Supporting Information

Efficient *N*-Heterocyclic Carbene Catalysed *O*- to C-acyl transfer

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Experimental Procedures and Analytical Data

General Information

All reactions involving moisture sensitive reagents were performed under an atmosphere of nitrogen via standard vacuum line techniques and with freshly distilled solvents. All glassware was flame dried and allowed to cool under vacuum. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were distilled from sodium benzophenone ketyl under nitrogen. Potassium bis(trimethylsilyl)amide (KHMDs) was used as a 0.5M solution in toluene as supplied (Aldrich). Petrol is defined as petroleum ether 40-60°C. All solvents and commercial reagents were used as supplied without further purification. Room temperature refers to 20-25°C. Temperatures of 0°C were obtained using an ice/water bath and reaction reflux conditions using an oil bath equipped with a contact thermometer. *In vacuo* refers to the use of a Büchi Rotavapor R-2000 rotary evaporator with a Vacubrand CVC₂ vacuum controller. Analytical thin layer chromatography was performed on aluminium sheets coated with 60 F₂₅₄ silica. TLC visualisation was carried out with ultraviolet light (254 nm), followed by staining with 1% aqueous KMnO₄ solution. Column chromatography was performed on Kieselgel 60 silica in the solvent system stated. ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were acquired on either a Bruker Avance 300 (300 MHz ¹H, 75.4 MHz ¹³C) or a Bruker Avance 500 (500 MHz ¹H, 125.7 MHz ¹³C) spectrometer and in the deuterated solvent stated. Coupling constants (*J*) are reported in Hz. Multiplicities are indicated by: s (singlet), d (doublet), t (triplet), tt (triplet of triplets), sept (septet) and m (multiplet). The abbreviation Ar is used to denote aromatic. Infrared spectra ($\nu_{\max}$) were recorded on a Perkin-Elmer Spectrum GX FT-IR Spectrometer using either thin films on NaCl plates (thin film) or KBr discs (KBr disc) as stated. Only the characteristic peaks are quoted. Microanalyses were carried out on a Carlo Erba CHNS analyser. Mass spectrometric (*m/z*) data was acquired by electrospray ionisation (ESI) and chemical ionisation (CI). Low and high resolution ESI MS was carried out on a Micromass LCT spectrometer. Low and high resolution CI MS was carried out on a Micromass GCT spectrometer. Melting points were recorded on an Electrothermal apparatus and are uncorrected.

Literature procedures were used for the preparation of compounds **1**,¹ **3**,² **4**,² **9**,¹ **10**¹ and **12**³ and gave spectroscopic data consistent with the literature. Rearrangement products **15**,¹ **16**³ and **18**³ have been fully characterised previously.

General Experimental Procedures

General Procedure A – Carbene catalysed rearrangement protocol

KHMDS was added to a solution of triazolium salt **5** in THF under nitrogen and stirred at room temperature for 30 minutes. The desired oxazole was added, either as a solution in THF or as a solid, and stirred for 5 minutes before concentration *in vacuo*. Chromatographic purification (silica) gave the desired product.

General Procedure B – Preparation of rearrangement substrates

Triethylamine (1.1 eq) was added to a stirred solution of oxazalone (1 eq) in THF under nitrogen at 0 °C, followed by addition of the desired chloroformate (1.06 eq) and stirred at 0 °C for 30 minutes before warming to room temperature and stirring overnight. The resulting solution was poured into H₂O and the aqueous phase extracted with Et₂O (x 3). The organic extracts were combined, washed with aqueous 0.1M HCl, saturated aqueous NaHCO₃ solution, brine, dried (MgSO₄), filtered and concentrated *in vacuo*.

4-Methyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydro-oxazole-4-carboxylic acid methyl ester **2**

Following general procedure A, KHMDS (0.040 mL, 0.020 mmol, 0.9 mol %), triazolium salt **5** (0.006 g, 0.022 mmol, 1.0 mol %), THF (5 mL) and oxazole **1** (0.585 g, 2.222 mmol) gave, after chromatography (petrol-Et₂O 70:30), (±)-**2** (0.497 g, 84%) as a white solid. $\nu_{\max}$ (KBr disc)/cm⁻¹ 2954 (C-H), 1751 (C=O), 1645 (C=O), 1497 (C=N) and 1262 (C-O); *m.p.* 58-60 °C; δ_{H} (300 MHz; CDCl₃) 8.00-7.95 (2H, m, 4-OMeAr(2,6)*H*), 7.01-6.96 (2H, m, 4-OMeAr(3,5)*H*), 3.89 (3H, s, OCH₃), 3.79 (3H, s, OCH₃) and 1.77 (3H, s, CH₃); δ_{C} (75 MHz; CDCl₃) 175.2, 166.8, 163.7, 162.9, 130.3, 117.4, 114.3, 72.7, 55.6, 53.7 and 20.7; *m/z* (ESI+) 264.1 (100, M+H⁺) and 286.1 (35, M+Na⁺); HRMS (ESI+) C₁₃H₁₄NO₅ requires 264.0872, found 264.0874 (+0.9 ppm).

