Supporting Information for
A Diastereodivergent Synthetic Strategy for the Syntheses of
Communesin F and Perophoramidine.

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Materials and Methods.

Unless otherwise stated, reactions were performed in flame-dried glassware under an argon or nitrogen atmosphere using dry, deoxygenated solvents. Reaction progress was monitored by thin-layer chromatography (TLC). THF, Et₂O, CH₂Cl₂, toluene, benzene, CH₃CN, and dioxane were dried by passage through an activated alumina column under argon. Triethylamine was distilled over CaH₂ prior to use. Purified water was obtained using a Barnstead NANOpure Infinity UV/UF system. Brine solutions are saturated aqueous solutions of sodium chloride. Commercially available reagents were purchased from Sigma-Aldrich, Acros Organics, Strem, or Alfa Aesar and used as received unless otherwise stated. Reaction temperatures were controlled by an IKA® temperature modulator unless otherwise indicated. Microwave-assisted reactions were performed in a Biotage Initiator 2.5 microwave reactor. Glove box manipulations were performed under a N₂ atmosphere. TLC was performed using E. Merck silica gel 60 F254 precoated glass plates (0.25 mm) and visualized by UV fluorescence quenching, p-anisaldehyde, or PMA (phosphomolybdic acid) staining. Silicycle SiliaFlash P60 Academic Silica gel (particle size 0.040-0.064 mm) was used for flash column chromatography. ¹H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer and are reported relative to residual CHCl₃ (δ 7.26 ppm), or (CD₃)₂CO (δ 2.05 ppm). ¹³C NMR spectra are recorded on a Varian Inova 500 MHz spectrometer (125MHz) and are reported relative to CHCl₃ (δ 77.16 ppm), or (CD₃)₂CO (δ 29.84 ppm). Data for ¹H NMR are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, sept = septuplet, m = multiplet, br s = broad singlet, br d= broad doublet, app = apparent. Data for ¹³C are reported in terms of chemical shifts (δ ppm). IR spectra were obtained using a Perkin Elmer Paragon 1000 spectrometer using thin films deposited on NaCl plates and reported in frequency of absorption (cm⁻¹). High resolution mass spectra (HRMS) were obtained from Agilent 6200 Series TOF with an Agilent G1978A Multimode source in electrospray ionization (ESI+), atmospheric pressure chemical ionization (APCI+), or mixed ionization mode (MM: ESI-APCI+).
Experimental Procedures and Spectroscopic Data

**Oxoacetate SI-1.** To a solution of 4-bromoindole 9 (8.0 g, 40.8 mmol, 1.0 equiv) in Et₂O (204 mL) was added oxalyl chloride (9.25 mL, 102 mmol, 2.5 equiv) dropwise at 0 °C. The reaction mixture was stirred for 16 h at 23 °C. The resulting suspension was filtered and washed with cold ether. The filter cake was dried in vacuo to afford the oxoacetyl chloride, which was used without further purification.

To a solution of oxoacetyl chloride in Et₂O (204 mL) was added MeOH (10 mL) at 0 °C, and stirred for 2 h. The resulting mixture was concentrated in vacuo and purified by flash column chromatography (4:1 hexanes:EtOAc) on silica gel to give oxoacetate SI-1 (9.0 g, 78% yield, 2 steps).

R_f = 0.23 (1:1 hexane:EtOAc); ^1H NMR (500 MHz, CDCl₃) δ 9.01 (br, s, 1H), 8.27 (d, J = 3.2 Hz, 1H), 7.52 (dd, J = 7.6, 0.8 Hz, 1H), 7.42 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 7.8Hz, 1H), 3.95 (s, 3H); ^13C NMR (125 MHz, CDCl₃) δ 178.3, 164.0, 137.8, 136.2, 128.3, 125.3, 125.2, 115.3, 115.0, 111.0, 53.0; IR (Neat Film NaCl) 3206, 1656, 1500, 1410, 1306, 1252, 1196, 1139, 1104, 789, 770, 731 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C₁₁H₉BrNO₃ [M+H]^⁺: 281.9760; found: 281.9760.

**Alcohol SI-2.** To a solution of oxoacetate SI-1 (6.8 g, 24.1 mmol, 1.0 equiv) in THF (120 mL) was added LiAlH₄ (2.8 g, 72.3 mmol, 3.0 equiv) in portions at 0 °C. The reaction mixture was refluxed for 4 h. When the reaction was done, the solution was
cooled to 0 °C, and quenched by Fieser work-up. The suspension was filtered and the filter cake was washed with EtOAc. The combined organic phases were concentrated in vacuo, and extracted with EtOAc (3 x 100 mL). The combined organic layer was washed with brine, dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (1:1 hexane:EtOAc) on silica gel to give alcohol SI-2 (5.3 g, 91% yield).

Rₛ = 0.27 (1:1 hexane:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.18 (br, s, 1H), 7.31 (dd, J = 7.6, 0.8 Hz, 1H), 7.28 (dd, J = 7.6, 0.8 Hz, 1H), 7.12 (dd, J = 2.8 Hz, 1H), 7.01 (t, J = 7.8 Hz, 1H), 3.97 (t, J = 6.4 Hz, 2H), 3.28 (dt, J = 6.4, 0.8 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 137.8, 125.4, 124.1, 123.0, 114.4, 113.1, 110.6, 63.6, 29.5; IR (Neat Film NaCl) 3369, 2929, 1899, 1613, 1478, 1425, 1335, 1185, 1029, 913, 815, 770, 736 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C₁₀H₁₁BrNO [M+H]⁺: 240.0019; found: 240.0021.

Silyl ether 10. To a solution of alcohol SI-2 (8.1 g, 33.7 mmol, 1.0 equiv) in DMF (112 mL) was added imidazole (5.0 g, 74.2 mmol, 2.2 equiv) and TIPSCl (10.7 mL, 50.6 mmol, 1.5 equiv). After stirring for 3 h at 23 °C, water (10 mL) was added. The aqueous phase was extracted with Et₂O (3 x 100 mL). The combined organic phases were washed with brine, dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (9:1 hexanes:EtOAc) on silica gel to give silyl ether 10 (13.1 g, 98% yield).

Rₛ = 0.56 (4:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.06 (br, s, 1H), 7.30–7.25 (m, 2H), 7.12 (d, J = 2.4 Hz, 1H), 6.99 (t, J = 7.8 Hz, 1H), 4.00 (t, J = 7.1 Hz, 2H), 3.27 (t, J = 7.1 Hz, 2H), 1.05-1.07 (m, 21H); ¹³C NMR (125 MHz, CDCl₃) δ 137.4, 125.7, 124.4, 123.9, 122.6, 114.3, 114.1, 110.4, 64.9, 29.9, 18.1, 12.0; IR (Neat Film NaCl) 3425, 3286, 2942, 1614, 1516, 1549, 1463, 1425, 1382, 1336, 1246,
1184, 1102, 1064, 913, 883, 826, 772, 738 cm\(^{-1}\); HRMS (MM: ESI-APCI+) \(m/z\) calc’d for C\(_{19}\)H\(_{31}\)BrNOSi [M+H]\(^+\): 396.1353; found: 396.1357.

3-Bromooxindole 7. To a solution of indole 10 (5.0 g, 12.6 mmol, 1.0 equiv) in \(t\)-BuOH (100 mL), THF (25 mL), and water (1.1 mL) was added pyridinium tribromide (7.9 g, 24.6 mmol, 1.95 equiv). The reaction mixture was stirred for 30 min and then diluted with EtOAc (50 mL) and water (80 mL). The aqueous phase was extracted with EtOAc (3 x 150 mL). The combined organic phases were washed with brine, dried over MgSO\(_4\) and concentrated \(\textit{in vacuo}\). The residue was purified by flash column chromatography (4:1 hexanes:EtOAc) on silica gel to give 3-bromooxindole 7 (5.5 g, 89% yield).

\(R_f = 0.31\) (4:1 hexanes:EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 8.64 (br, s, 1H), 7.19 (dd, \(J = 8.1, 1.0\) Hz, 1H), 7.13 (t, \(J = 7.9\) Hz, 1H), 6.86 (dd, \(J = 7.6, 1.0\) Hz, 1H), 3.66 (ddd, \(J = 10.4, 5.5, 3.3\) Hz, 1H), 3.46 (td, \(J = 10.5, 3.8\) Hz, 1H), 3.08 (dt, \(J = 13.9, 3.5\) Hz, 1H), 2.90 (ddd, \(J = 13.9, 10.6, 5.4\) Hz, 1H), 0.87 (m, 21H); \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 175.8, 142.3, 131.2, 127.5, 127.0, 120.8, 109.5, 60.6, 56.1, 39.6, 17.8, 11.8; IR (Neat Film NaCl) 2941, 2864, 2109, 1728, 1613, 1583, 1312, 1102, 882, 744 cm\(^{-1}\); HRMS (MM: ESI-APCI+) \(m/z\) calc’d for C\(_{19}\)H\(_{30}\)Br\(_2\)NO\(_2\)Si [M+H]\(^+\): 490.0407; found: 490.0340.

