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Asymmetric Thio-Michael/Nucleophilic Addition Domino Reaction with Chiral *N*-Sulfinimines

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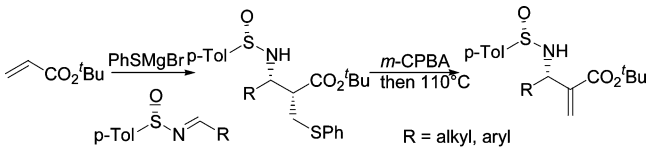

Optically active *N*-sulfinimines underwent stereoselective Michael/nucleophilic addition domino reaction triggered by magnesium thiolate to give α-phenylthiomethyl-*β*-(*N*-sulfinylamino) esters in high diastereomeric excess. The adducts were readily converted into optically active α-methylene-*β*-(*N*-sulfinylamino)esters so that this reaction provides a useful asymmetric aza-Baylis−Hillman-equivalent method.

The Baylis−Hillman reaction has been recognized as a potentially useful organic reaction because it provides one-step preparation of α-methylene-*β*-hydroxy carbonyl compounds from readily available α,*β*-unsaturated carbonyl compounds and aldehydes.[1] Catalytic asymmetric modification of the reaction has been of interest among organic chemists and a number of reports have been published so far.[2] Use of imines instead of aldehydes gives *β*-amino-α-methylene esters so the aza-variation of the reaction is also regarded as an important method for organic synthesis. Recently, Shi,[3] Adolfsson,[4] Hatakeyama,[5] Li,[6] Aggarwal,[7] Sasai,[8] Jacobsen,[9] and Leitner[10] have reported various attempts to obtain the asymmetric aza-Baylis−Hillman adducts; however, use of imines is only limited for aromatic imines. Recently we have developed an alternative stereoselective Baylis−Hillman strategy, that is the domino-Michael/aldol method with a sulfur-centered anion and analogous conditions.[11] With the extension of our method for asymmetric synthesis of amino compounds, we focused on the use of chiral sulfinimines which were devised by Davis[12] and Ellman.[13] In this paper we report a stereoselective asymmetric Michael/nucleophilic addition domino reaction, which provided a general method for the asymmetric aza-Baylis−Hillman-equivalent reaction for aromatic as well as aliphatic imines.

(*S*)-Sulfinimines **1** were prepared through the reported method in >95% ee.[14] Exposure of imine **1** to a mixture of magnesium thiolate and *tert*-butyl acrylate resulted in the smooth formation of domino adduct **2** in good yields (Scheme 1). The results are summarized in Table 1.

Magnesium thiolate was generated from the corresponding thiol and methyl Grignard reagent. *tert*-Butyl acrylate and chiral sulfinimine **1a** were added at −50 °C to the mixture. After usual workup, desired domino adduct **2a** was obtained in 99% yield (entry 1). The adduct **2a** contained two diastereomers whose ratio was 81/19. The major isomer was isolated by the usual chromatographic purification and recrystallization. The obtained crystals of major **2a** allowed us to perform an X-ray crystallographic analysis that unambiguously indicated that its absolute configuration was 2*R*,3*R*. Use of lithium thiolate also promoted the reaction but the yield of **2a** decreased to 43% although the level of diastereoselectivity was almost the same (entry 2). Other sulfinimines **1** also underwent the reaction smoothly to give **2** in good yields (entry 3−8). It should be mentioned that not only aromatic sulfinimines but also aliphatic sulfinimines gave the adduct **2** in good yields. The absolute stereochemistry of major-**2e** was also confirmed by X-ray crystallographic analysis,

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(1) (a) Drews, S. E.; Roo, G. H. P. *Tetrahedron* **1988**, *44*, 4653. (b) Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001. (c) Ciganek, E. In *Organic Reactions*; Paquette, L. A., Ed.; Wiley: New York, 1997; Vol. 51, p 201. (d) Langer, P. *Angew. Chem., Int. Ed.* **2000**, *39*, 3049. (e) Iwabuchi, Y.; Hatakeyama, S. *J. Synth. Org. Chem. Jpn.* **2002**, *60*, 2. (f) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811.

