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Unexpected Role of *p*-Toluenesulfonylmethyl Isocyanide (TosMIC) as a Sulfonylating Agent in Reactions with α -Bromo Carbonyl Compounds

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ABSTRACT:

The reactions of *p*-toluenesulfonylmethyl isocyanide (TosMIC) with α -bromo carbonyl compounds lead efficiently to α -sulfonated ketones, esters, and amides were reported, in which an explicit new role of TosMIC as the sulfonylating agent was uncovered for the first time. Mechanistic study by control experiments and DFT calculations suggested that the reaction is initiated by Cu(OTf)₂-catalyzed hydration of TosMIC to form a formamide intermediate, which undergoes facile C-S bond cleavage under the mediation of Cs₂CO₃ additive.

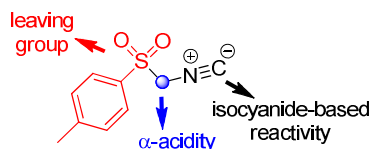
1. INTRODUCTION

The *p*-toluenesulfonylmethyl isocyanide (TosMIC) is a useful and versatile reagent in organic chemistry.¹ Among different types of transformations, the α -acidity of TosMIC has been widely employed as results of strong electron-withdrawing effect of the two groups attached to this carbon (Scheme 1a). Thus, a variety of heterocycles,² such as oxazolidines,³ oxazoles,⁴ indoles,⁵ pyrroles,⁶ thiazoles,⁷ triazoles⁸ etc., are readily accessible by base-induced cycloadditions of TosMIC with different heteroatom-containing unsaturated functionalities. In these reactions the 1,3-dipolar character of TosMIC was exploited (Scheme 1b). In the absence of a dipolarophile, TosMIC is a carbon nucleophile under basic conditions and undergoes substitution reactions readily with halides (Scheme 1c).⁹ Due to the facile cleavage of C-S bond, in most reactions the tosyl moiety of TosMIC substrate is finally released into the reaction media as a leaving group,¹⁰ however, the using of TosMIC as a sulfonating agent is rare.¹¹

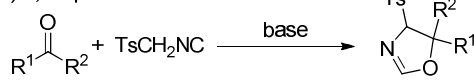
To search for new reactivity of TosMIC in organic transformations,¹² in the current manuscript we reported a new substitution reaction of TosMIC with α -bromo carbonyl compounds (**1**) in the presence of Cs₂CO₃. Instead of working as a three-atom-component in cycloaddition reaction with the carbonyl functionality (Scheme 1b) or as a carbon nucleophile in substitution with the bromide (Scheme 1c), we found that TosMIC is a sulfonylating agent to afford α -sulfonated carbonyl compounds with the isocyanide-substituted methylene moiety being a leaving group (Scheme 1d).

Scheme 1. Different Roles of TosMIC in Organic Reactions

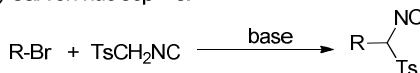
a) Possible reaction sites of TosMIC:



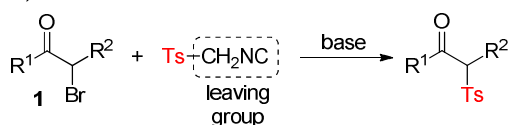
b) 1,3-dipole:



c) Carbon nucleophile:



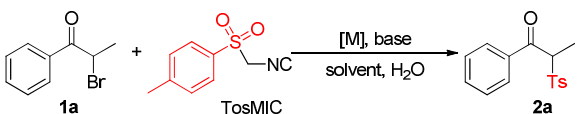
d) This work:



2. RESULTS AND DISCUSSION

Our study started with condition optimization of the reaction between 2-bromo-1-phenylpropan-1-one (**1a**) and TosMIC (Table 1). First we carried out the reaction in toluene solution under catalyst-free conditions. When 1.5 equiv of Cs_2CO_3 was used as the base, α -sulfonylation product **2a** was obtained in 40% yield at room temperature (entry 1). Slightly increased yield (44%) was achieved when carrying out the reaction at 50 °C (entry 2). Interestingly, the yield of **2a** could be increased to 52% with a slightly reduced amount of Cs_2CO_3 (entry 3). When the reaction temperature was further elevated to 70 and 90 °C, the same yield (56%) was obtained (entries 4 and 5), indicating the reaction temperature only has limited effect on the reaction efficiency. It was found that no better yields could be obtained when other solvents such as DCE and acetonitrile were used (entries 6 and 7). However, when 5 mol % $\text{Cu}(\text{OTf})_2$ was added as a catalyst, the yield of **2a** was dramatically increased to 84% (entry 8), and the yield could be further improved to 87% when the reaction was stirred for a longer time (entry 9). No catalytic activity was found when other metal salts such as $\text{Pd}(\text{OAc})_2$ and AgOTf were used (entries 10 and 11). The yield was only 70% when the Cu-catalyzed reaction was run in dioxane solution (entry 12). Replacing Cs_2CO_3 with DBU resulted in poor reactivity (entry 13). No reaction was observed when using 1.2 equiv Et_3N (entry 14), K_2CO_3 (entry 15), or NaO^tBu (entry 16) as the base source, and the using of CsOAc lead to a complex mixture (entry 17).

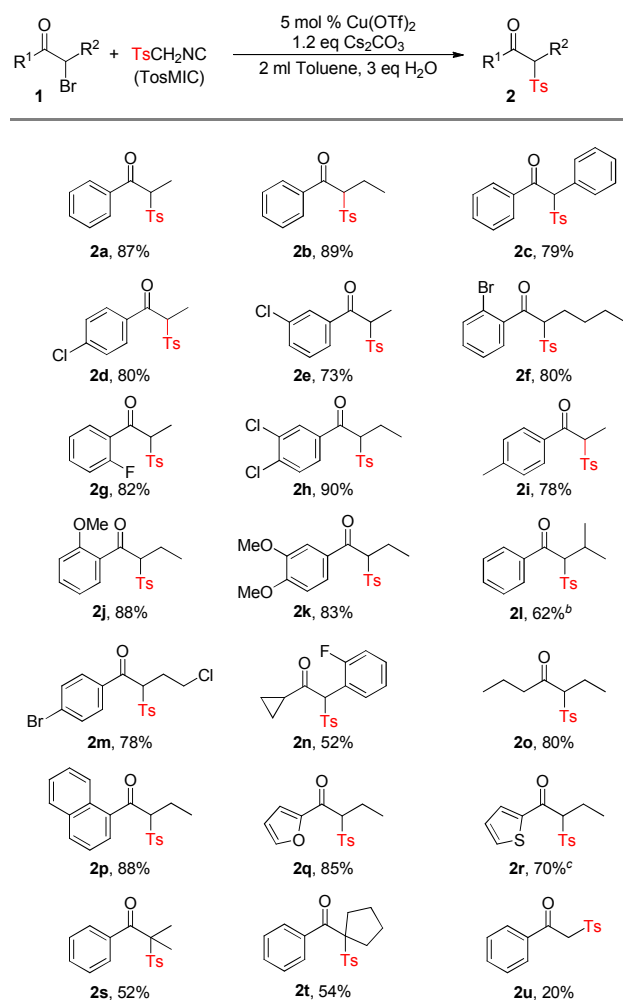
Table 1. Screening of the Reaction Conditions^a



Entry	Base [equiv]	[M]	Solvent	Yield [%] ^b
1 ^c	Cs ₂ CO ₃ (1.5)	-	Toluene	40
2 ^d	Cs ₂ CO ₃ (1.5)	-	Toluene	44
3 ^d	Cs ₂ CO ₃ (1.2)	-	Toluene	52
4	Cs ₂ CO ₃ (1.2)	-	Toluene	56
5 ^e	Cs ₂ CO ₃ (1.2)	-	Toluene	56
6 ^c	Cs ₂ CO ₃ (1.5)	-	DCE	33
7 ^c	Cs ₂ CO ₃ (1.5)	-	Acetonitrile	36
8	Cs ₂ CO ₃ (1.2)	Cu(OTf) ₂	Toluene	84
9 ^f	Cs ₂ CO ₃ (1.2)	Cu(OTf) ₂	Toluene	87
10	Cs ₂ CO ₃ (1.2)	Pd(OAc) ₂	Toluene	59
11	Cs ₂ CO ₃ (1.2)	AgOTf	Toluene	46
12	Cs ₂ CO ₃ (1.2)	Cu(OTf) ₂	1,4-Dioxane	70
13	DBU (1.2)	Cu(OTf) ₂	Toluene	49
14	Et ₃ N (1.2)	Cu(OTf) ₂	Toluene	NR
15	K ₂ CO ₃ (1.2)	Cu(OTf) ₂	Toluene	Trace
16	NaO ^t Bu (1.2)	Cu(OTf) ₂	Toluene	Trace
17	CsOAc (1.2)	Cu(OTf) ₂	Toluene	Trace ^g

^a Reaction conditions: **1a** (0.3 mmol), TosMIC (0.9 mmol), catalyst (5 mol %), H₂O (3 equiv), and anhydrous solvent (2 mL) at 70 °C for 9 h. ^b Isolated yields. ^c At room temperature. ^d At 50 °C. ^e At 90 °C. ^f Reaction for 20 h. ^g Complex mixture.

