Pergamon

Tetrahedron Letters 43 (2002) 9105–9109

TETRAHEDRON LETTERS

Lewis acid-mediated cyclization of allenyl-aldehyde dimethyl acetals: synthesis of *cis*- and *trans*-2-haloalkenylcycloalkyl methyl ethers

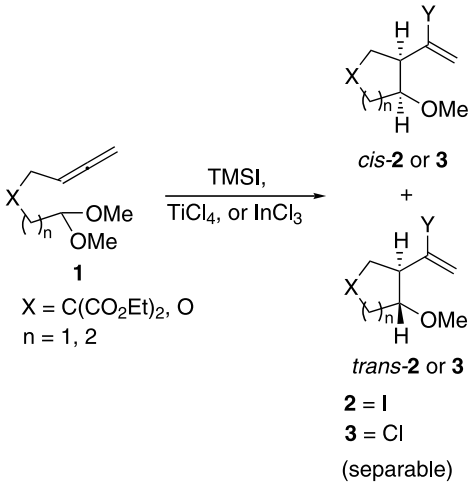
Suk-Ku Kang,[a,*] Young-Mook Kim,[a] Young-Hwan Ha,[a] Chan-Mo Yu,[a] Heejung Yang[b] and Yoongho Lim[b,*]

[a]*Department of Chemistry, Lab for Metal-Catalyzed Reactions, Sungkyunkwan University, Suwon 440-746, Republic of Korea*
[b]*Bio/Molecular Informatics Center and Department of Applied Biology and Chemistry Konkuk University, Seoul 143-701, Republic of Korea*

Received 24 September 2002; revised 8 October 2002; accepted 10 October 2002

Abstract—Treatment of allenyl-aldehyde dimethyl acetals with iodotrimethylsilane, titanium tetrachloride, and indium trichloride afforded a mixture of separable *cis*- and *trans*-2-haloalkenyl substituted 2-haloalkenylcycloalkyl methyl ethers by intramolecular nucleophilic attack of allene moiety to the oxonium ion generated by the reaction of TMSI, $TiCl_4$, or $InCl_3$ to dimethyl acetal moiety.

The development of new methods for the synthesis of cyclic compounds is quite important in organic chemistry since there are many biologically active compounds having a cyclic structure. The Lewis acid-promoted carbon–carbon bond forming cyclization of alkenyl-aldehyde acetals to prepare carbocycles and heterocycles is well documented,[1] particularly through the pioneering and extensive investigation of Johnson's mono- and polyene cyclization of ene acetals.[2] However few examples are known for the intramolecular Lewis acid-mediated cyclization of alkynyl-aldehyde acetals with direct participation of alkyne moiety as a nucleophile. Overman et al.[3a] reported $SnCl_4$-promoted involvement of alkynyl-aldehyde acetals with concomitant ring expansion to form the substituted cyclopentanol methyl ethers. Thomspon et al.[3b] report $TiCl_4$-mediated cyclization of MEM acetals derived from 2-ethylcyclohexanols to give chlorovinyl-substituted bicyclic ether. Recently, Ham et al.[3c] reported $TiCl_4$-mediated Prins-type cyclization reaction of β-hydroxy alkynyl-aldehyde acetals to give 1-chlorocyclohexene derivatives with high diastereoselectivity. Alternatively, Oshima et al.[3d] reported Lewis acid-mediated cyclization of 6-alkyl-aldehyde acetals to form six-membered iodo-substituted *exo*-vinyl ethers using TMSI as a Lewis acid. To the best of our knowledge Lewis acid-mediated cyclization reactions of allenyl-aldehyde acetals have not be described previously. In our ongoing studies, aimed at developing the utility of allenes in organic synthesis,[4] we found that Lewis acid-mediated cyclization reactions of tethered allenyl-aldehyde dimethyl acetals serve as the precursors of 2-haloalkenyl substituted cycloalkanols utilizing TMSI,[5] $TiCl_4$, or $InCl_3$ as Lewis acid (Scheme 1).



Scheme 1.

