A New Application of Hypervalent Iodine (λ^5) Reagents with Organosulfonic Acids for Direct α-Organosulfonyloxylation Carbonyl Compounds

Ulhas S. Mahajan, Krishnacharya G. Akamanchi*

Department of Pharmaceutical Sciences & Technology, Institute of Chemical Technology, Matunga, Mumbai 400 019, India
Fax +91(22)24145614; E-mail: kgap@rediffmail.com

Received 22 November 2007

Abstract: Hypervalent iodine (λ^5) reagents in combination with *p*-toluenesulfonic acid when reacted with ketones under reflux temperature in acetonitrile gave α-tosyloxy ketones in moderate to excellent yields. The reaction was developed further for both ketones and dicarbonyl compounds using Dess–Martin periodinane reagent in combination with *p*-toluenesulfonic acid and methanesulfonic acid, to give mono-α-tosyloxy and mono-α-mesyloxy products in very high to excellent yields.

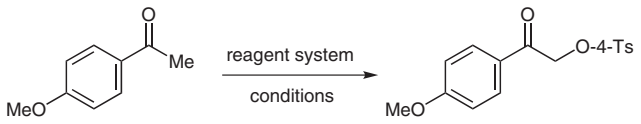
Key words: hypervalent iodine reagents, Dess–Martin periodinane, carbonyl compounds, organosulfonic acids, α-organosulfonyloxylation

Hypervalent iodine reagents are known for direct oxidative α-carbon–heteroatom bond formation in carbonyl compounds.[1] The reagents being nonmetallic, highly selective, and mild oxidants have attracted considerable attention towards exploration and development of new methodologies.[2] The α-tosyloxy and α-mesyloxy carbonyl compounds are versatile precursors for construction of biologically important heterocyclic ring systems such as thiazoles, imidazoles, oxazoles pyrazines, pyrazoles, lactones, benzofurans, benzopyrazines, benzoxazines, benzothiazines, imidazo[2,1-*b*]thiazoles and thiazolo[3,2-*a*]benzimidazoles.[3]

Our group has been working extensively on the development of novel methodologies using hypervalent iodine (λ^5) reagents, mainly, *o*-iodoxybenzoic acid (IBX) and Dess–Martin periodinane (DMP).[4] Throughout the literature there is no report on α-organosulfonyloxylation of carbonyl compounds using these reagents. However trivalent iodine (λ^3) reagents are known to promote direct α-organosulfonyloxylation of carbonyl compounds. Among them are (hydroxy tosyloxy iodo) benzene (HTIB),[5] (diacetoxyiodo)benzene organosulfonic acid under solvent-free conditions,[6a] (diacetoxyiodo)benzene and *p*-toluenesulfonic acid under microwave irradiation,[6b] iodosylbenzene/*p*-toluenesulfonic acid monohydrate,[6c] *m*-chloroperbenzoic acid/*p*-toluenesulfonic acid in presence of PhI,[6d] poly(4-hydroxy tosyloxy iodo)styrenes,[6e] and recently enantioselective α-tosyloxylation using enantioenriched iodoarenes/*m*-chloroperbenzoic acid.[6f] Other methods for direct α-*p*-tosyloxylation include thallium *p*-tolylsulfonate[6g] and *N*-methyl-*O*-tosylhydroxylamine.[6h]

In continuation of our studies towards the development of novel applications of hypervalent iodine (λ^5) regents, we wish to report direct α-organosulfonyloxylation of various ketones and dicarbonyl compounds using these reagents in combination with organosulfonic acids. The added advantage of this method is that there is no need for prior preparation of sulfonyloxy reagents as in the case of HTIB.[5] For preliminary experiments, 4-methoxyacetophenone was chosen as a model substrate and reactions were carried out using 1.5 equivalents of DMP in combination with 2.0 equivalents of *p*-toluenesulfonic acid at room temperature in acetonitrile. The expected reaction did not occur and unreacted starting material was recovered. When the reaction was performed at reflux temperature, it proceeded smoothly and the corresponding α-tosyloxy ketone was obtained in 94% yield with complete consumption of starting material (Table 1, entry 2).

