Supporting Information for

A systematic study on the Z-enoate assisted Meyer-Schuster rearrangement

Prabhakararao Tharra*, and Beeraiah Baire*

*Department of Chemistry, Indian Institute of Technology Madras, Chennai, Tamilnadu, INDIA-600036.

E-mail: beeru@iitm.ac.in

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General procedure:

To a solution of the z-enoate-propargylic alcohol\(^1\) (1equi.) and the arene (5 equiv.) in dichloromethane (5 mL / 0.2 mmol, 0.04 \(M\)) under nitrogen atmosphere was added an acid (1.3 equi.). The reaction tube was stirred either at prescribed temperature (0 °C or 55 °C or higher temperature) for 1-8 h. After completion of the reaction (by TLC analysis), saturated NaHCO\(_3\), and DCM were added to reaction mixture and extracted with DCM. The combined organic layer was washed with the brine, dried (MgSO\(_4\)) and solvent was evaporated under reduced pressure. The crude material was purified by flash column chromatography using hexane-ethyl acetate mixture as eluent to yield the corresponding \(\alpha\)-OMs or \(\alpha\)-OTs or \(\alpha\)-Cl-enone derivatives and arene trapped products.

Ethyl 6-methyl-5-(methylsulfonyloxy)-4-oxohept-5-enoate (12)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 4.12\) (q, \(J = 7.2\) Hz, 2 H), 3.19 (s, 3 H), 2.99 (t, \(J = 6.7\) Hz, 2 H), 2.64 (t, \(J = 6.5\) Hz, 2 H), 2.15 (s, 3 H), 2.01 (s, 3 H) and 1.25 (t, \(J = 7.2\) Hz, 3 H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 194.9,172.9, 142.4, 139.8, 60.8, 38.6, 35.4, 28.3, 21.8, 20.6\) and 14.3 ppm.

IR (neat): 2980, 2936, 1735 (C=O), 1699 (C=O), 1625, 1408, 1358, 1348, 1200, 1107, 968 and 821 cm\(^{-1}\).

HR ESI-MS: [C\(_{11}\)H\(_{19}\)O\(_6\)S]\(^+\) = [M+H]\(^+\) requires 279.0897; found 297.0894.

TLC: \(R_f = 0.4\) (3:1, Hex/EtOAc)

Ethyl 6-methyl-4-oxo-5-(tosyloxy)hept-5-enoate (21)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.80\) (d, \(J = 8.4\) Hz, 2 H), 7.25 (d, \(J = 8.2\) Hz, 2 H), 4.12 (q, \(J = 7.2\) Hz, 2 H), 2.93 (t, \(J = 6.8\) Hz, 2 H), 2.58 (t, \(J = 6.6\) Hz, 2 H), 3.07 (s, 3 H), 2.47 (s, 3 H), 1.99 (s, 3 H) and 1.25 (t, \(J = 7.2\) Hz, 3 H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 195.8, 172.8, 145.9, 141.3, 140.2, 132.7, 130.1, 128.7, 60.7, 35.2, 28.4, 21.9, 20.7, 20.2\) and 14.3 ppm.
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IR (neat): 2980, 2936, 2927, 2858, 1731 (C=O), 1626, 1607, 1598, 1444, 1395, 1377, 1373, 1191, 1178, 1089, 997 and 812 cm⁻¹.

HR ESI-MS: [C₁₇H₂₅O₆S]⁺ = [M+H]⁺ requires 355.1210; found 355.1206.

TLC: Rₚ = 0.4 (4:1, Hex/EtOAc).

M. P.; 93-97 °C.

Ethyl 5-chloro-6-methyl-4-oxohept-5-enoate (22)

¹H NMR (400 MHz, CDCl₃): δ = 4.14 (q, J = 7.1 Hz, 2 H), 3.08 (t, J = 6.6 Hz, 2 H), 2.60 (t, J = 6.6 Hz, 2 H), 2.13 (s, 3 H), 2.02 (s, 3 H) and 1.26 (t, J = 7.2 Hz, 3 H) ppm

¹³C NMR (100 MHz, CDCl₃): δ = 196.4, 172.9, 145.8, 125.6, 60.7, 36.3, 28.6, 24.7, 22.8 and 14.3 ppm.

IR (neat): 2965, 2926, 2875, 2854, 1736 (C=O), 1691 (C=O), 1596, 1493, 1461, 1375, 1340, 1268, 1188, 1061, 965 and 819 cm⁻¹.

