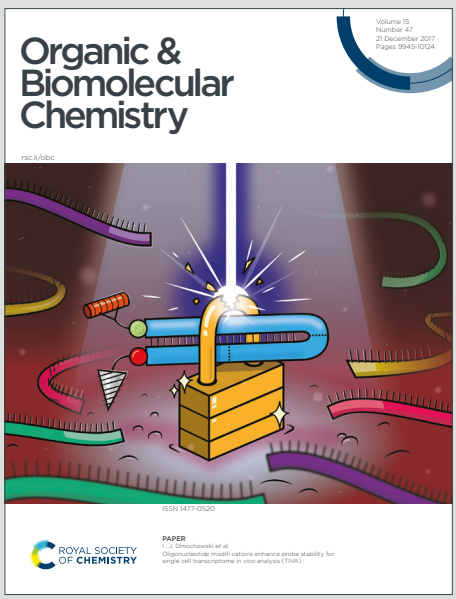
Organic & Biomolecular Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: H. Wang, P. Lian, Y. Zheng, J. Li and X. Wan, *Org. Biomol. Chem.*, 2020, DOI: 10.1039/D0OB00091D.



ROYAL SOCIETY OF CHEMISTRY

rsc.li/obc

View Article Online
DOI: 10.1039/D0OB00091D

ARTICLE

Cross Coupling of Sulfonyl Radical with Silver-Based Carbene: A Simple Approach to β-Carbonyl Arylsulfones

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

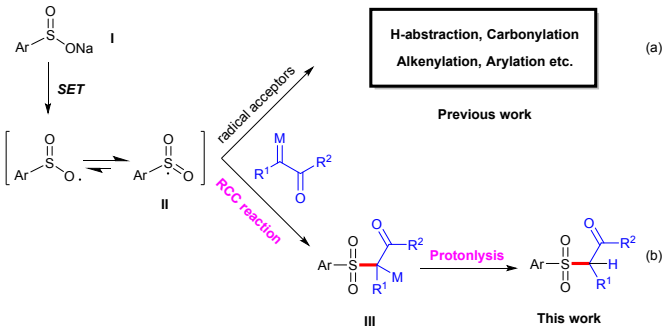
Hanghang Wang, Pengcheng Lian, Yonggao Zheng, Jingjing Li, Xiaobing Wan*

A coupling reaction between sulfonyl radical and silver-based carbene has been well established. This simple radical-carbene coupling (RCC) process provided an efficient approach to a variety of β-carbonyl arylsulfones from sodium arylsulfinates and diazo compounds, which was distinguished by wide substrate scopes, easy scale-up, simple manipulation, accessible starting materials, and mild reaction conditions.

Introduction

Radicals are generally considered as highly reactive and multifunctional intermediates,[1] which play vital roles in a wide range of transformations such as functionalization of alkenes,[2] alkynes,[3] and (hetero)arenes[4] and C–H bond[5] etc. On the other hand, transition-metal carbenes,[6] usually generated *in situ* from metal-induced decomposition of diazo compounds, are also highly efficient species, which are confirmed by X–H insertion,[7a-c] cross-coupling,[7d] cyclization and ylide reactions.[7e-k] Although great progress have been made in the research of radicals or transition metal carbenes, reactions based-upon radical-carbene coupling strategy still in its infancy. This might be due to the high reactivity and low concentration of radicals and carbenes, making them difficult to achieve highly selective cross-couplings. Clearly, synthetic strategies based upon radical-carbene coupling (RCC) reactions will provide a conceptually novel and efficient approach to multifunctional molecules. In recent years, we have obtained a series of functional molecules such as β-ester-γ-amino ketones,[8a,b] indoles,[8c] isoxazolines,[8d] and perfluoroalkanesulfinate esters[8e] through this strategy, and initially verified its potential in synthetic chemistry.

Arylsulfone motifs are ubiquitous in biologically active molecules, drugs and functional materials and also served as versatile building blocks in many transformations.[9] Thererfore, a handful of methods have been developed to introduce arylsulfonyl groups into organic molecules with sulfonylation reagents.[10] Among these reagents, sodium arylsulfinate is a stable, inexpensive and easy to prepare compound that can form sulfonyl radical by single electron transfer (SET) process, making it a classical sulfonylation reagent for a variety of radical acceptors (Scheme 1a).[9g,9h,10d-j] As a continuation of our research interest in exploiting the cross coupling of radicals with carbenes, we reported herein the construction of arylsulfone using this strategy as shown in Scheme 1b. Cross-coupling of sulfonyl radical **II** with a transition metal carbene yields intermediate **III**, which then provides the desired β-carbonyl arylsulfones by protonlysis. To the best of our knowledge, there have been no reports of cross-coupling of sulfonyl radical and metal-carbene to form arylsulfone compounds.[11] Considering the important use of arylsulfone compounds and the shortcomings of existing methods, this methodology provides a valuable alternative for their synthesis.



Scheme 1 Synthetic application of sodium arylsulfinate.

Results and discussion

Considering that $AgNO_3/K_2S_2O_8$ were often used to generate sulfonyl radical from sodium benzensulfinate **1a**,[10e,h,j] we tested their reaction with ethyl diazoacetate **2a** to form β-ester sulfones **3aa**. With this in mind, we firstly screened a range of solvents (For details, see Supporting Information, Table S1, entries 1–6) and found trace amount of desired product **3aa** in MeCN. To our delight, the yield of **3aa** could be increased to 36% by the 1:1 mixture of MeCN and H_2O as reaction medium (Table S1, entry 7). This result prompted us to adjust the ratio of MeCN to H_2O, and the best result was

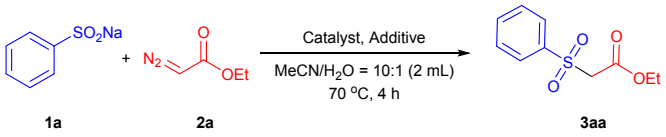
*Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. China. E-mail: wanxb@suda.edu.cn

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

View Article Online
DOI: 10.1039/D0OB00091D

obtained at a ratio of 10:1 (Table S1, entry 10). Next, we screened the amount of $K_2S_2O_8$ used. To our surprise, even with 0.5 equivalents of $K_2S_2O_8$, the yield of **3aa** could be further increased to 68% (Table 1, entry 1). Other silver catalysts and oxidants resulted in a reduced **3aa** yield (Table 1, entries 2-7). A series of *N*, *N*-bidentate ligands could promote the formation of product **3aa** (Table 1, entries 8-10). Control experiments showed that both $AgNO_3$ and $K_2S_2O_8$ were essential to this coupling reaction (Table 1, entries 18-19), indicating sulfonyl radical and silver-based carbene were involved in this transformation. After extensive screenings, we found the optimum conditions: using 10 mol% $AgNO_3$, 10 mol% 1,10-phenanthroline and 0.5 equiv. $K_2S_2O_8$, reacting in MeCN/H_2O at 70 °C for 4 h to obtain the coupling product **3aa** in a high yield of 80% (Table 1, entry 13).

