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Manganese(III)-Mediated and -Catalyzed Decarboxylative Hydroxysulfonylation of Arylpropiolic Acids with Sodium Sulfinates in Water

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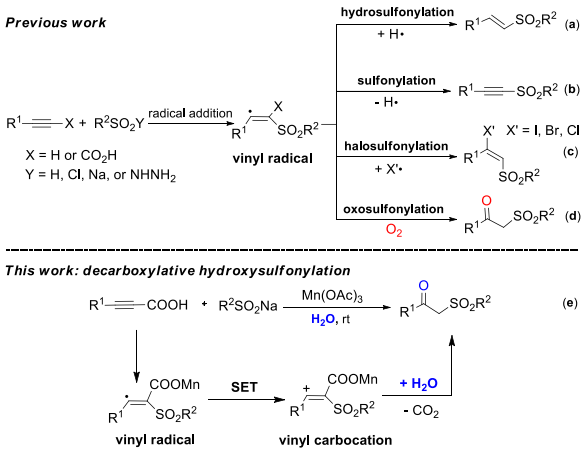
Abstract: With water as both solvent and reactant, a novel manganese(III)-mediated and -catalyzed synthesis of β-ketosulfones through decarboxylative hydroxysulfonylation reactions of arylpropiolic acids with sodium sulfinates is described. This protocol has the advantages of mild reaction conditions, short reaction time, easy to handle reagents, purification simplicity, and being environmentally benign, which demonstrate the practical utility of this methodology.

Keywords: Decarboxylative Hydroxysulfonylation; β-Ketosulfones; Arylpropiolic Acids; Manganese; Water

Organosulfones are common structural motifs present in pharmaceuticals, agrochemicals and natural products.[1] They also serve as useful intermediates in organic synthesis.[2] Considerable efforts have been devoted to developing efficient methods for the preparation of organosulfones.[3] Conventional synthetic methods, including sulfide oxidation[4] and direct C-SO_2 bond formation (e.g., sulfonylation that uses sulfonyl precursors)[5] are well established. Recently, direct functionalization of alkenes[6] or alkynes[7-10] with sulfonyl precursors (e.g., RSO_2X, RSO_2Na and RSO_2NHNH_2) has emerged as a promising tool for the synthesis of functionalized organosulfones and has attracted considerable attention because of its high synthetic efficiency and diversity. In particular, a wide range of organosulfone compounds can be prepared from alkynyl and sulfonyl derivatives under different conditions. Some representative synthetic strategies are showed in Scheme 1. Generally, the reactive vinyl radical is generated *in situ* through sulfonyl radical addition to alkynes, and then this key radical intermediate is trapped by different reagents to afford various sulfones. For example, vinyl sulfones could be prepared by subsequent H-atom abstraction (Scheme 1a),[7] whereas acetylenic sulfones are obtained upon the elimination of hydrogen radical (Scheme 1b).[8] The vinyl radical could also be attacked by halogen species to form β-haloalkenyl



Scheme 1. Strategies for functionalization of alkynes with sulfonyl derivatives

sulfones (Scheme 1c).[9] Recently, Lei's group[10a] reported the trapping of the sulfonyl vinyl radical by dioxygen to construct β-ketosulfones (Scheme 1d), which are versatile synthetic precursors.[10] Later, Lipshutz and coworkers developed an environmentally benign aerobic oxidative synthesis of β-ketosulfones in aqueous media using TPGS-750-M as surfactant and 2,6-lutidine as base.[10b] Despite these improvements, alternative strategies that use bench-stable and nontoxic reagents under green and mild conditions are still highly desirable.[11]

Alkynylcarboxylic acids have been widely used as coupling partners in organic synthesis because of their commercial availability, good stability and easy handling. In the meantime, the use of water as solvent in organic synthesis has become one of the latest challenges and has attracted much attention in recent years.[12] Continuing our ongoing research on organosulfone chemistry,[13] we herein report a new decarboxylative hydroxysulfonylation of arylpropiolic acids with sodium sulfinates using pure water as both solvent and reactant. We envisioned that the sulfonyl vinyl radical could be further

