4-MeC_6H_4I-Mediated Efficient α-Tosyloxylation of Ketones with Oxone® and *p*-Toluenesulfonic Acid in Acetonitrile

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Abstract: Various alkyl aryl ketones, dialkyl ketones, and cycloheptanone were efficiently converted into the corresponding α-tosyloxy ketones in good yields by using Oxone® and *p*-toluenesulfonic acid monohydrate in the presence of *p*-iodotoluene in acetonitrile. 4-Methoxyacetophenone and 2-acetylthiophene bearing an electron-rich aromatic group could be also converted into the corresponding α-tosyloxyketones smoothly in good yields with the present method. Here, *p*-iodotoluene works as catalyst and *p*-[(hydroxy)(tosyloxy)]iodotoluene is formed in situ as a reactive species for the α-tosyloxylation of ketones. However, one equivalent of *p*-iodotoluene was required to obtain α-tosyloxyketones in good yields and was recovered in 80–20% yields, depending on the reaction conditions.

Key words: *p*-iodotoluene, Oxone®, α-tosyloxyketone, ketone, *p*-toluenesulfonic acid, catalyst

The use of hypervalent iodines in organic synthesis has been studied widely.[1] Especially, (diacetoxyiodo)benzene and [(hydroxy)(tosyloxy)iodo]benzene (Koser's reagent) are the most popular and useful trivalent iodine reagents for organic synthesis because they are good alternatives to toxic heavy-metal oxidants.[2] Among them, [(hydroxy)(tosyloxy)iodo]benzene is a highly efficient and sole reagent for the direct α-tosyloxylation of ketones.[3a,b] α-Tosyloxyketones are very important strategic precursors for the preparation of various heteroaromatics, such as thiazoles, imidazoles, oxazoles, selenazoles, pyrazoles, and benzofurans.[3] Therefore, we have been studying the synthetic uses of [(hydroxy)(tosyloxy)iodo]arenes, 1-(arenesulfonyloxy)benziodoxolones, and poly[4-(hydroxy)(tosyloxy)iodo]styrenes for the construction of thiazoles, imidazoles, imidazo[1.2-*a*]pyridines, and 2,1-benzothiazines.[4] On the other hand, the ArI-catalyzed oxidative conversion of substrates, such as ketones, hydroquinones, and alcohols, with *m*-chloroperbenzoic acid (MCPBA) or Oxone® has become very popular[5] because it is a metal-free oxidative reaction and thus conforms to environmentally benign organic synthesis. Recently, we also reported an efficient means to prepare various [(hydroxy)(sulfonyloxy)iodo]arenes directly from iodoarenes with MCPBA and sulfonic acids at room temperature;[6] the PhI-catalyzed, polymer-supported PhI-catalyzed, and ion-supported PhI-catalyzed α-tosyloxylation of ketones with MCPBA and *p*-toluenesulfonic acid monohydrate;[7a–c] and the PhI-catalyzed and ion-supported PhI-catalyzed preparation of 3,4-dihydro-1*H*-2,1-benzothiazine 2,2-dioxides from *N*-methoxy-2-arylethanesulfonamides with MCPBA.[7d,e] Among those reactions, the ArI-catalyzed oxidative conversion of substrates with Oxone® is very attractive[5g,j,l,m,5q–s] as Oxone® is an inorganic nonmetal oxidant and is much less expensive than MCPBA. Here, as part of our study on the catalytic use of organoiodines(I) in organic synthesis,[7] we would like to report the 4-MeC_6H_4I-mediated α-tosyloxylation of ketones with Oxone® and *p*-toluenesulfonic acid monohydrate in acetonitrile.

Table 1 shows the effect of the amount of PhI on the yield of α-tosyloxyacetophenone from the reaction of acetophenone with Oxone® and *p*-toluenesulfonic acid monohydrate in chloroform at 60 °C. The yield of α-tosyloxyacetophenone was extremely poor without PhI, while good yield was obtained by using 1.0 equivalent of PhI at 60 °C (entries 1–3). Moreover, the amounts of *p*-toluenesulfonic acid monohydrate and Oxone® are important. α-Tosyloxyacetophenone was obtained in good yield when 3 or 5 equivalents of *p*-toluenesulfonic acid monohydrate and 1.5 equivalents of Oxone® were used at 60 °C (entries 3–8, and 14).

