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DABCO-Promoted Unexpected Regioselective Ring Opening and Stereoselective Addition Reactions of Sulfonylaziridines with Cyanoacetylenes: Access to Functionalized Enenitriles

Ling-Guo Meng[a] and Lei Wang[a,b,*]

[a] Department of Chemistry, Huaibei Normal University, Huaibei, Anhui 235000, People's Republic of China
Fax: (+86)-561-309-0518; phone: (+86)-561-380-2069; e-mail: leiwang@chnu.edu.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Shanghai 200032, People's Republic of China

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Abstract: A highly regioselective ring opening and stereoselective addition reaction of sulfonylaziridines with cyanoacetylenes promoted by 1,4-diazabicyclo-[2.2.2]octane (DABCO) was investigated. A variety of functionalized (*Z*)-enenitriles could be obtained in good yields through regioselective cleavage of carbon-nitrogen bonds in sulfonylaziridines.

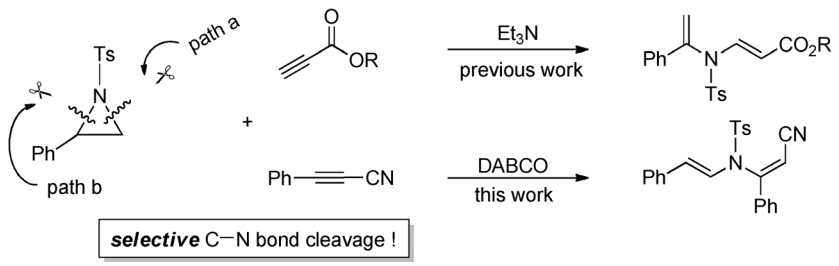
Keywords: cleavage; cyanoacetylenes; DABCO; ring-opening; sulfonylaziridines

Introduction

Aziridines have received increasing attention as important intermediates due to the high strain energy associated with the three-membered ring and have undergone many interesting reactions,[1] such as ring expansion,[2] cyclization,[3] alkylation,[4] substitution,[5] isomerization,[6] *N*-arylation,[7] *N*-acylation and *N*-alkylation,[8] etc. Apart from the above reactions, the ring opening of aziridines has also been studied intensively and applied to prepare a large number of functionalized nitrogen-containing compounds.[9] However, the ring opening pattern in the aziridines is the cleavage of the carbon-nitrogen bond often using transition metals or Lewis acids as catalyst or promoter.[10]

Over the past decade, reactions based on nucleophilic catalysis through conjugate additions of N and P nucleophiles to electron-deficient alkynes have proven to be useful in the construction of multifunctional molecules.[11] In those reactions, attention was frequently paid to the resulting electron-deficient alkynes, such as dialkyl acetylenedicarboxylates, terminal alkynoates, alkynyl ketones, etc.[12] Cyanoacetylenes, easily prepared from bromoalkynes with CuCN,[13] are one class of the important intermediates and versatile building blocks in organic synthesis.[14] However, there are a few reports about the applications of cyanoacetylenes as electron-deficient alkynes to form zwitterionic adducts in the presence of an organic base as catalyst.[15]

Most recently, we reported the Et_3N-promoted tandem ring opening reaction of *N*-tosylaziridines with terminal alkynoates involving C–N bond cleavage to give functionalized enamines (Scheme 1, path a).[16] To the best of our knowledge, there are only



Scheme 1. Regioselective C–N bond cleavage of sulfonylaziridines.

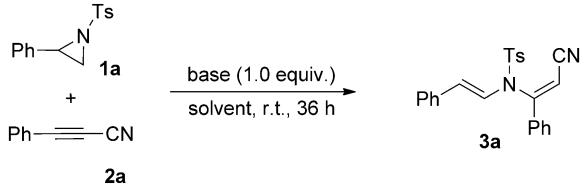
few reports about the C–N bond cleavage in sulfonylaziridines using organic bases as catalyst or promoter.[17] In continuation of our interest in developing C–N bond cleavage reactions, we further investigate the possibility of the reaction between cyanoacetylenes and sulfonylaziridines in the presence of an organic base. To our delight, an unexpected regioselective ring opening and stereoselective addition was observed in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO), through C–N bond cleavage of aziridines in a different way (Scheme 1, path b). The reaction generated functionalized enenitriles, which are the important intermediates in organic synthesis[18] under simple reaction conditions and in good yields. Herein, we wish to report this DABCO-promoted reaction of sulfonylaziridines with cyanoacetylenes.

