SUPPORTING INFORMATION

Multicomponent Access to Indolo[3,3a-c]isoquinolin-3,6-diones: Formal Synthesis of Plicamine

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Experimental Methods

General information.

All reagents and solvents were obtained from Aldrich and Fluka, and used without further purification unless specified otherwise. 2,2,2-trifluoroethanol was dried by refluxing it with excess calcium hydride under nitrogen and was freshly distilled before use. Tetrahydrofuran was dried by refluxing it with excess sodium metal under nitrogen and was freshly distilled before use. All laboratory material was oven dried at 130°C for 12 hours prior use. Melting points were determined on a Fisher apparatus and are uncorrected. Reaction progress was monitored by analytical thin layer chromatography using GF silica plates. Visualization was achieved by short-wave UV light (254 nm). Flash column chromatography was conducted under silica gel (230-400 mesh) and mixtures of hexane/ethyl acetate as eluents. 1H and 13C NMR spectra were recorded on a JEOL Eclipse-300 model spectrometer using CDCl3 or DMSO-d6 as solvents. Chemical shifts are reported as parts per million downfield from an internal tetramethylsilane standard (δ = 0.0 for 1H) or from solvent references. NMR coupling constants are reported in hertz (Hz). High-resolution electron impact mass spectra were obtained on JEOL JMS-AX505HA spectrometer. X-ray crystal structure analysis was undertaken on a Bruker Smart Apex diffractometer (CCD detector).

General procedure for the Ugi multicomponent condensation.

To a 0.20 M solution of 4-hydroxybenzaldehyde (1.0 equivalents) in methanol, was added piperonyl amine (1.1 equivalents) and reacted for 5 min at 60 °C under microwave assistance in a sealed vessel. Then the corresponding carboxylic acid (1.2 equivalents) and the corresponding isocyanide (1.2 equivalents) were injected successively and the reaction was taken to 60 °C under microwave assistance for 3 hours. Then, the volatiles were removed in vacuo and the crude subjected to flash column chromatography (SiO2, EtOAc/Hexanes) to obtain the pure Ugi adducts.

Ugi adduct 8a, amorphous white solid (m. p.: 197-199°C), 80 % yield.

1H NMR (300 MHz, CDCl3) δ 9.10 (s, 1H), 7.22-6.41 (m, 11H), 5.96 (s, 1H), 5.88 (s, 2H), 5.85 (s, 1H), 4.59 (d, J = 17.1, 1H), 4.42 (d, J = 17.1, 1H), 3.77 (s, 3H), 3.51 (m, 2H), 1.29 (s, 9H). 13C NMR (75 MHz, CDCl3) δ
172.68, 169.37, 158.09, 157.21, 147.39, 146.09, 132.14, 130.75, 129.77, 126.81, 125.85, 118.97, 115.29, 113.64, 107.76, 106.45, 100.68, 61.74, 55.00, 50.93, 48.90, 28.38. \textbf{HRMS-FAB+} (M+1) m/z: found. 505.2342, calcd for C$_{29}$H$_{33}$N$_2$O$_6$: 505.2339.

\[ \text{Ugi adduct 8b, amorphous pale yellow solid (m. p.: 90-93°C), 78% yield.} \]

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.24-6.39 (m, 16H), 6.18 (s, 1H), 5.84 (s, 2H), 5.74 (s, 1H), 4.61 (d, $J = 17.0$, 1H), 4.41 (m, 3H), 3.73 (s, 3H), 3.60 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 173.50, 170.18, 158.60, 156.75, 147.95, 146.76, 137.89, 131.35, 130.01, 128.71, 127.71, 127.49, 126.59, 126.04, 119.58, 115.90, 114.19, 108.25, 106.91, 101.08, 63.18, 55.33, 50.09, 43.83, 40.52. \textbf{HRMS-FAB+} (M+1) m/z: found. 539.2185, calcd for C$_{32}$H$_{31}$N$_2$O$_6$: 539.2182.

\[ \text{Ugi adduct 8c, amorphous white solid (m. p.: 117-120°C), 73% yield.} \]

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.62 (s, 1H), 7.13-6.40 (m, 11H), 5.83 (s, 2H), 5.76 (s, 1H), 5.56 (d, $J = 7.5$, 1H), 4.55 (d, $J = 17.0$, 1H), 4.33 (d, $J = 17.0$, 1H), 3.72 (s, 1H), 3.51 (m, 3H), 1.81 (m, 2H), 1.55 (m, 2H), 1.23 (m, 2H), 1.0 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 173.08, 168.99, 158.36, 157.53, 147.76, 146.52, 131.21, 129.98, 126.90, 125.74, 119.41, 115.85, 114.07, 108.13, 106.84, 100.97, 62.62, 55.31, 49.66, 48.53, 40.50, 32.82, 25.54, 24.87. \textbf{HRMS-FAB+} (M+1) m/z: found. 531.2499, calcd for C$_{31}$H$_{35}$N$_2$O$_6$: 531.2495.

\[ \text{Ugi adduct 8d, amorphous white solid (m. p.: 159-160°C), 61% yield.} \]

$^1$H NMR (300 MHz, CDCl$_3$) δ 8.97 (s, 1H), 7.06 (d, $J = 8.4$Hz, 2H), 6.97 (d, $J = 8.4$Hz, 2H), 6.71 (d, $J = 8.4$Hz, 2H), 6.64 (d, $J = 8.4$Hz, 2H), 6.53 (d, $J = 8.0$Hz, 1H), 6.51 (d, $J = 15.6$Hz, 1H), 3.96 (hept, $J = 6.8$Hz, 1H), 3.51 (d, $J = 15.6$Hz, 1H), 3.43 (d, $J = 15.6$Hz, 1H), 0.98 (m, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 173.03, 169.14, 158.27, 157.44, 147.64, 146.33, 131.66, 131.02, 128.83, 126.71, 125.42, 119.20, 115.66, 113.86, 107.93, 106.64, 100.79, 62.35, 55.12, 49.40, 41.50, 22.30. \textbf{HRMS-FAB+} (M+1) m/z: found. 491.2185, calcd for C$_{28}$H$_{31}$N$_2$O$_6$: 491.2182.

\[ \text{Ugi adduct 8e, amorphous white solid (m. p.: 93-95°C), 61% yield.} \]

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.11 (d, $J = 8.3$ Hz, 2H), 7.05 (d, $J = 8.3$ Hz, 2H), 6.77 (d, $J = 8.5$ Hz, 2H), 6.69 (d, $J = 8.5$ Hz, 2H), 6.62 (d, $J = 8.0$ Hz, 1H), 6.51 (d, $J = 8.1$ Hz, 1H), 6.45 (s, 1H), 5.85 (s, 2H), 5.66 (s, 1H), 4.63 (d, J
= 17.6 Hz, 1H), 4.40 (d, J = 17.6 Hz, 1H), 3.73 (s, 3H), 3.63 (d, J = 15.5 Hz, 1H), 3.56 (d, J = 15.5 Hz, 1H), 2.71 (m, 3H). 13C NMR (75 MHz, CDCl3) δ 173.05, 169.00, 158.89, 157.44, 147.64, 146.33, 131.66, 131.02, 129.83, 126.71, 125.42, 119.20, 115.66, 113.86, 107.93, 106.64, 100.79, 62.35, 55.12, 49.40, 28.30. HRMS-FAB+ (M+1) m/z: found. 463.1865, calcd for C26H27N2O6: 463.1869.

Ugi adduct 8f, amorphous pale yellow solid (m. p.: 194-196°C), 74 % yield. 1H NMR (300 MHz, CDCl3) δ 9.07 (s, 1H), 7.14 (d, J = 8.2 Hz, 2H), 6.72 (d, J = 8.2 Hz, 2H), 6.60 (m, 1H), 6.40 (m, 2H), 5.97 (s, 1H), 5.88 (s, 2H), 4.59 (d, J = 17.7 Hz, 1H), 4.44 (d, J = 17.7 Hz, 1H), 3.05 (s, 3H), 2.16 (s, 1H), 2.02 (s, 3H), 1.31 (s, 9H). 13C NMR (75 MHz, CDCl3) δ 172.26, 169.61, 157.32, 147.46, 146.05, 132.14, 130.88, 125.91, 119.06, 115.47, 107.78, 106.50, 100.70, 61.61, 51.11, 49.67, 28.51, 22.58. HRMS-FAB+ (M+1) m/z: found. 399.1924, calcd for C22H27N2O5: 399.1920.

