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An efficient transition-metal free iodine-mediated tuneable disulfonylation and sulfinylsulfonylation of alkynes with sodium arylsulfinate under visible light irradiation has been developed. This photochemical protocol offers broad substrate scope of 1,2-bissulfonylethenes with high functional group tolerance and good yields under mild reaction conditions. In addition, it was found that β -sulfinyl alkenylsulfones can be obtained in the absence of base. It is proposed that the reactions proceed *via* sulfonyl and sulfinyl radicals.

Organosulfur compounds are attractive scaffolds with numerous applications in organic chemistry,¹ agrochemicals,² material science,³ and medicinal chemistry.⁴ Among them, vinyl sulfones are an important class of organosulfur molecules as targets and versatile intermediates in organic chemistry.⁵ Recently, vinyl sulfones have been used in visible-light mediated reactions as radical acceptors.⁶ Due to their importance, there are many synthetic strategies to synthesise vinyl sulfones.⁷ Radical difunctionalisation of alkynes is one of the most efficient and direct approaches to access functionalised vinylsulfones with high step- and atom-economy.⁸ In 2020, Ning and Tang independently reported direct disulfonylation of terminal alkynes with sodium arylsulfinate using either copper(I) and bromodifluoroacetate or an iodine(III) reagent, respectively (Scheme 1a and b).^{9,10} Despite many advantages, these methods suffer from their scope being limited to terminal alkynes, harsh reaction conditions, use of copper or iodine(III), and high stoichiometric loading of arylsulfinate. To overcome these limitations, the development of a sustainable and simple method for disulfonylation of alkynes with readily available chemicals is highly sought-after.

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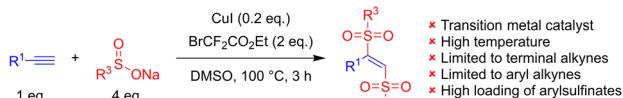
Iodine-mediated photoinduced tuneable disulfonylation and sulfinylsulfonylation of alkynes with sodium arylsulfinate[†]

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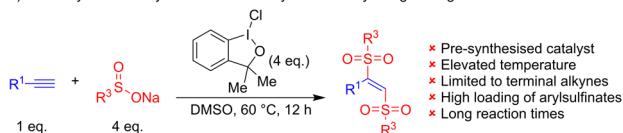
Visible-light photocatalysis is playing an increasing role in organic synthesis because of demonstrated complex bond constructions under mild reaction conditions and visible light is environmentally benign.¹¹ Recently, visible-light-initiated iodine mediated reactions have become attractive because these reactions avoid external transition-metal based photocatalysts and access the desired products by addition-elimination mechanisms.¹² E.g., Wang demonstrated photochemical iodine-catalysed electrophilic cyclisation reaction of alkynes for oxazole aldehydes.¹³ Separately, an environmentally friendly iodine-promoted synthesis of (*E*)- β -iodo vinylsulfones in water was developed by Liu¹⁴ and, recently, Bi reported the synthesis of β -sulfinyl alkenylsulfones by sulfinylsulfone radical additions to unsaturated hydrocarbons.¹⁵ Inspired by these, and related results¹⁶ herein we report the iodine-mediated tuneable synthesis of 1,2-bissulfonylethenes and β -sulfinyl alkenylsulfones under transition metal-free, mild photochemical conditions (Scheme 1c).

Previous work:

a) Disulfonylation of alkynes with sodium arylsulfinate by using Cu-catalyst⁹

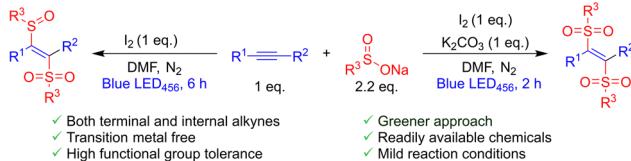


b) Disulfonylation of alkynes with sodium arylsulfinate by using I^{III} reagent¹⁰



This work:

c) Visible-light-induced and iodine-mediated difunctionalisation of alkynes with sodium arylsulfinate



Scheme 1 Background and context of this work.



