Synthesis of vinyl sulfoxides using sulfinyl chlorides and olefins

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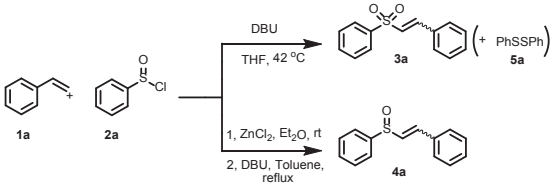
A general method for synthesis of vinyl sulfoxides, using sulfinyl chlorides and olefins as starting materials and DBU as an HCl scavenger, has been developed. Vinyl sulfoxides were obtained from the $ZnCl_2$ catalysed addition of sulfinyl chlorides to olefins followed by the elimination with DBU. However, the direct reaction of sulfinyl chlorides with olefins in the presence of DBU, usually leads to generation of vinyl sulfones. The sulfonyl radicals generated from the DBU-mediated disproportionation of the sulfinyl radicals undergo addition-elimination reaction with olefins to give vinyl sulfones.

Keywords: vinyl sulfoxide, vinyl sulfone, DBU, olefin, sulfinyl chloride

Vinyl sulfoxides are useful building blocks in the synthesis of biologically active compounds.[1] There have been several methods for the synthesis of vinyl sulfoxides including the Wittig reaction,[2-3] the Horner–Wadsworth–Emmons reaction,[4] the Andersen reaction,[5] reduction of alkynyl sulfoxides,[6] oxidation of vinyl sulfides.[7] and addition–oxidation of thiols with alkynes.[8] We now report an approach to vinyl sulfoxides using sulfinyl chlorides[9-12] and olefins as starting materials.

In our initial work, the reaction of styrene **1a** with benzenesulfinyl chloride **2a** did not occur. When DBU (1,8-diazabicyclo[5.4.0] undec-7-ene) was added to the reaction mixture, however, the reaction did occur. The isolated product was identified by spectroscopy as [2-(phenylsulfonyl)vinyl]benzene (**3a**) instead of the targetted product, [2-(phenylsulfinyl)vinyl]benzene (**4a**). However, **4a** could be obtained by the reaction of styrene (**1a**) with benzenesulfinyl chloride (**2a**) in the presence of $ZnCl_2$ followed by the treatment with DBU (Scheme 1). Inspired by these preliminary findings, we investigated the optimal conditions of this protocol for the synthesis of vinyl sulfoxides and vinyl sulfones. Firstly, a series of bases (*e.g.*, DBU, Et_3N, DABCO (1,4-diazabicyclo[2.2.2] octane), pyridine, *etc.*) was screened. Among them, DBU was the most effective, the other bases giving lower yields. Additionally, we found that **1a** and **2a** did not react in the absence of base. Various reaction conditions, such as solvents and temperature, were also examined for the optimum. Thus, the standard conditions for the synthesis of vinyl sulfoxides were established: treatment of the mixture obtained by the reaction of olefins with sulfinyl chlorides in the presence of $ZnCl_2$ at room temperature, with DBU as a scavenger in toluene under reflux produced vinyl sulfoxides. The intermediate saturated sulfoxide {**4ab**, [1-chloro-2-(phenylsulfinyl) ethyl]benzene} could be isolated from the reaction. This indicates that the reaction proceeds by $ZnCl_2$-catalysed addition of sulfinyl chlorides to olefins followed by elimination with DBU to form vinyl sulfoxides.

We investigated the scope of this protocol for the synthesis of vinyl sulfoxides. The results are listed in Table 1. It was discovered that a wide range of styrene derivatives can react to provide the corresponding vinyl sulfoxides in good yields (Table 1).



Scheme 1 Synthesis of vinyl sulfones and vinyl sulfoxides.

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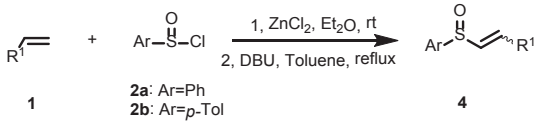
In addition, an alternative method for the preparation of vinyl sulfones was provided by reaction of olefins with sulfinyl chlorides. The results are summarised in Table 2.