Ugi adduct 8g, amorphous pale yellow solid (m. p.: 202-204°C), 66 % yield. 1H NMR (300 MHz, DMSO-d6) δ 9.55 (s, 1H), 8.56 (m, 1H), 7.30-6.48 (m, 12H), 6.02 (s, 1H), 5.93 (s, 2H), 4.55 (m, 1H), 4.38 (m, 1H), 4.29 (m, 2H), 2.08 (s, 1H), 1.89 (s, 2H), 1.31 (s, 9H). 13C NMR (75 MHz, DMSO-d6) δ 171.38, 170.18, 157.09, 147.05, 145.57, 139.29, 132.83, 130.91, 130.21, 128.20, 128.06, 127.35, 127.08, 125.80, 118.91, 115.00, 107.69, 106.37, 100.63, 60.76, 48.49, 41.99, 22.33. HRMS-FAB+ (M+1) m/z: found. 433.1765, calcd for C25H25N2O5: 433.1763.

Ugi adduct 8h, amorphous pale yellow solid (m. p.: 181-183°C), 79 % yield. 1H NMR (300 MHz, CDCl3) δ 8.82 (s, 1H), 6.83 (d, J = 7.9 Hz, 2H), 6.41 (d, J = 7.9 Hz, 2H), 6.31-6.14 (m, 3H), 5.65 (s, H), 5.55 (s, 2H), 4.26 (d, J = 17.2 Hz, 1H), 4.11 (d, J = 17.2 Hz, 1H), 3.38 (m, 1H), 2.86 (s, 3H), 1.76 (m, 2H), 1.52 (m, 2H), 1.34 (m, 12H), 0.98 (m, 2H), 0.82 (m, 2H). 13C NMR (75 MHz, CDCl3) δ 171.84, 168.81, 156.87, 147.00, 145.97, 139.29, 132.83, 130.91, 130.21, 128.20, 128.06, 127.35, 127.08, 125.80, 118.91, 115.00, 107.69, 106.37, 100.63, 60.76, 48.49, 41.99, 22.33. HRMS-FAB+ (M+1) m/z: found. 425.2078, calcd for C24H29N2O5: 425.2076.

Ugi adduct 8i, amorphous pale yellow solid (m. p.: 198-200°C), 61 % yield. 1H NMR (300 MHz, DMSO-d6) δ 9.05 (s, 1H), 7.16 (d, J = 8.0 Hz, 2H), 6.74 (d, J = 8.0 Hz, 2H), 6.62-6.28 (m, 3H), 5.93 (s, 1H), 5.88 (s, 2H), 4.58 (d, J = 17.0 Hz, 1H), 4.44 (d, J = 17.0 Hz, 9H), 4.05 (m, 1H), 2.09 (m, 3H), 1.12 (d, J = 7.7 Hz, 3H), 1.08 (d, J = 7.7 Hz, 3H). 13C NMR (75 MHz, DMSO-d6) δ 172.13, 169.05, 157.20, 145.92, 131.72, 130.72, 125.45, 118.92, 115.36, 107.63, 106.36, 100.51, 61.41, 49.63, 41.12, 22.30, 22.09. HRMS-FAB+ (M+1) m/z: found. 385.1766, calcd for C22H25N2O5: 385.1763.
Ugi adduct 8j, amorphous white solid, (m. p.: 118-120°C) 47% yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.78 (s, 1H), 7.13 (m, 2H), 6.63 (m, 2H), 6.71 (d, $J = 8.4$ Hz, 2H), 6.64 (d, $J = 8.4$ Hz, 2H), 6.58 (m, 1H), 6.41 (m, 2H), 5.97 (s, 1H), 5.86 (m, 2H), 4.60 (d, $J = 17.0$ Hz, 1H), 4.42 (d, $J = 17.0$ Hz, 1H), 2.92 (m, 1H), 2.84 (m, 2H), 1.54 (m, 2H), 1.28 (m, 1H), 0.81 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 175.22, 169.77, 157.44, 147.59, 146.25, 132.20, 131.05, 125.85, 119.20, 115.69, 107.93, 106.64, 100.83, 62.33, 51.40, 49.28, 33.78, 28.58, 27.28, 22.35, 13.85. HRMS-FAB+ (M+1) m/z: found. 441.2393, calcd for C$_{25}$H$_{33}$N$_2$O$_5$: 441.2389.

Ugi adduct 8k, amorphous pale yellow solid (m. p.: 68-70°C), 69 % yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.23-7.06 (m, 8H), 6.72 (m, 3H), 6.42 (m, 2H), 5.79 (s, 2H), 5.74 (s, 1H), 4.58 (d, $J = 17.5$ Hz, 1H), 4.36 (m, 3H), 2.25 (m, 2H), 1.54 (m, 2H), 1.23 (m, 2H), 0.78 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 175.76, 170.70, 157.49, 147.84, 146.61, 137.83, 131.41, 131.23, 128.65, 127.61, 127.42, 127.26, 125.35, 119.48, 116.00, 108.17, 108.08, 106.82, 101.01, 63.14, 49.88, 43.77, 33.86, 27.34, 22.44, 13.87. HRMS-FAB+ (M+1) m/z: found. 475.2236, calcd for C$_{28}$H$_{31}$N$_2$O$_5$: 475.2233.

Ugi adduct 8l, white semisolid, 56 % yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.84 (s, 1H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.71 (d, $J = 8.0$ Hz, 2H), 6.62 (d, $J = 7.8$ Hz, 1H), 6.48 (m, 2H), 5.87 (s, 2H), 5.87 (m, 1H), 5.74 (s, 1H), 4.60 (d, $J = 17.5$ Hz, 1H), 4.40 (d, $J = 17.5$ Hz, 1H), 3.74 (m, 1H), 2.29 (m, 2H), 1.86 (m, 2H), 1.61 (m, 4H), 1.28 (m, 4H), 1.05 (m, 3H), 0.84 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 175.66, 169.56, 157.15, 147.91, 146.66, 131.65, 131.17, 126.11, 119.54, 115.96, 108.24, 106.89, 101.10, 33.98, 32.81, 27.48, 25.57, 24.86, 24.79, 22.55, 13.95. HRMS-FAB+ (M+1) m/z: found. 467.2550, calcd for C$_{27}$H$_{35}$N$_2$O$_5$: 467.2546.

Ugi adduct 8m, amorphous pale yellow solid (m. p.: 94-96°C), 62 % yield. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.16 (d, $J = 8.3$ Hz, 2H), 6.71 (d, $J = 8.3$ Hz, 2H), 6.61 (d, $J = 8.0$ Hz, 1H), 6.43 (d, $J = 8.0$ Hz, 1H), 6.40 (s, 1H), 5.87 (s, 2H), 5.79 (s, 1H), 5.68 (s, 1H), 4.62 (d, $J = 17.4$ Hz, 1H), 4.42 (d, $J = 17.4$ Hz, 1H), 2.54 – 2.14 (m, 2H), 1.76-1.39 (m, 9H), 1.31 (s, 9H), 1.00 (m, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 175.45, 169.72, 157.38, 147.63, 146.28, 132.17, 131.10, 125.88, 119.25, 115.75, 107.98, 106.68, 100.85, 62.41, 51.50, 49.41, 39.70, 33.45, 32.43, 31.41, 28.60, 25.08. HRMS-FAB+ (M+1) m/z: found. 481.2703, calcd for C$_{28}$H$_{37}$N$_2$O$_5$: 481.2702.
**Ugi adduct 8n**, amorphous pale yellow solid (m. p.: 170-173°C), 40 % yield. 

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.14 (s, 1H), 7.38-7.00 (m, 8H), 6.76 – 6.40 (m, 4H), 6.00 (s, 1H), 5.88 (s, 2H), 4.60 (d, $J = 7.5$ Hz, 1H), 4.41 (m, 3H), 2.25 (m, 2H), 1.79-1.35 (m, 9H), 0.99 (s, 2H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 175.06, 170.57, 157.40, 147.48, 146.08, 138.55, 132.25, 131.12, 128.31, 127.46, 126.93, 125.57, 119.10, 115.50, 107.82, 106.54, 100.73, 61.83, 49.05, 43.11, 33.28, 32.28, 31.32, 24.95. HRMS-FAB+ (M+1) m/z: found. 515.2547, calcd for C$_{31}$H$_{35}$N$_2$O$_5$: 515.2546.

**Ugi adduct 8o**, pale yellow semisolid, 51 % yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.15 (d, $J = 8.1$ Hz, 2H), 6.74 (d, $J = 8.1$ Hz, 2H), 6.63 (d, $J = 7.8$ Hz, 1H), 6.59 – 6.39 (m, 2H), 5.87 (s, 2H), 5.87 (m, 1H), 5.76 (s, 1H), 4.61 (d, $J = 17.3$ Hz, 1H), 4.41 (d, $J = 17.3$ Hz, 1H), 3.76 (m, 1H), 2.32 (m, 2H), 1.93 – 0.89 (m, 21H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 175.82, 169.58, 157.16, 147.92, 146.65, 131.69, 131.16, 126.10, 119.56, 115.97, 108.24, 106.90, 101.09, 62.94, 50.04, 48.77, 39.82, 33.60, 32.81, 32.53, 31.61, 25.56, 25.21, 24.85, 24.79. HRMS-FAB+ (M+1) m/z: found. 507.2864, calcd for C$_{30}$H$_{39}$N$_2$O$_5$ : 507.2859.

