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Palladium-catalyzed three-component tandem reaction of sulfonyl hydrazones, aryl iodides and allenes: highly stereoselective synthesis of (*Z*)-α-hydroxymethyl allylic sulfones†

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Sulfonyl hydrazones have been identified as an excellent sulfonyl anion surrogate in the base and Pd^0-catalyzed three-component tandem reaction with aryl iodides and allenes for the synthesis of functionalized allylic sulfones. By forming a stabilized six-membered palladacycle intermediate, the reaction led to the desired higher substituted allylic sulfones with excellent *Z* selectivities and high yields.

Selective construction of carbon-heteroatom bonds is an ongoing challenge in organic synthesis. Although a variety of methods for forming C–O and C–N bonds have been developed, similar reactions to form C–S bonds have received comparably less attention.[1] However, the formation of C–S bonds is a fundamental transformation in the synthesis of organosulfur compounds. Sulfone, the most attractive sulfur-containing fragment, has emerged as a building block in several bioactive natural products, pharmaceuticals and agrochemicals (Fig. 1, **I–IV**).[2] For example, intepirdine (Fig. 1, **III**), a selective 5-HT6 receptor antagonist, is currently undergoing phase III clinical trials for application in different types of Alzheimer's disease (AD),[3] while rigosertib (Fig. 1, **IV**) is a potent, polo-like kinase 1 (PLK1) pathway modulator for treating lymphocytic leukemia.[4] In addition, sulfones are widely used as polymeric compounds (Fig. 1, **V**) and intermediates in organic synthesis.[5] Accordingly, the efficient incorporation of a sulfonyl group into organic molecules has attracted considerable interest among organic chemists.

Traditional sulfone syntheses are mainly based on the oxidation of the corresponding sulfide,[6] or the reaction of either organomagnesium halides or organolithiums with sulfonate esters (Scheme 1, eqn (1)).[7] However, these methods have certain drawbacks, including limited substrate sources, toxic by-products, and harsh reaction conditions. Recently, sulfonyl

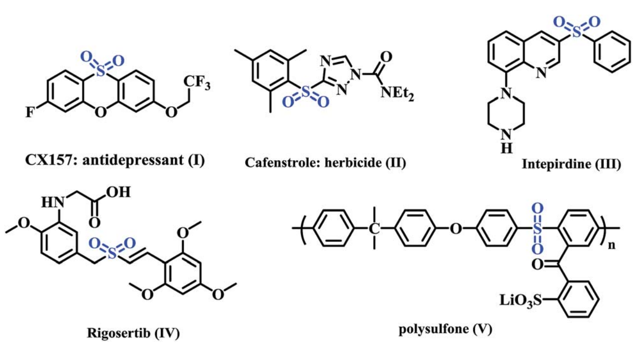
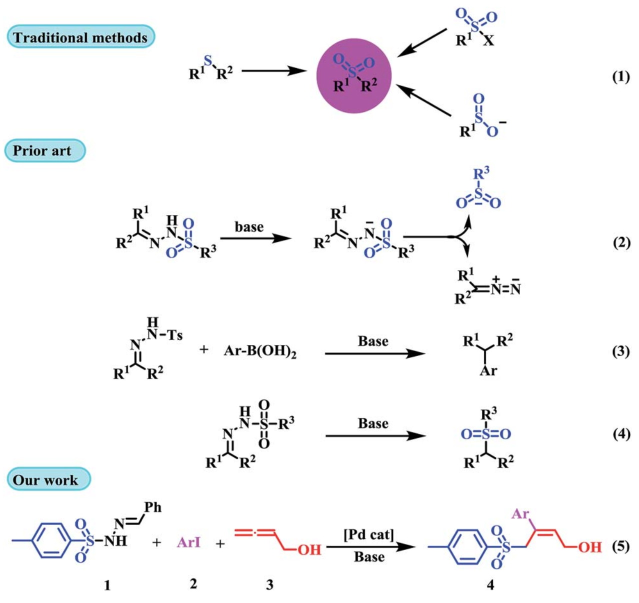


Fig. 1 Representative medicinally relevant agents, and polymeric agent containing sulfones.



Scheme 1 Strategies for the synthesis of sulfones and studies on the sulfonyl hydrazones.

