Pergamon

Tetrahedron, Vol. 53, No. 48, pp. 16253-16276, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)01013-2

Enantioselective Allene/Enone Photocycloadditions: The Use of an Inexpensive Optically Active 1,3–Disubstituted Allene

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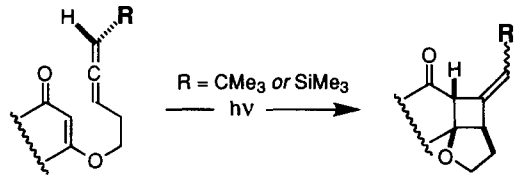
Abstract. We report the preparation and use of an inexpensive readily prepared optically active 1,3–disubstituted allene that may be utilized for enantioselective intramolecular allene/enone photocycloadditions. In addition, we describe novel substrates for intramolecular [2+2] photocycloadditions which substantially expand the scope of the process to include amino- and thio- tethered allene/enones. © 1997 Elsevier Science Ltd.

Introduction. The [2+2] photocycloaddition reaction of allenes and α,β–unsaturated carbonyl compounds is a powerful and important reaction for the construction of complex multi-ring systems. The fused exomethylenecyclobutane moiety in the products of such photocycloadditions is amenable to subsequent synthetic manipulations, affording a wide range of derivatives.[1] We have been interested in developing and studying enantioselective versions of the intramolecular allene/enone photocycloadditions as a means of preparing optically active polycyclic systems. In this regard, we have reported that the asymmetric [2+2] photocycloaddition of 1,3–disubstituted allenes with enones and enoates gives photoadducts in useful levels of enantioselectivity.[2] These photocycloaddition reactions prescribed the use of optically active allenes bearing *tert*–butyl– or trimethylsilyl– moieties as the stereochemical controlling groups (Eq 1).

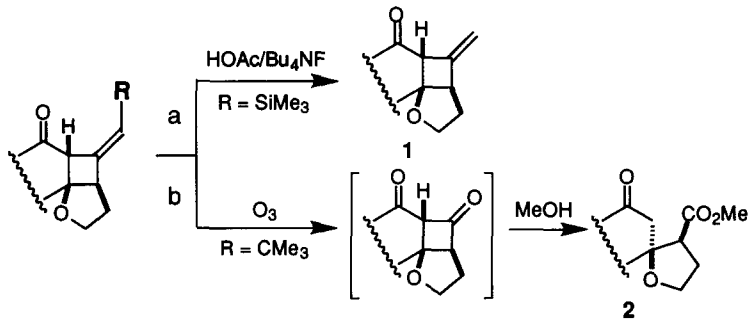


(1)

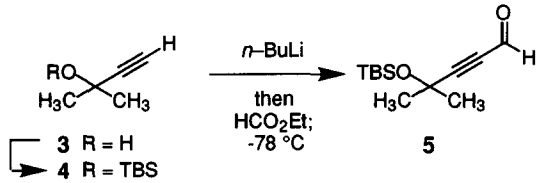
As shown in Scheme 1, when the unsubstituted exomethylenecyclobutane adducts **1** are desired, the trimethylsilyl substituted allenes are the optically active reagent of choice for the photocycloaddition reaction, since the vinylsilane photoproducts are conveniently protodesilylated (Path a, Scheme 1).[2b] In a complementary fashion, when products derived from the corresponding reactive cyclobutanones are desired, the *tert*–butyl substituted allenes afford photoproducts which may be ozonolyzed in MeOH to give ketoesters **2** (Path b, Scheme 1). A drawback to the use of the *tert*–butyl substituted allenes in the latter process stems from inconveniences associated with the volatility and the expense of this allene class. Herein, we report the use of an optically active 1,3–disubstituted allene with a novel stereochemical controlling group (Eq 1, R = $CMe_2OSi^tBuMe_2$). This allene provides a useful alternative to the *tert*–butyl substituted allenes initially reported and, importantly, gives photoadducts in equally high enantioselectivities and yields. In contrast to the

preparation of the *tert*–butyl substituted allene which requires expensive, volatile *tert*–butyl acetylene (≈ \$5/g), the preparation of the novel optically active allene described herein utilizes inexpensive 3–methyl–1–butyn–3–ol **3** (\$0.04/g). In addition, the preparation of the chiral allene is facilitated by the application of the catalytic, enantioselective acetate aldol addition we have previously reported.[3] Using this efficient catalytic process, we synthesized optically active secondary propargyl alcohol **8** which functions as the precursor to the chiral 1,3–disubstituted allene used in this study.

Scheme 1



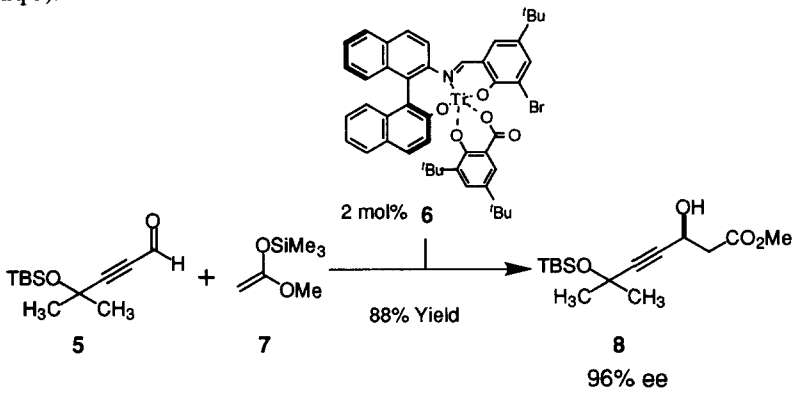
Results and Discussion. The synthesis of optically active allene alcohol **12** (Scheme 2) commences with the commodity chemical butynol **3** (Eq 2). Protection of the tertiary alcohol (^{t}BuMe$_2$SiCl, DMAP, Im) yielded **4**, which gave aldehyde **5** upon deprotonation (*n*–BuLi, THF) and reaction with ethyl formate (-78 °C). This convenient direct synthesis of ynal **5** may be conducted on large scale and avoids intermediates requiring subsequent oxidation (1° propargyl alcohol → aldehyde) or reduction (alkynoate → aldehyde).[4] With aldehyde **5** in hand, we investigated the enantioselective, catalytic acetate aldol addition reaction.



(2)

At the outset of this study, it was unclear whether such propynals could be successfully employed as substrates in this reaction to afford optically active propargyl alcohols. Two general approaches have been described for the enantioselective synthesis of secondary propargyl alcohols: (1) ynone reductions, and (2) aldehyde additions. The stereoselective reduction of α,β–alkynyl ketones has been carried out with several stoichiometric reductants including Alpine–Borane,[5] Chirald–$LiAlH_4$,[6,7] lithium NB–Enantrane,[8] BINAL–H,[9] and DIP–Cl;[10] and, more recently, a catalytic oxazaborolidine•catecholborane system has been reported.[11] As an alternative method for the preparation of propargyl alcohols, enantioselective additions of alkylmetal and alkynylmetal reagents to alkynyl and aliphatic aldehydes, respectively, have been reported.[12,13] The catalytic, enantioselective acetate–aldol addition reaction of ynals has only been described in a single study. Using 20–30 mol% of a catalyst prepared from $Sn(OTf)_2$ and a chiral diamine, addition of the *O*–trimethylsilyl enol ether

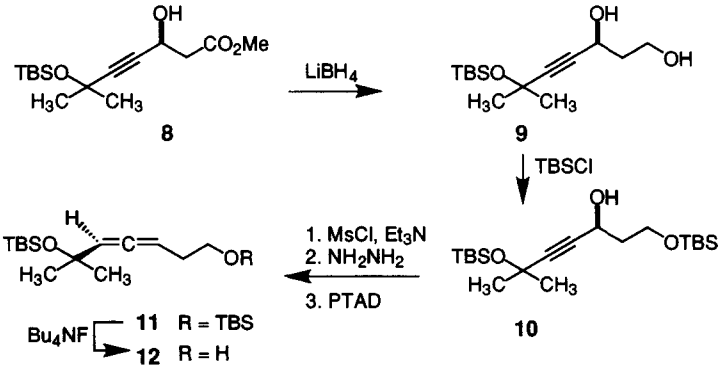
derivative of *S*–ethyl thioacetate with α,β–heptynal, phenyl propynal, and trimethylsilyl propynal proceeded in 77–88% ee's and 71-78% yields.[14,15] Application of the catalytic procedure we have described previously proved useful.[16] In the event, using catalyst **6**, enantioselective acetate aldol addition of the *O*–silyl ketene acetal **7** to aldehyde **5** afforded hydroxy ester **8** (88% yield). The optical purity (96% ee) of this adduct was readily determined upon conversion to the corresponding (*S*)–MTPA ester and analysis by ^{1}H NMR spectroscopy (Eq 3).[17]



(3)

The final steps in the synthesis of allene **12** commenced with reduction of ester **8** with $LiBH_4$ (0°C, Et_2O) giving diol **9** in 99% yield (Scheme 2). Selective monoprotection (^{t}BuMe$_2$SiCl, DMAP, CH_2Cl_2) of the primary alcohol in **9** afforded **10** (83%). Stereospecific conversion of alcohol **10** to optically active allene **11** was effected using the Myers allene synthesis procedure.[18] Finally, the primary *O*–silyl ether **11** was selectively desilylated (Bu_4NF) to give allenyl alcohol **12** in 86% yield. Although the conversion of optically active propargyl alcohols analogous to **10** to the corresponding allenes has been shown to occur

Scheme 2

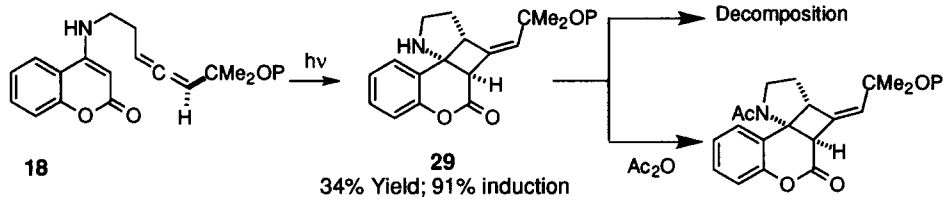


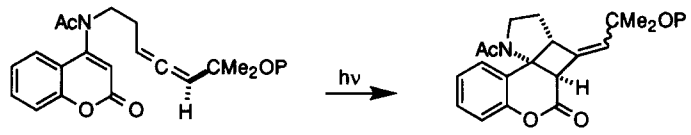
stereospecifically,[18] we verified that allene **12** had been produced with complete stereocontrol by its conversion to the corresponding (*S*)–MTPA ester and subsequent comparison by ^{19}F NMR to authentic racemic material.

With the optically active allenyl alcohol in hand, the substrates for photocycloadditions were prepared. Allene–alcohol **12** could be readily appended to the desired enones and enoates following procedures previously described.[2a] These involved either Mitsunobu coupling (Ph_3P, $EtO_2CN{=}NCO_2Et$) of **12** to the β–dicarbonyl derivative or alkylation of the protected β–amino–α,β–unsaturated enones and enoates to give the desired photosubstrates.

All photocycloaddition reactions were performed in cyclohexane or dichloromethane at ambient temperature with a Hanovia 450 W Hg medium-pressure UV–lamp through a Pyrex filter. As shown in Table 1, the [2+2] photoadducts were isolated in 50–100% yield and 54–>99% asymmetric induction. In only one case, Entry 6, was it necessary to carry out the cycloaddition reaction under modified conditions. When **18** was subjected to the photocycloaddition conditions, [2+2] adduct **29** was obtained with good levels of asymmetric induction; however, it proved difficult to isolate and unstable towards storage (Scheme 3). We speculated that these complications arose form the presence of a strained β–amino lactone in the product which could undergo retromannich fragmentation,[19] leading to the formation of polar products. As a possible solution to this problem, **18** was acetylated (H_3CCO, DMAP) and subjected to the photocyclization conditions (Eq 4). The acetylated [2+2] photoadducts were obtained in good yield (72%) as a 3:1 E/Z mixture of

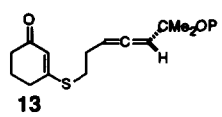
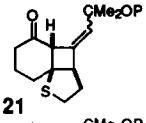
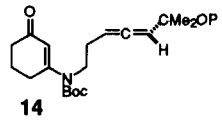
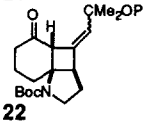
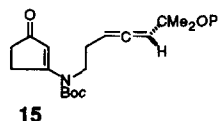
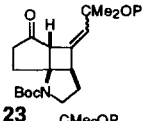
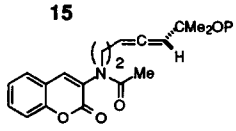
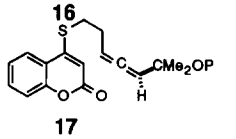
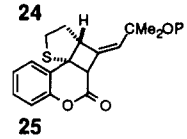
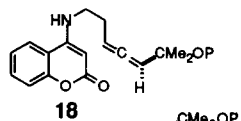
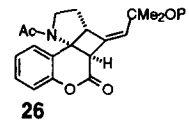
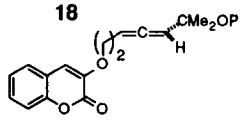
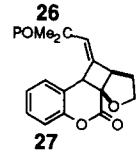
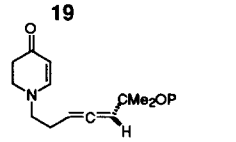
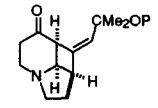
Scheme 3





(4)

Table 1. Intramolecular Photocycloadditions of Optically Active Allene/Enones; P = Si^tBuMe_2.

