

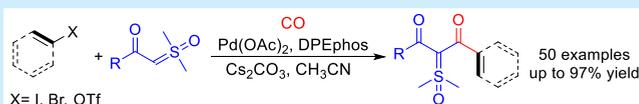
Direct Access to 1,1-Dicarbonyl Sulfoxonium Ylides from Aryl Halides or Triflates: Palladium-Catalyzed Carbonylation

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S Supporting Information

ABSTRACT: The synthesis of 1,1-dicarbonyl sulfoxonium ylides by palladium-catalyzed carbonylation of aryl halides or triflates with α -carbonyl sulfoxonium ylides has been developed for the first time. This method provides a general approach to synthetically useful 1,1-dicarbonyl sulfoxonium ylides in high efficiency. The protocol displays a wide substrate scope, showing that the resulting 1,1-dicarbonyl sulfoxonium ylides have been converted into the corresponding 1,3-dicarbonyl compounds.

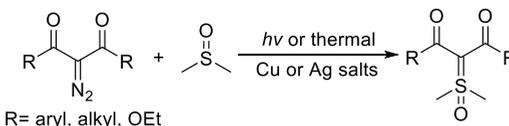


The transition-metal-catalyzed carbonylation reaction has now emerged as one of the most powerful methods for the synthesis of carbonyl-containing compounds, and a variety of value-added bulk and fine chemicals are available by this transformation.¹ Since the pioneering work of Heck and coworkers in 1974, palladium-catalyzed carbonylative coupling reactions of aromatic halides have undergone rapid development during the recent years.² Palladium-catalyzed carbonylations of aryl halides, followed by the attack of different types of nucleophiles such as alcohols, amines, and water, are known as alkoxycarbonylation, aminocarbonylation, and hydroxycarbonylation.³ In particular, they have been used for the synthesis of a wide range of valuable esters,⁴ amides,⁵ carboxylic acids,⁶ aldehydes,⁷ ketones,⁸ and heterocycles.⁹

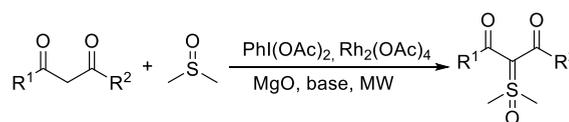
Sulfur (sulfonium and sulfoxonium) ylides¹⁰ have served as significant synthetic precursors in many organic transformations, such as aziridinations, epoxidations, cyclopropanations, olefinations, and rearrangements.¹¹ Their synthetic potential was demonstrated in the synthesis of various natural products, pharmaceuticals, and chemical materials as well.¹² In addition, sulfoxonium ylides¹³ were used as versatile carbenoid precursors in X–H (X = C, N, O, S) insertion reactions,¹⁴ and transition-metal-catalyzed C–H functionalization has been well developed.¹⁵ Consequently, it would be desirable to develop general protocols for the preparation of sulfoxonium ylides. Here it is important to mention that Aïssa and coworkers developed an interesting palladium-catalyzed procedure for the synthesis of bis-substituted sulfoxonium ylides in 2018.^{11g} By directly cross-coupling aryl halides and aryl triflates with α -ester sulfoxonium ylides, good yields of the desired ylides can be obtained. In 1964, König and Metzger reported their work on the acylation of trimethylsulfoxonium ylide with benzoic anhydride.^{16a} However, methods to synthesize 1,1-dicarbonyl sulfoxonium ylides were still limited. In general, these ylides can be prepared from the generation of carbenoids by transition-metal-catalyzed decomposition of diazo compounds or iodonium ylides. In 1970, Dost and Gosselck reported the decomposition of diazo compounds to provide sulfoxonium ylides by using copper and silver salts

(Figure 1, eq 1),^{16b} and intramolecular transformations using rhodium catalysts were studied by the research group of

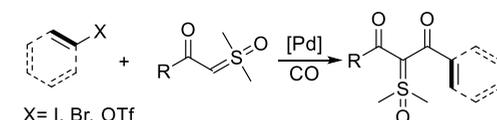
1. Synthesis of 1,1-dicarbonyl sulfoxonium ylides from diazo compounds



2. Synthesis of 1,1-dicarbonyl sulfoxonium ylides from iodonium ylides



3. This work



- ✓ High yield (up to 98% yield)
- ✓ Scalable
- ✓ Broad substrate scope
- ✓ Late-stage modification

Figure 1. Synthesis of 1,1-dicarbonyl sulfoxonium ylides.

