Masaatsu Adachi, Eiji Yamauchi, Takema Komada, Minoru Isobe\*

Laboratory of Organic Chemistry, School of Bioagricultural Sciences, Nagoya University, Chikusa, Nagoya 464-8601, Japan Fax +81(52)7894111; E-mail: isobem@ff.iij4u.or.jp

Received 22 January 2009

**Abstract:** We have demonstrated a new cyclobutane ring formation from the *trans*-1,2-disubstituted epoxides through intramolecular carbanion opening process. In this reaction, the nucleophilic carbanion is generated not via  $\alpha$ -proton abstraction but via heteroconjugate addition. These studies indicate that the different configuration of each epoxide (*syn* and *anti*) do not affect its reactivity and the reaction velocity in the cyclization step, providing multifunctionalized cyclobutanes in a regio- and stereospecific manner.

Key words: heteroconjugate addition, sulfonyl carbanion, epoxides, cyclization, cyclobutanes

Cyclobutanes are an important element in many natural products with intriguing physical, conformational, and biological activities.<sup>1</sup> Additionally, cyclobutane derivatives are potentially interesting intermediates for constructing a diverse array of compounds through transformations such as ring openings and ring expansions.<sup>2</sup> However, the construction of cyclobutanes is one of the most challenging synthetic problems in cycloaliphatic chemistry - primarily due to the inherent ring strain of the cyclobutane moiety. The standard strategy for constructing fourmembered cycloaliphatic rings has remained, for a century, an inter- or intramolecular [2+2]-photochemical cycloaddition between two alkenes, since its discover by Ciamician in 1908.<sup>3,4</sup> Unfortunately, the resulting regioand stereochemistry has proven difficult to control, and often dependent on various factors such as reaction solvent and temperature.<sup>5</sup> In addition, thermal [2+2] cycloadditions proceed inefficiently unless ketenes or haloketens with highly electrophilicity are chosen as substrates.<sup>6</sup> To date, alternative synthetic strategies for the formation of four-membered rings include an intramolecular cyclization,<sup>7</sup> a rearrangement of an oxonium ylide,<sup>8</sup> 'Cp<sub>2</sub>Zr' or SmI<sub>2</sub>/Pd(0)-mediated ring contraction of a vinylfuranoside,<sup>9</sup> and aluminum- or cobalt-mediated ring contraction of a dihydropyran.<sup>10,11</sup>

In 1974, Stork reported the first example of intramolecular nucleophilic opening of epoxides 1 with a carbanion stabilized by nitrile group to provide cyclobutane 3 but not cyclopentane 4.12 This reaction was further examined with various kinds of epoxides to culminate in regioselectivity as that the cis-1,2-disubstituted epoxides provided predominantly the cyclobutane products rather than cyclopentene derivatives.<sup>13</sup> Epoxide opening by 1,3dithiane anion is an alternative.<sup>14</sup> Many other examples of ionic intramolecular cyclobutane ring cyclization were limited to have little substituents on this ring. We found that similar epoxide opening took place with a carbanion 6 stabilized by phenylsulfonyl group. In this paper, we report a new cyclobutane ring formation from the trans-1,2disubstituted epoxides through intramolecular carbanionopening process. In this case, nucleophilic carbanion was generated not via  $\alpha$ -proton abstraction<sup>15</sup> but via heteroconjugate addition.



Scheme 1 Opening of epoxides with in situ generated carbanions via HCA leading to cyclobutane ring formation