Then, the effect of iodoarenes, such as PhI, 4-ClC_6H_4I, 3-$HO_2CC_6H_4I$, 4-$HO_2CC_6H_4I$, and 4-MeC_6H_4I, was studied at 60 °C as shown in entries 3 and 9–12, and PhI and 4-MeC_6H_4I showed the best reactivity among these iodoarenes to provide α-tosyloxyacetophenone in high yield. Finally, the effect of solvent was studied. Acetonitrile was a slightly better solvent than chloroform, while 1,2-dichloroethane and ethyl acetate were not good solvents (entries 12–18). Instead of *p*-toluenesulfonic acid monohydrate, the α-sulfonyloxylation of acetophenone with 5 and 3 equivalents of *p*-chlorobenzenesulfonic acid and DL-camphorsulfonic acid with Oxone® (1.5 equiv) in acetonitrile at 60 °C was carried out to form the corresponding α-sulfonyloxyacetophenones in good yields, respectively, as shown in Table 2.

Based on these results, various ketones, such as alkyl aryl ketones, dialkyl ketones, and cycloheptanone, were treated with Oxone® and *p*-toluenesulfonic acid monohydrate in the presence of 4-MeC_6H_4I in acetonitrile to provide the corresponding α-tosyloxyketones in good yields,[8] as shown in Table 3.[8]

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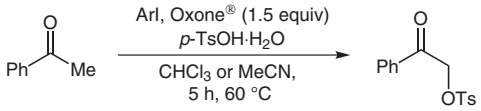
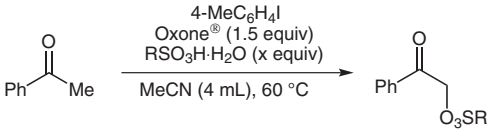
Table 1 ArI-Mediated α-Tosyloxylation of Acetophenone with Oxone® and PTSA·H_2O



Entry	ArI (equiv)	PTSA·H_2O (equiv)		Yield (%)
1	–	3.0	A	4 (70)[a]
2	PhI (0.5)	3.0	A	7 (82)[a]
3	PhI (1.0)	3.0	A	82 (7)[a]
4	PhI (1.0)[b]	0	A	0 (95)[a]
5	PhI (1.0)[b]	1.0	A	14 (78)[a]
6	PhI (1.0)[b]	2.0	A	14 (80)[a]
7	PhI (1.0)[b]	3.0	A	70 (11)[a]
8	PhI (1.0)[c]	3.0	A	76 (6)[a]
9	4-ClC_6H_4I (1.0)	3.0	A	17 (69)[a]
10	3-$HO_2CC_6H_4I$ (1.0)	3.0	A	57 (86)[a]
11	4-$HO_2CC_6H_4I$ (1.0)	3.0	A	4 (23)[b]
12	4-MeC_6H_4I (1.0)	3.0	A	81 (21)[a]
13	4-MeC_6H_4I (1.0)[d]	5.0	A	82 (4)[a]
14	PhI (1.0)[d]	5.0	A	50 (43)[a]
15	PhI (1.0)	5.0	B	84
16	4-MeC_6H_4I (1.0)	5.0	B	95 (1)[a]
17	PhI (1.0)	5.0	C	33 (55)[a]
18	PhI (1.0)	5.0	D	15 (62)[a]

[a] Yield of starting material.
[b] Oxone® (1.1 equiv) was used.
[c] Oxone® (1.3 equiv) was used.
[d] Reaction time was 3 h. A: $CHCl_3$ (4 mL), B: MeCN (4 mL), C: DCE (4 mL), D: $MeCO_2Et$ (4 mL).

