One-pot synthesis of asymmetric annulated bis(pyrrole)s

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General Experimental

All chemicals and reagents were purchased from commercial sources and were used as received, unless otherwise noted. Ethyl acetate, hexanes and dichloromethane were obtained crude and purified *via* distillation, under air and at 1 atm pressure, before use. HPLC grade methanol and chloroform were employed in reactions where stated. Anhydrous dichloromethane was purchased from Aldrich or EMD Chemicals. Column chromatography was performed using 230-400 mesh Silicycle Ultra Pure Silica Gel or 150 mesh Brockmann III, activated, neutral aluminium oxide, as indicated. TLC was performed on silica gel or neutral aluminium oxide plates and visualised using UV light (254 nm) and/or developed with Vanillin stain. NMR spectra were recorded using a Bruker AVANCE 500 or a Bruker AC-250 spectrometer. All ^{1}H and ^{13}C NMR chemical shifts are expressed in parts per million (ppm) using the solvent signal

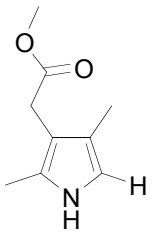
[$CDCl_3$ (^{1}H 7.26 ppm; ^{13}C 77.16 ppm); CD_2Cl_2 (^{1}H 5.32 ppm; ^{13}C 53.5 ppm); DMSO (^{1}H 2.50 ppm; ^{13}C 39.52 ppm)] as the internal reference. Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; at, apparent triplet; q, quartet; m, multiplet. All coupling constants (*J*) are reported in Hertz (Hz). Mass spectra were recorded using ion trap (ESI TOF) instruments. Compounds **3b**, **3d** and indole are commercially available. Where NMR and mass spectral data are not given, the relatively unstable pyrroles were immediately used in subsequent reactions.

Synthesis of α-Free Pyrroles

General Procedure for the Synthesis of α-Free Pyrroles (GP1)

Sodium hydroxide (9 equiv.) was added to a suspension of the appropriate 2-ethoxy carbonyl pyrrole (1.0 g, 1 equiv.) in ethylene glycol ([0.25 M]) and the reaction mixture was heated to 210 °C in a sand bath, with stirring for 1 hour. After cooling to room temperature, the reaction mixture was diluted with water and extracted with hexanes (3 x 30 mL). The organic extracts were combined and washed with brine, dried over anhydrous magnesium sulfate, filtered through a short pad of silica, washing with 10% diethyl ether in hexanes, and concentrated *in vacuo*. This gave the corresponding α-free pyrrole without the need for further purification.

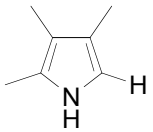
Methyl 2-(2,4-dimethyl-1H-pyrrol-3-yl)acetate (3a)



TFA (4.4 mL, 57.28 mmol, 11 eq.) was added dropwise to a solution of the corresponding 5-carboxy pyrrole[1] (1.1 g, 5.207 mmol) in freshly distilled dichloromethane (20 mL), with stirring at 0 °C under N_2 for 30 minutes. The reaction mixture was then poured into ice-water (50 mL) and sodium hydroxide solution (6 M, 6.9 mL 41.66 mmol, 8 eq.) was slowly added before extracting with chloroform (3 x 50 mL). The organic extracts were combined and carefully washed with 5% aq. $NaHCO_3$ solution (2 x 80 mL), water (80 mL) and brine (80 mL), before being dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* to give the crude product, which was purified using column chromatography on silica, eluting with 30% ethyl

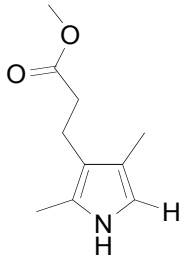
acetate in hexanes, to give the title compound **3a** as a pale yellow oil (687 mg, 79% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57-7.76 (br s, 1H, NH), 6.36 (s, 1H, PyH), 3.63 (s, 3H, OMe), 3.36 (s, 2H, CH_2), 2.15 (s, 3H, CH_3), 1.99 (s, 3H, CH_3); LRMS: 190.1 $(M+Na)^+$; HRMS: 190.0839 Found, 190.0838 Calculated for $C_9H_{13}NO_2Na$.

2,3,4-Trimethyl-1H-pyrrole (3c)[2]



Compound **3c** was synthesized from the corresponding 2-ethoxy pyrrole[3] using GP1 as an off-white solid (326 mg, 54% yield). M.p. 28–30 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (br s, 1H, NH), 6.40 (s, 1H, PyH), 2.17 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.94 (s, 3H, CH_3).

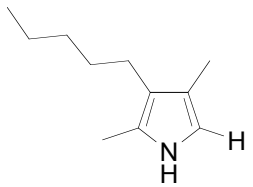
Methyl 3-(2,4-dimethyl-1H-pyrrol-3-yl)propanoate (3e)



TFA (37 mL, 479.8 mmol, 27 eq.) was added dropwise over 20 minutes to a solution of the corresponding 5-butoxy carbonyl pyrrole[4] (5.0 g, 17.77 mmol) in freshly distilled dichloromethane (16 mL), with stirring at 0 °C under N_2 for 30 minutes. The reaction mixture was then poured into ice-water (200 mL) and sodium hydroxide solution (6 M, 60 mL) was slowly added over 10 minutes before the mixture was extracted with dichloromethane (3 x 200 mL). The organic extracts were combined and carefully washed with 5% aq. $NaHCO_3$ solution (2 x 200 mL), water (200 mL) and brine (200 mL), before being dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* to give the crude product, which was purified using column chromatography on silica, eluting with 20% ethyl acetate in hexanes, to give the title compound **3e** as a pale yellow solid (2.361 g, 73% yield). M.p. 35–37 °C; ^{1}H NMR ($CDCl_3$, 500

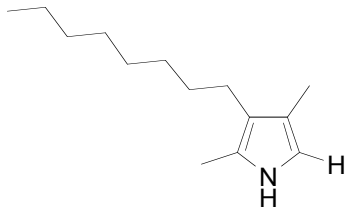
MHz) δ 7.60 (br s, 1H, NH), 6.39 (s, 1H, PyH), 3.69 (s, 3H, OMe), 2.73 (t, 2H, J = 8.0 Hz, CH_2*CH_2*CO_2Me), 2.47 (t, 2H, J = 8.0 Hz, *CH_2*CH_2CO_2Me), 2.19 (s, 3H, CH_3), 2.04 (s, 3H, CH_3).

2,4-Dimethyl-3-pentyl-1H-pyrrole (3f)[5]



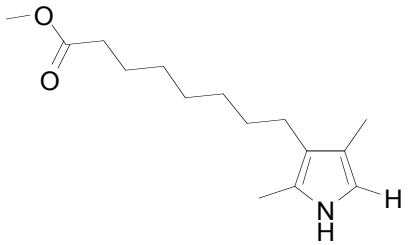
Compound **3f** was synthesized from the corresponding 2-ethoxy pyrrole[6] using GP1 as an pale yellow oil (184 mg, 26% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.48 (br s, 1H, NH), 6.40 (s, 1H, PyH), 2.36 (t, 2H, J = 7.8 Hz, CH_2), 2.18 (s, 3H, CH_3), 2.04 (s, 3H, CH_3), 1.49-1.43 (m, 2H), 1.36-1.31 (m, 4H), 0.91 (t, 3H, J = 7.0 Hz, CH_3).

2,4-Dimethyl-3-octyl-1H-pyrrole (3g)



Compound **3g** was synthesized from the corresponding 2-ethoxy pyrrole[7] using GP1 as an pale yellow oil (363 mg, 32% yield). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.47 (br s, 1H, NH), 6.39 (s, 1H, PyH), 2.36 (t, 2H, J = 7.8 Hz, CH_2), 2.17 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.48-1.42 (m, 2H), 1.33-1.28 (m, 10H), 0.89 (t, 3H, J = 7.0 Hz, CH_3). LRMS: 208.2 $(M+H)^+$; HRMS: 208.2054 Found, 208.2060 Calculated for $C_{14}H_{26}N$.

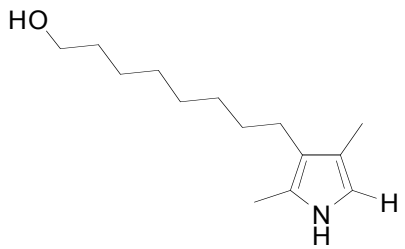
Methyl 8-(2,4-dimethyl-1H-pyrrol-3-yl)octanoate (3h)



8-(5-(Ethoxycarbonyl)-2,4-dimethyl-1H-pyrrol-3-yl)octanoic acid was converted to the corresponding α-free pyrrole using GP1, extracting with ethyl acetate instead of hexanes. Sulfuric acid (0.22 mL) was then added to a solution of the resulting 3-octylcarboxylic acid in

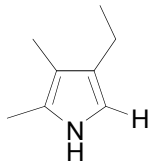
methanol (350 mL) and the reaction mixture was heated to reflux temperature, with stirring for 6 hours, before concentrating and separating the residue between [0.5 M] aqueous sodium hydroxide solution (30 mL) and dichloromethane (50 mL). The aqueous phase was extracted with dichloromethane (2 x 30 mL) and the combined organic extracts were washed with brine (80 mL), dried over anhydrous sodium sulfate and concentrated *in vacuo* to give the crude product, which was purified using column chromatography on silica gel, eluting with 20% ethyl acetate in hexanes, to give the product **3h** (408 mg, 36% overall yield) as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.50 (br s, 1H, NH), 6.39 (s, 1H, PyH), 3.67 (s, 3H, OMe), 2.36-2.29 (m, 4H), 2.16 (s, 3H, CH_3), 2.02 (s, 3H, CH_3), 1.66-1.60 (m, 2H), 1.47-1.41 (m, 2H), 1.35-1.29 (m, 6H); LRMS: 274.2 $(M+Na)^+$; HRMS: 274.1784 Found, 274.1778 Calculated for $C_{15}H_{25}NO_2Na$.

8-(2,4-dimethyl-1H-pyrrol-3-yl)octan-1-ol (3i)



Compound **3i** was synthesized from the corresponding 2-ethoxy pyrrole using GP1, extracting with ethyl acetate instead of hexanes, as an pale yellow oil (358 mg, 95% yield). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.53 (br s, 1H, NH), 6.39 (s, 1H, PyH), 3.64 (t, 2H, J = 6.6 Hz, CH_2), 2.35 (t, 2H, J = 7.3 Hz, CH_2), 2.17 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 1.59-1.54 (m, 2H), 1.47-1.41 (m, 2H), 1.38-1.27 (m, 8H).

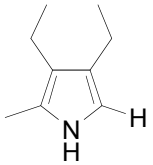
4-Ethyl-2,3-dimethyl-1H-pyrrole (3j)[8]



Compound **3j** was synthesized from the corresponding 2-ethoxy pyrrole[9] using GP1 as an pale yellow oil (634 mg, 67% yield). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.52 (br s, 1H, NH), 6.43 (s, 1H,

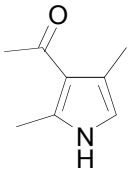
PyH), 2.46 (q, 2H, J = 7.5 Hz, CH_2CH_3), 2.20 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.22 (t, 3H, J = 7.5 Hz, CH_2CH_3).

3,4-Diethyl-2-methyl-1H-pyrrole (3k)[10]



TFA (4.7 mL, 60.8 mmol, 11 eq.) was added dropwise to a solution of the corresponding 5-carboxy pyrrole[11] (1.0 g, 5.53 mmol) in freshly distilled dichloromethane (5 mL), with stirring at 0 °C under N_2 for 20 minutes. The reaction mixture was then poured into ice-water (50 mL) and sodium hydroxide solution (6 M, 10 mL) was slowly added before extracting with hexane (3 x 50 mL). The organic extracts were combined and carefully washed with 5% aq. $NaHCO_3$ solution (100 mL) and brine (100 mL), dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo* to give the title compound **3k** as a pale yellow oil (337 mg, 45% yield). ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.56 (br s, 1H, NH), 6.41 (s, 1H, PyH), 2.51-2.38 (m, 4H), 2.19 (s, 3H, CH_3), 1.21 (t, 3H, J = 7.5 Hz, CH_2CH_3), 1.10 (t, 3H, J = 7.5 Hz, CH_2CH_3).

3-Acetyl-2,4-dimethylpyrrole[12]



TFA (8.76 mL, 113.8 mmol, 27 eq.) was added dropwise over 20 minutes to a solution of the corresponding 5-butoxy carbonyl pyrrole[13] (1.0 g, 4.21 mmol) in freshly distilled dichloromethane (4 mL), with stirring at 0 °C under N_2 for 30 minutes. The reaction mixture was then poured into ice-water (50 mL) and sodium hydroxide solution (6 M, 15 mL) was slowly added over 5 minutes before extracting with dichloromethane (3 x 50 mL). The organic extracts were combined and carefully washed with 5% aq. $NaHCO_3$ solution (100 mL), water (100 mL) and brine (100 mL), before being dried over anhydrous sodium sulfate, filtered and concentrated *in vacuo* to give the title compound as a white solid (575 mg, 99% yield). ^{1}H NMR (DMSO-*d6*,

250 MHz) δ 10.89 (br s, 1H, NH), 6.38 (s, 1H, PyH), 2.38 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.14 (s, 3H, CH_3).