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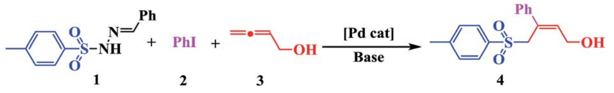
hydrazones are well-known as useful synthons in organic synthesis, and they can be easily prepared in solid form through condensation of ketones or aldehydes with sulfonyl hydrazide in high yields. Sulfonyl hydrazones are in general stable, and in many cases they are crystalline compounds and easy to purify, and used as an *in situ* source of diazo compounds in a variety of transition-metal-catalyzed and transition-metal-free reactions, which affords novel methodologies for the formation of carbon–carbon and carbon–heteroatom bonds (Scheme 1, eqn (2)).[8] Valdés and co-workers have reported the metal-free coupling of tosylhydrazones with boronic acids to form C–C bonds (Scheme 1, eqn (3)).[9] More recently, Yu *et al.* and Zhao *et al.* explored a new organocatalytic strategy to synthesize sulfones *via* loss of intramolecular nitrogen from sulfonyl hydrazones (Scheme 1, eqn (4)).[10] Despite the fact that it is well-known in the literature that sulfonyl hydrazones undergo dissociation in the presence of a base to generate a sulfinate anion and a diazo compound, all of the reported methodologies have used this reactivity for the generation of carbene species from the released diazoalkane reagent. In this sense, literature precedent illustrating the possibility of using this behavior for the generation of an S-based nucleophile (sulfonyl anion) that can be used in a subsequent transformation are rare.[11]

Multi-component reactions (MCRs) involving domino processes have emerged as powerful tools for the efficient and atom-economic formation of a diverse range of carbon-heteroatom bonds.[12] In addition, functionalized allenes have been established as starting materials for the efficient synthesis of potentially useful carbo- and heteroatom bonds.[13] Drawing from our recent experience in the field of sulfonyl hydrazones and allenes,[14f] and with regard to the importance of sulfones in organic synthesis, we herein report the ability of sulfonyl hydrazones to participate as a source of a sulfonyl anion equivalent towards (*Z*)-α-hydroxymethyl allylic sulfones by the assembly of aryl iodides (**2**) and buta-2,3-dien-1-ol (**3**) (Scheme 1, eqn (5)).

Initially, we investigated the model reaction of sulfonyl hydrazones (**1**) with iodobenzene (**2**) and buta-2,3-dien-1-ol (**3**) in the presence of 5 mol% of [Pd(OAc)$_2$] at 80 °C in THF (Table 1). Using these conditions, and with K_2CO_3 as the base, allylic sulfone 4 was obtained in 23% yield. The effect of the ligand on the catalytic activity was also investigated, and the presence of PPh_3 was found to promote the catalytic reaction (Table 1, entries 1 *vs.* 2–5). In order to improve the yield, different catalysts (Pd(PPh$_3$)$_4$, Pd(dppf)Cl$_2$, and Pd(PPh$_3$)$_2$Cl$_2$) were tested (Table 1, entries 6–8). Use of Pd(PPh$_3$)$_4$ (5 mol%) significantly improved the yield to 68%. No product was detected in the absence of a catalyst (Table 1, entry 9). To further improve the reaction efficiency, several bases were evaluated (Table 1, entries 10–14). As shown, Na_2CO_3, CsF, or Cs_2CO_3 showed no improvement compared with K_2CO_3. The use of stronger bases (*e.g.*, *t*-BuOLi and NaOH) did not result in any allylic sulfone **4** at all. Based on previous studies, different additives were investigated. Using either the phase-transfer catalyst *n*-Bu$_4$NBr (Table 1, entry 15) or the Lewis acid (Cu(OTf)$_2$) (Table 1, entry 16) did not increase the yield, nor did increasing the number of equivalents of allene 3 from 1.2 to 3.0 (Table 1, entries 5 *vs.* 17).

Table 1 Optimization of reaction conditions[a]



Entry	Cat.	Base	Additive	Yield[b] (%)
1	Pd(OAc)$_2$	K_2CO_3	—	23
2	Pd(OAc)$_2$	K_2CO_3	PPh_3	41
3	Pd(OAc)$_2$	K_2CO_3	dppf	28
4	Pd(OAc)$_2$	K_2CO_3	XantPhos	20
5	Pd(OAc)$_2$	K_2CO_3	BINAP	25
6	**Pd(PPh$_3$)$_4$**	**K_2CO_3**	**—**	**68**
7	Pd(PPh$_3$)$_2$Cl$_2$	K_2CO_3	—	42
8	Pd(dppf)Cl$_2$	K_2CO_3	—	44
9	—	K_2CO_3	—	n.d.
10	Pd(PPh$_3$)$_4$	Na_2CO_3	—	n.d.
11	Pd(PPh$_3$)$_4$	CsF	—	48
12	Pd(PPh$_3$)$_4$	Cs_2CO_3	—	39
13	Pd(PPh$_3$)$_4$	*t*-BuOLi	—	Trace
14	Pd(PPh$_3$)$_4$	NaOH	—	n.d.
15	Pd(PPh$_3$)$_4$	K_2CO_3	*n*-Bu$_4$NBr	63
16	Pd(PPh$_3$)$_4$	K_2CO_3	Cu(OTf)$_2$	55
17[c]	Pd(PPh$_3$)$_4$	K_2CO_3	—	69
18[d]	Pd(PPh$_3$)$_4$	K_2CO_3	—	23

[a] Reaction conditions: under N_2 atmosphere, **1** (1 equiv.), **2** (1.2 equiv.), **3** (1.2 equiv.), [Pd Cat.] (5 mol%), base (3 equiv.), THF (5.0 mL). [b] Isolated yield. [c] Allenes **3** (3.0 equiv.) was used. [d] Under air.

