Electronic Supplementary Information (ESI)

"N-Heterocyclic Carbene Catalyzed highly regioselective oxo-acyloxylation of

alkenes: a facile entry to α-acyloxy carbonyls"

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1. General Information

Solvents were purified and dried by standard procedures before use. IR spectra were recorded on a Perkin-Elmer model 683 B and absorption is expressed in cm⁻¹. ¹H NMR and ¹³C NMR spectra were recorded on Brucker AC-200 spectrometer unless mentioned otherwise. Purification was done using column chromatography (100-200 mesh). ESI-MS were recorded on a Thermo Finnigan LCQ Advantage spectrometer in ESI mode with a spray voltage of 4.8 kV. All chemicals are purchased from Sigma-Aldrich and used without further purification.

2. Experimental section

2.1. General experimental procedure:

To a stirred solution of alkene (5 mmol) in dry DMSO (35 mL), NBS (5 mmol), *N*-heterocyclic carbene precursor **1g** (10 mol %) and Et₃N (6 mmol), aromatic aldehyde (5.5 mmol) was added and the reaction mixture was then stirred at 25 °C under an O₂ atmosphere. After completion of the reaction as monitored by TLC, it was quenched with H₂O (50 mL) at 0 °C. It was then extracted with EtOAc (3 x 50 mL) followed by washing with brine (3x50 mL) and the combined organic layers were dried over anhydrous Na₂SO₄. Removal of solvent gave the crude product, which was purified by column chromatography over silica gel using pet ether/EtOAc (9:1) as eluent to obtain α -acyloxy carbonyl compounds **4a-v** in high purity.

2-Oxo-2-phenylethyl 4-nitrobenzoate (4a): Yield: 92%, colorless solid, Mp: 123-124 °C ; **IR** (Nujol, cm⁻¹): 719, 1104, 1229, 1294, 1376, 1462, 1524, 1598, 1696, 1727, 275, 2840, 2923; ¹H **NMR** (200 MHz, CDCl₃): δ 5.64 (s, 2H), 7.51 - 7.55 (m, 2H), 7.63 - 7.65 (m, 1H), 7.97 (d, J = 8.5 Hz, 2H), 8.33 (s, 4H); ¹³C **NMR** (50 MHz, CDCl₃) : δ 66.9, 123.4, 127.7, 128.9, 130.9, 133.8, 134.0, 134.7, 150.6, 164.0, 191.0: **HRMS** (**ESI**): [M+H]⁺ calcd for C₁₅H₁₁NO₅+H: 286.0715; found: 286.0726.

2-(4-Methylphenyl)-2-oxoethyl 4-nitrobenzoate (4b): Yield: 77%, colorless solid, Mp: 114-115 °C; IR (Nujol, cm⁻¹): 713, 1135, 1231, 1289, 1374, 1459, 1525, 1604, 1692, 1725, 2840, 2923; ¹H NMR (200 MHz, CDCl₃): δ 2.46 (s, 3H), 5.62 (s, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 8.33 (s, 4H); ¹³C NMR (50 MHz, CDCl₃): δ 21.8, 66.9, 123.5, 127.8, 129.6, 131.1, 131.5, 134.8, 145.1, 150.7, 164.1, 190.6; HRMS (ESI): [M+H]⁺ calcd for: C₁₆H₁₃NO₅+H : 300.0872; found: 300.0881.

2-(4-Bromophenyl)-2-oxoethyl 4-nitrobenzoate (4c): Yield: 71%, colorless solid, Mp: 117-118 °C; **IR** (CHCl₃, cm⁻¹): 717, 967, 1106, 1124, 1346, 1521, 1701, 1723, 2850, 2920; ¹H NMR (200 MHz, CDCl₃): δ 5.58 (s, 2H), 7.67 (m, J = 8.5 Hz, 2H), 7.83 (m, J = 8.5 Hz, 2H), 8.32 (s, 4H); ¹³C NMR (100 MHz, CDCl₃) : δ 66.7, 123.6, 129.2, 129.5, 131.1, 132.4, 132.6, 134.6, 150.8, 164.0, 190.0; **HRMS (ESI)**: [M+H]⁺ calcd for C₁₅H₁₀BrNNaO₅+H: 363.9820; found: 363.9834.

