Iodoarene-Mediated α**-Tosyloxylation of Ketones with MCPBA and** *p***-Toluenesulfonic Acid**

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Abstract: Alkyl aryl ketones and dialkyl ketones could be converted into the corresponding α -tosyloxy ketones by the reaction with MCPBA and p-toluenesulfonic acid monohydrate (PTSA·H₂O) in the presence of a catalytic amount of molecular iodine (I_2) in a mixture of acetonitrile and 2,2,2-trifluoroethanol, although the yields were dependent on the ketones (method A). The same conversion of alkyl aryl ketones and dialkyl ketones into the corresponding α tosyloxy ketones could be smoothly carried out by the reaction with MCPBA and PTSA·H₂O in the presence of catalytic amounts of iodine and tert-butylbenzene in a mixture of acetonitrile and 2,2,2trifluoroethanol (method B). In those reactions, p-iodotoluene and 4-tert-butyl-1-iodobenzene were formed at first in method A and method B, respectively, and then they were converted into p-[(hydroxy)(tosyloxy)]iodotoluene and 4-tert-butyl-1-[(hydroxy)(tosyloxy)iodo]benzene by the reaction with MCPBA and PTSA·H₂O. p-[(Hydroxy)(tosyloxy)]iodotoluene and 4-tert-butyl-1-[(hydroxy)-(tosyloxy)iodo]benzene worked as an α -tosyloxylation reagent of ketones.

Key words: molecular iodine, *tert*-butylbenzene, MCPBA, α -tosyloxy ketone, ketone, *p*-toluenesulfonic acid, catalyst

 α -Tosyloxy ketones are very important strategic precursors for the construction of various heteroaromatics, such as 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 -tosyloxylation of ketones. Generally, HTIB is prepared via two steps: the initial oxidation of iodobenzene to (diacetoxyiodo)benzene, followed by the treatment with *p*-toluenesulfonic acid monohydrate.^{1a,b} We have studied the synthetic uses of [(hydroxy)(tosyloxy)iodo]arenes, 1-(arenesulfonyloxy)benziodoxolones, and poly[4-(hydroxy)(tosyloxy)iodo]styrenes for the α tosyloxylation of ketones and the construction of thiazoles, imidazoles, and imidazo[1,2-a]pyridines.² On the other hand, the ArI-catalyzed oxidative conversion of substrates, such as ketones, hydroquinones, alkenes, alcohols, and amides, with *m*-chloroperbenzoic acid (MCPBA) or Oxone[®] has become very popular³ because it is a metalfree oxidative reaction and hypervalent iodines are formed in situ. In this regard, environmentally benign organic synthesis may be carried out. Previously, we reported an efficient method for the preparation of various [(hydroxy)(sulfonyloxy)iodo]arenes directly from iodo-

SYNLETT 2011, No. 13, pp 1853–1858 Advanced online publication: 14.07.2011 DOI: 10.1055/s-0030-1260948; Art ID: U03711ST © Georg Thieme Verlag Stuttgart · New York arenes with sulfonic acids and MCPBA.⁴ Based on these results, the PhI-catalyzed, polymer-supported PhI-catalyzed, and ion-supported PhI-catalyzed a-tosyloxylation of ketones with MCPBA and p-toluenesulfonic acid monohydrate;^{5a-c} the PhI-catalyzed and ion-supported PhI-catalyzed preparation of 3,4-dihydro-1H-2,1-benzothiazine 2,2-dioxides from N-methoxy-2-arylethanesulfonamides with MCPBA,^{5d-f} the PhI-catalyzed preparation of oxazoles with MCPBA^{5g} or Oxone[®], ^{5h} and the PhI-catalyzed α-tosyloxylation of ketones with Oxone[®] and *p*-toluenesulfonic acid monohydrate⁵ⁱ were carried out. Among those reactions, the ArI-catalyzed oxidative conversion of substrates with MCPBA is very attractive as MCPBA is a rather strong nonmetal oxidant and the formed *m*-chlorobenzoic acid (MCBA) can be removed easily by extraction with an aqueous basic solution. Here, as part of our study on the use of molecular iodine (I₂) for organic synthesis⁶ and ArI-catalyzed organic reactions,⁵ we would like to report the iodoarene-mediated α -tosyloxylation of ketones with MCPBA and ptoluenesulfonic acid monohydrate both in the absence and in the presence of tert-butylbenzene in a mixture of acetonitrile and 2,2,2-trifluoroethanol.

