Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Synthesis of the 2-Formylpyrrole Spiroketal Pollenopyrroside A and Structural Elucidation of Xylapyrroside A, Shensongine A and Capparisine B

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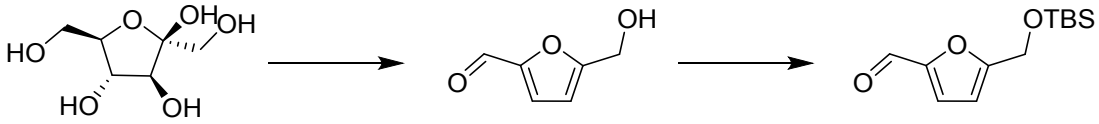
General Experimental

Unless otherwise noted, all reactions were performed under an oxygen-free atmosphere of nitrogen using standard techniques. All reagents were used as received unless otherwise noted. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin layer chromatography (TLC) carried out on silica gel plates using UV light as visualizing agent, followed by staining with vanillin, potassium permanganate or ninhydrin. Silica gel (60, 230-400 mesh) was used for flash column chromatography. Melting points are uncorrected. Optical rotations were measured with an Autopol® IV automatic polarimeter, using the Na-D line (589 nm) with the concentration of the solution measured in g/100 mL. Infrared (IR) spectra were recorded using a Perkin Elmer Spectrum 100 FT-IR spectrometer on a film ATR sampling accessory. Absorption maxima are expressed in wavenumbers (cm^{-1}) and recorded using a range of 450-4000 cm^{-1}. NMR spectra were recorded at room temperature in $CDCl_3$, on a spectrometer operating at 400 MHz for ^{1}H nuclei and 100 MHz for ^{13}C nuclei. Chemical shifts are reported in parts per million (ppm) on the δ scale and coupling constants, *J*, are in hertz (Hz). Multiplicities are reported as "s" (singlet), "br s" (broad singlet), "d" (doublet), "dd" (doublet of doublets), "t" (triplet), "m" (multiplet), "ABq" (AB quartet), and ABX. ^{1}H and ^{13}C NMR resonances were assigned using a combination of DEPT 135, COSY, HSQC, and HMBC spectra. High-resolution mass spectra (HRMS) were obtained using a Bruker microTOF-Q II mass spectrometer operating at a nominal accelerating voltage of 70 eV.



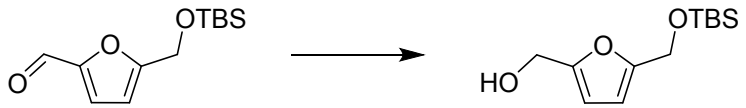
S1 **18**

5-tert-Butyldimethylsilyloxymethyl-furan-2-carbaldehyde (18)

A stirred solution of D-fructose (21.6 g, 120 mmol) and oxalic acid dihydrate (1.5 g, 11.9 mmol) in DMSO (60 mL) was heated at 150 °C for 6 h, then cooled to room temperature. The reaction was diluted with water (150 mL) and then extracted with EtOAc (4 × 150 mL). The combined organic extracts were washed with brine (2 × 75 mL), dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude extract was passed through a plug of silica, washing with EtOAc-petroleum ether (3:1) and concentrated *in vacuo* to afford crude 5-hydroxymethyl furfural (**S1**) which was used directly in the next step.

To a stirred solution of 5-hydroxymethyl furfural (**S1**) in CH_2Cl_2 (240 mL) was added imidazole (9.1 g, 134 mmol) and the mixture cooled to 0 °C. TBSCl (19.7 g, 131 mmol) was added portionwise and the reaction stirred for 18 h at r.t. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ (120 mL) and the layers separated. The aqueous layer was extracted with CH_2Cl_2 (120 mL) and the combined organic layers were washed with brine (100 mL), dried over Na_2SO_4 and concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 20:1) afforded the *title compound* **18** (26.4 g, 110 mmol, 92 % over two steps) as a colourless oil. R_f 0.45 (petroleum ether-EtOAc 7:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 7.19 (d, 1H, J = 3.7 Hz), 6.46 (d, 1H, J = 3.7 Hz), 4.73 (s, 2H), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7 (CH), 161.6 (C), 152.4 (C), 122.5 (CH), 109.5 (CH), 58.7 (CH_2), 25.9 (3 × CH_3), 18.5 (C), −5.2 (2 × CH_3); the spectroscopic data were in agreement with those reported in the literature.[1]

[1] McNelis, B. J.; Sternbach, D. D.; MacPhail, A. T. *Tetrahedron* **1994**, *50* (23), 6767–6782

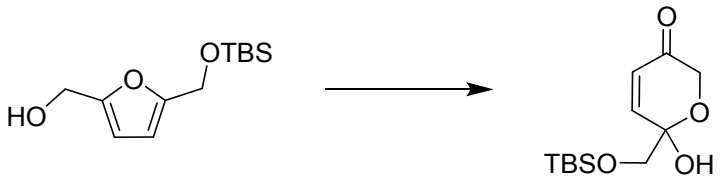


18 **17**

2-tert-Butyldimethylsilyloxymethyl-5-hydroxymethyl-furan (17)

To a stirred solution of aldehyde **18** (11.4 g, 48 mmol) in MeOH (150 mL) at 0 °C was added $NaBH_4$ (3.5 g, 93 mmol) portionwise. After stirring at 0 °C for 15 min, the reaction was quenched by the addition of H_2O (10 mL) and MeOH was removed under reduced pressure. The residue was partitioned with H_2O (100 mL) and EtOAc (150 mL). The organic layer was separated and the aqueous layer further extracted with EtOAc (2 × 150 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to afford the *title compound* **17** (11.2 g, 46 mmol, 98%) as a colourless oil that was used in the next step without further purification. R_f 0.33 (petroleum ether-EtOAc 7:1) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.22 (d, 1H, J = 3.2 Hz), 6.17 (d, 1H, J = 3.2 Hz), 4.62 (s, 2H), 4.57 (br s, 2H), 1.81 (br s, 1H), 0.90 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.6 (C), 153.7 (C), 108.6 (CH), 108.1 (CH), 58.4 (CH_2), 57.8 (CH_2), 26.0 (3 × CH_3), 18.6 (C), −5.1 (2 × CH_3); the spectroscopic data were in agreement with those reported in the literature.[2]

[2] Celanire, S.; Marlin, F.; Baldwin, J. E.; Adlington, R. M. *Tetrahedron* **2005**, *61* (12), 3025–3032

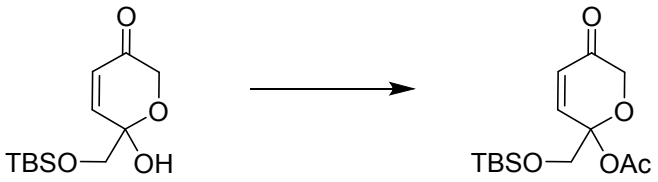


17 **14**

6-tert-Butyldimethylsilyloxymethyl-6-hydroxy-2H-pyran-3(6H)-one (14)

To a stirred solution of alcohol **17** (7.06 g, 29 mmol) in CH_2Cl_2 (230 mL) was added *m*-CPBA (6.44 g, 37 mmol, 75% *w/w*) at 0 °C. After stirring at 0 °C for 30 min, the reaction mixture was warmed to r.t. with stirring for an additional 30 min. The reaction was quenched by the addition of sat. aq. Na_2SO_3 (200 mL) followed by neutralisation with 1 M NaOH solution to reach pH 7-8. The resulting mixture was extracted with CH_2Cl_2 (2 × 150 mL) and concentrated *in vacuo* to give the *title compound* **14** (6.47 g, 25.1 mmol, 86 %) as a white solid. R_f 0.50 (petroleum ether-EtOAc 3:1); m.p. 82.3-84.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, 1H , J = 10.4 Hz), 6.15 (d, 1H, J = 10.4 Hz), 4.59 (d, 1H, J = 16.9 Hz), 4.14 (d, 1H, J = 16.9 Hz), 3.73 (ABq, 2H), 3.70 (br s, 1H), 0.93 (s, 9H), 0.12 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2 (C), 145.9 (CH), 128.7 (CH), 92.6 (C), 68.0 (CH_2), 66.8 (CH_2), 26.0 (3 × CH_3), 18.5 (C), −5.1 (CH_3), −5.3 (CH_3); the spectroscopic data were in agreement with those reported in the literature.[3]

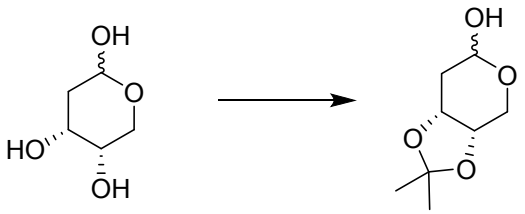
[3] Geng, H. M.; Chen, J. L.-Y.; Furkert, D. P.; Jiang, S.; Brimble, M. A. *Synlett* **2012**, *23* (6), 855–858



14 **22**

6-tert-Butyldimethylsilyloxymethyl-6-acetoxy-2H-pyran-3(6H)-one (22)

To a stirred solution of dihydropyranone **14** (1.04 g, 4.0 mmol) in CH_2Cl_2 (48 mL) at 0 °C was added acetic anhydride (8 mL, 85 mmol), pyridine (4 mL, 50 mmol) and DMAP (49 mg, 0.40 mmol). The resultant mixture was stirred at 0 °C for 90 min, then washed successively with 0.1 M HCl (50 mL), sat. aq. $NaHCO_3$ (50 mL) and brine (60 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo* to afford the *title compound* **22** (1.10 g, 3.7 mmol, 91 %) as a pale yellow oil which was used without further purification. R_f 0.68 (petroleum ether-EtOAc 3:1); IR (neat) ν_{max} 2930, 2858, 1741, 1701, 1464, 1368, 1239, 1114, 834, 777 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, 1H, J = 10.5 Hz), 6.12 (d, 1H, J = 10.5 Hz), 4.50 (d, 1H, J = 17.1 Hz), 4.17 (d, 1H, J = 17.1 Hz), 4.03 (d, 1H, J = 10.6 Hz), 3.74 (d, 1H, J = 10.6 Hz), 1.99 (s, 3H), 0.80 (s, 9H), 0.00 (s, 3H), −0.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8 (C), 169.3 (C), 144.9 (CH), 127.3 (CH), 98.7 (C), 68.0 (CH_2), 66.1 (CH_2), 25.7 (3 × CH_3), 21.3 (CH_3), 18.2 (C), −5.4 (CH_3), −5.5 (CH_3); HRMS (ESI+) *m/z* [M + Na]+ calcd for $C_{14}H_{24}NaO_5Si$ 323.1285, found 323.1285.

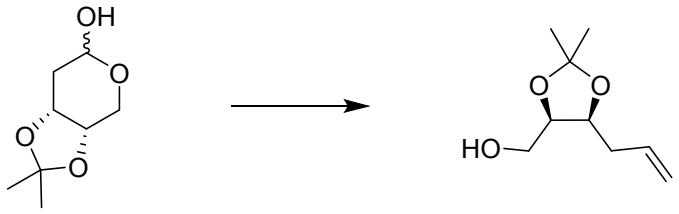


S2

(4R,5S)-4,5-iso-Propylidenebisoxy-tetrahydro-2H-pyran-2-ol (S2)

To a stirred solution of 2-deoxy-D-ribose (2 g, 14.9 mmol) in DMF (30 mL) was added $CaSO_4$ (1.01 g, 7.5 mmol) and the mixture was cooled to −10 °C. 2,2-dimethoxypropane (3.7 mL, 29.8 mmol) and PTSA (28 mg, 1.50 mmol) were added and the resulting mixture was stirred at −10 °C for 24 hours. The reaction mixture was passed through a plug of silica using *n*-hexane-EtOAc (1:1) as eluent and the filtrate concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 3:1 to 1:1) afforded the *title compound* **S2** (2.54 g, 14.6 mmol, 98 %) as a colourless oil comprised of a 3:1 mixture of anomers. R_f 0.30 (petroleum ether-EtOAc 1:1); ^{1}H NMR (400 MHz, $CDCl_3$) (major anomer) δ 5.23 (ddd, 1H, J = 7.1, 4.2, 4.2 Hz), 4.46 (ddd, 1H, J = 6.5, 4.2, 4.2 Hz), 4.18-4.13 (m, 1H), 3.96-3.91 (m, 1H), 3.72-3.65 (m, 1H), 2.22 (ddd, 1H, J = 14.8, 4.2, 4.2 Hz), 1.76 (ddd, 1H, J = 14.8, 7.1, 4.2 Hz), 1.48 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (major anomer) δ 108.9 (C), 91.1 (CH), 71.7 (CH), 70.6 (CH), 62.2 (CH_2), 32.3 (CH_2), 27.3 (CH_3), 25.5 (CH_3); the spectroscopic data were in agreement with those reported in the literature.[4]

[4] Geng, X.; Danishefsky, S. J. *Org. Lett.* **2004**, *6* (3), 413–416

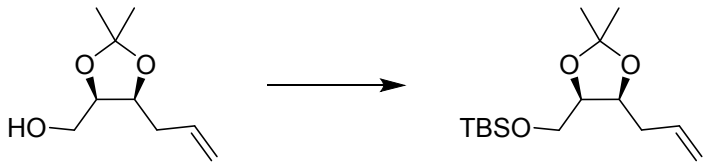


S2 **S3**

(2R,3S)-2,3-iso-propylidenebisoxy-hex-5-ene-1-ol (S3)

To a stirred solution of methyltriphenylphosphonium bromide (10.2 g, 28.5 mmol) in THF (40 mL) at −78 °C was added *n*-BuLi (26.0 mL, 28.6 mmol, 1.1 M in hexanes). The mixture was allowed to warm to r.t. and stirred for 30 min before being cooled to −78 °C and treated with a solution of **S2** (1.66 g, 9.53 mmol) in THF (20 mL). The reaction was warmed slowly to r.t. and stirred for 16 h, after which it was quenched by the addition of sat. aq. NH_4Cl (100 mL) and diluted with EtOAc (100 mL). The organic phase was separated and washed with brine (2 × 50 mL), then dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 4:1) afforded the *title compound* **S3** (1.13 g, 6.56 mmol, 69 %) as a colourless oil. R_f 0.48 (hexanes-EtOAc 1:1); $[\alpha]_D^{20}$ +17.9 (*c* 0.71, $CHCl_3$), (lit.[3] $[\alpha]_D^{20}$ +15.5 (*c* 6.3, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (ddt, 1H, *J* = 17.2, 10.3, 6.7 Hz), 5.18-5.09 (m, 2H), 4.26 (dt, 1H, *J* = 8.0, 5.9 Hz), 4.18 (dt, 1H, *J* = 5.9, 5.9 Hz), 3.65 (t, 2H, *J* = 6.0, 5.9 Hz), 2.45-2.37 (m, 1H), 2.32-2.25 (m, 1H), 1.89 (t, 1H, *J* = 6.0 Hz), 1.48 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 134.4 (CH), 117.5 (CH_2), 108.4 (C), 77.9 (CH), 76.4 (CH), 61.8 (CH_2), 33.8 (CH_2), 28.3 (CH_3), 25.6 (CH_3); the spectroscopic data were in agreement with those reported in the literature.[4]

[4] Geng, X.; Danishefsky, S. J. *Org. Lett.* **2004**, *6* (3), 413–416

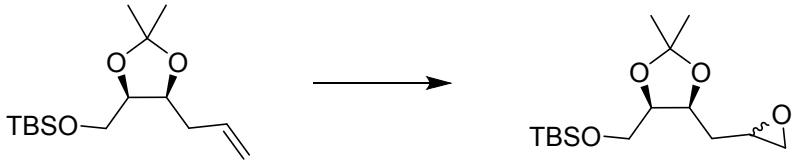


S3 **15**

(2R,3S)-1-tert-Butyldimethylsilyloxy-2,3-iso-propylidenebisoxy-hex-5-ene (15)

To a stirred solution of alcohol **S3** (1.10 g, 6.4 mmol) in CH_2Cl_2 (60 mL) at 0 °C was added TBSCl (1.44 g, 9.6 mmol) and imidazole (0.87 g, 12.8 mmol). The resultant mixture was allowed to warm to r.t. and stir for 2 h, after which it was diluted with CH_2Cl_2 (40 mL) and washed successively with 1M HCl (35 mL), sat. aq. $NaHCO_3$ (50 mL) and brine (35 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 10:1) afforded the *title compound* **15** (1.57 g, 5.5 mmol, 86 %) as a colourless oil. R_f 0.74 (petroleum ether-EtOAc 4:1); $[\alpha]_D^{20}$ −24.2 (*c* 1.68, $CHCl_3$) (lit.[3] $[\alpha]_D^{20}$ −21.4 (*c* 5.4, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (ddt,1H, *J* = 17.4, 10.2, 6.8 Hz), 5.15-5.07 (m, 2H), 4.23-4.18 (m, 1H), 4.11 (dt, 1H, *J* = 7.0, 5.0 Hz), 3.66 (ABX, 2H, *J* = 10.4, 7.4, 5.1 Hz), 2.45-2.29 (m, 2H), 1.43 (s, 3H), 1.34 (s, 3H), 0.89 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.4 (CH), 116.9 (CH_2), 108.1 (C), 77.9 (CH), 76.8 (CH), 62.0 (CH_2), 34.0 (CH_2), 28.3 (CH_3), 26.0 (3 × CH_3), 25.7 (CH_3), 18.4 (C), −5.2 (CH_3), −5.3 (CH_3); the spectroscopic data were in agreement with those reported in the literature.[5]

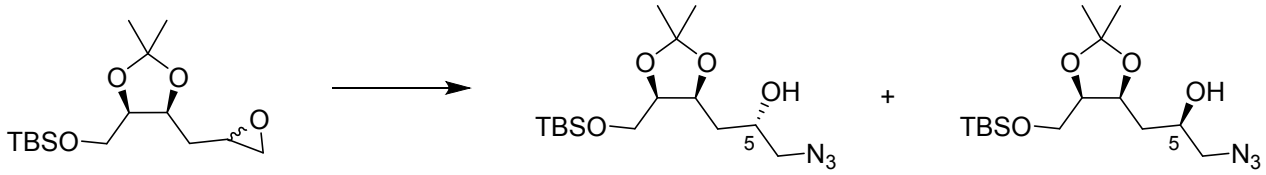
[5] Bolte, B.; Basutto, J. A.; Bryan, C. S.; Garson, M. J.; Banwell, M. G.; Ward, J. S. *J. Org. Chem.* **2015**, *80* (1), 460–470



15 **19**

(2R,3S)-1-tert-Butyldimethylsilyloxy-2,3-iso-propylidenebisoxy-5,6-epoxyhexane (21)

To a stirred solution of **15** (1.50 g, 5.24 mmol) in CH_2Cl_2 (90 mL) at 0°C was added *m*-CPBA (1.81 g, 7.85 mmol). The reaction was stirred at r.t. for 16 h and quenched by the addition of sat. aq. Na_2SO_3 (80 mL). The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (80 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ (2 × 50 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 10:1) afforded the *title compound* **19** (1.49 g, 4.92 mmol, 94 %, 1.3:1 mixture of diastereomers) as a colourless oil. R_f 0.49 hexanes-EtOAc 4:1); IR (neat) ν_{max} 2931, 2859, 1473, 1464, 1380, 1369, 1252, 1093, 833, 776 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.39 (ddd, 1H, J = 9.8, 5.9, 3.2 Hz), 4.29* (dt, 1H, J = 8.8, 5.5 Hz), 4.14-4.09 (m, 1H), 3.67-3.59 (m, 2H), 3.15-3.09 (m, 1H), 2.83 (dd, 1H, J = 4.9, 4.9 Hz), 2.77* (dd, 1H, J = 4.8, 4.8 Hz), 2.56* (dd, 1H, J = 4.8, 2.6 Hz), 2.51 (dd, 1H, J = 4.9, 2.7 Hz), 1.97-1.69 (m, 2H), 1.42 (s, 3H), 1.35 (s, 3H), 1.34* (s, 3H), 0.87 (s, 9H), 0.05 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.3 (C), 77.6 (CH), 74.8 (CH), 61.9 (CH_2), 50.29 (CH), 50.26* (CH), 47.9 (CH_2), 46.9* (CH_2), 33.2 (CH_2), 32.2* (CH_2), 28.3 (CH_3), 26.0 (3 × CH_3), 25.6 (CH_3), 18.3 (C), −5.3 (CH_3), −5.3 (CH_3); HRMS (ESI+) *m/z* [M + Na]+ calcd for $C_{15}H_{30}NaO_4Si$ 325.1806, found 325.1813; * denotes minor isomer.



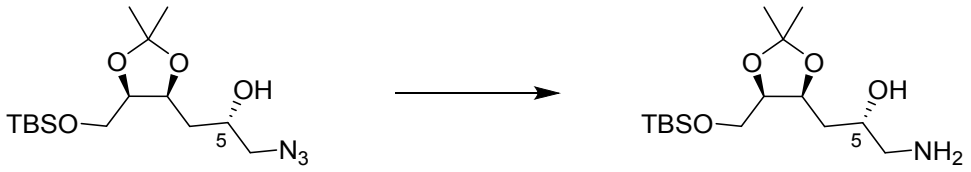
19 (5*S*)-**20** (5*R*)-**20**

(2R,3S)-5-Azido-1-tert-butyldimethylsilyloxy-2,3-iso-propylidenebisoxy-hexan-5-ol (20)

To a stirred solution of **19** (4.64 g, 15.3 mmol) in DMF/H_2O (10:1, 155 mL) was added NaN_3 (4.00 g, 61.4 mmol) and NH_4Cl (4.10 g, 76.7 mmol). The resultant mixture was heated at 80 °C for 16 h. The reaction was allowed to cool to r.t., then diluted with H_2O (200 mL) and the aqueous phase extracted with EtOAc (2 × 200 mL). The combined organic extracts were washed with brine (150 mL), dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 9:1 to 4:1) afforded two separable diastereomeric alcohols: (5*S*)-**20** (2.56 g, 7.4 mmol, 48 %) and (5*R*)-**20** (1.89 g, 5.5 mmol, 36%) as colourless oils.