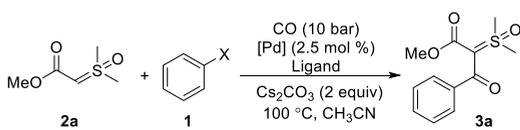
Moody.¹⁷ In 2017, Vaitla and coworkers demonstrated the direct synthesis of 1,1-dicarbonyl sulfoxonium ylides from malonates and sulfoxides via an iodonium ylide generated in situ (Figure 1, eq 2).¹⁸ The groups of Nemykin and Zhdankin developed a highly soluble iodonium ylide, which could be transformed into sulfoxonium ylides with DMSO by using $Rh_2(OAc)_4$ as the catalyst.¹⁹ On the basis of our continuous interest in carbonylations, and to the best of our knowledge, sulfoxonium ylides as the nucleophiles in the carbonylative reactions have not been reported until recently. Herein, we think a complementary practical approach to this interesting

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1,1-dicarbonyl sulfoxonium ylides can be achieved by the carbonylation of aryl halides with sulfoxonium ylides.

To verify our hypothesis, we initially chose α -estersulfoxonium ylide (**2a**) and iodobenzene (**1a**) as the model substrates, with Pd(PPh₃)₄ as the catalyst. We discovered that the desired product **3a** was formed in 72% yield using Cs₂CO₃ (2 equiv) as the base in CH₃CN under 10 bar of CO gas pressure at 100 °C (Table 1, entry 1). The yield of **3a** could be increased to

Table 1. Screening of Reaction Conditions^a



entry	X	[Pd]	ligand (mol %)	yield (%)
1	I	Pd(PPh ₃) ₄		72
2	I	Pd(PPh ₃) ₄		80 ^b
3	Br	Pd(PPh ₃) ₄		48
4	OTf	Pd(PPh ₃) ₄		28
5	I	Pd ₂ (dba) ₃	PPh ₃ (10)	33
6	I	Pd(OAc) ₂	PPh ₃ (10)	65
7	I	Pd(OAc) ₂	PCy ₃ (10)	trace
8	I	Pd(OAc) ₂	BUPAd ₂ (10)	48
9	I	Pd(OAc) ₂	^t Bu ₃ P·HF ₄ (10)	63
10	I	Pd(OAc) ₂	DPPE	<5
11	I	Pd(OAc) ₂	Xantphos	69
12	I	Pd(OAc) ₂	DPEPhos	78
13	I	Pd(OAc) ₂	DPEPhos	88 ^c
14	I	Pd(OAc) ₂	DPEPhos	89 ^{c,d}
15	Br	Pd(OAc) ₂	DPEPhos	80 ^{c,d}
16	OTf	Pd(OAc) ₂	DPEPhos	81 ^{c,d}
17	I	Pd(OAc) ₂	DPEPhos	86 ^{c,d,e}

