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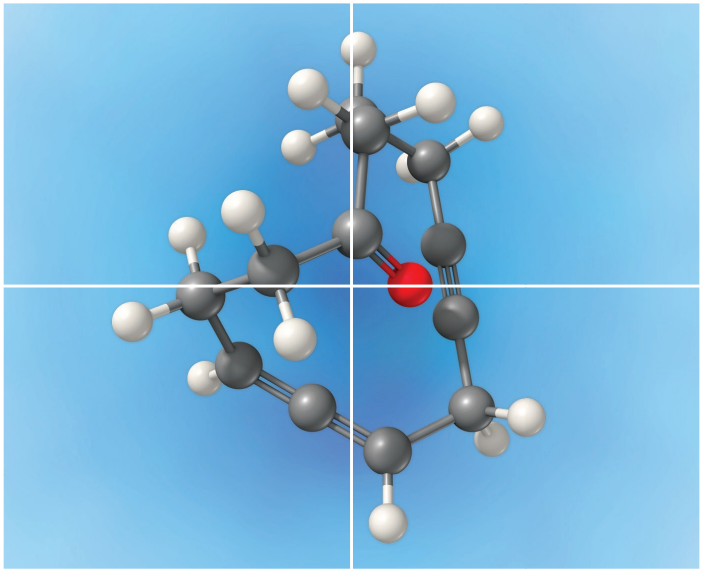

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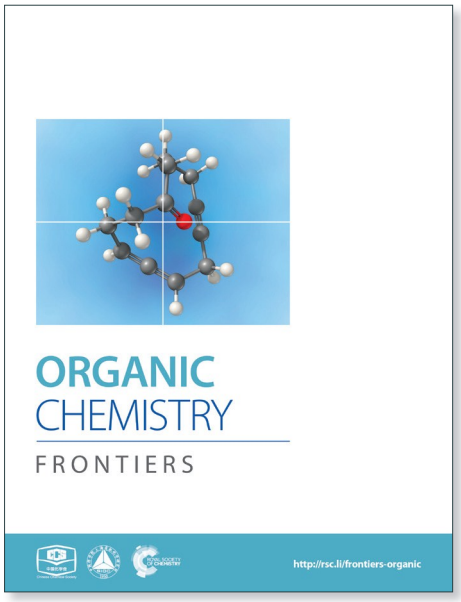

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Journal Name

ARTICLE

Palladium-Catalysed Coupling Reaction of Aminals with *N*-Sulfonyl Hydrazones to Allylic Sulfones

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Jiawen Li,[a,b] Guiping Qin,[a,b] Yang Liu,[a,b] and Hanmin Huang*,[a]

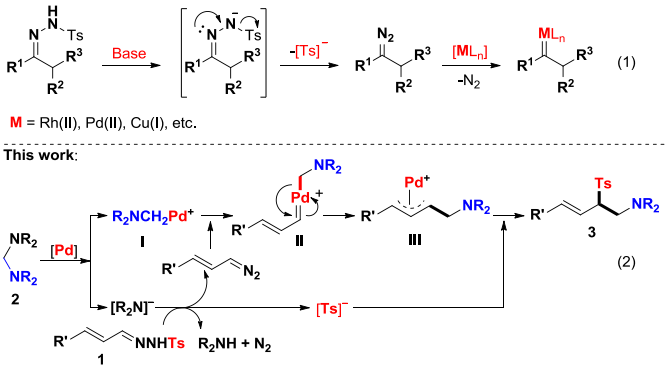
Palladium-catalysed cross-coupling of aminals with *N*-sulfonyl hydrazones has been established via C-N bond activation under base-free conditions, in which one C-C and one C-S bond was simultaneously generated. It was successfully applied in the construction of a variety of aminomethyl substituted allylic sulfones. Preliminary mechanistic studies indicated that the unique electrophilic cyclopalladated complex was involved in the catalytic cycle.

Introduction

Transition-metal catalysed insertion of metal carbenes into X-H (X = N, O, S, B, Si, et al) bond is a powerful tool for constructing carbon-heteroatom bonds, which has been extensively explored and considerable progress has been achieved.[1] In contrast, the selective insertion of metal carbenes into C-X bond via the stepwise ylide formation mechanism remains largely elusive since the selective controlling the migration of two distinct carbon moieties attached in heteroatom is challenging.[2] To circumvent this problem, we recently developed a novel palladium-catalysed protocol for the formal insertion of carbenoids into aminals via C-N bond activation, which led to generation of *α,β*-diaminoacidesters with quarternary carbon-centers. Mechanistic studies disclosed that the C-N bond of aminal was selectively cleaved by the palladium catalyst to generate the cyclopalladated complex which was then trapped by diazoacetate to form the Pd-carbene complex to facilitate the C-C and C-N bond formation.[3]

The *N*-sulfonyl hydrazones are easily synthesized from simple starting materials and have been widely utilized in the past decades.[4] In the presence of strong base, the unstable diazo compound could be generated *in situ* and one molecule of Ts^- was released from an *N*-sulfonyl hydrazone. In this regard, *N*-sulfonyl hydrazone could act as a surrogate of diazo compound (Scheme 1, eq 1). Indeed, the first example of employing *N*-sulfonyl hydrazone as a diazo compound precursor in palladium-catalysed cross-coupling reaction with aryl halides was discovered by Barluenga in 2007.[5] This pioneer work opened a new way for development of metal-carbene chemistry. Since then, a number of transition-metal catalysed cross-coupling reactions with *N*-sulfonyl hydrazones as carbene precursors were developed.[6,7] However, a stoichiometric amounts of external base was generally required in these reactions.

Inspired by these results and on the basis of our recent work in Pd-catalyzed C-N bond activation chemistry,[3,8] we hypothesized that the *N*-sulfonyl hydrazone would act as a useful surrogate of diazo intermediate to react with an aminal under the palladium catalysis, since the released R_2N^- can act as a strong base to facilitate producing diazo intermediate, which could be further reacted with the cyclopalladated complex **I** (Scheme 1, eq 2). Herein, we report a palladium-catalysed C-C, C-S bonds formation reactions between aminals and *N*-sulfonyl hydrazones via C-N bond activation, which provides an unusual and reliable approach to aminomethyl allylic sulfones. Notably, the allylic sulfone motif exists in numerous bioactive compounds, such as antibacterial agents and herbicides.[9]



Scheme1. A new strategy for synthesis of aminomethyl substituted allylic sulfones

