Remarkable Stereoselectivity in Intramolecular Borono-Mannich Reactions : Synthesis of Conduramines

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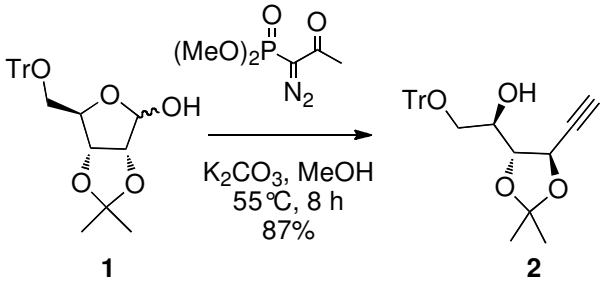
Supporting Information

I. General Experimental

General. Unless otherwise stated, all reactions were carried out under argon. Tetrahydrofuran was distilled under Argon on sodium-benzophenone. Dichloromethane was distilled under Argon on CaH_2. Reactions were monitored with analytical thin-layer chromatography (TLC) on silica gel 60 F_{254} plates and visualized under UV (254 nm) and/or by staining with $KMNO_4$ or Vanillin or Ninhydrin. Silica gel SDS 60 ACC 35-70 mm was used for column chromatography. NMR spectra were recorded with AM 300, AVANCE 300 and AVANCE 500 Brüker spectrometers. Chemical shifts are given in parts per million, referenced to the solvent peak of $CDCl_3$, defined at 77.2 ppm (^{13}C NMR) and 7.24 ppm (^{1}H NMR). Melting points (uncorrected) were determined with the aid of a Büchi B-540 apparatus. IR spectra were recorded on a Perkin-Elmer Spectrum BX instrument with an FT-IR system. Optical rotations were measured on a JASCO-810 polarimeter using a cell of 1 dm-length path.

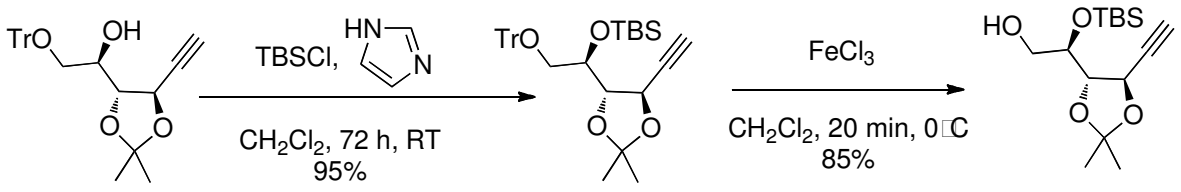
II. Experimental and Spectral data



1 **2**

(3R,4R,5R)-3,4-(i-propylidenedioxy)-6-(triphenylmethoxy)hex-1-yne 2:

To a solution of **1** (9.2 g, 21.3 mmol) and K_2CO_3 (8.8 g, 63.8 mmol, 3 equiv.) in distilled MeOH (200 mL) at 55 °C, was added with a seringe pump a solution of dimethyl (1-diazo-2-oxopropyl)phosphonate (10.2 g, 53.2 mmol, 2.5 equiv.) in MeOH (40 mL) for 8 h. After addition of saturated aqueous NH_4Cl (100 mL), the solvent was evaporated. The aqueous phase was extracted with EtOAc (3 x 100 mL) and the combined organic layers were washed with brine (100 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 100/0 to 85/15) to afford desired compound **2** (7.9 g, 87%): $[\alpha]_D^{25}$ +6.3 (*c* 1, $CHCl_3$); ν_{max}: 3492, 3285, 3086, 3058, 3024, 2988, 2933, 2881, 1597, 1490, 1448, 1381, 1372, 1212, 1158, 1056, 854 cm^{-1}; **^{1}H NMR** (300 MHz, CDCl3): δ (ppm) 7.54-7.19 (m, 15H, H_{ar}), 4.73 (dd, 1H, $J_{1,3}$ 2 and $J_{3,4}$ 6 Hz, H-3), 4.23 (t, 1H, $J_{4,5} = J_{4,3}$ 6 Hz, H-4), 3.96-3.86 (m, 1H, H-5), 3.36 (d, 2H, $J_{5,6}$ 5 Hz, H-6), 2.50 (d, 1H, $J_{1,3}$ 2 Hz, H-1), 2.46 (d, 1H, *J* 4 Hz, O*H*), 1.54 (s, 3H, C(CH_3)$_2$)), 1.41 (s, 3H, C(CH_3)$_2$); **^{13}C** NMR (75 MHz, CDCl3): δ (ppm) 143.7 (C_{ar}), 128.7 (C_{ar}), 127.9 (C_{ar}), 127.2 (C_{ar}), 110.9 (C(CH$_3$)$_2$), 87.1 (CPh$_3$), 82.0 (C-4), 81.9 (C-2), 74.4 (C-1), 71.0 (C-5), 67.0 (C-3), 64.4 (C-6), 26.9 (C(CH$_3$)$_2$), 26.0 (C(CH$_3$)$_2$); **ESIMS**: *m/z* = 451.2 [(M+Na)$^+$, 100%], **ESIHRMS**: *m/z* = 451.1873. $C_{28}H_{28}O_4Na$ requires 451.1885.



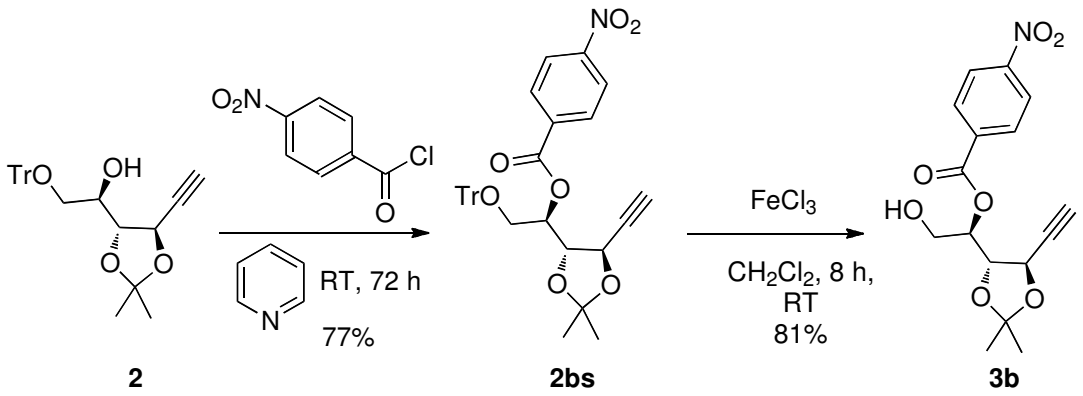
2 **2as** **3a**

(3R,4S,5R)-5-(t-butyldimethylsilyloxy)-3,4-(i-propylidenedioxy)-6-(triphenylmethoxy)hex-1-yne 2as:

Imidazole (1.42 g, 21.00 mmol, 3.00 equiv), and TBSCl (1.60 g, 10.50 mmol, 1.50 equiv) were added to a solution of alcohol **2** (2.95 g, 7.10 mmol, 1.00 equiv) in CH_2Cl_2 (50 mL) and the resulting mixture was stirred for 72 hours at room temperature. The solvent was removed in *vacuo* and the residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 100:0 to 95:5) to afford desired compound **2as** as a colorless oil (3.65 g, 95%): $\mathbf{[\alpha]_D^{25}}$ +8.4 (*c* 1, $CHCl_3$); $\boldsymbol{\nu_{max}}$: 3291, 2356, 1597, 1490, 1471, 1448, 1380, 1371, 1251, 1211, 1141, 1071, 832, 775, 808 cm^{-1}; **^{1}H NMR** (300 MHz, CDCl3): δ (ppm) 7.20-7.25 (m, 15H, H_{ar}), 4.64 (dd, 1H, $J_{1,3}$ 2 and $J_{3,4}$ 7 Hz, H-3), 4.39 (dd, 1H, $J_{4,5}$ 3 and $J_{4,3}$ 7 Hz, H-4), 4.02-3.95 (m, 1H, H-5), 3.23-3.08 (m, 2H, H-6), 2.33 (d, 1H, $J_{1,3}$ 2 Hz, H-1), 1.47 (s, 3H, C(CH_3)$_2$), 1.37 (s, 3H, C(CH_3)$_2$), 0.79 (s, 9H, SiC(CH_3)$_3$), 0.00 (s, 3H, SiCH_3), -0.12 (s, 3H, SiCH_3); **^{13}C** NMR (75 MHz, CDCl3): δ (ppm) 144.1 (C_{ar}), 129.0 (C_{ar}), 127.9 (C_{ar}), 121.2 (C_{ar}), 110.3(C(CH$_3$)$_2$), 87.3 (CPh$_3$), 82.8 (C-4), 82.6 (C-2), 74.5 (C-1), 70.9 (C-5), 65.4 (C-3), 65.3 (C-6), 26.9 (C(CH$_3$)$_2$), 26.0 (SiC(CH$_3$)$_3$), 25.9 (C(CH$_3$)$_2$), 18.2 (SiC(CH$_3$)$_3$), -4.5 (SiCH$_3$); **ESIMS**: *m/z* = 565 [(M+Na)$^+$, 100%], **ESIHRMS**: *m/z* = 565.2763. $C_{34}H_{42}O_4NaSi$ requires 565.2750; **Anal.** Calcd for $C_{34}H_{42}O_4Si$: C, 75.24; H, 7.80; O, 11.79; Si, 5.17. Found: C, 74.37; H, 7.94.

(2R,3S,4R)-2-(t-butyldimethylsilyloxy)-3,4-(i-propylidenedioxy)-hex-5-ynyl-1-ol 3a:

Compound **3as** (2.80 g, 5.16 mmol, 1.00 equiv), $FeCl_3$ (0.28 g, 1.72 mmol, 10 % wt) in CH_2Cl_2 (500 mL) was stirred for 20 minutes at 0 °C. After addition of a saturated aqueous $NaHCO_3$ (100 mL), the aqueous layer was extracted with CH_2Cl_2 (3 x 75 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 85:15) to afford desired compound **3a** as a white solid (1.31 g, 85%): **mp** 42-43°C; $\mathbf{[\alpha]_D^{25}}$ +16.5 (*c* 1, $CHCl_3$); $\boldsymbol{\nu_{max}}$: 3458, 3308, 2359, 2113, 1471, 1462, 1382, 1372, 1252, 1210, 1141, 1050 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 4.49 (dd, $J_{4,6}$ 2 and $J_{3,4}$ 7 Hz, H-4), 4.10 (dd, 1H, $J_{2,3}$ 5 and $J_{3,4}$ 7 Hz, H-3), 3.75 (q, 1H, $J_{1,2} = J_{2,3}$ 5 Hz, H-2), 3.49 (d, 2H, $J_{1,2}$ 5 Hz, H-1), 2.41 (d, 1H, $J_{4,6}$ 2 Hz, H-6), 1.37 (s, 3H, C(CH_3)$_2$), 1.30 (s, 3H, C(CH_3)$_2$), 0.79 (s, 9H, SiC(CH_3)$_3$), 0.01 (s, 3H, SiCH_3), 0.00 (s, 3H, SiCH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) 110.6, 82.2, 74.3, 72.6, 66.9, 64.3, 26.8, 25.8, 25.7, 18.0, -4.4, -4.6; **ESIMS**: *m/z* = 323 [(M+Na)$^+$, 100%], **ESIHRMS**: *m/z* = 323.1660. $C_{15}H_{18}O_4NaSi$ requires 323.1655; **Anal**. Calcd for $C_{15}H_{28}O_4Si$: C, 59.96; H, 9.39; O, 21.30; Si, 9.35. Found: C, 59.98; H, 9.39.



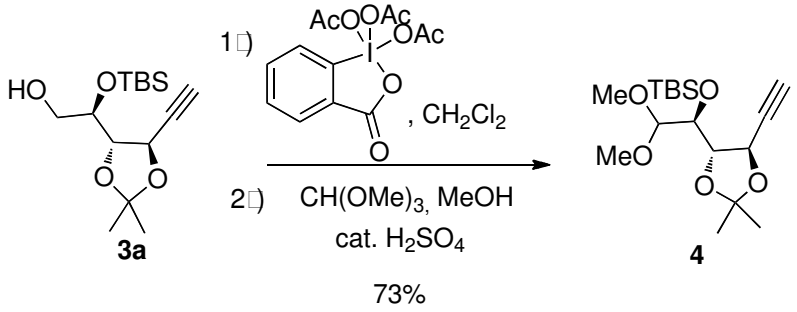
(3R,4R,5R)-5-(p-nitrobenzoate)-3,4-(i-propylidenedioxy)-6-(triphenylmethoxy)hex-1-yne 2bs:

To a solution of the alcohol **2** (56 mg, 0.131 mmol, 1.00 equiv) in pyridine (1 mL) was added *p*-nitrobenzoyl chloride (242 mg, 1.3 mmol, 10 equiv) and the resulting mixture was stirred for 72 hours at room temperature. After removal of the solvent in *vacuo*, the residue was diluted with EtOAc (15 mL) and successively washed with a saturated aqueous K_2CO_3 (10 mL) and brine (10 mL). The organic layer wads dried over Na_2SO_4 and concentrated. The resulting residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 100:0 to 90:10) to afford the desired compound **2bs** as an amorphous solid (58 mg, 77%): $\mathbf{[\alpha]_D^{25}}$ +6.1 (*c* 1, $CHCl_3$); $\boldsymbol{\nu_{max}}$: 3290, 2990, 1728, 1608, 1528, 1490, 1448, 1268, 1215, 1099, 1055, 750 cm^{-1}; **^{1}H NMR** (300 MHz, CDCl3): δ (ppm) 8.35 (d, 2H, *J* 9 Hz, H_{ar}), 8.27 (d, 2H, *J* 9 Hz, H_{ar}), 7.49-7.41 (m, 6H, H_{ar}), 7.33-7.21 (m, 9H, H_{ar}), 5.55 (q, 1H, $J_{5,6} = J_{5,4}$ 5 Hz, H-5), 4.75 (dd, 1H, $J_{3,1}$ 2 and $J_{3,4}$ 7 Hz, H-3), 4.48 (dd, 1H, $J_{4,5}$ 5 and $J_{4,3}$ 7 Hz, H-4), 3.52 (d, 2H, $J_{6,5}$ 5 Hz, H-6), 2.48 (d, 1H, $J_{1,3}$ 2 Hz, H-1), 1.52 (s, 3H, C(CH_3)$_2$), 1.32 (s, 3H, C(CH_3)$_2$); **^{13}C** NMR (75 MHz, CDCl3): δ (ppm) 163.8 (*C*O), 150.7 (Cq_{ar}), 143.5 (Cq_{ar}), 135.3 (Cq_{ar}), 130.9 (C_{ar}), 128.6 (C_{ar}), 127.9 (C_{ar}), 127.8 (C_{ar}), 127.2 (C_{ar}), 123.6 (C_{ar}), 111.3 (*C*(CH_3)$_2$), 87.1 (*C*Ph_3), 81.0 (C-2), 80.2 (C-4), 75.0 (C-1), 73.7 (C-5), 67.4 (C-3), 62.5 (C-6), 26.7 (C(*C*H_3)$_2$), 26.1 (C(*C*H_3)$_2$); **ESIMS**: *m/z* = 600.2 [(M+Na)$^+$, 100%], **ESIHRMS**: *m/z* = 600.2001. $C_{35}H_{31}NO_7Na$ requires 600.1998; **Anal.** Calcd for C35H31NO_7: C, 72.78; H, 5.41; N, 2.42; O, 19.39. Found: C, 72.70; H, 5.58; N, 2.18.

(2R,3S,4R)-2-(p-nitrobenzoate)-3,4-(i-propylidenedioxy)-hex-5-ynyl-1-ol 3b :

Compound **2as** (45 mg, 0.078 mmol, 1.00 equiv), $FeCl_3$ (8 mg, 0.047 mmol, 0.6 equiv) in CH_2Cl_2 (8 mL) was stirred for 8 h at RT. After addition of a saturated aqueous $NaHCO_3$ (10 mL), the aqueous layer was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers

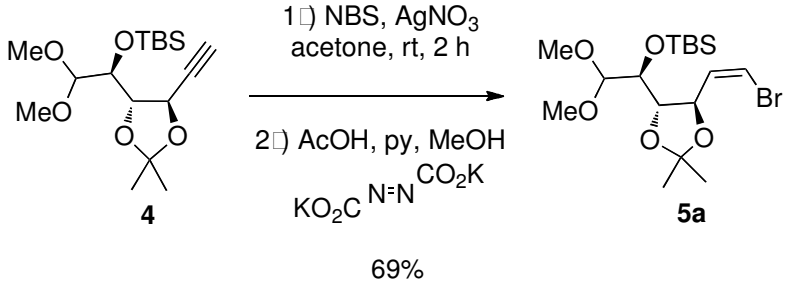
were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 90:10 to 70:30) to afford desired compound **3a** as a white solid (21 mg, 80%): **mp** 121-122 °C; $[\alpha]_D^{25}$ -5.7 (*c* 0.8, $CHCl_3$); ν_{max}: 3588, 3227, 2918, 2115, 1719, 1609, 1524, 1453, 1348, 1285, 1043, 712 cm^{-1}; **^{1}H NMR** (300 MHz, CDCl3): δ (ppm) 8.28 (d, 2H, *J* 9 Hz, H_{ar}), 8.22 (d, 2H, *J* 9 Hz, H_{ar}), 5.35-5.25 (m, 1H, H-2), 4.69 (dd, 1H, $J_{4,6}$ 2 and $J_{4,3}$ 7 Hz, H-4), 4.42 (t, 1H, $J_{3,4} = J_{3,2}$ 7 Hz, H-3), 4.04 (dd, 1H, $J_{1,2}$ 4 and $J_{1,1'}$ 12 Hz, H-1), 3.95 (dd, 1H, $J_{1',2}$ 5 and $J_{1',1}$ 12 Hz, H-1'), 2.50 (d, 1H, $J_{6,4}$ 2 Hz, H-6), 1.50 (s, 3H, C(CH_3)$_2$), 1.38 (s, 3H, C(CH_3)$_2$); **^{13}C** NMR (75 MHz, CDCl3): δ (ppm) 164.2 (*C*O), 150.8 (Cq_{ar}), 134.9 (Cq_{ar}), 131.0 (C_{ar}), 123.6 (C_{ar}), 111.5 (*C*(CH_3)$_2$), 80.7 (C-5), 80.0 (C-3), 75.4 (C-2), 75.1 (C-6), 67.9 (C-4), 62.0 (C-1), 26.8 (C(*C*H_3)$_2$), 26.8 (C(*C*H_3)$_2$); **ESIMS**: *m/z* = 334.1 [(M-H)$^-$], **ESIHRMS**: *m/z* = 334.0941. $C_{16}H_{16}NO_7$ requires 334.0927; **Anal**. Calcd for $C_{16}H_{17}NO_7$: C, 57.31; H, 5.11; N, 4.18; O, 33.40. Found: C, 57.27; H, 5.09; N, 4.19; O, 33.24.



(2S,3S,4R)-2-(t-butyldimethylsilyloxy)-3,4-(i-propylidenedioxy)hex-5-ynyl-1,1-dimethylacetal 4:

DMP (2.33 g**,** 5.50 mmol, 1.30 equiv) was added to solution of alcohol **3a** (1.26 g, 4.23 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) at 0 °C and the resulting mixture was stirred for 2 hours at 0°C. The homogeneous solution was poured into a saturated aqueous $NaHCO_3$ (10 mL) and $Na_2S_2O_3$ (10 mL)**.** The layers were separated, and the aqueous one was extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The crude residue was dissolved in trimethyl orthoformate (1.85 mL, 16.92 mmol, 4.00 equiv) and H_2SO_4 (11 μl, 0.21 mmol, 0.05 equiv) was added at 0°C. The mixture was stirred for 1 hour and $NaHCO_3$ (1.42 g, 16.92 mmol, 4.00 equiv) was added. The mixture was stirred for 30 minutes at room temperature and the solution was filtered and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 80:20) to afford desired compound **4** as a colorless oil (1.49 g, 73%): $[\alpha]_D^{25}$ +13.7 (*c* 1, $CHCl_3$); ν_{max}:

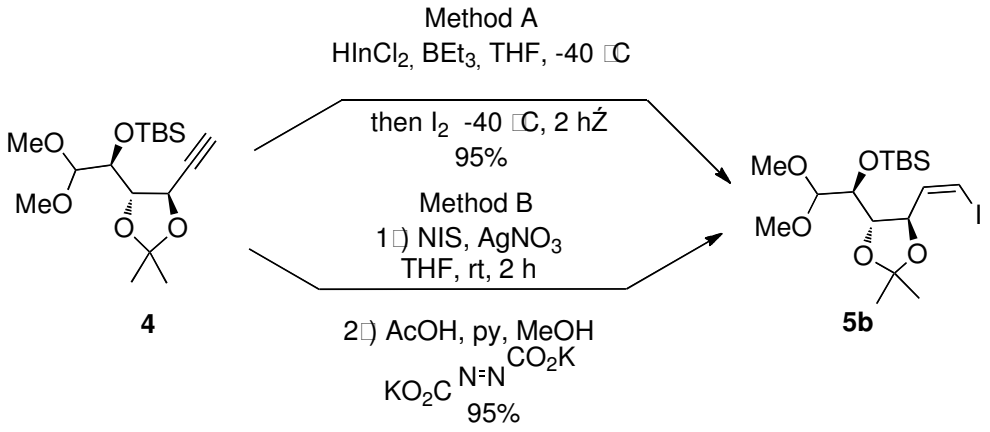
3308, 2930, 2358, 1471, 1462, 1380, 1250, 1208, 1157, 1135, 1059, 1001 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 4.72 (dd, 1H, $J_{4,6}$ 2 and $J_{3,4}$ 7 Hz, H-4), 4.32 (dd, 1H, $J_{2,3}$ 2 and $J_{3,4}$ 7 Hz, H-3), 4.16 (d, 1H, $J_{1,2}$ 6 Hz, H-1), 3.92 (dd, 1H, $J_{2,3}$ 2 and $J_{1,2}$ 6 Hz, H-2), 3.44 (s, 3H, OCH_3), 3.41 (s, 3H, OCH_3), 2.49 (d, 1H, $J_{4,6}$ 2 Hz, H-6), 1.44 (s, 3H, C(CH_3)$_2$), 1.40 (s, 3H, C(CH_3)$_2$), 0.88 (s, 9H, SiC(CH_3)$_3$), 0.08 (s, 3H, SiCH_3), 0.07 (s, 3H, SiCH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) 109.8 (*C*(CH$_3$)$_2$), 105.9 (C-1), 82.9(C-5), 81.9 (C-3), 73.8 (C-6), 71.8 (C-2), 64.8 (C-3), 56.8 (O*C*H$_3$), 55.6 (O*C*H$_3$), 26.7 (C(*C*H$_3$)$_2$), 26.1 (SiC(*C*H$_3$)$_3$), 25.6 (C(*C*H$_3$)$_2$), 18.0 (Si*C*(CH$_3$)$_3$), -4.2 (Si*C*H$_3$), -4.3 (Si*C*H$_3$); **ESIMS**: *m/z* = 367 [(M+Na)$^+$, 100%], **ESIHRMS**: *m/z* = 367.1920. $C_{17}H_{32}O_5NaSi$ requires 367.1917; **Anal**. Calcd for $C_{17}H_{32}O_5Si$: C, 59.27 H, 9.36; O, 23.22; Si, 8.15. Found: C, 59.37; H, 9.31.



