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Iron(III)-Catalyzed Aerobic Oxidation and Cleavage/Formation of a C–S Bond

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A new iron(III)-catalyzed synthesis of β-oxo sulfones is described that employs vinylarenes and readily available dimethyl sulfoxide (DMSO) with hydrazine and oxygen as the oxidant. The reaction tolerates various functional group substituents on the vinylarene substrates to afford β-oxo sulfones in moderate to good yields. The cleavage and formation of the C–S bond are the key steps of this transformation.

Introduction

The development of methods for the direct conversion of C–C bonds into C–S bonds remains a critical challenge in organic chemistry.[1,2] The cleavage and formation of a C–S bond through a transition-metal-catalyzed approach is a very attractive and fascinating branch of synthetic chemistry with few reports until now.[3] In 2006, Yu described the copper(II)-catalyzed thioetherification of 2-phenylpyridine by using PhSH and MeSSMe under oxygen.[4] In addition, Qing reported a copper(II)-mediated methylthiolation of aryl C–H bonds by using dimethyl sulfoxide (DMSO).[5] Furthermore, Yuan disclosed the synthesis of aryl methyl sulfones from aryl halides and DMSO through a copper-catalyzed aerobic oxidation.[6] Recently, a variety of methods have been developed that employ sulfonyl hydrazides,[7] sulfinic acids,[8] sulfonyl chlorides, and sulfonyl bromides[9] as substrates for the formation of the C–S bond. These approaches proceed through a radical addition that is catalyzed by iron, copper, or iodine or in the absence of a catalyst. In spite of these advances, there still remain great challenges in the formation of a C–S bond by using DMSO as the substrate because of the difficulties in the cleavage of a C–S bond.

Compounds that contain a sulfone group have been widely used for a variety of reactions such as C–C bond formations,[10] eliminations,[11] and rearrangements[12]. Among the derivatives of sulfones, β-oxo sulfones cannot only act as a versatile intermediates in Michael additions and Knoevenagel reactions[13,14] but also work as valuable precursors in the preparation of ketones, chalcones,[15] allenes, acetylenes, vinyl sulfones,[16] and polyfunctionlized 4*H*-pyrans.[17] Additionally, β-oxo sulfones play an important role in the synthesis of optically active β-hydroxy sulfones and α-halomethyl sulfones.[18,19] Generally, β-oxo sulfones can be prepared by either a Claisen condensation,[20] the reaction of an α-halo ketone with a sodium alkane-/arenesulfinate,[21] or an acid-catalyzed reaction between sulfonyl chlorides and arylacetylenes.[22] Although several methods have been explored, tremendous limitations remain in the syntheses of β-oxo sulfones, such as long reaction times, unavailability of starting materials, harsh reaction conditions, and low yields. Therefore, a direct, mild, and efficient process to access β-oxo sulfones is highly desired. Recently, we discovered a significant method to obtain β-oxo sulfones that employs an iron-catalyzed reaction of vinylarenes and commercially available DMSO as the sulfur source. Moreover, various β-oxo sulfones could be produced in moderate to good yields by using this strategy. Herein, we wish to report our preliminary results on this topic.

Results and Discussion

Initially, we investigated the possibility of a cross-coupling reaction between styrene and DMSO, which was also the solvent, along with benzohydrazide as an additive. To our surprise, the preparation of a β-oxo sulfone was successful. The desired 2-(methylsulfonyl)-1-phenylethanone (**2a**) was obtained from the reaction of styrene (**1a**, 0.2 mmol) and DMSO (1.0 mL) in the presence of $FeCl_2$ and benzohydrazide (1 mmol) at 20 °C in air for 36 h (see Table 1, Entry 1). Among the examined catalysts, $FeCl_3$ demonstrated the highest activity (see Table 1, Entries 2–4). No product, however, was observed in the absence of benzohydrazide, which suggests that it served an important role in this reaction (see Table 1, Entry 5). In addition, re-

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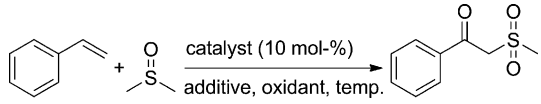
Table 1. Optimization of reaction conditions.[a]



