OL0491890

Supporting Information

Synthesis of 4-Azido-4-deoxy-Neu5,7,8,9Ac$_4$2en1Me. A Key Intermediate for the Synthesis of GG167 from D-Glucono-δ-lactone

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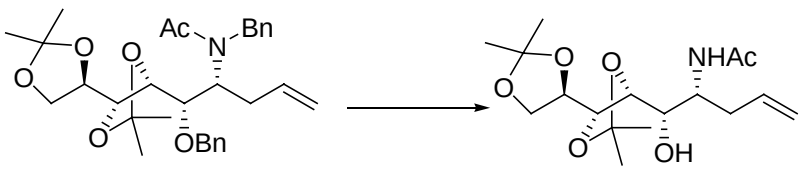
1. Experimental details with full characterization of compounds

General: ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or CD_3OD, $(CD_3)_2CO$ with TMS as internal standard. Elemental analyses were carried out at the Micro-analytical Laboratory of Shanghai Institute of Organic Chemistry. HRMS (EI and ESI) spectra were recorded on an APEXIII 7.0 Tesla FTMS mass spectrometer. Flash column chromatography was performed on silica gel H (10-40 μm).

Compound 6

Compound **6** was prepared from D-Glucono-δ-lactone according to the previously reported procedures in multiple steps. (See: Liu, K.-G.; Zhou, H.-B.; Wu, Y.-L.; Yao, Z.-J. *J. Org. Chem.* **2003**, *68*, 9528-9531.)

Compound 7

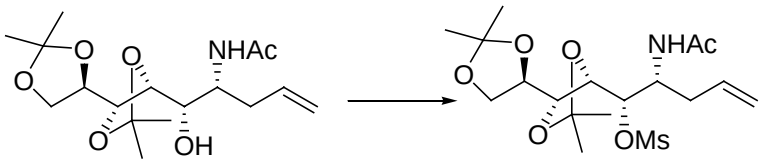


6 **7**

To liquid NH_3 (15 mL, collected first) at -78 ^{o}C was added a solution of **6** (530 mg, 1 mmol) in THF (5 mL). Solid lithium was then added until the solution turned deeply blue. The reaction mixture was stirred for 1h at -40 ^{o}C. Solid ammonium chloride was added carefully to quench the reaction. The reaction was allowed to warm up to rt naturally and ammonia was evaporated. The solid residue was dissolved into MeOH and dichloromethane. The organic layer was concentrated *in vacuo* to give a residue. Purification on silica gel flash chromatography (hexane-ethyl acetate=1:5) gave **7** (280 mg, 82%) as a colorless solid. $[\alpha]_D$ = +14.9 (*c* 1.75, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$): δ 5.76 (m, 1H), 5.73 (d, 1H, J=7.2Hz), 5.16-5.08 (m, 2H), 4.16-4.02 (m, 3H), 3.99 (dd, 1H, J=7.2, 3.0Hz), 3.92 (dd, 1H, J= 8.1, 4.8Hz), 3.85 (t, 1H, J=7.8Hz), 3.75 (m, 1H), 2.92 (d, 1H, J=7.8Hz), 2.39 (m, 2H), 1.98 (s, 3H), 1.41 (s, 6H), 1.37 (s, 3H), 1.34 (s, 3H) ppm. EI-MS (m/z, %): 328 (M^{+}-Me, 21.16), 302 (9.49), 184 (25.39), 149 (13.66), 143 (86.16), 113 (42.53), 70 (97.39), 43 (100.00). IR (film): 3301,

3079, 2988, 2937, 1649, 1552, 1373, 1216, 1068 cm^{-1}. HREIMS calcd for $C_{17}H_{29}NO_6$: 343.1995. Found: 343.2013.

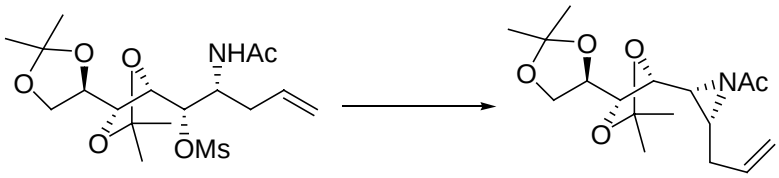
Compound 8



7 **8**

To a solution of **7** (230 mg, 0.67 mmol) in dichloromethane (5 mL) containing triethylamine (2.01 mmol) was added dropwise methanesulfonyl chloride (0.804 mmol). After being stirred at 20 ^{o}C for 2 h, the reaction mixture was poured into ice-water. The aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified on silica gel flash chromatography (hexane-ethyl acetate=1:4) to afford compound **8** (235 mg, 84%) as a yellowish oil. $[\alpha]_D$ = +16.4 (c 0.7, $CHCl_3$). ^{1}H NMR(300MHz, $CDCl_3$): δ 5.77 (m, 1H), 5.72 (d, 1H, J=6.9Hz), 5.21-5.14 (m, 2H), 4.86 (dd, 1H, J=4.8, 4.2Hz), 4.46 (m, 1H), 4.17-4.07 (m, 3H), 3.98-3.88 (m, 2H), 3.14 (s, 3H), 2.45 (m, 1H), 2.34 (m, 1H), 1.99 (s, 3H), 1.44 (s, 3H), 1.41 (s, 3H), 1.38 (s, 3H), 1.35 (s, 3H) ppm. EI-MS (m/z, %): 406 (M^+-Me, 25.35), 380 (4.21), 262 (26.18), 150 (10.16), 143 (93.71), 112 (56.53), 70 (71.96), 43 (100.00). IR (film): 3309, 2989, 2941, 1651, 1545, 1371, 1173, 909 cm^{-1}. Anal. calcd for $C_{18}H_{31}NO_8S$: C, 51.29; H, 7.41; N, 3.32. Found: C, 51.29; H, 7.36; N, 3.11.

Compound 9

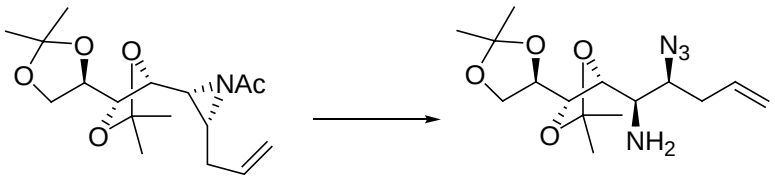


8 **9**

To a solution of **8** (520 mg, 1.3 mmol) in THF (7 mL) was added sodium hydride (60%, 300 mg) under N_2. The reaction mixture was heated to 40 ^{o}C and stirred for 24h. Saturated aq. NH_4Cl solution was added at 0 ^{o}C to quench the reaction. Aqueous phase was extracted with ether. The combined organic layers were washed with brine and dried over $MgSO_4$,

concentrated. Purification on silica gel flash chromatography (hexane: ethyl acetate=4:1) gave **9** (350 mg, 87%) as a colorless oil. $[\alpha]_D$ = +56.5 (c 0.7, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$): δ 6.00-5.89 (m, 1H), 5.23 (dd, 1H, J=17.1, 0.9Hz), 5.15 (dd, 1H, J =10.2, 0.9Hz), 4.23 –4.17 (m, 2H), 4.08 (dd, 1H, J=8.7, 6.0Hz), 3.96 (dd, 1H, J=9.0, 6.0Hz), 3.82 (dd, 1H, J=8.1, 6.0Hz), 2.70 (dd, 1H, J=8.1, 5.4Hz), 2.57-2.51 (m, 1H), 2.52-2.34 (m, 2H), 2.15 (s, 3H), 1.47 (s, 3H), 1.43 (s, 3H), 1.40 (s, 3H), 1.36 (s, 3H) ppm. EI-MS (m/z, %): 310 (M^+-Me, 59.31), 268 (5.70), 210 (15.68), 166 (22.34), 124 (65.87), 101 (64.23), 43 (100.00). IR (film): 2988, 2938, 2893, 1702, 1455, 1382, 1215, 1158, 847 cm^{-1}. Anal. calcd for $C_{17}H_{27}NO_5$: C, 62.75; H, 8.36; N, 4.30. Found: C, 62.89; H, 8.58; N, 4.15.