(2S,3S,4R,Z)-2-(t-butyldimethylsilyloxy)-6-bromo-3,4-(i-propylidenedioxy)hex-5-enyl-1,1-dimethylacetal 5a:

NBS (140 mg, 0.78 mmol, 1.50 equiv) and $AgNO_3$ (35 mg, 0.20 mmol, 0.40 equiv) were added to a solution of alkyne **4** (180 mg, 0.52 mmol, 1.00 equiv) in acetone (5 mL) and the resulting mixture was stirred for 2 hours at room temperature. The suspension was filtered through a pad of silica gel that was carefully rinsed with Et_2O (10 mL). The combined filtrates were concentrated *in vacuo*. To a solution of the crude residue in MeOH (5 mL), potassium azodicarboxylate (760 mg, 3.9 mmol, 7.5 equiv) and pyridine (0.55 mL, 6.8 mmol, 13.00 equiv) was added acetic acid (0.25 mL, 5.7 mmol, 11.0 equiv) over 2 hours with a syringe pump. After stirring for 12 h, the mixture was poured into a saturated aqueous NH_4Cl (5 mL) and the aqueous layer was extracted with AcOEt (3 x 15 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 98:2 to 96:4) to afford desired compound **5a** as a colorless oil (153 mg, 69%): $[\alpha]_D^{25}$ -6.2 (*c* 0.5, $CHCl_3$); ν_{max}: 2986, 2930, 2856, 1627, 1472, 1462, 1380, 1370, 1249, 1157, 1135, 1057, 999, 835, 776, 690 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 6.42 (d, 1H, $J_{6,5}$ 7.5 Hz, H-6), 6.16 (dd, 1H, $J_{5,4}$ 8.5 and $J_{5,6}$ 7.5 Hz, H-5), 5.04 (t, 1H, $J_{4,3} = J_{4,5}$ 8.5 Hz, H-4), 4.08 (d, 1H, $J_{1,2}$ 7 Hz, H-1), 4.03 (dd, 1H, $J_{3,4}$ 8.5 and

$J_{3,2}$ 2 Hz, H-3), 3.99 (dd, 1H, $J_{2,3}$ 2 and $J_{1,2}$ 7 Hz, H-2), 3.43 (s, 3H, OCH_3), 3.30 (s, 3H, OCH_3), 1.43 (s, 3H, C(CH_3)$_2$), 1.37 (s, 3H, C(CH_3)$_2$), 0.93 (s, 9H, SiC(CH_3)$_3$), 0.10 (s, 3H, SiCH_3), 0.09 (s, 3H, SiCH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) 133.3 (C-5), 111.6 (C-6), 108.69 (*C*(CH$_3$)$_2$) 105.6 (C-1), 80.2 (C-3), 72.6 (C-4), 71.0 (C-2), 56.8 (O*C*H$_3$), 54.3 (O*C*H$_3$), 27.0 (C(*C*H$_3$)$_2$), 26.7 (SiC(*C*H$_3$)$_3$), 26.0 (C(*C*H$_3$)$_2$), 18.5 (*C*(CH$_3$)$_2$), -4.3 (Si*C*H$_3$), -4.5 (Si*C*H$_3$); **ESIMS**: *m/z* = 444.2 [(M+Na)$^+$, 100%], 449.2 [(M+Na)$^+$, 70%], 450.1[(M+Na)$^+$, 18%], **ESIHRMS**: *m/z* = 447.1178. $C_{17}H_{33}BrO_5NaSi$ requires 447.1179; **Anal**. Calcd for $C_{17}H_{33}BrO_5Si$: C, 47.99 H, 7. 82; Br, 18.78; O, 18.80; Si, 6.60. Found: C, 48.46; H, 7.82.

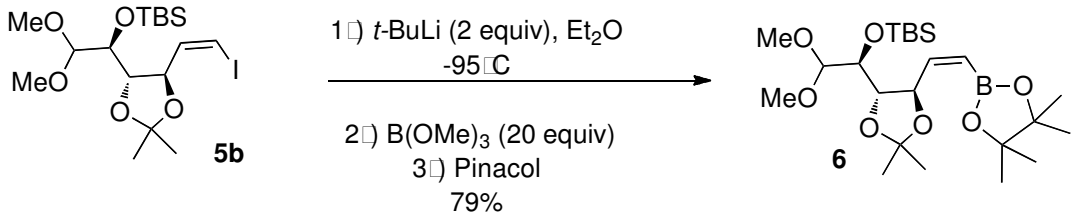


(2S,3S,4R,Z)-2-(t-butyldimethylsilyloxy)-6-iodo-3,4-(i-propylidenedioxy)hex-5-enyl-1,1-dimethylacetal 5b:

Method A: Anhydrous indium trichloride (600 mg, 2.71 mmol, 1.35 equiv) was placed in a Schlenk tube and heated with a hair dryer in *vacuo* for 2 minutes. The indium salt was dissolved in THF (6 mL) at 25 °C under an argon atmosphere. The solution turned to a white suspension upon cooling to -78 °C. Diisobutylaluminium hydride (1.0 M in hexane, 2.6 mL, 2.61 mmol, 1.30 equiv) was then added dropwise to the suspension at -78 °C. The mixture was stirred for 30 min to prepare dichloroindium hydride. Alkyne **4** (692 mg, 2.01 mmol, 1.00 equiv) and triethylborane (1.0 M hexane solution, 0.4 mL, 0.40 mmol, 0.20 equiv) were added in sequence and the resulting mixture was stirred for 2.5 hours at -78°C. Iodine (4.08 g, 16.08 mmol, 8.00 equiv) was added to the reaction mixture. After being stirred for 30 min at -78°C, the reaction mixture was poured into a saturated sodium hydrogen carbonate solution. Sodium thiosulfate solution was added to consume the excess of iodine. The aqueous layer was extracted with AcOEt (3 x 20 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel

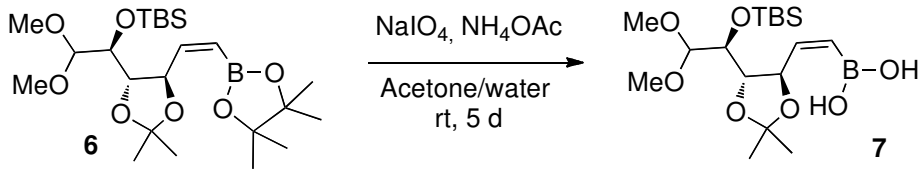
(heptane-ethyl acetate, 98:2) to afford desired compound **5** as a colorless oil (847 mg, 90% for (*Z*) and 47 mg, 5% for (*E*)).

Method B: NIS (1.02 g, 4.52 mmol, 1.25 equiv) and $AgNO_3$ (67 mg, 0.39 mmol, 0.11 equiv) were added to a solution of alkyne **4** (1.25 g, 3.62 mmol, 1.00 equiv) in THF (36 mL) and the resulting mixture was stirred for 2 hours at room temperature. The suspension was filtered through a pad of silica gel that was carefully rinsed with Et_2O (40 mL). The combined filtrates were concentrated *in vacuo*. To the residue in methanol (40 mL) were added pyridine (2.2 mL, 27.43 mmol, 7.6 equiv) and potassium azodicarboxylate (2.86 g, 14.71 mmol, 4.1 equiv). After addition of acetic acid (1.1 mL, 24.24 mmol, 6.7 equiv) over 2 hours with a syringe pump, the mixture was poured into AcOEt (30 mL) and a saturated aqueous NH_4Cl (20 mL). The aqueous layer was extracted with AcOEt (3 x 30 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 98:2) to afford desired compound **5** as a colorless oil (1.61 g, 95%): $[\alpha]_D^{25}$ -5.8 (*c* 1, $CHCl_3$); ν_{max}: 2984, 2927, 2854, 1613, 1470, 1461, 1379, 1370, 1246, 1213, 1189, 1155, 1056, 999, 835, 813, 677 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 6.55 (d, 1H, $J_{5,6}$ 7.5 Hz, H-6), 6.23 (dd, 1H, $J_{4,5}$ 8.5 and $J_{5,6}$ 7.5 Hz, H-5), 4.83 (t, 1H, $J_{3,4}$ and $J_{4,5}$ 8.5 Hz, H-4), 4.00-4.06 (m, 2H, H-1 and H-3), 3.99 (dd, 1H, $J_{2,3}$ 2 and $J_{1,2}$ 7 Hz, H-2), 3.44 (s, 3H, OCH_3), 3.28 (s, 3H, OCH_3), 1.42 (s, 3H, $C(CH_3)_2$), 1.36 (s, 3H, $C(CH_3)_2$), 0.93 (s, 9H, $SiC(CH_3)_3$), 0.10 (s, 3H, $SiCH_3$), 0.09 (s, 3H, $SiCH_3$); **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) 139.3 (C-5), 108.8 ($C(CH_3)_2$), 105.9 (C-1), 86.3 (C-6), 80.2 (C-3), 77.1 (C-4), 71.3 (C-2), 57.1 (OCH_3), 54.4 (OCH_3), 27.1 ($C(CH_3)_2$), 26.8 ($SiC(CH_3)_3$), 26.2 ($C(CH_3)_2$), 18.5 ($C(CH_3)_2$), -4.0 ($SiCH_3$), -4.3 ($SiCH_3$); **ESIMS**: *m/z* = 495 [$(M+Na)^+$, 100%], **ESIHRMS**: *m/z* = 495.1028. $C_{17}H_{33}IO_5NaSi$ requires 495.1040; **Anal**. Calcd for $C_{17}H_{33}IO_5Si$: C, 43.22 H, 7.04; I, 26.86; O, 16.93; Si, 5.94. Found: C, 43.49; H, 6.94.



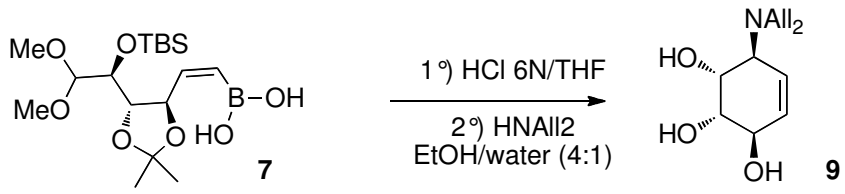
(2S,3S,4R,Z)-2-(t-butyldimethylsilyloxy)-3,4-(i-propylidenedioxy)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)hex-5-enyl-1,1-dimethylacetal 6:

A solution of iodovinyl **5** (750 mg, 1.58 mmol, 1.00 equiv) and a catalytic amount of bipyridine (2.5 mg, 0.01 mmol, 0.01 equiv) in dry Et_2O (5 mL) was cooled to -95 °C under argon. *t*-BuLi (2.0 mL, 1.6 M in hexane, 3.17 mmol, 2.00 equiv) was added dropwise, and the solution was stirred for 2 hours at this temperature. Freshly distilled trimethylborate (3.3 mL, 28.57 mmol, 18.00 equiv) was then added at -95°C. The solution was allowed to warm to 0 °C and was stirred at this temperature for 3 hours. Pinacol (3.56 g, 30.16 mmol, 19.00 equiv) and Na_2SO_4 (3.56 g) were then added and the solution was stirred at room temperature for 12 hours. The resulting mixture was poured into a saturated aqueous solution of NH_4Cl (15 mL). The aqueous layer was extracted with AcOEt (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (heptane-ethyl acetate, 80:20) to afford desired compound **6** as a colorless oil (590 mg, 79%): $[\alpha]_D^{25}$ 18.6 (*c* 1, $CHCl_3$); ν_{max}: 2980, 2929, 2855, 1637, 1426, 1378, 1370, 1336, 1249, 1211, 1142, 835, 756, 669 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 6.30 (dd, 1H, $J_{4,5}$ 9 and $J_{5,6}$ 13 Hz, H-5), 5.55 (d, 1H, $J_{5,6}$ 13 Hz, H-6), 5.10(t, 1H, $J_{3,4}$ and $J_{4,5}$ 9 Hz, H-4), 4.00-4.04 (m, 1H, H-2), 3.90-3.97 (m, 2H, H-3 and H-1), 3.39 (s, 3H, OCH_3), 3.24 (s, 3H, OCH_3), 1.42 (s, 3H, C(CH_3)$_2$), 1.36 (s, 3H, C(CH_3)$_2$), 0.92 (s, 9H, SiC(CH_3)$_3$), 0.82 (s, 12H, (B(OC(CH_3)$_2$)$_2$), 0.079 (s, 3H, SiCH_3), 0.08 (s, 3H, SiCH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) 150.8 (C-5), 108.5 (*C*(CH_3)$_2$), 105.8 (C-1), 83.6 (B(O*C*(CH_3)$_2$)$_2$), 81.0 (C-2 or C-3), 74.3 (C-4), 71.3 (C-2 or C-3), 56.6 (O*C*H_3), 54.5 (O*C*H_3), 27.0 (C(*C*H_3)$_2$), 26.9 (C(*C*H_3)$_2$), 26.1 (SiC(*C*H_3)$_3$), 24.8 (B(OC(*C*H_3)$_2$)$_2$), 18.5 (Si*C*(CH_3)$_3$), -3.9 (Si*C*H_3), -4.2 (Si*C*H_3); **ESIMS**: *m/z* = 495 [(M+Na)$^+$, 100%], **ESIHRMS**: *m/z* = 495.2919. $C_{23}H_{45}O_7BNaSi$ requires 495.2925; **Anal**. Calcd for $C_{23}H_{45}BO_7Si$: C, 58.47 H, 9.60; B, 2.29; O, 23.70; Si, 5.94. Found: C, 58.42; H, 9.59.



(3R,4S,5S,Z)-5-(t-butyldimethylsilyloxy)-6,6-dimethoxy-3,4-(i-propylidenedioxy)hex-1-enylboronic acid 7:

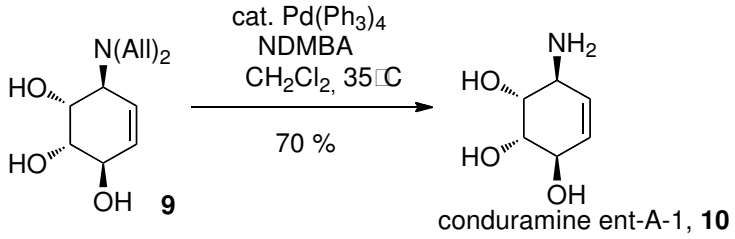
To a stirred solution of boronate ester **6** (345 mg, 0.73 mmol, 1.00 equiv) in acetone (25 mL) was added an aqueous solution of NH_4OAc (0.1 N, 15mL) and $NaIO_4$ (469 mg, 2.10 mmol, 3.00 equiv). The mixture was stirred at room temperature for 4 days. The acetone was removed *in vacuo*, the aqueous phase was diluted with aqueous NaOH (2 N, 10 mL) and washed with a mixture of Hept/AcOEt (9:1, 5 ml). After cautious acidification to pH=3 with aqueous HCI (2N), the aqueous phase was extracted with CH_2Cl_2 (4 x 30 mL). The combined organic layers were combined, dried (Na_2SO_4), filtered and concentrated to afford crude product **7**. $[\alpha]_D^{25}$ +12.3 (*c* 1, $CHCl_3$); ν_{max}: 3399, 2930, 2856, 1732, 1635, 1460, 1419, 1378, 1251, 1211, 1159, 1057, 1003, 837, 814, 778 cm^{-1}; **^{1}H NMR** (300 MHz, $CDCl_3$): δ (ppm) 6.34 (dd, 1H, $J_{2,3}$ 6 and $J_{2,1}$ 14.5 Hz, H-2), 5.89 (bs, 2H, B(O*H*)$_2$), 5.64 (dd, 1H, $J_{1,3}$ 1.5 $J_{1,2}$ 14.5 Hz, H-1), 4.81(ddd, 1H, $J_{3,1}$ 1.5, $J_{3,2}$ 6 and $J_{3,4}$ 8 Hz, H-3), 4.16 (d, 1H, $J_{6,5}$ 5 Hz, H-6), 4.05 (dd, 1H, $J_{4,5}$ 2 and $J_{4,3}$ 8 Hz, H-4), 4.00 (dd, 1H, $J_{5,4}$ 2 and $J_{5,6}$ 5 Hz, H-5), 3.42 (s, 3H, OCH_3), 3.36 (s, 3H, OCH_3), 1.44 (s, 3H, C(CH_3)$_2$), 1.37 (s, 3H, C(CH_3)$_2$), 0.89 (s, 9H, SiC(CH_3)$_3$), 0.11 (s, 3H, SiCH_3), 0.10 (s, 3H, SiCH_3); **^{13}C NMR** (75 MHz, $CDCl_3$): δ (ppm) 147.8 (C-2), 109.2 (*C*(CH$_3$)$_2$), 106.4 (C-6), 81.1 (C-4 or C-5), 76.0 (C-3), 72.9 (C-4 or C-5), 57.3 (OCH$_3$), 55.9 (OCH$_3$), 27.4 (C(*C*H$_3$)$_2$), 27.3 (C(*C*H$_3$)$_2$), 26.7 (SiC(*C*H$_3$)$_3$), 18.9 (Si*C*(CH$_3$)$_3$), -3.8 (Si*C*H$_3$), -3.9 (Si*C*H$_3$); **ESIMS**: *m/z* = 413 [(M+Na)$^+$, 100%], **ESIHRMS**: *m/z* = 413.2144. $C_{17}H_{35}O_7BNaSi$ requires 413.2143.



(1R,2S,3S,4S)-4-(diallylamino)cyclohex-5-ene-1,2,3-triol 9 :

A solution of boronic acid **7** (120 mg, 0.307 mmol, 1.00 equiv) in HCl (6N in THF, 4 mL) was stirred at room temperature for 2 hours. After evaporation and coevaporation with toluene, the residue was dissolved in a mixture of EtOH/water (4:1, 6 mL) and diallylamine (95 µL, 0.769, 2.50 equiv) was added. The solution was stirred at 80 °C in a sealed flask for 8

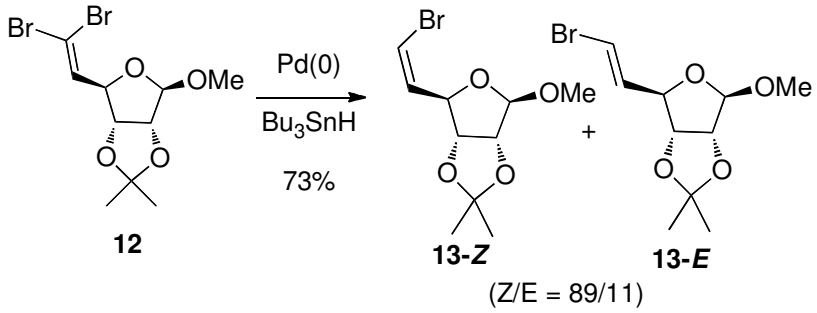
days. After removal of volatiles, the residue was purified by flash chromatography on Act I neutral alumina (CH_2Cl_2-MeOH-ammonia, 99:0:1 to 84:14:2) to afford product **9** as yellow oil (50 mg, 72%): $[\alpha]_D^{25}$ -34.2 (*c* 1, water); **^{1}H NMR** (300 MHz, MeOD): 5.99-5.82 (m, 2H, NCH_2CH=CH_2), 5.79 (s, 2H, H-5 and H-6), 5.29-5.09 (m, 4H, NCH_2CH=CH_2), 4.10-4.02 (m, 1H, H-1), 3.90 (dd, $J_{3,2}$ 2.5 and $J_{3,4}$ 7 Hz, H-3), 3.85 (t, 1H, $J_{2,3} = J_{2,1}$ 2.5, H-2), 3.58 (d, 1H, $J_{4,3}$ 7 Hz, H-4), 3.39-3.29 (m, 2H, NCH_2CH=CH_2), 3.21 (dd, 2H, *J* 7 and *J* 13 Hz, NCH_2CH=CH_2). **^{13}C NMR** (75 MHz, MeOD): δ (ppm) 138.0 (2*NCH_2CH=CH_2),130.1 and 130.0 (C-5 and C-6), 117.6 (2*NCH_2CH=CH_2), 75.0 (C-2), 70.2 (C-1), 68.4 (C-3), 60.7 (C-4), 54.8 (NCH_2CH=CH_2); **ESIMS**: *m/z* = 226.1 [$(M+H)^+$, 100%], **ESIHRMS**: *m/z* = 226.1441. $C_{12}H_{20}NO_3$ requires 226.1443.



