Supporting Information for:

Synthesis of Tailored Hydrodipyrrins and Examination in Directed Routes to Bacteriochlorins and Tetradehydrocorrins

Shaofei Zhang, Muthyala Nagarjuna Reddy, Olga Mass, Han-Je Kim, Gongfang Hu, and Jonathan S. Lindsey

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I. Synthesis of hydrodipyrrins

The eight hydrodipyrrins that were prepared and tested but found not to afford a viable macrocycle are shown in Chart 1. We first describe the synthesis and characterization of the eight hydrodipyrrins (Schemes S1–S6), followed by exploratory routes to several desired hydrodipyrrins (Scheme S7). The examination of the eight hydrodipyrrins in exploratory routes to macrocycles is described in the subsequent section.

Scheme S1. Route to a protected tetrahydrodipyrrin–acetal and use in α-lithiation.

1,1-Dimethoxy-4,4-dimethyl-5-nitro-6-(N-p-tosylpyrrol-2-yl)hexan-2-one (S10).

Following a general procedure, a mixture of S9 (0.937 g, 3.19 mmol), 13b (1.01 g, 6.37 mmol) and DBU (1.0 mL, 6.4 mmol) was stirred at room temperature for 16 h. The reaction mixture was diluted with ethyl acetate (50 mL) and washed with water (3 × 50 mL). The organic phase was dried, concentrated and chromatographed [silica, hexanes/ethyl acetate (3:1)] to afford a yellow solid (0.86 g, 60%): $^1$H NMR δ 1.15 (s, 3H), 1.23 (s, 3H), 2.42 (s, 3H), 2.59, 2.70 (AB, $^2$J = 18.9 Hz, 2H), 3.21 (ABX, $^3$J = 2.0 Hz, $^2$J = 13.1 Hz, 1H), 3.36 (ABX, $^3$J = 4.5 Hz, $^2$J = 13.1 Hz, 1H), 3.42 (s, 6H), 4.37 (s, 1H), 5.17 (ABX, $^3$J = 2.0 Hz, $^2$J = 11.7 Hz, 1H), 6.02 (m, 1H), 6.16 (m, 1H), 7.26 (m, 1H), 7.32 (d, $J$ = 8.2 Hz, 2H), 7.61 (d, $J$ = 8.2 Hz, 2H). $^{13}$C NMR δ 21.9, 23.9, 26.7, 36.6, 44.7, 55.2, 94.1, 104.8, 112.1, 114.8, 123.8, 126.7, 128.3, 130.4, 138.3, 145.5, 203.3; ESI-MS obsd 453.1189, calcd 453.1690 [(M + H)$^+$], M = C$_{21}$H$_{28}$N$_2$O$_7$S.

S1
2,3,4,5-Tetrahydro-1-(1,1-dimethoxymethyl)-3,3-dimethyl-N\textsuperscript{11}-p-tosyl dipyrin (S1).
Following a general procedure,\textsuperscript{25} a mixture of S10 (0.862 g, 1.91 mmol) and NH\textsubscript{4}Cl (0.303 g, 5.72 mmol) in THF/H\textsubscript{2}O (20 mL, 1:1) was treated with fresh zinc dust (1.25 g, 19.1 mmol) in one portion and stirred at room temperature for 1 h. The reaction mixture was filtered through filter paper. The filtrate was diluted with ethyl acetate (50 mL). The organic layer was washed with brine, dried, concentrated and chromatographed [silica, hexanes/ethyl acetate (4:1)] to afford a yellow oil (0.40 g, 52%). \textsuperscript{1}H NMR δ 0.90 (s, 3H), 1.08 (s, 3H), 2.40 (s, 3H), 2.37–2.49 (m, 2H), 2.72 (ABX, \textsuperscript{3}J = 9.6 Hz, \textsuperscript{2}J = 16.0 Hz, 1H), 2.98 (ABX, \textsuperscript{3}J = 4.8 Hz, \textsuperscript{2}J = 16.0 Hz, 1H), 3.38 (s, 3H), 3.39 (s, 3H), 3.81–3.85 (m, 1H), 4.79 (s, 1H), 6.21–6.24 (m, 2H), 7.27 (d, J = 8.4 Hz, 2H), 7.29–7.31 (m, 1H), 7.65 (d, J = 8.4 Hz, 2H); \textsuperscript{13}C NMR δ 21.8, 22.8, 27.2, 28.2, 41.8, 48.7, 54.8, 78.2, 103.1, 111.9, 113.9, 122.6, 127.0, 130.2, 133.8, 136.6, 145.0, 174.2; ESI-MS obsd 405.1845, calecd 405.1842 [(M + H)], M = C\textsubscript{21}H\textsubscript{28}N\textsubscript{2}O\textsubscript{4}S.

2,3,4,5-Tetrahydro-9-(hydroxy(p-toly)methyl)-1-(1,1-dimethoxymethyl)-3,3-dimethyl-N\textsuperscript{11}-p-tosyl dipyrin (S11). In an oven-dried flask, a solution of S1 (42.8 mg, 0.106 mmol) in dry THF (4.0 mL) was bubbled with argon for at least 45 min. Then the solution was cooled to −78 °C (dry ice/acetone bath) and treated dropwise with LDA solution (2.0 M in heptanes/THF/ethylbenzene, 106 µL, 0.212 mmol) under argon. The reaction mixture was stirred at −78 °C for 45 min. Then, p-tolualdehyde (22 µL, 0.21 mmol) was added via syringe. After 30 min, the dry ice/acetone bath was removed and the reaction mixture was stirred at room temperature for 2 h. The mixture was quenched by the addition of water and extracted with ethyl acetate (3 × 50 mL). The organic extract was washed, dried and concentrated. Purification by gradient chromatography [silica, hexanes/ethyl acetate (3:1 to 1:1)] afforded a yellow oil (20 mg, 36%). \textsuperscript{1}H NMR δ 0.88 (s, 3H), 1.09 (s, 3H), 2.34 (s, 3H), 2.41 (m, 5H), 2.75 (m, 1H), 3.02 (m, 1H), 3.37 (m, 6H), 3.47 (br, 1H), 3.82 (m, 1H), 4.78 (s, 1H), 5.68 (m, 1H), 6.12 (m, 2H), 7.12 (d, J = 7.8 Hz, 2H), 7.18 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 8.7 Hz, 2H), 7.56 (d, J = 8.7 Hz, 2H); ESI-MS obsd 525.2409, calecd 525.2353 [(M + H)], M = C\textsubscript{29}H\textsubscript{36}N\textsubscript{2}O\textsubscript{2}S\textsubscript{2}.

Scheme S2. Synthesis of a dihydridipyrin bearing a 1-dicyanovinyl group.

