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PhI- and polymer-supported PhI-catalyzed oxidative conversion of ketones and alcohols to α-tosyloxyketones with *m*-chloroperbenzoic acid and *p*-toluenesulfonic acid

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Abstract—Various ketones were converted to the corresponding α-tosyloxyketones with *m*CPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount of iodobenzene. Moreover, secondary alcohols were directly converted to the corresponding α-tosyloxyketones using *m*CPBA and catalytic amounts of iodobenzene and potassium bromide, followed by treatment with *p*-toluenesulfonic acid in a one-pot manner. Poly(4-iodostyrene) could be also used as a recyclable catalyst for the same α-tosyloxylation of ketone

1. Introduction

Synthetic use of hypervalent iodines for organic synthesis has been studied widely.[1] Especially, (diacetoxyiodo)benzene, [bis(trifluoroacetoxy)iodo]benzene, iodosylbenzene, and [(hydroxy)(tosyloxy)iodo]benzene (Koser's reagent) are the most popular and useful trivalent iodine reagents for organic synthesis as alternatives to toxic heavy-metal reagents.[2] Among them, [(hydroxy)(tosyloxy)iodo]benzene is an efficient and sole reagent for the direct α-tosyloxylation of ketones.[3a,b] α-Tosyloxyketones are very important strategic precursors for the construction of various heteroaromatics such as thiazoles, imidazoles, oxazoles, selenazoles, pyrazoles, and benzofurans.[3] We have also studied the synthetic uses of [(hydroxy)(tosyloxy)iodo]arenes, 1-(arenesulfonyloxy)benziodoxolones, and poly[4-(hydroxy)(tosyloxy)iodo]styrene for the construction of thiazoles, imidazoles, imidazo[1.2-*a*]pyridines, and 2,1-benzothiazines.[4] Recently, PhI-catalyzed efficient α-acetoxylation of ketones with *m*-chloroperbenzoic acid (*m*CPBA) in AcOH in the presence of $BF_3 \cdot Et_2O$ and water was reported to provide the corresponding α-acetoxyketones in moderate isolated yields.[5] Moreover, hypervalent iodine(III)-catalyzed oxidative cyclization of β-(4-hydroxyaryl)propanoic acids with *m*CPBA was also reported to give the corresponding spirolactones.[6] Recently, we also reported an efficient preparation of various [(hydroxy)(sulfonyloxy)iodo]arenes directly from iodoarenes with *m*CPBA and sulfonic acids at room temperature.[7] Here, as a part of our study on catalytic use of organoiodines(I) for organic synthesis, we would like to report PhI-catalyzed and polymer-supported PhI-catalyzed α-tosyloxylation of ketones and alcohols with *m*CPBA and *p*-toluenesulfonic acid.[8] Recently, study on the synthetic use of organic catalysts has become important, due to their less toxicity than that of organometallic catalysts.

2. Results and discussion

2.1. PhI-catalyzed and poly(4-iodostyrene)-catalyzed α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid

Table 1 shows the effect of the amount of PhI to provide α-tosyloxyacetophenone from acetophenone with *m*CPBA and *p*-toluenesulfonic acid in acetonitrile at warming temperature, and it indicates α-tosyloxyacetophenone was obtained in good yields using PhI in the range of 0.1–1.0 equiv (entries 1–6). It was more effective to use acetonitrile than chloroform as a solvent and the best reaction temperature was 50 °C (entry 8). The present reaction does not proceed at all without PhI (entry 7). Among *p*-$CH_3C_6H_4I$, PhI, *p*-ClC_6H_4I, and *p*-$CH_3OC_6H_4I$, PhI is the most effective for the α-tosyloxylation of acetophenone (entries 8–11). Under the present conditions, the formation of Baeyer–Villiger oxidation products was not observed.