(1R,2S,3R,4S)-4-aminocyclohex-5-ene-1,2,3-triol or Conduramine -(ent)-A-1 10:

A solution of **9** (29 mg, 0.13 mmol, 1.00 equiv) in dry degassed CH_2Cl_2 (2 mL) was added to a flask containing tetrakis(triphenylphosphino)palladium (32 mg, 0.03 mmol, 0.20 equiv) and *N,N'*-dimethylbarbituric acid (131 mg, 0.84 mmol, 6.00 equiv) under an argon atmosphere. The reaction mixture was stirred for 12 hours at 45 °C. After removal of volatiles, the residue was purified by flash chromatography on silica gel (CH_2Cl_2/MeOH 1:0 to 1:1) to afford Conduramine *ent*-A1 (13 mg, 0.09 mmol, 70%) as a brown oil.

$[\alpha]_D^{25}$ +19.0 (*c* 0.1, MeOH). **ν_{max}**: 3291, 2925, 2836, 1650, 1587, 1449, 1406, 1017 cm^{-1}. **^{1}H NMR** (300 MHz, MeOD) δ 5.66-5.58 (m, 2H, H-5 and H-6), 4.05-3.99 (dd, 1H, H-1), 3.73 (dd, 1H, $J_{2,3}$ 2.5 and $J_{2,1}$ 4 Hz, H-2), 3.54 (dd, $J_{3,4}$ 7 and $J_{3,2}$ 2.5 Hz, H-3), 3.33 (d, 1H, $J_{4,3}$ 7 Hz, H-4). ^{13}C NMR (75 MHz, MeOD) δ 132.2 (C-6), 128.9 (C-5), 74.5 (C-3), 74.4 (C-2), 71.0 (C-4), 52.2 (C-1). **ESIMS**: *m/z* = 146 [$(M+H)^+$ 100%]. **ESIHRMS**: *m/z* = 146.0818. $C_6H_{12}NO_3$ requires 146.0817.

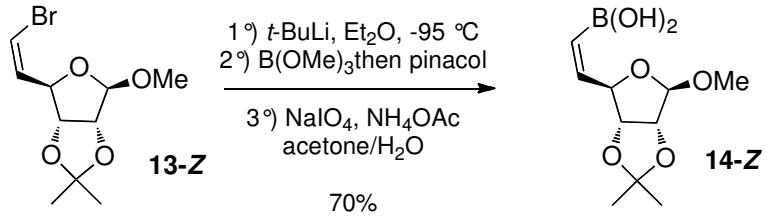


Methyl (5Z)-6-bromo-5,6-dideoxy-2,3-O-(i-propylidene)-β-D-ribo-hex-5-enofuranoside 13-Z and Methyl (5E)-6-bromo-5,6-dideoxy-2,3-O-(i-propylidene)-β-D-ribo-hex-5-enofuranoside 13-E

A mixture of PPh_3 (571 mg, 2.18 mmol, 0.30 equiv) and $Pd(OAc)_2$ (130 mg, 0.58 mmol, 0.08 equiv) in dry and degassed CH_2Cl_2 (40 mL) was stirred at room temperature for 20 min to generate a yellow solution. A solution of **12** (2.60 g, 7.26 mmol, 1.00 equiv) and Bu_3SnH (3.90 mL, 14.5 mmol, 2.00 equiv) in CH_2Cl_2 (20 mL) were added. The mixture was stirred for 30 min at room temperature, diluted with heptane (200 mL), washed with water (3 x 200 mL) and brine (200 mL), dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (heptane/AcOEt 98:2) to afford compound **13-*E*** (1.31 g, 4.72 mmol, 65 %) as a colorless oil and compound **13-*Z*** (158 mg, 0.58 mmol, 8 %) as a colorless oil.

13-*Z* : $[\alpha]_D^{25}$ −49.3 (*c* 1.2, $CHCl_3$). ν_{max} : 2936, 1618, 1373, 1210, 1086, 867, 723 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.33 (d, 1H, $J_{5,6}$ 7.5 Hz, H-6), 6.28 (t, 1H, $J_{5,6} = J_{4,5}$ 7.5 Hz, H-5), 5.08 (d, 1H, $J_{4,5}$ 7.5 Hz, H-4), 5.00 (s, 1H, H-1), 4.67 (d, $J_{2,3}$ 6.0 Hz, 1H, H-2 or H3), 4.63 (d, $J_{2,3}$ 6.0 Hz, 1H, H-2 or H3), 3.36 (s, 3H, OCH_3), 1.53 (s, 3H, CCH_3), 1.34 (s, 3H, CCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 134.7 (C-5), 112.8 ($C(CH_3)_2$), 110.04 (C-6, C-1), 85.5 (C-3 or C-2), 84.9 (C4), 84.5 (C-2 or C-3), 54.9 (OCH$_3$), 26.6 (CCH$_3$), 25.2 (CCH$_3$). **Anal.** Calcd for $C_{10}H_{15}BrO_4$: C, 43.03; H, 5.42; O, 22.93. Found: C, 43.26; H, 5.61; O, 22.76.

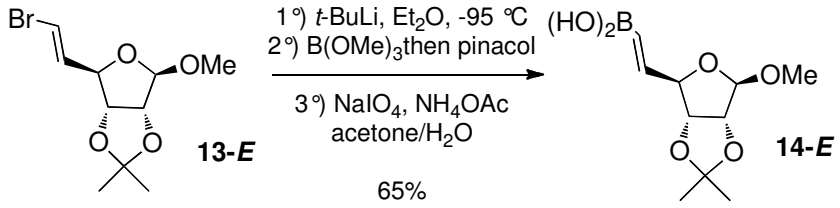
13-*E* : $[\alpha]_D^{25}$ −22.0 (*c* 1.2, $CHCl_3$). ν_{max} : 2936, 1618, 1373, 1210, 1086, 867, 723 cm^{-1}. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.39 (d, $J_{5,6}$ 14 Hz, 1H, H-6), 6.26 (dd, $J_{5,6}$ 14 Hz, $J_{4,5}$ 9 Hz, 1H, H-5), 4.98 (s, 1H, H-1), 4.62 (s, 2H, H-2 and H-3), 4.60 (d, $J_{4,5}$ 9 Hz, 1H, H-4), 3.35 (s, 3H, OCH_3), 1.48 (s, 3H, CCH_3), 1.31 (s, 3H, CCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 137.1 (C-5), 112.8 ($C(CH_3)_2$), 109.6 (C-6, C-1), 87.3 (C-4), 85.5 (C-2 or C-3), 84.1 (C-3 or C-2), 55.0 (OCH$_3$), 26.6 (CCH$_3$), 25.2 (CCH$_3$). **Anal.** Calcd for $C_{10}H_{15}BrO_4$: C, 43.03; H, 5.42; O, 22.93. Found: C, 43.30; H, 5.62; O, 22.82.



Methyl (5Z)-5,6-dideoxy-6-(dihydroxyboranyl)-2,3-O-(i-propylidene)-β-D-ribo-hex-5-enofuranoside 14-Z

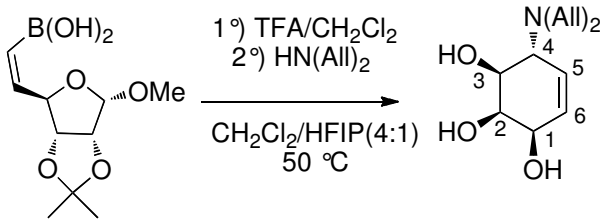
A solution of bromovinyl **13-*Z*** (1.40 g, 5.02 mmol, 1.00 equiv) and bipyridine (5 mg, 0.03 mmol, 0.01 equiv) in dry Et_2O (18 mL) was cooled to -95 °C under argon. A solution of *t*-BuLi (7.2 mL, 1.6 M in hexane, 11.5 mmol, 2.30 equiv) was added dropwise, and the mixture was stirred for 2 hours at this temperature. Freshly distilled trimethylborate (9.7 mL, 90.3 mmol, 18.00 eq) was then added at -95°C. The solution was allowed to warm to 0 °C and was stirred at this temperature for 3 hours. Pinacol (11.3 g, 95.3 mmol, 19.00 equiv) and Na_2SO_4 (11.3 g) were then added and the solution was stirred at room temperature for 12 hours. The resulting mixture was poured into a saturated aqueous solution of NH_4Cl (50 mL). The aqueous layer was extracted with AcOEt/heptane (2:8, 3 x 50 mL) and the combined organic layers were washed with water (6 x 150 mL), brine (150 mL), dried over Na_2SO_4 and concentrated *in vacuo* to give the boronate ester as a yellow oil (1.6 g).

To the crude mixture in acetone (162 mL) was added an aqueous solution of NH_4OAc (0.1 N, 93 mL) and $NaIO_4$ (3.14 g, 14.7 mmol, 3.00 equiv). The mixture was stirred at room temperature for 4 days. The acetone was removed *in vacuo*, the aqueous phase was diluted with aqueous NaOH (2 N, 60 mL) and washed with a mixture of AcOEt/heptane (2:8, 3 x 60 mL). After cautious acidification to pH=3 with aqueous HCl (2N), the aqueous phase was extracted with AcOEt (2 x 60 mL). The combined organic layers were combined, dried over Na_2SO_4, filtered and concentrated to afford product **14** (290 mg, 1.19 mmol, 70 %) as a yellow oil. $\mathbf{[\alpha]_D^{25}}$ +26.0 (*c* 0.8, $CHCl_3$). $\boldsymbol{\nu_{max}}$: 3410, 2939, 1737, 1627, 1413, 1373, 1084, 867, 777 cm^{-1}. **^{1}H NMR** (300 MHz, CD_3CN) δ 6.27 (dd, $J_{5,4}$ 9 and $J_{5,6}$ 14 Hz, 1H, H-5), 5.92 (s, 2H, B(O*H*)$_2$), 5.46 (d, $J_{6,5}$ 14 Hz, 1H, H-6), 5.15 (d, $J_{4,5}$ 9 Hz, 1H, H-4), 4.92 (s, 1H, H-1), 4.59 (s, 2H, H-2, H-3), 3.22 (3H, OC*H*$_3$), 1.37 (s, 3H, CC*H*$_3$), 1.23 (s, 3H, CC*H*$_3$). **^{13}C NMR** (75 MHz, CD_3CN) δ 149.6 (C-5), 110.5 (C-1), 86.5 (C-2 and C-3), 86.3 (C-4), 54.9 (O*C*H$_3$), 26.8 (C*C*H$_3$), 25.1 (C*C*H$_3$). **Anal.** Calcd for $C_{10}H_{17}BO_6$: C, 49.80; H, 7.02; B, 4.43; O, 39.33. Found: C, 49.49; H, 7.31.



Methyl (5E)-5,6-dideoxy-6-(dihydroxyboranyl)-2,3-O-(i-propylidene)-β-D-ribo-hex-5-enofuranoside 14-E

A solution of bromovinyl **13-*E*** (430 mg, 1.54 mmol, 1.00 eq) and bipyridine (2 mg, 0.02 mmol, 0.01 eq) in dry Et_2O (5 mL) was cooled to -95 °C under argon. A solution of *t*-BuLi (2.2 mL, 1.6 M in hexane, 3.54 mmol, 2.30 equiv) was added dropwise, and the mixture was stirred for 2 hours at this temperature. Freshly distilled trimethylborate (3.1 mL, 27.7 mmol, 18.00 eq) was then added at -95 °C. The solution was allowed to warm to 0 °C and was stirred at this temperature for 3 hours. Pinacol (3.46 g, 29.3 mmol, 19.00 equiv) and Na_2SO_4 (3.46 g) were then added and the solution was stirred at room temperature for 12 hours. The resulting mixture was poured into a saturated aqueous solution of NH_4Cl (10 mL). The aqueous layer was extracted with AcOEt/heptane (2:8, 3 x 10 mL) and the combined organic layers were washed with water (6 x 40 mL), brine (40 mL), dried over Na_2SO_4 and concentrated *in vacuo*. To the crude mixture in acetone (60 mL) was added an aqueous solution of NH_4OAc (0.1 N, 34 mL) and $NaIO_4$ (0.98 g, 4.6 mmol, 3.00 equiv). The mixture was stirred at room temperature for 4 days. The acetone was removed *in vacuo*, the aqueous phase was diluted with aqueous NaOH (2 N, 20 mL) and washed with a mixture of AcOEt/heptane (2:8, 3 x 20 mL). After cautious acidification to pH=3 with aqueous HCl (2N), the aqueous phase was extracted with AcOEt (2 x 20 mL). The combined organic layers were combined, dried over Na_2SO_4, filtered and concentrated to afford **14-*E*** (244 mg, 0.1 mmol, 65 %) as a yellow oil. $[\alpha]_D^{25}$ -43.7 (*c* 1.0, $CHCl_3$). ν_{max}: 3410, 2939, 1737, 1627, 1413, 1373, 1084, 867, 777 cm^{-1}. **^{1}H NMR** (300 MHz, CD_3CN) δ 6.85 (dd, 0.6H, $J_{5,6}$ 18 and $J_{5,4}$ 6.5 Hz, H-5), 6.43 (dd, 0.4H, $J_{5,6}$ 18 and $J_{5,4}$ 6.5 Hz, H-5), 5.73 (d, 0.6H, $J_{6,5}$ 18 Hz, H-6), 5.68 (s, B(O*H*)$_2$), 5.57 (d, 0.4H, $J_{6,5}$ 18 Hz, H-6), 4.97 (s, 0.6H, H-1), 4.94 (s, 0.4H, H-1), 4.70 (d, 1H, $J_{4,5}$ 6.5 Hz, H-4), 4.66-4.56 (m, 2H, H-2, H-3), 3.33 (s, 1.8H, OCH_3), 3.31 (s, 1.2H, OCH_3), 1.43 (s, 1.8H, CCH_3), 1.42 (s, 1.2H, CCH_3), 1.29 (s, 1.8H, CCH_3),1.28 (s, 1.2H, CCH_3). **^{13}C NMR** (75 MHz, CD_3CN) δ 155.5 (C-5), 150.0 (C-5), 113.1 (*C*$(CH_3)_2$), 110.6 (C-1), 110.4 (C-1), 89.9 (C-2 or C-3), 89.3 (C-4), 86.3 (C-2 or C-3), 85.3 (C-4), 55.2 (O*C*H_3), 26.8 (C*C*H_3), 25.2 (C*C*H_3). **ESIMS**: *m/z* = 243.1 [$(M-H)^-$ 100%]. **ESIHRMS**: *m/z* = 243.1034. $C_{10}H_{16}BO_6$ requires 243.1040.

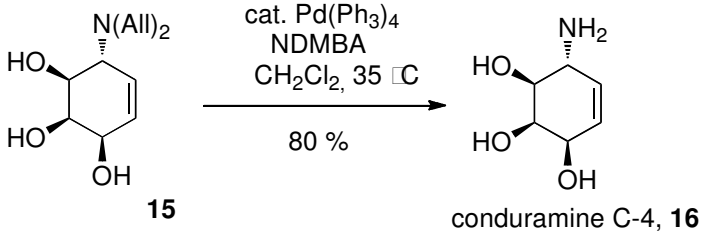


14 **15**, 60%

(1R,2R,3S,4R)-4-(diallylamino)cyclohex-5-ene-1,2,3-triol 15

A solution of boronic acid **14 (**57 mg, 0.23 mmol, 1.00 equiv) in H_2O (0.13 mL) and TFA (0.32 mL) was stirred at room temperature for 4 hours. After coevaporation with CH_2Cl_2 (6 x 5 mL), the residue was dissolved in a mixture of CH_2Cl_2/HFIP (4:1, 2 mL) and diallylamine (57 μL, 0.47 mmol, 2.00 equiv) was added. The solution was stirred at 50 °C in a sealed flask for 65 h. After removal of volatiles, the residue was purified by flash chromatography on Act I neutral alumina (CH_2Cl_2/MeOH/NH_4OH 99:0:1 to 80:15:5) to afford product **15** (31 mg, 0.14 mmol, 60 %) as a brown oil.

$[\alpha]_D^{25}$ −153 (*c* 0.3, MeOH). **ν_{max}**: 3355, 2912, 1641, 1417, 1026, 916, 823, 677 cm^{-1}. **^{1}H NMR** (300 MHz, MeOD) δ 5.88-5.75 (m, 2H, NCH_2CH=CH_2), 5.65 (dt, 1H, $J_{6,5}$ 10.5 and $J_{6,1}$ = $J_{6,4}$ 2 Hz, H-6), 5.52 (dq, 1H, $J_{5,6}$ 10.5 and $J_{5,4}$ = $J_{5,1}$ = $J_{5,3}$ 2 Hz, H-5), 5.21-4.98 (m, 4H, NCH_2CH=CH_2), 4.16-4.13 (m, 1H, H-1), 3.99 (dt, 1H, $J_{2,3}$ 2 and $J_{2,1}$ 4 Hz, H-2), 3.64 (dd, 1H, $J_{3,4}$ 9 and $J_{3,2}$ 2 Hz, H-3), 3.57 (dq, 1H, $J_{4,3}$ 9 and $J_{4,5}$ = $J_{4,6}$ = $J_{4,1}$ 2 Hz, H-4), 3.29-3.19 (m, 2H, NCH_2CH=CH_2), 3.04 (dd, 2H, *J* 7 and *J* 13 Hz, NCH_2CH=CH_2). **^{13}C NMR** (75 MHz, MeOD) δ 138.5 (2*NCH_2CH=CH_2), 131.8 (C-5), 128.2 (C-6), 117.5 (2*NCH_2CH=CH_2), 74.4 (C-2), 71.4 (C-3), 69.7 (C-1), 60.7 (C-4), 55.3 (NCH_2CH=CH_2); **ESIMS**: *m/z* = 226 [$(M+H)^+$ 100%]. **ESIHRMS**: *m/z* = 226.1434. $C_{12}H_{20}NO_3$ requires 226.1443.



