Supporting Information

for

α-Aroyloxyaldehydes; scope and limitations as alternatives to α-haloaldehydes for NHC-catalysed redox transformations

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General Experimental

All reactions involving moisture sensitive reagents were performed under an atmosphere of argon using standard vacuum line techniques and with anhydrous solvents. All glassware was flame dried and allowed to cool under vacuum.

Anhydrous solvents were obtained from a solvent purification system (MBraun, SPS-800). Petrol refers to the fraction of petroleum ether boiling between 40 °C and 60 °C. All N-methyl-O-aryloxythymylamine hydrochloride salts were prepared following the procedures outlined by Tomkinson et al.1 α-Ketoester 27 was prepared following the procedure of Zhang et al.2 All other reagents were used directly as supplied without further purification. Ozonolysis was performed using a Fischer Technology Ozone Generator, OZ 500/5.

Flash column chromatography was carried out on silica gel 60 (0.043–0.060 mm) (Merck) in the solvent system stated. Analytical thin layer chromatography was performed on commercially available pre-coated aluminium-backed plates (Merck silica Kieselgel 60 F_{254}). TLCs were visualised either by UV fluorescence (254 nm), or by staining with basic KMnO_{4} solution.

Melting points were recorded on an Electrothermal apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR Spectrometer and analysed either as thin films between NaCl plates (film) or KBr discs (KBr disc) as stated. Absorption maxima (ν_{max}) are quoted in wavenumbers (cm^{-1}) and only structurally significant peaks are quoted.

H and C nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance 300 (300 MHz H, 75.4 MHz C) or a Bruker Avance 400 (400 MHz H, 100 MHz C) spectrometer in the deuterated solvent stated. C NMR spectra were recorded with proton decoupling. Chemical shifts (δ) are quoted in parts per million (ppm) and referenced to residual
solvent peaks or to SiMe$_4$ as an internal standard ($\delta = 0.00$). Coupling constants, $J$, are quoted in Hz. The abbreviations s, d, dd, dt, td, q and m denote singlet, doublet, doublet of doublets, doublet of triplets, triplet of doublets, quartet and multiplet respectively. The abbreviation Ar is used to denote aromatic.

Mass spectrometric ($m/z$) data was acquired by electrospray ionisation (ESI) or chemical ionisation (CI), either at the University of St Andrews Mass Spectrometry facility ([M+Na]$^+$ quoted) or at the EPSRC National Mass Spectrometry Service Centre, Swansea ([M+H]$^+$, [2M+H]$^+$, [M+Na]$^+$ or [2M+Na]$^-$ quoted). At the University of St Andrews, low and high resolution ESI MS was carried out on a Micromass LCT spectrometer. At the EPSRC National Mass Spectrometry Service Centre, CI MS was carried out on a Micromass Quattro II spectrometer. High resolution ESI was carried out on a Finnigan MAT 900 XLT; a Thermofisher LTQ Orbitrap XL spectrometer was used to obtain high resolution ESI MS for accurate mass determination but also provided fragmentation data for the characterisation of samples. Values are quoted as a ratio of mass to charge in Daltons.
Preparation of α-benzzyloxyaldehyde I:

Following the procedure of Schreiner et al.\textsuperscript{3} Styrene oxide (1.14 mL, 10 mmol) was added to a stirred solution of mandelic acid (15.2 mg, 0.10 mmol) and \(N, N\)-bis-[3,5-bis-(trifluoromethyl)phenyl]-thiourea (50.0 mg, 0.10 mmol) in benzyl alcohol (12.4 mL, 120 mmol) at RT and the mixture stirred for 24 hrs then concentrated \textit{in vacuo}. The mixture was heated at \(\sim 70^\circ\text{C}\) under high vacuum to remove as much benzyl alcohol as possible, then purified by flash column chromatography (silica, 10% EtOAc/petrol) to give 2-(benzyloxy)-2-phenylethanol as a colourless oil (525 mg, 23\%). To a stirred solution of 2-(benzyloxy)-2-phenylethanol (456 mg, 2.00 mmol) in CH\(_2\)Cl\(_2\) (20 mL) was added Dess-Martin periodinane (1.02, 2.40 mmol) and the mixture stirred at RT for 30 mins (TLC monitoring). Et\(_2\)O (20 mL) and sodium thiosulphate (3.5 g, \(\sim 11\) eq) in sat. aq. NaHCO\(_3\) (20 mL) were added and the mixture stirred until both layers became homogenous. The aqueous layer was extracted with Et\(_2\)O (3 \(\times\) 20 mL) then the combined organics were washed with sat. aq. NaHCO\(_3\) (50 mL) and brine (50 mL), dried, filtered and concentrated \textit{in vacuo}. Purification by flash column chromatography (silica, petrol \(\rightarrow\) 15% EtOAc/petrol) gave 2-(benzyloxy)-2-phenylacetaldehyde I as a colourless oil (237 mg, 52\%) with spectroscopic data in accordance with the literature:\textsuperscript{4} \(\delta_H\) (400MHz, CDCl\(_3\)) 4.56 (1H, d, \(J\) 11.8, OCH\(_A\)H\(_B\)Ph), 4.69 (1H, d, \(J\) 11.8, OCH\(_A\)H\(_B\)Ph), 4.81 (1H, d, \(J\) 1.7, C(2)\(H\)), 7.27-7.43 (10H, m, Ph), 9.64 (1H, d, \(J\) 1.7, C(1)\(H\)).
**Procedure for the attempted NHC-mediated redox rearrangement of 1:**

![Chemical structure of 1 and its rearrangement product]

To a flame-dried Schlenk flask under an atmosphere of N₂ was added catalyst 2 (13.7 mg, 0.050 mmol), Cs₂CO₃ (14.7 mg, 0.045 mmol) and toluene or CH₂Cl₂ (2.50 mL) and the mixture stirred at RT for 15 mins. A solution 2-(benzyloxy)-2-phenylacetaldehyde 1 (113 mg, 0.50 mmol) in toluene or CH₂Cl₂ (2.50 mL) was added, the mixture allowed to stir at RT for 16 hrs then concentrated *in vacuo* to give the crude product. superscript{1}H NMR analysis showed that in both cases the reaction conversion was <5%.
Preparation of α-phenoxyaldehyde 4:

