Supporting Information
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Supporting information

Synthetic Utility of Sugar Derived Cyclic Nitrones: A Diastereoselective Synthesis of Linear 4-Azatriquinanes

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1. Experimental Section:

General methods

Unless and otherwise noted, all starting materials and reagents were obtained from commercial suppliers and used after further purification. Tetrahydrofuran was distilled from sodium benzophenone ketyl and toluene from sodium. Dichloromethane, N,N-dimethylformamide, hexanes and pyridine were freshly distilled from calcium hydride. All solvents for routine isolation of products and chromatography were of reagent grade and glass distilled. Reaction flasks were dried in oven at 120 °C for 12 h. Air and moisture sensitive reactions were performed under an argon/UHP nitrogen atmosphere. Chromatography was performed using silica gel (100-200 mesh, Aceme, for gravity column chromatograph; 230-400 mesh, Aceme, for Biotage flash column chromatography) with indicated solvents. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica plates (60F-254) using UV light as visualizing agent, and charring solution (prepared by drop wise addition of Conc. H₂SO₄ (5 mL) to a solution of phosphomolybdic acid (1 g) and ceric sulphate (2 g) in water (95 mL)), alkaline KMnO₄ solution (prepared by dissolving KMnO₄ (2 g) and NaHCO₃ (4 g) in water (100 mL)), and heat as developing agents. Optical rotation was recorded on Autopol IV automatic polarimeter. IR spectra were recorded on Thermo Nicolet Avater 320 FT-IR and Nicolete Impact 400 machine. Mass spectra were obtained from Waters Micromass-Q-Tof micro™ (YA105) spectrometer. ¹H and ¹³C NMR spectra were recorded Bruker 400. NMR data is in the order of chemical shifts, multiplicity (s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant in hertz (Hz) and number of protons.

General Procedure A for vinyl Grignard addition:

To a stirred solution of nitrone (1 mmol) in THF (10 mL) at -20 °C, 1 M solution of vinyl magnesium bromide in THF (6 mmol) was slowly added under nitrogen atmosphere. After stirring at 0 °C for 1.5 h, 10 mL of saturated aqueous NH₄Cl was added and was extracted with ethyl acetate (2 x 10 mL). The combined organic layers were dried (NaSO₄) and concentrated to afford hydroxylamine after purification by silica gel column chromatography.
(2S,3S,4S,5S)-3,4-bis(benzyloxy)-2-(benzyloxyethyl)-5-vinylpyrrolidin-1-ol (16)

Following the general procedure A, starting from the nitrone 9\(^8\) (500 mg), hydroxyl amine 16 was obtained as a viscous liquid (517 mg, 97\%) after purification by silica gel column chromatography (6-8\% ethyl acetate/hexanes). R\(_f\) = 0.7 (30\% ethyl acetate in hexanes); [\(\alpha\)]\(^D\)\(^{20}\) 16.6 (c 1.05, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.34-7.25 (m, 15H), 6.03 (ddd, \(J = 17.2, 10.3, 8.3\) Hz, 1H), 5.32 (d, \(J = 17.2\) Hz, 1H), 5.27 (dd, \(J = 10.3, 0.8\) Hz, 1H), 4.60-4.45 (m, 6H), 3.98 (dd, \(J = 3.9, 3.2\) Hz, 1H), 3.90 (dd, \(J = 5.3, 3.0\) Hz, 1H), 3.82-3.74 (m, 2H), 3.64 (dd, \(J = 9.6, 6.4\) Hz, 1H), 3.53 (dd, \(J = 10.6, 4.7\) Hz, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.3, 138.2, 138.0, 135.6, 128.5, 128.0, 127.9, 127.8, 119.5, 86.2, 83.9, 73.5, 73.1, 72.0, 71.8, 69.7, 68.0; IR (neat) \(cm^{-1}\) 3420, 2923, 2857, 1666, 1653, 1458, 1362, 1216, 1096, 753, 698; HRMS (ESI) calcd. for C\(_{28}\)H\(_{32}\)NO\(_4\) (M+1)\(^+\) \(m/z\) 446.2331, found \(m/z\) 446.2328.

(2R,3R,4R,5R)-3,4-bis(benzyloxy)-2-(benzyloxyethyl)-5-vinylpyrrolidin-1-ol (ent-16)

Following the general procedure A, starting from the nitrone ent-9\(^8\) (500 mg), hydroxyl amine ent-16 was obtained as a viscous liquid (500 mg, 94\%) after purification by silica gel column chromatography (6-8\% ethyl acetate/hexanes). R\(_f\) = 0.7 (30\% ethyl acetate in hexanes); [\(\alpha\)]\(^D\)\(^{20}\) -15.1 (c 2.00, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.36-7.26 (m, 15H), 6.46 (brs, 1H), 6.06 (ddd, \(J = 17.2, 10.3, 8.3\) Hz, 1H), 5.34 (d, \(J = 17.2\) Hz, 1H), 5.29 (dd, \(J = 10.3, 0.8\) Hz, 1H), 4.59-4.47 (m, 6H), 4.0 (dd, \(J = 3.9, 3.2\) Hz, 1H), 3.93 (dd, \(J = 5.3, 3.0\) Hz, 1H), 3.83-3.77 (m, 2H), 3.66 (dd, \(J = 9.6, 6.4\) Hz, 1H), 3.57-3.53 (m, 1H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.3, 138.2, 138.0, 135.7, 128.5, 128.1, 128.0, 127.9, 127.8, 119.5, 86.1, 83.9, 73.5, 73.0, 72.0, 71.8, 69.7, 68.0; IR (neat) \(cm^{-1}\) 3435, 3030, 2924, 2855, 1648, 1455, 1362, 1216, 1216, 1096, 753, 698; HRMS (ESI) calcd. for C\(_{28}\)H\(_{32}\)NO\(_4\) (M+1)\(^+\) \(m/z\) 446.2331, found \(m/z\) 446.2336.