2-(4-Fluorophenyl)-2-oxoethyl 4-nitrobenzoate (4d): Yield: 79%, colorless solid, Mp:117-118 °C; IR (CHCl₃, cm⁻¹): 717, 871, 1131, 1155, 1231, 1320, 1521, 1595, 1698, 1722, 1746; ¹H
NMR (400 MHz, CDCl₃): δ 5.59 (s, 2H), 7.21 (t, J = 8.6 Hz, 2H), 8.01 (dd, J = 8.6, J = 5.0 Hz, 2H), 8.32 (d, J = 2.7 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 66.7, 116.1, 116.4, 130.5, 130.5,

131.1, 134.6, 150.8, 164.0, 165.0, 167.5, 189.3; **HRMS (ESI)**: $[M+H]^+$ calcd for $C_{15}H_{10}FNO_5+H$: 304.0621; found: 304.0627.

2-(4-Acetoxyphenyl)-2-oxoethyl 4-nitrobenzoate (4e): Yield: 82%, colorless solid, Mp: 128-129 °C; **IR** (Nujol, cm⁻¹): 716, 1166, 1212, 1294, 1374, 1459, 1525, 1596, 1690, 1717, 1753, 2846, 2917; ¹**H NMR** (200 MHz, CDCl₃): δ 2.35 (s, 3H), 5.61 (s, 2H), 7.26 (d, *J* = 8.6 Hz, 2H), 8.01 (d, *J* = 8.6 Hz, 2H), 8.32 (s, 4H); ¹³**C NMR** (100 MHz, CDCl₃): δ 21.0, 66.7, 122.2, 123.5, 129.3, 131.0, 131.3, 134.6, 150.6, 155.0, 164.0, 168.4, 189.9; **HRMS (ESI)**: [M+H]⁺ calcd for C₁₇H₁₃NO₇+H: 344.0770; found: 344.0778.

2-(3, 4 Dimethoxyphenyl)-2-oxoethyl 4-nitrobenzoate (4f): **Yield**: 74%, colorless solid, Mp: 162-163 °C; **IR** (Nujol, cm⁻¹): 720, 1021, 1131, 1255, 1376, 1460, 1524, 1684, 1725, 2855, 2925; ¹**H NMR** (200 MHz, CDCl₃): δ 3.95 (s, 3H), 3.98 (s, 3H), 5.60 (s, 2H), 6.92 (d, *J* = 8.3 Hz, 1H), 7.51 - 7.54 (m, 2H), 8.33 (s, 4H); ¹³**C NMR** (100 MHz, CDCl₃): δ 55.9, 56.0, 66.6, 110.0, 110.1, 122.1, 123.6, 127.1, 131.0, 134.9, 149.5, 150.8, 154.1, 164.1, 189.5; **HRMS (ESI)**: [M+H]⁺ calcd for C₁₇H₁₅NO₇+H: 346.0922; found: 346.0927.

1-Oxo-2, 3-dihydro-1H-inden-2-yl 4-nitrobenzoate (4g): Yield: 72%, colorless solid, Mp: 199-200 °C ; **IR** (Nujol, cm⁻¹): 713, 1122, 1273, 1349, 1374, 1522, 1604, 1709, 1722, 2846, 2923; ¹H NMR (200 MHz, CDCl₃): δ 3.23 (dd, J = 17.0, 4.9 Hz, 1H), 3.82 (dd, J = 17.0, 8.1 Hz, 1H), 5.70 (dd, J = 8.1, 4.9 Hz, 1H), 7.44 - 7.53 (m, 2H), 7.68 (d, J = 7.7 Hz, 1H), 7.86 (d, J = 7.7 Hz, 1H), 8.30 (s, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 33.4, 75.0, 123.6, 124.7, 126.7, 128.4, 131.1, 134.5, 134.7, 136.1, 150.1, 150.9, 164.1, 199.3; **HRMS (ESI)**: [M+H]⁺ calcd for: C₁₆H₁₂NO₅+H: 298.0715; found: 298.0720.

2-Oxo-1,2-diphenylethyl 4-nitrobenzoate (4h): Yield: 81%, colorless solid, Mp: 114-115 °C; **IR** (Nujol, cm⁻¹): 762, 1097, 1288, 1341, 1374, 1462, 1522, 1692, 1720, 2851, 2923; ¹H NMR (200 MHz, CDCl₃): δ 7.13 (s, 1H), 7.41 - 7.58 (m, 8H), 7.99 (d, *J* = 7.2 Hz, 2H), 8.28 (s, 4H); ¹³C NMR (50 MHz, CDCl₃): δ 78.7, 123.5, 128.7, 128.8, 129.3, 129.7, 131.1, 133.2, 133.6, 134.4, 134.8, 150.7, 164.0, 192.6: **HRMS (ESI)**: [M+Na]⁺ calcd for: C₂₁H₁₅NO₅+Na: 384.0848; found: 384.0853.

