Iodine-Mediated α-Sulfonyloxylation of Alkyl Aryl Ketones with Oxone® and Sulfonic Acids

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Abstract: Alkyl aryl ketones are converted into the corresponding α-sulfonyloxyketones, in moderate to excellent yields, via a novel procedure that utilizes Oxone®, *p*-toluenesulfonic acid or methanesulfonic acid and molecular iodine in a mixture of acetonitrile and 2,2,2-trifluoroethanol. The yield is found to be dependent on the nature of the ketone. A mechanism is proposed in which the key intermediates are an α-iodoketone and a subsequently formed α-iodosylketone. The latter reacts with the sulfonic acid to afford the α-sulfonyloxyketone product.

Key words: α-sulfonyloxyketones, Oxone®, molecular iodine, *p*-toluenesulfonic acid, methanesulfonic acid

α-Sulfonyloxyketones are very important precursors for the construction of various heteroaromatics, including thiazoles, imidazoles, imidazo[1,2-*a*]pyridines, oxazoles, selenazoles, pyrazoles, and benzofurans.[1] [(Hydroxy)(tosyloxy)iodo]benzene (HTIB) is the sole reagent for the direct α-sulfonyloxylation of ketones.[1a,b] We have previously studied the synthetic uses of [(hydroxy)(tosyloxy)iodo]arenes, 1-(arenesulfonyloxy)benziodoxolones, and poly[4-(hydroxy)(tosyloxy)iodo]styrenes (PS-HTIB) for the α-tosyloxylation of ketones and the construction of thiazoles, imidazoles, and imidazo[1,2-*a*]pyridines.[2] On the other hand, the oxidative conversion of substrates such as ketones, hydroquinones, alkenes, alcohols, and amides, with *m*-chloroperbenzoic acid (*m*CPBA) or Oxone® ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), catalyzed by aryl iodides, has become very popular[3] since the procedure employed represents a metal-free oxidative reaction, and trivalent iodides such as (diacetoxy)iodoarenes, are formed in situ. Using these methods, environmentally benign organic syntheses have been carried out smoothly. Previously, we reported an efficient procedure for the direct preparation of various [(hydroxy)(sulfonyloxy)iodo]arenes from iodoarenes with sulfonic acids and *m*CPBA.[4] Based on this method, the iodobenzene-catalyzed, polymer-supported iodobenzene-catalyzed, and ion-supported iodobenzene-catalyzed α-tosyloxylations of ketones with *m*CPBA and *p*-toluenesulfonic acid (PTSA),[5] the iodobenzene-catalyzed and ion-supported iodobenzene-catalyzed preparation of 3,4-dihydro-1*H*-2,1-benzothiazine 2,2-dioxides from *N*-methoxy-2-arylethanesulfonamides with *m*CPBA,[6] the iodobenzene-catalyzed preparation of oxazoles with *m*CPBA[7] or Oxone®,[8] the iodobenzene-catalyzed α-tosyloxylation of ketones with Oxone® and *p*-toluenesulfonic acid,[9] and the iodoarene-mediated α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid,[10] were successfully carried out. In all the above reactions, the key reagent was [(hydroxy)(tosyloxy)iodo]benzene, formed in situ, which enabled the α-tosyloxylation of the ketones.

In comparison with *m*CPBA, Oxone® is a very attractive reagent for the iodoarene-catalyzed oxidative conversion of substrates[3h,i,l,m,p–r] because it is an inorganic, non-transition metal oxidant, and is less expensive than *m*CPBA. In continuation of our research on the use of molecular iodine (I_2) for organic synthesis,[11] we herein report the molecular iodine mediated α-sulfonyloxylation of ketones with Oxone® and *p*-toluenesulfonic acid or methanesulfonic acid in a mixture of acetonitrile and 2,2,2-trifluoroethanol.