Table 1 Optimization of the reaction conditions[a]



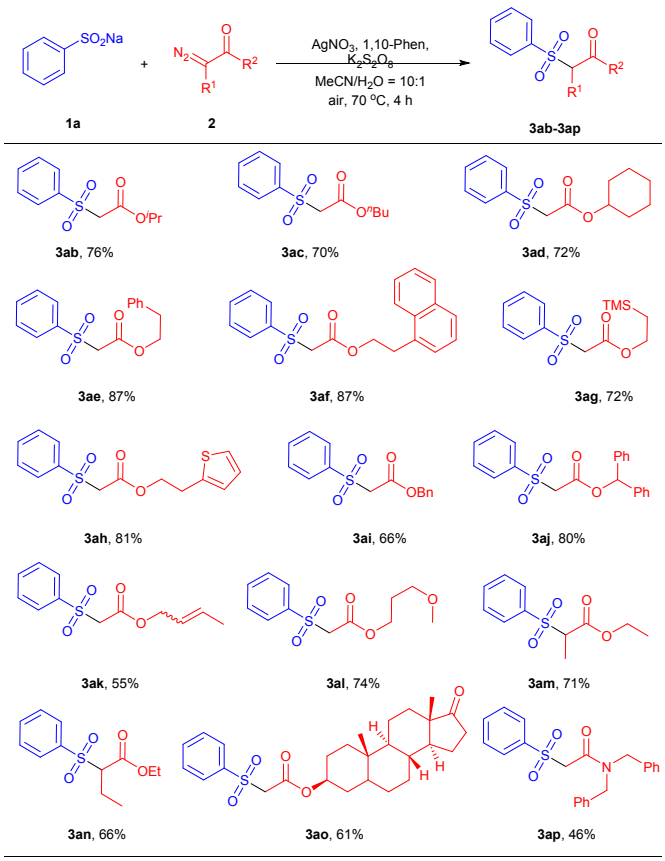
1a **2a** **3aa**

Entry	Catalyst (mol%)	Additive	Ligand (mol%)	Yield [%][b]
1	$AgNO_3$ (20)	$K_2S_2O_8$	—	68
2	CF_3CO_2Ag (20)	$K_2S_2O_8$	—	62
3	AgOAc (20)	$K_2S_2O_8$	—	58
4	Ag_2CO_3 (20)	$K_2S_2O_8$	—	63
5	AgF (20)	$K_2S_2O_8$	—	59
6	$AgNO_3$ (20)	$Na_2S_2O_8$	—	65
7	$AgNO_3$ (20)	$(NH_4)_2S_2O_8$	—	48
8	$AgNO_3$ (20)	$K_2S_2O_8$	**L1** (20)	76
9	$AgNO_3$ (20)	$K_2S_2O_8$	**L2** (20)	73
10	$AgNO_3$ (20)	$K_2S_2O_8$	**L3** (20)	68
11	$AgNO_3$ (20)	$K_2S_2O_8$	**L1** (15)	77
12	$AgNO_3$ (20)	$K_2S_2O_8$	**L1** (10)	77
13	**$AgNO_3$ (10)**	**$K_2S_2O_8$**	**L1 (10)**	**80**
14	$AgNO_3$ (5)	$K_2S_2O_8$	**L1** (10)	72
15	$AgNO_3$ (10)	$K_2S_2O_8$	**L4** (10)	68
16	$AgNO_3$ (10)	$K_2S_2O_8$	**L5** (10)	70
17	$AgNO_3$ (10)	$K_2S_2O_8$	**L6** (10)	57
18	—	$K_2S_2O_8$	**L1** (10)	< 5
19	$AgNO_3$ (10)	—	**L1** (10)	< 5

[a]Unless otherwise noted, all the reactions were run with **1a** (0.5 mmol), **2a** (1 mmol) and additive (0.25 mmol) in MeCN/H_2O = 10: 1 (2.0 mL) at 70 °C under air. [b]isolated yields. **L1** = 1,10-phenanthroline, **L2** = 2,2'-bipyridine, **L3** = 2,2':6',2''-terpyridine, **L4** = 4,7-dimethoxy-1,10-phenanthroline, **L5** = 4,7-diphenyl-1,10-phenanthroline, **L6** = 3,8-dibromo-1,10-phenanthroline.

With the optimal reaction conditions in hand, we set out to explore the substrate scope of this transformation. A varity of *α*-diazo carbonyl compounds were tested and the results are listed in Table 2. It turned out that all the selected *α*-diazo carbonyl compounds could take part in this transformation well, leading to the corresponding products in moderate to excellent yields (**3ab**-**3ap**). Notably, functional groups such as naphthyl (**3af**), TMS (**3ag**), thienyl (**3ah**) and methyl ether (**3al**) were compatible with this reaction. To our delight, the substrate bearing internal olefin was also good reaction partner for this transformation and the product **3ak** was obtained in satisfactory output. α-Fully substituted diazo compounds **2m** and **2n** were well tolerated in this reaction, furnishing the corresponding product **3am** and **3an** in 71% and 66% yields, respectively. This transformation was also illustrated with diazo amide and delivered the target product **3ap** in 46% yield. To showcase the synthetic utility of this methodology, diazo ester **2o** from epiandrosterone was utilized as the substrate, leading to the target product **3ao** in satisfactory 61% yield.

Table 2 Scope of diazo compounds[a,b]

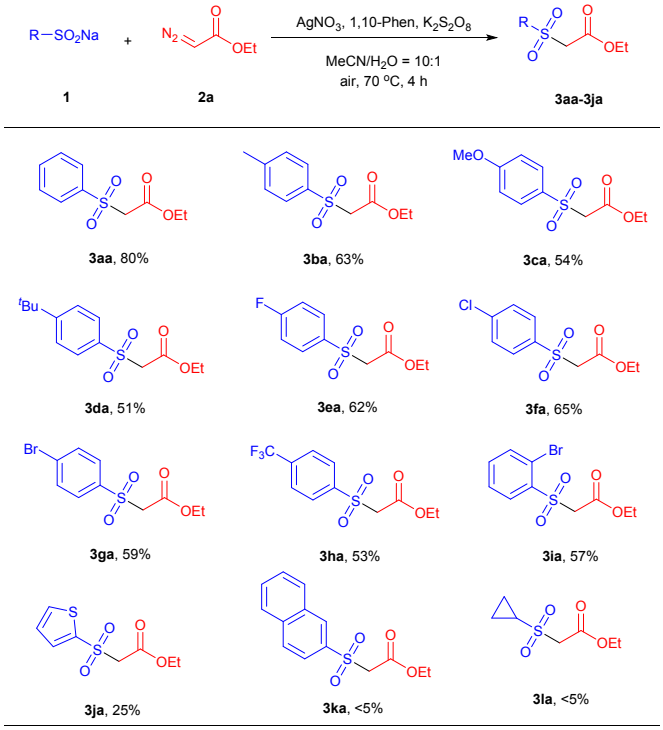


[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), $AgNO_3$ (0.05 mmol), 1,10-Phen (0.05 mmol), $K_2S_2O_8$ (0.25 mmol), stirred in MeCN/H_2O = 10: 1 (2 mL) at 70 °C for 4 h under air. [b]Isolated yields.