Diallyl 2-(2-nitrophenyl)malonate 8. A 500 mL round-bottom flask with a magnetic stir bar was charged with diallyl malonate SI-3 (22.0 g, 118 mmol, 1.0 equiv), 1-fluoro-2-nitrobenzene (13.7 mL, 129 mmol, 1.1 equiv), and K\(_2\)CO\(_3\) (48.9 g, 354
mmol, 3.0 equiv). DMF (120 mL) was added and the brown suspension was heated to 90 °C for 16 h. The reaction mixture was cooled to ambient temperature and diluted with ice water (250 mL) and Et₂O (300 mL). The aqueous phase was extracted with Et₂O (3 x 300 mL). The combined organic phases were washed with brine, dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (9:1 hexanes:EtOAc) on silica gel to give arylated malonate 8 (32.1 g, 89% yield).

R_f = 0.51 (1:1 hexane:Et₂O); ¹H NMR (500 MHz, CDCl₃) δ 8.08 (dd, J = 8.5, 1.4 Hz, 1H), 7.66 (td, J = 7.6, 1.4 Hz, 1H), 7.55–7.51 (m, 2H), 5.90 (ddt, J = 17.3, 10.4, 5.7 Hz, 2H), 5.38 (s, 1H), 5.34–5.23 (m, 4H), 4.70 (dt, J = 5.8, 1.4 Hz, 4H); ¹³C NMR (125MHz, CDCl₃) δ 166.8, 148.7, 133.6, 131.4, 131.1, 129.3, 127.9, 125.3, 119.1, 66.8, 54.3; IR (Neat Film NaCl) 3086, 2950, 1738, 1611, 1530, 1447, 1350, 1154, 991, 937, 852, 787, 722 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C₁₅H₁₆NO₆ [M+H]⁺: 306.0972; found: 306.0930.

Oxindole 5. To a solution of 3-bromooxindole 7 (5.6 g, 11.4 mmol, 1.0 equiv) and malonate 8 (5.2 g, 17.1 mmol, 1.5 equiv) in THF was added Cs₂CO₃ (7.4 g, 22.8 mmol, 2.0 equiv) at 0 °C. The reaction mixture was stirred for 1 h at 0 °C. Solids were removed via a filtration through a celite plug and the resulting solution was concentrated under reduced pressure. The residue was purified by flash column chromatography (9:1 → 4:1 hexanes:EtOAc) on silica gel to give desired alkylated product 5 (5.4 g, 95% yield).

R_f = 0.18 (3:1 hexane:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 9.01 (dd, J = 8.3, 1.3 Hz, 1H), 7.90 (dd, J = 8.1, 1.5 Hz, 1H), 7.68 (ddd, J = 8.5, 7.4, 1.6 Hz, 1H), 7.55 (d, J = 5.3 Hz, 1H), 7.51 (td, J = 7.7, 1.2 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 6.93 (dd, J = 8.1, 1.0 Hz, 1H), 6.78 (dd, J = 7.6, 1.0 Hz, 1H), 5.92–5.81 (m, 2H), 5.76–5.68 (m, 1H), 5.26–5.18 (m, 2H), 5.17–5.10 (m, 2H), 4.76–4.69 (m, 1H), 4.68–4.63 (m, 1H),
Methyloxindole SI-4. To a solution of oxindole 5 (5.6 g, 11.2 mmol, 1.0 equiv) in THF (56 mL) was added Cs₂CO₃ (10.9 g, 33.6 mmol, 3.0 equiv) and MeI (4.3 mL, 67.2 mmol, 6.0 equiv) at 0 °C. Then, the reaction mixture was stirred for 12 h at 23 °C. After the reaction was done, sat. NH₄Cl was added. The aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic phases were washed with brine (50 mL), dried over MgSO₄ and concentrated \textit{in vacuo}. The residue was purified by flash column chromatography (7:1 hexanes:EtOAc) on silica gel to give methylated oxindole SI-4 (7.5 g, 92% yield).

\begin{align*}
\text{R}_f &= 0.38 \text{ (4:1 hexanes:EtOAc)}; \\
\text{H NMR (500 MHz, CDCl}_3\text{)} &\delta 9.01 \text{ (dd, } J = 8.3, 1.3 \\
\text{Hz, 1H)}, 7.91 \text{ (dd, } J = 8.1, 1.6 \text{ Hz, 1H)}, 7.69 \text{ (ddd, } J = 8.5, 7.3, 1.6 \text{ Hz, 1H)}, 7.54–7.50 \text{ (m, 1H)}, 7.10 \text{ (t, } J = 8.0 \text{ Hz, 1H)}, 6.95 \text{ (dd, } J = 8.1, 1.0 \text{ Hz, 1H)}, 6.78 \text{ (dd, } J = 7.8, 1.0 \text{ Hz, 1H}), 5.88 \text{ (ddt, } J = 16.5, 10.4, 5.8 \text{ Hz, 1H}), 5.71 \text{ (ddt, } J = 16.7, 10.2, 6.3 \text{ Hz, 1H}), 5.27–5.11 \text{ (m, 4H)}, 4.78 \text{ (ddt, } J = 13.1, 6.0, 1.4 \text{ Hz, 1H}), 4.68 \text{ (ddt, } J = 13.1, 5.6, 1.5 \text{ Hz, 1H}), 4.47 \text{ (ddt, } J = 12.7, 6.3, 1.2 \text{ Hz, 1H}), 4.21 \text{ (ddt, } J = 12.8, 6.4, 1.2 \text{ Hz, 1H}), 3.24 \text{ (s, 3H)}, 3.20–3.15 \text{ (m, 3H)}, 3.00–2.93 \text{ (m, 1H)}, 0.91 \text{ (s, 21H)}; \\
\text{C NMR (125 MHz, CDCl}_3\text{)} &\delta 176.14, 167.03, 165.81, 152.74, 147.67, 147.67, 133.81, 131.78, 131.42, 131.19, 129.73, 129.21, 128.45, 126.99, 126.85, 126.54, 121.57, 119.44, 106.83, 67.43, 66.37, 65.91, 59.57, 57.96, 32.75, 26.77, 17.90, 11.85; \text{IR (Neat Film NaCl)} 2917, 2863, 1721, 1600, 1529, 1450, 1350, 1231, 1088, 923, 883, 852 \text{ cm}^{-1};
\end{align*}
HRMS (MM: ESI-APCI+) m/z calc’d for C_{35}H_{46}BrN_{2}O_{8}Si [M+H]^+ : 729.2201; found: 729.2240.

Lactone 11. To a 20 mL microwave vial with a magnetic stir bar were added oxindole SI-4 (500 mg, 0.69 mmol, 1.0 equiv), p-TsOH (520 mg, 2.7 mmol, 4.0 equiv), and benzene (20 mL). The reaction was sealed with a microwave crimp cap and subjected to microwave irradiation in a Biotage Initiator microwave reactor (temperature: 85 °C, sensitivity: low) with a gradual temperature increase over 10 min (10 °C increments). After 20 min of stirring, the vial was cooled to ambient temperature and uncapped. The reaction was diluted with EtOAc (10 mL) and quenched by addition of sat. NaHCO_3. The phases were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic phases were dried over MgSO_4, and concentrated in vacuo. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford lactone 11 (300 mg, 85% yield).

