Supporting Information

Gold-Catalyzed Intermolecular Oxidation of Terminal Alkynes: Simple and Efficient Synthesis of α-Mesyloxy Ketones

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General information

Ethyl acetate (ACS grade), hexanes (ACS grade) were purchased from J&K Scientific Ltd. and used without further purification. Commercially available reagents were used without further purification. Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed over silicycle silica gel (230-400 mesh). $^1$H NMR and $^{13}$C NMR spectra were recorded on a Brucker ARX 400 FT NMR plus spectrometer using residue solvent peaks as internal standards. Infrared spectra were recorded with FD-5DX spectrometer and are reported in reciprocal centimeter (cm$^{-1}$). High resolution mass spectra were obtained using GCT-TOF instrument with EI or ESI source.

General procedure

4f $N$-oxide (0.39 mmol, 63.96mg), MsOH (0.36mmol, 34.60mg) and Cy$_3$(PPh$_3$)NTf$_2$ (11.1 mg, 0.015 mmol) were added to a solution of alkynes (0.30 mmol) 1 in chlorobenzene (6 mL) at room temperature. The reaction mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction typically took 8 h. Upon completion, the mixture was concentrated and the residue was purified by chromatography on silica gel (eluent: hexanes/ethyl acetate) to afford the desired products 2.
Characterization data for the products

2-oxo-2-phenylethyl methanesulfonate (2a)

Compound 2a was prepared in 79% yield according to the general procedure and its spectroscopic data match well with those reported.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J=8.0, 2H), 7.66 (t, J=8.0, 1H), 7.52 (t, J=8.0, 2H), 5.53 (s, 2H), 3.30 (s, 3H); ¹³C NMR (100 Mz, CDCl₃) δ 191.09, 134.41, 133.45, 129.04, 127.76, 70.19, 39.15; IR(neat): 2956, 1702, 1560, 1338, 1156, 801; HRMS(EI) m/z calcd. C₉H₁₀O₄S: 214.0300, Found: 214.0297.

2-oxo-2-(p-tolyl)ethyl methanesulfonate (2b)

Compound 2b was prepared in 81% yield according to the general procedure and its spectroscopic data match well with those reported.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J=8.0, 2H), 7.32 (d, J=8.0, 2H), 5.51 (s, 2H), 3.30 (s, 3H), 2.44 (s, 3H); ¹³C NMR (100 Mz, CDCl₃) δ 190.64, 145.55, 130.96, 129.70, 127.85, 70.17, 39.14, 21.74; IR(neat): 2952, 1699, 1556, 1304, 1168, 804; HRMS(EI) m/z calcd. C₁₀H₁₂O₄S: 228.0456, Found: 228.0452.

2-(4-(tert-butyl)phenyl)-2-oxoethyl methanesulfonate (2c)

Compound 2c was prepared in 84% yield according to the general procedure.¹ ¹H NMR (400 MHz, CDCl₃) δ 7.84 (d, J=8.0, 2H), 7.53 (d, J=8.0, 2H), 5.51 (s, 2H), 3.29 (s, 3H), 1.35 (s, 9H); ¹³C NMR (100 Mz, CDCl₃) δ 190.70, 158.48, 130.71, 127.71, 126.01, 70.27, 39.15, 35.28, 30.91; IR(neat): 2966, 1704, 1601, 1360, 1176, 805; HRMS(EI) m/z calcd. C₁₃H₁₈O₄S: 270.0926, Found: 270.0923.

2-(4-methoxyphenyl)-2-oxoethyl methanesulfonate (2d)
Compound 2d was prepared in 82% yield according to the general procedure and its spectroscopic data match well with those reported.\(^2\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.88 (d, \(J=8.0, 2\)H), 6.98 (d, \(J=8.0, 2\)H), 5.49 (s, 2H), 3.90 (s, 3H), 3.29 (s, 3H); \(^13\)C NMR (100Mz, CDCl\(_3\)) \(\delta\) 189.41, 164.37, 130.08, 126.19, 114.18, 70.10, 55.55, 39.11; IR(neat): 2948, 1701, 1556, 1342, 1166, 804; HRMS(EI) m/z cacl. C\(_{10}\)H\(_{12}\)O\(_5\)S: 224.0405, Found: 224.0401.