To a stirred solution of 2-phenoxypropionic acid (3.32 g, 20.0 mmol) in Et₂O (50 mL) at 0 °C was added LiAlH₄ (2.0M in THF, 18.0 mL, 36.0 mmol) and the mixture stirred at RT for 16 hrs. The reaction was then quenched by the sequential addition of H₂O (1.4 mL), 15% aq. NaOH (1.4 mL) and H₂O (4.2 mL). The resulting mixture was stirred vigorously for 30 mins then filtered through Celite (eluent; MeOH). The filtrate was concentrated in vacuo, dissolved in Et₂O then dried, filtered and concentrated in vacuo to give a crude product which was purified by flash column chromatography (silica, 10% EtOAc/petrol) to give 2-phenoxypropan-1-ol as a colourless oil (2.80 g, 92%) with spectroscopic data in accordance with the literature; δ_H (300MHz, CDCl₃) 1.30 (3H, d, J 6.2, C(3)H₃), 3.71-3.80 (2H, m, C(1)H₂), 4.54 (1H, quintet d, J 6.2, 3.9, C(2)H), 6.95-7.02 (3H, m, Ph), 7.29-7.34 (2H, m, Ph). To a stirred solution of oxalyl chloride (0.51 mL, 6.00 mmol) in CH₂Cl₂ (40 mL) at −78 °C was added DMSO (0.71 mL, 10.0 mmol) dropwise. After 5 mins, a solution of 2-phenoxypropan-1-ol (761 mg, 5.00 mmol) in CH₂Cl₂ (10 mL) was added dropwise via syringe. The solution was stirred at −78 °C for 30 mins then triethylamine (2.79 mL, 20 mmol) was added and the resulting mixture allowed to warm to RT over 30 mins. H₂O (25 mL) was added and the aqueous layer extracted with CH₂Cl₂ (3 × 25 mL). The combined organics were washed with 0.1 M aq. HCl (100 mL), H₂O (100 mL), sat. aq. NaHCO₃ (100 mL) and brine (100 mL), then dried, filtered and concentrated in vacuo to give 2-phenoxypropanal 4 as a colourless oil (706 mg, 94%) with spectroscopic data in accordance with
the literature;\(^6\) \(\delta_H\) (300MHz, CDCl\(_3\)) 1.50 (3H, d, \(J 6.9\), C(3)\(H_3\)), 4.65 (1H, qd, \(J 6.9, 2.0\), C(2)\(H\)), 6.88-6.92 (2H, m, \(Ph\)), 6.99 -7.04 (1H, m, \(Ph\)), 7.27-7.35 (2H, m, \(Ph\)), 9.74 (1H, d, \(J 2.0\), C(1)\(H\)).

Procedure for the NHC-mediated redox rearrangement of \(\alpha\)-phenoxyaldehyde 4:

![Chemical structure](image)

To a flame-dried Schlenk flask under an atmosphere of N\(_2\) was added catalyst 2 (13.7 mg, 0.050 mmol), Cs\(_2\)CO\(_3\) (14.7 mg, 0.045 mmol) and toluene (2.50 mL) and the mixture stirred at RT for 15 mins. A solution 2-phenoxypropanal 4 (75 mg, 0.50 mmol) in toluene (2.50 mL) was added, the mixture allowed to stir at RT for 16 hrs, then concentrated in vacuo to give the crude product. \(^1\)H NMR analysis showed that the reaction conversion was >98% to give phenyl propionate 5 with spectroscopic data in accordance with the literature;\(^7\) \(\delta_H\) (400MHz, CDCl\(_3\)) 1.26 (3H, t, \(J 7.6\), C(3)\(H_3\)), 2.58 (2H, q, \(J 7.6\), C(2)\(H_2\)), 7.06-7.09 (2H, m, \(Ph\)), 7.19-7.23 (1H, m, \(Ph\)), 7.34-7.38 (2H, m, \(Ph\)).

Note - The above reaction also works under identical conditions with CH\(_2\)Cl\(_2\) as the solvent.
Preparation of α-aryloxyaldehydes 6-9, 12 and 13

General Procedure A: used for the preparation of 6–9

Following the procedure outlined by Tomkinson et al. To a stirred solution of isovaleraldehyde (1.0 eq) in DMSO (0.5 M) at RT was added the requisite N-methyl-O-acylhydroxylamine hydrochloride salt (1.1–1.2 eq) in one portion, and the mixture stirred at RT for 24–48 hrs. The mixture was then diluted with EtOAc and washed with brine (5x) then dried, filtered and concentrated in vacuo to give a crude product which was purified by flash column chromatography using the solvent system stated.

3-Methyl-1-oxobutan-2-yl benzoate 6: Isovaleraldehyde (0.54 mL, 5.00 mmol) and O-benzoyl-N-methylhydroxylamine hydrochloride (1.13 g, 6.00 mmol) in DMSO (10 mL) for 24 hrs gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a colourless oil (630 mg, 61%); νmax (film) 2969, 1721 (br), 1602, 1452, 1275, 1112, 711; δH (400MHz, CDCl3) 1.12 (3H, d, J 6.9, C(3)MeA MeB), 1.14 (3H, d, J 6.9, C(3) MeA MeB), 2.42 (1H, quintet d, J 6.9, 4.6, C(3)H), 5.08 (1H, dd, J 4.6, 0.9, C(2)H), 7.47-7.50 (2H, m, Ph), 7.59-7.65 (1H, m, Ph), 8.10-8.12 (2H, m, Ph), 9.66 (1H, d, J 0.9, C(1)H); δC (100MHz, CDCl3) 17.3, 18.9, 29.3, 82.7, 128.4, 129.3, 129.8, 133.5, 166.2, 198.9; m/z (NSI) 207 ([M+H]+, 100%); HRMS (NSI) C12H15O3 ([M+H]+ requires 207.1016, found 207.1016 (+0.1 ppm).
3-Methyl-1-oxobutan-2-yl o-nitrobenzoate 7: Isovaleraldehyde (0.54 mL, 5.00 mmol) and N-methyl-O-(o-nitrobenzoyl)hydroxylamine hydrochloride (1.28 g, 5.50 mmol) in DMSO (10 mL) for 24 hrs gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a pale yellow oil (752 mg, 60%); ν_{max} (film) 2971, 2936, 2879, 1732 (br), 1540, 1352, 1286, 1128, 1075, 736; δ_{H} (400MHz, CDCl_{3}) 1.01 (3H, d, J 6.9, C(3)Me_{A}Me_{B}), 1.10 (3H, d, J 6.9, C(3)Me_{A}Me_{B}), 2.37 (1H, quintet d, J 6.9, 4.4, C(3)H), 5.11 (1H, dd, J 4.4, 0.5, C(2)H), 7.66-7.75 (2H, m, Ar), 7.86 (1H, dd, J 7.4, 1.6, Ar), 7.95 (1H, dd, J 7.8, 1.4, Ar), 9.66 (1H, d, J 0.5, C(1)H); δ_{C} (100MHz, CDCl_{3}) 17.0, 19.7, 29.1, 84.0, 124.0, 126.8, 130.3, 132.2, 133.1, 148.1, 165.2, 197.9; m/z (NSI) 252 ([M+H]^{+}, 20%), 301 ([M+MeOH+NH_{4}^{+}], 100%); HRMS (NSI) C_{12}H_{14}NO_{5} ([M+H]^{+} requires 252.0866, found 252.0870 (+1.4 ppm).

