Designing New Chiral Ketone Catalysts. Asymmetric Epoxidation of *cis*-Olefins and Terminal Olefins

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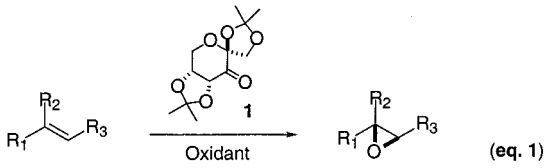
This paper describes a new class of chiral oxazolidinone ketone catalyst for asymmetric epoxidation. High ee values have been obtained for a number of cyclic and acyclic *cis*-olefins. The epoxidation was stereospecific with no isomerization observed in the epoxidation of acyclic systems. Encouragingly high ee values have also been obtained for a number of terminal olefins. Mechanistic studies show that electronic interactions play an important role in stereodifferentiation.

Asymmetric epoxidation of olefins presents a powerful strategy for the synthesis of enantiomerically enriched epoxides.[1−3] Great success has been achieved in the epoxidation of allylic alcohols.[1] For asymmetric epoxidation of unfunctionalized olefins, metal catalysts such as chiral salen and porphyrin complexes provide very high enantioselectivities, particularly for *cis*-olefins, conjugated trisubstituted olefins, and certain terminal olefins.[2,4] Dioxiranes generated in situ from chiral ketones have been shown to be highly enantioselective for the asymmetric epoxidation of *trans*-olefins and trisubstituted olefins.[5−7] However, it has been extremely challenging for chiral dioxiranes to epoxidize *cis*-olefins and terminal olefins with high enantioselectivity. Recently, we reported a class of promising chiral oxazolidinone ketones that provided high ee values for the epoxidation of *cis*-olefins and terminal olefins.[8] Herein we wish to report our detailed studies on this subject.

Catalyst Design and Synthesis

Earlier, we reported that the fructose-derived ketone **1** is an effective epoxidation catalyst and gives high ee values for a variety of *trans*- and trisubstituted olefins (eq 1).[7] However, epoxidation of *cis*- and terminal olefins using this ketone led to rather poor enantioselectivity.[7c]



(eq. 1)

For example, epoxidation of *cis*-*β*-methylstyrene and styrene using ketone **1** gave only 39% and 24% ee,

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(1) For recent reviews on highly enantioselective epoxidation of allylic alcohols, see: (a) Johnson, R. A.; Sharpless, K. B. In *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH: New York, 1993; Chapter 4.1. (b) Katsuki, T.; Martin, V. S. *Org. React.* **1996**, *48*, 1.

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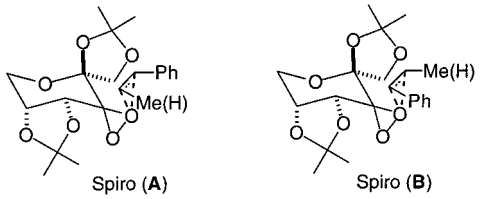
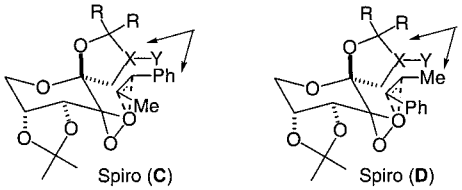
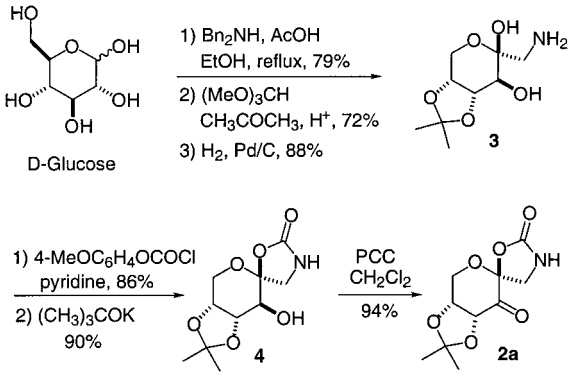
Scheme 1



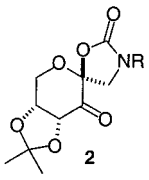
Scheme 2



Scheme 3



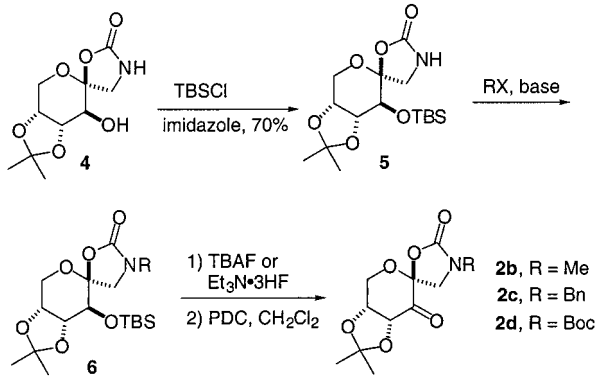
respectively. On the basis of our earlier transition state analysis,[7c] spiro **A** and **B** are likely to be the two major competing transition states (Scheme 1). The low ee obtained indicates that the ketone catalyst does not provide the necessary structural environment to differentiate between the phenyl and methyl (or hydrogen) groups of the olefin (Scheme 1). Since the spiro ketal of ketone **1** is in the proximity of one of the substituents on reacting olefins in the transition state, it was envisioned that replacement of the spiro ketal by other moieties would enhance selectivity by creating an environment in which the substituents on the olefin could be sufficiently differentiated sterically and/or electronically (Scheme 2). In line with this notion, ketone **2**, a nitrogen analogue of **1**, was among the ketones investigated for epoxidation.



Ketone **2** replaces the spiro ketal of **1** with an oxazolidinone. Ketones **2a**−**d** were prepared for our initial studies, and their syntheses are outlined in Schemes 3 and 4. Briefly, the Amadori rearrangement was carried out by refluxing D-glucose in ethanol with dibenzylamine in the presence of acetic acid (Scheme 3).[9] The resulting rearranged product was converted into aminodiol **3** by

(9) Hodge, J. E.; Fisher, B. E. *Methods Carbohydr. Chem*. **1963**, *2*, 99.

Scheme 4



ketalization and hydrogenation. Compound **3** was then converted to ketone **2a** by a two-step formation of the oxazolidinone, followed by PCC oxidation, as shown. The N-substituted ketones **2b**−**d** were prepared as shown in Scheme 4. Alcohol **4** was protected as TBS ether **5**, and the substituents were then introduced onto the nitrogen by alkylation or acylation. The resulting TBS ether **6** was then converted into ketones **2b**−**d** by desilylation and oxidation.

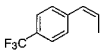
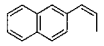
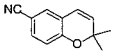
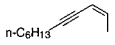
Asymmetric Epoxidation Studies

The catalytic properties of ketones **2a**−**d** were then investigated. Although our initial studies showed that these ketones did not give an enantioselectivity as high as **1** for *trans*-olefins, the ee's for *cis*-olefins were higher. When the epoxidation of *cis*-β-methylstyrene was carried out in DMM (dimethoxymethane)−CH_3CN (2/1), ketones **2a**−**d** gave the epoxide in 47%, 75%, 59%, and 84% ee, respectively. The ee could be further enhanced by using different solvents and running the epoxidation at lower temperature. For example, when the epoxidation was carried out with 15 mol % ketone **2d** in DME−DMM (3/1), at −10 °C, (1*R*,2*S*)-*cis*-β-methylstyrene oxide was obtained in 87% yield with 91% ee (Table 1, entry 1). Furthermore, like other dioxirane-mediated epoxidations, the epoxidation of *cis*-β-methylstyrene was found to be stereospecific, with no *trans*-β-methylstyrene oxide formed during the reaction, as judged by ^{1}H NMR and GC assays of the crude reaction mixture.

Encouraged by this result, we investigated the epoxidation for a variety of *cis*-olefins to explore the generality of ketone **2d**. The enantiomeric excesses were generally high for a variety of acyclic and cyclic *cis*-olefins conjugated with aromatics (Table 1, entries 1−11). Further studies showed that the enantioselectivity of the epoxidation did not significantly vary with substitution on the phenyl group of the olefin (Table 1, entries 2−6). The epoxidation of *cis*-1-cyclohexyl-1-propene with ketone **2d** resulted in the formation of the (2*R*,3*S*)-2-cyclohexyl-3-methyloxirane in 67% ee, indicating that a conjugated aromatic group is beneficial for enantioselectivity. The epoxidation of acyclic *cis*-enynes was also found to be both highly enantioselective and stereospecific, providing *cis*-epoxides with high ee values (Table 1, entries 12−13).[10]

(10) For leading references on asymmetric epoxidations of enynes using (salen)Mn(III), see: (a) Lee, N. H.; Jacobsen, E. N. *Tetrahedron Lett*. **1991**, *32*, 6533. (b) Brandes, B. D.; Jacobsen, E. N. *J. Org. Chem*. **1994**, *59*, 4378. (c) Hamada, T.; Irie, R.; Katsuki, T. *Synlett*, **1994**, 479. (d) Sasaki, H.; Irie, R.; Hamada, T.; Suzuki, K.; Katsuki, T. *Tetrahedron* **1994**, *50*, 11827. (e) Hamada, T.; Daikai, K.; Irie, R.; Katsuki, T. *Synlett* **1995**, 407.

Table 1. Asymmetric Epoxidation of *cis*-Olefins by Ketone 2d[a]

entry	substrate	yield (%)[b]	ee (%)	configuration
1[c]		87	91[i]	(-)-(1R,2S)[n,15a,b]
2[c]		76[h]	92[i]	(1R,2S)[o,15c]
3[c]		79[h]	88[i]	(1R,2S)[o]
4[c]		58[h]	93[i]	ND
5[c]		74[h]	92[i]	(1R,2S)[o]
6[d]		63[h]	90[i]	(1R,2S)[o]
7[c]		91	92[j]	(-)-(1R,2S)[p]
8[e]		88	83[k]	(-)-(1R,2S)[n,15d]
9[c]		88	84[k]	(+)-(1R,2S)[n,15b,10d]
10[e]		77	91[l]	(-)-(5R,6S)[n,15e,f]
11[f]		61	91[m]	(+)-(3R,4R)[n,15g,h]
12[g]		82	91[m]	(-)-(2S,3R)[q,10a,d]
13[d]		77	87[m]	(-)-(2S,3R)[q]
14[d]		47	96[i]	(+)
15[d]		61	97[i]	(+)[15i]
16[d]		88	94[i]	(+)

[a] All reactions were carried out with olefin (0.5 mmol), ketone (0.075−0.15 mmol), Oxone (0.89 mmol), and K_2CO_3 (2.01 mmol) in DME/DMM (3:1, v/v) (7.5 mL) and buffer (0.2 M K_2CO_3−AcOH, pH 8.0) (5 mL) at −10 or 0 °C. The reactions were stopped after 3.5 h. [b] The epoxides were purified by flash chromatography and gave satisfactory spectroscopic characterization. [c] With 0.075 mmol ketone at −10 °C. [d] With 0.15 mmol ketone at 0 °C. [e] With 0.10 mmol ketone at −10 °C. [f] With 0.075 mmol ketone at 0 °C. [g] With 0.15 mmol ketone at −10 °C. [h] The olefin substrate contains a mixture of *cis*- and *trans*-isomers. The yield is for the mixture of *cis*- and *trans*-epoxides. [i] Enantioselectivity was determined by chiral GC (Chiraldex G-TA). [j] Enantioselectivity was determined by chiral HPLC (Chiralcel OJ). [k] Enantioselectivity was determined by chiral HPLC (Chiralcel OB). [l] Enantioselectivity was determined by chiral HPLC (Chiralpak AD). [m] Enantioselectivity was determined by chiral HPLC (Chiralcel OD). [n] The absolute configurations were determined by comparing the measured optical rotations with the reported ones. [o] The epoxide was reduced to the benzylic alcohol with $LiAlH_4$, and the absolute configuration was determined by comparing the measured optical rotation of the alcohol with the reported one (ref 16). [p] The epoxide was reduced to 1-(2-naphthyl)propanol with $LiAlH_4$, and the absolute configuration was determined by comparing the measured optical rotation of the alcohol with the reported one (ref 16). [q] The epoxide was reduced with $LiAlH_4$ to the corresponding homopropargyl alcohol, and the absolute configuration was determined by a correlation of the resulting alcohol with a prepared authentic sample by a different route (ref 10a).

High ee's were obtained for 3,3-ethylenedioxycycloalkenes as well (Table 1, entries 14−16).[11]

(11) Up to 40% ketone could be recovered after extracting the aqueous layer of the reaction mixture with CH_2Cl_2−EtOAc and purification by flash chromatography. The recovered ketone gave a similar conversion and ee for the epoxidation.

Table 2. Asymmetric Epoxidation of Terminal Olefins, *trans*-Olefins, and Trisubstituted Olefins by Ketone 2d[a]

entry	substrate	yield (%)[b]	ee (%)	configuration [h]
1[c]		92	81[f]	(-)-(R)[17a]
2[d]		61	81[f]	(-)-(R)[17a]
3[d]		74	83[f]	(-)-(R)[17a]
4[d]		90	85[f]	(-)-(R)[17a]
5[d]		93	71[f]	ND[17b,c]
6[d]		88	30[g]	(+)-(S)[17a]
7[d]		87	58[f]	(+)[17d]
8[e]		65	94[g]	(+)-(R,R)[18,7c]
9[c]		91	77[f]	(+)-(R,R)[15a,7c]
10[c]		78	95[f]	(+)[7c]
11[c]		68	42[f]	(-)-(S,S)[7c]
12[c]		55	80[g]	(+)[7c]

[a] All reactions were carried out with olefin (0.5 mmol), ketone (0.075−0.15 mmol), Oxone (0.89 mmol), and K_2CO_3 (2.01 mmol) in DME/DMM (3:1, v/v) (7.5 mL) and buffer (0.2 M K_2CO_3−AcOH, pH 8.0) (5 mL) at −10 or 0 °C. The reactions were stopped after 3.5 h. [b] The epoxides were purified by flash chromatography and gave satisfactory spectroscopic characterization. [c] With 0.075 mmol ketone at −10 °C. [d] With 0.15 mmol ketone at −10 °C. [e] With 0.15 mmol ketone at 0 °C. [f] Enantioselectivity was determined by chiral GC (Chiraldex G-TA). [g] Enantioselectivity was determined by chiral HPLC (Chiralcel OD). [h] The absolute configurations were determined by comparing the measured optical rotations with the reported ones.