(2) (a) Barrett, A. G. M.; Cook, A. S.; Kamimura, A. *Chem. Commun.* **1998**, 2533. (b) Iwabuchi, Y.; Nakatani, M.; Yokoyama, N.; Hatakeyama, S. *J. Am. Chem. Soc.* **1999**, *121*, 10219. (c) McDougal, N. T.; Schaus, S. E. *J. Am. Chem. Soc.* **2003**, *125*, 12094.

(3) (a) Shi, M.; Xu, Y.-M. *Angew. Chem., Int. Ed.* **2002**, *41*, 4507. (b) Shi, M.; Chen, L.-H. *Chem. Commun.* **2003**, 1310. (c) Shi, M.; Xu, Y.-M.; Shi, Y.-L. *Chem. Eur. J.* **2005**, *11*, 1794. (d) Shi, M.; Chen, L.-H.; Li, C.-Q. *J. Am. Chem. Soc.* **2005**, *127*, 3790. (e) Shi, M.; Chen, L.-H.; Teng, W.-D. *Adv. Synth. Catal.* **2005**, *347*, 1781. (f) Shi, M.; Li, C.-Q. *Tetrahedron*: *Asymmetry* **2005**, *16*, 1385. (g) Shi, Y.-L.; Shi, M. *Tetrahedron* **2006**, *62*, 461. (g) Liu, Y.-H.; Chen, L.-H.; Shi, M. *Adv. Synth. Catal.* **2006**, *348*, 973.

(4) Balan, D.; Adolfsson, H. *Tetrahedron Lett.* **2003**, *44*, 2521.

(5) Kawahara, S.; Nakano, A.; Esumi, T.; Iwabuchi, Y.; Hatakeyama, S. *Org. Lett.* **2003**, *5*, 3103.

(6) Li, G.; Wei, H.-X.; Whittlesey, B. R.; Batrice, N. N. *J. Org. Chem.* **1999**, *64*, 1061.

(7) Aggarwal, V. K.; Castro, A. M. M.; Mereu, A.; Adams, H. *Tetrahedron Lett.* **2002**, *43*, 1577.

(8) (a) Matsui, K.; Takizawa, S.; Sasai, H. *J. Am. Chem. Soc.* **2005**, *127*, 3680. (b) Matsui, K.; Takizawa, S.; Sasai, H. *Synlett* **2006**, 761. (c) Matsui, K.; Tanaka, K.; Horii, A.; Takizawa, S.; Sasai, H. *Tetrahedron*: *Asymmetry* **2006**, *17*, 578.

(9) Raheem, I. T.; Jacobsen, E. N. *Adv. Synth. Catal.* **2005**, *347*, 1701.

(10) Gausepohl, R.; Buskens, P.; Kleiner, J.; Bruckmann, A.; Lehmann, C. W.; Klankermayer, J.; Leitner, W. *Angew. Chem., Int. Ed.* **2006**, *45*, 3689.

(11) (a) Kamimura, A.; Mitsudera, H.; Asano, S.; Kakehi A.; Noguchi, M. *Chem. Commun.* **1998**, 1095. (b) Kamimura, A. *J. Synth. Org. Chem. Jpn.* **2004**, *62*, 705.

(12) (a) Davis, F. A.; Zhou, P.; Chen, B.-C. *Chem. Soc. Rev.* **1998**, *27*, 13. (b) Zhou, P.; Chen, B.-C.; Davis, F. A. *Tetrahedron* **2004**, *60*, 8003. (c) Senanayake, C. H.; Krishnamurthy, D.; Lu, Z.-H.; Han, Z.; Gallou, I. *Aldrichim. Acta* **2005**, *38*, 93.

(13) Ellman, J. A.; Owens, T. D.; Tang, T. P. *Acc. Chem. Res.* **2002**, *35*, 984.

