HETEROANNELATIONS WITH PINANE-DERIVED β-ENAMINOALDEHYDE

Sergey A. Popov, Alexey V. Tkachev*

Department of Natural Sciences, Novosibirsk State University.
Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences
Academician Lavrentjev Ave. 9, Novosibirsk, 630090, Russia
Fax: +7 3832 344752; e-mail: atkachev@nioch.nsc.ru

Abstract: Synthesis of new chiral fused pyridines and pyrimidines with pinane carbon frame prospective as bioactive compounds is described. Heterocylisations of pinane-derived β-enaminoaldehyde, need generally more rigid conditions than for o-aminobenzaldehyde, probably, both due to sterical and electronic reasons.

Introduction.

Readily accessible monoterpenes α-pinene and β-pinene are of interest as starting material for preparation of certain chiral derivatives, annelated heterocycles in particular. Recently utilisation of pinane-derived α,β-unsaturated ketones for the synthesis of phenantrolines (1) and pyridines (2) fused with pinane frame were reported. The heterocycles cited are prospective chiral auxiliaries. The alternative route to heterocycles annelated with the pinane carbon frame is the use of pinocarvone oxime, which is readily prepared *via* nitrosochlorination of α-pinene. We reported earlier preparation of pyrazole and isoxazole-type heterocycles annelated with pinane skeleton (3). Isoxazoles and β-enaminocarbonyl compounds are known to be the convenient starting material for preparation of different types of azaheterocycles (4, 5, 6). Now we report the synthesis of pinane-derived enaminoaldehyde and new annelated heterocycles of pyridine and pyrimidine type.

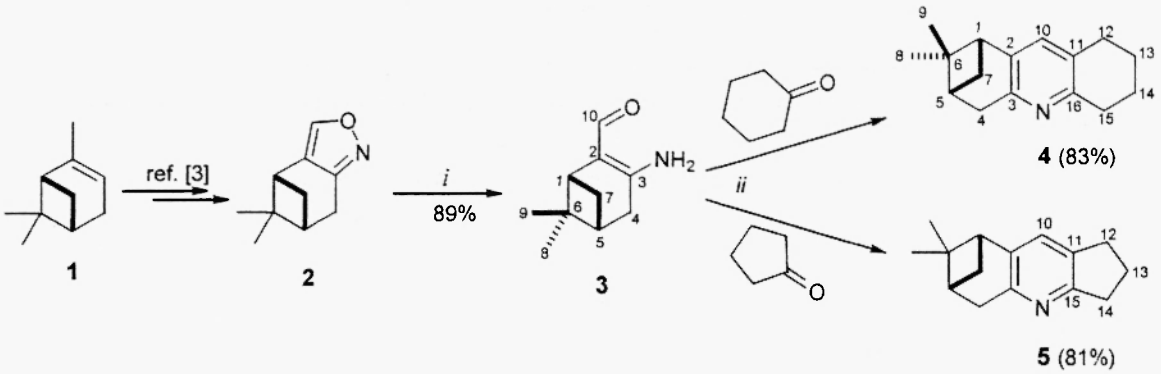
Results and discussion.

Isoxazole **2** (both optically active and racemic) was prepared from (–)-α-pinene and (±)-α-pinene correspondingly according to published procedure (3). In order to obtain β-enaminocarbonyl derivative of pinane type we studied hydrogenolysis of isoxazole **2** (Scheme 1). Surprisingly, hydrogenation of isoxazole **2** proceeds at ambient pressure to give enaminoaldehyde **3** in noticeable yield only in the presence of significant amount of the catalyst 5% Pd/C (1:1 w/w). However, hydrogenation of compound **2** at 4-5 atm H_2 over 5% Pd/C catalyst (10:1 w/w) gave enaminoaldehyde **3** in 89% yield.

Despite chemistry of aminoaldehydes has been scrupulously reviewed, only few examples of the use of aliphatic enaminoaldehydes for preparation of heterocyclic compounds are known(7). Reactions of chiral

enaminoaldehydes with ketones are of interest from the viewpoint of preparation of a new antitumour drugs (8). We have found that reaction of cyclopentanone or cyclohexanone with enaminoaldehyde **3** in boiling toluene in the presence of an excess of *p*-toluenesulphonic acid monohydrate resulted in formation of annelated pyridines **4** and **5** in very good yields (Scheme 1). Treatment of enaminoaldehyde **3** with less reactive acetophenone or propiophenone resulted in formation of complex mixtures of products. Derivatives **4** and **5** are prospective synthones for preparation of chiral tacrine-related AChE inhibitors (9).