Further studies showed that encouragingly high ee's could also be obtained for styrenes. When the reaction was carried out with 15 mol % ketone **2d** at −10 °C, (*R*)-styrene oxide was obtained in 92% yield with 81% ee (Table 2, entry 1). The ee values are somewhat dependent on substitution of the phenyl groups of the olefins (Table 2, entries 2−4), with 85% ee obtained for 4-chlorostyrene (Table 2, entry 4). Aliphatic terminal olefins gave lower enantioselectivity, as 71% ee was obtained when a phenyl group of styrene was replaced with a cyclohexyl group (Table 2, entry 5). The ee's for 1,1-disubstituted olefins were rather poor (Table 2, entries 6 and 7).

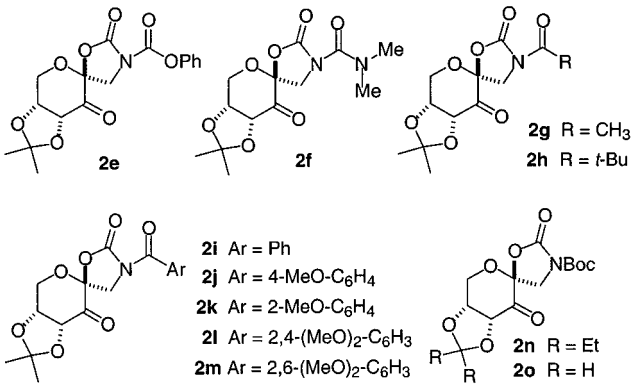
Studies with *trans*- and trisubstituted olefins showed that the enantioselectivity was substrate dependent (Table 2). In general, ketone **2d** is a less effective catalyst than ketone **1** for these classes of olefins. However, in certain cases, **2d** gives a higher ee than **1**. For example, 95% ee is obtained for 2,2-dimethylstyrene with **2d** (Table 2, entry 10), while only 76% ee was obtained with **1**.[7c] The epoxidation of 1-phenylcyclohexene and 1-phenyl-3,4-dihydronaphthalene was rather interesting. For these two olefins, 42% and 80% ee were obtained respectively with **2d** in contrast to 98% and 95% ee with **1**. Strikingly, the configuration of the epoxide obtained with **2d** was opposite to the one obtained with **1** (vide infra).

Table 3. Asymmetric Epoxidation of Olefins by Ketones 2, 16, and 17[a]

entry	ketone	Ph conv (ee)[b]	Ph conv (ee)[c]	Ph conv (ee)[d]	Ph conv (ee)[e]	Ph conv (ee)
1	**2a**	100 (62)	100 (59)	100 (76)	100 (79)	100 (55) (R,R)
2	**2b**	100 (72)	100 (79)	100 (79)	100 (92)	100 (40) (R,R)
3	**2c**	100 (65)	100 (70)	100 (81)	100 (90)	100 (59) (R,R)
4	**2d**	100 (79)	100 (87)	100 (77)	100 (94)	100 (23) (S,S)
5	**2e**	100 (75)	100 (89)	100 (73)	100 (94)	100 (46) (S,S)
6	**2f**	88 (61)	100 (59)	97 (72)	100 (69)	100 (65) (R,R)
7	**2g**	87 (73)	100 (87)	100 (73)	100 (95)	100 (44) (S,S)
8	**2h**	99 (70)	100 (78)	100 (75)	100 (89)	100 (51) (R,R)
9	**2i**	94 (73)	100 (86)	85 (73)	100 (95)	100 (18) (S,S)
10	**2j**	100 (73)	100 (87)	100 (74)	100 (93)	100 (14) (S,S)
11	**2k**	100 (66)	97 (78)	100 (71)	100 (90)	100 (12) (R,R)
12	**2l**	100 (63)	100 (74)	100 (69)	100 (88)	100 (6) (R,R)
13	**2m**	100 (52)	100 (47)	100 (70)	100 (54)	100 (69) (R,R)
14	**2n**	100 (77)	100 (80)	100 (75)	100 (91)	100 (23) (S,S)
15	**2o**	100 (69)	100 (79)	100 (73)	100 (93)	100 (29) (S,S)
16[f]	**16**	100 (47)	100 (39)	100 (61)	100 (78)	100 (2) (R,R)
17[g]	**17**	49 (<1)	91 (16)[h]	83 (32)	64 (3)	66 (64) (R,R)

[a] All reactions were carried out with olefin (1 equiv), ketone (0.15 equiv), Bu_4NHSO_4 (0.05 equiv), Oxone (1.6 equiv), and K_2CO_3 (4.2 equiv) in DME/DMM (3:1, v/v) and buffer (0.2 M K_2CO_3−AcOH, pH 8.0) at 0 °C. The reactions were stopped after 3.5 h. Enantioselectivity was determined by chiral GC (Chiraldex G-TA). [b] The epoxide has the (*R*) configuration. [c] The epoxide has the (1*R*,2*S*) configuration unless otherwise noted. [d] The epoxide has the (*R*,*R*) configuration. [e] The epoxide has the (*R*) configuration. [f] 0.3 equiv of ketone used. [g] 1.0 equiv of ketone used. [h] The epoxide has the (1*S*,2*R*) configuration.

Scheme 5



The substituents on the nitrogen of the ketone displayed some effect on enantioselectivity of the epoxidation. To further study such an effect, ketones with a variety of substituents on nitrogen were synthesized and investigated for the epoxidation (Scheme 5). Ketones **2e**−**m** were prepared as described in Scheme 4. Their catalytic properties were tested with five substrates representing terminal, *cis*-, *trans*-, and trisubstituted olefins. As shown in Table 3, the substituents on the nitrogen had a significant effect on the enantioselectivity of the epoxidation. Overall, ketones **2d**, **2e**, **2g**, **2i**, and **2j** were found to be the most effective catalysts. One noticeable feature of these ketones is that in the case of 1-phenylcyclohexene not only the ee but also the configuration of the epoxide significantly varied with the N-substituents.

Among these ketones, we were able to obtain the crystal structures for ketones **2a**, **2b**, **2d**, and **2e** (Figures 1 and 2). From these structures, it appears that the

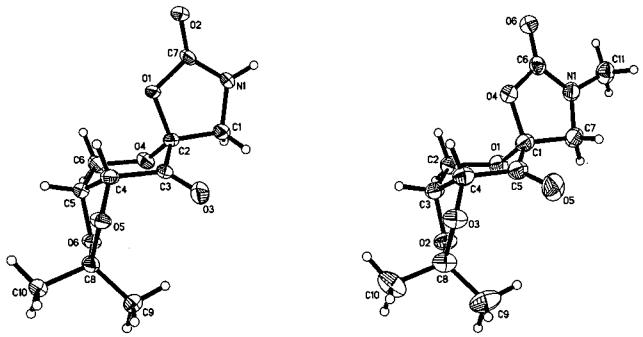


Figure 1. X-ray structure of ketones **2a** (left) and **2b** (right) (ORTEP view).

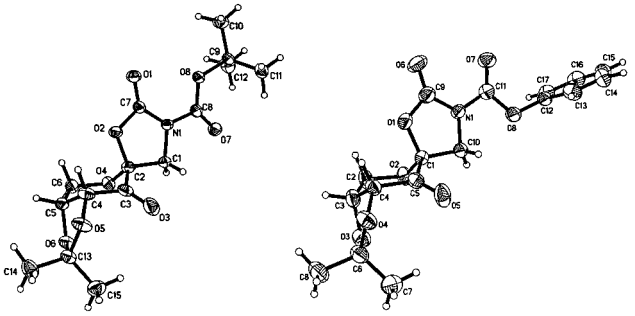
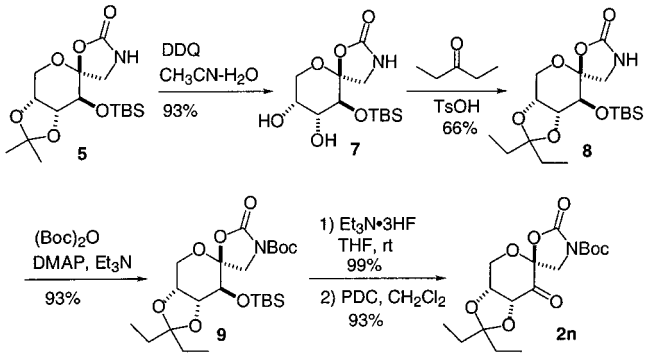


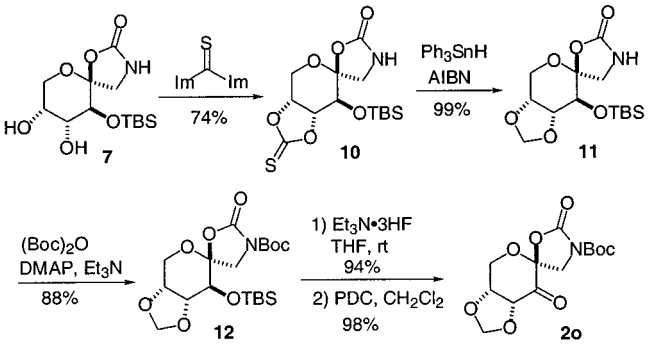
Figure 2. X-ray structure of ketones **2d** (left) and **2e** (right) (ORTEP view).

substituents on the nitrogen are away from the reacting center (dioxirane) (at least in the solid state). Their influence on the enantioselectivity of the epoxidation could be through a conformational or electronic effect rather than a steric effect. The structures of **2d** and **2e**

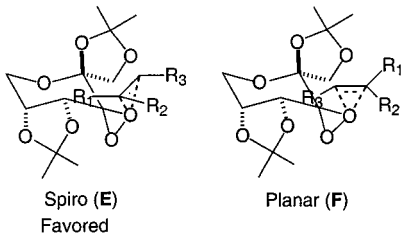
Scheme 6



Scheme 7



Scheme 8

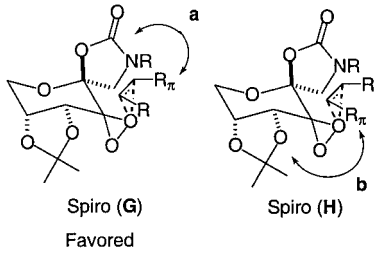


also showed that the carbonyl groups of N−Boc and N−COOPh are coplanar with the oxazolidinone, which could be important for enantioselectivity. To test the effect of the fused ketal of the ketone on epoxidation, ketones **2n** and **2o** were prepared as described in Schemes 6 and 7. The comparison studies between **2d**, **2n**, and **2o** showed that the dimethyl ketal was better than the diethyl and methylene ketals (Table 3, entries 4, 14, and 15).

Discussion

Understanding the reaction mode of the dioxirane-mediated epoxidation is critical for developing a useful model to predict the stereochemical outcome of the reaction and for designing effective ketone catalysts. The epoxidation of *trans*- and trisubstituted olefins with catalyst **1** has been shown to proceed mainly via spiro transition state **E** (Scheme 8).[7a,7c,12] The main competing transition state is believed to be planar transition state **F** (Scheme 8).[7c] The nature of the substituents on the olefins have noticeable effects on the competition between the two transition states, consequently affecting the enantioselectivities of the epoxidation.[7c] In general, higher ee can be obtained by decreasing the size of R_1 (favoring spiro **E**) and increasing the size of R_3 (disfavoring planar **F**).[13]

Scheme 9



The high ee values obtained with ketone **2** for *cis*-olefins is rather intriguing. Spiro **G** and **H** are the two plausible competing transition states (Scheme 9). The determination of the absolute configurations of some selected epoxides (Table 1) revealed that R groups with π system (R_π), regardless of its size, preferred to be proximal of the spiro oxazolidinone of the ketone. Thus, spiro **G** is favored over **H**. This observation is clearly difficult to explain solely based on steric interaction. It seems that there exists some electronic interaction between R_π and the ketone catalyst in the transition state. As a result, groups with π systems (R_π) could be significantly differentiated from those without π electrons (R), leading to high enantioselectivity for the reaction.[14] The interaction could involve attractive interaction between R_π and the oxazolidinone moiety of the ketone (interaction **a**) and/or some repulsive interaction between R_π and the fused ketal moiety of the ketone (interaction **b**).

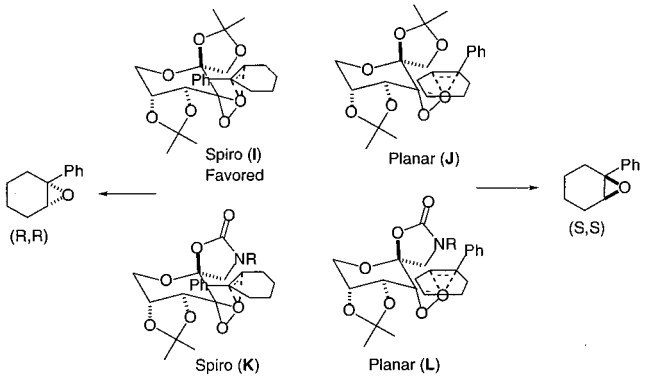
Although repulsive interaction **b** is difficult to assess at the moment, the epoxidation data provides a clear indication of the involvement of attractive interaction **a**. For example, when the epoxidation of 1-phenylcyclohexene was carried out with ketone **1**, the epoxide was obtained in 98% ee in (*R,R)* configuration, showing that spiro **I** is greatly favored over planar **J** (Scheme 10).[7c] However, as shown in Table 3, when the epoxidation was carried out with ketone **2**, the reaction outcome varies dramatically with the substituents on the nitrogen of the ketone. In some cases, the (*S,S*) isomer is obtained, suggesting that planar **L** eventually becomes a major transition state. The flip between spiro **K** and planar **L** is consistent with the attractive interaction between the Ph group and the oxazolidinone (interaction **a**). Such interaction can be significantly affected by the N-substituent on the ketone. The X-ray structures of ketones **2d** and **2e** show that the N−R groups are distant from the reacting center (dioxirane); thus, they have little steric effect on the epoxidation. The epoxidation data

(12) For leading references on the transition states of the dioxirane-mediated epoxidation, see: (a) Baumstark, A. L.; McCloskey, C. J. *Tetrahedron Lett.* **1987**, *28*, 3311. (b) Baumstark, A. L.; Vasquez, P. C. *J. Org. Chem.* **1988**, *53*, 3437. (c) Bach, R. D.; Andres, J. L.; Owensby, A. L.; Schlegel, H. B.; McDouall, J. J. W. *J. Am. Chem. Soc.* **1992**, *114*, 7207. (d) refs 6f and 6m. (e) Houk, K. N.; Liu, J.; DeMello, N. C.; Condroski, K. R. *J. Am. Chem. Soc.* **1997**, *119*, 10147. (f) Jenson, C.; Liu, J.; Houk, K. N.; Jorgensen, W. L. *J. Am. Chem. Soc.* **1997**, *119*, 12982. (g) Armstrong, A.; Washington, I.; Houk, K. N. *J. Am. Chem. Soc.* **2000**, *122*, 6297.

