A Novel One-Pot Method for α-Tosyloxylation of Ketones Using a Catalytic Amount of Ammonium Iodide

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Abstract: A novel one-pot procedure was designed for the preparation of various α-tosyloxy ketones in good yields by the reaction of ketones with *m*-chloroperoxybenzoic acid and *p*-toluenesulfonic acid monohydrate in the presence of catalytic amounts of ammonium iodide and benzene in a mixture of acetonitrile and 2,2,2-trifluoroethanol (8:2) at room temperature for 24 hours.

Key words: α-tosyloxylation, α-tosyloxy ketones, hypervalent iodine intermediate, ammonium iodide

Over the past two decades, hypervalent iodine reagents have been increasingly explored as environmentally benign oxidation reagents in place of rare or toxic heavy metal oxidants.[1] They are usually used as mild oxidants[2] and also as electrophilic reagents.[3] Among these hypervalent iodine reagents, [hydroxy(tosyloxy)iodo]benzene (HTIB, Koser's reagent) is the most popular and useful reagent for the direct α-tosyloxylation of ketones, and the prepared α-tosyloxy ketones are important strategic precursors for the construction of various heteroaromatic compounds such as thiazoles, oxazoles, selenazoles, imidazoles, pyrazoles, benzofurans and lactones.[4]

In recent years, the catalytic utilization of hypervalent iodine reagents has been increasing in importance, with growing interest in the development of environmentally benign synthetic transformations.[5] In these catalytic reactions, a catalytic amount of an iodine-containing molecule together with a stoichiometric oxidant is used. The oxidant generates the hypervalent iodine reagent in situ and, after the oxidative transformation, the reduced iodine-containing molecule is reoxidized. With iodobenzene as catalyst, Togo and co-workers have reported several methods for the catalyzed α-tosyloxylation of ketones in the presence of *m*-chloroperoxybenzoic acid and *p*-toluenesulfonic acid.[6] Based on these results, more recently they investigated a new way for the α-tosyloxylation of ketones using molecular iodine (I_2) as the catalyst, which was demonstrated via a hypervalent iodine intermediate; this method avoided the need for expensive aryl iodides and good yields were obtained.[7] Olofsson's group have also reported the one-pot preparation of hypervalent iodine compounds from molecular iodine and arenes.[8] In contrast, the one-pot reaction mediated by a hypervalent iodine species generated in situ from iodides, especially inorganic iodides, a method which is more environmentally benign, has been quite limited[9] and, to our knowledge, the α-tosyloxylation of ketones using catalytic amounts of iodide has not been reported before. Thus, the development of a simple and efficient method for the preparation of α-tosyloxy ketones with catalytic amounts of iodides under mild reaction conditions remains highly desirable. Herein, we wish to report a novel and efficient α-tosyloxylation of ketones using a catalytic amount of ammonium iodide (NH_4I).

At the onset of the research, we investigated the reaction of acetophenone with *m*-chloroperoxybenzoic acid (MCPBA) and *p*-toluenesulfonic acid monohydrate ($TsOH·H_2O$) in the presence of catalytic amounts of NH_4I and benzene in several organic solvents at room temperature for 24 hours. Generally, the reaction proceeded well and afforded the desired product (Table 1).

In light of the successful formation of α-tosyloxyacetophenone, the reaction conditions were optimized; the results are summarized in Table 1. It was shown that the yield depends greatly on the solvent (entries 1–13). When 1.0 equivalent of acetophenone was mixed and stirred with 2.2 equivalents of MCPBA, 2.1 equivalents of $TsOH·H_2O$ and 0.2 equivalents of NH_4I in the presence of benzene in a mixture of acetonitrile and 2,2,2-trifluoroethanol (MeCN–TFE, 8:2) at room temperature for 24 hours, the reaction gave a good yield of 84% (Table 1, entry 12). When oxidant Oxone® or $NaBO_3·4H_2O$ was used in place of MCPBA under similar reaction conditions, a moderate or poor yield was obtained (entries 14, 15). The amount of added NH_4I was also investigated (Table 1, entries 12, 16–19). When 0.3 equivalents of NH_4I were added, the yield reached the best value of 86% (entry 17); however, in the absence of NH_4I, no product was observed (entry 19). Other iodides, such as sodium iodide and potassium iodide, were active in the reaction and led to the product in good yields (Table 1, entries 20, 21).

