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Unexpected Role of *p*-Toluenesulfonylmethyl Isocyanide as a Sulfonylating Agent in Reactions with α-Bromocarbonyl Compounds

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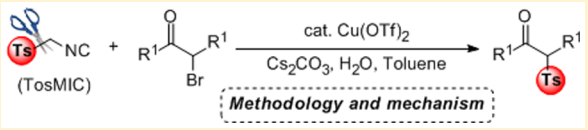
Supporting Information

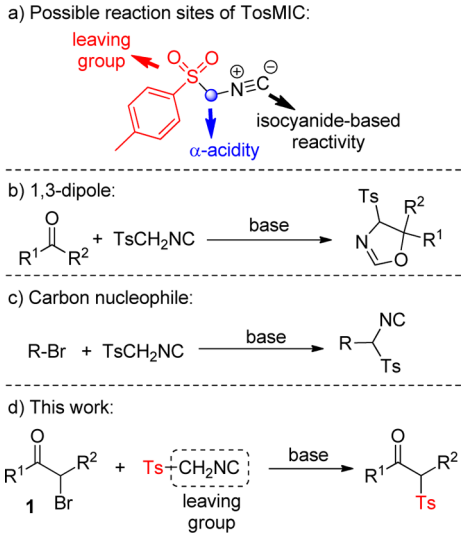
ABSTRACT: The reactions of *p*-toluenesulfonylmethyl isocyanide (TosMIC) with α-bromocarbonyl compounds leading efficiently to α-sulfonated ketones, esters, and amides were reported, in which an explicit new role of TosMIC as the sulfonylating agent was uncovered for the first time. Mechanistic study 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 a Cs_2CO_3 additive.



INTRODUCTION

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 a result of the strong electron-withdrawing effect of the two groups attached to the carbon (Scheme 1a). Thus, a variety of heterocycles,[2] such as oxazolidines,[3] oxazoles,[4] indoles,[5] pyrroles,[6] thiazoles,[7] triazoles,[8] etc., are readily accessible by base-induced cycloaddition 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 the C−S bond, in most reactions, the tosyl moiety of TosMIC is finally released into the reaction medium as a leaving group;[10] however, the use of TosMIC as a sulfonating agent is rare.[11]

Scheme 1. Different Roles of TosMIC in Organic Reactions



To search for new reactivity of TosMIC in organic transformations,[12] in this paper, we report a new substitution reaction of TosMIC with α-bromocarbonyl compounds (**1**) in the presence of Cs_2CO_3. Instead of working as a three-atom component in the cycloaddition reaction with the carbonyl functionality (Scheme 1b) or as a carbon nucleophile in the substitution with 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).

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-sulfonation product **2a** was obtained in 40% yield at room temperature (entry 1). Slightly increased yield (44%) was achieved when the reaction was carried out 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 increased to 70 and 90 °C, the same yield (56%) was obtained (entries 4 and 5), indicating that the reaction temperature only has a 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 % of $Cu(OTf)_2$ was added as a catalyst, the yield of **2a** was dramatically increased to 84% (entry 8), and the yield could be

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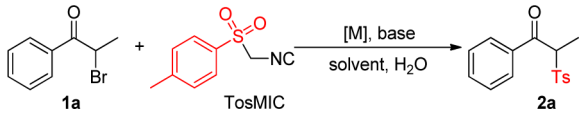
Table 1. Screening of the Reaction Conditions[a]



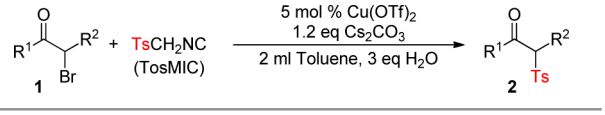
entry	base (equiv)	[M]	solvent	yield (%)[b]
1[c]	Cs_2CO_3 (1.5)		toluene	40
2[d]	Cs_2CO_3 (1.5)		toluene	44
3[d]	Cs_2CO_3 (1.2)		toluene	52
4	Cs_2CO_3 (1.2)		toluene	56
5[e]	Cs_2CO_3 (1.2)		toluene	56
6[c]	Cs_2CO_3 (1.5)		DCE	33
7[c]	Cs_2CO_3 (1.5)		acetonitrile	36
8	Cs_2CO_3 (1.2)	$Cu(OTf)_2$	toluene	84
9[f]	Cs_2CO_3 (1.2)	$Cu(OTf)_2$	toluene	87
10	Cs_2CO_3 (1.2)	$Pd(OAc)_2$	toluene	59
11	Cs_2CO_3 (1.2)	AgOTf	toluene	46
12	Cs_2CO_3 (1.2)	$Cu(OTf)_2$	1,4-dioxane	70
13	DBU (1.2)	$Cu(OTf)_2$	toluene	49
14	Et_3N (1.2)	$Cu(OTf)_2$	toluene	NR
15	K_2CO_3 (1.2)	$Cu(OTf)_2$	toluene	trace
16	NaO^tBu (1.2)	$Cu(OTf)_2$	toluene	trace
17	CsOAc (1.2)	$Cu(OTf)_2$	toluene	trace[g]

