LETTERS

Catalytic Diazosulfonylation of Enynals toward Diazoindenes via Oxidative Radical-Triggered 5-exo-trig Carbocyclizations

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Supporting Information

ABSTRACT: Catalytic diazosulfonylation of enynals with arylsulfonyl hydrazides has been established by using *tert*-butyl hydroperoxide (TBHP) as the oxidant with tetrabutylammonium iodide (TBAI) under a convenient system. The reaction occurred through oxidative radical-triggered *5-exo-trig* carbocyclization cascading to afford sulfonylated diazoindenes regioselectively. The new diazosulfonylation reaction features a broad substrate scope readily accessible starting materials and a simple



a broad substrate scope, readily accessible starting materials, and a simple one-pot process.

iazo compounds have been widely utilized in organic synthesis and appear as ubiquitous structural motifs that exist in many natural products and therapeutic agents.¹ For example, the kinamycins (e.g., A–D, F, and J) are endowed with a diazofluorene unit which is responsible for potent biological properties including antibiotic and antitumor activities.² There have been numerous examples in which diazo compounds served as versatile building blocks due to their accessibility and attractive functionalization potential via dediazoniation.³ Among them, transition-metal-catalyzed reactions of diazo compounds have taken a dominant position, enabling powerful access to the formations of carbon-carbon and carbon-heteroatom bonds via additions and insertions of highly reactive metal carbene intermediates.⁴ The significant biological interests and synthetic profiles of diazo compounds have triggered the development of novel methods to incorporate diazo functionality into more challenging structures.⁵ So far, the vast majority of wellestablished routes for accessing diazo compounds have been represented by the following: diazotization of activated methylene compounds (Scheme 1, Route I)⁶ and primary amines (Route II),⁷ alkaline cleavage of N-alkyl-N-nitrosoureas (Route III),⁸ dehydrogenation of hydrazones (Route IV),⁹ cleavage by treating sulfonylhydrazones with bases (Route V),¹⁰ and structural modifications of an existing diazo compound (Route

Scheme 1. Synthetic Routes to Diazo Compounds



VI).¹¹ Although significant advances have been made in the past several decades, a few crucial issues still remain in regard to the limited substrate scopes, the use of expensive and toxic transition metals, and the thermal lability of pregenerated diazo precursors and their potential safety concerns. Therefore, the exploration of an efficient access toward new diazo compounds associated with these challenges would be among the most attractive but intractable tasks. Radical-based cascades offer a strategic platform for the construction of densely functionalized structures in convergent manners through orchestrated multiple C-C/C-X bond formations.¹² Over the years, alkynes act as good radical acceptors and allow radical-triggered addition across a triple bond to access their functionalization with high compatibility.¹³ Recently, sulfonylation of alkynes via sulfonyl radicals generated in situ from sulfonohydrazides has attracted special attention, because it can provide an effective pathway to sulfones with significant synthetic potential under mild conditions.¹⁴ Very recently, our groups have also reported the addition of arylsulfonyl radicals to 1,5-enynes as a way to trigger a sulfonylation/5-exo-dig/6-endo-trig bicyclization sequence.¹⁵ Considering the direct conversion of sulfonylhydrazones into diazo compounds¹⁰ and our ongoing project on radical-based methodologies,¹⁶ we envisioned that introducing an sulfonylhydrazone group onto the *ortho* position of the aromatic ring of an aryl alkyne would be able to control the regioselectivity of the initial radical addition to the C \equiv C conjugate system,¹³ enabling C–S and C–C bond forming events across alkynes to assemble densely functionalized carbocycles. Herein, we would like to report the successful realization of this analysis with the introduction of an arylsulfonyl radical for the flexible synthesis of unprecedented sulfonylated diazoindenes in a highly selective and functional-group-compatible fashion (Scheme 2). In this



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Scheme 2. Exploration of New Reactivity of Enynal



reaction, arylsulfonyl hydrazides were found to play dual roles as both diazo source and arylsulfonyl radical precursor.