Entry	Catalyst	Additive	Oxidant	T [°C]	t [h]	Yield [%]
1	$FeCl_2$	benzohydrazide	air	20	36	18
2	$Ni(dppe)Cl_2$[b]	benzohydrazide	air	20	36	<5
3	$PdCl_2$	benzohydrazide	air	20	36	22
4	$FeCl_3$	benzohydrazide	air	20	36	45
5	$FeCl_3$	none	air	20	36	n.r.[c]
6	$FeCl_3$	hydrazine dihydrochloride	air	20	36	42
7	$FeCl_3$	hydrazine hydrate	air	20	36	58
8	$FeCl_3$	hydrazine hydrate	DDQ	20	36	66
9	$FeCl_3$	hydrazine hydrate	O_2	20	36	68
10	$FeCl_3$	hydrazine hydrate	H_2O_2	20	36	33
11	$FeCl_3$	hydrazine hydrate	TBHP	20	36	23
12	$FeCl_3$	hydrazine hydrate	O_2	0	36	15
13	$FeCl_3$	hydrazine hydrate	O_2	10	36	20
14	$FeCl_3$	hydrazine hydrate	O_2	30	36	65
15	$FeCl_3$	hydrazine hydrate	O_2	40	36	72
16	$FeCl_3$	hydrazine hydrate	O_2	60	36	52
17	$FeCl_3$	hydrazine hydrate	O_2	80	36	39
18	$FeCl_3$	hydrazine hydrate	O_2	40	24	53
19	$FeCl_3$	hydrazine hydrate	O_2	40	48	68
20[d]	$FeCl_3$	hydrazine hydrate	O_2	40	36	26
21[e]	$FeCl_3$	hydrazine hydrate	O_2	40	36	52
22[f]	$FeCl_3$	hydrazine hydrate	O_2	40	36	40
23[g]	$FeCl_3$	hydrazine hydrate	O_2	40	36	35

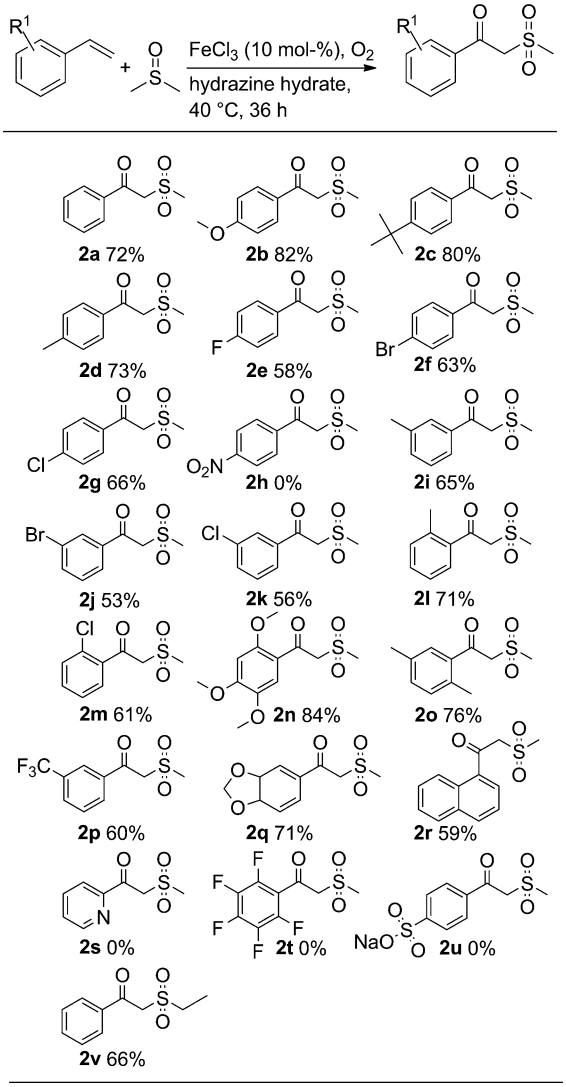
[a] Reagents and conditions: styrene (0.2 mmol), DMSO (1.0 mL), catalyst (10 mol-%), additive (1.0 mmol), and oxidant (0.2 mmol). [b] dppe = 1,2-bis(diphenylphosphino)ethane. [c] n.r. = no reaction. [d] Additive (0.4 mmol). [e] DMSO (0.6 mmol), 1,4-dioxane as solvent. [f] DMSO (0.6 mmol), xylene as solvent. [g] DMSO (0.6 mmol), toluene as solvent.

