Tetrahedron 67 (2011) 9957–9965

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Three types of products by carbon nucleophiles toward methoxyphenylacetylenic sulfones

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ARTICLE INFO

Article history:
Received 1 August 2011
Received in revised form 16 September 2011
Accepted 19 September 2011
Available online 24 September 2011

Keywords:
Acetylenic sulfone
α-Addition
β-Addition
Displacement
Conjugate addition
Chelation effect
Isomerization
trans-Elimination

ABSTRACT

Methoxy-arylacetylenic sulfones were examined to react with various carbanion nucleophiles to result in the three types of products; thus, (i) nucleophiles (MeLi·LiBr, Vinyl MgBr, $LiCH_2CN$) showed the α-addition, however, (ii) Li–C≡C–TMS afforded β-addition (conjugate addition) products. The (iii) displacement reaction through α-addition/isomerization/trans-elimination was enhanced by the presence of *ortho*-methoxy group at high temperature. The heteroatom nucleophiles (nitrogen, oxygen or sulfur atom) in a protic solvent provided only conjugate addition products as reported.

1. Introduction

We have been studying on the vinylic sulfone system as **1** as one of the key reactions for stereocontrolled C–C bond formation in the total syntheses of various natural products, such as maytansine,[1,2] okadaic acid,[3] tautomycin,[3,4] ciguatoxin,[5] etc. When one uses alkyllithium, alkenyllithium or alkynyllithium as Nu–Li in tetrahydrofuran (THF) solvent, extremely high stereoselectivity results to afford *syn* products **2** due to chelation effects, which is called heteroatom directed conjugate addition (HADCA)[6,7] (Scheme 1). HADCA can switch the selectivity to give *anti* product **3** under stereoelectronic control in polar solvents.[8–11] The selectivity is due to the significant neighboring group effect by the oxygen atom.[12–16] In cases without the oxygen atom presenting around the vinylsulfone moiety, low reactivity is observed in a rate of slower than 1/100 due to no chelation nor stereoelectronic effects.[11] The function of the oxygen atom is thus significant for reactivity and selectivity in HADCA. On the other hand, further enhanced reactivity and selectivity was observed under chelation control by adding NaBr in case of lithium acetylides as nucleophile.[6,7] The salt-effects suggested that reactivity was very much depending upon the counter cations of the carbon nucleophiles. We became interested in controlling the reactivity of acetylenic sulfone **4** with the carbanion nucleophiles during the course of solanoeclepin synthesis.[6,7] But, alkylacetylenic sulfones are easy to equilibrate to the corresponding allenic or propargylic sulfones, so that it is too complex to understand the mechanism of alkynylsulfone moiety with alkyllithium or Grignard reagent. Extensive studies have been accumulated in a review article.[17] In this paper, we focused on the reactivity of acetylenic sulfone **4a**,**b** with special reference to the roles of the oxygen atom (Scheme 1).

2. Results of carbon nucleophiles to acetylenic sulfones

An acetylenic sulfone with an alkyl substituent in general, e.g. $PhSO_2C{\equiv}C{-}CH_3$, was reported undergoing rapid equilibration to the corresponding allenic sulfone $PhSO_2{-}CX{=}C{=}CH_2$ with various metal complexes showing very different reactivity[18,19] (for details see reviews[17]). Here we studied alternative system having the aromatic substituents to the acetylenic sulfones; thus, $PhSO_2C{\equiv}C{-}Ar$ **4**, to avoid such equilibria. The acetylenic sulfones **4a** and **4b** were synthesized from commercially available 1-bromo-2-methoxybenzene **9** and 1-bromo-4-methoxybenzene **10** under (a) Sonogashira cross-coupling,[20,21] (b) retro-Favorskii reaction,[22] (c) lithium acetylide with *S*-phenyl benzenesulfonothioate, and (d) oxidized with *m*-CPBA to obtain 39% and 47% yield in four steps, respectively (Scheme 2). To investigate the chelation

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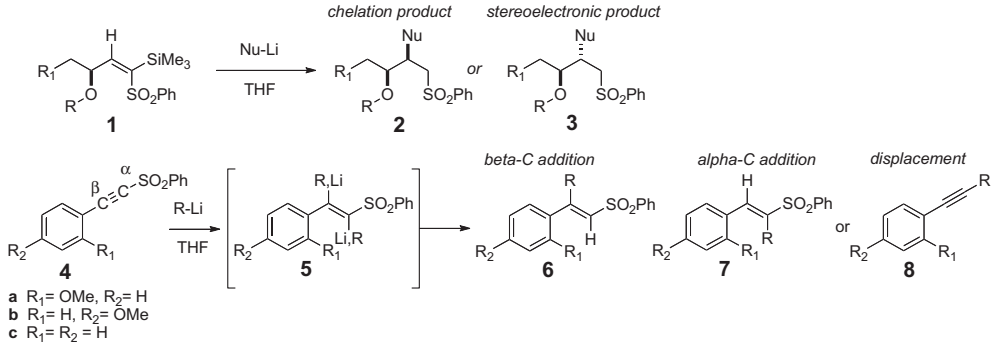
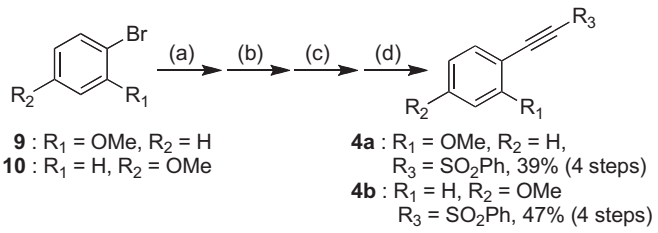
doi:10.1016/j.tet.2011.09.078



Scheme 1. Reactivity types for vinylic sulfone and arylacetylenic sulfone.



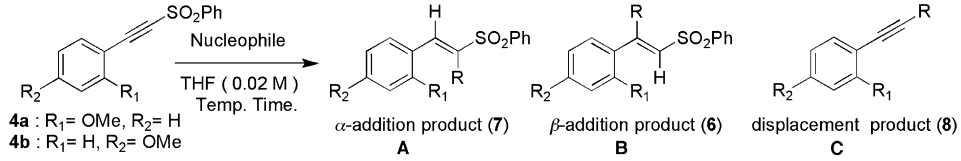
Scheme 2. Preparation of arylacetylenic sulfones **4a** and **4b**. Reagent and condition: (a) 2-methylbut-3-yn-2-ol, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, reflux, 5 h. (b) KOH, toluene, reflux, 1.5 h. (c) *n*-BuLi, $PhSO_2$–SPh, THF, −78 °C, 5 h. (d) *m*-CPBA, DCM, 0 °C, 2 h.

effects, a methoxy group was placed at the *ortho*-position **4a** and also *para*-position **4b** for comparison onto this aromatic ring, which would keep the same electronic situation to the acetylenic sulfone moiety (Scheme 1). The plan was first to add lithium carbanions to **4a**,**b**, and to see the difference in the oxygen-effects to afford the three types of the products **6**–**8**. But the product **7** was often found with amazing different selectivity from our expectation. The results are summarized in Table 1 with several nucleophiles.