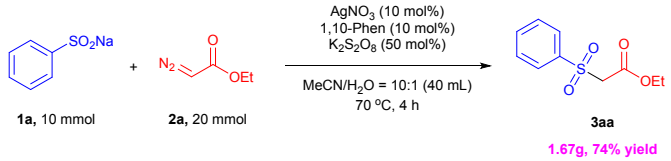
Next, we tried to expand the substrate scope by investigating different sodium sulfinate, as shown in Table 3. Satisfactorily, the benzene ring carrying both electron-withdrawing and electron-donating groups were well tolerated, affording the corresponding β-carbonyl arylsulfones **3ba-3ia** in moderate to good yields. The halogens such as F, Cl, and Br at *para*- or *ortho*- positions were tolerated to this process and gave the desired products in good yields (**3ea-3ga**, **3ia**). The reaction revealed low efficiency when thienyl-substituted sodium arylsulfinate (**3ja**) was used as substrate. Unfortunately, naphthyl and alkyl-substituted sodium sulfinate failed to get the corresponding products **3ka** and **3la**. To further demostrate the practicability of this coupling reaction,

the template reaction was carried on 10 mmol scale and the desired product **3aa** was obtained in 74% isolated yield, as shown in Scheme 2.

Table 3 Scope of sodium sulfinates[a,b]

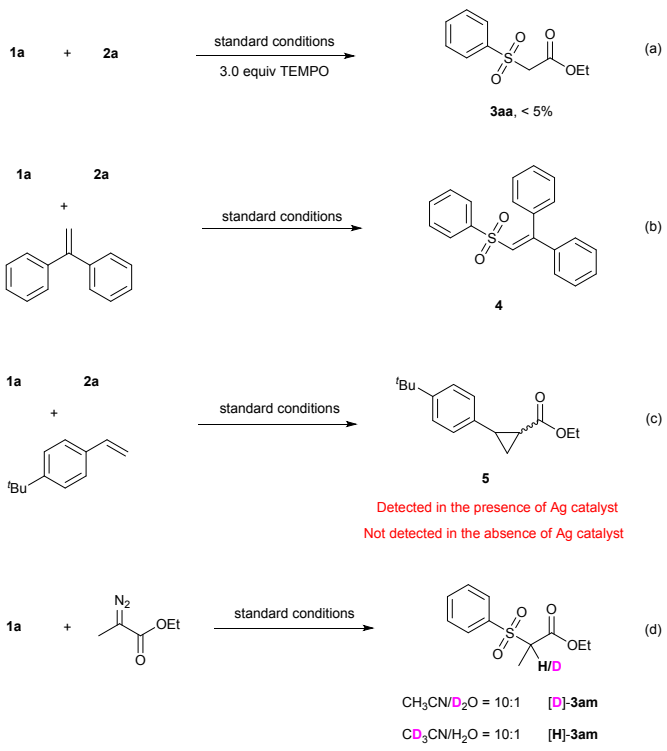


[a]Reaction conditions: **1a** (0.5 mmol), **2** (1.0 mmol), $AgNO_3$ (0.05 mmol), 1,10-Phen (0.05 mmol), $K_2S_2O_8$ (0.25 mmol), stirred in $MeCN/H_2O$ = 10: 1 (2 mL) at 70 °C for 4 h under air. [b]Isolated yields.



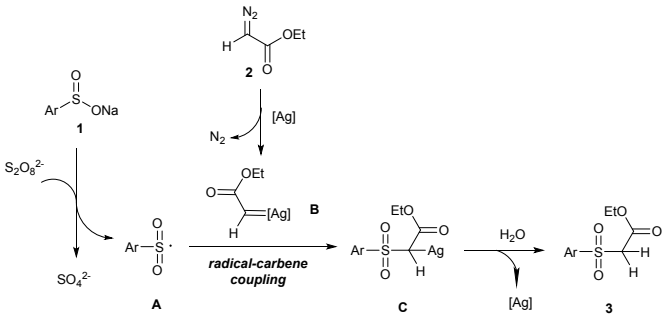
Scheme 2 Gram-Scale Reaction.

Further experiments were conducted to gain insight into the mechanism of this β-carbonyl arylsulfones formation reaction. The formation of product **3aa** was inhibited significantly by adding 2,2,6,6-tetramethylpiperidinoxy (TEMPO) to the reaction mixture (Scheme 3a). The addition of 1,1-diphenylethylene to the reaction system delivered the sulfonyl radical adduct **4** (Scheme 3b). By adding 4-*tert*-butylstyrene to the reaction system under the standard conditions, the cyclopropanation product **5** was detected by LCMS. However, it failed to detect the cyclopropanation product **5** in the absence of Ag catalyst (Scheme 3c). The results indicated the Ag catalyst was essential and Ag-based carbene was generated *in situ* in this transformation. When 2,6-di-*tert*-butyl-4-methylphenol (BHT) was subjected to the reaction system, the adduct **6** of sulfonyl radical and BHT was obtained in 10% yield (see Supporting Information, Scheme S3). It is particularly worth mentioning that compound **7** was detected by LCMS, indicating that cross-coupling of the sulfonyl radical and silver-based carbene occurred in the reaction. In order to determine the source of hydrogen in the *β*-carbonyl arylsulfones, $MeCN/D_2O$ or CD_3CN/H_2O were used as solvent for this transformation and the results indicated that water participates in the final protonation process (Scheme 3d). Taken together, these results provided clear evidence that the *in situ* generation of sulfonyl radical and silver-based carbene and their highly selective cross-coupling were invovled in this *β*-carbonyl arylsulfones formation reaction.



Scheme 3 Probe for the possible mechanism.

Based upon above results and literatures, a plausible reaction mechanism was proposed, as shown in Scheme 4. Sulfonyl radical **A** was produced by the single electron transfer oxidation of sodium sulfinate **1** promoted by $K_2S_2O_8$,[10d,h-j] and then cross coupled with silver carbene **B**[12] to form the intermediate **C**. Finally, the intermediate **C** underwent protonolysis and gave the desired β-carbonyl arylsulfones **3**.



