

Supporting Information

Phenanthridine Synthesis via [2+2+2] Cyclootrimerization Reactions

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Experimental Protocols for compounds 10-13:

10: To a solution of **9** (150 mg, 0.94 mmol) in THF (4 mL) at -78°C was added *n*-BuLi (2.4 M in hexanes, 450 μ L, 1.08 mmol) dropwise, and the solution stirred for 30 min. Propargyl bromide (80% in toluene, 150 μ L, 1.13 mmol) was added and the solution was allowed to warm to room temperature overnight. The reaction mixture was quenched with NH₄Cl and extracted with Et₂O, washed with water and brine, dried (MgSO₄) and concentrated under reduced pressure. The crude material was purified by silica gel chromatography to give the diyne **10** (167 mg, 90%). δ_{H} (300 MHz, CDCl₃) 1.86 (3 H, s), 2.16 (1 H, t, *J* = 2.0 Hz), 3.26 (1 H, s), 3.95 (1 H, dd, *J* = 13.2 Hz, 2.0 Hz), 5.05 (1 H, dd, *J* = 13.2 Hz, 2.0 Hz), 7.34-7.60 (3 H, m), 7.58 (1 H, d, *J* = 6.3 Hz); *m/z* (LCMS) requires [M + H]⁺ C₁₃H₁₂NO 198.0909, found 198.0913.

11: To a solution of **9** (200 mg, 1.25 mmol) in THF (5 mL) at -78°C was added *n*-BuLi (2.4 M in hexanes, 600 μ L, 1.44 mmol) dropwise, and the solution stirred for 30 min. 1-Bromo-2-butyne (200 μ L, 1.63 mmol) was added and the solution was allowed to warm to room temperature overnight. The reaction mixture was quenched with NH₄Cl and extracted with Et₂O, washed with water and brine, dried (MgSO₄) and concentrated under reduced pressure. The crude material was purified by silica gel chromatography to give the diyne **11** (255 mg, 96%). δ_{H} (300 MHz, CDCl₃) 1.74, (3 H, t, *J* = 2.4 Hz), 1.86 (3 H, s), 3.25 (1 H, s), 3.91 (1 H, dq, *J* = 17.0 Hz, 2.4 Hz), 4.94 (1 H, dq, *J* = 2.4 Hz, 17.0 Hz), 7.33-7.48 (3 H, m), 7.56-7.63 (1 H, m); *m/z* (LCMS) requires [M + H]⁺ C₁₄H₁₄NO 212.1071, found 212.1069.

12: To a solution of **9** (100 mg, 0.63 mmol) in THF (3 mL) at -78°C was added *n*-BuLi (2.5 M in hexanes, 315 μ L, 0.76 mmol) dropwise, and the solution stirred for 30 min. 3-Bromo-1-trimethylsilyl-1-propyne (180 μ L, 0.94 mmol) was added and the solution was allowed to warm to room temperature overnight. The reaction mixture was quenched with NH₄Cl and extracted with Et₂O, washed with water and brine, dried (MgSO₄) and concentrated under reduced pressure. The crude material was purified by silica gel chromatography to give the diyne **12** (160 mg, 93%). δ_{H} (300 MHz, CDCl₃) 0.08 (9 H, s), 1.85 (3 H, s), 3.23 (1 H, s), 4.04 (1 H, d, *J* = 17.6 Hz), 5.03 (1 H, d, *J* = 17.6 Hz), 7.30-7.46 (3 H, m), 7.58 (1 H, d, *J* = 5.7 Hz); *m/z* (LCMS) requires [M + H]⁺ C₁₆H₂₀NOSi 270.1310, found 270.1308.

13: To a solution of **8** (57 mg, 0.25 mmol) in THF (1.1 mL) at -78°C was added *n*-BuLi (2.1 M in hexanes, 128 μ L, 0.27 mmol) dropwise, and the solution stirred for 30 min. Propargyl bromide (80% in toluene, 44 μ L, 0.50 mmol) was added and the solution was allowed to warm to room temperature overnight. The reaction mixture was quenched with NH₄Cl and extracted with Et₂O, washed with water and brine, dried (MgSO₄) and concentrated under reduced pressure. The crude material was purified by silica gel chromatography to give the diyne **13** (59 mg, 89%). δ_{H} (300 MHz, CDCl₃) 0.22 (9 H, s), 1.85 (3 H, s), 2.15 (1 H, t, *J* = 2.4 Hz), 3.95 (1 H, dd, *J* = 17.4 Hz, 2.4 Hz), 7.32-7.41 (3 H, m), 7.51-7.58 (1 H, m); *m/z* (LCMS) requires [M + H]⁺ C₁₆H₂₀NOSi 270.1310, found 270.1308.