At first, iodine, p-toluenesulfonic acid monohydrate, and MCPBA were dissolved in a mixture of acetonitrile and 2,2,2-trifluoroethanol. The resulting solution was stirred at room temperature until the color of iodine faded completely. Then, a solution of acetophenone in acetonitrile was added to the resulting solution, and the mixture was stirred for three hours at 60 °C to give α -tosyloxyacetophenone in 71% yield as shown in Table 1 (entry 1, method A).⁷ α -Tosyloxyacetophenone was not obtained at all in the absence of iodine (entry 3, method A). When the reaction was carried out in acetonitrile alone, the yield of α -tosyloxyacetophenone was low (entry 2, method A). On the other hand, the addition of 2,2,2-trifluoroethanol as co-solvent enhanced the reaction to provide α -tosyloxyacetophenone in good yield. Moreover, the yield of α-tosyloxyacetophenone was low when Oxone[®], instead of MCPBA as an oxidant, was used under the same conditions (entry 4, method A). Today, it is well known that 2,2,2-trifluoroethanol promotes the oxidative reactions with hypervalent iodines^{8,9} and therefore, the promotion of the oxidative α-tosyloxylation of acetophenone was observed in the present reaction. In further detailed studies, it became clear that *p*-iodotoluene was formed at first in the present reaction, and it was further oxidized to *p*-[(hydroxy)(tosyloxy)iodo]toluene by the reaction with

MCPBA and *p*-toluenesulfonic acid monohydrate. Practically, the treatment of *p*-toluenesulfonic acid monohydrate (2.1 mmol) and MCPBA (2.2 mmol) in the presence of molecular iodine (2.4 mmol) in a mixture of acetonitrile (3 mL) and 2,2,2-trifluoroethanol (3 mL) at 60 °C for five hours provided 4-iodotoluene in 54% yield.¹⁰ On the other hand, when the α -sulforyloxylation of acetophene (1.0 mmol) with MCPBA (2.2 mmol) and molecular iodine (0.1 mmol) in the presence of camphorsulfonic acid (2.1 mmol), an aliphatic sulfonic acid, was carried out at 60 °C for 24 hours under the same conditions, only trace amount of α -camphorsulfonyloxyacetophenone was obtained. Thus, the present reaction requires aromatic sulfonic acids, not aliphatic sulfonic acids. Once p-iodotoluene is formed, it is easily oxidized to *p*-[(hydroxy)(tosyloxy)iodoltoluene by the reaction with MCPBA and *p*-toluenesulfonic acid monohydrate at room temperature.⁴ Thus, the real key species in method A is p-[(hydroxy)(tosyloxy)iodo]toluene. Based on these results, the α -tosyloxylation of various ketones, such as alkyl aryl ketones and dialkyl ketones, with MCPBA and *p*-toluenesulfonic acid monohydrate in the presence of iodine in a mixture of acetonitrile and 2,2,2-trifluoroethanol (method A) was carried out to provide the corresponding a-tosyloxy ketones in good yields (entries 6-10), moderate yields (entries 5, 11, 15, 16), and low yields (entries 12–14, 17, 18),



Scheme 1 Reaction mechanism for iodoarene-mediated α -tosyloxylation of ketones (methods A and B)

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depending on the ketones. On the whole, the yields of α -tosyloxy ketones with alkyl aryl ketones bearing an electron-donating group on the aromatic ring were low, and those of dialkyl ketones were likewise low. The results suggest that the smooth formation of the enol form is important. However, the nucleophilicity of the enol form of β -keto esters is not sufficiently high due to the presence of an ester group (entries 15, 16).

Table 1 Preparation of α -Tosyloxy Ketones from Ketones with
Methods A and B

Method A: **I**₂ (0.1 equiv), MCPBA (2.2 equiv), *p*-TsOH·H₂O (2.1 equiv) Method B: **I**₂ (0.1 equiv), *t*-BuPh (0.2 equiv), MCPBA (1.7 equiv), *p*-TsOH·H₂O (1.5 equiv)

Method A or Method B $\stackrel{(1) \text{ MeCN-CF}_3\text{CH}_2\text{OH} (1:1), r.t.}{2)} \stackrel{O}{\underset{R^1}{\longrightarrow}} R^2 \stackrel{O}{\underset{OTs}{\longrightarrow}} R^1 \stackrel{O}{\underset{OTs}{\longrightarrow}} R^1$