Scheme 4 Proposed Reaction Mechanism.

View Article Online
DOI: 10.1039/D0OB00241D

Conclusions

In summary, by careful control of the reaction conditions, we achieved a highly selective cross-coupling of sulfonyl radicals with silver-based carbene to form β-carbonyl arylsulfones. This strategy was also featured by simple manipulation, easy scale-up, wide substrate scopes and mild reaction conditions. Investigations on other radical carbene coupling (RCC) reactions are underway in our laboratory.

Experimental

General information

All manipulations were carried out under air atmosphere. Column chromatography was generally performed on silica gel (300-400 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light to visualize the course of the reactions. The ^{1}H NMR (400MHz), ^{13}C NMR (100 MHz) data were recorded using $CDCl_3$ as solvent at room temperature. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.00 ppm) as internal reference.

General procedures

Sodium arylsulfinates (0.5 mmol), $AgNO_3$ (0.05 mmol), 1,10-phen (0.05 mmol) and $K_2S_2O_8$ (0.25 mmol) were added to test tube charged with stir bar. MeCN/H_2O =10:1 (2.0 mL) and diazo compound (1.0 mmol) were added via syringe. The reaction mixture was heated at 70 °C for 4 h, which was then quenched with saturated Na_2SO_3 solution and extracted with ethyl acetate (20 mL × 3). The organic layers were combined and dried with anhydrous Na_2SO_4. Removal of the organic solvent followed by flash column chromatographic purification afforded the desired products using petroleum and ethyl acetate.

Ethyl 2-(phenylsulfonyl)acetate (3aa) petroleum ether/ ethylacetate = 5:1, colorless oil, 80% yield (91.0 mg), 10.0 mmol, 74% yield (1.67 g). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.95 (m, 2H), 7.72-7.68 (m, 1H), 7.61-7.57 (m, 2H), 4.17-4.12 (m, 4H), 1.19 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 138.7, 134.2, 129.2, 128.5, 62.3, 61.0, 13.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{12}O_4S+Na^+$: 251.0349, Found: 251.0353. IR (neat, cm^{-1}): υ 3066, 2984, 2926, 2852, 1736, 1447, 1276, 1149.

Isopropyl 2-(phenylsulfonyl)acetate (3ab) petroleum ether/ ethylacetate = 6:1, colorless oil, 76% yield (91.4 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.71-7.67 (m, 1H), 7.60-7.57 (m, 2H), 4.99-4.93 (m, 1H), 4.12 (s, 2H), 1.15 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 138.6, 134.1, 129.0, 128.3, 70.2, 61.0, 21.2. HRMS (ESI-TOF): Anal. Calcd. For $C_{11}H_{14}O_4S+Na^+$: 265.0505, Found: 265.0511. IR (neat, cm^{-1}): υ 3067, 2984, 2940, 2881, 1731, 1448, 1278, 1151.

Butyl 2-(phenylsulfonyl)acetate (3ac) petroleum ether/ ethylacetate = 6:1, colorless oil, 70% yield (88.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.71-7.67 (m, 1H), 7.60-7.56 (m, 2H), 4.15 (s, 2H), 4.07 (t, *J* = 6.7 Hz, 2H), 1.55-1.48 (m, 2H), 1.31-1.22 (m, 2H), 0.87 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 138.6, 134.1, 129.0, 128.2, 65.9, 60.7, 30.0, 18.6, 13.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{16}O_4S+Na^+$: 279.0662, Found: 279.0668. IR (neat, cm^{-1}): υ 2960, 2937, 2875, 1736, 1448, 1279, 1150, 1083.

Cyclohexyl 2-(phenylsulfonyl)acetate (3ad) petroleum ether/ ethylacetate = 5:1, colorless oil, 72% yield (101.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.71-7.67 (m, 1H), 7.60-7.56 (m, 2H), 4.76-4.57 (m, 1H), 4.12 (s, 2H), 1.77-1.64 (m, 4H), 1.53-1.48 (m, 1H), 1.37-1.18 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 138.7, 134.1, 129.1, 128.4, 75.0, 61.1, 31.0, 25.0, 23.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{18}O_4S+Na^+$: 305.0818, Found: 305.0822. IR (neat, cm^{-1}): υ 3065, 2937, 2860, 1731, 1448, 1281, 1150, 1083.

Phenethyl 2-(phenylsulfonyl)acetate (3ae) petroleum ether/ ethylacetate = 5:1, white solid, 87% yield (131.6 mg), melting point: 69.5-71.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89-7.87 (m, 2H), 7.65-7.61 (m, 1H), 7.53-7.49 (m, 2H), 7.28-7.24 (m, 2H), 7.22-7.18 (m, 1H), 7.13-7.11 (m, 2H), 4.25 (t, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 2.82 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 138.4, 136.8, 134.1, 129.0, 128.6, 128.3, 128.2, 126.5, 66.4, 60.6, 34.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{16}H_{16}O_4S+Na^+$: 327.0662, Found: 327.0652. IR (neat, cm^{-1}): υ 3005, 2968, 2935, 1737, 1448, 1270, 1161, 1082.

2-(naphthalen-1-yl)ethyl 2-(phenylsulfonyl)acetate (3af) petroleum ether/ ethylacetate = 5:1, white solid, 87% yield (154.2 mg), melting point: 71.4-72.9 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.88-7.83 (m, 3H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.52-7.45 (m, 4H), 7.39-7.35 (m, 1H), 7.27-7.26 (m, 1H), 4.38 (t, *J* = 7.3 Hz, 2H), 4.09 (s, 2H), 3.29 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 138.5, 134.2, 133.7, 132.7, 131.7, 129.1, 128.8, 128.3, 127.5, 127.0, 126.2, 125.6, 125.4, 123.2, 66.0, 60.8, 31.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{20}H_{18}O_4S+Na^+$: 377.0818, Found: 377.0817. IR (neat, cm^{-1}): υ 3060, 3005, 2968, 2935, 1733, 1448, 1270, 1160.

2-(trimethylsilyl)ethyl 2-(phenylsulfonyl)acetate (3ag) petroleum ether/ ethylacetate = 5:1, colorless oil, 72% yield (107.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (m, 2H), 7.69-7.67 (m, 1H), 7.60-7.56 (m, 2H), 4.18-4.14 (m, 2H), 4.11 (s, 2H), 0.93-0.89 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 138.7, 134.1, 129.1, 128.4, 64.7, 60.9, 17.0, -1.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{13}H_{20}O_4SSi+Na^+$: 323.0744, Found: 323.0743. IR (neat, cm^{-1}): υ 3066, 2954, 2899, 1736, 1448, 1274, 1150, 1084.

