Pergamon

Tetrahedron, Vol. 53, No. 15, pp. 5433-5454, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00238-X

Palladium-Mediated Asymmetric Synthesis of 3β,5β,7β-Trihydroxycycloheptene Derivatives

Hiroki Yoshizaki, Kumiko Yoshioka, Yoshihiro Sato, and Miwako Mori*

Faculty of Pharmaceutical Sciences, Hokkaido University, Sapporo 060, Japan

Abstract: Asymmetric alkylation of 3,5,7-trihydroxycycloheptene derivative **15** was developed using a palladium catalyst with a chiral ligand. The reaction site of π-allylpalladium complex **18** is controlled by steric repulsion between the nucleophile and the substituents on the cycloheptene ring. When **15b** was reacted with lithium dimethyl malonate using a catalytic amount of $[Pd(C_3H_5)Cl]_2$ in the presence of (*S*)-BINAPO in THF, alkylated product **17** was obtained in 71% yield with 42% ee. However, the reaction of **15b** with a large nucleophile, diethyl 2-lithio-2-(2-propenyl)malonate, in the presence of $[Pd(C_3H_5)Cl]_2$ and (*S*)-BINAP in THF gave alkylated product **21d** in 41% yield with 94% ee. In a similar manner, the reaction of **15b** with dimethyl 2-(3-butenyl)-2-lithiomalonate **5e** gave **21e** in 64% yield with 82% ee.
© 1997 Elsevier Science Ltd.

Palladium-catalyzed alkylation is a useful method for forming carbon-carbon bonds, and many asymmetric alkylations that employ the π-allylpalladium complex in the presence of a chiral ligand have been reported.[1] We previously described catalytic asymmetric syntheses of cyclopentanoids from a cyclopentenediol derivative[2a] and of cyclohexene derivatives from a cyclohexenediol derivative[2b]. Using this procedure, (+)-γ-lycorane was synthesized from a 3,6-dibenzoyloxycyclohexene derivative in a short series of steps. We report here the palladium-catalyzed asymmetric alkylation of cycloheptene derivatives **1** and **15** in the presence of a chiral ligand. In the formation of a π-allylpalladium complex, a C-O bond of the leaving group is approximately parallel to the p atom orbitals of the C=C bond.[3] This means that the leaving group must occupy the axial position of the cycloheptene ring for the formation of the π-allylpalladium complex. Based on caluculations of the molecular mechanics of cycloheptenediol derivative **1a**, it was clear that the lower energy form **1a-I** is in a state of equilibrium with the higher energy form **1a-II**, which has two axial substituents, at room temperature (Fig. 1).[4] This means that a π-allylpalladium complex would be formed from **1** and palladium catalyst. Furthermore, in cycloheptene diol derivatives **1**, the 1-position and/or the 3-position, on the π-allylpalladium complex **I** is attacked by the nucleophile, while in the case of a cyclopentenediol derivative and a cyclohexenediol derivative, the nucleophile attacks at the 1-position of the π-allylpalladium complex because of steric repulsion.

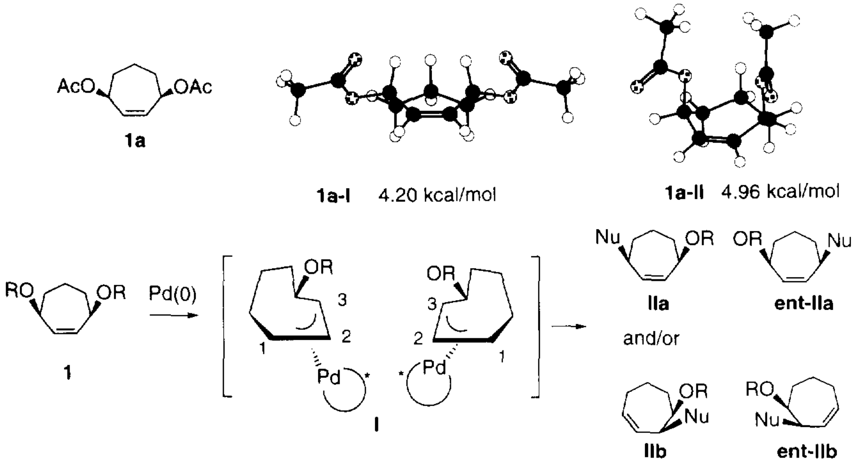
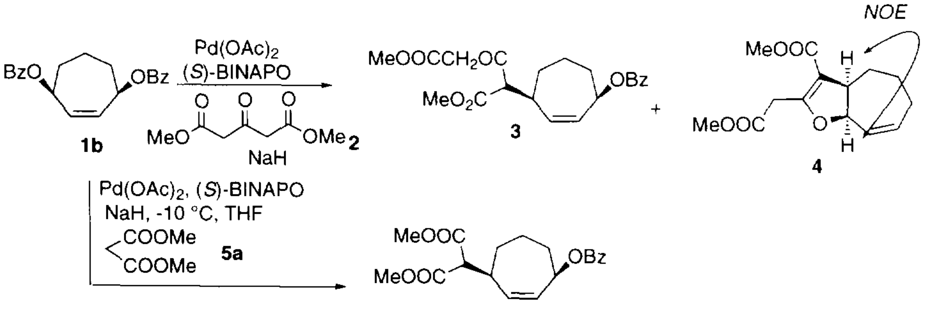


Figure 1 Conformational analysis of cycloheptenediol derivative **1a**

Palladium-Catalyzed Asymmetric Synthesis of 3β, 7β-DihydroxyCycloheptenes

First, we examined the palladium-catalyzed asymmetric alkylation of cycloheptenediol derivatives **1b**. When an CH_3CN solution of **1b** (1 equiv.) and dimethylketoglutarate **2** (2.5 equiv.) was stirred in the presence of NaH (2.5 equiv.), $Pd(OAc)_2$ (6 mol %) and (*S*)-BINAPO[5] (12 mol %) at 40 °C for 14 h, furan derivative **4** was obtained in 79% yield with 18% ee.[6] An NOE experiment indicated that the ring junction of **4** is *cis*. The same reaction was carried out in THF to give alkylated product **3** in 40% yield with 41% ee after 4 h along with **4** in 18% yield with 1% ee. The low ee of **4** suggests that kinetic resolution would occur in this reaction.[2a] A longer reaction time gave **4** with 68% yield with 31 % ee (Table 1).



Scheme 1

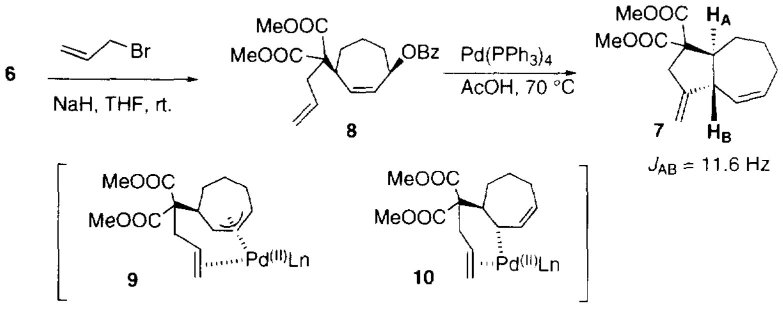
Table 1 Reaction of **1b** with **2** under various conditions[a)]

Run	Solvent	Time (h)	Yield (%) 3	Yield (%) 4	ee (%) 3	ee (%) 4
1	CH_3CN	20	-	79	-	18
2	THF	4	40	18	41	1
3	THF	93	5	68	-	31

a) All reactions were carried out in the presence of NaH (2.5 equiv.), $Pd(OAc)_2$ (6 mol %), and (*S*)-BINAPO (12 mol %) at 40 °C.

Dimethyl malonate **5a** was used as the nucleophile and the desired alkylated product **6** was obtained in 40% yield with 24% ee when the reaction was carried out at -10 ℃.[6] The regio- and stereochemistries of **6** were determined by ^{1}H-NMR and ^{13}C-NMR spectra. These results indicate that alkylation took place at the C-1 position on π-allylpalladium complex **I** to produce **IIa**.

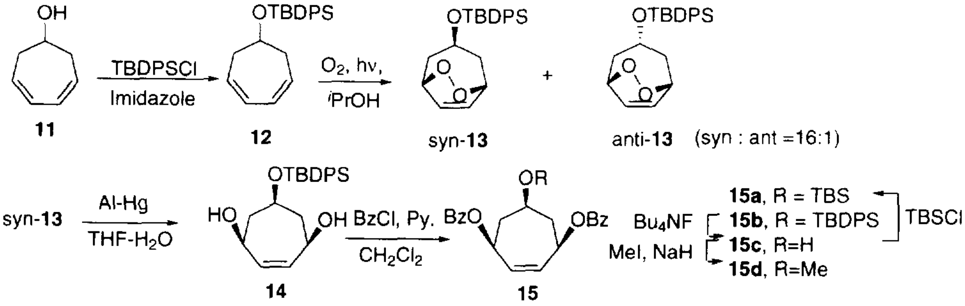
Oppolzer previouly reported that when compound **8** was treated with $Pd(PPh_3)_4$ in AcOH, *trans*-hydroazulene **7** was obtained *via* π-allylpalladium complex **9** and σ-allylpalladium complex **10**.[7] Thus, the stereochemistry of **6** was further confirmed by conversion of **6** into **7**; i.e., compound **6** was treated with allyl bromide in the presence of NaH to give allylated product **8**, which was treated with $Pd(PPh_3)_4$ in AcOH according to the Oppolzer's procedure[7] to give the cyclized product **7** in 51% yield. The spectral data of **7**, particularly the *J* value of the ring junction protons in the ^{1}H-NMR spectrum, agreed with those of the compound obtained by Oppolzer.[7] This means that the palladium-catalyzed alkylation of **1b** proceeds stereoselectively with the retention of configuration. Although the ee was modest, asymmetric alkylation was realized in cycloheptenediol derivative **1b**.



Scheme 2

Palladium-Mediated Asymmetric Synthesis of 3β, 5β, 7β-Trihydroxycycloheptene Derivatives

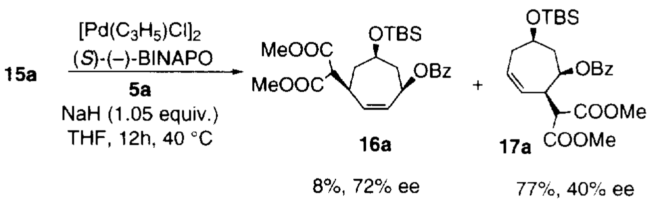
Next, we investigated the asymmetric alkylation of cycloheptenetriol derivative **15**, which has an alkoxy group at the C-5 position. For synthesis of the substrate, protection of 6-hydroxy-1,3-cycloheptadiene **11**[8] with TBDPSCl (^{t}butyldiphenylchlorosilane) was followed by photo-oxidation to give endo-peroxide **13** in 50% yield (syn:anti=16:1).



Scheme 3 Synthesis of the Substrates

Reduction of syn-**13** with Al-Hg gave diol **14**, which was treated with benzoyl chloride in pyridine to give

15b in 70% yield. Deprotection of the silyl group of **15b** gave alcohol **15c**, which was treated with TBSCl (^{t}Butyldimethylchlorosilane) to give **15a**, and with MeI and NaH to give **15d**. When a THF solution of **15a** and dimethyl malonate (1.05 equiv.) was stirred in the presence of NaH (1.05 equiv.), [(Pd(C$_3$H$_5$)Cl]$_2$ (2.5 mol %), and (*S*)-BINAPO (10 mol %) as a chiral ligand at 40 ℃ for 11.5 h, the two alkylated products **16a** and **17a** were obtained in the yields of 8% and 77%, respectively (ratio of **16a** to **17a**, 9 to 91). The structures of these compounds were determined by ^{1}H-NMR, NOESY, HMBC, HSQC, H-H COSY, and ^{13}C-NMR spectra. The ees were determined to be 72% for the minor product **16a** and to be 40% for the major product **17a** by HPLC.[6] They were produced from π-allylpalladium complex **18** derived from **15a** and palladium catalyst. The major product **17a** was obtained by an attack of the nucleophile at the C-iii position of π-allylpalladium complex **18**, and the minor product **16a** was the C-i alkylation product of π-allylpalladium complex **18** (Fig. 2). It is believed that the nucleophile attacks at the C-iii position of π-allylpalladium complex **18** in the formation of the major product **17** due to steric repulsion between the nucleophile and the protected hydroxy group, even though **16a** is more stable than **17a** (Fig. 2).



Scheme 4

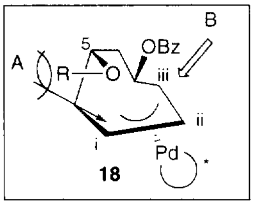


Figure 2

Various protecting groups on the hydroxy group were examined and the results are shown in Table 2.[9] Alkylation of cycloheptenetriol derivatives **15** with an alkoxy group at the C-5 position proceeded smoothly to give alkylation products **16** and **17** in high yields, except for the reaction of **15c**. In each case, the major product was **17**, which was attacked by the nucleophile at the C-iii position of **18**, and the minor product with high ee was the C-i alkylation product **16**.

