Revisiting a Classic Approach to the *Aspidosperma* Alkaloids: An Intramolecular Schmidt Reaction-Mediated Synthesis of (+)-Aspidospermidine

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Details on Characterization of Selected Compounds

Compound 28. In **28**, the CH₃ of the ethyl group appeared as a triplet at 0.88 ppm (J = 7.5 Hz) in its ¹H NMR (Figure 1). ¹H–¹H COSY then allowed the determination of the positions of the CH₂ of the ethyl group as being buried in the multiplets at 1.65 and 1.80 ppm. The ring fusion proton H_a was



again distinctive, appearing as a doublet at 1.81 ppm (J = 5.1 Hz, the only proton expected to appear as a doublet in the molecule). That in turn coupled into the proton on the carbon bearing the side chain at 2.55 ppm. Using similar correlations, the protons on the side chain were identified. In order to determine the relative stereochemistry of the major isomer in **28**, the compound was subjected to 2D-NOE experiments, which revealed that the azide-containing side chain, H_a, and the ethyl group were cis to each other. Hence the major isomer was determined as the one in which the side chain occupies a β -orientation as depicted.

Compound 6. The point of entry for establishing the proton signals in **6** was the CH₃ (triplet at 1.0 ppm) of the ethyl group (Figure 2). COSY data then unambiguously established the positions of the CH₂ of the ethyl group (1.50 ppm), and protons at C-7 (triplet, J COSY correlations in **6**



= 5.9 Hz, 2.86 ppm) and C-21 (doublet, J = 5.0 Hz, 3.63 ppm, furthest downfield). The protons at C-7, C-21 and the ethyl group at C-22 in **6** were determined to be *cis* to one other (¹H NOE data, aspidospermidine numbering), thus establishing the stereochemistry of **6** as shown.

Compound 29 was subjected to X-ray crystallographic analysis. The cif file of this structure is included as a separate piece of Supporting Information.



Compound 7. Selected ¹H NOE correlations in 7 are shown below.



Compound 31. The molecular weight of 31 was determined to be 280 and thus having the probable molecular formula $C_{19}H_{24}N_2$ (2 protons fewer than aspidospermidine). Also apparent from the ¹³C NMR of the compound was the presence of 8 aromatic signals indicating an intact



indole ring system. DEPT analysis indicated the presence of 7 methylenes, 2 methines, 4 aromatic protons, and 1 methyl group in the molecule. In addition to the more routine signals, a key feature of the proton spectrum was 2 geminal protons (H_a and H_b , 2.51 and 2.79 ppm, J = 15.0 Hz) that were coupled only to each other (Figure 5). HMQC (singlebond 1H–13C correlations) assigned all the protons to their respective carbons and HMBC data (2,3-bond 1H–13C correlations) showed that Ha and Hb correlated into the indole system, the carbon bearing the ethyl group, and the carbon of Hc. Hc was coupled to Hd as determined by 1H-1H COSY experiments. These results set up **32** to be the probable partial structure. Stereochemical assignments were then deduced by 1D and 2D NOE experiments as depicted.

Additional Experimental Details

General. ¹H and ¹³C NMR spectra were recorded at the field strengths noted for particular compounds. All NMR samples were dissolved in CDCl₃, and the chemical shifts are expressed in parts per million (δ) relative to tetramethylsilane as an internal reference. Abbreviations are s, singlet; d, doublet; t, triplet; q, quartet; br, broad; m, multiplet. Melting points are uncorrected. All mass spectra measurements were carried out in-house. Optical rotations were taken on at ambient temperature; the concentrations are reported in g/100 mL. Elemental analyses were performed in-house. All chromatography was performed using silica gel (32-63 mesh) with the indicated solvent mixtures. Tetrahydrofuran was distilled from sodium benzophenone ketyl, dichloromethane and triethylamine were distilled from calcium hydride, and all other solvents were used without further purification. Reaction flasks were flame-dried and cooled under argon, and all reactions were conducted under a positive pressure of dry argon.

4-Benzyloxy-1-butanol.¹ 1,4-Butanediol (20.3 g, 226 mmol) was added dropwise to an ice-cooled suspension of sodium hydride (4.33 g, 180 mmol) in DMF (200 mL). The resulting mixture was warmed to rt, treated with benzyl bromide (30.9 g, 180 mmol), and allowed to react for 20 h. The reaction mixture was then poured into H₂O, and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo to yield a light yellow oil (27.9 g, 86%). IR (film) 3390 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.72 (m, 4H), 2.40 (br s, 1H), 3.54 (t, *J* = 5.6 Hz, 2H), 3.66 (t, *J* = 5.7 Hz, 2H), 4.55 (s, 2H), 7.34 (m, 5H); ¹³C NMR (75 MHz, CDCl₃) δ 27.1, 30.5, 63.1, 70.8, 73.5, 128.1, 128.2, 128.8, 138.6; CIMS *m/z* (relative intensity) 181 (MH⁺, 100), 136 (50), 91 (95).

4-Benzyloxybutyraldehyde.¹ PCC (40.5 g, 188 mmol) was added in a single portion to a solution of the above alcohol (22.5 g, 125 mmol) in CH_2Cl_2 (300 mL)

maintained at rt. After 3 h, the reaction mixture was diluted with Et₂O (300 mL) and filtered through a silica gel plug. The filtrate was concentrated to approximately 50 mL and the resulting solution was distilled under high vacuum to yield 12.9 g (58%) of the title compound (bp 115–118 °C/1.0 Torr) as a clear liquid. IR (film) 1715 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 1.95 (m, 2H), 2.55 (t, *J* = 7.1 Hz, 2H), 3.50 (t, *J* = 6.1 Hz, 2H), 4.50 (s, 2H), 7.30 (m, 5H), 9.78 (s, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 22.6, 40.9, 69.2, 72.9, 127.6, 128.4, 138.3, 202.2; CIMS *m/z* (relative intensity) 179 (MH⁺, 60), 91 (100).

6-Benzyloxy-1-hexen-3-ol. A solution of the above aldehyde (10.9 g, 61.0 mmol) in THF (20 mL) was added dropwise to a rt solution of vinyl magnesium bromide (1 M in THF, 80.0 mL, 80.0 mmol). The reaction mixture was stirred for an additional 30 min before it was carefully poured over ice-cold 1 M HCl and extracted with Et₂O. The combined organic layers were washed successively with H₂O and brine, dried over MgSO₄ and concentrated in vacuo. The resulting oil was distilled under high vacuum to yield 11.1 g (88%) of the title compound (bp 145-155 °C/1.0 Torr) as a clear thin oil. IR (film) 3400 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.82-1.60 (m, 4H), 2.50 (br s, 1H), 3.54 (t, *J* = 5.9 Hz, 2H), 4.16 (q, *J* = 5.9 Hz, 1H), 4.54 (s, 2H), 5.12 (d, *J* = 10.4 Hz, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.90 (ddd, *J* = 17.0, 10.6, 6.1 Hz, 1H), 7.32 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 26.2, 34.7, 70.8, 73.1, 73.4, 114.9, 128.06, 128.12, 128.8, 138.6, 141.5; CIMS *m/z* (relative intensity) 207 (MH⁺, 15), 189 (100), 171 (50). Anal. calcd for C₁₃H₁₈O₂: C, 75.69; H, 8.79, found: C, 75.57; H, 9.00.

