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AgOTf-catalyzed reaction of sulfonyl hydrazones with ynamides led to stereoselective synthesis of α-amino alkenyl-substituted hydrazone derivatives

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ABSTRACT

A novel method for the synthesis of α-amino alkenyl-substituted hydrazone derivatives was disclosed through silver-catalyzed reaction of sulfonyl hydrazones with ynamides. The present method features mild conditions, high stereoselectivity and good yields. The proposed mechanism involves silver-mediated generation of a keteniminium ion intermediate to facilitate the stereoselective addition of hydrazones in the presence of K_2CO_3, while pyrazole ring could not be constructed under the current conditions.

1. Introduction

N-Tosylhydrazones are a class of important organic intermediates, and have been utilized in a large number of organic transformations [1]. For example, *N*-tosylhydrazones can act as efficient diazo precursors for various carbene or carbenoid-participated reactions like the cyclopropanation of alkenes and alkylation of X–H bonds (Scheme 1a) [2,3]. The *in-situ* generated diazo compounds was also frequently used as good 1,3-dipolars in cycloaddition or related reactions (Scheme 1b) [4]. However, the utilization of *N*-tosylhydrazones has not yet been fully explored, especially for the applications as nucleophiles or electrophiles. Our research interest is in the N–H functionalization of hydrazones as nucleophiles (Scheme 1c). In this respect, the alkylation of N–H bonds of hydrazones was readily achieved through substitution reaction and addition reaction [5,6]. Copper-catalyzed reactions of diaryliodonium salts or arylboronic acids with hydrazones could lead to *N*-arylation products [7,8]. By contrast, the *N*-alkenylation of hydrazones were rarely reported. One of major reasons responsible for this fact is that hydrazones are readily converted into diazo intermediate under base conditions. Recently, Shi and Hashemi independently reported the aza-Michael addition reactions of hydrazones with propiolate derivatives in the presence of DABCO and PPh_3 respectively, achieving the synthesis of *N*-alkenylation derivatives [9]. Even so, the development of new reactions to build the *N*-alkenylation products is still meaningful to expand hydrazone chemistry. In addition, as a class of structurally new sulfonamide products, they possess potential applications in pharmaceuticals [10], bioactive compounds [11], dyes and herbicides [12].

Ynamides are also a class of useful building blocks for various organic transformations [13,14]. The addition to alkyne motif is one of the most important transformations of ynamides, and is an efficient method for introducing α-amino alkenyl groups (Scheme 2). In this context, various nucleophilic substrates were examined for achieving such a type of reactions [15–17]. For example, free amines or protected amides have been used for providing a variety of interesting products under metal-catalyzed or metal-free conditions (Scheme 2(a,b)) [18–20]. Recently, our group reported the

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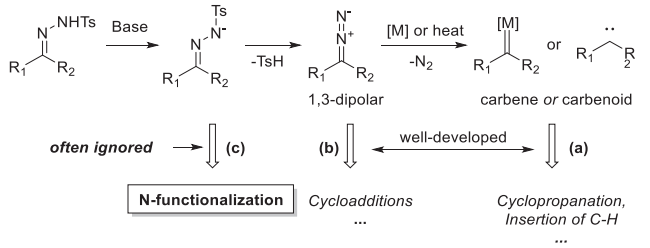
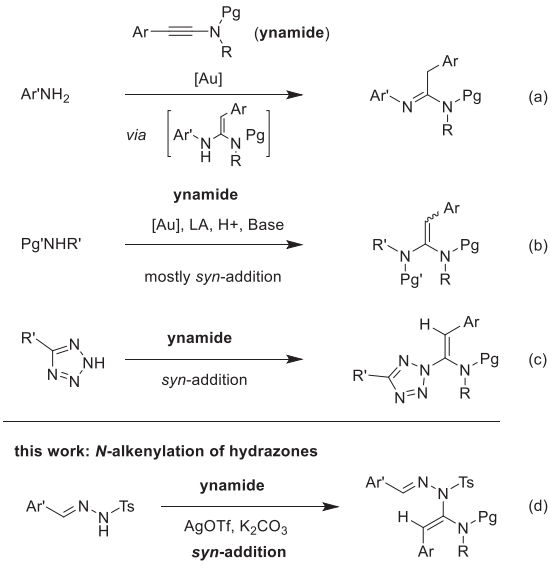


Scheme 1. The reactivities of *N*-tosylhydrazones for various organic transformations.



Scheme 2. The reactions of *N*-containing nucleophiles with ynamides.

reactions of nitrogen-containing heterocycles (2*H*-tetrazole) with ynamides in the absence of any catalyst [21], which facilitates the chemical modification of tetrazole drugs (Scheme 2(c)). Following our ongoing interests in the alkyne chemistry [22], we envisage that the reaction of *N*-tosylhydrazones with ynamides can realize the alkenylation of the N–H bond of hydrazones (Scheme 2(d)). Herein we reported the synthesis of α-amino alkenyl-substituted hydrazone derivatives by silver catalysis. The mechanism was proposed to involve the nucleophilic addition to the keteniminium intermediates *in situ* generated from ynamides by silver catalysis. This process is different from the well-known cycloaddition route of alkynes and hydrazones to give the pyrazole product [23]. To the best of our knowledge, this reactivity of *N*-tosylhydrazones with ynamides has not yet been reported.

2. Results and discussion

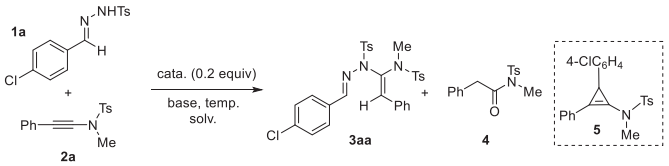
Initial experiments were carried out with sulfonyl hydrazone **1a** (0.39 mmol, 1.3 equiv) and ynamide **2a** (0.3 mmol, 1.0 equiv) as the substrates, using AgOTf (0.2 equiv) as a catalyst and NaH (2.0 equiv) as a base in 1,2-dichloroethane (DCE, 0.5 mL) at 40 °C for providing the aminocyclopropene product **5** [2b]. However, no reaction occurred (Table 1, entry 1). By replacing NaH with K_2CO_3, to our delight, a new product can be obtained in 81% yield and characterized as a simple adduct **3aa** possessing an *E*-type alkene motif, along with a small amount of hydrolytic by-product **4** (Table 1, entry 2). Notably, the addition reaction can proceed in a highly stereoselective manner. It should be also mentioned that neither cyclopropene nor pyrazole products could be observed under such a condition.