(14) Davis, F. A.; Zhang, Y.; Andemichael, Y.; Fang, T.; Fanelli, D. L.; Zhang, H. *J. Org. Chem.* **1999**, *64*, 1403.

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SCHEME 1. Michael/Aldol Domino Reaction of 1

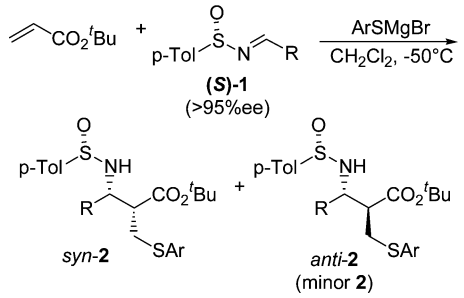


TABLE 1. Michael/Nucleophilic Addition Domino Reaction of 1

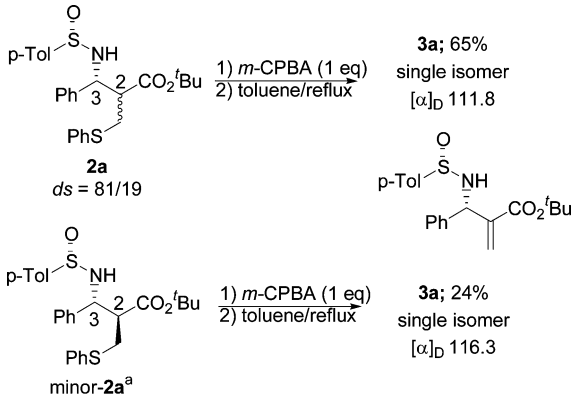
entry	Ar	R	2	yield (%)[a]	*syn*/*anti*[b]
1	Ph	Ph	**2a**	99	81/19
2	Ph	Ph	**2a**	43[c]	81/19
3	Ph	*p*-ClC_6H_4	**2b**	100	88/12
4	Ph	Et	**2c**	84	89/11
5	Ph	Pr	**2d**	85	95/5
6	Ph	^{i}Pr	**2e**	75	83/17
7	Ph	^{i}Bu	**2f**	96	97/3
8	Ph	C_5H_{11}	**2g**	84	89/11
9	*o*-$CH_3C_6H_4$	Ph	**2h**	79	79/21

[a] Isolated yields. [b] Determined by HPLC analyses (ODS-column, MeOH/H_2O 70:30 or 80:20). [c] Lithium thiolate (PhSLi) was used instead of magnesium thiolate.

which unambiguously indicated its configuration was identical with that of major-**2a**.[15] The HPLC pattern for compounds **2** made from aliphatic imines was the same so that these results clearly supported that the configurations for all of major-**2** were *syn*.[16] The presence of a substituent at the *ortho* position of thiolate sometimes enhanced the stereoselectivity[17] so we examined the magnesium salt of *o*-thiocresol for the reaction. Unfortunately, a slight decrease of the diastereoselectivity was observed (entry 9).

We next examined the conversion of **2a** to aza-Baylis−Hillman adducts through thermal elimination of sulfoxide. Treatment of **2a** (dr = 81/19) with 1 equiv of *m*-CPBA at 0 °C gave the corresponding sulfoxide, which afforded the desired aza-Baylis−Hillman adduct **3a** in 65% yield by treatment at 110 °C in toluene. ^{1}H and ^{13}C NMR spectra and HPLC analysis supported that obtained **3a** was diastereomerically pure so that these results suggested that both of the diastereomers of **2a** might have the same *R* configuration at the C3 carbon (Scheme 2). To confirm the absolute configuration of the minor isomer of **2a**, we performed a further experiment. The minor isomer of **2a** was purified by very careful chromatographic operation, and treated under similar oxidation/thermal elimination conditions. This operation also gave diastereomerically pure **3a**, which showed the same positive optical rotation as well as the identical NMR spectra to the product obtained from *syn*-**2a**. These results

SCHEME 2. Conversion to β-Amino-α-methylene Ester 3a



[a] Separated through chromatographic treatment.

