

Mechanochemical-Assisted Decarboxylative Sulfonylation of α,β -Unsaturated Carboxylic Acids with Sodium Sulfinite Salts

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Abstract: Developing a green and efficient method for synthesizing vinyl sulfones is challenging and highly desirable. We hereby report a green, sustainable, and unprecedented mechanochemical-assisted approach for the decarboxylative sulfonylation of α,β -unsaturated carboxylic acids with sodium sulfinates using only potassium iodide (50 mol%) as an activator under water-assisted grinding conditions. A library of alkyl and aryl vinyl sulfone derivatives was synthesized successfully up to 92% yield with excellent functional group compatibility under a short reaction time. This sulfonylation strategy is well tolerated by aryl α,β -unsaturated carboxylic acids, and alkyl and aryl sodium sulfinite salts. The advantages of this strategy are (i) metal catalyst-, base-, oxidant-, and solvent-free, (ii) operationally simple with a short reaction time, (iii) excellent effective mass yield, atom economy, *E*-factor, and EcoScale score. The practicality of this method is also demonstrated in the gram-scale synthesis of vinyl sulfones.

Keywords: Mechanochemistry, Ball mill, Vinyl sulfones, Decarboxylation

Introduction

Owing to their easy accessibility, high stability, and low toxicity, decarboxylative cross-coupling reactions with biomass feedstocks of α,β -unsaturated carboxylic acids have emerged as an efficient tool for the construction of C(sp²)-C and C(sp²)-X (X = N, P, S, Se) bonds. This can be achieved by utilizing the carbon bond adjacent to the -COOH group in α,β -unsaturated carboxylic acids into synthetically important molecules with the release of a non-toxic and easily removable CO₂ as the by-product.¹ Consequently, in the past few years, the construction of C-S bond *via* decarboxylative coupling strategy despite being an underdeveloped process, continues to capture a considerable attention from the synthetic community.²

Vinyl sulfones (α,β -unsaturated sulfones) are a valuable framework in organic synthesis, displaying excellent biological and pharmaceutical properties, as shown in Fig. 1.³ Thus, the synthesis of vinyl sulfones has garnered a great deal of interest, and different strategies for their preparation have emerged. Classic vinyl sulfone preparations are based on the Knoevenagel condensation of aromatic aldehydes with sulfonyl acetic acids and the Horner–Emmons reaction involving α -sulfonyl phosphonium ylides.⁴ A promising strategy, however, is the direct sulfonylation of olefins, alkynes, vinyl halide, vinyl tosylate, vinyl triflates and alkenyl boronic acids with sulfonyl sources. Several sulfonyl sources, such as DABSO, thiosulfonates, sulfinic acids/salts, and sulfonyl hydrazides, have been employed in these reactions.⁵

In this line, decarboxylative sulfonylation of cinnamic acids with sodium aryl sulfinates is a very promising method for the preparation of vinyl sulfones. This is due to easily available starting materials and CO₂ as the only by-product, thereby making this approach sustainable and environmentally benign. However, in the beginning of this approach, the decarboxylative sulfonylation of α,β -unsaturated carboxylic acids have been achieved by the use of transition metal (TM) catalysts such as Pd, Cu, or Mn with expensive and toxic ligands and strong oxidants (Scheme 1).⁶

Some metal-free approaches have also come to the fore,⁷ such as using iodine-containing reagents like I₂ and PhI(OAc)₂.^{7a-c} However, these reactions are marred by the use of stoichiometric amounts of the oxidant and the base, high reaction temperatures, prolonged reaction time, and limited substrate scope restricted only to aryl vinyl sulfones. On similar lines, Wang and co-workers in 2016, disclosed an electrochemical decarboxylative sulfonylation of cinnamic acid with sodium sulfinates for the synthesis of vinyl sulfones.^{7e} However, this method failed in the synthesis of alkyl vinyl sulfones. Thereafter, Wang and co-workers, in 2019, established a photocatalyzed synthesis of vinyl sulfones from cinnamic acid and sodium sulfinates with high regioselectivity.^{7f} This strategy also suffer in term of the requirement of high-intensity irradiation, expensive photocatalyst, and stoichiometric amount of an oxidant, and failure towards alkyl vinyl sulfones synthesis. Overall, a general, environmentally sustainable and mild approach for decarboxylative sulfonylation of cinnamic acids can be highly desirable.

In the arsenals of synthetic chemists, mechanochemistry has become an attractive alternative method for synthesizing organic compounds.⁸ Mechanochemistry enables chemical synthesis sustained by mechanical forces. It offers a new opportunity in synthesizing organic compounds, with solvent-free organic mechanochemical reactions and unlocking new routes towards numerous compounds that are not attainable by other conventional methods.⁹ In continuation to our interest in sustainable, green, and novel synthetic methodologies,¹⁰ we hereby report an unprecedented mechanochemical-assisted

decarboxylative sulfonylation of α,β -unsaturated carboxylic acids with sodium sulfonates using only potassium iodide as an activator with water ($\eta = 0.32 \mu\text{L}/\text{mg}$) as the liquid-assisted grinding additives (LAGs)¹¹ at ambient temperature, under ball milling in 10 min. The method works equally well on alkyl and aryl sulfonates at room temperature without needing any metal catalyst, oxidant, base, or inert environment.