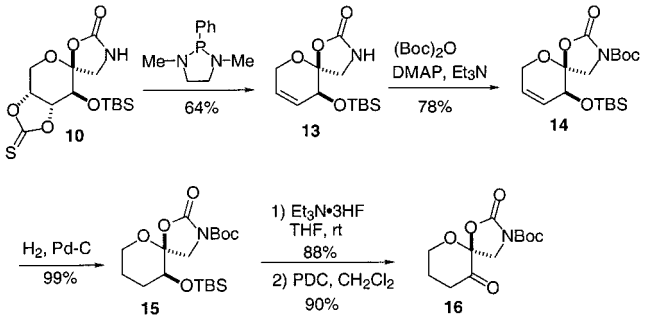
(13) Planar transition state **F** could become the major reaction mode if a large R_1 group is chosen to strongly discourage spiro **E** and a small R_3 group is chosen to strongly encourage planar **F**. One such an example has been observed. The epoxidation of (*Z*)-3,3-dimethyl-1-phenyl-2-trimethylsiloxy-1-butene with **1** led to the formation of (*S*)-3,3-dimethyl-1-hydroxy-1-phenyl-2-butanone in 43% ee (see ref 6k). The *S* configuration of the product suggested that a planar transition state is favored.

(14) For an observation of electronic interaction in ketone-catalyzed asymmetric epoxidation, see ref 6n.

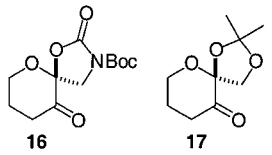
Scheme 10



Scheme 11



Scheme 12



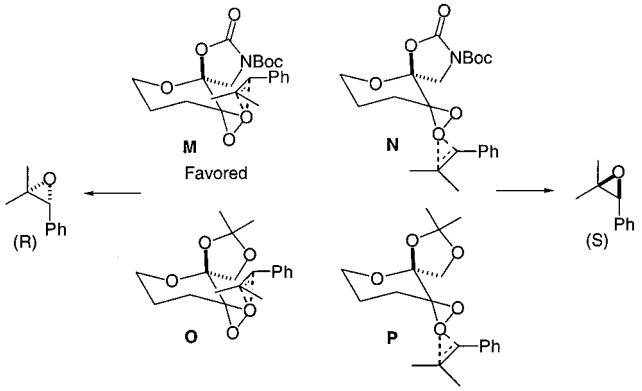
obtained with **2g**, which contains a small CH_3 group (Table 3, entry 7), further supports the hypothesis.

To further study the interaction between R_π and the oxazolidinone, ketone **16**, lacking the fused ketal moiety, was investigated and its synthesis is outlined in Scheme 11. As a comparison, ketone **17**[7g] was also tested for the epoxidation (Scheme 12) (Table 3, entries 16 and 17). The epoxidation results further support that there is a strong interaction between R_π and the oxazolidinone. For example, in the case of 2,2-dimethylstyrene, 78% ee was obtained with ketone **16** in stark contrast to 3% ee with **17**. This result suggests that transition state **M** is greatly favorable compared to **O** due to the attractive interaction between the Ph group with the oxazolidinone (Scheme 13). At this moment, the exact nature of the interaction between R_π and the oxazolidinone is not clear and awaits further study.

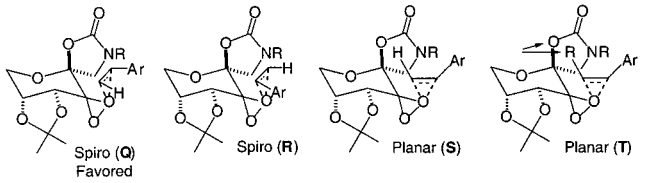
On the basis of the above transition state model, a similar analysis could also be applied to terminal olefins. Transition state spiro **Q** appears to be major transition state, but planar transition state **S** could also be operating (Scheme 14). On the other hand, the corresponding planar **T** would be less feasible for *cis*-olefins due to the steric effect, which could explain why higher ee's were obtained for *cis*-olefins than terminal olefins with ketone **2**.

The epoxidation of 1,1-disubstituted olefins with ketone **2** was rather low. For example, only 30% ee was obtained for α-methylstyrene (Table 2, entry 6). The low ee could be attributed to the destabilizing interaction between the

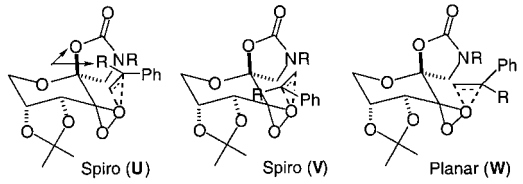
Scheme 13



Scheme 14



Scheme 15



R group of the olefin and the oxazolidinone in spiro **U** (Scheme 15). The *S* configuration of the resultant epoxide suggests that spiro **U** is no longer the major transition state. Spiro **V** and planar **W** are among the possible competing modes, giving the *S* isomer. Planar **W** might become a major transition state since in this transition state the Ph group could still have the attractive interaction with the spiro oxazolidinone of the ketone. If this is true, one would expect that a larger R group on the olefin would further destabilize spiro **U**, leading to a higher ee (Scheme 15). A 58% ee obtained with α-isopropylstyrene provides support to this hypothesis (Table 2, entry 7). A better understanding of the transition states for this type of olefins awaits further study.

In summary, we report a new class of chiral oxazolidinone ketone catalysts for asymmetric epoxidation. High ee values have been obtained for a number of cyclic and acyclic *cis*-olefins. The epoxidation was stereospecific with no isomerization observed in the epoxidation of acyclic systems. Encouragingly high ee's have also been obtained for a number of terminal olefins. Although the exact factors for stereodifferentiation need further investigation, mechanistic studies suggest that electronic interactions play an important role in the transition state. The results described show that chiral dioxiranes can also epoxidize *cis*-olefins and terminal olefins in addition to *trans*-olefins and trisubstituted olefins with a high degree of enantioselectivity. The transition state information gained from the current study provides us useful insight to design new ketone catalysts. Future efforts will be devoted to the optimization of the ketone structure to enhance both enantioselectivity and reactivity.

Experimental Section

General Methods. Oxone was purchased from Aldrich (it has been found that the oxidation activity of the purchased Oxone occasionally varies with different batches). All glassware used for the epoxidation was carefully washed to be free of any trace metals that catalyze the decomposition of Oxone. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. X-ray crystallographic analyses of ketones **2a**, **2b**, **2d**, and **2e** were performed at the X-ray Crystallographic Laboratory of Colorado State University.

Preparation of Aminodiol 3. To a suspension of D-glucose (36.0 g, 200.0 mmol) and Bn_2NH (39.5 g, 200.0 mmol) in absolute EtOH (200 mL) was added AcOH (12.0 g, 200.0 mmol). Upon refluxing for 3 h, the reaction mixture was cooled and filtered with suction. The resulting filter cake was washed with EtOH to colorless and dried in a desiccator over calcium chloride to give 1-dibenzylamino-1-deoxy-D-fructose as a white solid (57.0 g, 79%).[9]

To a suspension of 1-dibenzylamino-1-deoxy-D-fructose (2.5 g, 6.96 mmol) and trimethyl orthoformate (2.0 mL, 18.3 mmol) in acetone (80 mL) at 0 °C was added concentrated HCl (0.6 mL). Upon stirring at 0 °C for 2 h, the reaction mixture was neutralized with NH_4OH, filtered, concentrated, and purified by flash chromatography to give the dibenzylaminodiol as a syrup (2.01 g, 72%): $[\alpha]^{20}_D = -87.9$ (*c* 0.655, $CHCl_3$); IR (KBr) 3446 cm^{-1}; ^1H NMR δ 7.42−7.24 (m, 10H), 4.22−3.91 (m, 6H), 3.52−3.48 (m, 2H), 3.30 (d, $J = 7.5$ Hz, 1H), 3.08 (d, $J = 13.6$ Hz, 1H), 2.71 (d, $J = 13.6$ Hz, 1H), 1.53 (s, 3H), 1.36 (s, 3H); ^{13}C NMR δ 138.2, 129.2, 128.4, 127.3, 109.0, 96.4, 77.5, 73.7, 72.1, 59.1, 58.8, 56.6, 28.2, 26.3. Anal. Calcd for $C_{23}H_{29}NO_5$: C, 69.15; H, 7.32; N, 3.51. Found: C, 69.38; H, 7.28; N, 3.49.

A solution of dibenzylaminodiol (15.0 g, 37.41 mmol) in ethanol (250 mL) was purged with N_2, and 10% Pd/C (2.5 g) was added. Upon stirring under H_2 at room temperature overnight, the reaction mixture was filtered through a short Celite column and concentrated. The resulting residue was recrystallized from CH_2Cl_2−hexane in a freezer to give aminodiol **3** as a white crystal (7.25 g, 88%): mp 100−103 °C; $[\alpha]^{20}_D = -158.1$ (*c* 0.21, $CHCl_3$); IR (KBr) 3470, 3361, 1216 cm^{-1}; ^1H NMR δ 4.24−4.12 (m, 3H), 3.94 (d, $J = 13.5$ Hz, 1H), 3.47 (d, $J = 6.9$ Hz, 1H), 2.95 (d, $J = 11.7$ Hz, 1H), 2.89 (d, $J = 11.7$ Hz, 1H), 1.55 (s, 3H), 1.38 (s, 3H); ^{13}C NMR δ 109.2, 96.2, 77.7, 73.9, 72.5, 59.4, 46.3, 28.4, 26.4. Anal. Calcd for $C_9H_{17}NO_5$: C, 49.31; H, 7.82; N, 6.39. Found: C, 49.32; H, 7.60; N, 6.20.

Preparation of Alcohol 4. To a solution of **3** (17.15 g, 78.31 mmol) and pyridine (100 mL) in CH_2Cl_2 (350 mL) was added dropwise 4-methoxyphenyl chloroformate (16.07 g, 86.14 mmol) at 0 °C. Upon stirring at 0 °C for 5 h, the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give the carbamate as a colorless oil (24.71 g, 86%): $[\alpha]^{20}_D = -93.71$ (*c* 0.53, $CHCl_3$); IR (KBr) 3356, 1719, 1205 cm^{-1}; ^1H NMR δ 7.02 (m, 2H), 6.87 (m, 2H), 5.65 (dd, $J = 7.2$, 6.0 Hz, 1H,), 4.23−4.16 (m, 3H), 3.99 (d, $J = 12.9$ Hz, 1H), 3.79 (s, 3H), 3.62 (d, $J = 6.0$ Hz, 1H), 3.56 (dd, $J = 14.7$, 7.2 Hz, 1H), 3.40 (dd, $J = 14.7$, 6.0 Hz, 1H), 1.55 (s, 3H), 1.38 (s, 3H); ^{13}C NMR δ 157.1, 144.2, 122.4, 114.4, 109.2, 96.7, 76.2, 73.3, 70.9, 60.0, 55.7, 47.3, 28.2, 26.1.

To a solution of the carbamate (10.4 g, 28.01 mmol) in CH_3CN (125 mL) was added $(CH_3)_3COK$ (0.38 g, 3.39 mmol). Upon stirring at room temperature for 0.5 h, the reaction mixture was concentrated and purified by flash chromatography to give alcohol **4** as a white solid (6.15 g, 90%): mp 171−173 °C; $[\alpha]^{20}_D = -146.25$ (*c* 0.12, $CHCl_3$); IR (KBr) 3346, 1760, 1077 cm^{-1}; ^1H NMR (CD_3OD) δ 4.37−4.34 (m, 1H), 4.27−4.21 (m, 2H), 4.10 (d, $J = 13.8$ Hz, 1H), 3.83 (d, $J = 9.9$ Hz, 1H), 3.64 (d, $J = 7.8$ Hz, 1H), 3.36 (d, $J = 9.9$ Hz, 1H), 1.53 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (CD_3OD) δ 160.7, 111.2, 107.1, 78.6, 75.5, 73.0, 63.3, 50.1, 29.3, 27.3. Anal. Calcd for $C_{10}H_{15}NO_6$: C, 48.98; H, 6.17; N, 5.71. Found: C, 49.12; H, 6.15; N, 5.67.

Preparation of Ketone 2a. To a mixture of alcohol **4** (1.07 g, 4.37 mmol) and powdered 3 Å MS (4.0 g) in CH_2Cl_2 (19 mL) was added PCC (2.16 g, 10.02 mmol) portionwise over 15 min. Upon stirring under N_2 for 3 h, the reaction mixture was filtered through Celite and washed with Et_2O. The filtrate was concentrated and purified by flash chromatography to give the ketone **2a** as a white solid (0.997 g, 94%): mp 144.5−145.5 °C; $[\alpha]^{20}_D = -118.0$ (*c* 0.27, $CHCl_3$); IR (KBr) 3378, 3319, 1759, 1731 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.51 (s, 1H), 4.84 (d, $J = 5.4$ Hz, 1H), 4.66−4.52 (m, 2H), 4.32 (d, $J = 10.7$ Hz, 1H), 4.23 (d, $J = 13.5$ Hz, 1H), 3.38 (d, $J = 10.7$ Hz, 1H), 1.46 (s, 3H), 1.42 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 195.2, 156.0, 111.0, 102.7, 77.5, 75.5, 61.0, 45.3, 27.2, 26.1; HRMS calcd for $C_{10}H_{14}NO_6$ ($M^+ + 1$) 244.0821, found 244.0824. Anal. Calcd for $C_{10}H_{13}NO_6 \cdot 0.7H_2O$: C, 46.95; H, 5.67; N, 5.48. Found: C, 47.16; H, 5.86; N, 5.43.

Preparation of TBS Ether 5. To a solution of alcohol **4** (10.4 g, 42.45 mmol) in CH_3CN (300 mL) were added imidazole (4.33 g, 63.67 mmol) and TBSCl (6.72 g, 44.57 mmol). Upon stirring at room temperature for 24 h, the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give TBS ether **5** as a white solid (10.66 g, 70%): mp 153−155 °C; $[\alpha]^{20}_D = -92.92$ (*c* 0.12, $CHCl_3$); IR (KBr) 3286, 1770 cm^{-1}; ^1H NMR δ 5.87 (s, 1H), 4.31−4.18 (m, 3H), 4.08 (d, $J = 12.9$ Hz, 1H), 3.68 (d, $J = 9.3$ Hz, 1H), 3.65 (d, $J = 6.6$ Hz, 1H), 3.39 (dd, $J = 9.3$, 1.0 Hz, 1H), 1.53 (s, 3H), 1.36 (s, 3H), 0.87 (s, 9H), 0.17 (s, 3H), 0.10 (s, 3H); ^{13}C NMR δ 157.8, 109.3, 104.9, 77.0, 73.5, 73.3, 61.9, 48.9, 28.4, 26.4, 25.9, 18.2, −3.7, −5.2. Anal. Calcd for $C_{16}H_{29}NO_6Si$: C, 53.46; H, 8.13; N, 3.90. Found: C, 53.58; H, 7.89; N, 4.03.

