Supporting Information

Stereoselective Synthesis of the A,E-ring Bicyclic Core of Calyciphylline B Type Alkaloids

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Experimental procedure        S2-S10

$^1$H and $^{13}$C NMR spectra        S11-S27
EXPERIMENTAL SECTION

(R)-Cyclohex-2-enol 10. To a solution of (R)-cyclohex-2-en-1-yl acetate (8.8 g, 62.8 mmol) in methanol (63 mL) was added Na₂CO₃ (20 mol%, 1.73 g, 12.56 mmol), and the mixture stirred for 6 h at rt. The reaction mixture was filtered through a small pad of Celite and washed with EtOAc (15 mL). The solvent was evaporated in vacuum, water (10 mL) was added to the residue and product was extracted into DCM (3 × 20 mL). The combined organic layers were washed with saturated brine (15 mL), dried over anhydrous Na₂SO₄ and the solvent was evaporated in vacuum. The crude product was purified by column chromatography over 100-200 mesh silica gel (10% EtOAc/hexane) to afford compound 10 (5.3 g, 54 mmol) in 86% yield as a yellow color oil. TLC: Rf 0.6 (10% EtOAc/hexane); [α]D₂₀ +0.5 (c 0.4, CHCl₃); IR (neat) 3450, 2932, 2865, 1644, 1453, 1383, 1182, 1079 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.84 (dt, J = 10.0, 3.6, 1.1 Hz, 1H), 5.78 – 5.72 (m, 1H), 4.25 – 4.12 (m, 1H), 2.10 – 1.95 (m, 2H), 1.94 – 1.82 (m, 1H), 1.80 – 1.68 (m, 1H), 1.66-1.54 (m, 2H); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 130.2, 129.6, 65.3, 31.7, 24.9, 18.9; MS (ESI – TOF) m/z: 137 [M + K]⁺.

(R)-Cyclohex-2-en-1-yl propionate 11. To a solution of cyclohexenol 10 (5.2 g, 53 mmol) in anhydrous DCM (106 mL) cooled to 0 °C, was added Et₃N (12.2 mL, 87.45 mmol) and propanoyl chloride (5.2 mL, 58.3 mmol) dropwise. The reaction mixture was allowed to warm to rt and stirred further at the same temperature for 1 h. The solvent was evaporated in vacuum, water (15 mL) was added to the residue and the product was extracted into DCM (3 × 20 mL). The combined organic layers were washed with saturated brine (15 mL), dried over anhydrous Na₂SO₄ and the solvent was evaporated in vacuum. The crude product was purified by column chromatography over 100-200 mesh silica gel (5% EtOAc/hexane) to afford compound 11 (8.0
**2-((S)-Cyclohex-2-en-1-yl)propanoic acid 12.** To a solution of diisopropylamine (10.2 mL, 75 mmol) in anhydrous THF (45 mL) cooled to 0 °C, n-BuLi (2.5 M in hexane, 30 mL, 75 mmol) was added. This mixture was stirred for 30 min at 0 °C, and subsequently cooled to -78 °C and HMPA (10.3 mL, 23%) was added. A solution of propanoyl ester 11 (7.7 g, 50 mmol) in anhydrous THF (30 mL) was added slowly over a period of 10 min under vigorous stirring. After 1 h, the reaction mixture was quenched by the addition of a solution of Me₃SiCl (9.5 mL, 75 mmol) in anhydrous THF (35 mL). The mixture was gradually allowed to warm to rt, then heated at 65 °C for 1 h, and cooled to rt. Methanol (15 mL) was added and the reaction mixture was stirred for 10 min at 25 °C to effective hydrolysis of silyl ester. The reaction mixture was added to 5% sodium hydroxide solution (100 mL). The layers were separated and the aqueous layer was extracted with ether (2 × 25 mL). The aqueous layer was acidified with hydrochloric acid (11 M, 12 mL), and extracted with DCM (3 × 50 mL). The combined organic extracts were washed with brine solution (20 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuo to afford compound 12 and 13 (3.85 g, 25 mmol) as an inseparable mixture in 50% yield as a yellow color viscous oil along with the recovered starting material 11 (3.08 g, 20 mmol). TLC: Rₛ 0.5 (10% EtOAc/hexane); IR (neat) 3457, 3022, 2935, 2876, 2657, 1704, 1456, 1411, 1254,
1205, 1078, 847 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl\(_3\)) Note: The signals for the minor isomer are denoted by an asterisk) \(\delta\) 5.82 – 5.74 (m, 1H), 5.60-5.57 (m, 1H)*, 5.53-5.49 (m, 1H), 5.32-5.23 (m, 1H)*, 2.55-2.35 (m, 4H), 2.02-1.91 (m, 4H), 1.81-1.69 (m, 4H), 1.62-1.47 (m, 2H), 1.42 – 1.23 (m, 2H), 1.17 (d, \(J = 6.8\) Hz, 3H)*, 1.14 (d, \(J = 6.8\) Hz, 3H); \(^{13}\)C \({}^1\)H NMR (125 MHz, CDCl\(_3\)) \(\delta\) 182.7*, 182.6, 129.6*, 129.3*, 129.2, 128.8, 44.1, 44.0*, 37.9, 37.9*, 27.4*, 27.1, 25.0*, 24.9, 21.5, 21.4*, 13.5*, 13.1; MS (ESI – TOF) \(m/z\): 155 [M + H] \(^+\); HRMS (ESI – TOF) \(m/z\): [M + H] \(^+\) calcd for C\(_9\)H\(_{15}\)O\(_2\), 155.1072; found, 155.1065.

