Experimental

General

Solvents and reagents were purchased from Fluka or Aldrich. Pyridine was dried over KOH and freshly distilled. Ammonium acetate was dried for several days under vacuum. Diethylether and THF were distilled from sodium/benzophenone prior to use.

NMR spectra were recorded on a 'Varian Gemini 300' (300.075 MHz) or on a 'Bruker Avance DRX400' (400.13 MHz) spectrometer, chemical shifts are given in ppm using the solvent itself as internal standard, coupling constants *J* are given in Hertz. Attribution of the ^{1}H- and ^{13}C signals was performed by ^{1}H,^{1}H-COSY, DEPT, ^{13}C-^{1}H-HECTOR, ^{1}H-^{13}C-HMQC and ^{1}H-^{13}C-HMBC techniques. The numeration of the ligands is given in Fig. 2. The diastereotopic protons at carbon 9 of the pinene-moieties are labelled as H_a for the *endo*-oriented protons and H_b for the *exo*-oriented protons. The *exo* methyl groups are assigned as 12 and 12', the *endo* oriented ones as 13 and 13', respectively. The diastereotopic protons at carbon 1'' are labelled as H_a and H_b. For the methoxy-phenyl derivatives, the proton 8', 9', 11' and 12' form a spin-coupling system AA'XX', they are just labelled as doublets with the coupling constant $^{3}J_{A,X}$. Mass spectral data were acquired a) on 'VG Instrument 7070E' equipped with a FAB inlet system, b) on Hewlett Packard 5988A quadrupol mass spectrometer with an electron ionisation (EI) source and c) on a Bruker FTMS 4.7 T BioApex II using a standard electrospray ion source (ESI). Elemental analysis was obtained from EIF (Ecole d'ingénieurs de Fribourg, Switzerland).

S,S-{5'-p-Methoxyphenyl}-[5,6]-CHIRAGEN[p-xyl] (1a)

To dry THF (40 ml) at –40 °C diisopropylamine (0.2 ml, 1.4 mmole) was added, followed by *n*-butyllithium (0.85 ml, 1.35 mmole, 1.6 M in hexane). The temperature was allowed to increase to 0 °C for 30 minutes and then lowered to –40 °C. *S,S*-{5'-*p*-methoxyphenyl}-[5,6]-pinene-bpy (**4a**) (400 mg, 1.12 mmole) dissolved in dry THF (10 ml) was added dropwise over 1 hour. After stirring the solution at –40 °C for 2 hours, *a,a'*-dibromo-*p*-xylene (148 mg, 0.56 mmole) dissolved in THF (10 ml) was injected slowly (1 hour). The solution was warmed gradually to room temperature, quenched by water (50 ml). The aqueous solution was extracted three times with diethylether. The combined organic layers were dried over magnesium sulfate, and the solvent was evaporated. The residual solid was further purified by column chromatography or recrystallisation (hexane/ethylacetate/triethylamine: 1/1/0.5), yielding a slightly yellow powder (303 mg, 64%) .

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.86 (dd, 2H, H(6'), $^{4}J_{6',4'}$ = 2.4 Hz, $^{5}J_{6',3'}$ = 0.6 Hz); 8.50 (b, 2H, H(3') $^{3}J_{3',4'}$ = 8.3 Hz, $^{5}J_{3',6'}$ = 0.6 Hz); 8.14 (d, 2H, H(3), $^{3}J_{3,4}$ = 7.8 Hz); 7.94 (dd, 2H, H(4'), $^{3}J_{4',3'}$ = 8.3 Hz, $^{4}J_{4',6'}$ = 2.4 Hz); 7.59 (d, 2H, H(9'), H(11'), $^{3}J_{9',8'}$ = 8.7 Hz); 7.35 (d, 2H, H(4), $^{3}J_{4,3}$ = 7.8 Hz); 7.28 (s, 4H, H(3''), H(4''), H(5''), H(6'')); 7.01 (d, 4H, H(8'), H(12'), $^{3}J_{8',9'}$ = 8.8 Hz); 3.86 (m, 2H, H(1_b'')); 3.85 (s, 6H, H(13')); 3.43 (ddd, 2H, H(7) $^{3}J_{7,1a''}$ = 10.8 Hz, $^{3}J_{7,1b''}$ = 2.7 Hz, $^{3}J_{7,8''}$ = 2.7 Hz); 2.82 (dd, 2H, H(10), $^{3}J_{10,9b}$ = 5.6 Hz, $^{4}J_{10,8}$ = 5.6 Hz); 2.76 (dd, 2H, H(1_a''), $^{2}J_{1a'',1b''}$ = 13.6 Hz, $^{3}J_{1a'',7}$ = 10.8 Hz); 2.59 (ddd, 2H, H(9_b), $^{2}J_{9b,9a}$ = 9.8 Hz, $^{3}J_{9b,10}$ = 5.6Hz, $^{3}J_{9b,8}$ = 5.6 Hz); 2.18 (ddd, 2H, H(8), $^{3}J_{8,9b}$ = 5.6 Hz, $^{4}J_{8,10}$ = 5.6 Hz, $^{3}J_{8,7}$ = 2.7 Hz); 1.45 (d, 2H, H(9_a), $^{2}J_{9a,9b}$ = 9.8 Hz); 1.36 (s, 6H, H(12)); 0.64 (s, 6H, H(13)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.7 (Cq); 158.8 (Cq); 155.1 (Cq); 153.1 (Cq); 147.1 (CH, C(6')); 142.2 (Cq); 138.6 (Cq); 135.4 (Cq)); 134.5 (CH, C(4')); 133.7 (CH, C(4)); 130.3 (Cq); 129.3 (CH, C(3'')); 128.1 (CH, C(9'), C(11')); 120.7 (CH, C(3')); 117.8 (CH, C(3)); 114.6 (CH, C(8'), C(12')); 55.4 (CH_3, C(13')); 46.9 (CH, C(10)); 46.2 (CH, C(7)); 42.7 (CH_2, C(8)); 41.2 (Cq, C(11)); 38.5 (CH_2, C(1'')); 28.4 (CH_2, C(9)); 26.3 (CH_3, C(12)); 20.9 (CH_3, C(13)). MS(ESI): m/z = 815 (M^+). UV/Vis: $?_{max}$ ($CHCl_3$)/ nm 317 (e/ dm^3 mol^{-1} cm^{-1} 7.1*10^4), 272 (2.6 *10^4; sh). Elemental analysis: Found: C:81.59%, H:7.10%, N: 6.63%, $C_{56}H_{54}N_4O_2$ requires C:82.52%; H:7.10%, N: 6.87%.

***S,S*-{6'-Phenyl }-[5,6]-CHIRAGEN[p-xyl] (1b)**

Analogous to the procedure for **1a**, LDA was prepared with diisopropylamine (0.41 ml, 2.9 mmole) and *n*-butyllithium (1.6 ml, 1.9 mmole, 1.2 M in hexane) in dry THF (5 ml) at –20 °C. Further *S,S*-{6'-phenyl}-[5,6]-pinene-bpy (**4b**) (500 mg, 1.53 mmole) and *a,a'*-dibromo-*p*-xylene (202 mg, 0.77 mmole) were used for the formation of **1b**. After the extraction with dichloromethane, the residual solid was further purified by column chromatography (hexane/ ethylacetate/ triethylamine: 2/1/0.1) yielding the desired product **1b** (395 mg, 68%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.48 (d, 2H, H(3'), $^3J_{3',4'}$ = 7.7 Hz); 8.39 (d, 2H, H(3), $^3J_{3,4}$ =7.7 Hz); 8.17 (dd, 4H, H (8'), H(12'), $^3J_{8',9'}$ = 7.0 Hz); 7.90 (dd, 2H, H (4'), $^3J_{4',3'}$ = 7.7 Hz, $^3J_{4',5}$= 7.8 Hz); 7.76 (d, 2H, H (5') $^3J_{5',4'}$ = 7.8 Hz); 7.52 (dd, 4H, H (9'), H(11'), $^3J_{9',10'}$ = 7.8 Hz, $^3J_{9',8'}$ = 7.0 Hz); 7.47-7.36 (m, 2H, H(10'), $^3J_{10',9'}$ = 7.8 Hz); 7.38 (s, 4H, H(3''), H(4''), H(5''), H(6'')); 3.87 (dd, 2H, H (1''b), $^2J_{1b'',1a''}$ = 13.5 Hz, $^3J_{1b'',7}$ = 3.6 Hz); 3.44 (d (broad), 2H, H(7) $^3J_{7,1a''}$ = 11.0 Hz, $^3J_{7,1b''}$ = 3.6 Hz); 2.83 (dd, 2H, H (10), $^3J_{10,9b}$ = 5.5 Hz, $^3J_{10,8}$ = 5.5 Hz); 2.75 (dd, 2H, H(1''a), $^2J_{1a'',1b''}$ = 13.5 Hz, $^3J_{1a'',7}$ = 11.0 Hz); 2.58 (ddd 2H, H(9b), $^2J_{9b,9a}$ = 9.9 Hz, $^3J_{9b,8}$ = 5.5 Hz, $^3J_{9b,10}$ = 5.5 Hz); 2.18 (m, 2H, H(8)); 1.46 (d, 2H, H(9a), $^2J_{9a,9b}$ = 9.9 Hz); 1.37 (s, 6H, H(12)); 0.70 (s, 6H, H(13)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): δ 158.8 (Cq); 156.5 (Cq); 153.6 (Cq); 142.6 (Cq); 139.8 (Cq); 138.8 (Cq); 137.7 (CH, C(4')); 134.0 (CH, C(4)); 132.4 (Cq); 129.5 (CH, C(3'')); 129.1 (CH, C(8')); 128.9 (CH, C(10')); 127.1 (CH, C(3')); 119.9 (CH, C(5')); 119.4 (CH, C(3)); 118.5 (CH, C(9')); 47.2 (CH, C10); 46.4 (CH, C7); 43.0 (CH, C8); 41.4 (Cq, C11); 38.7 (CH_2, C1''); 28.6 (CH_2, C9); 26.5 (CH_3, C12); 21.2 (CH_3, C13). FAB-MS (Matrix: NBA): m/z = 755 (M^+); 325 (M^+-$C_{24}H_{28}N_2$).