Results and Discussion

In the initial exploration of the regioselective ring opening and stereoselective addition of sulfonylaziridines with cyanoacetylenes, 2-phenyl-1-tosylaziridine (**1a**) and 3-phenylpropiolonitrile (**2a**) were chosen as model substrates for our investigation and the results are summaried in Table 1. The reaction of **1a** with **2a** in the presence of DABCO (1.0 equiv.) at room temperature for 36 h afforded **3a** as a pale yellow oil in 72% yield (Table 1, entry 1), and it was characterized by ^{1}H and ^{13}C NMR spectroscopy and HR-MS analysis. The amount of DABCO has an obvious effect on this ring opening reaction. When 0.5 equiv. of DABCO was used, the desired product **3a** was isolated in 53% yield, and the yield of **3a** was not improved by further increasing the amount of DABCO (Table 1, entries 2 and 3). The yield of **3a** was not successfully improved when the reaction was conducted at 0 °C or 60 °C, respectively (Table 1, entries 4 and 5). DABCO as a promoter was crucial in the model reaction. No reaction was observed when other tertiary amines, such as DMAP, pyridine, *N*-methylimidazole, Et_3N and DBU, were used instead of DABCO (Table 1, entries 6–10). Meanwhile, no desired product was detected when the reaction was run in the presence of tertiary phosphines (Table 1, entries 11 and 12). On the other hand, when the model reaction was carried out in the presence of DABCO, a significant solvent effect was observed (Table 1, entries 13–18). Among the tested solvents, CH_2Cl_2 was found to be the best one. THF, CH_3CN and toluene were inferior and afforded 18–55% yields of **3a**. When the solvent was switched to $CHCl_3$ or DMF, only a trace amount of **3a** was detected. No desired product was detected when DMSO was used as solvent.

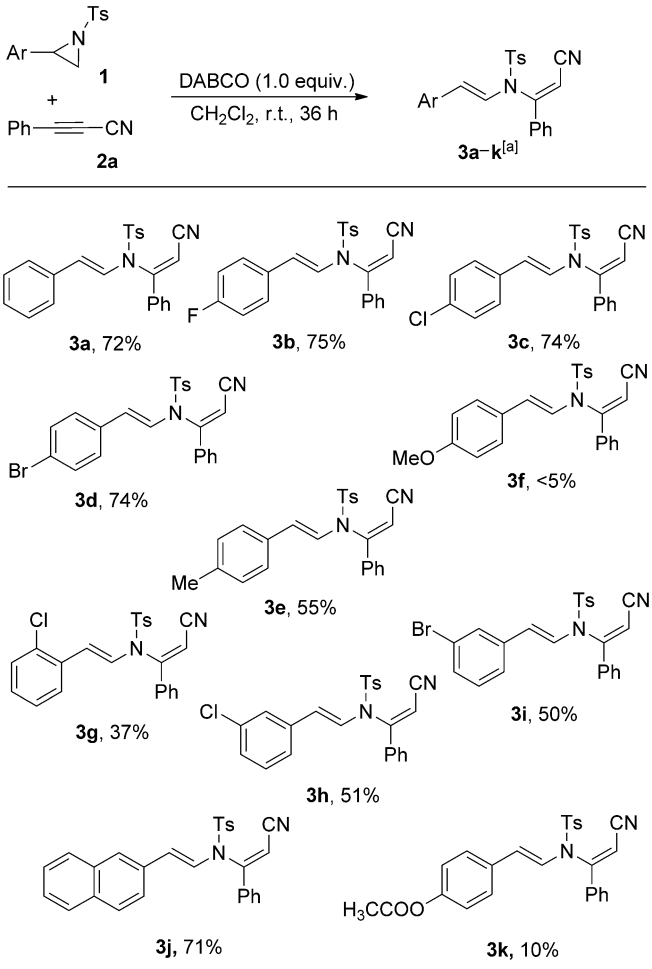
Under the optimized reaction conditions, the reaction scope of aromatic *N*-tosylaziridines was examined. Basically, a variety of aromatic *N*-tosylaziridines could react with 3-phenylpropiolonitrile (**2a**) smoothly to give the desired functionalized enenitriles in moderate to good yields (Scheme 2). Clearly, aromatic *N*-tosylaziridines with an electron-withdrawing group on the aromatic ring gave better yields than those with an electron-donating group on the aromatic ring. For example, **1** with an electron-withdrawing group, such as F, Cl or Br at the *para*-position of benzene ring reacted with **2a**, providing the desired products **3b–d** in good yields. On the other hand, the reaction of substrate **1** with a CH_3 group attached on the benzene ring with **2a** generated the corresponding product **3e** in 55% yield; only a trace amount of the product **3f** was detected when a CH_3O group was on the *para*-position of the benzene ring. The *ortho*-position effect of *N*-tosylaziridines was observed in the reaction of 2-(2-chlorophenyl)-1-tosylaziridine with **2a**. Treatment of 2-(3-chlorophenyl)-, 2-(3-bromophenyl)-, and 2-(naphthalen-2-yl)-1-tosylaziridines with **2a** afforded

Table 1. Ring-opening reaction of 2-phenyl-1-tosylaziridine (**1a**) with 3-phenylpropiolonitrile (**2a**).[a]



