

Design, Synthesis, and Antifouling Activity of Glucosamine-based Isocyanides

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7a. **7a** was synthesized according to the general procedure in the main text (69% yield).

$[\alpha]_D^{26} +65.3$ (c 7.51, CHCl_3); IR (neat) 3327, 3024, 2959, 1747, 1692, 1529, 1432, 1370, 1220, 1145, 1031, 937, 755, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.03 (3H, s), 2.05 (3H, s), 2.08 (3H, s), 2.18 (3H, s), 4.00 (1H, ddd, $J = 2.4, 3.9, 9.8$ Hz), 4.06 (1H, dd, $J = 1.8, 12.6$ Hz), 4.25 (1H, dd, $J = 3.9, 12.2$ Hz), 4.55 (1H, td, $J = 2.9, 9.7$ Hz), 5.18 – 5.31 (2H, m), 5.73 – 5.31 (1H, m), 6.20 (1H, t, $J = 3.9$ Hz), 8.13 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 20.4, 20.9, 21.0, 21.2, 49.8, 61.7, 67.7, 70.4, 70.7, 90.6, 160.9, 168.8, 169.4, 171.0, 171.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{21}\text{O}_{10}\text{NNa}$, 398.1057; Found 398.1050.

6a. **6a** was synthesized according to the general procedure in the main text (82% yield).

$[\alpha]_D^{16} +145.5$ (c 2.01, CHCl_3); IR (neat) 3024, 2963, 2854, 2148, 1757, 1432, 1371, 1214, 1144, 1090, 1014, 973, 937, 889, 756, 668 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.04 (3H, s), 2.07 (3H, s), 2.11 (3H, s), 2.24 (3H, s), 3.98 (1H, dd, $J = 3.9, 10.7$ Hz), 4.03 (1H, dd, $J = 2.4, 12.2$ Hz), 4.07 – 4.11 (1H, m), 4.28 (1H, dd, $J = 3.9, 12.2$ Hz), 5.01 (1H, t, $J = 9.7$ Hz), 5.54 (1H, t, $J = 10.7$ Hz), 6.40 (1H, t, $J = 3.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.5, 20.6, 54.7, 61.1, 67.1, 69.7, 70.0, 88.3, 168.3, 169.3, 169.7, 170.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{O}_9\text{NNa}$, 380.0958; Found 380.0951.

7b. **7b** was synthesized according to the general procedure in the main text (45% yield).

$[\alpha]_D^{26} +24.5$ (c 1.02, CHCl_3); IR (neat) 2955, 2918, 2850, 1743, 1684, 1520, 1467, 1377, 1243, 1220, 1166, 1113, 1029, 931, 758, 721 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.87 (12H, t, $J = 6.8$ Hz), 1.25 – 1.71 (104H, m), 2.23 – 2.55 (8H, m), 3.99 – 4.33 (4H, m), 5.15 – 5.33 (2H, m), 5.63 – 5.70 (1H, m), 6.21 (1H, t, $J = 3.4$ Hz), 8.11 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.7, 24.7, 24.8, 29.09, 29.12, 29.23, 29.36, 29.44, 29.48, 29.51, 29.62, 29.66, 29.70, 31.9, 49.7, 61.1, 61.3, 61.5, 61.7, 62.6, 63.6, 65.8, 66.8, 67.0, 69.9, 90.0, 90.1, 95.3, 119.9, 158.7, 159.8, 171.31, 171.35, 172.4, 173.4, 174.6.

6b. **6b** was synthesized according to the general procedure in the main text (54% yield).

$[\alpha]_D^{16} +59.3$ (c 0.91, CHCl_3); IR (neat) 2955, 2917, 2850, 2150, 1754, 1467, 1379, 1265, 1243, 1220, 1168, 1108, 1032, 924, 721, cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.88 (12H, t, $J = 6.8$ Hz), 1.25 – 1.71 (104H, m), 2.23 – 2.55 (8H, m), 3.96 (1H, dd, $J = 3.4, 10.7$ Hz), 4.03 – 4.09 (2H, m), 4.22 (1H, dd, $J = 4.4, 10.7$ Hz), 5.03 (1H, t, $J = 9.7$ Hz), 5.56 (1H, t, $J = 10.2$ Hz), 6.41 (1H, t, $J = 3.9$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.1, 22.7, 24.68, 24.71, 29.0, 29.1, 29.21, 29.25, 29.3, 29.45, 29.49, 29.61, 29.66, 29.7, 31.9, 33.88, 33.91, 33.94, 54.9, 61.0, 66.8, 69.6, 70.1, 88.1, 171.2, 172.0, 172.4, 173.2.

9c. **9c** was synthesized according to the general procedure in the main text (33% yield).

$[\alpha]_D^{27} +57.9$ (c 4.52, CHCl₃); IR (neat) 3481, 3027, 2947, 1747, 1718, 1590, 1494, 1468, 1429, 1384, 1337, 1220, 1173, 1082, 1040, 973, 900, 873, 818, 794, 756, 725, 691, 667, 639 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.88 (3H, s), 2.04 (3H, s), 2.11 (3H, s), 4.01 (1H, ddd, J = 2.4, 4.9, 10.2 Hz), 4.17 (1H, dd, J = 2.4, 12.2 Hz), 4.35 (1H, dd, J = 5.4, 10.7 Hz), 4.60 (1H, dd, J = 8.3, 10.7 Hz), 5.22 (1H, dd, J = 9.3, 10.2 Hz), 5.88 (1H, dd, J = 9.3, 10.7 Hz), 5.98 (1H, d, J = 8.3 Hz), 6.90 (1H, dd, J = 1.0, 8.9 Hz), 6.99 (1H, t, J = 7.8 Hz), 7.20 (2H, dd, J = 7.3, 7.8 Hz), 7.72 (2H, t, J = 3.4, 5.3 Hz), 7.84 (1H, t, J = 2.9, 5.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.4, 20.5, 20.6, 54.4, 61.9, 68.9, 70.6, 72.0, 96.2, 117.0, 123.2, 123.6, 129.4, 131.2, 134.3, 156.3, 169.4, 170.0, 170.6; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₂₆H₂₅O₁₀NNa, 534.1370; Found 534.1365.

7c. **7c** was synthesized according to the general procedure in the main text (10% overall yield).

$[\alpha]_D^{25} +12.9$ (c 0.28, CHCl₃); IR (neat) 3749, 3734, 3674, 3648, 3336, 2958, 2883, 2374, 2348, 2310, 1748, 1671, 1590, 1520, 1374, 1224, 1070, 1043, 903, 758, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.03 (3H, s), 2.05 (3H, s), 2.06 (3H, s), 3.88 (1H, ddd, J = 2.4, 5.3, 7.8 Hz), 4.13 – 4.23 (1H, m), 4.29 (1H, dd, J = 5.3, 12.2 Hz), 4.89 (1H, d, J = 8.3 Hz), 5.10 – 5.18 (1H, m), 5.26 (1H, d, J = 8.3 Hz), 5.44 (1H, dd, J = 9.3, 10.7 Hz), 5.75 – 5.81 (1H, m), 6.97 – 7.13 (3H, m), 7.28 (2H, dd, J = 1.4, 8.4 Hz), 8.20 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 20.5, 20.6, 20.7, 53.6, 56.8, 61.9, 62.0, 68.0, 68.5, 71.5, 71.8, 71.9, 72.0, 98.8, 99.8, 116.8, 117.0, 123.2, 123.7, 129.5, 129.7, 156.6, 156.8, 161.0, 164.8, 169.4, 170.5, 170.6, 170.8; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₉H₂₃O₉NNa, 432.1265; Found 432.1260.

6c. **6c** was synthesized according to the general procedure in the main text (51% yield).

$[\alpha]_D^{25} +8.0$ (c 0.13, CHCl₃); IR (neat) 2959, 2361, 2342, 2147, 1757, 1591, 1493, 1368, 1221, 1051, 898, 817, 757, 692 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.04 (3H, s), 2.08 (3H, s), 2.14 (3H, s), 3.86 (1H, ddd, J = 2.4, 5.3, 7.3 Hz), 3.94 (1H, dd, J = 7.8, 10.2 Hz), 4.15 (1H, dd, J = 2.4, 12.7 Hz), 4.31 (1H, dd, J = 5.3, 12.2 Hz), 5.02 (1H, t, J = 9.8 Hz), 5.09 (1H, d, J = 8.3 Hz), 5.39 (1H, dd, J = 9.3, 10.2 Hz), 7.09 (2H, dd, J = 1.0, 8.8 Hz), 7.13 (1H, t, J = 7.3 Hz), 7.35 (2H, t, J = 7.3 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 20.7, 20.8, 20.9, 57.4, 61.9, 67.8, 72.3, 72.5, 99.5, 117.9, 124.5, 130.0, 156.7, 169.7, 169.9, 170.8; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₁₉H₂₁O₈NNa, 414.1159; Found 414.1168.

9d. **9d** was synthesized according to the general procedure in the main text (54% yield).

$[\alpha]_D^{28} +7.9$ (c 0.32, CHCl₃); IR (neat) 2928, 2342, 1752, 1718, 1379, 1369, 1228, 1139, 1079, 1040, 975, 899, 722, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.86 (3H, s), 2.02 (3H, s), 2.13 (3H, s), 3.86 (1H, ddd, J = 2.4, 4.4, 10.2 Hz), 4.20 (1H, dd, J = 2.0, 12.4 Hz), 4.32 – 4.37 (1H, m), 4.38

(1H, t, $J = 10.7$ Hz), 4.53 (1H, d, $J = 12.2$ Hz), 4.85 (1H, d, $J = 11.7$ Hz), 5.19 (1H, t, $J = 9.8$ Hz), 5.37 (1H, d, $J = 8.3$ Hz), 5.78 (1H, dd, $J = 9.3, 10.7$ Hz), 7.07 – 7.16 (5H, m), 7.71 – 7.79 (4H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 20.7, 20.9, 21.1, 54.9, 62.3, 69.3, 70.9, 72.1, 97.4, 123.8, 128.0, 128.1, 128.5, 134.4, 136.2, 169.8, 170.4, 171.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{27}\text{O}_{10}\text{NNa}$, 548.1527; Found 548.1519.

7d. **7d** was synthesized according to the general procedure in the main text (41% overall yield). $[\alpha]_{\text{D}}^{25} -31.6$ (c 1.57, CHCl_3); IR (neat) 2928, 2342, 2342, 1752, 1718, 1379, 1369, 1228, 1139, 1079, 1040, 975, 899, 722, 701 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.02 (3H, s), 2.10 (3H, s), 2.16 (3H, s), 3.61 – 3.71 (1H, m), 4.03 (1H, dt, $J = 2.9, 12.2$ Hz), 4.24 – 4.37 (2H, m), 4.58 – 4.72 (2H, m), 4.90 (1H, d, $J = 11.7$ Hz), 5.09 (1H, td, $J = 2.4, 9.8$ Hz), 5.27 (1H, t, $J = 9.3$ Hz), 5.46 – 5.49 (1H, m), 7.36 – 7.28 (5H, m), 8.13 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 20.8, 20.9, 21.0, 21.1, 21.1, 31.2, 53.0, 57.2, 62.2, 62.3, 68.4, 68.8, 71.0, 71.5, 72.1, 72.2, 72.2, 72.4, 99.4, 99.8, 128.4, 128.4, 128.5, 128.7, 128.8, 128.9, 136.8, 161.2, 165.1, 169.7, 170.9, 171.0, 171.0, 170.2; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{27}\text{O}_{10}\text{NNa}$, 446.1421; Found 446.1415.

6d. **6d** was synthesized according to the general procedure in the main text (61% yield). $[\alpha]_{\text{D}}^{25} +4.5$ (c 0.09, CHCl_3); IR (neat) 3035, 2952, 2881, 2360, 2147, 1754, 1497, 1455, 1367, 1226, 1164, 1109, 1054, 969, 898, 752, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.03 (3H, s), 2.10 (3H, s), 2.10 (3H, s), 3.68 (1H, ddd, $J = 2.2, 4.4, 10.7$ Hz), 3.71 (1H, dd, $J = 7.8, 10.7$ Hz), 4.14 (1H, dd, $J = 2.0, 12.8$ Hz), 4.28 (1H, dd, $J = 4.4, 12.8$ Hz), 4.60 (1H, d, $J = 8.3$ Hz), 4.70 (1H, d, $J = 11.7$ Hz), 4.95 (1H, d, $J = 11.7$ Hz), 4.96 (1H, d, $J = 8.8$ Hz), 5.27 (1H, t, $J = 9.3$ Hz), 7.32 – 7.44 (5H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 20.7, 20.8, 21.0, 54.3, 54.4, 61.9, 68.0, 71.7, 72.3, 72.4, 98.8, 128.6, 128.8, 129.0, 135.9, 169.7, 169.9, 170.8; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{23}\text{O}_8\text{NNa}$, 428.1216; Found 428.1324.

9e. **9e** was synthesized according to the general procedure in the main text (66% yield). $[\alpha]_{\text{D}}^{27} +42.1$ (c 1.04, CHCl_3); IR (neat) 3480, 3022, 2925, 1747, 1716, 1468, 1428, 1384, 1225, 1128, 1079, 1038, 899, 772, 725 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.80 (3H, s), 1.97 (3H, s), 2.06 (3H, s), 3.80 (1H, ddd, $J = 2.4, 4.9, 10.2$ Hz), 4.00 (1H, dd, $J = 6.8, 13.2$ Hz), 4.12 (1H, dd, $J = 2.0, 12.2$ Hz), 4.20 – 4.34 (3H, m), 5.04 (2H, ddd, $J = 1.0, 10.2, 14.6$ Hz), 5.12 (1H, t, $J = 10.2$ Hz), 5.35 (1H, d, $J = 8.3$ Hz), 5.62 – 5.71 (1H, m), 5.73 (1H, dd, $J = 9.3, 10.7$ Hz), 5.73 (1H, dd, $J = 9.3, 10.7$ Hz), 7.68 (2H, dd, $J = 2.9, 5.4$ Hz), 7.80 (2H, dd, $J = 2.9, 5.4$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.8, 20.9, 21.0, 54.9, 62.3, 69.3, 70.5, 71.0, 72.1, 97.4, 118.2, 123.9, 131.7, 133.5, 134.6, 169.8, 170.5, 171.1; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{25}\text{O}_{10}\text{NNa}$, 498.1370; Found 498.1366.

7e. **7e** was synthesized according to the general procedure in the main text (20% overall yield).

$[\alpha]_D^{26} +26.0$ (c 0.41, CHCl_3); IR (neat) 3084, 2941, 2881, 2148, 1752, 1366, 1223, 1170, 1110, 1053, 929, 771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.02 (3H, s), 2.08 (3H, s), 2.11 (3H, s), 3.67 (1H, dd, $J = 8.3, 10.2$ Hz), 3.67 – 3.75 (1H, m), 4.17 (1H, dd, $J = 2.4, 12.2$ Hz), 4.20 (1H, dd, $J = 6.8, 12.6$ Hz), 4.27 (1H, dd, $J = 4.4, 12.2$ Hz), 4.62 (1H, d, $J = 9.8$ Hz), 4.95 (1H, d, $J = 7.8$ Hz), 5.41 – 5.26 (3H, m), 5.92 (1H, ddd, $J = 5.8, 11.2, 17.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.1, 20.2, 20.4, 29.4, 57.0, 61.2, 67.3, 67.4, 70.4, 70.5, 71.7, 71.8, 98.5, 98.6, 118.6, 132.3, 169.1, 169.3, 170.2; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_8\text{NNa}$, 378.1159; Found 378.1166.

6e. **6e** was synthesized according to the general procedure in the main text (32% yield).

$[\alpha]_D^{26} +26.0$ (c 0.41, CHCl_3); IR (neat) 3084, 2941, 2881, 2148, 1752, 1366, 1223, 1170, 1110, 1053, 929, 771 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 2.02 (3H, s), 2.08 (3H, s), 2.11 (3H, s), 3.67 (1H, dd, $J = 8.3, 10.2$ Hz), 3.67 – 3.75 (1H, m), 4.17 (1H, dd, $J = 2.4, 12.2$ Hz), 4.20 (1H, dd, $J = 6.8, 12.6$ Hz), 4.27 (1H, dd, $J = 4.4, 12.2$ Hz), 4.62 (1H, d, $J = 9.8$ Hz), 4.95 (1H, d, $J = 7.8$ Hz), 5.41 – 5.26 (3H, m), 5.92 (1H, ddd, $J = 5.8, 11.2, 17.0$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.1, 20.2, 20.4, 29.4, 57.0, 61.2, 67.3, 67.4, 70.4, 70.5, 71.7, 71.8, 98.5, 98.6, 118.6, 132.3, 169.1, 169.3, 170.2; $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{21}\text{O}_8\text{NNa}$, 378.1159; Found 378.1166.

9f. **9f** was synthesized according to the general procedure in the main text (31% yield).

$[\alpha]_D^{26} +21.8$ (c 4.31, CHCl_3); IR (neat) 3481, 3024, 2972, 1754, 1718, 1613, 1468, 1428, 1384, 1335, 1217, 1170, 1144, 1113, 1072, 1029, 973, 932, 900, 873, 829, 795, 756, 725, 667, 640, 629, 602 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.83 (3H, d, $J = 5.8$ Hz), 1.10 (3H, d, $J = 5.8$ Hz), 1.81 (3H, s), 1.98 (3H, s), 2.05 (3H, s), 3.85 – 3.80 (2H, m), 4.11 (1H, dd, $J = 2.4, 12.2$ Hz), 4.24 (1H, dd, $J = 8.4, 10.7$ Hz), 4.27 (1H, dd, $J = 4.8, 12.2$ Hz), 5.11 (1H, t, $J = 9.2$ Hz), 5.38 (1H, d, $J = 8.4$ Hz), 5.74 (1H, dd, $J = 9.2, 10.7$ Hz), 7.70 (2H, dd, $J = 2.9, 5.3$ Hz), 7.81 (2H, dd, $J = 3.4, 5.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.7, 20.9, 21.0, 22.0, 23.4, 55.1, 62.5, 69.4, 71.1, 71.9, 72.8, 97.07, 123.8, 131.6, 134.5, 169.7, 170.4, 170.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{23}\text{H}_{27}\text{O}_{10}\text{NNa}$, 500.1527; Found 500.1525.

7f. **7f** was synthesized according to the general procedure in the main text (31% overall yield).

$[\alpha]_D^{26} -7.9$ (c 2.23, CHCl_3); IR (neat) 3325, 2974, 2876, 1748, 1671, 1528, 1435, 1372, 1320, 1230, 1159, 1112, 1065, 1038, 986, 935, 904, 835, 754, 667 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 1.08 – 1.25 (6H, m), 2.01 (3H, s), 2.04 (3H, s), 2.06 (3H, s), 3.33 – 3.80 (1H, m), 3.89 – 4.00 (1H, m), 4.08 – 4.14 (1H, m), 4.23 – 4.31 (1H, m), 4.38 – 4.42 (1H, m), 4.82 (1H, d, $J = 8.3$ Hz), 4.96 – 5.10 (1H, m), 5.40 (1H, t, $J = 10.7$ Hz), 5.78 – 6.13 (1H, m), 7.98 – 8.14 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 20.5, 20.6, 20.7, 20.7, 21.8, 21.9, 23.2, 23.2, 57.1, 62.0, 62.3, 68.4, 68.4, 71.6,

71.6, 71.9, 72.0, 72.6, 73.4, 98.9, 100.1, 161.0, 165.3, 169.4, 169.5, 170.6, 170.7, 170.8; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{16}H_{25}O_9NNa$, 398.1421; Found 398.1419.

6f. **6f** was synthesized according to the general procedure in the main text (49% yield).

$[\alpha]_D^{24} +27.0$ (c 1.02, $CHCl_3$); IR (neat) 3852, 3837, 3801, 3734, 3674, 3648, 3628, 2976, 2146, 1749, 1683, 1652, 1635, 1558, 1540, 1520, 1507, 1456, 1373, 1224, 1107, 1055, 965, 772 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 1.23 (1H, d, $J = 6.3$ Hz), 1.27 (1H, d, $J = 6.3$ Hz), 2.02 (3H, s), 2.06 (3H, s), 2.10 (3H, s), 3.60 (1H, dd, $J = 7.8, 10.2$ Hz), 3.70 (1H, ddd, $J = 2.4, 4.9, 10.3$ Hz), 4.00 - 4.05 (1H, m), 4.25 (1H, dd, $J = 4.9, 12.2$ Hz), 4.61 (1H, d, $J = 7.8$ Hz), 4.91 (1H, t, $J = 9.8$ Hz), 5.30 (1H, t, $J = 10.7$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.9, 23.4, 58.0, 62.1, 68.1, 71.9, 72.2, 72.4, 72.5, 73.9, 99.3, 169.7, 169.9, 170.9; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{16}H_{23}O_8NNa$, 380.1315; Found 380.1324.

9g. **9g** was synthesized according to the general procedure in the main text (77% yield).

$[\alpha]_D^{27} +30.4$ (c 7.38, $CHCl_3$); IR (neat) 3484, 3027, 2956, 1752, 1719, 1387, 1227, 1164, 1082, 1043, 972, 900, 760, 723 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 1.86 (3H, s), 2.03 (3H, s), 2.12 (3H, s), 3.90 (1H, ddd, $J = 1.5, 4.4, 11.2$ Hz), 3.91 (1H, dd, $J = 8.3, 11.2$ Hz), 4.08 (1H, dd, $J = 8.8, 12.7$ Hz), 4.18 (1H, dd, $J = 2.4, 12.7$ Hz), 4.30 - 4.39 (2H, m), 5.18 (1H, dd, $J = 9.3, 10.2$ Hz), 5.49 (1H, d, $J = 8.3$ Hz), 5.49 (1H, d, $J = 8.3$ Hz), 5.81 (1H, dd, $J = 8.9, 10.7$ Hz), 7.74 (2H, dd, $J = 3.4, 5.9$ Hz), 7.85 (2H, dd, $J = 3.4, 5.9$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.7, 20.9, 21.0, 54.5, 62.0, 66.2, 66.5, 68.9, 70.6, 72.4, 98.5, 123.9, 131.5, 134.7, 169.7, 170.4, 170.9; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{22}H_{22}O_{10}NF_3Na$, 540.1088; Found 540.1079.

7g. **7g** was synthesized according to the general procedure in the main text (37% overall yield).

$[\alpha]_D^{27} +18.2$ (c 0.12, $CHCl_3$); IR (neat) 3316, 2921, 2851, 1745, 1691, 1678, 1547, 1529, 1441, 1369, 1220, 1161, 1038, 965, 907, 773 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 2.03 (3H, s), 2.05 (3H, s), 2.09 (3H, s), 3.74 (1H, ddd, $J = 2.4, 4.9, 9.8$ Hz), 3.91 - 4.05 (1H, m), 4.10 - 4.20 (1H, m), 4.26 - 4.31 (1H, m), 4.47 (1H, d, $J = 7.8$ Hz), 5.04 - 5.28 (2H, m), 5.38 (1H, d, $J = 10.7$ Hz), 5.60 - 5.87 (1H, m), 8.17 (1H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 20.9, 21.0, 30.0, 50.5, 53.8, 57.0, 61.9, 62.0, 65.7, 67.9, 68.5, 68.9, 70.5, 71.8, 72.5, 98.1, 100.5, 161.1, 161.3, 169.6, 170.0, 171.0; $[M + Na]^+$ Calcd for $C_{15}H_{20}O_9NF_3Na$, 438.0982; Found 438.0978.

6g. **6g** was synthesized according to the general procedure in the main text (54% yield).

$[\alpha]_D^{27} +18.8$ (c 0.17, $CHCl_3$); IR (neat) 2923, 2852, 2148, 1754, 1442, 1369, 1281, 1222, 1164, 1113, 1062, 970, 902, 772 cm^{-1} ; 1H NMR (400 MHz, $CDCl_3$) δ 2.03 (3H, s), 2.09 (3H, s), 2.12 (3H, s), 3.70 (1H, dd, $J = 8.2, 10.7$ Hz), 3.74 (1H, ddd, $J = 2.0, 4.4, 10.7$ Hz), 4.05 (1H, dd, $J =$

2.1, 8.3 Hz), 4.15 – 4.22 (2H, m), 4.27 (1H, dd, $J = 4.4, 12.2$ Hz), 4.71 (1H, d, $J = 8.3$ Hz), 4.96 (1H, t, $J = 9.8$ Hz), 5.32 (1H, dd, $J = 9.3, 10.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 20.7, 20.8, 20.9, 61.6, 67.6, 72.0, 72.7, 76.9, 100.2, 131.2, 169.6, 169.8, 170.7; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_8\text{NF}_3\text{Na}$, 420.0876; Found 420.0876.

7h. **7h** was synthesized according to the general procedure in the main text (24% overall yield). $[\alpha]_{\text{D}}^{25} -3.9$ (c 1.02, CHCl_3); IR (neat) 3335, 2956, 2926, 2856, 2360, 1741, 1698, 1668, 1558, 1540, 1520, 1507, 1456, 1418, 1385, 1220, 1165, 1112, 1084, 1029 cm^{-1} ; ^1H -NMR (400 MHz, CDCl_3) δ 0.85 – 0.89 (12H, m), 1.10 – 1.35 (27H, m), 1.54 – 1.62 (6H, m), 2.18 – 2.40 (6H, m), 3.62 – 3.80 (1H, m), 3.82 – 3.99 (1H, m), 4.12 – 4.24 (1H, m), 4.28 – 4.47 (1H, m), 4.64 – 4.82 (1H, m), 5.10 – 5.18 (1H, m), 5.35 – 5.59 (1H, m), 7.98 – 8.14 (1H, m); ^{13}C NMR (100 MHz, CDCl_3) δ 14.3, 14.4, 22.1, 22.2, 22.3, 22.9, 22.9, 23.5, 23.6, 23.6, 25.1, 25.2, 25.2, 25.2, 26.0, 29.2, 29.2, 29.2, 29.3, 29.3, 29.4, 29.5, 31.9, 31.9, 32.0, 34.3, 34.3, 34.4, 34.5, 34.5, 37.2, 54.8, 55.0, 57.6, 62.3, 62.5, 63.4, 68.3, 68.9, 69.7, 71.8, 72.1, 72.2, 72.3, 72.6, 72.8, 73.7, 74.4, 75.2, 99.4, 100.0, 100.6, 161.1, 165.3, 172.4, 172.4, 173.3, 173.8, 174.0, 174.8, 175.2; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{61}\text{O}_9\text{NNa}$, 650.4239; Found 650.4257.

