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$PhI(OAc)_2$/KI-Mediated Reaction of Aryl Sulfinates with Alkenes, Alkynes, and α,β-Unsaturated Carbonyl Compounds: Synthesis of Vinyl Sulfones and β-Iodovinyl Sulfones

Praewpan Katrun,[a] Supanimit Chiampanichayakul,[a] Kanokwan Korworapan,[a] Manat Pohmakotr,[a] Vichai Reutrakul,[a] Thaworn Jaipetch,[b] and Chutima Kuhakarn*[a]

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(Diacetoxyiodo)benzene [$PhI(OAc)_2$, DIB] was able to promote the reaction of sodium aryl sulfinate and potassium iodide (KI) with alkenes and alkynes to afford the corresponding vinyl sulfones and β-iodovinyl sulfones, respectively, in good yields. The salient features of this reaction are that it employs a commercially available and environmentally benign hypervalent iodine(III) reagent, a one-step reaction, a short reaction time, and mild reaction conditions.

Introduction

Vinyl sulfones are important units in organic synthesis due to the chemical versatility of the sulfonyl moiety.[1] The sulfonyl group, similar to the carbonyl group, has an activating effect to the adjacent double bonds or triple bonds, which enables these compounds to serve as Michael acceptors[2] and electron-deficient ene partners[3] in cycloaddition reactions. Vinyl sulfone containing molecules have been shown to exhibit important biological activities; for example, cysteine protease inhibitors,[4] HIV-1 inhibitors,[5] and inhibitors of a transpeptidase required for cell wall protein anchoring and virulence in *Staphylococcus aureus*.[6] In addition, the sulfonyl group can be exchanged by hydrogen, an alkyl group, a hydroxy group, a carbonyl group, or a nucleophile, and it is also susceptible to β-elimination and sulfur dioxide extrusion, allowing the sulfonyl group to function as a temporary activating functional group.[7] A number of synthetic routes are available toward the synthesis of vinyl sulfones including: a two-step method involving β-elimination of and sulfur oxidation or vice versa,[8] addition of $PhSO_2X$ (X = I, Cl, SePh, ONO_2, HgCl, etc.) to alkenes followed by β-elimination,[9] addition of $PhSO_2X$ (X = I, Cl, etc.) to alkynes,[10] Horner–Wadsworth–Emmons reaction of carbonyl compounds and sulfonyl phosphoranes,[11] hydrozirconation reaction of acetylenic sulfones,[12] hydrozirconation of terminal alkynes followed by reaction with sulfonyl chloride,[13] hydrotelluration of acetylenic sulfones,[14] selenosulfonation to alkynes,[15] nucleophilic addition to 1-phenylseleno-2-(arenesulfonyl)-ethyne,[16] addition of sodium benzenesulfinate to alkynylselenonium salts,[17] displacement of β-bromostyrene derivatives with sodium arenesulfinate,[18] reaction of alkenyltriphenylbismuthonium tetrafluoroborates with aryl sulfinate,[19] reaction of β-haloalkenylphenyliodonium salts with sodium benzenesulfinate,[20] palladium-catalyzed reactions,[21] copper-catalyzed reactions,[22] cross-metathesis reactions,[23] carbomagnesiation of acetylenic sulfones,[24] and reaction of 1,2-dibromoalkanes with sulfinic acid sodium salts.[25] Considering the importance of vinyl sulfones both as reactive synthons and as biologically active moieties in vinyl sulfone containing compounds, it is still of high interest to develop simple and efficient methods for the synthesis of vinyl sulfones.

During the past two decades, the versatility of hypervalent iodine reagents in organic synthesis is well recognized owing to their mild, highly selective, and environmentally benign properties for effecting a number of oxidative transformations.[26] Currently, both iodine(V) and iodine(III) reagents are widely used in organic synthesis. Despite their intriguing synthetic applications, widely used iodine(V) reagents are potentially explosive. As a result, iodine(III) reagents have received much more attention and have found broad application in organic synthesis.[27] One of the most important and commercially available iodine(III) reagents is (diacetoxyiodo)benzene [$PhI(OAc)_2$], which has several commonly used abbreviations, such as BAIB, DIB, PIDA, IBD, or IBDA. It is easy to handle, nontoxic, commercially available, and comparable in reactivity to heavy metal containing reagents. The synthetic utilities of $PhI(OAc)_2$ as an efficient oxidizing agent have been demonstrated by several groups.[28] The combination of $PhI(OAc)_2$ with halide salts has been reported for electrophilic halogenations of sub-

[a] Department of Chemistry and Center for Innovation in Chemistry (PERCH-CIC), Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand
E-mail: scckk@mahidol.ac.th
[b] Mahidol University, Kanchanaburi Campus, Saiyok, Kanchanaburi 71150, Thailand
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strates, particularly olefins, followed by nucleophilic-assisted halonium ion ring opening.[29]

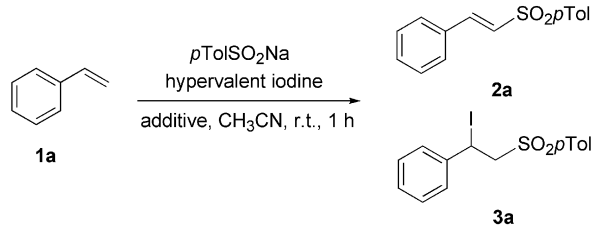
Results and Discussion

As a part of our ongoing research on the chemistry of hypervalent iodine reagents,[30] we herein describe our work on the development of a vinyl sulfone protocol by PhI(OAc)$_2$/KI-mediated reaction of aryl sulfinates with alkenes and alkynes. Our experiment was first conducted by using styrene and sodium *p*-toluenesulfinate as model substrates to search for optimum reaction conditions (Table 1).

