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Tetrahedron: *Asymmetry* 15 (2004) 1409–1417

Asymmetric *meta*-arene–alkene photocycloaddition controlled by a 2,4-pentanediol tether

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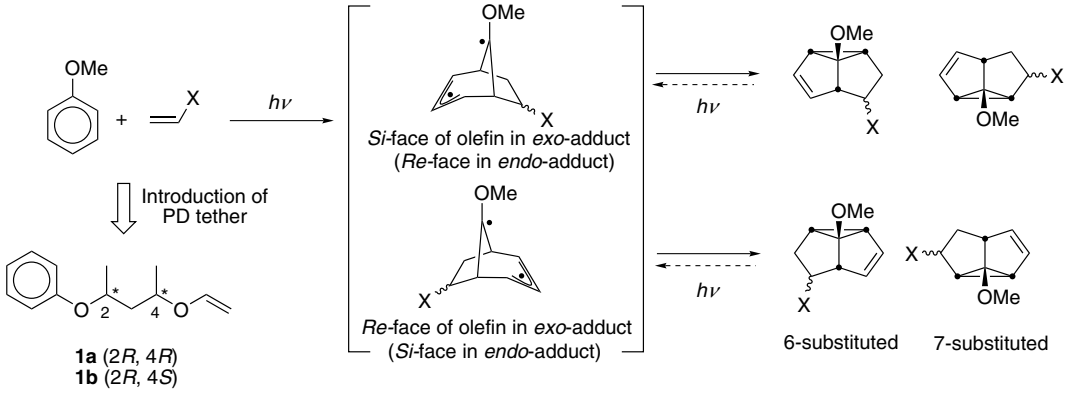
Received 13 January 2004; revised 2 March 2004; accepted 2 March 2004

Available online 9 April 2004

Abstract—Photo-irradiation of a substrate having phenyl and vinyl groups resulted in a stereocontrolled *meta*-arene–alkene cycloaddition when the two groups were connected by a chiral 2,4-pentanediol tether. The regioselectivity during the ring closing step after the initial addition was dependent on the stereochemistry of the tether and the photolysis conditions. The substrate bearing a *p*-tolyl or 3,5-xylyl group instead of the phenyl also underwent strict stereocontrolled addition. In the case of the *o*- and *m*-tolyl substrates, the regioselectivity due to the unsymmetric substitution of the arene moiety was also fully controlled.

1. Introduction

Photoreactions are useful for organic synthesis because of their characteristic products, which are unobtainable by ground-state reactions. Many of the photoreactions consist of cleavage of a photo-excited π-bond to produce a new σ-bond, and thus, convert a flat and achiral reaction site to a three-dimensional and chiral moiety. Accordingly, an optically active compound can be obtained by incorporation of an appropriate chiral source into a photoreaction, though induction of a sufficient differential activation energy to attain high stereoselectivity is expected to be difficult due to its highly energetic excited state process having a low energy barrier. Nevertheless, several photocycloadditions proceed under sufficient stereocontrol especially when the two reaction sites are connected by a chiral tether and the addition is intermolecular.[1] In 1994, we reported such an example using 2,4-pentanediol (PD) as a chiral tether for the *meta*-arene–alkene photocycloaddition, which produced synthetically useful tricyclic products having five new stereogenic centers (Scheme 1).[2,3] The



Scheme 1.

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doi:10.1016/j.tetasy.2004.03.017

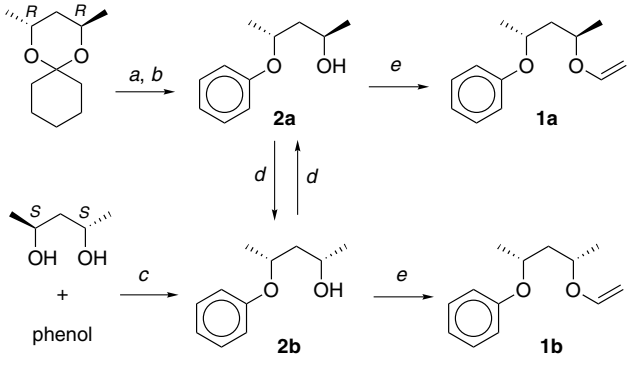
observed addition was strictly stereocontrolled, and when the arene moiety was unsymmetrical, the regioselectivity was also very high.

The photo-irradiation of benzene or benzenoid in the presence of an appropriate alkene results in *meta*-arene–alkene-cycloaddition, the effectiveness of which depends on the combination of aromatic and olefinic compounds. Anisole is a good aromatic substrate and can regioselectively react with various nonelectron deficient alkenes at the 2,6-positions.[3a–c] Reaction with a monosubstituted alkene proceeds through the formation of enantiomeric pairs of the initial adducts. Each of the adducts gives a pair of regioisomers, 6- and 7-substituted tricyclic products, which may interconvert under photochemical conditions, as shown in Scheme 1. Introduction of a PD tether to the reactants provides substrates **1a** and **1b**. The tether is sufficiently flexible and long enough to allow the addition without notable strain, but is not too long to give *endo*-stereochemistry at the X-substituent. The PD tether is a promising stereocontroller judging from other ground state reactions using it,[4] though it may be too long to perform the *meta*-arene–alkene-cycloaddition based on the known examples.[5]

2. Results and discussion

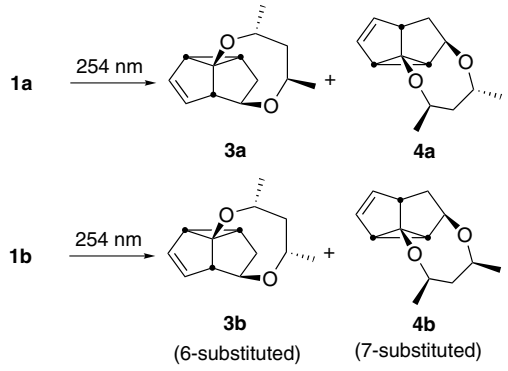
2.1. Stereochemical effect of the PD tether

Substrates **1a** and **1b** were synthesized from stereochemically pure PD as illustrated in Scheme 2. The cyclohexanone acetal prepared from (*R*,*R*)-PD (98% yield) was converted to the α,α′-dibromoacetal with excess pyridinium perbromide (79%) followed by treatment with excess sodium methoxide in DMSO to give **2a** in 93% yield. Its diastereomer **2b** was synthesized from **2a** by the Mitsunobu inversion at the hydroxy group (92%). Alternatively, **2b** was prepared in one step from (*S*,*S*)-PD by the addition of phenol under Mitsunobu conditions.[6] Formation of **2b** proceeded under complete inversion (99% yield), and was faster than the reaction of **2b** with a second phenol molecule. The conversion of **2b** to **2a** was also possible (94%). The vinyl ether exchange by the conventional method gave **1a** (79%) and **1b** (75%); the stereochemical purities of both **1a** and **1b** were confirmed to be over 99.6% by the GLC analysis.



Scheme 2. Reagents and conditions: (a) pyridinium perbromide (3 equiv)/CH_2Cl_2; (b) NaOMe/DMSO; (c) diethyl azodicarboxylate/PPh_3; (d) diethyl azodicarboxylate/PPh_3/PhCOOH, then aq NaOH; (e) ethyl vinyl ether/$Hg(OAc)_2$.

