Concise Total Synthesis of (±)-Aloperine and *epi*-Aloperine

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Experimental Section

2-[(Methoxy-methyl-carbamoyl)-methyl]-piperidine-1-carboxylic acid *tert*-butyl ester (8). To a solution of carboxylic acid **7** (1 g, 4.11 mmol), *N,O*-dimethylhydroxylamine hydrochloride (401 mg, 4.11), DMPA (840 mg, 6.85 mmol) in THF (150 ml), DCC (850 mg, 4.13 mmol) dissolved in THF (20 ml) was added dropwise . After 17 h at room temperature the reaction mixture was filtered and the solvent was evaporated. The resulting oil was purified by column chromatography (EtOAc-hexane 1:2) to give **8** (834 mg, 71%). R_f (EtOAc-hexane, 1:1) 0.13; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.80 – 4.60 (1H, m), 3.99 (1H, bd, J = 13 Hz), 3.68 (3H, s), 3.13 (3H, s), 2.80 (1H, bt, J = 13 Hz), 2.62 (1H, A portion of AB system), 2.58 (1H, B portion of AB system), 1.68 – 1.55 (4H, m), 1.45 (9H, s), 1.54 – 1.33 (2H, m). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 155.0, 79.5, 60.5, 48.7, 47.6, 39.1, 34.1, 33.0, 28.4 (3C), 25.2, 18.9. Anal. Calcd. for $C_{14}H_{26}N_2O_4$: C, 58.72; H, 9.16; N, 9.78. Found: C, 58.79. H, 9.22. N, 9.67.

2-(2-Oxo-4-trimethylsilanyl-but-3-ynyl)-piperidine-1-carboxylic acid *tert*-butyl ester (9) from 8. A solution of trimethylsilylacetylene (372 µl, 2.64 mmol) in THF (9 ml) was treated with n-BuLi (993 µl, 2 mmol) at –78 °C. After 30 minutes the resulting solution was added to a solution of amide **8** (300 mg, 1.05 mmol) in THF-MeOH (15 ml-414 µl) at –50 °C. After 1 h at –5 °C AcOH (90 µl) was added at –70 °C. After 5 minutes NaCl was added and the mixture was extracted with EtOAc. By column chromatography (EtOAc-hexane, 1:3) compound **9** (150 mg, 42%) was obtained as an oil. R_f (EtOAc-hexane, 1:3) 0.4; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.75-4.15 (1H, m), 3.98 (1H, bd, J= 13 hz), 2.85-2.65 (3H, m), 1.75-1.30 (6H, m), 1.44 (9H,s), 0.29 (9H, s). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 185.2, 154.4, 102.1, 97.9, 79.5, 47.5, 45.5, 39.0, 28.4, 28.2 (3C), 25.1, 18.8, -0.9 (3C). Anal. Calcd. for $C_{17}H_{29}NO_3Si$: C, 63.12; H, 9.04; N, 4.33. Found: C, 63.21. H, 9.10. N, 4.38.

2-(2-Oxo-but-3-ynyl)-piperidine-1-carboxylic acid *tert*-butyl ester (10)

To a solution of compound **9** (112mg, 0.34 mmol) in THF-MeOH (5 ml-138 µl), TBAF (1M in THF, 130 µl) was added at –20°C. After 30 min, NH_4Cl solution was added and the solution was extracted with CH_2Cl_2. Evaporation of the organic solvent, gave compound **10** as an oil (71mg, 84%). R_f (EtOAc-hexane, 1:4) 0.2; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.88-4.77 (1H, m), 4.08-3.93 (1H, bd, J=13 Hz), 2.90-2.65 (3H, m), 1.80-1.30 (7H, m), 1.45 (9H, s). ^{13}C NMR (50.3 MHz, $CDCl_3$) δ 184.9, 154.5, 81.6, 79.8, 78.8, 47.3, 45.8, 39.2, 28.7, 28.3 (3C), 25.1, 18.8. Anal. Calcd. for $C_{14}H_{21}NO_3$: C, 66.91; H, 8.42; N, 5.57. Found: C, 66.85. H, 8.48. N, 5.50.

