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Oxidative Rearrangement via 1,2-Aryl Migration using Hydroxy-(tosyloxy)iodobenzene in a Polar Aprotic Solvent

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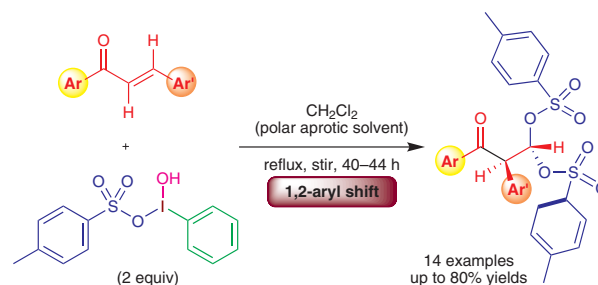
14 examples
up to 80% yields

Abstract A series of geminal β,β-ditosyloxy ketones were synthesized in moderate to good yields through hydroxy(tosyloxy)iodobenzene-mediated ditosyloxylation of readily accessible α,β-unsaturated ketones in a polar aprotic solvent. A mechanism has been proposed for the synthesis of the geminal β,β-ditosyloxy ketones, and entails an oxidative rearrangement involving a 1,2-aryl migration.
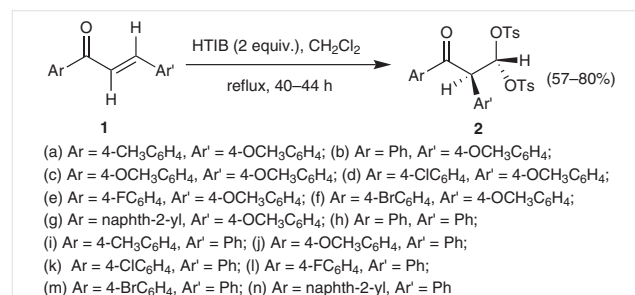
The intriguing role of hypervalent iodine reagents in synthetic transformations has amazed organic chemists over the years.[1–5] Beside their highly selective oxidizing properties, hypervalent iodine reagents are also associated with inherent low toxicity, an environmentally benign character, high stability, and mild reaction conditions, which make them good or superior alternatives to toxic transition-metal-based oxidants.[6,7] Hypervalent iodine moieties, as hypernucleofuges, exhibit an electrophilic character and generate cationic intermediates.[8,9] This permits their use as versatile reagents for many organic transformations, including oxidative functionalization, cyclization, dearomatization, fragmentation, atom-transfer, and coupling reactions, as well as rearrangements through ring contractions, ring expansions, or aryl migrations, etc.[10–22]

Oxidative 1,2-aryl migration reactions form a unique class of organic transformations that are used extensively in synthetic chemistry. Many elegant studies mediated by 1,2-aryl migration reactions or by combinations of these with other transformations have been established as alternative methods for accessing compounds whose synthesis would otherwise be quite complex and which are not otherwise easily accessible. Examples of such transformations include stereocontrolled total syntheses of numerous natural products,[23–25] various heterocycles,[26–29] intricate carbocycles,[30–31] and drugs.[32–35] The attractive and exceptional features of 1,2-aryl migration reactions continually inspire synthetic chemists to utilize the synthetic potential of these reaction in generating structurally complex entities from such precursors as unsaturated carbonyl compounds. Unsaturated carbonyl compounds are readily accessible through aldol condensations between aryl methyl ketones and aryl aldehydes. Numerous elegant studies on carbonyl compounds make these entities the most exploited building blocks in synthetic chemistry.

The synthetic utility of hypervalent iodine moieties in the oxidation of α,β-unsaturated carbonyl compounds has been well investigated and remains a promising area of research.[36] Hypervalent iodine reagents, when treated with α,β-unsaturated carbonyl compounds, serve as electrophiles Ph(L)I[+] and generate phenyliodinated intermediates that are available for further nucleophilic attack and give rearranged product through 1,2-aryl migration.[37,38] Here, we describe a stereoselective oxidative 1,2-aryl migration following the reaction of an α,β-unsaturated carbonyl com-


