JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Synthesis of Allenyl Sulfones via a TBHP/TBAI-Mediated Reaction of Propargyl Alcohols with Sulfonyl Hydrazides

Zheng Yang,[†] Wen-Juan Hao,*[,†] Shu-Liang Wang,[†] Jin-Peng Zhang,[‡] Bo Jiang,*[,†] Guigen Li,[§,∥] and Shu-Jiang Tu*[,†]

[†]School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory of Green Synthetic Chemistry for Functional Materials, Jiangsu Normal University, Xuzhou, Jiangsu, 221116, People's Republic of China

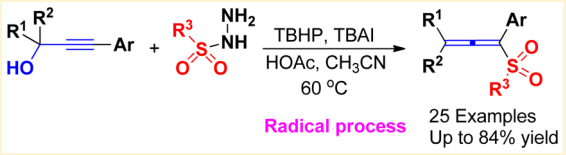
[‡]Department of Public Health, Xuzhou Medical College, Xuzhou, Jiangsu 221000, People's Republic of China

[§]Institute of Chemistry & BioMedical Sciences, Collaborative Innovation Center of Chemistry for Life Sciences, Nanjing University, Nanjing, Jiangsu, 210093, People's Republic of China

[∥]Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, United States

Supporting Information

ABSTRACT: A new TBHP/TBAI-mediated reaction of propargyl alcohols with sulfonyl hydrazides in the presence of HOAc has been established, in which a wide variety of allenyl sulfones were obtained in moderate to excellent yields. Mechanistic studies indicate that this transformation involves HOAc-promoted sulfonohydrazide intermediate formation, sequential C−O, C−N, and N−S bond cleavage, and C−S bond formation. Significantly, this sulfonohylation proceeds in a radical process and shows highly functional group compatibility and excellent regioselectivity, with a short reaction time and inexpensive reagents.

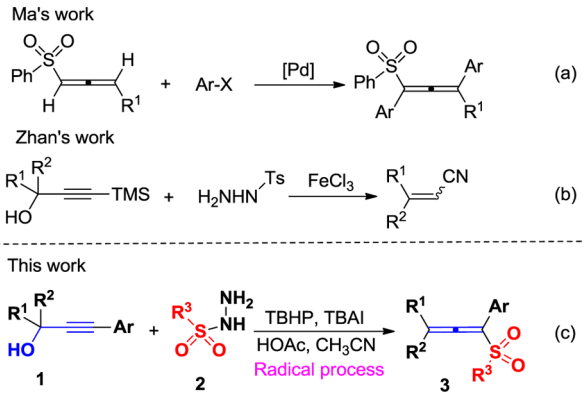


INTRODUCTION

Allenes represent a privileged structural unit in a wide range of non-naturally and naturally occurring products.[1] Furthermore, allenes serve as an important and useful building block for substrate-specific domino cyclizations and have been widely utilized for numerous challenging and intriguing syntheses.[2,3] They can readily result in various compounds with multifunctionalities via synergistic cascade processes across C═C bonds system in one-pot fashions.[4] So far, enormous efforts have been focused on the high-efficiency synthesis of allenes, which has made it more powerful and applicable.[5−7] Moreover, functional allenyl sulfones have been extensively applied in conjugate additions and cycloadditions,[8] because these molecules not only behave high and unique reactivity but also the sulfone functionality can be removed by various desulfonylation methods.[9] The increasing applications of allenyl sulfones have stimulated investigations on new methodologies for their synthesis.[10] For instance, Fu and Ma developed Heck-type cross-coupling reaction of allenes with aryl halides, leading to polysubstituted 1,2-allenyl sulfones (Scheme 1a).[11] Despite these advances, the development of a more flexible protocol toward allenyl sulfones with broad functional group tolerability is still highly desirable.

In the past decades, propargyl alcohols have proven to be versatile synthons and have been efficiently employed in various transformations and the preparation of bioactive molecules.[12] Wang et al. reported the synthesis of allenephosphoramides through the $Yb(OTf)_3$-catalyzed reaction of propargyl alcohols and diethyl arylphosphoramides.[13] However, in sharp contrast, a facile metal-free sulfonylation of

Scheme 1. Profiling Applications of Propargylic Alcohols



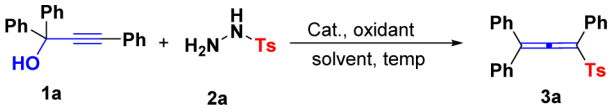
allenes initiated by a sulfonyl radical from propargyl alcohols is virtually unexplored. Very recently, Zhang et al. employed propargylic alcohols to react with *p*-tolylsulfonohydrazide to access acrylonitriles using $FeCl_3$ as a catalyst (Scheme 1b).[14] Inspired by these useful transformations and our recent studies on oxidative coupling reactions,[15] we envisioned that, under the right set of oxidative conditions, the reaction of propargylic alcohols with sulfonyl hydrazides would proceed in a radical process to form allenyl sulfones. Herein, we report the successful realization of this concept with the introduction of sulfonyl radicals for the flexible synthesis of polysubstituted

Received: July 21, 2015
Published: August 17, 2015

ACS Publications © 2015 American Chemical Society

DOI: 10.1021/acs.joc.5b01684
J. Org. Chem. 2015, 80, 9224−9230

Table 1. Optimization of Reaction Conditions[a]



entry	oxidant (equiv)	catalyst (mol %)	additive (mL)	solvent	t (°C)	yield[b] (%)
1	TBHP (2.0)	TBAI (20)		MeCN	40	26
2	H_2O_2 (2.0)	TBAI (20)		MeCN	40	ND
3	DTBP (2.0)	TBAI (20)		MeCN	40	ND
4	TBHP (2.0)	TBAI (20)		MeCN	60	52
5	TBHP (2.0)	TBAI (20)		MeCN	80	37
6	TBHP (2.0)	I_2 (20)		MeCN	60	ND
7	TBHP (2.0)	CuI (20)		MeCN	60	ND
8	TBHP (2.0)	KI (20)		MeCN	60	ND
9	TBHP (2.0)	TBAI (20)	HOAc (1.0)	MeCN	60	71
10	TBHP (2.0)	TBAI (20)	HOAc (2.0)	MeCN	60	84
11	TBHP (2.0)	TBAI (20)	HOAc (2.0)	EtOH	60	ND
12	TBHP (2.0)	TBAI (20)	HOAc (2.0)	THF	60	48
13	TBHP (2.0)	TBAI (20)	HOAc (2.0)	DCE	60	62
14	TBHP (2.0)	TBAI (20)	HOAc (2.0)	1,4-dioxane	60	59
15	TBHP (2.0)	TBAI (20)	HOAc (2.0)	EA	60	41
16	TBHP (2.0)	TBAI (10)	HOAc (2.0)	MeCN	60	31
17	TBHP (3.0)	TBAI (20)	HOAc (2.0)	MeCN	60	56
18	TBHP (4.0)	TBAI (20)	HOAc (2.0)	MeCN	60	41
19	TBHP (2.0)	TBAI (10)	–	HOAc	60	43
20	–	TBAI (20)	HOAc (2.0)	MeCN	60	ND

[a]Reaction conditions: **1a** (1.0 mmol), **2a** (2.0 mmol), additive, catalyst (0.2 equiv), oxidant (2.0 equiv) in solvent (4 mL). [b]Isolated yield is based on **1a**. ND = Not detected.

allenyl sulfones using tetrabutylammonium iodide (TBAI) and *tert*-butyl hydroperoxide (TBHP) (Scheme 1c).