2-(2-Oxo-4-trimethylsilanyl-but-3-ynyl)-piperidine-1-carboxylic acid *tert*-butyl ester (9) from 11. Trimethylsilylacetylene (373 mg, 3.80 mmol) was added to a cold (0°C) solution of ethylmagnesiumbromide (506 mg, 3.80 mmol) dissolved in THF (10 ml). This solution was stirred for 1 h at 5-15°C and for 15 min at room temperature. A solution of the aldehyde **11** (724 mg, 3.18 mmol) in THF (6 ml) was then added dropwise over a 30-min period. The reaction solution was allowed to stir for an additional 30 min before being quenched with $NH_4Cl_{(satd)}$ and concentrated.

The resulting mixture was extracted with AcOEt, the organic phase was washed with $NH_4Cl_{(satd)}$ and brine. The evaporation of the solvent gave a mixture of diastereoisomers **12** (890 mg, 86%) that were directly used for the next step. A DMSO solution (280 µl, 3.91 mmol) in CH_2Cl_2 (2 ml) was added to a solution of oxalyl chloride (170 µl, 1.96 mmol) in CH_2Cl_2 (13 ml) at –78°C over a period of 5 min. After the mixture was stirred for 30 min, a solution of **12** (198 mg, 0.61 mmol) was added to the CH_2Cl_2 solution and the reaction mixture was stirred at the same temperature for 90 min. Et_3N (115 µl, 8.15 mmol) was then added to the reaction mixture, which was gradually warmed to room temperature and diluted with CH_2Cl_2. The CH_2Cl_2 solution was washed with water and brine, dried and concentrated to dryness to give **9** as a brown oil (172 mg, 87%) that was directly used for the next step.

2-(2-Hydroxy-4-trimethylsilanyl-but-3-ynyl)-piperidine-1-carboxylic acid *tert*-butyl ester (12)
A small amount of diastereomeric mixture **12** was purified by chromatography (AcOEt:cyclohexane 1:4). **12a** R_f (AcOEt:cyclohexane 1:4) 0.38; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.64 (1H, bs), 4.50-4.20 (1H, m), 4.17-4.13 (1H, m), 4.01-3.90 (1H, m), 2.75 (1H, td, J=10, 3 Hz), 2.28-2.15 (1H, td, J=10, 3 Hz), 1.80-1.39 (25H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 154.5, 106.5, 80.8, 77.4 (tentatively assigned), 59.5, 46.5, 39.9, 39.0, 29.6, 28.8 (3C), 25.7, 19.6, 0.3 (3C). Anal. Calcd. for $C_{17}H_{31}NO_3Si$: C, 62.72; H, 9.60; N, 4.30. Found: C, 62.68. H, 9.62. N, 4.27. **12b** R_f (AcOEt:cyhexane 1:4) 0.30; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.82-4.77 (1H, bs), 4.62-4.39 (2H, m), 4.02-3.84 (1H, m), 2.98-2.80 (1H, m), 2.24 (1H, ddd, J=14, 11, 3 Hz), 1.74 (1H, ddd, J=15, 5, 4), 1.70-1.40 (24H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 154.5, 106.5, 80.8, 77.4 (tentatively assigned), 60.2, 46.3, 39.9, 37.0, 29.9, 28.9 (3C), 25.9, 19.7, 0.4 (3C). Anal. Calcad. for $C_{17}H_{31}NO_3Si$: C, 62.72; H, 9.60; N, 4.30. Found: C, 62.74. H, 9.58. N, 4.27.

