

HOTf-Catalyzed, Solvent-Free Oxyarylation of Ynol Ethers and Thioethers

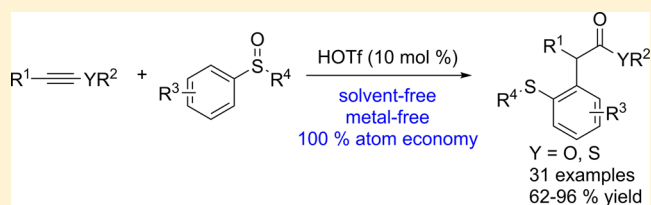
Liang Hu,[†] Qingwen Gui,[†] Xiang Chen,[†] Ze Tan,^{*,†} and Gangguo Zhu^{*,§}

[†]State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China

[§]Department of Chemistry, Zhejiang Normal University, 688 Yingbin Road, Jinhua 321004, China

S Supporting Information

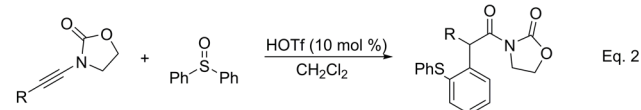
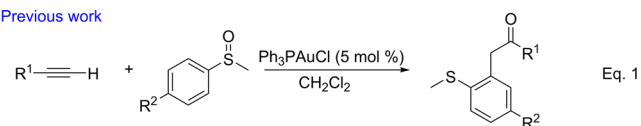
ABSTRACT: A novel HOTf-catalyzed oxyarylation of ynol ethers and thioethers has been realized with aryl sulfoxides as the oxyarylating reagents, providing α -arylated esters or thioesters in good to excellent yields. Notably, all atoms of the starting materials were incorporated in the product (100% atom economy) and the reaction proceeded under very mild conditions. It was found that the reaction can be ran under air and that the best yields are obtained under solvent-free conditions.



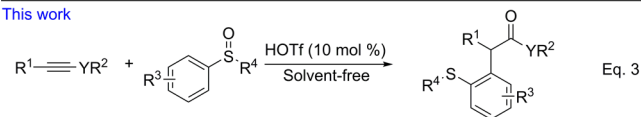
α -Arylated carbonyl compounds are common structural motifs found in a number of natural products and bioactive molecules.¹ As such, the development of new methods for their synthesis is of great importance in organic chemistry.^{2–14} Traditionally α -arylated carbonyl compounds are synthesized either through transition metal catalyzed couplings between a carbonyl compound^{2,7e,10a,12e} and an aryl electrophile, such as the notable Buchwald-Hartwig arylation reaction,³ or through the reaction of pregenerated enolate anion with electrophilic aromatic derivatives of Bi(V),⁴ Pb(IV),⁵ I(III),⁶ and benzyne.⁷ Alternatively, α -arylated carbonyl compounds can be efficiently synthesized from alkynes via Claisen rearrangement.⁸ For example, Toste reported that benzothiepinones could be synthesized via intramolecular rearrangement reaction between an aryl sulfoxide and a tethered alkyne using IMesAuCl as the catalyst.⁹ Zhang also independently reported a similar transformation using dichloro(pyridine-2-carboxylato)gold(III) as the catalyst.¹⁰ Later on gold catalyzed intermolecular versions of this reaction were developed by the groups of Asensio and Ujaque, and Davies and Grainger (Scheme 1, eq 1).¹¹ Even though these Au-catalyzed methods do allow the rapid construction of α -arylated carbonyl compounds from simple starting materials, the use of an expensive Au catalyst can limit their practical applications. Undoubtedly, the exploration of a metal-free method is highly desirable.^{8d,e,12–14} In this context, Maulide has demonstrated that they were able to synthesize α -arylated carbonyl compounds by coupling the corresponding amide or ketoester with arylsulfoxides using Tf₂O as a promoter.¹³ It is proposed that these reactions go through a [3,3]-sigmatropic rearrangement process. Even more impressively, they were able to couple ynamides with aryl sulfoxides as well under the catalysis of HOTf (trifluoromethanesulfonic acid) (Scheme 1, eq 2).¹⁴ Through the generation of a keteniminium intermediate followed by its coupling with

Scheme 1. Approaches to α -Arylated Carbonyl Compounds from Alkyne Derivatives

Previous work



This work

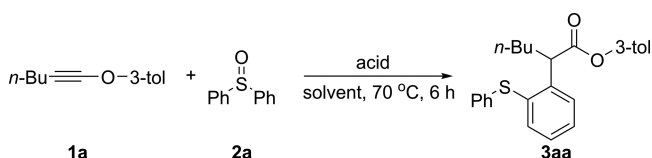


sulfoxide and a subsequent [3,3]-sigmatropic rearrangement, a variety of α -arylated oxazolidinones were obtained in good yields. As part of our continuing interest in ynol ethers,^{15,16} we wondered whether ynol ethers, the structures of which are analogous to ynamides, can participate in the reaction or not. Herein we describe that not only ynol ethers and thioethers can react efficiently with aryl sulfoxides to produce various α -arylated esters using HOTf as the catalyst, the reaction can also be ran under solvent-free condition (Scheme 1, eq 3).^{17,18}

Initially, ynol ether **1a**, which was easily prepared by Evano's method,¹⁹ was chosen for evaluating the reaction parameters. As a result, treating **1a** with 1.0 equiv of diphenyl sulfoxide (**2a**), 10 mol % of HOTf in CH₂Cl₂ at 70 °C for 6 h generated α -arylated ester **3aa** in 13% yield (Table 1, entry 1).

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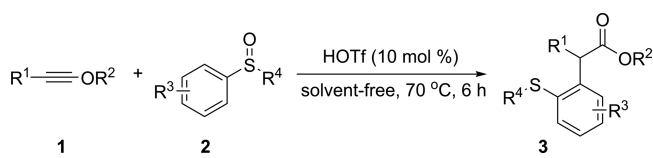
Table 1. Screening of the Reaction Conditions for HOTf-Catalyzed, Solvent-Free Oxyarylation of Ynol Ethers of **1a**^a

entry	2a (equiv)	acid (equiv)	solvent	yield (%) ^b
1	1.0	HOTf (0.1)	CH ₂ Cl ₂	13
2	1.0	HOTf (0.1)	DCE	5
3	1.0	HOTf (0.1)	MeCN	12
4	1.0	HOTf (0.1)	toluene	trace
5	1.0	HOTf (0.1)	dioxane	trace
6	2.0	HOTf (0.1)	CH ₂ Cl ₂	27(32) ^c
7	2.0	HOTf (1.0)	CH ₂ Cl ₂	42
8	2.0	HOTf (1.0)	no solvent	50
9	2.0	HOTf (0.2)	no solvent	72
10	2.0	HOTf (0.1)	no solvent	85(84) ^d
11	1.5	HOTf (0.1)	no solvent	77
12	2.0	TFA (0.1)	no solvent	45 ^e
13	2.0	TsOH (0.1)	no solvent	14
14	2.0	AcOH (0.1)	no solvent	6

^aReaction conditions: **1a** (0.25 mmol), **2a** (m equiv), acid (n equiv), 70 °C, 6 h. ^bIsolated yield. ^cThe reaction was run at 100 °C for 6 h. ^dThe reaction was run under an air atmosphere. ^eTFA = trifluoroacetic acid.

Encouraged by this result, we further investigated other conditions for this reaction. Replacing CH₂Cl₂ with dichloroethane or MeCN afforded **3aa** in lower yields whereas toluene and dioxane failed completely (entries 2–5). Increasing the amount of **2a** to 2.0 equiv or HOTf to 1.0 equiv appeared to be beneficial, providing **3aa** in 27% and 42% yields, respectively (entries 6–7). Gratifyingly, a better yield of 50% was obtained in the absence of solvent with 1 equiv of HOTf (entry 8). On the other hand, running the reaction under solvent free condition while decreasing the amount of HOTf back to 10 mol % turned out to be the best reaction condition, which delivered **3aa** in 85% yield (entries 9 and 10). Subsequent study of other acids proved HOTf to be the optimal one while acids such as TFA (TFA = trifluoroacetic acid), TsOH, and AcOH all performed less efficiently (entries 12–14). Notably, the reaction could be performed under an air atmosphere without loss of the yield. Therefore, further substrate screening was carried out using 10 mol % of HOTf and 2.0 equiv of **2a** in the absence of solvent at 70 °C under an air atmosphere for 6 h.