RESULTS AND DISCUSSION

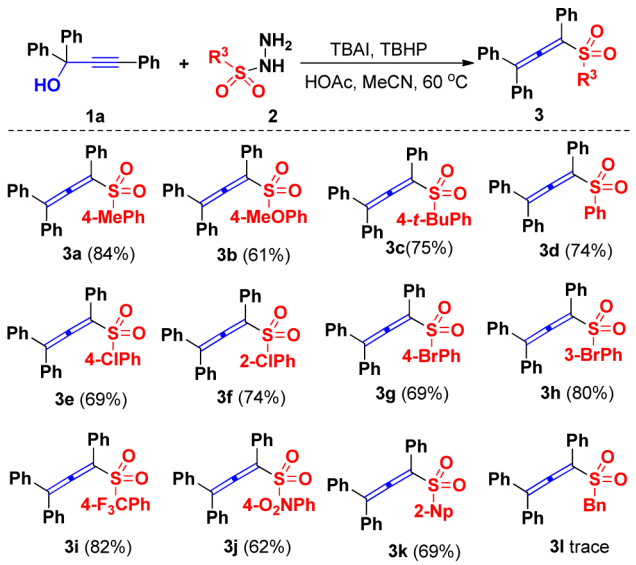
Optimization of the reaction conditions was performed by taking 1,1,3-triphenylprop-2-yn-1-ol (**1a**) and *p*-toluenesulfonyl hydrazide (**2a**) as the model substrates. Initially the reaction of **1a** with **2a** was performed employing a combination of TBAI (20 mol %) and TBHP (2.0 equiv, 70% in water) in acetonitrile at 40 °C, and the desired product **3a** was afforded, albeit with a low yield of 26% (Table 1, entry 1). Other oxidants, such as H_2O_2 and di-*t*-butyl peroxide (DTBP), were proven to be ineffective for this transformation (Table 1, entries 2 and 3). An increase in the reaction temperature to 60 °C delivered a higher yield of **3a** (entry 4); however, a higher reaction temperature (80 °C) decreased the chemical yield (entry 5). A subsequent investigation of other catalysts was conducted in CH_3CN. As illustrated in entries 6−8, different types of catalysts including I_2, CuI, and KI were investigated in the model reaction, and it turned out that these catalysts hardly facilitate the reaction (entries 6−8). Next, we found that the use of HOAc (1.0 mL) as an additive delivered **3a** in 71% yield (entry 9). Notably, with the use of TBAI (20 mol %) and TBHP (2.0 equiv), properly increasing the amount of HOAc (2.0 mL) could efficiently improve the yield to 84%, and the starting material **1a** was completely consumed (entry 10). Other solvents such as EtOH, tetrahydrofuran (THF), dichloroethane (DCE), 1,4-dioxane, and ethyl acetate (EA) were inferior to acetonitrile in terms of reaction yields (entries 11−15). Lowering the loading of TBAI or increasing the amount of TBHP gave unsatisfactory results (31−56% yields; entries 16−18). Using HOAc as a solvent did not improve the yield of **3a** (entry 19). Without oxidant, no product **3a** was observed (entry 20).

Having identified this acceptable optimization, we next set out to expand the scope of this reaction by utilizing different sulfonyl hydrazides. First, the influence of substituents in the phenyl ring of sulfonyl hydrazides **2** was investigated, which found that the sulfonylation reaction tolerated a broad spectrum of substituted sulfonyl hydrazides carrying either electron-donating, electron-neutral, or electron-withdrawing groups under the optimized conditions (Scheme 2). The variant of substituents resided at different positions on the phenyl ring, such as Me, MeO, *t*-Bu, Cl, and Br, were compatible, giving access to the expected allenyl sulfones **3a**−**h** with yields ranging 61−84%. Notably, the sterically more demanding 2-chlorophenyl and 2-naphthalenyl (2-Np) sulfonyl hydrazides were found to have no influence on the course of the reaction, with allenyl sulfones **3f** and **3k** afforded in 74% and 69% yields, respectively. Even for challenging cases in which a strong electron-withdrawing effect exists on the para position on the aromatic ring (**3i** and **3j**), good yields of 82% and 62% were provided. Obviously, this sulfonylation can tolerate structurally diverse substrates with steric bulk and a different electronic nature. Unluckily, aliphatic sulfonyl hydrazide (**2l**) was not an adaptable substrate for this, which may be ascribed to the relative instability of the sulfonyl radicals generated in situ from aliphatic sulfonyl hydrazides.

After the successful utilization of various sulfonyl hydrazides, we next extended our investigation to the electronic nature of substituents on the phenyl ring of propargyl alcohols. As per our expectation, propargyl alcohols bearing both electron-donating and electron-withdrawing groups on the aromatic alkyne moiety could take part in

DOI: 10.1021/acs.joc.5b01684
J. Org. Chem. 2015, 80, 9224−9230

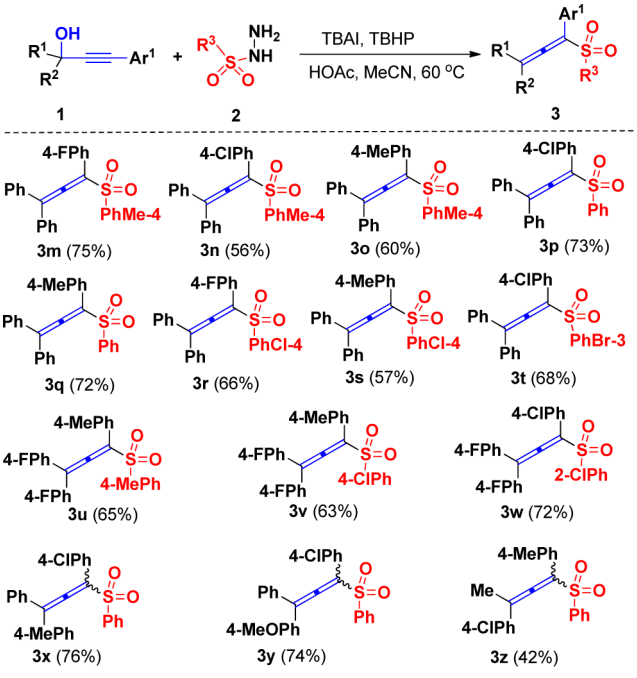
Scheme 2. Scope of the TBHP/TBAI-Mediated Sulfonylation Reaction[a]



