



Transition-Metal-Free Benzannulation for Diverse and Polyfunctionalized Biaryl Formation

Tej Narayan Poudel and Yong Rok Lee*

School of Chemical Engineering, Yeungnam University, Gyeongsan 712-749, Republic of Korea

(5) Supporting Information



ABSTRACT: A novel and efficient synthesis of highly functionalized and diverse biaryls via mild base-promoted transitionmetal-free benzannulation was achieved in good yield from readily available β -ketoesters, β -ketoamides, or 1,3-diketones with cinnamaldehydes or aryl aldehydes. This transformation comprises a sequence of the formation of three new bonds through multicomponent reactions as a one-pot procedure. This novel biaryl formation proceeds through domino Michael addition/ intramolecular and intermolecular aldol/[1,5]-hydrogen shift/tautomerization. This protocol provides a great advantage in introducing various functional groups on the aromatic ring of biaryls.

B iaryl units are one of the most important structural motifs found in biologically active natural products, pharmaceuticals, and agrochemicals.¹ They are used widely as important scaffolds and building blocks for the construction of optical and functional materials.² Several methods for aryl-aryl bond formation have been reported. Among these, transition-metalcatalyzed traditional cross-coupling (Suzuki, Stille, Hiyama, etc.) has become a useful tool for constructing an Ar-Ar bond by the reaction of aryl halides and aryl metals (path a, Scheme 1).³

Scheme 1. Transition-Metal-Catalyzed Biaryl Formation Using Cross-Coupling Reactions



Recently, transition-metal-catalyzed C–H arylation (path b, Scheme 1)⁴ and the oxidative cross-coupling of arenes (path c, Scheme 1)⁵ have emerged as an important cross-coupling strategy to form Ar–Ar bonds. This direct arylation reduces the number of synthetic steps and has the advantages of lower cost and environmental benignity. Although a number of methods for the direct formation of an Ar–Ar bond by transition-metal-catalyzed reactions have been well developed, the loading of catalyst tends to have a high economic cost in industrial processes.

Therefore, the development of a facile transition-metal-free process is essential and quite significant. Recently, several transition-metal-free methods for the formation of aryl-aryl bonds have been developed.⁶ These approaches include the arylation of arenes by aryl halides in the presence of strong alkali metal bases and ligand, which proceed via a radical-type mechanism. These reactions provide biaryl molecules by cross-coupling between the two aromatic rings of the aryl metals and aryl halides, arenes and aryl halides, or arenes and arenes.⁷

Recently, direct biaryl formation through the hydroarylation of arynes (path a, Scheme 2)⁸ or hexadehydro Diels–Alder reaction





(path b, Scheme 2)⁹ has been reported without cross-coupling reactions between two aromatic compounds. These reactions provide various complex molecules bearing biaryl skeletons by benzannulation through aryne intermediates.

Currently, benzannulation is one of the most important reactions for the formation of substituted benzenes.¹⁰ Over the past decade, several synthetic methods for benzannulation have been reported by Diels–Alder reaction,¹¹ Bergman cyclization,¹²

Received:February 10, 2015Published:April 15, 2015

Danheiser annulation,¹³ ring-closing metathesis,¹⁴ Dötz [3 + 2 + 1] reaction,¹⁵ Wulff [5 + 1] ortho benzannulation,¹⁶ and rhodium(II)-catalyzed benzannulation.¹⁷ Moreover, synthesis of phenol derivatives by benzannulation from 1,3-dicarbonyls and Michael acceptors have been also reported.¹⁸ Herein, we report a novel, facile and efficient one-pot biaryl formation through a three-component reaction starting from commercially available β -ketoesters, β -ketoamides, or 1,3-diketones with α , β -unsaturated aldehydes (eq 1) or α , β -unsaturated aldehydes (eq 2, Scheme 3) in the presence of mild base.

