SUPPORTING INFORMATION

Mild Oxidative One-Carbon Homologation of Aldehyde to Amide

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General information

Melting points were recorded using Reichert melting point apparatus.

Mass spectra were obtained either from an AEI MS-50 instrument using electron impact ionization (EI), from an AEI MS-9 using electron spray (ES), or from a MALDI-TOF type of instrument for the high resolution mass spectra (HRMS).

Proton NMR (^1H) spectra were recorded at 300 MHz on a Bruker AC-300 spectrometer. Carbon NMR (^{13}C) spectra were similarly recorded at 75 MHz on a Bruker AC-300 spectrometer, using a broadband decoupled mode with the multiplicities obtained using a JMOD or DEPT sequence.

Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane. NMR experiments were carried out in deuteriochloroform (CDCl_3). The following abbreviations are used for the multiplicities: s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, brs: broad singlet for proton spectra. Coupling constants (J) are reported in Hertz (Hz).

Infrared spectra were recorded on a Nicolet 205 FT-IR spectrometer.

Flash chromatography was performed using Kieselgel Si 60, 40-63 μm particle sized silica gel (200-400 mesh). Visualization was achieved under a UVP mineralight UVGL-58 lamp, and by developing the plates with Draggendorf's reagent or potassium permanganate (KMnO_4).

All reagents were obtained from commercial suppliers unless otherwise stated.

Experimental procedures

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*Experimental procedure for the N-formylation*¹: To a stirred solution of the corresponding amino ester hydrochloride salt (500 mg, 2.16 mmol, 1.0 eq.) in dry acetonitrile (2 mL) was added anhydrous ammonium formate (286 mg, 4.53 mmol, 2.1 eq.). The resulting heterogeneous reaction mixture was refluxed for 12 h. The solvent was evaporated and the crude mixture was diluted with water, extracted with ethyl acetate, dried over anhydrous sodium sulphate and concentrated *in vacuo*. *N*-formyl-4-methoxyphenylglycine methyl ester **15** was purified by column chromatography on silica gel (30 % ethyl acetate in heptane) to give pure title compound as a white solid (375 mg, 78 %); mp 85-87°C; IR (film): 3287, 2954, 1739, 1658, 1509, 1246, 1208, 1175 and 1028 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 3.89 (3H, s, OCH₃), 3.95 (3H, s, Ar-OCH₃), 5.76 (1H, d, *J* = 7.0 Hz, CH), 6.87 (1H, brd, *J* = 7.0 Hz, NH), 7.04 (2H, d, *J* = 8.7 Hz, Ar-H), 7.44 (2H, d, *J* = 8.7 Hz, Ar-H), 8.37 (1H, s, CHO); ¹³C NMR (75 MHz, CDCl₃) δ 52.9 (q), 54.5 (d), 55.3 (q), 114.4 (d), 128.1 (s), 128.5 (d), 159.8 (s), 160.1 (d) and 171.2 (s); *m/z* (ES⁺) 246 [(M+Na)⁺, 100 %] and 179 (90).

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To a solution of the formamide **15** (4.3 g, 19.3 mmol, 1.0 eq.) and diisopropylamine (7.3 mL, 52.0 mmol, 2.7 eq.) in dry dichloromethane (60.0 mL) at -30°C under argon atmosphere was added dropwise phosphoryl chloride (2.0 mL, 21.2 mmol, 1.1 eq.). Stirring was continued for 1 h at -30°C. A solution of potassium carbonate (8.0 g) in water (40.0 mL) was added to the reaction mixture. More water (50.0 mL) and dichloromethane (30.0 mL) were added and the organic layer was washed with water (2 × 30 mL), dried with anhydrous sodium sulphate and evaporated. The residue was then chromatographed (silica, eluant : ethyl acetate/heptane 1:4)

to give methyl 2-isocyano-2-(4-methoxyphenyl)acetate **16** as a colourless oil (3.4 g, 86 %); IR (film): 2956, 2146, 1751, 1610, 1511, 1247, 1211, 1175 and 1027 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 3.79 (3H, s, OCH_3), 3.82 (3H, s, Ar- OCH_3), 5.31 (1H, s, CH), 6.94 (2H, d, $J = 6.4$ Hz, Ar-H), 7.39 (2H, d, $J = 6.4$ Hz, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ 53.7 (q), 55.4 (q), 59.7 (d), 114.5 (d), 123.9 (s), 128.7 (d), 160.5 (s), 161.0 (s) and 166.3 (s).