With the optimized condition in hand, we next set out to explore the scope and limitation of our reaction and the results are summarized in Table 2. From the table, we can see that the reaction was suitable for a wide range of aryl sulfoxides, which generally afforded the α -arylated ester **3aa**–**3ak** in good to excellent yields under very mild conditions (Table 2, entries 1–11). Functional groups, such as methyl, methoxy, chloro, aldehyde, and nitro groups, were well tolerated on the phenyl ring of aryl sulfoxides (Table 2, entries 2–9). Moreover, alkyl aryl sulfoxides **2e**–**2j** also proved to be competent reaction partners for this transformation, leading to the generation of **3ae**–**3aj** in excellent yields ranging from 72 to 92% (Table 2, entries 5–10). Notably, an alkylpyridine sulfoxide can also participate in the α -arylation well, affording the desired product **3ak** in 81% yield (Table 2, entry 11). Unfortunately, aryl sulfoxide **2l** bearing an amino group on the phenyl ring failed to

Table 2. Scope of HOTf-Catalyzed, Solvent-Free Oxyarylation of Ynol Ethers^a

entry	1	2	3	yield (%) ^b
1	<i>n</i> -Bu/3-tol (1a)	Ph/Ph (2a)	84 (3aa)	
2	1a	4-MeC ₆ H ₄ /4-MeC ₆ H ₄ (2b)	89 (3ab)	
3	1a	4-ClC ₆ H ₄ /4-ClC ₆ H ₄ (2c)	71 (3ac)	
4	1a	4-NO ₂ C ₆ H ₄ /4-NO ₂ C ₆ H ₄ (2d)	67 (3ad) ^c	
5	1a	Ph/Me (2e)	79 (3ae)	
6	1a	4-MeC ₆ H ₄ /Me (2f)	77 (3af)	
7	1a	4-MeOC ₆ H ₄ /Me (2g)	83 (3ag)	
8	1a	4-ClC ₆ H ₄ /Me (2h)	70 (3ah)	
9	1a	4-HCOC ₆ H ₄ /Me (2i)	75 (3ai)	
10	1a	Ph/ <i>i</i> -Pr (2j)	92 (3aj)	
11	1a	Py/Me (2k)	81 (3ak)	
12	1a	4-NH ₂ C ₆ H ₄ /Me (2l)	trace	
13	1a	Ph/vinyl (2m)	trace	
14	<i>n</i> -Bu/Ph (1b)	2a	80 (3ba)	
15	<i>n</i> -Bu/4-ClC ₆ H ₄ (1c)	2a	68 (3ca)	
16	H/Ph (1d)	2a	81 (3da)	
17	H/3-tol (1e)	2a	84 (3ea)	
18	allyl/Ph (1f)	2a	81 (3fa)	
19	allyl/3-tol (1g)	2a	83 (3ga)	
20	allyl/2-naphthyl (1h)	2a	73 (3ha)	
21	Ph/3-tol (1i)	2a	78 (3ia)	
22	Ph/Et (1j)	2a	66 (3ja)	
23	4-CF ₃ C ₆ H ₄ /Et (1k)	2a	68 (3ka)	
24	BnCH ₂ /3-tol (1l)	2a	64 (3la) ^d	
25	Cy/3-tol (1m)	2a	65 (3ma)	
26	Cy/4-ClC ₆ H ₄ (1n)	2a	60 (3na)	
27	H/Et (1o)	2a	83 (3oa) ^e	

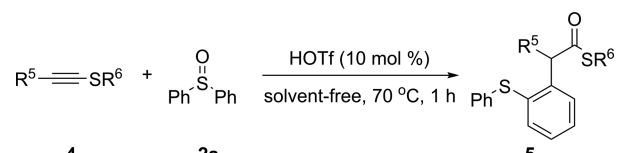
^aReaction conditions: **1** (0.25 mmol), **2** (2 equiv), HOTf (0.1 equiv), under air, 70 °C, 6 h. ^bIsolated yield. ^cCH₂Cl₂ (0.2 mL) was added to the standard conditions. ^dRun at 80 °C for 10 h. ^eRun at room temperature for 6 h.

participate in the reaction (Table 2, entry 12). This is to be expected since the unprotected amine group can neutralize HOTf, thus shutting down the desired reaction. In addition, an α,β -unsaturated aryl sulfoxide **2m** was also found not to be compatible with our reaction (Table 2, entry 13). On the other hand, as shown in Table 2, various ynol ethers were successfully applied to the current reaction. Specifically, the R² group of **1** had little impact on this reaction, as shown by the production of **3ba** and **3ca** (Table 2, entries 14 and 15). Pleasingly, terminal alkynyl ether **1d** and **1e** also underwent the reaction smoothly, giving rise to **3da** and **3ea** in satisfactory yield (Table 2, entries 16 and 17). We are also pleased to see that substrates **1f**–**1h**, possessing both C–C triple and double bonds, reacted uneventfully to form **3fa**–**3ha** in high yields (Table 2, entries 18–20). Besides alkyl ynol ethers, aryl alkynyl ethers also proved to be viable substrates, affording the corresponding α -arylated products in good yields (Table 2, entries 21–23). Additionally, good yields were obtained with sterically more demanding substrates such as **1m** and **1n**, showing that the reaction tolerates a tertiary center at the propargylic position (Table 2, entries 25 and 26). Remarkably, the commercially available ethyl ethynyl ether was also an effective substrate,

giving **30a** in 83% yield after the reaction was run at room temperature for 6 h (Table 2, entry 27).

Subsequently, we explored the acid-promoted oxyarylation reaction of thioethers (Table 3). As a result, we found that the

Table 3. Scope of HOTf-Catalyzed, Solvent-Free Oxyarylation of Thioethers^a



entry	R ⁵ /R ⁶	yield (%) ^b
1	Ph/Ph (4a)	84 (5aa)
2	Ph/Et (4b)	77 (5ba)
3	<i>n</i> -Bu/Ph (4c)	92 (5ca)
4	<i>n</i> -Bu/Me (4d)	91 (5da)
5	<i>n</i> -C ₆ H ₁₃ /Et (4e)	95 (5ea)
6	<i>n</i> -C ₈ H ₁₇ /Et (4f)	96 (5fa)

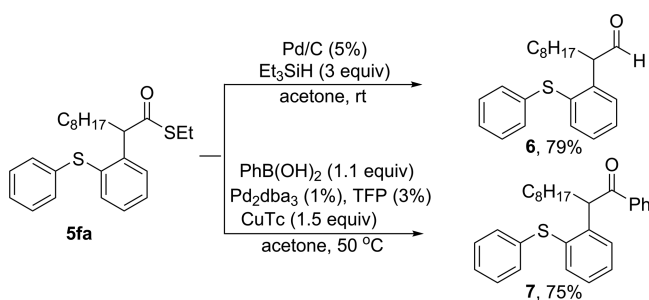
^aReaction conditions: **1a** (0.25 mmol), **2a** (2 equiv), HOTf (0.1 equiv), under air, 70 °C, 1 h. ^bIsolated yield.

oxyarylation process exhibited good compatibility with a wide variety of substrates under the optimal reaction conditions which are consisted of using 2.0 equiv of diphenyl sulfoxide and 10 mol % HOTf at 70 °C for 1 h in solvent-free condition. Both aryl thioethers and alkyl thioethers were successfully converted into the desired products in excellent yields (Table 3, entries 1–4). Furthermore, substrates **4e–4f** with longer alkyl

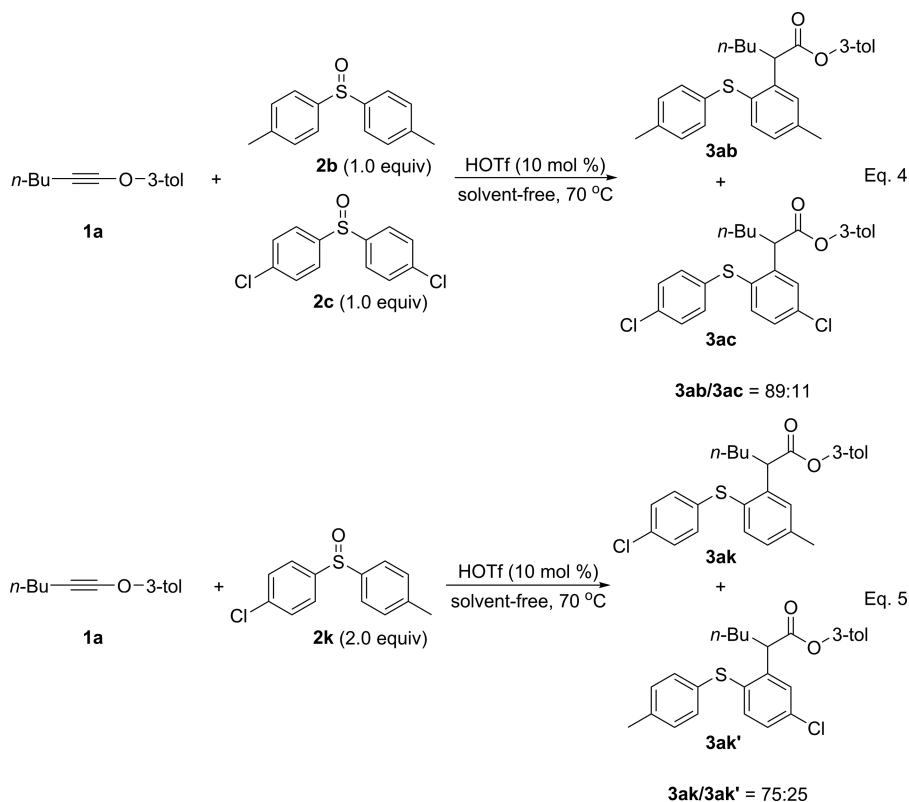
chains produced **5e–5f** in >95% yields (Table 3, entries 5 and 6), suggesting that the oxyarylation of alkynylether is a highly regioselective process.

