Cope's group.[1e,13] [b]Experimental value of $\Delta G^{\ddagger}_{(298\ K)}$. [c]Calculated value of $\Delta G^{\ddagger}_{(298\ K)}$ reported by Hoppe's group.[14] [d]Estimated values of half-lives of the optical activity based on $\Delta G^{\ddagger}_{(298\ K)}$. [e]Experimental value of the half-life of the optical activity at 298 K.

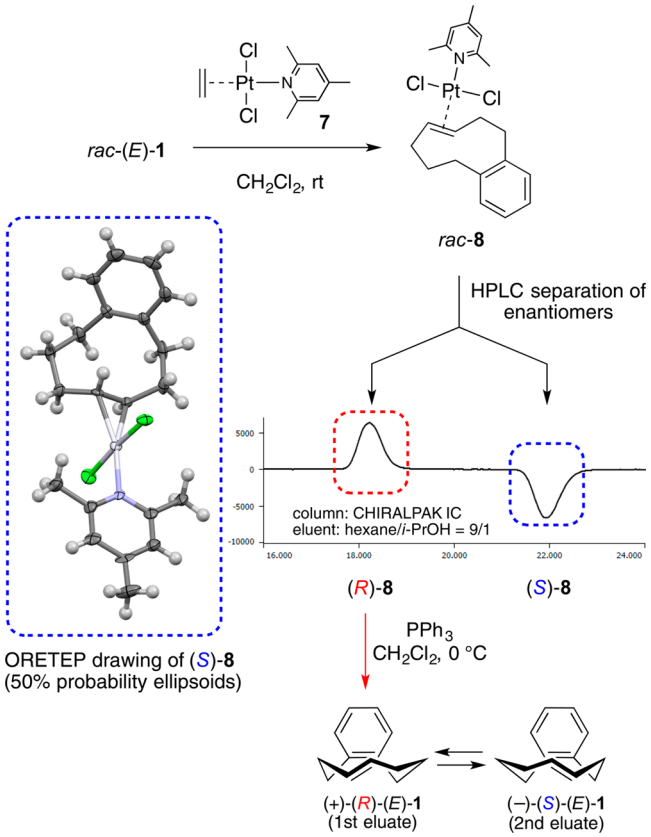
the conformational flexibility of the ring because of the introduction of additional trigonal carbons into the ring, and its degree depends on the bond length of trigonal carbons. The bond length of the (*Z*)-alkene of 1,5-(*E*,*Z*)-cyclononadiene is shorter than that of the benzene ring of (*E*)-**1**.

Determination of the Absolute Stereochemistry of (*E*)-1. Because a straightforward determination of the absolute configuration of noncrystalline (*E*)-**1** was difficult, the Pt complexes of the enantiomers were prepared by our previously developed method as shown in Scheme 4.[3g,15] The reaction of *rac*-(*E*)-**1** with $PtCl_2$(2,4,6-trimethylpyridine) (CH_2=CH_2) (**7**) provided *rac*-**8** in 97% yield, and its separation by HPLC using chiral stationary column CHIRALPAK IC or AD-H afforded both enantiomers of **8** in enantiopure crystalline form. An X-ray crystallographic analysis showed the stereochemistry of the second eluate of **8** with an IC column to be (*S*) and that of the first eluate of **8** to be (*R*).[16] The treatment of (*R*)-**8** with PPh_3 in CH_2Cl_2 at 0 °C provided (*E*)-**1** in an enantioenriched form, and its CD signal was identical to that of (+)-(*E*)-**1**. Therefore, it was unequivocally determined that (+)-(*E*)-**1** has an (*R*) configuration.

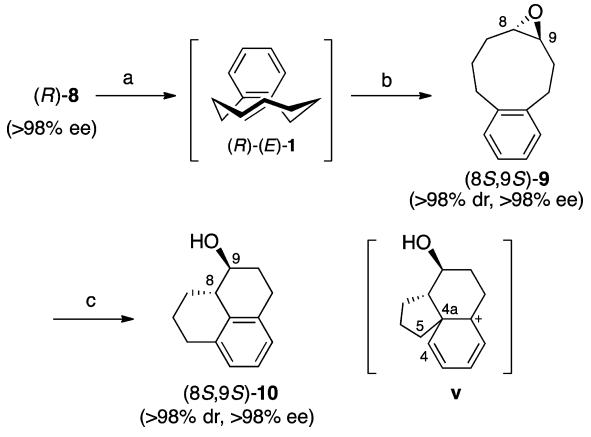
Transformation of the Planar Chirality of (*E*)-1 into the Central Chirality of Carbon. Enantioenriched orthocyclophene (*E*)-**1** has the potential to be a chiral building block for chiral compounds with the central chirality of carbon by proper reactions.