With the optimal reaction conditions in hand, the reaction scope for this Cu(OTf)₂-catalyzed and Cs₂CO₃-promoted sulfonylation of α-bromo ketones with TosMIC was then explored. As shown in Table 2, the sulfonylation products could be afforded from a variety of α-bromo ketones. In comparison with **1a**, when the alkyl group (R²) attached to the α carbon is one carbon longer (**1b**), product **2b** was obtained with a comparable yield of 89%. The alkyl group could be changed to a phenyl group (**1c**) to generate **2c** in 79% yield. The electronic property of the phenyl group attached directly to the carbonyl functionality does not have dramatic influence on the reaction efficiency. For example, for reactions of electron-withdrawing halide containing substrates, the corresponding sulfonylation products **2d-2g** could be formed with yields around 80%. Interestingly, a higher yield of 90% of **2h** was obtained when both meta and para positions of the phenyl group are occupied with chloride atoms. When the phenyl group is substituted with electron-donating substituent at para and ortho positions, **2i** and **2j** were formed in

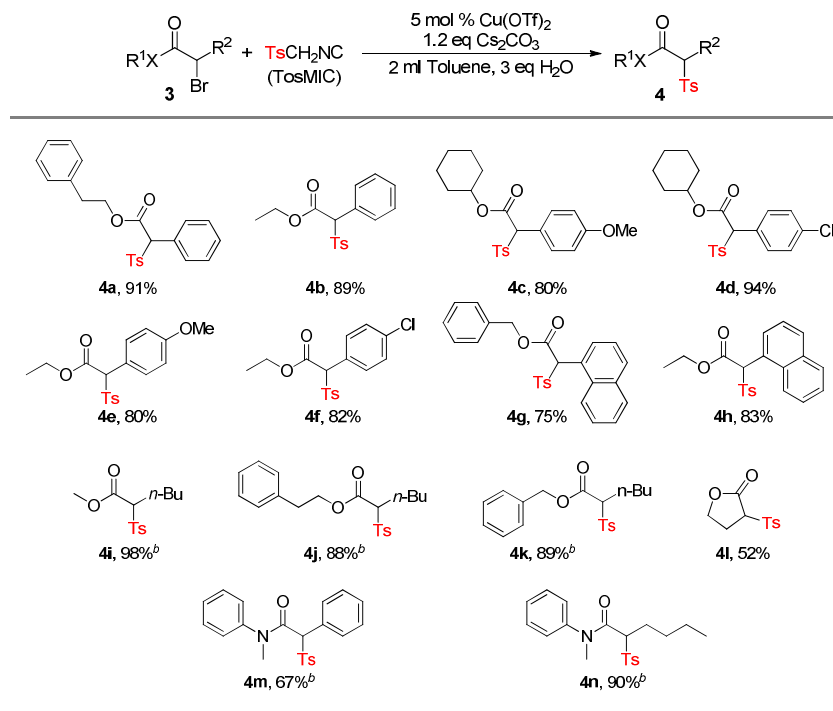
Table 2. Scope of α -Bromo Ketones^a

^a Reaction conditions: **1** (0.3 mmol), TosMIC (0.9 mmol), Cs₂CO₃ (1.2 equiv), Cu(OTf)₂ (5 mol %), H₂O (3 equiv), and toluene (2 mL) at 70 °C for 20 h. ^b At 100 °C for 42 h. ^c In 2 mL 1,4-dioxane for 12 h.

78 and 88% yields, respectively. When 3,4-dimethoxy-substituted phenyl is contained, 83% yield of **2k** was obtained. As expected for substitution reactions, increasing the steric hindrance at the α -carbon lowers the efficiency of the reaction, and **2l** was formed in a decreased yield of 62% when an isopropyl is attached to this carbon. A chloride substituent at the end of the alkyl chain does not disturb the reaction, and **2m** was formed in 78% yield. The phenyl group (R¹) in the ketone substrate could be replaced with alkyl groups, thus **2n** and **2o** were obtained in 52 and 80% yields, respectively. The lower efficiency for generation of **2n** may be attributed to the steric effect of the 2-fluorophenyl group at the α -carbon. The reactions of other aryl alkyl ketones were tested,

which showed that good yields could be achieved in reactions affording products containing 1-naphthalenyl (**2p**), 2-furanyl (**2q**), and 2-thiophenyl (**2r**) substituents. When tertiary bromides were used, substitution products **2s** and **2t** were obtained with moderate yields. The reaction of ketone with a primary bromide only afforded **2u** in 20% yield along with some unknown mixtures, indicating ketones with a primary bromide at the α -carbon are too reactive and thus are not compatible with the current conditions.

Table 3. Reactions of α -Bromo Esters and Amides^a



^a Reaction conditions: **3** (0.3 mmol), TosMIC (0.9 mmol), Cs₂CO₃ (1.2 equiv), Cu(OTf)₂ (5 mol %), H₂O (3 equiv), and toluene (2 mL) at 70 °C for 15 h. ^b In 2.0 mL dioxane for 9h.

After establishing the unique reactivity of TosMIC as a sulfonylating agent in reactions with α -bromo ketones, its reactions with other carbonyl compounds (**3**), such as esters and amides, were next studied (Table 3), and even higher efficiency of the reactions was observed in several cases. In contrast to the relative lower reactivity of α -phenyl substituted ketones (**2c** and **2n**), the sulfonylation reactions of α -phenyl substituted esters gave rise to **4a** and **4b** with yields around 90%. Substrates with α -phenyl groups of different electronic properties worked well under the current condition, as good yields were obtained for reactions producing **4c-f**. The obviously lower yield of **4c** than **4d** suggested that the substrate is more reactive when the α -substituent is an electron-poor aryl group. The α -1-naphthyl group containing substrates were compatible, generating **4g** and **4h** in 75% and 83% yields,

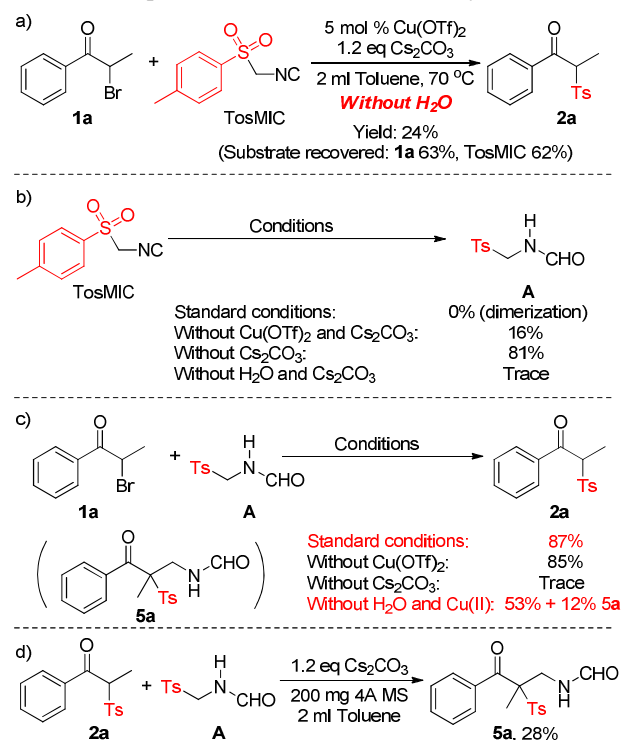
respectively. These slightly decreased yields compared with **4a** and **4b** indicated that the reaction is marginally influenced by steric effect of the 1-naphthyl group. When methyl 2-bromohexanoate was used as a substrate, **4i** was obtained in 98% yield. High yields were also achieved with other ester derivatives with alkyl substituent at the α -carbon (**4j** and **4k**). Interestingly, γ -lactone could also be sulfonylated with TosMIC, albeit only moderate yield of **4l** was obtained. The reaction could be applied to α -bromo amides, which lead to sulfonylation products **4m** and **4n** in 70% and 90% yields, respectively.

The reaction mechanism was next studied by control experiments. When the reaction of **1a** and TosMIC was run under conditions without water additive, only 24% of **2a** was produced (Scheme 2a), demonstrating the importance of water for realizing the reaction. It was assumed that the hydration of TosMIC to form intermediate **A** may occur in the first step (Scheme 2b); however, when TosMIC was stirred under the standard condition, no **A** was observed but only a small amount of dimerization product was found.¹³ Interestingly, if no $\text{Cu}(\text{OTf})_2$ and Cs_2CO_3 were used in the reaction, hydration intermediate **A** could be isolated in 16% yield. Further investigation indicated that a remarkably increased yield of **A** (81%) could be achieved when TosMIC was stirred in the absence of Cs_2CO_3 (only 5 mol % $\text{Cu}(\text{OTf})_2$ and 1 equiv H_2O were added). As expected, only trace amount of **A** was observed if no water additive was used. The experiments in Scheme 2b clearly showed that the hydration of TosMIC could occur in the reaction, but intermediate **A** is unstable in presence of Cs_2CO_3 . Next, the reactions between **1a** and **A** were studied under different conditions (Scheme 2c). Under standard conditions, the reaction of **1a** with **A** leads efficiently to **2a** in 87% yield, confirming that **A** is an intermediate to the sulfonylation product. A comparable yield of 85% was obtained if no $\text{Cu}(\text{OTf})_2$ catalyst was added, suggesting $\text{Cu}(\text{OTf})_2$ is not required for the C-S bond cleavage and the substitution steps. Instead, the base additive was proved to be crucial for the transformation from **A**, as no product was formed in the absence of Cs_2CO_3 . Interestingly, water was found to have some promoting effect on the formation of **2a** from **1a** and **A**, as notable decreasing of the yield to 53% was observed when no water was added. In this case, an unexpected byproduct **5a** was formed in 12% yield. The structure of **5a** suggests it may be resulted from Michael addition of product **2a** to *N*-methyleneformamide, a by-product generated from the C-S bond cleavage of **A**, under basic conditions. This assumption was supported by the reaction between **2a** and **A** under water-free condition (Scheme 2d), which gave rise to **5a** in 28% yield. Possibly, under standard conditions, the generated *N*-methyleneformamide was scavenged by facile reaction with water, thus more product **2a** was isolated.