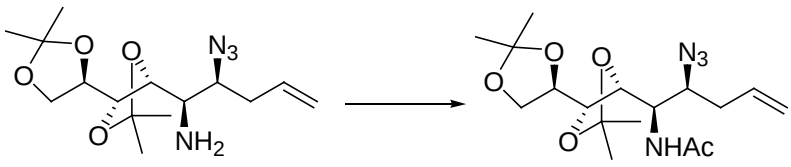
Compound 10



9 **10**

To a solution of **9** (40 mg, 0.12 mmol) in ethanol (1.2 mL) and water (0.3mL) was added solid ammonium chloride (26 mg, 0.50 mmol) and sodium azide (32 mg, 0.50 mmol) respectively. The reaction mixture was heated to reflux for 4h, then it was cooled to rt. Water was added. The aqueous phase was extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated. The residue was purified on silica gel flash chromatography (hexane-ethyl acetate=3:1) to afford **10** (27 mg, 68%) as a colorless oil. $[\alpha]_D$ = +48.0 (c 0.7, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$): δ 5.89-5.78 (m, 1H), 5.26-5.14 (m, 2H), 4.19-4.08 (m, 2H), 3.97 (dd, 1H, J=7.5, 5.1Hz), 3.89-3.78 (m, 3H), 2.79 (dd, 1H, J =8.7, 5.1Hz), 2.57-2.51 (m, 1H), 2.50-2.40 (m, 1H), 1.43 (s, 3H), 1.38 (s, 3H), 1.36 (s, 6H) ppm. EI-MS (m/z, %): 311 (M^+-Me, 13.58), 230 (100), 172 (54.19), 125 (41.49), 101 (16.20), 43 (82.50). IR (film): 3386, 2989, 2937, 2109, 1643, 1382, 12576, 1070, 848 cm^{-1}. Anal. calcd for $C_{15}H_{26}N_4O_4$: C, 55.20; H, 8.03; N, 17.17. Found: C, 55.22; H, 8.33; N, 16.71.

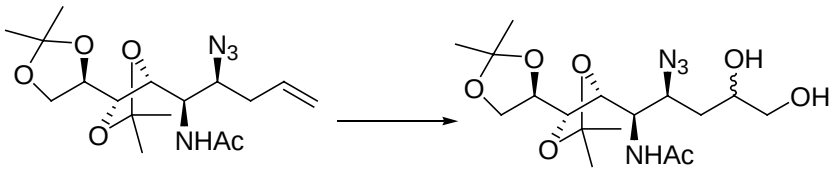
Compound 11



10 **11**

To a solution of **10** (18 mg, 0.055 mmol) in dichloromethane (1 mL) was added Et_3N (0.166 mmol) and Ac_2O (0.11 mmol) respectively. The reaction mixture was stirred for 30 min at rt. Water was added to quench the reaction. The aqueous phase was extracted with ether. The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated .The residue was purified on silica gel flash chromatography (hexane- ethyl acetate=(3:1) to afford **11** (20 mg, 99%) as a colorless solid. $[\alpha]_D$ = +17.7 (c 0.95, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91 - 5.79 (m, 1 H), 5.58 (d, 1 H, *J* = 9.3 Hz), 5.26 - 5.16 (m, 2 H), 4.23 (t, 1 H, J = 9.9 Hz), 4.14 (dd, 1 H, J = 9.9, 6.3 Hz), 4.05 - 3.93 (m, 3 H), 3.88 -3.80 (m, 2 H), 2.33 (m, 2 H), 2.00 (s, 3 H), 1.38 (s, 9 H), 1.36 (s, 3 H) ppm. ESI-MS (m/z, %): 369 (M^++1, 80), 391 (M^++Na, 100). IR (film): 3267, 2987, 2938, 2098, 1653, 1546, 1239, 1069 cm^{-1}. HRESIMS calcd for $C_{17}H_{28}N_4O_5$+Na: 391.1952；Found: 391.1958.

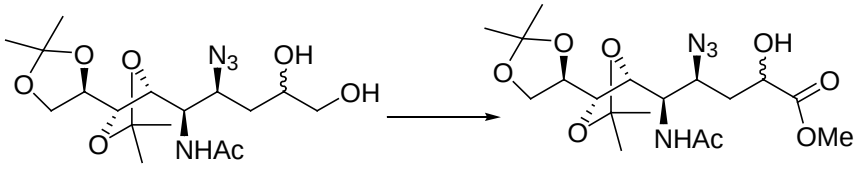
Compound 12



11 **12**

To a solution of **11** (100 mg, 0.27 mmol) in acetone (4.5 mL) and water (0.9 mL) was added NMO monohydrate (100 mg, 0.75 mmol), and a catalytic amount of OsO_4 in *t*-BuOH. The reaction mixture was stirred for 14 h at rt. Sat. aqueous Na_2SO_3 was added to quench the reaction. The mixture was filtered through a pad of celite and washed with ethyl acetate. The filtrate was extracted with ethyl acetate. The combined organic phases were washed with brine, dried over $MgSO_4$ and concentrated. The crude compound **12** (105 mg, 96%) was used directly for the next step.

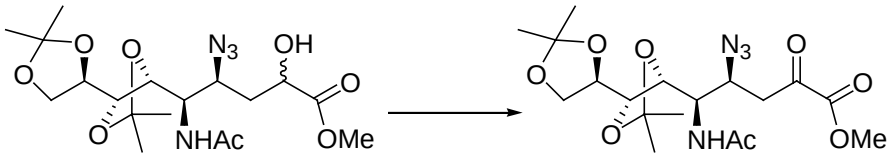
Compound 13



12 **13**

To a stirred mixture of alcohol **12** (141 mg, 0.35 mmol), KBr (16 mg), TBAB (16 mg) in sat. aq. $NaHCO_3$ (5 mL) was added solid $Ca(ClO)_2$ (265 mg) at 15-18 ^oC. After 5 min, TEMPO (15 mg) was added in portions and the mixture was vigorously stirred at 16-20 ^oC. After completion of the reaction monitored by TLC, solid $NaHSO_3$ was added to remove the excess $Ca(ClO)_2$. The solution was lyophilized and the solid residue was suspended in DMF (5 mL), and treated with MeI (0.1 mL) for 4h at rt. Water was added and the mixture was extracted with chloroform. The combined extracts were washed with brine, dried over $MgSO_4$ and concentrated. The residue was purified on silica gel flash chromatography (hexane-ethyl acetate = 1:1-1:2) to give **13** (120 mg, 80%) as a yellowish oil. ^1H NMR (300MHz, $CDCl_3$): δ 5.72-5.64 (m, 1H), 4.41-3.70 (m, 8H), 3.72 (s, 3H), 3.28 (d, 0.5H, J=5.1Hz), 3.17 (s, 0.5H), 2.02 (s, 3H), 1.97-1.75 (m, 2H), 1.42-1.19 (s, m, 12H) ppm. IR (film): 3300, 2988, 2118, 1744, 1661, 1539, 1373, 1258, 1072 cm^{-1}. ESI-MS (m/z, %): 431 (M^++1, 45), 453 (M^++Na, 100). HRMS (MALDI) calcd. for $C_{18}H_{30}N_4O_8Na^+$ (M^++Na): 453.1956; Found: 453.1972.