* Corresponding authors. Tel.: +82-31-290-7064; fax: +82-31-290-7079; e-mail: skkang@chem.skku.ac.kr

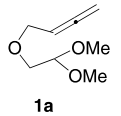
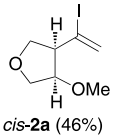
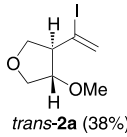
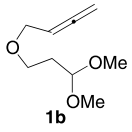
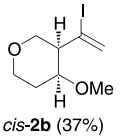
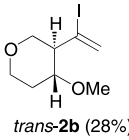
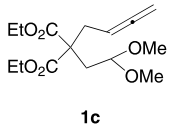
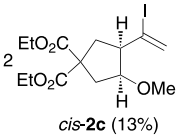
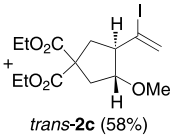
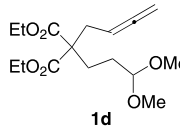
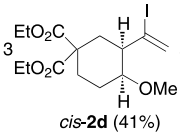
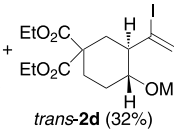
0040-4039/02/$ - see front matter
PII: S0040-4039(02)02241-4

The results of TMSI-induced cyclization of allenyl-aldehyde dimethyl acetals are summarized in Table 1.

To find optimum conditions, ether-linked allenyl-aldehyde dimethylacetal **1a** was used as a model compound and a series of experiments was performed with Lewis acids TMSI, TMSOTf, TMSCl/NaI, TMSCl/LiI, and allyltrimethylsilane/I_2. Among the Lewis acids TMSI gave the best results. The other Lewis acids did not work. Of the solvents tested toluene, THF, CH_3CN, HMPA, and $CHCl_3$, toluene was the best solvent. The allenyl-aldehyde dimethyl acetal **1a** reacted with TMSI (2.2 equiv.) in toluene at −78°C to rt for 14 h to give a separable mixture of *cis*-**2a**[6] (46%) and *trans*-**2a**[6] (38%) in 84% total yield (entry 1, Table 1). The stereochemistry was unambiguously determined by comparing the results of a NOESY spectrum analysis. In the NOESY spectra of *cis*-**2a** and *trans*-**2a**, NOE crosspeaks between the protons at ring junctions and the vinyl protons were investigated. In the spectrum of *trans*-**2a**, crosspeaks were observed between the protons at ring junctions and one of the vinyl protons. However, in the case of *cis*-**2a** a crosspeak was not observed between the proton adjacent to the methoxy group and the vinyl protons, which confirmed that there were isomer. This cyclization was extended to synthesize six-membered cyclohexanol derivatives, and under the same conditions, the reaction of **1b** with TMSI gave *cis*-**2b** (37%) and *trans*-**2b** (28%) in 65% total yield (entry 2). The cyclization was also applied to diethyl malonate-branched allenyl-aldehyde dimethyl acetal **1c**. When the compound **1c** was treated with TMSI in toluene separable isomers *cis*-**2c** and *trans*-**2c**, were isolated in 71% yield. For allenyl-aldehyde dimethyl acetal **1d** the cyclohexanol ethers *cis*-**2d** and *trans*-**2d** were afforded (entry 4). The *cis*- and *trans*-stereochemistry of *cis*-**2d** and *trans*-**2d** was confirmed by the comparison of the coupling constants ($J=3.3$ Hz for *cis* and $J=9.7$ Hz for *trans*) at ring juncture.