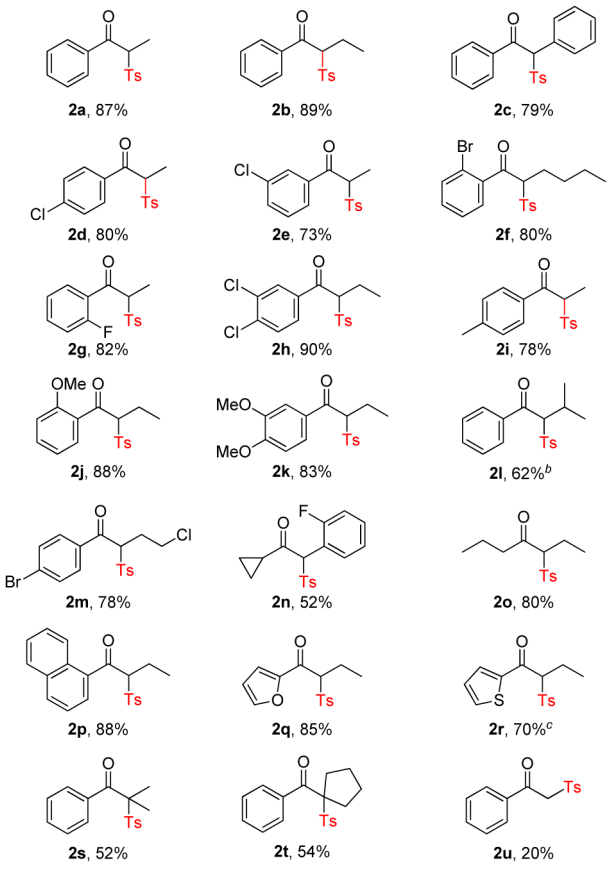
[a]Reaction conditions: **1a** (0.3 mmol), TosMIC (0.9 mmol), catalyst (5 mol %), H_2O (3 equiv), and anhydrous solvent (2 mL) at 70 °C for 9 h. [b]Isolated yields. [c]At room temperature. [d]At 50 °C. [e]At 90 °C. [f]Reaction for 20 h. [g]Complex mixture.

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 $Pd(OAc)_2$ 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 of Et_3N (entry 14), K_2CO_3 (entry 15), or NaO^tBu (entry 16) as the base source, and the use of CsOAc led to a complex mixture (entry 17).

With the optimal reaction conditions in hand, the reaction scope for this $Cu(OTf)_2$-catalyzed and Cs_2CO_3-promoted sulfonylation of α-bromoketones with TosMIC was then explored. As shown in Table 2, the sulfonylation products could be afforded from a variety of α-bromoketones. In comparison with **1a**, when the alkyl group (R^2) 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 a 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 were occupied with chloride atoms. When the phenyl group was substituted with an electron-donating substituent at para and ortho positions, **2i** and **2j** were formed in 78 and 88% yields, respectively. When 3,4-dimethoxyl-substituted phenyl was 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 isopropyl was attached to the

Table 2. Scope of α-Bromoketones[a]





[a]Reaction conditions: **1** (0.3 mmol), TosMIC (0.9 mmol), Cs_2CO_3 (1.2 equiv), $Cu(OTf)_2$ (5 mol %), H_2O (3 equiv), and toluene (2 mL) at 70 °C for 20 h. [b]At 100 °C for 42 h. [c]In 2 mL of 1,4-dioxane for 12 h.

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 (R^1) 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.