6h. **6h** was synthesized according to the general procedure in the main text (60% yield). $[\alpha]_{\text{D}}^{29} +15.1$ (c 9.50, CHCl_3); IR (neat) 3351, 2956, 2928, 2857, 2146, 1818, 1746, 1670, 1520, 1465, 1416, 1382, 1224, 1162, 1109, 1061, 922, 724 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.83 – 0.92, (12H, m), 1.18 – 1.40 (27H, m), 1.55 – 1.64 (6H, m), 2.18 – 2.42 (6H, m), 3.60 (1H, dd, $J = 8.3, 10.7$ Hz), 3.70 (1H, ddd, $J = 2.4, 4.9, 9.8$ Hz), 3.97 – 4.04 (1H, m), 4.11 (1H, dd, $J = 2.4, 12.2$ Hz), 4.19 (1H, dd, $J = 2.4, 12.2$ Hz), 4.61 (1H, d, $J = 7.8$ Hz), 4.93 (1H, t, $J = 9.8$ Hz), 5.32 (1H, t, $J = 10.7$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 14.1, 21.6, 22.5, 23.1, 24.6, 24.7, 28.8, 28.9, 29.0, 31.5, 31.6, 33.7, 33.9, 57.8, 61.7, 67.5, 71.8, 72.0, 73.5, 76.6, 98.9, 172.1, 172.4, 173.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{34}\text{H}_{59}\text{O}_8\text{NNa}$, 632.4133; Found 632.4127.

7i. **7i** was synthesized according to the general procedure in the main text (16% overall yield). $[\alpha]_{\text{D}}^{23} +6.5$ (c 0.20, CHCl_3); IR (neat) 3306, 2918, 2850, 1739, 1665, 1538, 1468, 1372, 1243, 1222, 1163, 1036, 720 cm^{-1} ; ^1H NMR (CDCl_3 , 400 MHz) δ 0.87 (9H, t, $J = 6.8$ Hz), 1.12-1.18 (78H, m), 1.62-1.80 (6H, m), 2.21-2.33 (6H, m), 3.92 (1H, septet, $J = 6.3$ Hz), 4.06-4.19 (2H, m), 4.78 (1H, d, $J = 8.3$ Hz), 5.04 (1H, t, $J = 9.8$ Hz), 5.37 (1H, dd, $J = 10.7, 9.3$ Hz), 5.43 (1H, d, $J = 8.3$ Hz), 5.65 (1H, m), 8.14 (1H, s); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.1, 14.2, 22.0, 22.67, 22.72, 23.27, 23.31, 24.78, 24.79, 24.9, 29.1, 29.27, 29.28, 29.3, 29.5, 29.65, 29.69, 30.2, 31.91, 31.95, 34.0, 34.1, 55.5, 62.3, 68.6, 71.79, 71.82, 72.5, 99.3, 170.0, 172.1, 173.5, 173.6; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$; Calcd for $\text{C}_{57}\text{H}_{113}\text{O}_9\text{NNa}$ 978.8308; Found 978.8330.

6i. **6i** was synthesized according to the general procedure in the main text (54% yield).

$[\alpha]_D^{23} +8.3$ (c 0.03, CHCl₃); IR (neat) 2917, 2849, 2350, 2148, 1749, 1559, 1541, 1507, 1463, 1147, 1046 cm⁻¹; ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (9H, t, $J = 6.3$ Hz), 1.25 (78H, s), 1.59 (6H, s), 2.19-2.39 (6H, m), 3.60 (1H, dd, $J = 10.2, 8.3$ Hz), 3.71 (1H, ddd, $J = 12.2, 9.8, 2.4$ Hz), 4.01 (1H, septet, $J = 5.9$ Hz), 4.11 (1H, dd, $J = 12.2, 2.0$ Hz), 4.19 (1H, dd, $J = 12.2, 4.9$ Hz), 4.91 (1H, d, $J = 8.3$ Hz), 4.93 (1H, dd, $J = 9.8, 9.3$ Hz), 5.32 (1H, dd, $J = 10.3, 9.8$ Hz); ¹³C NMR (CDCl₃, 100 MHz) δ 14.12, 14.14, 21.7, 22.68, 22.70, 23.2, 24.68, 24.79, 24.83, 29.11, 29.13, 29.28, 29.30, 29.4, 29.47, 29.50, 29.65, 29.69, 29.7, 31.92, 31.94, 33.9, 34.0, 57.8, 61.7, 67.6, 71.8, 72.1, 73.6, 99.0, 160.3, 172.2, 172.4, 173.3; HRMS (ESI) m/z : $[M + Na]^+$; Calcd for C₅₈H₁₀₇O₈NNa 968.7889; Found 968.7903.

7j. **7j** was synthesized according to the general procedure in the main text (46% overall yield).

$[\alpha]_D^{27} -19.4$ (c 0.28, CHCl₃); IR (neat) 3307, 3065, 2974, 2874, 2360, 2341, 1725, 1631, 1601, 1584, 1537, 1491, 1452, 1384, 1315, 1270, 1177, 1111, 1069, 1026, 985, 936, 852, 803, 755, 709, 686 cm⁻¹; ¹H-NMR (400 MHz, CDCl₃) δ 1.19 (3H, d, $J = 5.9$ Hz), 1.25 (3H, d, $J = 5.9$ Hz), 3.95 – 4.15 (2H, m), 4.46 (1H, ddd, $J = 3.9, 9.2, 12.2$ Hz), 4.55 - 4.64 (2H, m), 5.03 (1H, d, $J = 9.8$ Hz), 5.55 – 5.78 (2H, m), 5.87 – 6.00 (1H, m), 7.28 – 7.42 (6H, m), 7.42 – 7.60 (3H, m), 7.85 – 8.08 (6H, m), 8.15 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 21.5, 21.6, 21.9, 22.9, 54.5, 57.2, 60.1, 63.1, 69.7, 71.5, 71.6, 71.9, 72, 73.3, 98.9, 100.2, 127.9, 128.1, 129.4, 132.7, 133.2, 160.8, 164.9, 165.7, 166.0; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₃₁H₃₁O₉NNa, 584.1891; Found 584.1903.

6j. **6j** was synthesized according to the general procedure in the main text (35% yield).

$[\alpha]_D^{29} -26.2$ (c 0.30, CHCl₃); IR (neat) 3064, 2975, 2877, 2145, 1729, 1601, 1452, 1316, 1267, 1177, 1108, 1068, 1025, 708 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 1.29 (3H, d, $J = 6.3$ Hz), 1.29 (3H, d, $J = 5.9$ Hz), 3.87 (1H, dd, $J = 7.8, 10.7$ Hz), 4.14 – 4.04 (2H, m), 4.45 (1H, dd, $J = 5.9, 12.2$ Hz), 4.57 (1H, dd, $J = 3.4, 12.2$ Hz), 4.82 (1H, d, $J = 7.8$ Hz), 5.45 (1H, t, $J = 9.8$ Hz), 5.85 (1H, t, $J = 9.8$ Hz), 7.30 – 7.42 (6H, m), 7.47 – 7.56 (3H, m), 7.87 (4H, m), 7.96 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ 22.0, 23.4, 58.3, 63.3, 69.3, 72.4, 72.6, 74.1, 99.5, 128.6, 128.7, 128.8, 129.7, 129.9, 130.1, 130.2, 133.4, 133.9, 165.4, 165.4, 166.3; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for C₃₁H₂₉O₈NNa, 566.1758; Found 566.1787.

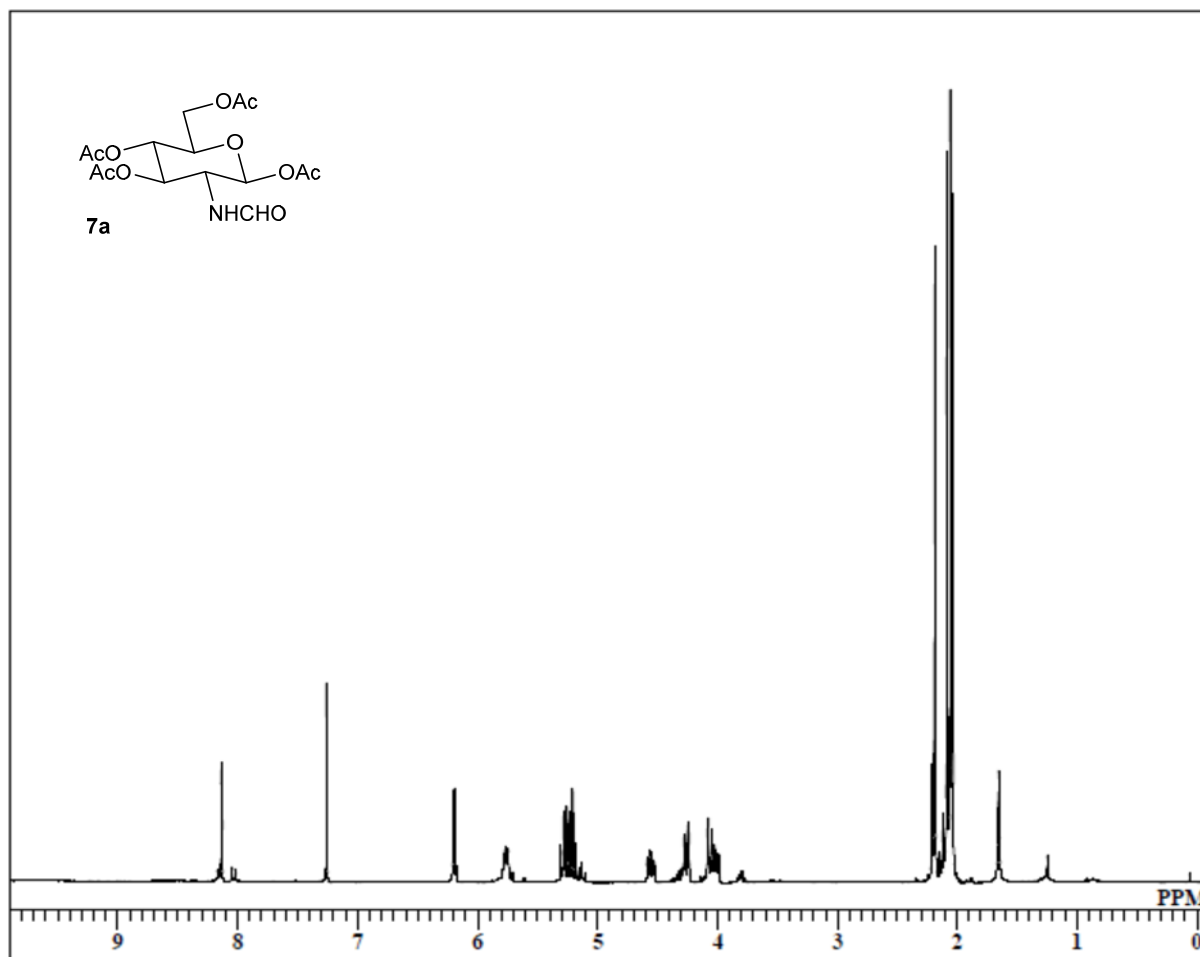
7k. **7k** was synthesized according to the general procedure in the main text (43% overall yield).

$[\alpha]_D^{29} -13.8$ (c 0.24, CHCl₃); IR (neat) 3091, 3853, 3838, 3819, 3750, 3734, 3674, 3648, 3628, 3586, 3566, 2954, 2930, 2885, 2857, 1698, 1684, 1653, 1617, 1558, 1540, 1520, 1507, 1473, 1457, 1386, 1361, 1255, 1095, 1065, 1039, 836, 776, 669 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ

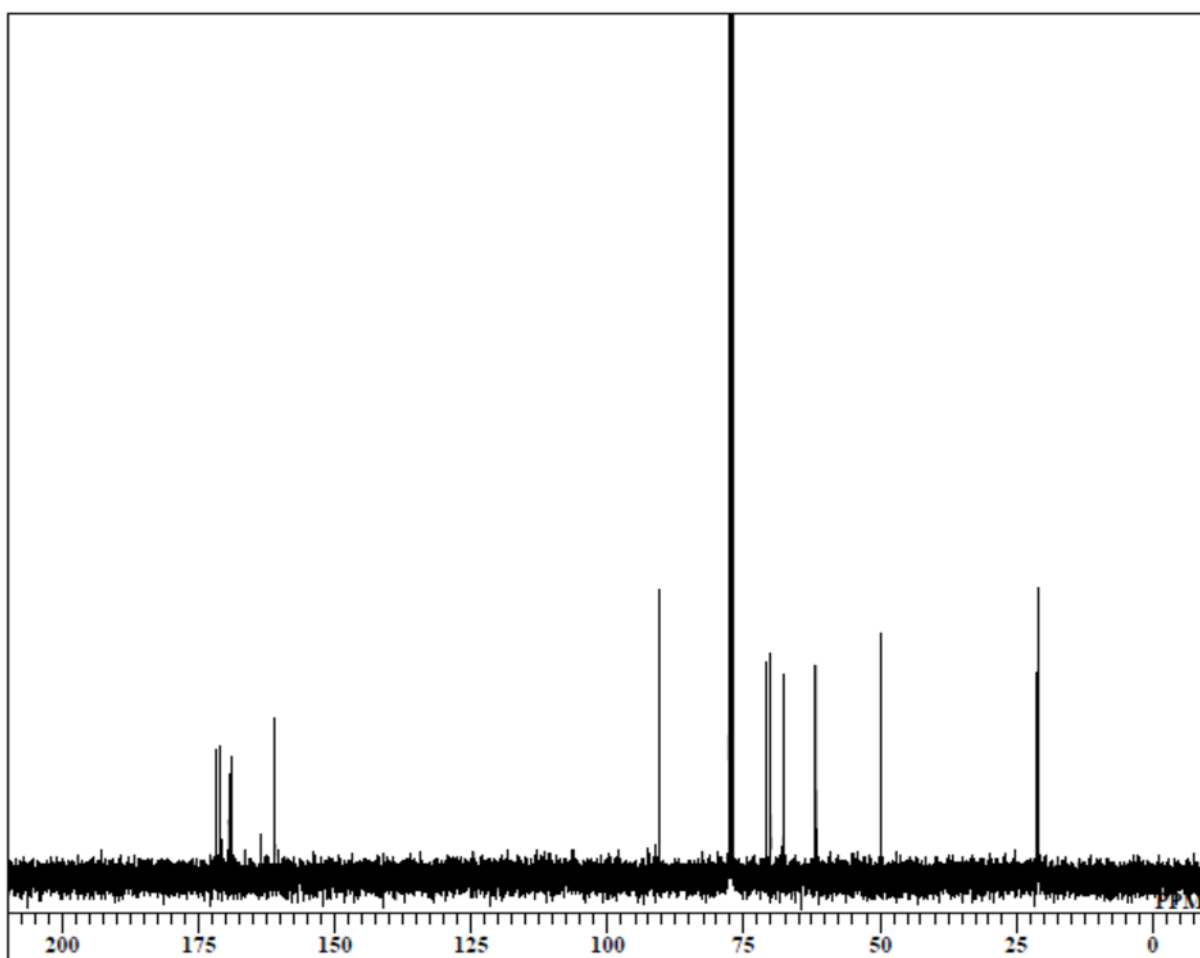
0.03 (3H, s), 0.04 (3H, s), 0.09 (3H, s), 0.11 (3H, s), 0.11 (3H, s), 0.12 (3H, s), 0.88 (9H, s), 0.89 (9H, s), 0.91 (9H, s), 1.10 (3H, d, $J = 6.3$ Hz), 1.14 (1H, d, $J = 6.3$ Hz), 3.66 (1H, dd, $J = 4.9, 9.8$ Hz), 3.72 – 3.80 (2H, m), 3.90 (1H, dd, $J = 4.9, 11.2$ Hz), 3.94 – 3.97 (1H, m), 4.08 (1H, d, $J = 9.3$ Hz), 4.32 (1H, t, $J = 9.8$ Hz), 4.60 – 4.72 (1H, m), 6.86 (1H, d, $J = 9.5$ Hz), 8.10 (1H, s); ^{13}C NMR (100 MHz, CDCl_3) δ –5.4, –5.3, –5.1, –5.0, –5.0, –4.8, 17.8, 17.9, 18.1, 21.6, 23.0, 25.6, 25.8, 25.8, 25.9, 49.3, 63.9, 68.4, 69.5, 70.1, 71.0, 78.7, 96.1, 159.7; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{61}\text{O}_6\text{NNaSi}_3$, 614.3699; Found 614.3697.

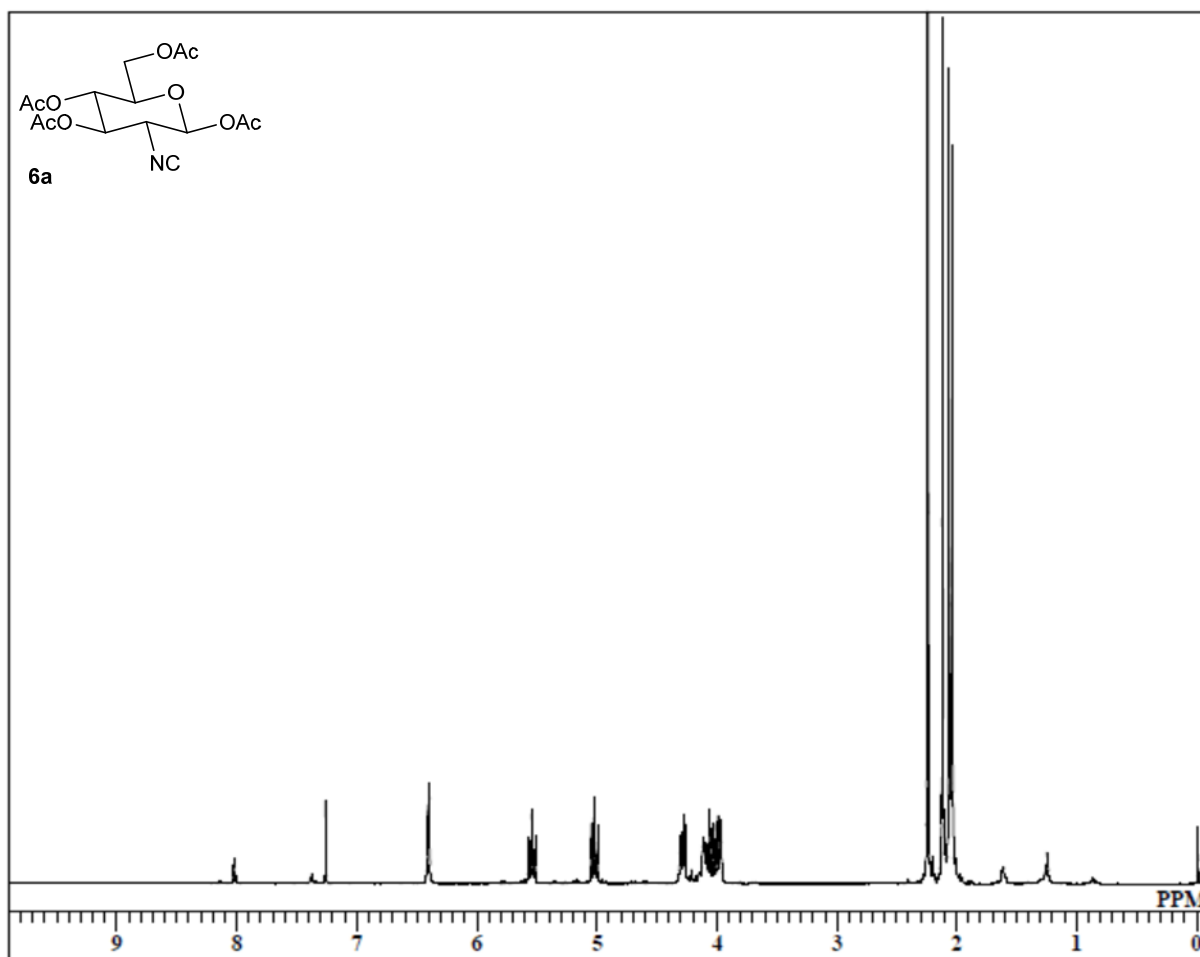
6k. **6k** was synthesized according to the general procedure in the main text (27% yield).

$[\alpha]_{\text{D}}^{27} +6.7$ (c 1.25, CHCl_3); IR (neat) 2959, 2933, 2886, 2855, 2740, 2711, 2140, 1736, 1470, 1408, 1384, 1358, 1346, 1257, 1100, 977, 939, 879, 836, 780, 673, 616 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 0.04 (3H, s), 0.06 (3H, s), 0.11 (3H, s), 0.12 (3H, s), 0.12 (3H, s), 0.16 (3H, s), 0.88 (9H, s), 0.90 (9H, s), 0.92 (9H, s), 1.22 (3H, d, $J = 6.3$ Hz), 1.25 (1H, d, $J = 6.3$ Hz), 3.43 (1H, dd, $J = 2.4, 7.3$ Hz), 3.69 – 3.79 (2H, m), 3.83 (1H, dd, $J = 1.5, 3.9$ Hz), 3.97 (1H, t, $J = 6.3$ Hz), 3.96 – 4.04 (1H, m), 4.96 (1H, d, $J = 7.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ –5.3, –4.6, –4.5, –4.4, –4.3, 1.0, 17.8, 18.0, 18.2, 21.5, 23.2, 25.7, 25.8, 63.4, 69.5, 71.9, 81.6, 97.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{28}\text{H}_{59}\text{O}_5\text{NNaSi}_3$, 596.3693; Found 596.3593.