Scheme 3. Diverse and Polysubstituted Biaryl Formation by Benzannlation through Three-Component Reactions



Multicomponent reactions of 1,3-dicarbonyls have received great attention in the past few years in the sythesis of diverse and complex organic molecules.¹⁹ A number of Michael additions of 1,3-dicarbonyl compounds to α,β -unsaturated aldehydes have been explored by many groups to afford various useful organic molecules.^{20,21} Among these, representative approaches include *N*-heterocyclic carbene-catalyzed Michael addition for dihydropyranones,²⁰ organocatalytic domino reactions for epoxycyclohexanones, and multicatalytic cascade reactions to furnish cyclopentanes.²¹

To afford the Michael addition products, the reactions of methyl acetoacetate (1a) with cinnamaldehyde (2a) were first attempted under several bases and solvents. The results are listed in Table 1. Reaction of methyl acetoacetate (1a, 0.5 mmol) and

 Table 1. Reaction of Methyl Acetoacetate (1a) with

 Cinnamaldehyde (2a) under Several Conditions

_	0 0 OCH ₃ + 1a		onditions		°OCH₃
entry	mmol (1a:2a)	base	solvent	condition	yield (%)
1	0.5:0.5	TEA (0.5 mmol)	toluene	reflux, 12 h	0
2	0.5:0.5	DBU (0.5 mmol)	toluene	reflux, 12 h	15
3	0.5:1.0	DBU (0.5 mmol)	toluene	reflux,12 h	35
4	0.5:1.0	NaOMe(0.5 mmol)	toluene	reflux, 6 h	63
5	0.5:1.0	K ₂ CO ₃ (0.5 mmol)	toluene	reflux, 6 h	71
6	0.5:1.0	Cs ₂ CO ₃ (0.5 mmol)	toluene	reflux, 4 h	83
7	0.5:1.0	Cs ₂ CO ₃ (1.0 mmol)	toluene	reflux, 4 h	80
8	0.5:1.0	Cs ₂ CO ₃ (0.05 mmol)	toluene	reflux, 12 h	30
9	0.5:1.0	Cs ₂ CO ₃ (0.1 mmol)	toluene	reflux, 12 h	42
10	0.5:1.0	Cs ₂ CO ₃ (0.5 mmol)	benzene	reflux, 12 h	61
11	0.5:1.0	Cs ₂ CO ₃ (0.5 mmol)	DCE	reflux, 12 h	10
12	0.5:1.0	Cs ₂ CO ₃ (0.5 mmol)	DMSO	reflux, 12 h	0
13	0.5:1.0	Cs ₂ CO ₃ (0.5 mmol)	water	reflux, 12 h	0

cinnamaldehyde (2a, 0.5 mmol) in the presence of triethylamine (1.0 equiv) in refluxing toluene for 12 h did not give any products; instead, the starting materials were recovered (entry 1, Table 1). Upon treatment of 1a (0.5 mmol) with 2a (0.5 mmol) in the presence of DBU (1.0 equiv) in refluxing toluene for 12 h, unexpected aromatic compound 3 was produced in 15% yield through a pseudo-three-component reaction between methyl acetoacetate and two cinnamaldehydes (entry 2). With 2 equiv of

cinnamaldehyde (2a), the yield of 3 was increased to 35%. To increase the yield, other bases were next examined. With NaOMe (1.0 equiv) and K_2CO_3 (1.0 equiv) in refluxing toluene, product 3 was formed in 63 and 71% yield, respectively. Importantly, the yield of 3 was increased to 83% when the reaction was carried out in the presence of Cs_2CO_3 (1.0 equiv) in refluxing toluene for 4 h. Cs₂CO₃ was found to be superior to other bases in this cascade process. Recently, Cs₂CO₃ has been widely used as an excellent base in various organic transformations because of its mild base strength.²² With the use of higher (2.0 equiv) or lower (0.2 equiv)catalytic amounts of Cs_2CO_3 in refluxing toluene, the yield of 3 did not increase. For other solvents, the reaction in refluxing benzene or 1,2-dichloroethane (DCE) provided compound 3 in 61 and 10% yield, respectively. However, product 3 was not formed in polar solvents, such as dimethyl sulfoxide (DMSO) or water. The structure of 3 was determined by analyzing the spectral data. The ¹H NMR spectrum of **3** showed a characteristic singlet peak for the -OH group at δ 10.88 ppm, benzylic methylene protons at δ 3.60 ppm (I = 6.0 Hz) as a doublet, two vinylic protons at δ 6.46–6.37 ppm as multiplets, and at δ 6.50 ppm as a doublet (J = 15.9 Hz). The coupling constant value of 15.9 Hz suggests the E-configuration of the double bond. The regio- and stereochemistry of 3 was deduced from the X-ray crystallographic analysis of structurally related compound 14 (see the Supporting Information).