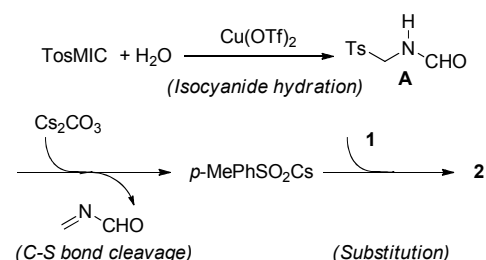
Based on the above experiments, the plausible mechanism for the current transformation was outlined in Scheme 3. In the first step, hydration of TosMIC to form **A** occurs under the catalysis of Lewis acidic $\text{Cu}(\text{OTf})_2$.

Then, from formamide **A**, the C-S bond cleavage is mediated by Cs_2CO_3 to form cesium sulfinate and *N*-methyleneformamide concurrently. The involvement of cesium sulfinate as an intermediate was supported by its reaction with **1a** without Cu(II) catalyst and water additive, which affords product **2a** in 88% yield. Finally the sulfonylation product **2** is generated by substitution of the α -bromo ketone **1** with sulfinate salt. Although reduced yields were obtained in presence of radical scavengers (given in SI), it is not unclear if the last step occurs via a radical or ionic mechanism because decomposition of the bromide starting materials may occur when exposed to radicals.¹⁴

Scheme 2. Experiments for Mechanistic Study



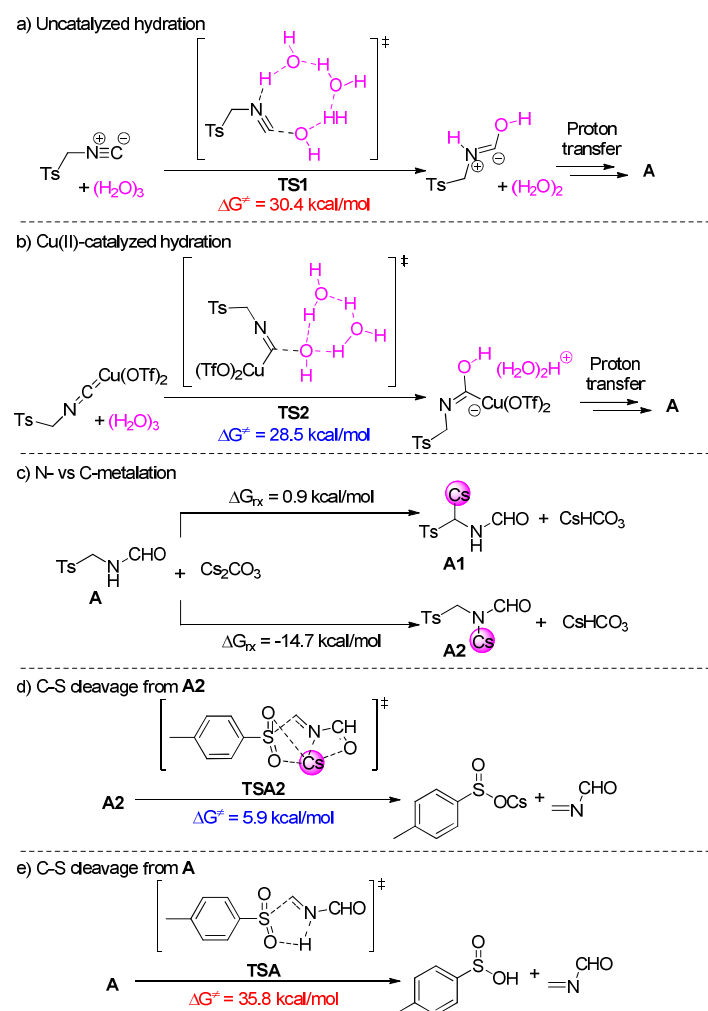
Scheme 3. Plausible Mechanism



To better understand the details for the $\text{Cu}(\text{OTf})_2$ -catalyzed isocyanide hydration and Cs_2CO_3 -mediated C-S bond cleavage processes, DFT calculations¹⁵ at the M062X/6-31+G(d)/SDD level were performed (Scheme 4). For the hydration step, the uncatalyzed reaction between TosMIC and a water cluster via **TS1** requires an activation free

energy of 30.4 kcal/mol (Scheme 4a). When the isocyanide moiety is σ -coordinated to $\text{Cu}(\text{OTf})_2$, the addition of water occurs via **TS2** with a reduced barrier of 28.5 kcal/mol (Scheme 4a), showing the hydration is catalyzed by Lewis acidic Cu(II) salt. In experiments no α -substitution of TosMIC (or **A**) was observed, and consistently, calculated reaction free energies in Scheme 4c showed that the deprotonation of the methylene in **A** by Cs_2CO_3 to form **A1** (*C*-metalation, 0.9 kcal/mol) was much less favorable thermodynamically than the deprotonation of the amide moiety to form **A2** (*N*-metalation, -14.7 kcal/mol). From **A2**, the C-S bond cleavage could be realized via **TSA2** with a very small activation barrier of 5.9 kcal/mol (Scheme 4d), in good agreement with the facile decomposition of intermediate **A** in presence of Cs_2CO_3 . In sharp contrast, the direct C-S bond cleavage from **A** requires much higher activation energy of 35.8 kcal/mol (**TSA**, Scheme 4e). The geometric structure of **TSA2** (given in SI) shows that the Cs atom has strong interactions with both the sulfinate and formamide moieties, thus facilitating the C-S bond cleavage.

Scheme 4. Computational Results¹⁵



3. CONCLUSION

In summary, we found a new type of reaction of TosMIC with a wide range of α -bromo carbonyl compounds including ketones, esters, and amides, in which for the first time TosMIC acts implicitly as a sulfonylating agent. Mechanistic studies by control experiments and DFT calculations suggested that the reaction is initiated by $\text{Cu}(\text{OTf})_2$ -catalyzed hydration of TosMIC to form a formamide intermediate, which undergoes facile C-S bond cleavage under the mediation of Cs_2CO_3 , and finally the in situ generated sulfinate salt is trapped by α -bromo carbonyl compound to afford α -sulfonated ketones, esters, and amides. Novel transformations involving efficient C-S bond cleavage/formation are ongoing in our laboratory.

4. EXPERIMENTAL SECTION

General Information. All reactions were conducted under nitrogen atmosphere. Toluene and dioxane solvents were distilled by standard procedures. TosMIC, **1a**, **1n**, **1u**, **3i**, and **3l** were purchased from commercial available resources and were used as received. All other α -bromo ketones were synthesized according to literature method. Column chromatography was performed using 200–300 mesh silica with the proper solvent system according to TLC analysis using UV light to visualize the reaction components. Nuclear magnetic resonance spectra were recorded on a 500 MHz spectrometer (^1H : 500 MHz, ^{13}C : 125 MHz), using CDCl_3 as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. NMR data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, and brs = broad singlet), coupling constant in Hz, and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuteriochloroform (77.0 ppm) as the internal standard. High resolution mass spectra were recorded on an ESI-Q-TOF mass spectrometer. Melting points were measured on X4 melting point apparatus.

Typical Procedure for the Preparation of 2-Bromo-1-phenylbutan-1-one 1b. To a 50 mL flask changed with a magnetic stirring bar were added 1-phenylbutan-1-one (3 mmol) and DCM solvent (5 mL). Br_2 (mg, 3.3 mmol) was first diluted in DCM (5 mL) and then transferred dropwisely to the ketone solution at room temperature. After the reaction being stirred overnight, the mixture was poured into ethyl acetate (20 mL), which was washed with saturated NaHCO_3 (15 mL), saturated $\text{Na}_2\text{S}_2\text{O}_3$ (15 mL), and brine (15 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by column chromatography (petroleum ether/ethyl acetate) to afford **2b** as a colorless liquid. All other α -bromoketones were prepared by similar procedures except for **2o**, which was prepared by reaction of heptan-4-one with NBS.

2-Bromo-1-phenylbutan-1-one (1b)^{16a}: colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 8.02 (d, J = 7.4 Hz, 2H),

7.59 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 2H), 5.08 (dd, $J = 7.4$, 6.7 Hz, 1H), 2.29–2.20 (m, $J = 14.3$, 7.2 Hz, 1H), 2.19–2.09 (m, $J = 14.8$, 7.4 Hz, 1H), 1.09 (t, $J = 7.3$ Hz, 3H).

2-Bromo-1,2-diphenylethanone (1c)^{16b}: white solid; ¹H NMR (500 MHz, CDCl₃) δ 7.99 (d, $J = 7.3$ Hz, 2H), 7.59–7.49 (m, 3H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.40–7.28 (m, 3H), 6.38 (s, 1H).

2-Bromo-1-(4-chlorophenyl)propan-1-one (1d)^{16c}: white solid; ¹H NMR (500 MHz, CDCl₃) δ 7.97 (d, $J = 8.6$ Hz, 2H), 7.47 (d, $J = 8.7$ Hz, 2H), 5.23 (q, $J = 6.6$ Hz, 1H), 1.90 (d, $J = 6.6$ Hz, 3H).