Table 2 Alkylation of trihydroxycycloheptene derivatives **15**

run	15, R=	Ratio **16** / **17** (Yield %)	ees (%) **16**	 **17**
1	TBS (**15a**)[a]	9 / 91 (85)	72	40
2	TBDPS (**15b**)[a]	26 / 74 (72)	80	32
3	H (**15c**)	14 / 86 (28)	22	24
4	CH$_3$ (**15d**)[b]	24 / 76 (68)	56	26

Reactions were carried out in THF in the presence of NaH (1.05 equiv.) [Pd(C$_3$H$_5$)Cl]$_2$ (2.5 mol %) and (*S*)-(-)-BINAPO (10 mol %) at 40 °C for 12 h . a) Enantioselectivities were determined converting **15a**, **15b**, and **15d** into **15c** by desilylation or demethylation

To improve the regioselectivity and the ees, **15b** was reacted with **5a** under various conditions (Table 3). Changing the palladium catalyst appeared to have no effect (Runs 1-3) and various solvents can be used. As a solvent, CH$_3$CN gave the alkylated products **16b** and **17b** in high yields, with 72% ee and 30% ee, respectively, but in a ratio of 1 to 1 (Run 4). The reason for the difference in the ees of these compounds **16** and **17** is not clear.

Next, various chiral ligands were examined in the reaction of **15b** with **5a** (Table 4, Figure 3). The use of (*R*,*R*)-DIOP, (*R*,*S*)-BPPFA and (*S*)-BINAP gave **17b** regioselectively (runs 1-3), but the ees were low.

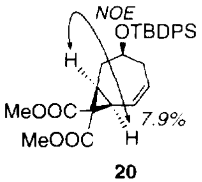
Table 3 Reaction of **15b** with **5a** under various conditions[a)]

			Ratio (Yield %)	ees (%)	
Run	Pd catalyst	Solvent	**16b / 17b**	**16b**	**17b**
1	$[Pd(C_3H_5)Cl]_2$	THF	26 / 74 (72)	80	32
2	$Pd(OAc)_2$	THF	26 / 74 (69)	74	32
3	$Pd_2(dba)_3{\bullet}CHCl_3$	THF	29 / 71 (83)	77	32
4	$[Pd(C_3H_5)Cl]_2$	CH_3CN	52 / 48 (96)	72	30
5	$[Pd(C_3H_5)Cl]_2$	CH_2Cl_2	40 / 60 (43)	62	26
6	$[Pd(C_3H_5)Cl]_2$	DMF	35 / 65 (48)	76	26
7	$[Pd(C_3H_5)Cl]_2$	toluene	23 / 77 (48)	84	46

a) Reactions were carried out in the presence of NaH (1.05 equiv.), palladium catalyst (2.5 mol %) and (*S*)-(-)-BINAPO (10 mol %) at 40 °C for 12 h .

Table 4 Reaction of **15b** with **5a**[a)]

			Ratio	ees (%)	
Run	Ligand	Base	**16b/17b** (Yield %)	**16b**	**17b**
1	(*R*,*R*)-DIOP	NaH	0 / 100 (92)	–	6
2	(*R*,*S*)-BPPFA	NaH	0 / 100 (46)	–	32
3	(*S*)-BINAP	NaH	0 / 100 (48)	–	40
4	(S)-BINAPO	NaH	26 / 74 (72)	80	32
5	(S)-BINAPO	LDA	20[b)]/80 (89)	N.D.[c)]	42
6	(*S*,*S*)-BPPM	NaH	3 / 97 (62)	N.D.[c)]	18
7[d)]	(*S*,*R*)-PPFA	NaH	26 /74 (49)	27	8



20

a) Reactions were carried out in THF in the presence of NaH (1.05 equiv.), $[Pd(C_3H_5)Cl]_2$ (2.5 mol %) and (S)-BINAPO (10 mol %) at 40 °C for 12 h. b) 18% of **20** was obtained. c) Enantiomeric excess was not determined. d) 20 mol % of ligand was used.

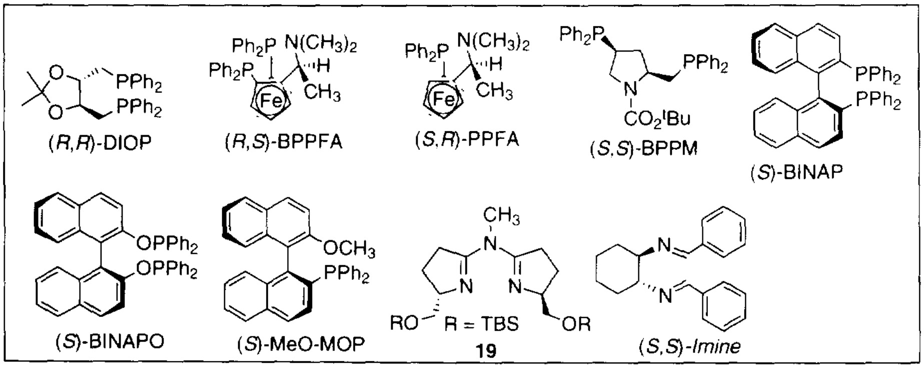
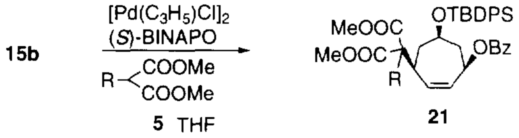


Figure 3

When (*S*)-MeO-MOP,[10] (*S*,*S*)-imine[1d] and **19**[11] were used for this reaction, none of the product was obtained. With these ligands, (*S*)-BINAPO gave good results. In the asymmetric alkylation of cycloalkenediol derivatives, we found that the base used for this reaction affected the ee.[2b] When **15b** was reacted with dimethyl malonate **5a** in the presence of LDA instead of NaH, $[Pd(C_3H_5)Cl]_2$ and (*S*)-BINAPO, compound **17b** was obtained in 71% yield with 42% ee (Run 5), which means that the product distribution is affected by the base used.

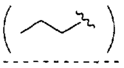
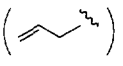
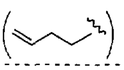
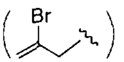
Reaction of Trihydroxycycloheptene Derivatives with Alkylated Methyl Malonate

Dimethyl alkylmalonate **5** was then used as a nucleophile for this reaction (Table 5).[11] The results were very interesting in that only the C-i alkylated product **21** with a fairly high ee was obtained in each case.



Scheme 5

Table 5 Reaction of **15b** with **5**[a)]

Run	R	Base (equiv.)	Yield	ee (%)[c)]
1	methyl (**5b**)	NaH (1.05)	65	54
2		LDA (2.5)	73[b)]	44
3	propyl (**5c**)	NaH (1.05)	81	60
4		LDA (2.5)	82	66
5	allyl (**5d**) [d)]	NaH (1.05)	80	54
6		LDA (2.5)	99	70
7	1-butenyl (**5e**)	NaH (1.05)	39	61
8		LDA (2.5)	57	56
9	2-bromo- allyl (**5f**) 	NaH (1.05)	20	64

a) Reactions were carried out at 40 °C for 12 h in the presence of NaH (1.05 equiv.), $[Pd(C_3H_5)Cl]_2$ (2.5 mol %) and (S)-(-)-BINAPO (10 mol %).
b) 10% of **22b** was obtained. c) The ees were determined after deprotection of the silyl group. d) Diethyl propenylmalonate was used as a nucleophile.

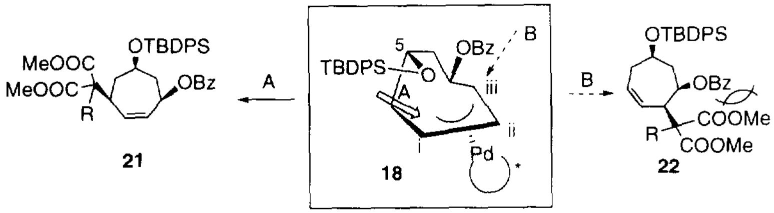
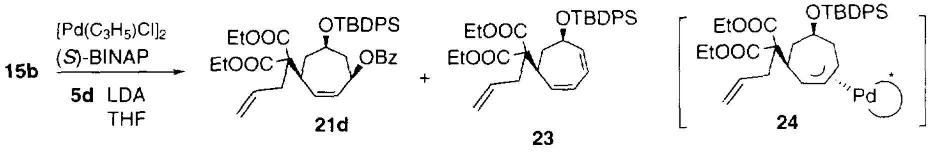


Figure 4

The reaction of **15b** with diethyl propenylmalonate **5d** gave **21d** in 99% yield with 70% ee when LDA was used as the base (Run 3). It is believed that the C-i alkylated product was the only product formed when the bulky nucleophiles were used for this reaction due to the steric repulsion between the benzyloxy group and the nucleophile (Fig. 4).



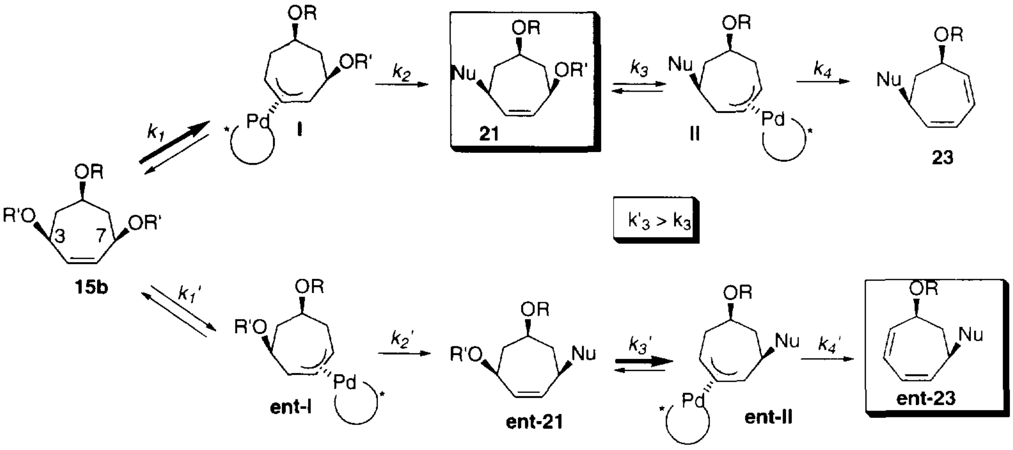
Scheme 6

Table 6 Reaction of **15b** with **5d**[b]under various conditions[a]

Run	Ligand	Temp. (°C)	Time (h)	Yield (%) 21d	Yield (%) 23	ee (%) 21d	ee (%) 23
1	(*S,S*)-BPPM	40	12	62	-	22	-
2	(*R,S*)-BPPFA	40	10	61	-	38	-
3	(*S*)-BINAPO	40	12	99	-	70	-
4	(*S*)-BINAP	40	6	21	43	98	22
5	(*S*)-BINAP	40	0.5	54	23	72	30
6	(*S*)-BINAP	25	13	66	13	86	30
7	(*S*)-BINAP	25	25	41	25	94	10
8	(*S*)-BINAP	25	1.5	64	-	70	-

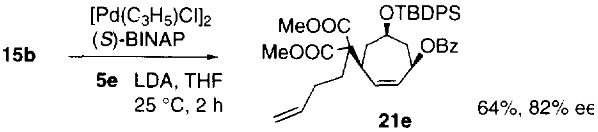
a) Reactions were carried out in THF in the presence of LDA (2.5 equiv.), $[Pd(C_3H_5)Cl]_2$ (2.5 mol %), and the chiral ligand (10 mol %).
b) Diethyl propenylmalonate was used.

To realize a synthetic approach to the hydroazulene derivative, the alkylated product **21d** was useful. The asymmetric alkylation of **15b** with **5d** was further investigated using various chiral ligands in the presence of LDA and $[Pd(C_3H_5)Cl]_2$ (Table 6). In each case, the alkylation product was obtained in good yield (Runs 1-4). Surprisingly, when the reaction was carried out using (*S*)-BINAP as the chiral ligand for 6 h, the desired alkylated product **21d** with 98% ee was obtained although the yield was 21% (Run 4). In this case, diene **23**, which was derived from π-allylpalladium complex **24** by β-hydride elimination, was obtained in 43% yield with 22% ee. When the same reaction was carried out for 30 min, **21d** and diene **23**[13] were obtained in 54% yield with 72% ee and in 23% yield with 30% ee, respectively (Run 5). A lower temperature gave **21d** with 86% ee in 66% yield after 13 h, and with 94% ee in 41% yield after 25 h (Runs 6 and 7). These results indicate that kinetic resolution would occur in this reaction. The plausible reaction mechanism is shown in Scheme 7. In this reaction, diene was formed from **21** or **ent-21** *via* π-allylpalladium complex **II** or **ent-II**. If **I** is formed faster than **ent-I**, the next π-allylpalladium complex **ent-II** should be formed faster than **II**. As a result, alkylated product **21** with high ee was obtained along with diene **23** with low ee.



