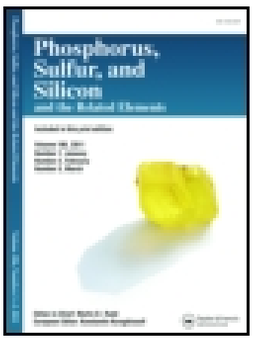

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SHORT COMMUNICATION

Synthesis of (E)-β-iodovinyl sulfones via DTBP/I_2 promoted difunctionalization of alkynes with sodium benzenesulfinates

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ABSTRACT

The present reaction provides a simple and convenient synthetic strategy to construct β-iodovinyl sulfones through molecular iodine and DTBP (di-tert-butyl peroxide) promoted difunctionalization of alkynes with sodium benzenesulfinates under mild and environmentally-benign conditions. A series of substituted (E)-β-iodovinyl sulfones were synthesized with excellent stereo- and regio-selectivities.

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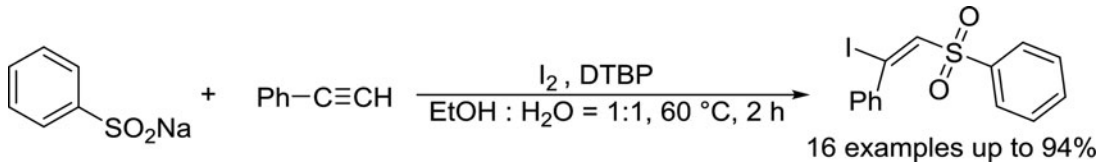
KEYWORDS
β-Iodovinyl sulfones; alkynes; sodium benzenesulfinates; molecular iodine

GRAPHICAL ABSTRACT



Introduction

β-Iodovinyl sulfones have drawn great attention from chemists due to their biological activities[1] and are widely used as building blocks for various organic transformations in synthetic chemistry (Scheme 1).[2–4] Recently, Wnuk *et al.* reported that β-iodovinyl sulfones undergo efficient stereoselective nucleophilic substitution with amines or thiols to provide (Z)-β-aminovinyl or (E)-β-thiovinyl sulfones tethered to the C5 position of the uracil ring (Scheme 1, eq. (1)).[2] Xie *et al.* reported that (E)-β-iodovinyl sulfones were used to synthesize sulfonyl-substituted 1,3-enynes via Sonogashira coupling reaction with terminal alkynes and the sulfonyl group could be further transformed to various substitutents by desulfonylation coupling reactions (Scheme 1, eq. (2)).[3] Inomata *et al.* reported the (E)-β-iodovinyl sulfones could be converted to their corresponding allylic sulfones in the presence of 5% Pd-C under hydrogen atmosphere in methanol or DBU (1,8-diazabicycloundec-7-ene) in CH_3CN. (Scheme 1, eqs. (3) and (4)).[4]

