Note

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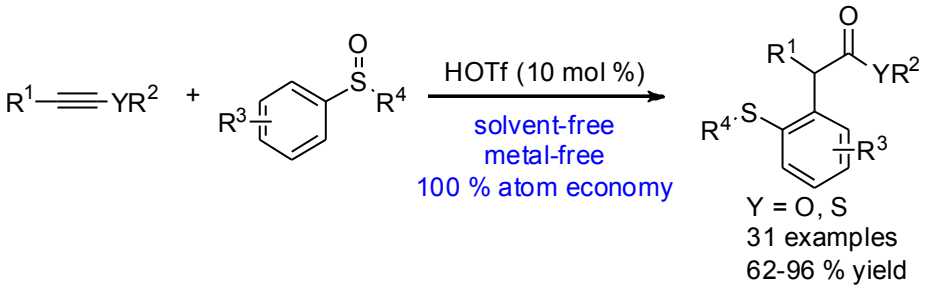
HOTf-Catalyzed, Solvent-free Oxyarylation of Ynol Ethers and Thioethers

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*

ztanze@gmail.com gangguo@zjnu.cn



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 proceeds under very mild conditions. It was found that the reaction can be run under air and best yields are obtained under solvent-free condition.

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 Tf_2O 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 sulfoxide and subsequent [3,3]-sigmatropic rearrangement, a variety of α-arylated oxazolidinones were obtained in good yields. As part of our continuing interest on 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 run under solvent-free condition (Scheme 1, Eq. 3).[17,18]

Scheme 1. Approaches to α-arylated carbonyl compounds from alkyne derivatives

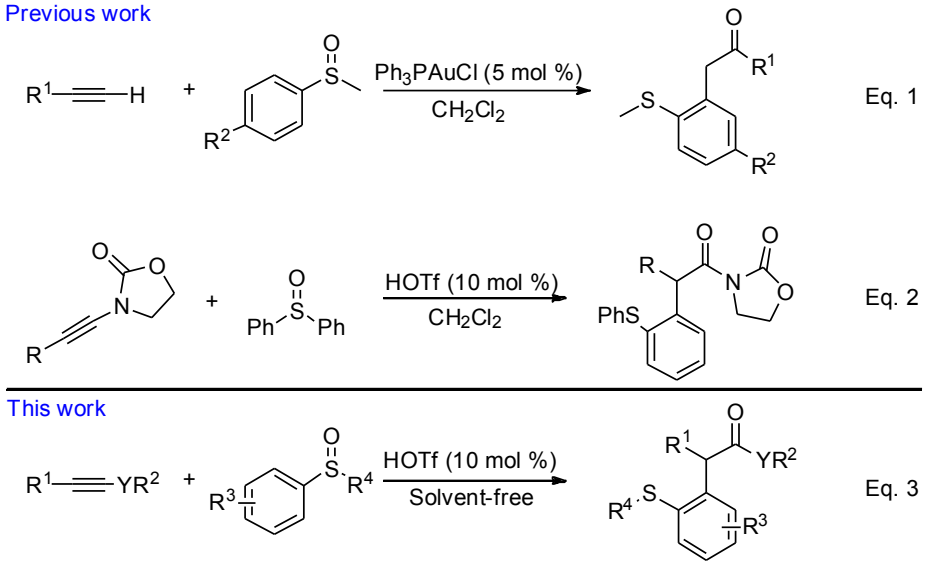
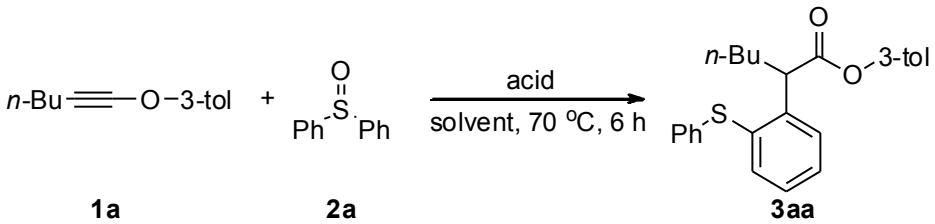