2-Bromo-1-(3-chlorophenyl)propan-1-one (1e)^{16c}: colorless liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.99 (s, 1H), 7.89 (d, $J = 7.8$ Hz, 1H), 7.56 (dd, $J = 8.0$, 0.9 Hz, 1H), 7.43 (t, $J = 7.9$ Hz, 1H), 5.22 (q, $J = 6.6$ Hz, 1H).

2-Bromo-1-(2-bromophenyl)hexan-1-one (1f): faint yellow liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.60 (d, $J = 8.0$ Hz, 1H), 7.49 (dd, $J = 7.6$, 1.6 Hz, 1H), 7.41–7.36 (m, 1H), 7.35–7.29 (m, 1H), 5.09 (dd, $J = 8.5$, 5.7 Hz, 1H), 2.29–2.18 (m, 1H), 2.15–2.02 (m, 1H), 1.63–1.53 (m, 1H), 1.52–1.32 (m, 3H), 0.94 (t, $J = 7.2$ Hz, 3H); ¹³C NMR (125 MHz; CDCl₃) δ 197.1, 139.7, 133.4, 131.9, 130.1, 127.4, 118.7, 52.0, 32.6, 29.4, 22.2, 13.8; HRMS (ESI) calcd for C₁₂H₁₅Br₂O⁺ ([M + H]⁺): 332.9484, found 332.9487.

2-Bromo-1-(2-fluorophenyl)propan-1-one (1g)^{16a}: faint yellow liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.90 (td, $J = 7.7$, 1.5 Hz, 1H), 7.55 (dd, $J = 14.6$, 7.7 Hz, 1H), 7.26 (t, $J = 7.6$ Hz, 1H), 7.15 (dd, $J = 10.8$, 8.9 Hz, 1H), 5.30 (q, $J = 6.7$ Hz, 1H), 1.90 (d, $J = 6.6$ Hz, 3H).

2-Bromo-1-(3,4-dichlorophenyl)butan-1-one (1h)^{16d}: colorless liquid; ¹H NMR (500 MHz, CDCl₃) δ 8.09 (d, $J = 2.1$ Hz, 1H), 7.84 (dd, $J = 8.4$, 2.1 Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 1H), 4.95 (dd, $J = 7.8$, 6.3 Hz, 1H), 2.27–2.09 (m, 2H), 1.09 (t, $J = 7.3$ Hz, 3H).

2-Bromo-1-p-tolylpropan-1-one (1i)^{16c}: white solid; ¹H NMR (500 MHz, CDCl₃) δ 7.93 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.0$ Hz, 2H), 5.28 (q, $J = 6.6$ Hz, 1H), 2.43 (s, 3H), 1.90 (d, $J = 6.6$ Hz, 3H).

2-Bromo-1-(2-methoxyphenyl)butan-1-one (1j): colorless liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.71 (dd, $J = 7.7$, 1.6 Hz, 1H), 7.51–7.45 (m, 1H), 7.05–6.94 (m, 2H), 5.34 (dd, $J = 7.9$, 5.9 Hz, 1H), 3.91 (s, 3H), 2.29–2.18 (m, 1H), 2.08–1.98 (m, 1H), 1.08 (t, $J = 7.3$ Hz, 3H); ¹³C NMR (125 MHz; CDCl₃) δ 196.3, 158.0, 133.9, 131.5, 126.3, 121.0, 111.6, 55.7, 55.6, 27.1, 12.2; HRMS (ESI) calcd for C₁₁H₁₃BrNaO₂⁺ ([M + Na]⁺): 278.9991, found 278.0004.

2-Bromo-1-(3,4-dimethoxyphenyl)butan-1-one (1k)^{16f}: white solid; ¹H NMR (500 MHz, CDCl₃) δ 7.65 (dd, $J = 8.4$, 2.0 Hz, 1H), 7.59 (d, $J = 2.0$ Hz, 1H), 6.91 (d, $J = 8.4$ Hz, 1H), 5.07 (dd, $J = 7.5$, 6.7 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 2.23 (dq, $J = 14.1$, 7.1 Hz, 1H), 2.15 (dq, $J = 14.6$, 7.4 Hz, 1H), 1.08 (t, $J = 7.3$ Hz, 3H).

2-Bromo-3-methyl-1-phenylbutan-1-one (1l)^{16a}: white solid; ¹H NMR (500 MHz, CDCl₃) δ 8.00 (d, $J = 7.3$ Hz,

2H), 7.60 (t, $J = 7.4$ Hz, 1H), 7.49 (t, $J = 7.7$ Hz, 2H), 4.94 (d, $J = 8.6$ Hz, 1H), 2.54–2.41 (m, 1H), 1.22 (d, $J = 6.6$ Hz, 3H), 1.03 (d, $J = 6.6$ Hz, 3H).

2-Bromo-1-(4-bromophenyl)-4-chlorobutan-1-one (1m): white solid; m.p. 91–93 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.90 (d, $J = 8.7$ Hz, 2H), 7.65 (d, $J = 8.7$ Hz, 2H), 5.41 (dd, $J = 8.1, 5.8$ Hz, 1H), 3.90–3.70 (m, 2H), 2.56 (dd, $J = 8.2, 5.2$ Hz, 2H). ^{13}C NMR (125 MHz; CDCl_3) δ 191.5, 132.8, 132.2, 130.4, 129.3, 43.5, 42.3, 35.6; HRMS (ESI) calcd for $\text{C}_{10}\text{H}_{10}\text{Br}_2\text{ClO}^+$ ($[\text{M} + \text{H}]^+$): 338.8781, found 338.8783.

3-Bromoheptan-4-one (1o)^{16g}: colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 4.19 (dd, $J = 8.0, 6.4$ Hz, 1H), 2.72–2.57 (m, 2H), 2.09–2.01 (m, 1H), 2.00–1.90 (m, 1H), 1.69–1.61 (m, 2H), 1.02 (t, $J = 7.3$ Hz, 3H), 0.94 (t, $J = 7.4$ Hz, 3H).

2-Bromo-1-(naphthalen-1-yl)butan-1-one (1p): faint yellow solid; ^1H NMR (500 MHz, CDCl_3) δ 8.45 (d, $J = 8.6$ Hz, 1H), 8.01 (d, $J = 8.2$ Hz, 1H), 7.92–7.83 (m, 2H), 7.66–7.46 (m, 3H), 5.14 (dd, $J = 7.5, 6.6$ Hz, 1H), 2.39–2.28 (m, 1H), 2.22–2.12 (m, 1H), 1.13 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 196.6, 134.4, 134.0, 133.2, 130.8, 128.5, 128.2, 126.8, 125.6, 124.2, 53.2, 27.3, 12.2; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{14}\text{BrO}^+$ ($[\text{M} + \text{H}]^+$): 277.0223, found 277.0222.

2-Bromo-1-(furan-2-yl)butan-1-one (1q)^{16h}: brown liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 1.0$ Hz, 1H), 7.34 (d, $J = 3.4$ Hz, 1H), 6.60 (dd, $J = 3.6, 1.7$ Hz, 1H), 4.94 (dd, $J = 7.7, 6.7$ Hz, 1H), 2.26–2.16 (m, 1H), 2.15–2.05 (m, 1H), 1.07 (t, $J = 7.3$ Hz, 3H).

*2-Bromo-1-(thiophen-2-yl)butan-1-one (1r)*¹⁶ⁱ: faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.83 (dd, $J = 3.8, 0.9$ Hz, 1H), 7.71 (dd, $J = 4.9, 1.0$ Hz, 1H), 7.17 (dd, $J = 4.9, 3.9$ Hz, 1H), 4.92 (dd, $J = 7.6, 6.7$ Hz, 1H), 2.29–2.19 (m, 1H), 2.18–2.07 (m, 1H), 1.08 (t, $J = 7.3$ Hz, 3H).

2-Bromo-2-methyl-1-phenylpropan-1-one (1s)^{16e}: colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 8.14 (d, $J = 7.3$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.43 (t, $J = 7.7$ Hz, 2H), 2.03 (s, 6H).

(1-Bromocyclopentyl)(phenyl)methanone (1t)^{16j}: white solid; ^1H NMR (500 MHz, CDCl_3) δ 8.16 (d, $J = 7.5$ Hz, 2H), 7.55 (t, $J = 7.4$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 2.58–2.38 (m, 4H), 2.07 (dd, $J = 11.9, 5.1$ Hz, 2H), 1.80 (t, $J = 7.2$ Hz, 2H).

Typical Procedure for the Preparation of phenethyl 2-bromo-2-phenylacetate 3a. The phenethyl 2-phenylacetate (9 mmol), AIBN (73.9 mg, 0.45 mmol) and 20 mL CCl_4 were placed in a 50 mL flask equipped with a magnetic stir bar. After the reaction was stirred overnight at 70 °C, the precipitation was filtered and washed with CCl_4 . Then the filtrate was evaporated under vacuum and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to afford the desired product **3a**. Other α -bromo esters and amides

were prepared from the corresponding ester and amide precursors by similar procedures.