(3\(R\),3a\(R\),7\(S\),7a\(S\))-7-bromo-3-methylhexahydrobenzofuran-2(3H)-one **14** and

(3\(S\),3a\(R\),7\(S\),7a\(S\))-7-Bromo-3-methylhexahydrobenzofuran-2(3H)-one **15**. To a solution of mixture of acids 12 and 13 (dr = 5:1), (3.42 g, 22.2 mmol) in anhydrous CHCl\(_3\) (89 mL) was added NBS (5.92 g, 33.3 mmol), and the mixture stirred in the dark at rt for 8 h. The reaction mixture was diluted with DCM (70 mL), washed with water (20 mL), saturated NaHCO\(_3\) (20 mL) saturated brine (15 mL), dried over anhydrous Na\(_2\)SO\(_4\) and the solvent was evaporated *in vacuum*. The crude product was purified by column chromatography over 100-200 mesh silica gel (10% EtOAc/hexane) to afford compound **14** and **15** as separable mixture of (5:1) in 84% yield.

**Compound 14** was isolated in 69% yield (3.54 g, 15.2 mmol) as a pale yellow color solid. TLC: \(R_f\) 0.2 (10% EtOAc/hexane); m.p: 83-85 °C; [\(\alpha\)]\(_D\)\(^{20}\) +84.0 (c 0.67, CHCl\(_3\) ); IR (KBr) 2944, 2871, 1779, 1445, 1348, 1174, 1137, 1091, 973, 924, 621 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.59 (dd, \(J = 7.7, 6.3\) Hz, 1H), 4.00 (ddd, \(J = 10.5, 7.8, 4.2\) Hz, 1H), 2.47 – 2.34 (m, 2H), 2.27 – 2.19 (m, 1H), 1.88-1.78 (m, 1H), 1.78 – 1.67 (m, 3H), 1.52 – 1.38 (m, 1H), 1.24 (d, \(J = 6.7\) Hz, 3H); \(^{13}\)C \({}^1\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 178.3, 82.0, 50.6, 43.1, 37.7, 33.3, 24.4, 20.6, 13.5; MS
Compound 15 was isolated in 13% yield as a colorless oil. TLC: Rf 0.4 (10% EtOAc/hexane); [α]D20 +45.1 (c 0.47, CHCl3); IR (neat) 2942, 2872, 1779, 1346, 1172, 1090, 972, 926, 677 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.63 (dd, J = 5.2, 2.6 Hz, 1H), 4.52 (t, J = 3.0 Hz, 1H), 2.81 – 2.74 (m, 1H), 2.70 – 2.6 (m, 1H), 2.01 – 1.90 (m, 2H), 1.86 – 1.67 (m, 2H), 1.63-1.57 (m, 1H), 1.16 (d, J = 7.0 Hz, 3H), 1.09 – 0.96 (m, 1H); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 178.3, 78.8, 47.8, 41.9, 35.5, 28.0, 22.4, 17.6, 8.8; MS (ESI – TOF) m/z: 233 [M + H]⁺; HRMS (ESI – TOF) m/z: [M + H]⁺ calcd for C₉H₁₄O₂Br, 233.0177; found, 233.0168.