Entry	Substrate	Photoadduct	Yield	Induction[c,d]
1	 13	 21	73%[a]	99% (E)[e] > 99% (Z)
2	 14	 22	78%[a]	90% (E)[f] 90% (Z)[g]
3	 15	 23	62%[a]	65% (E)[h] 66% (Z)
4	 16	 24	77%[a]	94% (E)[i] 87% (Z)
5	 17	 25	100%[b]	88% (E)[j]
6	 18	 26	50%[b]	93%(E)[i]
7	 19	 27	60%[b]	95% (E)[i]
8	 20	 28	77%[a]	54% (E)[e] 64% (Z)[k]

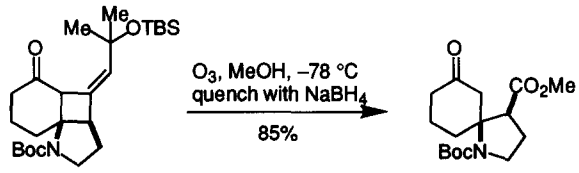
[a] Yields are reported for combined mixture of alkene diastereomers, following purification by chromatography on silica gel. [b] Isolated as a single alkene diastereomer. [c] % ee's were determined by comparison to authentic racemate. [d] Asymmetric induction (%ee adduct/% ee allene) is reported. The % ee's were determined as follows: [e] reduction to the corresponding alcohol and analysis by GC on a Cyclodex-B column; [f] reduction to the corresponding alcohol, preparation of the (*S*)-MTPA ester, and analysis by ^{19}F NMR spectroscopy; [g] The optical purity of *Z*-**22** could not be determined accurately as a consequence of carbamate rotamers; the asymmetric induction is only an estimate; [h] reduction to the corresponding alcohol, preparation of the (*S*)-MTPA ester, and analysis by ^1H NMR spectroscopy; [i] reduction to the corresponding phenol-alcohol, preparation of the bis-(*S*)-MTPA ester, and analysis by ^{19}F NMR spectroscopy; [j] reduction to the corresponding phenol-alcohol, preparation of the bis-(*S*)-MTPA ester, and analysis by ^1H NMR spectroscopy; [k] analysis by GC on a Cyclodex-B column.

alkene diastereomers and proved stable towards isolation and storage. However, the major E–adduct was isolated with only 64% induction and the Z-adduct with 95% induction. We surmised that it might be possible to carry out the photocycloaddition reaction on **18** itself provided the amine product was trapped at a faster rate than it underwent decomposition. To this end, irradiation of **18** was carried out in the presence of excess acetic anhydride, giving **26** as the sole diastereomer product in 50% yield and 93% asymmetric induction.

With the exception of **16**, coumarins **17–19** gave products **25–27** as single alkene diastereomers as determined by ^{1}H NMR spectroscopy. By contrast, the alicyclic enoates formed products as 2.7–1:1 mixtures of alkene diastereomers **21–23** and **28**. Although, for the purposes of this investigation, the formation of such alkene diastereomers is inconsequential, each of these could be separated by chromatography on silica gel and the enantioselectivity assayed individually as shown in Table 1.[20] The determination of asymmetric induction of the products required the development of various protocols, since it was possible to assay directly the optical purity for only one adduct **28Z** (Entry 8). The stereoisomeric purity of adducts **21** and **28E** was established upon reduction to the corresponding secondary alcohols and their analysis by gas chromatography on a Cyclodex–B column. For adducts **22** and **23** the enantioselectivity was assayed upon reduction of the ketones ($NaBH_4$, MeOH), conversion of the isolated secondary alcohols to the corresponding (*S*)–MTPA esters and analysis by ^{19}F NMR and ^{1}H NMR spectroscopy, respectively. Coumarin adducts **24**, **26**, and **27** were reduced to the phenol-alcohol products which upon preparation of the bis (*S*)–MTPA esters permitted the extent of asymmetric induction to be determined by ^{19}F NMR spectroscopy.

The extent of asymmetric induction in these cycloadditions is quite high for the wide range of substrates utilized. Moreover, the use of photosubstrates which incorporate *O*– and *N*–tethered allenes appended at the enoate C(α) position, to the best of our knowledge, represents the first investigation of such substrates in preparative allene–enone photochemistry. As such, it further expands the class of substrates that will participate in enantioselective [2+2] photocycloadditions.

The hindered exomethylenecylobutanes isolated from the photoreactions were found to be stable and amenable to storage for an extended time period without evidence of decomposition. We have found that these compounds undergo ozonolytic cleavage and retro–Claisen fragmentation to give spiro–fused bicyclic structures (Eq 5). As a representative example, treatment of **22** with a dilute stream of ozone at -78 °C followed by reductive work up with $NaBH_4$ at –78 °C afforded **30** in 85% isolated yield upon chromatography on silica gel.



22 **30** (5)

Conclusion. The ability of 1,3–disubstituted allenes to undergo asymmetric, intramolecular photocycloadditions with high enantioselectivity provides access to optically active polycyclic ring systems which are not otherwise easily synthesized using currently available asymmetric reaction methodology. The novel, optically active allene bearing a $CMe_2OSi^tBuMe_2$ moiety as a stereochemical controlling group has advantages over the previously employed *tert*–butyl substituted allenes since the former is readily prepared from inexpensive commodity chemicals using a strategy involving catalytic, enantioselective aldol addition and stereospecific conversion of a propargyl alcohol to an allene. In addition, this study has examined substrates for the [2+2] allene–enone photocycloaddition reaction which have not been investigated previously. As such, the examination of C(α)–substituted allene/enones including amino–tethered substrates further expands the scope of complex, optically active ring systems that may be readily accessed. Further methodological studies and applications to complex molecule synthesis are in progress and will be reported in due course.

EXPERIMENTAL SECTION

General Procedures. All reagents were commercially obtained except where noted. Where appropriate, reagents were purified prior to use. All nonaqueous reactions were performed using oven-dried glassware under an atmosphere of dry nitrogen. Air- and moisture-sensitive liquids and solutions were transferred *via* syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation below 35 °C at ~25 mmHg (water aspirator). Photoreactions were performed in Pyrex flasks ($\lambda > 293$ nm) using a Hanovia 450-W Hg medium-pressure UV lamp in a water-cooled quartz immersion apparatus as the light source. Diethyl ether and tetrahydrofuran (THF) were distilled from sodium benzophenone ketyl prior to use. N,N-Diisopropylethylamine, dichloromethane, pyridine, and triethylamine were distilled from calcium hydride prior to use. Dimethyl sulfoxide and dimethylformamide were distilled under reduced pressure from calcium hydride and stored over 4 Å molecular sieves. Methanol was distilled from magnesium methoxide prior to use. Spectroscopy grade cyclohexane or reagent grade dichloromethane was used in photoreactions. Spectroscopy grade chloroform (with 1% EtOH) was used for all optical rotation data. Chromatographic purification of products was accomplished using forced flow chromatography on Baker 7024-R silica gel or EM Science Geduran silica gel 60 according to the method of Still.[21] Thin-layer chromatography was performed on EM Reagents 0.25 mm silica gel 60F plates (230-400 mesh). Visualization of the developed chromatogram was performed by either fluorescence quenching, ethanolic *p*-anisaldehyde stain, or aqueous ceric ammonium molybdate (CAM) stain.

NMR spectra were recorded on a Bruker AM-500 operating at 500, 470, and 126 MHz for ^1H, ^{19}F, and ^{13}C, respectively, or a General Electric QE Plus operating at 300 and 75 MHz for ^1H and ^{13}C, respectively. Data for ^1H are reported as follows: chemical shift (δ in ppm), multiplicity (s, singlet; d, doublet; t, triplet; q quartet; m, multiplet), integration, coupling constant (J in Hz), and assignment. NOE difference spectra were recorded on degassed samples and were quantitated by integrating the difference spectra. IR spectra were recorded on a Perkin Elmer 1600 series or a paragon 1000 FTIR spectrometer using NaCl salt plates and are reported in terms of frequency of absorption (ν, cm^{-1}). Optical rotations were determined on a JASCO DIP-181 or DIP-1000 digital polarimeter operating at the sodium D line and are reported as follows: $[\alpha]_{Na}$,

concentration (g/100 mL), and solvent. Gas chromatographic analyses were performed on a Hewlett-Packard 6890 gas chromatograph with a flame ionization detector and a 30 m J&W Cyclodex-B capillary column. High-resolution mass spectra were obtained from the UC Irvine Mass Spectral facility.

Acetylene 4. To a solution of **3** (19 mL, 200 mmol, 1.0 equiv) in 100 mL DMF was added ^{t}BuMe$_2$SiCl (30 g, 200 mmol, 1.0 equiv), imidazole (19 g, 280 mmol, 1.4 equiv), and 4-N,N-dimethylaminopyridine (2.4 g, 20 mmol, 0.1 equiv). The reaction mixture was heated to 65 °C for 25 h and then was cooled and partitioned between 400 mL H_2O and 400 mL Et_2O. The aqueous layer was extracted with Et_2O (2 X 150 mL) and the combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification of the product by chromatography on silica gel (2% Et_2O in pentane) afforded 34 g (85%) of alkyne **4**: TLC R_f = 0.91 (8:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.39 (s, 1H, H_{alkyne}), 1.47 (s, 6H, $(CH_3)_2C$), 0.86 (s, 9H, $(CH_3)_3CSi$), 0.17 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 89, 71, 66, 33, 26, 18, -3.0; IR (thin film) ν 3310, 2931, 2858, 1473, 1463, 1361, 1253, 1221, 1166, 1044, 1005, 835, 777.

Aldehyde 5. To a solution of **4** (20 g, 100 mmol, 1.1 equiv) in Et_2O at 0 °C was added a solution of ^{n}BuLi (1.6 M in hexanes, 57 mL, 92 mmol, 1.0 equiv). After stirring at 0 °C for 30 min the mixture was cooled to -78 °C. Ethyl formate (8.9 mL, 110 mmol, 1.2 equiv) was quickly added and the mixture was stirred at -78 °C for 30 min and then at 0 °C for 15 min. The reaction was quenched with 100 mL H_2O and the aqueous layer was extracted with Et_2O (3 X 50 mL). The combined organic extracts were washed with 75 mL saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resultant oil was purified by chromatography on silica gel (gradient elution, 1% Et_2O in pentane to 2% Et_2O in pentane) to afford 18 g (88%) of aldehyde **5**: TLC R_f = 0.56 (8:1 hexanes/EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 9.23 (s, 1H, $H_{aldehyde}$), 1.52 (s, 6H, $(CH_3)_2C$), 0.86 (s, 9H, $(CH_3)_3CSi$), 0.17 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 177, 101, 82, 66, 32, 26, 18, -3.0; IR (thin film) ν 2931, 2858, 1473, 1463, 13610, 1253, 1221, 1166, 1044, 1005, 835, 777; HRMS (FAB$^+$) calcd for $C_{12}H_{23}O_2Si^+$ (MH^+) 227.1467, found 227.1468.