**Ugi adduct 8p**, amorphous white solid (m. p.: 102-105°C), 89 % yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.40 (s, 1H), 7.13 (m, 2H), 6.71 – 6.43 (m, 4H), 6.12 (m, 2H), 5.92 (m, 2H), 4.89 (d, $J = 16.0$ Hz, 1H), 4.63 (d, $J = 16.0$ Hz, 1H), 1.31 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.54, 162.08, 151.79, 148.76, 147.91, 147.60, 132.01, 126.15, 124.10, 123.80, 107.14, 106.92, 106.72, 106.31, 101.60, 77.58, 77.16, 76.74, 63.26, 52.02, 40.88, 28.63. HRMS-FAB+ (M+1) m/z: found. 385.1765, calcd for C$_{21}$H$_{25}$N$_2$O$_5$ : 385.1763.

**Ugi adduct 8q**, amorphous white solid (m. p.: 125-127°C), 97 % yield. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.25 and 8.14 (s, 1H, conformers), 7.12 - 6.49 (m, 7H), 5.93 (m, 3H), 4.47 (m, 1H), 4.23 (m, 1H), 2.79 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.54, 162.08, 151.79, 148.76, 147.91, 147.60, 132.01, 126.15, 124.10, 123.80, 107.14, 106.92, 106.72, 106.31, 101.60, 77.58, 77.16, 76.74, 60.55, 55.88, 52.15, 28.53. HRMS-FAB+ (M+1) m/z: found. 343.1296, calcd for C$_{18}$H$_{19}$N$_2$O$_5$ : 343.1294.
General procedure for the One-Pot oxidative dearomative phenol coupling/Michael addition protocol.

Preparation of solution A. An oven dried round bottom flask provided with a magnetic stirrer was charged with 1.0 equivalents of [bis(trifluoroacetoxy)iodo]benzene, and purged with N₂. Then, freshly distilled 2,2,2-trifluoroethanol was injected (1 mL/0.09 mmol) and a colorless solution formed.

Preparation of solution B. An oven dried conical flask was charged with 1.0 equivalents of Ugi adduct 8, and purged with N₂. Then, freshly distilled 2,2,2-trifluoroethanol was injected (1 mL/0.05 mmol) and a pale yellow solution formed. In some cases, sonication and/or heating was needed for complete dissolution of the material. Both solutions were placed in a -25°C bath (o-xylene/dry ice) for 20 min, and then the solution B was transferred to solution A via cannula over 30 seconds approximately, with constant magnetic stirring and under N₂. The reaction solution was let reacting for 40 seconds, and the volatiles were readily removed with no delay under reduced pressure and without heating. The crude spyrodienone intermediate was redissolved in acetonitrile (1 mL/0.035 mmol) and 4.0 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene were added, and the reaction was stirred at room temperature until the complete consumption of the intermediate as judged by TLC. Finally, the reaction was concentrated in vacuo and flash chromatography (SiO₂, EtOAc/Hexanes) furnished the plicamines.

Plicamine 9a, white solid (m. p.: 107-108°C), 56% yield from Ugi adduct 8a. ¹H NMR (300 MHz, CDCl₃) diasteromeric mixture, d.r.= 1.5*: 1.0°. δ 7.18° (d, J = 8.5 Hz, 2H), 7.10° (d, J = 8.4 Hz, 2H), 6.85° (d, J = 8.6 Hz, 2H), 6.78° (d, J = 8.6 Hz, 2H), 6.58° (s, 1H), 6.57° (dd, J = 10.3 Hz, 1H), 6.56° (s, 1H), 6.41° (s, 1H), 6.41° (s, 1H), 6.14° (d, J = 10.2 Hz, 1H), 5.97° (s, 2H), 5.95° (s, 2H), 5.93° (s, 1H), 5.61° (d, J = 10.2 Hz, 1H), 5.25° (d, J = 17.2 Hz, 1H), 4.91° (s, 1H), 4.60° (d, J = 16.1 Hz, 1H), 4.50° (d, J = 16.1 Hz, 1H), 4.16° (s, 2H), 3.85° (s, 2H), 3.81° (m, 2H), 3.78° (s, 2H), 3.77° (s, 3H), 2.97° (m, 2H), 2.78° (dd, J = 15.7, 12.3 Hz, 1H), 2.43° (dd, J = 15.9, 12.3 Hz, 1H), 1.24° (s, 9H), 1.24° (s, 9H). ¹³C NMR (75 MHz, CDCl₃). δ 196.46, 195.78, 171.68, 171.66, 168.33, 167.89, 159.16, 158.65, 150.00, 148.85, 147.87, 147.79, 147.76, 147.49, 130.08, 129.77, 129.74, 129.63, 128.63, 127.74, 127.30, 127.23, 126.78, 126.70, 126.49, 126.24, 114.73, 114.40, 114.38, 114.36, 107.12, 106.50, 106.39, 105.81, 101.70, 101.59, 62.09, 61.75, 61.49, 57.33, 55.64, 55.48, 55.44, 55.38, 45.14, 45.08, 44.98, 44.41, 44.05, 41.37, 41.26, 40.37, 27.93, 27.90. HRMS-FAB+ (M+1) m/z: found. 503.2184, calcd for C₂₉H₃₁N₂O₆: 503.2182.
Plicamine 9b, white solid (m. p.: 96-98°C), 58% yield from Ugi adduct 8b. 
1H NMR (300 MHz, CDCl₃) diasteromeric mixture, d.r. = 1.7*: 1.0°. δ 7.28 - 7.01° (m, 14H), 6.85° (d, J = 8.4 Hz, 2H), 6.79° (d, J = 8.4 Hz, 2H), 6.73° (s, 1H), 6.72° (s, 1H), 6.62° (s, 1H), 6.53° (d, J = 10.2 Hz, 1H), 6.45° (s, 1H), 6.24° (s, 1H), 6.10° (m, 2H), 5.91° (s, 2H), 5.90° (s, 2H), 5.64° (d, J = 10 Hz, 1H), 5.34° (d, J = 17.4 Hz, 1H), 5.00° (s, 1H), 4.92° (d, J = 14.0 Hz, 1H), 4.87° (d, J = 14.0 Hz, 1H), 4.67° (d, J = 16.7 Hz, 1H), 4.60° (d, J = 16.7 Hz, 1H), 4.19° (d, J = 17.5 Hz, 1H), 3.96-3.65° (m, 6H), 3.88° (s, 2H), 3.77° (s, 3H), 3.76° (s, 3H), 2.81° (m, 2H), 2.60° (d, J = 15.3, 12.4 Hz, 1H), 2.30° (m, 1H). 13C NMR (75 MHz, CDCl₃) δ 195.89, 195.20, 171.66, 171.48, 168.28, 167.90, 159.24, 158.76, 148.88, 147.95, 147.79, 147.65, 147.38, 134.96, 134.58, 129.75, 129.67, 129.17, 128.76, 128.70, 128.36, 128.30, 128.15, 128.05, 127.91, 127.74, 127.65, 127.28, 127.19, 126.78, 126.61, 126.13, 125.43, 114.78, 114.45, 107.69, 106.97, 106.38, 105.55, 105.54, 101.64, 61.29, 60.57, 56.39, 55.40, 45.15, 45.07, 45.01, 44.84, 41.58, 41.30, 41.10, 40.44. HRMS-FAB+ (M+1) m/z: found. 537.2028, calcd for C32H29N2O6: 537.2026.