Results and discussion

Initially, we started our investigation by employing *N*-tosylhydrazone **1a** and *N,N,N′,N′*-tetrabenzylmethanediamine **2a** as the model substrates (Table 1, entry 1). As might be expected, the reaction took place and gave the desired product **3a** in 39% isolated yield in the presence of a catalytic amount of $Pd(PPh_3)_4$ in 1,4-dioxane at 80 °C for 12 h. With the

[a] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China. E-mail: hmhuang@licp.cas.cn;
[b] University of Chinese Academy of sciences, Beijing 100049, P. R. China

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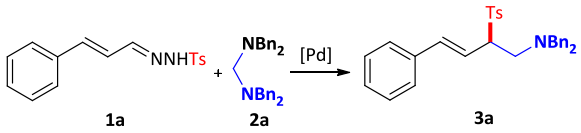
initial result in hand, we proceeded to optimize the reaction conditions. At the beginning, the yield of **3a** couldn't be improved by using different palladium catalysts (Table 1, entries 2-5). To our delight, when the cationic palladium-catalyst, $Pd(DPEphos)(CH_3CN)_2(OTf)_2$, was introduced into the reaction system, the yield of **3a** was promoted to 50% (Table 1, entry 6). Further screening of solvents (see Supporting Information) demonstrated that strong polar organic solvents and protic solvents were failing to give satisfied results and *n*-Bu_2O proved to be the best solvent, giving 3a in 56% yield (entries 6-10). Since the *N*-tosylhydrazone **1a** might be decomposed fast under high temperature. Thus, the reaction temperature was tested, we found the yield of **3a** was reduced at 60 °C (Table 1, entry 11) even prolonged the reaction time (see SI). However, the desired product could be given in a better yield through slightly elevating the temperature (Table 1, entry 12). To further improve the efficiency of the reaction, the impact of the additive was investigated (see Supporting Information). 3Å MS emerged as the choice to give **3a** in good yield (Table 1, entry 13). It's worth noting that the reaction could occur faster under higher concentration (Table 1, entry 14). Last but not least, we examined the effect of reaction time and found 10 hours was the best choice for this transformation, providing the desired product in 68% isolated yield (Table 1, entry 15).

Table 1 Optimization of reaction conditions[a]



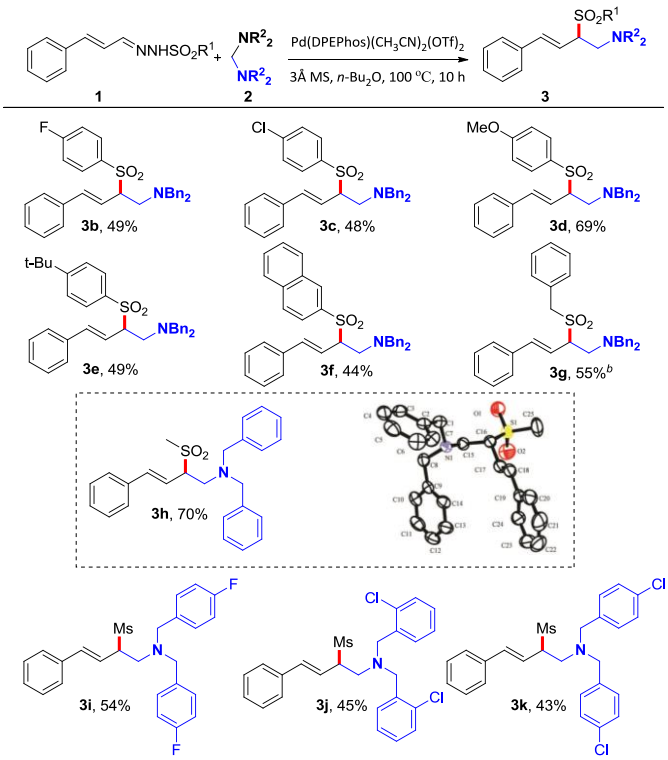
1a 2a 3a

Entry	Pd	Solvent	Additive	Yeild (%)
1	$Pd(PPh_3)_4$	1,4-dioxane	-	39
2	$Pd(OAc)_2$	1,4-dioxane	-	35
3	$Pd(XantPhos)Cl_2$	1,4-dioxane	-	40
4	$Pd(DPEPhos)Cl_2$	1,4-dioxane	-	28
5	$Pd(XantPhos)(CH_3CN)_2(OTf)_2$	1,4-dioxane	-	34
6	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	1,4-dioxane	-	50
7	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	DMF	-	0
8	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	DMSO	-	0
9	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	MeOH	-	12
10	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	*n*-Bu_2O	-	56
11[b]	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	*n*-Bu_2O	-	26
12[c]	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	*n*-Bu_2O	-	60
13[c,d]	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	*n*-Bu_2O	3Å MS	63
14[c,d,e]	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	*n*-Bu_2O	3Å MS	63
15[c,d,e,f]	$Pd(DPEPhos)(CH_3CN)_2(OTf)_2$	*n*-Bu_2O	3Å MS	68

[a] Reaction conditions: **1a** (0.4 mmol), **2a** (0.8 mmol), [Pd] (2.5 mol%), solvent (2.0 mL), 80 °C, 12 h, isolated yield. [b] 60 °C. [c] 100 °C. [d] 3Å MS (20 mg). [e] *n*-Bu_2O (1.0 mL). [f] 10 h.

With the optimized reaction conditions in hand, the substrate scope was next investigated by employing various *N*-sulfonyl hydrazones and aminals. Firstly, the effect of the sulfonyl group was investigated. As illustrated in Table 2, hydrazones bearing electron-donating or electron-withdrawing groups on the phenyl ring of sulfonyl groups can be transformed into corresponding products smoothly. As might be expected, *N*-sulfonyl hydrazones with electron-donating groups underwent the reaction to give the desired products (**3d**, **3e**) in 49% and 60% yields, respectively. On the contrary, relatively lower yields were obtained when substrates bear electron-withdrawing groups (**3b**, **3c**). The reason should be assigned to the nucleophilicity of the corresponding sulfinate anions. It's interesting to note that the reaction of the *N*-mesylhydrazone **1h** with **2a** proceeded smoothly, giving the desired product **3h** in 70% yield. Besides, The solid state structure of **3h** was unambiguously characterized by single-crystal X-ray crystallographic analysis (see Supporting Information).[10] As for the aminal component, fluoro and chloro functional groups attached in the phenyl ring of aminal can tolerate current reaction conditions to give the corresponding products in moderate yields (43-54% yields, **3i**-**3k**).