[a]Yields of isolated products after column chromatography on a silica gel are given. Compound **1a** (1.0 mmol) and **2** (2.0 mmol), TBAI (0.2 mmol), TBHP (2.0 mmol, 70% in water), HOAc (2.0 mL), MeCN (4.0 mL), under an air atmosphere at 60 °C, 0.5 h.

these reactions. Functional groups such as fluoride, chloride, and methyl were well-tolerated (Scheme 3, **3m**−**3t**). Likewise, different substituents on the aromatic rings directly bounded to the hydroxyl group can enable the reaction to occur steadily, efficiently converting into the corresponding products

Scheme 3. Scope of the TBHP/TBAI-Mediated Sulfonylation Reaction[a]

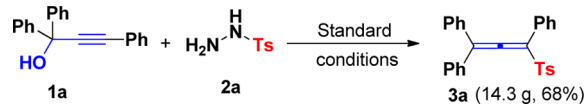


[a]Yields of isolated products after column chromatography on silica gel are given. Compound **1** (1.0 mmol) and **2** (2.0 mmol), TBAI (0.2 mmol), TBHP (2.0 mmol, 70% in water), HOAc (2.0 mL), MeCN (4.0 mL), under an air atmosphere at 60 °C, 0.5 h.

3u−**3y** in 63−76% yields. Additionally, a significant drop in the yield was observed for substrate with a hydroxyl group linked to a methyl group as has been demonstrated with propargyl alcohol **1i**, giving its expected product **3z** in a 42% yield. These observations showed that most functionalities of synthetic allenyl sulfones offer a flexible protocol to their further structural modifications. The structures of products **3** were unambiguously determined by their NMR and high-resolution mass spectrometry (HR-MS). Moreover, the structure of compound **3a** was further confirmed by single-crystal X-ray diffraction analysis. In general, these sulfonylation-based domino reactions provide a new example for forming richly decorated allenes, which are widespread structural cores in many bioactive compounds and serve as important synthons for further applications.

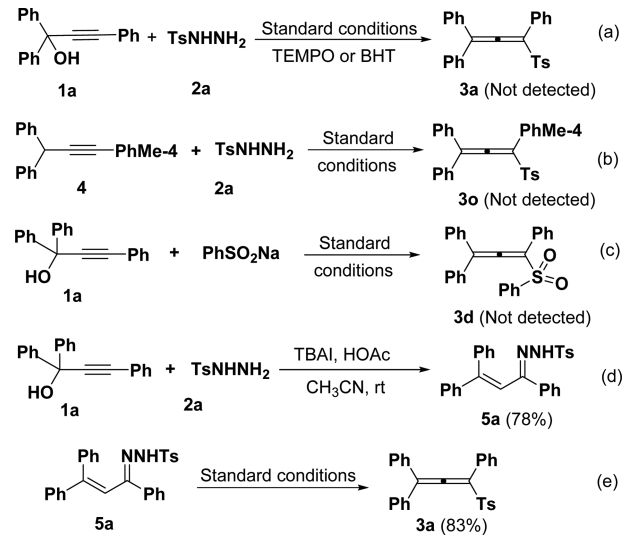
Noteworthy, when using easily prepared propargylic alcohol **1a** as the substrate to develop the efficiency of our method, a gram-scale reaction of **1a** (50 mmol) with **2a** (100 mmol) could be carried out under the standard conditions to provide **3a** in a 68% yield (Scheme 4), which offered a potential application in organic synthesis.

Scheme 4. Scale-Up Experiment



To understand the mechanism, several control experiments were conducted. Treatment of propargyl alcohol **1a** with tosylhydrazide **2a** in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) or butylhydroxytoluene (BHT) (2.0 equiv) under the standard conditions gave complex mixtures without observation of desired product **3a**, which indicates a possible radical mechanism (Scheme 5a). The preformed prop-2-yne-1,1,3-triyltribenzene **4** was subjected to the reaction with **2a**, but no expected product **3o** was observed (Scheme 5b), confirming the hydroxyl group is essential for the success of this transformation. The reaction of **1a** and sodium benzensulfinate under the standard conditions failed to access the desired product **3a**, indicating that hydrazides

Scheme 5. Controlling Reactions

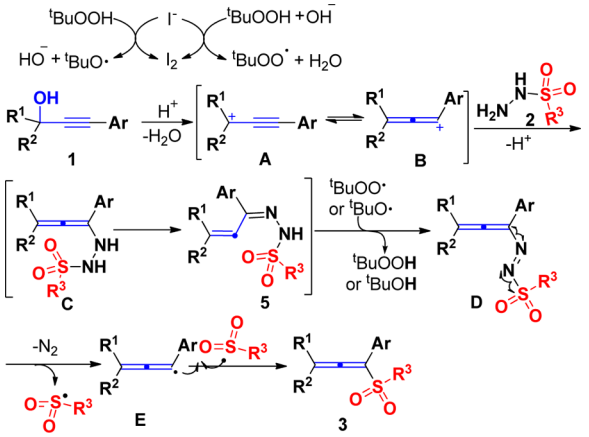


DOI: 10.1021/acs.joc.5b01684
J. Org. Chem. 2015, 80, 9224−9230

may participate in this reaction process (Scheme 5c). Without TBHP, propargyl alcohol **1a** was treated with tosylhydrazide **2a** under the standard conditions at room temperature, providing sulfonohydrazide **5a** in 78% yield (Scheme 5d). Subsequently, the reaction of sulfonohydrazide **5a** under the standard conditions generated the corresponding allenyl sulfone **3a** in an 83% chemical yield (Scheme 5c). This observation proves that the reaction process involved the formation of a sulfonohydrazide intermediate.

On the basis of the above analysis and literature survey,[12,13] a reasonable mechanism is outlined in Scheme 6. Propargyl

Scheme 6. Possible Mechanism



alcohols **1** are first converted to the allenic carbocation **B** via a Meyer−Schuster rearrangement.[16] Then, **B** is trapped by **2** to afford the key intermediate allenyl sulfonhydrazides **C**, followed by tautomerization to yield sulfonohydrazides **5**. The sulfonohydrazides **5** convert into allenyl sulfonyldiazenes **D** via H-abstractions by ^{t}BuO or ^{t}BuOO radical generated from TBAI-accelerated decomposition of TBHP.[17,18] Intermediate **D** undergoes a sequential homolysis and radical coupling process to afford target products **3**. Although the catalytic formation of allenyl sulfones has been achieved well,[10,11] sulfonyl radical initiated functionalization of propargyl alcohols toward allenyl sulfones is very rare in organic chemistry as mentioned earlier.