(2S,3R,4R,5R)-3,4-bis(benzyloxy)-2-(benzyloxyethyl)-5-vinylpyrrolidin-1-ol (18)

Following the general procedure A, starting from the nitrone 10\(^8\) (500 mg), hydroxyl amine 18 was obtained as a white solid (490 mg, 92\%) after purification by silica gel column chromatography (6-8\% ethyl acetate/hexanes). R\(_f\) = 0.7 (30\% ethyl acetate in hexanes); Mp: 106-109 \(^\circ\)C; [\(\alpha\)]\(^D\)\(^{20}\) -0.64 (c 1.00, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.36-7.26 (m, 15H), 5.95 (dd,
17.1, 10.2, 8.3 Hz, 1H), 5.41 (dd, 17.1, 0.72, 1H), 5.27 (dd, 10.2, 1.2 Hz, 1H), 4.59-4.43 (m, 6H), 4.02 (dd, 6.5, 1.9 Hz, 1H), 3.91 (dd, 9.0, 7.8 Hz, 1H), 3.81 (dd, 9.1, 5.3 Hz, 1H), 3.70 (dd, 6.7, 1.9 Hz, 1H), 3.40-3.30 (m, 2H); 13C NMR (100 MHz, CDCl3): δ 138.2, 137.9, 137.5, 128.6, 128.0, 127.9, 127.8, 119.4, 85.9, 80.3, 76.4, 73.6, 72.3, 72.0, 69.3, 68.1; IR (neat) cm⁻¹ 3337, 3029, 2921, 2866, 2107, 1966, 1660, 1453, 1217, 1116, 1023, 920, 761, 693, 638; HRMS (ESI) calcd. for C28H32NO4 (M+1)+ m/z 446.2331, found m/z 446.2339.

(2S,3R,4S,5S)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-5-vinylpyrrolidin-1-ol (22)

Following the general procedure A, starting from the nitrone 11 (500 mg), hydroxyl amine 22 was obtained as a viscous liquid (517 mg, 97%) after purification by silica gel column chromatography (6-8% ethyl acetate/hexanes). Rf = 0.7 (30% ethyl acetate in hexanes); [α]D²⁰ -11.8 (c 1.00, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.34-7.24 (m, 15H), 5.96 (ddd, J = 17.2, 10.3, 7.8 Hz, 1H), 5.30 (ddd, J = 17.2, 1.5, 1.1 Hz, 1H), 5.23 (ddd, J = 10.3, 1.5, 0.5 Hz, 1H), 4.74-4.46 (m, 6H), 4.73 (d, J = 11.8 Hz, 1H), 4.68-4.46 (m, 5H), 4.18 (t, J = 4.9, 1H), 3.94-3.85 (m, 2H), 3.83-3.66 (m, 2H), 3.55 (dd, J = 11.9, 6.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 138.5, 138.3, 138.1, 135.4, 128.5, 128.4, 128.0, 127.9, 127.8, 127.7, 118.9, 82.2, 73.7, 73.6, 72.5, 72.3, 69.1, 67.7; IR (neat) cm⁻¹ 3412, 3020, 2929, 2401, 2102, 1966, 1658, 1216, 1028, 919, 760, 670, 669; HRMS (ESI) calcd. for C28H32NO4 (M+1)+ m/z 446.2331, found m/z 446.2343.

(2S,3S,4S)-3,4-bis(benzyloxy)-2-vinylpyrrolidin-1-ol (26)

Following the general procedure A, starting from the nitrone 12 (500 mg), hydroxyl amine 26 was obtained as a pale yellow solid (520 mg, 95%) after purification by silica gel column chromatography (8-10% ethyl acetate/hexanes). Rf = 0.8 (40% ethyl acetate in hexanes); Mp: 66-69 °C; [α]D²¹ +44.7 (c 2.00, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.36-7.25 (m, 10H), 5.94 (ddd, J = 17.2, 10.2, 8.1 Hz, 1H), 5.4 (dd, J = 17.2, 0.7 Hz, 1H), 5.28 (dd, J = 10.2, 1.2 Hz), 4.57-4.41 (m, 4H), 3.97 (dt, J = 6.7, 2 Hz, 1H), 3.79-3.77 (m, 1H), 3.43 (d, J = 10.9 Hz, 1H), 3.27 (t, J = 7.7 Hz, 1H), 3.08 (dd, J = 10.9, 6.7 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 137.9, 137.0, 128.6, 128.0, 127.9, 119.8, 86.7, 80.3, 76.4, 72.2, 71.4, 61.4; IR (neat) cm⁻¹ 3304, 2918, 2852, 1646, 1455, 1362, 1210, 1125, 1086, 731, 694; HRMS (ESI) calcd. for C20H24NO3 (M+1)+ m/z 326.1756, found m/z 326.1763.
(3aS,4S,6R,6aR)-4-(((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-vinylidihydro-3aH-[1,3]dioxolo[4,5-c]pyrrol-5(4H)-ol (30)

Following the general procedure A, starting from the nitrone 13 \(^8\) (500 mg), hydroxyl amine 30 was obtained as a white solid (480 mg, 87\%) after purification by silica gel column chromatography (6-8\% ethyl acetate/hexanes). R\(_f\) = 0.6 (30\% ethyl acetate in hexanes); Mp: 71-74 °C; [\(\alpha\)]\(^D\) \(_{0}\) 0.4 (c 1.00, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 5.90 (ddd, \(J = 17.2, 10.3, 0.7\) Hz, 1H), 4.35 (dd, 11.9, 6.5 Hz, 1H), 4.28-4.21 (m, 2H), 4.10 (dd, 8.7, 6.6 Hz, 1H), 3.95 (dd, 8.7, 6.6 Hz, 1H), 3.42 (t, 6.8 Hz, 1H), 3.14 (dd, 4.7, 6.4 Hz, 1H), 1.54 (s, 3H), 1.49 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 136.1, 119.2, 114.0, 110.1, 80.5, 77.6, 76.6, 76.0, 74.4, 66.4, 27.4, 26.6, 25.4, 25.3; IR (neat) cm\(^{-1}\) 3428, 3084, 2987, 2933, 1792, 1705, 1643, 1449, 1377, 1257, 1213, 1156, 1077, 922, 858, 757, 515; HRMS (ESI) C\(_{24}\)H\(_{30}\)NO\(_5\)(M+1)\(^+\) m/z 286.1654, found m/z 286.1649.

**General Procedure B for N-O bond cleavage:**

A saturated solution of NH\(_3\)Cl (20 mL), powdered Zn (4.5 mmol) and a catalytic amount of indium powder (0.2 mmol) were added to a stirred solution of hydroxylamine (1.12 mmol) in methanol (15 mL), at 25 °C. The mixture was refluxed overnight. Then, solvent was evaporated in vacuo and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were washed with Na\(_2\)CO\(_3\) solution, brine, dried (Na\(_2\)SO\(_4\)), and concentrated. The crude product was purified by silica gel column chromatography.