Table 2 Substrate scope of *N*-sulfonyl hydrazones and aminals[a]

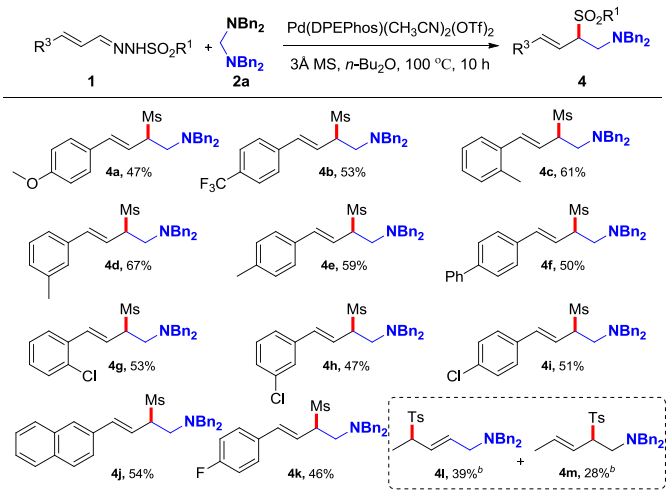


[a] Reaction conditions: **1** (0.4 mmol), **2** (0.8 mmol), $Pd(DPEphos)(CH_3CN)_2(OTf)_2$ (2.5mol%), 3Å MS (20 mg), *n*-Bu_2O (1.0 mL), 100 °C, 10 h, isolated yield. [b] 60 °C, 24 h.

After investigating the effect of the sulfonyl group and aminals, various types of *N*-mesylhydrazones derived from cinnamaldehydes, which bear a variety of substituents on the phenyl ring were also investigated in the reaction with **2a**. As shown in Table 3, the reaction proceeded smoothly to give the products in moderated yields in the presence of both electron-rich and -deficient aromatic systems. Generally, hydrazones with electron-donating groups on the phenyl ring provided higher yields than those with electron-withdrawing groups. Typical functional groups such as methoxyl (**4a**), methyl (**4c**-**4e**), fluoride (**4k**) and chloride (**4g**-**4i**) were well tolerated under the optimized reaction conditions. In addition, 2-naphthyl-substituted hydrazone was also compatible with this transformation, generating the corresponding product **4j** in 54% yield. After the exploration of the reaction scope of aryl hydrazones, we turned our attention to more challenging

crotonaldehyde derived hydrazone. The *N'*-((*E*)-but-2-enylidene)-4-methylbenzenesulfonohydrazide proceeded smoothly, producing the corresponding adducts (**4l**, **4m**) in 39% and 28% yields with lower regioselectivity, respectively.

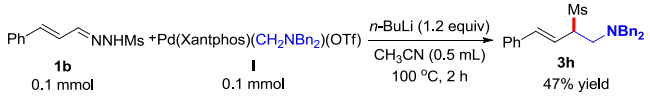
Table 3 Substrate scope of *N*-sulfonyl hydrazones [a]



[a] Reaction conditions: **1** (0.4 mmol), **2a** (0.8 mmol), Pd(DPEphos)$(CH_3CN)_2(OTf)_2$ (2.5 mol%), 3Å MS (20 mg), *n*-Bu_2O (1.0 mL), 100 °C, 10 h, isolated yield. [b] Pd(Xantphos)$(CH_3CN)_2(OTf)_2$ (2.5 mol%), 1,4-dioxane (1.0 mL).

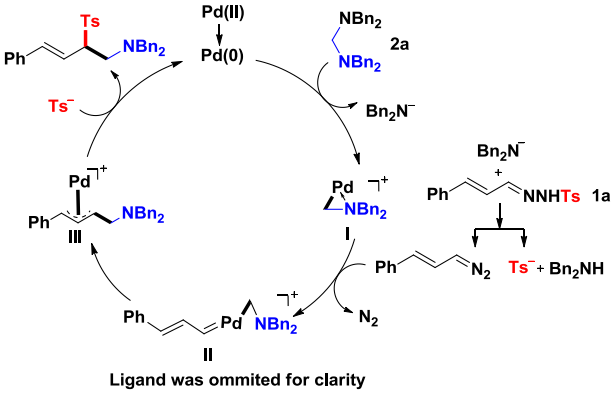
To gain insight into the mechanism of this reaction, a stoichiometric reaction of cyclopalladated complex **I** with *N'*-((*E*)-3-phenylallylidene)methanesulfonohydrazide **1b** was conducted in CH_3CN at 100 °C for 2 h in the presence of *n*-BuLi. This transformation provided the desired product **3h** in 47% yield, suggesting metal complex **I** was most likely to be involved in the catalytic cycle (Scheme 2).

Scheme 2 Plausible mechanistic study



On the basis of the results described above and previous reports,[3,6] a plausible mechanism of this novel reaction was proposed as the following catalytic cycle (Figure 1). The catalyst precursor Pd(II) species were reduced to Pd(0) species, which reacted with aminal **2a** through oxidative addition to produce the Pd(II) complex **I** and release one molecule of R_2N^-. The R_2N^- acted as a strong base to react with *N*-tosylhydeazone **1** to produce the (*E*)-(3-diazoprop-1-en-1-yl)benzene together with TS^-. The (*E*)-(3-diazoprop-1-en-1-yl)benzene was then trapped by the cyclopalladated complex **I** to generate the carbene intermediate **II,** which underwent subsequently migratory insertion of the aminomethyl group to form π-allylpalladium intermediate **III**. The intermediate **III** was then attacked by Ts^- to produce the desired product and regenerate the active Pd(0) for the next catalytic cycle.

Figure 1 Plausible reaction mechanism



Conclusions

In summary, we have established an unprecedented palladium-catalysed cross-coupling of aminals with *N*-sulfonyl hydrazones under external base-free conditions, in which one C-C and one C-S bond was simultaneously constructed. It was successfully applied in the construction of a variety of aminomethyl substituted allylic sulfones under mild conditions. A series of aminals and *N*-sulfonyl hydrazones with different substituents were smoothly transformed to the corresponding products. Asymmetric catalysis and reactions of aminals with other types of *N*-sulfonyl hydrazones are currently in progress in our group.