When a solution of **1a** in pentane (1 mmol dm^{-3}) was irradiated by a low pressure mercury lamp through a Vycor filter, two intramolecular adducts were produced with total consumption of **1a**. Column chromatography of the reaction mixture after the irradiation over 9 h gave **3a** and **4a** in 40% and 15% yield, respectively. The side reactions were those at the vinyl ether group to give **2a** and insoluble polymeric products as detected from the product analysis. Thus, the intramolecular photocycloaddition with **1a** was found to be highly stereocontrolled with the initial addition at the *Si*-face of the vinyl moiety (Scheme 3).



Scheme 3.

The reaction with **1b** was more effective with the substrate consumed within 4 h under similar conditions. In this case, the formation of **3b** was minimal (<2%) and **4b** was obtained in 70% yield after the column chromatography. The relative stereochemistry between **4a** and **4b** was determined to be the same based on the CD spectra (Fig. 1). Their stereochemistries as well as that of **3a** were determined by the chemical correlation as indicated in Section 2.3.

2.2. Analysis of factors controlling the reaction

From the photoreaction of **1a** and **1b**, the two diastereomeric PD tethers were found to have strict stereocontrollability, which is mainly due to the chirality at the 2-position of the tether, since the (2*R*)-configuration at the tether forces the reaction to occur at the *Si*-face of the vinyl group irrespective of the configuration at the 4-position. The lower total yield with **1a** than that with **1b** suggests that the (4*S*)-configuration cooperates to achieve the stereocontrol with the (2*R*)-configuration, while the (4*R*)-configuration does not. The difference in the efficiency of the photocycloaddition was confirmed by monitoring the reaction. A solution of the substrate was irradiated under controlled conditions in the presence of an internal standard (decane) for analysis and the reaction course was monitored by GLC. The conversion of **1b** (Fig. 2b) was confirmed to be faster than that of **1a** (Fig. 2a) while the reactivity ratio **1b**/**1a**

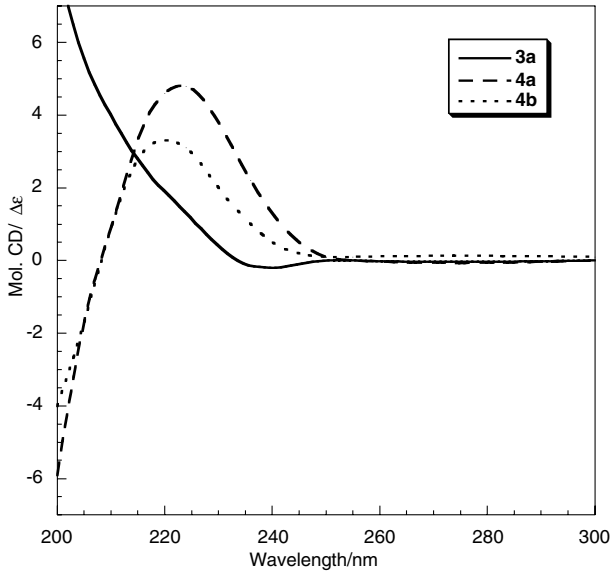


Figure 1. CD spectra of **3a**, **4a**, and **4b** in pentane.

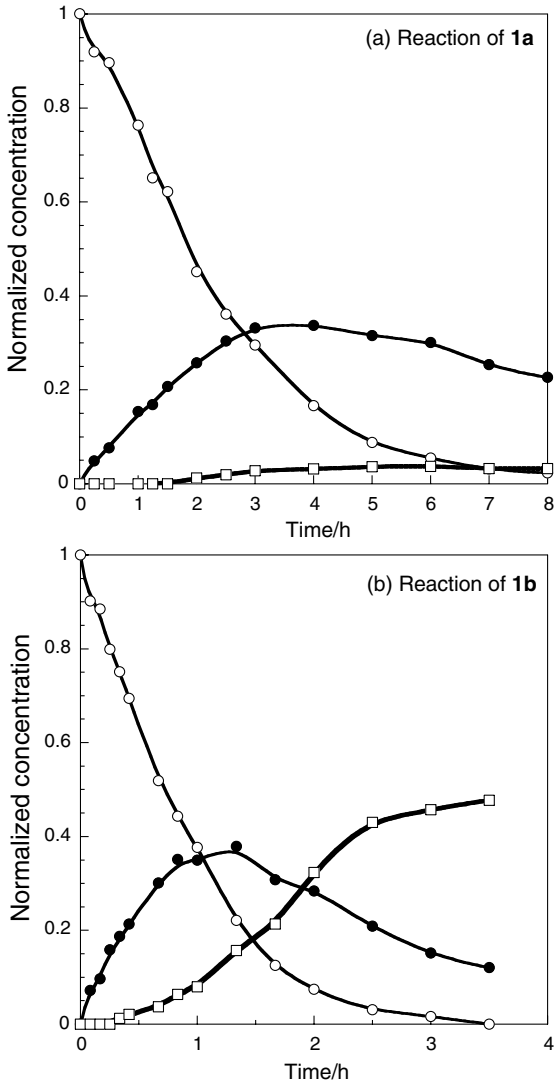


Figure 2. Normalized concentration of **1** (open circles), **3** (filled circles), and **4** (open squares) during the photoreactions.

was determined to be 2:6. Since the UV absorption of **1a** and **1b** at 254 nm are almost the same, the ratio can be attributed to the quantum yield of the photoreaction.

During this study, it was also found that **4** is not the initial product from **1**, but **3** is in the reactions of both **1a** and **1b**, while the isomerization rate of **3** to **4** is much different between the two substrates. Such an interconversion between the *meta*-adducts is attributable to the secondary photoreaction, and the ratio of the product governing the regioselectivity must be controlled by the absorption coefficient of the product. In fact, **3b** has a stronger absorption at 254 nm than **4b** as shown in Figure 3. Photochemical conversion of **3b** to **4b** as well as interconversion between **3a** and **4a** was confirmed independently.

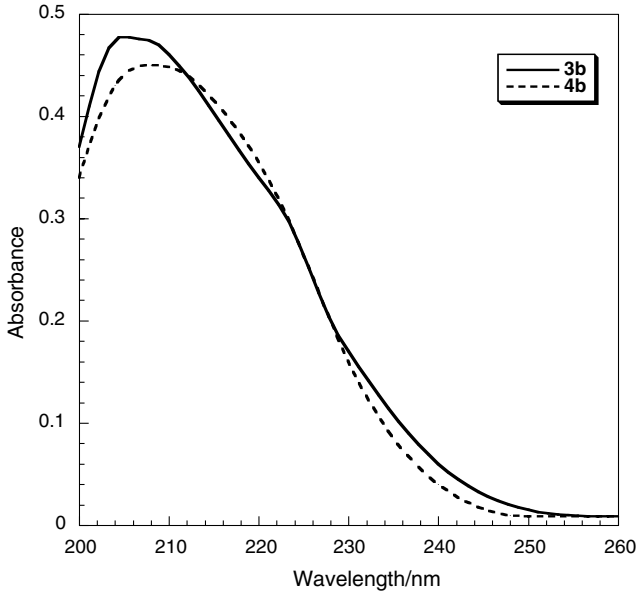
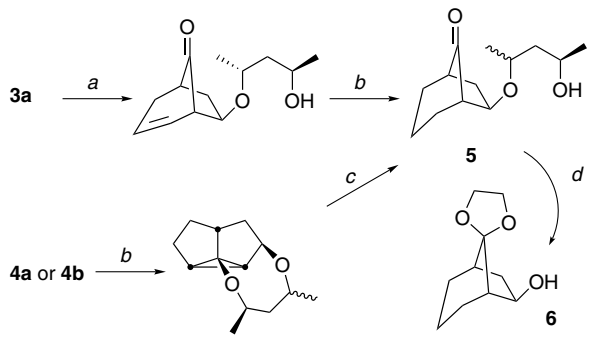


Figure 3. UV spectra of **3b** and **4b** in pentane.