Scheme 7 Plausible Mechanism for Kinetic Resolution

On the other hand, when compound **15b** was treated with dimethyl butenylmalonate **5e** in the presence of (*S*)-BINAP as a chiral ligand and LDA as the base, alkylated product **21e** was obtained in 64% yield with 82% ee (Scheme 8). In this case, diene was not produced.

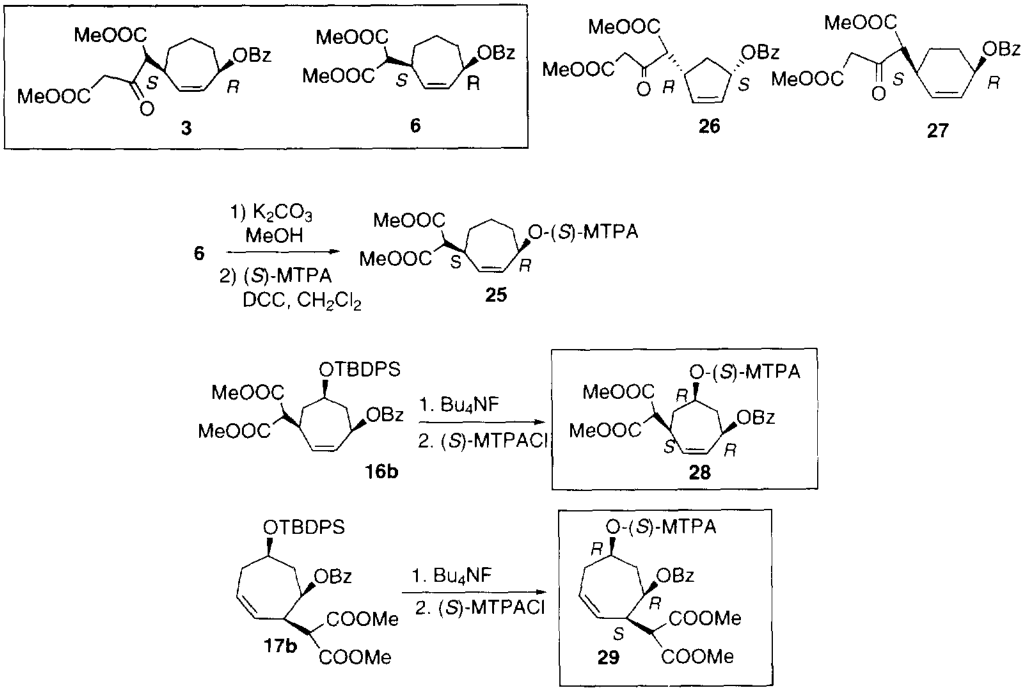


Scheme 8

Determination of the Absolute Configuration

The absolute configurations of mono alkylated products **3** and **6**, which were obtained from **1b**, were determined by the application of the CD exiton chirality method[14] to be (3*R*,7*S*) and (3*R*,7*S*), respectively. Since it has not yet been determined whether the CD exiton chirality method is applicable for allylbenzoate in a seven-membered ring compound, we next used an improved Mosher's method[15] to determine the absolute configuration of **6**. Each diastereomer on the route to MTPA ester **25** was separated. The δΔ values for these diastereomers were calculated from their NMR spectra. The absolute configuration of **6** was determined to be (3*R*,7*S*) by this method. Thus, the results of the CD exiton chirality method is the same as that of the improved Mosher's method. The absolute configurations of the alkylated products **16b** and **17b** were determined to be

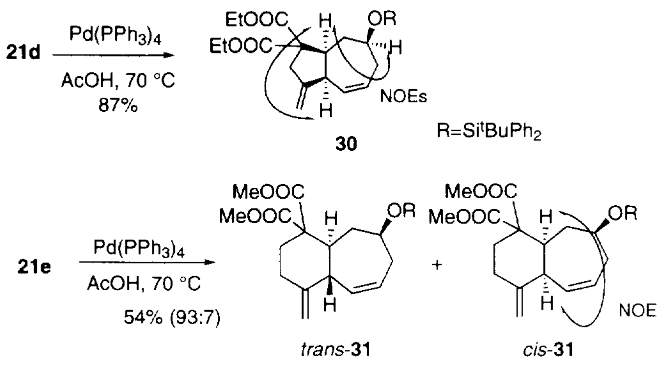
(3*R*,5*R*,7*S*) and (3*S*,4*R*,6*R*), respectively, also leading to MTPA esters **28** and **29**. We previously determined the absolute configurations of the products **26** and **27**, which were obtained by palladium-catalyzed asymmetric alkylation, to be (3*S*,5*R*) and (3*R*,6*S*), respectively.[2] These results indicate that the asymmetric inductions in cycloheptene derivatives **3** and **6** occur in the same site as in the cyclohexene derivative **27**.



Scheme 9

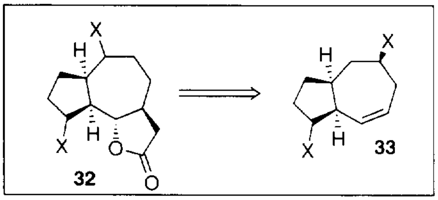
Synthetic Approach to the Hydroazulene Skeletons

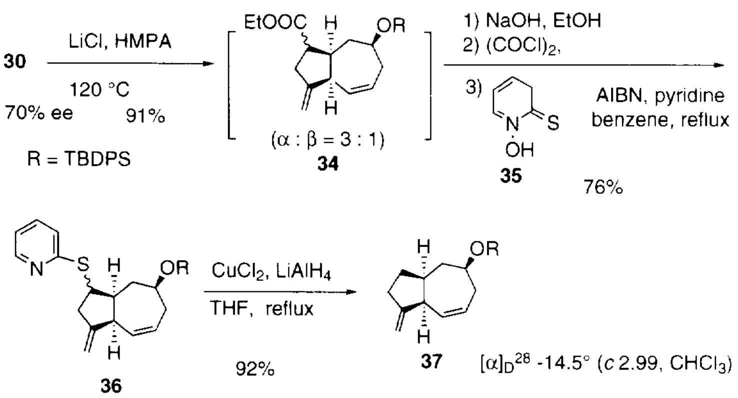
Hydroazulene and hydroxybenzocycloheptene skeletons are very interesting and useful for natural product syntheses.[16] To prepare these skeletons, compound **21d** was treated with $Pd(PPh_3)_4$ in AcOH to give hydroazulene **30** in 87% yield. The ring junction of **30** was determined to be *cis* by an NOE experiment. In a similar manner, compound **21e** was treated with $Pd(PPh_3)_4$ in AcOH at 70 ℃ to give *trans*- and *cis*-hydrobenzocycloheptene **31** in 54% yield in a ratio of 93 to 7. From an NOE experiment of the minor product, the ring junction of this compound is *cis*. Many natural products have a *cis*-hydroazulene skeleton, such as compressanolide[16a], grosshemin[16b], dehydrocostus lactone[16c] and estafiatin[16a,c,d]. Compound **33** should be an important key intermediate in the syntheses of these compounds. Thus, we tried to convert compound **30** into **33**. Decarbomethoxylation of **30** proceeded smoothly by treatment with LiCl in HMPA at 120 ℃ to give ester **34** in 91% yield. To remove the other ethoxycarbonyl group, Barton's method[17] was applied. Compound **34** was converted into the acid chloride and then reacted with **35**. A benzene solution of the resulting product was refluxed in the presence of AIBN and Bu_3SnH. However, a trace amount of **37** was obtained along with the thioether **36**.



Scheme 10

Various attempts were made to convert the acid chloride directly into **37**, but the main product was **36**. Thus, compound **36** was treated with LiAlH$_4$ in the presence of CuCl$_2$[18] to give compound **37** in high yield, which should be a useful key intermediate for the synthesis of biologically active substances.





Scheme 11

Thus, we realized the asymmetric alkylation of cycloheptenediol derivative using palladium catalyst and (*S*)-BINAPO or (*S*)-BINAP as a chiral ligand. The reaction site is controlled by the protecting group of the hydroxy group at the C-5 position and the size of the nucleophiles. The alkylation of a cycloheptenediol derivative with a large protecting group at the C-5 position by a large nucleophile gave a high yield and a high ee. The alkylated products could lead to the optically active hydroazulene and hydrobenzocycloheptene derivatives.

EXPERIMENTAL SECTION

All manipulations were performed under an argon atmosphere using standard Schlenk techniques, and all the reaction solutions were degassed through freeze-pump-thaw cycle. Solvents were distilled under an argon atmosphere from sodium benzophenone ketyl (THF) or CaH_2(DMF and CH_2Cl_2). All other reagents and solvents were purified when necessary using standard procedures. Column chromatography was performed on silica gel 60 (70-230 mesh, 60 Å), and flash chromatography was performed on silica gel 60 (230-400 mesh, 60 Å) using the indicated solvent. Melting points are uncorrected. The enantioselectivities were determined using chiral stationary-phse HPLC, which was shown in References and Notes.

General Procedure for the Asymmetric Alkylation. To a solution of the substrate, palladium catalyst and the ligand was added a solution of dimethyl ketoglutarate or dimethyl malonate derivative and the base and the solution was stirred at an appropriate temperature. After cooling, 10% HCl solution was added and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to give the desired alkylated product.

(3*R*,7*S*)-3-Benzoyloxy-7-[1',3'-di(methoxycarbonyl)-2'-oxopropyl]cycloheptene (3). IR (neat) ν 1742, 1716 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.40 (m, 1 H), 1.62 (m, 1 H), 1.73 (m, 1 H), 1.84 (m, 1 H), 2.00 (m, 1 H), 2.07 (m, 1 H), 3.11 (m, 1H), 3.64 (m, 9 H), 5.62 (m, 1 H), 5.71 (m, 1 H), 5.86 (dt, *J* = 11.0, 2.5 Hz, 1 H), 7.77 (dd, *J* = 7.7, 7.7 Hz, 2 H), 7.55 (d, *J* = 7.4 Hz, 1 H), 8.05 (m, 2 H); HRMS calcd for $C_{21}H_{24}O_7$ 388.1522, found 388.1551; Anal Calcd For $C_{21}H_{24}O_7$ for C, 64.94; H, 6.22, found C, 64.84; H,6.39.

(1*R*, 7*R*)-8-Methoxycarbonyl-9-(methoxycarbonyl)methyl-10-oxabicyclo[5.3.0]deca-2,8-diene (4). IR (neat) ν 1746, 1698, 1650, 1436 cm^{-1};^{1}H NMR (500 MHz, $CDCl_3$) δ 1.51-1.60 (m, 3H), 1.73-1.76 (m, 1H), 2.07-2.10 (m, 2H), 3.54 and 3.78 (ABq, *J* = 2.0, 15.9 Hz, 2H), 3.64 (dt, *J* = 2.1, 6.1 Hz, 1H), 3.64 (s, 3 H), 3.65 (s, 3H), 5.28 (dd, *J* = 0.8, 9.9 Hz, 1H) 5.61-571 (m, 2H); MS (EI, *m/z*) 266 (M$^+$), 235, 237, 92; HRMS calcd for $C_{14}H_{18}O_5$ 266.1175, found 266.1181; Anal. Calcd for $C_{14}H_{18}O_5$: C, 63.15; H, 6.81. Found: C, 62.98; H, 6.96; $[\alpha]_D^{27}$ +13.0 °(c 1.00, $CHCl_3$, 24% ee).

(3*R*,7*S*)-3-Benzoyloxy-7-[di(methoxycarbonyl)methyl]cycloheptene (6). IR (neat) ν 1734, 1716, 1654, 1450 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.37-2.13 (m, 6 H), 3.02-3.08 (m, 1H), 3.50 (d, *J* = 7.7 Hz, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 5.71 (brdd, *J* = 3.4 , 12.6 Hz, 2H), 5.85 (m, 1H), 7.43 (dd, *J* = 7.5, 7.5 Hz, 2H), 7.55 (m, 1H), 8.05 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 29.7, 30.7, 32.2, 39.6, 52.5, 56.7, 74.4, 128.3, 129.6, 130.5, 131.5, 132.0, 134.4, 165.7, 168.7, 168.8; MS (EI, *m/z*) 346 (M$^+$), 214. 237, 105, 105, 91, 77; .(EI, *m/z*) HRMS calcd for $C_{19}H_{22}O_6$ 346.1423, found 346.1432; Anal. Calcd for $C_{19}H_{22}O_6$: C, 65.88; H, 6.40. Found: C, 65.88; H, 6.55.

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-(*tert*-butyldimethylsilyloxy)-7-[di(methoxycarbonyl)methyl]cycloheptene (16a). IR (neat) ν 1736, 1718, 1640 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.89 (s, 9H), 1.75 (dd, *J* = 3.3, 8.8 Hz, 1H), 1.98 (m, 1H), 2.12 (dd, *J* = 2.1, 12.2 Hz, 1H), 2.25 (m, 1H), 3.36-3.43 (m, 1H), 3.50 (d, *J* = 7.7 Hz, 1H), 3.74 (s, 3H), 3.75 (s, 3H), 4.25 (m 1H), 5.58 (brd, *J* = 11.0 Hz, 1H), 5.72 (s, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 7.7 Hz, 2H); MS (EI, *m/z*) 445 (M$^+$-CH_3O), 419, 387, 323, 297, 223, 179, 105 ; HRMS (EI, *m/z*) calcd for $C_{24}H_{33}O_6Si$ (M$^+$-CH_3O) 445.2046, found 445.2026; Anal. Calcd for $C_{25}H_{36}O_7Si$: C, 63.00; H, 7.61. Found: C, 62.96; H, 7.45.