The results of the α-sulfonyloxylation of acetophenone with Oxone® and *p*-toluenesulfonic acid, methanesulfonic acid, or ethanesulfonic acid in a mixture of acetonitrile and 2,2,2-trifluoroethanol are shown in Table 1. Thus, acetonitrile or 2,2,2-trifluoroethanol by themselves were not good solvents for the present α-tosyloxylation (Table 1, entries 3 and 4). However, a mixture of acetonitrile and 2,2,2-trifluoroethanol (1:1) proved to be favorable solvent system, due to the moderate acidity and the solubility of the substrate and Oxone® (Table 1, entry 2). No reaction occurred in the absence of Oxone®, even after a long reaction time at 60 °C, whilst the use of two equivalents of Oxone® were required to give the α-tosyloxyacetophenone in good yield (Table 1, entry 2). On the other hand, when the α-tosyloxylation of acetophenone with *p*-toluenesulfonic acid, in the absence and presence of molecular iodine (0.1 equiv, 0.7 equiv, and 1.0 equiv) in a mixture of acetonitrile and 2,2,2-trifluoroethanol, was carried out at 60 °C, α-tosyloxyacetophenone was not obtained when molecular iodine was not present (Table 1, entry 6); the best yield (79%) was obtained in the presence of 0.7 equivalents of molecular iodine (Table 1, entries 2, 7 and 8). The potassium iodide (KI) mediated α-tosyloxylation of acetophenone did not proceed as efficiently (Table 1, entry 9), whilst the potassium bromide (KBr) mediated α-tosyloxylation of acetophenone provided α-bromoacetophenone in 78% yield, instead of the desired α-tosyloxyacetophenone (Table 1, entry 10). Moreover, when methanesulfonic acid and ethanesulfonic acid were used under the same conditions, α-methanesulfonyloxyacetophenone and α-ethanesulfonyloxyacetophenone

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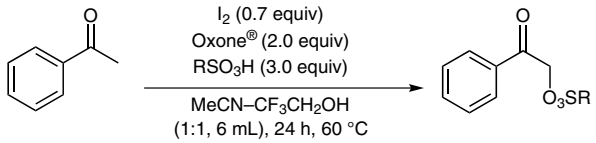
were obtained in fair to good yields (Table 1, entries 11 and 12).

Table 1 α-Sulfonyloxylation of Acetophenone with Iodine, Oxone® and Sulfonic Acids

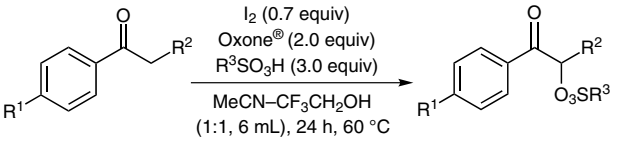


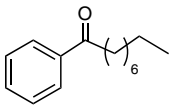
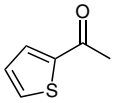
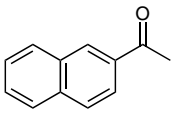
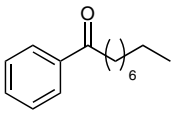
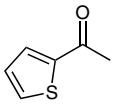
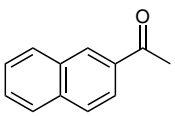
Entry	R	Yield (%)
1[a]	*p*-MeC_6H_4	41
2	*p*-MeC_6H_4	79
3[b]	*p*-MeC_6H_4	18
4[c]	*p*-MeC_6H_4	48
5[d]	*p*-MeC_6H_4	64
6[e]	*p*-MeC_6H_4	0 (37)[j]
7[f]	*p*-MeC_6H_4	45
8[g]	*p*-MeC_6H_4	51
9[h]	*p*-MeC_6H_4	57
10[i]	*p*-MeC_6H_4	0 (78)[k]
11	Me	78
12	Et	62

[a] Oxone® (1.1 equiv) was used.
[b] CF_3CH_2OH (6 mL) was used as the solvent.
[c] MeCN (6 mL) was used as the solvent.
[d] *p*-TsOH (1.0 equiv) was used.
[e] I_2 was not used.
[f] I_2 (0.1 equiv) was used.
[g] I_2 (1.0 equiv) was used.
[h] KI (0.7 equiv) was used instead of I_2.
[i] KBr (0.7 equiv) was used instead of I_2.
[j] Yield of recovered acetophenone.
[k] Yield of α-bromoacetophenone.