Keywords: Iodobenzene; Poly(4-iodostyrene); α-Tosyloxyketone; Ketone; *m*CPBA; *p*-Toluenesulfonic acid; Catalyst.
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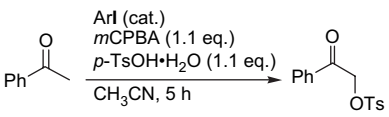
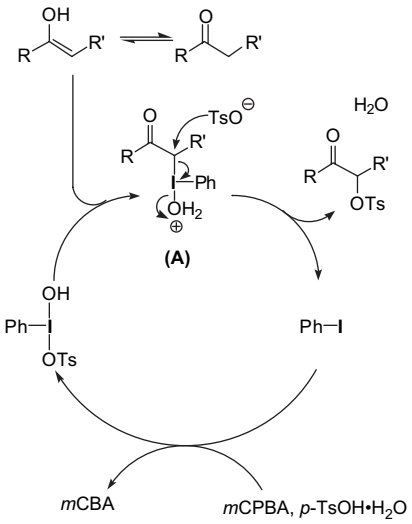
Table 1. ArI-catalyzed α-tosyloxylation of acetophenone with *m*CPBA and *p*-toluenesulfonic acid



Entry	ArI (equiv)	Temp (°C)	Yield[a] (%)
1	PhI (1.0)	80	89
2	PhI (0.5)	80	83
3	PhI (0.2)	80	80
4	PhI (0.1)	80	76
5	PhI (0.05)	80	66
6	PhI (0.01)	80	19
7	PhI (0)	80	0
8	PhI (0.1)	50	85
9	*p*-$CH_3C_6H_4I$ (0.1)	50	80
10	*p*-ClC_6H_4I (0.1)	50	52
11	*p*-$CH_3OC_6H_4I$ (0.1)	50	53

[a] Isolated yield.



Scheme 1. Reaction pathway for PhI-catalyzed α-tosyloxylation of ketones.

Instead of *p*-toluenesulfonic acid, *p*-chlorobenzenesulfonic acid, camphorsulfonic acid, and methanesulfonic acid could be also used under the same conditions to give the corresponding α-(*p*-chlorobenzenesulfonyloxy)-, α-(camphorsulfonyloxy)-, and α-(methanesulfonyloxy)-acetophenones in good yields, respectively, as shown in Table 2 (entries 2–4). Based on these results, various ketones: alkyl aryl ketones, dialkyl ketones, cyclic ketone were treated with *m*CPBA and *p*-toluenesulfonic acid in the presence of 0.1 equiv of PhI to provide the corresponding α-tosyloxyketones in good yields (entries 5–16). Aldehydes were also treated under the same conditions. However, the corresponding α-tosyloxyaldehydes were not obtained at all due to the instability of the products under the present reaction conditions. Though acetylacetone did not give the corresponding α-tosyloxyacetylacetone due to the instability of α-tosyloxyacetylacetone under the present reaction conditions, ethyl benzoylacetate and methyl acetoacetate gave the corresponding α-tosyloxy products in 68% and 70% yields, respectively (entries 13 and 14). In unsymmetrical methyl ketones, α-tosyloxylation at the alkyl group is favored over that of the methyl group (entries 15 and 16). A catalytic cycle for the α-tosyloxylation of ketones is shown in Scheme 1. Thus, PhI is oxidized by *m*CPBA in the presence of *p*-toluenesulfonic acid to generate [(hydroxy)(tosyloxy)iodo]benzene in situ, which then reacts with the enol form of ketone to provide α-tosyloxyketone via the intermediate [**A**], together with regeneration of PhI. Thus, PhI is repeatedly oxidized and reduced, i.e., PhI acts as a catalyst.

Then, polymer-supported PhI, instead of iodobenzene, was used under the same conditions to recover the polymer catalyst by simple filtration of the reaction mixture. Here, two kinds of polymer-supported PhI, i.e., standard linear poly(4-iodostyrene) and macroporous cross-linked poly(4-iodostyrene), were used. Consequently, excess amount of poly(4-iodostyrene) (1.3 equiv) was used to get moderate yield of the products, and the standard linear poly(4-iodostyrene) showed better reactivity than macroporous cross-linked poly(4-iodostyrene) as shown in Table 3 (entries 1–3). In the former case, poly(4-iodostyrene) used was recovered in ~90% yield and in the latter case, macroporous cross-linked poly(4-iodostyrene) was recovered quantitatively by the simple filtration of the reaction mixtures. Other ketones were also converted to the corresponding α-tosyloxyketones in moderate yields under the same conditions (entries 5–12). Recovered poly(4-iodostyrene) could be reused for the same reaction to provide the corresponding α-tosyloxyketone in good yields (entries 7–9).