***S,S*-{6'-p-Methoxyphenyl}-[5,6]-CHIRAGEN[p-xyl] (1c)**

Analogous to the procedure for **1a**, LDA was prepared with diisopropylamine (0.6 ml, 4 mmole) and *n*-butyllithium (2.1 ml, 3.4 mmole, 1.6 M in hexane) in dry THF (20 ml) at –20 °C. Further *S,S*-{6'-*p*-methoxyphenyl}-[5,6]-pinene-bpy (**4c**) (1.0 g, 2.8 mmole) and *a,a'*-dibromo-*p*-xylene (0.37 g, 1.4 mmole) were used for the formation of **1c**. After the extraction with dichloromethane, the residual solid was further purified by filtration over silica gel (hexane/ethylacetate/triethylamine : 8/1/0.5), yielding of **1c** (1.35 g, 95%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.39 (d, 2H, H(3'), $^3J_{3',4'}$ = 7.8 Hz); 8.35 (d, 2H, H(3), $^3J_{3,4}$ = 7.8 Hz); 8.12 (d, 4H, H(8'), H(12'), $^3J_{8',9'}$ = 8.8 Hz); 7.83 (dd, 2H, H(4'), $^3J_{4',3'}$ = 7.8 Hz, $^3J_{4',5'}$ = 7.8 Hz); 7.67 (d, 2H, H(5'), $^3J_{5',4'}$ = 7.8 Hz); 7.37 (d, 2H, H(4), $^3J_{4,3}$ = 7.8 Hz); 7.29 (s, 4H, H(3''), H(4''), H(6''), H(7'')); 7.02 (d, 4H, H(9'), H(11''), $^3J_{9',8'}$ = 8.8 Hz); 3.87 (s, 6H, H(13')); 3.86 (m, 2H, H(1_b'')); 3.43 (ddd, 2H, H(7), $^3J_{7,1b''}$ = 10.8 Hz, $^3J_{7,1a''}$ = 2.7 Hz, $^3J_{7,8}$ = 2.7 Hz); 2.82 (dd, 2H, H(10), $^3J_{10,9b}$ = 5.6 Hz, $^4J_{10,8}$ = 5.6 Hz); 2.74 (dd, 2H, H(1a''), $^2J_{1a'',1b''}$ = 13.6 Hz, $^3J_{1a'',7}$ = 10.8 Hz); 2.59 (ddd, 2H, H(9_b), $^2J_{9b,9a}$ = 9.8 Hz, $^3J_{9b,10}$ = 5.6 Hz, $^3J_{9b,8}$ = 5.6 Hz); 2.18 (ddd, 2H, H(8), $^3J_{8,9b}$ = 5.6 Hz, $^4J_{8,10}$ = 5.6 Hz, $^3J_{8,7}$ = 2.7 Hz); 1.45 (d, 2H, H(9a) $^2J_{9a,9b}$ = 9.8 Hz); 1.37 (s, 6H, H(12)); 0.65 (s, 6H, H(13)). ^{13}C-NMR (75MHz, $CDCl_3$): δ 160.4 (Cq); 158.6 (Cq); 156.2 (Cq); 155.9 (Cq); 153.6 (Cq); 142.2 (Cq); 138.6 (Cq); 137.4 (CH, C(4')); 133.6 (CH, C(4)); 132.3 (Cq); 129.2 (CH, C(3'), C(4'), C(6'), C(7')); 128.2 (CH, C(8'), C(12')); 118.9 (CH, C(5')); 118.4 (CH, C(3')); 118.1 (CH, C(3)); 114.0 (CH, C(9'), C(11')); 55.4 (CH_3, C(13')); 47.0 (CH, C(10)); 46.2 (CH, C(7)); 42.7 (CH, C(8)); 41.2 (Cq, C(11)); 38.5 (CH_2, C(1'')); 28.4 (CH_2, C(9)); 26.3 (CH_3, C(12)); 20.9 (CH_3, C(13)). MS-FAB (Matrix: NBA): m/z = 816 (MH^+, 82%); 355 (M^+/2-bridge, 100%); 341 (M^+/2-bridge- CH_2, 95%); 154 ($C_{11}H_8N^+$, 23%). UV/Vis: ?$_{max}$ ($CHCl_3$)/ nm 279 (e/ dm^3 mol^{-1} cm^{-1} 5.2*10^4). Elemental analysis: Found: C: 82.40%, H: 6.76%, N: 6.2%, $C_{56}H_{54}N_4O_2$ requires C: 82.52%, H: 6.68%, N: 6.87%.

***S,S*-{5'-p-Methoxyphenyl}-[5,6]-CHIRAGEN[0] (2a)**

Similar to the procedure for **1a**, LDA was prepared with diisopropylamine (0.2 ml, 1.4 mmole) and *n*-butyllithium (0.85 ml, 1.35 mmole, 1.6 M in hexane) in dry THF (40 ml) at –20 °C. Further *S,S*-{5'-*p*-methoxyphenyl}-[5,6]-pinene-bpy (**4a**) (400 mg, 1.12 mmole) and iodine (148 mg, 0.56 mmole) were used for the formation of **2a**. After the extraction with dichloromethane, the residual solid was further purified by column chromatography (hexane/ ethylacetate/ triethylamine: 1/1/0.5) and recrystallisation yielding the desired product (63 mg, 16%) .

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.81 (br, 2H, H(6')); 8.37 (br, 2H, H(3')); 8.14 (d, 2H, H(3), $^3J_{3,4}$ = 7.7 Hz); 7.89 (dd, 2H, H(4'), $^3J_{4',3'}$ = 8.3 Hz, $^4J_{4',6'}$ = 2.2 Hz); 7.55 (d, 4H, H(9'), H(11'), $^3J_{9',8'}$ = 8.7 Hz); 7.37 (d, 2H, H(4), $^3J_{4,3}$ = 7.7 Hz); 6.99 (d, 4H, H(8'), H(12'), $^3J_{8',9'}$ = 8.7 Hz); 4.60 (br, 2H, H(7)); 3.84 (s, 6H, H(13')); 2.81 (dd, 2H, H(10), $^3J_{10,9b}$ = 5.5 Hz, $^4J_{10,8}$ = 5.5 Hz); 2.51 (m, 2H, H(9_b)); 2.16 (dd, 2H, H(8) $^3J_{8,9b}$ = 5.5 Hz, $^4J_{8,10}$ = 5.5 Hz); 1.43 (d, 2H, H(9_a)); 1.34 (s, 6H, H(12)); 0.79 (s, 6H, H(13)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.7 (Cq); 158.3 (Cq); 155.1 (Cq); 152.6 (Cq); 146.8 (CH, C(6')); 143.0 (Cq); 135.4 (Cq); 134.6 (CH, C(4')); 133.6 (CH, C(4)); 130.2 (Cq); 128.0 (CH, C(9'), C(11')); 120.7 (CH, C(3')); 117.6 (CH, C(3)); 114.5 (CH, C(8'), C(12')); 55.4 (CH_3, C(13')); 46.5 (CH, C(7)); 46.2 (CH, C(10)); 42.70 (Cq, C(11)); 41.9 (CH, C(8)); 29.0 (CH_2, C(9)); 26.3 (CH_3, C(12)); 21.0 (CH_3, C(13)). MS(ESI): m/z = 711 (M^+). UV/Vis: ?$_{max}$ ($CHCl_3$)/ nm 319 (e/ dm^3 mol^{-1} cm^{-1} 7.1*10^4), 274 (2.5 *10^4; sh). CD: ?$_{max}$ ($CHCl_3$)/ nm 332 (?e/ dm^3 mol^{-1} cm^{-1} -87), 300 (61). Elemental analysis: Found C: 79.93%, H: 6.72%, N: 7.70%, $C_{48}H_{46}N_4O_2$ requires C: 81.10%, H: 6.52%, N: 7.88%.

***S,S*-{6'-Phenyl }- [5,6]-CHIRAGEN[0] (2b)**

Similar to the procedure for **1a**, LDA was prepared with diisopropylamine (0.33 ml, 2.3 mmole) and *n*-butyllithium (1.9 ml, 2.1 mmole, 1.1 M in hexane) in dry THF (5 ml) at –20 °C. Further *S,S*-{6'-phenyl}-[5,6]-pinene-bpy (**4b**) (494 mg, 1.5 mmole) and iodine (192 mg, 0.76 mmole) were used for the formation of **2b**. After the extraction with dichloromethane, the residual solid was further purified by recrystallisation (methanol/ dichloromethane) yielding the pure compound **2b** (345 mg, 70 %) .