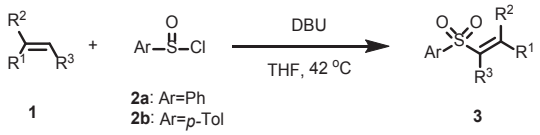
Table 1 Synthesis of vinyl sulfoxides from sulfinyl chlorides and olefins[a]



Entry	Product **4**	Yield/%[b]
1	**4a**, $R^1 = C_6H_5$, Ar=Ph	67
2	**4b**, $R^1 = p\text{-}CH_3C_6H_4$, Ar=Ph	85
3	**4c**, $R^1 = m\text{-}CH_3OC_6H_4$, Ar=Ph	76
4	**4d**, $R^1 = m\text{-}NO_2C_6H_4$, Ar=Ph	70
5	**4e**, $R^1 = C_6H_5$, Ar=*p*-Tol	46
6	**4f**, $R^1 = p\text{-}CH_3C_6H_4$, Ar=*p*-Tol	71
7	**4g**, $R^1 = m\text{-}CH_3OC_6H_4$, Ar=*p*-Tol	72
8	**4h**, $R^1 = m\text{-}NO_2C_6H_4$, Ar=*p*-Tol	63

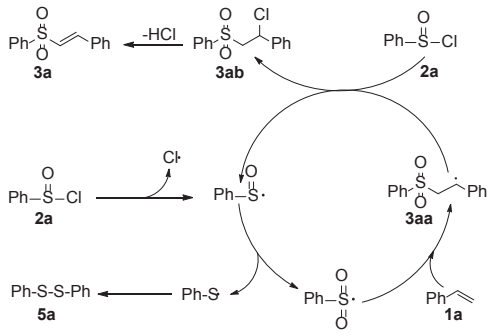
[a]Standard conditions: (1) olefin (1 mmol), sulfinyl chloride (1 mmol), $ZnCl_2$ (1 mmol, dissolved in 5 mL ethyl ether), solvent ethyl ether (5 mL) with a nitrogen balloon at room temperature for 30–50 min; (2) DBU (1 mmol), solvent toluene (10 mL) at reflux for 5 h.
[b]Isolated yield, *E* major configuration mixed products except **4a** and **4e**.

Table 2 Synthesis of vinyl sulfones from sulfinyl chlorides and olefins[a]



Entry	Product **3**	Yield/%[b]
1	**3a**, $R^1 = C_6H_5$, $R^2 = R^3$ = H, Ar=Ph	73
2	**3b**, $R^1 = p\text{-}CH_3C_6H_4$, $R^2 = R^3$ = H, Ar=Ph	72
3	**3c**, $R^1 = m\text{-}CH_3OC_6H_4$, $R^2 = R^3$ = H, Ar=Ph	65
4	**3d**, $R^1 = C_6H_5$, $R^2 = CH_3$, R^3 = H, Ar=Ph	54
5	**3e**, $R^1 = OCH_2CH_3$, $R^2 = R^3$ =H, Ar=Ph	50
6	**3f**, $R^1 = O(CH_2)_3CH_3$, $R^2 = R^3$ =H, Ar=Ph	53
7	**3g**, R^1, R^3=-OCH_2CH_2-, R^2 = H, Ar=Ph	57
8	**3h**, $R^1 = C_6H_5$, $R^2 = R^3$ = H, Ar=*p*-Tol	61
9	**3i**, $R^1 = p\text{-}CH_3C_6H_4$, $R^2 = R^3$ = H, Ar=*p*-Tol	60
10	**3j**, $R^1 = m\text{-}CH_3OC_6H_4$, $R^2 = R^3$ = H, Ar=*p*-Tol	59
11	**3k**, $R^1 = C_6H_5$, $R^2 = CH_3$, R^3 = H, Ar=*p*-Tol	60
12	**3l**, $R^1 = OCH_2CH_3$, $R^2 = R^3$ =H, Ar=*p*-Tol	45
13	**3m**, $R^1 = O(CH_2)_3CH_3$, $R^2 = R^3$ =H, Ar=*p*-Tol	48
14	**3n**, R^1, R^3= -OCH_2CH_2-, R^2 = H, Ar=*p*-Tol	40

[a] Standard conditions: olefin (1 mmol), sulfinyl chloride (2 mmol, dissolved in 2 mL THF), DBU (1.5 mmol), solvent THF (5 mL) at 42°C for 3–8 h.
[b] Isolated yields based on **1**.