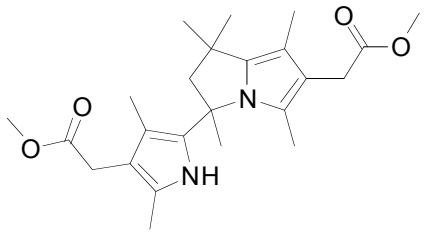
Synthesis of Annulated Pyrroles

General Procedure for the Synthesis of Annulated Pyrroles (GP2)

TFA (0.55 mmol, 0.5 eq.) was added dropwise to a stirred solution of pyrrole (1.10 mmol, 1.00 eq.) and ketone (1.16 mmol, 1.05 eq.) in dichloromethane (5 mL), at room temperature under nitrogen, with continued stirring for 18 hours. After this time, the reaction mixture was diluted with dichloromethane (50 mL), washed with saturated aqueous sodium hydrogen bicarbonate solution (30 mL) and brine (30 mL), dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo* to give the crude product, which was purified immediately over neutral alumina.

Annulated Pyrroles

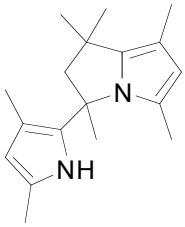
Methyl 2-(5-(6-(2-methoxy-2-oxoethyl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)acetate (5a)



Compound **5a** was synthesized from pyrrole **3a** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 5% ethyl acetate in hexanes, to give the product **5a** (212 mg, 86% yield) as a pale yellow solid. M.p. 110–113 °C; ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.06 (br s, 1H, NH), 3.63 (s, 3H, OMe), 3.61 (s, 3H, OMe), 3.34 (s, 2H, CH_2CO_2Me), 3.29 (s, 2H, CH_2CO_2Me), 2.56 (d, 1H, J = 12.5 Hz, CH_2), 2.38 (d, 1H, J = 12.5 Hz, CH_2), 2.06 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.74 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.07 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 173.2, 173.0, 139.3, 129.5, 122.4, 119.6, 116.5, 113.1, 112.7, 106.6, 62.2, 61.1, 51.83, 51.80,

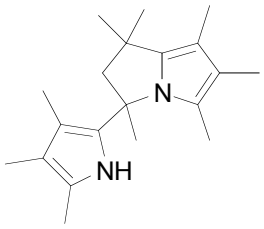
37.3, 30.7, 30.5, 29.8, 28.3, 27.9, 11.2, 10.1, 9.7, 8.8; LRMS: 437.3 $(M+Na)^+$; HRMS: 437.2411 Found, 437.2411 Calculated for $C_{24}H_{34}N_2O_4Na$. A crystal suitable for x-ray crystallography was obtained from recrystallization of compound **5a** from a solution of 10% ether in hexanes at -20 °C. Data for **5a**: $C_{24}H_{34}N_2O_4$, M = 414.54, pale yellow needle, 0.19 x 0.08 x 0.03 mm^3, monoclinic, space group $P2_1/n$, a = 12.705(10) Å, b = 9.521(6) Å, c = 19.280(4) Å, V = 2326(2) $Å^3$, Z = 4, T = 213.1 K, ρ = 1.184 gcm^{-3}, $\mu(MoK\alpha)$ = 0.801 cm^{-1}, 16495 reflections (8342 unique, R_{int} = 0.053), R = 0.0596, Rw = 0.0674, GOF = 1.127.

3-(3,5-Dimethyl-1H-pyrrol-2-yl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizine (5b)



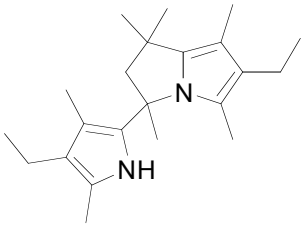
Compound **5b** was synthesized from pyrrole **3b** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 5% ethyl acetate in hexanes, to give the product **5b** (279 mg, 85% yield) as a yellow oil. ^1H NMR (CD_2Cl_2, 500 MHz) δ 7.02 (br s, 1H, NH), 5.68 (s, 1H, PyH), 5.59 (s, 1H, PyH), 2.57 (d, 1H, *J* = 12.5 Hz, CH_2), 2.39 (d, 1H, *J* = 12.5 Hz, CH_2), 2.08 (s, 3H, CH_3), 2.01 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.10 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 140.0, 130.3, 124.2, 121.2, 113.5, 113.1, 110.2, 106.7, 61.9, 61.3, 37.1, 29.7, 28.4, 27.9, 12.9, 12.2, 12.0, 10.6; LRMS: 293.2 $(M+Na)^+$; HRMS: 293.1975 Found, 293.1988 Calculated for $C_{18}H_{26}N_2Na$.

1,1,3,5,6,7-Hexamethyl-3-(3,4,5-trimethyl-1H-pyrrol-2-yl)-2,3-dihydro-1H-pyrrolizine (5c)



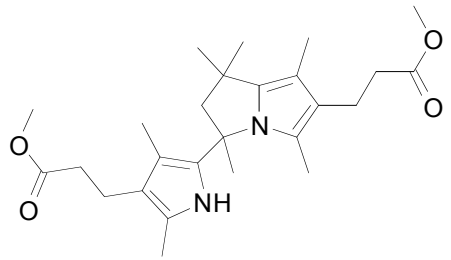
Compound **5c** was synthesized from pyrrole **3c** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 5% ethyl acetate in hexanes, to give the product **5c** (199 mg, 73% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.90 (br s, 1H, NH), 2.53 (d, 1H, *J* = 12.8 Hz, CH_2), 2.35 (d, 1H, *J* = 12.8 Hz, CH_2), 2.02 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.35 (s, 3H, CH_3), 1.07 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 139.1, 129.8, 120.4, 119.1, 117.5, 115.5, 112.3, 106.4, 62.3, 61.6, 37.4, 29.9, 28.8, 28.5, 11.3, 10.3, 10.2, 9.7, 9.4, 9.1; LRMS: 321.2 $(M+Na)^+$; HRMS: 321.2288 Found, 321.2301 Calculated for $C_{20}H_{30}N_2Na$.

6-Ethyl-3-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizine (5d)



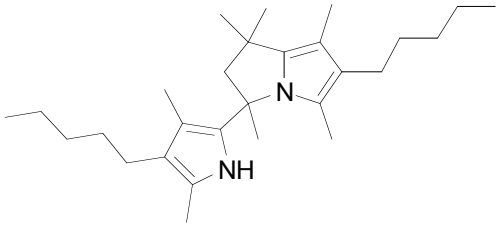
Compound **5d** was synthesized from pyrrole **3d** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 2% ethyl acetate in hexanes, to give the product **5d** (268 mg, 85% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.88 (br s, 1H, NH), 2.56 (d, 1H, *J* = 12.5 Hz, CH_2), 2.38-2.35 (m, 1H+2H), 2.31 (q, 2H, *J* = 7.5 Hz, CH_2CH_3), 2.04 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.92 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.38 (s, 3H, CH_3), 1.07 (s, 3H, CH_3), 1.04 (t, 3H, *J* = 7.5 Hz, CH_2CH_3), 1.00 (t, 3H, *J* = 7.5 Hz, CH_2CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 139.0, 129.6, 126.0, 122.3, 119.7, 117.1, 111.5, 105.5, 62.1, 61.3, 37.2, 29.8, 28.4, 28.1, 18.2, 17.9, 16.3, 16.0, 11.0, 9.9, 9.7, 8.8; LRMS: 349.3 $(M+Na)^+$; HRMS: 349.2600 Found, 349.2614 Calculated for $C_{22}H_{34}N_2Na$.

Methyl 3-(5-(6-(3-methoxy-3-oxopropyl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-3,5-dimethyl-1H-pyrrol-2-yl)propanoate (5e)



Compound **5e** was synthesized from pyrrole **3e** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 5% ethyl acetate in hexanes, to give the product **5e** (212 mg, 87% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.94 (br s, 1H, NH), 3.60 (s, 3H, OMe), 3.59 (s, 3H, OMe), 2.65 (t, 2H, *J* = 7.5 Hz, CH_2*CH_2*CO_2Me), 2.60 (t, 2H, *J* = 8.0 Hz, CH_2*CH_2*CO_2Me), 2.53 (d, 1H, *J* = 12.5 Hz, CH_2), 2.46-2.32 (m, 1H+2H+2H), 2.04 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.34 (s, 3H, CH_3), 1.03 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 174.03, 173.98, 139.2, 129.6, 121.9, 120.9, 118.5, 118.0, 111.6, 105.6, 62.0, 61.1, 51.6, 51.5, 37.2, 36.1, 35.8, 29.7, 28.2, 27.9, 20.7, 20.3, 11.0, 10.0, 9.7, 8.7; LRMS: 465.3 $(M+Na)^+$; HRMS: 465.2718 Found, 465.2724 Calculated for $C_{26}H_{38}N_2O_4Na$.

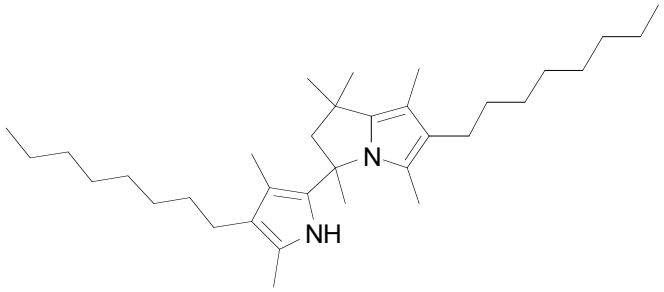
3-(3,5-Dimethyl-4-pentyl-1H-pyrrol-2-yl)-1,1,3,5,7-pentamethyl-6-pentyl-2,3-dihydro-1H-pyrrolizine (5f)



Compound **5f** was synthesized from pyrrole **3f** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 2% ethyl acetate in hexanes, to give the product **5f** (112 mg, 56% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.85 (br s, 1H, NH), 2.55 (d, 1H, *J* = 12.5 Hz, CH_2), 2.34 (d, 1H, *J* = 12.5 Hz, CH_2), 2.32-2.29 (m, 2H), 2.27 (t, 2H, J = 7.8 Hz, CH_2), 2.01 (s, 3H, CH_3), 1.97 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.45-1.38 (m, 4H), 1.36 (s, 3H, CH_3), 1.34-1.24 (m, 8H), 1.05 (s, 3H, CH_3), 0.91-0.86 (m, 6H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 139.0, 129.5, 124.5, 120.8, 120.0, 117.5, 111.8, 105.7, 62.0, 61.2, 37.2, 32.14, 32.08, 31.6, 31.3, 29.80,

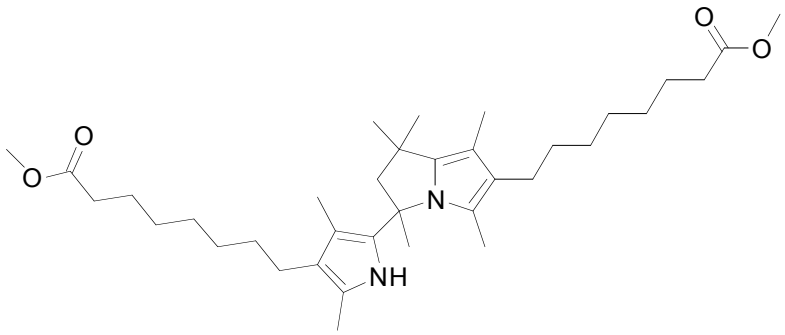
29.78, 28.3, 27.9, 24.9, 24.6, 23.1, 23.0, 14.3, 11.2, 10.1, 9.8, 8.9; LRMS: 411.4 $(M+H)^+$; HRMS: 411.3739 Found, 411.3734 Calculated for $C_{28}H_{47}N_2$.

3-(3,5-Dimethyl-4-octyl-1H-pyrrol-2-yl)-1,1,3,5,7-pentamethyl-6-octyl-2,3-dihydro-1H-pyrrolizine (5g)



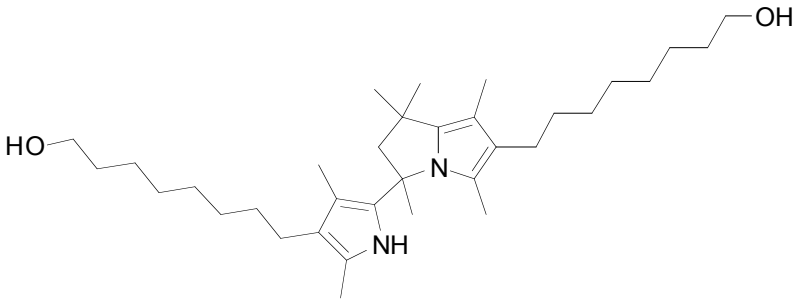
Compound **5g** was synthesized from pyrrole **3g** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 2% ethyl acetate in hexanes, to give the product **5g** (121 mg, 51% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.84 (br s, 1H, NH), 2.54 (d, 1H, J = 12.5 Hz, CH_2), 2.34 (d, 1H, J = 12.5 Hz, CH_2), 2.32-2.24 (m, 4H), 2.01 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.42-1.34 (m, 4H), 1.36 (s, 3H, CH_3), 1.30-1.25 (m, 20H), 1.05 (s, 3H, CH_3), 0.89-0.86 (m, 6H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 139.0, 129.5, 124.5, 120.8, 120.0, 117.5, 111.8, 105.7, 62.0, 61.2, 37.2, 32.34, 32.29, 31.9, 31.6, 30.2, 30.03, 29.95, 29.9, 29.83, 29.78, 29.76, 28.3, 27.9, 25.7, 25.0, 24.7, 23.1, 22.9, 14.3, 11.2, 10.1, 9.8, 8.9; LRMS: 495.5 $(M+H)^+$; HRMS: 495.4650 Found, 495.4673 Calculated for $C_{34}H_{59}N_2$.