Plicamine 9c, pale yellow semisolid, 43% yield from Ugi adduct 8c. 1H NMR (300 MHz, CDCl₃) diasteromeric mixture d.r. = 1.6*: 1.0°. δ 7.19° (dt, J = 8.8, 3.0, 2.0 Hz, 2H), 7.11° (d, J = 8.5 Hz, 2H), 6.85° (dt, J = 8.7, 3.0, 2.0 Hz, 2H), 6.79° (dt, J = 8.7, 3.0, 2.0 Hz, 2H), 6.56° (s, 1H), 6.54° (d, J = 10.3 Hz, 1H), 6.54° (s, 1H), 6.43° (s, 1H), 6.40° (s, 1H), 6.14° (d, J = 10.2 Hz, 3H), 6.01° (s, 1H), 5.95° (d, J = 10 Hz, 1H), 5.94° (dd, J = 7.2, 1.3 Hz, 2H), 5.93° (dd, J = 9.2, 1.2 Hz, 2H), 5.63° (d, J = 10.2 Hz, 1H), 5.26° (d, J = 17.4 Hz, 1H), 4.98° (s, 1H), 4.60° (d, J = 16.3 Hz, 1H), 4.50° (d, J = 16.3 Hz, 1H), 4.14° (d, J = 17.4 Hz, 1H), 4.21 - 3.97° (m, 2H), 3.86° (s, 2H), 3.77° (s, 3H), 3.77° (s, 3H), 3.77° (m, 4H) 2.96° (m, 2H), 2.75° (dd, J = 15.7, 12.2 Hz, 1H), 2.42° (dd, J = 15.9, 12.1 Hz, 1H), 1.86 - 1.53° (m, 8H), 1.34 - 1.13° (m, 8H), 1.06 (m, 4H). 13C NMR (75 MHz, CDCl₃) δ 196.46, 195.78, 171.65, 171.57, 167.89, 167.41, 159.22, 158.70, 149.60, 148.46, 147.91, 147.81, 147.72, 147.46, 129.70, 129.64, 128.50, 127.67, 127.24, 127.03, 126.70, 126.62, 126.54, 126.17, 114.76, 114.42, 107.34, 106.61, 106.54, 105.82, 101.68, 101.58, 61.04, 60.65, 60.01, 56.57, 55.42, 55.37, 52.74, 52.62, 45.53, 45.40, 45.10, 44.19, 43.77, 41.47, 41.28, 40.44, 32.23, 29.73, 25.79, 25.43, 25.36. HRMS-FAB+ (M+1) m/z: found. 529.2343, calcd for C31H33N2O6: 529.2339.

Plicamine 9d, white solid (m. p.: 104-105°C), 50% yield from Ugi adduct 8d. 1H NMR (300 MHz, CDCl₃) diasteromeric mixture, d.r. = 1.5*: 1.0°. δ 7.25° (d, J = 8.8 Hz, 1H), 7.19° (dt, J = 8.3, 3.0, 2.0 Hz, 2H), 7.11° (d, J = 8.3 Hz, 1H), 6.90° (dt, J = 8.8, 3.0, 2.0 Hz, 1H), 6.84° (d, J = 8.3, 3.0, 2.0 Hz, 2H), 6.79° (d, J = 8.7 Hz, 1H), 6.57° (s, 1H), 6.56° (s, 1H), 6.55° (d, J = 10.4 Hz, 1H), 6.45° (s, 1H), 6.41° (s, 1H), 6.40° (d, J = 10.4 Hz, 1H), 6.15° (d, J = 10.2 Hz, 3H), 6.01° (d, J = 0.7 Hz, 1H), 5.94° (m, 4H), 5.82° (d, J = 11.0
Hz, 1H), 5.64° (d, J = 10.3 Hz, 1H), 5.26° (d, J = 17.4 Hz, 1H), 4.98° (s, 1H), 4.60° (d, J = 16.4 Hz, 1H), 4.51° (d, J = 16.4 Hz, 1H), 4.10° (d, m, 4H), 3.87° (d, J = 16.0, 1H), 3.86° (s, 2H), 3.77° (s, 3H), 3.77° (d, J = 16.0, 1H), 2.95° (m, 2H), 2.79° (dd, J = 15.7, 12.1 Hz, 1H), 2.44° (dd, J = 15.9, 12.1 Hz, 2H), 2.22° (dd, J = 16.5, 11.4 Hz, 1H), 1.13° (d, J = 6.8 Hz, 3H), 1.12° (d, J = 7.0 Hz, 3H), 0.81° (d, J = 6.8 Hz, 3H), 0.80° (d, J = 6.8 Hz, 3H). ¹³C NMR (75 MHz, CDCl₃). δ 196.33, 195.65, 176.65, 171.62, 171.51, 167.86, 167.39, 165.72, 159.20, 158.98, 158.69, 149.56, 148.58, 148.42, 147.92, 147.82, 147.73, 147.47, 129.99, 129.71, 129.63, 128.72, 128.41, 128.25, 127.67, 127.24, 126.94, 126.69, 126.56, 126.17, 125.77, 121.14, 114.74, 114.59, 114.40, 108.84, 107.95, 107.34, 106.61, 106.53, 105.80, 101.67, 101.57, 101.48, 61.05, 59.57, 56.59, 55.41, 55.35, 45.29, 45.06, 44.67, 44.52, 44.07, 43.64, 41.46, 41.25, 40.40, 21.75, 21.66, 21.56, 19.35, 19.28. HRMS-FAB+ (M+1) m/z: found. 489.2031, calcd for C₂₈H₂₉N₂O₆: 489.2026.

Plicamine ⁹e, white solid, (m. p.: 103-105°C) 58% yield from Ugi adduct ⁸e. ¹H NMR (300 MHz, CDCl₃) diasteromeric mixture d.r. = 1.7°: 1.0°. δ 7.17° (d, J = 8.7 Hz, 2H), 7.10° (d, J = 8.4 Hz, 2H), 6.84° (dt, J = 8.4, 3.0, 2.0 Hz, 2H), 6.79° (dt, J = 8.4, 3.0, 2.0 Hz, 2H), 6.60° (s, 1H), 6.54° (d, J = 10.2 Hz, 1H), 6.42° (s, 1H), 6.42° (s, 1H), 6.40° (s, 1H), 6.16° (d, J = 10.2 Hz, 1H), 5.94° (s, 5H), 5.89° (d, J = 10.2 Hz, 1H), 5.69° (d, J = 10.2 Hz, 1H), 5.33° (d, J = 17.1 Hz, 1H), 4.89° (s, 1H), 4.61° (d, J = 16.4 Hz, 1H), 4.46° (d, J = 16.2 Hz, 1H), 4.04° (d, J = 16.2 Hz, 1H), 4.00 – 3.88° (m, 5H), 3.87° (s, 2H), 3.77° (d, 3H), 3.77° (m, 3H), 3.04° (ddt, J = 15.8, 5.7, 0.5 Hz, 1H), 2.94° (dd, J = 16.0, 6.0 Hz, 1H), 2.78° (s, 6H), 2.60° (dd, J = 15.5, 12.1 Hz, 1H), 2.60° (dd, J = 15.5, 12.0 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃). δ 195.94, 195.23, 168.18, 167.84, 159.13, 158.66, 149.20, 148.08, 147.90, 147.78, 147.54, 129.71, 129.64, 128.67, 127.72, 127.25, 126.83, 126.62, 126.10, 114.69, 114.36, 107.80, 107.13, 106.77, 105.90, 101.70, 101.61, 64.43, 63.92, 60.50, 56.05, 55.42, 55.36, 45.06, 44.13, 41.26, 41.10, 40.93, 40.35, 40.25, 29.80, 28.46. HRMS-FAB+ (M+1) m/z: found. 461.1715, calcd for C₂₆H₂₅N₂O₆: 461.1713.