7-(4-Bromophenyl)-1-(2,2-dicyanovinyl)-2,3-dihydro-3,3-dimethyl dipyrin (S2). A sample of 21 (78 mg, 0.20 mmol) was treated with SeO\textsubscript{2} (67 mg, 0.60 mmol) in 1,4-dioxane at room temperature for 90 min. The reaction mixture was diluted with ethyl acetate. The organic phase was washed (saturated aqueous NaHCO\textsubscript{3} solution then brine), dried (Na\textsubscript{2}SO\textsubscript{4}) and concentrated. The residue was dissolved in ethanol (8.0 mL) and then treated with malononitrile (20. mg, 0.30 mmol) and Et\textsubscript{2}NH (10. µL, 0.10 mmol) at room temperature. After 30 min, the reaction mixture was concentrated and then diluted with CH\textsubscript{2}Cl\textsubscript{2}. The organic layer was washed with brine, dried (Na\textsubscript{2}SO\textsubscript{4}), concentrated and chromatographed (silica, CH\textsubscript{2}Cl\textsubscript{2}) to afford a blue solid (24 mg, 29%). \textsuperscript{1}H NMR (300 MHz) δ 1.24 (s, 6H), 2.91 (s, 2H), 6.34 (s, 1H), 6.35 (m, 1H),
7.05 (m, 1H), 7.28 (d, J = 6.3 Hz, 2H), 7.54–7.57 (m, 3H), 10.88 (br, 1H); ESI-MS obsd 405.0706, calcd 405.0709 [(M + H)+, M = C21H17BrN4]; λabs (CH2Cl2) 608 nm.

Scheme S3. Synthesis of a dihydodiaryle bearing an ethyl acrylate group at the 1-position.

9-tert-Butoxycarbonyl-1-(3-ethoxy-3-oxoprop-1-yl)-2,3-dihydro-3,3,7,8-tetramethyldiaryle (S3). A mixture of S12 (34.4 mg, 0.100 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (38.3 mg, 0.110 mmol) in dry CH2Cl2 (1.0 mL) was stirred at room temperature for 16 h. The resulting mixture was concentrated and chromatographed (silica, CH2Cl2) to give an orange solid (34.0 mg, 82%): 1H NMR (300 MHz) δ 1.26 (s, 6H), 1.34 (t, J = 6.9 Hz, 3H), 1.61 (s, 9H), 2.06 (s, 3H), 2.26 (s, 3H), 2.59 (s, 2H), 4.27 (q, J = 6.9 Hz, 2H), 5.93 (s, 1H), 6.28 (d, J = 16.2 Hz, 1H), 7.58 (d, J = 16.2 Hz, 1H), 10.98 (br, 1H); ESI-MS obsd 401.2436, calcd 401.2435 [(M + H)+, M = C23H32N2O4].

Scheme S4. Synthesis of a dihydodiaryle bearing a 9-phenylthio group.

4-Ethoxycarbonyl-3-p-tolyl-2-(phenylthio)pyrole (S14a). Following a general procedure,30 a mixture of S13 (6.90 g, 50.0 mmol), PhSSPh (5.45 g, 25.0 mmol) and CuI (0.47 g, 2.5 mmol) was treated with DMSO (50 mL). The reaction mixture was stirred at 110 °C for 20 h. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (400 mL) and washed with water (300 mL × 4). The organic layer was dried (Na2SO4), concentrated, and chromatographed (silica, CH2Cl2), which afforded two isomers. The title compound was isolated.
as a brown solid (6.03 g, 50%): ¹H NMR (300 MHz) δ 1.21 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 4.18 (q, J = 7.2 Hz, 2H), 6.96–6.99 (m, 2H), 7.10–7.22 (m, 7H), 7.61 (d, J = 3.0 Hz, 1H), 8.6 (br, 1H); ESI-MS obsd 338.1209, calcld 338.1209 [(M + H)⁺, M = C₂₀H₁₉NO₂S]. Isomer S₁₄b was isolated as a yellow solid (3.01 g, 25%): ¹H NMR (300 MHz) δ 1.11 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 4.18 (q, J = 7.2 Hz, 2H), 6.96–7.52 (m, 10H), 7.96 (br, 1H); ESI-MS obsd 338.1209, calcld 338.1216 [(M + H)⁺, M = C₂₀H₁₉NO₂S].

4-Ethoxycarbonyl-5-(2-nitroethyl)-3-p-tolyl-2-(phenylthio)pyrrole (S₁₅). Following a general procedure,¹⁹ a solution of S₁₄a (6.0 g, 25 mmol) in CH₂Cl₂ (50 mL) and DMF (7.7 mL) was treated dropwise with POC₃ (3.5 mL, 38 mmol) under argon at 0 °C (ice bath). After 1 h, the ice-bath was removed and the reaction mixture was allowed to warm to room temperature. The mixture was stirred for 20 h and then cooled to 0 °C again, whereupon aqueous NaOH solution (2M, 50 mL) was added. The mixture was extracted with CH₂Cl₂. The organic phase was washed with brine, dried and concentrated. Chromatography [silica, CH₂Cl₂/hexanes (1:1)] afforded a yellow oil (0.61 g, 31%): Chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a yellow solid (0.61 g, 1.07 mmol) in THF (10 mL) was bubbled with argon for 10 min and then treated with NaOCH₃ (0.290 g, 5.35 mmol). The mixture was stirred at room temperature for 50 min. In a second flask, TiCl₃ solution (20 wt% in 3% HCl, 5.4 mL, 8.6 mmol) and water (40 mL) were mixed and bubbled with argon for 15 min. Then NH₄OAc (8.2 g, 107 mmol) was added to adjust the pH to 6, followed by 3.0 mL of THF. The resulting mixture was bubbled with argon for further 30 min. The solution in the first flask was transferred via cannula into the second one.
After 20 h, saturated aqueous NaHCO₃ solution (300 mL) was added to the reaction mixture. The mixture was extracted with ethyl acetate. The extract was washed with brine and water, dried (Na₂SO₄) and concentrated. Chromatography (silica, CH₂Cl₂) afforded a yellow oil (230 mg, 41%): \(^1\)H NMR (300 MHz) δ 1.10 (t, J = 7.2 Hz, 3H), 1.26 (s, 6H), 2.34 (s, 3H), 2.64 (s, 2H), 3.37 (s, 6H), 4.12 (q, J = 7.2 Hz, 2H), 4.90 (s, 1H), 6.86 (s, 1H), 7.07–7.20 (m, 9H), 11.3 (br, 1H); ESI-MS obsd 519.2322, calcd 519.2312 [(M + H)\(^+\), M = C\(_{30}\)H\(_{34}\)N\(_2\)O\(_4\)S].