3-Methyl-1-oxobutan-2-yl m-nitrobenzoate 8: Isovaleraldehyde (0.27 mL, 2.50 mmol) and N-methyl-O-(m-nitrobenzoyl)hydroxylamine hydrochloride (640 mg, 2.75 mmol) in DMSO (5 mL) for 24 hrs gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a pale yellow oil (410 mg, 65%); ν_{max} (film) 2970, 2878, 1731 (br), 1538, 1351, 1267, 1136, 719; δ_{H} (400MHz, CDCl_{3}) 1.14 (3H, d, J 6.9, C(3)Me_{A}Me_{B}), 1.17 (3H, d, J 6.9, C(3)Me_{A}Me_{B}), 2.48 (1H, quintet d, J 6.9, 4.6, C(3)H), 5.19 (1H, d, J 4.6, C(2)H), 7.70 (1H, t, J 8.0, Ar), 8.42 (1H, dt, J 7.8, 1.3, Ar), 8.47 (1H, ddd, J 8.2, 2.3, 1.1, Ar), 8.90 (1H, t, J 1.9, Ar), 9.67 (1H, s, C(1)H); δ_{C} (100MHz, CDCl_{3}) 17.3, 18.9, 29.0, 83.4, 124.7, 127.9, 129.9, 131.3, 135.5, 148.3, 164.0, 197.6; m/z (NSI) 252 ([M+H]^{+}, 45%); HRMS (NSI) C_{12}H_{14}NO_{5} ([M+H]^{+} requires 252.0866, found 252.0869 (+1.0 ppm).
3-Methyl-1-oxobutan-2-yl \(p\)-nitrobenzoate 9: Isovaleraldehyde (0.27 mL, 2.50 mmol) and \(N\)-methyl-\(O\)-(\(p\)-nitrobenzoyl)hydroxylamine hydrochloride (640 mg, 2.75 mmol) in DMSO (5 mL) for 24 hrs gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol \(\rightarrow\) 20% EtOAc/petrol), the title compound as a pale yellow solid (421 mg, 67%); m.p. 50–52 °C; \(\nu_{\text{max}}\) (KBr) 1728 (br), 1531, 1345, 1280, 1118, 1104, 719; \(\delta_{\text{H}}\) (400MHz, CDCl\(_3\)) 1.13 (3H, d, \(J=6.9\), C(3)Me\(_A\)Me\(_B\)), 1.17 (3H, d, \(J=6.9\), C(3)Me\(_A\)Me\(_B\)), 2.47 (1H, quint d, \(J=6.9\), 4.5, C(3)\(H\)), 5.18 (1H, dd, \(J=4.5\), 0.5, C(2)\(H\)), 8.25-8.28 (2H, m, \(Ar\)), 8.32-8.35 (2H, m, \(Ar\)), 9.66 (1H, d, \(J=0.5\), C(1)\(H\)); \(\delta_{\text{C}}\) (100MHz, CDCl\(_3\)) 17.3, 18.9, 29.0, 83.4, 123.7, 131.0, 134.7, 150.8, 164.2, 197.3; \(m/z\) (ASAP) 252 ([M+H]\(^+\), 100%); HRMS (ASAP) \(\text{C}_{12}\text{H}_{14}\text{NO}_5\) ([M+H]\(^+\) requires 252.0866, found 252.0860 (-2.6 ppm).

**General Procedure B: used for the preparation of 12, 13, 22 and 24:**

To a stirred solution of the requisite aldehyde or ketone (1.0 eq) in THF (0.5M) at \(-78\) °C was added vinylmagnesium bromide (1.0M in THF, 1.1 eq) dropwise and the resulting solution stirred at \(-78\) °C for 30 mins. 4-nitrobenzoyl chloride (1.2 eq) was then added portionwise over 5 mins and the mixture stirred at RT for 2–18 hrs (until tlc shows complete consumption of the vinyl alcohol). Purification by flash column chromatography afforded the \(O\)-\(p\)-nitrobenzoyl vinyl alcohol.
A solution of the requisite O-p-nitrobenzoyl vinyl alcohol (1.0 eq) in CH₂Cl₂ (0.025M) at −78 °C was subjected to ozonolysis, followed by addition of dimethyl sulfide (2.0 eq). The resulting mixture was concentrated in vacuo and the crude product purified by flash column chromatography using the solvent system stated.

**1-phenylbut-3-en-2-yl p-nitrobenzoate:** Phenylacetaldehyde (0.58 mL, 5.00 mmol), vinylmagnesium bromide (1.0M in THF, 5.50 mL, 5.50 mmol) and p-nitrobenzoyl chloride (1.11 g, 6.00 mmol) in THF (10 mL) gave, after purification by flash column chromatography (silica, petrol → 10% EtOAc/petrol), the title compound as a yellow oil (1.08 g, 72%); \( \nu_{\text{max}} \) (film) 1725, 1527, 1271, 1116, 1103, 720; \( \delta_H \) (400MHz, CDCl₃) 3.10 (2H, qd, \( J = 12.7, 6.7 \), C(1)H₂), 5.25 (1H, dt, \( J = 10.5, 1.1 \), CH=CH₂H₁), 5.32 (1H, dt, \( J = 17.2, 1.1 \), CH=CH₂H₂), 5.71-5.76 (1H, m, C(2)H), 5.94 (1H, ddd, \( J = 17.2, 10.5, 6.5 \), CH=CH₂), 7.22-7.31 (5H, m, Ph), 8.15-8.17 (2H, m, Ar), 8.26-8.29 (2H, m, Ar); \( \delta_C \) (75MHz, CDCl₃) 41.0, 77.0, 118.0, 123.7, 126.9, 128.6, 129.7, 130.8, 135.3, 135.9, 136.5, 150.6, 163.8; m/z (ASAP) 315 ([M+NH₄]⁺, 100%); HRMS (ASAP) C₁₇H₁₉N₂O₄ ([M+NH₄]⁺) requires 315.1339, found 315.1336 (-1.1 ppm).

**1-oxo-3-phenylpropan-2-yl p-nitrobenzoate 12:** Ozonolysis of 1-phenylbut-3-en-2-yl p-nitrobenzoate (1.35 g, 4.56 mmol) in CH₂Cl₂ (180 mL) at −78 °C, followed by addition of dimethylsulfide (0.67 mL, 9.12 mmol) gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 30% EtOAc/petrol), the title compound as a white solid (940 mg, 69%); m.p. 64–66 °C; \( \nu_{\text{max}} \) (KBr) 1739, 1721, 1525, 1349, 1293, 1120, 1104; \( \delta_H \) (400MHz, CDCl₃) 3.15 (1H, dd, \( J = 14.5, 8.4 \), C(3)H₃H₂), 3.28 (1H, dd, \( J = 14.5, 4.9 \), C(3)H₂H₂), 5.44 (1H, dd, \( J = 8.4, 4.9 \), C(2)H), 7.18-7.27
(5H, m, Ph), 8.11 (2H, d, J 8.9, Ar), 8.22 (2H, d, J 8.9, Ar), 9.60 (1H, s, C(1)H); δC (75MHz, CDCl₃) 35.2, 79.8, 123.7, 127.4, 128.9, 129.4, 131.0, 134.4, 135.0, 150.9, 164.1, 196.9; m/z (NSI) 299 ([M]⁺, 25%); HRMS (NSI) C₁₆H₁₄NO₅ ([M+H]⁺ requires 300.0869, found 300.0869 (+0.8 ppm).