Having optimized the reaction conditions, the molecular iodine mediated α-tosyloxylation of various acetophenone derivatives, including *p*-chloro-, *p*-bromo-, *p*-nitro-, *p*-methyl-, and *p*-phenylacetophenone with *p*-toluenesulfonic acid and Oxone®, was carried out to give the corresponding α-tosyloxyketones in moderate to excellent yields, as shown in Table 2 (entries 1–5). The same treatment of propiophenone, *p*-chloropropiophenone, and *p*-methylpropiophenone also provided the corresponding α-tosyloxypropiophenones in good to moderate yields (Table 2, entries 6–8). The reactions of nonanophenone, 2-acetylthiophene, and 2-acetylnaphthalene, with *p*-toluenesulfonic acid and Oxone® in the presence of molecular iodine in acetonitrile–2,2,2-trifluoroethanol at 60 °C, furnished the corresponding α-tosyloxyketones in moderate yields (Table 2, entries 9–11), despite the fact that the starting ketones were almost completely consumed. Next,

Table 2 α-Sulfonyloxylation of Ketones with Iodine, Oxone® and-Sulfonic Acids

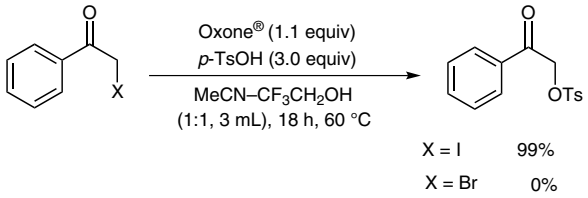


Entry	R^1	R^2	R^3	Time (h)	Yield (%)
1	Cl	H	*p*-MeC_6H_4	24	88
2	Br	H	*p*-MeC_6H_4	24	51
3	NO_2	H	*p*-MeC_6H_4	24	97
4	Me	H	*p*-MeC_6H_4	10	42
5	Ph	H	*p*-MeC_6H_4	19	63
6	H	Me	*p*-MeC_6H_4	24	67
7	Cl	Me	*p*-MeC_6H_4	24	90
8	Me	Me	*p*-MeC_6H_4	24	58
9			*p*-MeC_6H_4	24	44
10			*p*-MeC_6H_4	24	52
11			*p*-MeC_6H_4	6	54
12	Cl	H	Me	24	98
13	Br	H	Me	24	51
14	NO_2	H	Me	24	58
15	Me	H	Me	24	48
16	Ph	H	Me	24	47
17[a]	H	Me	Me	24	66
18	Cl	Me	Me	24	90
19	Me	Me	Me	24	79
20[a]			Me	10	47
21			Me	24	36
22[a]			Me	8	46

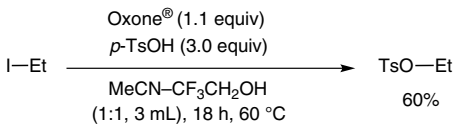
[a] I_2 (1.0 equiv) and $MeSO_3H$ (5.0 equiv) were used in a mixture of MeCN–CF_3CH_2OH (1:2, 6 mL).

the molecular iodine mediated α-methanesulfonyloxylation of various acetophenone and propiophenone derivatives with methanesulfonic acid and Oxone®, under the optimized conditions, provided the corresponding α-methanesulfonyloxyketones in moderate to excellent yields (Table 2, entries 12–19). The reactions of nonaphenone, 2-acetylthiophene, and 2-acetylnaphthalene with methanesulfonic acid and Oxone® in the presence of molecular iodine in acetonitrile–2,2,2-trifluoroethanol under the same conditions provided the corresponding α-methanesulfonyloxyketones in moderate yields (Table 2, entries 20–22). Overall, the yields of the α-sulfonyloxyketones with *p*-toluenesulfonic acid were slightly higher than those with methanesulfonic acid. As *p*-toluenesulfonic acid is a stronger acid than methanesulfonic acid, it probably promoted enolization of the ketone substrates more efficiently.