15 conduramine C-4, **16**

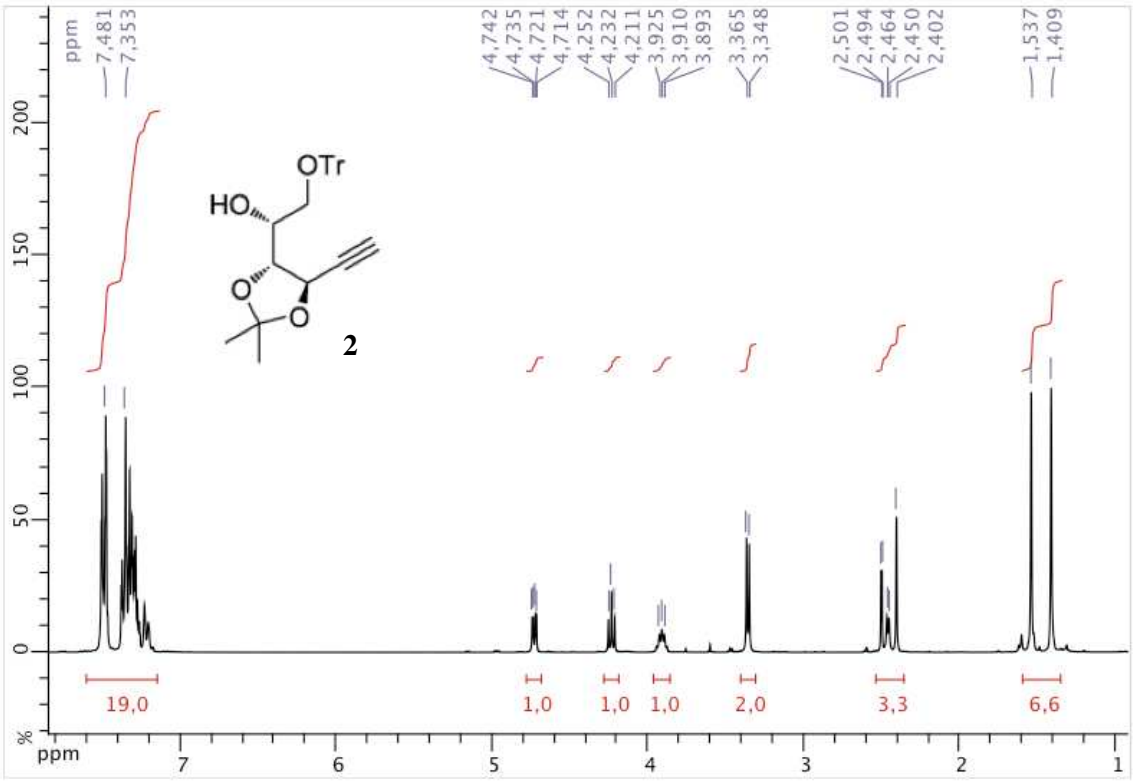
(1R,2R,3S,4R)-4-aminocyclohex-5-ene-1,2,3-triol (Conduramine C-4) 16

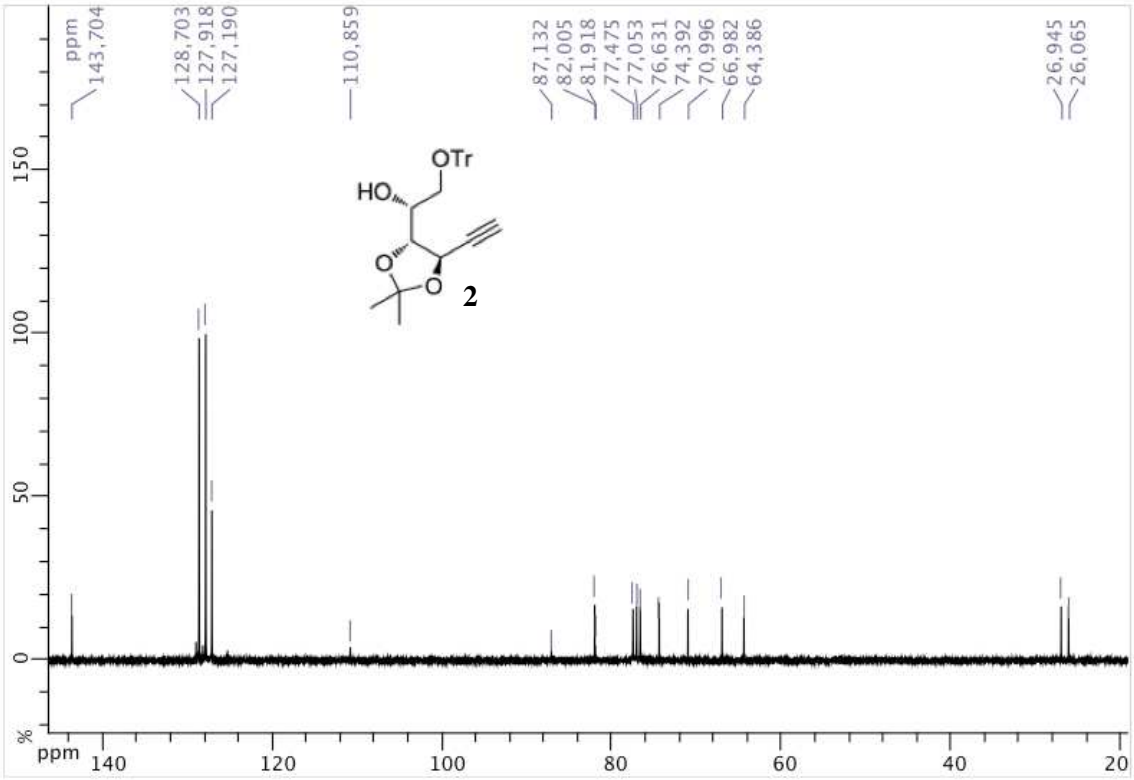
A solution of **15** (35 mg, 0.16 mmol, 1.00 equiv) in dry degassed CH_2Cl_2 (2 mL) was added to a flask containing tetrakis(triphenylphosphino)palladium (36 mg, 0.03 mmol, 0.20 equiv.) and *N,N'*-dimethylbarbituric acid (145 mg, 0.93 mmol, 6.00 equiv) under an argon atmosphere. The reaction mixture was stirred for 12 hours at 45 °C. After removal of volatiles, the residue

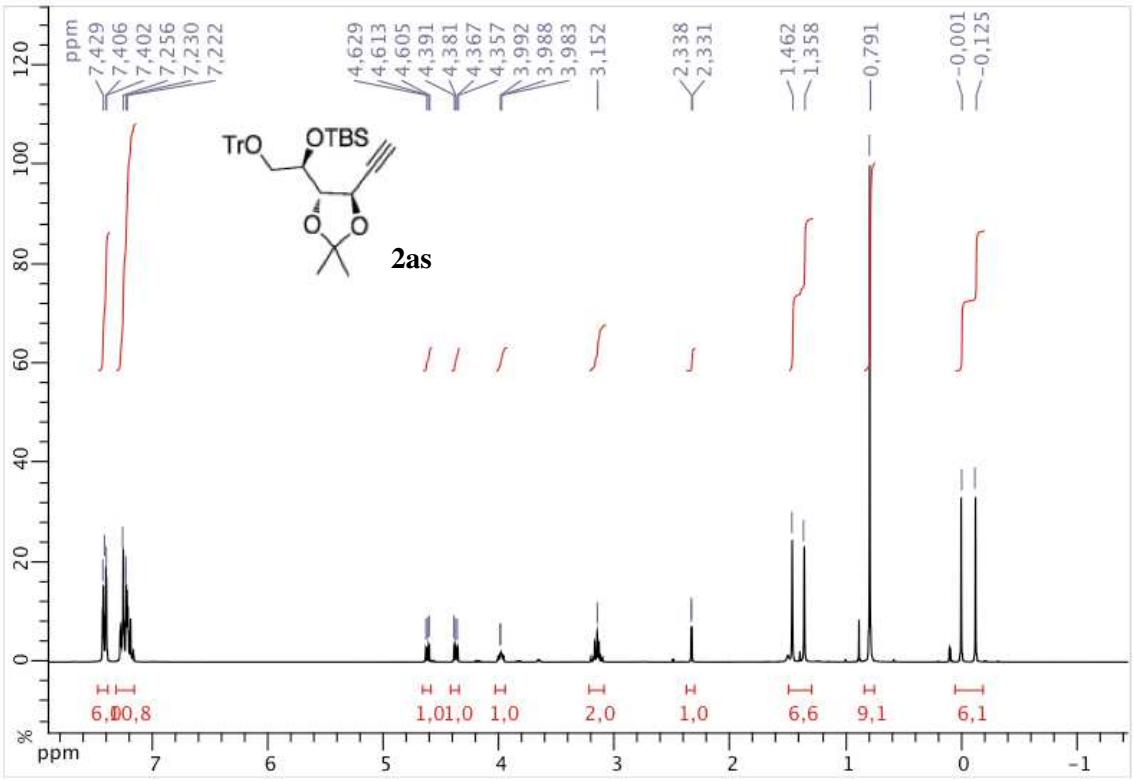
was purified by flash chromatography on silica gel (CH_2Cl_2/MeOH 1:0 to 1:1) to afford Conduramine C4 (18 mg, 0.12 mmol, 80%) as a white solid.

$[\alpha]_D^{25}$ −170 (*c* 0.3, MeOH). **ν_{max}**: 3338, 3279, 1613, 1305, 1048, 1019, 846, 689 cm^{-1}. **^{1}H NMR** (300 MHz, D_2O) δ 5.65 (dt, 1H, $J_{6,5}$ 10.5 and $J_{6,1} = J_{6,4}$ 2 Hz, H-6), 5.59 (dq,1 H, $J_{5,6}$ 10.5 and $J_{5,4} = J_{5,1} = J_{5,3}$ 2 Hz, H-5), 4.42-4.39 (m, 1H, H-1), 4.08 (m, 1H, H-2), 3.56 (dd, 1H, $J_{3,4}$ 9 and $J_{3,2}$ 2 Hz, H-3), 3.47 (dq, $J_{4,3}$ 9 and $J_{4,5} = J_{4,6} = J_{4,1}$ 2 Hz, H-4). **^{13}C NMR** (75 MHz, D_2O) δ 129.6 (C-6), 128.1 (C-5), 74.6 (C-3), 72.3 (C-2), 68.2 (C-1), 49.7 (C-4). **ESIMS**: *m/z* = 146 [$(M+H)^+$ 100%]. **ESIHRMS**: *m/z* = 146.0812. $C_6H_{12}NO_3$ requires 146.0817.

