Organic LETTERS

Letter

pubs.acs.org/OrgLett

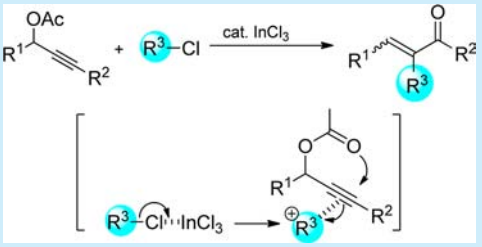
Indium Chloride Catalyzed Alkylative Rearrangement of Propargylic Acetates Using Alkyl Chlorides, Alcohols, and Acetates: Facile Synthesis of α-Alkyl-α,β-Unsaturated Carbonyl Compounds

Yoshiharu Onishi, Yoshihiro Nishimoto, Makoto Yasuda, and Akio Baba*

Department of Applied Chemistry, Graduate School of Engineering, Osaka University 2-1, Yamada-oka, Suita, Japan

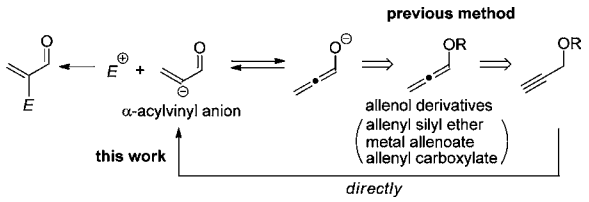
Supporting Information

ABSTRACT: Indium chloride catalyzed alkylative rearrangement of propargylic acetates into α-alkyl-α,β-unsaturated carbonyl compounds has been achieved. Propargylic acetates functioned as α-acylvinyl anion equivalents to react with carbocations generated from alkyl chlorides. Other alkyl electrophiles such as alcohols and acetates were also applicable.



An α-acylvinyl anion, which couples with various electrophiles to afford a beneficial α-substituted-α,β-unsaturated carbonyl compound, is one of the most useful nucleophiles in carbon−carbon bond-forming reactions (Scheme 1).[1,2]

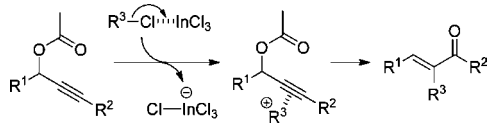
Scheme 1. Utilization of Propargylic Ester as α-Acylvinyl Anion



Recently, the strategy using propargylic alcohols and their derivatives as α-acylvinyl anion equivalents has been intensively studied because these are so readily available. In many cases, the rearrangement of them to allenol derivatives is employed due to the tautomerization between an α-acylvinyl anion and an allenoxy anion. Scheidt reported that allenyl silyl ethers, which are produced by Brook and retro-Brook rearrangements of propargylic alcohols and silyl ethers, respectively, coupled with carbonyl compounds.[3,4] Trost developed a coupling reaction employing Meyer−Schuster rearrangement of propargylic alcohols into vanadium allenoates.[5] Although methods using Au- and Ag-catalyzed rearrangements of propargylic esters to allenyl carboxylates have also attracted much attention,[6] these have been limited to acyl migration[7] and cyclization using intramolecular electrophilic moieties such as alkenes, alkynes, and imines.[8−12] A Au-catalyzed intermolecular reaction using isochromane acetal analogues was recently reported.[13] Also noteworthy has been the development of a Au-catalyzed coupling of propargylic acetates with arylboronic acids by Zhang, and a copper-catalyzed arylative Meyer−Schuster rearrangement of propargylic alcohols was developed by Gaunt, in which an allenyl carboxylate intermediate is uninvolved.[14,15] Despite these remarkable developments, however, we were unable to find a report of the reaction between an α-acylvinyl anion equivalent and a carbocation.

Herein, we report the $InCl_3$-catalyzed alkylative rearrangement of propargylic acetates using alkyl chlorides (Scheme 2).

Scheme 2. Alkylative Rearrangement of Propargylic Acetates Using Alkyl Chlorides



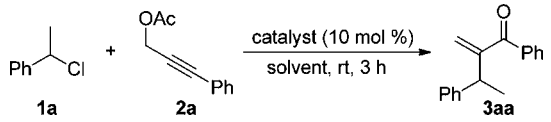
In the present reaction, propargylic acetate directly reacts with the carbocation generated from an alkyl chloride by indium catalyst to give the corresponding α-alkylated-α,β-unsaturated ketone.