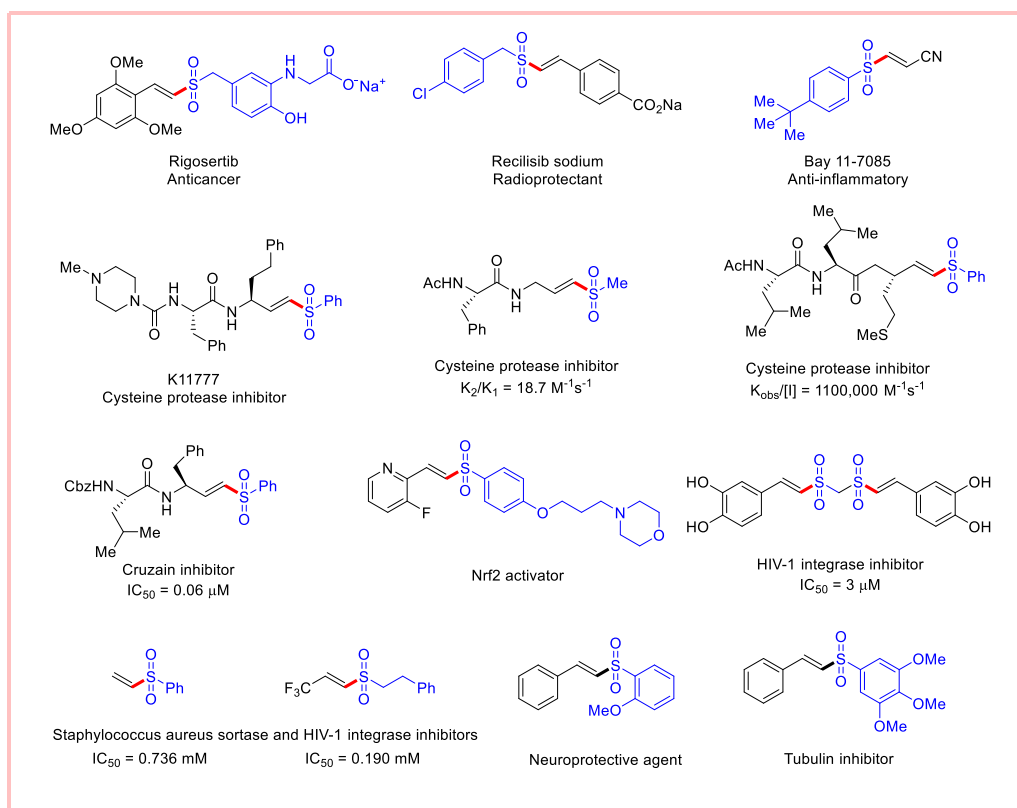
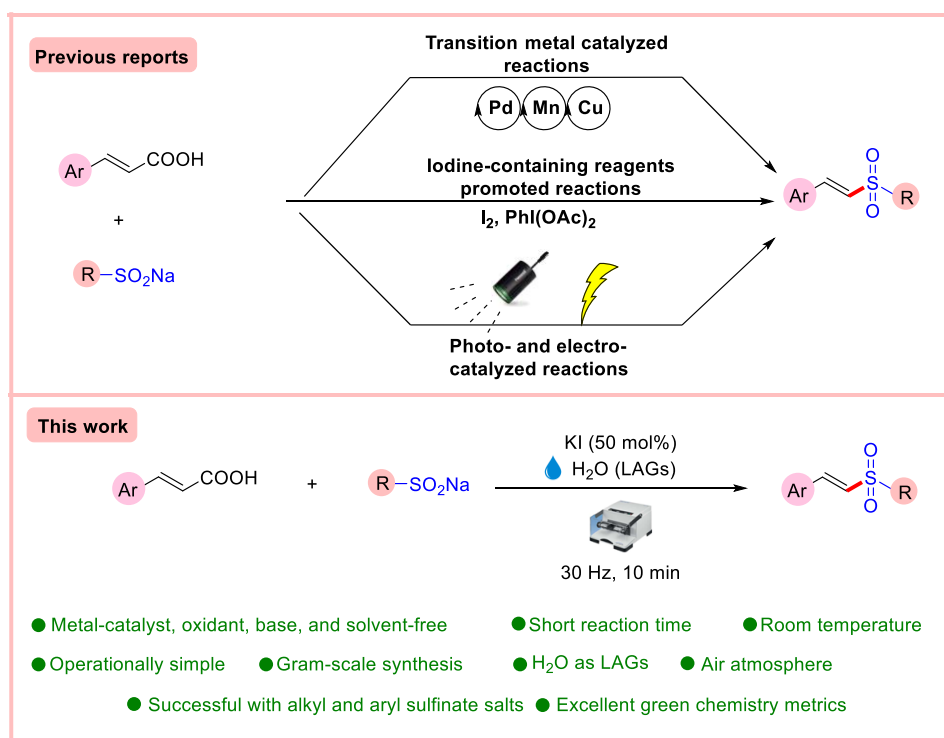
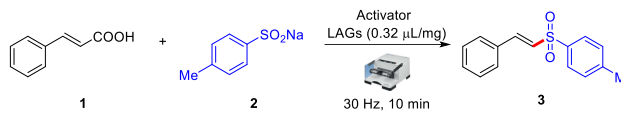


Figure. 1 Example of biologically active vinyl sulfones



Scheme 1. Background and summary of research work

Table 1 Optimization of reaction parameters for the reaction of cinnamic acid and sodium 4-methylbenzenesulfinate^a

Reaction scheme: Cinnamic acid (1) + Sodium 4-methylbenzenesulfinate (2) $\xrightarrow[\text{LAGs (0.32 } \mu\text{L/mg)}]{\text{Activator}}$ Product (3) (30 Hz, 10 min)

