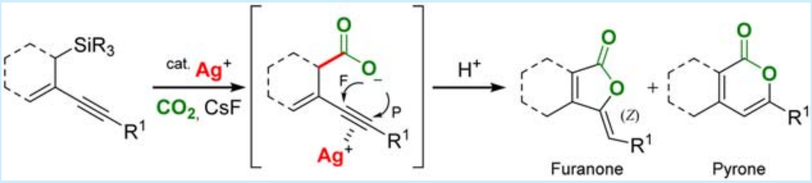
Organic LETTERS
Letter
pubs.acs.org/OrgLett

SilverCatalyzed Cascade Carboxylation and Cyclization of Trimethyl(2-methylenebut-3-yn-1-yl)silane Derivatives

Kohei Sekine, Yuta Sadamitsu, and Tohru Yamada*

Department of Chemistry, Keio University, Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

S *Supporting Information*



ABSTRACT: C−C bond-forming carboxylation and cyclization of trimethyl(2-methylenebut-3-yn-1-yl)silane derivatives and carbon dioxide was developed. Silver catalysts and CsF promoted the reaction to afford the corresponding 2-furanone and 2-pyrone derivatives in good-to-high yields. The structure of the 2-furanone was confirmed by single-crystal X-ray crystallography, which revealed that the geometry of the *exo*-olefin was that of a *Z*-isomer. When an aromatic ring-substituted alkyne was used, 2-furanone derivatives were selectively obtained via 5-*exo-dig* cyclization, whereas the reaction of alkyl-substituted alkynes produced 2-pyrone derivatives with high selectivity.

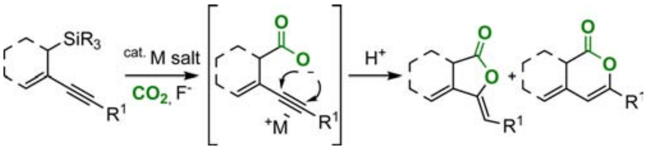
Carbon dioxide has been utilized as a carbon source for the synthesis of fine chemicals due to its abundant supply and easy handling, despite its thermodynamic stability. Methods to transform carbon dioxide into high-value chemicals have been developed,[1] and carbon dioxide has been incorporated into alkyne derivatives during the synthesis of heterocyclic compounds.[2] Propargyl alcohols[3] and propargyl amines[4] were converted to the corresponding cyclic carbonates and oxazolidinones in the presence of a transition metal, organic base, phosphine, or carbene catalyst. Though cyclic carbonates and oxazolidinones are important structures in materials and pharmaceutical sciences, their hydrolysis would readily promote decarboxylation. To incorporate carbon dioxide into organic molecules, formation of C−C bonds between the substrate and carbon dioxide is important. Cyclization following C−C bond-forming carboxylation can afford the corresponding lactones that are not easily decarboxylated. However, few examples of cyclization following carboxylation of alkyne derivatives with C−C bond formation have been reported.[5,7g]

Organosilane compounds, such as allylsilane, arylsilane, and vinylsilane, are useful reagents for new C−C bond formation. For example, Hosomi−Sakurai allylation[6] has been used to provide homoallyl alcohols, which are an important framework for the total synthesis of natural products and medicinal compounds. Studies related to the carboxylation of organosilane compounds using carbon dioxide have been reported; fluoride-mediated or Lewis acid mediated carboxylation afforded the corresponding carboxylic acids or esters.[7] However, for allylsilane compounds, only one system involving Lewis acid mediated carboxylation has been reported.[6c] Therefore, allylsilane compounds have additional potential for carbon dioxide incorporation.

Recently, carbon dioxide incorporation into propargyl alcohols,[8a,b,e] propargylamines,[8c−e] and *o*-alkynylanilines[8f,g] using silver catalysts and base was reported. In these reactions, silver catalysts, acting as a π-Lewis acid, activate C−C triple bonds to promote cyclization of the intermediates, such as carbonates and carbamates. Activation of C−C triple bonds by silver salts was a crucial step; otherwise, the intermediates would readily revert back to starting materials. The silver catalytic system was applied to ketone-containing alkynes to give the corresponding lactones[9a] or furans having a carboxyl group[9b] in good-to-high yields via C−C bond formation between the substrates and carbon dioxide. Next, organosilane compounds were utilized as a nucleophile for carbon dioxide, which led to C−C bond-forming carboxylation and cyclization.