In order to gain some information on the reaction mechanism, some control experiments were conducted (Scheme 2). When **1a** was reacted with a mixture of equal-molar amount of electron-rich (di-*p*-tolylsulfoxide **2b**) and electron-poor (di-*p*-chlorophenyl)-sulfoxide **2c**) sulfoxides, we found that a mixture of product **3ab** and **3ac** was obtained and the ratio of **3ab**:**3ac** is 89:11 (eq 4). On the other hand, when an unsymmetrical sulfoxide like **2k** was subjected to the reaction with **1a**, the reaction afforded two regioisomers **3ak** and **3ak'** in a 75:25 ratio favoring **3ak** (eq 5). From both cases, we can see that the rearrangement on the more electron rich arenes is preferred and this is consistent with the proposed mechanism (see Scheme 4 below). According to the proposed

Scheme 3. Synthesis of Multifunctional Aldehyde and Ketone from Thioester

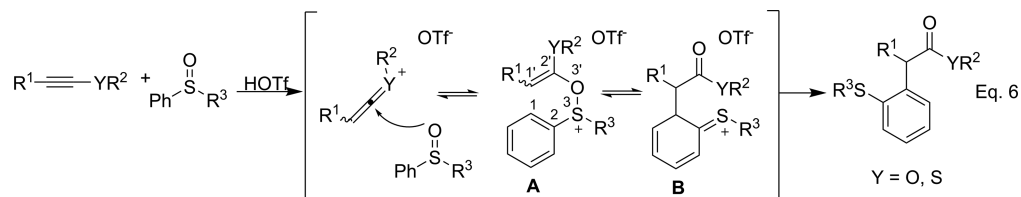


Scheme 2. Control Experiments with **2b^a, **2c**^a, and **2k**^b**



^aReaction conditions: **1a** (0.25 mmol), **2b** (1 equiv), **2c** (1 equiv), HOTf (0.1 equiv), under air, 70 °C, 6 h. ^bTwo equiv of **2k** were used instead of **2b** and **2c**.

Scheme 4. Possible Reaction Mechanism



mechanism, the cationic intermediate **B** is formed after rearrangement and it can be stabilized by electron donating substituents on the phenyl ring. This high preference for transferring the most electron-rich aromatics is a remarkable feature of this sulfoxide-mediated arylation reaction.

The synthetic utility of this reaction was then investigated. By treating **5fa** with triethylsilane in the presence of 5% Pd/C in acetone at room temperature for 10 h, aldehyde **6** was generated in 79% yield through the Fukuyama reduction (Scheme 3).²⁰ Furthermore, ketone **7** could be obtained in 75% yield via Pd-catalyzed thiol ester-boronic acid cross-coupling (Scheme 3).²¹ As such, we have developed an operationally simple and highly efficient method for the synthesis of multifunctional aldehydes and ketones, an important class of building blocks in medicinal and biochemistry.

In summary, we have developed a HOTf-catalyzed, solvent-free oxyarylation of alkynyl ethers and thioethers for the synthesis of α -arylated esters. The reaction proceeds under very mild reaction conditions and produces a wide range of α -arylated esters in high yields with excellent functional group tolerance. It represents a highly atom-economical and efficient method for the synthesis of α -arylated carbonyl compounds.

EXPERIMENTAL SECTION

General. Unless otherwise noted, materials obtained from commercial suppliers were used directly without further purification. Dioxane, toluene, and THF were distilled from sodium prior to use. Column chromatography was carried out using silica gel (300–400 mesh) with petroleum ethers/EtOAc as the eluent. ¹H and ¹³C NMR spectra were measured on a 600 or 400 MHz NMR spectrometer using CDCl₃ as the solvent. The chemical shifts are given in δ relative to TMS, and the coupling constants are given in Hertz. The high-resolution mass spectra (HRMS) analyses were conducted using a TOF MS instrument with an ESI source. Melting points were measured by a melting point instrument and were uncorrected.

General Procedure for Synthesis of Vinyl Dibromides from Aldehydes (First Step).²² Under an atmosphere of argon, a solution of triphenylphosphine (4 equiv) and tetrabromomethane (2 equiv) in abs. DCM (0.15 M) was stirred at 0 °C for 30 min. The aldehyde was added over a period of 5 min, and the mixture as stirred at 0 °C for 1 h. After addition of water, the layers were separated, and the aqueous layer was extracted with DCM (three times). The combined organic layers were dried over MgSO₄ and the solvent was removed under reduced pressure. The crude product was dry-loaded on silica and subjected to flash chromatography (silica, *n*-pentane/DCM).

General Procedure for Synthesis of Vinyl Ethers from Vinyl Dibromides (Second Step).⁹ A 15 mL pressure tube was charged with the phenol (6.7 mmol), 2,2'-bipyridine (310 mg, 2.0 mmol), K₃PO₄ (6500 mg, 31.0 mmol), and copper(I) iodide (190 mg, 1.0 mmol); if solid, the 1,1-dibromo-1-alkene (10.0 mmol) was also introduced at this stage. The tube was fitted with a rubber septum, evacuated under high vacuum and backfilled with argon. Dry and degassed toluene (20 mL) was next added as well as the 1,1-dibromo-1-alkene (10.0 mmol) which was added at this stage if liquid. The rubber septum was replaced by a Teflon-coated screw cap and the heterogeneous suspension was heated at 110 °C for 2 days, cooled to room temperature, diluted with dry dioxane (20 mL), and treated with

potassium tert-butoxide (1880 mg, 16.7 mmol). The resulting mixture was stirred overnight at room temperature, filtered through a plug of silica gel (washed with EtOAc), and concentrated in vacuo. The crude residue was purified by flash column chromatography.

1-(Hex-1-yn-1-yloxy)-3-methylbenzene (1a).²³ 73% yield (919 mg, 93% purity, determined by GC); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.23–7.19 (m, 1H), 7.06–7.04 (m, 2H), 6.92 (d, *J* = 7.7 Hz, 1H), 2.36 (s, 3H), 2.28 (t, *J* = 6.9 Hz, 2H), 1.57–1.43 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H).

(Hex-1-yn-1-yloxy)benzene (1b).²³ 52% yield (610 mg, 95% purity, determined by GC); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.32 (m, 2H), 7.26–7.24 (m, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 2.28 (t, *J* = 6.9 Hz, 2H), 1.58–1.43 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H).

(Hex-1-yn-1-yloxy)benzene (1c).²³ 68% yield (948 mg, 94% purity, determined by GC); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.27 (m, 2H), 7.23–7.14 (m, 2H), 2.27 (t, *J* = 7.0 Hz, 2H), 1.56–1.43 (m, 4H), 0.94 (t, *J* = 7.2 Hz, 3H).

1-Methyl-3-(pent-4-en-1-yn-1-yloxy)benzene (1g).²⁴ 85% yield (975 mg, 98% purity, determined by GC); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.25–7.20 (m, 1H), 7.08–7.06 (m, 2H), 6.93 (d, *J* = 7.6 Hz, 1H), 5.90 (m, 1H), 5.42–5.33 (m, 1H), 5.15–5.15 (m, 1H), 3.08–3.06 (m, 2H), 2.36 (s, 3H).

1-((Cyclohexylethynyl)oxy)-3-methylbenzene (1m).²⁴ 77% yield (1104 mg, 94% purity, determined by GC); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.24–7.19 (m, 1H), 7.06–7.05 (m, 2H), 6.92 (d, *J* = 7.6 Hz, 1H), 2.50–2.47 (m, 1H), 2.36 (s, 3H), 1.88–1.82 (m, 2H), 1.75–1.70 (m, 3H), 1.54–1.46 (m, 2H), 1.34–1.29 (m, 3H).

General Procedure for Synthesis of Alkynyl Sulfoxides from Terminal Alkynes.²⁵ To a THF solution of terminal alkynes (9.0 mmol), BuLi/Hex (8.5 mmol) was added at 0 °C. The mixture was stirred for 30 min. Dialkyl disulfide (8.0 mmol) was then added to the solution and the mixture was stirred for 2 h. The reaction was quenched with 2-bromoethanol (10 mmol) and stirred for an additional 2 h. Water (10 mL) was poured into the flask. The product was extracted with ethyl acetate (20 mL \times 3). The combined organic layer was washed with brine and then dried over Na₂SO₄ and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography (with hexane) to provide alkynyl sulfoxides.

Ethyl(phenylethynyl)sulfane (4b).²⁶ 68% yield (991 mg, > 99% purity, determined by GC); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.44–7.36 (m, 2H), 7.29–7.28 (m, 3H), 2.82 (q, *J* = 7.3 Hz, 2H), 1.45 (t, *J* = 7.3 Hz, 3H).

Hex-1-yn-1-yl(phenyl)sulfane (4c).²⁶ 62% yield (1060 mg, > 99% purity, determined by GC); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.40 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.7 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 2.45 (t, *J* = 7.1 Hz, 2H), 1.62–1.56 (m, 2H), 1.49–1.45 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H).

Dec-1-yn-1-yl(ethyl)sulfane (4f).²⁶ 74% yield (1319 mg, > 99% purity, determined by GC); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 2.68 (q, *J* = 7.3 Hz, 2H), 2.30 (t, *J* = 7.1 Hz, 2H), 1.54–1.49 (m, 2H), 1.39–1.36 (m, 4H), 1.32–1.25 (m, 9H), 0.88 (t, *J* = 7.0 Hz, 3H).

