JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Iron/Copper Co-Catalyzed Synthesis of Vinyl Sulfones from Sulfonyl Hydrazides and Alkyne Derivatives

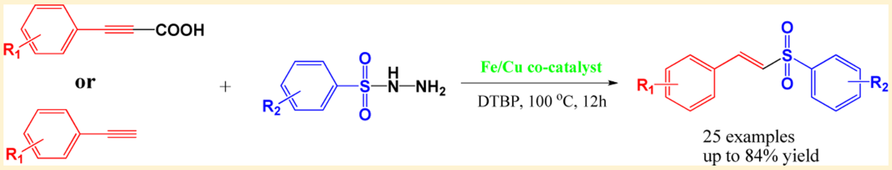
Guangwei Rong,[†] Jincheng Mao,*[,†,‡] Hong Yan,[†] Yang Zheng,[†] and Guoqi Zhang*[,§]

[†]Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering, and Materials Science, Soochow University, Suzhou 215123, P. R. China

[‡]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu, 610500, P. R. China

[§]Department of Sciences, John Jay College and The Graduate Center, The City University of New York, New York, New York 10019, United States

Supporting Information



ABSTRACT: A new approach to the selective synthesis of (*E*)-vinyl sulfones has been developed via a Fe/Cu co-catalyzed sulfonylation of arylpropiolic acid or phenylacetylene with sulfonyl hydrazides. A variety of vinyl sulfones have been obtained in moderate to good yields, comparable to the best results reported so far. The inexpensive Fe/Cu co-catalyzed method features a simple experimental procedure and good tolerance of substrate.

■ INTRODUCTION

Vinyl sulfones have attracted considerable interests in the area of synthetic organic chemistry in recent years, owing to their important role in serving as key structural units of many biological active compounds or medicines[1] as well as versatile building blocks for various organic transformations.[2] An overview of previously related work on the preparation of such vinyl sulfones resulted in the finding that generally the sulfone unit of this compound could be originated from sulfonyl chloride, sulfinic acid, sodium sulfinate, and sulfonyl hydrazide, of which sodium sulfinate and sulfonyl hydrazide have been predominantly utilized, probably due to their good stability and ease of handling. On the other hand, styrene and cinnamic acid derivatives were popularly chosen as the reaction partners to provide the alkene moiety. The main methodologies that were recently developed for the synthesis of vinyl sulfones have been illustrated in Figure 1. In 2001, a facile one-pot synthesis of vinyl sulfones via a CAN-mediated reaction of aryl sulfinates and alkenes was reported by the Nair group, and similar works were independently revealed by the Chutima group and others by using potassium iodide or iodine as catalysts.[3a−d] Very recently, Jiang group proposed an alternative way to prepare vinyl sulfones through a catalytic reaction between styrene and benzenesulfonyl hydrazide using copper(I) chloride as a catalyst.[3e] Relevant results on the decarboxylative sulfonylation of cinnamic acids with sodium sulfinates have been reported by Guo and Jiang groups, respectively, according to two different protocols, while Jiang's approach has advantages of transition-metal-free reaction conditions and relatively higher yields over the Guo's one.[3e−g]

Alternatively, vinyl sulfones can also be achieved through the addition of sulfone radical to alkyne.[4] Relevant work has been reported more recently by Wang and co-workers who introduced a copper-catalyzed selective hydrosulfonylation of alkynes with arylsulfinic acids (Figure 1).[4a] Yet this method suffers from major issues such as limited substrate scope and poor stability and availability of sulfinic acid. In the same year, Jiang group revealed a chemoselective synthesis of unsymmetrical internal alkynes or vinyl sulfones via palladium-catalyzed cross-coupling reaction of sodium sulfinates with alkynes.[4c] In contrast, the latter protocol shows better functional group tolerance for a wide range of alkynes including aliphatic substrates. However, the use of precious metal palladium as a catalyst will necessarily increases the cost of this procedure, and therefore, it would be less likely to be employed for large-scale applications, in particular in industrial manufacturing. Recent research has addressed the importance of the replacement of precious metals (Pd, Pt, or Ru) with earth-abundant catalysts containing iron, copper, or cobalt in the fields of chemical synthesis and energy conversion.[5] Consequently, major progress has been made in earth-abundant metal-catalyzed reactions, and in particular, copper and iron catalysts have found widespread applications in decarboxylation reactions of phenylpropiolic acids.[6]

However, the combination of two kinds of earth-abundant metals as effective catalyst systems was only scarcely explored very recently, in a few types of reactions.[7] Herein, we wish to

Received: March 15, 2015
Published: April 16, 2015

DOI: 10.1021/acs.joc.5b00558
J. Org. Chem. 2015, 80, 4697−4703

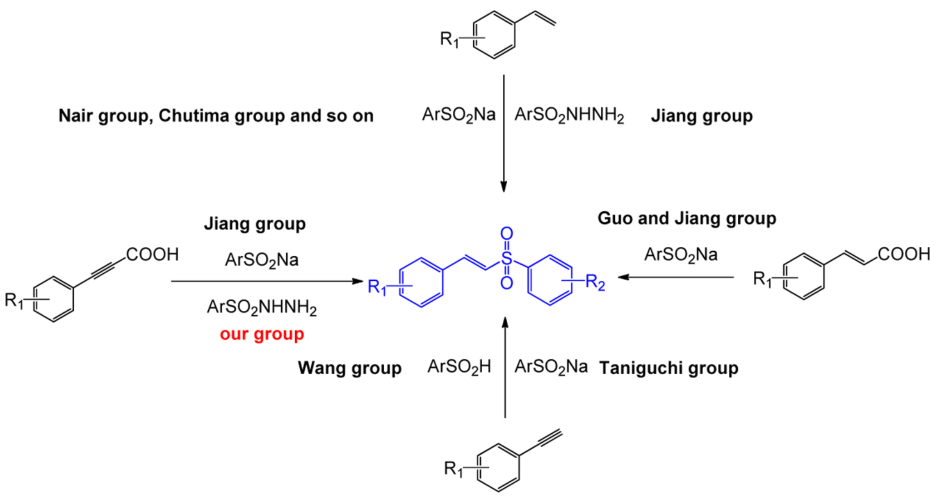
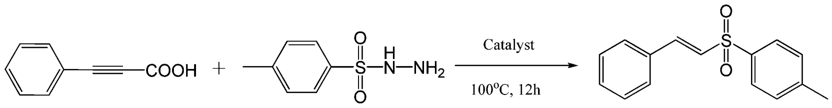


Figure 1. Diverse approaches to prepare useful vinyl sulfones.