β-Hydroxyester 8. To a 5.5 mM solution of the Schiff base ligand (0.044 equiv) in toluene was added Ti(^{i}PrO)$_4$ (0.020 equiv). The orange solution was stirred for 1 h at 23 °C before adding 3,5-di-*tert*-butylsalicylic acid (0.024 equiv) in toluene (12 mM). Stirring was continued for an additional 1 h at 23 °C. The solvent was removed *in vacuo* and the solid orange residue was dissolved in Et_2O to give a 5.0 mM solution of catalyst **6** (relative to Ti). After cooling the solution to 0 °C, 2,6-lutidine (0.20 equiv), aldehyde **5** (1.0 equiv) and silyl ketene acetal **7** (1.2 equiv) were added sequentially. The flask was then kept at 0 °C for 4 h before it was quenched by pouring onto water. The mixture was extracted with Et_2O after diluting with a saturated aqueous NaCl solution. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was treated with 10% trifluoroacetic acid (TFA) in THF to effect desilylation. Once complete, the solution was partitioned between Et_2O and water. The organic layer was separated and washed with a 1.0 M NaOH solution. The organic solutions were dried over anhydrous

Na_2SO_4 and concentrated *in vacuo*. The resultant mixture was purified by flash chromatography on silica gel (10:1 CH_2Cl_2/hexanes, then 10:1 CH_2Cl_2/Et_2O) to afford adduct **8** in 88% yield: TLC R_f = 0.09 (10:1 hexanes/EtOAc); $[\alpha]_{Na}$ -20.6° (c = 1.1, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.78 (q, 1H, *J* = 6.0 Hz, $H_{propargyl}$), 3.73 (s, 3H, OCH_3), 3.03 (d, 1H, *J* = 6.0 Hz, O*H*), 2.73 (d, 2H, *J* = 6.0 Hz, $CH_2CO_2CH_3$), 1.43 (s, 6H, $(CH_3)_2C$), 0.85 (s, 9H, $(CH_3)_3CSi$), 0.14 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 172, 91, 81, 66, 59, 52, 41, 33, 26, 18, -2.9; IR (thin film) ν 3378 (br), 2978, 1731 (s), 1643, 1437, 1361, 1279, 1226, 1161, 1049, 1014, 950, 850; HRMS (FAB^+) calcd for $C_{15}H_{28}O_4SiNa^+$ ($M+Na^+$) 323.1654, found 323.1650.

Diol 9. To a solution of ester **8** (0.90 g, 3.0 mmol, 1.0 equiv) in 15 mL Et_2O at 0 °C was added 5.0 mL of $LiBH_4$ solution (2.0 M in THF, 10 mmol, 3.3 equiv), followed by 0.31 mL (7.5 mmol, 2.5 equiv) MeOH. The reaction mixture was stirred at 0 °C for 60 min and then was quenched by slow addition of 1.0 mL acetone. After warming slowly to 23 °C over 3 h, the mixture was cooled to 0 °C and treated with 15 mL 1M aqueous KH_2PO_4 solution. The organic layer was washed with 15 mL 1M aqueous KH_2PO_4 and 15 mL saturated aqueous NaCl. The combined aqueous fractions were extracted with 10% MeOH in CH_2Cl_2 (5 X 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (4:1 hexanes/EtOAc) provided 0.81 g (99%) of diol **9** as a pale yellow oil: TLC R_f = 0.22 (4:1 hexanes/EtOAc); $[\alpha]_{Na}$ -16.7° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.68-4.64 (m, 1H, $H_{propargyl}$), 3.98-3.94 (m, 1H, C*H*HO), 3.86-3.83 (m, 1H, CH*H*O), 2.94 (br s, 1H, O*H*), 2.52 (br s, 1H, O*H*), 1.99-1.90 (m, 2H, $CHCH_2CH_2O$), 1.44 (s, 6H, $(CH_3)_2C$), 0.85 (s, 9H, $(CH_3)_3CSi$), 0.15 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 91, 82, 66, 62, 60, 39, 33, 26, 18, -2.9; IR (thin film) ν 3354 (br), 2955, 2930, 2857, 2248 (w), 1472, 1462, 1360, 1246, 1162, 1041, 836, 776; HRMS (FAB^+) calcd for $C_{14}H_{29}O_3Si^+$ (MH^+) 273.1886, found 273.1909.

Propargyl Alcohol 10. To 8.6 g of diol **9** (32 mmol, 1.0 equiv) in 300 mL CH_2Cl_2 at 0 °C were added triethylamine (6.6 mL, 47 mmol, 1.5 equiv), $^tBuMe_2SiCl$ (5.2 g, 35 mmol, 1.1 equiv), and 4-N,N-dimethylaminopyridine (0.19 g, 1.6 mmol, 0.05 equiv) successively. The reaction mixture was allowed to warm slowly to 23 °C and then was stirred at that temperature for 14 h. The reaction mixture was poured onto 250 mL H_2O and the layers were separated. The organic layer was washed with 200 mL 1.0 M aqueous KH_2PO_4 and 200 mL saturated aqueous NaCl. The combined aqueous washes were extracted with 280 mL Et_2O, and the combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (10% Et_2O in hexanes) afforded 10 g (83%) of alcohol **10**: TLC R_f = 0.23 (10% Et_2O in hexanes); $[\alpha]_{Na}$ -11.8° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 4.65-4.61 (m, 1H, $H_{propargyl}$), 4.05-3.99 (m, 1H, C*H*HOTBS), 3.86-3.79 (m, 1H, CH*H*OTBS), 3.35 (d, 1H, *J* = 5.9 Hz, O*H*), 2.02-1.93 (m, 1H, C*H*HCH$_2$OTBS), 1.88-1.84 (m, 1H, CH*H*CH$_2$OTBS), 1.45 (s, 6H, $(CH_3)_2C$), 0.90 (s, 9H, $(CH_3)_3CSi$), 0.86 (s, 9H, $(CH_3)_3CSi$), 0.16 (s, 3H, C*H*$_3$Si), 0.10 (s, 3H, C*H*$_3$Si), 0.09 (s, 3H, C*H*$_3$Si), 0.08 (s, 3H, C*H*$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 90, 83, 66, 62, 61, 39, 33, 25.8, 25.7, 18.1, 17.9, -2.9, -5.6; IR (thin film) ν 3418 (br), 2955, 2929,

2857, 1472, 1360, 1253, 1162, 1096, 1041, 939, 837, 776; HRMS (FAB$^+$) calcd for $C_{20}H_{42}O_3Si_2$ 386.2673, found 386.2700.

Allene 11. To alcohol **10** (10 g, 26 mmol, 1.0 equiv) in 100 mL CH_2Cl_2 at 0 °C was added triethylamine (4.3 mL, 31 mmol, 1.2 equiv) and methanesulfonyl chloride (2.4 mL, 31 mmol, 1.2 equiv). The clear solution became opaque as it was stirred at 0 °C for 20 min. The suspension was transferred *via* cannula to a mixture of 100 mL MeOH and 100 mL anhydrous hydrazine. The resultant mixture was stirred at 23 °C for 28 h and then was poured onto 500 mL H_2O. The small organic layer was collected and the aqueous layer was extracted with 15% MeOH in CH_2Cl_2 (5 X 100 mL). The combined organic extracts were washed with 100 mL saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The oil thus obtained was dissolved in 250 mL CH_2Cl_2 and 250 mL Et_2O and cooled to 0 °C. 4-Phenyl-1,2,4-triazoline-3,5-dione (9.1 g, 52 mmol, 2.0 equiv) was added in one portion whereupon effervescence occurred. After 15 min 1 L cold pentane was added and the mixture was stirred at 0 °C for 10 min and then was filtered through a pad of Celite. The precipitate was washed with 1 L cold 20% CH_2Cl_2 in pentane and the combined filtrates were concentrated *in vacuo*. Purification of the residue by chromatography on silica gel (1% Et_2O in pentane) afforded 6.2 g (65%) of allene **11**: TLC R_f = 0.79 (8:1 hexanes/EtOAc); $[\alpha]_{Na}$ +30.0° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.26-5.19 (m, 2H, H_{allene}), 3.67 (t, 2H, *J* = 7.0 Hz, CH_2OTBS), 2.23 (qt, 2H, *J* = 6.9, 3.0 Hz, CH_2CH_2OTBS), 1.30 (s, 3H, CH_3C), 1.29 (s, 3H, CH_3C), 0.90 (s, 9H, $(CH_3)_3CSi$), 0.85 (s, 9H, $(CH_3)_3CSi$), 0.07 (s, 6H, CH_3Si), 0.06 (s, 6H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201, 101, 90, 72, 63, 32, 30.9, 30.8, 25.9, 25.8, 18.4, 17.9, -2.3, -5.3; IR (thin film) ν 2956, 2929, 2857, 1966, 1472, 1361, 1254, 1148, 1102, 1041, 835, 774; HRMS (FAB$^+$) calcd for $C_{20}H_{42}O_2Si_2$ 370.2723, found 370.2746.

Allene Alcohol 12. To 0.73 g of allene **11** (2.0 mmol, 1.0 equiv) in 20 mL THF at 0 °C was added 2.0 mL Bu_4NF solution (1.0 M in THF, 2.0 mmol, 1.0 equiv). The reaction mixture was stirred at 0 °C for 2 h and then was poured onto 25 mL saturated aqueous NaCl and 25 mL Et_2O. The aqueous phase was extracted with Et_2O (3 X 10 mL) and the combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and placed in a freezer at -20 °C for 12 h. The crystals of TBSF that formed were filtered off and the supernatant was concentrated *in vacuo*. The resultant oil was purified by chromatography on silica gel (3:1 pentane/Et_2O) to afford 0.44 g (86%) of allene alcohol **12**: TLC R_f = 0.27 (4:1 hexanes/EtOAc); $[\alpha]_{Na}$ +51.1° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.33-5.29 (m, 1H, H_{allene}), 5.23 (q, 1H, *J* = 6.5 Hz, H_{allene}), 3.72 (q, 2H, *J* = 6.0 Hz, CH_2OH), 2.28 (qd, 2H, *J* = 6.3, 3.0 Hz, CH_2CH_2OH), 1.63 (t, 1H, *J* = 6.0 Hz, O*H*), 1.323 (s, 3H, CH_3C), 1.315 (s, 3H, CH_3C), 0.85 (s, 9H, $(CH_3)_3CSi$), 0.079 (s, 3H, CH_3Si), 0.074 (s, 3H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201, 102, 90, 72, 62, 32, 30.9, 30.7, 26, 18, -2.3; IR (thin film) ν 3328 (br), 2956, 2929, 2857, 1966, 1472, 1361, 1253, 1148, 1102, 1042, 835, 774; HRMS (FAB$^+$) calcd for $C_{14}H_{28}O_2Si$ 256.1859, found 256.1880.

Analysis of Optical Purity of 12. A sample of **12** (1.6 mg, 6.3 μmol, 1 equiv) was dried by azeotropic removal of water with toluene. The resultant residue was dissolved in 0.1 mL CH_2Cl_2 and treated

with triethylamine (10 μL, 72 μmol, 11 equiv), 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 2.5 equiv), and a solution of (R)-Mosher's acid chloride[22] (0.12 M in CH_2Cl_2, 150 μL, 18 μmol, 3 equiv), successively. The mixture was stirred at 23 °C for 30 min and then was purified by chromatography on silica gel (3% EtOAc in hexanes) to afford the (S)-MTPA-ester. Integration of the ^{19}F NMR resonances ($CDCl_3$, 470 MHz) at δ -71.56 ppm (minor) and δ -71.59 ppm (major) indicated a 99% enantiomeric excess.

Allene Mesylate. To allene alcohol **12** (0.40 g, 1.3 mmol, 1.0 equiv) in CH_2Cl_2 at 0 °C was added 260 μL (1.9 mmol, 1.5 equiv) triethylamine followed by 120 μL (1.5 mmol, 1.2 equiv) methanesulfonyl chloride. The reaction mixture was stirred at 0 °C for 15 min and was poured onto 5 mL pH 7 phosphate buffer. The aqueous layer was extracted with Et_2O (3 X 2 mL) and the combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resultant oil was purified by chromatography on silica gel (1:1 CH_2Cl_2/hexanes) to afford 0.35 g (83%) of the mesylate: TLC R_f = 0.64 (5:1 CH_2Cl_2/hexanes); $[\alpha]_{Na}$ +45.8° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.35-5.32 (m, 1H, H_{allene}), 5.20 (q, 1H, *J* = 6.6 Hz, H_{allene}), 4.26 (t, 2H, *J* = 6.7 Hz, CH_2OMs), 3.01 (s, 3H, OSO_2CH_3), 2.46 (qd, 2H, *J* = 6.7, 2.8 Hz, CH_2CH_2OMs), 1.31 (s, 3H, CH_3C), 1.30 (s, 3H, CH_3C), 0.84 (s, 9H, $(CH_3)_3CSi$), 0.065 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202, 103, 88, 72, 69, 37, 30.9, 30.6, 28.7, 25.7, 18, -2.3; IR (thin film) ν 3027 (w), 2930, 2857, 1966, 1772, 1360, 1253, 1175, 1149, 1040, 961, 916, 835, 774; HRMS (FAB^+) calcd for $C_{15}H_{30}O_4SSi$ 334.1634, found 334.1613.