2-(Phenylethynyl)benzaldehyde 1a was initially selected as the benchmark substrate to study the radical addition-cyclization reaction with p-toluenesulfonyl hydrazide 2a. This model reaction was first performed by using different oxidants, such as tert-butyl hydroperoxide (TBHP), tert-butyl peroxybenzoate (TBPB), and di-tert-butyl peroxide (DTBP) in the presence of tetrabutylammonium iodide (TBAI) in an acetonitrile solution. The use of 70% TBHP in aqueous solution gave the unprecedented diazoindene 3a, albeit with a low yield of 21%. An increased yield was obtained when TBPB was employed as the oxidant. The reaction did not give product 3a by using the DTBP oxidant. Delightedly, the anhydrous TBHP showed the best performance (41%), indicating that water inhibited this reaction. We thus utilized the anhydrous system for further optimization. Replacing TBAI with KI or CuI resulted in relatively lower yields of 3a, whereas iodine can hardly facilitate the reaction speed. Next, different dry solvents, such as DMSO, EtOH, and toluene, were examined. We observed diazoindene 3a in 33% yield together with some unreacted sulforylhydrazones (entry 8). Other solvents including EtOH and toluene were found to be less effective (entries 9-10). Then, 4 Å molecular sieves (MS) were added into the reaction system, resulting in a higher yield of 46% (entry 11). Eventually, the combination of acetonitrile with DMSO allowed us to isolate 3a in 53% yield, as shown in Table 1, entry 12 (see Supporting Information (SI)).

Tal	ole	1. (Optimization	Conditions f	or	Forming 3a ⁴⁴	
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	CHO 1a	H₂NHN 2a Ts + H₂NHN ^{∕Ts} 2a	cat., oxidant solvent, 70 °C N2 Ph 3a	
entry	cat. (mol %)	oxidant	solvent	yield (%) ^b
1	TBAI (20)	TBHP ^c	CH ₃ CN	21
2	TBAI (20)	TBPB	CH ₃ CN	32
3	TBAI (20)	DTBP	CH ₃ CN	N.D.
4	TBAI (20)	TBHP ^d	CH ₃ CN	41
5	KI (20)	TBHP ^d	CH ₃ CN	17
6	$I_2(10)$	TBHP ^d	CH ₃ CN	N.D.
7	CuI (5)	TBHP ^d	CH ₃ CN	27
8	TBAI (20)	TBHP ^d	DMSO	33
9	TBAI (20)	TBHP ^d	EtOH	trace
10	TBAI (20)	TBHP ^d	toulene	7
11	TBAI (20)	TBHPd	CH ₃ CN	46 ^e
12	TBAI (20)	TBHP ^d	CH ₃ CN/DMSO ^f	53 ^e

^{*a*}Reaction conditions: **1** (0.5 mmol), **2a** (1.5 mmol), oxidant (2.0 mmol), solvent (3.0 mL), 2.5 h. ^{*b*}Isolated yields based on **1**. ^{*c*}TBHP (70% in water). ^{*d*}TBHP (5.5 M in nonane). ^{*c*}The use of 4 Å MS (200 mg). ^{*f*} V_{MeCN}/V_{DMSO} = 30:1. N.D. = no detected.

Scheme 3. Substrate Scope for Synthesis of $3^{a,b}$



^{*a*}Reaction conditions: enynals (1, 0.5 mmol), sulfonyl hydrazide (2, 1.5 mmol), TBAI (0.1 mmol), TBHP (5.5 M in nonane, 2.0 mmol), CH₃CN (3.0 mL), DMSO (0.1 mL), 70 °C, 2.5 h. ^{*b*}Isolated yields based on 1.

With the established optimal conditions, we turned to evaluate the generality of this metal-free radical cyclization with respect to a variety of envnals 1 and sulfonyl hydrazides 2 (Scheme 3). Those substituents on the phenyl ring of both enynals 1 and sulfonyl hydrazides 2 were proven not to hamper this catalysis, and a wide range of arylsulfonylated diazoindenes 3b-3x can be generated in acceptable yields and a functional-group-compatible fashion using sulfonyl hydrazides as the diazo source. For instance, all the reactions of methyl- methoxy-, or chlorosubstituted substrates 2 with 1a can lead to the formation of desired products 3b-3d in 46%-59% yields. With a pmethoxyphenyl (PMP) group (1b) or a 1-naphthyl (1-Np) substituent (1d) on the alkynyl moiety, functional groups including methyl, tert-butyl, chloride, and bromide at different positions of the aromatic ring (Ar^2) directly bound to sulforyl hydrazides were well tolerated under this system, providing the corresponding sulfonated diazoindenes 3e-3k and 3m-3q with yields ranging from 43% to 64%. Among them, a sterically demanding o-chlorophenyl analogue (2i) proved to be more reluctant to undergo the reaction, in which 3p was obtained in 43% yield, whereas strongly electron-withdrawing aromatic rings (nitro, 2j) would be accommodated, confirming the reaction efficiency, as **3q** was generated in 61% yield. Next, the electronic nature of substituents on the arylalkynyl (Ar¹) moiety was systematically investigated, and it was found that the reaction proceeded readily with various functional groups attached by the arylalkynyl moiety of enynals 1. The variant of substituents on the arylalkynyl moiety, including methyl, methoxy, chloro, and fluoro, would be compatible with the present catalytic oxidation system. Generally, electron-donating groups on the arylalkynyl moiety afforded much better yields than those with electron-withdrawing