When the reaction was conducted in air instead of nitrogen, a relatively lower yield was obtained (Table 1, entry 18).

The effect of the solvent and reaction temperature was also examined (Table 2). It was found that the solvent played a critical role in this process (Table 2, entries 1–6). The tested solvents, including DMSO, DMF, toluene, ethyl acetate, and DCM, did not show any improvement in the transformation yield. However, when the reaction was conducted in dioxane, **4** was obtained in a relatively higher yield of 75% (Table 2, entry 7). When the reaction temperature was raised to 100 °C, the rate and conversion were not significantly affected (Table 2, entry 8). However, conversion decreased upon lowering the temperature

Table 2 Solvent and temperature effect on the Pd^0-catalyzed three-component tandem reaction of **1**, **2**, and **3**[a]

Entry	Solvent	*T* [°C]	Time (h)	Yield[b] (%)
1	THF	Reflux	12	68
2	DMF	80	12	41
3	DMSO	80	12	48
4	Ethyl acetate	Reflux	12	25
5	Toluene	80	12	33
6	DCM	Reflux	24	n.d.
7	**Dioxane**	**80**	**12**	**75**
8	Dioxane	100	10	76
9	Dioxane	40	48	28

[a] Reaction conditions: under N_2 atmosphere, **1** (1 equiv, **2** (1.2 equiv.), **3** (1.2 equiv.), [Pd(PPh$_3$)$_4$] (5 mol%), K_2CO_3 (3 equiv.), solvent (5.0 mL). [b] Isolated yield.

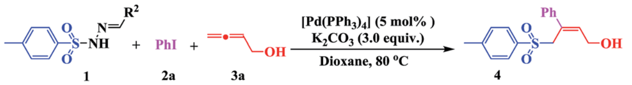
to 40 °C, even when the reaction time was extended to 48 h (Table 2, entry 9). Consequently, the standard reaction conditions used in further investigations were **1** (1 equiv.), **2** (1.2 equiv.), and **3** (1.2 equiv.) with K_2CO_3 (3 equiv.) in dioxane at 80 °C, using $[Pd(PPh_3)_4]$ (5 mol%) as the catalyst.

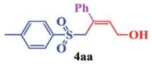
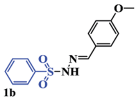
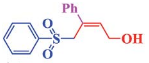
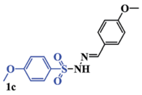
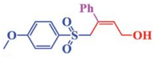
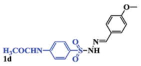
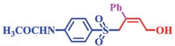
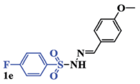
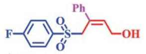
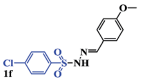
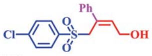
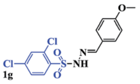
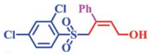
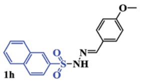
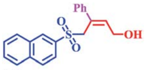
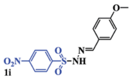
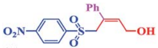
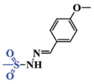
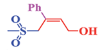
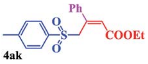
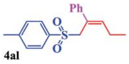
With the optimal conditions in hand, the scope of this protocol was explored for a series of sulfonyl hydrazones, accessible from the corresponding substituted aldehydes with *p*-toluenesulfonyl hydrazide as a standard substrate (Table 3). Reaction with an electronically diverse range of aryl hydrazones provided the corresponding allylic sulfones **4** in moderate to good yields. Electron-rich substrates provided higher yields, and the reaction time could be reduced to 8 h (Table 3, entries 5 *vs.* 3). Use of a heteroaryl group (Table 3, entry 7, R^2 = 2-thienyl), slightly reduced the yield to 65%, perhaps due to the electronic properties of the thiophene ring. Thus, sulfonyl hydrazone **1a**, derived from *p*-methoxybenzaldehyde, was used as the standard substrate for further investigations. Furthermore, sulfonyl hydrazones **1b-1h**, derived from aryl sulfonyl hydrazide and *p*-methoxybenzaldehyde, were also suitable substrates for the assembling reaction, and furnished the corresponding allylic sulfones in 65–85% yields (Table 3, entries 8–14). However, *p*-nitrophenyl sulfonyl hydrazone **1i** and methyl sulfonyl hydrazone **1j** gave only trace amounts of products **4ai** and **4aj**, respectively, making it unsuitable for further investigation (Table 3, entries 15–16). In order to investigate the scope of allenes, ethyl 2,3-butadienoate and 1,2-pentadiene were evaluated as representative compounds. As presented in Table 3 (entries 17–18), no product was observed, which suggested that the terminal substituent group of the allenes had a great effect on the three-component tandem reaction. The configuration of the product was supported by ^{1}H NOESY analysis of **4aa** as the *Z*-isomer (ESI, SI†), and those of the other products were assigned by analogy.