Scheme 1



Reagents and conditions: i) 4 atm H_2, Pd/C, 15°C, 30 min; *ii*) $PhCH_3$-TsOH, reflux, 2 h

The numbering scheme of the carbons does not coincide with the numbering of the system according to IUPAC and is given for NMR interpretation only

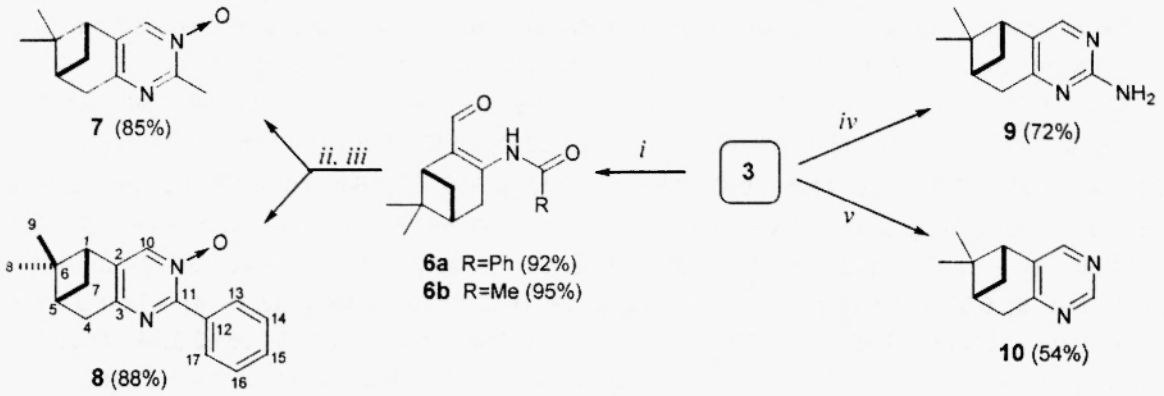
We studied also a possibility of synthesis of pyrimidines annelated with pinane carbon frame. Reaction of *o*-aminobenzaldehyde with hydroxylamine followed by N-acylation of the amino-moiety was reported as a convenient method for preparation of 2-substituted quinazoline-N-oxides (5). We failed to prepare enaminoaldehyde oxime by treatment of enaminoaldehyde **3** with hydroxylamine in the presence of KOH (by analogy with the procedure described in ref (5)), the starting compound was isolated unchanged. The following alternative reaction sequence was found to be a facile method for preparation of annelated pyrimidine-N-oxides **7** and **8**: N-acylation with an acyl halide followed by treatment with NH_2OH and intramolecular cyclocondensation in the presence of Py×HCl (scheme 2). N-Acylation of enaminoaldehyde **3** proceeds smoothly and results in high yields of N-acyl derivatives **6a**,**b** that are very active in the reaction with NH_2OH. N-Benzyl derivative **6a** was isolated and characterised by spectroscopic methods, whereas N-acetyl derivative **6b** was used without further purification. Compounds **7** and **8** are analogues of quinazoline alkaloids known due to their physiological activity.

Treatment of aliphatic enaminocarbonyl compounds with hot aqueous cyanamide was reported to be an expedient route for preparation of 2-aminopyrimidines (10). We have found that enaminoaldehyde **3** was inert under the conditions cited, although the reaction is possible under more drastic conditions (scheme 2).

In order to obtain annelated 2-unsubstituted pyrimidine we studied. The reaction of enaminoaldehyde **3** with trimethylorthoformate in the presence of NH_4OAc under reflux in benzene provided only poor yield (<35 %) of fused pyrimidine because of formation of a large quantities of tar-like products. However, treatment of enaminoaldehyde **3** with excessive formamide in boiling toluene in the presence of *p*-TsOH gave fused pyrimidine **10** in quite good yield.

As compared to the examples published, α-pinene-derived β-enaminoaldehyde **3**, in general, is less reactive than *o*-aminobenzaldehyde (5), probably, due to sterical and electronic reasons.

