SUPPLEMENTARY MATERIAL

MATERIALS AND METHODS

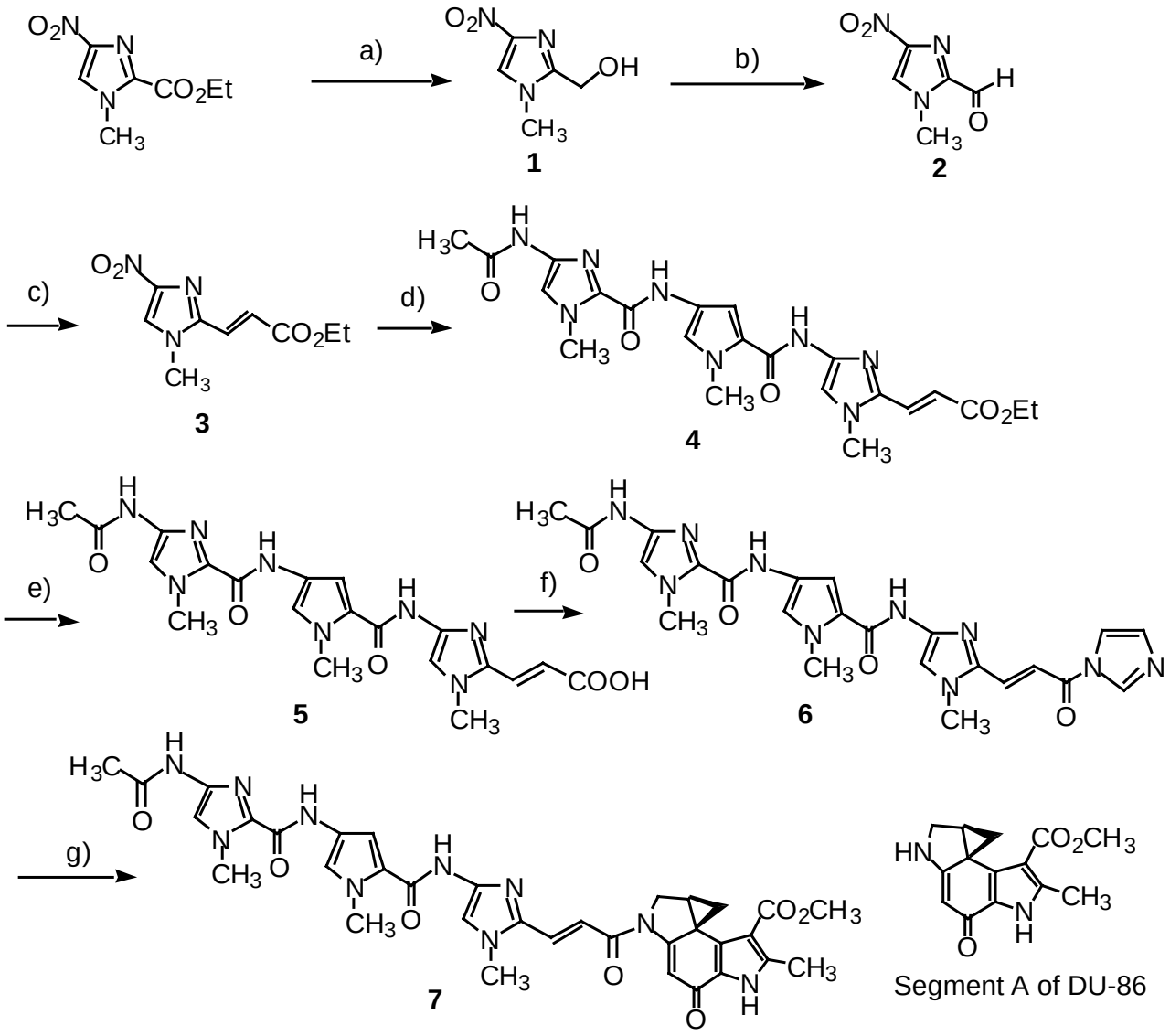
Materials

Reagents and solvents were purchased from standard suppliers and used without further purification. Abbreviations of reagents: DBU, 1,8-diazabicyclo[5.4.0]undec-7-ene; CDI, 1,1'-carbonyldiimidazole; $^{i}Pr_2NEt$, N,N-diisopropylethylamine; DMF, N,N-dimethylformamide; FDPP, pentafluorophenyl diphenylphosphinate. Reactions were monitored by thin-layer chromatography (TLC) using 0.25-mm silica gel 60 plates (Merck). ^{1}H- and ^{13}C-NMR spectra were recorded with a JEOL JNM-A 500 spectrometer; chemical shifts are in ppm relative to internal tetramethylsilane. Electrospray ionization mass spectra (ESMS) were measured with a PE SCIEX API 165 mass spectrometer. High-resolution mass spectra (HREIMS) were measured with a JEOL-JMS-SX102A mass spectrometer.

The synthesis of ImPyImLDu86 (7) and ImImPyLDu86 (14)