*SYNLETT* 2009, No. 7, pp 1157–1161 Advanced online publication: 26.03.2009 DOI: 10.1055/s-0028-1088108; Art ID: U00609ST © Georg Thieme Verlag Stuttgart · New York During the course of our synthetic studies toward natural products, such as maytansine, okadaic acid, tautomycin, etc., we have developed an efficient synthetic methodology that we named 'heteroconjugate addition (HCA, 5 to 6)'.<sup>16,17</sup> Several more generations of the HCA have upgraded this methodology to provide either syn or anti and D- or L-isomer, which we call switching of diastereo- and enantioselectivity.<sup>18</sup> A typical stereochemical course in THF solvent results in the syn-diastereomer in 5-10 minutes at -78 °C. This intermediate carbanion 6 is stabilized by the  $\alpha$ -sulforyl group, and it is potentially changeable further to dicarbanion through Si-C to Si-O rearrangement.<sup>19</sup> Usage of this carbanion might intramolecularly open the trans-epoxide to yield cyclobutanes 7. The current concept is summarized in Scheme 1, which includes (i) the in situ generation of a carbanion with stereocontrolled introduction of a nucleophile during HCA and (ii) intramolecular epoxide opening to result in the highly functionalized cyclobutane ring formation.

The vinylsulfone-epoxide **8** was synthesized as an approximately 1:1 mixture of diastereomers of epoxides from the corresponding *trans*-olefin. Treatment of this vinylsulfone-epoxide **8** with lithium acetylide (generated from trimethylsilylacetylene and MeLi-LiBr complex) at -78 °C was followed by gradually increasing the reaction temperature to provide three kinds of products **9**, **10**, and **11** in 73% yield (in a ratio of 48:45:7), respectively (Scheme 2).<sup>20–22</sup> As a result, *syn/anti* diastereomeric epoxides were allowed to open and yield stereospecifically the corresponding products **9** and **10**, respectively.

Treatment of the *anti*-epoxide **8** (*syn/anti* = 1:23) with lithium acetylide, under the same conditions, afforded the expected cyclobutane **9** as the major product in 80% yield along with cyclobutane **11** in 3%. Also treatment of the *syn*-epoxide **8** (*syn/anti* = 2.4:1) with lithium acetylide yielded three isomers **9**, **10**, and **11** in 16%, 38%, and 5% yield, respectively. These results support the reaction pathway is stereospecific, and show that different configurations of the epoxide **8** do not affect its reactivity in, or

the reaction velocity of, the intramolecular cyclization step.

The current cyclobutane ring formation proved to be regio- and stereospecific through in situ generated  $\alpha$ -sulfonyl carbanion, which prompted us to examine more complex systems having oxymethyl group at the  $\gamma$ -position. As shown in Scheme 3, the starting allyl epoxide 12, which was reported by Marshall<sup>23</sup> from D-mannitol in eight steps in 88% ee. We employed Sharpless's improved epoxidation method.<sup>24</sup> Addition of phenylthioacetylide in the presence of BF<sub>3</sub>·OEt<sub>2</sub> afforded the adduct 13. Hydrosilylation was achieved under catalytic condition by a biscobalthexacarbonyl complex 14, which yielded regioselectively the vinylsilylsulfide 15.25 After its oxidation to the sulfonyl group, many attempts for selective epoxidation failed,<sup>26</sup> so we have converted to allylic alcohol 17 and employed Sharpless asymmetric epoxidation, which led to the epoxyalcohol **19** (Scheme 3).

Treatment of this *syn*-vinylsulfone-epoxide **19** with lithium acetylide at -78 °C, was followed by increasing the temperature to -23 °C to provide cyclobutane **20** as a single product in 45% yield.<sup>27</sup> In the homologous cases, we have prepared both *syn*- and *anti*-epoxides (**21** and **23**) under similar manner as **19**, and treated with lithium trimethylsilylacetylide to obtain the cyclobutanes (**22**, **24**) in 51% and 42% yields, respectively (Scheme 4).<sup>28</sup> Notably, formation of oxetane and tetrahydrofuran rings was not observed through nucleophilic attacks of a resulting alkoxide to the neighboring epoxide.

