Palladium-Catalyzed Stereoselective Formation of α-*O*-Glycosides

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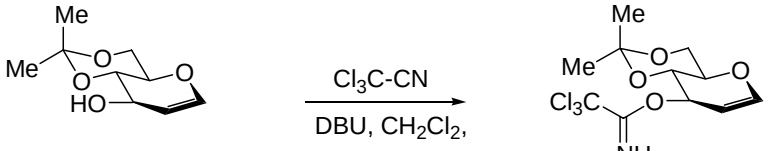
Supporting Information

Methods and Reagents. All reactions were performed in oven-dried Schlenk flasks fitted with glass stoppers under a positive pressure of argon. Organic solutions were concentrated by rotary evaporation below 40 ^{o}C at 25 torr. Analytical thin-layer chromatography (TLC) was routinely used to monitored the progress of all reactions and performed using pre-coated glass plates with 230-400 mesh silica gel impregnated with a fluorescent indicator (250 nm). Visualization was achieved using UV light, iodine, or ceric ammonium molybdenate. Flash chromatography was performed and employed 230-400 mesh silica gel. Dichloromethane and toluene were distilled from calcium hydride under an argon atmosphere at 760 torr. Buchwald's biaryl phosphine ligands, $Pd(CH_3CN)_2Cl_2$ and $Pd(PhCN)_2Cl_2$ were purchased from Strem Chemicals. All other chemicals were obtained from commercial vendors and used without further purification.

Instrumentation. All proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance spectra were recorded on a Bruker 300 (300 MHz and 75 MHz) or Bruker 500 (500 MHz and 125 MHz) NMR spectrometer. Chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to the residual protium in the NMR solvent ($CDCl_3$: δ 7.26 ppm, δ 77.23 ppm; C_6D_6: δ 7.16 ppm, δ 128.39 ppm). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and bs = broad singlet), integration, and coupling constant in hertz (Hz). Infrared (IR) spectra were obtained using a Jasco FT/IR-4100 spectrophotometer, and absorption frequencies are reported in cm^{-1}. High resolution (ESI) mass spectrometry was performed by the mass spectrometry laboratory at Montana State University.

General procedure for the synthesis of glycal imidates:

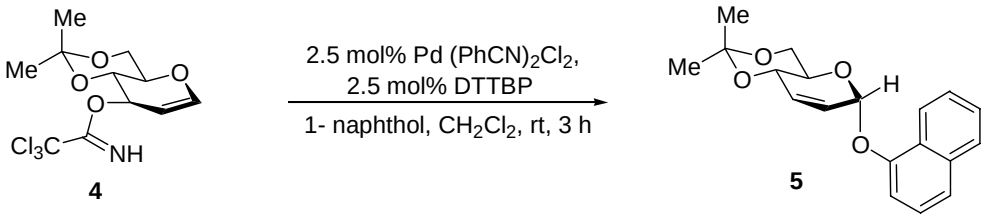


32 **4**

Preparation of glucal imidate 4. A 50 mL oven-dried Schlenk flask was charged with glucal **32** (480 mg, 2.58 mmol, 1 equiv) and CH_2Cl_2 (15 mL). The solution was cooled to 0 ^{o}C, and trichloroacetonitrile (0.78 mL, 7.74 mmol, 3 equiv) and DBU (0.12 mL, 0.77 mmol, 0.3 equiv) were sequentially added to the solution. The resulting mixture was stirred at 0 ^{o}C for 1 h and concentrated. The residue was purified by silica gel flash chromatography (5/1, hexane/ethyl acetate with 1% triethylamine) to give **4** (644 mg, 76%) as a white solid.

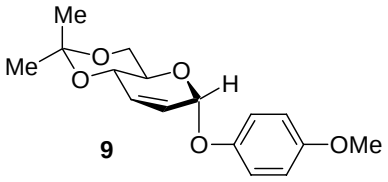
R_f = 0.68 (5/1, Hexane/Ethyl Acetate)
MP: 72 ^oC
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.35 (s, 1H), 6.39 (d, *J* = 6 Hz, 1H), 5.54 (d, *J* = 7.5 Hz, 1H), 4.89 (dd, *J* = 6.0, 2.0 Hz, 1H), 4.18 (dd, *J* = 10.0, 8.0 Hz, 1H), 3.99-3.97 (m, 1H), 3.88-3.83 (m, 1H), 1.51 (s, 3H), 1.40 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MZ): δ = 162.2, 145.9, 99.9, 99.4, 73.9, 70.0, 69.8, 61.7, 28.8, 19.0
IR (film, cm^{-1}): *ν* = 3337, 2995, 2951, 2890, 2870, 1664, 1641, 1333, 1266, 1235, 1109, 1093, 1062, 1015, 992, 796.

General procedure for the synthesis of *O*-aryl-glycosides:



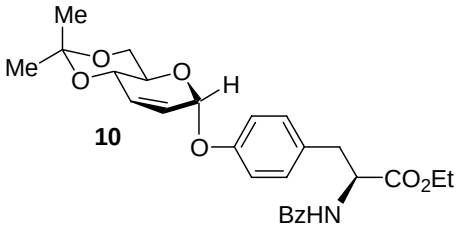
Preparation of *O*-aryl-glycoside 5. A 10 mL oven-dried Schlenk flask was charged with $Pd(PhCN)_2Cl_2$ (1.9 mg, 0.005 mmol, 2.5 mol%), DTTBP (2.1 mg, 0.005 mmol, 2.5% mol), and CH_2Cl_2 (0.5 mL). The resulting solution was stirred at room temperature for 3 h, 1-naphthol (58 mg, 0.4 mmol, 2 equiv), glucal imidate **4** (66 mg, 0.2 mmol, 1 equiv), and CH_2Cl_2 (0.5 mL) were sequentially added to the solution. The resulting mixture was stirred for 3 h, diluted with benzene (1 mL), and purified by silica gel flash chromatography (15/1, hexane/ethyl acetate) to give **5** (84%, α:β = 20:1) as a white solid.

R_f = 0.52 (8/1, Hexane/Ethyl Acetate)
MP: 134.7° C – 134.9° C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.21 (dd, *J* = 6.5, 3.0 Hz, 1H), 7.79 (dd, *J* = 3.5, 3.0 Hz, 1H), 7.51-7.45 (m, 3H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.20 (d, J = 10.0 Hz, 1H), 5.98 (dt, J = 10.0, 2.5 Hz, 1H), 5.85 (s, 1H), 4.29 (dd, J = 9.0, 1.0 Hz, 1H), 3.96-3.91 (m, 1H), 3.87-3.78 (m, 2H), 1.54 (s, 3H), 1.44 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 150.0, 134.6, 132.7, 127.5, 126.4, 126.2, 125.9, 125.8, 125.5, 122.0, 121.8, 108.8, 99.9, 93.7, 67.5, 66.2, 62.9, 29.2, 19.0
IR (film, cm^{-1}): ν = 3051 (w), 2992 (w), 2935 (w), 2878 (w), 1578 (w), 1396 (m), 1375 (m), 1264 (m), 1084 (s), 1081 (s), 935 (w), 858 (m), 792 (w), 771 (m).
HRMS (ESI): calc. for $C_{19}H_{20}O_5Na$ [M+Na] 335.1254; found: 335.1250.



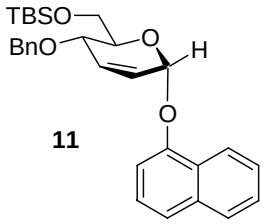
R_f = 0.40 (5/1, Hexane/Ethyl Acetate)
MP: 107.1° C – 108.5° C

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.97 (d, J = 8.5 Hz, 2H), 6.81 (d, J = 9.0 Hz, 2H), 6.10 (d, J = 10.0 Hz, 1H), (dt, J = 10.0, 2.5 Hz, 1H), 5.51 (s, 1H), 4.22 (d, 7.5 Hz, 1H), 3.88 – 3.79 (m, 3H), 3.75 (s, 3H), 1.51 (s, 3H), 1.42 (s, 3H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ = 155.1, 151.2, 132.5, 126.0, 118.5, 114.6, 100.0, 94.4, 67.5, 65.8, 63.0, 55.7, 29.2, 19.0.
IR (film, cm^{-1}): ν = 3054 (w), 2993 (m), 2941 (m), 2918 (m), 2868 (m), 2837 (m), 1508 (s), 1375 (m), 1219 (s), 1093 (m), 1031 (m), 993 (s), 859 (m), 822 (s)
HRMS (ESI): calc. for $C_{16}H_{21}O_5$ [M+] 293.1384; found: 293.1383.



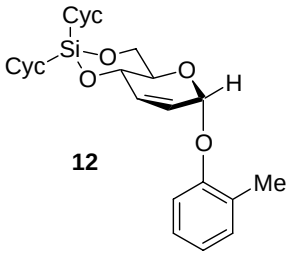
10

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.71 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.58 (d, *J* = 7.0 Hz, 1H), 6.10 (d, *J* = 10.0 Hz, 1H), 5.86-5.79 (m, 1H), 5.60 (s, 1H), 5.00 (dd, *J* = 12.0, 5.5 Hz, 1H), 4.19 (q, *J* = 7.0 Hz, 2H), 3.89- 3.73 (m, 3H), 3.22 (dd, *J* = 14.0, 6.0 Hz, 1H), 3.16 (dd, *J* = 14.0, 5 Hz, 1H), 1.50 (s, 3H), 1.41 (s, 3H), 1.26 (t, *J* = 7.0 Hz, 3H).
^{13}C NMR ($CDCl_3$, 125 MZ): δ = 171.6, 166.8, 156.4, 132.6, 131.7, 130.4, 129.5, 128.6, 126.9, 125.7, 116.8, 99.9, 93.3, 67.4, 65.9, 62.8, 61.6, 53.6, 37.1, 29.1, 18.9, 14.2.
IR (film, cm^{-1}): *ν* = 3330 (w), 2992 (w), 2935 (w), 2867 (w), 1737 (s), 1644 (s), 1509 (vs), 1486 (m), 1375 (s), 1267 (m), 1219 (vs), 1198 (s), 1150 (m), 1090 (s), 1036 (m), 859 (m), 731 (m).
HRMS (ESI): calc. for $C_{27}H_{32}NO_7$ [M+] 482.2173; found: 482.2184.



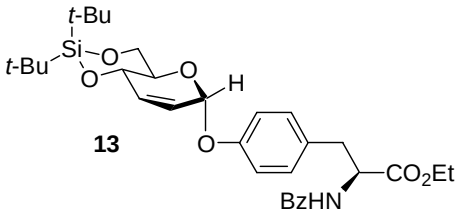
11

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.22 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 8 Hz, 1H), 7.49-7.43 (m, 3H), 7.40-7.7.35 (m, 5H), 7.31-7.24 (m, 2H), 6.26 (d, *J* = 10.0 Hz, 1H), 6.03 (d, *J* = 10.0 Hz, 1H), 5.84 (s, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.64 (d, *J* = 11.5 Hz, 1H), 4.26 (d, *J* = 9.5 Hz, 1H), 4.02 (d, *J* = 7.0 Hz, 1H), 3.89 (dd, *J* = 11.5, 4 Hz, 1H), 3.82 (d, *J* = 11.5 Hz, 1H), 0.86 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 153.3, 138.2, 134.5, 132.1, 128.5, 127.9, 127.8, 127.5, 126.2, 125.9, 125.8, 125.3, 122.1, 121.5, 109.2, 93.4, 71.8, 71.5, 69.9, 62.4, 25.9, 18.4, -5.15, -5.35.
IR (film, cm^{-1}): *ν* = 3049 (w), 2929 (s), 1595 (w), 1579 (m), 1464 (m), 1394 (s), 1260 (s), 1088 (vs), 970 (vs).
HRMS (ESI): calc. for $C_{29}H_{36}O_4SiK$ [M+K] 515.2014; found: 515.1990.



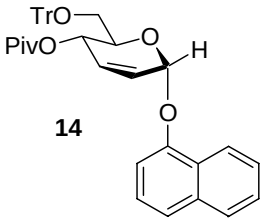
12

R_f = 0.32 (40/1, Hexane/Ethyl Acetate)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.13 (t, J = 8.0 Hz, 2H), 7.07 (d, J = 7.5 Hz, 1H), 6.92 (t, J = 7.0 Hz, 1H), 6.12 (d, J = 10.5 Hz, 1H), 5.83 (dt, J = 10.0, 2.5 Hz, 1H), 5.55 (s, 1H), 4.35 (d, J = 5.0 Hz, 1H), 4.09 – 4.08 (m, 1H), 3.86 – 3.82 (m, 2H), 2.23 (s, 3H), 1.75 – 1.68 (m, 12H), 1.28 – 1.19 (m, 12H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 155.7, 134.6, 130.8, 128.0, 126.9, 124.8, 122.2, 115.4, 93.7, 69.7, 68.5, 66.7, 31.6, 27.8, 27.7, 27.6, 26.9, 26.8, 26.8, 26.7, 26.2, 25.3, 23.8, 22.6, 16.3.
IR (film, cm^{-1}): ν = 2921 (s), 2847 (m), 1493 (m), 1449 (m), 1400 (w), 1234 (m), 1195 (w), 1138 (m), 1127 (m), 1114(m), 1103 (m), 1087 (s), 1021 (m), 994 (m), 891 (m), 862 (s), 749 (m), 717 (m), 668 (vs).
HRMS (ESI): calc. for $C_{25}H_{36}O_4SiNa$ [M+Na] 451.2275; found: 451.2250.



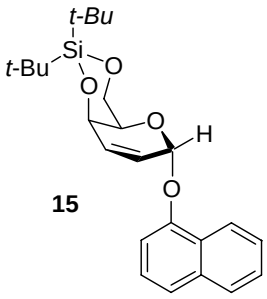
13

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.71 (d, J = 7.5, 2H), 7.48 (t, J = 7.5, 1H), 7.40 (t, J = 7.5, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.96 (d, J = 8.5 Hz, 2H), 6.65 (d, J = 7.5 Hz, 1H), 6.14 (d, J = 10.5 Hz, 1H), 5.76 (m, 1H), 5.54 (s, 1H), 5.0 (q, J = 6.0 Hz, 1H), 4.40 (d, J = 6.5 Hz, 1H), 4.20 (q, J = 7.0 Hz, 2H), 4.09 (q, J = 5.0 Hz, 1H), 3.87 (q, J = 5.5 Hz, 2H), 3.19 (qd, J = 15.5, 5.5 Hz, 2H), 1.27 (t, J = 7.0 Hz, 3H), 1.04 (s, 9H), 0.96 (s, 9H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.7, 166.8, 156.6, 135.3, 133.9, 131.8, 130.5, 129.5, 128.6, 127.0, 124.1, 116.9, 93.3, 70.1, 68.1, 67.0, 61.7, 53.6, 37.1, 27.4, 27.0, 22.7, 20.0, 14.1.
IR (film, cm^{-1}): ν = 3342 (m), 3298 (m), 3183 (w), 3060 (w), 2964 (m), 2934 (s), 2896 (m), 2860 (s), 1732 (s), 1649 (s), 1611 (m), 1580 (m), 1530 (m), 1510 (s), 1486 (m), 1474 (m), 1445 (m), 1397 (m), 1375 (m), 1365 (m), 1350 (m), 1318 (m), 1306 (m), 1272 (m), 1226 (s), 1186 (m), 1132 (vs), 1107 (s), 1090 (s), 1073 (m), 1025 (s), 993 (s), 938 (w), 911 (m), 884 (w), 859 (s), 826 (s), 761 (m), 734 (m), 714 (m), 693 (m), 653 (m).
HRMS (ESI): calc. for $C_{32}H_{43}NO_7SiNa$ [M+Na] 604.2701; found: 604.2709.



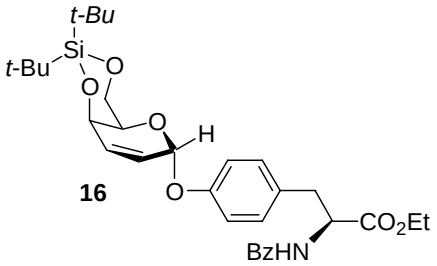
14

R_f = 0.48 (9/1, Hexane/Ethyl Acetate)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.29 (dd, J = 8.3, 1.5 Hz, 1H), 7.84 (dd, J = 8.3, 1.5 Hz, 1H), 7.53 (dd, J = 8.0, 4.0 Hz, 2H), 7.49 (t, J = 7.5 Hz, 1H), 7.41 (d, J = 8 Hz, 2H), 7.37 (d, J = 7 Hz, 6H), 7.22 – 7.17 (m, 9H), 6.15 (dt, J = 10, 2.5 Hz, 1H), 6.04 (d, J = 10 Hz, 1H), 6.00 (s, 1H), 5.41 (d, J = 9 Hz, 1H), 4.33-4.30 (m, 1H), 3.16 (dd, J = 10.0, 6.0 Hz, 1H), 3.11 (dd, J = 10, 1.5 Hz, 1H) 0.99 (s, 9H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 177.5, 153.1, 143.8, 134.6, 131.2, 128.8, 128.7, 128.5, 127.8, 127.7, 127.6, 127.0, 126.9, 126.8, 126.3, 126.1, 125.8, 125.4, 122.1, 121.9, 121.8, 109.6, 93.2, 86.3, 69.8, 65.1, 62.6, 38.6, 27.0, 26.9.
IR (film, cm^{-1}): ν = 3057 (m), 2973 (m), 2931 (m), 2874 (m), 1732 (s), 1596 (m), 1578 (m), 1507 (m), 1490 (m), 1479 (m), 1463 (m), 1448 (m), 1396 (m), 1280 (m), 1263 (m), 1237 (m), 1149 (s), 1085 (m), 1051 (m), 1016 (m), 976 (s), 910 (m), 792 (m), 772 (m), 733 (m), 706 (m), 667 (m).
HRMS (ESI): calc. for $C_{40}H_{38}O_5Na$ [M+Na] 621.2611; found: 621.2609.



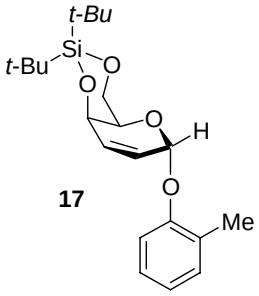
15

MP: 141 ° C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 8.16 (d, J = 8 Hz, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.50 – 7.38 (m, 4H), 7.32 (d, J = 7.5 Hz, 1H), 6.31 (dd, J = 9.5, 5.5 Hz, 1H), 6.14 (dd, J = 10.0, 3.0 Hz, 1H), 5.92 (d, J = 3 Hz, 1H), 4.42 (dd, J = 5.0, 2.5 Hz, 1H), 4.33 (d, J = 12.5 Hz, 1H), 4.14 (d, J = 12.5 Hz, 1H), 4.08 (d, J = 1.5 Hz, 1H), 1.05 (s, 9H), 1.03 (s, 9H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 153.1, 134.5, 130.3, 127.6, 126.2, 126.1, 126.0, 125.3, 121.9, 121.6, 109.2, 93.7, 68.1, 66.3, 64.7, 27.5, 27.1, 23.1, 20.6.
IR (film, cm^{-1}): ν = 3052 (w), 2963 (m), 2932 (s), 2886 (m), 2858 (s), 1598 (w), 1578 (m), 1507 (w), 1464 (m), 1398 (s), 1362 (w), 1264 (m), 1238 (m), 1195 (m), 1140 (s), 1124 (m), 1075 (s), 1049 (s), 1016 (m), 966 (s), 906 (s), 888 (s), 826 (m), 795 (s), 771 (s), 743 (s), 706 (m).
HRMS (ESI): calc. for $C_{24}H_{32}O_4SiNa$ [M+Na] 435.1962; found: 435.1951.