Isomerization of compound 14 to 15. To a solution of diisopropylamine (3.1 mL, 22.8 mmol) in anhydrous THF (10 mL) cooled to 0 °C, n-BuLi (2.5 M in hexane, 9.1 mL, 22.8 mmol) was added. This mixture was stirred for 30 min at 0 °C, and subsequently cooled to -78 °C. A solution of bromolactone 14 (3.54 g, 15.2 mmol) in anhydrous THF (15 mL) was added slowly over a period of 5 min under vigorous stirring. After 1 h, the reaction mixture was quenched by the addition of a solution of diethyl malonate (3.5 mL, 22.8 mmol) in anhydrous THF (10 mL). The reaction mixture allowed to warm to rt, and diluted with water (10 mL), and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with brine solution (10 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The crude product was purified by column chromatography over 100-200 mesh silica gel (10% EtOAc/Haxane) to afford compound 15 (3.26 g, 14 mmol) in 92% yield as a colorless oil.

(S)-2-((S)-Cyclohex-2-en-1-yl)propanoic acid 13. To a solution of bromolactone 15 (3.2 g, 13.7 mmol) in a mixture of EtOH : H₂O (9 : 1, 93.5 mL) was added Zn powder (1.64 g, 27.4 mmol) and the mixture was heated at 80 °C for 6 h. After consumption of starting material, the reaction
mixture was filtered through a small pad of Celite, and the filtrate was evaporated in vacuum. The residue was diluted with water (20 mL), and extracted with EtOAc (3 × 15 mL). The combined organic extracts were washed with aqueous 1N HCl (10 mL), brine solution (10 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The crude product was purified by column chromatography over 100-200 mesh silica gel (10% EtOAc/hexane) to afford compound 13 (1.69 g, 11 mmol) in 80% yield as a colorless oil. TLC: R$_f$ 0.4 (10% EtOAc/hexane); [α]$_D^{20}$ – 3.7 (c 0.41, CHCl₃); IR (neat) 3457, 2934, 2882, 1703, 1454, 1391, 1251, 1095, 847, 667 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl₃) δ 5.77 (ddd, J = 9.6, 5.9, 3.5 Hz, 1H), 5.62 (dd, J = 10.2, 1.9 Hz, 1H), 2.50 – 2.38 (m, 2H), 2.01 – 1.95 (m, 2H), 1.81 – 1.69 (m, 2H), 1.61 – 1.50 (m, 1H), 1.43 – 1.35 (m, 1H), 1.18 (d, J = 6.8 Hz, 3H); $^{13}$C {1H} NMR (100 MHz, CDCl₃) δ 181.8, 128.1, 126.7, 43.2, 37.3, 25.9, 23.7, 20.3, 12.6; MS (ESI – TOF) m/z: 155 [M + H]$^+$. HRMS (ESI – TOF) m/z: [M + H]$^+$ calcd for C₉H₁₅O₂, 155.1072; found, 155.1065.