**Scheme S5.** Synthesis of a dihydrodipyrrin–acetal bearing a pinacol boronate at the 9-position.

2,3-Dihydro-1-(1,1-dimethoxymethyl)-9-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,3-dimethyl-7-p-tolylidipyrrin (S5). Following a reported procedure, \(^{31}\) samples of S17 (339 mg, 1.00 mmol), B\(_2\)(pin)\(_2\) (152 mg, 0.598 mmol), [Ir(cod)(OMe)]\(_2\) (6.6 mg, 0.010 mmol) and 4,4′-di-tert-butyl-2,2′-dipyridyl (dtpy) (5.4 mg, 0.020 mmol) were placed in a Schlenk flask, which then was evacuated and purged with argon, and then charged with dried THF (3.0 mL). The mixture was stirred at 80 °C for 18 h. The resulting mixture was concentrated to a green oil. The green oil was dissolved in CH₂Cl₂ and filtered through a short silica column (2 cm high, eluent CH₂Cl₂) to remove the catalyst and salts. The filtrate was concentrated, and the resulting residue was dried in vacuum to give a yellow solid (265 mg, 75%): \(^1\)H NMR (300 MHz) δ 1.19 (s, 6H), 1.32 (s, 12H), 2.38 (s, 3H), 2.63 (s, 2H), 3.53 (s, 6H), 5.06 (s, 1H), 6.09 (s, 1H), 6.86 (d, J = 2.7 Hz, 1H), 7.22 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 11.13 (br, 1H); ESI-MS obsd 465.2919, calcd 465.2922 [(M + H)\(^+\), M = C\(_{27}\)H\(_{37}\)N\(_2\)O\(_4\)B].
**Scheme S6.** Synthesis of dihydrodipyrrins bearing 1-methoxy or 1-methylthio groups.

### 4-Ethoxycarbonyl-2-iodo-3-p-tolypyrrole (S18).
Following a general procedure, a stirred solution of S13 (2.29 g, 10.0 mmol) in dry DMF (25 mL) was treated dropwise with a solution of NIS (2.25 g, 10.0 mmol) in DMF (25 mL) at room temperature. The reaction mixture was stirred for 2 h. Then, the mixture was diluted with ethyl acetate (200 mL) and washed with brine and water. The organic layer was dried (Na$_2$SO$_4$), concentrated and chromatographed (silica, CH$_2$Cl$_2$) to give a bright-white solid (2.90 g, 82%): $^1$H NMR (300 MHz) δ 1.18 (t, $J$ = 7.2 Hz, 3H), 2.39 (s, 3H), 4.10 (q, $J$ = 7.2 Hz, 2H), 7.21 (m, 4H), 7.56 (d, $J$ = 3.0 Hz, 1H), 8.40 (br, 1H); ESI-MS obsd 356.0141, calcd 356.0142 [(M + H)$^+$, M = C$_{14}$H$_{14}$INO$_2$].

### 4-Ethoxycarbonyl-2-[(4,4-dimethyl-5-oxodihydrofuran-2(3H)-ylidene)methyl]-3-p-tolypyrrole (S20).
Following a general procedure, a solution of S18 (1.78 g, 5.00 mmol), S19 (1.26 g, 10.0 mmol) and BnNEt$_3$Cl (1.14 g, 5.00 mmol) in dry acetonitrile (20.0 mL) and Et$_3$N (5.0 mL) was degassed by three freeze-pump-thaw cycles. Then Pd(PPh$_3$)$_4$ (289 mg, 0.250 mmol) was added under argon. The reaction mixture was refluxed for 24 h, and then concentrated under high vacuum. The residue was dissolved in CH$_2$Cl$_2$. The resulting solution was washed with brine and water, dried (Na$_2$SO$_4$), concentrated, and chromatographed [silica, hexanes/ethyl acetate (2:1)] to afford a yellow solid (1.20 g, 68%): $^1$H NMR (300 MHz) δ 1.18 (s, 6H), 1.92 (t, $J$ = 7.2 Hz, 3H), 2.34 (s, 3H), 2.38 (d, $J$ = 2.4 Hz, 2H), 4.17 (q, $J$ = 7.2 Hz, 2H), 6.07 (m, 1H), 7.16 – 7.19 (m, 4H), 7.41 (d, $J$ = 3.3 Hz, 1H), 8.98 (br, 1H); $^{13}$C NMR (100 MHz) δ 179.8, 165.0, 148.3, 136.5, 131.4, 130.7, 128.7, 125.2, 124.8, 124.6, 115.1, 97.6, 59.9, 40.2, 40.0, 31.2, 25.1, 21.4, 14.5; ESI-MS obsd 354.1703, calcd 354.1700 [(M + H)$^+$, M = C$_{21}$H$_{23}$NO$_4$].

### 8-Ethoxycarbonyl-1,10,2,3-tetrahydro-2,2-dimethyl-7-p-tolylidipyrin-1-one (S6).
Following a general procedure, a solution of S20 (704 mg, 2.00 mmol) in THF (4.0 mL) was treated with 30% NH$_4$OH (4.0 mL, ~30 mmol) at room temperature for 20 h. The solution was
then concentrated to dryness at 50 °C under reduced pressure. The resulting residue was placed in a 20-mL vial, which was then heated to 120 °C under high vacuum to effect dehydration. After 2 h, the residue was allowed to cool to room temperature. Chromatography [silica, hexanes/ethyl acetate (1:1)] gave the unsaturated lactams as a mixture of geometric isomers (molar ratio Z:E = 1:1); the Z and E isomers exhibited TLC (silica, ethyl acetate) Rf values of 0.70 and 0.84, respectively. The title compound (Z-isomer) was isolated as a white solid (190 mg, 27%). 1H NMR (300 MHz) δ 1.14 (s, 6H), 1.18 (t, J = 7.2 Hz, 3H), 2.34 (s, 3H), 2.53 (d, J = 2.1 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H), 5.63 (m, 1H), 7.14 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 3.0 Hz, 1H), 7.95 (br, 1H), 8.66 (br, 1H); ESI-MS obsd 353.1860, calcd 353.1860 [(M + H)+, M = C21H24N2O3]. Data for the E-isomer of S6: 1H NMR (300 MHz) δ 1.18 (t, J = 7.2 Hz, 3H), 1.27 (s, 6H), 2.39 (s, 3H), 2.64 (d, J = 1.5 Hz, 2H), 4.14 (q, J = 7.2 Hz, 2H), 5.36 (m, 1H), 7.20 – 7.23 (m, 4H), 7.48 (d, J = 3.3 Hz, 1H), 10.08 (br, 1H), 10.13 (br, 1H); ESI-MS obsd 353.1862, calcd 353.1860 [(M + H)+, M = C21H24N2O3].

