Supporting Information

Regioselective Palladium$^{II}$ Catalyzed Desulfitative Heck-Type Reaction: To Access $\alpha$-Benzyl-$\beta$-Keto Esters from Baylis-Hillman Adducts with Sodium Sulfinates

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1. General Information:

All solvents and reagents were used, as received from the suppliers. TLC was performed on Merck Kiesel gel 60, F254 plates with the layer thickness of 0.25 mm. Column chromatography was performed on silica gel (100-200 mesh) using a gradient of ethyl acetate and hexane as mobile phase. Melting points were determined on a Fisher John’s melting point apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer RX-1 FT-IR system. ¹H NMR spectral data were collected at 300, 400 & 500 MHz, while ¹³C NMR were recorded at 75, 100, 150 MHz. ¹H NMR spectral data are given as chemical shifts in ppm followed by multiplicity (s- singlet; d- doublet; t- triplet; q- quartet; m- multiplet), number of protons and coupling constants. ¹³C NMR chemical shifts are expressed in ppm. HRMS (ESI) spectral data were collected using ORBITRAP High Resolution Mass Spectrometer. Starting materials were prepared as previously reported [Butyl-2-(hydroxy(p-tolyl)methyl)acrylate, ¹a Butyl-2-(hydroxy(4-nitrophenyl)methyl)acrylate, ¹b Butyl-2-((4bromophenyl)(hydroxy) methyl)acrylate, ¹a Butyl-2-(furan-2-yl(hydroxy)methyl)acrylate, ¹a Butyl-2-(hydroxy(phenyl)methyl)acrylate, ¹a Butyl-2-(hydroxy(4-methoxyphenyl)methyl)acrylate, ¹a Methyl-2-(hydroxy(phenyl)methyl)acrylate, ¹c Ethyl-2-(hydroxy(phenyl)methyl)acrylate ¹d].

2. General procedure for the synthesis of α-benzyl-β-keto esters from Baylis-Hillman adducts:

A mixture of sulfinic acid sodium salt (0.60 mmol), PdCl₂ (0.10 equiv), Baylis Hillman adduct (0.50 mmol), and CuCl₂ (1.0 equiv) was dissolved in 1,4-dioxane (3.0 mL) in a 10 mL RB flask. The mixture was vigorously stirred at 90 °C for 8 h. After cooling to room temperature, the reaction mixture was partitioned between ethyl acetate (25.0 mL) and water (25.0 mL) and filtered through a celite pad. The filtrate was transferred to a separatory funnel. The organic layer
was washed with water, and brine, dried over anhydrous Na₂SO₄ (s) and concentrated in vacuo. The residue was purified by column chromatography using a gradient of hexane and ethyl acetate (eluent system) to afford the pure product.

3. Analytical data for the products

**Butyl 2-benzyl-3-oxo-3-p-tolylpropanoate (1):**

![Butyl 2-benzyl-3-oxo-3-p-tolylpropanoate (1)](image)

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.158 g, 97%); ¹H NMR (300 MHz, CDCl₃); δ 7.88 (d, J = 8.3 Hz, 1H), 7.36 – 7.13 (m, 8H), 4.62 (t, J = 7.3 Hz, 1H), 4.05 (t, J = 6.5 Hz, 2H), 3.34 (d, J = 7.3 Hz, 2H), 2.42 (s, 3H), 1.56 – 1.40 (m, 2H), 1.18 (m, 2H), 0.83 (t, J = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 194.1, 169.5, 144.4, 138.5, 133.7, 129.4, 128.9, 128.8, 128.5, 126.6, 65.3, 56.1, 34.7, 30.4, 21.6, 18.8, 13.5 ppm; IR (Neat): 3026, 2960, 2930, 1733, 1681, 1606, 1454, 1273, 1215, 1181, 909, 748, 698, 666, 595 cm⁻¹; ESI-MS: m/z = 325 [M+H]^+, 347 [M+Na]^+. HRMS (ESI) calcd for C₂₁H₂₄O₃Na [M+Na]^+ 325.17976, found 325.17982.