(3*R*, 4*R*, 6*R*)-4-Benzoyloxy-6-(*tert*-butyldimethylsilyloxy)-3-[di(methoxycarbonyl)methyl]cycloheptene (17a). IR (neat) ν 1732, 1602, 1454, 1120 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.03 (s, 6H), 0.85 (s, 9H), 2.25-2.45 (m, 4H), 3.43 (m, 1H), 3.55 (s, 3H), 3.67 (s, 3H), 3.89 (d, *J* = 10.5 Hz, 1H), 3.91-4.02 (m, 1H), 5.23-5.31 (m, 1H), 5.66 (dd, *J* = 6.1, 11.7 Hz, 1H), 5.75-5.64 (m, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.96 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ -4.8, -4.8, , 18.0, 25.7, 25.7, 37.4, 41.4, 41.5, 52.5, 52.6, 52.7, 67.8, 71.1, 128.0, 128.3, 128.3, 129.2, 129.6, 129.6, 129.7, 133.0, 165.3, 168.4, 168.5; MS (EI, *m/z*) 445 (M^+-CH_3O), 419, 387, 323, 297, 223, 179, 105; HRMS (EI, *m/z*) calcd for $C_{24}H_{33}O_6Si$ (M^+-CH_3O) 445.2046, found 445.2026; Anal. Calcd for $C_{25}H_{36}O_7Si$: C, 63.00; H, 7.61. Found: C, 62.99; H, 7.55.

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-(*tert*-butyldiphenylsilyloxy)-7-[di(methoxycarbonyl)methyl]cycloheptene (16b). IR (neat) ν 1736, 1718, 1640 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.00 (s, 9H), 2.23-2.46 (m, 4H), 3.39-3.42 (m, 1H), 3.53 (s, 3H), 3.64 (s, 3H), 3.86 (d, *J* = 10.6 Hz, 1H), 3.97 (m, 1H), 5.13-5.27 (m, 1H), 5.57-5.66 (m, 2H), 7.34-7.40 (m, 9H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 3H), 7.96 (d, *J* = 7.7 Hz, 2H); MS (EI, *m/z*) 569 (M^+-CH_3O), 543, 361, 105.

(3*R*, 4*R*, 6*R*)-4-Benzoyloxy-6-(*tert*-butyldiphenylsilyloxy)-3-[di(methoxycarbonyl)methyl]cycloheptene (17b). IR (neat) ν 1756, 1737, 1716, 1428 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.93 (s, 9H), 2.27 (dt, *J* = 4.0, 14.5 Hz, 1H), 2.33 (m, 1H), 2.37 (dd, *J* = 4.8, 9.4 Hz, 1H), 2.44 (dt, *J* = 8.4, 14.3 Hz, 1H), 3.41 (m, 1H), 3.45 (s, 3H), 3.56 (s, 3H), 3.78 (d, *J* = 10.5 Hz, 1H), 3.96-4.05 (m, 1H), 5.05-5.11 (m, 1H), 5.48-5.55 (m, 2H), 7.34-7.40 (m, 9H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.65 (t, *J* = 7.9 Hz, 3H), 7.99 (d, *J* = 7.2 Hz, 2H); MS (EI, *m/z*) 569 (M^+-CH_3O), 543, 361, 105; Anal. Calcd for $C_{35}H_{40}O_7Si$: C, 69.97; H, 6.71. Found: C, 70.03; H, 6.81.

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-hydroxy-7-[di(methoxycarbonyl)methyl]cycloheptene (16c). IR (neat) ν 3507, 1738, 1733, 1717, 1451, 1436, 1315 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.69 (ddd, *J* = 11.4 11.4, 11.4 Hz, 1H), 1.63 (brs, 1H), 1.78 (dd, *J* = 11.3, 11.2 Hz, 1H), 2.00 (dd, *J* = 3.3, 12.5. Hz, 1H), 2.34 (brd, *J* = 11.7 Hz, 1H), 2.95 (m, 1H), 3.53 (d, *J* = 7.7 Hz, 1H), 3.75 (s, 3H), 3.76 (s, 3H), 4.01-4.09 (m, 1H) 5.69 (brd, *J* = 11.5 Hz, 1H), 5.71 (ddd, *J* = 2.0, 5.4, 9.3Hz, 1H), 5.80 (brdd, *J* = 2.2, 12.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 3H), 8.02 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 34.5, 39.6, 41.3, 52.6, 52.7, 56.3, 69.6, 70.6, 128.4, 129.7, 130.2, 130.7, 133.1, 134.0, 165.7, 168.6,; MS (EI, *m/z*) 331 (M^+-CH_3O), 240, 105; Anal. Calcd for $C_{19}H_{22}O_7$: C, 62.93; H, 6.12. Found: C, 63.13; H, 6.11. $[\alpha]_D^{19}$ -7.2° (*c* 0.892, $CHCl_3$, 58% ee).

(3*R*, 4*R*, 6*R*)-4-Benzoyloxy-6-hydroxy-3-[di(methoxycarbonyl)methyl]cycloheptene (17c). IR (neat) ν 3507, 1738, 1733, 1717, 1451, 1436, 1315 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.97 (brs, 1H), 2.22 (dt, *J* = 3.5, 14.5 Hz, 1H), 2.51-2.61 (m, 3H), 3.55 (m, 1H), 3.65 (s, 3H), 3.68 (s, 3H), 3.75 (d, *J* = 11.0 Hz, 1H), 3.99-4.12 (m, 1H), 5.05-5.43 (m, 1H), 5.75 (dd, *J* = 5.5, 11.0 Hz, 1H), 5.86-5.93 (m, 1H), 7.42 (t, *J* = 7.6 Hz, 3H), 7.96 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 35.5, 40.8, 41.9, 52.7, 52.8. 53.5, 66.4, 71.2, 128.5, 128.7, 129.6, 129.9, 133.2, 165.5. 168.4, 168.5; MS (EI, *m/z*) 331 (M^+-CH_3O), 240, 105; Anal. Calcd for $C_{19}H_{22}O_7$: C, 62.93; H, 6.12. Found: C, 63.02; H, 6.18; $[\alpha]_D^{28}$ -12.9° (*c* 1.38, $CHCl_3$, 32% ee).

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-methoxy-7-[di(methoxycarbonyl)methyl]cycloheptene (16d).(3*R*, 4*R*, 6*R*)-4-Benzoyloxy-6-methoxy-3-[di(methoxycarbonyl)methyl]cycloheptene

(**17d**). They are inseparable two isomers. To the CH_2Cl_2 solution of the reaction mixture was treated with BBr_3 at -78 °C for 3 h. After the usual work up, the alcohol **16c** and **17c** were obtained.

(1*R*, 5*S*, 7*S*)-5-(*tert*-Butyldiphenylsilyl)oxy-8,8-di(methoxycarbonyl)bicyclo[5.1.0]octa-2-ene (20). IR (neat) ν 1732, 1428, cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (s, 9H), 1.53 (dd, *J* = 10.5, 14.8 Hz, 1H), 1.65 (ddd, *J* = 6.6, 9.1, 11.0 Hz, 1H), 2.00 (brd, *J* =9.1 Hz, 1H), 2.14-2.23 (m, 2H), 2.57 (brd *J* = 17.0 Hz, 1H), 3.68 (s, 3H), 3.73 (s, 3H), 4.08 (m, 1H), 5.50 (m, 1H), 5.66 (brd, *J* = 11.0 Hz, 1H), 7.37 (t, *J* = 7.5 Hz, 4H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.64 (t, *J* = 7.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 26.9, 29.6, 32.8, 33.5, 37.8, 38.9, 52.2, 52.7, 69.3, 123.4, 127.6, 128.5, 129.6, 134.1, 134.2, 135.7, 166.8, 170.6; MS (EI, *m/z*) 478 (M^+), 447, 421; HRMS (EI, *m/z*) calcd for $C_{24}H_{25}O_5Si$ (M^+-^{t}Bu) 421.1422, found 421.1447.

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-(*tert*-butyldiphenylsilyloxy)-7-[1',1'-di(methoxycarbonyl)ethyl]cycloheptene (21b). IR (neat) ν 1732, 1602, 1452, 1428 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (s, 9H), 1.28 (s, 3H), 1.40 (dd, *J* = 12.5, 11.6, 10.8 Hz, 1H), 1.83 (dd, *J* = 11.6, 11.6, 10.8 Hz, 2H), 2.16 (brd, *J* = 12.0 Hz, 1H), 2.72 (m, 1H), 3.60 (s, 3H), 3.62 (s, 3H), 4.10 (m, 1H), 5.49 (brd, *J* = 11.4 Hz, 1H), 5.55 (brd, *J* = 11.3 Hz, 1H), 5.74 (brd, *J* = 11.3 Hz, 1H), 7.31-7.39 (m, 7H), 7.43 (t, *J* = 7.7 Hz, 1H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.65 (t, *J* = 6.5 Hz, 4H), 8.02 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.3, 19.1, 26.9, 38.7, 39.0, 41.6, 52.5, 52.6, 57.3, 69.4, 72.5, 127.5, 127.6, 128.3, 129.6, 129.7, 130.1, 130.3, 132.9, 133.5, 134.0, 134.1, 135.8, 135.8, 165.4, 171.4; MS (EI, *m/z*) 583 (M^+-CH_3O), 557, 492, 412, 303; HRMS (EI, *m/z*) calcd for $C_{35}H_{39}O_6Si$ (M^+-CH_3O) 583.2526, found 583.2521; Anal. Calcd for $C_{38}H_{42}O_4Si$: C, 70.33; H, 7.15. Found: C, 70.23; H, 6.89; $[\alpha]_D^{23}$ -2.2° (*c*1.01, $CHCl_3$, 54% ee).

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-hydroxy-7-[1',1'-di(methoxycarbonyl)ethyl]cycloheptene (21b-hydroxy). IR (neat) ν 3508, 1732, 1602, 1452, 1434 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.33 (ddd, *J* = 11.3, 11.3,11.3 Hz, 1H), 1.48 (s, 3H), 1.73 (dd, *J* = 11.3, 11.3 Hz, 1H), 1.95 (dd, *J* = 2.6, 11.3 Hz, 2H), 1.95 (m, 1 H), 2.32 (d, *J* = 11.3 Hz, 1H), 2.98 (dd, *J* = 4.6, 9.6 Hz, 1H), 3.71 (s, 3H), 3.75 (s, 3H), 4.09 (m, 1H), 5.61 (ddd, *J* = 1.8, 5.2, 11.3 Hz, 1H), 5.69 (brd, *J* = 9.2 Hz, 1H), 5.85 (brd, *J* = 11.4 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.51 (t, *J* = 7.4 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 17.1, 38.4, 38.9, 41.2, 52.6, 52.7, 57.2, 69.6, 70.9, 128.3, 129.5, 129.9, 130.1, 133.0, 133.7, 165.6, 171.5; $[\alpha]_D^{24}$ -6.0° (*c* 1.13, $CHCl_3$, 54% ee).

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-(*tert*-butyldiphenylsilyl)oxy-7-[1',1'-di(methoxycarbonyl)butyl]cycloheptene (21c). IR (neat) ν 1738, 1733, 1451, 1429 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (t, *J* = 7.3 Hz, 3H), 1.04 (s, 9H), 1.30 (m, 2H), 1.58-1.72 (m, 2H), 1.80 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H), 1.86 (dd, *J* = 7.8, 15.6 Hz, 2H), 1.97 (brdd, *J* = 3.3, 12.5 Hz, 1H), 2.16 (brd, *J* = 11.7 Hz, 1H), 3.61 (s, 3H), 3.68 (s, 3H), 4.05-4.09 (m, 1H), 5.48 (brd, *J* = 11.5, 1H), 5.71 (s, 2H), 7.36-7.67 (m, 13H), 8.02 (d, *J* = 7.2 Hz, 2H); MS (EI, m/z) 553 (M^+-BzO), 527, 405, 303; Anal. Calcd for $C_{39}H_{46}O_7Si$: C, 71.00; H, 7.21. Found C, 71.06; H, 7.40; $[\alpha]_D^{27}$ -4.1° (*c*1.81, $CHCl_3$, 60% ee).