Table 1 shows optimisation results using phenylacetylene **1a** and sodium *p*-toluenesulfinate **2a** as model substrates for the photochemical difunctionalisation. After screening, it was found that 1 equiv. of I_2 and 1 equiv. of K_2CO_3 in DMF under a nitrogen atmosphere for 2 h were the best conditions, yielding **3a** in 88% (entry 1). We screened different solvents: MeCN was found to be less efficient than DMF (entry 2) and other solvents such as EtOH and H_2O failed to afford **3a** (entries 3 and 4). No significant change in yields was observed on replacing the K_2CO_3 with Cs_2CO_3 , but organic bases DIPEA and DBU gave only 15% and 20% yield of **3a**, respectively (entries 5–7). To our delight, in the absence of base we observed β -sulfinyl alkenylsulfones **6a** in 30% yield (entry 8). Furthermore, increasing the reaction time to 6 h and doubling the dilution of the reaction mixture afforded **6a** in 55% yield (entry 9). Decreasing the equivalents of iodine was found to lower the yield (entry 10). Air instead of a nitrogen atmosphere gave only 20% of the desired product **3a** (entry 11). No product was observed in the absence of Iodine (entry 12) or blue light (35% of iodovinylsulfone **3a'** was obtained, entry 13).

Having found suitable reaction conditions, we examined the generality of this photochemical difunctionalisation reaction (Table 2). Phenylacetylenes bearing electron-donating groups underwent the photochemical difunctionalisation with **2a** smoothly, affording 1,2-bissulfonylethenes **3b–3e** in 68–84% yield. Phenylacetylenes bearing halogens and stronger electron-withdrawing groups effectively reacted with **2a** giving the products **3f–3n** in 74–88%. Notably, aromatic heterocyclic pyridine and thiophene-substituted alkynes, and an aliphatic alkyne were also well tolerated and gave the corresponding products **3o–3s** in good yields.

Next, we explored the scope of internal alkynes. To our delight, ethyl and methyl 3-phenylpropiolates smoothly reacted with **2a** under this protocol and gave alkenes **4a** and **4b** in 75% and 72% yield, respectively. Ynone **2c** was also well tolerated, giving 1,2-bissulfonylethene **4c** in moderate yield. Remarkably, prop-1-yn-1-ylbenzene was also reactive under these conditions, giving the target **4d** in 48% yield. In contrast, electronically symmetrical diphenylacetylene failed to produce alkene **4e**. We extended the substrate scope to the ester derivates of bio-active menthol, borneol and cholesterol; these reacted smoothly affording alkenes **4f–4h** in 58–73% yield.

We established the *E*-geometry from an X-Ray structure of **4a** (see ESI†). To the best of our knowledge, this is the first time tetrasubstituted alkenes of this general structure have been reported. Finally, we varied the sulfinate. Aryl sulfonates gave high yields (**5a–5d**). However, pyrimidine-2-sulfinate failed to give the target **5f**. Sodium ethane sulfinate also reacted to give **5e** in 53% yield. Overall, our new method gives direct access from alkyne to disulfonylated alkene with excellent control of geometry, and uses milder conditions compared to previous methods. The substrate scope is broader, with amines tolerated, and especially access to tetra-substituted alkenes being noteworthy.

Next, we explored the observation that in the absence of base the major product was β -sulfinyl alkenylsulfone **6a** (Table 1, entries 8–9). The scope of this tuneable synthesis of β -sulfinyl alkenylsulfones is shown in Table 3. Various alkynes and sodium arylsulfonates were screened under optimised conditions, β -sulfinyl alkenylsulfones **6a–6h** were obtained in moderate-to-good yields. In contrast, phenylacetylenes bearing strong electron-withdrawing groups failed to give targets **6i** and **6j**; the competing pathway producing bissulfonylethenes dominated (see ESI† for other unsuccessful substrates). Tetrasubstituted **6k** was obtained in low yield.