After the screening of catalysts in the reaction of alkyl chloride **1a** with propargylic acetate **2a**, $InCl_3$, $InBr_3$, and InI_3 smoothly accelerated the formation of the corresponding enone **3aa** in 79%, 82%, and 78% yields, respectively (Table 1, entries 1−3). Indium halides, in contrast to other Lewis acids, can generate the corresponding carbocation from an alkyl chloride even in the presence of oxygen-containing functional groups such as an acetoxy group.[16] The use of $ZnCl_2$ and $FeCl_3·6H_2O$, which are effective catalysts in the carbohalogenation of alkynes with alkyl chlorides,[17] gave lower yields of **3aa** (entries 4 and 5). No reaction took place in the presence of representative Lewis acids such as $BF_3·OEt_2$, $AlCl_3$, and $TiCl_4$ (entries 6−8). While $AuCl_3$, $PtCl_2$, and $AgBF_4$ are known to promote the rearrangement of propargylic carboxylates to give allenyl carboxylates,[18] they did not catalyze this reaction (entries 9−11). Low yields of **3aa** were obtained in nonpolar solvents such

Received: January 7, 2014
Published: February 4, 2014

   dx.doi.org/10.1021/ol500046e | Org. Lett. 2014, 16, 1176−1179

Table 1. Screening of Catalysts[a]



1a 2a 3aa

entry	catalyst	solvent	yield[b] (%)
1	$InCl_3$	CH_2Cl_2	79 (70)[c]
2	$InBr_3$	CH_2Cl_2	82
3	InI_3	CH_2Cl_2	78
4	$ZnCl_2$	CH_2Cl_2	22
5	$FeCl_3$ $6H_2O$	CH_2Cl_2	17
6	BF_3 OEt_2	CH_2Cl_2	0
7	$AlCl_3$	CH_2Cl_2	0
8	$TiCl_4$	CH_2Cl_2	0
9	$AuCl_3$	CH_2Cl_2	0
10	$PtCl_2$	CH_2Cl_2	0
11	$AgBF_4$	CH_2Cl_2	9
12	$InCl_3$	hexane	27
13	$InCl_3$	toluene	7
14	$InCl_3$	MeCN	0
15	$InCl_3$	THF	0
16	$InCl_3$	CH_2Cl_2	60

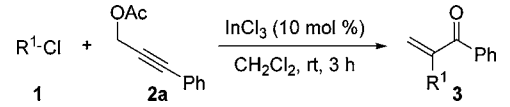
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (0.05 mmol), CH_2Cl_2 (1 mL), rt, 3 h. [b]Yield by ^1H NMR analysis. Internal standard is 1,1,2,2-tetrachloroethane. [c]Isolated yield. [d]**1a** was considerably recovered. [e]**2a** (0.5 mmol).

as hexane and toluene, and the employment of MeCN and THF completely disturbed the reaction because of their coordination toward $InCl_3$ (entries 12−15). The use of 1 equivalent of **2a** slightly decreased the yield of **3aa** (entry 16). For all of these results, $InCl_3$, which is cheaper and easier to handle than other indium halides, was chosen as a standard catalyst.

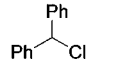
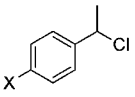
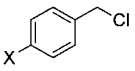
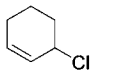
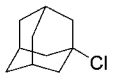
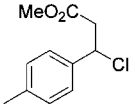
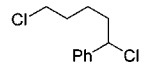
Using $InCl_3$ as a catalyst, the scope and limitations of alkyl chlorides were investigated (Table 2). Benzhydryl chloride **1b** gave an excellent result (Table 2, entry 1). Both secondary benzylic chlorides bearing electron-withdrawing and -donating groups reacted with propargylic acetate **2a** to produce α,β-unsaturated ketones **3ca** and **3da** in 63% and 74% yields, respectively (entries 2 and 3). Primary benzyl chloride **1e** did not afford the coupling product, even under the harsh conditions (entry 4). By contrast, the reaction of *p*-methylbenzyl chloride **1f** proceeded smoothly under the same harsh conditions, although only 20% yield was achieved at room temperature (entry 5). These results indicate that the stability of carbocations generated from alkyl chlorides is significant. Allylic chloride **1g** was also a suitable electrophile, and it provided the corresponding product **3ga** in a good yield (entry 6). Although the reaction of adamantyl chloride **1h** resulted in only 34% yield because the corresponding carbocation is hardly generated, the corresponding product **3ha** was obtained in high yield under heating conditions (entries 7 and 8). In the reaction of alkyl chloride **1i**, 4 equiv of **2a** were required to obtain a moderate yield of **3ia** because the electron-withdrawing effect of the intramolecular ester moiety makes the corresponding carbocation intermediate unstable (entry 9). Primary alkyl chloride moieties tolerated the reaction conditions (entry 10).