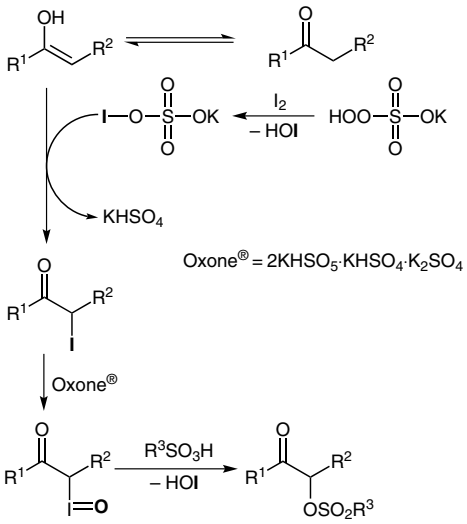
To uncover the present reaction mechanism, α-iodoacetophenone was treated with Oxone® and *p*-toluenesulfonic acid in a mixture of acetonitrile and 2,2,2-trifluoroethanol, using similar conditions to those applied previously, to generate α-tosyloxyacetophenone in 99% yield (Equation 1). In this reaction, α-tosyloxyacetophenone was not formed in the absence of Oxone®. On the other hand, similar treatment of α-bromoacetophenone did not afford α-tosyloxyacetophenone, and instead α-bromoacetophenone was recovered, quantitatively. It is well known that Oxone® is a powerful oxidant; iodoarenes and perfluoroiodoalkanes (monovalent iodine)[12] are oxidized into trivalent iodine species by Oxone®. Therefore, we believe the present α-sulfonyloxylation reaction proceeds through the α-iodination of the enol form of the ketone with a hypoiodite–sulfate species (i.e., $IOSO_3^-$), formed from the reaction of molecular iodine with Oxone®. Once the α-iodoketone is formed, it is smoothly oxidized into an α-iodosylketone, a very reactive intermediate, which reacts rapidly with the sulfonic acid to produce the corresponding α-sulfonyloxyketone (Scheme 1). When iodoethane was treated with Oxone® in the presence of *p*-toluenesulfonic acid in a mixture of acetonitrile and 2,2,2-trifluoroethanol, ethyl *p*-toluenesulfonate was obtained in 60% yield, as shown in Equation 2, whereas ethyl *p*-toluenesulfonate was not formed from the reaction of iodoethane and *p*-toluenesulfonic acid in the absence of Oxone®.



Equation 1



Equation 2



Scheme 1 A plausible reaction mechanism

In conclusion, α-sulfonyloxyketones have been prepared in moderate to excellent yields via the reactions of alkyl aryl ketones with Oxone® and *p*-toluenesulfonic acid or methanesulfonic acid in the presence of molecular iodine in a mixture of acetonitrile and 2,2,2-trifluoroethanol. The present procedure for the α-sulfonyloxylation of ketones does not require [(hydroxy)(tosyloxy)iodo]benzene, or related reagents, and the reaction mechanism is not the same as that when [(hydroxy)(tosyloxy)iodo]benzene is involved. We believe that the described method for the α-sulfonyloxylation is very attractive and opens new possibilities in the reactions of alkyl iodides with Oxone®, and further synthetic studies on these reactions are underway in our laboratory.

Melting points were determined with a Yamato MP-21 melting point apparatus. IR spectra were measured with a JASCO FT/IR-4100 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with JEOL JNM-ECS400 and JEOL JNM-ECA500 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from TMS. Mass spectra were recorded on JMS T100GCV and Thermo LTQ Orbitrap XL spectrometers. Merck silica gel $60F_{254}$ was used for TLC, and column chromatography was carried out with silica gel 60 from Kanto Kagaku Co.