HR ESI-MS: [C₁₀H₁₆ClO₃]⁺ = [M+H]⁺ requires 219.0782; found 219.0779

TLC: Rₚ = 0.4 (18:1, Hex/EtOAc).

Ethyl 5-(4-hydroxyphenyl)-6-methyl-4-oxohept-5-enoate (13)

The hydroxyester¹ (40 mg, 0.22 mmol), phenol (77 mg, 0.82 mmol), in DCM (4 mL), and MsOH (27.4 mg, 0.02 mmol, 0.29 ml of 1.4 M in DCM) were stirred for 24 h at 0 °C to RT. Purification by flash column chromatography (8:1 hexanes:EtOAc) gave the 1,4-keto-ester 13 (18 mg, 0.065 mmol, 30%) as a pale yellow oil and α-OMs-enone 12 (22 mg, 0.08 mmol, 36%) as a pale yellow oil.

¹H NMR (400 MHz, CDCl₃): δ = 7.30-7.37 (m, 2 H), 7.00 (t, J = 7.3 Hz, 1 H), 6.89 (d, J = 7.8 Hz, 1 H), 4.09 (q, J = 7.1 Hz, 2 H), 2.75 (t, J = 6.6 Hz, 2 H), 2.49 (t, J = 6.6 Hz, 2 H), 2.22 (s, 3 H), 1.781 (s, 3 H) and 1.22 (t, J = 7.1 Hz, 3 H) ppm.
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$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 197.7, 173.0, 157.5, 143.0, 139.6, 130.1, 122.1, 114.7, 60.6, 35.1, 28.0, 20.7, 20.1$ and 14.3 ppm.

IR (neat): 2952, 2854, 1734 (OC=O), 1699 (C=O), 1611, 1548, 1442, 1364, 1312, 1281, 1155, 1105, 1054, 954 and 817 cm$^{-1}$.

HR ESI-MS: $[\text{C}_{16}\text{H}_{20}\text{O}_{4}\text{Na}]^+ = [\text{M+Na}]^+$ requires 299.1254; found 299.1258

TLC: $R_f = 0.4$ (8:1, Hex/EtOAc).

Ethyl 5-(2,3-dimethoxyphenyl)-6-methyl-4-oxohept-5-enoate (15)

The hydroxyester (40 mg, 0.22 mmol), 1,2-dimethoxybenzene (113 mg, 0.82 mmol), in DCM (4 mL), and MsOH (27.4 mg, 0.02 mmol, 0.29 ml of 1.4 $M$ in DCM) were stirred for 5 h at 0 °C to RT. Purification by flash column chromatography (6:1 hexanes:EtoAc) gave the 1,4-keto-ester 15 (24 mg, 0.075 mmol, 34%) as a pale yellow oil and $\alpha$-OMs-enone 12 (33 mg, 0.12 mmol, 54%) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 6.87$ (d, $J = 8.2$ Hz, 1 H), 6.71 (dd, $J = 8.2 & 1.8$ Hz, 1 H), 6.67 (m, 1 H), 4.09 (q, $J = 7.1$ Hz, 2 H), 3.89 (s, 3 H), 3.86 (s, 3 H), 2.57 (t, $J = 6.6$ Hz, 2 H), 2.49 (t, $J = 6.3$ Hz, 2 H), 2.02 (s, 3 H), 1.68 (s, 3 H) and 1.23 (t, $J = 7.1$ Hz, 3 H) ppm.

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 203.1, 173.1, 149.0, 148.3, 143.3, 137.9, 131.1, 122.3, 112.8, 111.3, 60.6, 56.0, 55.9, 37.4, 28.4, 23.6, 22.4$ and 14.3 ppm.

IR (neat): 2923, 2853, 1734 (OC=O), 1687 (C=O), 1618, 1568, 1514, 1445, 1374, 1312, 1282, 1153, 1112, 1034, 957 and 813 cm$^{-1}$.

HR ESI-MS: $[\text{C}_{18}\text{H}_{24}\text{O}_{5}\text{Na}]^+ = [\text{M+Na}]^+$ requires 343.1516; found 343.1516

TLC: $R_f = 0.4$ (6:1, Hex/EtOAc).