The reaction of (*R*)-(*E*)-**1**, prepared *in situ* from (*R*)-**8** (>98% ee) by treatment with PPh_3, with DMDO provided epoxide (8*S*,9*S*)-**9** as the sole product in >98% dr and >98% ee (Scheme 5). This result attests to the fact that the epoxidation reaction occurs from the outer peripheral face. The transannular reaction of **9** proceeds in a stereospecific manner. Namely, the BF_3·OEt_2-promoted reaction of (8*S*,9*S*)-**9** afforded a unique tricyclic compound, (8*S*,9*S*)-**10**, in an excellent yield (85%) in >98% dr and >98% ee.[17] This reaction should involve cationic intermediate **v**, which was formed by epoxide cleavage, followed by an intramolecular Friedel−Crafts reaction. Then, the 1,2-migration of the C5 atom from the C4a position to the C4 position will provide (8*S*,9*S*)-**10**.

Scheme 4



Scheme 5[a]



[a]Reagents and conditions: (a) PPh_3, CH_2Cl_2, −78 to −60 °C; (b) DMDO, CH_2Cl_2, −78 to 0 °C, 71% (two steps); (c) BF_3·OEt_2, CH_2Cl_2, 0 °C, 85%.

CONCLUSIONS

A concise synthesis of (*E*)-4-[7]orthocyclophene (*E*)-**1** was performed. The main feature of the synthesis is the efficient photochemical isomerization of (*Z*)-**1** in the presence of $AgNO_3/SiO_2$. The detailed stereochemical behavior of (*E*)-**1** was analyzed; its thermodynamic parameters for racemization were as follows: $\Delta H^{\ddagger}$ = 22.8 kcal mol^{-1}, and $\Delta S^{\ddagger}$ = −3.31 cal mol^{-1} K^{-1}. The absolute stereochemistry of the enantiomers of (*E*)-**1** was adequately determined by the X-ray diffraction analysis of Pt complex derivative **8**. Furthermore, it was found that the planar chirality of (*E*)-**1** can be converted into the

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central chirality of carbon in a stereospecific manner. Studies of further synthetic applications of the planar-chiral orthocyclophene are underway.

EXPERIMENTAL SECTION

General Method. All reactions were performed in heat gun-dried glassware under an argon atmosphere unless otherwise noted. The dehydrated solvent (THF, CH_2Cl_2, DMF, benzene, and MeOH) and the solvent for spectroscopy (CH_3CN and pentane) were purchased and used without further purification. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded at ambient temperature using $CDCl_3$ as a solvent. Chemical shifts (δ) in parts per million were referenced to the solvent residual peak as an internal standard: $CHCl_3$ for ^{1}H NMR (δ 7.26) and $CDCl_3$ for ^{13}C NMR (δ 77.1). The peak multiplicities were given as follows: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Infrared spectra was recorded on an FT-IR spectrometer as neat liquid on NaCl plates or as crystals by use of a diffuse reflector. Analytical thin-layer chromatography (TLC) was conducted on silica gel plates with a fluorescent indicator, and developed plates were visualized by UV (254 nm) and by heating on a hot plate after staining with a 4% solution of phosphomolybdic acid in ethanol or a 2.5% solution of *p*-anisaldehyde in ethanol. Column chromatography was performed using neutral and spherical silica gel. Melting points (mp) were measured on a micro melting point apparatus. HPLC analyses were performed on an UV detector and a CD detector. Preparative GPC was performed with an UV detector and an RI detector. X-ray crystallographic data were recorded using a CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) at 123 K. HRMS was performed on a high-resolution mass spectrometer employing a quadrupole doublet-based lens system.