2.3. Reaction of the photoproducts 3 and 4

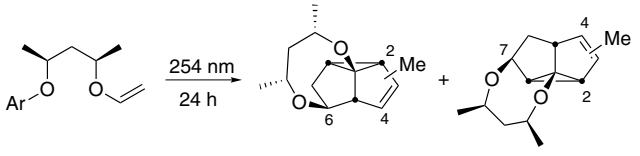
The cycloadducts **3** and **4** were converted into the bicyclic acetal **6**, of which the absolute stereochemistry has been established.[7] Acid treatment of **3a** and **3b** resulted in the cleavage at the cyclopropyl group, regioselectively,[8] with subsequent hydrogenation over a Pd–C catalyst giving **5** in 40% yield (Scheme 4). The structure of the intermediate was determined by the spin–decoupling experiments. Since the same acid treatment of **4a** and **4b** only resulted in complex mixtures, the olefinic function in **4** was first removed by hydrogenation over Pd–C, and then the cyclopropyl group was cleaved regioselectivity by the oxymercuration/reduction procedure to give **5** (50%).[9] Protection of the ketone in **5** followed by the conventional elimination of the PD moiety resulted in **6**, the specific rotation of which is negative and indicates its stereochemistry to be (1*R*,5*S*,6*R*).



Scheme 4. Reagents and conditions: (a) 4 M HCl/acetone; (b) H_2/Pd–C; (c) $Hg(OAc)_2$/THF–H_2O then $NaBH_4$; (d) i. ethylene glycol/H^+, ii. PCC/CH_2Cl_2, and iii. K_2CO_3/methanol/H_2O.

2.4. Application to substituted aromatic groups

The effectiveness and stereocontrollability in the *meta*-arene–alkene photocycloaddition of **1b** prompted us to study the generality of this reaction design. Substrates **7** and antipodes of **1b** in the tether moiety, were prepared from (*R*,*R*)-PD via a Mitsunobu reaction. The use of *o*-cresol, *m*-cresol, *p*-cresol, and 3,5-dimethylphenol gave **7a**, **7b**, **7c**, and **7d**, respectively, as stereochemically pure forms in 63–73% yield in two steps. Photo-irradiation of **7a** under the same conditions for the synthetic runs with **1** took 24 h to consume the substrate, with the two cycloadducts **8** and **9** isolated in 18% and 11% yield, respectively (Scheme 5). Products **8** and **9** are photo-convertible regioisomers corresponding to the antipodes of **3b** and **4b** confirmed by the comparison of their CD spectra and were determined to be the 8-methyl **8** and 5-methyl derivative **9** by ^1H NMR analysis. Neither the diastereomers nor other regioisomers were found in the reaction mixture. Thus, the PD tether controls the addition to both stereofaces of the alkene and the arene to produce only two products out of eight possible ones. It should be noted that many more isomers of intramolecular cycloadducts are possible if the reaction occurred at other positions than the 2,6-positions on the aromatic moiety.



7a. Ar = *o*-MePh
7b. Ar = *m*-MePh
7c. Ar = *p*-MePh
7d. Ar = 3,5-diMePh

8a. 8-Me (18%)
8b. 2-Me (16%)
8c. 3-Me (13%)
8d. 2,4-diMe (11%)

9a. 5-Me (11%)
9b. 4-Me (17%)
9c. 3-Me (16%)
9d. 2,4-diMe (8%)

Scheme 5.

The strict stereo- and regiocontrol during the initial addition step was extended to the *meta*-substituted substrate **7b** to give only a pair of regioisomers. Spectral analysis of isolated **8b** and **9b** showed the same stereochemistry as those of **8a** and **9a** except for the methyl-substituted positions, 2 and 4, respectively. The regioselectivity found with **7b** was not observed in the corresponding intermolecular reaction of *m*-methylanisole and ethyl vinyl ether.[10] Hence, the advantage of the intramolecular reaction in controlling the reaction selectivity was again disclosed. The regio- and stereo-controlled addition caused as a result of the stereoface differentiation both at the arene and alkene moieties is schematically expressed in Figure 4. The photo-irradiation of **7c** and **7d** gave similar results though these reactions did not require the stereoface-differentiation at the aromatic moiety. The low total yields with the methyl-substituted **7a**–**d** are attributable to the low quantum yield for the addition probably due to the faster internal conversion process of the excited aromatic rings having a substituent.

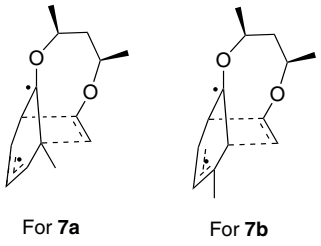


Figure 4. Schematic expression of the photo-addition of **7a** and **7b**.

3. Conclusion

Asymmetric *meta*-arene–alkene photocycloaddition has been found to be efficiently stereocontrolled by the PD tether. The PD-tethered reactions have been extensively developed after the first report for the *meta*-arene–alkene photocycloaddition with **1a** and **1b**,[2] and the reaction selectivity is now believed to be controlled by the differential activation entropy.[11] The two methyl groups in the PD tether cooperate or compete with each other for the stereocontrol of the reaction, and the cooperating case (**1b** in the present reaction) showed a higher acceleration of the intramolecular reaction to give a major stereoisomer mainly due to the entropy term. The acceleration by the methyl substitutions on the tether in **1b** (and even **7**) is obvious because general intramolecular *meta*-arene–alkene photocycloadditions are not effective when the arene and alkene moieties are separated by five or six bonds.[5] Entropy-control may be a reason why the PD tether sufficiently controls the highly exothermic and very fast photocycloaddition process. Although the substitution on the arene reduces the product yield from 70% with unsubstitued **1b** to 29–33% with the mono-substituted **7a**–**c** and to 19% with the bis-substituted **7d**, the present method is still useful because no other asymmetric synthesis is yet available for *meta*-arene–alkene additions to perform the short-step syntheses of polyquinane terpenoids.[12]

4. Experimental

4.1. General

All the products were characterized by NMR spectrometry using a JEOL EXcaliber-400 spectrometer at

400 MHz for the proton spectra and 100 MHz for the carbon spectra, and by IR with a JASCO IR-88 spectrophotometer. Optical rotations were measured with a Perkin–Elmer 243B polarimeter. CD spectra were obtained using a JASCO J-720. High resolution MS was obtained by a JEOL JMS-AX505HF or a JEOL JMS-T100LC. Analytical GLC was performed on a Shimadzu GC17A. MPLC was carried out using FMI pump (10 mL min^{-1}) and a Lover column (Merck Si-60, type B). All solvents were purified by distillation with proper drying agents.