(5*S*)-**20**: R_f 0.43 (hexanes-EtOAc 4:1); IR (neat) ν_{max} 3446, 2931, 2886, 2100, 1473, 1253, 1093, 837, 777 cm^{-1}; $[\alpha]_D^{20}$ −7.6 (*c* 1.8, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.40 (dt, 1H, *J* = 6.6, 6.2 Hz), 4.19-4.11 (m, 1H), 3.99-3.91 (m, 1H), 3.62 (ABX, 2H, *J* = 10.3, 8.9, 4.1 Hz), 3.33-3.29 (m, 2H), 3.13-3.10 (m, 1H), 1.92-1.81 (m, 2H), 1.39 (s, 3H), 1.34 (s, 3H), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.7 (C), 77.7 (CH), 75.0 (CH), 69.1 (CH), 61.9 (CH_2), 57.5 (CH_2), 33.2 (CH_2), 28.3 (CH_3), 26.0 (3 × CH_3), 25.6 (CH_3), 18.5 (C), −5.3 (CH_3), −5.3 (CH_3); HRMS (ESI+) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{31}N_3NaO_4Si$ 368.1976, found 368.1978.

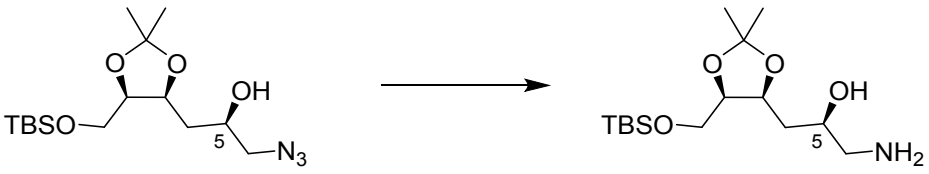
(5*R*)-**20**: R_f 0.34 (hexanes-EtOAc 4:1); IR (neat) ν_{max} 3483, 2931, 2859, 2101, 1473, 1371, 1254, 1095, 837, 778 cm^{-1}; $[\alpha]_D^{20}$ −30.0 (*c* 1.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.38 (ddd, 1H, *J* = 9.8, 6.3, 3.6 Hz), 4.15 (dt, 1H, *J* = 6.4, 6.3 Hz), 4.05-4.00 (m, 1H), 3.68-3.60 (m, 2H), 3.50 (s, 1H), 3.30 (m, 2H), 1.89-1.73 (m, 2H), 1.44 (s, 3H), 1.35 (s, 3H), 0.89 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.8 (C), 77.8 (CH), 77.4 (CH), 71.0 (CH), 61.6 (CH_2), 56.5 (CH_2), 33.3 (CH_2), 28.1 (CH_3), 25.9 (3 × CH_3), 25.6 (CH_3), 18.3 (C), −5.3 (CH_3), −5.4 (CH_3); HRMS (ESI+) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{31}N_3NaO_4Si$ 368.1976, found 368.1963.



(5*S*)-**20** (5*S*)-**13**

(2R,3S,5S)-6-Amino-1-tert-butyldimethylsilyloxy-2,3-iso-propylidenebisoxy-hexan-5-ol ((5S)-13)

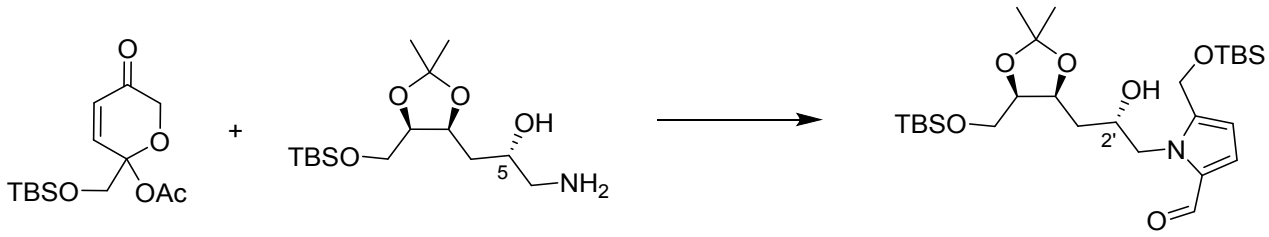
A mixture of (5*S*)-**20** (500 mg, 1.45 mmol) and Pd/C (10 % wt., 230 mg) in MeOH (25 mL) was stirred under H_2 at r.t. for 16 h. The reaction mixture was passed through Celite®, washing with MeOH (2 × 10 mL) and concentrated *in vacuo*. Purification by flash chromatography (CH_2Cl_2-MeOH saturated with NH_3 9:1 to 6:1) afforded the *title compound* (5*S*)-**13** (416 mg, 1.30 mmol, 90 %) as a colourless oil. R_f 0.56 (CH_2Cl_2-MeOH saturated with NH_3 9:1); IR (neat) ν_{max} 3362, 2931, 2859, 1746, 1473, 1380, 1253, 1096, 837, 778 cm^{-1}; $[\alpha]_D^{20}$ −4.3 (*c* 2.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.43 (dt, 1H, *J* = 6.7, 6.0 Hz), 4.14 (ddd, 1H, *J* = 8.3, 5.7, 4.6 Hz), 3.72-3.67 (m, 1H), 3.61 (ABX, 2H, *J* = 10.3, 8.2, 4.5 Hz), 2.71 (dd, 1H, *J* = 12.7, 3.3 Hz), 2.52 (dd, 1H, *J* = 12.7, 8.3 Hz), 2.03 (br s, 3H), 1.74 (dd, 2H, *J* = 6.8, 6.0 Hz), 1.39 (s, 3H), 1.34 (s, 3H), 0.88 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 107.6 (C), 77.9 (CH), 74.9 (CH), 70.4 (CH), 62.1 (CH_2), 48.5 (CH_2), 33.7 (CH_2), 28.3 (CH_3), 26.0 (3 × CH_3), 25.6 (CH_3), 18.4 (C), −5.30 (CH_3), −5.34 (CH_3); HRMS (ESI+) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{33}NNaO_4Si$ 342.2071, found 342.2069.



(5*R*)-**20** (5*R*)-**13**

(2R,3S,5R)-6-Amino-1-tert-butyldimethylsilyloxy-2,3-iso-propylidenebisoxy-hexan-5-ol ((5R)-13)

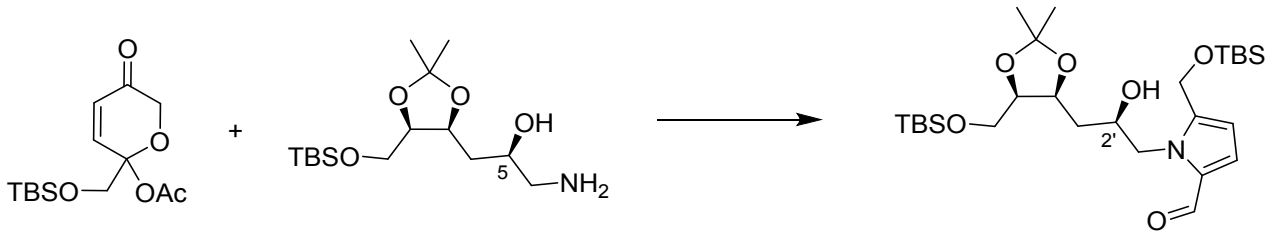
The reduction of (5*R*)-**20** (277 mg, 0.80 mmol) was carried out using analogous conditions to the preparation of (5*S*)-**13**. (5*R*)-**13** (200 mg, 0.63 mmol, 79 %) was obtained as a colourless oil after purification by flash chromatography (CH_2Cl_2-MeOH saturated with NH_3 9:1 to 6:1). R_f 0.53 (CH_2Cl_2-MeOH saturated with NH_3 9:1); IR (neat) ν_{max} 3367, 2930, 2860, 1369, 1474, 1370, 1252, 1216, 1094, 1006, 775 cm^{-1}; $[\alpha]_D^{20}$ −19.3 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 4.36 (ddd, 1H, *J* = 9.8, 5.8, 3.9 Hz), 4.11 (dt, 1H, *J* = 7.6, 5.8 Hz), 3.81-3.75 (m, 1H), 3.70-3.60 (m, 2H), 2.78-2.64 (m, 2H), 2.29 (br s, 3H), 1.80-1.64 (m, 2H), 1.41 (s, 3H), 1.33 (s, 3H), 0.86 (s, 9H), 0.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 108.4 (C), 77.9 (CH), 76.8 (CH), 72.1 (CH), 61.8 (CH_2), 47.8 (CH_2), 33.6 (CH_2), 28.2 (CH_3), 26.0 (3 × CH_3), 25.6 (CH_3), 18.3 (C), −5.3 (CH_3), −5.4 (CH_3); HRMS (ESI+) *m/z* $[M + Na]^+$ calcd for $C_{15}H_{33}NNaO_4Si$ 342.2071, found 342.2065.



22 (5*S*)-**13** (2'*S*)-**23**

1-((2S,4S,5R)-6-tert-Butyldimethylsilyloxy-4,5-isopropylidenebisoxy-2-hydroxyhexyl)-5-tert-butyldimethylsilyloxymethyl-1H-pyrrole-2-carbaldehyde ((2'S)-23)

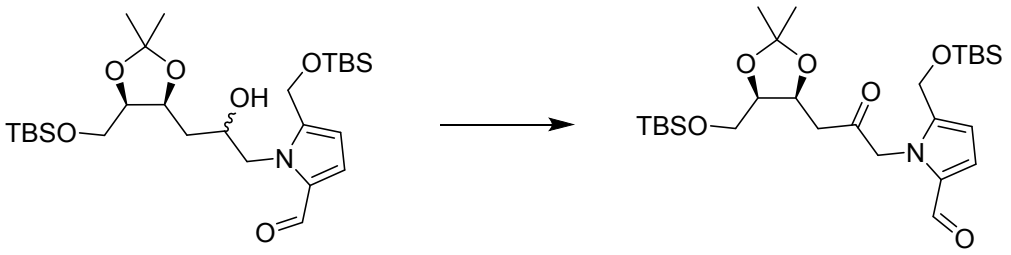
To a stirred solution of (5*S*)-**13** (630 mg, 1.97 mmol) and **22** (296 mg, 0.98 mmol) in CH_3CN (10 mL) at r.t. was added PPTS (62 mg, 0.25 mmol). After 20 h, the reaction was quenched by the addition of sat. aq. $NaHCO_3$ (and 5 mL), diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined organic extracts were dried over Na_2SO_4, filtered and concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 4:1) afforded the *title compound* (2'*S*)-**23** (249 mg, 0.46 mmol, 47 %) as a pale yellow oil. R_f 0.75 (petroleum, ether-EtOAc 3:1) IR (neat) ν_{max} 3447, 2929, 2857, 1729, 1662, 1463, 1369, 1253, 1070, 835, 776 cm^{-1}; $[\alpha]_D^{20}$ +7.6 (*c* 0.75, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 6.89 (d, 1H, *J* = 4.0 Hz), 6.18 (d, 1H, *J* = 4.0 Hz), 4.73 (ABq, 2H), 4.62 (dd, 1H, *J* = 14.0, 3.1 Hz), 4.47-4.42 (m, 1H), 4.23 (dd, 1H, *J* = 14.0, 9.3 Hz), 4.16-4.06 (m, 2H), 3.71-3.59 (m, 2H), 3.28 (d, 1H, *J* = 6.8 Hz), 1.91-1.77 (m, 2H); 1.41 (s, 3H), 1.33 (s, 3H), 0.91 (s, 9H), 0.90 (s, 9H), 0.10 (s, 3H), 0.09 (s, 6H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0 (CH), 142.8 (C), 132.8 (C), 125.1 (CH), 110.5 (CH), 107.9 (C), 77.9 (CH), 74.6 (CH), 70.2 (CH), 62.1 (CH_2), 57.6 (CH_2), 52.1 (CH_2), 34.2 (CH_2), 28.3 (CH_3), 26.1 (3 × CH_3), 26.0 (3 × CH_3), 25.7 (CH_3), 18.5 (C), 18.4 (C), −5.2 (CH_3), −5.2 (CH_3), −5.2 (CH_3), −5.3 (CH_3); HRMS (ESI+) *m/z* $[M + Na]^+$ calcd for $C_{27}H_{51}NNaO_6Si_2$ 564.3147, found 564.3156.



22 (5*R*)-**13** (2'*R*)-**23**

1-((2R,4S,5R)-6-tert-Butyldimethylsilyloxy-4,5-isopropylidenebisoxy-2-hydroxyhexyl)-5-tert-butyldimethylsilyloxymethyl-1H-pyrrole-2-carbaldehyde ((2'R)-23)

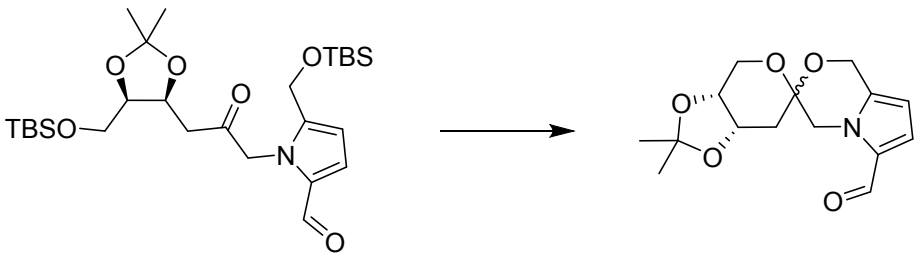
The reaction of (5*R*)-**13** (64 mg, 0.20 mmol) and **22** (30 mg, 0.10 mmol) was carried out under analogous conditions to the preparation of (2′*S*)-**23**. (2′*R*)-**23** (22 mg, 0.04 mmol, 41%) was obtained as a pale yellow oil after purification by flash chromatography (hexanes-EtOAc 4:1). R_f 0.65 (petroleum, ether-EtOAc 3:1); IR (neat) ν_{max} 3435, 2955, 1730, 1664, 1488, 1365, 1219, 1068, 836 cm^{-1}; $[\alpha]_D^{20}$ −8.0 (*c* 1.35, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 6.89 (d, 1H, *J* = 4.0 Hz), 6.18 (d, 1H, *J* = 4.0 Hz), 4.87 (d, 1H, *J* = 13.3 Hz), 4.72 (d, 1H, *J* = 13.3 Hz), 4.59 (dd, 1H, *J* = 13.9, 2.8 Hz), 4.42 (ddd, 1H, *J* = 10.5, 5.9, 2.9 Hz), 4.32-4.20 (m, 1H), 4.17-4.09 (m, 2H), 3.69-3.59 (m, 2H), 3.57 (br s, 1H), 1.95 (ddd, 1H, *J* = 14.3, 2.9, 2.9 Hz), 1.79-1.70 (m, 1H), 1.42 (s, 3H), 1.32 (s, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.10 (s, 3H), 0.07 (s, 6H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7 (CH), 143.7 (C), 132.4 (C), 125.1 (CH), 110.0 (CH), 108.5 (C), 78.1 (CH), 76.4 (CH), 71.9 (CH), 62.0 (CH_2), 57.9 (CH_2), 51.5 (CH_2), 33.5 (CH_2), 28.1 (CH_3), 26.0 (3 × CH_3), 26.0 (3 × CH_3), 25.6 (CH_3), 18.4 (C), 18.4 (C), −5.2 (CH_3), −5.2 (CH_3), −5.3 (CH_3), −5.3 (CH_3); HRMS (ESI+) *m/z* $[M + Na]^+$ calcd for $C_{27}H_{51}NNaO_6Si_2$ 564.3147, found 564.3131.



23 **12**

1-((4S,5R)-6-tert-Butyldimethylsilyloxy-4,5-isopropylidenebisoxy-2-oxohexyl)-5-tert-butyldimethylsilyloxymethyl-1H-pyrrole-2-carbaldehyde (12)

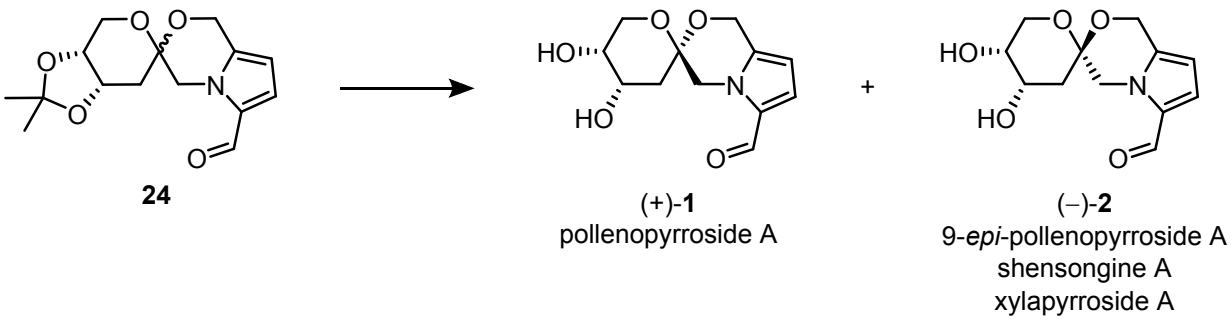
To a stirred solution of alcohols (2′*S*)-**23** (26 mg, 49 μmol) and (2′*R*)-**23** (26 mg, 49 μmol) in CH_2Cl_2 (4 mL) at 0 °C was added activated 4 Å MS (60 mg), TPAP (3.4 mg, 9.8 μmol) and NMO (42.4 mg, 360 μmol). After stirring at r.t. for 30 min, the reaction mixture was passed through a plug of silica, washing with EtOAc (2 × 20 mL) and the filtrate concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 30:1) afforded the *title compound* **12** (41 mg, 76 μmol, 77 %) as a pale yellow oil. R_f 0.43 (petroleum, ether-EtOAc 6:1); IR (neat) ν_{max} 2930, 2857, 1732, 1660, 1463, 1363, 1253, 1070, 836, 777 cm^{-1}; $[\alpha]_D^{20}$ −12.6 (*c* 0.82, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 6.89 (d, 1H, *J* = 4.0 Hz), 6.19 (d, 1H, *J* = 4.0 Hz), 5.33 (ABq, 2H), 4.64 (dt, 1H, *J* = 7.8, 5.8 Hz), 4.59 (s, 2H), 4.16 (dt, 1H, *J* = 6.0, 5.8 Hz), 3.63 (d, 2H, *J* = 6.0 Hz), 2.84-2.86 (m, 2H), 1.44 (s, 3H), 1.34 (s, 3H), 0.90 (s, 9H), 0.87 (s, 9H), 0.08 (s, 6H), 0.05 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6 (C), 179.9 (CH) 142.2 (C), 132.5 (C), 124.2 (CH), 10.2 (CH), 108.5 (C), 77.4 (CH), 73.1 (CH), 62.0 (CH_2), 57.4 (CH_2), 55.4 (CH_2), 40.5 (CH_2), 28.1 (CH_3), 26.1 (3 × CH_3), 25.9 (3 × CH_3), 25.5 (CH_3), 18.4 (C), 18.4 (C), −5.2 (3 × CH_3), −5.3 (CH_3); HRMS (ESI+) *m/z* $[M + Na]^+$ calcd for $C_{27}H_{49}NNaO_6Si_2$ 562.2991, found 562.2998.



12 **24**

(4S,5R)-4,5-iso-Propylidenebisoxy-1',3,4,4',5,6-hexahydrospiro[pyran-2,3'-pyrrolo[2,1-c][1,4]oxazine]-6'-carbaldehyde (24)

To a stirred solution of **12** (126 mg, 233 μmol) in THF (2.5 mL) at 0 °C was added 3HF·Et_3N (76 μL, 466 μmol). The reaction was allowed to warm to r.t. and stirred for 24 h, then diluted with H_2O (2 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 5 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude residue was dissolved in CH_2Cl_2 (2.5 mL) at r.t. and PPTS (14.7 mg, 58 μmol) was added. The reaction was stirred for 24 h, then additional PPTS (14.7 mg, 58 μmol) was added. The reaction was stirred at r.t. for 48 h and quenched with sat. aq. $NaHCO_3$ (2 mL). The aqueous phase was extracted with CH_2Cl_2 (4 × 5 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (hexanes-EtOAc 1:1) afforded the *title compound* **24** (43.1 mg, 63 %, 1.2:1 mixture of diastereomers) as a colourless oil. R_f 0.63 (EtOAc); IR ν_{max} (neat) 2985, 2935, 1726, 1652, 1444, 1373, 1312, 1187, 1039, 756 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.45* (s, 1H), 9.44 (s, 1H), 6.91 (d, 1H, J = 4.2 Hz), 6.89* (d, 1H, J = 4.2 Hz) 6.00 (d, 1H, J = 4.1 Hz), 5.98* (d, 1H, J = 4.1 Hz), 4.91-4.77 (m, 2H), 4.59 (d, 1H J = 13.9 Hz), 4.53* (ddd, 1H, J = 6.0, 5.9, 5.9 Hz), 4.41 (ddd, 1H, J = 5.4, 5.4, 3.5 Hz), 4.25-4.17 (m, 1H), 4.04 (d, 1H, J = 13.9 Hz), 4.01* (d, 1H, J = 14.1 Hz), 3.95-3.80* (m, 2H), 3.75-3.63 (m, 2H), 2.34 (dd, 1H, J = 15.4, 3.5 Hz), 2.06-2.04 (m, 1H), 1.54 (s, 3H), 1.53* (s, 3H), 1.37 (s, 3H), 1.35* (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9 (CH), 178.8* (CH) 134.5 (C), 134.4* (C), 131.3* (C), 131.2 (C), 124.2 (CH), 124.0* (CH), 109.5 (C), 109.2* (C), 104.9 (CH), 104.8* (CH), 94.6* (C), 93.1 (C), 71.7* (CH), 70.5 (CH), 69.5 (CH), 69.4* (CH), 61.9* (CH_2), 60.4 (CH_2), 58.2 (CH_2), 58.2* (CH_2), 53.6* (CH_2), 52.2 (CH_2), 34.9* (CH_2), 34.2 (CH_2), 28.4 (CH_3), 27.3* (CH_3), 25.9 (CH_3), 25.7* (CH_3); HRMS (ESI+) *m/z* [M + Na]+ calcd for $C_{15}H_{19}NNaO_5$ 316.1155, found 316.1155.* denotes minor isomer where distinguishable.



pollenopyrroside A ((+)-1), 9-epi-pollenopyrroside A/xylapyrroside A/shensongine A ((−)-2)

To a stirred solution of **24** (14.0 mg, 51.2 µmol) in MeOH (0.5 mL) was added PPTS (12.9 mg, 51.2 µmol) and the reaction was stirred at r.t. for 72 h. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ (1.5 mL) and extracted with CH_2Cl_2 (4 × 5 mL). The combined organic phases were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography (CH_2Cl_2-MeOH 40:1) afforded the *title compounds* (+)-**1** (9.2 mg, 36.3 µmol, 71 %) and (−)-**2** (1.3 mg, 5.2 µmol, 10 %) as colourless solids.

