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Direct oxidation of *N*-ynylsulfonamides into *N*-sulfonyloxoacetamides with DMSO as a nucleophilic oxidant†

 Jun Dong,^{ab} Duo Fu,^a Dongning Sheng,^a Jiayi Wang^a and Jiaxi Xu^{id}*^a

N-Arylethynylsulfonamides are oxidized into *N*-sulfonyl-2-aryloxoacetamides directly and efficiently with dimethyl sulfoxide (DMSO) as both an oxidant and solvent with microwave assistance. DFT calculations indicate that DMSO nucleophilically attacks the ethylic triple bond and transfers its oxygen atom to the triple bond to form zwitterionic anionic *N*-sulfonyliminiums to trigger the reaction. Then it nucleophilically attacks the generated iminium intermediates to accomplish the oxidation *via* the second oxygen atom transfer. The current method provides a straightforward and efficient strategy to transform various *N*-arylethynylsulfonamides into *N*-sulfonyl-2-aryloxoacetamides, sulfonyl oxoacetimides, without any other electrophilic activators or oxidants.

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Introduction

Dimethyl sulfoxide (DMSO) has become increasingly important in recent years. The importance is due not only to its high solvent power for lots of organic and inorganic compounds, but also to its ability to act as a substrate, building block, synthon, or reagent in organic chemistry. DMSO has been employed as a versatile, cheap, and safe reagent in various organic transformations. DMSO can be used as a one carbon source,¹ and a sulfur source, such as S(O)_{*n*}Me (*n* = 0, 1, 2)² and S(O)Me₂ (ref. 2*e* and 3) for the incorporation of functional groups into target molecules.

The reaction of alkynes and DMSO has been explored during the recent years.^{2*b*,4} These reactions can be divided into two categories: (1) transition metal or Brønsted acid-catalyzed reactions of alkynes and DMSO.^{4*a,b,c,d,e*} (2) Direct nucleophilic addition of electron-deficient alkynes with DMSO.^{4*f,g*}

Ynamides have emerged as remarkably useful building blocks for organic synthesis because of their combined stability and peculiar reactivity, and their readily availability and low prices.⁵ The oxidation of ynamides is a straightforward and efficient method to prepare α -ketoimides which are biologically active molecules and have widespread applications in organic synthesis.⁶ For example, HIV inhibitor chloropeptin I,⁷ bestatin

analogues as inhibitors of serine proteinase elastase.⁸ In the past years, several methods have been developed for the synthesis of α -ketoimides from ynamides.^{4*e,9*} Among these methods, the combination of electrophilic activating reagents (I₂, NIS, Cu, Au *etc.*) and oxidants (organic or inorganic) provides a useful approach to generate α -ketoimides from ynamides. They can be representatively divided into the radical oxidation transformation (Scheme 1*a*)^{4*e,9,10*} and ionic oxidation transformation (Scheme 1*b*).¹¹ For the radical oxidative transformation, O₂ is usually as an oxidant and converted into peroxy radical species.^{4*e,9b-d,10a*} Differing from the radical oxidative conversion, S_N2' is the major path for the ionic transformation with *N*-oxides or sulfoxides as organic oxidants. In addition, for the gold-catalyzed oxidative transformation, there are two possible pathways: (1) intermolecular S_N2' process which is similar to other ionic reactions using electrophilic activating reagents (I₂, Cu(CH₃CN)₄PF₆, ArSCL, ArSeCl, ArTeBr, and so on);¹² (2) the pathway involving highly electrophilic α -oxo gold-carbene intermediates^{11*a-d,12b,13*} (Scheme 1*b*).

For the radical and ionic classes of oxidative transformations, both electrophilic activating reagents and external oxidants are necessary. Considering ynamides are not really electron-rich alkynes, they are also a class of relatively electron-deficient alkynes. In recent years, DMSO has been widely applied as a nucleophilic oxidant in organic reactions rather than only as a solvent.¹⁴ Ynamides are also relatively electron-deficient alkynes due to the attached amido or sulfonamido group. We envisioned that nucleophilic zwitterionic DMSO could serve as a nucleophilic oxidant in the reaction with relatively electron-deficient *N*-ynylsulfonamides under microwave-assisted conditions because microwave irradiation can accelerate some organic reactions.¹⁵ Herein, we present a direct and efficient oxidation of *N*-arylethynylsulfonamides into α -

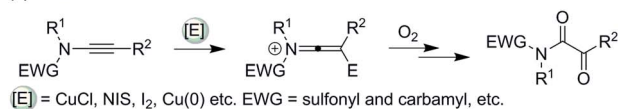
^aState Key Laboratory of Chemical Resource Engineering, Department of Organic Chemistry, College of Chemistry, Beijing University of Chemical Technology, Beijing 100029, P. R. China. E-mail: jxxu@mail.buct.edu.cn; Fax: +86 10 64435565

^bSchool of Chemistry and Environmental Engineering, Yancheng Teachers University, Yancheng 224007, People's Republic of China

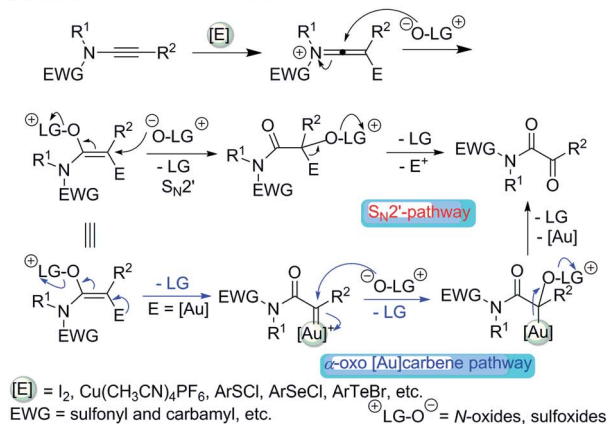
† Electronic supplementary information (ESI) available: Details on calculation on the reaction mechanism and copies of ¹H, ¹³C, and ¹⁹F NMR spectra of compounds 1, 2, 3, and 4. See DOI: 10.1039/d1ra04816c



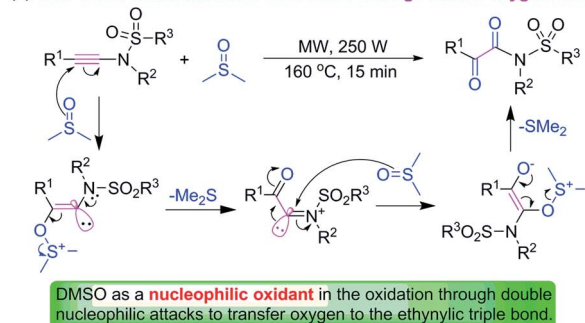
(a) Radical oxidative transformation:



(b) Ionic oxidative transformation:



(c) This Work: Direct oxidation with DMSO through double oxygen transfer

Scheme 1 Synthesis of α -keto-imides through the oxidation of ynamides.

ketoimides under the microwave irradiation without the addition of any other electrophilic activating reagents (such as I_2 , NIS, $\text{Cu(CH}_3\text{CN)}_4\text{PF}_6$ and so on) and external oxidants (for instant, N-oxide , O_2).

Results and discussion

Optimization of reaction conditions

Initially, a model reaction of *N*,4-dimethyl-*N*-(phenylethynyl) benzenesulfonamide (**1a**) and anhydrous DMSO (1 mL) was performed under microwave irradiation in a 10 mL microwave reaction tube, as outlined in Table 1.

Gratifyingly, the desired product **2a** was obtained in 78% yield (Table 1, entry 1). When commercial DMSO (without anhydrous treatment) was used, the yield of product **2a** was dropped sharply to 27% (Table 1, entry 2). In addition, the yield was also dropped slightly to 72% when the reaction was conducted under N_2 protection (Table 1, entry 3). The reaction was further optimized in anhydrous DMSO and it was found that when the temperature was increased to 170 °C or decreased to 150 °C, the yield dropped slightly. Product **2a** was obtained in 77% and 69% yields, respectively (Table 1, entries 4 and 5).

Table 1 Optimization of the reaction conditions^a

Entry	DMSO (mL)	Temp. (°C)	<i>t</i> (min)	2a ^b (%)
1	1	160	15	78
2	1 ^c	160	15	27
3 ^d	1	160	15	72
4	1	170	15	77
5	1	150	15	69
6	0.5	160	15	85, 83 ^e
7	1.5	160	15	71
8	0.1 ^f	160	15	70
9	0.5	160	10	50
10	0.5	160	20	50

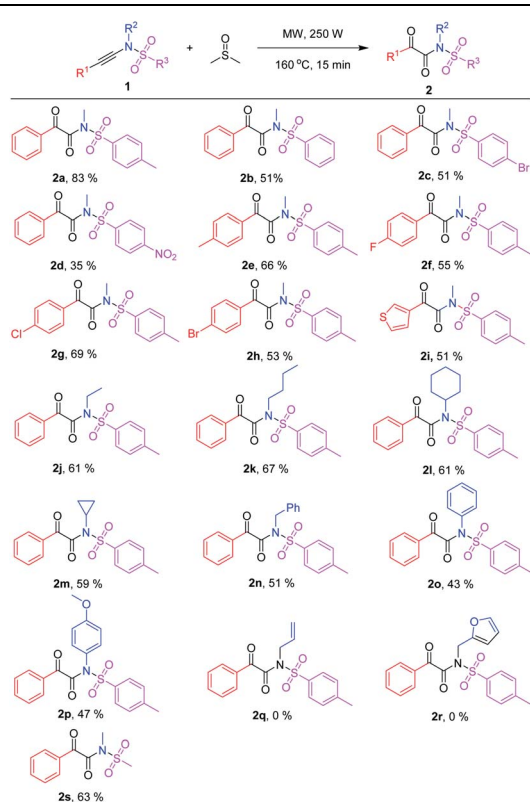
^a General conditions: **1a** (0.125 mmol, 36 mmg) in a capped 10 mL microwave reaction tube under microwave irradiation. ^b Yield on the basis of ^1H NMR analysis of the reaction mixture with 1,3,5-trimethoxybenzene as an internal standard. ^c Commercial DMSO as a solvent without waterless treatment. ^d Nitrogen protection. ^e Yield of the isolated product **2a**. ^f 0.1 mL of DMSO is enough to dissolve ynamide **1a**.