A solution of *ortho*-methoxyphenylacetylenic sulfone **4a** in THF solvent was added 1.5 equiv of MeLi·LiBr at 0 °C to afford displacement product **11** in 45% yield, together with recovery of 44% **4a** (entry 1). Addition of 1.5 equiv MeLi·LiBr into **4a** at −78 °C afforded a displacement product **11** in 61% yield (entry 3).

In case of *para*-methoxyphenylacetylenic sulfone **4b**, we obtained similar displacement product **12** in 60% yield at 0 °C (entry 2) or in 63% by excess amount 5 equiv of MeLi·LiBr at −78 °C (entry 5). Amazingly, the product obtained from **4b** with 1.5 equiv MeLi·LiBr

Table 1
Products by carbon nucleophiles to the acetylenic sulfones **4a** and **4b**



Entry[a]	Substrate	Nucleophile (equiv)	Temp (°C)	Time (h)	R	Products			Yield[b] (%)
						A	**B**	**C**	
1[c]	**4a**	MeLi·LiBr (1.5)	0	1	Me	—	—	**11**	45[d]
2	**4b**	MeLi·LiBr (1.5)	0	1	Me	—	—	**12**	60
3	**4a**	MeLi·LiBr (1.5)	−78	1	Me	—	—	**11**	61
4	**4b**	MeLi·LiBr (1.5)	−78	1	Me	**15b**	—	—	25
5	**4b**	MeLi·LiBr (5.0)	−78	1	Me	—	—	**12**	63
6	**4a**	MgBr (5.0)	−40	4.5		—	—	**17**	40
7	**4b**	MgBr (5.0)	−40	4.5		**19**	—	—	80
8	**4a**	MgBr (5.0)	−78	4.5		**18**	—	—	30[e]
9	**4b**	MgBr (5.0)	−78	4.5		**19**	—	—	18[f]
10	**4a**	MgBr (10.0)	−78	4.5		**18**	—	—	60[g]
11	**4b**	MgBr (10.0)	−78	4.5		**19**	—	—	25[f]
12	**4a**	$LiCH_2CN$[h] (3.0)	−78	0.25	$-CH_2CN$	**20**	—	—	37[i]

Table 1 (*continued*)

Entry[a]	Substrate	Nucleophile (equiv)	Temp (°C)	Time (h)	R	Products			Yield[b] (%)
						A	B	C	
13	**4b**	$LiCH_2CN$[h] (3.0)	−78	0.25	$-CH_2CN$	**21**	—	—	21[j]
14	**4a**	$LiCH_2CN$[h] (9.0)	−78	0.1	$-CH_2CN$	**20**	—	—	40
15	**4b**	$LiCH_2CN$[h] (9.0)	−78	0.1	$-CH_2CN$	**21**	—	—	27
16	**4a**	Li≡TMS[k] (10.0)	−40	5	≡H	—	**22**	**24**	25+44[l]
17	**4b**	Li≡TMS[k] (10.0)	−78 −40	2 3	≡H	—	**23**	—	50

[a] Every reaction is 100 mg scale.
[b] Isolated yield.
[c] The solution of **4a** in THF was added into MeLi·LiBr in THF solution.
[d] The **4a** was recovered in 44% yield.
[e] The **4a** was recovered in 43% yield.
[f] The conversion yield was determined by ^1H NMR.
[g] The **4a** was recovered in 18% yield.
[h] Acetonitrile was deprotonated with *n*-BuLi at 0 °C for 1 h.
[i] High polar byproduct (42 mg) was obtained.
[j] High polar byproduct (65 mg) was obtained.
[k] Trimethylsilylacetylene was deprotonated with MeLi·LiBr at 0 °C for 1 h.
[l] The yield of displacement products ≡X (X=H, TMS, combined yield).

at −78 °C in 25% was **15b** (entry 4), which showed different NMR from those of reported data for **12**,[23,24] **13**, **14** nor **16**. Particularly the vinylic proton of **15b** appeared at around δ 7.75 ppm, while the reported data of **13**[25] is δ 6.58 ppm. The structure of this adduct **15b**[26] was proven from the NMR data (HMBC and NOESY spectra) as shown in Fig. 1. So **15b** is a *anti*-addition at the α-carbon but not a *syn*-addition as **16**.[27] These authentic data[25–27] were taken from the compounds prepared by completely different way. The chemical shift data are summarized in Table 2.

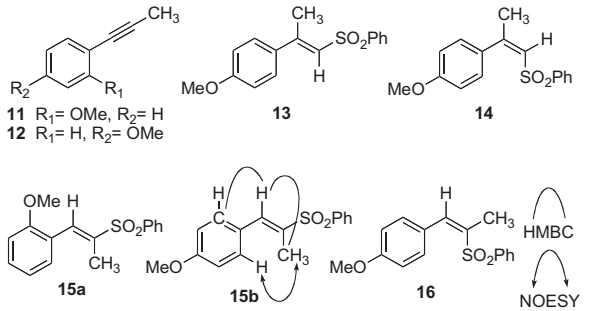


Fig. 1. Products of MeLi·LiBr addition to **4a** and **4b**.

Table 2
Chemical shifts of vinylic proton

R	δ ppm	δ ppm	δ ppm	δ ppm
$-CH_3$		(7.74)[a] 7.75		6.58[b]
$-CH=CH_2$	8.15[a]	7.81[c]		
$-CH_2CN$	8.19	7.99		
$-C\equiv C-H$			7.54	7.04

[a] Taken from Ref. 26.
[b] Taken from Ref. 25.
[c] Structures confirmed by X-ray crystallographic analysis.

Next, we employed vinylmagnesium bromide as the second nucleophile (Table 1, entries 6–11). Its reactivity was relatively lower than MeLi·LiBr,[6,7] so large excess reagents were used in 5–10 equiv to the acetylenic sulfones **4a** and **4b** to complete the reaction. Addition of vinylmagnesium bromide (5 equiv) to **4a** at −40 °C for 4.5 h afforded the displacement product **17** (entry 6). The same reaction at −78 °C gave **18** in 30% yield with 43% recovery of **4a** (entry 8), so increasing the nucleophile to 10 equiv increased the yield of **18**—60% (entry 10). On the other hand, addition of vinylmagnesium bromide to **4b** gave **19** in 80% yield at −40 °C (entry 7). But the same reaction at lower temperature (−78 °C) or larger excess (10 equiv) afforded lower yields (entry 9 and 11). Both of the addition products **18** and **19** became crystalline, so the structures were determined by X-ray crystallographic analysis to result in the structure as shown in Fig. 2. The addition took place at the α-carbon in *anti* mode in these cases.

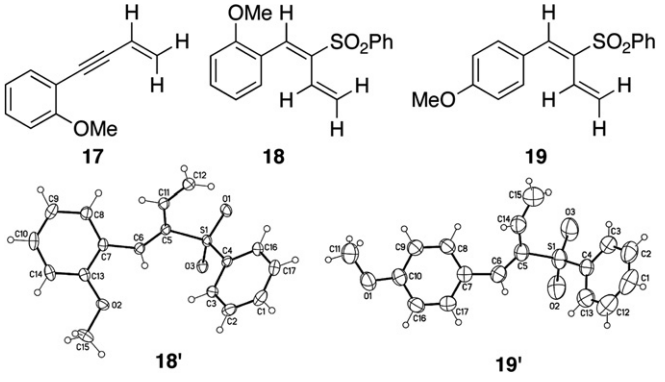


Fig. 2. Products of vinylmagnesium bromide to **4a** and **4b**.