Plicamine ⁹f, light gray semisolid, 43% yield from Ugi adduct ⁸f. ¹H NMR (300 MHz, CDCl₃) diasteromeric mixture, d.r. = 3°:1°, δ 6.76° (d, J = 10.2 Hz, 1H), 6.62° (d, J = 10.2 Hz, 1H), 6.62° (s, 1H), 6.59° (s, 1H), 6.58° (s, 1H), 6.57° (s, 1H), 6.21° (d, J = 10.2 Hz, 1H), 6.14° (d, J = 10.2 Hz, 1H), 5.98° (dd, J = 6.7, 1.3 Hz, 2H), 5.97° (dd, J = 7.5, 1.3 Hz, 2H), 5.90° (s, 1H), 5.26° (d, J = 17.5 Hz, 1H), 4.85° (s, 1H), 4.62° (d, J = 16.2 Hz, 1H), 4.53° (d, J = 16.2 Hz, 1H), 4.30° (dd, J = 12.0, 6.0 Hz, 1H), 4.25° (dd, J = 12.2, 5.7 Hz, 1H), 4.07° (d, J = 17.5 Hz, 1H), 3.07° (dd, J = 5.6 Hz, 1H), 3.01° (dd, J = 16.0, 5.8 Hz, 1H), 2.80° (dd, J = 16.0, 12.2 Hz, 1H), 2.70° (dd, J = 16.0, 12.2 Hz, 1H), 2.27° (s, 3H), 2.19° (s, 3H), 1.26° (s, 9H), 1.25° (s, 9H). ¹³C NMR (75 MHz, CDCl₃) Mezcla de diasterómeros. δ 196.47, 195.95, 170.85, 170.50, 168.33, 167.64, 149.98, 147.90, 147.83, 147.57, 128.73, 128.01, 127.78, 127.63, 127.31, 126.70, 107.19, 106.61, 106.48, 105.87, 101.75, 101.64, 62.85, 62.08, 61.74.
Plicamine 9g, pale yellow solid (m. p.: 123-124°C), 54% yield from Ugi adduct 8g. \(^1\)H NMR (300 MHz, CDCl\(_3\)) diasteromeric mixture, d. r. = 2.6*: 1.0°. \(\delta\) 7.17* (m, 6H), 6.77° (d, \(J = 10.3\) Hz, 1H), 6.74** (m, 4H), 6.63° (s, 1H), 6.59* (s, 1H), 6.59* (d, \(J = 10.3\) Hz, 1H), 6.29* (s, 1H), 6.27° (s, 1H), 6.20° (d, \(J = 10.2\) Hz, 1H), 6.12* (d, \(J = 10.2\) Hz, 13H), 6.02* (s, 1H), 5.93* (s, 2H), 5.36° (d, \(J = 16.4\) Hz, 1H), 4.61* (d, \(J = 16.3\) Hz, 1H), 4.13° (d, \(J = 17.3\) Hz, 1H), 4.10° (d, \(J = 14.2\) Hz, 1H), 3.89* (d, \(J = 15.0\) Hz, 1H) 3.85° (m, 1H) 3.81* (dd, \(J = 12.0, 6.0\) Hz, 1H), 2.89° (dd, \(J = 15.6, 5.9\) Hz, 1H), 2.62° (dd, \(J = 15.6, 12.3\) Hz, 1H), 2.59° (dd, \(J = 12.3\) Hz, 1H), 2.31° (s, 1H), 2.25° (s, 1H), 1.96–1.52° (m, 8H), 1.46–0.79° (m, 12H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)). \(\delta\) 195.87, 195.29, 170.72, 170.32, 168.27, 167.74, 148.80, 148.56, 148.02, 147.68, 147.43, 134.95, 134.57, 128.76, 128.65, 128.40, 128.14, 128.04, 127.86, 127.62, 126.84, 126.59, 107.75, 107.16, 106.35, 105.55, 101.65, 101.55, 61.86, 61.20, 60.79, 56.09, 45.40, 44.96, 44.77, 41.19, 41.02, 40.53, 21.81, 21.55. HRMS-FAB+ (M+1) m/z: found. 431.1593, calcd for C\(_{22}\)H\(_{25}\)N\(_2\)O\(_5\): 431.1607.

Plicamine 9h, white semisolid, 47% yield from Ugi adduct 8h. \(^1\)H NMR (300 MHz, CDCl\(_3\)) diasteromeric mixture, d.r. = 2.6*: 1.0°. \(\delta\) 6.74° (d, \(J = 10.2\) Hz, 1H), 6.60° (d, \(J = 10.3\) Hz, 1H), 6.57° (s, 1H), 6.54° (s, 2H), 6.22° (d, \(J = 10.2\) Hz, 1H), 6.15° (d, \(J = 10.2\) Hz, 1H), 5.97° (d, \(J = 16.9\) Hz, 1H), 4.65° (d, \(J = 16.9\) Hz, 1H), 4.55° (d, \(J = 16.3\) Hz, 9H), 4.19° (d, \(J = 12.0\), 6.0 Hz, 1H), 4.14° (d, \(J = 12.0\), 6.0 Hz, 1H), 4.10° (d, \(J = 17.0\) Hz, 1H), 3.87–3.67°* (m, 2H), 3.06° (ddd, \(J = 5.9, 0.7\) Hz, 1H), 3.0° (ddd, \(J = 15.8, 6.0\), 0.7 Hz, 1H), 2.76° (dd, \(J = 15.8, 12.1\) Hz, 1H), 2.68° (dd, \(J = 16.0, 12.0\) Hz, 1H), 2.29° (d, \(J = 3.86\), 1H), 2.21° (s, 3H), 1.96–1.52°* (m, 8H), 1.46–0.79°* (m, 12H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)). \(\delta\) 196.52, 195.99, 195.29, 170.80, 170.45, 167.90, 167.18, 149.57, 149.41, 147.89, 147.76, 147.51, 128.57, 128.14, 128.04, 127.86, 127.62, 126.84, 126.59, 107.75, 107.16, 106.35, 105.55, 101.65, 101.55, 61.86, 61.20, 60.79, 56.09, 45.40, 44.96, 44.77, 41.19, 41.02, 40.53, 21.81, 21.55. HRMS-FAB+ (M+1) m/z: found. 423.1921, calcd for C\(_{24}\)H\(_{27}\)N\(_2\)O\(_5\): 423.1920.

Plicamine 9i, white solid (m. p.: 80-82°C), 44% yield from Ugi adduct 8i. \(^1\)H NMR (300 MHz, CDCl\(_3\)) diasteromeric mixture, d.r. = 3.2*: 1.0°. \(\delta\) 6.75° (d, \(J = 10.2\) Hz, 1H), 6.61* (d, \(J = 10.3\) Hz, 1H), 6.60* (s, 1H), 6.58° (s, 1H), 6.56° (s, 1H), 6.54* (s, 1H), 6.23* (d, \(J = 10.2\) Hz, 1H), 6.16° (d, \(J = 10.2\) Hz, 1H), 5.97*° (m, 5H), 5.30° (d, \(J = 17.4\) Hz, 1H), 4.88° (s, 1H), 4.65° (d, \(J = 16.3\) Hz, 3H), 4.55° (d, \(J = 16.3\) Hz, 3H), 4.26–4.05°* (m, 5H), 3.06° (ddd, 6.0, 0.7 Hz, 1H), 3.0° (ddd, 15.7, 6.7, 0.8 Hz, 1H).
Hz, 1H), 2.78° (dd, 15.7, 12.1 Hz, 1H), 2.69° (dd, 16.0, 12.1 Hz, 1H), 2.28° (d, 3H), 2.19° (d, 3H), 1.16° (d, J = 6.7 Hz, 3H), 0.85° (d, J = 7.0 Hz, 3H), 0.82° (d, J = 7.0 Hz, 3H). ^13^C NMR (75 MHz, CDCl_3) Mezcla diasteromérica. δ 196.42, 195.87, 170.80, 170.42, 167.90, 167.18, 149.55, 149.40, 147.94, 147.81, 128.50, 128.07, 127.74, 127.53, 126.97, 126.61, 107.43, 106.82, 106.51, 105.88, 101.75, 101.15, 62.10, 60.18, 59.87, 56.31, 45.36, 45.28, 44.81, 44.51, 44.08, 43.92, 41.13, 29.83, 21.89, 21.70, 21.56, 19.32. HRMS-FAB+ (M+1) m/z: found. 383.1612, calcd for C_{21}H_{23}N_2O_5: 383.1607.

Plicamine 9j, white solid (m. p.: 104-106°C), 40% yield from Ugi adduct 8j. ^1^H NMR (300 MHz, CDCl_3) diasteromérico mixture d.r. = 3.3°: 1.0°. δ 6.73° (d, J = 10.2 Hz, 1H), 6.59 (d, J = 10.2 Hz, 1H), 6.59° (s, 1H), 6.58° (s, 1H), 6.55° (s, 1H), 6.54° (s, 1H), 6.20° (d, J = 10.2 Hz, 1H), 6.13° (d, J = 10.2 Hz, 1H), 5.95° (m, 4H), 5.91° (s, 1H), 5.82° (dd, J = 10.7, 0.4 Hz, 1H), 5.26° (d, J = 17.3 Hz, 1H), 4.87° (s, 2H), 4.56° (s, 2H), 4.27° (dd, J = 11.8, 5.7 Hz, 1H), 4.22° (dd, J = 12.2, 5.7 Hz, 1H), 4.05° (d, J = 17.4 Hz, 2H), 3.05° (dd, J = 16.0, 0.5 Hz, 1H), 2.99° (dd, J = 16.0, 0.5 Hz, 1H), 2.77° (d, J = 15.8, 12.2 Hz, 1H), 2.67° (dd, J = 16.1, 12.2 Hz, 1H), 2.48° (m, 4H), 1.65° (m, 4H), 1.38° (m, 4H), 1.24° (d, J = 10.2 Hz, 1H). ^13^C NMR (75 MHz, CDCl_3) δ 196.45, 195.97, 173.52, 173.05, 168.48, 167.75, 150.10, 149.40, 147.87, 147.80, 147.52, 128.90, 128.23, 127.90, 127.69, 127.42, 126.94, 107.21, 106.60, 106.52, 105.86, 101.71, 101.59, 62.08, 61.97, 61.74, 57.15, 55.45, 45.06, 44.66, 44.42, 41.14, 33.47, 32.84, 28.07, 27.93, 27.36, 27.23, 22.58, 13.99. HRMS-FAB+ (M+1) m/z: found. 439.2235, calcd for C_{25}H_{31}N_2O_5: 439.2233.