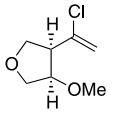
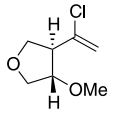
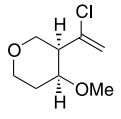
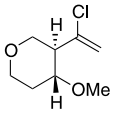
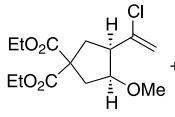
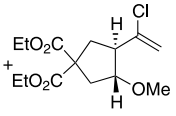
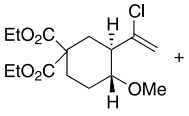
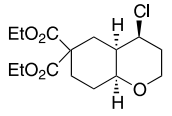
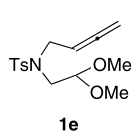
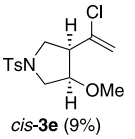
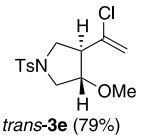
We have employed $TiCl_4$ (1.1 equiv.) as the Lewis acid for the cyclization of allenyl-aldehyde dimethyl acetals.[3] In contrast to TMSI, the reaction did not proceed at −78°C but at 0°C the reaction went to completion without any starting material remained for 3 h. The use of $SnCl_4$ did not give the product. The results of $TiCl_4$-mediated cyclization of allenyl-aldehyde dimethyl acetals are summarized in Table 2. The treatment of the acetal **1a** with $TiCl_4$ (1.1 equiv.) at 0°C for 3 h afforded a mixture of separable *cis*-**3a**[6] (70%) together with *trans*-**3a**[6] (19%) in 89% total yield (entry 1, Table 2). Under the same conditions the ether-linked allenyl-aldehyde dimethyl acetal **1b** reacted with $TiCl_4$ to afford *cis*-**3b** (47%) and *trans*-**3b** (32%) in 79% yield (entry 2, Table 2). The stereochemistry was determined by the coupling constant of the two protons at ring junction ($J=2.8$ Hz for *cis* and $J=9.1$ Hz for *trans*). With the malonate-branched allenyl-aldehyde dimethyl acetal **1c**, the *cis*-**3c** (24%) and *trans*-**3c** (65%) were afforded (entry 3). The *cis*-**3c** and *trans*-**3c** was deduced by 1D-NOESY experiments together with the calculation of the distance between the protons at ring junction (2.20 Å for *cis* and 3.15 Å for *trans*) by NOE values and molecular modeling calculation. However,

Table 1. TMSI-induced cyclization of allenyl-aldehyde dimethyl acetals[a]

Entry	Substrate	Time (h)	Product	Total Yields(%)[b]
1	 **1a**	14	 *cis*-**2a** (46%) +  *trans*-**2a** (38%)	84
2	 **1b**	18	 *cis*-**2b** (37%) +  *trans*-**2b** (28%)	65
3	 **1c**	12	 *cis*-**2c** (13%) +  *trans*-**2c** (58%)	71
4	 **1d**	13	 *cis*-**2d** (41%) +  *trans*-**2d** (32%)	73

[a]The reactions were run with allenyl - aldehyde dimethyl acetals (1.0 equiv) and TMSI (2.2 equiv) in toluene at -78 °C —rt. [b]The yields are isolated yields.

Table 2. $TiCl_4$-induced cyclization of allenyl-aldehyde dimethyl acetals[a]

Entry	Substrate	Time (h)	Product	Total Yields(%)[b]
1	**1a**	3	 *cis*-**3a** (70%) +  *trans*-**3a** (19%)	89
2	**1b**	3	 *cis*-**3b** (47%) +  *trans*-**3b** (32%)	79
3	**1c**	2	 *cis*-**3c** (24%) +  *trans*-**3c** (65%)	89
4	**1d**	2	 *trans*-**3d** (28%) +  **4** (52%)	80
5	 **1e**	2	 *cis*-**3e** (9%) +  *trans*-**3e** (79%)	88

[a]The reactions were run with allenyl-aldehyde dimethyl acetals (1.0 equiv) and $TiCl_4$ (1.1 equiv) in CH_2Cl_2 at 0 °C. [b]The yields are isolated yields.

the reaction of **1d** under the same conditions gave *trans*-**3d** (28%) and unexpected bicyclic pyran **4**[6] (52%) (entry 4). For this particular case, presumably the formation of bicyclic pyran **4** could be ascribed to the cyclization of *cis*-**3d** initially formed under the reaction conditions. The proposed reaction mechanism is shown in Scheme 2.

Finally nitrogen-linked allenyl-aldehyde dimethyl acetal **1e** gave a mixture of separable *cis*-**3e** (9%) and *trans*-**3e** (79%) in 88% yield (entry 5).