1,1-Bis(phenylsulfonyl)-3-butene.[18] To a solution of bis(phenylsulfonyl)methane (500 mg, 1.68 mmol) in DMF (10 mL) at 0 °C was added NaH (55 wt % in mineral oil, 80.2 mg, 1.84 mmol). After the mixture had been stirred at that temperature for 30 min, allyl bromide (144 μL, 1.68 mmol) was added. The resulting mixture was stirred at rt for 4 h. The reaction was quenched with saturated aqueous NH_4Cl and the mixture extracted three times with AcOEt. The combined organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (2:1 hexane/AcOEt) to afford 534 mg of 1,1-bis(phenylsulfonyl)-3-butene (94%) as colorless crystals: ^{1}H NMR (300 Hz, $CDCl_3$) δ 7.99−7.95 (m, 4H), 7.71 (tt, J = 7.5, 1.7 Hz, 2H), 7.61−7.56 (m, 4H), 5.81 (ddt, J = 17.0, 10.1, 6.9 Hz, 1H), 5.09−5.00 (m, 2H), 4.46 (t, J = 6.0 Hz, 1H), 2.95−2.90 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.8, 134.7, 132.3, 129.7, 129.1, 119.1, 83.6, 29.8; IR (reflection) 2919, 1643, 1583, 1449, 1311, 1142, 1077, 998, 928, 728, 686, 620, 564, 514 cm^{-1}; mp 116.5−117.0 °C; HRMS (EI, positive) $[M]^+$ calcd for $C_{16}H_{16}O_4S_2$ m/z 336.0490, found m/z 336.0484.

3-{*o*-[2,2-Bis(phenylsulfonyl)-4-penten-1-yl]phenyl}-1-propanol (4). To a solution of 2-(hydroxymethyl)benzenepropanol (**3**) (600 mg, 3.61 mmol), 1,1-bis(phenylsulfonyl)-3-butene (1.46 g, 4.33 mmol), Et_3N (1.00 mL, 7.21 mmol), and tri-*n*-butylphosphine (1.78 mL, 7.12 mmol) in benzene (36 mL) at 0 °C was added TMAD (930 mg, 5.40 mmol). The resulting mixture was stirred at rt for 23 h. The solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (3:1 to 2:1 hexane/AcOEt) to afford 1.80 g of **4** (quant.) as colorless crystals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92 (dd, J = 8.7, 1.2 Hz, 4H), 7.65 (tt, J = 7.5, 1.2 Hz, 2H), 7.50 (dd, J = 8.7, 7.5 Hz, 4H), 7.27 (d, J = 8.1 Hz, 1H), 7.22−7.14 (m, 2H), 6.99−6.91 (m, 1H), 5.97 (ddt, J = 17.1, 10.2, 6.3 Hz, 1H), 5.13−5.05 (m, 2H), 3.75 (s, 2H), 3.64 (dt, J = 5.7, 6.0 Hz, 2H), 3.09 (d, J = 6.6 Hz, 2H), 2.78 (t, J = 7.8 Hz, 2H), 1.78 (tt, J = 7.8, 6.0 Hz, 2H), 1.41 (t, J = 5.7 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.3, 137.2, 134.3, 131.5, 131.4, 131.2, 130.4, 129.9, 128.4, 127.8, 125.9, 120.0, 92.6, 62.1, 34.8, 34.0, 30.4, 29.3; IR (reflection) 3543, 2924, 1582, 1446, 1143, 1076, 911, 730, 686, 615, 586, 538 cm^{-1}; mp 139.0−139.8 °C; HRMS (FAB, positive, matrix of 3-nitrobenzyl alcohol) $[M + H]^+$ calcd for $C_{26}H_{29}O_5S_2$ m/z 485.1456, found m/z 485.1454.