III. Copies of ^{1}H NMR and ^{13}C NMR



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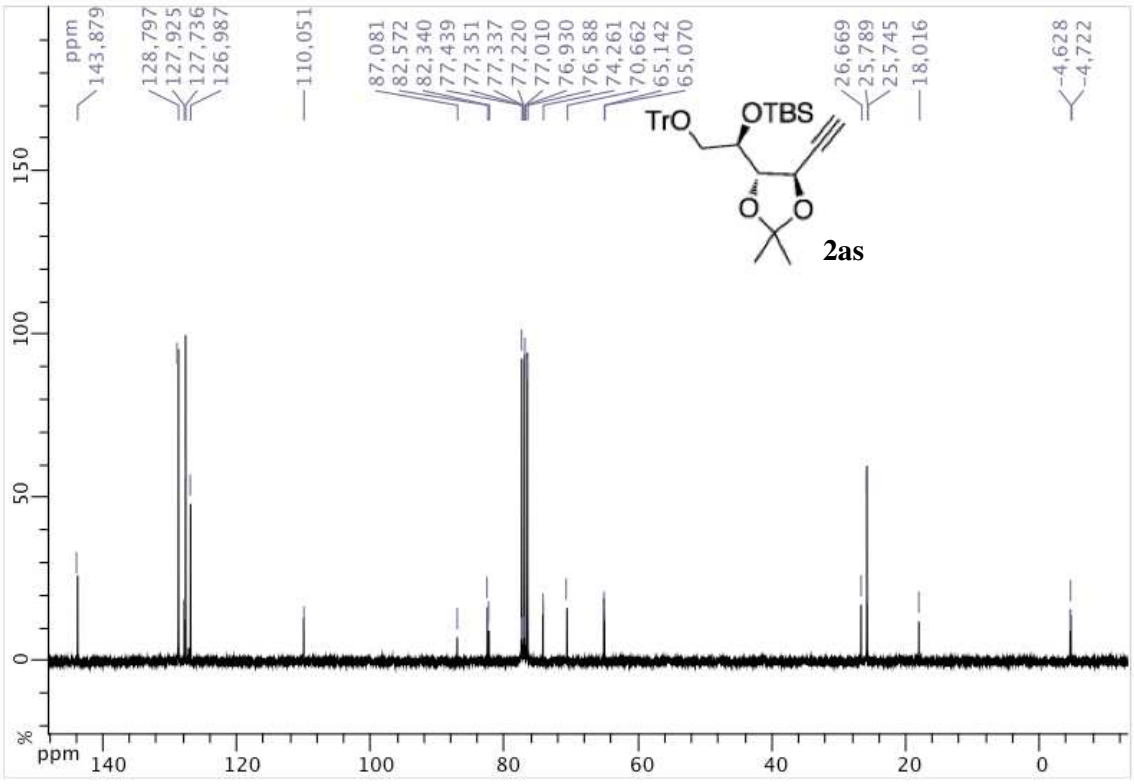
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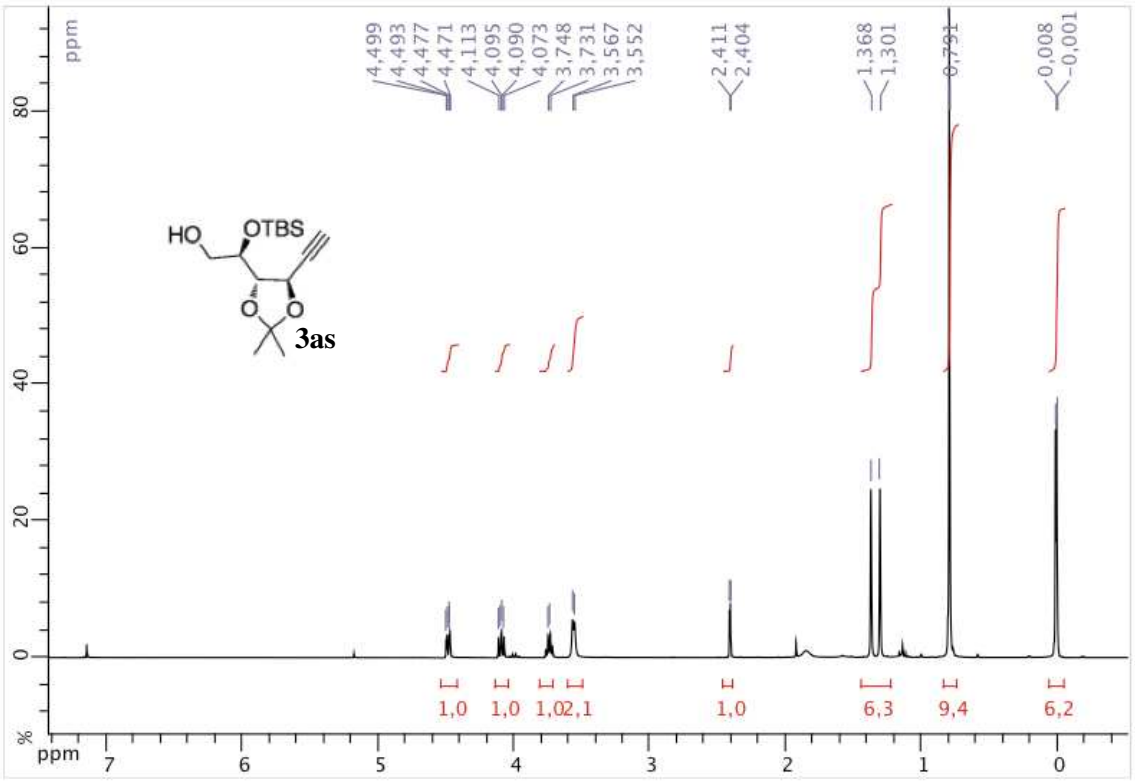
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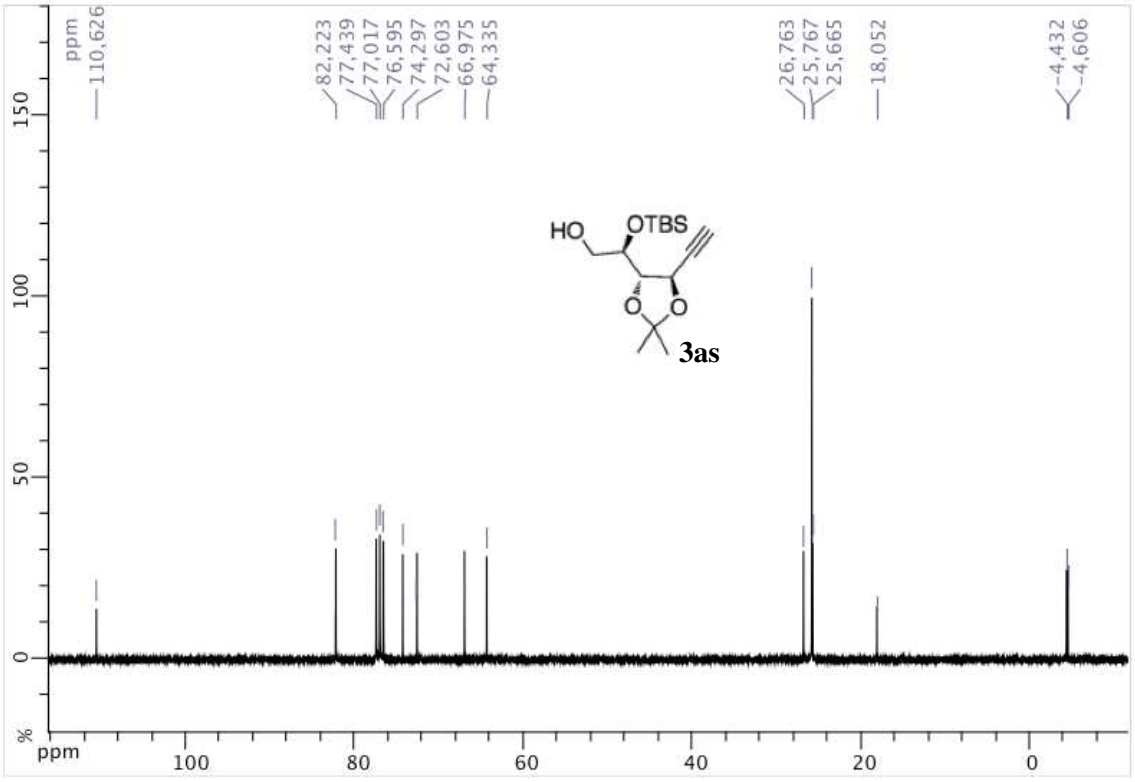
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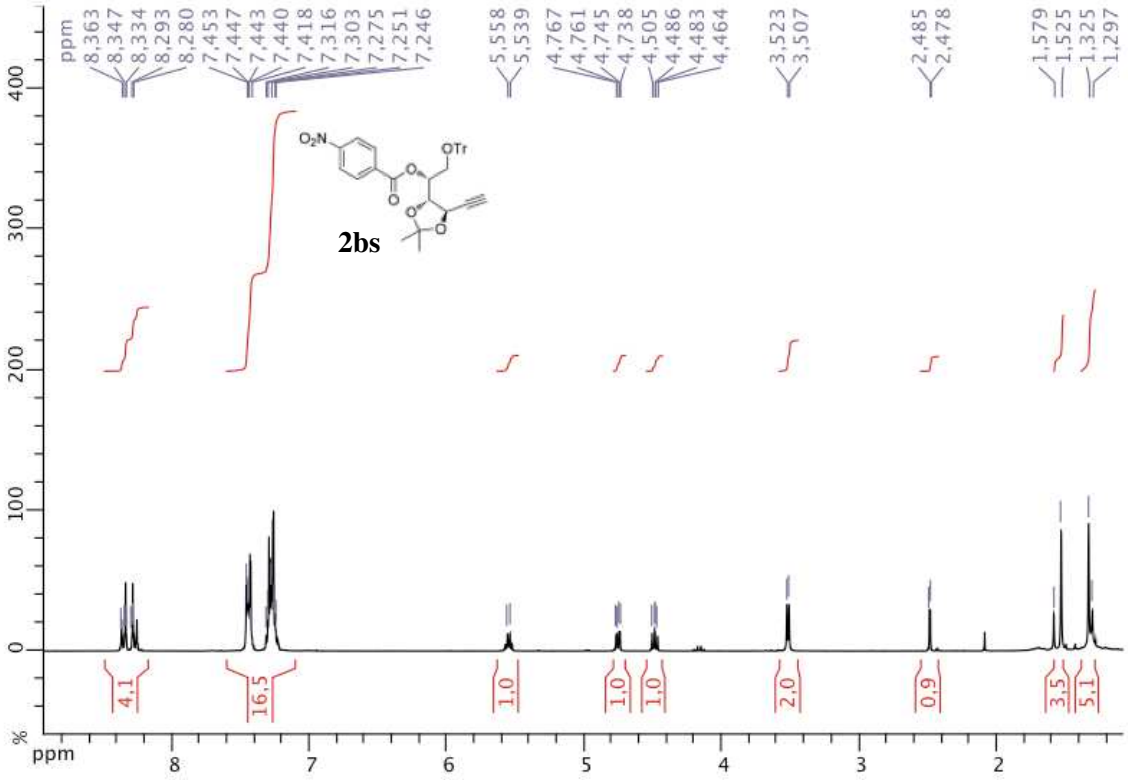
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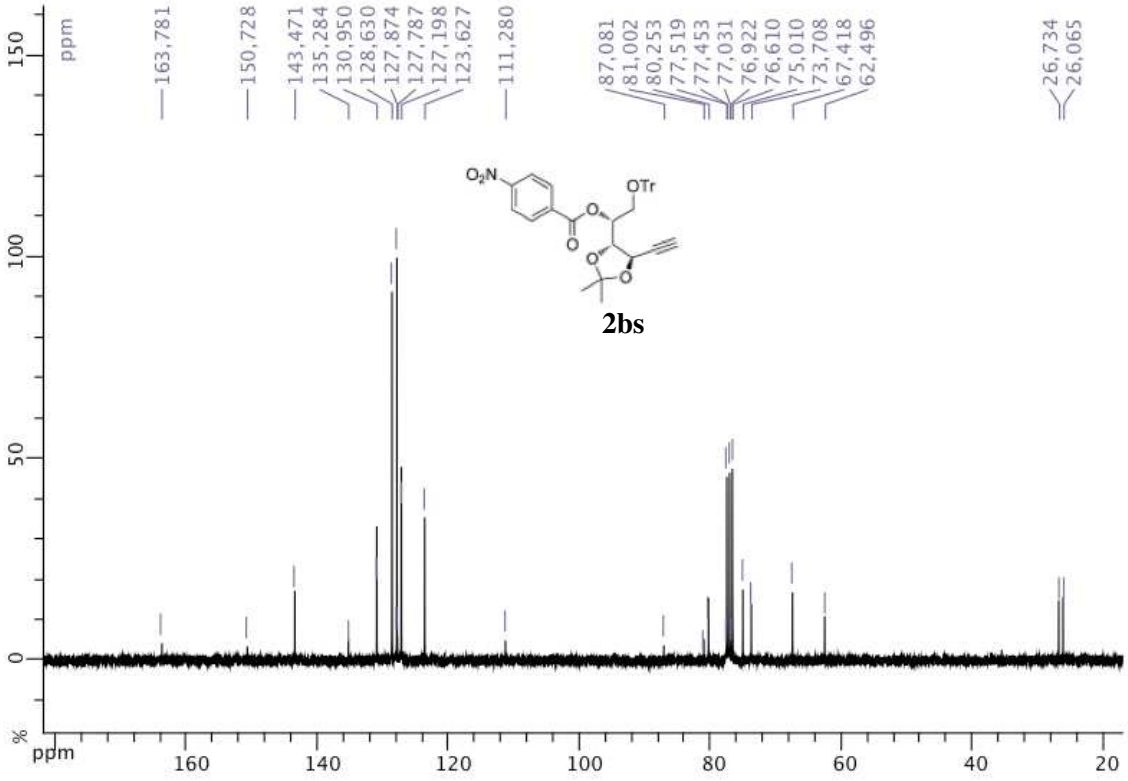
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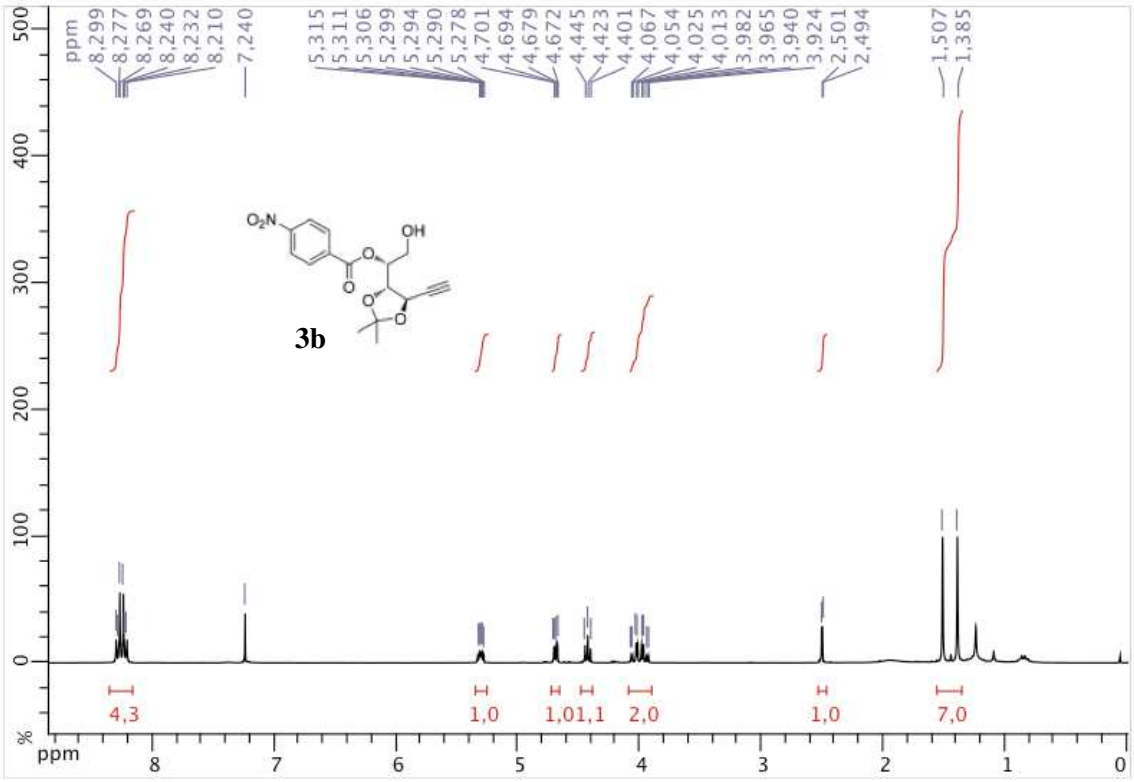
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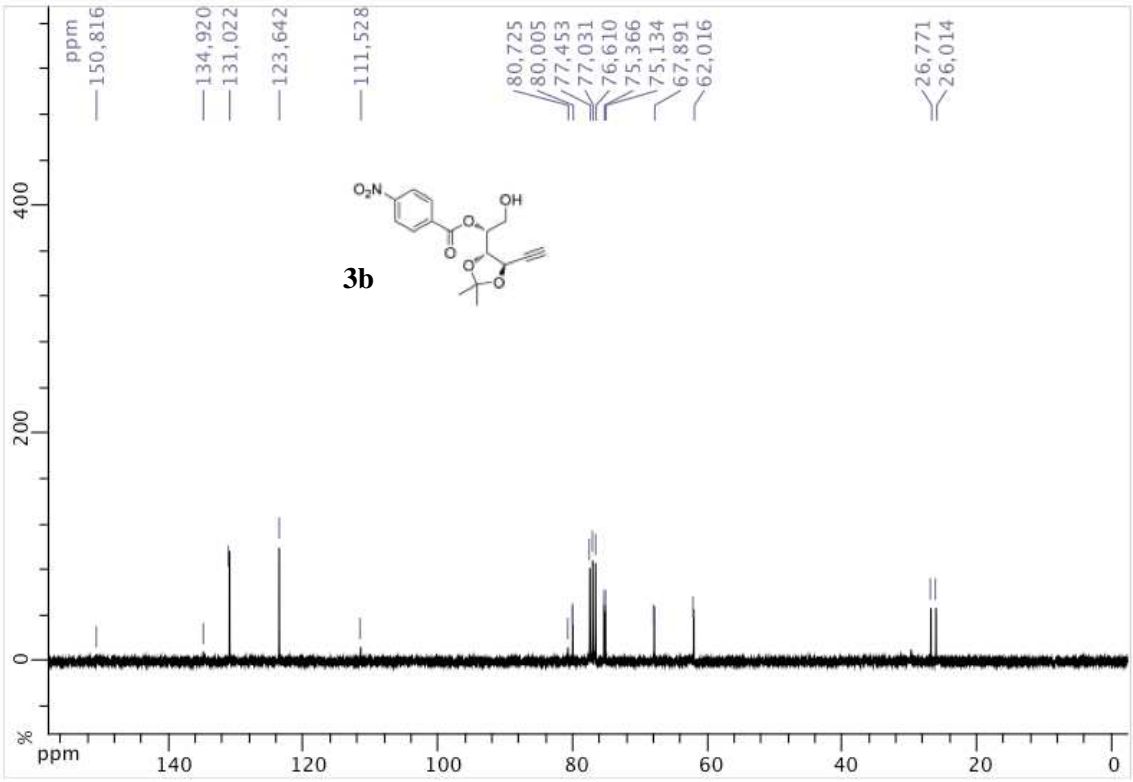
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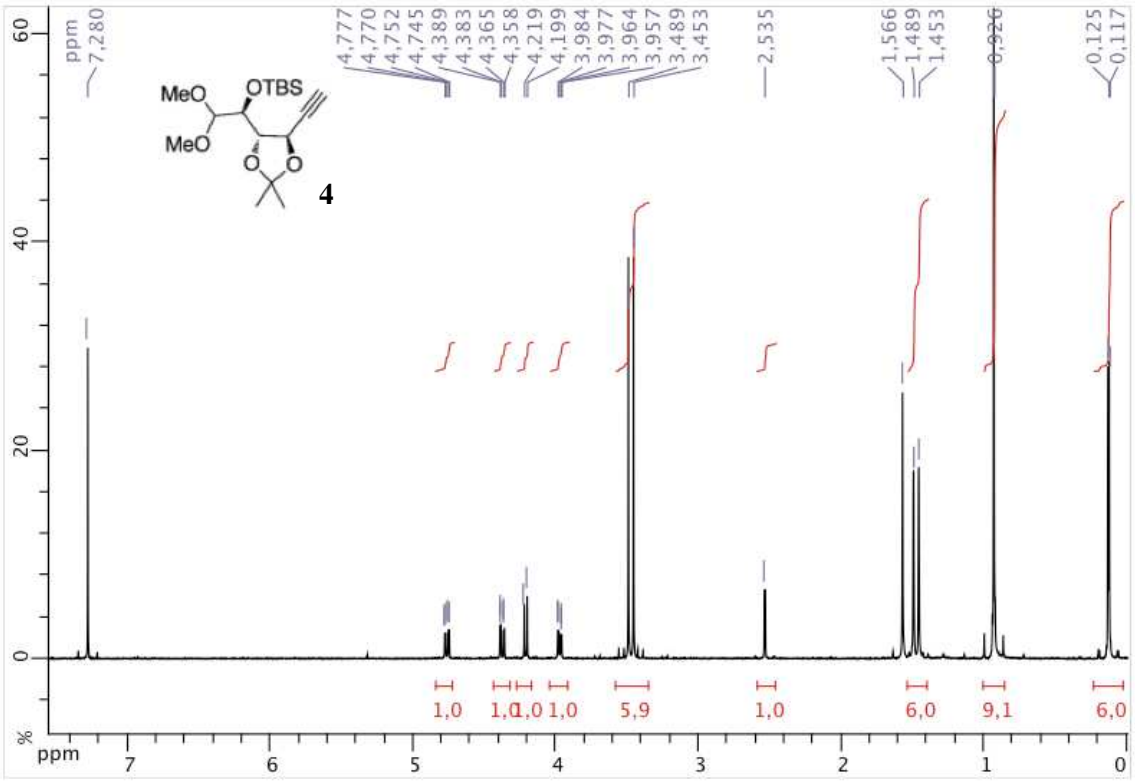
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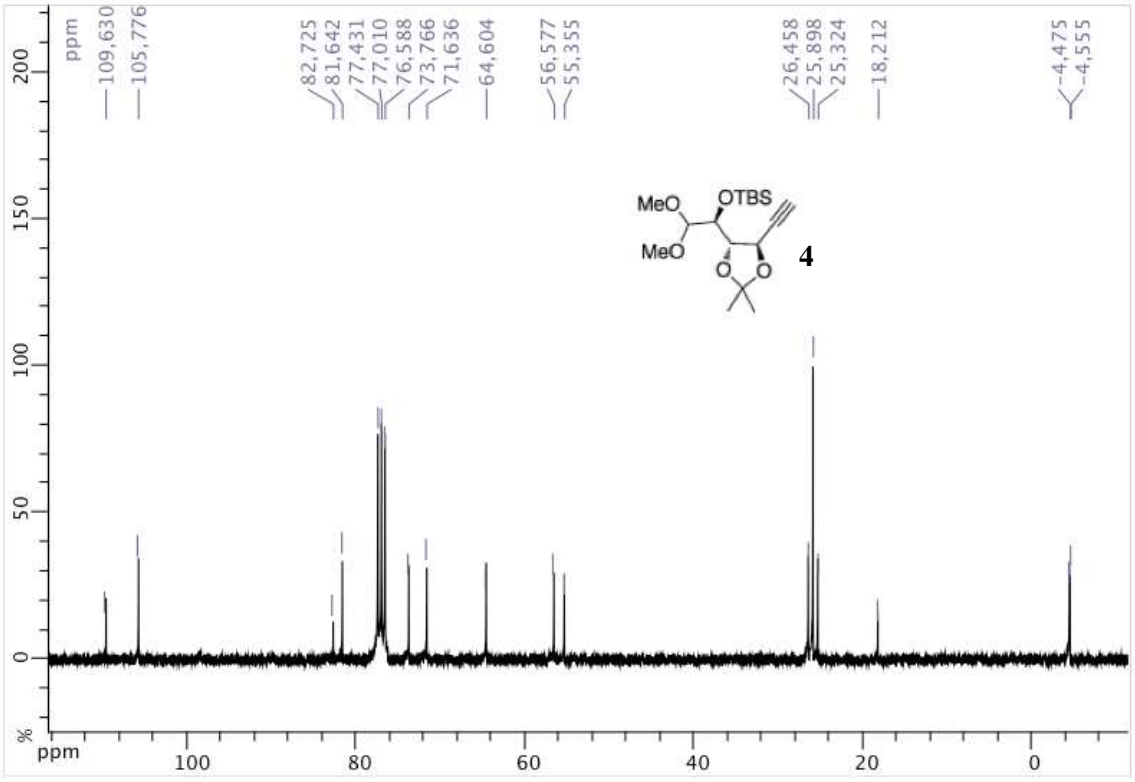