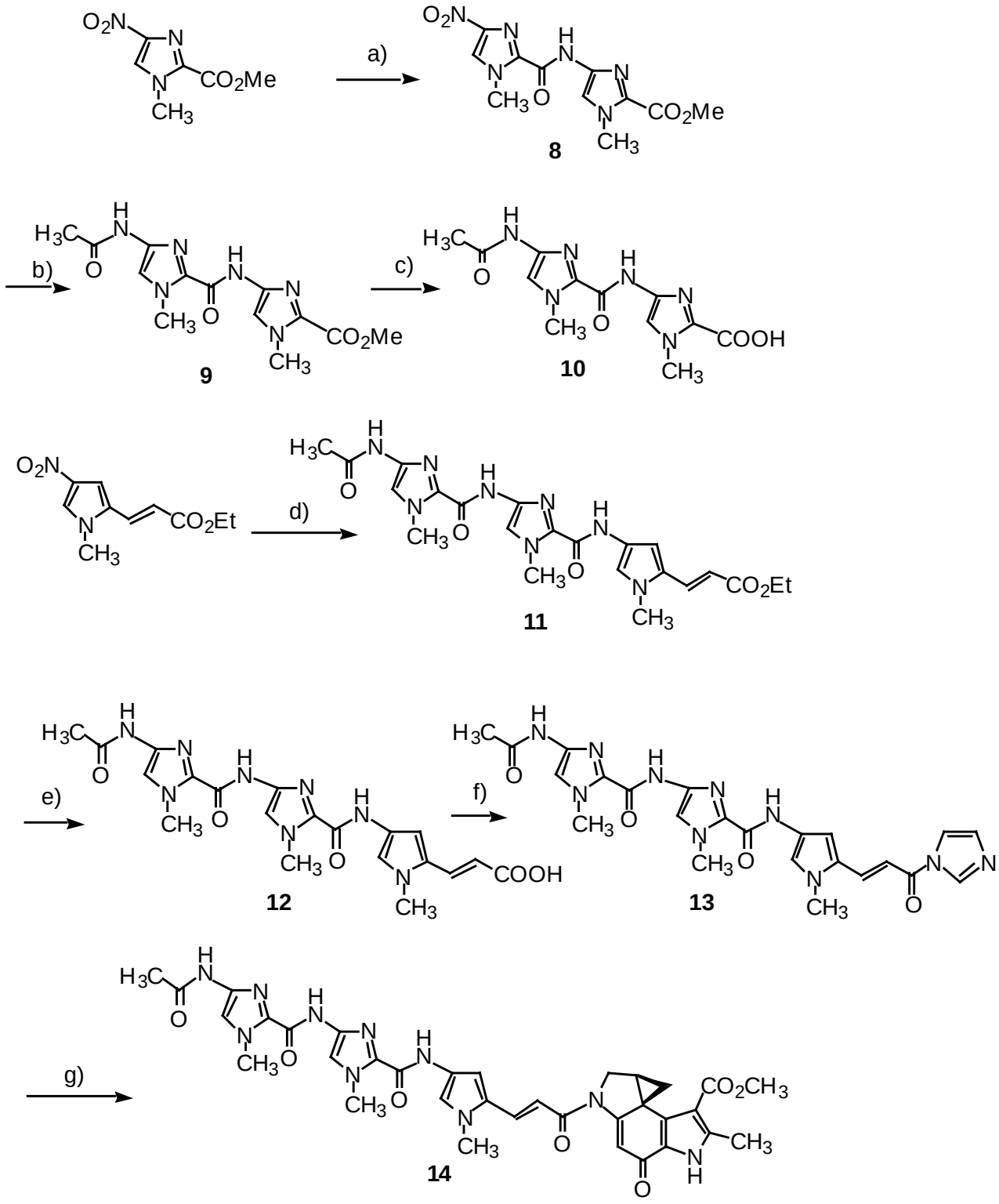
The synthesis of ImPyImLDu86 (**7**) is shown schematically in Scheme 1. Ethyl 1-methyl-4-nitroimidazol-2-carboxylate was efficiently reduced by $NaBH_4$ (1,2) to produce alcohol **1**. Vinyl ester **3** was obtained through the oxidation of **2** followed by the Horner–Wadsworth–Emmons reaction (3), with a good yield. Selective reduction of the nitro group in **4** to the corresponding amine was achieved with $NaBH_4$, using Pd-C in aqueous methanol as a catalyst (4). The resulting amine was coupled *in situ* with an activated benzotriazole ester, which was prepared *in situ* from the acid and BOP reagent (5,6) in the presence of Hunig's base, to produce triamide ester **4** with a 33% yield in three steps. Subsequent hydrolysis of ester **4** with an aqueous solution of DBU and activation of the resulting acid **5** produced amide **6**. Coupling of activated amide **6** and segment A of DU-86 (7) was effected by NaH in dry DMF, and the target molecule ImPyImLDu86 (**7**) was produced with a total yield of 8.4% in nine steps. This is the first CPI–polyamide conjugate bridged by an imidazolyl acrylic amino acid. The synthetic route to ImImPyLDu86 (**14**) is shown in Scheme 2. The Im dimer, conjugate **8**, was synthesized by the reduction of 2-(methoxycarbonyl)-1-methyl-4-nitroimidazole coupled with 2-(trichloroacetyl)-1-methyl-4-nitroimidazole. Hydrogenation of **8** and subsequent acetylation and hydrolysis produced the free carboxylic acid, **10**. The coupling of **10** with reduced ethyl (1-methyl-4-nitro-pyrrol)-2(*E*)-propenoate produced **11**. Hydrolysis of **11** and its subsequent activation and coupling with segment A of DU-86 produced conjugate **14** with a 15% yield in seven steps.