Scheme 2



Reagents and conditions: i) RCOCl-Py-CCl_4, 15°C, 30 min; *ii*) NH_2OH×HCl -NaHCO-MeOH, r.t. 1 h → reflux 4 h; *iii*) Py×HCl-MeOH, r.t. overnight; *iv*) $CNNH_2$-C_6H_6-TsOH, reflux, 30 min; *v*) $HCONH_2$-$PhCH_3$-TsOH, reflux, 8 h

The numbering scheme of the carbons does not coincide with the numbering of the system according to IUPAC and is given for NMR interpretation only

Experimental.

Melting points were determined using a *Kofler* hot-stage. IR spectra were recorded on a *Specord M-80* spectrophotometer. ^1H and ^{13}C NMR spectra were recorded for 5-10% solutions on a *Bruker AC 200* spectrometer (200.13 MHz for ^1H and 50.32 MHz for ^{13}C). Chemical shifts (in ppm) were calculated relative to signals of the solvent ($CDCl_3$) used as the internal standards: δ_H 7.240 ppm and δ_C 76.900 ppm. Optical rotations were measured on a *Polamat A* polarimeter (λ = 578 nm). MS spectra were recorded on a *Finnigan MAT 8200* mass spectrometer using electron impact ionization technique (70 ev). All reagents and solvents were of commercial quality. Preparative column chromatography was carried out using silica gel or alumina (0.10-0.30 mm) and freshly distilled solvents.

(1S,5R)-3-Amino-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde **3**. A mixture of isoxazole **2** (2.0 g, 12 mmol) and 5% Pd/C (0.2 g) in MeOH (300 ml) was hydrogenated under 4 atm of H_2 at 15°C for 12h. The catalyst was filtered off and the filtrate was concentrated at reduced pressure. The residue was chromatographed (Al_2O_3, EtOAc) to afford 1.8 g (89 %) of compound **3** as yellow crystals with m.p. 102°C (decomp.) and $[\alpha]^{26}$ -110 (c 4.8, $CHCl_3$). MS, *m/z* (%): 165.1153 (M^+, 94 %, $C_{10}H_{15}NO$ requires 165.1154) 150 (40), 136 (31), 122 (99), 109 (29), 105 (24), 94 (46), 81 (100), 68 (18), 41 (35). IR ($CHCl_3$) ν/cm^{-1}: 3480, 3375, 3250, 1625, 1585, 1500, 1425, 1415, 1375, 1240, 1170, 1040, 930, 845. UV (EtOH) λ_{max}/nm: 336 (ε 30280). ^1H NMR: 2.60 (m, 1 H, H-1); 2.45 (m, 1H, H-4); 2.06 (dddd, J = 6.0, 5.9, 3.0 and 2.8 Hz, 1H, H-5), 1.19 (d, J = 9.0 Hz, 1H, H-7a), 2.52 (m, 1H, H-7b), 0.82 (s, 3H, H-8), 1.35 (s, 3H, H-9), 8.8 (s, 1H, H-10), 7.08 (br.s, $W_{1/2}$ = 20 Hz, 1H, N-H), 9.47 (br.s, $W_{1/2}$ =20 Hz, 1H, N-H). ^{13}C NMR: 39.32 (C-1), 111.58 (C-2), 161.53 (C-3), 34.99 (C-4), 41.73 (C-5), 41.50 (C-6), 34.49 (C-7), 21.69 (C-8), 26.51 (C-9), 185.23 (C-10).

(±)-3-Amino-6,6-dimethylbicyclo[3.1.1]hept-2-ene-2-carbaldehyde **3**. M.p. 101-105°C (decomp.)