Methyl 8-(5-(6-(8-methoxy-8-oxooctyl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)octanoate (5h)



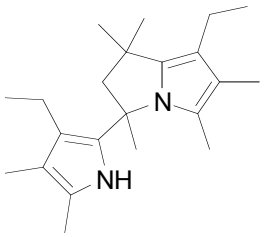
Compound **5h** was synthesized from pyrrole **3h** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 40% ethyl acetate in hexanes, to give the product **5h** (151 mg, 65% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.85 (br s, 1H, NH), 3.62 (s, 3H, OMe), 3.61 (s, 3H, OMe), 2.53 (d, 1H, *J* = 12.5 Hz, CH_2), 2.33 (d, 1H, *J* = 12.5 Hz, CH_2), 2.30-2.24 (m, 8H), 2.00 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.60-1.55 (m, 4H), 1.35 (s, 3H, CH_3), 1.32-1.28 (m, 14H), 1.04 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 174.3 (2C), 138.9, 129.5, 124.3, 120.7, 120.0, 117.5, 111.8, 105.7, 65.5, 62.0, 61.2, 51.6, 37.2, 34.3, 31.8, 31.5, 29.7, 29.63, 29.60, 29.57, 29.5, 28.3, 27.9, 25.34, 25.29, 24.9, 24.6, 22.8, 11.2, 10.1, 9.8, 8.9 (2 peaks missing); LRMS: 605.4 $(M+Na)^+$; HRMS: 605.4279 Found, 605.4289 Calculated for $C_{36}H_{58}N_2O_4Na$.

8-(5-(6-(8-Hydroxyoctyl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)octan-1-ol (5i)



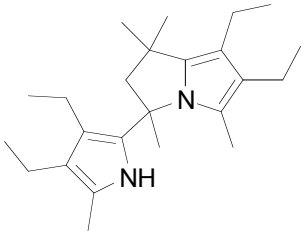
Compound **5i** was synthesized from pyrrole **3i** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 40% ethyl acetate in hexanes, to give the product **5i** (180 mg, 51% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.91 (br s, 1H, NH), 3.58-3.55 (m, 4H, CH_2OH), 2.54 (d, 1H, *J* = 12.5 Hz, CH_2), 2.34 (d, 1H, *J* = 12.5 Hz, CH_2), 2.31-2.29 (m, 2H), 2.27-2.24 (m, 2H), 2.01 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.65 (br s, 2H, 2 x OH), 1.52-1.50 (m, 4H), 1.35 (s, 3H, CH_3), 1.34-1.27 (m, 20H), 1.06 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 138.9, 129.5, 124.3, 120.7, 120.1, 117.5, 111.8, 105.6, 63.2, 62.0, 61.2, 37.2, 33.2, 31.9, 31.6, 30.0, 29.9, 29.8, 29.7, 28.34, 28.32, 27.9, 26.2, 26.1, 24.9, 24.6, 11.2, 10.06, 10.05, 9.79, 8.87 (3 peaks missing); LRMS: 549.4 $(M+Na)^+$; HRMS: 549.4396 Found, 549.4391 Calculated for $C_{34}H_{58}N_2O_2Na$.

7-Ethyl-3-(3-ethyl-4,5-dimethyl-1H-pyrrol-2-yl)-1,1,3,5,6-pentamethyl-2,3-dihydro-1H-pyrrolizine (5j)



Compound **5j** was synthesized from pyrrole **3j** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 2% ethyl acetate in hexanes, to give the product **5j** (219 mg, 83% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.75 (br s, 1H, NH), 2.51 (d, 1H, *J* = 12.5 Hz, CH_2), 2.44-2.32 (m, 1H+2H+2H), 2.00 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.93 (s, 3H, CH_3), 1.88 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.08 (t, 3H, *J* = 7.5 Hz, CH_2*CH_3*), 1.04 (t, 3H, *J* = 7.5 Hz, CH_2*CH_3*), 1.03 (s, 3H, CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 138.8, 129.3, 120.5, 118.9, 118.5, 117.8, 114.9, 113.9, 62.4, 62.1, 37.4, 30.5, 29.0, 28.8, 18.5, 17.9, 16.8, 15.8, 11.0, 10.3, 9.5, 9.2; LRMS: 349.3 $(M+Na)^+$; HRMS: 349.2607 Found, 349.2614 Calculated for $C_{22}H_{34}N_2Na$.

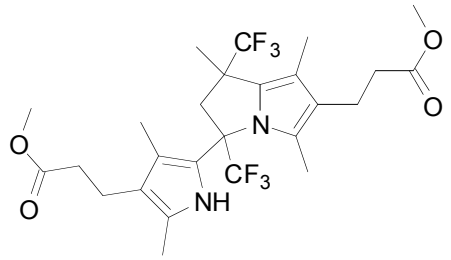
3-(3,4-Diethyl-5-methyl-1H-pyrrol-2-yl)-6,7-diethyl-1,1,3,5-tetramethyl-2,3-dihydro-1H-pyrrolizine (5k)



Compound **5k** was synthesized from pyrrole **3k** and acetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 2% ethyl acetate in hexanes, to give the product **5k** (105 mg, 51% yield) as a yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 6.72 (br s, 1H, NH), 2.53 (d, 1H, *J* = 12.5 Hz, CH_2), 2.44-2.29 (m, 1H+4 x 2H), 2.00 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.12-1.02 (m, 5 x 3H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 138.7, 129.1, 125.6, 121.8, 120.2, 118.5, 117.6, 113.4,

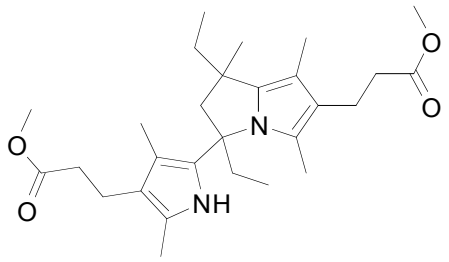
62.4, 61.9, 37.4, 30.5, 28.8, 28.7, 28.5, 18.13, 18.05, 17.8, 17.73, 17.70, 16.7, 16.4, 11.1, 10.2; LRMS: 377.3 $(M+Na)^+$; HRMS: 377.2944 Found, 377.2927 Calculated for $C_{24}H_{38}N_2Na$.

Methyl 3-(5-(6-(3-methoxy-3-oxopropyl)-1,5,7-trimethyl-1,3-bis(trifluoromethyl)-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)propanoate (9)

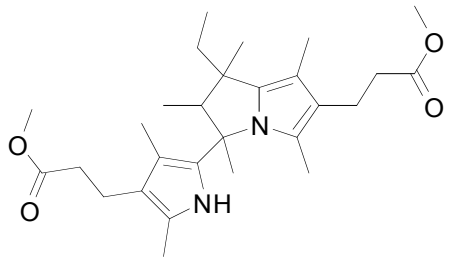


Compound **9** was synthesized from pyrrole **3e** and 1,1,1-trifluoroacetone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 5% ethyl acetate in hexanes, to give the product **9** (212 mg, 87% yield) as a yellow oil, as a mixture of diastereoisomers in a 1:0.7 ratio. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.58 (br s, 1H, NH), 7.30 (br s, 1H, NH), 3.62 (s, 3H, OMe), 3.60 (s, 3H, OMe), 3.60 (s, 3H, OMe), 3.59 (s, 3H, OMe), 3.30 (d, 1H, J = 14 Hz, CH_2), 3.04 (d, 1H, J = 15 Hz, CH_2), 2.89 (d, 1H, J = 15 Hz, CH_2), 2.73-2.60 (m, 9H), 2.42-2.33 (m, 8H), 2.13 (s, 3H, CH_3), 2.09 (s, 3H, CH_3), 1.99 (s, 3H, CH_3), 1.98 (s, 6H, CH_3), 1.85 (s, 3H, CH_3), 1.58 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.25 (s, 3H, CH_3); LRMS: 573.3 $(M+Na)^+$; HRMS: 573.2175 Found, 573.2158 Calculated for $C_{26}H_{32}N_2O_4F_6Na$

Methyl 3-(1,3-diethyl-3-(4-(3-methoxy-3-oxopropyl)-3,5-dimethyl-1H-pyrrol-2-yl)-1,5,7-trimethyl-2,3-dihydro-1H-pyrrolizin-6-yl)propanoate (10a) and Methyl 3-(1-ethyl-3-(4-(3-methoxy-3-oxopropyl)-3,5-dimethyl-1H-pyrrol-2-yl)-1,2,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-6-yl)propanoate (10b)



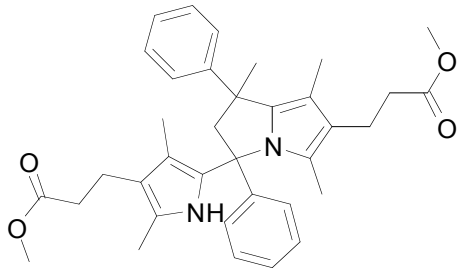
10a



10b

Compound **10** was synthesized from pyrrole **3e** and 2-butanone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 5% ethyl acetate in hexanes, to give **10a** (186 mg, 36% yield) and **10b** (127 mg, 24% yield) as yellow oils. **10a** appears to be a mixture of isomers; For ^{1}H NMR (CD_2Cl_2, 500 MHz) see spectrum on page 33; LRMS: 493.3 $(M+Na)^+$; HRMS: 493.3030 Found, 493.3037 Calculated for $C_{28}H_{42}N_2O_4Na$. **10b** ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.38 (br s, 1H, NH), 3.60 (s, 3H, OMe), 3.59 (s, 3H, OMe), 2.70 (q, 1H, *J* = 7.5 Hz, *CH*CH_3), 2.63-2.59 (m, 4H, CH_2), 2.38-2.33 (m, 4H, CH_2), 2.11 (s, 3H, CH_3), 2.00 (s, 3H, CH_3), 1.94 (s, 3H, CH_3), 1.65-1.61 (m, 5H), 1.52 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 0.92 (d, 3H, *J* = 7.5 Hz, CH_3), 0.84 (t, 3H, *J* = 7.5 Hz, CH_3); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 174.1, 174.0, 142.6, 136.3, 129.1, 121.7, 121.1, 118.3, 113.5, 105.8, 54.8, 51.54, 51.50, 43.3, 36.1, 35.8, 32.7, 23.7, 21.6, 20.6, 20.3, 14.4, 11.1, 10.2, 9.7, 9.4, 9.0, 8.8; LRMS: 493.3 $(M+Na)^+$; HRMS: 493.3040 Found, 493.3037 Calculated for $C_{28}H_{42}N_2O_4Na$.

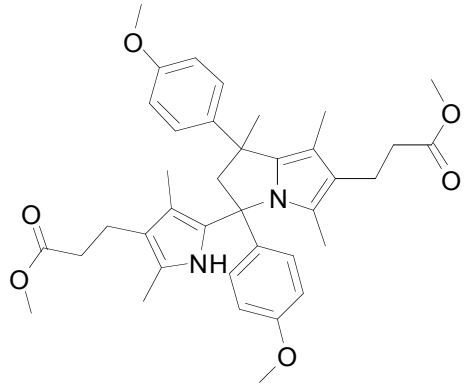
Methyl 3-(5-(6-(3-methoxy-3-oxopropyl)-1,5,7-trimethyl-1,3-diphenyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)propanoate (11)



Compound **11** was synthesized from pyrrole **3e** and acetophenone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 5% ethyl acetate in hexanes, to give the product **11** (285 mg, 91% yield) as a yellow oil, as a mixture of diastereoisomers in a 1:0.8 ratio. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.54 (br s, 1H, NH),

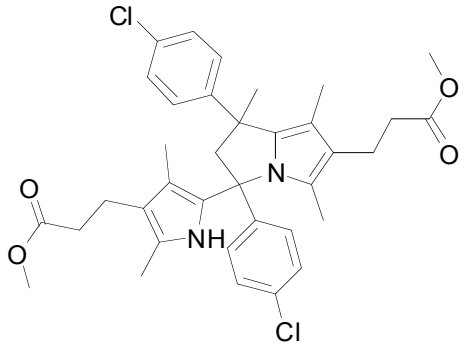
7.37-7.30 (m, 4H, ArH), 7.20-7.15 (m, 10H, ArH), 7.14-7.10 (m, 4H, ArH), 7.07-7.00 (m, 2H, ArH), 6.90 (br s, 1H, NH), 3.62 (s, 3H, OMe), 3.62 (s, 3H, OMe), 3.61 (s, 3H, OMe), 3.60 (s, 3H, OMe), 3.38 (d, 1H, *J* = 12.5 Hz, CH_2), 3.31 (d, 1H, *J* = 12.5 Hz, CH_2), 3.21 (d, 1H, *J* = 12.5 Hz, CH_2), 3.04 (d, 1H, *J* = 12.5 Hz, CH_2), 2.74-2.66 (m, 8H), 2.50-2.40 (m, 8H), 2.14 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.85 (s, 3H, CH_3), 1.75 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.40 (s, 3H, CH_3); LRMS: 589.3 $(M+Na)^+$; HRMS: 589.3059 Found, 589.3037 Calculated for $C_{36}H_{42}N_2O_4Na$.