2-Phenyl-6,7-dihydro-5H-pyrrolo[2,1-c][1,2,4]triazol-2-ium tetrafluoroborate **5**

5

Based upon a literature procedure,⁴ trimethyloxonium tetrafluoroborate (2.96 g, 20.0 mmol) was added to a solution of pyrrolidin-2-one (1.40 mL, 18.1 mmol) in CH₂Cl₂ (120 mL) and stirred at room temperature overnight. Phenylhydrazine (1.80 mL, 18.1 mmol) was added and stirred for 2 days before concentration *in vacuo*. The residue was dissolved in MeOH (10 mL) and triethylorthoformate (40 mL) and refluxed overnight at 100°C. The resultant solid was filtered and recrystallised from MeOH to give **5** (3.50 g, 85 %) as a tan solid. Found: C, 48.2; H, 4.5; N, 15.3%; C₁₁H₁₂BF₄N₃ requires C, 48.4; H, 4.4; N, 15.4%; $\nu_{\max}$ (KBr disc)/cm⁻¹ 2887 (C-H), 1602 (C=N) and 1589 (C=N); *m.p.* 154-156 °C; δ_{H} (300 MHz; d₆-DMSO) 10.69 (1H, s, CH), 7.90-7.86 (2H, m, *o*-PhH), 7.73-7.60 (3H, m, *m*-PhH, *p*-PhH), 4.41 (2H, t, *J* 7.4, CH₂), 3.21 (2H, t, *J* 7.4, CH₂) and 2.75 (2H, tt, *J* 7.4, CH₂); δ_{C} (75 MHz; d₆-DMSO) 163.0, 138.3, 135.6, 130.4, 130.2, 120.6, 46.9, 26.5 and 21.2; *m/z* (CI) 186.1 (100, C₁₁H₁₂N₃⁺); HRMS (CI) C₁₁H₁₂N₃ requires 186.1031, found 186.1033 (+1.2 ppm).

5-Methoxycarbonyloxy-4-benzyl-2-(4-methoxyphenyl)-oxazole **11**

11

Following general procedure B, triethylamine (1.60 mL, 11.4 mmol), 2-(4-methoxyphenyl)-4-benzylloxazalone (2.86 g, 10.2 mmol), THF (30 mL) and methyl chloroformate (0.87 mL, 10.8 mmol) gave, after recrystallisation (Et₂O-petrol), oxazole **11** (3.10 g, 90 %) as a white solid. $\nu_{\max}$ (KBr disc)/cm⁻¹ 2965 (C-H), 1790 (C=O), 1614 (C=C), 1500 (C=N), 1256 (C-O) and 1224 (C-O); *m.p.* 58-60 °C; δ_{H} (300 MHz; CDCl₃) 7.83-7.78 (2H, m, 4-OMeAr(2,6)H), 7.24-7.12 (5H, m, PhH), 6.88-6.83 (2H, m, 4-OMeAr(3,5)H), 3.80-3.78 (5H, m, CH₂Ph, OCH₃) and 3.77 (3H,

s, OCH_3); δ_{C} (75 MHz; CDCl_3) 161.8, 155.7, 152.5, 146.3, 138.0, 129.3, 128.8, 128.1, 126.9, 123.4, 120.3, 114.5, 56.8, 55.8 and 31.9; m/z (ESI+) 362.2 (100, $\text{M}+\text{Na}^+$) and 340.2 (15, $\text{M}+\text{H}^+$); HRMS (ESI+) $\text{C}_{19}\text{H}_{17}\text{NO}_5\text{Na}$ requires 362.1004, found 362.1000 (-1.3 ppm).