SCHEME 3. Conversion of 2 to α-Methylene Aminoester 3

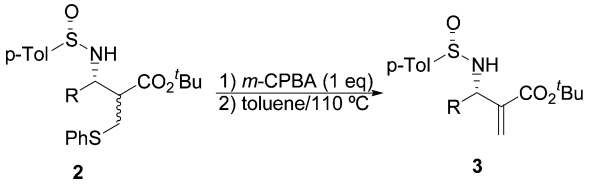


TABLE 2. Conversion to Aza-Baylis−Hillman Adducts 3

entry	R	3	yield (%)[a]	de[b]
1	Ph	**3a**	65	>99
2	*p*-ClC_6H_4	**3b**	65	>99
3	Et	**3c**	69	90
4	Pr	**3d**	67	94
5	^{i}Pr	**3e**	47	97
6	^{i}Bu	**3f**	58	99
7	C_5H_{11}	**3g**	51	98

[a] Isolated yields. [b] Determined by HPLC analyses (ODS-column, MeOH/H_2O 70:30 or 80:20).

clearly supported that minor-**2a** also contained the same *R* configuration at C3. Thus, the diastereomeric difference between the two isomers of **2a** came from the difference of configuration at C2 so that the stereochemistry of minor-**2a** has clearly determined to be 2*S*,3*R anti*. It should be mentioned that the level of diastereoselectivity at C3, which was derived from the chiral sulfinimine unit, was almost 100%.

Other adducts of **2** were also converted into α-methylene derivatives **3** in good yields (Scheme 3).[18] The results are summarized in Table 2. This transformation was useful for not only aromatic-imine adducts **2a** and **2b**, but also aliphatic-imines adducts **2c** to **2g** (entry 3−7). It should be noted that the temperature of the thermal elimination of sulfoxide was crucial to avoid partial epimerization at the C3 carbon. For example, when the elimination of the sulfoxide from **2d** was performed under vigorously refluxing conditions (bath temperature was about 150 °C), **3d** was obtained in 54% yield but became a mixture of two diastereomers, the ratio of which was 68:32. After an extensive search for optimized elimination conditions we found the best elimination conditions, 110 °C for the oil bath temperature for 1 h, and under these conditions we succeeded in suppressing the undesired epimerization to less than the 5% level. Thus, the present method provides the first general method for the preparation of the optically active aza-Baylis−Hillman adducts of aliphatic imines.

(15) Due to the sequential rule, adducts *syn*-**2a**, *syn*-**2b**, and *syn*-**2h** from aromatic imines are assigned to be 2*R*,3*R*, while adducts *syn*-**2c** to *syn*-**2g** from aliphatic imines are assigned to be 2*R*,3*S*, but all of them have the same absolute stereochemistry as shown in Scheme 1.

(16) In HPLC analyses performed by usual ODS column (4.6 mm id × 150 mm length), *syn*-**2** was eluted earlier than *anti*-**2**. For example, t_R for *syn*-**2f** was 60.7 min, while t_R for *anti*-**2f** was 70.8 min (flow rate = 0.7 mL/min, MeOH:H_2O = 70:30).

(17) For example: Nishimura, K.; Ono, M.; Nagaoka, Y.; Tomioka, K. *J. Am. Chem. Soc.* **1997**, *119*, 12974.

(18) Due to the sequential rule, assignment at C3 is *S* in all of compounds **3** but the absolute stereochemistry at C3 is maintained during the conversion from **2** to **3**.