1c

To a solution of the ester **18** (3.0 g, 14.6 mmol) in THF (40.0 mL) and water (10.0 mL) was added potassium hydroxide (820 mg, 14.6 mmol) and the resulting mixture was stirred at room temperature for 5 h. The solvent was then removed *in vacuo* and the resulting salt **1c** (3.3 g, 100 %) was used as such without further purification.

^1H NMR (300 MHz, $\text{DMSO}-d_6$) δ 3.73 (3H, s, OCH_3), 4.87 (1H, s, CH), 6.87 (2H, d, $J = 8.7$ Hz, Ar-H), 7.29 (2H, d, $J = 8.7$ Hz, Ar-H); ^{13}C NMR (75 MHz, CD_3OD) δ 55.0 (q), 63.1 (d), 113.2 (d), 127.4 (d), 129.9 (s), 158.3 (s), 165.2 (s); m/z (ES+) 262 $[(\text{M}+\text{MeOH}+\text{H})^+]$, 100 %].

5a

Typical Procedure: Dimethylamine hydrochloride (35 mg, 1.2 eq.) was added to a solution of cyclohexanal (44 μL , 1.0 eq.) in dry toluene (2 mL). The mixture was then stirred for 10 min at room temperature. Potassium 2-isocyano-2-(4-methoxyphenyl)acetate freshly prepared (100 mg, 1.2 eq.) was added and the reaction was allowed to stir for 15 h at room temperature under argon atmosphere.

The reaction was then evaporated to dryness. The crude product obtained was redissolved in ethyl acetate (5 mL), washed with water (3 mL), dried over anhydrous Na₂SO₄ and concentrated *in vacuo*. 2-(2-cyclohexylacetylimino)-2-(4-methoxyphenyl)-N,N-dimethylacetamide **5a** was purified by column chromatography on silica gel (30 % ethyl acetate in heptane) to give pure title compound as a colourless oil (96 mg, 81 %); IR (film): 2929, 2854, 1680, 1647, 1493, 1448, 1405 and 1149 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.95-1.39 (5H, m, Cy-H), 1.59-1.94 (6H, m, Cy-H), 2.45 (2H, d, *J* = 6.9 Hz, CH₂), 2.93 (3H, s, NCH₃), 3.06 (3H, s, NCH₃), 3.89 (3H, s, OCH₃), 6.96 (2H, d, *J* = 8.7 Hz, Ar-H), 7.75 (2H, d, *J* = 8.7 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ 26.1 (t), 26.2 (t), 33.1 (t), 33.7 (q), 34.2 (d), 38.0 (q), 45.8 (t), 55.5 (q), 114.4 (d), 125.1 (s), 130.2 (d), 160.4 (s), 163.3 (s), 165.7 (s) and 188.7 (s); [Found (ES⁺): [M+Na]⁺ 353.1852, C₁₉H₂₆N₂O₃Na requires 353.1841].

6a

Hydrochloric acid 1N (480 μ L, 5.0 eq.) was added to a solution of **5a** (32 mg, 1.0 eq.) in tetrahydrofuran (2 mL). The reaction was stirred at room temperature for 30 minutes. The mixture was then quenched with saturated NaHCO₃ and extracted with ethyl acetate (3 $\times$ 5 mL). The organic fractions were then combined, dried over anhydrous Na₂CO₃ and evaporated. 2-Cyclohexylacetamide **6a** was purified by column chromatography on silica gel (50 % ethyl acetate in heptane) to give pure title compound as a colourless solid (13.0 mg, 95 %); mp 165-167°C (lit.,² 185-186°C); ¹H NMR (300 MHz, CDCl₃) δ 0.82-1.32 (5H, m, Cy-H), 1.63-1.82 (6H, m, Cy-H), 2.07 (2H, d, *J* = 6.0 Hz, CH₂), 5.39 and 5.47 (2H, 2 $\times$ brs, NH₂); ¹³C NMR (75 MHz, CDCl₃) δ 26.1 (t), 26.3 (t), 33.2 (t), 35.2 (d), 44.1 (t) and 175.2 (s).