placing benzohydrazide with hydrazine dihydrochloride or hydrazine hydrate improved the yields of the desired product; however, hydrazine hydrate showed the best activity (see Table 1, Entries 6 and 7). Notably, the addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) increased the yield from 58 to 66% (see Table 1, Entry 8), but by using O_2 as the oxidant, we obtained the β-oxo sulfone in a higher yield (see Table 1, Entry 9). The yields did decrease when hydrogen peroxide or *tert*-butyl hydroperoxide (TBHP) were used as the oxidant (see Table 1, Entries 10 and 11). In addition, the screening of various reaction temperatures showed it to be a crucial factor, as the yield of **2a** decreased when the reaction was conducted at a higher and lower temperature than 40 °C. These results suggest that 40 °C was favorable for the formation of the target product, and the desired β-oxo sulfone was finally obtained in 72% yield (see Table 1, Entries 12–17). Furthermore, when the reaction time was changed to either 24 or 48 h, the yield decreased (see Table 1, Entries 18 and 19). Taking all of these results into account, the conditions listed in Table 1, Entry 15 were chosen as the optimal reaction conditions.

With these optimized conditions in hand, we examined the reactions of various vinylarenes. As shown in Table 2, a wide range of substrates, which include those with electron-donating and -withdrawing substituents, exhibited reactivity; however, those substrates with electron-rich substituents provided better yields of the product. In addition, the reactions of vinylarenes with substituents at the *ortho*, *meta*, and *para* positions proceeded smoothly, but those with groups at the *para* position gave higher yields. Of the *para*-substituted vinylarenes, those with the electron-donating methoxy, *tert*-butyl, and methyl groups promoted the reaction and led to the formation of the products (i.e., **2b**, **2c**, and **2d**, respectively) in higher yields than those obtained from the halogenated vinylarenes (to give **2e**, **2f**, and **2g**). The reaction was enhanced by the *para*-substituted methoxy group to give **2b** in the highest yield of 82%. On the other hand, the vinylarene with a *para*-substituted nitro group exhibited very low activity, and none of the desired product **2h** was obtained. Similarly, electron-rich analogues with a *meta* or *ortho* substituent also afforded products (i.e., **2i** and **2l**) in higher yields than those obtained from electron-deficient substrates (to give **2j**, **2k**, and **2m**). Moreover, substrates with two or three electron-donating substituents on the aromatic ring afforded better yields of product (i.e., **2n** and **2o**). With the electron-deficient trifluoromethyl group at the *meta* position, the yield of the β-oxo sulfone (i.e., **2p**) decreased. It is noteworthy that the bulky substrates 5-vinylbenzo[*d*][1,3]dioxole and 1-vinylnaphthalene also efficiently underwent the reaction with DMSO to give the product (i.e., **2q** and **2r**) in 71 and 59% yield, respectively. In addition, when styrene was replaced with 2-vinylpyridine, the transformation did not proceed (to give **2s**), which, suggests that heterocyclic compounds were not reac-

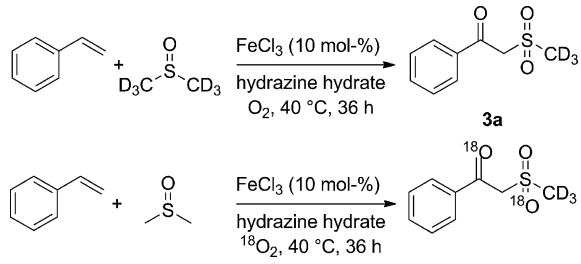
tive under these conditions. Furthermore, 1,2,3,4,5-pentafluoro-6-vinylbenzene and sodium 4-vinylbenzenesulfonate failed to furnish the desired products (i.e., **2t** and **2u**, respectively) because of their strong electron-withdrawing substituents. These results demonstrate that the electronic properties of the substituents on the aromatic ring had considerable influence on the formation of the target products. To explore the applicability of this significant method further, we then examined the scope of the sulfoxides. The reaction of styrene with diethyl sulfoxide afforded the corresponding product **2v** in 66% yield.

Table 2. Synthesis of 2-(methylsulfonyl)-1-phenylethanones from substituted styrenes and sulfoxides.[a]



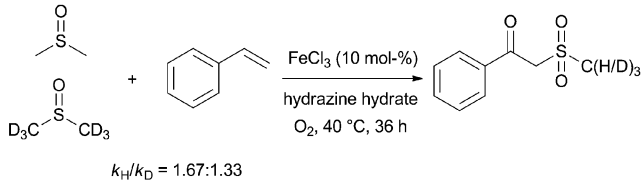
[a] Reagents and conditions: styrene (0.2 mmol), DMSO (1.0 mL), $FeCl_3$ (10 mol-%), and hydrazine hydrate (1.0 mmol) under O_2 at 40 °C for 36 h.