R_f = 0.23 (1:1 hexane:EtOAc); ^1H NMR (300 MHz, CDCl_3) δ 8.11 (dd, J = 8.1, 1.6 Hz, 1H), 7.99 (dd, J = 8.1, 1.3 Hz, 1H), 7.71 (dd, J = 9.1, 7.6 Hz, 1H), 7.59 (dd, J = 8.1, 7.4, 1.3 Hz, 1H), 7.11 (t, J = 8.0 Hz, 1H), 6.96 (dd, J = 8.1, 1.0 Hz, 1H), 6.87 (dd, J = 7.8, 1.0 Hz, 1H), 5.71 (ddt, J = 17.2, 10.4, 6.1 Hz, 1H), 5.18–5.07 (m, 3H), 4.71 (td, J = 11.0, 10.4, 7.4 Hz, 1H), 4.55 (ddt, J = 12.9, 5.9, 1.3 Hz, 1H), 4.26 (ddt, J = 12.9, 6.2, 1.3 Hz, 1H), 3.63 (ddd, J = 15.2, 13.1, 7.3 Hz, 1H), 3.34 (s, 3H), 1.67 (dd, J = 15.2, 5.3 Hz, 1H); ^13C NMR (125 MHz, CDCl_3) δ 175.1, 165.3, 165.1, 152.1, 146.0, 133.4, 132.0, 131.0, 130.4, 130.1, 130.0, 127.7, 127.7, 127.5, 119.1, 107.8, 67.8, 67.0, 64.8, 60.4, 54.5, 27.0, 24.2; IR (Neat Film NaCl) 2929, 1742, 1713, 1601, 1532, 1456, 1353, 1192, 1112, 1058, 1033, 993, 936, 856, 767 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C_{25}H_{20}BrN_{2}O_{7} [M+H]^+ : 515.0448; found: 515.0450.
Allyl 4. To a 250 mL round-bottom flask with a magnetic stir bar was added lactone 11 (2.5 g, 4.9 mmol, 1.0 equiv). The flask was brought into a N₂-filled glove box, and then Pd(PPh₃)₄ (0.1 g, 0.097 mmol, 0.02 equiv) was added. The reaction mixture was brought out from the glove box and treated with THF (97 mL). After 5 min stirring, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford allylated product 4 (2.0 g, 97% yield).

Rᵥ = 0.24 (1:1 hexane:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 7.66 (dd, J = 8.0, 1.6 Hz, 1H), 7.40 (t, J = 7.7 Hz, 1H), 7.20 (dd, J = 9.6, 6.5 Hz, 2H), 7.01 (d, J = 8.1 Hz, 1H), 6.92 (d, J = 7.7 Hz, 1H), 6.48 (d, J = 8.1 Hz, 1H), 5.52 (ddt, J = 16.6, 12.0, 6.4 Hz, 1H), 5.43–5.35 (m, 1H), 4.79–4.72 (m, 3H), 4.32 (td, J = 13.7, 7.2 Hz, 1H), 3.31 (s, 3H), 3.13 (dd, J = 15.6, 5.0 Hz, 1H), 2.43–2.36 (m, 1H), 1.73 (dd, J = 14.7, 5.0 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 175.5, 169.8, 152.4, 146.0, 134.7, 134.3, 130.9, 130.7, 130.4, 128.5, 128.3, 126.0, 125.2, 124.0, 117.8, 107.6, 64.7, 56.7, 54.2, 42.9, 26.4, 23.8; IR (Neat Film NaCl) 3418, 2923, 1709, 1601, 1532, 1455, 1361, 1292, 1201, 1113, 1069, 986, 917, 777, 736 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C₂₂H₂₀BrN₂O₅ [M+H]⁺: 471.0550; found: 471.0552.

Bis-oxindole 12. To a solution of lactone 4 (2.4 g, 5.6 mmol, 1.0 equiv) in H₂O (282 mL) and MeOH (565 mL) were added NH₄OAc (43.5 g, 564 mmol, 100.0 equiv) and TiCl₃ (10% w/w, 70.3 mL, 56.4 mmol, 10.0 equiv). Then, the reaction was stirred for 12 h at 23 °C. The reaction mixture was diluted with EtOAc (500 mL) and then the phases were separated and the aqueous phase was extracted with EtOAc (3 x 300
mL). The combined organic phases were dried over MgSO\(_4\), and concentrated \textit{in vacuo}. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford bis-oxindole 12 (1.99 g, 80% yield).

R\(_f\) = 0.10 (1:1 hexane:EtOAc); \(^1\)H NMR (500 MHz, DMSO) \(\delta\) 10.33 (s, 1H), 6.98 (dd, \(J = 8.1, 1.0\) Hz, 1H), 6.96–6.87 (m, 2H), 6.77–6.67 (m, 2H), 6.58 (dd, \(J = 7.8, 1.0\) Hz, 1H), 6.45 (d, \(J = 7.6\) Hz, 1H), 4.96 (ddt, \(J = 16.7, 9.7, 6.9\) Hz, 1H), 4.86 (dd, \(J = 17.0, 2.5\) Hz, 1H), 4.74 (dd, \(J = 9.9, 2.6\) Hz, 1H), 4.39 (t, \(J = 5.0\) Hz, 1H), 3.41–3.32 (m, 2H), 3.22–3.13 (m, 1H), 3.03 (s, 3H), 2.86 (dd, \(J = 10.3, 7.9, 5.5\) Hz, 1H), 2.76 (dd, \(J = 13.5, 6.8\) Hz, 1H), 2.24 (dt, \(J = 13.2, 7.9\) Hz, 1H); \(^{13}\)C NMR (125 MHz, DMSO) \(\delta\) 177.5, 175.8, 146.5, 142.8, 133.4, 130.2, 128.5, 128.1, 126.9, 126.8, 123.5, 120.4, 119.3, 118.9, 108.9, 107.4, 58.4, 57.2, 56.0, 33.5, 28.9, 26.3; IR (Neat Film NaCl) 2917, 2356, 1697, 1599, 1574, 1455, 1349, 1184, 910, 752 cm\(^{-1}\); HRMS (MM: ESI-APCI+) \(m/z\) calc’d for C\(_{22}\)H\(_{22}\)BrN\(_2\)O\(_3\) [M+H\(^+\)]: 441.0808; found 441.0812.

**Silyl ether SI-5.** Bis-oxindole 12 (1.66 g, 3.76 mmol, 1.0 equiv) was dissolved in DMF (18.8 mL) to which TIPSCI (1.61 mL, 7.52 mmol, 2.0 equiv) and imidazole (1.02 g, 15.0 mmol, 4.0 equiv) were added at 0 °C. The reaction was slowly warmed to 23 °C, and stirred for 12 h. The reaction mixture was extracted with EtOAc (3 x 40 mL), and washed with brine. The combined organic phases were dried over MgSO\(_4\), and concentrated \textit{in vacuo}. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford TIPS protected compound SI-5 (2.02 g, 90% yield).

R\(_f\) = 0.20 (4:1 hexanes:EtOAc); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.70 (s, 1H), 6.97 (dd, \(J = 8.2, 1.0\) Hz, 1H), 6.94 (tt, \(J = 7.6, 1.1\) Hz, 1H), 6.86 (d, \(J = 7.5\) Hz, 1H), 6.84–6.80 (m, 1H), 6.76 (t, \(J = 7.5\) Hz, 1H), 6.49 (d, \(J = 7.8\) Hz, 1H), 6.28 (dd, \(J = 7.8, 1.0\) Hz, 1H), 5.10 (ddt, \(J = 16.9, 9.9, 7.1\) Hz, 1H), 4.97 (dd, \(J = 17.1, 2.1\) Hz, 1H), 4.77 (dd, \(J = 9.9, 2.2\) Hz, 1H), 3.73 (ddd, \(J = 8.7, 5.7, 2.6\) Hz, 1H), 3.57 (dd, \(J = 13.6, 7.1\) Hz, 1H).
Hz, 1H), 3.47–3.41 (m, 2H), 3.05 (s, 3H), 2.97 (dd, J = 13.6, 7.1 Hz, 1H), 2.60 (ddd, J = 15.0, 11.5, 5.6 Hz, 1H), 0.87–0.82 (m, 2H); 13C NMR (125 MHz, CDCl3) δ 178.1, 175.8, 146.3, 140.9, 132.6, 128.2, 127.0, 126.8, 123.7, 120.6, 119.4, 119.1, 108.5, 106.2, 60.9, 57.7, 56.8, 33.0, 28.8, 25.9, 17.8, 17.8, 11.8; IR (Neat Film NaCl) 3191, 3081, 2942, 2865, 2251, 2699, 1602, 1471, 1337, 1236, 1108, 995, 920, 736 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C33H45BrN2O3Si [M+H]+: 655.2143; found 655.2141.