In conclusion, we have successfully developed an interesting method for the construction of polysubstituted allenyl sulfones in a highly functional-group-compatible manner via TBHP/TBAI-mediated reaction of propargyl alcohols with commercially available sulfonyl hydrazide in the presence of HOAc. The reaction pathway may involve a Meyer−Schuster rearrangement/key sulfonohydrazide intermediate formation/H-abstractions/homolysis of sulfonyldiazenes/radical coupling sequence by the sequential cleavage of C−O, C−N, and N−S bonds. This novel method not only extends the applications of propargyl alcohols in organic chemistry but also provides an invaluable access to structurally diverse allenyl sulfones. Moreover, this reaction could be enlarged to the gram scale in a satisfactory yield of 68%, which might display potential application in industrial production.

EXPERIMENTAL SECTION

General. All one-pot reactions were carried out in a 25 mL Schlenk tube equipped with a magnetic stir bar under air. Arylsulfonyl hydrazides **3** were prepared according to the known literature.[19] All other reagents were obtained from commercial sources and used as received, if not stated otherwise. All melting points are uncorrected. The NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz instrument with TMS as the internal standard. Chemical shifts (δ) were reported in parts per million with respect to TMS. Data are represented as follows: chemical shift, mutiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J, Hz), and integration. HR-MS analyses were carried out using a time-of-flight (TOF)-MS instrument with an electrospray ionization (ESI) source. X-ray crystallographic analysis was performed with a SMART CCD and a P4 diffractometer.

General Procedure for the Synthesis of 3. *Example for the Synthesis of* ***3a****.* 1,1,3-Triphenylprop-2-yn-1-ol (**1a**, 1.0 mmol, 284 mg) was introduced in a 25 mL Schlenk tube, *p*-toluenesulfonyl hydrazide (**2a**, 2.0 mmol, 372 mg), TBAI (0.2 mmol, 74 mg), *tert*-butyl hydroperoxide (2.0 mmol, 70% in water, 257 mg), acetic acid (2.0 mL), and acetonitrile (4.0 mL) were then successively added, and the mixture was stirred at 60 °C. After the completion of the reaction (monitored by TLC), the solvent was removed under vacuum. The residue was separated by flash column chromatography on silica gel (eluent, petroleum ether/ethyl acetate 12:1 v/v) to afford the pure product **3a**.

*(3-Tosylpropa-1,2-diene-1,1,3-triyl)tribenzene (**3a**).* White solid, 354 mg, 84% yield. mp 122−124 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.65 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 9.6 Hz, 2H), 7.39−7.32 (m, 13H), 7.10 (s, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.0, 144.3, 137.5, 133.8, 129.9, 129.5, 129.3, 129.0, 128.8, 128.8, 128.7, 128.7, 128.1, 118.9, 117.8, 21.6. HR-MS (ESI-TOF) m/z calcd for $C_{28}H_{22}NaO_2S$, 445.1233 $[M + Na]^+$; found: 445.1239.

*(3-((4-Methoxyphenyl)sulfonyl)propa-1,2-diene-1,1,3-triyl)-tribenzene (**3b**).* White solid, 267 mg, 61% yield. mp 141−143 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.69 (d, J = 8.8 Hz, 2H), 7.61−7.59 (m, 2H), 7.38−7.32 (m, 13H), 6.78 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 206.6, 163.5, 133.8, 131.9, 130.3, 129.3, 129.0, 128.8, 128.8, 128.7, 128.7, 128.7, 118.8, 118.0, 114.0, 55.6. HR-MS (ESI-TOF) m/z calcd for $C_{28}H_{22}NaO_3S$, 461.1182 $[M + Na]^+$; found 461.1178.

*(3-((4-(tert-Butyl)phenyl)sulfonyl)propa-1,2-diene-1,1,3-triyl)-tribenzene (**3c**).* White solid, 348 mg, 75% yield. mp 123−125 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.89−7.64 (m, 4H), 7.50−7.31 (m, 15H), 1.30 (d, J = 15.2 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 206.8, 157.3, 137.4, 133.7, 131.7, 131.0, 129.8, 128.7, 128.6, 128.1, 128.0, 125.8, 124.8, 118.9, 117.9, 35.1, 31.0. HR-MS (ESI-TOF) m/z calcd for $C_{31}H_{28}NaO_2S$, 487.1703 $[M + Na]^+$; found 487.1706.

*(3-(Phenylsulfonyl)propa-1,2-diene-1,1,3-triyl)tribenzene (**3d**).* White solid, 302 mg, 74% yield. mp 150−152 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.78−7.76 (m, 2H), 7.59−7.57 (m, 2H), 7.50−7.46 (m, 1H), 7.38−7.29 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.0, 140.3, 133.6, 133.4, 129.1, 128.9, 128.8(5), 128.8(0), 128.7(8), 128.7(6), 128.7, 128.1, 119.1, 117.5. HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{20}NaO_2S$, 431.1077 $[M + Na]^+$; found 431.1090.

*(3-((4-Chlorophenyl)sulfonyl)propa-1,2-diene-1,1,3-triyl)-tribenzene (**3e**).* White solid, 305 mg, 69% yield. mp 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.69−7.66 (m, 2H), 7.60−7.58 (m, 2H), 7.40−7.32 (m, 13H), 7.28 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.2, 140.1, 138.9, 133.4, 129.4, 129.3, 129.1(3), 129.0(5), 128.9, 128.8, 128.7, 119.5, 117.5. HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{19}ClNaO_2S$, 465.0687 $[M + Na]^+$; found 465.0691.

*(3-((2-Chlorophenyl)sulfonyl)propa-1,2-diene-1,1,3-triyl)-tribenzene (**3f**).* White solid, 327 mg, 74% yield. mp 123−125 °C .^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.15−8.13 (m, 1H), 7.63−7.61 (m, 2H), 7.38−7.27 (m, 15H), 7.18−7.16 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.1, 137.4, 134.3, 133.5, 133.3, 131.7, 131.6, 129.2, 129.0(5), 129.0(0), 128.8(5), 128.8, 128.7, 126.8, 120.4, 116.5. HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{19}ClNaO_2S$, 465.0687 $[M + Na]^+$; found 465.0692.

DOI: 10.1021/acs.joc.5b01684
J. Org. Chem. 2015, 80, 9224−9230

*(3-((4-Bromophenyl)sulfonyl)propa-1,2-diene-1,1,3-triyl)-tribenzene (**3g**).* White solid, 335 mg, 69% yield. mp 120−122 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.60−7.57 (m, 4H), 7.44−7.31 (m, 15H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.3, 139.5, 133.4, 132.1, 129.5, 129.3, 129.1, 128.9, 128.8, 128.7, 128.7, 119.5, 117.4. HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{19}BrNaO_2S$, 509.0182 $[M + Na]^+$; found 509.0187.

*(3-((3-Bromophenyl)sulfonyl)propa-1,2-diene-1,1,3-triyl)-tribenzene (**3h**).* White solid, 389 mg, 80% yield. mp 87−89 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.93−7.92 (m, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.63−7.60 (m, 3H), 7.43−7.34 (m, 13H), 7.24−7.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.3, 142.3, 136.4, 133.3, 130.9, 130.3, 129.3, 129.1, 128.9, 128.9, 128.8, 128.7, 128.6, 126.6, 123.0, 119.6, 117.3. HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{19}BrNaO_2S$, 509.0182 $[M + Na]^+$; found 509.0185.