Next, a series of metal catalysts were screened to improve the yield of **3aa** (Table 1, entries 2–11). Other silver salts such as $AgNO_3$ and $AgNTf_2$ also leaded to the formation of product **3aa** but with lower yields (Table 1, entries 2–6). The addition of 4 Å molecular sieves lowered the yield of **3aa** to only 13% (Table 1, entry 7). Among other metal catalysts examined, $CuOTf•C_6H_6$ was less reactive than AgOTf and afforded the adduct **3aa** in 50% yield, whereas $FeCl_3$, $In(OTf)_3$ and $AuCl_3$ did not work for the addition reaction (Table 1, entries 8–11). Subsequently, the examination of solvents indicated that no better yield of product was obtained (Table 1, entries 12–16). Various carbonates as the bases such as Na_2CO_3 and Cs_2CO_3 were proven to be suitable to current reaction albeit with low efficiencies, whereas the stronger bases (KO^tBu) were inefficient for the formation of **3aa** (Table 1, entries 17–20). The utility of several organic bases (Et_3N, DIPEA, DABCO and DBU) cannot afford the adduct **3aa** in better yields (Table 1, entries 21–24). Furthermore, temperature effects were rapidly tested, and the product **3aa** could be obtained in 56 and 75% yields at the temperatures of 25 and 60 °C, respectively (Table 1, entries 25–26). Finally, the optimal reaction conditions were established involving with the use of AgOTf and K_2CO_3 in DCE at 40 °C (Table 1, entry 2).

With the optimized conditions in hand, the scope of ynamide substrates was firstly investigated and summarized in Table 2. It could be found that the substrates **2b-d** containing an electron-donor or electron-deficient group on phenyl of aryl ynamides with hydrazone **1a** could be readily converted into the desired adducts **3 ab-ad** in 36–74% yields. The *meta*-substituted aryl ynamide **2e** was also a good substrate to form the product **3ae**. Alkyl substituted ynamides such as **2f** could lead to the formation of **3af** in 73% yield. In particular, the reaction of the bulky *tert*-butyl-substituted ynamide **2g** with **1a** could proceed efficiently to give the α-amino alkenyl-substituted hydrazone **3 ag** in moderate yield. In addition, the nitrogen substituents of ynamides were examined as well. The results showed that ynamide **2h** bearing with a linear alkyl group was reactive under current conditions, leading to synthesis of **3ah** in 64% yield, whereas the larger isopropyl substituent could not be suitable. The protected sulfonyl of ynamides could be replaced with *para*- or *ortho*-nitrobenzenesulfonyl (*p*-Ns or *o*-Ns, **3ai-aj**), or alkylsulfonyl (**3ak**) groups. However, the oxazolidin-2-one derived ynamides such as **2l** could be not good substrate for current reaction, affording an inseparable mixture. In addition, the terminal ynamides such as *N*-ethynyl-*N*,4-dimethylbenzenesulfonamide were incompatible for this reaction, leading to the formation of hydrolytic amides.

Next, various arylaldehyde-derived hydrazones were examined (Table 2). The substrate **1b** with a methoxyl group can react with ynamide **2a** to produce α-amino alkenyl-substituted hydrazone **3ba** efficiently. Somewhat surprisingly, the addition of *p*-tolylaldehyde-derived hydrozone **1c** with **2a** could not proceed under the optimized conditions. This limitation in reactivity could be overcome by changing the protecting group (Ts-) of hydrazones for *para*-nitrobenzenesulfonyl. Thus, the reaction of hydrazone **1d** with **2a** could proceed smoothly, affording the desired product **3da** in good efficiency. This change was also required for other hydrazones for achieving the present transformations efficiently. As exemplified, *p*-Ns-protecting hydrazones **1e-f** bearing with electron-deficient halo-substituents were tolerated to form the addition product **3ea** and **3fa** in 79% and 59% yields, respectively. *m*-Tolylaldehyde-derived hydrozone **1g** was suitable for this reaction, leading to the formation of **3ga** in 69% yield. It should be noted that the addition reaction could be also readily achieved in good yields with the utilization of hydrozones **1h** and **1i** that have a sterically hindered *ortho*-substituent. In addition, a heteroarene-substituted hydrozone **1j** was compatible to current reaction, and the desired α-

Table 1
The optimization of reaction conditions.[a]



Entry	Cata.(0.2 equiv)	Base (2.0 equiv)	Solvent (0.5 mL)	Time (h)	Yield **3aa** (%)[b]
1	AgOTf	NaH	DCE	12	0
2	AgOTf	K_2CO_3	DCE	4	81
3	$AgNO_3$	K_2CO_3	DCE	12	62
4	$AgNTf_2$	K_2CO_3	DCE	24	54
5	$AgSbF_6$	K_2CO_3	DCE	12	64
6	$AgBF_4$	K_2CO_3	DCE	5	45
7[c]	AgOTf	K_2CO_3	DCE	24	13
8	$FeCl_3$	K_2CO_3	DCE	12	0
9	$In(OTf)_3$	K_2CO_3	DCE	12	0
10	$CuOTf•C_6H_6$	K_2CO_3	DCE	4	50
11	$AuCl_3$	K_2CO_3	DCE	12	0
12	AgOTf	K_2CO_3	CH_3CN	12	0
13	AgOTf	K_2CO_3	THF	12	0
14	AgOTf	K_2CO_3	toluene	12	15
15	AgOTf	K_2CO_3	DMF[d]	12	0
16	AgOTf	K_2CO_3	DCM	4	80
17	AgOTf	Cs_2CO_3	DCE	4	40
18	AgOTf	Na_2CO_3	DCE	4	45
19	AgOTf	$KHCO_3$	DCE	4	72
20	AgOTf	KO^tBu	DCE	12	0
21	AgOTf	Et_3N	DCE	12	16
22	AgOTf	DIPEA	DCE	12	20
23	AgOTf	DABCO	DCE	12	0
24	AgOTf	DBU	DCE	12	0
25[e]	AgOTf	K_2CO_3	DCE	2.5	75
26[f]	AgOTf	K_2CO_3	DCE	6	56

[a] All the reactions were carried out with hydrazone **1a** (120.4 mg, 0.39 mmol, 1.3 equiv), ynamide **2a** (85.6 mg, 0.3 mmol, 1.0 equiv), Base (2.0 equiv) with catalyst (0.2 equiv) in the indicated solvent (0.5 mL), unless otherwise noted.
[b] Yield of isolated product **3aa**; The amide **4** of less than 10% were observed for all of reactions.
[c] 4 Å MS (30 mg) was added.
[d] Dry DMF was used.
[e] At 60 °C.
[f] At 25 °C.

amino alkenyl-substituted hydrazone **3ja** can be provided in 70% yield. The structure of **3ja** was also confirmed by X-ray crystal analysis (Fig. 1, left part), indicating the *syn*-addition of hydrozone**1j** to ynamide **2a** to afford the *E*-type product. [24] The use of NOESY ^{1}H NMR data (**3ja**) allowed for further confirmation of the assigned alkenyl-hydrozone geometry (Fig. 1, right part). The configurations of alkene unit of other products (Table 2) were tentatively assigned by analogy with that of **3ja**.