(+)-**1:** R_f 0.23 (CH_2Cl_2-MeOH 40:1); m.p. 188.5-190.9 °C (lit. 188-189 °C)[4], (lit. 159-165 °C)[5]; IR ν_{max} (neat) 3543, 3437, 2922, 2794, 1653, 1500, 1473, 1409, 1316, 1191, 1136, 1091, 1027, 862, 820, 777 cm^{-1}; $[\alpha]_D^{20}$ +235.9 (*c* 0.09, MeOH) (lit. $[\alpha]_D^{20}$ +125.9 (*c* 0.08, MeOH))[4], (lit. $[\alpha]_D^{25}$ +121.5 (*c* 0.08, MeOH)[5], (lit. $[\alpha]_D^{25}$ +65 (*c* 0.01, MeOH))[6]; ^{1}H NMR (400 MHz, CD_3COCD_3) δ 9.46 (s, 1H), 6.98 (d, 1H, *J* = 4.1 Hz), 6.06 (d, 1H, *J* = 4.1 Hz), 4.91 (d, 1H, *J* = 15.6 Hz), 483 (d, 1H, *J* = 15.6 Hz), 4.46 (d, 1H, *J* = 14.2 Hz), 4.02 (m, 1H), 4.00 (d, 1H, *J* = 14.2 Hz), 3.74 (dd, 1H, *J* = 10.5, 10.5 Hz), 3.71-3.66 (m, 1H), 3.55 (br s, 1H), 3.55-3.51 (m, 1H), 2.81, (br s, 1H), 2.22 (dd, 1H, *J* = 14.6, 3.5 Hz), 2.07 (dd, 1H, *J* = 14.6, 3.5 Hz); ^{13}C NMR (100 MHz, CD_3COCD_3) δ 179.1 (CH), 135.1 (C), 132.2 (C), 124.1 (CH), 105.4 (CH), 95.0 (C), 67.6 (CH), 66.9 (CH), 61.0 (CH_2), 58.2 (CH_2), 52.4 (CH_2), 38.5 (CH_2); HRMS (ESI+) *m/z* [M + Na]+ calcd for $C_{12}H_{15}NNaO_5$ 276.0842, found 276.0834. The spectroscopic data were in agreement with those reported in the literature.[6,7]

(−)-**2:** R_f 0.15 (CH_2Cl_2-MeOH 40:1); m.p. 165.1-168.3 °C (lit. 161.8-165.1 °C)[7]; IR ν_{max} (neat) 3313, 2921, 2853, 1728, 1651, 1472, 1403, 1315, 1181, 1080, 1035, 974, 752 cm^{-1}; $[\alpha]_D^{22.2}$ −135.2 (*c* 0.071,

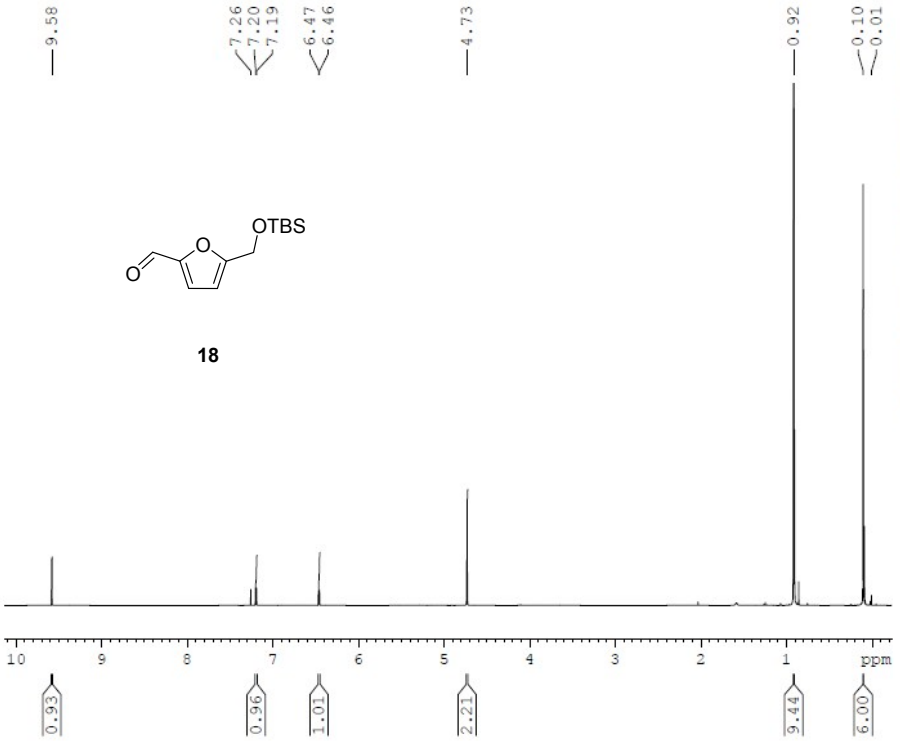
[6] Guo, J.-L.; Feng, Z.-M.; Yang, Y.-J.; Zhang, Z.-W.; Zhang, P.-C. *Chem. Pharm. Bull. (Tokyo)* **2010** *58* (7), 983–985
[7] Cao, Z.; Li, Y.; Wang, S.; Guo, X.; Wang, L.; Zhao, W. *Synlett* **2015**, *26* (7), 921–926

MeOH) (lit. $[\alpha]_D^{22}$ −189, *c* 0.1, MeOH)[6], (lit. $[\alpha]_D^{27}$ −12.7, *c* 0.05, MeOH)[8]; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.45 (s, 1H), 6.91 (d, 1H, *J* = 4.1 Hz), 6.01 (d, 1H, *J* = 4.1 Hz), 4.82 (d, 1H, *J* = 15.6 Hz), 4.73 (d, 1H, *J* = 15.6 Hz), 4.70 (d, 1H, *J* = 14.2 Hz), 4.19-4.15 (m, 1H), 4.02 (d, 1H, *J* = 14.2 Hz), 3.90-3.87 (m, 2H), 3.81 (dd, 1H, *J* = 12.7, 1.2 Hz), 2.23 (br s, 1H), 2.13 (br s, 1H), 2.04 (dd, 1H, *J* = 12.9, 5.4 Hz), 1.91 (dd, 1H, *J* = 12.9, 11.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 178.9 (CH), 134.2 (C), 131.3 (C), 124.2 (CH), 105.0 (CH), 95.5 (C), 67.5 (CH), 65.2 (CH), 64.7 (CH_2), 57.9 (CH_2), 52.3 (CH_2), 35.9 (CH_2); HRMS (ESI+) *m/z* [M + Na]+ calcd for $C_{12}H_{15}NNaO_5$ 276.0842, found 276.0844. The spectroscopic data were in agreement with those reported in the literature.[8-10]

[8] Li, M.; Xiong, J.; Huang, Y.; Wang, L.-J.; Tang, Y.; Yang, G.-X.; Liu, X.-H.; Wei, B.-G.; Fan, H.; Zhao, Y.; Zhai, W.-Z.; Hu, J.-F. *Tetrahedron* **2015**, *71* (33), 5285–5295

[9] Yang, T.; Wang, C.; Chou, G.; Wu, T.; Cheng, X.; Wang, Z. *Food Chem.* **2010**, *123* (3), 705–710

[10] Ding, B.; Dai, Y.; Hou, Y.-L.; Yao, X.-S. *J. Asian Nat. Prod. Res.* **2015**, *17* (5), 559–566



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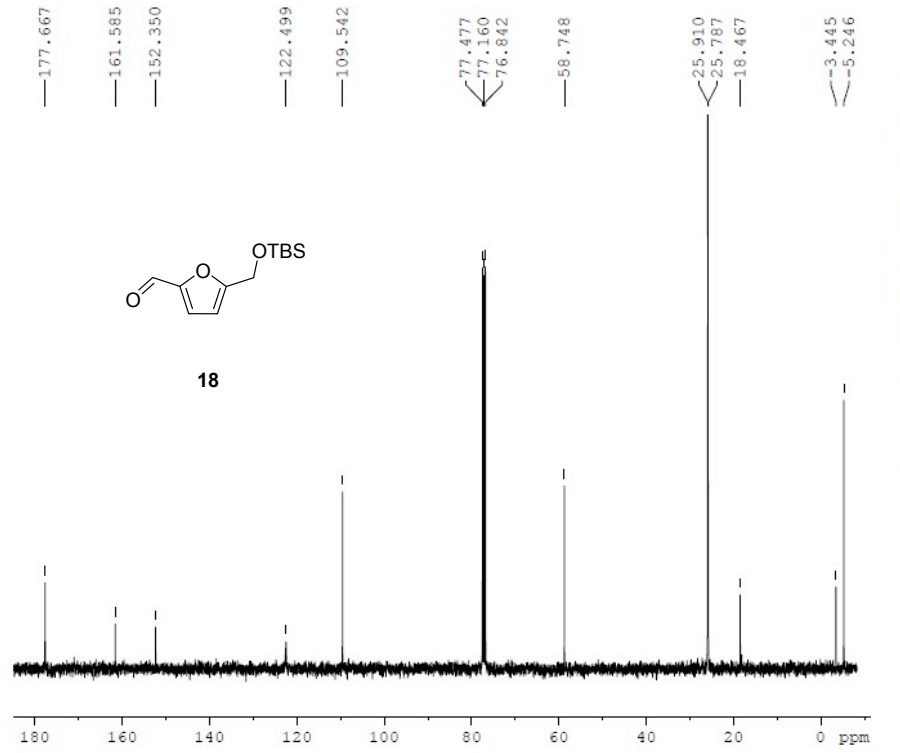

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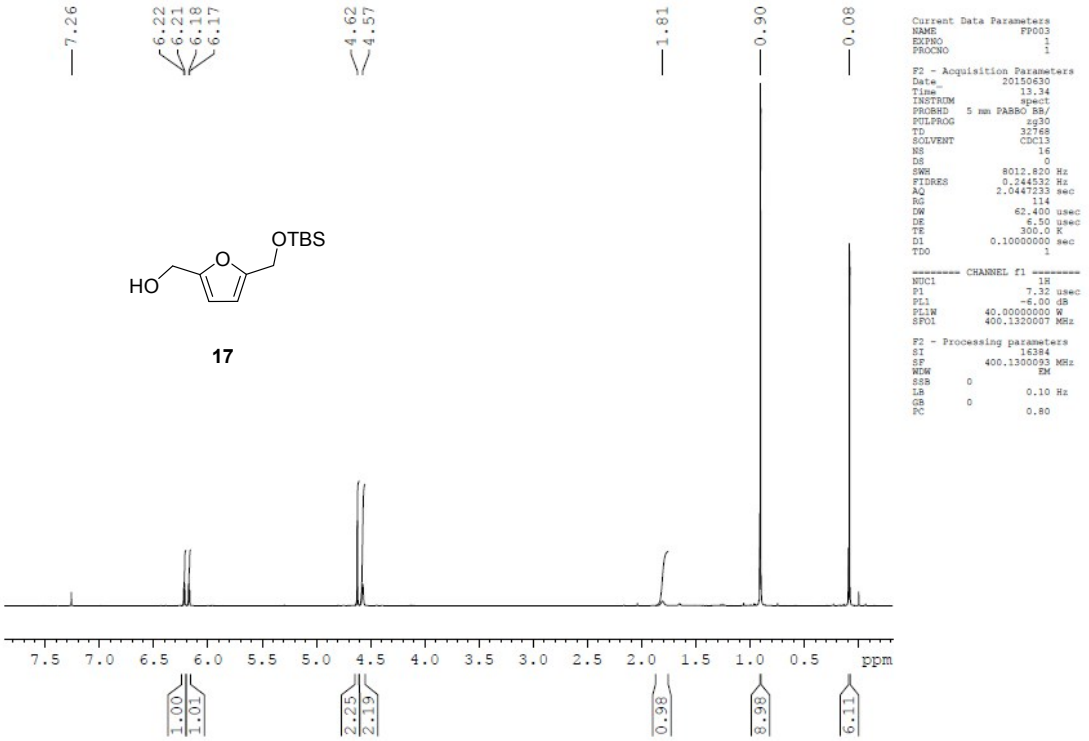
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF                100.6127546 MHz
WDW                       EM
SSB       0
LB                     2.00 Hz
GB        0
PC                     0.80
```

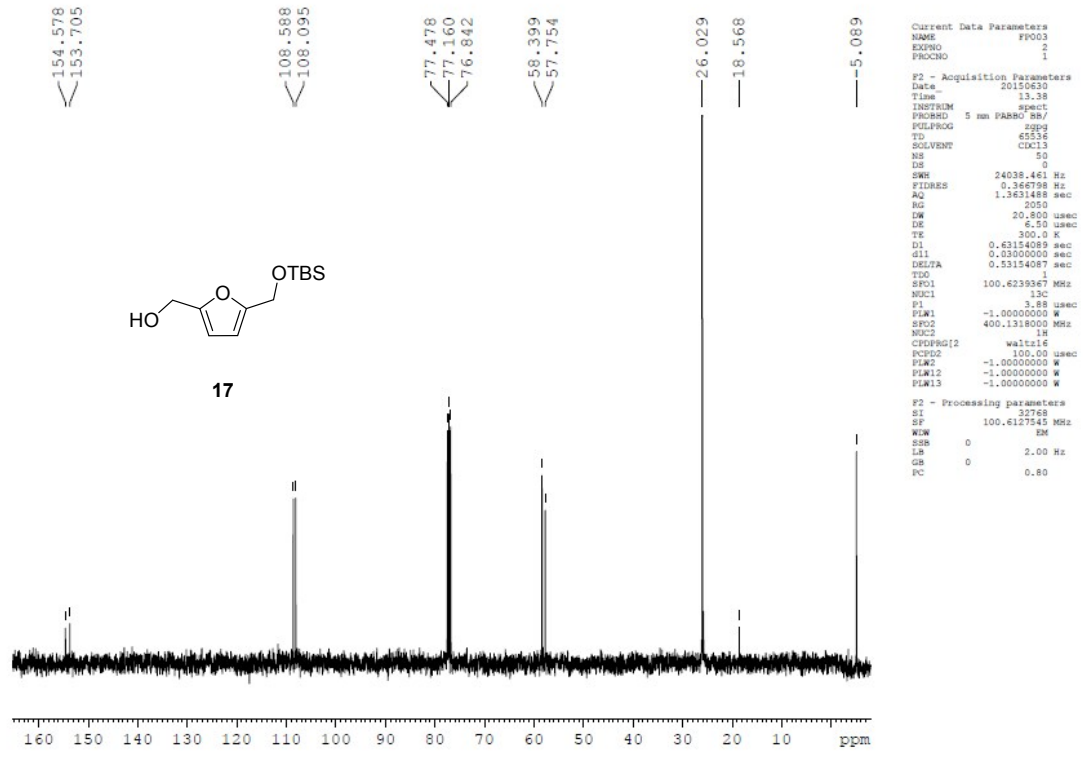



```
Current Data Parameters
NAME                  FP003
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150630
Time                  13.34
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 2.0447233 sec
RG                      114
DW                   62.400 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     7.32 usec
PL1                   -6.00 dB
PL1W          40.00000000 W
SFO1          400.1320007 MHz

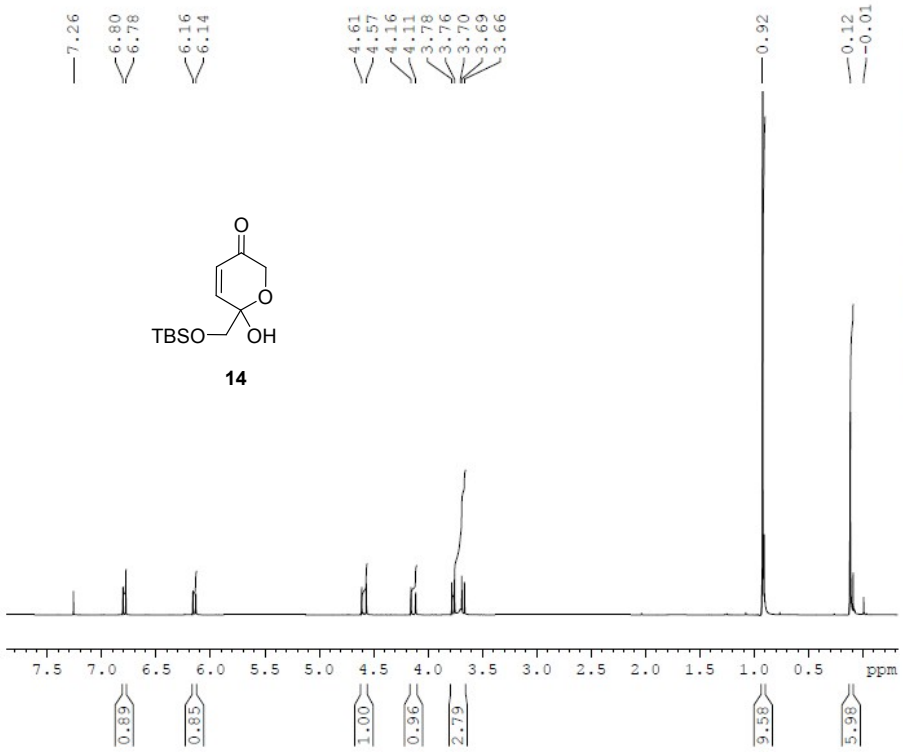
F2 - Processing parameters
SI                    16384
SF                400.1300093 MHz
WDW                       EM
SSB       0
LB                     0.10 Hz
GB        0
PC                     0.80
```




```
Current Data Parameters
NAME                  FP003
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150630
Time                  13.38
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg
TD                    65536
SOLVENT               CDCl3
NS                       50
DS                        0
SWH                24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                      2050
DW                   20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.63154089 sec
d11               0.03000000 sec
DELTA             0.53154087 sec
TD0                       1
SFO1          100.6239367 MHz
NUC1                     13C
P1                     3.88 usec
PLW1          -1.00000000 W
SFO2          400.1318000 MHz
NUC2                     1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF                100.6127545 MHz
WDW                       EM
SSB       0
LB                     2.00 Hz
GB        0
PC                     0.80
```

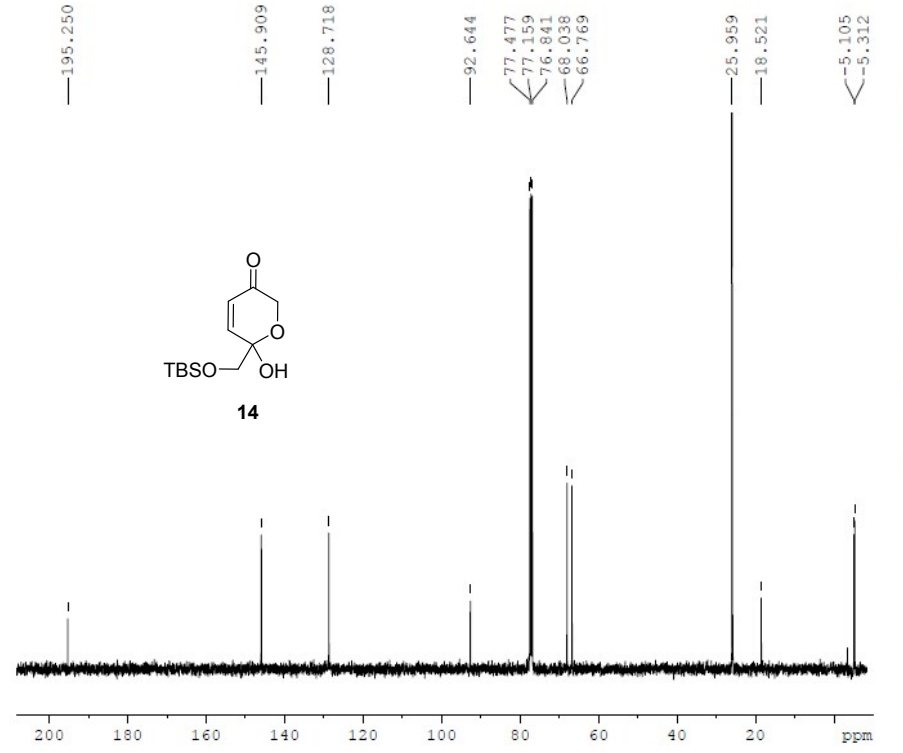



```
Current Data Parameters
NAME                  FP004
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150923
Time                   9.34
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       0
SWH               8169.935 Hz
FIDRES               0.249327 Hz
AQ                2.0054016 sec
RG                     114
DW                  61.200 usec
DE                   6.50 usec
TE                   300.0 K
D1              0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.90 usec
PL1                  -1.70 dB
PL1W           12.92942619 W
SFO1           399.8720993 MHz

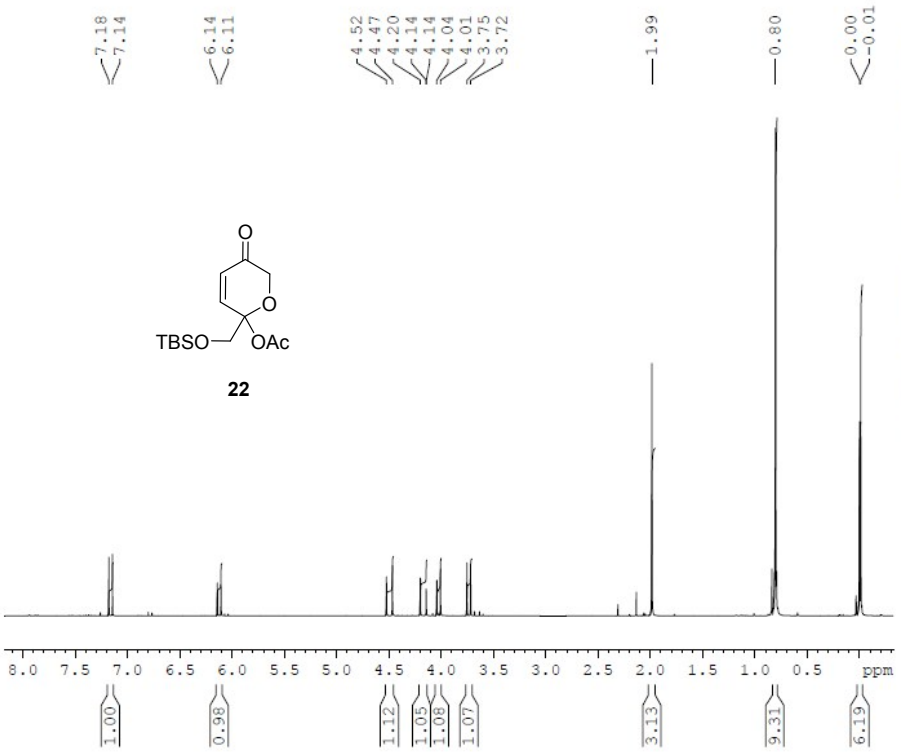
F2 - Processing parameters
SI                    16384
SF               399.8700133 MHz
WDW                      EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    0.80
```