2-(thiophen-2-yl)ethyl 2-(phenylsulfonyl)acetate (3ah) petroleum ether/ ethylacetate = 5:1, yellowish oil, 81% yield (125.0 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.90 (m, 2H), 7.68-7.65 (m, 1H), 7.57-7.53 (m, 2H), 7.14-7.13 (m, 1H), 6.92-6.90 (m, 1H), 6.80-6.79 (m, 1H), 4.28 (t, *J* = 6.8 Hz, 2H), 4.13 (s, 2H), 3.05 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 138.8, 138.5, 134.2, 129.1, 128.3, 126.9, 125.6, 124.0, 66.1, 60.7, 28.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{14}O_4S_2+Na^+$: 333.0226, Found: 333.0226. IR (neat, cm^{-1}): υ 3104, 3006, 2962, 2853, 1736, 1449, 1270, 1160.

DOI: 10.1039/D0OB00001D

Benzyl 2-(phenylsulfonyl)acetate (3ai) petroleum ether/ ethylacetate = 5:1, colorless oil, 66% yield (94.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.64-7.60 (m, 1H), 7.49-7.45 (m, 2H), 7.35-7.31 (m, 3H), 7.25-7.23 (m, 2H), 5.09 (s, 2H), 4.15 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 138.4, 134.3, 134.1, 129.1, 128.54, 128.47, 128.4, 128.3, 67.8, 60.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{15}H_{14}O_4S+Na^+$: 313.0505, Found: 313.0507. IR (neat, cm^{-1}): υ 3065, 3006, 2943, 2849, 1737, 1448, 1273, 1148.

Benzhydryl 2-(phenylsulfonyl)acetate (3aj) petroleum ether/ ethylacetate = 5:1, yellowish oil, 80% yield (145.1 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 2H), 7.57-7.53 (m, 1H), 7.40-7.36 (m, 2H), 7.32-7.24 (m, 10H), 6.82 (s, 1H), 4.17 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 138.7, 138.2, 134.1, 129.1, 128.4, 128.3, 128.1, 127.1, 78.9, 60.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{21}H_{18}O_4S+Na^+$: 389.0818, Found: 389.0804. IR (neat, cm^{-1}): υ 3063, 3007, 2929, 2853, 1738, 1448, 1265, 1149.

But-2-en-1-yl 2-(phenylsulfonyl)acetate (3ak) petroleum ether/ ethylacetate = 5:1, colorless oil, 55% yield (69.5 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.93 (m, 2H), 7.71-7.67 (m, 1H), 7.59-7.56 (m, 2H), 5.79-5.70 (m, 1H), 5.48-5.40 (m, 1H), 4.64-4.63 (m, 0.3H), 4.50-4.48 (m, 1.7H), 4.144 (s, 0.3H), 4.137 (s, 1.7H), 1.70-1.68 (m, 2.55H), 1.66-1.64 (m, 0.45H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 162.0, 138.5, 134.13, 134.10, 132.6, 130.7, 129.05, 129.03, 128.41, 128.38, 123.6, 122.7, 66.7, 61.5, 60.8, 17.6, 12.9. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{14}O_4S+Na^+$: 277.0505, Found: 277.0517. IR (neat, cm^{-1}): υ 3064, 3009, 2944, 2856, 1736, 1448, 1273, 1149.

3-methoxypropyl 2-(phenylsulfonyl)acetate (3al) petroleum ether/ ethylacetate = 3:1, colorless oil, 74% yield (100.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.91 (m, 2H), 7.72-7.68 (m, 1H), 7.61-7.57 (m, 2H), 4.18 (t, *J* = 6.5 Hz, 2H), 4.14 (s, 2H), 3.36 (t, *J* = 6.5 Hz, 1H), 3.30 (s, 3H), 1.85-1.79 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 138.6, 134.2, 129.1, 128.3, 68.4, 63.4, 60.8, 58.5, 28.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{16}O_5S+Na^+$: 295.0611, Found: 295.0619. IR (neat, cm^{-1}): υ 3065, 2930, 2878, 1737, 1448, 1278, 1151, 1083.

Ethyl 2-(phenylsulfonyl)propanoate (3am) petroleum ether/ ethylacetate = 6:1, colorless oil, 71% yield (85.3 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.71-7.67 (m, 1H), 7.60-7.56 (m, 2H), 4.11 (dq, *J* = 0.6, 7.2 Hz, 2H), 4.06 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 136.9, 134.1, 129.2, 128.9, 65.3, 62.1, 13.7, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{11}H_{14}O_4S+Na^+$: 265.0505, Found: 265.0509. IR (neat, cm^{-1}): υ 3066, 2985, 2942, 1734, 1448, 1260, 1145, 1083.

Ethyl 2-(phenylsulfonyl)butanoate (3an) petroleum ether/ ethylacetate = 6:1, colorless oil, 66% yield (83.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.88 (m, 2H), 7.71-7.67 (m, 1H), 7.60-7.56 (m, 2H), 4.11 (dq, *J* = 0.6, 7.2 Hz, 2H), 4.06 (q, *J* = 7.2 Hz, 1H), 1.58 (d, *J* = 7.2 Hz, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1, 136.9, 134.1, 129.2, 128.9, 65.3, 62.1, 13.7, 11.6. HRMS (ESI-TOF): Anal. Calcd. For $C_{12}H_{16}O_4S+Na^+$: 279.0662, Found: 279.0669. IR (neat, cm^{-1}): υ 3069, 2979, 2852, 1731, 1451, 1187, 1162, 1079.

(3S,8R,9S,10S,13S,14S)-10,13-dimethyl-17-oxohexadecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 2-(phenylsulfonyl)acetate (3ao) petroleum ether/ ethylacetate = 5:1, white solid, 61% yield (141.1 mg), melting point: 146.2-148.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96-7.94 (m, 2H), 7.71-7.68 (m, 1H), 7.60-7.57 (m, 2H), 4.71-4.65 (m, 1H), 4.09 (s, 2H), 2.47-2.40 (m, 1H), 2.11-2.01 (m, 1H), 1.92-1.91 (m, 1H), 1.77 -1.13 (m, 16H), 0.98-0.94 (m, 1H), 0.85 (s, 3H), 0.82 (s, 3H), 0.71-0.68 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 221.0, 161.7, 138.6, 134.1, 129.0, 128.4, 75.8, 61.1, 54.0, 51.1, 47.6, 44.3, 36.3, 35.7, 35.4, 34.8, 33.3, 31.3, 30.5, 28.0, 26.8, 21.6, 20.3, 13.6, 12.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{27}H_{36}O_5S$ $+Na^+$: 495.2176, Found: 495.2160. IR (neat, cm^{-1}): υ 3010, 2928, 2848, 1742, 1448, 1279, 1160, 1086.