Table 1. Catalytic Decarboxylative and Dehydrazine Reactions between Phenylpropiolic Acids and Sulfonyl Hydrazide[a]



1a **2a** **3a**

entry	catalyst	additive	oxidant	solvent	yield (%)
1	CuI	–	–	DMSO	45
2	Cu	–	–	DMSO	29
3	CuO	–	–	DMSO	27
4	CuBr	–	–	DMSO	41
5	$CuBr_2$	–	–	DMSO	25
6	$CuSO_4$	–	–	DMSO	38
7	CuAy	–	–	DMSO	60
8	CuAy	–	–	Dioxane	22
9	CuAy	–	–	Etanol	34
10	CuAy	–	–	CH_3CN	NR
11	CuAy	$FeCl_3$	TBHP	DMSO	67
12	CuAy	TBAI	TBHP	DMSO	64
13	CuAy	$FeCl_2{\cdot}4H_2O$	TBHP	DMSO	68
14	CuAy	Fe	TBHP	DMSO	51
15	CuAy	$FeCl_2{\cdot}4H_2O$	DCP	DMSO	52
16	CuAy	$FeCl_2{\cdot}4H_2O$	TBPB	DMSO	63
17	CuAy	$FeCl_2{\cdot}4H_2O$	DTBP	DMSO	70
18[b]	CuAy	$FeCl_2{\cdot}4H_2O$	DTBP	DMSO	75
19[b,c]	CuAy	$FeCl_2{\cdot}4H_2O$	DTBP	DMSO	81
20	CuAy	$FeCl_2{\cdot}4H_2O$	–	DMSO	57
21	CuAy	–	DTBP	DMSO	61
22	–	$FeCl_2{\cdot}4H_2O$	DTBP	DMSO	NR

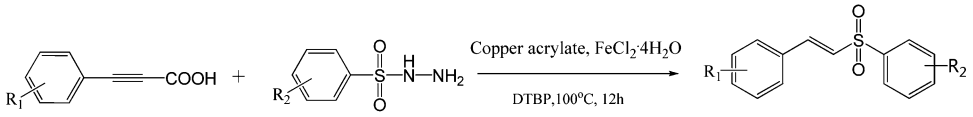
[a] Reaction conditions: Phenylpropiolic acid **1a** (0.3 mmol), 4-methylbenzenesulfonhydrazide **2a** (0.6 mmol), copper acrylate (20 mol %), DMSO (2 mL), additive (10 mol %), oxidant (0.6 mmol), 100 °C, 12 h, air. DTBP: *tert*-butyl peroxide; TBHP: *tert*-butyl hydroperoxide; DCP: dicumyl peroxide. CuAy: copper acrylate. [b] Additive (15 mol %). [c] Oxidant (0.9 mmol).

report our findings of novel Cu/Fe co-catalyzed sulfonylation of aromatic propiolic acids with sulfonyl hydrazides via a combined decarboxylative and dehydrazine process. In addition, similar reactions were carried out by replacing propiolic acids with aryl acetylenes. A variety of (*E*)-vinyl sulfones have been selectively accessed in reasonable yields.

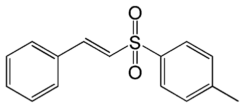
■ RESULTS AND DISCUSSION

We initially started our investigation by choosing phenylpropiolic acid (**1a**) to react with *p*-toluenesulfonyl hydrazide (**2a**; 2.0 equiv) in the presence of CuI (20 mol %) in dimethyl sulfoxide (DMSO) at 100 °C for 12 h, and to our delight the desired vinyl sulfone **3a** was harvested in 45% yield as shown in Table 1 (entry 1). Subsequently, various copper salts such as cupric oxide, cuprous bromide, and copper acrylate were tested as the catalysts, copper acrylate was proved to be the best choice, and the target product **3a** was selectively achieved in 60% yield with an *E* configuration (entries 2−7, Table 1 and SI). Other solvents than DMSO usually dropped the yield to a much lower level (entries 8−10 and SI). In order to further

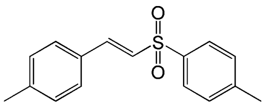
Table 2. Substrate Scope of the Reactions between Aromatic Propiolic Acids and Sulfonyl Hydrazides[a]