The scope and limitations of the transformation were also evaluated for the reaction of **1a** with various aryl iodides **2** (Table 4), under the optimized reaction conditions. Electron-withdrawing groups on the phenyl ring decreased the reaction efficiency, suggesting the importance of an electron-rich phenyl ring (Table 4, **4ea**, **4fa**, **4ja**). Further studies showed that steric hindrance of the aryl iodides had a negative effect on the reaction. For example, *p*-iodoanisole afforded the desired product **4ca** in 88% yield under the optimized conditions. However, the use of *o*-iodoanisole dramatically decreased the conversion, perhaps due to the steric hindrance of the methoxy group (Table 4, **4da**). Interestingly, the heterocyclic compound 2-iodothiophene reacted smoothly, affording the corresponding allylic sulfone **4la** in 80% yield. 1-Iodonaphthalene gave only trace amounts of product **4na**, probably because its rigid and bulky structure disfavors the transformation. However, diversely substituted aliphatic iodides were not suitable substrates (Table 4, **4oa**).

In order to investigate the limitations of aryl halides, phenyl bromide and phenyl chloride were evaluated as representative compounds. As shown in Table 5, phenyl bromide **2b** also reacted with **1a** and **3a** to give the expected products **4aa**, although the yields were slightly lower than the corresponding aryl iodides (Table 5, entry 2). Phenyl chloride **2c** and phenyl fluoride **2d** with **1a** and **3a** gave irreproducible results (Table 5, entries 3 and 4). These results indicate that the cleavage of the C–I and C–Br bonds is much faster than that of the C–Cl and C–F bonds.

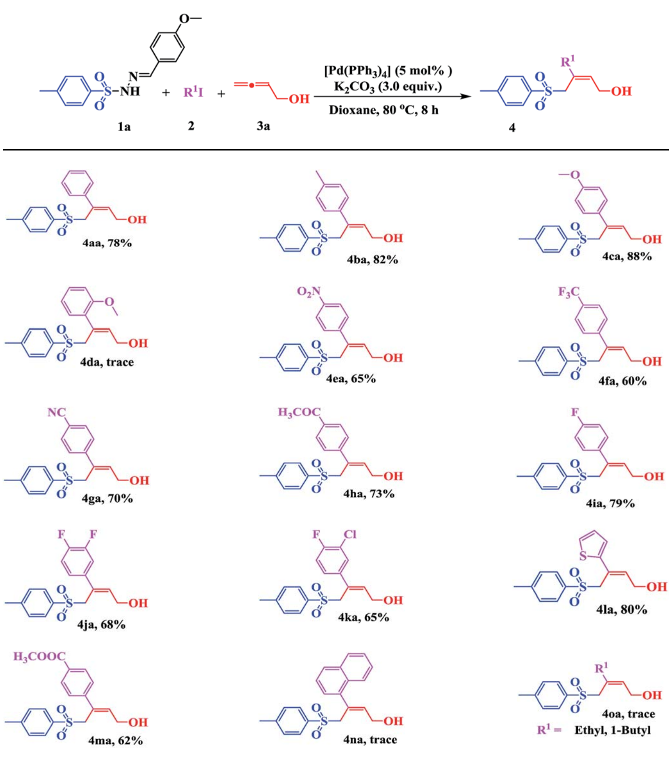
Table 3 Pd^0-catalyzed three-component tandem reaction of iodobenzene **2a**, **3a**, and different sulfonyl hydrazones^a



Entry	1	4	Time (h)	Yield^b (%)
1	(R^2 = Ph)	 **4aa**	12	75
2	(R^2 = *p*-$NO_2C_6H_4$)	**4aa**	16	70
3	(R^2 = *p*-$CF_3C_6H_4$)	**4aa**	16	65
4	(R^2 = *p*-MeC_6H_4)	**4aa**	12	73
5	(R^2 = *p*-$MeOC_6H_4$)	**4aa**	8	78
6	(R^2 = *p*-BrC_6H_4)	**4aa**	16	70
7	(R^2 = 2-thienyl)	**4aa**	18	65
8	 **1b**	 **4ab**	8	65
9	 **1c**	 **4ac**	8	81
10	 **1d**	 **4ad**	8	79
11	 **1e**	 **4ae**	8	78
12	 **1f**	 **4af**	8	80
13	 **1g**	 **4ag**	8	73
14	 **1h**	 **4ah**	8	85
15	 **1i**	 **4ai**	24	Trace
16	 **1j**	 **4aj**	24	Trace
17^c	(R^2 = *p*-$MeOC_6H_4$)	 **4ak**	24	Trace
18^d	(R^2 = *p*-$MeOC_6H_4$)	 **4al**	24	Trace