The cyclization process can be extended to $InCl_3$[7,8] as Lewis acid and refluxing conditions in CH_2Cl_2 are needed to produce the cyclized products. The results are summarized in Table 3. The allenyl-aldehyde dimethyl acetal **1a** reacted with $InCl_3$ (2.2 equiv.) in CH_2Cl_2 at reflux for 3 h to afforded *cis*-**3a** (59%) and *trans*-**3a** (18%) in 77% total yield (entry 1, Table 3). However, treatment of **1d** with $InCl_3$ (1.1 equiv.) gave the *trans*-**3a** (35%) along with the bicyclic pyran **4** (32%) (entry 4), presumably formed from the cyclization reaction of *cis*-**3d**. The structure of the pyran **4** was determined by a 2D-NOESY technique, coupled with molecular mechanics calculations. It is notable that *N*-sulfonamide substituted tethered allenyl-aldehyde dimethyl acetal **1e** gave a mixture of separable *cis*-**3e** (6%) and *trans*-**3e** (45%) (entry 5).

Although the exact mechanism remains unclear, the pathway shown in Scheme 3 is plausible. Iodotrimethylsilane abstracts the methoxy acetal **1** to give the oxonium intermediate **A** and then intramolecular nucleophilic attack by the allene moiety would occur. The resulting intermediate vinyl carbocation **B** will be trapped by the halides to afford **2** or **3**.

In summary TMSI-, $TiCl_4$-, and $InCl_3$-induced cyclization of allenyl-aldehyde dimethyl acetals to form readily separable *cis*- and *trans*-halovinyl substituted homoallylic cyclopentanols and cyclohexanols mono methyl ethers was achieved.

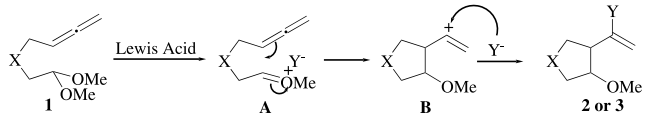
Supplementary material

The characterization for **1a–e**, **2b–d**, **3b**, **3c**, **3e**, NOESY spectrum analysis coupled with molecular dynamics calculation data and NOE experiments for *cis*-**2a**, *trans*-**2a**, *cis*-**2d**, *trans*-**2d**, *cis*-**3b**, *trans*-**3b**, *cis*-**3c**, *trans*-**3c**, *trans*-**3d** and **4**.

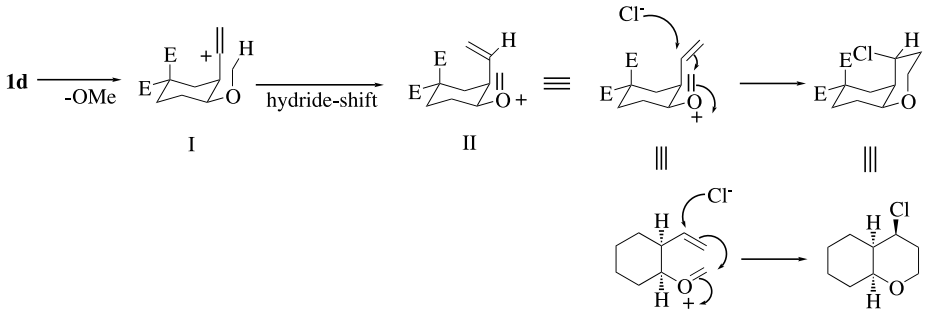
Table 3. $InCl_3$-induced cyclization of allenyl-aldehyde dimethyl acetals[a]

Entry	Substrate	Time (h)	Product	Total Yields(%)[b]
1	**1a**[c]	3	*cis*-**3a** (59%) + *trans*-**3a** (18%)	77
2	**1b**[c]	6	*cis*-**3b** (38%) + *trans*-**3b** (21%)	59
3	**1c**	4	*cis*-**3c** (33%) + *trans*-**3c** (54%)	87
4	**1d**	5	*trans*-**3d** (35%) + **4** (32%)	67
5	**1e**[c]	2	*cis*-**3e** (6%) + *trans*-**3e** (45%)	51

[a]The reactions were run with allenyl - aldehyde dimethyl acetals (1.0 equiv) and $InCl_3$ (1.1 equiv) in CH_2Cl_2 at reflux. [b]The yields are isolated yields.
[c]The reactions were carried out by using $InCl_3$ (2.2 equiv).