The reaction was initially carried out in water by using PhI(OAc)$_2$ (2.2 equiv.) and Et$_4$NI (1 equiv.) as an additive and sodium *p*-toluenesulfinate (4 equiv.; Table 1, Entry 1). A facile reaction took place within 30 min to yield β-iodosulfone **3a** and expected α,β-unsaturated sulfone **2a** in a ratio of 19:1. Higher conversion to α,β-unsaturated sulfone **2a** was observed when the reaction time was extended from 0.5 to 3 h (Table 1, Entry 2). The reactions conducted in aqueous CH$_3$CN, aqueous THF, and CH$_3$OH gave comparable results, and a mixture of **2a** and **3a** was obtained (Table 1, Entries 3–5). Gratifying, when EtOAc was employed as the solvent, **2a** was obtained as the major product (**2a**/**3a** = 2:1). Among organic solvents screened, CH$_3$CN gave the best result (Table 1, Entries 7–10), yielding **2a** in 90% yield after chromatographic purification (Table 1, Entry 10). A slightly lower yield was observed when the reaction was carried out with a shorter reaction time or with a decrease in the loading of PhI(OAc)$_2$ from 2.2 to 1.1 equiv. (Table 1, Entries 11 and 12). Decreasing the stoichiometry of sodium *p*-toluenesulfinate led to a dramatic decrease in the reaction yield (Table 1, Entry 13). An excellent yield of **2a** was observed when the amount of PhI(OAc)$_2$ employed was as low as 1.5 equiv., however, with a prolonged reaction time (Table 1, Entry 14 vs. 10).

Having established the most efficient reaction conditions (Table 1, Entry 14), we next investigated the efficiency of some hypervalent iodine reagents and types of additives, and the results are listed in Table 2. When using Et$_4$NI as

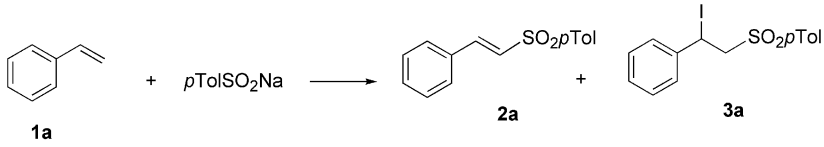
Table 2. Optimization of hypervalent iodine reagents and additives.[a]



Entry	Hypervalent iodine	Additive	Ratio[b] **2a**/**3a**	Yield of **2a**[c] [%]
1	PhI(OAc)$_2$	Et$_4$NI		91[d]
2	IBX	Et$_4$NI		62[d]
3	PhI(OCOCF$_3$)$_2$	Et$_4$NI	1:3	
4	PhI(OAc)$_2$	Bu$_4$NI		88[d]
5	PhI(OAc)$_2$	LiI	2:1	
6	PhI(OAc)$_2$	NaI	4:1	
7	PhI(OAc)$_2$	KI		85[d]

[a] All reactions were performed by using styrene (0.5 mmol), *p*TolSO$_2$Na (4 equiv.), hypervalent iodine reagent (1.5 equiv.), and additive (1 equiv.) in CH$_3$CN at room temperature for 1 h. [b] Product ratios were calculated from integration of the signals in the ^{1}H NMR (300 MHz) spectrum of the crude product. [c] Isolated yields after chromatographic purification. [d] The formation of **3a** was not observed by ^{1}H NMR (300 MHz) spectroscopic analysis of the crude products.

Table 1. Optimization of reaction conditions.[a]



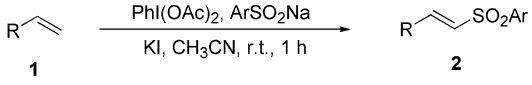
Entry	PhI(OAc)$_2$ [equiv.]	*p*TolSO$_2$Na [equiv.]	Solvent	Time [h]	Ratio[b] **2a**/**3a**	Yield of **2a**[c] [%]
1	2.2	4	H$_2$O	0.5	1:19	
2	2.2	4	H$_2$O	3	1:7	
3	2.2	4	H$_2$O/CH$_3$CN (1:3)	0.5	2:5	
4	2.2	4	H$_2$O/THF (1:3)	0.5	2:3	
5	2.2	4	CH$_3$OH	0.5	1:3	
6	2.2	4	EtOAc	3	2:1	
7	2.2	4	DMSO	0.5		64[d]
8	2.2	4	CHCl$_3$	0.5		60[d]
9	2.2	4	CH$_2$Cl$_2$	5		58[d]
10	2.2	4	CH$_3$CN	0.5		90[d]
11	2.2	4	CH$_3$CN	0.25		80[d]
12	1.1	4	CH$_3$CN	0.5		79[d]
13	2.2	2	CH$_3$CN	0.5		33[d]
14	1.5	4	CH$_3$CN	1		91[d]

[a] All reactions were performed by using styrene (0.5 mmol) and Et$_4$NI (1 equiv.) at room temperature. [b] Product ratios were calculated from integration of the signals in the ^{1}H NMR (300 MHz) spectrum of the crude product. [c] Isolated yield after chromatographic purification. [d] The formation of **3a** was not observed by ^{1}H NMR (300 MHz) spectroscopic analysis of the crude products.

an additive, the iodine(V) reagent IBX gave inferior results (Table 2, Entry 2) and the reaction conversion was lowered dramatically by utilizing $PhI(OCOCF_3)_2$ (Table 2, Entry 3). Among the hypervalent iodine reagents tested, and on the basis of both efficiency and availability of hypervalent iodine compounds, $PhI(OAc)_2$ was chosen as the oxidant for this reaction. The effect of additives was also briefly investigated. Even though tetraalkylammonium iodide salts gave excellent yields of vinyl sulfone **2a**, their highly hygroscopic nature was a major drawback (Table 2, Entries 1 and 4). The ease of handling the alkali metal iodides prompted us to examine their reactivity (Table 2, Entries 5–7). Both LiI and NaI gave a mixture of **2a** and **3a** as can be seen from the ^{1}H NMR spectrum of the crude product. To our delight, KI gave comparable results to those obtained by using tetraalkylammonium iodide salts as additives (Table 2, Entry 7).

On the basis of the results shown in Table 2 (Entry 7), the optimized reaction conditions were chosen for further exploration of the substrate scope and the arenesulfinate sodium salts of this reaction.[32] It was found that most styrene derivatives underwent the reaction to provide the corresponding vinyl sulfones in good yields (Table 3). *p*-Toluenesulfinate and benzenesulfinate sodium salts worked equally well in this reaction. Moderate yields were observed for electron-releasing-substituted styrene (Table 3, Entries 6 and 13).