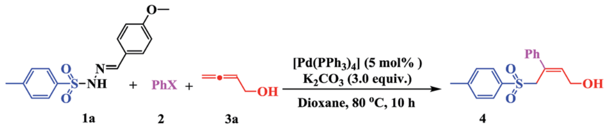
^{a} Reaction conditions: under N_2 atmosphere, **1** (1 equiv.), **2** (1.2 equiv.), **3** (1.2 equiv.), $[Pd(PPh_3)_4]$ (5 mol%), K_2CO_3 (3 equiv.), dioxane (5.0 mL). ^{b} Isolated yield. ^{c} **3a** = ethyl 2,3-butadienoate. ^{d} **3a** = 1,2-pentadiene.

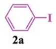
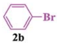
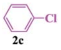
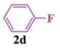
Table 4 Pd^0-catalyzed three-component tandem reaction of **1a**, **3a**, and different aryl iodides[a]



[a] Reaction conditions: under N_2 atmosphere, **1** (1 equiv.), **2** (1.2 equiv.), **3** (1.2 equiv.), [Pd(PPh$_3$)$_4$] (5 mol%), K_2CO_3 (3 equiv.), dioxane (5.0 mL).

Table 5 Pd^0-catalyzed three-component tandem reaction of **1**, **3**, and different aryl halides[a]



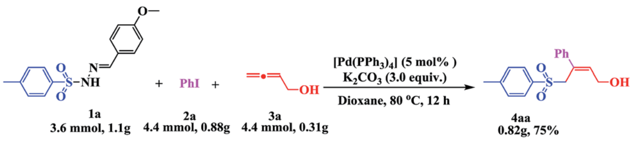
Entry	2	4	Time (h)	Yield[b] (%)
1		**4aa**	8	78
2		**4aa**	16	65
3		**4aa**	48	Trace
4		**4aa**	48	Trace

[a] Reaction conditions: under N_2 atmosphere, **1** (1 equiv.), **2** (1.2 equiv.), **3** (1.2 equiv.), [Pd(PPh$_3$)$_4$] (5 mol%), K_2CO_3 (3 equiv.), dioxane (5.0 mL). [b] Isolated yield.

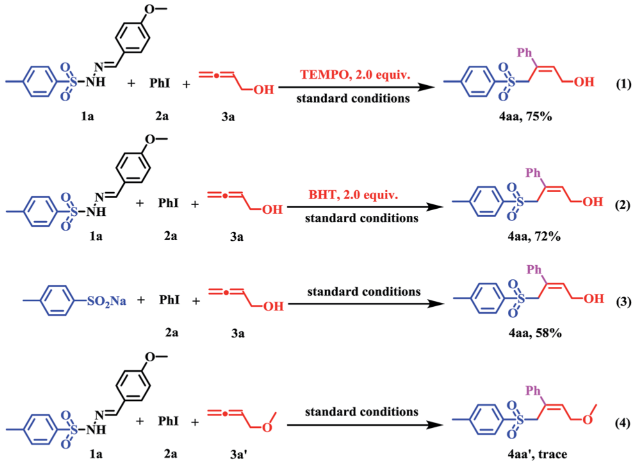
Encouraged by this three-component tandem reaction and sustainable synthesis, we conducted scale-up experiments to examine the synthetic utility of the reaction. When 3.6 mmol of 4-methylphenyl-sulfonylhydrazide **1a** was treated with 4.4 mmol aryl iodides (**2a**) and 4.4 mmol buta-2,3-dien-1-ol (**3a**), the corresponding product **4aa** was obtained with a satisfactory yield of 75%, although an extended reaction time was required (Scheme 2).

