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o-Iodoxybenzoic Acid (IBX)–Iodine Mediated One-Pot Deacylative Sulfonylation of 1,3-Dicarbonyl Compounds: A Synthesis of β-Carbonyl Sulfones

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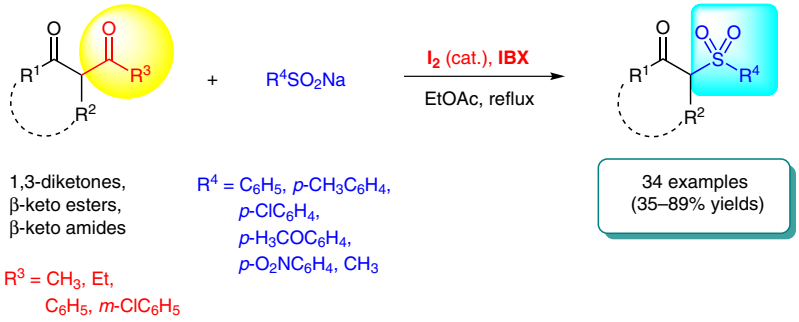

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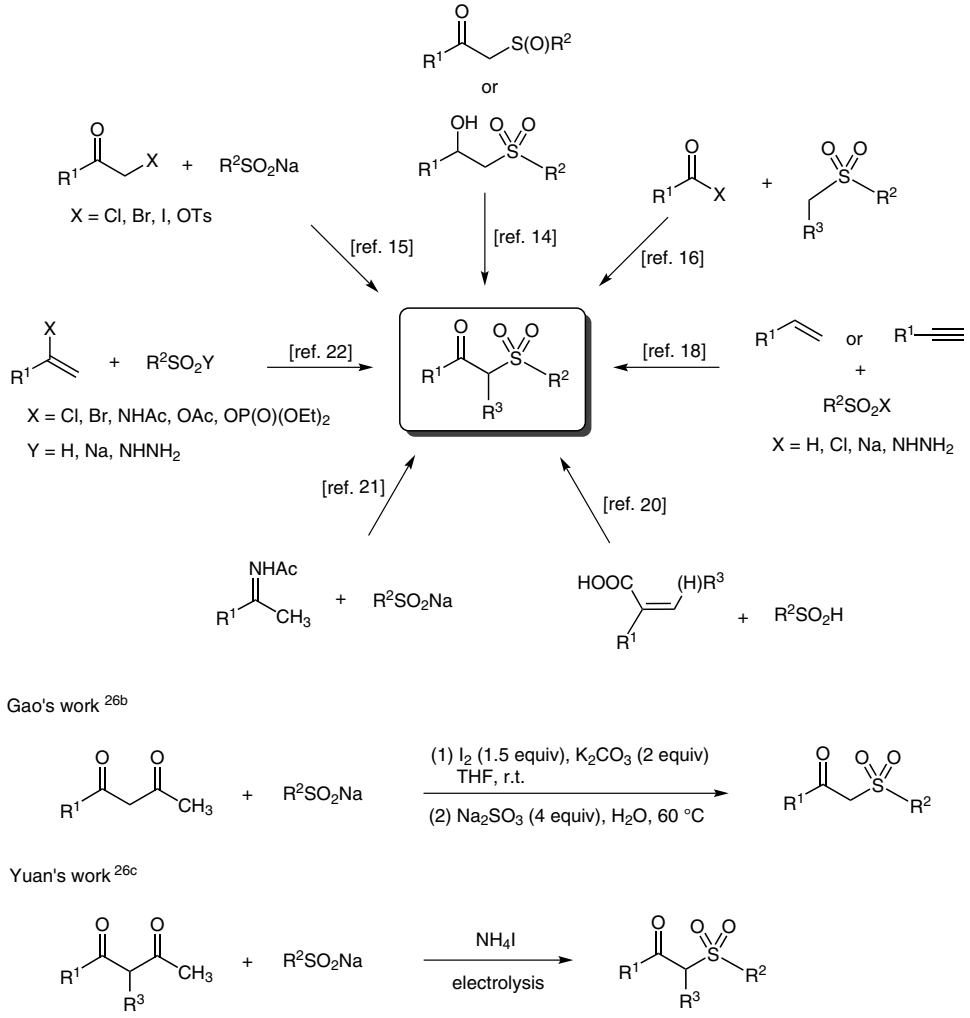
Abstract A combination of *o*-iodoxybenzoic acid (IBX) and a catalytic amount of iodine is found to promote a facile one-pot deacylative sulfonylation reaction of 1,3-dicarbonyl compounds with sodium sulfinates to yield β-carbonyl sulfones. The present method provides the target products bearing a wide variety of functional groups in one step and in good yields.

Key words deacylation, sulfonylation, β-keto sulfone, *o*-iodoxybenzoic acid, iodine

β-Carbonyl sulfones, particularly β-keto sulfones, are a class of organosulfur compound that has found different applications in various fields including polymeric materials, medicinal chemistry and synthetic organic chemistry.[1] β-Keto sulfones are desirable units and the presence of the sulfonyl moiety aids in enhancing their biological properties,[2] which include fungicidal,[2a] antibacterial[2d] and the inhibition of 11β-hydroxysteroid dehydrogenase type 1.[2b,c] In view of the synthetic applications, a variety of compounds, for example, olefins,[3] disubstituted alkynes,[4] allenes,[5] flavanones,[6] vinyl sulfones,[7] amides,[8] aromatic amines,[9] 2,3-dihydrofurans,[10] naphthols,[11] naphthalenes,[11] quinolines[12] and ketones[13] have been prepared via the intermediacy of β-keto sulfones. The numerous applications of β-keto sulfones have driven the development of several synthetic strategies toward the synthesis of β-keto sulfones including: (a) oxidation of β-keto sulfides, β-keto sulfoxides and β-hydroxy sulfones,[14] (b) alkylation of sodium sulfinates with either α-halo ketones or α-tosyloxy ketones,[15] (c) acylation of alkyl sulfones,[16] (d) sulfonylation of alkyl ketones or silyl enol ethers,[17] (e) oxysulfonylation of alkenes or alkynes,[18] (f) reactions of diazo sulfones with aldehydes,[19] (g) reactions of 2-arylacrylic acids with sulfinic acids,[20] (h) reactions of oxime acetates with sodium sulfinates,[21] (i) reactions of activated alkenes with sulfinic acids, sodium sulfinates or sulfonyl hydrazides,[22] (j) free-radical rearrangement of enol sulfonates,[23] (k) reactions of alkyl- and arylacetylenes with polystyrene-supported areneselenosulfonates,[24] and (l) reactions of arylboronic acids with arenesulfonylacetonitriles.[25] Recently, the straightforward synthesis of β-keto sulfones by the reaction of 1,3-dicarbonyl compounds with sodium sulfinates was also described.[26] Gao and co-workers first reported the C-sulfonylation of 1,3-dicarbonyl compounds mediated by I_2 to form both β-dicarbonyl sulfones and β-keto sulfones.[26a,b] They claimed that β-keto sulfones were formed through I_2-mediated sulfonylation followed by Na_2SO_3-mediated deacylation of β-dicarbonyl sulfones.[26b] In the same year, Yuan et al. demonstrated an efficient and convenient electrochemical synthesis of β-keto sulfones from sulfinates and 1,3-dicarbonyl compounds by using ammonium iodide as a supporting electrolyte (Scheme 1).[26c] From the perspective view of synthetic methodology toward β-keto sulfone synthesis, it is still desirable to develop alternative methods to access β-keto sulfones employing fast and convenient experimental procedures.