4.2. Synthesis of 2a from (*R*,*R*)-PD

(*R*,*R*)-2,4-Pentanediol acetal of cyclohexanone (5.2 g) was dissolved in THF (200 mL), and cooled to −50 °C. To this solution was added pyridinium perbromide (32.0 g, 3 equiv). After the mixture was warmed up to rt over 1.5 h, at which point pyridine (5 mL), satd aqueous $NaHCO_3$ (125 mL) and Na_2SO_3 (2 g) were added in this order. The mixture was extracted with benzene (100 mL × 3), dried over $MgSO_4$, concentrated and purified by a column chromatography on silica gel (3% ethyl acetate in hexane) to afford 7.7 g of 2,6-dibromide as a diastereomeric mixture (79% yield). A part of this (2.5 g) was added to a mixture of NaOMe (4 equiv) and DMSO (35 mL) at rt, and allowed to stand overnight. Extraction and silica gel column chromatography (30% ethyl acetate in hexane) gave 1.1 g of **2a** (93% yield). Mp 39.0–39.8 °C; $[\alpha]_D^{20} = -79.2$ (*c* 1.1, methanol); IR(KBr) 3400, 2950, 2830, 1600, 1580, 1240, 1170, 1150, 1100, 1040 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.26 (m, 2H), 6.95–6.90 (m, 3H), 4.67 (m, 1H), 4.11 (m, 1H), 2.59 (br s, 1H), 1.86–1.68 (m, 2H), 1.31 (d, $J = 6.4$ Hz, 3H), 1.22 (d, $J = 6.4$ Hz, 3H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.87; H, 8.92.

4.3. Synthesis of 2b from 2a

Inversion of the hydroxy group in **2a** by the Mitsunobu reaction using benzoic acid/triphenylphosphine/diethyl azodicarboxylate followed by the hydrolysis was carried out by the reported method.[4] $[\alpha]_D^{20} = -15.3$ (*c* 1.1, methanol); IR (KCl, neat), 3370, 2950, 1600, 1490, 1240, 1110 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.30–7.25 (m, 2H), 6.98–6.91 (m, 3H), 4.60 (m, 1H), 4.05 (m, 1H), 2.19 (br s, 1H), 1.95 (m, 1H), 1.69 (ddd, $J = 6.4$, 4.6, 3.2 Hz, 1H), 1.31 (d, $J = 6.4$ Hz, 3H), 1.22 (d, $J = 6.4$ Hz, 3H). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72.93; H, 8.67.

4.4. Syntheses of 2b from (*S*,*S*)-PD

To a solution of (*S*,*S*)-2,4-pentanediol (2.77 g), phenol (2.12 g, 1.0 equiv), and triphenylphosphine (7.01 g, 1.2 equiv) in THF (100 mL) was added a solution of diisopropyl azodicarboxylate (5.02 mL, 1.2 equiv) in THF (50 mL) for 90 min at rt. After 24 h, the mixture was concentrated and purified by column chromatography on silica gel (30% ethyl acetate in hexane) to give 3.76 g of **2b** as a colorless oil (93.1% yield).

4.5. Synthesis of 1a and 1b

A solution of **2a** (10.27 g) in ethyl vinyl ether (300 mL) was heated with mercuric acetate (3.47 g, 0.2 equiv) to reflux for 23 h. Pentane (50 g) was added and a mixed solvent (ca. 50 mL) containing generated ethanol was distilled off. This co-distillation procedure was repeated two more times, and then all the solvent removed under vacuum. The residue was purified by column chromatography on alumina (activity 3, hexane) to give 9.29 g of **1a** (79% yield). $[\alpha]_D^{20} = -81.6$ (*c* 1.2, methanol); IR (KCl, neat) 2950, 1640, 1600, 1590, 1500, 1380, 1240, 1180, 1150, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 2H), 6.95–6.89 (m, 3H), 6.23 (dd, $J = 14.2$, 6.6 Hz, 1H), 4.58 (m, 1H), 4.26 (dd, $J = 14.2$, 4.5 Hz, 1H), 4.16 (m, 1H), 3.29 (dd, $J = 14.2$, 1.5 Hz, 1H), 4.16 (m, 1H), 3.92 (dd, $J = 6.6$, 1.5 Hz, 1H), 1.86–1.81 (m, 2H), 1.29–1.24 (m, 6H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 75.64; H, 8.77. The diastereomer **1b** was prepared by the same procedure (74.3% yield). $[\alpha]_D^{20} = -35.9$ (*c* 0.9, methanol); IR (KCl, neat) 2970, 1640, 1600, 1500, 1240, 1200, 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.25 (m, 2H), 6.93–6.88 (m, 3H), 6.32 (dd, $J = 14.4$, 6.6 Hz, 1H), 4.50 (m, 1H), 4.31 (dd, $J = 14.4$, 1.5 Hz, 1H), 4.11 (m, 1H), 4.01 (dd, $J = 6.6$, 1.5 Hz, 1H), 2.18 (m, 1H), 1.64 (m, 1H), 1.31 (d, $J = 6.1$ Hz, 3H), 1.23 (d, $J = 6.4$ Hz, 1H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found: C, 74.87; H, 8.62.

4.6. Photoreaction of 1 (synthetic runs)

A solution of **1** in pentane (ca. 1 mmol dm^{-3}) was placed in a quartz photoreactor and de-aerated by argon bubbling. This was irradiated by a low pressure mercury lamp (100 W, Eiko-sha, Japan) at room temperature. The reaction was continued until all the reactant was consumed as monitored by TLC analysis. The concentrate was purified by MPLC on silica gel (15% ethyl acetate in hexane). The primary adduct **3b** was obtained by the reaction interrupted before the consumption of **1b**. Compound **3a**: $[\alpha]_D^{25} = +120$ (*c* 1.0, methanol); IR (KCl, neat) 2950, 2925, 1400, 1380, 1240, 1190, 1140, 1080, 780 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.53 (dd, $J = 5.6$, 2.2 Hz, 1H), 5.49 (ddd, $J = 5.6$, 2.2, 1.5 Hz, 1H), 4.45 (m, 1H), 4.33 (m, 1H), 4.22 (dm, $J = 4.4$ Hz, 1H), 3.48 (m, 1H), 2.38 (dm, $J = 7.6$ Hz, 1H), 2.06–2.00 (m, 2H), 1.94 (ddd, $J = 15.4$, 6.6, 2.7 Hz, 1H), 1.74 (dm, $J = 13.7$ Hz, 1H), 1.67 (ddd, $J = 15.4$, 6.6, 3.5 Hz, 1H), 1.26 (d, $J = 6.6$ Hz, 3H), 1.17 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 129.6, 128.1, 88.0, 85.1, 70.4, 66.3, 58.2, 45.6, 39.5, 34.8, 27.8, 26.2, 21.8; HRMS ($M + Na^+$) *m*/*z* calcd for $C_{13}H_{18}O_2Na$ 229.1205, found 229.1179. Compound **4a**: $[\alpha]_D^{25} = +68.8$ (*c* 0.8, methanol); IR (KCl, neat) 2950, 1720, 1460, 1380, 1140, 1100, 1060, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.72 (ddm, $J = 5.5$, 2.9 Hz, 1H), 5.45 (dd, $J = 5.5$, 2.2 Hz, 1H), 4.63 (d, $J = 6.3$ Hz, 1H), 4.21 (m, 1H), 4.12 (m, 1H), 3.31 (dt, $J = 8.5$, 2.2 Hz, 1H), 2.45 (ddd, $J = 15.5$, 8.5, 0.9 Hz,