4a

2-Cyclohexyl-2-dimethylino-*N*-(1-(4-methoxyphenyl)-2-dimethylamino-2-oxo)ethyl)acetamide (mixture of stereoisomers) is a by-product of the homologation reaction of cyclohexanal and was isolated as a colourless oil (4.7 mg, 7 %); IR (film): ^1H NMR (300 MHz, CDCl_3) δ 0.63-1.14 (5H, m), 1.50-1.74 (6H, m, $3 \times \text{CH}_2$), 2.12 (6H, s, $\text{N}(\text{CH}_3)_2$), 2.39 (1H, d, $J = 6.9$ Hz, CH), 2.82 (3H, s, $\text{CH}_3\text{NC}=\text{O}$), 2.91 (3H, s, $\text{CH}_3\text{NC}=\text{O}$), 3.72 (3H, s, OCH_3), 5.75 (1H, d, $J = 7.8$ Hz, NH), 6.80 (2H, d, $J = 8.7$ Hz, Ar-H), 7.26 (2H, d, $J = 8.7$ Hz, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ 26.2 (t), 26.6 (t), 26.7 (t), 28.6 (t), 30.5 (t), 35.9 (q), 36.9 (q), 37.6 (d), 42.7 (q), 52.9 (d), 55.3 (q), 75.4 (d), 114.2 (d), 129.2 (d), 130.0 (s), 159.3 (s), 169.9 (s) and 170.4 (s); m/z (ES $^+$) 376 $[(\text{M}+\text{H})^+]$, 51 %], 398 (85) and 140 (100).

7c

mp 75-76°C (lit.,³ 74-76°C); IR (film): 2939, 1660, 1632, 1597, 1571, 1509, 1245, 1143, 1024, 991, 858 and 773; ^1H NMR (300 MHz, CDCl_3) δ 2.89 (3H, s, NCH_3), 3.04 (3H, s, NCH_3), 3.82 (3H, s, OCH_3), 6.91 (2H, d, $J = 9.0$ Hz, Ar-H), 7.84 (2H, d, $J = 9.0$ Hz, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ 34.0 (q), 37.1 (q), 55.6 (q), 114.3 (d), 126.2 (s), 132.1 (d), 164.8 (s), 167.4 (s) and 190.5 (s); m/z (ES $^+$) 230 $[(\text{M}+\text{Na})^+]$, 94 %], 437 (100) and 262 (7).

5b

IR (film): 2932, 2858, 1681, 1642, 1601, 1574, 1263, 1178, 1139 and 1093 cm^{-1} ; ^1H NMR (300 MHz, CDCl_3) δ 0.80 (3H, t, $J = 6.9$ Hz, CH_3), 1.23 (8H, m, $4 \times \text{CH}_2$), 1.59 (2H, m, CH_2), 2.48 (2H, t, $J = 7.2$ Hz, CH_2), 2.84 (3H, s, NCH_3), 2.97 (3H, s, NCH_3), 3.80 (3H, s, OCH_3), 6.87 (2H, d, $J = 9.0$ Hz, Ar-H), 7.66 (2H, d, $J = 9.0$ Hz, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ 14.1 (q), 22.6 (t), 24.2 (t), 29.0 (t), 29.2 (t), 31.7 (t), 33.8 (q), 38.0 (q), 38.1 (t), 55.5 (q), 114.4 (d), 125.1 (s), 130.2 (d), 160.6 (s), 163.3 (s), 165.8 (s) and 189.6 (s); [Found (ES $^+$): $[\text{M}+\text{Na}]^+$ 355.1983, $\text{C}_{19}\text{H}_{28}\text{N}_2\text{O}_3\text{Na}$ requires 355.1998].