Scheme S1



a) $NaBH_4$, MeOH ; b) MnO_2, THF; c) Triethyl phosphonoacetate, NaH, THF; d) Pd-C, aq. $NaBH_4$, MeOH, H_2O then AcImPyCOOH, BOP (benzotriazole-1-yloxytris (dimethylamino)-phosphonium hexafluorophosphate), $^{i}Pr_2NEt$, DMF; e) DBU, H_2O; f) CDI, DMF; g) Segment A of DU-86, NaH, DMF

Scheme S2



a) Pd-C, H_2, AcOEt, then $NO_2ImCOCCl_3$, $^iPr_2NEt$, CH_2Cl_2; b) Pd-C, H_2, AcOEt-CH_2Cl_2, then Ac_2O, $^iPr_2NEt$, CH_2Cl_2; c) aq. NaOH, MeOH then 1% aq. HCl; d) Pd-C, aq. $NaBH_4$, MeOH, then **10**, $^iPr_2NEt$, FDPP, CH_2Cl_2; e) NaOH, MeOH-H_2O; f) CDI, DMF; g) Segment A of DU-86, NaH, DMF

2-(Hydroxymethyl)-1-methyl-4-nitroimidazole (1)

To a solution of ethyl 1-methyl-4-nitroimidazol-2-carboxylate (1.62 g, 8.1 mmol) in CH_3OH (70 ml) was added $NaBH_4$ (620 mg, 16.4 mmol) dropwise. The mixture was stirred for 2 h at 25 °C and then concentrated to a residue, which was purified by flash chromatography using ethyl acetate (AcOEt) as eluent, to produce **1** (1.07 g, 84% yield). ^{1}H NMR (DMSO-d_6) δ 8.34 (s, 1H), 5.57 (t, *J*=6.0 Hz, 1H), 4.51 (d, *J*=6.0 Hz, 2H), 3.76 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 147.4, 144.9, 123.8, 55.3, 33.6. HREIMS m/e calcd. for $C_5H_7N_3O_3$ 157.0487, found 157.0485.

1- Methyl-4-nitroimidazol-2-carboxoaldehyde (2)

To a solution of **1** (40 mg, 0.25 mmol) in 8 ml tetrahydrofuran (THF) was added MnO_2 (180 mg, 2.1 mmol), and the mixture was stirred for 15 h at 25 °C. The solid was filtered with celite and the filtrate was concentrated to a residue, which was purified by flash chromatography using AcOEt as eluent, to produce **2** (28 mg, 71% yield). ^{1}H NMR (DMSO-d_6) δ 9.74 (s, 1H), 8.69 (s, 1H), 4.00 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 182.2, 146.1, 140.5, 127.2, 35.6. HREIMS m/e calcd for $C_5H_5N_3O_3$ 155.0331, found 155.0333.

Ethyl (1-methyl-4-nitroimidazol)-2(*E*)-propeoate (3)

To a suspension of NaH (212 mg, 5.30 mmol, 60% oil suspension) in THF (10 ml) was injected triethyl phosphonoacetate dropwise (1.1 ml, 5.55 mmol), and the mixture was stirred for 5 min at 25 °C. Compound **2** (521 mg, 3.36 mmol) was added dropwise to the reaction mixture and the mixture was stirred for 10 min. H_2O (10 ml) was added to quench the reaction. THF was removed by evaporation, and the solution was diluted with H_2O (20 ml) and extracted with AcOEt. Evaporation of the solvents gave a crude residue, which was further purified by flash chromatography using AcOEt as eluent, to produce **3** (705 mg, 93% yield). ^{1}H NMR (DMSO-d_6) δ 8.50 (s, 1H), 7.53 (d, *J*=15.5 Hz, 1H), 6.70 (d, *J*=15.5 Hz, 1H), 4.23 (q, *J*=7.5 Hz, 2H), 3.87 (s, 3H), 1.27 (t, *J*=7.5 Hz, 3H). ^{13}C NMR (DMSO-d_6) δ 165.2, 146.2, 141.9, 128.4, 125.0, 123.0, 60.6, 33.8, 14.1. HREIMS m/e calcd for $C_9H_{11}N_3O_4$ 225.0749, found 225.0745.

AcImPyImLCO$_2$Et (4)

^{i}Pr$_2$NEt (0.1 ml, 0.57 mmol) was added to a suspension of 4-[[4-(acetylamino)-1-methylimidazole-2-yl]carbonylamino]-1-methylpyrrole-2-carboxylic acid (77 mg, 0.25 mmol), BOP reagent (135 mg, 0.26 mmol) in DMF (2 ml), and the solution was stirred for 2 h at 25 °C to produce activated benzotriazole ester. Separately, 1 M (aq) $NaBH_4$ (800 µl) was added to a mixture of **3** (78.8 mg, 0.35 mmol), 10% palladium on activated carbon (Pd-C) (45 mg) in CH_3OH (8 ml), and the mixture was stirred for 5 min at 25 °C. The Pd-C solid was removed by a short chromatographic separation. After evaporation of the