Furthermore, the volume of DMSO was screened, indicating that the concentration of **1a** had a slight effect on the yield of the product **2a** (Table 1, entries 6–8). When the solvent of DMSO was 0.5 mL, the product **2a** was obtained in 85% NMR yield and 83% yield of the isolated product (Table 1, entry 6). Next, when the volume of DMSO was increased to 1.5 mL or decreased to 0.1 mL, resulting in slightly lower yields of **2a** (71 and 70% yields, respectively) (Table 1, entries 7 and 8). At last, the reaction time was also optimized (Table 1, entries 9 and 10). When the reaction time was shortened from 15 min to 10 min, the yield was dropped to 50% (Table 1, entries 6 vs. 9). The yield of **2a** dropped to 50% as well when the reaction time was extended to 20 min because some products decomposed slightly (Table 1, entry 10).

Scope of ynamide oxidation

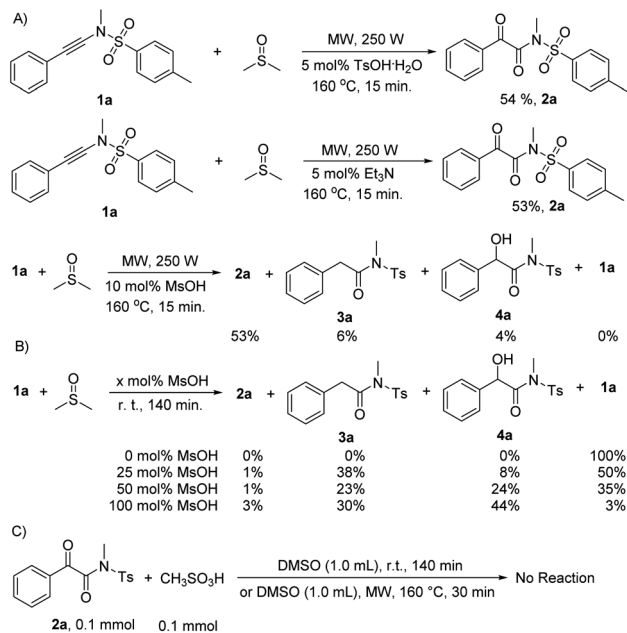
With the optimized reaction conditions in hand (Table 1, entry 5), various *N*-arylethynylarenesulfonamides **1** were tested to react with dimethyl sulfoxide (Table 2). The reactions proceeded smoothly with different arene (R^3) substituted ynamides **1a–1d** to generate the corresponding α -keto imides **2a–2d** in moderate to good yields (Table 2). Electron-rich *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide (**1a**) gave the corresponding product *N*-methyl-2-oxo-2-phenyl-*N*-tosylacetamide (**2a**) in 83% yield. Furthermore, both *N*-methyl-*N*-(phenylethynyl)benzenesulfonamide (**1b**) and 4-bromo-*N*-methyl-*N*-(phenylethynyl)benzenesulfonamide (**1c**) generated the corresponding products **2b** and **2c** in a moderate yield of 51%. For electron-deficient *N*-methyl-4-nitro-*N*-(phenylethynyl)benzenesulfonamide (**1d**), the desired *N*-methyl-*N*-((4-nitrophenyl)sulfonyl)-2-oxo-2-phenylacetamide (**2d**) was only isolated in 35% yield under



Table 2 Reaction scope for the formation of α -ketoimides **2**^a

^a Reaction conditions: **1** (0.125 mmol) in 0.5 mL of anhydrous DMSO in a 10 mL capped microwave reaction tube was heated under microwave irradiation. Yield of the isolated product.

the optimized reaction conditions. Moreover, the reaction scope was explored by using various aryl-substituted ynamides **1e–h** ($R^1 = \text{aryl}$), and the desired products **2e–h** were obtained in 53–69% yields which illustrated the substituent on the aryl have not an obvious electronic effect on this reaction. In addition, after replacing the phenyl group with thienyl, *N*,4-dimethyl-*N*-(thiophen-3-ylethynyl)benzenesulfonamide (**1i**) worked well to deliver the desired product **2i** in 51% yield. Next, different R^2 -substituted ynamides **1j–p** were attempted. The corresponding α -keto imides **2j–p** were formed in 43–67% yields. When R^2 was alkyl groups, such as ethyl, butyl, cyclohexyl, cyclopropyl, benzyl, the α -keto imides **2j–2n** were isolated in moderate yields (Scheme 2). Replacing the aryl substitution with the alkyl substitution, the yields of desired α -keto imides were dropped slightly and 2-oxo-*N*,2-diphenyl-*N*-tosylacetamide (**2o**), *N*-(4-methoxyphenyl)-2-oxo-2-phenyl-*N*-tosylacetamide (**2p**) were obtained in 43% and 47% yields, respectively. However, more electron-rich substrates *N*-allyl and *N*-(furan-2-yl)methyl ynamides **1q** and **1r** gave complex products due to their electron-rich allyl and furanyl groups. *N*-Methyl-*N*-phenylethynylmethanesulfonamide (**1s**) also worked well to generate the desired product **2s** in 63% yield (Table 2).



Scheme 2 Control experiments.

Mechanistic investigation

Control experiments. It was documented that DMSO decomposed into acidic methanesulfonic acid (MsOH) in the presence of air or oxygen and the acid promoted oxidative debenzoylation of *N*-benzylanilines with DMSO.^{14d} To verify whether some acid promoted our oxidation, three control experiments were conducted, with 5 mol% TsOH·H₂O, with 5 mol% Et₃N, and 10 mol% possible generated methanesulfonic acid as additives, respectively. The results indicated that the reactions with 5 mol% TsOH·H₂O or 5 mol% Et₃N as an additive gave the desired product **2a** in similar yields (54% and 53% from ¹H NMR analysis of the reaction mixtures with 1,3,5-trimethoxybenzene as an internal standard), lower than that under acid- and base-free conditions, revealing that acid and base cannot promote the reaction. For the reaction with 10 mol% MsOH as an additive, detailed analysis of the reaction mixture showed that two new byproducts, *N*-methyl-2-phenyl-*N*-tosylacetamide (**3a**) and 2-hydroxy-*N*-methyl-2-phenyl-*N*-tosylacetamide (**4a**), generated in 6% and 4% yields, respectively, without recovery of ynamide **1a** (Scheme 2A). Because byproducts **3a** and **4a** were observed without recovery of ynamide **1a** under the catalysis of acid at high temperature, we further conducted the reaction at mild room temperature under the catalysis of different amounts of possible generated MsOH. Importantly, no reaction occurred without MsOH as an additive at room temperature. However, in the presence of 25 mol%, 50 mol%, and 100 mol% MsOH, the yield of the desired product **2a** decreased obviously to 1–3% yields, but byproducts **3a** and **4a** were obtained in 23–38% yields and 8–44% yields, respectively, with recovery of ynamide **1a** in 3–50% (Scheme 2B). Furthermore, the product **2a** was treated with MsOH under the standard reaction conditions. No reaction was observed, revealing that the product **2a** was stable in the presence of MsOH (Scheme



2C). Finally, DMSO was irradiated with microwave at 160 °C for 15 min. The resulting solvent and its 1 : 1 diluted mixture with water were tested with pH paper. No acidic substance was observed. The experimental results indicated that no acid generated under our reaction conditions. The results are in good accordance with the previously reported observation,¹⁶ in which dimethyl sulfoxide was refluxed for 3 days, generating volatile materials, paraformaldehyde, dimethyl sulfide, dimethyl disulfide, bismethylthiomethane, and water with methanethiol as one of intermediates. The decomposition increased when diols or primary amides were heated in dimethyl sulfoxide at 190 °C for 36 h.¹⁶ Although DMSO decomposed into MsOH under the catalysis of relatively strong acids ($pK_a > 3.02$) and subsequent oxidation,¹⁷ another detailed investigation indicated that DMSO did not decompose for heating at 180 °C for 68 h without air or radical initiator under acid-free conditions. But it completely decomposed into dimethyl sulfide (42%), bis(methylthio)methane (31%), methyl disulfide (8%), paraformaldehyde, and water as major products with numerous unknown identities when it was heated at 180 °C for 68 h under either an atmosphere of air or one enriched in oxygen. MsOH might generate under these conditions.¹⁸ For our current synthetic method, all reactions were conducted at 160 °C for only 15 min under limited air and acid-free conditions in a 10 mL sealed microwave reaction tube, revealing that the reactions were performed without enough air source. Thus, on the basis of our control experiments and above analyses, the acid-catalyzed oxidation mechanism can be ruled out completely for our synthetic method.