6b

mp 104-105°C (lit.,⁴ 106°C); ¹H NMR (300 MHz, CDCl₃) δ 0.81 (3H, t, J = 6.9 Hz, CH₃), 1.23 (8H, m, 4 $\times$ CH₂), 1.56 (2H, p, J = 7.2 Hz, CH₂), 2.15 (2H, t, J = 7.2 Hz, CH₂), 5.40 and 5.55 (2H, 2 $\times$ brs, NH₂); ¹³C NMR (75 MHz, CDCl₃) δ 12.7 (q), 21.2 (t), 24.2 (t), 27.6 (t), 27.8 (t), 30.3 (t), 34.6 (t) and 174.3 (s).

6h

mp 156-157°C (lit.,⁵ 157-158°C); ¹H NMR (300 MHz, CDCl₃) δ 3.60 (2H, s, CH₂), 5.44 and 5.48 (2H, 2 $\times$ brs, NH₂), 7.28-7.40 (5H, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ 42.3 (t), 126.4 (d), 128.0 (d), 128.4 (d), 133.9 (s), 172.7 (s).

5d

IR (film): 2936, 2858, 1673, 1643, 1600, 1574, 1513, 1264, 1177 and 1146 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.20-1.54 (5H, m, Cy-H), 1.63-1.81 (3H, m, Cy-H), 2.01 (2H, m, Cy-H), 2.50 (1H, tt, J = 11.4 Hz and 3.6 Hz, CH), 2.92 (3H, s, NCH₃), 3.05 (3H, s, NCH₃), 3.88 (3H, s, OCH₃), 6.96 (2H, d, J = 9.0 Hz, Ar-H), 7.76 (2H, d, J = 9.0 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ 25.6 (t), 25.9 (t), 28.7 (t), 33.8 (q), 38.0 (q), 46.6 (d), 55.5 (q), 114.4 (d), 125.2 (s), 130.2 (d), 161.1 (s), 163.3 (s), 166.1 (s), 192.2 (s); [Found (ES⁺): [M+Na]⁺ 339.1694, C₁₈H₂₄N₂O₃Na requires 339.1685].

6d

mp 185-187°C (lit.,⁶ 188-189°C); ¹H NMR (300 MHz, CDCl₃) δ 1.17-1.47 (5H, m, Cy-H), 1.67-1.92 (5H, m, Cy-H), 2.15 (1H, tt, J = 3.2 Hz and 11.6 Hz, CH), 5.49 and 5.62 (2H, 2 $\times$ brs, NH₂); ¹³C NMR (75 MHz, CDCl₃) δ 25.6 (t), 25.7 (t), 29.7 (t), 44.8 (d) and 178.7 (s).

5n

IR (film): 2999, 2930, 1687, 1643, 1602, 1574, 1513, 1463, 1264 and 1175 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.82 (3H, d, J = 6 Hz, CH₃), 1.02-1.12 and 1.23-1.32 (2H, 2 $\times$ m, CH₂), 1.23-1.32 (2H, m, CH₂), 1.52 (3H, s, CH₃), 1.60 (3H, s, CH₃), 1.68 (1H, m, CH), 1.80-2.00 (2H, m, CH₂CH=), 2.45-2.52 (2H, m, CH₂C=O), 2.83 (3H, s, NCH₃), 2.97 (3H, s, NCH₃), 3.80 (3H, s, OCH₃), 5.02 (1H, m, CH=), 6.87 (2H, d, J = 9.0 Hz, Ar-H), 7.65 (2H, d, J = 9.0 Hz, Ar-H); ¹³C NMR (75 MHz, CDCl₃) δ 17.6 (q), 19.2 (q), 25.5 (t), 25.7 (q), 31.1 (t), 32.1 (d), 33.8 (q), 35.9 (t), 36.8 (t), 38.0 (q), 55.5 (q), 114.4 (d), 124.8 (d), 125.0 (s), 130.2 (d), 131.1 (s), 160.7 (s), 163.3 (s), 165.8 (s) and 189.8 (s); [Found (ES⁺): [M+Na]⁺ 395.2303, C₂₂H₃₂N₂O₃Na requires 395.2311].