To get an insight into the mechanism of the sulfonylation process, several controlled experiments were conducted. Firstly, radical trapping experiments were conducted to elucidate whether the reaction involves radical species. When the radical scavenger (2,2,6,6-tetramethyl-piperidinyloxy, TEMPO; butylated hydroxytoluene, BHT) was employed under standard conditions, the reaction afforded **4aa** in 75% and 72% yields, which indicated that the transformation did not proceed *via* a free-radical pathway (Scheme 3, eqn (1) and (2). Subsequently, when using *p*-toluene sulfinic acid sodium salt as the substrate instead of **1a** under standard conditions, the reaction proceeded with a 58% yield (Scheme 3, eqn (3)), which indicated that the sulfinate anion should be an intermediate in this transformation. Finally, the corresponding reaction of 4-methoxybuta-1,2-diene **3a′**, which can be viewed as the hydroxy group in **3a** was protected as the methoxy group, with PhI (**2a**) and sulfonyl hydrazine (**1a**) did not afford the corresponding (*Z*)-allylic sulfones **4aa′** (Scheme 3, eqn (4)).

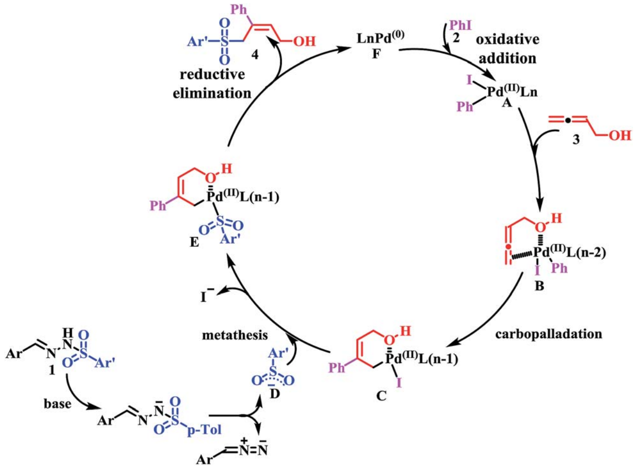
On the basis of the aforementioned investigations and previous reports,[10,14] a plausible mechanism for the cross-coupling reaction is proposed in Scheme 4. First, oxidative addition of iodobenzene (**2**) gives Pd^{II} intermediate **A.** Presumably, buta-2,3-dien-1-ol (**3**) plays two roles: (1) enhancing the reactivity of the allene component by coordinating to the palladium–aryl species **A** prior to insertion; and (2) controlling the regioselectivity of the allene insertion by forming a stabilized six-membered palladacycle intermediate **C.** Then, *N*-tosylhydrazones (**1**) undergo thermal decomposition in the presence of a base to generate diazo compound and sulfinate anion **D.** Metathesis of **C** with sulfinate anion **D** furnishes intermediate **E.** Finally, intermediate **E** converts to product **4** *via* reductive elimination, regenerating the Pd^0 catalyst **F.** The high stereoselectivity for the (*Z*)-α-hydroxymethyl allylic sulfone construction might be due to the formation of a stabilized, six-membered palladacycle intermediate **C.** In order to investigate this hypothesis, ethyl 2,3-butadienoate, 1,2-pentadiene and 4-methoxybuta-1,2-diene instead of buta-2,3-dien-1-ol (**3**) were evaluated. As presented in Table 3 (entries 17–18) and Scheme 3 (eqn (4)), no product was observed, which suggested that the terminal hydroxy group of the allenes played an important role on the three-component tandem reaction.



Scheme 2 Large scale experiment: under a N_2 atmosphere, **1a** (3.6 mmol), **2a** (4.4 mmol), **3a** (4.4 mmol), [Pd(PPh$_3$)$_4$] (5 mol%), K_2CO_3 (10.8 mmol) in 20 mL of dioxane, 80 °C, 12 h. Product **4aa** was isolated in 75% yield.



Scheme 3 Control experiments.



Scheme 4 Plausible reaction mechanism.

Conclusions

An efficient, Pd^0-catalyzed MCR for the synthesis of substituted (*Z*)-α-hydroxymethyl allylic sulfone derivatives has been developed. This reaction tolerates a broad range of functional groups in sulfonyl hydrazones with aryl iodides and buta-2,3-dien-1-ol to afford various allylic sulfones. In addition, we have demonstrated that sulfonyl hydrazones can be used as an excellent sulfonyl anion surrogate for performing tandem reactions. As all three building blocks are readily available, this study is expected to advance the transition-metal-catalyzed chemistry of allenes. Further studies regarding the scope and synthetic applications of this reaction are being pursued in our laboratory and will be reported in due course.