With the optimal conditions in hand, a series of alkyl aryl ketones and dialkyl ketones were investigated in the reaction with NH_4I, MCPBA and $TsOH·H_2O$, in the presence of benzene in a mixture of MeCN and TFE (8:2), in order to assess the scope of this method. As shown in Table 2, the reaction was compatible with most of the alkyl aryl ketones, except 2-acetylthiophene (**1k**), and provided the

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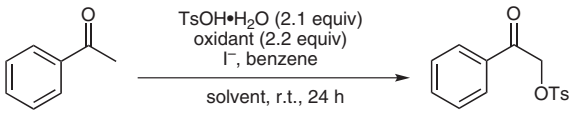
Table 1 Optimization of the α-Tosyloxylation of Acetophenone Using a Catalytic Amount of NH_4I



Entry	Solvent	Oxidant	I^- (equiv)	Yield[a] (%)
1	CH_2Cl_2	MCPBA	NH_4I (0.2)	57
2	MeOH	MCPBA	NH_4I (0.2)	13
3	EtOAc	MCPBA	NH_4I (0.2)	62
4	DMF	MCPBA	NH_4I (0.2)	49
5	EtOH	MCPBA	NH_4I (0.2)	40
6	THF	MCPBA	NH_4I (0.2)	60
7	TFE	MCPBA	NH_4I (0.2)	69
8	MeCN	MCPBA	NH_4I (0.2)	70
9	MeCN–TFE (5:5)	MCPBA	NH_4I (0.2)	77
10	MeCN–TFE (6:4)	MCPBA	NH_4I (0.2)	79
11	MeCN–TFE (7:3)	MCPBA	NH_4I (0.2)	79
12	MeCN–TFE (8:2)	MCPBA	NH_4I (0.2)	84
13	MeCN–TFE (9:1)	MCPBA	NH_4I (0.2)	79
14	MeCN–TFE (8:2)	Oxone®	NH_4I (0.2)	61
15	MeCN–TFE (8:2)	$NaBO_3·4H_2O$	NH_4I (0.2)	37
16	MeCN–TFE (8:2)	MCPBA	NH_4I (0.1)	64
17	MeCN–TFE (8:2)	MCPBA	NH_4I (0.3)	86
18	MeCN–TFE (8:2)	MCPBA	NH_4I (0.4)	77
19	MeCN–TFE (8:2)	MCPBA	–	0
20	MeCN–TFE (8:2)	MCPBA	NaI (0.3)	73
21	MeCN–TFE (8:2)	MCPBA	KI (0.3)	76

[a] Isolated yield.

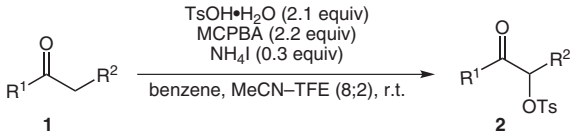
corresponding α-tosyloxy ketones in good yields (entries 1–9, 11). From these alkyl aryl ketones, it was found that substituents on the aromatic ring, no matter if they were electron-donating or electron-withdrawing groups, did not have an influence on the yield; however, ketones bearing an electron-donating group on the aromatic ring usually required somewhat longer reaction time than those bearing an electron-withdrawing group (Table 2, entries 2–7). Some dialkyl ketones were also investigated (Table 2, entries 12, 13, 15). Thus, acetone and 3-pentanone gave the corresponding products in 84% and 62% yield after 24 hours; the reaction with butanone was completed in only 6 hours, but afforded a mixture of products in a low yield of 38%. Cyclic ketones were checked and most of them were not active in the reaction; only 1-indanone (**1j**) gave the corresponding product in moderate yield (Table 2, entry 10). β-Dicarbonyl compounds, such as ethyl acetoacetate (**1n**), were not active at room temperature; when the reaction was carried out at 60 °C, a 92% yield of product was obtained after 12 hours (Table 2, entry 14).