From a synthetic standpoint, the most straightforward and useful strategies to synthesize β-halovinyl sulfones were the direct difunctionalization of alkynes with sulfonyl halides.[5] However, the instability of sulfonyl iodide greatly limited the application of this method to construct β-iodovinyl sulfones.[6] In recent years, stable sulfone precursor, such as sulfonylhydrazides,[7] benzenesulfonyl chlorides,[8] and sulfinic acids,[9] were employed for the direct difunctionalization of alkynes to construct β-iodovinyl sulfones. Unfortunately, these reported methods suffered from some obvious disadvantages such as the low atom economy, low reaction yields, high reaction temperature and long reaction time. Meanwhile, the direct difunctionalization of alkynes with sodium benzenesulfinates to construct (E)-β-iodovinyl sulfones were also well developed. Nair *et al.* reported the synthesis of (E)-β-iodovinyl sulfones via a cerium(IV) ammonium nitrate (CAN) mediated difunctionalization of alkynes in the presence of NaI (Scheme 2, eq. (a)).[10] Kuhakarn *et al.* reported a (diacetoxyiodo)benzene [$PhI(OAc)_2$, DIB] promoted reaction to afford β-iodovinyl sulfones from sodium aryl sulfinate and alkenes under mild reaction conditions (Scheme 2, eq. (b)).[11] In 2013, they reported an improved synthesis of β-iodovinyl sulfones by a molecular iodine-mediated one-pot reaction in the presence of 1.5 eq. of NaOAc (Scheme 2, eq. (c)).[12] Very recently, Taniguchi's group demonstrated an aerobic copper-catalyzed synthesis of β-iodovinyl sulfones via iodosulfonylation of alkynes with aryl sulfinates (Scheme 2, eq. (d)).[13] However, these above mentioned methods suffer from some obvious drawbacks such as the use of transition-metal catalyst, stoichiometric amounts of bases, toxic or potentially dangerous oxidants. Therefore, it is still highly desired to develop a simple, mild, efficient, atomeconomic and environmentally-benign method to construct β-iodovinyl sulfones. Herein, we report a simple and convenient method to synthesize (E)-β-iodovinyl sulfones through molecular iodine and DTBP promoted difunctionalization of alkynes with sodium benzenesulfinates under mild and environmentally-benign conditions (Scheme 2).

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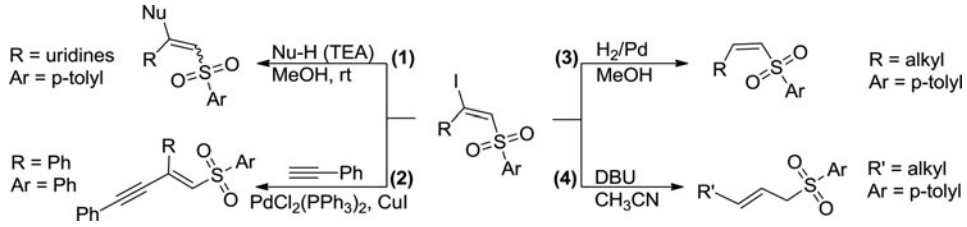
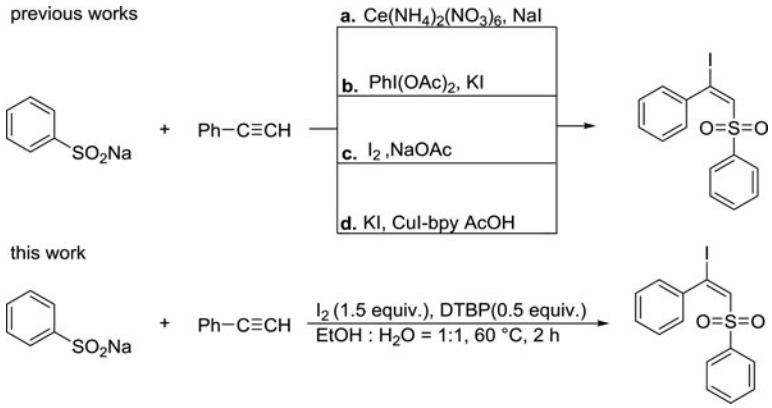
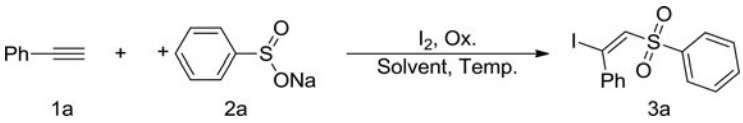


Scheme 1. Application of some (E)-β-iodovinyl sulfone derivatives.