α-Tosyloxylation; Typical Procedure

To a soln of acetophenone (120 mg, 1 mmol) in MeCN–CF_3CH_2OH (1:1, 6 mL) were added I_2 (178 mg, 0.7 mmol), *p*-TsOH·H_2O (571 mg, 3.0 mmol), and Oxone® (2.73 g, 2.0 mmol). The mixture was stirred for 24 h at 60 °C under an Ar atm. After the reaction was complete, the mixture was added to sat. aq $NaHCO_3$ soln (10 mL) and brine (10 mL), and extracted with $CHCl_3$ (3 × 20 mL). The combined organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by short flash column chromatography on silica gel (EtOAc–hexane, 1:2) to give α-tosyloxyacetophenone in 79% yield.

α-Methanesulfonyloxylation; Typical Procedure

To a soln of acetophenone (120 mg, 1 mmol) in MeCN–CF_3CH_2OH (1:1, 6 mL) were added I_2 (178 mg, 0.7 mmol), MsOH (288 mg, 3.0 mmol), and Oxone® (2.73 g, 2.0 mmol). The mixture was stirred for 24 h at 60 °C under an Ar atm. After the reaction was complete, the mixture was added to sat. aq $NaHCO_3$ soln (10 mL) and brine (10 mL), and extracted with $CHCl_3$ (3 × 20 mL). The combined organic

layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, the residue was purified by short flash column chromatography on silica gel (EtOAc–hexane, 1:2) to give α-methanesulfonyloxyacetophenone in 78% yield.

α-Tosyloxyacetophenone
Yield: 229.2 mg (79%); white solid; mp 90 °C (Lit.[1h] 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.78, 70.01, 128.09, 128.24, 129.01, 130.00, 132.72, 133.86, 134.29, 145.39, 190.39.

α-Methanesulfonyloxyacetophenone
Yield: 166.7 mg (78%); white solid; mp 78 °C (Lit.[13] 77–78 °C).

IR (neat): 1174, 1348, 1708 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.29 (s, 3 H), 5.52 (s, 2 H), 7.52 (t, *J* = 7.9 Hz, 2 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.89 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.26, 70.21, 127.77, 129.09, 133.41, 134.49, 191.10.

α-Ethanesulfonyloxyacetophenone
Yield: 141.4 mg (62%); white solid; mp 64–65 °C.

IR (neat): 1163, 1343, 1702 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.55 (t, *J* = 7.4 Hz, 3 H), 3.39 (q, *J* = 7.5 Hz, 2 H), 5.49 (s, 2 H), 7.51 (t, *J* = 7.9 Hz, 2 H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.89 (d, *J* = 7.1 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 8.13, 46.54, 69.67, 127.75, 129.01, 133.50, 134.36, 191.05.

HRMS–FAB: *m*/*z* $[M]^+$ calcd for $C_{10}H_{12}O_4S$: 228.0456; found: 228.0451.

α-Tosyloxy-*p*-chloroacetophenone
Yield: 285.0 mg (88%); white solid; mp 123 °C (Lit.[14] 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.67, 69.81, 128.11, 129.25, 129.47, 129.92, 132.06, 132.46, 140.75, 145.41, 189.46.

α-Tosyloxy-*p*-bromoacetophenone
Yield: 187.6 mg (51%); white solid; mp 129–131 °C (Lit.[15] 131–132 °C).

IR (neat): 1175, 1360, 1701 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 5.20 (s, 2 H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.9 Hz, 2 H), 7.71 (d, *J* = 8.9 Hz, 2 H), 7.84 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.70, 69.77, 128.13, 129.52, 129.93, 132.26, 132.46, 145.43, 189.68.