Preparation of Ketone 2b. To a solution of TBS ether **5** (2.0 g, 5.57 mmol) in THF (20 mL) was added NaH (0.267 g, 6.685 mmol) at 0 °C under N_2. Upon stirring for 0.5 h, MeI (1.58 g, 11.14 mmol) was added. After being stirred for 12 h, the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by chromatography to give **6b** as a white solid (2.04 g, 98%): mp 107−108 °C; $[\alpha]^{20}_D = -62.5$ (*c* 0.20, $CHCl_3$); IR (KBr) 1773 cm^{-1}; ^1H NMR δ 4.37−4.18 (m, 3H), 4.09 (d, $J = 13.2$ Hz, 1H), 3.65 (d, $J = 6.3$ Hz, 1H), 3.61 (d, $J = 9.3$ Hz, 1H), 3.34 (d, $J = 9.3$ Hz, 1H), 2.87 (s, 3H), 1.54 (s, 3H), 1.37 (s, 3H), 0.86 (s, 9H), 0.18 (s, 3H), 0.10 (s, 3H); ^{13}C NMR δ 156.4, 109.4, 101.5, 77.1, 73.6, 73.4, 61.9, 54.8, 30.6, 28.5, 26.5, 25.8, 18.2, −3.7, −5.2. Anal. Calcd for $C_{17}H_{31}NO_6Si$: C, 54.66; H, 8.37; N, 3.75. Found: C, 54.72; H, 8.26; N, 3.70.

To a solution of TBS ether **6b** (2.04 g, 5.47 mmol) in THF (20 mL) was added TBAF (1.0 M in THF) (5.5 mL, 5.5 mmol). Upon stirring at room temperature to the completion as judged by TLC, the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give the alcohol as a white solid (1.42 g, 99%): mp 144−146 °C; $[\alpha]^{20}_D = -158.8$ (*c* 0.08, $CHCl_3$); IR (KBr) 3422, 1747 cm^{-1}; ^1H NMR δ 4.31−4.23 (m, 3H), 4.10 (d, $J = 12.9$ Hz, 1H), 3.82 (d, $J = 9.6$ Hz, 1H), 3.71−3.65 (m, 1H), 3.36 (d, $J = 9.6$ Hz, 1H), 2.99−2.93 (m, 1H), 2.90 (s, 3H), 1.55 (s, 3H), 1.39 (s, 3H); ^{13}C NMR δ 156.3, 110.0, 101.4, 76.7, 73.4, 71.8, 61.8, 54.6, 30.8, 28.3, 26.2. Anal. Calcd for $C_{11}H_{17}NO_6$: C, 50.96; H, 6.61; N, 5.40. Found: C, 50.77; H, 6.40; N, 5.30.

To a solution of the above alcohol (0.145 g, 0.56 mmol) in CH_2Cl_2 (5 mL) were added PDC (0.32 g, 0.84 mmol), 3 Å molecular sieves (0.5 g), and AcOH (1 drop). Upon stirring at room temperature for 6 h, EtOAc was added. The resulting mixture was passed through a short silica gel plug, concentrated, and purified by flash chromatography to give ketone **2b** (0.144 g, 99%): $[\alpha]^{20}_D = -50.7$ (*c* 0.22, $CHCl_3$); IR (KBr) 3402, 1749 cm^{-1}; ^1H NMR δ 4.79 (d, $J = 5.7$ Hz, 1H), 4.60−4.50 (m, 2H), 4.23 (d, $J = 10.2$ Hz, 1H), 4.18 (d, $J = 13.5$ Hz, 1H), 3.27 (d, $J = 10.5$ Hz, 1H), 2.91 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H); ^{13}C NMR δ 195.2, 154.2, 111.0, 96.6, 77.5, 75.5, 60.9, 50.9, 30.8, 27.2, 26.1; HRMS calcd for $C_{11}H_{16}NO_6$ ($M^+ + 1$) 258.0978, found 258.0979.

Preparation of Ketone 2c. TBS ether **6c** was prepared from **5** (2.0 g, 5.57 mmol) in a way similar to **6b**: white solid (2.49 g, 99%); mp 101−103 °C; $[\alpha]^{20}_D = -64.8$ (*c* 0.16, $CHCl_3$); IR (KBr) 1769 cm^{-1}; ^1H NMR δ 7.46−7.23 (m, 5H), 4.49 (d, $J = 15.0$ Hz, 1H), 4.35 (d, $J = 15.0$ Hz, 1H), 4.31−4.18 (m, 3H), 4.06 (d, $J = 13.5$ Hz, 1H), 3.61 (d, $J = 6.6$ Hz, 1H), 3.52 (d, J

= 9.3 Hz, 1H), 3.20 (d, J = 9.3 Hz, 1H), 1.50 (s, 3H), 1.35 (s, 3H), 0.79 (s, 9H), 0.14 (s, 3H), −0.00 (s, 3H); ^{13}C NMR δ 156.4, 135.4, 129.1, 128.4, 128.2, 109.4, 102.0, 77.2, 73.4, 73.2, 61.7, 52.1, 48.2, 28.4, 26.4, 25.9, 18.1, −3.7, −5.2. Anal. Calcd for $C_{23}H_{35}NO_6Si$: C, 61.44; H, 7.85; N, 3.12. Found: C, 61.30; H, 7.70; N, 3.09.

TBS ether **6c** (2.49 g, 5.55 mmol) was desilylated in a way similar to **6b** to give the alcohol as a white solid (1.79 g, 96%): mp 171−172 °C; $[\alpha]^{20}_D$ = −171.4 (*c* 0.08, $CHCl_3$); IR (KBr) 3402, 1751 cm^{-1}; ^{1}H NMR δ 7.40−7.23 (m, 5H), 4.46 (s, 2H), 4.33−4.21 (m, 3H), 4.10 (d, J = 12.9 Hz, 1H), 3.67 (d, J = 9.6 Hz, 1H), 3.68−3.61 (m, 1H), 3.25 (d, J = 9.6 Hz, 1H), 1.50 (s, 3H), 1.37 (s, 3H). Anal. Calcd for $C_{17}H_{21}NO_6$: C, 60.89; H, 6.31; N, 4.18. Found: C, 60.90; H, 6.13; N, 4.14.

The above alcohol (0.041 g, 0.122 mmol) was oxidized with PDC to give ketone **2c** as a white solid (0.038 g, 93%): mp 176−178 °C; $[\alpha]^{20}_D$ = −85.7 (*c* 0.15, $CHCl_3$); IR (KBr) 3394, 1756 cm^{-1}; ^{1}H NMR δ 7.36−7.13 (m, 5H), 4.74 (d, J = 5.7 Hz, 1H), 4.57−4.30 (m, 4H), 4.12 (d, J = 13.2 Hz, 1H), 4.05 (d, J = 10.2 Hz, 1H), 3.10 (d, J = 10.2 Hz, 1H), 1.34 (s, 3H), 1.33 (s, 3H); ^{13}C NMR δ 195.1, 154.2, 134.6, 129.0, 128.3, 128.0, 111.0, 100.0, 77.5, 75.5, 61.0, 48.5, 48.2, 27.2, 26.1. Anal. Calcd for $C_{17}H_{19}NO_6 \cdot 0.4H_2O$: C, 59.96; H, 5.82; N, 4.12. Found: C, 59.78; H, 5.89; N, 4.16.

Preparation of Ketone 2d. To a solution of TBS ether **5** (2.0 g, 5.57 mmol) in THF (20 mL) were added Et_3N (2.82 g, 27.86 mmol), DMAP (0.136 g, 1.11 mmol), and $(Boc)_2O$ (2.43 g, 11.14 mmol). Upon stirring at room temperature for 24 h, the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give TBS ether **6d** as a white solid (2.53 g, 99%): mp 114−115 °C; $[\alpha]^{20}_D$ = −67.7 (*c* 0.118, $CHCl_3$); IR (KBr) 1828, 1808, 1727 cm^{-1}; ^{1}H NMR δ 4.27−4.08 (m, 4H), 3.94 (d, J = 10.8 Hz, 1H), 3.68 (d, J = 10.8 Hz, 1H), 3.65 (d, J = 6.9 Hz, 1H), 1.52 (s, 3H), 1.50 (s, 9H), 0.84 (s, 9H), 0.17 (s, 3H), 0.11 (s, 3H); ^{13}C NMR δ 150.3, 148.8, 109.4, 101.1, 84.0, 76.8, 73.8, 73.1, 62.3, 51.8, 28.4, 28.1, 26.4, 25.8, 18.1, −3.7, −5.3. Anal. Calcd for $C_{23}H_{37}NO_8Si$: C, 54.88; H, 8.11; N, 3.05. Found: C, 54.77; H, 7.98; N, 3.05.

To a solution of TBS ether **6d** (6.43 g, 14.0 mmol) in THF (100 mL) was added $Et_3N \cdot 3HF$ (22.6 g, 140.0 mmol). Upon stirring at room temperature to completion as judged by TLC (about 4 days), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give the alcohol as a white solid (4.47 g, 93%): mp 120.0−121.5 °C; $[\alpha]^{20}_D$ = −113.9 (*c* 0.33, $CHCl_3$); IR (KBr) 3481, 1812, 1733, 1718, 1222, 1162 cm^{-1}; ^{1}H NMR δ 4.26−4.23 (m, 3H), 4.13 (d, J = 11.2 Hz, 1H), 4.12 (d, J = 12.8 Hz, 1H), 3.75 (d, J = 11.2 Hz, 1H), 3.76−3.70 (m, 1H), 2.74 (d, J = 6.8 Hz, 1H, OH), 1.53 (s, 3H), 1.52 (s, 9H), 1.37 (s, 3H); ^{13}C NMR δ 150.5, 148.9, 109.9, 101.0, 84.3, 76.4, 73.1, 71.2, 62.0, 51.4, 28.2, 28.1, 26.2.

The above alcohol (1.9 g, 5.51 mmol) was oxidized with PDC to give ketone **2d** as a white solid (1.52 g, 80%): mp 139−140 °C; $[\alpha]^{20}_D$ = −47.9 (*c* 0.83, $CHCl_3$); IR (KBr): 3446 (hydrate), 1823, 1756, 1731 cm^{-1}; ^{1}H NMR δ 4.79 (d, J = 5.6 Hz, 1H), 4.61 (dd, J = 5.6, 1.8 Hz, 1H), 4.56 (d, J = 11.6 Hz, 1H), 4.51 (dd, J = 13.6, 1.8 Hz, 1H), 4.23 (d, J = 13.6 Hz, 1H), 3.71 (d, J = 11.6 Hz, 1H), 1.53 (s, 9H), 1.45 (s, 3H), 1.41 (s, 3H); ^{13}C NMR δ 194.9, 149.0, 148.6, 111.3, 98.9, 85.0, 77.4, 75.5, 61.3, 48.4, 28.0, 27.2, 26.0. Anal. Calcd for $C_{15}H_{21}NO_8$: C, 52.47; H, 6.17; N, 4.08. Found: C, 52.32; H, 5.94; N, 3.97.

Preparation of Ketone 2e. To a solution of TBS ether **5** (0.718 g, 2.0 mmol) in THF (20 mL) were added Et_3N (1.0 g, 10.0 mmol), DMAP (0.024 g, 0.2 mmol), and PhOCOCl (0.47 g, 3.0 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 2 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6e** as a white solid (0.95 g, 99%): mp 123−125 °C; $[\alpha]^{20}_D$ = −47.6 (*c* 1.19, $CHCl_3$); IR (KBr) 1839, 1806, 1743 cm^{-1}; ^{1}H NMR δ 7.47−7.41 (m, 2H), 7.33−7.29 (m, 1H), 7.20−7.17 (m, 2H), 4.37−4.19 (m, 4H), 4.19 (d, J = 11.0 Hz, 1H), 3.95 (d, J = 11.0 Hz, 1H), 3.77 (d, J = 6.9 Hz, 1H), 1.59 (s, 3H), 1.43 (s, 3H), 0.94 (s, 9H), 0.25 (s, 3H), 0.19 (s, 3H); ^{13}C NMR δ 150.0, 149.8, 149.0, 129.7, 126.6, 121.4, 109.6, 101.9, 76.8, 73.9, 73.0, 62.6, 52.1, 28.5, 26.5, 25.9, 18.2, −3.9, −5.2.

TBS ether **6e** (0.63 g, 1.32 mmol) was desilylated with $Et_3N \cdot 3HF$ (1.06 g, 6.58 mmol) in a way similar to **6d** to give the alcohol as a white solid (0.372 g, 78%) (about 3 days): mp 185−186 °C; $[\alpha]^{20}_D$ = −101.8 (*c* 1.02, $CHCl_3$); IR (KBr) 3474, 1829, 1744 cm^{-1}; ^{1}H NMR δ 7.39−7.32 (m, 2H), 7.26−7.19 (m, 1H), 7.17−7.12 (m, 2H), 4.32−4.11 (m, 5H), 3.92 (d, J = 10.8 Hz, 1H), 3.76 (m, 1H), 2.99 (s, 1H), 1.51 (s, 3H), 1.36 (s, 3H); ^{13}C NMR δ 150.0, 149.0, 129.6, 126.6, 121.4, 110.1, 101.7, 76.3, 73.0, 71.4, 62.4, 51.7, 28.3, 26.3. Anal. Calcd for $C_{17}H_{19}NO_8$: C, 55.89; H, 5.24; N, 3.83. Found: C, 56.03; H, 5.40; N, 3.95.