6n

IR (film): 3550, 3412, 2997, 2963, 2927, 1678, 1591, 1455 and 1380 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.83 (3H, d, J = 6.3 Hz, CH₃), 1.04-1.16 and 1.23-1.34 (2H, 2 $\times$ m, CH₂),

1.36-1.46 (2H, m, CH₂), 1.53 (3H, s, CH₃), 1.61 (3H, s, CH₃), 1.62 (1H, m, CH), 1.86-1.96 (2H, m, CH₂CH=), 2.07-2.25 (2H, m, CH₂C=O), 5.01 (1H, m, CH=), 5.39 and 5.51 (2H, 2 × brs, NH₂); ¹³C NMR (75 MHz, CDCl₃) δ 17.7 (q), 19.2 (q), 25.4 (t), 25.7 (q), 32.2 (d), 32.5 (t), 33.6 (t), 36.8 (t), 124.6 (d), 131.3 (s) and 175.9 (s); [Found (ES⁺): [M+Na]⁺ 206.1544, C₁₁H₂₁NONa requires 206.1521].

2o

IR (film): 2929, 1727, 1381, 1252, 1212, 1073 and 832; ¹H NMR (300 MHz, CDCl₃) δ 0.08 (6H, d, *J* = 1.5 Hz, 2 × SiCH₃), 0.91 (9H, s, 3 × CH₃), 1.36 (3H, s, CH₃), 1.56 (3H, s, CH₃), 2.74 (2H, dd, *J* = 2.1 Hz and *J* = 6.2 Hz, CH₂CHO), 3.73 (2H, d, *J* = 3.3 Hz, CH₂O), 4.11 (1H, q, *J* = 3.3 Hz, CH), 4.38 (2H, m, 2 × CH), 4.70 (1H, dd, *J* = 3.3 Hz and *J* = 6.2 Hz, CH), 9.80 (1H, t, *J* = 2.1 Hz, CHO); ¹³C NMR (75 MHz, CDCl₃) δ -5.5 (q), -5.3 (q), 18.3 (s), 25.5 (q), 25.9 (q), 27.5 (q), 47.3 (t), 63.6 (t), 79.9 (d), 81.9 (d), 84.7 (d), 84.9 (d), 114.1 (s), 200.3 (s); [Found (ES⁺): [M+Na]⁺ 353.1786, C₁₆H₃₀O₅SiNa requires 353.1760].

6o

The amide **6n** was isolated as a mixture of two diastereoisomers. IR (film): 3417, 3199, 2927, 2855, 1666, 1461, 1380, 1253, 1209 and 1073; ¹H NMR (300 MHz, CDCl₃) δ 0.07 (3H, s, SiCH₃), 0.08 (3H, 2 × s, SiCH₃), 0.91 (9H, 2 × s, 3 × CH₃), 1.36 (3H, s, CH₃), 1.51 and 1.54 (3H, 2 × s, CH₃), 1.88-2.08 (2H, m, CH₂), 2.39 (2H, q, *J* = 7.5 Hz, CH₂C=O), 3.71 (2H, dd, *J* = 12 Hz and *J* = 3.9 Hz, CH₂O), 3.89-4.10 (2H, m, 2 × CH), 4.29-4.32 and 4.79-4.81 (1H, 2 × m, CH), 4.63-4.66 (1H, m, CH), 5.38 and 5.75 (2H, 2 × brs, NH₂); ¹³C NMR (125 MHz,

CD₃OD) δ -5.6 (q), -5.5 (q), -5.4 (q), -5.3 (q), 18.2 (s), 18.4 (s), 25.0 (q), 25.4 (t), 25.5 (q), 25.8 (q), 25.9 (q), 26.3 (q), 27.5 (q), 29.2 (t), 32.1 (t), 32.7 (t), 63.6 (t), 64.5 (t), 81.4 (d), 81.9 (d), 82.1 (d), 83.2 (d), 83.7 (d), 84.1 (d), 84.5 (d), 84.8 (d), 112.2 (s), 114.1 (s), 174.8 (s), 175.1 (s); [Found (ES⁺): [M+Na]⁺ 382.2010, C₁₇H₃₃NO₅SiNa requires 382.2026].