Scheme 2 Proposed mechanism for the formation of vinyl sulfones.

It was discovered that a wide range of olefins could form vinyl sulfones in moderate yields. Aromatic alkenes bearing substituents such as methyl or methoxy on the ring, underwent the reaction to provide the corresponding vinyl sulfones in good yields (Table 2, entries 1–3, 8–11). Moderate yields were observed for styrene bearing an α-alkyl substituent (Table 2, entries 4, 11). However, attempted synthesis of vinyl sulfones using aliphatic alkenes gave unsatisfactory results under the standard conditions (Table 2, entries 5–7, 12–14).

Although the exact mechanism of the conversion of sulfinyl chlorides to sulfones (Scheme 2) is still not clear, some information has been gathered. When TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy, a well-known radical-capturing species) was added to the reaction system, the sulfonylation reaction was completely suppressed. This indicates presumably that the reaction presumably involves a radical process. Besides, it is noteworthy that no vinyl sulfoxide product was observed. Under the standard conditions, the reaction of **1a** with **2a** produced **3a** with 0.5 equiv. **5a** as the side product (Scheme 1). Moreover, the anaerobic reaction also generates vinyl sulfone **3a** instead of vinyl sulfoxide **4a**. These results might indicate that sulfonyl free radicals are produced from the disproportionation reaction of sulfinyl free radicals, which, meanwhile, generates an equivalent amount of Ph-S· (Scheme 2). This is supported by previous literature reports.[11, 13-15] On the basis of the above observations, we propose that a plausible mechanism (Scheme 2) consists of (i) disproportionation of sulfoxide free radicals to produce Ph–SO_2· and Ph–S free radicals·; (ii) electrophilic attack of the sulfonyl radical on the electron-rich styrene to generate a benzylic radical (**3aa**), which is trapped by Cl derived from the sulfinyl chloride; (iii) elimination of a molecule of hydrogen chloride from **3ab** to afford the corresponding vinyl sulfones (**3a**) in the presence of DBU. The side product PhSSPh, meanwhile, is obtained from the coupling of the reactive Ph–S· with another Ph–S·. [13,16]

In conclusion, we have demonstrated an alternative methodology for the preparation of substituted vinyl sulfoxides and vinyl sulfones. In view of the experimental simplicity and the mild reaction conditions, it is likely that this procedure will find various applications in organic synthesis.

Experimental

Commercially available reagents were used without further purification unless mentioned. All reactions were monitored by TLC. Visualisation of TLC plates was accomplished with a UV lamp. The column chromatography was performed using silica gel (200–300 mesh) with ethyl acetate/petroleum ether (b.p. 60–90 °C) as eluent. Melting points were recorded on a X-4 micro melting point apparatus. LRMS-EI and HRMS-ESI were recorded on ThermoFisher ITQ1100 or Agilent 6210 LC/TOF instrument. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a Bruker Spectrospin 500 MHz or 400 MHz spectrometer using TMS as internal standard.

Vinyl sulfones **3a–n***; general procedure*

Sulfinyl chloride **2** (2 mmol) in THF (2 mL) was added dropwise to a stirred solution of olefin **1** (1 mmol) and DBU (1.5 mmol) in THF (5 mL) . The resulting mixture was stirred at 42 °C until the reaction was completed as monitored by TLC (3:1 ethyl acetate/petroleum ether as eluent). Water was added to the reaction system, and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with dilute aqueous HCl (15 mL) and saturated NaCl solution (15 mL), dried over $MgSO_4$ and filtered. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (10:1 ethyl acetate/petroleum ether as eluent).