The starting material of **1d–1f**, **1h–1l**, **1n**, **4a**, and **4d–4e** have been prepared in our recent papers (references **15c** and **27**).

General Procedure for HOTf-Catalyzed, Solvent-Free Oxyarylation of Ynol Ethers. To a mixture of ynol ether **1a** (47.0 mg, 0.25 mmol) and diphenyl sulfoxide **2a** (101.0 mg, 0.5 mmol) was added HOTf (3.8 mg, 0.025 mmol) under an air atmosphere. After stirring at 70 °C for 6 h, the reaction mixture was quenched with NaHCO₃ (50.0 mg), extracted with EtOAc, washed with brine, dried

over anhydrous Na_2SO_4 and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:100) gave **3aa** as a colorless oil (81.9 mg, 84% yield).

M-Tolyl 2-(2-(Phenylthio)phenyl)hexanoate (3aa). ^1H NMR (600 MHz, CDCl_3) δ 7.52 (dd, J = 7.8, 1.3 Hz, 1H), 7.47 (dd, J = 7.8, 1.3 Hz, 1H), 7.38–7.35 (m, 1H), 7.26–7.15 (m, 7H), 6.99–6.97 (m, 1H), 6.74–6.73 (m, 2H), 4.63 (t, J = 7.5 Hz, 1H), 2.30 (s, 3H), 2.19–2.13 (m, 1H), 1.79–1.74 (m, 1H), 1.38–1.22 (m, 4H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.6, 150.7, 141.7, 139.4, 137.1, 135.1, 133.9, 129.3, 129.1, 128.9, 128.9, 128.1, 128.0, 126.4, 126.3, 121.9, 118.3, 48.0, 33.3, 29.7, 22.5, 21.2, 13.9; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{26}\text{NaO}_2\text{S}$ (M + Na) $^+$ 413.1551, found 413.1544.

M-Tolyl 2-(5-Methyl-2-(p-tolylthio)phenyl)hexanoate (3ab). 89% yield (93 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.36 (d, J = 7.9 Hz, 1H), 7.32–7.31 (m, 1H), 7.19–7.17 (m, 1H), 7.12–7.11 (m, 2H), 7.05–6.97 (m, 4H), 6.74–6.73 (m, 2H), 4.61 (t, J = 7.5 Hz, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 2.26 (s, 3H), 2.16–2.10 (m, 1H), 1.75–1.70 (m, 1H), 1.35–1.28 (m, 4H), 0.85 (t, J = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.8, 150.7, 141.5, 139.3, 138.9, 136.0, 135.0, 133.9, 130.8, 129.8, 129.3, 128.9, 128.6, 126.3, 121.9, 118.3, 47.8, 33.4, 29.7, 22.5, 21.3, 21.2, 20.9, 13.9; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{30}\text{NaO}_2\text{S}$ (M + Na) $^+$ 441.1864, found 441.1857.

M-Tolyl 2-(5-Chloro-2-(4-chlorophenylthio)phenyl)hexanoate (3ac). 71% yield (81 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.54–7.53 (m, 1H), 7.40–7.39 (m, 1H), 7.25–7.23 (m, 1H), 7.21–7.20 (m, 3H), 7.13–7.12 (m, 2H), 7.01–7.00 (m, 1H), 6.73–6.71 (m, 2H), 4.54 (t, J = 7.5 Hz, 1H), 2.32 (s, 3H), 2.19–2.13 (m, 1H), 1.78–1.74 (m, 1H), 1.34–1.31 (m, 4H), 0.87 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.9, 150.5, 143.4, 139.5, 136.2, 135.4, 135.1, 132.6, 132.0, 130.4, 129.3, 129.0, 128.6, 128.4, 126.6, 121.8, 118.1, 48.0, 33.3, 29.6, 22.4, 21.2, 13.8; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{24}\text{Cl}_2\text{NaO}_2\text{S}$ (M + Na) $^+$ 481.0772, found 481.0773.

M-Tolyl 2-(5-Nitro-2-(4-nitrophenylthio)phenyl)hexanoate (3ad). 67% yield (80 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 8.47–8.46 (m, 1H), 8.15–8.14 (m, 3H), 7.62–7.61 (m, 1H), 7.35–7.34 (m, 2H), 7.22–7.20 (m, 1H), 7.03–7.01 (m, 1H), 6.73–6.71 (m, 2H), 4.54 (t, J = 7.5 Hz, 1H), 2.31 (s, 3H), 1.97–1.89 (m, 1H), 1.39–1.24 (m, 5H), 0.89 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 171.0, 150.2, 148.4, 146.6, 144.1, 143.2, 140.4, 139.8, 135.2, 131.1, 129.4, 129.2, 126.9, 124.6, 124.5, 123.8, 123.1, 121.5, 117.9, 48.4, 33.0, 29.6, 22.3, 21.2, 13.8; HRMS (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{NaO}_6\text{S}$ (M + Na) $^+$ 503.1253, found 503.1255.

M-Tolyl 2-(2-(Methylthio)phenyl)hexanoate (3ae). 79% yield (65 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.41 (d, J = 7.6 Hz, 1H), 7.35 (d, J = 7.8 Hz, 1H), 7.27–7.25 (m, 1H), 7.22–7.19 (m, 2H), 7.00–6.98 (m, 1H), 6.81–6.79 (m, 2H), 4.46 (t, J = 7.4 Hz, 1H), 2.49 (s, 3H), 2.31 (s, 3H), 2.19–2.15 (m, 1H), 1.86–1.80 (m, 1H), 1.43–1.32 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.7, 150.7, 139.4, 138.3, 137.6, 129.0, 128.0, 127.8, 127.2, 126.5, 126.1, 122.0, 118.4, 47.5, 33.0, 29.7, 22.5, 21.2, 17.2, 13.9; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{24}\text{NaO}_2\text{S}$ (M + Na) $^+$ 351.1395, found 351.1391.

M-Tolyl 2-(5-Methyl-2-(methylthio)phenyl)hexanoate (3af). 77% yield (66 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.30–7.29 (m, 1H), 7.23–7.19 (m, 2H), 7.08–7.06 (m, 1H), 6.99–6.98 (m, 1H), 6.82–6.80 (m, 2H), 4.50 (t, J = 7.5 Hz, 1H), 2.46 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 2.18–2.14 (m, 1H), 1.83–1.75 (m, 1H), 1.43–1.34 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.8, 150.8, 139.4, 138.8, 136.4, 133.9, 129.4, 128.9, 128.6, 128.0, 126.4, 122.0, 118.4, 47.5, 33.2, 29.7, 22.5, 21.2, 21.0, 18.1, 13.9; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{26}\text{NaO}_2\text{S}$ (M + Na) $^+$ 365.1551, found 365.1548.

M-Tolyl 2-(5-Methoxy-2-(methylthio)phenyl)hexanoate (3ag). 83% yield (74 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.44 (d, J = 8.6 Hz, 1H), 7.22–7.20 (m, 1H), 7.01–6.99 (m, 2H), 6.83–6.80 (m, 3H), 4.63 (t, J = 7.5 Hz, 1H), 3.80 (s, 3H), 2.43 (s, 3H), 2.32 (s, 3H), 2.18–2.15 (m, 1H), 1.84–1.78 (m, 1H), 1.42–1.32 (m, 4H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.7, 159.2, 150.7, 141.9, 139.5, 133.4, 129.0, 128.0, 126.5, 122.0, 118.3, 113.6, 113.1, 55.4, 48.0, 33.4, 29.7, 22.6, 21.3, 19.7, 13.9; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{26}\text{NaO}_3\text{S}$ (M + Na) $^+$ 381.1500, found 381.1486.

M-Tolyl 2-(5-Chloro-2-(methylthio)phenyl)hexanoate (3ah). 70% yield (63 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.42–7.41 (m, 1H), 7.29–7.21 (m, 3H), 7.02–7.00 (m, 1H), 6.82–6.81 (m, 2H), 4.42 (t, J = 7.5 Hz, 1H), 2.48 (s, 3H), 2.33 (s, 3H), 2.20–2.15 (m, 1H), 1.83–1.81 (m, 1H), 1.40–1.38 (m, 4H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.1, 150.6, 139.9, 139.5, 136.2, 132.1, 129.4, 129.0, 127.9, 127.5, 126.6, 121.9, 118.3, 47.5, 33.0, 29.7, 22.5, 21.2, 17.4, 13.9; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{23}\text{ClNaO}_2\text{S}$ (M + Na) $^+$ 385.1005, found 385.1002.

M-Tolyl 2-(5-Formyl-2-(methylthio)phenyl)hexanoate (3ai). 75% yield (67 mg); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 9.95 (s, 1H), 7.91 (d, J = 1.7 Hz, 1H), 7.78 (dd, J = 8.2, 1.8 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.22 (t, J = 8.0 Hz, 1H), 7.01 (d, J = 7.4 Hz, 1H), 6.82–6.81 (m, 2H), 4.32 (t, J = 7.1 Hz, 1H), 2.58 (s, 3H), 2.32 (s, 3H), 2.27–2.20 (s, 1H), 1.97–1.87 (m, 1H), 1.47–1.33 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.4, 171.9, 150.6, 146.9, 139.6, 137.0, 133.2, 129.0, 128.7, 128.4, 126.7, 124.8, 121.9, 118.3, 47.2, 32.6, 29.7, 22.5, 21.2, 15.5, 13.9; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{24}\text{NaO}_3\text{S}$ (M + Na) $^+$ 379.1344, found 379.1352.