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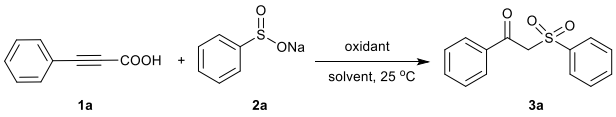
oxidized to a carbocation *via* a single electron transfer (SET) process (Scheme 1e); the *in-situ* generated active vinyl carbocation then undergoes sequential attack by water, keto-enol tautomerism, and decarboxylation to afford β-ketosulfones. It should be emphasized that here water acts as both solvent and a source of oxygen, which is different from the work reported by Lei[10a] and Lipshutz.[10b] They used O_2 as oxidant and the source of carbonyl oxygen (Scheme 1d). Moreover, the use of water as solvent also provides many benefits, such as improving reactivities and selectivities, simplifying the workup procedures, and allowing mild reaction conditions. On the other hand, using cheap, abundant, and non-toxic metal catalysts such as $Mn(OAc)_3$ to replace precious metal catalysts is one of the major targets of sustainable chemical synthesis.[14] Mn(III) acetate has proved to be an efficient and mild reagent for oxidative radical coupling reactions,[15] and it was therefore also expected to act as a green single-electron oxidant for this decarboxylative hydroxysulfonylation reaction.[16]

We chose bench-stable phenylpropiolic acid (**1a**) and sodium benzenesulfinate (**2a**) as model substrates. Initially, various single-electron oxidants were examined in 1,2-dichloroethane at room temperature under air (Table 1, entries 1-4). To our delight, the desired product *β*-ketosulfone **3a** was generated in 37% (^{1}H NMR yield) when $Mn(OAc)_3{\cdot}2H_2O$ (3.0 equiv.) was employed (Table 1, entry 1). In contrast, other metal salts such as $Cu(OAc)_2$, $FeCl_3$, and $AgNO_3$ were almost inactive for this transformation (Table 1, entries 2-4). Encouraged by this result, we then screened a series of manganese salts and found that changing the Mn oxidation state or the counterion of the salt could also promote this reaction, albeit with lower yields (Table 1, entries 5-9). Further optimization revealed that solvent played an important role in this reaction (Table 1, entries 10-15). The yield was improved to 57% when toluene was used (Table 1, entry 13). H_2O provided a yield comparable to that of toluene, and the reaction time was shortened to less than half an hour (Table 1, entry 15). Notably, the crude solid product could easily be separated from the aqueous media through simple filtration instead of organic extraction.[17] We further attempted to lower the loading of sulfinate salt **2a** and $Mn(OAc)_3{\cdot}2H_2O$ (Table 1, entries 16-20). The best isolated yield of **3a** (83%) was obtained when using 2.0 equiv. of $Mn(OAc)_3{\cdot}2H_2O$ and **2a** in water at room temperature (Table 1, entry 19). In addition, the control experiment showed that no product was formed when the reaction was performed in the absence of any oxidant (Table 1, entry 21).

With the optimized conditions in hand (Table 1, entries 19 and 20), we next explored the substrate scope of this reaction utilizing toluene and water as solvent respectively (Tables 2 and 3). A broad range of sodium benzenesulfinates that bearing electron-donating groups (-Me, -MeO and *t*-Bu) or electron-withdrawing groups (-F, -Cl, -Br, $-CF_3$ and $-NO_2$) on the phenyl ring, underwent the reaction efficiently, affording the corresponding β-ketosulfones **3b**-**3i** in

Table 1. Optimization of the reaction conditions[a]



Entry	Oxidant	Solvent	Time (h)	Yield (%)[b]
1	$Mn(OAc)_3{\cdot}2H_2O$ (3.0 eq.)	DCE	2-4	37
2	$Cu(OAc)_2{\cdot}H_2O$ (3.0 eq.)	DCE	2-4	N.D.
3	$FeCl_3$ (3.0 eq.)	DCE	2-4	N.D.
4	$AgNO_3$ (3.0 eq.)	DCE	2-4	trace
5	MnO_2 (3.0 eq.)	DCE	2-4	17
6	$Mn(OAc)_2$ (3.0 eq.)	DCE	2-4	22
7	$MnCl_2$ (3.0 eq.)	DCE	2-4	25
8	$Mn(acac)_3$ (3.0 eq.)	DCE	2-4	15
9	MnF_3 (3.0 eq.)	DCE	2-4	24
10	$Mn(OAc)_3{\cdot}2H_2O$ (3.0 eq.)	DME	2-4	25
11	$Mn(OAc)_3{\cdot}2H_2O$ (3.0 eq.)	MeCN	2-4	17
12	$Mn(OAc)_3{\cdot}2H_2O$ (3.0 eq.)	MeOH	2-4	trace
13	$Mn(OAc)_3{\cdot}2H_2O$ (3.0 eq.)	toluene	2-4	57(55)[c]
14	$Mn(OAc)_3{\cdot}2H_2O$ (3.0 eq.)	THF	2-4	12
15	$Mn(OAc)_3{\cdot}2H_2O$ (3.0 eq.)	H_2O	0.5	59(56)[c]
16	$Mn(OAc)_3{\cdot}2H_2O$ (2.0 eq.)	H_2O	0.5	79
17	$Mn(OAc)_3{\cdot}2H_2O$ (1.0 eq.)	H_2O	0.5	42
18[d]	$Mn(OAc)_3{\cdot}2H_2O$ (3.0 eq.)	H_2O	0.5	65
19[d]	$Mn(OAc)_3{\cdot}2H_2O$ (2.0 eq.)	H_2O	0.5	84(83)[c]
20[d]	$Mn(OAc)_3{\cdot}2H_2O$ (2.0 eq.)	toluene	4	78(73)[c]
21	-	H_2O	0.5	N.D.

