Synthesis M. Shiri et al. Paper

Cs_2CO_3-Mediated Regio- and Stereoselective Sulfonylation of 1,1-Dibromo-1-alkenes with Sodium Sulfinates

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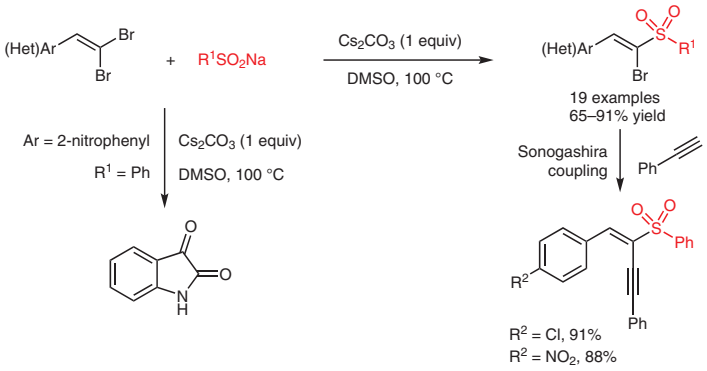
This paper is dedicated to Professor Majid M. Heravi on the occasion of his 68th birthday.



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Abstract A highly selective synthesis of (*Z*)-1-bromo-1-sulfonyl alkenes via Cs_2CO_3-promoted sulfonylation of 1,1-dibromo-1-alkenes with sodium sulfinates is described. Notably, using excess amounts of Cs_2CO_3 and sodium sulfinate in such a reaction regenerated the parent aldehyde. Interestingly, the reaction of 1-(2,2-dibromovinyl)-2-nitrobenzene in the presence of sulfinates and Cs_2CO_3 produced isatin. The Sonogashira cross coupling of synthesized (*Z*)-1-bromo-1-sulfonyl alkenes with phenylacetylene gave selectively the corresponding sulfonylalkynyl alkenes.

Key words 1,1-dibromo-1-alkenes, sodium sulfonates, regioselective, vinyl sulfone, cesium carbonate, isatin

Organosulfur compounds, particularly vinyl sulfone derivatives, have attracted considerable research interest because they are abundantly found in useful synthetic products and naturally occurring substances.[1] In addition, the vinyl sulfonyl group is extensively used as a synthetic intermediate in organic synthesis.[2] Usually, vinyl sulfones are prepared using sulfone agents such as sodium sulfinates, sulfonyl hydrazides, sulfinic acids, and tosyl methyl isocyanide (TosMIC), and alkene resources.[3] Among the sulfone agents, sodium sulfinates are readily available and stable; therefore, they are widely applied in organic transformations.[4]

Furthermore, 1,1-dibromo-1-alkenes have been extensively used as an efficient alkene and alkyne resource for generating complex alkene and alkyne derivatives.[5] They can easily be derived from aldehydes or ketones using CBr_4/PPh_3.[6] One common and practical method for synthesizing terminal alkynes (Corey–Fuchs reaction) and bromoacetylenes is the treatment of 1,1-dibromo-1-alkenes with a base.[7] Although *gem*-dibromoalkenes are widely used in organic transformations, the occurrence of the selective reaction that produces 1,1-difunctional alkenes by the remaining one Br atom is rare. For instance, the monoalkenylation,[8] selenation,[9] alkynylation,[10] arylation,[11] etherification,[12] and borylation[13] of germinal dibromoalkenes have been reported. Chen et al. established the synthesis of 2-arylbenzofurans(thiophenes) via the tandem reaction of 2-(*gem*-dibromovinyl)phenols(thiophenols) and sodium arylsulfinates in the presence of the TBAF–$PdCl_2$–$Cu(OAc)_2$–NEt_3 system.[14] A stereoselective synthesis of vinyl triflones starting from *gem*-dibromovinyl derivatives has been achieved via triflyl migration reactions.[15]

Although the synthesis of vinyl sulfones has been widely and intensively studied, the synthesis of 1-bromo-1-sulfonylalkenes has been shown only in few reports. For instance, sulfonylation of activated alkynes with sodium sulfinates,[16] as well as sulfinic acids[17] in water as the reaction medium have been developed. In both cases, ethyl 3-bromopropiolate reacted with sodium toluenesulfinate or toluenesulfinic acid to yield ethyl 3-bromo-3-tosylacrylate (Scheme 1, eq. 1). Fisher et al. have prepared α-bromovinylsulfone for their study in four steps starting from propylene oxide (Scheme 1, eq. 2).[18] In the first step, ring opening of the epoxide took place with a sulfinate salt producing an alcohol that was converted to the corresponding vinyl sulfones via treatment with methanesulfonyl chloride and base. The vinyl sulfone was dibrominated with Br_2 under radical conditions and subsequent dehydrobromination mediated by DBU afforded α-bromovinylsulfone. Condensation of bromomethyl sulfone and aldehyde generated the corresponding vinyl bromide.[19] Also diethyl bromo(phenyl-

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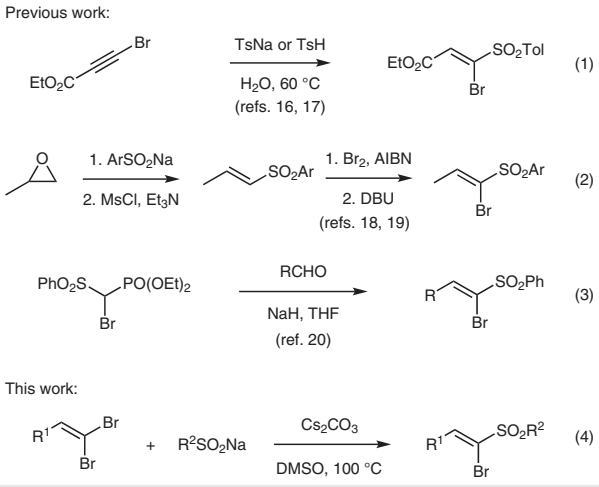
sulfonyl)methylphosphonate with an appropriate aldehyde in basic media produced the corresponding 1-bromo-1-sulfonylalkene (Scheme 1, eq. 3).[20]



