Studies towards synthesis of tetracyclic core of daphmanidin A-type alkaloids

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SUPPORTING INFORMATION

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Full experimental detail

All the products were characterized by IR, ^1H NMR, ^{13}C NMR and mass spectroscopy.

1,7-Allylspiro[bicyclo[2.2.2]oct[5]ene-2,2'-[1,3]dioxolan]-7-yl)prop-2-en-1-one (6)

To a stirred solution of compound **7** (0.15 g, 0.57 mmol) and *N*-methylmorpholine-*N*-oxide (NMO) (0.13 g, 1.12 mmol) in dry dichloromethane (25 mL) was added powdered molecular sieves (4Å, 0.5 g) and TPAP (0.01 g, 0.02 mmol) at room temperature under nitrogen atmosphere. After completion of the reaction (TLC, 10 h), it was filtered through a small pad of Celite and washed with dichloromethane (20 mL). Solvent was removed and the product was chromatographed on silica gel (petroleum ether/ethyl acetate 80:20) to

give the compound **6** (0.13 g, 87%) as a colorless liquid [R_f = 0.6 petroleum ether/ethyl acetate (80:20)]. IR (film) ν_{max} : 2930, 1696 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 6.74 (dd, J_1 = 16.9 Hz, J_2 = 10.3 Hz, 1H), 6.29 (dd, J_1 = 16.9 Hz, J_2 = 2.0 Hz, 1H), 6.23-6.12 (m, 2H), 5.64 (dd, J_1 = 10.3 Hz, J_2 = 2.0 Hz, 1H), 5.60-5.48 (m, 1H), 5.01-4.93 (m, 2H), 4.04-3.83 (m, 4H), 2.95 (d with structure, J = 6.3 Hz, 1H), 2.84-2.69 (m, 3H), 2.43 (dt, J_1 = 13.0 Hz, J_2 = 3.2 Hz, 1H), 1.85-1.75 (m, 2H), 1.39 (dd, J_1 = 13.0 Hz, J_2 = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 200.5, 134.7, 134.2, 132.4, 132.1, 128.8, 117.6, 113.4, 64.9, 63.2, 55.3, 43.2, 42.5, 42.0, 34.9, 31.3. HRMS (ESI): m/z $[\text{M} + \text{H}]^+$ calcd. for $\text{C}_{16}\text{H}_{21}\text{O}_3$: 261.1491; found: 261.1491.

Dispiro[cyclopent[4]enone-2,2'-bicyclo[2.2.2]oct[7]ene-6',2''-[1,3]dioxolane] (5)

To a degassed solution of compound **6** (0.1 g, 0.38 mmol) in dichloromethane (50 mL) was added Grubbs' 1st generation catalyst (0.015 g, 0.02 mmol) and the reaction mixture was stirred at ambient temperature under nitrogen atmosphere for 5 h. Removal of solvent followed by chromatography on silica gel [petroleum ether/ethyl acetate (70:30)] gave the product **5** (0.085 g, 96%) as a colorless liquid [R_f = 0.4 petroleum ether/ethyl acetate (80:20)]. IR (film) ν_{max} : 2931,

1704, 1124 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 7.66-7.62 (m, 1H), 6.38 (superimposed dd, $J_1 = J_2 = 7.8$ Hz, 1H), 6.29 (superimposed dd with structure, $J_1 = J_2 = 7.8$ Hz, 1H), 6.08 (dt, J_1 = 5.8 Hz, J_2 = 2.1 Hz, 1H), 4.01-3.80 (m, 4H), 3.57 (dt, J_1 = 19.6 Hz, J_2 = 2.5 Hz, 1H), 2.82-2.74 (m, 1H), 2.56 (dt, J_1 = 19.6 Hz, J_2 = 2.5 Hz, 1H), 2.38 (d, J = 6.6 Hz, 1H), 1.88-1.72 (m, 2H), 1.48 (dd, J_1 = 12.2 Hz, J_2 = 2.7 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 212.4, 162.3,

132.2, 131.9, 131.7, 112.9, 64.2, 63.1, 48.3, 45.5, 43.9, 40.3, 40.0, 31.4. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{14}H_{17}O_3$: 233.1178; found: 233.1168.

