Supporting Information

A general method for the α -acyloxylation of carbonyl compounds

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General Procedures. Commercially available solvents and reagents were used without further purification. Light petroleum refers to the fraction with bp 40-60 °C and ether refers to diethyl ether. Flash chromatography was carried out using Merck Kieselgel 60 H silica or Matrex silica 60. Analytical thin layer chromatography was carried out using aluminium-backed plates coated with Merck Kieselgel 60 GF₂₅₄ that were visualised under UV light (at 254 and/or 360 nm). Infra-red (IR) spectra were recorded in the range 4000-600 cm⁻¹ using KBr disks for solid samples and thin films between NaCl plates for liquid samples or as a nujol mull and are reported in cm⁻¹. Nuclear magnetic resonance (NMR) spectra were recorded in CDCl₃ at 18 °C unless stated otherwise and were reported in ppm; *J* values were recorded in Hz and multiplicities were expressed by the usual conventions. Low-resolution mass spectra (MS) were determined using atmospheric pressure chemical ionization (APCI) unless

otherwise stated. ES refers to electrospray ionization, CI refers to chemical ionization (ammonia) and EI refers to electron ionization. High-resolution mass spectra were obtained courtesy of the EPSRC Mass Spectrometry Service at University College of Wales, Swansea, UK using the ionization methods specified. *In vacuo* refers to evaporation at reduced pressure using a rotary evaporator and diaphragm pump, followed by the removal of trace volatiles using a vacuum (oil) pump.

Preparation of *N*-methyl-*O*-benzoyl hydroxylamine hydrochloride

N-Methyl-*N*-Boc hydroxylamine¹ (4)

Potassium carbonate (14.5 g, 0.1 mol) was added to an ice-cold solution of *N*-methyl hydroxylamine hydrochloride (30 g, 0.2 mol) in a 1:1 mixture of tetrahydrofuran and water (80 ml). A solution of di-*tert*-butyl dicarbonate (48 g, 0.22 mol) in tetrahydrofuran (60 ml) was then added dropwise to the mixture and stirring was continued for 2 hours at 0 °C and then at room temperature for 3 hours. After this period, the solution was concentrated *in vacuo* and the residue dissolved in dichloromethane (100 ml) before washing with water (3 × 40 ml) and brine (50 ml). The organic fraction was collected, dried and reduced *in vacuo* to yield an orange oil (29.3 g). The crude product was purified by distillation (< 1 mbar, 84-87 °C) to yield *N*-Boc-*N*-methylhydroxylamine as a colourless oil (28.5 g, 97%); IR (neat) 3257, 1699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.05 (brs, 1H), 3.31 (s, 3H), 1.63 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 157.4 (s), 80.6 (s), 37.5 (q), 27.5 (q),. MS (ES) *m/z* 148.2 [M+H]⁺; HRMS calculated for C₆H₁₃NO₃ 148.0973 [M+H]⁺, found 148.0974.

N-Methyl-*N*-Boc-*O*-benzoyl hydroxylamine² (6)

A solution of *N*-Boc-*N*-methyl hydroxylamine (25 g, 0.17 mol), dimethylaminopyridine (2 mol %) and triethylamine (17.2 g, 23.7 ml, 0.17 mmol) in dichloromethane (300 ml) was cooled to 0 °C prior to slow addition of benzoyl chloride (23.89 g, 19.7 ml, 0.17). The reaction mixture was allowed to warm to room temperature and stirred for 16 h. Evaporation of the solvent under reduced pressure

¹ Carrasco, M. R.; Brown, R. T.; Serafimova, I. M.; Silva, O. *J. Org. Chem.* **2003**, 68, 195.