8-Ethoxycarbonyl-2,3-dihydro-1-methoxy-2,2-dimethyl-7-p-tolylidihydridopyrrin (S7). Following a general procedure,27 a stirred solution of S6 (100 mg, 0.285 mmol) in CH2Cl2 (20 mL) was treated at room temperature under argon with Hünig’s base (990 µL, 5.70 mmol) and trimethyloxonium tetrafluoroborate (841 mg, 5.70 mmol). After 2 h, the mixture was diluted with CH2Cl2 (50 mL), washed twice with water (50 mL), dried (Na2SO4) and concentrated. Column chromatography [silica, CH2Cl2/ethyl acetate (1:1)] afforded a byproduct (S21) followed by the title compound. The title compound exhibited a TLC [silica, hexanes/ethyl acetate (1:1)] Rf value of 0.50 and was isolated as a yellow solid (63 mg, 62%): 1H NMR (300 MHz) δ 1.18 (t, J = 7.2 Hz, 3H), 1.20 (s, 6H), 2.34 (s, 3H), 2.71 (d, J = 1.8 Hz, 2H), 3.86 (s, 3H), 4.13 (q, J = 7.2 Hz, 2H), 6.25 (m, 1H), 7.14 (d, J = 8.1 Hz, 2H), 7.20 (d, J = 8.1 Hz, 2H), 7.42 (d, J = 3.3 Hz, 1H), 8.5 (br, 1H); 13C NMR (100 MHz) δ 182.7, 147.8, 135.9, 131.7, 130.8, 128.9, 128.4, 124.2, 124.0, 115.3, 104.7, 59.5, 56.6, 44.6, 44.3, 25.8, 25.7, 21.3, 14.4; ESI-MS obsd 367.2015, calcd 367.2016 [(M + H)+, M = C22H26N2O3].

8-Ethoxycarbonyl-1,10,2,3,-tetrahydro-2,2-trimethyl-7-p-tolylidipyrin-1-one (S21). This byproduct exhibited a TLC [silica, CH2Cl2] Rf value of 0.50 and was isolated as a solid (19 mg, 19%): 1H NMR (300 MHz) δ 1.19 (t, J = 7.2 Hz, 3H), 1.20 (s, 6H), 2.38 (s, 3H), 2.64 (d, J = 1.8 Hz, 2H), 4.01 (s, 3H), 4.15 (q, J = 7.2 Hz, 2H), 5.59 (s, 1H), 7.17 (d, J = 8.1 Hz, 2H), 7.26 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 3.0 Hz, 1H), 11.03 (br, 1H); ESI-MS obsd 367.2015, calcd 367.2016 [(M + H)+, M = C22H26N2O3].

8-Ethoxycarbonyl-2,3-dihydro-2,2-dimethyl-1-methylthio-7-p-tolylidihydridopyrrin (S8). Following a general procedure,25 a solution of S6 (100 mg, 0.285 mmol) and Lawesson’s reagent (70 mg, 0.17 mmol) in toluene (10 mL) was stirred for 1 h at 100 °C under argon. An additional 20 mg of Lawesson’s reagent was added and stirring was continued for 20 min. Then, the reaction mixture was cooled down. It was portioned between ethyl acetate and water. The organic layer was washed with brine, dried (Na2SO4) and concentrated. Column chromatography [silica, hexanes/ethyl acetate (1:1)] afforded 8-ethoxycarbonyl-1,10,2,3,-tetrahydro-2,2-dimethyl-7-p-tolylidipyrin-1-thione as a brown solid (76 mg, 71%). A stirred solution of the brown solid (34 mg, 0.092 mmol) in CH2Cl2 (9.2 mL) was treated under argon, with the Hünig’s base (320 µL, 1.84 mmol) and trimethyloxonium tetrafluoroborate (272 mg, 1.84 mmol). After 2 h, the mixture was diluted with CH2Cl2, washed with brine and water, dried (Na2SO4) and concentrated. Chromatography [silica, CH2Cl2/ethyl acetate (3:1)] afforded a pale-
yellow solid (32 mg, 91%): $^1$H NMR (300 MHz) $\delta$ 1.18 (t, $J = 6.9$ Hz, 3H), 1.26 (s, 6H), 2.36 (s, 3H), 2.46 (s, 3H), 2.73 (d, $J = 2.1$ Hz, 2H), 4.1 (q, $J = 6.9$ Hz, 2H), 6.41 (m, 1H), 7.15–7.24 (m, 4H), 7.48 (d, $J = 3.0$ Hz, 1H), 8.40 (br, 1H); ESI-MS obsd 383.1786, calcd 383.1788 [(M + H)$^+$, M = C$_{22}$H$_{26}$N$_2$O$_2$S].

Exploratory routes to hydrodipyrrin targets T1–T3 are shown in Schemes S7–S9.

**Scheme S7.** Exploratory route to hydrodipyrrin T1.

**Scheme S8.** Exploratory route to hydrodipyrrin T2.
Scheme S9. Exploratory route to hydrodipyrins T3.

3,3-Dimethyl-4-nitro-1-(1,3-dithiolan-2-yl)-5-(N-p-tosylpyrrol-2-yl)pentan-1-one (S22). Following a general procedure, a mixture of S9 (0.925 g, 3.15 mmol) and 13e (0.887 g, 4.72 mmol) was treated with DBU (2.60 mL, 9.45 mmol) at room temperature. The progress of the reaction was monitored by TLC analysis. After 3 h, the reaction mixture was diluted with ethyl acetate. The organic phase was washed (brine and water), dried (Na$_2$SO$_4$), and concentrated to a brown oil. Column chromatography [silica, hexanes/ethyl acetate (3:1)] afforded a yellow oil (0.431 mg, 28%): $^1$H NMR $\delta$ 1.19 (s, 3H), 1.24 (s, 3H), 2.42 (s, 3H), 2.75 (AB, $J = 17.6$ Hz, 1H), 2.82 (AB, $J = 17.6$ Hz, 1H), 3.23–3.40 (m, 7H), 5.06 (ABX, $^3J = 2.0$ Hz, $^2J = 11.6$ Hz, 1H), 6.02 (m, 1H), 6.17 (m, 1H), 7.24 (m, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.60 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (100 MHz) $\delta$ 202.3, 201.6, 145.5, 145.1, 136.3, 130.5, 130.4, 129.4, 129.2, 127.3, 126.6, 124.0, 123.8, 122.7, 115.1, 114.9, 112.4, 112.2, 94.9, 94.7, 59.1, 58.9, 58.6, 58.4, 46.8, 46.6, 45.5, 43.9, 41.9, 41.7, 39.2, 39.2, 38.9, 38.0, 37.2, 27.8, 26.9, 24.4, 23.8, 23.5, 22.0; ESI-MS obsd 483.1072, calcld 483.1077 [(M + H)$^+$, M = C$_{21}$H$_{26}$N$_2$O$_5$S$_3$].