Table 2 4-MeC_6H_4I-Mediated α-Sulfonyloxylation of Acetophenone with Oxone® and $RSO_3H·H_2O$



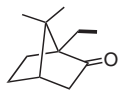
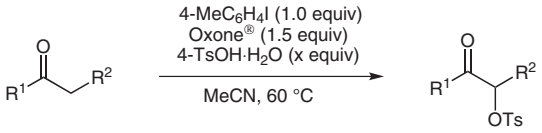
Entry	R	x	Time (h)	Yield (%)
1	4-MeC_6H_4	5	5	94
2		3	5	95
3	4-ClC_6H_4	5	2	72
4		3	22	82
5		5	3	70
6		3	7	76

Table 3 4-MeC_6H_4I-Mediated α-Tosyloxylation of Ketones with Oxone® and PTSA·H_2O



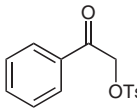
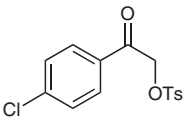
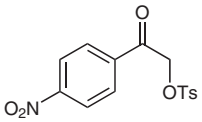
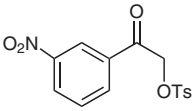
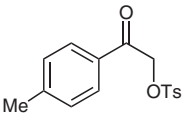
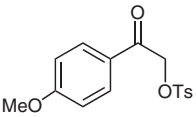
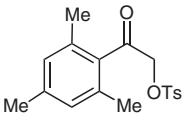
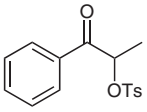
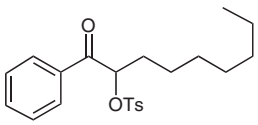
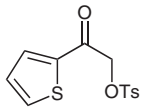
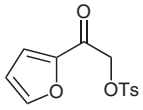
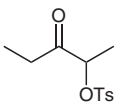
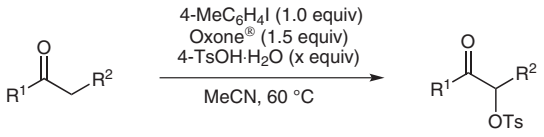
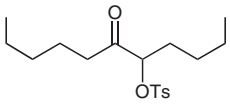
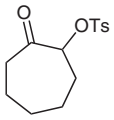
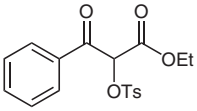
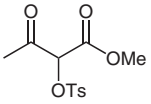
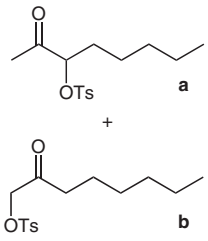
Entry	Product	x	Time (h)	Yield (%)
1		5	5	94
2		3	5	95
3		5	3	100
4		3	4	76
5		5	2	92
6		3	24	83
7		5	3	100
8		3	6	96
9		5	1	99
10		3	5	83
11		5	4	77
12		3	5	52 (26)[a]
13		5	5	71
14		3	48	65
15		5	3	90
16		3	24	84
17		5	4	80
18		3	27	92
19		5	4	100
20		3	24	92
21		5	3	41
22		3	3	45
23		5	4	75
24		3	2	68

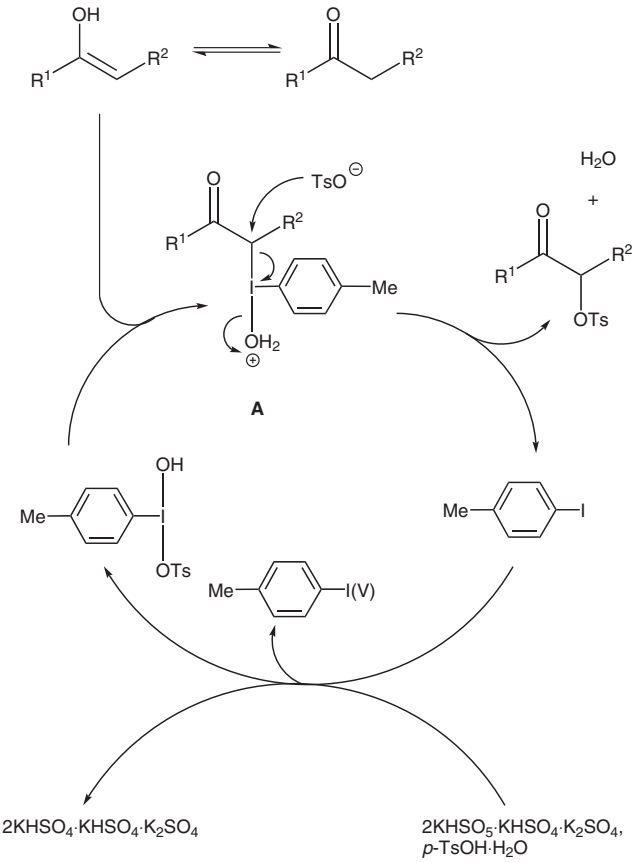
Table 3 4-MeC_6H_4I-Mediated α-Tosyloxylation of Ketones with Oxone® and PTSA·H_2O (continued)