*(*E*)-[2-(Phenylsulfonyl)vinyl]benzene* (**3a**): White solid, m.p. 74–76 °C (lit.[17] 68–70 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98–7.96 (m, 2H), 7.70 (d, *J* = 15.4 Hz, 1H), 7.64–7.61 (m, 1H), 7.57–7.38 (m, 7 H), 6.89 (d, *J* = 15.4 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 140.4, 133.2, 132.1, 131.0, 129.1, 128.9, 128.4, 127.4, 127.0 ppm. MS (EI): *m/z* 244 (5) [M^+], 179 (60), 119 (74), 102 (46), 91 (100), 77 (40), 65 (22), 51 (49).

*(*E*)-1-Methyl-4-[2-(phenylsulfonyl)vinyl]benzene* (**3b**): White solid, m.p. 136–138 °C (lit.[17] 130–132 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97–7.95 (m, 2H), 7.68 (d, *J* = 15.0 Hz, 1H), 7.64–7.39 (m, 5H), 7.22–7.20 (m, 2H), 6.82 (d, *J* = 15.0 Hz, 1H), 2.39 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.3, 141.6, 133.0, 129.6, 129.1, 128.4, 127.4, 126.4, 126.0, 125.1, 21.6 ppm.

1-Methoxy-3-[2-(phenylsulfonyl)vinyl]benzene (**3c**): *E*/*Z* = 92/8, white solid, m.p. 120–122 °C (lit.[18] 115–117 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.97–7.96 (m, 2H), 7.68–7.55 (m, 4H), 7.33–7.30 (m, 1H), 7.10–7.08 (m, 1H), 7.00–6.96 (m, 2H), 6.87 (d, *J* = 15.4 Hz, 1H), 3.82 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 142.2, 140.4, 133.2, 129.9, 129.2, 128.5, 127.5, 127.3, 121.1, 117.0, 113.2, 55.4 ppm.

*(*E*)-[(2-Phenylprop-1-en-1-yl)sulfonyl]benzene* (**3d**): White solid, m.p. 72–74 °C (lit.[19] 71–73 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.00–7.98 (m, 2H), 7.59–7.38 (m, 8H), 6.63 (s, 1H), 2.56 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, 141.9, 139.8, 133.0, 129.7, 129.0, 128.5, 127.1, 127.0, 126.1, 17.3 ppm.

*(*E*)-[(2-Ethoxyvinyl)sulfonyl]benzene* (**3e**):[20] Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.89–7.88 (m, 2H), 7.61–7.57 (m, 2H), 7.54–7.51 (m, 2H), 5.69 (d, *J* = 12.3 Hz, 1H), 3.91 (q, *J* = 7.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.5, 142.3, 132.6, 128.9, 126.7, 106.3, 67.6, 14.4 ppm.

*(*E*)-[(2-Butoxyvinyl)sulfonyl]benzene* (**3f**):[21]: White solid, m.p. 42–45 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87–7.85 (m, 2H), 7.56–7.25 (m, 4H), 5.68 (d, *J* = 12.4 Hz, 1H), 3.82 (t, *J* = 6.0 Hz, 2H), 1.71–1.64 (m, 2H), 1.44–1.34 (m, 2H), 0.92 (t, *J* = 7.2 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.4, 134.5, 129.5, 128.8, 127.9, 127.8, 66.7, 31.4, 19.2, 13.9 ppm.

4-(Phenylsulfonyl)-2,3-dihydrofuran (**3g**): White solid, m.p. 78–80 °C (lit.[22] 77–80 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.91–7.90 (m, 2H), 7.64–7.54 (m, 3H), 7.24 (s, 1H), 4.62 (t, *J* = 10.0 Hz, 2H), 2.81 (t, *J* = 10.0 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.5, 133.9, 129.2, 128.5, 98.6, 69.9, 67.1, 25.8 ppm.

*(*E*)-1-Methyl-4-(styrylsulfonyl)benzene* (**3h**): White solid, m.p. 118–120 °C (lit.[8] 118–119 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85–7.83 (m, 2H), 7.67 (d, *J* = 15.4 Hz, 1H), 7.50–7.49 (m, 2H), 7.48-7.35 (m, 5H), 6.86 (d, *J* = 15.4 Hz, 1H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 141.8, 137.5, 132.3, 130.9, 129.8, 128.9, 128.4, 127.6, 127.4, 21.7 ppm.