Plicamine 9k, pale yellow solid (m. p.: 175-176°C), 57% yield from Ugi adduct 8k. ^1^H NMR (300 MHz, CDCl_3) diasteromérico mixture d.r. = 3.0°: 1.0° = 2.9°: 1.0°. δ 7.20° (m, 4H), δ 6.71° (m, 4H), 6.61° (s, 1H), 6.61° (s, 1H), 6.56° (d, J = 10.2 Hz, 1H), 6.40° (d, J = 10.4 Hz, 2H), 6.27° (s, 1H), 6.25° (s, 1H), 6.20° (d, J = 10.1 Hz, 1H), 6.11° (d, J = 10.2 Hz, 1H), 6.04° (s, 1H), 5.95° (m, 4H), 4.97° (s, 1H), 4.88° (d, J = 15.2 Hz, 1H), 4.67° (s, 2H), 4.36° (d, J = 5.7 Hz, 1H), 4.26° (d, J = 5.7 Hz, 1H), 3.89° (d, J = 15.0 Hz, 1H), 3.81° (m, 2H), 3.85 – 3.74 (m, 19H), 2.84° (dd, J = 15.4, 5.7 Hz, 1H), 2.84° (dd, J = 15.4, 5.7 Hz, 1H), 2.55° (m, 6H), 1.67° (m, 4H), 1.40 (m, 4H), 0.93 (m, 6H). ^13^C NMR (75 MHz, CDCl_3) δ 196.01, 195.44, 173.59, 168.45, 148.94, 148.78, 148.00, 147.66, 134.90, 128.68, 128.42, 128.30, 128.07, 127.89, 127.60, 127.54, 127.39, 126.70, 108.19, 107.76, 105.75, 101.66, 101.10, 61.22, 56.17, 45.06, 44.96, 44.73, 44.44, 41.27, 41.01, 33.49, 32.96, 29.81, 27.33, 27.20, 22.55, 14.01. HRMS-FAB+ (M+1) m/z: found. 473.2077, calcd for C_{28}H_{29}N_2O_5: 473.2073.
Plicamine 9l, white solid (m. p.: 103-105°C), 39% yield from Ugi adduct 8l. $^1$H NMR (300 MHz, CDCl$_3$) diasteromeric mixture d.r. = 3.0*/: 1.0°. δ 6.72° (d, $J$ = 10.2, 1H), 6.59* (d, $J$ = 10.2 Hz, 1H), 6.58* (s, 1H), 6.57° (s, 1H), 6.54* (s, 1H), 6.53° (s, 1H), 6.22° (d, $J$ = 10.2 Hz, 1H), 6.15* (d, $J$ = 10.2 Hz, 1H), 5.97°,* (m, 5H), 5.89° (d, $J$ = 10.7 Hz, 1H), 5.30° (d, $J$ = 17.2 Hz, 1H), 4.95° (s, 1H), 4.59* (s, 2H), 4.35 – 4.01°,* (m, 3H), 3.76°,* (m, 2H), 3.06° (dd, $J$ = 15.8, 5.6 Hz, 1H), 3.06* (ddt, $J$ = 16.0, 5.9, 0.5 Hz, 1H), 2.75° (dd, $J$ = 15.7, 12.2 Hz, 1H), 2.67° (dd, $J$ = 16.0, 12.0 Hz, 1H), 2.51 (m, 4H), 2.02 – 0.70°,* (m, 34H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.59, 196.07, 173.51, 173.01, 168.03, 167.27, 149.73, 148.74, 147.86, 147.31, 128.71, 127.61, 126.81, 107.45, 105.87, 101.71, 101.61, 60.62, 56.37, 52.55, 45.35, 44.69, 44.17, 33.51, 32.20, 29.82, 29.72, 27.23, 25.78, 25.42, 25.35, 22.55, 14.01. HRMS-FAB+ (M+1) m/z: found. 465.2391, calcd for C$_{27}$H$_{33}$N$_2$O$_5$: 465.2389.

Plicamine 9m, white solid (m. p.: 105-106°C), 47% yield from Ugi adduct 8m. $^1$H NMR (300 MHz, CDCl$_3$) diasteromeric mixture d.r. = 2.9°: 1.0°. δ 6.60* (d, $J$ = 10.2, 1H), 6.60* (s, 1H), 6.60° (s, 1H), 6.57° (s, 1H), 6.56° (s, 1H), 6.51° (d, $J$ = 10.4 Hz, 1H), 6.21° (d, $J$ = 10.2 Hz, 1H), 6.14° (d, $J$ = 10.2 Hz, 3H), 5.98°,* (m, 2H), 5.92° (s, 3H), 5.28° (d, $J$ = 17.3 Hz, 1H), 4.89° (s, 1H), 4.60° (s, 1H), 4.28° (dd, $J$ = 12.4, 5.8 Hz, 1H), 4.23° (dd, $J$ = 12.2, 5.6 Hz, 1H), 4.06° (d, $J$ = 17.4 Hz, 1H), 3.07° (dd, $J$ = 15.8, 5.7 Hz, 1H), 3.0° (dd, $J$ = 15.8, 5.7 Hz, 1H), 2.79° (dd, $J$ = 15.7, 12.2 Hz, 1H), 2.68° (dd, $J$ = 16.0, 12.3 Hz, 1H), 2.50°,* (m, 24H), 1.90 – 1.48° (m, 22H), 1.25° (d, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.45, 195.95, 173.60, 173.15, 168.47, 167.72, 150.11, 149.39, 147.87, 147.79, 147.51, 128.91, 128.22, 127.87, 127.68, 126.94, 107.22, 106.59, 106.51, 105.85, 101.70, 101.59, 62.07, 61.73, 57.13, 55.68, 55.43, 45.07, 44.66, 44.42, 41.13, 39.94, 39.77, 33.08, 32.65, 32.40, 31.52, 31.32, 28.07, 27.92, 25.24. HRMS-FAB+ (M+1) m/z: found. 479.2540, calcd for C$_{28}$H$_{35}$N$_2$O$_5$: 479.2546.

Plicamine 9n, pale yellow semisolid, 53% yield from Ugi adduct 8n. $^1$H NMR (300 MHz, CDCl$_3$) diasteromeric mixture d.r. = 3.1 : 1.0. δ 7.11°,* (m, 6H), 6.72°,* (m, 4H), 6.60° (s, 1H), 6.58° (d, $J$ = 10.2 Hz, 1H), 6.28° (s, 1H), 6.25° (s, 1H), 6.21° (d, $J$ = 10.2 Hz, 1H), 6.12° (d, $J$ = 10.2 Hz, 1H), 6.05° (s, 1H), 5.94°,* (m, 4H), 5.37° (d, $J$ = 17.2 Hz, 1H), 4.95° (d, $J$ = 15.0 Hz, 1H), 4.90° (d, $J$ = 15.1 Hz, 1H), 4.71° (d, $J$ = 16.1 Hz, 1H), 4.64° (d, $J$ = 16.1 Hz, 1H), 4.13° (d, $J$ = 17.3 Hz, 5H), 3.84°,* (m, 4H), 2.91° (dd, $J$ = 15.7 Hz, 6.0, 0.6, 1H), 2.61° (dd, $J$ = 16.0, 12.0 Hz, 1H), 2.54°,* (m, 5H), 1.93 – 1.38°,* (m, 14H), 1.14°,* (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 196.02, 195.44, 173.66, 173.10, 168.46, 167.82, 148.99, 148.84, 148.01, 147.67, 134.94, 129.07, 128.69, 128.48,
Plicamine 9o, pale yellow solid (m. p.: 98-100°C), 40% yield from Ugi adduct 8o.  

\(^1\)H NMR (300 MHz, CDCl\(_3\)) diasteromeric mixture d.r. = 2.9*: 1.0°. \(\delta\) 6.59* (d, \(J = 10.1\) Hz, 1H), 6.58* (s, 1H), 6.55* (s, 1H), 6.54° (s, 1H), 6.22° (d, \(J = 10.2\) Hz, 5H), 6.15* (d, \(J = 10.2\) Hz, 13H), 5.97* (m, 2H), 5.94° (m, 2H), 5.30° (d, \(J = 17.2\) Hz, 1H), 4.95° (s, 1H), 4.60° (s, 5H), 4.58° (s, 5H), 4.56° (s, 4H), 4.51° (d, \(J = 16.6\) Hz, 1H), 4.26° (d, \(J = 10.2\) Hz, 1H), 3.99° (m, 2H), 3.76° (m, 2H), 3.61° (m, 2H), 2.70° (d, \(J = 16.2\) Hz, 1H), 1.23° (d, \(J = 6.2\) Hz, 1H).  