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.32 (d, 2H, H(3) $^3J_{3,4}$ = 7.8 Hz); 8.31 (br, 2H, H(3')); 8.14 (d, 4H, H(8'), H(12') , $^3J_{8',9'}$ = 7.3 Hz); 7.80 (dd, 2H, H(4'), $^3J_{4',3'}$ =7.8 Hz, $^3J_{4',5'}$ = 7.8 Hz); 7.69 (d, 2H, H(5'), $^3J_{5',4'}$ = 7.8 Hz); 7.49 (dd, 4H, H(9'), H(11'), $^3J_{9',8'}$ = 7.3 Hz, $^3J_{9',10'}$ =7.3 Hz); 7.41 (dd, 2H, H(10')); $^3J_{10',9'}$ =7.3 Hz); 7.38 (d, 2H, H(4) $^3J_{4,3}$ = 7.8 Hz); 4.65 (m, 2H, H(7)); 2.81 (dd, 2H, H(10), $^3J_{10,9b}$ = 5.6 Hz, $^4J_{10,8}$ = 5.6 Hz); 2.50 (ddd, 2H, H(9_b), $^2J_{9b,9a}$ = 9.8 Hz, $^3J_{9b,10}$ = 5.6Hz, $^3J_{9b,8}$ = 5.6 Hz)); 2.16 (dd, 2H, H(8), $^3J_{8,9b}$ = 5.6 Hz, $^4J_{8,10}$ = 5.6 Hz); 1.38 (b, 2H, H-C(9a)); 1.31 (s, 6H, H-C(12)); 0.79 (s, 6H, H(13)). ^{13}C-NMR (75 MHz, $CDCl_3$): δ 158.2 (Cq); 156.7 (Cq); 156.7.2 (Cq); 153.3 (Cq); 143.1 (Cq); 139.6 (Cq); 137.4 (CH, C(4')); 133.4 (CH, C(4)); 128.9 (CH, C(10')); 128.6 (CH, C(9'), C(11')); 126.9 (CH, C(8'), C(12')); 119.5 (CH, C(5')); 119.1 (CH, C(3')); 117.9 (CH, C(3)); 46.3 (CH, C(7)); 46.2 (CH, C(10)); 42.6 (CH, C(8)); 41.9 (Cq, C(11)); 29.1 (CH_2, C(9)); 26.3 (CH_3, C(12)); 21.0 (CH_3, C(13)). FAB-MS (matrix: NBA): m/z = 651.6 (M^+); 575.3 (M-$C_6H_5^+$); 557.7 (M-$C_{12}H_{10}^+$); 326.4 ($C_{23}H_{21}N_2$, M/2$^+$); 283.3 (M/2-$C_3H_7^+$); 218.2 ($C_{14}H_{14}N_2^+$); 154.1 ($C_{10}H_6N_2^+$). Elemental analysis: Found C 83.33%, H 6.55%, N 8.43%, $C_{46}H_{42}N_4$ requires C 84.89%, H 6.50%, N 8.61%.

***S,S*-{6'-p-Methoxyphenyl}-[5,6]-CHIRAGEN[0] (2c)**

Similar to the procedure for **1a**, LDA was prepared with diisopropylamine (0.6 ml, 4 mmole) and *n*-butyllithium (2.1 ml, 3.4 mmole, 1.6 M in hexane) in dry THF (20 ml) at –20 °C. Further *S,S*-{6'-*p*-methoxyphenyl}-[5,6]-pinene-bpy (**4c**) (1.0 g, 2.8 mmole) and iodine (0.37 g, 1.4 mmole) were used for the formation of **2c**. After the extraction with dichloromethane, the residual solid was further purified by recrystallisation (methanol/chloroform), yielding white crystals (0.53 g, 53%)

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.31 (d, 2H, H(3), $^3J_{3,4}$ = 7.8 Hz); 8.25 (b, 2H, H(3')); 8.11 (d, 4H, H(8'), H(12'), $^3J_{8',9'}$ = 8.8 Hz); 7.76 (dd, 2H, H(4'), $^3J_{4',3'}$ = 7.8 Hz, $^3J_{4',5'}$ = 7.8 Hz); 7.62 (d, 2H, H(5'), $^3J_{5',4'}$ = 7.8 Hz); 7.37 (d, 2H, H(4), $^3J_{4,3}$ = 7.8 Hz); 7.01 (d, 4H, H(9'), H(11'), $^3J_{9',8'}$ = 8.8 Hz); 4.65 (b, 2H, H(7)); 3.87 (s, 6H, H(13'); 2.80 (dd, 2H, H(10), $^3J_{10,9b}$ = 5.6 Hz, $^4J_{10,8}$ = 5.6 Hz); 2.50 (ddd, 2H, H(9_b), $^2J_{9b,9a}$ = *9.8 Hz*, $^3J_{9b,10}$ = 5.6 Hz, $^3J_{9b,8}$ = 5.6 Hz); 2.16 (dd, 2H, H(8), $^3J_{8,10}$ = 5.6 Hz, $^3J_{8,9b}$ = 5.6 Hz), 1.38 (b, 2H, H(9_a)); 1.31 (s, 6H, H(12)); 0.79 (s, 6H, H(13)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 160.4 (Cq); 158.2 (Cq); 156.5 (Cq); 155.8 (Cq); 153.3 (Cq); 143.0 (Cq); 137.4 (CH, C(4')); 133.4 (CH, C(4)); 132.3 (Cq); 128.2 (CH, C(8'), C(12')); 118.8 (CH, C(5'); 118.4 (CH, C(3')); 117.8 (CH, C(3)); 114.0 (CH, C(9'), C(11')); 55.4 (CH_3, C(13'); 46.3 (CH, C(7)); 46.2 (CH, C(10)); 42.6 (CH, C(8)); 41.8 (Cq, C(11)); 29.1 (CH_2, C(9)); 26.3 (CH_3, C(12)); 21.0 (CH_3,C(13)). MS-FAB (Matrix: NBA): m/z = 712 (M^+, 58%); 341 (M^+/2-Me, 26%); 307 (52%); 154 ($C_{11}H_8N^+$, 100%), 136 (93%). UV/Vis:

$?_{max}$ ($CHCl_3$)/ nm 280 (e/ dm^3 mol^{-1} cm^{-1} 5.3*10^4). CD: $?_{max}$ ($CHCl_3$)/ nm 310 (? e/ dm^3 mol^{-1} cm^{-1} -22), 287 (+32), 266 (-21.5). Elemental analysis: Found C: 80.37%, H: 6.41%, N: 7.37%, $C_{48}H_{46}N_4O_2$ requires C: 81.10%, H: 6.52%, N: 7.88%.

***S,S*-{2-*N,N*-Dimethylamino-isopropyl}-[5,6]-CHIRAGEN[0] (3)**

Similar to the procedure for **1a**, LDA was prepared with diisopropylamine (1.6 ml, 11.3 mmole) and *n*-butyllithium (5.8 ml, 9.3 mmole, 1.6 M in hexane) in dry THF (20 ml) at –20 °C. Further *S,S*-{2-DAMI}-[5,6]-pinene-py (**5**) (0.8 g, 3.1 mmole) and iodine (0.5 g, 0.2 mmole) were used for the formation of **3**. After the extraction with dichloromethane, the residual solid was further purified by recrystallisation (methanol/chloroform), yielding white crystals (0.16 g, 20%).

^{1}H-NMR (400 MHz, $CDCl_3$/CD_3CN): d 7.08 (d, 2H, H(3), $^3J_{3,4}$ = 7.8 Hz), 7.03 (d, 2H, H(4), $^3J_{4,3}$ = 7.8 Hz), 4.30 (s, br, 2H, H(7)), 2.56 (dd, 2H, H(10), $^3J_{10,9b}$ = 5.6 Hz, $^4J_{10,8}$ = 5.6 Hz), 2.27 (ddd, 2H, H(9b), $^2J_{9b,9a}$ = 9.4 Hz, $^3J_{9b,10}$ = 5.6 Hz, $^3J_{9b,8}$ = 5.6 Hz), 2.07 (s, 12H, H(6'), H(5')), 1.92-1.76 (m, 2H, H(8)), 1.31 (s, 6H, H(3')), 1.27 (s, 6H, H(4')), 1.14 (s, 6H, H(12)), 1.08 (s, br, 2H, H(9a)), 0.58 (s, 6H, H(13)). ^{13}C-NMR ($CDCl_3$/CD_3CN, 400 MHz): δ 163.54 (Cq, C(6)), 157.15 (Cq, C(2)), 140.28 (Cq, C(5)), 132.64 (CH, C(4)), 117.51 (CH, C(3)), 62.00 (Cq, C(2')), 46.11 (CH, C(10)), 41.52 (Cq, C(11)), 39.65 (CH_3, C(5'), C(6')), 26.54 (CH_3, C(12)), 24.72 (CH_3, C(3')), 22.71 (CH_3, C(4')), 31.30 (CH_3, C(13)). MS(ESI): m/z = 515.5 (HM^+). UV/Vis: $?_{max}$ ($CHCl_3$)/ nm 276 (e/ dm^3 mol^{-1} cm^{-1} 1.1*10^4). CD: $?_{max}$ ($CHCl_3$)/ nm 269 (?e/ dm^3 mol^{-1} cm^{-1} 13.7). Elemental analysis: Found C: 79.7%, H: 9.86%, N: 10.74%, $C_{34}H_{50}N_4$ requires: C: 79.33%, H: 9.79%, N: 10.88%.

***S,S*-{5'-p-Methoxyphenyl}-[5,6]-pinene-bpy (4a)**

A mixture of 1-(2-acetyl-5-(*p*-methoxyphenyl)-pyridyl)-pyridinium iodide (**18a**) (3.8 g, 8.79 mmole), ammonium acetate (6.93 g, dried under vacuum) and *R,R*-(+)-pinocarvone (1.35 g, 9.0 mmole) was suspended in acetic acid (5 ml) and slowly heated over 42 hours from 50 °C up to 115 °C. After addition of water, the pH was adjusted to 9 by addition of sodium carbonate. This aqueous solution was extracted ten times with hexane and the combined organic layers were washed with water and dried over magnesium sulfate with activated charcoal. The solvent was evaporated under reduced pressure. The residual solid was further purified by column chromatography (hexane/ ethylacetate/ triethylamine: 8/1/0.1) yielding a slightly yellow product **4a** (936mg, 30%) .