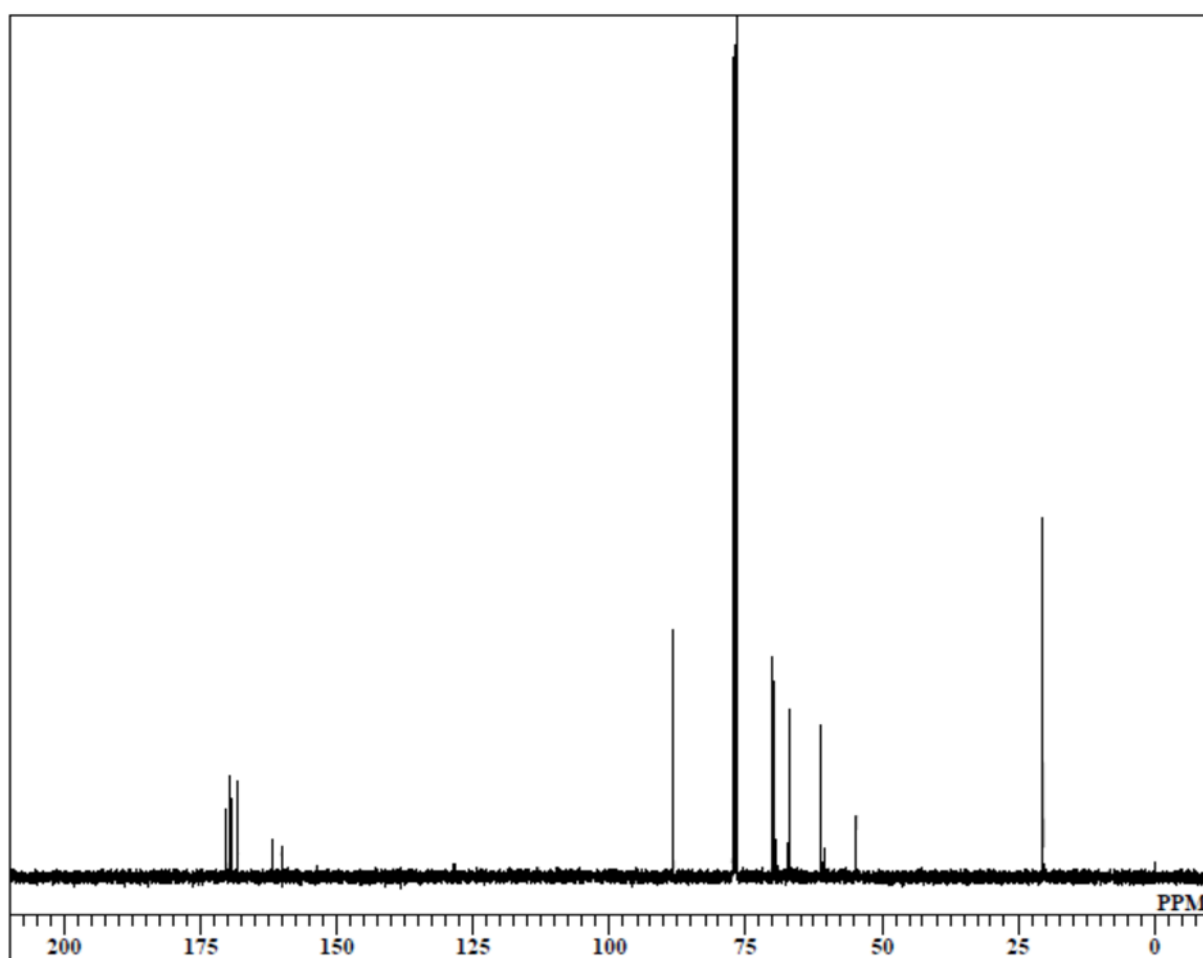


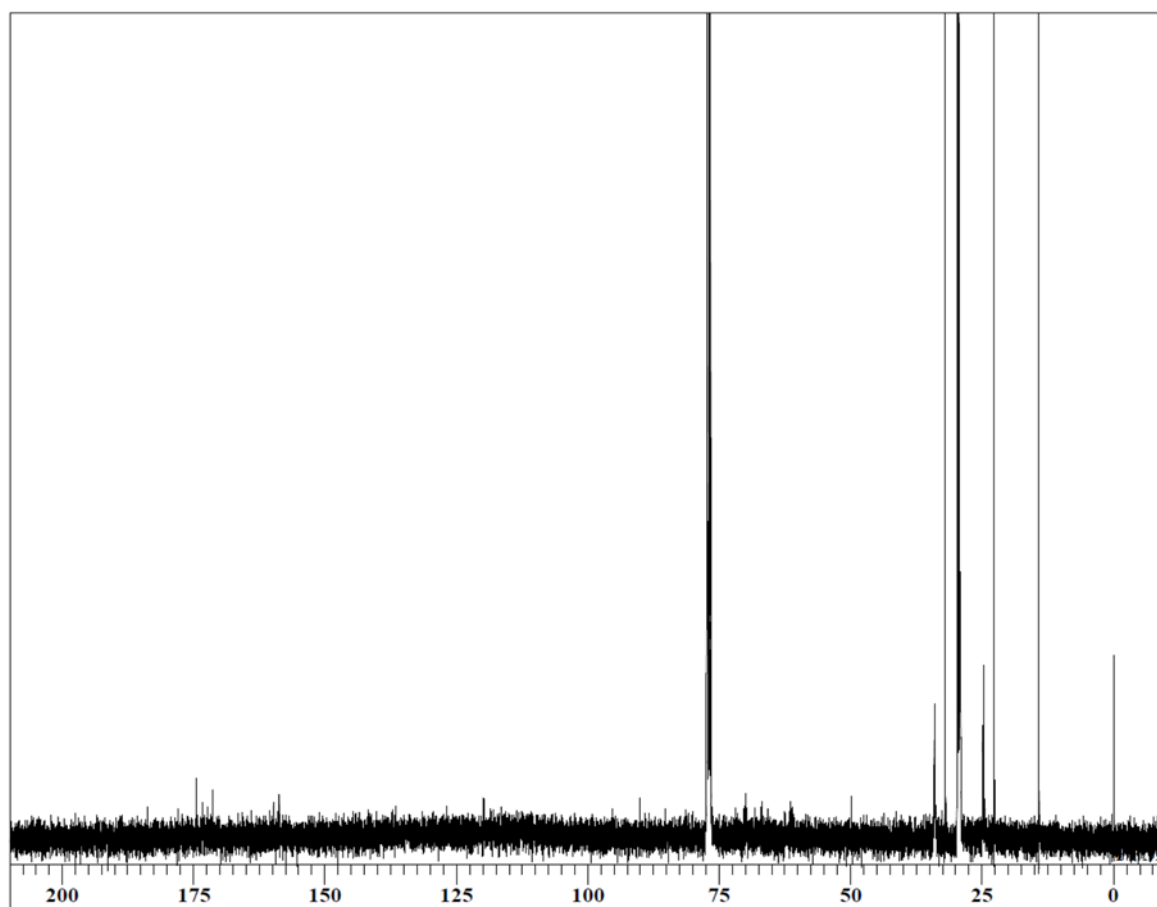
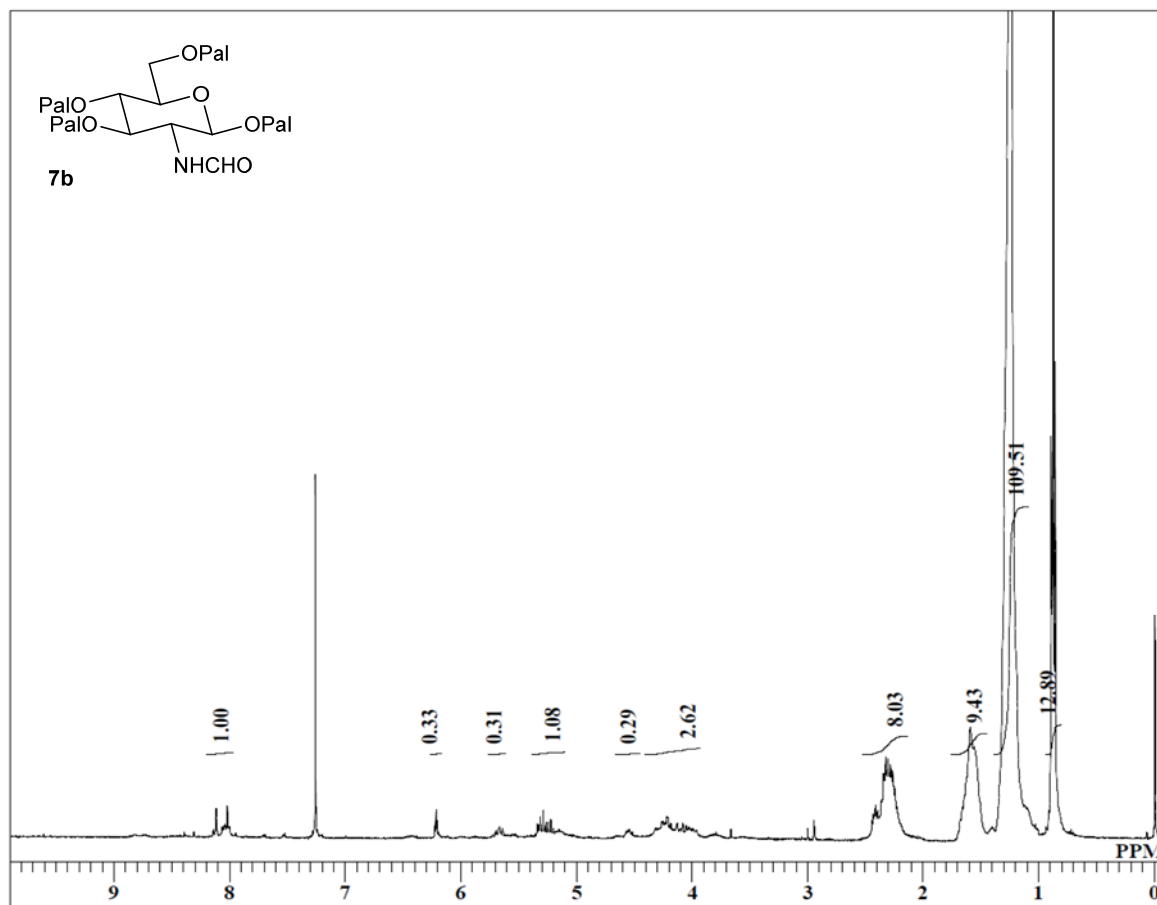
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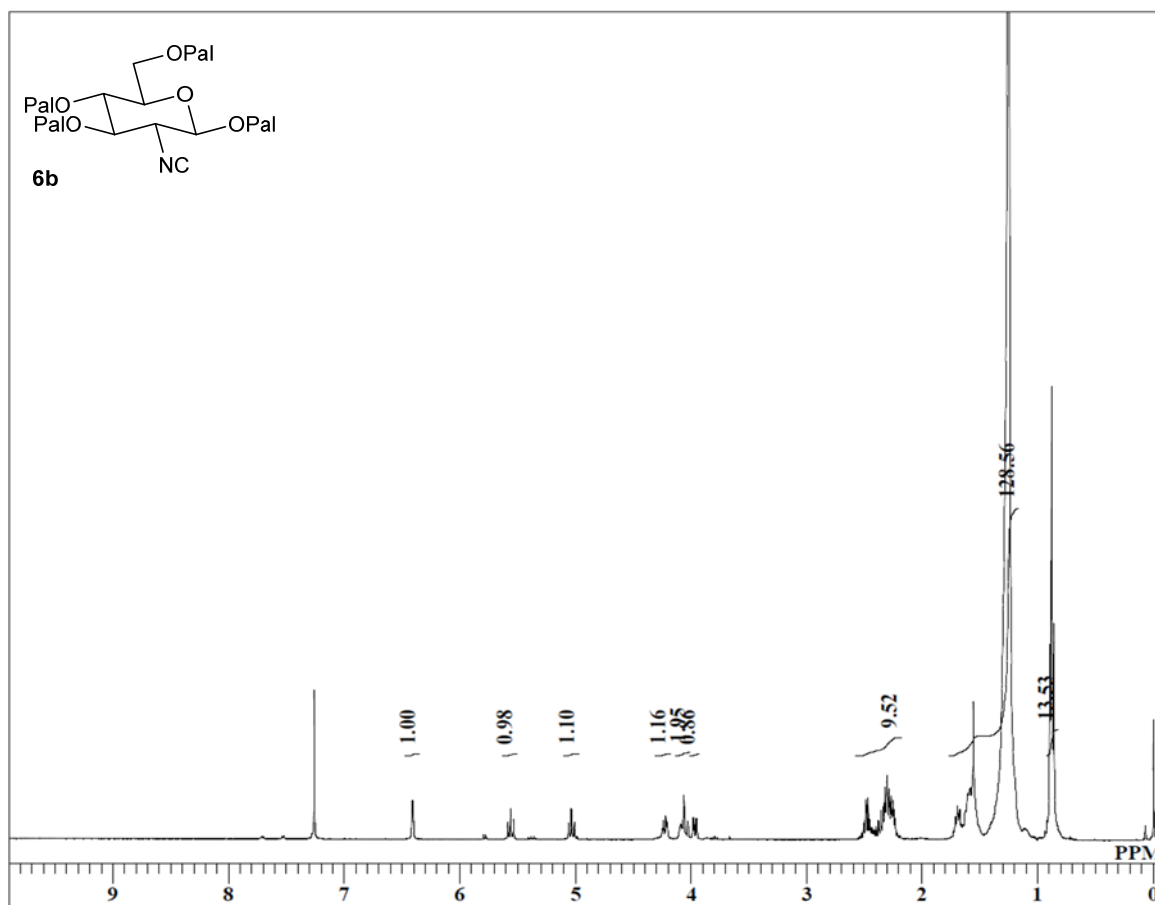




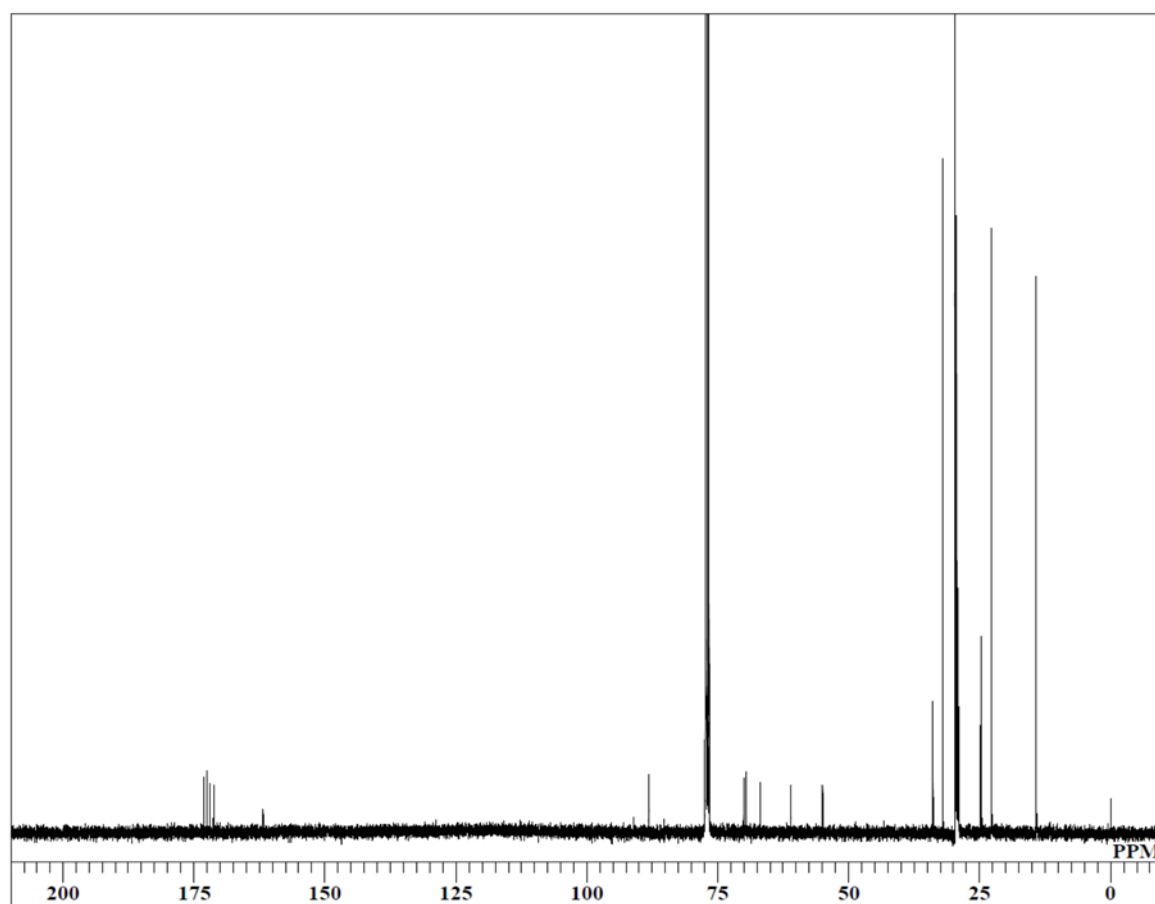
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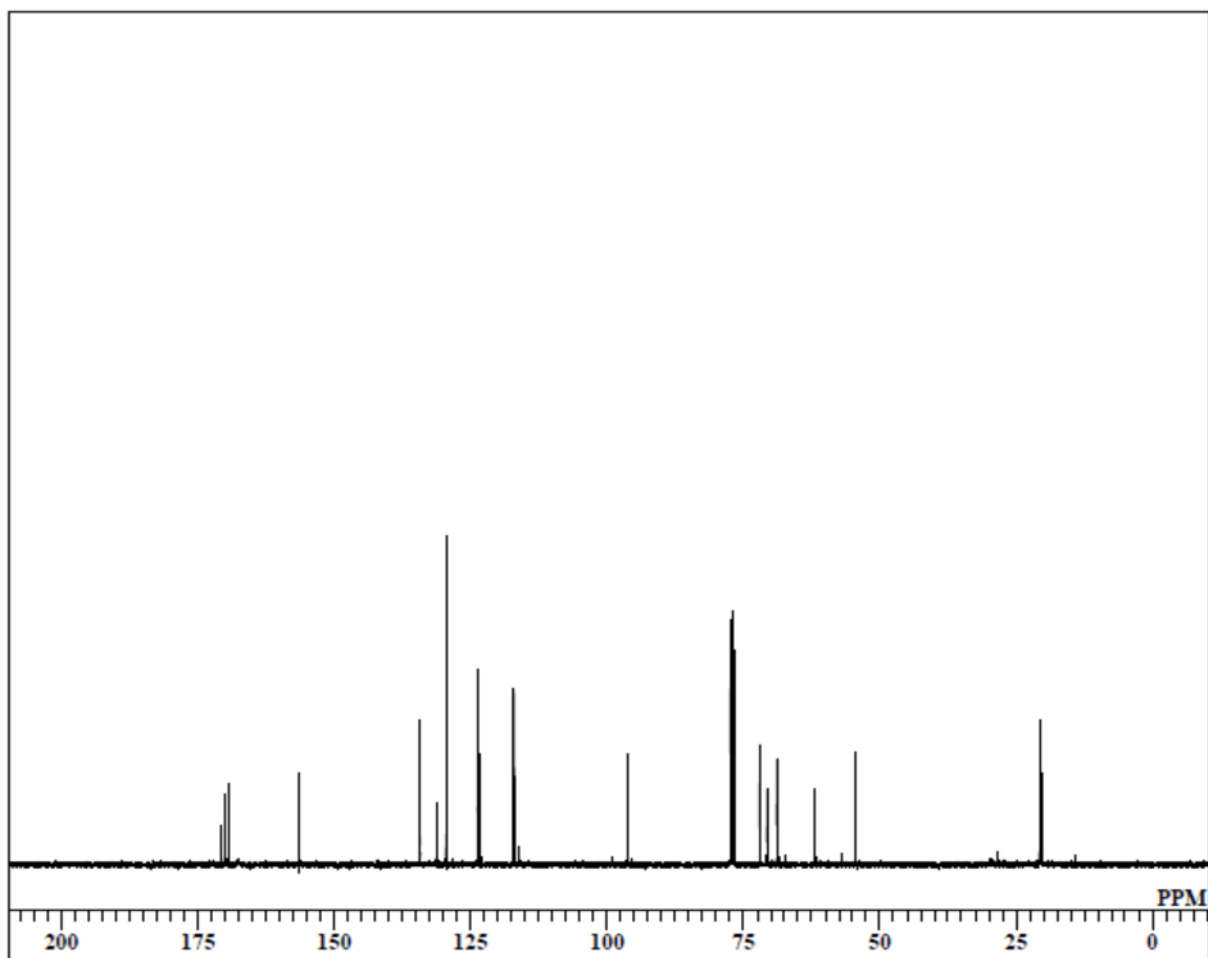
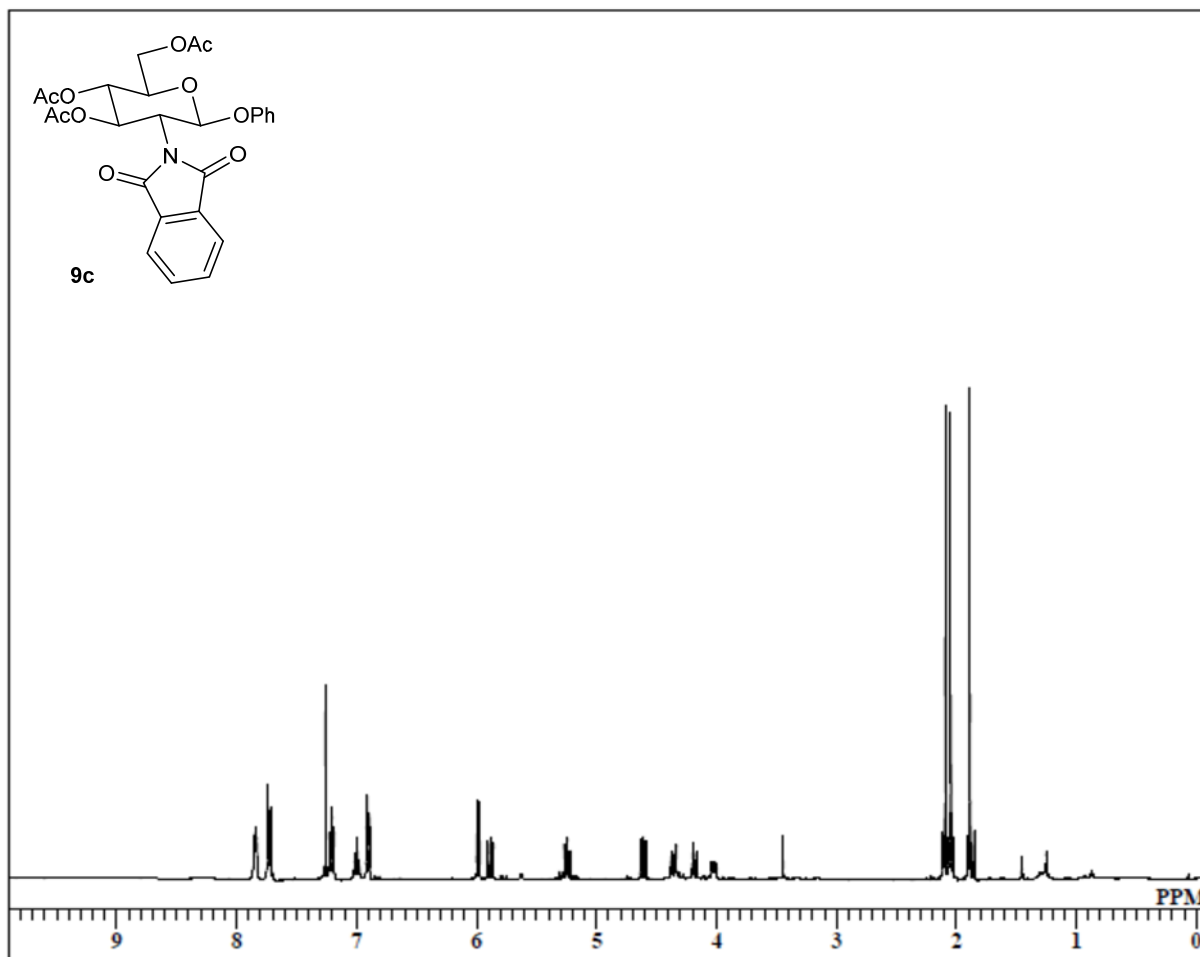