The proposed mechanism for silver-catalyzed synthesis of **3aa** is outlined in Scheme 3 [13,21]. On the one hand, the base-mediated deprotonation of sulfonyl hydrazone **1a** can afford anion **A** (or expressed as the resonance structure **A′**). On the other hand, the coordination of alkyne motif of **2a** to silver cation can form complex **B** which is in equilibrium with the reactive keteniminium ion intermediate **C**. Subsequently, the addition of nitrogen anion **A** to **C** and the protodemetalation afford the desired α-amino alkenyl-substituted hydrazone **3aa**. Notably, the formation of neither diazo nor silver carbene intermediates were observed, presumably because the highly reactive ynamides can rapidly capture the nitrogen anion **A**, thus preventing the further transformation of **A** to diazo intermediate (*via* **A′**). The addition of **A** to keteniminium **C** prefers the orientation **a** rather than the orientation **b** due to the greater steric effect of phenyl relative to [Ag], and thus leads to the formation of *syn*-adduct **3aa** (Scheme 3).

3. Conclusion

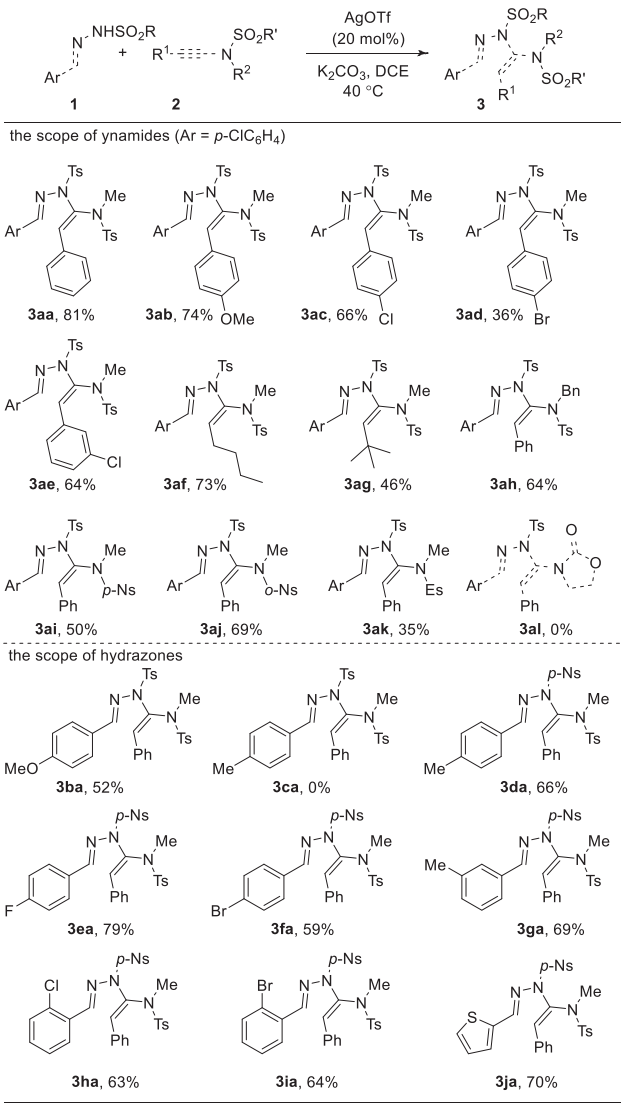
In summary, we have developed a silver-catalyzed stereoselective addition reaction of sulfonyl hydrazones with ynamides to prepare functionalized α-amino alkenyl-substituted hydrazone products in good yields. Compared with the previously-reported reactions of hydrazones with alkynes, the present reaction proceeds without the generation of diazo intermediate or silver carbene. This reaction was proposed to involve the silver-mediated generation of keteniminium intermediate and base-promoted formation of hydrazone anion, which may be often ignored as basic processes towards for the N−H functionalization of hydrazones. Further works will focus on the investigation of detailed mechanism and the bioactivity studies of these sulfonamide products.

4. Experimental section

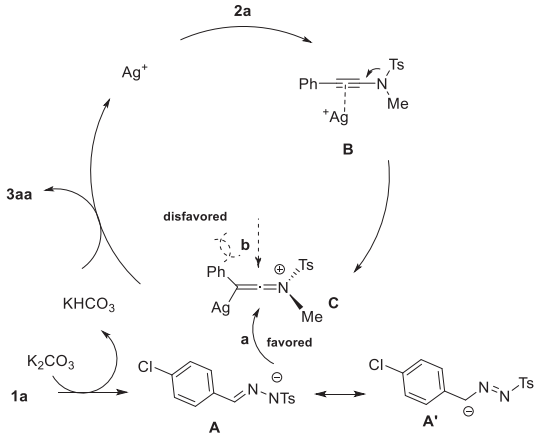
4.1. General methods

All reactions were carried out under air atmosphere, unless otherwise indicated. All reagents were purchased from commercial sources and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a *Bruker Avance III HD 500* (500.1 MHz, ^{1}H; 125.8 MHz, ^{13}C) instrument operating at the denoted spectrometer

Table 2
The scope of ynamide **2** and hydrazone **1** substrates[a,b].



frequency given in mega Hertz (MHz) for the specified nucleus. Chemical shifts are given in parts per million (ppm) relative to tetramethylsilane (TMS) as an external standard for ^{1}H and ^{13}C



Scheme 3. The proposed mechanism for the formation of **3aa** by silver catalysis.

NMR spectra and calibrated against the solvent residual peak. Multiplicities are reported as follows: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, or as combination of them. Coupling constants *J* are given in Hertz (Hz). Melting points were measured with an *X-4 microscope apparatus* and were uncorrected. High-resolution mass spectrometry with electrospray ionization (ESI-HRMS) was recorded on a *Bruke P-SIMS-Gly FT-ICR* mass spectrometer.