solvent, the residual amine was immediately mixed with the activated ester described above. The reaction mixture was stirred for a further 24 h at 25 °C and evaporated to give a black residue, which was subjected to flash chromatography using 5% CH_3OH in $CHCl_3$ as eluent, to produce **4** (40.2 mg, 33% yield). ^{1}H NMR (DMSO-d_6) δ 10.48 (s, 1H), 10.27 (s, 1H), 9.81 (s, 1H), 7.57 (s, 1H), 7.50 (d, *J*=15.0 Hz, 1H), 7.41 (s, 1H), 7.37 (d, *J*=1.5 Hz, 1H), 7.17 (d, *J*=1.5 Hz, 1H), 6.45 (d, *J*=15.0 Hz, 1H), 4.19 (q, *J*=7.5 Hz, 2H), 3.94 (s, 3H), 3.85 (s, 3H), 3.77 (s, 3H), 2.01 (s, 3H), 1.25 (t, *J*=7.5 Hz, 3H). HREIMS m/e calcd for $C_{22}H_{26}N_8O_5$ 482.2026, found 482.2020.

AcImPyImLCO$_2$H (5)

To a suspension of compound **4** (15.1mg, 0.03 mmol) in H_2O (0.6 ml) was added DBU (0.6 ml, 4.0 mmol). After the solution was stirred for 1 h at 25 °C, the reaction mixture was acidified to pH 3 at 0 °C. The precipitate was collected by filtration, washed with H_2O, and dried to produce **5** (10.1 mg, 72% yield). ^{1}H NMR (DMSO-d_6) δ 12.43 (s, brs, 1H), 10.49 (s, 1H), 10.28 (s, 1H), 9.78 (s, 1H), 7.56 (s, 1H), 7.46 (d, *J*=15.0 Hz, 1H), 7.42 (s, 1H), 7.39 (d, *J*=1.5 Hz, 1H), 7.18 (d, *J*=1.5 Hz, 1H), 6.43 (d, *J*=15.0 Hz, 1H), 3.95 (s, 3H), 3.86 (s, 3H), 3.77 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 167.4, 167.1, 158.4, 155.7, 138.9, 137.8, 136.2, 133.8, 128.7, 122.2, 121.1, 119.4, 118.7, 113.8, 112.9, 105.8, 36.3, 34.9, 32.6, 22.7. ESIMS m/e calcd for $C_{20}H_{21}N_8O_5$ (M-H) 453.4, found 453.3.

AcImPyImLCOIm (6)

To a solution of compound **5** (8.1 mg, 18 μmol) in DMF (1 ml) was added CDI (7.0 mg, 44 μmol). The mixture was stirred for 2 h at 25 °C. DMF was removed by vacuum evaporation, and H_2O (3 ml) was added. The yellow precipitate was collected, washed with H_2O, and dried to produce **6** (7.2 mg, 80% yield). ^{1}H NMR (DMSO-d_6) δ 10.51 (s, 1H), 10.24 (s, 1H), 9.78 (s, 1H), 8.51 (s, 1H), 7.85 (d, *J*=15.0 Hz, 1H), 7.81 (t, *J*=1.5 Hz, 1H), 7.71 (s, 1H), 7.42 (s, 1H), 7.40 (d, *J*=1.5 Hz, 1H), 7.30 (d, *J*=15.0 Hz, 1H), 7.21(d, *J*=1.5 Hz, 1H), 7.14 (s, 1H), 3.96 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 2.03 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 167.2, 161.9, 158.6, 155.7, 139.7, 137.7, 136.8, 136.2, 133.8, 132.6, 130.7, 122.1, 121.2, 119.7, 116.7, 115.0, 114.4, 113.8, 105.9, 36.3, 34.9, 32.9, 22.7. ESIMS m/e calcd for $C_{23}H_{23}N_{10}O_4$ (M-H) 503.5, found 503.4.

