Supporting Information

Microwave-Assisted Synthesis of New Polysubstituted Dienaminoesters and Their Cyclization to 3-Bromo-2(1*H*)-Pyridinones

Jeff Adams, Alison Hardin, Filisaty Vounatsos

Chemistry Process and Technology – Custom Synthesis Laboratory, Amgen Inc. One

Amgen Centre Drive, Thousand Oaks, CA, 91320

filisaty@amgen.com

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III. Materials and Reagents:

Flash chromatography was performed using silica gel (particle size 0.040-0.063 mm) as the stationary phase. ^1H NMR and ^{13}C NMR data were recorded using a 400 MHz or 100 MHz spectrometer. Chemical shifts are reported in ppm relative to CDCl_3 (0.1% (v/v) TMS as an internal standard). Microwave reactions were carried out in a commercial microwave with continuous monitoring of internal pressure and infrared temperature control. Optical rotations were measured using a polarimeter at the sodium D-line (589 nm) using spectroscopic grade CHCl_3 at 25 °C and at the concentrations (c) (g/100 mL) indicated. Melting points recorded are uncorrected.

General procedure for the synthesis of δ -dienaminoesters:

Microwave

A microwave process vial was charged with cyclohexyl amine (5 mmol) followed by methanol (5 mL) and methyl propiolate (12.5 mmol). The resulting mixture was sealed appropriately, placed into the microwave cavity and microwave irradiated at 120 °C for 30 minutes. The reaction mixture could be purified at this stage [solvent reduced *in vacuo* (silica gel chromatography) or telescoped into the next step.

Conventional Heating

For conventional heating, the reaction mixture is heated to 65 °C for 48 h.

Amino Acids

Amino acids were free based with 1 eq of NaOAc.

General procedure for the bromocyclisation:

Microwave

A microwave process vial was charged with δ -dienaminoester (5 mmol) followed by methanol (15 mL) and the portion-wise addition of NaH (5 mmol). The reaction mixture was cooled to 0 °C after which time NBS (6 mmol) was added in small portions. The resulting mixture was sealed appropriately, placed into the microwave cavity and microwave irradiated at 120 °C for 30 minutes. The solvent was reduced *in vacuo* and the residue quenched with aqueous NH_4Cl (10 mL) and extracted with CH_2Cl_2 (2×10 mL). The organic layers were combined, washed with brine (10 mL) and reduced *in vacuo* to give a dark yellow oil. The oil was chromatographed on silica gel (EtOAc/hexanes, gradient 0 to 30% EtOAc) to furnish **9** (790 mg, 51 % over two-steps).

Conventional Heating

For conventional heating, the reaction mixture is heated to 65 °C for 1 h .

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White crystalline solid, melting point: 99-101 °C.¹

¹H NMR (CDCl₃, 400 MHz): δ 9.00 (br s, 1H), 7.40 (d, *J*=15.65, 1H), 7.30 (d, *J*=13.89 Hz, 1H), 6.01 (d, *J*=15.65 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.20 (br s, 1H), 1.95 (m, 2H), 1.80 (m, 2H), 1.65 (m, 1H), 1.37 (m, 4H), 1.27 (m, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ 169.6, 169.3, 155.4, 143.6, 107.0, 94.1, 57.7, 51.0, 50.8, 33.9, 25.1, 24.4.

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White crystalline solid, melting point: 98-100 °C.

¹H NMR (CDCl₃, 400 MHz): δ 8.24 (d, *J*=2.15 Hz, 1 H), 8.21 (d, *J*=2.15 Hz, 1H), 5.26 (septet, *J*=6.85 Hz, 1H), 3.88 (s, 3H), 1.42 (d, *J*=6.85 Hz, 6H).

¹³C NMR (CDCl₃, 100 MHz): δ 163.9, 158.5, 139.5, 137.6, 115.6, 110.0, 52.3, 49.5, 21.9.

HRMS Calcd for C₁₀H₁₂BrNO₃: [M+H] *m/z* 274.0078. Found 274.0078.

White crystalline solid, melting point: 89-91 °C.

¹H NMR (CDCl₃, 400 MHz): δ 8.26 (d, *J*=2.15 Hz, 1H), 8.14 (d, *J*=2.15 Hz, 1H), 5.95 (m, 1H), 5.35 (m, 2H), 4.65 (d, *J*=6.26 Hz, 2H), 3.87 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 163.7, 158.6, 141.3, 140.3, 131.0, 120.4, 115.7, 110.0, 53.2, 52.3.

HRMS Calcd for C₁₀H₁₀BrNO₃: [M+H] *m/z* 271.9922. Found 271.9924.

White crystalline solid, melting point: 87-89 °C.

¹H NMR (CDCl₃, 400 MHz): δ 8.23 (d, *J*=2.35 Hz, 1H), 8.21 (d, *J*=2.35 Hz, 1H), 5.23 (m, 1H), 3.88 (s, 3H), 2.22 (m, 2H), 1.90 (m, 2H), 1.79-1.68 (m, 4H).