Allene Thiol. Hydrogen sulfide gas was bubbled through a solution of KOH (18 mg, 0.33 mmol, 1.1 equiv) in 1.5 mL absolute ethanol for 10 min before a solution of the allene mesylate in 0.5 mL ethanol was transferred *via* cannula into the mixture. Bubbling of H_2S was continued while the mixture was heated to 50 °C for 7.5 h. The resultant slurry was poured onto a solution of 7 mL H_2O and 3 mL saturated aqueous NaCl and then was extracted with Et_2O (3 X 8 mL). The combined ether extracts were concentrated *in vacuo* and the residue was purified by chromatography on silica gel (hexanes) to afford 75 mg (93%) of the desired product: TLC R_f = 0.87 (3:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.30 (m, 1H, H_{allene}), 5.21 (q, 1H, *J* = 6.4 Hz, H_{allene}), 2.60 (q, 2H, *J* = 7.4 Hz, CH_2SH), 2.34 (m, 2H, CH_2CH_2SH), 1.48 (t, 1H, *J* = 8.1 Hz, *SH*), 1.32 (s, 3H, CH_3COTBS), 1.31 (s, 3H, CH_3COTBS), 0.85 (s, 9H, $(CH_3)_3CSi$), 0.07 (s, 6H, $(CH_3)_2Si$); IR (thin film) ν 2956, 2929, 2856, 1964, 1472, 1360, 1252, 1417, 1041, 834, 774.

Photosubstrate 13. To 118 mg (1.06 mmol, 1.4 equiv) 1,3-cyclohexanedione in 7 mL pyridine at 0 °C was added *p*-toluenesulfonyl chloride (216 mg, 1.13 mmol, 1.5 equiv). The mixture was stirred at 0 °C for 30 min before a solution of the allene thiol (205 mg, 0.753 mmol, 1.0 equiv) in 2 mL pyridine was added *via* cannula. The reaction mixture was removed from the ice bath and stirred at 23 °C for 2 h and then at 50 °C for 16 h. After cooling to 23 °C, the mixture was poured onto 150 mL Et_2O and 50 mL 1M aqueous KH_2PO_4. The organic layer was washed with 1M aqueous KH_2PO_4 (5 X 15 mL) and 1M aqueous $CuSO_4$ (3 X 15 mL). The combined aqueous washes were extracted with Et_2O (3 X 25 mL). The combined organic layers were washed with saturated aqueous NaCl (2 X 20 mL), dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (gradient elution, 1% Et_2O in hexanes to 50% Et_2O

in hexanes) to provide 68 mg (25%) of substrate **13**: TLC R_f = 0.25 (3:1 hexanes/EtOAc); $[\alpha]_{Na}$ +78.5° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.85 (s, 1H, H_{vinyl}), 5.35 (m, 1H, H_{allene}), 5.23 (q, 1H, *J* = 6.4 Hz, H_{allene}), 2.88 (t, 2H, *J* = 7.3 Hz, CH_2S), 2.47-2.33 (m, 6H, $CH_2CH_2CH_2CO$, CH_2CH_2S), 2.03 (m 2H, CH_2CH_2CO), 1.31 (s, 6H, $(CH_3)_2COTBS$), 0.85 (s, 9H, $(CH_3)_3CSi$), 0.06 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201, 196, 165, 119, 103, 91, 72, 37, 31.1, 31.0, 30.7, 30.2, 27, 26, 23, 18, -2.2; IR (thin film) ν 2955, 2929, 2855, 1965, 1660, 1662 (s), 1574, 1251, 1186, 1148, 1042, 1007, 835, 774; HRMS (FAB^+) calcd for $C_{20}H_{34}O_2SSi$ 366.2049, found 366.2039.

Photoadduct 21. A solution of **13** (99% ee, 30 mg, 82 mmol) in 30 mL CH_2Cl_2 was deoxygenated by nitrogen sparge 5 min and then was sealed and irradiated 10 min (see General Procedures). The resultant solution was concentrated *in vacuo* and purified by chromatography on silica gel (gradient elution, 5% Et_2O in hexanes to 9% Et_2O in hexanes) to give 6 mg of the Z olefin and 16 mg of the E olefin (73%).

21Z: TLC R_f = 0.36 (8:1 hexanes/EtOAc); $[\alpha]_{Na}$ +71.8° (c = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.47 (t, 1H, *J* = 2.3 Hz, H_{vinyl}), 3.88 (br t, 1H, *J* ~ 3 Hz, *CH*CO), 3.54 (br s, 1H, *CH*$(CH_2)_2S$), 3.26 (td, 1H, *J* = 11.5, 5.1 Hz, *CH*HS), 2.97 (dd, 1H, *J* = 11.0, 6.3 Hz, CH*H*S), 2.49 (dm, 1H, *J* = 4.0 Hz, *CH*HCO), 2.3-1.9 (m, 7H), 1.43 (s, 3H, CH_3COTBS), 1.30 (s, 3H, CH_3COTBS), 0.85 (s, 9H, $(CH_3)_3$CSi), 0.07 (s, 3H, CH_3Si), 0.06 (s, 3H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 209, 136, 130, 74, 64, 62, 55, 40, 36, 33.4, 33.3, 31, 29, 26, 22, 18, -2.1; IR (thin film) ν 2928, 2855, 1713, 1251, 1153, 1042, 835, 773; HRMS (FAB^+) calcd for $C_{20}H_{34}O_2SSi$ 366.2049, found 366.2047.

21E: TLC R_f = 0.32 (8:1 hexanes/EtOAc); $[\alpha]_{Na}$ -10.0° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.35 (t, 1H, *J* = 2.4 Hz, H_{vinyl}), 3.64 (m, 1H, *CH*$(CH_2)_2S$), 3.56 (br t, 1H, *J* ~ 3 Hz, *CH*CO), 3.14 (td, 1H, *J* = 11.6, 5.0 Hz, *CH*HS), 3.00 (m, 1H, CH*H*S), 2.54 (dm, 1H, *J* ~ 19 Hz, *CH*HCO), 2.36 (dm, 1H, *J* ~ 13 Hz, *CH*HCH$_2$CH$_2$CO), 2.2-1.9 (m, 6H, CH*H*CH_2CH*H*CO, CH_2CH_2S), 1.32 (s, 3H, CH_3COTBS), 1.28 (s, 3H, CH_3COTBS), 0.84 (s, 9H, $(CH_3)_3CSi$), 0.06 (s, 3H, CH_3Si), 0.04 (s, 3H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 208, 134, 130, 74, 63, 58, 56, 39, 38, 33.5, 32.5, 31.5, 30.7, 26, 21, 18, -2.0; IR (thin film) ν 2928, 2854, 1701, 1253, 1154, 1038, 834, 773; HRMS (FAB^+) calcd for $C_{20}H_{34}O_2SSi$ 366.2049, found 366.2064.

Analysis of Asymmetric Induction. A sample of **21Z** (2 mg, 6 μmol, 1 equiv) in 0.5 mL MeOH at 23 °C was treated with 2.0 mg (53 μmol, 9 equiv) $NaBH_4$. After stirring for 25 min, the mixture was filtered through a plug of silica gel and the plug was washed with Et_2O. The filtrate was concentrated *in vacuo* and the resultant oil was purified by chromatography on silica gel (8:1 hexanes/EtOAc). GC analysis (200 °C, ret time 31.3 min (major), 32.5 min (minor)) indicated a 99% enantiomeric excess, or 100% asymmetric induction.

A sample of **21E** (4 mg, 10 μmol, 1 equiv) in 0.5 mL MeOH at 23 °C was treated with 2.0 mg (53 μmol, 5 equiv) $NaBH_4$. After stirring for 25 min, the mixture was filtered through a plug of silica gel and the plug was washed with Et_2O. The filtrate was concentrated *in vacuo* and the resultant oil was purified by chromatography on silica gel (8:1 hexanes/EtOAc). GC analysis (200 °C, ret time 32.7 min (major), 34.5 min (minor)) indicated a 98% enantiomeric excess, or 99% asymmetric induction.

N-Boc-3-amino-2-cyclohexenone. A 60% dispersion of NaH in mineral oil (0.80 g, 20 mmol, 1.1 equiv) was weighed into a flask, washed with hexanes (3 X 5 mL), and dried under vacuum. After an atmosphere of nitrogen was restored, 40 mL DMF was added and the mixture was cooled to 0 °C. 3-Amino-2-cyclohexenone[23] (2.0 g, 18 mmol, 1.0 equiv) was added and stirring was continued at 0 °C for 30 min. A solution of $(Boc)_2O$ (4.7 g, 22 mmol, 1.2 equiv) in 10 mL DMF was added *via* cannula, upon which effervescence occurred and the mixture became semisolid. As the bubbling ceased, stirring resumed. The mixture was stirred at 23 °C for 30 min and then was poured onto 200 mL H_2O and 200 mL Et_2O. The aqueous layer was extracted with Et_2O (4 X 50 mL). The combined organic layers were washed with 75 mL saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (gradient elution, 1:1 hexanes/EtOAc to 1:3 hexanes/EtOAc) to afford 1.5 g (39%) of a white solid: mp 185-188 °C; TLC R_f = 0.63 (19:1 EtOAc/MeOH); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.49 (br s, 1H, N*H*), 6.33 (s, 1H, H_{vinyl}), 2.50 (t, 2H, *J* = 6.0 Hz, CH_2CO), 2.35 (t, 2H, *J* = 6.6 Hz, $CH_2(CH_2)_2CO$), 2.05-1.99 (m, 2H, CH_2CH_2CO), 1.47 (s, 9H, $OC(CH_3)_3$).

Photosubstrate 14. A 60% dispersion of NaH in mineral oil (20 mg, 0.50 mmol, 1.2 equiv) was weighed into a flask, washed with hexanes, and dried under vacuum. After an atmosphere of nitrogen was restored, 2.5 mL DMF was added and the mixture was cooled to 0 °C. N-Boc-3-amino-2-cyclohexenone (110 mg, 0.50 mmol, 1.2 equiv) was added and stirring was continued at 0 °C for 20 min and then at 23 °C for 10 min. A solution of the allene mesylate (140 mg, 0.42 mmol, 1.0 equiv) in 1 mL DMF was added *via* cannula. The reaction was heated to 80 °C for 15 h before it was cooled to 23 °C and poured onto 50 mL H_2O and 50 mL Et_2O. The aqueous layer was extracted with Et_2O (4 X 10 mL). The combined organic layers were washed with 15 mL saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (5:1 CH_2Cl_2/hexanes, then 10:10:1 CH_2Cl_2/hexanes/EtOAc) to afford 56 mg (30%) of photosubstrate **14**: TLC R_f = 0.12 (5:1 CH_2Cl_2/hexanes); $[\alpha]_{Na}$ +54.3° (c = 0.95, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.71 (s, 1H, H_{vinyl}), 5.27 (m, 1H, H_{allene}), 5.15 (q, 1H, *J* = 6.6 Hz, H_{allene}), 3.63 (m, 2H, CH_2N), 2.72 (t, 2H, *J* = 6.0 Hz, CH_2CO), 2.38 (t, 2H, *J* = 6.6 Hz, $CH_2(CH_2)_2CO$), 2.28 (m, 2H, CH_2CH_2N), 2.0 (m, 2H, CH_2CH_2CO), 1.50 (s, 9H, $OC(CH_3)_3$), 1.30 (s, 3H, CH_3COTBS), 1.29 (s, 3H, CH_3COTBS), 0.84 (s, 9H, $(CH_3)_3CSi$), 0.06 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202, 199, 163, 153, 116, 102, 90, 82, 72, 49, 37, 31.1, 30.64, 30.57, 28.2, 27.7, 26, 23, 18, -2.2; IR (thin film) ν 2955, 2929, 2856, 1964, 1717, 1664, 1590, 1459, 1368, 1254, 1151, 1039, 834, 774; HRMS (FAB^+) calcd for $C_{25}H_{43}NO_4Si$ 449.2961, found 449.2976.