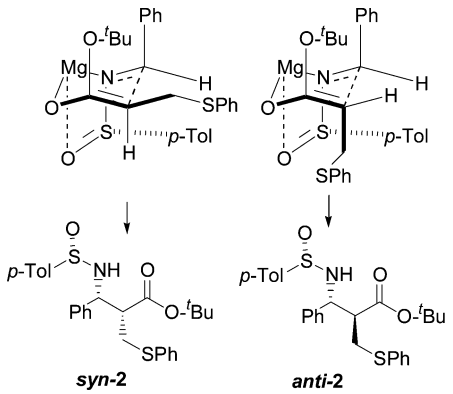
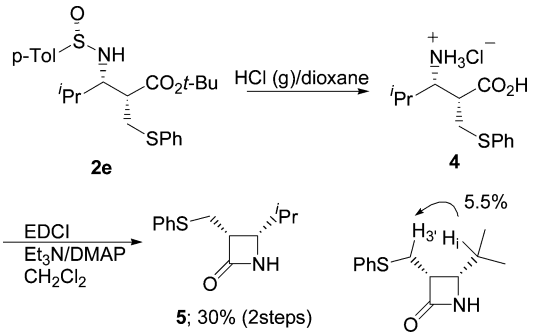


FIGURE 1. Plausible transition state of the reaction.

SCHEME 4. Removal of *N*- and *O*-Protection and Conversion to *β*-Lactam



The mechanistic origin for the present selectivity remains unclear. However, we assume that the reaction should proceed in a similar mechanism to what Davis proposed.[19] The magnesium cation should coordinate to both the oxygen atom of the sulfoxide and the nitrogen atom of the imine to fix a chelating structure that activates the imine unit toward the domino reaction as well as offer sufficient steric bias to achieve the present high diastereoselectivity in the *C*-nucleophilic attack on the C=N double bond (Figure 1). The *syn*/*anti* selectivity of the reaction, which should have depended on the *E*/*Z* formation of the enolate, ranged around 8:2 to 9:1, which was close to the *syn*/*anti* selectivity of the Michael/aldol domino reaction by lithium thiolate.[20]

The conversion of **2** to *β*-lactam was also examined. The sulfinyl group of the adduct was readily removed by acidic treatment. For example, treatment of **2e** with commercially available HCl solution in dioxane resulted in the smooth removal of both the *N*-sulfinyl group and the *O*-*tert*-butyl group to give **4**, which underwent cyclization to give *cis*-*β*-lactam **5** as a single isomer. The *syn*-configuration of **5** was supported by 5.5% of the NOE observed between H_i and $H_{3'}$ (Scheme 4).

Thus, the present method represents a useful synthesis of multifunctionalized *β*-aminoester derivatives from readily available chiral sulfinimines. The domino reaction formed a new carbon−carbon bond in a highly stereoselective manner, and installed the thio-functional group that should be useful for further transformation. The *N*-sulfinyl group was removed by acidic treatment.[21] The adducts of the present reaction were potentially useful for the conversion to the aza-Baylis−Hillman adducts. Further application of the reaction is now underway in our laboratory.

(19) Davis, F. A.; Yang, B. *J. Am. Chem. Soc.* **2005**, *127*, 8398.

(20) Kamimura, A.; Mitsudera, H.; Asano, S.; Kidera, S.; Kakehi, A. *J. Org. Chem.* **1999**, *64*, 6353.

(21) Davis reported the *N*-sulfinyl group was removed by acidic treatment and we have also succeeded in removing it from **3**. The optimized condition is now under investigation in our laboratory.