Table 1 α-Tosyloxylation Using Hypervalent Iodine (λ^5) Reagents[a]



Entry	Reagent	Reagent/PTSA molar ratio	Conditions	Yield (%)[b]
1	DMP	1.5/2	r.t., 10 h	NR
2	DMP	1.5/2	Reflux, 2.5 h	94
3	IBX	2/2	Reflux, 3 h	78
4	HIO_3	2.5/2.5	Reflux, 10 h	65[c]
5	HIO_4	2.5/2.5	Reflux, 10 h	55[c]

[a] Reactions were carried out on 5 mmol scale.
[b] Isolated yields using column chromatography.
[c] Unreacted starting material was recovered, NR = no reaction.

Encouraged by these results, other hypervalent iodine compounds IBX, HIO_3, and HIO_4 were also examined and all were found to be viable. However, the reactions were slow and in some cases unreacted starting material remained even after 10 hours and yields were moderate (Table 1, entries 4 and 5).

For further investigations DMP was chosen and selectivity, general applicability, and extension for other organosulfonic acids such as methanesulfonic acid were studied. Various ketones and dicarbonyl compounds were reacted

SYNLETT 2008, No. 7, pp 0987–0990
Advanced online publication: 17.03.2008
DOI: 10.1055/s-2008-1072508; Art ID: D37607ST

with DMP in combination with *p*-toluenesulfonic acid and methanesulfonic acid, respectively.[7,8] In all cases the corresponding α-organosulfonyloxylated compounds were obtained in very good to excellent isolated yields. The results are summarized in Table 2.

Table 2 DMP-Mediated α-Organosulfonyloxylation of Various Carbonyl Compounds[a]

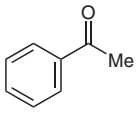
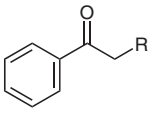
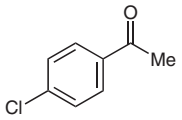
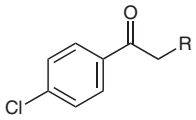
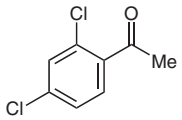
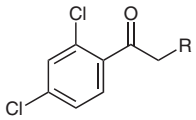
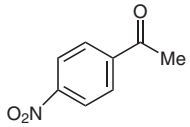
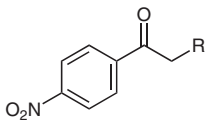
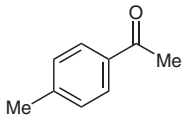
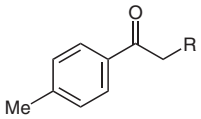
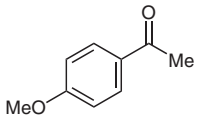
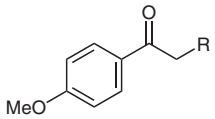
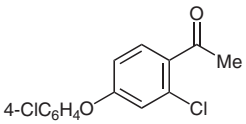
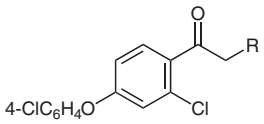
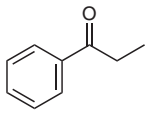
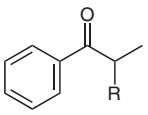
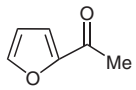
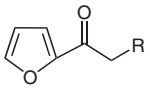
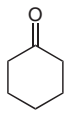
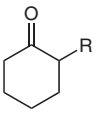
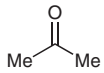
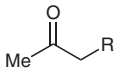
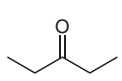
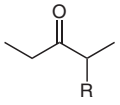
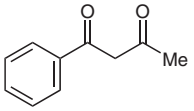
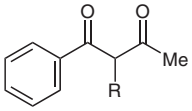
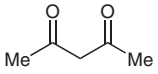
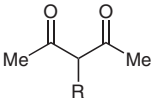
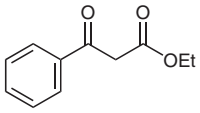
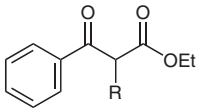
Entry	Substrate	Product[b]	Yield[c] (%, reaction time, h)	
			R = OMs	R = O-4-Ts
1			86 (2.5)	90 (2.5)
2			82 (3.0)	88 (3.0)
3			78 (3.5)	90 (3.5)
4			80 (3.5)	86 (3.5)
5			82 (3.5)	92 (3.5)
6			79 (2.5)	94 (2.5)
7			75 (4.5)	84 (4.5)
8			78 (3.0)	82 (3.0)
9			72 (3.0)	84 (3.0)
10			65 (4.5)	72 (4.5)
11			80 (2.5)	87 (2.5)
12			76 (3.0)	80 (3.0)