Entry	Product	x	Time (h)	Yield (%)
25		5	0.5	89
26		3	2	43
27		5	2	77
28		3	1.5	56
29		5	1.5	92
30		3	1	71
31		5	1.5	73
32		3	1	70
33	 **a/b** = 32:20	3	1	52

[a] Yield of *p*-methoxyphenol.

Especially, 4-methoxyacetophenone and 2-acetylthiophene bearing an electron-rich aromatic group reacted with Oxone® and *p*-toluenesulfonic acid monohydrate in the presence of 4-MeC_6H_4I in acetonitrile to provide the corresponding α-tosyloxyketones in good yields (entries 11, 19, and 20), although the treatment of 4-methoxyacetophenone and 2-acetylthiophene with the PhI-catalyzed MCPBA and *p*-toluenesulfonic acid monohydrate system gave the corresponding α-tosyloxyketones in 27% and 47% yields, respectively.[7a,b] Thus, the present system is much more effective than the PhI-catalyzed MCPBA and *p*-toluenesulfonic acid monohydrate system to give the corresponding α-tosyloxyketones from ketones. Ethyl benzoylacetate and methyl acetoacetate gave the corresponding α-tosyloxy products in good yields, respectively (entries 29–32). In unsymmetrical methyl ketones, α-tosyloxylation at the alkyl group is favored over that at the methyl group (entry 33). 4-MeC_6H_4-mediated formation of α-tosyloxyketones from ketones is shown in Scheme 1. 4-MeC_6H_4I is oxidized by Oxone® in the presence of *p*-toluenesulfonic acid monohydrate to generate [(hydroxy)(tosyloxy)iodo]toluene in situ, which then reacts with the



Scheme 1 Reaction mechanism for 4-MeC_6H_4I-mediated α-tosyloxylation of ketones

enol form of ketone to provide α-tosyloxyketone via intermediate **A**, together with the regeneration of 4-MeC_6H_4I.

Practically, when the reaction of *p*-iodotoluene and *p*-toluenesulfonic acid monohydrate with Oxone® was carried out in acetonitrile at room temperature, [hydroxy](tosyloxy)iodo]toluene was obtained in 32% yield. However, 4-MeC_6H_4I(I) may be partly further oxidized to 4-MeC_6H_4I(V), which is not applicable to the α-tosyloxylation of ketones, at the present conditions. Generally, 4-MeC_6H_4I was recovered in 80–20% yields depending on the reaction conditions and substrates, and this is probably the reason why 4-MeC_6H_4I could not be recovered quantitatively.

In conclusion, various α-tosyloxyketones were prepared in good yields from the reaction of ketones with Oxone® and *p*-toluenesulfonic acid monohydrate in the presence of 4-MeC_6H_4I in acetonitrile. The α-sulfonyloxylation of acetophenone was also achieved with Oxone® and *p*-chlorobenzenesulfonic acid and DL-camphorsulfonic acid in the presence of 4-MeC_6H_4I. In view of the synthetic utility of α-tosyloxyketones for the preparation of various heterocyclic compounds, we believe that the present α-tosyloxylation method is very useful due to the simplicity of operation and isolation of the product, and the fact that [(hydroxy)(tosyloxy)]iodobenzene is not required. Furthermore, Oxone® is an inorganic nonmetal oxidant and is much less expensive than MCPBA.

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(8) **Typical Procedure for 4-MeC_6H_4I-Mediated α-Tosyloxylation of Ketone with Oxone® and *p*-Toluenesulfonic Acid Monohydrate**

To a solution of acetophenone (120 mg, 1 mmol) in MeCN (4 mL) were added *p*-iodotoluene (218 mg, 1.0 mmol), PTSA·H_2O (951 mg, 5 mmol), and Oxone® (249 mg, 1.5 mmol). The mixture was stirred for 5 h at 60 °C under an argon atmosphere. After the reaction, the reaction mixture was poured into sat. aq $NaHCO_3$ solution and extracted with $CHCl_3$ (3 × 20 mL). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, α-tosyloxyacetophenone was obtained as a crude state. Pure α-tosyloxyacetophenone was obtained in 94% yield by short flash column chromatography on silica gel (EtOAc–hexane = 1:4).