***N,N*-dibenzyl-2-(phenylsulfonyl)acetamide (3ap)** petroleum ether/ ethylacetate = 5:1, white solid, 46% yield (86.0 mg), melting point: 83.9-85.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.65-7.62 (m, 1H), 7.53-7.49 (m, 2H), 7.36-7.26 (m, 6H), 7.24-7.22 (m, 2H), 7.11 (d, *J* = 7.1 Hz, 2H), 4.65 (s, 2H), 4.58 (s, 2H), 4.26 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 138.7, 136.1, 135.4, 134.0, 129.02, 128.99, 128.6, 128.4, 128.0, 127.8, 127.5, 126.1, 59.8, 50.8, 49.0. HRMS (ESI-TOF): Anal. Calcd. For $C_{22}H_{21}NO_3S+Na^+$: 402.1134, Found: 402.1136. IR (neat, cm^{-1}): υ 3086, 3002, 2955, 2916, 1650, 1445, 1284, 1142, 1089.

Ethyl 2-tosylacetate (3ba) petroleum ether/ ethylacetate = 6:1, colorless oil, 63% yield (75.6 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.10 (s, 2H), 2.46 (s, 3H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 145.3, 135.7, 129.7, 128.5, 62.3, 61.0, 21.6, 13.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{11}H_{14}O_4S+Na^+$: 265.0505, Found: 265.0515. IR (neat, cm^{-1}): υ 2983, 2929, 2854, 1737, 1400, 1276, 1147, 1084.

Ethyl 2-((4-methoxyphenyl)sulfonyl)acetate (3ca) petroleum ether/ ethylacetate = 4:1, colorless oil, 54% yield (68.8 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 9.0 Hz, 2H), 7.03 (d, *J* = 9.0 Hz, 2H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.09 (s, 2H), 3.89 (s, 3H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 162.5, 130.7, 130.1, 114.3, 62.2, 61.1, 55.6, 13.8. HRMS (ESI-TOF): Anal. Calcd. For $C_{11}H_{14}O_5S+Na^+$: 281.0454, Found: 281.0458. IR (neat, cm^{-1}): υ 3101, 2983, 2943, 2844, 1736, 1259, 1143, 1085.

Ethyl 2-((4-(tert-butyl)phenyl)sulfonyl)acetate (3da) petroleum ether/ ethylacetate = 6:1, colorless oil, 51% yield (70.9 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 4.17-4.11 (m, 4H), 1.35 (s, 9H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 158.2, 135.7, 128.3, 126.1, 62.1, 61.0, 35.2, 30.9, 13.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{14}H_{20}O_4S+Na^+$: 307.0975, Found: 307.0981. IR (neat, cm^{-1}): υ 3065, 2964, 2872, 1738, 1467, 1270, 1153, 1082.

Ethyl 2-((4-fluorophenyl)sulfonyl)acetate (3ea) petroleum ether/ ethylacetate = 6:1, colorless oil, 62% yield (75.2 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.96 (m, 2H), 7.30-7.24 (m, 2H), 4.18-4.13 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0 (d, *J* = 257.2 Hz), 162.2, 134.6 (d, *J* = 3.2 Hz), 131.5 (d, *J* = 9.8 Hz), 116.4 (d, *J* = 22.8 Hz), 62.3, 60.9, 13.8. ^{19}F

DOI: 10.1039/D0OB00091D

NMR (376 MHz, $CDCl_3$) δ -102.4. HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{11}FO_4S+Na^+$: 269.0254, Found: 269.0258. IR (neat, cm^{-1}): υ 3107, 3073, 2986, 2943, 1736, 1494, 1292, 1147.

Ethyl 2-((4-chlorophenyl)sulfonyl)acetate (3fa) petroleum ether/ ethylacetate = 6:1, colorless oil, 65% yield (84.4 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.92-7.88 (m, 2H), 7.58-7.55 (m, 2H), 4.18-4.13 (m, 4H), 1.21 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 140.9, 137.0, 130.0, 129.4, 62.4, 60.7, 13.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{11}{}^{35}ClO_4S+Na^+$: 284.9959, Found: 284.9968; Anal. Calcd. For $C_{10}H_{11}{}^{37}ClO_4S+Na^+$: 286.9929, Found: 286.9917. IR (neat, cm^{-1}): υ 3093, 2985, 2941, 1736, 1475, 1277, 1151, 1084.

Ethyl 2-((4-bromophenyl)sulfonyl)acetate (3ga) petroleum ether/ ethylacetate = 6:1, white solid, 59% yield (89.9 mg), melting point: 39.4-40.5 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 8.7 Hz, 2H), 4.18-4.13 (m, 4H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 137.5, 132.3, 130.0, 129.5, 62.3, 60.6, 13.7. HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{11}{}^{79}BrO_4S+Na^+$: 328.9454, Found: 328.9456; Anal. Calcd. For $C_{10}H_{11}{}^{81}BrO_4S+Na^+$: 330.9433, Found: 330.9441. IR (neat, cm^{-1}): υ 3093, 2987, 2850, 1732, 1463, 1268, 1147, 1079.

Ethyl 2-((4-(trifluoromethyl)phenyl)sulfonyl)acetate (3ha) petroleum ether/ ethylacetate = 6:1, colorless oil, 53% yield (77.8 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.2 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 4.20 (s, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 142.1, 135.7 (q, *J* = 33.2 Hz), 129.3, 126.2 (q, *J* = 3.6 Hz), 123.0 (q, *J* = 274.2 Hz), 62.5, 60.5, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3. HRMS (ESI-TOF): Anal. Calcd. For $C_{11}H_{11}F_3O_4S+Na^+$: 319.0222, Found: 319.0223. IR (neat, cm^{-1}): υ 3106, 2988 2944, 1739, 1404, 1279, 1154, 1086.

Ethyl 2-((2-bromophenyl)sulfonyl)acetate (3ia) petroleum ether/ ethylacetate = 6:1, white solid, 63% yield (75.6 mg), melting point: 44.0-45.2 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17-8.14 (m, 1H), 7.80-7.78 (m, 1H), 7.57-7.51 (m, 2H), 4.49 (s, 2H), 4.10 (q, *J* = 7.1 Hz, 2H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 137.6, 135.2, 135.0, 132.2, 127.8, 120.5, 62.1, 58.1, 13.5. HRMS (ESI-TOF): Anal. Calcd. For $C_{10}H_{11}{}^{79}BrO_4S+Na^+$: 328.9454, Found: 328.9456; Anal. Calcd. For $C_{10}H_{11}{}^{81}BrO_4S+Na^+$: 330.9433, Found: 330.9447. IR (neat, cm^{-1}): υ 3090, 3003, 2948, 1729, 1281, 1159, 1094, 1024.