The reaction mechanism proposed for HCA followed by cyclobutane ring formation is depicted in Scheme 5. The relative orientation between the  $sp^2$  plane and the allylic carbon atom in **25** should be highly populated as such that the allylic hydrogen atom becomes in this plane **26** due to A-strain. This has already been well established so that the conjugate addition largely provide the *syn*-addition product **27**. This carbanion intermediate would have a linear line up at the transition state for epoxide-opening step, so



Scheme 2 Cyclobutane ring formation through HCA from vinylsulfone-epoxide 8

Synlett 2009, No. 7, 1157-1161 © Thieme Stuttgart · New York



Scheme 3 Synthesis of a homologue syn-epoxide 19

the regioselective cyclization is explained not only by Baldwin's rules, but also by the steric factors between the reactive sites. The sulfonyl carbanion can overlap with the C4–O antibonding orbital of the epoxide in the transition state, resulting in the preferential 4-*exo-tet* cyclization. Notably, no five-membered ring was observed in the product through 5-*endo-tet* cyclization. The reaction courses for the cyclization seems to be dependent on steric hindrance of the substituents due to the *syn/anti* configurational difference. In the case of both the *anti*-epoxides (path a) and the *syn*-epoxides (path b), the steric interactions between the silyl group at C-1 and the side chain of the epoxide must restrict conformational mobility and forces the difference in intramolecular cyclization as two possible transition states **28** or **31**. Additionally, gradually increasing the temperature of the reaction stimulates the cyclizations and, for the *syn*-epoxides (path b), promotes an intramolecular anionic C-to-O migration of the silyl group. In the cyclobutane **29**, it seems that the C-to-O silicon-group migration would be slower than the case of **32** due to the diastereomeric difference. Protonation of the migration product in path b happened at the  $\alpha$ -position of sulfonyl group in a way that the phenylsulfonyl group became *trans* to the neighboring alkyl side chain.



Scheme 4 Synthesis of cyclobutane derivatives 20, 22, and 24 from syn-epoxide 19, 21, and anti-epoxide 23, respectively

Synlett 2009, No. 7, 1157-1161 © Thieme Stuttgart · New York



Scheme 5 Possible mechanism of the intramolecular cyclization utilizing the *syn*- and *anti*-epoxides

In conclusion, we have demonstrated the stereocontrolled synthesis of multifunctionalized cyclobutanes through intramolecular epoxide opening by carbanion intermediates of heteroconjugate addition. These studies indicate that the different configurations of each *trans*-1,2-disubstituted epoxide do not affect its reactivity and the reaction velocity in the cyclization step, providing multifunctionalized cyclobutanes in a regio- and stereospecific manner. Application of this method to the synthesis of various cyclobutanes<sup>1</sup> is now in progress.

**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

## Acknowledgment

This work was supported by a Grant-in-Aid for Specially Promoted Research [16002007(2004-8)] from Ministry of Education, Culture, Sports, Science and Technology (MEXT), and also by a grant from Asahi Kasei Pharma Award in Synthetic Organic Chemistry, Japan (to M. A.). We are thankful to Mr. K. Yoza (Bruker AXS) for X-ray diffraction.