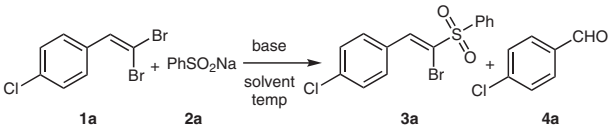
Scheme 1 Synthesis of α-bromovinyl sulfones

From the perspective of diversity-oriented synthesis, the incorporation of bromine and sulfone functional groups onto the terminal carbon atom of an alkene may be a significant achievement as it produces novel and more complex molecules. Inspired by the aforementioned results and based on our continued interest in exploring the application of *gem*-dibromoalkenes,[21] we envisioned that the selective debromosulfonation of 1,1-dibromo-1-alkenes can be performed. Herein, we report a practical protocol for the highly regioselective synthesis of (*Z*)-1-bromo-1-sulfonylalkenes **3** using sodium sulfinates and 1,1-dibromoalkenes in a basic medium (Scheme 1, Eq. 4).

In a preliminary study, 1-(2,2-dibromovinyl)-4-chlorobenzene (**1a**; 1 equiv) and sodium phenylsulfinate (**2a**; 1.2 equiv) reacted in DMSO at 100 °C without forming any desired product (Table 1, entry 1). By increasing the amount of $PhSO_2Na$ 3.6-fold under the same condition, (*Z*)-1-(2-bromo-2-(phenylsulfonyl)vinyl)-4-chlorobenzene (**3a**) and 4-chlorobenzaldehyde (**4a**) were obtained in 40% and 54% yields, respectively (entry 2). Notably, using Cs_2CO_3 (2 equiv) with $PhSO_2Na$ (3.6 equiv) in DMSO regenerated **4a** in 95% yield (entry 3). The amount of Cs_2CO_3 used played an important role in determining the success of this reaction. Upon reducing the amounts of Cs_2CO_3 and $PhSO_2Na$, the yield of the aldehyde decreased and that of **3a** increased (entries 4 and 5). Eventually, we determined the optimum amounts of Cs_2CO_3 and $PhSO_2Na$ as 1 and 1.2 equivalents, respectively, to afford **3a** as the main product (entry 6).

K_2CO_3 and Na_2CO_3 (2 equiv) formed **3a** in 60% and 45% yield, respectively; meanwhile, the reactions with CsF, Et_3N, NaOAc, and KO*t*-Bu produced **3a** in low-to-moderate yields (Table 1, entries 7–12). The screening of the solvents indicated that DMF yielded 78% **3a** along with 10% **4a**, whereas

Table 1 Optimization of the Reaction Conditions[a]



1a **2a** **3a** **4a**

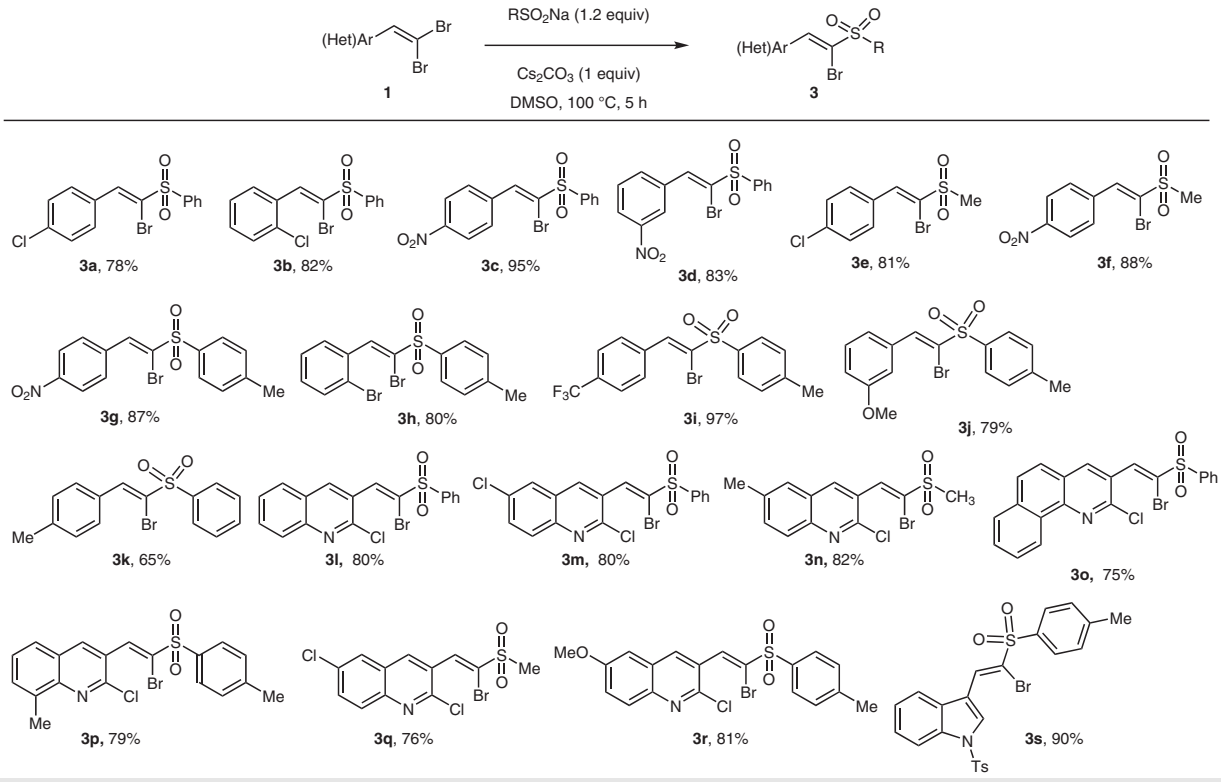
Entry	Base (equiv)	Solvent	Temp (°C)	Yield (%) of **3a**[b]	Yield (%) of **4a**[b]
1	–	DMSO	100	–	–
2[c]	–	DMSO	100	40	54
3[c]	Cs_2CO_3 (2)	DMSO	100	trace	95
4[d]	Cs_2CO_3 (2)	DMSO	100	40	56
5[d]	Cs_2CO_3 (1)	DMSO	100	63	31
6	Cs_2CO_3 (1)	DMSO	100	78	trace
7	K_2CO_3 (2)	DMSO	100	60	15
8	Na_2CO_3 (2)	DMSO	100	45	10
9	CsF (1)	DMSO	100	10	5
10	Et_3N (1)	DMSO	100	15	5
11	NaOAc (1)	DMSO	100	41	12
12	*t*-BuOK (1)	DMSO	100	50	14
13	Cs_2CO_3 (1)	DMF	100	78	10
14	Cs_2CO_3 (1)	toluene	reflux	–	––
15	Cs_2CO_3 (1)	MeCN	reflux	–	–
16	Cs_2CO_3 (1)	1,4-dioxane	reflux	–	–