Experimental section

General

All non-aqueous reactions and manipulations were using standard Schlenk techniques. All solvents before use were dried and degassed by standard methods and stored under nitrogen atmosphere. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on BRUKER Avence **III** 400 MHz spectrometers. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) were reported in Hz and refered to apparent peak multiplications. High resolution mass spectra (HRMS) were recorded on Bruker MicroTOF-Q**II** mass (ESI). Cinnamaldehyde, crotonaldehyde, solvents were purchased from Aldrich. Sulfonyl chlorides were purchased from Alfa Aesar. Aminals used here were known compounds and synthesized according to the reported methods.[11a,11b] 4-fluorobenzenesulfonohydrazide , 4-tert-butylbenzenesulfonohydrazide and *N*-sulfonyl hydrazones (**1c-1o)** were synthesized according to the literature procedure: 4-fluorobenzenesulfonohydrazide,[11c] 4-tert-butylbenzenesulfonohydrazide,[11c] **1c**,[11d] **1d**,[11d] **1e-1o**.[11e] *N'*-((*1E,2E*)-but-2-en-1-ylidene)-4-methylbenzenesulfonohydrazide was known compound and was prepared according to the feference.[11e] *N*-Sulfohydrazides used for preparation of hydrazones were synthesized according to the literature.[11f,11g] Substituted cinnamaldehydes

used for preparation of *N*-mesylhydrazones were known compounds and synthesized according to the literature.[11h]

General procedure for the reaction of aminals with *N*-sulfonyl hydrazones

N-Sulfonyl hydrazones **1** (0.4 mmol), aminals **2** (0.8 mmol), $Pd(DPEPhos)(CH_3CN)_2(OTf)_2$ (0.01mmol, 2.5 mol%), 3Å MS (20.0 mg), *n*-Bu_2O (1.0 mL) were added to a 25 mL flame-dried Young-type tube under nitrogen atmosphere. The mixture was degassed by the freeze-thaw method, and stirred at 100 °C for 10 h. After cooling to room temperature, the solvent was evaporated under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 50/1 - 5/1) to afford products.

4-fluoro-*N*′-((*E*)-3-phenylallylidene)benzenesulfonohydrazide (1c): The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (4.1 g, 72% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.88 (dd, J_1 = 16.0 Hz , J_2 = 9.2 Hz, 1H), 7.00 (d, *J* = 16.0 Hz, 1H), 7.29-7.38 (m, 3H), 7.45-7.50 (m, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 1H), 7.88-7.92 (m, 2H), 11.51 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 116.4, 116.6, 124.6, 127.1, 128.7, 128.9, 130.1, 130.2, 135.4, 135.6, 139.5, 149.7, 163.2, 165.7; ^{19}F NMR (376 MHz, DMSO-d_6) δ -105.8; HRMS (ESI) calcd. for $C_{15}H_{13}FN_2O_2SNa$ [M+Na]: 327.0574, found: 327.0567.

4-tert-butyl-*N*′-((*E*)-3-phenylallylidene)benzenesulfonohydrazide (1d): The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (5.0 g, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 1.27 (s, 9H), 6.88 (dd, J_1 = 16.0 Hz, J_2 = 9.2 Hz, 1H), 6.97 (d, *J* = 16.0 Hz, 1H), 7.27-7.36 (m, 3H), 7.55 (d, *J* = 7.2 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.75(d, *J* = 8.8 Hz, 1H), 7.80 (d, *J* = 10.4 Hz, 2H), 11.48 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 35.9, 40.1, 130.0, 131.3, 132.2, 132.3, 134.0, 134.1, 140.9, 141.6, 144.4, 154.4, 161.2; HRMS (ESI) calcd. for $C_{19}H_{23}N_2O_2S$ [M+H]: 343.1475, found: 343.1457.

***N*′-((*E*)-3-(4-methoxyphenyl)allylidene)methanesulfonohydrazide (1e)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (3.3 g, 92% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.03 (s, 3H), 3.77 (s, 3H), 6.85 (dd, J_1 = 16.0 Hz , J_2 = 8.8 Hz, 1H), 6.93-6.97 (m, 3H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 9.2 Hz, 1H), 10.87 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.4, 55.2, 114.3, 122.5, 128.4, 128.6, 138.8, 149.4, 159.9; HRMS (ESI) calcd. for $C_{11}H_{15}N_2O_3S$ [M+H]: 255.0798, found: 255.0792.

***N*′-((*E*)-3-(4-(trifluoromethyl)phenyl)allylidene)methanesulfonohydrazide (1f)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (2.8 g, 95% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.04 (s, 3H), 7.11-7.13 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.80-7.83 (m, 3H), 11.13 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.6, 122.8, 125.5, 125.6, 125.6, 127.6, 127.6, 128.3, 128.7, 136.9, 139.8, 148.1; ^{19}F NMR (376 MHz, DMSO-d6) δ -61.0; HRMS (ESI) calcd. for $C_{11}H_{11}F_3N_2O_2SNa$ [M+Na]: 315.0386, found: 315.0378.

***N*′-((*E*)-3-o-tolylallylidene)methanesulfonohydrazide (1g)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (2.3 g, 72% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.37 (s, 3H), 3.03 (s, 3H), 6.88 (dd, J_1 = 16.0 Hz , J_2 = 9.2 Hz, 1H), 7.20-7.25 (m, 4H), 7.65-7.67 (m, 1H), 7.85 (d, *J* = 9.6 Hz, 1H), 10.98 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 19.4, 38.5, 125.4, 125.8, 126.3, 128.7, 130.5, 134.4, 136.0, 136.4, 149.2; HRMS (ESI) calcd. for $C_{11}H_{15}N_2O_2S$ [M+H]: 239.0849, found: 239.0840.

***N*′-((*E*)-3-m-tolylallylidene)methanesulfonohydrazide (1h)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (155.0 mg, 47% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.32 (s, 3H), 3.02 (s, 3H), 6.90-7.01 (m, 2H), 7.15 (d, *J* = 7.6 Hz, 1H), 7.25-7.29 (m, 1H), 7.38-7.41 (m, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 10.95 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 20.9, 38.5, 124.2, 124.7, 127.6, 128.7, 129.6, 135.6, 137.9, 139.0, 148.9; HRMS (ESI) calcd. for $C_{11}H_{14}N_2O_2SNa$ [M+Na]: 261.0668, found: 261.0665.

***N*′-((*E*)-3-p-tolylallylidene)methanesulfonohydrazide (1i)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (2.0 g, 56% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.31 (s, 3H), 3.02 (s, 3H), 6.86-7.00 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.78 (d, *J*= 8.8 Hz, 1H), 10.92 (s, 1H); ^{13}C

NMR (100 MHz, DMSO-d_6) δ 20.9, 38.4, 123.8, 127.0, 129.4, 133.0, 138.5, 138.9, 149.1; HRMS (ESI) calcd. for $C_{11}H_{14}N_2O_2SNa$ [M+Na]: 261.0668, found: 261.0673.

***N'*-((*E*)-3-(biphenyl-4-yl)allylidene)methanesulfonohydrazide (1j)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (2.6 g, 87% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.03 (s, 3H), 6.98-7.10 (m, 2H), 7.36-7.40 (m, 2H), 7.46-7.50 (m, 2H), 7.72 (d, *J* = 8.4 Hz, 6H), 7.82 (d, *J* = 8.4 Hz, 1H), 10.99 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.5, 124.9, 126.5, 127.0, 127.7, 129.0, 134.9, 138.4, 139.4, 140.3, 148.9; HRMS (ESI) calcd. for $C_{16}H_{16}N_2O_2SNa$ [M+Na]: 323.0825, found: 323.0818.