Table 1 Preparation of α -Tosyloxy Ketones from Ketones with Methods A and B (continued)

Method A: I_2 (0.1 equiv), MCPBA (2.2 equiv), p-TsOH·H ₂ O (2.1 equiv)						
Method B: I ₂ (0.1 equiv), <i>t</i> -BuPh (0.2 equiv), MCPBA (1.7 equiv), <i>p</i> -TsOH·H ₂ O (1.5 equiv)						
Method A or Method B	1) MeCN-CF ₃ CH ₂ OH (1:1), r.t.	R ²				
	R^2 R^2 R^2 R^2	DTs				

Entry	Product ^a	Method A		Method B	
		Time (h)	Yield (%)	Time (h)	Yield (%)
12	OTs	20	21	5	58
13	O OTs	30	11	3	47
14	S OTs	24	21	5	49
15	O O OTs	3	43	3	63
16	O O OMe OTs	2	41	2.5	60
17	O OTs	1	31	3	62
18	O OTs	21	14	6	57
19	Ο (TsO) (OTs)	5	54	2.5	68
		$(\alpha/\gamma = 1:9.8)$		$(\alpha/\gamma=1{:}8.7)$	

^a Isolated yield.

^b Only MeCN was used as a solvent.

^c Reaction was carried out without I₂.

^d Oxone[®] was used instead of MCPBA.

This may be the reason why the yield with β -keto esters is not so high. Recently, a one-pot preparation of [(hydroxy)(tosyloxy)iodo]arenes from arenes with iodine, *p*-toluenesulfonic acid monohydrate, and MCPBA was reported.⁹ Based on that report and our previous report,⁴ we next studied the α -tosyloxylation of ketones with MCPBA and *p*-toluenesulfonic acid monohydrate in the presence of catalytic amounts of iodine and *tert*-butylbenzene in a mixture of acetonitrile and 2.2.2-trifluoroethanol. We noted improvements in the yields of α -tosyloxy ketones. In this case, 4-tert-butyl-1-iodobenzene was formed at first, and then 4-tert-butyl-1-[(hydroxy)(tosyloxy)iodo]benzene was generated from the reaction of 4tert-butyl-1-iodobenzene with MCPBA and p-toluenesulfonic acid monohydrate,⁴ and worked as an α -tosyloxylating reagent of ketones, similar to HTIB. Here, we do not have to use expensive iodoarenes and it is formed in situ and works as a catalyst. Thus, to a stirred solution of tert-butylbenzene in a mixture of acetonitrile and 2,2,2trifluoroethanol were added MCPBA, iodine, and p-toluenesulfonic acid monohydrate. The resulting solution was stirred at room temperature until color of iodine faded completely. Then, a solution of acetophenone in acetonitrile was added to the resulting solution, and the mixture was stirred for five hours at 60 °C to provide α-tosyloxyacetophenone in 70% yield (entry 1, method B).⁷ When anisole, benzene, and toluene instead of tert-butylbenzene was used for the α -tosyloxylation of acetophenone with MCPBA, iodine, and *p*-toluenesulfonic acid monohydrate under the same conditions, α -tosyloxyacetophenone was obtained in 48%, 45%, and 64% yields, respectively. Thus, tert-butylbenzene is the most effective among anisole, benzene, toluene, and tert-butylbenzene. In the reaction with acetophenone, the additive effect of tertbutylbenzene was not observed at all (entry 1, method A and B). However, α -tosyloxyacetophenone was not obtained at all in the absence of iodine (entry 3, method B). In other alkyl aryl ketones and dialkyl ketones under the same conditions, the corresponding α -tosyloxy ketones were obtained in good to moderate yields (entries 5-19, method B), and overall, the yields with method B were higher than those with method A. The plausible reaction mechanism, which is the same as that with HTIB, is shown in Scheme 1. Thus, *p*-iodotoluene is formed at first via the desulfonyloxyiodonation of *p*-toluenesulfonic acid by the reaction with MCPBA and molecular iodine in method A.¹⁰ On the other hand, 4-tert-butyl-1-iodobenzene is formed by the reaction of *tert*-butylbenzene with MCPBA and molecular iodine in method B.⁹ Once *p*-iodotoluene and 4-tert-butyl-1-iodobenzene are formed, p-[(hydroxy)(tosyloxy)iodo]toluene and 4-tert-butyl-1-[(hydroxy)(tosyloxy)iodo]benzene are generated in method A and method B, respectively, as the α -tosyloxylation reagent of ketones. α-Tosyloxy ketones are produced via intermediate I by the reaction of ketones with p-[(hydroxy)(tosyloxy)iodo]toluene and 4-tert-butyl-1-[(hydroxy)(tosyloxy)iodo]benzene, like HTIB^{1a}