4.2. General experimental procedure for synthesis of hydrazones ***1a-j***

A round-bottom flask charged with a stirring bar, aldehyde (10 mmol, 1.0 equiv) and sulfonyl hydrazide [25] (10 mmol, 1.0 equiv) in EtOH (10 mL) was placed into a bath oil of 70 °C for 2–3 h. After completion detected by TLC analysis, with cooling, white precipitate was formed, and then filtered and washed by cold alcohol for 3–5 times to afford pure hydrazone product in usually >80% yield.

4.3. General experimental procedure for synthesis of ynamides ***2a-l***

A Schlenk flask charged with a stirring bar, sulfonamide (12 mmol, 1.2 equiv), K_2CO_3 (20 mmol, 2.0 equiv), $CuSO_4{\cdot}5H_2O$ (1.0 mmol, 10 mol%), and 1,10-phenanthroline (2.0 mmol, 20 mol%) was vacuumed and backfilled with N_2, repeatedly for 3 times, and then a solution of alkynyl bromide [26] (10 mmol, 1.0 equiv) in toluene (10 mL, 1 M) was added to the mixture by a syringe. The

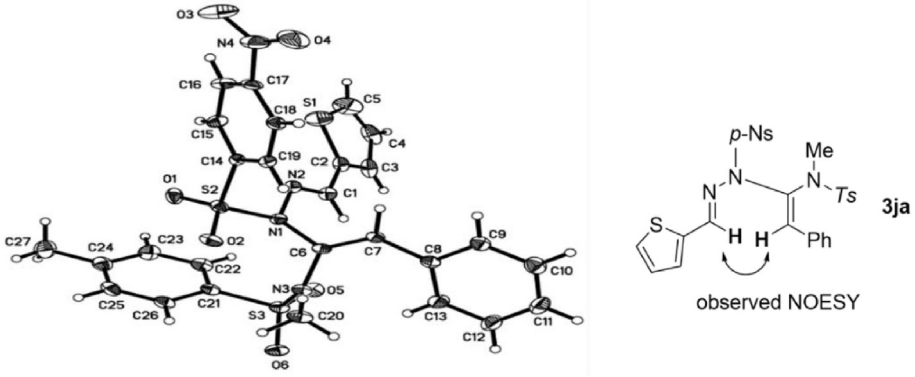


Fig. 1. X-ray structure of product **3ja** (left) and confirmation of geometry through NOESY ^{1}H NMR analysis (right).

resulting mixture was heated to 60 °C for 24–48 h. After completion, the mixture was filtered through celite pad, and the filtrate was concentrated under reduced pressure. The residue was subjected to column chromatography on silica gel (PE/EtOAc = 20/1–5/1) to give the ynamide product.

4.4. Typical experimental procedure for synthesis of *3aa*

An oven-dried Schlenk tube charged with a magnetic stirred bar, sulfonyl hydrazones **1a** (120.4 mg, 0.39 mmol, 1.3 equiv), ynamide **2a** (85.6 mg, 0.3 mmol, 1.0 equiv), K_2CO_3 (82.8 mg, 0.6 mmol, 2.0 equiv) and AgOTf (15.4 mg, 0.06 mmol, 0.2 equiv) was sealed with a stopper, then vacuumed and filled with N_2 repeatedly for three times. Subsequently, DCE (0.5 mL) was added by a syringe, followed by the mixture was stirred and placed into a preheated oil bath of 40 °C for about 4 h after the completion, the resulting mixture was quenched with water (2 mL), and extracted with DCM (5 mL) for three times. The combined organic phase was washed with brine and dried over anhydrous $MgSO_4$. After the filtration of desiccant, the solution was condensed by a rotary evaporator. The residue was suffered to column chromatography to give the addition product **3aa**.

4.5. Analytical data for all new compounds [27]

(E)-N'-(4-methylbenzylidene)-4-nitrobenzenesulfonohydrazide (**1d**): yellow solid, m.p. 147.4–148.2 °C, yield 83%; R_f = 0.60 (PE/EtOAc = 3/1); **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 11.76 (b, 1H), 8.43 (ddd, *J* = 9.0, 2.4, 2.0 Hz, 2H), 8.13 (ddd, *J* = 9.0, 2.1, 2.0 Hz, 2H), 7.92 (s, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR** (DMSO-d_6, *125*.8 Hz): δ 149.9, 148.4, 144.3, 140.2, 130.7, 129.4, 128.8, 126.9, 124.6, 21.0. **HRMS** (ESI) *m*/*z* calcd for $C_{14}H_{14}N_3O_4S$ (M + H)$^+$ 320.0700, found 320.0698.

(E)-N'-(4-fluorobenzylidene)-4-nitrobenzenesulfonohydrazide (**1e**): yellow solid, m.p. 149.5–150.4 °C, yield 87%; R_f = 0.21 (PE/EtOAc = 3/1); **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 11.87 (b, 1H), 8.43 (ddd, *J* = 8.9, 2.5, 2.0 Hz, 2H), 8.14 (ddd, *J* = 9.0, 2.4, 2.0 Hz, 2H), 7.97 (s, 1H), 7.69-7.59 (m, 2H), 7.23 (dd, *J* = 8.9, 8.9 Hz, 2H); **^{13}C NMR** (DMSO-d_6, *125*.8 MHz): δ 163.2 (d, *J* = 248.2 Hz), 150.0, 147.2, 144.2, 130.0 (d, *J* = 3.2 Hz), 129.2 (d, *J* = 8.5 Hz), 128.8, 124.6, 115.9 (d, *J* = 21.9 Hz). **HRMS** (ESI) *m*/*z* calcd for $C_{13}H_{11}FN_3O_4S$ (M + H)$^+$ 324.0449, found 324.0445.

(E)-N'-(4-bromobenzylidene)-4-nitrobenzenesulfonohydrazide (**1f**): yellow solid, m.p. 181.3–182.1 °C, yield 83%; R_f = 0.22 (PE/EtOAc = 3/1); **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 11.96 (b, 1H), 8.42 (d, *J* = 8.9 Hz, 2H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.95 (s, 1H), 7.63-7.56 (m, 2H), 7.53 (d, *J* = 8.6 Hz, 2H); **^{13}C NMR** (DMSO-d_6, *125*.8 MHz): δ 150.0, 147.1, 144.2, 132.6, 131.8, 128.8, 124.6, 123.6. **HRMS** (ESI) *m*/*z* calcd for $C_{13}H_{11}BrN_3O_4S$ (M + H)$^+$ 383.9648, found 383.9653.