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-hydroxy-7-[1',1'-di(methoxycarbonyl)butyl]cycloheptene (21c-hydroxy). IR (neat) ν 3507, 1738, 1733, 1717, 1451, 1436, 1315 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.97 (t, *J* = 7.3 Hz, 3H), 1.18-1.28 (m, 5H), 1.70 (ddd, *J* = 11.4, 11.4, 11.4 Hz, 1H), 1.85-1.94 (m, 2H)., 2.11 (brdd, *J* = 3.3, 12.5 Hz, 1H), 2.32 (brd, *J* = 11.7 Hz, 1H), 3.75 (s, 3H), 3.76 (s, 3H), 4.07 (m, 1H), 5.68 (brd, *J* = 11.5 Hz, 1H), 5.77 (ddd, *J* = 2.0, 5.4, 9.3 Hz, 1H), 5.83 (brd, *J* = 1.4, 12.4 Hz, 1H), 7.42 (t, *J*

= 7.6 Hz, 2H), 7.56 (t, *J* = 7.5 Hz, 1H), 8.02 (d, *J* = 7.3 Hz, 2H); MS (EI, *m/z*) 362, 331, 240, 105; HRMS (EI, *m/z*) calcd for $C_{19}H_{22}O_7$ (M^+-C_3H_6) 362.1315, found 362.1394; Anal. Calcd for $C_{22}H_{28}O_7$: C, 64.27; H, 7.19. Found: C, 64.34; H, 6.98; $[\alpha]_D^{21}$ -2.4°(*c* 1.26, $CHCl_3$, 60% ee)

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-(*tert*-butyldiphenylsilyloxy)-7-[1',1'-di(ethoxycarbonyl)-3'-butenyl]cycloheptene (21d). IR (neat) ν 2932, 1736, 1724, 1450, 1428 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.95 (s, 9H), 1.05-1.13 (m, 1H), 1.09 (t, *J* =6.9 Hz, 3H), 1.10 (t, *J* = 2.8 Hz, 3H), 1.25 (ddd, *J* = 11.3, 11.3, 11.3 Hz, 1H), 1.73 (ddd, *J* = 11.3, 11.3, 11.3 Hz, 1H), 1.93 (brd, *J* = 10.2 Hz, 1H), 2.12 (brd, *J* = 11.7 Hz, 1H), 2.36 (m, 1H), 2.43 (dd, *J* = 7.1, 14.3 Hz, 1H), 2.55 (m, 1H), 3.98 (q, *J* = 6.9 Hz, 2H), 4.05 (q, *J* = 6.9 Hz, 2H), 3.96-4.11 (m, 1H), 4.86 (dd, *J* = 10.0, 16.9 Hz, 1H), 5.40 (brd, *J* = 10.0, 1H), 5.51 (m, 1H), 5.66 (brd, *J* = 11.6 Hz, 1H), 5.70 (brdd, *J* = 4.8, 11.6 Hz, 1H), 7.21-7.34 (m, 8H), 7.58 (t, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 4H), 7.94 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.0, 19.1, 26.9, 37.8, 38.2, 41.6, 60.6, 61.0, 61.1, 69.3, 72.6, 118.8, 127.5, 127.6, 128.2, 129.5, 130.3, 130.8, 132.5, 132.6, 132.8, 134.0, 134.1, 135.7, 165.4, 169.8, 170.1; GCMC (*m/z*) 668 (M^+),611, 546, 489, 381, 303, 291, 217, 105, 91; Anal. Calcd for $C_{40}H_{48}O_7Si$: C, 71.82; H, 7.23. Found: C, 71.76; H, 7.42; $[\alpha]_D^{19}$ -4.7°(*c* 1.40, $CHCl_3$, 58% ee).

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-hydroxy-7-[1',1'-di(ethoxycarbonyl)-3'-butenyl]cycloheptene (21d-hydroxy). IR (neat) ν 3510, 1722, 1718, 1450, 1368 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 6H), 1.27 (m, 1 H), 1.69 (dd, *J* = 11.2, 11.2 Hz, 1H), 1.78 (brs, 1H), 2.15 (brdd, *J* = 3.3, 12.5 Hz, 1H), 2.32 (brd, *J* = 11.7 Hz, 1H), 2.70 (m, 2H), 2.81 (dd, *J* = 4.7, 10.5 Hz, 1H) 4.01 (m, 1H), 4.21 (q, *J* = 7.5Hz, 2H), 4.22 (q, *J* = 7.5 Hz, 2H), 5.08 (m, 2H), 5.67 (brd, *J* = 11.5 Hz, 1H), 5.77 (m, 1H), 5.83 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 2H): MS (EI, *m/z*) 430 (M^+), 429, 383, 355, 309, 264, 105; $[\alpha]_D^{26}$ -7.4°(*c* 0.31, $CHCl_3$, 98% ee).

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-(*tert*-butyldiphenylsilyl)oxy-7-[1',1'-di(methoxycarbonyl)-4'-pentenyl]cycloheptene (21e). IR (neat) ν 2932, 1736, 1724, 1450, 1428 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.03 (s, 9H), 1.31 (ddd, *J* = 10.9, 10.9, 10.9 Hz, 1H), 1.72-2.01 (m, 5H), 2.00 (brdd, *J* = 3.3, 10.9 Hz, 1H), 2.15 (brd, *J* = 10.9 Hz, 1H), 2.61 (brdd, *J* = 5.0, 10.0 Hz, 1H), 3.58 (s, 3H), 3.64 (s, 3H), 4.05 (m, 1H), 4.93-5.01 (m, 2H), 5.47 (brd, *J* = 11.3, 1H), 5.65-5.72 (m, 3H), 7.30-7.41 (m, 8H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.64 (t, *J* = 7.2 Hz, 4H), 8.02 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.1, 26.9, 29.0, 33.4, 38.8, 38.9, 41.7, 52.0, 60.8, 69.4, 72.7, 115.0, 127.0, 127.7, 128.3, 129.6, 130.4, 132.9, 133.1, 134.0, 134.2, 135.7, 135.8, 137.5, 165.5, 170.7, 170.9; MS (EI, *m/z*) 654 (M^+), 623 (M^+-CH_3O), 597 [M^+-$(CH_3)_3C$], 490, 476, 412, 368, 303, 105, 91; HRMS (EI, *m/z*) for $C_{35}H_{37}O_7Si$ [M^+-^{t}Bu], calcd 597.1369, found 597.1406; Anal. Calcd for $C_{39}H_{46}O_7Si$: C, 71.53; H, 7.08. Found: C, 71.36; H, 7.21; $[\alpha]_D^{23}$ -0.5°(*c* 1.06, $CHCl_3$, 82% ee)

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-hydroxy-7-[1',1'-di(methoxycarbonyl)-4'-pentenyl]cycloheptene (21e-hydroxy). IR (neat) ν 3510, 1722, 1718, 1450, 1368 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.2 Hz, 6H), 1.69 (ddd, *J* = 11.2, 11.2, 11.2 Hz, 1H), 1.78 (brs, 1H), 2.15 (brdd, *J* = 3.3, 11.2 Hz, 1H), 2.32 (brd, *J* = 11.2 Hz, 1H), 2.70 (m, 2H), 2.81 (dd, *J* = 4.7, 10.5 Hz, 1H), 4.01 (m, 1H), 4.21 (q, *J* = 7.5Hz, 2H), 4.22 (q, *J* = 7.5 Hz, 2H), 5.10 (m, 2H), 5.67 (brd, *J* = 11.5 Hz, 1H), 5.77 (ddd, *J* = 2.0, 5.4, 9.3 Hz, 1H), 5.83 (brd, *J* = 12.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 7.3 Hz, 2H); MS (EI, *m/z*) 416 (M^+), 384, 362, 145, 105; HRMS (EI, *m/z*) calcd for $C_{23}H_{28}O_7$ 416.1835, found 416.1851; Anal. Calcd for $C_{23}H_{28}O_7$: C, 66.33; H, 6.78. Found: C, 66.50; H, 7.14; $[\alpha]_D^{26}$ -3.6°(*c* 1.29, $CHCl_3$, 61% ee).

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-(*tert*-butyldiphenylsilyloxy)-7-[1',1'-di(methoxycarbonyl)-3'-bromo-3'-butenyl]cycloheptene (21f). IR (neat) ν 1732, 1624, 1450, 1362, 1272, 1178 cm^{-1}.; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.04 (s, 9H), 1.25 (dd, *J* = 10.7, 10.7 Hz, 1H), 1.82 (dd, *J*=11.3, 11.3 Hz, 1H), 2.05 (brdd, *J* = 3.1, 12.6 Hz, 1H), 2.21 (brd, *J* = 12.2 Hz, 1H), 2.76 (brdd, *J* = 1.9, 10.7 Hz, 1H), 2,86 (d, *J* = 15.2 Hz, 1H), 3.00 (d, *J* = 15.2 Hz, 1H), 3.01 (d, *J* = 7.9 Hz, 1H), 3.64 (s, 3H), 3.68 (s, 3H), 5.25 (brd, *J* = 10.1 Hz, 1H), 5.47 (dd, *J* = 1.7, 11.5 Hz, 2H), 5.75 (d, *J* = 2.2 Hz, 2H), 7.34-7.41 (m, 8H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.64 (d, *J* = 7.0 Hz, 4H), 8.02 (d, *J* = 7.2 Hz, 2H); MS (EI, *m/z*) 720, 718 (M^+),689, 687, 663, 661, 639, 583, 541, 539, 461, 459, 433, 431, 411, 303, 105, 91.

(3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-hydroxy-7-[1',1'-di(methoxycarbonyl)-3'-bromo-3'-butenyl]cycloheptene (21f-hydroxy). IR (neat) ν 3510, 1722, 1720, 1640, 1450, 1368, 1274, 1178 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.17 (dd, *J* = 10.9, 10.9 Hz, 1H), 1.69 (dd, *J* = 11.2, 22.5 Hz, 2H), 1.88 (brs 1H), 2.24 (dd, *J* = 3.0, 12.5 Hz, 1H), 2.32 (brd, *J* = 11.5 Hz, 1H), 3.02 (brdd, *J* = 4.1, 5.8 Hz, 1H), 3.16 (d, *J* = 7.0 Hz, 2H), 3.72 (s, 3H), 3.76 (s, 3H), 5.63 (dd, *J* = 1.7, 10.6 Hz, 1H), 5.64 (d, *J* = 1.7Hz, 1H), 5.71 (d *J* = 1.4Hz, 1H), 5.77 (ddd, *J* = 1.2, 5.7, 11.2 Hz, 1H), 5.84 (brd, *J* = 11.6 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) *d* 36.6, 38.4, 40.8, 44.3, 52.6 52.7, 59.7, 69.5, 71.1, 111.6., 123.1, 125.8, 128.4, 129.6, 130.1, 133.1, 133.6, 165.7, 169.8, 169.9; MS (EI, *m/z*) 401 (M^+-Br), 279, 105; HRMS (EI, *m/z*) for $C_{22}H_{25}O_7$ (M^+-Br), calcd 401.1617, found 401.1609; Anal. Calcd for $C_{22}H_{25}BrO_7$: C, 54.89; H, 5.23. Found: C, 54.94; H, 5.59.

(5*R*, 7*S*)-5-(*tert*-Butyldiphenylsilyl)oxy-7-[1',1'-di(ethoxycarbonyl)-3'-butenyl]cyclohepta-1,3-diene (23). IR (neat) ν 2960, 1732, 1640, 1472 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.18 (t, *J* = 7.1 Hz, 3H), 1.19 (t, *J* = 7.1 Hz, 3H), 2.37 (dd, *J* = 6.6, 14.3 Hz, 1H), 2.48 (dd, *J* = 6.6, 14.3 Hz, 2H), 2.66 (dd, *J* = 7.2, 14.2 Hz, 1H), 2.85-3.01 (m, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.1 Hz, 2H), 4.64 (brdd, *J* = 7.3, 14.9 Hz, 1H), 4.91 (m, 2H), 5.55-5.65 (m, 3H), 5.72-7.75 (m, 2H), 7.33-7.42 (m, 6H), 7.62-7.67 (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 14.0, 19.2, 26.9, 29.6, 36.8, 38.1, 39.5, 60.9, 61.0, 61.1, 72.9, 118.5, 122.1, 123.4, 127.6, 129.6, 133.0 133.7, 133.8, 134.0, 135.8, 137.3, 170.0, 170.3; MS (EI, *m/z*) 546 (M^+), 545 (M^+-1), 500, 488, 380, 345, 288, 198, 135; HRMS (EI, *m/z*) calcd for $C_{33}H_{42}O_5Si$ 546.2772, found 546.2787; Anal. Calcd for $C_{33}H_{42}O_5Si$: C, 72.49; H, 7.74. Found: C, 72.23; H, 7.83.

(5*R*,7*S*)-7-[1',1'-Di(ethoxycarbonyl)-3'-butenyl]-5-hydroxycyclohepta-1,3-diene (23-OH). IR (neat) ν 3396, 2928, 1724, 1446 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.25 (t, *J* = 6.9 Hz, 3H), 1.26 (t, *J* = 7.3 Hz, 3H), 1.95 (ddd, *J* = 11.3, 11.3, 11.3 Hz, 1H), 2.18 (dd, *J* = 3.1, 12.5 Hz, 1H), 2.52 (brs, 1H), 2.72 (ddd, *J* = 3.6, 7.4, 18.3 Hz, 2H), 3.14 (brd, *J* = 11.2 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 4H), 4.64 (brdd, *J* = 7.3, 14.9 Hz, 1H), 5.05-5.11 (m, 2H), 5.63-5.82 (m, 5H); MS (EI, *m/z*) 307 (M^+-1), 221, 91; $[\alpha]_D^{23}$ +1.7° (*c* 0.53, $CHCl_3$, 30% ee).