Phenethyl 2-bromo-2-phenylacetate (3a): white solid; m.p. 37 – 38 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.51–7.45 (m, 2H), 7.36–7.30 (m, 3H), 7.27–7.18 (m, 3H), 7.14 (d, J = 7.0 Hz, 2H), 5.32 (s, 1H), 4.38 (t, J = 7.0 Hz, 2H), 2.94 (t, J = 6.9 Hz, 2H); ^{13}C NMR (125 MHz; CDCl_3) δ 168.2, 137.2, 135.8, 129.2, 128.9, 128.8, 128.7, 128.6, 126.7, 66.8, 46.9, 34.8; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{BrO}_2^+$ ($[\text{M} + \text{H}]^+$): 319.0328, found 319.0327.

Ethyl 2-bromo-2-phenylacetate (3b)^{16k}: colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.57–7.30 (m, 5H), 5.34 (s, 1H), 4.30–4.17 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).

Cyclohexyl 2-bromo-2-(4-methoxyphenyl)acetate (3c): faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 5.32 (s, 1H), 4.92–4.73 (m, 1H), 3.80 (s, 3H), 1.90–1.75 (m, 2H), 1.76–1.64 (m, 2H), 1.55–1.40 (m, 3H), 1.39–1.22 (m, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 167.8, 160.2, 130.1, 128.1, 114.2, 74.7, 55.3, 47.3, 31.1, 25.3, 23.4, 23.4; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{19}\text{BrNaO}_3^+$ ($[\text{M} + \text{Na}]^+$): 349.0410, found 349.0413.

Cyclohexyl 2-bromo-2-(4-chlorophenyl)acetate (3d): faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, J = 8.6 Hz, 2H), 7.33 (d, J = 8.6 Hz, 2H), 5.28 (s, 1H), 4.87–4.80 (m, 1H), 1.89–1.75 (m, 2H), 1.75–1.62 (m, 2H), 1.55–1.40 (m, 3H), 1.40–1.24 (m, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 167.4, 135.2, 134.6, 130.1, 128.9, 75.1, 46.2, 31.1, 25.2, 23.4, 23.3; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{17}\text{BrClO}_2^+$ ($[\text{M} + \text{H}]^+$): 331.0095, found 331.0103.

Ethyl 2-bromo-2-(4-methoxyphenyl)acetate (3e)^{16k}: faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 5.33 (s, 1H), 4.33–4.17 (m, 2H), 3.80 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

Ethyl 2-bromo-2-(4-chlorophenyl)acetate (3f)^{16k}: faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.6 Hz, 2H), 5.30 (s, 1H), 4.28–4.19 (m, 2H), 1.28 (t, J = 7.1 Hz, 3H).

Benzyl 2-bromo-2-(naphthalen-1-yl)acetate (3g)^{16l}: faint yellow solid; m.p. 42–43 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, J = 8.5 Hz, 1H), 7.86 (dd, J = 13.8, 8.2 Hz, 2H), 7.74 (d, J = 7.2 Hz, 1H), 7.59–7.46 (m, 2H), 7.41 (t, J = 7.7 Hz, 1H), 7.33–7.20 (m, 5H), 6.19 (s, 1H), 5.22 (q, J = 12.3 Hz, 2H); ^{13}C NMR (125 MHz; CDCl_3) δ 168.2, 134.9, 134.0, 131.5, 130.4, 130.2, 129.1, 128.6, 128.5, 128.3, 127.3, 126.9, 126.2, 125.4, 123.1, 68.3, 45.2; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{15}\text{BrNaO}_2^+$ ($[\text{M} + \text{Na}]^+$): 377.0148, found 377.0150.

Ethyl 2-bromo-2-(naphthalen-1-yl)acetate (3h): faint yellow liquid; ^1H NMR (500 MHz, CDCl_3) δ 8.11 (d, J = 8.5 Hz, 1H), 7.86 (dd, J = 12.9, 8.2 Hz, 2H), 7.79 (d, J = 7.2 Hz, 1H), 7.61–7.57 (m, 1H), 7.51 (t, J = 7.1 Hz, 1H),

7.47–7.42 (m, 1H), 6.15 (s, 1H), 4.30–4.21 (m, 2H), 1.23 (t, $J = 7.1$ Hz, 3H).

Phenethyl 2-bromohexanoate (3j): colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.33–7.27 (m, 2H), 7.26–7.20 (m, 3H), 4.39 (td, $J = 7.0, 3.2$ Hz, 2H), 4.18 (t, $J = 7.4$ Hz, 1H), 2.98 (t, $J = 7.0$ Hz, 2H), 2.08–1.87 (m, 2H), 1.44–1.22 (m, 4H), 0.89 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 169.8, 137.4, 128.9, 128.5, 126.7, 66.2, 46.1, 34.9, 34.7, 29.3, 22.0, 13.8; HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{20}\text{BrO}_2^+$ ($[\text{M} + \text{H}]^+$): 299.0641, found 299.0645.

Benzyl 2-bromohexanoate (3k)^{16m}: colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.42–7.30 (m, 5H), 5.20 (s, 2H), 4.25 (t, $J = 7.4$ Hz, 1H), 2.16–2.04 (m, 1H), 2.04–1.94 (m, 1H), 1.50–1.22 (m, 4H), 0.89 (t, $J = 7.0$ Hz, 3H).

*2-Bromo-N-methyl-N,2-diphenylacetamide (3m)*¹⁶ⁿ: white solid; ^1H NMR (500 MHz, CDCl_3) δ 7.49–7.08 (m, 10H), 5.33 (s, 1H), 3.29 (s, 3H).

2-Bromo-N-methyl-N-phenylhexanamide (3n): colorless liquid; ^1H NMR (500 MHz, CDCl_3) δ 7.46 (t, $J = 7.6$ Hz, 2H), 7.40 (t, $J = 7.4$ Hz, 1H), 7.28 (d, $J = 7.8$ Hz, 2H), 4.08 (t, $J = 7.4$ Hz, 1H), 3.31 (s, 3H), 2.20–2.05 (m, 1H), 1.98–1.84 (m, 1H), 1.33–1.15 (m, 4H), 0.85 (t, $J = 6.3$ Hz, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 169.2, 143.0, 130.0, 128.5, 127.2, 44.2, 38.0, 35.1, 29.5, 22.1, 13.8; HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{18}\text{BrNNaO}^+$ ($[\text{M} + \text{Na}]^+$): 306.0464, found 306.0484.

Typical Procedure for Synthesis of 1-phenyl-2-tosylpropan-1-one 2a by $\text{Cu}(\text{OTf})_2$ -Catalyzed Reaction between TosMIC and 2-bromo-1-phenylpropan-1-one 1a. To a flame-dried Schlenk tube changed with a magnetic stirring bar was added **1a** (63.5 mg, 0.3 mmol), TosMIC (175.7 mg, 0.9 mmol), $\text{Cu}(\text{OTf})_2$ (5.4 mg, 0.015 mmol), Cs_2CO_3 (117.3 mg, 0.36 mmol), H_2O (16.2 μl , 0.9 mmol), and toluene (2 ml) under nitrogen atmosphere. The reaction mixture was stirred at 70°C for 20 h. The mixture was quenched with saturated NH_4Cl (15 ml) and then extracted with ethyl acetate (15 ml x 3). The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by column chromatography (petroleum ether/ethyl acetate or cyclohexane/dichloromethane/ethylacetate) to afford product **2a** (74.6 mg, 87% yield) as a white solid.

1-phenyl-2-tosylpropan-1-one (2a). Obtained as a white solid (74.6 mg, 87%); m.p. 93–95 °C; ^1H NMR (500 MHz; CDCl_3): δ 7.98 (d, $J = 7.3$ Hz, 2H), 7.66 (d, $J = 8.2$ Hz, 2H), 7.61 (d, $J = 7.4$ Hz, 1H) 7.49–7.46 (m, 2H) 7.31 (d, $J = 8.2$ Hz, 2H), 5.15 (q, $J = 6.9$ Hz, 1H) 2.43 (s, 3H) 1.56 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 192.6, 145.3, 136.3, 134.0, 133.1, 129.8, 129.5, 129.2, 128.7, 65.1, 21.7, 13.2; HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{O}_3\text{S}^+$ ($[\text{M} + \text{H}]^+$): 289.0893, found 289.0895.

1-phenyl-2-tosylbutan-1-one (2b). Obtained as a white solid (72.8 mg, 89%); m.p. 73–74 °C; ^1H NMR (500 MHz,

CDCl₃) δ 7.97 (d, J = 7.9 Hz, 2H), 7.65 (d, J = 8.2 Hz, 2H), 7.60 (t, J = 7.4 Hz, 1H), 7.47 (t, J = 7.8 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.01 (dd, J = 10.8, 3.6 Hz, 1H), 2.41 (s, 3H), 2.20–2.18 (m, 1H), 2.09–2.00 (m, 1H), 0.87 (t, J = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 192.8, 145.3, 137.5, 133.9, 133.6, 129.8, 129.5, 129.0, 128.7, 71.5, 22.0, 21.6, 11.5; HRMS (ESI) calcd for C₁₇H₁₉O₃S⁺ ([M + H]⁺): 303.1049, found 303.1049.

1,2-diphenyl-2-tosylethanone (2c). Obtained as a white solid (83.0 mg, 79%); m.p. 145–146 °C; ¹H NMR (500 MHz; CDCl₃): δ 7.87 (d, J = 7.8 Hz, 2H), 7.54–7.25 (m, 10H), 7.19 (d, J = 8.0 Hz, 2H), 6.15 (s, 1H), 2.39 (s, 3H); ¹³C NMR (125 MHz; CDCl₃) δ 190.8, 145.0, 136.1, 134.0, 133.9, 130.5, 130.3, 129.6, 129.1, 128.9, 128.8, 128.8, 128.7, 76.1, 21.7; HRMS (ESI) calcd for C₂₁H₁₉O₃S⁺ ([M + H]⁺): 351.1049, found 351.1052.