(a) Ar = 4-CH₃C₆H₄, Ar' = 4-OCH₃C₆H₄; (b) Ar = Ph, Ar' = 4-OCH₃C₆H₄;
(c) Ar = 4-OCH₃C₆H₄, Ar' = 4-OCH₃C₆H₄; (d) Ar = 4-ClC₆H₄, Ar' = 4-OCH₃C₆H₄;
(e) Ar = 4-FC₆H₄, Ar' = 4-OCH₃C₆H₄; (f) Ar = 4-BrC₆H₄, Ar' = 4-OCH₃C₆H₄;
(g) Ar = naphth-2-yl, Ar' = 4-OCH₃C₆H₄; (h) Ar = Ph, Ar' = Ph;
(i) Ar = 4-CH₃C₆H₄, Ar' = Ph; (j) Ar = 4-OCH₃C₆H₄, Ar' = Ph;
(k) Ar = 4-ClC₆H₄, Ar' = Ph; (l) Ar = 4-FC₆H₄, Ar' = Ph;
(m) Ar = 4-BrC₆H₄, Ar' = Ph; (n) Ar = naphth-2-yl, Ar' = Ph

Scheme 1 Synthetic protocol for β,β-ditosyloxy ketones **2**

pound with the hypervalent iodine reagent hydroxy(tosy-loxy)iodobenzene (HTIB) in an aprotic polar solvent (di-chloromethane) to give novel *gem*-β,β-ditosyloxy ketones.

Initially, we synthesized the *gem*-β,β-ditosyloxy ketone **2a** by treatment of (2*E*)-3-(4-methoxyphenyl)-1-(4-meth-ylphenyl)prop-2-en-1-one (**1a**) with two equivalents of HTIB by following the synthetic protocol shown in Scheme 1.[39]

The structure of product **2a** was confirmed by studying its spectral data (IR, ^{1}H, ^{13}C, HMBC 2D NMR). The IR spectrum of compound **2a** exhibited a characteristic absorption band at about 1666 cm^{−1} assigned to CO stretching. The ^{1}H NMR spectrum of compound **2a** showed characteristic doublets assigned to vicinal protons in the ranges δ = 4.95–4.97 and 6.95–6.98 ppm. Four singlets also appeared in the spectrum. The one corresponding to the three protons of the methoxy group in the *para*-position of the aryl group appeared at δ = 3.72 ppm, and the others, assigned to the three methyl groups (one substituent of the aryl group and two substituents of the tosyl group), appeared at δ = 2.31, 2.39, and 2.40 ppm. All aromatic protons resonated in the expected region δ = 6.62–7.78 ppm with similar values and patterns. The structure of compound **2a** was also analyzed by ^{13}C NMR spectroscopy, which showed a characteristic signal for the carbonyl carbon at δ = 193.96 ppm. Two more characteristic signals, one for the carbon in the position α to the carbonyl group and the other in the β-position appeared at δ = 56.86 and 99.69 ppm, respectively. The structure of compound **2a** was confirmed by HMBC 2D NMR spectroscopy, the results of which were in good agreement with the expected values (Figure 1).
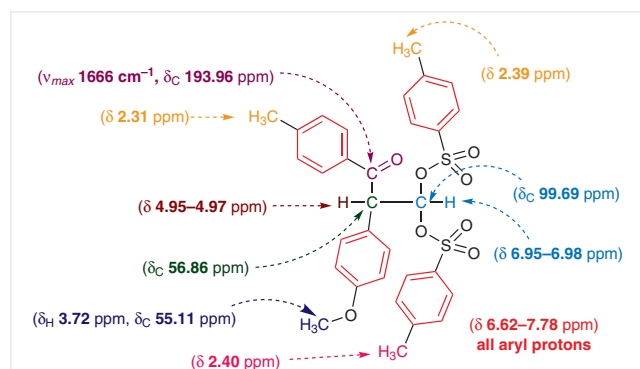

Figure 1 Overview of spectral data (^{1}H NMR, ^{13}C NMR, and IR) for 2-(4-methoxyphenyl)-3-(4-methylphenyl)-1,1-di(tosyloxy)propan-3-one (**2a**)