To gain insight into the reaction mechanism, we designed some experiments (see Scheme 1). The first isotope labeling experiment was conducted to elucidate the origin of the methylene hydrogen atoms of the β-oxo sulfone, and the second was carried out to verify the source of oxygen atoms. First, the reaction of styrene with deuterated DMSO under the standard reaction conditions generated deuterium-labeled product **3a** in 70% yield. The ^{1}H spectrum for this product displayed no signals in the range of δ = 2.0–4.0 ppm, but there was a single resonance at δ = 4.61 ppm. This result demonstrates that the methylene hydrogen atoms of the β-oxo sulfone came from styrene instead of DMSO. Therefore, both the C–S bond cleavage of DMSO and the C–S bond formation to give the β-oxo sulfone took place during the reaction. Second, the reaction of styrene and DMSO under $^{18}O_2$ and using the standard conditions afforded the ^{18}O-labeled product in 65% yield. This result illustrates that O_2 took part in this reaction, and the oxygen atom in the product came from O_2.



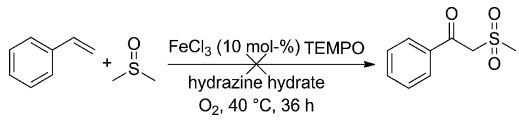
Scheme 1. Isotope labeling experiment.

To obtain some insight into the reaction mechanism, we performed a kinetic isotope effect study under the reaction conditions to reveal that the intermolecular kinetic isotope effect (k_H/k_D) is 1.25 (see Scheme 2).



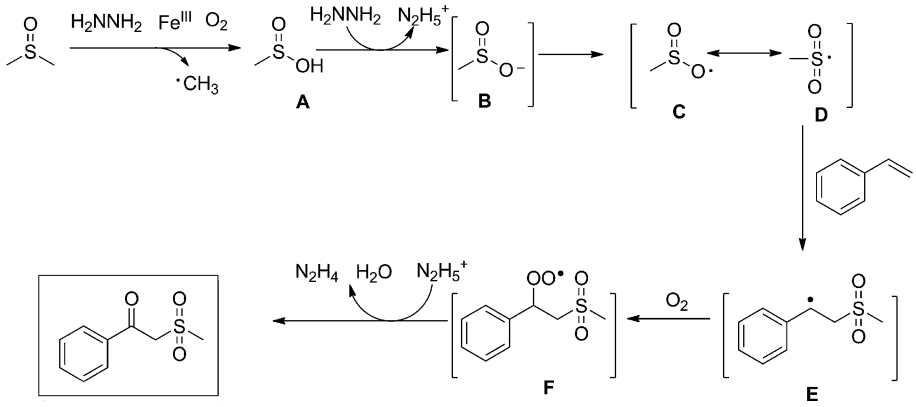
Scheme 2. Kinetic isotope effect study.

A radical pathway was supposedly involved in this transformation, and a radical trapping experiment further supported this assumption (see Scheme 3). This reaction was greatly inhibited in the presence of TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), a well-known radical scavenger, and this result suggests that the reaction presumably proceeded through a radical pathway (see radical trapping experiment in the Supporting Information).



Scheme 3. Radical trapping experiment.

On the basis of the aforementioned results and previous reports, a plausible mechanism is proposed for the formation of the β-oxo sulfone (see Scheme 4). The reaction may be initiated by DMSO and a high-valent iron complex that is generated from hydrazine hydrate and $FeCl_3$ to give **A**



Scheme 4. Plausible mechanistic pathway.

through an oxidative cleavage under O_2, in which the methyl group of DMSO is eliminated.[23] In this procedure, hydrazine hydrate acts as a ligand. Methanesulfinic acid (**A**) then undergoes a reaction with hydrazine to release the free sulfinyl anion **B**, which could be further oxidized by oxygen through a single-electron transfer (SET) to induce the formation of oxygen-centered radical **C** and its resonance structure sulfonyl radical **D**.[24] Moreover, the addition of radical **D** to styrene (**1a**) affords carbon-centered radical **E**, which is trapped by O_2 under diffusion control to give the corresponding peroxyl radical **F**, and a hydrogen atom from hydrazine is abstracted. The obtained hydroperoxyl compound is then dehydrated to give the product ketone.

To rationalize this possible mechanism, we carried out an additional experiment with methanesulfinic acid and styrene as substrates under the optimized conditions and obtained β-oxo sulfone. As a result, we assume that methanesulfinic acid is an intermediate in this transformation. Nevertheless, the applications of the reaction are wider with sulfoxide than sulfinic acid, and because of this, the sulfoxide is employed in the C–S bond cleavage, a process that is not easy to achieve.