**Butyl 2-(4-chlorobenzyl)-3-(4-cyanophenyl)-3-oxopropanoate (2):**

![Butyl 2-(4-chlorobenzyl)-3-(4-cyanophenyl)-3-oxopropanoate (2)](image)

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless solid (0.154 g, 83%). M.p. 76-80 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.06 – 7.99 (m, 2H), 7.80 – 7.73 (m, 2H), 7.30 – 7.22 (m, 2H), 7.20 – 7.12 (m, 2H), 4.56 (t, J = 7.4 Hz, 1H), 4.05 (t, J = 6.6 Hz, 2H), 3.32 (d, J = 7.4 Hz, 2H), 1.48 (m, 2H), 1.28 – 1.10 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 193.1, 168.4, 139.1,

**Butyl 2-(4-bromobenzyl)-3-(4-nitrophenyl)-3-oxopropanoate (3):**

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless solid (0.175 g, 81%). M.p. 89-92 °C; ¹H NMR (300 MHz, CDCl₃) δ 8.30 (d, J = 8.8 Hz, 2H), 8.08 (d, J = 8.8 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.3 Hz, 2H), 4.57 (t, J = 7.4 Hz, 1H), 4.04 (t, J = 6.6 Hz, 2H), 3.30 (t, J = 7.2 Hz, 2H), 1.52 – 1.40 (m, 2H), 1.26 – 1.10 (m, 2H), 0.82 (t, J = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 192.9, 168.4, 150.5, 140.6, 136.8, 131.7, 130.6, 129.5, 123.9, 120.9, 65.8, 56.5, 33.8, 30.3, 18.9, 13.5 ppm; IR (Neat): 3020, 1735, 1695, 1528, 1346, 1215, 1071, 1012, 931, 852, 743, 667, 624 cm⁻¹; ESI-MS: m/z = 434 [M+H]^+, 456 [M+Na]^+. HRMS (ESI) calcd for C₂₀H₂₀BrNO₅ [M+Na]^+ 456.0462, found 456.04010.

**Butyl 2-(4-bromobenzyl)-3-(4-methoxyphenyl)-3-oxopropanoate (4):**

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.194 g, 93%); ¹H NMR (300 MHz, CDCl₃) δ 8.01 – 7.91 (m, 2H), 7.41 – 7.36 (m, 2H), 7.12 (d, J = 8.4 Hz, 2H), 6.96 – 6.91 (m, 2H), 4.55 (t, J = 7.4 Hz, 1H), 4.05 (t, J = 6.6 Hz, 2H), 3.88 (s, 3H), 3.28 (d, J = 7.4 Hz, 2H), 1.54 – 1.41 (m, 2H), 1.18 (d, J = 14.8, Hz, 2H), 0.84 (t, J = 7.3 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 192.3,
Butyl 3-(4-bromophenyl)-2-(4-methylbenzyl)-3-oxopropanoate (5):

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4% ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.175 g, 87%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 8.5$ Hz, 1H), 7.85 − 7.78 (m, 2H), 7.63 − 7.56 (m, 2H), 7.43 (d, $J = 8.3$ Hz, 1H), 7.09 (q, $J = 8.2$ Hz, 2H), 4.55 (t, $J = 7.4$ Hz, 1H), 4.05 (t, $J = 6.6$ Hz, 2H), 3.30 (d, $J = 7.3$ Hz, 2H), 2.30 (s, 3H), 1.54 − 1.41 (m, 2H), 1.18 (dt, $J = 14.8$, 7.3 Hz, 2H), 0.84 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 193.6, 169.1, 136.2, 135.1, 132.1, 130.2, 130.1 129.2, 128.7, 127.1, 65.5, 56.3, 34.2, 30.3, 21.1, 18.9, 13.5 ppm; IR (Neat): 2959, 2926, 1735, 1688, 1584, 1515, 1455, 1378, 1271, 1220, 1172, 1070, 1008, 931, 841, 810, 772, 653, 571 cm$^{-1}$; ESI-MS: m/z = 403 [M+H$^+$], 425 [M+Na$^+$]. HRMS (ESI) calcd for C$_{21}$H$_{23}$O$_3$Br [M+Na$^+$] 425.07228, found 425.07176.