AcImPyImLDu86 (7)

To a solution of NaH (0.4 mg, 60% oil suspension) in DMF (0.2 ml) was added segment A of DU-86 (2.5 mg, 9.6 μmol) in DMF (0.3 ml), and the mixture was stirred for 2 h at –40 °C. Compound **6** (4.6 mg, 9.1 μmol) in DMF (0.7 ml) was added at –10 °C, and the reaction mixture was then stirred for 3 h at –10 °C. The reaction mixture was quenched by the addition of 10 mM sodium phosphate buffer (2 ml, pH 6.86) at 0 °C. Evaporation of the solvent produced a yellow residue, which was subjected to column

chromatography (silica gel, 0–5% CH_3OH in $CHCl_3$, gradient elution) to produce **7** (5.1 mg, 81% yield). ^{1}H NMR (DMSO-d_6) δ 12.39 (s, 1H), 10.57 (s, 1H), 10.29 (s, 1H), 9.76 (s, 1H), 7.60 (s, 1H), 7.56 (d, *J*=14.5 Hz, 1H), 7.43 (s, 1H), 7.40 (d, *J*=2.0 Hz, 1H), 7.26 (brs, 1H), 7.20 (d, *J*=2.0 Hz, 1H), 7.00 (d, *J*=14.5 Hz, 1H), 4.20 (m, 2H), 3.95 (s, 3H), 3.87 (s, 3H), 3.81 (s, 3H), 3.74 (s, 3H), 3.48 (m, 1H), 2.47 (s, 3H), 2.11 (dd, *J*=4.0 and 4.5 Hz, 1H), 2.02 (s, 3H), 1.36 (t, *J*=4.0 Hz, 1H). ESIMS m/e calcd for $C_{34}H_{33}N_{10}O_4$ (M-H) 693.7, found 693.6.

1- Methyl-4-[[(1-methyl-4-nitroimidazol-2-yl)carbonyl]amino]-imidazol-2-carboxylic acid (8)

A suspension of 2-(methoxycarbonyl)-1-methyl-4-nitroimidazole (4.0 g, 21.6 mmol) and Pd-C (500 mg) in AcOEt (80 ml) was stirred for 4 h at 25 °C under an H_2 atmosphere. The reaction mixture was filtered through celite. The filtrate was concentrated to produce a crude amino compound. To a solution of the crude amine in CH_2Cl_2 (50 ml) was added 2-(trichloroacetyl)-1-methyl-4-nitroimidazole (6.0 g, 22.0 mmol) and ^{i}Pr$_2$NEt (7.6 ml, 43.7 mmol) at 25 °C, and the solution was stirred overnight at 25 °C. After removal of the solvent, the residue was washed with diethyl ether (Et_2O) to produce **8** (5.72 g, 86% yield). ^{1}H NMR (DMSO-d_6) δ 10.84 (s, 1H), 8.61(s, 1H), 7.70 (s, 1H), 4.02 (s, 3H), 3.94 (s, 3H), 3.82 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 158.8, 155.2, 144.4, 137.1, 135.9, 131.5, 126.6, 116.3, 51.8, 36.3, 35.6. ESMS m/e calcd for $C_{11}H_{12}N_6O_5$ (M-H) 307.1, found 307.2.

Methyl 1-methyl-4-[[[1-methyl-4-(1-oxo-ethyl)-imidazol-2-yl]carbonyl]amino]-1-imidazol-2-carboxylate (9)

A suspension of **8** (2.0 g, 6.24 mmol) and Pd-C (300 mg) in AcOEt (50 ml) and CH_2Cl_2 (15 ml) was stirred for 5 h at 25 °C under an H_2 atmosphere. The reaction mixture was filtered through celite, and the residue was washed with CH_2Cl_2. The combined filtrate was concentrated to produce a crude amino compound. To a solution of the amine in CH_2Cl_2 (20 ml) was added acetic anhydride (4.0 ml, 36.1 mmol) and ^{i}Pr$_2$NEt (6.3 ml, 36.1 mmol) at 25 °C, and the solution was stirred overnight at 25 °C. After removal of the solvent, the residue was washed with H_2O/CH_3OH to produce **9** (1.50 g, 72% yield). ^{1}H NMR (DMSO-d_6) δ 10.37 (s, 1H), 9.69 (s, 1H), 7.67 (s, 1H), 7.47 (s, 1H), 3.94 (s, 3H), 3.93 (s, 3H), 3.81 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 167.2, 158.74 155.7, 136.5, 136.1, 132.7, 131.3, 115.3, 114.4, 51.8, 35.6, 34.9, 22.7. ESMS m/e calcd for $C_{13}H_{16}N_6O_4$ (M+H) 321.1, found 321.2.