(E)-N'-(3-methylbenzylidene)-4-nitrobenzenesulfonohydrazide (**1g**): yellow solid, m.p. 147.9–148.5 °C, yield 85%; R_f = 0.14 (PE/EtOAc = 5/1); **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 11.84 (b, 1H), 8.43 (d, *J* = 8.8 Hz, 2H), 8.14 (d, *J* = 8.9 Hz, 2H), 7.93 (s, 1H), 7.38 (s, 1H), 7.37 (d, *J* = 7.8 Hz, 1H), 7.27 (dd, *J* = 7.6, 7.6 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR** (DMSO-d_6, *125*.8 MHz): δ 149.9, 148.4, 144.3, 138.1, 133.3, 131.1, 128.8, 128.7, 127.3, 124.6, 124.2, 20.8. **HRMS** (ESI) *m*/*z* calcd for $C_{14}H_{14}N_3O_4S$ (M + H)$^+$ 320.0700, found 320.0695.

(E)-N'-(2-chlorobenzylidene)-4-nitrobenzenesulfonohydrazide (**1h**): yellow solid, m.p. 166.6–167.2 °C, yield 90%; R_f = 0.23 (PE/EtOAc = 5/1); **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 12.17 (b, 1H), 8.43 (ddd, *J* = 8.9, 2.4, 1.9 Hz, 2H), 8.30 (s, 1H), 8.14 (ddd, *J* = 8.9, 2.4, 1.8 Hz, 2H), 7.78 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.47 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.42 (ddd, *J* = 7.9, 7.3, 1.7 Hz, 1H), 7.37 (dd, *J* = 7.6, 7.5 Hz, 1H); **^{13}C NMR** (DMSO-d_6, *125*.8 MHz): δ 150.0, 144.1, 143.9, 133.0, 131.8, 130.5, 129.9, 128.8, 127.7, 126.7, 124.7. **HRMS** (ESI) *m*/*z* calcd for $C_{13}H_{11}ClN_3O_4S$ (M + H) 340.0153, found340.0157.

(E)-N'-(2-bromobenzylidene)-4-nitrobenzenesulfonohydrazide (**1i**): Yellow solid, m.p. 180.1–180.9 °C, yield 85%; R_f = 0.19 (PE/EtOAc = 5/1); **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 12.18 (b, 1H), 8.44 (ddd, *J* = 9.0, 2.4, 2.0 Hz, 2H), 8.26 (s, 1H), 8.14 (ddd, *J* = 8.9, 2.4, 2.0 Hz, 2H), 7.76 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.41 (dd, *J* = 7.5, 7.2 Hz, 1H), 7.34 (ddd, *J* = 7.9, 7.5, 1.8 Hz, 1H); **^{13}C NMR** (DMSO-d_6, *125*.8 MHz): δ 150.0, 146.2, 144.1, 133.1, 132.1, 132.0, 128.8, 128.2, 127.1, 124.7, 123.3. **HRMS** (ESI) *m*/*z* calcd for $C_{13}H_{11}BrN_3O_4S$ (M + H)$^+$ 383.9648, found 383.9651.

(E)-4-Nitro-N'-(thiophen-2-ylmethylene)benzenesulfonohydrazide (**1j**): yellow solid, m.p. 152.1–153.0 °C, yield 92%; R_f = 0.17 (PE/EtOAc = 5/1); **^{1}H NMR** (DMSO-d_6, 500 MHz): δ 11.80 (b, 1H), 8.44 (ddd, *J* = 9.0, 2.4, 2.1 Hz, 2H), 8.14 (s, 1H), 8.09 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 5.0 Hz, 1H), 7.39 (dd, *J* = 3.6, 1.0 Hz, 1H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 1H); **^{13}C NMR** (DMSO-d_6, *125*.8 MHz): δ 150.0, 144.1, 143.5, 137.8, 131.3, 129.1, 128.8, 127.9, 124.6. **HRMS** (ESI) *m*/*z* calcd for $C_{11}H_{10}N_3O_4S_2$ (M + H)$^+$ 312.0107, found 312.0104.

N-methyl-N-(phenylethynyl)ethanesulfonamide (**2k**): white solid, m.p. 59.8–60.5 °C, yield 51%; R_f = 0.38 (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 7.40-7.35 (m, 2H), 7.30-7.23 (m, 3H), 3.33-3.27 (m, 5H), 1.44 (t, *J* = 6.7 Hz, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 131.3, 128.2, 127.9, 122.5, 83.3, 69.0, 45.6, 39.4, 7.9. **HRMS** (ESI) *m*/*z* calcd for $C_{11}H_{14}NO_2S$ (M + H)$^+$ 224.0740, found 224.0735.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-2-phenylvinyl)-N,4-dimethylbenzenesulfonamide (**3aa**): white solid, m.p. 88.3–89.1 °C, yield 144.2 mg, 80.9%; R_f = 0.58 (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.41 (s, 1H), 7.82 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.5 Hz, 2H), 7.43-7.39 (m, 4H), 7.38-7.30 (m, 7H), 5.34 (s, 1H), 3.07 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 148.2, 144.8, 144.0, 136.2, 135.5, 135.0, 132.5, 132.3, 132.0.129.6, 129.3, 129.2, 128.94, 128.93, 128.88, 128.6, 128.0, 127.6, 37.0, 21.71, 21.67. **HRMS** (ESI) *m*/*z* calcd for $C_{30}H_{29}ClN_3O_4S_2$ (M + H)$^+$ 594.1283, found 594.1286.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-2-(4-methoxyphenyl)vinyl)-N,4-dimethylbenzenesulfonamide (**3 ab**): white solid, m.p. 110.1–112.2 °C, yield 137.8 mg, 73.6%; R_f = 0.49 (PE/EtOAc = 3/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.39 (s, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 7.38-7.29 (m, 6H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.33 (s, 1H), 3.84 (s, 3H), 3.11 (s, 3H), 2.46 (s, 3H), 2.43 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 160.4, 147.4, 144.7, 143.9, 136.1, 135.5, 132.6, 132.2, 130.3, 129.6, 129.24, 129.17, 128.90, 128.86, 128.3, 127.9, 124.4, 114.4, 55.4, 36.8, 21.69, 21.65. **HRMS** (ESI) *m*/*z* calcd for $C_{31}H_{31}ClN_3O_5S_2$ (M + H)$^+$ 624.1388, found 624.1385.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-2-(4-chlorophenyl)vinyl)-N,4-dimethylbenzenesulfonamide (**3ac**): white solid, m.p. 92.6–93.2 °C, yield 124.5 mg, 66.1%; R_f = 0.57 (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.30 (s, 1H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.65 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 2H), 7.30-7.19 (m, 8H), 7.16 (s, 2H), 5.23 (s, 1H), 2.96 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 148.6, 144.9, 144.2, 136.4, 135.5, 135.3, 135.1, 132.4, 132.3, 130.6, 129.8, 129.6, 129.29, 129.23, 129.18, 129.0, 128.9, 128.0, 126.4, 36.9, 21.71, 21.67. **HRMS** (ESI) *m*/*z* calcd for $C_{30}H_{28}Cl_2N_3O_4S_2$ (M + H)$^+$ 628.0893, found 628.0894.