DFT calculation. To best understand the direct oxidation mechanism of ynamides with DMSO, we performed DFT calculation investigation with *N*-methyl-*N*-phenylethynylmethanesulfonamide (**1s**) as a model substrate to minimize the calculational consumption. After many attempts on the possible reaction mechanisms, including DMSO first as electrophile to activate ynamides and then as nucleophilic oxidant, and DMSO first as an ene and ynamides as enophiles to trigger the reaction in the Alder-ene-like reaction, even in different configurations and conformations, finally, the double nucleophilic oxidation mechanism was established as shown in Fig. 1 and Scheme 3. DMSO first nucleophilically attacks relatively electron-deficient ynamides **1** on their β -carbon atom to generate zwitterionic intermediates **INT1** through transition states **TS1**, for **TS1s** with the activation energy of 37.2 kcal mol⁻¹, under microwave irradiation. The intermediates **INT1** further release a molecule of dimethyl sulfide to generate new acyl *N*-sulfonyl anionic zwitterionic iminium intermediates **INT2** via transition states **TS2**, in which the structure of **TS2** is similar to that of **INT1** due to early transition state, while, in **INT2**, the lone pair of electrons locate in the favorable *s*-transoid form due to the hyperconjugation of $n - \sigma_{C-O}^*$, for **TS2s** with 9.1 kcal mol⁻¹ free energy as its activation energy. This step is the rate-determining step because **TS1s** locates at the highest potential free energy of 45.2 kcal mol⁻¹. For the microwave-assisted reaction, it is reasonable because the polar reactants and intermediates generally locate at relatively higher temperature regions (so

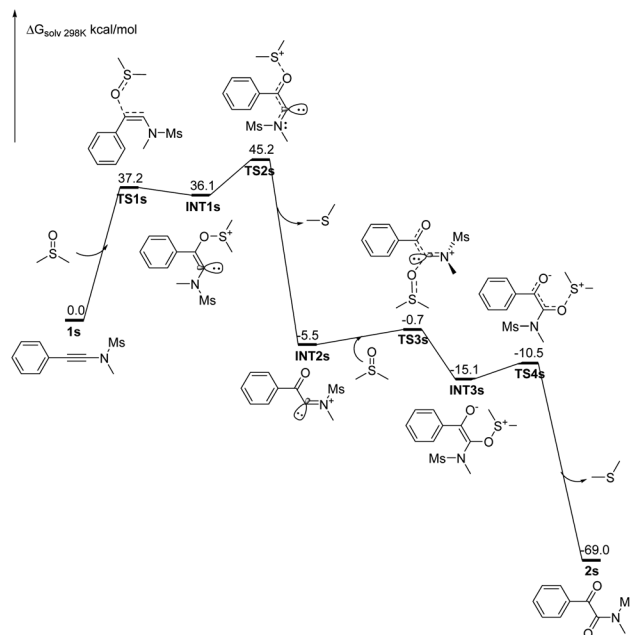
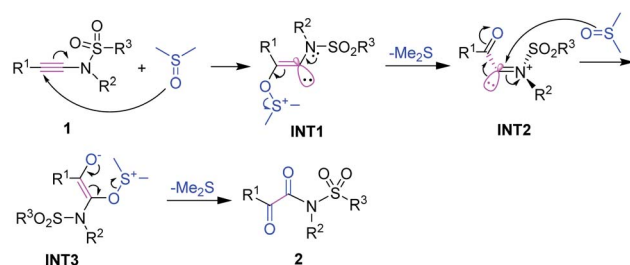


Fig. 1 Calculated potential energy surface for the DMSO oxidation of ynamides **1s** at the B3LYP/6-31+G(d,p) level of theory for all the intermediates and transition states, using the IEFPCM model in DMSO as a solvent.

called hot-spots) due to microwave selected heating.¹⁹ The second DMSO nucleophilically attacks the more electron-deficient iminiums **INT2** readily from the top or bottom of the iminium plane perpendicularly to form zwitterionic *cis*-enolate intermediates **INT3** through transition state **TS3**, with only 4.8 kcal mol⁻¹ as the activation energy for **TS1s**. For both **INT3** and **TS3**, they exist in their *cis*- and *cisoid* forms due to the weak electrostatic action between the enolate anion and sulfonium. The intermediates **INT3** favorably generate much stable final products **2** through transition states **TS3**, with 4.6 kcal mol⁻¹ of the activation energy for **TS1s**. The mechanism is a double nucleophilic oxidation of ynamides **1** with DMSO through the nucleophilic transfer its oxygen atom to ynamides twice.

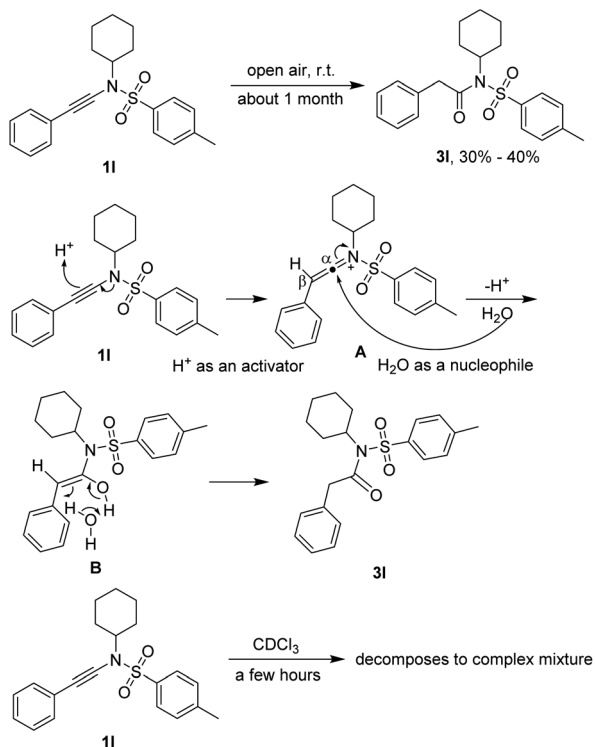
Stability of ynamides

It is worthy to note that the starting materials ynamides **1** are unstable enough, especially in their chloroform solutions, and should be stored in their pure states at low temperature (for instance -20 °C) under the protection of nitrogen. For example,



Scheme 3 Plausible reaction mechanism.



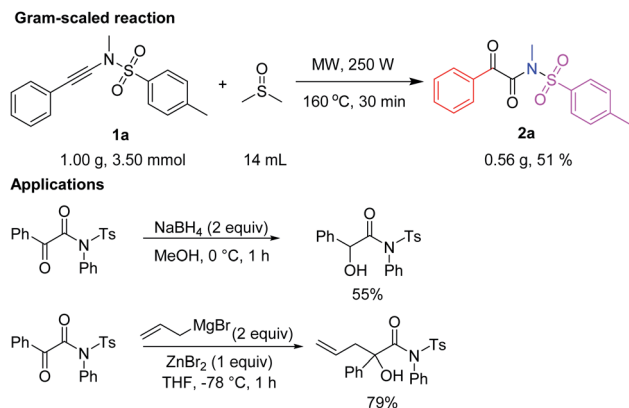


Scheme 4 Stability of ynamide 11.

ynamide **11** converted into *N*-cyclohexyl-2-phenyl-*N*-tosylacetamide (**3**) in 30% to 40% yield in open air at room temperature for about one month. The transformation was an acid-catalyzed water addition followed by a tautomerization through a water-participating six-membered transition state. The acid might come from glassware and water from environment. For the NMR determination of the structures of ynamides **1**, they should be determined soon after dissolved in deuterio chloroform because they decomposed completely to a complex mixture in a few hours (Scheme 4).

Gram-scaled reaction and application

More practically, this reaction can be performed at a 3.50 mmol scale, which clearly shows the potential application on a gram-scale preparation (Scheme 5).



Scheme 5 Gram-scaled reaction and selected reported applications.

For example, 3.50 mmol (1.00 g) of *N*,4-dimethyl-*N*-(phenylethynyl)benzenesulfonamide (**1a**) were reacted in 14 mL of DMSO at 160 °C under microwave irradiation (35 mL microwave reaction tube, 250 W) for 30 min to afford **2a** in 51% yield (562 mg) by flash column chromatography on silica gel.

Selected applications of α -keto imides, such as 2-oxo-*N*,2-diphenyl-*N*-tosylacetamide from the literature,^{14f} are listed in Scheme 5, one for synthesis of α -hydroxyl imide, and the other for quaternary carbon-containing α -hydroxyl imide (Scheme 5).

Conclusions

In summary, we have developed a new and efficient electrophile and external oxidant-free method to prepare α -keto-imides from ynamides with DMSO as a nucleophilic oxidant and solvent. In the reaction, DMSO serves as a nucleophilic oxidant to transfer its oxygen atom directly to ynamides twice. The current method is a simple and direct oxidation without any transition metal catalysts, electrophilic activators, and external oxidants. It is a less cost and economic synthetic method for α -keto-imides from ynamides.

Experimental

General information

Unless otherwise noted, all starting materials were purchased from commercial suppliers. DMSO was stirred overnight with NaH at room temperature and distilled freshly prior under vacuum to use. The microwave-assisted reactions were conducted on a CEM discovery SP microwave reactor. The attempted solvents were freshly distilled prior to use. Column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Branch of Qingdao Haiyang Chemical, with petroleum ether (PE, 60–90 °C fraction) and ethyl acetate (EA) as eluent. Reactions were monitored by thin-layer chromatography on GF254 silica gel plates (0.2 mm) from Institute of Yantai Chemical Industry. The plates were visualized under UV light, as well as other TLC stains (10% phosphomolybdic acid in ethanol; 1% potassium permanganate in water; 10 g of iodine absorbed on 30 g of silica gel). The IR spectra (KBr pellets, ν [cm⁻¹]) were taken on a Bruker Tensor 27 FTIR spectrometer. ¹H, ¹⁹F, and ¹³C NMR spectra were recorded on a Bruker 400 MHz spectrometer, usually in CDCl₃ as an internal standard, and the chemical shifts (δ) are reported in parts per million (ppm). And multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), dd (double doublet), m (multiplet). Coupling constants (*J*) are reported in hertz (Hz). HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected.