Table 1. Screening of the Reaction Conditions for HOTf-catalyzed, solvent-free oxyarylation of ynol ethers of 1a[a]



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

entry	**2a** (equiv)	acid (equiv)	solvent	yield (%)[b]
1	1.0	HOTf (0.1)	CH_2Cl_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_2Cl_2	27(32)[c]
7	2.0	HOTf (1.0)	CH_2Cl_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

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (m equiv), acid (n equiv), 70 °C, 6 h. [b]Isolated yield. [c]The reaction was run at 100 °C for 6 h. [d]The reaction was run under an air atmosphere. [e]TFA = trifluoroacetic acid.

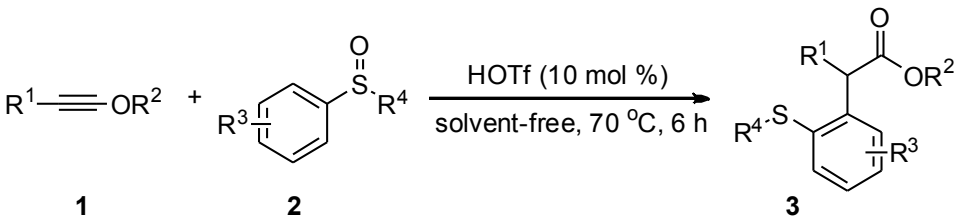
Initially, ynol ether **1a**, which was easily prepared by Evano's method,[19] was chosen for evaluating the reaction parameters. As a result, treating **1a** with 1.0 equiv of diphenyl sulfoxide (**2a**), 10 mol % of HOTf in CH_2Cl_2 at 70 °C for 6 h generated α-arylated ester **3aa** in 13% yield (Table 1, entry 1). Encouraged by this result, we further investigated other conditions for this reaction. Replacing CH_2Cl_2 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, 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 ^{o}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 methyl, methoxy, chloro, aldehyde, 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 72-92% (Table 2, entries 5-10). Notably, an alkyl pyridine 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 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 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 R^2 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 was also an effective substrate, giving **3oa** in 83% yield after the reaction was run at room temperature for 6 h

(Table 2, entry 27).

Table 2. Scope of HOTf-catalyzed, solvent-free oxyarylation of ynol ethers[a]



1 **2** **3**

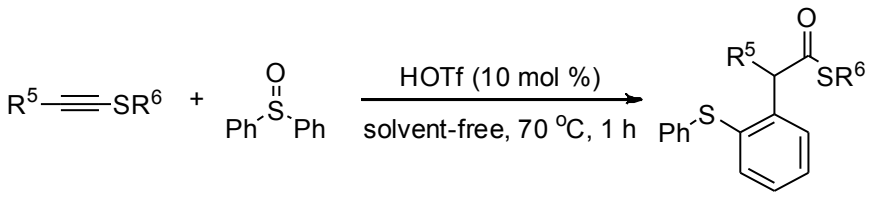
entry	R^1/R^2	R^3/R^4	yield (%)[b]
1	*n*-Bu/3-tol (**1a**)	Ph/Ph (**2a**)	84 (**3aa**)
2	**1a**	4-MeC_6H_4/4-MeC_6H_4(**2b**)	89 (**3ab**)
3	**1a**	4-ClC_6H_4/4-ClC_6H_4 (**2c**)	71 (**3ac**)
4	**1a**	4-$NO_2C_6H_4$/4-$NO_2C_6H_4$(**2d**)	67 (**3ad**)[c]
5	**1a**	Ph/Me (**2e**)	79 (**3ae**)
6	**1a**	4-MeC_6H_4/Me (**2f**)	77 (**3af**)
7	**1a**	4-$MeOC_6H_4$/Me (**2g**)	83 (**3ag**)
8	**1a**	4-ClC_6H_4/Me (**2h**)	70 (**3ah**)
9	**1a**	4-$HCOC_6H_4$/Me (**2i**)	75 (**3ai**)
10	**1a**	Ph/*i*-Pr (**2j**)	92 (**3aj**)
11	**1a**	Py/Me (**2k**)	81 (**3ak**)
12	**1a**	4-$NH_2C_6H_4$/Me (**2l**)	trace
13	**1a**	Ph/vinyl (**2m**)	trace
14	*n*-Bu/Ph (**1b**)	**2a**	80 (**3ba**)
15	*n*-Bu/4-ClC_6H_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-$CF_3C_6H_4$/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_6H_4 (**1n**)	**2a**	60 (**3na**)
27	H/Et (**1o**)	**2a**	83 (**3oa**)[e]