Table 3. Oxidative sulfonylation of styrene derivatives.[a]

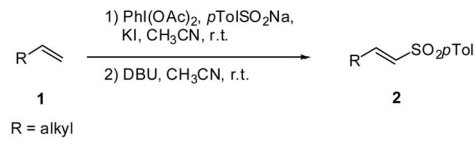


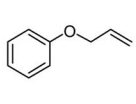
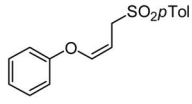
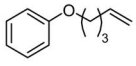
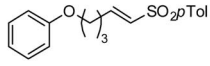
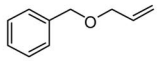
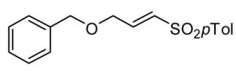
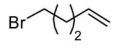
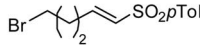
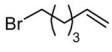
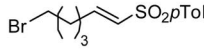
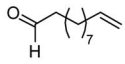
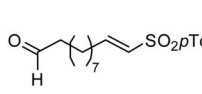
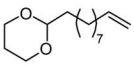
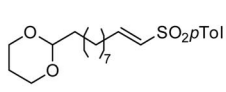
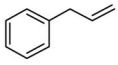
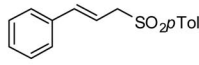
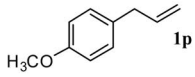
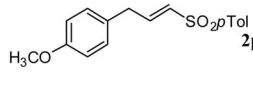
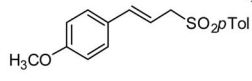
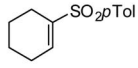
Entry	R	Substrate	Ar	Product	Yield [%][b]
1	C_6H_5	**1a**	*p*Tol	**2a**	85
2	4-BrC_6H_4	**1b**	*p*Tol	**2b**	88
3	4-ClC_6H_4	**1c**	*p*Tol	**2c**	86
4	2-ClC_6H_4	**1d**	*p*Tol	**2d**	77
5	4-$CH_3C_6H_4$	**1e**	*p*Tol	**2e**	67
6	4-$CH_3OC_6H_4$	**1f**	*p*Tol	**2f**	48
7	4-$CH_3OCOC_6H_4$	**1g**	*p*Tol	**2g**	80
8	C_6H_5	**1a**	Ph	**2aa**	90
9	4-BrC_6H_4	**1b**	Ph	**2bb**	87
10	4-ClC_6H_4	**1c**	Ph	**2cc**	88
11	2-ClC_6H_4	**1d**	Ph	**2dd**	82
12	4-$CH_3C_6H_4$	**1e**	Ph	**2ee**	82
13	4-$CH_3OC_6H_4$	**1f**	Ph	**2ff**	55
14	4-$CH_3OCOC_6H_4$	**1g**	Ph	**2gg**	84

[a] All reactions were performed by using the substrate (0.5 mmol), *p*TolSO_2Na or PhSO_2Na (4 equiv.), $PhI(OAc)_2$ (1.5 equiv.), and KI (1 equiv.) in CH_3CN at room temperature for 1 h. [b] Isolated yield.

The sulfonylation of aliphatic alkenes as well as cyclic alkenes was also investigated, and the results are summarized in Table 4. Under standard reaction conditions, aliphatic alkenes and cyclic alkenes afforded mixtures of vinyl sulfones and β-iodosulfones as observed by analysis of the ^{1}H NMR spectra of the crude products. Vinyl sulfones could be obtained by treatment of the crude mixtures with DBU in CH_3CN at room temperature for 30 min. A variety of aliphatic alkenes including those containing an oxygen atom (Table 4, Entries 1–3), a bromine atom (Table 4, Entries 4 and 5), an aldehyde function (Table 4, Entry 6), and a 1,3-dioxane moiety (Table 4, Entry 7) gave the corresponding products in good yields (70–89%). Allyl phenyl ether and allylbenzene derivatives yielded products derived from double bond isomerization as major products (Table 4, Entries 1, 8, and 9). It is also worth noting that allylsulfone **2h** was obtained as a *cis* alkene, whose stereochemistry was assigned on the basis of its spectroscopic

Table 4. Oxidative sulfonylation of aliphatic alkenes and cyclic alkene.[a]



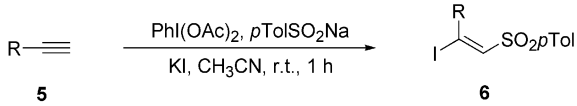
Entry	Alkene		Product		Yield [%][b]
1		**1h**		**2h**	70
2		**1i**		**2i**	84
3		**1j**		**2j**	75
4		**1k**		**2k**	80
5		**1l**		**2l**	89
6		**1m**		**2m**	80
7		**1n**		**2n**	81
8		**1o**		**2o**	72
9		**1p**		**2p**	11
				**4p**	63
10		**1q**		**2q**	56

[a] Reagents and conditions: 1) Alkene (0.5 mmol), *p*TolSO_2Na (4 equiv.), $PhI(OAc)_2$ (1.5 equiv.), KI (1 equiv.), CH_3CN, room temp., 1 h; 2) DBU, CH_3CN, room temp., 30 min. [b] Isolated yield after two steps.

data (NOE experiments).[33] Finally, cyclic vinylsulfone **2q** could also be prepared in moderate yield (56%) from cyclohexene.

The methodology works equally well with alkynes (Table 5). The optimized reaction conditions were applied to the reaction of arylacetylenes possessing substituents with different electronic properties on the phenyl rings (Table 5, Entries 1–4) and 1-octyne (Table 5, Entry 5). Facile reactions occurred, giving rise to the corresponding β-iodovinyl sulfones in high yields, each as a single geometrical isomer. On the basis of the spectroscopic data of the β-iodovinyl sulfone derived from 1-octyne (NOE experiments), the iodine atom was confirmed to be *anti* to the sulfonyl group. The stereochemistry of compounds **6a**–**d** was then assigned on the basis of that of **6e**.

Table 5. Sulfonylation of alkynes.[a]



5 6

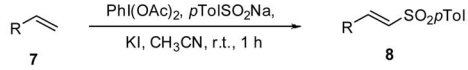
Entry	R	Substrate	Product	Yield [%][b]
1	C_6H_5	**5a**	**6a**	81
2	4-$CH_3C_6H_4$	**5b**	**6b**	86
3	4-$CH_3OC_6H_4$	**5c**	**6c**	77
4	4-$NO_2C_6H_4$	**5d**	**6d**	77
5	$CH_3(CH_2)_5$	**5e**	**6e**	64

[a] All reactions were performed by using the substrate (0.5 mmol), *p*TolSO$_2$Na (4 equiv.), PhI(OAc)$_2$ (1.5 equiv.), and KI (1 equiv.) in CH_3CN at room temperature for 1 h. [b] Isolated yields.