To examine the generality and scope of this methodology, additional reactions of β -ketoesters, β -ketoamides, or 1,3-diketones with several cinnamaldehydes were next carried out under optimized conditions. The results are summarized in Table 2. The reactions between methyl acetoacetate (1a) and

Table 2. Additional Reactions for the Synthesis	s of Various
Polysubstituted Diaryl Compounds ^a	

	R1	+ R ² O R ³ 2		Cs ₂ CO ₃ toluene reflux	→_R ³	R ² 4-29	R ²	R ¹					
entry		1		2		time (h)	product	yield (%)					
,		R'		R²	R°								
1	1a	OMe	2b	н	OMe	7.0	4	77					
2	1a	OMe	2c	н	F	5.0	5	78					
3	1b	OEt	2a	Н	H	4.0	6	79					
4	1b	OEt	2b		OMe	6.U 5.0	7	/1					
5	1b	OEt	2c		F	3.0	8	81					
6	1c	OCH ₂ CH=CH ₂	2a	п ц	н	4.0	10	00 70					
7	1c	OCH ₂ CH=CH ₂	2c	п 0М-	F	4.5	10	79					
8	1d	OCH ₂ Ph	2d	OMe	н	6.5	11	/4					
9	1e	PhNH	2a		н	4.5	12	04					
10	1e	PhNH	2c	н	F	5.5	13	78					
11	1f	4-MeOC ₆ H ₄ NH	2a		н	4.5	14	70					
12	11	4-MeOC ₆ H ₄ NH	2b	н	OMe	7.5	16	73					
13	1f	4-MeOC ₆ H ₄ NH	2C	н	F	5.5	10	81					
14	1g	4-MeC ₆ H ₄ NH	2a	н	н	5.5	17	76					
15	1g	4-MeC ₆ H ₄ NH	26	н	OMe	8.0	18	76					
16	1g	4-MeC ₆ H ₄ NH	20	н	F	4.5	19	80					
17	1h	2-MeC ₆ H ₄ NH	2a	н	н	5.5	20	74					
18	1h	2-MeC ₆ H ₄ NH	20	н	F	5.0	21	78					
19	1i	4-CIC ₆ H ₄ NH	2a	н	н	5.0	22	76					
20	1i	4-CIC ₆ H ₄ NH	2b	н	OMe	7.5	23	78					
21	1i	4-CIC ₆ H ₄ NH	20	H	F	4.5	24	78					
22	11		20		н	5.5	25	75					
23	11		2a 25	н	н	5.0	26	74					
24	1)		20	н	OMe	8.0	27	71					
25	11	Z-CIC6H4NH	20	н	F	5.0	28	/6					
20	1K	We	Za	п	н	0.0	29	48					
^a Reaction conditions: 1,3-diketones (1, 0.5 mmol), cinnamaldehydes													
(2.10)	mmo	(2, 10 mmol) Cs.CO. $(0.5 mmol)$ and toluene $(5.0 mL)$											

cinnamaldehydes **2b**,**c** bearing electron-donating (-OMe) or electron-withdrawing group (-F) on the 4-position of the benzene ring in the presence of Cs_2CO_3 in refluxing toluene provided products **4** and **5** in good yields (entries 1 and 2, Table 2). Similarly, reactions of ethyl acetoacetate (**1b**) with cinnamaldehydes **2a**-**c** were also successful and afforded the

products 6-8 in good yields (entries 3-5, Table 2). With allyl 3oxobutanoate (1c) or benzyl 3-oxobutanoate (1d), the expected products 9-11 were produced in a range of 74-80% yield (entries 6-8). The substrate scope was also extended successfully with various β -ketoamides. The treatment of **2a** or **2c** with 3-oxo-N-phenylbutanamide (1e) provided compounds 12 and 13 in good yields (entries 9–10). With β -ketoamides bearing an electron-donating (-OMe, -Me) or electron-withdrawing group (-Cl) at the 2- or 4-position on benzene, the desired products were obtained with good yields. For example, with N-(4-methoxyphenyl)-3-oxobutanamide (1f), 3-oxo-N-p-tolylbutanamide (1g), and 3-oxo-*N*-*o*-tolylbutanamide (1h) having electron-donating groups on the benzene ring, products 14-21 were produced in the range of 73-81% yield (entries 11-18). When N-(4-chlorophenyl)-3-oxobutanamide (1i) and N-(2chlorophenyl)-3-oxobutanamide (1j) bearing electron-withdrawing groups were used, products 22-28 were isolated in good yields (entries 19-25). On the other hand, reaction of 2,4pentanedione (1k) with cinnamaldehyde (2a) provided desired compound 29 with decreased yield (48%) (entry 26) compared to that of ketoesters or ketoamides.