After the unique reactivity of TosMIC as a sulfonylating ageant in reactions with α-bromoketones was established, 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

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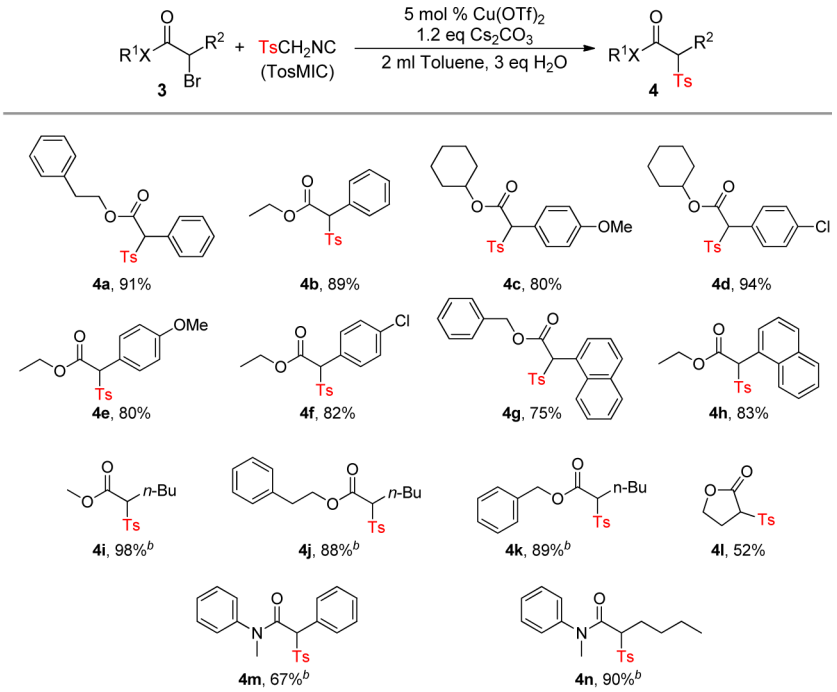
Table 3. Reactions of α-Bromoesters and Amides[a]

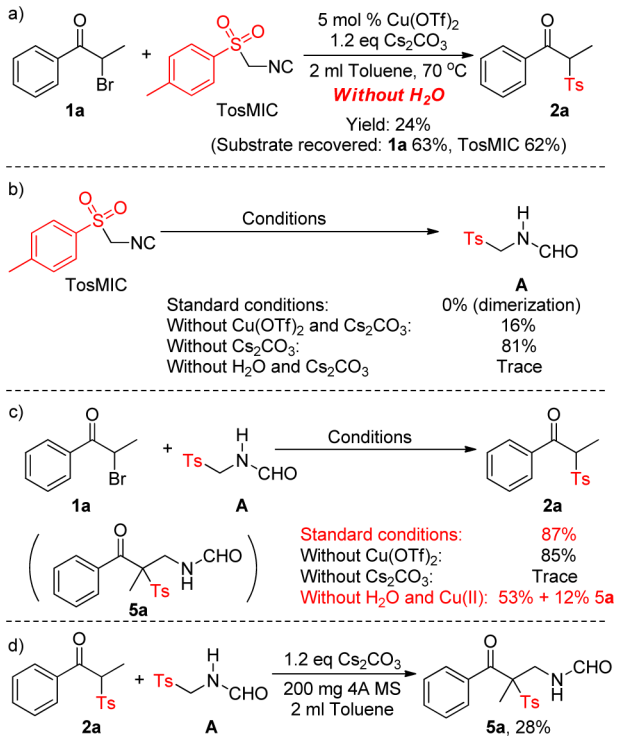


[a]Reaction conditions: **3** (0.3 mmol), TosMIC (0.9 mmol), Cs_2CO_3 (1.2 equiv), $Cu(OTf)_2$ (5 mol %), H_2O (3 equiv), and toluene (2 mL) at 70 °C for 15 h. [b]In 2.0 mL of dioxane for 9 h.