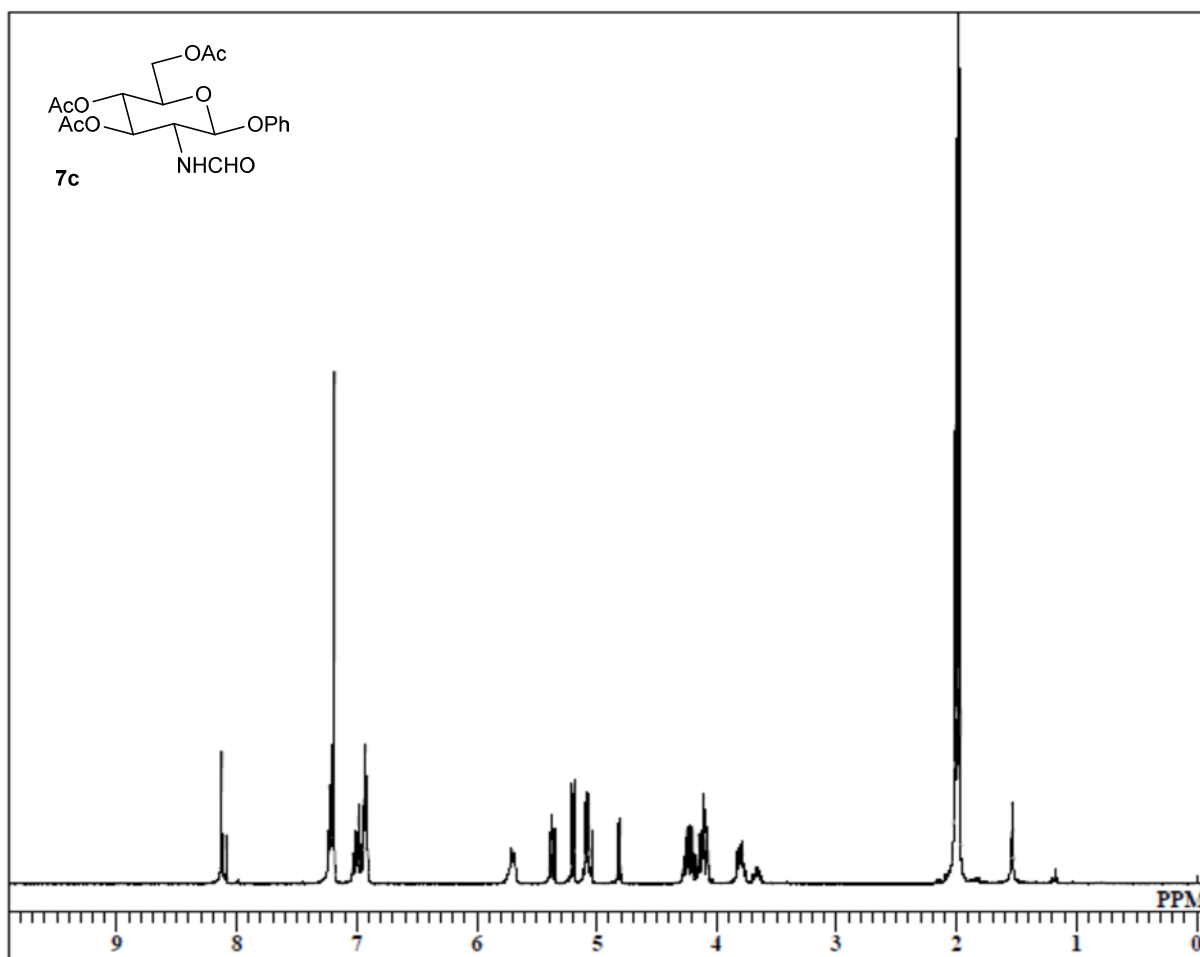


6b

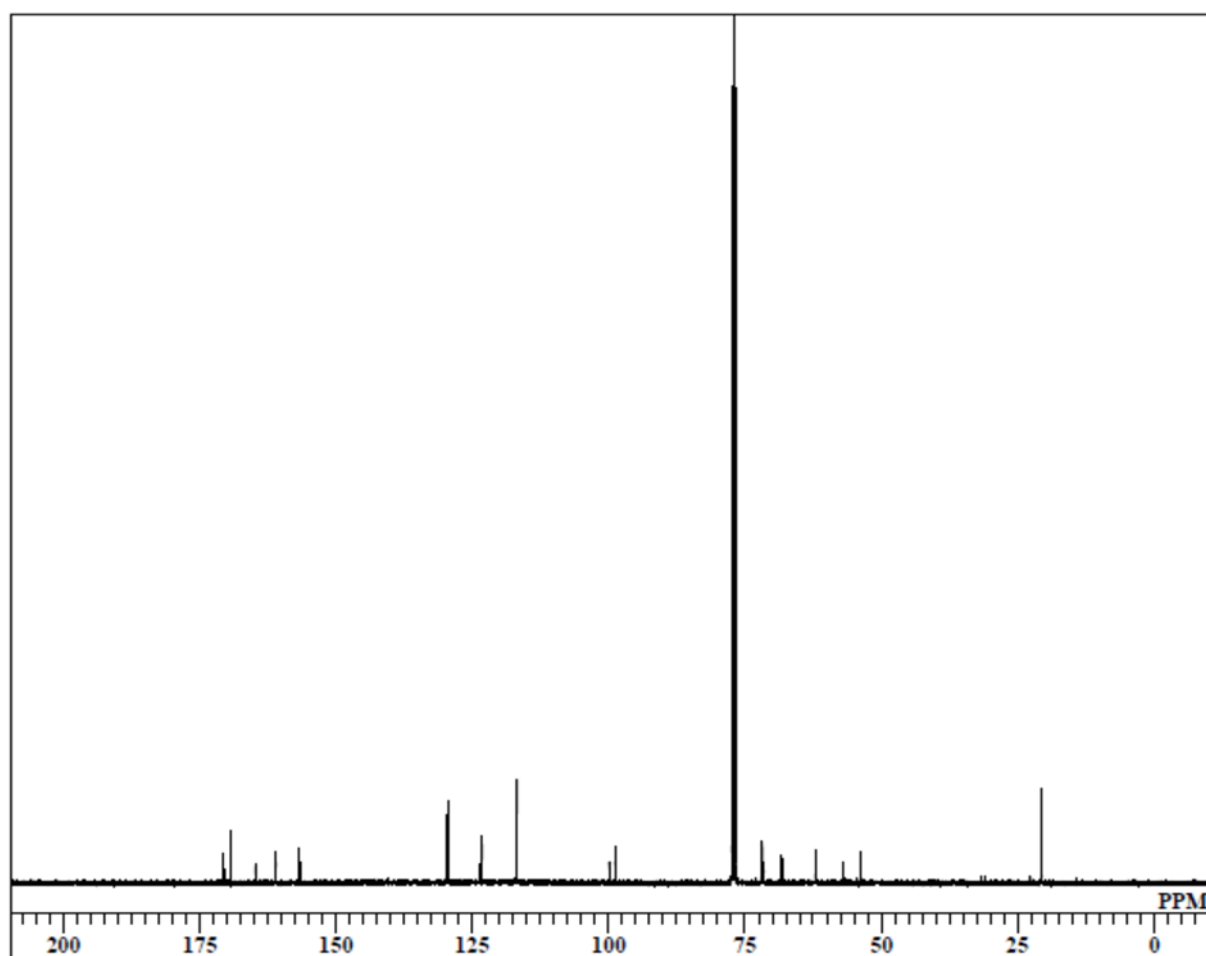


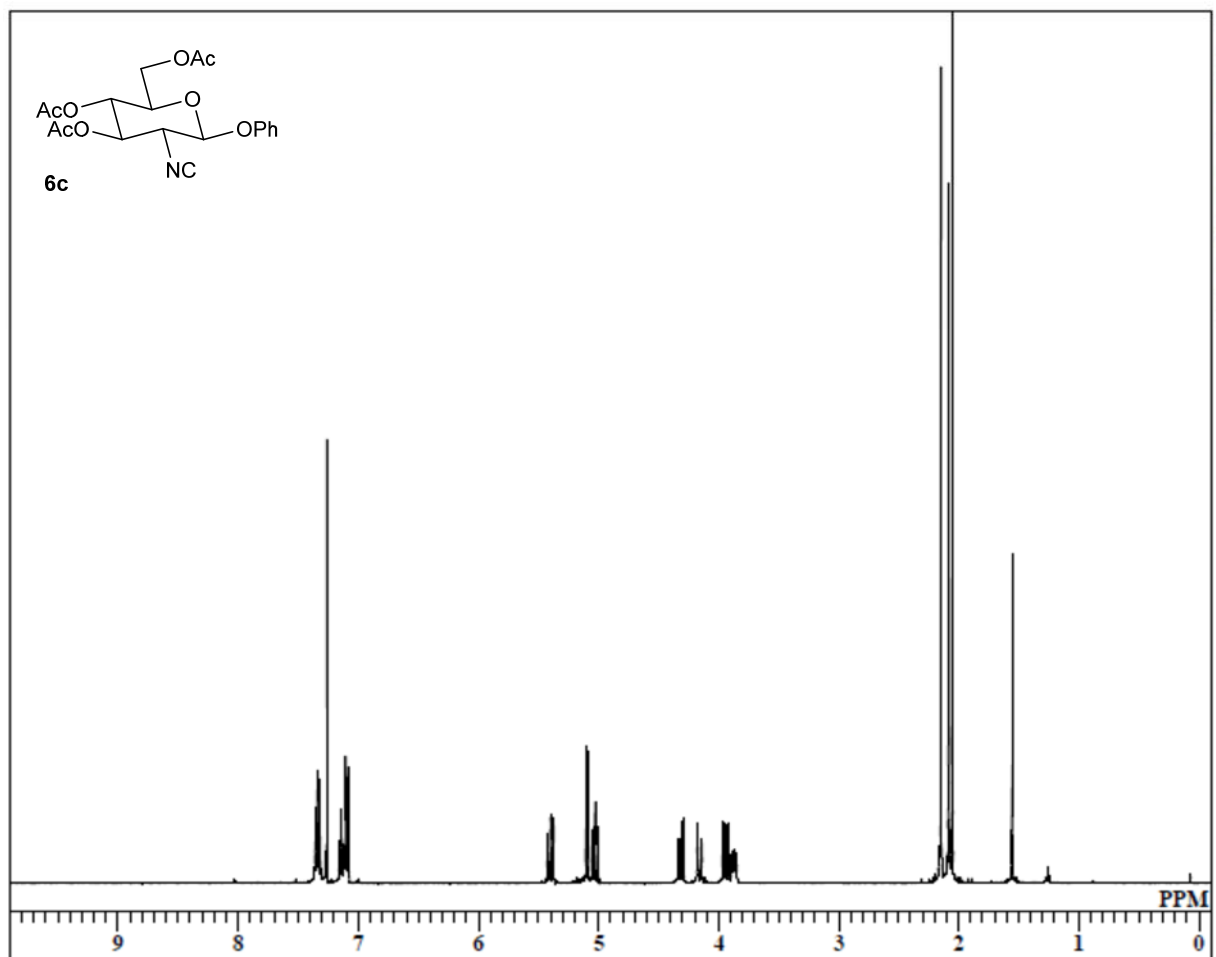


9c

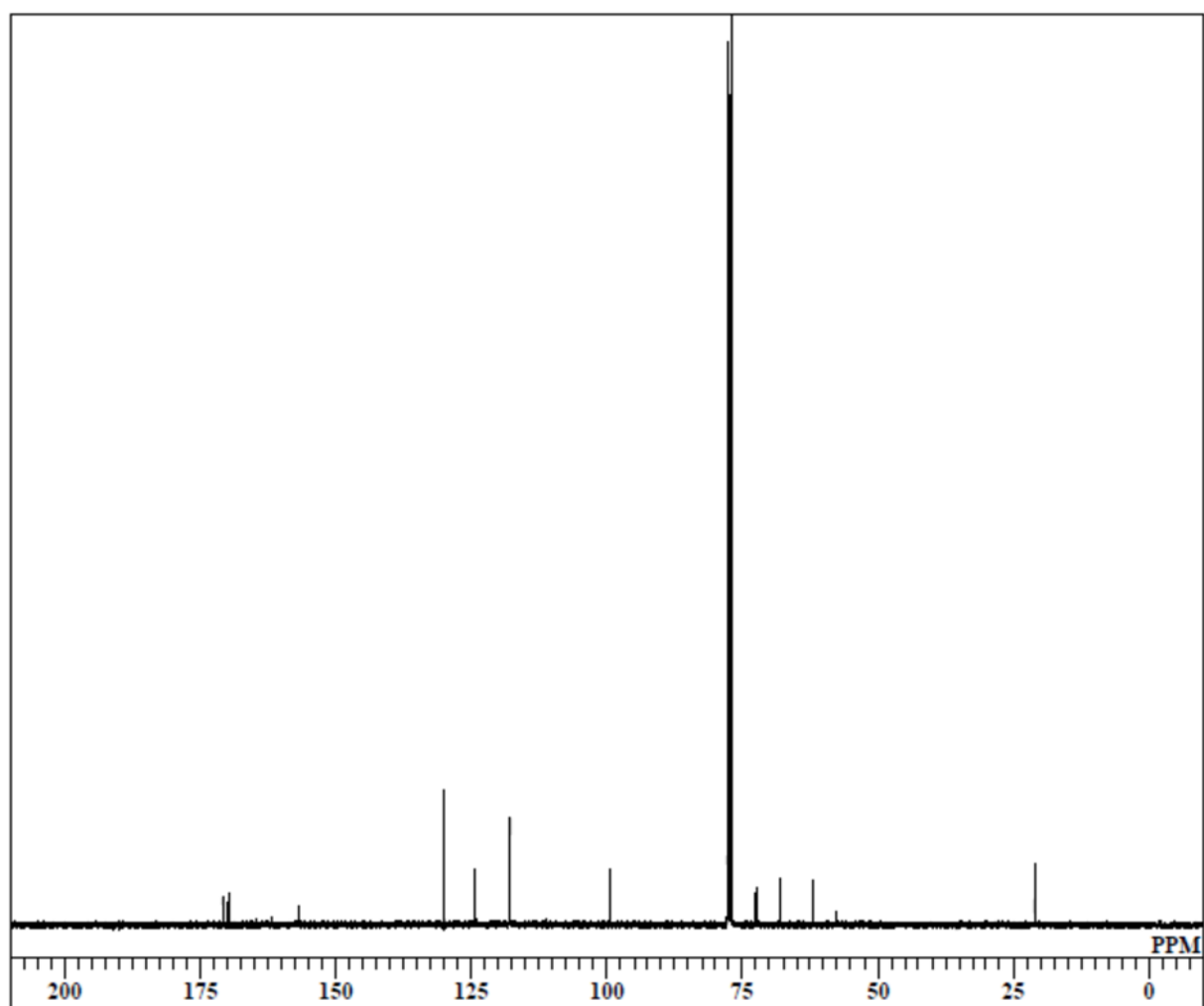


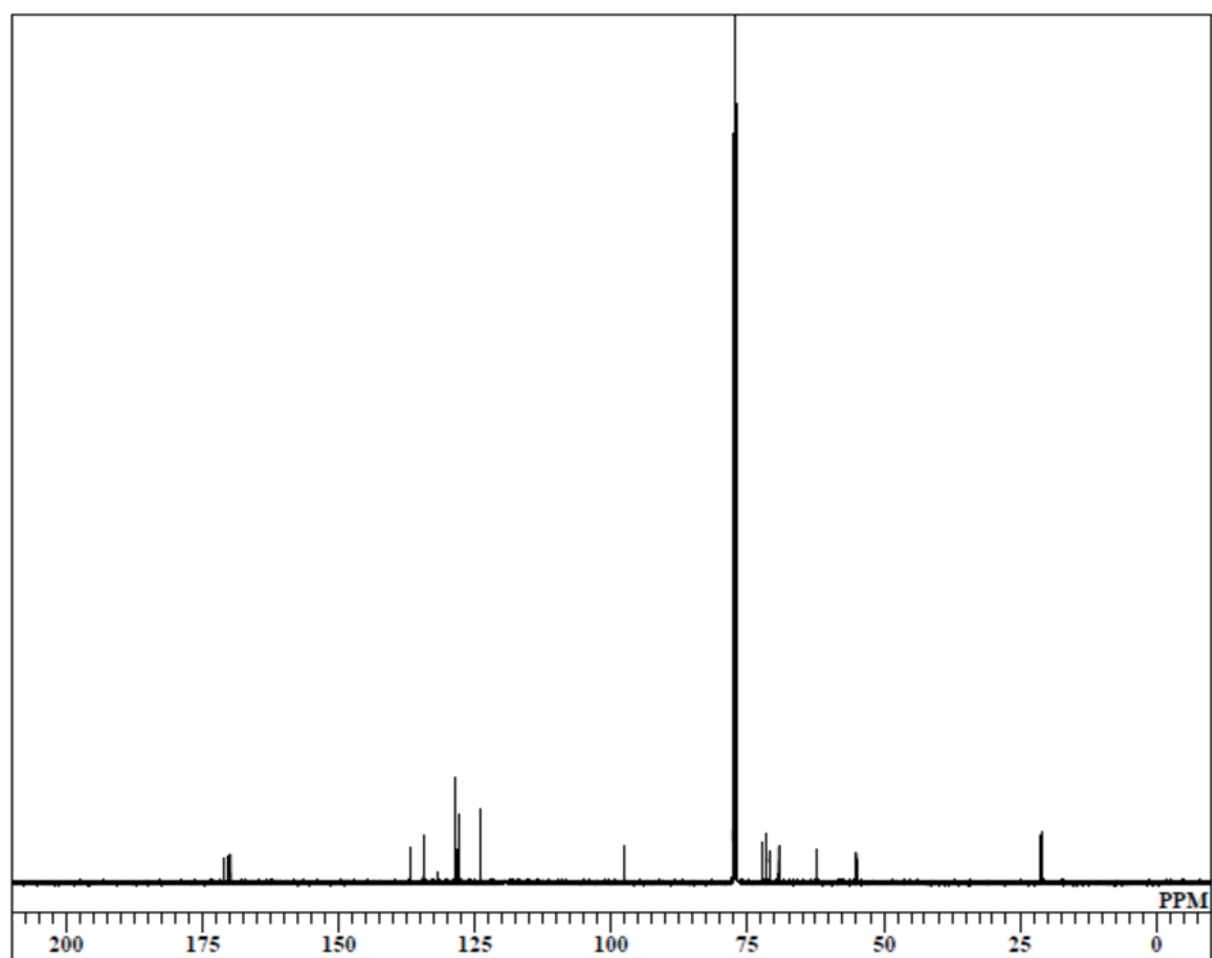
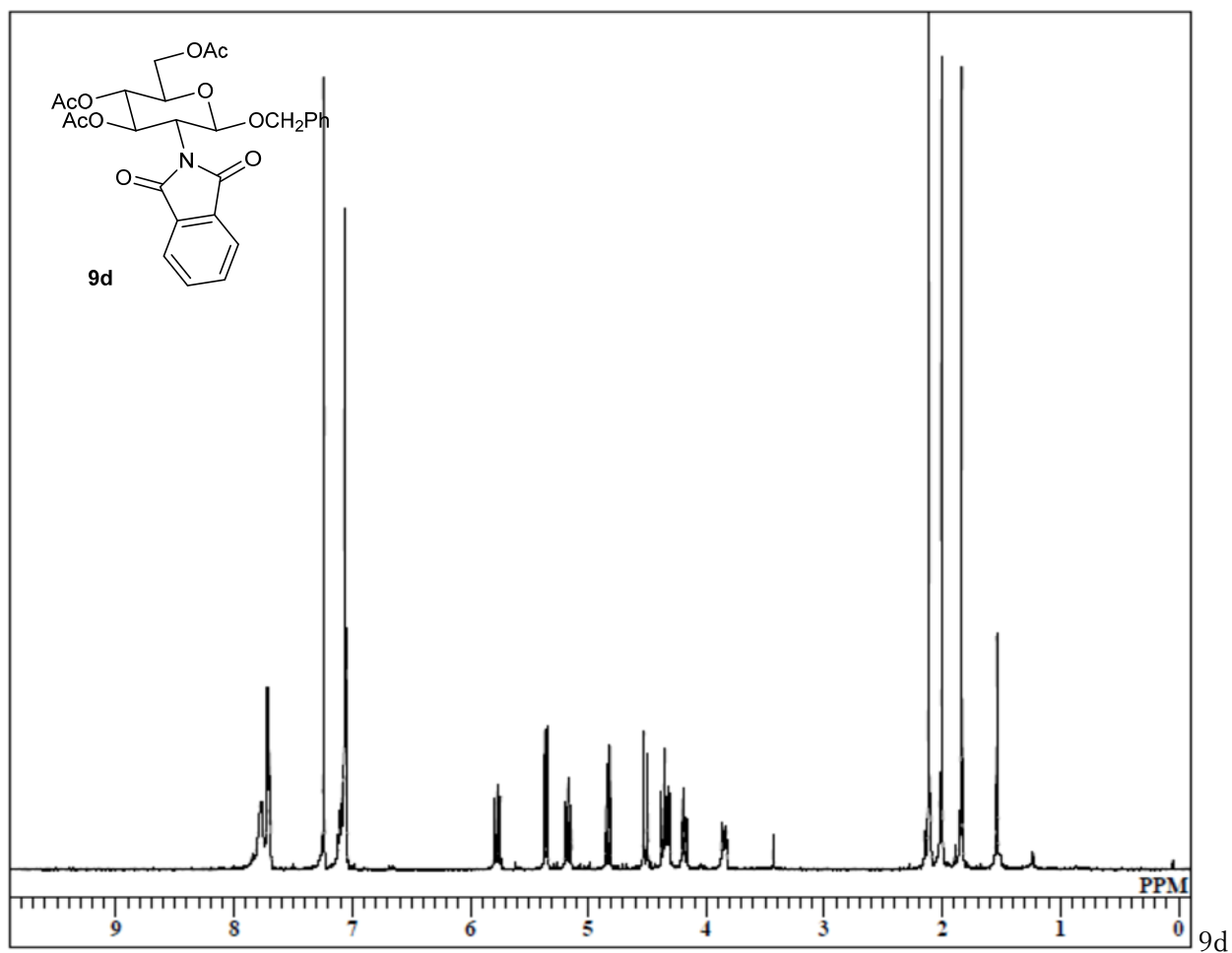
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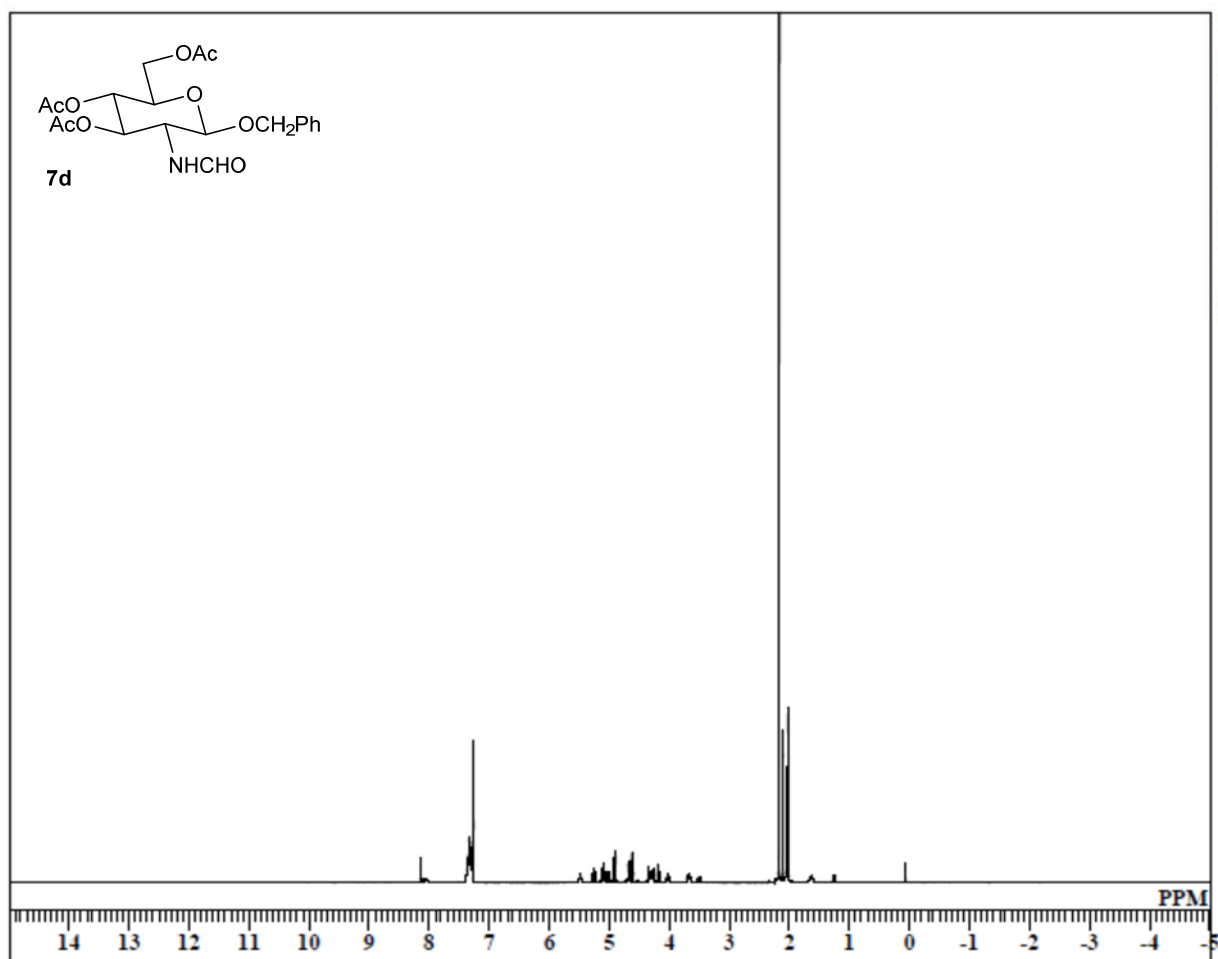




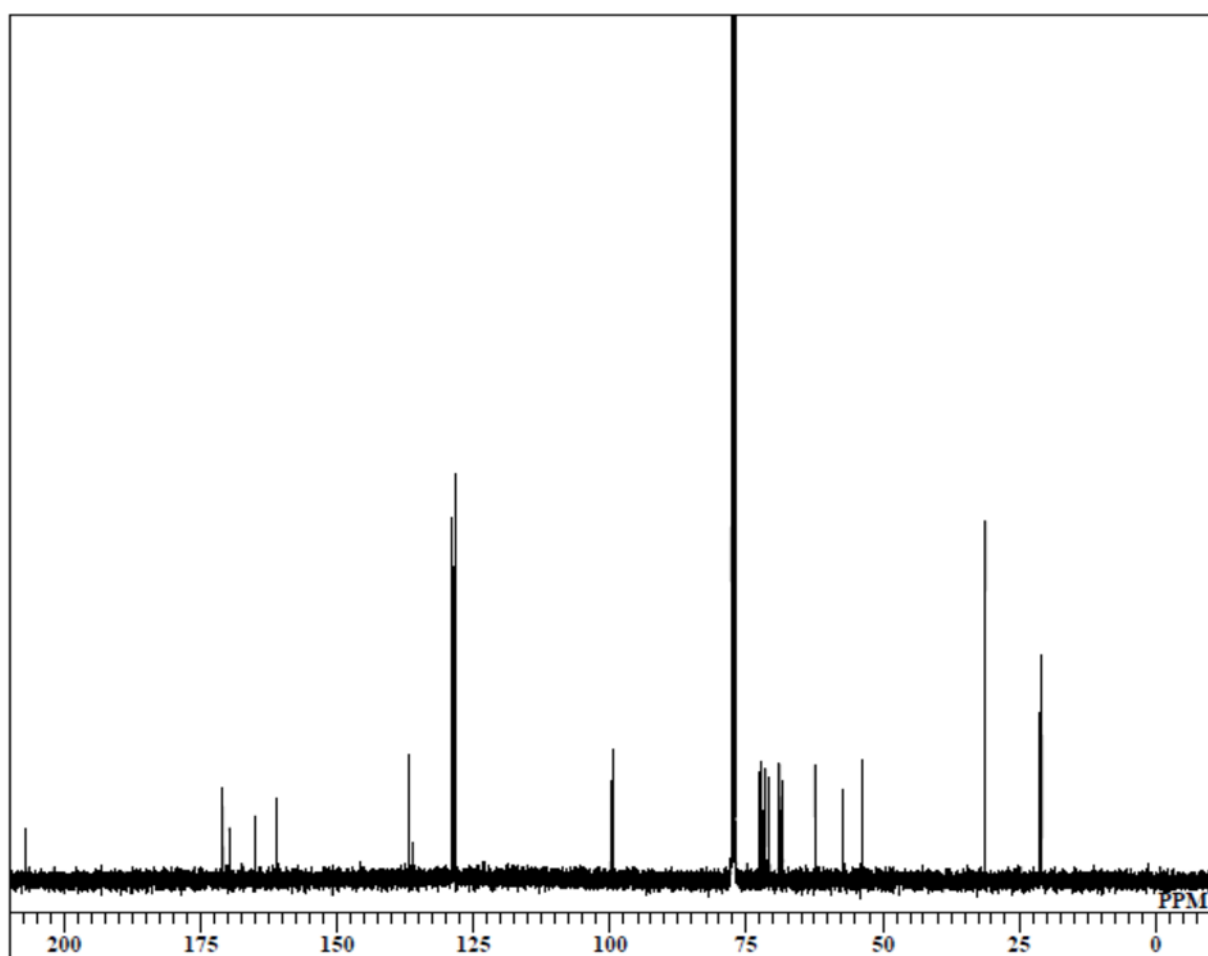
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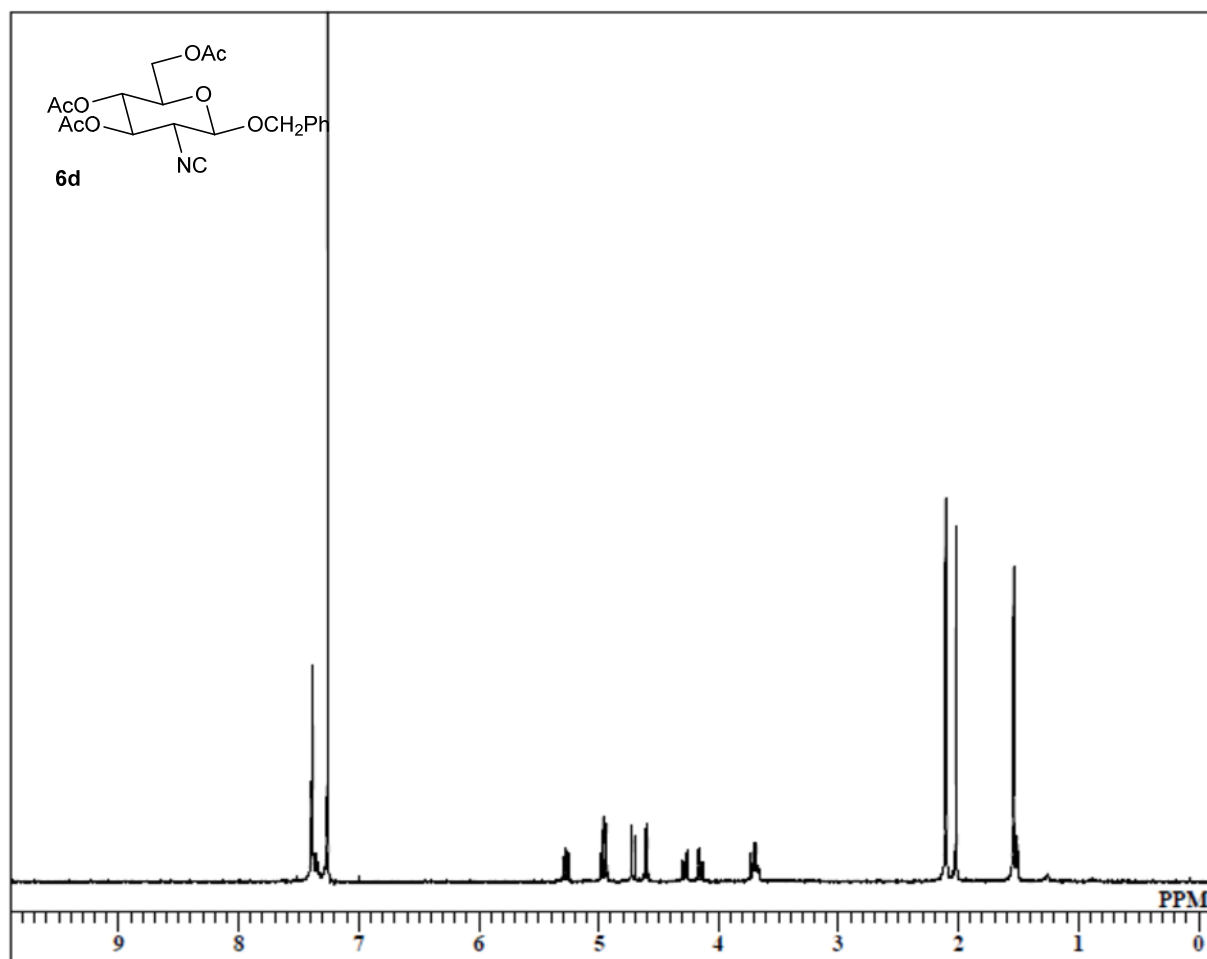