Experimental Section

Preparation of Thio-Michael/Nucleophilic Addition Domino Adducts 2: Preparation of (2*R*,3*R*)-*tert*-Butyl 3-phenyl-2-(phenylthio)methyl- 3-(*N*-*p*-toluenesulfinyl)aminopropionate [2a] (*syn*-2a). To a solution of thiophenol (0.102 mL, 1 mmol) in CH_2Cl_2 (2 mL) was added methylmagnesium bromide (0.86 mL, 1.2 mmol, 1.4 M in toluene/tetrahydrofuran (75:25)) at −50 °C. After the solution was stirred for 10 min, *tert*-butyl acrylate (0.146 mL, 1 mmol) and (*S*)-benzalsulfinimine **1a** (0.243 g, 1 mmol) were added to the mixture at −50 °C and the mixture was allowed to stir for 6 h at −50 °C. The reaction was quenched by adding saturated NH_4Cl (30 mL) and the mixture was allowed to warm to 0 °C. The mixture was extracted with EtOAc (3 × 30 mL) and the combined organic phase was washed with brine (1 × 10 mL) and dried over Na_2SO_4. After filtration, crude product was obtained by concentration. Purification by flash column chromatography (silica gel, hexane:EtOAc = 7:1) afforded **2a** in 99% yield (0.477 g, *syn*/*anti* = 81/19). White solid; mp 102−103 °C; $[\alpha]_D$ +79.8 ($CHCl_3$, *c* 0.88); ^{1}H NMR ($CDCl_3$) *δ* 1.25 (s, 9 H), 2.42 (s, 3 H), 2.81−2.99 (m, 2 H), 3.08 (dd, 1 H, *J* = 4.5, 12.9 Hz), 4.74 (t, 1 H, *J* = 6.0 Hz), 4.84 (d, 1 H, *J* = 4.9 Hz), 7.16−7.36 (m, 12 H), 7.57 (d, 2 H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) *δ* 21.3, 27.8, 32.7, 52.4, 58.9, 82.0, 125.3, 126.5, 128.1, 128.2, 128.5, 129.0, 129.7, 129.8, 135.3, 139.0, 141.6, 142.3, 172.1; IR (KBr) *ν* 3200, 2990, 1740, 1170, 1100, 1040, 690 cm^{-1}. Anal. Calcd for $C_{27}H_{31}NO_3S_2$: C, 67.33; H, 6.49; N, 2.91. Found: C, 67.15; H, 6.60; N, 2.94.

(2*S*,3*R*)-*tert*-Butyl 3-phenyl-2-(phenylthio)methyl-3-(*N*-*p*-toluenesulfinyl)aminopropionate [2a] (*anti*-2a). Yellow oil; $[\alpha]_D$ + 31.0 ($CHCl_3$, *c* 0.51); ^{1}H NMR ($CDCl_3$) *δ* 1.29 (s, 9 H), 2.42 (s, 3 H), 2.76−2.84 (m, 1 H), 3.04 (dd, 1 H, *J* = 5.9, 13.5 Hz), 3.16 (dd, 1 H, *J* = 8.4, 13.4 Hz), 4.72 (t, 1 H, *J* = 6.4 Hz), 5.41 (d, 1 H, *J* = 6.4 Hz), 7.15−7.45 (m, 12 H), 7.57 (d, 2 H, *J* = 8.4 Hz); ^{13}C NMR ($CDCl_3$) *δ* 22.1, 27.9, 33.9, 52.0, 59.0, 82.2, 12.54, 126.5, 127.1, 127.8, 128.5, 129.0, 129.6, 129.8, 135.2, 140.3, 141.4, 142.2, 171.8.

Preparation of *β*-(*N*-*p*-toluenesulfinyl)amino-α-metyleneester 3: Preparation of (3*S*)-*tert*-Butyl 2-methylene-3-phenyl-3-(*N*-*p*-toluenesulfinyl)aminopropionate [3a]. To a solution of **2a** (0.481 g, 1 mmol, *syn*/*anti* = 81/19) in CH_2Cl_2 (10 mL) at 0 °C was added *m*-CPBA (80 wt %, 0.173 g, 1 mmol), and the reaction mixture was allowed to stir at the same temperature for 30 min. The reaction was monitored by TLC analysis. After disappearance of **2a**, the reaction mixture was diluted with EtOAc and washed with saturated $NaHCO_3$ (1 × 20 mL) and dried over Na_2SO_4. Filtration followed by concentration in vacuo gave crude sulfoxide, which was solved in toluene (10 mL) and allowed to heat at 110 °C for 1 h. The progress of the reaction was carefully monitored by TLC. The mixture was concentrated in vacuo and residue was purified through flash chromatography (silica gel, hexane/ethyl acetate = 10:1 v/v) to give **3a** in 65% yield (0.241 g). White solid; mp 125−126 °C; $[\alpha]_D$ +111.8 ($CHCl_3$, *c* 1.00); ^{1}H NMR ($CDCl_3$) *δ* 1.30 (s, 9 H), 2.41 (s, 3 H), 4.80 (d, 1 H, *J* = 7.0 Hz), 5.39 (d, 1 H, *J* = 7.0 Hz), 5.67 (s, 1 H), 6.21 (s, 1 H), 7.24−7.61 (m, 9 H); ^{13}C NMR ($CDCl_3$) *δ* 21.4, 27.8, 58.0, 81.5, 125.7, 125.9, 127.5, 127.6, 128.5, 129.5, 140.0, 141.4, 141.7, 142.3, 164.6; IR (KBr) *ν* 3150, 2990, 1720, 1150, 1090 cm^{-1}. Anal. Calcd. for $C_{21}H_{25}NO_3S$: C, 67.89; H, 6.78; N, 3.77. Found: C, 67.94; H,6.71; N, 3.74.