Interestingly, when methanesulfonic acid, an aliphatic sulfonic acid, was used in place of $TsOH·H_2O$ in the reaction with acetophenone under similar conditions, the product **3a** was obtained in 21% yield (Table 3, entry 1). This result is different to Togo's report that the α-tosyloxylation of ketones using molecular iodine as catalyst was only suitable for aromatic sulfonic acids, and that when an aliphatic sulfonic acid was used, the reaction gave a trace amount of product.[7]

Enlightened by the above research, the reaction of several ketones with NH_4I, MCPBA and methanesulfonic acid or camphorsulfonic acid in the presence of benzene in a mixture of MeCN and TFE (8:2) at room temperature was ex-

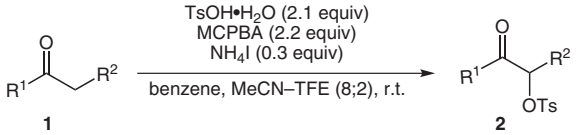
amined, and the corresponding α-sulfonyloxy ketones **3** were obtained (Table 3). Although the yields are variable, the present method extends the scope of the preparation of α-sulfonyloxy ketones and it suits not only aromatic sulfonic acids, but also aliphatic sulfonic acids.

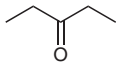
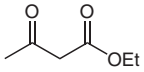
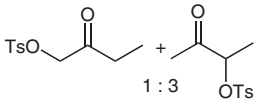
Table 2 Preparation of α-Tosyloxy Ketones **2**



Entry	Substrate	Time (h)	Product	Yield[a] (%)
1	**1a**	24	**2a**	86
2	**1b**	25	**2b**	81
3	**1c**	26	**2c**	80
4	**1d**	24	**2d**	71
5	**1e**	24	**2e**	95
6	**1f**	23	**2f**	92
7	**1g**	23	**2g**	82
8	**1h**	25	**2h**	75
9	**1i**	24	**2i**	73
10	**1j**	24	**2j**	55
11	**1k**	21	**2k**	30
12	**1l**	24	**2l**	84

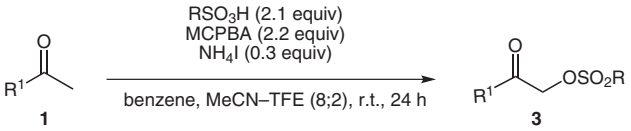
Table 2 Preparation of α-Tosyloxy Ketones **2** (continued)

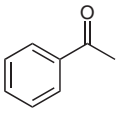
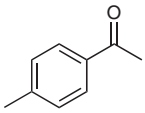
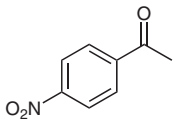
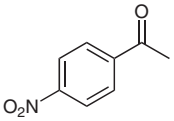


Entry	Substrate	Time (h)	Product	Yield[a] (%)
13	**1m** 	24	**2m**	62
14	**1n** 	12	**2n**	92[b]
15	**1o** 	6	 **2o** + **2p**	38[c]

[a] Isolated yield.
[b] Reaction was carried out at 60 °C.
[c] Determined by ^{1}H NMR spectroscopy.