Ethyl 2-(4-bromobenzyl)-3-oxo-3-phenylpropanoate (6):

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 4-5% ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.167 g, 92%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.95 (d, $J = 7.8$ Hz, 2H), 7.57 (t, $J = 7.3$ Hz, 1H), 7.45 (t, $J = 7.7$ Hz, 2H), 7.37 (d, $J = 8.3$ Hz, 2H), 7.11 (d, $J = 8.3$ Hz, 2H), 4.58 (t, $J = 7.3$ Hz, 1H), 4.12 − 4.07 (t, 6.9 Hz, 2H), 3.28 (d, $J =$
7.3 Hz, 2H), 1.11 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.1, 169.1, 137.4, 136.1, 133.7, 131.6, 130.7, 128.8, 128.6, 120.5, 61.6, 55.9, 34.1, 13.9 ppm; IR (Neat): 3021, 2982, 2929, 2871, 1733, 1686, 1596, 1488, 1446, 1403, 1368, 1302, 1268, 1215, 1181, 1153, 1100, 966, 931, 852, 813, 746, 688, 665, 620 cm$^{-1}$; ESI-MS: m/z = 363 [M$+$H]$^+$, 385 [M$+$Na]$^+$. HRMS (ESI) calcd for C$_{18}$H$_{17}$BrO$_3$ [M$+$Na]$^+$ 385.02976, found 385.02978.

**Butyl 2-benzyl-3-(4-bromophenyl)-3-oxopropanoate (7)**

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 4-5 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.168 g, 87%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.86 – 7.75 (m, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.31 – 7.15 (m, 5H), 4.56 (t, J = 7.3 Hz, 1H), 4.02 (t, J = 15.1, 8.5 Hz, 2H), 3.32 (d, J = 7.4 Hz, 2H), (1.54 – 1.39 (m, 2H), 1.21 (m, 2H), 0.82 (t, J = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 193.5, 169.1, 138.2, 135.1, 132.1, 130.1, 128.8, 128.6, 126.7, 65.5, 56.2, 34.6, 30.4, 18.9, 13.5 ppm; IR (Neat): 2958, 2927, 1736, 1689, 1584, 1488, 1454, 1396, 1273, 1219, 1180, 1071, 1008, 940, 840, 771, 699 cm$^{-1}$; ESI-MS: m/z = 389 [M$+$H]$^+$, 411 [M$+$Na]$^+$. HRMS (ESI) calcd for C$_{20}$H$_{22}$O$_3$Br [M$+$H]$^+$ 389.07528, found 389.07468.

**Ethyl 2-(4-chlorobenzyl)-3-oxo-3-phenylpropanoate (8)**

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 4-5 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.144 g, 91%); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.96 (d, J = 7.8 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.45 (t, J = 7.6
Hz, 2H), 7.27 – 7.13 (m, 4H), 4.59 (t, J = 7.3 Hz, 1H), 4.10 (t, J = 6.7 Hz, 2H), 3.29 (d, J = 7.3 Hz, 2H), 1.11 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 194.2, 169.1, 136.9, 136.1, 133.7, 132.5, 130.4, 128.7, 128.6, 61.7, 55.9, 34.1, 13.9 ppm; IR (Neat): 3063, 3024, 2981, 2927, 2852, 1732, 1684, 1596, 1492, 1446, 1408, 1368, 1324, 1267, 1227, 1180, 1151, 1092, 1058, 1015, 966, 931, 896, 851, 815, 739, 688, 639, 600 cm$^{-1}$; ESI-MS: m/z = 317 [M+H]$^+$, 339 [M+Na]$^+$. HRMS (ESI) calcd for C$_{18}$H$_{17}$ClO$_3$ [M+Na]$^+$ 339.34190, found 339.34186.