[a] Reaction conditions: **1a** (1 mmol), **2a** (1.2 mmol), and solvent (5 mL) reacted at 100 °C for 5 h, unless otherwise noted.
[b] Isolated yield.
[c] Sulfinate **2a**: 3.6 equiv.
[d] Sulfinate **2a**: 2.4 equiv.

toluene, MeCN, and 1,4-dioxane did not yield any products (entries 13–16). Note that the reaction did not occur below 100 °C.

Under the established optimal conditions, the scope of this reaction with a variety of aromatic and heteroaromatic dibromoalkanes with aliphatic and aromatic sodium sulfinates was examined. As shown in Scheme 2, the tandem reaction of β,β-dibromostyrenes containing Br, Cl, NO_2, OMe, Me, or CF_3 substituents in *para*-, *meta*-, or *ortho*-position with sodium phenyl, methyl, or tolyl sulfinate produced the corresponding β-bromo-β-sulfonylstyrenes **3a–k** in 65–91% yields.

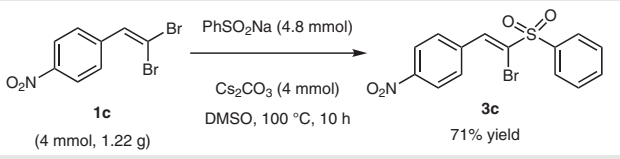
Next, we focused on the reaction of sodium phenylsulfinate with 2-chloro-3-(*gem*-dibromovinyl)quinoline because it bears an active C–Cl bond in the 2 position of quinoline. Interestingly, debromosulfonation occurred in the same way as described in the previous results and the C–Cl bond remained intact to yield **3l**. When the other vinylquinolines were employed, the selectivity was identical for the aliphatic and aromatic sodium sulfinates to afford the corresponding products **3m–r** in good to excellent



Scheme 2 Scope of various 1,1-dibromo-1-alkenes and sodium sulfinates

yields. (*Z*)-3-(2-Bromo-2-tosylvinyl)-1-tosyl-1*H*-indole (**3s**) was isolated in 90% yield from **2a** and the corresponding dibromoalkene.

To test the efficiency of this method in gram-scale synthesis, *gem*-dibromoalkene **1c** (1.22 g) was chosen to react with sodium phenylsulfinate (0.778 g) in the presence of Cs_2CO_3 (4 mmol) in DMSO (20 mL), which gave **3c** in 71% yield after 10 hours (Scheme 3).



Scheme 3 Gram-scale synthesis of **3c**

The debromosulfonylation reaction proceeded regioselectively and stereoselectively to produce the corresponding *Z*-brominated alkenyl sulfone **3** in good yields, and no *E*-isomer was observed. Although the reason for this high selectivity is not clear, the formation of an intramolecular hydrogen bond between C2-H and Br atom may be a factor.

The structure of compound **3c** was confirmed via X-ray crystallographic analysis (Figure 1).[22]

Further, 1-(2,2-dibromovinyl)-2-nitrobenzene (**1l**) was converted to isatin (**5**) in the presence of sodium phenylsulfinate and Cs_2CO_3 in 90% yield (Scheme 4). The same results were obtained when sodium tolylsulfinate was used as the sulfone source. Considering the removal of two oxygens of the nitro group and the appearance of oxygen on positions 2 and 3 of isatin, we propose the mechanism outlined in Scheme 4. The reaction commences from the base-promoted HBr elimination of **1l** to generate bromoacetylene **A**.[5b,7b] To approve this step, **1l** was treated to Cs_2CO_3 in DMSO, which yielded **A**. Subsequently, the α-addition of $ArSO_2^-$ to intermediate **A** formed **B**.[16,23] Intermediate B was subjected to intramolecular oxa-Michael addition to yield C.[24] The ring opening of **C** followed by base promoted the intramolecular hydroalkylation of nitroso group to afford **E**.[25] Final-