Next the reaction mechanism was investigated (Scheme 2a and b). Addition of the radical scavenger TEMPO stopped the production of **3a** and **6a** (Scheme 2a), and the tosyl radical-TEMPO adduct was detected (see ESI†). Addition of BHT also lowered the yield of **3a** and the tosyl radical-BHT adducts were detected (see ESI†). Thus, both reactions are proposed to proceed *via* a tosyl radical intermediate. When the disulfonylation reaction mixture was quenched and isolated after 1 h, 55% of **3a'** and 20% of **3a** were observed (Scheme 2ba).¹⁰ Subjecting **3a'** to the disulfonylation conditions gave **3a** in 82% yield, suggesting that **3a'** may be an intermediate in the synthesis of 1,2-bissulfonylethenes (Scheme 2bb). In the presence of TEMPO **3a'** failed to produce **3a** (Scheme 2bc), indicating that the conversion of **3a'** to **3a** proceeds *via* a radical pathway. When **3a'** was subjected to the disulfonylation conditions without I_2 the reaction failed to produce **3a** (Scheme 2bd), while KI instead of I_2 did give the target **3a** in 80% yield (Scheme 2be), suggesting that I_2 or iodide was needed for the second sulfonylation step. In contrast, subjecting **3a'** to the sulfinylsulfonylation conditions did not produce **6a**; implying that **6a** is not formed *via* intermediate **3a'**.

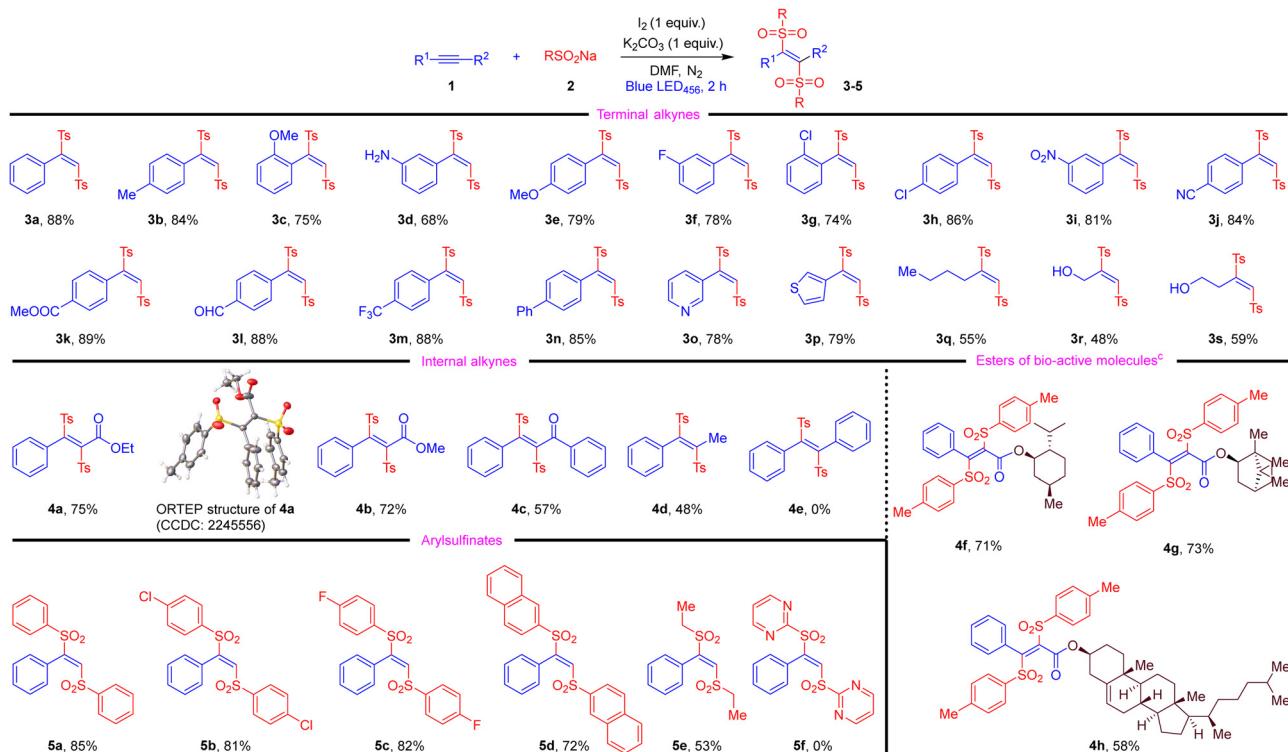
Based on the above experiments and earlier literature,¹⁷ we propose the pathway shown in Scheme 3. Initially, sodium