1H), 2.28–2.18 (m, 3H), 1.63 (m, 1H), 1.41 (d, $J = 14.7$ Hz, 1H), 1.35 (d, $J = 6.8$ Hz, 3H), 1.24 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 139.7, 123.4, 83.3 (2C), 74.0, 61.9, 53.5, 45.4, 44.3, 40.1, 39.5, 26.1, 21.9; HRMS ($M + Na^+$) m/z calcd for $C_{13}H_{18}O_2Na$ 229.1205, found 229.1205. Compound **3b**: (colorless oil) $[\alpha]_D^{20} = +70.7$ (c 0.9, methanol); IR (KCl, neat) 2970, 1380, 1200, 1140, 1100 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.57 (dd, $J = 5.4$, 2.0 Hz, 1H), 5.40 (ddd, $J = 5.4$, 2.4, 1.5 Hz, 1H), 4.22 (m, 1H), 4.09 (s like, 1H), 4.01 (m, 1H), 3.82 (s like, 1H), 2.31 (dm, $J = 8.3$ Hz, 1H), 2.07 (t like, $J = 7.3$ Hz, 1H), 1.91–1.83 (m, 2H), 1.57 (d, $J = 14.6$ Hz, 1H), 1.47 (dd, $J = 14.6$ Hz, 2.9 Hz, 1H), 1.20 (d, $J = 6.3$ Hz, 3H), 1.17 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 129.2, 127.9, 85.0, 85.6, 73.2, 70.7, 52.4, 47.1, 38.4, 33.4, 32.5, 24.9, 23.9; MS (M^+), m/z (%) 206 (13.8), 191 (61.5), 175 (61.5), 121 (77.7), 105 (96.2), 94 (76.9), 77 (52.4), 69 (100); HRMS, m/z (M^+) calcd for $C_{13}H_{18}O_2$ 206.1307, found 206.1334. Compound **4b**: mp 66.5–67.5 °C; $[\alpha]_D^{25} = +21.3$ (c 0.2, methanol); IR (KBr) 2950, 1420, 1380, 1220, 1160, 1100, 760 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.61 (dd, $J = 5.6$, 1.7 Hz, 1H), 5.43 (dd, $J = 5.6$, 1.7 Hz, 1H), 4.48 (dd, $J = 6.8$, 2.4 Hz, 1H), 4.30 (m, 1H), 4.05 (m, 1H), 3.25 (dd, $J = 8.3$, 2.7 Hz, 1H), 2.49–2.43 (m, 3H), 2.32 (m, 1H), 2.08 (ddd, $J = 14.1$, 6.8, 1.0 Hz, 1H), 1.58 (d, $J = 17.3$ Hz, 1H), 1.22 (d, $J = 6.3$ Hz, 6H). Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.69; H, 8.79. Found C, 75.24; H, 8.79.

4.7. Time course of the reaction of 1 to give 3 and 4

Solutions of **1a** and **1b** (1.58 mg) in pentane (2.50 mL) containing decane (0.46 mg) were placed in UV cells, de-aerated by argon bubbling and photo-irradiated by a low pressure mercury lamp under the same conditions. A part of the solution was taken out by a microsyringe every hour during the photo-irradiation and subjected to the GLC analysis. When a OV-1 column (i.d. 0.25 mm × 25 m, 120 °C, 30 cm s^{-1}) was employed, the retention times were as follows (min), decane: 5.14, **1a**: 10.7, **1b**: 12.9, **3a**: 21.7, **4a**: 18.3, **3b**: 20.1, **4b**: 16.3. Concentrations of **1**, **3**, and **4** were determined by the ratio of the peak integration using the decane peak as a standard. The sensitivities among **1**, **3**, and **4** were assumed to be the same. The results are shown in Figure 1. Conversion reactions of **3a** to **4a**, **4a** to **3a**, and **3b** to **4b** were also performed in pentane (0.5–0.9 mM) under photo-irradiation and products obtained analyzed by NMR.

4.8. Acid-catalyzed ring opening of 3a and 3b

A solution of **3a** (83 mg) in acetone (12 mL) and 4 M HCl (3 mL) was heated to 40 °C for 20 h. Extraction with dichloromethane and MPLC purification on silica gel (60% ethyl acetate in hexane) afforded a colorless oil (30 mg, 34%). $[\alpha]_D^{25} = -118$ (c 0.8, methanol); IR (KCl, neat) 3450, 2975, 2950, 1760, 1120, 1080 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.86 (m, 1H), 5.46 (td, $J = 6.3$, 3.2 Hz, 1H), 4.01–3.99 (m, 2H), 3.76 (m, 1H), 2.93 (m, 1H), 2.66–2.56 (m, 3H), 2.31 (m, 1H), 1.93 (m, 1H), 1.62–1.50 (m, 2H), 1.16 (d, $J = 6.2$ Hz, 3H), 1.15 (d, $J = 6.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 214.9, 133.8, 125.0, 78.8, 71.9, 64.6, 50.9, 45.5, 45.1, 41.3, 39.6, 24.0, 20.2. Hydrogenation of this in ethyl acetate (13 mL) over 5% Pd-on-carbon resulted in 31 mg of essentially pure **5a**. $[\alpha]_D^{25} = -73.5$ (c 0.8, methanol); IR (KCl, neat) 3430, 2955, 2930, 1745, 1160, 1120, 1080, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.08–4.02 (m, 2H), 3.79 (m, 1H), 2.42 (dq, $J = 9.4$, 2.4 Hz, 1H), 2.26–2.16 (m, 2H), 2.08–1.85 (m, 6H), 1.65–1.46 (m, 4H), 1.17 (d, $J = 6.4$ Hz, 3H), 1.16 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 221.2, 75.6, 71.3, 65.8, 52.8, 45.7, 36.5, 34.6, 33.9, 31.1, 24.4, 20.0, 18.2; HRMS ($M + Na^+$) m/z calcd for $C_{13}H_{20}O_3Na$ 247.1310, found 247.1300.

By the same acid-catalyzed procedure, **3b** was converted to the bicyclic compound. $[\alpha]_D^{25} = -3.4$ (c 1.6, methanol); IR (KCl, neat) 3450, 2980, 2950, 1760, 1380 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.87 (m, 1H), 5.47 (td, $J = 6.3$, 3.2 Hz, 1H), 4.09 (dd, $J = 8.5$, 4.4 Hz, 1H), 3.92 (m, 1H), 3.67 (m, 1H), 2.96 (m, 1H), 2.67 (dd, $J = 13.3$, 8.5 Hz, 1H), 2.62–2.57 (m, 2H), 2.37 (m, 1H), 1.90 (m, 1H), 1.66–1.46 (m, 3H), 1.16 (d, $J = 6.1$ Hz, 3H), 1.14 (d, $J = 6.3$ Hz, 3H); HRMS ($M + Na^+$) m/z calcd for $C_{13}H_{22}O_3Na$ 249.1467, found 249.1452. The hydrogenation of this gave **5b** identical with that obtained below.