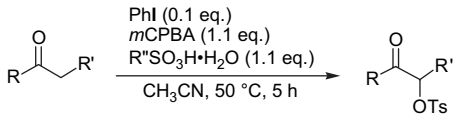
2.2. PhI-catalyzed and poly(4-iodostyrene)-catalyzed oxidative α-tosyloxylation of alcohols with *m*CPBA and *p*-toluenesulfonic acid

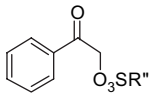
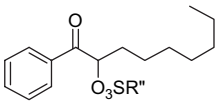
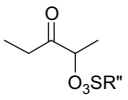
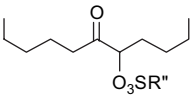
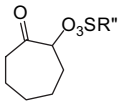
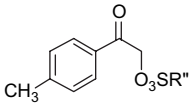
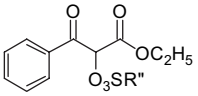
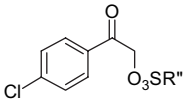
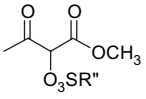
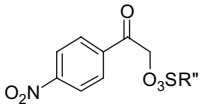
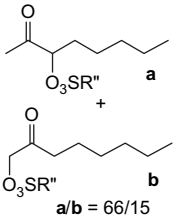
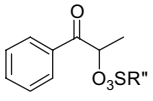
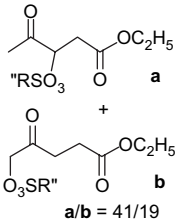
Then, to extend the present catalytic reaction, oxidative α-tosyloxylation of alcohols with *m*CPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount of iodobenzene was carried out. Oxidative α-tosyloxylation of alcohols with iodosylbenzene and *p*-toluenesulfonic acid has been previously reported to give the corresponding α-tosyloxyketones, and direct preparation of thiazoles, imidazoles, and imidazo[1,2-*a*]pyridines from alcohols has also succeeded.[4d] However, in this reaction, excess amount (3.0 equiv) of expensive iodosylbenzene was required for effective conversion. To establish optimal conditions for the reaction, 1-phenylethyl alcohol was treated as a substrate. Thus, 1-phenylethyl alcohol was treated with a catalytic amount of iodobenzene and a stoichiometric amount of *m*CPBA and *p*-toluenesulfonic acid in acetonitrile under various conditions, i.e., changing the amounts of iodobenzene, *m*CPBA, and *p*-toluenesulfonic acid. However, α-tosyloxyacetophenone was not obtained in good yield without any additive.

To improve the yield, a catalytic amount of 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) was added to the reaction mixture. It is well known that reactive *N*-oxoammonium salt is generated in situ by the oxidation of TEMPO with an oxidant and it oxidizes primary and secondary alcohols to the corresponding carbonyl derivatives.[9]

Table 4 shows the effect of TEMPO. When 1-phenylethyl alcohol and 1-(*p*-chlorophenyl)ethyl alcohol were treated as

Table 2. PhI-catalyzed α-tosyloxylation of ketones with *m*CPBA and sulfonic acids

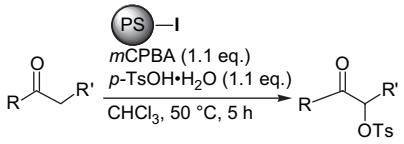


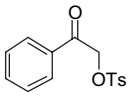
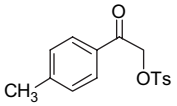
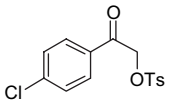
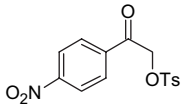
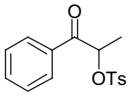
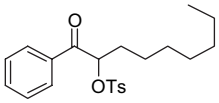
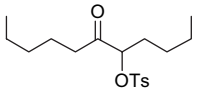
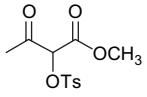
Entry	Product	R"–	Yield[a] (%)	Entry	Product	R"–	Yield[a] (%)
1		*p*-$CH_3C_6H_4$–	85	9		*p*-$CH_3C_6H_4$–	63
2		*p*-ClC_6H_4–	78	10		*p*-$CH_3C_6H_4$–	76
3			78	11		*p*-$CH_3C_6H_4$–	67
4		CH_3–	88	12		*p*-$CH_3C_6H_4$–	44
5		*p*-$CH_3C_6H_4$–	78	13		*p*-$CH_3C_6H_4$–	68
6		*p*-$CH_3C_6H_4$–	88	14		*p*-$CH_3C_6H_4$–	70
7		*p*-$CH_3C_6H_4$–	88	15	 **a/b** = 66/15	*p*-$CH_3C_6H_4$–	81
8		*p*-$CH_3C_6H_4$–	74	16	 **a/b** = 41/19	*p*-$CH_3C_6H_4$–	60