2-(4-fluorophenyl)-2-oxoethyl methanesulfonate (2e)

Compound 2e was prepared in 74% yield according to the general procedure and its spectroscopic data match well with those reported.\(^3\) \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96-7.93 (m, 2H), 7.21 (d, \(J=8.0, 2\)H), 5.49 (s, 2H), 3.30 (s, 3H); \(^13\)C NMR (100Mz, CDCl\(_3\)) \(\delta\) 189.59, 167.66, 165.11, 130.64, 130.54, 129.94, 129.91, 116.46, 116.24, 69.91, 39.13; IR(neat): 2917, 1699, 1561, 1336, 1172, 802; HRMS(EI) m/z cacl. C\(_9\)H\(_9\)FO\(_4\)S: 232.0206, Found: 232.0204.

2-(4-bromophenyl)-2-oxoethyl methanesulfonate (2f)

Compound 2f was prepared in 72% yield according to the general procedure.\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.76 (d, \(J=8.0, 2\)H), 7.67 (d, \(J=8.0, 2\)H), 5.47 (s, 2H), 3.28 (s, 3H); \(^13\)C NMR (100Mz, CDCl\(_3\)) \(\delta\) 191.00, 134.43, 133.21, 129.00, 127.69, 70.30, 39.09; IR(neat): 2920, 1701, 1561, 1338, 1169, 802; HRMS(EI) m/z cacl. C\(_9\)H\(_9\)BrO\(_4\)S: 291.9405, Found: 291.9403.

2-oxo-2-(4-(trifluoromethyl)phenyl)ethyl methanesulfonate (2g)
Compound 2g was prepared in 61% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl₃) δ 8.02 (d, $J$=8.0, 2H), 7.80 (d, $J$=8.0, 2H), 5.52 (s, 2H), 3.30 (s, 3H); $^{13}$C NMR (100Mz, CDCl₃) δ 190.45, 133.82, 130.23, 129.84, 128.26, 126.19, 126.15, 69.95, 39.22; IR(neat): 2924, 1698, 1554, 1344, 1163, 802; HRMS(EI) m/z cacl. C₁₀H₉F₃O₄S: 282.0174, Found: 282.0172.

methyl 4-(2-((methylsulfonyl)oxy)acetyl)benzoate(2h)

Compound 2h was prepared in 74% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl₃) δ 8.18 (d, $J$=8.0, 2H), 7.96 (d, $J$=8.0, 2H), 5.54 (s, 2H), 3.97 (s, 3H), 3.30 (s, 3H); $^{13}$C NMR (100Mz, CDCl₃) δ 190.76, 165.74, 136.35, 134.97, 130.13, 127.73, 70.21, 39.17; IR(neat): 2938, 1687, 1560, 1344, 1164, 800; HRMS(EI) m/z cacl. C₁₁H₂₂O₆S: 272.0355, Found: 272.0355.

2-oxo-2-(m-tolyl)ethyl methanesulfonate(2i)

Compound 2i was prepared in 72% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl₃) δ 7.69 (t, $J$=7.2, 2H), 7.46 (d, $J$=8.0, 2H), 7.40 (t, $J$=7.2, 1H), 5.51 (s, 2H), 3.29 (s, 3H), 2.43 (s, 3H); $^{13}$C NMR (100Mz, CDCl₃) δ 191.54, 139.05, 135.27, 133.37, 128.92, 128.25, 124.92, 70.28, 39.21, 21.30; IR(neat): 2951, 1700, 1554, 1302, 1165, 802; HRMS(EI) m/z cacl. C₁₀H₁₂O₄S: 228.0456, Found: 228.0453.