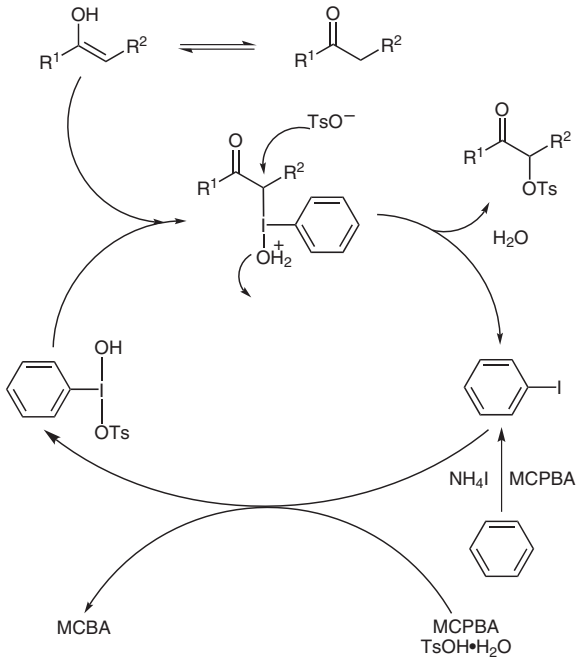
Table 3 Preparation of α-Sulfonyloxy Ketones **3**



Entry	Substrate	RSO_3H	Product	Yield[a] (%)
1	**1a** 	MsOH	**3a**	21
2	**1b** 	MsOH	**3b**	90
3	**1e** 	MsOH	**3c**	28
4	**1l** 	MsOH	**3d**	30
5	**1e** 	camphorsulfonic acid	**3e**	67
6	**1l** 	camphorsulfonic acid	**3f**	36

[a] Isolated yield.

A plausible reaction pathway for the present reaction is shown in Scheme 1. Thus, iodobenzene is formed at first by the reaction of NH_4I with benzene and MCPBA, which is followed by the generation in situ of the α-tosyloxylation reagent HTIB by the continuing oxidation with MCPBA. Then, the ketone reacts with HTIB to provide the corresponding α-tosyloxy ketone.



Scheme 1 Proposed reaction mechanism for the α-tosyloxylation of ketones

In summary, we have developed a novel and efficient one-pot method for the synthesis of various α-tosyloxy ketones in good yields by the reaction of ketones with MCPBA and $TsOH·H_2O$ in the presence of catalytic amounts of NH_4I and benzene in a mixture of MeCN and TFE (8:2) at room temperature for 24 hours. This method has some advantages, such as mild reaction conditions with a simple procedure, and it is suitable for preparing not only α-tosyloxy ketones but also other α-sulfonyloxy ketones. Furthermore, the use of inorganic iodide in place of expensive aryliodane will extend the scope of hypervalent iodine reagents in organic synthesis, and makes this method more environmentally benign.

Melting points were measured with an XT-4 melting point apparatus and are uncorrected. IR spectra were recorded on a Thermo Nicolet 6700 instrument. ^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance III (500 MHz) spectrometer. Mass spectra were determined on a Thermo ITQ 1100 mass spectrometer. Ammonium iodide, MCPBA, ketones and sulfonic acids were commercially available.

α-Tosyloxylation of Ketones Using a Catalytic Amount of Ammonium Iodide; General Procedure

To a solvent mixture of MeCN (8 mL) and TFE (2 mL), a ketone (1 mmol), MCPBA (2.2 mmol), NH_4I (0.3 mmol), $TsOH·H_2O$ (2.1 mmol) and benzene (2 drops) were added. The resulting solution was stirred at r.t. for 24 h. Then, the reaction mixture was poured into a soln of sat. aq $Na_2S_2O_3$ and Na_2CO_3. The mixture was extracted with CH_2Cl_2 (3 × 20 mL) and the combined organic layer was dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by short flash column chromatography on silica gel (hexane–EtOAc, 3:1) to provide the pure α-tosyloxy ketone.

α-Tosyloxyacetophenone (2a)

Yield: 249 mg (86%); yellow solid; mp 90–91 °C (Lit.[4h] 90–91 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 5.28 (s, 2 H), 7.36 (d, *J* = 8.1 Hz, 2 H), 7.47–7.50 (m, 2 H), 7.61–7.64 (m, 1 H), 7.85–7.88 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.63, 69.93, 127.96, 128.10, 128.88, 129.89, 132.64, 133.76, 134.16, 145.28, 190.30.