Scheme 4 presents a proposed mechanism for the formation of 3 through Cs_2CO_3 -mediated multicomponent cascade reaction.

Scheme 4. Proposed Mechanism for the Formation of 3



In basic medium, the Michael addition of the enolate 30 to 2a forms intermediate 31, which then undergoes intramolecular aldol reaction to give another intermediate 32. The aldol-type reaction of 32 with 2a in the basic medium produces 33, which further undergoes 1,5-H shift followed by tautomerization to form the final product 3.

To prove this mechanism, control experiments were carried out. Isolation of the intermediate **31** under several bases such as K_2CO_3 , NaHCO₃, and Na₂CO₃ at room temperature was not successful. Therefore, we performed an additional experiment using cinnamaldehyde-3-*d* (**2e**) under optimized reaction conditions (Scheme 5). Importantly, reaction of **1f** with **2e** in





refluxing toluene for 5 h provided the desired product 34 bearing a deuterium on each of the benzylic carbons in 71% yield. This result shows that the reaction pathway proceeds through the formation of intermediate 33 followed by [1,5]-H shift.

The additional control experiments of Michael donor ability of two different 1,3-dicarbonyl compounds **1a** and **1e** were explored (Scheme 6). The reaction of β -ketoester **1a** (0.5 mmol) and β -





ketoamide 1e (0.5 mmol) with cinnamaldehyde (2a, 1.0 mmol) in the presence of 0.5 mmol of Cs_2CO_3 in refluxing toluene for 6 h provided products 3 and 12 in 30 and 45% yield, respectively (eq 1, Scheme 6). This result did not show a significant difference in the Michael donor ability between β -ketoester and β -ketoamide, but *N*-phenyl-substituted β -ketoamide was found to be a slightly better Michael donor than β -ketoester. A further control experiment was attempted to explore the reactivity of different cinnamaldehydes. The reactions of 1a (0.5 mmol) with three different cinnamaldehydes 2a-c (1.0 mmol, each) bearing no substituent, electron-donating, and electron-withdrawing groups in refluxing toluene for 6 h provided compound 5 in 60% yield (eq 2, Scheme 6). This result suggests that the electronwithdrawing group on the cinnamaldehyde moiety acts as an excellent Michael acceptor compared to cinnamaldehyde bearing no substituent or electron-donating groups.

Having seen the general applicability of the multicomponent reactions between β -ketoesters or β -ketoamides and cinnamaldehydes, other cross-cascade reactions were next attempted for the synthesis of the benzyl-substituted biaryls (Scheme 7). The

Scheme 7. Additional Synthesis for Biaryls 36–39 by Three-Component Reactions of 1,3-Dicarbonyl Compounds and Arylaldehydes with 4-Methoxycinnamaldehyde



reaction of β -ketoester 1a with cinnamaldehyde (2a) and benzaldehyde (35a) did not observe any desired biaryl product with 2a and 35a being incorporated; instead, product 3 was isolated in 36% yield. With 4-fluorocinnamaldehyde (2c) and benzaldehyde (35a), compound 5 was produced in 37% yield. However, the reaction of 1a with 4-methoxycinnamaldehyde (2b) and 2-chlorobenzaldehyde (35b) in refluxing toluene for 6.5 h provided product 36 in 66% yield. The combinations of β ketoester 1b or β -ketoamides 1g and 1i with 2b and 35b or 35c provided the corresponding products 37–39 in 68, 65, and 63% yield, respectively.

To further demonstrate the versatility of this multicomponent reaction, we examined the reactions with 3-(furan-2-yl)-acrylaldehyde (2f) or 3-(anthracen-9-yl)acrylaldehyde (2g) for the synthesis of various biaryls bearing furanyl or anthracenyl ring (Scheme 8). The reactions of 1a-c or 1i with 2f in refluxing toluene for 4-5 h afforded the corresponding products 40-43 in

Scheme 8. Additional Reactions for the Synthesis of Diverse Biaryls 40–45 Bearing Furanyl or Anthracenyl Rings



Scheme 9. Synthetic Applications of the Synthesized Compounds 3 and 14



the range of 74–77% yield. With **2g** bearing an anthracenyl ring, the desired products **44** and **45** were isolated in 62% and 60% yield, respectively.