2-[2-Benzyl-6-oxo-1,4,5,6-tetrahydro-pyridin-3-yl)-2-oxo-ethyl]-piperidine-1-carboxylic acid *tert*-butyl ester (13)
Benzylamine (354 µl, 3.25 mmol) was added to a solution of **10** (743 mg, 2.96 mmol) at 0°C. After the solution was warmed to room temperature, stirring was maintained for 18 h. Acryloyl chloride (263 µl, 3.25 mmol) was added at room temperature. After being heated for 18 h at reflux, the solution was washed with a saturated aqueous $NaHCO_3$ and the organic layer extracted with EtOAc. Evaporation of the solvent and column chromatography (AcOEt-cyhexane, 1:3) gave a yellow oil (683 mg, 56%). R_f (EtOAc) 0.55; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70-7.20 (6H, m), 4.92 (1H, A portion of AB system), 4.68 (1H, B portion of AB system), 4.60-4.52 (1H, m), 3.90 (1H, bd, J=13 Hz), 2.82-2.65 (5H, m), 2.57 (2H, bs), 1.98-1.40 (6H, m), 1.45 (9H, s). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 195.8, 169.8, 155.1, 136.6, 128.8 (2C), 128.0, 127.8 (3C), 118.5, 79.6, 50.2, 49.1, 39.8, 38.4, 30.7, 28.4 (3C), 27.5, 25.1, 18.8, 18.6. Anal. Calcd. for $C_{24}H_{32}N_2O_4$: C, 69.88; H, 7.82; N, 6.79. Found: C, 69.93. H, 7.80. N, 6.82. EIMS 412 (6%), 356 (10%), 339 (16%), 312 (100%), 214 (80%).

1-Benzyl-6-(1-*tert*-butoxycarbonyl-piperidin-2-yl)-2-oxo-1,2,3,4,6,7,8,8a-octahydro-quinoline-8-carboxylic acid methyl ester (16 and 17)
To a solution of **13** (424 mg, 1.03 mmol) in THF-MeOH (1:2, 30 ml), $NaBH_4$ (56 mg, 1.48 mmol) was added at 0°C. After 2 h, the reaction mixture was poured into a $NH_4Cl_{(satd)}$ and extracted with AcOEt. The crude **14** was directly dissolved in toluene (10 ml) and refluxed in presence of pTSA (8 mg, 0.043 mmol) and methyl acrylate (6 ml, 66.7 mmol). After 10 days, the solution was concentrated in vacuum and the residue was purified by chromatography (AcOEt-hexane, 1:1) to give **16** (280 mg, 56%) and **17** (140 mg, 28%). **16**: R_f (AcOEt-hexane 1:1) 0.22; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.10 (5H, m), 5.50 (1H, bs), 5.42 (1H, A portion of AB system), 4.05 (1H, bd, J=11 Hz), 4.02 (1H, B portion of AB system), 3.92-3.82 (1H, m), 3.59 (3H, s), 3.22-3.12 (1H, m), 2.90-2.80 (1H, m), 2.54-2.30 (8H, m), 1.85-1.70 (2H, m), 1.70-1.45 (4H, m), 1.45 (9H, s). ^{13}C NMR

(75.4 MHz, $CDCl_3$) δ 172.9, 172.0, 155.0, 137.0, 135.5, 128.6-126.8 (5C), 123.2, 79.2, 55.9, 51.8, 46.1, 42.8, 40.0, 39.0, 34.6, 32.2, 29.5, 28.7, 28.3 (3C), 25.8, 25.3, 18.8. Anal. Calcd. for $C_{28}H_{38}N_2O_5$: C, 69.78; H, 7.94; N, 5.80. Found: C, 69.84. H, 7.91. N, 5.76. **17**: R_f (EtOAc) 0.19; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.15 (5H, m), 5.42 (1H, bs), 5.31 (1H, A portion of AB system), 4.15-3.85 (3H, m), 3.59 (3H, s), 3.15-3.05 (1H, m), 2.75-2.25 (9H, m), 1.95-1.20 (6H, m), 1.45 (9H, s). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 172.9, 172.0, 155.0, 137.0, 135.5, 128.6-126.8 (5C), 122.8, 77.4, 56.4, 53.4, 46.5, 42.3, 40.0, 39.8, 32.6, 29.6, 28.5 (3C), 25.9, 25.3, 18.7. Anal. Found. for $C_{28}H_{38}N_2O_5$:: C, 69.83. H, 7.90. N, 5.79.