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.84 (d, 1H, H(6'), $^4J_{6',4'}$ = 2.0 Hz); 8.35 (d, 1H, H(3'), $^3J_{3',4'}$ = 8.3 Hz); 8.04 (d, 1H, H(3), $^3J_{3,4}$ = 7.8 Hz); 7.91 (dd, 1H, H(4'), $^3J_{4',3'}$ = 8.3 Hz, $^4J_{4',6'}$ = 2.0 Hz) ; 7.56 (d, 2H, H(9'), H(11'), $^3J_{9',8'}$ = 8.8 Hz); 7.30 (d, 1H, H(4), $^3J_{4,3}$ = 7.8 Hz); 6.99 (dd, 2H, H(8'), H(12'), $^3J_{8',9'}$ = 8.8 Hz); 3.84 (s, 3H, H(13')); 3.18 (d, 1H, H(7), $^3J_{7,8}$ = 2.8 Hz); 2.82 (dd, 1H, H(10), $^3J_{10,9b}$ = 5.7 Hz, $^4J_{10,8}$ = 5.7 Hz); 2.69 (ddd, 1H, H(9_b), $^2J_{9b,9a}$ = 9.6 Hz, $^3J_{9b,10}$ = 5.7 Hz, $^3J_{9b,8}$ = 5.7 Hz); 2.38 (ddt, 1H, H(8) $^3J_{8,9b}$ = 5.7 Hz, $^4J_{8,10}$ = 5.7 Hz, $^3J_{8,7}$ = 2.8 Hz)); 1.40 (s, 3H, H(12)); 1.30 (d, 1H, H(9_a), $^2J_{9a,9b}$ = 9.6 Hz); 0.66 (s, 3H, H(13)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 160.2 (Cq); 157.0 (Cq); 155.4 (Cq); 153.8 (Cq); 147.6 (CH, C(6')); 142.6 (Cq); 135.8 (Cq); 135.0 (CH, C(4')); 134.2 (CH, C(4)); 130.7 (Cq); 128.5 (CH, C(9'), C(11')); 121.1 (CH, C(3')); 118.2 (CH, C(3)); 115.0 (CH, C(8'), C(12')); 55.8 (CH_3, C(13')); 47.0 (CH, C(10)); 40.7 (CH, C(8)); 40.0 (Cq, C(11)); 37.2 (CH_2, C(7)); 32.4 (CH_2, C(9)); 26.5 (CH_3, C(12)); 21.7 (CH_3, C(13)). MS(EI): m/z = 356 (M^+, 54%), 341 (M^+-CH_3, 12%), 313 (M^+-$COCH_3$; 100%), 298 (M^+-C_3H_6O,18%). UV/Vis: $?_{max}$ ($CHCl_3$)/ nm 317 (e/ dm^3 mol^{-1} cm^{-1} 3.3*10^4), 273 (1.3 *10^4; sh). Elemental analysis: Found C: 80.41%, H: 6.68%, N: 7.75%, $C_{24}H_{24}N_2O$ requires C: 80.87%, H 6.79 %, N: 7.86 %.

***S,S*-{6'-Phenyl}-[5,6]-pinene-bpy (4b)**

Analogous to the procedure for **4a** and the literature,[9b] a mixture of 1-(2-acetyl-6-phenylpyridyl)-pyridinium iodide (**18b**) (1.02 g, 2.5 mmole), ammonium acetate (1.7 g, dried under vacuum) and *R,R*-(+)-pinocarvone (0.38 g, 2.5 mmole) in acetic acid (5 ml) was used for the formation of **4b**. After a similar work-up, the residual solid was further purified by recrystallisation yielding a yellow powder (586 mg 71%). The spectral properties of **4b** correspond to those reported by literature.[9b]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.37 (d, 1H, H(3'), $^3J_{3',4'}$ = 8.0 Hz); 8.31 (d, 1H, H(3), $^3J_{3,4}$ = 8.0 Hz); 8.13 (dd, 2H, H(8'), H(12'), $^3J_{8',9'}$ = 8.0 Hz, $^4J_{8',10'}$ = 2.1 Hz,); 7.85 (dd, 2H, H(4'), ^3J = 7.4 Hz,); 7.72 (dd, 1H, H(5'), $^3J_{5',4'}$ = 7.8 Hz, ^4J = 0.8 Hz); 7.48 (dd, 2H, H(9'),H(11'), ^3J = 7.4 Hz); 7.42 (dd, 1H, H(10'), ^3J = 7.9 Hz,); 7.37 (d, 1H, H(4), ^3J = 8.0 Hz); 3.22 (m, 2H, H(7)); 2.83 (dd, 1H, H(10), ^3J = 5.6 Hz); 2.71 (ddd, 1H, H(9_b)); 2.40 (ddt, 1H, H(8), ^3J = 3.2 Hz); 1.42 (s, 3H, H(12)); 1.32 (d, 1H, H(9_a), $^3J_{9a,9b}$ = 9.5Hz); 0.68 (s, 3H, H(13)).

_S,S_-{6'-_p_-Methoxyphenyl}-[5,6]-pinene-bpy (4c)

A mixture of {6'-bromo}-[5,6]-pinene-bpy (**4d**) (3.3 g, 10 mmole), *p*-methoxyphenyl-boronic acid (1.65 g, 10 mmole) and $Pd(PPh_3)_4$ (0.2% eq) as catalyst, was heated at 120 °C for 4 days in a mixture of toluene (100 ml) and an aqueous solution of K_2CO_3 (50 ml, 8.5 M). After cooling to room temperature the two layers were separated and the aqueous layer extracted three times with dichloromethane. The combined organic layers were washed until pH=7 with water, dried over magnesium sulfate and the solvent was evaporated. Without further purification pure **4c** (3.59 g, 99%) was obtained.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.29 (d, 1H, H(3), $^3J_{3,4}$ = 7.8 Hz); 8.28 (d, 1H, H(3'), $^3J_{3',4'}$ = 7.8 Hz,) 8.10 (d, 2H, H(8'), H(12'), $^3J_{8',9'}$ = 8.8 Hz); 7.81 (dd, 1H, H(4'), $^3J_{4',5'}$ = 7.8 Hz, $^3J_{4',3'}$ = 7.8 Hz); 7.42 (d, 1H, H(5'), $^3J_{5',4'}$ = 7.8 Hz); 7.35 (d, 1H, H(4), $^3J_{4,3}$ = 7.8 Hz); 7.01 (d, 2H, H(9'), H(11'), $^3J_{9',11'}$ = 8.8 Hz); 3.87 (s, 3H, H(13')); 3.19 (d, 1H, H(7), $^3J_{7,8}$ = 2.8 Hz); 2.82 (dd, 1H, H(10), $^3J_{10,9b}$ = 5.8 Hz, $^4J_{10,8}$ = 5.8 Hz); 2.71 (ddd, 1H, H(9_b), $^2J_{9b,9a}$ = 9.6 Hz, $^3J_{9b,10}$ = 5.8 Hz, $^3J_{9b,8}$ = 5.8 Hz); 2.40 (ddt, 1H, H(8) $^3J_{8,9b}$ = 5.8 Hz, $^4J_{8,10}$ = 5.8 Hz, $^3J_{8,7}$ = 2.8 Hz); 1.42 (s, 3H, H(12)); 1.32 (d, 1H, H(9_a), $^2J_{9a,9b}$ = 9.6 Hz); 0.69 (s, 3H, H(13)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 160.4 (Cq); 156.2 (Cq); 156.1 (Cq); 155.9 (Cq); 153.8 (Cq); 142.2 (Cq); 137.4 (CH, C(4')); 133.7 (CH, C(4)); 132.2 (Cq); 128.2 (CH, C(8'), C(12')); 118.9 (CH, C(5')); 118.3 (CH, C(3)); 118.0 (CH, C(3')); 114.0 (CH, C(9'), C(11')); 55.3 (CH_3, C(13')); 46.5 (CH, C(10)); 40.3 (CH, C(8)); 39.5 (Cq, C(11)); 36.7 (CH_2, C(7)); 31.9 (CH_2, C(9)); 26.1 (CH_3, C(12)); 21.3 (CH_3, C(13)). MS-FAB (Matrix: NBA) : m/z = 357 (M^+, 100%); 154 ($C_{11}H_8N^+$, 10%), 136 (6%). UV/Vis: ?$_{max}$ ($CHCl_3$)/ nm 281 (e/ dm^3 mol^{-1} cm^{-1} 2.8*10^4). Elemental analysis: Found C: 81.22%, H: 6.80%, N: 7.45%, $C_{24}H_{24}N_2O$ requires C: 80.87%, H: 6.79%, N : 7.86%.

_S,S_-{6'-Bromo}-[5,6]-pinene-bpy (4d)

Analogous to the procedure for **4a**, a mixture of 1-(2-acetyl-6-bromopyridyl)-pyridinium iodide (**18d**) (27.75 g, 47 mmole), ammonium acetate (31.3 g, dried under vacuum) and *R,R*-(+)-pinocarvone (7.0 g, 47 mmole) in acetic acid (40 ml) was used for the formation of **4d**. After a similar work-up, the residual solid was further purified by filtration (chloroform) yielding a white powder of **4d** (7.69 g, 50%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.34 (d, 1H, H(3'), $^3J_{3',4'}$ = 7.8 Hz); 8.07 (d, 1H, H(3), $^3J_{3,4}$ = 7.8 Hz); 7.61 (dd, 1H, H(4'), $^3J_{4',3'}$ = 7.8 Hz, $^3J_{4',5'}$ = 7.8 Hz); 7.42 (d, 1H, H(5'), $^3J_{5',4'}$ = 7.8 Hz); 7.31; (d, 1H, H(4), $^3J_{4,3}$ = 7.8 Hz); 3.16 (d, 1H, H(7), $^3J_{7,8}$ = 2.8 Hz); 2.81 (dd, 1H, H(10), $^3J_{10,9b}$ = 5.7 Hz, $^4J_{10,8}$ = 5.7 Hz); 2.69 (ddd, 1H, H(9_b), $^2J_{9b,9a}$ = 9.6 Hz, $^3J_{9b,8}$ = 5.7 Hz, $^3J_{9b,10}$ = 5.7 Hz); 2.38 (ddt, 1H, H(8), $^3J_{8,9b}$ = 5.7 Hz, $^4J_{8,10}$ = 5.7 Hz, $^3J_{8,7}$ = 2.8 Hz); 1.40 (s, 3H, H(12)); 1.28 (d, 1H, H(9_a), $^2J_{9a,9b}$ = 9.6 Hz); 0.65 (s, 3H, H(13)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 158.0 (Cq); 156.6 (Cq); 151.8 (Cq); 143.0 (Cq); 141.5 (Cq); 139.0 (CH, C(4')); 133.8 (CH, C(4)); 127.2 (CH, C(5')); 120.7 (CH, C(6)); 119.4 (CH, C(3')); 118.4 (CH, C(3)); 46.5 (CH, C(10)); 40.2 (CH, C(8)); 39.5 (Cq, C(11)); 36.6 (CH_2, C(7)); 31.9 (CH_2, C(9)); 26.0 (CH_3, C(12)); 21.3 (CH_3, C(13)). MS-FAB (Matrix: NBA) : m/z = 331,329 (M^+, 100%) ; 285,287 (M^+-i-Pr, 40%), 154 ($C_{11}H_8N^+$, 50%), 136 (30%). UV/Vis: ?$_{max}$ ($CHCl_3$)/ nm 303 (e/ dm^3 mol^{-1} cm^{-1} 2.0*10^4), 252 (0.9*10^4). Elemental analysis: Found C: 61.57%, H: 5.22%, N: 7.91%, $C_{17}H_{17}BrN_2$ requires C: 62.02%, H: 5.20%, N: 8.51%.