Table 3 shows the results of the reactions for various propargylic acetates **2**. Propargylic acetates **2b** and **2c** furnished the corresponding α,β-unsaturated ketones **3bb** and **3bc** in 99% and 91% yields, respectively (Table 3, entries 1 and 2). Propargylic acetate **2d** bearing a thiophene ring gave thienyl

Table 2. Reaction of Various Alkyl Chlorides 1 with Propargylic Acetate 2a[a]



1 2a 3

entry	1		3	yield (%)[b]
1		**1b**	**3ba**	99 (93)
2	 X = Cl	**1c**	**3ca**	63 (29)
3	Me	**1d**	**3da**	77 (76)
4[e]	 X = H	**1e**	**3ea**	0
5[e]	Me	**1f**	**3fa**	59 (51)
6		**1g**	**3ga**	54 (45)
7		**1h**	**3ha**	34
8[d]				76 (58)
9[e]		**1i**	**3ia**	47 (47)
10		**1j**	**3ja**	59 (45)

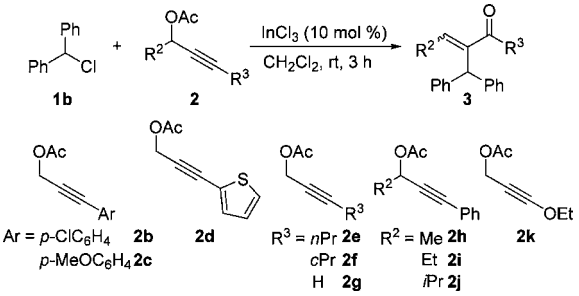
[a]Reaction conditions: **1** (1 equiv), **2a** (2 equiv), $InCl_3$ (0.1 equiv), CH_2Cl_2 (1 mL), rt, 3 h. [b]Yield by ^1H NMR analysis. Internal standard is 1,1,2,2-tetrachloroethane. Values in parentheses are isolated yields. [c]$InCl_3$ (0.3 equiv), $ClCH_2CH_2Cl$ (1 mL), 83 °C, 3 h. [d]1,4-Dichlorobutane, 150 °C, 3 h. [e]**2a** (4 equiv), $ClCH_2CH_2Cl$ (1 mL), 83 °C, 1 h.

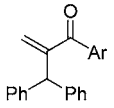
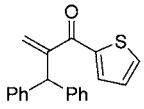
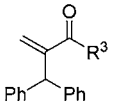
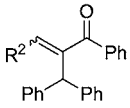
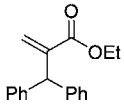
ketone product **3bd** in 92% yield (entry 3). This system was also applicable to propargylic acetates possessing aliphatic alkyne moieties. In particular, the cyclopropyl-substituted **2f** provided the desired product in an excellent yield (entries 4 and 5). Unfortunately, a reaction using **2g** did not afford the corresponding α,β-unsaturated aldehyde, and the starting materials were recovered (entry 6). Secondary propargylic acetates **2h**, **2i**, and **2j** reacted with alkyl chloride **1b** to afford trisubstituted olefin products **3bh**, **3bi**, and **3bj** in 53%, 56%, and 30% yields, respectively, with high *E*-selectivities (entries 7−9).[19] The low yield of the reaction using **3bj** indicates that the steric hindrance of the isopropyl group disturbed the reaction process. The reaction using propargylic acetate **2k** with an alkoxy acetylene moiety successfully produced the corresponding α,β-unsaturated ester **3bk** in 74% yield (entry 10).