Photoadduct 22. A solution of substrate **14** (93% ee, 50 mg, 0.11 mmol) in 50 mL CH_2Cl_2 was deoxygenated by nitrogen sparge 10 min and then was sealed and irradiated 5 min (see General Procedures). The resultant yellow solution was concentrated *in vacuo* and purified by chromatography on silica gel (10% EtOAc in hexanes) to give 13 mg of the Z olefin and 26 mg of the E olefin (78%).

22Z: TLC R_f = 0.53 (4:1 hexanes/EtOAc); $[\alpha]_{Na}$ +151° (c = 0.65, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) (peaks broadened due to rotamers) δ 5.54 (s, 1H, H_{vinyl}), 3.93, 3.74 (m, 1H, C*H*CO), 3.6 (br m, 2H, CH_2N), 3.25 (m, 1H, $CH(CH_2)_2N$), 2.6-2.2 (m, 3H, $CHHCH_2CH_2CO$), 2.2-1.9 (m, 1H,

CH*H*CH_2CH_2CO), 1.9-1.8 (m, 2H, C*H*$_2CH_2N$), 1.8-1.5 (m, 2H, $CH_2CH_2CH_2CO$), 1.47 (s, 9H, OC(CH_3)$_3$), 1.40 (s, 3H, C*H*$_3$COTBS), 1.35 (s, 3H, C*H*$_3$COTBS), 0.84 (s, 9H, (CH_3)$_3$CSi), 0.05 (s, 6H, (CH_3)$_2$Si); ^{13}C NMR ($CDCl_3$, 75 MHz) (some peaks broadened due to rotamers) δ 208, 154, 136, 132, 80, 77.2, 74, 59, 50, 48, 40, 32, 30, 29, 26.1, 25.8, 22, 21, 18, -2.1; IR (thin film) ν 2955, 2928, 2861, 1693 (s), 1459, 1376 (s), 1250, 1172, 1114, 1042, 834, 773; HRMS (FAB$^+$) calcd for $C_{25}H_{44}NO_4Si^+$ (MH^+) 450.3040, found 450.3073.

22E: TLC R_f = 0.47 (4:1 hexanes/EtOAc); $[\alpha]_{Na}$ +46° (c = 1.3, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz) (peaks are broadened due to rotamers) δ 5.37 (s, 1H, H_{vinyl}), 3.9 (s, 1H, C*H*CO), 3.5-3.3 (m, 3H, C*H*$_2$(CH_2)$_2$CO, C*H*(CH_2)$_2$N, 2.5 (m, 1H, C*H*HCO), 2.3-1.6 (m, 7H), 1.41 (s, 9H, OC(CH_3)$_3$), 1.30 (s, 3H, C*H*$_3$COTBS), 1.29 (s, 3H, C*H*$_3$COTBS), 0.83 (s, 9H, (CH_3)$_3$CSi), 0.04 (s, 3H, C*H*$_3$Si), 0.03 (s, 3H, C*H*$_3$Si); ^{13}C NMR ($CDCl_3$, 75 MHz) (some peaks are broadened due to rotamers) δ 208, 154, 134, 131, 80, 77.2, 73, 59, 52, 48, 38, 31.2, 30.6, 30.4, 29.7, 28, 26, 18, -2.1; HRMS (FAB$^+$) calcd for $C_{25}H_{44}NO_4Si^+$ (MH^+) 450.3040, found 450.3022.

Analysis of Asymmetric Induction. A sample of **22E** (12 mg, 27 μmol, 1 equiv) in 1.2 mL MeOH at 23 °C was treated with 2.0 mg (53 μmol, 2 equiv) $NaBH_4$. After stirring for 35 min, the mixture was poured onto 20 mL pH 7 phosphate buffer and 20 mL Et_2O. The aqueous layer was extracted with Et_2O (2 X 3 mL). The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resultant oil was purified by chromatography on silica gel (gradient elution, 12% EtOAc in hexanes to 15% EtOAc in hexanes) to afford <1 mg of the minor alcohol epimer (R_f = 0.35, 4:1 hexanes/EtOAc). The alcohol (2 μmol) was dried by azeotropic removal of water with toluene and then was dissolved in 0.1 mL CH_2Cl_2. Triethylamine (10 μL, 72 μmol, 36 equiv) was added to the reaction mixture, followed by addition of 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 8 equiv) and a solution of (R)-Mosher's acid chloride (0.12 M in CH_2Cl_2, 200 μL, 23 μmol, 10 equiv). The reaction was stirred at 23 °C for 30 min and then was purified by chromatography on silica gel (10% EtOAc in hexanes). Integration of the ^{19}F NMR resonances ($CDCl_3$, 470 MHz) at δ -71.3 ppm (minor) and δ -71.4 ppm (major) indicated an 83% enantiomeric excess, or 90% asymmetric induction.

N-Boc-3-Amino-2-cyclopentenone. A 60% dispersion of NaH in mineral oil (0.54 g, 14 mmol, 1.1 equiv) was weighed into a flask, washed with hexanes (3 X 5 mL), and dried under vacuum. After an atmosphere of nitrogen was restored, 25 mL DMF was added and the mixture was cooled to 0 °C. 3-Amino-2-cyclopentenone[23] (1.2 g, 12 mmol, 1.0 equiv) was added and stirring was continued at 0 °C for 15 min and then at 23 °C for 5 min. A solution of $(Boc)_2O$ (3.0 g, 14 mmol, 1.1 equiv) in 5 mL DMF was added *via* cannula, upon which effervescence occurred and the mixture became semisolid. As the bubbling ceased, stirring resumed. After 15 min, the reaction was poured onto 200 mL H_2O and 200 mL Et_2O. The aqueous layer was extracted with 10% MeOH in CH_2Cl_2 (4 X 50 mL). The combined organic layers were washed with 50 mL saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (1:3 hexanes/EtOAc) to afford 1.0 g (42%) of a yellow solid: TLC R_f = 0.57 (20:1 EtOAc/MeOH); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.08 (br s, 1H, N*H*), 6.08 (s, 1H, H_{vinyl}),

2.77-2.74 (m, 2H, CH_2CO), 2.42-2.39 (m, 2H, CH_2CH_2CO), 1.50 (s, 9H, $OC(CH_3)_3$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 207, 169, 151, 112, 83, 33, 29, 28; IR (thin film) ν 3183, 3084, 3033, 1737, 1654, 1602, 1552, 1212, 1167.

Photosubstrate 15. A 60% dispersion of NaH in mineral oil (14 mg, 0.36 mmol, 1.2 equiv) was weighed into a flask, washed with hexanes, and dried under vacuum. After an atmosphere of nitrogen was restored, 1.5 mL DMF was added and the mixture was cooled to 0 °C. The N-Boc-enaminone (59 mg, 0.30 mmol, 1.0 equiv) was added and stirring was continued at 0 °C for 25 min and then at 23 °C for 5 min. A solution of the allene mesylate (100 mg, 0.30 mmol, 1.0 equiv) in 1 mL DMF was added *via* cannula. The reaction was heated to 75 °C for 20 h and then was cooled to 23 °C and poured onto 20 mL H_2O and 20 mL Et_2O. The aqueous layer was extracted with Et_2O (4 X 5 mL). The combined organic layers were washed with 5 mL saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (2:1 hexanes/EtOAc) to afford 80 mg (62%) of **15**: TLC R_f = 0.23 (2:1 hexanes/EtOAc); $[\alpha]_{Na}$ +51.4° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.61 (s, 1H, H_{vinyl}), 5.32-5.28 (m, 1H, H_{allene}), 5.17 (q, 1H, *J* = 6.6 Hz, H_{allene}), 3.70 (m, 2H, CH_2N), 3.10 (m, 2H, CH_2CO), 2.42 (m, 2H, CH_2CH_2CO), 2.34-2.26 (m, 2H, CH_2CH_2N), 1.53 (s, 9H, $OC(CH_3)_3$), 1.29 (s, 3H, CH_3COTBS), 1.28 (s, 3H, CH_3COTBS), 0.84 (s, 9H, $(CH_3)_3CSi$), 0.05 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 206, 201, 173, 151, 112, 102, 89, 83, 72, 48, 34, 31, 30.7, 30.6, 28, 27, 26, 18, -2.3; IR (thin film) ν 2976, 2929, 2856, 1965, 1733, 1702, 1683, 1572 (s), 1462, 1369, 1246, 1149 (s), 1040, 834, 774; HRMS (FAB^+) calcd for $C_{24}H_{41}NO_4Si$ 435.2805, found 435.2813.

Photoadduct 23. A solution substrate **15** (93% ee, 60 mg, 0.14 mmol) in 60 mL CH_2Cl_2 was deoxygenated by nitrogen sparge 10 min and then was sealed and irradiated 15 min (see General Procedures). The resultant yellow solution was concentrated *in vacuo* and purified by chromatography on silica gel (10% EtOAc in hexanes) to give 19 mg of the Z olefin and 18 mg of the E olefin (62%).

23Z: TLC R_f = 0.75 (2:1 hexanes/EtOAc); $[\alpha]_{Na}$ +132° (c = 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) (peaks broadened due to rotamers) δ 5.50 (t, 1H, *J* = 2.1 Hz, H_{vinyl}), 3.68-3.60 (m, 2H, CH_2N), 3.42 (br s, 1H, $CHCO$), 3.37-3.34 (m, 1H, $CHCH_2CH_2N$), 2.61-2.56 (m, 3H, $CHHCH_2CO$), 2.10-2.05 (m, 1H, $CHHCH_2CO$), 1.92-1.84 (m, 2H, CH_2CH_2N), 1.44 (s, 12H, $OC(CH_3)_3$, CH_3COTBS), 1.28 (s, 3H, CH_3COTBS), 0.84 (s, 9H, $(CH_3)_3CSi$), 0.04 (s, 3H, CH_3Si), 0.03 (s, 3H, CH_3Si);^{13}C NMR ($CDCl_3$, 75 MHz) (some peaks broadened due to rotamers) δ 213, 155, 137, 130, 80, 73, 56, 53, 49, 39, 32, 30.2, 29.8, 29.4, 28.4, 27.9, 26, 18, -2.3, -2.2; IR (thin film) ν 2956, 2930, 2852, 1739, 1701, 1461, 1393, 1366, 1254, 1164, 1115, 1038, 835, 773; HRMS (FAB^+) calcd for $C_{24}H_{42}NO_4Si^+$ (MH^+) 436.2883, found 436.2865.

23E: TLC R_f = 0.68 (2:1 hexanes/EtOAc); $[\alpha]_{Na}$ +36.3° (c = 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) (peaks broadened due to rotamers) δ 5.50 (t, 1H, *J* = 1.7 Hz, H_{vinyl}), 3.8 (m, 1H, $CHCO$), 3.54-3.39 (m, 2H, CH_2N), 3.20 (t, 1H, *J* = 1.6 Hz, $CHCH_2CH_2N$), 2.65-2.50 (m, 3H, $CHHCH_2CO$), 2.33-2.26 (m, 1H, $CHHCH_2CO$), 2.10-1.96 (m, 2H, CH_2CH_2N), 1.43 (s, 9H, $OC(CH_3)_3$), 1.31 (s, 3H, CH_3COTBS), 1.29 (s, 3H, CH_3COTBS), 0.84 (s, 9H, $(CH_3)_3CSi$), 0.05 (s, 3H, CH_3Si), 0.03 (s, 3H, CH_3Si);^{13}C NMR

($CDCl_3$, 75 MHz) (some peaks broadened due to rotamers) δ 213, 154, 136, 130, 80, 73, 58, 54, 49, 38 (2), 32 (2), 31, 30, 28, 26, 18, -2.1; HRMS (FAB^+) calcd for $C_{24}H_{41}NO_4Si$ 435.2805, found 435.2826.

Analysis of Asymmetric Induction. A sample of **23Z** (6.0 mg, 14 μmol, 1 equiv) in 0.6 mL MeOH at 0 °C was treated with 2.0 mg (53 μmol, 4 equiv) $NaBH_4$. After stirring at 0 °C for 35 min, the mixture was poured onto pH 7 phosphate buffer and Et_2O. The aqueous layer was extracted with Et_2O (3 X 2 mL). The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resultant oil was purified by chromatography on silica gel (6:1 hexanes/EtOAc) to afford 2 mg of one alcohol epimer (**a**, R_f = 0.38, 6:1 hexanes/EtOAc) and 1 mg of the other epimer (**b**, R_f = 0.19, 6:1 hexanes/EtOAc). The epimer **a** (5 μmol) was dried by azeotropic removal of water with toluene and then was dissolved in 0.1 mL CH_2Cl_2. Triethylamine (10 μL, 72 μmol, 14 equiv) was added, followed by 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 3 equiv) and a solution of (R)-Mosher's acid chloride (0.085 M in CH_2Cl_2, 500 μL, 43 μmol, 9 equiv). The reaction was stirred at 23 °C for 12 h and then was purified by chromatography on silica gel (10% EtOAc in hexanes). Integration of the ^1H NMR resonances ($CDCl_3$, 500 MHz) at δ 0.06 ppm (minor) and δ 0.04 ppm (major) indicated a 61% enantiomeric excess, or 66% asymmetric induction.