Dispiro[[1,3]-dioxolane-2,6'-bicyclo[2.2.2]octane-2',2''-cyclopentanone] (9)

To a solution of compound **5** (0.5 g, 2.15 mmol) in EtOH (35 mL) was added Pd on carbon (5 % wt/wt, 0.08 g) at room temperature. The resulting mixture was stirred under hydrogen atmosphere (balloon) for 3 h. The reaction mixture was filtered through a pad of Celite and the filtrate was concentrated in vacuum. The resulting product was purified by

column chromatography on silica gel. Elution with petroleum ether/ethyl acetate (90:10) gave the desired compound **9** (0.485 g, 95%) as a colorless liquid, [R_f = 0.4 petroleum ether/ethyl acetate (90:10)]. IR (film) ν_{max} : 2924, 1732, 1094 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 4.06-3.81 (m, 4H), 2.79-2.71

(m, 1H), 2.31 (dd of part of an AB system with structure, $J_1 = 19.2$ Hz, $J_2 = 9.4$ Hz, $J_3 = 4.8$ Hz, 1H), 2.22-2.11 (m, 1H), 1.97-1.91 (m, 1H), 1.90-1.77 (m, 4H), 1.76-1.62 (m, 4H), 1.59-1.50 (m, 2H), 1.46-1.37 (m, 1H), 1.20 (dt, $J_1 = 13.0$ Hz, $J_2 = 3.0$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.3, 110.6, 64.1, 63.1, 49.3, 40.7, 38.2, 36.3, 34.6, 34.4, 26.9, 23.4, 17.7, 17.4. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{14}H_{21}O_3$: 237.1491; found: 237.1482.

5''-Allyl-dispiro[[1,3]-dioxolane-2,6'-bicyclo[2.2.2]octane-2',2''-cyclopentanone] (11) and diallylated compound (10)

To a freshly prepared solution of LDA (0.63 mmol) in THF (prepared from *n*-BuLi and diisopropylamine at -78 °C) was added a solution of compound **9** (0.1 g, 0.42 mmol) in THF at -78 °C under nitrogen. The reaction mixture was stirred at -78 °C for 1 h after which allyl bromide (0.05 mL, 0.41 mmol) was added dropwise. After further stirring for 1 h, the reaction mixture was quenched by saturated solution of ammonium chloride and organic layer was separated. The aqueous layer was extracted with ether (2×20 mL). Combined organic extract was washed with brine (15 mL) and dried over anhydrous Na_2SO_4 . Removal of solvent followed by column chromatography [petroleum ether/ethyl

acetate (97:3)] gave the minor diallylated compound **10** (0.007 g, 5%) as a colorless liquid [R_f = 0.2 petroleum ether/ethyl acetate (90:10)]. IR (film) ν_{max} : 2925, 1724, 1120 cm^{-1} . 1H NMR (400 MHz, $CDCl_3$): δ 5.74-5.62 (m, 2H), 5.09-4.99 (m, 4H), 4.02-3.80 (m, 4H), 2.70-2.62 (m, 1H), 2.23-2.08 (m, 4H), 1.95-1.71 (m, 5H), 1.70-1.48 (m, 5H), 1.46-1.35 (m, 1H), 1.33-1.23 (m, 1H), 1.18 (dt, $J_1 = 13.2$ Hz, $J_2 = 3.0$ Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 224.1, 134.4, 134.1, 118.4, 118.3, 110.7, 64.1, 63.1, 51.8, 49.7, 41.5, 41.4, 40.8, 36.5, 35.5, 35.1,

28.3, 27.1, 23.5, 17.2. HRMS (ESI): m/z $[M + H]^+$ calcd. for $C_{20}H_{29}O_3$: 317.2117; found: 317.2116.