3-{*o*-[2,2-Bis(phenylsulfonyl)-4-penten-1-yl]phenyl}propanal (5). To a solution of **4** (1.94 g, 4.00 mmol) in CH_2Cl_2 (80 mL) at rt were added molecular sieve 4A powder (2.64 g) and PCC (1.29 g, 5.98 mol). The resulting mixture was stirred at that temperature for 1 h, and hexane (52 mL) and silica gel (51 g) were added. The resulting slurry was transferred onto the top of a silica gel column and chromatographed (3:1 to 2:1 hexane/AcOEt) to afford 1.61 g of **5** (83%) as colorless crystals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.76 (t, J = 1.4 Hz, 1H), 7.89 (dd, J = 8.7, 1.2 Hz, 4H), 7.66 (tt, J = 7.4, 1.2 Hz, 2H), 7.50 (dd, J = 8.7, 7.4 Hz, 4H), 7.25 (d, J = 7.5 Hz, 1H), 7.21−7.14 (m, 2H), 6.99−6.93 (m, 1H), 6.01 (ddt, J = 16.7, 10.4, 6.6 Hz, 1H), 5.16−5.07 (m, 2H), 3.75 (s, 2H), 3.09 (d, J = 6.6 Hz, 2H), 2.99 (t, J = 7.5 Hz, 2H), 2.68 (dt, J = 1.4, 7.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.5, 141.3, 137.7, 134.9, 132.0, 131.98, 131.92, 130.9, 130.1, 129.0, 128.5, 126.8, 120.6, 93.0, 45.3, 35.4, 31.0, 25.8; IR (reflection) 3081, 1714, 1581, 1448, 1328, 1142, 930, 752, 572 cm^{-1}; mp 132.9−133.9 °C; HRMS (ESI, positive) $[M]^+$ calcd for $C_{26}H_{26}O_5S_2$ m/z 482.1222, m/z found 482.1217.

4-{*o*-[2,2-Bis(phenylsulfonyl)-4-penten-1-yl]phenyl}-1-butene (2a). To a solution of methyltriphenylphosphonium iodide (824 mg, 2.03 mmol) in THF (10 mL) at 0 °C was added *n*-BuLi (1.4 M in hexane, 1.36 mL, 1.90 mmol). After the mixture had been stirred at rt for 1 h, a solution of **5** (655 mg, 1.36 mmol) in THF (15 mL) was added. After the mixture had been stirred at that temperature for 30 min, the reaction was quenched with saturated aqueous NH_4Cl and the mixture extracted three times with AcOEt. The combined organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (20:1 to 4:1 hexane/AcOEt) to afford 574 mg of **2a** (88%) as colorless crystals: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, J = 8.7, 1.5 Hz, 4H), 7.64 (tt, J = 7.2, 1.5 Hz, 2H), 7.47 (dd, J = 8.7, 7.2 Hz, 4H), 7.23 (d, J = 7.8 Hz, 1H), 7.17−7.15 (m, 2H), 6.96−6.88 (m, 1H), 6.02 (ddt, J = 16.8, 10.2, 6.9 Hz, 1H), 5.81 (ddt, J = 17.3, 10.4, 6.6 Hz, 1H), 5.17−5.00 (m, 4H), 3.72 (s, 2H), 3.10 (d, J = 6.9 Hz, 2H), 2.74 (t, J = 7.8 Hz, 2H), 2.24 (dt, J = 6.6, 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.4, 137.7, 137.4, 134.3, 131.5, 131.4, 131.2, 130.6, 130.1, 128.5, 127.8, 126.0, 120.2, 115.2, 92.7, 35.5, 35.0, 32.6, 30.5; IR (reflection) 3069, 1582, 1446, 1310, 1141, 1075, 914, 730, 583, 544 cm^{-1}; mp 100.5−101.5 °C; HRMS (ESI, positive) $[M]^+$ calcd for $C_{27}H_{28}O_4S_2$ m/z 480.1429, m/z found 480.1423.

(*Z*)-6,6-Bis(phenylsulfonyl)-6,7,10,11-tetrahydro-5*H*-benzocyclononene (6). To a refluxed solution of **2a** (179 mg, 0.373 mmol) in CH_2Cl_2 (35 mL) was added a solution of Grubbs' first-generation catalyst (15.4 mg, 0.0187 mmol) in CH_2Cl_2 (7 mL) over an 8 h period. The resulting mixture was stirred for 22 h, and the solvent was removed under reduced pressure. To the residue in CH_2Cl_2 (15 mL) was added active charcoal (770 mg). After being stirred for 12 h, the resulting mixture was filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (3:1 hexane/AcOEt) to afford 168 mg of **6** (quant.) as colorless crystals. ^{1}H NMR analysis of **6** shows broadening peaks, and the ^{13}C NMR signal of the sulfonyl α-carbon was not detected probably because of the very low intensity of the peak under standard measurement conditions. These observations would be caused by the interconversion of the conformers on the measurement time scale: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (dd, J = 9.0, 1.5 Hz, 4H), 7.76−7.68 (m, 3H), 7.60 (dd, J = 9.0, 7.5 Hz, 4H), 7.22−7.11 (m, 2H), 7.01 (dd, J = 7.4, 2.0 Hz, 1H), 5.76 (dt, J = 10.5, 8.4 Hz, 1H), 5.48 (br, 1H), 3.69 (s, 2H), 3.05 (d, J = 8.4 Hz, 2H), 2.57 (br, 2H), 2.39−2.32 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.8, 137.4, 134.6, 134.5, 133.0 (br), 131.9, 131.4, 128.7, 128.0, 125.4, 123.8, 33.9, 32.0 (br), 28.7, 26.8; IR (reflection) 3064, 1582, 1447, 1309, 1142, 1076, 910, 733, 686, 629, 585 cm^{-1}; mp 90.5−91.0 °C; HRMS (ESI, positive) $[M]^+$ calcd for $C_{25}H_{24}O_4S_2$ m/z 452.1116, m/z found 452.1112.