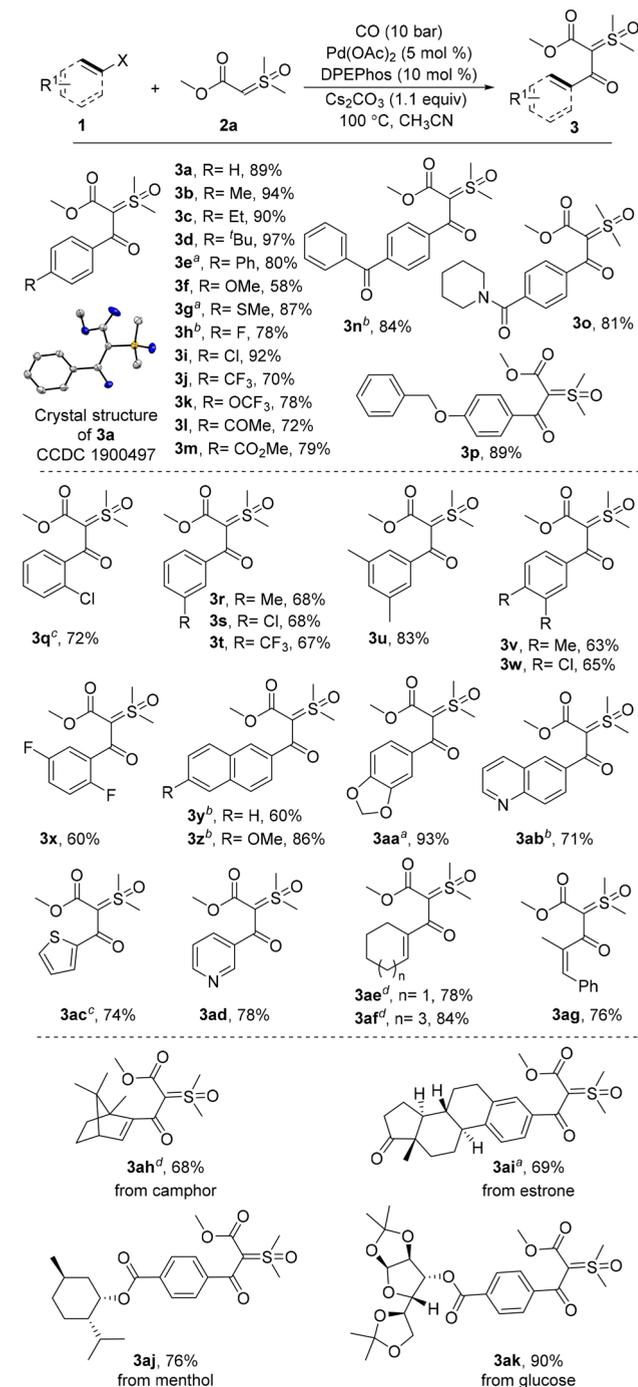
^aReaction conditions: **2a** (0.2 mmol), **1** (0.3 mmol), [Pd] (2.5 mol %), ligand (5.0 mol % or 10 mol %), CH₃CN (1.0 mL), Cs₂CO₃ (2.0 equiv), CO (10 bar), 100 °C, 20 h, isolated yield. ^bPd(PPh₃)₄ (5.0 mol %). ^cPd(OAc)₂ (5.0 mol %), DPEPhos (10 mol %). ^dCs₂CO₃ (1.1 equiv). ^e80 °C.

80% with 5 mol % Pd(PPh₃)₄ (Table 1, entry 2). Gratifyingly, the reaction could also give **3a** in 48% yield and 28% yield when the bromobenzene or phenyl triflate was used as the substrate (Table 1, entries 3 and 4). However, product **3a** was always mixed with small amounts of triphenylphosphine oxide, even after two applications of flash chromatography. Therefore, we decided to identify alternative conditions to avoid the impurity. We thus evaluated different palladium precursors in the presence of PPh₃ ligand, and Pd(OAc)₂ proved to be more efficient than Pd₂(dba)₃ (Table 1, entries 5 and 6). Subsequently, the screening of various monodentate and bidentate phosphine ligands showed that DPEPhos was the optimal ligand for this transformation (Table 1, entries 7–12). An increase in the catalyst loading to 5 mol % Pd(OAc)₂ and 10 mol % DPEPhos gave **3a** in 88% yield (Table 1, entry 13). Reducing the base Cs₂CO₃ to 1.1 equiv furnished the product **3a** in 89% isolated without any impurity (Table 1, entry 14). Further exploration of the bases resulted only in a significant decrease in the yield of **3a** (Table S1). In particular, bromobenzene and phenyl triflate were also well applicable to this transformation to give the desired product **3a** in high yield (Table 1, entries 15 and 16). Therefore, the optimal reaction conditions were defined as Pd(OAc)₂ (5 mol %),

DPEPhos (10 mol %), and Cs₂CO₃ (1.1 equiv) in CH₃CN at 100 °C under CO (10 bar) for 20 h.