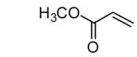
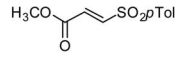
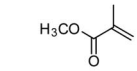
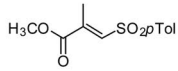
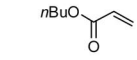
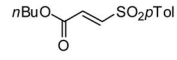
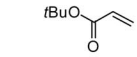
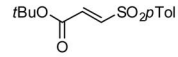
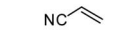
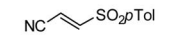
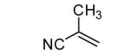
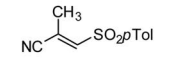
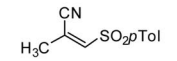
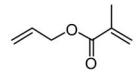
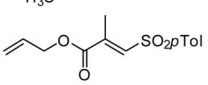
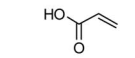
Finally, oxidative β-sulfonylation of α,β-unsaturated carbonyl derivatives was investigated, and the results are summarized in Table 6. We found that the optimized conditions prove to be suitable for a range of alkyl ester derivatives, and these reactions went smoothly to provide the β-toluenesulfonyl-α,β-unsaturated esters in good yields (62–81% yield; Table 6, Entries 1–4). A low yield (33%) was observed with acrylonitrile (Table 6, Entry 5). However, methacrylonitrile afforded a mixture of two possible geometrical isomers, which could be separated by column chromatography [**8fa**(*E*)/**8fb**(*Z*) = 3:1] in good yields (Table 6, Entry 6). Allyl methacrylate reacted solely at the electron deficient alkene moiety to give the corresponding product **8g** in moderate yield (59%; Table 6, Entry 7). Acrylic acid gave no identifiable product (Table 6, Entry 8).

A probable mechanism for the formation of vinyl sulfones is outlined in Scheme 1. DIB promotes the oxidation of the iodide anion, yielding acetylhypoiodite (**A**) as a putative intermediate. Subsequent reaction of **A** with aryl sulfinate gives arylsulfonyl iodide (**B**), which readily mediates iodosulfonylation of the alkene.[31] Spontaneous elimination of HI then takes place when the R group is an aryl or conjugated functional group. Aliphatic alkenes require a two-step reaction involving β-iodosulfonylation followed by base-induced dehydroiodination. To support our proposed mechanistic pathway, NMR spectroscopic experiments were

Table 6. Oxidative β-sulfonylation of α,β-unsaturated carbonyl derivatives and acrylonitrile compounds.[a]

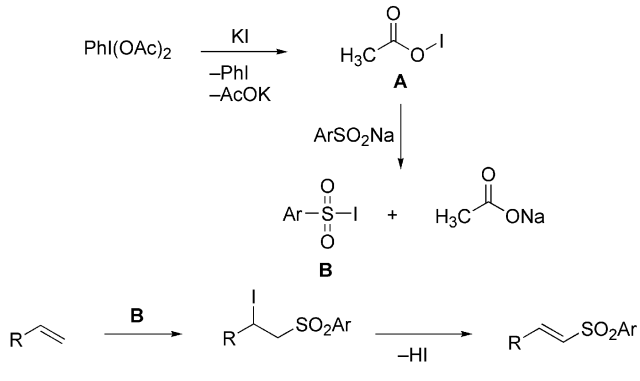


7 8

Entry	Alkene		Product		Yield [%][b]
1		**7a**		**8a**	62
2		**7b**		**8b**	81
3		**7c**		**8c**	78
4		**7d**		**8d**	62
5		**7e**		**8e**	33
6		**7f**		**8fa** (*E*)	53
				**8fb** (*Z*)	18
7		**7g**		**8g**	59
8		**7h**			–

[a] All reactions were performed by using the substrate (0.5 mmol), *p*TolSO$_2$Na (4 equiv.), PhI(OAc)$_2$ (1.5 equiv.), and KI (1 equiv.) in CH_3CN at room temperature for 1 h. [b] Isolated yields.

performed. When a 1:1 mixture of DIB/KI in $CDCl_3$ was examined by ^{1}H NMR spectroscopy, a new peak at δ = 2.10 ppm (s) gradually appeared and replaced the acetyl signal of DIB at δ = 2.02 ppm (s). The new singlet at δ = 2.10 ppm was assigned to acetylhypoiodite (AcOI).[34]



Scheme 1. Plausible mechanistic pathway.

Finally, to probe the efficiency and generality of the present method against those previously reported utilizing reactive arenesulfonyl iodides prepared in situ by oxidation of the arenesulfinate sodium salts with oxidizing agents, comparative studies were conducted. By following the method described by Nair et al. employing CAN as an oxidant, it was found that α,β-unsaturated carbonyl derivatives were not suitable substrates and vinyl sulfones **8a** and **8c** were obtained in 17 and 40% yield, respectively.[9d] The efficiency of the reaction dramatically depends on the type of solvent when molecular iodine was employed as the oxidizing reagent. Acetone gave poor results, which is in good agreement with those described by Julia and co-workers.[9b] When acetonitrile was used as the solvent by employing pTolSO$_2$Na (4 equiv.) and I_2 (1.5 equiv.) at room temperature for 1 h, styrene derivatives gave β-iodosulfones as major products along with vinyl sulfones, whereas the reactions of aliphatic alkenes did not work well and led to recovery of starting materials in 61–90% yield. In contrast to that reported by Yus, the reactions of **1a**, **1k**, and **7a** performed in dichloromethane by using pTolSO$_2$Na (4 equiv.) and I_2 (1.5 equiv.) at room temperature for 1 h gave the corresponding β-iodosulfones exclusively in good yields. However, an additional elimination step mediated by base is required to obtain the vinyl sulfones.

Conclusions

In conclusion, we have demonstrated the synthetic application of (diacetoxyiodo)benzene (DIB)/KI to promote the reaction of sodium arenesulfinates with alkenes and alkynes. The method is simple and be conducted in one pot under non-anhydrous conditions and tolerates a variety of functional groups. The results, in many aspects, are superior to those previously reported. In view of the experimental simplicity and the mild reaction conditions, the present method is an important alternative to existing methods for the synthesis of vinyl sulfones and β-iodovinyl sulfones, which are an important class of compounds in organic chemistry.

Experimental Section

General Remarks: All reagents were obtained from commercial sources and used without further purification. Thin-layer chromatography was carried out on TLC alumina sheets with silica gel 60 F254 (Merck). Chromatographic purification of products was accomplished by using column chromatography on silica gel with hexanes/EtOAc as eluent and all solid compounds were recrystallized from hexanes/CH_2Cl_2. Melting points were recorded with a digital Electrothermal Melting 9100 apparatus. ^{1}H NMR spectra were recorded with a Bruker DPX-300 (300 MHz), Bruker Avance-300 (300 MHz), or Bruker Avance-500 (500 MHz) spectrometer in $CDCl_3$ by using tetramethylsilane (δ = 0 ppm) as an internal standard. ^{13}C NMR spectra were recorded with a Bruker Avance-300 (75 MHz) spectrometer by using tetramethylsilane as an internal standard. Infrared spectra were recorded with a Perkin–Elmer 683 GX FTIR System spectrometer. High-resolution mass spectra (HRMS) were recorded with a Bruker micro TOF spectrometer in the ESI mode.