1-Methyl-4-(4-methylstyrylsulfonyl)benzene (**3i**): *E*/*Z* = 71/29, white solid, m.p. 149–154 °C (lit.[17] 152–155 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.84–7.83 (m, 2H), 7.64 (d, *J* = 15.4 Hz, 1H), 7.38–7.19 (m, 6 H), 6.81 (d, *J* = 15.4 Hz, 1H), 2.44 (s, 3H), 2.37 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.0, 141.8, 141.5, 137.7, 130.5, 129.7, 129.6, 128.3, 127.4, 126.2, 21.7, 21.6 ppm.

1-Methoxy-3-(2-tosylvinyl)benzene (**3j**):[8] *E*/*Z* = 94/6, colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.83–7.82 (m, 2H), 7.62 (d, *J* = 15.4 Hz,

1H), 7.34–7.26 (m, 3H), 7.06–7.05 (m, 1H), 6.98–6.93 (m, 2H), 6.87 (d, *J* = 15.4 Hz, 1H), 3.79 (s, 3H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 144.0, 141.5, 137.3, 133.3, 129.7, 129.6, 127.5, 127.3, 120.8, 116.7, 113.0, 55.1, 21.5 ppm.

(E)-1-Methyl-4-[(2-phenylprop-1-en-1-yl)sulfonyl]benzene (**3k**): White solid, m.p. 101–103 °C (lit.[23] 102–103 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88–7.86 (m, 2H), 7.42–7.35 (m, 7H), 6.61 (s, 1H), 2.53 (s, 3H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.0, 144.2, 140.3, 139.3, 130.0, 129.5, 128.8, 127.9, 127.4, 126.4, 22.0, 17.5 ppm.

(E)-1-[(2-Ethoxyvinyl)sulfonyl]-4-methylbenzene (**3l**): White solid, m.p. 57–59 °C (lit.[24] 57–58 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75–7.74 (m, 2H), 7.56 (d, *J* = 12.3 Hz, 1H), 7.31–7.28 (m, 2H), 5.67 (d, *J* = 12.3 Hz, 1H), 3.88 (q, *J* = 7.1 Hz, 1H), 2.41 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 143.3, 139.4, 129.5, 126.7, 106.7, 67.5, 21.6, 14.4 ppm.

(E)-1-[(2-Butoxyvinyl)sulfonyl]-4-methylbenzene (**3m**): White solid, m.p. 39–42 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.78–7.76 (m, 2H), 7.59 (d, *J* = 12.2 Hz, 1H), 7.33–7.31 (m, 2H), 5.68 (d, *J* = 12.2 Hz, 1H), 3.82 (t, *J* = 6.6 Hz, 2H), 2.44 (s, 1H), 1.71–1.65 (m, 2H), 1.44–1.36 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.3, 129.8, 129.1, 127.7, 127.6, 127.5, 66.6, 31.3, 21.5, 19.0, 13.6 ppm. HRMS (ESI) calcd for $C_{13}H_{19}O_3S$ $[M+H]^+$: 255.1049; found: 255.1067.

4-Tosyl-2,3-dihydrofuran (**3n**): White solid, m.p. 106–108 °C (lit.[25] 106–107 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.79–7.77 (m, 2H), 7.35–7.34 (m, 2H), 7.21 (s, 1H), 4.61 (t, *J* = 9.6 Hz, 2H), 2.82–2.78 (m, 2H), 2.45 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.0, 134.5, 129.8, 128.6, 98.6, 70.1, 67.0, 25.9, 21.8 ppm.