16

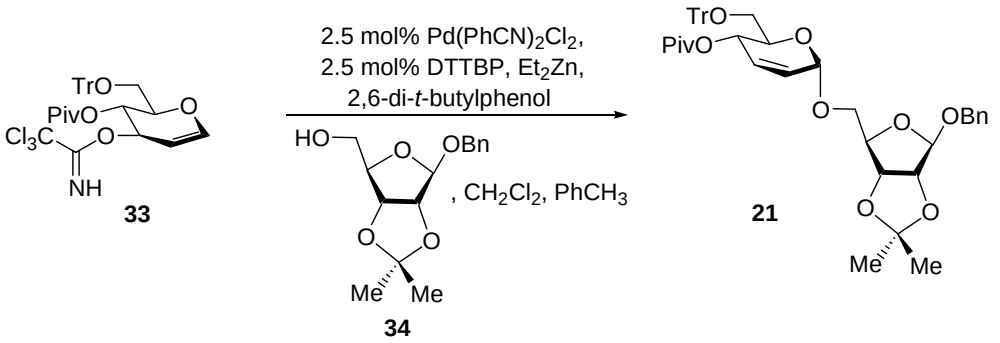
MP: 47 ° C
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.72 (d, J = 11.5 Hz, 2H), 7.50 – 7.39 (m, 3H), 7.056 – 6.991 (m, 4H), 6.59 (d, J = 12.0 Hz, 1H), 6.22 (q, J = 8.5 Hz, 1H), 5.98 (dd, J = 16.5, 5.5 Hz, 1H), 5.69 (d, J = 4.5 Hz, 1H), 5.02 (q, J = 12.0 Hz, 1H), 4.37 – 4.31 (m, 2H), 4.21 (q, J = 12.0 Hz, 2H), 4.11 (d, J = 21.0 Hz, 1H), 3.97 (s, 1H), 3.20 (hept., J = 8.5 Hz, 2H), 1.28 (t, J = 12.0 Hz, 3 H), 1.03 (s, 9H), 0.99 (s, 9H).
^{13}C-NMR ($CDCl_3$, 75 MHz): δ = 171.7, 156.6, 131.8, 130.5, 130.3, 129.4, 128.7, 127.1, 126.0, 116.9, 93.4, 67.9, 66.2, 64.7, 61.7, 53.7, 37.2, 27.5, 27.1, 23.1, 20.6, 14.2.
IR (film, cm^{-1}): ν = 3344 (m), 3282 (m), 3183 (m), 2963 (m), 2933 (s), 2893 (m), 2858 (s), 1726 (s), 1650 (s), 1602 (m), 1509 (s), 1474 (m), 1374 (m), 1227 (s), 1142 (s), 1076 (s), 980 (s), 905 (m), 887 (m), 826 (s), 792 (m), 714 (m).
HRMS (ESI): calc. for $C_{32}H_{43}NO_7Si$ [M+] 582.2882; found: 582.2854.



17

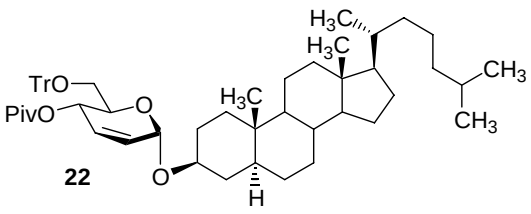
MP: 58 ° C
^{1}H-NMR ($CDCl_3$, 300 MHz): δ = 7.22 (s, 1H), 7.17-7.11 (m, 2H), 6.91 (t, J = 12.0 Hz, 1H), 6.23 (dd, 16.5, 9.0 Hz, 1H), 6.01 (dd, 16.5, 5.0 Hz, 1H), 5.68 (d, 4.5 Hz, 1H), 4.38- 4.32 (m, 2H), 4.15 (d, J = 21.0 Hz, 1H), 4.02 (d, J = 3.0 Hz, 1H), 2.18 (s, 3H), 1.04 (s, 9H), 1.0 (s, 9H).
^{13}C-NMR ($CDCl_3$, 300 MHz): δ = 130.7, 130.0, 127.0, 126.4, 122.0, 115.5, 93.9, 67.9, 66.3, 64.8, 27.5, 27.1, 23.2, 20.7, 16.3.
IR (film, cm^{-1}): ν = 3050 (w), 2933 (s), 2890 (m), 2858 (s), 1591 (m), 1493 (s), 1473 (m), 1400 (m), 1363 (m), 1339 (w), 1301 (w), 1236 (s), 1188 (m), 1144 (vs), 1123 (m), 1096 (m), 1077 (s), 1049 (w), 986 (vs), 905 (m), 887 (m), 858 (w), 826 (m), 796 (m), 782 (w), 750 (s), 711 (m).
HRMS (ESI): calc. for $C_{21}H_{32}O_4SiNa$ [M+Na] 399.1962; found: 399.2002.

General procedure for the synthesis of *O*-glycosides:



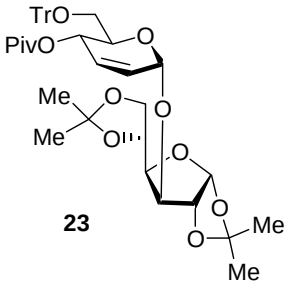
Preparation of *O*-glycoside 21. A 10 mL oven-dried Schlenk flask was charged with $Pd(PhCN)_2Cl_2$ (1.9 mg, 0.005 mmol, 2.5 mol%), DTTBP (2.1 mg, 0.005 mmol, 2.5% mol), and CH_2Cl_2 (0.5 mL). A second 10 mL oven-dried Schlenk flask was charged with alcohol acceptor **34** (120 mg, 0.27 mmol, 1.5 equiv, azeotroped three times with toluene), CH_2Cl_2 (0.5 mL), and toluene (0.5 mL), and Et_2Zn (1M in hexane, 135 μL, 0.135 mmol, 0.75 equiv) was then added to the solution. After the $Pd(PhCN)_2Cl_2$ and DTTBP complex solution had been stirring at room temperature for 3 h, it was added to the zinc alkoxide solution followed by glucal imidate **33** (111 mg, 0.18 mmol, 1 equiv) and 2,6-di-*t*-butylphenol (18.5 mg, 0.09 mmol, 0.5 equiv). The resulting mixture was stirred for 10 h and purified by silica gel flash chromatography (9/1, hexane/ethyl acetate) to give **21** (118.8 mg, 88%) as a white solid.

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.45 (d, J= 8.0 Hz, 6H), 7.28 – 7.25 (m, 9H), 7.21 – 7.17 (m, 5H), 5.79 (s, 2H), 5.21 (d, J = 9.5 Hz, 1H), 5.16 (s, 1H), 5.09 (s, 1H), 4.75 (q, 46.0, 6.0 Hz, 2H), 4.61 (d, 12.0 Hz, 1H), 4.51 (q, J = 4.5 Hz, 1H), 4.40 (d, J= 12.0 Hz, 1H), 4.15 – 4.10 (m, 2H), 3.63 (t, J = 10.0 Hz, 1H), 3.12 – 3.10 (m, 2H), 1.43 (s, 3H), 1.30 (s, 3H), 0.95 (s, 9H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 177.5, 143.9, 137.1, 129.9, 128.7, 128.4, 128.0, 127.8, 127.4, 126.9, 112.4, 107.3, 96.5, 94.7, 86.4, 85.5, 85.4, 85.4, 85.3, 82.5, 82.2, 74.9, 69.1, 69.0, 68.8, 68.4, 65.3, 64.7, 62.9, 38.6, 26.9, 26.8, 26.4, 25.0.
IR (film, cm^{-1}): ν = 3061 (w), 3031 (w), 2976 (m), 2935 (m), 2901 (w), 2874 (w), 1732 (s), 1490 (w), 1450 (m), 1372 (w), 1278 (m), 1210 (m), 1152 (s), 1077 (s), 1040 (s), 1016 (s), 913 (s), 870 (m), 744 (s), 699 (s), 668 (m), 633 (m).
HRMS (ESI): calc. for $C_{45}H_{50}O_9Na$ [M+Na] 757.3347; found: 757.3359.



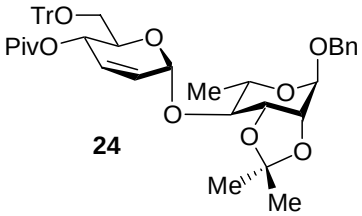
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.46 (d, J =7.0 Hz, 6H), 7.27 – 7.24 (m, 6H), 7.20 (t, J = 7.0 Hz, 3H), 5.79-5.78 (m, 1H), 5.27 (d, J = 10.0 Hz, 1H), 5.14 (d, J = 10.0 Hz, 1H), 4.20 – 4.17 (m, 1H), 4.19 (hex, J = 5.0 Hz, 1H), 3.22 – 3.08 (m, 2H), 1.95 (d, J = 12.5 Hz, 1H), 1.80 – 0.96 (m, 24H), 0.94 (s, 9H), 0.88 (d, J = 7.0 Hz, 3H), 0.84 (dd, J = 7.0, 2.5 Hz, 6H), 0.63 (s, 3H), 0.51 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ = 144.0, 129.5, 128.7, 128.4, 127.7, 126.9, 91.9, 68.5, 65.5, 63.4, 56.5, 56.3, 54.3, 45.1, 40.0, 39.5, 36.9, 36.3, 36.2, 35.8, 35.5, 32.1, 28.7, 28.3, 28.0, 27.7, 26.9, 26.8, 24.2, 23.8, 22.8, 22.5, 21.2, 18.7, 12.3, 12.1.
IR (film, cm^{-1}): ν = 3059 (w), 2932 (vs), 2868 (s), 1733 (s), 1499 (m), 1448 (m), 1382 (m), 1280 (m), 1150 (s), 1035 (m), 1075 (m), 1035 (vs), 909 (m), 764 (m), 734 (s), 705 (s).
HRMS (ESI): calc. for $C_{57}H_{78}O_5Na$ [M+Na] 865.5741; found: 865.5746.



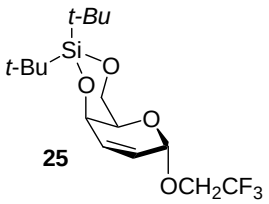
23

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.45 (d, J = 7.5 Hz, 6H), 7.27 (t, J = 7.5 Hz, 6H), 7.20 (t, J = 7.5 Hz, 3H), 5.92 (d, J = 3.5 Hz, 1H), 5.80 (s, 2H), 5.14 (d, J = 10 Hz, 1H), 4.85 (d, J = 3.0 Hz, 1H), 4.42 (d, J = 2.5 Hz, 1H), 4.23 – 4.20 (m, 1H), 4.15 – 4.10 (m, 3H), 4.00 – 3.97 (m, 1H), 3.15 (m, 2H), 1.48 (s, 3H), 1.43 (s, 3H), 1.34 (s, 3H), 1.02 (s, 3H), 0.95 (s, 9H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 177.5, 143.7, 129.9, 128.8, 127.8, 127.0, 126.9, 105.4, 95.9, 84.3, 82.0, 81.4, 72.6, 69.2, 67.8, 65.3, 63.4, 27.7, 27.0, 26.8, 26.2, 25.4.
IR (film, cm^{-1}): ν = 3060 (w), 3023 (w), 2984 (m), 2981 (m), 2963 (m), 2931 (m), 1734 (s), 1490 (w), 1449 (m), 1372 (m), 1280 (m), 1252 (w), 1217 (m), 1150 (s), 1073 (s), 1035 (s), 983 (s), 850 (m), 765 (m), 745 (m), 706 (s)
HRMS (ESI): calc. for $C_{42}H_{50}O_{10}Na$ [M+Na] 737.3296; found: 737.3283.



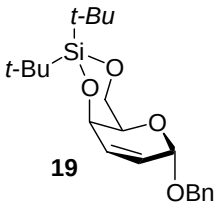
24

R_f = 0.4 (9/1, Hexanes/Ethyl acetate)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.5-7.12 (m, 20H), 5.86 (dd, *J* = 10, 9.5 Hz, 1H), 5.80 (bd, *J* = 10 Hz, 1H), 5.57 (d, *J* = 9.5 Hz, 1H), 5.28 (bs, 1H), 5.01 (s, 1H), 4.68 (d, *J* = 11.5 Hz, 1H), 4.50 (d, *J* = 11.5 Hz, 1H), 4.34 (apparent t, *J* = 6.3 Hz, 1H), 4.16 (dd, *J* = 8.5, 4.3 Hz, 1H), 4.06 (d, *J* = 5.5 Hz, 1H), 3.82-3.71 (m, 1H), 3.46 (dd, *J* = 10, 7.5 Hz, 1H), 3.29 (bd, *J* = 10 Hz, 1H), 3.17 (bdd, *J* = 10, 4.5 Hz, 1H), 1.29 (d, *J* = 6 Hz, 3H), 1.22 (s, 3H), 0.97 (s, 9H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ = 177.5, 143.9, 137.1, 129.9, 128.9, 128.7, 128.5, 128.2, 127.9, 127.8, 127.3, 126.8, 109.0, 96.3, 95.0, 86.3, 81.4, 77.3, 75.8, 69.1, 68.5, 65.0, 64.9, 62.6, 38.6, 28.2, 26.9, 26.4, 17.7.
IR (film, cm^{-1}): ν = 3058 (w), 3033 (w), 2979 (m), 2933 (m), 2872 (w), 1731 (vs), 1489 (m), 1449 (m), 1381 (m), 1281 (m), 1220 (m), 1150 (s), 1050 (s), 1024 (s).
HRMS (ESI): calc. for $C_{46}H_{52}NaO_9$ [M+ Na] 771.3509; found : 771.3514.



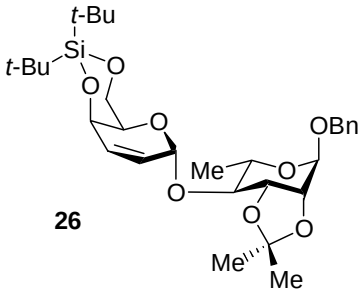
25

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.15 (dd, J = 9.8, 5.4 Hz, 1H), 5.88 (dd, J = 10.0, 3.0 Hz, 1H), 5.11 (d, J = 3.0 Hz, 1H), 4.37 (dd, J = 12.6, 1.5 Hz, 1H), 4.30 (dd, J = 5.4, 2.7 Hz, 1H), 4.16 (dd, J = 12.6, 1.5 Hz, 1H), 4.08 – 3.92 (m, 2H), 3.86 (d, J = 2.1 Hz, 1H), 1.03 (s, 9H), 0.96 (s, 9H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ = 130.4, 125.5, 95.1, 67.6, 66.1, 64.9, 64.6, 64.4, 27.5, 27.1, 23.2, 20.6.
IR (film, cm^{-1}): ν = 2935 (s), 2891 (m), 2856 (s), 1475 (m), 1428 (w), 1400 (w), 1384 (w), 1363 (w), 1342 (w), 1284 (s), 1200 (m), 1162 (s), 1147 (vs), 1127 (s), 1063 (vs), 1001 (s), 981 (s), 936 (m), 899 (m), 882 (m), 848 (w), 827 (s), 794 (s), 772 (w), 752 (w), 718 (w), 681 (m).
HRMS (ESI): calc. for $C_{16}H_{27}O_4F_3Si$ [M+Na] 391.1523; found: 391.2843.



19

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.33 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 6.09 (dd, J = 10.0, 5.0 Hz, 1H), 5.88 (dd, J = 10.0, 3.5 Hz, 1H), 5.13 (d, J = 3.0 Hz, 1H), 4.68 (q, 12.0 Hz, 2H), 4.33 (dd, 12.5, 2.0 Hz, 1H), 4.27 (dd, 5.0, 2.5 Hz, 1H), 4.11 (dd, J = 12.5, 1.5 Hz, 1H), 3.89 – 3.88 (m, 1H), 1.03 (s, 9H), 0.97 (s, 9H).
^{13}C NMR ($CDCl_3$, 500 MHz): δ = 138.1, 129.5, 128.4, 127.9, 127.6, 126.9, 94.0, 69.8, 67.2, 66.3, 64.9, 30.3, 27.5, 27.1, 23.1, 20.5.
IR (film, cm^{-1}): ν = 2935 (s), 2886 (m), 2858 (s), 1470 (m), 1363 (m), 1195 (m), 1142 (vs), 1121 (m), 1079 (m), 1040 (s), 1025 (s), 987 (m), 825 (m), 795 (s), 745 (m), 696 (m).
HRMS (ESI): calc. for $C_{21}H_{32}O_4SiNa$ [M+Na] 399.1962; found: 399.1946.



26

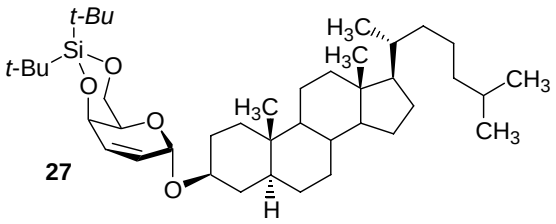
R_f = 0.36 (9/1, Hexane/Ethyl acetate)
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.35-7.25 (m, 5H), 6.10 (dd, *J* = 10.0, 5.5 Hz, 1H), 5.86 (dd, *J* = 10.0, 3.5 Hz, 1H), 5.09 (d, *J* = 3.5 Hz, 1H), 5.03 (s, 1H), 4.67 (d, *J* = 11.5 Hz, 1H), 4.48 (d, *J* =

11.5 Hz, 1H), 4.35 (bd, *J* = 10.5 Hz, 1H), 4.27 (s, 1H), 4.26 (bd, *J* = 10.5 Hz, 1H), 4.12 (d, *J* = 5.5 Hz, 1H), 4.05 (dd, *J* = 7.5, 2 Hz, 1H), 4.02 (bd, *J* = 2 Hz, 1H), 3.71 (dq, *J* = 10, 6 Hz, 1H), 3.51 (dd, *J* = 10, 7.5 Hz, 1H), 1.57 (s, 3H), 1.3 (s, 3H), 1.26 (d, *J* = 6 Hz, 3H), 1.03 (s, 9H), 0.96 (s, 9H).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 137.2, 129.9, 128.4, 128.1, 127.9, 126.3, 109.1, 96.2, 94.9, 79.3, 77.4, 76.1, 69.1, 66.8, 66.3, 65.4, 64.9, 60.3, 28.2, 27.4, 27.1, 26.5, 23.0, 20.6, 17.4, 14.2.