A sample of **23E** (6.0 mg, 14 μmol, 1 equiv) in 1.0 mL THF at 0 °C was treated with a solution of L-Selectride (1.0 M in THF, 30 μL, 30 μmol, 2 equiv). After stirring at 0 °C for 15 min, the mixture was poured onto water and Et_2O. The organic layer was washed with saturated aqueous NaCl. The combined aqueous washes were extracted with Et_2O (3 X 2 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The resultant oil was purified by chromatography on silica gel (6:1 hexanes/EtOAc) to afford 3 mg of one alcohol epimer (R_f = 0.13, 6:1 hexanes/EtOAc). The alcohol (7 μmol) was dried by azeotropic removal of water with toluene and then was dissolved in 0.1 mL CH_2Cl_2. Triethylamine (10 μL, 72 μmol, 10 equiv) was added, followed by 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 2 equiv) and a solution of (R)-Mosher's acid chloride (0.085 M in CH_2Cl_2, 200 μL, 17 μmol, 2 equiv). The reaction was stirred at 23 °C for 40 min and then was purified by chromatography on silica gel (1:6 EtOAc/hexanes). Integration of the ^1H NMR resonances ($CDCl_3$, 300 MHz) at δ 3.55 ppm (minor) and δ 3.52 ppm (major) indicated a 60% enantiomeric excess, or 65% asymmetric induction.

Photosubstrate 16. A 60% dispersion of NaH in mineral oil (72 mg, 1.8 mmol) was weighed into a flask, washed with hexanes, and dried under vacuum. An atmosphere of nitrogen was restored and 6.0 mL DMSO was added. The resultant mixture was heated at 65 °C for 60 min and then cooled to 23 °C to give a 0.3 M solution of sodium dimsylate, 5.1 mL of which (1.5 mmol, 1.1 equiv) was added to a mixture of 3-acetamidocoumarin[24] (0.34 g, 1.7 mmol, 1.2 equiv) in 3.4 mL DMSO. As the mixture was stirred at 23 °C for 60 min the coumarin dissolved, producing a brown solution. A solution of the allene mesylate (0.47 g, 1.4 mmol, 1.0 equiv) in 1.0 mL DMSO was added *via* cannula. The reaction was heated to 65 °C for 34 h and then cooled to 23 °C and poured onto 350 mL H_2O and 175 mL Et_2O. The aqueous layer was extracted with Et_2O (4 X 75 mL). The combined organic layers were washed with 150 mL saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica

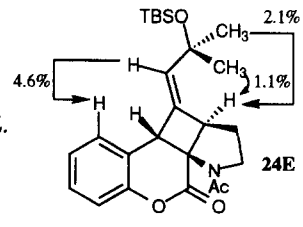
gel (29% EtOAc in hexanes) to give a mixture of product and 3-acetamidocoumarin starting material. The mixture was treated with Et_2O and the starting material was filtered off. Concentration of the filtrate *in vacuo* followed by chromatography on silica gel then afforded 79 mg (13%) of **16**: TLC R_f = 0.27 (2:1 hexanes/EtOAc); $[\alpha]_{Na}$ +58.9° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) (peaks are broadened due to rotamers) δ 7.66 (s, 1H, H_{vinyl}), 7.62-7.32 (m, 4H, H_{aryl}), 5.2 (m, 2H, H_{allene}), 3.95-3.88 (m, 1H, C*H*HN), 3.56-3.46 (m, 1H, CH*H*N), 2.29 (m, 2H, CH_2CH_2N), 2.00 (br s, 3H, H_{acyl}), 1.26 (s, 6H, $(CH_3)_2$COTBS), 0.80 (s, 9H, $(CH_3)_3$CSi), 0.00 (s, 6H, $(CH_3)_2$Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201, 170, 159, 153, 141, 132, 129, 128, 125, 118, 117, 102, 90, 72, 47 (br), 31.0, 30.7, 27, 26, 22, 18, -2.3; IR (thin film) ν 3049 (w), 2955, 2928, 2855, 1960, 1736 (s), 1672 (s), 1610, 1458, 1390, 1249, 1187, 1042, 834, 774; HRMS (CI^+) calcd for $C_{25}H_{36}NO_4Si^+$ (MH^+) 442.3413, found 442.2395.

Photoadduct 24. A solution of substrate **16** (99% ee, 30 mg, 68 μmol) in 30 mL CH_2Cl_2 was deoxygenated by nitrogen sparge 10 min and then was sealed and irradiated 5 min (see General Procedures). The resultant yellow solution was concentrated *in vacuo* and purified by chromatography on silica gel (2:1 hexanes/EtOAc) to give 9 mg of the Z olefin and 14 mg of the E olefin (77%).

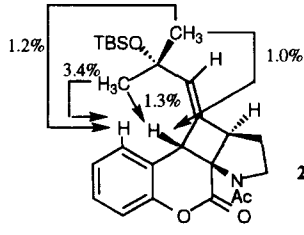
24Z: TLC R_f = 0.42 (1:1 hexanes/EtOAc); $[\alpha]_{Na}$ +179° (c = 0.33, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.64 (d, 1H, *J* = 7.7 Hz, H_{aryl}), 7.24 (t, 1H, *J* = 7.6 Hz, H_{aryl}), 7.10 (t, 1H, *J* = 7.6 Hz, H_{aryl}), 7.04 (d, 1H, *J* = 7.9 Hz, H_{aryl}), 5.35 (t, 1H, *J* = 1.7 Hz, H_{vinyl}), 4.62 (br s, 1H, H_{benzyl}), 4.00-3.92 (m, 2H, C*H*CH_2C*H*HN), 3.87-3.80 (m, 1H, CH*H*N), 2.27-2.21 (m, 1H, C*H*HCH_2NAc), 2.1-2.0 (m, 1H, CH*H*CH_2N), 2.12 (s, 3H, CH_3CON), 1.48 (s, 3H, CH_3COTBS), 1.45 (s, 3H, CH_3COTBS), 0.87 (s, 9H, $(CH_3)_3$CSi), 0.17 (s, 3H, $(CH_3)_2$Si), 0.13 (s, 3H, $(CH_3)_2$Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169, 165, 150, 136, 133, 130, 129, 124, 122, 118, 75, 64, 54, 49, 48, 32, 31, 26, 22, 18, -1.5, -1.7; IR (thin film) ν 3072 (w), 2955, 2929, 2860, 1767 (s), 1654 (s), 1488, 1455, 1407, 1239, 1213, 1182, 1151, 1037, 834, 775; HRMS (CI^+) calcd for $C_{25}H_{36}NO_4Si^+$ (MH^+) 442.2412, found 442.2413.

24E: TLC R_f = 0.30 (1:1 hexanes/EtOAc); $[\alpha]_{Na}$ +36° (c = 0.8, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.26-7.04 (m, 4H, H_{aryl}), 5.46 (t, 1H, *J* = 2.2 Hz, H_{vinyl}), 4.1 (m, 1H, C*H*$(CH_2)_2$N), 4.01-3.86 (m, 3H, H_{benzyl}, CH_2N), 2.52-2.39 (m, 2H, CH_2CH_2N), 2.11 (s, 3H, CH_3CON), 1.31 (s, 3H, CH_3COTBS), 1.27 (s, 3H, CH_3COTBS), 0.78 (s, 9H, $(CH_3)_3$CSi), -0.06 (s, 3H, CH_3Si), -0.13 (s, 3H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 169, 167, 150, 136, 135, 128.3, 127.6, 125, 122, 118, 73, 63, 54, 49.5, 48.9, 32.2, 31.6, 30, 26, 22, 18, -2.3; IR (thin film) ν 3060 (w), 2955, 2929, 2856, 1759 (s), 1651 (s), 1588, 1490, 1455, 1413, 1360, 1252, 1161, 1036, 835, 774, 754; HRMS (CI^+) calcd for $C_{25}H_{36}NO_4Si^+$ (MH^+) 442.2412, found 442.2405.

NOE Data for 24E and 24Z.



24E



24Z

Analysis of Asymmetric Induction. A sample of **24Z** (5.0 mg, 11 μmol, 1 equiv) in 0.5 mL THF at 23 °C was treated with a solution of $LiBH_4$ (2.0 M in THF, 25 μL, 50 μmol, 5 equiv). After stirring at 23 °C for 11 h, the reaction was quenched cautiously with a few drops 1M aqueous KH_2PO_4 solution. The reaction mixture was purified by chromatography on silica gel (1:1 hexanes/EtOAc) to afford 4 mg of the diol (R_f = 0.26, 1:1 hexanes/EtOAc). The diol (5 μmol) was dried by azeotropic removal of water with toluene and then was dissolved in 0.2 mL CH_2Cl_2. Triethylamine (15 μL, 110 μmol, 22 equiv) was added, followed by 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 3 equiv) and a solution of (R)-Mosher's acid chloride (0.1 M in CH_2Cl_2, 150 μL, 15 μmol, 3 equiv). The reaction was stirred at 23 °C for 2 h and then was purified by chromatography on silica gel (4:1 hexanes/EtOAc). Integration of the ^{19}F NMR resonances ($CDCl_3$, 470 MHz) at δ -71.4 ppm (minor) and δ -71.6 ppm (major) indicated an 86% enantiomeric excess, or 87% asymmetric induction.

A sample of **24E** (6.0 mg, 14 μmol, 1 equiv) in 0.6 mL THF at 23 °C was treated with a solution of $LiBH_4$ (2.0 M in THF, 50 μL, 100 μmol, 7 equiv). After stirring at 23 °C for 13 h, the reaction was quenched cautiously with a few drops 1M aqueous KH_2PO_4 solution. The reaction mixture was purified by chromatography on silica gel (2:3 hexanes/EtOAc) to afford 1 mg of the diol (R_f = 0.16, 1:1 hexanes/EtOAc). The alcohol (2 μmol) was dried by azeotropic removal of water with toluene and then was dissolved in 0.2 mL CH_2Cl_2. Triethylamine (15 μL, 110 μmol, 55 equiv) was added, followed by 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 8 equiv) and a solution of (R)-Mosher's acid chloride (0.1 M in CH_2Cl_2, 100 μL, 10 μmol, 5 equiv). The reaction was stirred at 23 °C for 1 h and then was purified by chromatography on silica gel (4:1 hexanes/EtOAc). Integration of the ^{19}F NMR resonances ($CDCl_3$, 470 MHz) at δ -71.3 ppm (minor) and δ -71.6 ppm (major) indicated a 93% enantiomeric excess, or 94% asymmetric induction.

***p*-Toluenesulfonate Ester of 4-Hydroxycoumarin.** A solution of 4-hydroxycoumarin (240 mg, 1.5 mmol, 1.0 equiv) in 7.5 mL pyridine was cooled to 0 °C. *p*-Toluenesulfonyl chloride (320 mg, 1.7 mmol, 1.1 equiv) was added and the reaction mixture was stirred at 0 °C for 35 min. The pyridine was removed by evaporation *in vacuo* and the resulting residue was purified by chromatography on silica gel (3:1 hexanes/EtOAc) to give 450 mg of the desired product (95%): TLC R_f = 0.24 (3:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.90 (d, 1H, *J* = 8.3 Hz, H_{aryl}), 7.66-7.55 (m, 1H, H_{aryl}), 7.40 (d, 1H, *J* = 8.3 Hz, H_{aryl}), 7.33-7.25 (m, 1H, H_{aryl}), 6.31 (s, 1H, H_{vinyl}), 2.47, (s, 3H, CH_3Ar).