Ethyl 5-(2,4-dimethoxyphenyl)-6-methyl-4-oxohept-5-enoate (16)

The hydroxyester (30 mg, 0.16 mmol), 1,3-dimethoxybenzene (113 mg, 0.82 mmol), in DCM (3 mL), and MsOH (19.2 mg, 0.02 mmol, 0.14 ml of 1.4 $M$ in DCM) were stirred for 4 h at 0 °C to RT. Purification by
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flash column chromatography (6:1 hexanes:EtOAc) gave the 1,4-keto-ester 16 (35 mg, 0.11 mmol, 68%) as a pale yellow oil and α-OMs-enone 12 (6 mg, 0.02 mmol, 10%) as a pale yellow oil.

\textbf{1H NMR} (400 MHz, CDCl$_3$): \( \delta = 7.01 \) (d, \( J = 8.0 \) Hz, 1 H), 6.51-6.47 (m, 2 H), 4.11 (q, \( J = 7.1 \) Hz, 2 H), 3.83 (s, 3 H), 3.75 (s, 3 H), 2.51-2.45 (m, 4 H), 2.90 (s, 3 H), 1.64 (s, 3 H) and 1.23 (t, \( J = 7.1 \) Hz, 3 H) ppm.

\textbf{13C NMR} (100 MHz, CDCl$_3$): \( \delta = 202.3, 173.3, 160.8, 158.3, 145.9, 133.7, 132.4, 120.4, 104.6, 98.8, 60.5, 55.6, 55.5, 36.7, 28.6, 24.2, 22.6 \) and 14.3 ppm.

\textbf{IR} (neat): 2923, 2851, 1735 (OC=O), 1684 (C=O), 1608, 1578, 1504, 1443, 1372, 1302, 1272, 1155, 1114, 1033 and 800 cm$^{-1}$.

\textbf{HR ESI-MS}: \([C_{18}H_{24}O_5Na]^+ = [M+Na]^+\) requires 343.1516; found 343.1509

\textbf{TLC}: R$_f$ = 0.4 (6:1, Hex/EtOAc).

Ethyl 6-methyl-4-oxo-5-(2,4,6-trimethoxyphenyl)hept-5-enoate (18)

The hydroxyester (30 mg, 0.16 mmol), 1,3,5-trimethoxybenzene (138 mg, 0.82 mmol), in DCM (3 mL), and MsOH (19.2 mg, 0.02 mmol, 0.14 ml of 1.4 \( M \) in DCM) were stirred for 6 h at 0 °C to RT.

Purification by flash column chromatography (4:1 hexanes:EtOAc) gave the 1,4-keto-ester 18 (42 mg, 0.12 mmol, 75%) as a pale yellow oil.

\textbf{1H NMR} (500 MHz, CDCl$_3$): \( \delta = 6.15 \) (s, 2 H), 4.08 (q, \( J = 7.0 \) Hz, 2 H), 3.84 (s, 3 H), 3.75 (s, 6 H), 2.45 (s, 4 H), 2.14 (s, 3 H), 1.56 (s, 3 H) and 1.22 (t, \( J = 7.0 \) Hz, 3 H) ppm.

\textbf{13C NMR} (125 MHz, CDCl$_3$): \( \delta = 201.8, 173.5, 161.3, 158.8, 148.2, 128.4, 109.0, 90.6, 60.4, 55.8, 55.4, 36.2, 28.7, 24.3, 22.5 \) and 14.3 ppm.

\textbf{IR} (neat): 2932, 2854, 1734 (OC=O), 1689 (C=O), 1605, 1585, 1495, 1462, 1414, 1371, 1336, 1205, 1153, 1061, 952 and 813 cm$^{-1}$.

\textbf{HR ESI-MS}: \([C_{19}H_{26}O_6Na]^+ = [M+Na]^+\) requires 373.1622; found 373.1618
TLC: $R_f = 0.4$ (4:1, Hex/EtOAc).

**Ethyl 6-methyl-4-oxo-5-(thiophen-2-yl)hept-5-enoate (20)**

The hydroxyester (40 mg, 0.22 mmol), thiophene (69 mg, 0.82 mmol), in DCM (4 mL), and MsOH (27.4 mg, 0.02 mmol, 0.29 ml of 1.4 $M$ in DCM) were stirred for 2 h at 0 °C to RT. Purification by flash column chromatography (9:1 hexanes:EtOAc) gave the 1,4-keto-ester 20 (23 mg, 0.086 mmol, 39%) as a pale yellow oil and $\alpha$-OMs-enone 12 (24 mg, 0.086 mmol, 40%) as a pale yellow oil.