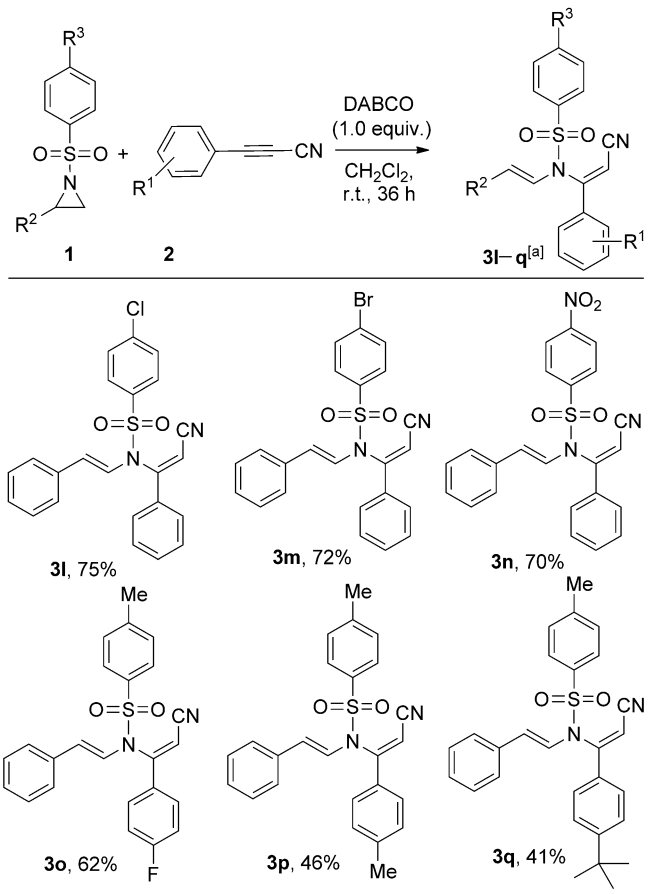
Entry	Solvent	Base	Yield [%][b]
1	CH_2Cl_2	DABCO	72
2	CH_2Cl_2	DABCO	53[c]
3	CH_2Cl_2	DABCO	72[d]
4	CH_2Cl_2	DABCO	30[e]
5	CH_2Cl_2	DABCO	17[f]
6	CH_2Cl_2	DMAP	NR[g]
7	CH_2Cl_2	pyridine	NR[g]
8	CH_2Cl_2	*N*-methylimidazole	NR[g]
9	CH_2Cl_2	Et_3N	NR[g]
10	CH_2Cl_2	DBU	NR[g]
11	CH_2Cl_2	PPh_3	ND[h]
12	CH_2Cl_2	$(n\text{-}Bu)_3P$	ND[h]
13	THF	DABCO	55
14	CH_3CN	DABCO	21
15	toluene	DABCO	18
16	$CHCl_3$	DABCO	<5
17	DMF	DABCO	<5
18	DMSO	DABCO	ND[h]

[a] *Reaction conditions:* **1a** (0.30 mmol), **2a** (0.20 mmol), base (0.20 mmol), solvent (2.0 mL), room temperature, in air, 36 h.
[b] Isolate yields.
[c] DABCO (0.50 equiv.).
[d] DABCO (1.2 equiv.).
[e] At 0 °C.
[f] At 60 °C.
[g] NR = no reaction observed.
[h] ND = no desired product detected.



[a] Isolated yields.

Scheme 2. DABCO-promoted ring-opening reaction of aromatic *N*-tosylaziridines with 3-phenylpropiolonitrile (**2a**). *Reaction conditions:* **1** (0.30 mmol), **2a** (0.20 mmol), DABCO (0.20 mmol), CH_2Cl_2 (2.0 mL), room temperature, in air, 36 h.



[a] Isolated yields.

Scheme 3. DABCO-promoted ring-opening reaction of aziridines with cyanoacetylenes. *Reaction conditions:* aziridine (0.30 mmol), cyanoacetylene (0.20 mmol), DABCO (0.20 mmol), CH_2Cl_2 (2.0 mL), room temperature, in air, 36 h.

the desired products (**3h–j**) in 50–71% yields. 4-(1-Tosylaziridin-2-yl)phenyl acetate also could be converted to the corresponding product **3k**, albeit the yield was so low.

To further evaluate the scope of this reaction, other aziridines and cyanoacetylenes were examined under the optimized reaction conditions. As can be seen from Scheme 3, sulfonylaziridines with other different groups, e.g., 1-(4-chlorophenyl)sulfonyl-, 1-(4-bromophenyl)sulfonyl- and 1-(4-nitrophenyl)sulfonyl-2-phenylaziridines, reacted with **2a** smoothly to generate the desired products (**3l–n**) in 70–75% yields. As expected, other cyanoacetylenes with different functional groups, including F, CH_3, and *t*-Bu groups on the *para*-position of the benzene rings, also gave the desired products (**3o–q**) in 41–62% yields. However, the reactions gave the poor results when 2-methyl-2-phenyl-1-tosylaziridine or 2-butyl-1-tosylaziridine was used as the aziridine substrate.

The structure of compound **3d** was determined as having the *Z*-configuration and this was confirmed unambiguously by single crystal X-ray analysis and the corresponding CIF data were presented in the Supporting Information.[19]

Conclusions

In conclusion, a novel regioselective ring opening and stereoselective addition of sulfonylaziridines with cyanoacetylenes promoted by DABCO has been developed. This reaction has simple conditions and produces functionalized enenitriles in moderate to good yields. Further studies on reactions with electron-deficient alkynes and aziridines catalyzed or promoted by organic bases are currently underway.