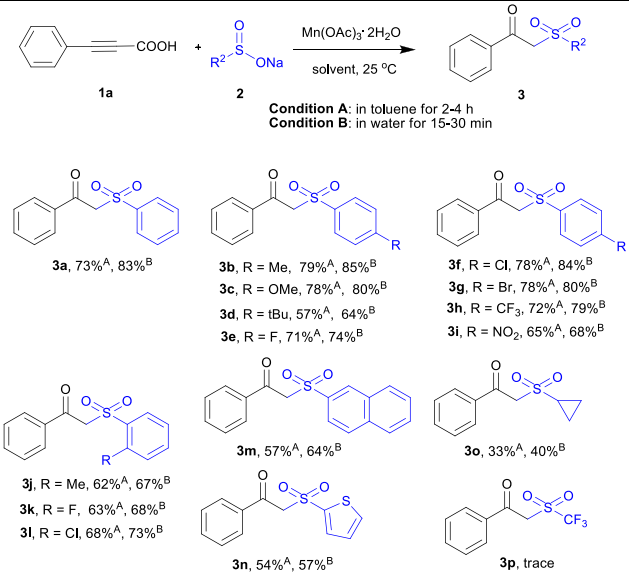
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), metal oxidant and solvent (2 mL), 25 °C under air. [b] Yields were determined by ^{1}H NMR spectroscopy using methyl 4-bromobenzoate as an internal standard. [c] Isolated yields are given in parentheses. [d] **2a** (0.4 mmol) was used. N.D. = not detected; DCE = 1,2-dichloroethane; DME = 1,2-dimethoxyethane.

high yields (Table 2). Moreover, the position of the substituent also had an effect on the reaction. Sodium benzenesulfinates that bear either electron-donating group (-Me) or electron-withdrawing groups (-F and -Cl) at the *para*-position of the phenyl ring were superior to their *ortho*-substituted counterparts in isolated yields (Table 2, **3b** *vs* **3j**; **3e** *vs* **3k**; **3f** *vs* **3l**), which is probably due to the steric hindrance effect of *ortho*-position substitution. In addition, sodium naphthalene-2-sulfinate and sodium thiophene-2-sulfinate also proved to be suitable substrates, providing the corresponding products **3m** and **3n** in good yields. Apart from aromatic sodium sulfinates, less reactive aliphatic sodium sulfinates, such as sodium cyclopropanesulfinate, were tolerated in this transformation, affording product **3o** in moderate yield. However, no desired product **3p** was obtained when sodium trifluoromethanesulfinate served as the substrate, which might be caused by the instability of the corresponding sulfonyl radical.

Further exploration of the substrate scope was focused on different arylpropiolic acids (Table 3). It was found that not only electron-donating groups, such as methyl (**3q**), tertiary butyl (**3r**), and methoxy (**3s**), but also electron-withdrawing groups, such as trifluoromethyl (**3t**), acetyl (**3u**), ester (**3v**), and