Carbamate 13. To a stirred solution of bis-oxindole SI-5 (350 mg, 0.59 mmol, 1.0 equiv) in CH2Cl2 (5.86 mL) were added DMAP (7 mg, 0.059 mmol, 0.1 equiv), Et3N (0.812 mL, 5.9 mmol, 10.0 equiv), and methyl chloroformate (0.16 mL, 1.76 mmol, 3.0 equiv) at 0 °C. The reaction was slowly warmed to 23 °C, and stirred for 12 h. The solvent was concentrated in vacuo, and then the residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford carbamate 13 (377 mg, 98% yield). Rf = 0.61 (4:1 hexanes:EtOAc); 1H NMR (500 MHz, CDCl3) δ 7.53 (dt, J = 8.2, 0.8 Hz, 1H), 7.05 (ddd, J = 8.1, 6.1, 2.9 Hz, 1H), 6.96 (dd, J = 8.2, 1.0 Hz, 1H), 6.92–6.91 (m, 2H), 6.82 (t, J = 7.9 Hz, 1H), 6.25 (dd, J = 7.8, 1.0 Hz, 1H), 5.06 (ddt, J = 16.6, 9.6, 6.9 Hz, 1H), 5.00 – 4.95 (m, 1H), 4.81–4.78 (m, 1H), 4.00 (s, 3H), 3.72 (ddd, J = 10.2, 5.7, 3.1 Hz, 1H), 3.61 (ddt, J = 13.8, 6.9, 1.0 Hz, 1H), 3.43 (td, J = 10.4, 3.9 Hz, 1H), 3.33–3.28 (m, 1H), 3.02 (m, 4H), 2.62 (ddd, J = 14.0, 10.6, 5.7 Hz, 1H), 0.87–0.81 (m, 21H); 13C NMR (125 MHz, CDCl3) δ 175.3, 174.2, 151.3, 146.1, 139.5, 132.0, 129.6, 128.6, 127.1, 126.5, 126.2, 123.2, 122.7, 119.9, 119.0, 113.9, 106.3, 60.7, 58.4, 57.3, 53.7, 33.4, 28.9, 26.0, 17.7, 11.8; IR (Neat Film NaCl) 2942, 2865, 2089, 1722, 1612, 1463, 1348, 1201, 1243, 1166, 1104, 1026, 920, 883, 736, 772 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C33H45BrN2O3Si [M+H]+: 655.2197; found 655.2199.
Aldehyde 14. To a 25 mL round bottom flask with magnetic stir bar was added alkene 13 (260 mg, 0.40 mmol, 1.0 equiv) and CH$_2$Cl$_2$ (2.0 mL). The flask was connected to an ozone generator, and purged with oxygen gas (flow: 0.5), for 5 min at –78 °C and then ozone gas (flow: 0.5) was bubbled through into the reaction solution for 10 min at –78 °C. After the reaction was done, oxygen gas was bubbled into the reaction mixture for 20 min and PPh$_3$ (313 mg, 1.19 mmol, 3.0 equiv) was added. The reaction mixture was slowly warmed to ambient temperature, stirred for 16 h, and then concentrated under reduced pressure. The residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford aldehyde 14 (245 mg, 94% yield).

R$_f$ = 0.13 (4:1 hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) δ 9.46 (d, $J$=1.0 Hz, 1H), 7.56 (d, $J$ = 8.1 Hz, 1H), 7.06–7.01 (m, 1H), 6.99 (d, $J$ = 8.1 Hz, 1H), 6.88–6.82 (m, 2H), 6.75 (d, $J$ = 7.6 Hz, 1H), 6.23 (d, $J$ = 7.8 Hz, 1H), 4.33 (d, $J$ = 19.4 Hz, 1H), 4.02 (s, 3H), 3.72 (ddd, $J$ = 9.3, 5.6, 2.7 Hz, 1H), 3.58 (dd, $J$ = 19.3, 1.2 Hz, 1H), 3.42 (td, $J$ = 10.3, 3.4 Hz, 1H), 3.23 (dt, $J$ = 14.0, 3.4 Hz, 1H), 2.99 (s, 3H), 2.56–2.48 (m, 1H), 0.86–0.79 (m, 21H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 197.9, 175.4, 174.4, 151.3, 146.0, 140.0, 129.9, 128.8, 127.2, 126.5, 125.2, 122.6, 121.4, 119.3, 114.1, 106.5, 60.6, 58.2, 53.8, 52.8, 44.6, 28.9, 26.0, 17.7, 11.8; IR (Neat Film NaCl) 2942, 2865, 2255, 1773, 1718, 1603, 1576, 1459, 1351, 1295, 1245, 1163, 1108, 914, 883, 771, 732 cm$^{-1}$; HRMS (MM: ESI-APCI+) m/z calc’d for C$_32$H$_{41}$BrN$_2$O$_6$Si [M+H]$^+$: 657.1990; found: 657.1991.
Amide 16. To a solution of aldehyde 14 (100 mg, 0.13 mmol, 1.0 equiv) and o-nitrobenzylammonium acetate 15 (97 mg, 0.38 mmol, 3.0 equiv) in MeOH (7.6 mL) was added NaBH$_3$CN (21 mg, 0.26 mmol, 2.0 equiv) in THF (3.8 mL) at 0 °C. The reaction mixture was slowly warmed to ambient temperature and stirred for 12 h. Then, H$_2$O (5 mL) was added and extracted with EtOAc (3 x 20 mL), and washed with brine. The combined organic phases were dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford o-nitrobenzyl protected amide 16 (116 mg, 97% yield).

R$_f$ = 0.35 (2:1 hexanes:EtOAc); (Due to the distinct presence of rotameric isomers, the $^1$H NMR and $^{13}$C NMR contained extra peaks. See the attached spectrum), $^1$H NMR (500 MHz, CDCl$_3$) δ 11.63 (s, 1H), 8.06–7.97 (m, 2H), 7.51 (td, $J$ = 7.6, 1.5 Hz, 1H), 7.42 (t, $J$ = 8.0 Hz, 1H), 7.25–7.18 (m, 2H), 7.13 (dd, $J$ = 14.1, 8.2 Hz, 2H), 7.05 (t, $J$ = 7.9 Hz, 1H), 6.97–6.90 (m, 1H), 6.53 (d, $J$ = 7.6 Hz, 1H), 5.32 (d, $J$ = 16.5 Hz, 1H), 4.71 (dd, $J$ = 16.4, 6.5 Hz, 1H), 3.70–3.63 (m, 2H), 3.57 (td, $J$ = 6.3, 2.9 Hz, 1H), 3.55–3.51 (m, 1H), 3.35–3.26 (m, 2H), 2.92 (ddd, $J$ = 13.1, 5.4, 3.3 Hz, 1H), 2.84 (s, 1H), 2.69 (ddd, $J$ = 19.4, 8.7, 5.3 Hz, 2H), 2.63 (s, 3H), 0.85 (t, $J$ = 4.1 Hz, 21H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 176.0, 175.4, 154.4, 148.7, 147.1, 139.7, 134.1, 132.1, 131.2, 130.0, 129.4, 128.8, 128.7, 127.6, 126.6, 126.0, 125.3, 122.1, 121.8, 121.3, 107.3, 60.9, 60.6, 60.4, 51.6, 46.0, 45.1, 31.8, 31.6, 25.9, 17.9, 11.9; IR (Neat Film NaCl) 3418, 2943, 2865, 1717, 1601, 1527, 1456, 1338, 1313, 1282, 1227, 1113, 1069, 911, 883, 857, 730 cm$^{-1}$; HRMS (MM: ESI-APCI+) m/z calc’d for C$_{39}$H$_{50}$BrN$_4$O$_7$Si [M+H]$^+$: 793.2627; found: 793.2658.