Continued elution with petroleum ether/ethyl acetate (95:5) furnished the mono alkylated product **11** (0.08 g, 75%, mixture of diastereoisomers) as a colorless liquid [R_f = 0.3 petroleum ether/ethyl acetate (90:10)]. IR (film) ν_{max} : 2928, 2875, 1726 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): 5.79-5.65 (m, 1H), 5.07-4.95 (m, 2H), 4.03-3.78 (m, 4H), 2.90-2.82 and 2.51-2.34 (m, 2H), 2.32-2.23 (m, 1H), 2.20-1.87 (m, 4H), 1.86-1.72 (m, 3H), 1.70-1.60 (m, 3H), 1.59-1.32 (m, 3H), 1.16 (dt, J_1 = 12.9 Hz, J_2 = 3.0 Hz, 1H) (signals due to both isomers). ^{13}C NMR (100 MHz, $CDCl_3$): δ 222.1, 136.4, 136.1, 116.5, 116.4, 110.5, 64.2, 64.1, 63.2, 49.9, 49.1,

47.7, 46.7, 40.8, 40.7, 37.3, 36.6, 36.4, 36.1, 35.8, 35.5, 35.0, 33.5, 27.2, 26.9, 24.5, 24.0, 23.5, 23.4, 17.4, 17.2 (signals due to both isomers). HRMS (ESI): m/z $[M + Na]^+$ calcd. for $C_{17}H_{24}O_3Na$: 299.1623; found: 299.1630.

5''-([2]Oxopropyl)dispiro[[1,3]-dioxolane-2,6'-bicyclo[2.2.2]octane-2',2''-cyclopentanone] (**12**)

To a mixture of $PdCl_2$ (0.015 g, 0.08 mmol), $CuCl_2$ (0.035 g, 0.36 mmol) in N,N -dimethyl formamide (DMF) and H_2O (4:2 mL) oxygen gas was bubbled for 15 min. A solution of compound **11** (0.1 g, 0.36 mmol) in DMF (4 mL) was added to the reaction mixture and it was stirred for 24 h under oxygen atmosphere. After which water (10 mL)

was added to the reaction mixture and stirred. Reaction mixture was extracted with ethyl acetate (3×15 mL) and organic layer was washed with brine (10 mL) and dried over Na_2SO_4 . Removal of solvent followed by chromatography [petroleum ether/ethyl acetate (70:30)] gave compound **12** (0.04 g, 40%, mixture of diastereoisomers) as colorless liquid [R_f = 0.5 petroleum ether/ethyl acetate (70:30)]. IR (film) ν_{max} : 2932, 2879, 1718 cm^{-1} .

1H NMR (400 MHz, $CDCl_3$): 4.05-3.81 (m, 4H), 2.97-2.84 (m, 1H), 2.76-2.67 (m, 1H), 2.58-2.35 (m, 2H), 2.22-2.09 (m merged with s, 4H), 1.95-1.83 (m, 2H), 1.82-1.78 (m, 2H), 1.77-1.60 (m, 4H), 1.58-1.48 (m, 1H), 1.47-1.31 (m, 2H), 1.27-1.20 (m, 1H) (signals due to both isomers). ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.9, 221.8, 207.2, 206.7, 110.7, 110.4, 64.1, 64.0, 63.2, 63.1, 48.5, 45.3, 44.3, 44.0, 43.2, 40.7, 40.6, 37.6, 37.0, 36.6, 36.3, 35.9, 34.1, 30.3, 30.0, 27.2, 26.9, 25.5, 25.2, 23.5, 23.3, 17.4, 17.1 (signals due to both isomers). HRMS (ESI): m/z $[M + Na]^+$ calcd. for $C_{17}H_{24}O_4Na$: 315.1572; found: 315.1565.