(2S,3S,4S,5S)-3,4-bis(benzyloxy)-2-(benzyloxyethyl)-5-vinylpyrroldidine (17)

Following the general procedure B, starting from the hydroxyl amine 16 (400 mg), amine 17 was obtained as a viscous liquid (325 mg, 84\%) after purification by silica gel column chromatography (12-15\% ethyl acetate/hexanes). R\(_f\) = 0.4 (30\% ethyl acetate in hexanes); [\(\alpha\)]\(^D\) \(_{0}\) -9.6 (c 1.00, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.37-7.25 (m, 15H), 5.92 (ddd, \(J = 17.1, 10.2, 7.2\) Hz, 1H), 5.26 (dt, \(J = 17.1, 1.4\) Hz, 1H), 5.12 (ddd, \(J = 10.2, 1.4, 1.1\) Hz, 1H), 4.69-4.49 (m, 6H), 3.89-3.84 (m, 2H), 3.68 (dd, \(J = 6.7, 5.9\) Hz, 1H), 3.55-3.48 (m, 2H), 3.45-3.41 (m, 1H), 1.81 (brs, 1H); \(^1^3\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.9, 138.3, 128.6, 128.5, 128.0, 127.9, 127.8, 116.3, 89.5, 86.1, 73.4,
72.2, 72.0, 71.1, 64.6, 61.5; IR (neat) cm\(^{-1}\) 3422, 3031, 2924, 2854, 2343, 1967, 1649, 1455, 1363, 1217, 1098, 925, 757, 699, 581; HRMS (ESI) calcd. for C\(_{28}\)H\(_{32}\)NO\(_3\) (M+1\(^+\)) \(m/z\) 430.2382, found \(m/z\) 430.2375.

(2R,3R,4R,5R)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-5-vinylpyrrolidine (ent-17)

Following the general procedure B, starting from the hydroxyl amine ent-16 (400 mg), amine ent-17 was obtained as a viscous liquid (310 mg, 80\%) after purification by silica gel column chromatography (12-15\% ethyl acetate/hexanes). \(R_f = 0.4\) (30\% ethyl acetate in hexanes); \([\alpha]^{21}_D\) 6.8 (c 1.00, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.40-7.25 (m, 15H), 5.93 (ddd, \(J = 17.1, 10.2, 7.2\) Hz, 1H), 5.26 (dt, \(J = 17.1, 1.4\) Hz, 1H), 5.13 (ddd, \(J = 10.2, 1.4, 1.1\) Hz, 1H), 4.61-4.49 (m, 6H), 3.90-3.85 (m, 2H), 3.68 (dd, \(J = 6.7, 5.9\) Hz, 1H), 3.56-3.48 (m, 2H), 3.46-3.42 (m, 1H), 2.63 (brs, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.7, 138.3, 138.2, 128.6, 128.5, 128.0, 127.9, 127.8, 116.5, 89.3, 85.9, 77.4, 73.4, 72.2, 72.0, 70.9, 64.6, 61.5; IR (neat) cm\(^{-1}\) 3400, 3030, 2922, 2856, 2343, 1967, 1646, 1455, 1363, 1214, 1098, 921, 752, 698, 487; HRMS (ESI) calcd. for C\(_{28}\)H\(_{32}\)NO\(_3\) (M+1\(^+\)) \(m/z\) 430.2382, found \(m/z\) 430.2370.

(2S,3R,4R,5R)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-5-vinylpyrrolidine (19)

Following the general procedure B, starting from the hydroxyl amine 18 (400 mg), amine 19 was obtained as a viscous liquid (300 mg, 78\%) after purification by silica gel column chromatography (12-15\% ethyl acetate/hexanes). \(R_f = 0.4\) (30\% ethyl acetate in hexanes); \([\alpha]^{21}_D\) 13.4 (c 1.00, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.36-7.25 (m, 15H), 5.93 (ddd, \(J = 17.1, 10.1, 7.6\) Hz, 1H), 5.27 (dt, \(J = 17.1, 1.3\) Hz, 1H), 5.10 (ddd, \(J = 10.1, 1.3, 0.8\) Hz, 1H), 4.58-4.44 (m, 6H), 3.95 (dd, \(J = 5.0, 2.0\) Hz, 1H), 3.76 (dd, \(J = 5.3, 2.0\) Hz, 1H), 3.75 (dd, \(J = 9.2, 5.3\) Hz, 1H), 3.64 (dd, \(J = 9.2, 7.1\) Hz, 1H), 3.56 (dd, \(J = 7.6, 5.2\) Hz, 1H), 3.51 (t, \(J = 5.3\) Hz, 1H), 3.49 (t, \(J = 5.3\) Hz, 1H), 1.86 (brs, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 139.4, 138.4, 138.2, 128.6, 128.5, 128.0, 127.9, 127.8, 116.5, 88.7, 83.6, 73.6, 72.0, 71.6, 69.9, 67.0, 60.7; IR (neat) cm\(^{-1}\) 3434, 2928, 2857, 2109, 1966, 1658, 1454, 1218, 1096, 925, 756, 698, 569; HRMS (ESI) calcd. for C\(_{28}\)H\(_{32}\)NO\(_3\) (M+1\(^+\)) \(m/z\) 430.2382, found \(m/z\) 430.2379.

(2S,3R,4S,5S)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-5-vinylpyrrolidine (23)

Following the general procedure B, starting from the hydroxyl amine 22 (400 mg), amine 23 was obtained as a viscous liquid (312 mg, 81\%) after
purification by silica gel column chromatography (12-15% ethyl acetate/hexanes). R\textsubscript{f} = 0.4 (30% ethyl acetate in hexanes); [\alpha]\textsuperscript{20D} = -23.9 (c 1.4, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 7.35-7.25 (m, 15H), 5.79 (ddd, \(J = 17.2, 10.1, 7.3\) Hz, 1H), 5.26 (dt, \(J = 17.2, 1.5\) Hz, 1H), 5.10 (ddd, \(J = 10.2, 1.5, 1.0\) Hz, 1H), 4.78-4.48 (m, 6H), 4.05 (t, \(J = 4.3\) Hz, 1H), 3.83 (t, \(J = 7.3\) Hz, 1H), 3.71-3.65 (m, 2H), 3.60 (dd, \(J = 9.0, 7.3\) Hz, 1H), 3.55-3.50 (m, 1H), 1.77 (brs, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 139.6, 138.8, 138.4, 138.3, 128.6, 128.4, 128.0, 127.8, 127.7, 116.5, 84.7, 73.5, 73.5, 72.5, 70.2, 62.7, 58.7; IR (neat) cm\textsuperscript{-1} 3429, 3067, 3019, 2928, 2862, 2402, 1966, 1646, 1455, 1362, 1217, 1089, 929, 699, 669, 469; HRMS (ESI) calcd. for C\textsubscript{28}H\textsubscript{32}N\textsubscript{2}O\textsubscript{3} (M+1)\textsuperscript{+} \textit{m/z} 430.2382, found \textit{m/z} 430.2366.