Experimental Section

General Remarks

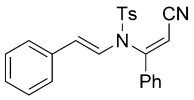
All reactions were conducted in oven-dried glassware with magnetic stirring. Chromatographic purification was performed on silica gel (100~200 mesh) and analytical thin layer chromatography (TLC) on silica gel 60-F_{254} (Qindao), which was detected by fluorescence. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured with a Bruker AC 400 spectrometer with $CDCl_3$ as solvent and recorded in ppm relative to internal tetramethylsilane standard. ^{1}H NMR data are reported as follows: δ, chemical shift; coupling constants (*J* are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectra were obtained with a Micromass GCT-TOF mass spectrometer. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

Typical Procedure for the Regioselective Ring Opening and Stereoselective Addition Reaction of Aziridines with Cyanoacetylenes Promoted by DABCO

To a solution of aziridine (0.30 mmol) with cyanoacetylene (0.20 mmol) in CH_2Cl_2 (2.0 mL) was added DABCO (22.4 mg, 0.20 mmol). The mixture was then stirred at room temperature for 36 h in a reaction flask. Then the solvent was removed under vacuum and residue was purified by column chromatography on silica gel (10:1, petroleum ether/EtOAc) to give the desired product.

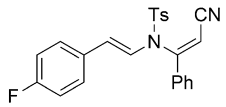
Characterization Data for all Products

***N*-[(*Z*)-2-Cyano-1-phenylvinyl]-4-methyl-*N*-[(*E*)-styryl]benzenesulfonamide (3a):** Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 14.0 Hz, 1H), 7.52–7.45 (m, 3H), 7.39–7.20 (m, 9H), 6.08 (s, 1H),



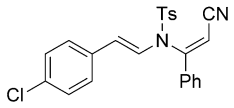
5.89 (d, *J* = 14.0 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 145.1, 135.3, 135.2, 133.6, 131.6, 130.0, 129.0, 128.7, 127.9, 127.2, 127.1, 126.8, 125.7, 114.7, 114.3, 99.8, 21.7; HR-MS (ESI): *m/z* = 423.1142, calcd. for $C_{24}H_{20}N_2O_2SNa$ $(M+Na)^+$: 423.1137.

***N*-[(*Z*)-2-Cyano-1-phenylvinyl]-*N*-[(*E*)-4-fluorostyryl]-4-methylbenzenesulfonamide (3b):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.76 (d, *J* = 8.0 Hz, 2H), 7.51–7.45 (m, 4H), 7.39–7.21 (m, 6H), 6.99 (t, *J* = 8.4 Hz, 2H), 6.07 (s, 1H), 5.88 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR



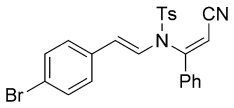
(100 MHz, $CDCl_3$): δ = 163.2 (d, *J* = 245.1 Hz), 154.3, 145.1, 135.2, 133.7, 131.6, 131.5 (d, *J* = 3.3 Hz), 130.0, 129.0, 127.9, 127.3, 127.2, 126.7 (d, *J* = 2.1 Hz), 115.7 (d, *J* = 21.7 Hz), 114.7, 113.3, 99.8, 21.6; HR-MS (ESI): *m/z* = 441.1044, calcd. for $C_{24}H_{19}N_2O_2SFNa$ $(M+Na)^+$: 441.1043.

***N*-[(*E*)-4-Chlorostyryl]-*N*-[(*Z*)-2-cyano-1-phenylvinyl]-4-methylbenzenesulfonamide (3c):** Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 14.4 Hz, 1H), 7.50–7.45 (m, 3H), 7.39–7.17 (m, 8H), 6.08 (s, 1H), 5.83 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR



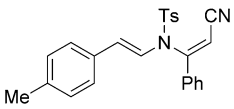
(100 MHz, $CDCl_3$): δ = 154.1, 145.2, 135.1, 133.9, 133.5, 132.5, 131.7, 130.0, 129.1, 128.7, 127.9, 127.3, 127.2, 126.9, 114.6, 112.7, 99.9, 21.6; HR-MS (ESI): *m/z* = 457.0752, calcd. for $C_{24}H_{19}N_2O_2S^{35}ClNa$ $(M+Na)^+$: 457.0748.

***N*-[(*E*)-4-Bromostyryl]-*N*-[(*Z*)-2-cyano-1-phenylvinyl]-4-methylbenzenesulfonamide (3d):** Yellow solid; mp 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.6 Hz, 2H), 7.58 (d, *J* = 14.4 Hz, 1H), 7.50–7.45 (m, 3H), 7.40–7.27



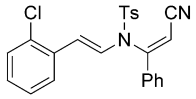
(m, 6H), 7.13 (d, *J* = 7.6 Hz, 2H), 6.08 (s, 1H), 5.80 (d, *J* = 14.4 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.1, 145.3, 135.0, 134.3, 133.5, 131.7, 131.7, 130.1, 129.1, 127.8, 127.4, 127.2, 127.2, 120.6, 114.6, 112.6, 99.9, 21.7; HR-MS (ESI): *m/z* = 501.0243, calcd. for $C_{24}H_{19}N_2O_2S^{79}BrNa$ $(M+Na)^+$: 501.0242.