² White, E. H.; Reefer, J.; Erickson, R. H.; Dzadzic, P. M. *J. Org. Chem.* **1984**, 49, 4872.

gave a yellow solid, which was triturated with light petroleum, filtered, diluted with dichloromethane (200 ml), washed with saturated sodium hydrogen carbonate solution (2 x 60 ml), water (60 ml) and brine (60 ml). The organics were dried over MgSO_4 and concentrated to give the *title compound* as a colourless liquid (40.58 g, 95%) which can be purified if necessary by vacuum distillation (1 mbar, 122-124 °C); IR (thin film) 1763, 1721 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 8.01 (d, J 8.5 = Hz, 2H), 7.61 (t, J = 7.05 Hz, 1H), 7.46 (dd, J = 8.5 7.05 Hz, 2H), 3.34 (s, 3H), 1.46 (s, 9H); ^{13}C NMR (125 MHz, CDCl_3) δ 164.74, 155.38, 133.86, 129.89, 128.62, 127.64, 82.40, 38.00, 28.13; MS (APCI) m/z 252 $[\text{M}+\text{H}]^+$; HRMS calculated for $\text{C}_{13}\text{H}_{17}\text{NO}_4$ 252.1236 $[\text{M}+\text{H}]^+$, found 252.1236.

***N*-Methyl-*O*-benzoyl hydroxylamine hydrochloride³ (10)**

Gaseous hydrogen chloride, generated from the slow addition of concentrated sulfuric acid (ca. 50 ml) to ammonium chloride (ca. 50 g) was bubbled through a solution of *N*-Boc-*N*-methyl-*O*-benzoyl hydroxylamine (25 g, 0.1 mol) in 1,4-dioxane for 2 hours. The resulting white precipitate was filtered and washed with cold ether and dried under high vacuum to give the *title compound* (17.83 g, 95%) as a colourless solid; Mp 129-129.5 °C; IR (thin film) 3458, 3056, 1712, 1600, 1550, 1422, 1264 cm^{-1} ; ^1H NMR (400 MHz, $\text{DMSO-}d^6$) δ 11.95 (brs, 2H), 7.95 (d, J = 7.0 Hz, 2H), 7.73 (t, J = 7.5 Hz, 1H), 7.57 (dd, J = 7.0 7.5 Hz, 2H), 2.93 (3H, s); ^{13}C NMR (100 MHz, $\text{DMSO-}d^6$) δ 164.33, 134.86, 129.69, 129.60, 127.15, 37.49; MS (APCI) m/z 152 $[\text{M}+\text{H}]^+$; HRMS calculated for $\text{C}_8\text{H}_9\text{NO}_2$ 152.0711 $[\text{M}+\text{H}]^+$, found 152.0712.

Typical experimental procedure for cyclic ketones

1,4-Cyclohexanedione mono-ethylene ketal (100 mg, 0.64 mmol) and *N*-Methyl-*O*-benzoyl hydroxylamine hydrochloride (111 mg, 0.64 mmol) were dissolved in dimethylsulfoxide (1.5 ml) and the resultant mixture allowed to stir at room temperature for two hours, after which time TLC analysis showed the reaction to be complete. The solution was subsequently diluted with ethyl acetate (50 ml) and washed repeatedly with saturated aqueous brine to remove the reaction solvent (5 ×

³ Wathen, S. P.; Czarnik, A. W. *J. Org. Chem.* **1992**, 57, 6129.

50 ml). The organic fraction was dried (magnesium sulfate), concentrated *in vacuo*, and the crude product purified by flash column chromatography (4:1 light petroleum/ethyl acetate) to yield benzoic acid 8-oxo-1,4-dioxaspiro[4.5]dec-7-yl ester as colourless microcrystals (122 mg, 70%); Mp 114-116 °C; IR (dichloromethane) 2915, 1714, 1448, 1260, 1101, 1036 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.01 (d, *J* = 8 Hz, 2H), 7.51 (t, *J* = 8 Hz, 1H), 7.38 (t, *J* = 8 Hz, 2H), 5.57–5.69 (m, 1H), 3.95–4.11 (m, 4H), 2.66–2.80 (m, 1H), 2.35–2.49 (m, 2H), 2.20 (t, *J* = 13 Hz, 1H), 1.90–2.09 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 203.4 (s), 165.4 (s), 133.3 (d), 129.9 (d), 129.4 (s), 128.4 (d), 107.3 (s), 73.7 (d), 65.0 (t), 64.9 (t), 40.3 (t), 35.6 (t), 34.6 (t); MS (APCI) *m/z* 277 [M+H]⁺; HRMS calculated for C₁₅H₁₆O₅ [M+H]⁺ 277.1071, found 277.1073.