Methyl 3-(5-(6-(3-methoxy-3-oxopropyl)-1,3-bis(4-methoxyphenyl)-1,5,7-trimethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)propanoate (12)



Compound **12** was synthesized from pyrrole **3e** and 4'-methoxyacetophenone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 10% ethyl acetate in hexanes, to give the product **12** (300 mg, 87% yield) as a yellow oil, as a mixture of diastereoisomers in a 1:0.9 ratio. ^1H NMR (CD_2Cl_2, 500 MHz) δ 7.28-7.26 (m, 1H, ArH), 7.14-7.13 (m, 2H, ArH), 7.10-7.08 (m, 1H, ArH), 7.07-7.05 (m, 4H, ArH), 7.02 (br s, 1H, NH), 6.88-6.85 (m, 3H), 6.73-6.68 (m, 6H, ArH), 3.79 (s, 3H, OMe), 3.72 (s, 6H, OMe), 3.71 (s, 3H, OMe), 3.62 (s, 3H, OMe), 3.61 (s, 3H, OMe), 3.60 (s, 6H, OMe), 3.31 (d, 1H, *J* = 12.5 Hz, CH_2), 3.21 (d, 1H, *J* = 12.5 Hz, CH_2), 3.10 (d, 1H, *J* = 12.5 Hz, CH_2), 2.97 (d, 1H, *J* = 12.5 Hz, CH_2), 2.73-2.66 (m, 8H), 2.49-2.39 (m, 8H), 2.06 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 1.84 (s, 3H, CH_3), 1.80 (s, 3H, CH_3), 1.76 (s, 3H, CH_3), 1.62 (s, 3H, CH_3), 1.44 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.37 (s, 3H, CH_3); LRMS: 649.3 $(M+Na)^+$; HRMS: 649.3249 Found, 649.3248 Calculated for $C_{38}H_{46}N_2O_6Na$.

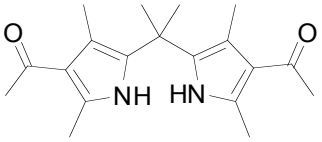
Methyl 3-(1,3-bis(4-chlorophenyl)-3-(4-(3-methoxy-3-oxopropyl)-3,5-dimethyl-1H-pyrrol-2-yl)-1,5,7-trimethyl-2,3-dihydro-1H-pyrrolizin-6-yl)propanoate (13)



Compound **13** was synthesized from pyrrole **3e** and 4'-chloroacetophenone using GP2. Purification was carried out using column chromatography on neutral alumina (Brockmann type III), eluting with 10% ethyl acetate in hexanes, to give the product **13** (265 mg, 76% yield) as a pale yellow solid, as a mixture of diastereoisomers in a 1:0.6 ratio. M.p. 35–38 °C; ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.52 (br s, 1H, NH), 7.33-7.29 (m, 3H, ArH), 7.17-7.14 (m, 3H, ArH), 7.13-7.09 (m, 4H, ArH), 7.09-6.99 (m, 6H, ArH), 6.81 (br s, 1H, NH), 3.62 (s, 3H, OMe), 3.61 (s, 6H, OMe), 3.60 (s, 3H, OMe), 3.35 (d, 1H, J = 12.5 Hz, CH_2), 3.29 (d, 1H, J = 13.0 Hz, CH_2), 3.09 (d, 1H, J = 13.0 Hz, CH_2), 2.98 (d, 1H, J = 12.5 Hz, CH_2), 2.73-2.65 (m, 8H), 2.50-2.39 (m, 8H), 2.05 (s, 3H, CH_3), 1.95 (s, 3H, CH_3), 1.89 (s, 3H, CH_3), 1.83 (s, 3H, CH_3), 1.73 (s, 3H, CH_3), 1.60 (s, 3H, CH_3), 1.52 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.41 (s, 3H, CH_3); LRMS: 657.2 $(M+Na)^+$; HRMS: 657.2260 Found, 657.2257 Calculated for $C_{36}H_{40}N_2O_4Cl_2Na$.

Dimethyldipyrromethanes

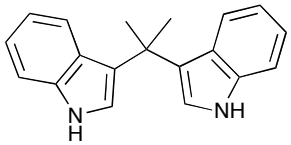
1,1'-(5,5'-(Propane-2,2-diyl)bis(2,4-dimethyl-1H-pyrrole-5,3-diyl))diethanone (6)[14]



Compound **6** was synthesized from 3-acetyl-2,4-dimethylpyrrole[12] and acetone using GP2. Purification was carried out using column chromatography on silica gel, eluting with 60% ethyl acetate in hexanes, to give the product **6** (173 mg, 75% yield) as a white solid. M.p. 199–203 °C;

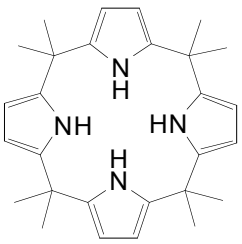
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.83 (br s, 2H, NH), 2.47 (s, 6H, CH_3), 2.40 (s, 6H, CH_3), 2.02 (s, 6H, CH_3), 1.67 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 196.0, 131.7, 131.2, 123.1, 115.6, 35.6, 31.4, 28.3, 15.4, 12.4; LRMS: 337.2 $(M+Na)^+$; HRMS: 337.1875 Found, 337.1886 Calculated for $C_{19}H_{26}N_2O_2Na$.

3,3'-(1-Methylethylidene)bis(1H-indole) (7)



Compound **7** was synthesized from indole and acetone using GP2. Purification was carried out using column chromatography on silica gel, eluting with 25% ethyl acetate in hexanes, to give the product **7** (159 mg, 68% yield) as a white solid. M.p. 157–161 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.89 (br s, 2H, NH), 7.43 (d, 2H, J = 8.5 Hz, ArH), 7.32 (d, 2H, J = 8.0 Hz, ArH), 7.09 (at, 2H, J = 8.0 Hz, ArH), 7.06 (d, 2H, J = 2.5 Hz, ArH), 6.90 (at, 2H, J = 8.0 Hz, ArH), 1.93 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 137.2, 126.4, 125.6, 121.5, 121.4, 120.6, 118.8, 111.1, 35.0, 30.1; LRMS: 297.1 $(M+Na)^+$; HRMS: 297.1354 Found, 297.1362 Calculated for $C_{19}H_{18}N_2Na$. the data matched the literature data for this compound:
Shiri, M.; Zolfigol, M.A.; Ayazi-Nasrabadi, R. *Tetrahedron Lett*. **2010**, *51*, 264-268.

***meso*-Octamethylcalix[4]pyrrole (8a)[15]**

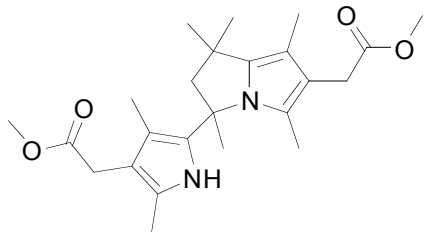


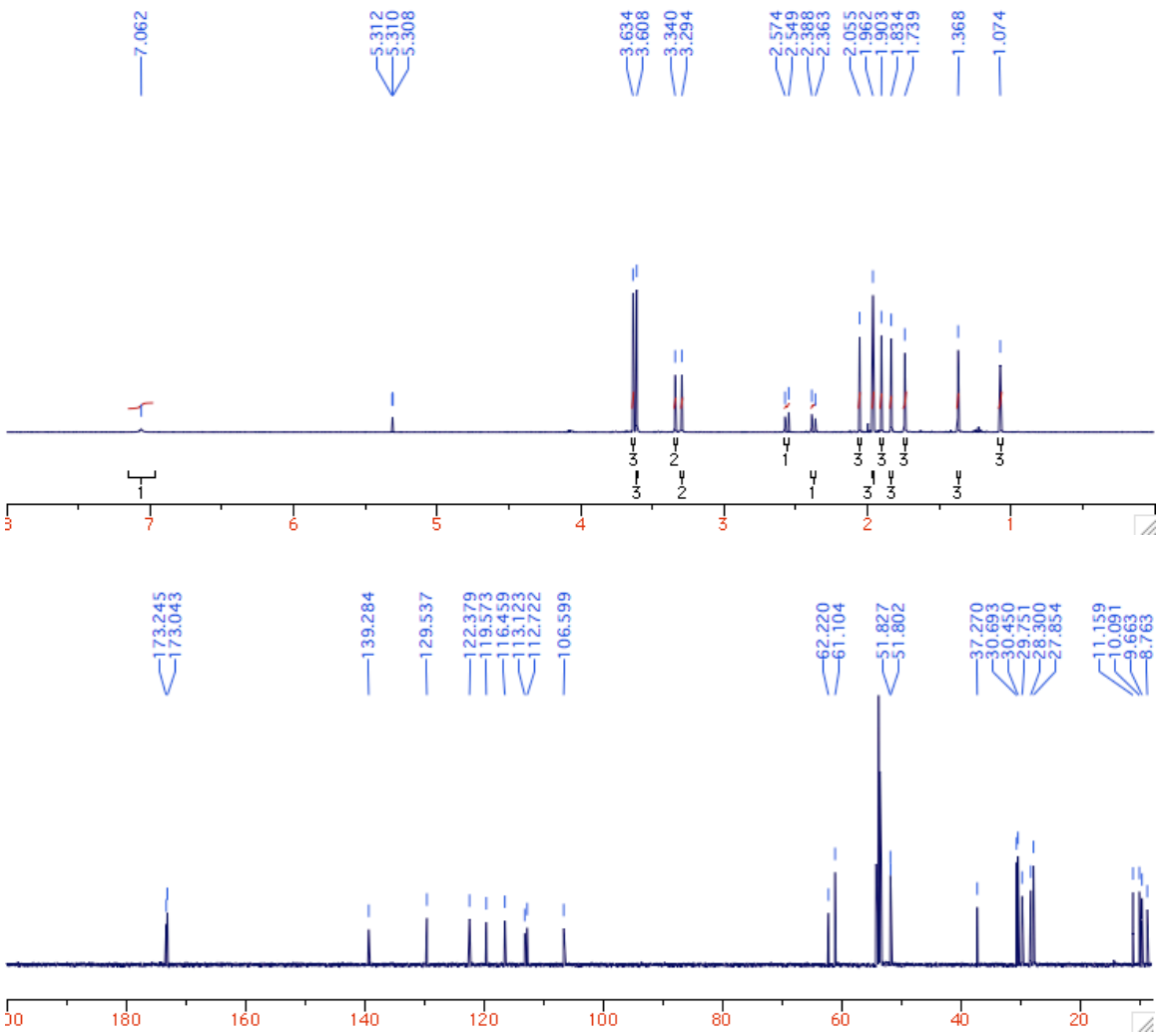
Compound **7** was synthesized from pyrrole and acetone using GP2. Purification was carried out using column chromatography on silica gel, eluting with 25% ethyl acetate in hexanes, to give the product **7** (159 mg, 68% yield) as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.99 (br s, 4H, NH), 5.90 (d, 8H, J = 2.5 Hz, PyH), 1.51 (s, 24H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 138.5, 103.0, 35.3, 29.2; LRMS: 429.3 $(M+H)^+$.

NMR Spectra

Annulated Pyrroles

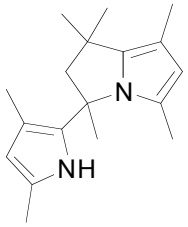
Methyl 2-(5-(6-(2-methoxy-2-oxoethyl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)acetate (5a)

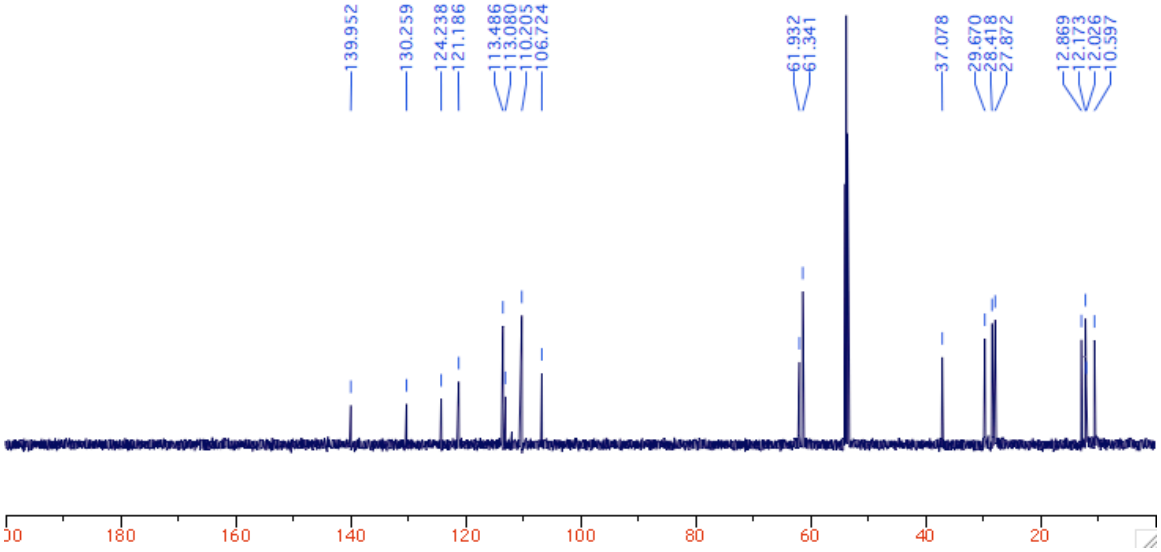




Top: ^{1}H NMR (CD_2Cl_2, 500 MHz); Bottom ^{13}C NMR (CD_2Cl_2, 125 MHz).