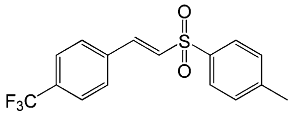
1 2 3



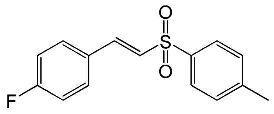
3a ,81%



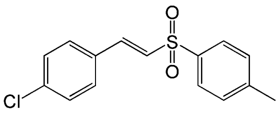
3b, 60%



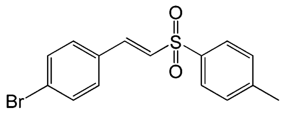
3c, 41%



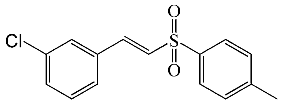
3d, 72%



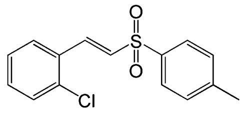
3e, 75%



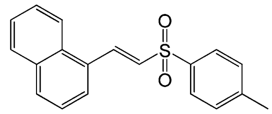
3f, 64%



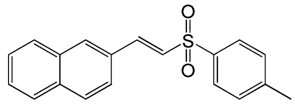
3g, 65%



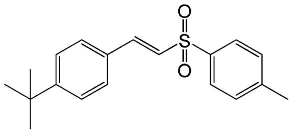
3h, 30%



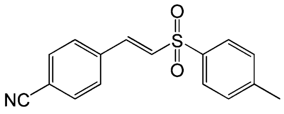
3i,Trace



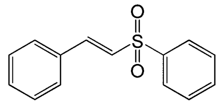
3j,66%



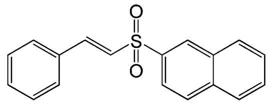
3k, 72%



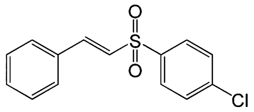
3l, 53%



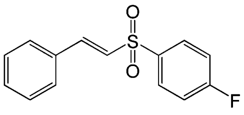
3m, 80%



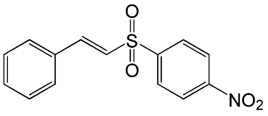
3n, 76%



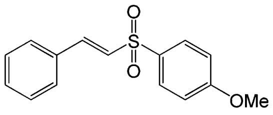
3o, 42%



3p, 41%



3q, 42%



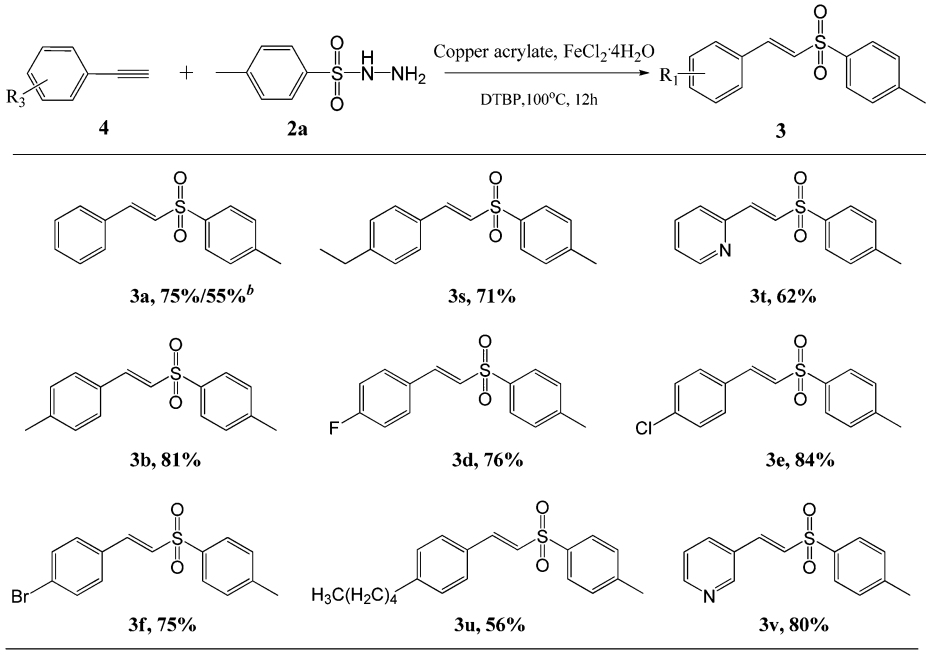
3r, 72%

[a]Reaction conditions: Phenylpropiolic acid **1** (0.3 mmol), benzenesulfonhydrazide **2** (0.6 mmol), copper acrylate (20 mol %), $FeCl_2·4H_2O$ (15 mol %), DTBP (0.9 mmol), DMSO (2 mL), 100 °C, air.

improve the results, we next attempted to use different types of additives, except for the copper acrylate catalyst. Some organic or inorganic bases (Na_2CO_3, Et_3N, etc.), co-ligands (such as PPh_3 and L-proline), and extra iron catalysts in the presence of various oxidants have been screened (Table 1 and SI for details), and it was pleasing to find that when a second metal catalyst $FeCl_2·4H_2O$ (10 mol %) and an oxidant TBHP (2.0 equiv) were added into the reaction, the yield was increased to 68% (entries 11−17, Table 1). Furthermore, the reaction was promoted with increased amount of $FeCl_2·4H_2O$ (15 mol %) and the oxidant DTBP (3.0 equiv), affording **3a** in 81% yield. The controlled experiments revealed that the concurrent addition of both the copper/iron catalyst and oxidant is crucial for an improved conversion of the starting materials (entries 20−22, Table 1), highlighting the importance of copper/iron catalysis in the present reaction. Although we were unable to further improve the yield of **3a** through a thorough screening of reaction conditions (see SI), the yield obtained is well comparable to the best results for the synthesis of vinyl sulfones that were reported heretofore.[3,4]

With the optimized reaction conditions in hand, we sought to expand the substrate scope that is applicable for the current reaction. Therefore, a range of substituted aromatic propiolic acids and benzenesulfonyl hydrazides were chosen to react with the Cu/Fe co-catalyst, and the results are summarized in Table 2. It was found that moderate to good yields ranging from 30% to 81% for a variety of vinyl sulfones were achieved. Although phenylpropiolic acids bearing strong electron-withdrawing groups (−CF_3 and −CN) on the benzene rings led to the corresponding products in slightly lower yields (**3c**, **3l**), halogen or alkyl substitution generally favored the conversion under standard conditions giving the products in good yields, except that an *ortho*-chloro substituent lowered the yield to 30% (**3h**), because probably of increasing steric hindrance. This was further confirmed by the fact that only trace amount of **3i** was detected when the bulky 3-(naphthalen-1-yl)propiolic acid

Table 3. Cu/Fe Catalytic Synthesis of Vinyl Sulfones from Aromatic alkynes and *p*-Toluenesulfonyl Hydrazides[a]



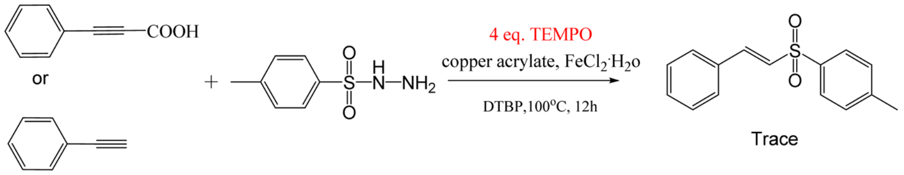
3a, 75%/55%[b] **3s, 71%** **3t, 62%**

3b, 81% **3d, 76%** **3e, 84%**

3f, 75% **3u, 56%** **3v, 80%**

[a]Reaction conditions: Phenylacetylene **4** (0.3 mmol), 4-methylbenzenesulfonhydrazide **2a** (0.6 mmol), copper acrylate (20 mol %), $FeCl_2 \cdot 4H_2O$ (15 mol %), DTBP (0.9 mmol), DMSO (2 mL), 100 °C, air. [b]In the absence of $FeCl_2 \cdot 4H_2O$.