*(3-((4-(Trifluoromethyl)phenyl)sulfonyl)propa-1,2-diene-1,1,3-triyl)tribenzene (**3i**).* White solid, 409 mg, 82% yield. mp 119−121 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.86 (d, J = 8.0 Hz, 2H), 7.61−7.59 (m, 2H), 7.54 (d, J = 8.0 Hz, 2H), 7.39−7.29 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.6, 144.1, 135.0 (J_{CF} = 32.9 Hz), 134.7, 133.2, 129.4, 129.2, 128.9, 128.9, 128.8, 128.6, 128.5, 125.9 (J_{CF} = 3.7 Hz), 123.1 (J_{CF} = 271.3 Hz), 119.8, 117.2. HR-MS (ESI-TOF) m/z calcd for $C_{28}H_{19}F_3NaO_2S$, 499.0951 $[M + Na]^+$; found 499.0965.

*(3-((4-Nitrophenyl)sulfonyl)propa-1,2-diene-1,1,3-triyl)tribenzene (**3j**).* White solid, 281 mg, 62% yield. mp 167−169 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.11−8.09 (m, 2H), 7.91−7.88 (m, 2H), 7.60−7.57 (m, 2H), 7.41−7.32 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 208.1, 150.4, 146.3, 133.0, 129.6, 129.4, 129.2, 129.0, 129.0, 128.8, 128.6, 128.4, 124.0, 120.2, 117.0. HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{19}NNaO_4S$, 476.0927 $[M + Na]^+$; found 476.0929.

*1-((1,3,3-Triphenylpropa-1,2-dien-1-yl)sulfonyl)naphthalene (**3k**).* White solid, 316 mg, 69% yield. mp 134−136 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.35 (s, 1H), 7.81 (d, J = 8.4 Hz, 1H), 7.73−7.68 (m, 3H), 7.62−7.52 (m, 4H), 7.35−7.28 (m, 13H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.5, 137.4, 135.1, 133.6, 132.0, 129.1, 129.4, 129.2, 129.1(1), 129.0(7), 129.0, 128.9, 128.8, 128.8, 128.7(5), 128.6(9), 127.8, 127.4, 122.8, 119.2, 117.6. HR-MS (ESI-TOF) m/z calcd for $C_{31}H_{22}NaO_2S$, 481.1233 $[M + Na]^+$; found 481.1237.

*3-(4-Fluorophenyl)-3-tosylpropa-1,2-diene-1,1-diyl)dibenzene (**3m**).* White solid, 330 mg, 75% yield. mp 132−134 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.86 (m, 4H), 7.50−7.35 (m, 10H), 7.10−7.05 (m, 4H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 215.7, 161.8 ($^1J_{CF}$ = 243.4 Hz), 159.7, 144.8, 135.5, 133.8 ($^3J_{CF}$ = 8.5 Hz), 133.1, 131.2, 129.8, 128.7, 128.5, 128.(4)5, 128.2, 118.1, 115.9 ($^2J_{CF}$ = 22.1 Hz), 21.7. HR-MS (ESI-TOF) m/z calcd for $C_{28}H_{21}FNaO_2S$, 463.1139 $[M + Na]^+$; found 463.1140.

*(3-(4-Chlorophenyl)-3-tosylpropa-1,2-diene-1,1-diyl)dibenzene (**3n**).* White solid, 255 mg, 56% yield. mp 147−149 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.85−7.83 (m, 4H), 7.41−7.37 (m, 4H), 7.37−7.34 (m, 8H), 7.08 (d, J = 8.4 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.1, 144.8, 135.4, 135.3, 133.1, 133.0, 132.9, 131.1, 129.8, 128.9, 128.7, 128.4, 128.2, 120.5, 21.7. HR-MS (ESI-TOF) m/z calcd for $C_{28}H_{21}ClNaO_2S$, 479.0843 $[M + Na]^+$; found 479.0853.

*(3-(p-Tolyl)-3-tosylpropa-1,2-diene-1,1-diyl)dibenzene (**3o**).* White solid, 262 mg, 60% yield. mp 90−92 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.38−7.33 (m, 10H), 7.18−7.12 (m, 4H), 2.36 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 206.9, 144.2, 139.1, 137.6, 133.9, 129.4, 128.7, 128.1, 126.2, 118.7, 117.7, 21.6, 21.3. HR-MS (ESI-TOF) m/z calcd for $C_{29}H_{24}NaO_2S$, 459.1390 $[M + Na]^+$; found 459.1409.

*(3-(4-Chlorophenyl)-3-(phenylsulfonyl)propa-1,2-diene-1,1-diyl)-dibenzene (**3p**).* White solid, 323 mg, 73% yield. mp 127−129 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.77−7.75 (m, 2H), 7.54−7.48 (m, 3H), 7.38−7.28 (m, 14H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.0, 140.2, 135.2, 133.5, 133.4, 130.1, 129.0, 128.9, 128.8, 128.7, 128.06, 127.7, 119.5, 116.7. HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{19}ClNaO_2S$, 465.0687 $[M + Na]^+$; found 465.0689.

*(3-(Phenylsulfonyl)-3-(p-tolyl)propa-1,2-diene-1,1-diyl)dibenzene (**3q**).* White solid, 304 mg, 72% yield. mp 130−132 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.79−7.77 (m, 2H), 7.51−7.47 (m, 3H), 7.36−7.31 (m, 12H), 7.16 (d, J = 8.0 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm) 206.9, 140.5, 139.2, 133.8, 133.3, 129.4, 128.8, 128.7, 128.7, 128.1, 126.1, 118.9, 117.5, 21.3. HR-MS (ESI-TOF) m/z calcd for $C_{28}H_{22}NaO_2S$, 445.1233 $[M + Na]^+$; found 445.1245.

*(3-((4-Chlorophenyl)sulfonyl)-3-(4-fluorophenyl)propa-1,2-diene-1,1-diyl)dibenzene (**3r**).* White solid, 305 mg, 66% yield. mp 146−148 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.66 (d, J = 8.4 Hz, 2H), 7.59−7.55 (m, 2H), 7.41−7.39 (m, 6H), 7.32−7.29 (m, 6H), 7.09−7.05 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.0, 163.2 ($^1J_{CF}$ = 248.5 Hz), 140.2, 138.7, 133.3, 130.8 ($^3J_{CF}$ = 8.4 Hz), 129.4, 129.2, 129.1, 128.9, 128.6, 124.8, 119.6, 116.6, 116.0 ($^2J_{CF}$ = 21.7). HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{18}ClFNaO_2S$, 483.0593 $[M + Na]^+$; found 483.0596.