[a] Isolated yield.

a substrate, the reaction proceeded effectively to provide the corresponding α-tosyloxyketones in good yields. However, the results in other substrates were disappointing, especially, in 1-(*p*-nitrophenyl)ethyl alcohol and 1-(*p*-methylphenyl)-ethyl alcohol. As another oxidation way, it is reported that iodosylbenzene and (diacetoxy)iodobenzene oxidize alcohols to the corresponding ketones or carboxylic acids in high yields with a catalytic amount of KBr.[10] Thus, oxidative α-tosyloxylation of alcohols with a catalytic amount of PhI and KBr with *m*CPBA was carried out. Table 5 shows the

Table 3. Poly(4-iodostyrene)-catalyzed α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid

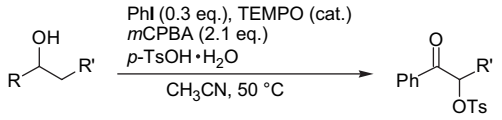


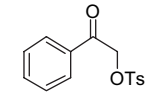
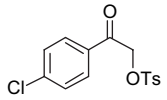
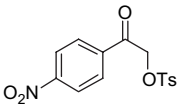
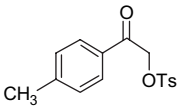
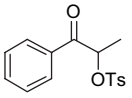
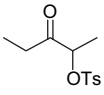
Entry	Product	PS—I	Yield[a] (%)
1		0.1	37
2		1.3	64
3		1.3[b]	36
4		1.3[c]	65
5		1.3	60
6		1.3[c]	65
7		1.3[c]	80
8		1.3[c,d]	77
9		1.3[c,e]	76
10		1.3[c]	75
11		1.3[c]	60
12		1.3[c]	64

[a] Isolated yield.
[b] Macroporous cross-linked poly(4-iodostyrene) was used.
[c] *p*-TsOH·H_2O (3.0 equiv) was used.
[d] Yield with the first recovered poly(4-iodostyrene).
[e] Yield with the second recovered poly(4-iodostyrene).

results using a KBr system. Totally, the yield of products was improved better than that with a TEMPO system. When all the substrate and reagents including *p*-toluenesulfonic acid were mixed initially, the yield of the product was slightly decreased (entries 2 and 3). Therefore, it is better to add *p*-toluenesulfonic acid to the reaction mixture, after the oxidation of alcohols to the ketones was completed. Thus, the best reaction conditions are as follows: a mixture of alcohol, PhI (0.3 equiv), KBr (0.1 equiv), and *m*CPBA (2.1 equiv) in acetonitrile was initially stirred for 0.5–1.5 h to oxidize alcohol to the corresponding ketones, then *p*-toluenesulfonic acid was added to the reaction mixture and the obtained mixture was warmed at 50 °C for 5 h. Moreover, the yields of α-tosyloxyketones were increased when an extra amount of *p*-toluenesulfonic acid was used (entries 7 and 8). The reactive species for the oxidation of alcohols to ketones in the present reactions may be PhI(Br)OH, formed in situ by

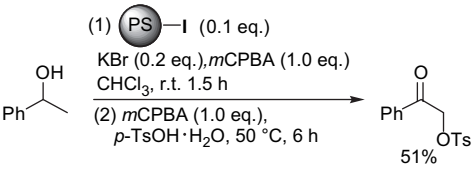
Table 4. PhI-catalyzed oxidative α-tosyloxylation of alcohols with *m*CPBA and *p*-toluenesulfonic acid in the presence of TEMPO