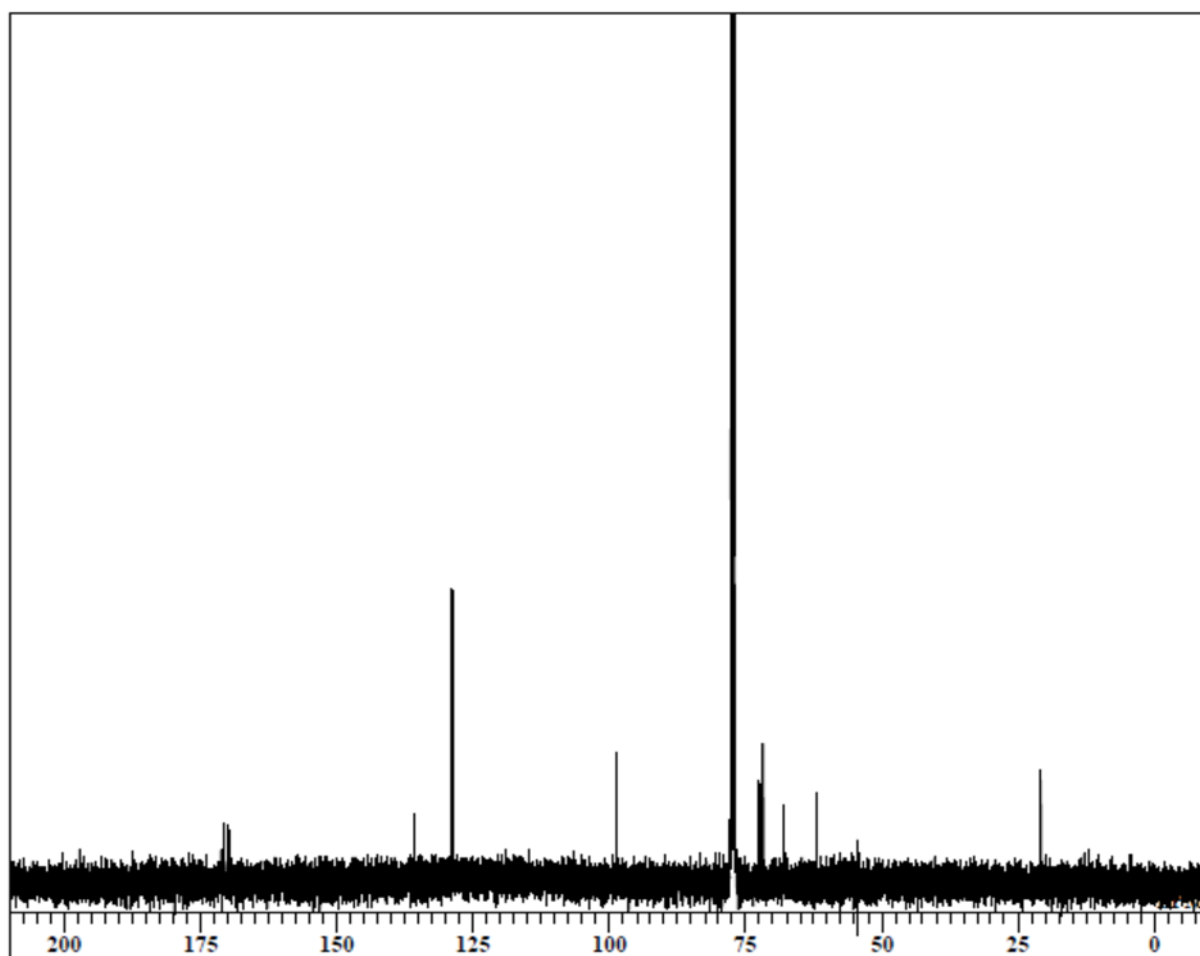


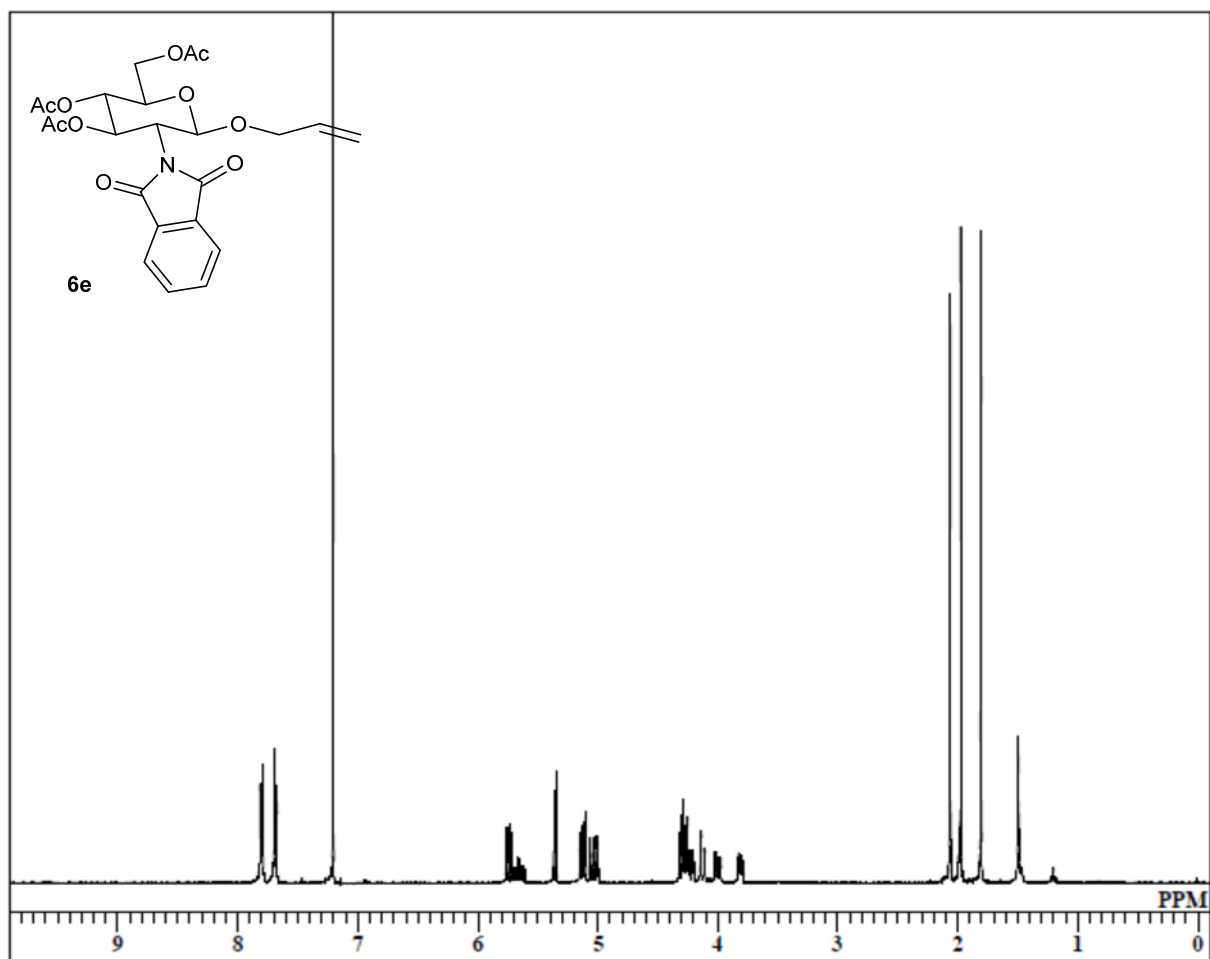
7d



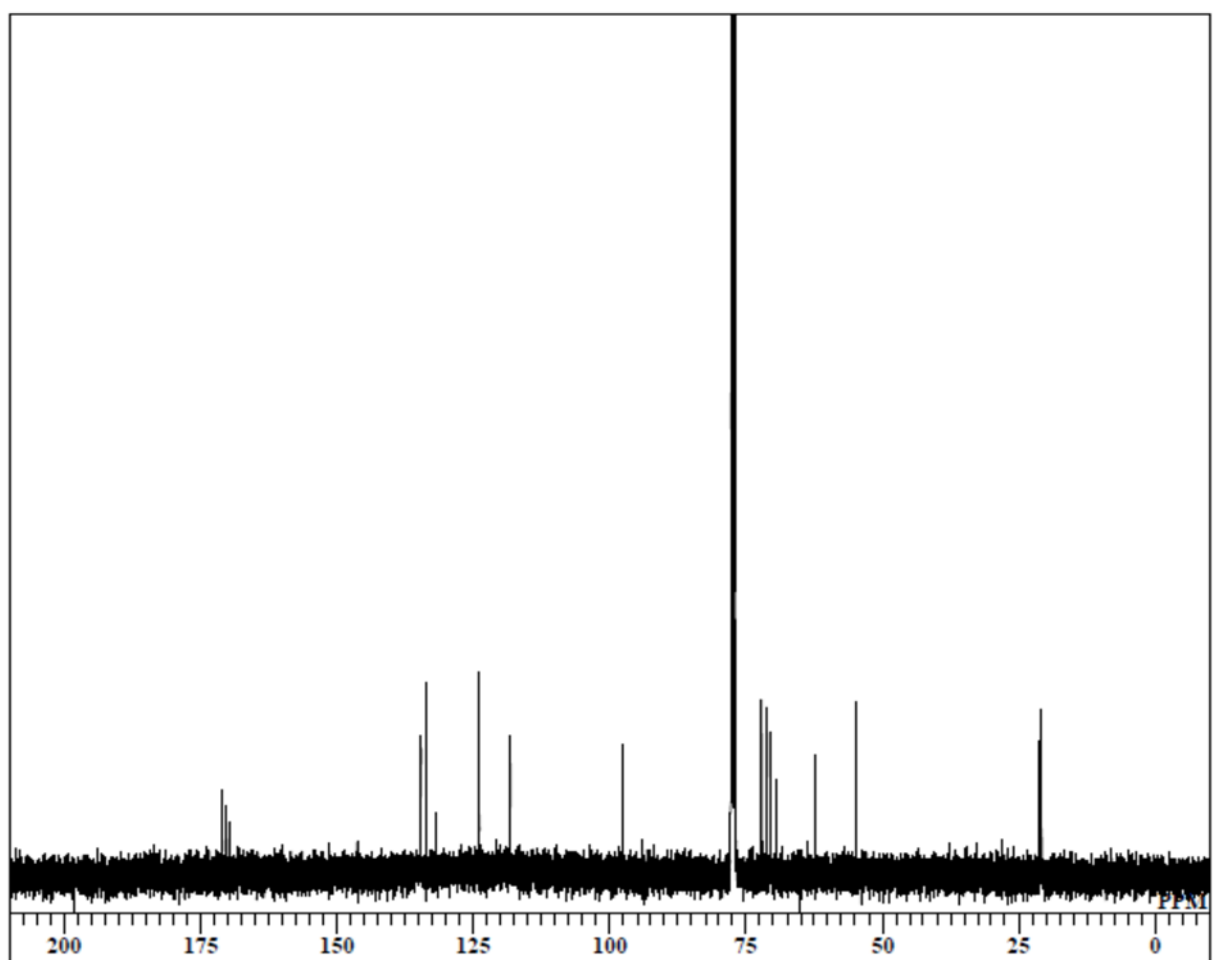


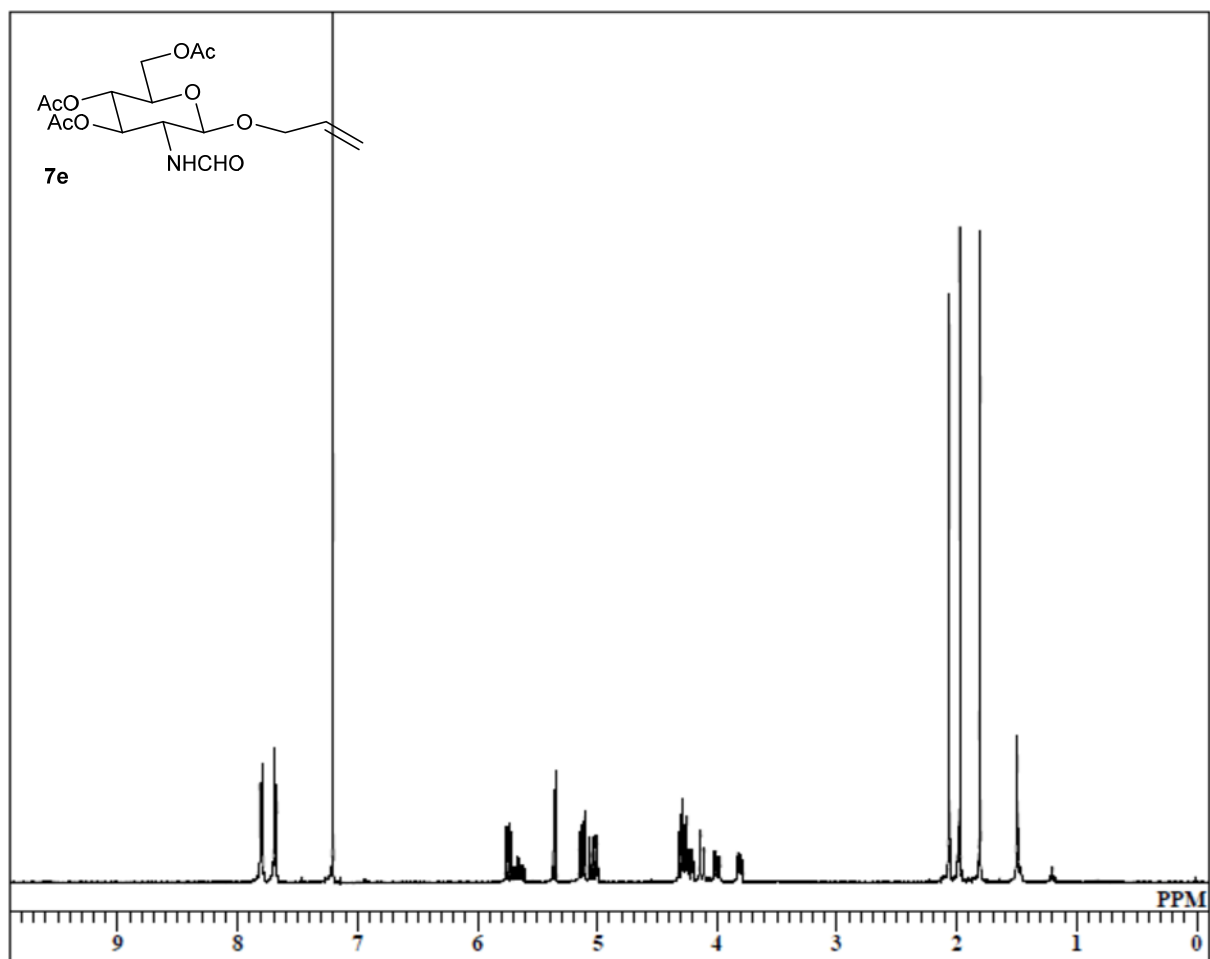
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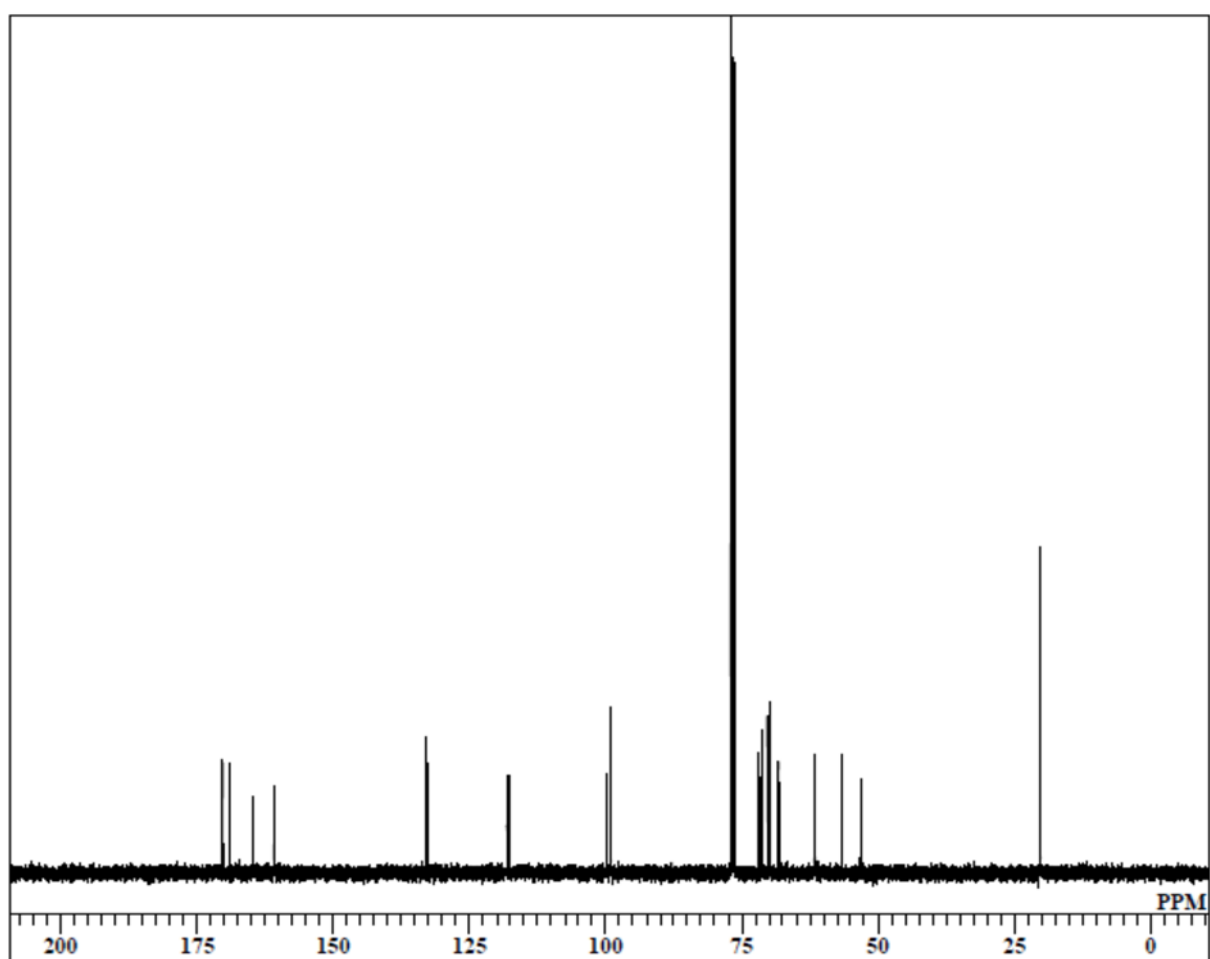


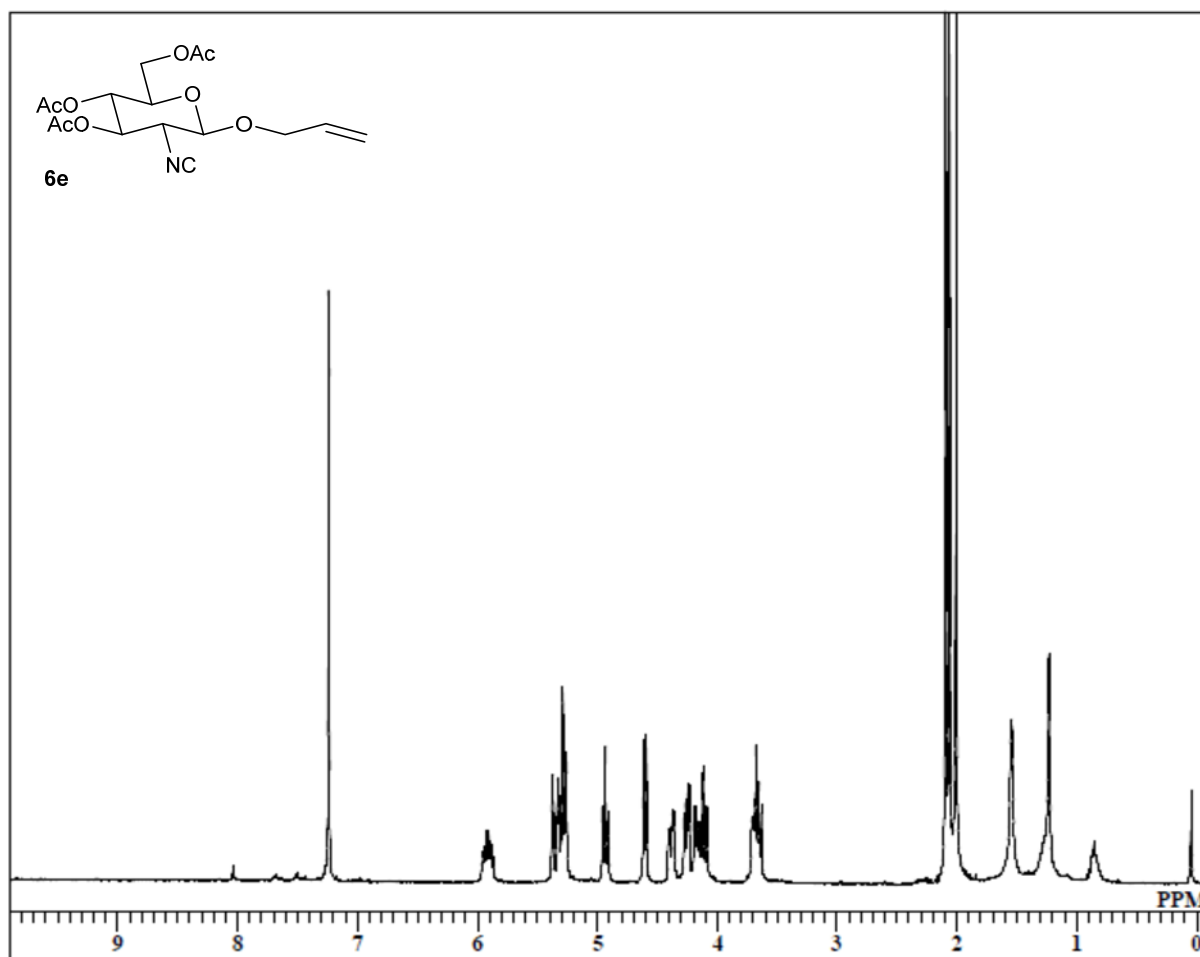
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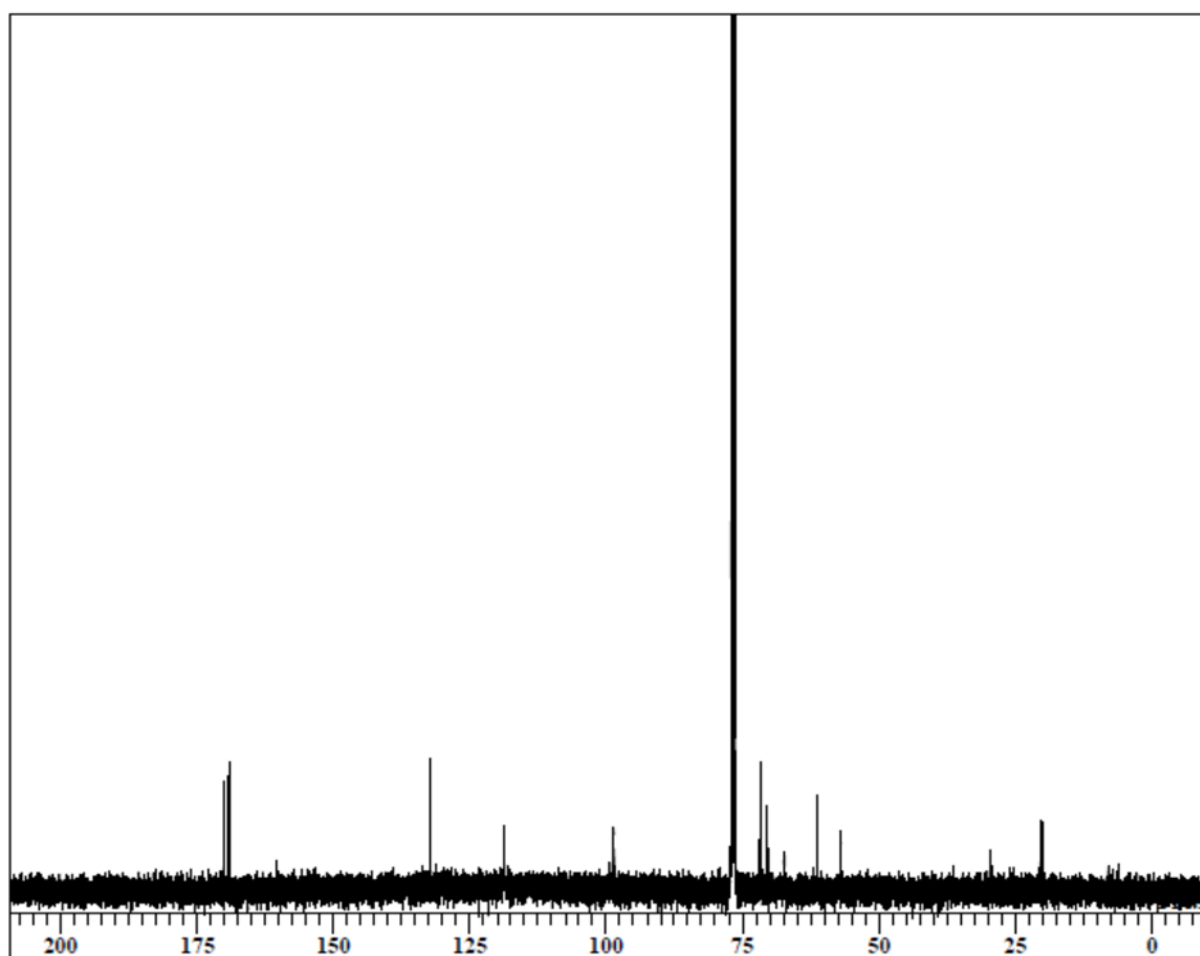