Table 2 DMP-Mediated α-Organosulfonyloxylation of Various Carbonyl Compounds[a] (continued)

Entry	Substrate	Product[b]	Yield[c] (%, reaction time, h)	
			R = OMs	R = O-4-Ts
13			68 (2.5)	72 (2.5)
14			73 (2.5)	78 (2.5)
15			72 (3.0)	80 (3.0)

[a] Reactions were conducted on 5 mmol scale in MeCN at reflux temperature with DMP (1.5 equiv) and organosulfonic acid (2.0 equiv).
[b] Compounds were characterized by IR, ^{1}H NMR and physical constants.[8]
[c] Isolated yield after column chromatography.

As illustrated in Table 2, the reactivity profile of the substituted ketones was remarkable. The reaction was equally facile with all aromatic ketones irrespective of whether they contain electron-withdrawing or electron-donating substituents (entries 1–8) and 2-acetylfuran (entry 9). The cyclic ketone cyclohexanone and aliphatic ketones including acetone, diethyl ketone (entries 10–12), and 1,3-dicarbonyl compounds including benzoylacetone, acetylacetone, ethyl benzoylacetate underwent α-sulfonyloxylation smoothly with good to high yields (entries 13–15). Esters such as ethyl butyrate and ethyl phenylacetate did not react under the optimized reaction conditions.

In conclusion, it has been shown that hypervalent iodine (λ5) reagents in combination with organosulfonic acids are suitable for direct α-organosulfonyloxylation. The general applicability of the reaction was demonstrated by using DMP in combination with *p*-toluenesulfonic acid and methanesulfonic acid. Direct α-tosyloxylation and α-mesyloxylation of various carbonyl compounds has been achieved. The method is clean, efficient, and useful for a wide range of carbonyl compounds.

Acknowledgment

The authors wish to thank the University Grants Commission (UGC), and AICTE India, for financial support.

References and Notes

(1) (a) Lodaya, J. S.; Koser, G. F. *J. Org. Chem.* **1988**, *53*, 210. (b) Moriarty, R. M.; Vaid, R. K.; Ravikumar, V. T.; Vaid, B. K.; Opkins, T. E. *Tetrahedron* **1988**, *44*, 1603. (c) Moriarty, R. M.; Prakash, O. *Acc. Chem. Res.* **1986**, *19*, 244. (d) Mizukami, E.; Ando, M.; Tanaka, T.; Imamura, J. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 335. (e) Koser, G. F.; Lodaya, J. S.; Ray, D. G. III; Kokil, P. B. *J. Am.Chem. Soc.* **1988**, *110*, 2987.