General procedure for the synthesis of *N*-arylethynylsulfonamides 1.^{20a} In the dark, to a solution of a terminal alkyne (3 mmol) in acetone (10 mL) was added NBS (641.0 mg, 3.6 mmol) and AgNO₃ (25.5 mg, 0.15 mmol). The resulting mixture was stirred at room temperature for 3 h. After filtration the filtrate was evaporated. Then 20 mL of petroleum ether (60–90 °C) was added. After filtration again the filtrate was evaporated under



vacuum to give the corresponding alkynyl bromide. Arene-sulfonamide (2.0 mmol), copper sulfate pentahydrate (50.0 mg, 0.2 mmol), 1,10-phenanthroline (72.0 mg, 0.4 mmol), K_2CO_3 (691.0 mg, 5 mmol), and toluene (10 mL) were added under nitrogen atmosphere. The reaction flask was evacuated under vacuum and flushed with nitrogen three times, then sealed under nitrogen and heated to 80 °C. The reaction mixture was stirred overnight at the same temperature, then cooled down to room temperature, filtered through Celite. The filtrate was evaporated and the residue was purified by flash silica gel column chromatography to give the desiredynamide **1**.

Note: most compounds **1** are unstable in air, or in their deuterated chloroform and chloroform solution. We usually store them in their pure states at -20 °C.

N,4-Dimethyl-N-(phenylethynyl)benzenesulfonamide (1a).^{20b} Colorless needle crystals, mp 79–81 °C, Lit.^{20b} mp 72–74 °C; yield: 32% (820 mg); $R_f = 0.33$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, $J = 8.2$ Hz, 2H), 7.35 (d, $J = 7.9$ Hz, 4H), 7.32–7.21 (m, 3H), 3.13 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 133.0, 131.2, 129.7, 128.2, 127.8, 127.7, 122.6, 83.9, 68.9, 39.2, 21.5.

N-Methyl-N-(phenylethynyl)benzenesulfonamide (1b).^{20b} Colorless crystals, mp 46–47 °C, Lit.^{20b} mp 45–47 °C; yield: 72% (1.52 g); $R_f = 0.26$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 8.08–7.97 (m, 2H), 7.86–7.67 (m, 3H), 7.46–7.26 (m, 5H), 3.19 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) (δ , ppm) = 136.2, 134.1, 131.1, 129.5, 128.5, 128.0, 127.8, 127.7, 84.1, 68.6, 39.0.

4-Bromo-N-methyl-N-(phenylethynyl)benzenesulfonamide (1c).^{20b} Colorless crystals, mp 50–51 °C, Lit.^{20b} mp 79–81 °C; yield: 35% (342 mg); $R_f = 0.26$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 7.96–7.90 (m, 4H), 7.40–7.33 (m, 5H), 3.21 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) (δ , ppm) = 135.9, 133.5, 131.9, 130.3, 129.4, 129.2, 128.8, 123.2, 84.4, 69.6, 39.8.

N-Methyl-4-nitro-N-(phenylethynyl)benzenesulfonamide (1d).^{20c} Colorless crystals, mp 119–120 °C, Lit.^{20c} mp 150–153 °C; yield: 15% (128 mg); $R_f = 0.39$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 8.58 (d, $J = 8.8$ Hz, 2H), 8.31 (d, $J = 8.8$ Hz, 2H), 7.42–7.35 (m, 5H), 3.28 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) (δ , ppm) = 135.9, 133.5, 131.9, 130.3, 129.4, 129.2, 128.8, 123.2, 84.4, 69.5, 39.8.

N,4-Dimethyl-N-(4-methylphenylethynyl)benzenesulfonamide (1e).^{20b} Colorless crystals, mp 55–56 °C, Lit.^{20b} mp 72–74 °C; yield: 38% (265 mg); $R_f = 0.46$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 7.82 (d, $J = 8.3$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.25 (d, $J = 8.1$ Hz, 2H), 7.08 (d, $J = 7.9$ Hz, 2H), 3.12 (s, 3H), 2.43 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (δ , ppm) = 144.9, 138.1, 133.2, 131.5, 129.9, 129.1, 127.9, 119.6, 83.3, 69.0, 39.4, 21.7, 21.5.

N-((4-Fluorophenyl)ethynyl)-N,4-dimethylbenzenesulfonamide (1f).^{20b} Colorless crystals, mp 86–88 °C, Lit.^{20b} mp 87–89 °C; yield: 36% (818 mg); $R_f = 0.43$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, $CDCl_3$) (δ , ppm) = 7.83 (d, $J = 8.3$ Hz, 2H), 7.49–7.29 (m, 4H), 7.08–6.81 (m, 2H), 3.14 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (δ , ppm) = 162.3 (d, $J_{F-C} = 249.1$ Hz), 144.9, 133.5 (d, $J_{F-C} = 8.3$ Hz), 133.2, 129.9, 127.8, 118.7 (d, $J_{F-C} = 3.1$

Hz), 115.6 (d, $J_{F-C} = 22.0$ Hz), 83.6, 68.0, 39.3, 21.7. ^{19}F NMR (377 MHz, $CDCl_3$) (δ , ppm) = -111.41.

N-((4-Chlorophenyl)ethynyl)-N,4-dimethylbenzenesulfonamide (1g).^{20b} Golden crystals, mp 97–98 °C, Lit.^{20b} mp 105–107 °C; yield: 51% (975 mg); $R_f = 0.28$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 7.88 (d, $J = 8.4$ Hz, 2H), 7.53 (d, $J = 8.0$ Hz, 2H), 7.38 (s, 4H), 3.17 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) (δ , ppm) = 146.1, 134.0, 133.3, 130.8, 129.5, 128.6, 122.4, 85.1, 68.4, 39.7, 21.4.

N-((4-Bromophenyl)ethynyl)-N,4-dimethylbenzenesulfonamide (1h).^{20b} Colorless crystals, mp 111–112 °C, Lit.^{20b} mp 116–118 °C; yield: 53% (845 mg); $R_f = 0.39$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 7.82 (d, $J = 8.3$ Hz, 2H), 7.44–7.32 (m, 4H), 7.20 (d, $J = 8.4$ Hz, 2H), 3.14 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) (δ , ppm) = 145.0, 133.2, 132.8, 131.5, 129.9, 127.8, 121.9, 121.8, 85.1, 68.2, 39.3, 21.1.

N,4-Dimethyl-N-(thiophen-3-ylethynyl)benzenesulfonamide (1i).^{20b} Colorless crystals, mp 102–103 °C, Lit.^{20b} mp 79–81 °C; yield: 59% (1.4 g); $R_f = 0.31$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 7.83 (d, $J = 8.3$ Hz, 2H), 7.42–7.30 (m, 3H), 7.24 (dd, $J = 5.0, 3.0$ Hz, 1H), 7.05 (dd, $J = 5.0, 1.0$ Hz, 1H), 3.13 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) (δ , ppm) = 144.8, 133.3, 130.2, 129.8, 128.8, 127.9, 125.2, 121.4, 83.3, 64.1, 39.3, 21.7.

N-Ethyl-4-methyl-N-(phenylethynyl)benzenesulfonamide (1j).^{20d} Colorless crystals, mp 69–70 °C, yield: 44% (1.067 g); $R_f = 0.43$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 7.75 (d, $J = 8.3$ Hz, 2H), 7.37 (d, $J = 8.2$ Hz, 2H), 7.28–7.06 (m, 5H), 3.37 (q, $J = 7.2$ Hz, 2H), 2.32 (s, 3H), 1.11 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) (δ , ppm) = 146.0, 134.8, 131.0, 130.0, 128.6, 127.8, 127.6, 123.0, 82.4, 70.6, 46.8, 20.7, 12.7.

N-Butyl-4-methyl-N-(phenylethynyl)benzenesulfonamide (1k).^{20b} Colorless oil, yield: 72% (1.79 g); $R_f = 0.41$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, CD_3COCD_3) (δ , ppm) = 7.93 (d, $J = 8.3$ Hz, 2H), 7.50 (d, $J = 8.1$ Hz, 2H), 7.45–7.28 (m, 5H), 3.47 (t, $J = 7.1$ Hz, 2H), 2.46 (s, 3H), 1.72 (quintet, $J = 7.2$ Hz, 2H), 1.41 (sextet, $J = 7.2$ Hz, 2H), 0.94 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CD_3COCD_3) (δ , ppm) = 145.0, 134.7, 130.9, 129.9, 128.5, 127.8, 127.6, 123.0, 82.7, 70.2, 51.2, 29.8, 20.6, 19.2, 12.9.

N-Cyclohexyl-4-methyl-N-(phenylethynyl)benzenesulfonamide (1l).^{20b} Colorless crystals, mp 82–83 °C, Lit.^{20b} mp 67–69 °C; yield: 50% (1.217 g); $R_f = 0.48$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, $CDCl_3$) (δ , ppm) = 7.85 (d, $J = 8.3$ Hz, 2H), 7.39–7.36 (m, 2H), 7.33–7.23 (m, 5H), 3.89–3.80 (m, 1H), 2.42 (s, 3H), 1.77–1.69 (m, 4H), 1.61–1.48 (m, 3H), 1.36–1.25 (m, 2H), 1.11–0.99 (m, 1H), ^{13}C NMR (101 MHz, $CDCl_3$) (δ , ppm) = 144.3, 136.2, 131.2, 129.6, 128.1, 127.5, 127.3, 123.2, 80.2, 72.3, 59.5, 31.1, 25.3, 24.8, 21.5.