(1S,13R)-10-Aza-14,14-dimethyltetracyclo[11.1.1.0^{2,11}0^{4,9}]pentadeca-2(11),3,9-triene 4. A mixture of enaminoaldehyde **3** (1.0 g, 6.1 mmol) and cyclohexanone (3.5 g, 36 mmol) were added to boiling toluene (15 ml) containing *p*-TsOH monohydrate (2.0 g, 10 mmol). The resulting mixture was refluxed for 2h under water distillation conditions followed by cooling to room temperature and extraction with 1M aq. H_2SO_4 (2×20 ml). The combined aqueous extracts were neutralised with an excess of aq. NH_3 and extracted with $CHCl_3$ (2×30 ml). The combined chloroformic extracts were dried (Na_2SO_4) and concentrated under reduced pressure affording annelated pyridine 4 (1.15 g, 83%) as yellow crystals with m.p. 68-70°C (MeCN) and $[\alpha]^{24}$ +39 (c 1.1, $CHCl_3$). MS (*m/z*, %): 226.1585 (M^+, 52%. $C_{16}H_{20}N$ requires 226.1596), 212 (82), 198 (25), 184 (100), 172 (13), 156 (9), 143 (8), 128 (5), 115 (6), 99 (5), 77 (6), 65 (3), 53 (2), 41 (6). IR ($CHCl_3$) ν/cm^{-1}: 1565, 1465, 1440, 1420, 1410, 1375, 1365, 1150, 1125, 1090, 1075, 1025, 1005, 950, 920, 840. UV (EtOH) λ_{max}/nm: 283 (ε 6735), 285 (ε 6425), 321 (ε 310). ^{1}H NMR: 2.56 (m, 1H, H-1), 2.93 (m, 2H, H-4), 2.26 (dddd, J = 6.1, 5.8, 3.0 and 2.6 Hz, 1H, H-5), 1.19 (ddd, J = 9.1, 3.2 and 2.3 Hz, 1 H, H-7a), 2.54 (m, 1H, H-7b), 0.62 (s, 3H, H-8), 1.34 (s, 3H, H-9), 6.67 (s, 1H, H-10), 2.59 (t, J = 6.2 Hz, 2H, H-12), 1.76 (m, 4H, H-13, H-14), 2.77 (t, J = 6.3 Hz, 2H, H-15). ^{13}C NMR: 47.08 (C-1), 138.83 (C-2) or (C-11), 154.46 (C-3) or (C-16), 36.82 (C-4), 41.30 (C-5), 40.34 (C-6), 33.19 (C-7), 22.41 (C-8), 27.22 (C-9), 133.94 (C-10), 128.22 (C-11) or (C-2), 29.46 (C-12), 24.00 (C-13), 24.34 (C-14), 32.85 (C-15), 154.08 (C-16) or (C-3).

(1S,12R)-9-Aza-13,13-dimethyltetracyclo[10.1.1.0^{2,10}0^{4,8}]tetradeca-2(10),3,8-triene **5** was prepared from enaminoaldehyde **3** and cyclopentanone in 81% yield. Yellow crystals with m.p. 76-78°C (MeCN) and $[\alpha]^{25}$ +41 (c 1.8, $CHCl_3$). MS (*m/z*, %): 212.1443 (M^+, 45 %, $C_{15}H_{18}N$ requires 212.1439), 198 (94), 170 (100), 157 (11), 142 (3), 128 (5), 115 (5), 99 (2), 92 (7), 84 (4), 77 (5), 65 (3), 53 (2), 41 (6). IR ($CHCl_3$) ν/cm^{-1} 1565, 1465, 1420, 1410, 1375, 1362, 1295, 1145, 1120, 1090, 1070, 1055, 1025, 1000, 930, 920, 905, 850, 840. UV (EtOH) λ_{max}/nm: 287 (ε 8790). ^{1}H NMR: 2.62 (dd, J = 5.9 and 5.9 Hz, 1H, H-1), 3.02 (dm, J = 2.9 Hz, 2H, H-4), 2.29 (ddt, J = 5.9, 5.9 and 2.9 Hz, 1H, H-5), 1.22 (d, J = 8.6 Hz, 1H, H-7a), 2.59 (ddd, J = 8.6, 5.9 and 5.9 Hz, 1H, H-7b), 0.62 (s, 3H, H-8), 6.93 (s, 1H, H-10), 1.35 (s, 3H, H-9), components of the AA`MM`XX` spin system: δ_A=$\delta_{A'}$=2.05 (tt, J = 7.5 and 7.5 Hz, 2H-13), δ_M=$\delta_{M'}$– 2.80 (t, J =7.5 Hz, 2H-12), δ_X=$\delta_{X'}$=2.91 (dd, J= 7.1 and 8.5, 2H, H-14). ^{13}C NMR: 46.48 (C-1), 138.40 (C-2) or (C-11), 161.66 (C-3) or (C-15), 35.97 (C-4), 40.12 (C-5), 39.23 (C-6), 32.00 (C-7), 21.16 (C-8), 26.00 (C-9), 129.30 (C-10), 132.57 (C-11) or (C-2), 30.29 (C-12), 23.00 (C-13), 33.61 (C-14), 153.93 (C-15) or (C-3).