Scheme 3.



Scheme 2.

Acknowledgements

This work was supported by National Research Laboratory Project administrated and by the Ministry of Science and Technology, KOSEF-CMDS, and Korea Health 21 R & D Project, Ministry of Health & Welfare (01-PJ2-PG6-01NA-002). Y.-M. Kim thanks the financial support by BK21 program.

References

1. (a) For a review, see: Mukaiyama, T.; Murakami, M. *Synthesis* **1987**, 1043–1053; (b) Trost, B. M.; Chem, D. W. C. *J. Am. Chem. Soc.* **1996**, *118*, 12541–12554; (c) Trost, B. M.; Lee, D. C. *J. Am. Chem. Soc.* **1988**, *110*, 6556–6558; (d) Sammakia, T.; Smith, R. S. *J. Am. Chem. Soc.* **1994**, *116*, 7915–7916; (e) Denmark, S. E.; Almstead, N. G. *J. Am. Chem. Soc.* **1991**, *113*, 8089–8110.
2. (a) For a review, see: Johnson, W. S. *Bioorg. Chem.* **1976**, *5*, 51–98; (b) Johnson, W. S.; Ward, C. E.; Book, S. G.; Gravestock, M. B.; Markazich, R. L.; McCarry, B. E.; Okorie, D. A.; Parry, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 88–98; (c) Johnson, W. S.; Plummer, M. S.; Reddy, S. P.; Bartlett, W. R. *J. Am. Chem. Soc.* **1993**, *115*, 515–521.
3. (a) Johnson, T. O.; Overman, L. E. *Tetrahedron Lett.* **1991**, *32*, 7361–7364; (b) Melany, M. L.; Lock, G. A.; Thomspon, D. W. *J. Org Chem.* **1985**, *50*, 3925–3927; (c) Kim, Y.-H.; Lee, K.-Y.; Oh, C.-Y.; Yang, J.-G.; Ham, W.-H. *Tetrahedron Lett.* **2002**, *43*, 837–841; (d) Takami, K.; Yorimitsu, H.; Shinokubo, H.; Matsubara, S.; Oshima, K. *Synlett* **2001**, 293–295.
4. (a) Kang, S.-K.; Ha, Y.-H.; Ko, B.-S.; Lim, Y.; Jung, J. *Angew. Chem., Int. Ed.* **2002**, *41*, 343–345; (b) Ha, Y.-H.; Kang, S.-K. *Org. Lett.* **2002**, *4*, 1143–1146; (c) Kang, S.-K.; Kim, K.-J.; Hong, Y.-T. *Angew. Chem., Int. Ed.* **2002**, *41*, 1584–1586; (d) Kang, S.-K.; Lee, S.-W.; Jung, J.; Lim, Y. *J. Org. Chem.* **2002**, *67*, 4376–4379.
5. *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: Chichester, 1995; Vol. 4, pp. 2854–2860.
6. *Typical procedure*: To a stirred solution of allenyl-aldehyde dimethyl acetal **1a** (100 mg, 0.63 mmol) in dry toluene (3.0 mL) at −78°C was added iodotrimethylsilane (0.5 M in hexane, 1.40 mL, 0.70 mmol) under an argon atmosphere for 1 h. The reaction mixture was warmed to room temperature and stirred for 12 h and then cooled to −78°C and then iodotrimethylsilane (0.5 M in hexane, 1.4 mL, 0.70 mmol) was added for 1 h warmed to room temperature, stirred for 2 h. The mixture was quenched with saturated $NaHCO_3$ (20 mL), extracted with diethyl ether (3×20 mL), dried over $MgSO_4$, and evaporated in