2-[2-Benzyl-6-oxo-1,4,5,6-tetrahydro-pyridin-3-yl)-vinyl]-piperidine-1-carboxylic acid *tert*-butyl ester (15). A solution of **14** (50 mg, 0.13 mmol) in toluene (3 ml) was heated at 70ºC. After 30 min, the solvent was evaporated and the residue was purified by chromatography (AcOEt:hexane 1:1) to give **15** (45 mg, 88%). **15** (AcOEt-cyhexane, 1:1. R_f = 0.32). ^1H NMR (200 MHz, $CDCl_3$) δ 7.55 - 7.15 (5H, m), 6.05 (1H, s), 5.96 (1H, d, J=16 Hz), 5.45 (1H, dd, J=16, 5 Hz), 4.84 (1H, m), 4.70 (2H, s), 3.92 (1H, bd, J=12Hz), 2.81 (1H, bt, J=12 Hz), 2.62 (2H, t, J=9 Hz), 2.47 (2H, t, J=9 Hz), 1.82 – 1.50 (6H, m), 1.40 (9H, s); ^{13}C NMR (50.2 MHz, $CDCl_3$) δ 179.2, 155.5, 136.7, 130.9, 128.6 (5C), 127.5, 125.5, 117.8, 79.5, 52.0, 49.1, 39.7, 30.7, 29.5, 28.3 (3C), 25.4, 20.5, 19.5. Anal. Calcd. for $C_{24}H_{32}N_2O_3$: C, 72.70; H, 8.13; N, 7.06. Found: C, 72.68. H, 8.17. N, 7.04.

1-Benzyl-2-oxo-6-piperidin-2-yl -1,2,3,4,6,7,8,8a-octahydro-quinoline-8-carboxylic acid methyl ester (18)
1-Benzyl-2-oxo-6-piperidin-2-yl -1,2,3,4,6,7,8,8a-octahydro-quinoline-8-carboxylic acid methyl ester (19)
To a solution of **16** or **17** (150 mg, 0.27 mmol) in CH_2Cl_2 (9 ml), CF_3COOH (2.1 ml, 27 mmol) was added. After 2 h at room temperature, water was added and the solution was basificated with NH_4OH. Evaporation of the organic layer gave **18** or **19** in quantitative yield. **18**: R_f (CH_2Cl_2:EtOH-NH_4OH conc. 5% 4:1) 0.5; ^1H NMR (300 MHz, $CDCl_3$) δ 7.40-7.05 (5H, m), 5.50 (1H, bs), 5.20 (1H, A portion of AB system), 4.31 (1H, B portion of AB system), 3.92-3.83 (1H, m), 3.56 (3H, s), 3.12-2.95 (2H, m), 2.70-0.85 (16H, m). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 172.7, 172.2, 137.2, 133.6, 128.6 (2C), 127.8 (2C), 127.3, 123.1, 59.8, 56.7, 51.5, 47.2, 46.6, 39.3, 38.1, 32.7, 30.4, 29.3, 26.3, 26.1, 25.4. Anal. Calcd. for $C_{23}H_{30}N_2O_3$: C, 72.22; H, 7.91; N, 7.32. Found: C, 72.27. H, 7.95. N, 7.32. EIMS 382 (23%), 322 (48%), 299 (100%). **19**: R_f (AcOEt: MeOH: Et_3N 15:1:2) 0.45; ^1H NMR (300 MHz, $CDCl_3$) δ 7.35-7.05 (5H, m), 5.64 (1H, bs), 5.24 (1H, A portion of AB system), 4.09 (1H, B portion of AB system), 3.90-3.85 (1H, m), 3.54 (3H, s), 3.12-3.01 (2H, m), 2.65-0.85 (16H, m). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 172.7, 172.2, 137.1, 133.3, 129.6 (2C), 127.6 (2C), 127.3, 122.4, 60.4, 56.4, 51.5, 47.5, 46.5, 39.4, 37.9, 32.6, 30.7, 29.2, 26.7, 26.2, 24.1. Anal. Calcd. for $C_{23}H_{30}N_2O_3$: Found: C, 72.28. H, 7.95. N, 7.30.