***N*-[(*Z*)-2-Cyano-1-phenylvinyl]-4-methyl-*N*-[(*E*)-4-methylstyryl]benzenesulfonamide (3e):** Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 2H), 7.48–7.41 (m, 4H), 7.35–7.24 (m, 4H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.08



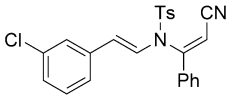
(d, *J* = 8.0 Hz, 2H), 6.02 (s, 1H), 5.87 (d, *J* = 14.4 Hz, 1H), 2.41 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.5, 145.0, 137.0, 135.4, 133.8, 132.4, 131.5, 129.9, 129.3, 129.0, 127.9, 127.3, 126.0, 125.7, 115.0, 114.8, 99.6, 21.6, 21.1; HR-MS (ESI): *m/z* = 437.1299, calcd. for $C_{25}H_{22}N_2O_2SNa$ $(M+Na)^+$: 437.1294.

***N*-[(*E*)-2-Chlorostyryl]-*N*-[(*Z*)-2-cyano-1-phenylvinyl]-4-methylbenzenesulfonamide (3g):** Pale yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.4 Hz, 2H), 7.55–7.45 (m, 5H), 7.39–7.13 (m, 7H), 6.23 (d, *J* = 14.4 Hz, 1H), 6.08 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.3, 145.2, 135.1, 133.8, 133.7, 132.7, 131.6, 130.0, 129.6,



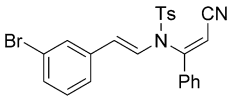
129.0, 128.8, 128.1, 127.9, 127.3, 126.9, 126.2, 114.5, 110.5, 100.0, 21.6; HR-MS (ESI): $m/z = 457.0746$, calcd. for $C_{24}H_{19}N_2O_2S^{35}ClNa$ $(M+Na)^+$: 457.0748.

***N*-[(*E*)-3-Chlorostyryl]-*N*-[(*Z*)-2-cyano-1-phenylvinyl]-4-methylbenzenesulfonamide (3h):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.76$ (d, $J = 8.4$ Hz, 2H), 7.59 (d, $J = 14.4$ Hz, 1H), 7.50–7.45 (m, 3H), 7.39–7.31 (m, 4H), 7.27–



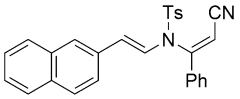
7.12 (m, 4H), 6.09 (s, 1H), 5.80 (d, $J = 14.4$ Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.0$, 145.2, 137.3, 135.1, 134.6, 133.5, 131.7, 130.0, 129.8, 129.1, 127.9, 127.9, 127.1, 126.9, 125.6, 123.8, 114.5, 112.2, 100.0, 21.6; HR-MS (ESI): $m/z = 457.0753$, calcd. for $C_{24}H_{19}N_2O_2S^{35}ClNa$ $(M+Na)^+$: 457.0748.

***N*-[(*E*)-3-Bromostyryl][-*N*-[(*Z*)-2-cyano-1-phenylvinyl]-4-methylbenzenesulfonamide (3i):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$ (d, $J = 8.0$ Hz, 2H), 7.59 (d, $J = 14.4$ Hz, 1H), 7.49–7.45 (m, 3H), 7.40–7.30 (m, 6H), 7.19–



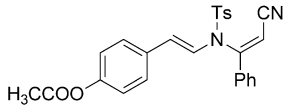
7.12 (m, 2H), 6.09 (s, 1H), 5.79 (d, $J = 14.4$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.9$, 145.2, 137.6, 135.1, 133.4, 131.7, 130.1, 130.0, 129.8, 129.1, 128.6, 127.9, 127.9, 127.1, 124.2, 122.8, 114.5, 112.1, 100.0, 21.6; HR-MS (ESI): $m/z = 501.0247$, calcd. for $C_{24}H_{19}N_2O_2S^{79}BrNa$ $(M+Na)^+$: 501.0242.

***N*-[(*Z*)-2-Cyano-1-phenylvinyl[-4-methyl-*N*-[(*E*)-2-(naphthalen-2-yl)vinyl]benzenesulfonamide (3j):** Yellow solid; mp 55–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.80$–7.75 (m, 5H), 7.74 (d, $J = 14.4$ Hz, 1H), 7.60 (s, 1H), 7.55–7.31 (m,



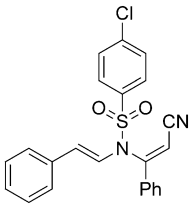
10H), 6.11 (s, 1H), 6.08 (d, $J = 14.4$ Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.3$, 145.1, 135.3, 133.7, 133.6, 132.8, 132.6, 131.6, 130.0, 129.0, 128.3, 127.9, 127.6, 127.3, 127.1, 126.4, 125.7, 125.3, 123.1, 114.7, 114.6, 99.9, 21.6; HR-MS (ESI): $m/z = 473.1300$, calcd. for $C_{28}H_{22}N_2O_2SNa$ $(M+Na)^+$: 473.1294.