Sulfone reaction from which diphenyl disulfide was isolated

Benzenesulfinyl chloride **2a** (2 mmol) in THF (2 mL) was added dropwise to a stirred solution of styrene **1a** (1 mmol) and DBU (1.5 mmol) in THF (5 mL) The resulting mixture was stirred at 42 °C until the reaction was completed as monitored by TLC (3:1 ethyl acetate/petroleum ether as eluent). Water was added to reaction system and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with diluted aqueous HCl (15 mL) and saturated NaCl solution (15 mL), dried over $MgSO_4$ and filtered. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (10:1 ethyl acetate/petroleum ether as eluent) to provide diphenyl disulfide **5a** (0.080 g, 0.37 mmol) and (E)-[2-(phenylsulfonyl)vinyl]benzene **3a** (0.178 g, 0.73 mmol).

Diphenyl disulfide (**5a**): White solid, m.p. 58–60 °C (lit.[26] 59 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53–7.52 (d, 4H), 7.33–7.31 (t, 4H), 7.27–7.24 (t, 2H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 137.2, 129.2, 127.7, 127.3 ppm.

Reaction in the presence of TEMPO

Benzenesulfinyl chloride **2a** (2 mmol) in THF (2 mL) was added dropwise to a stirred solution of styrene **1a** (1 mmol), DBU (1.5 mmol) and TEMPO (0.15 mmol) in THF (5 mL) . The resulting mixture was stirred at 42 °C for 3 h, from which no product **3a** was isolated. It was shown that the sulfonylation reaction was completely suppressed, monitored by TLC.

Vinyl sulfoxides **4a–h***; general procedure*

Anhydrous $ZnCl_2$ (1 mmol) dissolved in anhydrous ethyl ether (5 mL) was added to a stirred solution of olefin **1** (1 mmol) and sulfinyl chloride **2** (1 mmol) in anhydrous ethyl ether (5 mL) . The resulting mixture was stirred at room temperature with a nitrogen balloon for 30–50 min. The whole mixture was poured into a mixture of ice water (5 g) and toluene (10 mL) and separated. The organic layer, after addition of DBU (1 mmol), was refluxed to eliminate hydrogen chloride completely as monitored by TLC (2:1 ethyl acetate/petroleum ether as eluent). Water was added to the reaction system and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with diluted aqueous HCl (15 mL) and saturated NaCl solution (15 mL), dried over $MgSO_4$ and filtered. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (6:1 ethyl acetate/petroleum ether as eluent).

(Z)-[2-(Phenylsulfinyl)vinyl]benzene (**4a**):[27] Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69–7.67 (m, 2H), 7.62–7.60 (m, 2H), 7.55–7.41 (m, 6 H), 7.14 (d, *J* = 10.6 Hz, 1H), 6.46 (d, *J* = 10.6 Hz, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 138.8, 136.4, 133.5, 130.7, 129.6, 129.4, 129.2, 128.5, 124.1 ppm. MS (EI): *m/z* 229 (4) $[M^+ +1]$, 199 (60), 180 (100), 179 (76), 165 (44), 91 (34), 77 (25), 65 (13), 51 (36).

(E)-1-Methyl-4-[2-(phenylsulfinyl)vinyl]benzene (**4b**):[28] Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70–7.67 (m, 2H), 7.53–7.47 (m, 3H), 7.37–7.34 (m, 3H), 7.18–7.16 (m, 2H), 6.79 (d, *J* = 15.6 Hz, 1H), 3.35 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.8, 140.0, 136.6, 131.5, 130.8, 130.6, 129.3, 129.1, 127.5, 124.4, 21.4 ppm.

(E)-1-Methoxy-3-[2-(phenylsulfinyl)vinyl]benzene (**4c**):[28] Colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.64–7.63 (m, 2H), 7.46–7.41 (m, 3H), 7.30 (d, *J* = 15.5 Hz, 1H), 7.22–7.18 (m, 1H), 7.22–7.19 (m, 1H), 6.99–6.80 (m, 4H), 3.71 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 143.1, 135.4, 134.3, 132.5, 130.5, 129.2, 128.8, 124.0, 119.7, 114.9, 112.3, 54.7 ppm.