2,3,4,5-Tetrahydro-3,3-dimethyl-1-(1,3-dithiolan-2-yl)-N$^p$-tosyldipyr  (S23). Following a general procedure, a sample of S22 (0.43 g, 0.89 mmol) in THF/H$_2$O (4.5 mL/4.5 mL) was treated with NH$_4$Cl followed by zinc dust. The reaction mixture was stirred vigorously at room temperature for 1 h. Then ethyl acetate (10 mL) was added and the resulting mixture was filtered. The filtrate was washed (brine), dried (Na$_2$SO$_4$), concentrated and chromatographed [silica, CH$_2$Cl$_2$/ethyl acetate (1:1)] to afford a white solid (219 mg, 56%): $^1$H NMR $\delta$ 1.00 (s, 3H), 1.08 (s, 3H), 2.40 (s, 3H), 2.54 (AB, $J = 18$ Hz, 1H), 2.61 (AB, $J = 18$ Hz, 1H), 3.08 (ABX, $^3J = 9.9$ Hz, $^2J = 15.9$ Hz, 1H), 3.31 (m, 4H), 3.45 (ABX, $^3J = 3.9$ Hz, $^2J = 15.9$ Hz, 1H), 4.12 (m, 1H), 5.95 (s, 1H), 6.11 (m, 1H), 6.21 (m, 1H), 7.27 (m, 1H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.67 (d, $J = 8.4$ Hz, 2H); $^{13}$C NMR (100 MHz) $\delta$ 146.0, 136.0, 145.1, 136.3, 130.5, 130.4, 129.4, 129.2, 127.1, 126.9, 123.3, 123.2, 115.0, 114.9, 111.9, 80.3, 44.6, 44.5, 42.0, 40.1, 40.0, 37.3, 28.2, 27.3, 24.7, 22.8, 21.9; ESI-MS obsd 434.1151, calcld 434.1157 [(M + H)$^+$, M = C$_{21}$H$_{26}$N$_2$O$_5$S$_3$].

1-Ethoxy-4,4-dimethyl-5-nitro-6-[3-(p-tolyl)pyrrol-2-yl]hexan-1,2-dione (S25). Following a general procedure, a mixture of S24 (380 mg, 1.64 mmol) and 13d (635 mg, 4.96
mmol) in DBU (0.50 mL, 3.3 mmol) was stirred for 16 h at room temperature. The reaction mixture was diluted with ethyl acetate and then washed with brine and water. The organic phase was dried, concentrated and chromatographed [silica, hexanes/ethyl acetate (3:1)] to afford a yellow oil (51 mg, 10%): ¹H NMR (300 MHz) δ 1.12 (s, 3H), 1.21 (s, 3H), 1.38 (t, 3H), 2.37 (s, 3H), 2.79, 3.01 (AB, 2J = 18.4 Hz, 2H), 3.28 (ABX, 3J = 3.0 Hz, 2J = 15.8 Hz, 1H), 3.36 (ABX, 3J = 11.6 Hz, 2J = 15.8 Hz, 1H), 4.12 (m, 2H), 5.02 (ABX, 3J = 3.0 Hz, 2J = 11.2 Hz, 1H), 6.24 (m, 1H), 6.68 (m, 1H), 7.20 (m, 4H), 8.80–8.08 (br, 1H); ¹³C NMR (100 MHz) δ 192.2, 129.4, 128.4, 122.3, 117.8, 109.7, 95.1, 63.0, 46.7, 37.3, 25.4, 24.4, 24.0, 21.3, 14.20; ESI-MS obsd 387.1908, calcd 387.1914 [(M + H)⁺, M = C₁₂H₂₆N₂O₅].

**Methyl 3,3-dimethyl-4-nitro-5-(N-p-tosyl-2-pyrrolyl)pentanoate (S27).** Following a general procedure,¹⁹ a mixture of S9 (270 mg, 0.918 mmol) and methyl 3,3-dimethylacrylate (13e, 0.67 mL, 5.5 mmol) was treated with DBU (0.54 mL, 2.8 mmol) and stirred at room temperature under argon for 24 h. The crude reaction mixture was diluted with ethyl acetate. The organic phase was washed (water and brine), dried (Na₂SO₄), and concentrated to a dark brown oil. Column chromatography [silica, CH₂Cl₂/hexanes (2:1)] afforded a yellow oil (132 mg, 35%): ¹H NMR δ 1.18 (s, 3H), 1.22 (s, 3H), 2.36, 2.46 (AB, 2J = 15.1 Hz, 2H), 2.42 (s, 3H), 3.22 (ABX, 3J = 2.5 Hz, 2J = 15.8 Hz, 1H), 3.36 (ABX, 3J = 11.6 Hz, 2J = 15.8 Hz, 1H), 3.68 (s, 3H), 5.01 (ABX, 3J = 2.5 Hz, 2J = 11.6 Hz, 1H), 6.03–6.05 (m, 1H), 6.16–6.19 (m, 1H), 7.24–7.27 (m 1H), 7.32 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H); ¹³C NMR δ 21.8, 24.0, 26.9, 36.6, 42.6, 51.7, 95.1, 112.2, 115.1, 123.9, 126.5, 129.0, 130.4, 136.2, 145.4, 171.2; ESI-MS obsd 431.1250, calcd 431.1247 [(M + Na)⁺, M = C₁₉H₂₄N₂O₆S].

**1,10,2,3,4,5-Hexahydro-3,3-dimethyl-N⁸⁻p-tosylpyrrin-1-one (S28).** Following a general procedure,²⁵ a solution of S27 (215 mg, 0.527 mmol) in ethanol/formic acid (4.8 mL, 4:1) was treated with zinc dust (856 mg, 13.2 mmol) and stirred overnight at room temperature. The reaction mixture was diluted with ethyl acetate and filtered through Celite. The filtrate was washed (saturated aqueous NaHCO₃, water, and brine), dried (Na₂SO₄) and concentrated to a light pink solid. Chromatography (silica, ethyl acetate) afforded a white solid (45 mg, 25%): mp 124–126 °C; ¹H NMR δ 1.08 (s, 3H), 1.20 (s, 3H), 2.12–2.23 (m, 2H), 2.42 (s, 3H), 2.51 (ABX, 3J = 11.0 Hz, 2J = 15.0 Hz, 1H), 3.01 (ABX, 3J = 2.6 Hz, 2J = 15.0 Hz, 1H), 3.56 (ABX, 3J = 2.6 Hz, 2J = 11.0 Hz, 1H), 5.36 (br, 1H), 6.04–6.06 (m, 1H), 6.22–6.23 (m, 1H), 7.30 (m, 3H), 7.60 (d, J = 8.4 Hz, 2H); ¹³C NMR δ 22.1, 23.2, 27.7, 29.5, 38.9, 46.5, 62.7, 112.3, 114.4, 124.1, 127.0, 130.7, 132.1, 136.7, 145.8, 176.8.