As an application of this methodology, consequently, the conversion of the synthesized compounds 3 and 14 to new molecules using catalytic hydrogenation and cyclization reaction was attempted (Scheme 9). The catalytic hydrogenation of 3 and 14 over Pd/C (30 psi) at room temperature for 8 h provided 46 and 47 in high yields. Treatment of 3 and 14 in the presence of DDQ in refluxing benzene for 12 h afforded the corresponding chromenes 48 and 49 in 63 and 65% yield, respectively.

In summary, we have developed a simple, cost-effective, transition-metal-free, and mild base-promoted novel cascade reaction for the synthesis of diverse and polysubstituted biaryls starting from readily available β -ketoesters, β -ketoamides, or 1,3-diketones with α , β -unsaturated aldehydes or arylaldehydes in good yield. This novel benzannulation involves the domino Michael addition/intramolecular and intermolecular aldol/[1,5]-hydrogen shift and tautomerization.

ASSOCIATED CONTENT

Supporting Information

Experimental procedures, characterization data, and ¹H NMR and ¹³C NMR spectra for synthesized compounds. X-ray data for **14** (CCDC 1047083). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: yrlee@yu.ac.kr.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the Nano Material Technology Development Program of the Korean National Research Foundation (NRF) funded by the Korean Ministry of Education, Science, and Technology (Grant No. 2012-049675). This work was also supported by the Korean National Research Foundation (NRF) grant funded by the Korean government (MSIP) (NRF-2014R1A2A1A11052391).

REFERENCES

(1) Bringmann, G.; Gulder, T.; Gulder, T. A. M.; Breuning, M. Chem. Rev. 2011, 111, 563.

(2) (a) Ashenhurst, J. A. *Chem. Soc. Rev.* **2010**, 39, 540. (b) Corbet, J.-P.; Mignani, G. *Chem. Rev.* **2006**, 106, 2651.

(3) (a) Suzuki, A.; Miyaura, N. *Chem. Rev.* **1995**, *95*, 2457. (b) Seechurn, C. C. C. J.; Kitching, M. O.; Colacot, T. J.; Snieckus, V. *Angew. Chem., Int. Ed.* **2012**, *51*, 5062.

(4) (a) Alberico, D.; Scott, M. E.; Lautens, M. Chem. Rev. 2007, 107, 174.
(b) Seregin, I. V.; Gevorgyan, V. Chem. Soc. Rev. 2007, 36, 1173.
(c) Ackermann, L.; Vicente, R.; Kapdi, A. R. Angew. Chem., Int. Ed. 2009, 48, 9792.

(5) (a) Zhao, X.; Yeung, C. S.; Dong, V. M. J. Am. Chem. Soc. 2010, 132, 5837. (b) Wei, Y.; Su, W. J. Am. Chem. Soc. 2010, 132, 16377. (c) Cho, S. H.; Kim, J. Y.; Kwak, J.; Chang, S. Chem. Soc. Rev. 2011, 40, 5068. (d) Kuhl, N.; Hopkinson, M. N.; Wencel-Delord, J.; Glorius, F. Angew. Chem., Int. Ed. 2012, 51, 10236.

(6) (a) Sun, C.-L.; Li, H.; Yu, D.-G.; Yu, M.; Zhou, X.; Lu, X.-Y.; Huang, K.; Zheng, S.-F.; Li, B.-J.; Shi, Z.-J. Nat. Chem. 2010, 2, 1044.
(b) Shirakawa, E.; Itoh, K.-i.; Higashino, T. J. Am. Chem. Soc. 2010, 132, 15537. (c) Liu, W.; Cao, H.; Zhang, H.; Zhang, H.; Chung, K. H.; He, C.; Wang, H.; Kwong, F. Y.; Lei, A. J. Am. Chem. Soc. 2010, 132, 16737.

(7) (a) Yanagisawa, S.; Ueda, T.; Taniguchi, T.; Itami, K. Org. Lett.
2008, 10, 4673. (b) Stunder, A.; Curran, D. P. Angew. Chem., Int. Ed.
2011, 50, 5018. (c) Shirakawa, E.; Zhang, X.; Hayashi, T. Angew. Chem., Int. Ed. 2011, 50, 4671.