_S,S_-{2-_N,N_-Dimethylamino-isopropyl}-[5,6]-pinene-py (5)

Analogous to the procedure for **4a**, a mixture of 1-(3-dimethylamino-3-methyl-2-oxo-butyl)-pyridinium iodide (**19**) (8.6 g, 25 mmole), ammonium acetate (23.1 g, dried under vacuum) and *R,R*-(+)-pinocarvone (4.5 g, 47 mmole) in acetic acid (100 ml)

was used for the formation of **5**. After a similar work-up, a viscous liquid (1.6 g, 29 %) was obtained after purification by column chromatography: (hexane/ ethylacetate/ triethylamine: 5/1/0.1).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.2 (d, 1H, H(3), $^3J_{3,4}$ = 7.8 Hz); 7.09 (d, 1H, H(4), $^3J_{4,3}$ = 7.8 Hz); 3.06 (d, 1H, H(7), $^3J_{7,8}$ = 2.7 Hz); 2.69 (dd, 1H, H(10), $^3J_{10,9b}$ = 5.7 Hz, $^4J_{10,8}$ = 5.7 Hz); 2.62 (ddd, 1H, H(9_b), $^2J_{9b,9a}$ = 9.2 Hz, $^3J_{9b,10}$ = 5.7 Hz, $^3J_{9b,8}$ = 5.7 Hz); 2.38 (ddt, 1H, H(8) $^3J_{8,9b}$ = 5.7 Hz, $^4J_{8,10}$ = 5.7 Hz, $^3J_{8,7}$ = 2.8 Hz); 2.18 (s, 6H, H(5'), H(6')); 1.38 (s, 6H, H(2'), H(3')); 1.37 (s, 3H, H(12)); 1.25 (d, 1H, H(9_a), $^2J_{9a,9b}$ = 9.2 Hz); 0.61 (s, 3H, H(13)). MS(ESI): m/z = 259.2(HM^+). Elemental analysis: Found C: 79.52%, H: 10.1%, N: 11.91%, $C_{17}H_{26}N_2$ requires C: 79.02%, H: 10.14%, N: 10.84%.

_S,S_-{5'-_p_-Methoxyphenyl}-[4,5]-pinene-bpy (6a)

A mixture of 1-(2-acetyl-5-(*p*-methoxyphenyl)-pyridyl)-pyridinium iodide (**18a**) (223 mg, 0.52 mmole), ammonium acetate (560 mg, dried under vacuum) and *R,R*-(-)-myrtenal (90mg, 0.6 mmole) was suspended in formamide (20 ml) and stirred at room temperature for 5 days, then it was slowly heated over 24 hours from 50 °C up to 100 °C. To the reaction mixture 50 ml of water was added and extracted five times with hexane and the combined organic layers were washed with water and dried over magnesium sulfate with activated charcoal. The solvent was evaporated under reduced pressure. The residual solid was further purified by column chromatography (hexane/ ethylacetate/ triethylamine: 4/1/0.25), yielding the desired product (85 mg, 24 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.84 (d, 1H, H(6'), $^4J_{6',4'}$ = 2.0 Hz); 8.35 (d, 1H, H(3'), $^3J_{3',4'}$ = 8.3 Hz); 8.20 (s, 2H, H(3), H(6)); 7.93 (dd, 1H, H(4'), $^3J_{4',3'}$ = 8.3 Hz, $^4J_{4',6'}$ = 2.0 Hz); 7.57 (d, 2H, H(9'), H(11'), $^3J_{9',8'}$ = 8.8 Hz); 7.00 (d, 2H, H(8'), H(12'), $^3J_{8',9'}$ = 8.8 Hz); 3.85 (s, 3H, H(13')); 3.05 (d, 1H, H(7), $^3J_{7,8}$ = 2.7 Hz); 2.86 (dd, 1H, H(10), $^3J_{10,9b}$ = 5.7 Hz, $^4J_{10,8}$ = 5.7 Hz); 2.70 (ddd, 1H, H(9_b), $^2J_{9b,9a}$ = 9.6 Hz, $^3J_{9b,10}$ = 5.7 Hz, $^3J_{9b,8}$ = 5.7 Hz); 2.30 (ddt, 1H, H(8) $^3J_{8,9b}$ = 5.7 Hz, $^4J_{8,10}$ = 5.7 Hz, $^3J_{8,7}$ = 2.7 Hz)); 1.41 (s, 3H, H(12)); 1.23 (d, 1H, H(9_a), $^2J_{9a,9b}$ = 9.6 Hz); 0.65 (s, 3H, H(13)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.8 (Cq); 154.8 (Cq); 154.2 (Cq); 147.0 (CH, C(6')); 145.6 (CH, C(6)); 145.5 (Cq); 142.9 (Cq); 135.6 (Cq); 134.6 (CH, C(4')); 130.1 (Cq); 128.1 (CH, C(9'), C(11')); 120.7 (CH, C(3')); 120.4 (CH, C(3)); 114.6 (CH, C(8'), C(12')); 55.4 (CH_3, C(13')); 44.5 (CH, C(10)); 40.1 (CH, C(8)); 39.3 (Cq, C(11)); 32.9 (CH_2, C(7)); 31.8 (CH_2, C(9)); 26.0 (CH_3, C(12)); 21.4 (CH_3, C(13)). MS(ESI): m/z = 357 (M^+). UV/Vis: ?$_{max}$ ($CHCl_3$)/ nm 314 (e/ dm^3 mol^{-1} cm^{-1} 2.9*10^4), 274 (1.2 *10^4; sh). Elemental analysis: Found C: 79.82%, H: 6.59%, N: 7.73%, $C_{24}H_{24}N_2O$ requires C: 80.87%, H: 6.79%, N: 7.86%.

_S,S_-{6'-Phenyl}-[4,5]-pinene-bpy (6b)

Analogous to the procedure for **6a**, a mixture of (2-acetyl-6-phenylpyridyl)-pyridinium iodide (**18b**) (0.80 g, 2.0 mmole), ammonium acetate (0.8 g, dried under vacuum) and *R,R*-(-)-myrtenal (**2**) (0.30 g, 2.0 mmole) in formamide (10 ml) was used for the formation of **6b**. After a similar work-up, the residual solid was further purified by column chromatography: (hexane/ ethylacetate/ triethylamine: 4/1/0.25) yielding the desired product **6b** (0.19 g, 52 %).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.41 (s, 1H, H(3)); 8.33 (d, 1H, H(3'), $^3J_{3',4'}$ = 7.8 Hz); 8.21 (s, 1H, H(6)); 8.14 (dd, 2H, H(8'), H(12'), $^3J_{8',9'}$ = 8.2 Hz); 7.85 (dd, 2H, H(4'), $^3J_{4',5'}$ = 7.8 Hz. $^3J_{4',3'}$ = 7.8 Hz); 7.72 (d, 1H, H(5'), $^3J_{5',4'}$ = 7.8 Hz); 7.50 (dd, 2H, H(9'), H(11'), $^3J_{9',8'}$ = 8.2 Hz, $^3J_{9',10}$ = 8.2 Hz); 7.42 (dd, 1H, H(10'), $^3J_{10',9'}$ = 8.2 Hz); 3.09 (d, 1H, H(7), $^3J_{7,8}$ = 2.8 Hz); 2.87 (dd, 1H, H(10), $^3J_{10,9b}$ = 5.6 Hz, $^4J_{10,8}$ = 5.6 Hz); 2.70 (ddd, 1H, H(9_b), $^2J_{9b,9a}$ = 9.6 Hz, $^3J_{9b,8}$ = 5.6 Hz, $^3J_{9b,10}$ = 5.6 Hz); 2.33 (ddt, 1H, H(8), $^3J_{8,9b}$ = 5.5 Hz, $^4J_{8,10}$ = 5.6 Hz, $^3J_{8,7}$ = 2.8 Hz); 1.42 (s, 3H, H(12)); 1.25 (d, 1H, H(9_a), $^3J_{9a\text{-}9b}$ = 9.6 Hz); 0.66 (s, 3H, H(13)). ^{13}C-NMR (100MHz, $CDCl_3$): δ 156.4 (Cq); 156.1 (Cq); 154.5 (Cq); 145.5 (Cq); 145.3 (CH, C(6)); 143.1 (Cq); 139.5 (Cq); 137.6 (CH, C(4')); 128.9 (CH, C(10')); 128.7 (CH, C(9'), C(11')); 127.0 (CH, C(8'), C(12')); 120.7 (CH, C(3)); 119.9 (CH, C(5')); 119.1 (CH, C(3')); 44.6 (CH, C(10)); 40.1 (CH, C(8)); 39.3 (Cq, C(11)); 33.1 (CH_2, C(7)); 31.8 (CH_2, C(9)); 26.0 (CH_3, C(12)); 21.4 (CH_3, C(13)). MS(ESI): m/z = 327 (M^+). V/Vis: (?$_{max}$ ($CHCl_3$)/ nm 300 (e/ dm^3 mol^{-1} cm^{-1} 1.7*10^4), 253 (2.4*10^4). Elemental analysis: Found C: 84.47%, H: 7.05%, N: 8.48%,$C_{23}H_{22}N_2$ requires C: 84.63% H: 6.79% N: 8.58%.