Typical experimental procedure for acyclic ketones

Pentan-3-one (60 µl, 0.57 mmol) and *N*-Methyl-*O*-benzoyl hydroxylamine hydrochloride (100 mg, 0.57 mmol) were dissolved in dimethylsulfoxide (1 ml) and the resultant mixture allowed to stir at 50 °C for sixteen hours. After this period the solution was diluted with ethyl acetate (50 ml) and washed repeatedly with saturated aqueous brine (5 × 50 ml). The organic fraction was dried (magnesium sulfate) and concentrated *in vacuo*, and the crude product purified by flash chromatography (dichloromethane) to yield benzoic acid 1-methyl-2-oxo-butyl ester⁴ as a pale yellow oil (81 mg, 74%); IR (dichloromethane) 2353, 1719, 1262, 1097 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8 Hz, 2H), 7.53 (t, *J* = 8 Hz, 1H), 7.40 (t, *J* = 8 Hz, 2H), 5.29 (q, *J* = 7 Hz, 2H), 2.39-2.66 (m, 2H), 1.47 (d, *J* = 7 Hz, 3H), 1.03 (t, *J* = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 208.6 (s), 165.96 (s), 133.4 (d), 129.8 (d), 129.5 (s), 128.5 (d), 75.2 (d), 31.5 (t), 16.5 (q), 7.3 (q); MS (APCI) *m/z* 207 [M+H]⁺. HRMS calculated for C₁₂H₁₅O₃ [M+H]⁺ 207.1016, found 207.1016.

Typical experimental procedure for aldehydes

1-Heptanal (79 µl, 0.57 mmol) and *N*-Methyl-*O*-benzoyl hydroxylamine hydrochloride (100 mg, 0.57 mmol) were dissolved in dimethylsulfoxide (1 ml) and

⁴ Defosseux, M.; Blanchard, N.; Meyer, C.; Cossy, J. *J. Org. Chem.* **2004**, *69*, 4626.

the resultant mixture allowed to stir at 50 °C for sixteen hours. After this period the solution was diluted with ethyl acetate (50 ml) and washed repeatedly with saturated aqueous brine (5 × 50 ml). The organic fraction was dried (magnesium sulfate) and concentrated *in vacuo*, and the crude product subjected to flash chromatography (1:1 dichloromethane/light petroleum) to furnish benzoic acid 1-formyl-hexyl ester⁵ as a colourless oil (110 mg, 83%); IR (neat) 2910, 1715, 1250, 1030 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.53 (s, 1H), 7.99 (d, *J* = 8, 2H), 7.50 (t, *J* = 8 Hz, 1H), 7.37 (t, *J* = 8 Hz, 2H), 5.07–5.14 (m, 1H), 1.71–1.90 (m, 2H), 1.35–1.46 (m, 2H), 1.17–1.29 (m, 4H), 0.79 (t, *J* = 8 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 198.6 (s), 166.2 (s), 133.6 (d), 129.9 (d), 129.2 (s), 128.6 (d), 78.8 (d), 31.5 (t), 28.9 (t), 24.7 (t), 22.4 (t), 14.0 (q); MS (APCI) *m/z* 235 [M+H]⁺; HRMS calculated for C₁₄H₁₉O₃ [M+H]⁺ 235.1329, found 235.1329.

⁵ Rubottom, G. M.; Gruber, J. M.; Mong, G. M. *J. Org. Chem.* **1976**, *41*, 1673.