**Butyl 2-(4-bromobenzyl)-3-oxo-3-(thiophen-2-yl)propanoate (9):**

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.155 g, 79%); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.76 (dd, J = 3.9, 1.0 Hz, 1H), 7.68 (dd, J = 5.0, 1.0 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.14 – 7.07 (m, 3H), 4.45 – 4.35 (t, J = 7.3 Hz, 1H), 4.06 (t, J = 6.6 Hz, 2H), 3.28 (d, J = 7.4 Hz, 2H), 1.49 (ddd, J = 14.0, 8.8, 6.6 Hz, 2H), 1.29 – 1.12 (m, 2H), 0.84 (t, J = 7.5 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 186.5, 168.7, 143.3, 137.3, 135.1, 133.1, 131.6, 130.7, 128.3, 120.6, 65.6, 57.2, 34.1, 30.4, 18.9, 13.5 ppm; IR (Neat): 3019, 1733, 1664,1413, 1215, 1070, 1012, 744, 667 cm$^{-1}$; ESI-MS: m/z = 395 [M+H]$^+$, 417 [M+Na]$^+$. HRMS (ESI) calcd for C$_{18}$H$_{19}$O$_3$BrS [M+Na]$^+$ 417.01053, found 417.01019.

**Butyl 2-benzyl-3-(furan-2-yl)-3-oxopropanoate (10):**

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.130 g, 86%); $^1$H NMR (300 MHz, CDCl$_3$) δ 7.60 (dd, J = 1.6, 0.7 Hz, 1H), 7.34 – 7.09 (m, 6H), 6.54 (dd, J = 3.6, 1.7 Hz, 1H), 4.43 (t, J = 7.5 Hz, 1H),
Butyl 3-(furan-2-yl)-2-(4-methylbenzyl)-3-oxopropanoate (11): Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.127 g, 80%); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.60 (dd, \(J = 1.6, 0.7\) Hz, 1H), 7.29 – 7.23 (m, 2H), 7.10 (dd, \(J = 17.7, 8.1\) Hz, 4H), 6.54 (dd, \(J = 3.6, 1.7\) Hz, 1H), 4.40 (t, \(J = 7.5\) Hz, 1H), 4.08 (t, \(J = 6.6\) Hz, 2H), 3.29 (d, \(J = 7.4\) Hz, 2H), 2.30 (s, 3H), 1.51 (dt, \(J = 14.6, 6.7\) Hz, 2H), 1.31 – 1.16 (m, 2H), 0.85 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 183.2, 169.1, 152.1, 146.9, 136.1, 135.2, 129.2, 128.8, 118.5, 112.5, 65.3, 33.7, 30.4, 21.1, 18.9, 13.6 ppm; IR (Neat): 2960, 2928, 1733, 1676, 1566, 1515, 1464, 1391, 1216, 1155, 1015, 880, 771, 667, 592 cm\(^{-1}\); ESI-MS: m/z = 315 [M+H]\(^+\), 337 [M+Na]\(^+\). HRMS (ESI) calcd for C\(_{19}\)H\(_{22}\)O\(_4\) [M+Na]\(^+\) 337.14103, found 337.14072.

Butyl 2-benzyl-3-oxo-3-(thiophen-2-yl)propanoate (12): Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a pale yellow liquid oil (0.145 g, 92%); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.79 – 7.66 (d, \(J = 7.1\) Hz, 1H), 7.68 (d, \(J = 4.9\) Hz, 1H), 7.31 – 7.18 (m, 5H), 7.13 (dd, \(J = 8.6, 4.6\) Hz, 1H), 4.47 (t, \(J = 7.4\) Hz, 1H), 4.08 (t, \(J = 6.6\) Hz, 2H), 3.35 (d, \(J = 7.4\) Hz, 2H), 1.58 – 1.45 (m, 2H), 1.30 – 1.14
(m, 2H), 0.85 (t, J = 7.4 Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 186.8, 169.1, 143.2, 138.5, 134.9, 133.1, 128.9, 128.5, 128.3, 126.7, 65.5, 57.4, 34.7, 30.4, 18.9, 13.6 ppm; IR (Neat): 2959, 2928, 1732, 1661, 1516, 1454, 1412, 1356, 1274, 1221, 1148, 1063, 847, 772, 726, 699, 595 cm$^{-1}$; ESI-MS: m/z = 317 [M+H]$^+$, 339 [M+Na]$^+$. HRMS (ESI) calcd for C$_{18}$H$_{20}$O$_3$S [M+Na]$^+$ 339.10254, found 325.10177.