N-Cyclopropyl-4-methyl-N-(phenylethynyl)benzenesulfonamide (1m).^{20b} Colorless crystals, mp 66–67 °C, Lit.^{20b} mp 64–66 °C; yield: 58% (548 mg); $R_f = 0.29$ (PE/EtOAc 10 : 1, v/v). 1H NMR (400 MHz, $CDCl_3$) (δ , ppm) = 7.88 (d, $J = 8.3$ Hz, 2H), 7.37–7.35 (m, 4H), 7.31–7.25 (m, 3H), 2.83 (tt, $J = 7.0, 3.5$ Hz, 1H), 2.46 (s, 3H), 0.93–0.89 (m, 2H), 0.84–0.76 (m, 2H). ^{13}C NMR (101



MHz, CDCl₃) (δ , ppm) = 144.8, 133.9, 131.3, 129.7, 128.2, 128.0, 127.7, 122.8, 81.8, 70.5, 32.9, 21.7, 6.5.

***N*-Benzyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide**

(1n).^{20e} Colorless crystals, mp 76–78 °C, Lit.^{20e} mp 82–83 °C. yield: 71% (779 mg); R_f = 0.27 (PE/EtOAc 10 : 1, v/v). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 7.79 (d, J = 8.2 Hz, 2H), 7.36–7.29 (m, 7H), 7.23 (s, 5H), 4.58 (s, 2H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 144.6, 134.6, 134.4, 131.1, 129.7, 128.8, 128.5, 128.3, 128.2, 127.7, 127.6, 122.8, 82.6, 71.3, 55.7, 21.6.

4-Methyl-*N*-phenyl-*N*-(phenylethynyl)benzenesulfonamide

(1o).^{20e} Colorless crystals, mp 94–96 °C, Lit.^{20e} mp 68–70 °C; yield: 7% (137 mg); R_f = 0.37 (PE/EtOAc 10 : 1, v/v). ¹H NMR (400 MHz, CD₃COCD₃) (δ , ppm) = 7.66 (d, J = 8.0 Hz, 2H), 7.46 (d, J = 8.0 Hz, 2H), 7.44–7.40 (m, 5H), 7.38–7.34 (m, 5H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CD₃COCD₃) (δ , ppm) = 146.4, 139.8, 133.8, 132.0, 130.6, 130.1, 129.3, 129.2, 129.0, 126.8, 123.3, 83.9, 71.1, 21.5.

***N*-(4-Methoxyphenyl)-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (1p).**^{20b} Colorless crystals, mp 117–118 °C, Lit.^{20b} mp 106–108 °C; yield: 38% (292 mg); R_f = 0.60 (PE/EtOAc 3 : 1, v/v). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 7.63 (d, J = 8.3 Hz, 2H), 7.40–7.36 (m, 2H), 7.30–7.27 (m, 5H), 7.18 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 3.80 (s, 3H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 159.5, 144.9, 132.9, 131.5, 131.3, 129.5, 128.3, 128.2, 127.9, 127.8, 122.7, 114.2, 83.4, 69.9, 55.5, 21.7.

***N*-Allyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide**

(1q).^{20a} Light yellow oil; yield: 38% (769 mg); R_f = 0.35 (PE/EtOAc 10 : 1, v/v). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 7.83 (d, J = 8.4 Hz, 2H), 7.45–7.30 (m, 4H), 7.27–7.19 (m, 3H), 5.77 (ddt, J = 16.6, 10.2, 6.3 Hz, 1H), 5.28 (dq, J = 17.0, 1.4 Hz, 1H), 5.21 (dq, J = 10.1, 1.2 Hz, 1H), 4.03 (dt, J = 6.3, 1.3 Hz, 2H), 2.40 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 144.6, 134.4, 131.1, 130.7, 129.6, 128.1, 127.6, 127.5, 122.6, 119.9, 82.2, 54.2, 21.4.

***N*-(Furan-2-ylmethyl)-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (1r).**²¹ Colorless oil; yield: 62% (665 mg); R_f = 0.25 (PE/EtOAc 10 : 1, v/v). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 7.79 (d, J = 8.4 Hz, 2H), 7.38–7.20 (m, 8H), 6.31 (d, J = 3.3 Hz, 1H), 6.28 (dd, J = 3.3, 1.8 Hz, 1H), 4.65 (s, 2H), 2.43 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 147.9, 144.6, 143.0, 134.5, 131.2, 129.6, 128.2, 127.8, 127.7, 122.7, 110.5, 110.4, 82.1, 48.2, 21.6.

***N*-Methyl-*N*-(phenylethynyl)methanesulfonamide (1s).**^{14e}

Colorless crystals, mp 48–49 °C, yield: 68% (712 mg); R_f = 0.50 (PE/EtOAc 3 : 1, v/v). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 7.44–7.36 (m, 2H), 7.29–7.28 (m, 3H), 3.26 (s, 3H), 3.09 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 131.3, 128.2, 127.9, 122.2, 83.0, 69.2, 39.0, 36.5.

General procedure for the synthesis of α -keto imides 2. *N*-Arylethynylsulfonamide **1** (0.125 mmol) was dissolved in anhydrous DMSO (0.5 mL). The reaction mixture was further stirred at 160 °C for 15 min under microwave irradiation (250 W) in a 10 mL microwave reaction tube. After cooling and addition of water (5 mL), the mixture was extracted with DCM (5 \times 3 mL), and combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting residue was purified by silica gel column

chromatography with petroleum ether (60–90 °C) and ethyl acetate (50 : 1 to 10/1, v/v) as eluent to afford α -keto imide **2**.

***N*-Methyl-2-oxo-2-phenyl-*N*-tosylacetamide (2a).**^{12a} Colorless crystals, mp 85–86 °C, yield: 83% (33 mg); R_f = 0.24 (PE/EtOAc 10 : 1, v/v). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 7.96–7.93 (m, 2H, ArH), 7.91–7.87 (m, 2H, ArH), 7.69–7.60 (m, 1H, ArH), 7.56–7.51 (m, 2H, ArH), 7.38 (d, J = 8.5 Hz, 2H, ArH), 3.24 (s, 3H), 2.45 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 188.0, 167.2, 145.9, 134.4, 133.4, 132.8, 130.1, 129.7, 128.8, 128.4, 30.7, 21.7.

***N*-Methyl-2-oxo-2-phenyl-*N*-(phenylsulfonyl)acetamide (2b).** Colorless crystals, mp 79–80 °C, yield: 51% (31 mg); R_f = 0.21 (PE/EtOAc 10 : 1, v/v). IR (KBr): 1684, 1597, 1450, 1373, 1329, 1231, 1168, 1088, 1051, 947, 726, 985, 601, 573 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 8.05–8.01 (m, 2H, ArH), 7.98–7.93 (m, 2H, ArH), 7.75–7.69 (m, 1H, ArH), 7.68–7.59 (m, 3H, ArH), 7.57–7.51 (m, 2H, ArH), 3.26 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 188.0, 167.2, 136.4, 134.6, 134.5, 132.6, 129.7, 129.5, 128.9, 128.3, 30.8. HRMS (ESI-TOF) m/z : [M + Na]⁺ calcd for C₁₅H₁₃NNaO₄S⁺ 326.0457, found 326.0451.

***N*-((4-Bromophenyl)sulfonyl)-*N*-methyl-2-oxo-2-phenylacetamide (2c).**^{12a} Yellow crystals, mp 78–81 °C, yield: 51% (24 mg); R_f = 0.26 (PE/EtOAc 10 : 1, v/v). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 7.96–7.92 (m, 2H, ArH), 7.93–7.84 (m, 2H, ArH), 7.80–7.72 (m, 2H, ArH), 7.71–7.63 (m, 1H, ArH), 7.54 (t, J = 7.7 Hz, 2H, ArH), 3.26 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 188.0, 167.0, 135.5, 134.7, 132.9, 132.5, 130.1, 129.8, 129.7, 128.9, 30.9.

***N*-Methyl-*N*-((4-nitrophenyl)sulfonyl)-2-oxo-2-phenylacetamide (2d).** Colorless crystals, mp 128–130 °C, yield: 35% (15 mg); R_f = 0.14 (PE/EtOAc 10 : 1, v/v). IR (KBr): 1687, 1534, 1378, 1350, 1229, 1167, 946, 738, 715, 617, 582 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 8.48–8.43 (m, 2H, ArH), 8.26–8.21 (m, 2H, ArH), 7.97–7.93 (m, 2H, ArH), 7.72–7.66 (m, 1H, ArH), 7.56 (t, J = 7.7 Hz, 2H, ArH), 3.32 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 187.8, 166.7, 151.1, 142.1, 134.9, 132.3, 129.8, 129.0, 124.6, 31.2. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₅H₁₃N₂O₆S⁺ 349.0489, found 349.0480.

***N*-Methyl-2-oxo-2-(4-methylphenyl)-*N*-tosylacetamide (2e).**^{12a} Colorless crystals, mp 134–135 °C, yield: 66% (27 mg); R_f = 0.26 (PE/EtOAc 10 : 1, v/v). ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 7.89 (d, J = 8.4 Hz, 2H, ArH), 7.83 (d, J = 8.2 Hz, 2H, ArH), 7.39 (d, J = 7.7 Hz, 2H, ArH), 7.33 (d, J = 7.7 Hz, 2H, ArH), 3.23 (s, 3H), 2.46 (s, 3H), 2.44 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 187.7, 167.4, 145.8, 145.7, 133.5, 130.3, 130.1, 129.8, 129.6, 128.4, 30.7, 21.9, 21.7.