On the basis of previous studies, 5-membered ring lactones and 6-membered ring lactones were expected from the reaction of carbon dioxide and an allylsilane containing a C−C triple bond (Scheme 1). The present report describes a silver-catalyzed cyclization following carboxylation of trimethyl(2-methylenebut-3-yn-1-yl)silane derivatives with carbon dioxide.

Scheme 1. Cyclization Following Carboxylation of Allylsilanes Containing Alkynes

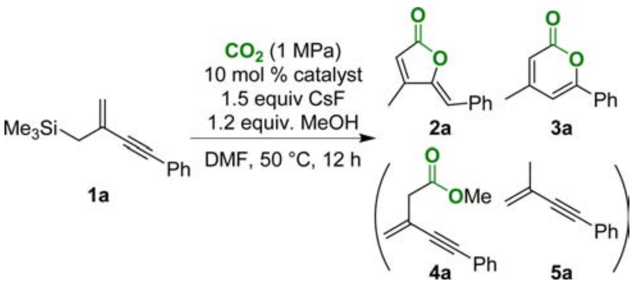


Received: October 19, 2015
Published: November 4, 2015

DOI: 10.1021/acs.orglett.5b03023
Org. Lett. 2015, 17, 5706−5709

Enyne compound **1a** containing an allylsilane moiety was employed as a model substrate in the presence of CsF and MeOH in DMF under 1 MPa CO_2 atmosphere. Methanol was added as a proton source for complete turnover of the catalytic cycle. Initially, various metal salts were examined (Table 1).

Table 1. Examination of Metal Salts

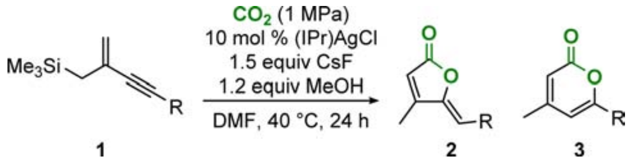


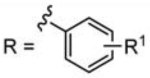
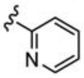
entry[a]	catalyst	yield **2** + **3**[b] (%)	2:3[c]
1	none	trace[d]	
2	CuI	trace[e]	
3	$(PPh_3)AuCl$	17	95:5
4	$Pd(OAc)_2$	49	89:11
5	AgF	70	77:23
6	AgOTf	79	88:12
7[f]	AgOTf	28	87:13
8[g]	AgOTf	73	83:19
9	AgOAc	73	89:11
10	$AgBF_4$	73	91:9
11	(IMes)AgCl	80	93:7
12	(IPr)AgCl	80	94:6
13[h]	**(IPr)AgCl**	**78**	**> 95:5**

[a] The reaction was carried out with 0.15 mmol of substrate in 1.5 mL of solvent. [b] Isolated yield. [c] Determined by ^1H NMR. [d] **4a** was obtained in 54% yield after methylation. [e] **4a** was produced in 63% yield after methylation. [f] KF was used intsead of CsF. [g] TBAT (tetrabutylammonium difluorotriphenylsilicate) was used intsead of CsF. [h] 40 °C for 24 h.

Without any catalysts or with CuI, a trace amount of 2-furanone **2a** was detected, although methyl ester **4a** was obtained after methylation by trimethylsilyldiazomethane (Table 1, entries 1 and 2). The results indicated that carboxylation of **1a** proceeded; in contrast, cyclization was minimal. The metal salts $(PPh_3)AuCl$ and $Pd(OAc)_2$ promoted the reaction to give 2-furanone **2a** and 2-pyrone **3a** in 17% and 49% yields, respectively (Table 1, entries 3 and 4). In the presence of AgF, the reaction proceeded smoothly to afford a 70% yield of a mixture of 77:23 furanone **2a**/pyrone **3a** (Table 1, entry 5). In this case, (3-methylbut-3-en-1-yn-1-yl)benzene **5a** was obtained in 8% yield, which was produced by protonation of a carbanion equivalent generated from substrate and CsF. For fluoride sources, CsF was the most suitable for this reaction (Table 1, entries 6–8).[10] Various silver salts were screened to improve the selectivity for **2a** (Table 1, entries 5, 6, and 9–12). The results indicated that an *N*-heterocyclic carbene ligand slightly improved selectivity for the furanone **2a**; (IMes)AgCl and (IPr)AgCl produced **2a** and **3a** in ratios of 93:7 and 94:6, respectively (Table 1, entries 11 and 12). Examination of the reaction temperature[10] revealed that the ratio of furanone **2a** to pyrone **3a** was >95:5 if the reaction was conducted at 40 °C, which afforded a mixture of **2a** and **3a** in 78% yield (Table 1, entry 13).