General cyclotrimerization procedure:

To a flame-dried microwave vial equipped with a stir bar was added the diyne (0.071 mmol), the mono-alkyne (0.71 mmol), catalyst (0.0071 mmol), and dry toluene (0.8 mL). The vial was flushed with nitrogen, capped with a microwave vial septum, and irradiated for 10 min. in a CEM Discover microwave synthesizer at 300 W. After cooling to room temperature, the reaction mixture was concentrated, and the residue was purified by silica gel chromatography, eluting with hexanes/EtOAc to give the pure cyclotrimerization product.

Analytical data for compounds 14-30 and 33-41:

¹³C NMRs were not taken due to the presence of mixtures of regioisomers.

14: δ_{H} (300 MHz, CDCl_3)¹ 0.90-0.97 (3 H, m), 1.30-1.43 (2 H, m), 1.51-1.70 (2 H, m), 2.18 (3 H, s), 2.58-2.71 (2 H, m), 4.90 (2 H, br s), 7.09-7.34 (5 H, m), 7.59 (0.5 H, s), 7.67 (0.5 H, d, $J = 7.8$ Hz), 7.71-7.85 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{19}\text{H}_{22}\text{NO}$ 280.1695, found 280.1695.

15: δ_{H} (300 MHz, CDCl_3)¹ 2.12 (3 H, s), 4.99 (2 H, br s), 7.26-7.70 (10 H, m), 7.80-7.92 (1 H, m), 7.99 (1 H, s); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{21}\text{H}_{18}\text{NO}$ 300.1381, found 300.1382.

16: δ_{H} (300 MHz, CDCl_3)¹ 1.96-2.09 (2 H, m), 2.19 (3 H, s), 2.30-2.42 (2 H, m), 2.75-2.90 (2 H, m), 4.91 (2 H, br s), 7.08-7.37 (5 H, m), 7.60 (0.5 H, s), 7.71 (0.5 H, d, $J = 7.8$ Hz), 7.75-7.82 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}$ 291.1489, found 291.1491.

17: δ_{H} (300 MHz, CDCl_3)¹ 1.75-1.90 (4 H, m), 2.19 (3 H, s), 2.63-2.73 (2 H, m), 3.52-3.61 (2 H, m), 4.90 (2 H, br s), 7.08-7.37 (5 H, m), 7.59 (0.5 H, s), 7.68 (0.5 H, d, $J = 8.1$ Hz), 7.74-7.83 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{19}\text{H}_{21}\text{NOCl}$ 314.1303, found 314.1306.

18: δ_{H} (300 MHz, CDCl_3)¹ 1.46 (9 H, s), 2.16 (3 H, s), 4.26-4.40 (2 H, m), 4.90 (2 H, br s), 7.19-7.38 (5 H, m), 7.68-7.81 (2 H, m); m/z (LCMS) requires $[\text{M} + \text{Na}]^+$ $\text{C}_{21}\text{H}_{24}\text{N}_2\text{O}_3\text{Na}$ 375.1677, found 375.1679.

19: δ_{H} (300 MHz, CDCl_3)¹ 0.13 (6 H, s), 0.97 (9 H, s), 2.19 (3 H, s), 4.76 (1 H, s), 4.80 (1 H, s), 4.92 (2 H, br s), 7.25-7.38 (5 H, m), 7.72-7.83 (2 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{22}\text{H}_{30}\text{NO}_2\text{Si}$ 368.2038, found 368.2040.

20: δ_{H} (300 MHz, CDCl_3) 1.20-1.33 (6 H, m), 2.18 (3 H, s), 2.65-2.76 (4 H, m), 4.89 (2 H, br s), 7.11 (1 H, s), 7.21-7.35 (3 H, m), 7.75-7.85 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{19}\text{H}_{22}\text{NO}$ 280.1696, found 280.1695.

21: δ_{H} (300 MHz, CDCl_3) 2.18 (3 H, s), 3.43 (3 H, s), 3.45 (3 H, s), 4.54 (2 H, s), 4.58 (2 H, s), 4.96 (2 H, br s), 7.30-7.35 (4 H, m), 7.80-7.85 (2 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{19}\text{H}_{22}\text{NO}_3$ 312.1591, found 312.1594.