4-((*E*)-2-{*N*-[(*Z*)-2-Cyano-1-phenylvinyl]-4-methylphenylsulfonamido}vinyl)-phenyl acetate (3k): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.75$ (d, $J = 8.0$ Hz, 2H), 7.50–7.44 (m, 4H), 7.39–7.25 (m, 6H), 7.02 (d, $J = 8.4$ Hz,



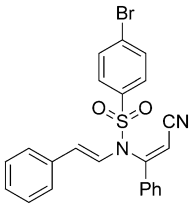
2H), 6.05 (s, 1H), 5.87 (d, $J = 14.4$ Hz, 1H), 2.44 (s, 3H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 169.3$, 154.3, 149.6, 145.1, 135.2, 133.7, 133.1, 131.6, 130.0, 129.0, 127.9, 127.2, 127.0, 126.7, 121.8, 114.6, 113.6, 99.7, 21.6, 21.0.; HR-MS (ESI): $m/z = 481.1211$, calcd. for $C_{26}H_{22}N_2O_4SNa$ $(M+Na)^+$: 481.1206.

4-Chloro-*N*-[(*Z*)-2-cyano-1-phenylvinyl]-*N*-[(*E*)-styryl]-benzenesulfonamide (3l): Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.80$ (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 14.4$ Hz, 1H), 7.51–7.47 (m, 5H), 7.40–7.23 (m, 7H), 6.09 (s, 1H),



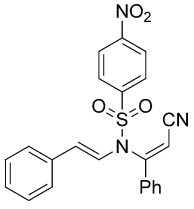
5.98 (d, $J = 14.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 154.1, 140.6, 136.8, 135.0, 133.4, 131.8, 129.7, 129.2, 129.1, 128.7, 127.3, 127.2, 126.4, 125.9, 115.3, 114.7, 100.1; HR-MS (ESI): $m/z = 443.0596$, calcd. for $C_{23}H_{17}N_2O_2S^{35}ClNa$ $(M+Na)^+$: 443.0591.

4-Bromo-*N*-[(*Z*)-2-cyano-1-phenylvinyl]-*N*-[(*E*)-styryl]-benzenesulfonamide (3m): Yellow solid; mp 50–52 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.72$ (d, $J = 8.4$ Hz, 2H),



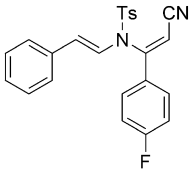
7.65 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 14.4$ Hz, 1H), 7.50–7.46 (m, 3H), 7.40–7.36 (m, 2H), 7.30–7.22 (m, 5H), 6.08 (s, 1H), 5.97 (d, $J = 14.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta =$ 154.1, 137.3, 135.0, 133.4, 132.6, 131.8, 129.2, 129.2, 129.1, 128.7, 127.3, 127.2, 126.3, 125.9, 115.4, 114.6, 100.0; HR-MS (ESI): $m/z = 487.0087$, calcd. for $C_{23}H_{17}N_2O_2S^{79}BrNa$ $(M+Na)^+$: 487.0086.

***N*-[(*Z*)-2-Cyano-1-phenylvinyl]-4-nitro-*N*-[(*E*)-styryl]benzenesulfonamide (3n):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.35$ (d, $J = 8.8$ Hz, 2H), 8.05 (d, $J = 8.8$ Hz, 2H), 7.58–7.48 (m, 4H), 7.42 (t, $J = 7.6$ Hz, 2H), 7.31–7.24 (m,



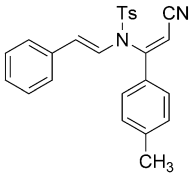
5H), 6.10 (s, 1H), 6.02 (d, $J=14.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=153.9, 150.7, 143.8, 134.6, 133.2, 132.0, 129.2, 129.0, 128.8, 127.7, 127.2, 126.0, 125.7, 124.6, 116.6, 114.5, 100.1; HR-MS (ESI): m/z=432.1012, calcd. for $C_{23}H_{18}N_3O_4S$ $(M+H)^+$: 432.1018.

***N*-[(*Z*)-2-Cyano-1-(4-fluorophenyl)vinyl]-4-methyl-*N*-[(*E*)-styryl]benzenesulfonamide (3o):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.78 (d, $J=8.0$ Hz, 2H), 7.54–7.49



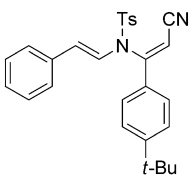
(m, 3H), 7.34–7.19 (m, 7H), 7.09 (t, $J=8.4$ Hz, 2H), 5.99 (s, 1H), 5.88 (d, $J=14.4$ Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=165.9 (d, $J=252.7$ Hz), 153.3, 145.2, 135.2, 135.2, 130.1 (d, $J=3.3$ Hz), 130.0, 129.5 (d, $J=8.8$ Hz), 128.6, 127.9, 127.2, 126.6, 125.8, 116.4 (d, $J=22.1$ Hz), 114.7, 114.5, 99.4 (d, $J=1.9$ Hz), 21.6; HR-MS (ESI): m/z= 419.1235, calcd. for $C_{24}H_{20}N_2O_2SF$ $(M+H)^+$: 419.1230.

***N*-[(*Z*)-2-Cyano-1-(*p*-tolyl)vinyl]-4-methyl-*N*-[(*E*)-styryl]-benzenesulfonamide (3p):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.79 (d, $J=8.0$ Hz, 2H), 7.56 (d, $J=14.4$ Hz,



1H), 7.43 (d, $J=8.0$ Hz, 2H), 7.34 (d, $J=8.0$ Hz, 2H), 7.29–7.25 (m, 4H), 7.22–7.17 (m, 3H), 6.03 (s, 1H), 5.88 (d, $J=$ 14.4 Hz, 1H), 2.45 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=154.2, 145.0, 142.4, 135.4, 135.4, 130.9, 129.9, 129.8, 128.6, 127.9, 127.2, 127.0, 126.8, 125.7, 114.9, 114.2, 98.5, 21.6, 21.4; HR-MS (ESI): m/z=415.1480, calcd. for $C_{25}H_{23}N_2O_2S$ $(M+H)^+$: 415.1480.