## **References and Notes**

- (a) Grandisol is a histrical example of pheromone having a cyclobutane moiety, see: Petschen, I.; Parrilla, A.; Bosch, M. P.; Amela, C.; Botar, A. A.; Camps, F.; Guerreo, A. *Chem. Eur. J.* **1999**, *5*, 3299. (b) Solanoeclepin may be another example having three-, four-, five-, six-, and seven-membered rings including cyclobutane moiety of fully functional groups, see: Schenk, H.; Driessen, R. A. J.; de Gelder, R.; Goubitz, K.; Nieboer, H.; Brüggemann-Rotgans, I. E. M.; Diepenhorst, P. *Croat. Chem. Acta* **1999**, *72*, 593.
- (2) For recent reviews on application of cyclobutane, see:
  (a) Bellus, D.; Ernst, B. Angew. Chem., Int. Ed. Engl. 1988, 27, 797. (b) Lee-Ruff, E.; Mladenova, G. Chem. Rev. 2003, 103, 1449. (c) Namyslo, J. C.; Kaufmann, D. E. Chem. Rev. 2003, 103, 1485. (d) Sadana, A. K.; Saini, R. K.; Billups, W. E. Chem. Rev. 2003, 103, 1539.
- (3) Ciamician, G.; Silber, P. Ber. Dtsch. Chem. Ges. **1908**, 41, 1928.
- (4) For recent reviews on [2+2] photocycloaddition, see:
  (a) Demuth, M.; Mikhail, G. Synthesis 1989, 145. (b) Bach, T. Synthesis 1998, 683.
- (5) (a) Roberts, J. D.; Sharts, C. M. Org. React. 1962, 12, 1.
  (b) Crimmins, M. T.; Reinhold, T. L. Org. React. 1993, 44, 297. (c) Arseniyadis, S.; Kyler, K. S.; Watt, D. S. Org. React. 1984, 31, 1.
- (6) (a) Vogel, E.; Müller, K. *Liebigs. Ann. Chem.* **1958**, *615*, 29.
  (b) Ghosez, L.; Montaigne, R.; Roussel, A.; Vanlierde, H.; Mollet, P. *Tetrahedron* **1971**, *27*, 615.
- (7) (a) Wenkert, E.; Bakuzis, P.; Baumgarten, R. J.; Leicht, C. L.; Schenk, H. P. J. Am. Chem. Soc. 1971, 93, 3208.
  (b) Schumacher, W.; Hanack, M. Synthesis 1981, 490.
  (c) Casadei, M. A.; Galli, C.; Mandolini, L. J. Am. Chem. Soc. 1984, 106, 1051. (d) Mori, K.; Fukamatsu, K. Liebigs Ann. Chem. 1992, 489. (e) Ihara, M.; Ohnishi, M.; Takano, M.; Makita, K.; Taniguchi, N.; Fukumoto, K. J. Am. Chem. Soc. 1992, 114, 4408. (f) Kim, D.; Kwak, Y. S.; Shin, K. J. Tetrahedron Lett. 1994, 35, 9211. (g) Tanino, K.; Aoyagi, K.; Kirihara, Y.; Ito, Y.; Miyashita, M. Tetrahedron Lett. 2005, 46, 1169.
- (8) Roskamp, E. J.; Johnson, C. R. J. Am. Chem. Soc. 1986, 108, 6062.
- (9) (a) Ito, H.; Motoki, Y.; Taguchi, T.; Hanzawa, Y. J. Am. Chem. Soc. 1993, 115, 8835. (b) Hanzawa, Y.; Ito, H.; Taguchi, T. Synlett 1995, 299. (c) Paquette, L. A.; Cunière, N. Org. Lett. 2002, 4, 1927. (d) Paquette, L. A. J. Organomet. Chem. 2006, 691, 2083. (e) Aurrecoechea, J. M.; López, B.; Arrate, M. J. Org. Chem. 2000, 65, 6493.