We then explored the substrate scope of aryl halides with sulfoxonium **2a** (Scheme 1). A variety of aryl iodides bearing electron-donating substituents at the para positions were successfully converted to the desired products **3a–3g** and **3p**

Scheme 1. Substrate Scope of Various Aryl Halides and Triflates^a

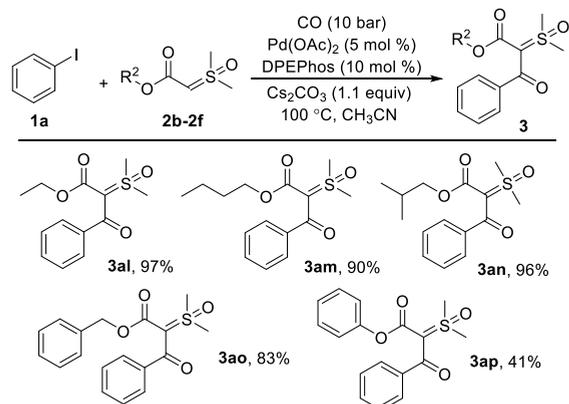


^aReaction conditions: **2a** (0.2 mmol), **1** (0.3 mmol), Pd(OAc)₂ (5 mol %), DPEPhos (10 mol %), CH₃CN (1.0 mL), Cs₂CO₃ (1.1 equiv), CO (10 bar), 100 °C, 20 h, isolated yield. [a] Use aryl triflates. [b] Use aryl bromides. [c] Use 5 mol % Pd(PPh₃)₄ as catalyst. [d] Use vinyl triflate.

in good to excellent yield. The structure of **3a** was confirmed by X-ray crystallography.²⁰ Various electron-withdrawing substituents such as fluoro, chloro, and trifluoromethyl, esters, as well as ketones at the para positions of aryl iodides were all well tolerated and afforded the corresponding substituted products **3h–3o** in 70–92% yield. Ortho- or meta-substituted aryl halides were able to give the corresponding products in moderate yield as well (**3q–3t**). Moreover, disubstituted aryl iodides and bromonaphthalenes also reacted smoothly to furnish the desired products **3u–3z** in 60–86% yield. Fortunately, benzodioxole- and quinoline- containing substrates were successfully compatible under the reaction conditions (**3aa, 3ab**, 71–93% yields). Importantly, heteroiodides such as 2-iodothiophene and 3-iodopyridine also worked well, furnishing **3ac** and **3ad** in 74–78% yield. Vinyl triflates were also well applicable in this transformation to give the desired products **3ae–3ag** in good yield, and these vinyl triflates could be easily prepared from the corresponding carbonyl compounds.²¹ To demonstrate the potential applications, the late-stage modification of natural products and pharmaceutical derivatives was investigated. Camphor-, estrone-, menthol-, and glucose-derived **3ah–3ak** were all isolated in good yield (68–90% yield, **Scheme 1**).

Under the optimized conditions, the scope of different α -estersulfoxonium ylides **2** was subsequently examined (**Scheme 2**). The sulfoxonium ylides bearing an alkyl group gave the

Scheme 2. Substrates Scope of α -Estersulfoxonium Ylides^a

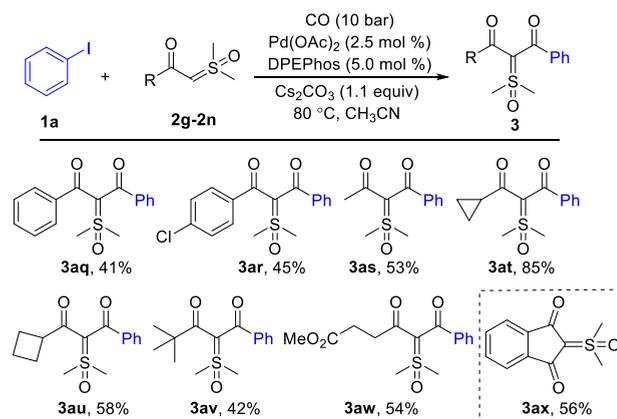


^aReaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol), Pd(OAc)₂ (5 mol %), DPEPhos (10 mol %), CH₃CN (1.0 mL), Cs₂CO₃ (1.1 equiv), CO (10 bar), 100 °C, 20 h, isolated yield.

expected products (**3al–3ao**) in excellent yield. However, sulfoxonium ylide with an aryl group provided only the corresponding product **3ap** in 41% isolated yield.