Acetonitrile anion was generated with *n*-butyllithium and then added to **4a** and **4b**, respectively. In these cases (entries 12–15), the α-addition products **20** and **21** were isolated. The yields were 21–40% with some polar side products. These structures were confirmed by NMR with HMBC (Fig. 3). None of the conjugate addition product nor displacement product was observed under the conditions shown in Table 1.

Trimethylsilyl acetylene was lithiated by MeLi·LiBr and then added to **4a** and **4b**, respectively. We obtained the conjugate addition products **22** and **23** in relatively moderate yields. The case of **4a** we obtained the displacement product **24** only on the *ortho*-methoxy case. The ratios of addition product **22** and displacement product **24** were isolated in a ratio of 1:2 in 69% total yield. The HMBC experiments of **22** and **23** showed that the addition products took place at the β-carbon, thus conjugate addition (Fig. 3).

Structure assignments of the products by the carbon nucleophiles were performed from NMR and X-ray crystallographic

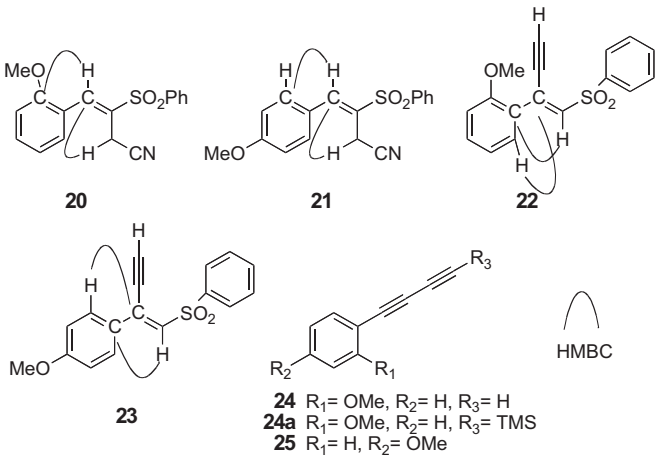


Fig. 3. Products of acetonitrile and acetylide anions to **4a** and **4b**.

analysis. In addition to confirming these structures, the vinylic protons of the α- or β-positions are summarized in Table 2. Chemical shifts of the β-H to the vinylsulfones appear between δ 7.75 and 8.19 ppm, while those of the α-H are located between δ 6.58 and 7.54 ppm. Namely the lower chemical shifts than δ 7.75 ppm can be assigned as the β-proton, thus α-addition.

3. Results of heteroatom nucleophiles to 4a and 4b

After we examined the four kinds of carbon nucleophiles to the arylacetylenic sulfones, we performed the addition by heteroatom nucleophiles, such as nitrogen, sulfide, and oxygen as shown in Fig. 4. In fact, various nucleophiles were added to arylacetylenic sulfones in ethanol or methanol solvent at 0 °C to room temperature to afford selectively the addition products. All of them are conjugate addition to the β-carbon of the acetylenic sulfones in high yields (70–88% yields) as summarized in Table 3. Judging from the higher yields with these heteroatom nucleophiles, neither displacement nor very little addition took place at the α-carbon of the acetylenic sulfones **4a** and **4b**.

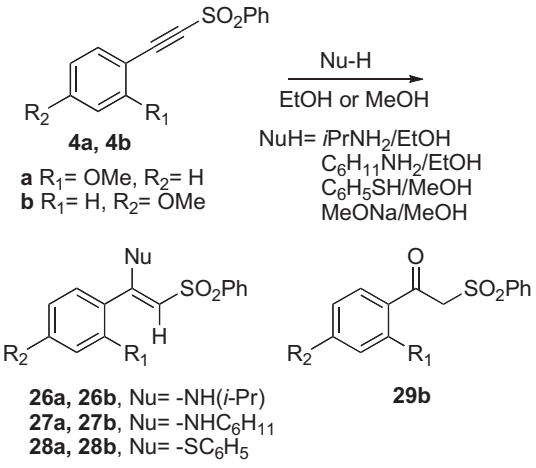


Fig. 4. Heteroatom nucleophiles addition in ethanol and methanol to **4a** and **4b**.

Heteroatom nucleophiles have already been reported in terminal acetylenic sulfone (H–C≡C–SO_2Ar) or alkylacetylenic sulfones to results in the conjugate addition.[17,19,28] The arylacetylenic sulfones show similar but simple conjugate addition with *Z*-isomers. The enamines **26a**, **26b** and **27a**, **27b** were isolated only in *anti*-selective addition at the β-carbon of the acetylenic sulfones **4a** and **4b**. The addition of sulfide took place similarly at the β-carbon to provide **28a**, **28b**. The sodium methoxy addition product was converted to the keto-sulfones **29b** only on *para*-methoxy case. The case of **4a**, we obtained stereoisomer mixture addition products. The conjugate adduct **27b** became crystalline, and the structure was determined by X-ray crystallographic analyzed as shown in Fig. 5.

4. Discussions

The three carbon nucleophiles toward arylacetylenic sulfones **4a**, **4b** showed either α-addition in *anti*-manner or displacement, but no α-*syn*-addition nor β-addition product was obtained (Table 1, entries 1–15). The displacement products **11** and **12** with MeLi·LiBr (Table 1, entries 2 and 3) were obtained in a tendency of conditions (1) at relatively higher temperature (0 °C), (2) in larger excess amounts (5 equiv) and/or with substrates (3) the *ortho*-methoxy compound **4a** rather than *para*-methoxy **4b**. A *anti*-adduct **15b** was isolated from **4b** but not corresponding adduct **15a** from the *ortho*-methoxy precursor **4a**. These results suggest that the α-addition **D** of methyllithium to **4a** first gives the anionic intermediate **E**, lithium cation of which would chelate with the *ortho*-methoxy oxygen atom. Under the conditions, *E*-isomer might isomerize to *Z*-isomer at this sp^2 carbanion atom to **F**, which could kick out the phenylsulfonyl group by *trans*-elimination to provide **G**, ending up with the formation of formal displacement product. This α-addition, however, takes place without the *ortho*-methoxyl group under more drastic conditions (longer reaction time or larger amount of nucleophiles). Therefore, *ortho*-methoxyl group is not essential to α-addition but enhancing the isomerization reaction leading to the *trans*-elimination ending up with the displacement. Russel has proposed a radical mechanism under photochemical reaction condition of arylacetylenic sulfonyl compounds.[29,30] Fuchs suggested similar radical mechanism with acetylenic triflones.[31]

In the current cases, an ionic mechanism is proposed to include α-addition/isomerization/trans-elimination mechanism for this displacement reaction as shown in Fig. 6. This is also supported by the fact in the vinylmagnessium bromide case (Table 1, entry 6) that the displacement product **17** was obtained at −40 °C but never observed at −78 °C, and that only α-*anti*-addition products **18** and **19** were obtained at that lower temperature conditions. In the meantime, we utilized 5 equiv vinylmagnessium bromide to react with phenylethynyl-sulfonyl benzene **4c** at −40 or −78 °C for 4.5 h, and that only α-addition product **32** was gained but no displacement product. The product **I** was proposed the α-addition intermediate **H** through α-attack to **4c**, but no isomerization/elimination, as shown in Fig. 6 and Scheme 3.