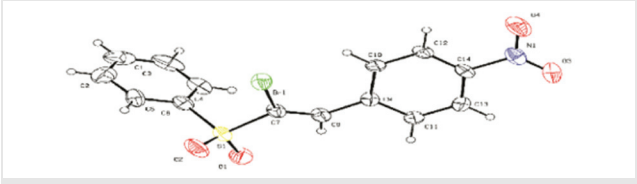
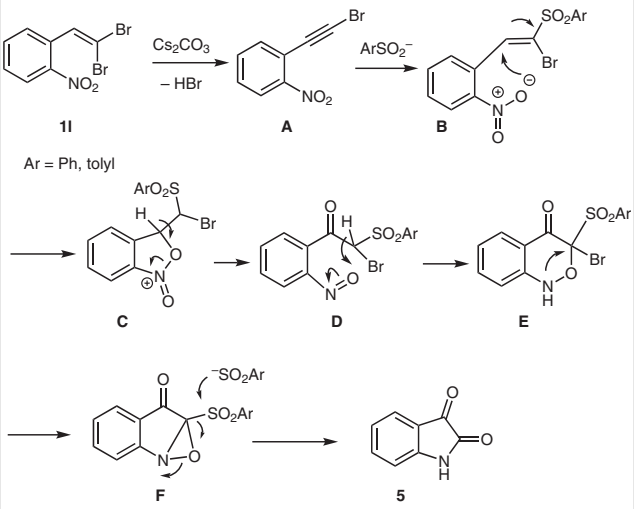


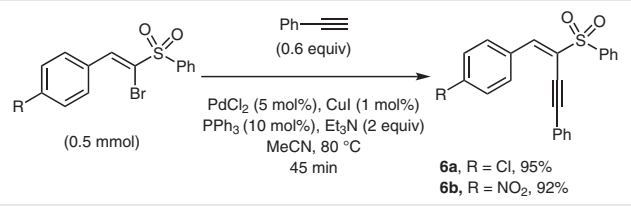
Figure 1 Single-crystal ORTEP drawing of **3c**

ly, HBr elimination via oxaziridine formation led to the ring opening of **F** assisted by the removal of sulfonyl, eventually affording **5** (Scheme 4).



Scheme 4 Plausible mechanism for the formation of isatin (**5**) from **1l**

Furthermore, the feasibility of using **3** to obtain more complex molecules was investigated. In this regard, the Sonogashira cross coupling of **3a** and **3c** with phenylacetylene resulted in the corresponding alkynylated products **6a** and **6b** in 91% and 88% yield, respectively (Scheme 5).



Scheme 5 Synthetic utility of (*Z*)-α-bromovinyl sulfones

In summary, we have developed a robust transition-metal-free synthetic method for the highly regioselective and stereoselective debromosulfonylation of 1,1-dibromo-1-alkenes using sodium sulfinates. The Cs_2CO_3-mediated reaction of a wide range of aromatic, and heteroaromatic substrates has wide applicability with good functional-group compatibility. From the reaction of 1-(2,2-dibromovinyl)-2-nitrobenzene with sodium phenyl- and tolylsulfinate, isatin was isolated as the sole product. As an example of the synthetic potential of **3**, the selective palladium-catalyzed alkynylation of these compounds with phenyl acetylene was demonstrated.

The solvents and chemicals were purchased from Merck and Aldrich chemical companies. Unless otherwise mentioned they were used without further purification. The 1,1-dibromoalkenes were prepared according to the reported procedures.[26] Melting points are taken on an Electrothermal 9100 apparatus and are uncorrected. FT-IR spectra were recorded on a Shimadzu Infra-Red Spectroscopy IR-435. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE Spectrometer 400 MHz for ^{1}H,100 MHz for ^{13}C) in DMSO-d_6 as solvent. Mass spectra recorded on Agilent Technology (HP) 5973 Network Mass Selective Detector operating at an ionization potential of 70 eV and a Leco CHNS, model 932 was used for elemental analysis.

Cs_2CO_3-Promoted Sulfonylation of 1,1-Dibromo-1-alkenes with Sodium Sulfinates; General Procedure

To a mixture of respective *gem*-dibromoalkene **1** (1.0 mmol) and Cs_2CO_3 (326 mg, 1.0 mmol) in DMSO (5.0 mL) was added the corresponding sodium sulfinate (1.2 mmol). The mixture was stirred at 100 °C for 5 h. Upon completion of the reaction, H_2O (20 mL) was added and the whole was extracted with CH_2Cl_2 (20 mL). The organic layer was washed with brine and dried ($MgSO_4$). The solvent was removed and the residue was purified by column chromatography using *n*-hexane/EtOAc (9:1) to obtain **3** in pure form.

(*Z*)-1-[2-Bromo-2-(phenylsulfonyl)vinyl]-4-chlorobenzene (3a)

Yield: 277 mg (78%); white solid; mp 116–118 °C.

FT-IR (KBr): 3089, 3066, 1649, 1593, 1398, 1317, 1154, 882 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.48 (s, 1 H), 8.01 (d, *J* = 8.0 Hz, 2 H), 7.96 (d, *J* = 8.4 Hz, 2 H), 7.82 (t, *J* = 7.4 Hz, 1 H), 7.72 (t, *J* = 7.6 Hz, 2 H), 7.60 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.7, 137.3, 136.3, 135.1, 132.3, 131.0, 130.2, 129.4, 129.1, 121.7.

MS (EI): *m*/*z* calcd for $C_{14}H_{10}BrClO_2S$: 355.93; found: 357.

Anal. Calcd for $C_{14}H_{10}BrClO_2S$: C, 47.02; H, 2.82; S, 8.97. Found: C, 47.3; H, 3.0; S, 8.85.

(*Z*)-1-[2-Bromo-2-(phenylsulfonyl)vinyl]-2-chlorobenzene (3b)

Yield: 291 mg (82%); white solid; mp 118–120 °C.

FT-IR (KBr): 3061, 3022, 2955, 1583, 1388, 1206, 1150, 751 cm^{-1}.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.51 (s, 1 H), 8.02 (d, *J* = 8.0 Hz, 2 H), 7.86 (t, *J* = 7.2 Hz, 1 H), 7.77 (q, *J* = 7.6 Hz, 3 H), 7.64 (d, *J* = 8.0 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.48 (t, *J* = 7.4 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 137.6, 136.9, 135.3, 133.7, 132.5, 131.1, 130.4, 130.2, 129.1, 127.9, 125.4.

MS (EI): *m*/*z* calcd for $C_{14}H_{10}BrClO_2S$: 355.93; found: 357.