1-Nitro-3-[2-(phenylsulfinyl)vinyl]benzene (**4d**): *E*/*Z* = 90/10, pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29–8.28 (m, 1H), 8.17–8.15 (m, 1H), 7.75–7.68 (m, 3H) , 7.57–7.51 (d, 3H), 7.41 (d, *J* = 15.4 Hz, 1H), 7.02 (d, *J* = 15.4 Hz, 1H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.6, 143.1, 136.5, 135.5, 133.5, 132.3, 131.5, 129.9, 129.6, 124.7, 123.9, 121.9 ppm. HRMS (ESI) calcd for $C_{14}H_{12}NO_3S$ $[M]^+$, 274.0532; found: 274.0533.

(Z)-1-Methyl-4-(styrylsulfinyl)benzene (**4e**):[8, 29] Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59–7.57 (m, 4H), 7.47–7.40 (m, 3H), 7.34–7.32 (m, 2H), 7.11 (d, *J* = 10.6 Hz, 1H), 6.45 (d, *J* = 10.6 Hz, 1H), 2.42 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 141.1, 138.3, 136.7, 133.6, 129.9, 129.6, 129.3, 128.5, 124.2, 21.5 ppm.

1-Methyl-4-(4-methylstyrylsulfinyl)benzene (**4f**):[8] *E*/*Z* = 93/7, colourless oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58–7.56 (m, 2H), 7.34–7.28 (m, 5H), 7.16–7.14 (m, 2H), 6.77 (d, *J* = 15.6 Hz, 1H), 2.39 (s, 3H), 2.34 (s, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 140.4, 139.6, 135.9, 131.5, 130.6, 129.7, 129.2, 127.3, 124.4, 21.3 ppm.

(E)-1-Methoxy-3-[2-(p-tolylsulfinyl)vinyl]benzene (**4g**):[8] Pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48–7.47 (m, 2H), 7.22 (d, *J* = 15.5 Hz, 1H), 7.19–7.17 (m, 2H), 7.15–7.12 (m, 1H), 6.92–6.87 (m, 2H), 6.78–6.75 (m, 2H), 3.64 (s, 3H), 2.25 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 159.1, 140.6, 140.2, 134.5, 134.4, 133.0, 129.2, 129.0, 123.9, 119.4, 114.6, 112.1, 54.3, 20.4 ppm.

1-Nitro-3-[2-(p-tolylsulfinyl)vinyl]benzene (**4h**): *E*/*Z* = 98/2, pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.29–8.28 (m, 1H), 8.17–8.15 (m, 1H), 7.75–7.74 (d, *J* = 7.8 Hz, 1H), 7.58–7.53 (m, 3H) , 7.41–7.33 (d, 3H), 7.00 (d, *J* = 15.4 Hz, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ 148.6, 142.2, 139.9, 136.7, 135.6, 133.5, 132.0, 130.3, 129.9, 124.9, 124.5, 123.8, 121.9, 21.3 ppm. HRMS (ESI) calcd for $C_{15}H_{14}NO_3S$ $[M+H]^+$:288.0689; found: 288.0699.

Synthesis of **4ab***; general procedure*

Anhydrous $ZnCl_2$ (1 mmol) dissolved in anhydrous ethyl ether (5 mL) was added to a stirred solution of styrene **1a** (1 mmol) and benzenesulfinyl chloride **2a** (1 mmol) in anhydrous ethyl ether (5 mL). The resulting mixture was stirred at room temperature with a nitrogen balloon for 30 min. Water was added to the reaction system and the mixture was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with diluted aqueous HCl (15 mL) and saturated NaCl solution (15 mL), dried over $MgSO_4$ and filtered. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (5:1 ethyl acetate/petroleum ether as eluent) provide the product **4ab** (0.216 g) in 82% yield. *[1-Chloro-2-(phenylsulfinyl)ethyl]benzene* (**4ab**): White solid, m.p. 80–82 °C (lit.[30] 84–85 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69–7.64 (m, 2H), 7.56–7.52 (m, 3H), 7.49–7.40 (m, 4H), 7.40–7.32 (m, 1H), 5.46–5.18 (m, 1H), 3.71–3.26 (m, 2H) ppm.

Electronic Supplementary Information

The ^{1}H and ^{13}C NMR and mass spectra of the products have been deposited in the ESI available through stl.publisher.ingentaconnect.com/content/stl/jcr/supp-data.