_S,S_-{6'-Bromo}-[4,5]-pinene-bpy (6d)

Analogous to the procedure for **6a**, a mixture of 1-(2-acetyl-6-bromopyridyl)-pyridinium iodide (**18d**) (3.0 g, 7.4 mmole), ammonium acetate (6.0g, dried under vacuum) and *R,R*-(-)-myrtenal (1.1 g, 7.5 mmole) in formamide (100 ml) was used for the formation of **6d**. After a similar work-up, the residual solid was further purified by column chromatography (hexane/ ethylacetate/ triethylamine: 5/1/0.1) as a white powder (706 mg, 29 %).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.30 (dd, 1H, H(3'), $^3J_{3',4'}$ = 7.8 Hz, $^3J_{3',5'}$ = 0.8 Hz); 8.19 (s, 2H, H(3), H(6)); 7.61 (dd, 1H, H(4'), $^3J_{4',3'}$ = 7.8 Hz, $^3J_{4',5'}$ = 7.8 Hz); 7.42 (d, 1H, H(5'), $^3J_{5',4'}$ = 7.8 Hz, $^3J_{5',3'}$ = 0.8 Hz); 3.01 (d, 1H, H(7), $^3J_{7,8}$ = 2.7 Hz); 2.84 (dd, 1H, H(10), $^3J_{10,9b}$ = 5.5 Hz, $^4J_{10,8}$ = 5.5 Hz) ; 2.68 (ddd, 1H, H(9_b), $^2J_{9b,9a}$ = 9.6 Hz, $^3J_{9b,8}$ = 5.7 Hz, $^3J_{9b,10}$ = 5.7 Hz)); 2..29 (ddt, 1H, H(8)), $^3J_{8,9b}$ = 5.7 Hz, $^4J_{8,10}$ = 5.8 Hz, $^3J_{8,7}$ = 2.7 Hz); 1.39 (s, 3H, H(12)); 1.19 (d, 1H, H(9_a), $^2J_{9a,9b}$ = 9.6 Hz); 0.61 (s, 3H, H(13)). ^{13}C-NMR (100 MHz, $CDCl_3$): δ 157.9 (Cq); 152.7 (Cq); 145.6 (Cq); 145.5 (CH, C(3) or C(6)); 143.7 (Cq); 141.4 (Cq); 139.1 (CH, C(4')); 127.4 (CH, C(5')); 120.8 (CH, C(6) or C(3)); 119.4 (CH, C(3')); 118.4 (CH, C(3)); 44.5 (CH, C(10)); 40.1 (CH, C(8)); 39.2 (Cq, C(11)); 32.9 (CH_2, C(7)); 31.7 (CH_2, C(9)); 26.0 (CH_3, C(12)); 21.3 (CH_3, C(13)). UV/Vis: $?_{max}$ ($CHCl_3$)/ nm 297 (e/ dm^3 mol^{-1} cm^{-1} 2.0*10^4), 253 (1.0*10^4). Elemental analysis: Found C: 62.35%, H: 5.30%, N: 8.28%, $C_{17}H_{17}BrN_2$ requires C: 62.02%, H: 5.2%, N:8.51%.

2-Acetyl-5-(*p*-methoxyphenyl)-pyridine (7a)

The introduction of the acetyl function starting from 2-bromo-5-(p-methoxyphenyl) pyridine (**11**) was carried out in similar manner as described for compound **7d**.[9b] 2-Bromo-5-(p-methoxyphenyl)-pyridine (**11**) (2g, 7.6 mmole) was dissolved in dry diethylether (250 ml) under argon and cooled to –60°C, *n*-butyllithium (5 ml, 1.6M in hexane) was added dropwise over 45 minutes. After stirring for 1 ¼ hours, *N,N*-dimethyl-acetamide (0.75 ml, 8mmole) in diethylether (10 ml) was added over an hour. Overnight, the solution was allowed to warm to room temperature, quenched with saturated ammonium chloride solution and extracted five times with diethylether. Further purification was carried out by column chromatography (hexane/ ethylacetate/ triethylamine: 8/1/0.5) yielding a white solid (1.04g, 60 %). The spectral data was in accordance to the literature.[15]

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.88 (d, 1H, H(6), $^4J_{6,4}$ = 2.2 Hz, $^5J_{6,3}$ = 1.0 Hz), 8.07 (dd, 1H, H(4), $^3J_{4,3}$ = 8.1 Hz, $^4J_{4,6}$ = 2.2 Hz), 7.94 (d, 1H, H(3), $^3J_{3,4}$ = 8.1 Hz $^5J_{3,6}$ = 1.1 Hz), 7.62 (d, 2H, H(9), H(11), $^3J_{8,9}$ = 8.9 Hz), 7.04 (d, 2H, H(8), H(12), $^3J_{9,8}$ = 8.9 Hz), 3.87 (s, 3H, H(13)), 2.75 (s, 3H, H(15)).

2-Acetyl-6-phenyl pyridine (7b)

The synthesis was carried out according to the published method.[9b] 2-Acetyl-6-bromopyridine (**7d**) (7.75 g, 38.74 mmole) was dissolved in dry xylene (75 ml). Phenylboronic acid (7.09 g, 58.11 mmole), freshly purified $Pd(PPh_3)_4$ (5% eq) and potassium carbonate (10.71 g, 77.48 mmole) were added, stirred for 2hours at room temperature. Water (500 ml) was added and the reaction mixture was extracted by dichloromethane (500 ml). The resulting organic layers were dried over sodium sulfate and the solvent was evaporated to afford, after recrystallisation in hexane/ethylacetate, the desired compound (6.95 g, 91%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.03 (dd, 2H, H(8), (12)), 7.91-7.8 (m, 3H, H(3), H(4), H(5)), 7.44-7.38 (m, 3H, H(9), H(10), H(11)), 2.75 (s, 3H, H(14)). MS-EI: 197(100), 154(80), 127(25), 77(15).

2-Acetyl-6-(*p*-methoxyphenyl)-pyridine (7c)

A mixture of 2-acetyl-6-bromopyridine (**7d**) (2.00 g, 10 mmole), *p*-methoxyphenyl-boronic acid (347 mg, 10 mmole), and $Pd(PPh_3)_4$ (0.2% eq, 0.02 mmole) as catalyst, was heated at 120°C for 15 hours in a solvent mixture of toluene (100 ml) and an aqueous solution of K_2CO_3 ((50 ml, 8.5 M). After cooling to room temperature the two layers were separated and the aqueous layer extracted three times with dichloromethane. The combined organic layers were washed with water until pH=7

with water, dried over magnesium sulfate and the solvent was evaporated. Further purifications by recrystallisation (ethylacetate/hexane: 1/4) yielded compound **7c** (1.45 g, 64%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.04 (d, 2H, H(8), H(12)), $^3J_{8,9}$ = 8.9 Hz); 7.89 (dd, 1H, H(4); ^3J = 6.0 Hz, ^3J = 2.8 Hz); 7.83 (d, 1H, H(5) or H(3), ^3J = 2.5 Hz); 7.81 (d, 1H, H(3) or H(5) ^3J = 6.0 Hz); 7.01 (d, 2H, H(9), H(11), $^3J_{10,11}$ = 8.9 Hz); 3.87 (s, 3H, H(13)); 2.80 (s, 3H, H(15)). ^{13}C-NMR (75 MHz, $CDCl_3$): 200.8 (Cq, C(14)); 160.9 (Cq); 156.2 (Cq); 153.3 (Cq); 137.5 (CH, C(5) or C(3)); 131.1 (Cq); 128.2 (CH, C(8), C(12)); 122.7 (CH, C(3) or C(5)); 119.1 (CH, C(4)); 114.3 (CH, C(9), C(11)); 55.4 (CH_3, C(13)); 25.8 (CH_3, C(15)). MS-EI: m/z = 227 (100%); 199 (51%); 170 (58%); 142 (16%).

2-*N,N*-Dimethylamino-2-methyl-butan-3-one (8)

The synthesis was carried out according the published procedure by Gaset.[24] To a to 0 °C cooled solution of 2-bromo-2-methyl-butan-3-one (**23**) (10g, 0.06 mmole), dimethylamine (22 ml, 0.12 mmole, 5.6 M in ethanol) was added over a period of 5 minutes. The reaction solution was stirred overnight at 0 °C, then warmed to 40 °C for 70 minutes. After cooling to room temperature the reaction mixture was filtered and the residual solid was washed with cold ethanol. To the filtrate hydrochloric acid (66 ml, 4M) was added. Ethanol was removed under reduced pressure. To the acidic solution, sodium hydroxide (2M) was added, until the pH > 7. The alkaline solution was extracted three times with diethylether. The combined organic extracts were dried over magnesium sulfate and the solvent was removed under reduced pressure. The desired product was obtained (5.87 g, 76%). The spectral properties correspond to those reported.[24]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.18 (s, 3H, H(4)), 2.13 (s, 6H, H(6), H(8)), 1.06 (s, 6H, H(1), H(5)).

2-Bromo-5-(*p*-methoxyphenyl) pyridine (11)

A mixture of 2-bromo-5-iodopyridine (**10**) (5.67 g, 20 mmole), *p*-methoxyphenyl-boronic acid (3.34 g, 20 mmole) and $Pd(PPh_3)_4$ (0.02 mmole) as catalyst, was heated at 120 °C for 4 days in a mixture of toluene (80 ml) and an aqueous solution of K_2CO_3 (80 ml, 80g, 8.5 M). After cooling to room temperature, the two layers were separated and the aqueous layer extracted three times with dichloromethane. The combined organic layers were washed until pH = 7 with water, dried over magnesium sulfate and the solvent was evaporated. Further purification was carried out by column chromatography (hexane/ ethylacetate/ triethylamine: 5/1/0.1), yielding the desired product (5.3g, 99 %) .