(*Z*)-6,7,10,11-Tetrahydro-5*H*-benzocyclononene [(*Z*)-1]. To a suspension of **6** (307 mg, 0.678 mmol) in MeOH (23 mL) at rt were added Mg turnings (569 mg, 23.7 mmol). The resulting mixture was stirred for 1 h. The reaction was quenched with aqueous HCl (1.0 M, 35 mL) and the mixture extracted twice with pentane. The combined organic phase was dried over Na_2SO_4 and filtered, and the solvent was

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removed under reduced pressure. The residue was purified by silica gel chromatography (pentane) to afford 107 mg of (*Z*)-**1** (92%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−7.08 (m, 4H), 5.84 (dt, J = 10.5, 8.4 Hz, 1H), 5.50 (dt, J = 10.5, 7.8 Hz, 1H), 2.67 (t, J = 5.4 Hz, 2H), 2.59 (t, J = 5.7 Hz, 2H), 2.24 (br, 2H), 1.79−1.68 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.7, 140.4, 130.6, 130.2, 130.1, 129.5, 126.1, 126.0, 33.9, 32.0, 29.0, 28.1, 24.2; IR (neat) 3009, 2924, 2863, 1490, 1463, 1094, 782, 747, 700, 598 cm^{-1}; HRMS (ESI, positive) $[M]^+$ calcd for $C_{13}H_{16}$ m/z 172.1252, m/z found 172.1253.

Preparation of $AgNO_3/SiO_2$. To a solution of $AgNO_3$ (1 g) in distilled water (100 mL) in an aluminum foil-wrapped one-neck round-bottom flask (300 mL) was added silica gel (9 g). The mixture was stirred for 20 min, and then water was evaporated under reduced pressure with a rotary evaporator at 55 °C. The residue in the flask was further dried under reduced pressure with a rotary vacuum pump for 2 h at 90−110 °C by heating with an oil bath.

(*E*)-6,7,10,11-Tetrahydro-5*H*-benzocyclononene [(*E*)-1]. The reaction was performed in a three-neck round-bottom Pyrex flask equipped with a cylindrical Teflon-coated magnetic stir bar. The left neck was capped with a rubber septum, the center neck fitted with a Teflon connecter holding a quartz photoinlet adapter, and the right neck fitted with a three-direction cock connected to an argon balloon. The flask was charged with a 0.02 M solution of (*Z*)-**1** (34.8 mg, 0.202 mmol) and DEIP (91.7 mg, 0.412 mmol) in pentane and 500 mg of $AgNO_3/SiO_2$.[11] A 280 nm UV light (Asahi Spectra MAX-301) was introduced into the flask through the glass fiber inserted into the photoinlet adapter. The reaction mixture was gently stirred at ambient temperature for 42 h. To the reaction mixture was added NH_4OH (NH_3 content of 28−30%, 10 mL), and then the organic compounds were extracted with Et_2O. The combined organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (pentane). GC analysis of the resulting mixture provided an (*E*)-**1** assay yield of 78.6% and a (*Z*)-**1** assay yield of 9.7% [89:11 (*E*)-**1**/(*Z*)-**1**] with dodecane as an internal standard [column, Supelco Astec CHIRALDEX B-DP (0.25 mm × 30 m × 0.12 μm); oven temperature, 130 °C; injector and detector temperature, 160 °C; carrier gas, He; pressure, 100 kPa; flow rate, 2.5 mL/min; detector, FID; t_R = 11.5 min for (*Z*)-**1** and 12.0 min for (*E*)-**1**]. The resulting mixture was purified by $AgNO_3/SiO_2$ chromatography (20:1 pentane/Et_2O to Et_2O only) to afford 26.4 mg of (*E*)-**1** (76%) as a colorless oil: HPLC analysis [column, CHIRALCEL OD-H (0.46 cm × 25 cm); eluent, hexane; flow rate, 0.5 mL/min; detector, UV 254 nm; temperature, rt; retention time, t_R = 14.7 min for (−)-(*S*)-(*E*)-**1** and 16.3 min for (+)-(*R*)-(*E*)-**1**]; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−7.04 (m, 4H), 5.52 (ddd, J = 15.4, 10.7, 5.0 Hz, 1H), 4.65 (ddd, J = 15.4, 11.0, 3.9 Hz, 1H), 2.81−2.75 (m, 1H), 2.59−2.47 (m, 3H), 2.45−2.24 (m, 3H), 2.05−1.86 (m, 2H), 1.77−1.65 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.3, 138.2, 131.37, 131.31, 130.7, 130.5, 126.2, 125.6, 36.01, 35.99, 34.1, 33.6, 29.7; IR (neat) 3012, 2929, 2856, 1488, 1443, 976, 801, 754, 699, 516, 455 cm^{-1}; HRMS (ESI, positive) $[M]^+$ calcd for $C_{13}H_{16}$ m/z 172.1252, m/z found 172.1252.