**Butyl 2-benzyl-3-oxooctanoate (13):**

![Butyl 2-benzyl-3-oxooctanoate](image)

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.145 g, 96%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26 (t, J = 7.3 Hz, 2H), 7.21 – 7.13 (m, 3H), 4.08 (t, J = 6.6 Hz, 2H), 3.78 (t, J = 7.6 Hz, 1H), 3.15 (t, J = 7.2, Hz, 2H), 2.51 (dt, J = 17.1, 7.4 Hz, 1H), 2.32 (dd, J = 17.4, 7.3 Hz, 1H), 1.58 – 1.45 (m, 4H), 1.34 – 1.13 (m, 6H), 0.86 (dt, J = 19.1, 7.3 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 204.8, 169.3, 138.3, 128.8, 128.5, 126.6, 65.3, 60.5, 42.8, 34.1, 31.1, 30.5, 29.7, 23.1, 22.4, 19.1, 13.8, 13.6 ppm; IR (Neat): 3029, 2958, 2929, 2871, 2255, 1738, 1713, 1604, 1495, 1456, 1360, 1312, 1243, 1164, 1064, 1029, 963, 908, 729, 699, 648, 594 cm$^{-1}$; ESI-MS: m/z = 305 [M+H]$^+$, 327 [M+Na]$^+$. HRMS (ESI) calcd for C$_{19}$H$_{28}$O$_3$ [M+Na]$^+$ 327.19307, found 327.19208.

**Butyl 2-benzyl-3-oxodecanoate (14):**

![Butyl 2-benzyl-3-oxodecanoate](image)

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product
as a colourless liquid (0.156 g, 94%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.26 (t, $J = 7.3$ Hz, 2H), 7.18 (dd, $J = 16.5$, 7.6 Hz, 3H), 4.08 (t, $J = 6.6$ Hz, 1H), 3.78 (t, $J = 7.6$ Hz, 2H), 3.15 (dd, $J = 7.5$, 4.2 Hz, 2H), 2.51 (dt, $J = 17.1$, 7.3 Hz, 1H), 2.32 (dt, $J = 17.2$, 7.2 Hz, 1H), 1.59 – 1.46 (m, 4H), 1.33 – 1.17 (m, 10H), 0.88 (dt, $J = 11.5$, 7.3 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 204.8, 169.2, 138.3, 128.8, 128.5, 126.6, 65.3, 60.5, 42.9, 34.1, 31.6, 30.5, 28.8, 28.9, 23.3, 22.6, 19.1, 14.1, 13.6 ppm; IR (Neat): 2957, 2927, 2856, 2255, 1740, 1713, 1604, 1495, 1456, 1376, 1310, 1262, 1202, 1163, 1065, 1028, 907, 729, 699, 648 cm$^{-1}$; ESI-MS: m/z = 333 [M+H]$^+$, 355 [M+Na]$^+$. HRMS (ESI) calcd for C$_{21}$H$_{32}$O$_3$ [M+Na]$^+$ 355.22437, found 355.22340.

Butyl 3-(4-cyanophenyl)-2-(4-methylbenzyl)-3-oxopropanoate (15):

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.152 g, 87%); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.99 (d, $J = 8.3$ Hz, 2H), 7.72 (d, $J = 8.3$ Hz, 2H), 7.06 (q, $J = 8.1$ Hz, 2H), 4.55 (t, $J = 7.3$ Hz, 1H), 4.04 (t, $J = 6.6$ Hz, 2H), 3.29 (d, $J = 7.3$ Hz, 2H), 2.27 (s, 3H), 1.45 (dt, $J = 13.3$, 6.6 Hz, 2H), 1.21 – 1.11 (m, 2H), 0.82 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 193.6, 168.7, 139.4, 136.4, 134.7, 132.5, 129.3, 128.9, 128.7, 117.7, 116.6, 65.6, 56.6, 34.2, 30.3, 21.1, 18.8, 13.5 ppm; IR (Neat): 3021, 2960, 2930, 2232, 1734, 1692, 1515, 1460, 1404, 1269, 1218, 1113, 1063, 1018, 931, 850, 808, 770, 667 cm$^{-1}$; ESI-MS: m/z = 350 [M+H]$^+$, 372 [M+Na]$^+$. HRMS (ESI) calcd for C$_{22}$H$_{23}$O$_3$N [M+Na]$^+$ 372.15701, found 372.15659.