Entry	Activator (50 mol%)	LAGs (0.32 $\mu\text{L/mg}$)	Yield %
1	-	-	N.R.
2	NH ₄ I	-	N.R.
3	NH ₄ I	DMSO	24
4	NH ₄ I	DMA	trace
5	NH ₄ I	DMF	trace
6	NH ₄ I	H ₂ O	39
7	NH ₄ I	DCM	trace
8	NH ₄ I	EtOH	N.R.
9	TBAI	H ₂ O	62
10	CuI	H ₂ O	40
11	KI	H ₂ O	92
12	I ₂	H ₂ O	76
13	PhI(OAc) ₂	H ₂ O	59
14	NaCl	H ₂ O	N.R.
15	TBAB	H ₂ O	N.R.
16	KI	H ₂ O	88 ^b
17	KI	H ₂ O	65 ^c
18	KI	H ₂ O	73 ^d

^aReaction conditions: **1** (0.5 mmol), **2** (0.75 mmol), activator (50 mol%), LAGs (0.32 $\mu\text{L/mg}$). The reaction was milled for 10 mins at 30 Hz frequency using a 10 mL Retsch stainless steel jar, and 5 mm, 2.5 gm stainless steel grinding balls (5 x 5 mm grinding balls) at room temperature. ^bKI (1 equiv.), ^cKI (30 mol%), ^dKI (40 mol%).

To commence our studies, we chose cinnamic acid **1** and sodium 4-methylbenzenesulfinate **2** as the model substrates to investigate this mechanochemical-mediated decarboxylative sulfonation reaction, and different conditions were screened, as shown in Table 1. Although the primary attempts did not lead to the desired product on milling of pure reagents (entry 1). Moreover, no desired product was observed when we added NH₄I as an iodine-based activator. Interestingly, after the addition of a liquid ($\eta = 0.32 \mu\text{L/mg}$) so called liquid assisted grinding additives or LAGs, the desired product **3** was formed in 24% yield (Table 1, entry 3). Furthermore, given the significance of LAGs for the chemical transformation, a series of experiments was performed to optimize the best LAGs for the present reaction and the results revealed that H₂O was the best among DMA, DMF, DCM, EtOH (Table 1, entries 4–8), in which the desired product was obtained as 39% yield using NH₄I in a sub-stoichiometric amount (50 mol%) with H₂O (entry 6). Next, the screening of other iodine-containing reagents, such as TBAI, CuI, KI, I₂, and PhI(OAc)₂ (entries 9–13), revealed that KI displayed the efficiency to yield the desired product **3** in 92% yield (entry 11). Next, we focused on other halide-based activators, such as NaCl and TBAB. Unfortunately, no product was obtained (entries 14-15). Next, changing the loading of KI to 1 equiv., 30 mol%, and 40 mol% had a negative impact on the yield of the desired product (entries 16-18).

Screening of reaction temperature reveals that 92% yield of desired product **3** was obtained under standard conditions at room temperature (internal jar temperature, 25.4 °C) (fig. 2a), while applying an external heat source using a heat gun on the mixing jar for 10 min, didn't seem to impact the reaction yield (90% yield of **3**) (internal jar temperature, 103.0 °C) (fig. 2b). Furthermore, a hand grinding reaction between **1** and **2** for 10 min with H₂O gave access to the desired product **3** in lower yield (42% yield) (fig. 2c). Lastly, a solution-based heating reaction of **1** and **2** in H₂O at 80 °C for 24 h resulted in the required product **3** in 29% yield (fig. 2d). All these parameters established that a combination of inexpensive and readily available KI with H₂O as LAGs at 30 Hz frequency for 10 min. at ambient temperature was optimal and displayed the highest efficiency in catalyzing the reaction. For other parameters such as concentration of sodium sulfinate salt, jar size, grinding balls, time and frequency, see ESI† for more details.