Our research group has a long-standing interest in the synthesis of sulfur-containing molecules mediated by iodine and hypervalent iodines.[15i,27] In 2012, we reported a facile two-step synthesis, in one pot, of β-keto sulfones from alkenes mediated by a combination of *o*-iodoxybenzoic acid (IBX) and iodine in the presence of sodium arenesulfinates.[15i] We report herein a one-pot synthesis of β-carbonyl sulfones by deacylative sulfonylation of 1,3-dicarbonyl compounds with sodium sulfinates mediated by a combination of *o*-iodoxybenzoic acid (IBX) and molecular iodine (I_2). It is worth mentioning here that hypervalent io-

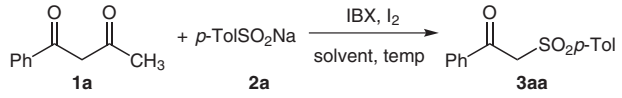


Scheme 1 The synthetic strategies toward β-keto sulfone synthesis

dines and molecular iodine are widely employed as reagents to promote sulfonylation reactions for organosulfone synthesis.[28]

To begin with, benzoylacetone (**1a**) and sodium *p*-toluenesulfinate (**2a**) were chosen as the substrates in the model reactions. On the basis of our previous work,[15i] a combination of molecular iodine and *o*-iodoxybenzoic acid (IBX) was primarily employed to screen for optimized reaction conditions. A variety of reaction factors including the solvent, reagent stoichiometry, reaction time, temperature, oxidizing agent and iodide source were screened. First, various solvents were examined and the reactions were performed using benzoylacetone (**1a**) (0.5 mmol), sodium *p*-toluenesulfinate (**2a**) (3 equiv), IBX (2 equiv) and iodine (0.5 equiv) at 80 °C or at reflux temperature for two hours (Table 1). Although the reaction did not proceed in water (Table 1, entry 1), β-keto sulfone **3aa** was obtained in variable yields (40–85%) when the reactions were carried out in organic solvents including 1,4-dioxane, DCE, DMF, EtOH, MeOH, acetone, THF and EtOAc (Table 1, entries 2–9). Among these, EtOAc was found to be the optimum solvent yielding β-keto sulfone **3aa** in 85% yield (Table 1, entry 9). With the best solvent (EtOAc) in hand, we further attempted to optimize the molar ratios of **2a**, IBX and I_2 and the results are summarized in Table 1 (entries 10–14). While increasing the stoichiometry of **2a** (from 3 to 4 equiv) did not improve the yield of **3aa**, lowering the amount of **2a** (from 3 to 2 or 1 equiv) significantly decreased the product yields to 60% and 35%, respectively (Table 1, entries 10–12). Furthermore, while molecular iodine can be employed in a lesser amount (from 0.5 to 0.25 equiv), a further decrease in the quantity of IBX (from 2 to 1.2 equiv) caused a decrease in the yield of the desired product from 85% to 68% (Table 1, entries 13 and 14). No improvement was observed when the reaction time was extended (from 2 h to 5 h) (Table 1, entry 15). Finally, the reaction proceeded with poorer efficiency at room temperature (Table 1, entry 16).

Table 1 Optimization of the Reaction Conditions[a]



1a **2a** **3aa**

Entry	**2a** (equiv)	IBX (equiv)	I_2 (equiv)	Solvent	Temp (°C)	Yield (%)[b]
1	3	2	0.5	H_2O	80	NR
2	3	2	0.5	1,4-dioxane	80	69
3	3	2	0.5	DCE	80	49
4	3	2	0.5	DMF	80	41
5	3	2	0.5	EtOH	reflux	62
6	3	2	0.5	MeOH	reflux	40
7	3	2	0.5	acetone	reflux	52
8	3	2	0.5	THF	reflux	79
9	3	2	0.5	EtOAc	reflux	85
10	4	2	0.5	EtOAc	reflux	80
11	2	2	0.5	EtOAc	reflux	60
12	1	2	0.5	EtOAc	reflux	35
13	3	1.2	0.5	EtOAc	reflux	68
14	**3**	**2**	**0.25**	**EtOAc**	**reflux**	**85**
15[c]	3	2	0.25	EtOAc	reflux	83
16[d]	3	2	0.25	EtOAc	r.t.	70

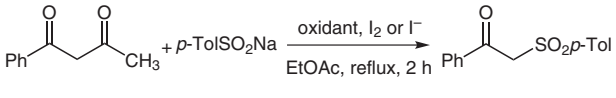
[a] Reaction conditions: **1a** (0.5 mmol), solvent (3 mL), open air, 2 h.
[b] Yield of isolated product after column chromatography (SiO_2); NR = no reaction.
[c] Reaction time = 5 h.
[d] Reaction time = 16 h.

Having established the primary reaction conditions (Table 1, entry 14), different types of oxidizing agent and iodide source were next investigated and the results are listed in Table 2.

Among the oxidizing agents screened including IBX, *o*-iodosobenzoic acid (IBA), (diacetoxyiodo)benzene (DIB), *tert*-butyl hydroperoxide (TBHP), OXONE® and $K_2S_2O_8$, IBX was the optimum oxidizing agent for the present reaction (Table 2, entries 1–6). When iodine was replaced with other iodide sources including KI, NaI, Et_4NI and Bu_4NI, **3aa** was obtained in lower yields (55–71%) (Table 2, entries 7–10). When IBX was excluded from the reactions performed by employing variable molar ratios of I_2 (0.25, 0.5 and 1.0 equiv), a significant decrease in the product yield was observed (Table 2, entries 11–13). Based on the results shown in Tables 1 and 2, the optimum reaction conditions were chosen as the following: substrate **1** (1 equiv), sodium sulfinate **2** (3 equiv), IBX (2 equiv) and I_2 (0.25 equiv) in refluxing EtOAc for two hours (Table 1, entry 14).

With optimized reaction conditions in hand, a series of 1,3-dicarbonyl compounds including 1,3-diketones, β-keto esters and β-keto amides, sodium sulfinates and the limitations of the procedure were investigated and the results are summarized in Scheme 2 and Scheme 3. Initially, the reactions of sodium *p*-toluenesulfinate (**2a**) with aroylacetone derivatives bearing electronically different substituents on the phenyl ring were investigated. Benzoylacetone derivatives containing electron-donating groups on the phenyl ring including *m*-CH_3, *p*-*t*-Bu, *m*-CH_3O, *p*-CH_3O and 3,5-$(CH_3O)_2$ gave the corresponding β-keto sulfones **3ba–fa** in good yields (70–78%). It is evident that the steric and electronic nature of the chlorine atom at *ortho*-, *meta*- and *para*-positions of the phenyl ring affected the yields of the corresponding β-keto sulfones; products **3ga**, **3ha** and **3ia** were obtained in 51%, 58% and 72% yields, respectively. The benzoylacetone bearing a strong electron-attracting group (*m*-NO_2) was also a suitable substrate although it was converted into the corresponding product **3ja** in moderate yield (44%). Compound **1k** bearing a furfuryl group also worked well and could be converted into the desired product **3ka** under standard reaction conditions in 59% yield. When 2-methyl-1-phenylbutane-1,3-dione (**1l**) was used as a substrate, no desired product **3la** was observed and 2-methyl-1-phenylbutane-1,3-dione (**1l**) was recovered in 59% yield. Acetylacetone was employed as a representative substrate for aliphatic 1,3-diketones. Unfortunately, it could only be transformed into β-keto sulfone **3ma** with relatively low efficiency (38% yield). In addition to the 1,3-diketone

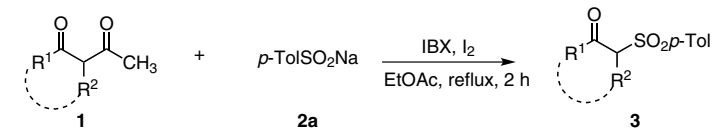
Table 2 Optimization of the Reaction Conditions[a]