*(3-((4-Chlorophenyl)sulfonyl)-3-(p-tolyl)propa-1,2-diene-1,1-diyl)dibenzene (**3s**).* White solid, 260 mg, 57% yield. mp 102−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.69 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.42−7.33 (m, 10H), 7.30−7.28 (m, 2H), 7.19 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm) 207.1, 140.0, 139.4, 139.0, 133.6, 129.5, 129.4, 129.1, 129.0, 128.8, 128.7, 128.6, 125.8, 119.2, 117.4, 21.3. HR-MS (ESI-TOF) m/z calcd for $C_{28}H_{21}ClNaO_2S$, 479.0843 $[M + Na]^+$; found 479.0850.

*(3-((3-Bromophenyl)sulfonyl)-3-(4-chlorophenyl)propa-1,2-diene-1,1-diyl)dibenzene (**3t**).* White solid, 353 mg, 68% yield. mp 105−107 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.90 (s, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H), 7.41−7.29 (m, 12H), 7.24−7.20 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 207.3, 142.0, 136.6, 135.5, 133.1, 130.9, 130.4, 130.0, 129.2(4), 129.1(5), 129.0, 128.6, 127.3, 126.5, 123.1, 120.0, 116.5. HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{18}BrClNaO_2S$, 544.9766 $[M + Na]^+$; found 544.9775.

*4,4′-(3-(p-Tolyl)-3-tosylpropa-1,2-diene-1,1-diyl)bis(fluoro-benzene) (**3u**).* White solid, 307 mg, 65% yield. mp 108−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.62 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.32−7.27 (m, 4H), 7.17−7.13 (m, 4H), 7.09−7.05 (m, 4H), 2.36 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 206.6, 164.3, 161.7 ($^1J_{CF}$ = 252.0 Hz), 144.4, 139.3, 137.5, 130.4 ($^3J_{CF}$ = 8.3 Hz), 129.8, 129.8, 129.5, 129.5, 128.6, 128.0, 126.0, 117.9, 117.0, 115.9 ($^2J_{CF}$ = 22.7 Hz), 21.6, 21.3. HR-MS (ESI-TOF) m/z calcd for $C_{29}H_{22}F_2NaO_2S$, 495.1201 $[M + Na]^+$; found 495.1205.

*4,4′-(3-((4-Chlorophenyl)sulfonyl)-3-(p-tolyl)propa-1,2-diene-1,1-diyl)bis(fluorobenzene) (**3v**).* White solid, 307 mg, 65% yield. mp 108−110 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.65 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.32−7.28 (m, 6H), 7.19−7.07 (m, 6H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; δ, ppm) 206.8, 163.2 ($^1J_{CF}$ = 248.2 Hz), 140.2, 139.7, 138.9, 130.4, ($^3J_{CF}$ = 8.4 Hz), 129.6, 129.5 ($^4J_{CF}$ = 3.0 Hz), 129.4, 129.2, 128.7, 125.6, 117.6, 117.5, 116.0 ($^2J_{CF}$ = 21.7), 21.3. HR-MS (ESI-TOF) m/z calcd for $C_{28}H_{19}ClF_2NaO_2S$, 515.0655 $[M + Na]^+$; found 515.0660.

*4,4′-(3-(4-Chlorophenyl)-3-((2-chlorophenyl)sulfonyl)propa-1,2-diene-1,1-diyl)bis(fluorobenzene) (**3w**).* White solid, 369 mg, 72% yield. mp 151−153 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 8.13−8.11 (m, 1H), 7.51 (d, J = 8.4 Hz, 2H), 7.42−7.29 (m, 8H), 7.24 (d, J = 8.0 Hz, 1H), 7.10−7.06 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm) 206.9, 163.3 ($^1J_{CF}$ = 248.2 Hz), 137.2, 135.5, 134.5, 133.1, 131.7, 131.6, 130.7 ($^3J_{CF}$ = 8.4 Hz), 130.1, 129.2 ($^4J_{CF}$ = 3.3 Hz), 129.1, 127.3, 127.0, 119.0, 115.9 ($^2J_{CF}$ = 21.7). HR-MS (ESI-TOF) m/z calcd for $C_{27}H_{16}Cl_2F_2NaO_2S$, 535.0109 $[M + Na]^+$; found 535.0111.

*1-Chloro-4-(3-phenyl-1-(phenylsulfonyl)-3-(p-tolyl)propa-1,2-dien-1-yl)benzene (**3x**).* White solid, 347 mg, 76% yield. mp 98−100 °C. ^{1}H NMR (400 MHz, $CDCl_3$; δ, ppm) 7.77 (d, J = 7.2 Hz, 2H), 7.54−7.51 (m, 3H), 7.38−7.31 (m, 9H), 7.19 (s, 4H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6; δ, ppm) 207.0, 140.2, 139.1, 135.2,

DOI: 10.1021/acs.joc.5b01684
J. Org. Chem. 2015, 80, 9224−9230

133.6, 133.5, 130.3, 130.0, 129.5, 129.0, 128.9, 128.9, 128.8, 128.7, 128.6, 128.1, 127.8, 119.5, 116.5, 100.0, 21.3. HR-MS (ESI-TOF) *m*/*z* calcd for $C_{28}H_{21}ClNaO_2S$, 479.0843 $[M + Na]^+$; found 479.0854.

*1-Chloro-4-(3-(4-methoxyphenyl)-3-phenyl-1-(phenylsulfonyl)-propa-1,2-dien-1-yl)benzene (**3y**).* White solid, 349 mg, 74% yield. mp 114−116 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.77 (d, *J* = 7.6 Hz, 2H), 7.54−7.49 (m, 3H), 7.39−7.28 (m, 9H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 207.0, 160.3, 140.2, 135.1, 133.7, 133.5, 130.0(4), 129.9(9), 129.0, 128.9, 128.8, 128.7, 128.0, 127.9, 125.3, 119.3, 116.4, 114.3, 55.4. HR-MS (ESI-TOF) *m*/*z* calcd for $C_{28}H_{21}ClNaO_2S$, 479.0843 $[M + Na]^+$; found 479.0854.

*1-Chloro-4-(4-(phenylsulfonyl)-4-(p-tolyl)buta-2,3-dien-2-yl)-benzene (**3z**).* White solid, 165 mg, 42% yield. mp 102−104 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.68−7.56 (m, 5H), 7.45−7.41 (m, 2H), 7.36−7.29 (m, 4H), 7.19 (d, *J* = 8.0 Hz, 2H), 2.40 (s, 3H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 139.5, 135.3, 134.6, 134.0, 133.1, 131.6, 131.0, 130.5, 129.2, 128.2, 128.2, 118.6, 90.0, 85.2, 22.2, 21.6. HR-MS (ESI-TOF) *m*/*z* calcd for $C_{23}H_{19}ClNaO_2S$, 417.0687 $[M + Na]^+$; found 417.0700.