The above alcohol (0.255 g, 0.70 mmol) was oxidized with PDC to give ketone **2e** as a white solid (0.25 g, 96%): mp 190−191 °C; $[\alpha]^{20}_D$ = −55.0 (*c* 0.93, $CHCl_3$); IR (KBr) 1843, 1759, 1720 cm^{-1}; ^{1}H NMR δ 7.45−7.38 (m, 2H), 7.32−7.26 (m, 1H), 7.22−7.18 (m, 2H), 4.83 (d, J = 5.4 Hz, 1H), 4.78 (d, J = 11.5 Hz, 1H), 4.65 (m, 1H), 4.55 (dd, J = 13.7, 2.1 Hz, 1H), 4.29 (d, J = 13.7 Hz, 1H), 3.95 (d, J = 11.5 Hz, 1H), 1.48 (s, 3H), 1.44 (s, 3H); ^{13}C NMR δ 194.5, 149.9, 148.4, 129.7, 126.8, 121.3, 111.5, 99.5, 77.3, 75.4, 61.7, 48.8, 27.3, 26.2. Anal. Calcd for $C_{17}H_{17}NO_8$: C, 56.20; H, 4.72; N, 3.86. Found: C, 56.12; H, 4.73; N, 3.82.

Preparation of Ketone 2f. To a solution of **5** (0.718 g, 2.0 mmol) in THF (20 mL) was added Et_3N (2.02 g, 20.0 mmol), DMAP (0.024 g, 0.2 mmol), and Me_2NCOCl (0.43 g, 4.0 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 12 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6f** as a white solid (0.83 g, 96%): mp 129−131 °C; $[\alpha]^{20}_D$ = −85.0 (*c* 0.81, $CHCl_3$); IR (KBr) 1782, 1688 cm^{-1}; ^{1}H NMR δ 4.26−4.05 (m, 5H), 3.71−3.68 (m, 2H), 2.99 (s, 6H), 1.52 (s, 3H), 1.35 (s, 3H), 0.86 (s, 9H), 0.16 (s, 3H), 0.11 (s, 3H); ^{13}C NMR δ 152.8, 152.1, 109.4, 102.7, 76.8, 73.0, 72.8, 62.0, 51.7, 28.2, 26.3, 25.9, 18.2, −3.8, −5.1.

TBS ether **6f** (0.617 g, 1.435 mmol) was desilylated with $Et_3N \cdot 3HF$ (2.31 g, 14.35 mmol) in a way similar to **6d** to give the alcohol as a white solid (0.346 g, 76%) (about 3 days): mp 167−169 °C; $[\alpha]^{20}_D$ = −102.3 (*c* 0.87, $CHCl_3$); IR (KBr) 3428, 1783, 1683 cm^{-1}; ^{1}H NMR δ 4.31 (d, J = 10.4 Hz, 1H), 4.28−4.23 (m, 3H), 4.12 (d, J = 13.5 Hz, 1H), 3.78 (m, 1H), 3.66 (d, J = 10.4 Hz, 1H), 3.20 (bs, 1H), 3.01 (s, 6H), 1.54 (s, 3H), 1.38 (s, 3H); ^{13}C NMR δ 153.0, 152.0, 109.9, 102.6, 76.2, 73.0, 71.2, 62.2, 51.7, 28.2, 26.2.

The above alcohol (0.217 g, 0.687 mmol) was oxidized with PDC to give ketone **2f** as a white solid (0.204 g, 95%): mp 115−117 °C; $[\alpha]^{20}_D$ = −72.3 (*c* 1.11, $CHCl_3$); IR (KBr) 3409, 1789, 1760, 1688 cm^{-1}; ^{1}H NMR δ 4.80 (d, J = 5.4 Hz, 1H), 4.65−3.94 (m, 4H), 3.70 (d, J = 11.1 Hz, 1H), 3.03 (s, 6H), 1.47 (s, 3H), 1.41 (s, 3H). Anal. Calcd for $C_{13}H_{18}N_2O_7 \cdot 0.4H_2O$: C, 48.56; H, 5.85; N, 8.72. Found: C, 48.85; H, 5.97; N, 8.46.

Preparation of Ketone 2g. To a solution of **5** (0.718 g, 2.0 mmol) in THF (20 mL) were added Et_3N (1.0 g, 10.0 mmol), DMAP (0.024 g, 0.2 mmol), and CH_3COCl (0.236 g, 3.0 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 12 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6g** as a white solid (0.727 g, 91%): mp 76−78 °C; $[\alpha]^{20}_D$ = −64.0 (*c* 0.97, $CHCl_3$); IR (KBr) 1794, 1709 cm^{-1}; ^{1}H NMR δ 4.28−4.13 (m, 4H), 3.99 (d, J = 11.5 Hz, 1H), 3.76 (d, J = 11.5 Hz, 1H), 3.69 (d, J = 6.9 Hz, 1H), 2.50 (s, 3H), 1.55 (s, 3H), 1.38 (s, 3H), 0.83 (s, 9H), 0.19 (s, 3H), 0.10 (s, 3H); ^{13}C NMR δ 169.9, 151.9, 109.6, 102.2, 76.8, 73.9, 73.0, 62.6, 51.2, 28.5, 26.5, 25.8, 23.7, 18.1, −3.6, −5.2. Anal. Calcd for $C_{18}H_{31}NO_7Si$: C, 53.84; H, 7.78; N, 3.49. Found: C, 54.03; H, 7.74; N, 3.41.

TBS ether **6g** (0.65 g, 1.62 mmol) was desilylated with $Et_3N \cdot 3HF$ (0.523 g, 3.24 mmol) in a way similar to **6d** to give the alcohol as a colorless oil (0.267 g, 57%) (about 5 days): $[\alpha]^{20}_D$ = −143.2 (*c* 0.9, $CHCl_3$); IR (KBr) 3447, 1793, 1709 cm^{-1}; ^{1}H NMR δ 4.28−4.17 (m, 4H), 4.15 (d, J = 11.7 Hz, 1H), 3.82 (d, J = 11.7 Hz, 1H), 3.75 (d, J = 5.7 Hz, 1H), 3.21 (s, 1H), 2.51 (s, 3H), 1.54 (s, 3H), 1.38 (s, 3H); ^{13}C NMR δ 170.2, 151.9,

110.1, 101.9, 76.4, 73.1, 71.4, 62.3, 50.6, 28.3, 26.3, 23.8. Anal. Calcd for $C_{12}H_{17}NO_7$: C, 50.17; H, 5.96; N, 4.88. Found: C, 50.09; H, 5.70; N, 4.77.

The above alcohol (0.18 g, 0.627 mmol) was oxidized with PDC to give ketone **2g** as a colorless oil (0.177 g, 99%): $[\alpha]^{20}_D = -56.8$ (*c* 2.77, CH_3CN); IR (KBr) 3427 (hydrate), 1798, 1711 cm^{-1}; **Ketone:** ^1H NMR (CD_3CN) δ 4.85 (d, $J = 6.0$ Hz, 1H), 4.43−4.15 (m, 3H), 3.71 (d, $J = 12.3$ Hz, 1H), 3.61 (d, $J = 12.3$ Hz, 1H), 2.40 (s, 3H), 1.47 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (CD_3CN) δ 196.3, 170.5, 152.4, 111.7, 103.1, 78.2, 76.1, 62.8, 48.9, 27.2, 26.0, 23.7. **Hydrate:** ^1H NMR (CD_3CN) δ 4.67 (d, $J = 5.1$ Hz, 1H), 4.43−4.15 (m, 4H), 3.81 (d, $J = 12.7$ Hz, 1H), 2.40 (s, 3H), 1.36 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (CD_3CN) δ 170.5, 151.5, 110.5, 100.4, 92.0, 76.6, 73.8, 64.5, 51.6, 26.5, 24.8, 23.8; HRMS calcd for $C_{12}H_{18}NO_8$ ($M{\cdot}H_2O + 1$) 304.1032, found 304.1026.

Preparation of Ketone 2h. To a solution of **5** (0.718 g, 2.0 mmol) in CH_2Cl_2 (20 mL) were added Et_3N (1.0 g, 10.0 mmol), DMAP (0.024 g, 0.2 mmol), and Me_3CCOCl (0.326 g, 3.0 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 12 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6h** as a white solid (0.884 g, 99%): mp 145−148 °C; $[\alpha]^{20}_D = -59.2$ (*c* 1.35, $CHCl_3$); IR (KBr) 1789, 1687 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.30−4.11 (m, 4H), 4.04 (d, $J = 11.9$ Hz, 1H), 3.79 (d, $J = 11.9$ Hz, 1H), 3.67 (d, $J = 6.9$ Hz, 1H), 1.54 (s, 3H), 1.37 (s, 3H), 1.36 (s, 9H), 0.83 (s, 9H), 0.18 (s, 3H), 0.10 (s, 3H); ^{13}C NMR δ 177.9, 150.4, 109.6, 101.6, 76.9, 73.6, 73.1, 62.2, 53.4, 41.6, 28.5, 26.5, 26.4, 25.9, 18.2, −3.6, −5.2. Anal. Calcd for $C_{21}H_{37}NO_7Si$: C, 56.86; H, 8.41; N, 3.16. Found: C, 57.00; H, 8.35; N, 3.23.

TBS ether **6h** (0.75 g, 1.69 mmol) was desilylated with $Et_3N{\cdot}3HF$ (0.546 g, 3.39 mmol) in a way similar to **6d** to give the alcohol as a colorless oil (0.506 g, 91%) (about 5 days): $[\alpha]^{20}_D = -64.2$ (*c* 1.15, $CHCl_3$); IR (KBr) 3458, 1793, 1691 cm^{-1}; ^1H NMR δ 4.28−4.12 (m, 5H), 3.84 (d, $J = 11.7$ Hz, 1H), 3.74 (d, $J = 5.7$ Hz, 1H), 3.06 (bs, 1H), 1.54 (s, 3H), 1.38 (s, 3H), 1.37 (s, 9H); ^{13}C NMR δ 178.2, 150.5, 110.1, 101.4, 76.4, 73.1, 71.4, 62.1, 53.1, 41.6, 28.3, 26.4, 26.2. Anal. Calcd for $C_{15}H_{23}NO_7$: C, 54.70; H, 7.04; N, 4.25. Found: C, 54.70; H, 7.11; N, 4.14.

The above alcohol (0.40 g, 1.22 mmol) was oxidized with PDC to give ketone **2h** as a white solid (0.372 g, 94%): mp 156−157 °C; $[\alpha]^{20}_D = -40.4$ (*c* 1.95, $CHCl_3$); IR (KBr) 3468 (hydrate), 1799, 1758, 1697 cm^{-1}; ^1H NMR δ 4.78 (d, $J = 5.4$ Hz, 1H), 4.62 (dd, $J = 5.4$, 1.8 Hz, 1H), 4.58 (d, $J = 12.6$ Hz, 1H), 4.48 (dd, $J = 13.5$, 1.8 Hz, 1H), 4.23 (d, $J = 13.5$ Hz, 1H), 3.82 (d, $J = 12.6$ Hz, 1H), 1.47 (s, 3H), 1.41 (s, 3H), 1.37 (s, 9H); ^{13}C NMR δ 194.8, 177.7, 149.0, 111.5, 99.5, 77.7, 75.4, 61.6, 50.3, 41.7, 27.3, 26.3, 26.2. Anal. Calcd for $C_{15}H_{21}NO_7$: C, 55.04; H, 6.47; N, 4.28. Found: C, 55.22; H, 6.31; N, 4.32.

Preparation of Ketone 2i. To a solution of **5** (0.718 g, 2.0 mmol) in THF (20 mL) were added Et_3N (1.0 g, 10.0 mmol), DMAP (0.024 g, 0.2 mmol), and PhCOCl (0.422 g, 3.0 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 12 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6i** as a white solid (0.867 g, 94%): mp 93−95 °C; $[\alpha]^{20}_D = -84.7$ (*c* 1.22, $CHCl_3$); IR (KBr) 1796, 1685 cm^{-1}; ^1H NMR δ 7.68−7.44 (m, 5H), 4.35−4.19 (m, 5H), 4.00 (d, $J = 11.4$ Hz, 1H), 3.81 (d, $J = 6.6$ Hz, 1H), 1.61 (s, 3H), 1.42 (s, 3H), 0.93 (s, 9H), 0.25 (s, 3H), 0.19 (s, 3H); ^{13}C NMR δ 169.0, 151.2, 132.8, 132.3, 130.2, 129.2, 129, 127.9, 109.6, 102.2, 76.8, 73.6, 73.1, 62.5, 51.7, 28.4, 26.4, 26.0, 18.3, −3.6, −5.1.

TBS ether **6i** (0.64 g, 1.382 mmol) was desilylated with $Et_3N{\cdot}3HF$ (0.569 g, 3.529 mmol) in a way similar to **6d** to give the alcohol as a white solid (0.448 g, 93%) (about 3 days): mp 120−123 °C; $[\alpha]^{20}_D = -134.1$ (*c* 1.09, $CHCl_3$); IR (KBr) 3444, 1794, 1685 cm^{-1}; ^1H NMR δ 7.67−7.41 (m, 5H), 4.43−4.17 (m, 5H), 3.97 (d, $J = 11.7$ Hz, 1H), 3.81 (d, $J = 6.6$ Hz, 1H), 3.06 (bs, 1H), 1.56 (s, 3H), 1.40 (s, 3H); ^{13}C NMR δ 169.3, 151.4, 132.5, 129.1, 128, 110.1, 102.1, 76.3, 73.0, 71.4, 62.4, 51.5, 28.3, 26.2. Anal. Calcd for $C_{17}H_{19}NO_7$: C, 58.45; H, 5.48; N, 4.01. Found: C, 58.38; H, 5.46; N, 3.95.

The above alcohol (0.326 g, 0.935 mmol) was oxidized with PDC to give ketone **2i** as a white solid (0.307 g, 95%): mp 66−68 °C; $[\alpha]^{20}_D = -91.2$ (*c* 1.06, $CHCl_3$); IR (KBr) 3452 (hydrate), 1799, 1687 cm^{-1}; ^1H NMR δ 7.69−7.43 (m, 5H), 4.81 (d, $J = 6.3$ Hz, 1H), 4.78 (d, $J = 12.5$ Hz, 1H), 4.65 (m, 1H), 4.51 (dd, $J = 13.8$, 2.1 Hz, 1H), 4.29 (d, $J = 13.8$ Hz, 1H), 3.98 (d, $J = 12.5$ Hz, 1H), 1.51 (s, 3H), 1.44 (s, 3H); ^{13}C NMR δ 194.7, 168.8, 150.0, 132.8, 132.2, 129.2, 128.1, 111.6, 99.9, 77.2, 75.4, 61.9, 48.9, 27.3, 26.2. Anal. Calcd for $C_{17}H_{17}NO_7$: C, 58.79; H, 4.93; N, 4.03. Found: C, 58.78; H, 5.12; N, 4.00.