***N'*-((*E*)-3-(2-chlorophenyl)allylidene)methanesulfonohydrazide (1k)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (1.8 g, 84% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.04 (s, 3H), 7.07 (dd, J_1 = 16.0 Hz , J_2 = 9.2 Hz, 1H), 7.28 (d, *J* = 16.0 Hz, 1H), 7.33-7.38 (m, 2H), 7.49-7.51 (m, 1H), 7.85-7.90 (m, 2H), 11.10 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.6, 127.3, 127.6, 127.9, 129.8, 130.2, 132.4, 133.3, 133.5, 148.4; HRMS (ESI) calcd. for $C_{10}H_{11}ClN_2O_2SNa$ [M+Na]: 281.0122, found: 281.0108.

***N'*-((*E*)-3-(3-chlorophenyl)allylidene)methanesulfonohydrazide (1l)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (2.7 g, 89% yield) ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.03 (s, 3H), 6.98-7.09 (m, 2H), 7.36-7.43 (m, 2H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.69 (s, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 11.06 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.6, 125.5, 126.5, 126.7, 128.4, 130.6, 133.6, 137.2, 138.0, 148.3; HRMS (ESI) calcd. for $C_{10}H_{11}ClN_2O_2SNa$ [M+Na]: 281.0122, found: 281.0110.

***N'*-((*E*)-3-(4-chlorophenyl)allylidene)methanesulfonohydrazide (1m)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (2.8 g, 95% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.03 (s, 3H), 6.95-7.05 (m, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.8 Hz, 2H), 7.76-7.78 (m, 1H), 11.02 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.5, 125.7, 128.7, 128.8, 133.2, 134.7, 137.4, 148.5; HRMS (ESI) calcd. for $C_{10}H_{11}ClN_2O_2SNa$ [M+Na]: 281.0122, found: 281.0114.

***N'*-((*E*)-3-(naphthalen-2-yl)allylidene)methanesulfonohydrazide (1n)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (2.9 g, 92% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.05 (s, 3H), 7.08-7.21 (m, 2H), 7.50-7.55 (m, 2H), 7.83-7.92 (m, 5H), 8.03 (s, 1H), 11.02 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.5, 123.6, 125.3, 126.6, 127.6, 128.1, 128.4, 133.0, 133.4, 138.9, 148.9; HRMS (ESI) calcd. for $C_{14}H_{15}N_2O_2S$ [M+H]: 275.0849, found: 275.0835.

***N'*-((*E*)-3-(4-fluorophenyl)allylidene)methanesulfonohydrazide (1o)**: The title compound was prepared according to the general procedure and purified by recrystallization to give a white needles (2.1 g, 82% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 3.02 (s, 3H), 6.90-7.04 (m, 2H), 7.20-7.24 (m, 2H), 7.64-7.68 (m, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 10.97 (s, 1H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 38.5, 115.6, 115.8, 124.7, 124.7, 129.1, 129.2, 132.4, 132.4, 137.7, 148.8, 161.1, 163.5; ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.3; HRMS (ESI) calcd. for $C_{10}H_{11}FN_2O_2SNa$ [M+Na]: 265.0417, found: 265.0407.

(*E*)-*N*,*N*-dibenzyl-4-phenyl-2-tosylbut-3-en-1-amine (3a): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (130.5 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.40 (s, 3H), 2.97-3.03 (m, 1H), 3.20 (dd, J_1 = 13.2 Hz, J_2 = 3.2 Hz, 1H), 3.45 (d, *J* = 13.6 Hz, 2H), 3.70-3.79 (m, 3H), 5.73 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.19 (d, *J* = 16.0 Hz, 1H), 7.20-7.36 (m, 17H), 7.58 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 51.7, 59.1, 67.9, 121.6, 126.6, 127.2, 128.2, 128.3, 128.6, 129.0, 129.0, 129.5, 134.7, 136.2, 137.9, 138.8, 144.5; HRMS (ESI) calcd. for $C_{31}H_{32}NO_2S$ [M+H]: 482.2148, found: 482.2151.

(*E*)-*N*,*N*-dibenzyl-2-(4-fluorophenylsulfonyl)-4-phenylbut-3-en-1-amine (3b): The title compound was prepared according to the general procedure and purified by column

chromatography to give a colorless oil (94.0 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97-3.03 (m, 1H), 3.22 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.48 (d, J = 13.6 Hz, 2H), 3.70-3.76 (m, 3H), 5.70 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.16 (d, J = 16.0 Hz, 1H), 7.08-7.12 (m, 2H), 7.21-7.24 (m, 11H), 7.28-7.37 (m, 4H), 7.70 (dd, J_1 = 8.8 Hz, J_2 = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.5, 59.2, 68.1, 116.0, 116.2, 121.2, 126.6, 127.2, 128.3, 128.4, 128.7, 129.0, 131.8, 131.9, 135.9, 138.2, 138.7; ^{19}F NMR (376 MHz, DMSO-d_6) δ -103.6; HRMS (ESI) calcd. for $C_{30}H_{29}FNO_2S$ [M+H]: 486.1898, found: 486.1886.

(*E*)-*N*,*N*-dibenzyl-2-(4-chlorophenylsulfonyl)-4-phenylbut-3-en-1-amine (3c): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (96.4 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96-3.02 (m, 1H), 3.20 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.48 (d, J = 13.6 Hz, 2H), 3.71-3.76 (m, 3H), 5.70 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.19 (d, J = 16.0 Hz, 1H), 7.23-7.26 (m, 12H), 7.31-7.35 (m, 3H), 7.41 (d, J = 8.8 Hz, 2H), 7.61 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.5, 59.2, 68.0, 121.0, 126.6, 127.3, 128.3, 128.4, 128.7, 129.0, 129.1, 130.5, 135.9, 136.1, 138.3, 138.6, 140.4; HRMS (ESI) calcd. for $C_{30}H_{29}ClNO_2S$ [M+H]: 502.1602, found: 502.1597.