- (10) (a) Menicagli, R.; Malanga, C.; Lardicci, L.; Tinucci, L. *Tetrahedron Lett.* **1980**, *21*, 4525. (b) Menicagli, R.; Malanga, C.; Lardicci, L. *J. Org. Chem.* **1982**, *47*, 2288.
  (c) Meek, S. J.; Pradaux, F.; Demont, E. H.; Harrity, J. P. A. *Org. Lett.* **2006**, *8*, 5597.
- (11) For review of contraction of carbohydrate, see: Redlich, H. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1345.
- (12) Stork, G.; Cohen, J. F. J. Am. Chem. Soc. 1974, 96, 5270.
- (13) (a) Lallemand, J. Y.; Onanga, M. *Tetrahedron Lett.* 1975, *16*, 585. (b) Petschen, I.; Parrilla, A.; Bosch, M. P.; Amela, C.; Botar, A. A.; Camps, F.; Guerrero, A. *Chem. Eur. J.* 1999, *5*, 3299.
- (14) Krohn, K.; Börner, G. J. Org. Chem. 1994, 59, 6063.
- (15) Direct generation of a carbanion by proton abstraction from  $\alpha$ -sulfonyl group cannot be achieved due to the fact that an epoxidic proton would be abstracted to convert the epoxide into an enolate under these conditions.
- (16) (a) Isobe, M.; Kitamura, M.; Goto, T. J. Am. Chem. Soc. 1982, 104, 4997. (b) Kitamura, M.; Isobe, M.; Ichikawa, Y.; Goto, T. J. Am. Chem. Soc. 1984, 106, 3252. (c) Isobe, M.; Ichikawa, Y.; Bai, D.-L.; Masaki, H.; Goto, T. Tetrahedron 1987, 43, 4767. (d) Ichikawa, Y.; Tsuboi, K.; Jiang, Y.; Naganawa, A.; Isobe, M. Tetrahedron Lett. 1995, 36, 7101. (e) Tsuboi, K.; Ichikawa, Y.; Jiang, Y.; Naganawa, A.; Isobe, M. Tetrahedron 1997, 53, 5123.
- (17) For reviews on the heteroconjugate addition, see: (a) Isobe, M. Nippon Nogeikagaku Kaishi 1981, 55, 47. (b) Isobe, M. J. Synth. Org. Chem. Jpn. 1983, 41, 51. (c) Isobe, M. In Perspective in the Organic Chemistry of Sulfur; Zwanenburg, B.; Klunder, A. J. H., Eds.; Elsevier Science Publishers B. V.: Amsterdam, 1986, 209–229. (d) Isobe, M. J. Synth. Org. Chem. Jpn. 1994, 52, 968. (e) Isobe, M.; Kira, K. J. Synth. Org. Chem. Jpn. 2000, 58, 99.
- (18) Tsuboi, K.; Ichikawa, Y.; Isobe, M. Synlett 1997, 713.
- (19) Isobe, M.; Kitamura, M.; Goto, T. *Tetrahedron Lett.* 1979, 20, 3465.
- (20) The cyclobutane ring structure of **9** was confirmed by X-ray crystallographic analysis (see Supporting Information), and other structures were confirmed through NMR spectroscopy.
- (21) General Procudure for the Synthesis of Cyclobutane by Heteroconjugate Addition Trimethylsilylacetylene (5 equiv) was dissolved in THF and

Trimetnyisiiyiacetyiene (5 equiv) was dissolved in THF and cooled to -78 °C under argon atmosphere. To this cold solution was added a solution of methyllithium–lithium bromide complex (4 equiv) dropwise with stirring. This stirring was continued at -78 °C for 30 min, and then a solution of vinylsulfone-epoxide (1 equiv) in THF was added to this mixture. After stirring for further 20 min, the reaction mixture was allowed to warm to -44 °C, and the temperature was kept at -44 °C for 40 min, then at -23 °C for 1 h. The reaction mixture was poured into an ice-cooled sat. aq NH<sub>4</sub>Cl. The aqueous layer was separated and extracted with Et<sub>2</sub>O. The extracts were combined, washed with H<sub>2</sub>O and brine, and then dried over Na<sub>2</sub>SO<sub>4</sub>. The solution was concentrated in vacuo, and the residue was purified by flash column chromatography to give the corresponding cyclobutane.

(22) Cyclobutane **9**: IR (KBr):  $v_{max} = 3448, 2957, 2858, 1448, 1284, 1252, 1134, 1117, 842 cm<sup>-1</sup>. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>): <math>\delta = -0.14$  (3 H, s), 0.08 (6 H, s), 0.17 (9 H, s), 0.47 (3 H, s), 0.94 (9 H, s), 3.41 (1 H, br d, J = 8.6 Hz), 3.51 (1 H, dt, J = 11.5, 8.4 Hz), 3.63 (1 H, t, J = 9.5 Hz), 3.79 (1 H, dd,