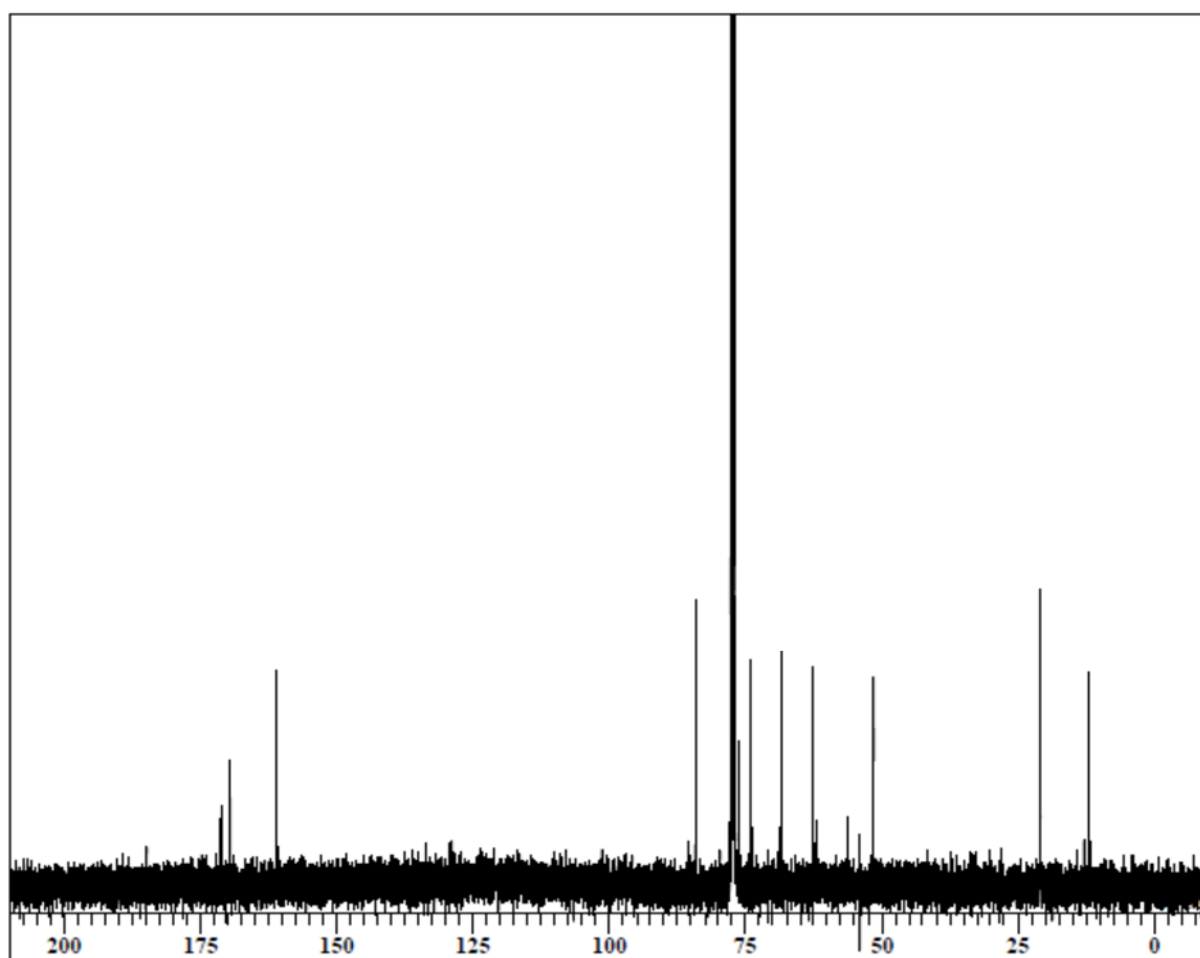
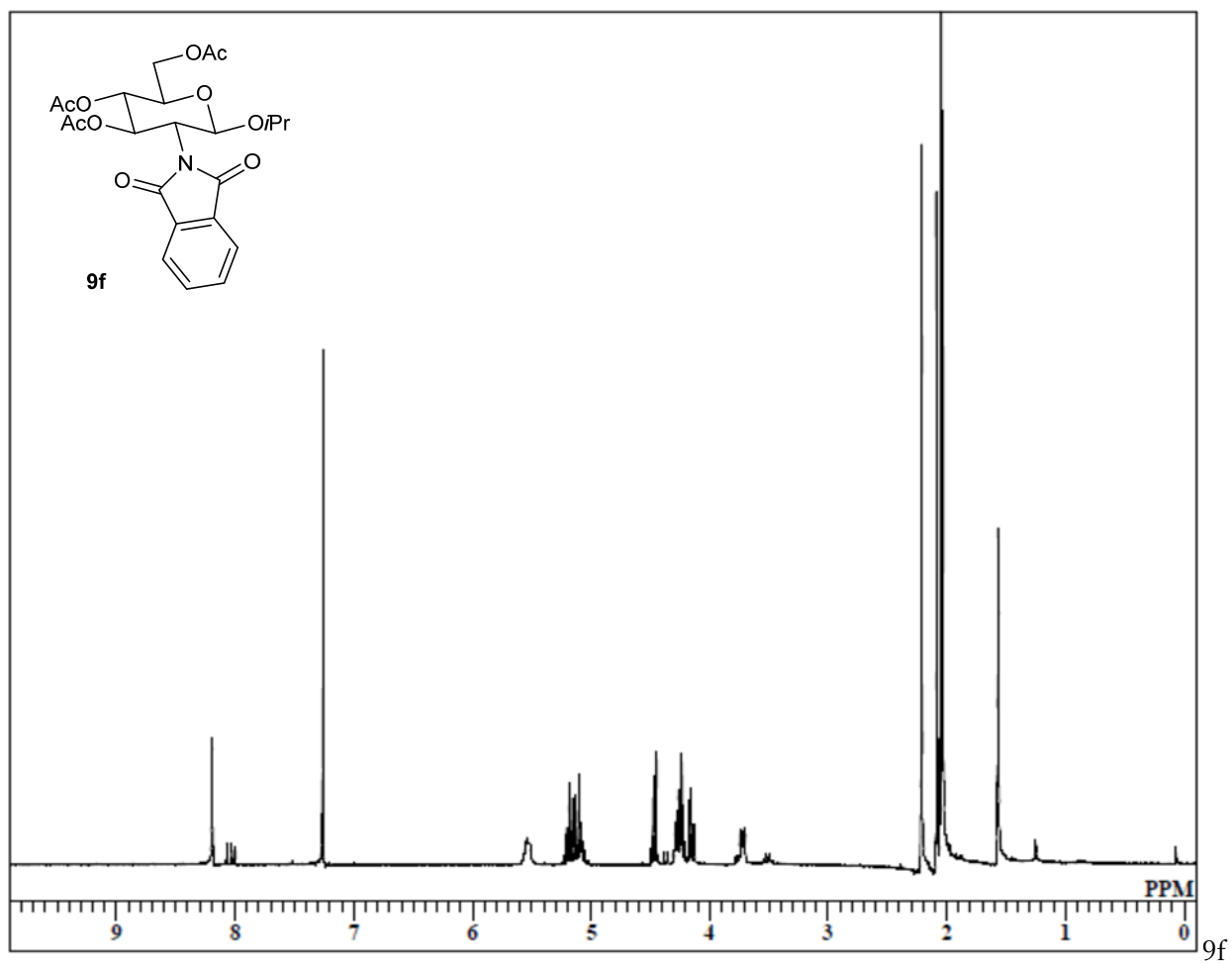
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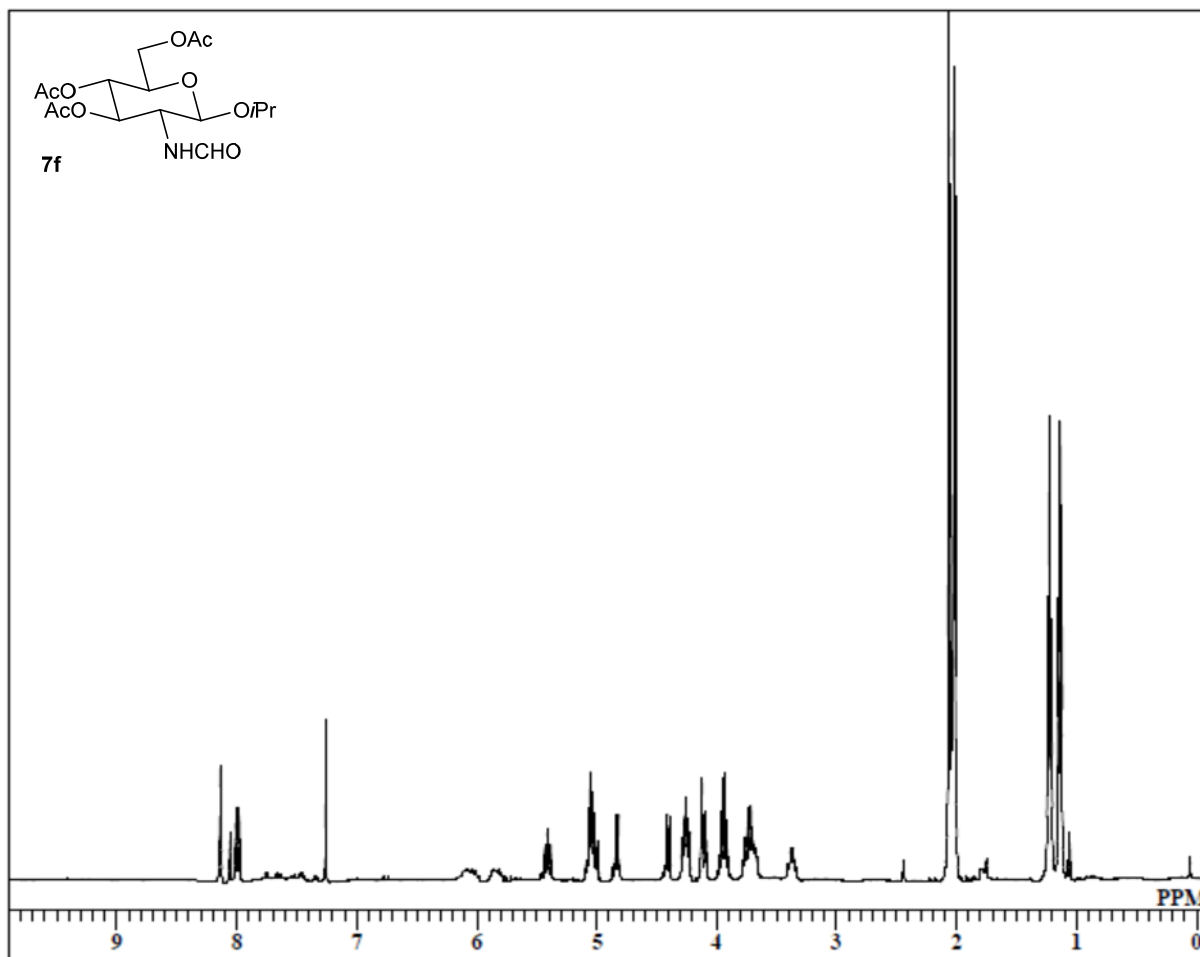




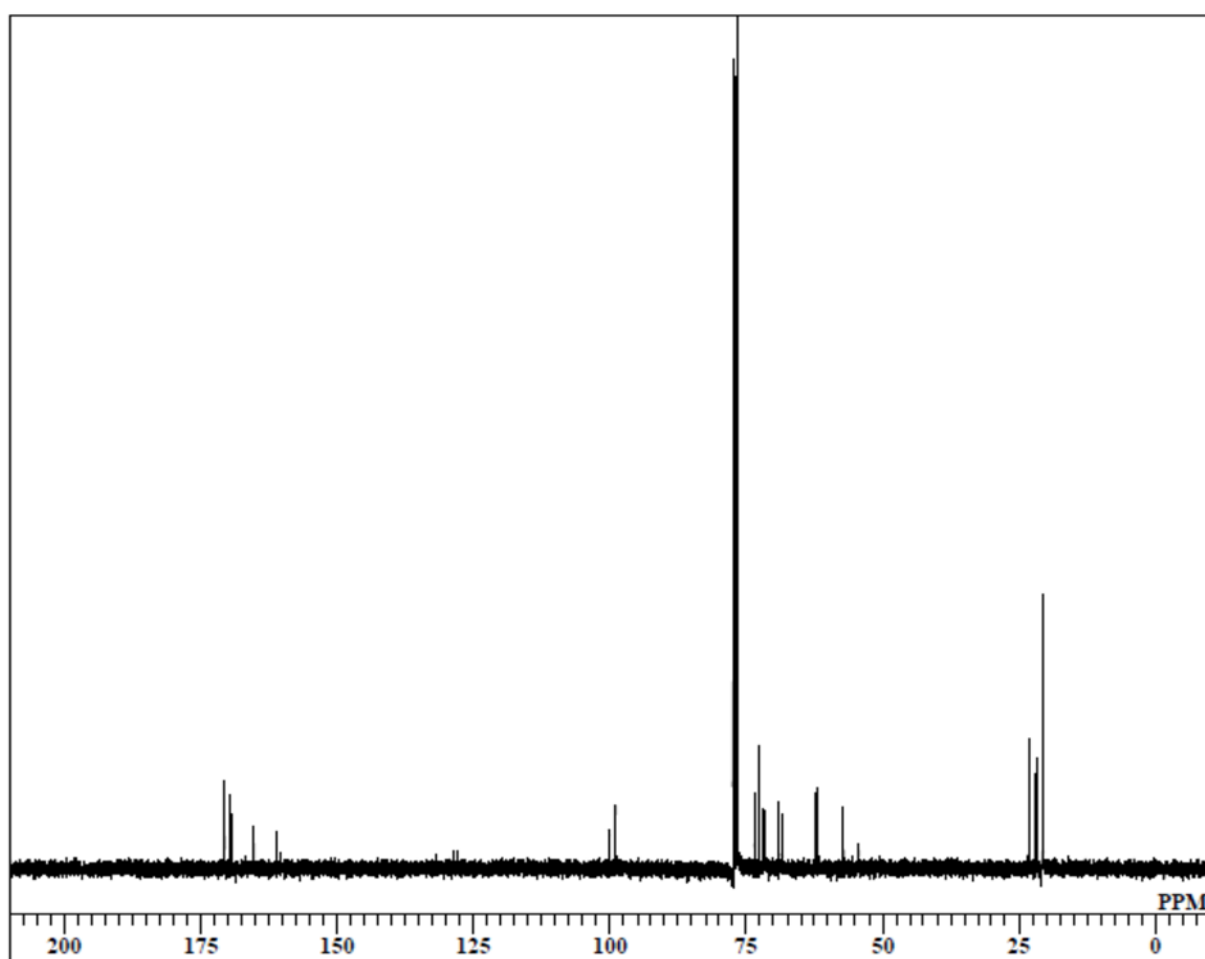
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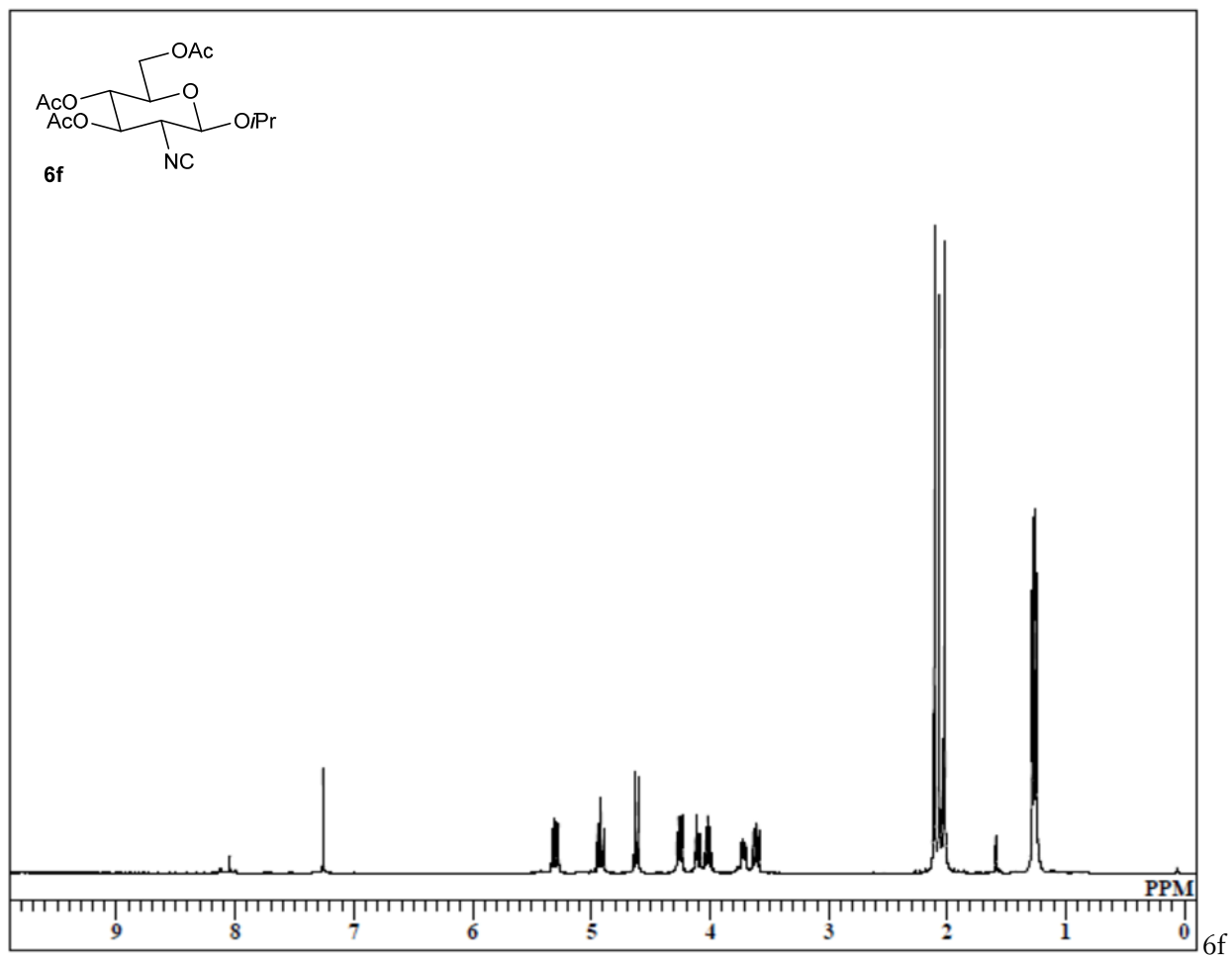




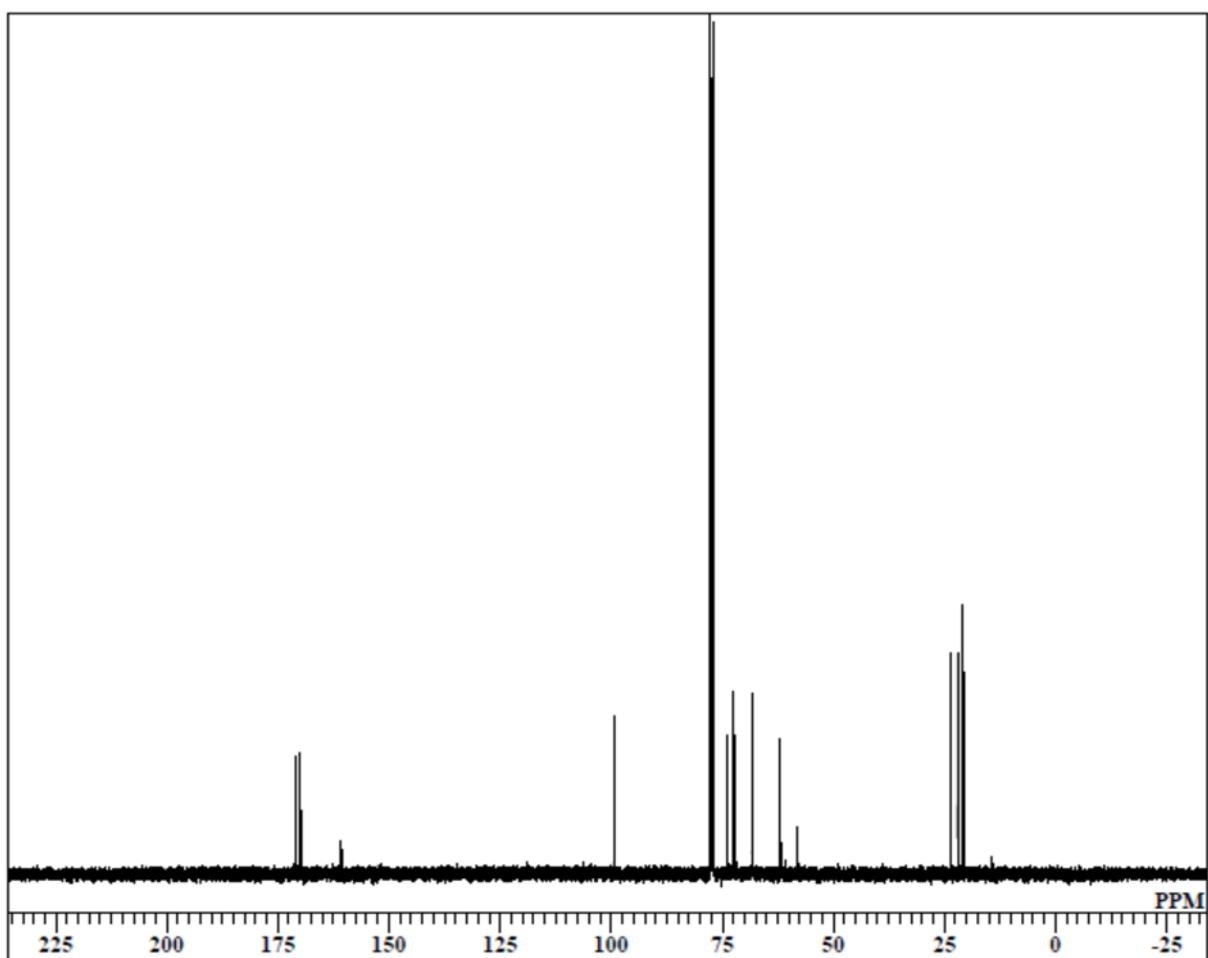


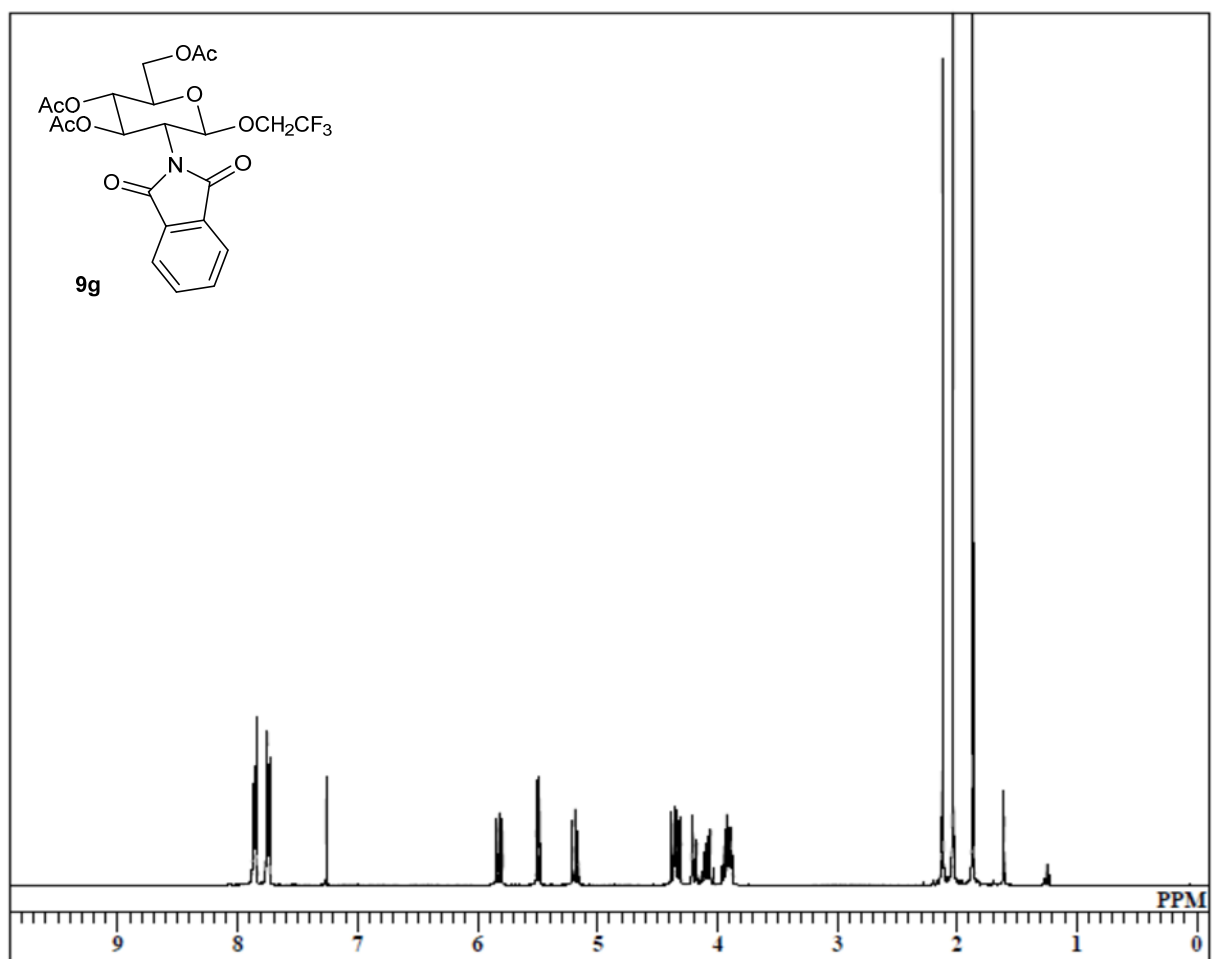
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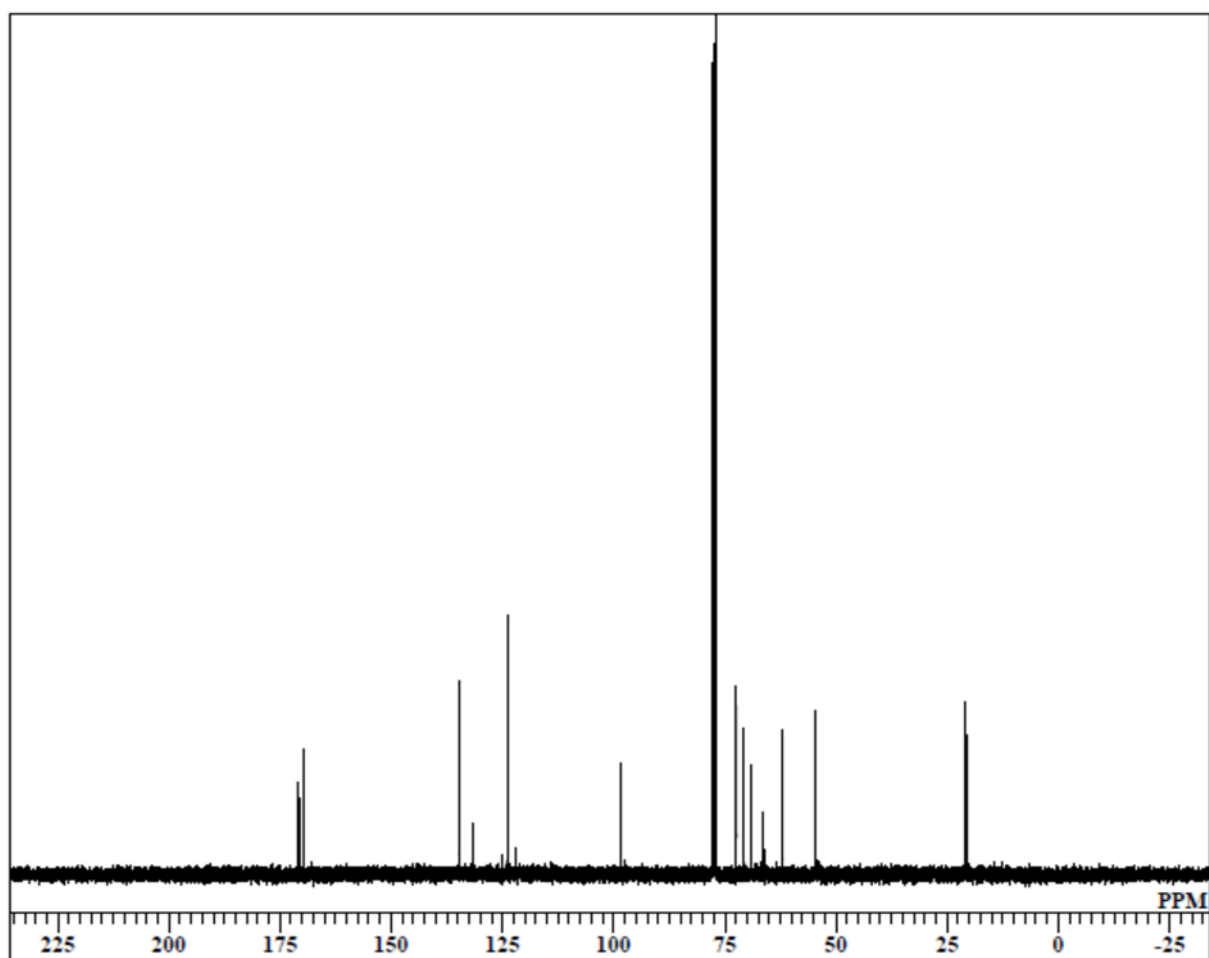