¹³C NMR (CDCl₃, 100 MHz): δ 163.8, 158.9, 139.5, 138.4, 115.4, 109.8, 59.3, 52.3, 32.2, 24.2.

HRMS Calcd for C₁₂H₁₄BrNO₃: [M+H] *m/z* 300.0235. Found 300.0233.

White crystalline solid, melting point: 149-151 °C.

¹H NMR (CDCl₃, 400 MHz): δ 8.23 (s, 1H), 8.20 (s, 1H), 4.87 (m, 1H), 3.88 (s, 3H), 1.97 (m, 4H), 1.77 (m, 1H), 1.57-1.49 (m, 5H), 1.26 (m, 1H).

¹³C NMR (CDCl₃, 100 MHz): δ 163.9, 158.6, 139.5, 138.2, 115.5, 109.8, 56.8, 52.3, 32.6, 25.6, 25.2.

HRMS Calcd for C₁₃H₁₆BrNO₃: [M+H] *m/z* 314.0391. Found 314.0394.

Beige crystalline solid, melting point: 103-105 °C.

Specific Rotation [α]_D −67.4 (*c* 0.27, CHCl₃).

¹H NMR (CDCl₃, 400 MHz): δ 8.27 (s, 1H), 8.12 (s, 1H), 5.44 (br s, 1H), 3.87 (s, 3H), 3.58 (br s, 3 H), 2.41 (br s, 1H), 2.15 (br s, 1H), 1.63 (br s, 1H), 1.49 (s, 9H).

¹³C NMR (CDCl₃, 100 MHz): δ 163.5, 158.7, 154.1, 140.1, 137.5, 115.7, 110.5, 80.3, 52.4, 28.4.

HRMS Calcd for C₁₆H₂₁BrN₂O₅: [M+H] *m/z* 401.0712. Found 401.0713.

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Colorless oil.

Specific Rotation $[\alpha]_D +1.5$ (*c* 0.2, CHCl₃).

¹H NMR (CDCl₃, 400 MHz): δ 8.30 (d, *J*=2.35 Hz, 1H), 8.21 (d, *J*=2.35 Hz, 1H), 5.54 (q, *J*=7.43 Hz, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 1.73 (d, *J*=7.24 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 170.0, 163.6, 158.5, 140.4, 139.4, 115.4, 110.3, 56.0, 52.4, 16.6.

HRMS Calcd for C₁₁H₁₂BrNO₅: [M+H] *m/z* 317.9977. Found 317.9973.

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Amorphous light yellow solid, melting point: 93-95 °C.

Specific Rotation $[\alpha]_D +9.0$ (*c* , CHCl₃).

¹H NMR (CDCl₃, 400 MHz): δ 8.40 (s, 1H), 8.27 (s, 1H), 5.46 (d, *J*=9.98 Hz, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 2.43 (m, 1H), 1.13 (d, *J*=6.46, 3H), 0.87 (d, *J*=6.65 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 169.9, 163.5, 158.7, 140.2, 139.7, 115.0, 109.9, 63.5, 52.6, 52.3, 31.0, 19.4, 18.6.

HRMS Calcd for C₁₃H₁₇BrNO₅: [M+H] *m/z* 346.0290. Found 346.0287.

Light yellow crystalline solid, melting point: 171-173 °C.

¹H NMR (CDCl₃, 400 MHz): δ 8.33 (s, 1H), 8.22 (s, 1H), 7.29 (d, *J*=8.61 Hz, 2H), 7.01 (d, *J*=8.22 Hz, 2H), 3.88 (s, 3H), 3.87 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 163.7, 160.0, 158.8, 142.6, 140.5, 132.9, 127.4, 116.3, 114.6, 109.8, 55.6, 52.4.

HRMS Calcd for C₁₄H₁₂BrNO₄: [M+H] *m/z* 338.0028. Found 338.0026.

Reference:

1. Bottomley, W.; *Tetrahedron Lett.* **1967**, 21, 1997.

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VerticalScaleFactor = 1

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CHLOROFORM-d

VerticalScaleFactor = 1

VerticalScaleFactor = 1

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CHLOROFORM-d

VerticalScaleFactor = 1

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28

CHLOROFORM-d

VerticalScaleFactor = 1

VerticalScaleFactor = 1

29

CHLOROFORM-d

VerticalScaleFactor = 1

9

VerticalScaleFactor = 1

9

CHLOROFORM-d

VerticalScaleFactor = 1

30

CHLOROFORM-d

VerticalScaleFactor = 1

31

VerticalScaleFactor = 1

CHLOROFORM-d

31

VerticalScaleFactor = 1

32

VerticalScaleFactor = 1

VerticalScaleFactor = 1

33

VerticalScaleFactor = 1

33

CHLOROFORM-d

VerticalScaleFactor = 1