In conclusion, alkyl aryl ketones and dialkyl ketones could be converted into the corresponding α -tosyloxy ketones by the reaction with MCPBA and *p*-toluenesulfonic acid monohydrate in the presence of a catalytic amount of iodine in a mixture of acetonitrile and 2,2,2-trifluoroethanol, and the yields were dependent on the ketones used. The same α -tosyloxylation of alkyl aryl ketones and dialkyl ketones occurred smoothly by the reaction with MCPBA and *p*-toluenesulfonic acid monohydrate in the presence of catalytic amounts of iodine and *tert*-butylbenzene in a mixture of acetonitrile and 2,2,2-trifluoroethanol. Both α -tosyloxylation reactions of ketones proceeded via the formation of [(hydroxy)(tosyloxy)iodo]arenes in situ and did not require expensive iodoarenes. Further synthetic study of the present reaction is under way in this laboratory.

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(7) Typical Procedure for Iodoarene-Mediated α-Tosyloxylation of Ketones with MCPBA and p-TsOH·H₂O Method A

I₂ (0.1 mmol), *p*-TsOH·H₂O (2.1 mmol), and MCPBA (2.2 mmol) were dissolved in a mixture of MeCN (3 mL) and 2,2,2-trifluoroethanol (3 mL) under argon atmosphere. The resulting solution was stirred at r.t. until the color of I₂ faded completely (1–2 h). Then, a solution of acetophenone (1 mmol) in MeCN (2 mL) was added, and the mixture was stirred for 3 h at 60 °C under argon atmosphere. After the reaction, the reaction mixture was poured into a solution of sat. aq NaHCO₃ and Na₂SO₃, and the whole was extracted with CHCl₃ (3 × 20 mL). The organic layer was dried over Na₂SO₄. After removal of the solvent under reduced pressure, α-tosyloxyacetophenone was obtained in the crude

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state. Pure α -tosyloxyacetophenone was obtained in 71% yield (206 mg) by short flash column chromatography on silica gel (EtOAc–hexane = 1:3).

Method B

To a stirred solution of tert-butylbenzene (0.2 mmol) in a mixture of MeCN (3 mL) and 2,2,2-trifluoroethanol (3 mL) under argon atmosphere were added MCPBA (1.7 mmol), I₂ (0.1 mmol), and *p*-TsOH·H₂O (1.5 mmol). The resulting solution was stirred at r.t. until the color of I₂ faded completely (1-2 h). Then, a solution of acetophenone (1 mmol) in MeCN (2 mL) was added, and the mixture was stirred for 5 h at 60 °C under argon atmosphere. After the reaction, the reaction mixture was poured into a solution of sat. aq NaHCO₃ and Na₂SO₃, and the whole was extracted with $CHCl_3$ (3 × 20 mL). The organic layer was dried over Na₂SO₄. After removal of solvent under reduced pressure, α tosyloxyacetophenone was obtained in the crude state. Pure a-tosyloxyacetophenone was obtained in 70% yield (204 mg) by short flash column chromatography on silica gel (EtOAc-hexane = 1:3).

α-Tosyloxyacetophenone

Mp 90 °C (lit.^{1h} mp 90–91 °C). IR (KBr): 1180, 1360, 1715 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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), 1³C NMR (100 MHz, CDCl₃): δ = 21.67, 69.90, 127.97, 128.13, 128.89, 129.89, 132.57, 133.71, 134.19, 145.28, 190.26.

α -Tosyloxy-*p*-methylacetophenone

Mp 105 °C (lit.¹¹ mp 82–83 °C). IR (KBr): 1170, 1350, 1700 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): δ = 21.68, 21.77, 69.85, 128.07, 128.14, 129.57, 129.87, 131.24, 132.62, 145.23, 145.28, 189.80.

α -Tosyloxy-*p*-chloroacetophenone

Mp 123 °C (lit.¹¹ mp 125 °C). IR (KBr): 1190, 1360, 1710 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): δ = 21.71, 69.79, 128.14, 129.28, 129.48, 129.94, 132.05, 132.44, 140.78, 145.43, 189.55.