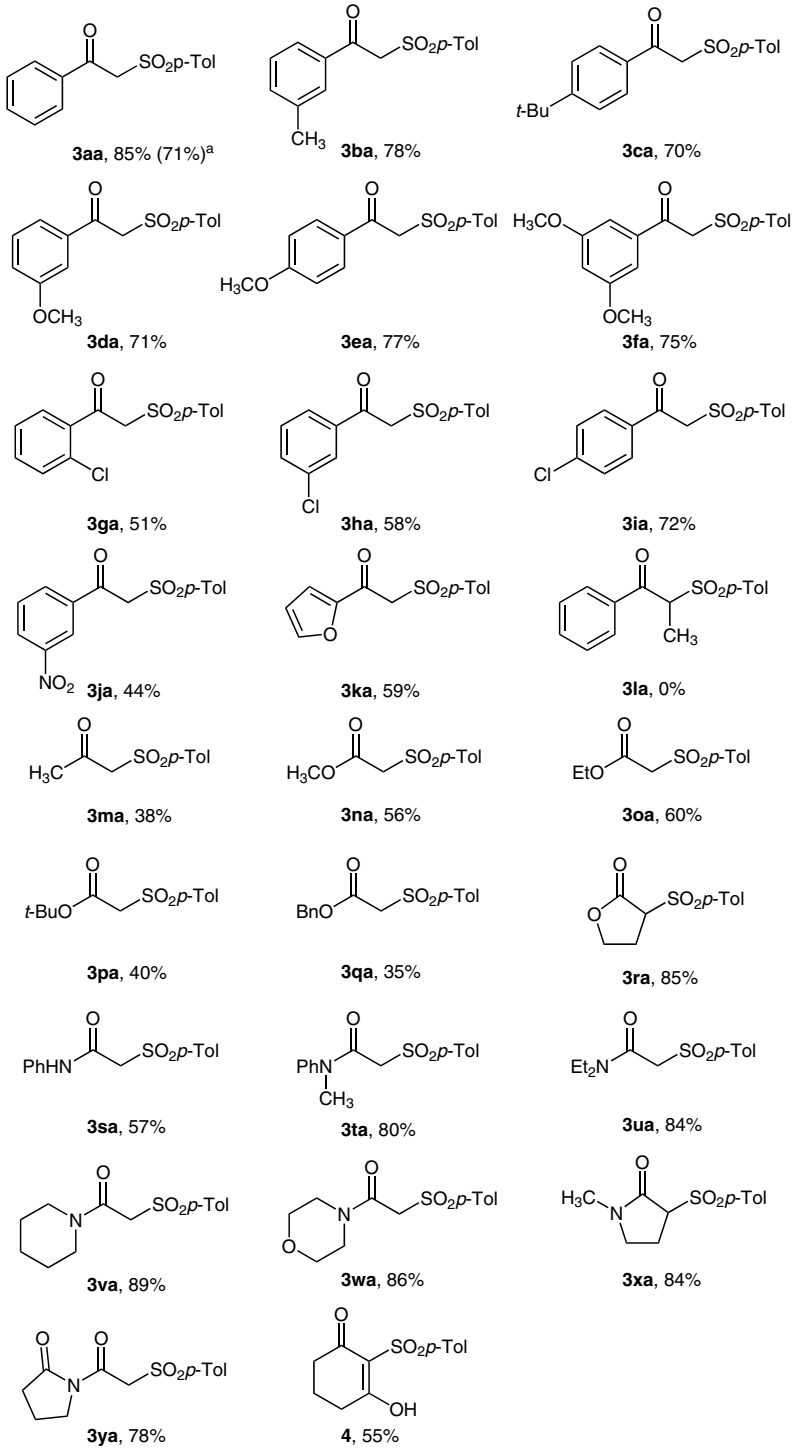


1a **2a** **3aa**

Entry	Oxidant	I_2 or I^- (equiv)	Yield (%)[b]
1	IBX	I_2 (0.25)	85
2	IBA	I_2 (0.25)	73
3	DIB	I_2 (0.25)	32
4	TBHP	I_2 (0.25)	49
5	OXONE®	I_2 (0.25)	25[c]
6	$K_2S_2O_8$	I_2 (0.25)	26[c]
7	IBX	KI (0.5)	71
8	IBX	NaI (0.5)	68
9	IBX	Et_4NI (0.5)	61
10	IBX	Bu_4NI (0.5)	55
11	–	I_2 (0.25)	10[c]
12	–	I_2 (0.5)	20[c]
13	–	I_2 (1.0)	23[c]

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (3 equiv), oxidant (2 equiv), EtOAc (3 mL), open air, 2 h.
[b] Yield of isolated product after column chromatography (SiO_2).
[c] Substrate **1a** was recovered in the range of 55–65%.





Scheme 2 Scope of 1,3-dicarbonyl compounds. *Reagents and conditions*: **1** (0.5 mmol), **2a** (3 equiv), IBX (2 equiv), I_2 (0.25 equiv), EtOAc (3 mL), open air, 2 h. Yields are those of isolated products after column chromatography (SiO_2). [a] 1-Phenylpentane-1,3-dione was employed as the substrate.

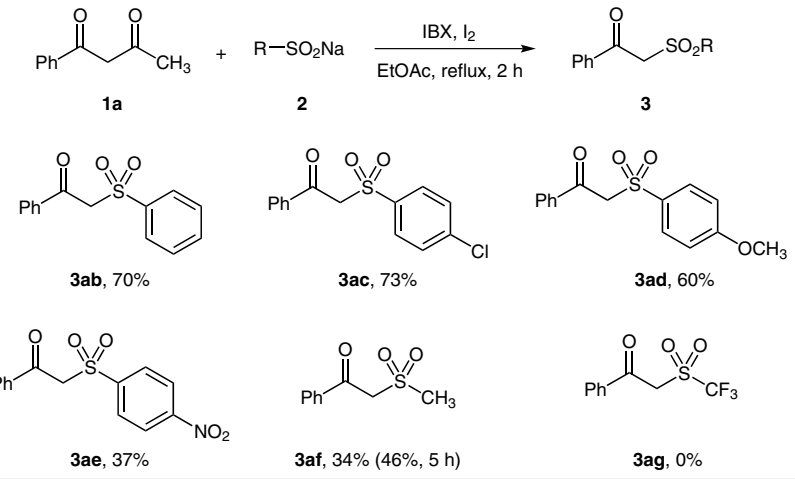
substrates, the present method was also found to be applicable to reactions employing β-keto esters as the substrates. Thus, methyl, ethyl, *tert*-butyl, and benzyl 3-oxobutanoates yielded the corresponding products **3na–qa** in low to moderate yields (35–60%). The reaction of 2-acetylbutyrolactone (**1r**) proceeded readily to yield the corresponding product **3ra** in 85% yield. β-Keto amides, including simple open-chain secondary and tertiary amides (**1s–u**), cyclic tertiary amides (**1v** and **1w**), 3-acetyl-1-methylpyrrolidin-2-one (**1x**) and 1-(2-oxopyrrolidin-1-yl)butane-1,3-dione (**1y**), provided the corresponding products **3sa–ya** in moderate to good yields (57–89%). Interestingly, when 1-phenylpentane-1,3-dione was employed as a substrate under standard reaction conditions, depropionylation took place to yield 1-phenyl-2-(*p*-tosyl)ethanone (**3aa**) in 71% yield. Finally, cyclohexane-1,3-dione did not provide the expected ring-opened product, but yielded 3-hydroxy-2-(*p*-tosyl)cyclohex-2-enone (**4**) in 55% yield.

Next, the reactions of benzoylacetone (**1a**) with a series of sodium sulfinates **2** were evaluated and the results are shown in Scheme 3. Sodium arenesulfinates bearing electronically different groups on the *para*-position (*p*-Cl, *p*-CH_3O, *p*-O_2N) gave the corresponding products **3ab–3ae** in variable yields (37–73%), the example with a strong electron-withdrawing group (*p*-O_2N) giving a poor yield (37%). Under the standard reaction conditions, sodium methanesulfinate gave the corresponding product **3af** in low yield (34%). A better yield of **3af** (46%) was obtained when the reaction was carried out over a prolonged reaction time (5 h). Finally, no formation of the corresponding product **3ag** was observed when sodium trifluoromethanesulfinate was employed as the sulfone source under the typical reaction conditions.

To further demonstrate the synthetic utility of the present methodology, the reactions of 1,3-diarylpropane-1,3-diones with sodium *p*-toluenesulfinate (**2a**) were investigated and the results are summarized in Table 3. Although a longer reaction time (6 h) followed by stirring with a mixture of saturated $Na_2S_2O_3$ and $NaHCO_3$ (1:1 v/v) was required, it was gratifying to observe that the symmetrical 1,3-diarylpropane-1,3-dione, 1,3-diphenylpropane-1,3-dione (**5a**), smoothly underwent debenzoylative sulfonylation to afford **3aa** in 61% yield (Table 3, entry 1). The reactions of unsymmetrical 1,3-diarylpropane-1,3-diones were also investigated. 1-(3-Chlorophenyl)-3-(4-methoxyphenyl)propane-1,3-dione (**5b**) exclusively yielded **3ea** derived from chemoselective cleavage of the 3-chlorobenzoyl group in 63% yield (Table 3, entry 2). However, 1-(4-methoxyphenyl)-3-phenylpropane-1,3-dione (**5c**) yielded an inseparable mixture of **3ea** and primarily formed sulfonylation adduct **6** (60% yield, **3ea**/**6** = 1:3) while 1-(4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)propane-1,3-dione (**5d**) exclusively gave an initially formed sulfonylation adduct **7** in 66% yield (Table 3, entries 3 and 4).