5''-Allyl-5''-methyl-dispiro[[1,3]-dioxolane-2,6'-bicyclo[2.2.2]octane-2',2''-cyclopentanone] (14)

NaH (0.1 g, 60% w/w suspension in mineral oil) was placed in a round bottom flask and washed with petroleum ether (3×5 mL), and dry THF (5 mL) was added to it. The reaction mixture was cooled and a solution of compound **11** (0.3 g, 1.09 mmol) in THF was added slowly to the reaction mixture and then it was refluxed for 1 h under nitrogen atmosphere. Methyl iodide (0.5 mL, excess) was added to the reaction mixture and the reaction mixture was further refluxed for ~3 h. After which the reaction mixture was cooled and quenched by careful addition of cold water. Solid NaCl was added to the reaction mixture and stirred. THF layer was separated and aqueous layer was extracted with ether (2×20 mL). The combined organic extract was washed with brine (10 mL) and dried over Na_2SO_4 . Solvent was removed under vacuum and residue was purified by column chromatography. Elution with petroleum ether/ethyl acetate (90:10) gave the product **14** (0.26 g, 82%, mixture of diastereoisomers) as a colorless liquid. [$R_f = 0.6$ petroleum ether/ethyl acetate (90:10)]. IR (film) ν_{max} : 2929, 2879, 1726 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.75-5.63 (m, 1H), 5.08-5.01 (m, 2H), 4.05-3.97 and 3.91-3.80 (m, total 4H), 2.80-2.71 and 2.62-2.54 (m, total 1H), 2.20-2.05 and 2.00-1.89 (m, total 4H), 1.88-1.70 (m, 4H), 1.70-1.62 (m, 2H), 1.62-1.47 (m, 3H), 1.47-1.37 and 1.27-1.18 (m, total 2H), 1.02 and 1.00 (s, total 3H) (signals due to both isomers). ^{13}C NMR (100 MHz, CDCl_3): δ 225.0, 224.8, 134.5, 134.2, 118.2, 118.1, 110.64, 110.58, 64.1, 64.0, 63.1, 63.0, 49.9, 49.5, 48.1, 48.0, 42.8, 42.7, 40.7, 40.6, 36.5, 36.3, 36.1, 35.7, 35.0, 34.3, 31.3, 30.9, 27.1, 27.0, 24.1, 23.9, 23.5, 17.3, 17.2 (signals due to both isomers). HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{26}\text{NaO}_3$: 313.1774; found: 313.1772.

5''-Methyl-5''-([2]oxopropyl)dispiro[[1,3]-dioxolane-2,6'-bicyclo[2.2.2]octane-2',2''-cyclopentanone] (15a,b)

To a mixture of CuCl_2 (0.065 g, 0.65 mmol) in DMF-water (4-1 mL), PdCl_2 (0.025 g, 0.14 mmol) was added and oxygen gas was bubbled for 15 min. A solution of compound **14** (0.2 g, 0.68 mmol) in DMF (3 mL) was added dropwise to the reaction mixture and it was stirred for 30 h under oxygen atmosphere at room temperature. After which water was added and the reaction mixture was extracted with ethyl acetate (3×20 mL). The combined organic extract was washed with brine (10 mL) and dried over Na_2SO_4 .

Solvent was removed and the product was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (70:30) gave the minor product **15a** (0.065 g, 31%) as a colorless liquid [R_f = 0.4 petroleum ether/ethyl acetate (80:20)]. IR (film) $\nu_{\max}$: 2930, 2875, 1720 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.05-3.96 (m, 1H), 3.95-3.81 (m, 3H), 2.67 (AB system, J = 17.4 Hz, 2H), 2.53-2.44 (m, 1H), 2.20-2.11 (m, 1H), 2.10 (s, 3H), 2.02-1.94 (m, 2H), 1.86-1.79 (m, 2H), 1.78-1.54 (m, 6H), 1.49-1.34 (m, 2H), 1.04 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 225.0, 206.8, 110.6, 64.0, 63.2, 51.3, 48.6, 46.8, 40.7, 38.2, 38.0, 36.6, 31.2, 31.1, 27.3, 23.9, 23.5, 17.2. HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{26}\text{NaO}_4$: 329.1723; found: 329.1723.