2-oxo-2-(3,4,5-trimethoxyphenyl)ethyl methanesulfonate(2j)
Compound 2j was prepared in 64% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.13 (s, 2H), 5.50 (s, 2H), 3.95-3.93 (m, 9H), 3.30 (s, 3H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 189.89, 153.22, 143.41, 128.30, 104.98, 70.09, 60.95, 56.24, 39.03; IR(neat): 2938, 1700, 1503, 1308, 1127, 808; HRMS(EI) m/z cacl. C$_{12}$H$_{16}$O$_7$S: 304.0617, Found: 304.0615.

2-oxo-4-phenylbutyl methanesulfonate(2k)

Compound 2k was prepared in 55% yield according to the general procedure and its spectroscopic data match well with those reported.$^1$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33-7.18 (m, 5H), 4.74 (s, 2H), 3.18 (s, 3H), 2.96 (t, $J$=8.0, 2H), 2.80 (t, $J$=8.0, 2H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 202.12, 139.90, 128.63, 128.25, 126.45, 71.57, 40.17, 38.73, 28.98; IR(neat): 2938, 1736, 1561, 1361, 1176, 805; HRMS(EI) m/z cacl. C$_{11}$H$_{14}$O$_4$S: 242.0613, Found: 242.0609.

2-oxopentyl methanesulfonate(2l)

Compound 2l was prepared in 58% yield according to the general procedure.$^1$ $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.80 (s, 2H), 3.22 (s, 3H), 2.46 (t, $J$=8.0, 2H), 1.65-1.59 (m, 2H), 1.35-1.23 (m, 10H), 0.87 (t, $J$=6.8, 3H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 203.08, 71.56, 38.91, 38.57, 31.74, 29.23, 29.04, 29.01, 23.07, 22.61, 14.09; IR(neat): 2929, 1732, 1556, 1364, 1172, 813; HRMS(EI) m/z cacl. C$_{11}$H$_{22}$O$_4$S: 250.1239, Found: 250.1235.

6-chloro-2-oxohexyl methanesulfonate(2m)
Compound 2m was prepared in 65% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.79 (s, 2H), 3.56-3.53 (m, 2H), 3.20 (s, 3H), 2.55-2.51 (m, 2H), 1.81-1.79 (m, 4H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 202.42, 71.45, 44.41, 38.75, 37.54, 31.49, 20.19; IR(neat): 2942, 1732, 1556, 1354, 1172, 805; HRMS(EI) m/z cacl. C$_7$H$_{13}$ClO$_4$S: 228.0223, Found: 228.0221.

6-((methylsulfonyl)oxy)-5-oxohexyl acetate(2n)

![6-((methylsulfonyl)oxy)-5-oxohexyl acetate](image)

Compound 2n was prepared in 52% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.78 (s, 2H), 4.07 (t, $J$=6.0, 2H), 3.20 (s, 3H), 2.52 (t, $J$=6.8, 2H), 2.05 (s, 3H), 1.73-1.64 (m, 4H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 202.52, 171.14, 71.46, 63.76, 38.80, 37.88, 27.79, 20.94, 19.42; IR(neat): 2933, 1732, 1556, 1343, 1172, 804; HRMS(EI) m/z cacl. C$_9$H$_{16}$O$_6$S: 252.0668, Found: 252.0665.

2-oxohexane-1,6-diyl dimethanesulfonate(2o)

![2-oxohexane-1,6-diyl dimethanesulfonate](image)

Compound 2o was prepared in 53% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.81 (s, 2H), 4.29 (t, $J$=6.0, 2H), 3.19 (s, 3H), 3.02 (s, 3H), 2.67 (t, $J$=8.0, 2H), 2.11-2.04 (m, 4H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 201.88, 71.44, 68.51, 38.61, 37.30, 34.01, 22.46; IR(neat): 2921, 1732, 1556, 1344, 1168, 805; HRMS(EI) m/z cacl. C$_8$H$_{16}$O$_7$S$_2$: 288.0337, Found: 288.0333.