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 conditions, 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-containing substrates were compatible, generating **4g** and **4h** in 75 and 83% yields, respectively. These slightly decreased yields compared with those of **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 an alkyl substituent at the α-carbon (**4j** and **4k**). Interestingly, γ-lactone could also be sulfonylated with TosMIC, although only a moderate yield of **4l** was obtained. The reaction could be applied to α-bromoamides, which leads to sulfonylation products **4m** and **4n** in 67 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 and only a small amount of dimerization product was found.[13] Interestingly, if no $Cu(OTf)_2$ 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 % of $Cu(OTf)_2$ and 1 equiv of H_2O were added). As expected, only a 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 the presence of Cs_2CO_3. Next, the reactions between **1a** and **A** were studied under different conditions (Scheme 2c). Under

Scheme 2. Experiments for Mechanistic Study



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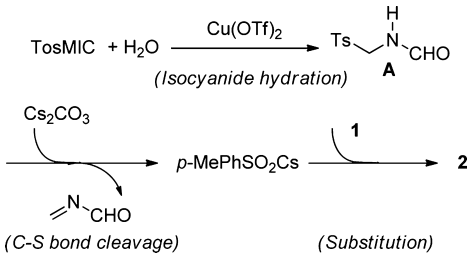
standard conditions, the reaction of **1a** with **A** leads efficiently to **2a** in 87% yield, confirming that **A** is an intermediate to the sulfonylation product. A comparable yield of 85% was obtained if no $Cu(OTf)_2$ catalyst was added, suggesting that $Cu(OTf)_2$ is not required for the C−S bond cleavage and the substitution steps. Instead, the base additive was proven 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 a notable decrease 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 that it may be a result from Michael addition of product **2a** to *N*-methyleneformamide, a byproduct 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 conditions (Scheme 2d), which gave rise to **5a** in 28% yield. Possibly, under standard conditions, the generated *N*-methyleneformamide was scavenged by a facile reaction with water, thus more product **2a** was isolated.

Based on the above experiments, the plausible mechanism for the current transformation is outlined in Scheme 3. In the first

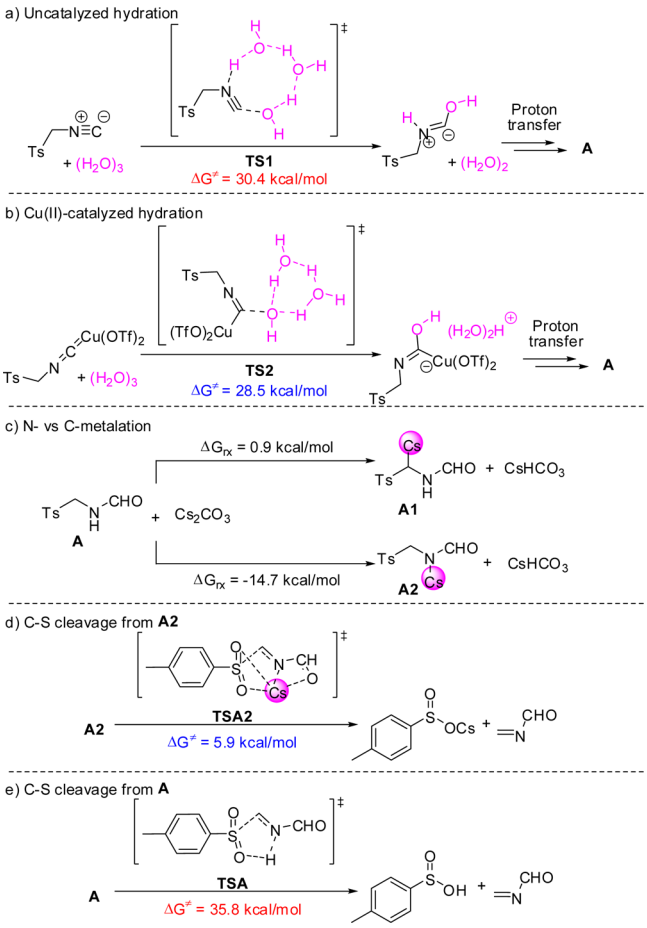
Scheme 3. Plausible Mechanism



step, hydration of TosMIC to form **A** occurs under the catalysis of Lewis acidic $Cu(OTf)_2$. Then, from formamide **A**, the C−S bond cleavage is mediated by Cs_2CO_3 to form celsium sulfinate and *N*-methyleneformamide concurrently. The involvement of celsium 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-bromoketone **1** with sulfinate salt. Although reduced yields were obtained in the presence of radical scanvengers (given in the Supporting Information), it is not clear 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]

To better understand the details for the $Cu(OTf)_2$-catalyzed isocyanide hydration and Cs_2CO_3-mediated C−S bond cleavage processes, DFT calculations[15] at the M062X/6-31+G(d)/SDD level were performed (Scheme 4). For the hydration step, the noncatalyzed 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 $Cu(OTf)_2$, the addition of water occurs via **TS2** with a reduced barrier of 28.5 kcal/mol (Scheme 4b), showing that the hydration is catalyzed by a 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/

Scheme 4. Computational Results[15]



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 the 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 the Supporting Information) shows that the Cs atom has strong interactions with both the sulfinate and formamide moieties, thus facilitating the C−S bond cleavage.