```
Current Data Parameters
NAME                  FP004
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150923
Time                   9.42
INSTRUM               spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     200
DS                       0
SWH              24038.461 Hz
FIDRES               0.366798 Hz
AQ                1.3631488 sec
RG                    1820
DW                  20.800 usec
DE                   6.50 usec
TE                   300.0 K
D1              0.63167691 sec
d11             0.03000000 sec
DELTA           0.53167689 sec
TD0                       1
SFO1           100.5585530 MHz
NUC1                    13C
P1                   14.72 usec
PLW1           -1.00000000 W
SFO2           399.8717994 MHz
NUC2                    1H
CPDPRG[2          waltz16
PCPD2                80.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                    32768
SF               100.5473787 MHz
WDW                      EM
SSB       0
LB                    2.00 Hz
GB        0
PC                    0.80
```



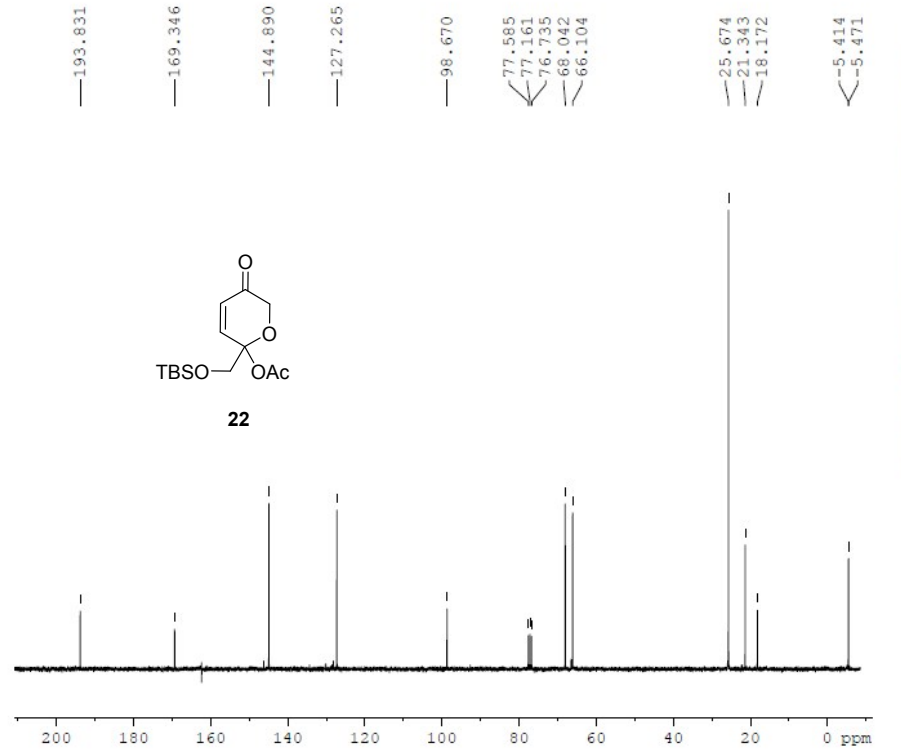
22

```
Current Data Parameters
NAME                  FP208
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150323
Time                  10.45
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                       16
DS                        0
SWH                5995.204 Hz
FIDRES            0.182959 Hz
AQ                 2.7328513 sec
RG                      25.4
DW                   83.400 usec
DE                    6.00 usec
TE                   294.5 K
D1                0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                     9.25 usec
PL1                   -1.20 dB
PL1W           21.52352333 W
SFO1           300.1315006 MHz

F2 - Processing parameters
SI                       16384
SF             300.1300054 MHz
WDW                      EM
SSB       0
LB                     0.10 Hz
GB        0
PC                     0.80
```

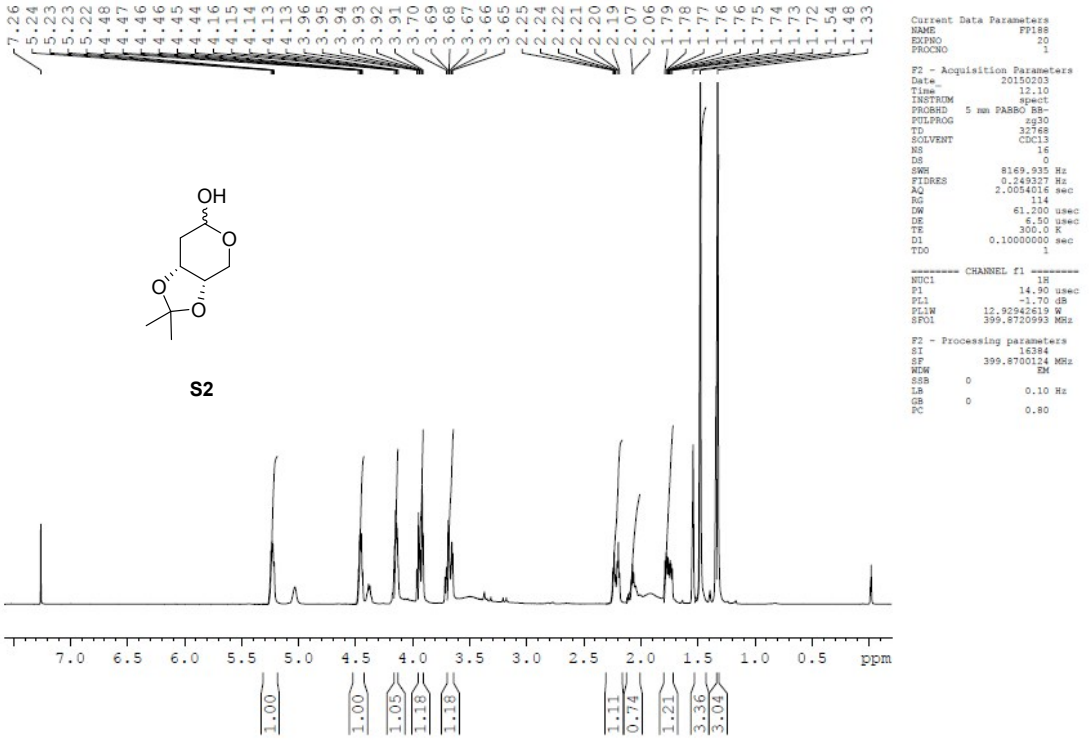


22

```
Current Data Parameters
NAME                  FP208
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150323
Time                  10.46
INSTRUM               spect
PROBHD   5 mm QNP 1H/13
PULPROG             zgpg
TD                   65536
SOLVENT              CDCl3
NS                       25
DS                        0
SWH               17985.611 Hz
FIDRES            0.274439 Hz
AQ                 1.8219008 sec
RG                    16384
DW                   27.800 usec
DE                    20.00 usec
TE                   294.6 K
D1                0.17593171 sec
d11               0.03000000 sec
DELTA             0.07593171 sec
TD0                       1
SFO1           75.4760973 MHz
NUC1                     13C
P1                     6.39 usec
PLW1          -1.00000000 W
SFO2           300.1312005 MHz
NUC2                     1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                       32768
SF             75.4677472 MHz
WDW                      EM
SSB       0
LB                     1.00 Hz
GB        0
PC                     1.00
```

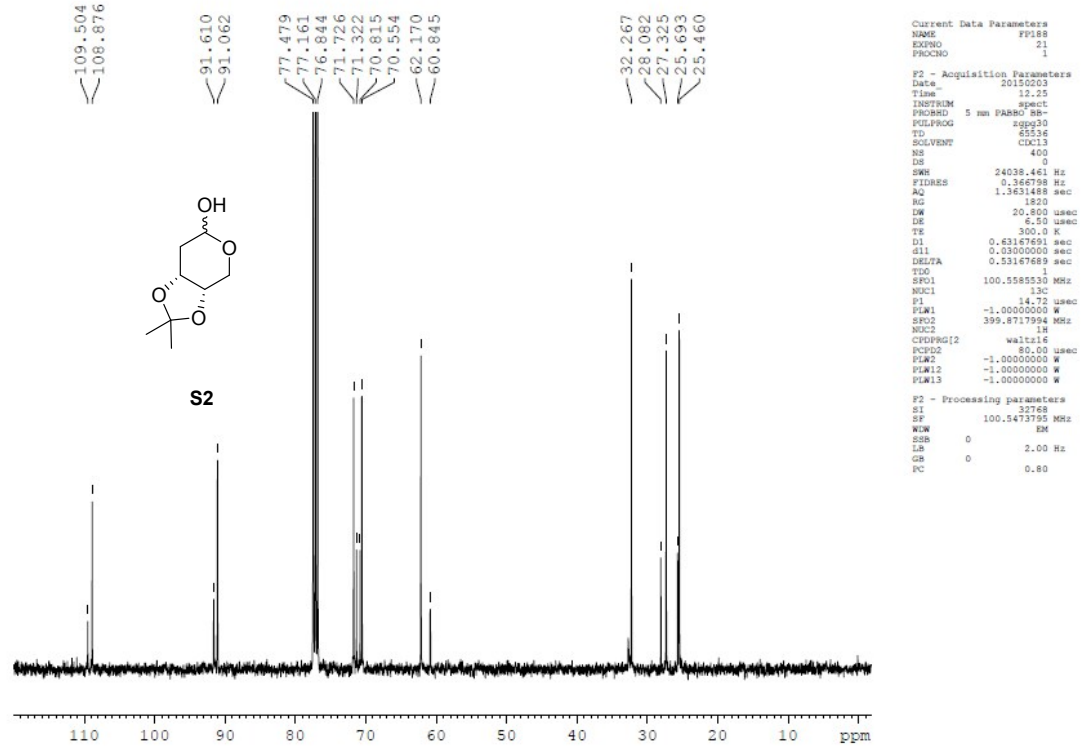



```
Current Data Parameters
NAME                  FP188
EXPNO                    20
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150203
Time                  12.10
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH               8169.935 Hz
FIDRES            0.249327 Hz
AQ                2.0054016 sec
RG                      114
DW                 61.200 usec
DE                  6.50 usec
TE                  300.0 K
D1              0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                  14.90 usec
PL1                 -1.70 dB
PL1W          12.92942619 W
SFO1          399.8720993 MHz

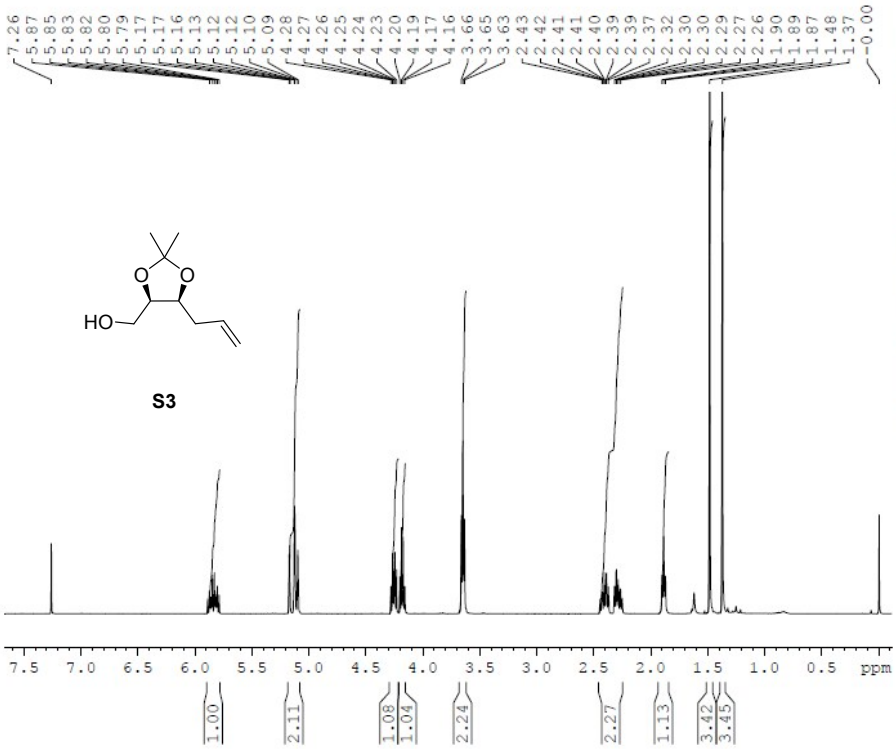
F2 - Processing parameters
SI                    16384
SF            399.8700124 MHz
WDW                     EM
SSB       0
LB                   0.10 Hz
GB        0
PC                   0.80
```




```
Current Data Parameters
NAME                  FP188
EXPNO                    21
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150203
Time                  12.25
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      400
DS                        0
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                     1820
DW                 20.800 usec
DE                  6.50 usec
TE                  300.0 K
D1              0.63167691 sec
d11             0.03000000 sec
DELTA           0.53167689 sec
TD0                       1
SFO1          100.5585530 MHz
NUC1                    13C
P1                  14.72 usec
PLW1           -1.00000000 W
SFO2          399.8717994 MHz
NUC2                    1H
CPDPRG[2            waltz16
PCPD2               80.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                    32768
SF            100.5473795 MHz
WDW                     EM
SSB       0
LB                   2.00 Hz
GB        0
PC                   0.80
```



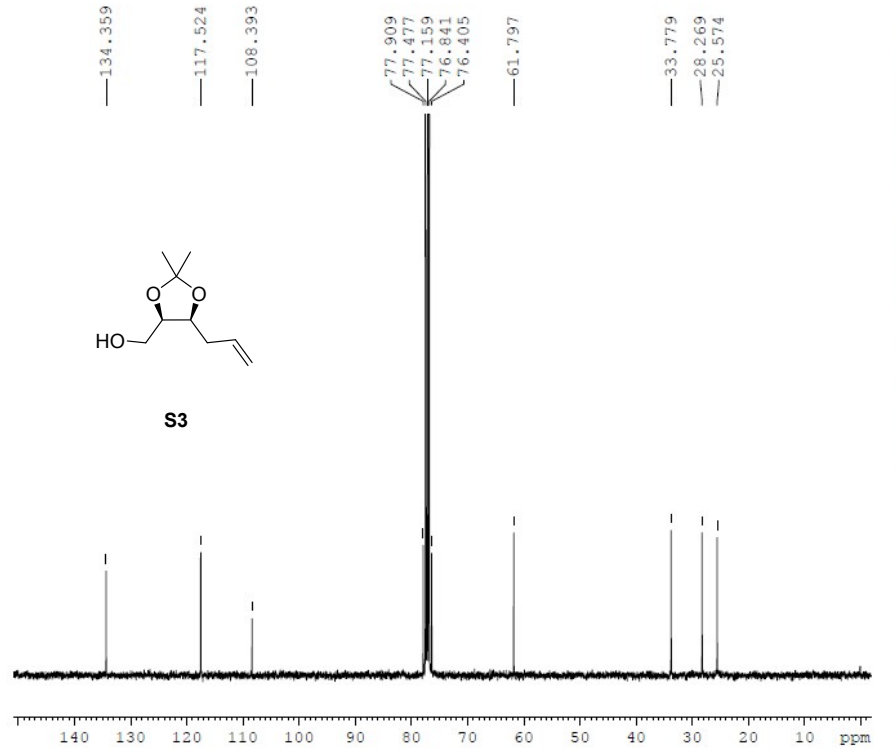
S3

```
Current Data Parameters
NAME                  FP189
EXPNO                    20
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150203
Time                  18.06
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      16
DS                       0
SWH              8169.935 Hz
FIDRES           0.249327 Hz
AQ               2.0054016 sec
RG                     161
DW                61.200 usec
DE                 6.50 usec
TE                 300.0 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.90 usec
PL1                -1.70 dB
PL1W         12.92942619 W
SFO1         399.8720993 MHz

F2 - Processing parameters
SI                   16384
SF           399.8700127 MHz
WDW                     EM
SSB      0
LB                  0.10 Hz
GB       0
PC                  0.80
```

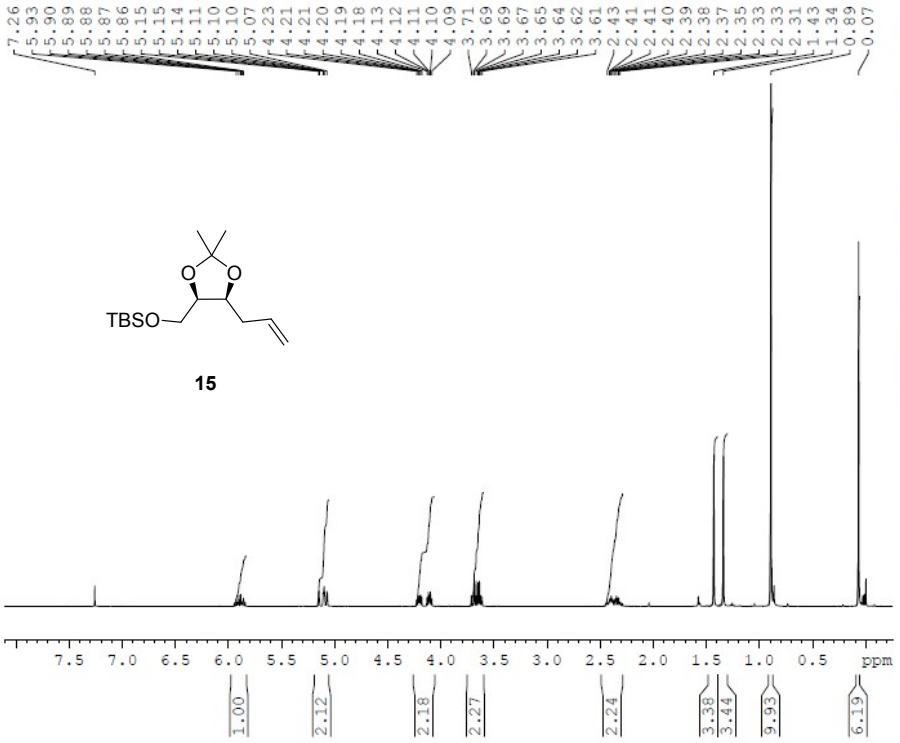


S3

```
Current Data Parameters
NAME                  FP189
EXPNO                    21
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150203
Time                  18.20
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     400
DS                       0
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631488 sec
RG                    1820
DW                20.800 usec
DE                 6.50 usec
TE                 300.0 K
D1              0.63167691 sec
d11             0.03000000 sec
DELTA           0.53167689 sec
TD0                      1
SFO1         100.5585530 MHz
NUC1                   13C
P1                 14.72 usec
PL1             -1.00000000 W
SFO2         399.8717994 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PLW2            -1.00000000 W
PLW12           -1.00000000 W
PLW13           -1.00000000 W

F2 - Processing parameters
SI                   32768
SF           100.5473781 MHz
WDW                     EM
SSB      0
LB                  2.00 Hz
GB       0
PC                  0.80
```



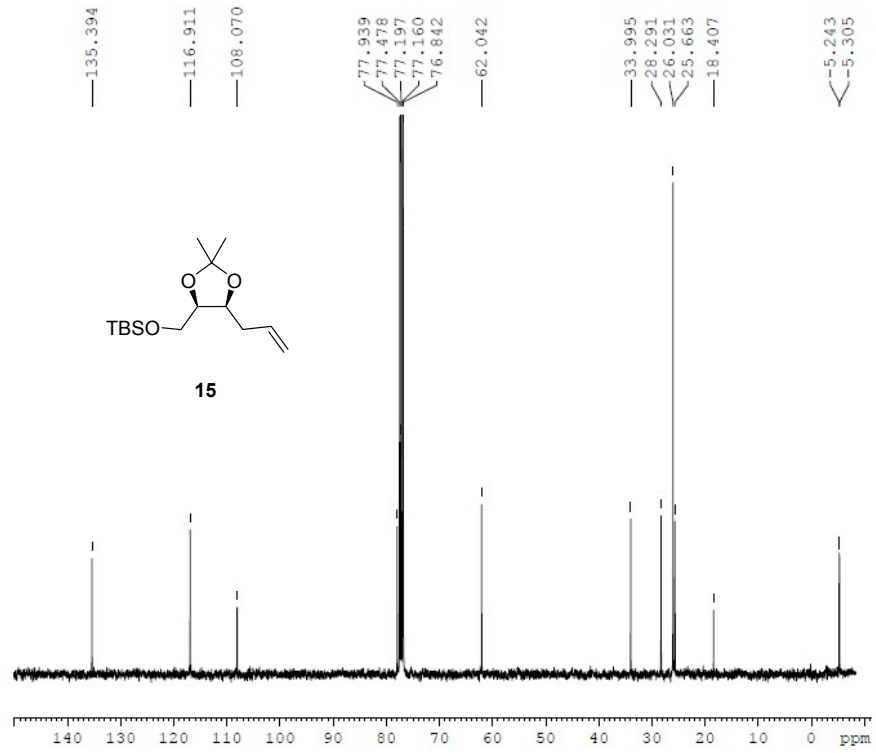
15

```
Current Data Parameters
NAME                  FP190
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150204
Time                  12.40
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8169.935 Hz
FIDRES                0.249327 Hz
AQ                 2.00054016 sec
RG                      128
DW                   61.200 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    14.90 usec
PL1                   -1.70 dB
PL1W           12.92942619 W
SFO1           399.8720993 MHz