1-Methyl-4-[[[1-methyl-4-(1-oxo-ethyl)-imidazol-2-yl]carbonyl]amino]-imidazol-2-carboxylic acid (10)

To a suspension of **9** (1.5 g, 4.69 mmol) in CH_3OH (15 ml) was added 1 N (aq) NaOH (30 ml), and the reaction mixture was stirred for 15 h at 25 °C. After removal of the CH_3OH, the residue was acidified (pH 2.0) with 20% (aq) HCl. The resulting precipitate was filtered to produce **10** (1.39 g, 97% yield). ^{1}H

NMR (DMSO-d_6) δ 10.36 (s, 1H), 9.61 (s, 1H), 7.63 (s, 1H), 7.48 (s, 1H), 3.95 (s, 3H), 3.93 (s, 3H), 3.62 (brs, 1H), 2.02 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 167.3, 158.8, 155.5, 136.5, 134.4, 132.4, 131.6, 114.8, 114.7, 35.9, 35.1, 22.7. ESMS m/e calcd for $C_{12}H_{14}N_6O_4$ (M+H) 307.1, found 307.1.

AcImImPyLCO$_2$Et (11)

To a suspension of ethyl (1-methyl-4-nitro-pyrrol)-2(*E*)-propenoate (128 mg, 0.57 mmol) and Pd-C (60 mg) in CH_3OH (10 ml) was added 1 M (aq) $NaBH_4$ (125 μl) at 25 °C. After the reaction mixture was stirred for 10 min, acetone was added. The mixture was separated chromatographically through silica gel with AcOEt/CH_3OH. After the eluent was evaporated, the residue, **10** (227 mg, 0.74 mmol), FDPP (856 mg, 2.23 mmol), and $^{i}Pr_2NEt$ (5.0 ml, 28.7 mmol) were dissolved in DMF (20 ml) and stirred overnight at 25 °C. After removal of the solvent, the residue was dissolved in H_2O and extracted with CH_2Cl_2. The extract was evaporated and separated chromatographically (silica gel, 50% AcOEt in CH_2Cl_2) to produce **11** (118 mg, 43% yield). ^{1}H NMR ($CDCl_3$) δ 9.20 (s, 1H), 9.01 (brs, 1H), 8.06 (s, 1H), 7.53 (d, *J* = 15.0 Hz, 1H), 7.42 (s, 1H), 7.41 (s, 1H), 7.34 (s, 1H), 6.55 (s, 1H), 6.10 (d, *J* = 15.0 Hz, 1H), 4.22 (q, *J* = 7.0 Hz, 2H), 4.05 (s, 3H), 4.02 (s, 3H), 3.66 (s, 3H), 2.17 (s, 3H), 1.30 (t, *J* = 7.0 Hz ,3H). ^{13}C NMR ($CDCl_3$) δ 167.7, 167.6, 155.9, 155.8, 136.5, 135.5, 134.4, 133.0, 131.5, 127.2, 123.1, 117.8, 114.5, 114.1, 113.3, 102.3, 60.2, 35.7, 35.6, 34.1, 23.2, 14.3. ESMS m/e calcd for $C_{22}H_{26}N_8O_5$ (M-H) 481.2, found 481.2.