IR (film, cm^{-1}): ν = 2968 (m), 2934 (m), 2896 (m), 2859 (m), 1473 (m), 1383 (m), 1220 (m), 1142 (s), 1080 (m), 1049 (s), 1026 (m), 999 (m).

HRMS (ESI): calc. for $C_{30}H_{46}NaO_8Si$ (M^+ Na) 585.2860; found: 582.2851.



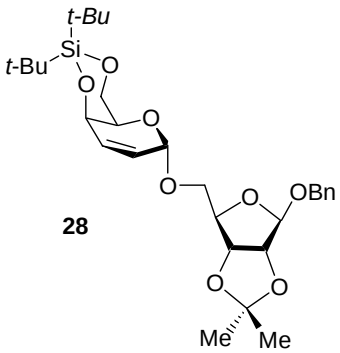
27

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 6.06 (dd, J = 10.0, 5.5 Hz, 1H), 5.83 (dd, 10.0, 3.0 Hz, 1H), 5.15, (d, 4.0 Hz, 1H), 4.36 (dd, J = 12.3, 1.5 Hz, 1H), 4.25 (q, J = 3.0 Hz, 1H), 4.13 (dd, J = 12.3, 1.5 Hz, 1H), 3.91 (d, 2.0Hz, 1H), 3.64 (hept., J = 5.0 Hz, 1H), 1.93 (dt, J = 13.0, 3.5 Hz, 1H), 1.82 – 1.75 (m, 2H), 1.69 (dt, J = 10.0, 3.0 Hz, 1H), 1.62 (dq, J = 9.5, 3.5 Hz, 1H), 1.56 – 1.05 (m, 22H), 1.04 – 1.00 (m, 1H), 1.03 (s, 9H), 0.99 – 0.94 (m, 2H), 0.96 (s, 9H), 0.87 (d, J = 6.5 Hz, 3H), 0.84 (dd, J = 6.5, 2.0 Hz, 6H), 0.76 (s, 3H), 0.62 (s, 3H).

^{13}C NMR ($CDCl_3$, 500 MHz): δ = 129.2, 127.5, 93.0, 76.9, 66.9, 66.4, 65.1, 56.5, 56.3, 54.4, 45.0, 42.6, 40.0, 39.5, 37.0, 36.4, 36.2, 35.8, 35.5, 32.1, 28.8, 28.2, 28.0, 27.5, 27.1, 24.2, 23.8, 23.1, 22.8, 22.5, 21.2, 18.7, 12.2, 12.1.

IR (film, cm^{-1}): ν = 2932 (vs), 2858 (s), 1172 (m), 1384 (m), 1143 (s), 1033 (s), 987 (m), 903 (m), 886 (m), 826 (m), 797 (m).

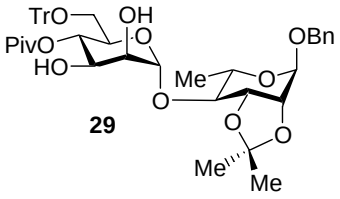
HRMS: calc. for $C_{41}H_{72}O_4SiNa$ $[M+Na]^+$ 679.5092; found: 679.5094.



28

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.34 – 7.26 (m, 5H), 6.06 (dd, J = 10.0, 5.5 Hz, 1H), 5.83 (dd, J = 10.0, 5.5 Hz, 1H), 5.13 (s, 1H), 5.03 (d, J = 3.0 Hz, 1H), 4.72 – 4.65 (m, 3H), 4.44 – 4.38 (m, 2H), 4.27 (dd, J = 12.5, 1.5 Hz, 1H), 4.24 (dd, J = 5.5, 2.5 Hz, 1H), 4.13 (dd, J = 12.5, 1.5 Hz, 1H), 3.83 – 3.80 (m, 2H), 3.57 (t, J = 10.0 Hz, 1H), 1.45 (s, 3H), 1.29 (s, 3H), 1.02 (s, 9H), 0.96 (s, 9H).

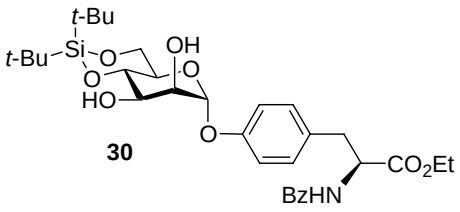
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 137.1, 129.4, 128.5, 127.9, 127.8, 126.7, 112.4, 107.2, 95.4, 85.5, 85.4, 82.2, 69.4, 69.1, 67.2, 66.2, 64.8, 27.5, 27.1, 26.5, 25.0, 23.1, 20.5.
IR (film, cm^{-1}): ν = 2934 (s), 2886 (m), 2859 (s), 1498 (w), 1473 (m), 1383 (m), 1373 (m), 1363 (m), 1271 (m), 1238 (m), 1210 (m), 1194 (m), 1142 (vs), 1121 (s), 1104 (s), 1078 (s), 1041 (vs), 1015 (s), 987 (s), 967 (m), 940 (m), 903 (m), 886 (m), 871 (m), 848 (m), 826 (m), 796 (m), 772 (m), 748 (m), 735 (m), 717 (m), 698 (m), 651 (m), 606 (w).
HRMS (ESI): calc. for $C_{29}H_{44}O_8SiNa$ [M+Na] 571.2698; found: 571.2683.



29

A scintillation vial was charged with **24** (81 mg, 0.108 mmol, 1 equiv) and acetone (0.6 mL). *N*-methyl morpholine *N*-oxide (18.9 mg, 0.162 mmol, 1.5 equiv) was then added to the solution followed by OsO_4 (4 wt% in H_2O, 13.5 μL, 0.00216 mmol, 2 mo%). The resulting mixture was stirred at rt overnight. The mixture was quenched with saturated aqueous $Na_2S_2O_3$ solution (30 mL), stirred for 30 min, and then extracted with ethyl acetate (3 x 40 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by silica gel flash chromatography (1/1, hexane/ethyl acetate) to give **29** (68.3 mg, 80%) as a white solid.

R_f = 0.45 (1/1, Hexane/Ethyl acetate)
MP: 98°C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.45-7.15 (m, 20H), 5.28 (apparent t, *J* = 9.7 Hz, 1H), 5.13 (s, 1H), 5.03 (s, 1H), 4.69 (d, *J* = 11.5 Hz, 1H), 4.51 (d, *J* = 11.5 Hz, 1H), 4.22 (apparent t, *J* = 6.2 Hz, 1H), 4.11-4.06 (m, 2H), 3.93 (bs, 1H), 3.86-3.80 (m, 1H), 3.74 (qd, *J* = 10, 6.5 Hz, 1H), 3.42 (dd, *J* = 9.5, 7.5 Hz, 1H), 3.32 (d, *J* = 9 Hz, 1H), 3.26 (d, *J* = 6 Hz, 1H), 3.11 (dd, *J* = 10, 4 Hz, 1H), 2.56 (d, *J* = 4.5 Hz, 1H), 1.29 (d, *J* = 6 Hz, 3H), 1.24 (s, 3H), 1.14 (s, 3H), 0.95 (s, 9H).
^{13}C NMR ($CDCl_3$, 75 MHz): δ = 179.8, 143.8, 137.0, 128.9, 128.5, 128.2, 128.0, 127.7, 126.8, 109.1, 100.3, 96.1, 86.3, 81.8, 76.0, 71.2, 71.0, 70.2, 69.4, 69.2, 64.8, 62.0, 38.7, 28.1, 26.9, 26.4, 17.5, 14.2.
IR (film, cm^{-1}): ν = 3472 (br, m), 3060 (w), 3033 (w), 2980 (m), 2934 (m), 1733 (m), 1449 (m), 1382 (m), 1280 (w), 1220 (m), 1146 (s), 1090 (vs), 1041 (vs).
HRMS (ESI): calc. for $C_{46}H_{54}NaO_{11}$ [M+ Na] 805.3564; found: 805.3580.

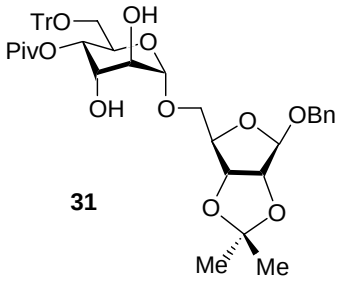


30

To a scintillation vial was charged with **13** (60 mg, 0.10 mmol, 1 equiv) and acetone (0.6 mL). *N*-methyl morpholine *N*-oxide (17.5 mg, 0.15 mmol, 1.5 equiv) was then added to the solution followed by OsO_4 (4 wt% in H_2O, 12.5 μL, 0.002 mmol, 2 mo%). The resulting mixture was stirred at rt overnight. The mixture was quenched with saturated aqueous $Na_2S_2O_3$

solution (30 mL), stirred for 30 min, and then extracted with ethyl acetate (3 x 30 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated. The resulting residue was purified by silica gel flash chromatography (1/1, hexane/ethyl acetate) to give **30** (50 mg, 81%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.71 (d, *J* = 7.0 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.61 (d, *J* = 7.5 Hz, 1H), 5.47 (s, 1H), 5.01 (dd, J = 13.0, 5.5 Hz, 1H), 4.21-4.17 (m, 3H), 4.09 (t, J = 9.5 Hz, 1H), 4.00 (dd, *J* = 8.5, 3.0 Hz, 1H), 3.97 (dd, J = 10.0, 5.0 Hz, 1H), 3.78 (td, J = 10.0, 5.5 Hz, 1H), 3.22 (dd, J = 14.0, 5.5 Hz, 1H), 3.16 (dd, J = 13.5, 5.0 Hz, 1H), 2.87 (s, 1H), 2.80 (d, J = 2.0 Hz, 1H), 1.25 (t, *J* = 7.5 Hz, 3H), 1.03 (s, 3H), 0.95 (s, 3H).
^{13}C NMR ($CDCl_3$, 125 MHz): δ = 171.6, 166.8, 155.4, 133.9, 131.8, 130.6, 129.9, 128.6, 126.9, 116.5, 98.0, 74.4, 71.6, 70.4, 67.4, 66.2, 61.6, 53.6, 37.2, 27.5, 26.9, 22.6, 19.9, 14.1.
IR (film, cm^{-1}): ν = 3419 (m), 3362 (m), 2933 (vs), 2858 (s), 1734 (s), 1646 (s), 1509 (vs), 1473 (m), 1229 (s), 1127 (m), 1092 (vs), 1011 (vs), 911 (w), 854 (w), 826 (m).
HRMS (ESI): calc. for $C_{32}H_{45}NO_9SiNa$ $[M+Na]^+$ 638.2756; found: 638.2770.



31

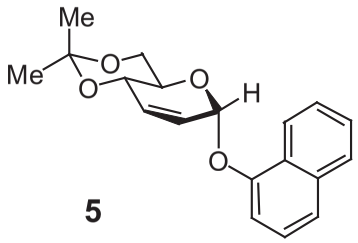
To a solution of **21** (43 mg, 0.059 mmol, 1 equiv) in acetonitrile (1.1 mL) was added a 0.4 mM solution of EDTA in H_2O (360 µL). The flask was cooled to 5 °C, and trifluoroacetone (134 µL, 1.5 mmol, 25 equiv) was added to the cloudy solution. A mixture of Oxone® (184 mg, 0.3 mmol, 5 equiv) and sodium bicarbonate (126 mg, 1.5 mmol, 25 equiv) was added in portions at intervals of 5 min over 1.25 h to the cooled heterogeneous mixture. After complete addition of the Oxone® mixture, the flask was allowed to warm to rt with continued stirring for 2 h. The reaction mixture was then filtered through Celite with a wash of ethyl acetate (10 mL). The filtrate was concentrated, and the residue was taken up with ethyl acetate (20 mL), dried over $MgSO_4$, and then concentrated to yield crude epoxide **31-A** (45 mg).

R_f = 0.45 (4/1, Hexane/Ethyl acetate)
^{1}H NMR (C_6D_6, 500 MHz): δ = 7.7-7.05 (m, 20H), 5.43 (s, 1H), 5.09 (d, *J* = 10 Hz, 1H), 4.94 (s, 1H), 4.84 (dd, *J* = 10, 5 Hz, 1H), 4.82-4.77 (m, 2H), 4.64 (d, *J* = 11.5, 1H), 4.42 (dd, *J* = 9.5, 5 Hz, 1H), 4.28 (d, *J* = 11.5, 1H), 4.24 (apparent t, *J* = 12 Hz, 1H), 3.63 (apparent t, *J* = 9.5, 1H), 3.38 (dd, *J* = 10, 7.5 Hz, 1H), 3.21 (bd, *J* = 8.5 Hz, 1H), 3.06 (d, *J* = 3.5 Hz, 1H), 2.84 (d, *J* = 3.5 Hz, 1H), 1.54 (s, 3H), 1.28 (s, 3H), 0.97 (s, 9H).

The crude epoxide (45 mg, 0.059 mmol, 1 equiv) was dissolved in dichloromethane (4 mL) within a schlenk reaction flask and cooled to −78 °C under an argon atmosphere. BF_3•OEt_2 (1 M in dichloromethane, 39 µL, 0.039 mmol, 0.65 equiv) was added to the cooled solution. The reaction was monitored regularly by TLC. Once the epoxide was mostly consumed at 6 h, a solution of water in THF (~0.5% v/v, 1 mL, 5 equiv) was added dropwise to the solution. The reaction mixture was allowed to warm slowly to rt with continued stirring over 12 h.

Triethylamine (30 μL, 2 equiv) was added and the solution was concentrated. The residue was purified by flash chromatography silica gel (gradient elution 2:1→1:1 hexane/ethyl acetate) to yield pure diol **31** (26 mg, 57%, 2 steps) as a white solid.

R_f = 0.44 (1/1, Hexane/Ethyl acetate)
MP: 79 ^{o}C
^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.49-7.15 (m, 20H), 5.16 (s, 1H), 4.99 (dd, *J* = 8.5, 3.5 Hz, 1H), 4.78 (d, *J* = 3 Hz, 1H), 4.74 (d, *J* = 11 Hz, 1H), 4.69 (d, *J* = 11 Hz, 1H), 4.63 (d, *J* = 12 Hz, 1H), 4.47 (d, *J* = 12 Hz, 1H), 4.45 (d, *J* = 12 Hz, 1H), 4.21 (apparent t, *J* = 6.5 Hz, 1H), 4.07 (dd, *J* = 10.5, 5.5 Hz, 1H), 3.99-3.93 (m, 1H), 3.87-3.82 (m, 1H), 3.60 (dd, *J* = 10, 7.2 Hz, 1H), 3.24 (dd, *J* = 10, 7 Hz, 1H), 3.15 (dd, *J* = 10, 2.5 Hz, 1H), 2.78 (d, *J* = 8 Hz, 1H), 2.24 (d, *J* = 5 Hz, 1H), 1.45 (s, 3H), 1.30 (s, 3H), 1.02 (s, 9H).
^{13}C NMR ($CDCl_3$, 75 MH): δ = 177.5, 143.7, 136.9, 128.7, 128.5, 128.1, 127.9, 127.1, 112.6, 107.7, 100.7, 86.8, 85.7, 85.0, 82.1, 70.4, 69.5, 69.3, 68.7, 67.9, 63.1, 38.8, 27.0, 26.5, 25.0.
IR (film, cm^{-1}): ν = 3478 (br, m), 3061 (w), 2933 (s), 2874 (m), 1730 (s), 1489 (w), 1449 (m), 1373 (m), 1283 (m), 1211 (m), 1159 (s), 1075 (vs), 1014 (s).
HRMS (ESI): calc. for $C_{45}H_{52}O_{11}$ (M^+ Na) 791.3402; found: 791.3408.

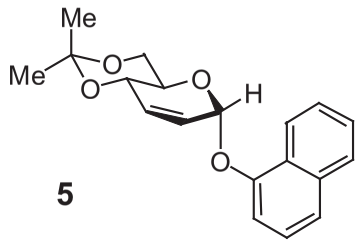

Me
Me
O
O
O
H
O

5

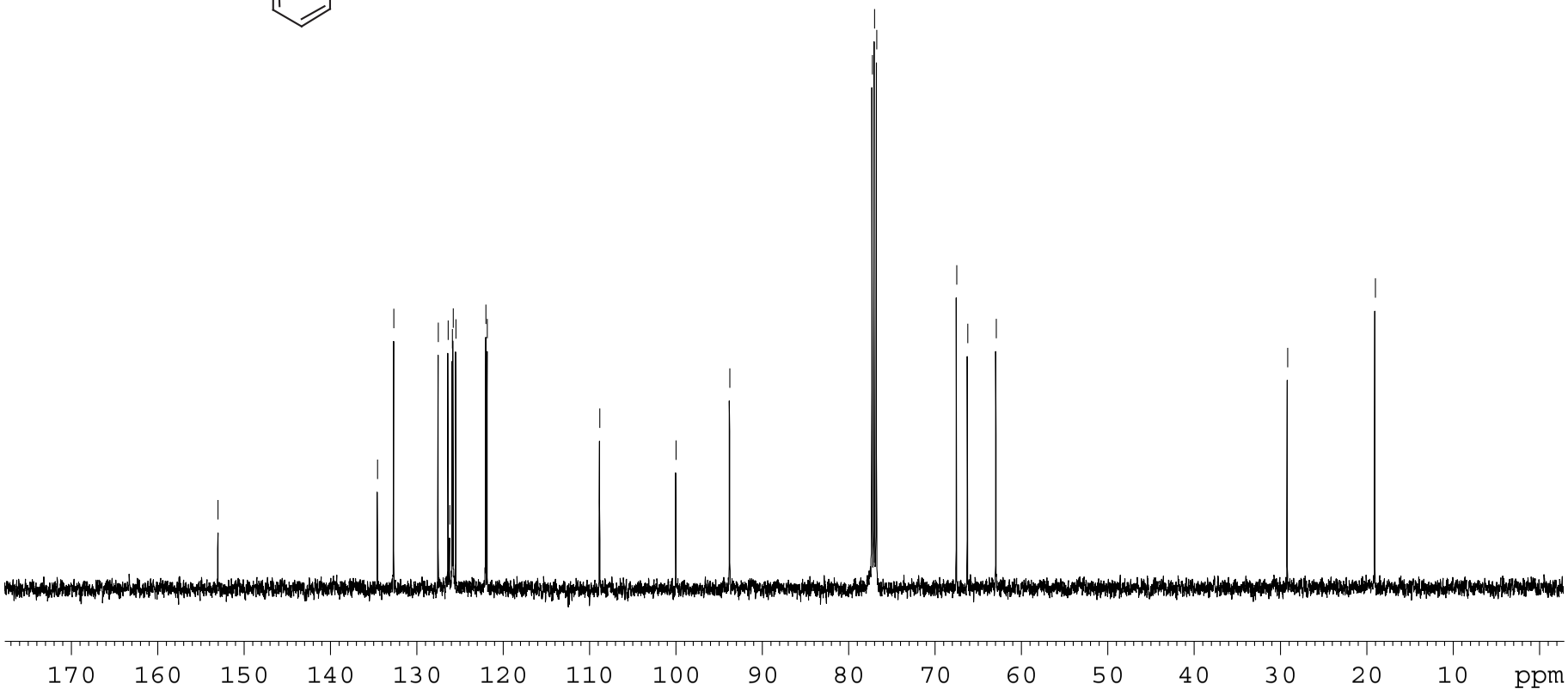
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.974
1.006
3.138
1.018
1.008
1.000
1.013
1.002
1.008
1.036
2.122
3.127
3.091