(1S,5R)-N-(2-Formyl-6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)-benzamide **6a**. A solution of benzoyl chloride (0.94 g, 6.7 mmol) in CCl_4 (5 ml) was added at 15°C to a solution of enaminoaldehyde **3** (1.0 g, 6.1 mmol) in a mixture of CCl_4 (15ml) and Py (0.55 g, 7 mmol). The resulting mixture was stirred for 0.5 h, washed consequently with 0.5M aq. $NaHCO_3$ (50 ml) and 1M aq. H_2SO_4 (20ml), dried and concentrated at reduced pressure to afford a crude acyl derivative which was then purified by column chromatography (SiO_2, benzene) to give N-benzoyl derivative **6a** as yellow viscous oil (yield 92 %) with $[\alpha]^{17}$ +8.2 (c 3.04, $CHCl_3$). MS (*m/z*, %): 269.1422 (M^+, 6 %, $C_{17}H_{19}NO_2$ requires 269.1415) 240 (2), 226 (4), 213 (0.4), 198 (1), 185 (2), 164 (62), 149 (1), 136 (4), 122 (4), 105 (100), 77 (56), 51 (12), 39 (6). IR ($CHCl_3$) ν/cm^{-1}: 1675,1630, 1560, 1490, 1455, 1420, 1390, 1360, 1320, 1150, 1130, 1105, 1075, 1055, 1010, 1000, 920, 875, 840. UV (EtOH) λ_{max}/nm: 246 (ε 11460). 348 (ε 12300). ^{1}H NMR: 2.59 (dd, J = 5.6 and 6.0 Hz, 1H, H-1), 3.40 (dd, J = 20.7 and 3.0 Hz, 1H, H-4a), 3.26 (dd, J = 20.7 and 3.0 Hz, 1H, H-4 b), 2.17 (dddd, J = 6.0, 6.0, 3.0 and 3.0 Hz, 1H, H-5), 1.15 (d, J = 9.0 Hz, 1H, H-7a), 2.50 (ddd, J = 9.0, 6.0 and 5.6 Hz, 1H, H-7 b), 0.80 (s, 3 H-8), 1.30 (s, 3H, H-9), 9.09 (s, 1H, H-10), 13.11 (br.s, 1H, N-H), aromatic protons at 7.45 (m, 3H) and 7.96 (m, 2H). ^{13}C NMR: 41.35 (C-1), 120.89 (C-2), 152.91 (C-3), 34.47 (C-4), 39.05 (C-5), 38.62 (C-6), 31.69 (C-7), 21.10 (C-8),

25.53 (C-9), 191.06 (C-10), 165.02 (C-11), 133.36 (C-12), signals of aromatic carbons: 127.74 (2C), 128.49 (2C), 132.12 (1C).

(1S,5R)-N-(2-Formyl-6,6-dimethylbicyclo[3.1.1]hept-2-en-3-yl)-acetamide **6b** was prepared from enaminoaldehyde **3** and AcCl as described above for the synthesis of benzamide **6a** and was used to prepare annelated N-oxides **7** and **8** without any purification.