1-Oxo-1-phenylpropan-2-yl 4-nitrobenzoate (4i): Yield: 81%, colorless solid, Mp: 119-120°C; IR (Nujol, cm⁻¹): 721, 965, 1122, 1270, 1374, 1462, 1522, 1599, 1692, 1725, 2851, 2923; ¹H NMR (200 MHz, CDCl₃): δ 1.72 (d, *J* = 6.9 Hz, 3H), 6.23 (q, *J* = 6.9 Hz, 1H), 7.52 - 7.63 (m, 3H), 7.97 - 8.01 (m, 2H), 8.29 - 8.30(m, 4H); ¹³C NMR (100 MHz, CDCl₃); δ 17.2, 72.6, 123.4, 128.4, 128.8, 130.9, 133.7, 134.8, 150.6, 163.9, 195.5; HRMS (ESI): [M+H]⁺ calcd for: C₁₆H₁₃NO₅+H :300.0872; found: 300.0877.

3-((Tert-butyldimethylsilyl)oxy)-1-oxo-1-phenylpropan-2-yl 4-nitro benzoate (4j): Yield: 92%, colorless solid, Mp: 77-78 °C; **IR** (Nujol, cm⁻¹): 718, 839, 1270, 1371, 1459, 1530, 1695, 1733, 2851, 2917; ¹**H NMR** (200 MHz, CDCl₃): δ 0.00 (s, 3H), 0.02 (s, 3H), 0.82 (s, 9H), 4.18 (d, *J* = 5.1 Hz, 2H), 6.25 (t, *J* = 5.1 Hz, 1H), 7.47 - 7.62 (m, 3H), 8.00 - 8.04 (m, 2H), 8.29 - 8.30 (m, 4H); ¹³**C NMR** (100 MHz, CDCl₃): δ -5.4, 18.1, 25.6, 29.7, 62.9, 77.3, 123.5, 128.5, 128.7, 131.0, 133.7, 134.8, 135.2, 150.7, 163.9, 194.4; **HRMS** (**ESI**): [M+H]⁺ calcd for: C₂₂H₂₇NO₆Si+H: 430.1686; found: 430.1689.

3-(Benzyloxy)-2-oxopropyl 4-nitrobenzoate (4k) Yield: 79%, colorless solid, Mp: 83-84 °C; **IR** (Nujol, cm⁻¹): 718, 1083, 1283, 1374, 1459, 1517, 1722, 1739, 2851, 2823; ¹H NMR (200 MHz, CDCl₃): δ 4.21 (s, 2H), 4.64 (s, 2H), 5.23 (s, 2H), 7.37 (s, 5H), 8.28 (d, *J* = 4.3 Hz, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 67.8, 73.8, 73.9, 123.5, 127.9, 128.3, 128.6, 130.9, 134.6, 136.5, 150.7, 163.8, 200.8; HRMS (ESI): [M+Na]⁺ calcd for C₁₇H₁₅NO₆+Na: 352.0796; found: 352.0801.

2-Oxooctyl 4-nitrobenzoate (4I): Yield: 71%, colorless solid, Mp: 75-76 °C: **IR** (Nujol, cm⁻¹): 717, 1121, 1272, 1352, 1377, 1463, 1536, 1543, 1722, 1733, 2854, 2923; ¹H NMR (200 MHz, CDCl₃): δ 0.87 - 0.93 (m, 3H), 1.26 - 1.31 (br. s, 6H), 1.67 - 1.70 (m, 2H), 2.49 (t, *J* = 7.3 Hz, 2H), 4.94 (s, 2H), 8.24 - 8.35 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 13.9, 22.4, 23.2, 28.7, 31.5, 38.7, 68.7, 123.5, 130.9, 134.6, 150.7, 163.8, 202.4: **HRMS (ESI)**: [M+H]⁺ calcd for C₁₅H₁₉NO₅+H: 294.1341; found: 294.1347.

2-Oxodecyl 4-nitrobenzoate (4m): Yield: 76%, colorless solid, Mp: 76-77 °C; **IR** (Nujol, cm⁻¹): 713, 1119, 1270, 1374, 1459, 1541, 1610, 1717, 1736, 2857, 2928; ¹H NMR (200 MHz, CDCl₃): δ 0.85 - 0.92 (m, 3H), 1.29 (br. s., 10H), 1.66 (t, *J* = 7.2 Hz, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 4.94 (s, 2H), 8.24 - 8.35 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): δ 14.0, 22.5, 23.2, 29.0, 29.0, 29.2, 31.7, 38.6, 68.6, 123.4, 130.8, 134.6, 150.6, 163.7, 202.2; **HRMS (ESI)**: [M+H]⁺ calcd for C₁₇H₂₃NO₅+H: 322.1654; found: 322.1656.