(*E*)-*N*,*N*-dibenzyl-2-(4-methoxyphenylsulfonyl)-4-phenylbut-3-en-1-amine (3d): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid (137.2 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.97-3.03 (m, 1H), 3.20 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.45 (d, J = 13.6 Hz, 2H), 3.71-3.78 (m, 3H), 3.84 (s, 3H), 5.74 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.19 (d, J = 15.6 Hz, 1H), 6.89 (d, J = 9.2 Hz, 2H), 7.20-7.25 (m, 12H), 7.29-7.36 (m, 3H), 7.62 (d, J = 8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.7, 55.6, 59.1, 68.1, 114.0, 121.7, 126.6, 127.2, 128.2, 128.3, 128.6, 129.0, 129.2, 131.2, 136.2, 137.8, 138.8, 163.6; HRMS (ESI) calcd. for $C_{31}H_{32}NO_3S$ [M+H]: 498.2097, found: 498.2093.

(*E*)-*N*,*N*-dibenzyl-2-(4-tert-butylphenylsulfonyl)-4-phenylbut-3-en-1-amine (3e): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (103.0 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 9H), 2.99-3.05 (m, 1H), 3.21 (dd, J_1 = 13.2 Hz, J_2 = 3.2 Hz, 1H), 3.45 (d, J = 13.6 Hz, 2H), 3.72-3.82 (m, 3H), 5.72 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.14 (d, J = 16.0 Hz, 1H), 7.18-7.25 (m, 11H), 7.28-7.35 (m, 4H), 7.44 (d, J = 8.4 Hz, 2H), 7.60-7.62 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 31.1, 35.2, 51.6, 59.0, 68.0, 121.6, 125.8, 126.6, 127.2, 128.2, 128.3, 128.6, 128.9, 129.0, 134.5, 136.2, 137.9, 138.8, 157.5; HRMS (ESI) calcd. for $C_{34}H_{38}NO_2S$ [M+H]: 524.2618, found: 524.2610.

(*E*)-*N*,*N*-dibenzyl-2-(naphthalen-2-ylsulfonyl)-4-phenylbut-3-en-1-amine (3f): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid (92.0 mg, 44% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.02-3.07 (m, 1H), 3.25 (dd, J_1 = 13.2 Hz, J_2 = 3.2 Hz, 1H), 3.47 (d, J = 13.6 Hz, 2H), 3.73 (d, J = 13.2 Hz, 2H), 3.82-3.88 (m, 1H), 5.78 (dd, J_1 = 15.6 Hz, J_2 = 9.2 Hz, 1H), 6.20 (d, J = 16.0 Hz, 1H), 7.15-7.20 (m, 12H), 7.25-7.33 (m, 3H), 7.57-7.61 (m, 1H), 7.64-7.68 (m, 2H), 7.86-7.90 (m, 3H), 8.28 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.8, 59.1, 68.0, 121.3, 123.7, 126.6, 127.2, 127.5, 127.9, 128.2, 128.6, 128.9, 128.9, 129.2, 129.5, 130.9, 132.0, 134.7, 135.3, 136.1, 138.2, 138.7; HRMS (ESI) calcd. for $C_{34}H_{32}NO_2S$ [M+H]: 518.2148, found: 518.2134.

(*E*)-*N*,*N*-dibenzyl-2-(benzylsulfonyl)-4-phenylbut-3-en-1-amine (3g): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (106.0 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.00-3.05 (m, 1H), 3.21 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.46 (d, J = 13.6 Hz, 2H), 3.67-3.73 (m, 3H), 4.11 (d, J = 14.0 Hz, 1H), 4.21 (d, J = 14.0 Hz, 1H), 5.93 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.45 (d, J = 16.0 Hz, 1H), 7.19-7.26 (m, 9H), 7.29-7.43 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 51.1, 57.5, 59.1, 64.6, 121.8, 126.8, 127.2, 127.3, 128.3, 128.6, 128.8, 128.9, 129.0, 130.9, 135.8, 138.1, 138.7; HRMS (ESI) calcd. for $C_{31}H_{32}NO_2S$ [M+H]: 482.2148, found: 482.2148.

(*E*)-*N*,*N*-dibenzyl-2-(methylsulfonyl)-4-phenylbut-3-en-1-amine (3h): The title compound was prepared according to the general procedure and purified by column chromatography to give a white solid (113.5 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 3.00-3.06 (m, 1H), 3.27 (dd, J_1 = 13.2 Hz, J_2 = 4.0 Hz, 1H), 3.53 (d, J = 13.6 Hz, 2H), 3.70-3.76 (m, 1H), 3.81 (d, J = 13.6 Hz, 2H), 5.94 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H),

6.58 (d, *J* = 16.0 Hz, 1H), 7.24-7.33 (m, 11H), 7.38-7.39 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 51.2, 59.2, 67.0, 121.7, 126.8, 127.3, 128.4, 128.6, 128.8, 129.0, 135.7, 138.0, 138.7; HRMS (ESI) calcd. for $C_{25}H_{28}NO_2S$ [M+H]: 406.1835, found: 406.1842.

(*E*)-*N*,*N*-bis(4-fluorobenzyl)-2-(methylsulfonyl)-4-phenylbut-3-en-1-amine (3i): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (95.0 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3H), 2.97-3.03 (m, 1H), 3.27 (dd, J_1 = 13.6 Hz, J_2 = 3.6 Hz, 1H), 3.48 (d, *J* = 13.6 Hz, 2H), 3.71-3.78 (m, 3H), 5.92 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.59 (d, *J* = 15.6 Hz, 1H), 6.92-6.96 (m, 4H), 7.22-7.26 (m, 4H), 7.33-7.42 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 50.7, 58.2, 66.9, 115.1, 115.3, 121.8, 126.7, 128.8, 128.9, 130.4, 130.5, 134.2, 134.2, 135.5, 137.9, 160.9, 163.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.2; HRMS (ESI) calcd. for $C_{25}H_{26}F_2NO_2S$ [M+H]: 442.1647, found: 442.1650.

(*E*)-*N*,*N*-bis(2-chlorobenzyl)-2-(methylsulfonyl)-4-phenylbut-3-en-1-amine (3j): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (85.0 mg, 45% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (s, 3H), 3.03-3.08 (m, 1H), 3.42 (dd, J_1 = 13.2 Hz, J_2 = 3.2 Hz, 1H), 3.76-3.84 (m, 5H), 5.94 (dd, J_1 = 16.0 Hz, J_2 = 10.0 Hz, 1H), 6.57 (d, *J* = 16.0 Hz, 1H), 7.10-7.18 (m, 4H), 7.25-7.38 (m, 7H), 7.46 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 51.9, 56.4, 67.0, 121.4, 126.7, 126.8, 128.5, 128.6, 128.7, 129.6, 131.2, 134.3, 135.7, 135.9, 138.3; HRMS (ESI) calcd. for $C_{25}H_{26}Cl_2NO_2S$ [M+H]: 474.1056, found: 474.1047.