Preparation of Ketone 2j. To a solution of **5** (0.718 g, 2.0 mmol) in THF (20 mL) were added Et_3N (2.6 mL, 20.0 mmol), DMAP (0.024 g, 0.2 mmol), and 4-methoxylbenzoyl chloride (0.41 g, 2.4 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 12 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6j** as a white solid (0.98 g, 99%): mp 139.0−140.5 °C; $[\alpha]^{20}_D = -75.5$ (*c* 1.78, $CHCl_3$); IR (KBr) 1794, 1680, 1607 cm^{-1}; ^1H NMR δ 7.69−7.64 (m, 2H), 6.93−6.89 (m, 2H), 4.32−4.15 (m, 4H), 4.22 (d, $J = 11.4$ Hz, 1H), 3.95 (d, $J = 11.4$ Hz, 1H), 3.86 (s, 3H), 3.76 (d, $J = 6.6$ Hz, 1H), 1.56 (s, 3H), 1.38 (s, 3H), 0.87 (s, 9H), 0.20 (s, 3H), 0.14 (s, 3H); ^{13}C NMR δ 168.3, 163.1, 151.6, 131.8, 124.6, 113.3, 109.6, 102.1, 76.9, 73.5, 73.1, 62.4, 55.6, 51.9, 28.5, 26.5, 26.0, 18.3, −3.6, −5.0.

TBS ether **6j** (0.746 g, 1.512 mmol) was desilylated with $Et_3N{\cdot}3HF$ (1.22 g, 7.56 mmol) in a way similar to **6d** to give the alcohol as a white solid (0.489 g, 85%) (about 3 days): mp 66−68 °C; $[\alpha]^{20}_D = -140.3$ (*c*, 0.94, $CHCl_3$); IR (KBr) 3447, 1793, 1680, 1606 cm^{-1}; ^1H NMR δ 7.71−7.66 (m, 2H), 6.94−6.89 (m, 2H), 4.41−4.17 (m, 5H), 3.95 (m, 1H), 3.86 (s, 3H), 3.82 (d, $J = 6.0$ Hz, 1H), 1.56 (s, 3H), 1.40 (s, 3H); ^{13}C NMR δ 167.5, 156.9, 150.7, 132.6, 128.8, 123.6, 120.6, 111.0, 110.1, 101.8, 76.3, 73.0., 71.6, 62.4, 56.0, 51.2, 28.3, 26.2. Anal. Calcd for $C_{18}H_{21}NO_8$: C, 56.99; H, 5.58; N, 3.69. Found: C, 56.76; H 5.74; N, 3.65.

The above alcohol (0.461 g, 1.216 mmol) was oxidized with PDC to give ketone **2j** as a white solid (0.429 g, 94%): mp 63−65 °C; $[\alpha]^{20}_D = -89.1$ (*c* 0.96, $CHCl_3$); IR (KBr) 1799, 1758, 1684, 1606 cm^{-1}; ^1H NMR δ 7.72−7.69 (m, 2H), 6.96−6.92 (m, 2H), 4.81 (d, $J = 5.4$ Hz, 1H), 4.78 (d, $J = 12.3$ Hz, 1H), 4.65 (m, 1H), 4.52 (dd, $J = 13.5$, 2.1 Hz, 1H), 4.29 (d, $J = 13.5$ Hz, 1H), 3.95 (d, $J = 12.3$ Hz, 1H), 3.87 (s, 3H), 1.51 (s, 3H), 1.44 (s, 3H); ^{13}C NMR δ 194.7, 168.0, 163.5, 150.4, 132.0, 126.8, 124.0, 118.0, 113.5, 77.3, 75.5, 61.9, 55.7, 49.1, 27.3, 26.2. Anal. Calcd for $C_{18}H_{19}NO_8$: C, 57.29; H, 5.08; N, 3.71. Found: C, 57.17; H, 5.24; N, 3.61.

Preparation of Ketone 2k. To a solution of **5** (0.718 g, 2.0 mmol) in THF (20 mL) were added Et_3N (2.6 mL, 20.0 mmol), DMAP (0.024 g, 0.2 mmol), and 2-methoxylbenzoyl chloride (0.41 g, 2.4 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 12 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6k** as a white solid (0.9 g, 91%): mp 114−116 °C; $[\alpha]^{20}_D = -92.0$ (*c* 1.12, $CHCl_3$); IR (KBr) 1802, 1685, 1603 cm^{-1}; ^1H NMR δ 7.42 (m, 1H), 7.25 (m, 1H), 7.00 (m, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 4.29−4.12 (m, 5H), 3.96 (d, $J = 11.7$ Hz, 1H), 3.81 (s, 3H), 3.75 (d, $J = 6.6$ Hz, 1H), 1.56 (s, 3H), 1.38 (s, 3H), 0.89 (s, 9H), 0.19 (s, 3H), 0.15 (s, 3H); ^{13}C NMR δ 167.4, 156.9, 150.5, 132.2, 128.4, 124, 120.5, 111, 109.6, 101.9, 76.8, 73.3, 73.1, 62.3, 55.9, 51.1, 28.4, 26.4, 26, 18.3, −3.6, −5.1.

TBS ether **6k** (0.696 g, 1.411 mmol) was desilylated with $Et_3N{\cdot}3HF$ (1.14 g, 7.05 mmol) in a way similar to **6d** to give the alcohol as a white solid (0.501 g, 94%) (about 3 days): mp 68−71 °C; $[\alpha]^{20}_D = -119.7$ (*c* 1.01, $CHCl_3$); IR (KBr) 3453, 1801, 1684, 1603 cm^{-1}; ^1H NMR δ 7.48−7.42 (m, 1H), 7.34 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.01 (t, $J = 7.8$ Hz, 1H), 6.92 (d, $J = 7.8$ Hz, 1H), 4.33 (d, $J = 11.7$ Hz, 1H), 4.29−4.15 (m, 4H), 3.99 (d, $J = 11.7$ Hz, 1H), 3.81 (s, 3H), 3.84−3.79 (m, 1H), 1.56 (s, 3H), 1.39 (s, 3H); ^{13}C NMR δ 167.5, 156.9, 150.7, 132.6, 128.8, 123.6, 120.6, 111.0, 110.1, 101.8, 76.3, 73.0, 71.6, 62.4, 56.0, 51.2, 28.3, 26.2.

The above alcohol (0.403 g, 1.063 mmol) was oxidized with PDC to give ketone **2k** as a white solid (0.391 g, 97%): mp 160−161 °C; $[\alpha]^{20}_D = -75.0$ (*c* 1.09, $CHCl_3$); IR (KBr) 3487 (hydrate), 1806, 1758, 1689, 1603 cm^{-1}; ^1H NMR δ 7.50−7.44 (m, 1H), 7.35 (dd, *J* = 7.4, 1.4 Hz, 1H), 7.05−7.00 (m, 1H), 6.93 (d, *J* = 8.4 Hz, 1H), 4.80 (d, *J* = 5.4 Hz, 1H), 4.74 (d, *J* = 12.3 Hz, 1H) 4.63 (m, 1H), 4.49 (dd, *J* = 13.8, 2.1 Hz, 1H), 4,27 (d, *J* = 13.8 Hz, 1H), 3.99 (d, *J* = 12.3 Hz, 1H), 3.83 (s, 3H), 1.50 (s, 3H), 1.43 (s, 3H); ^{13}C NMR δ 194.7, 167.1, 156.9, 149.2, 132.7, 128.9, 123.1, 120.6, 111.5, 110.9, 99.7, 77.2, 75.4, 61.8, 55.9, 48.4, 27.2, 26.1. Anal. Calcd for $C_{18}H_{19}NO_8$: C, 57.29; H, 5.08; N, 3.71. Found: C, 57.17; H, 5.18; N, 3.83.

Preparation of Ketone 2l. To a solution of **5** (0.718 g, 2.0 mmol) in THF (10 mL) were added Et_3N (1.01 g, 10.0 mmol), DMAP (0.024 g, 0.2 mmol), and 2,4-dimethoxylbenzoyl chloride (0.482 g, 2.4 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 5 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6l** as a white solid (0.973 g, 93%): mp 69−70 °C; $[\alpha]^{20}_D = -73.8$ (*c* 1.30, $CHCl_3$); IR (KBr) 1799, 1680, 1609 cm^{-1}; ^1H NMR δ 7.32−7.29 (m, 1H), 6.54 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.48 (d, *J* = 1.8 Hz, 1H), 4.34−4.17 (m, 5H), 3.98 (d, *J* = 11.4 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.78 (d, *J* = 6.6 Hz, 1H), 1.60 (s, 3H), 1.42 (s, 3H), 0.92 (s, 9H), 0.23 (s, 3H), 0.19 (s, 3H); ^{13}C NMR δ 167.0, 163.4, 159.0, 130.5, 116.5, 109.6, 104.7, 101.8, 98.5, 76.9, 73.3, 73.2, 62.3, 55.9, 55.7, 51.3, 28.5, 26.5, 26.0, 18.3, −3.6, −5.1.

TBS ether **6l** (0.93 g, 1.78 mmol) was desilylated with Et_3N·3HF (1.43 g, 8.89 mmol) in a way similar to **6d** to give the alcohol as a white solid (0.67 g, 92%) (about 3 days): mp 70−72 °C; $[\alpha]^{20}_D = -114.0$ (*c* 1.00, $CHCl_3$); IR (KBr) 3447, 1797, 1676, 1609 cm^{-1}; ^1H NMR δ 7.36 (d, *J* = 8.4 Hz, 1H), 6.52 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 4.32 (d, *J* = 11.7 Hz, 1H), 4.28−4.12 (m, 4H), 3.94 (d, *J* = 11.7 Hz, 1H), 3.84 (s, 3H), 3.79 (m, 1H), 3.77 (s, 3H), 1.55 (s, 3H), 1.39 (s, 3H); ^{13}C NMR δ 167.2, 163.6, 159.0, 150.9, 131.0, 116.0, 109.9, 104.8, 101.9, 98.4, 76.2, 73.0, 71.3, 62.2, 55.9, 55.6, 51.2, 28.2, 26.2.

The above alcohol (0.518 g, 1.267 mmol) was oxidized with PDC to give ketone **2l** as a white solid (0.44 g, 85%): mp 74−76 °C; $[\alpha]^{20}_D = -78.0$ (*c* 1.04, $CHCl_3$); IR (KBr) 1805, 1758, 1681, 1609 cm^{-1}; ^1H NMR δ 7.36 (d, *J* = 8.4 Hz, 1H), 6.53 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.44 (d, *J* = 2.1 Hz, 1H), 4.80 (d, *J* = 6.0 Hz, 1H), 4.72 (d, *J* = 12.3 Hz, 1H), 4.63 (m, 1H), 4.49 (dd, *J* = 13.5, 1.8 Hz, 1H), 4.27 (d, *J* = 13.5 Hz, 1H), 3.97 (d, *J* = 12.6 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.50 (s, 3H), 1.43 (s, 3H); ^{13}C NMR δ 194.8, 166.7, 163.9, 149.5, 131.2, 115.7, 111.6, 105.0, 99.8, 98.5, 77.3, 75.5, 61.9, 56.0, 55.7, 48.7, 27.3, 26.2. Anal. Calcd for $C_{19}H_{21}NO_9$: C, 56.02; H, 5.20; N, 3.44. Found: C, 56.20; H, 5.34; N, 3.39.

Preparation of Ketone 2m. To a solution of **5** (0.718 g, 2.0 mmol) in THF (10 mL) were added Et_3N (1.01 g, 10.0 mmol), DMAP (0.024 g, 0.2 mmol), and 2,6-dimethoxylbenzoyl chloride (0.482 g, 2.4 mmol) at 0 °C under N_2. Upon stirring to completion as judged by TLC (about 12 h), the reaction mixture was quenched with water, extracted with EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **6m** as a white solid (1.02 g, 97%): mp 63−67 °C; $[\alpha]^{20}_D = -74.9$ (*c* 1.07, $CHCl_3$); IR (KBr) 1800, 1698, 1598 cm^{-1}; ^1H NMR δ 7.34 (t, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 4.31−3.78 (m, 7H), 3.82 (s, 6H). 1.60 (s, 3H), 1.41 (s, 3H), 0.94 (s, 9H), 0.23 (s, 3H), 0.19 (s, 3H); ^{13}C NMR δ 165.3, 157.1, 150.3, 131.5, 109.5, 103.8, 101.7, 76.9, 73.14, 73.1, 62.2, 56.1, 50.9, 28.4, 26.4, 26.0, 18.3, −3.7, −5.1.

TBS ether **6m** (0.64 g, 1.22 mmol) was desilylated with Et_3N·3HF (0.99 g, 6.12 mmol) in a way similar to **6d** to give the alcohol as a white solid (0.498 g, 99%) (about 3 days): mp 75−78 °C; $[\alpha]^{20}_D = -87.6$ (*c* 1.02, $CHCl_3$); IR (KBr) 3447, 1799, 1694, 1597 cm^{-1}; ^1H NMR δ 7.35 (t, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 2H), 4.35−4.13 (m, 5H), 4.00 (d, *J* = 11.7 Hz, 1H), 3.82 (m, 1H), 3.81 (s, 6H), 1.57 (s, 3H), 1.41 (s, 3H); ^{13}C NMR δ 165.5, 157.2, 150.5, 131.7, 112.9, 109.9, 103.9, 101.8, 76.2, 73.0, 71.3, 62.3, 56.2, 50.8, 28.2, 26.2.

The above alcohol (0.308 g, 0.753 mmol) was oxidized with PDC to give ketone **2m** as a white solid (0.268 g, 87%): mp 72−73 °C; $[\alpha]^{20}_D = -60.6$ (*c* 1.12, $CHCl_3$); IR (KBr) 3481, 1805, 1758, 1698, 1597 cm^{-1}; ^1H NMR δ 7.34 (t, *J* = 8.4 Hz, 1H), 6.57 (d, *J* = 8.4 Hz, 2H), 4.79 (d, *J* = 5.4 Hz,1H), 4.74 (d, *J* = 12.3 Hz, 1H), 4.62 (m, 1H), 4.48 (dd, *J* = 13.5, 2.1 Hz, 1H), 4.26 (d, *J* = 13.5 Hz, 1H), 3.99 (d, *J* = 12.3 Hz, 1H), 3.80 (s, 6H), 1.50 (s, 3H), 1.43 (s, 3H); ^{13}C NMR δ 194.8, 157.3, 149.0, 143.8, 132.0, 112.5, 111.5, 103.9, 99.6, 77.3, 75.5, 61.8, 56.2, 48.1, 27.3, 26.2. Anal. Calcd for $C_{19}H_{21}NO_9$: C, 56.02; H, 5.20; N, 3.44. Found: C, 55.96; H, 5.26; N, 3.41.