(2S,3S,4S)-3,4-bis(benzyloxy)-2-vinylpyrrolidine (27)

Following the general procedure B, starting from the hydroxyl amine 26 (400 mg), amine 27 was obtained as a viscous liquid (312 mg, 82%) after purification by silica gel column chromatography (14-16% ethyl acetate/hexanes). R\textsubscript{f} = 0.6 (40% ethyl acetate in hexanes); [\alpha]\textsuperscript{20D} = 21.6 (c 2.00, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 7.37-7.26 (m, 10H), 5.93 (ddd, \(J = 17.2, 10.3, 7.0\) Hz, 1H), 5.28 (dt, \(J = 17.2, 1.4\) Hz, 1H), 5.13 (dt, \(J = 10.3, 1.3\) Hz, 1H), 4.59, 4.53 (ABq, 2H, \(J_{AB} = 11.8\) Hz), 4.53, 4.46 (ABq, 2H, \(J_{AB} = 11.9\) Hz), 4.01(dt, \(J = 4.7, 2.2\) Hz, 1H), 3.77 (ddd, \(J = 0.6, 1.9, 5.2\) Hz, 1H), 3.54 (dd, \(J = 6.7, 5.4\) Hz, 1H), 3.13 (dd, \(J = 12.2, 2.5\) Hz, 1H), 3.08 (dd, \(J = 12.2, 4.8\) Hz, 1H), 1.95 (s, 1H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 138.3, 138.2, 128.6, 128.5, 127.9, 127.8, 116.3, 89.4, 84.6, 72.1, 71.2, 67.3, 51.2; IR (neat) cm\textsuperscript{-1} 3350, 3031, 2923, 2857, 2109, 1967, 1644, 1454, 1363, 1215, 1097, 922, 738, 698; HRMS (ESI) calcd. for C\textsubscript{20}H\textsubscript{24}N\textsubscript{2}O\textsubscript{2} (M+1)\textsuperscript{+} \textit{m/z} 310.1807, found \textit{m/z} 310.1810.

(3aS,4S,6R,6aR)-4-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-6-vinyltetrahydro-3aH-[1,3]dioxolo[4,5-c]pyrrole (31)

Following the general procedure B, starting from the hydroxyl amine 30 (400 mg), amine 31 was obtained as a viscous liquid (272 mg, 72%) after purification by silica gel column chromatography (12-14% ethyl acetate/hexanes). R\textsubscript{f} = 0.65 (30% ethyl acetate in hexanes); [\alpha]\textsuperscript{20D} = 4.4 (c 1.00, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta\) 5.90 (ddd, \(J = 17.2, 10.3, 6.7\) Hz, 1H), 5.40 (ddd, \(J = 17.2, 2.6, 1.4\) Hz, 1H), 5.29 (dt, \(J = 10.3, 1.3\) Hz, 1H), 4.34-4.28 (m, 2H), 4.16-4.08 (m, 2H), 3.86 (dd, 7.8, 6.2 Hz, 1H), 3.63-3.60 (m, 1H), 3.16 (dd, 6.6, 4.3Hz, 1H), 1.53 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.32 (s, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): \(\delta\) 137.8, 116.7,
114.5, 109.6, 85.2, 81.9, 77.7, 66.7, 66.4, 27.5, 26.9, 25.5, 25.4; IR (neat) cm\(^{-1}\) 3422, 2983, 2926, 2106, 1656, 1459, 1381, 1262, 1214, 1159, 1073, 868, 758; HRMS (ESI) calcd. for C\(_{14}H_{24}NO\(_4\)) (M+1)\(^+\) m/z 270.1705, found m/z 270.1711.

**General Procedure C for N-propargylation:**

To a stirred solution of amine (1 mmol) in acetone (10 ml), K\(_2\)CO\(_3\) (2.5 mmol) was added followed by the addition of propargyl bromide (2.5 mmol) under nitrogen atmosphere. After refluxed for 4h at 50 °C, the solvent was evaporated in vacuo and added water and extracted with CH\(_2\)Cl\(_2\). The combined organic layers were washed with brine, dried (Na\(_2\)SO\(_4\)), and concentrated. The crude product was purified by silica gel column chromatography.

(2S,3S,4S,5S)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-1-(prop-2-ynyl)-5-vinylpyrrolidine (14)

Following the general procedure C, starting from the amine 17 (300 mg), enyne 14 was obtained as a viscous liquid (300 mg, 92%) after purification by silica gel column chromatography (4-6% ethyl acetate/hexanes). R\(_f\) = 0.75 (25% ethyl acetate in hexanes); [\(\alpha\)]\(_{20}^D\) 35.2 (c 1.00, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.37-7.24 (m, 15H), 5.85 (dt, \(J = 17.0, 9.7\) Hz, 1H), 5.35 (dd, \(J = 17.0, 1.6\) Hz, 1H), 5.24 (dd, \(J = 10.0, 1.8\) Hz, 1H), 4.58-4.45(m, 6H), 3.93(t, \(J = 3\) Hz, 1H), 3.83 (dd, \(J = 9.6, 5.0\) Hz, 1H), 3.69 (dd, \(J = 9.4, 4.6\) Hz,1H), 3.60 (dd, \(J = 9.6, 6.1\) Hz, 1H), 3.57 (dd, \(J = 17.2, 2.4\) Hz, 1H), 3.45-3.39 (m, 2H), 2.18 (t, \(J = 2.4\) Hz, 1H);

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 138.4, 138.3, 137.2, 128.5, 128.0, 127.9, 127.8, 127.7, 119.6, 88.0, 85.4, 81.1, 73.5, 72.4, 71.9, 71.7, 69.8, 69.2, 65.2, 37.2; IR (neat) cm\(^{-1}\) 3296, 3064, 3031, 2921, 2858, 2107, 1965, 1644, 1497, 1454, 1363, 1207, 1099, 1029, 926, 737, 698, 465; HRMS (ESI) calcd. for C\(_{31}H_{34}NO\(_3\)) (M+1)\(^+\) m/z 468.2539, found m/z 468.2522.