Entry	Product	*p*-TsOH·H_2O (equiv)	TEMPO (equiv)	Yield[a] (%)
1		1.05	—	14
2		1.05	0.5	29
3		1.05	0.1	57
4		1.05	0.05	64
5		1.3	0.05	77
6		1.5	0.05	40
7		1.3	0.05	71
8		1.5	0.05	79
9		1.5	0.05	25
10		1.3	0.05	32
11		1.3	0.05	51
12		1.3	0.05	46

[a] Isolated yield.

the reaction of [(hydroxy)(tosyloxy)iodo]benzene and KBr, as mentioned previously in the oxidation of alcohols with iodosylbenzene and KBr.[10b] Then, poly(4-iodostyrene)-catalyzed oxidative α-tosyloxylation of secondary alcohols with *m*CPBA and *p*-toluenesulfonic acid in the presence of TEMPO or KBr was carried out. However, the yield was less than 51% under the best conditions. A typical example is shown in Eq. 1.

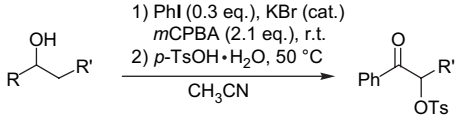


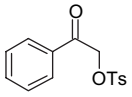
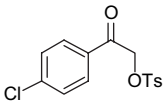
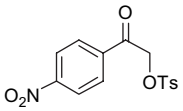
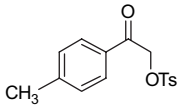
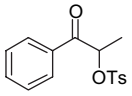
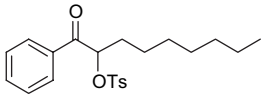
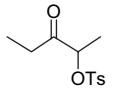
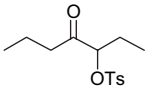
(1)

3. Conclusion

Various α-tosyloxyketones were prepared in good yields from the reaction of ketones with *m*CPBA and *p*-toluenesulfonic acid in the presence of a catalytic amount of iodobenzene. α-Sulfonyloxylation of ketones was also achieved with *m*CPBA and *p*-chlorobenzenesulfonic acid, camphorsulfonic acid, and methanesulfonic acid in the presence of

Table 5. PhI-catalyzed oxidative α-tosyloxylation of alcohols with *m*CPBA and *p*-toluenesulfonic acid in the presence of KBr



Entry	Product	*p*-TsOH·H_2O (equiv)	KBr (equiv)	Time		Yield[a] (%)
				(1)	(2)	
1		1.3	—	1 h	5 h	12
2		1.3	0.1	1 h	5 h	73
3		1.3[b]	0.1	1 h	5 h	61
4		1.5	0.1	1 h	5 h	67
5		1.5	0.1	1 h	5 h	60
6		1.3	0.2	30 min	5 h	63
7		3.0	0.2	40 min	5 h	63
8		5.0	0.2	40 min	5 h	51
9		1.3	0.2	1.5 h	5 h	63
10		1.3	0.2	1.5 h	5 h	53

[a] Isolated yield.
[b] A mixture of the substrate, PhI, *m*CPBA, KBr, and *p*-TsOH·H_2O in acetonitrile was stirred initially at room temperature, and then the reaction mixture was stirred at 50 °C.

a catalytic amount of iodobenzene. Poly(4-iodostyrene) could be also used as a recyclable catalyst instead of iodobenzene, and therefore after the reaction, it was recovered in high yields by simple filtration of the reaction mixture. PhI-catalyzed oxidative α-tosyloxylation of alcohols was carried out using a catalytic amount of KBr, and the corresponding α-tosyloxyketones were obtained in moderate yields. In view of the synthetic utility of α-tosyloxyketones for various heterocyclic compounds, we believe the present α-tosyloxylation method is very useful due to the simple operation, without using any hypervalent iodine reagents.

4. Experimental section

4.1. General

^1H and ^{13}C NMR spectra were obtained with JEOL-JNM-LA-400, JEOL-JNM-LA-400s, and JEOL-JNM-LA-500, spectrometers. Chemical shifts are expressed in ppm downfield from tetramethylsilane (TMS) in δ units. Mass spectra were recorded on JEOL-HX-110 and JEOL-JMS-ATII15 spectrometers. Melting points were determined on Yamato melting point apparatus Model MP-21. Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wakogel B-5F was used for preparative TLC.