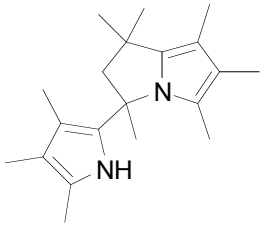
3-(3,5-Dimethyl-1H-pyrrol-2-yl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizine (5b)

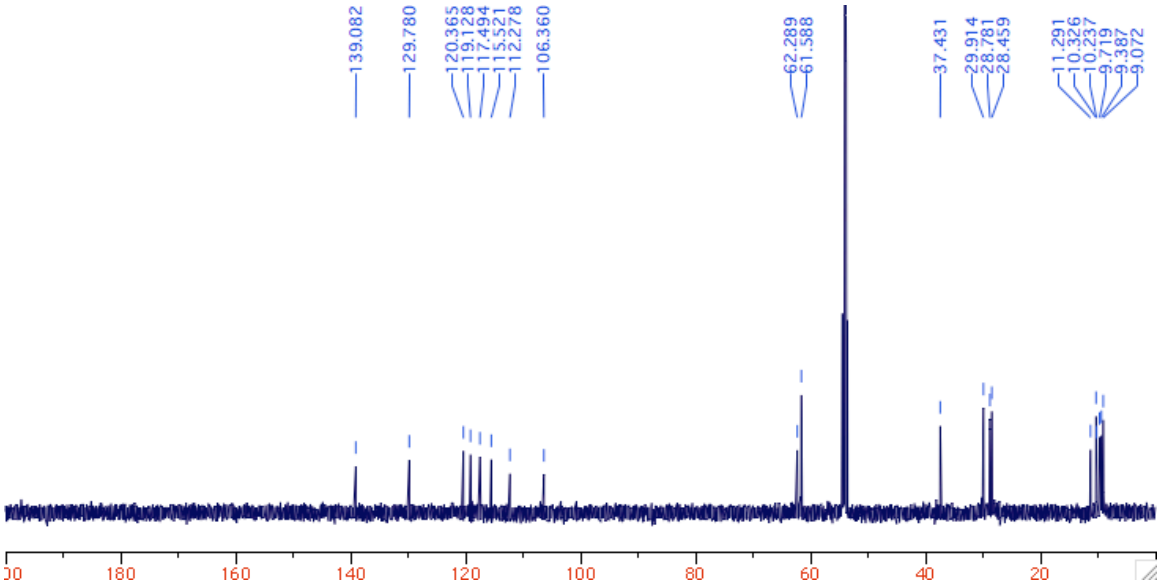




Compound **5b**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

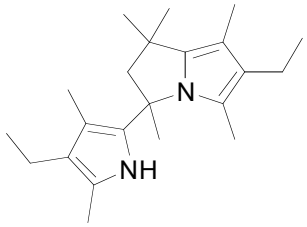
1,1,3,5,6,7-Hexamethyl-3-(3,4,5-trimethyl-1H-pyrrol-2-yl)-2,3-dihydro-1H-pyrrolizine (5c)

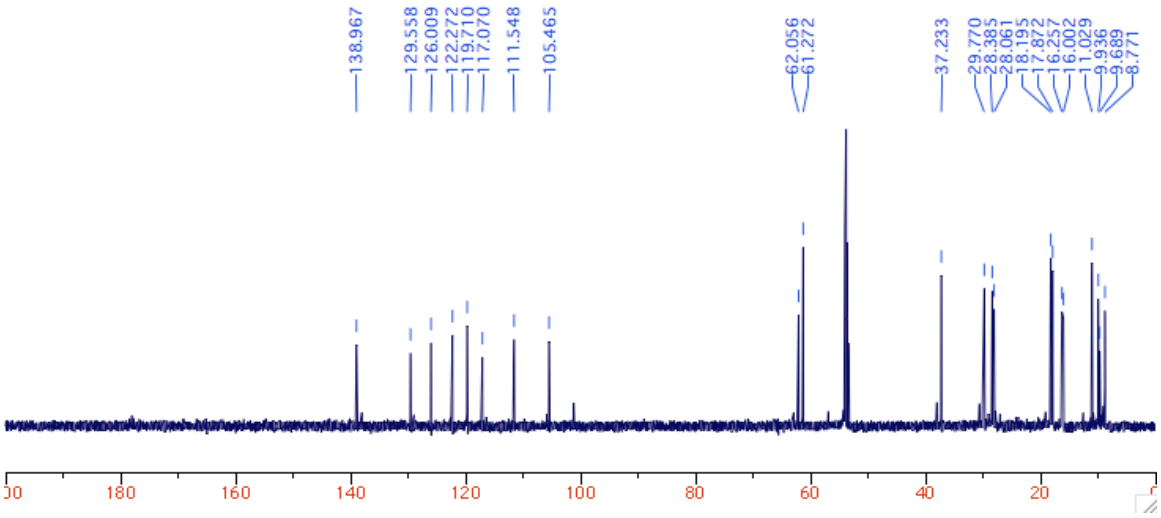




Compound **5c**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

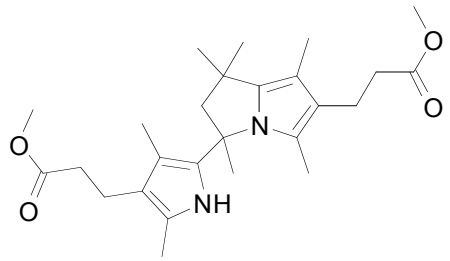
6-Ethyl-3-(4-ethyl-3,5-dimethyl-1H-pyrrol-2-yl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizine (5d)

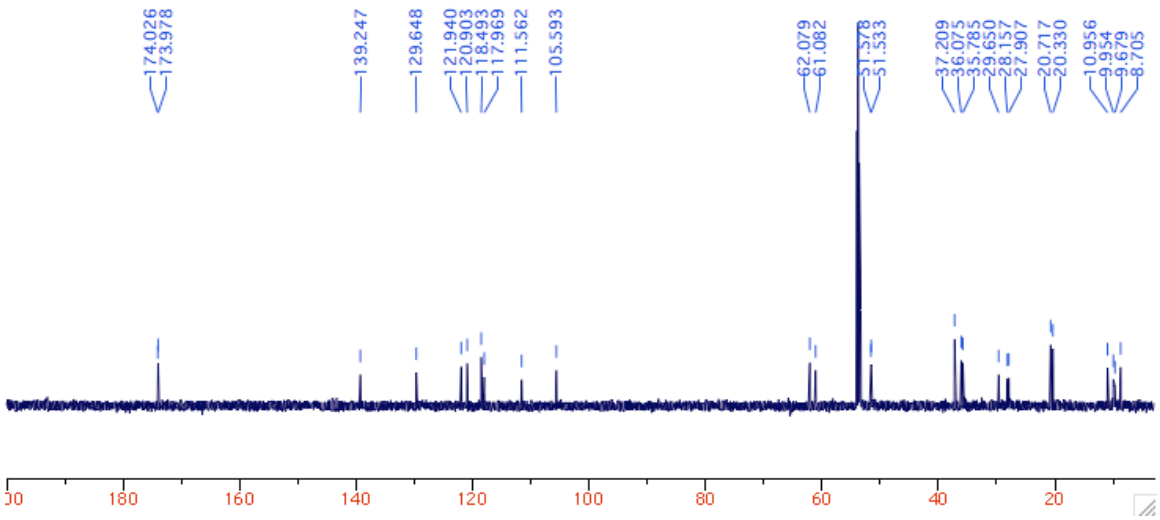




Compound **5d**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

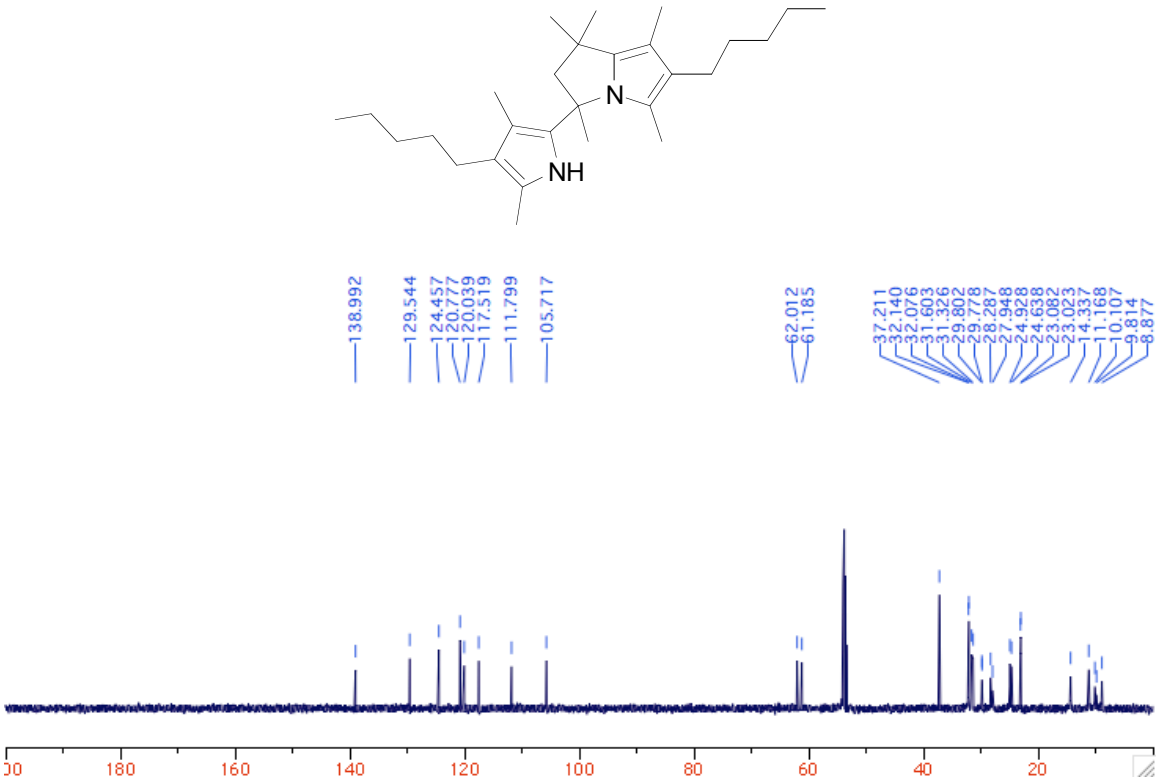
Methyl 3-(5-(6-(3-methoxy-3-oxopropyl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)propanoate (5e)





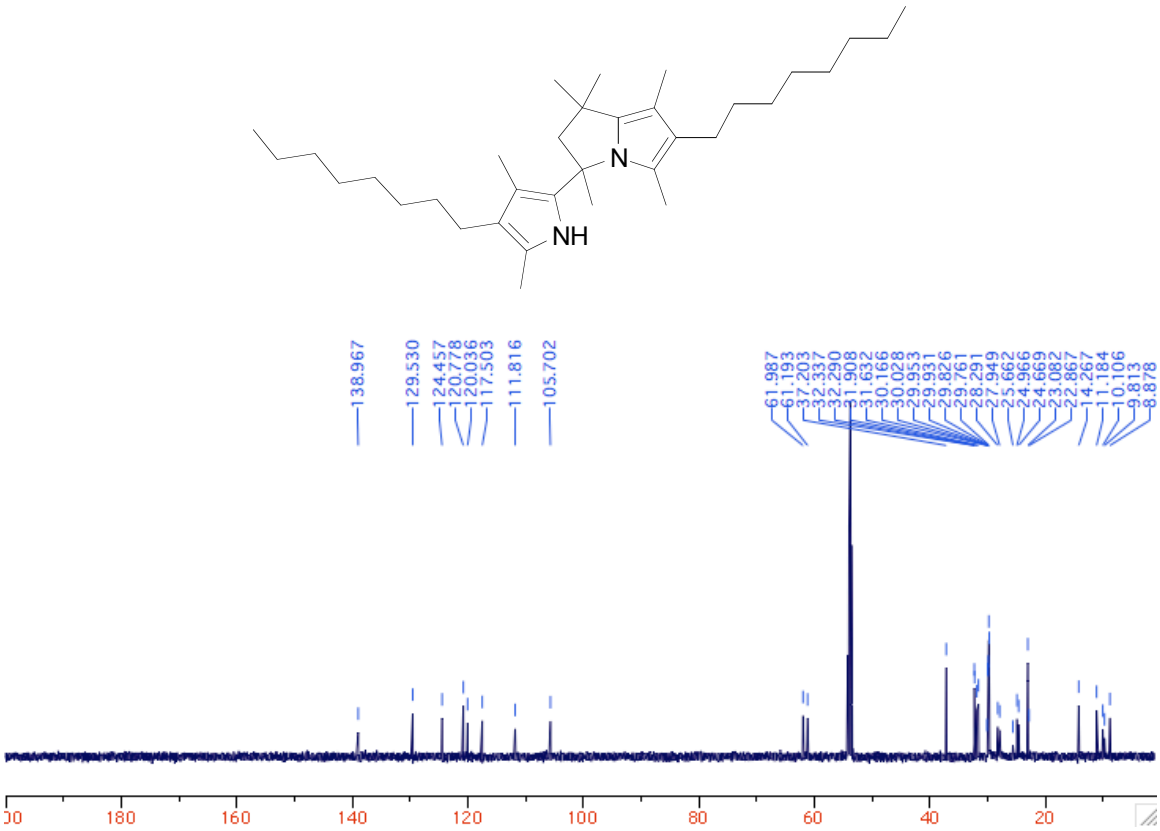
Compound **5e**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