2-(4-Fluorophenyl)-*N*-methyl-2-oxo-*N*-tosylacetamide (2f). Colorless crystals, mp 138–141 °C, yield: 55% (23 mg); R_f = 0.26 (PE/EtOAc 10 : 1, v/v). IR (KBr): 1672, 1598, 1370, 1236, 1164, 1051, 944, 667, 589, 546 cm⁻¹. ¹H NMR (400 MHz, CDCl₃) (δ , ppm) = 8.00–7.95 (m, 2H, ArH), 7.89 (d, J = 8.4 Hz, 2H, ArH), 7.40 (d, J = 8.0 Hz, 2H, ArH), 7.24–7.18 (m, 2H, ArH), 3.24 (s, 3H), 2.47 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) (δ , ppm) = 186.5, 167.7, 166.09 (d, J_{F-C} = 182.4 Hz), 146.0, 133.3, 132.37 (d, J_{F-C} = 9.8 Hz), 130.1, 129.3, 128.4, 116.24 (d, J_{F-C} = 22.4 Hz), 30.7, 21.7. ¹⁹F NMR (377 MHz, CDCl₃) (δ , ppm) = -102.2. HRMS (ESI-TOF) m/z : [M + H]⁺ calcd for C₁₆H₁₅FNO₄S⁺ 336.0700, found 336.0698.



2-(4-Chlorophenyl)-*N*-methyl-2-oxo-*N*-tosylacetamide (2g). Colorless crystals, mp 138–140 °C, yield: 69% (30 mg); $R_f = 0.24$ (PE/EtOAc 10 : 1, v/v). IR (KBr): 1685, 1665, 1587, 1372, 1233, 1164, 1052, 943, 762, 666, 594, 545 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.94–7.84 (m, 4H, ArH), 7.54–7.49 (m, 2H, ArH), 7.43–7.38 (m, 2H, ArH), 3.24 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 186.8, 166.9, 146.0, 141.0, 133.3, 131.2, 130.9, 130.2, 129.3, 128.4, 30.7, 21.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{ClNNaO}_4\text{S}^+$ 374.0224, found 374.0220.

2-(4-Bromophenyl)-*N*-methyl-2-oxo-*N*-tosylacetamide (2h). Colorless crystals, mp 130–132 °C, yield: 53% (26 mg); $R_f = 0.26$ (PE/EtOAc 10 : 1, v/v). IR (KBr): 1662, 1586, 1372, 1230, 1162, 1051, 941, 758, 665, 592, 546 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.89–7.86 (m, 2H, ArH), 7.84–7.76 (m, 2H, ArH), 7.72–7.64 (m, 2H, ArH), 7.40 (d, $J = 8.4$ Hz, 2H, ArH), 3.23 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 187.0, 166.8, 146.0, 133.2, 132.2, 131.6, 130.9, 130.1, 129.8, 128.3, 30.7, 21.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{14}\text{BrNNaO}_4\text{S}^+$ 417.9719, found 417.9714.

***N*-Methyl-2-oxo-2-(thiophen-3-yl)-*N*-tosylacetamide (2i).**^{11e} Yellow crystals, mp 65–67 °C, yield: 51% (41 mg); $R_f = 0.11$ (PE/EtOAc 10 : 1, v/v). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 8.14 (dd, $J = 2.9, 1.2$ Hz, 1H), 7.90 (d, $J = 8.4$ Hz, 2H), 7.59 (dd, $J = 5.1, 1.2$ Hz, 1H), 7.43–7.36 (m, 3H), 3.22 (s, 3H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 181.5, 166.9, 145.8, 137.7, 135.6, 133.5, 130.0, 128.4, 127.1, 126.9, 30.9, 21.7.

***N*-Ethyl-2-oxo-2-phenyl-*N*-tosylacetamide (2j).** Colorless oil, yield: 61% (25 mg); $R_f = 0.36$ (PE/EtOAc 10 : 1, v/v). IR (KBr): 1677, 1597, 1368, 1214, 1178, 1161, 1087, 1051, 972, 715, 660, 591, 552 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 8.01–7.86 (m, 4H), 7.73–7.62 (m, 1H), 7.58–7.54 (m, 2H), 7.41 (d, $J = 8.2$ Hz, 2H), 3.78 (q, $J = 7.0$ Hz, 2H), 2.48 (s, 3H), 1.29 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 187.8, 167.1, 145.7, 134.4, 134.4, 132.9, 130.1, 129.6, 128.8, 128.3, 77.3, 77.0, 76.7, 40.9, 21.7, 13.7. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{17}\text{H}_{17}\text{NNaO}_4\text{S}^+$ 354.0770, found 354.0765.

***N*-Butyl-2-oxo-2-phenyl-*N*-tosylacetamide (2k).** Colorless crystals, mp 62–63 °C, yield: 67% (30 mg); $R_f = 0.42$ (PE/EtOAc 10 : 1, v/v). IR (KBr): 2920, 1667, 1597, 1451, 1370, 1210, 1170, 1088, 1003, 919, 715, 664, 593, 546 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.95–7.89 (m, 4H, ArH), 7.67–7.61 (m, 1H, ArH), 7.56–7.50 (m, 2H, ArH), 7.39 (d, $J = 8.6$ Hz, 2H, ArH), 3.69–3.61 (m, 2H), 2.47 (s, 3H), 1.66 (tt, $J = 8.0, 6.6$ Hz, 2H), 1.32 (tq, $J = 7.4, 7.4$ Hz, 2H), 0.91 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 187.9, 167.3, 145.7, 134.4, 134.3, 132.9, 130.0, 129.6, 128.8, 128.4, 45.5, 30.2, 21.7, 20.0, 13.5. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{19}\text{H}_{21}\text{NNaO}_4\text{S}^+$ 382.1083, found 382.1077.

***N*-Cyclohexyl-2-oxo-2-phenyl-*N*-tosylacetamide (2l).**^{11e} Colorless crystals, mp 80–83 °C, yield: 61% (29 mg); $R_f = 0.38$ (PE/EtOAc 10 : 1, v/v). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.94 (d, $J = 8.3$ Hz, 4H), 7.62 (tt, $J = 7.2, 1.8$ Hz, 1H), 7.52 (t, $J = 7.7$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 3.78 (tt, $J = 12.2, 3.8$ Hz, 1H), 2.46 (s, 3H), 2.37–2.22 (m, 2H), 1.86–1.70 (m, 2H), 1.68–1.47 (m, 3H), 1.20 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) =

186.8, 167.9, 145.5, 134.8, 134.1, 132.9, 130.0, 129.7, 128.7, 128.3, 61.0, 29.1, 26.4, 24.9, 21.7.

***N*-Cyclopropyl-2-oxo-2-phenyl-*N*-tosylacetamide (2m).** Colorless crystals, mp 88–90 °C, yield: 59% (25 mg); $R_f = 0.49$ (PE/EtOAc 10 : 1, v/v). IR (KBr): 2234, 1597, 1369, 1174, 1090, 1027, 862, 814, 755, 672, 573, 548 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 8.00–7.94 (m, 4H), 7.66 (tt, $J = 7.6, 1.2$ Hz, 1H), 7.54 (t, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 2.77 (tt, $J = 6.8, 4.0$ Hz, 1H), 2.49 (s, 3H), 0.99–0.94 (tt, $J = 6.8, 4.0$ Hz, 1H, 2H), 0.77–0.72 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 187.4, 168.5, 145.6, 134.9, 134.4, 132.6, 129.9, 129.8, 128.8, 128.6, 27.2, 21.7, 7.8. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{18}\text{H}_{17}\text{NNaO}_4\text{S}^+$ 366.0770, found 366.0763.

***N*-Benzyl-2-oxo-2-phenyl-*N*-tosylacetamide (2n).**^{12a} Yellowish oil, yield: 51% (25 mg); $R_f = 0.56$ (PE/EtOAc 10 : 1, v/v). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.93–7.81 (m, 2H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.64–7.57 (m, 1H), 7.49 (dd, $J = 8.3, 7.1$ Hz, 2H), 7.29–7.21 (m, 7H), 4.98 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 187.7, 167.5, 145.6, 134.6, 134.4, 134.4, 132.8, 129.7, 129.6, 128.8, 128.4, 128.0, 127.7, 77.3, 77.0, 76.7, 48.2, 21.6.

2-Oxo-*N*,2-diphenyl-*N*-tosylacetamide (2o).^{11e} Colorless crystals, mp 131–132 °C, yield: 43% (20 mg); $R_f = 0.53$ (PE/EtOAc 3 : 1, v/v). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.98–7.95 (m, 2H), 7.78 (d, $J = 8.4$ Hz, 2H), 7.70–7.65 (m, 1H), 7.57–7.53 (m, 2H), 7.48–7.44 (m, 1H), 7.40 (t, $J = 8.0$ Hz, 2H), 7.37 (d, $J = 8.0$ Hz, 2H), 7.15 (dd, $J = 7.6, 1.6$ Hz, 2H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 187.6, 166.7, 145.9, 134.6, 134.0, 133.4, 132.7, 130.5, 130.2, 129.7, 129.6, 129.4, 129.0, 128.9, 21.8.

***N*-(4-Methoxyphenyl)-2-oxo-2-phenyl-*N*-tosylacetamide (2p).**^{9b} Colorless crystals, mp 44–46 °C, yield: 47% (21 mg); $R_f = 0.41$ (PE/EtOAc 3 : 1, v/v). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.91 (d, $J = 7.6, 2\text{H}$), 7.77 (d, $J = 8.1$ Hz, 2H), 7.64 (m, 1H), 7.53–7.49 (m, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.03 (d, $J = 8.3$ Hz, 2H), 6.85 (dd, $J = 8.4, 1.6$ Hz, 2H), 3.80 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 187.7, 166.8, 160.7, 145.8, 134.6, 134.1, 132.7, 131.7, 129.7, 129.6, 129.0, 128.9, 125.6, 114.7, 55.5, 21.8.