M-Tolyl 2-(2-(Isopropylthio)phenyl)hexanoate (3aj). 92% yield (82 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.55 (dd, J = 7.7, 0.9 Hz, 1H), 7.47 (dd, J = 7.7, 1.1 Hz, 1H), 7.30–7.29 (m, 1H), 7.28–7.19 (m, 2H), 7.00–6.98 (m, 1H), 6.80–6.77 (m, 2H), 4.77 (t, J = 7.5 Hz, 1H), 3.41–3.37 (m, 1H), 2.31 (s, 3H), 2.21–2.13 (m, 1H), 1.81–1.76 (m, 1H), 1.42–1.35 (m, 4H), 1.32 (d, J = 6.7 Hz, 3H), 1.29 (d, J = 6.6 Hz, 3H), 0.90 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.9, 150.8, 141.7, 139.4, 135.1, 134.2, 129.0, 127.9, 127.4, 127.4, 126.4, 121.9, 118.3, 47.7, 39.7, 33.5, 29.7, 23.2, 23.1, 22.6, 21.2, 13.9; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{28}\text{NaO}_2\text{S}$ (M + Na) $^+$ 379.1708, found 379.1701.

M-Tolyl 2-(2-(Methylthio)pyridin-3-yl)hexanoate (3ak). 81% yield (67 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 8.41 (dd, J = 4.8, 1.6 Hz, 1H), 7.63 (dd, J = 7.7, 1.6 Hz, 1H), 7.23–7.21 (t, J = 7.7 Hz, 1H), 7.05–7.01 (m, 2H), 6.83–6.81 (m, 2H), 4.16 (t, J = 7.5 Hz, 1H), 2.62 (s, 3H), 2.33 (s, 3H), 2.18–2.14 (m, 1H), 1.90–1.84 (m, 1H), 1.42–1.38 (m, 4H), 0.92 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.0, 158.5, 150.6, 147.9, 139.5, 134.0, 132.3, 129.0, 126.7, 121.9, 119.3, 118.3, 46.5, 32.6, 29.7, 22.4, 21.2, 13.9, 13.5; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{23}\text{NNaO}_2\text{S}$ (M + Na) $^+$ 352.1347, found 352.1346.

Phenyl 2-(2-(Phenylthio)phenyl)hexanoate (3ba). 80% yield (75 mg); colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.53–7.51 (m, 1H), 7.48–7.46 (m, 1H), 7.37–7.14 (m, 10H), 6.94–6.92 (m, 2H), 4.65 (t, J = 7.5 Hz, 1H), 2.18–2.12 (m, 1H), 1.82–1.74 (m, 1H), 1.39–1.22 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 172.5, 150.8, 141.6, 137.0, 135.1, 133.9, 129.3, 129.2, 129.0, 128.9, 128.0, 128.0, 126.3, 125.6, 121.3, 48.0, 33.3, 29.7, 22.5, 13.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{24}\text{NaO}_2\text{S}$ (M + Na) $^+$ 399.1395, found 399.1392.

4-Chlorophenyl 2-(2-(Phenylthio)phenyl)hexanoate (3ca). 68% yield (70 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.50–7.47 (m, 2H), 7.38–7.35 (m, 2H), 7.26–7.16 (m, 7H), 6.86–6.85 (m, 2H), 4.63 (t, J = 7.4 Hz, 1H), 2.18–2.11 (m, 1H), 1.80–1.74 (m, 1H), 1.40–1.27 (m, 4H), 0.85 (t, J = 7.0 Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 172.3, 149.2, 141.3, 136.9, 135.2, 133.8, 131.0, 129.2, 129.2, 129.1, 129.0, 128.1, 128.0, 126.3, 122.7, 47.9, 33.1, 29.6, 22.4, 13.9; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{23}\text{ClNaO}_2\text{S}$ (M + Na) $^+$ 433.1005, found 433.1008.

Phenyl 2-(2-(Phenylthio)phenyl)acetate (3da). 81% yield (65 mg); white solid, mp: 105–107 °C; ^1H NMR (600 MHz, CDCl_3) δ 7.45–7.42 (m, 2H), 7.34–7.31 (m, 3H), 7.29–7.18 (m, 7H), 7.03–7.02 (m, 2H), 4.06 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.6, 150.8, 136.4, 136.4, 134.6, 134.3, 131.2, 129.3, 129.3, 129.2, 128.6, 128.5, 126.4, 125.7, 121.4, 39.8; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{16}\text{NaO}_2\text{S}$ (M + Na) $^+$ 343.0769, found 343.0763.

M-Tolyl 2-(2-(Phenylthio)phenyl)acetate (3ea). 84% yield (70 mg); colorless oil; ^1H NMR (600 MHz, CDCl_3) δ 7.46–7.42 (m, 2H), 7.35–7.32 (m, 1H), 7.28–7.18 (m, 7H), 7.00–6.99 (m, 1H), 6.83–6.81 (m, 2H), 4.05 (s, 2H), 2.30 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 169.7, 150.7, 139.4, 136.5, 136.5, 134.7, 134.2, 131.2, 129.2, 129.1, 129.0, 128.6, 128.5, 126.5, 126.4, 122.0, 118.3, 39.8, 21.2;

HRMS (ESI) calcd for $C_{21}H_{18}NaO_2S$ ($M + H$)⁺ 357.0925, found 357.0919.

Phenyl 2-(2-(Phenylthio)phenyl)pent-4-enoate (3fa). 81% yield (73 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.52 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.48–7.47 (m, 1H), 7.38–7.35 (m, 1H), 7.32–7.26 (m, 3H), 7.24–7.16 (m, 6H), 6.94–6.93 (m, 2H), 5.82–5.75 (m, 1H), 5.08–5.05 (m, 1H), 5.02–5.00 (m, 1H), 4.76 (q, *J* = 6.8 Hz, 1H), 2.91–2.86 (m, 1H), 2.53–2.50 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 171.9, 150.7, 140.8, 136.9, 135.1, 134.8, 133.9, 129.3, 129.2, 129.1, 128.9, 128.2, 128.1, 126.4, 125.7, 121.3, 117.4, 47.8, 37.5; HRMS (ESI) calcd for $C_{23}H_{21}O_2S$ ($M + H$)⁺ 361.1257, found 361.1251.

M-Tolyl 2-(2-(Phenylthio)phenyl)pent-4-enoate (3ga). 83% yield (78 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.53 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.48 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.39–7.36 (m, 1H), 7.27–7.22 (m, 5H), 7.20–7.15 (m, 2H), 6.99–6.98 (m, 1H), 6.74–6.73 (m, 2H), 5.80–5.76 (m, 1H), 5.08–5.00 (m, 2H), 4.74 (q, *J* = 6.8 Hz, 1H), 2.91–2.86 (m, 1H), 2.54–2.49 (m, 1H), 2.30 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 171.9, 150.7, 140.9, 139.4, 136.9, 135.1, 134.9, 133.9, 129.3, 129.1, 128.9, 128.9, 128.2, 128.2, 126.5, 126.3, 121.9, 118.3, 117.4, 47.9, 37.5, 21.2; HRMS (ESI) calcd for $C_{24}H_{22}NaO_2S$ ($M + Na$)⁺ 397.1238, found 397.1220.

Naphthalen-2-yl 2-(2-(Phenylthio)phenyl)pent-4-enoate (3ha). 73% yield (75 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.80–7.76 (m, 2H), 7.73–7.72 (m, 1H), 7.58–7.56 (m, 1H), 7.51–7.50 (m, 1H), 7.48–7.35 (m, 5H), 7.28–7.22 (m, 3H), 7.18–7.16 (m, 1H), 7.08–7.06 (m, 1H), 5.84–5.81 (m, 1H), 5.11–5.03 (m, 2H), 4.82 (q, *J* = 7.0 Hz, 1H), 2.95–2.92 (m, 1H), 2.58–2.53 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 172.0, 148.3, 140.8, 136.9, 135.2, 134.9, 133.6, 131.3, 129.3, 129.2, 129.1, 129.0, 128.3, 128.2, 127.7, 127.6, 126.4, 126.4, 125.6, 120.9, 118.3, 117.5, 47.9, 37.5; HRMS (ESI) calcd for $C_{27}H_{22}NaO_2S$ ($M + H$)⁺ 433.1238, found 433.1237.

M-Tolyl 2-Phenyl-2-(2-(phenylthio)phenyl)acetate (3ia). 78% yield (80 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.48 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.38–7.30 (m, 7H), 7.28–7.24 (m, 3H), 7.22–7.17 (m, 4H), 7.00–6.99 (m, 1H), 6.80–6.78 (m, 2H), 5.92 (s, 1H), 2.31 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 171.0, 150.7, 141.1, 139.4, 137.5, 136.7, 135.1, 133.7, 129.9, 129.2, 129.1, 129.0, 128.9, 128.8, 128.8, 127.5, 126.6, 126.4, 121.9, 118.3, 54.2, 21.2; HRMS (ESI) calcd for $C_{27}H_{22}NaO_2S$ ($M + Na$)⁺ 433.1238, found 433.1229.