ones (3e vs 3s, 3f vs 3r), which indicates that the reactivity of the reaction may be dominated by the electronic nature of the substituents. In addition, we conducted fluorinated enynals 1 to expand their synthetic and phamaceutical utility. As anticipated, fluorinated enynals 1 proved to be adaptable substrates in this transformation, allowing sulfonyl radical-triggered additioncyclization to access the corresponding sulfonated diazoindenes 3t-3x, albeit with relatively lower yields as compared with those without the fluoro group, which might be ascribed to a strong inductive effect of fluorine functionality. The fluoro substituent located at the 4- or 5-position of the phenyl ring of enynals 1 enabled the reaction to occur smoothly. The resulting densely functionalized diazoindenes 3 were fully determined by NMR spectroscopy and HRMS. In the two cases of 3a, its structure was unambiguously confirmed by X-ray diffraction analysis (Figure 1).



Figure 1. ORTEP drawing of 3a.





After the successful formation of functional diazoindenes 3, we then attempted to render the potential applications of the resulting diazoindenes. The reaction between diazoindenes 3f and phenylboronic acid 5 was carried out in the presence of K_2CO_3 in 1,4-dioxane at 120 °C. Surprisingly, an unprecedented hydrazine-tethered bifluorenes 6 was afforded in a 76% yield (Scheme 4), confirmed by X-ray diffraction analysis (SI).

To gain insights into the reaction mechanism for forming diazoindenes 3, several control experiments were conducted (Scheme 5). The enynal 1a was subjected to reaction with 2a in the presence of the radical scavenger TEMPO (2,2,6,6tetramethyl-1-piperidinyloxy) or BHT (2,6-di-tert-butyl-4-methylphenol) (4.0 equiv), and sulfonohydrazones 4 was obtained in 89% yield without observation of the expected product 3a, indicating the possibility of a radical mechanism (Scheme 5a). To provide further support for the reaction pathway, treatment with 4 and 2a under standard conditions gave the desired product 3a in 52% yield (Scheme 5b), suggesting that the reaction involves the in situ formation of sulfonohydrazones 4. The reaction failed to proceed under standard conditions, and the preformed substrate 4 was recovered in this reaction system (Scheme 5c), confirming that the oxidative cleavage of the N-S bond did not take place. Moreover, when 4 was reacted with 2c, two products 3a and 3c as an inseparable mixture in a 1:2.75 ratio, as analyzed by their ¹H

Scheme 5. Control Experiments



Scheme 6. Proposed Mechanism for Forming 3



NMR, were isolated (Scheme 5d). Considering these experimental observations, we reasoned that arylsulfonyl radicals were *in situ* generated from arylsulfonyl hydrazides 2 by oxidation triggered addition—cyclization, which allowed the cleavage of N—S of sulfonohydrazones via a radical process. Obviously, the sulfonylation occurred prior to the carbocyclization step, which was followed by diazotization.

On the basis of our own observations and literature survey,¹⁷ a tentative mechanism for forming diazoindenes 3 was proposed in Scheme 6. The first step is to form sulfonohydrazones 4 derived from enynals 1 and sulfonohydrazides 2, which captures sulfonyl radicals generated in situ from the oxidative decomposition of sulfonyl hydrazides mediated by TBAI and TBHP,¹⁸ to give A. Intermediate A then undergoes 5-exo-trig cyclization and Habstraction to access arylsulfonyldiazene intermediate C, which releases sulfonyl radicals by a second H-abstraction and the cleavage of the N-S bond, leading to the formation of diazoindenes 3. Although the conversion of arylsulfonyl hydrazides into sulfonyl radicals by various oxidants has been documented well,^{17,18} in situ generated sulfonyl radical initiated addition-cyclization toward diazoindenes, in which sulfonyl hydrazides play dual roles as both a diazo source and an arylsulfonyl radical precursor, has not been reported yet.