***trans*-Dichloro(*trans*-2′,4′,6′-trimethylpyridine)[η^2-(*E*)-6,7,10,11-tetrahydro-5*H*-benzocyclononene]platinum (8).** To a solution of (*E*)-**1** (63.5 mg, 0.361 mmol) in CH_2Cl_2 (3 mL) at 40 °C was added *trans*-dichloro(ethylene)(2,4,6-trimethylpyridine)platinum (**7**) (150 mg, 0.368 mmol). The resulting mixture was stirred for 4 h at that temperature, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (hexane only to 5:1 hexane/AcOEt) to afford a mixture of **8** and **7**. The resulting mixture was purified by preparative GPC [column, JAIGEL-1H (2.0 cm × 60 cm); eluent, $CHCl_3$; flow rate, 3.7 mL/min; temperature, rt] to afford 196 mg of **8** (97%) as yellow crystals: preparative HPLC [column, CHIRALPAK AD-H (2.0 cm × 25 cm); eluent, 1:1 hexane/*i*-PrOH; flow rate, 4.0 mL/min; detector, UV 254 nm; temperature, rt; retention time, t_R = 77.0 min for (−)-(*S*)-**8** and 107 min for (+)-(*R*)-**8**]; HPLC analysis [column, CHIRALPAK IC (0.46 cm × 25 cm); eluent. 9:1 hexane/*i*Pr-OH; flow rate, 0.5 mL/min; detector, UV 254 nm; temperature, rt; retention time, t_R = 18.2 min for the (+)-(*R*) isomer and 21.9 min for the (−)-(*S*) isomer]; $[\alpha]_D^{20}$ − 130.18 (*c* 0.44, $CHCl_3$) for the (*S*) isomer (>98% ee); $[\alpha]_D^{20}$ + 130.14 (*c* 0.46, $CHCl_3$) for the (*R*) isomer (>98% ee); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−6.99 (m, 6H), 5.37 (br, 1H), 4.69 (br, 1H), 3.12 (s, 6H), 2.93−2.83 (m, 3H), 2.75−2.67 (m, 1H), 2.57−2.28 (m, 6H), 2.19−1.95 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.6, 151.1, 143.1, 137.5, 131.2, 130.5, 126.8, 126.5, 125.2, 94.3, 94.0, 35.2, 35.0, 34.1, 33.8, 28.4, 25.7, 20.7; IR (reflection) 2928, 1626, 1457, 1374, 1320, 1036, 924, 849, 758, 567, 501 cm^{-1}; mp >185 °C dec; HRMS (FAB, positive, matrix of 3-nitrobenzyl alcohol) $[M]^+$ calcd for $C_{21}H_{27}N^{35}Cl^{37}Cl^{194}Pt$ m/z 559.1118, found m/z 559.1115.