4.2. Typical procedure for PhI-catalyzed α-tosyloxylation of ketone with *m*CPBA and *p*-toluenesulfonic acid

To a solution of acetophenone (120 mg, 1 mmol) in CH_3CN (5 ml) were added iodobenzene (20 mg, 0.1 mmol), *p*-TsOH·H_2O (209 mg, 1.1 mmol), and *m*CPBA (65% purity, 292 mg, 1.1 mmol). The mixture was stirred for 5 h at 50 °C under an argon atmosphere. After the reaction, the reaction mixture was poured into satd aq $NaHCO_3$ solution and extracted with $CHCl_3$ (3×15 ml). The organic layer was dried over Na_2SO_4. After removal of the solvent under

reduced pressure, α-tosyloxyacetophenone was obtained in a crude state. Pure α-tosyloxyacetophenone was obtained by flash column chromatography on silica gel (AcOEt–hexane=1:4).

4.3. Typical procedure for poly(4-iodostyrene)-catalyzed α-tosyloxylation of ketones with *m*CPBA and *p*-toluenesulfonic acid

Poly(4-iodostyrene) was prepared based on our previous method.[11] To a solution of acetophenone (120 mg, 1 mmol) in $CHCl_3$ (5 ml) were added poly(4-iodostyrene) (400 mg, 1.33 mmol; C, 53.69%; H, 4.13%; I, 42.12%, loading rate of the iodophenyl group is 3.3 mmol/g), *p*-TsOH·H_2O (209 mg, 1.1 mmol), and *m*CPBA (65% purity, 292 mg, 1.1 mmol). The mixture was stirred for 6 h at 50 °C under an argon atmosphere. After the reaction, methanol (10 mL) was added and the obtained mixture was filtered and washed with ether. The filtrate was poured into satd aq $NaHCO_3$ solution and extracted with $CHCl_3$ (3×15 ml). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, α-tosyloxyacetophenone was obtained in a crude state. Pure α-tosyloxyacetophenone was obtained by flash column chromatography on silica gel (AcOEt–hexane=1:4).

Loading rate of the iodophenyl group in the recovered poly(4-iodostyrene) was 3.2 mmol/g (C, 54.84%; H, 4.40%; I, 41.12%).

4.4. Typical procedure for PhI-catalyzed oxidative α-tosyloxylation of alcohol with *m*CPBA, *p*-toluenesulfonic acid, and KBr

To a solution of 1-phenylethyl alcohol (120 mg, 1 mmol) in CH_3CN (5 ml) were added iodobenzene (61 mg, 0.3 mmol), KBr (12 mg, 0.1 mmol), and *m*CPBA (65% purity, 544 mg, 2.05 mmol). The mixture was stirred for 1 h at room temperature under an argon atmosphere. Then, *p*-TsOH·H_2O (26 mg, 1.35 mmol) was added and the reaction mixture was stirred for 5 h at 50 °C. After the reaction, the reaction mixture was poured into satd aq $NaHCO_3$ solution and extracted with $CHCl_3$ (3×15 ml). The organic layer was dried over Na_2SO_4. After removal of the solvent under reduced pressure, α-tosyloxyacetophenone was obtained in a crude state. Pure α-tosyloxyacetophenone was obtained by column chromatography on silica gel (AcOEt–hexane=1:4).

4.4.1. 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, 3H), 5.27 (s, 2H), 7.35 (d, *J*=8.5 Hz, 2H), 7.47 (t, *J*=8.2 Hz, 2H), 7.61 (t, *J*=8.2 Hz, 1H), 7.84 (d, *J*=8.2 Hz, 2H), 7.85 (d, *J*=8.2 Hz, 2H).

4.4.2. α-Tosyloxy-*p*-methylacetophenone. Mp: 80 °C (lit.[12] 82–83 °C); IR (KBr): 1170, 1350, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.41 (s, 3H), 2.45 (s, 3H), 5.24 (s, 2H), 7.26 (d, *J*=8.1 Hz, 2H), 7.35 (d, *J*=8.2 Hz, 2H), 7.74 (d, *J*=8.1 Hz, 2H), 7.86 (d, *J*=8.2 Hz, 2H).