F2 - Processing parameters
SI                     16384
SF                399.8700125 MHz
WDW                       EM
SSB       0
LB                     0.10 Hz
GB        0
PC                     0.80
```

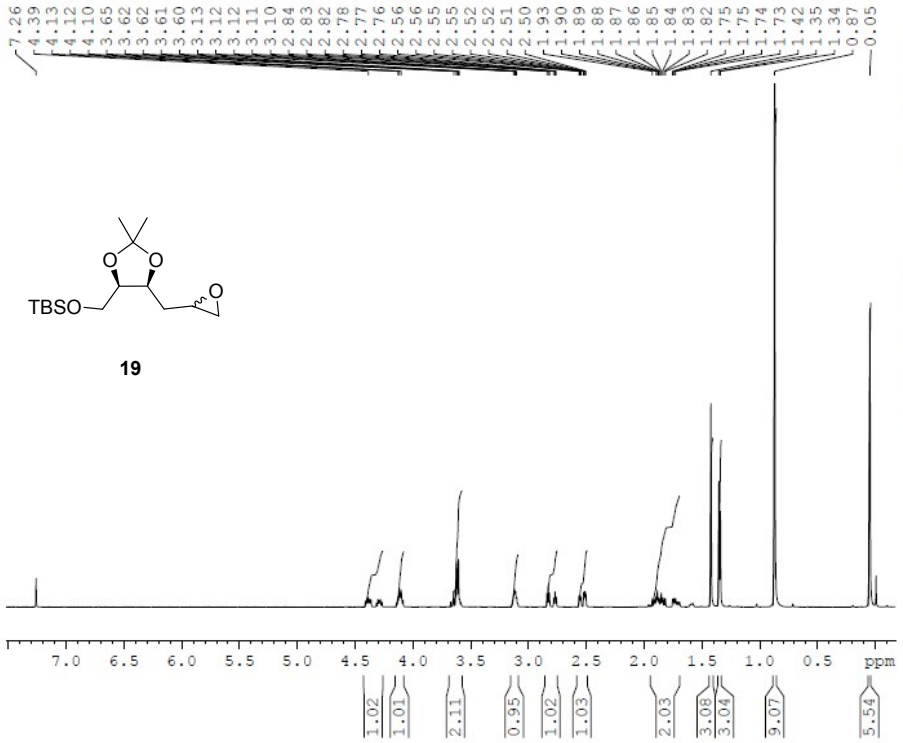


15

```
Current Data Parameters
NAME                  FP190
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150204
Time                  12.55
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      400
DS                        0
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                     1820
DW                   20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.63167691 sec
d11               0.03000000 sec
DELTA             0.53167689 sec
TD0                       1
SFO1           100.5585530 MHz
NUC1                     13C
P1                    14.72 usec
PLW1          -1.00000000 W
SFO2           399.8717594 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                 80.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                     32768
SF                100.5473773 MHz
WDW                       EM
SSB       0
LB                     2.00 Hz
GB        0
PC                     0.80
```



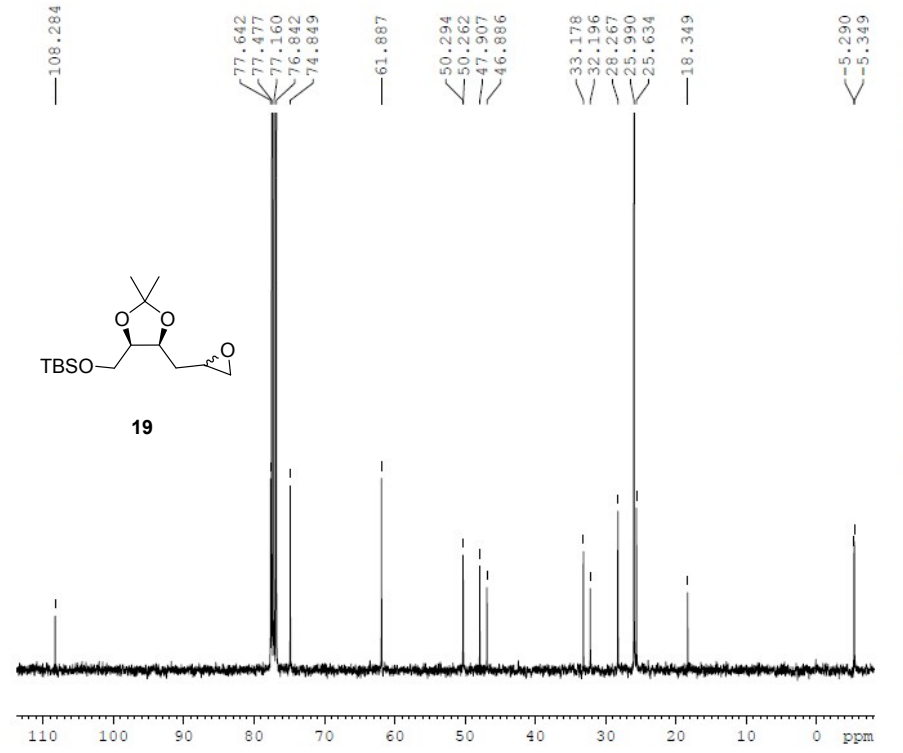
19

```
Current Data Parameters
NAME                  FP192
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150205
Time                 18.10
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT              CDCl3
NS                      16
DS                       0
SWH             8169.935 Hz
FIDRES             0.249327 Hz
AQ                2.0054016 sec
RG                     128
DW                61.200 usec
DE                 6.50 usec
TE                 300.0 K
D1              0.10000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.90 usec
PL1                -1.70 dB
PL1W          12.92942619 W
SFO1          399.8720993 MHz

F2 - Processing parameters
SI                   16384
SF            399.8700128 MHz
WDW                    EM
SSB       0
LB                  0.10 Hz
GB        0
PC                  0.80
```

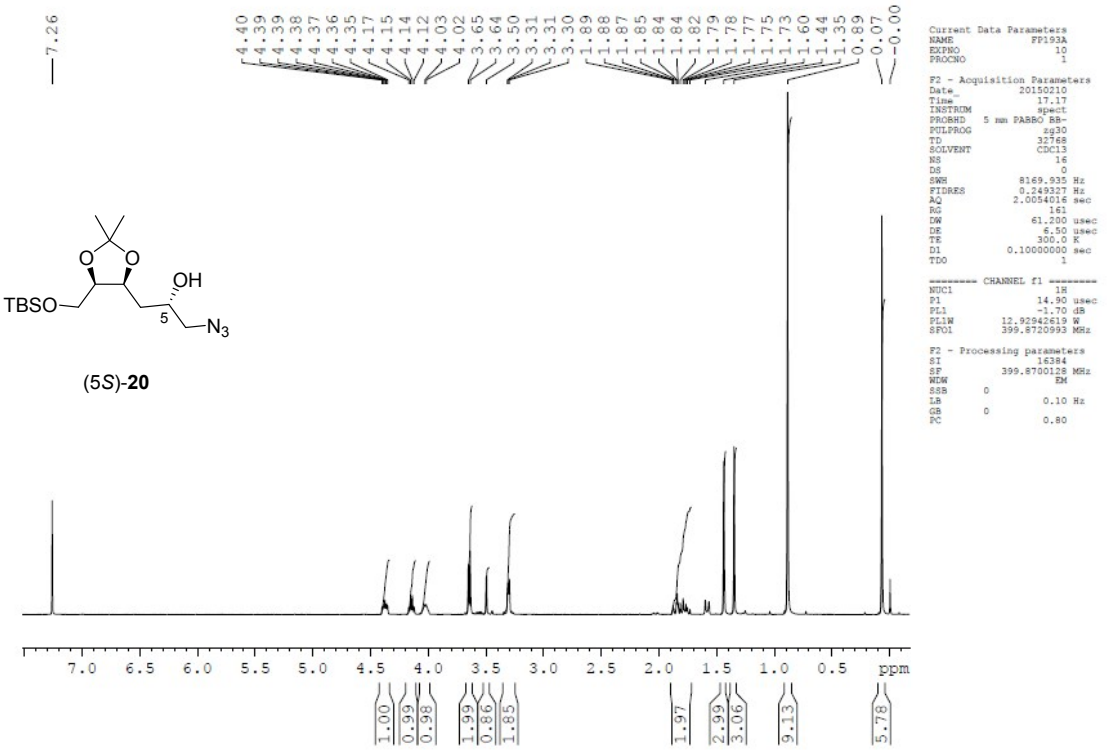


19

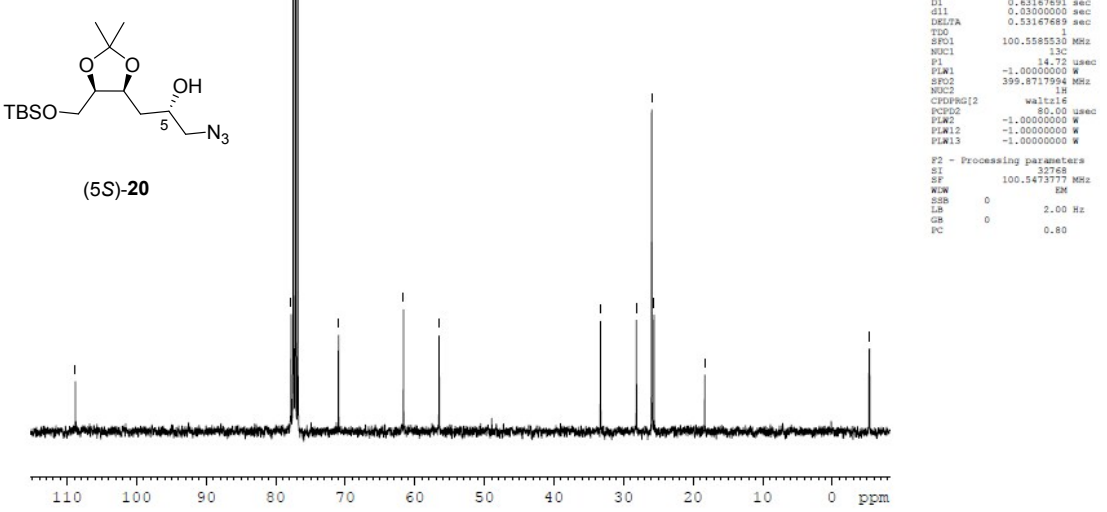
```
Current Data Parameters
NAME                  FP192
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150205
Time                 18.25
INSTRUM              spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                  65536
SOLVENT              CDCl3
NS                     400
DS                       0
SWH            24038.461 Hz
FIDRES             0.366798 Hz
AQ                1.3631488 sec
RG                    1820
DW                20.800 usec
DE                 6.50 usec
TE                 300.0 K
D1              0.63167691 sec
d11             0.03000000 sec
DELTA           0.53167689 sec
TD0                      1
SFO1          100.5585530 MHz
NUC1                   13C
P1                 14.72 usec
PL1             -1.00000000 W
SFO2          399.8717594 MHz
NUC2                   1H
CPDPRG[2          waltz16
PCPD2              80.00 usec
PL2             -1.00000000 W
PL12            -1.00000000 W
PL13            -1.00000000 W

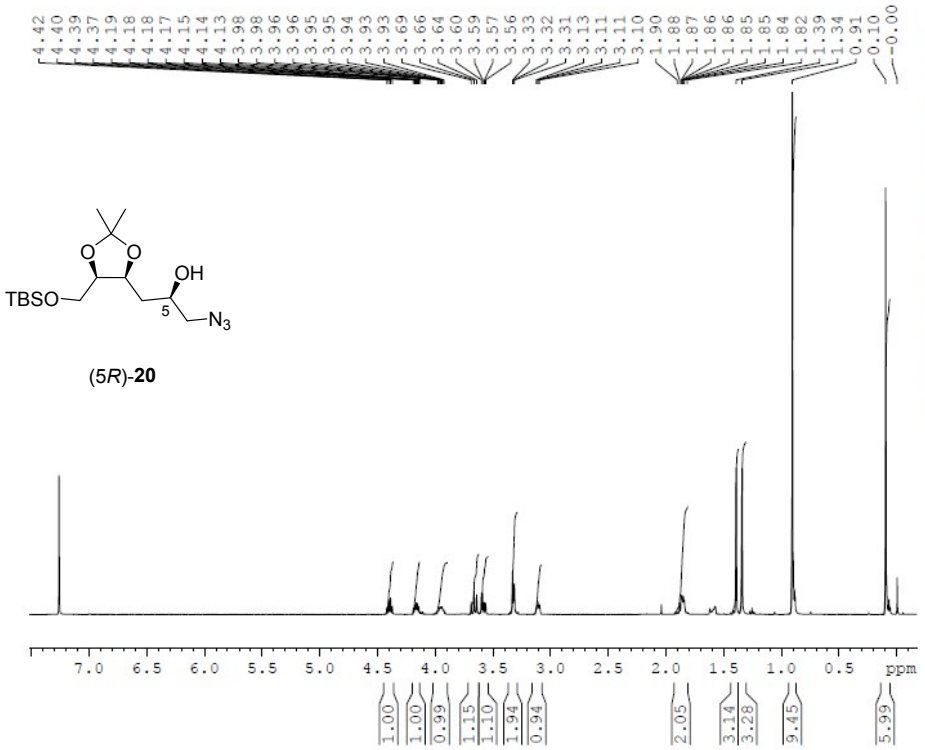
F2 - Processing parameters
SI                   32768
SF            100.5473777 MHz
WDW                    EM
SSB       0
LB                  2.00 Hz
GB        0
PC                  0.80
```


7.26
4.40 4.39 4.39 4.38 4.37 4.36 4.35 4.17 4.15 4.14 4.12 4.03 4.02 3.65 3.64 3.50 3.31 3.31 3.30 1.89 1.88 1.87 1.85 1.84 1.84 1.82 1.79 1.78 1.77 1.75 1.73 1.60 1.44 1.35 0.89 0.07 0.00
TBSO
OH
5
N3
7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.00 0.99 0.98 1.99 0.86 1.85 1.97 2.99 3.06 9.13 5.78

(5*S*)-**20**


108.810
77.807 77.479 77.365 77.162 76.843 70.984
61.641
56.513
33.310
28.148 25.949 25.620
18.328
5.306 5.380
TBSO
OH
5
N3
110 100 90 80 70 60 50 40 30 20 10 0 ppm

(5*S*)-**20**



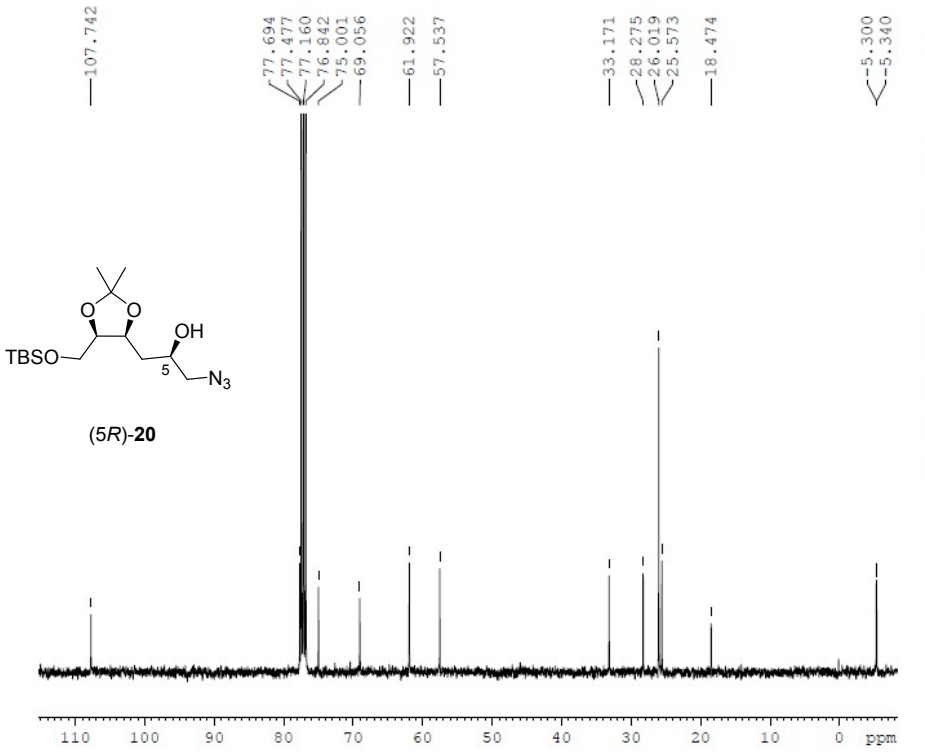
(5*R*)-**20**

```
Current Data Parameters
NAME                  FP193B
EXPNO                     10
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150210
Time                  17.45
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8169.935 Hz
FIDRES                0.249327 Hz
AQ                 2.0054016 sec
RG                      161
DW                   61.200 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    14.90 usec
PL1                   -1.70 dB
PL1W           12.92942619 W
SFO1           399.8720993 MHz

F2 - Processing parameters
SI                    16384
SF             399.8700131 MHz
WDW                      EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    0.80
```

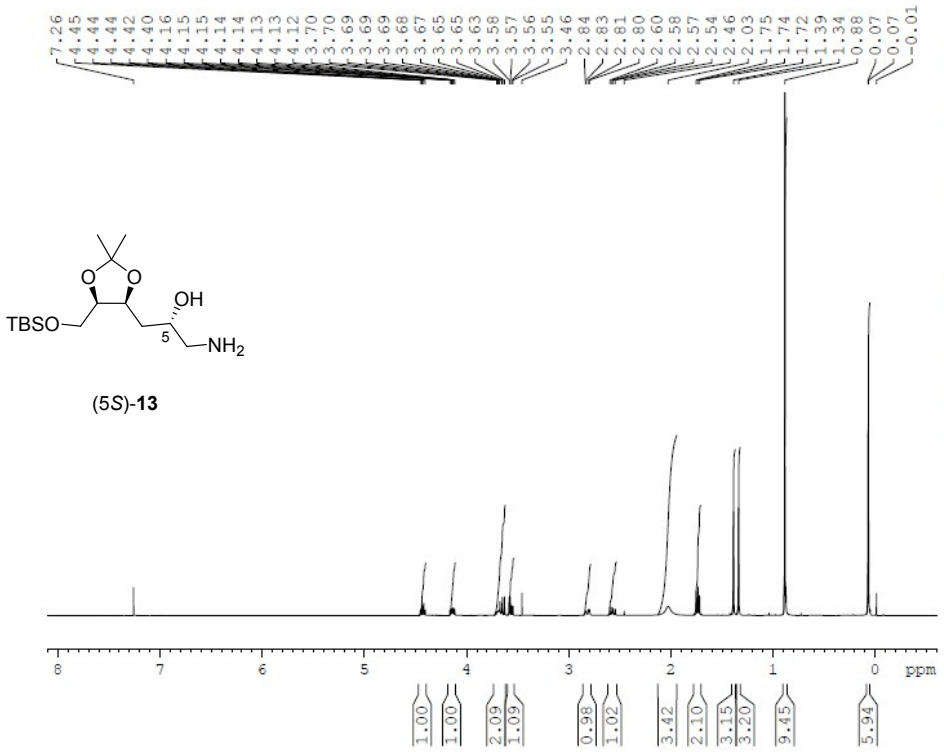


(5*R*)-**20**

```
Current Data Parameters
NAME                  FP193B
EXPNO                     11
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150210
Time                  18.00
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      400
DS                        0
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                     1820
DW                   20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.63167691 sec
d11               0.03000000 sec
DELTA             0.53167689 sec
TD0                       1
SFO1           100.5585530 MHz
NUC1                     13C
P1                    14.72 usec
PLW1          -1.00000000 W
SFO2           399.8717994 MHz
NUC2                      1H
CPDPRG[2              waltz16
PCPD2                 80.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             100.5473778 MHz
WDW                      EM
SSB       0
LB                    2.00 Hz
GB        0
PC                    0.80
```



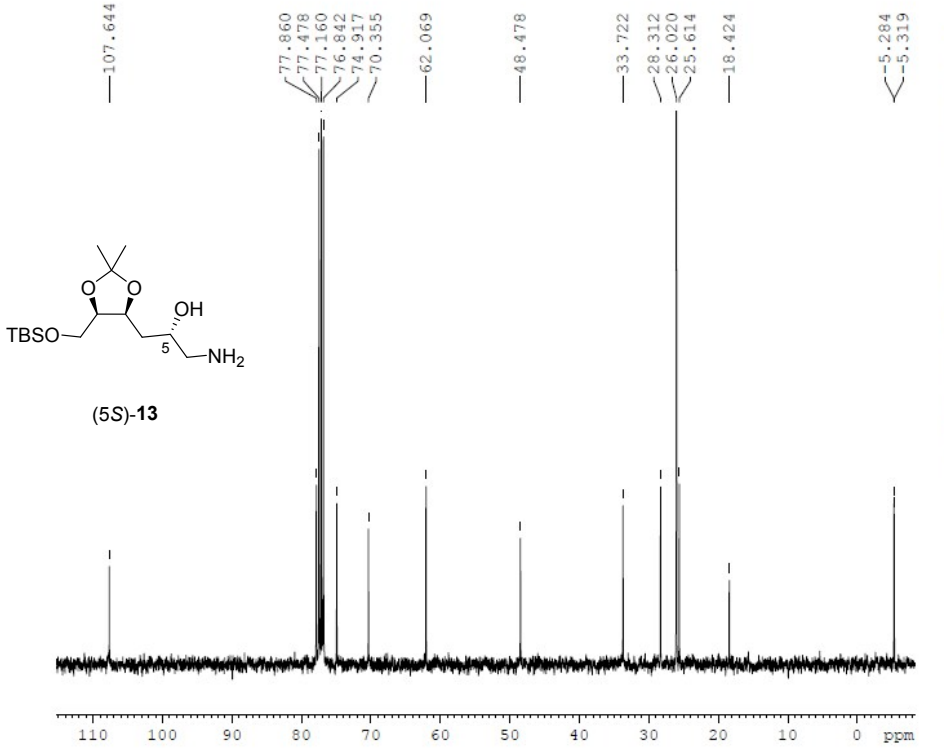
(5*S*)-**13**

```
Current Data Parameters
NAME                  FP195
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150219
Time                  11.27
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH              8169.935 Hz
FIDRES           0.249327 Hz
AQ               2.0054016 sec
RG                      101
DW                 61.200 usec
DE                  6.50 usec
TE                 300.0 K
D1              0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    1H
P1                   7.32 usec
PL1                 -6.00 dB
PL1W          40.00000000 W
SFO1          400.1321007 MHz