Compound **14**

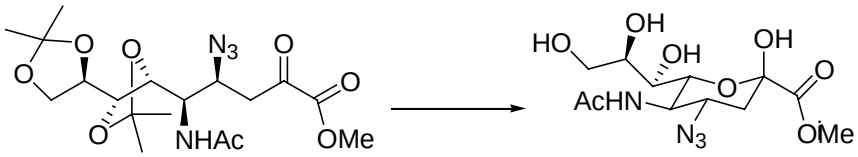


13 **14**

To a solution of **13** (280 mg, 0.65 mmol) in dichloromethane (5 mL) was added Dess-Matin periodinane (336 mg, 0.78 mmol) at 0 ^oC. The reaction mixture was stirred at the rt for 2 h. A solution of $Na_2S_2O_3$ (890 mg) in sat. aqueous $NaHCO_3$ (4 mL) was added to quench the reaction at 0 ^oC. The aqueous phase was extracted with dichloromethane. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated to afford **14** (280 mg), which was unstable and used to the next step immediately without any purification. ^1H NMR (300 MHz, $CDCl_3$): δ 5.66 (d, 1 H, J=8.1Hz), 4.50 (td, 1 H, *J* =7.8, 1.5 Hz), 4.18-3.97 (m, 4 H), 3.93 (s, 3 H), 3.84-3.77 (m, 2H), 3.20 (dd, 1H, J=19.2, 6.9Hz), 3.06 (dd, 1H, J=19.2,

7.5Hz), 2.00 (s, 3 H), 1.45(s, 3 H) 1.41 (s, 3 H), 1.39 (s, 3 H), 1.37 (s, 3 H) ppm.

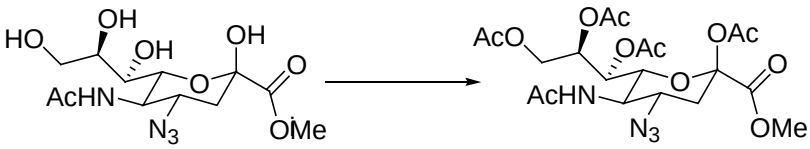
Compound 16



14 **16**

To a solution of **14** (280 mg, 0.65 mmol) in MeCN (20 mL) was added an aqueous solution of HF (40%, 4 mL). The reaction mixture was stirred at 30 ^{o}C for 4 h. An aqueous NaOH (1N) was added to adjust pH to 6. The solution was lyophilized and the solid residue was suspended in MeOH and filtered. The filtrate was dried over MgSO4, concentrated and purified on silica gel flash chromatography ($CHCl_3$: MeOH=4:1) to afford **16** (118 mg, 52% in two steps yield) as a white solid. $[\alpha]_D$ = -43.8 (c 0.69, MeOH). ^{1}H NMR (300 MHz, CD_3OD): δ 4.13-3.92 (m, 3H), 3.81-3.58 (m, 3H), 3.78 (s, 3H), 3.48 (d, 1 H, J=9.0Hz), 2.23 (dd, 1H, J=13.2, 4.5Hz), 2.00 (s, 3H), 1.90 (dd, 1H, J=13.2, 11.7Hz) ppm. IR (film): 3288, 2109, 1744, 1657, 1544, 1374, 1259, 1062 cm^{-1}. ESI-MS (m/z, %): 349 (M^++1, 2), 371 (M^++Na, 100), 387 (M^++K, 5). HRMS (MALDI) calcd. for $C_{12}H_{20}N_4O_8Na^+$ (M^++Na): 371.1173; Found: 371.1194.

Compound 17

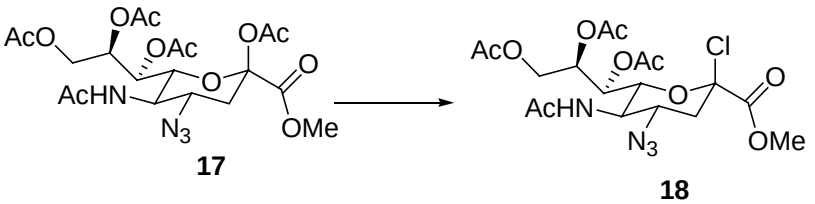


16 **17**

To a solution of **16** (100 mg, 0.30 mmol) in pyridine (1 mL) was added acetic anhydride (0.5 mL) at 0 ^{o}C. The reaction mixture was stirred for 12 h at rt. The solution was evaporated and the residue was purified on silica gel flash chromatography (hexane-ethyl acetate=1:4) to give **17** (100 mg, 65%) as a white solid. $[\alpha]_D$ = -8.8 (c 0.3, $CHCl_3$). ^{1}H NMR (300MHz, $CDCl_3$): δ 5.66 (d, 1H, J=8.1Hz), 5.35 (dd, 1H, J=6.0, 1.8Hz), 5.13 (td, 1H, J=6.0, 2.4Hz), 4.46 (dd, 1H, J=12.3, 2.4Hz), 4.44-4.37 (m, 2H), 4.19 (dd, 1H, J =12.3, 6.0Hz), 3.81 (s, 3H), 3.38 (m, 1H), 2.56 (dd, 1H, J=13.5, 4.5Hz), 2.18 (s, 3H), 2.17 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 2.02 (s,

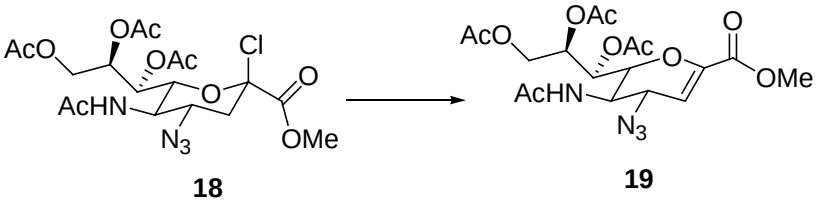
3H), 1.85 (dd, 1H, J=13.5, 12.0Hz) ppm. IR (film): 3274, 2958, 2014, 1750, 1663, 1225 cm^{-1}. ESI-MS (m/z, %): 539 (M^++Na, 100), 555 (M^++K, 11). HRMS (MALDI) calcd. for $C_{20}H_{28}N_4O_{12}Na^+$ (M^++Na): 539.1596; Found: 539.1618.

Compound 18



The solution of **17** (80 mg, 0.16 mmol) in dichloromethane (5 mL) was treated with HCl (g) (prepared from solid NH_4Cl and con. H_2SO_4) at -40 ^oC for 30 min. The reaction mixture was warmed to rt for 14 h, then the solvent was removed under reduced pressure to afford the crude product **18** (58 mg, 74%) as a white solid, which is not stable to store at 4 ^oC for a long time. The crude product was used for the next step without any further purification. ^1H NMR (300MHz, $CDCl_3$): δ 5.61 (d, 1H, J=9.3Hz), 5.47 (dd, 1H, J=7.5, 2.1Hz), 5.19 (ddd, 1H, J=7.5, 5.4, 2.4Hz), 4.51 (dd, 1H, J=10.5, 2.1Hz), 4.41 (dd, 1H, J=12.6, 2.4Hz), 4.25 (td, 1H, J =10.5, 4.5Hz), 4.10 (dd, 1H, J=12.6, 5.4Hz) 3.88 (s, 3H), 3.75 (m, 1H), 2.80 (dd, 1H, J=14.1, 4.5Hz), 2.14 (s, 3H) , 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.05 (dd, 1H, J=14.1, 10.5Hz) ppm. ESI-MS (m/z, %): 493 (M^++1, 66), 495 (M^++1, 22).