In summary, we have discovered a novel diazosulfonylation of enynals under catalytic oxidation conditions. The addition of sulfonyl radicals to the triple bond of enynals can trigger a domino *S-exo-trig* carbocyclization and H-abstraction sequence, giving access to unprecedented sulfonylated diazoindenes in multiple C-N/C-S/C-C bond-forming processes. The present new synthetic strategy paves the way for the collection of significant functional sulfones for potential applications in organic and medicinal chemistry.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.6b00655.

Experimental procedures and spectroscopic data for all new compounds **3a–3x**, **6** (PDF) X-ray crystal data for **3a** (CIF) X-ray crystal data for **6** (CIF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Woo, C. M.; Gholap, S. L.; Lu, L.; Kaneko, M.; Li, Z.; Ravikumar, P. C.; Herzon, S. B. *J. Am. Chem. Soc.* **2012**, *134*, 17262. (b) Nicolaou, K. C.; Li, H.; Nold, A. L.; Pappo, D.; Lenzen, A. *J. Am. Chem. Soc.* **2007**, *129*, 10356. (c) Marco-Contelles, J.; Molina, M. T. *Curr. Org. Chem.* **2003**, *7*, 1433.

(2) (a) Ito, S.; Matsuya, T.; Omura, S.; Otani, M.; Nakagawa, A. J. J. Antibiot. 1970, 23, 315. (b) Hata, T.; Omura, S.; Iwai, Y.; Nakagawa, A.; Otani, M. J. J. Antibiot. 1971, 24, 353. (c) Omura, S.; Nakagawa, A.; Yamada, H.; Hata, T.; Furusake, A. Chem. Pharm. Bull. 1973, 21, 931. (d) Furusaki, A.; Marsui, M.; Watanabe, T.; Omura, S.; Nakagawa, A.; Hata, T. Isr. J. Chem. 1972, 10, 173. (e) Gould, S. J.; Tamayo, N.; Melville, C. R.; Cone, M. C. J. Am. Chem. Soc. 1994, 116, 2207. (f) Mithani, S.; Weeratunga, G.; Taylor, N. J.; Dmitrienko, G. I. J. Am. Chem. Soc. 1994, 116, 2209.

(3) (a) Ford, A.; Miel, H.; Ring, A.; Slattery, C. N.; Maguire, A. R.; McKervey, M. A. Chem. Rev. 2015, 115, 9981. (b) Hu, F.; Xia, Y.; Ma, C.; Zhang, Y.; Wang, J. Chem. Commun. 2015, 51, 7986. (c) Qian, D.; Zhang, J. Chem. Soc. Rev. 2015, 44, 677. (d) Gillingham, D.; Fei, Na. Chem. Soc. Rev. 2013, 42, 4918. (e) Liu, Z.; Wang, J. J. Org. Chem. 2013, 78, 10024. (4) (a) Guo, X.; Hu, W. Acc. Chem. Res. 2013, 46, 2427. (b) Davies, H. M. L.; Beckwith, R. E. J. Chem. Rev. 2003, 103, 2861. (c) Xiao, Q.; Zhang, Y.; Wang, J. Acc. Chem. Res. 2013, 46, 236. (d) Padwa, A. Chem. Soc. Rev. 2009, 38, 3072.

(5) Maas, G. Angew. Chem., Int. Ed. 2009, 48, 8186.

(6) (a) Heydt, H. Science of Synthesis 2004, 27, 843–915. (b) Goddard-Borger, E. D.; Stick, R. V. Org. Lett. 2007, 9, 3797. (c) Davies, H. M.; Townsend, L.; R, J. J. Org. Chem. 2001, 66, 6595. (d) Taber, D. F.; Tian, N. J. Org. Chem. 2007, 72, 3207. (e) Ramachary, D. B.; Narayana, V. V.; Ramakumar, K. Tetrahedron Lett. 2008, 49, 2704.