Single-crystal x-ray diffraction analysis of product **2a** was also carried out and further explicitly confirmed the formation of the β,β-ditosyloxy ketone in this reaction. The β,β-ditosyloxy ketone **2a** crystallized in the monoclinic *P*1 21/*c*1 space group.[40] An ORTEP diagram of **2a** is shown in Figure 2.
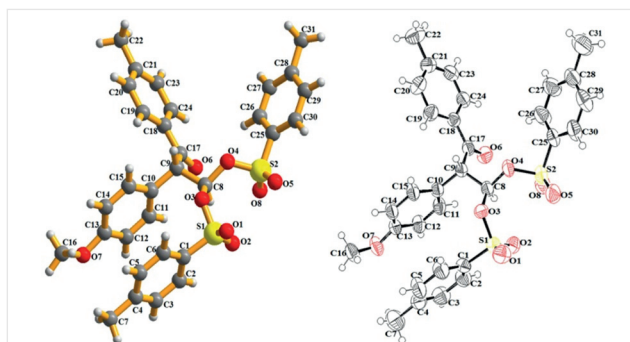
**Figure 2** Single-crystal ORTEP diagram for the β,β-ditosyloxy ketone **2a**

When the same synthetic protocol was attempted with various substituted chalcones, the reaction proceeded in a similar manner to give the corresponding β,β-ditosyloxy ketones **2b–n** (Scheme 1). However, it pertinent to mention here that Koser et al.[41] have reported an example of vicinal ditosyloxylation of the C=C double bond of α,β-unsaturated carbonyl compounds through treatment with HTIB and *syn*-addition to the double bond (Scheme 2).
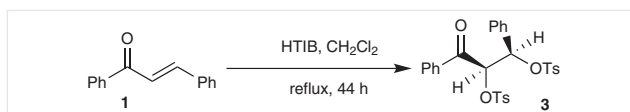
Scheme 2 Synthesis of an α,β-ditosyloxy ketone **3**

As a result, in many previous investigations, our research group assumed that the structure of the ditosyloxy ketones corresponded to that of the vicinal α,β-ditosyloxy ketone **3** (Scheme 3).[42–44]
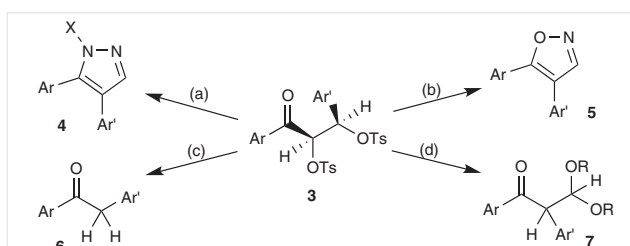
Conditions: (a) XNHNH$_2$ (where X = Ph, CONH$_2$, CSNH$_2$), DMF or EtOH;
(b) NH$_2$OH·HCl, NaOAc, EtOH, reflux;
(c) KOH (2 eq.), ROH (where R = H, Me, Et), reflux;
(d) KOH (cat. amt), MeOH, stirring, r.t.

Scheme 3 Reported syntheses of pyrazoles **4**, isoxazoles **5**, α-aryl β-keto dialkylacetals **6**, and desoxybenzoins **7**, assuming that the structure of the ditosyloxy ketone was that of the vicinal α,β-ditosyloxy ketone **3**

Reports in the literature and the results obtained from various reactions of ditosyloxy ketones performed by our research group encouraged us to study the actual mechanism of the ditosyloxylation of α,β-unsaturated ketones mediated by HTIB. As a result, we compared the physical and spectral data of the ditosyloxy ketones in powdered

and single-crystal forms. This investigation was performed to reveal the actual structure of the product formed during the reaction. The similar physical (color and melting point) and spectral data (IR, ^{1}H, ^{13}C, HMBC 2D NMR) for the powdered and crystalline forms led us to a new finding that the structure of these compounds is actually that of geminal β,β-ditosyloxy ketones rather than that of vicinal α,β-ditosyloxy ketones.

To support our experimental findings, we performed density functional theory (DFT) calculations with the *Gaussian 09* quantum-chemical package[45] to analyze the relative thermodynamic stability of both the geminal and vicinal forms of the ditosyloxy ketones, along with two conformations (*syn* and *anti*) of the vicinal ditosyloxy ketone. The various structures were optimized by using the 6-31+G(d,p) polarized split-valence basis set with diffuse functions for heavy atoms. A hybrid functional B3LYP[46] consisting of Becke's three-parameter exchange functional[47] and the Lee–Yang–Parr correlation functional[48] was used to treat the electron-exchange and correlation (*x–c*) interactions. The quantum-chemical calculations showed that the geminal structure for the ditosyloxy ketone is the most stable form, followed by the vicinal *syn* structure (Figure 3); the vicinal *anti*-configuration of the ditosyloxy ketone was found to be the thermodynamically least favored. The geminal structure was predicted to be lower in energy than the vicinal *syn*-configuration of the ditosyloxy ketone by 16.11 kJ/mol, and was therefore found to be thermodynamically favored over the previously reported *syn*-configuration. This extra stability of the geminal structure might originate from π–π stacking interactions between the two aryl rings, one bearing the tosylate group and the other bearing the methoxy substituent, whereas the vicinal configurations lack these π–π stacking interactions.