***p*-Methyl-α-tosyloxyacetophenone (2b)**

Yield: 246 mg (81%); red solid; mp 103–105 °C (Lit.[7] 105 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.44 (s, 3 H), 5.24 (s, 2 H), 7.26 (d, *J* = 7.9 Hz, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 7.85 (dd, *J* = 6.7, 1.7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.67, 21.76, 69.85, 128.11, 128.16, 129.58, 129.87, 131.33, 132.74, 145.22, 145.27, 189.80.

***o*-Methyl-α-tosyloxyacetophenone (2c)**

Yield: 243 mg (80%); red solid; mp 61–63 °C (Lit.[10] 60–62 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.37 (s, 3 H), 2.38 (s, 3 H), 5.09 (s, 2 H), 7.18–7.21 (m, 2 H), 7.27 (d, *J* = 8.2 Hz, 2 H), 7.34–7.36 (m, 1 H), 7.46 (d, *J* = 7.9 Hz, 1 H), 7.76 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.01, 21.61, 70.99, 125.84, 128.04, 128.45, 129.93, 132.27, 132.50, 132.70, 133.67, 139.26, 145.30, 193.69.

***p*-Chloro-α-tosyloxyacetophenone (2d)**

Yield: 230 mg (71%); white solid; mp 123–124 °C (Lit.[11] 125 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 5.22 (s, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.45 (d, *J* = 8.5 Hz, 2 H), 7.80 (d, *J* = 8.5 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.67, 69.79, 128.14, 129.28, 129.47, 129.94, 132.13, 132.55, 140.79, 145.42, 189.51.

***p*-Nitro-α-tosyloxyacetophenone (2e)**

Yield: 318 mg (95%); yellow solid; mp 136–137 °C (Lit.[7] 137 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.48 (s, 3 H), 5.25 (s, 2 H), 7.38 (d, *J* = 8.2 Hz, 2 H), 7.85 (d, *J* = 8.3 Hz, 2 H), 8.04 (dd, *J* = 7.0, 1.8 Hz, 2 H), 8.34 (dd, *J* = 7.0, 1.8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.72, 69.97, 124.08, 128.17, 129.38, 130.06, 132.34, 138.28, 145.71, 150.85, 189.83.

***m*-Nitro-α-tosyloxyacetophenone (2f)**

Yield: 308 mg (92%); white solid; mp 130–131 °C (Lit.[7] 129–130 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.48 (s, 3 H), 5.26 (s, 2 H), 7.38 (d, *J* = 8.0 Hz, 2 H), 7.73 (t, *J* = 8.0 Hz, 1 H), 7.86 (d, *J* = 8.4 Hz, 2 H), 8.21–8.24 (m, 1 H), 8.47–8.49 (m, 1 H), 8.65 (t, *J* = 1.9 Hz, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.70, 69.92, 123.07, 128.17, 128.27, 130.06, 130.28, 132.31, 133.74, 135.07, 145.72, 148.48, 189.22.

***p*-Bromo-α-tosyloxyacetophenone (2g)**

Yield: 303 mg (82%); yellow solid; mp 131–132 °C (Lit.[12] 129–130 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 5.21 (s, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.61–7.63 (m, 2 H), 7.70–7.73 (m, 2 H), 7.84 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.69, 69.76, 117.20, 128.15, 129.55, 129.95, 132.28, 132.42, 132.52, 145.44, 189.87.

α-Tosyloxypropiophenone (2h)
Yield: 228 mg (75%); white solid; mp 68–69 °C (Lit.[11] 68–69 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.59 (d, *J* = 7.0 Hz, 3 H), 2.40 (s, 3 H), 5.79 (q, *J* = 7.0 Hz, 1 H), 7.26 (d, *J* = 8.5 Hz, 2 H), 7.45 (t, *J* = 7.8 Hz, 2 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.75 (d, *J* = 8.3 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.73, 21.62, 77.38, 127.95, 128.75, 129.76, 133.50, 133.74, 133.82, 145.01, 194.83.