Both benzylic acetates and alcohols were applicable as electrophiles (eqs 1−3).[20] In particular, the reaction using alkyl acetate **6** is noteworthy because the alkyl chloride that corresponded to **6** was too unstable to be handled. This result implies that the variety of products might be broadened by the employment of alcohols and alkyl acetates.

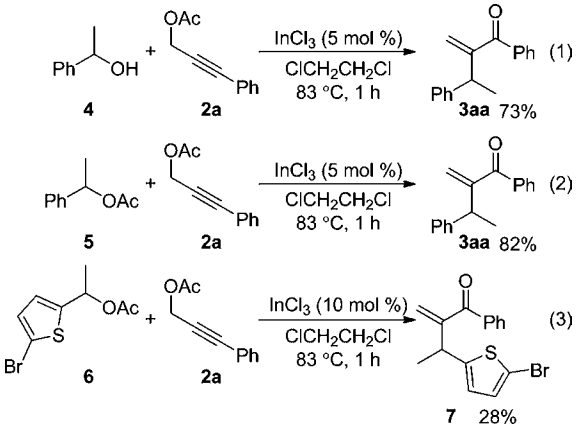
dx.doi.org/10.1021/ol500046e | *Org. Lett.* 2014, 16, 1176−1179

Table 3. Reaction of Diverse Propargylic Acetate 2 with Alkyl Chloride 1b[a]

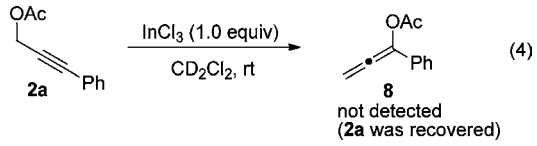


entry	2	3		yield (%)[b]
1	**2b**		**3bb**	99 (89)
2[c]	**2c**		**3bc**	91 (57)
3	**2d**		**3bd**	92 (43)
4[d]	**2e**		**3be**	25 (24)
5	**2f**		**3bf**	92 (80)
6	**2g**		**3bg**	0
7[e]	**2h**		**3bh**	53 (40)[f]
8[g]	**2i**		**3bi**	56 (42)[h]
9[g]	**2j**		**3bj**	30 (12)[i]
10	**2k**		**3bk**	74 (51)

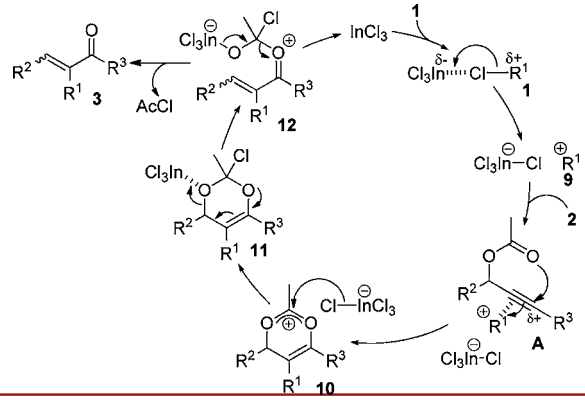
[a]Reaction conditions: **1b** (0.5 mmol), **2** (1.0 mmol), $InCl_3$ (0.05 mmol), CH_2Cl_2 (1 mL), rt, 3 h. [b]Yield by ^1H NMR analysis. Values in parentheses are isolated yields. [c]5 h. [d]40 °C. [e]30 min. [f]E/Z = 85:15. [g]**2** (2.5 mmol), rt, 30 min. [h]E/Z = 93:7. [i]E/Z = 77:23.



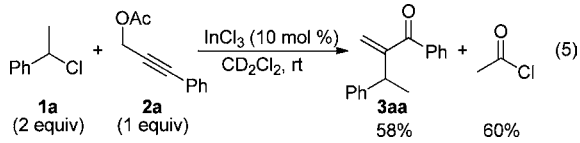
The treatment of propargylic acetates **2a** with $InCl_3$ did not give the corresponding allenyl acetates **8** and resulted in the recovery of **2a** in contrast with the rearrangement catalyzed by Au, Pt, and Ag catalysts (eq 4).[18,21] In addition, these transition-metal catalysts did not cause the present alkylative rearrangement (Table 1). These results imply that an allenyl acetate intermediate was not involved in the reaction mechanism.