1-Benzyl-8-hydroxymethyl-6-piperidin-2-yl-1,2,3,4,6,7,8,8a-octahydro-*1H*-quinoline (20)
1-Benzyl-8-hydroxymethyl-6-piperidin-2-yl-1,2,3,4,6,7,8,8a-octahydro-*1H*-quinoline (21)
To a suspension of $LiAlH_4$ (115mg, 3.03 mmol) in THF (15 ml), a solution of **18** or **19** (430 mg, 1.12 mmol) was added dropwise at 0°C. The reaction mixture was maintained at 0°C for 6 h. $LiAlH_4$ (402 mg, 10.58 mmol) was added in several portions and after 4 days at room temperature the reaction was concluded. AcOEt was added and after 2 h the reaction mixture was poured into water. The organic layer was concentrated to give a yellow oil (361 mg, 94%) that was directly used in the next step. A little amount was purified by chromatography (AcOEt:MeOH:Et_3N 15:1:1). **20**: R_f (AcOEt: MeOH: Et_3N 15:1:1) 0.13; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55-7.10 (5H, m), 5.51 (1H, bs), 4.00 (1H, A portion of AB system), 3.91 (1H, dd, J=12.5, 10 Hz), 3.65 (1H, dd, J=12.5, 10 Hz), 3.31 (1H, B portion of AB system), 3.22 (1H, bd, J=7.5 Hz), 3.13 (1H, bd, J=12.5 Hz), 2.88-2.75

(1H, m), 2.70-1.22 (19H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 139.2, 135.9, 128.8 (2C), 128.7 (2C), 127.3, 124.4, 63.3, 61.6, 60.9, 51.6, 47.2, 39.9, 36.4, 34.4 (2C), 31.0, 30.1, 26.3, 24.9, 23.4. Anal. Calcd. for $C_{22}H_{32}N_2O$: C, 77.60; H, 9.47; N, 8.23. Found: C, 77.62; H, 9.49; N, 8.20. **21**: R_f (AcOEt: MeOH: Et_3N 15:1:1) 0.23; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.15 (5H, m), 5.61 (1H, bs), 3.90 (1H, dd, J=12.5, 10 Hz), 3.88 (1H, A portion of AB system), 3.69 (1H, dd, J=12.5, 10 Hz), 3.52 (1H, B portion of AB system), 3.41-3.35 (1H, m), 3.18-3.08 (1H, m), 2.85-2.71 (1H, m), 2.70-2.55 (1H, m), 2.50-1.15 (18H, m). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.4, 135.1, 128.8 (2C), 128.4 (2C), 127.1, 123.1, 64.0, 61.3, 60.3, 54.5, 50.0, 47.0, 39.7, 36.6, 33.7, 29.6, 25.9, 25.7, 24.7, 21.6. Anal. Calcd. for $C_{22}H_{32}N_2O$: Found: C, 77.64; H, 9.51; N, 8.25.

Formation and reduction of N-C6 imine from compound 18. NCS (19 mg, 0.141 mmol) was stirred in THF (2 ml) at 0 ºC and a solution of **18** (50 mg, 0.130 mmol) in THF (1 ml) was added. After 1.5 h water was added and the organic layer was concentrated to give the crude N-Cl derivative as a colorless oil. The crude product was dissolved in CH_2Cl_2 (2 ml) and DBU (0.169 mmol, 26 mg, 26 µl) was added. After 8 h the solvent was evaporated, the crude mixture containing the imine product was directly dissolved in CH_2Cl_2 and $NaBH_3CN$ (16 mg, 0.25 mmol) was added. After 1 h the reaction mixture was poured into water and extracted with CH_2Cl_2 to give a mixture containing compounds **18** and **19**.