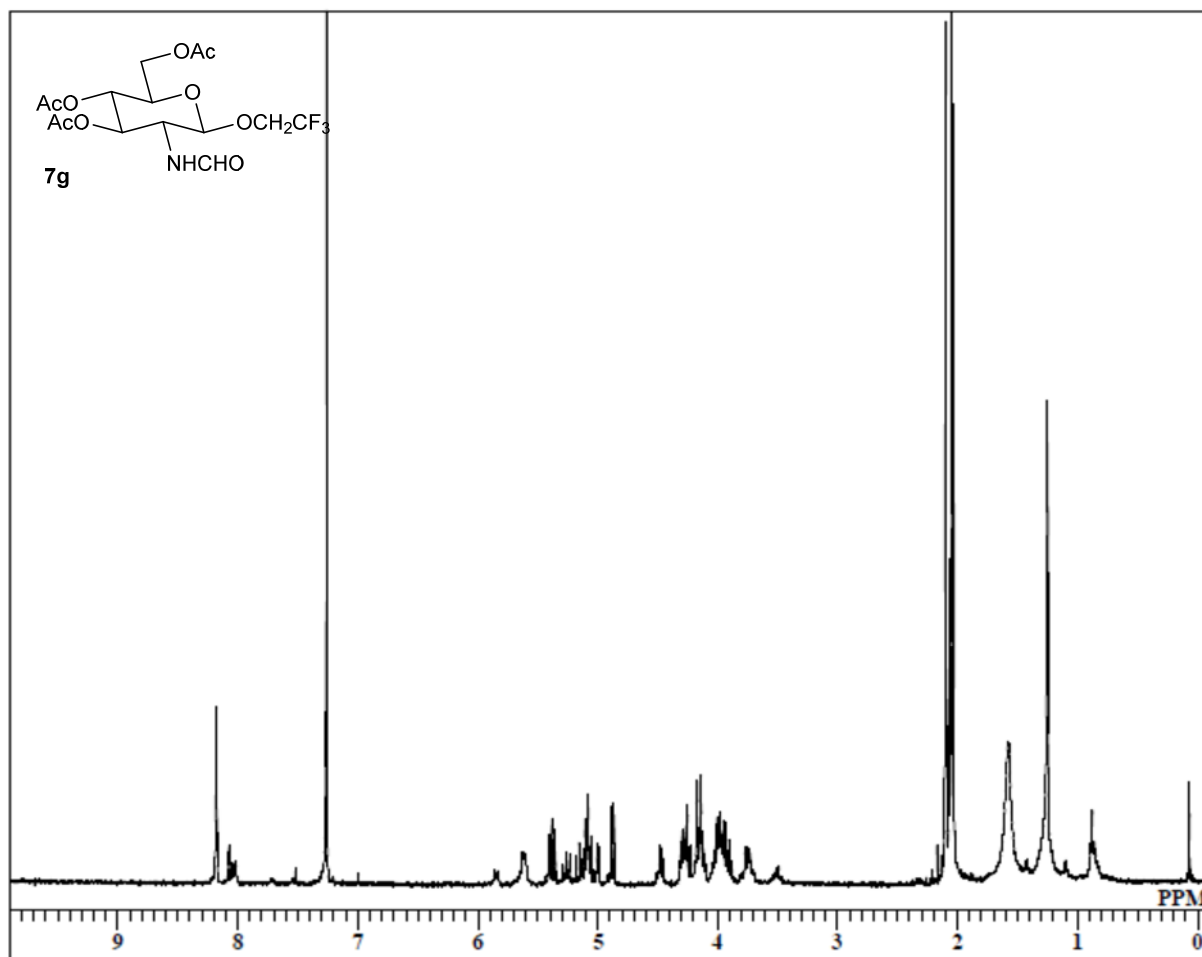
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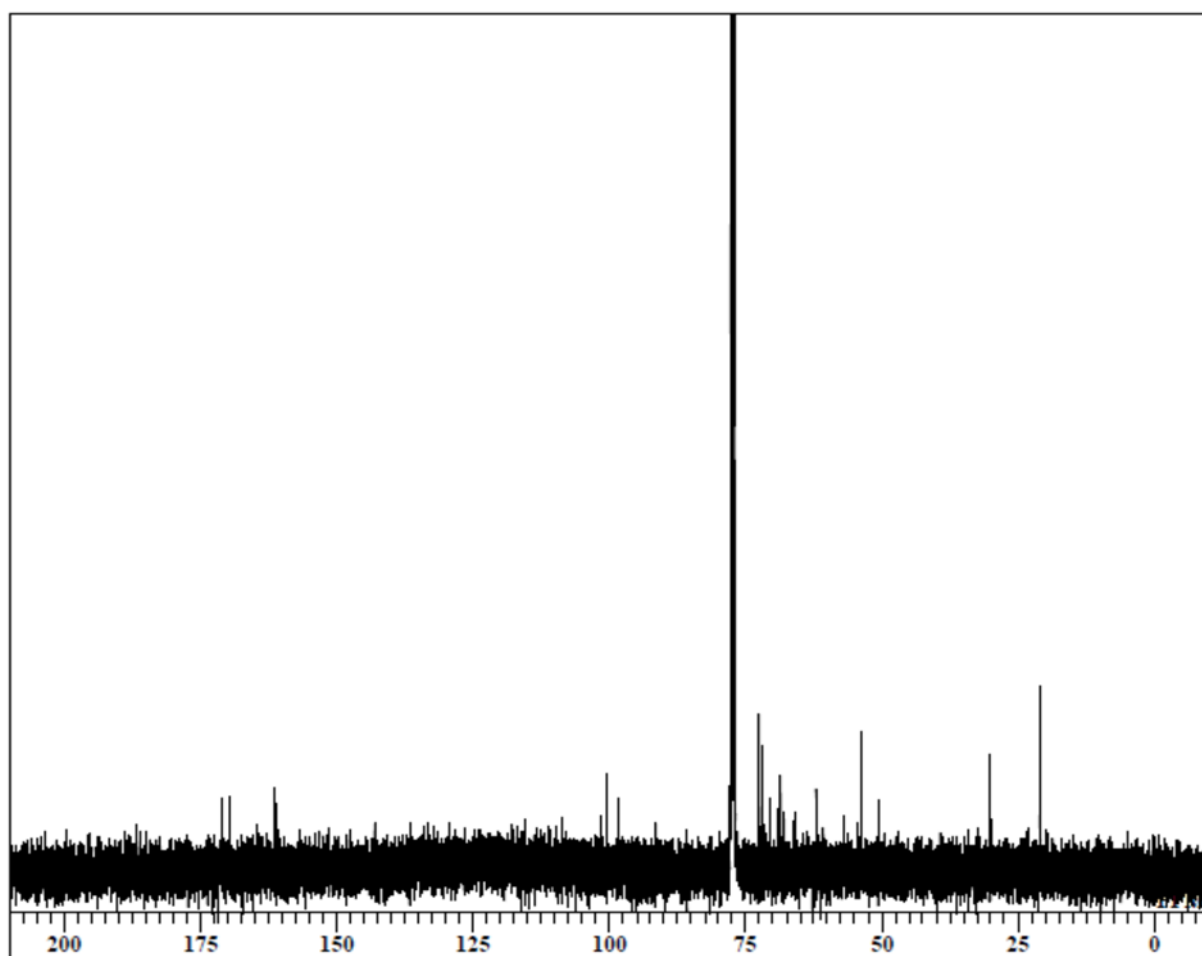


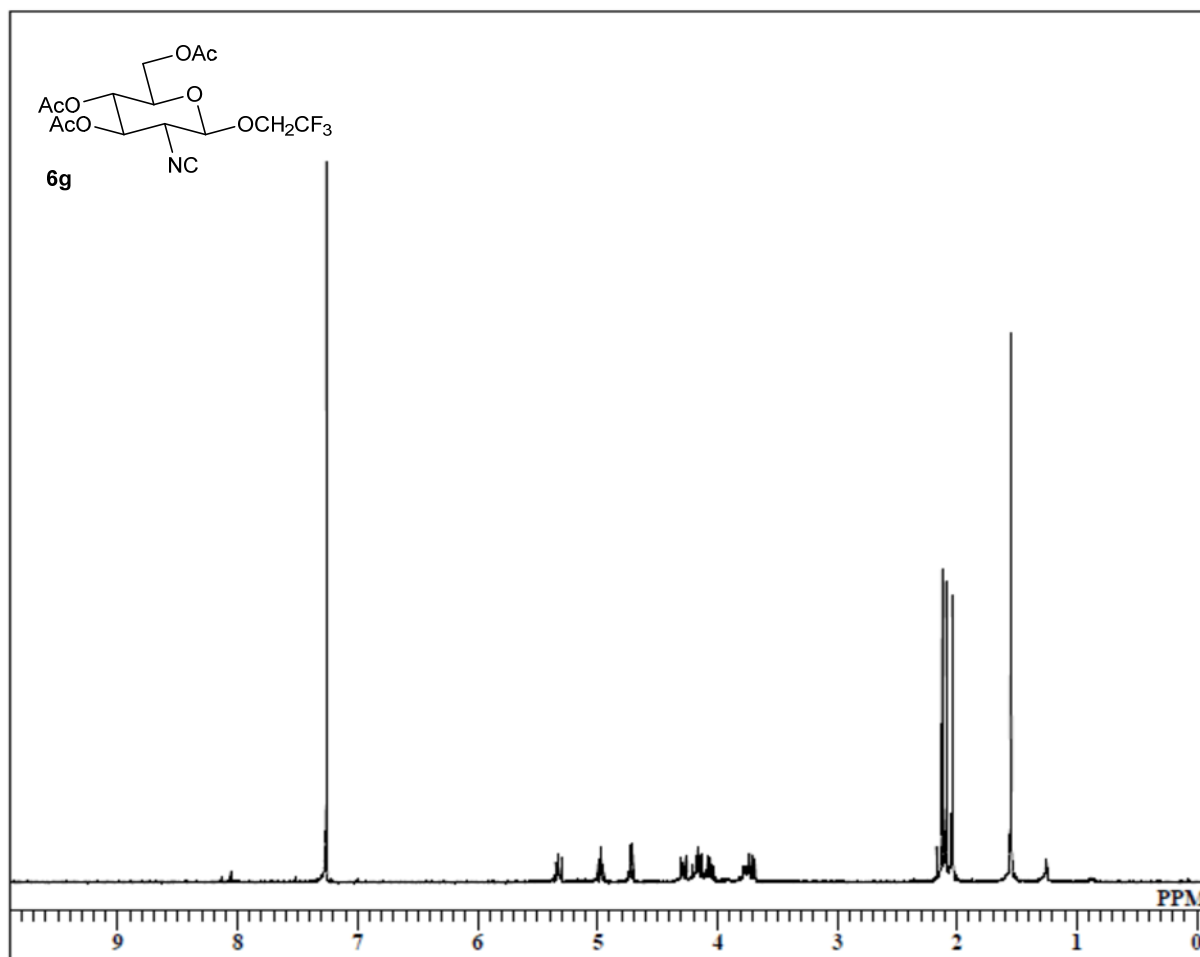
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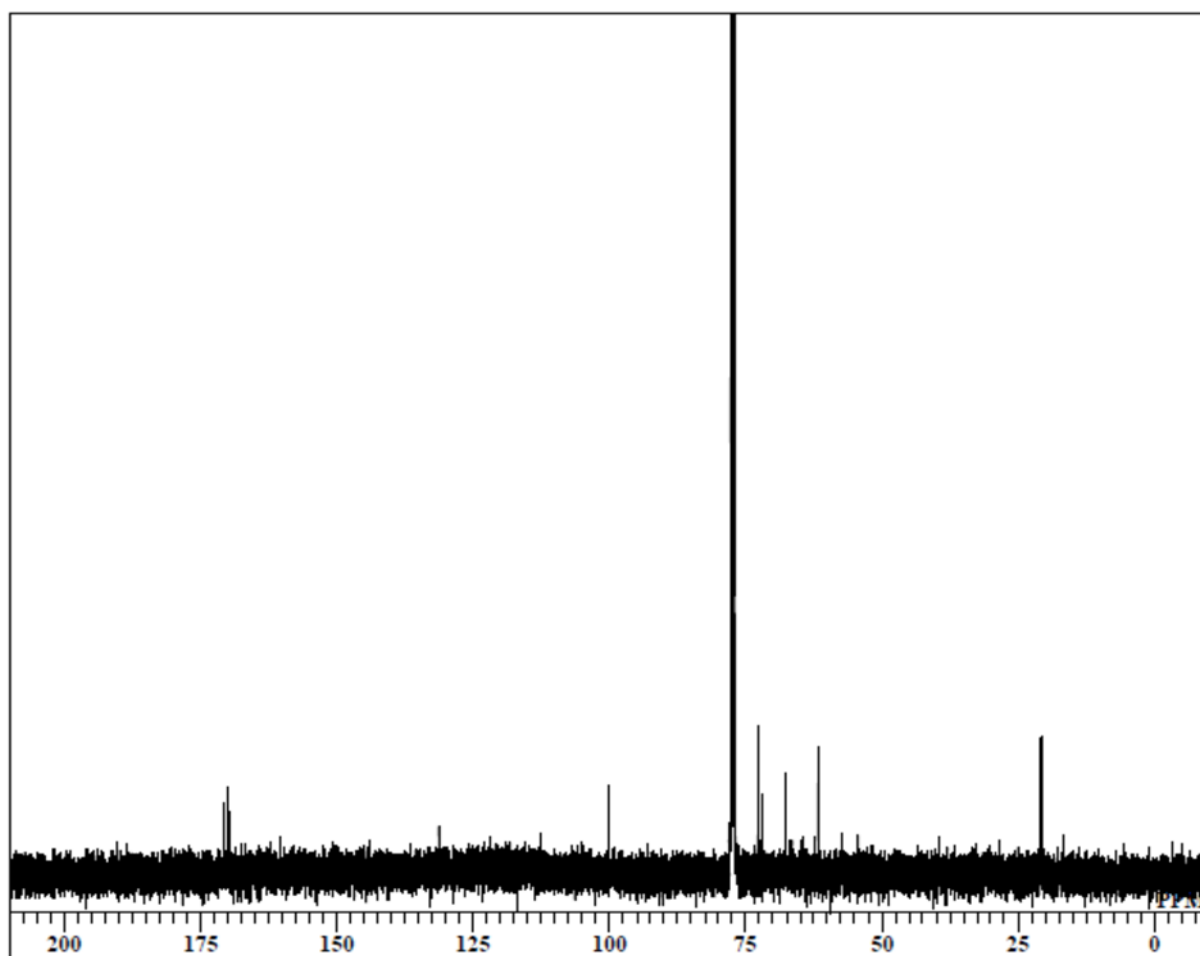


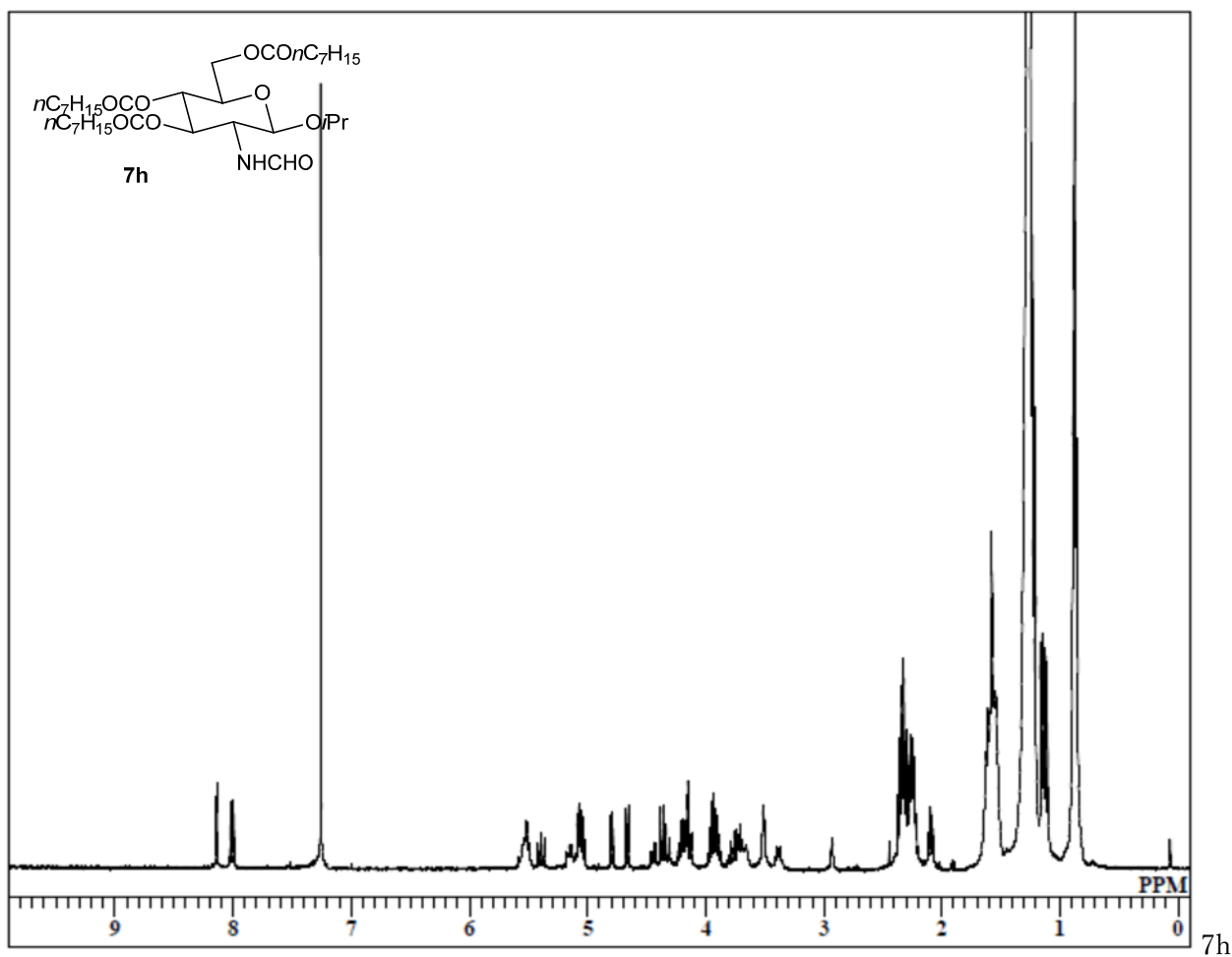
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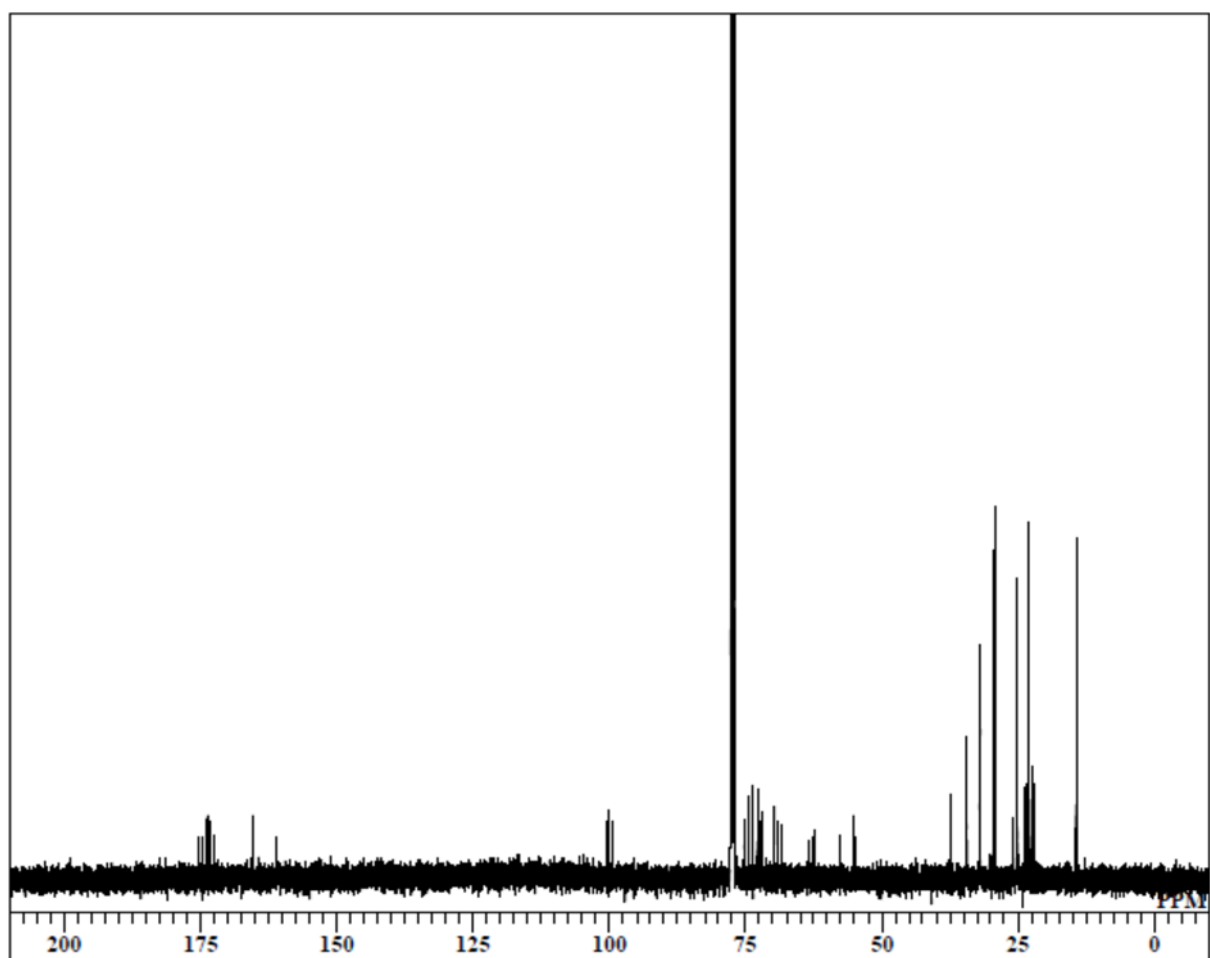


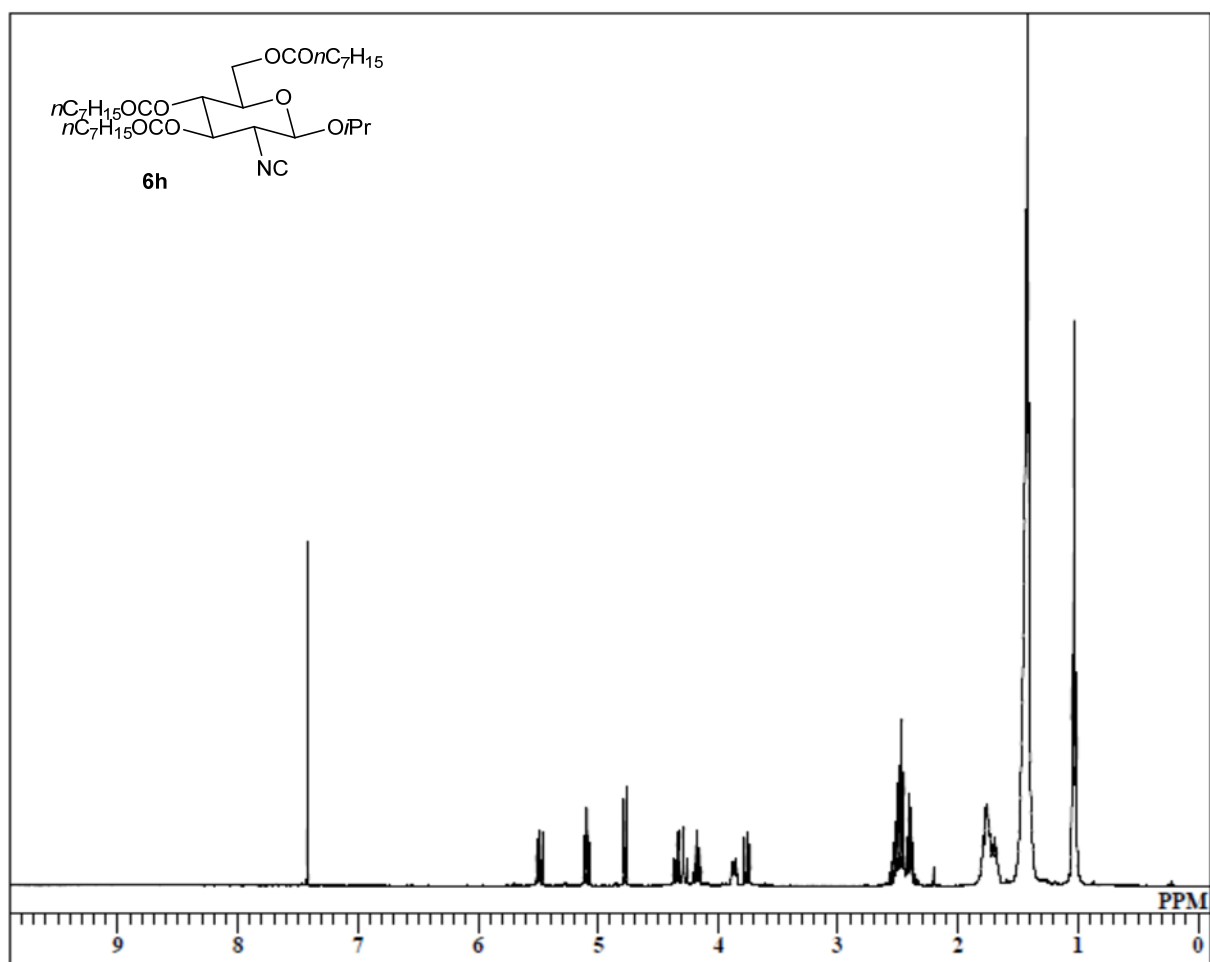
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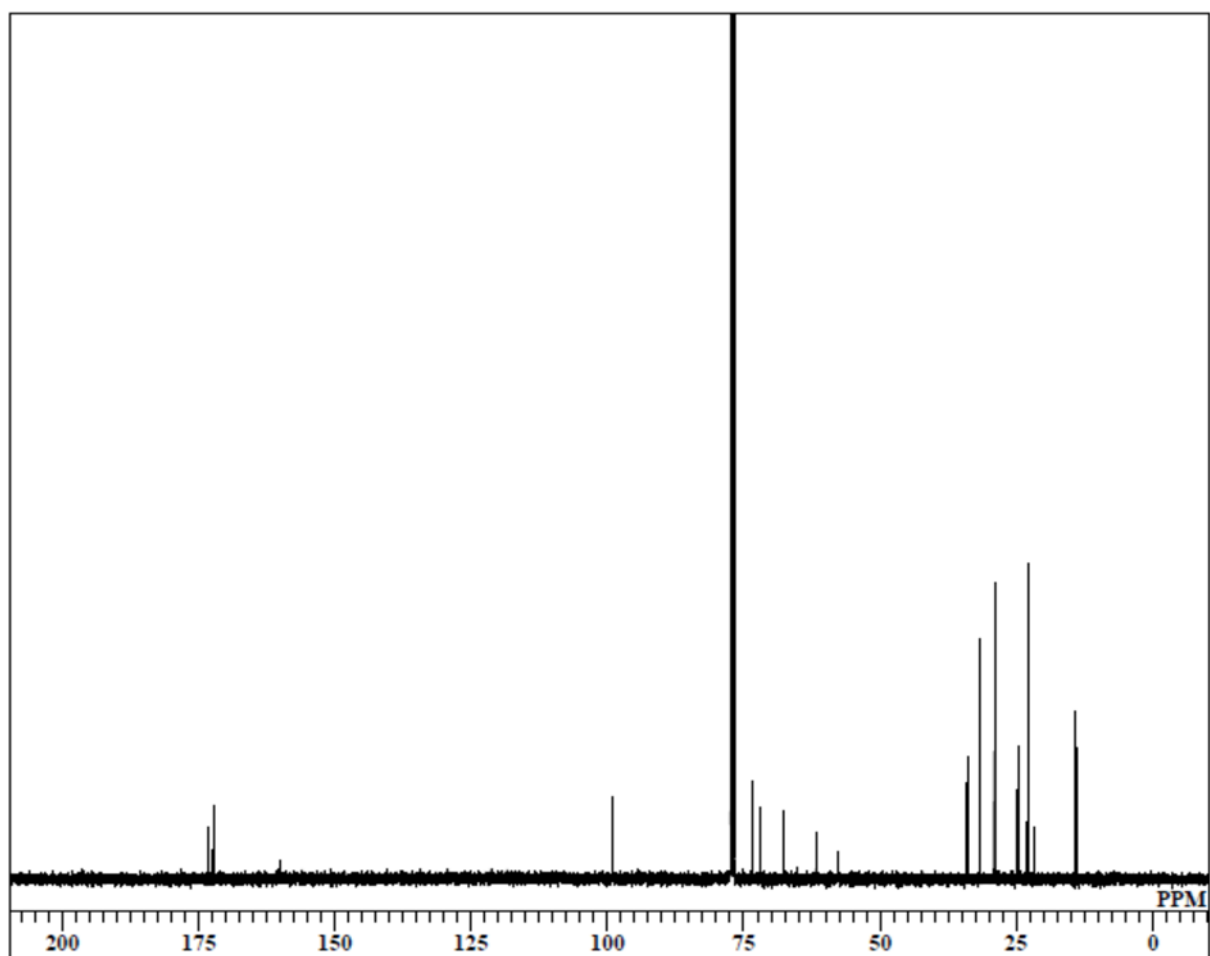