Anal. Calcd for $C_{14}H_{10}BrClO_2S$: C, 47.02; H, 2.82; S, 8.97. Found: C, 47.20; H, 2.73; S, 8.91.

(*Z*)-1-[2-Bromo-2-(phenylsulfonyl)vinyl]-4-nitrobenzene (3c)

Yield: 347.7 mg (95%); light yellow crystals; mp 167–169 °C.

FT-IR (KBr): 3103, 3014, 1595, 1516, 1445, 1342, 1153, 851, 804, 752 cm^{-1}.

^{1}H NMR (300 MHz, DMSO-d_6): δ = 8.61 (s, 1 H), 8.32 (d, *J* = 8.7 Hz, 2 H), 8.11 (d, *J* = 8.7 Hz, 2 H), 8.03 (d, *J* = 7.8 Hz, 2 H), 7.83 (t, *J* = 7.1 Hz, 1 H), 7.72 (t, *J* = 7.7 Hz, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 153.3, 143.4, 143.0, 141.6, 140.0, 136.2, 135.0, 133.9, 129.6, 128.9.

MS (EI): *m*/*z* calcd for $C_{14}H_{10}BrNO_4S$: 366.95; found: 366.9.

Anal. Calcd for $C_{14}H_{10}BrNO_4S$: C, 45.67; H, 2.74; N, 3.80; S, 8.71. Found: C, 45.51; H, 2.81; N, 3.84; S, 8.77.

(*Z*)-1-[2-Bromo-2-(phenylsulfonyl)vinyl]-3-nitrobenzene (3d)

Yield: 304 mg (83%); light yellow solid; mp 125–127 °C.

FT-IR (KBr): 3058, 1615, 1437, 1323, 1167, 1121, 814, 723, 695 cm^{-1}.

^1H NMR (400 MHz, DMSO-d_6): δ = 8.78 (s, 1 H), 8.65 (s, 1 H), 8.33 (t, *J* = 10.4 Hz, 2 H), 8.05 (d, *J* = 8.4 Hz, 2 H), 7.85–7.78 (m, 2 H), 7.73 (t, *J* = 7.6 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 148.2, 138.2, 137.1, 136.7, 135.2, 133.9, 130.8, 130.2, 129.2, 125.8, 124.7, 124.0.

MS (EI): *m*/*z* calcd for $C_{14}H_{10}BrNO_4S$: 355.93; found: 357.

Anal. Calcd for $C_{14}H_{10}BrNO_4S$: C, 45.67; H, 2.74; N, 3.80; S, 8.71. Found: C, 45.74; H, 2.65; N, 3.91; S, 8.63.

(*Z*)-1-[2-Bromo-2-(methylsulfonyl)vinyl]-4-chlorobenzene (3e)

Yield: 238 mg (81%); white solid; mp 80–82 °C.

FT-IR (KBr): 3081, 3023, 2924, 2851, 1639, 1607, 1403, 1310, 1147, 966, 818, 749 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.19 (s, 1 H), 7.95 (d, *J* = 8.4 Hz, 2 H), 7.62 (d, *J* = 8.7 Hz, 2 H), 3.35 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 137.8, 136.1, 132.2, 131.1, 129.4, 121.9, 39.7.

MS (EI): *m*/*z* calcd for $C_9H_8BrClO_2S$: 293.91; found: 295.58.

Anal. Calcd for $C_9H_8BrClO_2S$: C, 36.57; H, 2.73; S, 10.85. Found: C, 36.71; H, 2.81; S, 11.12.

(*Z*)-1-[2-Bromo-2-(methylsulfonyl)vinyl]-4-nitrobenzene (3f)

Yield: 268 mg (88%); white solid; mp 152–154 °C.

FT-IR (KBr): 3113, 3045, 3014, 2926, 2852, 1615, 1595, 1515, 1346, 1304, 1146, 968, 853 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.38 (s, 1 H), 8.34 (d, *J* = 3.9 Hz, 2 H), 8.11 (d, *J* = 8.7 Hz, 2 H), 3.37 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 148.5, 138.9, 137.4, 131.4, 125.1, 124.2, 39.9.

MS (EI): *m*/*z* calcd for $C_9H_8BrNO_4S$: 304.94; found: 306.

Anal. Calcd for $C_9H_8BrNO_4S$: C, 35.31; H, 2.63; N, 4.58; S, 10.47. Found: C, 35.52; H, 2.71; N, 4.47; S, 10.54.

(*Z*)-1-{[1-Bromo-2-(4-nitrophenyl)vinyl]sulfonyl}-4-methylbenzene (3g)

Yield: 330 mg (87%); white solid; mp 197–199 °C.

FT-IR (KBr): 2956, 1517, 1380, 1329, 1186, 843, 814 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.59 (s, 1 H), 8.34 (d, *J* = 8.7 Hz, 2 H), 8.12 (d, *J* = 9.0 Hz, 2 H), 7.92 (d, *J* = 8.4 Hz, 2 H), 7.54 (d, *J* = 8.1 Hz, 2 H), 2.45 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 148.6, 146.2, 138.8, 137.9, 134.0, 131.5, 130.8, 129.3, 125.4, 124.2, 21.7.

MS (EI): *m*/*z* calcd for $C_{15}H_{12}BrNO_4S$: 380.97; found: 382.

Anal. Calcd for $C_{15}H_{12}BrNO_4S$: C, 47.14; H, 3.16; N, 3.66; S, 8.39. Found: C, 46.95; H, 3.21; N, 3.48; S, 8.55.

(*Z*)-1-Bromo-2-(2-bromo-2-tosylvinyl)benzene (3h)

Yield: 330 mg (80%); white solid; mp 110–112 °C.