Table 1 Optimisation of reaction conditions^a

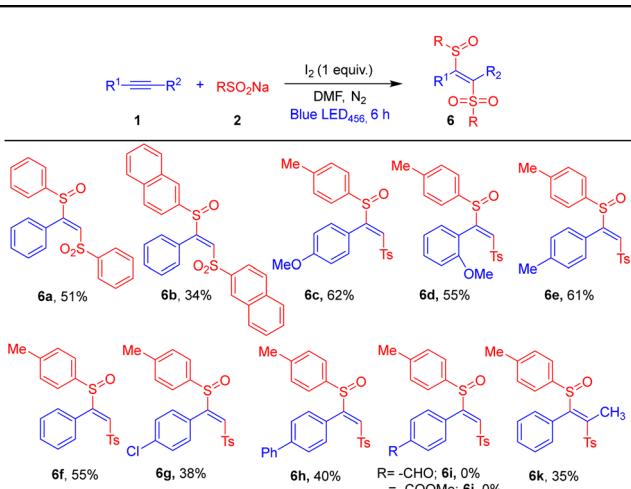
Entry	Variation from the standard conditions	Yield ^b (%)		
		3a	6a	3a'
1	None	88	0	0
2	MeCN instead of DMF	75	10	0
3	EtOH instead of DMF	Traces	0	25
4	H_2O instead of DMF	0	0	55
5	Cs_2CO_3 instead of K_2CO_3	88	0	0
6	iPr ₂ EtN instead of K_2CO_3	15	0	22
7	DBU instead of K_2CO_3	20	0	35
8	Absence of base	10	30	35
9 ^c	Absence of base, 6 h, dilute	15	55	20
10	0.5 equiv. of I_2	66	0	0
11	Air instead of N_2	20	0	35
12	Absence of I_2	n.r.	n.r.	n.r.
13	Absence of blue LED	0	0	35

^a Standard reaction conditions: **1a** (0.1 mmol), **2a** (0.22 mmol), I_2 (0.1 mmol), and K_2CO_3 (0.1 mmol) in DMF (1 mL) was irradiated with a blue LED (456 nm, 40 W) under a N_2 atmosphere. ^b Isolated yields.

^c Reaction mixture was irradiated for 6 h under blue LED and 2 mL DMF. n.r. = no reaction.

Table 2 Scope of synthesis of 1,2-bissulfonylalkenes^{a,b}

^a Reaction conditions: **1a** (0.1 mmol), **2a** (0.22 mmol), **I₂** (0.1 mmol), and **K₂CO₃** (0.1 mmol) in DMF (1 mL) was irradiated with a blue LED (456 nm, 40 W) under a **N₂** atmosphere. ^b Isolated yields. ^c Reaction mixture was irradiated for 4 h with a blue LED.

Table 3 Scope of the synthesis of β -sulfinyl alkenylsulfones^{a,b}

^a Reaction conditions: **1** (0.1 mmol), **2** (0.22 mmol) and **I₂** (0.1 mmol) in DMF (2 mL) was irradiated with a blue LED (456 nm, 40 W) under a **N₂** atmosphere. ^b Isolated yields.