\(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 196.59, 196.07, 173.61, 173.12, 168.04, 167.27, 149.74, 148.73, 1478.66, 147.73, 128.71, 128.44, 127.89, 127.61, 127.11, 126.81, 120.75, 108.90, 108.26, 107.45, 106.78, 106.55, 105.87, 101.71, 101.60, 101.11, 61.18, 60.61, 60.22, 56.36, 52.77, 52.54, 45.61, 45.36, 44.70, 44.17, 41.17, 39.90, 39.75, 33.99, 33.12, 32.65, 32.20, 31.48, 31.32, 29.81, 29.71, 25.78, 25.24, 25.00.  

HRMS-FAB+ (M+1) m/z: found. 513.2393, calcd for C\(_{31}\)H\(_{33}\)N\(_2\)O\(_5\): 513.2389.

Plicamine 9p, white solid (m. p.: 148-150°C), 71% yield from Ugi adduct 8p.  

\(^1\)H NMR (300 MHz, CDCl\(_3\)) diasteromeric mixture d.r. = 1.0°: 1.0°. \(\delta\) 8.43° (s, 1H), 8.17° (s, 1H), 6.69° (d, \(J = 10.2\) Hz, 1H), 6.59° (m, 5H), 6.20° (d, \(J = 10.2\) Hz, 1H), 6.2° (d, \(J = 10.2\) Hz, 1H), 5.98° (m, 4H), 5.61° (s, 1H), 5.1° (d, \(J = 17.2\) Hz, 1H), 4.58° (d, \(J = 16.5\) Hz, 1H), 4.38° (d, \(J = 16.5\) Hz, 1H), 4.33° (m, 2H), 4.11° (d, \(J = 17.2\) Hz, 2H), 3.05° (dd, \(J = 16.2, 6.2, 0.6\) Hz, 1H), 3.05° (dd, \(J = 16.2, 6.2, 0.6\) Hz, 1H), 2.75° (d, \(J = 15.7\) Hz, 1H), 2.7° (d, \(J = 16.0, 12.2\) Hz, 1H) 1.27 (d, 9H). \(^13\)C NMR (75 MHz, CDCl\(_3\)) δ 196.11, 195.77, 167.57, 167.48, 162.08, 149.49, 149.41, 148.12, 147.98, 147.88, 128.85, 128.16, 127.75, 126.50, 126.39, 107.50, 106.89, 106.40, 105.77, 101.78, 101.74, 77.58, 77.16, 76.74, 62.53, 62.19, 61.70, 56.21, 44.89, 44.60, 44.53, 44.45, 29.80, 27.91, 27.87. HRMS-FAB+ (M+1) m/z: found. 383.1606, calcd for C\(_{21}\)H\(_{23}\)N\(_2\)O\(_5\): 383.1607.

Plicamine 9q, white amorphous semisolid, 63% yield from Ugi adduct 8q.  

\(^1\)H NMR (300 MHz, CDCl\(_3\)) diasteromeric mixture d.r. = 1.4°: 1.0°. \(\delta\) 8.44° (s, 1H), 8.2° (s, 1H), 6.66° (d, \(J = 10.3\) Hz, 1H), 6.61 – 6.54° (m, 5H), 6.23° (d, \(J = 10.2\) Hz, 1H), 6.18° (d, \(J = 10.2\) Hz, 1H), 5.97° (s, 2H), 5.96° (s, 2H), 5.61° (s, 1H), 5.15° (d, \(J = 17.0\) Hz, 1H), 4.56° (d, \(J = 16.1\) Hz, 1H), 4.55° (s, 1H), 4.41° (d, \(J = 16.1\) Hz, 1H), 4.06° (m, 2H), 4.03° (d, \(J = 17.0\) Hz, 1H).
3.08° (m, 2H), 2.83° (s, 3H), 2.82° (s, 3H), 2.55° (m, 2H). 13C NMR (75 MHz, CDCl3) δ 195.61, 195.22, 167.39, 162.09, 161.85, 148.63, 148.39, 148.18, 148.06, 147.90, 128.80, 128.40, 127.87, 127.62, 126.43, 108.17, 107.63, 106.64, 105.92, 101.83, 101.78, 64.50, 64.11, 61.20, 54.84, 44.70, 43.99, 43.90, 41.03, 40.74, 39.78, 29.80, 28.69, 28.60. HRMS-FAB+ (M+1) m/z: found. 341.1141, calcd for C18H17N2O5: 341.1137.

Luche Reduction and Methylation procedure

A 25 mL round bottom flash with a magnetic stirrer was charged with diastereoisomeric enones 9q (50.5 mg, 0.1488 mmol, 1.0 equiv.) and dissolved with 7.5 mL of methanol. Then cerium trichloride heptahydrate (560.0 mg, 1.4881 mmol, 10.0 equiv.) was added and the resultant solution was placed in a in a -25°C bath (o-xylene/dry ice) for 10 min. Then, sodium borohydride (28.7 mg, 0.7440 mmol, 5.0 equiv.) was added in one operation. The reduction was finished in 15 minutes as judged by TLC. The reaction was quenched with saturated aqueous NH4Cl and extracted twice with CH2Cl2. The organic extracts were dried over anhydrous Na2SO4, and concentrated in vacuo. The crude alcohols were redisolved in 5 mL of freshly distilled THF, and this solution was placed in an ice/water bath at 0 °C for 10 min. Then sodium hydride (29.8 mg, 60% suspension, 0.7440 mmol, 5.0 equiv.) was added in a fast operation and the reaction was stirred over 20 min. Then iodomethane (0.094 mL, 1.4881 mmol, 10 equiv.) was slowly added and the reaction flask was removed from the ice bath after the addition, and let warm to room temperature for 2 hours until the reaction was finished as judged by TLC.

The reaction mixture was treated with 10 mL of H2O and extracted twice with 10 mL of EtOAc. The organic extracts were dried over anhydrous Na2SO4 and concentrated in vacuo. Flash column chromatography (SiO2, EtOAc/Hexanes) furnished 32.0 mg (60.3% yield overall) the endo ethers 11K as a 1.6 :1.0 diastereomeric mixture.
**Compound 11.** $^1$H NMR (300 MHz, CDCl$_3$) diastereomeric mixture d.r. = 1.6*: 1.0°. δ 8.41° (s, 1H), 8.14* (s, 1H), 6.70 – 6.34 (m, 4H), 6.04* (d, $J = 10.1$ Hz, 1H), 5.99° (d, $J = 10.2$ Hz, 1H), 5.96 – 5.90*° (m, 4H), 5.65* (dd, $J = 10.1$, 2.1 Hz, 1H), 5.60° (dd, $J = 10.2$, 2.2 Hz, 1H), 5.41* (s, 1H), 5.09° (d, $J = 16.9$ Hz, 1H), 4.47° (d, $J = 16.2$ Hz, 1H), 4.33° (d, $J = 16.2$ Hz, 1H), 4.32° (s, 1H), 4.14*.° (m, 2H), 4.00* (d, $J = 16.9$ Hz, 1H), 3.72* (dd, $J = 12.7$, 4.6 Hz, 1H), 3.68* (dd, $J = 12.7$, 4.6 Hz, 1H), 3.41° (d, 3H), 2.82* (s, 3H), 2.64*° (m, 2H), 1.47° (m, 2H). 13C NMR (75 MHz, CDCl$_3$) δ 167.81, 161.99, 147.52, 131.08, 130.75, 130.07, 129.68, 129.57, 126.35, 126.26, 108.12, 107.58, 106.07, 105.42, 101.50, 74.39, 64.72, 64.25, 62.47, 56.47, 56.15, 56.02, 44.78, 44.43, 44.12, 39.65, 32.25, 28.60, 28.49. HRMS-FAB+ (M+1) m/z: found. 357.1453, calcd for C$_{19}$H$_{21}$N$_2$O$_5$: 357.1450.

**Formamide hydrolysis**

The formamide 11 (22.2mg) was dissolved in 3 mL of 20% (v/v) methanolic NaOH in a sealed vessel and was reacted for 60 minutes at 70 °C under microwave assistance. The reaction then was diluted with 15 mL of H$_2$O and extracted with CH$_2$Cl$_2$ twice. The organic extracts were dried over anhydrous Na$_2$SO$_4$, filtrated and evaporated in vacuo. The crude product was chromatographed to obtain 13.6 mg of 12 as the only diasteromer.