(2) (a) Varvoglis, A. *Hypervalent Iodine in Organic Synthesis*; Academic Press: London, **1997**. (b) Zhdankin, V. V.; Stang, P. J. *Chem. Rev.* **2002**, *102*, 2523. (c) Zhdankin, V. V. *Curr. Org. Synth.* **2005**, *2*, 121. (d) Wirth, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 3656. (e) Nicolaou, K. C.; Montagnon, T.; Baran, P. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 993. (f) Nicolaou, K. C.; Gray, D. L.; Montagnon, F. T.; Harrison, S. T. *Angew. Chem. Int. Ed.* **2002**, *41*, 996. (g) Nicolaou, K. C.; Montagnon, T.; Baran, P. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 1386. (h) Katritzky, A. R.; Duell, B. L.; Durst, H. D.; Knier, B. L. *J. Org. Chem.* **1988**, *53*, 3972. (i) Zhdankin, V. V.; Arbit, R. M.; Lynch, B. L.; Kiprof, P. *J. Org. Chem.* **1998**, *63*, 6590.

(3) Reviews: (a) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. (b) Koser, G. F. *Aldrichimica Acta* **2001**, *34*, 89. (c) Prakash, O.; Saini, N.; Sharma, P. K. *Heterocycles* **1994**, *38*, 409. Papers: (d) Neilands, O.; Karele, B. *J. Org. Chem. USSR* **1970**, *6*, 885. (e) Koser, G. F.; Wettach, R. H.; Troup, J. M.; Bertram, A. F. *J. Org. Chem.* **1976**, *41*, 3609. (f) Koser, G. F.; Wettach, R. H. *J. Org. Chem.* **1977**, *42*, 1476. (g) Koser, G. F.; Wettach, R. H.; Smith, C. S. *J. Org. Chem.* **1980**, *45*, 1543. (h) Koser, G. F.; Relenyi, A. G.; Kalos, A. N.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1982**, *47*, 2487. (i) Moriarty, R. M.; Penmasta, R.; Awasthi, A. K.; Epa, W. R.; Prakash, I. *J. Org. Chem.* **1989**, *54*, 1101. (j) Moriarty, R. M.; Vaid, R. K.; Hopkins, T. E.; Vaid, B. K.; Prakash, O. *Tetrahedron Lett.* **1990**, *31*, 201. (k) Tuncay, A.; Dustman, J. A.; Fisher, G.; Tuncay, C. I. *Tetrahedron Lett.* **1992**, *33*, 7647. (l) Moriarty, R. M.; Vaid, B. K.; Duncan, M. P.; Levy, S. G.; Prakash, O.; Goyal, S. *Synthesis* **1992**, 845. (m) Prakash, O.; Goyal, S. *Synthesis* **1992**, 629. (n) Prakash, O.; Rani, N.; Goyal, S. *J. Chem. Soc., Perkin Trans. 1* **1992**, 707. (o) Prakash, O.; Saini, N.; Sharma, P. K. *Synlett* **1994**, 221. (p) Varma, R. S.; Kumar, D.; Liesen, P. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 4093. (q) Lee, J. C.; Choi, J.-H. *Synlett* **2001**, 234. (r) Moriarty, R. M.; Vaid, B. K.; Duncan, M. P.; Levy, S. G.; Prakash, O.; Goyal, S. *Synthesis* **1992**, 845. (s) Nicolaou, K. C.; Mantagnon, T.; Ulven, T.; Baren, P. S.; Zhong, Y. L.; Sarabia, F. *J. Am. Chem. Soc.* **2002**, *124*, 5718.

(4) (a) Bhalerao, D. S.; Mahajan, U. S.; Chaudhari, K. H.; Akamanchi, K. G. *J. Org. Chem.* **2007**, *73*, 662. (b) Arote, N. D.; Bhalerao, D. S.; Akamanchi, K. G. *Tetrahedron Lett.* **2007**, *48*, 5661. (c) Ramnarayanan, G. V.; Shukla, V. G.; Akamanchi, K. G. *Synlett* **2002**, 2059. (d) Shukla, V. G.; Salgaonker, P. D.; Akamanchi, K. G. *J. Org. Chem.* **2003**,

68, 5742. (e) Chaudhari, S. S.; Akamanchi, K. G. *Synthesis* **1999**, 760. (f) Chaudhari, S. S.; Akamanchi, K. G. *Tetrahedron Lett.* **1998**, *39*, 3209.