The oxidative rearrangements of aryl-substituted unsaturated carbonyl compounds mediated by hypervalent iodine reagents in polar protic solvent system had previously been established to give geminal β,β-substituted carbonyl compounds through 1,2-migration.[37,38] Moreover, Ollis et al.[49–51] reported an oxidative rearrangement of chalcone promoted by thallium(III) acetate in methanol in which the methoxy ion (CH$_3$O$^-$) served as the nucleophile, and which resulted in the formation of β,β-geminal disubstituted carbonyl compounds, i.e. acetals, through a 1,2-aryl shift. Furthermore, Moriarty et al.[38] also reported that acetals formed as oxidative products through a 1,2-aryl migration when chalcone was treated with HTIB in methanol. In this case, the methoxy ion (MeO$^-$), being more nucleophilic than the tosylate ion (TsO$^-$), which was also present in the reaction mixture, acted as nucleophile, resulting in the rearranged geminally substituted product.
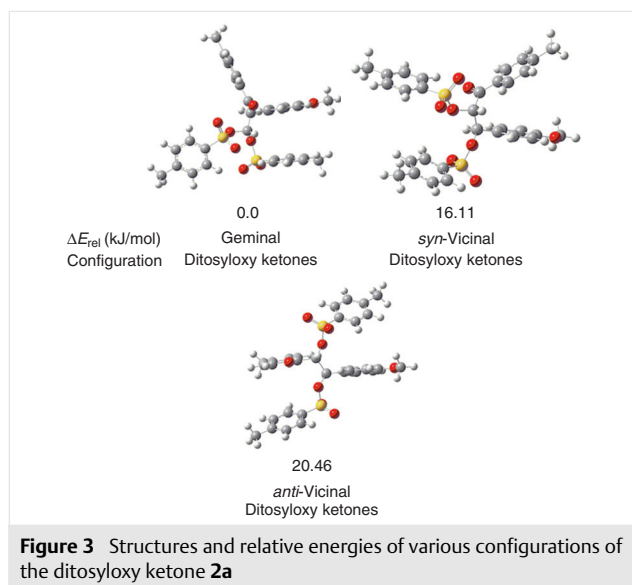
Figure 3 Structures and relative energies of various configurations of the ditosyloxy ketone **2a**

The solvent composition plays a crucial role in oxidative rearrangements mediated by hypervalent iodine reagents.[52] In polar protic solvent system, the solvent can serve as a competent nucleophile and can significantly influence the transformation,[38] whereas polar aprotic solvents do not possess such a nucleophilic nature. We can therefore state that ditosyloxylation of the C=C double bond of α,β-unsaturated carbonyl compounds in dichloromethane with HTIB entails an oxidative 1,2-aryl migration and, feasibly, results in a geminal β,β-ditosyloxy ketone.

A plausible mechanism for this transformation is suggested in Scheme 4. Initial electrophilic addition of Ph(OH)I$^+$ (generated by simple dissociation of HTIB)[53] to the double bond of the chalcone results in the cyclic organoiodine intermediate **8**. This intermediate undergoes nucleophilic attack by the tosylate ion (OTs$^-$), present in the reaction mixture. As the possibility of competitive nucleophilic attack by the tosylate ion at the carbon α to carbonyl group in structure **8** appears to be low due to the presence of the electron-withdrawing COAr group that restrict the development of a positive charge on the α-carbon, attack on the carbon β to the carbonyl group occurs instead to give the hydroxyiodinane **9**. Thereafter, release of a hydroxide ion (OH$^-$) and iodobenzene, and 1,2 migration of the aryl group, which might be facilitated by the lone pair of electrons on the oxygen atom, results in the formation of intermediate **10**. Nucleophilic attack by a second tosylate ion, generated by simple dissociation of HTIB, on the carbon β to the carbonyl group finally results in the formation of the geminal ditosyloxy ketone.