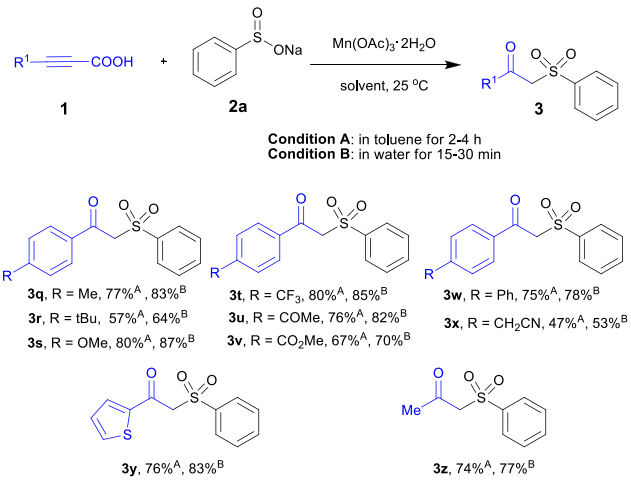
phenyl (**3w**) on the phenyl ring of the arylpropiolic acids at the *para*-position, were tolerated in this transformation, providing moderate to good yields. In addition, sensitive cyano group (**3x**) was compatible with the standard reaction conditions, which was meaningful for further transformation. Thiophene-2-propiolic acid and 2-butynoic acid were also tolerated well, providing the corresponding products **3y** and **3z** in good yields. It should be mentioned that all these products prepared in water could be separated by simple filtration instead of organic extraction.

Table 2. Substrate scope of sodium sulfonates **2**[a,b]



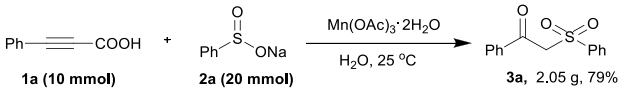
[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $Mn(OAc)_3$•$2H_2O$ (0.4 mmol) and solvent (2 mL), 25 °C under air. **Condition A**: in toluene for 2-4 h, **Condition B**: in water for 15-30 min. [b] Isolated yields.

Table 3. Substrate scope of arylpropiolic acids **1**[a,b]



[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), $Mn(OAc)_3$•$2H_2O$ (0.4 mmol) and solvent (2 mL), 25 °C under air. **Conditions A**: in toluene for 2-4 h, **Conditions B**: in water for 15-30 min. [b] Isolated yields.

Moreover, the present transformation could be smoothly scaled up to 10 mmol without a significant decrease in the yield (Scheme 2). This result demonstrated its potential in the large-scale preparation of β-ketosulfones under operationally simple and environmentally benign conditions.



Scheme 2. Gram-scale preparation of **3a**

To gain insight into the reaction mechanism, a series of control experiments were carried out (Scheme 3). Firstly, radical inhibition experiment was performed (Scheme 3a). The reaction was found to be strongly suppressed by the radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), indicating that the reaction might undergo a radical process. Secondly, performing the reaction under N_2 or O_2 atmosphere resulted in reasonable yields of **3a** (Scheme 3a), which implied that O_2 might not be the oxygen source in the product. To confirm that water was the origin of the carbonyl oxygen in the β-ketosulfones, several isotopic labelling experiments were performed (Schemes 3b-3d). When the reaction was conducted in the presence of $H_2{}^{18}O$ (10 equiv.) using dry toluene as the solvent under nitrogen atmosphere, the ^{18}O labelling products were observed (**3a**-^{18}O/**3a**-^{16}O = 71:29), which is almost consistent with the ratio of $H_2{}^{18}O$ to $Mn(OAc)_3$•$2H_2{}^{16}O$ in the reaction system (Scheme 3b). By contrast, less than 5% of the label was incorporated into **3a** when the reaction was performed in dry toluene under $^{18}O_2$ atmosphere (Scheme 3c, HRMS spectra in the SI). Furthermore, when unlabeled β-ketosulfone **3a** was exposed to ^{18}O-labeled water ($H_2{}^{18}O$), less than 5% of **3a**-^{18}O product was detected in the reaction mixture (Scheme 3d), which ruled out that the incorporation of the label occurred from the exchange with water. Overall, these results collectively illustrate that water was the sole oxygen source in this hydroxysulfonylation process. Furthermore, when ethynylbenzene (**4**) and 1-methyl-4((phenylethynyl)-sulfonyl)-benzene (**5**), rather than 3-phenylpropiolic acid (**1a**), were exposed to the standard conditions, the desired β-ketosulfones were obtained in extremely low yields (Schemes 3e and 3f), which indicated that arylacetylene and arylacetylenic sulfone might not be the main intermediates in this reaction. Besides, using methyl 3-phenylpropiolate (**6**) as substrate resulted in trace amounts of the desired product (Scheme 3g). These results also suggest that the COOH group in arylpropiolic acids plays an important role in promoting the hydroxysulfonylation reaction; presumably the chelation of COOH with Mn(III) can activate the triple bond and facilitate the subsequent transformation. Moreover, we have performed XPS measurement of Mn with the reaction mixture of crude **3a** (Figures S3 and S4 in the Supporting Information). There were two satellite peaks (646.0 eV and 657.5 eV) in Mn 2p spectrum, and a pair of split peaks with separation about 6.0 eV in Mn 3s spectrum. We are convinced that Mn(II) was formed after the reaction[18] and Mn(I) was not observed.