Meanwhile, we were wondering if this catalytic system could be extended to the β -ketosulfoxonium ylides. To our delight, in the reactions of iodobenzene **1a** with β -ketosulfoxonium ylide **2g** under the above reaction conditions, the reaction could furnish the target product **3aq** in moderate yield. Unfortunately, although a detailed exploration of reaction parameters, such as catalysts, bases, temperature, ligands, and solvents, was carried out (**Tables S2–S5**), the yield of **3aq** was only achieved with up to 52% NMR yield and isolated in 41% yield. Then, the substrate scope of β -ketosulfoxonium ylide (**2g–2n**) was examined (**Scheme 3**). The β -ketosulfoxonium ylides bearing an alkyl or aryl group gave the expected products (**3aq–3aw**)

Scheme 3. Carbonylation of β -Ketosulfoxonium Ylides^a

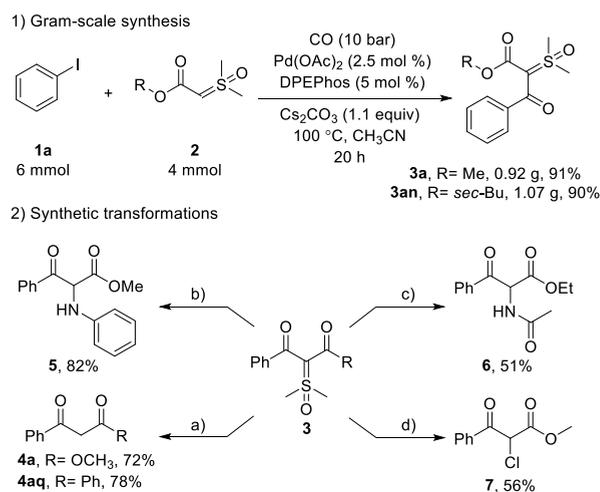


^aReaction conditions: **1a** (0.3 mmol), **2** (0.2 mmol), Pd(OAc)₂ (2.5 mol %), DPEPhos (5 mol %), CH₃CN (1.0 mL), Cs₂CO₃ (1.1 equiv), CO (10 bar), 80 °C, 20 h.

in 41–85% yield. Interestingly, intramolecular reactions could also smoothly proceed to form **3ax** in 56% yield.

The practicability of the presented methodology was demonstrated with a 4 mmol scale of reaction in the presence of 2.5 mol % palladium catalyst, and the desired products **3a** and **3an** were obtained in 91 and 90% yields, respectively (**Scheme 4**, eq 1). As an application of the ylides, some of them

Scheme 4. Gram-Scale Synthesis and Synthetic Transformations^a



^a(a) Raney nickel, IPA, reflux, 2 h. (b) Aniline, [Ir(COD)Cl]₂ (2 mol %), toluene, 150 °C. (c) Acetamide, [Ir(COD)Cl]₂ (2 mol %), toluene, 150 °C. (d) LiCl, MsOH, THF, 50 °C.

were subjected to a desulfurization reaction using Raney nickel in refluxing 2-propanol and provided respective 1,3-dicarbonyl compounds in good yield (72–78%, **Scheme 4**, eq 2a).²² Furthermore, some known transformations were performed, such as N–H and Cl–H insertions (**Scheme 4**, eqs 2b–d).²³ The treatment of sulfoxonium ylide **3** with aniline or acetamide in the presence of [Ir(COD)Cl]₂ (1 mol %) in toluene at 150 °C afforded N–H insertion products **5** or **6** successfully. Likewise, the treatment of **3a** with LiCl and MsOH in THF at 50 °C gave the Cl–H insertion product **7** in 56% isolated yield.

In conclusion, we have developed the first palladium-catalyzed carbonylation of α -estersulfoxonium ylides or β -ketosulfoxonium ylides for the synthesis of 1,1-dicarbonyl sulfoxonium ylides from easily available aryl halides and triflates. This method provides a general approach to a variety of synthetically useful 1,1-dicarbonyl sulfoxonium ylides in good yield with ease of scale up. Additionally, the desulfurization of representative sulfoxonium ylides successfully afforded the corresponding 1,3-dicarbonyl compounds. Moreover, we also demonstrated that these ylides can be readily diversified to other important dicarbonyl compounds of choice.

■ ASSOCIATED CONTENT

● Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.orglett.9b01926](https://doi.org/10.1021/acs.orglett.9b01926).

General comments, general procedure, optimization details, analytic data, and NMR spectra (PDF)

Accession Codes

CCDC 1900497 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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