Propellane hexacycle 17. To a solution of amide 16 (54.1 mg, 0.087 mmol, 1.0 equiv) in CH$_2$Cl$_2$ (6.82 mL), was added Tf$_2$O (34 mL, 0.26 mmol, 3.0 equiv) dropwise at 0 °C. The reaction mixture was slowly warmed to 23 °C, and stirred for 2 h. After the reaction was done, the solution was brought to pH 10.5-11.0 by addition of sat.
NaHCO₃. The reaction mixture was extracted with EtOAc (3 x 6 mL) and washed with brine. The combined organic phases were dried over MgSO₄ and concentrated *in vacuo*. The residue was purified by column chromatography (2:1 hexanes:EtOAc) on silica gel to afford propellane hexacycle 17 (39.6 mg, 75% yield). $R_f = 0.46$ (1:1 hexane:EtOAc); $^1$H NMR (500 MHz, CDCl₃) δ 7.82 (dd, $J = 7.9, 1.2$ Hz, 1H), 7.72–7.58 (m, 1H), 7.46–7.40 (m, 2H), 7.30 (ddd, $J = 8.0, 6.7, 2.2$ Hz, 1H), 7.21–7.14 (m, 1H), 6.99–6.93 (m, 2H), 6.81–6.76 (m, 1H), 6.64 (dd, $J = 7.4, 1.4$ Hz, 1H), 6.36 (dd, $J = 7.7, 1.3$ Hz, 1H), 4.61 (d, $J = 16.6$ Hz, 1H), 4.54 (d, $J = 18.2$ Hz, 1H), 4.45 (td, $J = 11.4, 6.5$ Hz, 1H), 4.18–4.11 (m, 1H), 3.72 (d, $J = 9.4$ Hz, 1H), 3.21 (s, 3H), 3.11–3.02 (m, 1H), 2.96–2.87 (m, 1H), 2.51 (dt, $J = 14.4, 9.0$ Hz, 2H), 1.94–1.81 (m, 2H); $^{13}$C NMR (125 MHz, CDCl₃) δ 177.6, 153.5, 148.9, 145.8, 144.4, 142.1, 136.2, 132.9, 131.0, 130.0, 129.6, 129.1, 128.1, 127.3, 125.1, 124.3, 123.1, 116.1, 111.9, 106.8, 64.5, 58.4, 56.5, 54.5, 52.6, 50.0, 47.9, 33.9, 26.5, 22.8; IR (Neat Film NaCl) 2953, 2360, 1721, 1599, 1573, 1524, 1483, 1455, 1367, 1242, 1134, 1088, 1134, 947, 856, 761, 733 cm⁻¹; HRMS (MM: ESI-APCI+) $m/z$ calc’d for C₃₀H₂₈BrN₄O₆ [M+H]+: 619.1187; found: 619.1188.

**Aminal 18.** To a solution of propellane hexacyclic oxindole 17 (14.6 mg, 0.024 mmol, 1.0 equiv) in CH₂Cl₂ (2.4 mL) was added DIBAL (1.0 M in THF; 0.12 mL, 0.12 mmol, 5 equiv) dropwise at −78 °C. After the reaction mixture was stirred for 1 h at −78 °C, the solution was warmed to 0 °C and DIBAL (1.0 M in THF; 24 mL, 0.024 mmol, 1.0 equiv) was added dropwise. The mixture was stirred for 1 h at 0 °C, and more DIBAL (1.0 M in THF; 24 mL, 0.024 mmol, 1.0 equiv) was added dropwise. The reaction mixture was stirred for 1 h at 0 °C, and warmed to 23 °C. To the reaction mixture was added Et₂AlCl (1.0 M in hexanes; 48 mL, 0.048 mmol, 2.0 equiv) dropwise. The reaction was stirred for 30 min and quenched with aq. NH₄Cl (1 mL) and aq. potassium sodium tartrate (1 mL). The reaction mixture was washed...
with EtOAc (3 x 3 mL), and brine. The combined organic phases were dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford aminal 18 (8.9 mg, 60% yield).

$R_f = 0.12$ (1:1 hexane:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 8.01 (dd, $J = 8.2, 1.3$ Hz, 1H), 7.58 (td, $J = 7.6, 1.3$ Hz, 1H), 7.50–7.48 (m, 1H), 7.44 (ddd, $J = 8.6, 7.4, 1.5$ Hz, 1H), 7.37–7.34 (m, 1H), 7.23–7.19 (m, 1H), 7.09–7.05 (m, 1H), 6.81 (t, $J = 7.9$ Hz, 1H), 6.69 (dd, $J = 8.0, 1.0$ Hz, 1H), 6.26 (s, 1H), 6.01 (dd, $J = 7.9, 0.9$ Hz, 1H), 5.41 (d, $J = 16.3$ Hz, 1H), 4.56 (d, $J = 16.2$ Hz, 1H), 3.86 (s, 3H), 3.73–3.64 (m, 2H), 3.56 (td, $J = 9.5, 7.4$ Hz, 1H), 3.24–3.18 (m, 1H), 3.09 (ddd, $J = 13.6, 8.6, 5.3$ Hz, 1H), 2.95 (ddd, $J = 14.2, 7.4, 1.7$ Hz, 1H), 2.48 (s, 3H), 2.35 (ddd, $J = 13.2, 8.5, 6.2$ Hz, 1H), 1.78 (dt, $J = 14.2, 9.4$ Hz, 1H), 1.74 (br, s, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 171.5, 171.3 152.6, 148.9, 138.8, 136.3, 133.7, 132.1, 130.4, 129.7, 128.4, 126.9, 126.2, 126.0, 125.0, 124.8, 122.7, 122.2, 104.6, 83.2, 64.4, 60.7, 60.4, 53.3, 53.1, 45.3, 44.5, 35.2, 33.0, 31.0; IR (Neat Film NaCl) 2955, 2357, 1694, 1595, 1524, 1444, 1335, 1281, 1073, 1032, 911, 857, 835, 730 cm$^{-1}$; HRMS (MM: ESI-APCI+) $m/z$ calc’d for C$_{30}$H$_{30}$BrN$_4$O$_6$ [M+H]$^+$: 621.1343; found: 621.1286.

**Amide 3.** A solution of aminal 18 (21.5 mg, 0.035 mmol, 1.0 equiv) in anhydrous MeOH (3.5 mL) in a Pyrex flask was purged with N$_2$ for 5 min. The reaction mixture was irradiated in a cylindrical photoreactor with 254 nm lamps under N$_2$ for 3 h and concentrated. The residue was purified by column chromatography (4:1 CH$_2$Cl$_2$:acetone) on silica gel to afford aminal 3 (6.7 mg, 40% yield). See below for characterization data.
Amide 3. To a solution of o-nitrobenzyl protected aminal 18 (10.8 mg, 0.017 mmol, 1.0 equiv) in MeOH (0.8 mL) was added 20% aq NaOH (0.2 mL) and the mixture was stirred for 4 h at 75 °C. After the reaction mixture was cooled to 23 °C, it was diluted with water and extracted with EtOAc (3 x 2 mL). The organic layer was washed with brine, dried over MgSO₄, concentrated in vacuo. The residue was purified by column chromatography (4:1 CH₂Cl₂:acetone) to afford compound 3 (5.9 mg, 70% yield).

R_f = 0.18 (4:1 CH₂Cl₂:acetone); ¹H NMR (500 MHz, CDCl₃) δ 7.51–7.45 (m, 1H), 7.19 (td, J = 7.6, 1.4 Hz, 1H), 7.05 (td, J = 7.7, 1.4 Hz, 1H), 6.80 (d, J = 7.9 Hz, 1H), 6.69 (dt, J = 8.0, 1.0 Hz, 1H), 6.60 (br, s, 1H), 6.25 (br, s, 1H), 5.99 (dd, J = 7.9, 0.9 Hz, 1H), 3.87 (s, 3H), 3.74–3.63 (m, 2H), 3.55 (td, J = 9.4, 7.3 Hz, 1H), 3.33 (ddd, J = 9.8, 8.8, 1.5 Hz, 1H), 3.17 (ddd, J = 13.6, 8.4, 5.6 Hz, 1H), 2.93–2.96 (m, 1H), 2.49 (s, 3H), 2.36 (ddd, J = 13.2, 8.2, 6.3 Hz, 1H), 1.92 (dt, J = 14.0, 9.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 174.8, 155.4, 152.9, 138.6, 136.4, 130.4, 126.9, 126.6, 126.1, 125.0, 122.4, 104.6, 83.2, 76.9, 60.9, 60.6, 53.5, 52.3, 40.4, 35.8, 35.2, 31.1; IR (Neat Film NaCl) 3418, 2955, 2357, 1693, 1593, 1446, 1335, 1282, 1032, 836, 754 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C₂₃H₂₅BrN₃O₄ [M+H]+ : 486.1023; found: 486.1004.

Diallyl 2-(4-bromo-2-nitrophenyl)malonate 24. A 500 mL round-bottom flask with a magnetic stir bar was charged with diallyl malonate SI-3 (15.0 g, 81.5 mmol, 1.0 equiv), 4-bromo-1-fluoro-2-nitrobenzene (11.0 mL, 89.7 mmol, 1.1 equiv), and
K₂CO₃ (33.8 g, 245 mmol, 3.0 equiv). DMF (163 mL) was added and the brown suspension was heated to 90 °C for 16 h. The reaction mixture was cooled to ambient temperature and diluted with ice water (250 mL) and Et₂O (300 mL). The aqueous phase was extracted with Et₂O (3 x 300 mL). The combined organic phases were washed with brine, dried over MgSO₄ and concentrated in vacuo. The residue was purified by flash column chromatography (9:1 hexanes:EtOAc) on silica gel to give arylated malonate 24 (32.1 g, 80% yield).