3-(3,5-Dimethyl-4-pentyl-1H-pyrrol-2-yl)-1,1,3,5,7-pentamethyl-6-pentyl-2,3-dihydro-1H-pyrrolizine (5f)



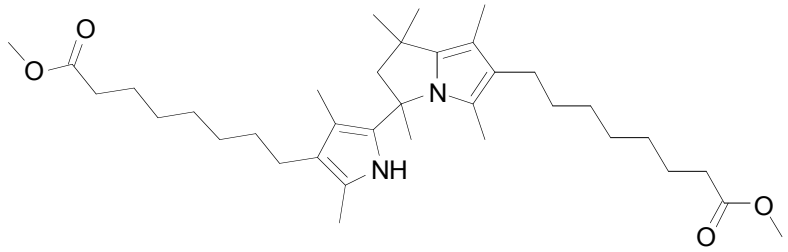
Compound **5f**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

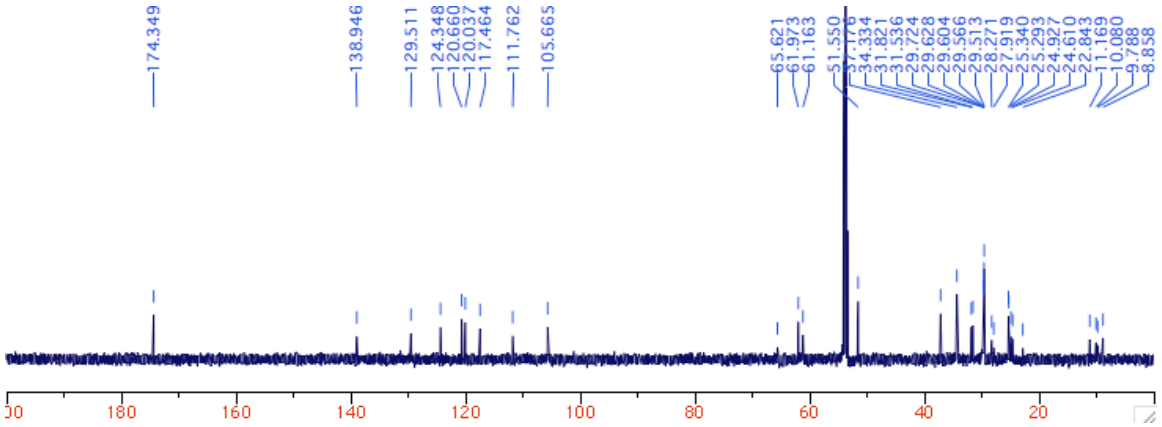
3-(3,5-Dimethyl-4-octyl-1H-pyrrol-2-yl)-1,1,3,5,7-pentamethyl-6-octyl-2,3-dihydro-1H-pyrrolizine (5g)



Compound **5g**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

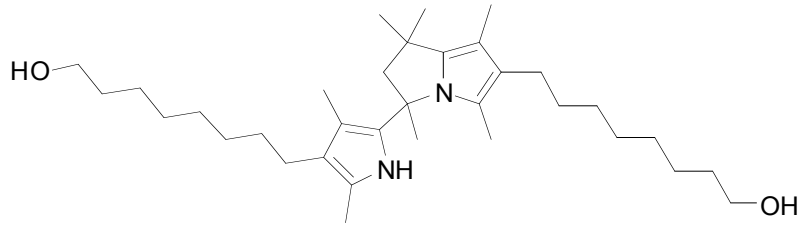
Methyl 8-(5-(6-(8-methoxy-8-oxooctyl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)octanoate (5h)

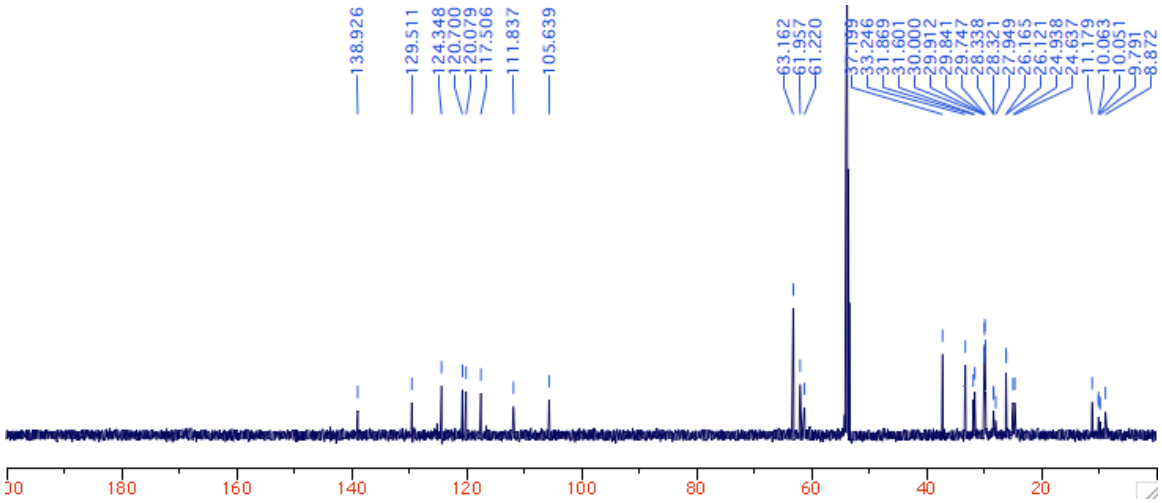




Compound **5h**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

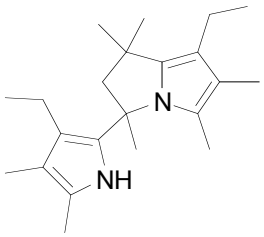
8-(5-(6-(8-Hydroxyoctyl)-1,1,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)octan-1-ol (5i)

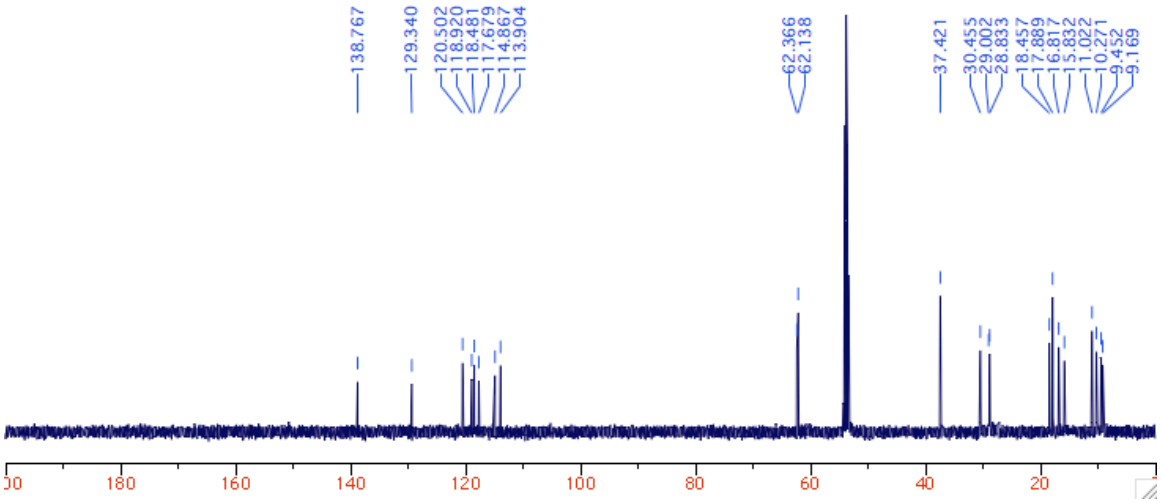




Compound **5i**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

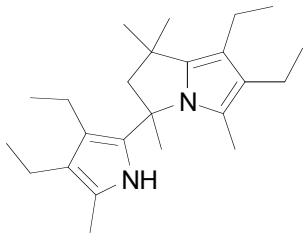
7-Ethyl-3-(3-ethyl-4,5-dimethyl-1H-pyrrol-2-yl)-1,1,3,5,6-pentamethyl-2,3-dihydro-1H-pyrrolizine (5j)

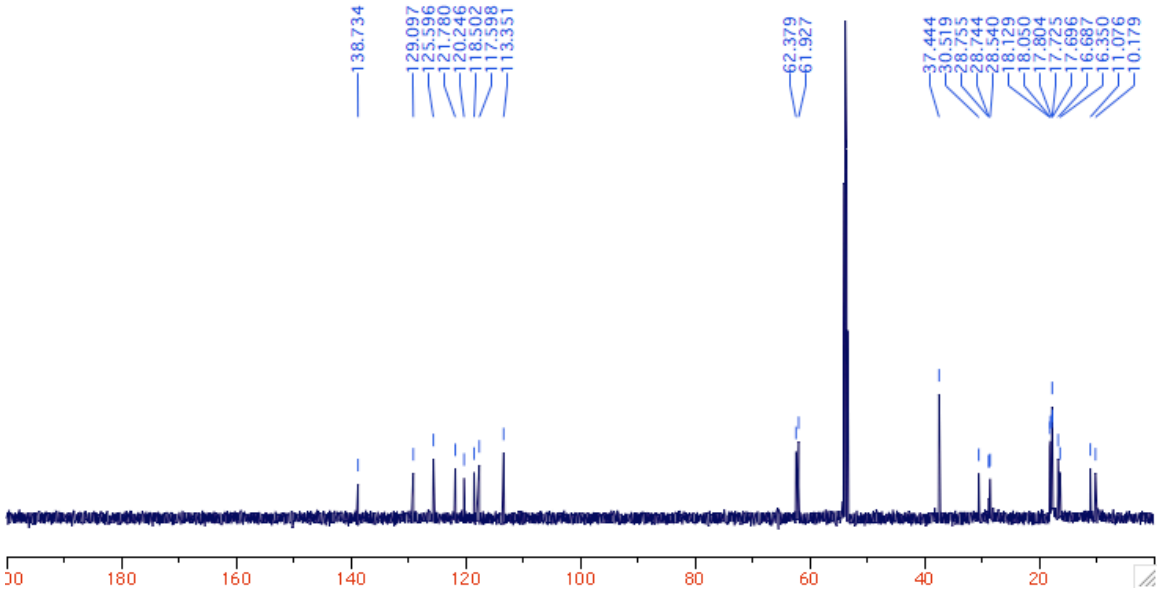




Compound **5j**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

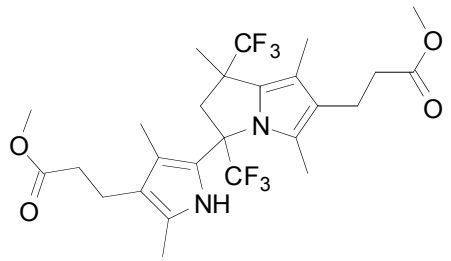
3-(3,4-Diethyl-5-methyl-1H-pyrrol-2-yl)-6,7-diethyl-1,1,3,5-tetramethyl-2,3-dihydro-1H-pyrrolizine (5k)