(2R,3R,4R,5R)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-1-(prop-2-ynyl)-5-vinylpyrrolidine (ent-14)

Following the general procedure C, starting from the amine ent-17 (300 mg), enyne ent-14 was obtained as a viscous liquid (297 mg, 91%) after purification by silica gel column chromatography (4-6% ethyl acetate/hexanes). R\(_f\) = 0.75 (25% ethyl acetate in hexanes); [\(\alpha\)]\(_{21}^{21}\) - 33.8 (c 1.00, CHCl\(_3\)); \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta\) 7.34-7.24 (m, 15H), 5.85 (dt, \(J = 17.0, 9.8\) Hz,
1H), 5.35 (dd, J = 17.0, 1.6 Hz, 1H), 5.24 (dd, J = 10.0, 1.8 Hz, 1H), 4.58-4.45 (m, 6H), 3.93 (t, J = 3 Hz, 1H), 3.83 (dd, J = 4.6, 2.8 Hz, 1H), 3.73 (dd, J = 9.6, 5.0 Hz, 1H), 3.69 (dd, J = 9.4, 4.6 Hz, 1H), 3.60 (dd, J = 9.6, 6.1 Hz, 1H), 3.57 (dd, J = 17.2, 2.4 Hz, 1H), 3.45-3.39 (m, 2H), 2.18 (t, J = 2.4 Hz, 1H); 13C NMR (100 MHz, CDCl3): δ 138.4, 138.3, 137.2, 128.5, 128.0, 127.9, 127.8, 127.7, 119.6, 88.0, 85.4, 81.1, 73.5, 72.4, 71.9, 71.7, 69.8, 69.2, 65.2, 37.2; IR (neat) cm⁻¹ 3296, 3060, 3022, 2922, 2853, 1964, 1657, 1455, 1362, 1098, 927, 753, 698; HRMS (ESI) calcd. for C₃₁H₄₃NO₃(M+1)⁺ m/z 468.2539, found m/z 468.2530.

(2S,3R,4R,5R)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-1-(prop-2-ylnyl)-5-vinylpyrrolidine (20)

Following the general procedure C, starting from the amine 19 (300 mg), enyne 20 was obtained as a viscous liquid (290 mg, 89%) after purification by silica gel column chromatography (4-6% ethyl acetate/hexanes). Rf = 0.75 (25% ethyl acetate in hexanes); [α]D²¹ -14.4 (c 1.00, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.24 (m, 15H), 5.75 (ddd, J = 17.1, 9.9, 8.9 Hz, 1H), 5.39 (dd, J = 17.1, 1.5 Hz, 1H), 5.25 (dd, J = 9.9, 1.8 Hz, 1H), 4.61-4.49 (m, 6H), 3.98 (dd, J = 6.4, 3.1 Hz, 1H), 3.80-3.76 (m, 2H), 3.64 (dd, J = 17.7, 2.3 Hz, 1H), 3.60 (dd, J = 9.8, 6.0 Hz, 1H), 3.45 (dd, J = 17.7, 2.3 Hz, 1H), 3.38 (dd, J = 12.1, 6.0 Hz, 1H), 3.28 (dd, J = 8.8, 6.2 Hz, 1H), 2.20 (t, J = 2.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 138.6, 138.4, 138.3, 138.2, 128.5, 128.0, 127.9, 127.8, 127.7, 119.7, 87.2, 82.9, 77.9, 73.8, 73.5, 72.3, 72.1, 69.8, 61.2, 38.4; IR (neat) cm⁻¹ 3293, 3031, 2924, 2852, 2108, 1966, 1660, 1454, 1362, 1263, 1217, 1096, 1029, 928, 758, 698, 469; HRMS (ESI) calcd. for C₃₁H₄₃NO₃(M+1)⁺ m/z 468.2539, found m/z 468.2545.

(2S,3R,4S,5S)-3,4-bis(benzyloxy)-2-(benzyloxymethyl)-1-(prop-2-ylnyl)-5-vinylpyrrolidine (24)

Following the general procedure C, starting from the amine 23 (300 mg), enyne 24 was obtained as a viscous liquid (295 mg, 90%) after purification by silica gel column chromatography (4-6% ethyl acetate/hexanes). Rf = 0.75 (25% ethyl acetate in hexanes); [α]D²¹ -14.4 (c 1.00, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.37-7.26 (m, 15H), 5.79 (ddd, J = 17.0, 10.0, 8.8 Hz, 1H), 5.32 (dd, J = 17.0, 1.5 Hz, 1H), 5.20 (dd, J = 10.0, 1.7 Hz, 1H), 4.69-4.47 (m, 6H), 4.09-4.06 (m, 1H), 3.86-3.78 (m, 2H), 3.79-3.73 (m, 2H), 3.71-3.67 (m, 1H), 3.62 (dd, J = 17.4, 2.3 Hz, 1H), 3.54 (dd, J = 17.4, 2.3 Hz, 1H), 2.18 (t, J = 2.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 138.8, 138.6,
138.5, 137.4, 128.4, 127.9, 127.8, 127.7, 127.6, 119.2, 82.5, 81.9, 77.7, 73.5, 72.9, 72.2, 72.1, 68.8, 68.7, 62.0, 37.9; IR (neat) cm⁻¹ 3298, 3030, 2924, 2855, 2109, 1966, 1657, 1496, 1454, 1365, 1216, 1093, 925, 756, 698; HRMS (ESI) calcd. for C₃₁H₃₄NO₃(M+1)⁺ m/z 468.2539, found m/z 468.2544.