 $J = 9.7, 5.4 \text{ Hz}), 4.27 (1 \text{ H}, d, J = 8.1 \text{ Hz}), 4.87 (1 \text{ H}, br \text{ dt}, J = 9.3, 4.8 \text{ Hz}), 4.94 (1 \text{ H}, d, J = 11.5 \text{ Hz}), 4.98 (1 \text{ H}, d, J = 4.1 \text{ Hz}), 7.26 (2 \text{ H}, t, J = 7.5 \text{ Hz}), 7.36 (1 \text{ H}, t, J = 7.5 \text{ Hz}), 7.49 (2 \text{ H}, t, J = 7.5 \text{ Hz}), 7.61-7.68 (3 \text{ H}, m), 7.91 (2 \text{ H}, d, J = 7.5 \text{ Hz}), 7.49 (2 \text{ H}, t, J = 7.5 \text{ Hz}), 7.61-7.68 (3 \text{ H}, m), 7.91 (2 \text{ H}, d, J = 7.5 \text{ Hz}), 1^3 \text{C} \text{ NMR} (150 \text{ MHz}, \text{CDCl}_3): \delta = -5.4, -5.4, -3.6, -2.6, -0.3, 18.3, 25.9, 45.8, 47.6, 57.4, 65.0, 70.9, 71.5, 91.6, 104.0, 127.8, 128.8, 129.0, 130.1, 134.0, 134.6, 135.8, 140.5. \text{ Anal. Calcd for } \text{C}_{31}\text{H}_{48}\text{O}_5\text{SSi}_3: \text{C}, 60.34; \text{H}, 7.84. \text{Found: C}, 60.34; \text{H}, 7.98.$ 