F2 - Processing parameters
SI                    16384
SF            400.1300098 MHz
WDW                     EM
SSB       0
LB                   0.10 Hz
GB        0
PC                   0.80
```

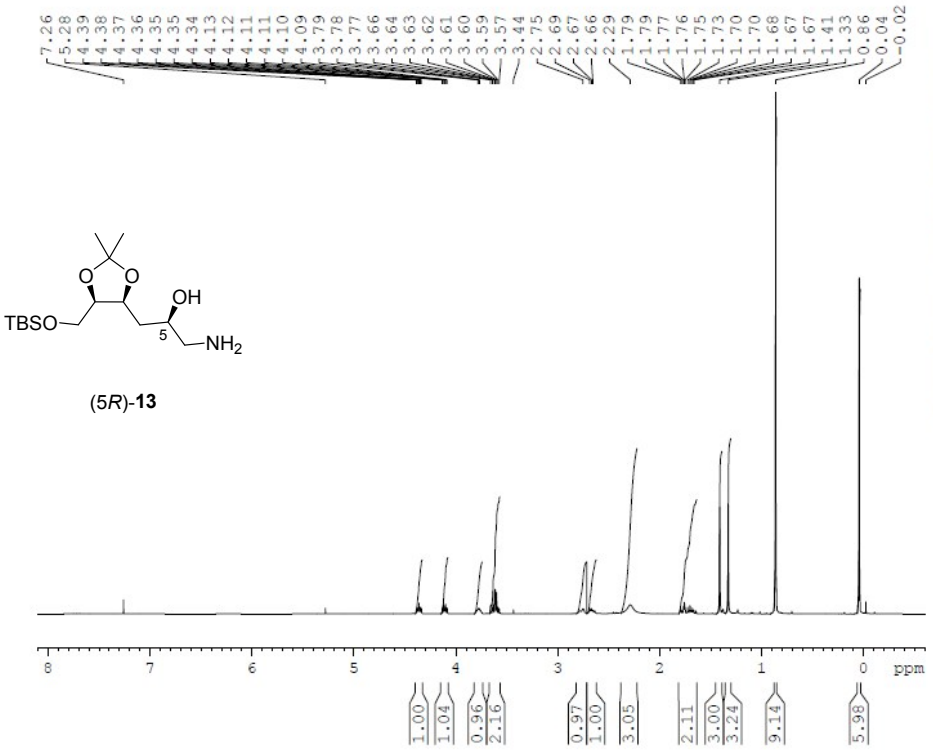


(5*S*)-**13**

```
Current Data Parameters
NAME                  FP195
EXPNO                     2
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150219
Time                  11.36
INSTRUM               spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      200
DS                        0
SWH             24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631488 sec
RG                     2050
DW                 20.800 usec
DE                  6.50 usec
TE                 300.0 K
D1              0.63167691 sec
d11             0.03000000 sec
DEL7A           0.53167689 sec
TD0                       1
SFO1          100.6239378 MHz
NUC1                    13C
P1                   6.98 usec
PLW1          -1.00000000 W
SFO2          400.1318006 MHz
NUC2                    1H
CPDPRG[2        waltz16
PCPD2              100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF            100.6127549 MHz
WDW                     EM
SSB       0
LB                   2.00 Hz
GB        0
PC                   0.80
```



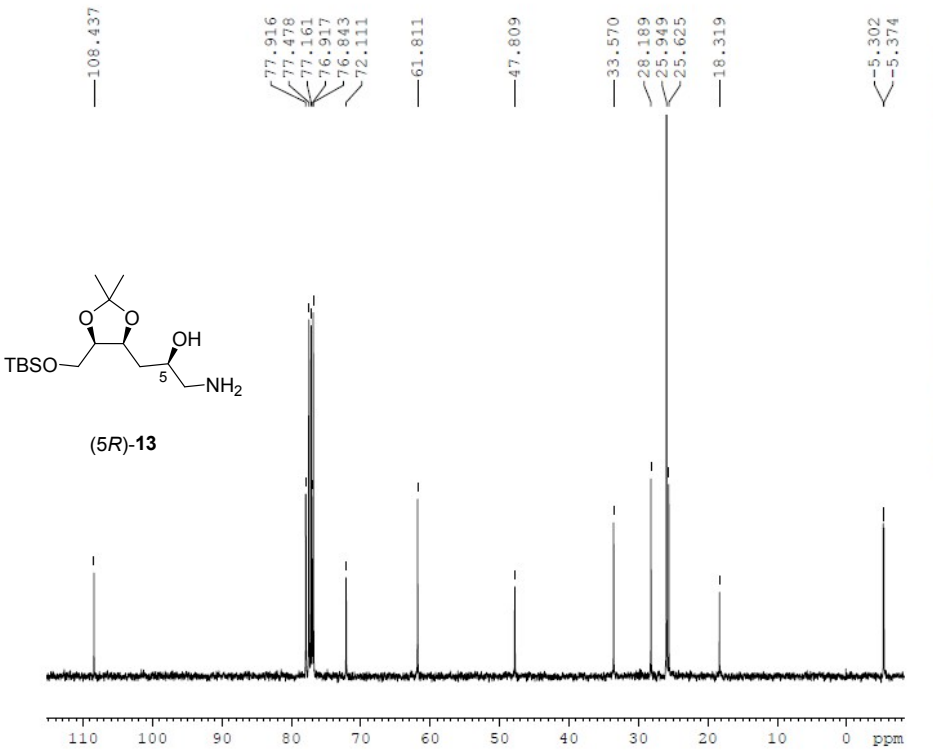
(5*R*)-**13**

```
Current Data Parameters
NAME                  FP195A
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150217
Time                  14.53
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8169.935 Hz
FIDRES                0.249327 Hz
AQ                 2.0054016 sec
RG                      71.8
DW                    61.200 usec
DE                     6.50 usec
TE                    300.0 K
D1                 0.10000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                      7.32 usec
PL1                    -6.00 dB
PL1W           40.00000000 W
SFO1           400.1321007 MHz

F2 - Processing parameters
SI                     16384
SF                400.1300098 MHz
WDW                       EM
SSB       0
LB                     0.10 Hz
GB        0
PC                     0.80
```

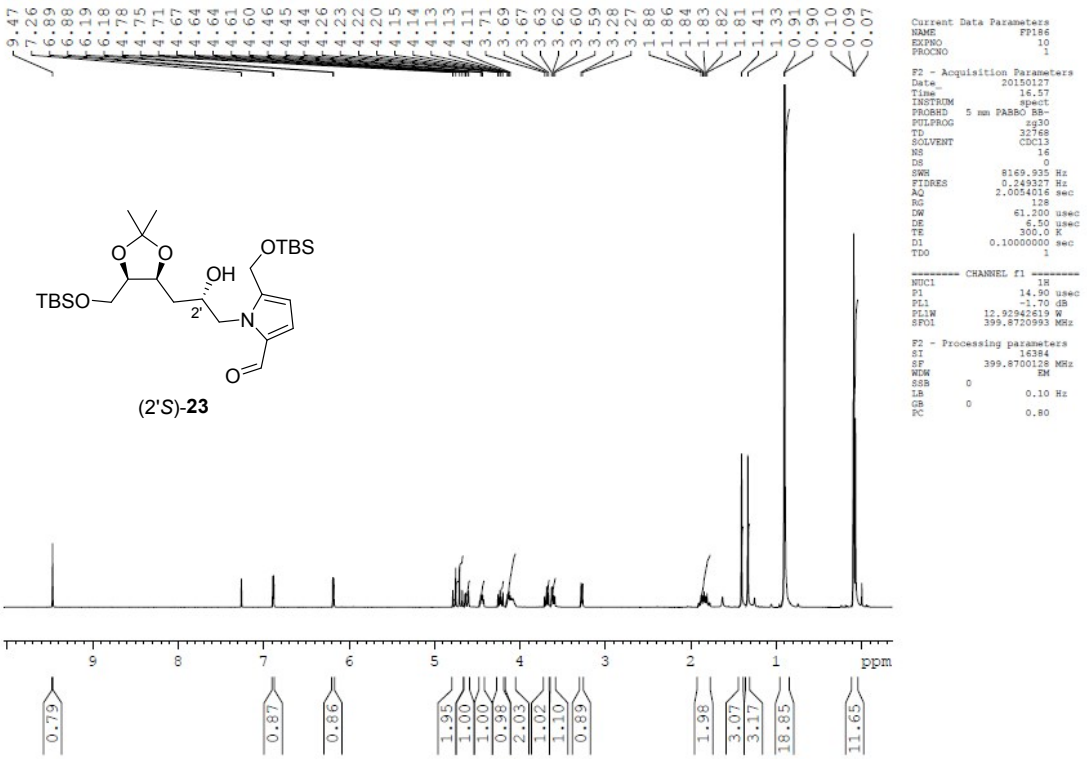


(5*R*)-**13**

```
Current Data Parameters
NAME                  FP195A
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150217
Time                  15.09
INSTRUM                spect
PROBHD    5 mm PABBO BB/
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                       400
DS                        0
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                      2050
DW                    20.800 usec
DE                     6.50 usec
TE                    300.0 K
D1                 0.63167691 sec
d11                0.03000000 sec
DELTA              0.53167689 sec
TD0                        1
SFO1           100.6239378 MHz
NUC1                      13C
P1                      6.98 usec
PLW1           -1.00000000 W
SFO2           400.1318006 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                 100.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                     32768
SF                100.6127560 MHz
WDW                       EM
SSB       0
LB                     2.00 Hz
GB        0
PC                     0.80
```

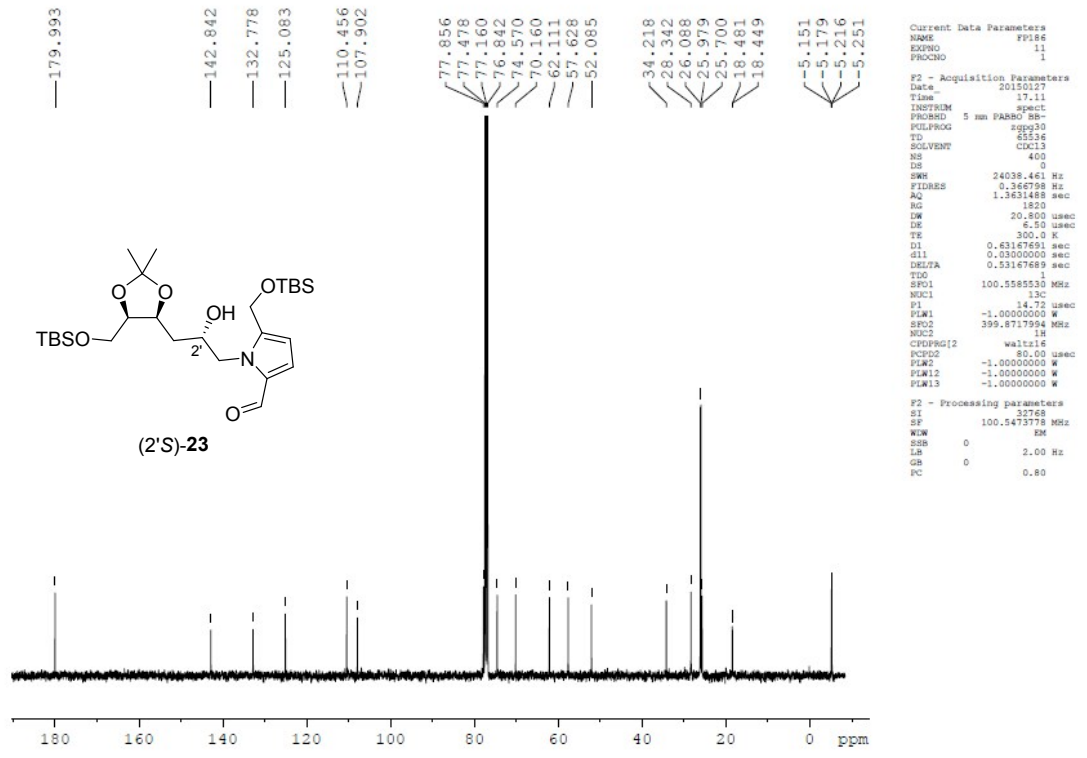



```
Current Data Parameters
NAME                  FP186
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150127
Time                  16.57
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       16
DS                        0
SWH                8169.935 Hz
FIDRES                0.249327 Hz
AQ                 2.0054016 sec
RG                      128
DW                   61.200 usec
DE                    6.50 usec
TE                   300.0 K
D1                 0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    14.90 usec
PL1                   -1.70 dB
PL1W           12.92942619 W
SFO1           399.8720993 MHz

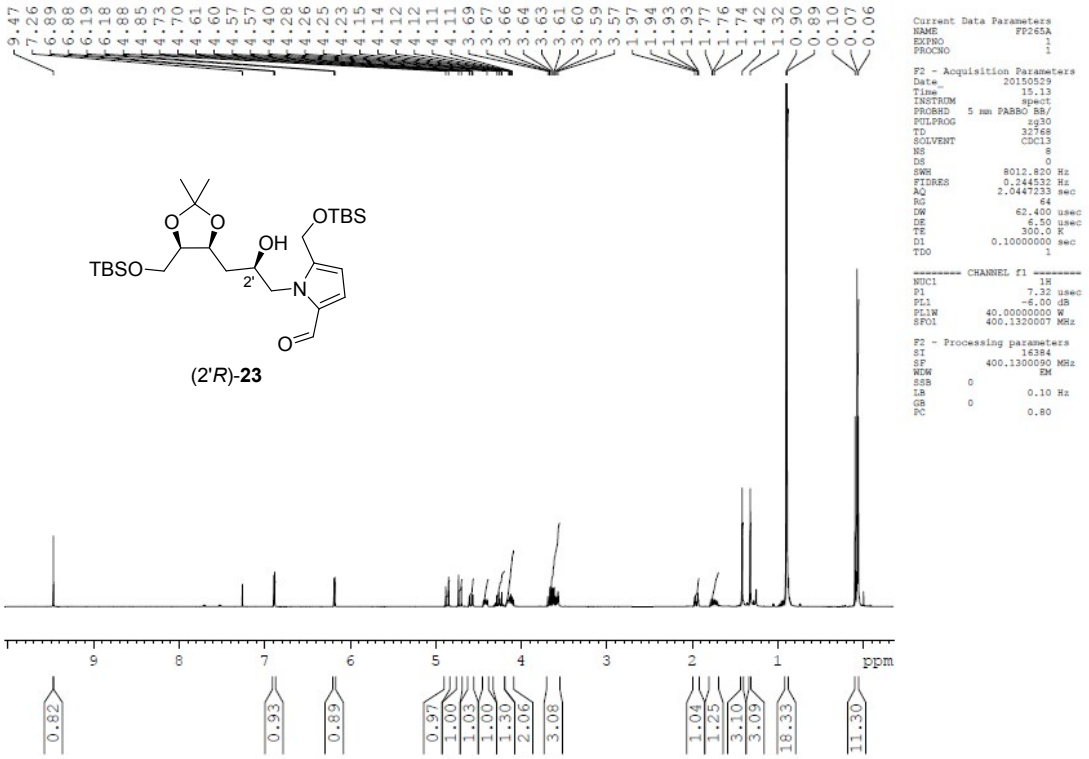
F2 - Processing parameters
SI                    16384
SF                399.8700128 MHz
WDW                      EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    0.80
```




```
Current Data Parameters
NAME                  FP186
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150127
Time                  17.11
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      400
DS                        0
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                     1820
DW                   20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1                 0.63167691 sec
d11                0.03000000 sec
DELTA              0.53167689 sec
TD0                       1
SFO1           100.5585530 MHz
NUC1                     13C
P1                    14.72 usec
PLW1           -1.00000000 W
SFO2           399.8717994 MHz
NUC2                     1H
CPDPRG[2          waltz16
PCPD2                 80.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                    32768
SF                100.5473778 MHz
WDW                      EM
SSB       0
LB                    2.00 Hz
GB        0
PC                    0.80
```

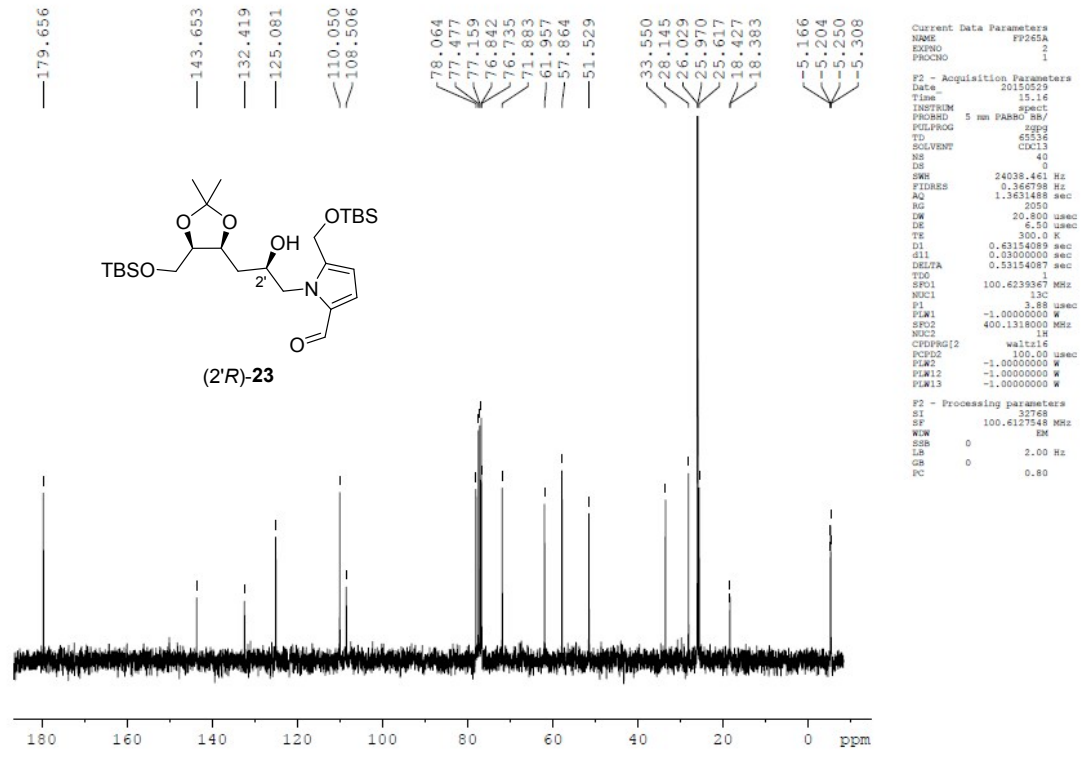



```
Current Data Parameters
NAME                  FP265A
EXPNO                      1
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150529
Time                  15.13
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                        8
DS                        0
SWH                8012.820 Hz
FIDRES            0.244532 Hz
AQ                2.0447233 sec
RG                       64
DW                   62.400 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.10000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     7.32 usec
PL1                   -6.00 dB
PL1W          40.00000000 W
SFO1          400.1320007 MHz

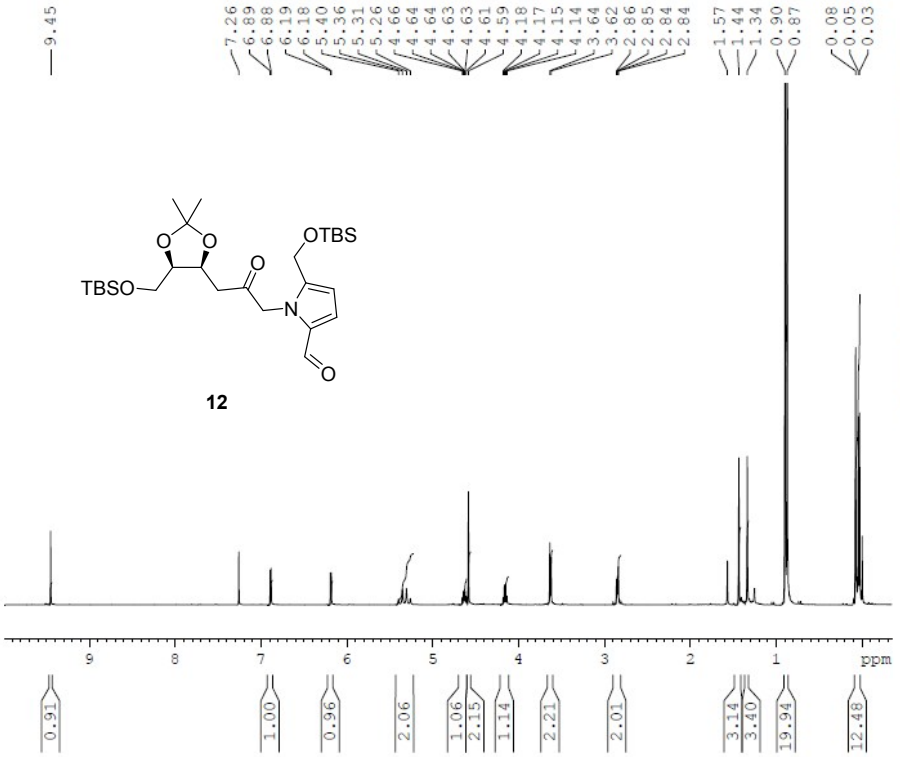
F2 - Processing parameters
SI                     16384
SF            400.1300090 MHz
WDW                       EM
SSB       0
LB                     0.10 Hz
GB        0
PC                     0.80
```




```
Current Data Parameters
NAME                  FP265A
EXPNO                      2
PROCNO                     1