^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.55 (d, 1H, H(6), $^4J_{6,4}$ = 2.6 Hz), 7.69 (dd, 1H, H(4), $^3J_{4,3}$ = 8.0 Hz, $^4J_{4,6}$ = 2.6 Hz), 7.51 (d, 1H, H(3), $^3J_{3,4}$ = 8.0 Hz), 7.47 (d, 2H, H(9), H(11), $^3J_{9,8}$ = 8.0 Hz), 7.01(d, 2H, H(8), H(12), $^3J_{8,9}$ = 8.0 Hz), 3.85 (s, 3H, H(13)). MS(EI): m/z = 265, 263 (M^+, 100%, 96%), 250, 248 (M^+- CH_3, 30%, 31 %), 222, 220 (M^+-C_2H_3O, 27%, 28%), 184 (M^+- Br, 19%), 169 (M^+- CH_3, 21%). Elemental analysis: Found C: 54.80%, H: 3.92%, N: 5.15%, $C_{12}H_{10}BrNO$ requires C: 54.57%, H:3.82% , N:5.30%.

2-Bromo-2-methyl-butan-3-one (14)

To a solution of 2-methylbutan-3-one (**13**) (25.85 g, 0.3 mole) in carbon tetrachloride (120 ml), bromine (48.0 g, 0.3 mole) in carbon tetrachloride (30 ml) was added dropwise under reflux over a period of 2 hours. After the addition the reaction mixture was kept under reflux for another 2 hours, then cooled to room temperature. Unreacted bromine was destroyed with sodium thiosulfate solution (10%). The organic layer was separated, dried with magnesium sulfate, the solvent was removed under reduced pressure. The crude product was further purified by vacuum distillation (100 mbar, 60°C), yielding a colourless liquid (30.1 g, 60%). The spectral properties correspond to those reported.[25]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.43 (s, 3H, H(4)), 1.84 (s, 6H, H(1), H(5)).

1-Bromo-1,1-diphenyl-propan-2-one (16)

To a solution of 1,1-diphenyl-propan-2-one (**15**) (15.0 g, 71mmole) in carbon tetrachloride (80 ml), bromine (12.5 g, 78 mmole) in carbon tetrachloride (20 ml) was added dropwise under reflux over a period of 2 hours. After the addition the reaction mixture was kept under reflux for another 2 hours, then cooled to room temperature. Unreacted bromine was destroyed with sodium thiosulfate. The organic layer was separated, dried with magnesium sulfate, the solvent was removed under reduced pressure. The crude product was further purified by recrystallisation, yielding a colourless solid (18.23 g, 82%).

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.25-7.38 (m, 10H, H(5), H(6), H(7)), 2.47 (s, 3H, H(1))

***N,N*-dimethyl- 3,3-diphenyl-propionamide (17)**

To a to 0 °C cooled solution of 1-bromo-1,1-diphenyl-propan-2-one (**16**) (2.0 g, 6.9 mmole), dimethylamine (2.5 ml, 13.8 mmole, 5.6 M in ethanol) was added over a period of 5 minutes. The reaction solution was stirred overnight at 0 °C, then warmed to 40 °C for 70 minutes. After cooling to room temperature, hydrochloric acid (50 ml, 4M) was added to the reaction mixture. Ethanol was removed under reduced pressure. To the acidic solution, sodium hydroxide (2M) was added, until the pH > 7. The alkaline solution was extracted three times with diethylether. The combined organic layers were dried over magnesium sulfate and the solvent was removed under reduced pressure, yielding product **26** (1.66 g 95%). The spectral properties correspond to those reported.[18]

^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.16-7.29 (m, 10H, H(5), H(6), H(7)), 4.68 (t, 1H, H(3), $^3J_{3,2}$ = 7.4 Hz), 3.03 (d, 2H, H(2), $^3J_{2,3}$ = 7.4 Hz), 2.84 (s, 6H, H(8)).

1-(2-Acetyl-5-(*p*-methoxyphenyl)-pyridyl)-pyridinium iodide (18a)

A mixture of pyridine (10 ml), iodine (280 mg, 1.1 mmole) and 2-acetyl-5-(*p*-methoxyphenyl)-pyridine (**7a**) (210 mg, 0.925 mmole) was kept at 100 °C for 2 hours and at 0 °C for 20 min. After addition of dry diethylether, the desired product and pyridinium iodide precipitated and was filtered. The crude product (305 mg) was used without further purification: The ratio between **18a** (1.3 eq, 223 mg, 59%) and the pyridinium iodide (1eq, 82 mg) was determined by ^{1}H-NMR-spectroscopy.

^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.19 (d, 1H, H(6), $^4J_{6,4}$ = 2.0 Hz), 9.01 (d, 2H, H(16), $^3J_{16,17}$ = 5.7 Hz), 8.73 (dd, 1H, H(18), $^3J_{18,17}$ = 7.8 Hz), 8.37 (dd, 1H, H(4), $^3J_{4,3}$ = 8.3 Hz, $^4J_{4,6}$ = 2.0 Hz), 8.27 (dd, 2H, H(17), $^3J_{17,18}$ = 7.8 Hz), 8.09 (d, 1H, H(3), $^3J_{3,4}$ = 8.3 Hz), 7.88 (d, 2H, H(9), H(11), $^3J_{9,8}$ = 8.8 Hz), 7.13 (d, 2H, H(8), H(12), $^3J_{8,9}$ = 8.8 Hz), 6.52 (s, 2H, H(14)), 3.84 (s, 3H, H(13')). MS(ESI): m/z = 305.14 M^+-I

Pyridinium iodide: ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.91 (d, 2H, H(a), $^3J_{a,b}$ = 6.6 Hz); 8.55 (dd, 1H, H(c), $J_{c,b}$ = 7.7 Hz); 8.03 (dd, 1H, H(b), $^3J_{b,a}$ = 6.6 Hz, $^3J_{b,c}$ = 7.7 Hz).

1-(2-Acetyl-6-phenylpyridyl)-pyridinium iodide (18b)

A mixture of pyridine (5 ml), iodine (0.64 g, 2.5 mmole) and 2-acetyl-6-phenylpyridine (**7b**) (0.5 g, 2.5 mmole) was kept at 120 °C for 3 hours and then at 0 °C for a night. The pyridine was evaporated under reduced pressure. The residual solid was suspended in dry diethylether and filtered to yield a black solid (1.36 g). The ratio between **18b** (1.2 eq, 0.95 g, 93%) and pyridinium iodide (1eq, 0.41 g) was determined by ^{1}H-NMR-spectroscopy.

^{1}H-NMR (300 MHz, DMSO-d_6): δ 9.02 (dd, 2H, H(16), $^3J_{16,17}$ = 6.6 Hz, $^4J_{16,17}$ = 1.2 Hz), 8.74 (dd, 1H, H(6), $^3J_{17,16}$ = 7.8 Hz, $^4J_{17,15}$ = 1.2 Hz), 8.42 (dd, 1H, (H(arom)), 8.33-8.25 (m, 4H, H(arom)), 8.22 (dd, 1H, H(arom)), 7.96 (dd, 1H, H(arom)), 7.64-7.51 (m, 3H, H(arom)), 6.69 (s, 2H, H(2)).

1-(2-Acetyl-6-bromopyridyl)-pyridinium iodide (18d)

A mixture of pyridine (200 ml), iodine (40.1g, 0.16 mol) and 2-acetyl-6-bromopyridine (**7d**) (31.2 g, 0.16 mol) was kept at 130 °C for 3 hours and then at 0 °C for 20 min. The pyridine was then removed by distillation (75 °C at 240 mbar). After addition of dry diethylether, the desired product and pyridinium iodide precipitated and was filtered. The crude product (84.5 g) was used without further purification: The ratio between **18d** (1.1 eq, 57.9g, 92%) and pyridinium iodide (1 eq, 26.6 g) was determined by ^{1}H-NMR-spectroscopy.

^{1}H-NMR (300 MHz, DMSO-d_6): δ 8.96 (d, 1H, H(10), $^3J_{10,11}$ = 5.5 Hz); 8.74 (m, 1H, H(12)); 8.28 (dd, 1H, H(11), $^3J_{11,10}$ = 5.5 Hz, $^3J_{11,12}$ = 6.8 Hz); 8.10 (m, 3H, H(3), H(4), H(5)); 6.46 (s, 2H, H(8)). MS-FAB (Matrix: NBA) : m/z = 279, 277 (M^+-I^-, 100%); 198, 200 (M^+-py, 30%, 20%) ; 154 (40%); 136 (48%).

1-(3-*N,N*-Dimethylamino-3-methyl-2-oxo-butyl)-pyridinium iodide (19)

A mixture of pyridine 160 ml), iodine (36.0 g, 142 mmole) and 2-*N,N*-dimethylamino-2-methyl-butan-3-one (**8**) (17.6 g, 136 mmole) was kept at 130 °C for 3 hours and then at 0 °C for 20 min. After addition of dry diethylether the desired product and pyridinium iodide precipitated and was filtered. The crude product was used without further purification: The ratio between **19** (1 eq, 16.2, 36 %) and pyridinium iodide (2.2 eq, 22.1 g) was determined by ^{1}H-NMR-spectroscopy.

^{1}H-NMR (400 MHz, DMSO-d_6): δ 9.10 (d, 2H, H(8), $^3J_{8,9}$ = 5.6 Hz), 8.78 (dd, 1H, H(10), $^3J_{10,9}$ = 7.8 Hz), 8.31 (dd, 2H, H(9), $^3J_{9,10}$ = 7.8 Hz), 6.43 (s, 2H, H(1)), 2.77 (s, 6H, H(6), H(7)), 1.72 (s, 6H, H(4), H(5)). MS(ESI): m/z = 207.16 (M^+-I^-).