Scheme 3. Plausible Mechanism



A plausible mechanism is shown in Scheme 3. First, $InCl_3$ does not activate propargylic acetates **2** but activates alkyl chloride **1** to generate carbocation **9**. Carbocation **9** interacts with propargylic acetate **2** to increase positive charge in the alkyne moiety. Then, the electrophilic addition of **9** and the nucleophilic addition of the intramolecular acetoxy group to the alkyne moiety occur to give cation intermediate **10** (**A**). The addition of a chloride anion to **10** provides oxyalkylated intermediate **11**. The coordination of the allylic oxygen atom of **11** to $InCl_3$ accelerates the cleavage of C−O bond to give zwitterionic species **12**. Then, the elimination of acetyl chloride from **12** affords α-alkyl-α,β-unsaturated carbonyl compound **3**, and $InCl_3$ is regenerated. It was observed the yield of acetyl chloride was equivalent to that of enone **3aa** (eq 5).[22]



In conclusion, we have achieved the $InCl_3$-catalyzed alkylative transformation of propargylic acetates, which provided α-alkyl-α,β-unsaturated carbonyl compounds. The novel usage of propargylic acetates as an α-acylvinyl anion equivalent has been demonstrated. The employment of carbocations as coupling partners, which were derived from alkyl chlorides, alcohols, and alkyl acetates, led to the success of this reaction.

■ ASSOCIATED CONTENT

Supporting Information

Experimental procedures, full characterization of new products, and copies of NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: baba@chem.eng.osaka-u.ac.jp.

Notes

The authors declare no competing financial interest.

dx.doi.org/10.1021/ol500046e | *Org. Lett.* 2014, 16, 1176−1179

■ ACKNOWLEDGMENTS

This work was supported by the Ministry of Education, Culture, Sports, Science and Technology (Japan). Y.O. thanks JSPS Research Fellowships for Young Scientists.

■ REFERENCES

(1) For recent reviews for Morita−Baylis−Hillman reaction, see: (a) Chinchilla, R.; Najera, C. *Chem. Rev.* **2000**, *100*, 1891−1928. (b) Basavaiah, D.; Rao, A. J.; Satyanarayana, T. *Chem. Rev.* **2003**, *103*, 811−891.

(2) For recent reports for the generation of α-acylvinyl anion equivalent by the conjugation addition of organometallic compounds to α,β-acetylenic carbonyl compounds, see: (a) Mueller, A. J.; Jennings, M. P. *Org. Lett.* **2007**, *9*, 5327−5329. (b) Mueller, A. J.; Jennings, M. P. *Org. Lett.* **2008**, *10*, 1649−1652. (c) Lakshmi, B. V.; Kazmaier, U. *Synlett* **2010**, 407−410.

(3) For recent reports for the generation of α-acylvinyl anion equivalent by Brook rearrangement of α-hydroxypropargyl silane, see: (a) Galliford, C. V.; Scheidt, K. A. *Chem. Commun.* **2008**, 1926−1928. (b) Reynolds, T. E.; Binkley, M. S.; Scheidt, K. A. *Org. Lett.* **2008**, *10*, 2449−2452. (c) Reynolds, T. E.; Binkley, M. S.; Scheidt, K. A. *Org. Lett.* **2008**, *10*, 5227−5230. (d) Brekan, J. A.; Reynolds, T. E.; Scheidt, K. A. *J. Am. Chem. Soc.* **2010**, *132*, 1472−1473.

(4) For recent reports for reactions using siloxyallenes generated by retro-Brook rearrangement, see: (a) Stergiades, I. A.; Tius, M. A. *J. Org. Chem.* **1999**, *64*, 7547−7551. (b) Yoshizawa, K.; Shioiri, T. *Tetrahedron Lett.* **2006**, *47*, 757−761.

(5) For reports for the generation of α-acylvinyl anion equivalent by vanadium-catalyzed Meyer−Schuster rearrangement of propargylic alcohols, see: (a) Trost, B. M.; Oi, S. *J. Am. Chem. Soc.* **2001**, *123*, 1230−1231. (b) Trost, B. M.; Chung, C. K. *J. Am. Chem. Soc.* **2006**, *128*, 10358−10359. (c) Trost, B. M.; Luan, X. *J. Am. Chem. Soc.* **2011**, *133*, 1706−1709. (d) Trost, B. M.; Luan, X.; Miller, Y. *J. Am. Chem. Soc.* **2011**, *133*, 12824−12833.