R_f = 0.69 (1:1 hexane:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, J = 2.1 Hz, 1H), 7.77 (dd, J = 8.4, 2.1 Hz, 1H), 7.43 (d, J = 8.4 Hz, 1H), 5.94–5.84 (m, 2H), 5.37–5.24 (m, 5H), 4.70 (dt, J = 5.9, 1.3 Hz, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 166.4, 149.1, 136.5, 132.8, 131.0, 128.2, 126.8, 122.8, 119.3, 66.9, 53.8; IR (Neat Film NaCl) 3085, 2986, 2951, 1733, 1649, 1538, 1348, 1283, 1218, 1148, 989, 936 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C₁₅H₁₃BrNO₆ [M+H]⁺: 384.0077; found: 384.0072.

**Oxindole SI-6.** To a solution of 3-bromooxindole 23 (2.0 g, 4.85 mmol, 1.0 equiv) and malonate 24 (3.7 g, 9.70 mmol, 2.0 equiv) in THF (49 mL) was added Cs₂CO₃ (3.2 g, 9.70 mmol, 2.0 equiv) at 0 °C. The reaction mixture was warmed to 23 °C and stirred overnight. Solids were removed via a filtration through a celite plug and the resulting solution was concentrated under reduced pressure. The residue was purified by flash column chromatography (9:1 → 4:1 hexanes:EtOAc) on silica gel to give desired alkylated product SI-6 (3.3g, 96% yield).

R_f = 0.33 (4:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.00 (br, s, 1H), 7.95 (d, J = 8.9 Hz, 1H), 7.86 (d, J = 2.3 Hz, 1H), 7.53 (dd, J = 8.8, 2.3 Hz, 1H), 7.43–7.39 (m, 1H), 7.16 (td, J = 7.7, 1.2 Hz, 1H), 6.92 (td, J = 7.7, 1.1 Hz, 1H), 6.75–6.72 (m, 1H), 5.79 (dddt, J = 33.6, 17.2, 10.4, 5.9 Hz, 2H), 5.26–5.14 (m, 4H), 4.66 (qdt, J = 13.2, 5.9, 1.4 Hz, 2H), 4.55–4.42 (m, 2H), 3.32 (dt, J = 9.7, 7.5 Hz, 1H), 3.09 (ddd, J
= 9.8, 8.5, 4.5 Hz, 1H), 2.89–2.82 (m, 1H), 2.63 (ddd, J = 12.7, 8.1, 4.5 Hz, 1H), 0.89 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 178.0, 166.6, 166.2, 150.9, 140.9, 134.3, 134.1, 131.3, 130.8, 129.0, 128.3, 127.2, 122.7, 122.2, 119.6, 119.0, 109.5, 67.2, 67.1, 66.9, 59.7, 57.0, 38.4, 18.0, 11.9; IR (Neat Film NaCl) 3203, 2943, 2865, 1716, 1619, 1538, 1471, 1357, 1229, 1111, 992, 935, 753, 735 cm$^{-1}$; HRMS (MM: ESI-APCI+) m/z calc’d for C$_{34}$H$_{44}$BrN$_2$O$_8$Si [M+H]$^+$: 715.2045; found: 715.2090.

Methyloxindole 22. To a solution of oxindole SI-6 (14.1 g, 0.0197 mol, 1.0 equiv) in THF (106 mL) was added Cs$_2$CO$_3$ (19.3 g, 0.0591 mol, 3.0 equiv) and MeI (7.40 mL, 0.118 mol, 6.0 equiv) at 0 °C. Then, the reaction mixture was stirred for 12 h at 23 °C. After the reaction was done, sat. NH$_4$Cl was added. The aqueous phase was extracted with EtOAc (3 x 100 mL). The combined organic phases were washed with brine (50 mL), dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by flash column chromatography (7:1 hexanes:EtOAc) on silica gel to give methylated oxindole 22 (13.2 g, 92% yield).

R$_f$ = 0.40 (4:1 hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.89 (d, J = 8.9 Hz, 1H), 7.76 (d, J = 2.3 Hz, 1H), 7.53–7.48 (m, 2H), 7.21 (td, J = 7.7, 1.2 Hz, 1H), 6.95 (td, J = 7.6, 1.1 Hz, 1H), 6.69–6.66 (m, 1H), 5.85 (ddt, J = 17.2, 10.4, 5.9 Hz, 1H), 5.74 (ddt, J = 17.2, 10.4, 5.9 Hz, 1H), 5.26–5.20 (m, 2H), 5.18 (ddt, J = 10.4, 2.2, 1.2 Hz, 2H), 4.72–4.63 (m, 2H), 4.54 (ddt, J = 13.1, 6.0, 1.4 Hz, 1H), 4.40 (ddt, J = 13.0, 6.0, 1.3 Hz, 1H), 3.18–3.13 (m, 1H), 3.13 (s, 3H), 3.05 (ddd, J = 9.9, 7.9, 4.7 Hz, 1H), 2.82 (dt, J = 13.0, 7.6 Hz, 1H), 2.71 (ddd, J = 12.8, 7.6, 4.7 Hz, 1H), 0.90–0.84 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 176.3, 166.3, 166.2, 150.8, 143.7, 134.4, 133.4, 131.1, 130.8, 128.8, 128.1, 128.0, 127.0, 122.5, 122.1, 119.4, 119.0, 107.6, 67.0, 66.9, 59.6, 56.8, 37.9, 26.3, 17.8, 17.8, 11.8; IR (Neat Film NaCl) 2943, 2865, 1747, 1619, 1538, 1471, 1357, 1229, 1111, 992, 935, 753, 735 cm$^{-1}$; HRMS (MM: ESI-APCI+) m/z calc’d for C$_{34}$H$_{44}$BrN$_2$O$_8$Si [M+H]$^+$: 715.2045; found: 715.2090.
Allyl 21. To a 500 mL round-bottom flask with a magnetic stir bar was added malonate 22 (11.1 g, 15.2 mmol, 1.0 equiv). The flask was brought into a N₂-filled glove box and then Pd(PPh₃)₄ (0.88 g, 0.761 mol, 0.05 equiv) was added. The reaction mixture was brought out from the glove box and treated with THF (152 mL). After 1 h stirring, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography (1:1 hexane:EtOAc) on silica gel to afford allylated product 21 (8.1 g, 78% yield).

Rf = 0.45 (4:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.28 (d, J = 8.7 Hz, 1H), 7.97 (d, J = 2.3 Hz, 1H), 7.80 (dd, J = 8.6, 2.2 Hz, 1H), 7.22 (td, J = 7.7, 1.1 Hz, 1H), 6.83–6.77 (m, 2H), 6.33 (d, J = 7.5 Hz, 1H), 5.66 (ddt, J = 16.9, 10.3, 6.2 Hz, 1H), 5.56 (ddt, J = 17.0, 10.1, 6.9 Hz, 1H), 5.16–5.09 (m, 2H), 4.91 (dq, J = 17.1, 1.5 Hz, 1H), 4.84 (ddd, J = 10.2, 1.9, 1.1 Hz, 1H), 4.38–4.26 (m, 2H), 3.37 (dd, J = 15.3, 7.0 Hz, 1H), 3.23 (s, 3H), 3.21–3.10 (m, 2H), 2.90 (ddd, J = 9.5, 8.5, 4.2 Hz, 1H), 2.59–2.51 (m, 1H), 2.16 (ddd, J = 12.5, 8.1, 4.3 Hz, 1H), 0.92–0.80 (m, 21H); ¹³C NMR (125 MHz, CDCl₃) δ 177.7, 169.6, 152.1, 144.3, 134.8, 134.5, 133.7, 131.3, 131.1, 128.9, 128.8, 128.70, 125.13, 121.9, 121.8, 119.5, 118.2, 108.1, 65.7, 60.7, 59.5, 55.5, 39.0, 36.6, 26.5, 18.0, 11.9; IR (Neat Film NaCl) 2942, 2865, 1713, 1610, 1538, 1495, 1471, 1353, 1106, 995, 918, 882, 750, 732 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C₃₄H₆₀BrN₂O₆Si [M+H⁺]: 685.2303; found: 685.2294.
**Bis-oxindole SI-7.** To a solution of oxindole 21 (7.65 g, 11.2 mmol, 1.0 equiv) in H$_2$O (187 mL) and i-PrOH (373 mL) were added NH$_4$OAc (43.2 g, 0.560 mol, 50 equiv) and TiCl$_3$ (20% w/w, 69.2 mL, 0.11 mol, 10 equiv). Then, the reaction was stirred for 12 h at 23 °C. The reaction mixture was diluted with EtOAc (200 mL) and then the phases were separated and the aqueous phase was extracted with EtOAc (3 x 300 mL). The combined organic phases were dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by column chromatography (2:1 hexanes:EtOAc) on silica gel to afford bis-oxindole SI-7 (6.10 g, 91% yield).