Typical Procedure for the Synthesis of MTPA ester (25). A solution of **6** (57.7 mg, 0.166 mmol) and K_2CO_3(229 mg, 10 equiv.) in MeOH (5.5 mL) was stirred at room temperature for 40.5 h. Solvent was removed and water was added. The aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/EtOAc=1/1) to give a colorless oil of alcohol (36.1 mg, 0.149 mmol, 88%), which was dissolved in CH_2Cl_2 (5 mL).To this solution was added (*S*)-MTPA (81.4 mg, 0.342 mmol), DMAP (42.5 mg, 0.342 mmol) and DCC (102 mg, 0.419 mmol) at 0 °C and the solution was stirred at room temperature for 90.5 h

The solution was washed with 10% HCl, aquous sat. $NaHCO_3$, and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt=5/1) to give **25** (53 mg, 77%), which was separated by preparative thin layer chromatography(hexane/AcOEt=10/1) to give **25-major** and **25-minor**.

(2'*S*, 3*R*, 7*S*)-3-[(2'-Methoxy-2'-phenyl-2'-trifluoromethyl)acetoxy]-7-[di(methoxycarbonyl)methyl]cycloheptene (25-major). IR ν (neat) 2952, 1734, 1436, 1262 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (m, 1H), 1.67 (m, 1H), 1.71 (m, 1H), 1.81 (m, 1H), 1.97 (m, 2H), 2.99 (m, 1H), 3.44 (d, *J* = 7.2 Hz, 1H), 3.48 (s, 3H), 3.64 (s, 6H), 5.54-5.73 (m, 3 H), 7.38 (m, 3H). 7.43-7.48 (m, 2H); MS (EI, *m/z*) 458 (M^+), 430, 326, 225, 189, 165, 133; HRMS (EI, *m/z*) calcd for $C_{22}H_{25}F_3O_7$ 458.1553, found 458.1579; Anal. Calcd for $C_{22}H_{25}F_3O_7$: C, 57.64; H, 5.50. Found: C, 57.85; H, 5.65.

(2'*S*, 3*S*, 7*R*)-3-[(2'-Methoxy-2'-phenyl-2'-trifluoromethyl)acetoxy]-7-[di(methoxycarbonyl)methyl]cycloheptene (25-minor). IR (neat) ν 2952, 1733, 1439, 1262 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.35 (m, 1H), 1.65 (ddd, *J* = 3.2, 3.2, 12.8 Hz, 1H), 1.69 (m, 1H), 1.77 (ddd, *J* = 2.2, 14.3, 26.2 Hz, 1H), 1.97 (brdd, *J* = 2.6, 12.2 Hz, 1H), 2.06 (m, 1H), 2.97 (m, 1H), 3.44 (d, *J* = 7.6 Hz, 1H), 3.55 (s, 3H), 3.73 (s, 3H), 3.74 (s, 3H), 5.60-5.75 (m, 3H), 7.36-7.40 (m, 3H), 7.51-7.55 (m, 2H); MS (EI, *m/z*) 458 (M^+), 430, 326, 225, 189, 165, 133; HRMS calcd for $C_{22}H_{25}F_3O_7$ 458.1553, found 458.1579; Anal. Calcd for $C_{22}H_{25}F_3O_7$: C, 57.64; H, 5.50. Found: C, 57.85; H, 5.65.

(2'*S*, 3*R*, 5*R*, 7*S*)-3-Benzoyloxy-5-[(2'-methoxy-2'-phenyl-2'-trifluoromethyl)acetoxy]-7-[di(methoxycarbonyl)methyl]cycloheptene (28-major). IR (neat) ν 1732, 1602, 1454, 1120 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.77 (ddd, *J* = 11.3, 11.3, 11.3 Hz, 1H), 1.94 (ddd, *J* = 11.0, 11.0, 11.0 Hz, 1H), 2.06 (dd, *J* = 3.4, 10.7 Hz, 1H), 2.32 (d, *J* = 12.1 Hz, 1H), 3.03 (m, 1H), 3.51 (s, 3H), 3.54 (d, *J* = 6.7 Hz, 1H), 3.76 (s, 3H), 3.77 (s, 3H), 5.38 (m, 1H), 5.73 (dd, *J* = 2.3, 11.0 Hz, 1H), 5.76 (m, 1H), 5.85 (ddd, *J* = 2.5, 2.6, 11.4 Hz, 1H), 7.35-7.39 (m, 2H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.47-7.49 (m, 3H), 7.56 (t, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.2, 35.7, 37.5, 52.6, 52.7, 55.4, 56.0, 68.8, 74.5, 127.2, 128.4, 129.6, 129.7, 129.8, 130.9, 132.2, 133.2, 133.6, 165.2. 165.5, 168.2, 168.3; MS (EI, *m/z*) 578 (M^+), 473, 457, 447, 212, 189, 163, 105; Anal. Calcd for $C_{29}H_{29}F_3O_9$: C, 60.21; H, 5.05. Found: C, 60.21; H, 5.16; $[\alpha]_D^{28}$ -24.7°(c 0.36, $CHCl_3$).

(2'*S*, 3*S*, 5*S*, 7*R*)-3-Benzoyloxy-5-[(2'-methoxy-2'-phenyl-2'-trifluoromethyl)acetoxy]-7-[di(methoxycarbonyl)methyl]cycloheptene (28-minor). IR (neat) ν 1732, 1602, 1454, 1120 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.64 (ddd, *J* = 11.3, 11.3, 11.3 Hz, 1H), 1.93 (dd, *J* = 3.3, 12.1 Hz, 1H), 2.02 (ddd, *J* = 11.7, 11.7, 11.7 Hz, 1H), 2.39 (dd, *J* = 0.7, 11.7 Hz, 1H), 3.00 (m, 1H), 3.52 (s, 3H), 3.75 (s, 3H) 3.75 (s, 3H), 3.76 (d, *J* = 2.6 Hz, 1H), 5.38 (m, 1H), 5.73 (dd, *J* = 2.3, 11.0 Hz, 1H), 5.75 (ddd, *J* = 2.1, 4.5 10.4 Hz, 1H), 5.86 (ddd, *J* = 2.5, 6.4, 11.6 Hz, 1H), 7.35-7.39 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.47-7.49 (m, 2H), 7.56 (t, *J* = 7.6 Hz, 1H), 8.02 (d, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 34.3, 36.0, 37.3, 52.6, 52.7, 55.3, 56.0, 68.8, 74.6, 127.3, 128.4, 128.4, 129.6, 129.7, 130.0, 130.9, 132.1, 133.1, 133.7, 165.3. 165.4, 168.2, 168.3; MS (EI, *m/z*) 578 (M^+), 489, 473, 457, 447, 425, 345, 212, 189, 163, 105, 91; Anal. Calcd for $C_{29}H_{29}F_3O_9$: C, 60.21; H, 5.05. Found: C, 60.12; H, 5.05; $[\alpha]_D^{28}$ -24.4°(*c* 0.69, $CHCl_3$).

(2'*S*, 3*S*, 4*R*, 6*S*)-4-Benzoyloxy-3-[di(methoxycarbonyl)methyl]-6-[(2'-methoxy-2'-phenyl-2'-trifluoromethyl)acetoxy]cycloheptene (29-major). IR (neat) ν1732, 1602, 1454, 1120cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.38 (m, 2H), 2.64 (d, *J* = 5.0 Hz, 1H), 2.67 (dd, *J* = 5.1, 11.0 Hz, 1H), 3.48 (s, 3H), 3.57 (s, 3H), 3.61 (m, 1H), 3.66 (s, 3H), 3.74 (d, *J* = 10.2 Hz, 1H), 5.29-5.35 (m, 2H), 5.72 (dd, *J*

= 5.7, 11.4 Hz, 1H), 5.84 (m, 1H), 7.28-7.42 (m, 5H), 7.52-7.57 (m, 2H), 7.68 (m, 1H), 7.91 (d, J = 7.2 Hz, 2H); MS (EI, m/z) 578 (M$^+$), 548, 457, 345, 223, 212, 189, 163, 105, 91; Anal. Calcd for $C_{29}H_{29}F_3O_9$: C, 60.21; H, 5.05. Found: C, 60.00; H, 5.24.

(2'*S*, 3*R*, 4*S*, 6*R*)-4-Benzoyloxy-3-[di(methoxycarbonyl)methyl]-6-[(2'-methoxy-2-phenyl-2'-trifluoromethyl)acetoxy]cycloheptene (29-minor). IR (neat) ν 1732, 1602, 1454, 1120 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 2.45 (m, 1H), 2.49 (m, 1H), 2.56 (m, 2H), 3.40 (s, 3H), 3.59 (m, 1H), 3.58 (s, 3H), 3.65 (s, 3H), 3.71 (d, J = 10.1 Hz, 1H), 5.30-5.36 (m, 2H), 5.63-5.65 (m, 2H), 7.28-7.42 (m, 5H), 7.52-7.57 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.92 (d, J = 7.2 Hz, 2H); MS (EI, m/z) 578 (M$^+$), 548, 473, 457, 345, 212, 189, 163, 105, 91; Anal. Calcd for $C_{29}H_{29}F_3O_9$: C, 60.21; H, 5.05. Found: C, 60.00; H, 5.24.

Synthesis of the Substrates

6-(*tert*-Butyldiphenylsilyloxy)-1,3-cycloheptadiene (12). To a solution of **11**[8] (15.13 g, 137.35 mmol) and imidazole (31 g, 452.9 mmol) in CH$_2$Cl$_2$ (100 mL) was added TBDPSCl (^{t}BuPh$_2$SiCl) (39.1 mL, 150.5 mmol) at 0 °C and the solution was stirred at room temperature for 2 h. The organic layer was washed with brine, dried over Na$_2$SO$_4$ and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt=20/1) to give colorless oil of **12** (45.5 g, 95%). IR (neat) ν 2954, 1613, 1471, 1254 1079 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.05 (s, 9H), 1.06-1.09 (m, 2H), 2.43-2.45 (m, 2H), 4.10 (m, 1H), 5.49-5.57 (m, 2H), 5.72-5.77 (m, 2H), 7.32-7.41 (m, 6H), 7.62-7.70 (m, 4H); MS (EI, m/z) 360 (M$^+$), 348, 303, 289, 259, 211, 199, 183, 167, 91; Anal. Calcd for $C_{23}H_{28}OSi$: C, 79.25; H, 8.09. Found: C, 79.13; H, 7.95.

5-(*tert*-Butyldiphenylsilyloxy)-3,7-epidioxycycloheptene (13). A solution of **12** (45.49g, 130.51 mmol) was irradiated with halogen lamp in 2-propanol (1 L) in the presence of rose bengal (60 mg) for 4 days under oxygen. The solution was passed through the short silica gel to remove rose bengal and the solvent was removed, The residue was purified by column chromatography on silica gel (hexane/Et$_2$O=15/1) to give *syn*-**13** (22.71 g, 46%) and *anti*-**13** (1.89 g, 4 %). *syn*-**13**. IR (neat) ν 2956, 1472, 1428, 1144, 1112 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.04 (s, 9H), 2.12-2.15 (m, 4H), 3.72 (m, 1H), 4.53-4.56 (m, 2H), 6.18 (dd, J = 3.1, 4.8 Hz, 2H), 7.34 (t, J = 7.0 Hz, 4H), 7.42 (t, J = 7.4 Hz, 2H), 7.65 (d, J = 7.9 Hz, 4H); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 19.0 , 26.8, 40.7, 65.8, 67.1, 73.3, 127.5, 128.4, 129.6, 134.1, 135.7; MS (EI, m/z) 323 [M$^+$-^{t}Bu], 306, 279, 245, 225, 215, 199, 183, 173; Anal. Calcd for $C_{23}H_{28}O_3Si$: C, 72.59; H, 7.41. Found: C, 72.67; H, 7.61. *anti*-**13**. IR (neat) ν 2956, 1472, 1428, 1144, 1112 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 1.09 (s, 9H), 1.08-1.13 (m, 1H), 1.68-1.74 (m, 3H), 4.06 (m, 1H), 4.56 (m, 2H), 6.50 (dddd, J = 1.0, 2.2, 6.9, 11.9 Hz, 2H), 7.34 (t, J = 7.0 Hz, 4H), 7.42 (t, J = 7.4 Hz, 2H), 7.65 (d, J = 7.9 Hz, 4H); ^{13}C NMR (67.8 MHz, CDCl$_3$) δ 19.1, 25.4, 26.8, 27.6, 74.2, 74.3, 80.6, 125.5, 127.6, 127.7, 129.4, 129.6, 129.7, 129.8, 133.5, 134.0; MS (EI, m/z) 323 [M$^+$-^{t}Bu], 306, 279, 245, 225, 215, 199, 183, 173; Anal. Calcd for $C_{23}H_{28}O_3Si$: C, 72.59; H, 7.41. Found: C, 72.67; H, 7.61.