(8*S*,9*S*)-6,7,8,9,10,11-Hexahydro-8,9-epoxy-5*H*-benzocyclononene [(8*S*,9*S*)-9]. To a solution of (+)-(*R*)-**8** (25.9 mg, 0.0462 mmol) in CH_2Cl_2 (4 mL) at −78 °C was added triphenylphosphine (25.6 mg, 0.0976 mmol). The resulting mixture was allowed to warm to −60 °C over 1.5 h. Then the mixture was recooled to −78 °C, and a DMDO solution (0.043 M in acetone, 10.7 mL, 0.460 mmol) was added at that temperature. After the mixture was allowed to warm to 0 °C over 6 h, the solvent was removed under reduced pressure at rt. The residue was purified by silica gel chromatography (20:1 to 10:1 hexane/AcOEt) to afford 6.2 mg of (8*S*,9*S*)-**9** (71%) in >98% dr and >98% ee as colorless crystals: HPLC analysis [column, CHIRALCEL OD-3 (0.46 cm × 25 cm); eluent, 95:5 hexane/EtOH; flow rate, 0.5 mL/min; detector, UV 254 nm; temperature, rt; t_R = 12.0 min for (8*S*,9*S*)-**9** and 13.3 min for (8*R*,9*R*)-**9**]; $[\alpha]_D^{20}$ − 173.68 (*c* 0.77, $CHCl_3$) for (8*S*,9*S*)-**9**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20−7.18 (m, 2H), 7.11−7.09 (m, 2H), 2.99−2.68 (m, 5H), 2.56−2.52 (m, 1H), 2.41−2.32 (m, 1H), 2.25−2.12 (m, 2H), 1.99−1.83 (m, 1H), 1.19−0.96 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.2, 139.1, 130.7, 130.1, 126.8, 126.1, 60.0, 56.6, 32.8, 31.8, 29.5, 28.6 (two peaks are overlapping); IR (reflection) 2932, 2862, 1491, 1446, 988, 945, 911, 882, 817, 757, 521 cm^{-1}; mp 32.0−33.0 °C; HRMS (ESI, positive) $[M]^+$ calcd for $C_{13}H_{16}O$ m/z 188.1201, m/z found 188.1201.

(1*S*,9a*S*)-2,3,7,8,9,9a-Hexahydro-1*H*-phenalen-1-ol [(8*S*,9*S*)-10]. To a solution of (8*S*,9*S*)-**9** (6.2 mg, 0.0329 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added $BF_3{\cdot}OEt_2$ (8.26 μL, 0.0658 mmol). The reaction mixture was stirred at that temperature for 30 min. The reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with CH_2Cl_2. The combined organic phase was dried over Na_2SO_4 and filtered, and the solvent was removed under reduced pressure. The residue was purified by silica gel chromatography (20:1 to 7:1 hexane/AcOEt) to afford 5.3 mg (85%) of (8*S*,9*S*)-**10** in >98% dr and >98% ee as colorless crystals: HPLC analysis [column, CHIRALCEL OD-3 (0.46 cm × 25 cm); eluent, 99:1 hexane/EtOH; flow rate, 0.9 mL/min; detection, UV 254 nm; temperature, rt; t_R = 18.8 min for (8*S*,9*S*)-**10** and 20.3 min for (8*R*,9*R*)-**10**]; $[\alpha]_D^{21}$ + 17.1 (*c* 0.36, $CHCl_3$) for (8*S*,9*S*)-**10**; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.05 (dd, J = 7.5, 7.5 Hz, 1H), 6.92 (d, J = 7.5 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 3.65 (ddd, J = 10.0, 9.9, 4.3 Hz, 1H), 3.01−2.87 (m, 2H), 2.85−2.73 (m, 2H), 2.55 (ddd, J = 10.5, 10.2, 4.5 Hz, 1H), 2.39 (dddd, J = 12.6, 4.5, 4.4, 3.9 Hz, 1H), 2.14 (dddd, J = 12.5, 5.6, 3.9, 3.6 Hz, 1H), 2.05−1.93 (m, 1H), 1.89−1.70 (m, 2H), 1.32 (dddd, J = 12.1, 12.0, 12.0, 3.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.7, 135.7, 135.1, 126.9, 126.4, 126.0, 73.3, 44.8, 32.8, 29.6, 28.7, 26.7, 22.6; IR (reflection) 3313, 2926, 1459, 1360, 1101, 1052, 913, 839, 801, 760, 740 cm^{-1}; mp 68.5−69.5 °C; HRMS (EI, positive) $[M]^+$ calcd for $C_{13}H_{16}O$ m/z 188.1201, m/z found 188.1202.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b01799.