F2 - Acquisition Parameters
Date_              20150529
Time                  15.16
INSTRUM                spect
PROBHD   5 mm PABBO BB/
PULPROG             zgpg
TD                    65536
SOLVENT               CDCl3
NS                       40
DS                        0
SWH               24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631488 sec
RG                     2050
DW                   20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.63154089 sec
d11               0.03000000 sec
DELTA             0.53154087 sec
TD0                        1
SFO1          100.6239367 MHz
NUC1                      13C
P1                     3.88 usec
PLW1          -1.00000000 W
SFO2          400.1318000 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                     32768
SF            100.6127548 MHz
WDW                       EM
SSB       0
LB                     2.00 Hz
GB        0
PC                     0.80
```

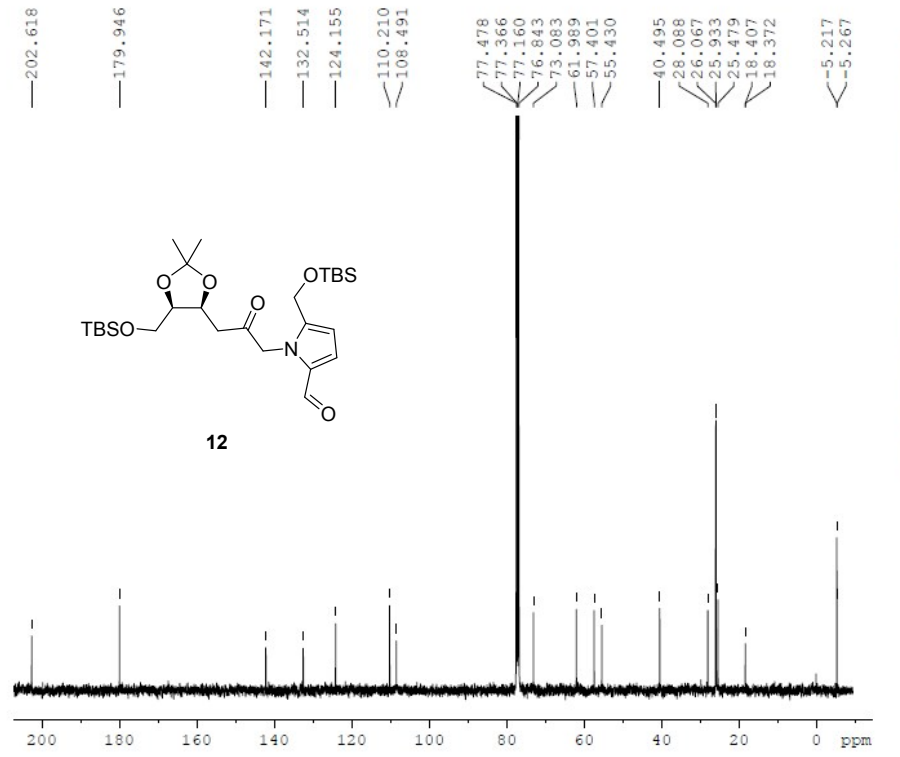



```
Current Data Parameters
NAME                  FP191
EXPNO                    10
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150209
Time                  16.28
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG                zg30
TD                    32768
SOLVENT               CDCl3
NS                       32
DS                        0
SWH                8169.935 Hz
FIDRES             0.249327 Hz
AQ                 2.0054016 sec
RG                      181
DW                   61.200 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                      1H
P1                    14.90 usec
PL1                   -1.70 dB
PL1W           12.92942619 W
SFO1           399.8720993 MHz

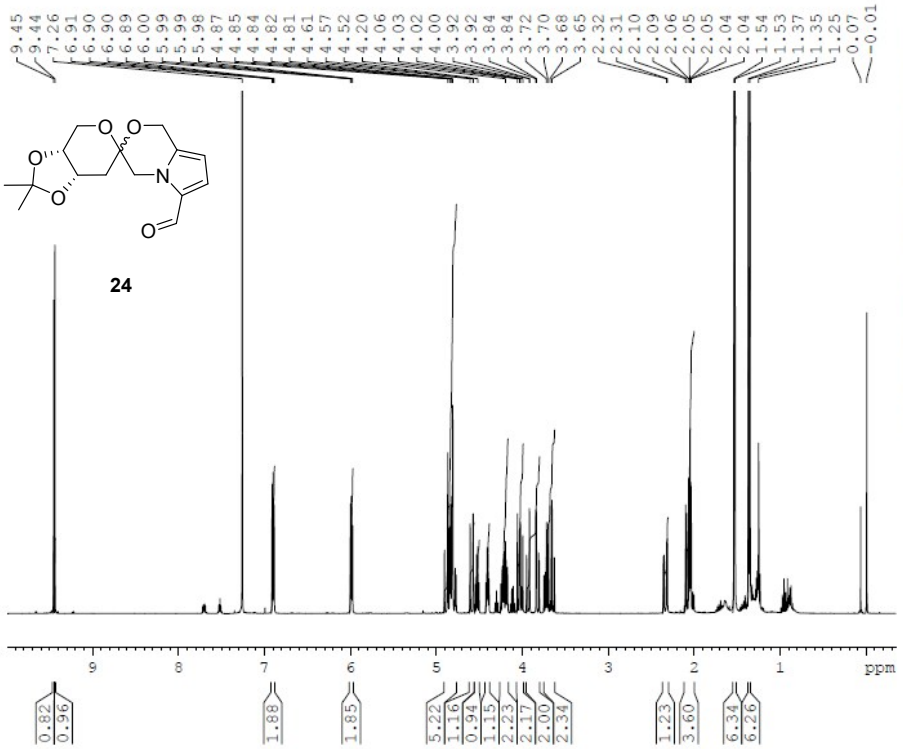
F2 - Processing parameters
SI                    16384
SF             399.8700129 MHz
WDW                      EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    0.80
```




```
Current Data Parameters
NAME                  FP191
EXPNO                    11
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150210
Time                   6.03
INSTRUM                spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                    65536
SOLVENT               CDCl3
NS                      800
DS                        0
SWH               24038.461 Hz
FIDRES             0.366798 Hz
AQ                 1.3631488 sec
RG                     1820
DW                   20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1                0.63167691 sec
d11               0.03000000 sec
DELTA             0.53167689 sec
TD0                       1
SFO1           100.5584512 MHz
NUC1                     13C
P1                    14.72 usec
PLW1          -1.00000000 W
SFO2           399.8717194 MHz
NUC2                      1H
CPDPRG[2          waltz16
PCPD2                 80.00 usec
PLW2          -1.00000000 W
PLW12         -1.00000000 W
PLW13         -1.00000000 W

F2 - Processing parameters
SI                    32768
SF             100.5473777 MHz
WDW                      EM
SSB       0
LB                    2.00 Hz
GB        0
PC                    0.80
```



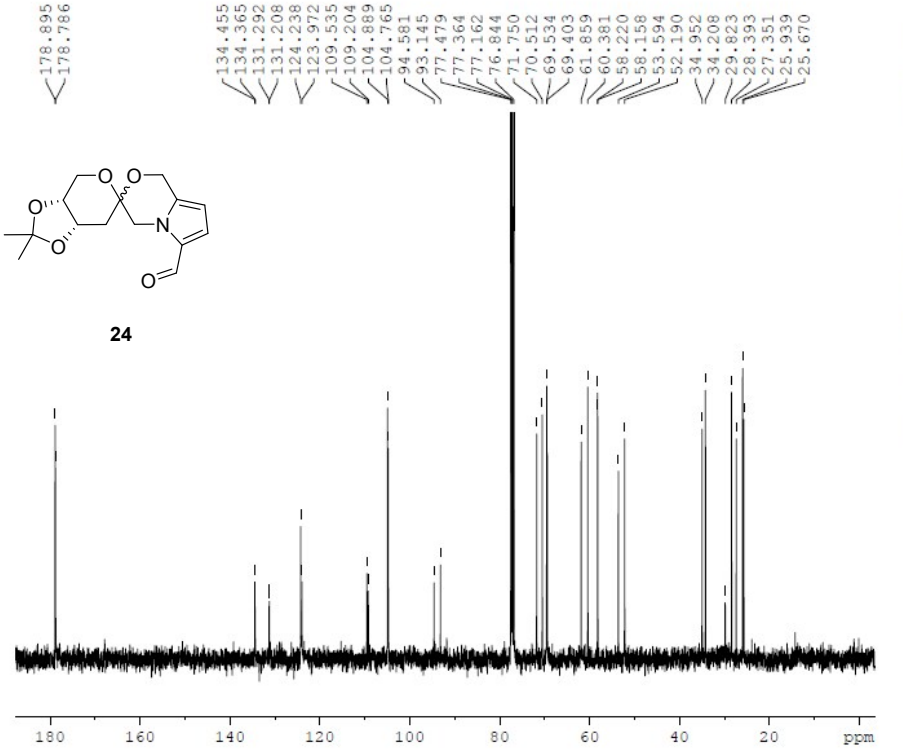
24

```
Current Data Parameters
NAME                  FP267
EXPNO                     1
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150523
Time                  14.31
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG               zg30
TD                   32768
SOLVENT              CDCl3
NS                      32
DS                       0
SWH                8012.820 Hz
FIDRES                0.244532 Hz
AQ                 2.0447233 sec
RG                      128
DW                   62.400 usec
DE                    6.50 usec
TE                   300.0 K
D1                 0.10000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                    7.32 usec
PL1                  -6.00 dB
PL1W           40.00000000 W
SFO1           400.1320007 MHz

F2 - Processing parameters
SI                    16384
SF               400.1300093 MHz
WDW                      EM
SSB       0
LB                    0.10 Hz
GB        0
PC                    0.80
```

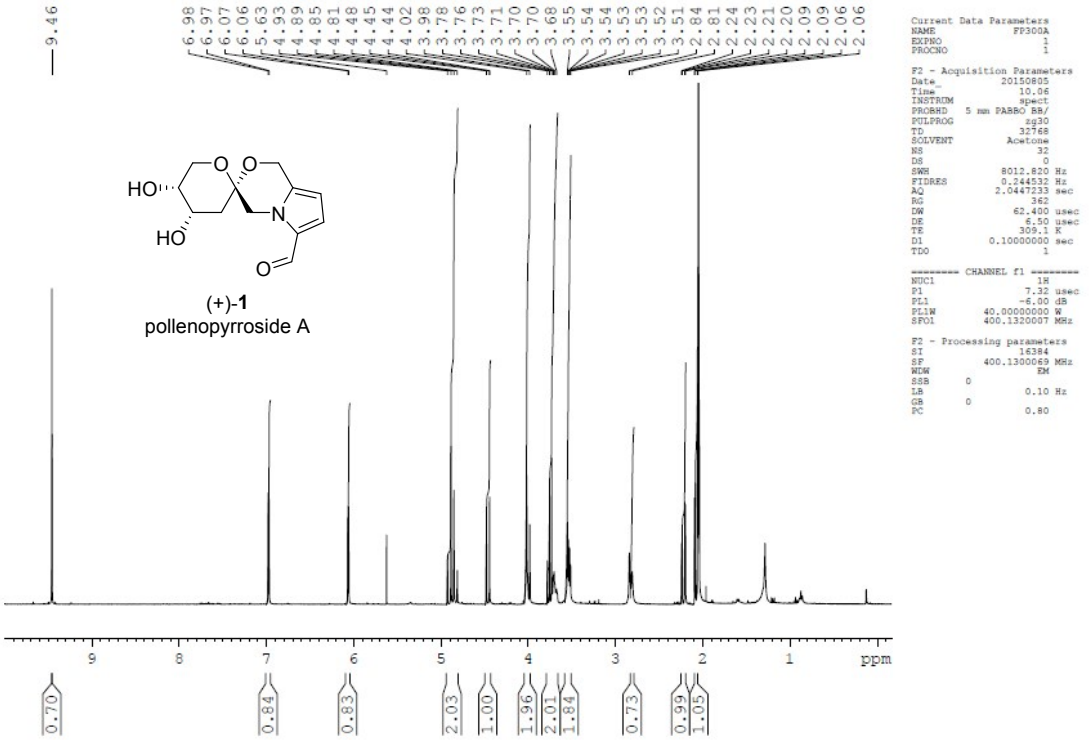


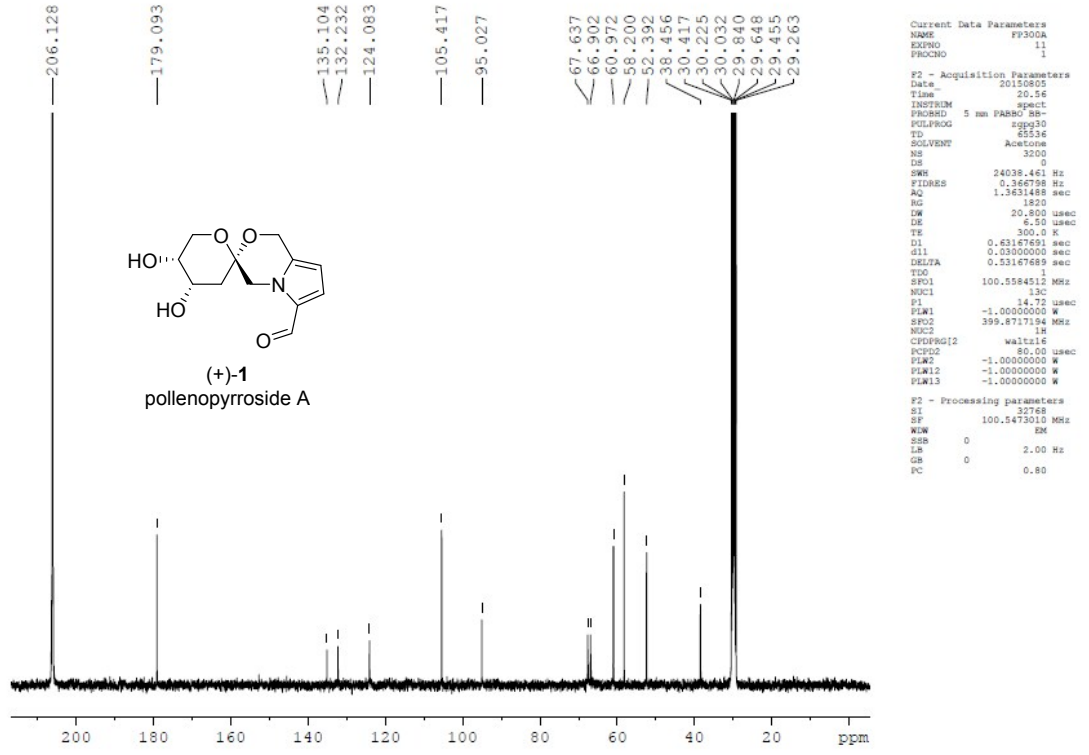
24

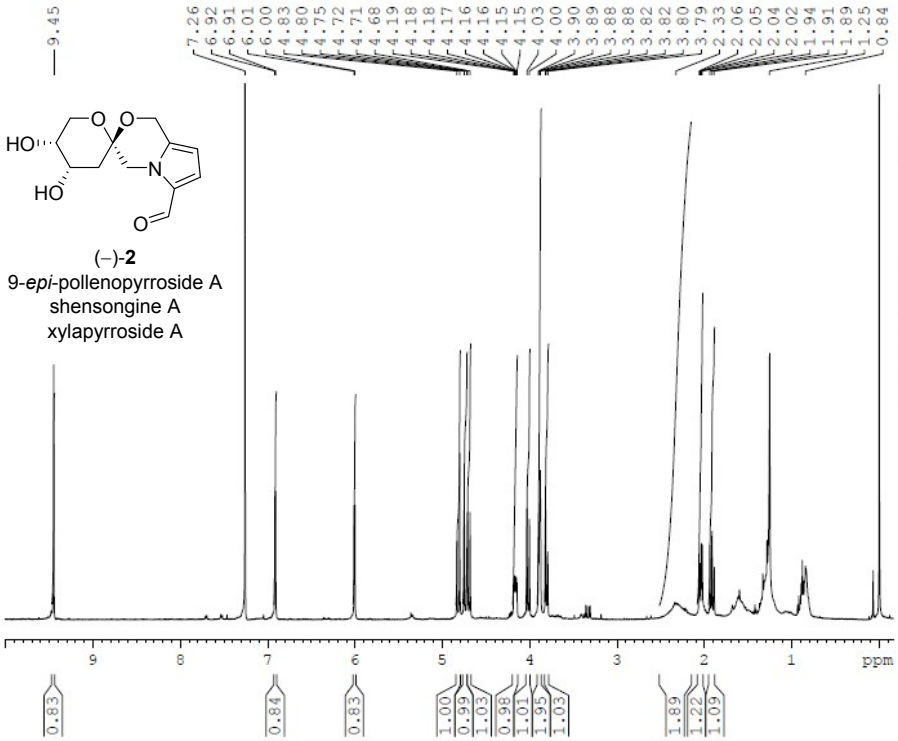
```
Current Data Parameters
NAME                  FP267
EXPNO                     5
PROCNO                    1

F2 - Acquisition Parameters
Date_              20150523
Time                  14.56
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG               zgpg
TD                   65536
SOLVENT              CDCl3
NS                      401
DS                       0
SWH               24038.461 Hz
FIDRES                0.366798 Hz
AQ                 1.3631488 sec
RG                      2050
DW                   20.800 usec
DE                    6.50 usec
TE                   300.0 K
D1                 0.63154089 sec
d11                0.03000000 sec
DELTA              0.53154087 sec
TD0                       1
SFO1           100.6239367 MHz
NUC1                     13C
P1                    3.88 usec
PLW1           -1.00000000 W
SFO2           400.1318000 MHz
NUC2                     1H
CPDPRG[2          waltz16
PCPD2                100.00 usec
PLW2           -1.00000000 W
PLW12          -1.00000000 W
PLW13          -1.00000000 W