4.9. Hydrogenation/oxymercuration procedure for ring opening of 4a and 4b

Hydrogenation of **4a** (50 mg) and **4b** (80 mg) in ethyl acetate over Pd-on-carbon proceeded smoothly to give the corresponding dihydro-derivatives without other side-reactions. This was treated with mercuric acetate (1.2 equiv) in THF/water (10 mL, ratio = 3:4) and stirred for 5 h at rt. The resulting mixture was treated with a saturated aqueous solution of sodium borohydride (ca. 200 μL). Extraction and purification by column chromatography on silica gel (20% ethyl acetate in hexane) afforded **5** (45–50% yield). The **5a** obtained was identical with that obtained from **3a** above. Compound **5b**: $[\alpha]_D^{25} = +21.9$ (c 0.8, methanol); IR (KCl, neat) 3450, 2950, 2850, 1760, 1380, 1120, 1080, 1060 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.04 (dd, $J = 8.3$, 2.5 Hz, 1H), 3.92 (m, 1H), 3.68 (m, 1H), 2.85 (m, 1H, OH), 2.43 (m, 1H), 2.34 (br s, 1H), 2.27 (dd, $J = 14.4$, 8.3 Hz, 1H), 2.04–1.90 (m, 5H), 1.66–1.55 (m, 5H), 1.49 (ddd, $J = 14.4$, 4.0, 2.8 Hz, 1H), 1.18 (d, $J = 5.9$ Hz, 3H), 1.14 (d, $J = 6.4$ Hz, 3H); HRMS (Na^+) m/z calcd for $C_{13}H_{22}O_3Na$ 249.1467, found 249.1447.

4.10. Elimination of the PD moiety in 5

A solution of **5a** (48 mg), ethylene glycol (1 mL) and catalytic amount of pyridinium p-toluenesulfonate in benzene (60 mL) was heated to reflux under removing water by a Dean–Stark apparatus. Extraction and purification by a silica gel column chromatography gave the acetal (58 mg, 84% yield). IR (KCl, neat) 3440, 2930, 2830, 1360, 1060, 1030 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.09 (m, 1H), 3.96–3.84 (m, 6H), 2.07 (m, 1H), 1.66 (m, 1H),

1.86–1.77 (m, 4H), 1.70–1.53 (m, 3H), 1.45–1.31 (m, 2H), 1.25–1.22 (m, 2H), 1.20 (d, $J = 6.4$ Hz, 3H), 1.16 (d, $J = 6.4$ Hz, 3H). Oxidation of this by PCC (70 mg) in dichloromethane (3 mL) at rt and a succeeding silica gel column chromatography (20% ethyl acetate in hexane) gave the precursor of **6** (45 mg, 81% yield). IR (KCl, neat) 2950, 2860, 1710, 1360, 1170, 1120, 1100, 1060 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.97–3.87 (m, 6H), 2.77 (dd, $J = 15.4$, 7.3 Hz, 1H), 2.40 (dd, $J = 15.4$, 5.4 Hz, 1H), 2.20 (s, 3H), 2.03 (s, 1H), 1.92–1.85 (m, 5H), 1.41–1.34 (m, 2H), 1.25–1.20 (m 2H), 1.17 (d, $J = 6.4$ Hz, 3H). This was dissolved in methanol (3 mL) with K_2CO_3 (ca. 50 mg) and stirred overnight. Extraction and purification by passing a short silica gel column (30% ethyl acetate in hexane) gave 28.6 mg of **6** (99% yield). $[\alpha]_D^{24} = -13.0$ (c 0.3, methanol, lit.[7]$= -16.0$); IR (KCl, neat) 2940, 2850, 1140, 1120, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.98–3.92 (m, 5H), 2.43 (br s, 1H), 2.10–2.03 (m, 2H), 1.83–1.77 (m, 2H), 1.75–1.70 (ddd, $J = 13.4$, 5.9, 2.7 Hz, 1H), 1.58 (m, 1H), 1.42–1.35 (m, 2H), 1.19 (m, 1H). By the same procedure with a smaller scale (24 mg) and without purification of the intermediate, **6** was obtained from **5b**. $[\alpha]_D^{24} = -14$ (c 0.1, methanol).

4.11. Preparation of 7a–d

By the procedure shown in Section 4.4, (*R*,*R*)-2,4-pentanediol was converted to the mono-ether under complete stereo-inversion. The reaction with *o*-cresol gave the mono-ether as a colorless oil in 79.1% yield. $[\alpha]_D^{20} = +25.1$ (c 1.0, methanol); IR (KCl, neat) 3400, 1500, 1460, 1380, 1290, 1240, 1120, 1050, 960, 750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16–7.13 (m, 2H), 6.90–6.85 (m, 2H), 4.62 (m, 1H), 4.07 (m, 1H), 2.74 (br s, 1H), 2.25 (s, 3H), 1.98 (ddd, $J = 14.4$, 9.0, 8.8 Hz, 1H), 1.73 (ddd, $J = 14.4$, 4.2, 2.9 Hz, 1H), 1.29 (d, $J = 6.1$ Hz, 3H), 1.23 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 155.1, 130.9, 127.8, 126.6, 120.8, 113.4, 73.8, 67.0, 45.7, 23.7, 20.1, 16.5; HRMS, m/z (M^+) calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1275. The reaction with *m*-cresol gave the mono-ether as a colorless oil in 90.2% yield. $[\alpha]_D^{20} = +13.5$ (c 1.0, methanol); IR (KCl, neat) 3430, 2940, 1590, 1460, 1260, 1120, 1050, 950, 880, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.12 (m, 1H), 6.77–6.63 (m, 3H), 4.57 (m, 1H), 4.06 (m, 1H), 2.32 (s, 3H), 1.93 (ddd, $J = 14.4$, 8.8, 8.8 Hz, 1H), 1.69 (ddd, $J = 14.4$, 4.4, 3.2 Hz, 1H), 1.30 (d, $J = 6.1$ Hz, 3H), 1.22 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 139.5, 129.2, 122.0, 117.2, 113.1, 100.5, 73.8, 67.0, 45.6, 23.8, 20.6, 20.1; HRMS, m/z (M^+) calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1309. The reaction with *p*-cresol gave the mono-ether as a colorless oil in 92.2% yield. $[\alpha]_D^{20} = +10.3$ (c 1.0, methanol); IR (KCl, neat) 3400, 2970, 1520, 1390, 1290, 1240, 1120, 1040, 820 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.08 (d, $J = 8.3$ Hz, 2H), 6.86–6.80 (m, 2H), 4.52 (m, 1H), 4.05 (m, 1H), 2.68 (br s, 1H), 2.32 (s, 3H), 1.92 (ddd, $J = 14.4$, 8.8, 8.8 Hz, 1H), 1.68 (ddd, $J = 14.4$, 4.4, 2.9 Hz, 1H), 1.28 (d, $J = 5.9$ Hz, 3H), 1.22 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 154.9, 130.5, 129.9, 116.3, 74.1, 66.9, 45.6, 23.7, 20.5, 20.0; MS m/z (%) 194 (15.3, M^+), 186 (16.6), 162 (43.7), 149 (23.2), 121 (26.8), 108 (100), 107 (22.0); HRMS, m/z (M^+) calcd for $C_{12}H_{18}O_2$ 194.1307, found 194.1286. The reaction with 3,5-dimethylphenol gave the mono-ether as a colorless oil in 81.5% yield. $[\alpha]_D^{20} = +14.6$ (c 1.2, methanol); IR (KCl, neat) 3400, 2980, 1620, 1480, 1380, 1320, 1160, 1060, 840 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.60 (s, 1H), 6.52 (s, 2H), 4.59 (m, 1H), 4.06 (m, 1H), 3.24 (br s, 1H), 2.31 (s, 6H), 2.02 (ddd, $J = 14.2$, 8.3, 5.9 Hz, 1H), 1.66 (ddd, $J = 14.2$, 8.3, 4.9 Hz, 1H), 1.32 (d, $J = 5.9$ Hz, 3H), 1.26 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 157.00, 138.78, 122.55, 113.69, 72.85, 66.14, 45.37, 23.46, 21.17, 17.84; HRMS, m/z (M^+) calcd for $C_{13}H_{20}O_2$ 208.1463, found 208.1502.