Reanalysis data of the racemization of (*E*)-cyclononene, ^{1}H and ^{13}C NMR spectra for all synthesized compounds, a thermal ellipsoid plot for the crystal structure of (*S*)-**8**, and HPLC chromatograms of compounds **8**−**10** (PDF)
Crystallographic information for (*S*)-**8** (CIF)

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Notes

The authors declare no competing financial interest.

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(7) A similar benzyl alcohol-selective Mitsunobu reaction has been observed in a reaction of **3** and tosylamide in our group (see ref 6). The studies for clarifying the generality and mechanism of the group-selective Mitsunobu reaction are now underway.

(8) It is well-known that (*Z*)-cycloalkenes are preferentially provided over (*E*)-cycloalkenes by RCM in medium-size ring formation. For representative reports, see: (a) Fürstner, A.; Radkowski, K.; Wirtz, C.; Goddard, R.; Lehmann, C. W.; Mynott, R. *J. Am. Chem. Soc.* **2002**, *124*, 7061−7069. (b) Matsui, R.; Seto, K.; Fujita, K.; Suzuki, T.; Nakazaki, A.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 10068−10073. (c) Tomooka, K.; Miyasaka, S.; Motomura, S.; Igawa, K. *Chem. - Eur. J.* **2014**, *20*, 7598−7602. For a representative review, see: (d) Deiters, A.; Martin, S. F. *Chem. Rev.* **2004**, *104*, 2199−2238.

(9) (a) Inoue, Y.; Takamuku, S.; Sakurai, H. *J. Phys. Chem.* **1977**, *81*, 7−11. (b) Inoue, Y.; Takamuku, S.; Kunitomi, Y.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 2* **1980**, 1672−1677.

(10) For reviews on chromatographic separation of alkenes with $AgNO_3/SiO_2$, see: (a) van Beek, T. A.; Subrtova, D. *Phytochem. Anal.* **1995**, *6*, 1−19. (b) Williams, C. M.; Mander, L. N. *Tetrahedron* **2001**, *57*, 425−447.

(11) As a related important study, Fox and colleagues have reported an efficient photochemical isomerization of (*Z*)- to (*E*)-cycloalkenes with the continuous circulation of the reaction mixture pumped through a packed column of $AgNO_3/SiO_2$: (a) Royzen, M.; Yap, G. P. A.; Fox, J. M. *J. Am. Chem. Soc.* **2008**, *130*, 3760−3761. (b) Royzen, M.; Taylor, M. T.; DeAngelis, A.; Fox, J. M. *Chem. Sci.* **2011**, *2*, 2162−2165.

(12) Because of the low solubility of DMIP in pentane, DEIP was used for the photochemical isomerization in the presence of $AgNO_3/SiO_2$.

(13) To clarify the order of stereochemical stability between the (*E*)-cycloalkenes, we reanalyzed Cope's reported data to obtain the thermodynamic parameters of (*E*)-cyclononene (see the Supporting Information for the details).

(14) Deiters, A.; Mück-Lichtenfeld, C.; Fröhlich, R.; Hoppe, D. *Chem. - Eur. J.* **2002**, *8*, 1833−1842.

(15) Tomooka, K.; Shimada, M.; Uehara, K.; Ito, M. *Organometallics* **2010**, *29*, 6632−6635.

(16) Selected crystal data for (*S*)-**8**: monoclinic, $P2_1$ (No. 4), a = 12.359(2) Å, b = 9.5073(15) Å, c = 18.697(3) Å, β = 105.044(3)°, V = 2121.5(6) Å^3, Z = 4, R_1 = 0.0375, wR_2 = 0.0610, Flack parameter = −0.013(7), CCDC 1483485.

(17) The stereochemistry of **9** and **10** was suggested by the reaction pathway. Similar transformations of planar-chiral cyclic amides have been reported. See: Tomooka, K.; Suzuki, M.; Shimada, M.; Ni, R.; Uehara, K. *Org. Lett.* **2011**, *13*, 4926−4929 and ref 6.

(18) 1,1-Bis(phenylsulfonyl)-3-butene was prepared by a procedure modified from the one described by: Du Penhoat, C. H.; Julia, M. *Tetrahedron* **1986**, *42*, 4807−4816.

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