*(3-(p-Tolyl)prop-2-yne-1,1-diyl)dibenzene (**4**) (Known Compound).*[20] White solid, mp 83−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.44 (d, *J* = 7.6 Hz, 4H), 7.38−7.24 (m, 7H), 7.22 (d, *J* = 7.2 Hz, 1H), 7.11 (d, *J* = 8.0 Hz, 2H), 5.20 (s, 1H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$; *δ*, ppm) 141.9, 138.0, 131.6, 129.0, 128.6, 127.9, 126.9, 120.4, 89.4, 85.0, 43.8, 21.5.

*1-(p-Tolyl)-2-(1,3,3-triphenylallylidene)hydrazine (**5a**) (Known Compound).* White solid, mp 177−179 °C (lit. mp 174−176 °C).[21] ^{1}H NMR (400 MHz, $CDCl_3$; *δ*, ppm) 7.85 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 4H), 7.42−7.33 (m, 5H), 7.30−7.23 (m, 5H), 7.17−7.12 (m, 1H), 7.05−6.93 (m, 4H), 6.38 (d, *J* = 4.8 Hz, 1H), 2.42 (s, 3H).

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for all pure products, and X-ray crystal data (CIF) for **3a**. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01684.

■ AUTHOR INFORMATION

Corresponding Authors

*(W.-J.H.) E-mail: wjhao@jsnu.edu.cn.
*(B.J.) E-mail: jiangchem@jsnu.edu.cn.
*(S.-J.T.) E-mail: laotu@jsnu.edu.cn.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful for financial support from the NSFC (Nos. 21332005, 21232004, 21272095, and 21472071), PAPD of Jiangsu Higher Education Institutions, the Qing Lan Project (12QLG006), the Outstanding Youth Fund of JSNU (YQ2015003), Robert A. Welch Foundation (D-1361, USA), NIH (R33DA031860, USA), the NSF of JSNU (14XLR005), and the Open Foundation of Jiangsu Key Laboratory (K201505).

■ REFERENCES

(1) (a) Yu, S.; Ma, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3074. (b) Hoffmann-Röder, A.; Krause, N. *Angew. Chem., Int. Ed.* **2004**, *43*, 1196.

(2) (a) Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; John Wiley & Sons: New York, 1984. (b) *The Chemistry of Ketenes, Allenes, and Related Compounds*, Part 1; Patai, S., Ed.; John Wiley & Sons: New York, 1980. (c) Krause, N.; Hashmi, A. S. K. *Modern Allene Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2004; Vols. *1 and 2*.

(3) For selected reviews, see: (a) Wang, K. K. *Chem. Rev.* **1996**, *96*, 207. (b) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067. (c) Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2000**, *39*, 3590. (d) Bates, R. W.; Satcharoen, V. *Chem. Soc. Rev.* **2002**, *31*, 12. (e) Brasholz, M.; Reissig, H. U.; Zimmer, R. *Acc. Chem. Res.* **2009**, *42*, 45. (f) Ma, S. *Acc. Chem. Res.* **2009**, *42*, 1679. (g) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev.* **2010**, *39*, 783. (h) Lopez, F.; Mascarenas, J. L. *Chem. - Eur. J.* **2011**, *17*, 418. (i) Zhao, Q.-Y.; Lian, Z.; Wei, Y.; Shi, M. *Chem. Commun.* **2012**, *48*, 1724. (j) Yu, S.; Ma, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3074. (k) Neff, R. K.; Frantz, D. E. *ACS Catal.* **2014**, *4*, 519. (l) Alcaide, B.; Almendros, P. *Chem. Soc. Rev.* **2014**, *43*, 2886. (m) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev.* **2014**, *43*, 3106.

(4) For selected examples, see: (a) Ghosh, P.; Zhang, Y.; Emge, T. J.; Williams, L. J. *Org. Lett.* **2009**, *11*, 4402. (b) Guan, X.-Y.; Wei, Y.; Shi, M. *Org. Lett.* **2010**, *12*, 5024. (c) Yuan, W.; Dong, X.; Shi, M.; McDowell, P.; Li, G. *Org. Lett.* **2012**, *14*, 5582. (d) Zeng, R.; Fu, C.; Ma, S. *J. Am. Chem. Soc.* **2012**, *134*, 9597. (e) Zhang, X.-N.; Shi, M. *ACS Catal.* **2013**, *3*, 507. (f) Yang, H.-B.; Yuan, Y.-C.; Wei, Y.; Shi, M. *Chem. Commun.* **2015**, *51*, 6430. (g) Mei, L.-Y.; Wei, Y.; Tang, X.-Y.; Shi, M. *J. Am. Chem. Soc.* **2015**, *137*, 8131. (h) Alcaide, B.; Almendros, P.; Herrera, F.; Luna, A.; de Orbe, M. E.; Torres, M. R. *J. Org. Chem.* **2015**, *80*, 4157.

(5) For reviews on the synthesis of allenes, see: (a) Krause, N.; Hoffmann-Röder, A. *Tetrahedron* **2004**, *60*, 11671. (b) Brummond, K. M.; DeForrest, J. E. *Synthesis* **2007**, *2007*, 795. (c) Ogasawara, M. *Tetrahedron: Asymmetry* **2009**, *20*, 259. (d) Yu, S.; Ma, S. *Chem. Commun.* **2011**, *47*, 5384. (e) Ye, J.; Ma, S. *Org. Chem. Front.* **2014**, *1*, 1210.

(6) For selected examples, see: (a) Liu, Z.; Gu, P.; Shi, M. *Chem. - Eur. J.* **2011**, *17*, 5796. (b) Kuş, M.; Artok, L.; Aygün, M. *J. Org. Chem.* **2015**, *80*, 5494. (c) Quinio, P.; François, C.; Escribano Cuesta, A.; Steib, A. K.; Achrainer, F.; Zipse, H.; Karaghiosoff, K.; Knochel, P. *Org. Lett.* **2015**, *17*, 1010. (d) Ambler, B. R.; Peddi, S.; Altman, R. A. *Org. Lett.* **2015**, *17*, 2506. (e) Zhang, H.; Wang, B.; Yi, H.; Zhang, Y.; Wang, J. *Org. Lett.* **2015**, *17*, 3322. (f) Kuang, J.; Tang, X.; Ma, S. *Org. Chem. Front.* **2015**, *2*, 470.