Ethyl 2-(thiophen-2-ylsulfonyl)acetate (3ja) petroleum ether/ ethylacetate = 5:1, colorless oil, 25% yield (29.0 mg). ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1H), 7.77-7.76 (m, 1H), 7.20-7.18 (m, 1H), 4.23 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 139.0, 135.1, 134.9, 127.8, 62.2, 61.8, 13.6. HRMS (ESI-TOF): Anal. Calcd. For $C_8H_{10}O_4S_2+Na^+$: 256.9913, Found: 256.9922. IR (neat, cm^{-1}): υ 3100, 2985, 2941, 1735, 1467, 1277, 1145, 1090.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

A Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD), NSFC (21971175, 21572148).

Notes and references

1 For selected reviews, see: (*a*) C. P. Jasperse, D. P. Curran and T. L. Fevig, *Chem. Rev.,* 1991, **91**, 1237; (*b*) A. Studer, *Chem. Soc. Rev.,* 2004, **033**, 267; (*c*) M. Yan, J. C. Lo, J. T. Edwards and P. S. Baran, *J. Am. Chem. Soc.,* 2016, **138**, 12692; (*d*) J. Xie, H. Jin and A. S. K. Hashmi, *Chem. Soc. Rev.,* 2017, **46**, 5193; (*e*) P. Sivaguru, Z. Wang, G. Zanoni and X. Bi, *Chem. Soc. Rev.,* 2019, **48**, 2615.

2 For selected examples on functionalization of alkene *via* radical process, see: (*a*) B. Yang, X.-H. Xu and F.-L. Qing, *Org. Lett.,* 2015, **17**, 1906; (*b*) E. Shi, J. Liu, C. Liu, Y. Shao, H. Wang, Y. Lv, M. Ji, X. Bao and X. Wan, *J. Org. Chem.,* 2016, **81**, 5878; (*c*) J. Hou, A. Ee, H. Cao, H.-W. Ong, J.-H. Xu and J. Wu, *Angew. Chem. Int. Ed.,* 2018, **57**, 17220; (*d*) G. S. Sauer and S. Lin, *ACS Catal.,* 2018, **8**, 5175; (*e*) X. Tang and A. Studer, *Angew. Chem. Int. Ed.,* 2018, **57**, 814; (*f*) J.-S. Lin, T.-T. Li, J.-R. Liu, G.-Y. Jiao, Q.-S. Gu, J.-T. Cheng, Y.-L. Guo, X. Hong and X.-Y. Liu, *J. Am. Chem. Soc.,* 2019, **141**, 1074.

3 For selected examples on functionalization of alkyne *via* radical process, see: (*a*) Q. Lu, J. Zhang, G. Zhao, Y. Qi, H. Wang and A. Lei, *J. Am. Chem. Soc.,* 2013, **135**, 11481; (*b*) A. Maji, A. Hazra and D. Maiti, *Org. Lett.,* 2014, **16**, 4524; (*c*) J. Hou, A. Ee, W. Feng, J.-H. Xu, Y. Zhao and J. Wu, *J. Am. Chem. Soc.,* 2018, **140**, 5257; (*d*) W. Jud, C. O. Kappe and D. Cantillo, *Org. Biomol. Chem.,* 2019, **17**, 3529; (*e*) B. Wang, Z. Yan, L. Liu, J. Wang, Z. Zha and Z. Wang, *Green Chem.,* 2019, **21**, 205.

4 For selected examples on functionalization of (hetero)arenes *via* radical process, see: (*a*) L. Song, L. Zhang, S. Luo and J.-P. Cheng, *Chem. Eur. J.,* 2014, **20**, 14231; (*b*) J. Genovino, Y. Lian, Y. Zhang, T. O. Hope, A. Juneau, Y. Gagné, G. Ingle and M. Frenette, *Org. Lett.,* 2018, **20**, 3229; (*c*) B. Yang, D. Yu, X.-H. Xu and F.-L. Qing, *ACS Catal.,* 2018, **8**, 2839; (*d*) W. Jud, S. Maljuric, C. O. Kappe and D. Cantillo, *Org. Lett.,* 2019, **21**, 7970.

5 (*a*) F.-L. Zhang, Y.-F. Wang and S. Chiba, *Org. Biomol. Chem.,* 2013, **11**, 6003; (*b*) Q. Qin and S. Yu, *Org. Lett.,* 2015, **17**, 1894; (*c*) G. J. Choi, Q. Zhu, D. C. Miller, C. J. Gu and R. R. Knowles, *Nature,* 2016, **539**, 268; (*d*) X.-Q. Hu, J.-R. Chen and W.-J. Xiao, *Angew. Chem. Int. Ed.,* 2017, **56**, 1960; (*e*) A. Hu, J.-J. Guo, H. Pan, H. Tang, Z. Gao and Z. Zuo, *J. Am. Chem. Soc.,* 2018, **140**, 1612.

6 For selected reviews on carbene chemistry, see: (*a*) D. M. Hodgson, F. Y. T. M. Pierard and P. A. Stupple, *Chem. Soc. Rev.,* 2001, **30**, 50; (*b*) H. M. L. Davies and R. E. J. Beckwith, *Chem. Rev.,* 2003, **103**, 2861; (*c*) M. P. Doyle, R. Duffy, M. Ratnikov and L. Zhou, *Chem. Rev.,* 2010, **110**, 704; (*d*) Q. Xiao, Y. Zhang and J. Wang, *Acc. Chem. Res.,* 2013, **46**, 236; (*e*) A. Ford, H. Miel, A. Ring, C. N. Slattery, A. R. Maguire and M. A. McKervey, *Chem. Rev.,* 2015, **115**, 9981; (*f*) Q.-Q. Cheng, Y. Deng, M. Lankelma and M. P. Doyle, *Chem. Soc. Rev.,* 2017, **46**, 5425; (*g*) Y. Xia, D. Qiu and J. Wang, *Chem. Rev.,* 2017, **117**, 13810; (*h*) Y. Xiang, C. Wang, Q. Ding and Y. Peng, *Adv. Synth. Catal.,* 2019, **361**, 919.