Conclusions

We have developed the first general method for the formation of β-oxo sulfones that proceeds through a C–S bond cleavage and formation. The procedure tolerates a wide range of functional groups and employs an inexpensive and nontoxic iron catalyst. The new synthetic approach proceeds without additional initiators and forms a new C–S bond by using DMSO as the substrate. These factors make this transformation sustainable and flexible. Further studies to clearly understand the reaction mechanism and the synthetic applications are ongoing by our group.

Experimental Section

General Methods: Column chromatography was carried out on silica gel. The ^{1}H NMR spectroscopic data were recorded at 400 MHz, and $CDCl_3$ was used as the solvent. The ^{13}C NMR spectroscopic data were recorded at 100 MHz with $CDCl_3$ as the solvent and TMS as the internal standard. IR spectra were recorded with an FTIR spectrometer, and only the major peaks are reported in cm^{-1}. All new compounds were further characterized by HRMS, and copies of their ^{1}H and ^{13}C NMR spectra are provided in the Supporting Information. Commercially available reagents and solvents were used without further purification. CCDC-960134 (for **2a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Typical Procedure for the Preparation of 2-(Methylsulfonyl)-1-phenylethanone (2a): A test tube was charged with styrene (**1a**, 0.2 mmol), $FeCl_3$ (0.04 mmol), and DMSO (1 mL). Then, hydrazine hydrate (1.0 mmol) was added, and the resulting mixture was stirred at 40 °C for 36 h under O_2. After cooling to room temperature, the mixture was diluted with ethyl acetate (10 mL), and the resulting solution was washed with brine (5 mL) and dried with anhydrous Na_2SO_4. After the solvent had been evaporated in vacuo, the residue was purified by column chromatography (petroleum ether/EtOAc) to afford pure **2a** (see Figure 1).

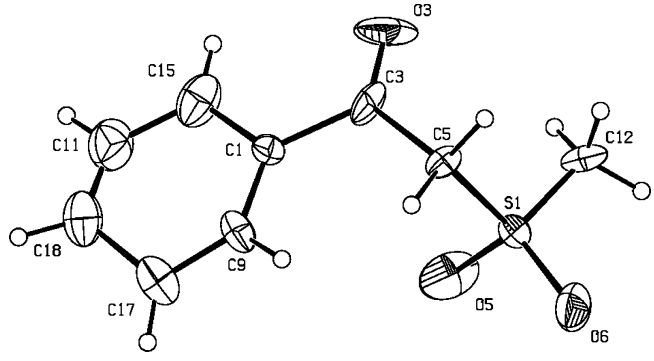


Figure 1. X-ray crystal structure of **2a**.

Characterization Data of Compounds 2:

2-(Methylsulfonyl)-1-phenylethanone (2a): Yellow solid (29 mg, 72%); m.p. 86–90 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.00 (dd, J = 8.8 Hz, J = 1.2 Hz, 2 H), 7.68–7.64 (m, 1 H), 7.55–7.51 (m, 2 H), 4.62 (s, 2 H), 3.16 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2, 135.6, 134.7, 129.2, 129.0, 61.2, 41.8 ppm. IR (neat): $\tilde{\nu}$ = 3333, 3023, 2998, 2949, 2929, 1675, 1616, 1597, 1301, 1219, 1152, 1118, 1006, 964, 907, 734, 689, 583, 495, 455 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{11}O_3S$ $[M + H]^+$ 199.0429; found 199.0431.

1-(4-Methoxyphenyl)-2-(methylsulfonyl)ethanone (2b): Yellow solid (37 mg, 82%); m.p. 132–138 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.8 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 4.55 (s, 2 H), 3.89 (s, 3 H), 3.13 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.3, 164.8, 131.8, 128.7, 114.3, 61.2, 55.6, 41.7 ppm. IR (neat): $\tilde{\nu}$ = 3350, 3051, 3017, 2973, 2923, 1603, 1572, 1513, 1450, 1422, 1300, 1263, 1176, 1128, 1028, 976, 911, 830, 797, 766, 735, 500 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{13}O_4S$ $[M + H]^+$ 229.0535; found 229.0538.

1-[4-(*tert*-Butyl)phenyl]-2-(methylsulfonyl)ethanone (2c): Yellow liquid (41 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.94 (d, J = 8.4 Hz, 2 H), 7.53 (d, J = 8.4 Hz, 2 H), 4.58 (s, 2 H), 3.15 (s, 3 H), 1.35 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.7, 158.9, 133.1, 129.3, 126.1, 61.3, 41.8, 35.2, 30.9 ppm. IR (neat): $\tilde{\nu}$ = 3615, 3335, 2963, 2909, 1677, 1604, 1464, 1410, 1365, 1314, 1219, 1130, 1105, 969, 900, 853, 802, 734, 540, 514, 484, 458 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{19}O_3S$ $[M + H]^+$ 255.1055; found 255.1058.