(5) Review: (a) Moriarty, R. M.; Vaid, R. K.; Koser, G. F. *Synlett* **1990**, 365. (b) Tuncay, A.; Dustman, J. A.; Fisher, G.; Tuncay, C. I. *Tetrahedron Lett.* **1992**, *33*, 7647. (c) Vrama, R. S.; Kumar, D.; Liesen, P. J. *J. Chem. Soc., Perkin Trans. 1* **1998**, 4093. (d) Lee, J. C.; Choi, J.-H. *Synlett* **2001**, 234. (e) Nabana, T.; Togo, H. *J. Org. Chem.* **2002**, *67*, 4362.

(6) (a) Yusubov, M. S.; Wirth, T. *Org. Lett.* **2005**, *7*, 519. (b) Lee, J. C.; Choi, J.-H. *Synlett* **2001**, 234. (c) Ueno, M.; Nabana, T.; Togo, H. *J. Org. Chem.* **2003**, *68*, 6424. (d) Yamamoto, Y.; Togo, H. *Synlett* **2006**, 798. (e) Abe, S.; Sakurantani, K.; Togo, H. *Synlett* **2001**, 22. (f) Richardson, R. D.; Page, T. K.; Altermann, S.; Paradine, S. M.; French, A. N.; Wirth, T. *Synlett* **2007**, 538. (g) Khanna, M. S.; Garg, C. P.; Kapoor, R. P. *Tetrahedron Lett.* **1992**, *33*, 1495. (h) Oliver, R. S.; John, N. M.; Killeen, D. A.; Sze, C. Y.; Mark, C. B.; Nicholas, C. O. T. *Org. Lett.* **2007**, *9*, 4009.

(7) **General Experimental Procedure for α-Organosulfonyloxylation**
To a stirred suspension of Dess–Martin periodinane (3.5 g, 7.5 mmol) and organosulfonic acid (10 mmol) in MeCN (15 mL) was added the substrate (5 mmol) in one portion and the reaction mixture was refluxed until complete consumption of starting material (monitored by TLC). After completion of reaction MeCN was removed under reduced pressure. The residue obtained was diluted by adding $CHCl_3$ (50 mL) and washed with sat. solutions of $NaHCO_3$ (2 × 30 mL) and brine (50 mL). The organic layer was dried over anhyd Na_2SO_4 and concentrated under reduced pressure to give the crude α-organosulfonyloxylated product. Pure product was obtained after column chromatography (SiO_2, mesh size 60–120, eluent, EtOAc–hexane, 15:85).