N-((E)-2-(4-bromophenyl)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)vinyl)-N,4-dimethylbenzenesulfonamide (**3ad**): white solid, m.p. 103.5–104.7 °C, yield 145.2 mg, 72.0%; R_f = 0.38 (PE/EtOAc = 10/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.40 (s, 1H), 7.79 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.39-7.31 (m, 6H), 7.29 (d, *J* = 8.4 Hz, 2H), 5.31 (s, 1H), 3.06 (s, 3H), 2.46 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 148.6, 144.9, 144.2, 136.4, 135.7, 135.3, 132.4, 132.2, 132.1, 131.0, 130.0, 129.6, 129.3, 129.2, 129.0, 128.9, 128.0, 126.4, 123.3, 36.9, 21.70, 21.66. **HRMS** (ESI) *m*/*z* calcd for

$C_{30}H_{28}BrClN_3O_4S_2$ $(M + H)^+$ 672.0388, found 672.0385.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-2-(3-chlorophenyl)vinyl)-N,4-dimethylbenzenesulfonamide (**3ae**): white solid, m.p. 78.1–79.0 °C, yield 119.7 mg, 63.5%; $R_f = 0.59$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.40 (s, 1H), 7.81 (d, $J = 8.3$ Hz, 2H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.45 (d, $J = 7.7$ Hz, 1H), 7.39-7.29 (m, 9H), 5.31 (s, 1H), 3.06 (s, 3H), 2.47 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 148.9, 145.0, 144.2, 136.5, 136.4, 135.2, 134.8, 134.0, 132.3, 132.2, 130.3, 129.7, 129.3, 129.2, 129.1, 129.0, 128.9, 128.6, 128.0, 126.3, 125.8, 37.0, 21.71, 21.67. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{28}Cl_2N_3O_4S_2$ $(M + H)^+$ 628.0893, found 628.0898.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)hex-1-en-1-yl*)-N,4-dimethylbenzenesulfonamide* (**3af**): white solid, m.p. 72.4–73.1 °C, yield 125.1 mg, 72.6%; $R_f = 0.51$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.23 (s, 1H), 7.74 (d, $J = 8.3$ Hz, 2H), 7.66 (d, $J = 8.3$ Hz, 2H), 7.58 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 8.5$ Hz, 2H), 7.28 (d, $J = 8.2$ Hz, 2H), 7.23 (d, $J = 8.2$ Hz, 2H), 5.04 (t, $J = 7.5$ Hz, 1H), 3.18 (s, 3H), 2.42 (s, 3H), 2.39 (s, 3H), 2.32 (q, $J = 7.2$ Hz, 2H), 1.42-1.30 (m, 4H), 0.92 (t, $J = 7.1$ Hz, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 146.3, 144.4, 143.8, 136.9, 136.0, 135.7, 133.5, 132.5, 129.6, 129.3, 128.9, 128.8, 128.7, 127.6, 37.5, 30.3, 27.8, 22.4, 21.6, 21.5, 13.8. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{33}ClN_3O_4S_2$ $(M + H)^+$ 574.1596, found 574.1593.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-3,3-dimethylbut-1-en-1-yl*)-N,4-dimethylbenzenesulfonamide* (**3 ag**): white solid, m.p. 127.5–128.3 °C, yield 78.9 mg, 45.8%; $R_f = 0.51$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.27 (s, 1H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.61 (d, $J = 8.2$ Hz, 2H), 7.60 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.5$ Hz, 2H), 7.26 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 4.73 (s, 1H), 3.24 (s, 3H), 2.41 (s, 3H), 2.39 (s, 3H), 1.19 (s, 9H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 146.9, 145.9, 144.4, 143.7, 136.0, 135.2, 133.0, 132.6, 130.4, 129.5, 129.2, 128.97, 128.96, 128.7, 127.6, 40.1, 33.9, 29.1, 21.62, 21.56. **HRMS** (ESI) *m/z* calcd for $C_{28}H_{33}ClN_3O_4S_2$ $(M + H)^+$ 574.1596, found 574.1599.

N-benzyl-N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-2-phenylvinyl)-4-methylbenzenesulfonamide (**3ah**): white solid, m.p. 107.6–109.1 °C, yield 128.1 mg, 63.7%; $R_f = 0.35$ (PE/EtOAc = 10/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.38 (s, 1H), 7.87 (d, $J = 8.2$ Hz, 2H), 7.58 (d, $J = 8.5$ Hz, 2H), 7.42 (d, $J = 8.3$ Hz, 2H), 7.39-7.33 (m, 8H), 7.30-7.27 (m, 3H), 7.09 (d, $J = 8.1$ Hz, 2H), 7.06 (d, $J = 7.4$ Hz, 1H), 7.00 (dd, $J = 7.6$, 7.2 Hz, 2H), 5.83 (s, 1H), 4.62 (s, 2H), 2.47 (s, 3H), 2.36 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 146.8, 144.8, 143.4, 137.1, 136.1, 134.1, 133.8, 133.2, 132.5, 132.3, 131.8, 130.9, 129.3, 129.2, 129.1, 128.89, 128.85, 128.81, 128.5, 127.7, 127.6, 127.5, 54.5, 21.7, 21.5. **HRMS** (ESI) *m/z* calcd for $C_{36}H_{33}ClN_3O_4S_2$ $(M + H)^+$ 670.1596, found 670.1594.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-2-phenylvinyl)-N-methyl-4-nitrobenzenesulfonamide (**3ai**): white solid, m.p. 77.1–78.0 °C, yield 85.8 mg, 49.8%; $R_f = 0.61$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.40-8.36 (m, 3H), 8.08 (ddd, $J = 8.9$, 2.3, 2.0 Hz, 2H), 7.73 (d, $J = 8.3$ Hz, 2H), 7.64 (d, $J = 8.6$ Hz, 2H), 7.46-7.32 (m, 9H), 5.36 (s, 1H), 3.16 (s, 3H), 2.47 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 150.4, 148.2, 145.3, 144.1, 136.6, 134.2, 132.2, 131.8, 131.6, 129.6, 129.4, 129.19, 129.17, 129.1, 129.02, 128.98, 128.5, 127.7, 124.3, 37.4, 21.7. **HRMS** (ESI) *m/z* calcd for $C_{31}H_{32}N_3O_4S_2$ $(M + H)^+$ 574.1829, found 574.1833.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-2-phenylvinyl)-N-methyl-2-nitrobenzenesulfonamide (**3aj**): white solid, m.p. 116.4–117.8 °C, yield 128.9 mg, 68.7%; $R_f = 0.49$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.36 (s, 1H), 8.21 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.82 (d, $J = 8.3$ Hz, 2H), 7.78-7.68 (m, 2H), 7.65 (dd, $J = 7.8$, 1.7 Hz, 1H), 7.60 (d, $J = 8.6$ Hz, 2H), 7.43-7.32 (m, 9H), 5.44 (s, 1H), 3.25 (s, 3H), 2.48 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 148.71, 148.68, 145.2, 136.5, 134.2, 133.9, 132.3, 132.2, 132.1, 131.9, 131.5, 131.0, 129.7, 129.4, 129.3, 129.05, 128.98, 128.94, 128.6, 128.5, 123.9, 37.5, 21.7. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{26}ClN_4O_6S_2$ $(M + H)^+$ 625.0977, found 625.0975.