Continued elution with petroleum ether/ethyl acetate (70:30) gave the major product **15b** as a colorless liquid (0.11 g, 52%) [R_f = 0.35 petroleum ether/ethyl acetate (80:20)]. IR (film) $\nu_{\max}$: 2932, 2878, 1723 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 4.04-3.82 (m, 4H), 2.95 (ddd, J_1 = 13.3 Hz, J_2 = 6.5 Hz, J_3 = 2.9 Hz, 1H), 2.64 (AB system, J = 17.6 Hz, 2H), 2.10 (s, 3H), 2.04-1.88 (m, 2H), 1.87-1.62 (m, 7H), 1.60-1.36 (m, 3H), 1.26 (dt, J_1 = 12.9 Hz, J_2 = 2.9 Hz, 1H), 1.01 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 224.8, 206.8, 110.9, 64.1, 63.1, 51.5, 49.8, 46.4, 40.9, 37.6, 35.2, 34.9, 31.8, 31.1, 27.1, 24.2, 23.6, 17.3. HRMS (ESI): m/z $[\text{M} + \text{Na}]^+$ calcd. for $\text{C}_{18}\text{H}_{26}\text{NaO}_4$: 329.1724; found: 329.1723.

5''-Methyl-dispiro[[1,3]-dioxolane-2,6'-bicyclo[2.2.2]octane-2',8''-bicyclo[3.3.0]^{1,5}octen-3-one] (**16b**)

To a solution of compound **15b** (0.2 g, 0.65 mmol) in t -BuOH (10 mL) was added KO^tBu (0.15 g, 1.33 mmol) and the reaction mixture was stirred at room temperature for 3 h. Solvent was removed and water (10 mL) was added to reaction mixture and it was extracted with ethyl acetate (3×20 mL). Combined organic layer was washed with brine (20 mL) and dried over Na_2SO_4 . Solvent was removed and the product was purified by column chromatography on silica gel. Elution with petroleum ether/ethyl acetate (70:30) gave the aldol product **16b** (0.155 g, 82%) as a colorless liquid [R_f = 0.5 petroleum ether/ethyl acetate (70:30)]. IR (film) $\nu_{\max}$: 2928, 2868, 1706 cm^{-1} . ^1H NMR (400 MHz, CDCl_3): δ 5.81 (s, 1 H), 4.05-3.81 (m, 4H), 2.41 (part of an AB system, J = 16.8 Hz, 1H), 2.31 (part of an AB system, J = 16.8 Hz, 1H), 2.14-2.06 (m, 1H), 2.06-1.96 (m, 2H), 1.96-1.87 (m, 1H), 1.88-1.80 (m, 3H), 1.79-1.76 (m, 3H), 1.71-1.66 (m, 1H), 1.62-1.58 (m, 1H), 1.58-1.42 (m, 2H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 211.4, 200.0, 121.4, 110.4, 63.8, 63.4, 54.9, 49.4,

44.9, 42.3, 40.2, 40.0, 38.9, 34.4, 30.1, 27.3, 23.9, 19.9. HRMS (ESI): m/z $[M + Na]^+$ calcd. for $C_{18}H_{24}NaO_3$: 311.1619; found: 311.1618.

5'-Methylspiro[bicyclo[2.2.2]octane-6-one-2,8'-bicyclo[3.3.0]^{1,5}octen-3-one] (17)

To a solution of compound **16b** (0.1 g, 0.35 mmol) in acetone-H₂O (20 mL, 4:1) was added HCl (10%, 1.0 mL) at 0-5 °C and the reaction mixture was stirred for 1 h at ambient temperature. After which the reaction mixture was neutralized with NaHCO₃ and acetone was removed under vacuum. It was diluted with water and extracted with ether (2 × 20 mL). The combined extract was washed with brine (10 mL) and dried over Na₂SO₄. Solvent was removed under vacuum and the product was chromatographed on silica gel. Elution with petroleum ether/ethyl acetate (60:40) gave the product **17** (0.081 g, 95%) as a colorless solid, mp 130-132 °C, [R_f = 0.4 petroleum ether/ethyl acetate (65:35)]. IR (KBr)