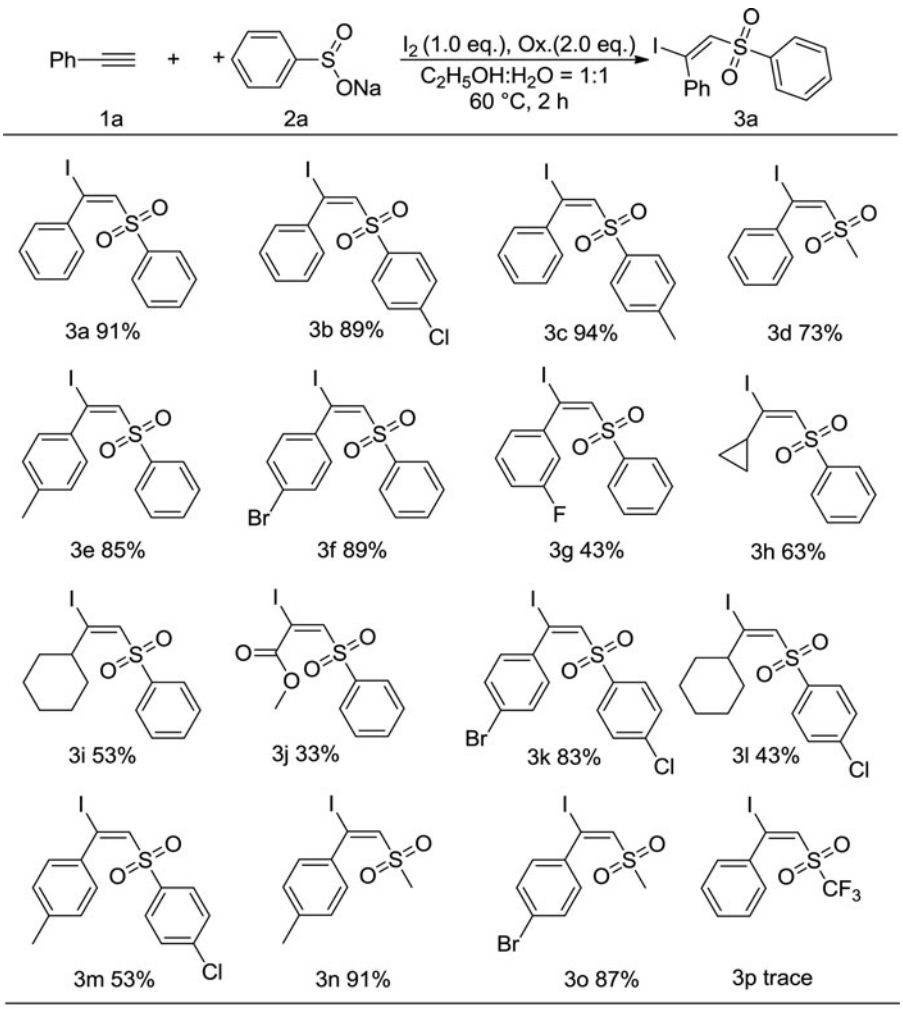
Scheme 2. Synthesis of (E)-β-iodovinyl sulfones from alkynes and sodium benzenesulfinates.

Table 1. Optimization of the reaction conditions.[a]