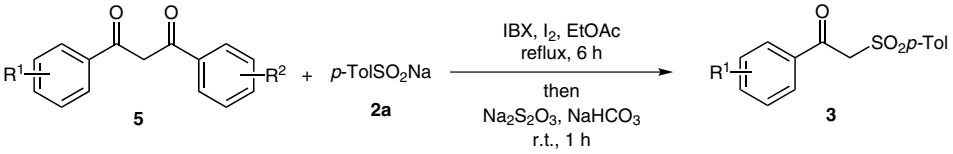
It is worth emphasizing here that scaling up experiments were also investigated (Scheme 4). The reactions took place readily and the β-carbonyl sulfones **3aa** and **3va** were obtained in somewhat lower efficiency (85% vs 74% for **3aa**; 89% vs 79% for **3va**). Pleasingly, product **3na** was isolated in a slightly better yield after a prolonged reaction time [56% (2 h) vs 68% (3 h)].

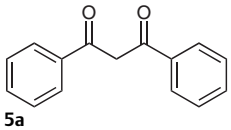
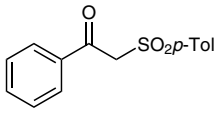
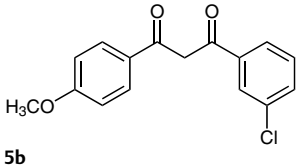
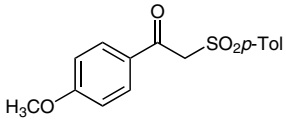
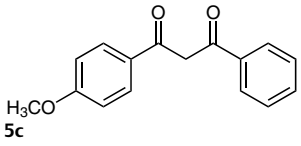
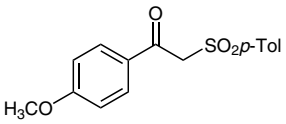
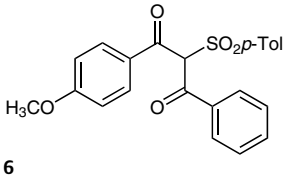
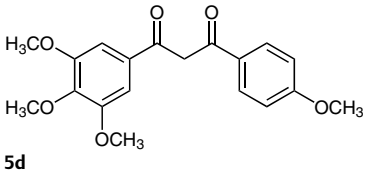
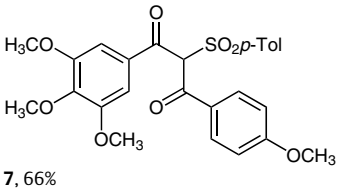
At this point, a series of control experiments was carried out in order to obtain some insights regarding the possible mechanism (Scheme 5). High-resolution mass spectrometry (HRMS) was employed as a tool for the detection and confirmation of some intermediates formed due to their instability (see the Supporting Information for mass



Scheme 3 The scope of sodium sulfinates. *Reaction conditions*: **1a** (0.5 mmol), **2** (3 equiv), IBX (2 equiv), I_2 (0.25 equiv), EtOAc (3 mL), open air, 2 h. Yields are those of isolated products after column chromatography (SiO_2).

Table 3 Reactions of 1,3-Diarylpropane-1,3-diones **5** with Sodium *p*-Toluenesulfinate (**2a**)[a]

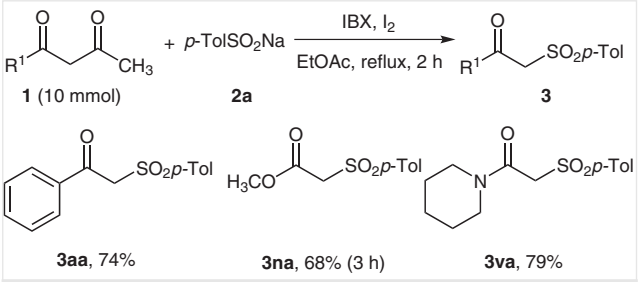


Entry	Substrate	Product[b]
1	 **5a**	 **3aa**, 61%
2	 **5b**	 **3ea**, 63%
3	 **5c**	 **3ea**  **6** inseparable mixture (60%, **3ea**/**6** = 1:3)
4	 **5d**	 **7**, 66%

[a] Reaction conditions: **5** (0.5 mmol), **2a** (3 equiv), IBX (2 equiv), I_2 (0.25 equiv), EtOAc (3 mL), open air, 6 h.
[b] Yields are those of isolated compounds after column chromatography (SiO_2).

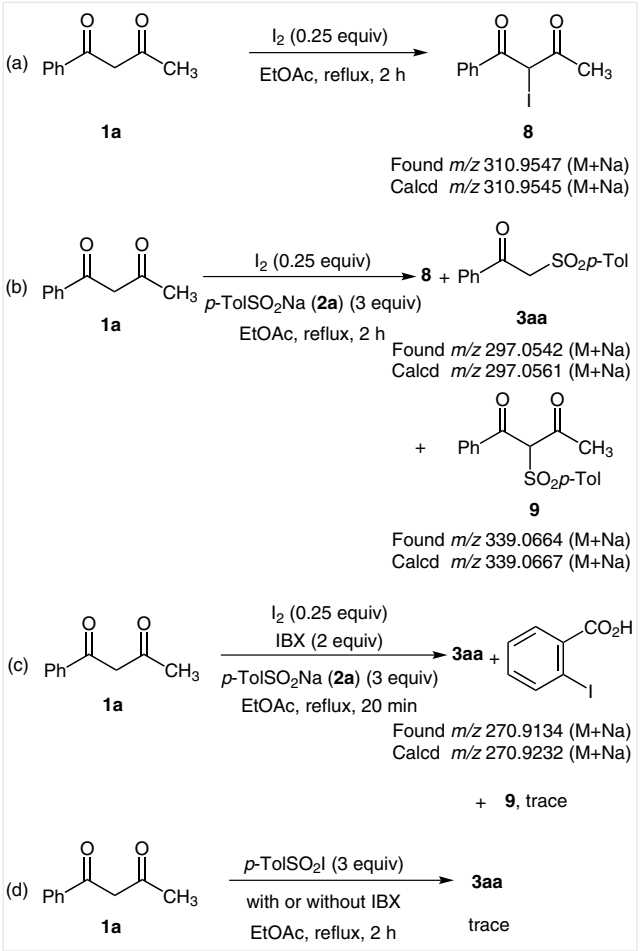
spectra). Primarily, when benzoylacetone (**1a**) was treated with molecular iodine (0.25 equiv) in EtOAc at 80 °C for two hours, the α-iodinated adduct **8** was detected by TLC and HRMS analysis (see the Supporting Information for the mass spectrum) (Scheme 5, a). Without aqueous work-up, the solvent was removed followed by chromatographic purification. The α-iodinated adduct **8** was isolated in 7% yield and **1a** was recovered in 88% yield. Next, the reaction of **1a** with **2a** was performed in the absence of IBX under the standard conditions and the reaction solution was taken for HRMS analysis after two hours (Scheme 5, b). The mass spectrum indicated the presence of **8**, **3aa** and **9** (see the Supporting Information for the mass spectrum). After solvent removal followed by chromatographic purification, **3aa** was isolated in 10% yield (see also Table 2, entry 11), while compounds **8** and **9** could not be isolated. In the conventional reaction of **1a** with **2a**, when the reaction solution was taken for HRMS analysis after 20 minutes, **3aa** was detected as a major component along with *o*-iodobenzoic acid, while compound **9** was hardly observed (Scheme 5, c) (see the Supporting Information for the mass spectrum). Since sulfonyl iodide was also possibly formed from sodium sulfinate under the present reaction conditions,[27b] the reaction of **1a** with *p*-toluenesulfonyl iodide (*p*-TolSO_2I) was evaluated (Scheme 5, d). It was found that **3aa** was detected in trace amount (TLC analysis) indicating that sulfonyl iodide was not an intermediate in this reaction.