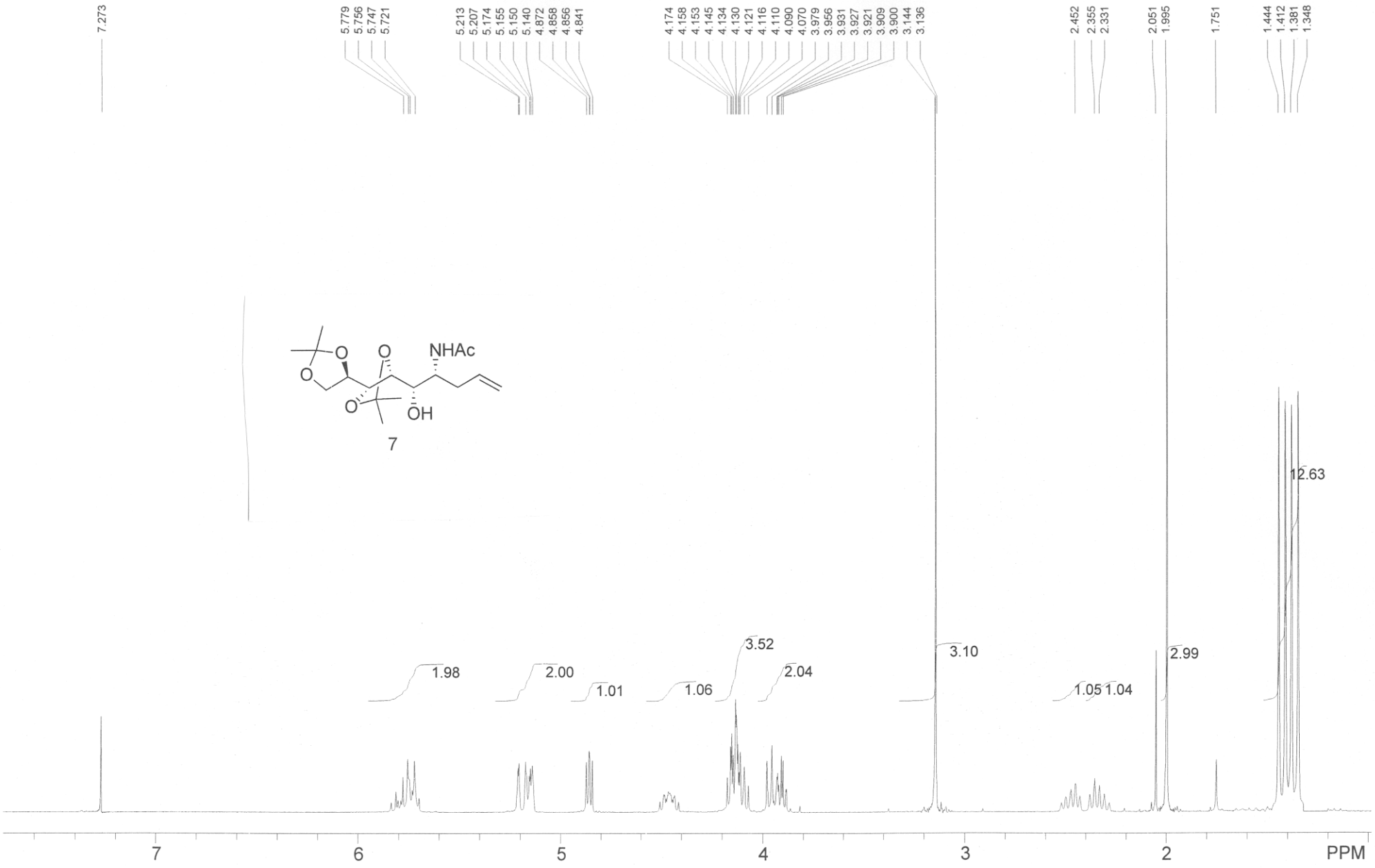
Compound 19



To a solution of **18** (19 mg, 0.039 mmol) in dichloromethane (1.5 mL) was added DBU (0.23 mmol) dropwise at 10 ^oC. The reaction mixture was stirred at the same temperature for 1h. An aqueous solution of NaOH (1N) was added to adjust pH to 6. The solution was extracted with ethyl acetate twice. The combined organic phases were washed with brine, dried over MgSO4, concentrated. Purification on silica gel flash chromatography (hexane-ethyl acetate=1:1) gave **19** (17 mg, 98%) as a white solid. $[\alpha]_D^{19}$ = +48.7 (c 0.71, DMSO); $[\alpha]_D^{22}$ = +108.8 (c 0.85,

$CHCl_3$). ^1H NMR (300 MHz, $(CD_3)_2CO$): δ 7.83 (d, 1H, J=9.3Hz), 5.94 (d, 1H, J=2.4Hz), 5.51 (dd, 1H, J=6.3, 2.1Hz), 5.33 (td, 1H, J=6.6, 3.0Hz), 4.55 (dd, 1H, J=12.3, 3.0Hz), 4.50 (dd, 1H, J=10.5, 2.1Hz), 4.40 (dd, 1H, J =9.6, 2.4Hz), 4.25 (q, 1H), 4.15 (dd, 1H, J=12.3, 6.9Hz), 3.78 (s, 3H), 2.05 (s, 3H) , 2.01 (s, 3H), 2.00 (s, 3H), 1.89 (s, 3H) ppm. ^{13}C NMR (300 MHz, $(CD_3)_2CO$): δ 170.3, 170.2, 169.9, 169.7, 161.5, 145.4, 108.3, 76.7, 70.3, 67.5, 62.0, 59.2, 52.0, 46.9, 22.2, 20.1, 20.0, 19.9 ppm. IR (film): 3277, 2957, 2100, 1747, 1662, 1541, 1372, 1219, 1047 cm^{-1}. ESI-MS (m/z, %): 479 (M^++Na, 100), 495 (M^++K, 12).