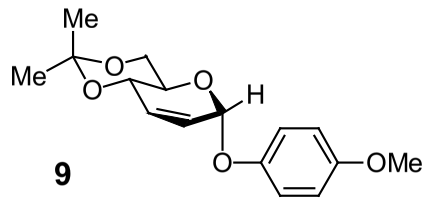
BS-I-29

153.025
134.550
132.666
127.518
126.373
126.185
125.884
125.784
125.474
122.005
121.845
108.819
99.988
93.762
77.254
77.001
76.748
67.484
66.208
62.908
29.168
19.009



5




Me
Me
O
O
O
H
O
OMe

9

7.5
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
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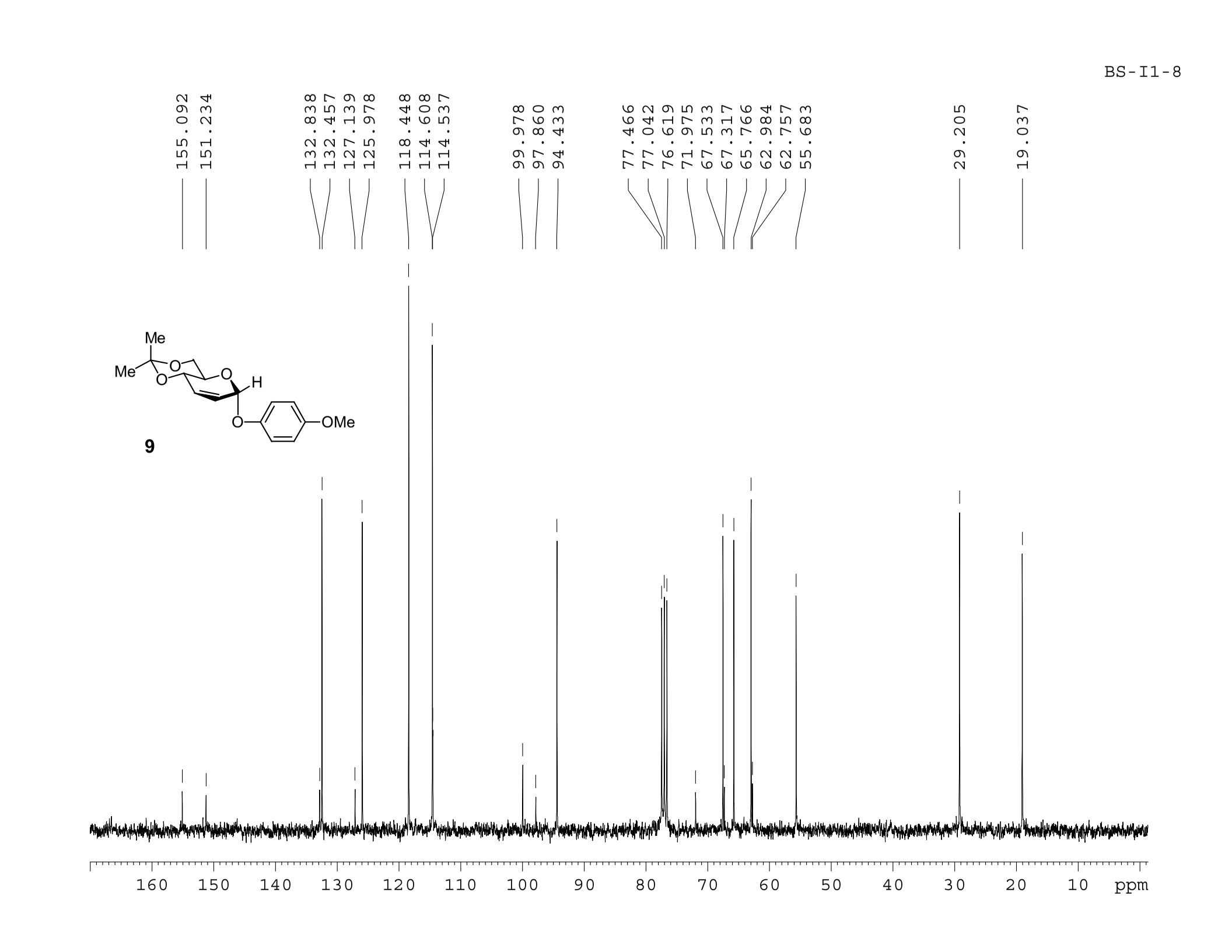
1.043
1.012
0.799
1.000
2.809
2.728
4.270
3.029

BS-I1-8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151.234
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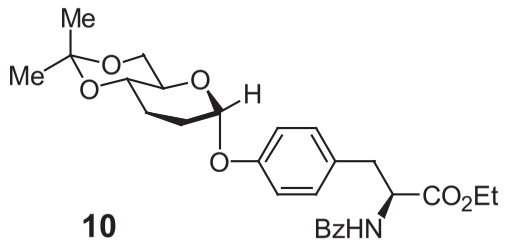
132.457
127.139
125.978
118.448
114.608
114.537
99.978
97.860
94.433
77.466
77.042
76.619
71.975
67.533
67.317
65.766
62.984
62.757
55.683
29.205
19.037
Me
Me
O
O
O
H
O
OMe
9
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

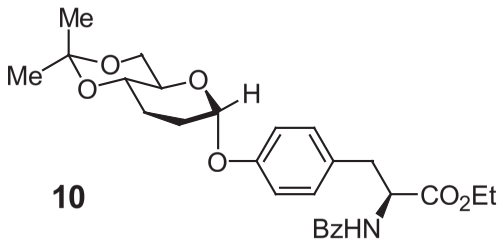

Me
Me
O
O
O
H
O
CO2Et
BzHN

10

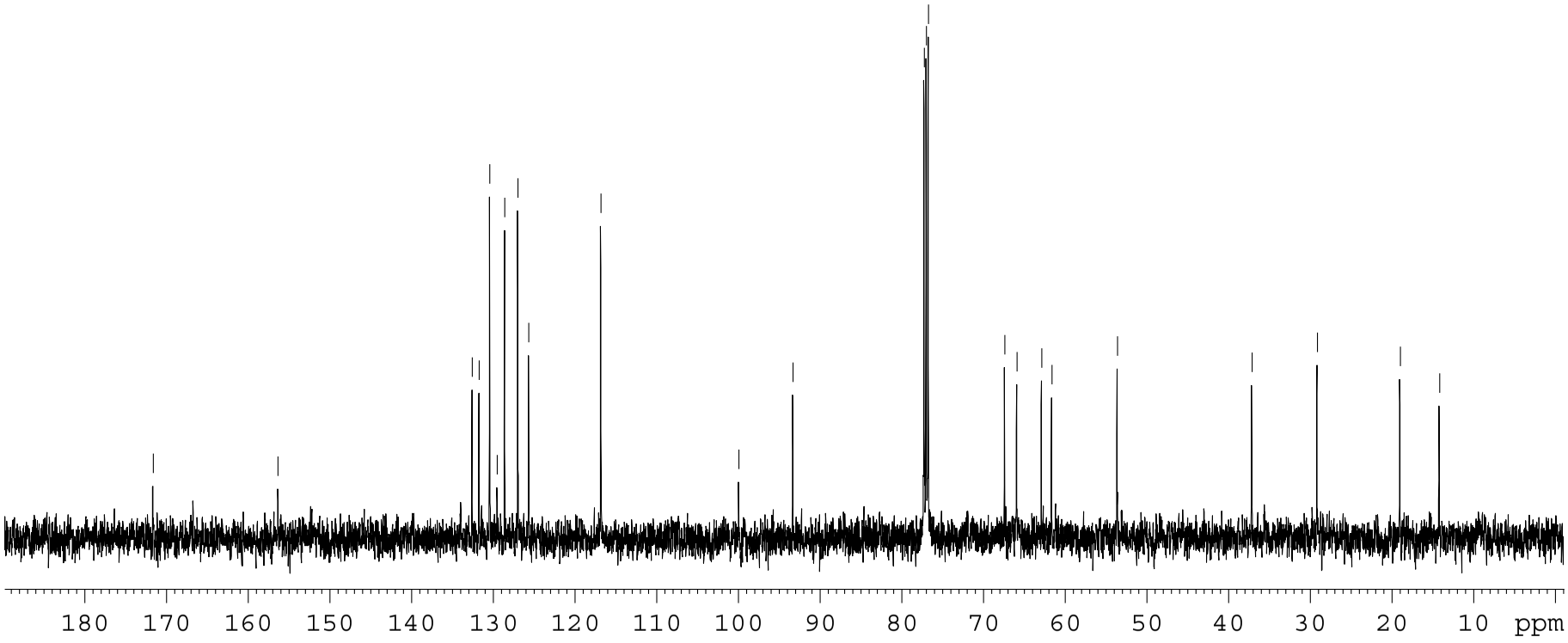
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.856
0.450
0.859
0.882
0.888
0.429
0.424
0.534
0.332
0.435
1.227
1.440
0.887
1.512
1.459
1.504

HN-I-78

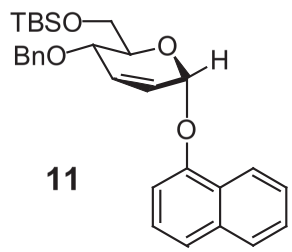
171.619
156.362
132.581
131.734
130.435
129.524
128.602
126.987
125.664
116.823
99.942
93.320
77.245
76.991
76.736
67.393
65.897
62.870
61.618
53.600
37.126
29.131
18.976
14.165



10



HN-II-12

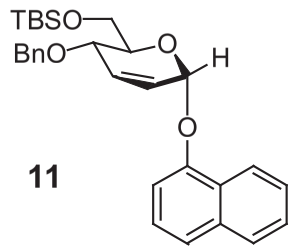

TBSO
BnO
O
H
O

11

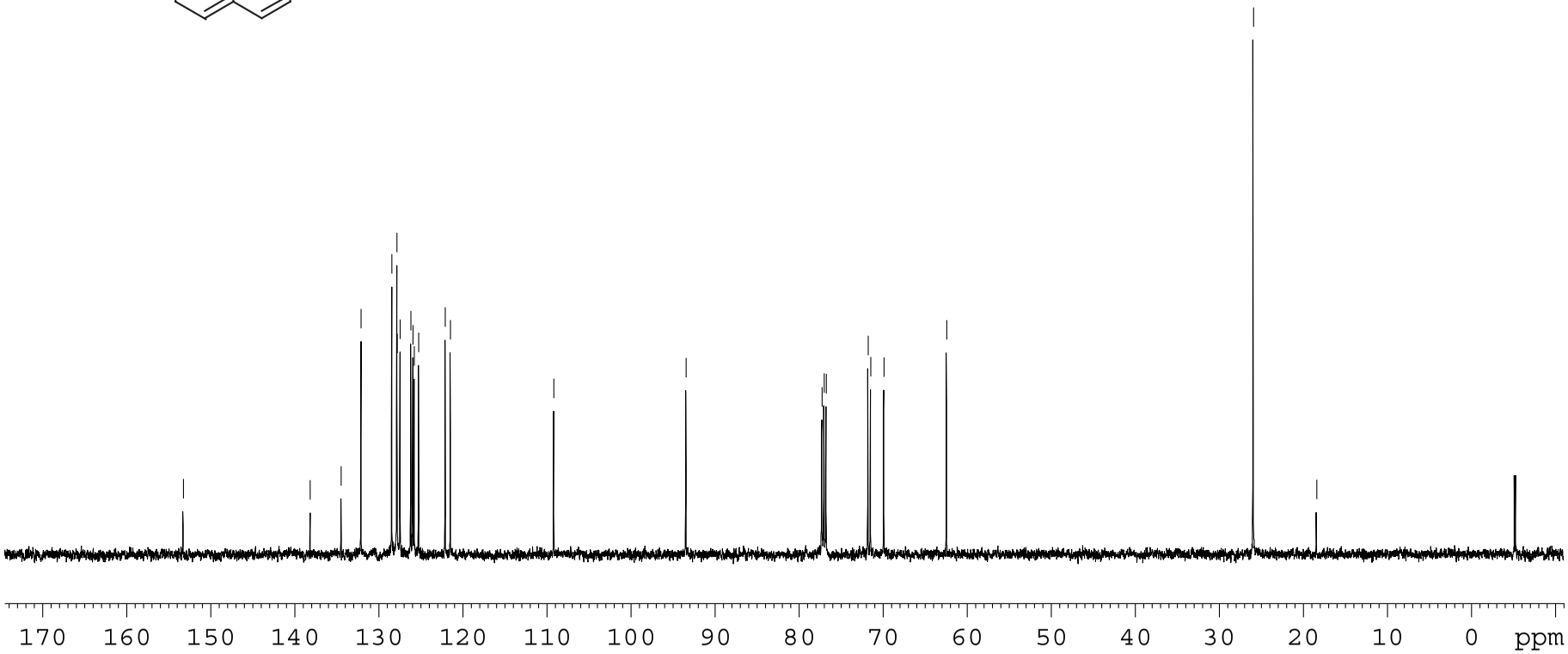
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.937
0.957
3.225
5.082
2.143
1.000
1.009
1.002
1.002
1.035
1.008
1.033
1.040
1.011
9.069
5.755

HN-II-12

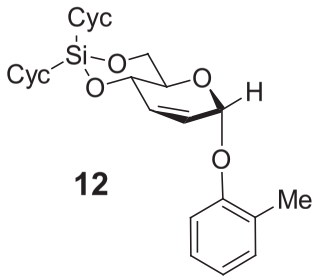
153.254
138.179
134.492
132.124
128.460
127.856
127.818
127.474
126.196
125.945
125.791
125.268
122.108
121.488
109.188
93.449
77.269
77.017
76.764
71.782
71.477
69.901
62.437
25.932
18.408



11



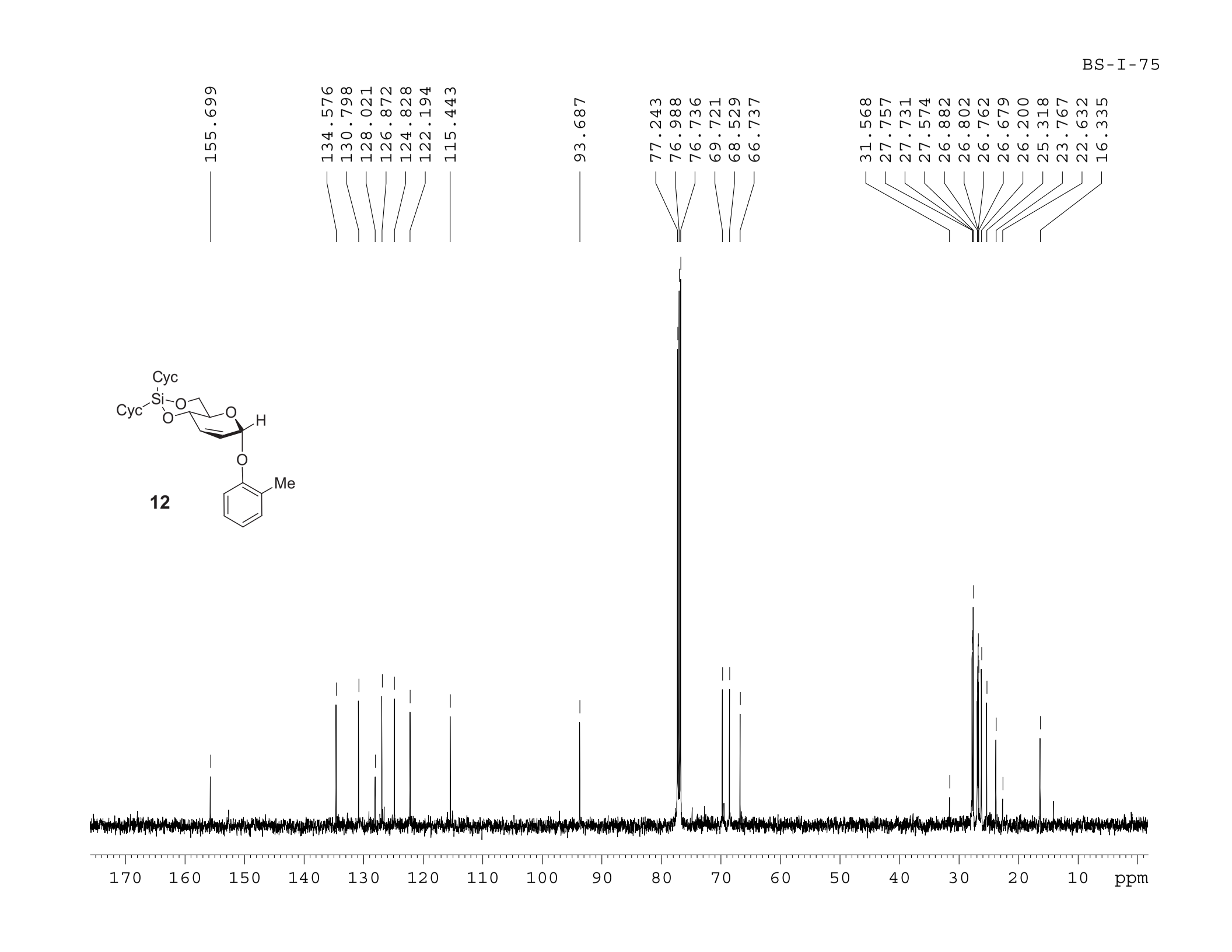
BS-I-71


Cyc
Si
Cyc
O
O
O
H
O
Me

12

7.5
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
2.229
1.142
1.210
1.154
1.079
1.000
1.072
1.155
1.857
2.606
15.727
17.400

BS-I-75


155.699
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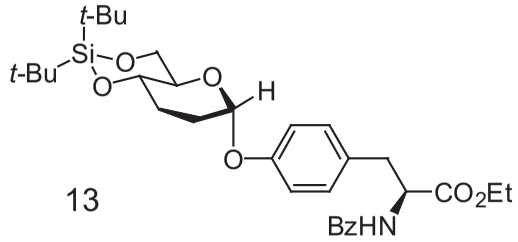
130.798
128.021
126.872
124.828
122.194
115.443
93.687
77.243
76.988
76.736
69.721
68.529
66.737
31.568
27.757
27.731
27.574
26.882
26.802
26.762
26.679
26.200
25.318
23.767
22.632
16.335
Cyc
Si
Cyc
O
O
O
H
O
Me
12
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