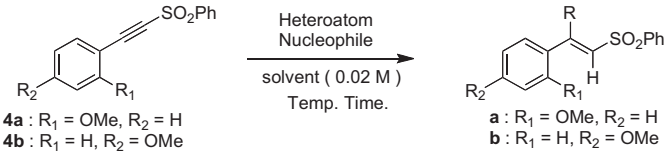
A clear *syn*-addition of lithium dimethylcuprate to phenyl trimethylsilylethynyl sulfone afforded the conjugate adduct, showing the vinylic H at δ 6.25 ppm. Addition of phenyllithium afforded benzenesulfenic acid in >70% yields meaning displacement reaction, but the product was detected by gas chromatography.[32]

An alternative carbon nucleophile was examined for a conjugate addition to the acetylenic sulfone **33**. The corresponding methylketone of **33** afforded under basic conditions largely a mixture of the dimeric products **35** instead of the pentanone **34**. So treatment of **33** under acidic conditions, such as *p*-toluenesulfonic acid monohydrate afforded a cyclopentanone product **34** in 25% isolated yield together with **35** in 35% yield, which should proceed via the intramolecular β-attack as shown by **33a** (Fig. 7).

5. Conclusion

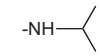
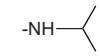
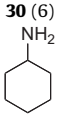
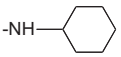
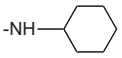
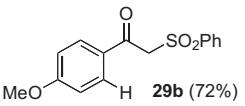
Addition reaction to acetylenic sulfones was studied to give three types of products: (i) α-addition products by those high p*Ka* carbon nucleophiles, such as MeLi·LiBr, vinyl MgBr and $LiCH_2CN$

Table 3
Heteroatom nucleophiles to the arylacetylenic sulfones **4a** and **4b**



4a : R_1 = OMe, R_2 = H
4b : R_1 = H, R_2 = OMe

a : R_1 = OMe, R_2 = H
b : R_1 = H, R_2 = OMe

Entry[a]	Substrate	Nucleophile (equiv)	Temp (°C)	Time (h)	Solvent	R	Result (yield %)
1[b]	**4a**	 **30** (6)	0 to rt (25)	4	EtOH		**26a** (88%)
2[b]	**4b**	**30** (6)	0 to rt (25)	4	EtOH		**26b** (75%)
3[b]	**4a**	 **31** (6)	0 to rt (25)	4	EtOH		**27a** (81%)
4[b]	**4b**	**31** (6)	0 to rt (25)	4	EtOH		**27b** (70%)
5	**4a**	$NaBH_4$ (6) PhS–SPh (6)	0	1	MeOH	–SPh	**28a** (82%)
6	**4b**	$NaBH_4$ (6) PhS–SPh (6)	0	1	MeOH	–SPh	**28b** (75%)
7	**4b**	NaOMe (3)	Reflux	1	MeOH	 **29b** (72%)	

[a] Every reaction is 100 mg scale.
[b] The solution of sulfones was added into the amine in EtOH solution at 0 °C.

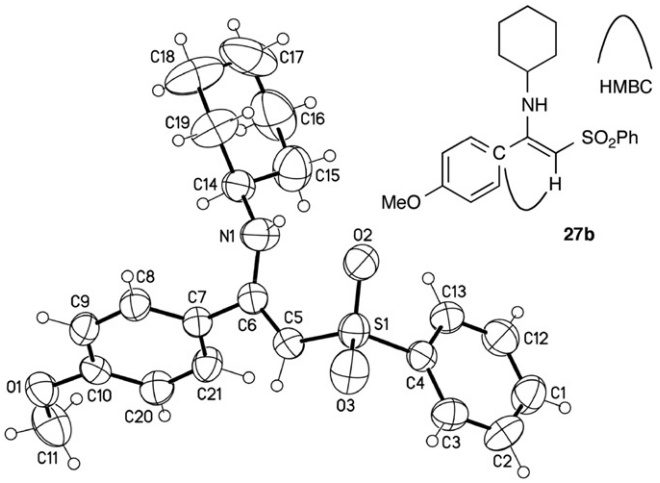


Fig. 5. HMBC and X-ray structure of **27b**.

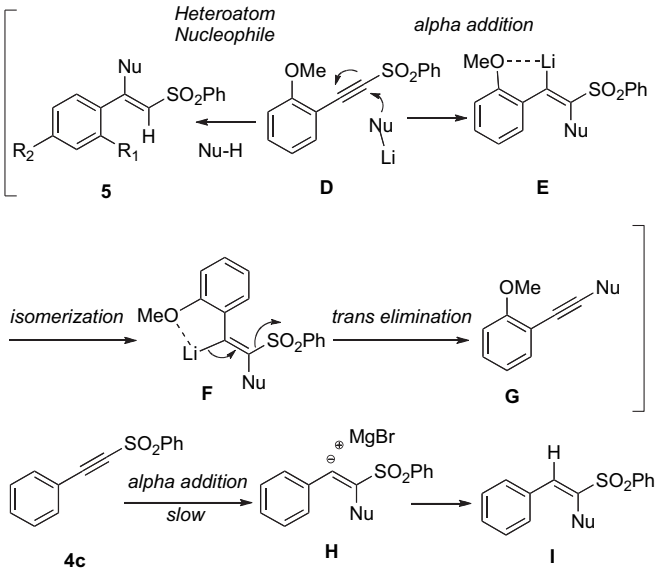
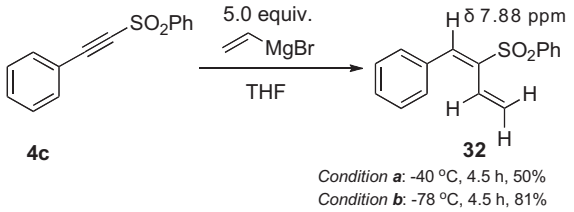


Fig. 6. Possible mechanism of the displacement products through α-addition.

(p*Ka* ≥25); (ii) β-addition products by Li–C≡C–TMS (p*Ka* ≈25); and (iii) the displacement products through α-addition/isomerization/*trans*-elimination. This isomerization was enhanced by the presence of *ortho*-methoxy group to afford displacement products, although it happened even without *o*-OMe under more drastic conditions using larger amount of nucleophiles or higher temperatures. The sulfonyl group made the α-carbon itself electrophilic due to its strongly electron withdrawing nature in THF solvent. This is striking contrast with the fact that lithium acetylide addition took place at the β-carbon, thus conjugate addition. It seems that lithium acetylide is the border of α- or β-carbon attacking. Recently, Xie and co-workers reported conjugate addition of alkyl- or aryl-



Scheme 3. *Anti*-Addition of vinylmagnesium bromide to phenylethynyl-sulfonyl benzene **4c**.