1-(4-chlorophenyl)-2-tosylpropan-1-one (2d). Obtained as a white solid (76.5 mg, 80%); m.p. 126–127 °C; ¹H NMR (500 MHz; CDCl₃): δ 7.93 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 5.10 (q, J = 6.9 Hz, 1H), 2.43 (s, 3H), 1.54 (d, J = 6.9 Hz, 3H); ¹³C NMR (125 MHz; CDCl₃) δ 191.4, 145.5, 140.7, 134.7, 132.9, 130.6, 129.8, 129.6, 129.1, 65.2, 21.7, 13.1; HRMS (ESI) calcd for C₁₆H₁₆ClO₃S⁺ ([M + H]⁺): 323.0503, found 323.0506.

1-(3-chlorophenyl)-2-tosylpropan-1-one (2e). Obtained as a white solid (71.1 mg, 73%); m.p. 105 – 106 °C; ¹H NMR (500 MHz; CDCl₃) δ 7.90–7.84 (m, 2H), 7.64 (d, J = 8.3 Hz, 2H), 7.58–7.52 (m, 1H), 7.42 (t, J = 8.2 Hz, 1H), 7.31 (d, J = 8.1 Hz, 2H), 5.08 (q, J = 6.9 Hz, 1H), 2.43 (s, 3H), 1.55 (d, J = 6.9 Hz, 3H); ¹³C NMR (125 MHz; CDCl₃) δ 191.5, 145.6, 137.8, 135.1, 133.8, 133.0, 130.0, 129.8, 129.6, 129.0, 127.3, 65.3, 21.7, 13.0; HRMS (ESI) calcd for C₁₆H₁₆ClO₃S⁺ ([M + H]⁺): 323.0503, found 323.0510.

1-(2-bromophenyl)-2-tosylhexan-1-one (2f). Obtained as a white solid (96.5 mg, 80%); m.p. 93–94 °C; ¹H NMR (500 MHz; CDCl₃) δ 7.76–7.67 (m, 3H), 7.63 (d, J = 8.0 Hz, 1H), 7.45–7.30 (m, 4H), 5.05 (dd, J = 10.0, 4.3 Hz, 1H), 2.45 (s, 3H), 2.09–1.98 (m, 2H), 1.41 – 1.24 (m, 4H), 0.85 (t, J = 7.2 Hz, 3H); ¹³C NMR (125 MHz; CDCl₃) δ 194.6, 145.3, 139.8, 134.4, 133.6, 132.8, 130.9, 129.8, 129.6, 127.5, 120.0, 73.4, 29.0, 28.3, 22.5, 21.7, 13.6; HRMS (ESI) calcd for C₁₉H₂₂BrO₃S⁺ ([M + H]⁺): 409.0468, found 409.0469.

1-(2-fluorophenyl)-2-tosylpropan-1-one (2g). Obtained as a white solid (75.5 mg, 82%); m.p. 83–84 °C; ¹H NMR (500 MHz; CDCl₃) δ 7.77–7.74 (m, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.56–7.51 (m, 1H), 7.29 (dd, J = 8.1 Hz, 2H), 7.25–7.20 (m, 1H), 7.12–7.08 (m, 1H), 5.20 – 5.15 (m, 1H), 2.42 (s, 3H), 1.57 (d, J = 6.9 Hz); ¹³C NMR (125 MHz; CDCl₃) δ 191.1 (d, J = 3.8 Hz), 161.5 (d, J = 252.5 Hz), 145.2, 135.4 (d, J = 8.8 Hz), 133.8, 131.1 (d, J = 1.3 Hz), 129.6, 129.5, 125.7 (d, J = 11.3 Hz), 124.7 (d, J = 2.5 Hz), 116.7 (d, J = 23.8 Hz), 69.2 (d, J = 8.8 Hz), 21.6, 12.4; HRMS (ESI) calcd for C₁₆H₁₆FO₃S⁺ ([M + H]⁺): 307.0799, found 307.0796.

1-(3,4-dichlorophenyl)-2-tosylbutan-1-one (2h). Obtained as a yellow solid (90.0 mg, 90%); m.p. 131–132 °C;

¹H NMR (500 MHz, CDCl₃) δ 8.01 (d, *J* = 2.0 Hz, 1H), 7.83 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.65–7.55 (m, 3H), 7.32 (d, *J* = 8.1 Hz, 2H), 4.87 (dd, *J* = 10.9, 3.5 Hz, 1H), 2.45 (s, 3H), 2.20–2.10 (m, 1H), 2.08–1.98 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 190.7, 145.7, 138.8, 136.9, 133.6, 133.2, 130.9, 130.8, 129.7, 129.6, 128.0, 71.9, 21.8, 21.7, 11.5; HRMS (ESI) calcd for C₁₇H₁₆Cl₂O₃SNa⁺ ([M + Na]⁺): 393.0089, found 393.0098.

1-p-tolyl-2-tosylpropan-1-one (2i). Obtained as a white solid (70.6 mg, 78%); m.p. 104–105 °C; ¹H NMR (500 MHz; CDCl₃): δ 7.88 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.31–7.26 (m, 4H), 5.13 (q, *J* = 6.6 Hz, 1H), 2.46–2.37 (m, 6H), 1.54 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (125 MHz; CDCl₃) δ 192.1, 145.3, 145.2, 133.9, 133.1, 129.8, 129.5, 129.4, 129.4, 64.9, 21.7, 21.7, 13.2; HRMS (ESI) calcd for C₁₇H₁₉O₃S⁺ ([M + H]⁺): 303.1049, found 303.1049.

1-(2-methoxyphenyl)-2-tosylbutan-1-one (2j). Obtained as a white solid (84.3 mg, 88%); m.p. 106 – 107 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.57 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.47–7.42 (m, 1H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.99–6.93 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.47 (dd, *J* = 10.0, 4.3 Hz, 1H), 3.87 (s, 3H), 2.39 (s, 3H), 2.15–2.03 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 194.5, 158.4, 144.8, 134.5, 134.5, 131.1, 129.5, 129.3, 128.3, 120.9, 111.8, 75.1, 55.6, 21.6, 21.6, 11.6; HRMS (ESI) calcd for C₁₈H₂₁O₄S⁺ ([M + H]⁺): 333.1155, found 333.1142.

1-(3,4-dimethoxyphenyl)-2-tosylbutan-1-one (2k). Obtained as a white solid (88.7 mg, 83%); m.p. 163–164 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.66 (d, *J* = 8.1 Hz, 3H), 7.51 (s, 1H), 7.31 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 4.94 (dd, *J* = 10.9, 3.5 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 2.44 (s, 3H), 2.20–2.10 (m, 1H), 2.07–1.95 (m, 1H), 0.87 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 190.7, 154.3, 149.2, 145.2, 133.6, 130.7, 129.8, 129.4, 124.5, 110.6, 110.1, 71.1, 56.2, 56.0, 22.1, 21.7, 11.5; HRMS (ESI) calcd for C₁₉H₂₃O₅S⁺ ([M + H]⁺): 363.1261, found 363.1261.

3-methyl-1-phenyl-2-tosylbutan-1-one (2l). Obtained as a white solid (58.4 mg, 62%); m.p. 81–82 °C; ¹H NMR (500 MHz; CDCl₃) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.43–7.39 (m, 2H), 7.23 (d, 8.1 Hz, 2H), 4.87 (d, *J* = 9.1 Hz, 1H), 2.60–2.49 (m, 1H), 2.36 (s, 3H), 1.33 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (125 MHz; CDCl₃) δ 193.9, 145.0, 137.8, 135.1, 133.6, 129.8, 129.4, 128.7, 128.6, 76.3, 29.6, 21.5, 21.4, 21.0; HRMS (ESI) calcd for C₁₈H₂₁O₃S⁺ ([M + H]⁺): 317.1206, found 317.1207.

1-(4-bromophenyl)-4-chloro-2-tosylbutan-1-one (2m). Obtained as a white solid (97.2 mg, 78%); m.p. 145–146 °C; ¹H NMR (500 MHz, CDCl₃) δ 7.83 (d, *J* = 8.7 Hz, 2H), 7.60 (t, *J* = 8.5 Hz, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.35 (dd, *J* = 8.1, 5.8 Hz, 1H), 3.73–3.60 (m, 1H), 3.40–3.26 (m, 1H), 2.62–2.49 (m, 2H), 2.43 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 190.9, 145.9, 135.5, 133.2, 132.1, 130.6, 129.8, 129.8, 129.6, 67.4, 41.6, 30.5, 21.7; HRMS (ESI)

calcd for $C_{17}H_{17}BrClO_3S^+$ ($[M + H]^+$): 414.9765, found 414.9764.

1-cyclopropyl-2-(2-fluorophenyl)-2-tosylethanone (2n). Obtained as a white solid (49.3 mg, 52%); m.p. 144–146 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.64–7.61 (m, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.36–7.32 (m, 1H), 7.22 (d, J = 7.6 Hz, 2H), 7.16–7.13 (m, 1H), 7.00–6.95 (m, 1H), 5.86 (s, 1H), 2.41 (s, 3H), 2.19–2.18 (m, 1H), 1.25–0.94 (m, 4H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 199.2, 160.9 (d, J = 248.8 Hz), 145.2, 134.6, 131.6 (d, J = 1.3 Hz), 131.2 (d, J = 8.8 Hz), 129.4, 129.3, 124.3 (d, J = 3.8 Hz), 116.2 (d, J = 13.8 Hz), 115.3 (d, J = 22.5 Hz), 71.5 (d, J = 1.3), 22.6, 21.6, 13.1, 13.1; HRMS (ESI) calcd for $C_{18}H_{18}FO_3S^+$ ($[M + H]^+$): 333.0955, found 333.0971.