Entry	I_2 (eq.)	Ox. (eq.)	Solvent	Temp. (°C)	2a (eq.)	Yield (%)[b]
1	0.25	$K_2S_2O_8$ (2)	CH_3OH-H_2O	30	1.2	13%
2	0.5	$K_2S_2O_8$ (2)	CH_3OH-H_2O	30	1.2	15%
3	0.75	$K_2S_2O_8$ (2)	CH_3OH-H_2O	30	1.2	19%
4	1.0	$K_2S_2O_8$ (2)	CH_3OH-H_2O	30	1.2	29%
5	1.25	$K_2S_2O_8$ (2)	CH_3OH-H_2O	30	1.2	26%
6	1.5	$K_2S_2O_8$ (2)	CH_3OH-H_2O	30	1.2	23%
7	1.0	m-CPBA (2)	CH_3OH-H_2O	30	1.2	25%
8	1.0	$(NH_4)_2S_2O_8$ (2)	CH_3OH-H_2O	30	1.2	11%
9	1.0	H_2O_2 (2)	CH_3OH-H_2O	30	1.2	30%
10	1.0	TBHP (2)	CH_3OH-H_2O	30	1.2	32%
11	1.0	DTBP (2)	CH_3OH-H_2O	30	1.2	49%
12	1.0	DTBP (1)	CH_3OH-H_2O	30	1.2	31%
13	1.0	DTBP (3)	CH_3OH-H_2O	30	1.2	34%
14	1.0	DTBP (2)	AcOH-H_2O	30	1.2	57%
15	1.0	DTBP (2)	DMF-H_2O	30	1.2	73%
16	1.0	DTBP (2)	C_2H_5OH-H_2O	30	1.2	78%
17	1.0	DTBP (2)	C_2H_5OH-H_2O	20	1.2	66%
18	1.0	DTBP (2)	C_2H_5OH-H_2O	40	1.2	72%
19	1.0	DTBP (2)	C_2H_5OH-H_2O	50	1.2	82%
20	1.0	DTBP (2)	C_2H_5OH-H_2O	60	1.2	85%
21	1.0	DTBP (2)	C_2H_5OH-H_2O	70	1.2	83%
22	1.0	DTBP (2)	C_2H_5OH-H_2O	80	1.2	76%
23	1.0	DTBP (2)	C_2H_5OH-H_2O	60	1.0	79%
24	1.0	DTBP (2)	C_2H_5OH-H_2O	60	1.5	76%
25	1.0	DTBP(2)	C_2H_5OH-H_2O	60	2.0	91%
26	1.0	DTBP (2)	C_2H_5OH-H_2O	60	2.5	77%
27	1.0	DTBP (2)	C_2H_5OH-H_2O	60	3.0	75%

[a]Reaction conditions: alkyne (0.5 mmol), I_2 (0.25–1.5 eq.), sodium benzenesulfinates (1.0–3.0 eq.), solvent (2 mL: 2 mL) at 20–80°C for 2 h.
[b]Isolated yields.



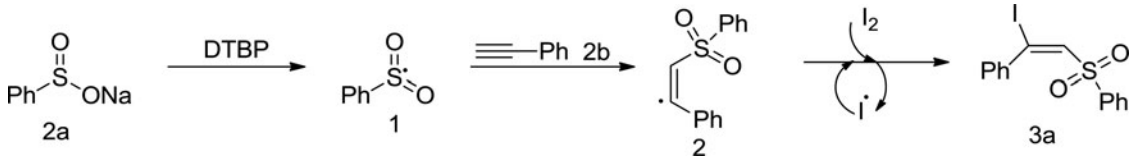
[a] Reaction conditions: alkyne (0.5 mmol), sodium benzenesulfinates (1.0 mmol), I_2 (0.5 mmol) in C_2H_5OH : H_2O (2 mL : 2 mL) at 60 °C for 2 h. [b] Isolated yields.

Scheme 3. Scope of the reaction.[a,b]