FT-IR (KBr): 3066, 3020, 1610, 1492, 1335, 1150, 756 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.47 (s, 1 H), 7.89 (d, *J* = 8.1 Hz, 2 H), 7.78 (dd, *J* = 1.8, 4.5 Hz, 1 H), 7.63 (dd, *J* = 1.2, 7.8 Hz, 1 H), 7.55 (d, *J* = 8.4 Hz, 3 H), 7.48 (dd, *J* = 2.1, 7.2 Hz, 1 H), 2.42 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 146.1, 137.0, 133.9, 133.6, 132.4, 131.1, 130.8, 130.3, 130.2, 129.2, 127.8, 125.8, 21.7.

MS (EI): *m*/*z* calcd for $C_{15}H_{12}Br_2O_2S$: 413.89; found: 416.13.

Anal. Calcd for $C_{15}H_{12}Br_2O_2S$: C, 43.30; H, 2.91; S, 7.70. Found: C, 43.42; H, 2.93; S, 7.62.

(*Z*)-1-({1-Bromo-2-[4-(trifluoromethyl)phenyl]vinyl}sulfonyl)-4-methylbenzene (3i)

Yield: 391 mg (97%); white solid; mp 110–112 °C.

FT-IR (KBr): 3057, 3027, 2922, 2852, 1600, 1492, 1325, 1155, 1087, 828, 756 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.55 (s, 1 H), 8.07 (d, *J* = 8.4 Hz, 2 H), 7.89 (q, *J* = 7.6 Hz, 4 H), 7.52 (d, *J* = 8.1 Hz, 2 H), 2.44 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 146.0, 138.3, 136.4, 134.1, 131.1, 131.0, 130.7, 129.3, 126.0 (q, *J* = 3.75 Hz), 124.3, 122.5, 21.6.

^{19}F NMR (283 MHz, DMSO-d_6): δ = –61.4.

MS (EI): *m*/*z* calcd for $C_{16}H_{12}BrF_3O_2S$: 403.97; found: 405.

Anal. Calcd For $C_{16}H_{12}BrF_3O_2S$: C, 47.42; H, 2.98; S, 7.91. Found: C, 47.5; H, 3.12; S, 8.07.

(*Z*)-1-(2-Bromo-2-tosylvinyl)-3-methoxybenzene (3j)

Yield: 288.4 mg (79%); white solid; mp 220–222 °C.

FT-IR (KBr): 3028, 2908, 2850, 1658, 1561, 1370, 1341, 1182, 780 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.85 (s, 1 H), 8.03 (d, *J* = 8.4 Hz, 2 H), 7.92 (q, *J* = 4.3 Hz, 1 H), 7.59 (m, 4 H), 7.45 (d, *J* = 3.0 Hz, 1 H), 3.91 (s, 3 H), 2.49 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 146.8, 146.2, 144.8, 143.4, 138.2, 131.1, 127.7, 127.3, 126.3, 112.3, 106.8, 56.3, 21.7.

MS (EI): *m*/*z* calcd for $C_{16}H_{15}BrO_3S$: 365.99; found: 367.26.

Anal. Calcd for $C_{16}H_{15}BrO_3S$: C, 52.33; H, 4.12; S, 8.73. Found: C, 52.13; H, 4.41; S, 8.49.

(*Z*)-1-[2-Bromo-2-(phenylsulfonyl)vinyl]-4-methylbenzene (3k)

Yield: 212 mg (65%); white solid; mp 101–110 °C.

FT-IR (KBr): 3056, 2912, 1609, 1585, 1313, 1125, 872 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.34 (s, 1 H), 7.94 (q, *J* = 8.3 Hz, 4 H), 7.84 (d, *J* = 7.8 Hz, 1 H), 7.38 (m, 4 H), 2.29 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 146.4, 134.1, 133.7, 130.9, 129.4, 127.6, 127.3, 126.2, 125.0, 120.4, 117.9, 113.6, 91.4, 21.5.

MS (EI): *m*/*z* calcd for $C_{15}H_{13}BrO_2S$: 335.98; found: 337.23.

Anal. Calcd for $C_{15}H_{13}BrO_2S$: C, 53.42; H, 3.89; S, 9.51. Found: C, 53.33; H, 3.96; S, 9.43.

(*Z*)-3-[2-Bromo-2-(phenylsulfonyl)vinyl]-2-chloroquinoline (3l)

Yield: 326 mg (80%); white solid; mp 183–185 °C.

FT-IR (KBr): 3060, 1646, 1611, 1447, 1384, 1324, 1154, 1084, 714 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.15 (s, 1 H), 7.81 (t, *J* = 4.9 Hz, 3 H), 7.67 (t, *J* = 5.6 Hz, 1 H), 7.59 (d, *J* = 2.7 Hz, 3 H), 7.48 (t, *J* = 5.9 Hz, 1 H), 7.37 (m, 1 H), 6.94 (d, *J* = 5.7 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 149.6, 138.8, 138.7, 136.1, 135.8, 135.5, 134.0, 132.4, 131.6, 130.3, 130.2, 129.7, 129.6, 128.7, 127.1.

MS (EI): *m*/*z* calcd for $C_{17}H_{11}BrClNO_2S$: 406.94; found: 408.

Anal. Calcd for $C_{17}H_{11}BrClNO_2S$: C, 49.96; H, 2.71; N, 3.43; S, 7.85. Found: C, 49.65; H, 2.63; N, 3.49; S, 7.94.

(*Z*)-3-[2-Bromo-2-(phenylsulfonyl)vinyl]-2,6-dichloroquinoline (3m)

Yield: 352 mg (80%); white solid; mp 147–149 °C.

FT-IR (KBr): 3031, 2950, 1597, 1577, 1369, 1324, 1184, 765 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.75 (s, 1 H), 8.48 (s, 1 H), 8.23 (d, *J* = 2.4 Hz, 1 H), 7.97 (t, *J* = 5.9 Hz, 3 H), 7.85 (dd, *J* = 5.4, 9.0 Hz, 1 H), 7.79 (d, *J* = 7.2 Hz, 1 H), 7.70 (t, *J* = 7.5 Hz, 2 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 149.0, 145.8, 139.3, 136.7, 136.5, 135.5, 133.2, 132.9, 130.4, 130.3, 129.3, 127.8, 127.5, 127.4, 127.0.