Preparation of the vinyl ether **7** from the mono-ether was achieved by the same method shown in Section 4.5. Compound **7a**: (colorless oil, 82.7%) $[\alpha]_D^{20} = +28.9$ (c 2.0, methanol); IR (KCl, neat) 2970, 1635, 1600, 1490, 1240, 1190, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.15–7.11 (m, 2H), 6.86–6.82 (m, 2H), 6.34 (dd, $J = 14.2$, 6.6 Hz, 1H), 4.53 (m, 1H), 4.32 (dd, $J = 14.2$, 1.7 Hz, 1H), 4.15 (m, 1H), 4.02 (dd, $J = 6.6$, 1.7 Hz, 1H), 2.23 (ddd, $J = 13.9$, 7.1, 6.8 Hz, 1H), 2.20 (s, 3H), 1.68 (ddd, $J = 13.9$, 6.4, 6.1 Hz, 1H), 1.33 (d, $J = 6.1$ Hz, 3H), 1.25 (d, $J = 6.1$ Hz, 3H); HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1470. Compound **7b**: (colorless oil, 69.1%) $[\alpha]_D^{20} = +35.2$ (c 1.0, methanol); IR (KCl, neat) 2970, 1635, 1600, 1490, 1240, 1190, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19–7.12 (m, 2H), 6.76–6.69 (m, 2H), 6.33 (dd, $J = 14.2$, 6.6 Hz, 1H), 4.48 (m, 1H), 4.33 (dd, $J = 14.2$, 1.5 Hz, 1H), 4.10 (m, 1H), 4.03 (dd, $J = 6.6$, 1.5 Hz, 1H), 2.32 (s, 3H), 2.19 (ddd, $J = 13.9$, 7.1, 6.8 Hz, 1H), 1.64 (ddd, $J = 13.9$, 6.1, 5.9 Hz, 1H), 1.32 (d, $J = 5.9$ Hz, 3H), 1.25 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 157.6, 150.5, 139.4, 129.1, 121.4, 116.6, 112.5, 111.89, 88.3, 72.7, 70.3, 43.0, 20.0, 20.0; HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1460. Compound **7c**: (colorless oil, 79.8%) $[\alpha]_D^{20} = +20.2$ (c 1.4, methanol); IR (KCl, neat) 2980, 1640, 1620, 1515, 1385, 1330, 1300, 1240, 1200, 1110, 1050, 980, 955, 830 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05 (d, $J = 8.3$ Hz, 2H), 6.78 (d, $J = 8.3$ Hz, 2H), 6.31 (dd, $J = 14.2$, 6.6 Hz, 1H), 4.44 (m, 1H), 4.30 (dd, $J = 14.2$, 1.5 Hz, 1H), 4.09 (m, 1H), 4.00 (dd, $J = 6.6$, 1.5 Hz, 1H), 2.26 (s, 3H), 2.16 (ddd, $J = 13.9$, 7.1, 6.8 Hz, 1H), 1.64 (ddd, $J = 13.9$, 6.1, 5.8 Hz, 1H), 1.29 (d, $J = 6.1$ Hz, 3H), 1.23 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 155.5, 150.5, 129.9, 129.9, 115.8, 88.3, 72.7, 70.7, 43.0, 20.5, 20.0, 19.9; HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1459. Compound **7d**: (colorless oil, 83.9%) IR (KCl, neat) 2974, 1594, 1460, 1378, 1320, 1295, 1155, 1055, 830, 690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.56 (s, 1H), 6.52 (s, 2H), 6.32 (dd, $J = 14.2$, 6.8 Hz, 1H), 4.46 (m, 1H), 4.31 (dd, $J = 14.2$, 1.5 Hz, 1H), 4.09 (m, 1H), 4.01 (dd, $J = 6.8$, 1.5 Hz, 1H), 2.26 (s, 6H), 2.17 (m, 1H), 1.62 (dt like, $J = 14.2$, 5.9 Hz, 1H), 1.29 (d, $J = 6.0$ Hz, 3H), 1.23 (d, $J = 5.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 157.7, 150.5, 139.1, 122.4, 113.5, 88.3, 72.7, 70.2, 43.0, 21.5, 20.0, 20.0; HRMS, m/z (M^+) calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1622.

4.12. Photoreaction of 7a–d

A pentane solution of **7** (30–40 mg, ca. 1 mmol dm^{-3}) was de-aerated by argon bubbling and then irradiated