Preparation of Ketone 2n. To a solution of **5** (2.48 g, 6.91 mmol) in CH_3CN-H_2O (9/1, v/v) (21 mL) was added DDQ (0.153 g, 0.691 mmol). Upon stirring at room temperature for 6 h, the reaction mixture was concentrated, redissolved in EtOAc, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give diol **7** as a pink solid (2.053 g, 93%):[7g] mp 210−213 °C; IR (KBr) 3340, 1752 cm^{-1}; ^1H NMR (CD_3CN) δ 5.78 (s, 1H), 3.94 (d, *J* = 12.9 Hz, 1H), 3.83 (m, 1H), 3.78−3.69 (m, 3H), 3.64 (d, *J* = 10.5 Hz, 1H), 3.29−3.23 (m, 3H), 0.87 (s, 9H), 0.15 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (CD_3CN) δ 157.9, 106.4, 73.1, 71.1, 70.1, 66.4, 49.7, 26.3, 19.0, −3.2, −5.1. Anal. Calcd for $C_{13}H_{25}NO_6Si$: C, 48.88; H, 7.89; N, 4.38. Found: C, 48.79; H, 7.65; N, 4.45.

To a solution of **7** (0.638 g, 2.0 mmol) in CH_2Cl_2 (5 mL) were added TsOH (0.038 g, 0.2 mmol) and 3-petanone (0.516 g, 6.0 mmol). Upon stirring at room temperature to completion as judged by TLC (about 24 h), the reaction mixture was diluted with EtOAc, washed with water and brine, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give compound **8** as a white solid (0.51 g, 66%): mp 158.5−159.5 °C; $[\alpha]^{20}_D = -84.1$ (*c* 1.68, $CHCl_3$); IR (KBr) 3333, 1770 cm^{-1}; ^1H NMR δ 6.06 (s, 1H), 4.28−4.04 (m, 4H), 3.68 (d, *J* = 6.0 Hz, 1H), 3.67 (d, *J* = 9.0 Hz, 1H), 3.40 (d, *J* = 9.0 Hz, 1H), 1.82−1.66 (m, 2H), 1.62 (q, *J* = 7.5 Hz, 2H), 0.97 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H), 0.88 (s, 9H), 0.19 (s, 3H), 0.10 (s, 3H); ^{13}C NMR δ 158.0, 113.6, 104.9, 76.8, 73.8, 72.9, 62.3, 49.1, 30.5, 28.4, 26.0, 18.3, 8.93, 8.87, −3.7, −5.2. Anal. Calcd for $C_{18}H_{33}NO_6Si$: C, 55.79; H, 8.58; N, 3.61. Found: C, 55.66; H, 8.49; N, 3.79.

Compound **9** was prepared in a way similar to **6d**: white solid (93%); mp 102−104 °C; $[\alpha]^{20}_D = -59.1$ (*c* 1.16, $CHCl_3$); IR (KBr) 1807, 1724 cm^{-1}; ^1H NMR δ 4.30−4.18 (m, 3H), 4.08 (d, *J* = 12.9 Hz, 1H), 3.94 (d, *J* = 10.5 Hz, 1H), 3.69 (d, *J* = 10.5 Hz, 1H), 3.68 (d, *J* = 6.6 Hz, 1H), 1.82−1.65 (m, 2H), 1.62 (q, *J* = 7.5 Hz, 2H), 1.52 (s, 9H), 0.98 (t, *J* = 7.5 Hz, 3H), 0.89 (t, *J* = 7.5 Hz, 3H), 0.86 (s, 9H), 0.19 (s, 3H), 0.12 (s, 3H); ^{13}C NMR δ 150.3, 148.9, 113.7, 101.1, 84.1, 76.7, 74.1, 72.7, 62.7, 52.0, 30.5, 28.4, 28.2, 25.9, 18.2, 8.9, −3.7, −5.3. Anal. Calcd for $C_{23}H_{41}NO_8Si$: C, 56.65; H, 8.47; N, 2.87. Found: C, 56.62; H, 8.24; N, 2.87.

TBS ether **9** (0.596 g, 1.224 mmol) was desilylated with Et_3N·3HF (0.986 g, 6.12 mmol) in a way similar to **6d** to give the alcohol as a colorless oil (0.451 g, 99%) (about 4 days): $[\alpha]^{20}_D = -92.1$ (*c* 0.70, $CHCl_3$); IR (KBr) 3478, 1817, 1728 cm^{-1}; ^1H NMR δ 4.26−4.11 (m, 3H), 4.06 (d, *J* = 10.8 Hz, 1H), 3.99 (d, *J* = 13.2 Hz, 1H), 3.84 (s, 1H, OH), 3.68 (d, *J* = 6.6 Hz, 1H), 3.63 (d, *J* = 10.8 Hz, 1H), 1.64 (q, *J* = 7.5 Hz, 2H), 1.54 (q, *J* = 7.5 Hz, 2H), 1.42 (s, 9H), 0.86 (t, *J* = 7.5 Hz, 3H), 0.80 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 150.5, 148.7, 113.6, 101.1, 84.0, 75.8, 72.6, 70.9, 62.2, 51.5, 30.0, 28.5, 27.9, 8.6, 8.5. Anal. Calcd for $C_{17}H_{27}NO_8$: C, 54.68; H, 7.29; N, 3.75. Found: C, 54.48; H, 7.18; N, 3.91.

The above alcohol (0.39 g, 1.05 mmol) was oxidized with PDC to give ketone **2n** as a colorless oil (0.361 g, 93%): $[\alpha]^{20}_D = -25.7$ (*c* 2.37, $CHCl_3$); IR (KBr) 3454 (hydrate), 1833, 1754, 1732 cm^{-1}; ^1H NMR δ 4.73 (d, *J* = 6.0 Hz, 1H), 4.63 (dd, *J* = 6.0, 1.8 Hz, 1H), 4.51 (d, *J* = 11.2 Hz, 1H), 4.46 (dd, *J* = 13.8, 1.8 Hz, 1H), 4.23 (d, *J* = 13.8 Hz, 1H), 3.70 (d, *J* = 11.2 Hz, 1H), 1.70−1.59 (m, 4H), 1.53 (s, 9H), 0.94−0.87 (m, 6H); ^{13}C NMR δ 194.9, 148.8, 148.4, 115.5, 98.7, 84.9, 76.8, 75.0, 61.7, 48.8, 29.8, 29.1, 28.1, 8.7, 8.4; HRMS calcd for $C_{17}H_{26}NO_8$ ($M^+ + 1$) 372.1658, found 372.1662. Anal. Calcd for $C_{17}H_{25}NO_8$: C, 54.98; H, 6.79; N, 3.77. Found: C, 55.06; H, 6.91; N, 3.71.

Preparation of Ketone 2o. A mixture of thiocarbonyldiimidazole (1.12 g, 6.3 mmol) and diol **7** (1.826 g, 5.724 mmol) in toluene (30 mL) was heated at reflux for 1 h. Upon cooling, the reaction mixture was washed with water and brine, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography to give **10** as a white solid (1.523 g, 74%): mp 219−222 °C; $[\alpha]^{20}_D = -102.5$ (*c* 0.49, $CHCl_3$); ^{1}H NMR δ 5.95 (s, 1H), 5.02−4.90 (m, 2H), 4.33 (s, 2H), 3.79 (d, $J = 6.0$ Hz, 1H), 3.73 (d, $J = 9.6$ Hz, 1H), 3.25 (d, $J = 9.6$ Hz, 1H), 0.90 (s, 9H), 0.24 (s, 3H), 0.17 (s, 3H); ^{13}C NMR δ 190.1, 156.9, 103.6, 82.2, 79.5, 71.4, 60.2, 48.6, 25.8, 18.3, −3.9, −5.1. Anal. Calcd for $C_{14}H_{23}NO_6SSi$: C, 46.52; H, 6.41; N, 3.87. Found: C, 46.70; H, 6.39; N, 4.03.

Compound **10** (0.5 g, 1.385 mmol), Ph_3SnH (0.972 g, 2.77 mmol), and AIBN (0.014 g, 0.085 mmol) were dissolved in anhydrous toluene (35 mL). Upon stirring at reflux to completion as judged by TLC, the reaction mixture was concentrated and purified by flash chromatography to give **11** as a white solid (0.457 g, 99%):[19] mp 179−182 °C; $[\alpha]^{20}_D = -95.5$ (*c* 1.17, $CHCl_3$); IR (KBr) 3295, 1767 cm^{-1}; ^{1}H NMR δ 6.27 (s, 1H), 5.18 (s, 1H), 5.00 (s, 1H), 4.31−4.25 (m, 2H), 4.16 (d, $J = 13.8$ Hz, 1H), 4.01 (dd, $J = 5.4$, 1.8 Hz, 1H), 3.69 (d, $J = 9.3$ Hz, 1H), 3.60 (d, $J = 7.2$ Hz, 1H), 3.39 (d, $J = 9.3$ Hz, 1H), 0.87 (s, 9H), 0.17 (s, 3H), 0.09 (s, 3H); ^{13}C NMR δ 158.0, 104.9, 94.8, 76.3, 74.4, 71.5, 61.6, 48.8, 25.9, 18.3, −3.8, −5.2. Anal. Calcd for $C_{14}H_{25}NO_6Si$: C, 50.73; H, 7.60; N, 4.23. Found: C, 50.86; H, 7.56; N, 4.22.

Compound **12** was prepared in a way similar to **6d**: white solid (0.522 g, 88%); mp 119.0−120.5 °C; $[\alpha]^{20}_D = -65.0$ (*c* 1.13, $CHCl_3$); IR (KBr) 1827, 1807, 1726 cm^{-1}; ^{1}H NMR δ 5.20 (s, 1H), 5.03 (s, 1H), 4.31−4.24 (m, 3H), 4.04 (m, 1H), 3.99 (d, $J = 10.8$ Hz, 1H), 3.72 (d, $J = 10.8$ Hz, 1H), 3.63 (d, $J = 7.2$ Hz, 1H), 1.54 (s, 9H), 0.88 (s, 9H), 0.20 (s, 3H), 0.13 (s, 3H); ^{13}C NMR δ 150.2, 148.8, 101.1, 94.8, 84.2, 76.0, 74.2, 71.8, 62.0, 51.7, 28.2, 25.9, 18.2, −3.9, −5.4. Anal. Calcd for $C_{19}H_{35}NO_8Si$: C, 52.88; H, 7.71; N, 3.25. Found: C, 52.92; H, 7.60; N, 3.40.

TBS ether **12** (0.522 g, 1.21 mmol) was desilylated with $Et_3N{\cdot}3HF$ (0.975 g, 6.06 mmol) in a way similar to **6d** to give the alcohol as a colorless oil (0.363 g, 94%) (about 4 days): $[\alpha]^{20}_D = -115.7$ (*c* 1.28, $CHCl_3$); IR (KBr) 3468, 1812, 1726 cm^{-1}; ^{1}H NMR δ 5.21 (s, 1H), 4.99 (s, 1H), 4.32 (dd, $J = 7.5$, 5.4 Hz, 1H), 4.24 (dd, $J = 13.5$, 2.0 Hz, 1H), 4.18 (d, $J = 13.5$ Hz, 1H), 4.14 (d, $J = 10.8$ Hz, 1H), 4.04 (dd, $J = 5.7$, 2.0 Hz, 1H), 3.72 (d, $J = 10.8$ Hz, 1H), 3.65 (dd, $J = 7.5$, 7.2 Hz, 1H), 3.41 (d, $J = 7.2$ Hz, 1H), 1.51 (s, 9H); ^{13}C NMR δ 150.6, 148.9, 101.1, 95.0, 84.5, 75.7, 74.2, 69.5, 61.6, 51.3, 28.1. Anal. Calcd for $C_{13}H_{19}NO_8$: C, 49.21; H, 6.04; N, 4.41. Found: C, 49.26; H, 5.96; N, 4.54.

The above alcohol (0.309 g, 0.974 mmol) was oxidized with PDC to give ketone **2o** as a colorless oil (0.30 g, 98%): $[\alpha]^{20}_D = -35.6$ (*c* 1.22, $CHCl_3$); IR (KBr) 3453, 1821, 1757, 1729 cm^{-1}; ^{1}H NMR δ 5.13 (s, 1H), 4.99 (s, 1H), 4.83 (d, $J = 5.4$ Hz, 1H), 4.52−4.42 (m, 3H), 4.26 (d, $J = 13.5$ Hz, 1H), 3.67 (d, $J = 11.7$ Hz, 1H), 1.49 (s, 9H); ^{13}C NMR δ 193.6, 148.7, 148.3, 98.7, 95.8, 84.9, 78.4, 74.6, 61.1, 48.4, 28.0; HRMS calcd for $C_{13}H_{18}NO_8$ ($M^+ + 1$) 316.1032, found 316.1040. Anal. Calcd for $C_{13}H_{17}NO_8$: C, 49.52; H, 5.43; N, 4.44. Found: C, 49.37; H, 5.60; N, 4.31.

Preparation of Ketone 16. A suspension of thiocarbonate **10** (0.565 g, 1.566 mmol) in 1,3-dimethyl-2-phenyl-1,3,2-diazaphospholidine (0.911 g, 4.698 mmol) was stirred under N_2 at 40 °C for 20 h. Upon cooling, the mixture was purified by flash chromatography to give olefin **13** as a colorless oil (0.287 g, 64%):[20] $[\alpha]^{20}_D = +9.63$ (*c* 1.6, $CHCl_3$); IR (KBr) 3281, 1763 cm^{-1}; ^{1}H NMR δ 6.53 (s, 1H), 5.77 (d, $J = 10.5$ Hz, 1H), 5.65 (d, $J = 10.5$ Hz, 1H), 4.48 (dd, $J = 16.5$, 1.2 Hz, 1H), 4.26 (s, 1H), 4.17 (dd, $J = 16.5$, 1.2 Hz, 1H), 3.64 (d, $J = 9.6$ Hz, 1H), 3.40 (d, $J = 9.6$ Hz, 1H), 0.88 (s, 9H), 0.12 (s, 3H), 0.10 (s, 3H); ^{13}C NMR δ 158.5, 126.1, 125.5, 102.6, 67.5, 63.0, 49.3, 25.8, 18.1, −3.7, −4.6.