Ethyl 2-Phenyl-2-(2-(phenylthio)phenyl)acetate (3ja). 66% yield (57 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.44–7.42 (m, 1H), 7.35–7.30 (m, 3H), 7.25–7.22 (m, 7H), 7.17–7.14 (m, 3H), 5.72 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 1.18 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 172.3, 141.4, 138.1, 136.8, 134.9, 133.6, 129.8, 129.1, 129.0, 128.8, 128.6, 128.5, 128.1, 127.1, 126.2, 61.2, 54.1, 14.0; HRMS (ESI) calcd for $C_{22}H_{20}NaO_2S$ ($M + Na$)⁺ 371.1082, found 371.1079.

Ethyl 2-(2-(Phenylthio)phenyl)-2-(4-(trifluoromethyl)phenyl)acetate (3ka). 68% yield (72 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.52–7.51 (m, 2H), 7.46–7.45 (m, 1H), 7.39–7.33 (m, 4H), 7.26–7.21 (m, 3H), 7.17–7.16 (m, 1H), 7.10–7.09 (m, 2H), 5.79 (s, 1H), 4.15–4.13 (m, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 171.7, 142.0, 140.5, 136.4, 135.3, 133.7, 129.5, 129.3, 129.1, 129.0, 128.9, 128.5, 126.4, 125.4 (q, *J* = 3.7 Hz), 61.5, 53.8, 14.0; ¹⁹F NMR (565 MHz, CDCl₃) δ –62.6; HRMS (ESI) calcd for $C_{23}H_{19}F_3NaO_2S$ ($M + Na$)⁺ 439.0956, found 439.0957.

M-Tolyl 4-Phenyl-2-(2-(phenylthio)phenyl)butanoate (3la). 64% yield (70 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.53 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.38–7.35 (m, 1H), 7.26–7.22 (m, 4H), 7.21–7.15 (m, 6H), 7.12–7.11 (m, 2H), 6.99–6.97 (m, 1H), 6.74–6.73 (m, 2H), 4.68 (q, *J* = 6.7 Hz, 1H), 2.73–2.68 (m, 1H), 2.58–2.54 (m, 1H), 2.50–2.46 (m, 1H), 2.30 (s, 3H), 2.09–2.04 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 172.3, 150.6, 141.4, 141.3, 139.4, 137.0, 135.2, 131.0, 129.2, 129.1, 129.0, 128.9, 128.4, 128.3, 128.2, 128.1, 126.5, 126.3, 125.9, 121.9, 118.3, 47.8, 35.2, 33.8, 21.2; HRMS (ESI) calcd for $C_{29}H_{26}NaO_2S$ ($M + Na$)⁺ 461.1551, found 461.1544.

M-Tolyl 2-Cyclohexyl-2-(2-(phenylthio)phenyl)acetate (3ma). 65% yield (68 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.67–7.66 (m, 1H), 7.44–7.43 (m, 1H), 7.36–7.32 (m, 1H), 7.24–7.22 (m, 5H), 7.17–7.15 (m, 2H), 6.97–6.96 (m, 1H), 6.71–6.70 (m, 2H), 4.53 (d, *J* = 10.4 Hz, 1H), 2.29 (s, 3H), 2.17–2.13 (m, 1H), 2.04–2.02 (m, 1H), 1.82–1.77 (m, 1H), 1.65–1.64 (m, 2H), 1.36–1.31 (m, 2H), 1.26–1.24 (m, 1H), 1.19–1.13 (m, 2H), 0.94–0.88 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 172.3, 150.6, 139.9, 139.3, 137.2, 135.0, 134.7, 129.6, 129.0, 128.9, 128.7, 128.4, 127.9, 126.4, 126.3, 122.0, 118.3, 53.8, 41.9, 31.9, 29.9, 26.2, 26.1, 26.0, 21.2; HRMS (ESI) calcd for $C_{27}H_{28}NaO_2S$ ($M + Na$)⁺ 439.1708, found 439.1694.

4-Chlorophenyl 2-Cyclohexyl-2-(2-(phenylthio)phenyl)acetate (3na). 60% yield (65 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.64–7.62 (m, 1H), 7.45–7.44 (m, 1H), 7.37–7.32 (m, 2H), 7.26–7.22 (m, 6H), 7.16–7.14 (m, 1H), 6.84–6.82 (m, 2H), 4.52 (d, *J* = 10.4 Hz, 1H), 2.14–2.11 (m, 1H), 2.00–1.97 (m, 1H), 1.79–1.77 (m, 1H), 1.64–1.62 (m, 2H), 1.35–1.25 (m, 3H), 1.19–1.14 (m, 2H), 0.95–0.87 (m, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 172.1, 149.1, 139.6, 137.1, 135.0, 134.8, 130.9, 129.5, 129.2, 129.1, 128.8, 128.4, 128.1, 126.3, 122.8, 53.7, 41.8, 31.9, 29.9, 26.2, 26.1, 26.0; HRMS (ESI) calcd for $C_{26}H_{25}ClNaO_2S$ ($M + Na$)⁺ 459.1161, found 459.1155.

Ethyl 2-(2-(Phenylthio)phenyl)acetate (3oa). 83% yield (56 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.41 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.33 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.31–7.28 (m, 1H), 7.25–7.22 (m, 3H), 7.17–7.14 (m, 3H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.83 (s, 2H), 1.20 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 171.1, 136.9, 136.6, 134.5, 134.2, 131.0, 129.2, 129.0, 128.4, 128.2, 126.3, 60.8, 39.7, 14.1; HRMS (ESI) calcd for $C_{16}H_{16}NaO_2S$ ($M + Na$)⁺ 295.0769, found 295.0766.

General Procedure for HOTf-Catalyzed, Solvent-Free Oxyarylation of Thioethers. To a mixture of thioalkyne **4a** (52.5 mg, 0.25 mmol) and diphenyl sulfoxide **2a** (101.0 mg, 0.5 mmol) was added HOTf (3.8 mg, 0.025 mmol) under an air atmosphere. After stirring at 70 °C for 1 h, the reaction mixture was quenched with NaHCO₃ (50.0 mg), extracted with EtOAc, washed with brine, dried over anhydrous Na₂SO₄, and concentrated. Column chromatography on silica gel (EtOAc/petroleum ether = 1:50) gave **5aa** (86.5 mg, 84% yield) as a colorless oil.

S-Phenyl 2-Phenyl-2-(2-(phenylthio)phenyl)ethanethioate (5aa). ¹H NMR (600 MHz, CDCl₃) δ 7.46 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.36–7.29 (m, 10H), 7.28–7.26 (m, 4H), 7.20–7.18 (m, 3H), 6.05 (s, 1H); ¹³C NMR (150 MHz, CDCl₃) δ 196.9, 140.6, 137.4, 136.8, 135.2, 134.4, 133.9, 130.1, 129.3, 129.2, 129.2, 129.1, 128.7, 128.7, 128.5, 128.0, 127.5, 126.4, 61.5; HRMS (ESI) calcd for $C_{26}H_{20}NaOS_2$ ($M + Na$)⁺ 435.0853, found 435.0859.

S-Ethyl 2-Phenyl-2-(2-(phenylthio)phenyl)ethanethioate (5ba). 77% yield (70 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.42 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.40 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.30–7.27 (m, 3H), 7.24–7.21 (m, 6H), 7.17–7.15 (m, 3H), 5.92 (s, 1H), 2.84 (q, *J* = 7.4 Hz, 2H), 1.19 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 198.9, 140.7, 137.8, 136.7, 134.9, 134.1, 129.9, 129.3, 129.1, 129.1, 128.5, 128.5, 128.3, 127.3, 126.3, 61.8, 24.0, 14.4; HRMS (ESI) calcd for $C_{22}H_{20}NaOS_2$ ($M + Na$)⁺ 387.0853, found 387.0859.

S-Phenyl 2-(2-(Phenylthio)phenyl)hexanethioate (5ca). 92% yield (90 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.48–7.45 (m, 2H), 7.35–7.34 (m, 4H), 7.30–7.23 (m, 7H), 7.20–7.17 (m, 1H), 4.73 (t, *J* = 7.4 Hz, 1H), 2.17–2.11 (m, 1H), 1.73–1.71 (m, 1H), 1.26–1.14 (m, 4H), 0.81 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 198.4, 140.7, 136.9, 134.9, 134.3, 134.2, 129.4, 129.1, 129.1, 129.0, 128.8, 128.5, 128.1, 128.0, 126.4, 56.0, 33.6, 29.5, 22.4, 13.8; HRMS (ESI) calcd for $C_{24}H_{24}NaOS_2$ ($M + Na$)⁺ 415.1166, found 415.1174.