2. ^{1}H NMR copies of compounds 7-11, 14, 17-19, and ^{13}C NMR copy of compound 19.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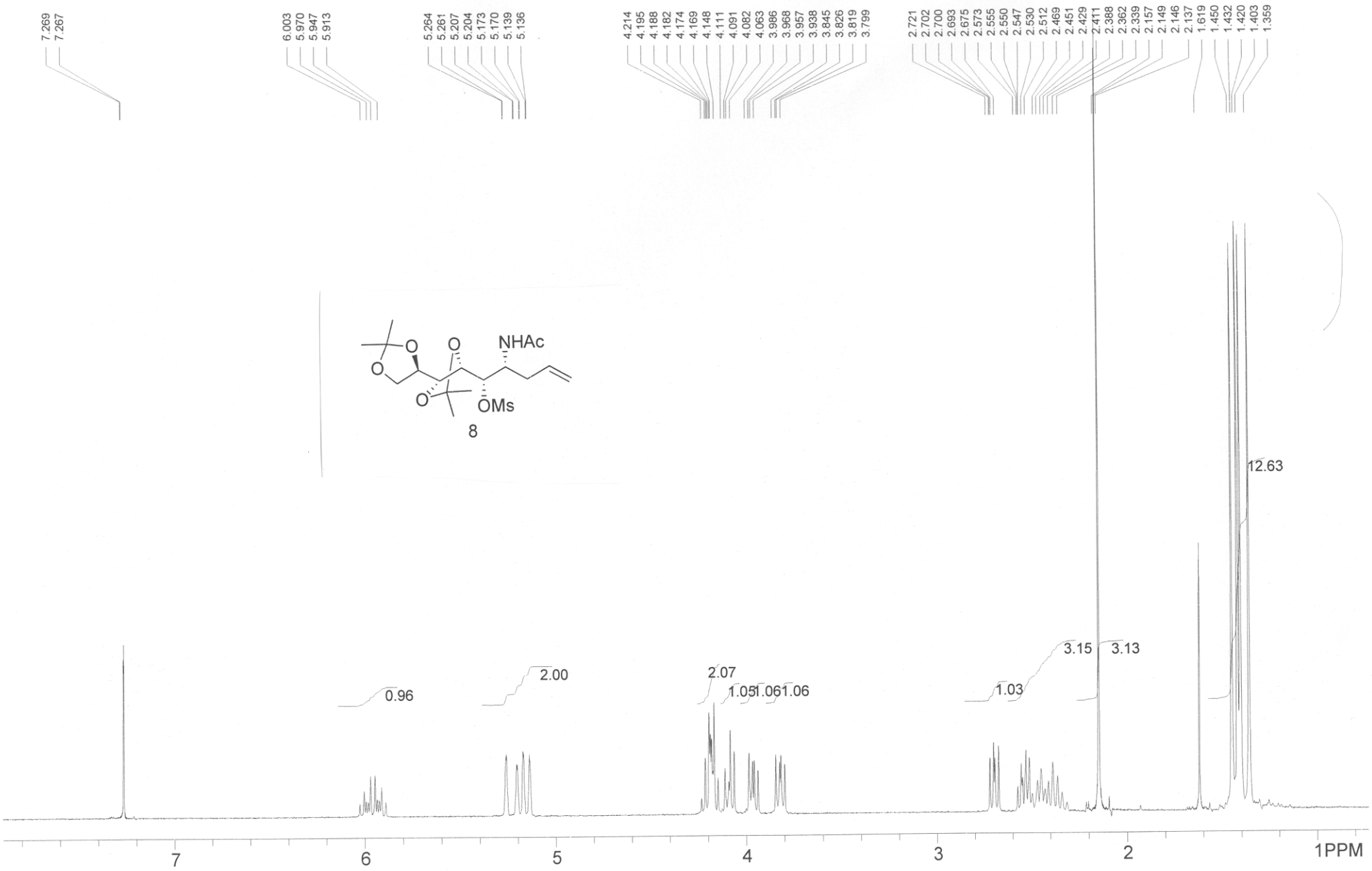
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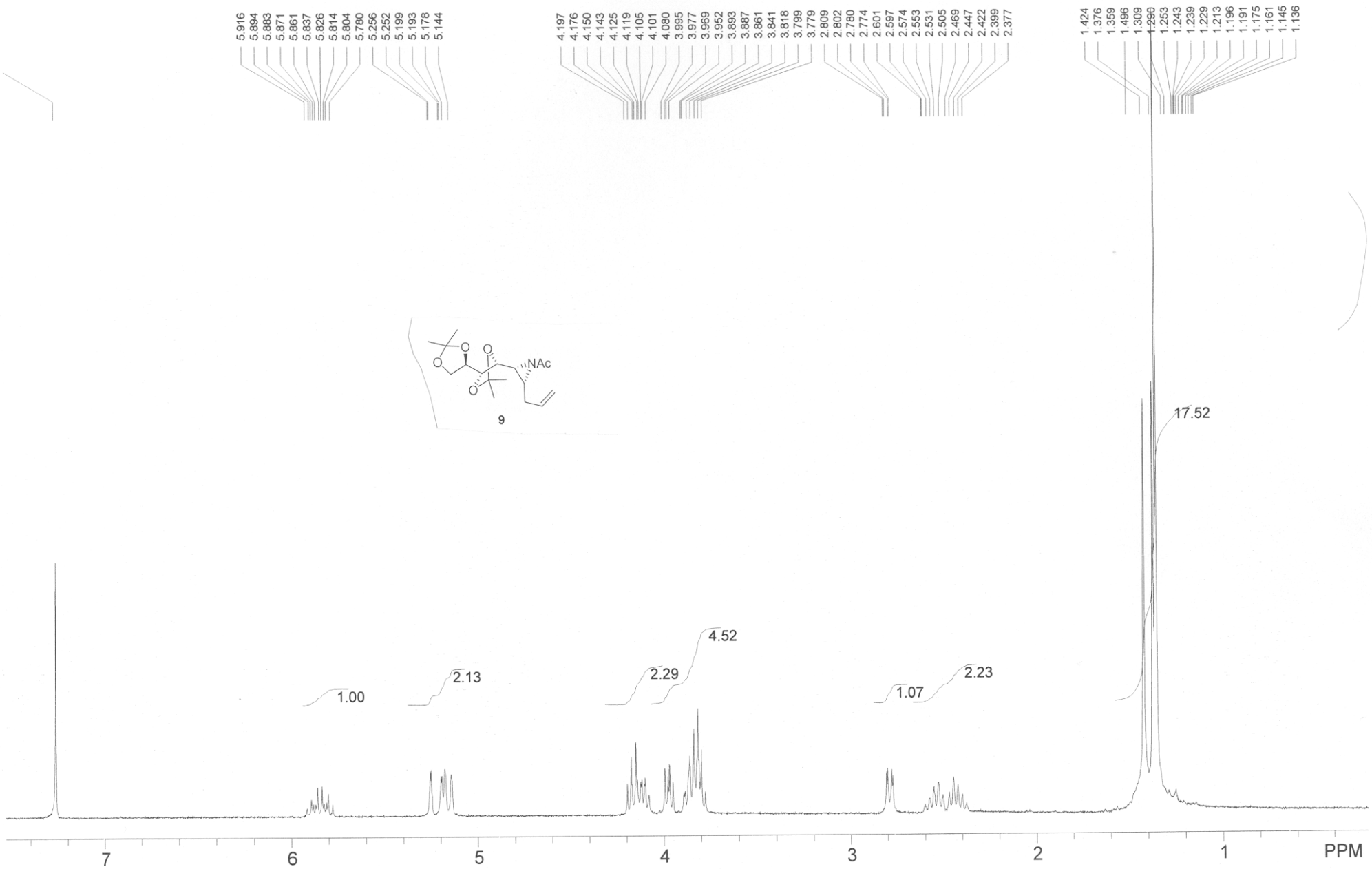