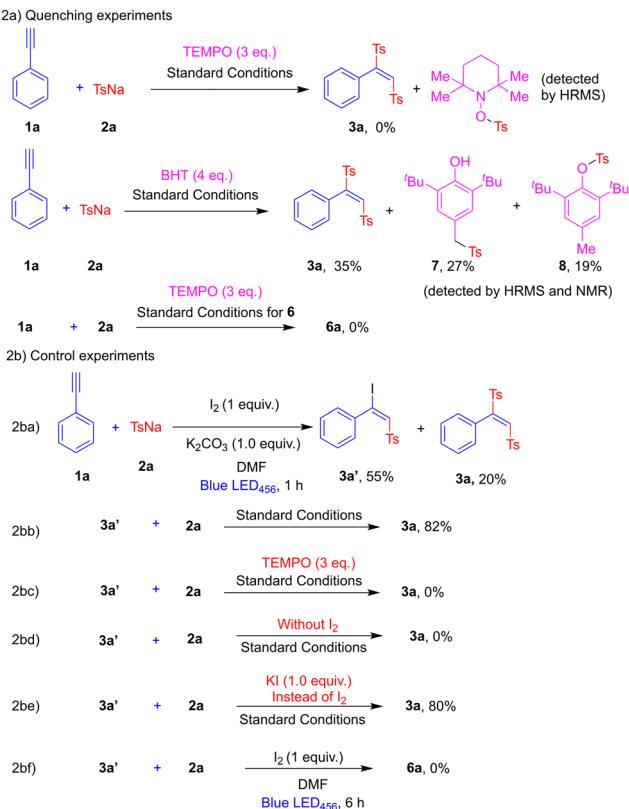
arylsulfinate **2** reacts with **I₂** to form intermediate **A**.¹⁸ Irradiation of **A** generates a sulfonyl radical **B**, which reacts with alkyne **1** to form a vinylsulfone radical **C**. Radical **C** could undergo radical–radical coupling with sulfonyl radical **B** to give the product **3**,¹⁰ or it could react with iodine or iodine radical

to give intermediate **3'** (which was isolated from quenched reactions).¹⁹ Intermediate **3'** can react with sulfonyl radical **B** in the presence of base and blue light to afford final compound **3** (Scheme 2bb). Given that 55% of **3a'** was isolated after 1 h of reaction (Scheme 2ba), it seems that this is likely to be the major pathway. The pathway for the formation of sulfinylsulfones **6** is less clear. The simplest explanation is that a sulfinyl radical forms and then follows the pathway proposed by Bi.¹⁵ One possibility is that in the absence of base, intermediate **A** reacts with iodide to generate intermediate **D** by elimination of **IO⁻**.²⁰ Intermediate **D** could then form a sulfinyl radical on irradiation.^{20b} Intermediate **D** or the sulfinyl radical could react with intermediate **C** to give the sulfinylvinylsulfone **6**.

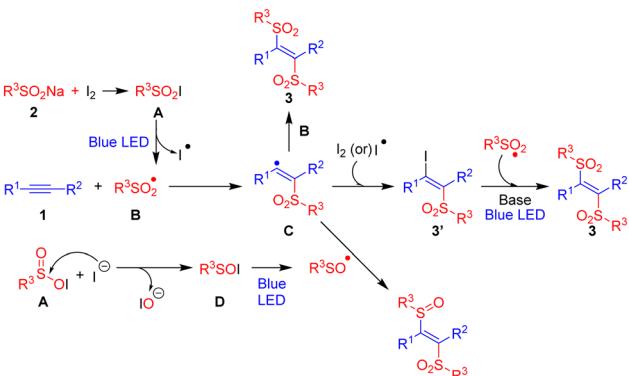
In conclusion, we have demonstrated a sustainable iodine-mediated tuneable disulfonylation and sulfinylsulfonylation of alkynes with sodium arylsulfinate. This photochemical difunctionalisation has a broad substrate scope and high functional group tolerance, and mild reaction conditions without transition-metal or external photocatalysts. A plausible mechanistic proposal was supported by control, quenching experiments and UV studies. We anticipate that this methodology will enable further applications of vinylsulfones, especially w.r.t. to the novel tetra-substituted alkene architectures that are accessible as a result of this work.

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Scheme 2 Mechanistic investigations.



Scheme 3 Plausible mechanism.

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Conflicts of interest

There are no conflicts to declare.

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