7aR-Ethyl-1,2,3,6,7,7a-hexahydroinden-5-one (9). A solution of 2ethylcyclopentanone² (5.36 g, 47.9 mmol), (S)- α -methylbenzylamine (5.22 g, 43.1 mmol) and p-TsOH (0.01 g) in benzene (50 mL) was thoroughly degassed and then allowed to reflux for 24 h using a Dean-Stark trap to remove H₂O. After the theoretical amount of H₂O had been removed, the remaining benzene was distilled off at atmospheric pressure and the crude imine pot residue was cooled to rt and used directly in the next step. Methyl vinyl ketone (3.93 g, 56 mmol) and hydroquinone (ca. 0.025 g) were added to the imine and the resulting solution was heated at 60 °C for 44 h, cooled to rt, diluted with aqueous acetic acid (10%, 30 mL) and MeOH (15 mL), and the resulting biphasic solution was stirred vigorously for 2 h. The mixture was then poured over 1 M HCl and extracted with Et₂O. The combined organic layers were successively washed with saturated aqueous NaHCO₃ and brine, dried over MgSO₄, and concentrated in vacuo. The resulting residue was added to a solution of sodium methoxide (3.0 g, 86.2 mmol) in methanol (70 mL) and allowed to reflux for 24 h. After this time, the reaction mixture was cooled to rt and 1N HCl was added in a dropwise manner until the pH was adjusted to 2.0 and the reaction mixture stirred for an additional 15 min. The aqueous layer was extracted with Et_2O (6 × 100 mL) and the organic layer washed with a saturated aqueous solution of NaHCO₃ (3 \times 100 mL), H₂O (1 \times 100 mL), brine (1 \times 100 mL), dried over MgSO₄, concentrated and purified by distillation to afford 2.2 g (31%) of 9 ($R_f = 0.72$, 30%) EtOAc/hexanes) as a clear oil. IR (neat) 2968, 2881, 1675 cm⁻¹; ¹H NMR (400 MHz, $CDCl_3$) $\delta 0.93$ (t, J = 7.4 Hz, 3H), 1.20-1.32 (m, 1H), 1.38-1.52 (m, 2H), 1.63 (dt, J =13.7, 5.2 Hz, 1H), 1.75-1.90 (m, 2H), 1.96-2.00 (m, 1H), 2.17-2.32 (m, 2H), 2.38-2.50 (m, 2H), 2.60-2.72 (m, 1H), 5.78 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) & 8.9, 20.9, 25.4,

30.8, 31.2, 33.2, 35.7, 45.8, 120.9, 179.2, 199.4; CIMS *m*/*z* (relative intensity) 165 (MH⁺, 100), 136 (16), 122 (18); HRMS calcd for C₁₁H₁₇O: 165.1279, found: 165.1267.

7aR-Ethyl-3R-hydroxy-1,2,3,6,7,7a-hexahydroinden-5-one. The enone **9** (0.039 g, 0.24 mmol) and *p*-TsOH (0.011 g, 0.06 mmol) were added to isopropenylacetate (5 mL) and the reaction mixture heated at 105 °C for 1.5 h. After this time the reaction mixture was cooled to room temperature and diluted with Et_2O (50 mL). The organic layer was washed with a saturated aqueous solution of NaHCO₃ (10 mL), H₂O (10 mL), dried over MgSO₄, concentrated to a light brown oil that was used in the next step without purification.

The crude dienol acetate was dissolved in acetone (3 mL), followed by the addition of H₂O (1 mL), a saturated aqueous solution of NaHCO₃ (1 mL) and Oxone (0.40 g). The resulting reaction mixture was stirred at rt for 45 min. The reaction mixture was diluted with H₂O (5 mL) and the aqueous layer was extracted with EtOAc (2 × 20 mL). The organic layer was washed with brine, dried over MgSO₄ and concentrated to give the title compound (R_f = 0.28, 30% EtOAc/hexanes) as a colorless oil that was used in the next step without purification. [α]_D = -66.2 (*c* 1.7, CH₂Cl₂); IR (neat) 3405, 2960, 1666 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.43-1.64 (m, 4H), 1.75-1.87 (m, 3H), 2.17 (ddd, *J* = 2.0, 5.0, 15.0 Hz, 1H), 2.25-2.29 (m, 1H), 2.35 (m, 1H), 2.42-2.46 (m, 1H), 4.78 (dt, *J* = 2.0, 8.0 Hz, 1H), 5.94 (d, *J* = 2.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 9.1, 29.1, 32.2, 32.5, 33.0, 33.7, 43.2, 73.2, 119.2, 178.9, 199.6; CIMS *m/z* (relative intensity) 181 (MH⁺, 100), 124 (14); HRMS calcd for C₁₁H₁₇O₂: 181.1228, found: 181.1231.

6-Benzyloxy-1-hexen-3-one (**10**).³ Jones reagent (8 M in H₂O, 21.0 mL, 168 mmol) was added dropwise to a 0 °C solution of the above alcohol (11.1 g, 53.8 mmol) dissolved in 20 mL of acetone. After the addition was complete the reaction was poured over H₂O and extracted with Et₂O. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo. The resulting residue was treated with ca. 200 mg of hydroquinone and distilled under high vacuum to yield 8.80 g (80%) of **10** (bp 135-145 °C/1.0 Torr) as a light yellow oil. IR (film) 1690, 1670 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.97 (m, 2H), 2.75 (t, *J* = 7.2 Hz, 2H), 3.54 (t, *J* = 6.1 Hz, 2H), 4.55 (s, 2H), 5.84 (dd, *J* = 10.4, 1.2 Hz, 1H), 6.25 (dd, *J* = 17.7, 1.2 Hz, 1H), 6.38 (dd, *J* = 17.7, 10.4 Hz, 1H), 7.35 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ 24.4, 36.6, 69.6, 69.7, 73.3, 116.5, 128.0, 128.1, 128.5, 128.8, 137.0, 138.8, 201.0; CIMS *m/z* (relative intensity) 205 (MH⁺, 20), 97 (90).