![Hept-1-en-3-yl p-nitrobenzoate](image)

**Hept-1-en-3-yl p-nitrobenzoate:** Valeraldehyde (0.53 mL, 5.00 mmol), vinylmagnesium bromide (1.0M in THF, 5.50 mL, 5.50 mmol) and p-nitrobenzoyl chloride (1.11 g, 6.00 mmol) in THF (10 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a pale yellow oil (997 mg, 76%); νmax (film) 2958, 2934, 2863, 1725, 1529, 1271, 1115, 1103, 720; δH (400MHz, CDCl₃) 0.89-0.93 (3H, m, C(6)H₃), 1.33-1.41 (4H, m, C(4)H₂ and C(5)H₂), 1.70-1.86 (2H, m, C(3)H₂), 5.24 (1H, dt, J 10.5, 1.1, CH=CH₂Hₐ), 5.34 (1H, dt, J 17.2, 1.1, CH=CH₂Hₐ), 5.50 (1H, app q, J 6.6, C(2)H), 5.89 (1H, ddd, J 17.2, 10.5, 6.6, CH=CH₂), 8.20-8.24 (2H, m, Ar), 8.27-8.31 (2H, m, Ar); δC (75MHz, CDCl₃) 14.1, 22.6, 27.3, 34.0, 76.8, 117.5, 123.6, 130.8, 136.1, 150.6, 164.1; m/z (ASAP) 264 ([M+H]⁺, 100%); HRMS (ASAP) C₁₄H₁₈NO₄ ([M+H]⁺ requires 264.1230, found 264.1224 (-2.4 ppm).

![1-oxohexan-2-yl p-nitrobenzoate 13](image)

**1-oxohexan-2-yl p-nitrobenzoate 13:** Ozonolysis of hept-1-en-3-yl p-nitrobenzoate (790 mg, 3.0 mmol) in CH₂Cl₂ (120 mL) at −78 °C, followed by addition of dimethylsulfide (0.44 mL, 6.0 mmol) gave, after purification by flash...
column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a pale yellow oil (640 mg, 80%); \( \nu_{\text{max}} \) (film) 2959, 2933, 2864, 1731 (br), 1608, 1530, 1350, 1271, 1004, 874, 844, 720; \( \delta_{\text{H}} \) (400MHz, CDCl\(_3\)) 0.95 (3H, t, J 7.2, C(6)H\(_3\)), 1.36-1.54 (4H, m, C(4)H\(_2\) and C(5)H\(_2\)), 1.88-2.07 (2H, m, C(3)H\(_2\)), 5.31 (1H, dd, J 8.3, 4.7, C(2)H), 8.26-8.28 (2H, m, Ar), 8.31-8.34 (2H, m, Ar), 9.64 (1H, d, J 0.4, C(1)H); \( \delta_{\text{C}} \) (75MHz, CDCl\(_3\)) 13.8, 22.4, 27.2, 28.4, 79.6, 123.7, 131.0, 134.6, 150.8, 164.3, 197.2; m/z (NSI) 265 ([M\(^+\)], 45%); HRMS (NSI) \( \text{C}_{13}\text{H}_{16}\text{NO}_5 \) ([M+H]\(^+\) requires 266.1023, found 266.1026 (+1.1 ppm).

**1-phenylallyl \( p \)-nitrobenzoate:** Benzaldehyde (0.51 mL, 5.00 mmol), vinylmagnesium bromide (1.0M in THF, 5.50 mL, 5.50 mmol) and \( p \)-nitrobenzoyl chloride (1.11 g, 6.00 mmol) in THF (10 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a pale yellow solid (1.10 g, 78%); m.p. 38–39 °C; \( \nu_{\text{max}} \) (KBr) 3120, 1719, 1526, 1348, 1270, 1119 1104, 716; \( \delta_{\text{H}} \) (400MHz, CDCl\(_3\)) 5.35 (1H, dt, J 10.5, 1.2, CH=CH\(_{\text{A}}\)H\(_{\text{B}}\)), 5.41 (1H, dt, J 17.1, 1.2, CH=CH\(_{\text{A}}\)H\(_{\text{B}}\)), 6.15 (1H, ddd, J 17.1, 10.5, 6.2, CH=CH\(_{\text{A}}\)H\(_{\text{B}}\)), 6.53 (1H, d, J 6.0, C(1)H), 7.33-7.47 (5H, m, Ph), 8.24-8.31 (4H, m, Ar); \( \delta_{\text{C}} \) (75MHz, CDCl\(_3\)) 78.0, 117.9, 123.7, 127.3, 128.7, 128.9, 135.8, 138.4, 150.7, 163.8; m/z (ASAP) 264 ([M\(^+\)], 55%); HRMS (ASAP) \( \text{C}_{16}\text{H}_{13}\text{NO}_4 \) ([M\(^+\)] requires 283.0839, found 283.0838 (-0.4 ppm).

**2-oxo-1-phenylethyl \( p \)-nitrobenzoate 22:** Ozonolysis of 1-phenylallyl \( p \)-nitrobenzoate (567 mg, 2.0 mmol) in CH\(_2\)Cl\(_2\) (80 mL) at \(-78 \) °C, followed by addition of dimethylsulfide (0.29 mL, 4.00 mmol) gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a white solid (479 mg, 84%); m.p. 108–110 °C; \( \nu_{\text{max}} \) (KBr) 1747, 1719, 1530,
1342, 1270, 1123, 1104, 720, 700; δ_H (400MHz, CDCl_3) 6.34 (1H, s, C(1)H), 7.48-7.50 (5H, m, Ph), 8.29-8.34 (4H, m, Ar), 9.67 (1H, s, C(2)H); δ_C (75MHz, CDCl_3) 81.6, 123.8, 128.3, 129.6, 130.6, 131.2, 134.6, 151.0, 163.8, 193.0; m/z (NSI) 285 ([M]^+, 10%); HRMS (NSI) C_{13}H_{16}NO_5 ([M+H]^+ requires 286.0710, found 286.0712 (+0.7 ppm).