(*E*)-N,N-bis(4-chlorobenzyl)-2-(methylsulfonyl)-4-phenylbut-3-en-1-amine (3k): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (81.0 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3H), 2.96-3.02 (m, 1H), 3.27 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.48 (d, *J* = 13.6 Hz, 2H), 3.70-3.78 (m, 3H), 5.90 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 7.19-7.26 (m, 8H), 7.34-7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 50.8, 58.3, 66.9, 121.8, 126.7, 128.6, 128.9, 130.2, 133.1, 135.4, 137.0, 138.0; HRMS (ESI) calcd. for $C_{25}H_{26}Cl_2NO_2S$ [M+H]: 474.1056, found: 474.1060.

(*E*)-*N*,*N*-dibenzyl-4-(4-methoxyphenyl)-2-(methylsulfonyl)but-3-en-1-amine (4a): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (82.0 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 2.98-3.04 (m, 1H), 3.26 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.52 (d, *J* = 13.6 Hz, 2H), 3.69-3.75 (m, 1H), 3.80 (d, *J* = 13.6 Hz, 2H), 3.85 (s, 3H), 5.79 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 6.53 (d, *J* = 15.6 Hz, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.23-7.33 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.1, 51.1, 55.4, 59.1, 67.1, 114.1, 119.3, 127.3, 128.1, 128.4, 128.5, 129.0, 137.4, 138.7, 160.0; HRMS (ESI) calcd. for $C_{26}H_{30}NO_3S$ [M+H]: 436.1941, found: 436.1942.

(*E*)-*N*,*N*-dibenzyl-2-(methylsulfonyl)-4-(4-(trifluoromethyl)phenyl)but-3-en-1-amine (4b): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (100.0 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 3.02-3.07 (m, 1H), 3.28 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 1H), 3.54 (d, *J* = 13.2 Hz, 1H), 3.69-3.75 (m, 1H), 3.81 (d, *J* = 13.6 Hz, 2H), 6.01 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 6.58 (d, *J* = 16.0 Hz, 1H), 7.26-7.30 (m, 10H), 7.46 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 51.3, 59.2, 66.9, 115.6, 115.9, 121.3, 121.3, 127.4, 128.3, 128.4, 128.4, 129.0, 131.9, 136.7, 138.6, 161.7, 164.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6; HRMS (ESI) calcd. for $C_{26}H_{27}F_3NO_2S$ [M+H]: 474.1709, found: 474.1700.

(*E*)-*N*,*N*-dibenzyl-2-(methylsulfonyl)-4-o-tolylbut-3-en-1-amine (4c): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (101.0 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.39 (s, 3H), 2.75 (s, 3H), 3.00-3.06 (m, 1H), 3.27 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.53 (d, *J* = 13.6 Hz, 2H), 3.70-3.81 (m, 3H), 5.92 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 6.56 (d, *J* = 15.6 Hz, 1H), 7.14-7.20 (m, 3H), 7.24-7.32 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.8, 39.1, 51.4, 59.2, 67.3, 123.1, 126.0, 126.3, 127.3, 128.4, 128.5, 129.0, 130.5, 134.8, 135.6, 135.9, 138.7; HRMS (ESI) calcd. for $C_{26}H_{30}NO_2S$ [M+H]: 420.1992, found: 420.1985.

(*E*)-*N*,*N*-dibenzyl-2-(methylsulfonyl)-4-m-tolylbut-3-en-1-amine (4d): The title compound was prepared according to the

general procedure and purified by column chromatography to give a colorless oil (112.0 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H), 2.76 (s, 3H), 3.01-3.06 (m, 1H), 3.28 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.54 (d, J = 13.6 Hz, 2H), 3.71-3.81 (m, 3H), 5.84 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 6.86 (d, J = 15.6 Hz, 1H), 7.20-7.28 (m, 9H), 7.28-7.33 (m, 4H), 7.41-7.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 39.1, 51.1, 59.2, 67.0, 121.6, 124.1, 127.3, 127.4, 128.4, 128.7, 129.0, 129.4, 135.6, 138.0, 138.4, 138.7; HRMS (ESI) calcd. for $C_{26}H_{30}NO_2S$ [M+H]: 420.1992, found: 420.1982.

(*E*)-*N*,*N*-dibenzyl-2-(methylsulfonyl)-4-p-tolylbut-3-en-1-amine (4e): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (99.0 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (s, 3H), 2.74 (s, 3H), 2.99-3.05 (m, 1H), 3.26 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.52 (d, J = 13.2 Hz, 2H), 3.70-3.80 (m, 3H), 5.89 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), *6.55* (d, J = 16.0 Hz, 1H), 7.18-7.25 (m, 2H), 7.27-7.32 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 39.1, 51.1, 59.1, 67.0, 120.7, 126.7, 127.3, 128.4, 129.0, 129.5, 133.0, 137.9, 138.7, 138.7; HRMS (ESI) calcd. for $C_{26}H_{30}NO_2S$ [M+H]:420.1992, found: 420.1990.

(*E*)-*N*,*N*-dibenzyl-4-(biphenyl-4-yl)-2-(methylsulfonyl)but-3-en-1-amine (4f): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (95.0 mg, 50% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (s, 3H), 3.02-3.08 (m, 1H), 3.29 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 1H), 3.54 (d, J = 13.6 Hz, 2H), 3.73-3.82 (m, 3H), 5.98 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.62 (d, J = 16.0 Hz, 1H), 7.25-7.40 (m, 11H), 7.45-7.49 (m, 4H), 7.62-7.65 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 51.2, 59.2, 67.1, 121.7, 127.0, 127.2, 127.3, 127.4, 127.6, 128.4, 128.9, 129.0, 134.7, 137.5, 138.7, 140.4, 141.4; HRMS (ESI) calcd. for $C_{31}H_{32}NO_2S$ [M+H]: 482.2148, found: 482.2129.

(*E*)-*N*,*N*-dibenzyl-4-(2-chlorophenyl)-2-(methylsulfonyl)but-3-en-1-amine (4g): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (94.0 mg, 53% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3H), 3.01-3.07 (m, 1H), 3.29 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.54 (d, J = 13.6 Hz, 2H), 3.70-3.76 (m, 1H), 3.81 (d, J = 13.6 Hz, 2H), 5.87 (dd, J_1 = 15.6 Hz, J_2 = 9.6 Hz, 1H), 7.04 (d, J = 15.6 Hz, 1H), 7.22-7.26 (m, 4H), 7.27-7.32 (m, 8H), 7.40-7.47 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.3, 51.0, 59.4, 67.0, 125.1, 127.1, 127.2, 127.3, 128.4, 129.1, 129.6, 129.8, 133.2, 133.9, 134.1, 138.6; HRMS (ESI) calcd. for $C_{25}H_{27}ClNO_2S$ [M+H]: 440.1446, found: 440.1433.