[a]Reaction conditions: **1** (0.25 mmol), **2** (2 equiv), HOTf (0.1 equiv), under air, 70 °C, 6 h. [b]Isolated yield. [c]CH_2Cl_2 (0.2 ml) was added to the standard conditions. [d]Run at 80 °C for 10 h. [e]Run at room temperature for 6 h.

Subsequently, we explored the acid-promoted oxyarylation reaction of thioethers (Table 3). As a result, we found that the oxyarylation process exhibited good compatibility with a wide variety of substrates under the optimal reaction conditions 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.

Table 3. Scope of HOTf-catalyzed, solvent-free oxyarylation of thioethers[a]



4 **2a** **5**

entry	R^5/R^6	yield (%)[b]
1	Ph/Ph (**4a**)	84 (**5aa**)
2	Ph/Et (**4b**)	77 (**5ba**)
3	*n*-Bu/Ph (**4c**)	92 (**5ca**)
4	*n*-Bu/Me (**4d**)	91 (**5da**)
5	*n*-C_6H_{13}/Et (**4e**)	95 (**5ea**)
6	*n*-C_8H_{17}/Et (**4f**)	96 (**5fa**)

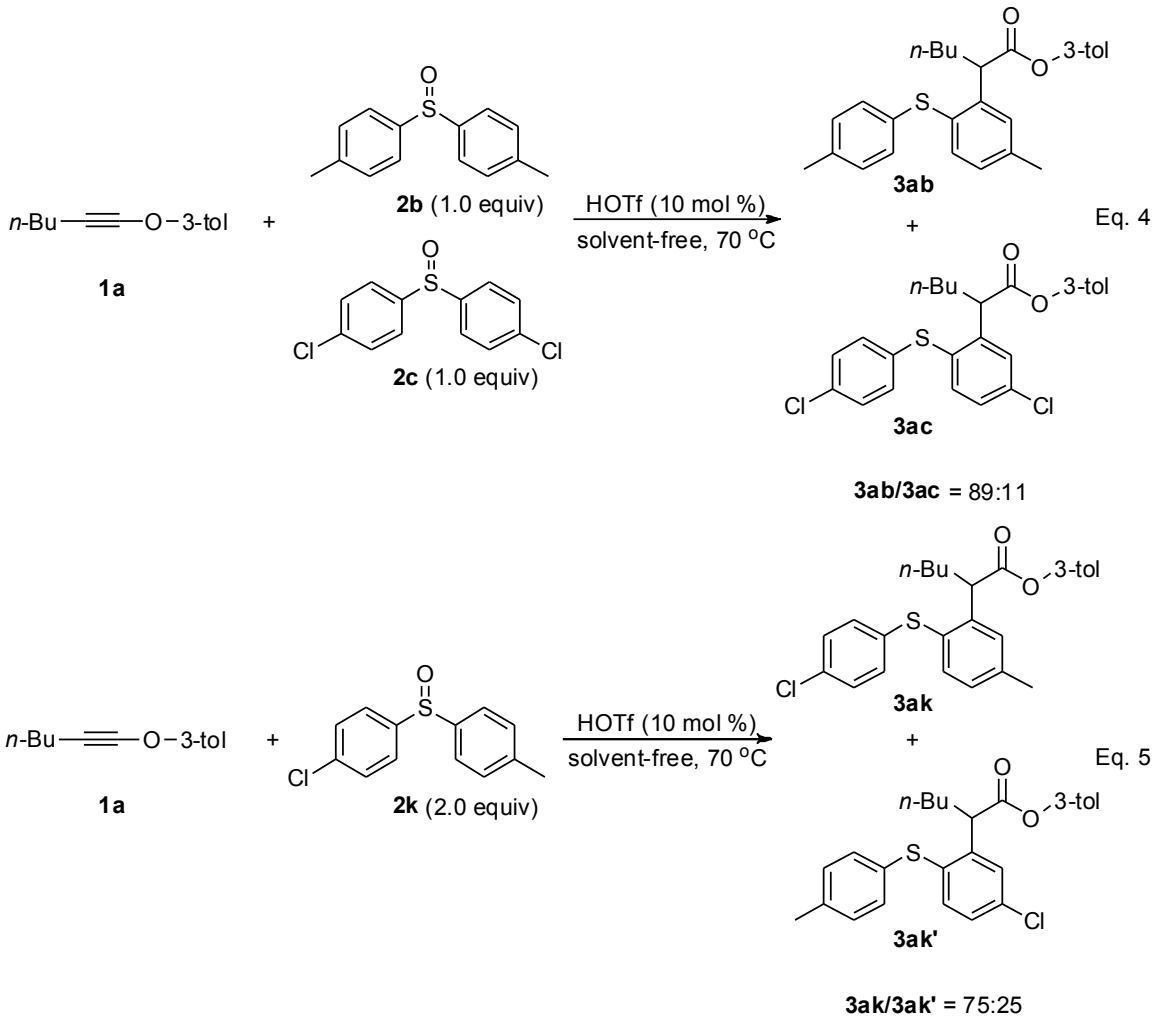
[a]Reaction conditions: **1a** (0.25 mmol), **2a** (2 equiv), HOTf (0.1 equiv), under air, 70 °C, 1 h. [b]Isolated yield.