2-(Methylsulfonyl)-1-(*p*-tolyl)ethanone (2d): Yellow solid (31 mg, 73%); m.p. 110–114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.0 Hz, 2 H), 7.32 (d, J = 8.0 Hz, 2 H), 4.59 (s, 2 H), 3.15 (s, 3 H), 2.44 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.7, 146.0, 133.1, 129.7, 129.4, 61.1, 41.7, 21.8 ppm. IR (neat): $\tilde{\nu}$ = 3042, 3018, 2960, 2932, 2915, 1687, 1604, 1298, 1206, 1220, 1189, 1175, 1126, 979, 901, 814, 733, 522, 462 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{13}O_3S$ $[M + H]^+$ 213.0585; found 213.0589.

1-(4-Fluorophenyl)-2-(methylsulfonyl)ethanone (2e): Yellow solid (25 mg, 58%); m.p. 92–100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07–8.04 (m, 2 H), 7.23–7.18 (m, 2 H), 4.59 (s, 2 H), 3.15 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.6, 167.9, 165.4, 132.2, 132.13, 132.05, 132.0, 116.5, 116.4, 116.3, 116.2, 61.3, 41.7 ppm. IR (neat): $\tilde{\nu}$ = 3325, 3112, 3073, 3018, 2958, 2931, 1671, 1595, 1508, 1420, 1311, 1235, 1167, 1134, 969, 910, 860, 797, 733, 568, 512, 488, 405 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{10}FO_3S$ $[M + H]^+$ 217.0335; found 217.0340.

1-(4-Bromophenyl)-2-(methylsulfonyl)ethanone (2f): Yellow solid (35 mg, 63%); m.p. 134–139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.87 (d, J = 8.4 Hz, 2 H), 7.68 (d, J = 8.4 Hz, 2 H), 4.56 (s, 2 H), 3.14 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.3, 134.4, 132.4, 130.7, 130.4, 61.4, 41.7 ppm. IR (neat): $\tilde{\nu}$ = 3331, 2955, 2921, 2852, 1672, 1581, 1459, 1400, 1293, 1213, 1160, 1108, 1067, 1024, 997, 966, 894, 796, 714, 581, 502, 462 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{10}BrO_3S$ $[M + H]^+$ 276.9534; found 276.9538.

1-(4-Chlorophenyl)-2-(methylsulfonyl)ethanone (2g): Yellow solid (31 mg, 66%); m.p. 122–128 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 8.4 Hz, 2 H), 7.52 (d, J = 8.4 Hz, 2 H), 4.49 (s, 2 H), 3.15 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.9, 131.6, 130.9, 129.5, 129.4, 61.3, 41.7 ppm. IR (neat): $\tilde{\nu}$ = 3327, 3014, 2955, 2924, 2853, 1676, 1596, 1448, 1418, 1306, 1215, 1123, 1117, 1109, 966, 909, 821, 734, 687, 651, 585, 512, 456 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{10}ClO_3S$ $[M + H]^+$ 233.0039; found 233.0044.

2-(Methylsulfonyl)-1-(*m*-tolyl)ethanone (2i): Yellow solid (28 mg, 65%); m.p. 112–116 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.93–7.91 (m, 2 H), 7.40 (d, J = 7.6 Hz, 1 H), 7.34 (t, J = 8.0 Hz, 1 H), 4.55 (s, 2 H), 3.14 (s, 3 H), 2.40 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 182.8, 138.3, 134.6, 130.7, 129.3, 128.3, 127.4, 61.2, 41.8, 21.2 ppm. IR (neat): $\tilde{\nu}$ = 3327, 3014, 2958, 2921, 2851, 1687, 1596, 1451, 1421, 1311, 1208, 1128, 1106, 1101, 964, 901, 820, 734, 687, 651, 583, 511, 452 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{13}ClO_3S$ $[M + H]^+$ 213.0585; found 213.0588.