4.4.3. α-Tosyloxy-*p*-chloroacetophenone. Mp: 123 °C (lit.[12] 125 °C); IR (KBr): 1190, 1360, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.46 (s, 3H), 5.21 (s, 2H), 7.35 (d, *J*=8.4 Hz, 2H), 7.45 (d, *J*=8.6 Hz, 2H), 7.80 (d, *J*=8.6 Hz, 2H), 7.84 (d, *J*=8.4 Hz, 2H).

4.4.4. α-Tosyloxy-*p*-nitroacetophenone. Mp: 137 °C (lit.[12] 130–131 °C); IR (KBr): 1180, 1340, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.47 (s, 3H), 5.25 (s, 2H), 7.37 (d, *J*=8.3 Hz, 2H), 7.83 (d, *J*=8.3 Hz, 2H), 8.03 (d, *J*=8.9 Hz, 2H), 8.32 (d, *J*=8.9 Hz, 2H).

4.4.5. α-Tosyloxypropiophenone. Mp: 68 °C (lit.[12] 68–69 °C); IR (KBr): 1170, 1370, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.60 (d, *J*=7.0 Hz, 3H), 2.41 (s, 3H), 5.79 (q, *J*=7.0 Hz, 1H), 7.29 (d, *J*=8.1 Hz, 2H), 7.46 (t, *J*=7.2 Hz, 2H), 7.60 (t, *J*=7.2 Hz, 1H), 7.75 (d, *J*=7.2 Hz, 2H), 7.88 (d, *J*=8.1 Hz, 2H).

4.4.6. 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, 3H), 1.20–1.43 (m, 10H), 1.84–1.91 (m, 2H), 2.40 (s, 3H), 5.59 (dd, *J*=8.2, 4.8 Hz, 1H), 7.24 (d, *J*=8.0 Hz, 2H), 7.45 (t, *J*=7.5 Hz, 2H), 7.59 (t, *J*=7.5 Hz, 1H), 7.74 (d, *J*=8.2 Hz, 2H), 7.86 (d, *J*=8.2 Hz, 2H).

4.4.7. α-Tosyloxy-3-pentanone. Oil (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, 3H), 1.35 (d, *J*=7.0 Hz, 3H), 2.47 (s, 3H), 2.60 (m, 2H), 4.80 (q, *J*=7.0 Hz, 1H), 7.37 (d, *J*=8.0 Hz, 2H), 7.81 (d, *J*=8.0 Hz, 2H).

4.4.8. 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, 3H), 0.86–1.75 (m, 15H), 2.46 (s, 3H), 2.51 (t, *J*=7.5 Hz, 2H), 4.64 (dd, *J*=8.0, 4.6 Hz, 1H), 7.36 (d, *J*=8.0 Hz, 2H), 7.80 (d, *J*=8.0 Hz, 2H).

4.4.9. α-Tosyloxycycloheptanone. Oil; IR (neat): 1190, 1590, 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.48–1.95 (m, 8H), 2.42–2.63 (m, 5H), 4.98 (t, *J*=5.1 Hz, 1H), 7.35 (d, *J*=8.0 Hz, 2H), 7.83 (d, *J*=8.0 Hz, 2H); ^{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): found *m*/*z*=283.0986, calcd for $C_{14}H_{19}O_4S$ M+1=283.1004.

4.4.10. Methyl α-tosyloxyacetoacetate. Oil; IR (neat): 1180, 1320, 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=2.30 (s, 3H), 2.48 (s, 3H), 3.71 (s, 3H), 5.20 (s, 1H), 7.38 (d, *J*=8.5 Hz, 2H), 7.83 (d, *J*=8.5 Hz, 2H); ^{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): found *m*/*z*=287.0596, calcd for $C_{14}H_{19}O_4S$ M+1=287.0589.

4.4.11. 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, 3H), 2.85 (s, 3H), 4.18 (m, 2H), 5.59 (s, 1H), 7.30 (d, *J*=8.4 Hz, 2H), 7.46 (t, *J*=7.5 Hz, 2H), 7.61 (t, *J*=7.5 Hz, 1H), 7.79 (d, *J*=8.5 Hz, 2H), 7.93 (d, *J*=8.5 Hz, 2H); ^{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): found m/z=363.0920, calcd for $C_{18}H_{19}O_6S$ M+1=363.0902.