CONCLUSION

In summary, we found a new type of reaction of TosMIC with a wide range of α-bromocarbonyl 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 $Cu(OTf)_2$-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 an α-bromocarbonyl compound to afford α-sulfonated ketones, esters, and amides. Novel transformations involving efficient C−S bond cleavage/formation are ongoing in our laboratory.

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

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from commercial available resources and were used as received. All other α-bromoketones were synthesized according to the 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 (500 MHz for ^{1}H, 125 MHz for ^{13}C), using $CDCl_3$ as the solvent with tetramethylsilane 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 br s = broad singlet), coupling constant in hertz, and integration. Chemical shifts for ^{13}C NMR spectra were recorded in parts per million from tetramethylsilane using the central peak of deuterochloroform (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 an X4 melting point apparatus.

Typical Procedure for the Preparation of 2-Bromo-1-phenylbutan-1-one ***1b.*** To a 50 mL flask charged 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 was transferred dropwise to the ketone solution at room temperature. After the reaction was stirred overnight, the mixture was poured into ethyl acetate (20 mL), which was washed with saturated $NaHCO_3$ (15 mL), saturated $Na_2S_2O_3$ (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; ^{1}H 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; ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{12}H_{15}Br_2O^+$ ($[M + H]^+$) 332.9484, found 332.9487.

*2-Bromo-1-(2-fluorophenyl)propan-1-one (**1g**):*[16a] faint yellow liquid; ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{1}H NMR (500 MHz, $CDCl_3$) 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**):*[16e] white solid; ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{11}H_{13}BrNaO_2^+$ ($[M + Na]^+$) 278.9991, found 278.0004.

*2-Bromo-1-(3,4-dimethoxyphenyl)butan-1-one (**1k**):*[16f] white solid; ^{1}H NMR (500 MHz, $CDCl_3$) 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; ^{1}H NMR (500 MHz, $CDCl_3$) 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; mp 91−93 °C; ^{1}H 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 $C_{10}H_{10}Br_2ClO^+$ ($[M + H]^+$) 338.8781, found 338.8783.

*3-Bromoheptan-4-one (**1o**):*[16g] colorless liquid; ^{1}H 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; ^{1}H 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 $C_{14}H_{14}BrO^+$ ($[M + H]^+$) 277.0223, found 277.0222.

*2-Bromo-1-(furan-2-yl)butan-1-one (**1q**):*[16h] brown liquid; ^{1}H 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; ^{1}H 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; ^{1}H 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; ^{1}H 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 of 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-bromoesters and amides were prepared from the corresponding ester and amide precursors by similar procedures.

*Phenethyl 2-Bromo-2-phenylacetate (**3a**):* white solid; mp 37−38 °C; ^{1}H 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 $C_{16}H_{16}BrO_2^+$ ($[M + H]^+$) 319.0328, found 319.0327.

*Ethyl 2-Bromo-2-phenylacetate (**3b**):*[16k] colorless liquid; ^{1}H 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; ^{1}H 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,

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130.1, 128.1, 114.2, 74.7, 55.3, 47.3, 31.1, 25.3, 23.4, 23.4; HRMS (ESI) calcd for $C_{15}H_{19}BrNaO_3^+$ ([M + Na]$^+$) 349.0410, found 349.0413.

*Cyclohexyl 2-Bromo-2-(4-chlorophenyl)acetate (**3d**):* faint yellow liquid; ^{1}H 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 $C_{14}H_{17}BrClO_2^+$ ([M + H]$^+$) 331.0095, found 331.0103.

*Ethyl 2-Bromo-2-(4-methoxyphenyl)acetate (**3e**):*[16k] faint yellow liquid; ^{1}H 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; ^{1}H 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; mp 42−43 °C; ^{1}H 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 $C_{19}H_{15}BrNaO_2^+$ ([M + Na]$^+$) 377.0148, found 377.0150.

*Ethyl 2-Bromo-2-(naphthalen-1-yl)acetate (**3h**):* faint yellow liquid; ^{1}H 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; ^{1}H 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 $C_{14}H_{20}BrO_2^+$ ([M + H]$^+$) 299.0641, found 299.0645.