1-(3-Bromophenyl)-2-(methylsulfonyl)ethanone (2j): Yellow solid (29 mg, 53%); m.p. 91–96 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 7.93 (d, J = 7.6 Hz, 1 H), 7.79 (d, J = 8.0 Hz, 1 H), 7.42 (t, J = 8.0 Hz, 1 H), 4.58 (s, 2 H), 3.16 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.1, 137.5, 132.0, 130.6, 128.8, 127.9, 123.4, 61.2, 41.8 ppm. IR (neat): $\tilde{\nu}$ = 3287, 2957, 2927, 2852, 1725, 1567, 1422, 1318, 1209, 1127, 1074, 967, 909, 733, 648, 447 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{10}BrO_3S$ $[M + H]^+$ 276.9534; found 276.9536.

1-(3-Chlorophenyl)-2-(methylsulfonyl)ethanone (2k): Yellow solid (26 mg, 56%); m.p. 88–97 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (s, 1 H), 7.88 (d, J = 8.0 Hz, 1 H), 7.62 (d, J = 9.2 Hz, 1 H), 7.45 (t, J = 8.0 Hz, 1 H), 4.56 (s, 2 H), 3.14 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.9, 135.2, 134.5, 130.2, 129.4, 127.4, 126.9, 62.2, 41.8 ppm. IR (neat): $\tilde{\nu}$ = 3281, 2953, 2926, 2851, 1724, 1561, 1421, 1308, 1200, 1124, 1070, 966, 901, 734, 640, 441 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{10}ClO_3S$ $[M + H]^+$ 233.0039; found 233.0040.

2-(Methylsulfonyl)-1-(*o*-tolyl)ethanone (2l): Yellow solid (30 mg, 71%); m.p. 92–98 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.07 (d, J = 8.0 Hz, 1 H), 7.47–7.43 (m, 1 H), 7.29–7.24 (m, 2 H), 4.55 (s, 2 H), 3.05 (s, 3 H), 2.67 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 141.4, 132.9, 131.9, 131.6, 128.4, 125.9, 62.1, 42.1, 22.1 ppm. IR (neat): $\tilde{\nu}$ = 3277, 2942, 2917, 2852, 1724, 1563, 1432, 1328, 1219, 1107, 1034, 957, 905, 731, 644, 443 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{13}O_3S$ $[M + H]^+$ 213.0585; found 213.0588.

1-(2-Chlorophenyl)-2-(methylsulfonyl)ethanone (2m): Yellow liquid (28 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.67 (dd, J = 7.6 Hz, J = 1.2 Hz, 1 H), 7.50–7.46 (m, 2 H), 7.43–7.39 (m, 1 H), 4.67 (s, 2 H), 3.19 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.5, 137.2, 133.6, 130.8, 130.5, 128.9, 127.4, 64.4, 42.2 ppm. IR (neat): $\tilde{\nu}$ = 2956, 2928, 2872, 2854, 1726, 1589, 1434, 1320, 1127, 1072, 967, 910, 733, 649, 496, 458 cm^{-1}. HRMS (ESI): calcd. for $C_9H_{10}ClO_3S$ $[M + H]^+$ 233.0039; found 233.0042.

2-(Methylsulfonyl)-1-(2,4,5-trimethoxyphenyl)ethanone (2n): Yellow solid (48 mg, 84%); m.p. 122–134 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.32 (s, 1 H), 6.49 (s, 1 H), 4.64 (s, 2 H), 3.98 (s, 3 H), 3.93 (s, 3 H), 3.88 (s, 3 H), 3.17 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 187.9, 158.6, 155.7, 143.5, 117.3, 108.9, 95.9, 62.6, 56.2, 56.15, 56.12, 31.1 ppm. IR (neat): $\tilde{\nu}$ = 3335, 3036, 2962, 1678, 1590, 1508, 1480, 1421, 1342, 1280, 1220, 1165, 1122, 1092, 1024, 1016, 988, 900, 836, 764, 620, 521, 470 cm^{-1}. HRMS (ESI): calcd. for $C_{12}H_{17}O_6S$ $[M + H]^+$ 289.0746; found 289.0749.

1-(2,5-Dimethylphenyl)-2-(methylsulfonyl)ethanone (2o): Yellow solid (34 mg, 76%); m.p. 100–104 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57 (s, 1 H), 7.28 (d, J = 10.4 Hz, 1 H), 7.19 (d, J = 7.6 Hz, 1 H), 4.56 (s, 2 H), 3.18 (s, 3 H), 2.50 (s, 3 H), 2.39 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.7, 136.9, 135.8, 135.5, 133.9, 132.4, 130.7, 63.2, 42.0, 21.2, 20.9 ppm. IR (neat): $\tilde{\nu}$ = 3349, 3038, 3013, 2962, 2949, 2926, 1684, 1496, 1306, 1230, 1153, 1137, 1112, 1017, 982, 967, 807, 499, 445 cm^{-1}. HRMS (ESI): calcd. for $C_{11}H_{15}O_3S$ $[M + H]^+$ 227.0742; found 227.0739.