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 a 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). Form 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 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 10h, aldehyde **6** was generated in 79% yield

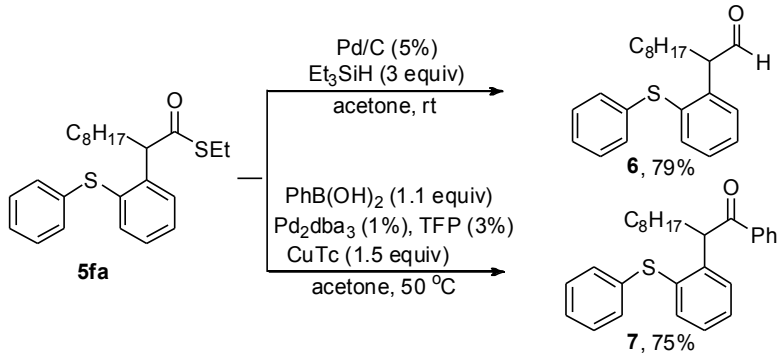
through the Fukuyama reduction (Scheme 3).[20] Furthermore, ketone **7** could be obtained in 75% yield via Pd-catalyzed thiol ester–boronic acid cross-coupling (Scheme 3).[21] As such, we have developed an operationally simple and highly efficient method for the synthesis of multifunctional aldehydes and ketones, an important class of building blocks in medicinal and biochemistry.

Scheme 2. Control experiments with 2b[a], 2c[a], and 2k[b]

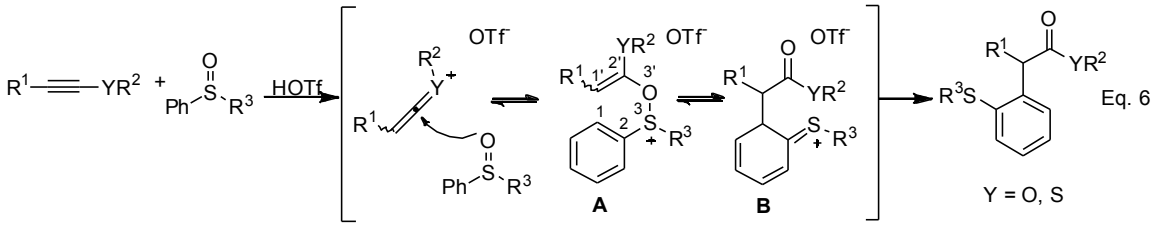


[a]Reaction conditions: **1a** (0.25 mmol), **2b** (1 equiv), **2c** (1 equiv), HOTf (0.1 equiv), under air, 70 °C, 6 h. [b]2 equiv of **2k** was used instead of **2b** and **2c**.