General Procedure A

One-Step Synthesis of Vinyl Sulfones: $PhI(OAc)_2$ (241.6 mg, 0.75 mmol) was added to a suspension of the alkene or alkyne (0.5 mmol), sodium arenesulfinate (2.0 mmol), and KI (83.0 mg, 0.5 mmol) in CH_3CN (2 mL), and the reaction mixture was vigorously stirred at room temperature for 1 h. Upon completion of the reaction, the reaction mixture was quenched by the addition of a saturated aqueous solution of $Na_2S_2O_3$ (5 mL) and basified with a saturated aqueous solution of $NaHCO_3$ (5 mL). Further stirring was followed by extraction with EtOAc (3 × 15 mL). The combined organic extract was washed with H_2O (15 mL) and brine (15 mL), dried ($MgSO_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography.

(*E*)-1-Methyl-4-(styrylsulfonyl)benzene (2a):[9a] According to general procedure A, styrene (**1a**; 52.0 mg, 0.5 mmol) and sodium p-toluenesulfinate (356.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 20% EtOAc in hexanes) gave **2a** (109.8 mg, 85% yield; white solid, m.p. 118–120 °C, ref.[9a] m.p. 120–121 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.85 (d, J = 8.3 Hz, 2 H, ArH), 7.68 (d, J = 15.4 Hz, 1 H, CH), 7.51–7.35 (m, 7 H, ArH), 6.87 (d, J = 15.4 Hz, 1 H, CH), 2.46 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 141.9, 137.8, 132.5, 131.1, 130.3, 129.9, 129.0, 128.5, 127.7, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3046, 2924, 1615, 1595, 1496, 1449, 1315, 1285, 1143, 1086, 973, 810, 748, 665 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{15}H_{14}O_2SNa$ [M + Na]$^+$ 281.0612; found 281.0646.

(*E*)-1-Bromo-4-(2-tosylvinyl)benzene (2b): According to general procedure A, 4-bromostyrene (**1b**; 91.9 mg, 0.5 mmol) and sodium p-toluenesulfinate (356.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 20% EtOAc in hexanes) gave **2b** (148.4 mg, 88% yield; white solid, m.p. 163–164 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.1 Hz, 2 H, ArH), 7.51 (d, J = 15.4 Hz, 1 H, CH), 7.44 (d, J = 8.4 Hz, 2 H, ArH), 7.29–7.24 (m, 4 H, ArH), 6.78 (d, J = 15.4 Hz, 1 H, CH), 2.36 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.5, 140.5, 137.5, 132.3, 131.4, 130.0, 129.8, 128.4, 127.7, 125.5, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3053, 1614, 1583, 1482, 1303, 1287, 1142, 1084, 1068, 1008, 861, 785, 671 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{15}H_{13}BrO_2SNa$ [M + Na]$^+$ 358.9717; found 358.9708.

(*E*)-[2-(Phenylsulfonyl)vinyl]benzene (2aa):[35] According to general procedure A, styrene (**1a**; 52.0 mg, 0.5 mmol) and sodium benzenesulfinate (328.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 20% EtOAc in hexanes) gave **2aa** (109.9 mg, 90% yield; white solid, m.p. 68–70 °C, ref.[35] m.p. 75–76 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.99–7.96 (m, 2 H, ArH), 7.69 (d, J = 15.4 Hz, 1 H, CH), 7.64–7.34 (m, 8 H, ArH), 6.89 (d, J = 15.4 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.5, 140.8, 133.3, 132.4, 131.2, 129.3, 129.1, 128.5, 127.6, 127.3 ppm. IR (KBr): $\tilde{\nu}$ = 3056, 1612, 1576, 1496, 1448, 1301, 1177, 1146, 1086, 972, 856, 818, 743, 690 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{14}H_{12}O_2SNa$ [M + Na]$^+$ 267.0456; found 267.0439.

(*E*)-1-Bromo-4-[2-(phenylsulfonyl)vinyl]benzene (2bb): According to general procedure A, 4-bromostyrene (**1b**; 91.9 mg, 0.5 mmol) and sodium benzenesulfinate (328.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 20% EtOAc in hexanes) gave **2bb** (140.6 mg, 87% yield; white solid, m.p. 152–154 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.96 (d, J = 7.4 Hz, 2 H, ArH), 7.65–7.48 (m, 6 H, ArH, CH), 7.34 (d, J = 8.6 Hz, 2 H, ArH), 6.91 (d, J = 15.5 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.0,

140.5, 133.5, 132.4, 131.3, 129.9, 129.4, 128.1, 127.7, 125.5 ppm. IR (KBr): $\tilde{\nu}$ = 3056, 1619, 1583, 1485, 1446, 1398, 1308, 1285, 1153, 1085, 1068, 1008, 976, 856, 784 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{14}H_{11}O_2SBrNa$ $[M + Na]^+$ 344.9561; found 344.9577.

(*E*)-1-Chloro-2-[2-(phenylsulfonyl)vinyl]benzene (2dd): According to general procedure A, 2-chlorostyrene (**1d**; 69.3 mg, 0.5 mmol) and sodium benzenesulfinate (328.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 10% EtOAc in hexanes) gave **2dd** (114.3 mg, 82% yield; pale-yellow solid, m.p. 98–100 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.08 (d, J = 15.4 Hz, 1 H, CH), 7.98–7.95 (m, 2 H, ArH), 7.66–7.49 (m, 4 H, ArH), 7.42–7.25 (m, 3 H, ArH), 6.93 (d, J = 15.4 Hz, 1 H, CH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.4, 138.4, 135.3, 133.5, 131.9, 130.7, 130.4, 130.1, 129.4, 128.4, 127.8, 127.2 ppm. IR (KBr): $\tilde{\nu}$ = 3051, 1607, 1591, 1470, 1448, 1304, 1201, 1148, 1086, 1042, 971, 824, 747, 689 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{14}H_{11}O_2SClNa$ $[M + Na]^+$ 301.0066; found 301.0059.