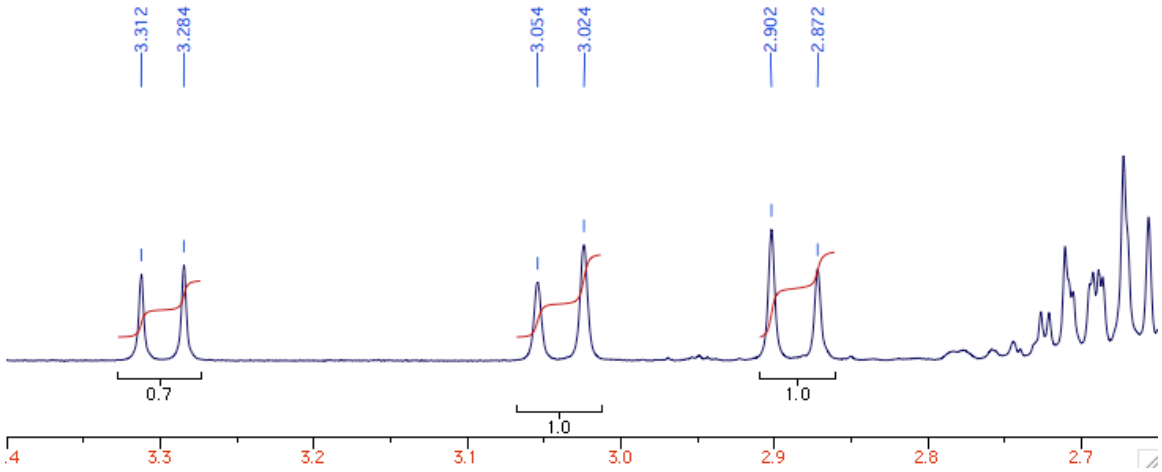




Compound **5k**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

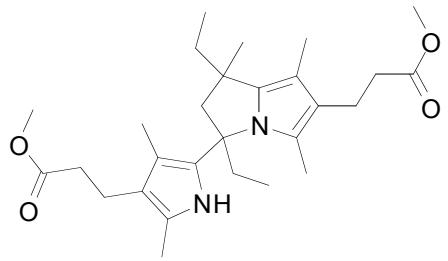
Methyl 3-(5-(6-(3-methoxy-3-oxopropyl)-1,5,7-trimethyl-1,3-bis(trifluoromethyl)-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)propanoate (9)



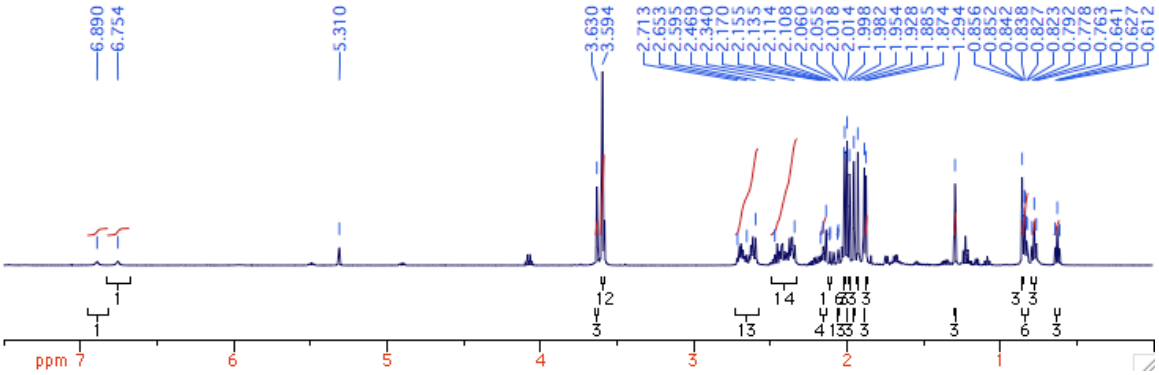


^{1}H NMR (CD_2Cl_2, 500 MHz); Section showing cyclic CH_2 peaks of both diastereoisomers in a 1:0.7 ratio.

Methyl 3-(1,3-diethyl-3-(4-(3-methoxy-3-oxopropyl)-3,5-dimethyl-1H-pyrrol-2-yl)-1,5,7-trimethyl-2,3-dihydro-1H-pyrrolizin-6-yl)propanoate (10a)

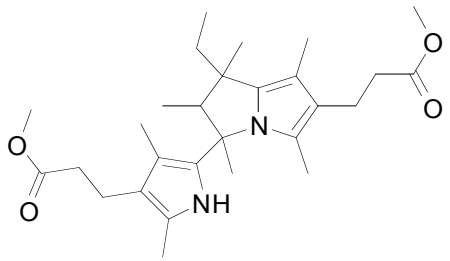


10a

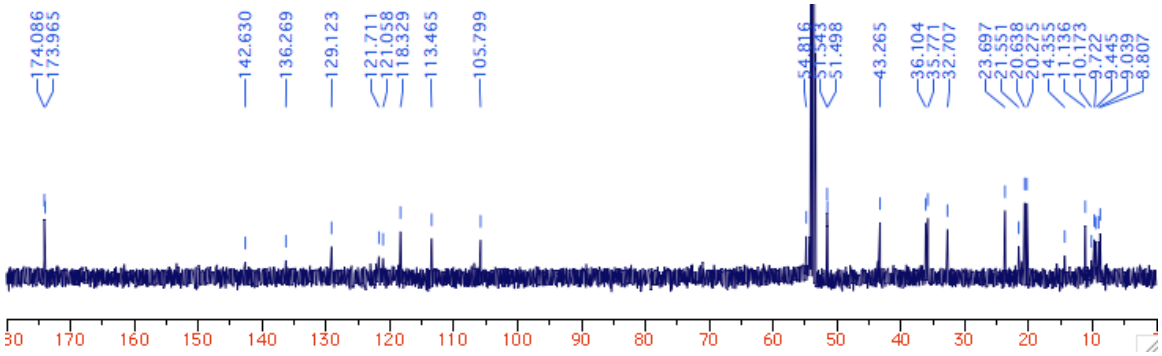


Isolated fraction 1: ^{1}H NMR (CD_2Cl_2, 500 MHz) showing 1:1 mixture of isomers.

Methyl 3-(1-ethyl-3-(4-(3-methoxy-3-oxopropyl)-3,5-dimethyl-1H-pyrrol-2-yl)-1,2,3,5,7-pentamethyl-2,3-dihydro-1H-pyrrolizin-6-yl)propanoate (10b)

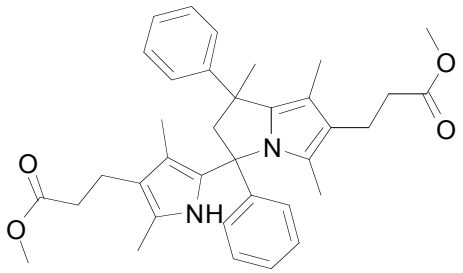


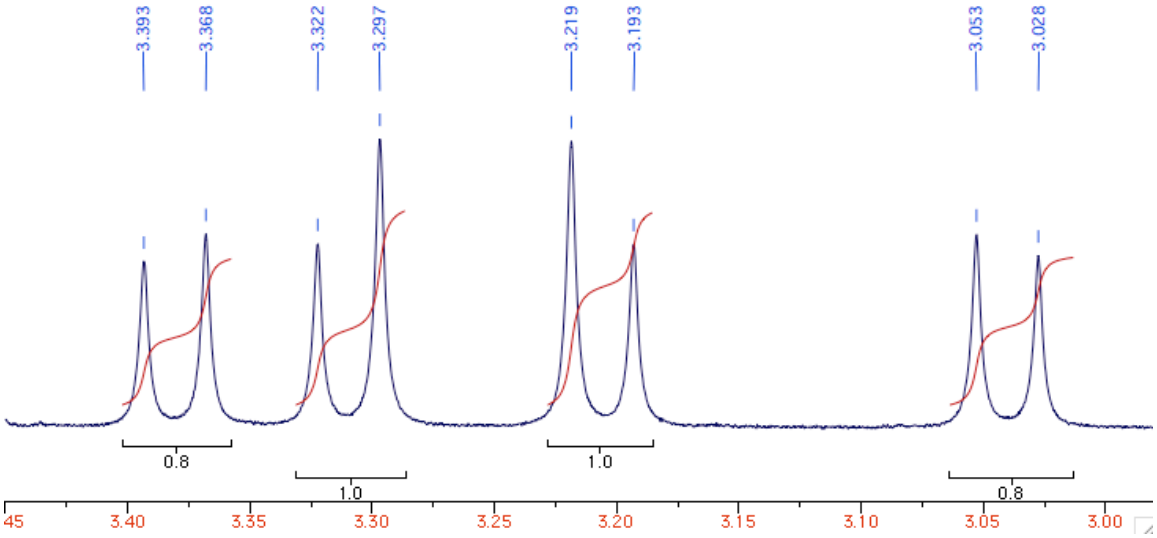
10b



Compound **10b**, ^{13}C NMR (CD_2Cl_2, 125 MHz).

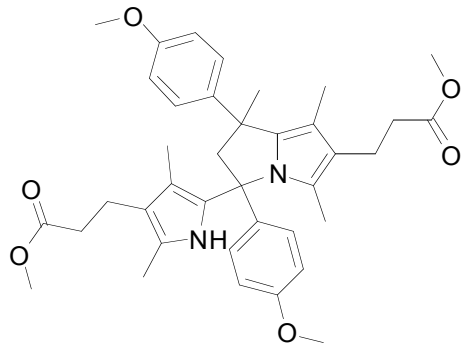
Methyl 3-(5-(6-(3-methoxy-3-oxopropyl)-1,5,7-trimethyl-1,3-diphenyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)propanoate (11)

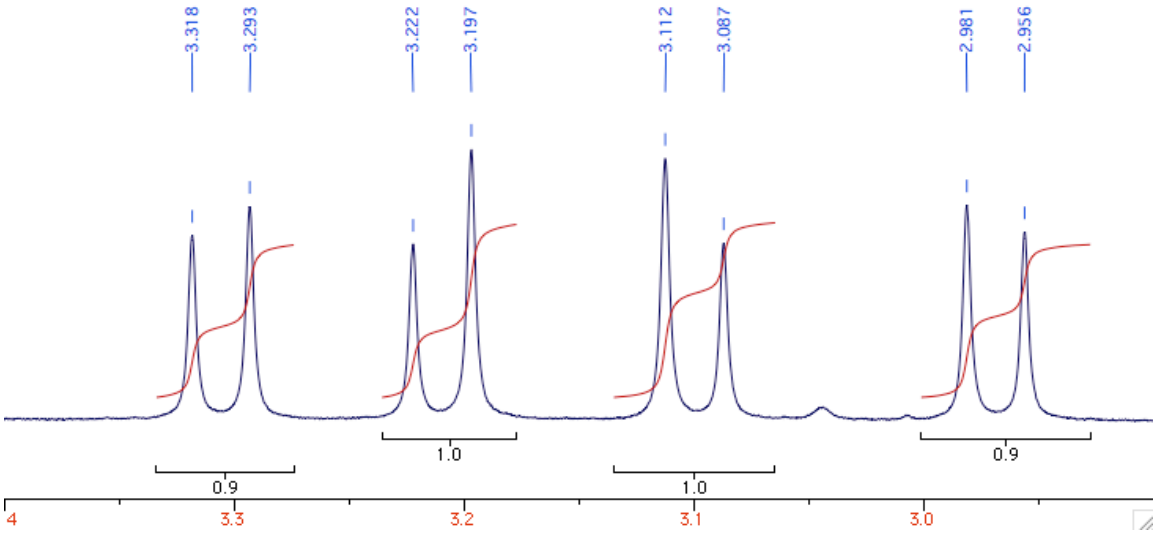




^{1}H NMR (CD_2Cl_2, 500 MHz): Section showing cyclic CH_2 peaks of both diastereoisomers in a 1:0.8 ratio.

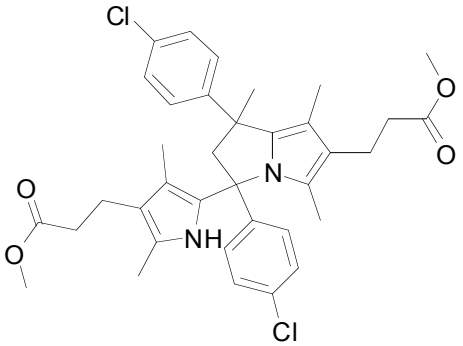
Methyl 3-(5-(6-(3-methoxy-3-oxopropyl)-1,3-bis(4-methoxyphenyl)-1,5,7-trimethyl-2,3-dihydro-1H-pyrrolizin-3-yl)-2,4-dimethyl-1H-pyrrol-3-yl)propanoate (12)

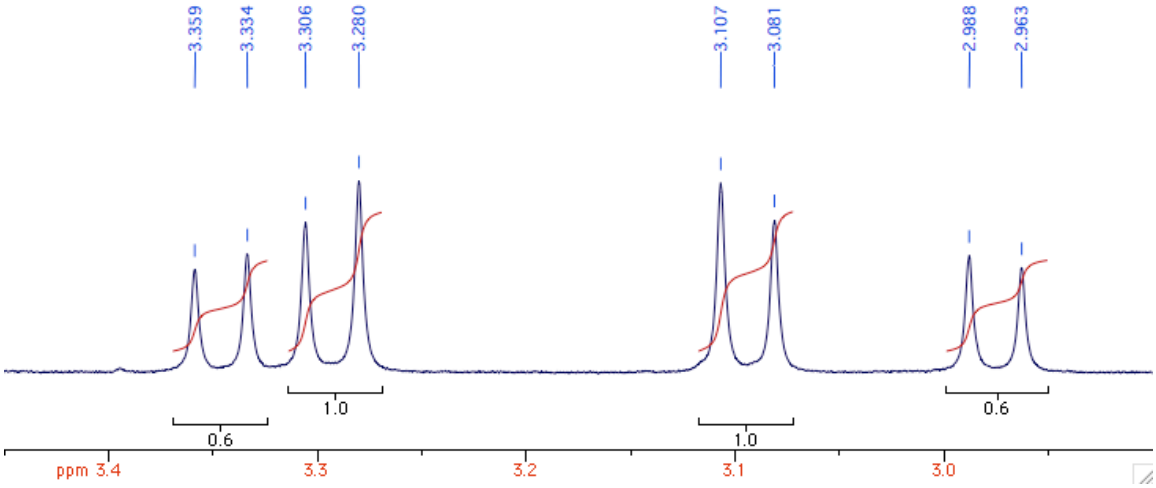




^{1}H NMR (CD_2Cl_2, 500 MHz): Section showing cyclic CH_2 peaks of both diastereoisomers in a 1:0.9 ratio.