3-tosylheptan-4-one (2o). Obtained as a white solid (62.3 mg, 80%); m.p. 64–65 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.65 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 4.05–3.96 (m, 1H), 2.88–2.77 (m, 1H), 2.62–2.50 (m, 1H), 2.45 (s, 3H), 1.98–1.79 (m, 2H), 1.61 (dt, J = 10.4, 6.9 Hz, 2H), 0.92 (t, J = 7.4 Hz, 3H), 0.85 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 202.4, 145.3, 133.6, 129.6, 129.4, 76.6, 47.0, 21.6, 20.8, 16.6, 13.4, 11.4; HRMS (ESI) calcd for $C_{14}H_{21}O_3S^+$ ($[M + H]^+$): 269.1206, found 269.1205.

1-(naphthalen-1-yl)-2-tosylbutan-1-one (2p). Obtained as a white solid (93.1 mg, 88%); m.p. 129–131 °C; 1H NMR (500 MHz; $CDCl_3$) δ 8.52 (d, J = 8.5 Hz, 1H), 8.04 (dd, J = 12.4, 7.8 Hz, 2H), 7.87 (d, J = 8.0 Hz, 1H), 7.69 (d, J = 8.2 Hz, 2H), 7.61–7.50 (m, 3H), 7.24 (d, J = 8.0 Hz, 2H), 5.04 (dd, J = 10.8, 3.8 Hz, 1H), 2.39 (s, 3H), 2.29–2.10 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (125 MHz; $CDCl_3$) δ 195.2, 145.2, 135.8, 134.0, 134.0, 133.9, 130.1, 129.7, 129.5, 128.6, 128.5, 126.8, 125.5, 124.3, 74.8, 22.4, 21.6, 11.6; HRMS (ESI) calcd for $C_{21}H_{21}O_3S^+$ ($[M + H]^+$): 353.1206, found 353.1205.

1-(furan-2-yl)-2-tosylbutan-1-one (2q). Obtained as a yellow solid (73.7 mg, 85%); m.p. 116 – 117 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.71–7.59 (m, 3H), 7.34–7.28 (m, 3H), 6.60–6.53 (m, 1H), 4.82–4.74 (m, 1H), 2.42 (m, 3H), 2.18–2.08 (m, 1H), 2.07–1.97 (m, 1H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 180.3, 153.0, 147.9, 145.2, 133.8, 129.6, 129.5, 119.7, 113.0, 72.3, 21.6, 21.0, 11.4; HRMS (ESI) calcd for $C_{15}H_{17}O_4S^+$ ($[M + H]^+$): 293.0842, found 293.0855.

1-(thiophen-2-yl)-2-tosylbutan-1-one (2r). Obtained as a yellow solid (64.0 mg, 70%); m.p. 107–108 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.81 (dd, J = 3.9, 1.0 Hz, 1H), 7.73 (dd, J = 4.9, 1.0 Hz, 1H), 7.67 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.16 (dd, J = 4.9, 3.9 Hz, 1H), 4.71 (dd, J = 11.0, 3.6 Hz, 1H), 2.42 (s, 3H), 2.20–2.11 (m, 1H), 2.03 (m, 1H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 184.6, 145.3, 144.8, 135.9, 134.3, 133.4, 129.8, 129.5, 128.6, 73.7, 21.7, 11.5; HRMS (ESI) calcd for $C_{15}H_{17}O_3S_2^+$ ($[M + H]^+$): 309.0614, found 309.0617.

2-methyl-1-phenyl-2-tosylpropan-1-one (2s). Obtained as a faint yellow liquid (47.7 mg, 52%); 1H NMR (500 MHz; $CDCl_3$) δ 7.93 (d, J = 7.5 Hz, 2H), 7.67 (d, J = 7.7 Hz, 2H), 7.52 (t, J = 7.0 Hz, 1H), 7.43 (t, J = 7.4 Hz, 2H),

7.31 (d, $J = 7.7$ Hz, 2H), 2.44 (s, 3H), 1.69 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 199.4, 145.2, 137.8, 132.3, 132.0, 130.5, 129.4, 128.9, 128.2, 73.3, 22.6, 21.7; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}_3\text{S}^+$ ($[\text{M} + \text{H}]^+$): 303.1049, found 303.1048.

Phenyl(1-tosylcyclopentyl)methanone (2t). Obtained as a colorless liquid (52.9 mg, 54%); ^1H NMR (500 MHz, CDCl_3) δ 8.07 (d, $J = 7.2$ Hz, 2H), 7.61–7.51 (m, 3H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.28 (d, $J = 8.1$ Hz, 2H), 2.72–2.64 (m, 2H), 2.49–2.39 (m, 5H), 1.91–1.80 (m, 2H), 1.59–1.48 (m, 2H); ^{13}C NMR (125 MHz; CDCl_3): 197.8, 145.1, 136.2, 133.0, 132.6, 130.3, 130.1, 129.3, 128.1, 84.3, 34.5, 26.0, 21.7; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{21}\text{O}_3\text{S}^+$ ($[\text{M} + \text{H}]^+$): 329.1206, found 329.1205.

1-phenyl-2-tosylethanone (2u). Obtained as a white solid (16.6 mg, 20%); m.p. 98–99 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.95 (d, $J = 7.5$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 2H), 7.62 (t, $J = 7.4$ Hz, 1H), 7.48 (t, $J = 7.8$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 4.72 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 188.2, 145.4, 135.8, 135.8, 134.4, 129.9, 129.4, 128.9, 128.6, 63.6, 21.7; HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{O}_3\text{S}^+$ ($[\text{M} + \text{H}]^+$): 275.0736, found 275.0738.

Phenethyl 2-phenyl-2-tosylacetate (4a). Obtained as a white solid (104.1 mg, 91%); m.p. 113–114 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.48–7.08 (m, 14H), 5.06 (s, 1H), 4.44–4.27 (m, 2H), 2.90 (t, $J = 7.1$ Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 164.9, 145.3, 137.1, 133.6, 130.3, 130.0, 129.6, 129.2, 128.9, 128.6, 128.5, 128.0, 126.7, 75.4, 66.8, 34.8, 21.7; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{23}\text{O}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$): 395.1312, found 395.1313.

Ethyl 2-phenyl-2-tosylacetate (4b). Obtained as a white solid (84.7 mg, 89%); m.p. 111–112 °C; ^1H NMR (500 MHz; CDCl_3): δ 7.48 (d, $J = 8.1$ Hz, 2H), 7.38–7.26 (m, 5H), 7.21 (d, $J = 8.1$ Hz, 2H), 5.08 (s, 1H), 4.21–4.18 (m, 2H), 2.41 (s, 3H), 1.23 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 164.9, 145.2, 133.6, 130.3, 130.0, 129.6, 129.2, 128.5, 128.1, 75.3, 62.4, 21.7, 13.9; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{19}\text{O}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$): 319.0999, found 319.1015.

Cyclohexyl 2-(4-methoxyphenyl)-2-tosylacetate (4c). Obtained as a faint yellow solid (94.4 mg, 80%); m.p. 104–105 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.49 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 8.8$ Hz, 2H), 7.22 (d, $J = 8.3$ Hz, 2H), 6.82 (d, $J = 8.8$ Hz, 2H), 5.00 (s, 1H), 4.87–4.75 (m, 1H), 3.80 (s, 3H), 2.42 (s, 3H), 1.87–1.61 (m, 4H), 1.53–1.23 (m, 6H); ^{13}C NMR (125 MHz; CDCl_3) δ 164.6, 160.6, 145.0, 133.8, 131.6, 129.9, 129.1, 120.1, 113.9, 75.1, 75.0, 55.3, 31.2, 31.1, 25.2, 23.5, 23.4, 21.6; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{27}\text{O}_5\text{S}^+$ ($[\text{M} + \text{H}]^+$): 403.1574, found 403.1570.

Cyclohexyl 2-(4-chlorophenyl)-2-tosylacetate (4d). Obtained as a white solid (112.4 mg, 94%); m.p. 89–90 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.50 (d, $J = 8.3$ Hz, 2H), 7.34–7.23 (m, 6H), 5.02 (s, 1H), 4.86–4.79 (m, 1H), 2.43 (s, 3H), 1.85–1.74 (m, 2H), 1.73–1.63 (m, 2H), 1.53–1.24 (m, 6H); ^{13}C NMR (125 MHz; CDCl_3) δ 164.0, 145.4, 135.8,

133.5, 131.6, 129.9, 129.3, 128.7, 126.8, 75.4, 74.8, 31.1, 31.1, 25.2, 23.4, 23.4, 21.7; HRMS (ESI) calcd for $C_{21}H_{24}ClO_4S^+$ ($[M + H]^+$): 407.1078, found 407.1080.