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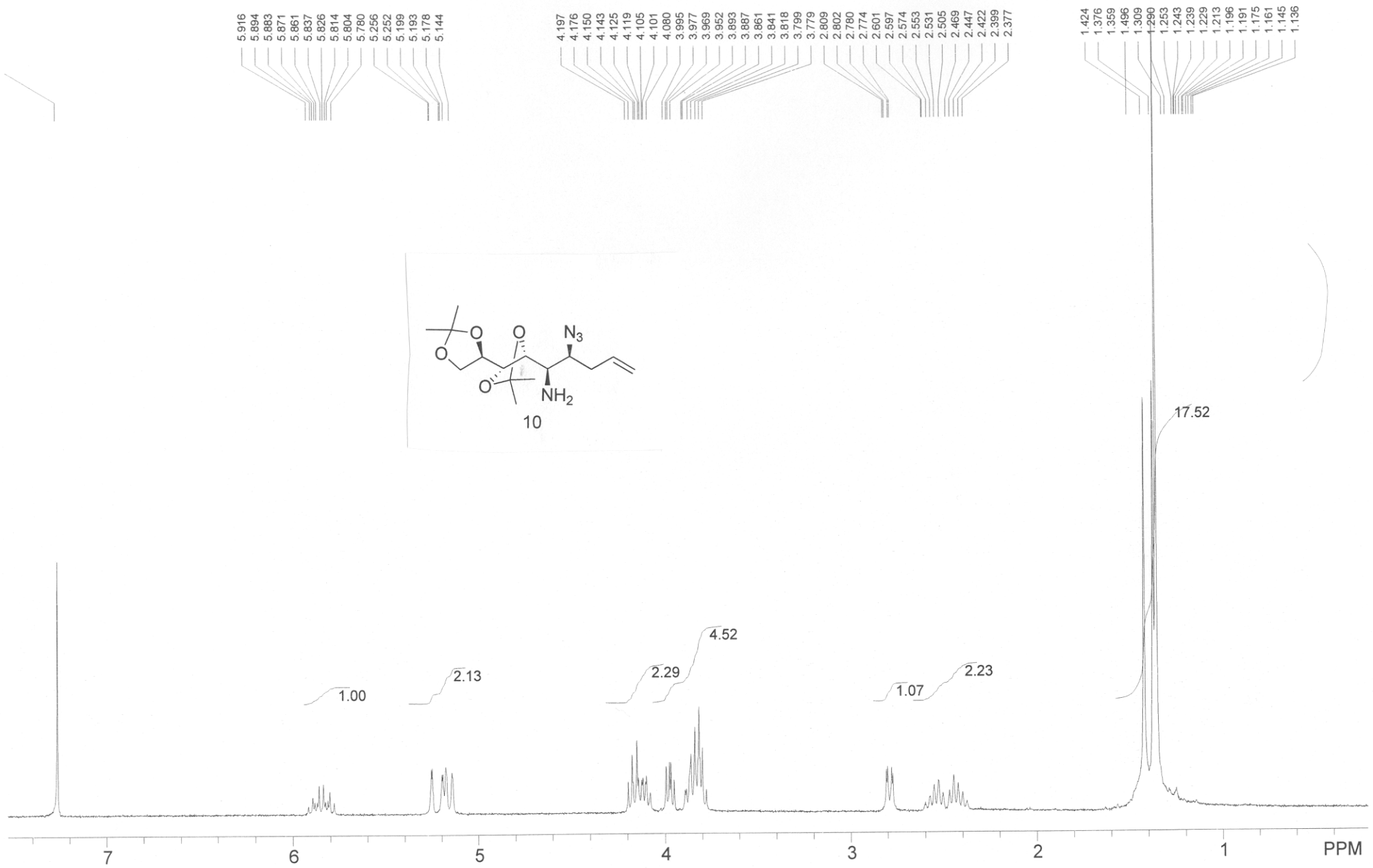
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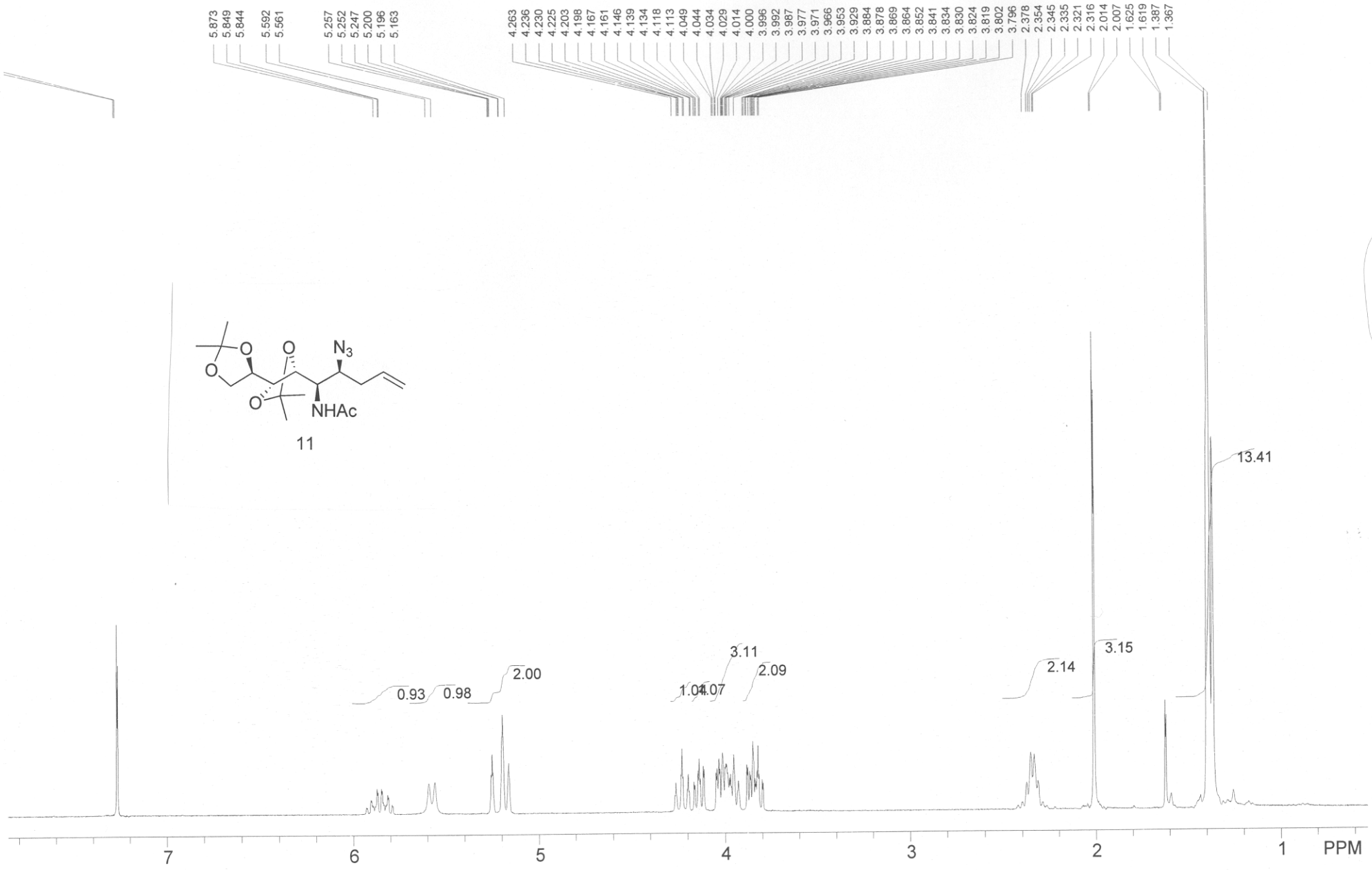
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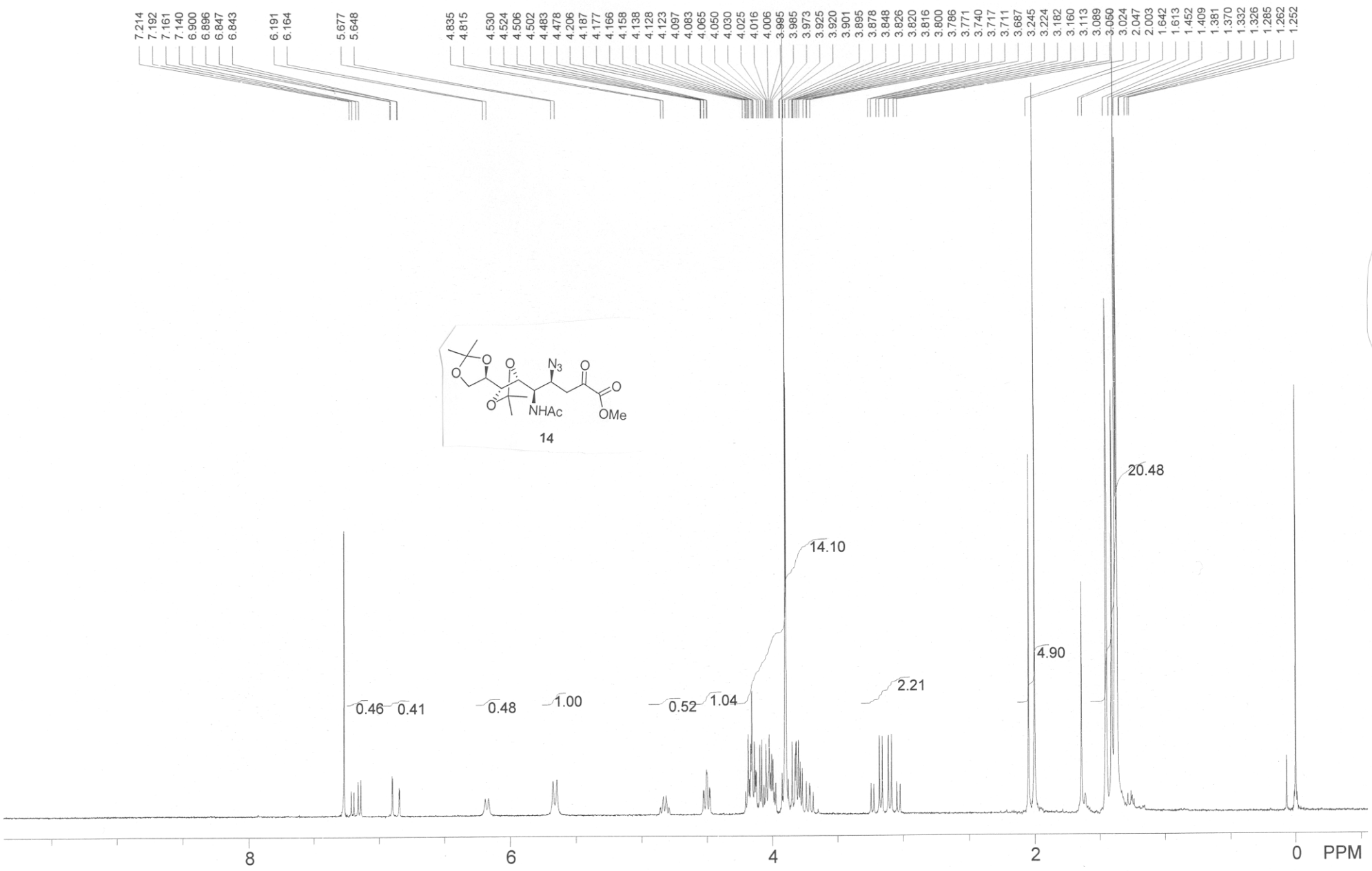
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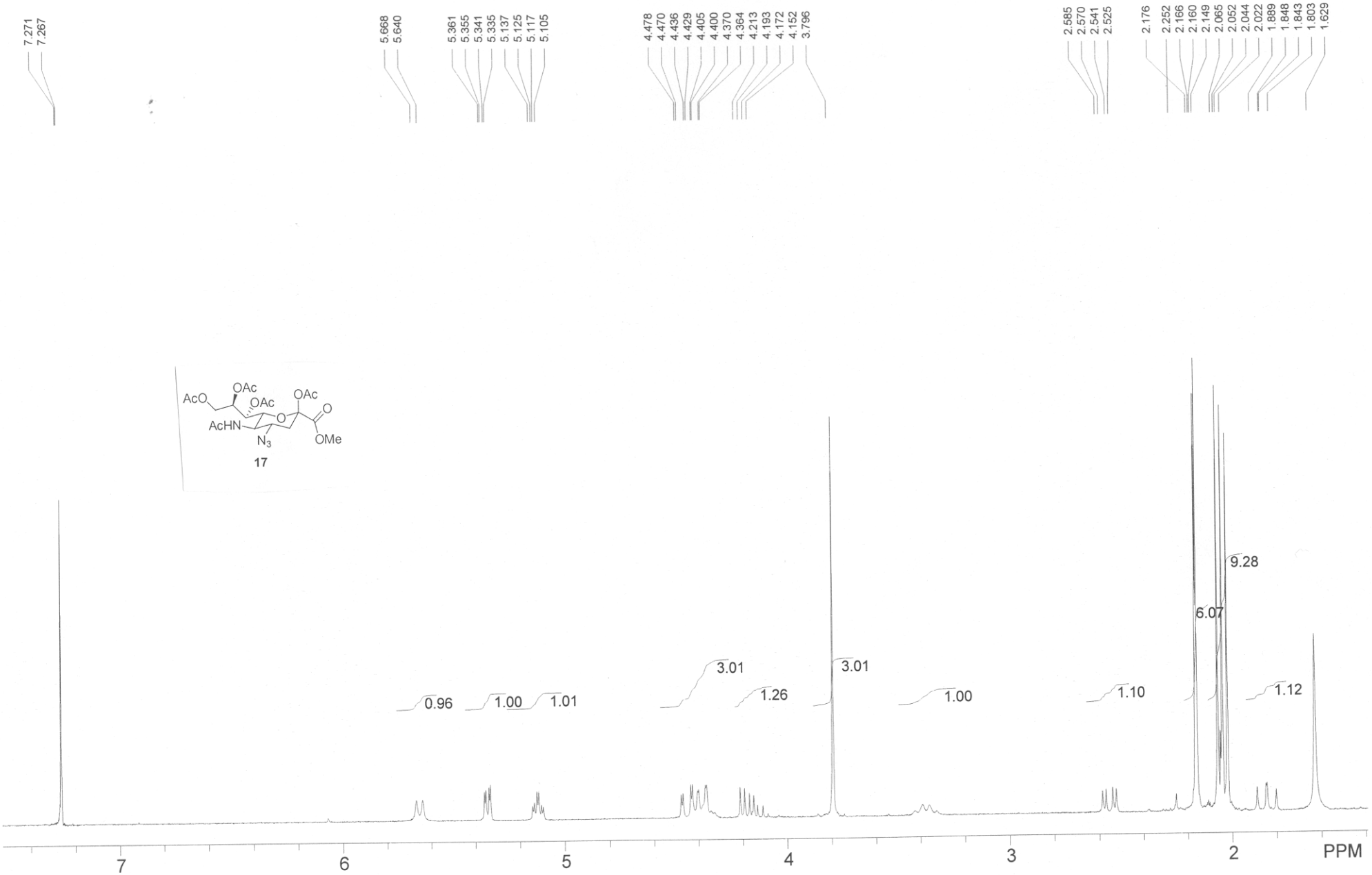