(2S,3S,4S)-3,4-bis(benzyloxy)-1-(prop-2-ynyl)-2-vinylpyrrolidine (28)

Following the general procedure C, starting from the amine 27 (300 mg), enyne 28 was obtained as a viscous liquid (300 mg, 89%) after purification by silica gel column chromatography (4-6% ethyl acetate/hexanes). Rᵣ = 0.75 (25% ethyl acetate in hexanes); [α]²⁰ᵪ D 70.2 (c 1.00, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 7.35-7.27 (m, 10H), 5.77 (ddd, J = 17.1, 10.0, 8.8 Hz, 1H), 5.40 (dd, J = 17.1, 1.7 Hz, 1H), 5.28 (dd, J = 10.0, 1.7 Hz, 1H), 4.60-4.44 (m, 4H), 3.95 (ddd, J = 6.0, 2.2, 1.3 Hz, 1H), 3.86 (dd, J = 6.8, 2.1 Hz, 1H), 3.45 (dd, J = 17.4, 2.3 Hz, 1H), 3.41 (dd, J = 17.4, 2.3 Hz, 1H), 3.09-3.01 (m, 2H), 2.93 (dd, J = 10.5, 6.1 Hz, 1H), 2.19 (t, J = 2.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 138.2, 137.6, 128.5, 128.1, 127.9, 127.8, 120.1, 89.5, 82.0, 77.7, 77.4, 73.7, 72.2, 71.4, 70.6, 55.4, 39.7; IR (neat) cm⁻¹ 3431, 3305, 2924, 2854, 2109, 1966, 1650, 1455, 1364, 1218, 1095, 929, 757, 698, 667, 484; HRMS (ESI) calcd. for C_{23}H_{26}NO_{2}(M+1)⁺ m/z 348.1964, found m/z 348.1959.

(3aS,4S,6R,6aR)-4-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-5-(prop-2-ynyl)-6-vinyltetrahydro-3aH-[1,3]dioxolo[4,5-c]pyrrole (32)

Following the general procedure C, starting from the amine 31 (300 mg), enyne 32 was obtained as a viscous liquid (305 mg, 89%) after purification by silica gel column chromatography (4-6% ethyl acetate/hexanes). Rᵣ = 0.8 (25% ethyl acetate in hexanes); [α]²⁰ᵪ D 7.2 (c 1.00, CHCl₃); ¹H NMR (CDCl₃, 400 MHz): δ 5.60 (ddd, J = 17.1, 10.0, 8.6 Hz, 1H), 5.37 (dd, J = 17.1, 1.7 Hz, 1H), 5.26 (dd, J = 10.0, 1.7 Hz, 1H), 4.26 (dd, J = 7.2, 5.7 Hz, 1H), 4.21 (dd, J = 7.2, 4.3 Hz, 1H), 4.16-4.11 (m, 1H), 4.07 (dd, J = 8.3, 6.7 Hz, 1H), 3.85 (dd, J = 8.3, 6.2 Hz, 1H), 3.80 (dd, J = 17.6, 2.3 Hz, 1H), 3.34 (dd, J = 17.6, 2.3 Hz, 1H), 3.31 (dd, J = 8.6, 5.6 Hz, 1H), 3.11 (dd, J = 7.4, 4.3 Hz, 1H), 2.21 (t, J = 2.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 136.7, 120.1, 113.8, 109.9, 83.4, 80.2, 78.0, 73.8, 71.0, 67.6, 66.6, 38.3, 27.6, 26.7, 25.8, 25.5; IR (neat) cm⁻¹ 3292, 2987, 2934, 2107, 1967, 1651, 1429, 1382, 1373, 1263, 1214, 1158, 1073,
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933, 864, 760, 693, 513; HRMS (ESI) calcd. for C_{17}H_{26}NO_{4}(M+1)^{+} m/z 308.1862, found m/z 308.1864.

**General Procedure D for Pauson-Khand reaction:**

To a stirred solution of enyne (1 mmol) in CH_{2}Cl_{2} (30 ml), Co_{2}(CO)_{8} (1.2 mmol) was added under nitrogen atmosphere at 25 °C. After stirring at 25 °C for 1 h, the solvent was removed to get the crude product. To a solution of above crude product in toluene (20 ml) DMSO (10 mmol) was added and refluxed for overnight at 80 °C. After completion, the reaction mixture was quenched with 50 ml of 1% HCl (except for compound 33, 34 which was quenched with water) and extracted with CH_{2}Cl_{2}. The combined organic layers were dried (Na_{2}SO_{4}), and concentrated. The crude product was purified by basic alumina column chromatography.

(1S,2S,3S,8aS,8bS)-1,2-bis(benzyloxy)-3-(benzyloxymethyl)-1,2,3,8,8a,8b-hexahydrocyclopenta[a]pyrrolizin-7(5H)-one (15)

Following the general procedure D, starting from the enyne 14 (100 mg), azatriquinane 15 was obtained as a viscous liquid (73 mg, 69%) after purification by neutral alumina column chromatography (20-23% ethyl acetate/hexanes). R_{f} = 0.4 (50% ethyl acetate in hexanes); [α]^{20}_D - 9.8 (c 1.00, CHCl_{3}); ^{1}H NMR (CDCl_{3}, 400 MHz): δ 7.37-7.26 (m, 15H), 6.0-5.99 (m, 1H), 4.69-4.44 (m, 6H), 4.08-4.02 (m, 3H), 3.71 (d, J = 16.9 Hz, 1H), 3.62 (dd, J = 9.4, 4.5 Hz, 1H), 3.52 (dd, J = 9.4, 6.5 Hz, 1H), 3.29-3.24 (m, 1H), 3.19 (dd, J = 10.5, 3.3 Hz, 1H), 3.12-3.08 (m, 1H), 2.60 (dd, J = 17.6, 6.2 Hz, 1H), 2.10 (dd, J = 17.6, 3.3 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_{3}): δ 209.3, 186.9, 138.4, 138.1, 137.7, 128.7, 128.6, 128.5, 128.1, 128.0, 127.9, 127.8, 125.1, 86.8, 86.1, 73.6, 73.0, 72.7, 72.5, 72.3, 70.2, 54.2, 48.5, 40.6; IR (neat) cm^{-1} 3872, 3030, 2924, 2854, 2109, 1966, 1703, 1646, 1454, 1367, 1306, 1215, 1106, 1028, 754, 698; HRMS (ESI) calcd. for C_{32}H_{34}NO_{4}(M+1)^{+} m/z 496.2488, found m/z 496.2469.