Butyl 2-benzyl-3-(4-methoxyphenyl)-3-oxopropanoate (16):

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl
acetate in hexane as eluent) to afford the title product as a colourless liquid (0.156 g, 92%); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.93 (d, $J = 8.8$ Hz, 2H), 7.27 – 7.11 (m, 5H), 6.88 (d, $J = 8.8$ Hz, 2H), 4.50 (t, $J = 7.7$ Hz, 1H), 4.06 – 3.98 (t, $J = 6.8$ Hz, 2H), 3.85 (s, 3H), 3.30 – 3.26, (d, $J = 3.4$ Hz, 2H), 1.51 – 1.43 (m, 2H), 1.24 – 1.17 (m, 2H), 0.84 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 191.9, 169.1, 163.6, 138.6, 130.9, 129.3, 128.8, 128.4, 126.4, 113.7, 96.2, 64.9, 55.8, 55.2, 34.7, 30.4, 29.7, 18.9, 13.6 ppm; IR (Neat): 2959, 2927, 2871, 1732, 1676, 1575, 1510, 1456, 1420, 1310, 1258, 1222, 1116, 1062, 1026, 968, 940, 840, 698, 635, 600, 563 cm$^{-1}$; ESI-MS: m/z = 353 $[M+H]^+$, 3375 $[M+Na]^+$. HRMS (ESI) calcd for C$_{23}$H$_{29}$O$_3$ $[M+H]^+$ 353.21112, found 356.21115.

Butyl 2-benzyl-3-(4-nitrophenyl)-3-oxopropanoate (17):

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless solid (0.143 g, 80%). M.p. 86-88 °C; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.27 (d, $J = 8.8$ Hz, 2H), 8.06 (d, $J = 8.8$ Hz, 2H), 7.33 – 7.12 (m, 5H), 4.62 (t, $J = 7.4$ Hz, 1H), 4.05 (t, $J = 6.6$ Hz, 2H), 3.36 (d, $J = 7.4$ Hz, 2H), 1.56 – 1.37 (m, 2H), 1.28 – 1.09 (m, 2H), 0.82 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 193.4, 168.6, 150.5, 140.8, 137.8, 129.5, 128.9, 128.7, 126.6, 123.8, 65.7, 56.6, 34.5, 30.3, 18.8, 13.5 ppm; IR (Neat): 3020, 1736, 1696, 1529, 1346, 1214, 742, 667 cm$^{-1}$; ESI-MS: m/z = 356 $[M+H]^+$, 378 $[M+Na]^+$. HRMS (ESI) calcd for C$_{20}$H$_{22}$O$_5$N $[M+H]^+$ 356.14925, found 356.14947.

Butyl 2-benzyl-3-oxo-3-o-tolylpropanoate (18):

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in
hexane as eluent) to afford the title product as a colourless liquid (0.127 g, 78%); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.55 (d, $J = 7.7$ Hz, 1H), 7.37 (dd, $J = 10.9$, 4.1 Hz, 2H), 7.27 – 7.17 (m, 5H), 7.01 (d, $J = 6.9$ Hz, 1H), 4.54 (t, $J = 7.5$ Hz, 1H), 4.17 (t, $J = 6.5$ Hz, 2H), 3.33 (d, $J = 6.4$ Hz, 2H), 2.44 (s, 3H), 1.55 – 1.41 (m, 2H), 1.28 – 1.12 (m, 2H), 0.87 – 0.83 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 198.1, 169.4, 138.4, 131.9, 131.6, 128.9, 128.5, 128.3, 126.6, 125.6, 65.2, 58.6, 34.7, 30.4, 20.9, 18.8 13.6 ppm; IR (Neat): 3023, 2960, 2929, 1733, 1690, 1606, 1454, 1258, 1216, 1160, 1061, 934, 909, 748, 666, cm$^{-1}$; ESI-MS: m/z = 325 [M+H]$^+$, 347 [M+Na]$^+$. HRMS (ESI) calcd for C$_{21}$H$_{25}$O$_3$ [M+H]$^+$ 325.17982, found 325.17970.