Scheme 1. Reactivity Tests by a Radical Scavenger



was employed to the reaction with *p*-toluenesulfonyl hydrazide, while the *ortho*-position free 3-(naphthalen-2-yl)propiolic acid furnished the reaction in 66% yield (**3j**).

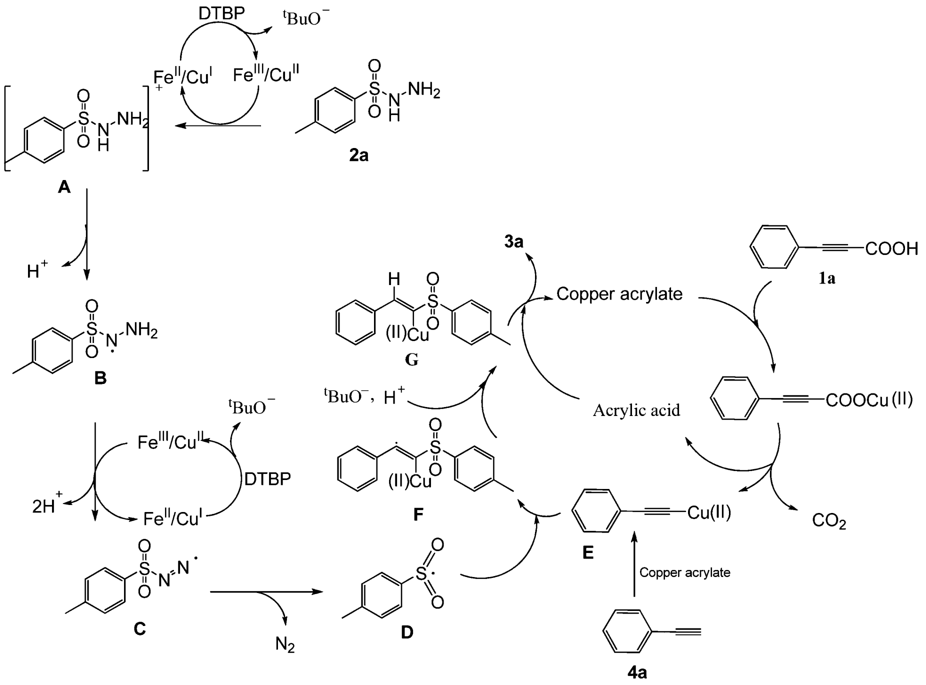
On the other hand, various substituted benzenesulfonyl hydrazides were also explored under optimal conditions. Likewise, reactions involving electron-withdrawing groups including halos were run slightly more sluggishly, generating the corresponding products in 41−42% yields after 12 h. Good yields were obtained when substrates with methoxyl or naphthyl substitutents were applied to the reaction with phenylpropiolic acid under the same conditions.

Encouraged by the results depicted above, we also attempted to extend our Cu/Fe co-catalysis system to a similar transformation for the synthesis of vinyl sulfones, yet utilizing aryl alkynes, the starting materials previously investigated by Wang and Taniguchi groups as precursors to react with sulfinic acid or sodium sulfinate.[4a,b] However, sulfonehydrazide was never used as a source of sulfonates in those reactions. We first tested the reaction between *p*-toluenesulfonyl hydrazide with phenylacetylene catalyzed by the same Cu/Fe system under standard conditions depicted above. Interestingly, the vinyl sulfone product **3a** was isolated again in 75% yield (Table 3). Likewise, co-catalyst $FeCl_2 \cdot 4H_2O$ was indispensable for this reaction, only 55% of **3a** was obatined when the additive was absent. Several substituted aryl alkynes were also examined under the same reaction conditions, and the results showed that all reactions proceeded smoothly affording the corresponding products in moderate to good yields, with exclusively *E* isomers obtained (Table 3). For example, substrates with alkyl and halo substituents furnished the reactions with desired products in yields ranging from 56% to 81%. Heterocyclic alkynes were also suitable substrates for this transformation and the corresponding vinyl sulfones were obtained in 80% and 62% yields, respectively (**3u**, **3v**).

In order to gain insights into the reaction details on the Cu/Fe catalytic reactions, further reactivity tests were performed by introducing TEMPO, a common radical scavenger into the reaction mixtures of *p*-toluenesulfonyl hydrazide with either phenylpropiolic acid or phenylacetylene under standard conditions (Scheme 1). After 12 h reactions at 100 °C, however, only a trace amount of product **3a** was detected in both cases, and the starting materials were recycled, indicating that the reactions were almost completely inhibited by TEMPO (4 equiv). This strongly suggests that the reactions have proceeded through a radical mechanism.

Based on previous reports on relevant reaction as well as our own findings as described above, we proposed a plausible reaction mechanism for the bimetallic Cu/Fe catalytic reaction. The reaction is likely to be initiated by a single-electron transfer between **2a** and Fe^{II}/Cu^{II} species in the presence of the oxidant DTBP to give an unstable cation radical **A**, which readily loses a proton to generate a new radical **B**. Radical **B** then undergoes similar deprotonation assisted by the Fe^{II}/Cu^{II} species, resulting in the formation of an azo radical **C**. Subsequently, a sulfonyl

Scheme 2. A Plausible Catalytic Mechanism Involving the Cu/Fe Co-Catalyst



radical **D** could be readily accessed with the release of molecular nitrogen.[8] Next, the addition of radical **D** to an active cuprate complex **E**,[9] which is generated by the reaction of copper acrylate and phenylpropiolic acid/phenylacetylene, would give an intermediate **F**.[9] Then, the protonolysis of intermediate **F** with *tert*-butanol which was generated in the process of the oxidation of sulfonyl hydrazide resulted in the generation of **G**.[10] Eventually, target product **3a** is obtained from **G** with the participation of a proton produced from previous steps, by releasing the Cu(II) species to fullfill the catalytic cycle (Scheme 2).