(*E*)-1-Methoxy-4-[2-(phenylsulfonyl)vinyl]benzene (2ff): According to general procedure A, 4-methoxystyrene (**1f**; 67.1 mg, 0.5 mmol) and sodium benzenesulfinate (328.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 20% EtOAc in hexanes) gave **2ff** (75.4 mg, 55% yield; white solid, m.p. 74–77 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.86–7.83 (m, 2 H, ArH), 7.54 (d, J = 15.4 Hz, 1 H, CH), 7.50–7.40 (m, 3 H, ArH), 7.33 (d, J = 8.8 Hz, 2 H, ArH), 6.79 (d, J = 8.5 Hz, 2 H, ArH), 6.64 (d, J = 15.4 Hz, 1 H, CH), 3.71 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.1, 142.3, 141.2, 133.1, 130.3, 129.2, 127.5, 125.0, 124.5, 114.5, 55.4 ppm. IR (KBr): $\tilde{\nu}$ = 3054, 2991, 2835, 1603, 1573, 1512, 1447, 1422, 1306, 1287, 1262, 1173, 1145, 1082, 1038, 979, 867, 803, 752, 685 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{15}H_{14}O_3SNa$ $[M + Na]^+$ 297.0561; found 297.0563.

(*E*)-1-[2-Iodo-2-(4-nitrophenyl)vinylsulfonyl]-4-methylbenzene (6d): According to general procedure A, 4-ethynylnitrobenzene (**5d**; 73.6 mg, 0.5 mmol) and sodium *p*-toluenesulfinate (356.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 20% EtOAc in hexanes) gave **6d** (165.3 mg, 77% yield; pale-yellow solid, m.p. 186–189 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.12 (d, J = 8.8 Hz, 2 H, ArH), 7.48 (d, J = 8.1 Hz, 2 H, ArH), 7.35 (d, J = 8.8 Hz, 2 H, ArH), 7.31 (s, 1 H, CH), 7.21 (d, J = 8.1 Hz, 2 H, ArH), 2.36 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 148.1, 145.9, 145.4, 142.5, 136.8, 130.1, 128.5, 127.8, 123.2, 109.1, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3077, 3041, 1602, 1583, 1519, 1345, 1321, 1290, 1145, 1082, 1016, 886, 845, 817, 761, 653 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{15}H_{12}INO_4SNa$ $[M + Na]^+$ 451.9429; found 451.9456.

(*E*)-Methyl 2-Methyl-3-tosylacrylate (8b): According to general procedure A, methyl methacrylate (**7b**; 50.0 mg, 0.5 mmol) and sodium *p*-toluenesulfinate (356.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 15% EtOAc in hexanes) gave **8b** (103.0 mg, 81% yield; colorless solid, m.p. 53–56 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.3 Hz, 2 H, ArH), 7.37 (d, J = 8.4 Hz, 2 H, ArH), 7.22 (q, J = 1.5 Hz, 1 H, CH), 3.77 (s, 3 H, CH_3), 2.45 (s, 3 H, CH_3), 2.32 (d, J = 1.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.0, 145.1, 140.5, 137.6, 137.6, 130.0, 127.6, 52.9, 21.5, 13.2 ppm. IR (KBr): $\tilde{\nu}$ = 3048, 2959, 1717, 1630, 1596, 1490, 1437, 1381, 1312, 1267, 1182, 1145, 1088, 973, 857, 817, 737 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{12}H_{14}O_4SNa$ $[M + Na]^+$ 277.0510; found 277.0459.

(*E*)-Butyl 3-Tosylacrylate (8c): According to general procedure A, *n*-butyl acrylate (**7c**; 56.1 mg, 0.5 mmol) and sodium *p*-toluenesulfinate (356.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 10% EtOAc in hexanes) gave **8c** (110.1 mg, 78% yield; colorless viscous liquid). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 8.3 Hz, 2 H, ArH), 7.37 (d, J = 8.0 Hz, 2 H, ArH), 7.31 (d, J = 15.1 Hz, 1 H, CH), 6.79 (d, J = 15.1 Hz, 1 H, CH), 4.17 (t, J = 6.6 Hz, 2 H, CH_2), 2.44 (s, 3 H, CH_3), 1.63 (quint., J = 6.6 Hz, 2 H, CH_2), 1.40–1.33 (m, 2 H, CH_2), 0.91 (t, J = 7.3 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 163.4, 145.5, 143.3, 135.4, 130.4, 130.1, 128.2, 65.7, 30.3, 21.5, 18.9, 13.4 ppm. IR (neat): $\tilde{\nu}$ = 3064, 2962, 2875, 1732, 1596, 1494, 1464, 1385, 1327, 1297, 1228, 1167, 1148, 1087, 963, 812, 708, 644 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{14}H_{18}O_4SNa$ $[M + Na]^+$ 305.0823; found 305.0772.

(*E*)-*tert*-Butyl 3-Tosylacrylate (8d): According to general procedure A, *tert*-butyl acrylate (**7d**; 56.1 mg, 0.5 mmol) and sodium *p*-toluenesulfinate (356.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 15% EtOAc in hexanes) gave **8d** (87.5 mg, 62% yield; white solid, m.p. 95–97 °C). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.3 Hz, 2 H, ArH), 7.39 (d, J = 8.0 Hz, 2 H, ArH), 7.23 (d, J = 15.1 Hz, 1 H, CH), 6.73 (d, J = 15.1 Hz, 1 H, CH), 2.48 (s, 3 H, CH_3), 1.49 (s, 9 H, 3 CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 162.6, 145.4, 142.5, 135.7, 132.4, 130.2, 128.3, 83.0, 27.9, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3070, 3039, 2986, 2967, 1713, 1625, 1595, 1480, 1393, 1368, 1311, 1249, 1156, 1087, 984, 828, 807, 720, 645 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{14}H_{18}O_4SNa$ $[M + Na]^+$ 305.0823; found 305.0859.