(±)-(1S,9R*)-4-N-Oxide-5,10,10-trimethyl-4,6-diazatricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene* **7**. A solution of racemic N-acylated enaminoaldehyde **6b** (4.8 mmol) in MeOH (10 ml) was added to a mixture of $NH_2OH \times HCl$ (2.0 g, 29 mmol) and $NaHCO_3$ (3.0 g, 35 mmol) in MeOH (15 ml). The mixture was stirred at ambient temperature for 1h and then at reflux for 4 h. The solvent was distilled off and the residue was treated with $CHCl_3$ (2×20 ml). The combined organic extracts were concentrated under reduced pressure, the residue was dissolved in dry MeOH (15 ml), a catalytic amount of Py×HCl (*ca* 10 mg) was added to the resulting solution and the mixture was allowed to stand overnight at room temperature. Powdered $NaHCO_3$ (1g, 12 mmol) was added and the mixture was concentrated at reduced pressure and extracted with $CHCl_3$ (2×30 ml). The combined extracts were concentrated in vacuum to afford crude pyrimidine-N-oxide, which was then crystallised from MeCN to give pure compound **7** (85 %) as pale yellow crystals with m.p. 112-114°C (decomp.) MS (*m/z*, %): 204.1260 (M^+, 100%, $C_{12}H_{16}N_2O$ requires 204.1262), 187 (39), 172 (12), 161 (34), 145(17), 131 (32), 118 (21), 105 (8), 91 (20), 77 (24), 65 (20), 53 (14), 41 (31). IR ($CHCl_3$) ν/cm^{-1}: 1530, 1480, 1435, 1370, 1340, 1300, 1280, 1135, 1115, 1065, 1015, 990, 940, 850. UV (EtOH) λ_{max}/nm: 225 (ε 10990), 269 (ε 7070), 313 (ε 6460). ^{1}H NMR: 2.72 (m, 2H, H-1, 7b), 2.97 (m, 2H, H-4), 2.36 (m, 1H, H-5), 1.29 (m, 1H, H-7a), 0.71 (s, 3H, H-8), 1.43 (s, 3H, H-9), 7.97 (s, 1 H, H-10), 2.62 (s, 3H, H-12). ^{13}C NMR: 42.81 (C-1), 137.66 (C-2), 151.57 (C-3), 34.93 (C-4), 39.41 (C-5), 39.25 (C-6), 31.26 (C-7), 25.47 (C-8), 20.95 (C-9), 139.82 (C-10), 156.40 (C-11), 18.91 (C-12).

(1S,9R)-4-N-Oxide-10,10-Dimethyl-5-phenyl-4,6-diazatricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene **8** was prepared from N-benzoylated enaminoaldehyde **6a** in 88 % yield by the same method. Pale yellow crystals with m.p. 158-166°C (decomp.). $[\alpha]^{17}$ +45.4° (c 1.6, $CHCl_3$). MS (m/z, %): 266.1414 (M^+, 100%, $C_{17}H_{18}N_2O$ requires 266.1419),249 (10), 223 (18), 207 (6), 196 (12), 180 (6), 168 (3), 146 (8), 129 (3), 120 (10), 105 (42), 91 (11), 77 (26), 65 (10), 51 (7), 41 (14). IR (KBr) ν/cm^{-1}: 1550, 1485, 1475, 1450, 1340, 1285, 1260, 1170, 1130, 1060, 970, 875, 810, 775, 730, 640. UV (EtOH) λ_{max}/nm: 217 (ε 14740), 253 (ε 29500), 295 (ε 10890). ^{1}H NMR: 2.71 (m, 2H, H-1, H-7b), 3.03 (m, 2H, H-4), 2.35 (m, 1H, H-5), 1.25 (m, 1 H, H-7a), 0.73 (s, 3H, H-8), 1.40 (s, 3H, H-9), 8.03 (s, 1H, H-10), signals of protons at aromatic carbons: 7.40 (m, 3H), 8.51 (m, 2H). ^{13}C NMR: 42.81 (C-1), 137.97 (C-2) or (C-12), 152.85 (C-3) or (C-11), 35.22 (C-4), 39.47 (2 C, C-5, C-6), 31.29 (C-7), 25.54 (C-8), 21.16 (C-9), 142.10 (C-10), 152.48 (C-11) or (C-3), 131.69 (C-12) or (C-2), signals of aromatic carbons:129.66 (2C), 127.34 (2C), 130.14 (1C).