(7) (a) Brehm, W. J.; Levenson, T. J. Am. Chem. Soc. 1954, 76, 5389.
(b) Myers, E. L.; Raines, R. T. Angew. Chem., Int. Ed. 2009, 48, 2359.
(c) Gonzalez, A.; Perez, D.; Puig, C.; Ryder, H.; Sanahuja, J.; Sole, L.; Bach, J. Tetrahedron Lett. 2009, 50, 2750.

(8) (a) Monguchi, K.; Itoh, T.; Hirai, K.; Tomioka, H. J. Am. Chem. Soc.
2004, 126, 11900. (b) Hu, Y.; Ishikawa, Y.; Hirai, K.; Tomioka, H. Bull. Chem. Soc. Jpn. 2001, 74, 2207. (c) Hirai, K.; Kamiya, E.; Itoh, T.; Tomioka, H. Org. Lett. 2006, 8, 1847. (d) Tomioka, H.; Watanabe, T.; Hattori, M.; Nomura, N.; Hirai, K. J. Am. Chem. Soc. 2002, 124, 474.
(e) Geng, Y.; Kumar, A.; Faidallah, H. M.; Albar, H. A.; Mhkalid, I. A.; Schmidt, R. R. Bioorg. Med. Chem. 2013, 21, 4793.

(9) (a) McGuiness, M.; Shechter, H. Tetrahedron Lett. 2002, 43, 8425.
(b) Wommack, A. J.; Moebius, D. C.; Travis, A. L.; Kingsbury, J. S. Org. Lett. 2009, 11, 3202. (c) Javed, M. I.; Brewer, M. Org. Lett. 2007, 9, 1789.
(d) Kang, B. C.; Nam, D. G.; Hwang, G.-S.; Ryu, D. H. Org. Lett. 2015, 17, 4810. (e) Moebius, D. C.; Kingsbury, J. S. J. Am. Chem. Soc. 2009, 131, 878. (f) Wommack, A. J.; Kingsbury, J. S. J. Org. Chem. 2013, 78, 10573.
(10) (a) Kaufman, G. M.; Cook, F. B.; Shechter, H.; Bayless, J. H.; Friedman, L. J. Am. Chem. Soc. 1967, 89, 5736. (b) Celebi, S.; Leyva, S.; Modarelli, D. A.; Platz, M. S. J. Am. Chem. Soc. 1993, 115, 8613.
(c) Bartrum, H. E.; Blakemore, D. C.; Moody, C. J.; Hayes, C. J. Chem. Eur. J. 2011, 17, 9586. (d) Costa, P.; Fernandez-Oliva, M.; Sanchez-Garcia, E.; Sander, W. J. Am. Chem. Soc. 2014, 136, 15625. (e) Emer, E.; Twilton, J.; Tredwell, M.; Calderwood, S.; Collier, T. L.; Liegault, B.; Taillefer, M.; Gouverneur, V. Org. Lett. 2014, 16, 6004.

(11) (a) Roy, V.; Smith, J. A. I.; Wang, J.; Stewart, J. E.; Bentley, W. E.; Sintim, H. O. J. Am. Chem. Soc. 2010, 132, 11141. (b) Smith, J. A. I.; Wang, J.; Nguyen-Mau, S.-M.; Lee, V.; Sintim, H. O. Chem. Commun. 2009, 7033. (c) Xiao, F.; Zhang, Z.; Zhang, J.; Wang, J. Tetrahedron Lett. 2005, 46, 8873. (d) Padwa, A.; Kulkarni, Y. S.; Zhang, Z. J. Org. Chem. 1990, 55, 4144. (e) Trost, B. M.; Malhotra, S.; Koschker, P.; Ellerbrock, P. J. Am. Chem. Soc. 2012, 134, 2075. (f) Panish, R.; Selvaraj, R.; Fox, J. M. Org. Lett. 2015, 17, 3978. (g) Peng, C.; Cheng, J.; Wang, J. J. Am. Chem. Soc. 2007, 129, 8708.

(12) (a) Studer, A.; Curran, D. P. Angew. Chem., Int. Ed. 2016, 55, 58.
(b) Tang, S.; Liu, K.; Liu, C.; Lei, A. Chem. Soc. Rev. 2015, 44, 1070.
(c) Chen, Z.-M.; Zhang, X.-M.; Tu, Y.-Q. Chem. Soc. Rev. 2015, 44, 5220.
(d) Walton, J. C. Acc. Chem. Res. 2014, 47, 1406. (e) Orlando, J. J.; Tyndall, G. S. Chem. Soc. Rev. 2012, 41, 6294. (f) Girard, S. A.; Knauber, T.; Li, C.-J. Angew. Chem., Int. Ed. 2014, 53, 74. (g) Li, C.-J. Acc. Chem. Res. 2009, 42, 335.