3a*S***-Ethyl-3,3a,4,5-tetrahydro-2H-inden-1,6-dione** (**15**). The above alcohol (1.52 mmol) was dissolved in CH₂Cl₂ (7 mL) and PCC (0.65 g, 3.04 mmol) was added in one portion. The reaction mixture was stirred at rt for 1.5 h after which time the organic layer was filtered through a pad of silica gel, concentrated and purified by chromatography (10% EtOAc/hexanes) to afford 0.226 g of **15** (84% from **9**) as a yellow solid. Mp = 107-109 °C; $[\alpha]_D = -289.2$ (*c* 0.204, CHCl₃); IR (neat) 2960, 2881, 1728, 1684 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.02 (t, *J* = 7.4 Hz, 3H), 1.53-1.64 (m, 3H), 1.84 (dt, *J* = 13.7, 5.5 Hz, 1H), 2.28-2.39 (m, 2H), 2.47-2.55 (m, 4H), 6.30 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 9.3, 26.8, 30.5, 32.8, 33.7, 36.0, 42.9, 122.7, 161.7, 200.1,

207.6; CIMS m/z (relative intensity) 179 (MH⁺, 100), 150 (37), 137 (28), 121 (16), 107 (11), 93 (11), 79 (15), 65 (12); HRMS calcd for $C_{13}H_{20}BrO$ (M⁺+H): 271.0698, found: 271.0710.

4-(2'-Bromoethyl)-7a*R***-ethyl-1,2,3,6,7,7a-hexahydroinden-5-one (16a).** Boron tribromide (1 M in CH₂Cl₂, 1.34 mL, 1.34 mmol) was added dropwise to a -78 °C solution of benzyl ether **8** (0.20 g, 0.67 mmol) in CH₂Cl₂ (2 mL). The reaction was then allowed to stir without external cooling for 3 h before it was poured over saturated aqueous NaHCO₃, extracted with CH₂Cl₂, dried over Na₂SO₄, and concentrated in vacuo. The resulting crude product residue was purified by chromatography (20% Et₂O/hexanes) to yield 0.10 g (55%) of **16a** (R_f = 0.30, 20% Et₂O/hexanes) as a clear oil. [α]_D = -27.4 (*c* 1.2, CH₂Cl₂); IR (film) 1650 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (t, *J* = 7.4 Hz, 3H), 1.30 (m, 1H), 1.46 (q, *J* = 7.5 Hz, 2H), 1.66 (td, *J* = 13.8, 5.4 Hz, 1H), 1.84 (m, 2H), 2.05 (m, 1H), 2.18 (ddd, J = 13.3, 5.3, 1.9 Hz, 1H), 2.34 (ddd, J = 18.2, 5.4, 1.9 Hz, 1H), 2.49 (ddd, *J* = 18.3, 14.2, 5.3 Hz, 1H), 2.58-2.84 (m, 4H), 3.48 (td, *J* = 7.0, 0.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 9.6, 22.0, 26.0, 30.5, 30.6, 31.2, 32.6, 33.8, 36.8, 47.0, 128.6, 176.5, 198.7; CIMS *m*/*z* (relative intensity) 273 (MH₂⁺, 100), 271 (M⁺, 100), 191 (25); HRMS calcd for C₁₃H₁₉O: 271.0698, found: 271.0710.

4-(2'-Chloroethyl)-7aR-ethyl-1,2,3,6,7,7a-hexahydroinden-5-one (16b). Boron trichloride (1 M solution in CH₂Cl₂, 3.40 mL, 3.40 mmol) was added dropwise to a -78 °C solution of benzyl ether **8** (0.60 g, 2.01 mmol) in CH₂Cl₂ (6 mL). The reaction was then allowed to stir without external cooling for 45 min before it was poured over saturated aqueous NaHCO₃, extracted with CH₂Cl₂, dried over Na₂SO₄, and concentrated in vacuo. The resulting crude product residue was purified by chromatography (20% Et₂O/hexanes), to yield 0.38 g (84%) of the chloride **16b** (R_f = 0.30, 20% Et₂O/hexanes) as a light yellow oil. [α]_D = -30.2 (*c* 4.1, CH₂Cl₂); IR (film) 1650 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.94 (t, *J* = 7.5 Hz, 3H), 1.30 (td, *J* = 12.4, 10.0 Hz, 1H), 1.47 (q, *J* = 7.4 Hz, 2H), 1.66 (td, *J* = 13.8, 5.3 Hz, 1H), 1.84 (m, 2H), 2.01 (dt, *J* = 12.5, 4.0 Hz, 1H), 2.18 (ddd, *J* = 13.3, 5.3, 1.9 Hz, 1H), 2.35 (ddd, *J* = 18.3, 5.4, 1.9 Hz, 1H), 2.49 (ddd, *J* = 18.3, 14.2, 5.3 Hz, 1H), 2.65 (m, 4H), 3.61 (td, *J* = 6.9, 2.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 9.6, 22.0, 26.0, 30.48, 30.55, 31.2, 33.8, 36.8, 44.0, 46.9, 127.8, 176.7, 198.8; CIMS *m*/*z* (relative intensity) 227 (MH⁺, 90), 191 (50), 161 (15), 91 (15). Anal. calcd for C₁₃H₁₉CIO: C, 68.86; H, 8.45, found: C, 68.98; H, 8.50.

7-(2'-Chloroethyl)-3aS-ethyl-3,3a,4,5-tetrahydro-2H-indene-1,6-dione (17). A solution of chloride 16b (0.70 g, 3.1 mmol) and isopropenyl acetate (12 mL) was treated with *p*-TsOH (0.30 g) and heated at reflux for 1.5 h. The reaction was then cooled to rt, diluted with Et₂O, washed successively with saturated NaHCO₃ and brine, and dried over Na₂SO₄. The resulting solution was concentrated in vacuo to yield 0.83 g (100%) of dienol acetate as a light yellow oil. [α]_D = +23.4 (*c* 2.3, CH₂Cl₂); IR (film) 1750 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.87 (t, *J* = 7.5 Hz, 3H), 1.58-1.31 (m, 4H), 1.95 (dd, *J* = 12.9, 6.3 Hz, 1H), 2.00 (dd, *J* = 12.6, 7.5 Hz, 1H), 2.12 (m, 1H), 2.20 (s, 3H), 2.33 (m, 1H), 2.48 (m, 2H), 2.60 (m, 1H), 2.67 (ddd, *J* = 13.5, 9.8, 7.1 Hz, 1H), 3.49 (m, 2H), 5.58 (s, 1H).