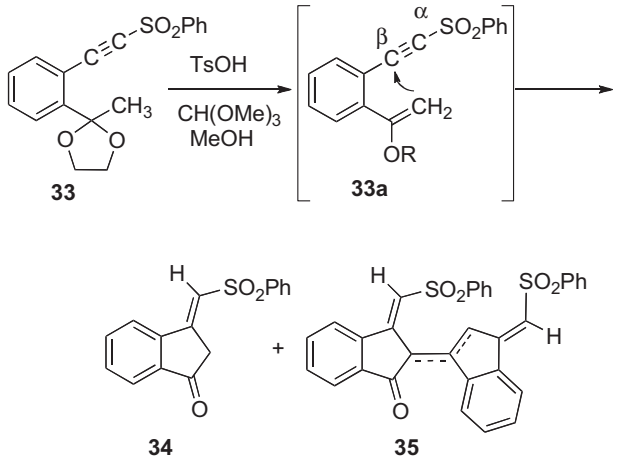


Fig. 7. Intramolecular nucleophile to form cyclopentanone by conjugate addition.

zinc halides to the acetylenic sulfones under toluene-refluxing condition in the presence of CuI to afford *syn*-addition products.[33,34] The alkynyl nucleophiles, however, cannot undergo the cuprate mediated conjugate addition due to greater *s*-character for the transformation to the electrophile.[35] Therefore, the conjugate addition of acetylide is a quite unique example. The finding of the addition product at the α-carbon in this study is also remarkable. Further studies on addition reaction to acetylenic sulfones with carbon nucleophiles having other counter metal ions are now in progress, which would be disclosed elsewhere.

6. Experimentals

6.1. General information

Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a BRUKER AV-400 (400 MHz) or a BRUKER DMX-600 (600 MHz). Data were reported as follows; chemical shift as δ values referenced to $CHCl_3$ (7.24), integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, br=broadened, m=multiplet), coupling constants in Hz, and assignment. Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a BRUKER AV-400 (100 MHz) or a BRUKER DMX-600 (150 MHz). Chemical shifts are reported in δ values and referenced to $CHCl_3$ (77.00). High resolution mass spectra (HRMS) were recorded on FINNIGAN MAT-95XL Mass spectrometers in *m*/*z* respectively in NSC Instrumentation Center at NTHU or a Bruker APEX II ESI/FT-MS Mass spectrometers in *m*/*z* respectively in NSC Instrumentation Center at NSYSU. Melting points were obtained with a SMP3 melting point apparatus. X-ray diffraction spectra were recorded on Siemens Smart CCD in NSC Instrumentation Center at NTHU. Infrared (IR) spectrum was recorded on a HORIBA FT-IR spectrometer using KBr salt plates, and reported in terms of wavenumber (cm^{-1}). Reactions were monitored by thin-layer chromatography carried out on 0.25 mm Silica Gel 60 F_{254} coated glass plates (Merck, Art 1.05715) using UV light as visualizing agent Ammonium molybdate tetrahydrate solution and heated as developing agents. Geduran® Silica Gel 60 (particle size 40–63 μm, purchased from E-Merck Chemicals, Inc.) was used for flash column chromatography.

*6.1.1. 1-(2(2-Methoxyphenyl)ethynylsulfonyl)benzene (**4a**)*[36]. As light yellow solid, R_f 0.28 (ethyl acetate/hexane=1:5). Mp 81.1–81.9 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.79 (s, 3H), 6.83–6.90 (m, 2H), 7.37–7.40 (m, 2H), 7.55 (t, *J*=7.6 Hz, 2H), 7.62–7.65 (m, 1H), 8.04–8.06 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.7, 88.6, 91.6, 106.9, 110.9, 120.4, 127.1, 129.2, 133.3, 133.9, 134.3, 142.0, 161.6; HRMS (EI) calcd for $C_{15}H_{12}O_3S$ (M^+) *m*/*z* 272.0507; found 272.0502.

*6.1.2. 1-(2-(4-Methoxyphenyl)ethynylsulfonyl)benzene (**4b**)*[37,38]. As light yellow solid, R_f 0.25 (ethyl acetate/hexane=1:3). Mp 74.7–75.2 °C; ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.81 (s, 3H), 6.85 (d, *J*=8.4 Hz, 2H), 7.45 (d, *J*=8.8 Hz, 2H), 7.57 (t, *J*=7.6 Hz, 2H), 7.65 (t, *J*=7.2 Hz, 1H), 8.05 (d, *J*=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 84.5, 94.7, 109.4, 114.4, 127.2, 129.3, 133.9, 134.7, 142.0, 162.1; HRMS (EI) calcd for $C_{15}H_{12}O_3S$ (M^+) *m*/*z* 272.0507; found 272.0510.

6.2. The general procedure for carbon nucleophile to the acetylenic sulfones 4a and 4b (Table 1, entries 2–11)

The acetylenic aulfones **4a** (or **4b**) was dissolved in dry THF (0.02 M), then the carbon nucleophile (MeLi·LiBr or vinylmagnessium bromide) was dropwise added into the mixture at the reaction temperature as shown in Table 1. After the reaction completed, the reaction mixture was poured into ice-cold saturated aqueous NH_4Cl, extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel with ethyl acetate and hexane.

*6.2.1. 1-Methoxy-2-(prop-1-ynyl)benzene (**11**).* As yellow liquid, R_f 0.80 (ethyl acetate/hexane=1:5). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.10 (s, 3H), 3.86 (s, 3H), 6.83–6.88 (m, 2H), 7.21 (d, *J*=8.0 Hz, 1H),7.35 (d, *J*=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.7, 55.7, 75.7, 89.9, 110.4, 113.0, 120.3, 128.8, 133.5, 159.7; HRMS (EI) calcd for $C_{10}H_{10}O$ (M^+) *m*/*z* 146.0732; found 146.0737.

*6.2.2. 1-Methoxy-4-(prop-1-ynyl)benzene (**12**).* As yellow liquid, R_f 0.70 (ethyl acetate/hexane=1:5). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.01 (s, 3H), 3.77 (s, 3H), 6.79 (d, *J*=8.0 Hz, 2H), 7.31 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 4.2, 55.2, 79.4, 84.0, 113.8, 116.1, 132.7, 158.9; HRMS (EI) calcd for $C_{10}H_{10}O$ (M^+) *m*/*z* 146.0732; found 146.0729.