22: δ_{H} (300 MHz, CDCl_3) 0.13 (6 H, s), 0.14 (6 H, s), 0.96 (9 H, s), 0.98 (9 H, s), 2.19 (3 H, s), 4.75 (2 H, s), 4.79 (2 H, s), 7.28-7.41 (4 H, m), 7.75-7.82 (1 H, m), 7.88 (1 H, s); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{29}\text{H}_{46}\text{NO}_3\text{Si}_2$ 512.3005, found 512.3010.

23: δ_{H} (300 MHz, CDCl_3)¹ 0.91-0.99 (3 H, m), 1.32-1.48 (2 H, m), 1.50-1.69 (2 H, m), 2.18 (3 H, s), 2.36-2.40 (3 H, m), 2.58-2.72 (2 H, m), 4.90-5.00 (2 H, m), 6.99 (1 H, s), 7.10-7.32 (3 H, m), 7.44 (1 H, s), 7.70-7.82 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{20}\text{H}_{24}\text{NO}$ 294.1850, found 294.1852.

24: δ_{H} (300 MHz, CDCl_3)¹ 2.21 (3 H, s), 2.50 (3 H, s), 5.03 (2 H, br s), 7.25-7.55 (7 H, m), 7.62 (2 H, d, $J = 8.1$), 7.78-7.84 (2 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{22}\text{H}_{20}\text{NO}$ 314.1541, found 314.1539.

25: δ_{H} (300 MHz, CDCl_3)¹ 1.90-2.06 (2 H, m), 2.18 (3 H, s), 2.30-2.44 (5 H, m), 2.69-2.84 (2 H, m), 4.90 (2 H, br s), 6.90-7.36 (4 H, m), 7.44 (1 H, s), 7.70-7.80 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{20}\text{H}_{21}\text{N}_2\text{O}$ 305.1644, found 305.1648.

¹ Mixture of regioisomers.

26: δ_{H} (300 MHz, CDCl_3)¹ 1.78-1.90 (4 H, m), 2.18 (3 H, s), 2.36-2.40 (3 H, m), 2.60-2.72 (2 H, m), 3.52-3.61 (2 H, m), 4.86-5.00 (2 H, m), 6.98 (1 H, s), 7.11-7.60 (4 H, m), 7.70-7.80 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{20}\text{H}_{23}\text{NOCl}$ 328.1458, found 328.1462.

27: δ_{H} (300 MHz, CDCl_3)¹ 1.45-1.49 (9 H, m), 2.19 (3 H, s), 2.36-2.43 (3 H, m), 4.30-4.40 (2 H, m), 4.60-5.05 (3 H, m), 7.07 (1 H, s), 7.16-7.40 (3 H, m), 7.52-7.64 (1 H, m), 7.76-7.82 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H} - \text{CH}_2\text{C}(\text{CH}_3)_2]^+ \text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_3$ 311.1396, found 311.1390.

28: δ_{H} (300 MHz, CDCl_3)¹ 0.11-0.15 (6 H, m), 0.95-0.99 (9 H, m), 2.18 (3 H, s), 2.31-2.43 (3 H, m), 4.73-4.78 (2 H, m), 4.81-5.02 (2 H, m), 7.10-7.80 (6 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{23}\text{H}_{32}\text{NO}_2\text{Si}$ 382.2194, found 382.2196.

29: δ_{H} (300 MHz, CDCl_3)¹ 0.00-0.03 (6 H, m), 0.82-0.91 (9 H, m), 2.17 (3 H, s), 2.37-2.41 (3 H, m), 2.80-2.95 (2 H, m), 3.75-3.90 (2 H, m), 4.80-5.01 (2 H, m), 7.00-7.80 (6 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{24}\text{H}_{34}\text{NO}_2\text{Si}$ 396.2351, found 396.2353.

30: δ_{H} (300 MHz, CDCl_3)¹ 0.04-0.09 (6 H, m), 0.87-0.95 (9 H, m), 1.78-1.91 (2 H, m), 2.18 (3 H, s), 2.35-2.41 (3 H, m), 2.62-2.79 (2 H, m), 3.60-3.70 (2 H, m), 4.80-5.00 (2 H, m), 6.98-7.80 (6 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{25}\text{H}_{36}\text{NO}_2\text{Si}$ 410.2499, found 410.2509.

33: δ_{H} (300 MHz, CDCl_3)¹ 0.43 (9 H, s), 0.94 (3 H, t, $J = 7.4$), 1.35-1.50 (2 H, m), 1.59-1.72 (2 H, m), 2.18 (3 H, s), 2.65 (2 H, t, $J = 7.8$ Hz), 5.01 (2 H, br s), 7.23-7.36 (4 H, m), 7.61 (1 H, s), 7.76-7.82 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{22}\text{H}_{30}\text{NOSi}$ 352.2091, found 352.2091.