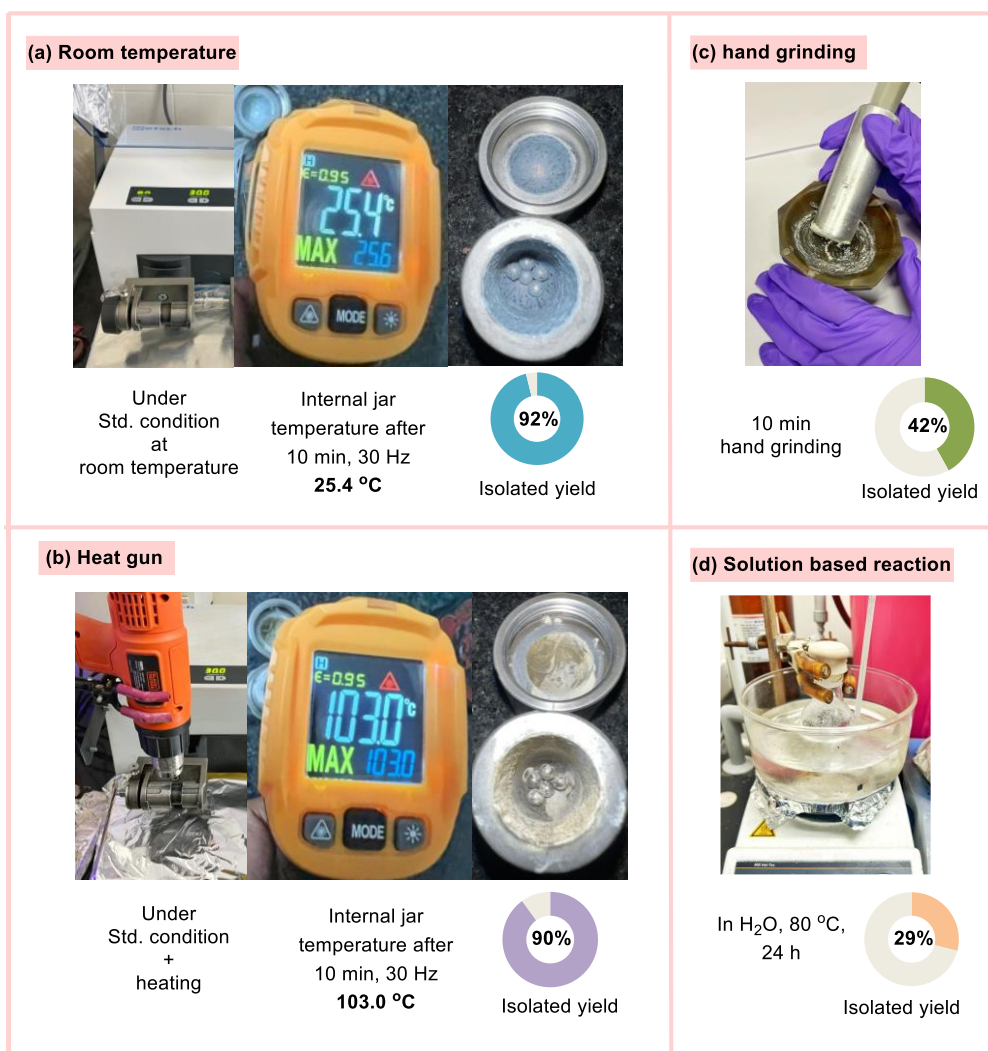


Figure 2: Various reactions setup. (a) Reaction at room temperature; (b) Heat gun-based reaction; (c) Hand grinding-based reaction; (d) Solution-based reaction.

Substrate Scope

With the optimized reaction conditions in hand, we explored the substrate scope of this novel mechanochemical-assisted decarboxylative sulfonylation reaction. As shown in Scheme 2, a library of aryl α,β -unsaturated carboxylic acids **1**, bearing electron-donating and electron-withdrawing functionalities, successfully underwent the mechanochemical-mediated decarboxylative sulfonylation reaction with sodium benzenesulfinate **2**, thus providing an ample opportunity for further derivatization of the products **4-53** in moderate to excellent yields. However, the experimental results suggested that both electronic and steric features of the substituted aryl α,β -unsaturated carboxylic acids **1** affected the efficacy of the decarboxylative sulfonylation reaction.

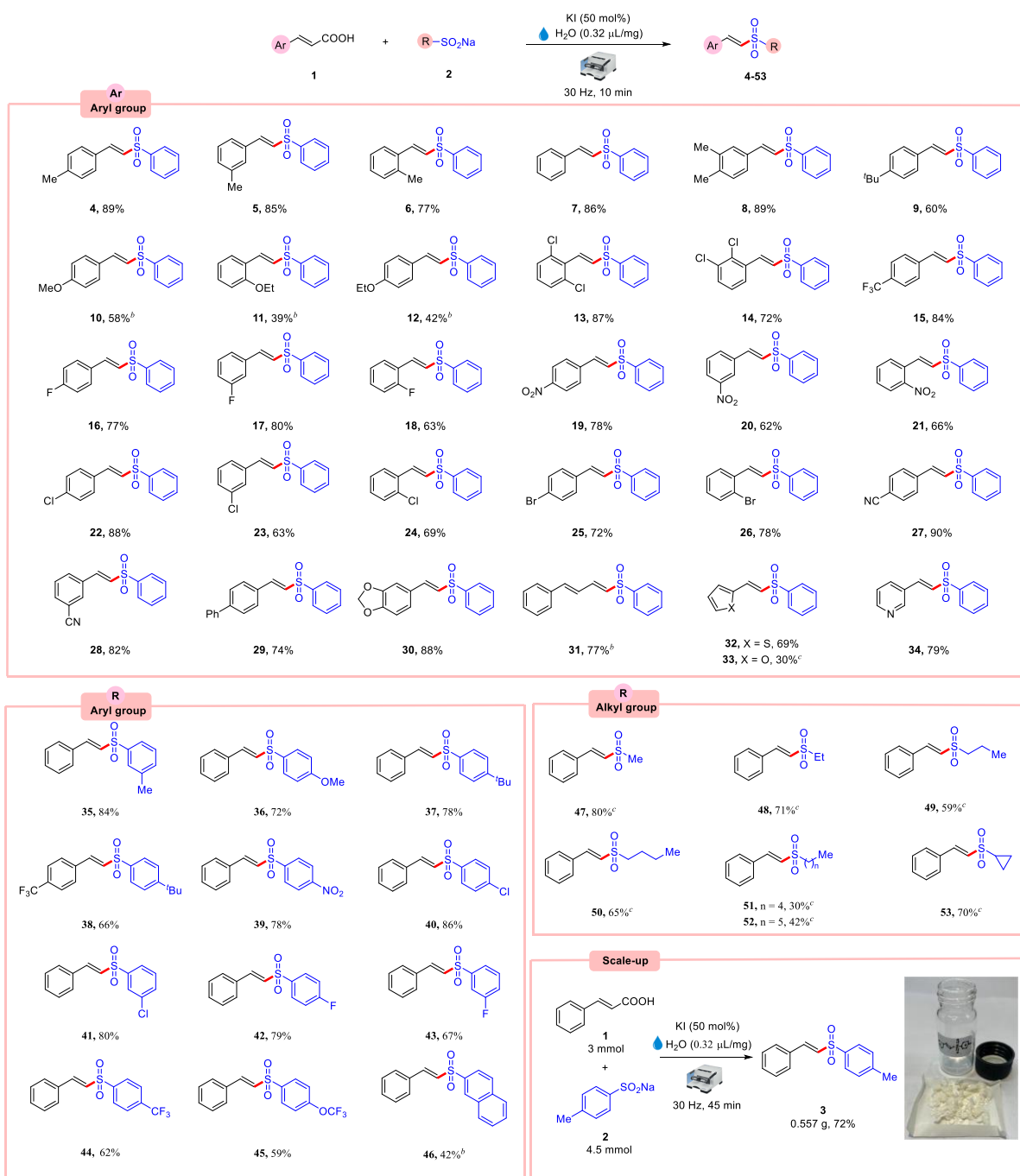
Aryl α,β -unsaturated carboxylic acids **1** bearing weak electron-donating groups (**4-9**) showed higher reactivity than those with strong electron-donating ones (**10-12**) albeit less efficiently. Additionally, *para*-substituted α,β -unsaturated carboxylic acids **4** furnished the desired product in higher yield than *meta*- and *ortho*-substituted α,β -unsaturated carboxylic acids (**5, 6**). Next, aryl α,β -unsaturated carboxylic acids **1**, bearing remote electron-withdrawing groups, were subsequently evaluated (**13-28**). Various functional groups such as chloro-, fluoro-, bromo-, nitro-, and cyano-functionalities at *ortho*-, *meta*-, and *para*-position smoothly reacted under this protocol to form the targeted products (**13-28**) in moderate to good yields. The reaction also worked well with biphenyl and 1,3-benzodioxole derived α,β -unsaturated carboxylic acids to afford the required product **29** and **30** in 74% and 88% yield, respectively. Interestingly, aryl α,β -unsaturated carboxylic acids having extended conjugation, also reacted well and afforded the desired product **31** in 77% yield. This strategy could also be expanded to other heteroaryl such as thiophene, furan, and pyridine derived α,β -unsaturated carboxylic acids, affording the corresponding products (**32-34**) in 69%, 30%, and 79% yield respectively. Unfortunately, aliphatic α,β -unsaturated carboxylic acids could not participate