***N*-Methyl-*N*-(methylsulfonyl)-2-oxo-2-phenylacetamide (2s).**^{11e} Colorless crystals, mp 74–75 °C, yield: 63% (19 mg); $R_f = 0.38$ (PE/EtOAc 3 : 1, v/v). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.91 (d, $J = 8.0$ Hz, 2H), 7.64 (td, $J = 7.6, 1.3$ Hz, 1H), 7.51 (t, $J = 7.6$ Hz, 2H), 3.39 (s, 3H), 3.29 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 188.4, 167.1, 134.8, 132.2, 129.9, 128.8, 40.8, 31.2.

***N*-Methyl-2-phenyl-*N*-tosylacetamide (3a).**²² Colorless oil, yield: 38% (11.5 mg) from 0.1 mmol of **1a**; $R_f = 0.68$ (PE/EtOAc 5 : 1, v/v). ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.62 (d, $J = 8.0$ Hz, 2H), 7.27–7.17 (m, 5H), 7.06 (d, $J = 8.0$ Hz, 2H), 3.97 (s, 2H), 3.20 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 171.4, 145.1, 136.1, 133.5, 123.0, 129.5, 128.7, 127.6, 127.3, 43.2, 33.4, 21.8.

2-Hydroxy-*N*-methyl-2-phenyl-*N*-tosylacetamide (4a). Colorless crystals, mp 136–138 °C; yield: 44% (14 mg); $R_f = 0.11$ (PE/EtOAc 5 : 1, v/v). IR (KBr): 3610, 1675, 1597, 1450, 1373, 1329, 1231, 1168, 1088, 1051, 947, 726, 985, 601, 573 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.55 (d, $J = 8.4$ Hz, 2H), 7.38–7.30 (m, 3H), 7.26 (d, $J = 8.1$ Hz, 2H), 7.21 (dd, $J = 7.7, 1.9$ Hz, 2H),



5.65 (d, $J = 7.8$ Hz, 1H), 3.92 (d, $J = 7.8$ Hz, 1H), 3.14 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 173.7, 145.3, 137.6, 134.8, 129.6, 129.1, 128.9, 128.1, 127.7, 73.6, 32.8, 21.6. HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{NaNO}_4\text{S}^+$ 342.0770, found 342.0778.

Gram-scaled synthesis of α -keto imide 2a. *N*-Phenylethynylsulfonamide **1a** (1.00 g, 3.5 mmol) was dissolved in anhydrous DMSO (14 mL). The reaction mixture was further stirred at 160 °C for 30 min under microwave irradiation (250 W) in a 35 mL microwave reaction tube. After cooling and addition of water (100 mL), the mixture was extracted with DCM (5×50 mL), and combined organic layer was washed with brine, dried over anhydrous sodium sulfate, and concentrated *in vacuo*. The resulting residue was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (50 : 1 to 10/1, v/v) as eluent to afford α -keto imide **2a** 562 mg, 51% yield.

Conversion of *N*-cyclohexyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (1l**) to *N*-cyclohexyl-2-phenyl-*N*-tosylacetamide (**3l**).** *N*-Cyclohexyl-4-methyl-*N*-(phenylethynyl)benzenesulfonamide (**1l**) (353 mg, 1 mmol) was placed in a sample bottle at room temperature under open air for about one month. The sample decomposed completely by TLC analysis (silica gel, PE : EtOAc, 10 : 1, v/v), showing one major component. It was purified by silica gel column chromatography with petroleum ether (60–90 °C) and ethyl acetate (15 : 1, v/v) as eluent to afford *N*-tosylacetamide **3l** 111 mg to 148 mg (30% to 40% yield).

***N*-Cyclohexyl-2-phenyl-*N*-tosylacetamide (**3l**).** Colorless crystals, mp 86–87 °C, yield: 30% to 40% (111 mg to 148 mg); $R_f = 0.28$ (PE/EtOAc 10 : 1, v/v). IR (KBr): 2934, 2855, 1691, 1454, 1359, 1169, 1089, 997, 591 cm^{-1} . ^1H NMR (400 MHz, CDCl_3) (δ , ppm) = 7.69 (d, $J = 8.4$ Hz, 2H), 7.36–7.15 (m, 5H), 7.15–7.04 (m, 2H), 4.00 (s, 2H), 3.97 (tt, $J = 12.0, 3.6$ Hz, 1H), 2.41 (s, 3H), 2.27 (qd, $J = 12.2, 3.5$ Hz, 2H), 1.80–1.69 (m, 2H), 1.65–1.51 (m, 3H), 1.31–1.02 (m, 3H). ^{13}C NMR (101 MHz, CDCl_3) (δ , ppm) = 171.5, 144.4, 137.1, 133.9, 129.6, 129.2, 128.3, 127.3, 126.9, 61.8, 44.5, 30.1, 26.6, 24.9, 21.4. HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{21}\text{H}_{26}\text{NO}_3\text{S}^+$ 372.1627, found 372.1633.

Conflicts of interest

There are no conflicts of interest to declare.

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References

- (a) P. Zhang, Y. Yang, Z. Chen, Z. Xu, X. Xu, Z. Zhou, X. Yu and W. Yi, *Adv. Synth. Catal.*, 2019, **361**, 3002–3007; (b) W.-M. Shu, J.-X. He, X.-F. Zhang, S. Wang and A.-X. Wu, *J. Org. Chem.*, 2019, **84**, 2962–2968; (c) R. Ebule,

- S. Mudshinge, M. H. Nantz, M. S. Mashuta, G. B. Hammond and B. Xu, *J. Org. Chem.*, 2019, **84**, 3249–3259; (d) X. Zhu, W. Li, X. Luo, G. Deng, Y. Liang and J. Liu, *Green Chem.*, 2018, **20**, 1970–1974; (e) R. Zhang, H. Yu, Z. Li, Q. Yan, P. Li, J. Wu, J. Qi, M. Jiang and L. Sun, *Adv. Synth. Catal.*, 2018, **360**, 1384–1388; (f) X. Xu, Y. Yang, X. Zhang and W. Yi, *Org. Lett.*, 2018, **20**, 566–569; (g) C. Xu, S.-F. Jiang, X.-H. Wen, Q. Zhang, Z.-W. Zhou, Y.-D. Wu, F.-C. Jia and A.-X. Wu, *Adv. Synth. Catal.*, 2018, **360**, 2267–2271; (h) M. Phanindrudu, S. B. Wakade, D. K. Tiwari, P. R. Likhari and D. K. Tiwari, *J. Org. Chem.*, 2018, **83**, 9137–9143; (i) R. A. Garza-Sanchez, T. Patra, A. Tlahuext-Aca, F. Strieth-Kalthoff and F. Glorius, *Chem.-Eur. J.*, 2018, **24**, 10064–10068; (j) H.-J. Ai, X. Qi, J.-B. Peng, J. Ying and X.-F. Wu, *Asian J. Org. Chem.*, 2018, **7**, 2045–2048.
- (a) W. C. Hu, F. Y. Zhang, C. Chen, T. H. Qi, Y. L. Shen, G. Y. Qian and Z. T. Rong, *Chem. Commun.*, 2021, **57**, 6995–6998; (b) D. Fu, J. Dong, H. G. Du and J. X. Xu, *J. Org. Chem.*, 2020, **85**, 2752–2758; (c) S. A. Rather, A. Kumar and Q. N. Ahmed, *Chem. Commun.*, 2019, **55**, 4511–4514; (d) H. Hazarika, K. Neog, A. Sharma, B. Das and P. Gogoi, *J. Org. Chem.*, 2019, **84**, 5846–5854; (e) J. Zhang, S. Cheng, Z. Cai, P. Liu and P. Sun, *J. Org. Chem.*, 2018, **83**, 9344–9352; (f) N. Xu, Y. Zhang, W. Chen, P. Li and L. Wang, *Adv. Synth. Catal.*, 2018, **360**, 1199–1208; (g) H.-R. Tan, L. Wang, J.-N. Zhu, Z.-H. Yang and S.-Y. Zhao, *Synthesis*, 2018, **50**, 4113–4123; (h) K.-S. Du and J.-M. Huang, *Green Chem.*, 2018, **20**, 1405–1411; (i) P. Dai, K. Luo, X. Yu, W.-C. Yang, L. Wu and W.-H. Zhang, *Adv. Synth. Catal.*, 2018, **360**, 468–473.
- (a) D. Fu and J. X. Xu, *Synthesis*, 2021, **53**, 4086–4096; (b) P. Zhao, X. Wu, X. Geng, C. Wang, Y. Zhou, Y.-D. Wu and A.-X. Wu, *J. Org. Chem.*, 2019, **84**, 8322–8329; (c) J. Vaitla, K. H. Hopmann and A. Bayer, *Org. Lett.*, 2017, **19**, 6688–6691.
- (a) H. Tong, C. Chen, W. Liu, Y. Pan and L. Duan, *Asian J. Org. Chem.*, 2019, **8**, 479–481; (b) Q. H. Nguyen, N. H. Nguyen, H. Kim and S. Shin, *Chem. Sci.*, 2019, **10**, 8799–8805; (c) S. Devari, A. Kumar, R. Deshidi and B. A. Shah, *Chem. Commun.*, 2015, **51**, 5013–5016; (d) Y. Jiang and T.-P. Loh, *Chem. Sci.*, 2014, **5**, 4939–4943; (e) T. Chikugo, Y. Yauchi, M. Ide and T. Iwasawa, *Tetrahedron*, 2014, **70**, 3988–3993; (f) M. Hanack and B. Wilhelm, *Angew. Chem.*, 1989, **101**, 1083–1084; *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1057–1059; (g) T. J. Chow, U.-K. Tan and S.-M. Peng, *Synth. Commun.*, 1988, **18**, 519–523.
- (a) B. Zhou, T.-D. Tan, X.-Q. Zhu, M. Shang and L.-W. Ye, *ACS Catal.*, 2019, **9**, 6393–6406; (b) G. Evano, N. Blanchard, G. Compain, A. Coste, C. S. Demmer, W. Gati, C. Guissart, J. Heimbürger, N. Henry, K. Jouvin, G. Karthikeyan, A. Laouiti, M. Lecomte, A. Martin-Mingot, B. Métayer, B. Michelet, A. Nitelet, C. Theunissen, S. Thibaudeau, J. J. Wang, M. Zarca and C. Y. Zhang, *Chem. Lett.*, 2016, **45**, 574–585; (c) G. Evano, A. Coste and K. Jouvin, *Angew. Chem., Int. Ed.*, 2010, **49**, 2840–2859; (d) K. A. DeKorver, H. Li, A. G. Lohse, R. Hayashi, Z. Lu, Y. Zhang and R. P. Hsung, *Chem. Rev.*, 2010, **110**, 5064–5106.