N-((E)-1-(2-((E)-4-chlorobenzylidene)-1-tosylhydrazinyl)-2-phenylvinyl)-N-methylethanesulfonamide (**3ak**): white solid, m.p. 79.4–80.3 °C, yield 55.6 mg, 34.8%; $R_f = 0.63$ (PE/EtOAc = 3/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.32 (s, 1H), 7.90 (d, $J = 8.3$ Hz, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.37 (d, $J = 7.3$ Hz, 2H), 7.36-7.30 (m, 5H), 5.28 (s, 1H), 3.40 (q, $J = 7.45$ Hz, 2H), 3.14 (s, 3H), 2.50 (s, 3H), 1.51 (t, $J = 7.45$ Hz, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 149.2, 145.2, 136.4, 135.5, 132.3, 132.0, 131.8, 129.4, 129.2, 129.0, 128.92, 128.89, 128.4, 126.3, 48.5, 37.3, 21.8, 7.7. **HRMS** (ESI) *m/z* calcd for $C_{25}H_{27}ClN_3O_4S_2$ $(M + H)^+$ 532.1126, found 532.1125.

N-((E)-1-(2-((E)-4-methoxybenzylidene)-1-tosylhydrazinyl)-2-phenylvinyl)-N,4-dimethylbenzenesulfonamide (**3ba**): white solid, m.p. 112.1–112.7 °C, yield 119.2 mg, 67.3%; $R_f = 0.41$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.46 (s, 1H), 7.84 (d, $J = 8.3$ Hz, 2H), 7.77 (d, $J = 8.3$ Hz, 2H), 7.64 (d, $J = 8.8$ Hz, 2H), 7.42-7.32 (m, 9H), 6.90 (d, $J = 8.8$ Hz, 2H), 5.32 (s, 1H), 3.83 (s, 3H), 3.08 (s, 3H), 2.46 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 161.5, 150.7, 144.6, 143.9, 135.9, 135.7, 132.3, 132.1, 129.6, 129.5, 129.4, 129.1, 129.0, 128.9, 128.5, 128.1, 127.0, 126.7, 114.0, 55.4, 37.0, 21.69, 21.67. **HRMS** (ESI) *m/z* calcd for $C_{31}H_{32}N_3O_5S_2$ $(M + H)^+$ 590.1778, found 590.1775.

N,4-dimethyl-N-((E)-1-(2-((E)-4-methylbenzylidene)-1-((4-nitrophenyl)sulfonyl)hydrazinyl)-2-phenylvinyl)benzenesulfonamide (**3da**): yellow solid, m.p. 108.9–110.2 °C, yield 119.5 mg, 65.8%; $R_f = 0.75$ (PE/EtOAc = 3/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.50 (s, 1H), 8.38 (d, $J = 8.8$ Hz, 2H), 8.08 (d, $J = 8.8$ Hz, 2H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 8.0$ Hz, 2H), 7.46-7.35 (m, 5H), 7.33 (d, $J = 8.1$ Hz, 2H), 7.21 (d, $J = 7.9$ Hz, 2H), 5.46 (s, 1H), 3.11 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 151.4, 150.6, 144.2, 141.4, 141.1, 135.6, 134.3, 131.7, 130.6, 130.5, 129.7, 129.6, 129.5, 129.0, 128.6, 128.1, 127.89, 127.87, 123.7, 37.0, 21.6, 21.5. **HRMS** (ESI) *m/z* calcd for $C_{30}H_{29}N_4O_6S_2$ $(M + H)^+$ 605.1523, found 605.1527.

N-((E)-1-(2-((E)-4-fluorobenzylidene)-1-((4-nitrophenyl)sulfonyl)hydrazinyl)-2-phenylvinyl)-N,4-dimethylbenzenesulfonamide (**3ea**): yellow solid, m.p. 127.7–128.4 °C, yield 143.6 mg, 78.6%; $R_f = 0.40$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.49 (s, 1H), 8.40 (d, $J = 8.8$ Hz, 2H), 8.08 (d, $J = 8.7$ Hz, 2H), 7.78 (d, $J = 8.3$ Hz, 2H), 7.71-7.64 (m, 2H), 7.47-7.35 (m, 5H), 7.33 (d, $J = 8.2$ Hz, 1H), 7.10 (dd, $J = 8.6$, 8.6 Hz, 3H), 5.48 (s, 1H), 3.11 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 164.3 (d, $J = 252.2$ Hz), 150.6, 149.8, 144.3, 141.1, 135.5, 134.0, 131.5, 130.4, 129.8 (d, $J = 8.9$ Hz), 129.7, 129.6 (d, $J = 3.3$ Hz), 129.1, 128.7, 128.4, 127.9, 123.8, 116.0 (d, $J = 22.2$ Hz), 115.9, 37.0, 21.6. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{26}FN_4O_6S_2$ $(M + H)^+$ 609.1272, found 609.1278.