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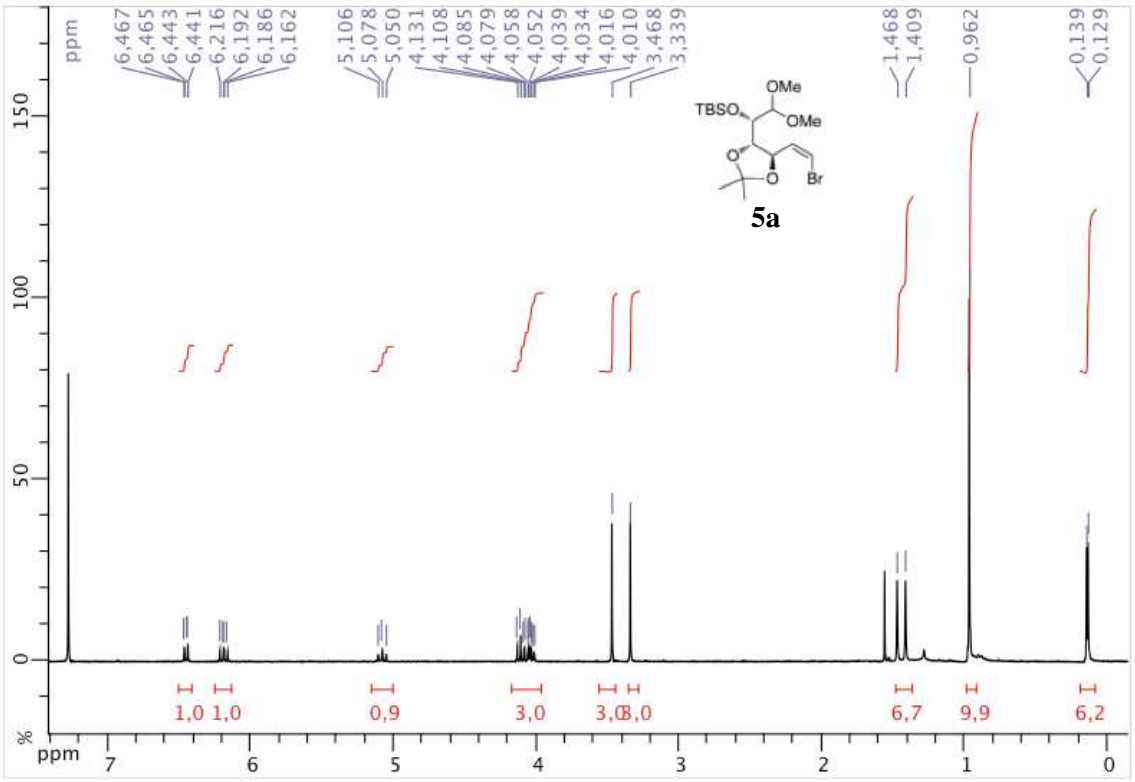
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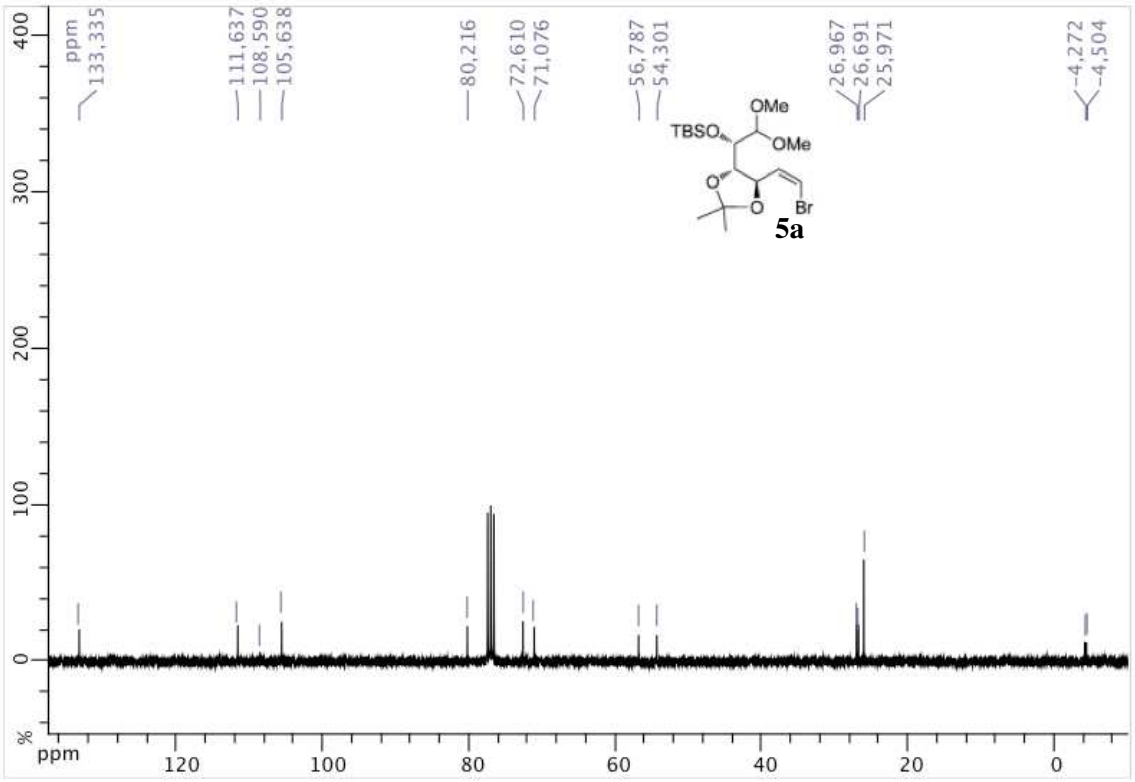
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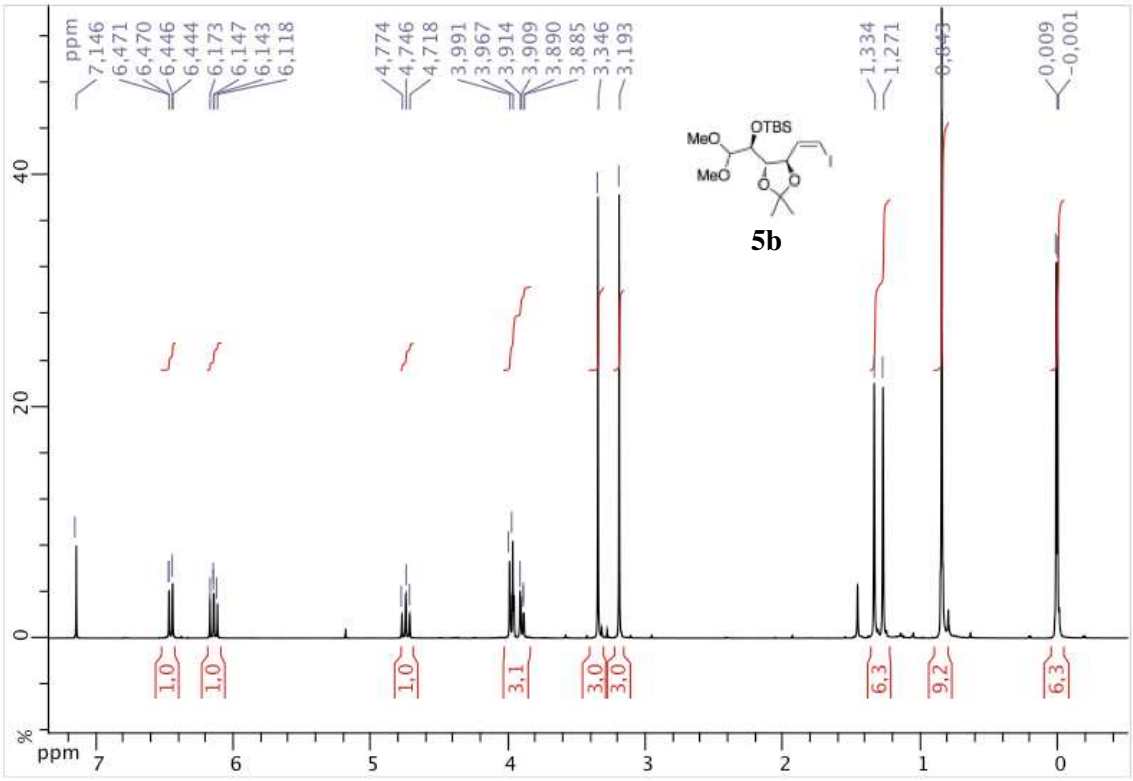
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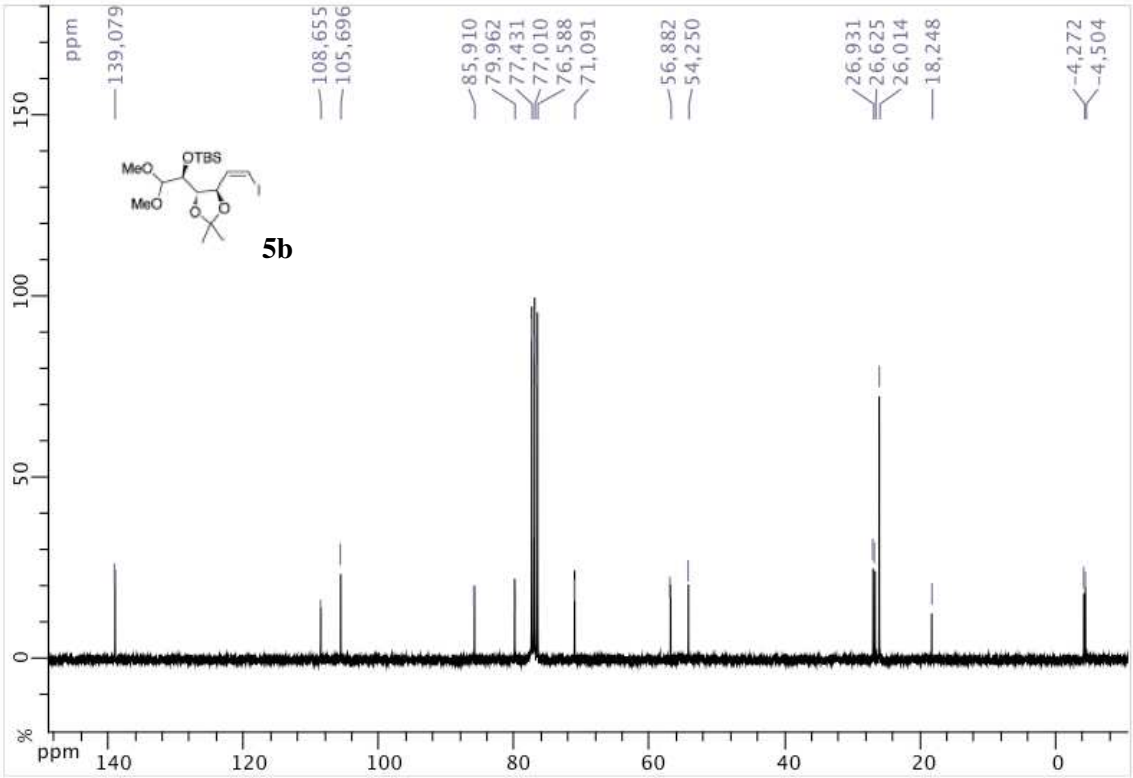
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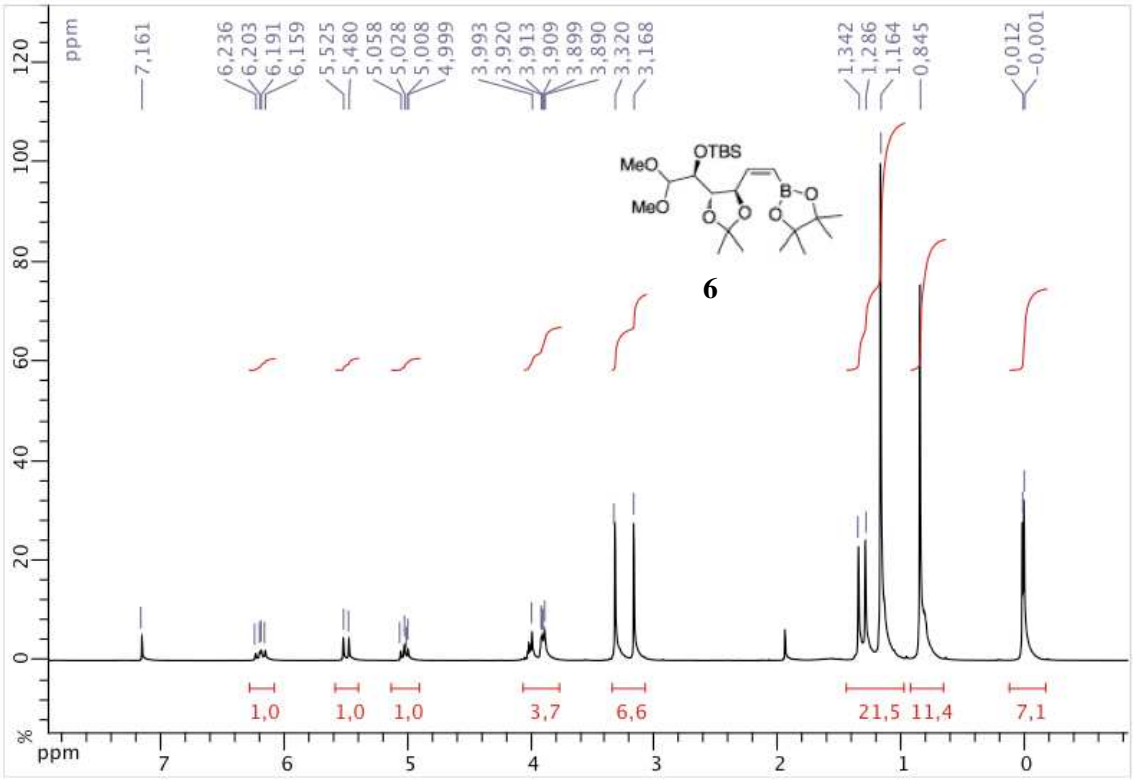
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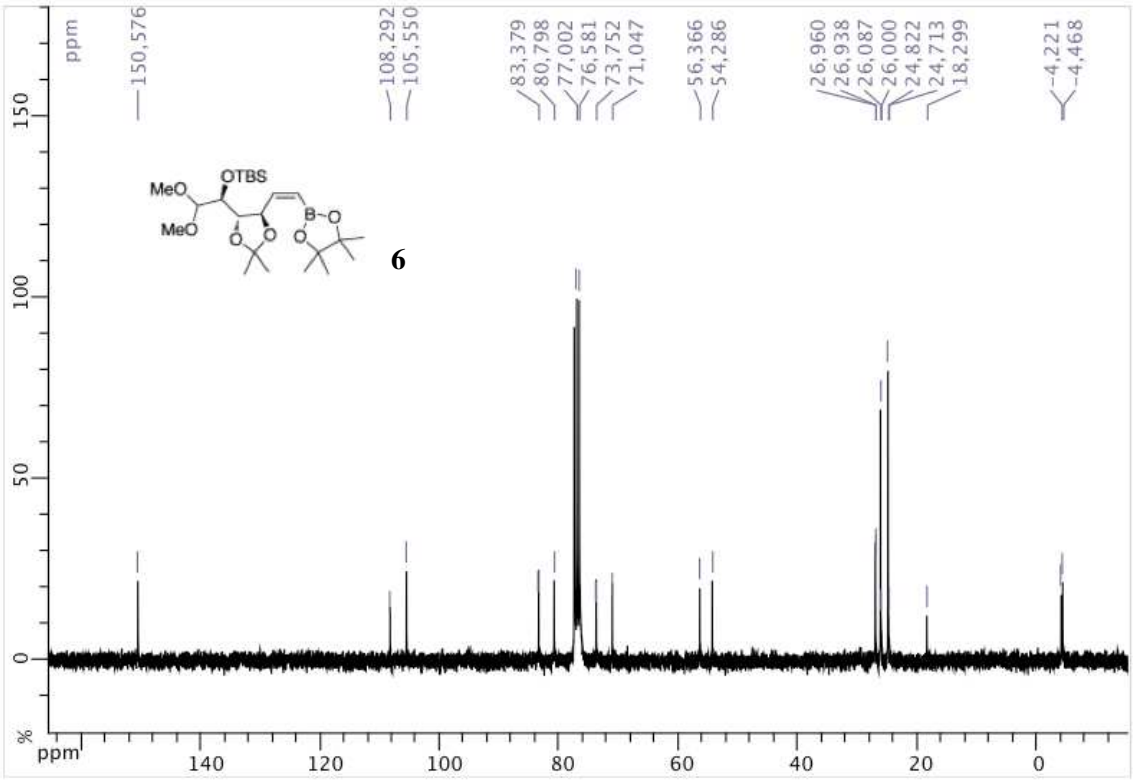
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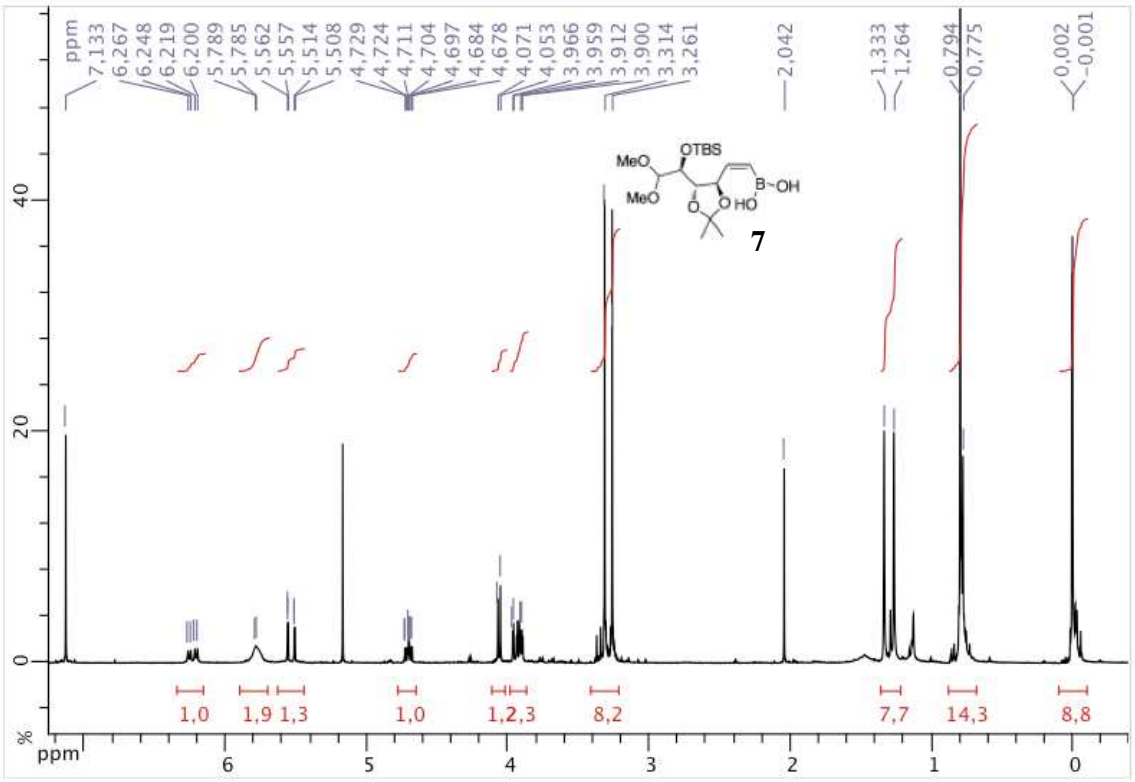
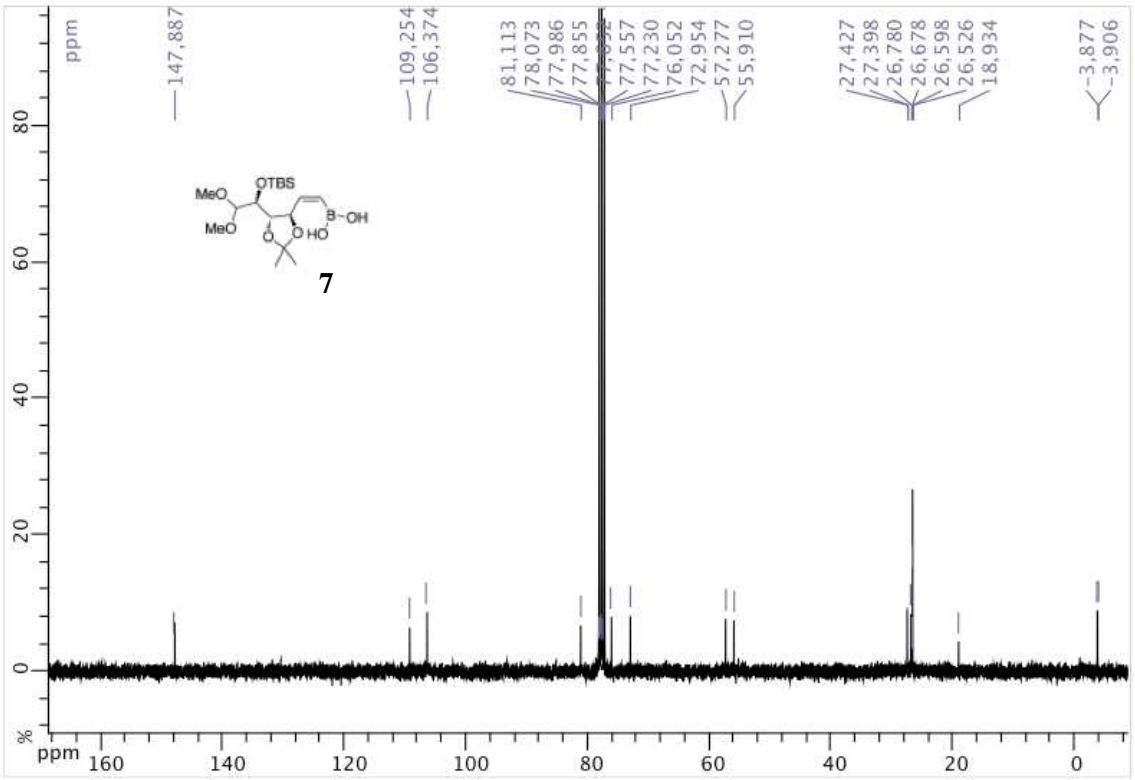
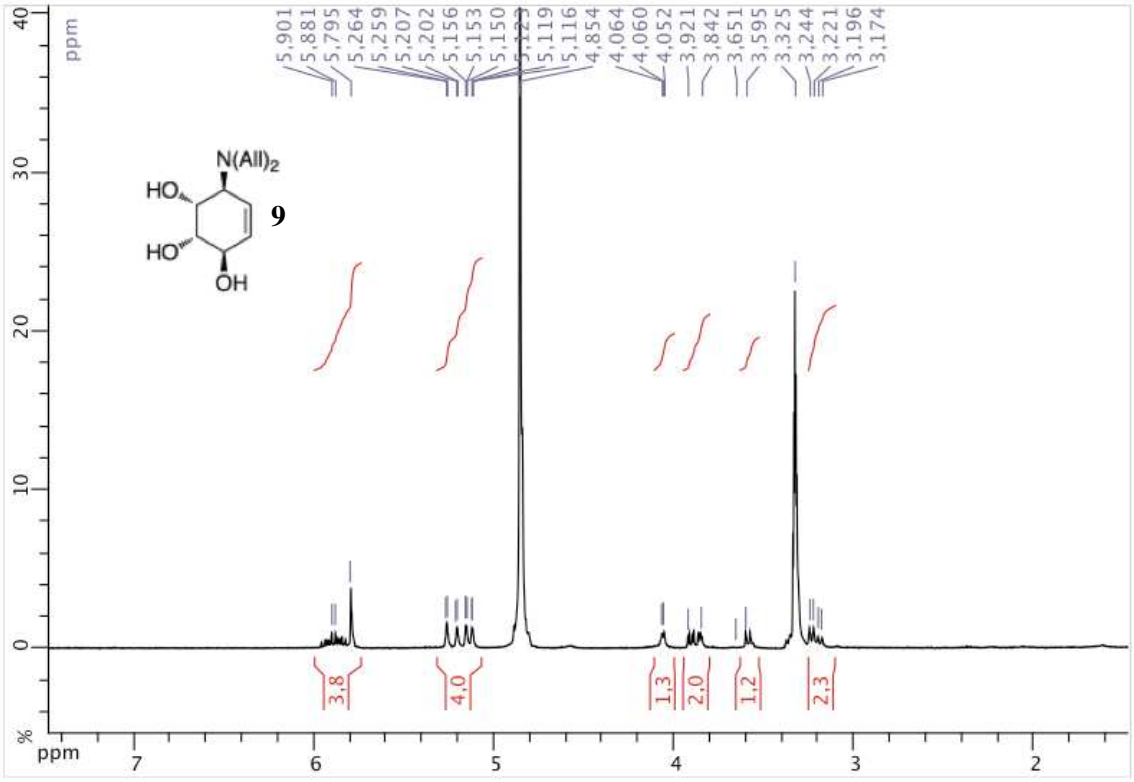
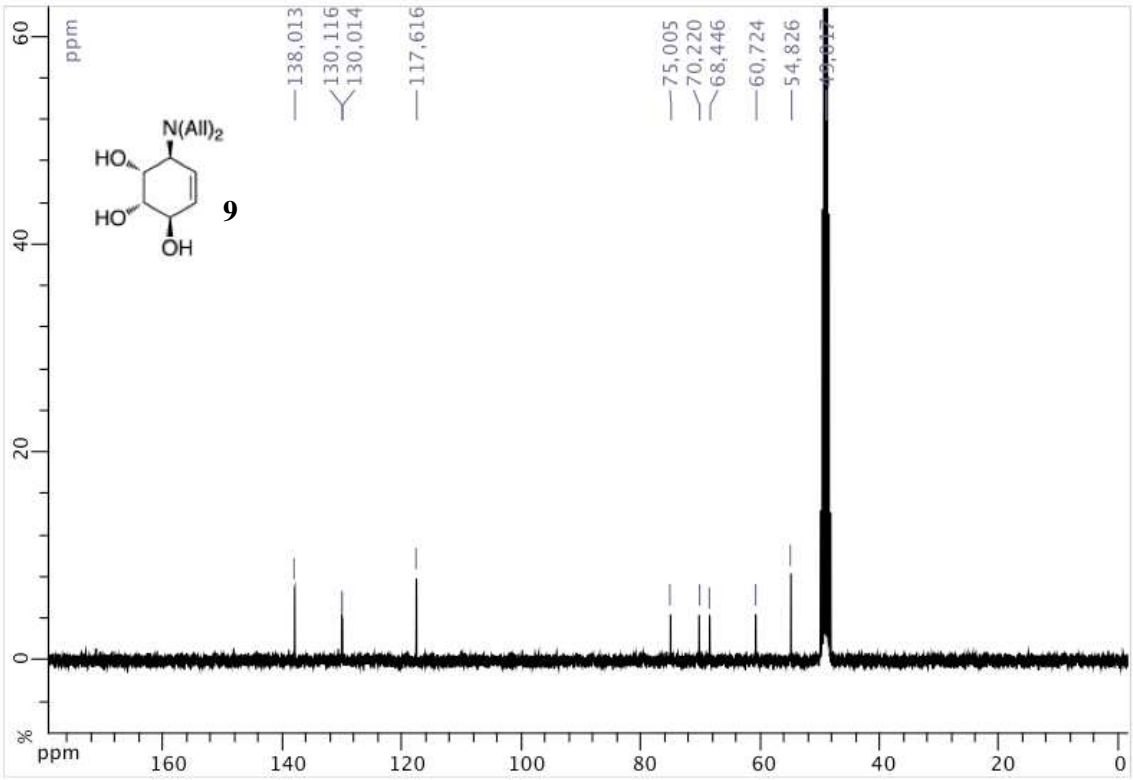
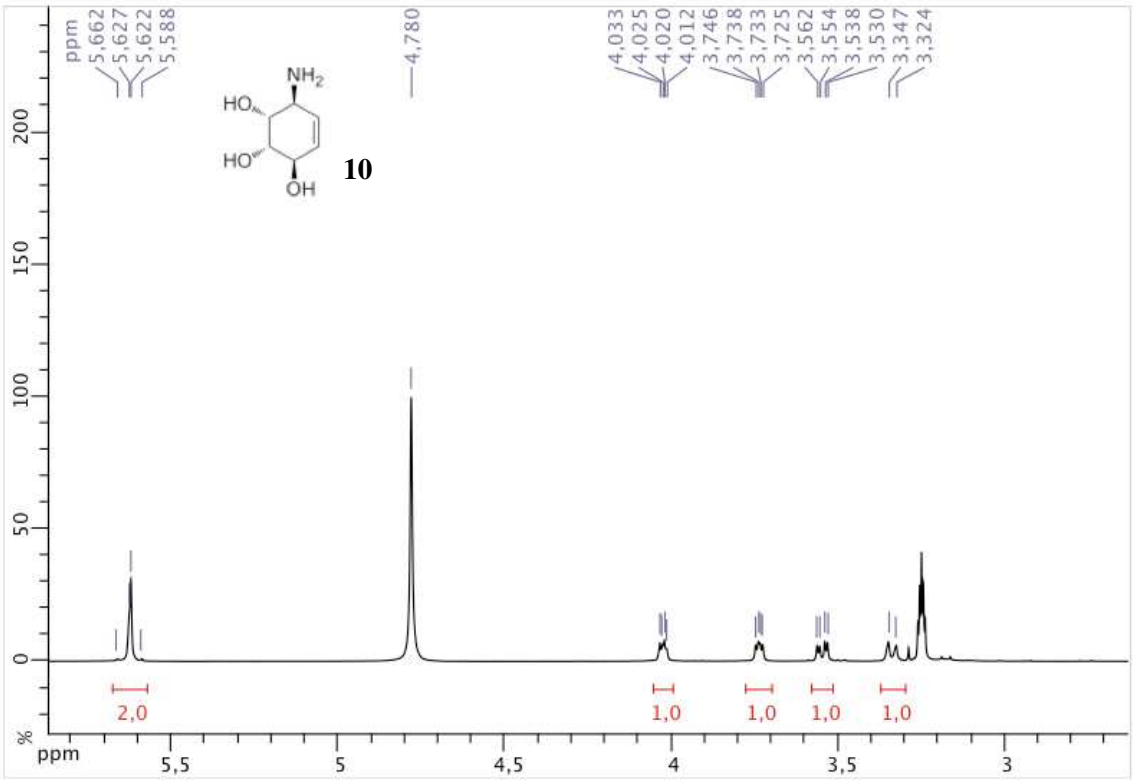
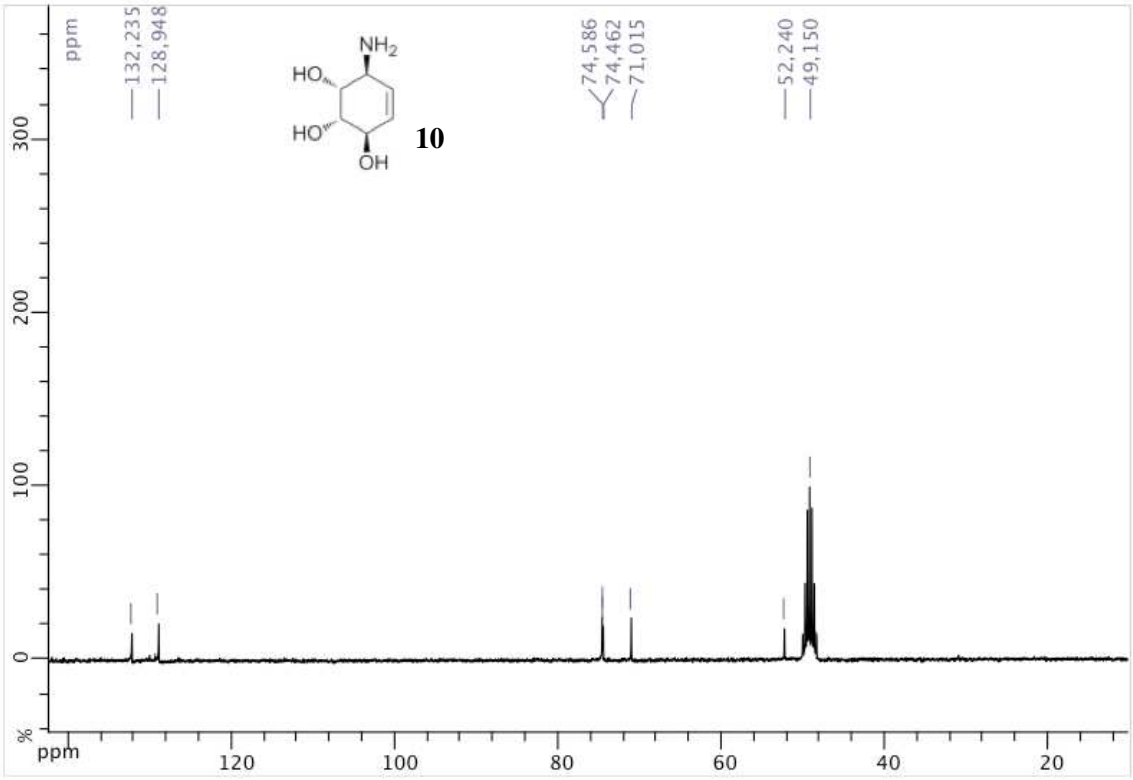