S-Methyl 2-(2-(Phenylthio)phenyl)hexanethioate (5da). 91% yield (75 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.45 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.41 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.33–7.31 (m, 1H), 7.28–7.27 (m, 1H), 7.26–7.25 (m, 1H), 7.23–7.19 (m, 4H), 4.63 (t, *J* = 7.4 Hz, 1H), 2.22 (s, 3H), 2.14–2.08 (m, 1H), 1.73–1.68 (m, 1H), 1.25–1.22 (m, 4H), 0.81 (t, *J* = 7.2 Hz, 3H); ¹³C NMR (150 MHz,

CDCl₃) δ 200.8, 140.9, 136.9, 134.7, 134.4, 129.6, 129.1, 128.7, 128.3, 128.0, 126.4, 56.1, 33.4, 29.5, 22.5, 13.8, 11.9; HRMS (ESI) calcd for C₁₉H₂₂NaOS₂ (M + Na)⁺ 353.1010, found 353.1008.

S-Ethyl 2-(2-(Phenylthio)phenyl)octanethioate (5ea). 95% yield (88 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.44 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.42 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.33–7.30 (m, 1H), 7.27–7.16 (m, 6H), 4.60 (t, *J* = 7.4 Hz, 1H), 2.84–2.76 (m, 2H), 2.10–2.08 (m, 1H), 1.70–1.67 (m, 1H), 1.20–1.16 (m, 11H), 0.83 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 200.5, 141.0, 137.0, 134.8, 134.2, 129.5, 129.0, 128.6, 128.3, 127.9, 126.3, 56.2, 33.6, 31.5, 29.0, 27.3, 23.5, 22.5, 14.5, 14.0; HRMS (ESI) calcd for C₂₂H₂₈NaOS₂ (M + Na)⁺ 395.1479, found 395.1491.

S-Ethyl 2-(2-(Phenylthio)phenyl)decanethioate (5fa). 96% yield (96 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 7.45–7.42 (m, 2H), 7.33–7.30 (m, 1H), 7.26–7.18 (m, 6H), 4.60 (t, *J* = 7.4 Hz, 1H), 2.83–2.77 (m, 2H), 2.10–2.08 (m, 1H), 1.69–1.67 (m, 1H), 1.30–1.15 (m, 15H), 0.87–0.85 (m, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 200.5, 141.0, 137.0, 134.8, 134.2, 129.5, 129.0, 128.6, 128.3, 127.9, 126.3, 56.2, 33.6, 31.8, 29.3, 29.3, 29.1, 27.3, 23.5, 22.6, 14.5, 14.1; HRMS (ESI) calcd for C₂₄H₃₂NaOS₂ (M + Na)⁺ 423.1792, found 423.1784.

General Procedure for the Synthesis of Multifunctional Aldehyde and Ketone from Thioester. To a reaction vessel was added thioester **5fa** (100 mg, 0.25 mmol), acetone (2 mL), triethylsilane (87.2 mg, 0.75 mmol), and Pd/C (4.4 mg, 0.0125 mmol) and the mixture was stirred for 10 h at rt. Et₂O (15 mL) was added and the suspension was washed with water (10 mL). The organic layer was dried over MgSO₄, filtered, and evaporated. Column chromatography on silica gel (EtOAc/petroleum ether =1:50) gave **6** (67.2 mg, 79% yield) as a colorless oil.

2-(2-(Phenylthio)phenyl)decanal (6). 79% yield (67.2 mg); colorless oil; ¹H NMR (600 MHz, CDCl₃) δ 9.57 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.29–7.25 (m, 3H), 7.20–7.16 (m, 4H), 4.28 (t, *J* = 7.0 Hz, 1H), 2.12–2.05 (m, 1H), 1.67–1.63 (m, 1H), 1.28–1.16 (m, 12H), 0.86 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 200.6, 139.6, 136.8, 135.2, 134.7, 129.3, 129.2, 129.2, 128.9, 128.3, 126.5, 55.9, 31.8, 29.9, 29.5, 29.3, 29.2, 27.1, 22.6, 14.1; HRMS (ESI) calcd for C₂₂H₂₈NaOS (M + Na)⁺ 363.1759, found 363.1764.

Thioester **5fa** (100 mg, 0.25 mmol), Cu (I) thiophene-2-carboxylate (71.6 mg, 0.375 mmol), boronic acid (33.6 mg, 0.275 mmol), Pd₂dba₃·CHCl₃ (2.6 g, 0.0025 mmol), and tris-2-furylphosphine (1.7 g, 0.0075 mmol) were placed in a reaction vessel that was flushed with argon. Acetone (5 mL) was added and the mixture was stirred for 18 h at 50 °C. Et₂O (15 mL) was added and the suspension was washed with 5% aq. HCl (10 mL) and water (10 mL). The organic layer was dried over MgSO₄, filtered, and evaporated. Column chromatography on silica gel (EtOAc/petroleum ether =1:50) gave **7** (78.2 mg, 75% yield) as a colorless oil.

1-Phenyl-2-(2-(phenylthio)phenyl)decan-1-one (7). 75% yield (78.2 mg); colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 8.01–7.93 (m, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.39 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.32–7.28 (m, 4H), 7.26–7.18 (m, 5H), 7.16–7.12 (m, 1H), 5.32 (dd, *J* = 8.0, 6.0 Hz, 1H), 2.19–2.08 (m, 1H), 1.60–1.56 (m, 1H), 1.33–1.16 (m, 12H), 0.86 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 200.3, 142.0, 136.9, 136.5, 134.7, 133.3, 132.8, 129.7, 129.7, 129.2, 128.7, 128.4, 128.4, 127.6, 126.6, 49.9, 34.2, 31.8, 29.6, 29.4, 29.2, 27.9, 22.6, 14.1; HRMS (ESI) calcd for C₂₈H₃₂NaOS (M + Na)⁺ 439.2072, found 439.2067.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00535.

Detailed experimental procedures for Scheme 2. Copies of ¹H NMR spectra of compounds **1a–1c**, **1g**, **1m**, **4b–4c**, and **4f**; ¹H NMR, ¹³C NMR spectra of compounds **3aa–3ak**, **3ba–3oa**, **5aa–5fa**, **6**, and **7** (PDF)

AUTHOR INFORMATION

Corresponding Authors

*ztanze@gmail.com.

*gangguo@zjnu.cn.

Notes

The authors declare no competing financial interest.

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REFERENCES

- (1) (a) Shen, T. Y. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 460. (b) Edmondson, S.; Danishefsky, S. J.; Sepp-Lorenzino, L.; Rosen, N. *J. Am. Chem. Soc.* **1999**, *121*, 2147. (c) Delorbe, J. E.; Lotz, M. D.; Martin, S. F. *Org. Lett.* **2010**, *12*, 1576. (d) Yang, Y.; Philips, D.; Pan, S. *J. Org. Chem.* **2011**, *76*, 1902. (e) Desai, L. V.; Hay, M. B.; Leahy, D. K.; Wei, C.; Fanfair, D.; Rosner, T.; Hsiao, Y. *Tetrahedron* **2013**, *69*, 5677.
- (2) For recent selected examples of using carbonyl compounds as arylation reagents, see: (a) Potukuchi, H. K.; Spork, A. P.; Donohoe, T. J. *Org. Biomol. Chem.* **2015**, *13*, 4367. (b) Yang, J.; Chen, X.; Wang, Z. *Tetrahedron Lett.* **2015**, *56*, 5673. (c) Zhang, S.-L.; Yu, Z.-L. *J. Org. Chem.* **2016**, *81*, 57.
- (3) For recent selected examples of Buchwald-Hartwig arylation reactions, see: (a) Shelby, Q.; Kataoka, N.; Mann, G.; Hartwig, J. F. *J. Am. Chem. Soc.* **2000**, *122*, 10718. (b) Hama, T.; Liu, X.; Culkun, D. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2003**, *125*, 11176. (c) Ge, S.; Arlow, S. I.; Mormino, M. G.; Hartwig, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 14401. (d) Vinogradova, E. V.; Zhang, C.; Spokoiny, A. M.; Pentelute, B. L.; Buchwald, S. L. *Nature* **2015**, *526*, 687. (e) Ruiz-Castillo, P.; Blackmond, D. G.; Buchwald, S. L. *J. Am. Chem. Soc.* **2015**, *137*, 3085. (f) Park, N. H.; Vinogradova, E. V.; Surry, D. S.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2015**, *54*, 8259.
- (4) For some examples of using organobismuth reagents as arylation reagents, see: (a) Barton, D. H. R.; Finet, J.-P. *Pure Appl. Chem.* **1987**, *59*, 937. (b) Finet, J.-P. *Chem. Rev.* **1989**, *89*, 1487. (c) Elliott, G. I.; Konopelski, J. P. *Tetrahedron* **2001**, *57*, 5683. (d) Ooi, T.; Goto, R.; Maruoka, K. *J. Am. Chem. Soc.* **2003**, *125*, 10494. (e) Matano, Y.; Imahori, H. *J. Org. Chem.* **2004**, *69*, 5505. (f) Koech, P. K.; Kriche, M. J. *J. Am. Chem. Soc.* **2004**, *126*, 5350.
- (5) For some examples of using organolead reagents, see: (a) Orito, K.; Sasaki, T.; Sugimoto, H. *J. Org. Chem.* **1995**, *60*, 6208. (b) Morgan, J.; Pinhey, J. T.; Rowe, B. A. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1005. (c) Elliott, G. I.; Konopelski, J. P.; Olmstead, M. M. *Org. Lett.* **1999**, *1*, 1867. (d) Deng, H.; Konopelski, J. P. *Org. Lett.* **2001**, *3*, 3001. (e) Xia, J.; Brown, L. E.; Konopelski, J. P. *J. Org. Chem.* **2007**, *72*, 6885.
- (6) For recent reviews and examples on polyvalent iodine, see: (a) Aggarwal, V. K.; Olofsson, B. *Angew. Chem., Int. Ed.* **2005**, *44*, 5516. (b) Zhdankin, V. V.; Stang, P. *Chem. Rev.* **2008**, *108*, 5299. (c) Merritt, E. A.; Olofsson, B. *Angew. Chem., Int. Ed.* **2009**, *48*, 9052. (d) Eastman, K.; Baran, P. S. *Tetrahedron* **2009**, *65*, 3149. (e) Norrby, P.-O.; Petersen, T. B.; Bielawski, M.; Olofsson, B. *Chem. - Eur. J.* **2010**, *16*, 8251. (f) Allen, A. E.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2011**, *133*, 4260. (g) Bigot, A.; Williamson, A. E.; Gaunt, M. J. *J. Am. Chem. Soc.* **2011**, *133*, 13778. (h) Harvey, J. S.; Simonovich, S. P.; Jamison, C. R.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2011**, *133*, 13782.
- (7) For recent selected examples of using arynes as arylation reagents, see: (a) Tambar, U. K.; Stoltz, B. M. *J. Am. Chem. Soc.* **2005**, *127*, 5340. (b) Ramtohl, Y.; Chartrand, A. *Org. Lett.* **2007**, *9*, 1029. (c) Liu, Y.-L.; Liang, Y.; Pi, S.-F.; Li, J.-H. *J. Org. Chem.* **2009**, *74*, 5691. (d) Tadross, P. M.; Gilmore, C. D.; Bugga, P.; Virgil, S. C.; Stoltz, B. M. *Org. Lett.* **2010**, *12*, 1224. (e) Dhokale, R. A.; Thakare, P. R.;