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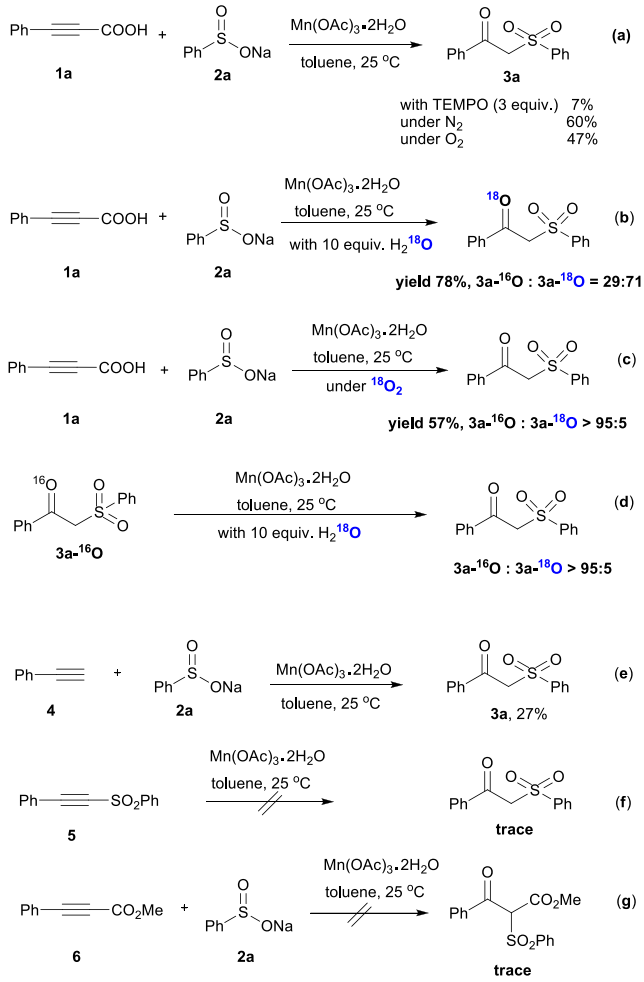
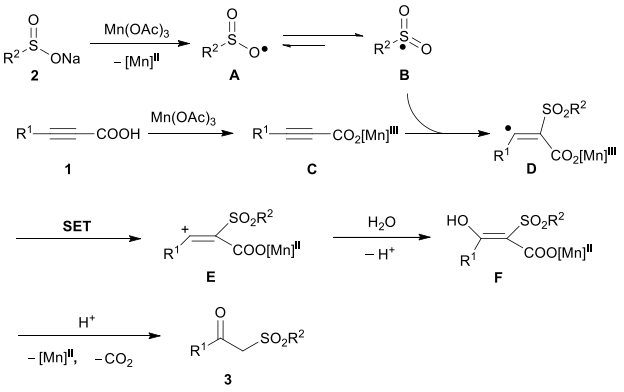


Scheme 3. Preliminary mechanistic studies

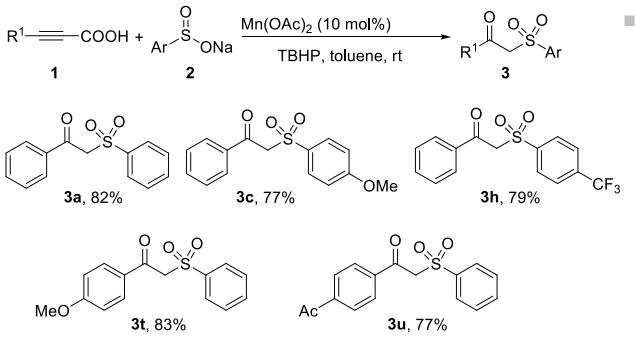
On the basis of the above experimental observations and previous reports,[19] a plausible mechanism is proposed for this $Mn(OAc)_3$-mediated decarboxylative hydroxysulfonylation reaction (Scheme 4). Initially, arylpropiolic acid **1** coordinates with Mn(III) to generate salt **C**, at the same time sulfinate sodium **2** is oxidized by Mn(III) to form the sulfonyl radical **B**. Subsequently, the intermolecular radical addition of **B** to **C** occurs regioselectively to form the vinyl radical **D**, which could be further transformed into vinyl carbocation **E** through a Mn(III)-mediated intramolecular SET process. Thereafter, **E** is trapped by water to deliver the enolate adduct **F**. Finally, keto-enol tautomerism and decarboxylation of **F** lead to the desired β-ketosulfone **3**.