***N*-Methyl-*N*-Boc hydroxylamine¹ (4)**

CC(=O)ON(C)C(=O)OC(C)(C)C(C)(C)C(C)C

***N*-Methyl-*N*-Boc-*O*-benzoyl hydroxylamine² (6)**

N-Methyl-N-Boc-O-(4-methoxybenzoyl) hydroxylamine (7)

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Current Data Parameters
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Time: 10:10:13
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Field 500 MHz

DEPT 90

DEPT 135

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***N*-Methyl-*O*-benzoyl hydroxylamine hydrochloride³ (10)**

N-Methyl-O-(4-methoxybenzoyl) hydroxylamine hydrochloride (11)

N-Methyl-O-pivaloyl hydroxylamine hydrochloride⁷ (12)

Chemical Name: N-Methyl-O-pivaloyl hydroxylamine hydrochloride
 CAS: 100000-00-0
 Molecular Weight: 173.17
 SMILES: CC(=O)OCN(C)[H+]Cl
 InChI: CC(=O)OCN(C)[H+]Cl
 InChI Key: CC(=O)OCN(C)[H+]Cl

⁷ Geffken, D. *Chem. Zeit* **1986**, *110*, 377.

^1H NMR of crude reaction mixture between 10 and cyclohexanone in CHCl_3 , THF, DMSO, THF/ H_2O .

CHCl_3 :

2-(Benzoyloxy)cyclopentanone⁸ (Table 1 entry 1)

⁸ Feng, X.; Shu, L.; Shi, Y. *J. Org. Chem.* **2002**, 67, 2813.

2-(Benzoyloxy)cyclohexanone⁸ (14)

2-(Benzoyloxy)cycloheptanone⁸ (Table 1 entry 3)

2-(Benzoyloxy)pentan-3-one⁴ (Table 1 entry 4)

3-(Benzyloxy)heptan-4-one (Table 1 entry 5)

2-(Benzoyloxy)isovaleraldehyde⁹ (Table 1 entry 6)

⁹ Beshara, C. S.; Hall, A.; Jenkins, R. L.; Jones, T. C.; Parry, R. T.; Thomas, S. P.; Tomkinson, N. C. *O. Chem. Commun.* **2005**, 1478.

2-(Benzoyloxy)heptanal⁵

Benzoyloxycyclohexanecarboxaldehyde¹⁰ (Table 1 entry 7)

¹⁰ Cummins, C. H.; Coates, R. M. *J. Org. Chem.* **1983**, *48*, 2070.

3-(Benzoyloxy)tetrahydro-4H-pyran-4-one⁸ (Table 1 entry 8)

3-(Benzoyloxy)tetrahydro-4H-thiopyran-4-one (Table 1 entry 9)

2-(Benzoyloxy)cyclohexane-1,4-dione monoethylene ketal (Table 1 entry 10)

***N*-Benzoyl-3-(benzyloxy)piperidin-4-one (Table 1 entry 11)**

O=C1CCN(C1)C(=O)OCC2=CC=CC=C2

Ethyl 2-(benzyloxy)-4-oxocyclohexanecarboxylate (Table 1 entry 13)

O=C1CCCCC1OBz

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SOLVENT: CDCl3
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AQ: 1.9921644
TE: 300.2
DS: 1.00000000

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2-(Benzoyloxy)-4-*tert*butylcyclohexanone (Table 1 entry 15)

2-(Benzoyloxy)propiophenone¹² (Table 1 entry 16)

¹² Nadkarni, D.; Hallissey, J.; Mijica, C. *J. Org. Chem.* **2002**, 68, 594.

1-(4-Methoxyphenyl)-2-(benzoyloxy)propan-1-one¹³ (Table 1 entry 17)

¹³ Hamana, M.; Endo, T.; Saeki, S. *Tetrahedron Lett.* **1975**, 16, 903.

CC(=O)c1ccc(Br)cc1OC(=O)c2ccccc2

1-(4-Hydroxyphenyl)-2-(benzyloxy)propan-1-one (Table 1 entry 19)

4-Methyl-3-benzoyloxypentan-2-one (Table 2 entry 1)

CC(=O)C(OBz)CC=C

1-(4-Hydroxyphenyl)-3-oxobutan-2-yl benzoate (Table 2 entry 3)

1-(4-Methoxyphenyl)-3-oxobutan-2-yl benzoate (Table 2 entry 4)