■ CONCLUSIONS

In summary, we have developed a new method to selectively synthesize (*E*)-vinyl sulfones through a Cu/Fe co-catalyzed sulfonylation of propiolic acid/phenylacetylene with sulfonyl hydrazides. In this work, for the first time sulfonyl hydrazides were applied to the preparation of a variety of vinyl sulfones in moderate to good yields. In contrast to previous work, this method utilizes readily available earth-abundant metal catalysts and features simple experimental procedure and good tolerance of substrates. Moreover, the fact that molecular carbon dioxide and dinitrogen are the only byproducts from the reactions makes this process a rather green synthesis. Further studies on the application of bimetallic co-catalysis systems based on earth-abundant metals for other organic transformations are in progress in our laboratory.

■ EXPERIMENTAL SECTION

General Information. All reactions were carried out under an air atmosphere condition. Various phenylpropiolic acid and various benzenesulfonyl hydrazide were commercial available. The copper acrylate (95%) and ferrous chloride tetrahydrate (99.95%) were purchased from Alfa Aesar and Aladdin, respectively. Flash column chromatography was performed using silica gel (100−200 mesh). Analytical thin-layer chromatography was performed using glass plates precoated with 200−300 mesh silica gel impregnated with a fluorescent indicator (254 nm). NMR spectra were recorded in $CDCl_3$ on 400 MHz NMR spectrometer or 300 MHz NMR spectrometer with TMS as an internal reference. Products were characterized by comparison of ^{1}H NMR, ^{13}C NMR, MS, and TOF-MS data in the literature.

General Procedure for the Reaction between Phenylpropiolic Acids/Phenylacetylenes and Benzenesulfonyl Hydrazides. To a Schlenk tube equipped with a magnetic stir bar was added phenylpropiolic acid (0.3 mmol) or phenylacetylenes (0.3 mmol), benzenesulfonyl hydrazide (0.6 mmol), copper acrylate (20 mol %, 0.06 mmol, 12.3 mg), $FeCl_2 \cdot 4H_2O$ (15 mol %, 0.045 mmol, 8.9 mg), DTBP (0.9 mmol, 164.5 uL), and DMSO (2.0 mL). The resulting reaction mixture was kept stirring at 100 °C for 12 h. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford the desired product in high purity.

(E)-1-Methyl-4-(styrylsulfonyl)benzene (**3a**).[3e] White solid, mp: 118−120 °C, yield 81% (62.8 mg); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.75 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 15.2 Hz, 1H), 7.39 (d, J = 7.6 Hz, 2H), 7.33−7.24 (m, 5H), 6.77 (d, J = 15.6 Hz, 1H), 2.35 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm) 144.4, 141.9, 137.8, 132.5, 131.1, 130.0, 129.1, 128.5, 127.7, 127.6, 21.6; MS (m/z) calcd for $C_{15}H_{14}O_2S$ 258.1, found 259.1 (M + H)$^+$.

(E)-1-Methyl-4-(4-methylstyrylsulfonyl)benzene (**3b**).[4b] White solid, mp: 152−154 °C, yield 60% (49.0 mg); ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.82 (d, J = 8.0 Hz, 2H), 7.62 (d, J = 15.6 Hz, 1H), 7.38−7.31 (m, 4H), 7.18 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 15.2 Hz, 1H), 2.42 (s, 3H), 2.36 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm) 144.3, 142.0, 141.8, 137.9, 130.0, 129.8, 129.7, 128.7, 127.7, 126.4, 21.6, 21.5; MS (m/z) calcd for $C_{16}H_{16}O_2S$ 272.1, found 273.1 (M + H)$^+$.

(E)-1-Methyl-4-(4-(trifluoromethyl)styrylsulfonyl)benzene (**3c**).[11] White solid, mp: 120−122 °C, yield 41% (40.1 mg); ^{1}H NMR (400 MHz, $CDCl_3$) 7.84 (d, J = 8.4 Hz, 2H), 7.56−7.71 (m, 5H), 7.36 (d, J = 8.0 Hz, 2H), 6.95 (d, J = 15.6 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) (δ, ppm) 144.8, 139.9, 137.1, 135.8, 132.5 (t, J = 32.6 Hz), 130.3, 130.1, 128.7, 127.9 126.0 (t, J = 3.7 Hz), 123.6 (d, J = 270.7 Hz), 21.6; MS (m/z) calcd for $C_{16}H_{13}F_3O_2S$ 326.1, found 327.1 (M + H)$^+$.

(E)-1-Fluoro-4-(2-tosylvinyl)benzene (**3d**).[11] White solid, mp: 96−98 °C, yield 72% (59.7 mg); ^{1}H NMR (400 MHz, $CDCl_3$) 7.82 (d, J =

8.4 Hz, 2H), 7.62 (d, *J* = 15.6 Hz, 1H), 7.51−7.44 (m, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.07 (t, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 15.2 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 164.3 (d, *J* = 251.3 Hz), 144.5, 140.6, 137.6, 130.6 (d, *J* = 8.6 Hz), 130.0, 128.7 (d, *J* = 3.3 Hz), 127.7, 127.4 (d, *J* = 2.4 Hz), 116.3 (d, *J* = 21.9 Hz), 21.6; MS (*m*/*z*) calcd for $C_{15}H_{13}F_3O_2S$ 276.1, found 277.1 (M + H)$^+$.

(E)-1-Chloro-4-(2-tosylvinyl)benzene (**3e**).[11] White solid, mp: 149−151 °C, yield 75% (65.9 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.82 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 15.6 Hz, 1H), 7.43−7.38 (m, 2H), 7.37−7.32 (d, *J* = 8.4 Hz, 4H), 6.85 (d, *J* = 15.6 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 144.6, 140.4, 137.5, 137.1, 130.9, 130.0, 129.7, 129.4, 128.2, 127.8, 21.6; MS (*m*/*z*) calcd for $C_{15}H_{13}ClO_2S$ 292.0, found 293.0 (M + H)$^+$.

(E)-1-Bromo-4-(2-tosylvinyl)benzene (**3f**).[11] White solid, mp: 162−164 °C, yield 64% (64.7 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.82 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 15.6 Hz, 1H), 7.53−7.48 (m, 2H), 7.37−7.31 (m, 4H), 6.86 (d, *J* = 15.2 Hz, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 144.6, 140.5, 137.4, 132.3, 131.4, 130.1, 128.3, 129.9, 127.8, 125.5, 21.7; MS (*m*/*z*) calcd for $C_{15}H_{13}BrO_2S$ 336.0, found 337.0 (M + H)$^+$.