4-Mercaptocoumarin. Gaseous H_2S was bubbled through a solution of KOH (7.0 mg, 0.13 mmol, 1.1 equiv) in 0.6 mL absolute ethanol for 15 min before freshly purified tosylate (36 mg, 0.11 mmol, 1.0 equiv) was added. The mixture was stirred at 23 °C with continued bubbling of H_2S for 5 h. Ethanol was removed by evaporation *in vacuo*. Diethyl ether was added to the resultant residue and the mixture was filtered. The filtrate was concentrated *in vacuo* and the resulting residue was used without purification: TLC R_f = 0.05 (5% MeOH in 1:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.91-7.24 (m, 4H, H_{aryl}), 6.42 (s, 1H, H_{vinyl}), 3.90, (br s, 1H, S*H*).

Photosubstrate 17. A solution of allene alcohol **12** (35 mg, 0.13 mmol, 1.0 equiv) in 0.8 mL THF was transferred *via* cannula to a solution of 4-mercaptocoumarin (30 mg, 0.17 mmol, 1.25 equiv) in 1.0 mL THF. Triphenyl phosphine (46 mg, 0.18 mmol, 1.3 equiv) was added, followed by 28 μL (0.18 mmol, 1.3 equiv) diethylazodicarboxylate. The resultant mixture was stirred at 23 °C for 10 min and then was concentrated *in vacuo*. The residue was purified by chromatography on silica gel (7:1 hexanes/EtOAc) to yield 30 mg (54%) of **17** as a white solid: m.p. 52-6 °C for; TLC R_f = 0.58 (3:1 hexanes/EtOAc); $[\alpha]_{Na}$ +66.9° (c = 0.675, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.74 (dd, 1H, *J* = 8.0, 1.2 Hz, H_{aryl}), 7.55 (t, 1H, *J* = 7.7 Hz, H_{aryl}), 7.35-7.25 (m, 2H, H_{aryl}), 6.15 (s, 1H, H_{vinyl}), 5.39 (m, 1H, H_{allene}), 5.30 (q, 1H, *J* = 6.4 Hz, H_{allene}), 3.11 (t, 2H, *J* = 7.2 Hz, CH_2S), 2.51 (m, 2H, CH_2CH_2S), 1.33 (s, 6H, $(CH_3)_2$COTBS), 0.84 (s, 9H, $(CH_3)_3$CSi), 0.07 (s, 3H, CH_3Si), 0.06 (s, 3H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201, 159, 156, 152, 132, 124.0, 123.8, 118, 117, 107, 103, 91, 72, 31.1, 30.7, 30.1, 27, 26, 18, -2.2; IR (thin film) ν 3067 (w), 2956, 2929, 2856, 1965, 1755, 1722 (s), 1686, 1596, 1551, 1343, 1253, 1188, 1149, 1040, 931, 834, 774; HRMS (FAB^+) calcd for $C_{23}H_{32}O_3SSi$ 416.1841, found 416.1845.

Photoadduct 25. A solution of substrate **17** (94% ee, 5.0 mg, 12 μmol) in 5 mL CH_2Cl_2 was deoxygenated by nitrogen sparge 5 min. The reaction vessel was sealed and the solution was irradiated 10 min (see General Procedures). After concentration *in vacuo* the residue was purified by chromatography on silica gel (10% EtOAc in hexanes) to afford 5.0 mg (100%) E-product: TLC R_f = 0.55 (6:1 hexanes/EtOAc); $[\alpha]_{Na}$ +53.2° (c = 0.6, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.58 (dd, 1H, *J* = 7.7, 1.6 Hz, H_{aryl}), 7.27 (t, 1H, *J* = 7.7 Hz, H_{aryl}), 7.16 (td, 1H, *J* = 7.7, 1.1 Hz, H_{aryl}), 7.03 (dd, 1H, *J* = 8.1, 1.1 Hz, H_{aryl}), 5.70 (t, 1H, *J* = 2.5 Hz, H_{vinyl}), 4.15 (t, 1H, *J* = 3.2 Hz, $CHCO$), 3.85 (m, 1H, $CHCH_2CH_2S$), 3.34-3.29 (m, 2H, CH_2S), 2.49-2.41 (m, 2H, CH_2CH_2S), 1.29 (s, 3H, CH_3COTBS), 1.27 (s, 3H, CH_3COTBS), 0.79 (s, 9H, $(CH_3)_3$CSi), 0.01 (s, 3H, CH_3Si), -0.02 (s, 3H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 164, 150, 136, 129.5, 129.0, 128.6, 125, 122, 118, 73, 65, 54, 39, 35, 31.3, 30.7, 26, 18, -2.1, -2.2; IR (thin film) ν 3060 (w), 3037 (w), 2955, 2928, 2854, 1761 (s), 1451, 1251, 1204 (s), 1157, 1036, 835, 774, 758; HRMS (FAB^+) calcd for $C_{23}H_{32}O_3SSi$ 416.1841, found 416.1849.

Analysis of Asymmetric Induction. A sample of **25** (5 mg, 10 μmol, 1 equiv) in 1.0 mL THF at 23 °C was treated with a solution of $LiBH_4$ (2.0 M in THF, 25 μL, 50 μmol, 5 equiv). After stirring at 23 °C for 2 h, the reaction was quenched cautiously with 3 drops 1M aqueous KH_2PO_4 solution. The reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel (3:1 hexanes/EtOAc) to afford 2 mg of the diol (R_f = 0.19, 3:1 hexanes/EtOAc). The diol (5 μmol) was dried by azeotropic removal of water with toluene and then was dissolved in 0.2 mL CH_2Cl_2. Triethylamine (10 μL, 70 μmol, 7 equiv) was added, followed by 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 1.6 equiv) and a solution of (R)-Mosher's acid chloride (0.1 M in CH_2Cl_2, 300 μL, 30 μmol, 3 equiv). The reaction was stirred at 23 °C for 30 min and then was purified by chromatography on silica gel (9:1 hexanes/EtOAc). Integration of the ^1H NMR resonances ($CDCl_3$, 500 MHz) at δ 3.74, 3.41 ppm (minor) and δ 3.68, 3.33 ppm (major) indicated an 83% enantiomeric excess, or 88% asymmetric induction.

Photosubstrate 18. A 60% dispersion of NaH in mineral oil (28 mg, 0.69 mmol, 1.1 equiv) was weighed into a flask, washed with hexanes, and dried under vacuum. An atmosphere of nitrogen was restored and 1.2 mL DMF was added. 4-Aminocoumarin[25] (120 mg, 0.75 mmol, 1.2 equiv) was added and the mixture was stirred at 23 °C for 45 min. A solution of the allene mesylate (210 mg, 0.63 mmol, 1.0 equiv) in 0.6 mL DMF was added *via* cannula. The reaction was heated to 75-80 °C for 35 h and then was cooled to 23 °C and poured onto 5 mL pH 7 phosphate buffer and 10 mL Et_2O. The aqueous layer was extracted with Et_2O (5 X 2 mL). The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (2:1 hexanes/EtOAc) to afford 84 mg (34%) of **18**: TLC R_f = 0.23 (2:1 hexanes/EtOAc); $[\alpha]_{Na}$ +73.8° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.53 (m, 1H, H_{aryl}), 7.37 (m, 2H, H_{aryl}), 7.25 (m, 1H, H_{aryl}), 5.41-5.37 (m, 1H, H_{allene}), 5.34 (s, 1H, H_{vinyl}), 5.27 (q, 1H, *J* = 6.5 Hz, H_{allene}), 5.19 (br m, δ changes with conc, 1H, N*H*), 3.39 (q, 2H, *J* = 6.2 Hz, CH_2N), 2.47 (m, 2H, CH_2CH_2N), 1.31 (s, 6H, $(CH_3)_2COTBS$), 0.84 (s, 9H, $(CH_3)_3CSi$), 0.06 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202, 163, 154, 153, 132, 123, 120, 118, 114, 103, 90, 84, 72, 42, 31.0, 30.7, 27, 26, 18, -2.3; IR (thin film) ν 3342, 3096 (w), 2956, 2929, 2857, 1965, 1678 (s), 1610 (s), 1559 (s), 1470, 1256, 1203, 1149, 1042, 933, 835, 763; HRMS (FAB^+) calcd for $C_{23}H_{34}NO_3Si^+$ (MH^+) 400.2308, found 400.2325.

Acylated Photoadduct 26. To a solution of substrate **18** (99% ee, 20 mg, 50 μmol, 1 equiv) in 20 mL CH_2Cl_2 was added acetic anhydride (190 μL, 2.0 mmol, 40 equiv) and 4-N,N-dimethylaminopyridine (12 mg, 0.10 mmol, 2 equiv). The solution was deoxygenated by N_2 sparge 10 min, sealed, and irradiated 3 X 30 min (see General Procedures). The resulting yellow solution was concentrated *in vacuo* and purified by chromatography on silica gel (40% hexanes in EtOAc) to afford 11 mg (50%) of product **26** (E isomer only): TLC R_f = 0.23 (1:1 hexanes/EtOAc); $[\alpha]_{Na}$ +164° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) (peaks are broadened due to rotamers) δ 7.34-7.03 (m, 4H, H_{aryl}), 5.75 (t, 1H, *J* = 2.3 Hz, H_{vinyl}), 4.3 and 4.1 (m, 1H, C*H*HNAc), 3.94 (m, 1H, CH*H*NAc), 3.83 (m, 1H, C*H*CO), 3.68 (m, 1H, $CH(CH_2)_2N$), 2.5 (m, 1H, C*H*HCH$_2$N), 2.4-2.2 (m, 1H, CH*H*CH$_2$N), 2.07 (s, 3H, CH_3CO), 1.27 (s, 6H, $(CH_3)_2COTBS$), 0.77 (s, 9H, $(CH_3)_3CSi$), -0.01 (s, 3H, CH_3Si), -0.07 (s, 3H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) (some rotamer pairs) δ 169, 162, 151, 137/136, 130.2, 129.5/129.1, 126, 125, 123, 118.0/117.6, 73, 61, 57, 51.2/51.0, 50.5/50.3, 31.8/31.3, 30.5/30.1, 26, 23/22, 18, -2.2, -2.4; IR (thin film) ν 3060 (w), 2955, 2929, 2856, 1759, 1644, 1451, 1413, 1209, 1035, 835, 774; HRMS (CI^+) calcd for $C_{25}H_{36}NO_4Si^+$ (MH^+) 442.2413, found 442.2401.

Analysis of Asymmetric Induction. A sample of **26** (12 mg, 25 μmol, 1 equiv) in 2 mL THF at 23 °C was treated with a solution of $LiBH_4$ (2.0 M in THF, 100 μL, 200 μmol, 8 equiv). After stirring at 23 °C for 11 h, the reaction was quenched cautiously with 4 mL 1M aqueous KH_2PO_4 solution. The aqueous layer was extracted with Et_2O (3 X 2 mL). The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The resultant oil was purified by chromatography on silica gel (2:1 hexanes/EtOAc) to afford 5 mg of the diol (R_f = 0.61, 1:1 hexanes/EtOAc). The alcohol (5 μmol) was dried by azeotropic removal of water with toluene and then was dissolved in 0.1 mL

CH_2Cl_2. Triethylamine (10 μL, 72 μmol, 12 equiv) was added, followed by 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 3 equiv) and a solution of (R)-Mosher's acid chloride (0.1 M in CH_2Cl_2, 200 μL, 20 μmol, 4 equiv). The reaction was stirred at 23 °C for 7 h and then was purified by chromatography on silica gel (gradient elution, 18% EtOAc in hexanes to 50% EtOAc in hexanes). Integration of the ^{19}F NMR resonances ($CDCl_3$, 470 MHz) at δ -70.0, -71.0 ppm (minor) and δ -70.4, -71.4 ppm (major) indicated a 92% enantiomeric excess, or 93% asymmetric induction.

Photosubstrate 19. To a solution of allene alcohol **12** (170 mg, 0.66 mmol, 1 equiv) in 6.6 mL THF were added 130 mg 3-hydroxycoumarin[24] (0.83 mmol, 1.25 equiv), 260 mg triphenyl phosphine (1.0 mmol, 1.5 equiv), and 140 μL diethylazodicarboxylate (0.92 mmol, 1.38 equiv). The reaction was stirred at 23 °C for 30 min and then was concentrated *in vacuo*. The residue was purified by chromatography on silica gel (78:10:8:4 hexanes/benzene/CH_2Cl_2/EtOAc) to afford 170 mg (64%) of substrate **19**: TLC R_f = 0.32 (2:1 CH_2Cl_2/hexanes); $[\alpha]_{Na}$ +51.3° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.40-7.23 (m, 4H, H_{aryl}), 6.82 (s, 1H, H_{vinyl}), 5.34 (m, 2H, H_{allene}), 4.09 (t, 2H, CH_2O), 2.61 (m, 2H, CH_2CH_2O), 1.32 (s, 6H, $(CH_3)_2$COTBS), 0.85 (s, 9H, $(CH_3)_3$CSi), 0.07 (s, 6H, $(CH_3)_2$Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 201, 157, 149, 144, 128, 126, 125, 120, 116, 113, 103, 89, 72, 68, 30.9, 30.7, 28, 26, 18, -2.3; IR (thin film) ν 3066 (w), 2955, 2929, 2856, 1966, 1778, 1740 (s), 1627, 1458, 1298, 1251, 1139, 1114, 1040, 835, 774, 753; HRMS (FAB^+) calcd for $C_{23}H_{33}O_4Si^+$ (MH^+) 401.2148, found 401.2149.