Experimental section

Representative procedure for the synthesis of (*Z*)-α-hydroxymethyl allylic sulfone products: buta-2,3-dien-1-ol **3a** (28 mg, 0.39 mmol) and iodobenzene **2a** (81 mg, 0.39 mmol, 1.2 equiv.) were consecutively added to a sealed tube charged with a mixture of K_2CO_3 (136 mg, 0.99 mmol, 3.0 equiv.), $[Pd(PPh_3)_4]$ (19 mg, 0.018 mmol, 5 mol%), and sulfonyl hydrazone **1a** (100 mg, 0.33 mmol, 1 equiv.) in dioxane (5 mL), under an atmosphere of nitrogen. The reaction mixture was stirred at 80 °C for 8 h and analyzed by TLC. After the reaction was complete, water (10 mL) was added, and the solution was extracted with dichloromethane. The organic phase was separated, washed with brine, dried ($MgSO_4$), filtered, and concentrated *in vacuo* to give the crude product, which was purified by column chromatography on silica gel with a mixture of ethyl acetate/petroleum (10 : 10, v/v) to afford the desired product **4aa.**

Conflicts of interest

There are no conflicts to declare.

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Notes and references

1 (*a*) M. Usman, Z. H. Ren, Y. Y. Wang and Z. H. Guan, *Synthesis*, 2017, **49**, 1419; (*b*) Q. Lu, J. Zhang, F. Wei, Y. Qi, H. Wang, Z. Liu and A. Lei, *Angew. Chem., Int. Ed.*, 2013, **52**, 7156; (*c*) S. Otocka, M. Kwiatkowska, L. Madalińska and P. Kiełbasiński, *Chem. Rev.*, 2017, **117**, 4147; (*d*) C. Shen, P. Zhang, Q. Sun, S. Bai, T. S. Andy Hor and X. Liu, *Chem. Soc. Rev.*, 2015, **44**, 291; (*e*) P. Ruiz-Castillo and S. L. Buchwald, *Chem. Rev.*, 2016, **116**, 12564; (*f*) C. Zhang, C. Tang and N. Jiao, *Chem. Soc. Rev.*, 2012, **41**, 3464; (*g*) S. R. Neufeldt and M. S. Sanford, *Acc. Chem. Res.*, 2012, **45**, 936; (*h*) L. H. Zou, J. Reball, J. Mottweiler and C. Bolm, *Chem. Commun.*, 2012, **48**, 11307.

2 (*a*) F. Reck, F. Zhou, M. Girardot, G. Kern, C. J. Eyermann, N. J. Hales, R. R. Ramsay and M. B. Gravestock, *J. Med. Chem.*, 2005, **48**, 499; (*b*) Y. Harrak, G. Casula, J. Basset, G. Rosell, S. Plescia, D. Raffa, M. G. Cusimano, R. Pouplana and M. D. Pujol, *J. Med. Chem.*, 2010, **53**, 6560; (*c*) W. M. Xu, F. F. Han, M. He, D. Y. Hu, J. He, S. Yang and B. A. Song, *J. Agric. Food Chem.*, 2012, **60**, 1036; (*d*) M. Lee, M. Ikejiri, D. Klimpel, M. Toth, M. Espahbodi, D. Hesek, C. Forbes, M. Kumarasiri, B. C. Noll, M. Chang and S. Mobashery, *ACS Med. Chem. Lett.*, 2012, **3**, 490; (*e*) N. W. Liu, S. Liang and G. Manolikakes, *Synthesis*, 2016, **48**, 1939; (*f*) S. Shaaban, S. Liang, N. W. Liua and G. Manolikakes, *Org. Biomol. Chem.*, 2017, **15**, 1947; (*g*) F. L. Yang and S. K. Tian, *Tetrahedron Lett.*, 2017, **58**, 487; (*h*) K. M. Elattar, A. Fekri, N. M. Bayoumy and A. A. Fadda, *Res. Chem. Intermed.*, 2017, **43**, 4227.

3 C. Julie, B. Guillaume, F. Sylvain, Z. Luc and B. Thierry, *J. Med. Chem.*, 2014, **57**, 3884.

4 (*a*) M. V. Ramana Reddy, P. Venkatapuram, M. R. Mallireddigari, V. R. Pallela, S. C. Cosenza,

K. A. Robell, B. Akula, B. S. Hoffman and E. P. Reddy, *J. Med. Chem.*, 2011, **54**, 6254; (*b*) O. Chahrour, A. Abdalla, F. Lam, C. Midgley and S. D. Wang, *Bioorg. Med. Chem. Lett.*, 2011, **21**, 3066.

5 M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla and J. E. McGrath, *Chem. Rev.*, 2004, **104**, 4587.

6 (*a*) A. Rostami and J. Akradi, *Tetrahedron Lett.*, 2010, **51**, 3501; (*b*) N. Fukuda and T. Ikemoto, *J. Org. Chem.*, 2010, **75**, 4629; (*c*) S. L. Jain, B. S. Rana, B. Singh, A. K. Sinha, A. Bhaumik, M. Nandi and B. Sain, *Green Chem.*, 2010, **12**, 374; (*d*) B. M. Choudary, C. R. V. Reddy, B. V. Prakash, M. L. Kantam and B. Sreedhar, *Chem. Commun.*, 2003, **6**, 754.