R$_f$ = 0.68 (1:1 hexane:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.57 (br, s, 1H), 7.31–7.26 (m, 1H), 6.98–6.90 (m, 2H), 6.88 (dd, $J$ = 2.7, 1.5 Hz, 1H), 6.82 (s, 1H), 6.73–6.69 (m, 1H), 6.21 (br, s, 1H), 5.14 (ddt, $J$ = 17.1, 10.0, 7.1 Hz, 1H), 4.96 (ddd, $J$ = 17.1, 2.0, 0.9 Hz, 1H), 4.86–4.80 (m, 1H), 3.42–3.31 (m, 2H), 3.25 (ddd, $J$ = 9.9, 7.5, 4.7 Hz, 1H), 3.05 (dt, $J$ = 14.5, 7.4 Hz, 1H), 2.90 (s, 3H), 2.79 (dd, $J$ = 13.0, 6.9 Hz, 1H), 2.34 (ddd, $J$ = 13.4, 6.8, 4.7 Hz, 1H), 0.92–0.81 (m, 21H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 177.14, 176.05, 144.65, 142.73, 131.37, 128.80, 127.92, 127.73, 125.58, 124.41, 124.20, 121.97, 121.73, 119.88, 112.70, 108.15, 59.61, 56.86, 54.80, 35.16, 32.66, 25.91, 17.82, 11.77; IR (Neat Film NaCl) 3270, 2942, 2865, 1716, 1611, 1471, 1377, 1241, 1105, 916, 883, 791, 734 cm$^{-1}$; HRMS (MM: ESI-APCI+) m/z calc’d for C$_{31}$H$_{42}$BrN$_2$O$_3$Si [M+H]$^+$: 597.2143; found: 597.2187.
Carbamate SI-8. To a stirred solution of bis-oxindole SI-7 (2.63 g, 4.40 mmol, 1.0 equiv) in MeCN (44 mL) were added DMAP (1.08, 8.80 mmol, 2.0 equiv) and Boc₂O (1.92 g, 8.80 mmol, 2.0 equiv) at 0 °C. The reaction was slowly warmed to 23 °C, and stirred for 12 h. The solvent was concentrated in vacuo and then the residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford protected compound SI-8 (2.6 g, 85% yield).

Rf = 0.52 (4:1 hexanes:EtOAc); 1H NMR (500 MHz, CDCl₃) δ 7.95 (d, J = 1.9 Hz, 1H), 7.25 (td, J = 7.7, 1.3 Hz, 1H), 7.14–7.09 (m, 1H), 6.90 (t, J = 7.5 Hz, 1H), 6.71–6.67 (m, 1H), 6.62–6.53 (m, 1H), 6.47 (s, 1H), 5.10 (ddt, J = 17.0, 9.9, 7.1 Hz, 1H), 4.99–4.92 (m, 1H), 4.83 (dd, J = 10.0, 2.0 Hz, 1H), 3.43 (dd, J = 13.3, 7.3 Hz, 1H), 3.35 (dt, J = 9.9, 7.2 Hz, 1H), 3.20 (ddd, J = 9.9, 7.7, 4.8 Hz, 1H), 2.94 (s, 3H), 2.90 (dd, J = 13.9, 8.0 Hz, 1H), 2.81–2.75 (m, 1H), 2.30 (ddd, J = 13.2, 7.2, 4.8 Hz, 1H), 1.51 (s, 9H), 0.89–0.84 (m, 21H); 13C NMR (125 MHz, CDCl₃) δ 175.60, 173.73, 148.46, 144.52, 141.67, 131.26, 128.95, 127.19, 126.28, 126.06, 125.32, 124.15, 122.43, 121.69, 120.23, 118.24, 108.06, 84.08, 59.56, 57.36, 55.29, 34.77, 32.70, 27.92, 25.97, 17.82, 11.76; IR (Neat Film NaCl) 2941, 2866, 1770, 1716, 1610, 1471, 1420, 1370, 1287, 1246, 1153, 1105, 1067, 1023, 919, 882, 845, 752, 733 cm⁻¹; HRMS (MM: ESI-APCI⁺) m/z calc’d for C₃₁H₄₂BrN₂O₃Si [M+H-Boc]⁺: 597.2143 found: 597.2181.

Aldehyde 20. To a 100 mL round bottom flask with magnetic stir bar was added alkene SI-8 (2.61 g, 0.00374 mol, 1.0 equiv) in CH₂Cl₂ (18.7 mL). The flask was connected to an ozone generator and purged with oxygen gas (flow: 0.5) for 5 min at −78 °C. Then, ozone gas (flow: 0.5) was bubbled through into the reaction solution for 30 min at −78 °C. After the reaction was done, oxygen gas was bubbled into the reaction mixture for 20 min and PPh₃ (2.95 g, 0.0112 mol, 3.0 equiv) was added. The reaction mixture was slowly warmed to ambient temperature, stirred for 16 h, and
then concentrated under reduced pressure. The residue was purified by column chromatography (4:1 hexanes:EtOAc) to afford aldehyde 20 (2.4 g, 90% yield).

$R_f = 0.23$ (4:1 hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.45 (s, 1H), 8.00 (d, $J = 1.8$ Hz, 1H), 7.31 – 7.26 (m, 1H), 7.21 (td, $J = 7.8$, 1.2 Hz, 1H), 6.93 (br, s, 1H), 6.77 (t, $J = 7.5$ Hz, 1H), 6.73 (d, $J = 7.8$ Hz, 1H), 5.99 (br, s, 1H), 4.43 (d, $J = 19.1$ Hz, 1H), 3.39 (dd, $J = 19.2$, 1.1 Hz, 1H), 3.31 (dt, $J = 9.9$, 7.3 Hz, 1H), 3.15 (ddd, $J = 9.9$, 8.0, 4.7 Hz, 1H), 3.10 (s, 3H), 2.64 (dt, $J = 12.8$, 7.6 Hz, 1H), 2.20 (ddd, $J = 12.6$, 7.5, 4.7 Hz, 1H), 1.43 (s, 9H), 0.91–0.82 (m, 21H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 197.38, 175.36, 173.47, 148.07, 144.01, 142.38, 129.18, 126.57, 126.04, 125.73, 124.51, 123.59, 122.99, 121.72, 118.74, 108.14, 83.83, 59.25, 53.78, 53.64, 44.47, 33.42, 27.83, 26.20, 17.80, 11.74; IR (Neat Film NaCl) 1941, 2865, 1771, 1722, 1609, 1471, 1422, 1370, 1345, 1291, 1245, 1152, 1109, 1070, 1015, 882, 845, 793, 749 cm$^{-1}$; HRMS (MM: ESI-APCI+) $m/z$ calc’d for C$_{30}$H$_{40}$BrN$_2$O$_4$Si [M+H-Boc]$^+$: 599.1935 found: 597.1971.

Amide 25. To a solution of aldehyde 20 (200 mg, 0.29 mmol, 1.0 equiv) and o-nitrobenzylammonium acetate 15 (182 mg, 0.86 mmol, 3.0 equiv) in MeOH (14.3 mL) was added NaBH$_3$CN (39 mg, 0.57 mmol, 2.0 equiv) in THF (7.2 mL) at 0 °C. The reaction mixture was slowly warmed to ambient temperature, and stirred for 12 h. Then, H$_2$O (10 mL) was added. The mixture was extracted with EtOAc (3 x 20 mL) and washed with brine. The combined organic phases were dried over MgSO$_4$, and concentrated in vacuo. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford o-nitrobenzyl protected amide 25 (221 mg, 91% yield).

$R_f = 0.22$ (4:1 hexanes:EtOAc); (Due to the distinct presence of rotameric isomers, the $^1$H NMR and $^{13}$C NMR contained extra peaks. See attached the spectrum behind); $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.47 (d, $J = 8.9$ Hz, 1H), 8.36 (d, $J = 2.3$ Hz, 1H), 8.09 (s, 1H).
Aminal 26. Oxindole 25 (20 mg, 0.0239 mmol, 1.0 equiv) was dissolved in THF (2.39 mL) and cooled to 0 °C. AlH₃-Me₂NEt (0.5 M in toluene; 0.096 mL, 0.0478 mmol, 2.0 equiv) was added dropwise at 0 °C. The solution was stirred for 2 h and quenched with MeOH. The solution was concentrated under reduced pressure and purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford cyclized compound 26 (8.23 mg, 42% yield; 66% yield, based on recovered starting material).