α-Tosyloxyacetophenone

Mp 90 °C (lit.[3h] 90–91 °C). IR (KBr): 1180, 1360, 1715 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 5.27 (s, 2 H), 7.35 (d, *J* = 8.5 Hz, 2 H), 7.47 (t, *J* = 8.2 Hz, 2 H), 7.61 (t, *J* = 8.2 Hz, 1 H), 7.84 (d, *J* = 8.2 Hz, 2 H), 7.85 (d, *J* = 8.2 Hz, 2 H).

α-Tosyloxy-*p*-methylacetophenone

Mp 105 °C (lit.[9] 82–83 °C). IR (KBr): 1170, 1350, 1700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.41 (s, 3 H), 2.45 (s, 3 H), 5.24 (s, 2 H), 7.26 (d, *J* = 8.1 Hz, 2 H), 7.35 (d, *J* = 8.2 Hz, 2 H), 7.74 (d, *J* = 8.1 Hz, 2 H), 7.86 (d, *J* = 8.2 Hz, 2 H).

α-Tosyloxy-*p*-chloroacetophenone

Mp 123 °C (lit.[9] 125 °C). IR (KBr): 1190, 1360, 1710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 5.21 (s, 2 H), 7.35 (d, *J* = 8.4 Hz, 2 H), 7.45 (d, *J* = 8.6 Hz, 2 H), 7.80 (d, *J* = 8.6 Hz, 2 H), 7.84 (d, *J* = 8.4 Hz, 2 H).

α-Tosyloxy-*p*-nitroacetophenone
Mp 137 °C (lit.[9] 130–131 °C). IR (KBr): 1180, 1340, 1710 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.47 (s, 3 H), 5.25 (s, 2 H), 7.37 (d, *J* = 8.3 Hz, 2 H), 7.83 (d, *J* = 8.3 Hz, 2 H), 8.03 (d, *J* = 8.9 Hz, 2 H), 8.32 (d, *J* = 8.9 Hz, 2 H).

α-Tosyloxypropiophenone
Mp 68 °C (lit.[9] 68–69 °C). IR (KBr): 1170, 1370, 1700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.60 (d, *J* = 7.0 Hz, 3 H), 2.41 (s, 3 H), 5.79 (q, *J* = 7.0 Hz, 1 H), 7.29 (d, *J* = 8.1 Hz, 2 H), 7.46 (t, *J* = 7.2 Hz, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 2 H).

α-(Tosyloxy)octyl Phenyl Ketone
Mp 59–61 °C (lit.[4d] 59–61 °C). IR (neat): 1180, 1340, 1700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 6.9 Hz, 3 H), 1.20–1.43 (m, 10 H), 1.84–1.91 (m, 2 H), 2.40 (s, 3 H), 5.59 (dd, *J* = 8.2, 4.8 Hz, 1 H), 7.24 (d, *J* = 8.0 Hz, 2 H), 7.45 (t, *J* = 7.5 Hz, 2 H), 7.59 (t, *J* = 7.5 Hz, 1 H), 7.74 (d, *J* = 8.2 Hz, 2 H), 7.86 (d, *J* = 8.2 Hz, 2 H).

α-Tosyloxy-3-pentanone
Mp 45–46 °C (lit.[3k] 43–44 °C). IR (neat): 1190, 1360, 1720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.03 (t, *J* = 7.3 Hz, 3 H), 1.35 (d, *J* = 7.0 Hz, 3 H), 2.47 (s, 3 H), 2.60 (m, 2 H), 4.80 (q, *J* = 7.0 Hz, 1 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.81 (d, *J* = 8.0 Hz, 2 H).