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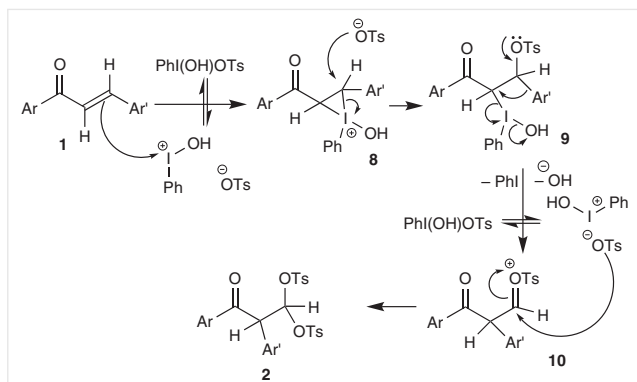
Scheme 4 Plausible mechanism for the ditosyloxylation of α,β-unsaturated ketones

Some features of the proposed mechanism need to be considered. First, the existence of the organoiodine intermediate **8** has already been established in an earlier investigation by Rebrovic and Koser[41] and confirmed by Moriarty et al.[38] The formation of intermediates **9** and **10** is supported by the rearrangement resulting from HTIB-mediated reaction of chalcones in methanol reported by Moriarty et al.[38] in which the more nucleophilic methoxy ion (MeO⁻), instead of the tosylate ion (TsO⁻), attacks the chalcone. However, in the absence of methanol, the tosylate ion (TsO⁻) should act as nucleophile.

At this stage it is important to mention that our previous investigations[42–44] that reported a vicinal structure for the ditosyloxy ketone **3** can also be justified in terms of the geminal β,β-ditosyloxy ketone structure **2**, as shown in Scheme 5.

As stated, the synthesis of 1,4,5-trisubstituted pyrazoles **4** and 4,5-disubstituted isoxazole **5** can be demonstrated to involve the geminal ditosyloxy ketone **2**. Although the mechanism for the conversion of **2** into **4** or **5** is a matter of investigation, the geminal ditosyloxy ketone **2** might either behave in an identical manner to the β-keto aldehyde **11** or act as a synthon for the latter. The proposed mechanism for the regioselective formation of 1,4,5-trisubstituted pyrazoles and 4,5-disubstituted isoxazoles is outlined in Scheme 5. The first step of the reaction might be nucleophilic substitution of one of the tosyloxy groups by an NH₂ group of the nucleophile (phenylhydrazine, semicarbazide, thiosemicarbazide, or hydroxylamine). This substitution might be followed by further elimination of another tosyloxy group with participation of the lone pair of electrons on the nitrogen or oxygen atom, resulting in the formation of intermediate **2-II** or **2-V**, which subsequently undergoes cyclization in the usual manner to afford the required product.

Moreover, the formation of α-aryl β-keto dialkyl acetals and desoxybenzoins can also be explained by assuming that the geminal ditosyloxy ketone **2** is a precursor (Scheme 5).
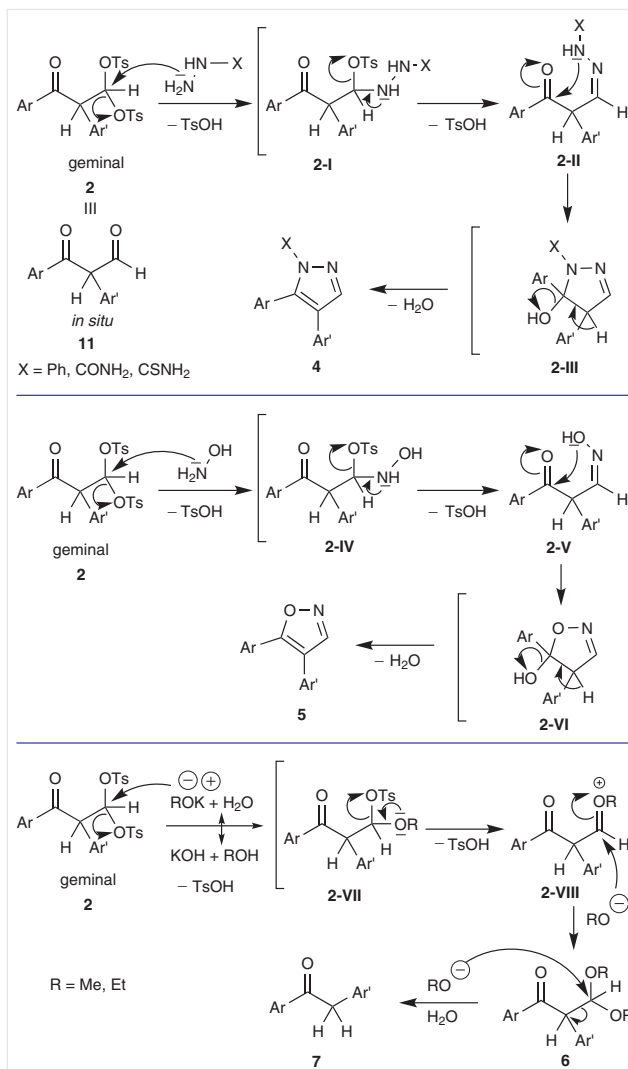
Scheme 5 Plausible mechanisms for the formation of pyrazoles, isoxazoles, α-aryl β-keto dialkyl acetals and desoxybenzoins from a β,β-ditosyloxy ketone as precursor