*6.2.3. 1-((E)-1-(4-Methoxyphenyl)prop-1-en-2-ylsulfonyl)benzene (**15b**)*.* As colorless liquid, R_f 0.23 (ethyl acetate/hexane=1:5). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.10 (s, 3H), 3.81 (s, 3H), 6.91 (d, *J*=8.4 Hz, 2H), 7.37 (d, *J*=8.4 Hz, 2H), 7.51 (t, *J*=7.2 Hz, 2H), 7.58 (t, *J*=7.2 Hz, 1H), 7.75 (s, 1H), 7.89 (d, *J*=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.3, 55.3, 114.1, 126.2, 128.0, 129.1, 131.5, 133.1, 134.4, 137.2, 139.4, 160.5; HRMS (EI) calcd for $C_{16}H_{16}O_3S$ (M^+) *m*/*z* 288.0820; found 288.0826. *Compound **15b** was reported by different synthetic route.[29]

*6.2.4. 1-(But-3-en-1-ynyl)-2-methoxybenzene (**17**).* As brown liquid, R_f 0.55 (ethyl acetate/hexane=1:5). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.87 (s, 3H), 5.51 (d, *J*=11.2 Hz, 1H), 5.73 (d, *J*=17.6 Hz, 1H), 6.06 (dd, *J*=11.2, 17.6 Hz, 1H), 6.84–6.91 (m, 2H), 7.27 (t, *J*=8.0 Hz, 1H), 7.40 (d, *J*=7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.8, 86.2, 92.1,

110.6, 112.3, 117.4, 120.4, 126.6, 129.8, 133.6, 159.8; HRMS (EI) calcd for $C_{11}H_{10}O$ (M^+) m/z 158.0732; found 158.0726.

*6.2.5. 1-((E)-1-(2-Methoxyphenyl)buta-1,3-dien-2- ylsulfonyl) benzene (**18**).* As white solid, mp 108.6–109.1 °C, R_f 0.28 (ethyl acetate/hexane=1:5). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.87 (s, 3H), 5.36 (d, J=11.6 Hz, 1H), 5.91 (d, J=18.0 Hz, 1H), 6.33 (dd, J=11.6, 18.0 Hz, 1H), 6.90–6.93 (m, 2H), 7.34 (t, J=8.0 Hz, 1H), 7.39 (d, J=7.2 Hz, 1H), 7.49 (t, J=7.6 Hz, 2H), 7.56 (t, J=7.2 Hz, 1H), 7.89 (d, J=8.0 Hz, 2H), 8.15 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.6, 110.8, 120.1, 122.2, 122.7, 126.6, 128.0, 128.8, 130.8, 131.5, 132.9, 135.3, 137.3, 140.2, 158.3; HRMS (EI) calcd for $C_{17}H_{16}O_3S$ (M^+) m/z 300.0820; found 300.0826.

*6.2.6. 1-((E)-1-(4-Methoxyphenyl)buta-1,3-dien-2- ylsulfonyl) benzene (**19**).* As yellow solid, mp 120.7–122.2 °C, R_f 0.20 (ethyl acetate/hexane=1:5). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.81 (s, 3H), 5.43 (d, J=11.6 Hz, 1H), 5.86 (d, J=18.0 Hz, 1H), 6.35 (dd, J=11.6, 18.0 Hz, 1H), 6.89 (d, J=8.0 Hz, 2H), 7.47–7.49 (m, 4H), 7.54–7.57 (m, 1H), 7.81 (s, 1H), 7.86 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 114.1, 123.4, 125.8, 126.7, 128.0, 128.8, 132.4, 133.0, 135.5, 138.3, 140.1, 161.1; HRMS (EI) calcd for $C_{17}H_{16}O_3S$ (M^+) m/z 300.0820; found 300.0815.

*6.2.7. (E)-4-(2-Methoxyphenyl)-3-(phenylsulfonyl)but-3-enenitrile (**20**).* Acetonitrile anion was generated from acetonitrile (58 mmL, 1.10 mmol) with *n*-butyllithium (2.5 M in hexane solution, 0.44 mL, 1.10 mmol) in dry THF (2.8 mL, 0.4 M) at 0 °C for 1 h, then added into the solution of **4a** (100 mg, 0.37 mmol) in dry THF (16 mL) at −78 °C dropwise. After 15 min, the reaction mixture was poured into ice-cold saturated NH_4Cl, extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel with ethyl acetate and hexane (1:5) as an eluent to afford **20** (43 mg, 37%) as yellow solid. mp 100.7–101.7 °C, R_f 0.25 (ethyl acetate/hexane=1:3). ^{1}H NMR (600 MHz; $CDCl_3$): δ 3.46 (s, 2H), 3.85 (s, 3H), 6.95 (d, J=8.4 Hz, 1H), 7.00 (t, J=7.2 Hz, 1H), 7.27 (d, J=7.8 Hz, 1H), 7.41 (t, J=7.8 Hz, 1H), 7.58 (t, J=7.2 Hz, 2H), 7.64–7.67 (m, 1H), 7.96 (d, J=8.4 Hz, 2H), 8.19 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 16.7, 55.5, 111.2, 115.3, 120.76, 120.82, 128.3, 129.5, 129.6, 131.0, 132.3, 134.0, 138.7, 139.7, 157.6; HRMS (EI) calcd for $C_{17}H_{15}NO_3S$ (M^+) m/z 313.0773; found 313.0775.

*6.2.8. (E)-4-(4-Methoxyphenyl)-3-(phenylsulfonyl)but-3-enenitrile (**21**).* As yellow solid, mp 99.3–100.4 °C, R_f 0.23 (ethyl acetate/hexane=1:3). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.59 (s, 2H), 3.84 (s, 3H), 6.98 (d, J=8.0 Hz, 2H), 7.42 (d, J=8.0 Hz, 2H), 7.58 (t, J=7.2 Hz, 2H), 7.65–7.68 (m, 1H), 7.95 (d, J=8.0, 2H), 7.99 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3, 55.4, 114.7, 115.2, 124.2, 127.7, 128.1, 129.6, 131.7, 134.0, 138.7, 142.3, 161.7; HRMS (EI) calcd for $C_{17}H_{15}NO_3S$ (M^+) m/z 313.0773; found 313.0769.

*6.2.9. 1-((E)-1-(2-Methoxyphenyl)but-1-en-3-yn-2-ylsulfonyl) benzene (**22**).* The trimethylsilyl acetylene (10.0 equiv, 0.52 mL, 3.63 mmol) was dissolved in dry THF (4 mL) and deprotonated with MeLi·LiBr (2.21 M in Et_2O solution, 10.0 equiv, 1.67 mL, 3.63 mmol) at 0 °C for 1 h, then added into the solution of **4a** (100 mg, 0.37 mmol) in dry THF (14.5 mL) at −40 °C. The mixture was stirred for 5 h, the reaction was poured into ice-cold saturated NH_4Cl, extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel with ethyl acetate and hexane (1:7) as an eluent to afford **22** (27 mg, 25%) as yellow liquid, R_f 0.18 (ethyl acetate/hexane=1:3) and **24** together with trace amount **24a** (24 mg, 44%). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.74 (s, 1H), 3.82 (s, 3H), 6.90 (d, J=8.4 Hz, 1H), 6.95 (t, J=7.6 Hz, 1H), 7.31–7.35 (m, 1H), 7.51 (d, J=7.6 Hz, 2H), 7.54 (s, 1H), 7.60 (d, J=6.8 Hz, 1H), 7.64 (d, J=8.0 Hz, 1H), 8.04 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.7, 78.2, 92.0, 111.6, 120.7, 123.7, 128.0, 128.8, 131.2, 131.3, 131.6, 133.3, 138.6, 141.4, 157.4; HRMS (EI) calcd for $C_{17}H_{14}O_3S$ (M^+) m/z 298.0664; found 298.0663.