**1-vinylcyclohexyl p-nitrobenzoate:** Cyclohexanone (0.50 mL, 5.00 mmol), vinylmagnesium bromide (1.0M in THF, 5.50 mL, 5.50 mmol) and p-nitrobenzoyl chloride (1.11 g, 6.00 mmol) in THF (10 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as an off-white solid (720 mg, 52%); m.p. 75–77 °C; ν_{max} (KBr) 2938, 1719, 1524, 1271, 1103, 717; δ_H (400MHz, CDCl_3) 1.25-1.32 (1H, m, C_H_2), 1.48-1.67 (7H, m, CH_2), 2.31 (2H, br d, J 12.7, CH_2), 5.13-5.21 (2H, m, CH=CH_2), 6.13 (1H, dd, J 17.6, 11.0, CH=CH_2), 8.12 (2H, d, J 8.9, Ar), 8.20 (2H, d, J 8.9); δ_C (100MHz, CDCl_3) 22.1, 25.4, 34.9, 84.1, 114.6, 123.6, 130.6, 137.1, 141.2, 150.4, 163.2; m/z (ASAP) 276 ([M+H]^+, 20%); HRMS (ASAP) C_{15}H_{18}NO_4 ([M+H]^+ requires 276.1230, found 276.1227 (-1.2 ppm).

**1-formylcyclohexyl p-nitrobenzoate 24:** Ozonolysis of 1-vinylcyclohexyl p-nitrobenzoate (720 mg, 2.62 mmol) in CH_2Cl_2 (105 mL) at −78 °C, followed by addition of dimethylsulfide (0.39 mL, 5.24 mmol) gave, after purification by flash column chromatography (silica, 10% EtOAc/petrol → 20% EtOAc/petrol), the title compound as a white solid (510 mg, 70%); m.p. 92–94 °C; ν_{max} (KBr) 2938, 1738, 1710, 1529, 1306, 1119, 1103, 718; δ_H (300MHz, CDCl_3) 1.32-1.44 (1H, m, CH_2), 1.60-1.84 (7H, m, CH_2), 2.14-2.19 (2H, m, CH_2), 8.23-8.28 (2H, m, Ar), 8.31-8.34 (2H, m, Ar), 9.62 (1H, s, CHO); δ_C (75MHz, CDCl_3) 21.1, 24.8, 29.4, 85.8, 123.7, 131.0, 134.9, 150.9, 163.8, 198.0; m/z (ASAP)
278 ([M+H]^+, 100%); HRMS (ASAP) C_{14}H_{16}NO_5 ([M+H]^+ requires 278.1023, found 278.1020 (-1.1 ppm).

**Preparation of catalyst 10:**

(a) Preparation of mesitylhydrazine hydrochloride:

To a stirred solution of di-tert-butyl dicarbonate (48.0 g, 220 mmol) in MeOH (50 mL), cooled to −10 °C, was added a solution of hydrazine monohydrate (4.86 mL, 200 mmol) in MeOH (50 mL) dropwise over ~30 mins via a pressure-equalised dropping funnel. The resulting mixture was allowed to stir at RT for 3 hrs then concentrated *in vacuo*. The resulting solid was triturated with hexane (250 mL) to give di-tert-butyl hydrazine-1,2-dicarboxylate as a white solid (19.4 g, 84%) with spectroscopic data in accordance with the literature;^8^ m.p. 121–122 °C {lit. m.p. 122 °C}; δ_H (300MHz, CDCl_3) 1.46 (18H, s, 2 × CMe_3), 6.26 (2H, br s, 2 × NH). [Note – Concentration of the mother liquor and repetition of the process generally affords a second crop of equal purity]

Following the procedure of Mäeorg et al.;^9^ To a stirred solution of di-tert-butyl hydrazine-1,2-dicarboxylate (11.6 g, 50 mmol) and pyridine (8.29 mL, 102 mmol) in CH_2Cl_2 (50 mL) at 0 °C was added a solution of Br_2 (2.82 mL, 55 mmol) in CH_2Cl_2 (20 mL) dropwise over ~15 mins *via*
a pressure-equalised dropping funnel. The resulting solution was stirred at 0 °C for 30 mins then
diluted with CH₂Cl₂ (50 mL) and washed with 1M aq. HCl (100 mL), sat. aq. NaHCO₃ (100 mL)
and brine (100 mL). The organic layer was dried, filtered and concentrated *in vacuo* to give the
crude product which was triturated with cold hexane (100 mL) to give di-tert-butyl
azodicarboxylate as a pale yellow solid (10.0 g, 87%) with spectroscopic data in accordance with
the literature; m.p. 85–87 °C {lit.¹⁰ m.p. 90–92 °C}; δ_H (300MHz, CDCl₃) 1.63 (18H, s, 2 × CMe₃). [Note – Concentration of the mother liquor and repetition of the process generally
affords a second crop of equal purity].

*Following the procedure of Demers and Klauber;¹¹* To a stirred solution of di-tert-butyl
azodicarboxylate (11.3 g, 49 mmol) in THF (200 mL) at −78 °C was added 2-mesitylmagnesium
bromide (1.0 M in Et₂O, 49 mL, 49 mmol) and the resulting solution stirred at −78 °C for 30
mins then quenched with acetic acid (2.9 mL, 50 mmol). The mixture was allowed to warm to
RT then H₂O (100 mL) was added and the mixture extracted with Et₂O (3 × 100 mL). The
combined organics were washed with brine (100 mL), dried, filtered and concentrated *in vacuo*
to give the crude product, which was used directly in the next step.

The crude product was dissolved in i-PrOH (125 mL) and HCl (4M in dioxane, 125 mL, 500
mmol) was added. The mixture was heated at reflux for 30 mins then cooled to 0 °C and diluted
with Et₂O (125 mL). The precipitate was collected by filtration, then washed with Et₂O (3×) and
dried under vacuum for several hours to give mesitylhydrazine hydrochloride as an off-white
solid (6.51 g, 71%) with spectroscopic data in accordance with the literature;¹² m.p. 192–194 °C
{lit.¹² m.p. 195–197 °C (dec)}; δ_H (300MHz, D₂O) 2.27 (3H, s, C(4)Me), 2.36 (6H, s, C(2,6)Me),
7.04 (2H, s, C(3,5)H).
(b) Procedure for obtaining free based mesitylhydrazine

To a mixture of 1 M aq. NaOH (50 mL) and Et₂O (50 mL) cooled to −10 °C was added mesitylhydrazine hydrochloride (1.87 g, 10 mmol) and the mixture stirred at −10 °C until almost all the solid has dissolved (typically ~15 mins). The layers were separated and the aqueous layer extracted with Et₂O (2 × 25 mL). The combined organics were dried (Na₂SO₄), filtered and concentrated in vacuo to give mesitylhydrazine as a pale yellow solid (1.22 g, 81%) which was used immediately without further purification; δ_H (300MHz, CDCl₃) 2.17 (6H, s, C(2,6)Me), 2.24 (3H, s, C(4)Me), 6.81 (2H, s, C(3,5)H); [In our hands, mesitylhydrazine was stable for a period of a few hours under an inert atmosphere but readily decomposed upon exposure to air].