Compound **14** was prepared in a way similar to **6d**: colorless oil (78%); $[\alpha]^{20}_D = +19.0$ (*c* 1.45, $CHCl_3$); IR (KBr) 1827, 1806, 1726 cm^{-1}; ^{1}H NMR δ 5.80−5.74 (m, 1H), 5.66−5.61 (m, 1H), 4.50−4.42 (m, 1H), 4.29−4.26 (m, 1H), 4.25−4.17 (m, 1H), 3.91 (d, $J = 10.5$ Hz, 1H), 3.71 (d, $J = 10.5$ Hz, 1H), 1.52 (s, 9H), 0.87 (s, 9H), 0.13 (s, 3H), 0.11 (s, 3H); ^{13}C NMR δ 150.5, 149.1, 125.7, 125.4, 98.8, 83.9, 67.8, 63.6, 52.2, 28.2, 25.8, 18.1, −3.6, −4.7.

A mixture of **14** (0.303 g, 0.787 mmol) and 10% Pd−C (0.0303 g) in MeOH (10 mL) was stirred under H_2 for 24 h. Upon filtration, the mixture was concentrated and purified by flash chromatography to give **15** as a colorless oil (0.301 g, 99%): $[\alpha]^{20}_D = -13.7$ (*c* 1.31, $CHCl_3$); IR (KBr) 1824, 1799, 1727 cm^{-1}; ^{1}H NMR δ 3.90 (d, $J = 8.0$ Hz, 1H), 3.93−3.86 (m, 1H), 3.72−3.68 (m, 1H), 3.61−3.57 (m, 1H), 3.57 (d, $J = 8.0$ Hz, 1H), 1.96−1.66 (m, 4H), 1.50 (s, 9H), 0.83 (s, 9H), 0.065 (s, 6H); ^{13}C NMR δ 150.9, 149.2, 101.4, 83.7, 71.6, 63.3, 52.3, 28.1, 28.0, 25.7, 24.4, 17.9, −3.5, −5.0; HRMS calcd for $C_{18}H_{34}NO_6Si$ ($M^+ + 1$) 388.2155, found 388.2163.

TBS ether **15** (0.3 g, 0.775 mmol) was desilylated with $Et_3N{\cdot}3HF$ (0.625 g, 3.876 mmol) in a way similar to **6d** to give the alcohol as a colorless oil (0.187 g, 88%) (about 4 days): $[\alpha]^{20}_D = -71.2$ (*c* 1.10, $CHCl_3$); IR (KBr) 3496, 1806, 1725 cm^{-1}; ^{1}H NMR δ 4.11 (d, $J = 8.1$ Hz, 1H), 3.85 (td, $J = 8.4$, 2.4 Hz, 1H), 3.70 (dd, $J = 8.4$, 2.4 Hz, 1H), 3.63 (d, $J = 8.1$ Hz, 1H), 3.52 (m, 1H), 2.59 (s, 1H), 2.06 (m, 1H), 1.82−1.71 (m, 3H), 1.50 (s, 9H); ^{13}C NMR δ 151.4, 149.1, 102.0, 84.1, 69.1, 62.9, 51.6, 28.15, 28.1, 24.7; HRMS calcd for $C_{12}H_{20}NO_6$ ($M^+ + 1$) 274.1291, found 274.1291.

The above alcohol (0.18 g, 0.659 mmol) was oxidized with PDC to give ketone **16** as a colorless oil (0.16 g, 90%): $[\alpha]^{20}_D = +15.1$ (*c* 1.24, $CHCl_3$); IR (KBr) 3475, 1827, 1736 cm^{-1}; ^{1}H NMR δ 4.47 (d, $J = 11.1$ Hz, 1H), 4.26 (td, $J = 11.4$, 3.6 Hz, 1H), 3.89−3.83 (m, 1H), 3.49 (d, $J = 11.1$ Hz, 1H), 2.86−2.75 (m, 1H), 2.61−2.55 (m, 1H), 2.27−2.08 (m, 2H), 1.45 (s, 9H); ^{13}C NMR δ 197.0, 149.1, 148.5, 99.0, 84.3, 62.7, 48.5, 35.8, 27.9, 27.0; HRMS calcd for $C_{12}H_{18}NO_6$ ($M^+ + 1$) 272.1134, found 272.1139.

Representative Asymmetric Epoxidation Procedure. To a solution of *cis*-β-methylstyrene (0.059 g, 0.5 mmol) and ketone **2d** (0.026 g, 0.075 mmol) in DME−DMM (3:1, v/v) (7.5 mL) were added buffer (0.2 M K_2CO_3–AcOH in 4×10^{-4} M aqueous EDTA, buffer pH = 8.0) (5 mL) and Bu_4NHSO_4 (0.0075 g, 0.02 mmol) with stirring. After the mixture was cooled to about −10 °C (bath temperature) via a NaCl−ice bath, a solution of Oxone (0.212 M in 4×10^{-4} M aqueous EDTA, 4.2 mL) (0.548 g, 0.89 mmol) and K_2CO_3 (0.479 M in 4×10^{-4} M aqueous EDTA, 4.2 mL) (0.278 g, 2.01 mmol) were added dropwise separately over a period of 3.5 h via a syringe pump. The reaction was then quenched with the addition of pentane and extracted with pentane. The combined organic layers were washed with brine, dried (Na_2SO_4), filtered, concentrated, and purified by flash chromatography [the silica

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gel was buffered with 1% Et_3N in pentane; pentane−ether (1/0 to 50/1) was used as eluent] to give *cis-β*-methylstyrene oxide as a colorless oil (0.058 g, 87% yield, 91% ee) (Table 1, entry 1).

(1*R*,2*S*)-*cis-β*-Methylstyrene oxide (Table 1, entry 1):[15a,b] colorless oil; $[\alpha]^{20}_D = -45.5$ (*c* 0.67, $CHCl_3$).

(1*R*,2*S*)-1-(4-Methylphenyl)-1-propene oxide (Table 1, entry 2):[15c] colorless oil; ^{1}H NMR δ 7.16 (m, 4H), 4.04 (d, J = 4.2 Hz, 1H), 3.29−3.26 (m, 1H), 2.40 (s, 3H), 1.14 (d, J = 5.1 Hz, 3H); ^{13}C NMR δ 128.8, 126.6, 57.7, 55.3, 21.4, 12.7.

(1*R*,2*S*)-1-(3-Methylphenyl)-1-propene oxide (Table 1, entry 3): colorless oil; ^{1}H NMR δ 7.26−7.09 (m, 4H), 4.04 (d, J = 4.2 Hz, 1H), 3.37−3.30 (m, 1H), 2.37 (s, 3H), 1.10 (d, J = 5.7 Hz, 3H); ^{13}C NMR δ 137.7, 128.3, 128.0, 127.3, 123.7, 57.7, 55.3, 21.6, 12.8; HRMS calcd for $C_{10}H_{12}O$ 148.0888, found 148.0888.

(1*R*,2*S*)-1-(3,5-Dimethylphenyl)-1-propene oxide (Table 1, entry 4): colorless oil; ^{1}H NMR δ 6.95−6.85 (m, 3H), 4.00 (d, J = 4.2 Hz, 1H), 3.32 (qd, J = 5.7, 4.2, 1H), 2.32 (s, 6H), 1.10 (d, J = 5.7 Hz, 3H); ^{13}C NMR δ 129.2, 124.4, 57.7, 55.2, 21.5, 12.8; HRMS calcd for $C_{11}H_{14}O$ 162.1045, found 162.1042.

(1*R*,2*S*)-1-(4-Fluorophenyl)-1-propene oxide (Table 1, entry 5): colorless oil; ^{1}H NMR δ 7.30−7.19 (m, 2H), 7.09−6.98 (m, 2H), 4.03 (d, J = 4.2 Hz, 1H), 3.33 (qd, J = 5.1, 4.2 Hz, 1H), 1.07 (d, J = 5.1 Hz, 3H); ^{13}C NMR δ 128.3, 128.2, 115.2, 115.0, 57.2, 55.3, 12.7. Anal. Calcd C_9H_9FO: C, 71.04; H, 5.96. Found: C, 71.21; H, 5.90.

(1*R*,2*S*)-1-(4-Trifluoromethylphenyl)-1-propene oxide (Table 1, entry 6): colorless oil; ^{1}H NMR δ 7.62 (d, J = 8.1 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 4.10 (d, J = 4.2 Hz, 1H), 3.39 (m, 1H), 1.08 (d, J = 5.4 Hz, 3H); ^{13}C NMR δ 127.0, 125.1, 57.2, 55.4, 12.7. Anal. Calcd $C_{10}H_9F_3$: C, 59.41; H, 4.49. Found: C, 59.19; H, 4.65.

(1*R*,2*S*)-1-(2-Naphthyl)-1-propene oxide (Table 1, entry 7): white solid; $[\alpha]^{20}_D = -13.5$ (*c* 1.31, $CHCl_3$); IR (KBr) 3051, 1511, 1341 cm^{-1}; ^{1}H NMR δ 7.86−7.77 (m, 4H), 7.50−7.44 (m, 3H), 4.23 (d, J = 4.5 Hz, 1H), 3.43 (qd, J = 5.4, 4.5 Hz, 1H), 1.12 (d, J = 5.4 Hz, 3H); ^{13}C NMR δ 133.1, 132.9, 127.9, 127.8, 126.3, 125.9, 125.6, 124.6, 57.9, 55.6, 12.8. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.60; H, 6.41.

(1*R*,2*S*)-Indene oxide (Table 1, entry 8):[15d] colorless oil; $[\alpha]^{20}_D$ = -38.3 (*c* 1.2, $CHCl_3$).

(1*R*,2*S*)-3,4-Dihydronaphthalene oxide (Table 1, entry 9):[15b,10d] colorless oil; $[\alpha]^{20}_D = +133.2$ (*c* 1.57, $CHCl_3$).

(5*R*,6*S*)-5,6-Epoxy-6,7,8,9-tetrahydro-5H-benzocycloheptene (Table 1, entry 10):[15e,f] colorless oil; $[\alpha]^{20}_D = -23.4$ (*c* 0.82, $CHCl_3$).

(3*R*,4*R*)-6-Cyano-3,4-epoxy-2,2-dimethylchromene (Table 1, entry 11): white solid; $[\alpha]^{20}_D = +62.7$ (*c* 0.71, $CHCl_3$).

(2*S*,3*R*)-2-Methyl-3-(phenylethynyl)oxirane (Table 1, entry 12):[10a,d] colorless oil; $[\alpha]^{20}_D$ = -33.0 (*c* 0.98, $CHCl_3$).

(2*S*,3*R*)-2-Methyl-3-(1-octynyl)oxirane (Table 1, entry 13): colorless oil; $[\alpha]^{20}_D = -31.4$ (*c* 0.29, $CHCl_3$); IR (KBr) 2215, 1347 cm^{-1}; ^{1}H NMR δ 3.45 (dt, J = 3.9, 1.8 Hz, 1H), 3.16 (qd, J = 5.1, 3.9 Hz, 1H), 2.70 (td, J = 7.2, 1.8 Hz, 2H), 1.63−1.25 (m, 8H), 1.45 (d, J = 5.1 Hz, 3H), 0.93 (t, J = 6.9 Hz, 3H); ^{13}C NMR δ 100.1, 86.8, 54.1, 46.1, 31.5, 30.1, 28.6, 22.7, 19.0, 14.9, 14.3. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.28; H, 10.95.

(+)-3,3-Ethylenedioxycyclopentene oxide (Table 1, entry 14): colorless oil; $[\alpha]^{20}_D = +12.7$ (*c* 0.132, $CHCl_3$); IR (KBr) 1347, 1130 cm^{-1}; ^{1}H NMR δ 4.10−3.85 (m, 4H), 3.51 (m, 1H), 3.25 (d, J = 3 Hz, 1H), 2.10 (m, 1H), 1.85−1.55 (m, 3H); ^{13}C NMR δ 114.8, 65.4, 65.0, 55.9, 55.7, 29.5, 25.2. Anal. Calcd for $C_7H_{10}O_3$: C, 59.14; H, 7.09. Found: C, 59.32; H, 7.18.

(+)-3,3-Ethylenedioxycyclohexene oxide (Table 1, entry 15):[15i] colorless oil; $[\alpha]^{20}_D = +9.7$ (*c* 2.3, hexane).

(+)-3,3-Ethylenedioxycycloheptene oxide (Table 1, entry 16): colorless oil; $[\alpha]^{20}_D = +6.5$ (*c* 0.71, $CHCl_3$); IR (KBr) 1147, 1087, 1061 cm^{-1}; ^{1}H NMR δ 4.10−3.86 (m, 4H), 3.09 (td, J = 5.3, 1.2 Hz, 1H), 2.95 (dd, J = 4.5, 1.2 Hz, 1H), 2.28−2.21 (m, 1H), 1.95−1.43 (m, 6H), 1.30−1.21 (m, 1H); ^{13}C NMR δ 110.9, 65.1, 64.9, 59.4, 54.3, 34.9, 28.0, 23.7, 22.9. Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.65; H, 8.50.

(*R*)-(−)-Styrene oxide (Table 2, entry 1):[17a] colorless oil; $[\alpha]^{20}_D = -19.2$ (*c* 1.34, $CHCl_3$).

(*R*)-(−)-2-Chlorostyrene oxide (Table 2, entrys 2):[17a] colorless oil; $[\alpha]^{20}_D = -49.7$ (*c* 0.7, $CHCl_3$).

(*R*)-(−)-3-Chlorostyrene oxide (Table 2, entry 3):[17a] colorless oil; $[\alpha]^{20}_D = -10.3$ (*c* 1.04, $CHCl_3$).

(*R*)-(−)-4-Chlorostyrene oxide (Table 2, entry 4):[17a] colorless oil; $[\alpha]^{20}_D = -21.8$ (*c* 0.83, $CHCl_3$).

Cyclohexyloxirane (Table 2, entry 5):[17b,c] colorless oil.

(*S*)-(+)-α-Methylstyrene oxide (Table 2, entry 6):[17a] colorless oil; $[\alpha]^{20}_D = +2.78$ (*c* 1.1, $CHCl_3$).

(+)-α-Isopropylstyrene oxide (Table 2, entry 7):[17d] colorless oil; $[\alpha]^{20}_D = +23.2$ (*c* 0.6, hexane); ^{1}H NMR δ 7.44−7.30 (m, 5H), 3.05 (d, J = 5.1 Hz, 1H), 2.77 (d, J = 5.1 Hz, 1H), 2.21−2.07 (m, 1H), 1.02 (d, J = 6.9 Hz, 3H), 1.00 (d, J = 6.9 Hz, 3H); ^{13}C NMR δ 139.4, 128.0, 127.4, 127.3, 64.7, 53.4, 33.4, 18.8, 18.1.

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Supporting Information Available: X-ray structural data of ketones **2a**, **2b**, **2d**, and **2e** containing atomic coordinates and bond lengths and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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