α-Tosyloxy-*p*-nitroacetophenone
Yield: 324.8 mg (97%); yellow solid; mp 137 °C (Lit.[14] 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.83, 70.04, 117.70, 124.17, 128.26, 129.45, 130.15, 132.32, 138.29, 145.81, 189.87.

α-Tosyloxy-*p*-methylacetophenone
Yield: 127.8 mg (42%); white solid; mp 105 °C (Lit.[14] 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.68, 21.77, 69.85, 128.07, 128.14, 129.57, 129.87, 131.24, 132.62, 135.23, 135.28, 189.80.

α-Tosyloxy-*p*-phenylacetophenone
Yield: 230.6 mg (63%); pale yellow solid; mp 139 °C (Lit.[16] 137–138 °C).

IR (neat): 1171, 1372, 1702 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.45 (s, 3 H), 5.29 (s, 2 H), 7.35 (d, *J* = 8.0 Hz, 2 H), 7.42 (t, *J* = 7.3 Hz, 1 H), 7.48 (t, *J* = 7.3 Hz, 2 H), 7.61 (d, *J* = 6.9 Hz, 2 H), 7.69 (d, *J* = 8.6 Hz, 2 H), 7.87 (d, *J* = 8.4 Hz, 2 H), 7.92 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.69, 69.96, 127.26, 127.48, 128.15, 128.54, 128.62, 129.02, 129.90, 132.40, 132.62, 139.43, 145.29, 146.89, 189.91.

α-Tosyloxypropiophenone
Yield: 203.9 mg (67%); white solid; mp 68 °C (Lit.[14] 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.84, 21.74, 128.04, 128.84, 129.85, 133.51, 133.77, 133.93, 143.48, 143.69, 145.10, 194.93.

α-Tosyloxy-*p*-chloropropiophenone
Yield: 304.0 mg (90%); white solid; mp 89 °C (Lit.[17] 94–96 °C).

IR (neat): 1176, 1359, 1695 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 6.9 Hz, 3 H), 2.42 (s, 3 H), 5.68 (q, *J* = 6.9 Hz, 1 H), 7.28 (d, *J* = 8.1 Hz, 2 H), 7.42 (d, *J* = 8.6 Hz, 2 H), 7.74 (d, *J* = 8.4 Hz, 2 H), 7.84 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.54, 21.62, 77.44, 127.90, 129.07, 129.79, 130.20, 131.93, 133.27, 140.37, 145.17, 193.83.

α-Tosyloxy-*p*-methylpropiophenone
Yield: 185.4 mg (58%); white solid; mp 83–84 °C (Lit.[18] 88–89 °C).

IR (neat): 1176, 1363, 1693 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.58 (d, *J* = 6.9 Hz, 3 H), 2.40 (s, 3 H), 2.41 (s, 3 H), 5.77 (q, *J* = 7.0 Hz, 1 H), 7.26 (t, *J* = 8.2 Hz, 4 H), 7.76 (d, *J* = 7.3 Hz, 2 H), 7.78 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.81, 21.62, 21.72, 77.33, 127.93, 128.85, 129.43, 129.72, 131.11, 133.50, 144.89, 144.93, 194.27.

α-(Tosyloxy)octyl Phenyl Ketone
Yield: 176.2 mg (44%); white solid; mp 59–61 °C (Lit.[2d] 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).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.00, 21.58, 22.53, 24.96, 28.75, 28.86, 31.58, 32.67, 81.39, 128.01, 128.61, 128.68, 129.65, 133.20, 133.71, 134.04, 144.91, 195.02.

α-Thienyl (Tosyloxy)methyl Ketone
Yield: 154.2 mg (52%); light brown solid; mp 92–93 °C (Lit.[1i] 94–96 °C).

IR (KBr): 730, 1180, 1370, 1685 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).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.66, 69.87, 128.17, 128.46, 129.94, 132.38, 133.13, 135.12, 140.12, 145.43, 183.64.