***r*-3,*c*-7-Dihydroxy-*c*-5-(*tert*-butyldiphenylsilyl)oxycycloheptene (14).** To a solution of *syn*-**13** (22.71 g, 56.675 mmol) in THF (200 mL) and H$_2$O (10 mL) was added Al-Hg untill the spot of the starting material was disappeared on TLC. The solution was passed through the short celite column and the solvent was removed. The residue was purified by column chromatography on silica gel (Et$_2$O) to give colorless crystals of **14** 15.98 g, 70 %), which was recrystalyzed from MeOH. mp 174-175 °C; IR (neat) ν 3331, 1373 cm^{-1};^{1}H NMR (270 MHz, CDCl$_3$) δ 1.04 (s, 9H), 1.80 (brd, J = 11.2 Hz, 1H), 1.86 (brd, J = 11.2 Hz, 1 H), 1.99-2.11 (m, 4H), 4.10 (m, 1H), 4.28 (brd, *J* = 11.0 Hz, 2H), 5.71 (s, 2H), 7.34 (t, *J* = 7.0 Hz, 4H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.65 (d, *J* = 7.9 Hz, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 19.0 , 26., 45.1, 67.0, 69.6, 127.6, 129.8, 133.7, 134.6, 135.8; MS (EI, *m/z*) 382 (M^+), 367, 354, 322, 199; Anal. Calcd for $C_{23}H_{30}O_3Si$: C, 72.20; H, 7.90. Found: C, 72.13; H, 7.97.

***r*-3,*c*-7-Dibenzoyloxy-*c*-5-(*tert*-butyldiphenylsilyl)oxycycloheptene (15b)**. To a solution of **14** (15.98 g, 41.76 mmol) and pyridine (23.6 mL, 292.32 mmol) in CH_2Cl_2 (120 mL) was added benzoyl chloride (24.6 mL, 212.97 mmol) at 0 ℃ and the solution was stirred at room temperature for 2 h. A solution of sat. NH_4Cl was added and the organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt=5/1) to give colorless crystals of **15b**, which was recrysatalyzed from AcOEt (19.74 g, 80%). mp 109-110 ℃; IR (neat) ν 1740, 1450 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.04 (s, 9H), 2.03 (ddd, *J* = 11.2, 15.0, 9.9 Hz, 2H), 2.23 (brd, *J* = 15.0 Hz, 2H), 4.17 (m, 1H), 5.03 (brd.d, *J* = 11.2 Hz, 2H), 5.78 (s, 2H), 7.32-7.68 (m, 16H), 8.03 (d, *J* = 7.6 Hz, 4H); MS (EI, *m/z*) 590 (M^+), 533, 468, 199; Anal. Calcd for $C_{37}H_{38}O_5Si$: C, 75.22; H, 6.48. Found: C, 75.44; H, 6.54.

***r*-3,*c*-7-Dibenzoyloxy-*c*-5-(*tert*-butyldimethylsilyl)oxycycloheptene (15a)**. mp 104-105 ℃; IR (neat) ν 1727, 1451 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 6H), 0.86 (s, 9H), 1.94 (ddd, *J* = 10.6, 12.2, 11.8 Hz, 2H), 2.24 (brd, 11.8 Hz, 2H), 4.18-4.24 (m, 1H), 5.61 (brd, 10.7 Hz, 2H), 5.86 (s, 2H), 7.45 (t, *J* = 7.7 Hz, 4H), 7.58 (t, *J* = 7.2 Hz, 2H), 8.07 (d, *J* = 7.2 Hz, 4H); MS (EI, *m/z*) 466 (M^+), 409, 344, 222;Anal. Calcd for $C_{27}H_{34}O_5Si$: C, 69.49; H, 7.34. Found: C, 69.44; H, 7.42.

***r*-3,*c*-7-Dibenzoyloxy-*c*-5-hydroxycycloheptene (15c)**. mp 107-108.5 ℃; IR (neat) ν 3505, 1727, 1451 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.67 (d, *J* = 2.2H, 1H), 1.93 (dd, *J* = 10.5, 12.1, 11.8 Hz, 2H), 2.11 (brdd, *J* = 11.8 Hz, 2H), 4.16 (m, 1H), 5.62 (brd, *J* = 10.5 Hz, 2H), 5.91 (s, 2H), 7.45 (d, *J* = 7.6 Hz, 4H), 7.58 (t, *J* = 7.2 Hz, 2H), 8.07 (t, *J* = 7.0 Hz, 4H); MS (EI, *m/z*) 352 (M^+), 334, 230, 108; Anal. Calcd for $C_{21}H_{20}O_5$: C, 71.57; H, 6.29. Found: C, 71.44; H, 6.42.

***r*-3,*c*-7-Dibenzoyloxy-*c*-5-methoxycycloheptene (15d)**. mp 136.5-137.5 ℃; IR (neat) ν 1727, 1451 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.86 (ddd, *J* = 11.1, 11.7, 10.7 Hz, 2H), 2.45 (brd, *J* = 11.7 Hz, 2H), 3.41 (s, 3H), 3.61-3.73 (m, 1H), 5.63 (brd, *J* = 10.7 Hz, 2H), 5.91 (s, 2H), 7.47 (d, *J* = 7.5 Hz, 4H), 7.57 (t, *J* = 7.9 Hz, 2H), 8.07 (t, *J* = 7.0 Hz, 4H); MS (EI, *m/z*) 364 (M^+), 346, 242, 120; Anal. Calcd for $C_{22}H_{22}O_5$: C, 72.51; H, 5.53. Found: C, 72.44; H, 5.42.

Typical Procedure for the Syntheses of Hydroazulene Derivatives and Hydrobenzocycloheptene Derivative

(7*S*,3a*R*,8a*S*)-7-(*tert*-Butyldiphenylsilyloxy)-1,1-di(methoxycarbonyl)-3-methylene-1,2,3,3a,6,7,8,8a-octahydroazulene (30). A solution of **21d** (930.1 mg, 1.390 mmol) and $Pd(PPh_3)_4$ (15.7 mg, 0.070 mmol) in AcOH (18 mL) was warmed at 70 ℃ for 39 h. The solvent was removed under reduced pressure and ethyl acetate was added to the residue. The organic layer was washed with sat. $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate=20/1) to give a colorless oil of **30** (661.6 mg, 87%). IR (neat) ν 1728, 1658, 1464, 1446, 1368, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.19 (t, *J* = 7.1 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H), 1.66 (m, 1H), 2.13 (dt, *J* = 2.4, 11.9 Hz, 1H), 2.23-2.45 (m, 2H), 2.60-2.66 (m, 2H), 3.10 (d, *J* = 7.3 Hz, 1H), 3.22 (brd, *J* = 11.3 Hz, 1H), 3.64 (tt, *J* = 3.0, 10.0 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.20 (q, *J* = 7.1 Hz, 2H), 4.85 (bs, 1H), 4.93 (bs, 1H), 5.42-5.48 (m, 1H), 5.76 (dd, *J* = 10.9 Hz, 1H), 7.35-7.45 (m, 6H), 7.66-7.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1, 19,.2, 27.0, 38.4, 41.1, 43.1, 47.0, 48.2, 61.0, 61.1, 61.4, 70.4, 105.9, 126.9, 127.5, 129.5, 134.3, 134.7, 135.7, 136.5, 151.2, 171.0, 171.1; MS (EI, *m/z*) 546 (M$^+$), 531, 501, 489; HRMS (EI, *m/z*) calcd for $C_{33}H_{42}O_5Si$ 546.2778, found 546.2790; Anal. Calcd for $C_{33}H_{42}O_5Si$: C, 72.48; H, 7.74. Found: C, 72.08; H, 7.93; $[\alpha]_D^{24}$ +19.2$_\circ$ (*c* 0.96, $CHCl_3$, 70% ee).

(3*R*,7*S*)-3-Benzoyloxy-7-[1',1'-di(methoxycarbonyl)-3'-butenyl]cycloheptene (8). To a suspension of NaH (6.2 mg, 0.155 mmol) in THF (0.3 mL) was added **6** (35.7 mg, 0.103 mmol) in THF (0.8 mL) at 0 ℃ and the solution was stirred at room temperature for 15 min. To this solution was added allyl bromide (10 μL, 0.206 mmol) in THF (0.2 mL) and the solution was stirred at room temperature for 24 h. A solution of sat. NH_4Cl was added ant the aqueous layer was extracted with ethyl ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (hexane/Et_2O=10/1) to give colorless oil of **8** (8.7 mg, 22%). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.18-2.50 (m, 1H), 1.65 (ddd, *J* = 3.0, 12.0, 14.0 Hz, 1H), 1.79-2.12 (m, 4H), 2.68 (brd, *J* = 7.3 Hz, 2H), 2.95 (dd, *J* = 2.7 10.7 Hz, 1H), 3.73 (s, 3H), 3.74 (s, 3H), 5.06-5.07 (m, 2H), 5.73-5.81 (m, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 8.05 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR (67.9 MHz, $CDCl_3$) δ 27.7, 29.2, 32.2, 38.4, 43.5, 52.1, 52.1, 61.5, 74.4, 118.9, 128.3, 129.5, 130.5, 131.1, 132.8, 133.7, 165.7, 170.9, 170.9; MS (EI, *m/z*) 386 (M$^+$), 327, 281, 265, 232, 214, 204, 145, 105, 91, 77; Anal. Calcd for $C_{22}H_{26}O_6$: C, 66.64; H, 7.98. Found: C, 66.98; H, 7.96.

(3a*S*,8a*S*)-1,1-Di(methoxycarbonyl)-3-methylene-1,2,3,3a,6,7,8,8a-octahydroazulene (7). IR (neat) ν1728, 1658, 1464, 1446, 1250 cm-1; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.32 (m, 2H), 1.77-1.82 (m, 1H), 1.98-2.05 (m, 1H), 2.08-2.15 (m, 2H), 2.31-2.40 (m, 1H), 2.75 (ddd, *J* = 2.6, 5.4, 17.2 Hz, 1H), 3.12 (d, *J* = 17.2 Hz, 1H), 3.26 (brd.d, *J* = 11.6 Hz, 1H), 3.72 (s, 6H), 4.96 (dd, *J* = 2.6, 4.6 Hz, 1H), 4.99 (bs, 1H), 5.75-5.95 (m, 2H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 26.0, 28.6, 33.1, 41.1, 47.5, 50.2, 52.7, 52.8, 61.5, 105.7, 132.4, 134.8, 151.6, 171.3, 171.5; MS (EI, *m/z*) 264 (M$^+$), 233, 202; Anal. Calcd for $C_{15}H_{20}O_4$: C 68.16; H, 7.62. Found: C, 68.04; H, 7.74.

(1*S*, 5*S*, 7*S*)-5-(*tert*-Butyldiphenylsilyl)oxy-8,8-di(methoxycarbonyl)-11-methylenebicyclo[5.4.0]undec-2-ene (*trans*-31). IR (neat) ν 1728, 1658, 1464, 1446, 13368, 1250 cm^{-1}; ^{1}H NMR (500MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.70 (ddd, *J* = 1.4, 6.4, 12.9 Hz, 1H), 1.94 (m, 2H), 2.03-2.11 (m, 2H), 2.28 (ddd, *J* = 2.9, 7.2, 9.2 Hz, 2H), 2.40 (ddd, *J* = 1.7, 3.7, 12.8 Hz, 2H), 2.78 (dd, *J* = 4.5, 11.9 Hz, 1H), 3,50 (s, 3H), 3.73 (s, 3H), 3.99 (m, 1H), 4.65 (d, *J* = 25.0 Hz, 2H), 5.51 (ddd, *J* = 1.9, 5.2, 10.5 Hz, 1H), 5.68 (m, 1H), 7.32-7.41 (m, 6H), 7.62 (t, *J* = 8.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 19.2 26.9, 32.1, 33.4, 34.7, 39.2, 43.7, 48.0, 51.9, 52.3, 60.7, 73.1, 107.7, 124.9, 127.7, 127.5, 127.6, 129.4, 130.7, 134.6, 134.7, 135.7, 135.8, 148.9, 170.8, 172.2; MS (EI, *m/z*) 532 (M$^+$), 517, 501, 475; HRMS (EI, *m/z*) calcd for $C_{28}H_{31}O_5Si$ (M$^+$-^{t}Bu) 475.1883, found 475.1912; Anal. Calcd for $C_{32}H_{40}O_5Si$: C, 72.14; H, 7.56. Found: C, 72.08; H, 7.75.