(c) Preparation of the triazolium salt 10

Following the general procedure of Rovis et al.¹³ To a stirred solution of pyrrolidin-2-one (0.52 mL, 6.8 mmol) in anhydrous CH₂Cl₂ (25 mL) was added trimethyloxonium tetrafluoroborate (1.03 g, 6.96 mmol) and the mixture stirred at RT for 18 hrs. Mesitylhydrazine (1.06 g, 6.96 mmol) was then added and the resulting orange solution stirred for a further 18 hours at RT. The mixture was then concentrated in vacuo and EtOAc (25 mL) was added. The solid was collected by filtration, washed with EtOAc (3 × 10 mL), then dried under vacuum for several hours to give the hydrazone as an off-white solid (1.06 g, 51%). To the hydrazone was added chlorobenzene (7 mL) and triethylorthoformate (2.89 mL, 17.4 mmol) and the mixture then heated at 120 °C for 72 hours. The mixture was concentrated in vacuo then EtOAc (15 mL) was added and the solid
collected by filtration, washed with EtOAc (3 × 10 mL), then dried under vacuum for several hours to give 2-mesityl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate 10 as an off-white solid (860 mg, 79%) with spectroscopic data in accordance with the literature;\textsuperscript{14} m.p. 174–176 °C; \(\delta_{\text{H}}\) (400MHz, CDCl\(_3\)) 2.07 (6H, s, 2 × o-ArMe), 2.36 (3H, s, p-ArMe), 2.90 (2H, quintet, \(J\) 7.6, \(CH_2\)), 3.25 (2H, t, \(J\) 7.8, \(CH_2\)), 4.70 (2H, t, \(J\) 7.4, \(CH_2\)), 6.99 (2H, s, 2 × m-ArH), 9.52 (1H, s, NCHN).
Procedure for the NHC-mediated redox esterification of α-aroyloxyaldehydes:

To a flame-dried Schlenk flask under an atmosphere of N\textsubscript{2} was added the appropriate α-aroyloxyaldehyde (1.0 eq), the requisite alcohol (2.0 eq), catalyst 10 (0.20 eq) and THF (0.1M) followed by triethylamine (1.5 eq). The resulting mixture was stirred at RT for 16 hrs then concentrated in vacuo to give a crude product, which was purified as described.

**Benzyl 3-methylbutanoate 11:** 9 (126 mg, 0.50 mmol), benzyl alcohol (0.10 mL, 1.00 mmol), catalyst 10 (31.5 mg, 0.10 mmol) and triethylamine (0.10 mL, 0.75 mmol) in THF (5.0 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (71 mg, 74%) with spectroscopic data in accordance with the literature;\textsuperscript{15} δ\textsubscript{H} (400MHz, CDCl\textsubscript{3}) 0.96 (6H, d, J 6.6, C(3)Me\textsubscript{2}), 2.08-2.18 (1H, m, C(3)H), 2.25 (2H, d, J 7.0, C(2)H\textsubscript{2}), 5.12 (2H, s, OCH\textsubscript{2}Ph), 7.31-7.39 (5H, m, Ph).

**Benzyl 3-phenylpropanoate 14:** 12 (75 mg, 0.25 mmol), benzyl alcohol (52 µL, 0.50 mmol), catalyst 10 (15.8 mg, 0.050 mmol) and triethylamine (52 µL, 0.375 mmol) in THF (2.5 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (40 mg, 67%) with spectroscopic data in accordance with the literature;\textsuperscript{14} δ\textsubscript{H} (400MHz, CDCl\textsubscript{3}) 2.68 (2H, dd, J 8.4, 7.2, C(2)H\textsubscript{2}), 2.96 (2H, t, J 7.8, C(3)H\textsubscript{2}), 5.10 (2H, s, OCH\textsubscript{2}Ph), 7.16-7.36 (10H, m, 2 × Ph).

**Benzyl hexanoate 15:** 13 (133 mg, 0.50 mmol), benzyl alcohol (0.10 mL, 1.00 mmol), catalyst 10 (31.5 mg, 0.10 mmol) and triethylamine (0.10 mL, 0.75 mmol) in THF (5.0 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (73 mg, 71%) with
spectroscopic data in accordance with the literature;\textsuperscript{16} $\delta_H$ (300MHz, CDCl\textsubscript{3}) 0.89 (3H, t, $J$ 6.9, C(6)H\textsubscript{3}), 1.27-1.34 (4H, m, C(4)H\textsubscript{2} and C(5)H\textsubscript{2}), 1.60-1.70 (2H, m, C(3)H\textsubscript{2}), 2.36 (2H, t, $J$ 7.6, C(2)H\textsubscript{2}), 5.12 (2H, s, OCH\textsubscript{2}Ph), 7.30-7.38 (5H, m, Ph).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{methyl_3-phenylpropanoate_16}
\caption{Methyl 3-phenylpropanoate 16: 12 (116 mg, 0.39 mmol), methanol (32 $\mu$L, 0.78 mmol), catalyst 10 (24.4 mg, 0.078 mmol) and triethylamine (81 $\mu$L, 0.58 mmol) in THF (3.9 mL) gave, after purification by flash column chromatography (silica, petrol $\rightarrow$ 5% EtOAc/petrol), the title compound as a colourless oil (42 mg, 66%) with spectroscopic data in accordance with the literature;\textsuperscript{14} $\delta_H$ (400MHz, CDCl\textsubscript{3}) 2.64 (2H, dd, $J$ 8.5, 7.2, C(2)H\textsubscript{2}), 2.96 (2H, t, $J$ 7.9, C(3)H\textsubscript{2}), 3.68 (3H, s, OMe), 7.19-7.23 (3H, m, Ph).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{ethyl_3-phenylpropanoate_17}
\caption{Ethyl 3-phenylpropanoate 17: 12 (150 mg, 0.50 mmol), ethanol (58 $\mu$L, 1.00 mmol), catalyst 10 (31.5 mg, 0.10 mmol) and triethylamine (0.10 mL, 0.75 mmol) in THF (5.0 mL) gave, after purification by flash column chromatography (silica, petrol $\rightarrow$ 5% EtOAc/petrol), the title compound as a colourless oil (52 mg, 58%) with spectroscopic data in accordance with the literature;\textsuperscript{14} $\delta_H$ (300MHz, CDCl\textsubscript{3}) 1.23 (3H, t, $J$ 7.1, OCH\textsubscript{2}CH\textsubscript{3}), 2.62 (2H, dd, $J$ 8.5, 7.1, C(2)H\textsubscript{2}), 2.95 (2H, t, $J$ 7.8, C(3)H\textsubscript{2}), 4.12 (2H, q, $J$ 7.1, OCH\textsubscript{2}CH\textsubscript{3}), 7.17-7.31 (5H, m, Ph).