(*E*)-2-Methyl-3-tosylacrylonitrile (8fa) and (*Z*)-2-Methyl-3-tosylacrylonitrile (8fb): According to general procedure A, methacrylonitrile (**7f**; 33.6 mg, 0.5 mmol) and sodium *p*-toluenesulfinate (356.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 10–20% EtOAc in hexanes) gave **8fa** and **8fb**. Data for **8fa**: Colorless solid (58.6 mg, 53% yield), m.p. 93–94 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.4 Hz, 2 H, ArH), 7.43 (d, J = 8.0 Hz, 2 H, ArH), 6.89 (q, J = 1.6 Hz, 1 H, CH), 2.50 (s, 3 H, CH_3), 2.42 (d, J = 1.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 143.1, 136.8, 130.4, 127.9, 123.2, 117.1, 21.6, 16.4 ppm. IR (KBr): $\tilde{\nu}$ = 3038, 2924, 2233, 1619, 1594, 1440, 1383, 1329, 1299, 1182, 1149, 1087, 1040, 856, 811, 670 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{11}H_{11}NO_2SNa$ $[M + Na]^+$ 244.0408; found 244.0381. Data for **8fb**: Colorless solid (19.9 mg, 18% yield), m.p. 112–114 °C. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.88 (d, J = 8.4 Hz, 2 H, ArH), 7.41 (d, J = 8.0 Hz, 2 H, ArH), 6.87 (q, J = 1.6 Hz, 1 H, CH), 2.47 (s, 3 H, CH_3), 2.16 (d, J = 1.6 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.9, 142.9, 135.9, 130.2, 128.2, 121.1, 114.2, 22.3, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3038, 2924, 2233, 1619, 1594, 1441, 1384, 1329, 1307, 1299, 1182, 1149, 1087, 1041, 857, 812, 670 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{11}H_{11}NO_2SNa$ $[M + Na]^+$ 244.0408; found 244.0376.

(*E*)-Allyl 2-Methyl-3-tosylacrylate (8g): According to general procedure A, allyl methacrylate (**7g**; 63.1 mg, 0.5 mmol) and sodium *p*-toluenesulfinate (356.4 mg, 2.0 mmol) were employed. Column chromatography (SiO_2, 10–15% EtOAc in hexanes) gave **8g** (82.7 mg, 59% yield; colorless viscous liquid). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.82 (d, J = 8.3 Hz, 2 H, ArH), 7.38 (d, J = 8.4 Hz, 2 H, ArH), 7.25 (d, J = 1.5 Hz, 1 H, CH), 5.95–5.84 (m, 1 H, CH), 5.33 (dd, J = 17.3, 1.3 Hz, 1 H, CH), 5.27 (dd, J = 11.6, 1.3 Hz, 1 H, CH), 4.66 (d, J = 5.9 Hz, 2 H, CH_2), 2.46 (s, 3 H, CH_3), 2.34 (d, J = 1.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 165.2, 145.1, 140.7, 137.7, 137.5, 131.1, 130.0, 127.6, 119.2, 66.6, 21.5, 13.2 ppm. IR (neat): $\tilde{\nu}$ = 3054, 2953, 1727, 1626, 1597, 1494, 1447, 1382, 1362, 1324, 1232, 1151, 1117, 1086, 997, 941, 817, 782, 708 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{14}H_{16}O_4SNa$ $[M + Na]^+$ 303.0667; found 303.0613.

General Procedure B

Two-Step Synthesis of Vinyl Sulfones: PhI(OAc)$_2$ (241.6 mg, 0.75 mmol) was added to a suspension of alkene (0.5 mmol), *p*-toluenesulfinate (356.4 mg, 2.0 mmol), and KI (83.0 mg, 0.5 mmol) in CH_3CN (2 mL), and the reaction mixture was vigorously stirred at room temperature for 1 h. The reaction mixture was quenched by the addition of a saturated aqueous solution of $Na_2S_2O_3$ (5 mL) and basified with a saturated aqueous solution of $NaHCO_3$ (5 mL). Further stirring was followed by extraction with EtOAc (3 × 15 mL). The combined organic extract was washed with H_2O (15 mL) and brine (15 mL), dried ($MgSO_4$), filtered, and concentrated (aspirator). ^{1}H NMR spectroscopy of the crude mixture revealed that it was mixture of β-iodosulfone and vinyl sulfone. Without purification, the crude mixture was diluted with CH_3CN (2 mL), and to this solution was added 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 76.1 mg, 0.5 mmol). The reaction mixture was vigorously stirred at room temperature for 30 min before it was quenched with a saturated aqueous solution of $NaHCO_3$ (5 mL). Further stirring was followed by extraction with EtOAc (2 × 15 mL). The combined organic extract was washed with H_2O (15 mL) and brine (15 mL), dried ($MgSO_4$), filtered, and concentrated (aspirator). The residue was purified by column chromatography.

(*Z*)-1-Methyl-4-[3-(phenoxy)allylsulfonyl]benzene (2h): According to general procedure B, allyl phenyl ether (**1h**; 67.1 mg, 0.5 mmol) was employed. Column chromatography (SiO_2, 15% EtOAc in hexanes) gave **2h** (100.9 mg, 70% yield; colorless solid, m.p. 83–85 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.2 Hz, 2 H, ArH), 7.29–7.22 (m, 4 H, ArH), 7.09–7.04 (m, 1 H, ArH), 6.66 (d, J = 7.5 Hz, 2 H, ArH), 6.51 (d, J = 6.0 Hz, 1 H, CH), 4.92 (td, J = 8.0, 6.0 Hz, 1 H, CH), 4.07 (d, J = 8.0 Hz, 2 H, CH_2), 2.37 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 156.4, 146.4, 144.4, 135.6, 129.5, 129.4, 128.6, 123.5, 116.5, 97.8, 52.6, 21.6 ppm. IR (KBr): $\tilde{\nu}$ = 3063, 2976, 1670, 1592, 1486, 1406, 1385, 1312, 1302, 1266, 1209, 1143, 1080, 983, 770, 742 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{16}H_{16}O_3SNa$ [M + Na]$^+$ 311.0718; found 311.0759.

(*E*)-1-Methyl-4-(5-phenoxypent-1-enylsulfonyl)benzene (2i): According to general procedure B, 4-pentenyl phenyl ether (**1i**; 81.1 mg, 0.5 mmol) was employed. Column chromatography (SiO_2, 20% EtOAc in hexanes) gave **2i** (132.9 mg, 84% yield; white solid, m.p. 73–75 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.74 (d, J = 8.3 Hz, 2 H, ArH), 7.32–7.22 (m, 4 H, ArH), 7.05–6.91 (m, 2 H, ArH, CH), 6.84–6.81 (m, 2 H, ArH), 6.35 (d, J = 15.1 Hz, 1 H, CH), 3.94 (t, J = 6.1 Hz, 2 H, CH_2), 2.48–2.41 (m, 5 H, CH_3, CH_2), 1.98–1.89 (m, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 158.6, 145.3, 144.2, 137.7, 131.4, 129.8, 129.4, 127.6, 120.8, 114.4, 66.4, 28.2, 27.4, 21.5 ppm. IR (KBr): $\tilde{\nu}$ = 3039, 2961, 2873, 1634, 1601, 1586, 1492, 1469, 1441, 1397, 1315, 1307, 1279, 1242, 1178, 1083, 1042, 979, 811, 761 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{18}H_{20}O_3SNa$ [M + Na]$^+$ 339.1031; found 339.1055.