ν_{max} : 2938, 2875, 1719, 1698 cm⁻¹. ¹H NMR (500 MHz, CDCl₃): δ 6.00 (s, 1H), 2.38 (part of an AB system, J = 13.9 Hz, 1H), 2.37-2.31 (m, 2H), 2.31-2.25 (m merged with part of an AB system, J = 13.9 Hz, total 3H), 2.14-2.09 (m, 2H), 2.05-1.92 (m, 2H), 1.91-1.84 (m, 2H), 1.81-1.76 (m, 1H), 1.73-1.64 (m, 2H), 1.53 (dd with structure, J_1 = 19.1 Hz, J_2 = 9.8 Hz, 1H), 1.24 (s, 3H).

¹³C NMR (125 MHz, CDCl₃): δ 214.1, 210.9, 198.4, 121.6, 52.6, 52.2, 51.4, 44.1, 43.4, 43.1, 41.9, 35.7, 29.1, 27.3, 24.3, 19.1. HRMS (ESI): m/z $[M + Na]^+$ calcd. for $C_{16}H_{20}NaO_2$: 267.1358; found: 267.1356.

Crystal data of compound **17**: $C_{16}H_{20}O_2$, M = 244.32, Triclinic, space group P -1, a = 8.853(2) Å, b = 12.257 (4) Å, c = 12.557 (4) Å, α = 87.650(11)°, β = 71.8650(10)°, γ = 81.881(10)°, V = 1281.9(7) Å³, D_c = 1.266 Mg m⁻³, Z = 4, $F(000)$ = 528, Size: 0.46 x 0.34 x 0.08 mm³, Wavelength = 0.71070 Å, GoF = 0.879, Absorption coefficient = 0.082 mm⁻¹, Total/unique reflections = 27062 / 6887 [R (int) = 0.1528], T = 100 (2) K, θ range = 3.15 to 29.17°, Final R [$I > 2s(I)$]: R_1 = 0.0659, wR_2 = 0.1495, R (all data): R_1 = 0.1091, wR_2 = 0.1858. Crystallographic data has been deposited with Cambridge Crystallographic data Centre, CCDC no. 1050400. Copy of the data can be obtained, free of charge, on application to CCDC. E-mail. Deposit@ccdc.cam.ac.Uk

NAME VKS-BD-Vketo-1H
EXPNO 9
PROCNO 1
Date_ 20120110
Time 10.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 23
DS 0
SWH 9615.385 Hz
FIDRES 0.146719 Hz
AQ 3.4079220 sec
RG 32
DW 52.000 usec
DE 6.50 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300051 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

¹H NMR (400 MHz, CDCl₃) spectrum of **6**

^{13}C NMR (100 MHz, CDCl_3) spectrum of **6**

¹H NMR (400 MHz, CDCl₃) spectrum of **5**

^{13}C NMR (100 MHz, CDCl_3) spectrum of **5**

NAME VKS-BD-Hydro-1H
EXPNO 33
PROCNO 2
Date_ 20120410
Time_ 15.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 40960
SOLVENT CDCl3
NS 21
DS 0
SWH 10416.667 Hz
FIDRES 0.254313 Hz
AQ 1.9661300 sec
RG 80.6
DW 48.000 usec
DE 6.50 usec
TE 293.3 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324008 MHz
SI 32768
SF 400.1299881 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

¹H NMR (400 MHz, CDCl₃) spectrum of **9**

^{13}C NMR (100 MHz, CDCl_3) spectrum of **9**

```
NAME      vks-bd-allyl-NaH-1ST-1H
EXPNO      4
PROCNO     1
Date_      20120416
Time       18.29
INSTRUM    spect
PROBHD     5 mm PABBO BB-
PULPROG    zg30
TD         65536
SOLVENT    CDCl3
NS         21
DS         0
SWH        8223.685 Hz
FIDRES     0.125483 Hz
AQ         3.9846387 sec
RG         114
DW         60.800 usec
DE         6.50 usec
TE         294.7 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         13.50 usec
PL1        -1.00 dB
PL1W       10.56200695 W
SF01       400.1324710 MHz
SI         32768
SF         400.1300094 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
```