***trans*-6f**

mp 225-226°C (lit.,⁷ 226-227°C); ¹H NMR (300 MHz, CD₃OD) δ 1.52-1.67 (4H, m, Cy-H), 1.93-2.02 (4H, m, Cy-H), 2.30 (1H, m, CH), 2.55 (1H, m, CH), 7.21-7.28 (5H, m, Ar-H); ¹³C NMR (75 MHz, CD₃OD) δ 31.0 (t), 34.7 (t), 45.1 (d), 45.5 (d), 127.0 (d), 127.7 (d), 129.4 (d), 148.3 (s) and 182.1 (s).

***cis*-6f**

mp 126-127°C; ¹H NMR (300 MHz, CD₃OD) δ 1.67-1.75 (4H, m, Cy-H), 1.81-1.90 (2H, m, Cy-H), 2.10-2.16 (2H, m, Cy-H), 2.60 (2H, m, Cy-H), 7.12-7.29 (5H, m, Ar-H); ¹³C NMR (75 MHz, CD₃OD) δ 28.8 (t), 31.4 (t), 40.6 (d), 44.2 (d), 126.8 (d), 127.9 (d), 129.3 (d), 148.3 (s) and 181.0 (s).

6j

mp 134-136°C (lit.,⁸ 139-140°C); ¹H NMR (300 MHz, CD₃OD) δ 3.68 (2H, s, CH₂), 7.58 (1H, t, *J* = 7.8 Hz, Ar-H), 7.72 (1H, d, *J* = 7.8 Hz, Ar-H), 8.15 (1H, d, *J* = 7.8 Hz, Ar-H), 8.22

(1H, s, Ar-H); ^{13}C NMR (75 MHz, CD_3OD) δ 42.5 (t), 122.8 (d), 125.1 (s), 130.6 (d), 136.7 (d), 139.2 (s), 149.7 (s) and 175.5 (s).

6i

mp 137-139°C (lit.,⁹ 138-139°C); ^1H NMR (300 MHz, CD_3OD) δ 3.51 (2H, s, CH_2), 7.21-7.30 (2H, m, Ar-H), 7.42 (1H, m, Ar-H), 7.51 (1H, m, Ar-H); ^{13}C NMR (75 MHz, CD_3OD) δ 42.8 (t), 123.3 (s), 129.1 (d), 131.0 (d), 131.3 (d), 133.2 (d), 139.5 (s) and 176.1 (s).

6k

mp 137-139°C (lit.,¹⁰ 138-139°C); ^1H NMR (300 MHz, CDCl_3) δ 3.48 (2H, s, CH_2), 3.74 (3H, s, OCH_3), 5.39 and 5.66 (2H, 2 $\times$ brs, NH_2), 6.75-6.80 (3H, m, Ar-H), 7.18-7.23 (1H, m, Ar-H); ^{13}C NMR (75 MHz, CDCl_3) δ 43.4 (t), 55.2 (q), 112.9 (d), 115.0 (d), 121.6 (d), 130.1 (d), 136.3 (s), 160.0 (s) and 173.4 (s).

6c

mp 129-131°C (lit.,¹¹ 132-134°C); ^1H NMR (300 MHz, CDCl_3) δ 0.90 (3H, s, CH_3), 0.92 (3H, s, CH_3), 2.03 (3H, m, CH, CH_2), 5.44 and 5.68 (2H, 2 $\times$ brs, NH_2); ^{13}C NMR (75 MHz, CDCl_3) δ 22.4 (q), 26.0 (t), 45.3 (d) and 175.4 (s).