BS-II-67


t-Bu
Si
t-Bu
O
O
O
H
O
CO2Et
BzHN

13

7.5
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
2.389
1.166
2.361
2.397
2.318
1.114
1.077
1.314
1.000
1.182
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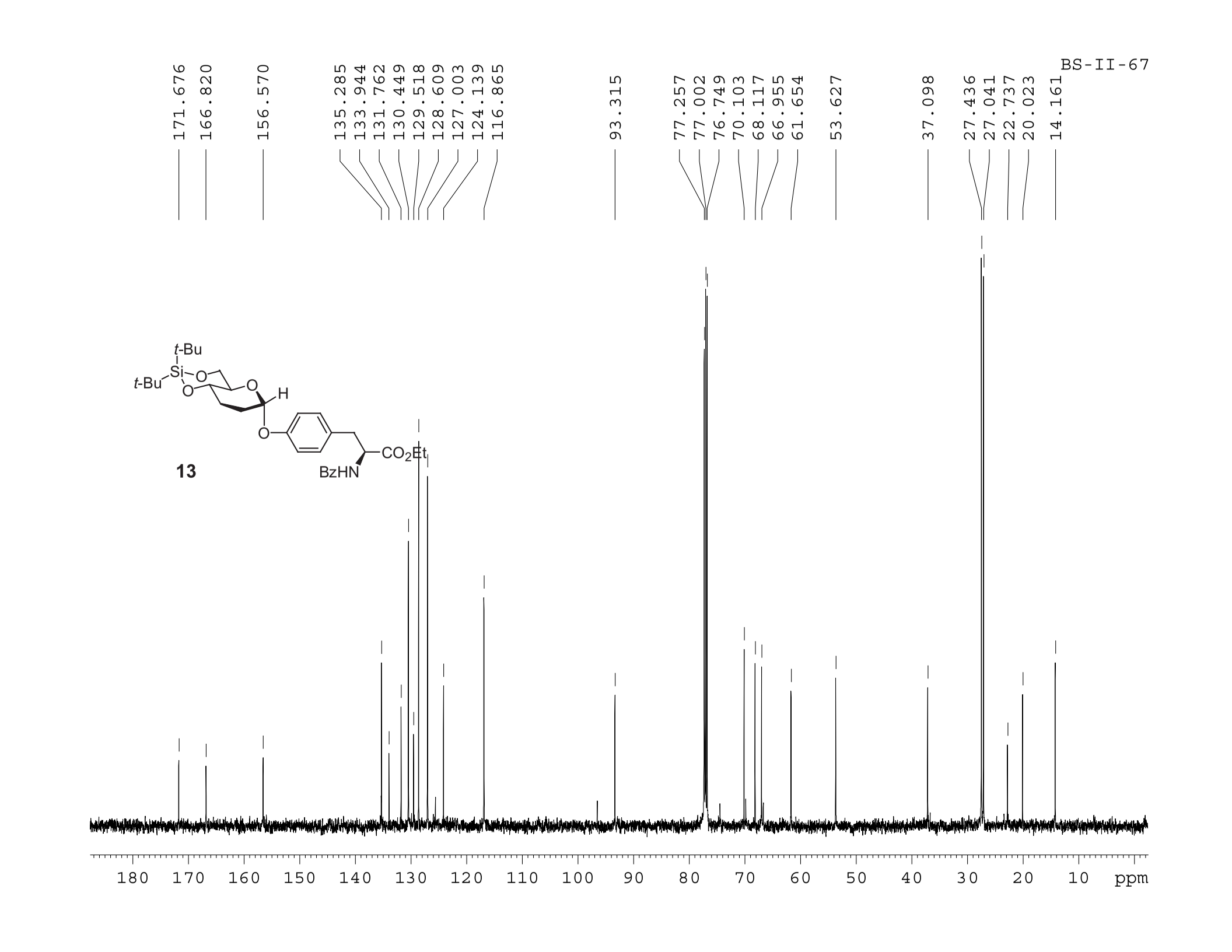
1.066
2.033
2.396
3.273
10.093
9.533


BS-II-67
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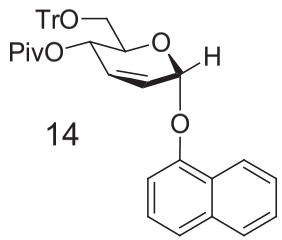
156.570
135.285
133.944
131.762
130.449
129.518
128.609
127.003
124.139
116.865
93.315
77.257
77.002
76.749
70.103
68.117
66.955
61.654
53.627
37.098
27.436
27.041
22.737
20.023
14.161
t-Bu
Si
t-Bu
O
O
O
H
O
CO2Et
BzHN
13
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

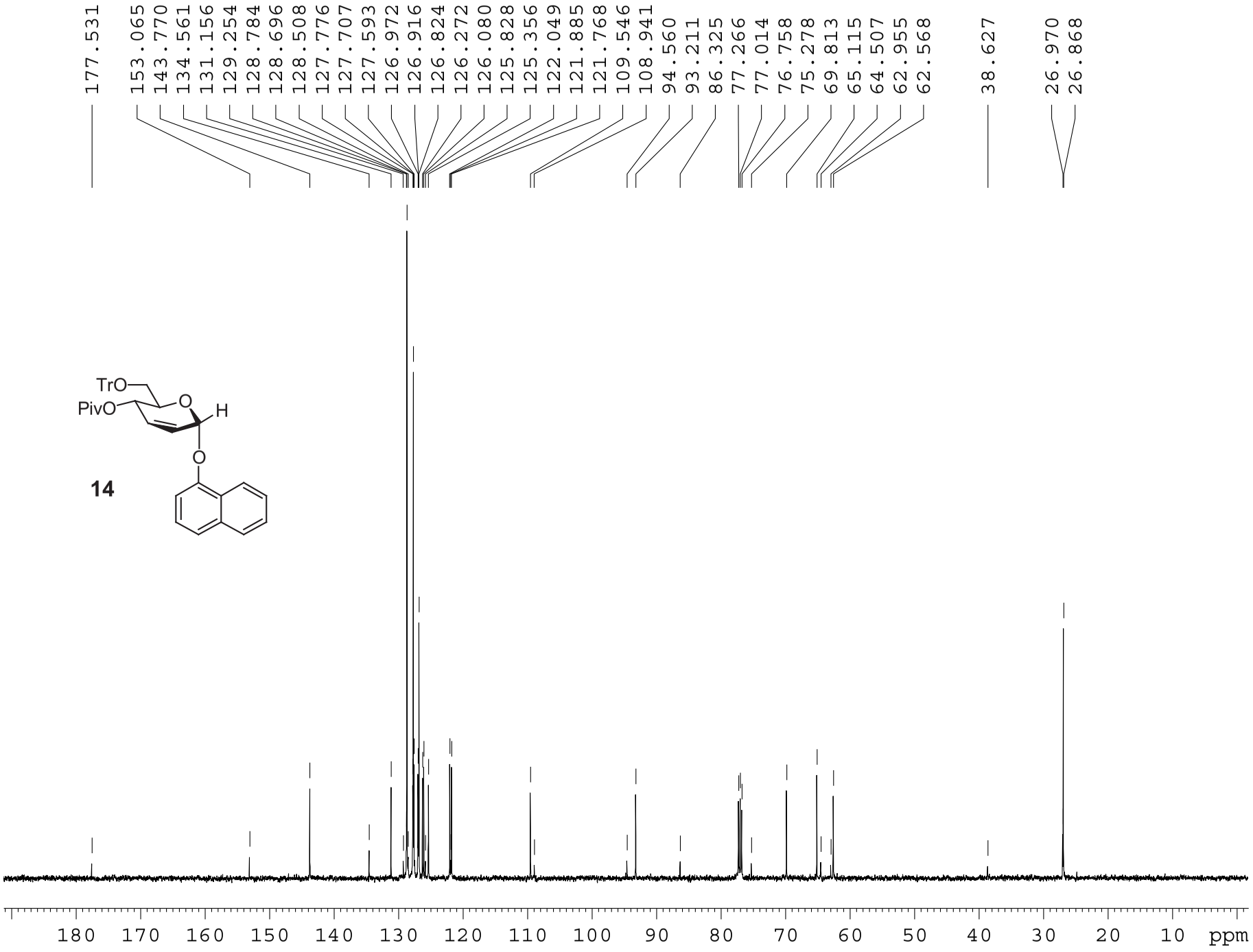
BS-II-45


TrO
PivO
O
H
O

14

8.0
7.5
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
0.807
0.808
2.012
1.792
1.527
5.526
9.361
0.986
0.926
1.000
1.017
0.860
0.883
0.878
7.759

BS-II-45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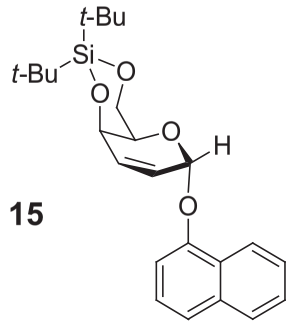
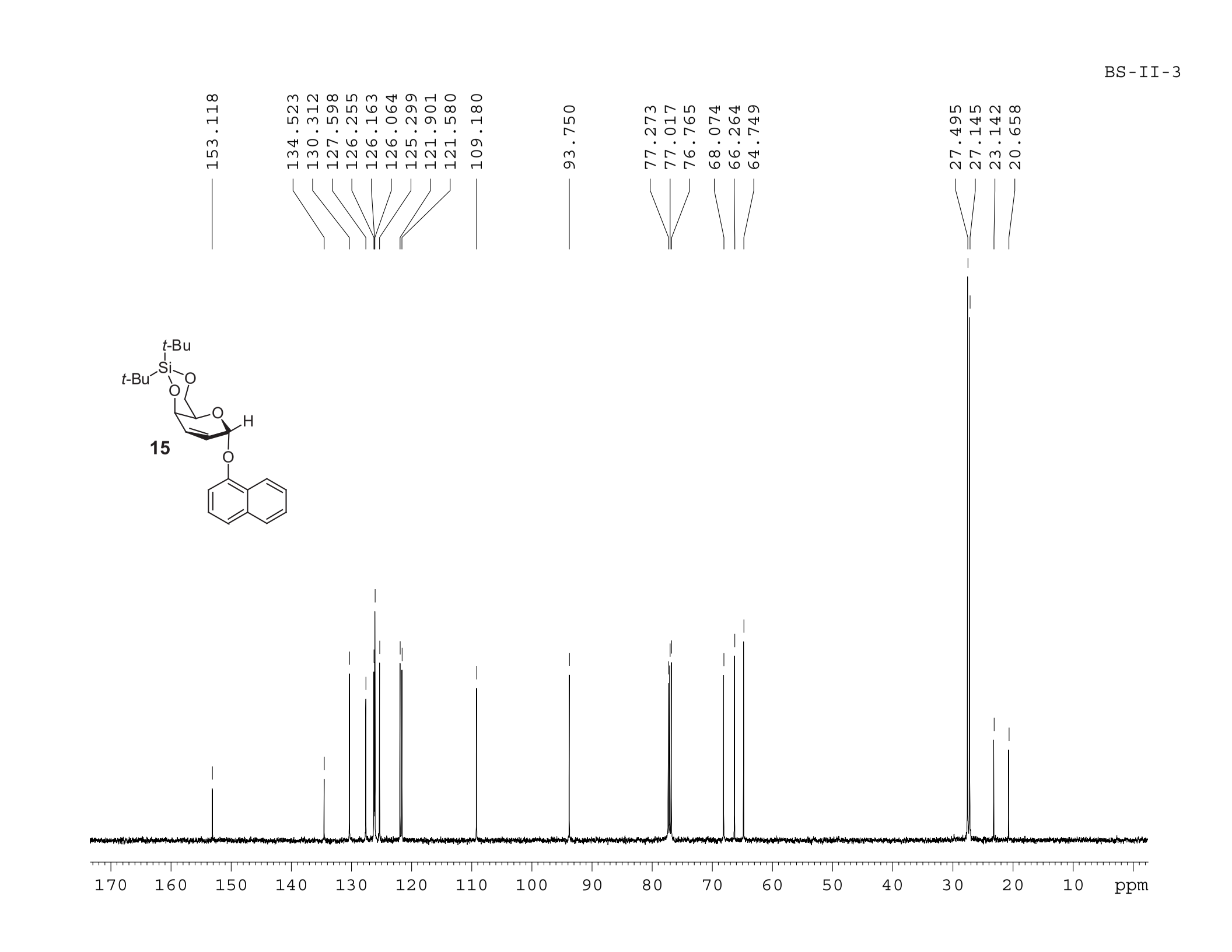
143.770
134.561
131.156
129.254
128.784
128.696
128.508
127.776
127.707
127.593
126.972
126.916
126.824
126.272
126.080
125.828
125.356
122.049
121.885
121.768
109.546
108.941
94.560
93.211
86.325
77.266
77.014
76.758
75.278
69.813
65.115
64.507
62.955
62.568
38.627
26.970
26.868
TrO
PivO
O
H
O
14
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


t-Bu
Si
t-Bu
O
O
O
H
O

15

8.0
7.5
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
0.998
1.000
4.178
1.052
1.015
1.018
1.000
1.019
1.043
1.052
1.039
9.320
8.921

BS-II-3


153.118
134.523
130.312
127.598
126.255
126.163
126.064
125.299
121.901
121.580
109.180
93.750
77.273
77.017
76.765
68.074
66.264
64.749
27.495
27.145
23.142
20.658
t-Bu
Si
t-Bu
O
O
O
H
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150
140
130
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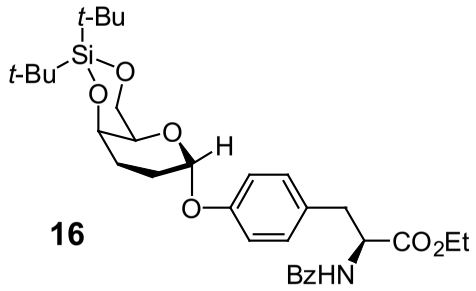
100
90
80
70
60
50
40
30
20
10
ppm

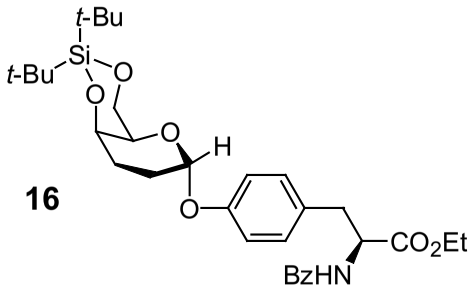

t-Bu
Si
t-Bu
O
O
O
H
O
CO2Et
BzHN

16

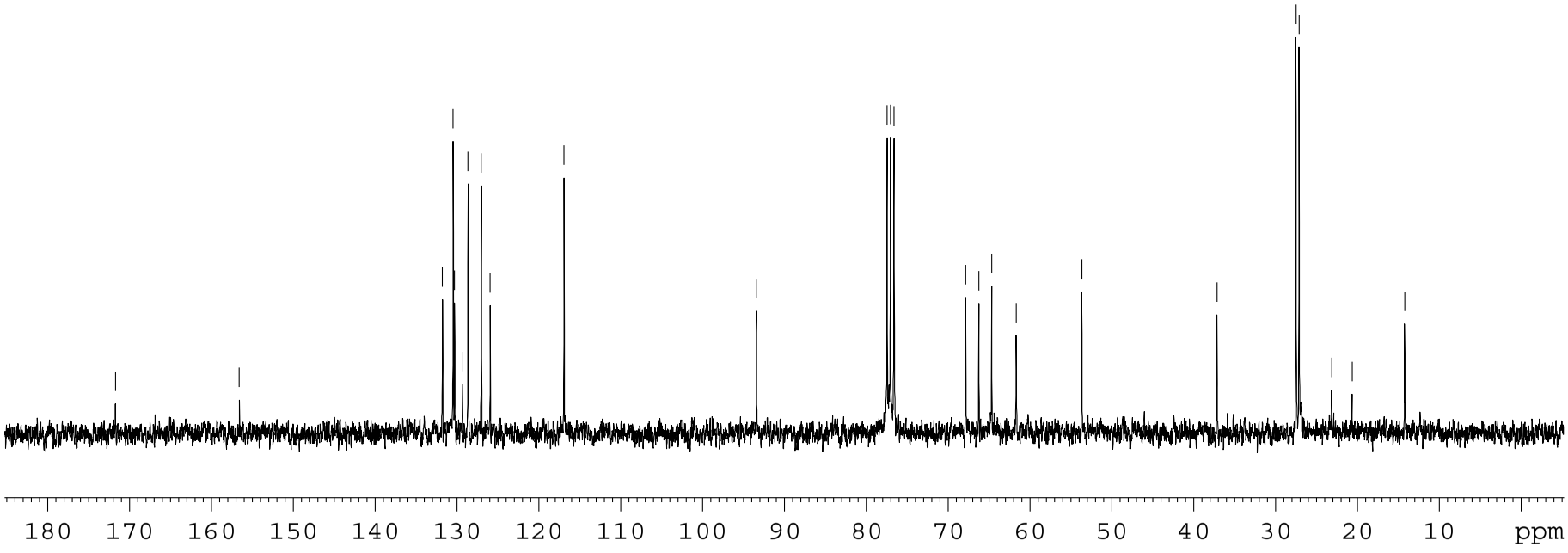
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.015
2.931
4.126
1.468
1.043
1.271
1.076
0.985
2.184
3.189
1.076
1.993
3.430
9.266
9.539

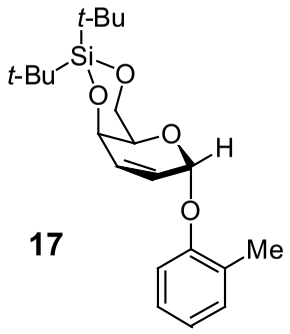
BS-II-1

171.714
156.616
131.799
130.493
130.317
129.378
128.676
127.049
125.964
116.939
93.441
77.465
77.040
76.617
67.862
66.249
64.677
61.684
53.661
37.151
27.492
27.123
23.138
20.637
14.219