It is possible that an alkoxy ion (RO⁻), being more nucleophilic than a tosylate ion, has a crucial role in the transformation.

In summary, we efficiently synthesized β,β-ditosyloxy ketone derivatives by the ditosyloxylation of α,β-unsaturated carbonyl compounds mediated by a hypervalent iodine reagent in a polar aprotic solvent. We also proposed a mechanistic pathway for the synthesis of geminal β,β-ditosyloxy ketones. These outcomes are noteworthy as they contradict earlier reported syntheses of α,β-ditosyloxy ketones through HTIB-mediated ditosyloxylation of unsaturated carbonyl compound. We also explained our earlier investigations that wrongly implicated an α,β-ditosyloxy ketone by invoking a β,β-ditosyloxy ketone as a precursor.

The chemical versatility and relative stability of β,β-ditosyloxy ketones, along with the ease of their preparation, make them unique synthons in synthetic chemistry. The products reported here can act as precursors of β-keto aldehydes, and therefore have widespread synthetic applications in organic chemistry. Investigations on the intriguing chemistry of ditosyloxy ketones, especially their use in syntheses of medicinally important heterocyclic and other compounds, are currently in progress.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0040-1708010.

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(39) **2-(4-Methoxyphenyl)-3-(4-methylphenyl)-3-oxopropane-1,1-diyl Ditosylate (2a); Typical Procedure**
HTIB (3.136 g, 0.008 mol, 2 equiv) was added to a solution of chalcone **1a** (1.008 g, 0.004 mol) in CH_2Cl_2 (30 mL), and the mixture was stirred at 40–42 °C. The HTIB, which was insoluble in CH_2Cl_2, gradually disappeared as the reaction proceeded. Stirring was continued for about 40 h, and then the solvent was evaporated in vacuo. The resulting gummy mass was triturated with PE (60–80 °C; 3 × 20 mL) to remove PhI. The white solid was then thoroughly washed with water (2 × 30 mL) to remove the TsOH byproduct and crystallized from MeCN; yield: 1.8 g (76%).
2a (**Powdered Form**)
White solid; mp 136–138 °C. IR (KBr): 1666 cm^{-1} (CO stretch). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.76–7.78 (d, J = 8.4 Hz, 2 H), 7.59–7.62 (d, J = 8.3 Hz, 2 H), 7.41–7.43 (d, J = 8.4 Hz, 2 H), 7.24–7.26 (d, J = 7.4 Hz, 2 H), 7.07–7.13 (m, 6 H), 6.95–6.98 (d, J = 8.1 Hz, 1 H), 6.62–6.64 (d, J = 8.8 Hz, 2 H), 4.95–4.97 (d, J = 8.1 Hz, 1

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H), 3.72 (s, 3 H), 2.40 (s, 3 H), 2.39 (s, 3 H), 2.31 (s, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$): δ = 193.96, 159.66, 144.94, 144.69, 144.45, 133.62, 133.13, 133.00, 130.47, 129.46, 129.22, 128.80, 128.27, 127.91, 123.42, 114.41, 99.69, 56.86, 55.11, 21.70, 21.65, 21.63. HRMS (ESI): *m/z* calcd [M + H]$^+$ for C$_{31}$H$_{31}$O$_8$S$_2$: 595.7003; found: 595.6971.

2a (Single Crystal)

Crystalline white solid; spectroscopic data matched those of the powdered form.

(40) CCDC 1862569 and 1862571 contain supplementary crystallographic data for crystals of compound **2a** obtained from MeCN and from MeCN with traces of Et$_3$N, respectively. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/getstructures.

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