(1R,2R,3R,8aR,8bR)-1,2-bis(benzyloxy)-3-(benzyloxymethyl)-1,2,3,8,8a,8b-hexahydrocyclopenta[a]pyrrolizin-7(5H)-one (ent-15)

Following the general procedure D, starting from the enyne ent-14 (100 mg), azatriquinane ent-15 was obtained as a viscous liquid (70 mg, 66%) after purification by neutral alumina column chromatography (20-23% ethyl acetate/hexanes). R_{f} = 0.4 (50% ethyl
acetate in hexanes); $[\alpha]^{20D}_{D} 7.9 (c 0.83, CHCl_3); ^1H NMR (CDCl_3, 400 MHz): $\delta$ 7.38-7.26 (m, 15H), 6.00 (dd, $J = 2.0, 1.1$ Hz 1H), 4.68-4.44 (m, 6H), 4.08-4.02 (m, 3H), 3.71 (d, $J = 16.5$ Hz, 1H), 3.62 (dd, $J = 9.4, 4.5$ Hz, 1H), 3.52 (dd, $J = 9.4, 6.5$ Hz, 1H), 3.28-3.24 (m, 1H), 3.19 (dd, $J = 10.6, 3.2$ Hz, 1H), 3.13-3.09 (m, 1H), 2.61 (dd, $J = 17.6, 6.1$ Hz, 1H), 2.10 (dd, $J = 17.6, 3.3$ Hz, 1H); $^1C$ NMR (100 MHz, CDCl_3): $\delta$ 209.3, 186.9, 138.4, 138.1, 137.7, 128.7, 128.6, 128.5, 128.2, 128.0, 127.9, 127.8, 125.1, 86.8, 86.1, 73.6, 73.0, 72.7, 72.5, 72.3, 70.2, 54.2, 48.5, 40.6; IR (neat) cm$^{-1}$: 3028, 2923, 2853, 2345, 1966, 1713, 1643, 1454, 1367, 1366, 1217, 1110, 757, 699, 668, 598; HRMS (ESI) calcd. for $C_{32}H_{34}NO_4$(M+1)$^+$ m/z 496.2488, found m/z 496.2484.

(1R,2R,3S,8aR,8bR)-1,2-bis(benzyloxy)-3-(benzyloxy methyl)-1,2,3,8a,8b-hexahydrocyclopenta[a]pyrrolizin-7(5H)-one (21)

Following the general procedure D, starting from the enyne 20 (100 mg), azatriquinane 21 was obtained as a viscous liquid (74 mg, 70%) after purification by neutral alumina column chromatography (20-23% ethyl acetate/hexanes). $R_f = 0.3$ (50% ethyl acetate in hexanes); $[\alpha]^{20D}_{D}$ 2.4 (c 0.60, CHCl_3); $^1H$ NMR (CDCl_3, 400 MHz): $\delta$ 7.35-7.24 (m, 15H), 5.75 (dd, $J = 17.1, 9.9$, 8.9 Hz, 1H), 5.39 (dd, $J = 17.1, 1.5$ Hz, 1H), 5.25 (dd, $J = 9.9, 1.8$ Hz, 1H), 4.61-4.49 (m, 6H), 3.98 (dd, $J = 6.4, 3.1$ Hz, 1H), 3.80-3.76 (m, 2H), 3.64 (dd, $J = 17.7, 2.3$ Hz, 1H), 3.60 (dd, $J = 9.8$, 6.0 Hz, 1H), 3.45 (dd, $J = 17.7, 2.3$ Hz, 1H), 3.38 (dd, $J = 12.1$, 6.0 Hz, 1H), 3.28 (dd, $J = 8.8$, 6.2 Hz, 1H), 2.20 (t, $J = 2.3$ Hz, 1H); $^{13}C$ NMR (100 MHz, CDCl_3): $\delta$ 209.8, 187.1, 138.3, 138.1, 138.0, 128.7, 128.6, 128.0, 127.9, 127.7, 124.9, 85.9, 85.1, 77.4, 73.6, 72.9, 72.7, 72.2, 65.9, 61.6, 48.2, 47.2, 41.1; IR (neat) cm$^{-1}$: 3030, 2929, 2853, 2345, 1966, 1713, 1643, 1454, 1367, 1366, 1217, 1110, 757, 699, 668, 598; HRMS (ESI) calcd. for $C_{32}H_{34}NO_4$(M+1)$^+$ m/z 496.2488, found m/z 496.2484.

(1S,2R,3S,8aS,8bS)-1,2-bis(benzyloxy)-3-(benzyloxy methyl)-1,2,3,8a,8b-hexahydrocyclopenta[a]pyrrolizin-7(5H)-one (25)

Following the general procedure D, starting from the enyne 24 (100 mg), azatriquinane 25 was obtained as a viscous liquid (72 mg, 68%) after purification by neutral alumina column chromatography (20-23% ethyl acetate/hexanes). $R_f = 0.3$ (50% ethyl acetate in hexanes); $[\alpha]^{20D}_{D}$ - 12.9 (c 1.00, CHCl_3); $^1H$ NMR (CDCl_3, 400 MHz): $\delta$ 7.38-7.27 (m, 15H), 5.97 (t, $J = 1.7$ Hz, 1H), 4.89-4.44 (m, 6H), 4.29 (t, $J = 3.4$ Hz, 1H), 3.74 (d, $J = 15.1$ Hz, 1H), 3.84 (dd, $J = 7.4$, 1H), 3.74 (d, $J = 15.1$ Hz, 1H), 3.84 (dd, $J = 7.4$, 1H).
3.6 Hz, 1H), 3.74 (dd, J = 9.0, 6.6 Hz, 1H), 3.58 (dd, J = 9.0, 6.3 Hz, 1H), 3.45-3.40 (m, 2H), 3.24 (dd, J = 6.6, 3.2 Hz, 1H), 2.82-2.77 (m, 1H), 2.62 (dd, J = 17.6, 6.4 Hz, 1H), 2.10 (dd, J = 17.6, 3.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 209.4, 186.0, 138.6, 138.3, 138.0, 128.7, 128.6, 128.4, 128.1, 127.9, 127.8, 127.7, 125.0, 85.7, 80.6, 77.4, 74.0, 73.7, 72.0, 70.9, 70.5, 68.2, 53.6, 48.8, 41.4; IR (neat) cm$^{-1}$ 3779, 3030, 2926, 2856, 1966, 1713, 1496, 1455, 1367, 1262, 1216, 1094, 1028, 880, 821, 754, 699, 666, 609; HRMS (ESI) calcd. for C$_{32}$H$_{34}$NO$_4$(M+1)$^+$ m/z 496.2488, found m/z 496.2491.