AcImImPyLCO$_2$H (12)

To a suspension of **11** (118 mg, 0.245 mmol) in CH_3OH (1 ml) was added 1 N (aq) NaOH (2 ml), and the reaction mixture was stirred at 25 °C for 15 h. After the removal of CH_3OH, the residue was acidified (pH 2.0) with 20% (aq) HCl, and the resulting precipitate was filtered to produce **12** (85.6 mg, 77% yield). ^{1}H NMR (DMSO-d_6) δ 10.35 (s, 1H), 10.30 (s, 1H), 9.34 (s, 1H), 7.56 (s, 1H), 7.49 (s, 1H), 7.46 (d, *J* = 15.5 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 6.01 (d, *J* = 15.5 Hz, 1H), 3.99 (s, 3H), 3.97 (s, 3H), 3.79 (brs, 1H), 3.67 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (DMSO-d_6) δ 167.9, 167.2, 155.3, 155.2, 136.5, 134.6, 134.3, 132.6, 131.9, 126.1, 123.5, 118.3, 114.6, 113.8, 112.9, 102.9, 35.2, 35.0, 22.8. ESMS m/e calcd for $C_{20}H_{22}N_8O_5$ (M+H) 455.2, found 455.1.

AcImImPyLCO$_2$Im (13)

A solution of **12** (20 mg, 44 μmol) and CDI (14.2 mg, 88 μmol) in DMF (5 ml) was stirred overnight at 25 °C. After removal of the solvent, the residue was washed with Et_2O five times to produce **13** (22.0 mg, 99% yield). ^{1}H NMR (DMSO-d_6) δ 10.43 (s, 1H), 10.29 (s, 1H), 9.34 (s, 1H), 8.68 (s, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 7.87 (d, *J* = 15.5 Hz, 1H), 7.58 (s, 1H), 7.50 (s, 1H), 7.48 (d, *J* = 2.0 Hz, 1H), 7.35 (s, 1H), 7.16 (d, *J* = 15.5 Hz, 1H), 7.10 (s, 1H), 4.01 (s, 3H), 3.98 (s, 3H), 3.78 (s, 3H), 2.04 (s, 3H). ^{13}C

NMR (DMSO-d_6) δ 167.2, 157.7, 155.6, 155.2, 139.9, 136.5, 134.8, 134.6, 134.2, 132.5, 130.2, 126.9, 124.2, 121.1, 116.7, 114.6, 113.9, 108.4, 105.9, 35.2, 35.0, 33.9, 22.8. ESMS m/e calcd for $C_{23}H_{24}N_{10}O_4$ (M+H) 505.2, found 505.2.

AcImImPyLDu86 (14)

To a solution of segment A of DU-86 (10.0 mg, 20 μmol) in DMF (2 ml) was added NaH (1.6 mg, 40 μmol) at –30 °C. After the solution was stirred for 2 h, conjugate **13** (12.2 mg, 20 μmol) in DMF (2 ml) was added dropwise to the reaction mixture at –30 °C. The reaction mixture was stirred for a further 10 h at 0 °C, then 10 mM sodium phosphate buffer (2 ml, pH 6.9) was added, and the mixture was stirred for 5 min at 25 °C. After removal of the solvent, the residue was separated chromatographically (silica gel, 0–5% CH_3OH in $CHCl_3$, gradient elution) to produce **14** (10.6 mg, 76% yield). ^{1}H NMR (DMSO-d_6) δ 12.35 (s, 1H), 10.34 (s, 1H), 10.29 (s, 1H), 9.33 (s, 1H), 7.57 (d, *J* = 15.5 Hz, 1H), 7.57 (s, 1H), 7.50 (s, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.83 (brs, 1H), 6.56 (d, *J* = 14.5 Hz, 1H), 4.29 (d, *J* = 10.0 Hz, 1H), 4.19 (dd, *J* = 4.5 and 10.0 Hz, 1H), 4.00 (s, 3H), 3.97 (s, 3H), 3.72 (s, 3H), 3.71 (s, 3H), 3.45 (m, 1H), 2.46 (s, 3H), 2.04 (s, 3H), 2.02 (dd, *J* = 4.0 and 4.5 Hz, 1H), 1.29 (t, *J* = 4.0 Hz, 1H). ESMS m/e calcd for $C_{34}H_{34}N_{10}O_7$ (M+H) 695.3, found 695.3.

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