Methyl 3-(1,3-bis(4-chlorophenyl)-3-(4-(3-methoxy-3-oxopropyl)-3,5-dimethyl-1H-pyrrol-2-yl)-1,5,7-trimethyl-2,3-dihydro-1H-pyrrolizin-6-yl)propanoate (13)

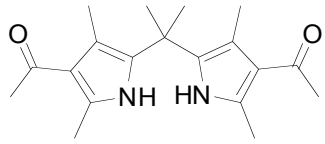


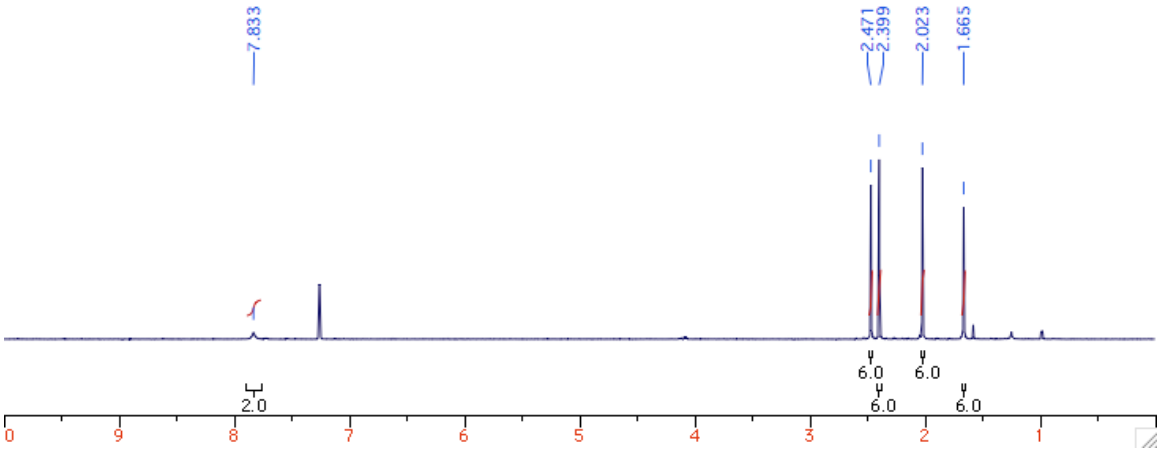


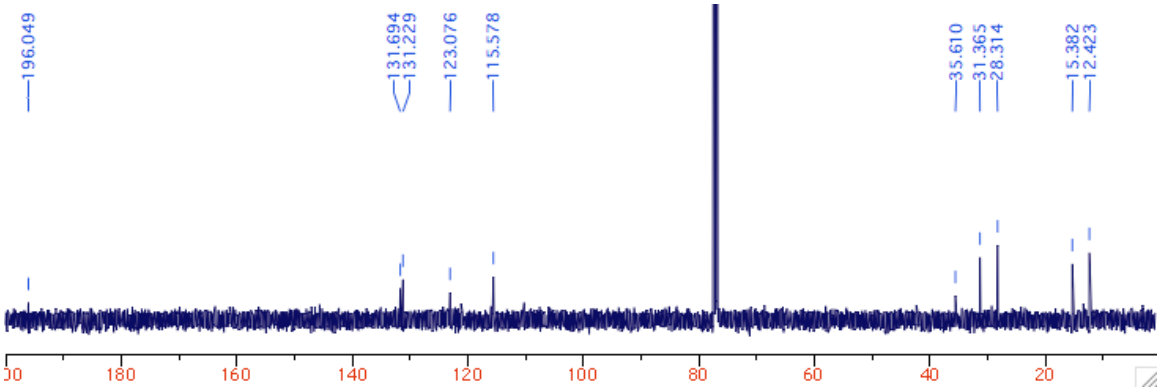
^{1}H NMR (CD_2Cl_2, 500 MHz): Section showing cyclic CH_2 peaks of both diastereoisomers in a 1:0.6 ratio.

Dimethyldipyrromethanes

1,1'-(5,5'-(Propane-2,2-diyl)bis(2,4-dimethyl-1H-pyrrole-5,3-diyl))diethanone (6)

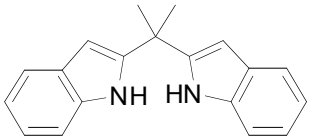


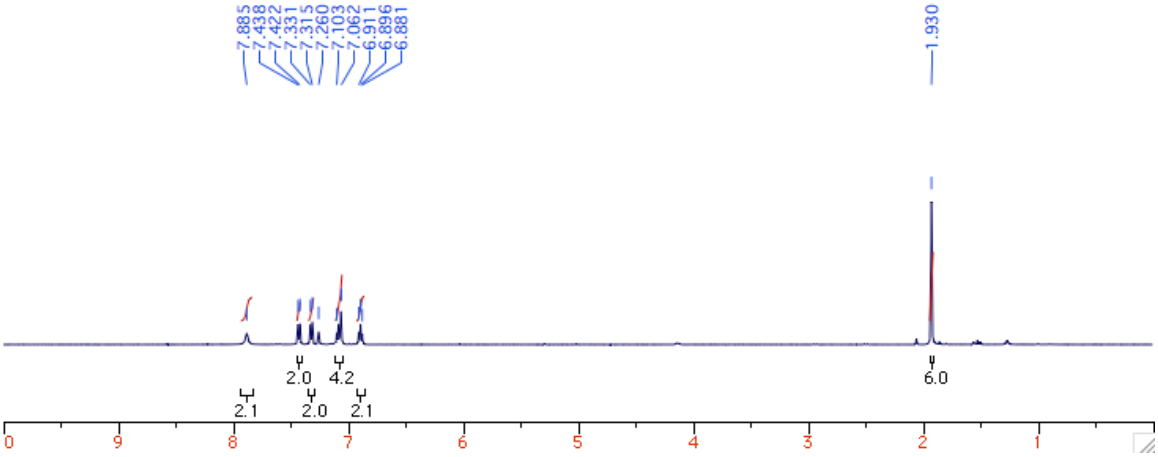


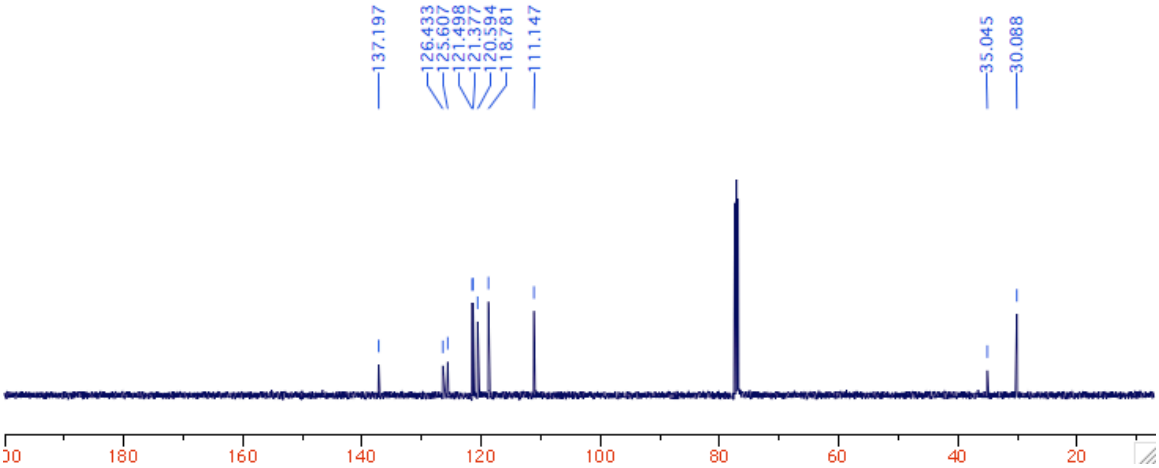


Top: ^{1}H NMR (CD_2Cl_2, 500 MHz); Bottom ^{13}C NMR (CD_2Cl_2, 125 MHz).

2,2'-(Propane-2,2-diyl)bis(1H-indole) (7)

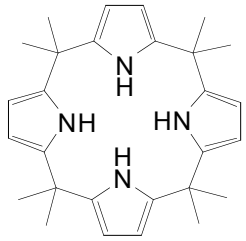


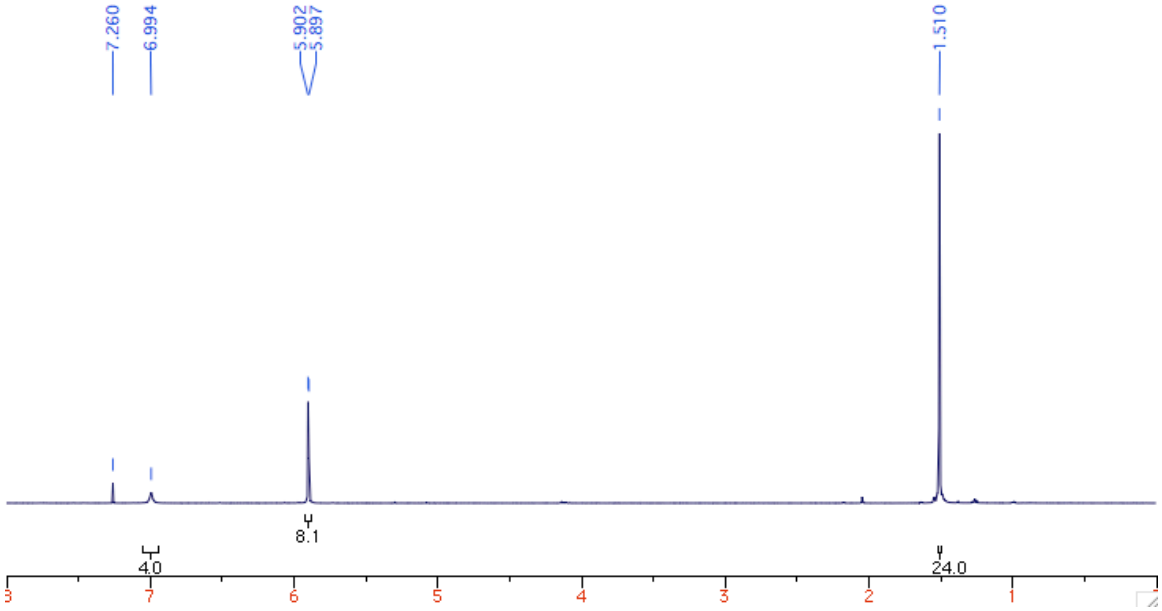


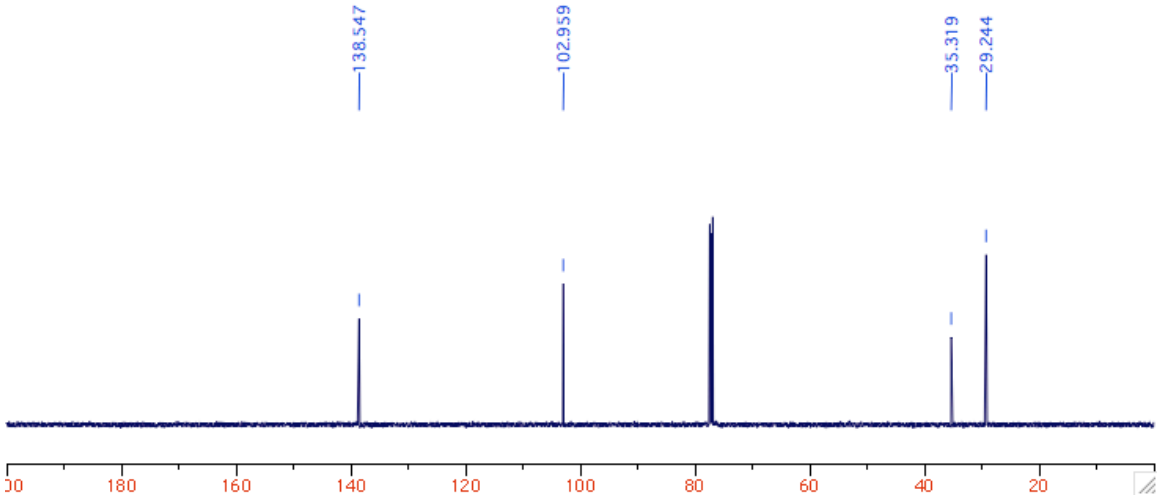


Top: ^{1}H NMR (CD_2Cl_2, 500 MHz); Bottom ^{13}C NMR (CD_2Cl_2, 125 MHz).

meso-Octamethylcalix[4]pyrrole (8a)







Top: ^{1}H NMR (CD_2Cl_2, 500 MHz); Bottom ^{13}C NMR (CD_2Cl_2, 125 MHz).

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