(1S,2S,8bS)-1,2-bis(benzyloxy)-1,2,3,8,8a,8b-hexahydrocyclopenta[a]pyrrolizin-7(5H)-one (29)

Following the general procedure D, starting from the enyne 28 (100 mg), azatricinane 29 was obtained as a viscous liquid (77 mg, 71%) after purification by neutral alumina column chromatography (20-23% ethyl acetate/hexanes). R$_f$ = 0.3 (50% ethyl acetate in hexanes); [$\alpha$]$^\text{D}_{20}$ 7.2 (c 1.00, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): δ 7.37-7.26 (m, 10H), 5.98 (s, 1H), 4.61-4.54 (m, 4H), 4.23 (dd, J = 8.8, 5.1 Hz, 1H), 4.03-3.99 (m, 2H), 3.61 (d, J = 15.8 Hz, 1H), 3.47 (dd, J = 10.8, 5.1 Hz, 1H), 3.16 (s, 2H), 2.98 (dd, J = 10.8, 5.3 Hz, 1H), 2.59 (dd, J = 17.4, 5.4 Hz, 1H), 2.10 (d, J = 17.4 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 209.4, 186.1, 138.0, 137.8, 128.7, 128.1, 128.0, 127.8, 127.7, 125.1, 86.0, 85.2, 73.2, 72.2, 72.1, 58.8, 54.5, 47.6, 40.9; IR (neat) cm$^{-1}$ 2926, 2857, 2338, 2107, 1966, 1660, 1455, 1265, 1217, 1026, 953, 760, 699, 668, 545; HRMS (ESI) calcd. for C$_{24}$H$_{26}$NO$_3$(M+1)$^+$ m/z 376.1913, found m/z 376.1916.

(3aS,4S,9aR,9bR,9cR)-4-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-3a,4,9,9a,9b,9c-hexahydrocyclopenta[f][1,3]dioxolo[4,5-a]pyrrolizin-8(6H)-one (33)

Following the general procedure D, starting from the enyne 32 (100 mg), azatricinane 33 was obtained as a viscous liquid (57 mg, 52%) after purification by neutral alumina column chromatography (18-20% ethyl acetate/hexanes). R$_f$ = 0.3 (50% ethyl acetate in hexanes); [$\alpha$]$^\text{D}_{20}$ 161.4 (c 1.00, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): δ 5.98 (dd, J = 3.8, 1.7 Hz, 1H), 4.44-4.38 (m, 2H), 4.17-4.12 (m, 2H), 4.07 (d, 17 Hz, 1H), 3.90-3.85 (m, 1H), 3.48 (d, 17 Hz, 1H), 2.88-2.81 (m, 2H), 2.67 (dd, 9.7, 4.8 Hz, 1H), 2.65 (dd, 17.5, 6.24 Hz, 1H), 2.26 (dd, 17.6, 3.7 Hz, 1H), 1.51 (s, 3H), 1.45 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 209.6, 187.9, 125.7, 114.7, 110.0, 84.8, 79.8, 76.0, 68.7, 66.7, 49.1, 47.7, 39.8,
27.4, 27.0, 25.6, 25.3; IR (neat) cm$^{-1}$ 3650, 2924, 2111, 1658, 1439, 1407, 1319, 1217, 1022, 953, 762, 712; HRMS (ESI) calcd. for C$_{18}$H$_{26}$NO$_5$(M+1)$^+$ m/z 336.1811, found m/z 336.1826.

(3aS,4S,9aS,9bR,9cR)-4-((S)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-3a,4,9,9a,9b,9c-hexahydrocyclopenta[f][1,3]dioxolo[4,5-a]pyrrolizin-8(6H)-one (34)

Following the general procedure D, starting from the enyne 32 (100 mg), azatriquinane 34 was obtained as a viscous liquid (14 mg, 13%) after purification by neutral alumina column chromatography (20-23% ethyl acetate/hexanes). R$_f$ = 0.2 (50% ethyl acetate in hexanes); [$\alpha$]$^D$$^2$ 15.5 (c 0.48, CHCl$_3$); $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 6.03 (t, $J$ = 1.4 Hz, 1H), 4.22 (dd, $J$ = 7.3, 5.4 Hz, 1H), 4.14 (dd, $J$ = 12.8, 6.3 Hz, 1H), 4.09 (dd, $J$ = 8.0, 6.6 Hz, 1H), 4.03 (dd, $J$ = 7.3, 5.3 Hz, 1H), 3.86 (dd, $J$ = 8.0, 6.3 Hz, 1H), 3.48 (t, $J$ = 5.2 Hz, 1H), 3.14 (t, $J$ = 5.7 Hz, 1H), 3.09-3.06 (m, 1H), 2.47 (dd, $J$ = 19.1, 6.8 Hz, 1H), 2.27 (dd, $J$ = 19.1, 2.1 Hz, 1H), 2.2 (s, 2H), 1.48 (s, 3H), 1.43 (s, 3H), 1.36 (s, 3H), 1.25 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 208.7, 179.3, 132.5, 114.7, 109.6, 81.8, 80.6, 77.6, 66.5, 66.2, 64.6, 46.5, 38.1, 27.5, 26.82, 25.4, 25.3, 18.6; IR (neat) cm$^{-1}$ 2986, 2928, 1710, 1619, 1459, 1380, 1262, 1213, 1159, 1071, 868, 764, 709, 558, 461; HRMS (ESI) calcd. for C$_{18}$H$_{26}$NO$_5$(M+1)$^+$ m/z 336.1811, found m/z 336.1813.

2. Spectral data
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^1$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
COSY (400 MHz, CDCl₃)
NOESY (400 MHz, CDCl₃)
$^1$H-NMR
(400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^{1}H$-NMR

(400 MHz, CDCl$_3$)

$^{13}C$-NMR (100 MHz, CDCl$_3$)

grease peak
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR
(400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^{1}\text{H-NMR}$
(400 MHz, CDCl$_3$)

$^{13}\text{C-NMR}$ (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR
(400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)

grease peak
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR
(400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR
(400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR (400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)
$^1$H-NMR
(400 MHz, CDCl$_3$)

$^{13}$C-NMR (100 MHz, CDCl$_3$)