ppm
7,133
6,267
6,248
6,219
6,200
5,789
5,785
5,562
5,557
5,514
5,508
4,729
4,724
4,711
4,704
4,697
4,684
4,678
4,071
4,053
3,966
3,959
3,912
3,900
3,314
3,261
2,042
1,333
1,264
0,794
0,775
0,002
-0,001
OTBS
MeO
MeO
B~OH
O
O
HO
7
1,0
1,9
1,3
1,0
1,2,3
8,2
7,7
14,3
8,8
%
ppm
6
5
4
3
2
1
0

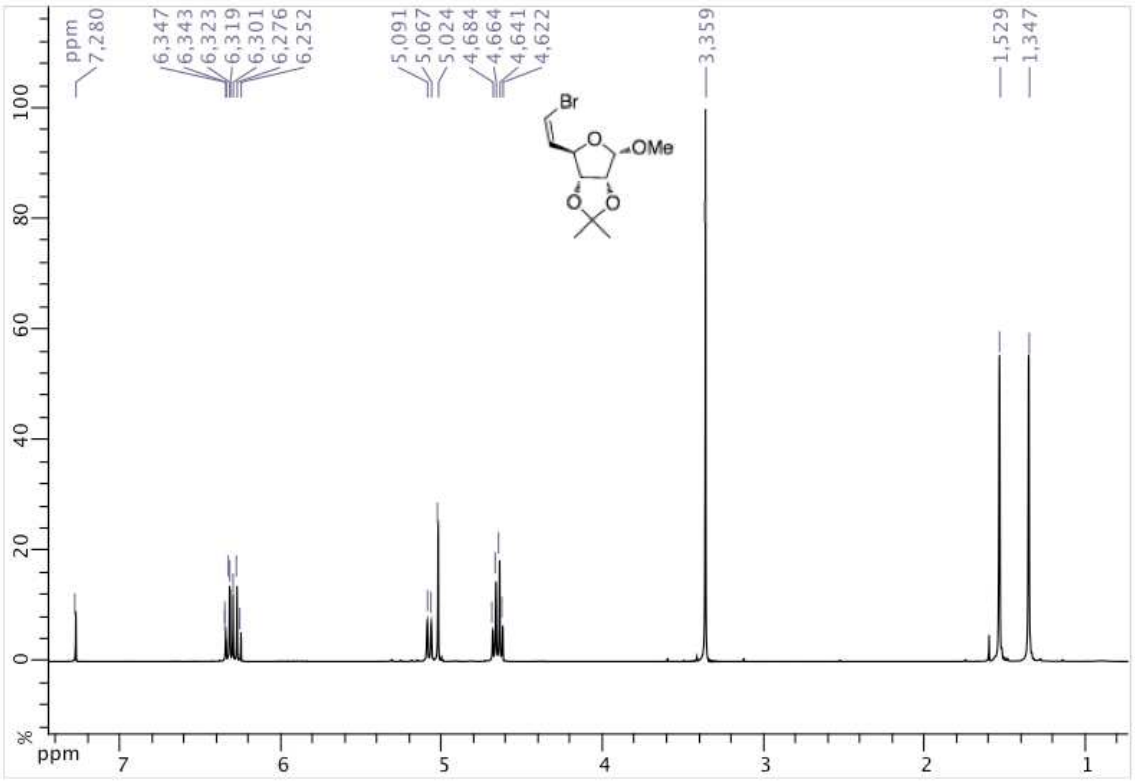

ppm
147,887
109,254
106,374
81,113
78,073
77,986
77,855
77,557
77,230
76,052
72,954
57,277
55,910
27,427
27,398
26,780
26,678
26,598
26,526
18,934
-3,877
-3,906
OTBS
MeO
MeO
B~OH
O
O
HO
7
%
ppm
160
140
120
100
80
60
40
20
0

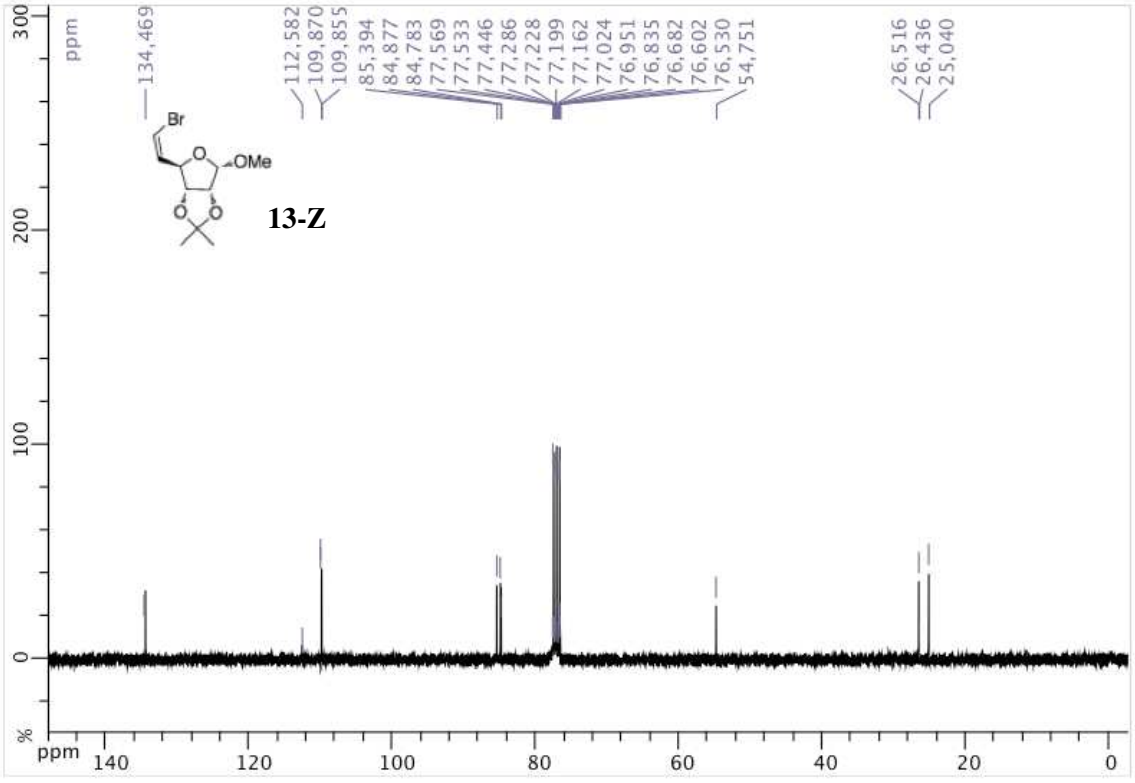

ppm
5,901
5,881
5,795
5,264
5,259
5,207
5,202
5,156
5,153
5,150
5,123
5,119
5,116
4,854
4,064
4,060
4,052
3,921
3,842
3,651
3,595
3,325
3,244
3,221
3,196
3,174
N(All)2
HO
HO
OH
9
3,8
4,0
1,3
2,0
1,2
2,3
%
ppm


ppm
138,013
130,116
130,014
117,616
75,005
70,220
68,446
60,724
54,826
N(All)2
HO
HO
OH
9
%
ppm

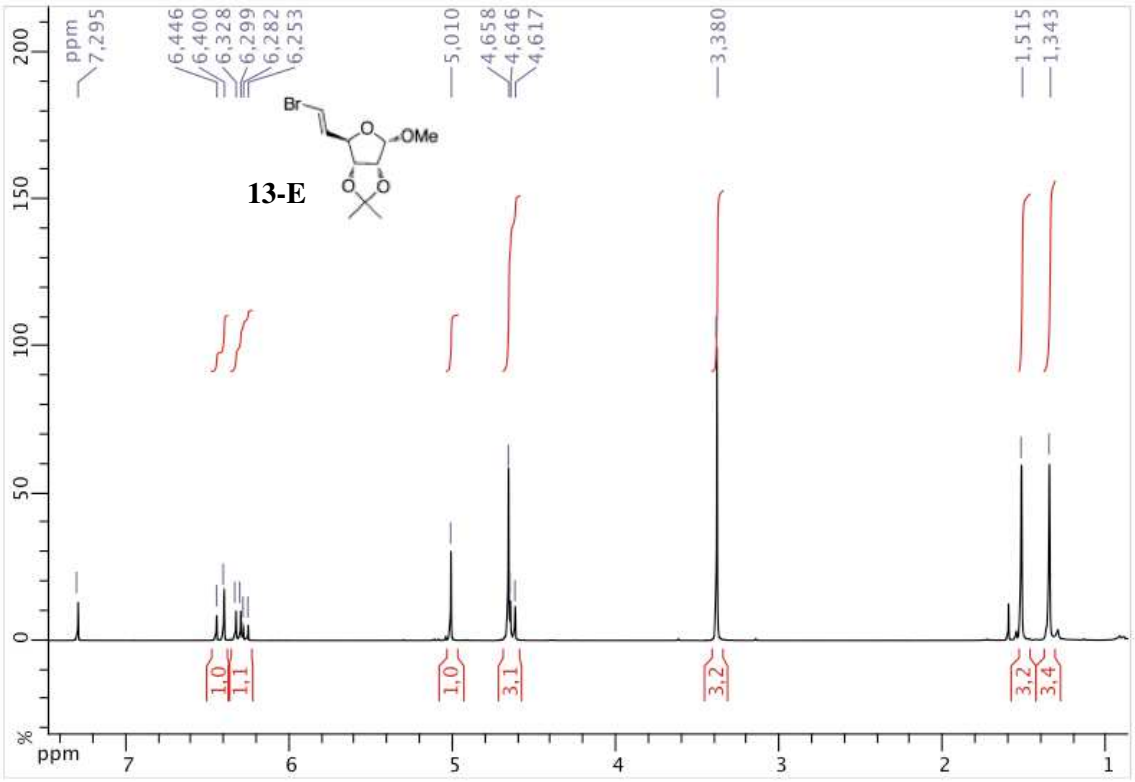

ppm
5,662
5,627
5,622
5,588
4,780
4,033
4,025
4,020
4,012
3,746
3,738
3,733
3,725
3,562
3,554
3,538
3,530
3,347
3,324
NH2
HO
HO
OH
10
2,0
1,0
1,0
1,0
1,0
%
ppm
5,5
5
4,5
4
3,5
3

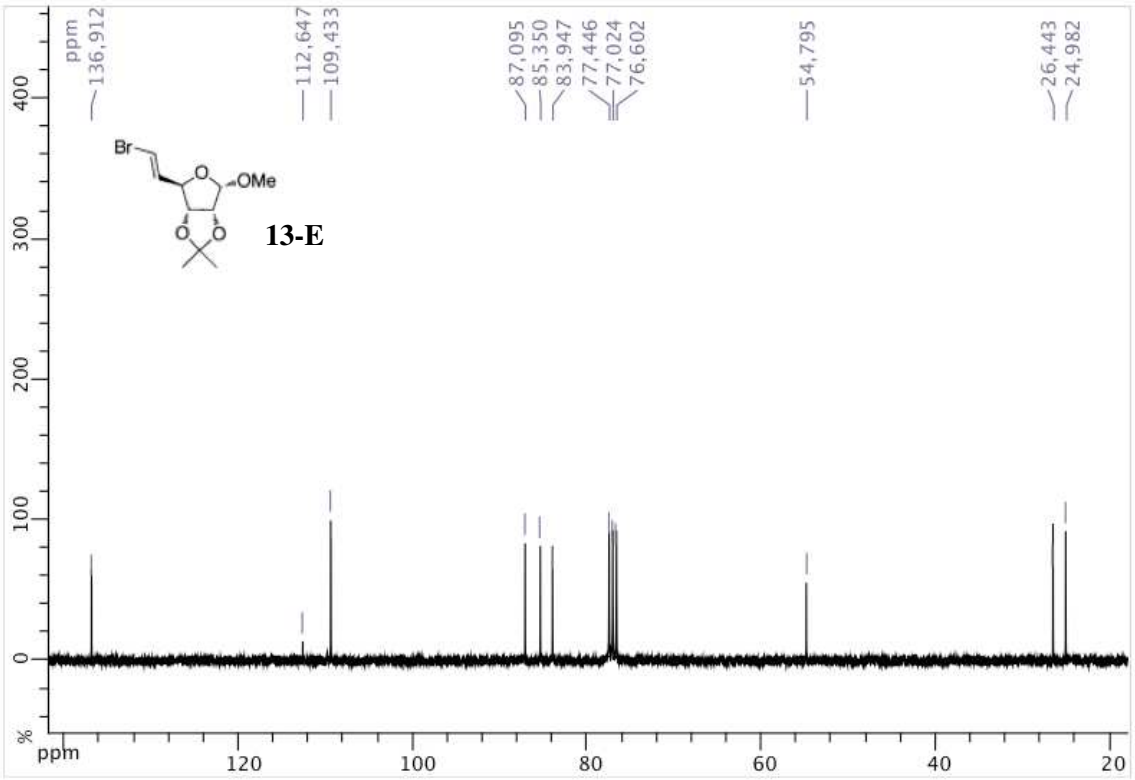

ppm
132,235
128,948
74,586
74,462
71,015
52,240
49,150
NH2
HO
HO
OH
10
%
ppm
120
100
80
60
40
20

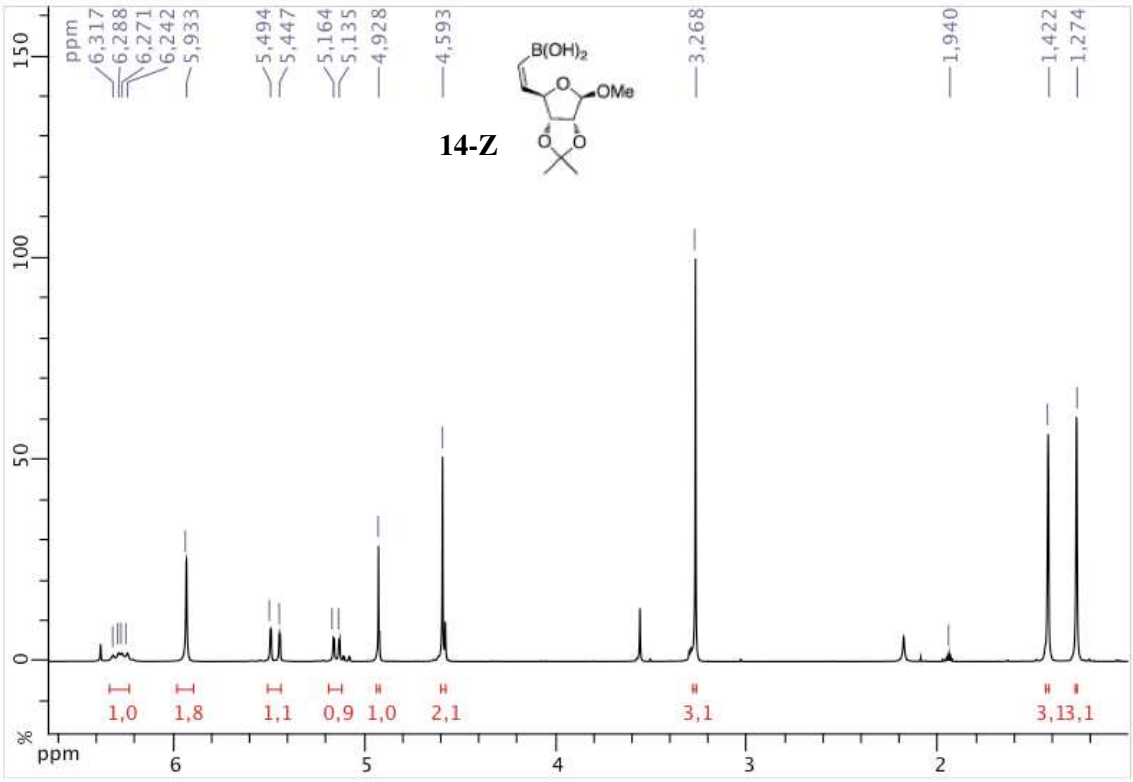

ppm
7,280
6,347
6,343
6,323
6,319
6,301
6,276
6,252
5,091
5,067
5,024
4,684
4,664
4,641
4,622
3,359
1,529
1,347
Br
OMe
O
O
O
%
ppm
7
6
5
4
3
2
1

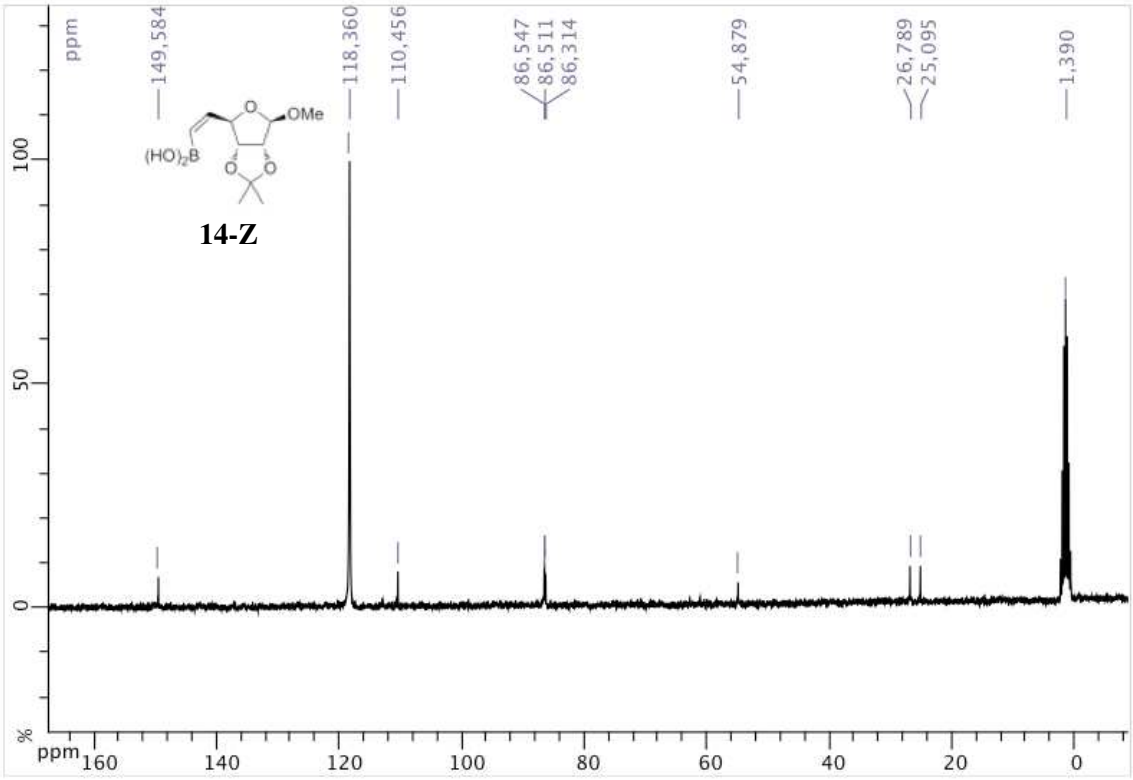

ppm
134,469
112,582
109,870
109,855
85,394
84,877
84,783
77,569
77,533
77,446
77,286
77,228
77,199
77,162
77,024
76,951
76,835
76,682
76,602
76,530
54,751
26,516
26,436
25,040
Br
OMe
O
O
O
%
ppm
140
120
100
80
60
40
20
0