in this decarboxylative sulfonylation reaction. We presume that the low stability of alkyl radical intermediates may be the reason for failure compared to benzyl radical intermediate in other cases. Next, the potential of this methodology on aryl sodium sulfinate salts **2** was investigated. Aryl sodium sulfinate derivatives **2** bearing electron-donating and electron-withdrawing functionalities such as methyl-, methoxy-, *t*-butyl, nitro-, chloro-, fluoro-trifluoromethyl, and trifluoromethoxy groups were well tolerated affording the corresponding products (**35-45**) in moderate to excellent yields. Besides, naphthyl substituted sulfinate salt also reacted well with cinnamic acid **1** to afford the desired product **46** in 42% yield.

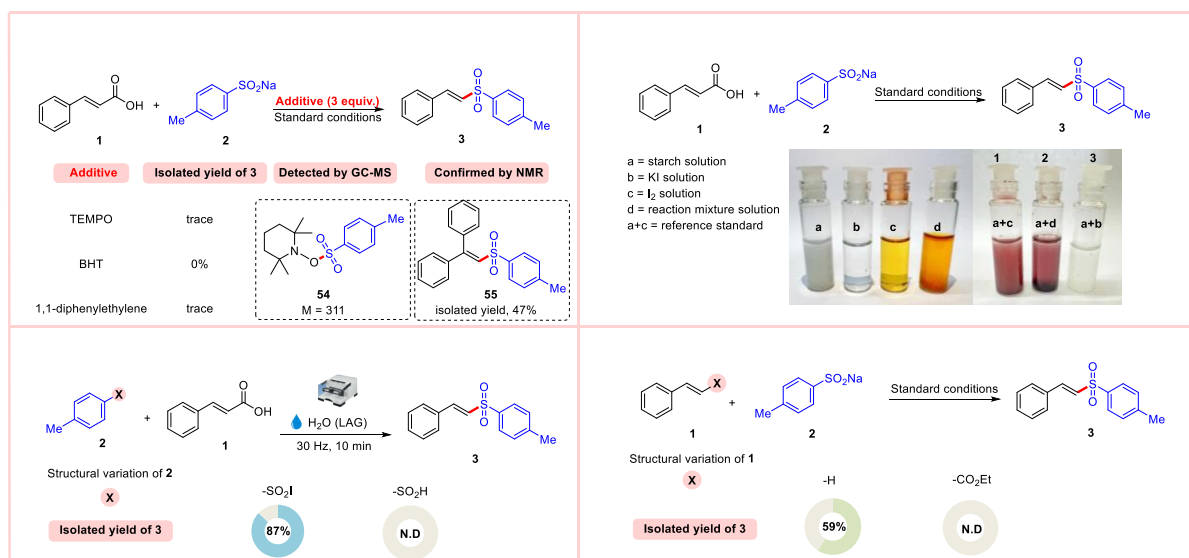
The compatibility of this protocol was further demonstrated by the reaction between aliphatic sodium sulfinate salts **2** and cinnamic acid **1** under our KI-promoted decarboxylative sulfonylation strategy. Methane-, ethane-, 1-propane-, 1-butane, 1-pentane-, and 1-hexane sulfinic acid sodium salts **2** were well tolerated under this protocol to afford the desired products (**47-52**) in 30-80% yield. Moreover, cyclopropane-sulfinic acid sodium salt also proceeded smoothly and afforded the desired vinyl sulfone (**53**) in 70% yield. Notably, this is the first report on decarboxylative sulfonylation synthesis of 1-propane-, 1-butane- 1-pentane-, and 1-hexane- bearing vinyl sulfones in good yields.

Scale-up

To demonstrate the practicality of this method, a gram-scale synthesis was performed with cinnamic acid **1** (0.444 g, 3 mmol) and 4-methylbenzenesulfinate **2** (0.801 g, 4.5 mmol) to afford the desired product **3** in 72% yield (0.557 g).