(E)-1-Chloro-3-(2-tosylvinyl)benzene (**3g**).[3b] White solid, mp: 90−92 °C, yield 65% (57.1 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.82 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 15.6 Hz, 1H), 7.44 (s, 1H), 7.38−7.31 (m, 5H), 6.87 (d, *J* = 15.2 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 144.7, 140.2, 137.3, 135.1, 134.3, 130.9, 130.0, 130.1, 129.2, 128.1, 127.8, 126.8, 21.6; MS (*m*/*z*) calcd for $C_{15}H_{13}ClO_2S$ 292.0, found 293.0 (M + H)$^+$.

(E)-1-Chloro-2-(2-tosylvinyl)benzene (**3h**).[3b] White solid, mp: 103−105 °C, yield 30% (26.3 mg); ^{1}H NMR (400 MHz, CDCl$_3$) ^{1}H NMR (400 MHz, CDCl$_3$) 8.08 (d, *J* = 15.6 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.52 (dd, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.40−7.32 (m, 3H), 7.30−7.26 (m, 1H), 6.90 (d, *J* = 15.6 Hz, 1H), 2.46 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 144.6, 137.9, 137.3, 135.3, 131.8, 130.8, 130.4, 130.0, 128.2, 127.9, 127.2, 21.6; MS (*m*/*z*) calcd for $C_{15}H_{13}ClO_2S$ 292.0, found 293.0 (M + H)$^+$.

(E)-2-(2-Tosylvinyl)naphthalene (**3j**).[3e] White solid, mp: 160−162 °C, yield 66% (61.1 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.90 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.84−7.77 (m, 4H), 7.55−7.49 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 15.2 Hz, 1H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 144.4, 142.0, 137.8, 134.5, 133.1, 130.9, 130.0, 129.9, 129.0, 128.7, 127.8, 127.8, 127.8, 127.7, 127.0, 123.4, 21.7; MS (*m*/*z*) calcd for $C_{19}H_{16}O_2S$ 308.1, found 309.1 (M + H)$^+$.

(E)-1-tert-Butyl-4-(2-tosylvinyl)benzene (**3k**).[11] White solid, mp: 125−127 °C, yield 72% (67.9 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.82 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 15.6 Hz, 1H), 7.44−7.38 (m, 4H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 15.2 Hz, 1H), 2.42 (s, 3H), 1.30 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 154.9, 144.3, 141.9, 138.0, 129.9, 128.4, 129.7, 127.6, 126.6, 126.1, 35.0, 31.1, 21.6; MS (*m*/*z*) calcd for $C_{19}H_{22}O_2S$ 314.1, found 315.1 (M + H)$^+$.

(E)-4-(2-Tosylvinyl)benzonitrile (**3l**). White solid, mp: 125−127 °C, yield 53% (45.0 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.83 (d, *J* = 8.0 Hz, 2H), 7.70−7.62 (m, 3H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 15.6 Hz, 1H), 2.45 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 145.0, 139.3, 136.8, 136.7, 132.8, 131.3, 130.2, 128.9, 127.9, 118.1, 114.2, 21.7; HRMS (TOF MS CI$^-$) calculated for $C_{16}H_{13}NO_2S$ 283.0667, found 283.0669.

(E)-(2-(Phenylsulfonyl)vinyl)benzene (**3m**).[3e] White solid, mp: 67−69 °C, yield 80% (58.6 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.98−7.93 (m, 2H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.63−7.58 (m, 1H), 7.56−7.52 (m, 2H), 7.49−7.45 (m, 2H), 7.41−7.35 (m, 3H), 6.87 (d, *J* = 15.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 142.5, 140.7, 133.4, 132.3, 131.3, 129.4, 129.1, 128.6, 127.6, 127.3; MS (*m*/*z*) calcd for $C_{14}H_{12}O_2S$ 244.1, found 245.1 (M + H)$^+$.

(E)-2-(Styrylsulfonyl)naphthalene (**3n**).[3e] White solid, mp: 140−142 °C, yield 76% (67.1 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 8.56 (s, 1H), 8.01−7.96 (m, 2H), 7.93−7.86 (m, 2H), 7.74 (d, *J* = 15.2 Hz, 1H), 7.68−7.60 (m, 2H), 7.50−7.46 (m, 2H), 7.42−7.35 (m, 3H), 6.92 (d, *J* = 15.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 142.6, 137.5, 135.2, 132.4, 132.3, 131.3, 129.7, 129.4, 129.3, 129.2, 129.1, 128.6, 128.0, 127.7, 127.3, 122.6; MS (*m*/*z*) calcd for $C_{18}H_{14}O_2S$ 294.1, found 295.1 (M + H)$^+$.

(E)-1-Chloro-4-(styrylsulfonyl)benzene (**3o**).[3g] White solid, mp: 82−84 °C, yield 42% (35.1 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.90−7.86 (m, 2H), 7.69 (d, *J* = 15.6 Hz, 1H), 7.53−7.46 (m, 4H), 7.43−7.36 (m, 3H), 6.85 (d, *J* = 15.6 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 143.1, 140.1, 139.2, 132.2, 131.5, 129.7, 129.2, 129.2, 128.7, 126.8; MS (*m*/*z*) calcd for $C_{14}H_{11}ClO_2S$ 278.0, found 279.0 (M + H)$^+$.

(E)-1-Fluoro-4-(styrylsulfonyl)benzene (**3p**).[3g] White solid, mp: 80−82 °C, yield 41% (32.3 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 8.00−7.94 (m, 2H), 7.68 (d, *J* = 15.6 Hz, 1H), 7.51−7.46 (m, 2H), 7.43−7.36 (m, 3H), 7.25−7.18 (m, 2H), 6.86 (d, *J* = 15.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 165.6 (d, *J* = 254.5 Hz), 142.7, 136.8 (d, *J* = 3.1 Hz), 132.2, 131.4, 130.5 (d, *J* = 9.6 Hz), 129.1, 128.6, 127.1, 116.7 (d, *J* = 22.5 Hz); MS (*m*/*z*) calcd for $C_{14}H_{11}FO_2S$ 262.0, found 263.0 (M + H)$^+$.