**Ethyl 2-(4-methylbenzyl)-3-oxo-3-phenylpropanoate (19)$^{2a}$:**

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 4-5 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.140 g, 95%); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.02 – 7.90 (d, $J = 7.5$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.44 (t, $J = 7.7$ Hz, 2H), 7.12 (d, $J = 7.9$ Hz, 2H), 7.06 (d, $J = 7.8$ Hz, 2H), 4.60 (t, $J = 7.3$ Hz, 1H), 4.10 (t, $J = 7.1$ Hz, 2H), 3.32 – 3.26 (d, $J = 6.2$ Hz, 1H), 2.29 (s, 3H), 1.12 (t, $J = 7.1$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.6, 169.3, 136.2, 136.2, 135.3, 133.5, 129.2, 128.8, 128.67, 61.5, 56.3, 34.3, 21.1, 13.9 ppm; IR (Neat): 2981, 2924, 2854, 2254, 1733, 1685, 1597, 1515, 1447, 1369, 1268, 1217, 1182, 1152, 1111, 1023, 906, 852, 808, 728, 689, 667, 649, 604 cm$^{-1}$; ESI-MS: m/z = 297 [M+H]$^+$, 319 [M+Na]$^+$. HRMS (ESI) calcd for C$_{19}$H$_{20}$O$_3$ [M+Na]$^+$ 319.13047, found 319.12958.

**Methyl 2-(4-methylbenzyl)-3-oxo-3-phenylpropanoate (20)$^{1d}$:**

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl
acetate in hexane as eluent) to afford the title product as a colourless liquid (0.125 g, 89%); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.95 (d, \(J = 7.3\) Hz, 2H), 7.55 (d, \(J = 7.3\) Hz, 1H), 7.44 (t, \(J = 7.5\) Hz, 2H), 7.15 – 7.01 (m, 4H), 4.63 (t, \(J = 7.3\) Hz, 1H), 3.63 (s, 3H), 3.29 (dd, \(J = 7.0, 3.3\) Hz, 2H), 2.28 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 194.5, 169.8, 136.2, 136.1, 135.3, 133.6, 129.3, 128.7, 128.4, 56.1, 52.5, 34.4, 21.1 ppm; IR (Neat): 2924, 2254, 1737, 1686, 1596, 1581, 1515, 1446, 1329, 1273, 1231, 1148, 904, 809, 723, 648, 584 cm\(^{-1}\); ESI-MS: m/z = 283 [M+H]\(^+\), 305 [M+Na]\(^+\). HRMS (ESI) calcd for C\(_{18}\)H\(_{18}\)O\(_3\) [M+Na]\(^+\) 305.11482, found 305.11386.

**Butyl 2-benzyl-3-(4-isopropylphenyl)-3-oxopropanoate (21):**

![Butyl 2-benzyl-3-(4-isopropylphenyl)-3-oxopropanoate (21)](image)