**1,10,2,3,4,5-Hexahydro-3,3-dimethyl-N⁸⁻p-tosylpyrrin-1-thione (S29).** Following a literature procedure,²⁵ a mixture of S28 (89 mg, 0.26 mmol) and Lawesson’s reagent (120 mg, 0.300 mmol) in toluene (5.2 mL) was stirred overnight at 100 °C. The reaction mixture was diluted with ethyl acetate. The organic phase was washed with water and brine, dried (Na₂SO₄), and concentrated to a yellow oil, which solidified on standing. Chromatography (silica, CH₂Cl₂) afforded a white solid (75 mg, 80%): mp 149–152 °C; ¹H NMR δ 1.06 (s, 3H), 1.20 (s, 3H), 2.42 (s, 3H), 2.61 (ABX, 3J = 11.3 Hz, 2J = 15.1 Hz, 1H), 2.72 (s, 2H), 3.00 (ABX, 3J = 2.5 Hz, 2J = 15.1 Hz, 1H), 3.85 (ABX, 3J = 2.5 Hz, 2J = 11.3 Hz, 1H), 6.09–6.12 (m, 1H), 6.24–6.27 (m, 1H), 7.30–7.34 (m, 3H), 7.62 (d, J = 8.5 Hz, 2H), the N–H signal was missing; ¹³C NMR δ 21.9, 22.3, 26.5, 28.1, 41.5, 58.4, 69.3, 112.2, 114.7, 124.2, 126.7, 130.5, 130.9, 136.3, 145.7, 204.9; Calcd for C₁₈H₂₂N₂O₂S₂: C, 59.64; H, 6.12; N, 7.73; Found: C, 60.01; H, 6.14; N, 7.40.
Following a literature procedure, samples of S29 (30 mg, 0.10 mmol), methyl acrylate (13f, 0.027 mL, 0.30 mmol) and a catalytic amount of NaOH were stirred in THF (1.4 mL) at room temperature for 2.5 h. The reaction mixture was diluted with ethyl acetate, and water was added. The organic extract was dried (Na₂SO₄) and concentrated to a colorless oil that was dried overnight under high vacuum. The resulting crude product (1,10,2,3,4,5-hexahydro-N₁₀-(3-methoxy-3-oxopropyl)-3,3-dimethyl-N₁₁-p-tosyldipyrrin-1-thione, S30) was dissolved in CH₃CN (1.4 mL) and treated with ethyl bromoacetate (0.033 mL, 0.30 mmol). The reaction mixture was stirred overnight at room temperature. A solution of Et₃N (0.016 mL, 0.12 mmol) and Ph₃P (31 mg, 0.12 mmol) in CH₂Cl₂ (0.3 mL) was added. The reaction mixture was stirred at room temperature under argon for 2 h. Concentration of the reaction mixture followed by chromatography [silica, CH₂Cl₂/hexanes (3:1) then CH₂Cl₂, then CH₂Cl₂/ethyl acetate (10:1)] afforded a light yellow oil (20 mg, 40%). ¹H NMR δ 0.94 (s, 3H), 0.98 (s, 3H), 1.26 (t, J = 6.8 Hz, 3H), 2.41 (s, 3H), 2.36–2.48 (m, 2H), 2.59 (ABX, ³J = 8.4 Hz, ²J = 15.2 Hz, 1H), 2.68 (d, J = 17.2 Hz, 1H), 2.79 (m, 1H), 2.88 (ABX, ³J = 5.4 Hz, ²J = 15.2 Hz, 1H), 3.12 (d, J = 17.2 Hz, 1H), 3.23 (m, 1H), 3.57 (ABX, ³J = 5.4 Hz, ²J = 8.4 Hz, 1H), 3.66 (s, 3H), 4.09 (q, J = 6.8 Hz, 2H), 4.46 (s, 1H), 6.00 (m, 1H), 6.22 (m, 1H), 7.30 (d, J = 8.4 Hz, 2H), 7.32 (m, 1H), 7.61 (d, J = 8.4 Hz, 2H); LD-MS obsd 503.5, calcd 503.2 [(M + H)⁺, M = C₂₆H₃₄N₂O₆S].

II. Exploration of directed routes to bacteriochlorins

Possible routes to unsymmetrically unsubstituted-bacteriochlorins were proposed and explored as outlined in the following schemes. In Scheme S10, the condensation between the respective hydrodipyrrin halves was envisaged to proceed via an organometallic reagent. The initial approach employed β-unsubstituted hydrodipyrrins, hence leading to a symmetrical bacteriochlorin. Each half is a tetrahydrodipyrrin and contains an N-p-tosyl protected pyrrolic unit. One hydrodipyrrin half contains a 9-carboxaldehyde unit whereas the other half contains an α-lithiated pyrrole (derived from S1). The required tetrahydrodipyrrin–carboxaldehyde (T1) was not reliably obtained. Exploratory reaction with the putative hydrodipyrrin derived from S1, envisaged to entail nucleophilic attack on the carboxaldehyde, failed to give the expected linear tetrapyrrole.

Scheme S10. Bacteriochlorin synthesis via an α-lithio pyrrolic species derived from S1.

In Scheme S11, a dihydrodipyrrin bears a Michael-like acceptor at the 1-position (S2). The Michael acceptor is the dicyanovinyl unit, akin to the ethyl acrylate 8 described in the body.
of the paper. The reactant 3 is a 9-bromodihydrodipyrrin-1-acetal. On the basis of the outcome of the reaction of 8 + 3 (Scheme 9, left), we anticipated the isolable product would be a tetradehydrocorrin bearing a dicyanovinyl moiety at the 19-position; such a macrocycle could also be expected to rearrange to give the corresponding 15-malonylbacteriochlorin. The route failed to give a characterizable macrocycle.

Scheme S11. Bacteriochlorin synthesis using a hydrodipyrinn bearing a Michael acceptor.

In Scheme S12, two routes to link the two hydrodipyrin halves were explored using Rh or Pd catalyzed coupling reactions. In each case, one half (S5) is a dihydrodipyrin bearing a pinacol boronate ester at the α-pyrrole position, whereas the pyrroline α-substituent of the other half varies from ethyl acrylate (S3, route A) to carboxaldehyde (S12, route B). No bacteriochlorin was formed in any case.

Scheme S12. Organometallic coupling to form linear tetrapyrrole precursors to bacteriochlorins.

In Scheme S13, the hydrodipyrin S4 contains a phenylthio group as the blocking unit at the α-pyrrolic position, whereas the other half (21) is a 1-methyldihydrodipyrin. The acid-catalyzed condensation failed to afford the expected linear intermediate or any macrocycle.
Scheme S13. Bacteriochlorin synthesis with a 9-(phenylthio)dihydrodipyrrin.

In Scheme S14, one half (5b) is a 9-methyldihydrodipyrrin-1-acetal whereas the other half contains a 1-oxo (S6), 1-methoxy (S7), or 1-methylthio (S8) group. The hydrodipyrrins described to this point all contain the gem-dimethyl unit at the 3-position, whereas the hydrodipyrrins here contain the gem-dimethyl unit at the 2-position. The latter were prepared via a new synthetic approach.\footnote{21} Regardless, none of the approaches led to the corresponding linear tetrapyrrole, a precursor to the desired bacteriochlorin.

Scheme S14. Bacteriochlorin routes via 2,2-dimethyl-substituted hydrodipyrrins.

In Scheme S15, like that in Scheme S10, the condensation between the respective hydrodipyrrin halves was envisaged to proceed via an organometallic reagent. The Grignard-mediated $\alpha$-acylation of a pyrrole unit of a dipyrromethane is a well established approach in the synthesis of porphyrins bearing distinct patterns of meso-substituents.\footnote{32} The acylation entails reaction of the pyrrole Grignard reagent of the tetrahydrodipyrrin (derived from S32) and an $S$-2-pyridyl thioester. Synthesis of the desired $S$-2-pyridyl thioester (T2) failed, however.
Scheme S15. Bacteriochlorin synthesis via α-acylation of a pyrrolic unit.