α-Tosyloxy-6-undecanone
Mp 72 °C (lit.[4d] 72 °C). IR (neat): 1190, 1380, 1720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.70–0.80 (m, 3 H), 0.86–1.75 (m, 15 H), 2.46 (s, 3 H), 2.51 (t, *J* = 7.5 Hz, 2 H), 4.64 (dd, *J* = 8.0, 4.6 Hz, 1 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 7.80 (d, *J* = 8.0 Hz, 2 H).

α-Tosyloxycycloheptanone
Oil. IR (neat): 1190, 1590, 1720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.48–1.95 (m, 8 H), 2.42–2.63 (m, 5 H), 4.98 (t, *J* = 5.1 Hz, 1 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.83 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 21.36, 22.30, 24.77, 27.45, 30.93, 39.98, 83.75, 127.61, 129.51, 133.00, 144.66, 206.05. HRMS–FAB: *m/z* calcd for $C_{14}H_{19}O_4S$ [M + 1]: 283.1004; found: 283.0986.

Methyl α-Tosyloxyacetoacetate
Oil. IR (neat): 1180, 1320, 1720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.30 (s, 3 H), 2.48 (s, 3 H), 3.71 (s, 3 H), 5.20 (s, 1 H), 7.38 (d, *J* = 8.5 Hz, 2 H), 7.83 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR(400 MHz, $CDCl_3$): δ = 21.66, 26.53, 53.27, 80.34, 128.18, 129.98, 132.02, 145.90, 163.86, 196.98. HRMS–FAB: *m/z* calcd for $C_{12}H_{15}O_6S$ [M + 1]: 287.0589; found: 287.0596.

Ethyl α-Tosyloxybenzoylacetate
Oil. IR (neat): 1440, 1590, 1690 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.0 Hz, 3 H), 2.85 (s, 3 H), 4.18 (m, 2 H), 5.59 (s, 1 H), 7.30 (d, *J* = 8.4 Hz, 2 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 2 H), 7.93 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13.75, 21.63, 62.80, 78.03, 128.24, 128.71, 129.34, 129.82, 132.34, 133.28, 134.36, 145.68, 164.12, 188.19. HRMS–FAB: *m/z* calcd for $C_{18}H_{19}O_6S$ [M + 1]: 363.0902; found: 363.0920.

1-Tosyloxy-2-octanone
Oil. IR (neat): 1180, 1360, 1590,1730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.87 (t, *J* = 7.0 Hz, 3 H), 1.20–1.32 (m, 6 H), 1.48–1.62 (m, 2 H), 2.45 (s, 3 H), 2.49 (t, *J* = 7.2 Hz, 2 H), 4.49 (s, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.82 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13.97, 21.68, 22.39, 22.76, 28.62, 31.43, 38.98, 71.78, 128.04, 130.00, 132.30, 145.44, 203.43. HRMS–FAB: *m/z* calcd for $C_{15}H_{23}O_4S$ [M + 1]: 299.1317; found: 299.1295.

3-Tosyloxy-2-octanone
Oil. IR (neat): 1180, 1360, 1600, 1740 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.3 Hz, 3 H), 1.00–1.30 (m, 6 H), 1.54–1.78 (m, 2 H), 2.23 (s, 3 H), 2.48 (s, 3 H), 4.58 (dd, *J* = 8.4, 4.6 Hz, 1 H), 7.36 (d, *J* = 8.7 Hz, 2 H), 7.81 (d, *J* = 8.7 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 13.91, 21.97, 22.35, 24.17, 26.01, 31.00, 31.52, 84.62, 128.13, 130.07. 132.98, 145.48, 205.78. HRMS–FAB: *m/z* calcd for $C_{15}H_{23}O_4S$ [M + 1]: 299.1317; found: 299.1315.

2-Thienyl (Tosyloxy)methyl Ketone
Mp 92–93 °C (lit.[3i] 94–96 °C). IR (KBr): 1685, 1370, 1180, 730 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 5.09 (s, 2 H), 7.16 (dd, *J* = 5.0, 3.9 Hz, 1 H), 7.35 (d, *J* = 8.1 Hz, 2 H), 7.73 (dd, *J* = 5.0, 1.0 Hz, 1 H), 7.79 (dd, *J* = 3.9, 1.0 Hz, 1 H), 7.85 (d, *J* = 8.1 Hz, 2 H).