Results and discussion

We initiated this study by establishing optimal experimental conditions using the model reaction of phenylacetylene (**1a**) with sodium benzenesulfinate (**2a**) as shown in Table 1. The amount of iodine employed in the model reaction was first investigated by reacting **1a** with **2a** in the presence of $K_2S_2O_8$ (2.0 eq.) at 30°C for 2 h (Table 1, entries 1-6). It can be seen that the yield increased over the amount of iodine range of 0.25 eq. to 1.0 eq. (entries 1-4), and then decreased (entries 5-6). The effects of some common oxidant reagents on the reaction were then investigated (entries 4, 7-11). $K_2S_2O_8$, m-CPBA, $(NH_4)_2S_2O_8$, H_2O_2 and TBHP (tert-butyl hydroperoxide) exhibited almost the same activity for the model reaction (entries 4, 7-10). Only DTBP (di-tert-butyl peroxide) afforded a moderate yield of **3a** (49%) (entriy 11). The investigation on the amount of DTBP (entries 11-13) indicated that 2 eq. of oxidant still gives the best yield of **3a**. The investigation of solvent system employed on the model reaction showed a significate increase in the yield of **3a** (49-78%) (entries 11, 14-16) when C_2H_5OH-H_2O (v:v = 1:1) were used. Then the influence of temperature on the model reaction showed that the yield increased over the temperature range of 20-60°C (entries 16-20), and then decreased (entries 21-22). At last, the exploration of the ideal amount of sodium benzenesulfinate (**2a**) showed that 2.0 eq. of **2a** gave the highest yield of **3a** (91%) (entries 20, 23-27). Therefore, the optimized reaction conditions for the construction of **3a** was 1.0 eq. of I_2, 2.0 eq. of DTBP and 2.0 eq. of sodium benzenesulfinate in C_2H_5OH-H_2O (v:v = 1:1) at 60°C for 2 h (entry 25).

With the optimized raction conditions in hand, the substrate scope of phenylacetylene and sodium benzenesulfinate was then examined as demonstrated in Scheme 3. As it can be seen, a variety of sodium benzenesulfinates reacted well with phenylacetylene itself, in addition to sodium methanesulfinate. We found that the substitute groups on sodium benzenesulfinate did not affect the yield of the correspongding compounds. Electron donating groups on phenylacetylene also gave excellent yields; while the electron withdrawing groups on phenylacetylene or acetylene significantly decreased the yields of β-iodovinyl



Scheme 4. A general pathway for the difunctionalization of alkynes.

sulfones. However, the yields of the corresponding β-iodovinyl sulfones were relatively low when aliphatic terminal alkynes were employed in this reaction and these reaction conditions were not suitable to convert sodium trifluoromethanesulfinate to its β-iodovinyl sulfones derivatives.

Based on the knowledge that sulfonyl radical species are easily generated from sodium benzenesulfinates under air oxidizing environment,[14] a general reaction pathway is proposed and demonstrated in Scheme 4. Firstly, the sulfonyl radical **1** was generated from sodium benzenesulfinates under DTBP. Then, the addition of sulfonyl radical to alkyne **2b** gave the alkenyl radical **2**, which further interacted with molecular iodine leading to the formation of the desired β-iodovinyl sulfone 3a.[6,10]

Conclusion

In conclusion, a simple and efficient approach for the synthesis of (E)-β-iodovinyl sulfones via the molecular iodine promoted direct difunctionalization of alkynes with sodium benzenesulfinates were developed. The new synthesis methodology provides an alternative route to various (E)-β-iodovinyl sulfones from easily available starting materials without transition-metal catalyst or potentially dangerous oxidants.

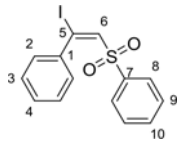
Experimental section

All the chemicals were obtained from Tianjin Kermel Chemical Reagent Co., Ltd., and Shanghai Aladdin Bio-Chem Technology Co., Ltd., and used as received. ^{1}H, and ^{13}C NMR spectra were recorded with a Bruker Avance 400 MHz spectrometer operating at 400.13 and 100.61 MHz, respectively, with ^{13}C NMR spectra being recorded with broad band proton decoupled. All NMR spectra were recorded in δ-DMSO at room temperature (20 $\pm$ 3°C). ^{1}H and ^{13}C chemical shifts are quoted in parts per million downfield from TMS. High resolution mass spectra (HR MS) were obtained with a Waters Micromass Q-Tof Micro instrument using the ESI technique. The Supplemental Materials contains sample ^{1}H and ^{13}C NMR spectra for the products 3 (Figures S1–S30).