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{allyl_3-phenylpropanoate_18}
\caption{Allyl 3-phenylpropanoate 18: 12 (75 mg, 0.25 mmol), allyl alcohol (34 $\mu$L, 0.50 mmol), catalyst 10 (15.8 mg, 0.050 mmol) and triethylamine (52 $\mu$L, 0.375 mmol) in THF (2.5 mL) gave, after purification by flash column chromatography (silica, petrol $\rightarrow$ 5% EtOAc/petrol), the title compound as a colourless oil (45 mg, 95%) with spectroscopic data in accordance with the literature;\textsuperscript{17} $\delta_H$ (400MHz, CDCl\textsubscript{3}) 2.68 (2H, dd, $J$ 8.5, 7.2, C(2)H\textsubscript{2}), 2.98 (2H, t, $J$ 7.8, C(3)H\textsubscript{2}), 4.59 (2H, dt, $J$ 5.7, 1.4, OCH\textsubscript{2}CH=CH\textsubscript{2}), 5.23 (1H, dq, $J$}
10.4, 1.3, OCH₂CH=CH₆H₆B), 5.29 (1H, dq, J 17.2, 1.5, OCH₂CH=CH₆H₆B), 5.90 (1H, ddt, J 17.2, 10.4, 5.7, OCH₂CH=CH₂), 7.19-7.23 (3H, m, Ph), 7.28-7.32 (2H, m, Ph).

Cyclohexyl 3-phenylpropionate 19: 12 (75 mg, 0.25 mmol), cyclohexanol (53 µL, 0.50 mmol), catalyst 10 (15.8 mg, 0.05 mmol) and triethylamine (52 µL, 0.375 mmol) in THF (2.5 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (13 mg, 22%) with spectroscopic data in accordance with the literature;¹⁸ δ_H (400MHz, CDCl₃) 1.13-1.76 (10H, m, 5 × CH₂), 2.52-2.56 (2H, m, C(2)H₂), 2.88 (2H, t, J 7.8, C(3)H₂), 4.68 (1H, td, J 8.8, 4.1, OCH), 7.18-7.23 (3H, m, Ph), 7.27-7.31 (2H, m, Ph).

Furan-2-ylmethyl 3-phenylpropanoate 20: 12 (39 mg, 0.13 mmol), furfuryl alcohol (22 µL, 0.26 mmol), catalyst 10 (8.2 mg, 0.026 mmol) and triethylamine (27 µL, 0.195 mmol) in THF (1.3 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (23 mg, 77%) with spectroscopic data in accordance with the literature;¹⁹ δ_H (300MHz, CDCl₃) 2.68 (2H, dd, J 8.4, 7.1, C(2)H₂), 2.97 (2H, t, J 7.8, C(3)H₂), 5.08 (2H, s, OCH₂Ar), 6.37-6.41 (2H, m, Ar), 7.18-7.24 (3H, m, Ph), 7.26-7.32 (2H, m, Ph), 7.44 (1H, dd, J 1.8, 0.9, Ar).

Furan-2-ylmethyl hexanoate 21: 13 (66 mg, 0.25 mmol), furfuryl alcohol (43 µL, 0.50 mmol), catalyst 10 (15.8 mg, 0.050 mmol) and triethylamine (52 mL, 0.375 mmol) in THF (2.5 mL) gave, after purification by flash column chromatography (silica, petrol → 5% EtOAc/petrol), the title compound as a colourless oil (31 mg, 63%); ν_max (film2959, 2933, 2873, 1740, 1243, 1229, 1164, 743; δ_H (300MHz, CDCl₃) 0.88 (3H, t, J 6.9, C(6)H₃), 1.26-1.31 (4H, m, C(4)H₂ and C(5)H₂), 1.58-1.67 (2H, m, C(3)H₂), 2.32
(2H, t, J 7.6, C(2)H2), 5.06 (2H, s, OCH2Ar), 6.35 (1H, dd, J 3.1, 1.8, Ar), 6.39 (1H, d, J 3.1, Ar),
7.41 (1H, dd, J 1.8, 0.7, Ar); δC (100MHz, CDCl3) 14.0, 22.4, 24.7, 31.4, 34.2, 58.0, 110.6,
110.7, 143.3, 149.8, 173.6; m/z (ASAP) 214 ([M+NH4]+, 45%); HRMS (ASAP) C11H20NO3
([M+NH4]+ requires 214.1438, found 214.1432 (-2.7 ppm).
Procedure for the base-mediated rearrangement of 22:

(a) under NHC-mediated redox esterification conditions:

To a flame-dried Schlenk flask under an atmosphere of N₂ was added 22 (71 mg, 0.25 mmol), benzyl alcohol (52 µL, 0.50 mmol), catalyst 10 (15.8 mg, 0.050 mmol), THF (2.5 mL) and triethylamine (52 µL, 0.375 mmol). The resulting mixture was stirred at RT for 16 hrs then concentrated in vacuo to give a crude product. \(^1\)H NMR analysis showed that 2-oxo-2-phenylethyl 4-nitrobenzoate 23 was the major product of the reaction.

(b) with triethylamine only:

To a stirred solution of 22 (71 mg, 0.25 mmol) in THF (2.5 mL) at RT was added triethylamine (52 µL, 0.375 mmol, 1.5 eq) and the mixture stirred at RT for 3 hrs then concentrated in vacuo to give 2-oxo-2-phenylethyl 4-nitrobenzoate 24 as a white solid (71 mg, quant.) with spectroscopic data in accordance with the literature;\(^20\) m.p. 120–121 °C;\(^{21}\) m.p. 124–125 °C; \(\delta\) (400MHz, CDCl₃) 5.65 (2H, s, CH₂), 7.51-7.56 (2H, m, Ph), 7.63-7.68 (1H, m, Ph), 7.96-7.98 (2H, m, Ph), 8.33 (4H, app s, Ar).
**Procedure for the NHC-mediated redox amination of 9 to give 26:**

![Chemical structure diagram]

To a flame-dried Schlenk flask under an atmosphere of N\textsubscript{2} was added 9 (63 mg, 0.25 mmol), phenol (47 mg, 0.50 mmol), catalyst 10 (15.8 mg, 0.050 mmol), THF (2.5 mL) and triethylamine (52 \(\mu\)L, 0.375 mmol). The resulting mixture was stirred at RT for 16 hrs then benzylamine (68 \(\mu\)L, 0.625 mmol, 2.5 eq) and DMAP (6 mg, 0.05 mmol) were added and the mixture stirred at RT for a further 48 hrs then concentrated in vacuo. Purification by flash column chromatography (silica, petrol \(\rightarrow\) 5% EtOAc/petrol) gave \(N\)-benzyl-3-methylbutanamide 26 as a colourless oil (30 mg, 63%) with spectroscopic data in accordance with the literature;\textsuperscript{22} \(\delta_H\) (400MHz, CDCl\textsubscript{3}) 0.89 (6H, d, \(J\) 6.4, C(3)Me\textsubscript{2}), 1.99-2.01 (2H, m, C(2)H\textsubscript{2}), 2.03-2.13 (1H, m, C(3)H), 4.37 (2H, d, \(J\) 5.7, NCH\textsubscript{2}Ph), 5.76 (1H, br s, NH), 7.18-7.21 (3H, m, Ph), 7.24-7.28 (2H, m, Ph).