On the basis of optimization of the reaction conditions (Table 2), the results of the control experiments (Scheme 5) and the previously reported literature,[26] we postulate two possible reaction mechanisms for the deacylative sulfonylation of 1,3-dicarbonyl compounds as depicted in Scheme 6. In the presence of I_2, iodination of 1,3-dicarbonyl compound **1** proceeds to form intermediate **A** followed by nucleophilic attack of sulfinate **2** to give β-dicarbonyl sulfone **B**. Subsequently, deacylation takes place following the attack of the nucleophilic species, possibly as the by-products derived from IBX or sodium sulfinate, to form the intermediate **C**, which then eliminates $NuCOCH_3$ followed by protonation to afford the final β-carbonyl sulfone **3** (Route A). Unfortunately, we were unable to isolate or determine the nature of any adducts derived from the deacylation process. Alternatively, due to the enhanced acidity of the methine proton of the dicarbonyl sulfone **B**, it is believed that **B′** could exist as a major tautomer which then undergoes iodination to produce fully substituted intermediate **D** (Route B). The intermediate **D** is highly susceptible to nucleophilic attack. Thus, deacylation leads to intermediate **E** followed by deiodination to afford the β-carbonyl sulfone **3**. Finally, the iodide ion generated in the reaction could be reoxidized by IBX or IBA leading to I_2 to resume the catalytic cycle.



Scheme 4 Gram-scale reactions

In summary, we have described a facile protocol for the formation of β-carbonyl sulfones through an IBX–I_2-mediated deacylative sulfonylation reaction of 1,3-dicarbonyl compounds with sodium sulfinates. The present procedure offers experimental simplicity as a one-pot reaction and is an important alternative to the existing methods for the synthesis of β-carbonyl sulfones.

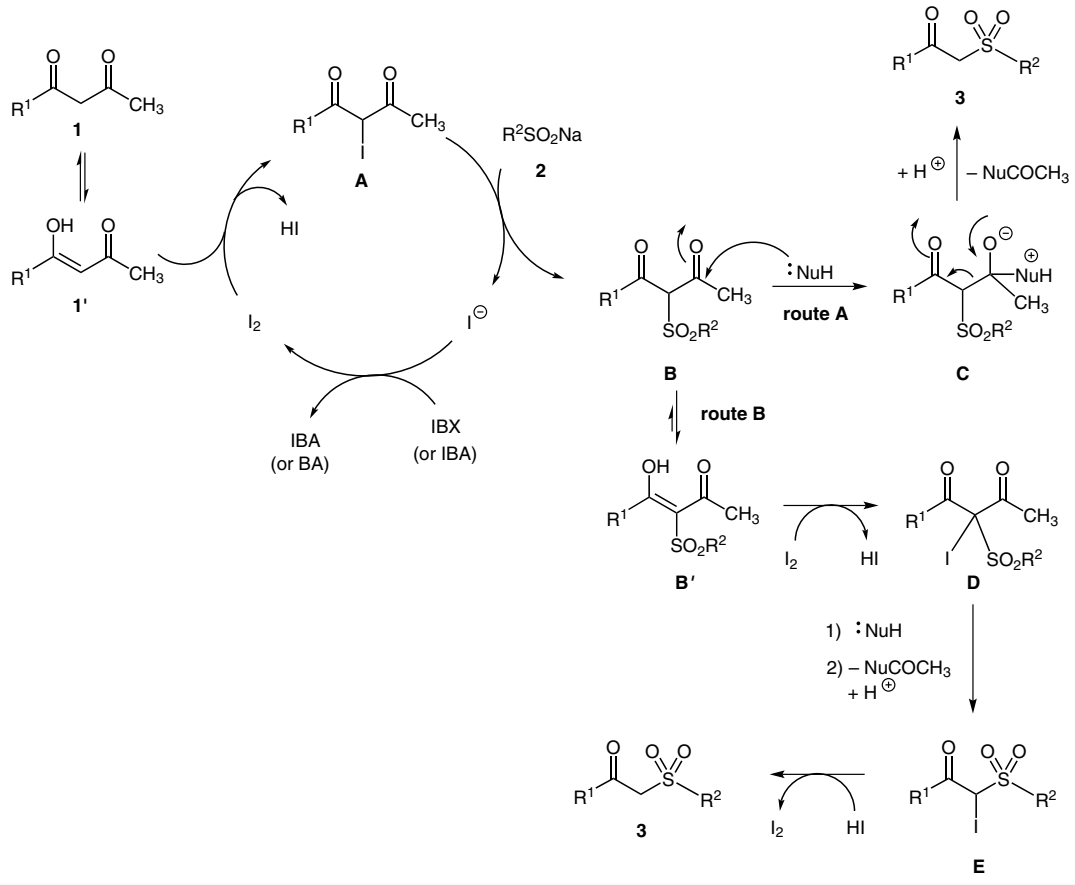


Scheme 5 Control experiments for mechanistic studies

1,3-Diketone compounds [**1a**,**m**,**n**,**p**–**s**,**z**, **5a**] and solvents were obtained from commercial sources and were used without further purification. Unless otherwise noted, 1,3-diketone derivatives (**1b**–**l**, **5b**–**d**), β-keto ester **1o** and β-keto amides **1t**–**y** were synthesized according to literature procedures.[29] Purification of the reaction products was carried out by column chromatography on Merck silica gel 60 (0.063–0.200 mm). After column chromatography, analytically pure solids were obtained by crystallization from CH_2Cl_2–hexanes. All isolated compounds were characterized on the basis of IR, ^1H NMR and ^{13}C NMR spectroscopy, and HRMS data. Reactions were monitored by thin-layer chromatography on Merck aluminium-backed silica gel 60 F_{254} TLC sheets, and samples were made visual under UV and with a solution of $KMnO_4$. Melting points were recorded with a Sanyo Gallenkamp apparatus. Infrared spectra were recorded on a Bruker ALPHA FT-IR spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker Ascend™ spectrometer and the chemical shifts are reported in ppm using tetramethylsilane (TMS) or residual non-deuterated solvent peaks as internal standards. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF spectrometer in ESI mode.

β-Keto Sulfones 3; General Procedure

Iodine (31.8 mg, 0.125 mmol) was added to a suspension of 1,3-dicarbonyl compound **1** or **5** (0.5 mmol), sodium sulfinate **2** (1.5 mmol) and *o*-iodoxybenzoic acid (IBX) (1.0 mmol) in EtOAc (3 mL), and the reaction mixture was stirred at reflux temperature for 2 h (6 h in the case of 1,3-diarylpropane-1,3-diones). After cooling to r.t., the reaction mixture was quenched by the addition of sat. aq $Na_2S_2O_3$ (5 mL) and sat. aq $NaHCO_3$ (5 mL). Further stirring was followed by extraction with EtOAc (2 × 20 mL). The combined organic extracts were washed with H_2O (20 mL) and brine (20 mL), dried over $MgSO_4$, fil-



Scheme 6 Possible reaction mechanisms

tered, and concentrated (aspirator). The residue was purified by column chromatography (EtOAc/hexanes) to afford the corresponding product.

1-Phenyl-2-(*p*-tosyl)ethanone (3aa)[15i]

Prepared from benzoylacetone (**1a**) (81.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol); yield: 116.5 mg (85%).

Prepared from 1,3-diphenylpropane-1,3-dione (**5a**) (112.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol); yield: 83.7 mg (61%).

White solid; mp 104.5–106.0 °C (Lit.[15i] 106.1–108.0 °C); R_f = 0.48 (40% EtOAc in hexanes).

IR (neat): 1676 (C=O), 1318, 1147 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.90 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.3 Hz, 2 H), 7.57 (t, *J* = 7.4 Hz, 1 H), 7.43 (t, *J* = 7.9 Hz, 2 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 4.70 (s, 2 H), 2.39 (s, 3 H).

1-(*m*-Tolyl)-2-(*p*-tosyl)ethanone (3ba)

Prepared from 1-(*m*-tolyl)butane-1,3-dione (**1b**) (88.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Pale yellow solid; yield: 112.3 mg (78%); mp 91.0–92.5 °C; R_f = 0.54 (40% EtOAc in hexanes).