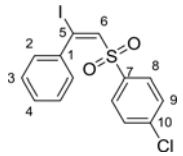
General procedure

Synthesis of (E)-β-iodovinyl sulfones

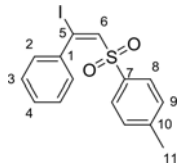
I_2 (0.5 mmol) was added to a solution of alkynes (0.5 mmol), sodium benzenesulfinates (1.0 mmol) and DTBP (1.0 mmol) in C_2H_5OH: H_2O (2 mL:2 mL), and the reaction mixture was stirred and heated at 60°C for 2.0 h. Then, the mixture was cooled to room temperature, quenched by $Na_2S_2O_3$, diluted with water and extracted by CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was removed in vacuum and the target compound was obtained by column chromatography on silica gel (petroleum ether: ethyl acetate = 15: 1, v: v).



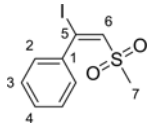
(E)-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (3a) Isolated Yield 91%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 7.17(t, 2H, 2-H), 7.33(t, 1H, 4-H), 7.56 (t, 2H, 3-H), 7.65(d, J = 7.6 Hz, 2H, 9-H), 7.68 (m, 2H, 8-H), 7.70(m, 1H, 10-H), 7.81(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 116.5(5-C), 127.6(2-C), 127.8(4-C), 128.4(3-C), 129.8(8-C), 129.9(9-C), 134.3(6-C), 140.2(10-C), 140.67(1-C), 140.71(7-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 370.9597, found: 370.9601.



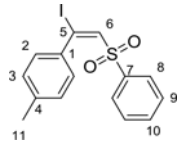
(E)-1-chloro-4-((2-iodo-2-phenylvinyl)sulfonyl)benzene (3b) Isolated Yield 89%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 7.17(t, 2H, 2-H), 7.31(t, 3H, 3, 4-H), 7.56 (d, J = 8.4 Hz, 2H, 9-H), 7.64(d, J = 8.4 Hz, 2H, 8-H), 7.81(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 116.9(5-C), 127.5(2-C), 128.4(3-C), 129.8(8-C), 129.9(4-C), 133.3(9-C), 139.3(6-C), 139.5(10-C), 139.9(1-C), 140.6(7-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 404.9207, found: 404.9211.



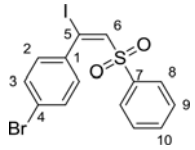
(E)-1-((2-iodo-2-phenylvinyl)sulfonyl)-4-methylbenzene (3c) Isolated Yield 94%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 2.35(s, 3H, 11-H), 7.17(dd, J = 2.0 Hz, J = 5.6 Hz, 2H, 3-H), 7.32-7.34(m, 5H, 2, 4, 9-H), 7.53(d, J = 8.4 Hz, 2H, 8-H), 7.74(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 21.6(11-C), 115.9(5-C), 127.6(2-C), 127.9(3-C), 128.3(8-C), 129.8(4-C), 130.4(9-C), 137.8(6-C), 140.4(10-C), 140.7(1-C), 144.9(7-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 384.9754, found: 384.9759.



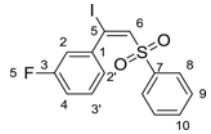
(E)-(1-iodo-2-(methylsulfonyl)vinyl)benzene (3d) Isolated Yield 73%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 2.95(s, 3H, 7-H), 7.36-7.37(m, 5H, 2, 3, 4-H) 7.71(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 43.5(7-C), 114.9(5-C), 128.0(2-C), 128.4(3-C), 130.0(4-C), 140.0(6-C), 140.8(1-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 308.9441, found: 308.9441.



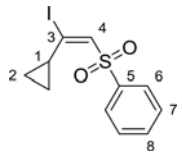
(E)-1-(1-iodo-2-(phenylsulfonyl)vinyl)-4-methylbenzene (3e) Isolated Yield 85%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 2.30(s, 3H, 11-H), 7.08-7.14(m, 4H, 2, 3-H), 7.52-7.56(m, 2H, 9-H), 7.65-7.72 (m, 3H, 8, 10-H), 7.75 (s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 21.4(11-C), 116.8(5-C), 127.7(2-C), 127.8(4-C), 128.9(3-C), 129.8(8-C), 134.2(9-C), 137.8(6-C), 139.7(10-C), 139.9(1-C), 140.7(7-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 384.9754, found: 384.9759.