Based on the proposed mechanism, we have developed a catalytic version of this transformation (for details of optimization of reaction conditions, see Supporting Information). Using 10 mol% of $Mn(OAc)_2$ in the presence of 3.0 equiv. of TBHP (*tert*-butyl hydroperoxide), β-ketosulfones **3a**, **3c**, **3h**, **3t** and **3u** were obtained in comparable yields to that with 2.0 equiv. of $Mn(OAc)_3•2H_2O$ (Table 4).



Scheme 4. Proposed mechanism

Table 4. Mn-catalyzed decarboxylative hydroxysulfonylation[a]



[a] Reaction conditions: **1** (0.2 mmol), **2** (0.4 mmol), $Mn(OAc)_2$ (0.02 mmol), TBHP (70% in water, 0.6 mmol) and toluene (2 mL), stirred at 25 °C under air for about 2-4 h.

In summary, we have developed an efficient manganese(III)-mediated and -catalyzed synthesis of β-ketosulfones through decarboxylative hydroxysulfonylation reactions of arylpropiolic acids with sodium sulfinates in water. This newly developed protocol has the advantages of mild reaction conditions, short reaction time, easy to handle reagents, purification simplicity, and being environmentally benign, which demonstrate the practical utility of this methodology. Preliminary mechanistic studies revealed that this reaction might involve a radical process, and the carbonyl oxygen in the target product originates from water. Further application of this methodology is underway in our laboratory.

Experimental Section

General Procedures for the Mn-Mediated Synthesis of β-Ketosulfones

Reaction Conditions A: To a 5 mL tube equipped with a magnetic stirring bar, arylpropiolic acid **1** (0.2 mmol), sodium benzenesulfinate **2** (0.4 mmol), $Mn(OAc)_3•2H_2O$ (0.4 mmol) and toluene (2 mL) were added. No special precautions were taken to exclude moisture and air. The reaction was stirred at room temperature until the complete consumption of **1** as monitored by TLC analysis (typically

2-4 h). The reaction mixture was then diluted with water and extracted with ethyl acetate. After the combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure, the residue was purified by flash column chromatography on silica gel to afford the pure product **3**.

Reaction Conditions B: To a 5 mL tube equipped with a magnetic stirring bar, arylpropiolic acid **1** (0.2 mmol), sodium benzenesulfinate **2** (0.4 mmol), $Mn(OAc)_3•2H_2O$ (0.4 mmol) and water (2 mL) were added. No special precautions were taken to exclude moisture and air. The reaction was stirred at room temperature until the complete consumption of **1** as monitored by TLC analysis (typically 15-30 minutes). The solid crude product was separated from the reaction mixture by simple filtration. The crude product was further purified by flash column chromatography on silica gel to afford the desired product **3**.

General Procedure for the Mn-Catalyzed Synthesis of β-Ketosulfones

To a 5 mL tube equipped with a magnetic stirring bar, arylpropiolic acid **1** (0.2 mmol), sodium benzenesulfinate **2** (0.4 mmol), $Mn(OAc)_2$ (0.02 mmol), TBHP (70% in water, 0.6 mmol) and toluene (2 mL) were added. The reaction was stirred at room temperature until the complete consumption of **1** as monitored by TLC analysis (typically 2-4 h). The solid crude product was separated from the reaction mixture by simple filtration. The crude product was further purified by flash column chromatography on silica gel to afford the desired product **3**.

Acknowledgements

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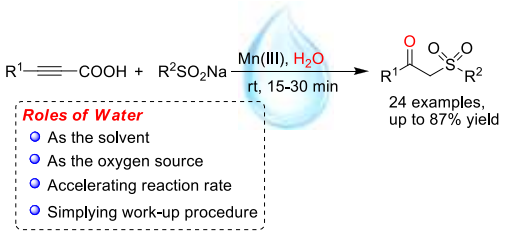
Manganese(III)-Mediated and -Catalyzed Decarboxylative Hydroxysulfonylation of Arylpropiolic Acids with Sodium Sulfinates in Water



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