Scheme 2. Substrate scope for the decarboxylative sulfonylation reaction. ^aReaction conditions, aryl α,β -unsaturated carboxylic acid **1** (0.5 mmol), sodium sulfinate **2** (0.75 mmol), KI (50 mol%), and H₂O ($\eta=0.32\mu\text{L}/\text{mg}$). The reaction was milled using a 10 mL Retsch stainless steel jar for 10 min at 30 Hz frequency with 5 mm, 2.5 gm stainless steel grinding balls (5 x 5 mm grinding balls) at room temperature. ^b30 min, 30 Hz. ^c40 min, 30 Hz.



Scheme 3 Mechanistic studies

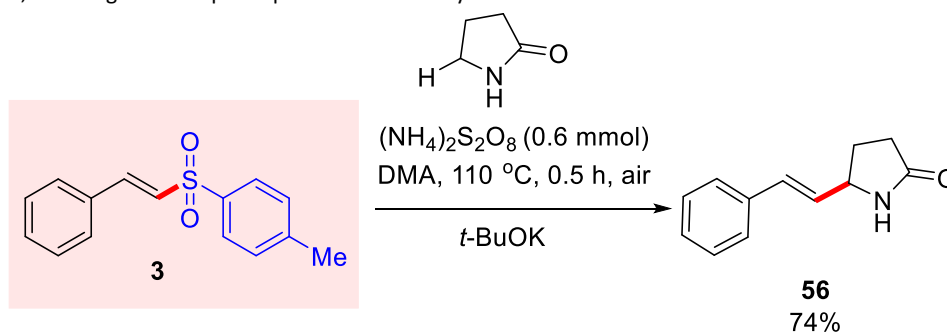
Mechanistic studies

To glean further insights into the mechanism, a series of control experiments and studies were performed and analyzed (Scheme 3). Radical trapping experiment with (2,2,6,6-tetramethylpiperidin-1-yl) oxy (TEMPO), butylated hydroxytoluene (BHT) or 1,1-diphenylethylene completely inhibited the reaction, and no sulfonated product was obtained (Scheme 3a). These results indicated that the sulfonation reaction may involve a radical process. The tosyl-TEMPO adduct **54** was detected by GC-MS ($M = 311$) and the 1,1-diphenylethylene adduct **55** was produced, isolated (47% yield) upon reaction of cinnamic acid **1** with 4-methylbenzenesulfonate **2**, and confirmed by NMR, corroborating the intermediacy of a sulfonyl radical species (See SI). Moreover, a starch-iodine test was performed, which indicated the formation of *in-situ* molecular iodine (I_2) in the reaction mixture (see SI). Next, 4-methylbenzenesulfonyl iodide substrate ($X = -SO_2I$) was subjected under ball mill conditions with H_2O and the desired product **3** was obtained in 87% yield, establishing the involvement of a possible sulfonyl iodide intermediate in the reaction medium (Scheme 3c).¹² However, the same reaction with aryl sulfonic acid ($X = -SO_2H$) did not yield the expected desired product under ball mill conditions. The above result indicates that the key sulfonyl iodide intermediate may be formed in the reaction medium and sulfonic acid may not be the intermediate.

Next, a series of controlled reactions with styrene and ethyl cinnamate were performed under standard conditions (Scheme 3d). The results revealed a 59% yield of the desired vinyl sulfones **3** was obtained when the reaction was performed with styrene. Whereas, ethyl cinnamate derivatives, did not yield the required products, which shows the importance of the carboxy group in the reaction protocol.

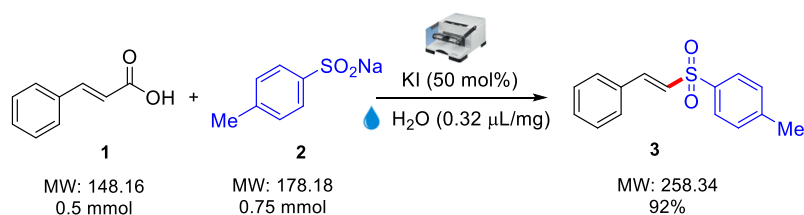
Diversification of vinyl sulfones

Compound **3** was subjected to a reaction with pyrrolidin-2-one in DMA at 110 °C with $(NH_4)_2S_2O_8$ as an oxidant under air environment, resulting in the required product **56** in 74% yield.¹³



Scheme 4 Synthetic applications

a) Green chemistry metrics evaluation for the synthesis of vinyl sulfone



$\text{EMY} (\%) = \frac{\text{Mass of product}}{\text{Mass of non - benign reagents}} \times 100 = \frac{0.118 \text{ g}}{0.0414 \text{ g}} \times 100 = 285.02\%$
$\text{AE} (\%) = \frac{\text{Molecular weight of product}}{\text{Total molecular weight of reactants}} \times 100 = \frac{258.34}{148.16 + 178.12} \times 100 = 79.17\%$
$\text{AEt} (\%) = \text{AE} \times \text{yield\%} = 79.17 \times 92\% = 72.84\%$
$\text{RME} (\%) = \frac{\text{Mass of isolated product}}{\text{Total mass of reactants}} \times 100 = \frac{0.118 \text{ g}}{0.074 \text{ g} + 0.133 \text{ g} + 0.0414 \text{ g}} \times 100 = 47.50\%$
$\text{E - factor} = \frac{\text{Total mass of wastes}}{\text{mass of product}} = \frac{0.074 \text{ g} + 0.133 \text{ g} + 0.0414 \text{ g} - 0.118 \text{ g}}{0.118 \text{ g}} = 1.105$
<p>EcoScale = 100 – sum of individual penalties Score on EcoScale: > 75, Excellent; >50, Acceptable; <50, Inadequate EcoScale score = 100 – 21 = 79^a (> 75: it is an excellent synthesis)</p>