R_f = 0.33 (4:1 hexanes:EtOAc); 'H NMR (600 MHz, CDCl₃) δ 7.96 (d, J = 7.9 Hz, 1H), 7.40 (s, 1H), 7.35 (dt, J = 19.0, 7.4 Hz, 2H), 7.06–7.03 (m, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.93–6.91 (m, 2H), 6.90–6.86 (m, 1H), 6.40 (t, J = 7.4 Hz, 1H), 6.20 (s, 1H), 6.12 (d, J = 7.8 Hz, 1H), 4.75 (q, J = 16.8, 16.1 Hz, 2H), 3.78 (td, J = 10.7, 10.3, 6.0 Hz).
Hz, 1H), 3.53 (q, J = 8.8 Hz, 1H), 3.46 (t, J = 9.3 Hz, 1H), 3.16–3.07 (m, 2H), 2.84(s, 3H), 2.75 (dd, J = 13.4, 6.0 Hz, 1H), 2.50 (td, J = 11.4, 5.6 Hz, 1H), 2.23–2.16 (m, 1H), 1.47 (s, 9H), 0.95 (m, 21H); 13C NMR (125 MHz, CDCl₃) δ 172.5, 153.6, 150.9, 148.7, 139.9, 133.5, 132.2, 131.0, 130.6, 128.9, 128.5, 128.2, 127.8, 125.2, 124.8, 123.2, 120.6, 116.2, 104.3, 80.9, 79.6, 59.6, 56.9, 54.12, 44.49, 43.5, 39.5, 31.0, 29.6, 28.2, 26.3, 17.9, 11.9; IR (Neat Film NaCl) 2941, 2865, 1697, 1603, 1528, 1491, 1333, 1302, 1168, 1100, 992, 882, 739 cm⁻¹; HRMS (MM: ESI-APCI+) m/z calc’d for C₄₂H₅₆BrN₄O₆Si [M+H]^+: 819.3147; found: 819.3153.

**Formyl 27.** To a solution of methyl protected compound 26 (11 mg, 0.0161 mmol, 1.0 equiv) in CH₂Cl₂ (1.61 mL) was added PDC (9.1 mg, 0.0241 mmol, 1.5 equiv) at 23 °C. After being stirred at 23 °C for 12 h, the reaction mixture was quenched with water. The reaction mixture was washed with CH₂Cl₂ (3 x 2 mL), and brine. The combined organic phases were dried over MgSO₄ and concentrated in vacuo. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford aldehyde 27 (7.0 mg, 62% yield; 93% yield, based on recovered starting material).

Rₕ = 0.55 (4:1 hexanes:EtOAc); ¹H NMR (500 MHz, CDCl₃) δ 8.90 (s, 1H), 7.96 (dd, J = 7.8, 2.5 Hz, 2H), 7.38 (q, J = 8.5, 8.0 Hz, 2H), 7.33 (s, br, 1H), 7.14–6.99 (m, 4H), 6.96–6.87 (m, 3H), 4.83 (s, br, 1H), 4.70 (d, 15Hz, 1H), 3.64–3.54 (m, 2H), 3.51 (t, J = 9.4 Hz, 1H), 3.26 (q, J = 10.0, 7.4 Hz, 1H), 3.11 (q, J = 10.9 Hz, 1H), 2.79 (dd, J = 13.2, 5.8 Hz, 1H), 2.58 (dt, J = 13.1, 7.8 Hz, 1H), 2.19 (ddd, J = 12.9, 7.9, 4.7 Hz, 1H), 1.44 (s, br, 9H), 0.98–0.76 (m, 21H); ¹³C NMR (125 MHz, CDCl₃) δ 172.1, 161.4, 153.1, 148.7, 141.3, 138.3, 133.5, 131.8, 131.5, 131.2, 129.3, 128.7, 128.4, 125.1, 124.9, 124.2, 123.5, 121.1, 116.0, 81.9, 75.1, 59.4, 57.2, 54.1, 44.6, 43.6, 39.6, 29.7, 28.1, 26.3, 17.9, 17.9, 11.8; IR (Neat Film NaCl) 2942, 2866, 1683, 1591, 1527,
1489, 1393, 1323, 1280, 1155, 1096, 911, 733 cm$^{-1}$; HRMS (MM: ESI-APCI+) $m/z$ calc’d for C$_{42}$H$_{54}$BrN$_4$O$_7$Si [M+H]$^+$: 833.2940; found: 833.2960.

**Amide 19.** To a solution of aldehyde 27 (14.8 mg, 0.0177 mmol, 1.0 equiv) in MeOH (0.4 mL) was added 20% aq NaOH (0.2 mL) and the reaction mixture was stirred for 4 h at 75 °C. The reaction mixture was diluted with EtOAc (1 mL) and the aqueous phase was extracted with EtOAc (3 x 1 mL). The combined organic phases were dried over MgSO$_4$ and concentrated in vacuo. The residue was purified by column chromatography (4:1 hexanes:EtOAc) on silica gel to afford desired amide 19 (5.9 mg, 50% yield).

$R_f = 0.21$ (4:1 hexanes:EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) δ 7.69 (s, 1H), 7.14 (dd, $J = 8.3$, 2.0 Hz, 1H), 7.06 (dt, $J = 7.7$, 3.7 Hz, 3H), 6.70 (t, $J = 7.4$ Hz, 1H), 6.60 (d, $J = 7.7$ Hz, 1H), 6.17 (s, 1H), 5.72 (s, 1H), 3.69–3.61 (m, 1H), 3.48 (dt, $J = 10.8$, 5.6 Hz, 1H), 3.07 (m, 1H), 2.85 (m, 1H), 2.77 (m, 2H), 2.33 (d, $J = 7.9$ Hz, 1H), 1.59 (s, 9H), 0.91 (m, 21H); $^{13}$C NMR (125 MHz, CDCl$_3$) δ 176.2, 153.9, 149.2, 138.2, 130.4, 128.9, 127.1, 126.8, 126.5, 124.4, 120.6, 119.5, 109.4, 82.5, 60.3, 55.6, 53.4, 38.9, 35.7, 31.2, 28.6, 18.4, 11.9; IR (Neat Film NaCl) 3401, 2941, 2865, 1696, 1487, 1465, 1314, 1163, 1094, 882, 740 cm$^{-1}$; HRMS (MM: ESI-APCI+) $m/z$ calc’d for C$_{34}$H$_{40}$BrN$_5$O$_4$Si [M+H]$^+$: 670.2670; found: 670.2679.
$^1$H NMR (500 MHz, CDCl$_3$) of compound SI-1.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound SI-1.
$^1$H NMR (500 MHz, CDCl$_3$) of compound SI-2.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound SI-2.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 10.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 10.
$^1$HNMR (500 MHz, CDCl$_3$) of compound 7.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 7.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 8.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 8.
^1H NMR (500 MHz, CDCl₃) of compound 5.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 5.
\(^1\)H NMR (500 MHz, CDCl\(_3\)) of compound SI-4.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound SI-4.
$^1$H NMR (300 MHz, CDCl$_3$) of compound 11.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 11.
\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) of compound 4.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 4.
$^1$H NMR (500 MHz, DMSO) of compound 12.
$^{13}$C NMR (125 MHz, DMSO) of compound 12.
$^1$H NMR (500 MHz, CDCl$_3$) of compound SI-5.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound SI-5.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 13.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 13.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 14.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 14.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 16.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 16.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 17.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 17.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 18.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 18.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 3.
\textsuperscript{13}C NMR (125 MHz, CDCl\textsubscript{3}) of compound 3.
$^{1}$H NMR (500 MHz, CDCl$_3$) of compound 24.
\(^{13}\text{C} \text{NMR (125 MHz, CDCl}_3\text{)} \text{ of compound 24.}\)
$^1$H NMR (500 MHz, CDCl$_3$) of compound S1-6.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound SI-6.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 22.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 22.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 21.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 21.
$^1$H NMR (500 MHz, CDCl$_3$) of compound S1-7.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound SI-7.
$^1$H NMR (500 MHz, CDCl$_3$) of compound SI-8.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound SI-8.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 20.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 20.
$^1$H NMR (300 MHz, CDCl$_3$) of compound 25.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 25.
^1^H NMR (600 MHz, CDCl₃) of compound 26.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 26.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 27.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 27.
$^1$H NMR (500 MHz, CDCl$_3$) of compound 19.
$^{13}$C NMR (125 MHz, CDCl$_3$) of compound 19.