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.161 g, 92%); \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.91 (d, \(J = 8.3\) Hz, 2H), 7.23 (ddd, \(J = 10.6, 8.3, 5.3\) Hz, 7H), 4.61 (t, \(J = 7.3\) Hz, 1H), 4.03 (t, \(J = 6.5\) Hz, 2H), 3.32 (d, \(J = 7.3\) Hz, 2H), 2.94 (m, 1H), 1.52 – 1.38 (m, 2H), 1.25 (d, \(J = 6.9\) Hz, 6H), 1.14 (d, \(J = 7.4\) Hz, 2H), 0.80 (t, \(J = 7.3\) Hz, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 193.9, 169.5, 155.2, 138.5, 134.1, 128.9, 128.5, 126.8, 126.6, 65.3, 56.1, 34.7, 34.3, 30.4, 29.7, 23.6, 18.9, 13.6 ppm; IR (Neat): 2962, 1733, 1681, 1604, 1457, 1273, 1217, 1057, 907, 847, 728, 698, 667 cm\(^{-1}\); ESI-MS: m/z = 353 [M+H]\(^+\), 375 [M+Na]\(^+\). HRMS (ESI) calcd for C\(_{23}\)H\(_{29}\)O\(_3\) [M+H]\(^+\) 353.21112, found 325.21115.

**Butyl 2-benzyl-3-oxo-3-phenylpropanoate (22):**

![Butyl 2-benzyl-3-oxo-3-phenylpropanoate (22)](image)

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4 % ethyl acetate in
hexane as eluent) to afford the title product as a colourless liquid (0.143 g, 92%); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 7.3$ Hz, 2H), 7.57 (dd, $J = 13.7$, 6.5 Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.30 – 7.16 (m, 5H), 4.63 (t, $J = 7.3$ Hz, 1H), 4.03 (t, $J = 6.6$ Hz, 2H), 3.33 (d, $J = 7.3$ Hz, 2H), 1.53 – 1.38 (m, 2H), 1.32 – 1.09 (m, 2H), 0.80 (t, $J = 7.3$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.4, 169.3, 138.5, 136.3, 133.5, 128.9, 128.6, 128.7, 128.5, 126.6, 65.6, 56.2, 34.7, 30.4, 18.8, 13.5 ppm; IR (Neat); 2959, 2929, 1733, 1684, 1450, 1220, 1181, 1148, 1078, 940, 772, 688, 576 cm$^{-1}$; ESI-MS: m/z = 311 [M+H]$^+$, 333 [M+Na]$^+$. HRMS (ESI) calcd for C$_{20}$H$_{23}$O$_3$ [M+H]$^+$ 311.16417, found 325.16400.

Butyl-2-(4-methylbenzyl)-3-oxo-3-phenylpropanoate (23)

Following the general procedure, the residue was purified by column chromatography (silica gel 100-200 mesh, 2-4% ethyl acetate in hexane as eluent) to afford the title product as a colourless liquid (0.154 g, 95%); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.96 (d, $J = 7.4$ Hz, 2H), 7.56 (t, $J = 7.3$ Hz, 1H), 7.44 (t, $J = 7.6$ Hz, 2H), 7.09 (dd, $J = 18.0$, 8.0 Hz, 4H), 4.60 (t, $J = 7.3$ Hz, 1H), 4.03 (t, $J = 6.6$ Hz, 2H), 3.29 (d, $J = 7.3$ Hz, 2H), 2.28 (s, 3H), 1.52 – 1.40 (m, 2H), 1.16 (dt, $J = 14.7$, 7.3 Hz, 2H), 0.80 (t, $J = 7.3$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.45, 169.38, 136.18, 136.08, 135.30, 133.44, 129.16, 128.73, 128.62, 65.27, 56.29, 34.23, 30.33, 20.97, 18.83, 13.51; (IR, Neat): 3021, 1733, 1687, 1515, 1448, 1213, 907, 728 cm$^{-1}$; HRMS (ESI): Calculated for [C$_{21}$H$_{24}$O$_3$ + Na]$^+$ 347.1617; Found 347.1609.
4. References:

1)  

2)  

5. Copies of $^1$H and $^{13}$C NMR Spectra for compounds
\begin{align*}
\text{Compound} & \quad \text{Shift} \\
10 & \quad 7.60 \\
 & \quad 7.22 \\
 & \quad 7.76 \\
 & \quad 7.22 \\
 & \quad 7.26 \\
 & \quad 7.22 \\
 & \quad 7.15 \\
 & \quad 6.85 \\
 & \quad 6.54 \\
 & \quad 6.53 \\
\end{align*}