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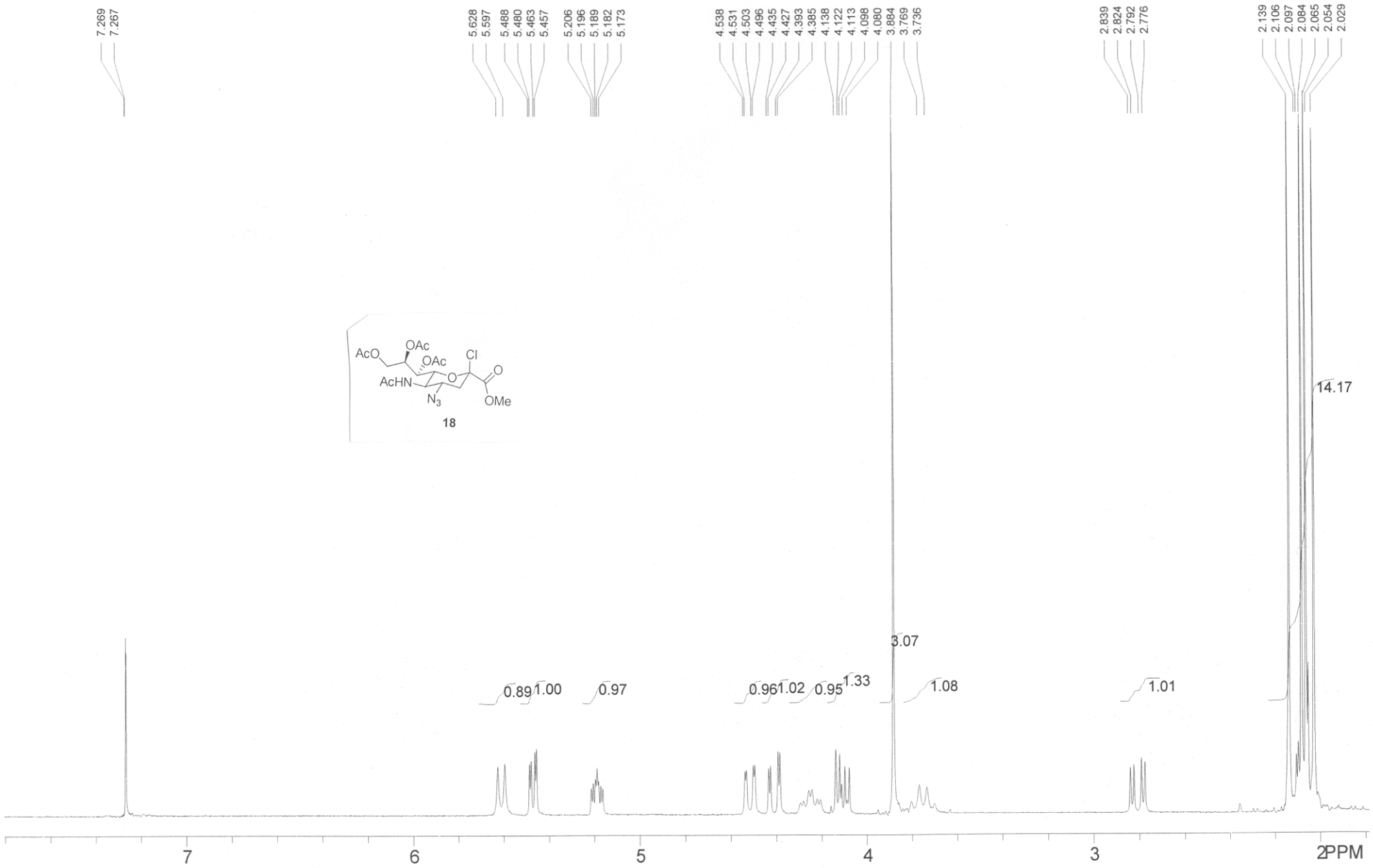
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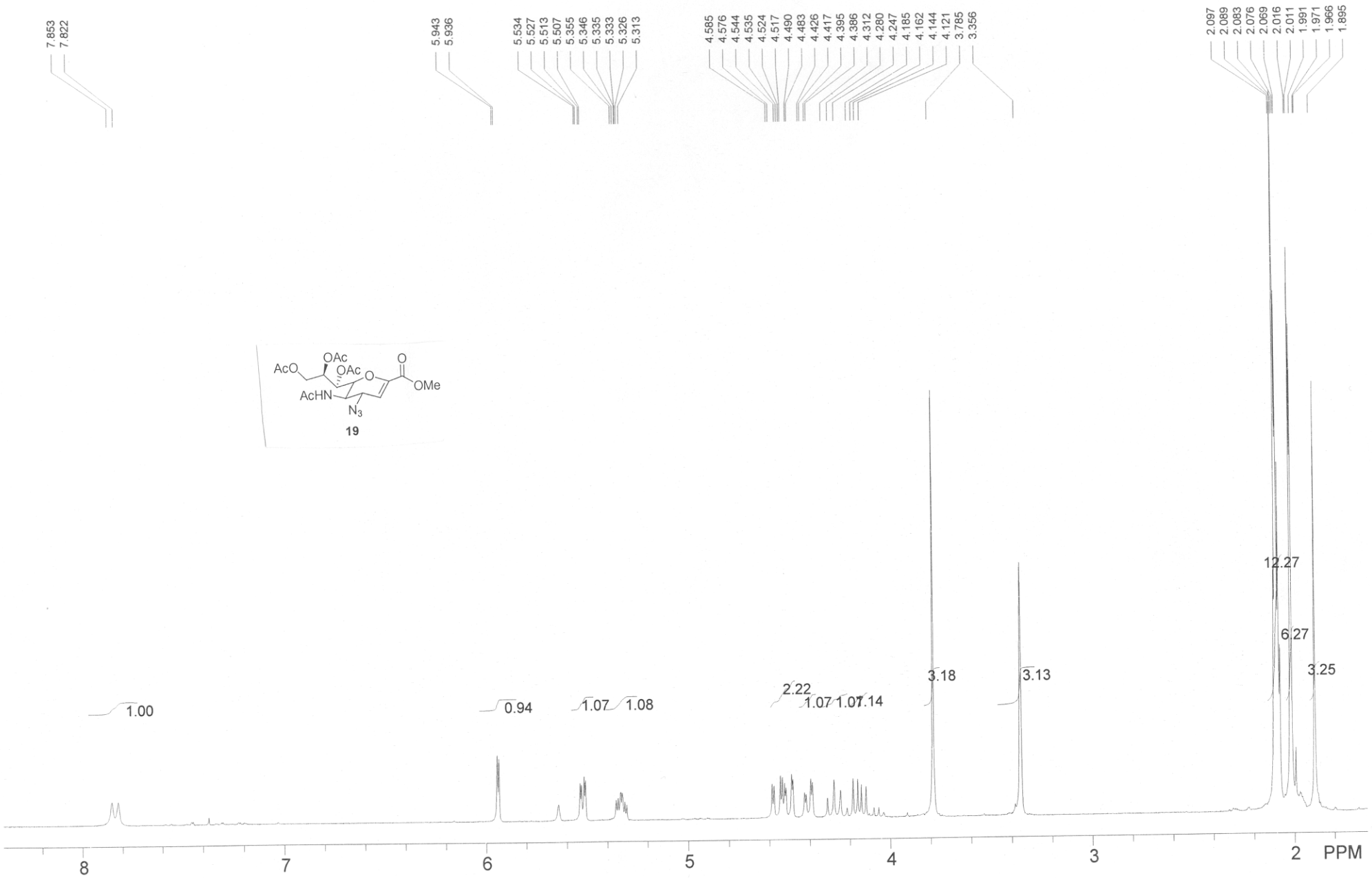
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2.069
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1.07
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PPM

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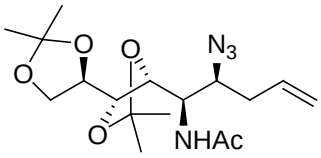
ppm

3. ORTEP drawing of compound 11 derived from X-ray crystallographic analysis



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