α-Naphthalen-2-yl (Tosyloxy)ethanone
Yield: 182.3 mg (54%); white solid; mp 118–120 °C (Lit.[16] 118–119 °C).

IR (neat): 1176, 1367, 1699 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 5.39 (s, 2 H), 7.33 (d, *J* = 8.0 Hz, 2 H), 7.57 (t, *J* = 6.9 Hz, 1 H), 7.63 (t, *J* = 6.9 Hz, 1 H), 7.87 (d, *J* = 8.3 Hz, 2 H), 7.87–7.90 (m, 3 H), 7.94 (d, *J* = 7.8 Hz, 1 H), 8.34 (s, 1 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.67, 70.00, 123.26, 127.16, 127.86, 128.16, 128.89, 129.13, 129.61, 129.90, 129.99, 131.09, 132.27, 132.68, 135.95, 145.28, 190.27.

α-Methanesulfonyloxy-*p*-chloroacetophenone
Yield: 243.9 mg (98%); white solid; mp 109–110 °C (Lit.[14] 125 °C).

IR (neat): 1170, 1344, 1698 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.29 (s, 3 H), 5.47 (s, 2 H), 7.50 (d, *J* = 8.7 Hz, 2 H), 7.84 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.23, 69.88, 129.20, 129.49, 131.75, 141.12, 190.04.

α-Methanesulfonyloxy-*p*-bromoacetophenone
Yield: 147.5 mg (51%); white solid; mp 119–120 °C (Lit.[19] 106 °C).

IR (neat): 1171, 1344, 1699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.28 (s, 3 H), 5.46 (s, 2 H), 7.67 (d, *J* = 8.9 Hz, 2 H), 7.76 (d, *J* = 8.7 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.24, 69.84, 129.24, 129.87, 132.15, 132.48, 190.26.

α-Methanesulfonyloxy-*p*-nitroacetophenone
Yield: 150.5 mg (58%); yellow solid; mp 123–124 °C (Lit.[13] 123 °C).

IR (neat): 1173, 1356, 1708 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.30 (s, 3 H), 5.51 (s, 2 H), 8.08 (d, *J* = 9.2 Hz, 2 H), 8.38 (d, *J* = 9.2 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.23, 69.85, 124.28, 129.05, 137.83, 151.02, 190.05.

α-Methanesulfonyloxy-*p*-methylacetophenone
Yield: 110.1 mg (48%); white solid; mp 88–89 °C (Lit.[13] 87 °C).

IR (neat): 1175, 1346, 1707 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 3.28 (s, 3 H), 5.49 (s, 2 H), 7.31 (t, *J* = 7.9 Hz, 2 H), 7.79 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.78, 39.21, 70.17, 127.86, 129.73, 130.94, 145.61, 190.68.

α-Methanesulfonyloxy-*p*-phenylacetophenone
Yield: 136.0 mg (47%); pale yellow solid; mp 141–142 °C (Lit.[20] 141–142 °C).

IR (neat): 1167, 1359, 1699 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.30 (s, 3 H), 5.54 (s, 2 H), 7.49 (t, *J* = 6.9 Hz, 1 H), 7.43 (t, *J* = 7.3 Hz, 2 H), 7.63 (d, *J* = 7.4 Hz, 2 H), 7.73 (d, *J* = 8.6 Hz, 2 H), 7.97 (d, *J* = 8.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.24, 70.20, 127.26, 127.64, 128.38, 128.61, 129.04, 132.05, 139.32, 147.17, 190.66.

α-Methanesulfonyloxypropiophenone
Yield: 150.5 mg (66%); white solid; mp 64 °C (Lit.[14] 68–69 °C).

IR (neat): 1178, 1362, 1702 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.67 (d, *J* = 7.1 Hz, 3 H), 3.14 (s, 3 H), 6.05 (q, *J* = 7.1 Hz, 1 H), 7.51 (t, *J* = 7.9 Hz, 2 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.94 (d, *J* = 7.3 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.69, 39.38, 77.11, 128.58, 128.97, 133.63, 134.14, 195.26.