MS (EI): *m*/*z* calcd for $C_{17}H_{10}BrCl_2NO_2S$: 440.90; found: 441.

Anal. Calcd for $C_{17}H_{10}BrCl_2NO_2S$: C, 46.08; H, 2.27; N, 3.16; S, 7.24. Found: C, 47.0; H, 2.34; N, 3.30; S, 7.24.

(*Z*)-3-[2-Bromo-2-(methylsulfonyl)vinyl]-2-chloro-6-methylquinoline (3n)

Yield: 294 mg (82%); white solid; mp 214–216 °C.

FT-IR (KBr): 3028, 2998, 2853, 1648, 1561, 1370, 1341, 1182, 753 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.80 (s, 1 H), 8.30 (dd, *J* = 0.9, 10.8 Hz, 1 H), 7.94 (q, *J* = 4.2 Hz, 2 H), 7.78 (dd, *J* = 1.8, 8.7 Hz, 1 H), 3.38 (s, 3 H), 2.55 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 147.7, 146.7, 146.0, 139.4, 138.4, 135.5, 128.0, 127.8, 126.7, 126.6, 126.5, 125.7, 39.8, 21.6.

MS (EI): *m*/*z* calcd for $C_{13}H_{11}BrClNO_2S$: 358.94; found: 360.

Anal. Calcd for $C_{13}H_{11}BrClNO_2S$: C, 43.29; H, 3.07; N, 3.88; S, 8.89. Found: C, 42.78; H, 2.95; N, 3.54; S, 8.74.

(*Z*)-3-[2-Bromo-2-(phenylsulfonyl)vinyl]-2-chlorobenzo[*h*]quinolone (3o)

Yield: 342 mg (75%); white solid; mp 150–152 °C.

FT-IR (KBr): 3055, 3021, 1517, 1383, 1148, 1079, 734, 684 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.34 (s, 1 H), 8.26 (s, 1 H), 8.11 (q, *J* = 13.6 Hz, 1 H), 8.00 (m, 1 H), 7.90 (m, 1 H), 7.80 (m, 2 H), 7.64 (m, 6 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 148.3, 147.9, 147.4, 141.3, 139.5, 138.4, 136.1, 136.0, 135.7, 133.0, 130.5, 130.3, 129.8, 129.2, 128.8, 128.6, 128.2, 126.1, 121.5.

MS (EI): *m*/*z* calcd for $C_{21}H_{13}BrClNO_2S$: 456.95; found: 458.

Anal. Calcd for $C_{21}H_{13}BrClNO_2S$: C, 54.98; H, 2.86; N, 3.05; S, 6.99. Found: C, 55.11; H, 2.91; N, 3.12; S, 7.13.

(*Z*)-3-(2-Bromo-2-tosylvinyl)-2-chloro-8-methylquinoline (3p)

Yield: 283 mg (79%); white solid; mp 165–167 °C.

FT-IR (KBr): 3060, 3030, 2950, 2849, 1578, 1369, 1325, 1184, 1151, 765 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.81 (s, 1 H), 8.54 (s, 1 H), 7.98 (d, *J* = 8.1 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 2 H), 7.77 (d, *J* = 6.9 Hz, 1 H), 7.62 (d, *J* = 8.1 Hz, 1 H), 7.58 (d, *J* = 8.1 Hz, 2 H), 2.68 (s, 3 H), 2.47 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 147.6, 146.4, 146.3, 140.3, 136.2, 136.1, 133.8, 132.7, 130.9, 129.3, 128.3, 127.1, 126.7, 125.6, 21.7, 17.7.

MS (EI): *m*/*z* calcd for $C_{19}H_{15}BrClNO_2S$: 434.97; found: 436.

Anal. Calcd for $C_{19}H_{15}BrClNO_2S$: C, 52.25; H, 3.46; N, 3.21; S, 7.34. Found: C, 51.85; H, 3.53; N, 3.41; S, 7.47.

(*Z*)-3-[2-Bromo-2-(methylsulfonyl)vinyl]-2,6-dichloroquinoline (3q)

Yield: 288 mg (76%); white solid; mp 230–232 °C.

FT-IR (KBr): 3058, 2918, 2850, 1650, 1561, 1370, 1331, 1282, 780 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 9.08 (s, 1 H), 8.52 (s, 1 H), 8.03 (s, 1 H), 8.0 (d, *J* = 8.4 Hz, 1 H), 7.54 (d, *J* = 8.1 Hz, 1 H), 2.46 (s, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 146.1, 145.6, 140.5, 135.3, 134.9, 131.7, 130.6, 129.6, 129.2, 129.1, 128.5, 39.6.

MS (EI): *m*/*z* calcd for $C_{12}H_8BrCl_2NO_2S$: 378.88; found: 380.07.

Anal. Calcd for $C_{12}H_8BrCl_2NO_2S$: C, 37.82; H, 2.12; N, 3.68; S, 8.41. Found: C, 37.76; H, 2.01; N, 3.57; S, 8.53.

(*Z*)-3-(2-Bromo-2-tosylvinyl)-2-chloro-6-methoxyquinoline (3r)

Yield: 365 mg (81%); white solid; mp 220–222 °C.

FT-IR (KBr): 3028, 2908, 2850, 1658, 1561, 1370, 1341, 1182, 780 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.72 (s, 1 H), 8.52 (s, 1 H), 7.93 (d, *J* = 8.4 Hz, 3 H), 7.57 (t, *J* = 7.4 Hz, 4 H), 3.91 (s, 3 H), 2.48 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 158.7, 146.3, 145.8, 143.4, 138.7, 136.3, 133.8, 130.9, 129.6, 129.3, 128.0, 127.0, 125.9, 125.1, 107.0, 56.2, 21.7.