Table 2. Substrate Scope Using the Silver Catalytic System



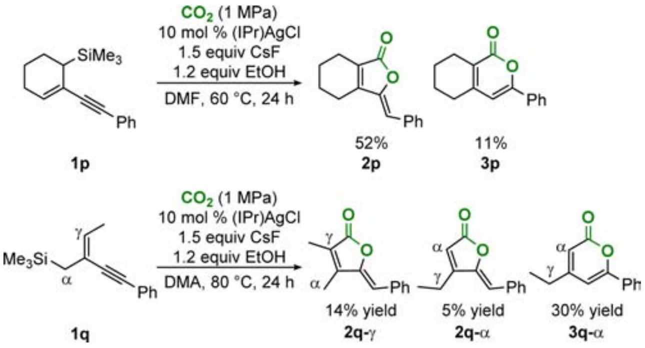
entry[a]	substrate		yield[b] 2 / %	3 / %	(2:3)[c]
1	R = 	R^1 = H(**1a**)	78	trace	
2		*p*-Me(**1b**)	76	5	(94:6)
3		*m*-Me(**1c**)	78	4	(95:5)
4[d,e]		*o*-Me(**1d**)	43	29	(60:40)
5		*p*-OMe(**1e**)	66	9	(88:12)
6[d]		*p*-COOEt(**1f**)	74	ND[f]	
7		*p*-Ac(**1g**)	72	ND[f]	
8		*p*-CN(**1h**)	92	ND[f]	
9		*p*-CF_3(**1i**)	78	ND[f]	
10	R = 1-naph (**1j**)		18	15	(56:44)
11	2-naph (**1k**)		80	trace	
12	 (**1l**)		73	ND[f]	
13[d]	^nBu (**1m**)		ND[f]	77	
14[d,g]	CH_2CH_2Ph (**1n**)		ND[f]	65	
15[d]	^tBu (**1o**)		14	43	(25:75)

[a] The reaction was carried out with 0.15 mmol of substrate in 1.5 mL of DMF. [b] Isolated yield. [c] The ratio was calculated based on isolated yields. [d] 50 °C. [e] 20 mol % (IPr)AgCl was employed. 48 h. [f] Not detected. [g] Using AgOTf instead of (IPr)AgCl.

Various alkynylaromatics were next explored under the optimized conditions (Table 2, entries 1–12). Electron-donating groups induced production of the pyrone **3**. For substrates **1b** (*p*-Me), **1c** (*m*-Me), and **1e** (*p*-OMe), the corresponding furanones **2b**, **2c**, and **2e**, and pyrones **3b**, **3c**, and **3e** were obtained with ratios of 94:6, 95:5, and 88:12, respectively (Table 2, entries 2, 3, and 5). The reaction of substrate **1d** (*o*-Me) required higher temperatures, compared to the optimized conditions, to afford the corresponding furanone **2d** and pyrone **3d** in 43% and 29% yields, respectively. A methyl group at the *ortho*-position should hinder the approach of silver catalysts, therefore requiring a greater amount of catalyst, higher temperatures, and a longer reaction time (Table 2, entry 4). In contrast, substrates containing electron-withdrawing groups such as *p*-COOEt (**1f**), *p*-Ac (**1g**), *p*-CN (**1h**), and *p*-CF_3 (**1i**) gave the corresponding furanones **2f–i** selectively in high yields, while pyrone derivatives **3f–i** were not observed (Table 2, entries 6–9). 1-Naphthyl and 2-naphthyl isomers affected yield and selectivity; substrate **1j** (1-naphthyl) could be converted to furanone **2j** and pyrone **3j** in 18% and 15% yields, respectively (Table 2, entry 10). In contrast, 2-naphthyl-substituted furanone **2k** (2-naphthyl) was produced selectively in 80% yield (Table 2, entry 11). The regioselectivity for substrates **1b** (*p*-Me), **1c** (*m*-Me), **1d** (*o*-Me), **1j** (1-naphthyl), and **1k** (2-naphthyl) was assumed to be due to steric effects from the substituent at the *ortho*-position; silver catalysts were hindered from occupying the appropriate position for 5-*exo* cyclization to promote 6-*endo* cyclization. For 2-pyridyl-substituted substrate **1l**, the reaction afforded only the furanone **2l** in 73% yield. The reaction of the alkyl-substituted alkynes substrates **1m** and **1n** also proceeded (Table 2, entries 13−15). Interestingly, the corresponding pyrones **3m** and **3n** were obtained exclusively in 77% and 65% yields, respectively (Table 2, entries 13 and 14). For *tert*-butyl (**1o**), pyrone **3o** was produced in a greater yield than that of the furanone **2o** (Table 2, entry 15). Selectivity for pyrone **3** when using alkyl-substituted substrates **1m**, **1n**, and **1o** was due to the electron-donating properties of the alkyl groups. A similar tendency was noticed upon introduction of electron-donating groups into alkynylaromatics (Table 2, entries 2−5).

Alkyl-substituted allylsilane **1p** also was investigated (Scheme 2). The reaction required a higher temperature to provide an adequate yield of furanone **2p** and pyrone **3p**. Only trace amounts of furanone **2p** and pyrone **3p** were observed at 40 °C. However, raising the temperature to 60 °C increased the yields of furanone **2p** and pyrone **3p** to 52% and 11%, respectively.

Scheme 2. Reactions of Alkyl-Substituted Allylsilanes



Next, we investigated the nucleophilic addition to carbon dioxide of substrate **1q**, which contains a trisubstituted alkene moiety (Scheme 2). Previous studies on fluoride-activated allylation[6c] indicated that a carbanion (ion pair or equivalent) was generated via Si−F bond formation. This was supported by the result that nucleophilic addition of multisubstituted allylsilanes occurred preferably from the less substituted carbon atom, which gave homoallylalcohols with loss of regioselectivity. In this case, **1q** was transformed to three isomers, **2q-γ** produced by attack from the γ-carbon, and **2q-α** and **3q-α** were produced by the addition from the α-carbon. These observations suggest that nucleophilic addition of a carbanion (ion pair or equivalent) to carbon dioxide occurred to produce the carboxylate. The structure of **2d** was confirmed by single-crystal X-ray crystallography (Figure 1). The geometry of the *exo*-olefin of **2d** was that of a *Z* isomer. The structure based on heteronuclear multiple bond correlation (HMBC) (see the Supporting Information for details) also agreed with that suggested by the X-ray analysis.

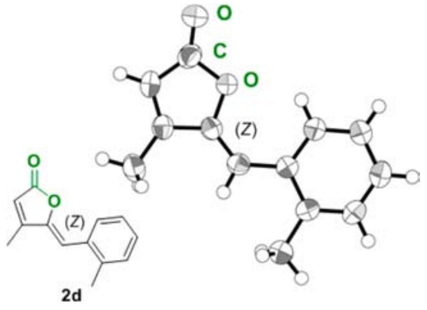


Figure 1. X-ray structure analysis of **2d**. Thermal ellipsoids are shown at 50% probability.[11]

In conclusion, a C−C bond-forming cyclization following carboxylation of trimethyl(2-methylenebut-3-yn-1-yl)silane derivatives and carbon dioxide was promoted by silver catalysts and CsF. It afforded the corresponding 2-furanone and 2-pyrone derivatives in good-to-high yields. The structure of the 2-furanone was confirmed by single-crystal X-ray crystallography and HMBC, which revealed that the geometry of the *exo*-olefin was that of a *Z*-isomer. Results also showed that, when using an aromatic ring-substituted alkyne, 2-furanone derivatives were selectively obtained via 5-*exo-dig* cyclization, whereas the reaction of alkyl-substituted alkynes produced 2-pyrone derivatives with high selectivity.

■ ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03023.

Experimental procedures and analytical data for new compounds (PDF)

X-ray crystallographic data for **2d** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: yamada@chem.keio.ac.jp.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was financially supported by JSPS Research Fellowships for Young Scientists.

■ REFERENCES

(1) Reviews about the utility of carbon dioxide: (a) Tsuji, Y.; Fujihara, T. *Chem. Commun.* **2012**, *48*, 9956−9964. (b) Cokoja, M.; Bruckmeier, C.; Rieger, B.; Herrmann, W. A.; Kühn, F. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 8510−8537. (c) Correa, A.; Martín, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 6201−6204. (d) Sakakura, T.; Kohno, K. *Chem. Commun.* **2009**, 1312−1330. (e) Sakakura, T.; Choi, J. C.; Yasuda, H. *Chem. Rev.* **2007**, *107*, 2365−2387.

(2) Yu, B.; He, L.-N. *ChemSusChem* **2015**, *8*, 52−62.

(3) (a) Iritani, K.; Yanagihara, N.; Utimoto, K. *J. Org. Chem.* **1986**, *51*, 5499−5501. (b) Inoue, Y.; Ishikawa, J.; Taniguchi, M.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1204−1206. (c) Fournier, J.; Bruneau, C.; Dixneuf, P. H. *Tetrahedron Lett.* **1989**, *30*, 3981−3982. (d) Inoue, Y.; Itoh, Y.; Yen, I.-F.; Imaizumi, S. *J. Mol. Catal.* **1990**, *60*, L1−L3. (e) Joumier, J. M.; Fournier, J.; Bruneau, C.; Dixneuf, P. H. *J. Chem. Soc., Perkin Trans. 1* **1991**, 3271−3274. (f) Gu, Y.; Shi, F.; Deng, Y. *J. Org. Chem.* **2004**, *69*, 391−394. (g) Kayaki, Y.; Yamamoto, M.; Ikariya, T. *J. Org. Chem.* **2007**, *72*, 647−649. (h) Kayaki, Y.; Yamamoto, M.; Ikariya, T. *Angew. Chem., Int. Ed.* **2009**, *48*, 4194−4197. (i) Minakata, S.; Sasaki, I.; Ide, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 1309−1311. (j) Song, Q. W.; Chen, W. Q.; Ma, R.; Yu, A.; Li, Q. Y.; Chang, Y.; He, L. N. *ChemSusChem* **2015**, *8*, 821−827.

(4) (a) Mitsudo, T.; Hori, Y.; Yamakawa, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 4417−4418. (b) Costa, M.; Chiusoli, G. P.; Taffurelli, D.; Dalmonego, G. *J. Chem. Soc., Perkin Trans. 1* **1996**, 1541−1546. (c) Shi, M.; Shen, Y. *J. Org. Chem.* **2002**, *67*, 16−21. (d) Feroci, M.; Orsini, M.; Sotgiu, G.; Rossi, L.; Inesi, A. *J. Org. Chem.*

2005, *70*, 7795−7798. (e) Kayaki, Y.; Yamamoto, M.; Suzuki, T.; Ikariya, T. *Green Chem.* **2006**, *8*, 1019−1021. (f) Maggi, R.; Bertolotti, C.; Orlandini, E.; Oro, C.; Sartori, G.; Selva, M. *Tetrahedron Lett.* **2007**, *48*, 2131−2134. (g) Yoshida, M.; Komatsuzaki, Y.; Ihara, M. *Org. Lett.* **2008**, *10*, 2083−2086. (h) Yoo, W. J.; Li, C. J. *Adv. Synth. Catal.* **2008**, *350*, 1503−1506. (i) Takeda, Y.; Okumura, S.; Tone, S.; Sasaki, I.; Minakata, S. *Org. Lett.* **2012**, *14*, 4874−4877. (j) Yoshida, M.; Mizuguchi, T.; Shishido, K. *Chem. - Eur. J.* **2012**, *18*, 15578−15581. (k) Zhao, J.; Huang, H.; Qi, C.; Jiang, H. *Eur. J. Org. Chem.* **2012**, *2012*, 5665−5667. (l) Hase, S.; Kayaki, Y.; Ikariya, T. *Organometallics* **2013**, *32*, 5285−5288.

(5) (a) Inoue, Y.; Itoh, Y.; Hashimoto, H. *Chem. Lett.* **1977**, 855−856. (b) Inoue, Y.; Itoh, Y.; Hashimoto, H. *Chem. Lett.* **1978**, 633−634. (c) Tsuda, T.; Morikawa, S.; Sumiya, R.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 3140−3145. (d) Tsuda, T.; Morikawa, S.; Hasegawa, N.; Saegusa, T. *J. Org. Chem.* **1990**, *55*, 2978−2981. (e) Louie, J.; Gibby, J. E.; Farnworth, M. V.; Tekavec, T. N. *J. Am. Chem. Soc.* **2002**, *124*, 15188−15189. (f) Ishii, M.; Mori, F.; Tanaka, K. *Chem. - Eur. J.* **2014**, *20*, 2169−2174. (g) Xin, Z.; Lescot, C.; Friis, S. D.; Daasbjerg, K.; Skrydstrup, T. *Angew. Chem., Int. Ed.* **2015**, *54*, 6862−6866.