by a low pressure mercury lamp for 24 h at rt. The concentrate was purified by silica gel column chromatography to give **8** and **9**, the yields of which are shown in Scheme 5. Compound **8a**: (colorless oil) $[\alpha]_D^{20} = -61.5$ (c 0.4, methanol); CD (methanol) λ_{ext} 220 nm ($\Delta\varepsilon + 6.3$); IR (KCl, neat) 2930, 1455, 1375, 1172, 1091, 738 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.62 (dd, $J = 5.4$, 2.4 Hz, 1H), 5.38 (dd, $J = 5.4$, 2.4 Hz, 1H), 4.17 (m, 1H), 4.05 (br s, 1H), 3.97 (m, 1H), 3.90 (br s, 1H), 1.87 (br s, 1H), 1.68 (dd, $J = 13.7$, 2.9 Hz, 1H), 1.59 (m, 1H), 1.65–1.51 (m, 2H), 1.58 (d, $J = 16.1$ Hz, 1H), 1.31 (s, 3H), 1.19 (d, $J = 6.4$ Hz, 3H), 1.15 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 130.8, 127.5, 87.9, 84.5, 72.9, 71.1, 52.4, 48.0, 44.1, 39.9, 38.4, 25.0, 24.3, 17.6; HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1466. Compound **9a**: (white solid) $[\alpha]_D^{20} = +20.2$ (c 0.4, methanol); CD (methanol) λ_{ext} 220 nm ($\Delta\varepsilon$ −17.2); IR (KBr) 2961, 1455, 1375, 1205, 1089, 753 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.45 (d, $J = 2.0$ Hz, 2H), 4.34 (dd, $J = 6.9$, 3.0 Hz, 1H), 4.28 (m, 1H), 4.04 (m, 1H), 2.50 (d, $J = 9.2$ Hz, 1H), 2.43 (dd, $J = 9.2$, 2.0 Hz, 1H), 2.21 (m, 1H), 2.09 (dd, $J = 14.2$, 3.0 Hz, 1H), 1.56 (d, $J = 17.6$ Hz, 1H), 1.29 (s, 3H), 1.21 (d, $J = 5.9$ Hz, 3H), 1.19 (t like, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 142.8, 121.9, 86.6, 78.4, 77.9, 72.7, 56.9, 56.4, 44.4, 41.1, 40.1, 26.8, 24.1, 19.0; HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1432. Compound **8b**: (colorless oil) $[\alpha]_D^{20} = -258.2$ (c 0.5, methanol); IR (KCl, neat) 2970, 2929, 1600, 1457, 1376, 1193, 1123, 763 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.44 (d, $J = 5.6$ Hz, 1H), 5.35 (dd, $J = 5.6$, 2.9 Hz, 1H), 4.14 (m, 1H), 4.07 (br d, $J = 3.0$ Hz, 1H), 4.02 (m, 1H), 3.76 (br s, 1H), 1.91 (m, 1H), 1.85 (ddd, $J = 14.2$, 6.5, 2.5 Hz, 1H), 1.60 (d, $J = 6.5$ Hz, 1H), 1.57 (d, $J = 15.6$ Hz, 1H), 1.50 (dd, $J = 14.2$, 3.0 Hz, 1H), 1.32 (s, 3H), 1.20 (d, $J = 6.4$ Hz, 3H), 1.18 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 134.0, 126.4, 86.8, 85.7, 73.5, 70.4, 54.1, 46.4, 43.0, 33.5, 31.0, 25.1, 23.8, 14.4; HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1461. Compound **9b**: (colorless oil) $[\alpha]_D^{20} = -32.9$ (c 0.5, methanol); IR (KCl, neat) 2968, 1716, 1419, 1376, 1140, 816, 692, 654, 592 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.99 (s, 3H), 4.47 (dd, $J = 6.9$, 2.1 Hz, 1H), 4.32–4.25 (m, 1H), 4.04 (m, 1H), 2.96 (d, $J = 8.4$ Hz, 1H), 2.46 (ddd, $J = 14.6$, 8.4, 2.1 Hz, 1H), 2.39–2.25 (m, 2H), 2.30 (d, $J = 7.9$ Hz, 1H), 2.06 (dd, $J = 14.6$, 6.9 Hz, 1H), 1.60 (s, 3H), 1.56 (d, $J = 16.6$ Hz, 1H), 1.21 (d, $J = 6.4$ Hz, 3H), 1.20 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 147.9, 117.3, 88.4, 79.8, 78.4, 72.7, 58.0, 48.4, 44.5, 40.2, 38.8, 26.8, 24.3, 15.1; HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1468. Compound **8c**: (colorless oil) $[\alpha]_D^{20} = -46.9$ (c 0.9, CH_2Cl_2); CD (methanol) λ_{ext} 250 nm ($\Delta\varepsilon + 0.9$), 210 nm ($\Delta\varepsilon$ −2.7); IR (KCl, neat) 2928, 1638, 1446, 1376, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.96 (d, $J = 1.0$ Hz, 1H), 4.241 (m, 1H), 4.07 (br s, 1H), 3.98 (m, 1H), 3.75 (br s, 1H), 2.14 (d, $J = 8.4$ Hz, 1H), 2.04 (dd, $J = 14.2$, 6.5 Hz, 1H), 1.88–1.82 (m, 2H), 1.69 (s, 3H), 1.55 (d, $J = 15.6$ Hz, 1H), 1.42 (dd, $J = 14.2$, 1.6 Hz, 1H), 1.20 (d, $J = 6.4$ Hz, 3H), 1.16 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 139.3, 130.0, 86.4, 86.0, 73.2, 70.8, 51.7, 47.3, 41.5, 41.5, 33.1, 25.0, 24.1, 16.8; HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1493. Compound **9c**: (colorless oil) $[\alpha]_D^{20} = -13.1$ (c 0.4, methanol); CD (methanol) λ_{ext} 250 nm ($\Delta\varepsilon + 0.9$), 210 nm ($\Delta\varepsilon$ −2.9); IR (KCl, neat) 2929, 1723, 1448, 1377, 1103 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.14 (s, 1H), 4.47 (dd, $J = 6.8$, 2.4 Hz, 1H), 4.28 (m, 1H), 4.01 (m, 1H), 3.15 (d, $J = 8.4$ Hz, 1H), 2.41 (ddd, $J = 14.7$, 8.4, 2.5 Hz, 1H), 2.39 (d, $J = 8.8$ Hz, 1H), 2.30 (m, 1H), 2.34 (d, $J = 8.8$ Hz, 1H), 2.07 (dd, $J = 14.7$, 6.9 Hz, 1H), 1.69 (s, 3H), 1.55 (d, $J = 16.1$ Hz, 1H), 1.21 (d, $J = 6.4$ Hz, 3H), 1.20 (d, $J = 6.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 133.6, 131.3, 88.0, 80.0, 78.4, 72.8, 54.6, 49.3, 44.6, 44.1, 39.9, 26.9, 24.3, 16.4; HRMS, m/z (M^+) calcd for $C_{14}H_{20}O_2$ 220.1463, found 220.1415. Compound **8d**: (colorless oil) $[\alpha]_D^{20} = -18.9$ (c 0.2, methanol); CD (methanol) λ_{ext} 230 nm ($\Delta\varepsilon + 4.8$), 205 nm ($\Delta\varepsilon + 4.5$); IR (KCl, neat) 2928, 1638, 1446, 1376, 1095 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.06 (d, $J = 1.6$ Hz, 1H), 4.18 (m, 1H), 4.13 (d, $J = 6.9$ Hz, 1H), 4.04 (m, 1H), 3.51 (s, 1H), 2.26 (br s, 1H), 1.93 (ddd, $J = 17.6$, 10.3, 7.3 Hz, 1H), 1.84 (ddd, $J = 14.2$, 6.9, 3.0 Hz, 1H), 1.66 (d, $J = 1.6$ Hz, 3H), 1.55 (d, $J = 17.6$ Hz, 1H), 1.54 (s, 3H), 1.50 (dm, $J = 14.2$ Hz, 1H), 1.20 (d, $J = 6.3$ Hz, 3H), 1.18 (d, $J = 6.3$ Hz, 3H); HRMS, m/z (M^+) calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1613. Compound **9d**: (colorless oil) $[\alpha]_D^{20} = -10.0$ (c 0.2, methanol); CD (methanol) λ_{ext} 215 nm ($\Delta\varepsilon$ −10.0); IR (KCl, neat) 2928, 1594, 1456, 1376, 1208, 1101, 817 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.87 (d, $J = 1.6$ Hz, 1H), 4.23 (dd, $J = 6.9$, 2.5 Hz, 1H), 4.26 (m, 1H), 3.95 (m, 1H), 2.94 (d, $J = 8.4$ Hz, 1H), 2.39 (ddd, $J = 14.6$, 8.4, 2.5 Hz, 1H), 2.26 (br s, 1H), 2.24 (m, 1H), 2.05 (dd, $J = 14.6$, 6.9 Hz, 1H), 1.57 (d, $J = 1.6$ Hz, 3H), 1.31 (s, 3H), 1.29 (d, $J = 16.8$ Hz, 1H), 1.22 (d, $J = 6.8$ Hz, 3H), 1.21 (d, $J = 5.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 145.9, 122.7, 90.6, 79.8, 79.4, 72.7, 58.9, 47.7, 44.9, 44.2, 30.9, 26.9, 24.3, 16.7, 14.8; HRMS, m/z (M^+) calcd for $C_{15}H_{22}O_2$ 234.1620, found 234.1644.

Acknowledgements

The authors would like to thank Professor G. Lodder of Leiden University for his helpful suggestions. A part of this study was supported by KAKENHI from JSPS (No 13440192).

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