F2 - Processing parameters
SI                    32768
SF               100.6127552 MHz
WDW                      EM
SSB       0
LB                    2.00 Hz
GB        0
PC                    0.80
```


9.46
6.98
6.97
6.07
6.06
5.63
4.93
4.89
4.85
4.81
4.48
4.45
4.44
4.02
3.98
3.78
3.76
3.73
3.71
3.70
3.70
3.68
3.55
3.54
3.54
3.53
3.53
3.52
3.51
2.84
2.81
2.24
2.23
2.21
2.20
2.09
2.09
2.06
2.06
HO
HO
O
O
N
O
(+)-1
pollenopyrroside A
ppm
0.70
0.84
0.83
2.03
1.00
1.96
2.01
1.84
0.73
0.99
1.05


206.128
179.093
135.104
132.232
124.083
105.417
95.027
67.637
66.902
60.972
58.200
52.392
38.456
30.417
30.225
30.032
29.840
29.648
29.455
29.263
HO
HO
O
O
N
O
(+)-1
pollenopyrroside A
ppm



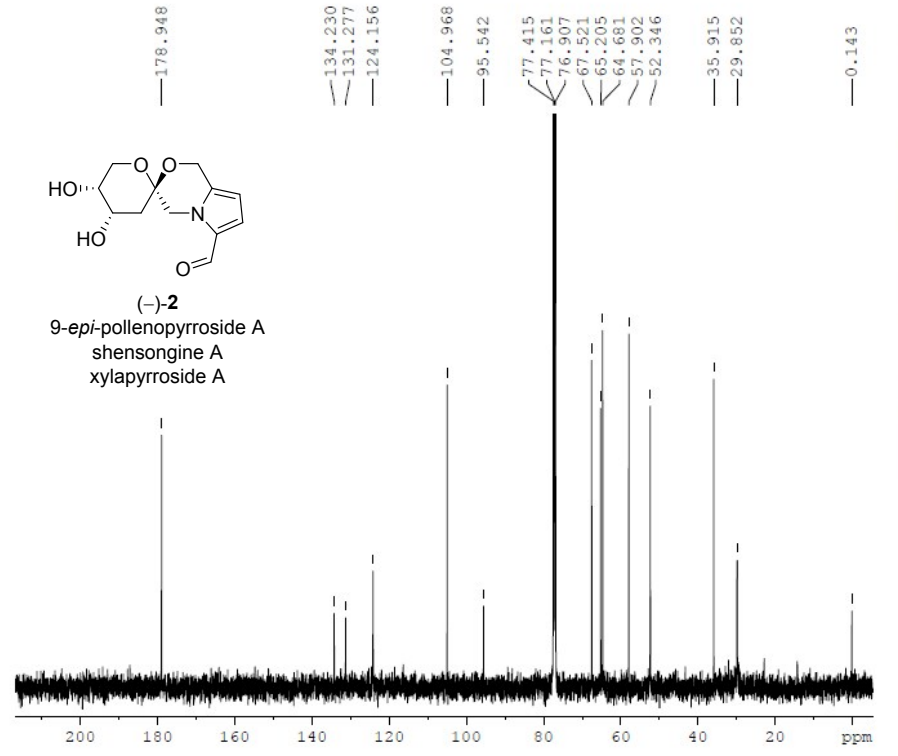
(–)-**2**
9-*epi*-pollenopyrroside A
shensongine A
xylapyrroside A

Current Data Parameters
NAME FP300B
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20150817
Time 18.04
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 0
SWH 10000.000 Hz
FIDRES 0.305176 Hz
AQ 1.6384000 sec
RG 222.74
DW 50.000 usec
DE 6.50 usec
TE 300.0 K
D1 0.10000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 500.1925007 MHz
NUC1 1H
P1 10.00 usec
PLW1 21.00000000 W

F2 - Processing parameters
SI 16384
SF 500.1900134 MHz
WDW EM
SSB 0
LB 0.10 Hz
GB 0
PC 0.80



(–)-**2**
9-*epi*-pollenopyrroside A
shensongine A
xylapyrroside A

Current Data Parameters
NAME FP300B
EXPNO 2
PROCNO 1

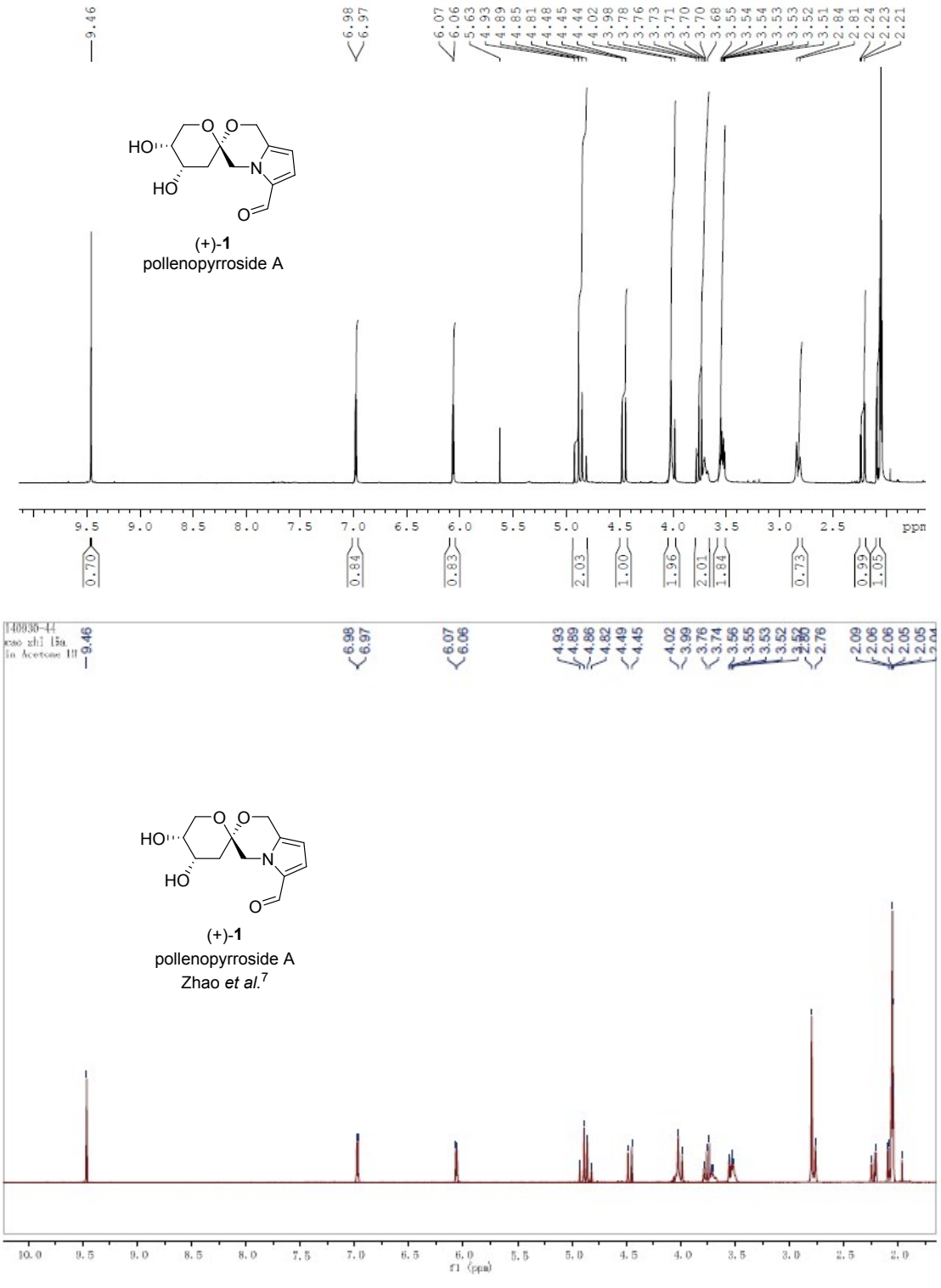
F2 - Acquisition Parameters
Date_ 20150817
Time 18.24
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 4000
DS 0
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 749.15
DW 16.800 usec
DE 6.50 usec
TE 300.0 K
D1 0.63058811 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
SFO1 125.7868349 MHz
NUC1 13c
P1 5.56 usec
PLW1 83.00000000 W

======== CHANNEL f2 ========
SFO2 500.1918000 MHz
NUC2 1H
CPDPRG[2 waltz16
PCPD2 80.00 usec
PLW2 21.00000000 W
PLW12 0.32813001 W
PLW13 0.20999999 W

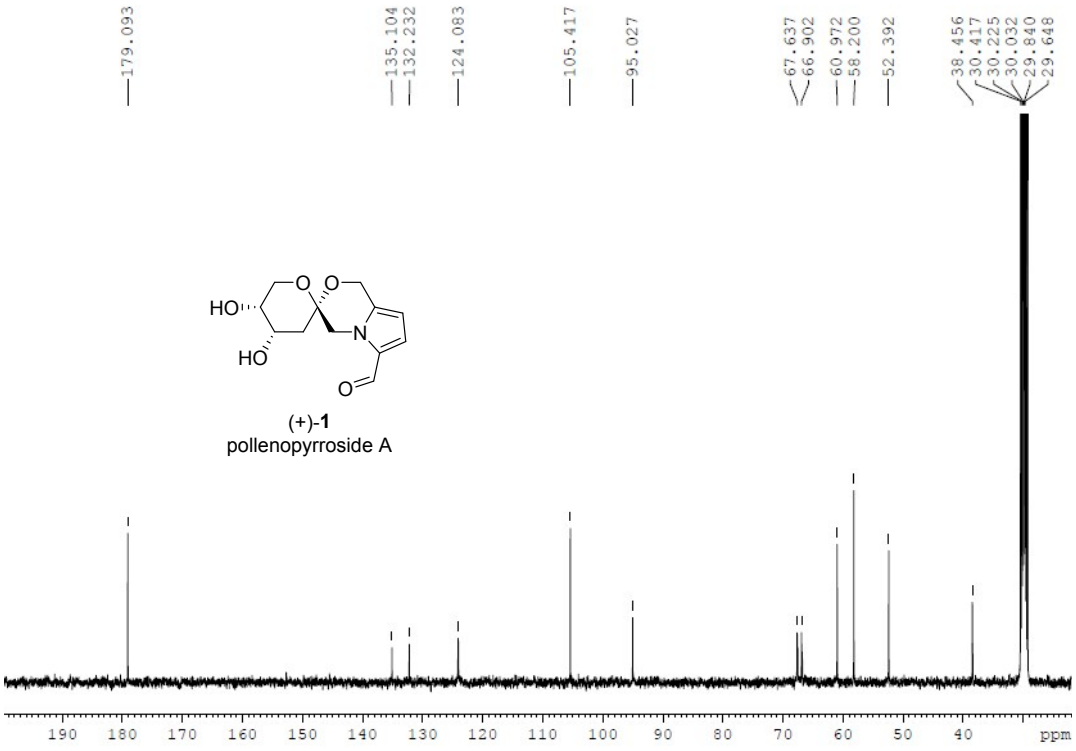
F2 - Processing parameters
SI 32768
SF 125.7728573 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 0.80

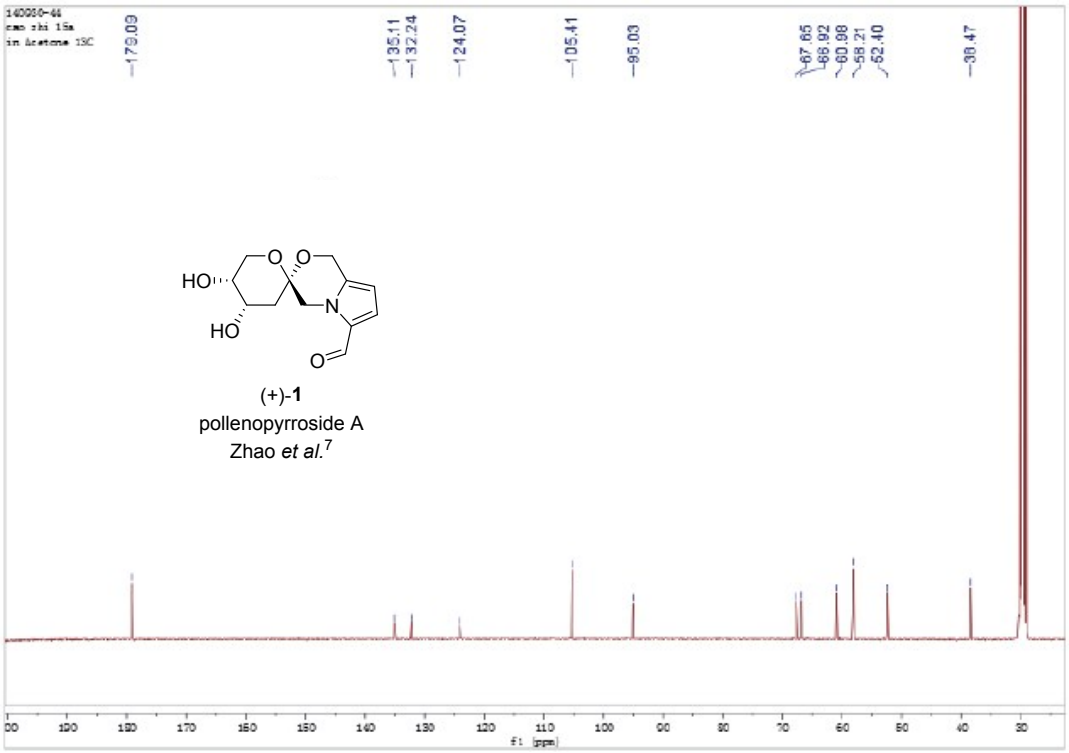
Comparison of ^{1}H NMR spectra for synthetic pollenopyrroside A ((+)-**1**) and pollenopyrroside A ((+)-**1**) synthesised by Zhao *et al.*[7]



[7] Cao, Z.; Li, Y.; Wang, S.; Guo, X.; Wang, L.; Zhao, W. *Synlett* **2015**, *26* (7), 921–926

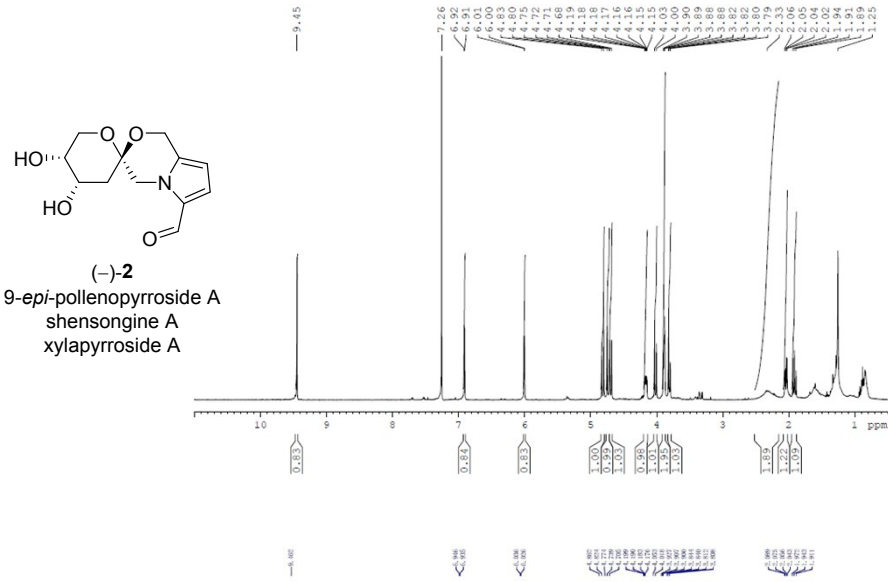
Comparison of ^{13}C NMR spectra for synthetic pollenopyrroside A ((+)-**1**) and pollenopyrroside A ((+)-**1**) synthesised by Zhao *et al.*[7]



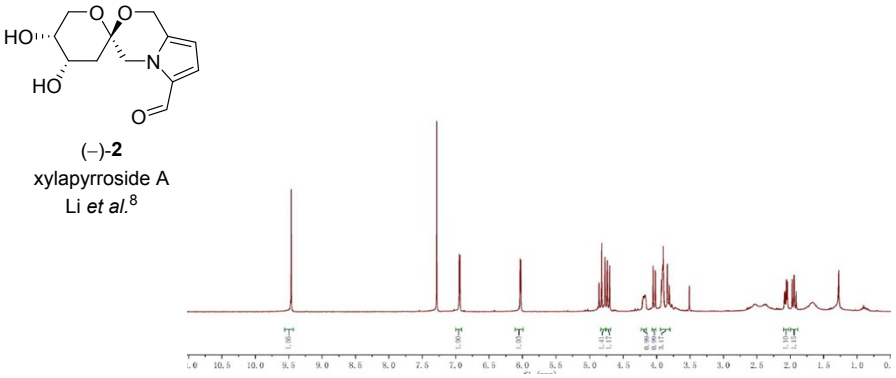


[7] Cao, Z.; Li, Y.; Wang, S.; Guo, X.; Wang, L.; Zhao, W. *Synlett* **2015**, *26* (7), 921–926

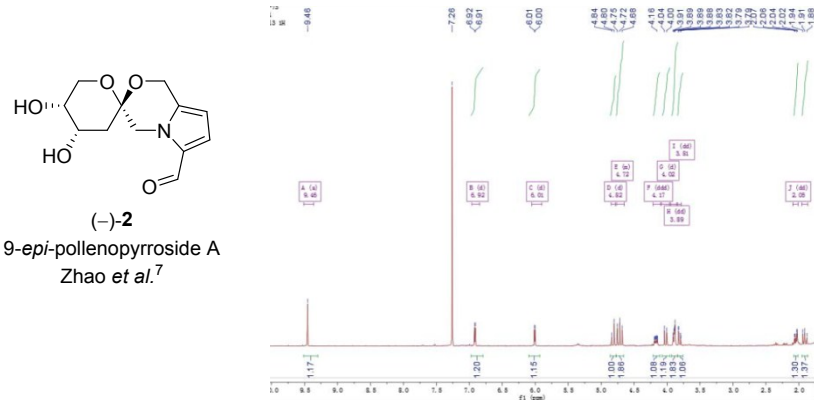
Comparison of ^{1}H NMR spectra for synthetic 9-*epi*-pollenopyrroside A ((−)-**2**), xylapyrroside A ((−)-**2**) isolated by Li *et al.*[8] and 9-*epi*-pollenopyrroside A ((−)-**2**) synthesised by Zhao *et al.*[7]



(−)-**2**
9-*epi*-pollenopyrroside A
shensongine A
xylapyrroside A



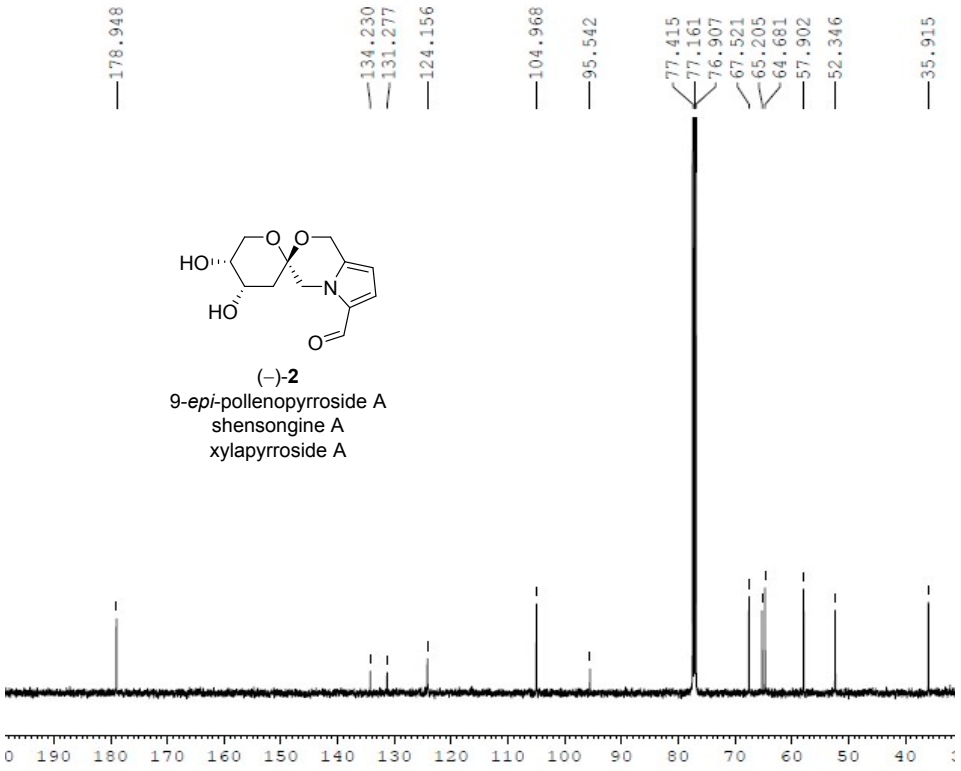
(−)-**2**
xylapyrroside A
Li *et al.*[8]

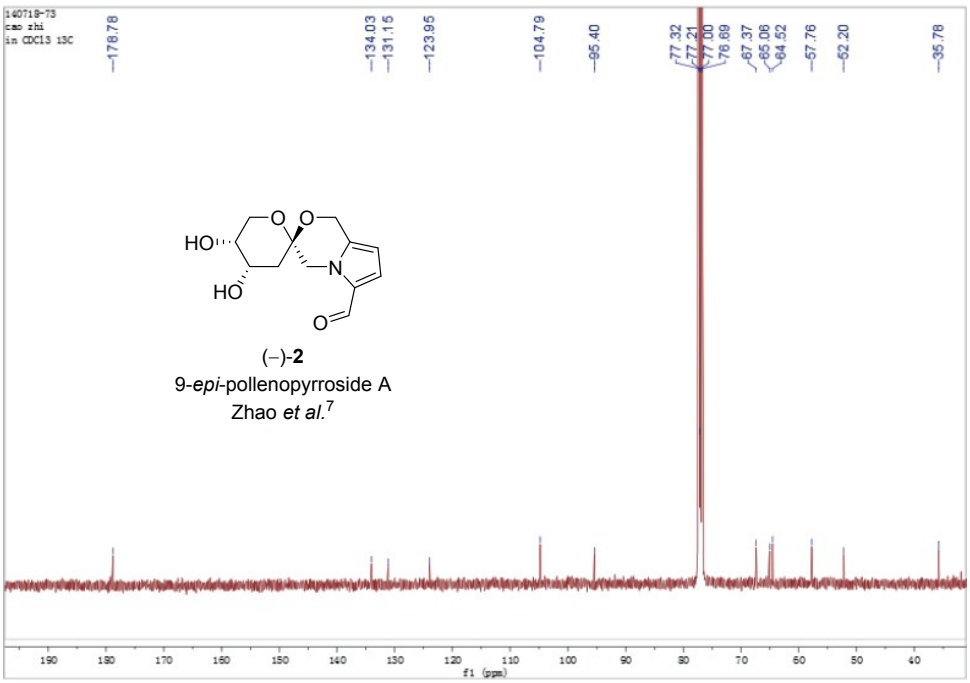


(−)-**2**
9-*epi*-pollenopyrroside A
Zhao *et al.*[7]

[7] Cao, Z.; Li, Y.; Wang, S.; Guo, X.; Wang, L.; Zhao, W. *Synlett* **2015**, *26* (7), 921–926
[8] Li, M.; Xiong, J.; Huang, Y.; Wang, L.-J.; Tang, Y.; Yang, G.-X.; Liu, X.-H.; Wei, B.-G.; Fan, H.; Zhao, Y.; Zhai, W.-Z.; Hu, J.-F. *Tetrahedron* **2015**, *71* (33), 5285–5295

Comparison of ^{13}C NMR spectra for synthetic 9-*epi*-pollenopyrroside A ((−)-**2**) and 9-*epi*-pollenopyrroside A ((−)-**2**) synthesised by Zhao *et al.*[7]





[7] Cao, Z.; Li, Y.; Wang, S.; Guo, X.; Wang, L.; Zhao, W. *Synlett* **2015**, *26* (7), 921–926

Comparison of ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data for synthetic 9-*epi*-pollenopyrroside A ((−)-**2**) reported by Zhao *et al.*[7], isolated capparisine B ((+)-**2**)[9] and isolated xylapyrroside A ((−)-**2**)[8] in $CDCl_3$

	δ_H (*J* values in Hz)			δ_C	
No.	9-*epi*-pollenopyrroside A[7]	capparisine B[9]	xylapyrroside A[8]	9-*epi*-pollenopyrroside A[7]	capparisine B[9]
2	-	-	-	131.2	131.2
3	6.92 (d, 4.1)	6.92 (d, 3.8)	6.90 (d, 4.0)	124.0	124.0
4	6.01 (d, 4.1)	6.01 (d, 3.5)	5.99 (d, 4.0)	104.8	104.8
5	-	-	-	134.1	134.1
6	4.82 (d, 15.3) 4.71 (m)	4.82 (d, 15.2) 4.74 (d, 15.7)	4.80 (d, 15.6) 4.71 (d, 15.6)	57.8	57.8
7	9.46 (s)	9.45 (s)	9.42 (s)	178.8	178.8
8	4.71 (m) 4.02 (d, 14.0)	4.70 (d, 14.4) 4.02 (d, 13.8)	4.70 (d, 13.9) 4.03 (d, 13.9)	52.2	52.2
9	-	-	-	95.4	95.4
10	1.91 (t, 13.0) 2.05 (dd, 13.0, 5.5)	1.91 (dd, 12.6, 11.8) 2.04 (dd, 12.8, 5.3)	1.90 (dd, 12.8, 11.6) 2.02 (dd, 12.8, 5.6)	35.8	35.8
11	4.17 (ddd. 11.4, 5.4, 3.2)	4.14 (m)	4.14 (ddd, 11.6, 5.6, 2.8)	65.1	65.1
12	3.88 (m, overlapped)	3.88 (m)	3.87 (m, overlapped)	67.4	67.4
13	3.89 (dd, overlapped) 3.81 (dd, 12.7, 1.2)	3.89 (d, 12.1) 3.81 (d, 12.1)	3.87 (dd, overlapped) 3.78 (dd, 12.8, 1.2)	64.5	64.5

Comparison of ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR data for isolated shensongine A ((−)-**2**)[10] and isolated xylapyrroside A ((−)-**2**)[8] in CD_3OD

	δ_H (*J* values in Hz)		δ_C	
No.	shensongine A[10]	xylapyrroside A[8]	shensongine A[10]	xylapyrroside A[8]
2	-	-	132.4	132.4
3	7.00 (d, 4.1)	7.04 (d, 4.0)	125.7	125.8
4	6.06 (d, 4.1)	6.09 (d, 4.0)	106.1	106.1
5	-	-	137.0	137.1
6	4.83 (m, overlapped) 4.73 (d, 15.8)	4.86 (d, 15.6) 4.74 (d, 15.6)	58.6	58.6
7	9.35 (s)	9.39 (s)	180.2	180.2
8	4.58 (d, 14.0) 3.96 (d, 14.0)	4.62 (d, 14.0) 4.00 (d, 14.0)	53.4	53.5
9	-	-	96.7	96.9
10	1.98 (t, 12.0) 1.89 (dd, 12.0, 5.3)	2.02 (dd, 12.8, 11.6) 1.92 (dd, 12.8, 5.2)	36.1	36.1
11	4.07 (ddd, 12.0, 5.3, 2.7)	4.10 (m)	66.0	66.0
12	3.78 (m, overlapped)	3.81 (m)	68.7	68.7
13	3.79 (dd, overlapped) 3.67 (dd, 18.5, 7.3)	3.83 (br d, 12.0) 3.78 (br d, 12.0)	66.3	66.3

[7] Cao, Z.; Li, Y.; Wang, S.; Guo, X.; Wang, L.; Zhao, W. *Synlett* **2015**, *26* (7), 921–926
[8] Li, M.; Xiong, J.; Huang, Y.; Wang, L.-J.; Tang, Y.; Yang, G.-X.; Liu, X.-H.; Wei, B.-G.; Fan, H.; Zhao, Y.; Zhai, W.-Z.; Hu, J.-F. *Tetrahedron* **2015**, *71* (33), 5285–5295
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[10] Ding, B.; Dai, Y.; Hou, Y.-L.; Yao, X.-S. *J. Asian Nat. Prod. Res.* **2015**, *17* (5), 559–566