16

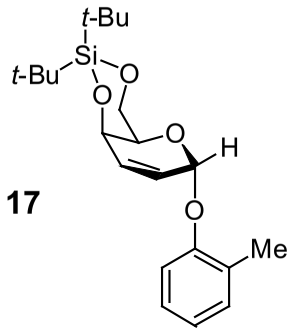



t-Bu
Si
t-Bu
O
O
O
H
O
Me

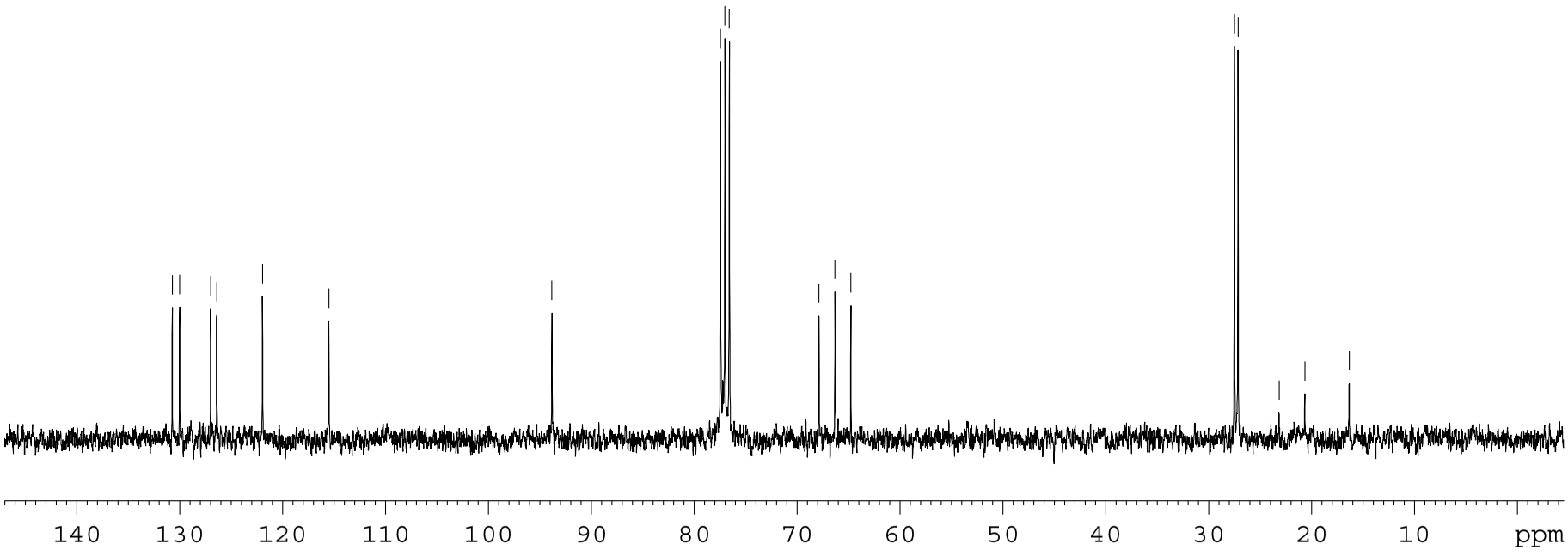
17

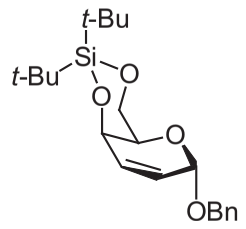
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.781
1.963
0.967
0.999
0.998
1.000
2.288
1.162
1.081
3.004
10.476
10.012

130.715
130.013
126.989
126.397
121.950
115.501
93.845
77.452
77.029
76.605
67.883
66.332
64.781
27.496
27.138
23.150
20.650
16.335



17

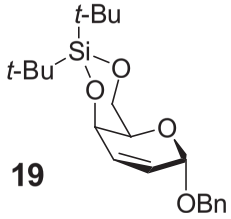



t-Bu
Si
t-Bu
O
O
O
OBn

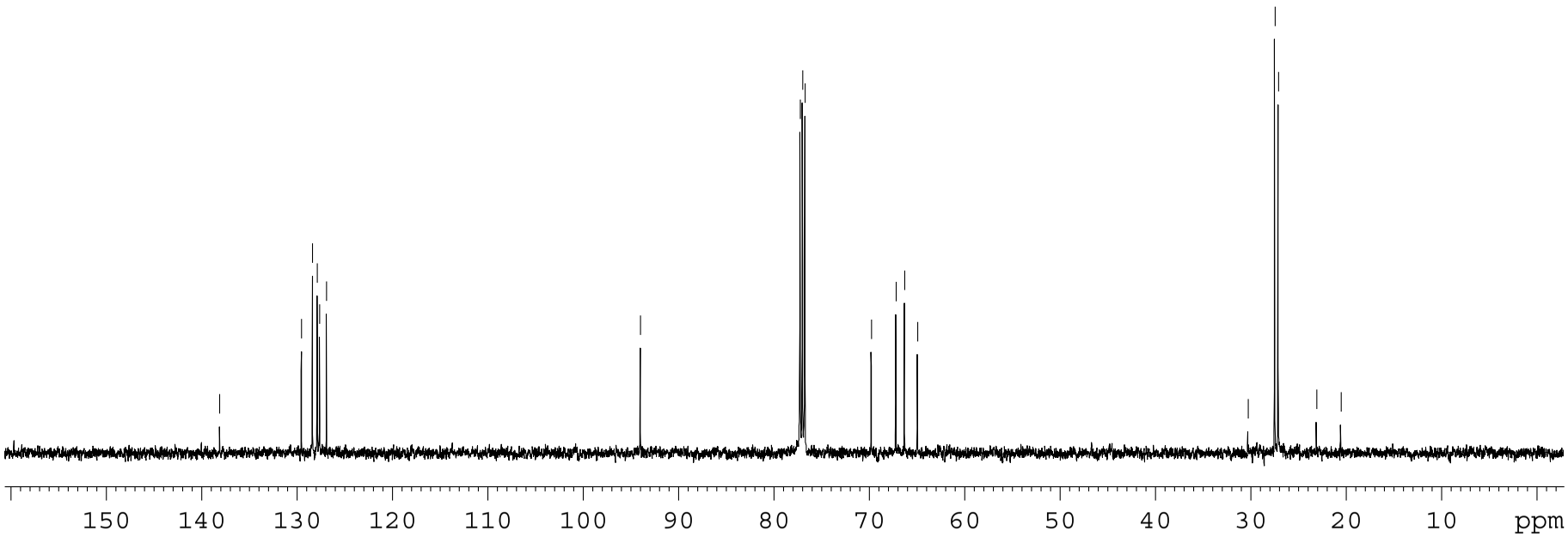
19

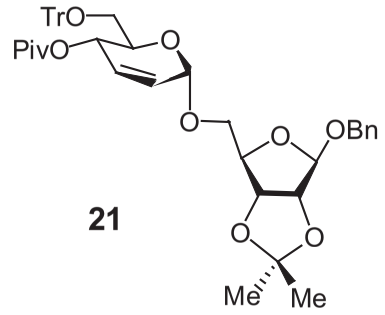
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
4.764
0.955
0.952
0.920
0.940
0.950
1.000
1.019
0.978
0.957
9.143
8.364

138.124
129.539
128.388
127.885
127.638
126.916
93.999
77.239
76.986
76.733
69.774
67.190
66.293
64.931
30.275
27.453
27.094
23.086
20.528



19

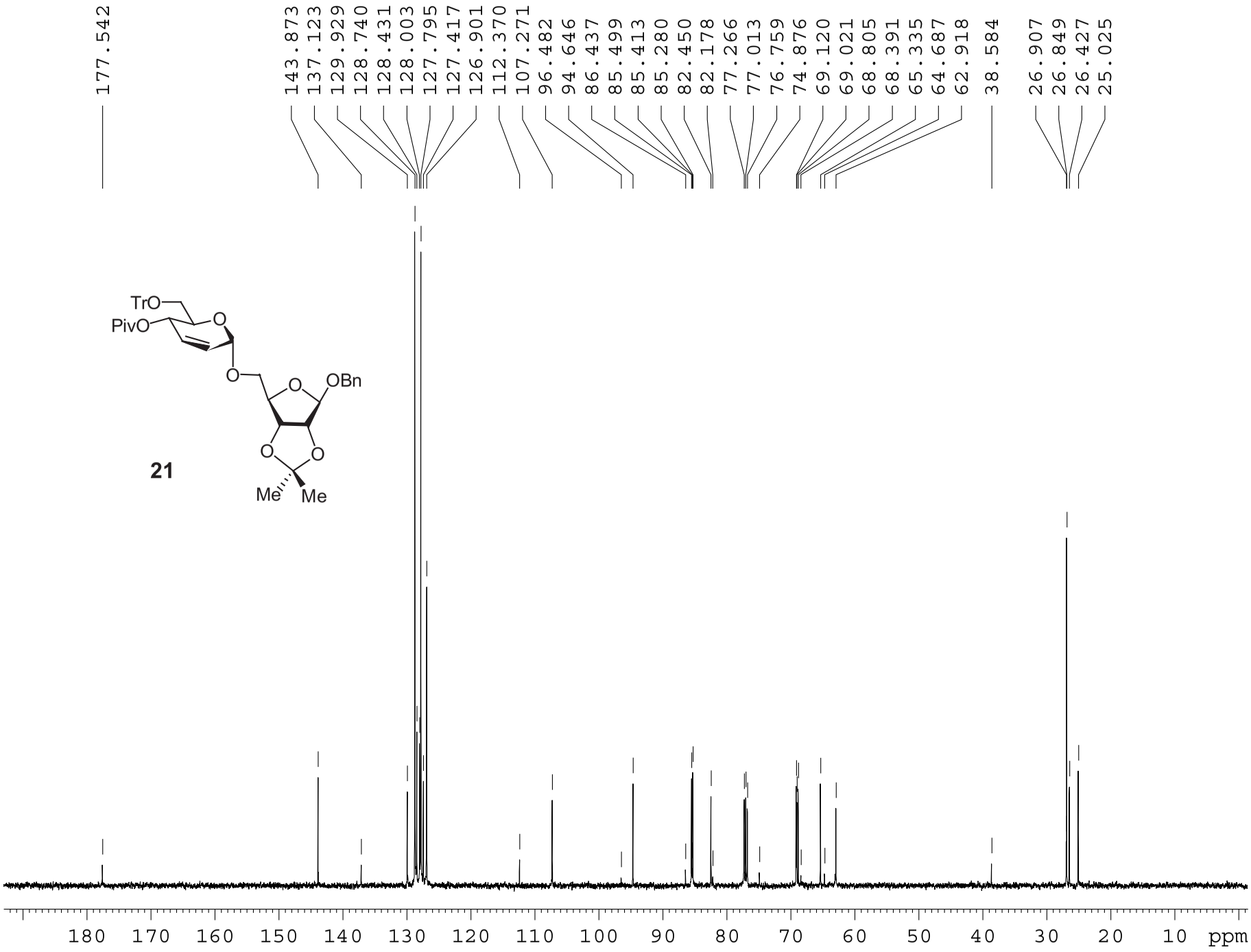


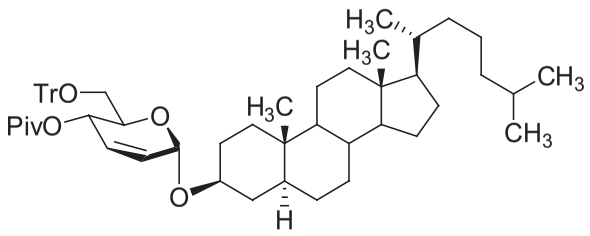

TrO
PivO
O
O
OBn
O
O
O
Me
Me

21

7.5
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
7.186
9.831
5.816
1.811
1.035
1.012
1.008
1.000
1.086
1.047
1.040
1.121
2.104
1.050
1.796
3.065
3.152
8.990

BS-II-59

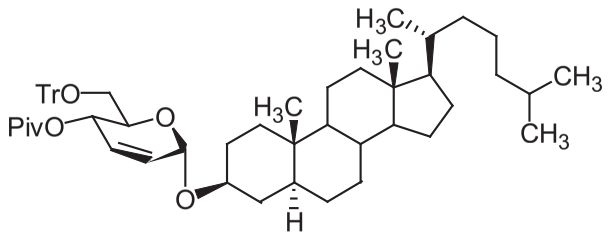

177.542
143.873
137.123
129.929
128.740
128.431
128.003
127.795
127.417
126.901
112.370
107.271
96.482
94.646
86.437
85.499
85.413
85.280
82.450
82.178
77.266
77.013
76.759
74.876
69.120
69.021
68.805
68.391
65.335
64.687
62.918
38.584
26.907
26.849
26.427
25.025
TrO
PivO
O
O
OBn
O
O
O
Me
Me
21
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


TrO
PivO
O
O
H3C
H3C
H3C
CH3
CH3
H

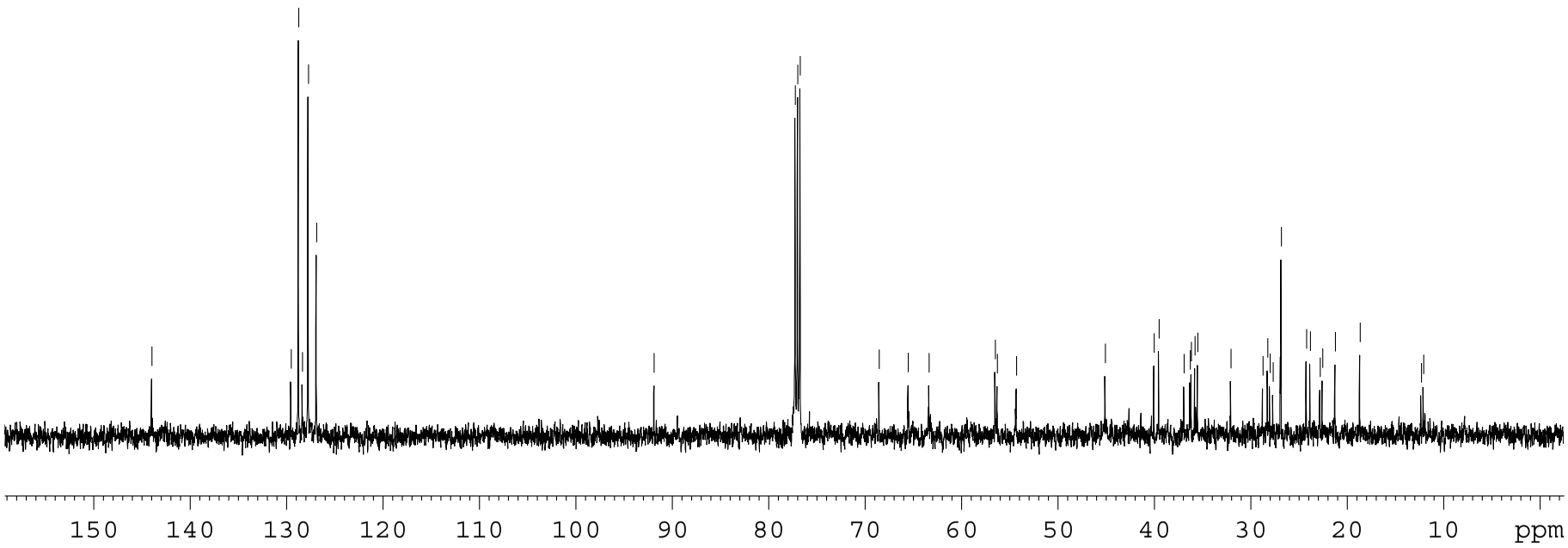
22

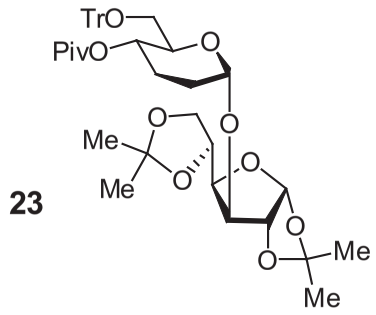
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
7.057
5.572
3.768
1.323
0.760
0.755
0.758
0.979
2.108
1.969
25.926
5.611
7.438
3.741
6.884
3.091
3.404

143.966
129.519
128.740
128.353
127.727
126.883
91.888
77.240
76.986
76.733
68.540
65.529
63.366
56.498
56.286
54.297
45.086
40.025
39.511
36.919
36.280
36.166
35.787
35.495
32.057
28.735
28.245
27.997
27.684
26.887
26.832
24.216
23.821
22.802
22.544
21.229



22



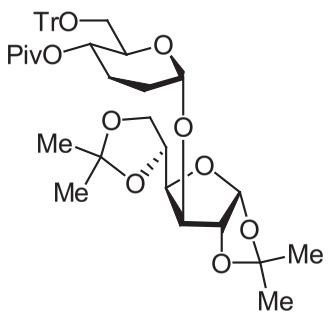

TrO
PivO
O
O
Me
Me
O
O
O
O
O
Me
Me

23

8.5
8.0
7.5
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
7.312
1.740
7.705
3.899
1.069
2.012
1.040
1.000
0.993
1.176
3.242
1.127
2.105
3.490
3.528
3.471
3.149
9.459

BS-II-023

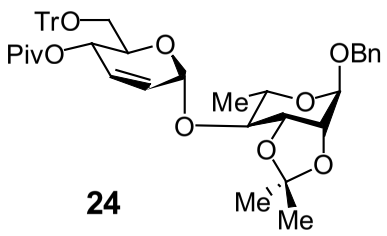
177.496
143.711
129.942
128.768
127.812
127.029
126.944
105.411
95.927
84.252
81.986
81.396
77.239
76.986
76.733
72.590
69.160
67.822
65.290
63.377
29.685
27.043
26.833
26.232
25.405



23

180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

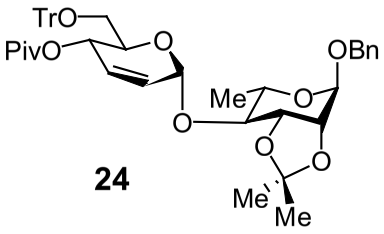
GJM-III-005



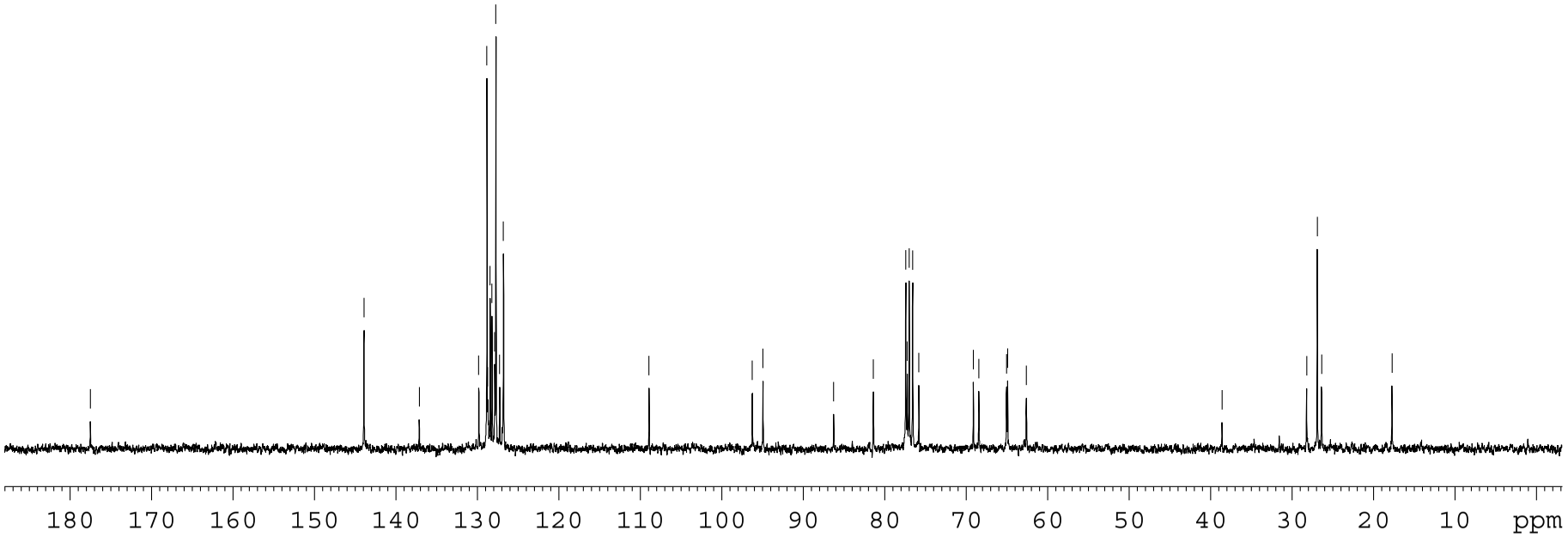
24

GJM-III-005

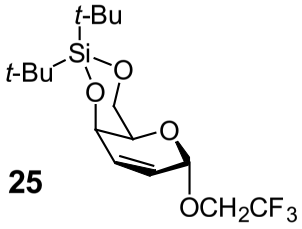
177.509
143.917
137.120
129.858
128.857
128.749
128.456
128.229
127.901
127.751
127.290
126.828
108.952
96.273
94.961
86.284
81.406
77.424
77.251
77.001
76.577
75.825
69.126
68.454
65.047
64.914
62.621
38.591
28.196
26.895
26.361
17.718