(*E*)-*N*,*N*-dibenzyl-4-(3-chlorophenyl)-2-(methylsulfonyl)but-3-en-1-amine (4h): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (82.0 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (s, 3H), 3.00-3.05 (m, 1H), 3.27 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.53 (d, J = 13.6 Hz, 2H), 3.65-3.71 (m, 1H), 3.80 (d, J = 13.6 Hz, 2H), 5.89 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.49 (d, J = 16.0 Hz, 1H), 7.21-7.23 (m, 1H), 7.25-7.31 (m, 12H), 7.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 51.3, 59.4, 66.8, 123.3, 125.0, 126.6, 127.4, 128.4, 128.5, 129.1, 130.0, 134.8, 136.4, 137.5, 138.6; HRMS (ESI) calcd. for $C_{25}H_{27}ClNO_2S$ [M+H]: 440.1446, found: 440.1445.

(*E*)-*N*,*N*-dibenzyl-4-(4-chlorophenyl)-2-(methylsulfonyl)but-3-en-1-amine (4i): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (89.0 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 2.99-3.05 (m, 1H), 3.26 (dd, J_1 = 13.2 Hz, J_2 = 4.0 Hz, 1H), 3.53 (d, J = 13.6 Hz, 2H), 3.67-3.80 (m, 3H), 5.89 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.51 (d, J = 15.6 Hz, 1H), 7.22-7.27 (m, 3H), 7.28-7.30 (m, 9H)，7.34-7.36 (m, 2H) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 51.3, 59.3, 66.9, 122.3, 127.4, 127.9, 128.4, 129.0, 129.0, 134.2, 134.4, 136.6, 138.6; HRMS (ESI) calcd. for $C_{25}H_{27}ClNO_2S$ [M+H]: 440.1446, found: 440.1442.

(*E*)-*N*,*N*-dibenzyl-2-(methylsulfonyl)-4-(naphthalen-2-yl)but-3-en-1-amine (4j): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (98.0 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.78 (s, 3H), 3.05-3.11 (m, 1H), 3.30 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 1H), 3.54 (d, J = 13.6 Hz, 2H), 3.76-3.83 (m, 3H), 6.05 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.74 (d, J = 16.0 Hz, 1H), 7.22-7.29 (m, 6H), 7.31-7.33 (m, 4H)，7.48-7.57 (m, 3H)，7.75（s, 1H）, 7.84-7.86 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 51.2, 59.2, 67.1, 122.1, 123.5, 126.5, 126.6, 127.2, 127.3, 127.8, 128.2, 128.4, 128.5, 129.0, 133.2, 133.4,

133.5, 138.0, 138.7; HRMS (ESI) calcd. for $C_{29}H_{30}NO_2S$ [M+H]: 456.1992, found: 456.1997.

(*E*)-*N*,*N*-dibenzyl-4-(4-fluorophenyl)-2-(methylsulfonyl)but-3-en-1-amine (4k): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (77.0 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.75 (s, 3H), 2.99-3.04 (m, 1H), 3.27 (dd, J_1 = 13.2 Hz, J_2 = 3.6 Hz, 1H), 3.53 (d, J = 13.6 Hz, 2H), 3.67-3.73 (m, 1H), 3.80 (d, J= 13.6 Hz, 2H), 5.83 (dd, J_1 = 16.0 Hz, J_2 = 9.6 Hz, 1H), 6.53 (d, J = 16.0 Hz, 1H), 7.05-7.09 (m, 2H), 7.24-7.27 (m, 3H), 7.28-7.35 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 39.2, 51.3, 59.2, 66.9, 115.6, 115.9, 121.3, 121.3, 127.4, 128.3, 128.4, 128.4, 129.0, 131.9, 136.7, 138.6, 161.7, 164.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.6; HRMS (ESI) calcd for $C_{25}H_{27}FNO_2S$ [M+H]: 424.1741, found: 424.1732.

(*E*)-*N*,*N*-dibenzyl-4-tosylpent-2-en-1-amine (4l): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (65.0 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (d, J = 6.8 Hz, 3H), 2.22 (s, 3H), 2.89-3.04 (m, 2H), 3.43 (q, J = 24.8 Hz, 4H), 3.65-3.72 (m, 1H), 5.48-5.66 (m, 2H), 7.15 (d, J = 8.0 Hz, 2H), 7.21-7.23 (m, 2H), 7.24-7.31 (m, 8H), 7.66 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 21.4, 55.2, 58.0, 63.6, 125.8, 126.9, 128.2, 128.7, 129.0, 129.5, 134.1, 139.3, 144.5; HRMS (ESI) calcd. for $C_{26}H_{30}NO_2S$ [M+H]: 420.1992, found: 420.1988.

(*E*)-*N*,*N*-dibenzyl-2-tosylpent-3-en-1-amine (4m): The title compound was prepared according to the general procedure and purified by column chromatography to give a colorless oil (47.0 mg, 28% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.68 (dd, J_1 = 6.4 Hz, J_2 = 1.2 Hz, 3H), 2.42 (s, 3H), 2.82-2.88 (m, 1H), 3.07 (dd, J_1 = 12.8 Hz, J_2 = 3.2 Hz, 1H), 3.43 (d, J = 13.6 Hz, 2H), 3.55-3.61 (m, 1H), 3.67 (d, J = 13.6 Hz, 2H), 5.07-5.13 (m, 1H), 5.34-5.43 (m, 1H), 7.20-7.28 (m, 12H), 7.57 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 18.2, 21.6, 51.6, 58.8, 67.7, 123.1, 127.1, 128.2, 128.9, 129.0, 129.3, 135.0, 138.8, 144.3; HRMS (ESI) calcd. for $C_{26}H_{30}NO_2S$ [M+H]: 420.1992, found: 420.1975.

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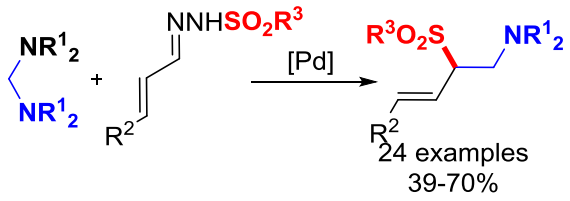
Table of contents:

Palladium-Catalysed Coupling Reaction of Aminals with *N*-Sulfonyl Hydrazones to Allylic Sulfones



Palladium-catalysed cross-coupling of aminals with *N*-sulfonyl hydrazones has been established via C-N bond activation under base-free conditions.