vacuo. The crude product was separated by SiO_2 column chromatography (EtOAc/hexane = 1:10) to afford *cis*-**2a** (74 mg, 46%) and *trans*-**2a** (61 mg, 38%) as colorless oils. *cis*-**2a**: TLC, SiO_2, EtOAc/hexanes 1:10, $R_f = 0.38$; IR (neat): ν 2930, 1461, 1111, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 2.93 (m, 1H, $J = 1$, 2.1, 2.7, 5.3, 7.2 Hz), 3.38 (s, 3H), 3.74 (ddd, 1H, $J = 0.7$, 5.3, 9.2 Hz), 3.79 (ddd, 1H, $J = 0.6$, 2.1, 6.9 Hz), 3.97 (ddd, 1H, $J = 0.6$, 2.8, 6.7 Hz), 3.96 (m, 1H), 3.99 (ddd, 1H, $J = 0.7$, 2.7, 11.0 Hz), 5.86 (d, 1H, $J = 1.9$ Hz), 6.25 (dd, 1H, $J = 1.0$, 1.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 127.6, 111.2, 86.6, 72.7, 72.6, 58.6, 57.7; HRMS calcd for $C_7H_{11}IO_2$: 253.9804, found: 253.9807.
trans-**2a**: TLC, SiO_2, EtOAc/hexanes 1:10, $R_f = 0.30$; IR (neat): ν 2927, 1452, 1065, 665 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.12 (m, 1H, $J = 1.6$, 1.8, 4.7, 7.3, 10.3 Hz), 3.41 (s, 3H), 3.93 (dd, 1H, $J = 0.7$, 7.8, 10.3 Hz), 3.94 (dd, 1H, $J = 4.1$, 10.2 Hz), 4.00 (m, 1H), 4.01 (dd, 1H, $J = 0.9$, 10.2 Hz), 4.01 (dd, 1H, $J = 7.3$, 7.8 Hz), 5.93 (dd, 1H, $J = 1.8$, 2.3 Hz), 6.00 (dd, 1H, $J = 1.6$, 2.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 127.2, 103.5, 82.7, 71.8, 68.4, 58.0, 57.4; HRMS calcd for $C_7H_{11}IO_2$: 253.9804, found: 253.9809.
Typical procedure: A solution of allenyl-aldehyde dimethyl acetal **1a** (100 mg, 0.63 mmol) in CH_2Cl_2 was stirred and added $TiCl_4$ (0.08 mL, 0.69 mmol) at 0°C. The reaction mixture was sttirred at 0°C for 3 h and quenched with saturated $NaHCO_3$. The organic layer was separated and the aqueous phase was extracted with diethyl ether (3×20 mL). The combined extracts were dried $MgSO_4$ and the solvent was evaporated in vacuo. The crude product was purified by SiO_2 column chromatography (EtOAc/hexane = 1:15) to afford *cis*-**3a** (72 mg, 70%) and *trans*-**3a** (20 mg, 19%) as colorless oils.
cis-**3a**: TLC, SiO_2, EtOAc/hexane 1:7, $R_f = 0.31$; IR (neat): ν 1632, 1461, 1099 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.32 (m, 1H), 3.38 (s, 3H), 3.83 (m, 2H), 3.93 (dd, 1H, $J = 5.3$, 9.9 Hz), 4.06 (m, 2H), 5.27 (d, 1H, 2.8 Hz), 5.35 (dd, 1H, $J = 0.6$, 1.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.4, 114.1, 85.3, 72.9, 70.9, 57.6, 54.6; HRMS calcd for $C_7H_{11}ClO_2$: 162.0448, found: 162.0448.