Ethyl 2-(4-methoxyphenyl)-2-tosylacetate (4e). Obtained as a white solid (84.2 mg, 80%); m.p. 147–148 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.49 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.5$ Hz, 2H), 7.23 (d, $J = 8.1$ Hz, 2H), 6.82 (d, $J = 8.5$ Hz, 2H), 5.03 (s, 1H), 4.27–4.09 (m, 2H), 3.79 (s, 3H), 2.41 (s, 3H), 1.22 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 165.1, 160.7, 145.1, 133.7, 131.6, 129.9, 129.2, 119.9, 114.0, 74.7, 62.3, 55.3, 21.6, 13.9; HRMS (ESI) calcd for $C_{18}H_{21}O_5S^+$ ($[M + H]^+$): 349.1104, found 349.1104.

Ethyl 2-(4-chlorophenyl)-2-tosylacetate (4f). Obtained as a white solid (87.2 mg, 82%); m.p. 134–135 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.50 (d, $J = 8.2$ Hz, 2H), 7.33–7.24 (m, 6H), 5.04 (s, 1H), 4.27–4.14 (m, 2H), 2.43 (s, 3H), 1.23 (t, $J = 7.1$, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 164.6, 145.5, 135.9, 133.3, 131.6, 129.9, 129.3, 128.8, 126.6, 62.6, 21.7, 13.9; HRMS (ESI) calcd for $C_{17}H_{18}ClO_4S^+$ ($[M + H]^+$): 353.0609, found 353.0625.

Benzyl 2-(naphthalen-1-yl)-2-tosylacetate (4g). Obtained as a brown solid (95.7 mg, 75%); m.p. 135–136 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.97–7.75 (m, 4H), 7.46 (d, $J = 7.1$ Hz, 4H), 7.37 (t, $J = 7.7$ Hz, 1H), 7.29 (s, 3H), 7.23 (s, 2H), 7.09 (d, $J = 7.7$ Hz, 2H), 6.10 (s, 1H), 5.25–5.07 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 165.3, 145.2, 134.7, 133.8, 133.7, 132.0, 130.4, 130.0, 129.2, 129.0, 128.8, 128.6, 128.5, 128.4, 127.1, 125.9, 124.9, 123.8, 122.6, 69.3, 68.1, 21.6; HRMS (ESI) calcd for $C_{26}H_{23}O_4S^+$ ($[M + H]^+$): 431.1312, found 431.1320.

Ethyl 2-(naphthalen-1-yl)-2-tosylacetate (4h). Obtained as a faint yellow solid (88.2 mg, 83%); m.p. 136–137 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.97 (d, $J = 8.0$ Hz, 1H) 7.88–7.82 (m, 2H), 7.75 (d, $J = 7.1$ Hz, 1H), 7.51–7.365 (m, 5H), 7.13 (d, $J = 8.0$ Hz, 2H), 6.07 (s, 1H), 4.26–4.21 (m, 1H), 4.19–4.12 (m, 1H), 2.35 (s, 3H), 1.20 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 165.4, 145.2, 133.8, 133.7, 132.0, 130.3, 130.1, 129.1, 129.0, 128.6, 127.0, 125.9, 124.9, 124.1, 122.6, 69.4, 62.5, 21.6, 13.9; HRMS (ESI) calcd for $C_{21}H_{21}O_4S^+$ ($[M + H]^+$): 369.1155, found 369.1156.

Methyl 2-tosylhexanoate (4i). Obtained as a white solid (81.3 mg, 98%); m.p. 46–47 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.74 (d, $J = 8.3$ Hz, 2H), 7.36 (d, $J = 8.3$ Hz, 2H), 3.92 (dd, $J = 11.3, 3.8$ Hz, 1H), 3.68 (s, 3H), 2.46 (s, 3H), 2.05–1.88 (m, 2H), 1.33–1.23 (m, 4H), 0.87 (t, $J = 7.0$ MHz, 3H); ^{13}C NMR (125 MHz; $CDCl_3$) δ 166.6, 145.3, 134.2, 129.6, 129.3, 71.0, 52.8, 29.0, 26.6, 22.1, 21.7, 13.6; HRMS (ESI) calcd for $C_{14}H_{21}O_4S^+$ ($[M + H]^+$): 285.1155, found 285.1156.

Phenethyl 2-tosylhexanoate (4j). Obtained as a white solid (94.1 mg, 88%); m.p. 35 – 36 °C; 1H NMR (500 MHz; $CDCl_3$) δ 7.71 (d, $J = 8.0$ Hz, 2H), 7.35–7.26 (m, 4H), 7.25–7.20 (m, 1H), 7.15 (d, $J = 7.5$ Hz, 2H), 4.34–4.20 (m, 2H), 3.88 (dd, $J = 11.3, 3.3$ Hz, 1H), 2.85 (t, $J = 7.0$ Hz, 2H), 2.44 (s, 3H), 2.03–1.94 (m, 1H), 1.93–1.82 (m, 1H),

1.30–1.10 (m, 4H), 0.82 (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.1, 145.3, 137.2, 134.3, 129.6, 129.4, 128.8, 128.5, 126.7, 71.1, 66.4, 34.7, 28.9, 26.6, 22.1, 21.7, 13.6; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{27}\text{O}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$): 375.1625, found 375.1626.

Benzyl 2-tosylhexanoate (4k). Obtained as a white solid (90.5 mg, 89%); m.p. 49–50 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.65 (d, $J = 8.0$ Hz, 2H), 7.33 (s, 3H), 7.25 (m, 4H), 5.08 (q, $J = 12.2$ Hz, 2H), 3.94 (dd, $J = 11.2, 3.4$ Hz, 1H), 2.41 (s, 3H), 2.10–2.01 (m, 1H), 2.00–1.91 (m, 1H), 1.34–1.17 (m, 4H), 0.83 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 166.1, 145.2, 134.8, 134.2, 129.6, 129.3, 128.5, 70.9, 67.7, 28.9, 26.5, 22.1, 21.7, 13.6; HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{25}\text{O}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$): 361.1468, found 361.1476.

3-tosyldihydrofuran-2(3H)-one (4l). Obtained as a white solid (30.4 mg, 52%); m.p. 74–75 °C; ^1H NMR (500 MHz; CDCl_3) δ 7.83 (d, $J = 8.3$ Hz, 2H), 7.40 (d, $J = 8.3$ Hz, 2H), 4.51–4.36 (m, 2H), 4.04–4.01 (m, 1H), 3.05–2.70 (m, 2H), 2.47 (s, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 168.3, 146.1, 133.7, 130.0, 129.4, 67.1, 63.6, 24.0, 21.8; HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{13}\text{O}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$): 241.0529, found 241.0534.

N-methyl-N,2-diphenyl-2-tosylacetamide (4m). Obtained as a white solid (76.3 mg, 67%); m.p. 150–151 °C; ^1H NMR (500 MHz; CDCl_3) δ 7.40–7.14 (m, 19H), 5.05 (s, 1H), 3.27 (s, 4H), 2.41 (s, 3H). ^{13}C NMR (125 MHz; CDCl_3) δ 164.2, 144.8, 142.7, 133.7, 130.5, 130.3, 130.0, 129.3, 129.2, 128.7, 128.7, 128.4, 127.6, 72.6, 37.7, 21.7; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{22}\text{NO}_3\text{S}^+$ ($[\text{M} + \text{H}]^+$): 380.1315, found 380.1312.

N-methyl-N-phenyl-2-tosylhexanamide (4n). Obtained as a white solid (96.6 mg, 90%); m.p. 110–112 °C; ^1H NMR (500 MHz, CDCl_3) δ 7.70 (d, $J = 7.7$ Hz, 2H), 7.51–7.27 (m, 7H), 4.00 (d, $J = 11.1$ Hz, 1H), 3.32 (s, 3H), 2.45 (s, 3H), 1.86–1.74 (m, 2H), 1.28–1.00 (m, 4H), 0.81 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 165.1, 144.9, 142.8, 134.3, 130.0, 129.2, 128.5, 66.7, 38.0, 28.8, 28.5, 22.3, 21.6, 13.6. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{26}\text{NO}_3\text{S}^+$ ($[\text{M} + \text{H}]^+$): 360.1628, found 360.1623.

N-(2-methyl-3-oxo-3-phenyl-2-tosylpropyl)formamide (5a). Obtained as a white solid (isolated yield: 28%); m.p. 148–150 °C; ^1H NMR (500 MHz, CDCl_3) δ 8.17 (s, 1H), 7.94–7.90 (m, 2H), 7.66 (d, $J = 8.3$ Hz, 2H), 7.55 (t, $J = 7.5$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 6.32 (s, 1H), 4.02 (dd, $J = 6.6, 3.3$ Hz, 2H), 2.45 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 198.0, 161.4, 146.0, 137.3, 132.6, 131.8, 130.3, 129.7, 128.9, 128.4, 76.5, 41.3, 21.7, 17.4; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_4\text{S}^+$ ($[\text{M} + \text{H}]^+$): 346.1108, found 346.1121.

N-(tosylmethyl)formamide (A). Obtained as a white solid (isolated yield: 81%); m.p. 107–108; ^1H NMR (500 MHz, CDCl_3) δ 8.06 (s, 1H), 7.77 (d, $J = 8.3$ Hz, 2H), 7.34 (d, $J = 8.1$ Hz, 2H), 7.18 (t, $J = 6.0$ Hz, 1H), 4.70 (d, $J = 6.9$ Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz; CDCl_3) δ 160.7, 145.7, 133.6, 130.1, 128.8, 58.9, 21.7.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge via the Internet at <http://pubs.acs.org>.

Computational details and results

Copies of ^1H and ^{13}C NMR spectra for all new compounds

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Notes

The authors declare no competing financial interest.

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