7 For selected examples on X–H insertion, see: (*a*) M. Austeri, D. Rix, W. Zeghida and J. Lacour, *Org. Lett.,* 2011, **13**, 1394; (*b*) Q.-Q. Cheng, S.-F. Zhu, Y.-Z. Zhang, X.-L. Xie and Q.-L. Zhou, *J. Am. Chem. Soc.,* 2013, **135**, 14094; (*c*) D. Chen, X. Zhang, W.-Y. Qi, B. Xu and M.-H. Xu, *J. Am. Chem. Soc.,* 2015, **137**, 5268. For selected examples on cross-coupling, see: (*d*) F. Ye, X. Ma, Q. Xiao, H. Li, Y. Zhang and J. Wang, *J. Am. Chem. Soc.,* 2012, **134**, 5742; For selected examples on

View Article Online DOI: 10.1039/D0OB00091B

cyclization and ylide reactions, see: (*e*) S. Son and G. C. Fu, *J. Am. Chem. Soc.,* 2007, **129**, 1046; (*f*) B. V. S. Reddy, E. P. Reddy, B. Sridhar and Y. J. Rao, *RSC Adv.,* 2016, **6**, 50497; (*g*) T. Douglas, A. Pordea and J. Dowden, *Org. Lett.,* 2017, **19**, 6396; (*h*) A. N. Koronatov, N. V. Rostovskii, A. F. Khlebnikov and M. S. Novikov, *J. Org. Chem.,* 2018, **83**, 9210; (*i*) H. Li, X. Wu, W. Hao, H. Li, Y. Zhao, Y. Wang, P. Lian, Y. Zheng, X. Bao and X. Wan, *Org. Lett.,* 2018, **20**, 5224; (*j*) D. Zhang, L. Lin, J. Yang, X. Liu and X. Feng, *Angew. Chem. Int. Ed.,* 2018, **57**, 12323; (*k*) S. Fang, Y. Zhao, H. Li, Y. Zheng, P. Lian and X. Wan, *Org. Lett.,* 2019, **21**, 2356.

8 (*a*) J. Zhang, J. Jiang, D. Xu, Q. Luo, H. Wang, J. Chen, H. Li, Y. Wang and X. Wan, *Angew. Chem. Int. Ed.,* 2015, **54**, 1231; (*b*) J. Ling, J. Zhang, Y. Zhao, Y. Xu, H. Wang, Y. Lv, M. Ji, L. Ma, M. Ma and X. Wan, *Org. Biomol. Chem.,* 2016, **14**, 5310; (*c*) H. Li, Y. Zhao, L. Ma, M. Ma, J. Jiang and X. Wan, *Chem. Commun.,* 2017, **53**, 5993; (*d*) R. Chen, Y. Zhao, S. Fang, W. Long, H. Sun and X. Wan, *Org. Lett.,* 2017, **19**, 5896; (*e*) H. Wang, H. Li, Y. Zheng, P. Lian and X. Wan, *Chem. Eur. J.,* 2019, **25**, 2195.

9 (*a*) C. Curti, M. Laget, A. O. Carle, A. Gellis and P. Vanelle, *Eur. J. Med. Chem.,* 2007, **42**, 880; (*b*) S. C. Söderman and A. L. Schwan, *J. Org. Chem.,* 2012, **77**, 10978; (*c*) F. Minghao, T. Bingqing, H. L. Steven and J. Xuefeng, *Curr. Top. Med. Chem.,* 2016, **16**, 1200; (*d*) C. Bosset, G. Lefebvre, P. Angibaud, I. Stansfield, L. Meerpoel, D. Berthelot, A. Guérinot and J. Cossy, *J. Org. Chem.,* 2017, **82**, 4020; (*e*) W. Wang and B. Wang, *Chem. Commun.,* 2017, **53**, 10124; (*f*) K. A. Scott and J. T. Njardarson, *Top. Curr. Chem.,* 2018, **376**, 5; (*g*) R. Chawla and L. D. S. Yadav, *Org. Biomol. Chem.,* 2019, **17**, 4761; (*h*) P. Kramer, S.-C. Krieg, H. Kelm and G. Manolikakes, *Org. Biomol. Chem.,* 2019, **17**, 5538.

10 For selected examples on sulfonyl hydrazide, see: (*a*) S. Tang, Y. Wu, W. Liao, R. Bai, C. Liu and A. Lei, *Chem. Commun.,* 2014, **50**, 4496; (*b*) S. Li, X. Li, F. Yang and Y. Wu, *Org. Chem. Front.,* 2015, **2**, 1076; (*c*) K. Xu, L. Li, W. Yan, Y. Wu, Z. Wang and S. Zhang, *Green Chem.,* 2017, **19**, 4494. For selected examples on sodium sulfinate, see: (*d*) R. Chawla, A. K. Singh and L. D. S. Yadav, *Eur. J. Org. Chem.*, 2014, **2014**, 2032; (*e*) A. K. Singh, R. Chawla and L. D. S. Yadav, *Tetrahedron Lett.,* 2014, **55**, 4742; (*f*) A. U. Meyer, S. Jäger, D. Prasad Hari and B. König, *Adv. Synth. Catal.,* 2015, **357**, 2050; (*g*) W.-C. Yang, P. Dai, K. Luo and L. Wu, *Adv. Synth. Catal.,* 2016, **358**, 3184; (*h*) W. Wu, S. Yi, W. Huang, D. Luo and H. Jiang, *Org. Lett.,* 2017, **19**, 2825; (*i*) L.-Y. Xie, S. Peng, F. Liu, G.-R. Chen, W. Xia, X. Yu, W.-F. Li, Z. Cao and W.-M. He, *Org. Chem. Front.,* 2018, **5**, 2604; (*j*) Y. Liu, Q.-L. Wang, Z. Chen, Q. Zhou, C.-S. Zhou, B.-Q. Xiong, P.-L. Zhang, C.-A. Yang and K.-W. Tang, *Org. Biomol. Chem.,* 2019, **17**, 1365. For selected examples on sulfonyl chloride, see: (*k*) S. K. Pagire, S. Paria and O. Reiser, *Org. Lett.,* 2016, **18**, 2106; (*l*) X.-F. Xia, S.-L. Zhu, D. Wang and Y.-M. Liang, *Adv. Synth. Catal.,* 2017, **359**, 859. For selected examples on other sulfonylation reagents, see: (*m*) C. C. Chen and J. Waser, *Org. Lett.,* 2015, **17**, 736; (*n*) A. S. Deeming, C. J. Russell and M. C. Willis, *Angew. Chem. Int. Ed.,* 2016, **55**, 747.

11 Recently, we reported the cross-coupling reaction between sulfonyl hydrazides and diazo to construct sulfones, see: Y. Wang, L. Ma, M. Ma, H. Zheng, Y. Shao and X. Wan, *Org. Lett.,* 2016, **18**, 5082.

12 For selected examples on silver-based carbene, see: (*a*) H. Luo, G. Wu, Y. Zhang and J. Wang, *Angew. Chem. Int. Ed.,* 2015, **54**, 14503; (*b*) J. Huang, L. Li, H. Chen, T. Xiao, Y. He and L. Zhou, *Org. Chem. Front.,* 2017, **4**, 529; (*c*) Z. Liu, P. Sivaguru, G. Zanoni, E. A. Anderson and X. Bi, *Angew. Chem. Int. Ed.,* 2018, **57**, 8927; (*d*) R. D. Kardile and R.-S. Liu, *Org. Lett.,* 2019, **21**, 6452.