N-((E)-1-(2-((E)-4-bromobenzylidene)-1-((4-nitrophenyl)sulfonyl)hydrazinyl)-2-phenylvinyl)-N,4-dimethylbenzenesulfonamide (**3fa**): yellow solid, m.p. 122.7–123.5 °C, yield 118.2 mg, 58.9%; $R_f = 0.47$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.44 (s, 1H), 8.40 (ddd, $J = 8.9$, 2.2, 1.8 Hz, 2H), 8.07 (ddd, $J = 8.9$, 2.2, 1.9 Hz, 2H), 7.76 (d, $J = 8.3$ Hz, 2H), 7.54 (b, 4H), 7.47-7.35 (m, 5H), 7.33 (d, $J = 8.2$ Hz, 2H), 5.49 (s, 1H), 3.10 (s, 3H), 2.45 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 150.7, 149.2, 144.3, 141.2, 135.4, 133.6, 132.3, 132.1, 131.5, 130.3, 129.8, 129.7, 129.2, 129.1, 128.70, 128.65, 127.8, 125.2, 123.8, 37.0, 21.7. **HRMS** (ESI) *m/z* calcd for $C_{29}H_{26}BrN_4O_6S_2$ $(M + H)^+$ 669.0472, found 669.0475.

N,4-dimethyl-N-((E)-1-(2-((E)-3-methylbenzylidene)-1-((4-nitrophenyl)sulfonyl)hydrazinyl)-2-phenylvinyl)benzenesulfonamide (**3ga**): yellow solid, m.p. 145.3–146.2 °C, yield 124.7 mg, 68.7%; $R_f = 0.55$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.49 (s, 1H), 8.39 (ddd, $J = 8.9$, 2.2, 1.8 Hz, 2H), 8.09 (ddd, $J = 8.8$, 2.2, 1.9 Hz, 2H), 7.79 (d, $J = 8.3$ Hz, 2H), 7.50 (d, $J = 7.7$ Hz, 1H), 7.47 (s, 1H), 7.45-7.39 (m, 4H), 7.39-7.34 (m, 1H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.30 (dd,

$J = 7.7$, 7.6 Hz, 1H), 7.23 (d, $J = 7.6$ Hz, 1H), 5.46 (s, 1H), 3.12 (s, 3H), 2.45 (s, 3H), 2.38 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 151.3, 150.6, 144.2, 141.2, 138.5, 135.6, 134.1, 133.3, 131.7, 131.6, 130.4, 129.7, 129.6, 129.1, 128.8, 128.69, 128.65, 128.3.127.9, 124.9, 123.7, 37.1, 21.7, 21.3. **HRMS** (ESI) *m*/*z* calcd for $C_{30}H_{29}N_4O_6S_2$ $(M + H)^+$ 605.1523, found 605.1525.

N-((E)-1-(2-((E)-2-chlorobenzylidene)-1-((4-nitrophenyl)sulfonyl)hydrazinyl)-2-phenylvinyl)-N,4-dimethylbenzenesulfonamide (**3ha**): yellow solid, m.p. 123.8–124.6 °C, yield 117.8 mg, 62.8%; $R_f = 0.43$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 M Hz): δ 8.91 (s, 1H), 8.40 (ddd, $J = 8.9$, 2.1, 1.9 Hz, 2H), 8.11 (d, $J = 8.9$ Hz, 2H), 7.95-7.89 (m, 1H), 7.77 (d, $J = 8.3$ Hz, 2H), 7.41-7.38 (m, 4H), 7.38-7.30 (m, 7H), 5.62 (s, 1H), 3.09 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 150.6, 147.0, 144.2, 141.4, 135.6, 135.2, 133.5, 131.6, 131.1, 130.4, 130.1, 129.7, 129.6, 129.1, 128.9, 128.6, 127.8, 127.3, 127.0, 123.8, 37.2, 21.6. **HRMS** (ESI) *m*/*z* calcd for $C_{29}H_{26}ClN_4O_6S_2$ $(M + H)^+$ 625.0977, found 625.0980.

N-((E)-1-(2-((E)-2-bromobenzylidene)-1-((4-nitrophenyl)sulfonyl)hydrazinyl)-2-phenylvinyl)-N,4-dimethylbenzenesulfonamide (**3ia**): yellow solid, m.p. 81.2–82.5 °C, yield 127.8 mg, 63.7%; $R_f = 0.46$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.89 (s, 1H), 8.39 (d, $J = 8.8$ Hz, 2H), 8.10 (d, $J = 8.9$ Hz, 2H), 7.91 (dd, $J = 7.9$, 1.6 Hz, 1H), 7.78 (d, $J = 6.1$ Hz, 2H), 7.54 (dd, $J = 8.0$, 0.8 Hz, 1H), 7.43-7.35 (m, 6H), 7.33 (d, $J = 8.2$ Hz, 2H), 7.28-7.21 (m, 1H), 5.62 (s, 1H), 3.09 (s, 3H), 2.44 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 150.6, 149.4, 144.2, 141.4, 135.6, 133.5, 133.3, 132.6, 131.8, 131.6, 130.4, 129.7, 129.6, 129.0, 128.9, 128.5, 127.8, 127.61, 127.59, 125.2, 123.8, 37.2, 21.6. **HRMS** (ESI) *m*/*z* calcd for $C_{29}H_{26}BrN_4O_6S_2$ $(M + H)^+$ 669.0472, found 668.0474.

N,4-dimethyl-N-((E)-1-(1-((4-nitrophenyl)sulfonyl)-2-((E)-thiophen-2-ylmethylene)hydrazinyl)-2-phenylvinyl)benzenesulfonamide (**3ja**): yellow solid, m.p. 140.6–141.5 °C, yield 124.5 mg, 69.5%; $R_f = 0.48$ (PE/EtOAc = 5/1); **^{1}H NMR** ($CDCl_3$, 500 MHz): δ 8.65 (s, 1H), 8.40 (dd, $J = 7.1$, 1.8 Hz, 2H), 8.09 (dd, $J = 7.1$, 1.9 Hz, 2H), 7.81 (d, $J = 8.4$ Hz, 2H), 7.46-7.38 (m, 5H), 7.39-7.31 (m, 3H), 7.28 (dd, $J = 3.6$, 0.7 Hz, 1H), 7.04 (dd, $J = 5.0$, 3.7 Hz, 1H), 5.46 (s, 1H), 3.09 (s, 3H), 2.46 (s, 3H); **^{13}C NMR** ($CDCl_3$, *125*.8 MHz): δ 150.7, 145.9, 144.3, 140.8, 138.4, 135.5, 134.7, 132.7, 131.9, 131.6, 130.7, 129.7, 129.6, 129.2, 129.1, 128.6, 127.9, 127.8, 123.6, 36.9, 21.7. **HRMS** (ESI) *m*/*z* calcd for $C_{27}H_{25}N_4O_6S_3$ $(M + H)^+$ 597.0931, found 597.0936.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.130534.

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