Scheme 3. Synthesis of multifunctional aldehyde and ketone from thioester



Scheme 4. Possible reaction mechanism



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. ^{1}H and ^{13}C NMR spectra were measured on a 600 or 400 MHz NMR spectrometer using $CDCl_3$ 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 eq.) and tetrabromomethane (2 eq.) in abs. DCM (0.15 M) was stirred at 0 °C for 30 minutes. The aldehyde was added over a period of five minutes, and the mixture as stirred at 0 °C for one hour. 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 $MgSO_4$ 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 ynol ethers from vinyl dibromides (Second step)[19]:

A 15 mL pressure tube was charged with the phenol (6.7 mmol), 2,2'-bipyridine (310 mg, 2.0 mmol), K_3PO_4 (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 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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 sulfides from terminal alkynes[25]:

To a THF solution of terminal alkynes (9.0 mmol), BuLi/Hex (8.5 mmol) was added at 0 ^{o}C. The mixture was stirred for 30 min. Dialkyl disulfides (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 x 3). The combined organic layer was washed with brine and then dried over Na_2SO_4 and concentrated in vacuo. The crude mixture was purified by silica gel column chromatography (with hexane) to provide Alkynyl Sulfides.

*Ethyl(phenylethynyl)sulfane (**4b**)*[26]. 68% yield (991 mg, >99% purity, determined by GC); colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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□ for 6 h, the reaction mixture was quenched with $NaHCO_3$ (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**)*. ^{1}H 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 $C_{25}H_{26}NaO_2S$ $(M + Na)^+$ 413.1551, found 413.1544.

*M-tolyl 2-(5-methyl-2-(p-tolylthio)phenyl)hexanoate (**3ab**)*. 89% yield (93 mg); colorless oil; ^{1}H 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 $C_{27}H_{30}NaO_2S$ $(M + Na)^+$ 441.1864, found 441.1857.

*M-tolyl 2-(5-chloro-2-((4-chlorophenyl)thio)phenyl)hexanoate (**3ac**)*. 71% yield (81 mg); colorless oil; ^{1}H 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 $C_{25}H_{24}Cl_2NaO_2S$ $(M + Na)^+$ 481.0772, found 481.0773.

*M-tolyl 2-(5-nitro-2-((4-nitrophenyl)thio)phenyl)hexanoate (**3ad**)*. 67% yield (80 mg); colorless oil; ^{1}H 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 $C_{25}H_{24}N_2NaO_6S$ $(M + Na)^+$ 503.1253, found 503.1255.

*M-tolyl 2-(2-(methylthio)phenyl)hexanoate (**3ae**)*. 79% yield (65 mg); colorless oil; ^{1}H 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 $C_{20}H_{24}NaO_2S$ $(M + Na)^+$ 351.1395, found 351.1391.

*M-tolyl 2-(5-methyl-2-(methylthio)phenyl)hexanoate (**3af**)*. 77% yield (66 mg); colorless oil; ^{1}H 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 $C_{21}H_{26}NaO_2S$ $(M + Na)^+$ 365.1551, found 365.1548.

*M-tolyl 2-(5-methoxy-2-(methylthio)phenyl)hexanoate (**3ag**)*. 83% yield (74 mg); colorless oil; ^{1}H 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 $C_{21}H_{26}NaO_3S$ $(M + Na)^+$ 381.1500, found 381.1486.

M-tolyl 2-(5-chloro-2-(methylthio)phenyl)hexanoate（***3ah***). 70% yield (63 mg); colorless oil; ^{1}H 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 $C_{20}H_{23}ClNaO_2S$ $(M + Na)^+$ 385.1005, found 385.1002.