This sensitive material was directly dissolved in a mixture of acetone (20 mL), saturated aqueous NaHCO₃ (10 mL), and H₂O (5 mL), and treated with 3.5 g of Oxone. After 30 min the reaction was poured over H₂O and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated in vacuo, and the resulting residue was purified by chromatography (50% Et₂O/hexanes), to yield 0.60 g (80%) of the allylic alcohol ($R_f = 0.20$, 50% Et₂O/hexanes) as a clear oil. [α]_D = -16.4 (*c* 1.8, CH₂Cl₂); IR (film) 3400, 1650 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.92 (t, *J* = 7.4 Hz, 3H), 1.42 (m, 2H), 1.63 (m, 1H), 1.76 (m, 1H), 1.83 (m, 1H), 1.92 (m, 1H), 2.04 (m, 1H), 2.14 (m, 1H), 2.21 (m, 1H), 2.42 (m, 1H), 2.48 (m, 1H), 2.80 (m, 1H), 2.98 (m, 1H), 3.70 (m, 2H), 4.97 (d, *J* = 6.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 9.8, 27.7, 30.4, 31.3, 33.6, 33.7, 33.9, 44.3, 46.6, 72.9, 130.5, 175.5, 199.9; CIMS *m/z* (relative intensity) 243 (MH⁺, 90), 207 (50), 180 (25).

A solution of allylic alcohol (0.67 g, 2.8 mmol) in CH₂Cl₂ (30 mL), maintained at rt, was treated with PCC (1.2 g, 5.5 mmol) and stirred for 3 h. The reaction was then diluted with Et₂O and filtered through a silica gel plug. The filtrate was concentrated in vacuo and the resulting crude product residue was purified by chromatography (30% Et₂O/hexanes), to yield 0.45 g (68%) of **17** ($R_f = 0.20$, 30% Et₂O/hexanes) as a yellow solid: mp = 54-55 °C; [α]_D = -211.6 (*c* 1.4, CH₂Cl₂); IR (film) 1705, 1665 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.01 (t, *J* = 7.4 Hz, 3H), 1.57 (m, 3H), 1.86 (td, *J* = 13.6, 6.0 Hz, 1H), 2.25 (ddd, *J* = 13.0, 7.9, 2.3 Hz, 1H), 2.31 (ddd, *J* = 13.5, 5.1, 2.3 Hz, 1H), 2.41-2.62 (m, 4H), 3.13 (m, 1H), 3.29 (dt, *J* = 12.5, 7.2 Hz, 1H), 3.56 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 26.3, 27.7, 30.5, 32.5, 33.7, 37.0, 43.6, 44.3, 135.6, 156.6, 200.3, 209.5; CIMS *m*/*z* (relative intensity) 241 (MH⁺, 30), 240 (M⁺, 50), 211 (40), 175 (100).

7-(2'-Chloroethyl)-3a*S***-ethyl-7a***R***-hexahydroindene-1,6-dione** (18). Concentrated HCl (12 M, 0.91 mL, 11.0 mmol) and sodium iodide (1.64 g, 11.0 mmol) were added to a solution of enedione **17** (0.33 g, 1.37 mmol) in acetone (50 mL) maintained at rt. After 15 min the reaction was diluted with Et₂O and washed successively with 10% aqueous Na₂S₂O₃ (until the organic layer remained colorless), H₂O, and brine. The resulting organic layer was dried over Na₂SO₄ and concentrated in vacuo to give a crude product residue that was purified by chromatography (30% Et₂O/hexanes), to yield 0.31 g (93%) of a ~1:1 diastereomeric mixture of **18** (R_f = 0.15) as a clear oil. IR (film) 1725, 1700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, J = 7.4 Hz, 3H), 1.05 (t, J = 7.4 Hz, 3H), 1.35-1.42 (sextet, J = 7.4 Hz, 1H), 1.49-1.53 (sextet, J = 7.4 Hz, 1H), 1.55-1.65 (m, 1H), 1.70-1.80 (m, 2H), 1.83-2.10 (m, 9H), 2.05-2.10 (m, 1H), 2.10-2.20 (m, 1H), 2.20-2.35 (m, 4H), 2.35-2.47 (m, 4H), 2.65-2.75 (m, 2H), 2.83 (q, J = 6.5 Hz, 1H), 3.50-3.58 (m, 1H), 3.61-3.67 (m, 3H); CIMS *m/z* (relative intensity) 243 (MH⁺, 30), 207 (50), 180 (90); HRMS calcd for C₁₃H₁₉O₂ (M⁺+H): 207.1385, found: 207.1385.

Cyclopropane (19). A solution of **18** (0.31 g, 1.28 mmol) in THF (18 mL) was treated with 14 drops of DBU and stirred overnight at rt. After 18 h the reaction was diluted with Et₂O, washed successively with 1M HCl and brine, dried over Na₂SO₄, and concentrated in vacuo. The resulting residue was purified by chromatography (30% Et₂O/hexanes) to yield 0.20 g (76%) of **19** ($R_f = 0.10$) as a clear oil. [α]_D = -100 (c 0.66,

CH₂Cl₂); IR (film) 1730, 1685 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.68 (ddd, J = 9.1, 7.1, 3.3 Hz, 1H), 0.94 (m, 1H), 1.02 (t, J = 7.5 Hz, 3H), 1.08 (ddd, J = 9.0, 7.2, 4.6 Hz, 1H), 1.60 (m, 1H), 1.69-1.93 (m, 6H), 2.01 (m, 1H), 2.24-2.45 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 8.6, 12.4, 20.7, 25.8, 29.3, 31.1, 31.11, 35.2, 36.2, 42.8, 61.3, 209.4, 217.3; CIMS *m*/*z* (relative intensity) 207 (MH⁺, 50), 150 (100).

Cyclopropane (20). To **16b** (0.277 g, 0.12 mmol) in THF (2 mL) was added DBU (0.036 g, 0.24 mmol) and the reaction mixture was heated under reflux for 5 h. After this time the reaction mixture was cooled to rt, diluted with H₂O (5 mL) and extracted with Et₂O (3 x 15 mL). The organic layer was dried over MgSO₄, concentrated in vacuo and the resulting oil was purified by chromatography (10% EtOAc/hexanes) to afford 18 mg (78%) of **20** (R_f = 0.86, 20% EtOAc/hexanes) as a clear oil. IR (neat) 1693 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, *J* = 7.4 Hz, 3H), 0.89 (buried m, 1H), 1.23 (m, 1H), 1.36 (m, 1H), 1.54-1.62 (m, 3H), 1.66-1.78 (m, 2H), 2.01-2.06 (m, 2H), 2.28 (m, 2H), 2.44 (m, 2H), 5.06 (t, *J* = 2.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 8.9, 16.8, 27.1, 28.5, 29.5, 30.8, 33.3, 36.1, 36.3, 49.8, 117.7, 149.0, 210.4; CIMS *m/z* (relative intensity) 191 (MH⁺, 100), 162 (42), 91 (11); HRMS calcd for C₁₃H₁₉O: 191.1436, found: 191.1460.