(±)-(1S,9R*)-10,10-Dimethyl-4,6-diazatricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-trien-5-ylamine* **9**. A mixture of racemic enaminoaldehyde **3** (0.7 g, 4 mmol) cyanamide (0.5 g, 12 mmol) was added to a stirred boiling mixture of p-TsOH monohydrate (0.8 g, 4 mmol) in C_6H_6 (10 ml) and the mixture was kept at reflux for 30 min. The cooled mixture was extracted with 1M aq. H_2SO_4 (2×15 ml) and the combined aqueous phase wase neutralised with an excess of aq. NH_3 and extracted with $CHCl_3$ (2×20 ml). The combined organic extracts were dried (Na_2SO_4) and concentrated under reduced pressure to give a brown solid which was crystallised from CH_3CN to give 2-aminopyrimidine **9** (0.43 g, 54 %) as pale yellow crystals with m.p. 151-153 °C. MS (m/z, %): 189.1272 (M^+, 37 %, $C_{11}H_{15}N_3$ requires 189.1266) 174 (41), 160 (7), 146 (100), 133 (11), 119 (26), 106 (3), 91 (4), 81 (2), 77 (8), 65 (3), 51 (4), 41 (7). IR ($CHCl_3$) ν/cm^{-1}: 3525, 3420, 3300, 3175, 1600, 1550, 1510, 1500, 1410, 1375, 1560, 1340, 1310, 1160, 1125, 1090, 1080, 1020, 950, 940, 840. UV (EtOH)

λ_{max}/nm: 234 (ε 18680), 312 (ε 4230). NMR ^{1}H: 0.58 s (3H, H-8), 1.11 dm (J = 9.4 Hz, 1 H, H-7a), 1.30 s (3H, H-9), 2.20 m (1H, H-5), 2.57 m (1H, H-7 b), 2.61 dd (J = 6.0 and 5.8 Hz, 1H, H-1), 2.80 d (J = 2.9 Hz, 2H, H-4), 5.32 br.s. ($W_{1/2}$ = 8 Hz, 2H, NH_2), 7.70 s (1H, H-10). NMR ^{13}C: 41.49 (C-1), 128.83 (C-2), 162.09 (C-3),.92 (C-4), 39.56 (C-5), 39.71 (C-6), 32.36 (C-7), 21.10 (C-8), 25.73 (C-9), 152.48 (C-10), 166.95 (C-11).

(±)-(1S,9R*)-10,10-Dimethyl-4,6-diazatricyclo[7.1.1.0^{2,7}]undeca-2(7),3,5-triene* **10**. A mixture of racemic enaminoaldehyde **3** (0.2 g, 1.2 mmol), *p*-TsOH monohydrate (0.23 g, 1.15 mmol), and formamide (4.0 g, 89 mmol) in toluene (10 ml) was refluxed under water distillation conditions for 8 h. The mixture was cooled to room temperature, washed with 0.5M aq. Na_2CO_3 (2×20 ml) and the aqueous phase was extracted with toluene (2×20 ml). The combined toluene solution was treated with AcCl (0.02 g, 0.26 mmol, stirring for 10 min at ambient temperature) and extracted with 2M aq. H_2SO_4 (2×20 ml). The combined aqueous extracts were neutralised with concentrated aq. NH_3 (40 ml) and extracted with CH_2Cl_2 (3×15 ml). The combined extracts were dried (Na_2CO_3) and concentrated at reduced pressure to give a brown oil (0.19 g) which was then purified by column chromatography (SiO_2, C_6H_6-pentane) to afford pure compound **10** as yellow oil (0.15 g, 72 %). MS (*m/z*, %): 174.1141 (M^+, 68 %, $C_{11}H_{14}N_2$ requires 174.1157), 173(71), 159 (100), 131 (90), 119 (15), 104 (40), 91 (8), 77 (21), 65 (9), 51 (12). IR ($CHCl_3$) ν/cm^{-1}: 1679, 1587, 1555, 1454, 1421, 1396, 1327, 1267, 1240, 1218, 1179. UV (EtOH) λ_{max}/nm: 258 (ε 4980). NMR ^{1}H: 0.56 s (3H, H-8), 1.16 d (J = 9.0 Hz, H-7a), 1.34 s (3H, H-9), 2.30 dddd (J = 6.0, 6.0, 3.1 and 2.9 Hz, 1H, H-5), 2.65 m (1H, H-7b), 2.70 dd (J = 6.0 and 6.0, 1H, H-1), 2.96 m (2H, H-4), 8.07 s (1H, H-10), 8.82 s (1H, H-11). NMR ^{13}C: 43.28(C-1), 139.06 (C-2), 164.70 (C-3), 36.05 (C-4), 39.62 (C-5), 39.32 (C-6), 31.69 (C-7), 21.25 (C-8), 25.82 (C-9), 156.60 (C-10 or C-11), 151.41 (C-11 or C-10).

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