2-Oxo-4-phenylbutyl 4-nitrobenzoate (4n): Yield: 74%, colorless solid, Mp: 112-113 °C; IR (Nujol, cm⁻¹): 724, 1089, 1131, 1273, 1347, 1377, 1462, 1523, 1600, 1718, 1732, 2855, 2926; ¹H NMR (200 MHz, CDCl₃) : δ 2.79 - 2.87 (m, 2H), 2.95 - 3.03 (m, 2H), 4.91 (s, 2H), 7.21 - 7.31 (m, 5H), 8.27 - 8.34 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): δ 29.2, 40.4, 68.8, 123.6, 126.4, 128.2, 128.6, 131.0, 138.0, 140.2, 150.8, 163.9, 201.7; HRMS (ESI): [M+Na]⁺ calcd for: C₁₇H₁₅NO₅+Na: 336.0848; found: 336.0856. **2-Ethoxy-2-oxoethyl 4-nitrobenzoate (4o): Yield:** 78%, yellow liquid; **IR** (neat, cm⁻¹): 2926, 2983, 1759, 1738, 1732, 1608, 1531, 1349, 1285, 1213, 1121, 1018, 857, 718; ¹H NMR (200 MHz, CDCl₃): δ 1.33 (t, *J* = 7.1 Hz, 3H), 4.28 (q, *J* = 7.1 Hz, 2H), 4.89 (s, 2H), 8.25 - 8.36 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): δ 14.1, 61.5, 123.5, 131.0, 134.5, 150.8, 163.9, 166.9; **HRMS** (ESI): [M+Na]⁺ calcd for C₁₁H₁₁NO₆+Na: 276.0484; found: 276.0446.

2-Oxotetrahydro-2H-pyran-3-yl 4-nitrobenzoate (4p): Yield: 69%, colorless solid, Mp: 136-137 °C; **IR** (Nujol, cm⁻¹): 718, 1124, 1273, 1377, 1456, 1511, 1602, 1725, 1753, 2857, 2912; ¹H **NMR** (200 MHz, CDCl₃): δ 2.14 - 2.20 (m, 3H), 2.51 - 2.76 (m, 1H), 4.43 - 4.49 (m, 2H), 5.61 -5.67 (m, 1H), 8.25 - 8.35 (m, 4H); ¹³C NMR (50 MHz, CDCl₃): δ 21.3, 24.8, 68.2, 68.2, 123.5, 131.0, 134.5, 150.7, 163.4, 168.1; **HRMS (ESI)**: [M+H]⁺ calcd for C₁₂H₁₁NO₆+H: 266.0664; found: 266.0663

2-(Methoxy)-2-oxo-1-phenylethyl 4-nitrobenzoate (4q): Yield: 72%, yellow liquid; **IR** (CHCl₃, cm⁻¹): 718, 1101, 1167, 1269, 1346, 1368, 1508, 1527, 1606, 1731, 1760; ¹H NMR (500 MHz, CDCl₃): δ 3.80 (s, 3H), 6.20 (s, 1H), 7.47 - 7.48 (m, 3H), 7.59 - 7.60 (m, 2H), 8.32 (s, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 52.6, 75.4, 123.5, 127.7, 128.9, 129.5, 131.0, 133.3, 134.5, 150.8, 163.7, 168.5; **HRMS (ESI)**: [M+Na]⁺ calcd for C₁₆H₁₃NO₆+Na: 338.0641; found: 338.0649.

2-Oxo-2-phenylethyl benzoate (4r): Yield: 68%, colorless solid, Mp: 119-120 °C ; **IR** (Nujol, cm⁻¹): 705, 1015, 1374, 1459, 1596, 1714, 1750, 2851, 2923; ¹H NMR (200 MHz, CDCl₃): δ 5.58 (s, 2H), 7.48 - 7.61 (m, 6H), 7.97 - 8.00 (m, 2H), 8.13 - 8.17 (m, 2H); ¹³C NMR (50 MHz, CDCl₃): δ 66.2, 127.6, 128.2, 128.73 , 129.8, 130.1, 133.1, 133.6, 134.1, 165.7, 191.6; **HRMS** (**ESI**): [M+Na]⁺ calcd for C₁₅H₁₂O₃+Na: 263.0683; found: 263.0692.