- Cyclobutane **10**: IR (KBr):  $v_{max} = 3493$ , 2956, 2172, 1428, 1247, 1147, 1023, 967, 848 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, 318 K):  $\delta = 0.09$  (6 H, s), 0.10 (9 H, s), 0.54 (3 H, s), 0.56 (3 H, s), 1.00 (9 H, s), 2.09 (1 H, d, J = 5.4 Hz), 3.08 (1 H, ddd, J = 9.4, 7.4, 2.3 Hz), 3.30 (1 H, dd, J = 9.1, 7.2 Hz), 3.37 (1 H, t, J = 9.1 Hz), 3.46 (1 H, dd, J = 10.5, 5.0 Hz), 3.56 (1 H, dd, J = 10.5, 5.0 Hz), 4.30 (1 H, td, J = 5.0, 2.3 Hz), 4.37 (1 H, td, J = 7.2, 5.5 Hz), 7.06–7.20 (3 H, m), 7.30–7.40 (3 H, m), 7.71–7.76 (2 H, m), 7.87–7.92 (2 H, m). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta = -5.4$ , -5.4, -1.7, -0.7, -0.1, 18.6, 26.1, 37.2, 48.2, 56.1, 66.5, 68.4, 71.6, 87.7, 103.8, 128.7, 128.8, 129.1, 129.9, 133.3, 133.9, 138.4, 139.6. Anal. Calcd for C<sub>31</sub>H<sub>48</sub>O<sub>5</sub>SSi<sub>3</sub>: C, 60.34; H, 7.84. Found: C, 60.34; H, 7.96.
- (23) Marshall, J. A.; Trometer, J. D.; Cleary, D. G. *Tetrahedron* 1989, 45, 391.
- (24) Kolb, H. C.; Sharpless, K. B. Tetrahedron 1992, 48, 10515.
- (25) For hydrosilylation with a catalytic amount of Co complex, see: (a) Isobe, M.; Nishizawa, R.; Nishikawa, T.; Yoza, K. *Tetrahedron Lett.* **1999**, *40*, 6972. (b) Liu, T.-Z.; Kirschbaum, B.; Isobe, M. *Synlett* **2000**, 587. (c) Liu, T.-Z.; Isobe, M. *Tetrahedron* **2000**, *56*, 5391. (d) Baba, T.; Isobe, M. *Synlett* **2003**, 547. (e) Baba, T.; Huang, G.; Isobe, M. *Tetrahedron* **2003**, *59*, 6851.
- (26) Isobe, M.; Kitamura, M.; Mio, S.; Goto, T. *Tetrahedron Lett.* 1982, 23, 221.
- (27) Cyclobutane **20**:  $[a]_D^{2^7}-14.5$  (*c* 1.15, CHCl<sub>3</sub>). IR (KBr):  $v_{max}$ = 3525, 3031, 2172, 1305, 1148 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = -0.02 (9 H, s), 0.40 (3 H, s), 0.41 (3 H, s), 2.61 (1 H, m), 2.91 (1 H, td, *J* = 9.0, 3.0 Hz), 2.95 (1 H, t, *J* = 9.0 Hz), 3.38 (2 H, d, *J* = 6.0 Hz), 3.48 (1 H, t, *J* = 9.0 Hz), 3.57 (1 H, dd, *J* = 11.5, 6.5 Hz), 3.64 (1 H, dd, *J* = 11.5, 6.5 Hz), 3.98 (1 H, td, *J* = 6.0, 3.0 Hz), 4.38 (1 H, d, *J* = 11.5 Hz), 4.44 (1 H, d, *J* = 11.5 Hz), 7.25-7.76 (15 H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = -1.4, -1.1, -0.1, 27.1, 39.6, 40.8, 60.5, 64.1, 70.5, 71.9, 73.4, 87.2, 104.0, 127.9, 127.9, 127.9, 128.4, 128.4, 129.1, 129.7, 133.5, 133.6, 137.4, 137.7, 138.3. Anal. Calcd for C<sub>33</sub>H<sub>42</sub>O<sub>5</sub>SSi<sub>2</sub>: C, 65.32; H, 6.98. Found: C, 65.32; H, 7.04.
- (28) Cyclobutane **24**:  $[\alpha]_D^{22}$  -34.2 (*c* 0.56, CHCl<sub>3</sub>). IR (KBr):  $v_{max} = 3358$ , 3066, 3030, 1287, 1136 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 0.03$  (9 H, s), 0.55–0.66 (2 H, m), 0.72– 0.84 (4 H, m), 0.89 (9 H, t, *J* = 7.5 Hz), 2.77 (1 H, tdd, *J* = 10.5, 7.5, 2.5 Hz), 3.26 (1 H, ddd, *J* = 10.5, 6.0, 1.0 Hz), 3.69 (1 H, dd, *J* = 12.5, 2.5 Hz), 3.73 (1 H, dd, *J* = 10.0, 5.0 Hz), 3.83 (1 H, dd, *J* = 10.0, 5.0 Hz), 3.86 (1 H, dd, *J* = 12.5, 7.5 Hz), 4.20 (1 H, dd, *J* = 11.5 Hz), 4.98 (1 H, dd, *J* = 11.5 Hz), 4.61 (1 H, d, *J* = 11.5 Hz), 4.98 (1 H, td, *J* = 6.0, 3.0 Hz), 7.28–7.39 (5 H, m), 7.48–7.54 (2 H, m), 7.61–7.67 (1 H, m), 7.92–7.96 (2 H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta = -0.4$ , 3.7, 8.2, 32.5, 43.2, 46.6, 60.7, 63.1, 67.6, 72.5, 73.2, 90.2, 104.8, 127.8, 127.9, 128.4, 128.9, 129.1, 133.8, 137.8, 140.9. Anal. Calcd for C<sub>31</sub>H<sub>46</sub>O<sub>5</sub>SSi<sub>2</sub>: C, 63.44; H, 7.90. Found: C, 63.44; H, 7.97.

Synlett 2009, No. 7, 1157–1161 © Thieme Stuttgart · New York

Copyright of Synlett is the property of Georg Thieme Verlag Stuttgart and its content may not be copied or emailed to multiple sites or posted to a listserv without the copyright holder's express written permission. However, users may print, download, or email articles for individual use.