Mhaske, S. B. *Org. Lett.* **2012**, *14*, 3994. (f) Mohanan, K.; Coquerel, Y.; Rodriguez, J. *Org. Lett.* **2012**, *14*, 4686.

(8) (a) Claisen, L. *Ber. Dtsch. Chem. Ges.* **1912**, *45*, 3157. (b) *The Claisen Rearrangement*; Hiersemann, M., Nubbemeyer, U., Eds.; Wiley-VCH: Weinheim, 2007. (c) Martín Castro, A. M. *Chem. Rev.* **2004**, *104*, 2939. (d) Eberhart, A. J.; Procter, D. J. *Angew. Chem., Int. Ed.* **2013**, *52*, 4008. (e) Pecak, W. H.; Son, J.; Burnstine, A. J.; Anderson, L. L. *Org. Lett.* **2014**, *16*, 3440. (f) Eberhart, A. J.; Shriver, H. J.; Álvarez, E.; Carrér, A.; Zhang, Y.; Procter, D. J. *Chem. - Eur. J.* **2015**, *21*, 7428.

(9) Shapiro, N. D.; Toste, F. D. *J. Am. Chem. Soc.* **2007**, *129*, 4160.

(10) (a) Li, G.; Zhang, L. *Angew. Chem., Int. Ed.* **2007**, *46*, 5156. (b) Lu, B.; Li, Y.; Wang, Y.; Aue, D. H.; Luo, Y. D.; Zhang, L. *J. Am. Chem. Soc.* **2013**, *135*, 8512.

(11) (a) Cuenca, A. B.; Montserrat, S.; Hossain, K. M.; Mancha, G.; Lledós, A.; Medio-Simón, M.; Ujaque, G.; Asensio, G. *Org. Lett.* **2009**, *11*, 4906. (b) Barrett, M. J.; Davies, P. W.; Grainger, R. S. *Org. Biomol. Chem.* **2015**, *13*, 8676.

(12) For recent selected examples of metal-free direct arylations, see: (a) Dichiarante, V.; Fagnoni, M. *Synlett* **2008**, 2008, 787. (b) Małosza, M. *Chem. Soc. Rev.* **2010**, *39*, 2855. (c) Eberhart, A. J.; Imbriglio, J. E.; Procter, D. J. *Org. Lett.* **2011**, *13*, 5882. (d) Beyer, A.; Buendia, J.; Bolm, C. *Org. Lett.* **2012**, *14*, 3948. (e) Xu, Q.-L.; Gao, H.; Yousufuddin, M.; Ess, D. H.; Kürti, L. *J. Am. Chem. Soc.* **2013**, *135*, 14048. (f) Thompson, A. D.; Huestis, M. P. *J. Org. Chem.* **2013**, *78*, 762. (g) Theunissen, C.; Métayer, B.; Henry, N.; Compain, G.; Marrot, J.; Martin-Mingot, A.; Thibaudeau, S.; Evano, G. *J. Am. Chem. Soc.* **2014**, *136*, 12528. (h) Hu, G.; Xu, J.; Li, P. *Org. Lett.* **2014**, *16*, 6036. (i) Yamaoka, Y.; Yoshida, T.; Shinozaki, M.; Yamada, K.-I.; Takasu, K. *J. Org. Chem.* **2015**, *80*, 957.

(13) (a) Huang, X.; Patil, M.; Farès, C.; Thiel, W.; Maulide, N. *J. Am. Chem. Soc.* **2013**, *135*, 7312. (b) Peng, B.; Geerdink, D.; Maulide, N. *J. Am. Chem. Soc.* **2013**, *135*, 14968. (c) Peng, B.; Geerdink, D.; Farès, C.; Maulide, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 5462.

(14) Peng, B.; Huang, X.; Xie, L.-G.; Maulide, N. *Angew. Chem., Int. Ed.* **2014**, *53*, 8718.

(15) For our recent works on ynol ethers, see: (a) Cui, W.; Yin, J.; Zheng, R.; Cheng, C.; Bai, Y.; Zhu, G. *J. Org. Chem.* **2014**, *79*, 3487. (b) Bai, Y.; Yin, J.; Liu, Z.; Zhu, G. *J. Org. Chem.* **2015**, *80*, 10226. (c) Hu, L.; Che, C.; Tan, Z.; Zhu, G. *Chem. Commun.* **2015**, 51, 16641.

(16) For selected reports on ynol ethers since 2015, see: (a) Babu, M. H.; Dwivedi, V.; Kant, R.; Reddy, M. S. *Angew. Chem., Int. Ed.* **2015**, *54*, 3783. (b) Fabig, S.; Haberhauer, G.; Gleiter, R. *J. Am. Chem. Soc.* **2015**, *137*, 1833. (c) Saito, N.; Sun, Z.; Sato, Y. *Chem. - Asian J.* **2015**, *10*, 1170. (d) Zhao, W.; Qian, H.; Li, Z.; Sun, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 10005. (e) Ng, K.; Tran, V.; Minehan, T. *Tetrahedron Lett.* **2016**, *57*, 415.

(17) For recent reviews and examples on solvent-free reactions, see: (a) Tanaka, K.; Toda, F. *Chem. Rev.* **2000**, *100*, 1025. (b) Martins, M. A. P.; Frizzo, C. P.; Moreira, D. N.; Buriol, L.; Machado, P. *Chem. Rev.* **2009**, *109*, 4140. (c) Chen, C.; Hecht, M. B.; Kavara, A.; Brennessel, W. W.; Mercado, B. Q.; Weix, D. J.; Holland, P. L. *J. Am. Chem. Soc.* **2015**, *137*, 13244.

(18) During the submission of this manuscript, Maulide reported the synthesis of α -arylated ketones via HOTf catalyzed reaction of simple alkynes with aryl sulfoxides under solvent free conditions: Kaiser, D.; Veiros, L. F.; Maulide, F. *Chem. - Eur. J.* **2016**, *22*, 4727.

(19) Jouvin, K.; Bayle, A.; Legrand, F.; Evano, G. *Org. Lett.* **2012**, *14*, 1652 Although a copper catalyzed method was employed to prepare the ynol ethers, many alternative transition-metal-free synthetic approaches are also available..

(20) Kimura, M.; Seki, M. *Tetrahedron Lett.* **2004**, *45*, 3219.

(21) Liebeskind, L. S.; Srogl, J. *J. Am. Chem. Soc.* **2000**, *122*, 11260.

(22) Hack, D.; Chauhan, P.; Deckers, K.; Hermann, G. N.; Mertens, L.; Raabe, G.; Enders, D. *Org. Lett.* **2014**, *16*, 5188.

(23) Jouvin, K.; Coste, A.; Bayle, A.; Legrand, F.; Karthikeyan, G.; Tadiparthi, K.; Evano, G. *Organometallics* **2012**, *31*, 7933.

(24) Bieber, L. W.; da Silva, M. F. *Tetrahedron Lett.* **2007**, *48*, 7088.

(25) Zheng, W.; Zheng, F.; Hong, Y.; Hu, L. *Heteroat. Chem.* **2012**, *23*, 105.

(26) Ding, S.; Jia, G.; Sun, J. *Angew. Chem., Int. Ed.* **2014**, *53*, 1877.

(27) Yang, Z.; Chen, X.; Kong, W.; Xia, S.; Zheng, R.; Luo, F.; Zhu, G. *Org. Biomol. Chem.* **2013**, *11*, 2175.