(*E*)-1-(5-Bromopent-1-enylsulfonyl)-4-methylbenzene (2k): According to general procedure B, 5-bromopentene (**1k**; 74.5 mg, 0.5 mmol) was employed. Column chromatography (SiO_2, 15% EtOAc in hexanes) gave **2k** (121.3 mg, 80% yield; colorless oil). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.67 (d, J = 8.2 Hz, 2 H, ArH), 7.26 (d, J = 8.0 Hz, 2 H, ArH), 6.84 (dt, J = 15.1, 6.8 Hz, 1 H, CH), 6.30 (d, J = 15.1 Hz, 1 H, CH), 3.31 (t, J = 6.3 Hz, 2 H, CH_2), 2.36–2.30 (m, 5 H, CH_3, CH_2), 1.93 (quint., J = 6.8 Hz, 2 H, CH_2) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.3, 143.9, 137.4, 131.9, 129.8, 127.5, 32.1, 30.3, 29.6, 21.5 ppm. IR (neat): $\tilde{\nu}$ = 3047, 2925, 1627, 1597, 1495, 1441, 1317, 1302, 1289, 1145, 1087, 961, 814, 660 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{12}H_{15}O_2SBrNa$ [M + Na]$^+$ 324.9874; found 324.9898.

(*E*)-11-Tosylundec-10-enal (2m): According to general procedure B, undec-10-enal (**1m**; 84.1 mg, 0.5 mmol) was employed. Column chromatography (SiO_2, 15% EtOAc in hexanes) gave **2m** (129.0 mg, 80% yield; colorless viscous liquid). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.75 (t, J = 1.8 Hz, 1 H, CHO), 7.74 (d, J = 8.3 Hz, 2 H, ArH), 7.32 (d, J = 8.5 Hz, 2 H, ArH), 6.94 (dt, J = 15.1, 6.8 Hz, 1 H, CH), 6.30 (d, J = 15.1 Hz, 1 H, CH), 2.44–2.38 (m, 5 H, CH_3, CH_2), 2.26–2.17 (m, 2 H, CH_2), 1.60–1.20 [m, 12 H, $(CH_2)_6$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 202.7, 146.4, 144.0, 137.8, 130.6, 129.7, 127.5, 43.7, 31.3, 29.0, 28.9, 28.8, 27.4, 21.9, 21.4 ppm. IR (neat): $\tilde{\nu}$ = 3048, 2929, 2856, 1712, 1634, 1597, 1495, 1456, 1403, 1317, 1303, 1287, 1144, 1087, 970, 814, 660 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{18}H_{26}O_3SNa$ [M + Na]$^+$ 345.1500; found 345.1558.

(*E*)-2-(10-Tosyldec-9-enyl)-1,3-dioxane (2n): According to general procedure B, 2-(dec-9-enyl)-1,3-dioxane (**1n**; 113.2 mg, 0.5 mmol) was employed. Column chromatography (SiO_2, 15% EtOAc in hexanes) gave **2n** (154.1 mg, 81% yield; colorless solid, m.p. 81–83 °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, J = 8.3 Hz, 2 H, ArH), 7.33 (d, J = 8.1 Hz, 2 H, ArH), 6.95 (dt, J = 15.1, 6.8 Hz, 1 H, CH), 6.29 (d, J = 15.1 Hz, 1 H, CH), 4.51 (t, J = 5.1 Hz, 1 H, CH), 4.13–4.08 (m, 2 H, 2 CH of OCH_2), 3.81–3.72 (m, 2 H, 2 CH of OCH_2), 2.44 (s, 3 H, CH_3), 2.25–2.18 (m, 2 H, CH_2), 2.10–2.05 (m, 1 H, CH of CH_2), 1.61–1.54 (m, 2 H, CH_2), 1.44–1.26 [m, 13 H, CH of CH_2, $(CH_2)_6$] ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.5, 144.0, 137.8, 130.5, 129.7, 127.5, 102.3, 66.8, 35.1, 31.3, 29.2, 29.1, 29.0, 28.9, 27.5, 25.8, 23.8, 21.5 ppm. IR (KBr): $\tilde{\nu}$ = 3055, 2934, 2857, 1632, 1597, 1492, 1450, 1410, 1334, 1301, 1287, 1244, 1147, 1117, 1098, 1085, 986, 968, 890, 742, 668 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{21}H_{32}O_4SNa$ [M + Na]$^+$ 403.1919; found 403.1949.

(*E*)-1-Methoxy-4-(3-tosylprop-1-enyl)benzene (4p): According to general procedure B, allyl anisole (**1p**; 74.1 mg, 0.5 mmol) was employed. Column chromatography (SiO_2, 10–20% EtOAc in hexanes) gave products **2p** (16.6 mg, 11% yield) and **4p** (95.3 mg, 63% yield). Data for **4p**: Brownish solid, m.p. 117–119 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, J = 8.2 Hz, 2 H, ArH), 7.23 (d, J = 8.0 Hz, 2 H, ArH), 7.14 (d, J = 8.7 Hz, 2 H, ArH), 6.75 (d, J = 8.6 Hz, 2 H, ArH), 6.24 (d, J = 15.8 Hz, 1 H, CH), 5.86 (dt, J = 15.8, 7.6 Hz, 1 H, CH), 3.82 (d, J = 7.6 Hz, 2 H, CH_2), 3.71 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.8, 144.6, 138.4, 135.6, 129.6, 128.6, 128.4, 127.8, 114.0, 112.7, 60.5, 55.2, 21.5 ppm. IR (KBr): $\tilde{\nu}$ = 3033, 2969, 2915, 1644, 1605, 1575, 1512, 1463, 1400, 1313, 1289, 1252, 1177, 1145, 1087, 978, 819, 733, 664 cm^{-1}. HRMS (ESI-TOF): calcd. for $C_{17}H_{18}O_3SNa$ [M + Na]$^+$ 325.0874; found 325.0860.

Supporting Information (see footnote on the first page of this article): Experimental procedures and spectroscopic data; NOE interactions of **2h**, **6e**, and **8fa/8fb**; copies of the ^{1}H and ^{13}C NMR spectra of all compounds.

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