24



BS-I-91

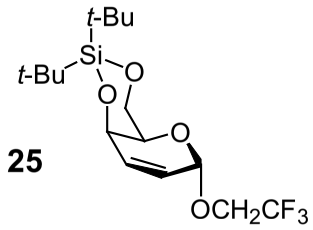

t-Bu
Si
t-Bu
O
O
O
OCH2CF3

25

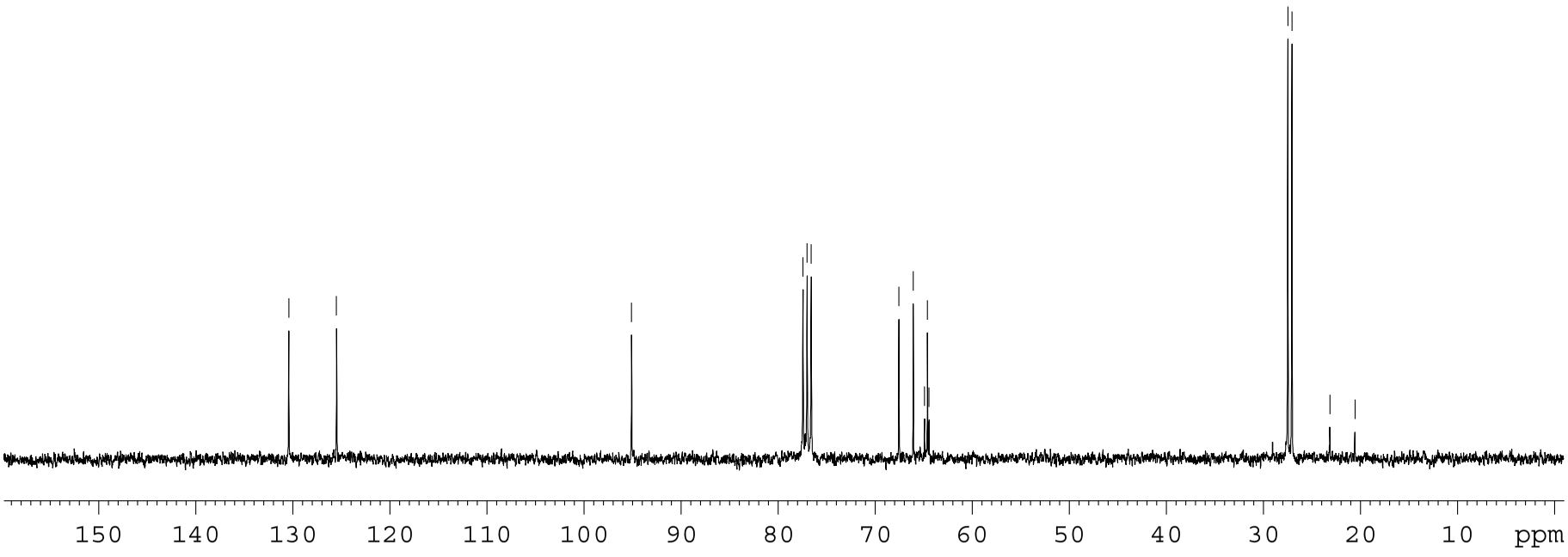
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.999
1.005
1.000
1.250
1.132
1.207
2.229
1.182
10.721
10.489

BS-I-91

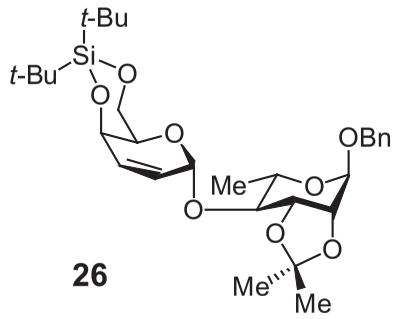
130.409
125.520
95.113
77.446
77.024
76.601
67.562
66.082
64.923
64.623
64.464
27.476
27.055
23.145
20.555



25



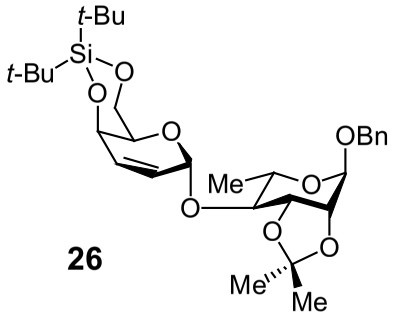
GJM-III-008



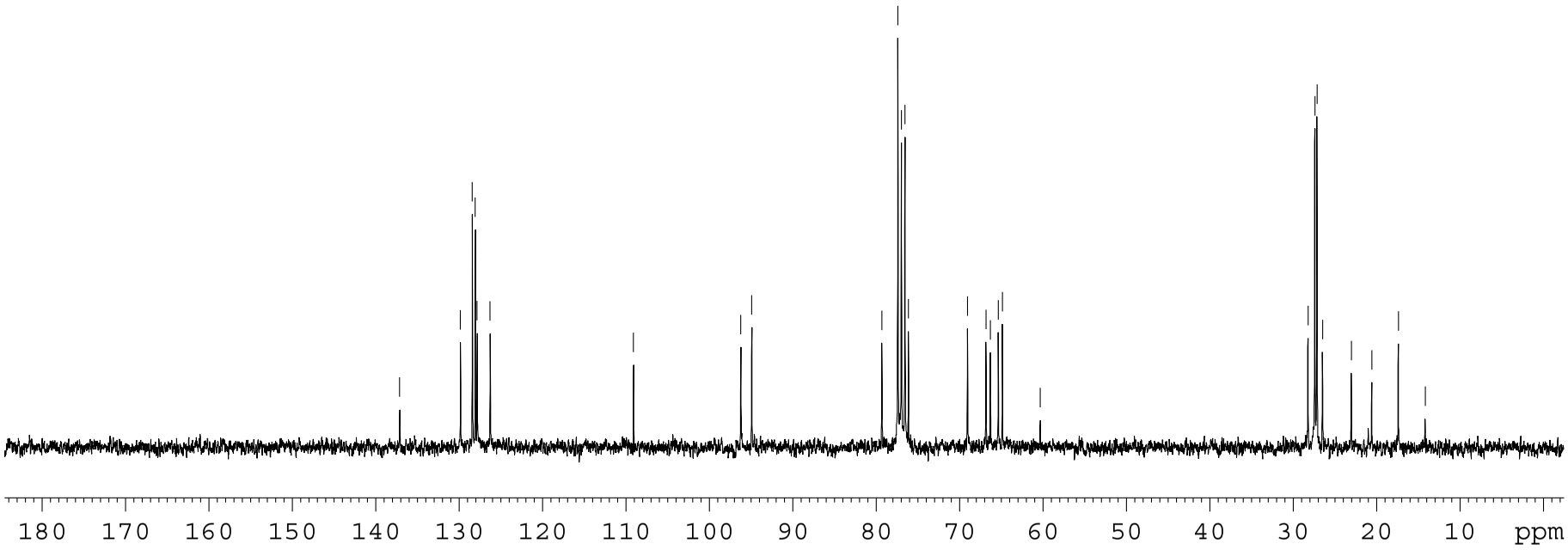
26

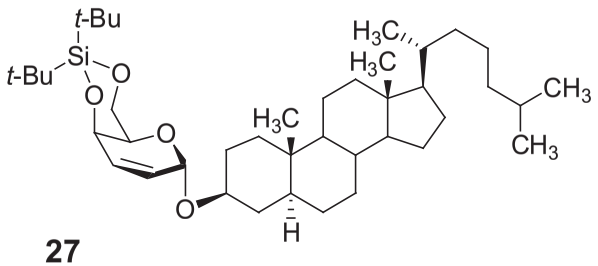
GJM-III-008

137.150
129.865
128.441
128.087
127.866
126.308
109.115
96.245
94.935
79.322
77.405
76.978
76.555
76.141
69.057
66.833
66.314
65.364
64.867
60.339
28.216
27.396
27.138
26.474
23.026
20.576
17.385
14.166



26



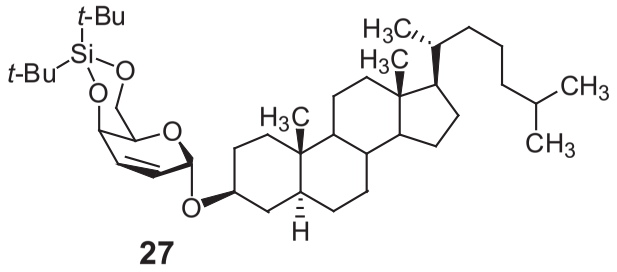

t-Bu
Si
t-Bu
O
O
O
O
H3C
H3C
H3C
CH3
CH3
H

27

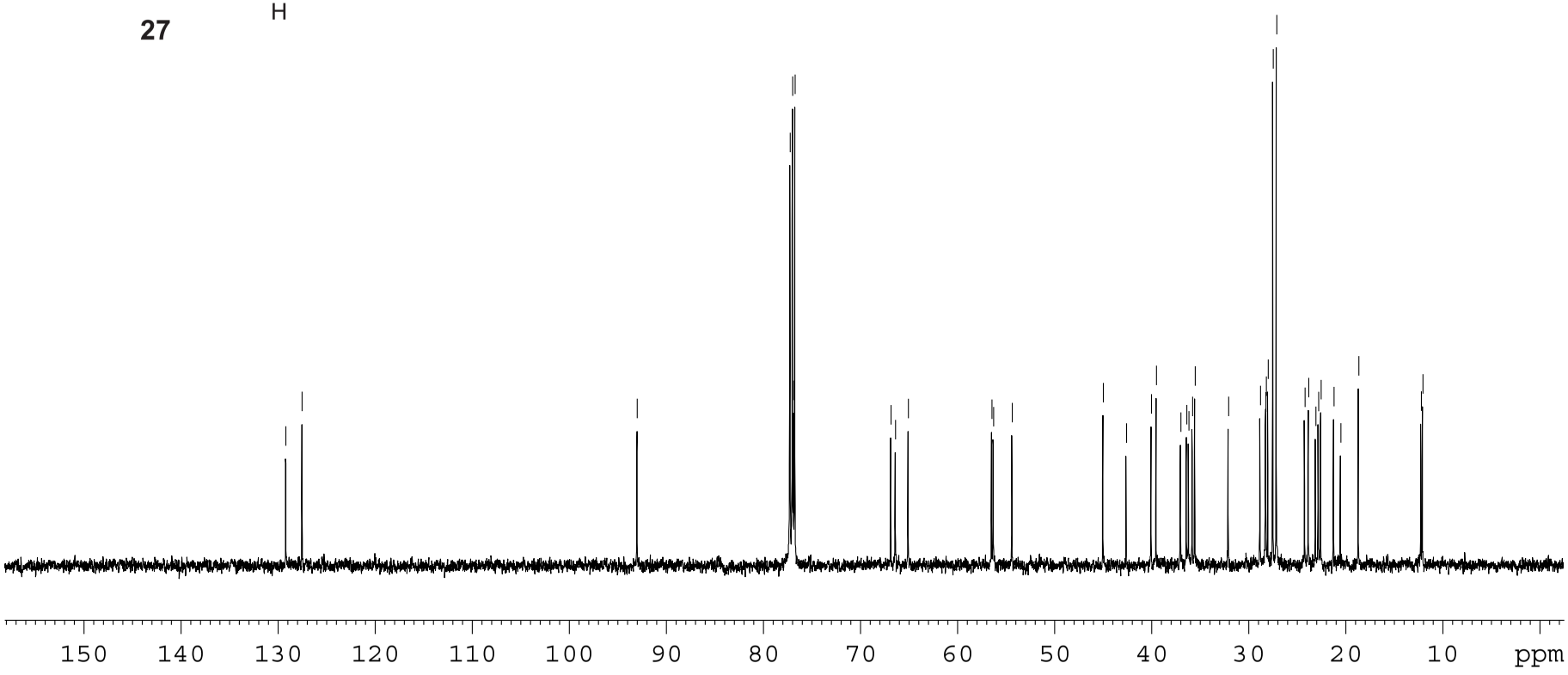
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.000
1.002
1.003
1.013
1.037
1.022
1.003
1.027
1.084
2.188
1.161
1.182
5.078
7.392
4.080
6.233
10.792
12.158
0.859
3.923
7.211
3.128
3.296
0.875

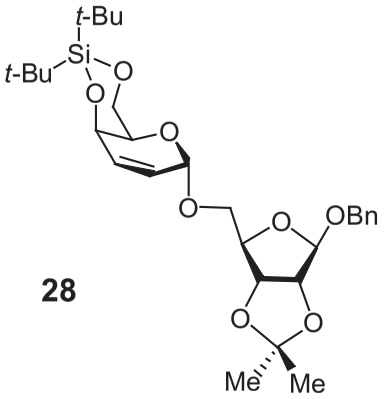
129.204
127.535

93.006
77.243
76.988
76.886
76.735
66.856
66.392
65.068
56.458
56.286
54.367
44.983
42.590
40.025
39.509
36.992
36.382
36.164
35.786
35.515
32.072
28.791
28.234
28.188
27.994
27.478
27.111
24.200
23.821
23.083
22.797
22.544



27

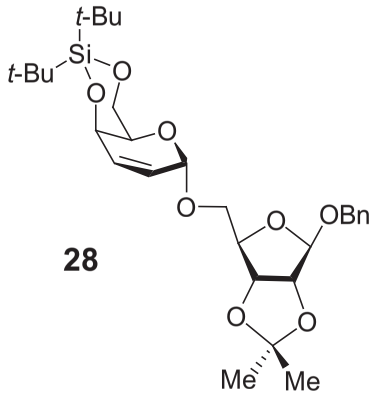



t-Bu
Si
t-Bu
O
O
O
O
OBn
O
O
Me
Me

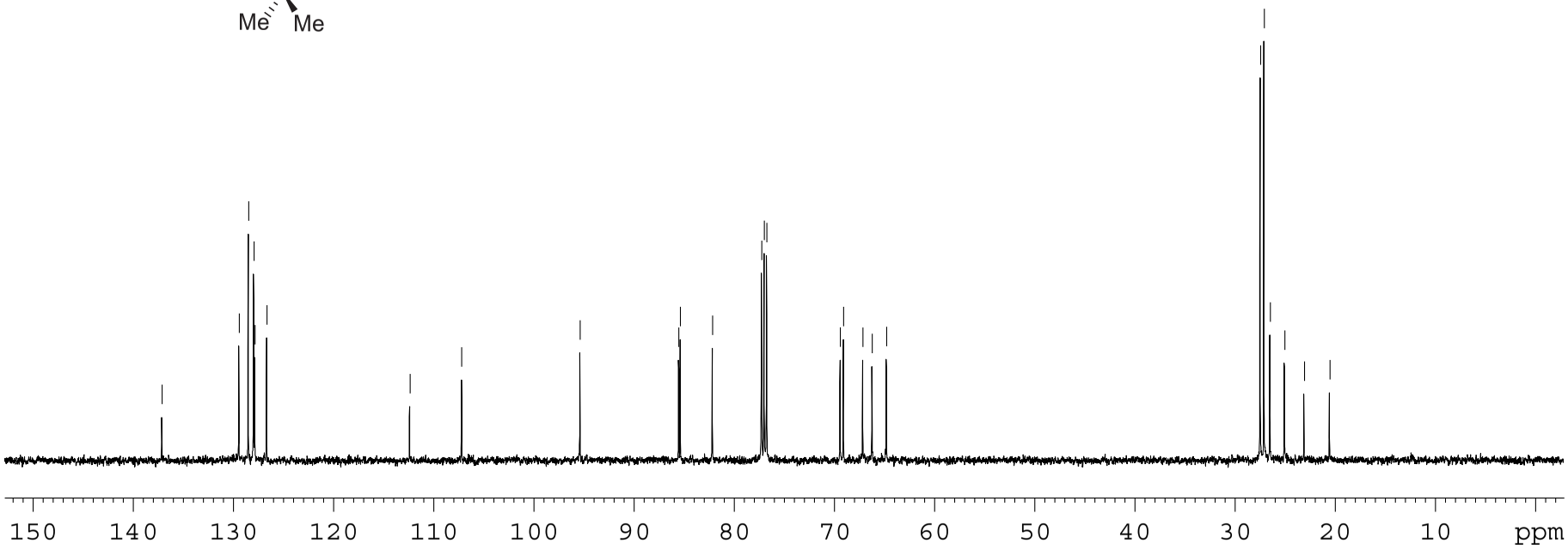
28

8.0
7.5
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
5.128
1.010
1.003
0.981
1.000
3.222
2.179
2.249
1.105
2.096
1.051
3.135
3.258
9.788
8.985

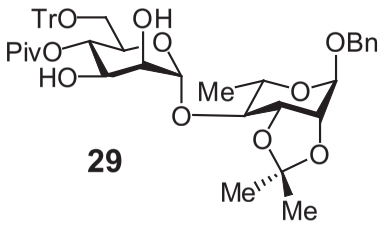
137.122
129.417
128.476
127.941
127.841
126.651
112.361
107.217
95.388
85.539
85.381
82.165
77.255
77.001
76.749
69.414
69.087
67.157
66.229
64.787
27.452
27.083
26.482
25.033
23.073
20.526