trans-**3a**: TLC, SiO_2, EtOAc/hexane 1:7, $R_f = 0.23$; IR (neat): ν 1631, 1462, 1092 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 3.08 (m, 1H), 3.39 (s, 3H), 3.91 (dd, 1H, $J = 7.9$, 10.5 Hz), 3.95 (d, 1H, $J = 4.1$ Hz), 3.97 (d, 1H, $J = 1.8$ Hz), 4.04 (m, 1H), 4.06 (m, 1H), 5.13 (dd, 1H, $J = 1.8$, 2.3 Hz), 5.38 (dd, 1H, $J = 1.2$, 2.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.6, 114.5, 81.7, 72.7, 69.0, 58.2, 52.9; HRMS calcd for $C_7H_{11}ClO_2$: 162.0448, found: 162.0449.
trans-**3d**: TLC, SiO_2, EtOAc/hexane 1:5, $R_f = 0.37$; IR (neat): ν 1733, 1374, 1262 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.23 (t, 3H, $J = 7.1$ Hz), 1.27 (t, 3H, $J = 7.1$ Hz), 1.27 (m, 1H), 1.77 (ddd, 1H, $J = 3.7$, 14.0, 14.0 Hz), 1.91 (dd, 1H, $J = 12.6$, 13.7 Hz), 2.17 (ddd, 1H, $J = 3.7$, 7.9, 13.2 Hz), 2.37 (m, 1H), 2.44 (dddd, 1H, $J = 0.6$, 3.6, 6.6, 14.0 Hz), 2.62 (ddd, 1H, $J = 3.7$, 10.2, 12.6 Hz), 3.25 (ddd, 1H, $J = 4.4$, 10.2, 11.0 Hz), 3.37 (s, 3H), 4.16 (m, 2H), 4.24 (m, 2H), 5.26 (dd, 1H, $J = 0.7$, 1.3 Hz), 5.30 (dd, 1H, $J = 0.4$, 1.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 171.8, 170.8, 143.8, 114.7, 78.7, 62.0, 61.8, 57.3, 54.8, 49.7, 35.3, 29.8, 27.1, 14.5, 14.4; HRMS calcd for $C_{15}H_{23}ClO_5$: 318.1234, found: 318.1232.
Compound **4**: TLC, SiO_2, EtOAc/hexane 1:5, $R_f = 0.26$; IR (neat): ν 1726, 1245, 732 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 1.25 (t, 3H, $J = 7.1$), 1.26 (t, 3H, $J = 7.1$), 1.66 (dddd, 1H, $J = 3.0$, 4.2, 14.3, 14.3), 1.81 (m, 1H), 1.89 (m, 1H), 1.94 (md, 1H, $J = 4.2$), 2.02 (m, 1H), 2.04 (m, 1H), 2.13 (md, 1H, $J = 5.2$), 2.15 (m, 1H), 2.48 (m, 1H), 3.45 (md, 1H, $J = 2.5$), 3.46 (m, 1H), 4.03 (ddd, 1H, $J = 1.3$, 5.2, 11.8), 4.17 (m, 2H), 4.20 (m, 2H), 4.23 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 172.2, 171.1, 74.6, 67.7, 61.7, 61.4, 60.1, 54.7, 39.5, 31.5, 28.5, 25.6, 25.1, 14.30, 14.26; HRMS calcd for $C_{15}H_{23}ClO_5$: 318.1234, found: 318.1236.

7. Recently, indium(III) chloride has emerged a powerful Lewis acid catalyst in a variety of organic transformations. For reviews, see: (a) Li, C.-J.; Chan, T.-H. *Tetrahedron* **1999**, *55*, 11149–11176; (b) Ranu, B. C. *Eur. J. Org. Chem.* **2000**, 2347–2356; (c) Chauhan, K. K.; Frost, C. G. *J. Chem. Soc. Perkin Trans. 1* **2000**, 3015–3019.

8. For $InCl_3$-mediated reactions, see: (a) Yang, X.-F.; Mague, J. T.; Li, C.-J. *J. Org. Chem.* **2001**, *66*, 739–747; (b) Yang, J.; Li, C.-J. *Synlett* **1999**, 717–718; (c) Li, J.; Li, C.-J. *Heterocycles* **2000**, *53*, 1691–1695; (d) Yang, J.; Viswanathan, G. S.; Li, C.-J. *Tetrahedron Lett.* **1999**, *40*, 1627–1630; (e) Viswanathan, G. S.; Yang, J.; Li, C.-J. *Org. Lett.* **1999**, *1*, 993–995.