*6.2.10. 1-(Buta-1,3-diynyl)-2-methoxybenzene (**24**)[39].* As brown liquid, R_f 0.63 (ethyl acetate/hexane=1:3). ^{1}H NMR (400 MHz; $CDCl_3$): δ 2.51 (s, 1H), 3.87 (s, 3H), 6.85–6.90 (m, 2H), 7.30–7.34 (m, 1H), 7.45 (dd, J=1.6, 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.8, 68.4, 71.8, 72.0, 77.2, 110.3, 110.7, 120.5, 131.0, 134.7, 161.8; HRMS (EI) calcd for $C_{11}H_8O$ (M^+) m/z 156.0575; found 156.0570.

*6.2.11. 1-((E)-1-(4-Methoxyphenyl)but-1-en-3-yn-2-ylsulfonyl) benzene (**23**).* As yellow liquid, R_f 0.15 (ethyl acetate/hexane=1:5). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.80 (s, 3H), 3.89 (s, 1H), 6.86 (d, J=8.8 Hz, 2H), 7.04 (s, 1H), 7.50–7.54 (m, 2H), 7.58–7.62 (m, 3H), 8.03 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 77.4, 93.5, 114.2, 127.0, 128.0, 128.8, 129.0, 132.3, 133.4, 134.3, 141.3, 162.0; HRMS (EI) calcd for $C_{17}H_{14}O_3S$ (M^+) m/z 298.0664; found 298.0672.

*6.2.12. N-((Z)-1-(2-Methoxyphenyl)-2-(phenylsulfonyl)vinyl) propan-2-amine (**26a**).* To a solution of **4a** (100 mg, 0.37 mmol) in EtOH (13 mL) was dropwise added into the solution of isopropylamine (0.19 mL, 2.20 mmol) in EtOH (5.5 mL, 0.4 M) at 0 °C. The stirring was allowed to warm to room temperature and continued for 4 h. The mixture was poured into ice-cold aqueous HCl (pH=4) and extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with saturated aqueous $NaHCO_3$, followed by brine, dried over $MgSO_4$, and concentrated. The resides was purified by chromatography on silica gel with ethyl acetate and hexane (1:3) as an eluent to afford **26a** (107 mg, 88%) as yellow syrup, R_f 0.30 (ethyl acetate/hexane=1:3). ^{1}H NMR (600 MHz; $CDCl_3$, 263 K): δ 0.92 (d, J=6.6 Hz, 3H)*, 1.07 (d, J=6.0 Hz, 3H)*, 3.08–3.13 (m, 1H), 3.71 (s, 3H), 4.41 (s, 1H), 6.82 (d, J=8.4 Hz, 1H), 6.86 (t, J=7.2 Hz, 1H), 7.05 (d, J=7.2 Hz, 1H), 7.27–7.31 (m, 2H), 7.41–7.44 (m, 2H), 7.46–7.48 (m, 1H), 7.88 (d, J=8.4 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$, 263 K): δ 23.3*, 24.5*, 46.2, 55.2, 87.6, 110.4, 120.3, 123.9, 125.4, 128.6, 129.2, 130.7, 131.8, 144.9, 155.6, 156.7; HRMS (EI) calcd for $C_{18}H_{21}NO_3S$ (M^+) m/z 331.1242; found 331.1240.

*The measurement of ^{1}H and ^{13}C NMR at 300 K afforded single broad signal of isopropyl methyl group, therefore, the data are measured at 263 °K.

*6.2.13. N-((Z)-1-(4-Methoxyphenyl)-2-(phenylsulfonyl)vinyl) propan-2-amine (**26b**).* As yellow syrup, R_f 0.35 (ethyl acetate/hexane=1:3). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.06 (d, J=6.4 Hz, 6H), 3.36–3.45 (m, 1H), 3.78 (s, 3H), 4.73 (s, 1H), 6.85 (d, J=8.4 Hz, 2H), 7.01–7.05 (m, 1H), 7.22 (d, J=8.4 Hz, 2H), 7.45–7.51 (m, 3H), 7.90 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.9, 46.4, 55.3, 92.3, 113.8, 125.7, 127.8, 128.8, 129.1, 132.0, 144.9, 159.7, 160.8; HRMS (EI) calcd for $C_{18}H_{21}NO_3S$ (M^+) m/z 331.1242; found 331.1243.

*6.2.14. N-((Z)-1-(2-Methoxyphenyl)-2-(phenylsulfonyl)vinyl) cyclohexanamine (**27a**).* As yellow liquid, R_f 0.33 (ethyl acetate/hexane=1:3). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.08–1.23 (m, 6H), 1.42 (br, 1H), 1.60–1.61 (m, 3H), 2.74–2.78 (m, 1H), 3.73 (s, 3H), 4.47 (s, 1H), 6.86 (d, J=8.4 Hz, 1H), 6.90 (t, J=7.6 Hz, 1H), 7.09 (d, J=7.2 Hz, 1H), 7.30–7.33 (m, 1H), 7.43–7.49 (m, 4H), 7.93 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.4, 24.5, 25.2, 52.9, 55.4, 88.5, 110.9, 120.5, 124.5, 125.5, 128.6, 129.4, 130.7, 131.7, 145.4, 156.0, 156.8; HRMS (EI) calcd for $C_{21}H_{25}NO_3S$ (M^+) m/z 371.1555; found 371.1553.

*6.2.15. N-((Z)-1-(4-Methoxyphenyl)-2-(phenylsulfonyl)vinyl) cyclohexanamine (**27b**).* As yellow solid mp 119.8–120.8 °C, R_f 0.45 (ethyl acetate/hexane=1:3). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.05–1.15

(m, 3H), 1.20–1.29 (m, 2H), 1.46–1.48 (m, 1H), 1.61–1.72 (m, 4H), 2.97–3.07 (m, 1H), 3.80 (s, 3H), 4.70 (s, 1H), 6.83–6.87 (m, 2H), 7.21–7.23 (m, 2H), 7.45–7.52 (m, 3H), 7.90–7.92 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 24.6, 25.1, 34.3, 53.1, 55.3, 91.9, 113.8, 125.7, 127.8, 128.8, 129.1, 131.9, 145.0, 159.7, 160.7; HRMS (EI) calcd for $C_{21}H_{25}NO_3S$ (M^+) m/z 371.1555; found 371.1551.