In Scheme S16, a 1-(ethoxycarbonylmethylene)hexahydrodipyrrin (T3) was desired for reaction with a 9-bromo-dihydrodipyrrin-1-acetal (3). The exocyclic α,β-unsaturated ester in T3 was envisaged as a means to shift the imine-enamine equilibrium to favor the enamine, whereas the bromo group served as a displaceable blocking group to thwart self-condensation of hydrodipyrrin 3. The resulting 15-ethoxycarbonyl group on the bacteriochlorin would serve as a convenient handle for subsequent elaboration, such as bioconjugation. The ethylidene embedded in the pyrrolidine motif of the hexahydrodipyrrin T3 is quite different from the Michael acceptor located at the 1-position of the dihydrodipyrrin S2 in Scheme S11 (or 8 in Scheme 9); the ethylidene moiety is attached to, and conjugated with, with pyrrolidine motif of the hexahydrodipyrrin T3, whereas the Michael acceptor is designed to promote attack at the β-carbon of the Michael acceptor. However, attempts to prepare T3 failed (Scheme S9); hence, the condensation and macrocyclization were not explored.

Scheme S16. Route to bacteriochlorins via a stabilized enamine-containing hydrodipyrrin.

In Scheme S17, a 1-methyltetrahydrodipyrrin (S33) or 1-methyltrihydrodipyrrin (S34) was used as one half whereas a dihydrodipyrrin-1-acetal (3, 5c) or tetrahydrodipyrrin-1-acetal (S35) was used as the other half. In route A, one half was a dihydrodipyrrin–acetal bearing a 9-bromo group (3); in routes B and C, the corresponding half was a tetrahydrodipyrrin–acetal bearing a 9-bromo group (S35); and in route D, a dihydrodipyrrin–acetal lacking any blocking group at the 9-position (5c) was used. No bacteriochlorin was formed in any case (routes A–D).
III. Screening of reaction parameters

Screening of reaction parameters was performed with analysis by absorption spectroscopy and LD-MS of crude reaction mixtures for the reaction of 22 + 5c. The results are shown in Table S1. During this process, attempts to isolate the linear tetrapyrrole intermediate failed, and the second reaction (cyclization) was performed directly using crude products from the first step (condensation). The best result (entry 8) was obtained using InCl₃ and 2,2,6,6-tetramethylpiperidine (TMPi) in toluene at 90 °C whereupon the bacteriochlorin InBC-1 was obtained in 8% yield (the isolated yield was determined spectroscopically). Some amount of tetradecahydrocorrin and a trace of a free base A₂-bacteriochlorin, a side-product obtained from self-condensation of 5c, were also observed. Various metal salts screened in addition to InCl₃ included NiCl₂, Zn(OAc)₂, Pd(OAc)₂, CdCl₂, MgBr₂, YbCl₃·6H₂O, CoCl₂, Cu(OAc)₂, ErCl₃ and SnCl₂·H₂O.

Table S1. Survey of conditions to prepare bacteriochlorin InBC-1

Scheme S17. Chlorin-inspired routes to bacteriochlorins.
<table>
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<tr>
<th>Entry</th>
<th>condensation conditions</th>
<th>cyclization conditions</th>
<th>solvent</th>
<th>base</th>
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<th>Yield, b %</th>
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*a* The condensation was performed for 20 min using 22 (10 mM) and 5c (10 mM) in the presence of Lewis acid in CH$_2$Cl$_2$ at room temperature. Then the reaction was neutralized with 2.2 molar equiv of Et$_3$N and concentrated to a solid. The crude solid was treated with InCl$_3$ (10 mol equiv) and base (10 mol equiv) in 0.5 mL of solvent for 1.5–2 h. b*Isolated yield determined by absorption spectroscopy (ε$_{\text{max}}$ nm = 100,000 M$^{-1}$cm$^{-1}$) in toluene. c*The condensation was carried out for 40 min. d*The condensation was carried out for 150 min. e*Tetramethylguanidine.

### IV. Spectral data for new compounds
4c-Lm
15b
Pulse Sequence: 2πpul
Solvent: CDCl₃
Ambient temperature
Mercury-400B "ncsumerc400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.355 sec
Width 5056.0 Hz
150 repetitions

Observe 1H, 400.1245660 MHz
Data Processing
FT size 32768
Total time 13 min, 21 sec

TDC-3
NiTDC-5
NiTDC-5

![Chemical Structure](image)
Copper-complex in Scheme 7C
Copper-complex

in Scheme 7C

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Report generated by: Lindsey Lab

Signature: ............
Copper-complex in Scheme 7D
Copper-complex in Scheme 7D

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<td>0000000000.0</td>
<td>-1.7977E308</td>
</tr>
</tbody>
</table>
Ambient temperature
Mercury-300BB "nsumerc300"

Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 3.996 sec
Width 4506.5 Hz
64 repetitions
Observe H1, 298.7918117 MHz
Data processing
FT size 32768
Total time 3 min, 18 sec
Pulse Sequence: s2pul
Solvent: CDCl3
Ambient temperature
Mercury-400R "nnumsmerc400"

Pulse 81.2 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
10000 repetitions
OBSERVE CI3, 100.6140585 MHz
DECOUPLE H1, 400.1371641 MHz
Power 44 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
line broadening 1.0 Hz
FF size 65536
Total time 4 hr, 4 min, 24 sec
DHDP(CN)2. Experimental and Theoretical Isotopic Distribution C_{21}H_{18}BrN_{3} [M+H]^+

The characteristic "A+2" peak at ~97% is added confirmation of the presence of 1 Br atom. S2
Solvent: CDCl3
Ambient temperature
Mercury-300BB "ncsumerc300"

Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 1.995 sec
Width 4560.5 Hz
128 repetitions
OBSERVE H1, 599.7918095 MHz
DATA PROCESSING
FT size 32768
Total time 6 min, 37 sec
Pulse Sequence: s2pu1
Solvent: CDCl3
Ambient temperature
Mercury-400BB "ncsumerc400"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.993 sec
Width 5065.8 Hz
8 repetitions
OBSERVE H1. 404.1245687 MHz
DATA PROCESSING
FT size 32768
Total time 9 min, 25 sec

S6
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.199 sec
Width 25125.0 Hz
512 repetitions
OBSERVE CI3, 100.6113782 MHz
DECOUPLE H1, 400.1268857 MHz
Power 44 dB
continuously on
GARP-1 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 45536
Total time 19 min, 32 sec

S6
Ambient temperature
Mercury-3000B "nclumerc638"

Relax, delay 1.000 sec
Pulse 50.4 degrees
Acc. time 1.905 sec
Width 4596.5 Hz
64 repetitions
OBSERVE H1, 300.1683340 MHz
DATA PROCESSING
FT size 32768
Total time 3 min, 18 sec