¹H NMR (400 MHz, CDCl₃) spectrum of **10**

^{13}C NMR (100 MHz, CDCl_3) spectrum of **10**

¹H NMR (400 MHz, CDCl₃) spectrum of **11**

¹³C NMR (100 MHz, CDCl₃) spectrum of **11**

¹H NMR (400 MHz, CDCl₃) spectrum of **12**

^{13}C NMR (100 MHz, CDCl_3) spectrum of **12**

NAME VKS-BD-Me-1H
EXPNO 4
PROCNO 1
Date_ 20130307
Time_ 11.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 56336
SOLVENT CDCl3
NS 15
DS 0
SWH 8802.817 Hz
FIDRES 0.156256 Hz
AQ 3.1999347 sec
RG 32
DW 56.800 usec
DE 6.50 usec
TE 293.3 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1299940 MHz
WDW EM
SSB 0
LB 0.00 Hz
GB 0
PC 1.00

¹H NMR (400 MHz, CDCl₃) spectrum of **14**

^{13}C NMR (100 MHz, CDCl_3) spectrum of **14**

```
NAME      VKS-BD-1stOx-1H
EXPNO     5
PROCNO    1
Date_     20130312
Time      10.46
INSTRUM   spect
PROBHD    5 mm PABBO BB-
PULPROG   zg30
TD        50986
SOLVENT   CDCl3
NS        27
DS        0
SWH       8223.685 Hz
FIDRES    0.161293 Hz
AQ        3.0999987 sec
RG        32
DW        60.800 usec
DE        6.50 usec
TE        294.2 K
D1        1.00000000 sec
TD0       1

===== CHANNEL f1 =====
NUC1      1H
P1        13.50 usec
PL1       -1.00 dB
PL1W      10.56200695 W
SFO1      400.1324710 MHz
SI        32768
SF        400.1300056 MHz
WDW       EM
SSB       0
LB        0.20 Hz
GB        0
PC        1.00
```

¹H NMR (400 MHz, CDCl₃) spectrum of **15a**

¹³C NMR (100 MHz, CDCl₃) spectrum of **15a**

NAME VKS-BD-2ND-OX-2-1)
EXPNO 13
PROCNO 1
Date 20131031
Time 23.55
INSTRUM spect
PROBHD 5 mm SEI 1H/D-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 15
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 se
RG 101
DW 60.800 us
DE 6.50 us
TE 294.4 K
D1 1.00000000 se
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 6.75 us
PL1 -3.00 dB
PL1W 16.73965454 W
SFO1 400.1324710 MH:
SI 32768
SF 400.1300106 MH:
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹H NMR (400 MHz, CDCl₃) spectrum of **15b**

^{13}C NMR (100 MHz, CDCl_3) spectrum of **15b**

NAME VKS-BD-ALDOL-1H
EXPNO 8
PROCNO 1
Date_ 20130318
Time_ 21.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 12
DS 0
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 128
DW 60.800 usec
DE 6.50 usec
TE 293.5 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 13.50 usec
PL1 -1.00 dB
PL1W 10.56200695 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300051 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹H NMR (400 MHz, CDCl₃) spectrum of **16b**

¹³C NMR (100 MHz, CDCl₃) spectrum of **16b**

Current Data Parameters
NAME VKS-BD-ALDOL-1H
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20140105
Time 11.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 18
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 134.65
DW 50.000 usec
DE 6.50 usec
TE 297.8 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
SFO1 500.1330885 MHz
NUC1 1H
P1 13.00 usec
PLW1 13.00000000 W

F2 - Processing parameters
SI 65536
SF 500.1300125 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹H NMR (500 MHz, CDCl₃) spectrum of **17**

 ^{13}C NMR (125 MHz, CDCl_3) spectrum of **17**