5-Methoxycarbonyloxy-4-isobutyl-2-(4-methoxyphenyl)-oxazole 13

13

Following general procedure B, triethylamine (0.93 mL, 6.67 mmol), 2-(4-methoxyphenyl)-4-isobutyloxazalone (1.50 g, 6.07 mmol), THF (20 mL) and methyl chloroformate (0.50 mL, 6.43 mmol) gave, after chromatography (petrol- Et_2O 85:15), oxazole **13** (1.74 g, 94 %) as a colourless oil. ν_{max} (thin film)/ cm^{-1} 2959 (C-H), 1791 (C=O), 1615 (C=C), 1501 (C=N) and 1240 (C-O); δ_{H} (300 MHz; CDCl_3) 7.91-7.86 (2H, m, 4-OMeAr(2,6)*H*), 6.96-6.91 (2H, m, 4-OMeAr(3,5)*H*), 3.97 (3H, s, OCH_3), 3.85 (3H, s, OCH_3), 2.33 (2H, d, J 6.7, CH_2), 2.05 (1H, sept, J 6.7, $\text{CH}(\text{CH}_3)_2$) and 0.95 (6H, d, J 6.7, $\text{CH}(\text{CH}_3)_2$); δ_{C} (75 MHz; CDCl_3) 161.3, 155.0, 152.4, 146.0, 127.6, 123.4, 120.0, 114.1, 56.5, 55.3, 33.8, 27.6 and 22.3; m/z (ESI+) 328.1 (100, $\text{M}+\text{Na}^+$) and 306.1 (15, $\text{M}+\text{H}^+$); HRMS (ESI+) $\text{C}_{16}\text{H}_{20}\text{NO}_5$ requires 306.1341, found 306.1342 (+0.2 ppm).

5-Methoxycarbonyloxy-4-isopropyl-2-(4-methoxyphenyl)-oxazole 14

14

Following general procedure B, triethylamine (1.30 mL, 9.43 mmol), 2-(4-methoxyphenyl)-4-isopropylloxazalone (2.00 g, 8.57 mmol), THF (25 mL) and methyl chloroformate (0.70 mL, 9.09 mmol) gave, after chromatography (petrol-Et₂O 85:15), oxazole **14** (2.22 g, 89 %) as a pale yellow oil. $\nu_{\max}$ (thin film)/cm⁻¹ 2968 (C-H), 1789 (C=O), 1615 (C=C), 1502 (C=N) and 1255 (C-O); δ_{H} (300 MHz; CDCl₃) 7.91-7.86 (2H, m, 4-OMeAr(2,6)*H*), 6.95-6.90 (2H, m, 4-OMeAr(3,5)*H*), 3.97 (3H, s, OCH₃), 3.85 (3H, s, OCH₃), 2.86 (1H, sept, *J* 7.0, CH(CH₃)₂) and 1.27 (6H, d, *J* 7.0, CH(CH₃)₂); δ_{C} (75 MHz; CDCl₃) 161.2, 154.9, 152.6, 143.9, 129.1, 127.6, 120.2, 114.1, 56.5, 55.4, 25.4 and 21.0; *m/z* (ESI+) 314.1 (100, M+Na⁺) and 292.1 (15, M+H⁺); HRMS (ESI+) C₁₅H₁₈NO₅ requires 292.1185, found 292.1176 (-3.2 ppm).

**4-Methyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydro-oxazole-4-carboxylic acid
benzyl ester **15****

Following general procedure A, KHMDs (0.030 mL, 0.015 mmol, 0.9 mol%), triazolium salt **5** (0.005 mg, 0.016 mmol, 1 mol %), THF (4 mL) and oxazole **9** (0.563 g, 1.665 mmol) gave, after chromatography (petrol-Et₂O 80:20), (±)-**15** (0.434 g, 77%) as a colourless oil with spectroscopic data consistent with the literature.¹

**4-Methyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydro-oxazole-4-carboxylic acid
phenyl ester **16****

Following general procedure A, KHMDs (0.030 mL, 0.015 mmol, 0.9 mol%), triazolium salt **5** (0.005 mg, 0.016 mmol, 1 mol %), THF (4 mL) and oxazole **10** (0.542 g, 1.665 mmol) gave, after chromatography (petrol-Et₂O 80:20), (±)-**16** (0.444 g, 82%) as a colourless oil with spectroscopic data consistent with the literature.³

4-Benzyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydro-oxazole-4-carboxylic acid methyl ester **17**

(±)-**17**

Following general procedure A, KHMDs (0.030 mL, 0.015 mmol, 0.9 mol%), triazolium salt **5** (0.005 mg, 0.016 mmol, 1 mol %), THF (4 mL) and oxazole **11** (0.565 g, 1.665 mmol) gave, after chromatography (petrol-Et₂O 80:20), (±)-**17** (0.465 g, 82%) as a colourless oil. $\nu_{\max}$ (thin film)/cm⁻¹ 2956 (C-H), 1753 (C=O), 1648 (C=O), 1513 (C=N) and 1261 (C-O); δ_{H} (300 MHz; CDCl₃) 7.85-7.80 (2H, m, 4-OMeAr(2,6)*H*), 7.20-7.14 (5H, m, Ph*H*), 6.94-6.89 (2H, m, 4-OMeAr(3,5)*H*), 3.85 (3H, s, OCH₃), 3.83 (3H, s, OCH₃), 3.62 (1H, ABq, *J* 13.7, CH_AH_BPh) and 3.49 (1H, ABq, *J* 13.7, CH_AH_BPh); δ_{C} (300 MHz; CDCl₃) 173.8, 166.4, 163.6, 162.7, 132.9, 130.4, 130.1, 128.2, 127.6, 117.2, 114.2, 77.4, 55.5, 53.7 and 40.3; *m/z* (ESI+) 362.1 (100, M+Na⁺) and 394.1 (95, M+MeOH+Na⁺); HRMS (CI) C₁₉H₁₈NO₅ requires 340.1185, found 340.1185 (+0.0 ppm).