***N*-{(*Z*)-1-[4-(*tert*-Butyl)phenyl]-2-cyanovinyl}-4-methyl-*N*-[(*E*)-styryl]benzenesulfonamide (3q):** Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.75 (d, $J=8.4$ Hz, 2H), 7.59 (d, $J=$ 14.4 Hz, 1H), 7.44 (d, $J=8.4$ Hz, 2H), 7.37 (d, $J=8.4$ Hz, 2H), 7.30–7.19 (m, 7H), 6.04 (s, 1H), 5.89 (d, $J=14.4$ Hz, 1H), 2.43 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=155.4, 154.1, 144.8, 135.5, 130.7, 129.9, 128.6, 127.9, 127.1, 126.9, 126.9, 126.0, 125.7, 114.8, 114.0, 98.8, 34.9, 31.0, 21.6; HR-MS (ESI): m/z=457.1947, calcd. for $C_{28}H_{29}N_2O_2S$ $(M+H)^+$: 457.1950.



Acknowledgements

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References

[1] a) *Aziridines and Epoxide in Organic Synthesis*, (Ed.: A. K.Yudin), Wiley-VCH, Weinheim, **2006**; b) D. Tanner, *Angew. Chem.* **1994**, *106*, 625–646; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 599–619; c) I. D. G. Watson, L. Yu, A. K. Yudin, *Acc. Chem. Res.* **2006**, *39*, 194–206; d) G. S. Singh, M. D′hooghe, N. De Kimpe, *Chem. Rev.* **2007**, *107*, 2080–2135.

[2] a) H. Alper, F. Urso, D. J. H. Smith, *J. Am. Chem. Soc.* **1983**, *105*, 6737–6738; b) S. Calet, F. Urso, H. Alper, *J. Am. Chem. Soc.* **1989**, *111*, 931–934.

[3] For selected examples, see: a) J.-O. Baeg, H. Alper, *J. Am. Chem. Soc.* **1994**, *116*, 1220–1224; b) P. D. Pohlhaus, R. K. Bowman, J. S. Johnson, *J. Am. Chem. Soc.* **2004**, *126*, 2294–2295; c) P. A. Wender, D. Strand, *J. Am. Chem. Soc.* **2009**, *131*, 7528–7529.

[4] a) T. A. Moss, D. R. Fenwick, D. Dixon, *J. Am. Chem. Soc.* **2008**, *130*, 10076–10077; b) C.-Y. Huang, A. G. Doyle, *J. Am. Chem. Soc.* **2012**, *134*, 9541–9544.

[5] D. M. Hodgson, P. G. Humphreys, J. G. Ward, *Org. Lett.* **2005**, *7*, 1153–1156.

[6] a) J. P. Wolfe, J. E. Ney, *Org. Lett.* **2003**, *5*, 4607–4610; b) D. M. Hodgson, P. G. Humphreys, S. M. Miles, C. A. J. Brierley, J. G. Ward, *J. Org. Chem.* **2007**, *72*, 10009–10021.

[7] M. Sadaki, S. Dalili, A. K. Yudin, *J. Org. Chem.* **2003**, *68*, 2045–2047.

[8] a) M. D′hooghe, V. Van Speybroeck, M. Waroquier, N. De Kimpe, *Chem. Commun.* **2006**, 1554–1556; b) M. D′hooghe, K. Vervisch, A. Van Nieuwenhove, N. De Kimpe, *Tetrahedron Lett.* **2007**, *48*, 1771–1774; c) M. D′hooghe, S. Catak, S. Stanković, M. Waroquier, Y. Kim, H.-J. Ha, V. Van Speybroeck, N. De Kimpe, *Eur. J. Org. Chem.* **2010**, 4920–4931.

[9] For selected examples, see: a) C. Schneider, *Angew. Chem.* **2009**, *121*, 2116–2118; *Angew. Chem. Int. Ed.* **2009**, *48*, 2082–2084; b) S. Stanković, M. D′hooghe, S. Catak, H. Eum, M. Waroquier, V. Van Speybroeck, N. De Kimpe, H.-J. Ha, *Chem. Soc. Rev.* **2012**, *41*, 643–665; c) H. J. Reich, A. W. Sanders, A. T. Fiedler, M. J. Bevan, *J. Am. Chem. Soc.* **2002**, *124*, 13386–13387.