*6.2.16. 1-((Z)-2-(2-Methoxyphenyl)-2-(phenylthio)vinylsulfonyl) benzene (**28a**).* To a mixture solution of **4a** (100 mg, 0.37 mmol) and phenyl disulfide (481 mg, 2.20 mmol) in MeOH (18.5 mL) was added $NaBH_4$ (84 mg, 2.20 mmol) at 0 °C and stirred for 1 h. The mixture solution was poured into ice-cold saturated aqueous NH_4Cl and extracted with ethyl acetate (20 mL×3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel with ethyl acetate and hexane (1:5) as an eluent to afford **28a** (115 mg, 82%) as colorless liquid, R_f 0.28 (ethyl acetate/hexane=1:3).^{1}H NMR (400 MHz; $CDCl_3$): δ 3.54 (s, 3H), 6.41 (s, 1H), 6.44 (d, J=8.4 Hz, 1H), 6.65–6.68 (m, 1H), 6.92–6.94 (m, 2H), 6.96–7.06 (m, 5H), 7.54–7.58 (m, 2H), 7.61–7.66 (m, 1H), 8.13–8.16 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.9, 110.2, 119.7, 124.7, 125.2, 127.4, 127.9, 128.5, 128.7, 129.9, 130.1, 130.4, 133.1, 134.6, 141.6, 155.5, 155.7; HRMS (EI) calcd for $C_{21}H_{18}O_3S_2$ (M^+) m/z 382.0697; found 382.0704.

*6.2.17. 1-((Z)-2-(4-Methoxyphenyl)-2-(phenylthio)vinylsulfonyl) benzene (**28b**).* As white solid, mp 116.2–117.1 °C, R_f 0.33 (ethyl acetate/hexane=1:3). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.66 (s, 3H), 6.62 (d, J=8.8 Hz, 2H), 6.72 (s, 1H), 6.83 (d, J=6.8 Hz, 2H), 6.96–7.01 (m, 3H), 7.19 (d, J=8.4 Hz, 2H), 7.51 (t, J=7.6 Hz, 2H), 7.57–7.61 (m, 1H), 8.14 (d, J=7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2, 113.6, 127.7, 128.0, 128.2, 128.5, 128.7, 128.8, 130.2, 131.8, 132.5, 133.2, 141.6, 155.3, 161.0; HRMS (EI) calcd for $C_{21}H_{18}O_3S_2$ (M^+) m/z 382.0697; found 382.0697.

*6.2.18. 1-(4-Methoxyphenyl)-2-(phenylsulfonyl)ethanone (**29b**).* The mixture solution of **4b** (100 mg, 0.37 mmol) and sodium methoxide (60 mg, 1.10 mmol) in methanol (18.5 mL) was heated to reflux for 1 h. The reaction solution was cooled to room temperature, and was neutralized to pH=7 by Dowex-50W-X4 then filtered. The filtrate was concentrated in vacuo. The residue was purified by chromatography on silica gel with ethyl acetate and hexane (1:5) as an eluent to afford **29b** (77 mg, 72%) as white solid, mp 113.0–113.5 °C, R_f 0.18 (ethyl acetate/hexane=1:3). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.86 (s, 3H), 4.66 (s, 2H), 6.92 (d, J=8.8 Hz, 2H), 7.50–7.54 (m, 2H), 7.62–7.65 (m, 1H), 7.85–7.87 (m, 2H), 7.90 (d, J=9.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.5, 63.2, 114.0, 128.4, 128.7, 129.1, 131.8, 134.1, 138.7, 164.5, 186.1; HRMS (EI) calcd for $C_{15}H_{14}O_4S$ (M^+) m/z 290.0613; found 290.0618.

*6.2.19. 1-((E)-1-Phenylbuta-1,3-dien-2-ylsulfonyl)benzene (**32**).* As white solid, mp 80.9–82.1 °C, R_f 0.48 (ethyl acetate/hexane=1:3). ^{1}H NMR (400 MHz; $CDCl_3$): δ 5.44 (d, J=11.6 Hz, 1H), 5.89 (d, J=17.6 Hz, 1H), 6.36 (dd, J=11.6, 17.6 Hz, 1H), 7.36 (s, 3H), 7.48–7.50 (m, 4H), 7.54–7.56 (m, 1H), 7.87 (s, 2H), 7.88 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 123.8, 126.3, 128.0, 128.5, 128.8, 129.9, 130.3, 133.06, 133.11, 138.0, 138.5, 139.7; HRMS (EI) calcd for $C_{16}H_{14}O_2S$ (M^+) m/z 270.0715; found 270.0711.

*6.2.20. 2-Methyl-2-(2-(2-(phenylsulfonyl)ethynyl)phenyl)-1,3-dioxolane (**33**).* As white solid, mp 97.5–98.9 °C, R_f 0.33 (ethyl acetate/hexane=1:5). ^{1}H NMR (400 MHz; $CDCl_3$): δ 1.54 (s, 3H), 3.58–3.67 (m, 2H), 3.87–3.95 (m, 2H), 7.26 (t, J=7.6 Hz, 1H), 7.39 (t, J=7.6 Hz, 1H), 7.50–7.57 (m, 4H), 7.62–7.65 (m, 1H), 8.08 (d, J=8.0 Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 25.9, 64.3, 88.8, 93.8, 107.9, 115.2, 126.2, 127.3, 128.0, 129.0, 131.1, 133.8, 134.8, 142.0, 147.0; HRMS (ESI) calcd for $C_{18}H_{16}O_4SNa$ (M+Na) m/z 351.0667; found 351.0665.

*6.2.21. (E)-2,3-Dihydro-3-((phenylsulfonyl)methylene)inden-1-one (**34**).* The mixture solution of **33** (55 mg, 0.17 mmol), *p*-toluenesulfonic acid monohydrate (318 mg, 1.67 mmol), trimethyl orthoformate (0.13 mL, 1.17 mmol), and MS 4 Å in methanol (8.5 mL, 0.02 M) was heated to reflux for 45 h. The reaction solution was cooled to room temperature, quenched by ice-cold saturated aqueous NH_4Cl, then filtered through Celite. The filtrate was concentrated in vacuo, then the water layers were extracted with ethyl acetate (15 mL×3). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified by chromatography on silica gel with ethyl acetate and hexane (1:4) as an eluent to afford **34** (12 mg, 25%) as a brown liquid, R_f 0.28 (ethyl acetate/hexane=1:2) together with dimmer byproduct **35** (32 mg, 35%) as yellow liquid, R_f 0.26 (ethyl acetate/hexane=1:2). ^{1}H NMR (400 MHz; $CDCl_3$): δ 3.77 (s, 2H), 6.93 (s, 1H), 7.54–7.69 (m, 5H), 7.73 (d, J=7.6 Hz, 1H), 7.83 (d, J=7.2 Hz, 1H), 7.96 (d, J=7.6 Hz, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 40.4, 121.5, 122.3, 124.0, 127.5, 129.5, 132.5, 133.8, 135.1, 137.8, 141.2, 146.6, 199.7; IR (KBr) ν:1723, 2850, 2922 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{12}O_3SNa$ (M+Na) m/z 307.0405; found 307.0403.

Acknowledgements

We are grateful to National Science Council, Taiwan and National Tsing Hua University for funds supported to the current studies.

Supplementary data

Copies of ^{1}H NMR, ^{13}C NMR and 2D NMR spectra are included as Supplementary data. The crystallographic data for the structures of **18**, **19** and **27b** have been deposited with the Cambridge Crystallographic Data Center as Supplementary publications no. CCDC 843905, no. CCDC 843909 and no. CCDC 843910. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (tel.: +44 (0) 1223 762911; e-mail: deposit@ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2011.09.078.

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