*\(N.B.\) It was also possible to isolate the intermediate phenyl ester in moderate yield:*

**Phenyl 3-methylbutanoate 25:** Concentration in vacuo after the first step, and purification by flash column chromatography (silica, petrol \(\rightarrow\) 5% EtOAc/petrol), gave the title compound as a colourless oil (18 mg, 40%) with spectroscopic data in accordance with the literature;\textsuperscript{23} \(\delta_H\) (400MHz, CDCl\textsubscript{3}) 0.99 (6H, d, \(J\) 6.7, C(3)Me\textsubscript{2}), 2.12-2.23 (1H, m, C(3)H), 2.36 (2H, d, \(J\) 7.2, C(2)H\textsubscript{2}), 7.00 (2H, dd, \(J\) 8.6, 1.1, \(o\)-Ph), 7.12-7.18 (1H, m, \(p\)-Ph), 7.28-7.33 (2H, m, \(m\)-Ph).
Procedure for the formal [4+2] cycloaddition reaction:

To a stirred solution of (E)-ethyl 2-oxo-4-phenylbut-3-enoate 27 (20.4 mg, 0.10 mmol), 12 (47 mg, 0.157 mmol) and catalyst 10 (9.9 mg, 0.031 mmol) in THF (1.5 mL) at RT was added triethylamine (21 µL, 0.15 mmol) and the mixture stirred at RT for 16 hrs then concentrated in vacuo. Purification by flash column chromatography (silica, 10% EtOAc/petrol) gave an inseparable 69:31 diastereoisomeric mixture of dihydropyranones 28a and 28b as a colourless oil (18 mg, 54% combined yield);  

(3RS,4RS)-Ethyl 3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate 28a (major diastereoisomer): δ_H (400MHz, CDCl₃) 1.35 (3H, t, J 7.1, OCH₂CH₃), 2.42 (1H, dd, J 15.8, 10.6, CH₃H₃Ph), 3.26-3.31 (2H, m, CH₃H₃Ph and C(3)H), 3.64 (1H, t, J 6.8, C(2)H), 4.32 (2H, q, J 7.1, OCH₂CH₃), 6.67 (1H, d, J 6.8, C(5)H), 7.02-7.09 (4H, m, Ph), 7.25-7.36 (6H, m, Ph); δ_C (75MHz, CDCl₃) 14.3, 32.2, 40.7, 44.9, 62.1, 118.6, 126.8, 127.5, 128.5, 128.7, 129.0, 129.3, 135.9, 138.2, 142.6, 160.6, 168.7.

(3RS,4SR)-Ethyl 3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2H-pyran-6-carboxylate 28b (minor diastereoisomer): δ_H (400MHz, CDCl₃) 1.37 (3H, t, J 7.1, OCH₂CH₃), 2.92 (1H, dt, J 12.6, 6.2, C(3)H), 3.05-3.14 (2H, m,
$CH_2Ph$, 3.60-3.65 (1H, m, C(2)$H$), 4.35 (2H, obsc q, OCH$_2$CH$_3$), 6.52 (1H, d, $J$ 5.0, C(5)$H$), 7.02-7.09 (2H, m, $Ph$), 7.16 (2H, m, $Ph$), 7.25-7.36 (6H, m, $Ph$); $\delta_C$ (75MHz, CDCl$_3$) 14.3, 35.7, 41.5, 47.8, 62.2, 116.4, 127.2, 128.1, 128.4, 128.8, 129.3, 129.4, 135.6, 137.4, 142.6, 160.6, 168.2.

$m/z$ (NSI) 278 ([M+NH$_4$]$^+$, 100%); HRMS (NSI) C$_{21}$H$_{24}$NO$_4$ ([M+NH$_4$]$^+$ requires 354.1700, found 354.1704 (+1.2 ppm).
References and notes


24 The relative configuration of the major isomer was tentatively assigned as syn by comparison with $^1$H NMR data of the corresponding $p$-tolyl derivative; see He, M., Uc, J. C. and Bode, J. W.; J. Am. Chem. Soc., 2006, 128, 15088-15089.
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δ_H (300MHz, CDCl₃)
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$\delta_C^{13}$ (100 MHz, CDCl$_3$)

- 197.955
- 165.249
- 148.160
- 133.194
- 132.379
- 128.366
- 124.054
- 84.116
- 77.478
- 77.160
- 76.842
- 29.183
- 18.772
- 17.133

$^{13}$C NMR spectrum of compound 7.
$\delta_C$ (100MHz, CDCl$_3$)
$\text{Boc}^2\text{N}^\text{H}^\text{N}\text{Boc}$

$\nu_0 (300\text{MHz, CDCl}_3)$
\[ \delta_H(300\text{MHz, CDCl}_3) \]

Boc-NH-NH-Boc
δ_H (300MHz, CDCl₃)
$\delta_4 (400\text{MHz, CDCl}_3)$
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δ_H (400MHz, CDCl_3)
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$\delta_H (400\text{MHz, CDCl}_3)$

Ph $\xrightarrow{\text{O}}$ O Ph

14
$^{1}H$ (400MHz, CDCl$_3$)
Ph\[O Me

\delta_H (400MHz, CDCl_3)
Ph\(-\)CO\(-\)O\(-\)CH₃

$\delta_H$ (300MHz, CDCl₃)
18

δ_H (400MHz, CDCl₃)
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\[
\delta_H (300\text{MHz, CDCl}_3)
\]
$\delta_H (300\text{MHz, CDCl}_3)$

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$\delta_C (75\text{MHz, CDCl}_3)$
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Ph

O

Ph

O

NO₂

δ\textsubscript{H} (400MHz, CDCl\textsubscript{3})
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$\delta_H (400\text{MHz, CDCl}_3)$

$\text{HCO}_2\text{Ph}$

25
26

δ_H (400MHz, CDCl_3)
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\[
\begin{align*}
\text{Ph} & \quad \text{CO}_2\text{Et} \\
\text{Ph} & \quad \text{CO}_2\text{Et} \\
\end{align*}
\]

\[\delta_C (100\text{MHz, CDCl}_3)\]