*Benzyl 2-Bromohexanoate (**3k**):*[16m] colorless liquid; ^{1}H 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; ^{1}H 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; ^{1}H 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 $C_{13}H_{18}BrNNaO^+$ ([M + Na]$^+$) 306.0464, found 306.0484.

*Typical Procedure for Synthesis of 1-Phenyl-2-tosylpropan-1-one **2a** by Cu(OTf)$_2$-Catalyzed Reaction between TosMIC and 2-Bromo-1-phenylpropan-1-one **1a**.* To a flame-dried Schlenk tube charged with a magnetic stirring bar were added **1a** (63.5 mg, 0.3 mmol), TosMIC (175.7 mg, 0.9 mmol), $Cu(OTf)_2$ (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 × 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/ethyl acetate) to afford product **2a** (74.6 mg, 87% yield) as a white solid.

*1-Phenyl-2-tosylpropan-1-one (**2a**):* white solid (74.6 mg, 87%); mp 93−95 °C; ^{1}H 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 $C_{16}H_{17}O_3S^+$ ([M + H]$^+$) 289.0893, found 289.0895.

*1-Phenyl-2-tosylbutan-1-one (**2b**):* white solid (72.8 mg, 89%); mp 73−74 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{17}H_{19}O_3S^+$ ([M + H]$^+$) 303.1049, found 303.1049.

*1,2-Diphenyl-2-tosylethanone (**2c**):* white solid (83.0 mg, 79%); mp 145−146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{21}H_{19}O_3S^+$ ([M + H]$^+$) 351.1049, found 351.1052.

*1-(4-Chlorophenyl)-2-tosylpropan-1-one (**2d**):* white solid (76.5 mg, 80%); mp 126−127 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{16}H_{16}ClO_3S^+$ ([M + H]$^+$) 323.0503, found 323.0506.

*1-(3-Chlorophenyl)-2-tosylpropan-1-one (**2e**):* white solid (71.1 mg, 73%); mp 105−106 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{16}H_{16}ClO_3S^+$ ([M + H]$^+$) 323.0503, found 323.0510.

*1-(2-Bromophenyl)-2-tosylhexan-1-one (**2f**):* white solid (96.5 mg, 80%); mp 93−94 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{19}H_{22}BrO_3S^+$ ([M + H]$^+$) 409.0468, found 409.0469.

*1-(2-Fluorophenyl)-2-tosylpropan-1-one (**2g**):* white solid (75.5 mg, 82%); mp 83−84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{16}H_{16}FO_3S^+$ ([M + H]$^+$) 307.0799, found 307.0796.

*1-(3,4-Dichlorophenyl)-2-tosylbutan-1-one (**2h**):* yellow solid (90.0 mg, 90%); mp 131−132 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{17}H_{16}Cl_2O_3SNa^+$ ([M + Na]$^+$) 393.0089, found 393.0098.

*1-p-Tolyl-2-tosylpropan-1-one (**2i**):* white solid (70.6 mg, 78%); mp 104−105 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{17}H_{19}O_3S^+$ ([M + H]$^+$) 303.1049, found 303.1049.

*1-(2-Methoxyphenyl)-2-tosylbutan-1-one (**2j**):* white solid (84.3 mg, 88%); mp 106−107 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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

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(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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{18}H_{21}O_4S^+$ ([M + H]$^+$) 333.1155, found 333.1142.

1-(3,4-Dimethoxyphenyl)-2-tosylbutan-1-one (**2k**): white solid (88.7 mg, 83%); mp 163−164 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{19}H_{23}O_5S^+$ ([M + H]$^+$) 363.1261, found 363.1261.

3-Methyl-1-phenyl-2-tosylbutan-1-one (**2l**): white solid (58.4 mg, 62%); mp 81−82 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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 $C_{18}H_{21}O_3S^+$ ([M + H]$^+$) 317.1206, found 317.1207.

1-(4-Bromophenyl)-4-chloro-2-tosylbutan-1-one (**2m**): white solid (97.2 mg, 78%); mp 145−146 °C; ^{1}H NMR (500 MHz, $CDCl_3$) 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); ^{13}C NMR (125 MHz, $CDCl_3$) 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**): white solid (49.3 mg, 52%); mp 144−146 °C; ^{1}H 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**): white solid (62.3 mg, 80%); mp 64−65 °C; ^{1}H 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**): white solid (93.1 mg, 88%); mp 129−131 °C; ^{1}H 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**): yellow solid (73.7 mg, 85%); mp 116−117 °C; ^{1}H 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**): yellow solid (64.0 mg, 70%); mp 107−108 °C; ^{1}H 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**): faint yellow liquid (47.7 mg, 52%); ^{1}H 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 $C_{17}H_{19}O_3S^+$ ([M + H]$^+$) 303.1049, found 303.1048.