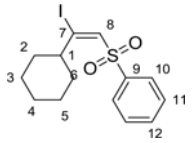
(E)-1-bromo-4-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (3f) Isolated Yield 89%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 7.15(d, J = 8.4 Hz, 2H, 2-H), 7.54-7.59(m, 4H, 3, 9-H), 7.68-7.73 (m, 3H, 8, 10-H) 7.83(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 114.6(5-C), 123.2(2-C), 127.9(4-C), 129.6(3-C), 130.0(8-C), 131.4(9-C), 134.4(6-C), 140.1(10-C), 140.4(1-C), 140.7(7-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 448.8702, found: 448.8707.



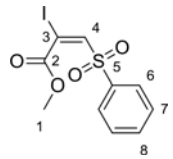
(E)-1-fluoro-3-(1-iodo-2-(phenylsulfonyl)vinyl)benzene (3g) Isolated Yield 43%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 6.99(t, 2H, 2, 2'-H), 7.15-7.20(m, 1H, 4-H), 7.37-7.42 (m, 1H, 3'-H), 7.58(t, 2H, 9-H), 7.67(d, J = 7.6 Hz, 2H, 8-H), 7.72(t, 1H, 10-H), 7.84(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 114.0(5-C), 114.3(J = 22.3 Hz, 2-C), 116.5(J = 20.4 Hz, 4-C), 123.6(J = 2.7 Hz, 2'-C), 127.8(8-C), 130.0 (9-C), 130.5(J = 8.4 Hz, 3'-C), 134.4(6-C), 140.4(10-C), 140.7(7-C), 142.8(J = 6.8 Hz, 1-C), 140.2(J = 243.4 Hz, 3-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 388.9503, found: 388.9507.



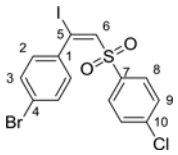
(E)-((2-cyclopropyl-2-iodovinyl)sulfonyl)benzene (3h) Isolated Yield 63%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 0.71-0.94(m, 4H, 2-H), 2.37(m, 1H, 1-H), 7.42 (s, 1H, 4-H), 7.67(t, 2H, 7-H), 7.74-7.78(m, 1H, 8-H), 7.95(d, J = 6.4 Hz, 2H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 12.0(2-C), 17.4(1-C), 127.4(6-C), 130.2(7-C), 134.3(4-C), 135.5(3-C), 137.6(8-C), 141.5(5-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 334.9597, found: 334.9599.



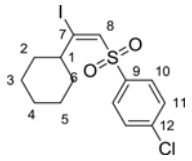
(E)-((2-cyclohexyl-2-iodovinyl)sulfonyl)benzene (3i) Isolated Yield 53%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 1.04-1.71(m, 10H, 2, 3, 4, 5, 6-H), 2.78(m, 1H, 1-H), 7.44 (s, 1H, 8-H), 7.69(t, 2H, 11-H), 7.77(t, 1H, 12-H), 7.94(d, J = 7.2 Hz, 2H, 10-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 24.8 (3-C), 25.4(4-C), 33.2(2-C), 43.2(1-C), 127.6(7-C), 130.3(11-C), 134.5(12-C), 137.0(8-C), 138.3(13-C), 141.5(10-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 377.0067, found: 377.0071.



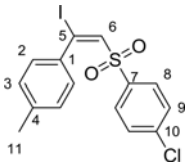
(E)-methyl 2-iodo-3-(phenylsulfonyl)acrylate (3j) Isolated Yield 33%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 3.84(s, 3H, 1-H), 7.71(t, 2H, 7-H), 7.79-7.81 (m, 2H, 4, 8-H), 7.88 (d, J = 7.6 Hz, 2H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 53.9(1-C), 103.7(3-C), 128.0(6-C), 130.3(7-C), 135.0(8-C), 139.2(5-C), 139.3(4-C), 166.4(2-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 352.9339, found: 352.9343.