4.4.12. 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, 3H), 1.20–1.32 (m, 6H), 1.48–1.62 (m, 2H), 2.45 (s, 3H), 2.49 (t, J=7.2 Hz, 2H), 4.49 (s, 2H), 7.37 (d, J=8.0 Hz, 2H), 7.82 (d, J=8.0 Hz, 2H); ^{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): found m/z=299.1295, calcd for $C_{15}H_{23}O_4S$ M+1=299.1317.

4.4.13. 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, 3H), 1.00–1.30 (m, 6H), 1.54–1.78 (m, 2H), 2.23 (s, 3H), 2.48 (s, 3H), 4.58 (dd, J=8.4, 4.6 Hz, 1H), 7.36 (d, J=8.7 Hz, 2H), 7.81 (d, J=8.7 Hz, 2H); ^{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): found m/z=299.1315, calcd for $C_{15}H_{23}O_4S$ M+1=299.1317.

4.4.14. δ-Tosyloxylevulinic acid ethyl ester. Oil; IR (neat): 1090, 1590, 1730 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.24 (t, J=7.3 Hz, 3H), 2.46 (s, 3H), 2.61 (t, J=6.3 Hz, 2H), 2.81 (t, J=6.3 Hz, 2H), 4.12 (q, J=7.3 Hz, 2H), 4.56 (s, 2H), 7.38 (d, J=8.4 Hz, 2H), 7.83 (d, J=8.4 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ=14.13, 21.70, 27.42, 33.69, 60.85, 71.82, 128.08, 130.07, 132.20, 145.55, 172.16, 201.86; HRMS (FAB): found m/z=315.0893, calcd for $C_{14}H_{19}O_6S$ M+1=315.0902.

4.4.15. β-Tosyloxylevulinic acid ethyl ester. Oil; IR (neat): 1180, 1590, 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=1.20 (t, J=7.2 Hz, 3H), 2.29 (s, 3H), 2.48 (s, 3H), 2.75 (dd, J=16.8, 5.4 Hz, 1H), 2.90 (dd, J=16.8, 5.4 Hz, 1H), 4.06 (m, 2H), 4.98 (t, J=5.4, 1H), 7.38 (d, J=7.0 Hz, 2H), 7.83 (d, J=7.0 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$): δ=14.01, 21.75, 26.86, 36.85, 61.33, 79.65, 128.04, 130.11, 132.87, 145.67, 168.66, 204.47; HRMS (FAB): found m/z=315.0893, calcd for $C_{14}H_{19}O_6S$ M+1=315.0902.

4.4.16. α-(*p*-Chlorobenzenesulfonyloxy)acetophenone. Mp: 96 °C (lit.[13] 97 °C); IR (KBr): 1180, 1540, 1700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=5.36 (s, 2H), 7.48 (t, J=7.5 Hz, 2H), 7.56 (d, J=8.9 Hz, 2H), 7.63 (t, J=8.9 Hz, 1H), 7.84 (d, J=7.5 Hz, 2H), 7.92 (d, J=8.9 Hz, 2H).

4.4.17. α-(Methanesulfonyloxy)acetophenone. Mp: 72–74 °C (lit.[14] 76–77 °C); IR (KBr): 1185, 1520, 1710 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=3.31 (s, 3H), 5.53 (s, 2H), 7.53 (t, J=7.6 Hz, 2H), 7.66 (t, J=7.6 Hz, 1H), 7.90 (d, J=7.6 Hz, 2H).

4.4.18. α-(Camphorsulfonyloxy)acetophenone. Oil (lit.[15] 60–61 °C); IR (neat): 1170, 1590, 1720 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ=0.92 (s, 3H), 1.14 (s, 3H), 1.42–1.51 (m, 1H), 1.74–1.85 (m, 1H), 1.95 (d, J=18.6 Hz, 1H), 2.04–2.16 (m, 2H), 2.36–2.55 (m, 2H), 3.35 (d, J=15.3 Hz, 1H), 3.82 (d, J=15.3 Hz, 1H), 5.53 (s, 2H), 7.52 (t, J=7.2 Hz, 2H), 7.64 (t, J=7.2 Hz, 1H), 7.92 (d, J=7.2 Hz, 2H).

Acknowledgements

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References and notes

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