4-(2'-Azidoethyl)-7aR-ethyl-1,2,3,6,7,7a-hexahydroinden-5-one (21). Cyclopropane **20** (0.030 g, 0.16 mmol), TMSN₃ (0.168 mL, 0.64 mmol) and Bu₄NF (0.64 mL, 0.64 mmol) were combined and heated at 66 °C for 25 h. The reaction mixture was cooled to rt and quenched with a saturated aqueous solution of NaHCO₃ (5 mL). The aqueous layer was extracted with Et₂O (3 x 25 mL), and the organic layer washed with a saturated solution of NaHCO₃ (5 mL), and H₂O (5 mL). The organic layer was dried over MgSO₄, concentrated in vacuo and the resulting oil was purified by chromatography (10% EtOAc/hexanes) to afford 30 mg (81%) of **21** (R_f = 0.59, 20% EtOAc/hexanes) as a clear oil. IR (neat) 2968, 2872, 2095, 1666 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.91 (t, *J* = 7.4 Hz, 3H), 1.22-1.32 (m, 1H), 1.44 (q, *J* = 7.4 Hz, 2H), 1.64 (dt, *J* = 13.8, 9.6 Hz, 1H), 1.80-1.88 (m, 2H), 1.97-2.04 (m, 1H), 2.17 (ddd, *J* = 1.6, 5.1, 13.3 Hz, 1H), 2.33 (ddd, *J* = 1.6, 5.2, 12.0 Hz, 1H), 2.40-2.58 (m, 3H), 2.64 (q, *J* = 8.3 Hz, 2H), 3.25-3.40 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 9.0, 21.4, 25.3, 26.7, 29.8, 30.6, 33.3, 36.1, 46.4, 50.1, 127.2, 175.8, 198.3; CIMS *m/z* (relative intensity) 234 (MH⁺, 100), 206 (54), 149 (16); HRMS calcd for C₁₃H₁₉N₃O: 234.1606, found: 234.1594.

4-(2'-Azidoethyl)-7a*R*-ethyl-3*S*-hydroxy-1,2,3,6,7,7a-hexahydroinden-5-one (22). Enone 21 (0.019 g, 0.08 mmol) and *p*-TsOH (0.003 g, 0.016 mmol) were placed in isopropenyl acetate (5 mL) and the reaction mixture heated at 105 °C for 1.5 h. After this time the reaction mixture was cooled to room temperature and diluted with Et_2O (50 mL). The organic layer was washed with a saturated aqueous solution of NaHCO₃ (10 mL), H₂O (10 mL), dried over MgSO₄, concentrated to a light brown oil that was used in the next step without purification.

The crude dienol acetate was dissolved in acetone (3 mL), followed by the addition of H_2O (1 mL), a saturated aqueous solution of NaHCO₃ (1 mL) and Oxone (0.40 g) and the resulting reaction mixture was stirred at rt for 45 min. The reaction mixture was diluted with H_2O (5 mL) and the aqueous layer was extracted with EtOAc (2 x 20

mL). The organic layer was washed with brine, dried over MgSO₄, concentrated, and purified by chromatography (50% EtOAc/hexanes) to afford 13 mg of **32** (65%) as a clear oil ($R_f = 0.28$, 20% EtOAc/hexanes). IR (neat) 3432, 2942, 2103, 1658 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.90 (t, J = 7.4 Hz, 3H), 1.34-1.40 (m, 2H), 1.61-1.75 (m, 2H), 1.77-1.91 (m, 2H), 2.00-2.08 (m, 2H), 2.20 (ddd, J = 2.0, 5.0, 13.3 Hz, 1H), 2.38-2.53 (m, 3H), 2.77 (td, J = 4.3, 13.8 Hz, 1H), 3.07 (br s, 1H), 3.48-3.57 (m, 2H), 4.84 (d, J = 6.0 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 9.4, 26.9, 27.2, 30.7, 32.8, 33.1, 33.5, 46.2, 50.0, 71.8, 129.5, 175.8, 199.4; CIMS m/z (relative intensity) 250 (MH⁺, 27), 222 (29), 204 (100); HRMS calcd for C₁₃H₂₀O₂N₃: 250.1555, found: 250.1567.

5aS-Ethyl-8aS-decahydro-3-oxa-indacen-8-one (24). NaBH₄ (0.49 g, 13.0 mmol) was added to a solution of **18** (4.32 mmol) in MeOH (25 mL) at 0 °C. After stirring the reaction mixture for 5 min it was allowed to warm to rt, stirred for an additional 20 min, quenched with acetone (2 mL), and poured into H₂O (50 mL). The aqueous layer was extracted with Et₂O (2 x 100 mL) and the organic layer was washed with H₂O (50 mL), dried over MgSO₄, and concentrated to **23** which was a thick oil that was used in the next step without purification.

NaN₃ (2.45 g, 37.7 mmol) was added to crude **23** (0.93 g, 3.77 mmol) in DMF (30 mL), and the reaction mixture heated at 78 °C for 17 h. The reaction was allowed to cool to rt and poured into H₂O (100 mL) and the aqueous layer was extracted with Et₂O (3 x 100 mL). The organic layer was washed with brine, dried over MgSO₄, and concentrated to afford 0.87 g of a clear oil that was reacted with PCC (2.97 g, 13.7 mmol). After stirring for 2 h at rt the reaction mixture was treated with silica gel (2 g) and diluted with Et₂O (100 mL). The reaction mixture was then filtered through a pad of silica gel and the organic layer was concentrated to a pale yellow oil. The crude product was purified by chromatography (30% EtOAc/hexanes) to afford 7 and **24** (4:1 mixture). For **24**: IR (neat) 2922, 1727 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.85-0.95 (m, 3H), 1.15-2.15 (m, 8H), 2.22-2.33 (m, 3H), 2.45-2.52 (m, 1H), 2.72-2.80 (m, 1H), 3.02-3.20 (m, 1H), 3.70-3.80 (m, 1H), 3.85-4.00 (m, 2H); CIMS *m/z* (relative intensity) 209 (MH⁺, 95), 191 (100).

References

- (1) Parker, K. A.; Iqbal, T. J. Org. Chem. 1987, 52, 4369-4377.
- (2) Bernady, K. F.; Poletto, J. F.; Nocera, J.; Mirando, P.; Schaub, R. E.; Weiss, M. J. J. Org. Chem. **1980**, 45, 4702-4715.
- (3) Yadav, J. S.; Prahlad, V.; Muralidhar, B. Synth. Commun. **1997**, 27, 3415-3418.