b) Summary of green chemistry metrics

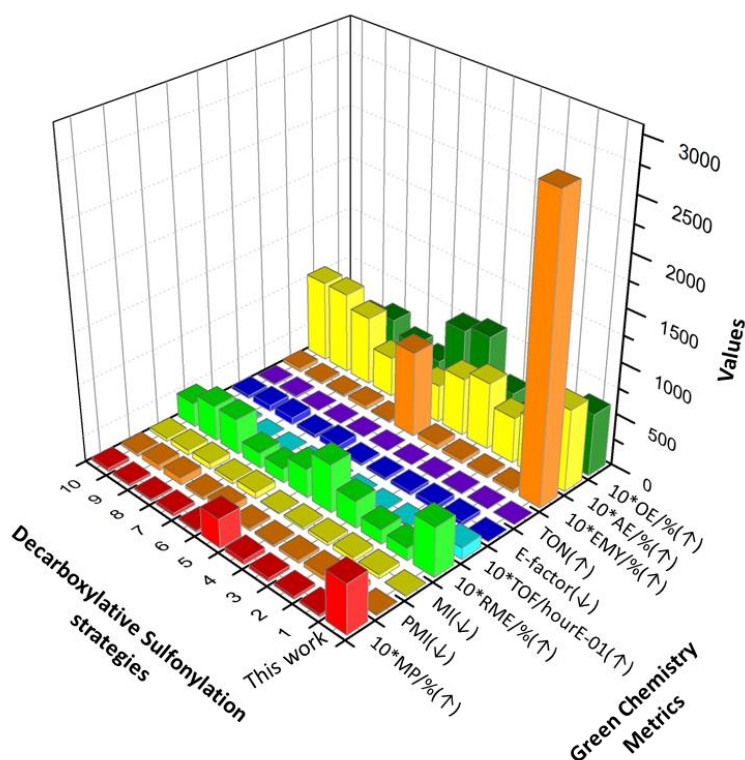
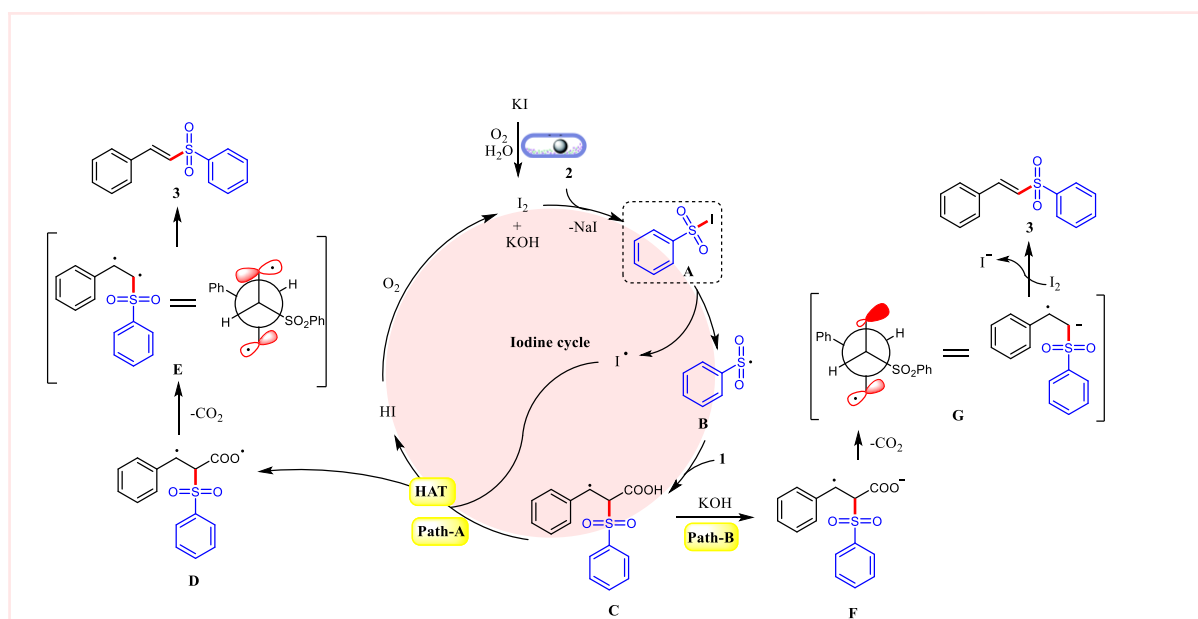


Figure 3 Green chemistry metrics analysis (a) Green chemistry metrics evaluation of our method's synthesis of vinyl sulfones. (b) Summary of green chemistry metrics of our method compared to previous methods (see ESI[†] for detailed calculation). Note; Atom Economy (AE), Atom Efficiency (AEf), Effective Mass Yield (EMY), Reaction Mass Efficiency (RME), Optimum

Efficiency (OE), Process Mass Intensity (PMI), Mass Intensity (MI), Mass Productivity (MP), E-factor, Turnover Number (TON), and Turnover Frequency (TOF). (↑) higher is better, (↓) lower is better. ^aSee ESI† for detailed calculations.