MS (EI): *m*/*z* calcd for $C_{19}H_{15}BrClNO_3S$: 450.96; found: 451.

Anal. Calcd for $C_{19}H_{15}BrClNO_3S$: C, 50.41; H, 3.34; N, 3.09; S, 7.08. Found: C, 50.33; H, 3.39; N, 2.98; S, 7.21.

(*Z*)-3-(2-Bromo-2-tosylvinyl)-1-tosyl-1*H*-indole (3s)

Yield: 477 mg (90%); white solid; mp 200–202 °C.

FT-IR (KBr): 3051, 3020, 2950, 2859, 1578, 1369, 1325, 1184, 1051, 745 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.25 (s, 1 H), 8.14 (s, 1 H), 8.05 (q, *J* = 3.9 Hz, 1 H), 7.91–7.87 (m, 4 H), 7.50 (d, *J* = 8.0 Hz, 2 H), 7.46 (d, *J* = 3.2 Hz, 1 H), 7.37 (q, *J* = 2.9 Hz, 2 H), 7.27 (d, *J* = 7.6 Hz, 1 H), 2.45 (s, 3 H), 2.36 (s, 3 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 144.8, 144.0, 139.4, 138.5, 135.1, 132.9, 130.4, 130.3, 129.9, 129.7, 129.0, 128.2, 127.5, 127.4, 126.2, 125.3, 124.4, 21.5, 21.4.

MS (EI): *m*/*z* calcd for $C_{24}H_{20}BrNO_4S_2$: 529.00; found: 530.45.

Anal. Calcd for $C_{24}H_{20}BrNO_4S_2$: C, 54.34; H, 3.80; N, 2.64; S, 12.09. Found: C, 54.17; H, 3.88; N, 2.53; S, 12.16.

Indoline-2,3-dione (5)

Yield: 132 mg (90%); orange crystals; mp 189–191 °C.

FT-IR (KBr): 3447, 3192, 3058, 1730, 1617, 1460, 1330, 1200, 1093 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 11.05 (s, 1 H), 7.59 (td, *J* = 7.7, 1.2 Hz, 1 H), 7.51 (dd, *J* = 7.5, 0.6 Hz, 1 H), 7.07 (td, *J* = 7.5, 0.9 Hz, 1 H), 6.92 (d, *J* = 7.8 Hz, 1 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 184.9, 159.8, 151.2, 138.8, 125.2, 123.2, 118.3, 112.7.

MS (EI): *m*/*z* calcd for $C_8H_5NO_2$: 147.03; found: 147.13.

Anal. Calcd for $C_8H_5NO_2$: C, 65.31; H, 3.43; N, 9.52. Found: C, 66.5; H, 3.57; N, 9.41.

Enynes 6a and 6b; General Procedure

To a mixture of (*Z*)-α-bromovinyl sulfone **3** (0.5 mmol) and phenylacetylene (61 mg, 0.6 mmol) in MeCN (5.0 mL) was added $PdCl_2$ (4.4 mg, 5 mol%), CuI (0.95 mg, 1 mol%), PPh_3 (13.9 mg, 10 mol%), and Et_3N (101 mg, 1 mmol). The resulting mixture was stirred at 80 °C for 45 min. After completion of reaction, H_2O (10 mL) was added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 (2 × 5 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the solvent was removed. The resulting crude product was purified by column chromatography with *n*-hexane/EtOAc (8:2) as eluent.

(*E*)-1-Chloro-4-[4-phenyl-2-(phenylsulfonyl)but-1-en-3-yn-1-yl]benzene (6a)

Yield: 361 mg (95%); white solid; mp 110–112 °C.

FT-IR (KBr): 3054, 2923, 2196, 1585, 1443, 1372, 1283, 847 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.14 (d, *J* = 8.4 Hz, 2 H), 8.04 (t, *J* = 5.0 Hz, 3 H), 7.81–7.68 (m, 3 H), 7.63 (d, *J* = 8.4 Hz, 2 H), 7.51–7.44 (m, 5 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 140.5, 138.7, 136.8, 134.9, 132.3, 131.9, 131.7, 130.8, 130.1, 129.7, 129.5, 128.9, 124.8, 121.0, 102.9, 81.8.

MS (EI): *m*/*z* calcd for $C_{22}H_{15}ClO_2S$: 378.05; found: 378.87.

Anal. Calcd for $C_{22}H_{15}ClO_2S$: C, 69.74; H, 3.99; S, 8.46. Found: C, 69.31; H, 3.82; S, 8.19.

(*E*)-1-Nitro-4-[4-phenyl-2-(phenylsulfonyl)but-1-en-3-yn-1-yl]benzene (6b)

Yield: 357 mg (92%); white solid; mp 120–122 °C.

FT-IR (KBr): 3107, 3061, 2191, 1592, 1541, 1380, 1342, 1153, 844 cm^{-1}.

^1H NMR (300 MHz, DMSO-d_6): δ = 8.39 (q, *J* = 8 Hz, 4 H), 8.21 (s, 1 H), 8.09 (d, *J* = 6.9 Hz, 2 H), 7.83–7.73 (m, 3 H), 7.61–7.50 (m, 5 H).

^{13}C NMR (75 MHz, DMSO-d_6): δ = 148.9, 139.2, 138.9, 138.2, 135.1, 132.2, 131.6, 131.1, 130.2, 129.5, 129.0, 127.8, 124.6, 120.7, 81.6, 73.0.

MS (EI): *m*/*z* calcd for $C_{22}H_{15}NO_4S$: 389.07; found: 389.42.

Anal. Calcd for $C_{22}H_{15}NO_4S$: C, 67.85; H, 3.88; N, 3.60; S, 8.23. Found: C, 67.59; H, 3.97; N, 3.51; S, 8.53.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1706295.

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