IR (neat): 1669 (C=O), 1317, 1148 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73–7.66 (m, 4 H), 7.37–7.26 (m, 4 H), 4.68 (s, 2 H), 2.38 (s, 3 H), 2.33 (s, 3 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 188.2 (C), 145.1 (C), 138.5 (C), 135.7 (C), 135.6 (C), 134.9 (CH), 129.6 (2 × CH), 129.5 (CH), 128.5 (CH), 128.4 (2 × CH), 126.4 (CH), 63.3 (CH$_2$), 21.5 (CH$_3$), 21.1 (CH$_3$).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for C$_{16}$H$_{16}$O$_3$SNa: 311.0718; found: 311.0720.

1-[4-(*tert*-Butyl)phenyl]-2-(*p*-tosyl)ethanone (3ca)

Prepared from 1-[4-(*tert*-butyl)phenyl]butane-1,3-dione (**1c**) (109.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Yellow solid; yield: 115.5 mg (70%); mp 93.5–95.0 °C; R_f = 0.63 (40% EtOAc in hexanes).

IR (neat): 1679 (C=O), 1300, 1140 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.86 (d, *J* = 8.5 Hz, 2 H), 7.74 (d, *J* = 8.3 Hz, 2 H), 7.46 (d, *J* = 8.5 Hz, 2 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 4.67 (s, 2 H), 2.42 (s, 3 H), 1.31 (s, 9 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 187.6 (C), 158.3 (C), 145.2 (C), 135.8 (C), 133.2 (C), 129.8 (2 × CH), 129.3 (2 × CH), 128.6 (2 × CH), 125.8 (2 × CH), 63.5 (CH$_2$), 35.3 (C), 31.0 (3 × CH$_3$), 21.7 (CH$_3$).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{19}H_{22}O_3SNa$: 353.1187; found: 353.1183.

1-(3-Methoxyphenyl)-2-(*p*-tosyl)ethanone (3da)[22a]

Prepared from 1-(3-methoxyphenyl)butane-1,3-dione (**1d**) (96.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Colorless solid; yield: 107.9 mg (71%); mp 92.0–93.0 °C; R_f = 0.45 (40% EtOAc in hexanes).

IR (neat): 1672 (C=O), 1316, 1147 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.47 (d, *J* = 7.7 Hz, 1 H), 7.39 (t, *J* = 1.8 Hz, 1 H), 7.35–7.28 (m, 3 H), 7.11 (dd, *J* = 8.2, 2.6 Hz, 1 H), 4.69 (s, 2 H), 3.78 (s, 3 H), 2.39 (s, 3 H).

1-(4-Methoxyphenyl)-2-(*p*-tosyl)ethanone (3ea)[15i]

Prepared from 1-(4-methoxyphenyl)butane-1,3-dione (**1e**) (96.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol); yield: 117.0 mg (77%).

Prepared from 1-(3-chlorophenyl)-3-(4-methoxyphenyl)propane-1,3-dione (**5b**) (144.4 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol); yield: 95.8 mg (63%).

White solid; mp 122.0–123.0 °C (Lit.[15i] 124.0–124.8 °C); R_f = 0.35 (40% EtOAc in hexanes).

IR (neat): 1665 (C=O), 1318, 1149 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.88 (d, *J* = 8.9 Hz, 2 H), 7.71 (d, *J* = 8.3 Hz, 2 H), 7.27 (d, *J* = 8.1 Hz, 2 H), 6.88 (d, *J* = 8.9 Hz, 2 H), 4.64 (s, 2 H), 3.81 (s, 3 H), 2.38 (s, 3 H).

1-(3,5-Dimethoxyphenyl)-2-(*p*-tosyl)ethanone (3fa)

Prepared from 1-(3,5-dimethoxyphenyl)butane-1,3-dione (**1f**) (111.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Colorless solid; yield: 125.3 mg (75%); mp 148.5–149.5 °C; R_f = 0.41 (40% EtOAc in hexanes).

IR (neat): 1673 (C=O), 1318, 1147 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.74 (d, *J* = 8.3 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 7.00 (d, *J* = 2.3 Hz, 2 H), 6.64 (t, *J* = 2.3 Hz, 1 H), 4.66 (s, 2 H), 3.77 (s, 6 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 187.8 (C), 160.8 (2 × C), 145.2 (C), 137.5 (C), 135.7 (C), 129.7 (2 × CH), 128.5 (2 × CH), 106.8 (2 × CH), 106.7 (CH), 63.5 (CH$_2$), 55.5 (2 × CH$_3$), 21.6 (CH$_3$).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{17}H_{18}O_5SNa$: 357.0773; found: 357.0775.

1-(2-Chlorophenyl)-2-(*p*-tosyl)ethanone (3ga)[15i]

Prepared from 1-(2-chlorophenyl)butane-1,3-dione (**1g**) (98.3 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Pale yellow solid; yield: 78.5 mg (51%); mp 90.5–92.0 °C (Lit.[15i] 96.0–97.0 °C); R_f = 0.48 (40% EtOAc in hexanes).

IR (neat): 1695 (C=O), 1307, 1139 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.51 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.42–7.28 (m, 5 H), 4.49 (s, 2 H), 2.40 (s, 3 H).

1-(3-Chlorophenyl)-2-(*p*-tosyl)ethanone (3ha)[15i]

Prepared from 1-(3-chlorophenyl)butane-1,3-dione (**1h**) (98.3 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Pale yellow solid; yield: 89.3 mg (58%); mp 120.0–121.0 °C (Lit.[15i] 123.8–125.5 °C); R_f = 0.50 (40% EtOAc in hexanes).

IR (neat): 1679 (C=O), 1314, 1146 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.81–7.78 (m, 2 H), 7.71 (d, *J* = 8.3 Hz, 2 H), 7.54–7.51 (m, 1 H), 7.38 (t, *J* = 8.2 Hz, 1 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 4.67 (s, 2 H), 2.41 (s, 3 H).

1-(4-Chlorophenyl)-2-(*p*-tosyl)ethanone (3ia)[15i]

Prepared from 1-(4-chlorophenyl)butane-1,3-dione (**1i**) (98.3 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Pale yellow solid; yield: 110.9 mg (72%); mp 131.0–132.5 °C (Lit.[15i] 135.7–136.5 °C); R_f = 0.54 (40% EtOAc in hexanes).

IR (neat): 1677 (C=O), 1313, 1145 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.85 (d, *J* = 8.7 Hz, 2 H), 7.70 (d, *J* = 8.3 Hz, 2 H), 7.39 (d, *J* = 8.7 Hz, 2 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 4.67 (s, 2 H), 2.39 (s, 3 H).

1-(3-Nitrophenyl)-2-(*p*-tosyl)ethanone (3ja)[15i]

Prepared from 1-(3-nitrophenyl)butane-1,3-dione (**1j**) (103.6 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Pale yellow solid; yield: 70.2 mg (44%); mp 126.0–127.0 °C (Lit.[15i] 128.0–128.7 °C); R_f = 0.34 (40% EtOAc in hexanes).

IR (neat): 1685 (C=O), 1146 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.68 (t, *J* = 1.9 Hz, 1 H), 8.42 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1 H), 8.30 (dt, *J* = 7.6, 1.2 Hz, 1 H), 7.72–7.67 (m, 3 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.77 (s, 2 H), 2.41 (s, 3 H).

1-(Furan-2-yl)-2-(*p*-tosyl)ethanone (3ka)[26c]

Prepared from 1-(furan-2-yl)butane-1,3-dione (**1k**) (76.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Yellow solid; yield: 77.9 mg (59%); mp 124.5–125.5 °C; R_f = 0.30 (40% EtOAc in hexanes).

IR (neat): 1645 (C=O), 1313, 1152 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.71 (d, *J* = 8.3 Hz, 2 H), 7.55 (t, *J* = 1.0 Hz, 1 H), 7.29–7.27 (m, 3 H), 6.52 (dd, *J* = 3.7, 1.7 Hz, 1 H), 4.53 (s, 2 H), 2.37 (s, 3 H).

1-(*p*-Tosyl)propan-2-one (3ma)[26b]

Prepared from acetylacetone (**1m**) (50.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Colorless oil; yield: 40.3 mg (38%); R_f = 0.38 (40% EtOAc in hexanes).

IR (neat): 1715 (C=O), 1317, 1146 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 4.11 (s, 2 H), 2.42 (s, 3 H), 2.37 (s, 3 H).