(E)-1-Nitro-4-(styrylsulfonyl)benzene (**3q**).[12] White solid, mp: 152−154 °C, yield 42% (36.4 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 8.40−8.37 (m, 2H), 8.17−8.13 (m, 2H), 7.77 (d, *J* = 15.2 Hz, 1H), 7.53−7.49 (m, 2H), 7.47−7.39 (m, 3H), 6.87 (d, *J* = 15.2 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 150.5, 146.6, 145.0, 131.9, 131.8, 129.3, 129.0, 128.9, 125.7, 124.6; MS (*m*/*z*) calcd for $C_{14}H_{11}NO_4S$ 289.0, found 290.0 (M + H)$^+$.

(E)-1-Methoxy-4-(styrylsulfonyl)benzene (**3r**).[3e] White solid, mp: 83−85 °C, yield 72% (59.3 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.90−7.85 (m, 2H), 7.63 (d, *J* = 15.2 Hz, 1H), 7.49−7.45 (m, 2H), 7.41−7.36 (m, 3H), 7.03−6.99 (m, 2H), 6.84 (d, *J* = 15.6 Hz, 1H), 3.87 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 163.6, 141.4, 132.5, 132.2, 131.0, 129.9, 129.1, 128.5, 127.9, 114.6, 55.7; MS (*m*/*z*) calcd for $C_{15}H_{14}O_3S$ 274.1, found 275.1 (M + H)$^+$.

(E)-1-Ethyl-4-(2-tosylvinyl)benzene (**3s**). White solid, mp: 80−82 °C, yield 71% (61.0 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.82 (d, *J* = 8.0 Hz, 2H), 7.63 (d, *J* = 15.6 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 15.6 Hz, 1H), 2.65 (q, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 148.0, 144.3, 142.1, 137.9, 130.0, 129.9, 128.7, 128.6, 127.6, 126.4, 28.8, 21.6, 15.3; HRMS (TOF MS CI$^-$) calculated for $C_{17}H_{18}O_2S$ 286.1028, found 286.1024.

(E)-2-(2-Tosylvinyl)pyridine (**3t**).[3b] White solid, mp: 84−86 °C, yield 62% (48.2 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 8.60 (d, *J* = 4.0 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.73 (td, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.62 (d, *J* = 15.2 Hz, 1H), 7.44 (d, *J* = 15.2 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.31−7.27 (m, 1H), 2.43 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 151.1, 150.3, 144.6, 140.1, 137.2, 137.1, 132.1, 130.0, 127.9, 125.4, 125.0, 21.6; MS (*m*/*z*) calcd for $C_{14}H_{13}NO_2S$ 259.1, found 260.1 (M + H)$^+$.

1-Methyl-4-(4-(prop-1-enyl)styrylsulfonyl)benzene (**3u**). Yellow oil, yield 56% (50.1 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 7.84 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 15.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.82 (d, *J* = 15.2 Hz, 1H), 2.63 (t, *J* = 7.6 Hz, 2H), 2.44 (s, 3H), 1.65−1.57 (m, 2H), 1.36−1.27 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 146.8, 144.3, 142.1, 138.0, 129.9, 129.9, 129.2, 128.6, 127.6, 126.4, 35.8, 31.4, 30.9, 22.5, 21.6, 14.0; HRMS (TOF MS CI$^-$) calculated for $C_{20}H_{24}O_2S$ 328.1497, found 328.1498.

(E)-3-(2-Tosylvinyl)pyridine (**3v**).[13] White solid, mp: 108−110 °C, yield 80% (62.2 mg); ^{1}H NMR (400 MHz, CDCl$_3$) 8.72 (s, 1H), 8.62 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.80 (dt, *J* = 8.0 Hz, 1.6 Hz, 1H), 7.66 (d, *J* = 15.6 Hz, 1H), 7.39−7.32 (m, 3H), 6.98 (d, *J* = 15.6 Hz, 1H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) (*δ*, ppm) 151.7, 149.9, 144.8, 138.2, 137.1, 134.8, 130.1, 129.9, 128.4, 127.8, 123.9, 21.7; MS (*m*/*z*) calcd for $C_{14}H_{13}NO_2S$ 259.1, found 260.1 (M + H)$^+$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all products. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jcmao@suda.edu.cn

*E-mail: guzhang@jjay.cuny.edu

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the grants from the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry, the Priority Academic Program Development of Jiangsu Higher Education Institutions, and the Key Laboratory of Organic Synthesis of Jiangsu Province. G.Z. acknowledges a PSC- CUNY award (no. 67312-0045) from the City University of New York.

REFERENCES

(1) (a) Uttamchandani, M.; Liu, K.; Panicker, R. C.; Yao, S. Q. *Chem. Commun.* **2007**, 1518. (b) Reddick, J. J.; Cheng, J.; Roush, W. R. *Org. Lett.* **2003**, *5*, 1967. (c) Wang, G.; Mahesh, U.; Chen, G. Y. J.; Yao, S. Q. *Org. Lett.* **2003**, *5*, 737. (d) Meadows, D. C.; Sanchez, T.; Neamati, N.; North, T. W.; Gervay-Hague, J. *Bioorg. Med. Chem.* **2007**, *15*, 1127. (e) Frankel, B. A.; Bentley, M.; Kruger, R. G.; McCafferty, D. G. *J. Am. Chem. Soc.* **2004**, *126*, 3404.

(2) (a) Kumamoto, H.; Deguchi, K.; Wagata, T.; Furuya, Y.; Odanaka, Y.; Kitade, Y.; Tanaka, H. *Tetrahedron.* **2009**, *65*, 8007. (b) Zhu, Q.; Lu, Y. *Org. Lett.* **2009**, *11*, 1721. (c) Arjona, O.; Menchaca, R.; Plumet, J. *Org. Lett.* **2001**, *3*, 107. (d) Noshi, M. N.; El-awa, A.; Torres, E.; Fuchs, P. L. *J. Am. Chem. Soc.* **2007**, *129*, 11242. (e) Wardrop, D. J.; Fritz. *J. Org. Lett.* **2006**, *8*, 3659. (f) Sulzer-Mossé, S.; Alexakis, A.; Mareda, J.; Bollot, G.; Bernardinelli, G.; Filinchuk, Y. *Chem.—Eur. J.* **2009**, *15*, 3204. (g) López-Pérez, A.; Robles-Machín, R.; Adrio, J.; Carretero, J. C. *Angew. Chem., Int. Ed.* **2007**, *46*, 9261.