α-Tosyloxy-*p*-nitroacetophenone

Mp 137 °C (lit.¹¹ mp 130–131 °C). IR (KBr): 1180, 1340, 1710 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 2.47$ (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). ¹³C NMR (100 MHz, CDCl₃): $\delta = 21.83$, 70.04, 117.70, 124.17, 128.26, 129.45, 130.15, 132.32, 138.29, 145.81, 189.87. **a** Tosylaxy m pitropeotophonome

α-Tosyloxy-*m*-nitroacetophenone

Mp 129–130 °C. IR (KBr): 1615, 1375, 1348, 1188 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): 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 C₁₅H₁₃O₆NSNa [M + Na]: 358.0356; found: 358.0347.

α-Tosyloxypropiophenone

Mp 68 °C (lit.¹¹ mp 68–69 °C). IR (KBr): 1170, 1370, 1700 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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), 7.75 (d, *J* = 7.2 Hz, 2 H), 7.88 (d, *J* = 8.1 Hz, 2 H). ¹³C NMR (100 MHz, CDCl₃): 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)octyl Phenyl Ketone

Mp 59–61 °C (lit.^{2d} mp 59–61 °C). IR (neat): 1180, 1340, 1700 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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).

Tosyloxymethyl Naphthyl Ketone

Oil (lit.¹²). IR (neat): 1176, 1365, 1700 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ = 2.40 (s, 3 H), 5.27 (s, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 7.50 (t, *J* = 8.3 Hz, 1 H), 7.53–7.60 (m, 2 H), 7.78 (dd, *J* = 1.2, 7.4 Hz, 1 H), 7.81 (d, *J* = 8.3 Hz, 2 H), 7.87 (d, *J* = 7.8 Hz, 1 H), 8.04 (d, *J* = 8.3 Hz, 1 H), 8.48 (dd, *J* = 0.9, 8.3 Hz, 1 H). ¹³C NMR (100 MHz, CDCl₃): δ = 21.65, 70.99, 124.13, 125.35, 126.82, 128.08, 128.34, 128.44, 128.50, 129.87, 130.16, 131.28, 132.60, 133.91, 134.05, 145.24, 193.91.

2,4,6-Trimethylphenyl (Tosyloxy)methyl Ketone

Mp 58 °C. IR (neat): 1191, 1377, 1608 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): 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. ESI-HRMS: *m/z* calcd for C₁₈H₂₁O₄SNa [M + Na]: 355.0980; found: 355.0946.

2-Furyl (Tosyloxy)methyl Ketone

Mp 63–64 °C (lit.^{1h} mp 65–67 °C). IR (KBr): 1695, 1370, 1170, 810, 750 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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).

2-Thienyl (Tosyloxy)methyl Ketone

Mp 92–93 °C (lit.¹ⁱ mp 94–96 °C). IR (KBr): 1685, 1370, 1180, 730 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): δ = 21.66, 69.87, 128.17, 128.46, 129.94, 132.38, 133.13, 135.12, 140.12, 145.43, 183.64.

Ethyl α-Tosyloxybenzoylacetate

Oil. IR (neat): 1440, 1590, 1690 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): 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 C₁₈H₁₉O₆S [M + 1]: 363.0902; found: 363.0920.

Methyl a-Tosyloxyacetoacetate

Oil. IR (neat): 1180, 1320, 1720 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): 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 C₁₂H₁₅O₆S [M + 1]: 287.0589; found: 287.0596.

2-Tosyloxy-3-pentanone

Mp 45–46 °C (lit.^{1k} mp 43–44 °C). IR (neat): 1190, 1360, 1720 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): 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). ¹³C NMR (100 MHz, CDCl₃): δ = 6.96, 17.58, 21.65, 31.16, 80.68, 127.85, 129.99, 133.16, 145.29, 207.81.

5-Tosyloxy-6-undecanone

Mp 72 °C (lit.^{2d} mp 72 °C). IR (neat): 1190, 1380, 1720 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.70-0.80$ (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).

1-Tosyloxy-2-octanone

Oil. IR (neat): 1180, 1360, 1590, 1730 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.87$ (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). ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.97$, 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 C₁₅H₂₃O₄S [M + 1]: 299.1317; found: 299.1295.

3-Tosyloxy-2-octanone

Oil. IR (neat): 1180, 1360, 1600, 1740 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): $\delta = 0.80$ (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). ¹³C NMR (100 MHz, CDCl₃): $\delta = 13.91$, 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 C₁₅H₂₃O₄S [M + 1]: 299.1317; found: 299.1315.

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