Current Data Parameters



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											PC	1.40
												11 - 120 MG
	1										10 NMA plo	t parameters
114	1 and the set of	السرد المشاتله ابان لاالتنصورا	والمنابع والمتحد ومراكل المراج	الاستعال فرطله فيداف المعدا	أد فيق بالمان فاستعاله	instally still be shown	والمتعادية والمتعادية والمتلك والمتعادية	in the real pale of here beet	Land Linner	A 1. 18 4. 18 10 11 10 10 10	CX	20.00 cm
6.14	No. Adulat	When additions distance was	11. 21 Maganing tot at 1. In	a high at a diduit and	darin her hade	diday in Law time	the the party of a d	de la de ser de la la	all all transit	Kal the party	F1P	220.036 ppm
0.0	WL LIN	indian at a lite a de alla de la	Lad Windowski and a state of the first of the state of th	which the at he takes before	U. band bied bluft	an barla a third have	an unselet the all all a so a so a	والقر أفأك الدهر بالمؤدر مار	L. In A to Britishind	and a state of the	F1	22138.41 Hz
									3959 S.C.		F2P	-5,000 ppm
											F2	-503.06 Hz
		200	75 45		5	100	5-132 1 1-1	50		1 J	PPMCM	11.25179 nnm/cm
1HH		100 1	10 10	12	.5	100	/5	00	20	0	HZCM	1132 07385 Hz/rm
												1100.07000 112/08







Current Data Parameters ks3.097 NAME EXPNO 1 1 PROCNO F2 - Acquisition Parameters 970423 Date_ 12.34 Time drx400 INSTRUM PROBHD 5 mm Multinu PULPROG zg30 32768 TD SOLVENT CDC13 NS 16 2 DS SWH 4789.272 Hz FIDRES 0.146157 Hz AG 3.4210291 sec RG 114 104.400 usec DW DE 4.50 usec TE 300.0 K 1.00000000 sec D1 P1 7.70 usec 4.50 usec DE 400.1320007 MHz SF01 NUC1 1H PL1 -6.00 dB F2 - Processing parameters SI 16384 SF 400.1300000 MHz EM WDW 0 SS8 0.30 Hz LB 0 GB PC 1.00 10 NMR plot parameters CX 20.00 cm F1P 9.500 ppm F1 3801.24 Hz F2P -0.500 ppm F2 -200.07 Hz PPMCM 0.50000 ppm/cm

200.06500 Hz/cm

HZCM



0.961

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FTTT

ppm 9

		Current Dat	a Parameters	
		NAME	ks3.097	
n c	5	EXPNO	2	
410	0 0	PROCNO	1	
in c	α			
2 4		F2 - Acquis	ition Paramete	rs
		Date_	970423	
	1	Time	12.45	
1	1	INSTRUM	drx400	
		PROBHD	5 mm Multinu	
	45	PULPROG	zgpg30	
		TD	65536	
		SOLVENT	CDC13	
		NS	526	
		DS	2	10
		SWH	23640.662 1	1Z
		FIDRES	0.360/28 1	1Z
		AU	1.3801304 3	Sec
		HG	32/08	
		UW DC	21.130 0	JSEL
		UE	4.00 1	JSEL
1		IC.	0.0000	N
		011	0.000000	500
		012	18 00 1	48
	1	D1	0 05000000	Sec
		CB06865	waltz16	
- 1	1	PCPD2	100.00	USEC
÷.,		SF02	400.1316005	MHZ
1		NUC2	1H	
		PL2	-6.00	dB
		PL 12	18.00	dB
		P1	6.90	USEC
		DE	4.50	USEC
1		SF01	100.6232933	MHZ
		NUC1	130	
- 1		PL1	-6.00	dB
		F2 - Proce	essing paramete	rs
		SI	32768	
		SF	100.6127290	MHZ
		WOW	EM	
1		SSB	0	
		18	1.00	HZ
- 1		GB	0	
		PL	1.40	
	1	ID NHD of	ot narameters	
. 1	1	10 MMM 01	20 00	C.B.
	the High and the	FIP	220,000	000
	ter han a lister part of	F1	22134.80	Hz
		F2P	-5.000	ppm
		F2	-503.07	Hz
		PPMCM	11.25000	ppm/cm
	U	HZCM	1131.89319	Hz/cm

270 435						767 450 132	296	750 235 246 107	999 322 757 757 700 413	. 581	expno Procno
ррг 17.						77.77.77.	61.	42 35 31	20 20 12 20 12	Ξ	F2 - Acc
						$\langle \rangle$		1111	1///		Date_ Time
11	¥2					Y) $)$ $)$	1///	1	INSTRUM PROBHD
										25	PULPROG
											SOLVENT
											NS DS
						1					SWH
						1		T.	1		AQ
						1		- 1			DW
	3. Se					i		•			DE TE
						1					d11 d12
										1	PL13
											CPDPRG2
											PCPD2 SF02
											NUC2 PL 2
	н										PL12
											DE
								- T			SF01 NUC1
											PL1
											F2 - P1
						-					SF
											WOW SSB
1 1											LB GB
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											10 NMA
the Hunge of a billing	locks which he applies and	ship have a had a faller	indentifies a the state of the second	N. Shaan M	Loyda billiol	Land Bir Anto Bird	with the liter i	and the Home in the		all all here with	F1P
and desired and the fight	and a state of the state of the second s	a di se la se l La se la s	lalle die Arthrice Reference in der	म ब्रह्मक विश्व नहाँ है।	akin alan katang	linger is in the	heline electric	alde i de de e de la	al idalite to a divise	to and have a first of	F1 F2P
			· · · · · · · ·			<u>- Ş-35</u>					F2 PPMCM
ppm	200 17	5 150	125	10]	100	75		50	25	0	HZCM





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ррт 10.469		9.032	7.764		7.316 6.999 6.681	9.836 6.320 6.198 6.198 3.324 9.544 9.527 7.197 7.197 6.841 8.903	Current [NAME EXPNO PROCNO)ata Parameters raj-3-84-prdt 2 1
	*	14	11				F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS	visition Parameters 1000217 16.06 drx400 5 mm Multinu zgpg30 65536 CDC13 1024 2
							SWH FIDRES AG RG DW DE	23148.148 Hz 0.353213 Hz 1.4156276 sec 1024 21.600 usec 4.50 usec
	а 4			5×	£		TE C'' d12 PL13 D1 CPDPRG2	300.0 K 0.0300000 sec 0.0000200 sec 18.00 dB 0.05000000 sec waltz16
л н к							PCPD2 SF02 NUC2 PL2 PL12 P1	100.00 usec 400.1316005 MHz H -6.00 dB 18.00 dB 6.90 usec
					1		DE SF01 NUC1 PL1	4.50 usec 100.6232933 MHz 13C -6.00 dB
							SI SF WDW SSB LB	32768 100.6127727 MHz EM 0 1.00 Hz
				19 fra 19 a fin star by the star			68 PC 10 NMR pi CX F1P	0 1.40 Lot parameters 20.00 cm 216.725 ppm
ppm 200	175	150	125	100	S+37 · · · · · · · · · · · · · · · · · · ·	50 25	F1 F2P F2 PPMCM HZCM	21805.33 Hz -2.285 ppm -229.92 Hz 10.95053 ppm/cm 1101.76270 Hz/cm



Ν3.