Phenyl(1-tosylcyclopentyl)methanone (**2t**): colorless liquid (52.9 mg, 54%); ^{1}H 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, $CDCl_3$) δ 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 $C_{19}H_{21}O_3S^+$ ([M + H]$^+$) 329.1206, found 329.1205.

1-Phenyl-2-tosylethanone (**2u**): white solid (16.6 mg, 20%); mp 98−99 °C; ^{1}H 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 $C_{15}H_{15}O_3S^+$ ([M + H]$^+$) 275.0736, found 275.0738.

Phenethyl 2-Phenyl-2-tosylacetate (**4a**): white solid (104.1 mg, 91%); mp 113 114 °C; ^{1}H 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 $C_{23}H_{23}O_4S^+$ ([M + H]$^+$) 395.1312, found 395.1313.

Ethyl 2-Phenyl-2-tosylacetate (**4b**): white solid (84.7 mg, 89%); mp 111−112 °C; ^{1}H 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 $C_{17}H_{19}O_4S^+$ ([M + H]$^+$) 319.0999, found 319.1015.

Cyclohexyl 2-(4-Methoxyphenyl)-2-tosylacetate (**4c**): faint yellow solid (94.4 mg, 80%); mp 104−105 °C; ^{1}H 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 $C_{22}H_{27}O_5S^+$ ([M + H]$^+$) 403.1574, found 403.1570.

Cyclohexyl 2-(4-Chlorophenyl)-2-tosylacetate (**4d**): white solid (112.4 mg, 94%); mp 89−90 °C; ^{1}H 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**): white solid (84.2 mg, 80%); mp 147−148 °C; ^{1}H 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**): white solid (87.2 mg, 82%); mp 134−135 °C; ^{1}H 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.

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*Benzyl 2-(Naphthalen-1-yl)-2-tosylacetate (**4g**):* brown solid (95.7 mg, 75%); mp 135−136 °C; ^{1}H 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**):* faint yellow solid (88.2 mg, 83%); mp 136−137 °C; ^{1}H 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**):* white solid (81.3 mg, 98%); mp 46−47 °C; ^{1}H 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**):* white solid (94.1 mg, 88%); mp 35−36 °C; ^{1}H 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 $C_{21}H_{27}O_4S^+$ ([M + H]$^+$) 375.1625, found 375.1626.

*Benzyl 2-Tosylhexanoate (**4k**):* white solid (90.5 mg, 89%); mp 49−50 °C; ^{1}H 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 $C_{20}H_{25}O_4S^+$ ([M + H]$^+$) 361.1468, found 361.1476.

*3-Tosyldihydrofuran-2(3H)-one (**4l**):* white solid (30.4 mg, 52%); mp 74−75 °C; ^{1}H 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 $C_{11}H_{13}O_4S^+$ ([M + H]$^+$) 241.0529, found 241.0534.

*N-Methyl-N,2-diphenyl-2-tosylacetamide (**4m**):* white solid (76.3 mg, 67%); mp 150−151 °C; ^{1}H 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 $C_{22}H_{22}NO_3S^+$ ([M + H]$^+$) 380.1315, found 380.1312.

*N-Methyl-N-phenyl-2-tosylhexanamide (**4n**):* white solid (96.6 mg, 90%); mp 110−112 °C; ^{1}H 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 $C_{20}H_{26}NO_3S^+$ ([M + H]$^+$) 360.1628, found 360.1623.

*N-(2-Methyl-3-oxo-3-phenyl-2-tosylpropyl)formamide (**5a**):* white solid (isolated yield: 28%); mp 148−150 °C; ^{1}H 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 $C_{18}H_{20}NO_4S^+$ ([M + H]$^+$) 346.1108, found 346.1121.

*N-(Tosylmethyl)formamide (**A**):* white solid (isolated yield: 81%); mp 107−108; ^{1}H 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 on the ACS Publications website at DOI: 10.1021/acs.joc.6b00844.

Computational details, results, and copies of ^{1}H and ^{13}NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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