α-Methanesulfonyloxy-*p*-chloropropiophenone
Yield: 236.3 mg (90%); white solid; mp 88–89 °C.

IR (neat): 1177, 1360, 1695 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.66 (d, *J* = 7.1 Hz, 3 H), 3.14 (s, 3 H), 5.97 (d, *J* = 7.0 Hz, 1 H), 7.49 (d, *J* = 8.7 Hz, 2 H), 7.89 (d, *J* = 8.9 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.54, 39.38, 76.78, 129.35, 130.02, 131.89, 140.74, 194.14.

HRMS–FAB: *m*/*z* $[M]^+$ calcd for $C_{10}H_{11}ClO_4S$: 262.0067; found: 262.0061.

α-Methanesulfonyloxy-*p*-methylpropiophenone
Yield: 190.5 mg (79%); white solid; mp 86–88 °C.

IR (neat): 1174, 1359, 1690 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 1.66 (d, *J* = 7.1 Hz, 3 H), 2.43 (s, 3 H), 3.13 (s, 3 H), 6.03 (q, *J* = 7.1 Hz, 1 H), 7.31 (d, *J* = 8.0 Hz, 2 H), 7.84 (d, *J* = 8.2 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.84, 21.73, 39.40, 77.13, 128.73, 129.68, 131.07, 145.30, 194.78.

HRMS–FAB: *m*/*z* $[M]^+$ calcd for $C_{11}H_{14}O_4S$: 242.0613; found: 242.0606.

α-(Methanesulfonyloxy)octyl Phenyl Ketone
Yield: 151.7 mg (47%); white solid; mp 53–54 °C.

IR (neat): 1176, 1357, 1701 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 (t, *J* = 7.0 Hz, 3 H), 1.25–1.38 (m, 8 H), 1.51 (quin, *J* = 7.4 Hz, 2 H), 1.84–1.96 (m, 2 H), 3.13 (s, 3 H), 5.92 (dd, *J* = 8.6, 4.0 Hz, 1 H), 7.51 (t, *J* = 7.7 Hz, 2 H), 7.64 (t, *J* = 7.5 Hz, 1 H), 7.92 (d, *J* = 7.2 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.02, 22.55, 25.04, 28.89, 31.62, 32.49, 39.30, 81.25, 128.48, 129.01, 134.11, 195.34.

HRMS–FAB: *m*/*z* $[M]^+$ calcd for $C_{16}H_{24}O_4S$: 312.1395; found: 312.1390.

α-Thienyl (Methanesulfonyloxy)methyl Ketone
Yield: 79.9 mg (36%); yellow solid; mp 83–84 °C.

IR (neat): 1176, 1365, 1674 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.27 (s, 3 H), 5.38 (s, 2 H), 7.20 (dd, *J* = 5.2, 4.0 Hz, 1 H), 7.76–7.79 (m, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 39.16, 69.68, 128.60, 132.59, 135.25, 139.46, 184.23.

HRMS–FAB: *m*/*z* $[M]^+$ calcd for $C_7H_8O_4S_2$: 219.9864; found: 219.9858.

α-Naphthalen-2-yl (Methanesulfonyloxy)ethanone
Yield: 113.8 mg (46%); white solid; mp 90–94 °C (Lit.[21] 105–106 °C).

IR (neat): 1169, 1357, 1711 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.32 (s, 3 H), 5.65 (s, 2 H), 7.60 (t, *J* = 7.1 Hz, 1 H), 7.66 (t, *J* = 7.0 Hz, 1 H), 7.90 (d, *J* = 8.2 Hz, 1 H), 7.95 (s, 2 H), 7.98 (d, *J* = 8.5 Hz, 1 H), 8.40 (s, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 39.23, 70.24, 122.95, 127.30, 127.91, 129.11, 129.26, 129.62, 129.76, 130.73, 132.28, 136.05, 191.01.

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