(13) (a) Wille, U. *Chem. Rev.* **2013**, *113*, 813. (b) Besset, T.; Poisson, T.; Pannecoucke, X. *Eur. J. Org. Chem.* **2015**, *2015*, 2765. (c) Wang, T.; Jiao, N. *Acc. Chem. Res.* **2014**, 47, 1137. (d) Leca, D.; Fensterbank, L.; Lacote, E.; Malacria, M. *Chem. Soc. Rev.* **2005**, *34*, 858.

(14) (a) Wen, J.; Wei, W.; Xue, S.; Yang, D.; Lou, Y.; Gao, C.; Wang, H. J. Org. Chem. 2015, 80, 4966. (b) Rong, G.; Mao, J.; Yan, H.; Zheng, Y.; Zhang, G. J. Org. Chem. 2015, 80, 4697. (c) Li, S.; Li, X.; Yang, F.; Wu, Y. Org. Chem. Front. 2015, 2, 1076. (d) Wei, W.; Wen, J.; Yang, D.; Guo, M.; Wang, Y.; You, J.; Wang, H. Chem. Commun. 2015, 51, 768. (e) Yang, Z.; Hao, W.-J.; Wang, S.-L.; Zhang, J.-P.; Jiang, B.; Li, G.; Tu, S.-J. J. Org. Chem. 2015, 80, 9224. (f) Li, X.; Shi, X.; Fang, M.; Xu, X. J. Org. Chem. 2013, 78, 9499.

(15) Chen, Z.-Z.; Liu, S.; Xu, G.; Wu, S.; Miao, J.-N.; Jiang, B.; Hao, W.-J.; Wang, S.-L.; Tu, S.-J.; Li, G. Chem. Sci. **2015**, *6*, 6654.

(16) (a) Qiu, J.-K.; Jiang, B.; Zhu, Y.-L.; Hao, W.-J.; Wang, D.-C.; Sun, J.; Wei, P.; Tu, S.-J.; Li, G. *J. Am. Chem. Soc.* **2015**, *137*, 8928. (b) Zhu, Y.-L.; Jiang, B.; Hao, W.-J.; Qiu, J.-K.; Sun, J.; Wang, D.-C.; Wei, P.; Wang, A.-F.; Li, G.; Tu, S.-J. Org. Lett. **2015**, *17*, 6078. (c) Jiang, B.; Ning, Y.; Fan, W.; Tu, S.-J.; Li, G. J. Org. Chem. **2014**, *79*, 4018. (d) Qiu, J.-K.; Hao, W.-J.; Wang, D.-C.; Wei, P.; Sun, J.; Jiang, B.; Tu, S.-J. Chem. Commun. **2014**, *50*, 14782.

(17) (a) Li, X.; Xu, X.; Zhou, C. Chem. Commun. 2012, 48, 12240.
(b) Rong, G.; Mao, J.; Yan, H.; Zheng, Y.; Zhang, G. J. Org. Chem. 2015, 80, 4697. (c) Li, X.; Xu, Y.; Wu, W.; Jiang, C.; Qi, C.; Jiang, H. Chem. - Eur. J. 2014, 20, 7911. (d) Tang, S.; Wu, Y.; Liao, W.; Bai, R.; Liu, C.; Lei, A. Chem. Commun. 2014, 50, 4496. (e) Taniguchi, T.; Sugiura, Y.; Zaimoku, H.; Ishibashi, H. Angew. Chem., Int. Ed. 2010, 49, 10154.

(18) (a) Zhang, J.; Šhao, Y.; Wang, H.; Luo, Q.; Chen, J.; Xu, D.; Wan, X. Org. Lett. **2014**, *16*, 3312. (b) Liu, Z.; Zhang, J.; Chen, S.; Shi, E.; Xu, Y.; Wan, X. Angew. Chem., Int. Ed. **2012**, *51*, 3231. (c) Wu, X.-F.; Gong, J.-L.; Qi, X. Org. Biomol. Chem. **2014**, *12*, 5807.