***p*-Chloro-α-tosyloxypropiophenone (2i)**
Yield: 247 mg (73%); white solid; mp 100–101 °C (Lit.[13] 94–96 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 6.9 Hz, 3 H), 2.44 (s, 3 H), 5.70 (q, *J* = 7.0 Hz, 1 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.43–7.46 (m, 2 H), 7.75 (d, *J* = 8.3 Hz, 2 H), 7.84–7.86 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.56, 21.64, 77.25, 127.93, 129.10, 129.81, 130.24, 132.01, 133.36, 140.41, 145.18, 193.86.

2-Tosyloxy-1-indanone (2j)
Yield: 166 mg (55%); yellow solid; mp 115–116 °C (Lit.[14] 110–112 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.48 (s, 3 H), 3.29 (dd, *J* = 17.2, 4.8 Hz, 1 H), 3.67 (dd, *J* = 17.2, 8.0 Hz, 1 H), 5.15 (dd, *J* = 8.0, 4.7 Hz, 1 H), 7.40–7.46 (m, 4 H), 7.65–7.68 (m, 1 H), 7.75 (d, *J* = 7.7 Hz, 1 H), 7.94 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.70, 33.81, 78.27, 124.60, 126.71, 128.17, 128.41, 129.91, 133.22, 133.57, 136.37, 145.24, 149.94, 197.52.

2-(α-Tosyloxyacetyl)thiophene (2k)
Yield: 89 mg (30%); yellow solid; mp 92–93 °C (Lit.[7] 92–93 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 5.10 (s, 2 H), 7.16 (dd, *J* = 5.0, 3.9 Hz, 1 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.72–7.75 (m, 1 H), 7.79 (dd, *J* = 3.9, 1.0 Hz, 1 H), 7.85 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.68, 69.89, 128.18, 128.47, 129.95, 132.43, 133.15, 135.13, 140.04, 145.44, 183.66.

α-Tosyloxyacetone (2l)
Yield: 192 mg (84%); yellow solid; mp 35–36 °C (Lit.[15] 35 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.18 (s, 3 H), 2.44 (s, 3 H), 4.48 (s, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.79 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.65, 26.49, 72.03, 128.02, 130.05, 132.31, 145.54, 201.03.

2-Tosyloxy-3-pentanone (2m)
Yield: 159 mg (62%); black solid; mp 45–46 °C (Lit.[7] 45–46 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.3 Hz, 3 H), 1.29 (d, *J* = 7.0 Hz, 3 H), 2.40 (s, 3 H), 2.53–2.57 (m, 2 H), 4.77 (q, *J* = 7.0 Hz, 1 H), 7.32 (d, *J* = 8.1 Hz, 2 H), 7.75 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 6.99, 17.60, 21.66, 31.18, 80.68, 127.89, 129.99, 133.80, 145.27, 207.74.

Ethyl 2-Tosyloxyacetoacetate (2n)[16]
Yield: 276 mg (92%); yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.12 (t, *J* = 7.2 Hz, 3 H), 2.20 (s, 3 H), 2.37 (s, 3 H), 4.02–4.10 (m, 2 H), 5.15 (s, 1 H), 7.29 (dd, *J* = 8.2, 3.9 Hz, 2 H), 7.74 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 6.96, 21.66, 26.55, 62.67, 80.36, 128.18, 129.98, 132.02, 145.90, 163.86, 196.98.

α-Tosyloxybutanone (2o)[16]
Yield: 10% (NMR); yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.3 Hz, 3 H), 2.44 (s, 3 H), 2.51 (q, *J* = 7.3 Hz, 2 H), 4.49 (s, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.79 (dd, *J* = 8.4, 2.8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 9.34, 21.69, 29.46, 80.68, 128.46, 130.05, 145.54, 207.81.

γ-Tosyloxybutanone (2p)[16]
Yield: 29% (NMR); yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 7.0 Hz, 3 H), 2.19 (s, 3 H), 2.44 (s, 3 H), 4.74 (q, *J* = 7.0 Hz, 1 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.79 (dd, *J* = 8.4, 2.8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.66, 26.53, 80.34, 128.18, 132.02, 140.12, 145.90, 207.81.