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References

1 K. Mori, K. Ohmori and K. Suzuki, *Angew. Chem. Int. Ed.*., 2009, **48**, 5633.
2 M. Mikolajczyk, W. Perlikowska, J. Omelanczuk, H. Cristau and A. Perraud-Darcy, *J. Org. Chem*., 1998, **63**, 9716.
3 J. H. Van Steenis, J. J. G. S. Van Es and A. Van der Gen, *Eur. J. Org. Chem*., 2000, 2787.
4 K. Kokin, S. Tsuboi, J. Motoyoshiya and S. Hayashi, *Synthesis*, 1996, 637.
5 G. H. Posner, and P. W. J. Tang, *J. Org. Chem*., 1978, **43**, 4131.
6 H. Kosugi, M. Kitaoka, K. Tagami, A. Takahashi and H. Uda, *J. Org. Chem*., 1987, **58**, 1078.
7 X. Huang, D. Duan and W. Zheng, *J. Org. Chem*., 2003, **68**, 1958.
8 Q. C. Xue, Z. J. Mao and C. J. Zhu, *Tetrahedron Lett*., 2012, **53**, 1851.
9 M.-L. Kee and I. B. Douglass, *Org. Prep. Proced. Int*., 1970, **2**, 235.
10 I. B. Douglass, R. V. Norton and B. S. Farah, *Org. Synth*., 1960, **40**, 62.
11 I. B. Douglass and R. V. Norton, *J. Org. Chem*., 1968, **33**, 2104.
12 J. Drabowicz, B. Bujnicki and B. Dudzinski, *Synth. Commun*., 1994, **24**, 1207.
13 P. Koch, E. Cuiffarin and A. Fava, *J. Am. Chem. Soc*., 1970, **92**, 5971.
14 G. A. Olah, S. C. Narang, L. D. Field and R. Karpeles, *J. Org. Chem.,* 1981, **46**, 2408.
15 G. W. Kabalka, M. S. Reddy and M.-L. Yao, *Tetrahedron Lett*., 2009, **50**, 7340.
16 C.M.M. da Silva Correa and W.A. Waters, *J. Chem. Soc. C,* 1968, 1874.
17 P. Katrun, S. Chiampanichayakul, K. Korworapan, M. Pohmakotr, V. Reutrakul, T. Jaipe*t*ch and C. Kuhakarn, *Eur. J. Org. Chem.,* 2010, 5633.
18 Y. L. Xu, X. D. Tang, W. G. Hu, W. Q. Wu and H. F. Jiang, *Green Chem*., 2014, **16**, 3720.
19 H. Guo and S. M. Ma, *Synthesis*, 2007, **17**, 2731.
20 F. Montanari, *Gazz. Chim. Ital*., 1956, **86**, 420.
21 G. V. Ratovskii, T. I. Rozova, M. A. Vasil'eva and T. I. Bychkova, *Theor. Exp. Chem.,* 1978, **14**, 194.
22 M. Ochiai, M. Kunishima, S. Tani and Y. Nagao, *J. Am. Chem. Soc*., 1991, **113**, 3135.
23 N. Kamigata, H. Sawada and M. Kobayashi, *J. Org. Chem*., 1983, **48**, 3793.
24 A. Padwa, W. H. Bullock, A. D. Dyszlewski, S. W. McCombie, B. B. Shankar and A. K. Ganguly, *J. Org. Chem*., 1991, **51**, 3556.
25 K. S. Feldman and M. L. Wrobleski, *J. Org. Chem*., 2000, **65**, 8659.
26 F. Barba, F. Ranz and B. Batanero, *Tetrahedron. Lett*., 2009, **50**, 6798.
27 P. Zhong; M-P. Guo and N-P. Huang, *Synth. Commun*., 2002, **23**, 175.
28 D. Craig, K. Daniels and A. R. MacKenzie, *Tetrahedron Lett*., 1991, **32**, 6973.
29 S. Diederichs, J. Delaunay, G. Mabon and J. Simonet, *Tetrahedron Lett*., 1995, **36**, 8423.
30 G. Glarosa and S. Sullivana, *Synth. Commun*., 1976, **6**, 495.