(6) For selected reports other than carbon−carbon bond formation, see: (a) Marion, N.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2750−2752. (b) Yu, M.; Li, G.; Wang, S.; Zhang, L. *Adv. Synth. Catal.* **2007**, *349*, 871−875. (c) Marco-Contelles, J.; Soriano, E. *Chem.—Eur. J.* **2007**, *13*, 1350−1357. (d) Marion, N.; Carlqvist, P.; Gealageas, R.; de Frémont, P.; Maseras, F.; Nolan, S. P. *Chem.—Eur. J.* **2007**, *13*, 6437−6451. (e) Yu, M.; Zhang, G.; Zhang, L. *Org. Lett.* **2007**, *9*, 2147−2150. (f) Yu, M.; Zhang, G.; Zhang, L. *Tetrahedron* **2009**, *65*, 1846−1855. (g) Wang, S.; Zhang, G.; Zhang, L. *Synlett* **2010**, 692−706.

(7) (a) Wang, S.; Zhang, L. *J. Am. Chem. Soc.* **2006**, *128*, 8414−8415. (b) Barluenga, J.; Riesgo, L.; Vincente, R.; López, L. A.; Tomás, M. *J. Am. Chem. Soc.* **2007**, *129*, 7772−7773.

(8) For reports for cyclization using an intramolecular alkyne moiety, see: (a) Zhao, J.; Hughes, C. O.; Toste, F. D. *J. Am. Chem. Soc.* **2006**, *128*, 7436−7437. (b) Oh, C. H.; Kim, A.; Park, W.; Park, D. I.; Kim, N. *Synlett* **2006**, 2781−2784. (c) Oh, C. H.; Kim, A. *New J. Chem.* **2007**, *31*, 1719−1721. (d) Lebœuf, D.; Simonneau, A.; Aubert, C.; Malacria, M.; Gandon, V.; Fensterbank, L. *Angew. Chem., Int. Ed.* **2011**, *50*, 6868−6871.

(9) For a report for cyclization using an intramolecular alkene moiety, see: Rao, W.; Susanti, D.; Chan, P. W. H. *J. Am. Chem. Soc.* **2011**, *133*, 15248−15251.

(10) For reports for cyclization using an intramolecular α,β-unsaturated carbonyl compound moiety, see: (a) Luo, T.; Schreiber, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 8250−8253. (b) Luo, T.; Schreiber, S. L. *J. Am. Chem. Soc.* **2009**, *131*, 5667−5674. (c) Cran, J. W.; Krafft, M. E. *Angew. Chem., Int. Ed.* **2012**, *51*, 9398−9402.

(11) For a report for cyclization using an imine moiety, see: Zhang, Z.; Shi, M. *Chem.—Eur. J.* **2012**, *18*, 3654−3658.

(12) For a report for cyclization using an aziridine moiety, see: Yang, J.-M.; Zhang, Z.; Wei, Y.; Shi, M. *Tetrahedron Lett.* **2012**, *53*, 6173−6176.

(13) Yu, Y.; Yang, W.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2013**, *52*, 7586−7589.

(14) (a) Zhang, G.; Peng, Y.; Cui, L.; Zhang, L. *Angew. Chem., Int. Ed.* **2009**, *48*, 3112−3115. (b) Cui, L.; Zhang, G.; Zhang, L. *Bioorg. Med. Chem. Lett.* **2009**, *19*, 3884−3887. (c) Collins, B. S. L.; Suero, M. G.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 5799−5802.

(15) Collins, B. S. L.; Suero, M. G.; Gaunt, M. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 5799−5802.

(16) (a) Nishimoto, Y.; Yasuda, M.; Baba, A. *Org. Lett.* **2007**, *9*, 4931−4934. (b) Nishimoto, Y.; Saito, T.; Yasuda, M.; Baba, A. *Tetrahedron* **2009**, *65*, 5462−5471.