N-Benzyl-aloperine (22)
1-Benzyl-1,3,4,6,6a,7,8,9,10,12,13,13a-dodecahydro-2H-6,13-methano-dipyrido[1,2-a,3',2'-e]azocine (23)
To a solution of **20** or **21** (361 mg, 1.06 mmol) in CH_2Cl_2 (40 ml), PPh_3 (695 mg, 2.65 mmol) and CBr_4 (421 mg, 1.27 mmol) were added and the reaction mixture was stirred at room temperature for 3 h. Dry Et_3N (361 µl, 2.60 mmol) was added and, after 15h, the solution was poured into HCl 1N. The aqueous solution was basified with NH_4OH conc. and extracted with CH_2Cl_2. Evaporation of the solvent and chromatographic purification (hexane: Et_3N 30:1) gave respectively **22** (153 mg, 45%) or **23** (143 mg, 42%). **22**: R_f (AcOEt: hexane: Et_3N 15:10:1) 0.48; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.11 (5H, m), 5.58 (1H, d, J=4.5 Hz), 4.12 (1H, A portion of AB system), 3.01 (1H, B portion of AB system), 2.98-1.25 (22H, m). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.6, 133.8, 128.6 (2C), 128.1 (2C), 127.9, 126.6, 65.6, 65.1, 57.8, 55.8, 52.5, 51.7, 35.7, 33.7, 32.6, 29.6, 25.6 (2C), 25.2, 23.5. Anal. Calcd. for $C_{22}H_{30}N_2$: C, 81.93; H, 9.38; N, 8.69. Found: C, 81.90. H, 9.41. N, 8.73. EIMS 322 (25%), 231 (100%). **23**: R_f (AcOEt: hexane: Et_3N 10:15:1) 0.7; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.11 (5H, m), 5.45 (1H, d, J=5 Hz), 4.14 (1H, A portion of AB system), 3.20 (1H, d, J=10 Hz), 2.90 (1H, B portion of AB system), 3.00-2.70 (2H, m), 2.32-2.15 (1H, m), 2.10-1.15 (18H, m). ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 139.7, 138.4, 128.7 (2C), 128.2 (2C), 126.6, 122.4, 65.9, 64.8, 58.2, 56.4, 56.3, 53.4, 35.6, 34.4, 32.8, 31.1, 30.5, 25.9, 25.6, 25.0. Anal. Calcd. for $C_{22}H_{30}N_2$. Found: C, 81.94. H, 9.39. N, 8.71.

(±)-Aloperine (1)
1,3,4,6,6a,7,8,9,10,12,13,13a-dodecahydro-2H-6,13-methano-dipyrido[1,2-a,3',2'-e]azocine (24)
To a solution of **22** or **23** (50 mg, 0.15 mmol) in THF (600 µl) maintained at room temperature, Et_3N (1.20 ml), lithium (53 mg, 7.57 mmol) and ethylendiamine (redistilled from Na, 123 µl, 1.82 mmol) were added. After 2 h, THF (600 µl), Et_3N (1.20 ml) and ethylendiamine (123 µl) were added. After 3 h, NH_4Cl 5% (5 ml) and water (5 ml) were added and the reaction mixture was stirred for 10 min. The aqueous layer was basified with Na_2CO_3 and extracted with $CHCl_3$. After evaporation of organic layer, a yellow oil was obtained. Chromatography purification (AcOEt: MeOH: Et_3N 15 :5 :2) gave respectively **1** (28 mg, 80%) or **24** (29 mg, 83%). **1**: R_f (AcOEt: MeOH: Et_3N 15 :5 :2) 0.15; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 5.50 (1H, d, J=6.5 Hz), 3.22 (1H, d, J=5.8

Hz), 3.15-3.05 (1H, m), 2.90 (1H, dd, J=11.4, 6 Hz), 2.87-2.75 (1H, m), 2.68 (1H, td, J=12.1, 2.8 Hz), 2.65-2.45 (2H, m), 2.40-1.15 (16H, m). ^{13}C NMR (300 MHz, $CDCl_3$) δ 136.1, 126.9, 60.1, 58.1, 55.1, 47.6, 46.0, 34.9, 32.5, 31.6, 29.6, 27.1, 25.4 (2C), 20.2. Anal. Calcd. for $C_{15}H_{24}N_2$: C, 77.53; H, 10.42; N, 12.05. Found: C, 77.58. H, 10.42. N, 12.02. **24**: R_f (AcOEt: MeOH: Et_3N 15 :5 :2) 0.21; ^{1}H NMR (300 MHz, CD_3COCD_3) δ 5.45 (1H, d, J=6.6 Hz), 3.18 (1H, d, J=6 Hz), 3.15-3.04 (1H, m), 2.98-2.86 (1H, m), 2.75-2.60 (2H, m), 2.38-2.25 (1H, m), 2.20-1.10 (17H, m). ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 140.7, 121.5, 66.6, 58.4, 57.6, 56.3, 47.2, 35.6, 33.8, 33.4, 32.7, 30.8, 30.4, 26.0, 24.9. Anal. Calcd. for $C_{15}H_{24}N_2$: C, 77.53; H, 10.42; N, 12.05. Found: C, 77.57. H, 10.38. N, 12.03.