(S)-2-(S)-Cyclohex-2-en-1-yl)propan-1-ol 16. To a suspension of LAH (1.42 g, 37.5 mmol), in anhydrous THF (5 mL) cooled at 0 °C, was added the solution of acid 13 (2.31 g, 15 mmol) in anhydrous THF (10 mL) and the mixture was stirred for 45 min, gradually allowing it to warm to rt. The reaction mixture was carefully quenched with ice cold water (1.5 mL), and filtered through a pad of Celite. The solid residue was washed with EtOAc (3 × 15 mL). The combined filtrates were washed with brine solution (10 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The crude product was purified by column chromatography over 100-200 mesh silica gel (10% EtOAc/hexane) to afford compound 16 (1.47 g, 10.5 mmol) in 70% yield as a colorless oil. TLC: R$_f$ 0.1 (10% EtOAc/hexane); [α]$_D^{20}$ –26.5 (c 0.31, CHCl₃); IR (neat) 3384, 2927, 2873, 1655, 1452, 1034, 721 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl₃) δ 5.74 (ddd, J = 10.1, 6.6, 3.1 Hz, 1H), 5.62 – 5.57 (m, 1H), 3.66 (dd, J = 10.7, 6.2 Hz, 1H), 3.49 (dd, J = 10.7,
6.8 Hz, 1H), 2.26 – 2.19 (m, 1H), 2.01 – 1.95 (m, 2H), 1.81 – 1.63 (m, 3H), 1.57-1.48 (m, 1H), 1.38-1.30 (m, 1H), 0.92 (d, J = 6.9 Hz, 3H); $^1$C {$^1$H}NMR (125 MHz, CDCl$_3$) δ 129.7, 128.3, 66.2, 40.1, 37.5, 26.2, 25.4, 22.3, 14.1; MS (ESI – TOF) m/z: 141 [M + H]$^+$. 

**N-((S)-2-((S)-Cyclohex-2-en-1-yl)propyl)-4-nitrobenzenesulfonamide 17.** To a solution of alcohol 16 (1.4 g, 10 mmol) in anhydrous THF (200 mL) was added Ph$_3$P (5.24 g, 20 mmol), p-nitrobenzenesulfonamide (4.04 g, 20 mmol) and DIAD (3.16 mL, 20 mmol) at 0 °C. The contents were stirred for 12 h at rt. Water (100 mL) was added to the reaction mixture, the layers were separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic extracts were washed with brine solution (20 mL), dried over anhydrous Na$_2$SO$_4$, and concentrated in vacuum. The crude product was purified by column chromatography over 100-200 mesh silica gel (10% EtOAc/hexane) to afford compound 17 (2.21 g, 6.5 mmol) in 65% yield as a colorless solid. TLC: R$_f$ 0.2 (15% EtOAc/hexane); m.p.: 98-100 °C; $[\alpha]_D^{20}$ –15.3 (c 0.31, CHCl$_3$); IR (neat) 3282, 2926, 2850, 1608, 1530, 1351, 1156, 753, 611 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 8.37 (d, $J = 8.8$ Hz, 2H), 8.05 (d, $J = 8.9$ Hz, 2H), 5.74 (ddd, $J = 9.7$, 6.5, 2.9 Hz, 1H), 5.43 (d, $J = 10.2$ Hz, 1H), 4.65 (t, $J = 6.1$ Hz, 1H), 3.07 – 2.98 (m, 1H), 2.92 – 2.83 (m, 1H), 2.18 – 2.07 (m, 1H), 2.00 – 1.89 (m, 2H), 1.77 – 1.68 (m, 1H), 1.67-1.59 (m, 2H), 1.53 – 1.41 (m, 1H), 1.31 – 1.13 (m, 1H), 0.88 (d, $J = 6.9$, Hz, 3H); $^1$C {$^1$H}NMR (100 MHz, CDCl$_3$) δ 150.1, 146.0, 129.2, 128.6, 128.31, 124.4, 46.8, 38.1, 37.6, 25.7, 25.2, 22.1, 14.8; MS (ESI – TOF) m/z: 325 [M + H]$^+$; HRMS (ESI – TOF) m/z: [M + H]$^+$ calcd for C$_{15}$H$_{21}$N$_2$O$_4$S, 325.1222; found, 325.1227.