(17) (a) Maroni, R.; Melloni, G. *Tetrahedron Lett.* **1972**, *13*, 2869−2870. (b) Maroni, R.; Melloni, G.; Modena, G. *J. Chem. Soc., Chem. Commun.* **1972**, 857−858. (c) Maroni, R.; Melloni, G.; Modena, G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 353−356. (d) Maroni, R.; Melloni, G.; Modena, G. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2491−2496. (e) Marcuzzi, F.; Melloni, G. *Tetrahedron Lett.* **1975**, *16*, 2771−2774. (f) Marcuzzi, F.; Melloni, G. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1517−1522. (g) Marcuzzi, F.; Melloni, G. *J. Am. Chem. Soc.* **1976**, *98*, 3295−3300. (h) Liu, Z.; Wang, J.; Zhao, Y.; Zhou, B. *Adv. Synth. Catal.* **2009**, *351*, 371−374.

(18) $AuCl_3$: (a) Zhang, L. *J. Am. Chem. Soc.* **2005**, *127*, 16804−16805. (b) Brummond, N. M.; Davis, M. M.; Huang, C. *J. Org. Chem.* **2009**, *74*, 8314−8320. $PtCl_2$: (c) Cariou, K.; Mainetti, E.; Fensterbank, L.; Malacria, M. *Tetrahedron* **2004**, *60*, 9745−9755. (d) Marion, N.; Díez-González, S.; de Frémont, P.; Noble, A. R.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 3647−3650. (e) Ji, K.-G.; Shu, X.-Z.; Chen, J.; Zhao, S.-C.; Zheng, Z.-J.; Lu, L.; Liu, X.-Y.; Liang, Y.-M. *Org. Lett.* **2008**, *10*, 3919−3922. (f) Cho, E. J. *Chem.—Eur. J.* **2012**, *18*, 4495−4498. $AgBF_4$: (g) Oelberg, D. G.; Schiavelli, M. D. *J. Org. Chem.* **1977**, *42*, 1804−1806. (h) Marion, N.; Lemière, G.; Correa, A.; Costabile, C.; Ramón, R. S.; Moreau, X.; de Frémont, P.; Dahmane, R.; Hours, A.; Lesage, D.; Tabet, J. C.; Goddard, J. P.; Gandon, V.; Cavallo, L.; Fensterbank, L.; Malacria, M.; Nolan, S. P. *Chem.—Eur. J.* **2009**, *15*, 3243−3260. (i) Shu, D.; Li, X.; Zhang, M.; Robichaux, P. J.; Tang, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 1346−1349.

(19) The major geometry of an olefin moiety was assigned as the *E*-configuration by NOESY.

(20) For our previous reports for coupling reactions using alcohols and alkyl acetates, see: (a) Yasuda, M.; Saito, T.; Ueba, M.; Baba, A. *Angew. Chem., Int. Ed.* **2004**, *43*, 1414−1416. (b) Saito, T.; Yasuda, M.; Baba, A. *Synlett* **2005**, 1737−1739. (c) Saito, T.; Nishimoto, Y.; Yasuda, M.; Baba, A. *J. Org. Chem.* **2006**, *71*, 8516−8522. (d) Yasuda, M.; Somyo, T.; Baba, A. *Angew. Chem., Int. Ed.* **2006**, *45*, 793−796. (e) Baba, A.; Yasuda, M.; Nishimoto, Y.; Saito, T.; Onishi, Y. *Pure Appl. Chem.* **2008**, *80*, 845−854. (f) Nishimoto, Y.; Kajioka, M.; Saito, T.; Yasuda, M.; Baba, A. *Chem. Commun.* **2008**, 6396−6398. (g) Babu, S. A.; Yasuda, M.; Tsukahara, Y.; Yamauchi, T.; Wada, Y.; Baba, A. *Synthesis* **2008**, 1717−1724. (h) Nishimoto, Y.; Onishi, Y.; Yasuda, M.; Baba, A. *Angew. Chem., Int. Ed.* **2009**, *48*, 9131−9134. (i) Onishi, Y.; Nishimoto, Y.; Yasuda, M.; Baba, A. *Chem. Lett.* **2011**, *40*, 1223−1225.

(21) The indium salt catalyzed rearrangement of propargylic carboxylates to allenyl carboxylates have never been reported.

(22) The generation of acetyl chloride was confirmed by ^1H and ^{13}C NMR analysis in the reaction mixture in situ.