Photoadduct 27. A solution of substrate **19** (99% ee, 63 mg, 0.16 mmol) in 63 mL cyclohexane was deoxygenated by nitrogen sparge 10 min and then was sealed and irradiated for 3.5 h (see General Procedures). The resultant yellow solution was concentrated *in vacuo* and purified by chromatography on silica gel (gradient elution, 2:1 CH_2Cl_2/hexanes to 4:1 CH_2Cl_2/hexanes) to give 38 mg of the Z olefin isomer (60%): TLC R_f = 0.19 (2:1 CH_2Cl_2/hexanes); $[\alpha]_{Na}$ +115° (c = 0.5, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 7.74 (d, 1H, *J* = 7.8 Hz, H_{aryl}), 7.25 (t, 1H, *J* = 7.6 Hz, H_{aryl}), 7.11 (t, 1H, *J* = 7.7 Hz, H_{aryl}), 7.02 (d, 1H, *J* = 8.0 Hz, H_{aryl}), 5.30 (t, 1H, *J* = 1.8 Hz, H_{vinyl}), 4.52 (m, 2H, H_{benzyl}, $CHHO$), 4.36 (q, 1H, *J* = 7.9 Hz, $CHHO$), 3.98 (m, 1H, $CHCH_2CH_2O$), 2.14-2.03 (m, 2H, CH_2CH_2O), 1.46 (s, 3H, CH_3COTBS), 1.44 (s, 3H, CH_3COTBS), 0.91 (s, 9H, $(CH_3)_3$CSi), 0.20 (s, 3H, CH_3Si), 0.17 (s, 3H, CH_3Si); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 167, 150, 137, 134, 131, 129, 124, 122, 117, 81, 75, 72, 57, 48, 31.7, 31.4, 31.2, 26, 18, -1.5, -1.6; IR (thin film) ν 3060 (w), 3037 (w), 2931, 2857, 1771 (s), 1587, 1453, 1361, 1239, 1164, 1063, 1038, 835, 774; HRMS (FAB^+) calcd for $C_{23}H_{33}O_4Si^+$ (MH^+) 4401.2148, found 401.2133.

Analysis of Asymmetric Induction. A sample of **27** (5.0 mg, 13 μmol, 1 equiv) in 0.5 mL THF at 23 °C was treated with a solution of $LiBH_4$ (2.0 M in THF, 25 μL, 50 μmol, 4 equiv). After stirring at 23 °C for 14 h, the reaction was quenched cautiously with 3 drops 1M aqueous KH_2PO_4 solution. The reaction mixture was concentrated *in vacuo* and purified by chromatography on silica gel (2:1 hexanes/EtOAc) to afford 1 mg of the diol (R_f = 0.13, 2:1 hexanes/EtOAc). The diol (3 μmol)was dried by azeotropic removal of water with toluene and then was dissolved in 0.2 mL CH_2Cl_2. Triethylamine (20 μL, 140 μmol, 47 equiv) was added, followed by 4-N,N-dimethylaminopyridine (2.0 mg, 16 μmol, 5 equiv) and a solution of (R)-Mosher's

acid chloride (0.1 M in CH_2Cl_2, 200 μL, 20 μmol, 7 equiv). The reaction was stirred at 23 °C for 20 min and then was purified by chromatography on silica gel (8:1 hexanes/EtOAc). Integration of the ^{19}F NMR resonances ($CDCl_3$, 470 MHz) at δ -70.9, -71.5 ppm (minor) and δ -71.2, -71.9 ppm (major) indicated a 94% enantiomeric excess, or 95% asymmetric induction.

Photosubstrate 20. A 60% dispersion of NaH in mineral oil (41 mg, 1.0 mmol, 1.1 equiv) was weighed into a flask, washed with hexanes, and dried under vacuum. After an atmosphere of nitrogen was restored, 0.5 mL DMF was added and the mixture was cooled to 0 °C. A solution of the dihydropyridone[26] (120 mg, 1.1 mmol, 1.2 equiv) in 0.7 mL DMF was added *via* cannula and stirring was continued at 0 °C for 5 min and then at 23 °C for 15 min. A solution of the allene mesylate (310 mg, 0.93 mmol, 1.0 equiv) in 0.7 mL DMF was added *via* cannula. The reaction was heated to 65 °C for 12 h and then was cooled to 23 °C and poured onto 10 mL pH 7 phosphate buffer and 20 mL Et_2O. The aqueous layer was extracted with Et_2O (10 X 3 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residue was purified by chromatography on silica gel (gradient elution, 2:1 Et_2O/EtOAc to EtOAc) to afford 195 mg (63%) of substrate **20**: TLC R_f = 0.47 (EtOAc); $[\alpha]_{Na}$ +75.3° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 6.98 (d, 1H, *J* = 7.4 Hz, $CH_{vinyl}N$), 5.29 (m, 1H, H_{allene}), 5.13 (q, 1H, *J* = 6.6 Hz, H_{allene}), 4.91 (d, 1H, *J* = 7.4 Hz, $CH_{vinyl}CO$), 3.44 (t, 2H, *J* = 7.8 Hz, NCH_2CH_2CO), 3.27 (m, 2H, NCH_2CH_2CH), 2.45 (t, 2H, *J* = 7.8 Hz, NCH_2CH_2CO), 2.28 (m, 2H, NCH_2CH_2CH), 1.28 (s, 3H, CH_3COTBS), 1.27 (s, 3H, CH_3COTBS), 0.82 (s, 9H, $(CH_3)_3CSi$), 0.04 (s, 6H, $(CH_3)_2Si$); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 202, 191, 154, 103, 98, 89, 72, 55, 47, 36, 30.9, 30.8, 28, 26, 18, -2.2; IR (thin film) ν 2928, 2855, 1963, 1637, 1591, 1466, 1360, 1249, 1176, 1038, 833, 734; HRMS (FAB^+) calcd for $C_{19}H_{34}NO_2Si^+$ (MH^+) 336.2359, found 336.2348.

Photoadduct 28. A solution of substrate **20** (99% ee, 73 mg, 0.22 mmol) in 75 mL CH_2Cl_2 was deoxygenated by N_2 sparge 15 min. The flask was sealed and irradiated 20 min (see General Procedures). The resultant yellow solution was concentrated *in vacuo* and purified by column chromatography (gradient elution, 50% hexanes in EtOAc to EtOAc to 5% MeOH in EtOAc) to yield 36 mg of the Z isomer and 20 mg of the E isomer (77%).

28Z: TLC R_f = 0.54 (20:1 EtOAc/MeOH); $[\alpha]_{Na}$ +136° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.54 (t, 1H, *J* = 2.5 Hz, H_{vinyl}), 4.02 (t, 1H, *J* = 5.3 Hz, C(7)H), 3.56 (m, 1H, C(8)H), 3.45-3.39 (m, 2H, C(6)H, C(4)H), 3.27-3.04 (m, 3H, C(4)H, $C(3)H_2$), 2.8 (m, 1H, C(5)H), 2.1 (dm, 1H, *J* = 14 Hz, C(5)H), 2.0-1.9 (m, 2H, $C(2)H_2$), 1.31 (s, 3H, CH_3COTBS), 1.17 (s, 3H, CH_3COTBS), 0.84 (s, 9H, $(CH_3)_3CSi$), 0.04 (s, 6H, $(CH_3)_2Si$), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 208, 137, 133, 73, 63, 54, 49.5, 48.9, 47.7, 35, 31, 30.1, 29.9, 26, 18, -2.2; IR (thin film) ν 2928, 2855, 1695, 1462, 1360, 1251, 1155, 1038, 834, 771; HRMS (FAB^+) calcd for $C_{19}H_{34}NO_2Si^+$ (MH^+) 336.2359, found 336.2341.

28E: TLC R_f = 0.42 (20:1 EtOAc/MeOH); $[\alpha]_{Na}$ +162° (c = 1.0, $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 5.33 (t, 1H, *J* = 2.5 Hz, H_{vinyl}), 4.00 (t, 1H, *J* = 5.6 Hz, C(7)H), 3.74 (m, 1H, C(8)H), 3.33 (m, 2H, C(6)H, C(4)H), 3.24-3.09 (m, 2H, C(4)H, C(3)H), 3.01 (t, 1H, *J* ~8 Hz, C(3)H), 2.72-2.65 (m, 1H, C(5)H), 2.21-1.95 (m, 3H, C(5)H, $C(2)H_2$), 1.31 (s, 3H, CH_3COTBS), 1.30 (s, 3H, CH_3COTBS),

0.86 (s, 9H, $(CH_3)_3CSi$), 0.09 (s, 3H, CH_3Si) 0.06 (s, 3H, CH_3Si), ^{13}C NMR ($CDCl_3$, 75 MHz) δ 207, 135, 134, 74, 60, 51, 48.2, 48.1, 45, 32, 31.3, 31.1, 30.9, 26, 18, -1.9; IR (thin film) ν 2926, 1694, 1462, 1360, 1252, 1150, 1028, 832, 772; HRMS (FAB^+) calcd for $C_{19}H_{34}NO_2Si^+$ (MH^+) 336.2359, found 336.2364.

Analysis of Asymmetric Induction. GC analysis of **28Z** (150 °C, ret time 142 min (minor), 145 min (major)) indicated a 63% enantiomeric excess, or 64% asymmetric induction.

A sample of **28E** (6.0 mg, 18 μmol, 1 equiv) in 0.5 mL MeOH at 23 °C was treated with 2.0 mg (53 μmol, 3 equiv) $NaBH_4$. After stirring for 20 min, the mixture was poured onto a solution of pH 7 phosphate buffer and saturated aqueous NaCl. The resultant mixture was extracted exhaustively with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. GC analysis of the resultant oil (165 °C, ret time 90.6 min (minor), 92.2 min (major)) indicated a 53% enantiomeric excess, or 54% asymmetric induction.

Methyl Ester 30. A solution of photoadduct **22Z** (14 mg, 31 μmol, 1.0 equiv) in 15 mL MeOH at -78°C was treated with a dilute stream of ozone for 10 min before $NaBH_4$ (6.0 mg, 160 μmol, 5 equiv) was added. Stirring was continued at -78 °C for 10 min before excess acetone was added and the mixture was allowed to warm to 23 °C. The resultant mixture was concentrated *in vacuo* and the residue was purified by chromatography on silica gel (3:1 hexanes/EtOAc) to afford 8.5 mg (85%) of ester **30**: TLC R_f = 0.40 (2:1 hexanes/EtOAc); ^1H NMR ($CDCl_3$, 300 MHz) (peaks broadened due to rotamers) δ 3.70-3.60 (m, 1H, C*H*HN), 3.64 (s, 3H, OCH_3), 3.47-3.42 (m, 1H, CH*H*N), 2.92-2.88 (m, 1H, C*H*CO_2Me), 2.7 (m, 1H, C*H*HCO), 2.32-2.78 (m, 3H, CH_2CO, CH*H*CO), 2.10-1.94 (m, 4H), 1.85-1.82 (m, 1H), 1.79-1.63 (m, 1H), 1.44 (s, 9H, $OC(CH_3)_3$); IR (thin film) ν 2927, 1735 (s), 1712 (s), 1686 (s), 1458, 1381 (s), 1365, 1169, 1103.

Acknowledgment. We are grateful to Dr. Robert Singer for carrying out the aldol addition reaction with substrate **5**. M.S.S. is grateful to the Office of Naval Research for a graduate fellowship. This research has been generously supported by awards from the Packard Foundation, Camille and Henry Dreyfus Foundation, and Sloan Foundation, as well as funds provided by the NIH, and NSF and gifts from Eli Lilly, Merck, Pfizer, Upjohn, and Zeneca.

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(*Received* 3 *January* 1997; *accepted* 2 *April* 1997)