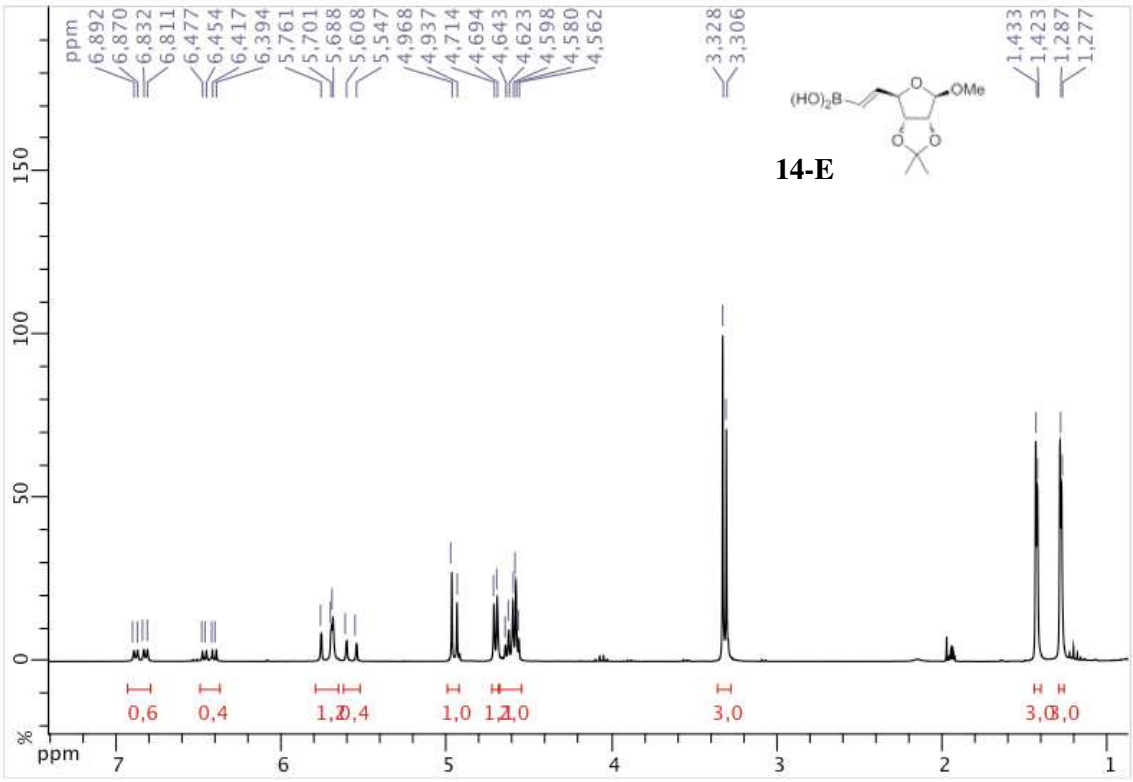
13-Z

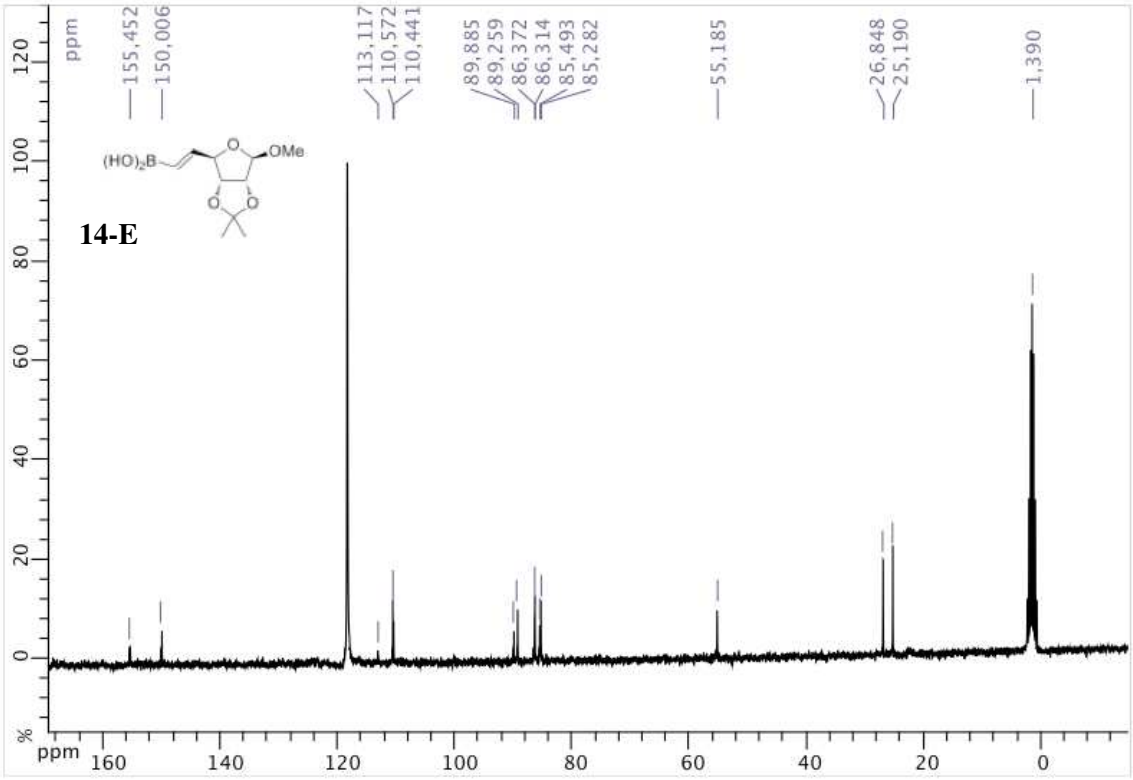

ppm
7,295
6,446
6,400
6,328
6,299
6,282
6,253
5,010
4,658
4,646
4,617
3,380
1,515
1,343
Br
OMe
O
O
O
13-E
1,0
1,1
1,0
3,1
3,2
3,2
3,4
%
ppm
7
6
5
4
3
2
1
200
150
100
50
0

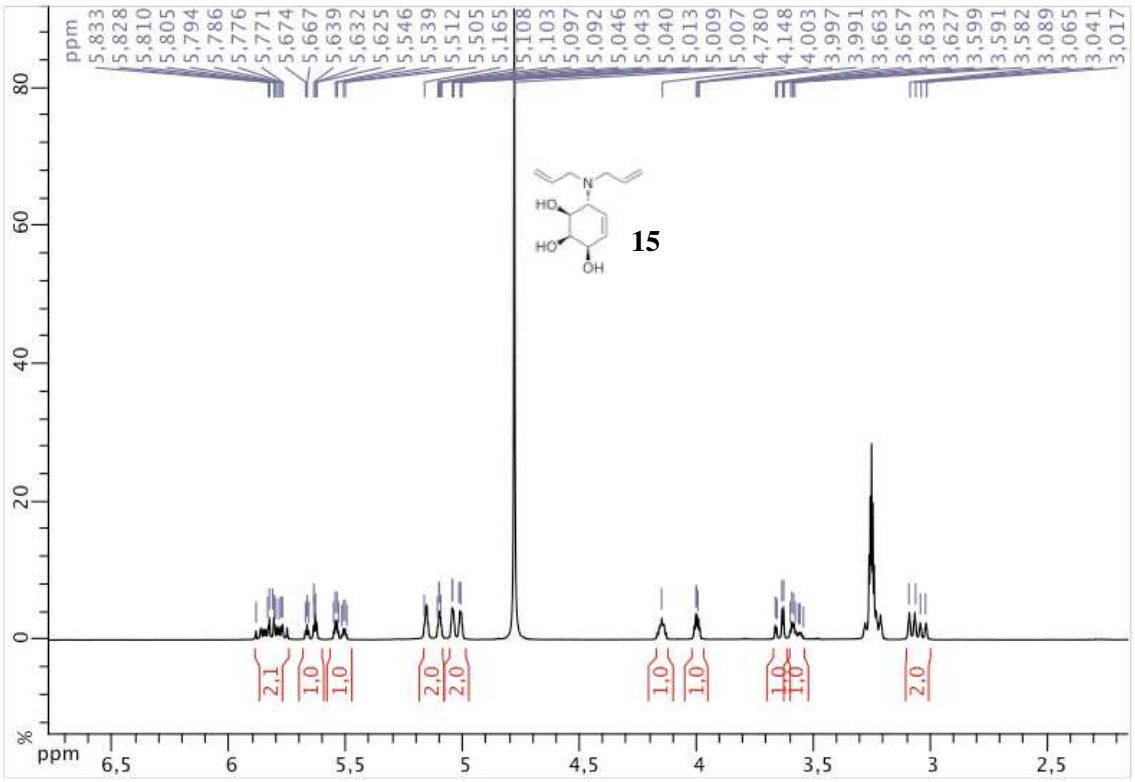

ppm
136,912
112,647
109,433
87,095
85,350
83,947
77,446
77,024
76,602
54,795
26,443
24,982
Br
OMe
O
O
O
13-E
%
ppm
120
100
80
60
40
20
400
300
200
100
0

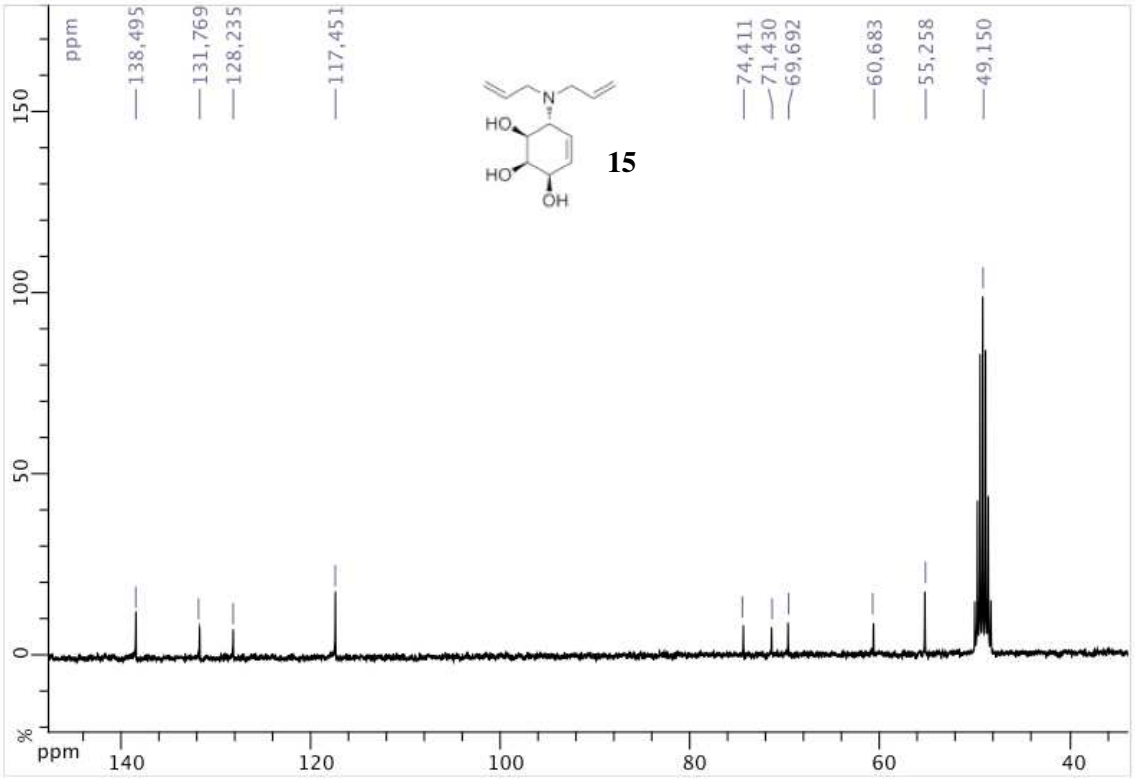

ppm
6,317
6,288
6,271
6,242
5,933
5,494
5,447
5,164
5,135
4,928
4,593
3,268
1,940
1,422
1,274
B(OH)2
OMe
14-Z
1,0
1,8
1,1
0,9
1,0
2,1
3,1
3,1
3,1
%
ppm
6
5
4
3
2

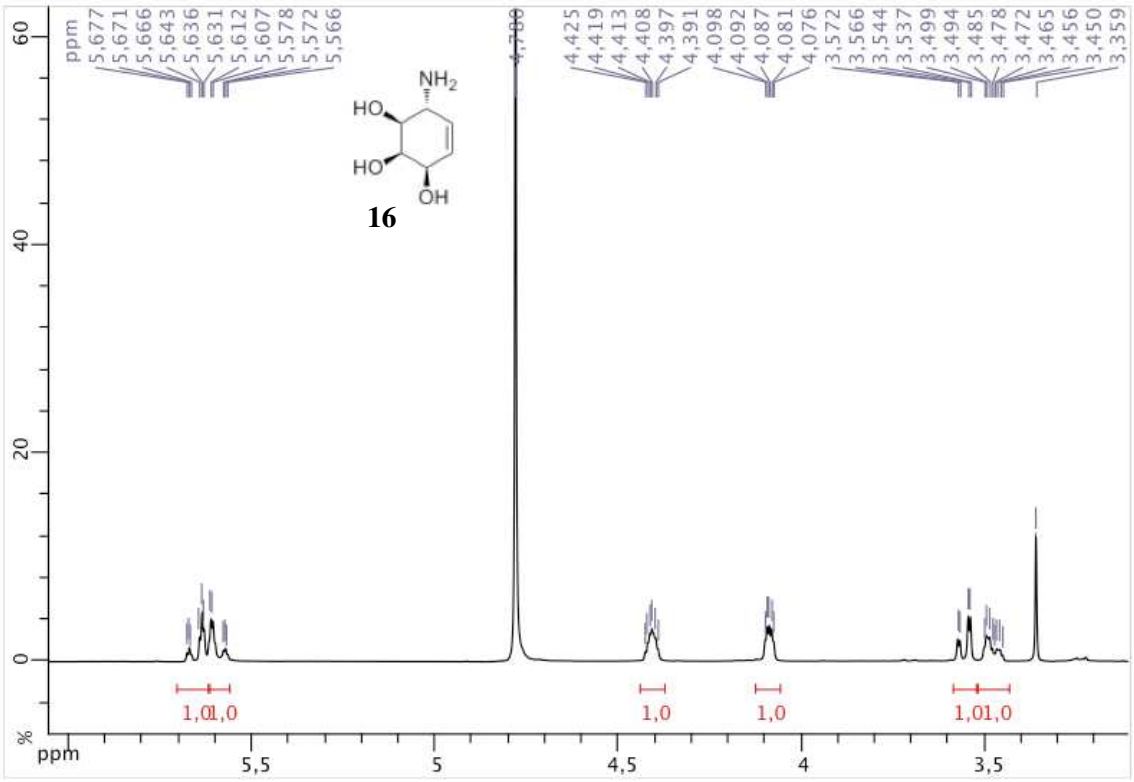

ppm
149,584
118,360
110,456
86,547
86,511
86,314
54,879
26,789
25,095
1,390
OMe
(HO)2B
14-Z
%
ppm
160
140
120
100
80
60
40
20
0

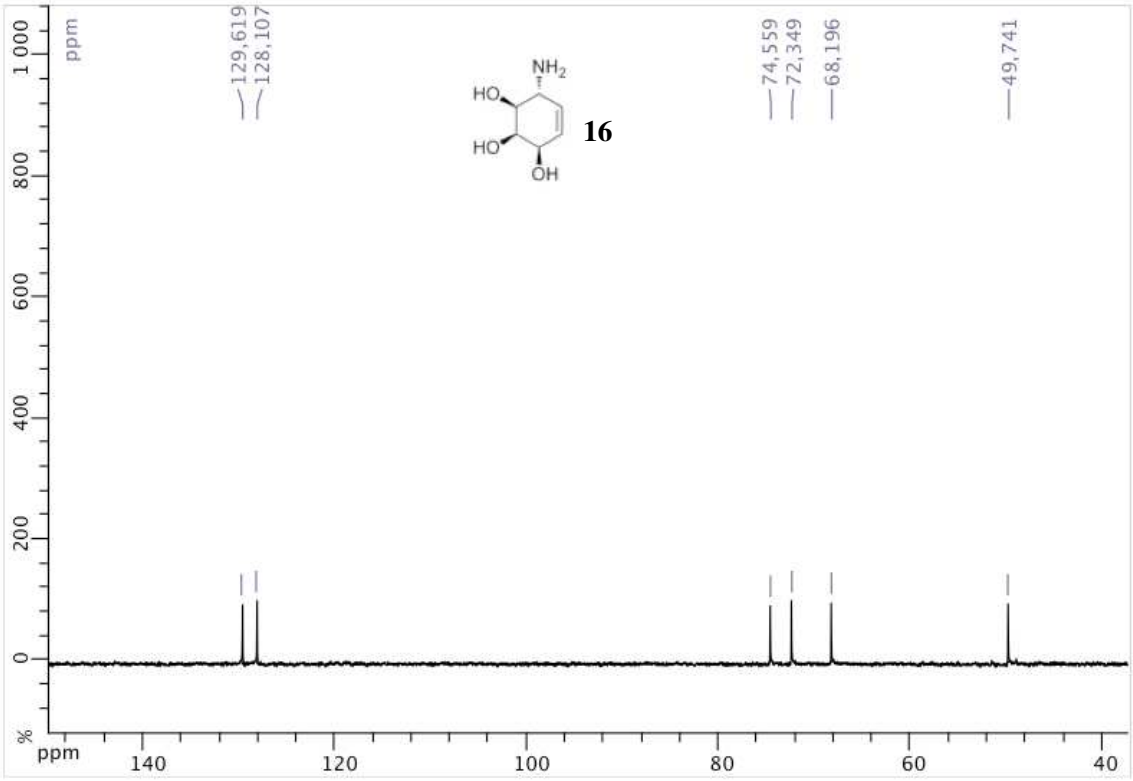

ppm
6,892
6,870
6,832
6,811
6,477
6,454
6,417
6,394
5,761
5,701
5,688
5,608
5,547
4,968
4,937
4,714
4,694
4,643
4,623
4,598
4,580
4,562
3,328
3,306
1,433
1,423
1,287
1,277
(HO)2B
OMe
14-E
0,6
0,4
1,2
0,4
1,0
1,2
1,0
3,0
3,0
3,0
%
ppm
7
6
5
4
3
2
1


ppm
155,452
150,006
113,117
110,572
110,441
89,885
89,259
86,372
86,314
85,493
85,282
55,185
26,848
25,190
1,390
(HO)2B
OMe
14-E
%
ppm
160
140
120
100
80
60
40
20
0


ppm
5,833
5,828
5,810
5,805
5,794
5,786
5,776
5,771
5,674
5,667
5,639
5,632
5,625
5,546
5,539
5,512
5,505
5,165
5,108
5,103
5,097
5,092
5,046
5,043
5,040
5,013
5,009
5,007
4,780
4,148
4,003
3,997
3,991
3,663
3,657
3,633
3,627
3,599
3,591
3,582
3,089
3,065
3,041
3,017
HO
HO
OH
15
2,1
1,0
1,0
2,0
2,0
1,0
1,0
1,0
1,0
2,0
%
ppm
6,5
6
5,5
5
4,5
4
3,5
3
2,5


ppm
138,495
131,769
128,235
117,451
74,411
71,430
69,692
60,683
55,258
49,150
HO
HO
OH
15
%
ppm
140
120
100
80
60
40


ppm
5,677
5,671
5,666
5,643
5,636
5,631
5,612
5,607
5,578
5,572
5,566
4,700
4,425
4,419
4,413
4,408
4,397
4,391
4,098
4,092
4,087
4,081
4,076
3,572
3,566
3,544
3,537
3,499
3,494
3,485
3,478
3,472
3,465
3,456
3,450
3,359
NH2
HO
HO
OH
16
1,0
1,0
1,0
1,0
1,0
%
ppm
5,5
5
4,5
4
3,5


ppm
129,619
128,107
74,559
72,349
68,196
49,741
NH2
HO
HO
OH
16
%
ppm
140
120
100
80
60
40