2-(Methylsulfonyl)-1-[3-(trifluoromethyl)phenyl]ethanone (2p): Yellow solid (32 mg, 60%); m.p. 88–92 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.27 (s, 1 H), 8.21 (d, J = 8.0 Hz, 1 H), 7.93 (d, J = 7.6 Hz, 1 H), 7.71 (t, J = 8.0 Hz, 1 H), 4.64 (s, 2 H), 3.17 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 188.2, 136.0, 132.5, 131.0, 129.8, 126.0, 125.9, 61.3, 41.8 ppm. IR (neat): $\tilde{\nu}$ = 3632, 3548, 3348, 3013, 2963, 2928, 2865, 1684, 1568, 1496, 1451, 1408, 1306, 1229, 1115, 1015, 967, 908, 808, 733, 649, 604, 498, 465, 447 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{10}F_3O_3S$ $[M + H]^+$ 267.0303; found 267.0300.

1-(Benzo[*d*][1,3]dioxol-5-yl)-2-(methylsulfonyl)ethanone (2q): Yellow solid (34 mg, 71%); m.p. 128–132 °C. ^{1}H NMR (400 MHz,

$CDCl_3$): δ = 7.41–7.39 (m, 1 H), 7.32 (s, 1 H), 6.92 (d, J = 8.0 Hz, 1 H), 6.06 (s, 2 H), 4.59 (s, 2 H), 3.18 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.2, 153.0, 148.6, 131.8, 128.5, 108.3, 106.8, 102.0, 59.9, 42.6 ppm. IR (neat): $\tilde{\nu}$ = 3068, 3013, 2852, 2972, 2848, 1670, 1664, 1598, 1511, 1495, 1423, 1323, 1267, 1113, 1030, 925, 882, 810, 745, 721, 613, 554, 468 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{11}O_5S$ $[M + H]^+$ 243.0327; found 243.0331.

2-(Methylsulfonyl)-1-(naphthalen-1-yl)ethanone (2r): Yellow solid (29 mg, 59%); m.p. 86–90 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 8.76 (d, J = 8.4 Hz, 1 H), 8.11–8.08 (m, 2 H), 7.92 (d, J = 8.0 Hz, 1 H), 7.69–7.65 (m, 1 H), 7.61–7.56 (m, 2 H), 4.72 (s, 2 H), 3.24 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.6, 131.1, 130.1, 130.9, 129.0, 128.9, 128.8, 128.7, 127.0, 125.4, 124.4, 64.0, 42.1 ppm. IR (neat): $\tilde{\nu}$ = 3332, 3059, 2955, 2927, 2871, 2852, 1676, 1596, 1576, 1507, 1435, 1381, 1289, 1131, 1076, 948, 909, 795, 770, 733, 649, 582, 562, 504, 436 cm^{-1}. HRMS (ESI): calcd. for $C_{13}H_{13}O_3S$ $[M + H]^+$ 249.0585; found 249.0588.

2-(Ethylsulfonyl)-1-phenylethanone (2v): Yellow solid (28 mg, 66%); m.p. 92–98 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (d, J = 7.2 Hz, 2 H), 7.62 (t, J = 7.6 Hz, 1 H), 7.51–7.47 (m, 2 H), 4.59 (s, 2 H), 3.10 (q, J = 14.8 Hz, J = 7.6 Hz, 2 H), 1.35 (t, J = 7.6 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2, 135.5, 134.7, 129.2, 129.0, 61.2, 48.8, 11.8 ppm. IR (neat): $\tilde{\nu}$ = 3330, 3049, 2995, 2947, 2929, 1727, 1676, 1596, 1311, 1225, 1161, 1016, 968, 909, 733, 694, 582, 504, 436 cm^{-1}. HRMS (ESI): calcd. for $C_{10}H_{13}O_3S$ $[M + H]^+$ 213.0585; found 213.0587.

Deuterated 2-(Methylsulfonyl)-1-phenylethanone (3a): Yellow solid (25 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$): δ = 8.01 (d, J = 7.2 Hz, 2 H), 7.67–7.65 (m, 1 H), 7.56–7.52 (m, 2 H), 4.61 (s, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2, 135.5, 134.7, 129.2, 129.0, 61.2, 42.1 ppm.

Supporting Information (see footnote on the first page of this article): ^1H and ^{13}C NMR spectra of the products.

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