(3) (a) Katrun, P.; Chiampanichayakul, S.; Korworapan, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Kuhakarn, C. *Eur. J. Org. Chem.* **2010**, 5633. (b) Sawangphon, T.; Katrun, P.; Chaisiwamongkhol, K.; Pohmakotr, M.; Reutrakul, V.; Jaipetch, T.; Soorukram, D.; Kuhakarn, C. *Synth. Commun.* **2013**, *43*, 1692. (c) Nair, V.; Augustine, A.; George, T. G.; Nair, L. G. *Tetrahedron Lett.* **2001**, *42*, 6763. (d) Das, B.; Lingaiah, M.; Damodar, K.; Bhunia, N. *Syhthesis* **2011**, 2941. (e) Li, X.; Xu, Y.; Wang, W.; Jiang, C.; Qi, C.; Jiang, H. *Chem.—Eur. J.* **2014**, *20*, 7911. (f) Jiang, Q.; Xu, B.; Jia, J.; Zhao, A.; Zhao, Y.-R.; Li, Y.-Y.; He, N.-N.; Guo, C.-C. *J. Org. Chem.* **2014**, *79*, 7372. (g) Xu, Y.; Tang, X.; Hu, W.; Jiang, H. *Green. Chem.* **2014**, *16*, 3720.

(4) (a) Wei, W.; Li, J.; Yang, D.; Wen, J.; Jiao, Y.; You, J.; Wang, H. *Org. Biomol. Chem.* **2014**, *12*, 1861. (b) Taniguchi, N. *Tetrahedron* **2014**, *70*, 1984. (c) Xu, Y.; Zhao, J.; Tang, X.; Wu, W.; Jiang, H. *Adv. Synth. Catal.* **2014**, *9*, 2029.

(5) (a) Park, J. H.; kim, S. Y.; Kim, S. M.; Chung, Y. K. *Org. Lett.* **2007**, *9*, 2465. (b) Yu, D.-G.; Gensch, T.; Azambuja, F.; Vasquez-Cespedes, S.; Glorius, F. *J. Am. Chem. Soc.* **2014**, *136*, 17722. (c) Grigorjeva, L.; Daugulis, O. *Org. Lett.* **2014**, *16*, 4684. (d) Bonnamour, J.; Bolm, C. *Org. Lett.* **2011**, *13*, 2012. (e) Cong, X.; Zeng, X. *Org. Lett.* **2014**, *16*, 3716.

(6) (a) Jia, W.; Jiao, N. *Org. Lett.* **2010**, *12*, 2000. (b) Priebbenow, D. L.; Becker, P.; Bolm, C. *Org. Lett.* **2013**, *15*, 6155. (c) Min, H.; Palani, T.; Park, K.; Hwang, J.; Lee, S. *J. Org. Chem.* **2014**, *79*, 6279. (d) Yu, M.; Pan, D.; Chen, W.; Jiao, N. *Tetrahedron Lett.* **2010**, *51*, 1287. (e) Kolarovic, A.; Faberova, Z. *J. Org. Chem.* **2009**, *74*, 7199. (f) Kumar, M. R.; Irudayanathan, F. M.; Moon, J. H.; Lee, S. *Adv. Synth. Catal.* **2013**, *355*, 3221. (g) Kolarovic, A.; Schnurch, M.; Mihovilovic, M. *J. Org. Chem.* **2011**, *76*, 2613. (h) Pan, D.; Zhang, C.; Ding, S.; Jiao, N. *Eur. J. Org. Chem.* **2011**, 4751.

(7) (a) Ji, Y.-L.; Lin, J.-H.; Xiao, J.-C.; Gu, Y.-C. *Eur. J. Org. Chem.* **2014**, 7948. (b) Saikia, A. K.; Unnava, R.; Indukuri, K.; Sarkar, S. *RSC Adv.* **2014**, *4*, 55296. (c) Wang, X.; Wang, Z. *Tetrahedron* **2014**, *70*, 6728. (d) Fan, B.; Li, S.; Chen, H.; Lu, Z.; Liu, S. *Adv. Synth. Catal.* **2013**, *355*, 2827. (e) Xiao, Q.; Sheng, J.; Ding, Q.; Wu, J. *Adv. Synth. Catal.* **2013**, *355*, 2321.

(8) (a) Li, X.; Xu, X.; Shi, X. *Tetrahedron Lett.* **2013**, *54*, 3071. (b) Taniguchi, T.; Idota, A.; Ishibashi, H. *Org. Biomol. Chem.* **2011**, *9*, 3151. (c) Li, X.; Xu, X.; Zhou, C. *Chem. Commun.* **2012**, *48*, 12240.

(9) (a) Hu, G.; Gao, Y.; Zhao, Y. *Org. Lett.* **2014**, *16*, 4464. (b) Lee, J.-E.; Kwon, J.; Yun, J. *Chem. Commun.* **2008**, 733. (c) Jia, W.; Jiao, N. *Org. Lett.* **2010**, *12*, 2000. (d) Allen, S. E.; Walvoord, R. R.; Padilla-Salinas, R.; Kozlowski, M. C. *Chem. Rev.* **2013**, *113*, 6234.

(10) (a) Zhang, Y.; Feng, J.; Li, C.-J. *J. Am. Chem. Soc.* **2008**, *130*, 2900. (b) Rong, G.; Liu, D.; Lu, L.; Yan, H.; Zheng, Y.; Chen, J.; Mao, J. *Tetrahedron* **2014**, *70*, 5033.

(11) Tang, S.; Wu, Y.; Liao, W.; Bai, R.; Liu, C.; Lei, A. *Chem. Commun.* **2014**, *50*, 4496.

(12) Obushak, N. D.; Bilaya, E. E.; Ganushchak, N. I. *Russian J. Org. Chem.* **1991**, *27*, 2372.

(13) Baliah, V.; Seshapathirao, M. *J. Org. Chem.* **1959**, *24*, 867.

DOI: 10.1021/acs.joc.5b00558
J. Org. Chem. 2015, 80, 4697−4703