(8) **Spectroscopic Data for Selected of α-Tosyloxylated and α-Mesyloxylated Products**
2-Oxo-2-phenylethyl-4-Methanebenzenesulfonate (Entry 1)
Solid; mp 90 °C (lit.[5d] 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), 7.23–7.88 (m, 5 H) ppm.
2-Oxo-2-phenylethyl Methanesulfonate (Entry 1)
Solid; mp 76–77 °C (lit.[1a] 76–78 °C). IR (KBr): ν_{max} = 1725 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 3.20 (s, 3 H), 5.43 (s, 2 H), 7.12–8.12 (m, 5 H) ppm.
2-(4-Chlorophenyl)-2-oxo-ethyl 4-Methanebenzenesulfonate (Entry 2)
Solid; mp 123 °C (lit.[6g] 125 °C). IR (KBr): 1190, 1360, 1700 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) ppm.
2-(2,4-Dichlorophenyl)-2-oxo-ethyl Methanesulfonate (Entry 3)
Solid; mp 87 °C. IR (KBr): ν_{max} = 1710 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 3.24 (s, 3 H), 5.44 (s, 2 H), 7.22–7.83 (m, 3 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 37.65, 69.83, 128.90, 129.92, 130.46, 131.63, 136.10, 136.57, 190.74. Anal. Calcd (%) for $C_9H_8Cl_2O_4S$: C, 38.16; H, 2.82. Found: C, 38.15; H, 2.81.
2-(4-Nitrophenyl)-2-oxo-ethyl 4-Methanebenzenesulfonate (Entry 4)
Solid; mp 137 °C (lit.[6g] 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) ppm.
2-Oxo-2-*p*-tolylethyl 4-Methylbenzenesulfonate (Entry 5)
Solid; mp 80 °C (lit.[6g] 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) ppm.
2-Oxo-2-*p*-tolylethyl Methanesulfonate (Entry 5)
IR (KBr): ν_{max} = 1710 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 2.44 (s, 3 H), 3.28 (s, 3 H), 5.48 (s, 2 H), 7.28 (d, *J* = 8.33 Hz, 2 H), 7.77 (d, *J* = 8.33 Hz, 2 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 190.68, 145.65, 130.93, 129.77, 127.86, 70.22, 39.27, 21.83. Anal. Calcd (%) for $C_{10}H_{12}O_4S$: C, 52.63; H, 5.26. Found: C, 52.64; H, 5.25.
2-(4-Methoxyphenyl)-2-oxo-ethyl Methanesulfonate (Entry 6)
Solid; mp 98 °C. IR (KBr): ν_{max} 1710 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 3.22 (s, 3 H), 3.88 (s, 3 H), 5.44 (s, 2 H), 7.28 (d, *J* = 7.8 Hz, 2 H), 7.74 (d, *J* = 7.8 Hz, 2 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 37.63, 70.35, 55.82, 114.24, 126.81, 129.86, 165.12, 190.92. Anal. Calcd (%) for $C_{10}H_{12}O_5S$: C, 49.18; H, 4.91. Found: C, 49.20; H, 4.92.
2-[2-Chloro-4 (4-chlorophenoxy)phenyl]-2-oxo-ethyl Methanesulfonate (Entry 7)
White solid; mp 118–119 °C. IR (KBr): ν_{max} = 1715 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 3.20 (s, 3 H), 5.44 (s, 2 H), 7.20–7.89 (m, 7 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 39.23, 73.64, 117.32, 121.62, 123.35, 124.14, 130.70, 130.73, 131.31, 132.32, 132.40, 158.12, 190.40. Anal. Calcd (%) for $C_{15}H_{13}Cl_2O_5S$: C, 47.87; H, 3.45. Found: C, 47.86; H, 3.42.
1-Oxo-1-phenylpropan-2-yl 4-Methanebenzenesulfonate (Entry 8)
Solid; mp 68 °C (lit.[6g] 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), 7.60 (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) ppm.
2-(Furan-2-yl)-2-oxo-ethyl 4-Methanebenzensulfonate (Entry 9)
Solid; mp 62 °C (lit.[5e] 65–67 °C). IR (KBr): ν_{max} = 1670 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 3.27 (s, 3 H), 5.53 (s, 1 H), 7.28–8.05 (m, 3 H) ppm.
2-Oxo-cyclohexyl 4-Methylbenzenesulfonate (Entry 10)
Solid; mp 76 °C (lit.[5e] 74–76 °C). IR (KBr): ν_{max} = 1744 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 1.30–2.70 (m, 11 H), 4.82 (s, 1 H), 7.10 (d, 2 H), 8.02 (d, 2 H) ppm.
2-Oxo-propyl Methanesulfonate (Entry 11)
Oil.[1a] IR (neat): ν_{max} = 1738, 1367, 1187 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 2.20 (s, 3 H), 3.16 (s, 3 H), 4.37 (s, 2 H) ppm.
Ethyl 2-(Methylsulfonyloxy)-3-oxo-3-phenylpropanoate (Entry 15)
Yellow oil.[1a] IR (KBr): ν_{max} = 1670 cm^{-1}. ^1H NMR (60 MHz, $CDCl_3$): δ = 1.13 (t, 3 H), 3.23 (s, 3 H), 4.24 (q, 2 H), 6.23 (s, 1 H), 7.23–8.20 (m, 5 H) ppm.