34: δ_{H} (300 MHz, CDCl_3)¹ 0.48 (9 H, s), 2.22 (3 H, s), 5.12 (2 H, br s), 7.15-7.54 (6 H, m), 7.63 (2 H, d, $J = 8.3$), 7.69 (1 H, d, $J = 1.8$), 7.84-7.90 (1 H, m), 7.99 (1 H, d, $J = 1.8$); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{24}\text{H}_{26}\text{NOSi}$ 372.1771, found 372.1778.

35: δ_{H} (300 MHz, CDCl_3)¹ 0.43 (9 H, s), 1.75-1.90 (4 H, m), 2.18 (3 H, s), 2.69 (2 H, t, $J = 7.2$ Hz), 3.59 (2 H, t, $J = 6.3$ Hz), 5.02 (2 H, br s), 7.22-7.38 (4 H, m), 7.60 (1 H, d, $J = 1.7$ Hz), 7.75-7.82 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{22}\text{H}_{29}\text{NOSiCl}$ 386.1699, found 386.1701.

36: δ_{H} (300 MHz, CDCl_3)¹ 0.82 (6 H, s), 0.43 (9 H, s), 0.93 (9 H, s), 1.82-1.97 (2 H, m), 2.19 (3 H, s), 2.73 (2 H, t, $J = 7.4$ Hz), 3.67 (2 H, t, $J = 6.1$ Hz), 5.03 (2 H, br s), 7.21-7.38 (4 H, m), 7.63 (1 H, d, $J = 1.7$ Hz), 7.76-7.83 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{27}\text{H}_{42}\text{NO}_2\text{Si}_2$ 468.2748, found 468.2748.

37: δ_{H} (300 MHz, CDCl_3)¹ 0.93-1.02 (3 H, m), 1.36-1.52 (2 H, m), 1.70-1.82 (2 H, m), 2.83-2.96 (2 H, m), 7.52-8.66 (6 H, m), 9.25 (1 H, s); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{17}\text{H}_{18}\text{N}$ 236.1436, found 236.1433.

38: δ_{H} (300 MHz, CDCl_3)¹ 7.40-7.68 (3 H, m), 7.70-7.90 (4 H, m), 7.94-8.26 (2.5 H, m), 8.59-8.72 (1.5 H, m), 8.80 (1 H, s), 9.31-9.39 (1 H, m); m/z (LCMS) requires $[\text{M} + \text{H}]^+ \text{C}_{19}\text{H}_{14}\text{N}$ 256.1118, found 256.1120.

39: δ_{H} (300 MHz, CDCl_3)¹ 2.09-2.19 (2 H, m), 2.36-2.45 (2 H, m), 3.01-3.14 (2 H, m), 7.58 (0.5 H, d, $J = 7.9$ Hz), 7.64-7.82 (2 H, m), 7.89 (1 H, s), 8.04 (0.5 H, d, $J = 7.9$ Hz), 8.21 (1 H, d, $J = 7.4$ Hz), 8.46 (0.5 H, s), 8.52-8.64 (1.5 H, m), 9.28 (1 H, s); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{17}\text{H}_{15}\text{N}_2$ 247.1228, found 247.1229.

40: δ_{H} (300 MHz, CDCl_3)¹ 1.80-2.05 (4 H, m), 2.88-3.04 (2 H, m), 3.56-3.68 (2 H, m), 7.58 (0.5 H, d, $J = 8.3$ Hz), 7.66-7.84 (2 H, m), 7.87 (1 H, s), 8.01 (0.5 H, d, $J = 8.3$ Hz), 8.21 (1 H, t, $J = 7.4$ Hz), 8.43 (0.5 H, s), 8.53-8.66 (1.5 H, m), 9.28 (1 H, s); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{17}\text{H}_{17}\text{NCl}$ 270.1042, found 270.1044.

41: δ_{H} (300 MHz, CDCl_3)¹ 1.49 (9 H, s), 4.52-4.64 (2 H, m), 5.10-5.23 (1 H, m), 7.60-7.82 (3 H, m), 7.93 (1 H, s), 8.01 (0.5 H, d, $J = 8.1$ Hz), 8.18 (1 H, d, $J = 8.1$ Hz), 8.48 (0.5 H, s), 8.54 (1 H, d, $J = 8.1$ Hz), 9.27 (1 H, s); m/z (LCMS) requires $[\text{M} + \text{H}]^+$ $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2$ 309.1598, found 309.1597.

¹H NMR spectra for compounds 10-30 and 33-41