7 H. Gilman, N. J. Beaver and C. H. Meyers, *J. Am. Chem. Soc.*, 1925, **47**, 2047.

8 (*a*) J. R. Fulton, V. K. Aggarwal and J. de Vicente, *Eur. J. Org. Chem.*, 2005, **8**, 1479; (*b*) J. L. Zhao, S. H. Guo, J. Qiu, X. F. Gou, C. W. Hua and B. Chen, *Tetrahedron Lett.*, 2016, **57**, 2375; (*c*) J. Barluenga, M. Escribano, P. Moriel, F. Aznar and C. Valdés, *Chem.–Eur. J.*, 2009, **15**, 13291; (*d*) J. Barluenga, P. Moriel, C. Valdés and F. Aznar, *Angew. Chem., Int. Ed.*, 2007, **46**, 5587; (*e*) J. Barluenga, M. Escribano, F. Aznar and C. Valdés, *Angew. Chem., Int. Ed.*, 2010, **49**, 6856; (*f*) J. Barluenga and C. Valdés, *Angew. Chem., Int. Ed.*, 2011, **50**, 7486; (*g*) Q. Xiao, Y. Zhang and J. Wang, *Acc. Chem. Res.*, 2013, **46**, 236; (*h*) Z. Shao and H. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 560; (*i*) Y. Xia and J. B. Wang, *Chem. Soc. Rev.*, 2017, **46**, 2306.

9 J. Barluenga, M. Tomás-Gamasa, F. Aznar and C. Valdés, *Nat. Chem.*, 2009, **1**, 494.

10 (*a*) X. W. Feng, J. Wang, J. Zhang, J. Yang, N. Wang and X. Q. Yu, *Org. Lett.*, 2010, **12**, 4408; (*b*) J. L. Zhao, S. H. Guo, J. Qiu, X. F. Gou, C. W. Hua and B. Chen, *Tetrahedron Lett.*, 2016, **57**, 2375.

11 M. Fernández, U. Uria, L. Orbe, J. L. Vicario, E. Reyes and L. Carrillo, *J. Org. Chem.*, 2014, **79**, 441.

12 (*a*) X. Chu, X. Xu and S. Ji, *Chem.–Eur. J.*, 2016, **22**, 14181; (*b*) M. Ghorbani, B. Mohammadi, M. Saraii, B. Masoumi, M. Abbasian, A. Ramazani, K. Slepokura and T. Lis, *Org. Lett.*, 2016, **18**, 4759; (*c*) J. Chu, B. Hu, Z. Liao and X. Zhang, *J. Org. Chem.*, 2016, **81**, 8647; (*d*) H. Dong, L. Xu, S. Li, L. Wang, C. Shao and J. Xiao, *ACS Comb. Sci.*, 2016, **18**, 604; (*e*) X. Lian, J. Meng and Z. Han, *Org. Lett.*, 2016, **18**, 4270.

13 (*a*) W. Yuan and S. Ma, *Org. Lett.*, 2014, **16**, 193; (*b*) C. Grandclaudon, V. Michelet and P. Y. Toullec, *Org. Lett.*, 2016, **18**, 676; (*c*) A. Tap, A. Blond, V. N. Wakchaure and B. List, *Angew. Chem., Int. Ed.*, 2016, **55**, 8962; (*d*) Y. Shigeo, Y. Kawaguchi, O. Yuta and M. Chisato, *Chem.–Eur. J.*, 2016, **22**, 12181.

14 (*a*) A. Khan, J. Xing, J. Zhao, Y. Kan, W. Zhang and Y. Zhang, *Chem.–Eur. J.*, 2015, **21**, 120; (*b*) Y. Yang, S. Zhang, L. Tang, Y. Hu, Z. Zha and Z. Wang, *Green Chem.*, 2016, **18**, 2609; (*c*) Y. Yang, Y. J. Bao, Q. Q. Guan, Q. Sun, Z. G. Zha and Z. Y. Wang, *Green Chem.*, 2017, **19**, 112; (*d*) Q. Xiao, B. Wang, L. Tian, Y. Yang, J. Ma, Y. Zhang, S. Chen and J. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 9305; (*e*) J. Le Bras and J. Muzart, *Chem. Soc. Rev.*, 2014, **43**, 3003; (*f*) Y. L. Hou, M. Z. Qin, X. X. Yang, Q. Shen, Y. F. Zhao, Y. J. Liu and P. Gong, *RSC Adv.*, 2017, **7**, 7401; (*g*) S. M. Ma and S. M. Zhao, *J. Am. Chem. Soc.*, 2001, **123**, 5578; (*h*) S. Kamijo, M. AI-Masum and Y. Yamamoto, *Tetrahedron Lett.*, 1998, **39**, 691.