Methyl 2-(*p*-Tosyl)acetate (3na)[26c]

Prepared from methyl acetoacetate (**1n**) (58.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Colorless oil; yield: 63.8 mg (56%); R_f = 0.38 (40% EtOAc in hexanes).

IR (neat): 1739 (C=O ester), 1146 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.77 (d, *J* = 8.3 Hz, 2 H), 7.33 (d, *J* = 8.1 Hz, 2 H), 4.07 (s, 2 H), 3.66 (s, 3 H), 2.41 (s, 3 H).

Ethyl 2-(*p*-Tosyl)acetate (3oa)[26c]

Prepared from ethyl acetoacetate (**1o**) (65.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Colorless oil; yield: 73.2 mg (60%); R_f = 0.30 (25% EtOAc in hexanes).

IR (neat): 1735 (C=O ester), 1323, 1146 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 8.3 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 4.08 (s, 2 H), 2.45 (s, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H).

tert-Butyl 2-(*p*-Tosyl)acetate (3pa)[26c]

Prepared from *tert*-butyl acetoacetate (**1p**) (79.1 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

Colorless oil; yield: 54.0 mg (40%); R_f = 0.56 (40% EtOAc in hexanes).

IR (neat): 1729 (C=O ester), 1324, 1141 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 3.98 (s, 2 H), 2.42 (s, 3 H), 1.34 (s, 9 H).

Benzyl 2-(*p*-Tosyl)acetate (3qa)[30a]

Prepared from benzyl acetoacetate (**1q**) (96.1 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

Pale yellow oil; yield: 53.2 mg (35%); R_f = 0.50 (40% EtOAc in hexanes).

IR (neat): 1736 (C=O ester), 1324, 1145 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.3 Hz, 2 H), 7.36–7.33 (m, 3 H), 7.29–7.25 (m, 4 H), 5.11 (s, 2 H), 4.13 (s, 2 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.3 (C), 145.3 (C), 135.5 (C), 134.4 (C), 129.8 (2 × CH), 128.61 (CH), 128.57 (2 × CH), 128.53 (2 × CH), 128.47 (2 × CH), 67.9 (CH_2), 61.0 (CH_2), 21.7 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{16}O_4SNa$: 327.0667; found: 327.0673.

3-(*p*-Tosyl)dihydrofuran-2(3*H*)-one (3ra)[26c]

Prepared from 2-acetylbutyrolactone (**1r**) (64.1 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

White solid; yield: 102.5 mg (85%); mp 76.0–78.0 °C; R_f = 0.23 (40% EtOAc in hexanes).

IR (neat): 1761 (C=O ester), 1315, 1142 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.1 Hz, 2 H), 4.40–4.28 (m, 2 H), 4.04 (dd, *J* = 10.0, 4.7 Hz, 1 H), 2.91–2.85 (m, 1 H), 2.72–2.64 (m, 1 H), 2.42 (s, 3 H).

***N*-Phenyl-2-(*p*-tosyl)acetamide (3sa)**[26c]

Prepared from 3-oxo-*N*-phenylbutanamide (**1s**) (88.6 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

White solid; yield: 82.4 mg (57%); mp 164.0–166.0 °C; R_f = 0.33 (40% EtOAc in hexanes).

IR (neat): 3326 (N–H), 1665 (C=O amide), 1314, 1150 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.54 (br s, 1 H), 7.78 (d, *J* = 8.3 Hz, 2 H), 7.48 (d, *J* = 8.7 Hz, 2 H), 7.35–7.30 (m, 4 H), 7.14 (t, *J* = 7.4 Hz, 1 H), 4.14 (s, 2 H), 2.42 (s, 3 H).

***N*-Methyl-*N*-phenyl-2-(*p*-tosyl)acetamide (3ta)**

Prepared from *N*-methyl-3-oxo-*N*-phenylbutanamide (**1t**) (95.6 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

White solid; yield: 121.2 mg (80%); mp 106.0–108.0 °C; R_f = 0.31 (50% EtOAc in hexanes).

IR (neat): 1660 (C=O amide), 1301, 1142 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.3 Hz, 2 H), 7.44–7.35 (m, 3 H), 7.33 (d, *J* = 8.3 Hz, 2 H), 7.18 (d, *J* = 7.3 Hz, 2 H), 3.96 (s, 2 H), 3.24 (s, 3 H), 2.43 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 161.4 (C), 144.9 (C), 142.6 (C), 136.5 (C), 130.1 (2 × CH), 129.5 (2 × CH), 128.6 (2 × CH), 128.5 (CH), 127.4 (2 × CH), 59.0 (CH_2), 37.6 (CH_3), 21.6 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{18}NO_3S$: 304.1007; found: 304.1008.

***N*,*N*-Diethyl-2-(*p*-tosyl)acetamide (3ua)**[26c]

Prepared from *N*,*N*-dimethyl-3-oxobutanamide (**1u**) (64.6 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

White solid; yield: 116.4 mg (84%); mp 84.0–85.0 °C (Lit.[26c] 87.0–88.0 °C); R_f = 0.59 (100% EtOAc).

IR (neat): 1641 (C=O amide), 1317, 1148 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.3 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 4.19 (s, 2 H), 3.48 (q, *J* = 7.2 Hz, 2 H), 3.34 (q, *J* = 7.1 Hz, 2 H), 2.44 (s, 3 H), 1.21 (t, *J* = 7.2 Hz, 3 H), 1.10 (t, *J* = 7.1 Hz, 3 H).

1-(Piperidin-1-yl)-2-(*p*-tosyl)ethan-1-one (3va)[30b]

Prepared from 1-(piperidin-1-yl)butane-1,3-dione (**1v**) (84.6 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

White solid; yield: 127.6 mg (89%); mp 117.0–119.0 °C; R_f = 0.56 (100% EtOAc).

IR (neat): 1639 (C=O amide), 1313, 1143 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.3 Hz, 2 H), 7.34 (d, *J* = 8.0 Hz, 2 H), 4.22 (s, 2 H), 3.55–3.49 (m, 4 H), 2.42 (s, 3 H), 1.70–1.60 (m, 4 H), 1.55–1.50 (m, 2 H).

1-Morpholino-2-(*p*-tosyl)ethan-1-one (3wa)[30c]

Prepared from 1-morpholinobutane-1,3-dione (**1w**) (85.6 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

White solid; yield: 121.8 mg (86%); mp 163.0–164.0 °C; R_f = 0.41 (100% EtOAc).

IR (neat): 1643 (C=O amide), 1308, 1145 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.2 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 4.21 (s, 2 H), 3.77 (t, *J* = 4.4 Hz, 2 H), 3.67 (t, *J* = 4.4 Hz, 2 H), 3.63 (t, *J* = 4.4 Hz, 2 H), 3.59 (t, *J* = 4.4 Hz, 2 H), 2.44 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.9 (C), 145.5 (C), 135.6 (C), 129.9 (2 × CH), 128.3 (2 × CH), 66.6 (CH_2), 66.5 (CH_2), 59.6 (CH_2), 47.5 (CH_2), 42.6 (CH_2), 21.7 (CH_3).

HRMS (ESI-TOF): *m*/*z* [M + H]$^+$ calcd for $C_{13}H_{18}NO_4S$: 284.0957; found: 284.0959.

1-Methyl-3-(*p*-tosyl)pyrrolidin-2-one (3xa)[30d]

Prepared from 3-acetyl-1-methylpyrrolidin-2-one (**1x**) (70.6 mg, 0.5 mmol) and *p*-$TolSO_2Na$ (**2a**) (267.3 mg, 1.50 mmol).

Yellow solid; yield: 105.8 mg (84%); mp 108.0–109.0 °C; R_f = 0.33 (100% EtOAc).

IR (neat): 1687 (C=O lactam), 1301, 1141 (–SO_2–) cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.3 Hz, 2 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 3.89 (dd, *J* = 10.0, 4.2 Hz, 1 H), 3.39–3.32 (m, 1 H), 3.25 (td, *J* = 9.1, 3.4 Hz, 1 H), 2.76 (s, 3 H), 2.70–2.61 (m, 1 H), 2.46–2.35 (m, 1 H), 2.39 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3 (C), 145.0 (C), 134.4 (C), 129.4 (2 × CH), 129.0 (2 × CH), 65.6 (CH), 46.9 (CH_2), 29.9 (CH_3), 21.5 (CH_3), 19.6 (CH_2).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{12}H_{15}NO_3SNa$: 276.0670; found: 276.0679.