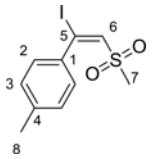
(E)-1-bromo-4-(2-((4-chlorophenyl)sulfonyl)-1-iodovinyl)benzene (3k) Isolated Yield 83%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 7.12(d, J = 8.4 Hz, 2H, 2-H), 7.54(d, J = 7.6 Hz, 2H, 3-H), 7.62-7.69 (m, 4H, 7, 8-H), 7.84(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 119.9(5-C), 128.0(4-C), 134.2(2-C), 134.6(3-C), 134.9(8-C), 136.2(9-C), 143.9(6-C), 144.3(10-C), 144.76(1-C), 140.78(7-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 482.8313, found: 482.8313.



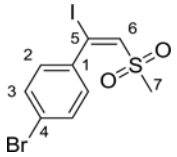
(E)-1-chloro-4-((2-cyclohexyl-2-iodovinyl)sulfonyl) benzene (3l) Isolated Yield 43%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 1.04-1.72(m, 10H, 2, 3, 4, 5, 6-H), 2.78(m, 1H, 1-H), 7.45 (s, 1H, 8-H), 7.76(d, J = 8.8 Hz, 2H, 10-H), 7.95(d, J = 7.2 Hz, 2H, 11-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 24.8 (3-C), 25.4(4-C), 33.3(2-C), 43.3(1-C), 129.6(7-C), 130.4(11-C), 137.5(12-C), 137.8(8-C), 139.6(13-C), 140.2(10-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 410.9677, found: 410.9677.



(E)-1-chloro-4-((2-iodo-2-(p-tolyl)vinyl)sulfonyl)benzene (3m) Isolated Yield 53%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 2.32(s, 3H, 11-H), 7.06(d, J = 8.4 Hz, 2H, 2-H), 7.13 (d, J = 8.0 Hz, 2H, 3-H), 7.60-7.65(m, 4H, 8, 9-H), 7.77(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 21.4(11-C), 117.3(5-C), 127.6(2-C), 128.9(3-C), 129.8(8-C), 130.0(9-C), 137.8(4-C), 139.3(6-C), 139.4(10-C), 139.5(1-C), 139.8(7-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 418.9364, found: 418.9368.



(E)-1-(1-iodo-2-(methylsulfonyl)vinyl)-4-methylbenzene (3n) Isolated Yield 91%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 2.32(s, 3H, 8-H), 2.94(s, 3H, 7-H), 7.19(d, J = 8.0 Hz, 2H, 2-H), 7.28(d, J = 7.6 Hz, 2H, 3-H), 7.66(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 21.3(8-C), 43.4(7-C), 115.2(5-C), 128.2(2-C), 128.9(3-C), 137.9(6-C), 139.6(1-C), 139.9(4-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 322.9597, found: 322.9599.



(E)-1-bromo-4-(1-iodo-2-(methylsulfonyl)vinyl)benzene (3o) Isolated Yield 87%. Yellow oil. ^{1}H NMR (400 MHz, δ-DMSO) δ: 3.40(s, 3H, 7-H), 7.31(d, J = 8.4 Hz, 2H, 2-H), 7.58(d, J = 8.4 Hz, 2H, 3-H), 7.75(s, 1H, 6-H). ^{13}C NMR (400 MHz, δ-DMSO) δ: 43.5(7-C), 113.1(5-C), 123.2(6-C), 130.0(2-C), 131.4(3-C), 140.1(1-C), 140.3(4-C). HR MS (ESI-Q-TOF): $[M+H]^+$, Cal.: 386.8546, found: 386.8549.

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