M-tolyl 2-(5-formyl-2-(methylthio)phenyl)hexanoate（***3ai***). 75% yield (67 mg); colorless oil; ^{1}H 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 $C_{21}H_{24}NaO_3S$ $(M + Na)^+$ 379.1344, found 379.1352.

*M-tolyl 2-(2-(isopropylthio)phenyl)hexanoate (**3aj**)*. 92% yield (82 mg); colorless oil; ^{1}H 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 $C_{22}H_{28}NaO_2S$ $(M + Na)^+$ 379.1708, found 379.1701.

*M-tolyl 2-(2-(methylthio)pyridin-3-yl)hexanoate (**3ak**)*. 81% yield (67 mg); colorless oil; ^{1}H 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 $C_{19}H_{23}NNaO_2S$ $(M + Na)^+$ 352.1347, found 352.1346.

*Phenyl 2-(2-(phenylthio)phenyl)hexanoate (**3ba**)*. 80% yield (75 mg); colorless oil; ^{1}H 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 $C_{24}H_{24}NaO_2S$ $(M + Na)^+$ 399.1395, found 399.1392.

*4-chlorophenyl 2-(2-(phenylthio)phenyl)hexanoate (**3ca**)*. 68% yield (70 mg); colorless oil; ^{1}H 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 $C_{24}H_{23}ClNaO_2S$ $(M + Na)^+$ 433.1005, found 433.1008.

*Phenyl 2-(2-(phenylthio)phenyl)acetate (**3da**)*. 81% yield (65 mg); white soild, mp: 105–107 ^{o}C; ^{1}H 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 $C_{20}H_{16}NaO_2S$ $(M + Na)^+$ 343.0769, found 343.0763.

*M-tolyl 2-(2-(phenylthio)phenyl)acetate (**3ea**)*. 84% yield (70 mg); colorless oil; ^{1}H 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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, 128.4, 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{19}F NMR (565 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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, 459.1155.

*Ethyl 2-(2-(phenylthio)phenyl)acetate (**3oa**)*. 83% yield (56 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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□ for 1 h, the reaction mixture was quenched with $NaHCO_3$ (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 = 1:50) gave **5aa** (86.5 mg, 84% yield) as a colorless oil.

S-phenyl 2-phenyl-2-(2-(phenylthio)phenyl)ethanethioate *(**5aa**)*. ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.9, 140.6, 137.4, 136.8, 135.2, 134.4, 133.9, 130.1, 129.3, 129.2, 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{19}H_{22}NaOS_2$ $(M + Na)^+$ 353.1010, found 353.1008.

*S-ethyl 2-(2-(phenylthio)phenyl)octanethioate (**5ea**)*. 95% yield (88 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{22}H_{28}NaOS_2$ $(M + Na)^+$ 395.1479, found 395.1491.

*S-ethyl 2-(2-(phenylthio)phenyl)decanethioate (**5fa**)*. 96% yield (96 mg); colorless oil; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{24}H_{32}NaOS_2$ $(M + Na)^+$ 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. Et_2O (15 mL) was added and the suspension was washed with water (10 mL). The organic layer was dried over $MgSO_4$, 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; ^{1}H NMR (600 MHz, $CDCl_3$) 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); ^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{22}H_{28}NaOS$ $(M + Na)^+$ 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), $Pd_2dba_3.CHCl_3$ (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. Et_2O (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 $MgSO_4$, 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; ^{1}H NMR (400 MHz, $CDCl_3$) 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); ^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{28}H_{32}NaOS$ $(M + Na)^+$ 439.2072, found 439.2067.

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Supporting Information: Detailed experimental procedures for Scheme 2**.** Copies of ^{1}H NMR spectra of compounds **1a-1c**, **1g**, **1m**, **4b-4c**, **4f**, ^{1}H NMR, ^{13}C NMR spectra of compounds **3aa-3ak**,

3ba-3oa, **5aa-5fa**, **6** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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