1-[2-(*p*-Tosyl)acetyl]pyrrolidin-2-one (3ya)[30e]

Prepared from 1-(2-oxopyrrolidin-1-yl)butane-1,3-dione (**1y**) (84.6 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Yellow solid; yield: 109.7 mg (78%); mp 78.0–80.0 °C; R_f = 0.19 (50% EtOAc in hexanes).

IR (neat): 1737 and 1687 (C=O lactam), 1315, 1136 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.78 (d, *J* = 8.2 Hz, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 4.88 (s, 2 H), 3.75 (t, *J* = 7.2 Hz, 2 H), 2.52 (t, *J* = 8.0 Hz, 2 H), 2.41 (s, 3 H), 1.97 (quin, *J* = 7.9 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 175.3 (C), 161.6 (C), 145.0 (C), 136.3 (C), 129.6 (2 × CH), 128.4 (2 × CH), 60.6 (CH$_2$), 45.5 (CH$_2$), 33.0 (CH$_2$), 21.5 (CH$_3$), 16.6 (CH$_2$).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{15}NO_4SNa$: 304.0619; found: 304.0622.

3-Hydroxy-2-(*p*-tosyl)cyclohex-2-en-1-one (4)

Prepared from cyclohexane-1,3-dione (**1z**) (56.1 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

Yellow solid; yield: 73.2 mg (55%); mp 145.0–147.0 °C; R_f = 0.19 (10% MeOH in EtOAc).

IR (neat): 1668 (C=O), 1114 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 12.46 (br s, 1 H), 7.91 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 2.67 (t, *J* = 6.0 Hz, 2 H), 2.42 (s, 3 H), 2.35 (t, *J* = 6.4 Hz, 2 H), 1.95 (quin, *J* = 6.4 Hz, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 191.4 (C), 183.5 (C), 144.8 (C), 137.6 (C), 129.3 (2 × CH), 128.4 (2 × CH), 114.0 (C), 37.3 (CH$_2$), 31.1 (CH$_2$), 21.6 (CH$_3$), 19.1 (CH$_2$).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{13}H_{14}O_4SNa$: 289.0510; found: 289.0511.

1-Phenyl-2-(phenylsulfonyl)ethanone (3ab)[26b]

Prepared from benzoylacetone (**1a**) (81.1 mg, 0.5 mmol) and PhSO$_2$Na (**2b**) (246.2 mg, 1.50 mmol).

Pale yellow solid; yield: 91.0 mg (70%); mp 88.0–89.0 °C (Lit.[26b] 90–92 °C); R_f = 0.48 (40% EtOAc in hexanes).

IR (neat): 1672 (C=O), 1307, 1153 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.90–7.85 (m, 4 H), 7.63–7.55 (m, 2 H), 7.50 (t, *J* = 7.6 Hz, 2 H), 7.43 (t, *J* = 7.7 Hz, 2 H), 4.73 (s, 2 H).

2-[(4-Chlorophenyl)sulfonyl]-1-phenylethanone (3ac)[22a]

Prepared from benzoylacetone (**1a**) (81.1 mg, 0.5 mmol) and 4-ClC$_6$H$_4$SO$_2$Na (**2c**) (297.9 mg, 1.50 mmol).

Yellow solid; yield: 107.3 mg (73%); mp 126.0–128.0 °C (Lit.[22a] 135–136 °C); R_f = 0.54 (40% EtOAc in hexanes).

IR (neat): 1686 (C=O), 1305, 1140 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.89 (d, *J* = 8.5 Hz, 2 H), 7.80 (d, *J* = 8.7 Hz, 2 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.49–7.43 (m, 4 H), 4.74 (s, 2 H).

2-[(4-Methoxyphenyl)sulfonyl]-1-phenylethanone (3ad)[22a]

Prepared from benzoylacetone (**1a**) (81.1 mg, 0.5 mmol) and 4-CH$_3$OC$_6$H$_4$SO$_2$Na (**2d**) (291.3 mg, 1.50 mmol).

Yellow solid; yield: 87.0 mg (60%); mp 99.0–101.0 °C (Lit.[22a] 93–94 °C); R_f = 0.35 (40% EtOAc in hexanes).

IR (neat): 1674 (C=O), 1143 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.92 (d, *J* = 8.2 Hz, 2 H), 7.78 (d, *J* = 9.0 Hz, 2 H), 7.59 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.4 Hz, 2 H), 6.96 (d, *J* = 9.0 Hz, 2 H), 4.70 (s, 2 H), 3.85 (s, 3 H).

2-[(4-Nitrophenyl)sulfonyl]-1-phenylethanone (3ae)

Prepared from benzoylacetone (**1a**) (81.1 mg, 0.5 mmol) and 4-O$_2$NC$_6$H$_4$SO$_2$Na (**2e**) (313.7 mg, 1.50 mmol).

Pale yellow solid; yield: 56.4 mg (37%); mp 168.5–169.5 °C; R_f = 0.45 (40% EtOAc in hexanes).

IR (neat): 1672 (C=O), 1307, 1152 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.38 (d, *J* = 9.0 Hz, 2 H), 8.11 (d, *J* = 9.0 Hz, 2 H), 7.92 (d, *J* = 8.3 Hz, 2 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.9 Hz, 2 H), 4.80 (s, 2 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 187.6 (C), 151.0 (C), 144.0 (C), 135.3 (C), 134.8 (CH), 130.3 (2 × CH), 129.2 (2 × CH), 129.1 (2 × CH), 124.3 (2 × CH), 62.9 (CH$_2$).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{14}H_{11}NO_5SNa$: 328.0256; found: 328.0253.

2-(Methylsulfonyl)-1-phenylethanone (3af)[26c]

Prepared from benzoylacetone (**1a**) (81.1 mg, 0.5 mmol) and CH$_3$SO$_2$Na (**2f**) (153.2 mg, 1.50 mmol).

Pale yellow solid; yield: 45.5 mg (46%); mp 98.5–100.0 °C; R_f = 0.29 (40% EtOAc in hexanes).

IR (neat): 1674 (C=O), 1297, 1151 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.97 (d, *J* = 8.6 Hz, 2 H), 7.63 (t, *J* = 7.4 Hz, 1 H), 7.50 (t, *J* = 7.4 Hz, 2 H), 4.59 (s, 2 H), 3.12 (s, 3 H).

1-(4-Methoxyphenyl)-2-(*p*-tosyl)-3-(3,4,5-trimethoxyphenyl)propane-1,3-dione (7)

Prepared from 1-(4-methoxyphenyl)-3-(3,4,5-trimethoxyphenyl)propane-1,3-dione (**5d**) (172.2 mg, 0.5 mmol) and *p*-TolSO$_2$Na (**2a**) (267.3 mg, 1.50 mmol).

White solid; yield: 163.5 mg (66%); mp 155.5–157.5 °C; R_f = 0.34 (50% EtOAc in hexanes).

IR (neat): 1693, 1655 (C=O), 1322, 1146 (–SO$_2$–) cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.06 (d, *J* = 8.8 Hz, 2 H), 7.89 (d, *J* = 8.4 Hz, 2 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.15 (s, 2 H), 7.13 (s, 1 H), 6.93 (d, *J* = 9.2 Hz, 2 H), 3.87 (s, 3 H), 3.83 (s, 3 H), 3.70 (s, 6 H), 2.40 (s, 3 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 185.3 (C), 184.6 (C), 164.4 (C), 152.8 (2 × C), 145.3 (C), 143.2 (C), 134.3 (C), 131.8 (2 × CH), 130.4 (2 × CH), 129.8 (C), 128.9 (2 × CH), 128.1 (C), 114.1 (2 × CH), 106.2 (2 × CH), 77.3 (CH), 60.6 (CH$_3$), 55.8 (2 × CH$_3$), 55.4 (CH$_3$), 21.4 (CH$_3$).

HRMS (ESI-TOF): *m*/*z* [M + Na]$^+$ calcd for $C_{26}H_{26}O_8SNa$: 521.1246; found: 521.1240.

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