4-Benzyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydro-oxazole-4-carboxylic acid phenyl ester **18**

(±)-**18**

Following general procedure A, KHMDs (0.030 mL, 0.015 mmol, 0.9 mol%), triazolium salt **5** (0.005 mg, 0.016 mmol, 1 mol %), THF (4 mL) and oxazole **12** (0.668g, 1.665 mmol) gave, after chromatography (petrol-Et₂O 80:20), (±)-**18** (0.534 g, 80%) as a colourless oil with spectroscopic data consistent with the literature.³

4-(2-Methylpropyl)-5-oxo-2-(4-methoxyphenyl)-4,5-dihydro-oxazole-4-carboxylic acid methyl ester **19**

(±)-**19**

Following general procedure A, KHMDs (0.040 mL, 0.020 mmol, 1.5 mol%), triazolium salt **5** (0.007 mg, 0.027 mmol, 2 mol %), THF (2 mL) and a solution of oxazole **13** (0.407 g, 1.333 mmol) in THF (2 mL) gave, after chromatography (petrol-Et₂O 80:20), (±)-**19** (0.323 mg, 79%) as a colourless oil. $\nu_{\max}$ (KBr disc)/cm⁻¹ 2959 (C-H), 1755 (C=O), 1649 (C=O), 1513 (C=N) and 1262 (C-O); δ_{H} (300 MHz; CDCl₃) 8.01-7.96 (2H, m, 4-OMeAr(2,6)*H*), 7.01-6.96 (2H, m, 4-OMeAr(3,5)*H*), 3.88 (3H, s, OCH₃), 3.78 (3H, s, OCH₃), 2.37 (1H, ABX, $J_{\text{A,B}}$ 14.2, $J_{\text{A,X}}$ 5.8, CH_AH_BCH(CH₃)₂), 2.05 (1H, ABX, $J_{\text{B,A}}$ 14.2, $J_{\text{B,X}}$ 7.2, CH_AH_BCH(CH₃)₂), 1.70 (1H, sept, J 6.7, CH(CH₃)₂) and 0.94-0.88 (6H, m, CH(CH₃)₂); δ_{C} (75 MHz; CDCl₃) 175.1, 166.8, 164.7, 162.4, 130.2, 117.5, 114.3, 76.2, 55.6, 53.6, 42.9, 24.6, 23.7 and 23.0; m/z (CI) 306.1 (100, M+H⁺); HRMS (CI) C₁₆H₂₀NO₅ requires 306.1341, found 306.1341 (-0.2 ppm).

4-Isopropyl-5-oxo-2-(4-methoxyphenyl)-4,5-dihydro-oxazole-4-carboxylic acid methyl ester **20**

(±)-20

Following general procedure A, KHMDS (0.080 mL, 0.040 mmol, 4 mol%), triazolium salt **5** (0.014 g, 0.051 mmol, 5 mol %), THF (2 mL) and a solution of oxazole **14** in THF (2 mL) gave, after chromatography (petrol-Et₂O 85:15), (±)-**20** (0.200 g, 67%) as a colourless oil which solidified on standing. $\nu_{\max}$ (KBr disc)/cm⁻¹ 2958 (C-H), 1736 (C=O), 1647 (C=O), 1513 (C=N) and 1261 (C-O); *m.p.* 68-70 °C; δ_{H} (300 MHz; CDCl₃) 8.02-7.97 (2H, m, 4-OMeAr(2,6)*H*), 7.00-6.95 (2H, m, 4-OMeAr(3,5)*H*), 3.88 (3H, s, OCH₃), 3.81 (3H, s, OCH₃), 2.78 (1H, sept, *J* 6.8, CH(CH₃)₂), 1.06 (3H, d, *J* 6.8, CH(CH₃)₂) and 0.97 (3H, d, *J* 6.8, CH(CH₃)₂); δ_{C} (75 MHz; CDCl₃) 173.7, 166.4, 163.6, 162.5, 130.3, 117.4, 114.3, 80.3, 55.5, 53.5, 34.8, 17.2 and 16.3; *m/z* (CI) 292.1 (100, M+H⁺); HRMS (CI) C₁₉H₁₇N₃Na requires 292.1185, found 292.1188 (+1.1 ppm).

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