	Current Da	ata Parameters	
	NAME	ks3.266	- 14
	EXPNO	1	
	PROCNO	1	
	F2 - Acqu	isition Paramet	ers
	Date_	970414	
	Time	11.58	
	INSTRUM	drx400	
	PROBHD	5 mm Multinu	
	PULPROG	zg30	
	TD	32768	
	SOLVENT	CDC13	
	NS	16	
	DS	2	
	SWH	4789.272	Hz
	FIDRES	0.146157	Hz
	AG	3.4210291	SEC
	RG	128	
	DW	104.400	USEC
	DE	4.50	usec
	TE	300.0	к
	D1	1.00000000	sec
	P1	7.70	usec
	DE	4.50	usec
	SF01	400.1320007	MHZ
	NUC1	íH	
	PL1	-6.00	dB
	F2 - Proc	essing paramete	ers
	SI	16384	
	SF	400.1300000	MHz
	NDW	EM	
	SSB	0	
	LB	0.30	Hz
	GB	0	
1	PC	1.00	
	10 NMR pl	lot parameters	
	CX	20.00	Cm
	F1P	9.500	ppm
~~~~~	F1	3801.24	Hz
	F2P	-0.500	ppm
	F2	-200.07	Hz
	PPMCM	0.50000	ppm/cm
	HZCM	200.06500	Hz/cm





BnO, HO,







Integral



19.019		38.461 28.216 28.102 27.502 27.370	8.575 66.780 7.318 7.000 6.682 2.827 2.827 0.563	6. 530 9. 630 5. 400 6. 195 6. 195	4.622 2.033 1.345	0.603 9.516 8.350 7.981 6.672	3.003 2.413 2.312 2.232 8.871 8.170	Currer NAME EXPND PROCNO	<b>26</b> _{`s} raj-2-254-prdt 2 1
								F2 - Acqu Date_ Time	uisition Parameters 990827 7.40
4		1	11					INSTRUM PROBHD	drx400 5 mm Multinu
								PULPROG TD	zgpg30 65536
	10							SOLVENT	CDC13
								DS	1024
								SWH	23148.148 Hz
								FIDRES	0.353213 Hz
							· ·	RG	4096
								DW	21.600 usec
	1.2							TE	4.50 USEC 300.0 K
				22				d11	0.0300000 sec
					-			d12	0.0000200 sec
								D1	0.05000000 sec
								CPDPAG2	waltz16
								PCPD2	100.00 usec
						_		NUC2	400.1316003 MHZ 1H
				Ť		1.		PL2	-6.00 dB
				1			1	PL12	18.00 dB
		1	24	11				P1 DF	6.90 USEC
								SF01	100.6232933 MHz
								NUC1	13C
								PL1	-6.00 dB
								F2 - Proc	essing parameters
								SI	32768
<i></i>								SF	100.6127791 MHz
1								WDW	EM
								LB	1 00 Hz
								68	0
								PC	1.40
1 L.			1						nt narameters
					HI U			CX	20.00 cm
Personal States	an an an an anna an anna an anna an anna an an			اجوز بإلدية فبالمام فتدجعهم	Service and States	hereiter and the states of the second	where has a state of the second	F1P	230.000 ppm
								F1	23140.94 Hz
								F2P	-10.534 ppm -1059 82 87
ppm	200 150		100	5-46	50			PPMCM	12.02668 ppm/cm
							v	HZCM	1210.03796 Hz/cm

mqq











	28
Current D	ata Parameters
NAME	raj-2-231-prot
EXPINU	2
PHUCNU	1
F2 - Acqu	isition Parameters
Date_	990730
Time	0.14
INSTRUM	drx400
PHOBHD	5 mm Multinu
PULPROG	zgpg30
10	65536
SOLVENT	CDC13
NS	1024
DS	2
SWH	23148.148 Hz
FIUHES	0.353213 HZ
AQ	1.41562/6 Sec
HG	1024
UW	21.600 USEC
DE	4.50 USEC
IE	300.0 K
011	0.0300000 Sec
012	0.0000200 sec
PL13	18.00 68
U1	0.05000000 sec
LPUPH62	Walt210
PUPU2	100.00 0500
3502	400.1310003 MHz
NUC2	-6 00 49
FLC DL 42	18 00 48
DI	6 90 user
DC	4 50 usec
DC CCO1	4.30 0320
MUCI	130
DIS	-6 00 dB
FLI	0.00 00
F2 - Pro	cessing parameters
51	32/68
SF	100.612//34 MHZ
NUW	EM
558	0
LB	1.00 HZ
PC	1.40
	lot parameters
10 NMR p	20 00 cm
10 NMR p CX	20.00 cm
10 NMR p CX F1P F1	20.00 cm 225.000 ppm 22637 B7 Hz
10 NMR p CX F1P F1 F2P	20.00 cm 225.000 ppm 22637.87 Hz -5.000 ppm
10 NMR p CX F1P F1 F2P F2	20.00 cm 225.000 ppm 22637.87 Hz -5.000 ppm -503.05 Hz
10 NMR p CX F1P F1 F2P F2 PPMCM	20.00 cm 225.000 ppm 22637.87 Hz -5.000 ppm -503.06 Hz 11.50000 ppm/cm

77.321 77.003 76.685 69.685 69.685 69.685 69.685 50.773 34.571 34.183 34.571 34.183 34.571 29.636 29.636 29.636 29.636 29.636 29.636 29.636 29.636 29.636 29.636 29.636 29.636 29.636 29.636 29.636 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.773 20.7743 20.7743 20.7743 20.7744 20.7744 20.7744 20.7744 20

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<u>Ş-50</u> 75

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50

-----218.945

ppm

200

175

150







raj-2-261-prdt

1

1

990913

14.29

drx400

zg30

32768

CDC13

4789.272 Hz

0.146157 Hz

3.4210291 sec

812.7

104.400 usec

300.0 K

1.00000000 sec

400.1320007 MHz

4.50 usec

7.70 usec

4.50 usec

1H

-6.00 dB

16384

EM

0

0.30 Hz

0

20.00 cm

10.217 ppm

-0.325 ppm

0.52711 ppm/cm

4088.30 Hz

-129.94 Hz

210.91219 Hz/cm

1.00

400.1300077 MHz

16

2

5 mm Multinu



mdd







mdd

NH H 6

		×		:2					H H G Current Data	Parameters
					77.316 76.999 76.681 68.470		29.676 29.192 27.926 25.169 22.060	7.360	NAME EXPNO PROCNO F2 - Acquisit Date_ Time INSTRUM PROBHD 5 PULPROG TD SOLVENT NS OS SWH FIDRES AQ RG DW DE TE d11 d12 PL13 D1 CPDPRG2 PCPD2 PCPD2	ks2.240 1 1 1 1 1 1 1 1 1 1 1 1 1