- 6 (a) J. Zhou, E. D. Mock, A. Martella, V. Kantae, X. Di, L. Burggraaff, M. P. Baggelaar, K. Al-Ayed, A. Bakker, B. I. Florea, S. H. Grimm, H. den Dulk, C. T. Li, L. Mulder, H. S. Overkleeft, T. Hankemeier, G. J. P. van Westen and M. van der Stelt, *ACS Chem. Biol.*, 2019, **14**, 164–169; (b) W. Qu, C. Niu, X. Zhang, W. Chen, F. Yu, H. Liu, X. Zhang and S. Wang, *Talanta*, 2019, **197**, 431–435; (c) S. Pacifico, V. Ferretti, V. Albanese, A. Fantinati, E. Gallerani, F. Nicoli, R. Gavioli, F. Zamberlan, D. Preti and M. Marastoni, *ACS Med. Chem. Lett.*, 2019, **10**, 1086–1092; (d) M.-M. Liu, X.-C. Yang, Y.-Z. Hua, J.-B. Chang and M.-C. Wang, *Org. Lett.*, 2019, **21**, 2111–2115; (e) J. Fu, J. Han, T. Meng, J. Hu and J. Yin, *Chem. Commun.*, 2019, **55**, 12904–12907.
- 7 Z. Wang, M. Bois-Choussy, Y. Jia and J. Zhu, *Angew. Chem., Int. Ed.*, 2010, **49**, 2018–2022.
- 8 T. D. Ocain and D. H. Rich, *J. Med. Chem.*, 1992, **35**, 451–456.
- 9 (a) M. Anitha, M. Shankar and K. C. Kumara Swamy, *Org. Chem. Front.*, 2019, **6**, 1133–1139; (b) A. Ragupathi, V. P. Charpe, A. Sagadevan and K. C. Hwang, *Adv. Synth. Catal.*, 2017, **359**, 1138–1143; (c) H. T. Qin, X. Xu and F. Liu, *ChemCatChem*, 2017, **9**, 1409–1412; (d) H. Huang, G. He, X. Zhu, X. Jin, S. Qiu and H. Zhu, *Eur. J. Org. Chem.*, 2014, 7174–7183.
- 10 (a) Y. Liu, W. Zhang, J. Zhang and Z. Xu, *Synlett*, 2013, **24**, 2709–2714; (b) Z. F. Al-Rashid, W. L. Johnson, R. P. Hsung, Y. Wei, P. Y. Yao, R. Liu and K. Zhao, *J. Org. Chem.*, 2008, **73**, 8780–8784.
- 11 (a) V. Claus, L. Molinari, S. Büllmann, J. Thusek, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Chem.-Eur. J.*, 2019, **25**, 9385–9389; (b) T. Baker and P. W. Davies, *Eur. J. Org. Chem.*, 2019, 5201–5204; (c) M. D. Santos and P. W. Davies, *Chem. Commun.*, 2014, **50**, 6001–6004; (d) F. Pan, S. Liu, C. Shu, R.-K. Lin, Y.-F. Yu, J.-M. Zhou and L.-W. Ye, *Chem. Commun.*, 2014, **50**, 10726–10729; (e) S. W. Kim, T.-W. Um and S. Shin, *J. Org. Chem.*, 2018, **83**, 4703–4711; (f) X. Liu, Z.-X. Zhang, B. Zhou, Z.-S. Wang, R.-H. Zheng and L.-W. Ye, *Org. Biomol. Chem.*, 2017, **15**, 10156–10159; (g) H. Huang, J. Fan, G. He, Z. Yang, X. Jin, Q. Liu and H. Zhu, *Chem.-Eur. J.*, 2016, **22**, 2532–2538.
- 12 (a) C. F. Xu, M. Xu, Y. X. Jia and C. Y. Li, *Org. Lett.*, 2011, **13**, 1556–1559; (b) K. B. Wang, R. Q. Ran, S. D. Xiu and C. Y. Li, *Org. Lett.*, 2013, **15**, 2374–2377; (c) H. Huang, L. Tang, Q. Liu, Y. Xi, G. He and H. Zhu, *Chem. Commun.*, 2016, **52**, 5605–5608.
- 13 (a) L.-Q. Yang, K.-B. Wang and C.-Y. Li, *Eur. J. Org. Chem.*, 2013, 2775–2779; (b) P. W. Davies, A. Cremonesi and N. Martin, *Chem. Commun.*, 2011, **47**, 379–381.
- 14 (a) X.-F. Wu and K. Natte, *Adv. Synth. Catal.*, 2016, **358**, 336–352; (b) E. Jones-Mensah, M. Karki and J. Magolan, *Synthesis*, 2016, **48**, 1421–1436; (c) Z. Tashrifi, M. M. Khanaposhtani, B. Larijani and M. Mahdavi, *Adv. Synth. Catal.*, 2020, **362**, 65–86; (d) T. Yoshinaga, T. Iwata and M. Shindo, *Chem. Lett.*, 2020, **49**, 191–194; (e) D. Fu, J. Dong, J. Y. Wang and J. X. Xu, *Asian J. Org. Chem.*, 2021, **10**, 1756–1764.
- 15 Reviews: (a) C. O. Kappe, D. Dallinger and S. S. Murphree, *Practical Microwave Synthesis for Organic Chemists: Strategies, Instruments, and Protocols*, Wiley-VCH, Weinheim, 2009; (b) Y. Coquerel, E. Colacino, J. Rodriguez, J. Martinez and F. Lamaty, in *Stereoselective Synthesis of Drugs and Natural Products*, ed. V. Andrushko and N. Andrushko, John Wiley & Sons, Hoboken, NJ, 2013, ch. 5, pp. 145–166; (c) C. O. Kappe, *Chem. Soc. Rev.*, 2008, **37**, 1127. Recent examples: ; (d) X. Y. Fu, X. Y. Li and J. X. Xu, *Org. Lett.*, 2021, **23**, 8733–8737; (e) X. P. Chen, Y. L. Lei, D. Fu and J. X. Xu, *Org. Biomol. Chem.*, 2021, **19**, 7678–7689; (f) X. P. Chen, Z. S. Huang and J. X. Xu, *Adv. Synth. Catal.*, 2021, **363**, 3098–3108; (g) Y. Luo, Z. C. Fu, X. Y. Fu, C. L. Du and J. X. Xu, *Org. Biomol. Chem.*, 2020, **18**, 9526–9537; (h) Y. Luo and J. X. Xu, *Org. Lett.*, 2020, **22**, 7780–7785.
- 16 V. J. Traynelis and W. L. Hergenrother, *J. Org. Chem.*, 1964, **29**, 221–222.
- 17 C.-T. Chen and S.-J. Yan, *Tetrahedron Lett.*, 1969, **10**, 3855–3856.
- 18 D. L. Head and C. G. McCarty, *Tetrahedron Lett.*, 1973, **14**, 1405–1408.
- 19 (a) X. H. Li and J. X. Xu, *Tetrahedron*, 2016, **72**, 5515–5520; (b) D. Q. Yang and J. X. Xu, *Curr. Microwave Chem.*, 2018, **5**, 120–127.
- 20 (a) X. Tian, L. Song, M. Rudolph, Q. Wang, X. Song, F. Rominger and A. S. K. Hashmi, *Org. Lett.*, 2019, **21**, 1598–1601; (b) F. Pan, X.-L. Li, X.-M. Chen, C. Shu, P.-P. Ruan, C.-H. Shen, X. Lu and L.-W. Ye, *ACS Catal.*, 2016, **6**, 6055–6062; (c) K. Shigenari, K. Azusa, Y. Hiroto, Y. Hideki and O. Koichiro, *Bull. Chem. Soc. Jpn.*, 2008, **81**, 506–514; (d) X. Zeng, Y. Tu, Z. Zhang, C. You, J. Wu, Z. Ye and J. Zhao, *J. Org. Chem.*, 2019, **84**, 4458–4466; (e) B. Yao, Z. Liang, T. Niu and Y. Zhang, *J. Org. Chem.*, 2009, **74**, 4630–4633.
- 21 Y. Yang, X. Meng, B. Zhu, Y. Jia, X. Cao and S. Huang, *Eur. J. Org. Chem.*, 2019, 1166–1169.
- 22 W.-F. Luo, L.-W. Ye, L. Li and P.-C. Qian, *Chem. Commun.*, 2021, **57**, 5032–5035.