$^1$H NMR (500 MHz, CDCl$_3$): $\delta = 7.32$ (dd, $J = 5.2$ & 1.2 Hz, 1 H), 7.03 (dd, $J = 5.2$ & 3.4 Hz, 1 H), 6.84 (dd, $J = 3.4$ & 1.2 Hz, 1 H), 4.11 (q, $J = 7.1$ Hz, 2 H), 2.69 (t, $J = 6.6$ Hz, 2 H), 2.52 (t, $J = 6.6$ Hz, 2 H), 2.05 (s, 3 H), 1.81 (s, 3 H) and 1.23 (t, $J = 7.1$ Hz, 3 H) ppm.

$^{13}$C NMR (125 MHz, CDCl$_3$): $\delta = 202.1$, 173.0, 147.4, 139.1, 130.7, 127.9, 127.3, 126.4, 60.6, 37.1, 28.4, 24.0, 22.8 and 14.3 ppm.

IR (neat): 2932, 2853, 1735 (OC=O), 1697 (C=O), 1614, 1568, 1514, 1443, 1374, 1312, 1283, 1153, 1115, 1044, 954 and 819 cm$^{-1}$.

HR ESI-MS: $[C_{14}H_{19}O_3S]^+ = [M+Na]^+$ requires 267.1049; found 267.1042.

TLC: $R_f = 0.4$ (9:1, Hex/EtOAc).

**5-(4-Chlorophenyl)-3-methylpent-1-yn-3-ol (S$_1$)**

The ketone$^2$ (150 mg, 0.82 mmol), anhydrous THF (5 mL), ethynyl magnesium bromide (3.3 ml, 1.6 mmol, 0.5 M in THF) were stirred for 2 h at 0 °C. Purification by flash column chromatography (9:1 hexane:EtOAc) gave alcohol S$_1$ (160 mg, 0.78 mmol, 95%) as a color less oil.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.24$ (d, $J = 8.4$ Hz, 2 H), 7.15 (d, $J = 8.4$ Hz, 2 H), 2.85-2.80 (m, 2 H), 2.51 (s, 1 H), 2.04 (br s, 1H), 2.01-1.90 (m, 2 H) and 1.55 (s, 3 H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 140.4$, 131.8, 129.9, 128.7, 87.3, 72.1, 68.0, 45.1, 30.6 and 30.2 ppm.
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IR (neat): 3387, 3298, 2980, 2932, 2865, 1491, 1454, 1371, 1158, 1093, 1016, 907 and 661 cm\(^{-1}\).

HR ESI-MS: \([\text{C}_{12}\text{H}_{13}\text{ClNaO}_3]^+ = [\text{M+Na}]^+\) requires 231.0547; found 231.0540

TLC: \(R_f = 0.4\) (5:1, Hex/EtOAc)

(Z)-Ethyl 8-(4-chlorophenyl)-6-hydroxy-6-methyloct-2-en-4-ynoate (23)

Iodo-ester\(^3\) (223 mg, 0.99 mmol), alcohol \(S_1\) (170 mg, 0.83 mmol), dry THF (8 mL), dry DIPA (2 ml), CuI (23.5 mg, 0.12 mmol) and PdCl\(_2\)(PPh\(_3\))\(_2\) (5.8 mg, 0.008 mmol) were stirred for 12 h at 0 °C to RT. Purification by flash column chromatography (4:1 hexane:EtOAc) gave the hydroxyester 23 (225 mg, 0.74 mmol, 89%) as a pale yellow oil.

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.25-7.22\) (m, 2 H), 7.18-7.16 (m, 2 H), 6.16 (d, \(J = 11.5\) Hz, 1 H), 6.12 (d, \(J = 11.5\) Hz, 1 H), 4.22 (q, \(J = 7.1\) Hz, 2 H), 2.94-2.83 (m, 2 H), 2.07-1.95 (m, 2 H), 1.71 (br s, 1H), 1.60 (s, 3 H) and 1.30 (t, \(J = 7.1\) Hz, 3 H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 164.7, 140.6, 131.7, 130.0, 129.2, 128.6, 122.6, 104.8, 80.9, 68.6, 60.6\) (C-OH), 45.2, 30.6, 30.0 and 14.4 ppm.

IR (neat): 3439 (OH), 2981, 2935, 2864, 1712 (C=O), 1610, 1491, 1410, 1386, 1188, 1091, 1020, 816 and 665 cm\(^{-1}\).