**Compound 12.** $^1$H NMR (300 MHz, CDCl$_3$) Only diasteromer. δ 6.53 (s, 1H), 6.46 (s, 1H), 5.98 (dt, $J = 10.1$, 1.4 Hz 1H), 5.90 (s, 2H), 5.84 (dd, $J = 10.1$, 2.0 Hz, 1H), 4.10 (m, 1H), 3.97 (d, $J = 15.2$ Hz, 1H), 3.75 (s, 1H), 3.68 (d, $J = 15.2$ Hz, 1H), 3.60 (dd, $J = 12.1$, 4.6 Hz, 1H), 3.46 (s, 3H), 2.81 (s, 3H), 2.56 (ddt, $J = 12.0$, 4.6, 1.2 Hz, 1H), 1.41 (dt, $J = 12.0$, 10.4 Hz, 1H). 13C NMR (75 MHz, CDCl$_3$) δ171.44, 146.83, 146.60, 132.94, 130.68, 129.73, 128.27, 108.11, 106.20, 101.12, 74.46, 64.52, 62.30, 56.34, 44.16, 43.40, 32.11, 28.16. HRMS-FAB+ (M+1) m/z: observ. 329.1508, calcd: 329.1501.
Spirodienones

Some spiromexadienones were isolated and characterized for the systematic demonstration of their actual existence and role as synthetic intermediates. The next compounds (S1-S3) were obtained from the corresponding Ugi adducts as described in the first part of the experimental procedure for the synthesis of the plicamines; subjecting the crude to a fast flash chromatographical isolation as the spirodienones were prone to a dienone-phenol fragmentation.

**Spirodienone S1**, quantitative yield from Ugi adduct 15a. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.26 (dd, $J = 10.2$, 3.1 Hz, 1H), 7.19 (dt, $J = 8.6$, 3.0, 2.0 Hz, 2H), 6.88 (dt, $J = 8.6$, 3.0, 2.0 Hz, 2H), 6.64 (dd, $J = 10.1$, 3.0 Hz, 1H), 6.56 (dd, $J = 10.3$, 1.9 Hz, 1H), 6.52 (s, 1H), 6.47 (s, 1H), 6.11 (dd, $J = 10.0$, 1.8 Hz, 1H), 5.91 (m, 2H), 5.07 (s, 1H), 4.86 (d, $J = 15.7$ Hz, 1H), 4.55 (d, $J = 16.0$ Hz, 1H), 5.91 (m, 2H), 5.07 (s, 1H), 4.86 (d, $J = 15.7$ Hz, 1H), 4.55 (d, $J = 16.0$ Hz, 1H), 4.86 (d, $J = 15.7$ Hz, 1H), 4.55 (d, $J = 16.0$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 185.22, 172.21, 166.15, 159.02, 153.7, 148.80, 147.80, 147.52, 132.19, 129.74, 126.40, 125.55, 124.45, 123.58, 114.64, 106.57, 106.32, 101.55, 57.03, 55.45, 51.85, 46.04, 45.50, 40.79, 28.63. HRMS-FAB+ (M+1) m/z: found. 503.2186, calcd for C$_{29}$H$_{31}$N$_2$O$_6$: 503.2182.

**Spirodienone S2**, 97% yield from Ugi adduct 15c. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.23 (dd, $J = 10.3$, 3.0 Hz, 1H), 7.18 (d, $J = 8.6$ Hz, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 6.64 (dd, $J = 10.3$, 3.0 Hz, 1H), 6.54 (dd, $J = 10.3$, 2.0 Hz, 1H), 6.53 (s, 1H), 6.47 (s, 1H), 6.11 (dd, $J = 10.1$, 1.8 Hz, 1H), 5.96 – 5.82 (m, 2H), 5.14 (s, 1H), 4.84 (d, $J = 16.0$, 1H), 4.63 (d, $J = 16.0$, 1H), 3.84 (s, 1H), 3.79 (s, 3H), 3.57 (m, 1H) 1.33 (m, 10H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 188.98, 185.16, 172.27, 166.10, 159.02, 153.71, 148.86, 147.80, 147.48, 132.19, 129.84, 126.57, 125.53, 124.61, 123.68, 114.60, 106.59, 106.32, 101.55, 77.58, 77.37, 77.16, 76.74, 55.41, 48.54, 46.10, 45.54, 40.72, 32.76, 25.48, 24.79. HRMS-FAB+ (M+1) m/z: found. 529.3342, calcd for C$_{31}$H$_{33}$N$_2$O$_6$: 529.3339.

**Spirodienone S3**, quantitative yield from Ugi adduct 15p. $^1$H NMR (30 MHz, CDCl$_3$) $\delta$ 8.41 (s, 1H), 8.23 (s, 1H), 7.16 (dd, $J = 10.3$, 2.5 Hz, 1H), 6.82 (dd, $J = 10.5$, 3.0 Hz, 1H), 6.71 (dd, $J = 10.0$, 2.9 Hz, 1H), 6.62 (s, 1H), 6.57 (d, $J = 10.2$ Hz, 1H), 6.47 (s, 1H), 6.14 (d, $J = 10.2$ Hz, 1H), 5.94 (m, 2H), 4.90 (d, $J = 16.0$ Hz, 1H), 4.85 (s, 1H), 4.63 (d, $J = 16.0$ Hz, 1H), 1.52 – 1.09 (m, 9H). HRMS-FAB+ (M+1) m/z: found. 383.1611, calcd for C$_{21}$H$_{23}$N$_2$O$_5$: 383.1607.
NMR Spectroscopy for the Ugi adducts 8
Compound 8a
Compound 8b

[Chemical Structure Image]

[Spectrum Image]
Compound 8c
Compound 8e
Compound 8g
Compound 8h

[Chemical structure image]

[Spectroscopic data]

[S25]
Compound 8i
Compound 8k
Compound 8I

[Chemical structure of Compound 8I]

[Spectroscopic data and analysis]
Compound 8m
Compound 8q
NMR spectroscopy for the spirodienones S1 to S3
Compound S1 COSY
Compound S2
Compound S3
NMR spectroscopy for the Plicamines 9
Compound 9a
Compound 9b COSY
Compound 9b HETCOR
Compound 9c
Compound 9c COSY
Compound 9d
Compound 9e

Chemical structures and spectra are shown for Compound 9e, along with details of the experimental setup and conditions, including the instrument used (Bruker Avance 300 MHz) and the date (27-09-2013).
Compound 9e COSY
Compound 9f COSY
Compound 9f HETCOR

HETCOR H-1^C
Compound 9g COSY

COSY $^1$H-$^1$H
Compound 9g HETCOR

HETCOR $^{13}$C
Compound 9h COSY
Compound 9h HETCOR
Compound 9i

UNAM, INSTITUTO DE QUÍMICA
Dr. Luis D. Miranda / Marco V. Mijangos
Clave: MM-101-036
Disolvente: CDCl3
Carbony-13
15-08-2013
No. Reg. 1213
Compound 9i COSY
Compound 9i HETCOR

HETCOR $^1$H- $^{13}$C
Compound 9k
Compound 9l COSY
Compound 9n

Mira e 1H
U.N.P. 1001-47
Dr. Luis D. Trefny / Mira Y. Hijmans
Cave: MIR-100-47
Experiments: 1H
Bruker Avance 300 MHz
30-08-2013
No. Reg. 1218

1218 Reg. 13
U.N.P. INSTITUTO DE BIOMÉDICA, saq
Dr. Luis D. Trefny / Mira Y. Hijmans
Cave: MIR-100-47
Experiments: 1H
Bruker Avance 75 MHz (F)

S76
Compound 9N HETCOR

HETCOR $^1$H-13C.
Compound 9o
Compound 9o HETCOR
Compound 9p
Compound 9p COSY

COSY H-H
Compound 9p HETCOR
Compound 9q
Compound 9q COSY
Compound 9q NOESY
NMR spectroscopy for the synthetic intermediates 11 and 12
Compound 11 COSY
Compound 11 HETCOR

HETCOR $^1$H-$^{13}$C
Compound 11 NOESY
Compound 12
Crystallographic data for compound 9p
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>087MGL13</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C$<em>{21}$H$</em>{22}$N$_2$O$_5$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>382.41</td>
</tr>
<tr>
<td>Temperature</td>
<td>298(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P-1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>8.4009(4) Å</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>94.7910(10)$^\circ$</td>
</tr>
<tr>
<td>b</td>
<td>10.4848(4) Å</td>
</tr>
<tr>
<td>$\beta$</td>
<td>103.0250(10)$^\circ$</td>
</tr>
<tr>
<td>c</td>
<td>11.8979(5) Å</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>108.5480(10)$^\circ$</td>
</tr>
<tr>
<td>Volume</td>
<td>954.23(7) Å</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.331 Mg/m$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.096 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>404</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.34 x 0.27 x 0.26 mm$^3$</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.78 to 25.29$^\circ$.</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-10$\leq$h$\leq$10, -12$\leq$k$\leq$12, -14$\leq$l$\leq$14</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>8877</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>3449 [R(int) = 0.0388]</td>
</tr>
<tr>
<td>Completeness to theta = 25.29$^\circ$</td>
<td>99.5 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>None</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>3449 / 0 / 256</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.030</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0406, wR2 = 0.0955</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0609, wR2 = 0.1061</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.153 and -0.220 e Å$^{-3}$</td>
</tr>
</tbody>
</table>