4-(benzyloxy)-2-oxobutyl methanesulfonate(2p)

![4-(benzyloxy)-2-oxobutyl methanesulfonate](image)

Compound 2p was prepared in 57% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.29 (m, 5H), 4.75 (s, 2H), 4.48 (s, 2H), 3.48 (t, $J$=6.0, 2H), 3.20 (s, 3H), 2.48 (t, $J$=6.02H), 1.76-1.72 (m, 2H), 1.67-1.62 (m, 2H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 202.78, 138.23, 133.66, 130.14, 129.78, 128.29, 127.63, 72.90, 71.51, 69.68, 38.79, 38.13, 28.81, 19.97; IR(neat): 2921, 1716, 1550, 1302, 1168, 800; HRMS(EI) m/z cacl. C$_{14}$H$_{20}$O$_5$S: 300.1031, Found: 300.1028.
4-(allyloxy)-2-oxobutyl methanesulfonate(2q)

Compound 2q was prepared in 51% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 5.95-5.85 (m, 1H), 5.28-5.16 (m, 2H), 4.79 (s, 2H), 3.95-3.93 (m, 2H), 3.43 (t, $J$=8.0, 4.0, 2H), 3.20 (s, 3H), 2.51 (t, $J$=8.0, 2H), 1.74-1.71 (m, 2H), 1.64-1.59 (m, 2H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 202.72, 134.75, 116.89, 71.79, 71.52, 69.71, 38.79, 38.20, 28.85, 20.01; IR(neat): 2913, 1704, 1507, 1354, 1164, 760; HRMS(EI) m/z calcd. C$_{10}$H$_{18}$O$_5$S: 280.0875, Found: 280.0873.

2-(cyclohex-1-en-1-yl)-2-oxoethyl methanesulfonate(2r):

Compound 2r was prepared in 63% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.85 (s, 1H), 5.22 (s, 2H), 3.23 (s, 3H), 2.28-2.24 (m, 4H), 1.66-1.62 (m, 4H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 191.45, 142.11, 136.77, 69.62, 39.10, 26.04, 22.68, 21.44, 21.21; IR(neat): 2933, 1683, 1550, 1356, 1176, 821; HRMS(EI) m/z calcd. C$_9$H$_{14}$O$_4$S: 218.0613, Found: 218.0611.

2-cyclohexyl-2-oxoethyl methanesulfonate(2s)

Compound 2s was prepared in 66% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.89 (s, 2H), 3.21 (s, 3H), 2.47-2.41 (m, 1H), 1.85-1.79 (m, 4H), 1.25-1.22 (m, 6H); $^{13}$C NMR (100Mz, CDCl$_3$) $\delta$ 205.51, 70.56, 46.90, 38.91, 27.95, 25.45, 25.24; IR(neat): 2928, 1702, 1550, 1342, 1164, 801; HRMS(EI) m/z calcd. C$_9$H$_{16}$O$_4$S: 220.0769, Found: 220.0766.

2-cyclopropyl-2-oxoethyl methanesulfonate(2t)
Compound 2t was prepared in 67% yield according to the general procedure. $^1$H NMR (400 MHz, CDCl$_3$) δ 4.97 (s, 2H), 3.18 (s, 3H), 2.00-1.96 (m, 1H), 1.16-1.14 (m, 2H), 1.06-1.02 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 202.71, 72.12, 38.77, 17.03, 12.04; IR (neat): 2922, 1700, 1552, 1344, 1161, 801; HRMS (EI) m/z calcd. C$_6$H$_{10}$O$_4$S: 178.0300; Found: 178.0297.

References:

$^1$H and $^{13}$C NMR spectra
2e

[Chemical structure image]

[1H NMR spectrum image]
2j
MsO-\(\text{C}^\text{3}\)-OMs

2o
2r

The diagram shows a chemical structure with peaks at 3.00, 1.97, 0.99, 4.07, and 4.10 PPM.