Crystal structure analysis

Compound **1b**, $C_{54}H_{50}N_4$, M_r = 754.98, colourless rod 0.60 x 0.20 x 0.10 mm^3. Orthorhombic, $P2_12_12_1$, Z = 4, a = 11.4989(5), b = 14.7712(8), c = 25.1410(16) Å, V = 4270.3(4) Å^3, $?_{calc}$ = 1174 kg m^3, μ= 0.068 mm^{-1}. Data were collected at 153K on a Stoe Image Plate Diffraction system equipped with a f circle, using Mo-Kα graphite monochromated radiation (0.71073Å). Image plate distance 70mm, f oscillation scans 0 - 200°, step Δf = 1°, 2θ range 3.27 – 52.1°, d_{max} -d_{min} = 12.45 - 0.81 Å. The structure was solved by direct methods using the programme SHELXS-97[23a] and refined SHELXL-97.[23b] The H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. From 31668 reflections, 8128 were independent and used to refine 724 parameters. 4620 reflections were observed ($I > 2s$ (I)). R_1 = 0.0326 (observed), 0.0760 (all data), wR_2 = 0.0487 (observed), 0.0558 (all data). Residual electron density –0.121/+0.142 e Å^{-3}. The absolute structure of the molecule in the crystal was assigned to the known absolute configuration of the pinene-moiety.

CCDC reference number 179705.

Compound **2c**, $C_{48}H_{48}N_4O_2$, M_r = 710.89, colourless rod 0.50 x 0.30 x 0.20 mm^3. Monoclinic, C2, Z = 2, a = 20.7692(18), b = 6.0863(4), c = 14.9639(13) Å, ß = 99.673(10)°, V = 1864.7(3) Å^3, $?_{calc}$ = 1266 kg m^3, μ= 0.078 mm^{-1}. Data were collected at 153K on a Stoe Image Plate Diffraction system equipped with a f circle, using Mo-Kα graphite monochromated radiation (0.71073Å). Image plate distance 70mm, f oscillation scans 0 - 200°, step Δf = 1°, 2θ range 3.27 – 52.1°, d_{max} -d_{min} = 12.45 - 0.81 Å. The structure was solved by direct methods using the programme SHELXS-97[23a] and refined SHELXL-97.[23b] The H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. From 7379 reflections, 3471 were independent and used to refine 337 parameters. 2907 reflections were observed ($I > 2s$ (I)). R_1 = 0.0334 (observed), 0.0425 (all data), wR_2 = 0.0819 (observed), 0.0847 (all data). Residual electron density –0.350/+0.344 e Å^{-3}. The absolute structure of the molecule in the crystal was assigned to the known absolute configuration of the pinene-moiety.

CCDC reference number 179706.

Compound **3**, $C_{34}H_{50}N_4$, M_r = 514.78, colourless rod 0.50 x 0.15 x 0.15 mm^3. Orthorhombic, $P2_12_12$, Z = 2, a = 11.4893(8), b = 20.8542(16), c = 6.4198(4) Å, V = 1538.19(19) Å^3, $?_{calc}$ = 1111 kg m^3, μ= 0.065 mm^{-1}. Data were collected at 153K on a Stoe Image Plate Diffraction system equipped with a f circle, using Mo-Kα graphite monochromated radiation (0.71073Å). Image plate distance 70mm, f oscillation scans 0 - 198°, step Δf = 1°, 2θ range 3.27 – 52.1°, d_{max} -d_{min} = 12.45 - 0.81 Å. The structure was solved by direct methods using the programme SHELXS-97[23a] and refined SHELXL-97.[23b] The H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. From 12014 reflections, 2938 were independent and used to refine 178 parameters. 1798 reflections were observed ($I > 2s$ (I)). R_1 = 0.0417 (observed), 0.0774 (all data), wR_2 = 0.0841 (observed), 0.0926 (all data). Residual electron density –0.196/+0.307 e Å^{-3}. The absolute structure of the molecule in the crystal was assigned to the known absolute configuration of the pinene-moiety.
CCDC reference number 196850.

Compound **4a**, $C_{24}H_{24}N_2O$, M_r = 356.45, colourless block 0.50 x 0.50 x 0.50 mm^3. Monoclinic, $P2_1$, Z = 2, a = 9.1016(9), b = 9.3289(7), c = 11.1653(12) Å, ß = 96.651(13)°, V = 941.64(15) Å^3, $?_{calc}$ = 1257 kg m^3, μ= 0.077 mm^{-1}. Data were collected at 153K on a Stoe Image Plate Diffraction system equipped with a f circle, using Mo-Kα graphite monochromated radiation (0.71073Å). Image plate distance 70mm, f oscillation scans 0 - 185°, step Δf = 1°, 2θ range 3.27 – 52.1°, d_{max} -d_{min} = 12.45 - 0.81 Å. The structure was solved by direct methods using the programme SHELXS-97[23a] and refined SHELXL-97.[23b] The H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. From 7352 reflections, 3477 were independent and used to refine 340 parameters. 2978 reflections were observed ($I > 2s$ (I)). R_1 = 0.0278(observed), 0.0351 (all data), wR_2 = 0.0639 (observed), 0.0664 (all data). Residual electron density –0.120/+0.133 e Å^{-3}. The absolute structure of the molecule in the crystal was assigned to the known absolute configuration of the pinene-moiety.
CCDC reference number 179702.

Compound **4b**, $C_{23}H_{22}N_2$, M_r = 326.43, colourless block 0.53 x 0.30 x 0.30 mm^3. Monoclinic , $P2_1$, Z = 4, a = 10.8641(16), b = 6.3600(8), c = 13.0544(17) Å, ß = 90.312(10)°, V = 902.0(2) Å^3, $?_{calc}$ = 1202 kg m^3, μ= 0.070 mm^{-1}. Data were collected at room temperature on a Stoe AED2 4-circle diffractometer using MoKα graphite monochromated radiation (λ = 0.71073 Å) with $\omega/2\Theta$ scans in the 2Θ range 5 - 55°. The structure was solved by direct methods using the programme SIR-97[23c] and refined SHELXL-97.[23b] The H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. From 4520 reflections, 2260 were independent and used to refine 315 parameters. 1520 reflections were observed ($I > 2s$ (I)). R_1 = 0.0494 (observed), 0.0850 (all data), wR_2 = 0.0967 (observed), 0.1118 (all data). Residual electron density –0.139/+0.136 e Å^{-3}. The absolute structure of the molecule in the crystal was assigned to the known absolute configuration of the pinene-moiety.
CCDC reference number 179703.

Compound **4c**, $C_{24}H_{24}N_2O$ * $CHCl_3$, M_r = 475.92, colourless plate 0.35 x 0.30 x 0.10 mm^3. Monoclinic, $P2_1$, Z = 2, a = 6.6825(5), b = 7.4085(4), c = 23.4403(18) Å, ß = 94.080(10)°, V = 1157.52(14) Å^3, $?_{calc}$ = 1365 kg m^3, μ= 0.416 mm^{-1}. Data were collected at 153K on a Stoe Image Plate Diffraction system equipped with a f circle, using Mo-Kα graphite monochromated radiation (0.71073Å). Image plate distance 70mm, f oscillation scans 0 - 200°, step Δf = 1°, 2θ range 3.27 – 52.1°, d_{max} -d_{min} = 12.45 - 0.81 Å. The structure was solved by direct methods using the programme SHELXS-97[23a] and refined SHELXL-97.[23b] The H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. From 9156 reflections, 4208 were independent and used to refine 380 parameters. 3453 reflections were observed ($I > 2s$ (I)). R_1 = 0.0299 (observed), 0.0403 (all data), wR_2 = 0.0657 (observed), 0.0684 (all data). Residual electron density –0.270/+0.262 e Å^{-3}. Owing to the anomalous dispersion of

the chlorine atoms in the $CHCl_3$ solvate molecule, present per molecule of **4c**. The absolute configuration of the molecule in the crystal could be determined crystallographically, the refined Flack factor was 0.06(5).
CCDC reference number 179704.

Compound **4d**, $C_{17}H_{17}BrN_2$, M_r = 329.24, colourless rod 0.50 x 0.10 x 0.08 mm^3. Orthorhombic, $P2_12_12_1$, Z = 4, a = 6.1546(5), b = 13.5496(13), c = 17.5877(16) Å, V = 1466.7(2) $Å^3$, $?_{calc}$ = 1491 kg m^3, μ= 2.794 mm^{-1}. Data were collected at 153K on a Stoe Image Plate Diffraction system equipped with a f circle, using Mo-Kα graphite monochromated radiation (0.71073Å). Image plate distance 70mm, f oscillation scans 0 - 185°, step Δf = 1°, 2θ range 3.27 – 52.1°, d_{max} -d_{min} = 12.45 - 0.81 Å. The structure was solved by direct methods using the programme SHELXS-97[23a] and refined SHELXL-97.[23b] The H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. From 10465 reflections, 2871 were independent and used to refine 249 parameters. 1760 reflections were observed ($I > 2s$ (I)). R_1 = 0.0315 (observed), 0.0705 (all data), wR_2 = 0.0384 (observed), 0.0574 (all data). Residual electron density –0.500/+0.142 e $Å^{-3}$. The absolute configuration of the molecule in the crystal could be determined crystallographically, the refined Flack factor was 0.002(13).
CCDC reference number 179707.

Compound **6d**, $C_{17}H_{17}BrN_2$, M_r = 329.24, colourless block 0.38 x 0.30 x 0.23 mm^3. Orthorhombic, $P2_12_12_1$, Z = 4, a = 6.5403(8), b = 11.3397(10), c = 20.395(2) Å, V = 1512.6(3) $Å^3$, $?_{calc}$ = 1446 kg m^3, μ= 3.619 mm^{-1}. at room temperature (293K) on a Stoe AED2 4-circle diffractometer using CuKα graphite monochromated radiation (λ = 1.54186 Å) with ω/2Θ scans in the 2Θ range 5 - 125°. The structure was solved by direct methods using the programme SHELXS-97[23a] and refined SHELXL-97.[23b] The H-atoms were located from difference Fourier maps and refined isotropically. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on F^2. From 6472 reflections, 2219 were independent and used to refine 184 parameters. 2163 reflections were observed ($I > 2s$ (I)). R_1 = 0.0314 (observed), 0.0320 (all data), wR_2 = 0.0801 (observed), 0.0808 (all data). Residual electron density –0.205/ +0.174 e $Å^{-3}$. The absolute configuration of the molecule in the crystal could be determined crystallographically, the refined Flack factor was 0.01(3).
CCDC reference number 196851.