α-Tosyloxy-*p*-methoxyacetophenone
Mp 131–132 °C. IR (KBr): 1684, 1376, 1171 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 3.88 (s, 3 H), 5.20 (s, 2 H), 6.93 (d, *J* = 8.5 Hz, 2 H), 7.34 (d, *J* = 8.8 Hz, 2 H), 7.83 (d, *J* = 8.8 Hz, 2 H), 7.85 (d, *J* = 8.5 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 30.89, 55.55, 69.77, 114.11, 125.88, 128.15, 129.87, 130.43, 133.52, 144.70, 163.52, 189.17. ESI-HRMS: *m/z* calcd for $C_{16}H_{16}O_5SNa$ [M + Na]: 343.0611; found: 343.0602.

α-Tosyloxy-*m*-nitroacetophenone
Mp 129–130 °C. IR (KBr): 1615, 1375, 1348, 1188 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 5.25 (s, 2 H), 7.37 (d, *J* = 8.0 Hz, 2 H), 7.72 (t, *J* = 8.0 Hz, 1 H), 7.84 (d, *J* = 8.0 Hz, 2 H), 8.21 (dt, *J* = 8.0, 1.2 Hz, 1 H), 8.46 (dt, *J* = 8.0, 1.2 Hz, 1 H), 8.63 (t, *J* = 1.2 Hz, 1 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 30.38, 69.87, 123.05, 128.15, 128.25, 130.03, 130.25, 132.35, 133.72, 135.29, 144.70, 145.88, 188.82. ESI-HRMS: *m/z* calcd for $C_{15}H_{13}O_6NSNa$ [M + Na]: 358.0356; found: 358.0347.

2,4,6-Trimethylphenyl (Tosyloxy)methyl Ketone
Mp 58 °C. IR (neat): 1191, 1377, 1608 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.12 (s, 6 H), 2.27 (s, 3 H), 2.45 (s, 3 H), 4.84 (s, 2 H), 6.81 (s, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.87 (d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$): δ = 18.96, 21.08, 21.65, 72.28, 128.05, 128.61. 129.81, 132.70, 133.83, 134.70, 139.82, 145.19, 201.17. Elemental Analysis: Calcd for $C_{18}H_{20}O_4S$. C 65.04, H 6.06%. Found: C 64.70, H 5.90%.

2-Furyl (Tosyloxy)methyl Ketone
Mp 63–64 °C (lit.[3h] 65–67 °C). IR (KBr): 1695, 1370, 1170, 810, 750 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 5.09 (s, 2 H), 6.58 (dd, *J* = 3.7, 1.7 Hz, 1 H), 7.33 (dd, *J* = 3.7, 0.7 Hz, 1 H), 7.36 (d, *J* = 8.2 Hz, 2 H), 7.61 (dd, *J* = 1.7, 0.7 Hz, 1 H), 7.86 (d, *J* = 8.2 Hz, 2 H).

α-(*p*-Chlorobenzenesulfonyloxy)acetophenone
Mp 96 °C (lit.[10] 97 °C). IR (KBr): 1180, 1540, 1700 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.36 (s, 2 H), 7.48 (t, *J* = 7.5 Hz, 2 H), 7.56 (d, *J* = 8.9 Hz, 2 H), 7.63 (t, *J* = 8.9 Hz, 1 H), 7.84 (d, *J* = 7.5 Hz, 2 H), 7.92 (d, *J* = 8.9 Hz, 2 H).

α-(Camphorsulfonyloxy)acetophenone
Oil (lit.[11] 60–61 °C). IR (neat): 1170, 1590, 1720 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.92 (s, 3 H), 1.14 (s, 3 H), 1.42–1.51 (m, 1 H), 1.74–1.85 (m, 1 H), 1.95 (d, *J* = 18.6 Hz, 1 H), 2.04–2.16 (m, 2 H), 2.36–2.55 (m, 2 H), 3.35 (d, *J* = 15.3 Hz, 1 H), 3.82 (d, *J* = 15.3 Hz, 1 H), 5.53 (s, 2 H), 7.52 (t, *J* = 7.2 Hz, 2 H), 7.64 (t, *J* = 7.2 Hz, 1 H), 7.92 (d, *J* = 7.2 Hz, 2 H).

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