α-Mesyloxyacetophenone (3a)
Yield: 45 mg (21%); red solid; mp 81–82 °C (Lit.[17] 80–82 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.30 (s, 3 H), 5.53 (s, 2 H), 7.53 (t, *J* = 7.8 Hz, 2 H), 7.66 (t, *J* = 7.4 Hz, 1 H), 7.90 (d, *J* = 7.8 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.23, 70.19, 127.80, 129.09, 133.50, 134.46, 191.12.

α-Mesyloxy-*p*-methylacetophenone (3b)
Yield: 205 mg (90%); white solid; mp 87–88 °C (Lit.[17] 87 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.43 (s, 3 H), 3.27 (s, 3 H), 5.48 (s, 2 H), 7.29 (d, *J* = 8.2 Hz, 2 H), 7.78 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.79, 39.22, 70.17, 127.89, 129.76, 131.00, 145.61, 190.68.

α-Mesyloxy-*p*-nitroacetophenone (3c)
Yield: 73 mg (28%); yellow solid; mp 122–123 °C (Lit.[17] 123 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 3.31 (s, 3 H), 5.53 (s, 2 H), 8.09–8.11 (m, 2 H), 8.37–8.40 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.22, 69.84, 124.28, 129.06, 151.05, 190.07.

α-Mesyloxyacetone (3d)
Yield: 46 mg (30%); black solid; mp 96–98 °C (Lit.[17] 98 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.22 (s, 3 H), 3.19 (s, 3 H), 4.79 (s, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 25.96, 38.80, 71.75, 200.44.

α-(Camphorsulfonyloxy)-*p*-nitroacetophenone (3e)
Yield: 265 mg (67%); yellow solid; mp 96–98 °C.

IR (neat): 746, 1173, 1710, 1746 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.86 (s, 3 H), 1.07 (s, 3 H), 1.40–1.45 (m, 1 H), 1.68–1.74 (m, 1 H), 1.91 (d, *J* = 18.6 Hz, 1 H), 1.99–2.05 (m, 1 H), 2.10–2.12 (m, 1 H), 2.32–2.41 (m, 2 H), 3.25 (d, *J* = 15.1 Hz, 1 H), 3.72 (d, *J* = 15.1 Hz, 1 H), 5.56 (d, *J* = 3.0 Hz, 2 H), 8.09 (d, *J* = 8.8 Hz, 2 H), 8.30 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.58, 25.01, 26.84, 42.45, 42.74, 48.19, 48.48, 58.05, 70.53, 124.11, 129.20, 138.18, 150.81, 190.12, 214.39.

MS (ESI): *m*/*z* (%) = 396 (100) $[M + 1]^+$.

HRMS–FAB: *m*/*z* $[M + 1]^+$ calcd for $C_{18}H_{22}NO_7S$: 396.1117; found: 396.1109.

α-(Camphorsulfonyloxy)acetone (3f)[18]
Yield: 104 mg (36%); yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (s, 3 H), 1.09 (s, 3 H), 1.43–1.48 (m, 1 H), 1.70–1.77 (m, 1 H), 1.95 (d, *J* = 18.5 Hz, 1 H), 2.03–

2.09 (m, 1 H), 2.12–2.14 (m, 1 H), 2.22 (s, 3 H), 2.35–2.45 (m, 2 H), 3.19 (d, J = 15.1 Hz, 1 H), 3.67 (d, J = 15.1 Hz, 1 H), 4.80 (d, J = 1.7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 19.66, 24.99, 26.24, 26.90, 42.50, 42.77, 48.12, 52.17, 57.99, 72.17, 200.74, 214.28.

MS (ESI): m/z (%) = 289.1 (100) $[M + 1]^+$.

HRMS–FAB: m/z $[M + 1]^+$ calcd for $C_{13}H_{21}O_5S$: 289.1110; found: 289.1105.

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