HR ESI-MS: \([\text{C}_{17}\text{H}_{19}\text{ClNaO}_3]^+ = [\text{M+Na}]^+\) requires 329.0915; found 329.0902

TLC: \(R_f = 0.4\) (4:1, Hex/EtOAc)

Ethyl 8-(4-chlorophenyl)-6-methyl-5-(methylsulfonyloxy)-4-oxooct-5-enoate (25)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\text{Major isomer}: \delta = 7.27-7.23\) (m, 2 H), 7.17-7.14 (m, 2 H), 4.17-4.11 (m, 2 H), 3.15 (s, 3 H), 2.96-2.91 (m, 2 H), 2.82-2.71 (m, 4 H), 2.66-2.58 (m, 2 H), 1.93 (s, 3 H) and 1.27-1.23 (m, 3 H) ppm.
**Beeraiah-Meyer-Schuster rearrangement**

**ESI**

**1H NMR** (400 MHz, CDCl$_3$): Minor: $\delta = 7.27$-$7.23$ (m, 2 H), 7.17-$7.14$ (m, 2 H), 4.17-$4.11$ (m, 2 H), 3.19 (s, 3 H), 2.96-$2.91$ (m, 2 H), 2.82-$2.71$ (m, 4 H), 2.66-$2.58$ (m, 2 H), 2.15 (s, 3 H) and 1.27-$1.23$ (m, 3 H) ppm.

**13C NMR** (100 MHz, CDCl$_3$): $\delta = 195.0$, 194.8, 172.9, 172.8, 144.9, 140.2, 139.4, 132.1, 130.1, 129.9, 128.8, 128.7, 60.9, 60.8, 38.8, 38.5, 36.8, 35.6, 35.5, 35.2, 34.2, 32.8, 28.3, 28.2, 19.9, 18.7 and 14.3 ppm.

**IR** (neat): 2935, 2858, 1734 (OC=O), 1698 (C=O), 1611, 1563, 1524, 1442, 1384, 1322, 1293, 1152, 1115, 1054, 957 and 819 cm$^{-1}$.

**HR ESI-MS**: [C$_{18}$NaClH$_{23}$O$_6$S]$^+ = [M+Na]^+$ requires 425.0796; found 425.0791.

**TLC**: $R_f = 0.4$ (4:1, Hex/EtOAc).

**Ethyl 4-(7-chloro-2-methyl-3,4-dihyronaphthalen-1-yl)-4-oxobutanoate (24)**

**1H NMR** (400 MHz, CDCl$_3$): $\delta = 7.11$-$7.05$ (m, 2 H), 6.89 (d, $J = 1.8$ Hz, 1 H), 4.18 (q, $J = 7.1$ Hz, 2 H), 2.97 (t, $J = 6.5$ Hz, 2 H), 2.76 (t, $J = 8.1$ Hz, 2 H), 2.68 (t, $J = 6.5$ Hz, 2 H), 2.28 (t, $J = 7.8$ Hz, 2 H), 1.92 (s, 3 H) and 1.29 (t, $J = 7.1$ Hz, 3 H) ppm.

**13C NMR** (100 MHz, CDCl$_3$): $\delta = 206.6$, 172.7, 137.8, 134.9, 133.6, 133.0, 132.4, 128.9, 126.9, 123.6, 60.9, 40.0, 29.9, 28.1, 27.4, 20.8 and 14.4 ppm.

**IR** (neat): 2976, 2928, 2855, 1733 (OC=O), 1699 (C=O), 1595, 1483, 1433, 1399, 1372, 1262, 1206, 1158, 1098, 937 and 736 cm$^{-1}$.

**HR ESI-MS**: [C$_{17}$H$_{26}$ClO$_3$]$^+ = [M+H]^+$ requires 307.1095; found 307.1112

**TLC**: $R_f = 0.4$ (9:1, Hex/EtOAc)
References:


Beeraiah-Meyer-Schuster rearrangement

ESI
Beeraiah-Meyer-Schuster rearrangement

![NMR Spectrum of Compound 22](image)
Beeraiah-Meyer-Schuster rearrangement

ESI
Beeraiah-Meyer-Schuster rearrangement

![Chemical Structure](image)

![NMR Spectrum](image)
Beeraiah-Meyer-Schuster rearrangement
Beeraiah-Meyer-Schuster rearrangement

\[ \text{Cl-} \text{C}_7 \text{H}_5 \text{-C} \equiv \text{CH-} \text{OH} \]

\[ S_1 \]

\[ \begin{array}{c}
\text{Cl} \\
\text{C}_7 \text{H}_5 \\
\text{C} \equiv \text{CH-} \\
\text{OH} \\
\text{S}_1
\end{array} \]

ESI
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