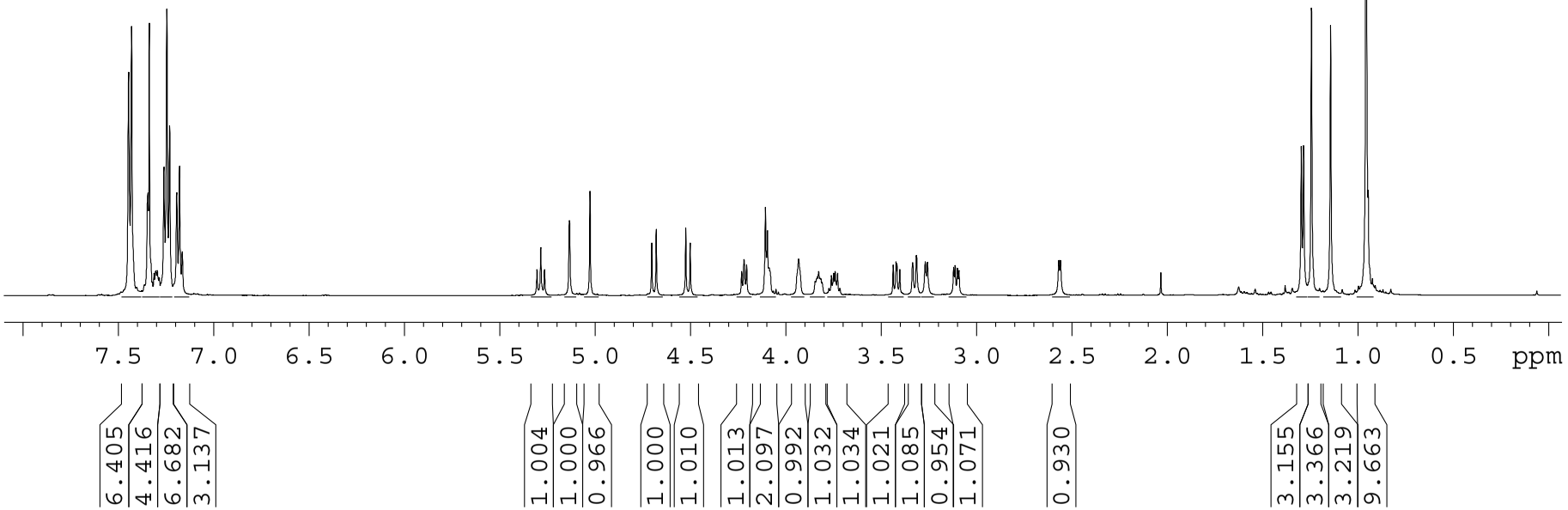
28



GJM-III-011

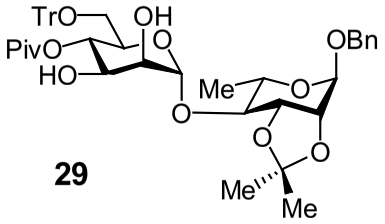


29

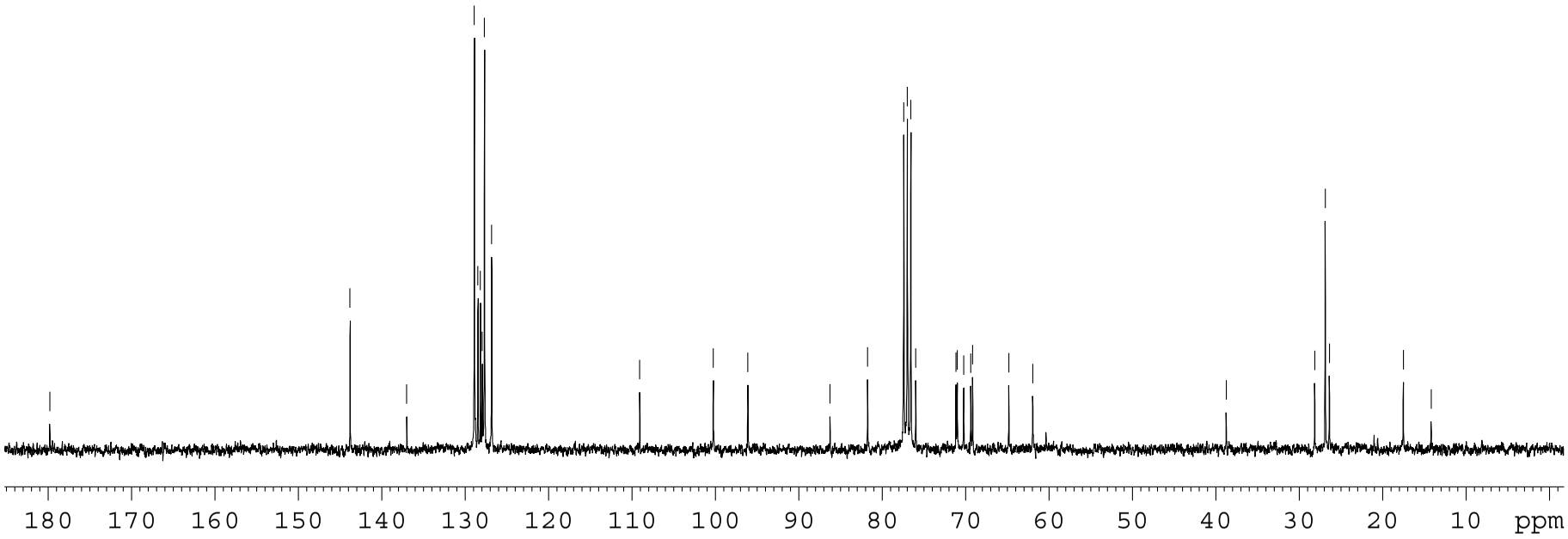


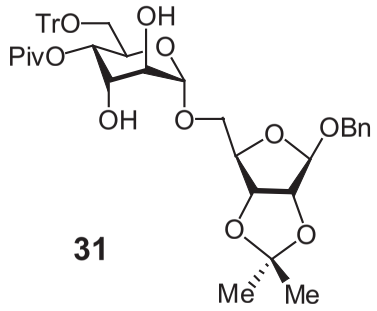
GJM-III-011

179.797
143.829
137.027
128.924
128.490
128.190
127.969
127.705
126.840
109.090
100.263
96.125
86.268
81.761
77.422
76.999
76.575
75.990
71.163
71.006
70.233
69.392
69.168
64.821
61.954
38.748
28.139
26.880
26.381
17.514
14.180



29

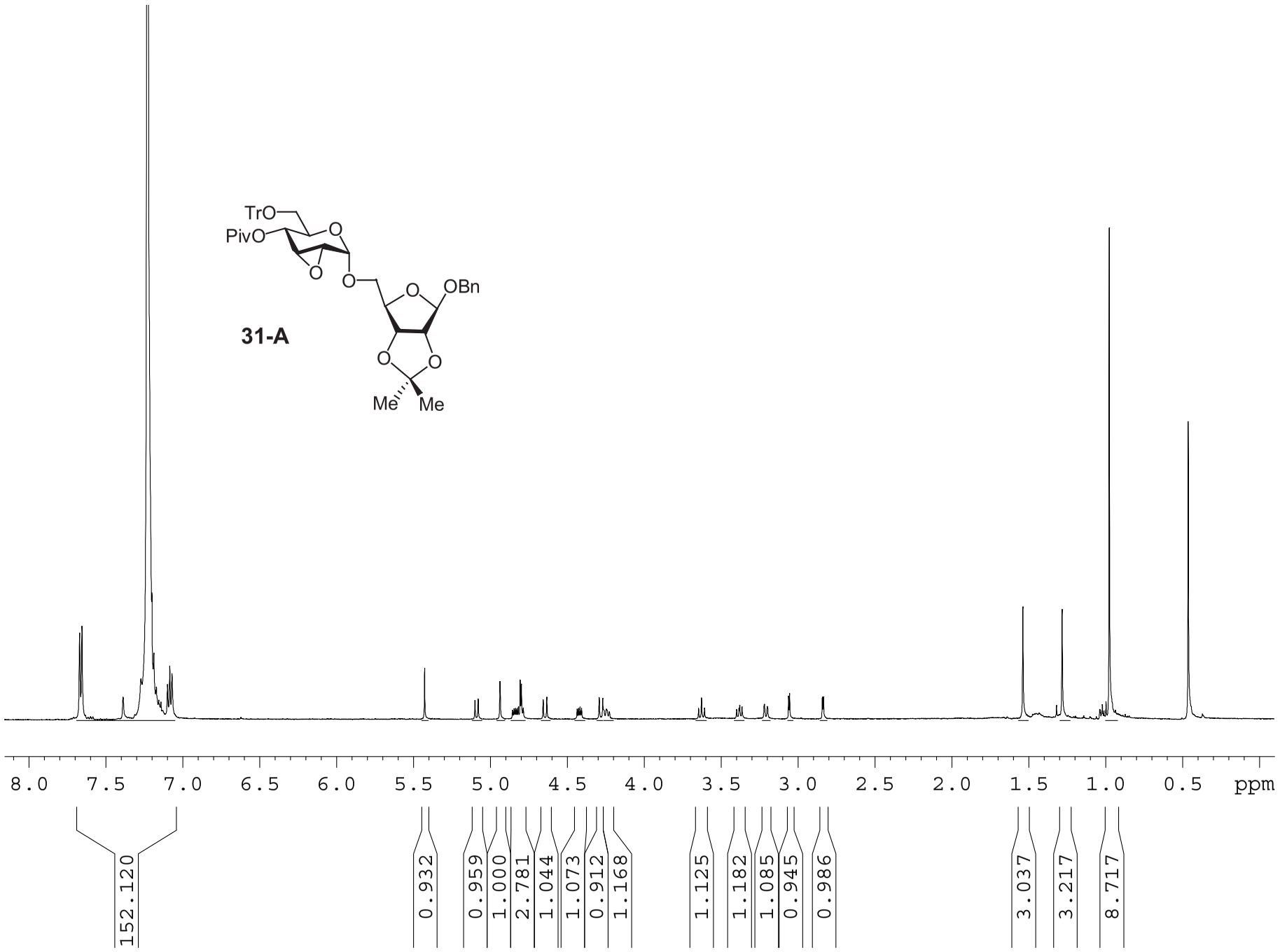



TrO
OH
PivO
O
OH
O
O
OBn
O
O
Me
Me

31

7.5
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
23.107
0.956
1.000
0.956
1.041
1.049
1.092
1.976
1.001
1.018
1.117
1.104
1.082
1.014
1.078
0.936
0.946
3.415
3.644
9.219

GJM-III-020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PivO
O
O
O
O
OBn
O
O
Me
Me
31-A
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7.5
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
152.120
0.932
0.959
1.000
2.781
1.044
1.073
0.912
1.168
1.125
1.182
1.085
0.945
0.986
3.037
3.217
8.717

HN-II-56

171.624
166.817
155.375
133.923
131.785
130.575
129.946
128.622
126.987
116.484
98.033
77.261
77.005
76.751
74.398
71.583
70.397
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66.208
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37.156
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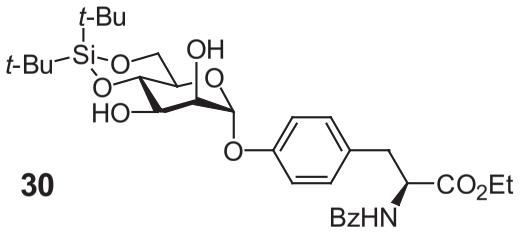
27.142
26.980
22.643
19.894
14.143



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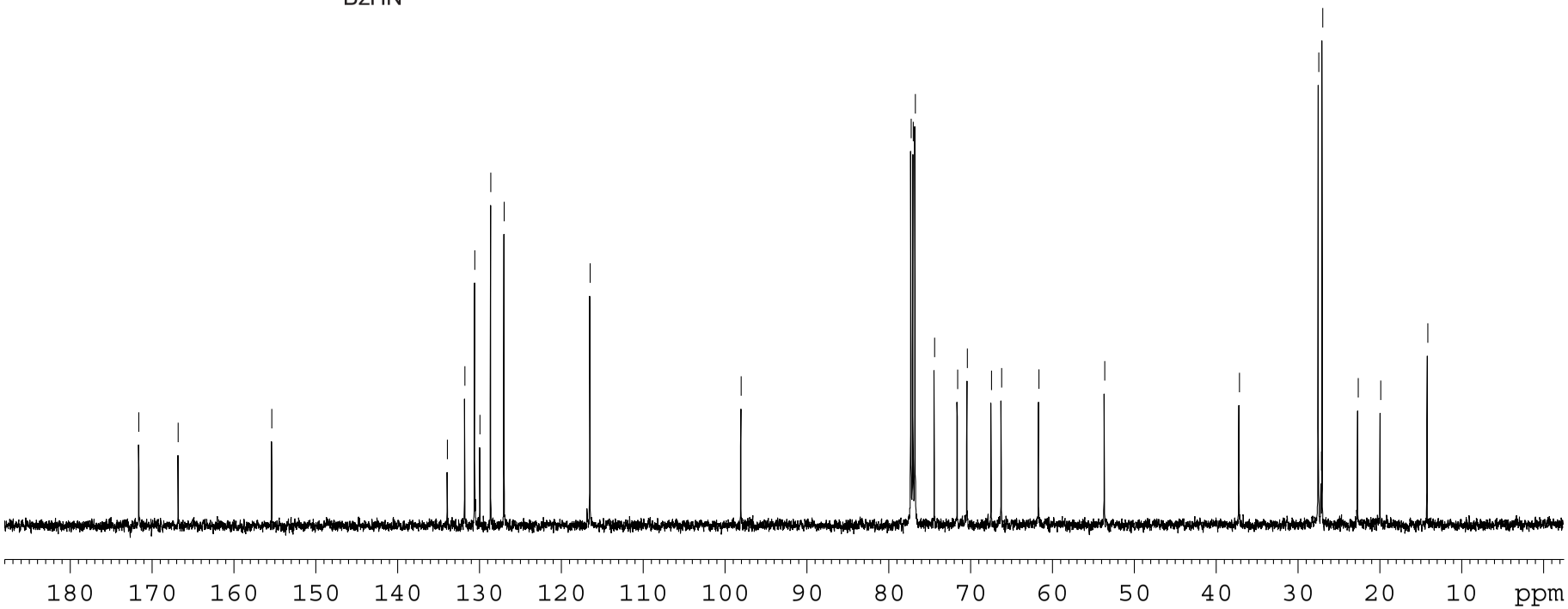

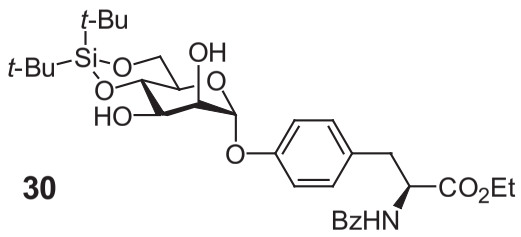
t-Bu
t-Bu
Si
O
O
OH
O
HO
O
CO2Et
BzHN

30

8.0
7.5
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
2.176
1.091
2.166
2.182
2.188
1.080
1.000
1.075
3.332
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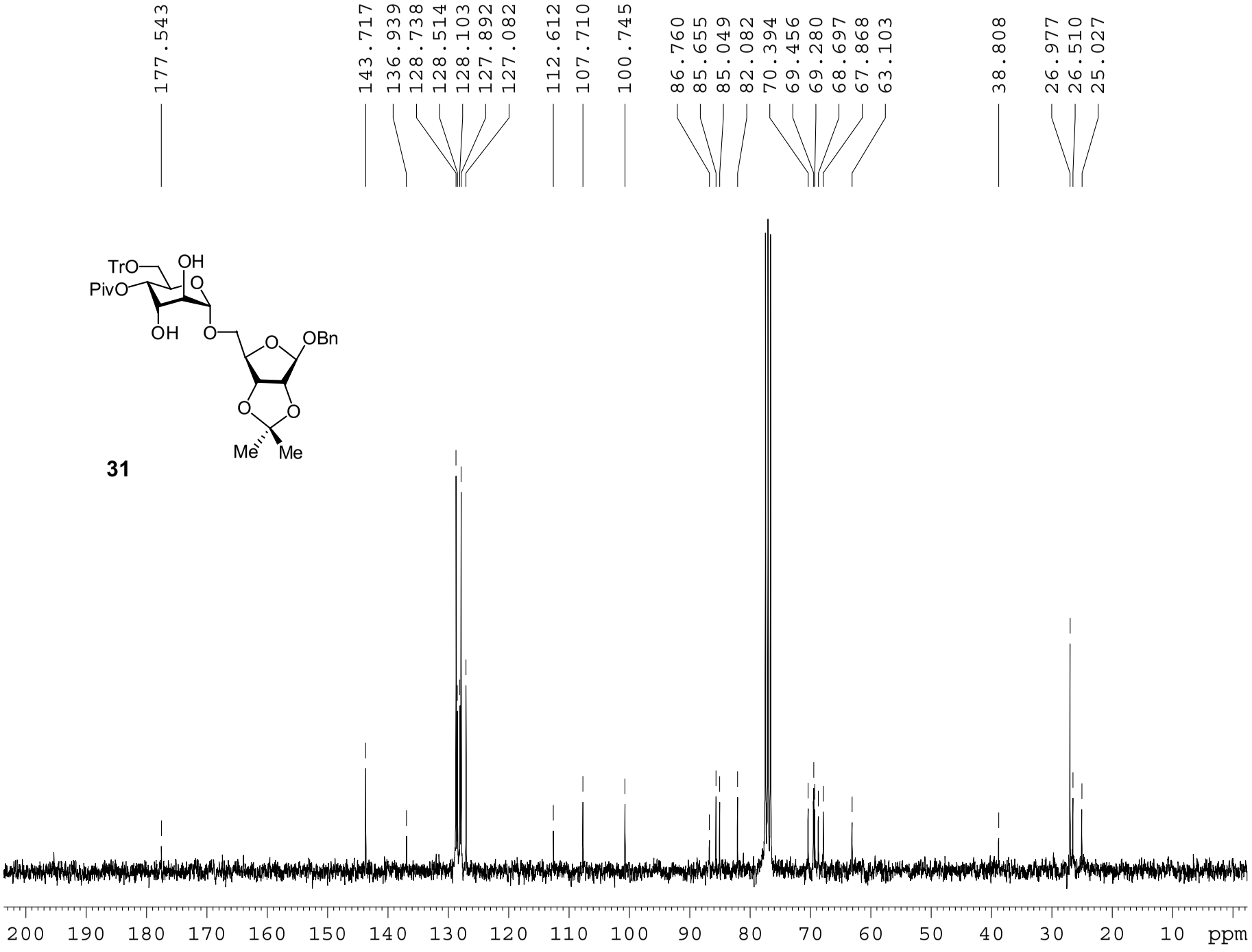
1.190
1.054
2.210
0.982
1.012
3.587
9.735
9.463

GJM-III-026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143.717
136.939
128.738
128.514
128.103
127.892
127.082
112.612
107.710
100.745
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85.655
85.049
82.082
70.394
69.456
69.280
68.697
67.868
63.103
38.808
26.977
26.510
25.027
TrO
OH
PivO
O
OH
O
O
OBn
O
O
Me
Me
31
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm