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Cobalt-Bisoxazoline-Catalyzed Enantioselective Cross-Coupling of α-Bromo Esters with Alkenyl Grignard Reagents

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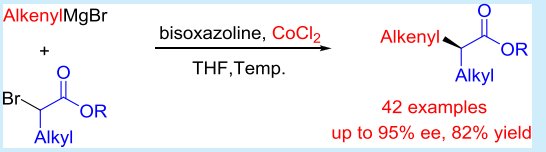
ABSTRACT: The first catalytic asymmetric Kumada cross-coupling of organic halides with alkenyl Grignard reagents has been developed. The reaction was promoted by the cobalt-bisoxazoline catalyst and afforded various α-alkyl-β,γ-unsaturated esters with excellent enantioselectivities and moderate to good yields (≤95% ee and ≤82% yields). The formal synthesis of the California red scale pheromone using this method was investigated, and radical clock experiments were performed.



Transition metal-catalyzed cross-coupling reactions of organic halides with alkenyl nucleophiles have emerged as a powerful strategy for preparing alkene-containing molecules, which are very important structural motifs in medicines, pesticides, and natural products.[1] Although some significant progress has been achieved in alkenylation of organic halides involving alkenyl Grignard reagents,[2] alkenylzinc halide or alkenylzirconium reagents,[3] alkenylboranes or boronic acids,[4] and alkenyltin reagents,[5] reports of catalytic asymmetric vinylation of organic halides are rare. There are only six examples: Hiyama cross-couplings of α-bromo esters,[6] Negishi cross-coupling of α-bromoketones, α-bromonitriles, and α-bromosulfonamides and -sulfones,[7] and Suzuki–Miyaura cross-couplings of 3-chlorocyclohex-1-ene.[8] As for catalytic asymmetric Kumada cross-coupling involving alkenyl Grignard reagents, to the best of our knowledge, there is still no successful approach.

Enantioriched α-alkyl-β,γ-unsaturated esters are versatile intermediates of bioactive natural products, such as (+)-jasplakinolide[9] and (−)-Vulcanolide.[10] Due to the limited number of methods for synthesizing these compounds,[11] devising a more general and effective asymmetric strategy is meaningful. Oshima, Yorimitsu, and Cahiez's cross-coupling of alkyl bromides with Grignard reagents showed that cobalt and iron-catalyzed procedures were efficient, environmentally friendly, and economical.[12a−c] In 2014, we have developed the first cobalt-catalyzed asymmetric Kumada cross-coupling, and various novel enantioriched α-arylalkanoic esters were obtained via cobalt-bisoxazoline-catalyzed enantioselective cross-coupling of α-bromo esters with aryl Grignard reagents.[12d] Herein, we report the first catalytic asymmetric Kumada cross-coupling of organic halides with alkenyl Grignard reagents, which affords an efficient approach for the enantioselective alkenylation of α-bromo esters. Furthermore, we have investigated the formal synthesis of the California red scale pheromone via this coupling and performed radical clock experiments.

We initially employed bisoxazoline ligand **L1**, previously the best ligand for the asymmetric arylation of α-bromo esters,[12d] in the enantioselective cross-coupling of racemic benzyl 2-bromopropanoate (**1a**) with isobutenyl magnesium bromide (**2a**). Fortunately, catalytic asymmetric alkenylation could be achieved in 84% ee and 65% yield. To find a more efficient ligand, a series of bisoxazoline ligands were screened (Scheme 1). Varying the groups on the backbone of the bisoxazoline ligand from methyls (**L1**) to hydrogens (**L2**) and benzyl groups (**L4**) led to a small decrease in yields and enantioselectivities (56−60% yield, 80−84% ee), while the replacement of the methyl groups with bulky isobutyl groups (**L3**) caused a significant drop in the yield (40%) and enantioselectivity (75%). On the basis of these results, we then modified the backbone benzyl groups of **L4**. 2-Fluorobenzyl bisoxazoline **L7** and 2-methyl bisoxazoline **L8** exhibited yields and enantioselectivities similar to those of the parent bisoxazoline **L4**, which indicated that the substitution at the *ortho* position of the benzyl group had a minor impact on this reaction. In contrast, the substitution at the *para* position significantly influenced the enantioselectivity of the coupling. 4-Fluorobenzyl bisoxazoline **L5** and 4-trifluorobenzyl bisoxazoline **L6** bearing electron-withdrawing groups decreased enantioselectivities to 68−70%, while 4-isobutylbenzyl bisoxazoline **L9** containing electron-donating group gave the best result (65% yield, 86% ee), a slight increase compared with

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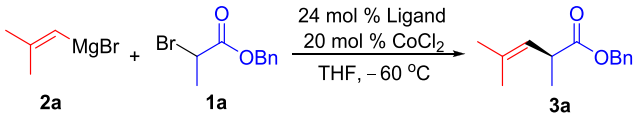
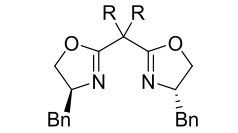
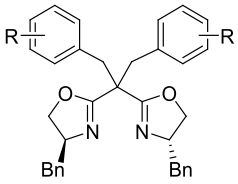
Scheme 1. Ligand Screening in the Enantioselective Kumada Cross-Coupling of Isobutenyl Magnesium Bromide[a]





L1: R = Me, 65% yield, 84% ee
L2: R = H, 56% yield, 80% ee
L3: R = *i*-Bu, 40% yield, 75% ee



L4: R = H, 60% yield, 84% ee
L5: R = 4-F, 61% yield, 70% ee
L6: R = 4-CF_3, 48% yield, 68% ee
L7: R = 2-F, 61% yield, 85% ee
L8: R = 2-Me, 63% yield, 82% ee
L9: R = 4-*t*-Bu, 65% yield, 86% ee
L10: R = 3,5-*t*-Bu_2, 43% yield, 45% ee
L11: R = 3,5-Me_2, 61% yield, 70% ee

[a]All reactions were performed for 5 h, and 4.0 equiv of **2a** was used. Isolated yields after chromatographic purification. Values of ee were determined by chiral HPLC.

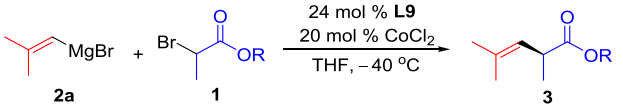
those of the parent bisoxazoline **L4**. However, 3,5-dimethyl bisoxazoline **L10** and 3.5-diisobutyl bisoxazoline **L11** furnished only 45−70% ee coupling product. The influence of other reaction parameters is depicted in Tables S1 and S2, and the absolute configuration of the cross-coupling product **3a** was confirmed as *S*.[11b]

A series of racemic α-bromo propionic esters could be coupled with isobutenyl magnesium bromide (**2a**) in the presence of $CoCl_2$ and bisoxazoline ligand **L9** (Table 1). All α-bromo propionic esters derived from aliphatic alcohols except cyclohexylmethanol (entry 8) exhibited good enantioselectivities (83−91%, entries 3−10). Likewise, esters derived from phenols (entries 11, 13, and 14), naphthol (entry 21), and benzyl alcohols (entries 1, 2, 15, 16, 18, and 19) afforded the alkenylation products with high enantioselectivities (81−90%). However, 3-fluorophenyl ester (**3l**) and 4-bromobenzyl ester (**3q**) gave only moderate enantioselectivity (74−76%, entries 12 and 17). It should be noted that 2-naphthenylmethyl ester was the best substrate and the coupling product **3t** was obtained with 93% ee in 79% yield (entry 20).

The scope of the substituents attached to the α-carbon of the bromo ester was next explored (Table 2). Excellent enantioselectivities and moderate to good yields were obtained (86−90% ee, 62−82% yield, entries 1−5) when the substituents were primary alkyl groups (Et, *n*-Bu, and *i*-Bu). Unfortunately, secondary substituents (*i*-Pr and cyclohexyl) gave poor results (32% ee, 28−46% yield, entries 6 and 7) due to their steric hindrance. α-Bromo ester bearing functionalized substituents, such as 2-bromoethyl (**5h**), allyl (**5i**), ester (**5j**), silyloxy (**5k**), and benzyl (**5l**), were tolerated with this coupling (66−88% ee, 52−65% yield, entries 8−12). However, the ester bearing 2-(5-methyl)furyl (**5m**) led to only 33% ee coupling product (entry 13).

To extend these enantioselective Kumada alkenylations with respect to the nucleophiles, we applied the same conditions to the cross-coupling of racemic benzyl 2-bromopropanoate (**1a**) with isopropenyl magnesium bromide (**2c**). However, desired alkenylation product **6c** was not obtained. Previous references[2d,13] demonstrated that HMTA could promote the

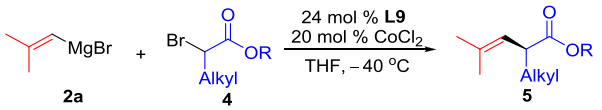
Table 1. Enantioselective Kumada Alkenylations of Racemic α-Bromo Propionic Esters[a]

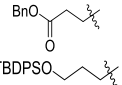
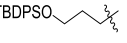
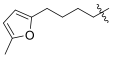


entry	R	product	yield (%)[b]	ee (%)[c]
1	Bn	**3a**	80	91
2	PMB	**3b**	60	90
3	*i*-Bu	**3c**	62	85
4	*i*-Pr	**3d**	70	91
5	*t*-Bu	**3e**	70	90
6	cyclopentyl	**3f**	75	83
7	cyclohexyl	**3g**	76	85
8	cyclohexylmethyl	**3h**	77	72
9	2-bromoethyl	**3i**	73	85
10	isopentenyl	**3j**	65	85
11	Ph	**3k**	61	86
12	3-F-C_6H_4	**3l**	63	76
13	4-Cl-C_6H_4	**3m**	59	81
14	4-Me-C_6H_4	**3n**	73	87
15	4-F-$C_6H_4CH_2$	**3o**	69	90
16	4-CF_3-$C_6H_4CH_2$	**3p**	58	86
17	4−Br-$C_6H_4CH_2$	**3q**	50	74
18	4-Me-$C_6H_4CH_2$	**3r**	75	90
19	4-*tert*-Bu-$C_6H_4CH_2$	**3s**	66	90
20	2-naphthenylmethyl	**3t**	79	93
21	2-naphthyl	**3u**	69	81

[a]All reactions were performed for 5 h, and 4.0 equiv of **2a** was used. [b]Isolated yields after chromatographic purification. [c]Values of ee were determined by chiral HPLC.

Table 2. Enantioselective Kumada Alkenylations of Racemic α-Bromo Esters[a]



entry	R	alkyl	product	yield (%)[b]	ee (%)[c]
1	PMB	Et	**5a**	82	90
2	Bn	Et	**5b**	76	90
3	PMB	*n*-Bu	**5c**	74	91
4	PMB	*i*-Bu	**5d**	62	86
5	Bn	*i*-Bu	**5e**	71	90
6	Bn	*i*-Pr	**5f**	46	32
7	PMB	cyclohexyl	**5g**	28	32
8	Et	2-bromoethyl	**5h**	52	73
9	PMB		**5i**	56	80
10	Bn		**5j**	56	85
11	Me		**5k**	65	66
12	PMB	Bn	**5l**	52	88
13	Me		**5m**	50	33

[a]All reactions were performed for 5 h, and 4.0 equiv of **2a** was used. [b]Isolated yields after chromatographic purification. [c]Values of ee were determined by chiral HPLC.

TMEDA-Fe-catalyzed cross-coupling of Grignard reagents. Fortunately, the promising result (44% yield, 53% ee) was

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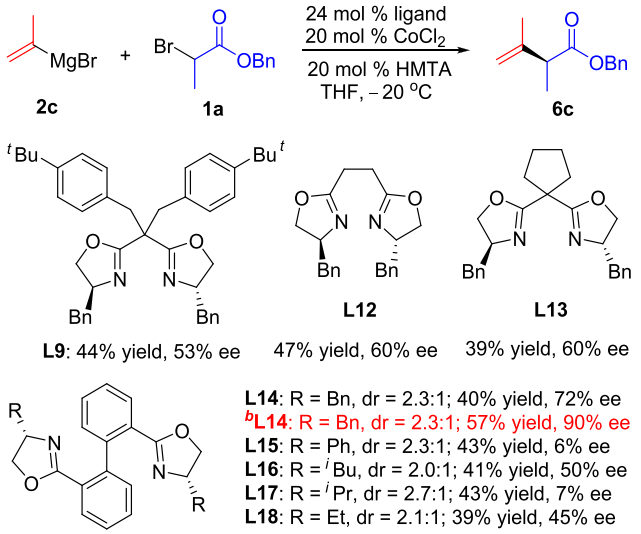
observed when we used HMTA as the additive. The other bisoxazoline ligands (**L12**–**L18**) were then surveyed (Scheme 2). Introduction of an ethanediyl (**L12**) and cyclopentane

Scheme 2. Ligand Screening in the Enantioselective Kumada Cross-Coupling of Isopropenyl Magnesium Bromide[a]



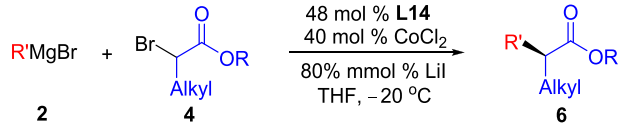
[a]All reactions were performed for 12 h, and 4.0 equiv of **2c** was used. Isolated yields after chromatographic purification. Values of ee were determined by chiral HPLC. [b]The reaction was conducted for 24 h; 80 mol % LiI, 40 mol % $CoCl_2$, and 48 mol % **L14** were used.

(**L13**) backbone resulted in a small increase in enantioselectivity, while biphenyl bisoxazoline **L14** afforded the alkenylation product with 72% ee. Varying the substitutions on oxazoline from benzyl to phenyl (**L15**), isobutyl (**L16**), isopropyl (**L17**), and ethyl (**L18**) significantly decreased the product ee. To optimize the reaction conditions, we tried LiI as the additive, which could improve the enantioselective alkenylation by stabilizing the cobalt ate complex.[12b,e,f] We were pleased to obtain an excellent result (57% yield, 90% ee), and the details about the optimizing reaction conditions are elaborated in Tables S3 and S4.

With the optimized conditions in hand, other alkenyl Grignard reagents were examined (Table 3). Vinyl magnesium bromide, as well as isopropenyl magnesium bromide, could be coupled with racemic α-bromo esters in high enantioselectivities and moderate yields (86–91% ee, 44–52% yield, entries 1–4 and 8). It was noteworthy that the commercial mixtures of (Z)- and (E)-alkenyl Grignard reagents could afford the (E)-coupling product with 92–95% ee, while lower enantioselectivities for (Z)-isomers were given (entries 5–7).

Taken together, these results show that the scope of this bisoxazoline-cobalt-catalyzed cross-coupling was broad. Thirty-four different α-bromo esters could be employed, while vinyl Grignard reagent, α- or β-monosubstituted, α,β-disubstituted, and β,β-disubstituted alkenylmagnesium were all suitable nucleophiles. However, there are some limitations associated with this new cross-coupling. Under the optimized conditions in Table 1, alkenylation products were detected by GC-MS in only 4%, 7%, and 2% when (1-bromoethyl)benzene, 2-bromo-1-phenylpropan-1-one, and 2-bromobutane, respectively, were used.

Table 3. Asymmetric Kumada Alkenylations of Racemic α-Bromo Esters with Alkenyl Grignard Reagents[a]

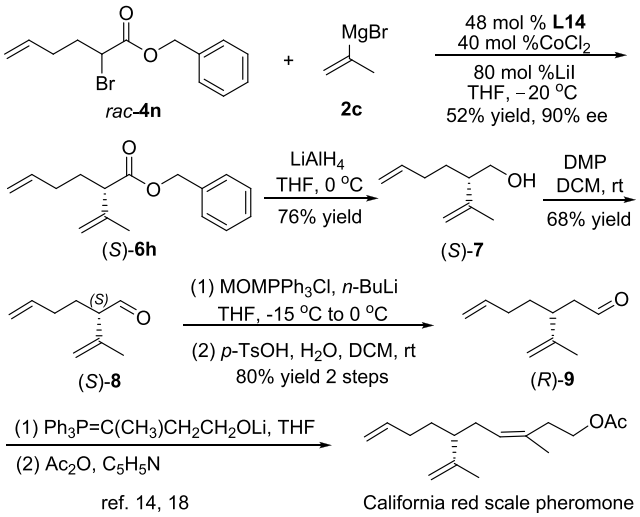


Entry	R'	R	alkyl	product	yield (%)[b]	E/Z	ee (%)[c]
1		Bn	Me	**6a**	50	–	90
2		PMB	Et	**6b**	44	–	86
3		Bn	Me	**6c**	57	–	90
4		PMB	Et	**6d**	54	–	91
5[d]		Bn	Me	**6e**	62	76/24	95(E) 78(Z)
6[d]		PMB	Et	**6f**	48	54/46	92(E) 44(Z)
7[d]		PMB	Et	**6g**	51	60/40	94(E) 88(Z)
8		Bn		**6h**	52	–	90

[a]All reactions were performed for 24 h, and 4.0 equiv of **2** was used. [b]Isolated yields after chromatographic purification. [c]Values of ee were determined by chiral HPLC. [d]**2** was a commercial mixtures of (Z)- and (E)-alkenyl magnesium bromide.

To demonstrate the utility of this enantioselective Kumada alkenylation, the formal synthesis of the California red scale pheromone, isolated from female *Aonidiella aurantii* (Maskell),[14] was investigated (Scheme 3). Our synthesis started

Scheme 3. Formal Synthesis of the California Red Scale Pheromone



from the enantioselective cross-coupling of racemic α-bromo ester **4n** with isopropenyl magnesium bromide (**2c**) to afford alkenylation product **6h** with 90% ee and 52% yield. Subsequent reduction with $LiAlH_4$[15] and Dess-Martin oxidation[16] generated chiral dienoic aldehyde **8**. The one-carbon elongation was then achieved via the Wittig reaction with methoxymethyltriphenylphosphonium chloride and the hydrolysis with p-toluenesulfonic acid,[17] and the key intermediate **9** was obtained in an 80% yield over two steps. The target California red scale pheromone could be prepared

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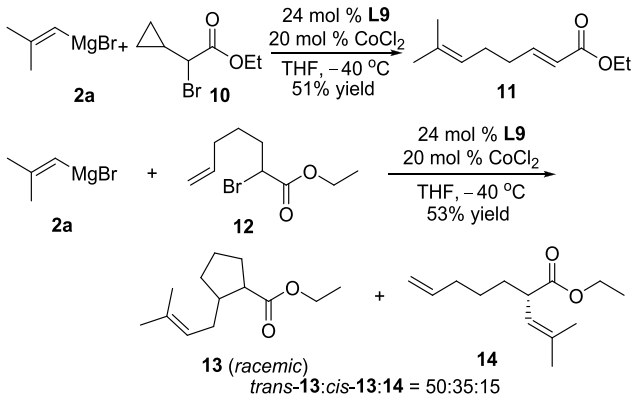
by Wittig alkenylation and acetylation according to the method described in the literature.[14,18]

To gain insight into the mechanism of this cobalt-bisoxazoline-catalyzed cross-coupling, radical clock experiments were performed (Scheme 4). The ring-opened product

Scheme 4. Cobalt-Catalyzed Reaction of Radical Probes 10 and 12 with Isobutenyl Magnesium Bromide



11 was obtained in 51% yield when α-bromocyclopropyl ester **10** was reacted with isobutenyl magnesium bromide (**2a**). However, another radical probe **12**, an α-bromo ester bearing a pendant olefin, afforded the mixtures of the cyclized cross-coupling product **13** and direct cross-coupling product **14** in 53% yield (85:15 **13**:**14**), which was similar to the nickel-catalyzed enantioselective Negishi reaction of α-bromosulfonamide.[7c] These results suggest that this Kumada enantioselective alkenylation mainly occurs via a radical intermediate consistent with other cobalt-catalyzed cross-coupling of alkyl halides.[12,19]

In conclusion, we have developed the first catalytic asymmetric Kumada cross-coupling of organic halides with alkenyl Grignard reagents. Various alkenyl Grignard reagents were coupled with 34 different α-bromo esters to afford highly enantioenriched α-alkyl-β,γ-unsaturated esters. Furthermore, this enantioselective Kumada alkenylation could be applied to the formal synthesis of the California red scale pheromone, and preliminary mechanistic investigations support the intermediacy of radicals.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01557.

Experimental procedures, optimization, characterization data, ^{1}H and ^{13}C NMR spectra, and HPLC chromatograms of the products. (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Dunkelblum, E.; Mendel, Z.; Gries, G.; Gries, R.; Zegelman, L.; Hassner, A.; Mori, K. *Bioorg. Med. Chem.* **1996**, *4*, 489. (b) Trost, B. M.; Burns, A. C.; Bartlett, M. J.; Tautz, T.; Weiss, A. H. *J. Am. Chem. Soc.* **2012**, *134*, 1474. (c) Hesse, M. J.; Butts, C. P.; Willis, C. L.; Aggarwal, V. K. *Angew. Chem., Int. Ed.* **2012**, *51*, 12444. (d) Zhou, Y.; Yang, P.; Li, S.; Wang, L.; Yin, J.; Zhong, J.; Dong, Y.; Liu, S.; Wang, M.; Bian, Q. *Tetrahedron: Asymmetry* **2017**, *28*, 338. (e) Murray, L. A. M.; Fallon, T.; Sumby, C. J.; George, J. H. *Org. Lett.* **2019**, *21*, 8312. (f) Itoh, H.; Inoue, M. *Chem. Rev.* **2019**, *119*, 10002. (g) Zhang, K.; Lu, L.-Q.; Xiao, W.-J. *Chem. Commun.* **2019**, *55*, 8716.

(2) (a) Nunomoto, S.; Kawakami, Y.; Yamashita, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2831. (b) Nunomoto, S.; Kawakami, Y.; Yamashita, Y. *J. Org. Chem.* **1983**, *48*, 1912. (c) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2006**, *8*, 3093. (d) Cahiez, G.; Duplais, C.; Moyeux, A. *Org. Lett.* **2007**, *9*, 3253. (e) Guerinot, A.; Reymond, S.; Cossy, J. *Angew. Chem., Int. Ed.* **2007**, *46*, 6521. (f) Shirakawa, E.; Imazaki, Y.; Hayashi, T. *Chem. Lett.* **2008**, *37*, 654.

(3) (a) Zhou, J.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 12527. (b) Wiskur, S. L.; Korte, A.; Fu, G. C. *J. Am. Chem. Soc.* **2004**, *126*, 82.

(4) (a) Miyaura, N.; Suzuki, A. *J. Chem. Soc., Chem. Commun.* **1979**, 866. (b) Miyaura, N.; Yamada, K.; Suzuki, A. *Tetrahedron Lett.* **1979**, *20*, 3437. (c) Miyaura, N.; Yano, T.; Suzuki, A. *Tetrahedron Lett.* **1980**, *21*, 2865. (d) Charette, A. B.; Giroux, A. *J. Org. Chem.* **1996**, *61*, 8718.

(5) (a) Shimizu, R.; Fuchikami, T. *Tetrahedron Lett.* **1996**, *37*, 8405. (b) Luh, T.-Y.; Leung, M.-k.; Wong, K.-T. *Chem. Rev.* **2000**, *100*, 3187. (c) Menzel, K.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 3718.

(6) Dai, X.; Strotman, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 3302.

(7) (a) Lou, S.; Fu, G. C. *J. Am. Chem. Soc.* **2010**, *132*, 5010. (b) Choi, J.; Fu, G. C. *J. Am. Chem. Soc.* **2012**, *134*, 9102. (c) Choi, J.; Martin-Gago, P.; Fu, G. C. *J. Am. Chem. Soc.* **2014**, *136*, 12161. (d) Pellissier, H.; Clavier, H. *Chem. Rev.* **2014**, *114*, 2775.

(8) Schafer, P.; Sidera, M.; Palacin, T.; Fletcher, S. P. *Chem. Commun.* **2017**, *53*, 12499.

(9) Grieco, P. A.; Hon, Y. S.; Perez-Medrano, A. *J. Am. Chem. Soc.* **1988**, *110*, 1630.
(10) Fehr, C.; Chaptal-Gradoz, N.; Galindo, J. *Chem. - Eur. J.* **2002**, *8*, 853.
(11) (a) Piva, O.; Henin, F.; Muzart, J.; Pete, J. P. *Tetrahedron Lett.* **1987**, *28*, 4825. (b) Piva, O.; Mortezaei, R.; Henin, F.; Muzart, J.; Pete, J. P. *J. Am. Chem. Soc.* **1990**, *112*, 9263. (c) Henin, F.; Letinois, S.; Muzart, J. *Tetrahedron: Asymmetry* **2000**, *11*, 2037. (d) Murphy, K. E.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 4690. (e) Murphy, K. E.; Hoveyda, A. H. *Org. Lett.* **2005**, *7*, 1255.
(12) (a) Someya, H.; Ohmiya, H.; Yorimitsu, H.; Oshima, K. *Org. Lett.* **2007**, *9*, 1565. (b) Cahiez, G.; Habiak, V.; Duplais, C.; Moyeux, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 4364. (c) Cahiez, G.; Chaboche, C.; Duplais, C.; Moyeux, A. *Org. Lett.* **2009**, *11*, 277. (d) Mao, J.; Liu, F.; Wang, M.; Wu, L.; Zheng, B.; Liu, S.; Zhong, J.; Bian, Q.; Walsh, P. J. *J. Am. Chem. Soc.* **2014**, *136*, 17662. (e) Bergbreiter, D. E.; Whitesides, G. M. *J. Org. Chem.* **1975**, *40*, 779. (f) Kreyenschmidt, F.; Koszinowski, K. *Chem. - Eur. J.* **2018**, *24*, 1168.
(13) Cahiez, G.; Habiak, V.; Duplais, C.; Moyeux, A. *Angew. Chem., Int. Ed.* **2007**, *46*, 4364.
(14) Roelofs, W.; Gieselmann, M.; Carde, A.; Tashiro, H.; Moreno, D. S.; Henrick, C. A.; Anderson, R. J. *J. Chem. Ecol.* **1978**, *4*, 211.
(15) Dai, X.; Strotman, N. A.; Fu, G. C. *J. Am. Chem. Soc.* **2008**, *130*, 3302.
(16) Lee, T.; Jones, J. B. *J. Am. Chem. Soc.* **1996**, *118*, 502.
(17) Xu, B.; Xun, W.; Wang, T.; Qiu, F. G. *Org. Lett.* **2017**, *19*, 4861.
(18) Hutchinson, J. H.; Money, T. *Can. J. Chem.* **1985**, *63*, 3182.
(19) (a) Tsuji, T.; Yorimitsu, H.; Oshima, K. *Angew. Chem., Int. Ed.* **2002**, *41*, 4137. (b) Ohmiya, H.; Tsuji, T.; Yorimitsu, H.; Oshima, K. *Chem. - Eur. J.* **2004**, *10*, 5640. (c) Ikeda, Y.; Nakamura, T.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2002**, *124*, 6514. (d) Ohmiya, H.; Yorimitsu, H.; Oshima, K. *J. Am. Chem. Soc.* **2006**, *128*, 1886.

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