(3a*R*, 7*S*,8a*S*)-7-(*tert*-Butyldiphenylsilyl)oxy-1-(2'-pyridylthio)-3-methylene-1,2,3,3a,6,7,8,8a-octahydroazulene (36). A solution of **30** (6.54 g, 11.96 mmol) and LiCl (1.01 g, 23.92 mmol) in HMPA (100 mL) was heated at 120 ℃ for 24 h. Ether was added and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (hexane/Et_2O=15/1) to give **34** (5.16g, 91%). IR (neat) ν 1733, 1446 cm^{-1}; HRMS (EI, *m/z*) calcd for $C_{30}H_{38}O_3Si$ 474.2590, found 474.2598; Anal. Calcd for $C_{30}H_{38}O_3Si$: C, 75.90; H, 8.06. Found: C, 75.61; H 8.03. A solution of **34** (3.881 g, 8.175 mmol) in EtOH (15 mL) and aqueous 15% NaOH (10 mL) was stirred at room temperature for 12 h. EtOH was removed and the aqueous layer was acidify by10% HCl at 0 ℃. The aqueous layer was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/AcOEt=5/1) to give a colorless oil of carboxylic acid (3.349 g, 93%, α:β=3:1). **α-isomer**: IR (neat) ν 3072, 1704, 1428, 1110, 1070 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.62 (m, 1H), 1.55-1.69 (m, 1H), 2.31-2.40 (m, 3H), 2.44 (m, 1H), 2.61 (m, 1H), 2.75 (m, 1H), 2.94 (brd, *J* = 8.9 Hz, 1H), 3.12 (m, 1H), 3.58 (m, 1H), 4.88 (dd, *J* = 1.9, 20.7 Hz, 2H), 5.54 (m, 1H), 5.78 (m, 1H), 7.29-7.42 (m, 6H), 7.61-7.69 (m, 4H); MS (EI, *m/z*) 446 (M^+), 400, 389, 371, 311, 267, 199, 145; HRMS (EI, *m/z*) for $C_{28}H_{34}O_3Si$, calcd 446.2277, found 446.2287; Anal. Calcd for $C_{28}H_{34}O_3Si$: C, 75.29; H, 7.67. Found: C, 75.16; H, 7.73. To a solution of carboxylic acid (659.3 mg, 1.476 mmol) in CH_2Cl_2 (5 mL) was added oxalyl chloride (281 mg, 2.214 mmol) at 0 ℃ and the solution was stirred at the same temperature for 15 min. Solvent was removed. To this residue was added a benzene solution of pyridine (143.2 mL, 1.771 mmol), AIBN (48.4 mg, 0.295 mmol), and **35** (225.3 mg, 1.771 mmol) and the solution was refluxed for 12 h. The organic layer was washed with sat. $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/Et_2O=20/1) to give **36** (575.4 mg, 76%) and **37** (25.6 mg, 4.3 %). **37**: ^1HNMR (500 MHz, $CDCl_3$) δ 1.06 (s, 9H), 1.90 (ddt, *J* = 2.2, 5.1, 7.3 Hz, 1H), 1.99 (m, 1H), 2.26 (ddd, *J* = 2.2, 10.3, 19.1 Hz, 2H), 2.35-2.43 (m, 1H), 2.61 (d, *J* = 17.5 Hz, 1H), 2.92 (ddd, *J* = 3.0, 6.3, 14.8 Hz, 1H), 3.21 (brd, *J* = 9.2 Hz, 1H), 3.58 (tt, *J* = 2.2, 10.1 Hz, 1H), 4.33 (t, *J* = 5.8 Hz, 1H), 4.92 (dd, *J* = 2.9, 5.6 Hz, 2H), 5.45-5.52 (m, 1H), 5.78 (dt, *J* = 3.0, 10.6 Hz, 1H), 6.94-6.96 (m, 1H), 7.29-7.45 (m, 7H), 7.61 (d, *J* = 7.9 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 3H), 8.37 (d, *J* = 4.7 Hz, 1H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 19.1, 27.0, 29.7, 38.6, 41.4, 43.7, 47.1, 47.4, 48.7, 70.5, 106.7, 119.4, 123.1, 126.8 , 127.5, 129.4,134.8, 134.6, 135.8, 136.8, 149.3, 153.1, 159.3; MS (EI, *m/z*) 510 (M^+-1), 453, 399, 342, 291, 265, 199, 145, 122; HRMS (EI, *m/z*)calcd for $C_{32}H_{37}NOSSi$ 511.2024, found 511.2017.

(3a*R*, 7*S*,8a*S*)-7-(tert-Butyldiphenylsilyl)oxy-3-methylene-1,2,3,3a,6,7,8,8a-octahydroazulene (37). To a suspension of $LiAlH_4$ (28.7 mg, 0.755 mmol) in THF (2 mL) was added $CuCl_2$ (50.7 mg, 0.377 mmol) at 0 ℃ and the solution was stirred at roome temperature for 1 h. To this solution was added a solution of **36** (48.2 mg, 0.094 mmol) in THF (1 mL) and the solution was refluxed for 3.5 h. To this solution was added 10% HCl at 0 ℃ and the organic layer was extracted with Et_2O. The organic layer was washed with sat. $NaHCO_3$ solution and brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (hexane/Et_2O=50/1) to give **37** (35.0 mg, 92%). IR (neat) ν1654, 1428, cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.05 (s, 9H), 1.25 (dd, *J* = 8.7, 20.3 Hz, 1H), 1.37 (ddd, *J* = 2.0, 6.0, 11.2 Hz, 1H), 1.59 (d, *J* = 8.2, 15.1 Hz, 1H), 1.61-1.66 (m, 1H), 2.19-2.29 (m, 4H), 2.25 (dd, *J* = 8.2, 15.1 Hz, 1H), 2.75 (brd, *J* = 8.1 Hz, 1H), 3.55 (m, 1H), 4.83 (dd, *J* = 2.0, 7.6 Hz, 2H), 5.47 (m, 1H), 5.80 (m, 1H), 7.33-7.43 (m, 6H), 7.65-7.69 (m, 4H); ^{13}C NMR (67.8 MHz, $CDCl_3$) δ 19.1, 27.0, 31.8, 32.7, 38.7, 44.2, 47.2, 49.5, 70.2, 123.4, 124.4, 126.5, 127.4, 129.4, 134.5, 134.6, 135.7, 155.8; MS (EI, *m/z*) 402 (M^+), 387, 345, 267, 199; HRMS (EI, *m/z*) calcd for $C_{27}H_{34}OSi$ 402.2375, found 402.2377; Anal. Calcd for $C_{27}H_{34}OSi$: C, 80.54; H, 8.51. Found: C, 80.18; H, 8.64; $[\alpha]_D^{28}$ -14.5°(*c* 2.99, $CHCl_3$).

REFERENCES AND NOTES

1. (a) B. M. Trost, *Angew. Chem.*, **1989**, *28*, 1173. Trost, B. M.; Verhoeven, T. R. *J. Am. Chem. Soc.* **1977**, *99*, 1649–1651. Trost, B. M.; Van. Vranken, D. L. *J. Am. Chem Soc.* **1990**, *112*, 1261–1263.

Trost, B. M.; Van Vranken, D. L. *J Am. Chem. Soc.*, **1993**, *115*, 444–458. Trost, B. M.; Van Vranken, D. L. *J. Am. Chem. Soc.* **1991**, *113*, 6317–6318. Trost, B. M.; Krische, M. J.; Radinov, R.; Zanoni, G, *J. Am. Chem. Soc.*, **1996**, *118*, 6297. (b) Hayashi, T.; Kumada, M. "*Asymmetric Synthesis*"; Morrison, J. D., Ed.; Academic Press, Oxford, **1985**; Vol.5, pp 147–169. Hayashi, T.; Hagihara, T.; Konishi, M; Kumada, M. *J Am. Chem. Soc.* **1983**, *105*, 7767–7768. Hayashi, T.; Yamamoto, A; Ito, Y. *Tetrahedron Lett.* **1988**, *29*, 669–672. Hayashi, T.; Yamamoto, A.; Ito, Y.; Nishioka, E.; Miura, H.; Yanagi, K. *J. Am. Chem. Soc.* **1989**, *111*, 6301–6303. (c) Reister, O. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 547–549. (d) Müller, D.; Umbricht, G.; Weber, B.; Pfaltz, A. *Helv. Chim. Acta* **1991**, *74*, 232–240. (e) Leutengger, U.; Umbricht, G.; Fahrni, C.; von Matt, P.; Pfaltz, A. *Tetrahedron* **1992**, *48*, 4123–4156. (f) Pfaltz, A. *Acc. Chem. Res.* **1993**, *26*, 339–345. (g) Kubota, H.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1993**, *34*, 8135–8138. (h) Takemoto, T.; Nishikimi, Y.; Sodeoka, M.; Shibasaki, M. *Tetrahedron Lett.* **1992**, *33*, 3531–3532.

2. a) Mori, M.; Nukui, S.; Shibasaki, M. *Chem. Lett.*, **1991**, 1797. b) Yoshizaki, H.; Satoh, H.; Sato, Y.; Seiji, N.; Shibasaki, M.; Mori, M. *J. Org. Chem.*, **1995**, *60*, 2016.
3. Fiaud, J-C.; A-Zouioueche, L. *J. Chem. Soc., Chem. Commun.*, **1986**, 390.
4. These were calculated using Molecular Mechanics (CAChe™) software.
5. (a) Grubbs, R. H.; Devries, R. A. *Tetrahedron Lett.*, **1977**, 1879-1880. (b) Trost, B. M.; Murphy, D. J. *Organometallics*, **1990**, *4*, 1143-1146.
6. The enantioselectivities were established by chiral stationary-phase HPLC (DAICEL CHIRALCEL OD eluted by hexane /^{i}PrOH (9/1).
7. Oppolzer, W.; Gaudin, J.-M.; Birkinshaw, T.-N. *Tetrahedron Lett.* **1988**, *29*, 4715–4708. Oppolzer, W. *Pure & Appl. Chem.* **1990**, *62*, 1941–1948. Oppolzer, W.; Gaudin, J.-M. *Helv. Chim. Acta* **1987**, *70*, 1477–1481.
8. (a) Radlick, P. *J. Org. Chem.* **1964**, *29*, 960. (b) Schuster, D. I.; Palmer, J. M.; Dickerman, S. C. *J. Org. Chem.* **1966**, *31*, 4281–4282.
9. The enantioselectivities of **16c** and **17c** were established by chiral stationary-phase HPLC (DAICEL CHIRALCEL OD eluted by hexane /^{i}PrOH (9/1). Converting of other compounds **16a**, **16b**, and **16d**, and compounds **17a**, **17b**, **17d** into **16c** and **17c**, respectively, the enantioselectivities of them were determined.
10. Uozumi, Y.; Hayashi, T. *J. Am. Chem. Soc.* **1991**, *113*, 9887–9888.
11. Trost, B. M.; Phan, L. T. *Tetrahedron Lett.* **1993**, *34*, 4735–4738.
12. The enantioselectivities were determined after deprotection of the silyl group using DAICEL CHIRALCEL OD eluted by hexane/^{i}PrOH (9/1).
13. The enantioselectivities of **23** was established by chiral stationary-phase HPLC (DAICEL CHIRALCEL OJ eluted by hexane /^{i}PrOH (9/1) after deprotection of silyl group.
14. Harada, N.; Nakanishi, K. *Circular Dichroic Spectroscopy-Exciton Coupling in Organic Stereochemistry*; University Science Books: Mill Valley, CA, **1983**.
15. Ohtani, I.; Kusumi, T.; Kashman, Y.; Kakisawa, H. *J. Am. Chem. Soc.* **1991**, *113*, 4092–4096.

16 (a) Devreese, A. A.; De Clercq, P. J.; Vandewalle, M. *Tetrahedron Lett.* **1980**, *21*, 4767–4769. (b) Rigby, J. H.; Senanayake, C. *J. Am. Chem. Soc.* **1987**, *109*, 3147–3149. (c) Ito, K.; Iida, T.; Kobayashi, T. *Phytochemistry* **1984**, *23*, 188–190. Mathur, S. B.; Kulkarni, G. H.; Keller, G. R.;

Bhatacharyya, S. C.; Sivnonovic, D.; Rao, A. S. *Tetrahedron* **1965**, *21*, 3575–3590. Rigby, J. H.; Wilson, J. Z. *J. Am. Chem. Soc.* **1984**, *106*, 8217–8224. (d) Devreese, A. A.; Demuynck, M.; De Clercq, P. J.; Vandewalle, M. *Tetrahedron* **1983**, *39*, 3049–3054. Demuynck, M.; Devreese, A. A.; De Clercq, P. J.; Vandewalle, M. *Tetrahedron Lett.* **1982**, *23*, 2501–2504. (e) Kobayashi, M.; Son, B. W.; Kido, M.; Kyogoku, Y.; Kitagawa, I. *Chem. Pharm. Bull. Jpn.* **1983**, *31*, 2160–2163. (f) Kobayashi, M.; Son, B. W.; Kyogoku, Y.; Kitagawa, I. *Chem. Pharm. Bull. Jpn.* **1984**, *32*, 1667–1670.

17. Barton, D. H. R.; Crich, D.; Motherwell, W. B. *J. Chem. Soc., Chem. Commun.* **1983**, 939–941.

18. Mukaiyama, T.; Narasawa, K.; Maekawa, K.; Furusato, M. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 2285.

(*Received in Japan* 22 *January* 1997; *accepted* 28 *February* 1997)