To determine the eco-friendliness and greenness of our developed strategy, the green chemistry metrics were evaluated for the synthesis of **3** (0.118 g, 92%) from cinnamic acid **1** (0.5 mmol, 0.074 g) and 4-methylbenzenesulfinate **2** (0.75 mmol, 0.133 g) using KI (50 mol%, 0.0414 g) under ball mill conditions. The results are presented in Figure 3a. For our method, the green chemistry metrics were found to be top-notch. In particular, effective mass yield (285.02%), atom economy (79.17%), atom efficiency (72.84%), and reaction mass efficiency (47.50%) were found excellent.¹⁴⁻¹⁷ The E-factor is calculated to be 1.105, which is the lowest compared to other reported methods. Moreover, the EcoScale score was calculated to be 79, which is excellent in terms of safety, economic, and ecological features.¹⁸ Besides, the advantage of a short reaction time of our method results in an excellent turnover frequency (TOF) and satisfactory turn-over number (TON), exhibiting the high catalytic ability of KI in the reaction system (see ESI†). In general, we observed that the green chemistry metrics of our method is exceptionally tailored towards sustainability. The green chemistry metrics of our strategy is compared to other decarboxylative sulfonylation methods is shown in Figure 3b.^{6,7} (see ESI† for detailed calculation).

In light of all experimental data and previous literature reports, the plausible mechanistic scenarios for this mechanochemical-mediated decarboxylative sulfonylation reaction is proposed and illustrated in Scheme 5. Initially, KI is oxidized in the presence of atmospheric air and H₂O to generate molecular iodine (I₂) which is supported by the starch-iodine test. It is easy to generate aryl sulfonyl iodide intermediate **A** from sodium sulfinate salt and iodine, which undergoes homolysis to give a sulfonyl radical **B** and an iodine radical.¹⁹ The addition of sulfonyl radical intermediate **B** to α,β -unsaturated carboxylic acid **1** affords the radical intermediate **C**. Two possible mechanistic pathways for product formation is shown in Scheme 5. In Path-A, the benzylic radical intermediate **C** undergoes hydrogen atom transfer reaction (HAT) with iodine radical to give diradical intermediate **D** and HI. Lastly, the final product **3** is obtained *via* decarboxylation of intermediate **D**. On the other hand (Path-B), the intermediate **C** undergoes deprotonation followed by decarboxylation to give a radical anion intermediate **F**. Lastly, the intermediate **F** can interact with iodine *via* a single electron transfer event to give the final product **3**. The excellent E/Z selectivity might originate from stereoelectronic and steric effects in the radical anion.²⁰



Scheme 5. Possible mechanistic pathway

Conclusions

In summary, we have successfully demonstrated a mechanochemical-mediated decarboxylative sulfonylation reaction to synthesize vinyl sulfones under ball milling conditions. The striking features of this method include: (a) the use of readily available α,β -unsaturated carboxylic acids, and sodium sulfonates; (b) use of inexpensive KI as an activator and H₂O as a LAGs; (c) operationally simple in term of room temperature reaction and a short reaction time; (d) metal catalyst-, oxidant-, additive-, solvent-free method; (e) successful with both alkyl and aryl sulfinate salts; (f) compatible under gram-scale. Moreover, the green chemistry parameters were found excellent in terms of safety, economical, and ecological consideration. We believe

the current method be applicable to late-stage functionalization and in the synthesis of valuable intermediates in organic synthesis in both academic and industrial levels.

Author Contributions

B. Saxena optimized the reaction conditions and synthesized all the derivatives including gram-scale synthesis. R. Patel synthesized the sodium sulfonates salts. S. Sharma synthesized cinnamic acids. B. Saxena and R. Patel performed the mechanistic studies and wrote the manuscript with the helpful insights of Prof. A. Sharma. Prof. A. Sharma supervised the whole work, interpreted the results, and edited the manuscript. All the authors have given their final approval to the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

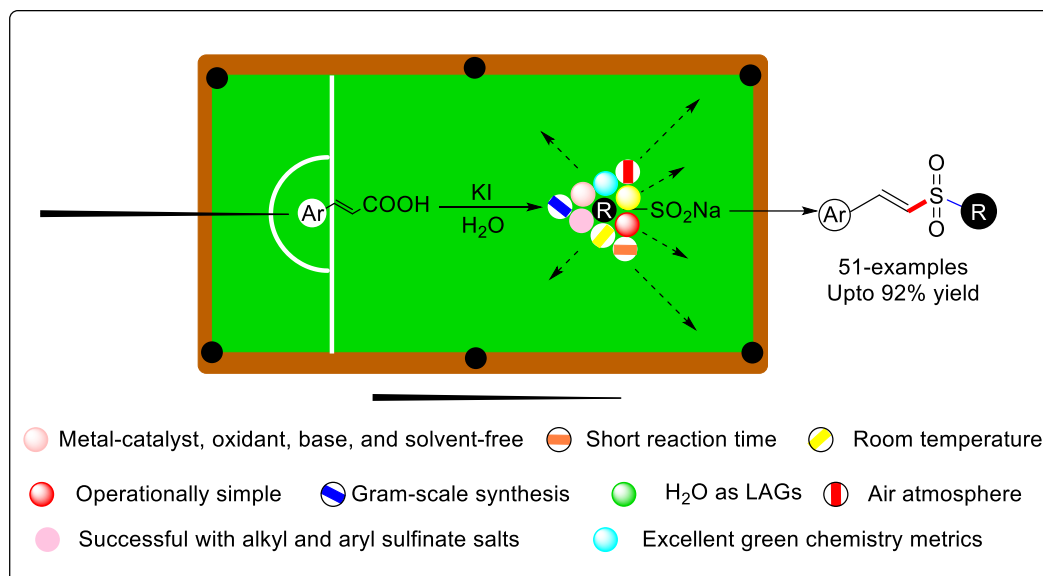
Acknowledgements

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Herein, we report a mechanochemical-assisted decarboxylative sulfonylation of α,β -unsaturated carboxylic acids with sodium sulfinate salts using potassium iodide as an activator under water-assisted grinding conditions.