**3S,3aR,6S,6aS)-3-Methyl-1-((4-nitrophenyl)sulfonyl)octahydrocyclopenta[b]pyrrole-6-carbaldehyde 18.** To a solution of sulfonamide 17 (770 mg, 2.2 mmol) in 1,4-dioxane and H$_2$O (3:1, 22.6 mL) was added 2,6-lutidine (0.52 mL), and OsO$_4$ (0.04 M in Toluene, 1.1 mL). After
stirring for 5 min at 0 °C, NaIO₄ (1.88g, 8.8 mmol) was added, and the resulting solution was stirred for 2 h at rt. A solution of 20% Na₂S₂O₃ (10 mL) was added and stirred for 10 min. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with 20% Na₂S₂O₃ (10 mL) saturated brine, (10 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The crude aldehyde was dissolved in anhydrous toluene (5 mL) and piperidinium acetate (37 mg, 0.25 mmol, 10 mol %) was added. The solution was heated at reflux for 1 h. The reaction mixture was cooled to rt, EtOAc (10 mL) was added to the reaction mixture and washed successively with 2 N HCl (2× 5 mL), saturated NaHCO₃ (5 mL) and brine (5 mL). The organic layer was dried over anhydrous Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography over 100-200 mesh silica gel (15% EtOAc/hexane) to afford the aldehyde 18 which was taken ahead to the next step immediately (295 mg, 0.87 mmol) in 45% overall yield for two steps as a pale yellow color oil. TLC: Rf 0.3 (20% EtOAc/hexane); [α]D²⁰ +55.7 (c 1.1, CHCl₃); IR (neat) 2964, 2930, 1720, 1530, 1351, 1164, 1095, 614 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.76 (s, 1H), 8.43 (d, J = 8.8 Hz, 2H), 8.03 (d, J = 8.8 Hz, 2H), 4.15 (dd, J = 8.5, 2.5 Hz, 1H), 3.70 (dd, J = 9.2, 6.2 Hz, 1H), 3.40 – 3.34 (m, 1H), 2.49 (t, J = 9.4 Hz, 1H), 2.12 – 2.02 (m, 2H), 2.01 – 1.92 (m, 2H), 1.85 – 1.78 (m, 1H), 1.61-1.46 (m, 1H), 0.87 (d, J = 6.5 Hz, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 201.6, 150.3, 141.2, 129.3, 124.4, 63.5, 59.1, 57.0, 51.7, 37.3, 28.5, 25.4, 16.4; MS (ESI – TOF) m/z: 339 [M + H]⁺. HRMS (ESI – TOF) m/z: [M + H]⁺ calcd for C₁₅H₁₉N₂O₅S, 339.1015; found, 339.1020.

(3S,3aR,6S,6aS)-3-Methyl-1-((4-nitrophenyl)sulfonyl)octahydrocyclopenta[b]pyrrole-6-carboxylic acid 19. To a solution of aldehyde 18 (70 mg, 0.2 mmol) in t-BuOH (2.5 mL) cooled to 0 °C, was added NaClO₂ (36 mg, 0.4 mmol) and NaH₂PO₄ (72 mg, 0.6 mmol), and the
resulting solution was stirred for 1 h at rt. The solvent was concentrated in vacuum, and the reaction mixture was extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine solution (10 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The crude product was purified by column chromatography over 100-200 mesh silica gel (30% EtOAc/hexane) to afford compound 19 (67 mg, 0.18 mmol) in 95% yield as a yellow color oil. TLC: Rₚ 0.3 (30% EtOAc/hexane); [α]D²⁰ +47.4 (c 1.0, CHCl₃); IR (neat) 3300, 3105, 2960, 2930, 1710, 1532, 1350, 1300, 1160, 1090, cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 8.42 (d, J = 8.8 Hz, 2H), 8.07 (d, J = 8.8 Hz, 2H), 4.10 (dd, J = 8.7, 3.3 Hz, 1H), 3.72 (dd, J = 9.3, 6.2 Hz, 1H), 3.33 – 3.23 (m, 1H), 2.57 (t, J = 9.2 Hz, 1H), 2.22 – 2.09 (m, 2H), 2.09 – 1.91 (m, 2H), 1.88-1.76 (m, 1H), 1.61-1.50 (m, 1H), 0.86 (d, J = 6.6 Hz, 3H); ¹³C {¹H} NMR (125 MHz, CDCl₃) δ 179.1, 150.3, 141.3, 129.3, 124.4, 67.0, 56.0, 52.1, 51.8, 38.0, 30.0, 29.5, 16.7; MS (ESI – TOF) m/z: 355 [M + H]⁺. HRMS (ESI – TOF) m/z: [M + H]⁺ calcd for C₁₅H₁₉N₂O₆S, 355.0964; found, 355.0959.