									SF02 PL2 PL12 P1 DE SF01 NUC1 PL1 F2 - Process SI SF WDW SSB LB GB PC 10 NMR plot CX F1P	14 -6.00 dB 18.00 dB 6.90 usec 4.50 usec 100.6232933 MHz 13C -6.00 dB ing parameters 32768 100.6127741 MHz EM 0 1.00 Hz 0 1.40 parameters 20.00 cm 215.000 ppm
ppm 200	, , , , , , , , , , , , , , , , , , ,	150	125	100		50	25	0	F1 F2P F2 PPMCM HZCM	21631.75 Hz -5.000 ppm -503.07 Hz 11.00000 ppm/c 1106.74060 Hz/cm



Current D	lata Parameters	
NAME	ks3.287	
EXPNO	1	
PROCNO	1	
F2 - Acqu	isition Paramet	ers
Date_	970501	
Time	15.05	
INSTRUM	drx400	
PROBHD	5 mm Multinu	
PULPROG	zg30	
TD	32768	
SOLVENT	COC13	
NS	16	
DS	5	
SWH	4789.272	Hz
FIDRES	0.146157	Hz
AQ	3,4210291	Sec
RG	90.5	
DW	104,400	usec
DE	4.50	USEC
TE	300.0	К
D1	1.00000000	Sec
P1	7.70	USEC
DE	4.50	usec
SF01	400.1320007	MHZ
NUC1	1H	
PL1	-6.00	dB
F2 - Proc	essing paramete	ers
SI	16384	
SF	400.1300000	MHz
NDW	EM	
SSB	0	
LB	0 30	Hz
GB	0	
PC	1.00	
10 NMR p1	ot parameters	
CX	20.00	Cm
F1P	9,500	DOM
	3801.24	Hz
F1		
F1 F2P	-0.500	mqq
F1 F2P F2	-0.500	ppm Hz
F1 F2P F2 PPMCM	-0.500 -200.07 0.50000	ppm Hz ppm/cm



-N H Н 3

			×.						3	
			3			77.756 77.438 77.120 73.973	53.641 53.339 48.581 37.237 35.144 30.483 30.483 26.479	7.550	Current Data NAME EXPNO PROCNO F2 - Acquis Date_ Time INSTRUM PROBHD PULPROG TO SOLVENT NS DS SWH FIDRES AO RG DW DE TE d11 d12 PL13 D1 CPDPRG2 PCPD2 SF02 NUC2 PL2 PL12 PL12 PL12 PL1 DE	Parameters ks3.287 2 1 ition Parameters 970501 15.25 drx400 5 mm Multinu zgpg30 65536 CDC13 512 2 23148.148 Hz 0.353213 Hz 1.4156276 sec 32768 21.600 usec 4.50 usec 300.0 K 0.0300000 sec 18.00 dB 0.0500000 sec waltz16 100.00 usec 400.1316005 MHz 1H -6.00 dB 18.00 dB 18.00 dB 18.00 dB 18.00 dB 18.00 dB 18.00 dB 5.90 usec 4.50 usec
		he allows - have to all		Washing and a time to a	ar island the stress of	autouri distriction per l		Biss da 1 Jose 20 Incaste 1 Maduli	SF01 NUC1 PL1 F2 - Proce SI SF WDW SSB LB G8 PC 1D NMR plc CX	100.6232933 MHz 13C -6.00 dB ssing parameters 32768 100.6127290 MHz EM 0 1.00 Hz 0 1.40 t parameters 20.00 cm
in the state	tallahelte (Lassification) dan Konseration (Lassification) Konseration (Lassification)	states and a source of the sou	ulaura gila stilada upuna gila stilada	hi shinani kana a kana ka Appiranj kana a kana ka	an a	S-58	nfarkeland 14 from teater for our service National and the total service for the service of the		F1P F1 F2P F2	220.000 ppm 22134.80 Hz -5.000 ppm -503.07 Hz
ppm	200	175	150	125	100	75	50 25		PPMCM HZCM	11.25000 ppm/cm 1131.89319 Hz/cm

.... Ĥ N : H H

(+)-Aspido	ospermidine	(1)
EXPNO	1	. /
PROCNO	1	
F2 - Acqui	isition Paramet	ers
Date_	500000	
Time	15.22	
INSTRUM	drx400	
PROBHD	5 mm Multinu	
PULPROG	zg30	
TD	32768	
SOLVENT	CDC13	
NS	16	
DS	2	
SWH	4789.272	Hz
FIDRES	0.146157	Hz
AQ	3.4210291	sec
RG	256	
DW	104.400	usec
DE	4.50	usec
TE	300.0	К
D1	1.00000000	Sec
P1	7.70	usec
DE	4.50	usec
SF01	400.1320007	MHz
NUC1	1H	
PL1	-6.00	dB
F2 - Proc	essing paramete	ens
SI	16384	
SF	400.1300094	MHZ
WDW	EM	
SS8	0	
LB	0.30	Hz
GB	0	
PC	1.00	
10 NMR pl	ot parameters	
CX	20.00	СШ
F1P	10.166	ppm
F1	4067.84	Hz
F2P	-0.272	ppm
F2	-108.74	Hz
PPMCM	0.52190	ppm/cm
HZCM	208.82909	Hz/cm

. <b>.</b>			н (*)		
		3			
Integra1	0.8454 0.8715 0.8758 0.8539		1.0000	2.8604 1.8290 2.8529 3.7610 1.8935 0.9646 0.9646	
ppm	8	6	4°S-59	2	0



(+)-Aspidospermidine (1)

5

1

2

4096

1H

6.90 usec

4.50 usec

130

EM

0

1.00 Hz

0 1.40

Current Data Parameters NAME raj-3-71-pndt -127.029 -122.802 -118.935 77.315 76.997 76.679 71.229 65.629 53.843 53.339 52.996 38.798 35.603 34.438 29.941 28.068 22.971 21.741 135.692 6.782 EXPNO 149.375 110.291 PROCNO F2 - Acquisition Parameters 500000 Date_ Time 17.29 INSTRUM drx400 PROBHD 5 mm Multinu PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 1024 DS SWH 23148.148 Hz FIDRES 0.353213 Hz AQ 1.4156276 sec RG 21.600 usec DW DE 4.50 usec TE 300.0 K 0.0300000 sec d11 0.0000200 sec d12 PL13 18.00 dB D1 0.05000000 sec waltz16 CPDPRG2 PCPD2 100.00 usec SF02 400.1316005 MHz 1 NUC2 -6.00 dB PL2 PL12 18.00 dB P1 DE SF01 100.6232933 MHz NUC1 PL1 -6.00 dB F2 - Processing parameters SI 32768 SF 100.6127741 MHz NDW SSB LB GB PC 1D NMR plot parameters CX 20.00 cm F1P 204.851 ppm F1 20610.64 Hz F2P -1.215 ppm S-60 F2 -122.26 Hz 75 ppm 175 150 125 100 50 25 PPMCM 10.30331 ppm/cm HZCM 1036.64478 Hz/cm

mdd