2-Oxo-2-phenylethyl 3-methylbenzoate (4s): Yield: 81%, colorless solid, Mp: 94-95°C; IR (Nujol, cm⁻¹): 743, 814, 957, 1083, 1198, 1369, 1451, 1585, 1684, 1714, 2857, 2917; ¹H NMR (200 MHz, CDCl₃): δ 2.38 (s, 3H), 5.52 (s, 2H), 7.31 - 7.48 (m, 5H), 7.90 - 7.95 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δ 21.1, 66.2, 127.0, 127.6, 128.2 128.7, 129.2, 130.3, 133.6, 133.9, 134.1, 137.9, 165.8, 191.7; HRMS (ESI): [M+Na]⁺ calcd for C₁₆H₁₄O₃+Na: 277.0840; found: 277.0848

2-Oxo-2-phenylethyl 4-bromobenzoate (4t) : Yield: 78%, colorless solid, Mp: 84-85°C; **IR** (Nujol, cm⁻¹): 766, 1012, 1126, 1327, 1588, 1643,1711, 1732, 2923, 2956; ¹H NMR (200 MHz, CDCl₃): δ 5.57 (s, 2H), 7.44 - 7.64 (m, 5H), 7.94 - 8.03 (m, 4 H); ¹³C NMR (50 MHz, CDCl₃): δ 66.4, 127.7, 128.3, 128.4, 128.8, 131.4, 131.7, 133.8, 134.1, 165.0, 191.4: **HRMS (ESI)**: [M+Na]⁺ calcd for C₁₅H₁₁BrO₃+Na: 340.9789; found: 340.9799

2-Oxo-2-phenylethyl 4-chlorobenzoate (4u): **Yield**: 75%, colorless solid, Mp: 127-128 °C ; **IR** (Nujol, cm⁻¹): 753, 1091, 1226, 1273, 1376, 1456, 1595, 1697, 1726, 2724, 2857, 2926; ¹H **NMR** (500 MHz, CDCl₃): δ 5.58 (s, 2H) 7.44- 7.56 (m, 5H), 7.97(d, J = 7.3Hz, 2H) 8.07 – 8.11 (d, J = 7.3 Hz, 2H); ¹³C **NMR** (125 MHz, CDCl₃): δ 66.5, 77.0, 127.8, 128.6, 128.8, 128.9, 131.3, 133.9, 134.2, 139.8, 165.0, 191.6; **HRMS (ESI)**: [M+Na]⁺ calcd for C₁₅H₁₁ClO₃+Na: 297.0294; found: 297.0294.

2-Oxo-2-phenylethyl nicotinate (4v): Yield: 73%, colorless solid, Mp: 64-65 °C**: IR** (CHCl₃, cm⁻¹): 753, 1076, 1342, 1463, 1591, 1650, 1695, 1726, 2854, 2870, 2923; ¹H NMR (400 MHz, CDCl₃); δ 5.61 (s, 2H), 7.44 (dd, *J* = 7.6, 4.9 Hz, 1H) 7.50 - 7.54 (m, 2H), 7.62 - 7.64 (m, 1H), 7.97 (d, *J* = 7.5 Hz, 2H), 8.40 (d, *J* = 7.7 Hz, 1H), 8.82 (br. s, 1H), 9.33 (br. s, 1H); ¹³C NMR

(100 MHz, CDCl₃) δ 66.6, 123.3, 125.6, 127.8, 128.9, 134.0, 134.1, 137.4, 151.2, 153.7, 164.6,
191.1; HRMS (ESI): [M+Na]⁺ calcd for C₁₄H₁₁NO₃+Na: 264.0637; found: 264.0648.

2, **3-Epoxy-1-(4-nitrophenyl)-3-phenylpropan-1-one (5):** Yield: 56%, colorless solid, Mp: 120-121 °C; **IR** (CHCl₃, cm⁻¹): 745, 1233, 1451, 1519, 1598, 1692, 2850, 2923; ¹H NMR (200 MHz, CDCl₃); δ 4.21 (d, *J* = 1.7 Hz 1H), 4.25 (d, *J* = 1.7 Hz, 1H), 7.52 - 7.56 (m, 4H), 7.58 (m, 1H), 8.02 (d, *J* = 8.7 Hz, 2H), 8.29 (d, *J* = 8.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 57.9, 60.8, 124.1, 126.6, 128.4, 129.0, 134.3, 135.2, 142.7, 148.3, 191.9: **HRMS (ESI)**: [M+H]⁺ calcd for C₁₅H₁₁NO₄+H: 270.0766; found: 270.0777.

















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<sup>1</sup>H and <sup>13</sup>C NMR spectra of 2-Oxo-1, 2-diphenylethyl 4-nitrobenzoate (4h)
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