(6) Hosomi−Sakurai allylation: (a) Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1976**, 941−942. (b) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, *17*, 1295−1298. (c) Hosomi, A.; Shirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, *19*, 3043−3046.

(7) Carboxylation of C(sp)−Si bond: (a) Yonemoto-Kobayashi, M.; Inamoto, K.; Tanaka, Y.; Kondo, Y. *Org. Biomol. Chem.* **2013**, *11*, 3773−3775. Carboxylation of C(sp^2)−Si bond: (b) Effenberger, F.; Spiegler, W. *Chem. Ber.* **1985**, *118*, 3900−3914. (c) Hattori, T.; Suzuki, Y.; Miyano, S. *Chem. Lett.* **2003**, *32*, 454−455. (d) Nemoto, K.; Yoshida, H.; Egusa, N.; Morohashi, N.; Hattori, T. *J. Org. Chem.* **2010**, *75*, 7855−7862. (e) Yoshida, H.; Fukushima, H.; Ohshita, J.; Kunai, A. *J. Am. Chem. Soc.* **2006**, *128*, 11040−11041. (f) Yoshida, H.; Morishita, T.; Ohshita, J. *Org. Lett.* **2008**, *10*, 3845−3847. (g) Yoo, W.-J.; Nguyen, T. V. Q.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 10213−10217. Carboxylation of C(sp^3)−Si bond: (h) Ohno, M.; Tanaka, H.; Komatsu, M.; Ohshiro, Y. *Synlett* **1991**, *1991*, 919−920. (i) Singh, R. P.; Shreeve, J. M. *Chem. Commun.* **2002**, *38*, 1818−1819. (j) Babadzhanova, L. A.; Kirij, N. V.; Yagupolskii, Y. L. *J. Fluorine Chem.* **2004**, *125*, 1095−1098. (k) Petko, K. I.; Kot, S. Y.; Yagupolskii, L. M. *J. Fluorine Chem.* **2008**, *129*, 301−306. (l) Mita, T.; Michigami, K.; Sato, Y. *Org. Lett.* **2012**, *14*, 3462−3465. (m) Mita, T.; Higuchi, Y.; Sato, Y. *Org. Lett.* **2014**, *16*, 14−17.

(8) (a) Yamada, W.; Sugawara, Y.; Cheng, H.-M.; Ikeno, T.; Yamada, T. *Eur. J. Org. Chem.* **2007**, *2007*, 2604−2607. (b) Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. *J. Am. Chem. Soc.* **2010**, *132*, 4072−4073. (c) Yoshida, S.; Fukui, K.; Kikuchi, S.; Yamada, T. *Chem. Lett.* **2009**, *38*, 786−787. (d) Ishida, T.; Kobayashi, R.; Yamada, T. *Org. Lett.* **2014**, *16*, 2430−2433. (e) Kikuchi, S.; Yoshida, S.; Sugawara, Y.; Yamada, W.; Cheng, H.-M.; Fukui, K.; Sekine, K.; Iwakura, I.; Ikeno, T.; Yamada, T. *Bull. Chem. Soc. Jpn.* **2011**, *84*, 698−717. (f) Ishida, T.; Kikuchi, S.; Tsubo, T.; Yamada, T. *Org. Lett.* **2013**, *15*, 848−851. (g) Ishida, T.; Kikuchi, S.; Yamada, T. *Org. Lett.* **2013**, *15*, 3710−3713.

(9) (a) Kikuchi, S.; Sekine, K.; Ishida, T.; Yamada, T. *Angew. Chem., Int. Ed.* **2012**, *51*, 6989−6992. (b) Sekine, K.; Takayanagi, A.; Kikuchi, S.; Yamada, T. *Chem. Commun.* **2013**, *49*, 11320−11322.

(10) See the Supporting Information for details.

(11) CCDC 1424535 (**2d**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.