(3S,3aR,6R,6aS)-Allyl 3-methyl-1-((4-nitrophenyl)sulfonyl)octahydrocyclopenta[b]pyrrole-6-carboxylate 8. To a solution of acid 19 (50 mg, 0.14 mmol) in anhydrous DCM (1.5 mL) cooled to 0 °C, was added Et₃N (80 μL, 0.56 mmol) and allyl bromide (25 μL, 0.28 mmol). The resulting solution was stirred for 30 min at rt. The reaction mixture was concentrated in vacuum, and the reaction mixture was extracted with EtOAc (3 × 5 mL). The combined organic extracts were washed with brine solution (10 mL), dried over anhydrous Na₂SO₄, and concentrated in vacuum. The crude product was purified by column chromatography over 100-200 mesh silica gel (10% EtOAc/hexanes) to afford compound 8 (44 mg, 0.11 mmol) in 80% yield as a colorless solid. TLC: Rₚ 0.6 (20% EtOAc/hexane); m.p: 124-126 °C; [α]D²⁰ +2.6 (c 1.3, CHCl₃); IR (KBr) 3096, 2927, 2860, 1727, 1531, 1351, 1167, 1115, 1026, 613 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ
8.42 (d, $J = 8.8$ Hz, 2H), 8.07 (d, $J = 8.8$ Hz, 2H), 5.99 (ddd, $J = 17.2$, 10.7, 5.7 Hz, 1H), 5.40 (dd, $J = 17.2$, 1.5 Hz, 1H), 5.31 (dd, $J = 10.4$, 1.2 Hz, 1H), 4.70 – 4.66 (m, 2H), 4.12 (dd, $J = 9.0$, 3.8 Hz, 1H), 3.73 (dd, $J = 9.3$, 6.3 Hz, 1H), 3.25 – 3.21 (m, 1H), 2.57 (t, $J = 9.3$ Hz, 1H), 2.21 – 2.11 (m, 2H), 1.99 - 1.90 (m, 2H), 1.83 – 1.75 (m, 1H), 1.55 – 1.50 (m, 1H), 0.86 (d, $J = 6.6$ Hz, 3H); $^{13}$C {$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 174.0, 150.3, 141.4, 132.2, 129.3, 124.3, 118.4, 67.0, 65.5, 57.5, 51.7, 38.0, 30.4, 30.0, 16.5; MS (ESI – TOF) $m/z$: 395 [M + H]$^+$. HRMS (ESI – TOF) $m/z$: [M + H]$^+$ calcd for C$_{18}$H$_{23}$N$_2$O$_6$S, 395.1277; found, 395.1275.
Compound 10

1H NMR (400 MHz, CDCl3)
Compound 11

\[ \text{HNM\text{R} (400 MHz, CDCl}_3) \]

\[ \text{C NMR (125 MHz, CDCl}_3) \]
Compound 12

$\text{SATHISH-M0010}$
Compound 13

$^{13}$C NMR (125 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
Compound 14
Compound 15
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
Compound 16

HH

$^1$H NMR (500 MHz, CDC$_3$)
Compound 17
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
Compound 18

$^1$H NMR (400 MHz, CDCl$_3$)
Compound 19

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (125 MHz, CDCl$_3$)
Compound 8

\[
\text{\textsuperscript{13}C NMR (125 MHz, CDCl₃)}
\]

\[
\text{\textsuperscript{1}H NMR (500 MHz, CDCl₃)}
\]
$^{13}$C NMR (100 MHz, CDCl3)
Compound 8 NOE a. full
b. Exp 1
c. Exp 2