6e

mp 174-175°C (lit.,¹² 179-180°C); ¹H NMR (300 MHz, CDCl₃) δ 1.49 (2H, m, CH₂), 1.62-1.84 (6H, m, 3 $\times$ CH₂), 2.53 (1H, p, J = 7.8 Hz, CH), 5.42 (2H, brs, NH₂); ¹³C NMR (75 MHz, CDCl₃) δ 25.9 (t), 30.4 (t), 45.1 (d) and 175.8 (s).

6l

mp 205-206°C ; ¹H NMR (300 MHz, CD₃OD) δ 3.70 (2H, s, CH₂), 7.47 (3H, m, Ar-H), 7.82 (4H, m, Ar-H); ¹³C NMR (75 MHz, CD₃OD) δ 43.6 (t), 126.7 (d), 127.2 (d), 128.3 (d), 128.6 (d), 128.8 (d), 129.1 (d), 133.9 (s), 134.4 (s), 135.0 (s) and 176.9 (s).

6m

mp 119-120°C (lit.,¹³ 121-123°C); ¹H NMR (300 MHz, CD₃OD) δ 3.59 (2H, s, CH₂), 7.41 (1H, dd, J = 5.1 Hz, J = 8.1 Hz, Ar-H), 7.82 (1H, m, Ar-H), 8.44 (1H, dd, J = 1.2 Hz, J = 5.1 Hz, Ar-H), 8.50 (1H, d, J = 1.2 Hz, Ar-H); ¹³C NMR (75 MHz, CD₃OD) δ 40.1 (t), 125.1 (d), 133.8 (s), 139.0 (d), 148.4 (d), 150.6 (d) and 171.2 (s).

12a (Z + E)

Synthesis of 2-benzylidene-4-phenyloxazol-5(2H)-one **11a** is accomplished according to procedure¹⁴ and is isolated as a yellow solid; mp 139-141°C; IR: 1772, 1638, 1447, 1167, 967 and 934 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 6.53 (1H, s, CH=), 7.39-7.62 (6H, m, Ar-H), 7.86 (1H, d, J = 7.2 Hz, Ar-H), 8.02 (1H, d, J = 7.2 Hz, Ar-H), 8.45 (1H, d, J = 6.6 Hz, Ar-H), 8.54 (1H, d, J = 6.6 Hz, Ar-H); ¹³C NMR (125 MHz, CDCl₃) δ 112.6 (d), 113.8 (d), 128.6 (d),

128.7 (s), 128.9 (d), 129.0 (d), 129.1 (d), 129.5 (d), 129.9 (d), 131.0 (d), 131.2 (d), 132.6 (d), 132.7 (s), 132.9 (s), 133.0 (d), 151.4 (s), 153.0 (s), 153.5 (s), 153.6 (s), 162.3 (s) and 162.9 (s).

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NL:
1.56E8
TIC MS
db458

Solvent = CH_2Cl_2
Helium flow = 1.5 mL/min
150°C (2 min) to 280°C (10°C/min)
Injector = 280°C
IE source = 250°C

db458#1155-1158 RT: 14.66-14.70 AV: 4 SB: 24 14.55-14.65, 14.70-14.86 NL: 4.81E5
T: c Full [60.00-700.00]

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db458#1163-1166 RT: 14.76-14.79 AV: 4 SB: 24 14.55-14.65, 14.70-14.86 NL: 1.59E6
T: c Full [60.00-700.00]

db458#1188-1190 RT: 15.05-15.07 AV: 3 SB: 14 14.92-15.02, 15.11-15.16 NL: 2.44E6
T: c Full [60.00-700.00]

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db458#1251-1261 RT: 15.80-15.91 AV: 11 SB: 31 15.54-15.69, 15.98-16.17 NL: 8.01E6

T: c Full [60.00-700.00]

05/04/05 10:56:02

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db458#1286-1290 RT: 16.21-16.26 AV: 5 SB: 27 16.06-16.19, 16.27-16.43 NL: 1.04E6

T: c Full [60.00-700.00]

Peak n°5

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05/04/05 10:56:02

db458#1344-1350 RT: 16.89-16.97 AV: 7 SB: 47 16.61-16.82, 16.98-17.30 NL: 8.23E6

T: c Full [60.00-700.00]