S10
Ambient temperature
Mercury-400B  "nscumerc400"

Pulse 81.2 degrees
Acq. time 1.199 sec
Width 25000.0 Hz
19000 repetitions

Observe CI1, 100.6160505 MHz
Decouple H1, 400.1371641 MHz
Power 44 dB
continuously on

WALTZ-16 modulated

Data Processing
Line broadening 1.0 Hz
FT size 65536
Total time 4 hr, 4 min, 24 sec

S10
Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.935 sec
Width 4566.5 Hz
64 repetitions
Observe H1, 300.1683387 MHz
Data Processing
FF size 32768
Total time 3 min, 18 sec

3.37 (m, 6H), 3.82 (m, 1H), 4.75 (s, 1H)
5.68 (m, 1H), 6.12 (m, 2H), 7.12 (d, 2H)
7.18 (d, 2H), 7.26 (d, 2H), 7.56 (d, 2H)

S11

2.32 1.95 2.34 0.94 0.78 1.11 1.31 0.64 1.56 4.81 3.73
3.87 5.97 1.90 5.70 2.65
User Spectra

Fragmentor Voltage 150
Collision Energy 0
Ionization Mode Esi

+ESI Scan (0.293-0.326 min, 3 scans) Frag=150.0V 122281.d Subtract

Counts vs. Mass-to-Charge (m/z)

525.2408
667.2810

Peak List

<table>
<thead>
<tr>
<th>m/z</th>
<th>z</th>
<th>Abund</th>
</tr>
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<tbody>
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<td>15642</td>
</tr>
<tr>
<td>525.2408</td>
<td>1</td>
<td>75775</td>
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<td>526.2444</td>
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<td>21012</td>
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<td>527.2432</td>
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<td>6262</td>
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<td>547.2234</td>
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<td>27404</td>
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<td>548.2265</td>
<td>1</td>
<td>8051</td>
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<td>645.2991</td>
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<td>646.3018</td>
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<td>667.2810</td>
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<td>12184</td>
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<td>668.2843</td>
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<td>4665</td>
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</tbody>
</table>
Ambient temperature
Mercury-300BB "ncsumerc638"
Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4506.5 Hz
16 repetitions
OBSERVE - H1, 300.1683397 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 45 sec

S18
Ambient temperature
Mercury-30000 "nccn100c300"

Relax. delay 1.000 sec
Pulse 36.0 degrees
Acq. time 1.000 sec
Width 4506.0 Hz
16 repetitions
OBSERVE Hz 299.7918088 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 49 sec

S20
Pulse Sequence: s2ps1
Solvent: CDCl3
Ambient temperature
Mercury-3000B "nsumcerc300"

Pulse 39.0 degrees
Acq. time 1.615 sec
Width 18741.7 Hz
100 repetitions

DECOUPLE C13, 7.593826925 MHz
DECOUPLE H1, 298.7932667 MHz
Power 40 db
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 min, 34 sec

S20
Pulse Sequence: 4pul
Solvent: CDC13
Ambient temperature
Mercury-3000S "notesmercury"

Relax. delay 1.000 sec
Pulse 90.0 degrees
Acq. time 1.995 sec
Width 4506.3 Hz
64 repetitions
Observe H2, 299.791810 MHz
Data PROCESSING
FIT size 32768
Total time 3 min, 15 sec

S21
S111
Pulse Sequence: s2pul
Solvent: CDC13
Ambient temperature
Mercury-300BB "ncsmuc638"

Relax. delay 1.000 sec
Pulse 50.4 degrees
Acq. time 1.995 sec
Width 4086.5 Hz
64 repetitions
OBSERVE R1, 368.1698255 MHz
DATA PROCESSING
FT size 32768
Total time 0 min, 0 sec

S23

1.88 2.78
0.96 0.86 1.93
1.36 3.76 1.17 2.80 2.80
2.86 3.03
S116

Solvent: CDCl3
Ambient temperature
Mercury-400B 400 MHz

Pulse 81.2 degrees
Acq. time 1.19 sec
Width 5000.0 Hz

6558 repetitions

INDEPENDENT: 125.12082956 MHz

DECoupling: 400.0 127.3641 MHz

Power 44.00
continuously on

WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 52536
Total time 6 hr, 6 min, 38 sec

S25
User Spectra

Fragmentor Voltage: 150
Collision Energy: 0
Ionization Mode: ESI

+ESI Scan (0.238-0.321 min, 6 scans) Frag=150.0V 121298.d Subtract

Counts vs. Mass-to-Charge (m/z)

<table>
<thead>
<tr>
<th>m/z</th>
<th>z</th>
<th>Abund</th>
<th>Formula</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
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<td>C21 H27 N2 O5</td>
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<td>387.1908</td>
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<td>C21 H27 N2 O5</td>
<td>(M+H)+</td>
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<td>388.1937</td>
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<td>(M+H)+</td>
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<tr>
<td>395.1568</td>
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<td>409.1727</td>
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<td>410.1764</td>
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<td>497.2275</td>
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<td>519.2095</td>
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<td>520.2132</td>
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<td>619.2986</td>
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User Spectra

Fragmentor Voltage 110
Collision Energy 0
Ionization Mode Esi

+ESI Scan (0.2357-0.2529 min, 2 scans) Frag=110.0V 100651.d Subtract 431.1250

Counts vs. Mass-to-Charge (m/z)

Peak List

<table>
<thead>
<tr>
<th>m/z</th>
<th>z</th>
<th>Abund</th>
<th>Formula</th>
<th>Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>409.1435</td>
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<td>C19 H25 N2 O6 S</td>
<td>(M+H)+</td>
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<td>431.1250</td>
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<td>447.0996</td>
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<td>8009</td>
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</table>

S27
**ATLANTIC MICROLAB, INC.**

**Sample No.** Je-Pyr-Thienes

**SUBMITTER**

Company/School: North Carolina State University
Address: NCSU Dept of Chemistry
Campus Box 8204, 2520 Yarbrough Dr
Raleigh, NC 27695-8204
NAME: Ola, MRS
DATE: 5/25/10

<table>
<thead>
<tr>
<th>Element</th>
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<tbody>
<tr>
<td>C</td>
<td>53.64</td>
<td>60.01</td>
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<td>H</td>
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<tr>
<td>N</td>
<td>7.73</td>
<td>7.40</td>
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</table>

**Element Present:** C, H, N, O, S

**Analyte for:** C, H, N

**Hygroscopic** [ ] **Explosive** [ ]

**M.P.** [ ] **B.P.** [ ]

**To be dried:** Yes [ ] No [ ]

**FAX Service** [ ] **EMAIL Service** [ ]

**FAX#** 219-513-2800 fax

**Rush Service** [ ] (SEE CURRENT PRICE LIST)

**Billing Address:**

**Date Received:** MAY 26 2010

**Date Completed:** MAY 31 2010

**email:** olamas@ncsu.edu