[10] a) Y. Fukuta, T. Mita, N. Fukuda, M. Kanai, M. Shibasaki, *J. Am. Chem. Soc.* **2006**, *128*, 6312–6313; b) Y. Xu, L. Lin, M. Kanai, S. Matsunaga, M. Shibasaki, *J. Am. Chem. Soc.* **2011**, *133*, 5791–5793; c) K. Ohmatsu, Y. Hamajima, T. Ooi, *J. Am. Chem. Soc.* **2012**, *134*, 8794–8797; d) M. K. Ghorai, K. Das, D. Shukla, *J. Org. Chem.* **2007**, *72*, 5859–5862; e) G. Sabitha, R. S. Babu, M. Rajkumar, J. S. Yadav, *Org. Lett.* **2002**, *4*, 343–345; f) S. E. Larson, J. C. Baso, G. Li, J. C. Antilla, *Org. Lett.* **2009**, *11*, 5186–5189; g) Z. Li, M. Fernández, E. N. Jacobsen, *Org. Lett.* **1999**, *1*, 1611–1613; h) Z. Zhang, Y. Wei, M. Shi, *Chem. Commun.* **2012**, *48*, 5334–5336.

[11] For recent reviews, see: a) X. Lu, C. Zhang, Z. Xu, *Acc. Chem. Res.* **2001**, *34*, 535–544; b) L.-W. Ye, J. Zhou, Y. Tang, *Chem. Soc. Rev.* **2008**, *37*, 1140–1152; c) V. Nair, R. S. Menon, A. R. Sreekanth, N. Abhilash, A. T. Biju, *Acc. Chem. Res.* **2006**, *39*, 520–530.

[12] For selected examples, see: a) C.-Q. Li, M. Shi, *Org. Lett.* **2003**, *5*, 4273–4276; b) R. Weiss, M. Bess, S. M. Huber, F. W. Heinemann, *J. Am. Chem. Soc.* **2008**, *130*, 4610–4617; c) Y.-G. Wang, S.-L. Cui, X.-F. Lin, *Org. Lett.* **2006**, *8*, 1241–1244; d) X. Jiang, D. Fu, X. Shi, S. Wang, R. Wang, *Chem. Commun.* **2011**, *47*, 8289–8291; e) H. Liu, Q. Zhang, L. Wang, X. Tong, *Chem. Commun.* **2010**, *46*, 312–314.

[13] S. R. Landor, P. D. Landor, Z. T. Fomum, G. W. Mpango, *J. Chem. Soc. Perkin Trans. 1* **1979**, 2289–2293.

[14] a) Y. Nakao, Y. Hirata, M. Tanaka, T. Hiyama, *Angew. Chem.* **2008**, *120*, 391–393; *Angew. Chem. Int. Ed.* **2008**, *47*, 385–387; b) S. Kamijo, C. Kanazawa, Y. Yamamoto, *J. Am. Chem. Soc.* **2005**, *127*, 9260–9266; c) K. Yoo, H. Kim, J. Yun, *Chem. Eur. J.* **2009**, *15*, 11134–11138; d) Z. Shi, C. Zhang, S. Li, D. Pan, S. Ding, Y. Cui, N. Jiao, *Angew. Chem.* **2009**, *121*, 4642–4646; *Angew. Chem. Int. Ed.* **2009**, *48*, 4572–4576.

[15] a) H. Duckert, V. Khedkar, H. Waldmann, K. Kumar, *Chem. Eur. J.* **2011**, *17*, 5130–5137; b) B. A. Trofimov, L. V. Andriyankova, K. V. Belyaeva, A. G. Mal′kina, L. P. Nikitina, A. V. Afonin, I. A. Ushakov, *J. Org. Chem.* **2008**, *73*, 9155–9157; c) B. A. Trofimov, L. V. Andriyankova, K. V. Belyaeva, A. G. Mal′kina, L. P. Nikitina, O. A. Dyachenko, O. N. Kazheva, G. G. Alexandrov, G. V. Shilov, A. V. Afonin, I. A. Ushakov, *Tetrahedron* **2011**, *67*, 1288–1293; d) B. A. Trofimov, L. V. Andriyankova, L. P. Nikitina, K. V. Belyaeva, A. G. Mal′kina, A. V. Afonin, I. A. Ushakov, *Synlett* **2012**, 2069–2072.

[16] L.-G. Meng, L. Wang, *Chem. Commun.* **2012**, *48*, 3242–3244.

[17] a) J.-Y. Wu, Z.-B. Luo, L.-X. Dai, X.-L. Hou, *J. Org. Chem.* **2008**, *73*, 9137–9139; b) X.-L. Hou, R.-H. Fan, L.-X. Dai, *J. Org. Chem.* **2002**, *67*, 5295–5300; c) R.-H. Fan, X.-L. Hou, *J. Org. Chem.* **2003**, *68*, 726–730; d) S. Minakata, Y. Okada, Y. Oderaotoshi, M. Komatsu, *Org. Lett.* **2005**, *7*, 3509–3512; e) H. Guo, Q. Xu, O. Kwon, *J. Am. Chem. Soc.* **2009**, *131*, 6318–6319.

[18] a) M. Yoshimatsu, Y. Timura, *J. Org. Chem.* **2002**, *67*, 5678–5682; b) H.-P. Deng, Y. Wei, M. Shi, *Org. Lett.* **2011**, *13*, 3348–3351; c) J. Feng, X. Lu, A. Kong, X. Han, *Tetrahedron* **2007**, *63*, 6035–6041.

[19] The X-ray crystal structure of **3d** is shown below. CCDC 915901 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.