(7) For selected examples, see: (a) Kuang, J.; Ma, S. *J. Am. Chem. Soc.* **2010**, *132*, 1786. (b) Ye, J.; Li, S.; Chen, B.; Fan, W.; Kuang, J.; Liu, J.; Liu, Y.; Miao, B.; Wan, B.; Wang, Y.; Xie, X.; Yu, Q.; Yuan, W.; Ma, S. *Org. Lett.* **2012**, *14*, 1346. (c) Ye, J.; Fan, W.; Ma, S. *Chem. - Eur. J.* **2013**, *19*, 716. (d) Lu, R.; Ye, J.; Cao, T.; Chen, B.; Fan, W.; Lin, W.; Liu, J.; Luo, H.; Miao, B.; Ni, S.; Tang, X.; Wang, N.; Wang, Y.; Xie, X.; Yu, Q.; Yuan, W.; Zhang, W.; Zhu, C.; Ma, S. *Org. Lett.* **2013**, *15*, 2254. (e) Zhang, X.; Qiu, Y.; Fu, C.; Ma, S. *Org. Chem. Front.* **2014**, *1*, 247. (f) Kitagaki, S.; Komizu, M.; Mukai, C. *Synlett* **2011**, *2011*, 1129. (g) Kuang, J.; Luo, H.; Ma, S. *Adv. Synth. Catal.* **2012**, *354*, 933.

(8) (a) Back, T. G. *Tetrahedron* **2001**, *57*, 5263. (b) Fujii, I.; Ryu, K.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1984**, 844. (c) Blechert, S. *Tetrahedron Lett.* **1984**, *25*, 1547. (d) Hilpert, H.; Dreiding, A. S. *Helv. Chim. Acta* **1984**, *67*, 1547. (e) Bosum, A.; Blechert, S. *Angew. Chem.* **1988**, *100*, 596. (f) Harmata, M.; Gamlath, C. B. *J. Org. Chem.* **1988**, *53*, 6154. (g) Harmata, M.; Gamlath, C. B.; Barnes, C. L.; Jones, D. E. *J. Org. Chem.* **1995**, *60*, 5077.

(9) (a) Najera, C.; Yus, M. *Tetrahedron* **1999**, *55*, 10547. (b) Bridges, A. J.; Ross, R. J. *Tetrahedron Lett.* **1983**, *24*, 4797. (c) Okamura, W. H.; Shen, G. Y.; Tapia, R. *J. Am. Chem. Soc.* **1986**, *108*, 5018. (d) Hojo, M.; Tomita, K.; Hirohara, Y.; Hosomi, A. *Tetrahedron Lett.* **1993**, *34*, 8123.

(10) (a) Hiroi, K.; Kato, F.; Nakasato, H. *Chem. Lett.* **1998**, 553. (b) Conrads, M.; Mattay, J. *Synthesis* **1991**, *1991*, 11. (c) Braverman, S.; Lior, Z. *Tetrahedron Lett.* **1994**, *35*, 6725. (d) Block, E.; Putman, D. *J. Am. Chem. Soc.* **1990**, *112*, 4072. (e) Hojo, M.; Tomita, K.; Hirohara, Y.; Hosomi, A. *Tetrahedron Lett.* **1993**, *34*, 8123.

DOI: 10.1021/acs.joc.5b01684
J. Org. Chem. 2015, 80, 9224−9230

(11) Fu, C.; Ma, S. *Org. Lett.* **2005**, *7*, 1605.
(12) Zhu, Y.; Sun, L.; Lu, P.; Wang, Y. *ACS Catal.* **2014**, *4*, 1911.
(13) Yin, G.; Zhu, Y.; Zhang, L.; Lu, P.; Wang, Y. *Org. Lett.* **2011**, *13*, 940.
(14) Hao, L.; Wu, F.; Ding, Z.-C.; Xu, S.-X.; Ma, Y.-L.; Chen, L.; Zhan, Z.-P. *Chem. - Eur. J.* **2012**, *18*, 6453.
(15) (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) Jiang, B.; Ning, Y.; Fan, W.; Tu, S.-J.; Li, G. *J. Org. Chem.* **2014**, *79*, 4018. (c) Qiu, J.-K.; Hao, W.-J.; Wang, D.-C.; Wei, P.; Sun, J.; Jiang, B.; Tu, S.-J. *Chem. Commun.* **2014**, *50*, 14782.
(16) Swaminathan, S.; Narayanan, K. V. *Chem. Rev.* **1971**, *71*, 429.
(17) For recent selected examples of TBAI/TBHP-mediated reactions; see: (a) Wei, W.; Zhang, C.; Xu, Y.; Wan, X. *Chem. Commun.* **2011**, *47*, 10827. (b) Majji, G.; Guin, S.; Gogoi, A.; Rout, S. K.; Patel, B. K. *Chem. Commun.* **2013**, *49*, 3031. (c) Uyanik, M.; Suzuki, D.; Yasui, T.; Ishihara, K. *Angew. Chem., Int. Ed.* **2011**, *50*, 5331. (d) Ma, L.; Wang, X.; Yu, W.; Han, B. *Chem. Commun.* **2011**, *47*, 11333. (e) Froehr, T.; Sindlinger, C. P.; Kloeckner, U.; Finkbeiner, P.; Nachtsheim, B. J. *Org. Lett.* **2011**, *13*, 3754. (f) Li, L.-T.; Huang, J.; Li, H.-Y.; Wen, L.-J.; Wang, P.; Wang, B. *Chem. Commun.* **2012**, *48*, 5187. (g) Wong, Y.-C.; Tseng, C.-T.; Kao, T.-T.; Yeh, Y.-C.; Shia, K.-S. *Org. Lett.* **2012**, *14*, 6024. (h) Mai, W.-P.; Wang, H.-H.; Li, Z.-C.; Yuan, J.-W.; Xiao, Y.-M.; Yang, L.-R.; Mao, P.; Qu, L.-B. *Chem. Commun.* **2012**, *48*, 10117. (i) Xie, J.; Jiang, H.; Cheng, Y.; Zhu, C. *Chem. Commun.* **2012**, *48*, 979. (j) Tan, B.; Toda, N.; Barbas, C. F., III *Angew. Chem., Int. Ed.* **2012**, *51*, 12538.
(18) (a) Zhang, J.; Shao, Y.; Wang, H.; Luo, Q.; Chen, J.; Xu, D.; Wan, X. *Org. Lett.* **2014**, *16*, 3312. (b) Wu, X.-F.; Gong, J.-L.; Qi, X. *Org. Biomol. Chem.* **2014**, *12*, 5807. (c) Zhang, J.; Jiang, J.; Li, Y.; Zhao, Y.; Wan, X. *Org. Lett.* **2013**, *15*, 3222. (d) Liu, Z.; Zhang, J.; Chen, S.; Shi, E.; Xu, Y.; Wan, X. *Angew. Chem., Int. Ed.* **2012**, *51*, 3231.
(19) Tripathi, C. B.; Mukherjee, S. *Org. Lett.* **2014**, *16*, 3368.
(20) Ren, K.; Li, P.; Wang, L.; Zhang, X. *Tetrahedron* **2011**, *67*, 2753.
(21) Hao, L.; Wu, F.; Ding, Z.-C.; Xu, S.-X.; Ma, Y.-L.; Chen, L.; Zhan, Z.-P. *Chem. - Eur. J.* **2012**, *18*, 6453.

DOI: 10.1021/acs.joc.5b01684
J. Org. Chem. 2015, 80, 9224−9230