(8) Lee, N.-K.; Yun, S. Y.; Mamidipalli, P.; Salzman, R. M.; Lee, D.; Zhou, T.; Xia, Y. J. Am. Chem. Soc. 2014, 136, 4363.

(9) Hoye, T. R.; Baire, B.; Niu, D.; Willoughby, P. H.; Woods, B. P. *Nature* **2012**, *490*, 208.

(10) (a) Zhu, S.; Xiao, Y.; Guo, Z.; Jiang, H. Org. Lett. 2013, 15, 898.
(b) Zatolochnaya, O. V.; Gevorgyan, V. Org. Lett. 2013, 15, 2562.

(11) (a) Evans, D. A.; Chapman, K. T.; Bisaha, J. J. Am. Chem. Soc. 1988,

110, 1238. (b) Corey, E. J.; Shibata, T.; Lee, T. W. J. Am. Chem. Soc. 2002, 124, 3808. (c) Ahrendt, K. A.; Borths, C. J.; MacMillan, D. W. C. J. Am. Chem. Soc. 2000, 122, 4243.

(12) (a) Jones, R. R.; Bergman, R. G. J. Am. Chem. Soc. 1972, 94, 660.
(b) Bergman, R. G. Acc. Chem. Res. 1973, 6, 25. (c) Mohamed, R. K.; Peterson, P. W.; Alabugin, I. V. Chem. Rev. 2013, 113, 7089.

(13) Danheiser, R. L.; Carini, D. J.; Basak, A. J. Am. Chem. Soc. 1981, 103, 1605.

(14) Yoshida, K.; Imamoto, T. J. Am. Chem. Soc. 2005, 127, 10470.

(15) (a) Dötz, K. H. Angew. Chem., Int. Ed. 1975, 14, 644. (b) White, J. D.; Smits, H. Org. Lett. 2005, 7, 235. (c) Dötz, K. H. Angew. Chem., Int. Ed. 1984, 23, 587.

(16) (a) Wulff, W. D.; Tang, P.-C.; McCallum, J. S. J. Am. Chem. Soc. 1981, 103, 7677. (b) Rawat, M.; Wulff, W. D. Org. Lett. 2004, 6, 329. (c) Lian, Y.; Wulff, W. D. J. Am. Chem. Soc. 2005, 127, 17162.

(17) Dawande, S. G.; Kanchupalli, V.; Kalepu, J.; Chennamsetti, H.; Lad, B. S.; Katukojvala, S. *Angew. Chem., Int. Ed.* **2014**, *53*, 4076.

(18) (a) Geirsson, J. K. F.; Johannesdottir, J. F. J. Org. Chem. **1996**, 61, 7320. (b) Covarrubias-Zuniga, A.; Rios-Barrios, E. J. Org. Chem. **1997**, 62, 5688. (c) Terzidis, M. A.; Tsoleridis, C. A.; Stephanidou-Stephanatou, J.; Terzis, A.; Raptopoulou, C. P.; Psycharis, V. Tetrahedron **2008**, 64, 11611.

(19) (a) Simon, C.; Constantieux, T.; Rodriguez, J. *Eur. J. Org. Chem.* **2004**, 4957. (b) Lieby-Muller, F.; Simon, C.; Thierry Constantieux, T.; Rodriguez, J. *QSAR Comb. Sci.* **2006**, *25*, 432. (c) Bonne, D.; Coquerel, Y.; Constantieux, T.; Rodriguez, J. *Tetrahedron: Asymmetry* **2010**, *21*, 1085. (d) Bugaut, X.; Constantieux, T.; Coquerel, Y.; Rodriguez, J. *Multicomponent Reactions in Organic Synthesis*; Zhu, J., Wang, Q., Wang, M.-X., Eds.; Wiley-VCH: Weinheim, 2014; Chapter 5, p 109.

(20) (a) Sarkar, S. D.; Studer, A. Angew. Chem., Int. Ed. 2010, 49, 9266.
(b) Rong, Z.-Q.; Jia, M.-Q.; You, S.-L. Org. Lett. 2011, 13, 4080.

(21) (a) Lathrop, S. P.; Rovis, T. J. Am. Chem. Soc. 2009, 131, 13628.
(b) Marigo, M.; Bertelsen, S.; Landa, A.; Jorgensen, K. A. J. Am. Chem. Soc. 2006, 128, 5475.

(22) Poudel, T. N.; Lee, Y. R. Org. Biomol. Chem. 2014, 12, 919.