The same treatment of *anti*-**2a** gave **3a**. $[\alpha]_D$ +116.3 ($CHCl_3$, *c* 0.99); ^{1}H NMR and ^{13}C NMR were identical with **3a**.

Preparation of (4*S*,3*R*)-4-Isopropyl-3-phenylthiomethyl-2-azetidinone [5]. Compound **2e** (0.4370 g, 0.977 mmol) was

dissolved in HCl−dioxane (4 M, 25 mL) at room temperature. The reaction mixture was allowed to stir for 6 h and disappearance of **2e** was monitored by TLC. After the reaction was completed, solvent was removed to give **4** as the residue. The residue was added to a solution of EDCI (0.7860 g, 4 mmol), Et_3N (0.75 mL), and DMAP (0.01 g) in CH_2Cl_2 (100 mL) and the resulting solution was allowed to stir for 72 h. The reaction mixture was poured into dilute HCl (40 mL) and the mixture was extracted with EtOAc (3 × 50 mL). The organic phases were combined, washed with $NaHCO_3$ aq (30 mL), and dried over Na_2SO_4. After filtration, the organic solution was concentrated in vacuo. The residue was purified through flash chromatography (silica gel, hexane−EtOAc 10:1, 5:1, then 3:1 v/v) and the desired β-lactam **5** was isolated in 30% yield (69.5 mg). White solid; mp 104−105 °C; $[\alpha]_D$ +16.8 ($CHCl_3$, *c* 0.25); ^{1}H NMR ($CDCl_3$) δ 0.97 (d, 3 H, J = 6.4 Hz), 1.03 (d, 3 H, J = 6.5 Hz), 1.78−1.92 (m 1 H), 3.16 (dd, 1 H, J = 6.9, 13.3 Hz), 3.31−3.48 (m, 3 H), 6.00 (s, 1 H), 7.18−7.41 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 19.7, 19.8, 28.6, 29.0, 52.0, 59.1, 126.5, 129.1, 129.7, 135.6, 169.4. Anal. Calcd for $C_{13}H_{17}NOS$: C, 66.34; H, 7.28; N, 5.95. Found: C, 66.23; H, 7.22; N, 6.12.

Supporting Information Available: Preparation of aliphatic chiral sulfinimine **1**, physical data for compounds *syn*-**2b**, *syn*-**2c**, *syn*-**2d**, *syn*-**2e**, *syn*-**2f**, *syn*-**2g**, *syn*-**2h**, **3b**, **3c**, **3d**, **3e**, **3e**, **3f**, and **3g**, ^{1}H NMR and ^{13}C NMR spectra for compounds *syn*-**2a**, *anti*-**2a**, *syn*-**2b**, *syn*-**2c**, *syn*-**2d**, *syn*-**2e**, *syn*-**2f**, *syn*-**2g**, *syn*-**2h**, **3a**, **3b**, **3c**, **3d**, **3e**, **3e**, **3f**, **3g**, and **5**, and X-ray crystallographic data for compounds *syn*-**2a** and *syn*-**2e**. This material is available free of charge via the Internet at http://pubs.acs.org.

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