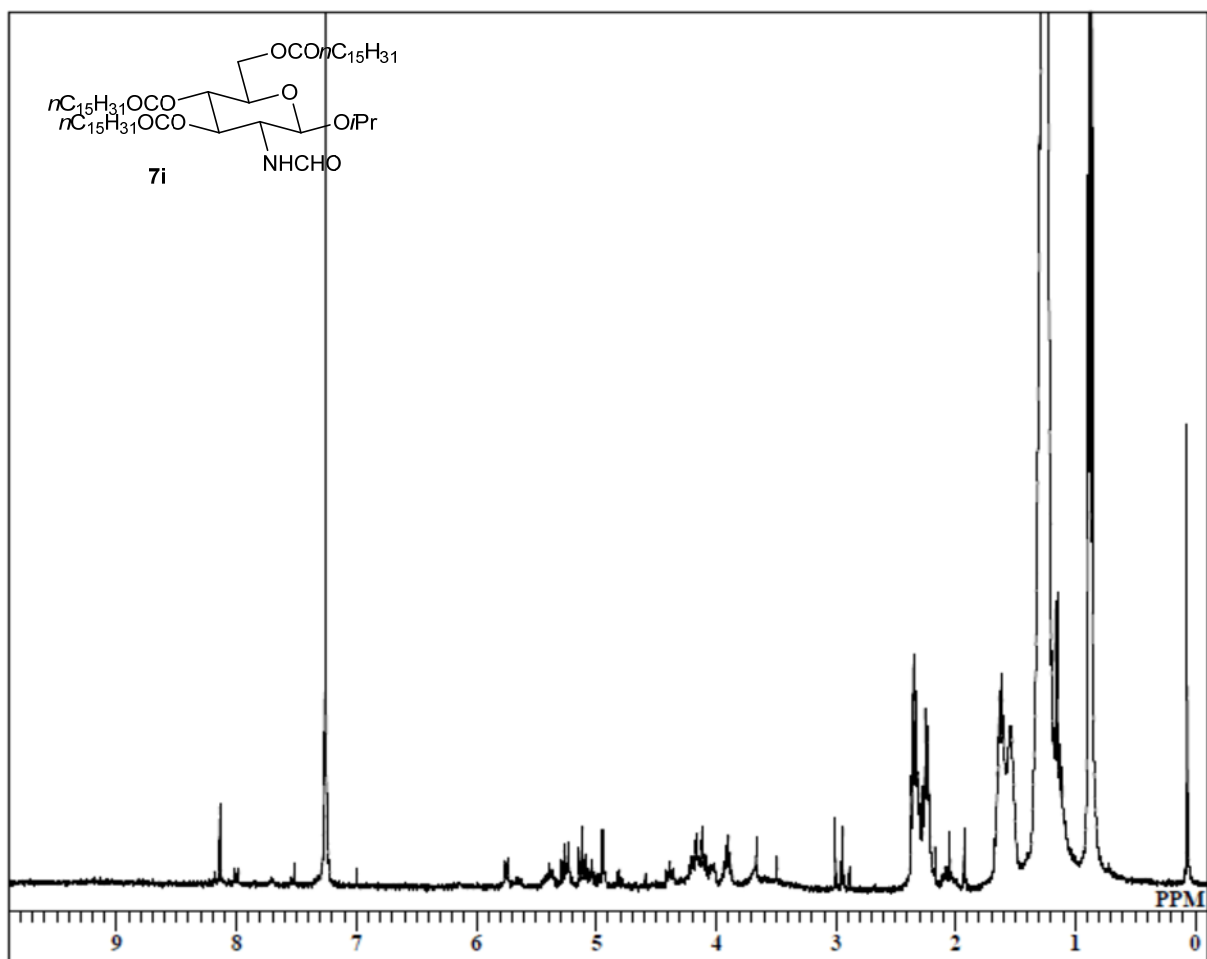
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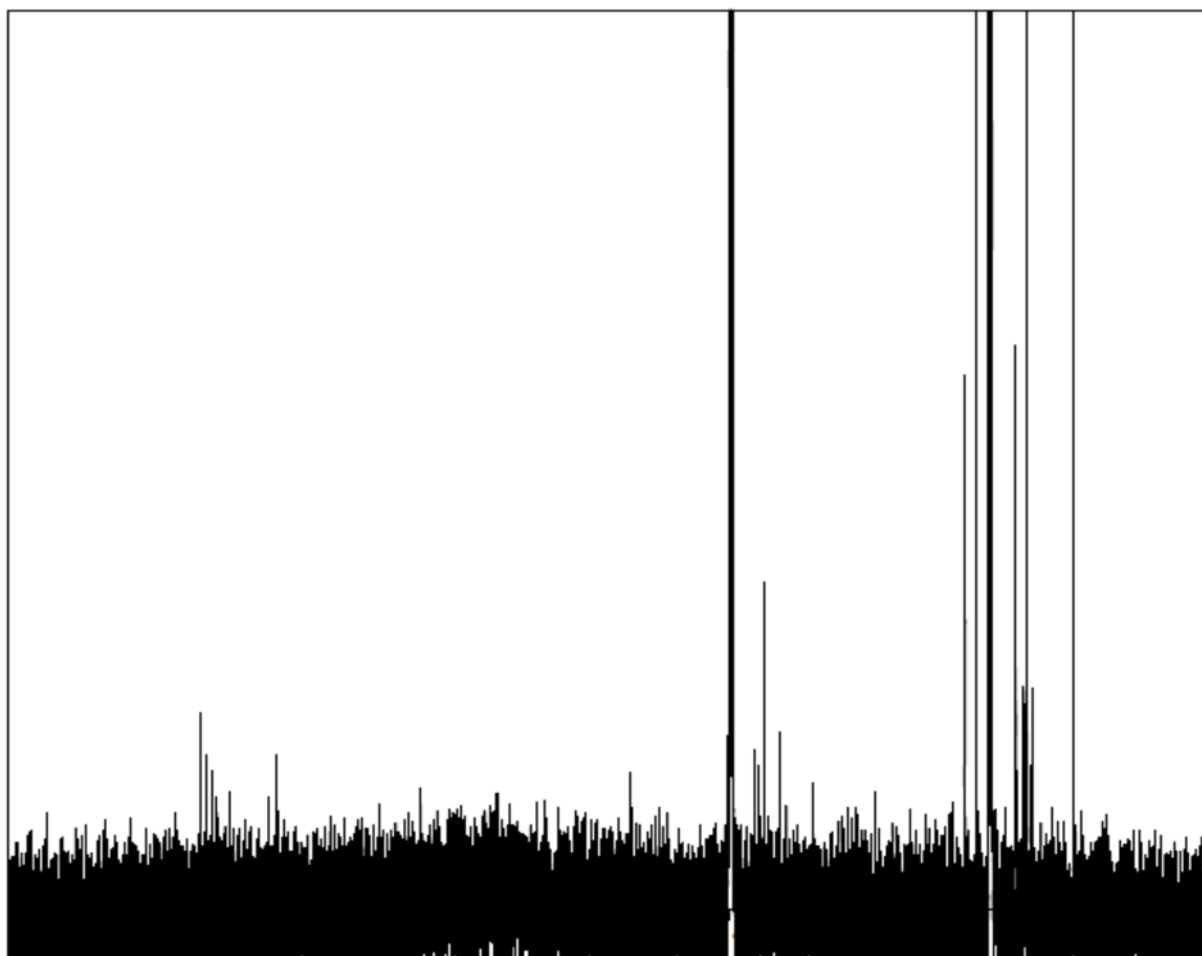


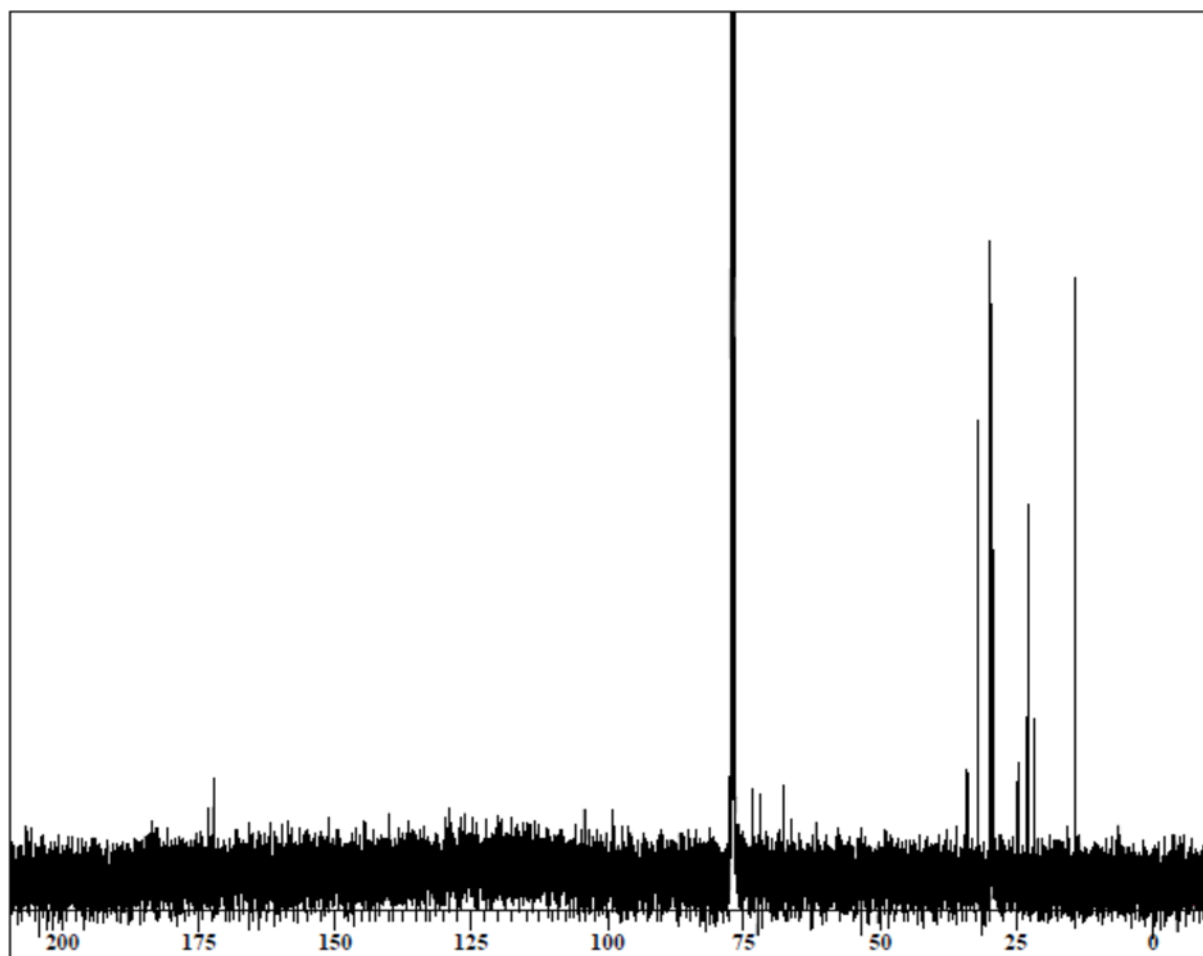
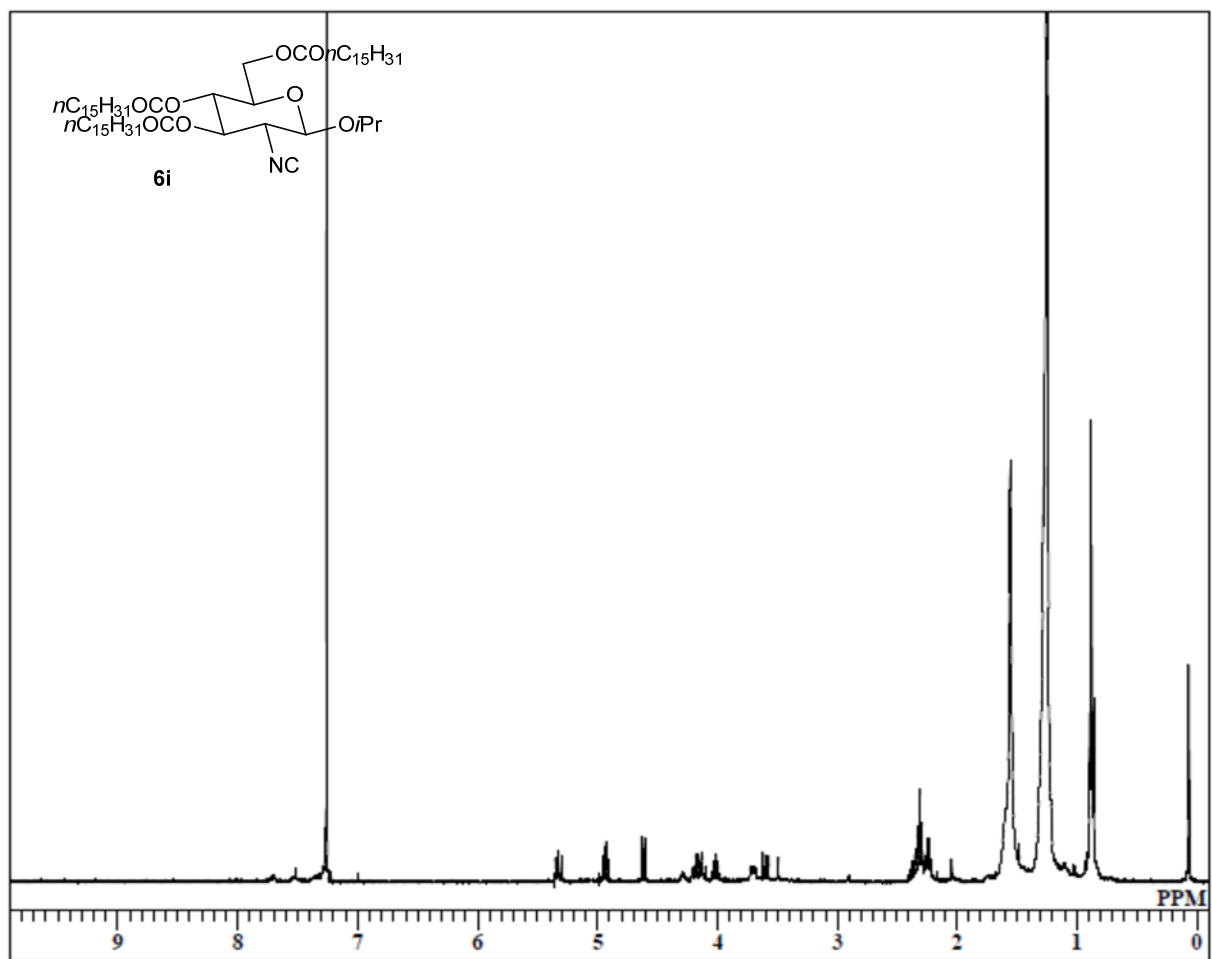
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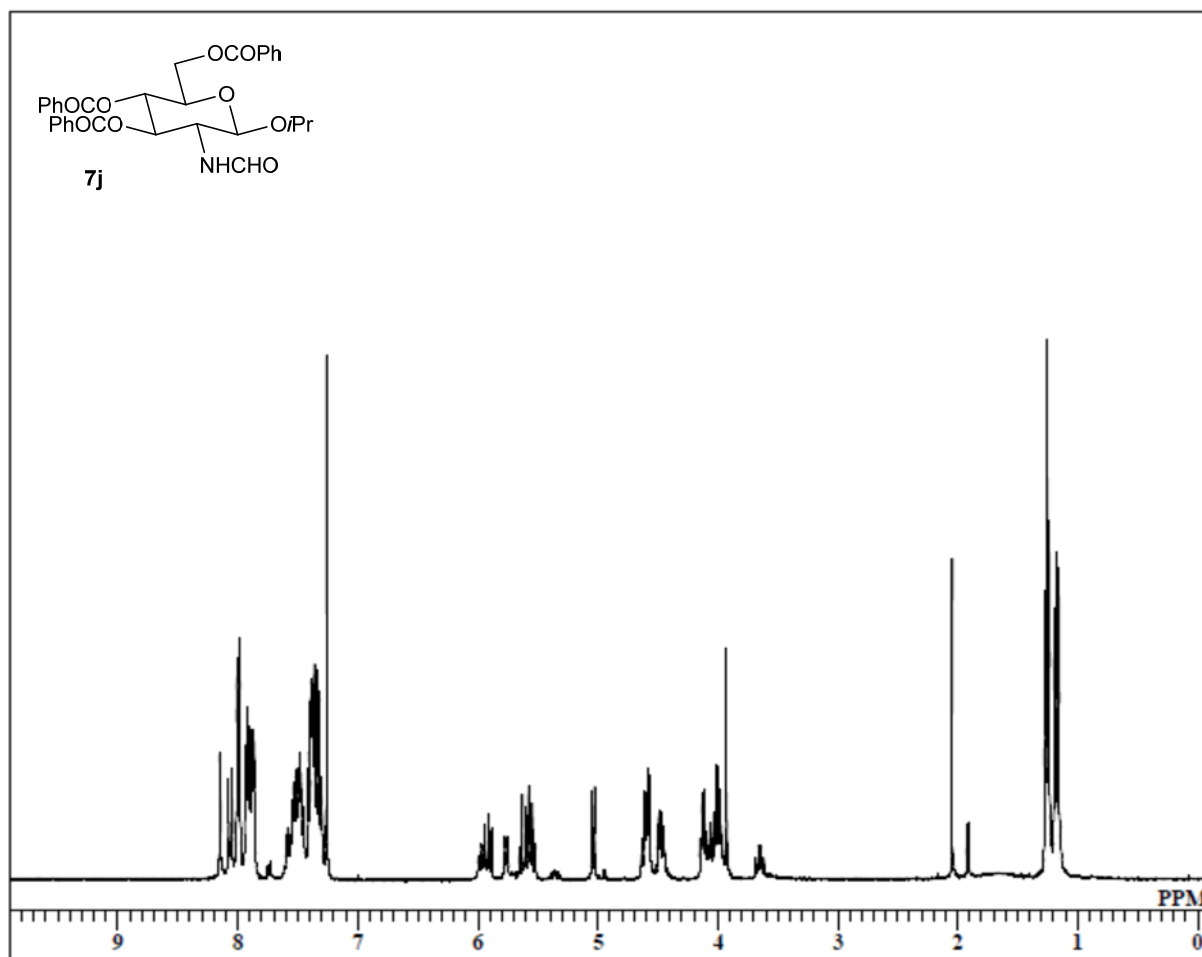




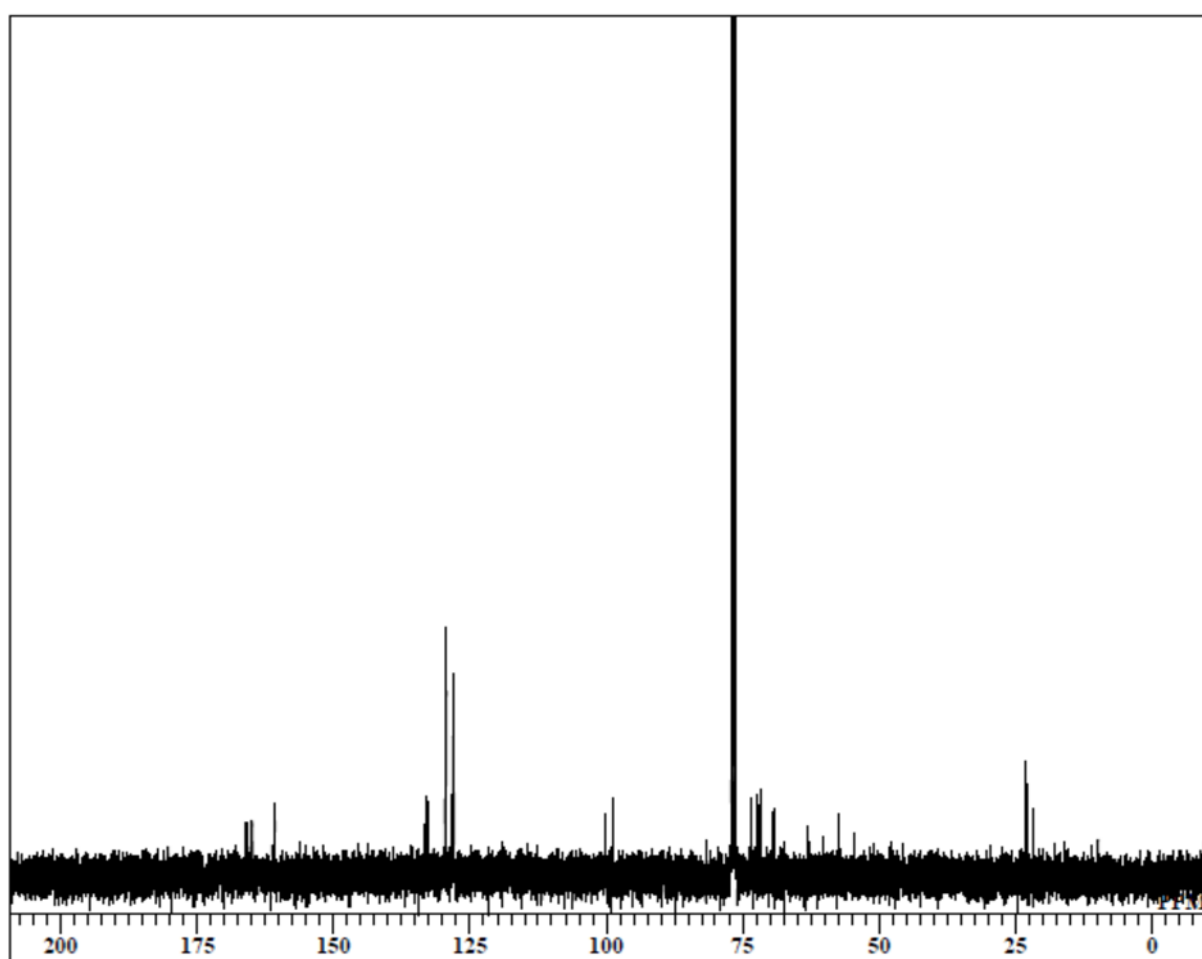
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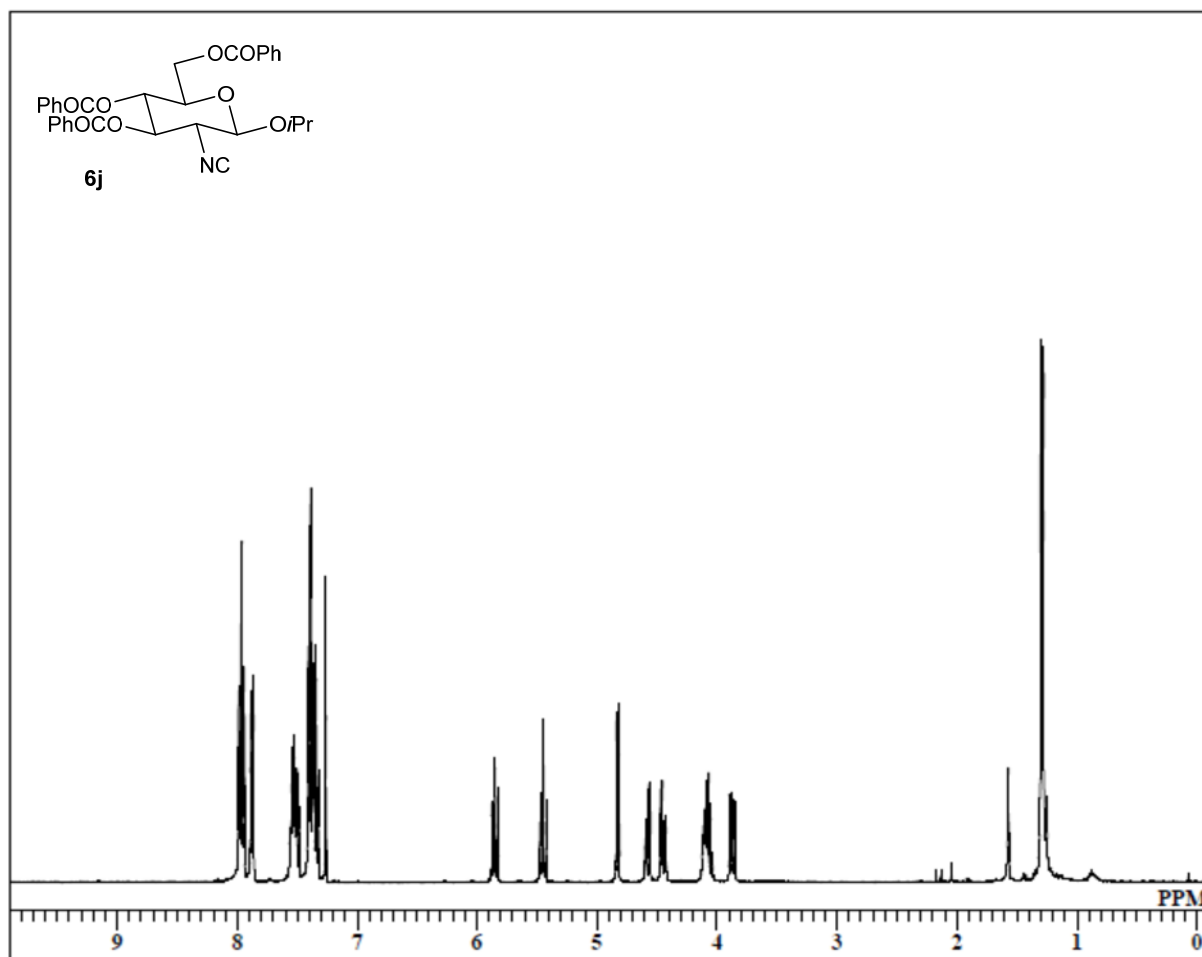




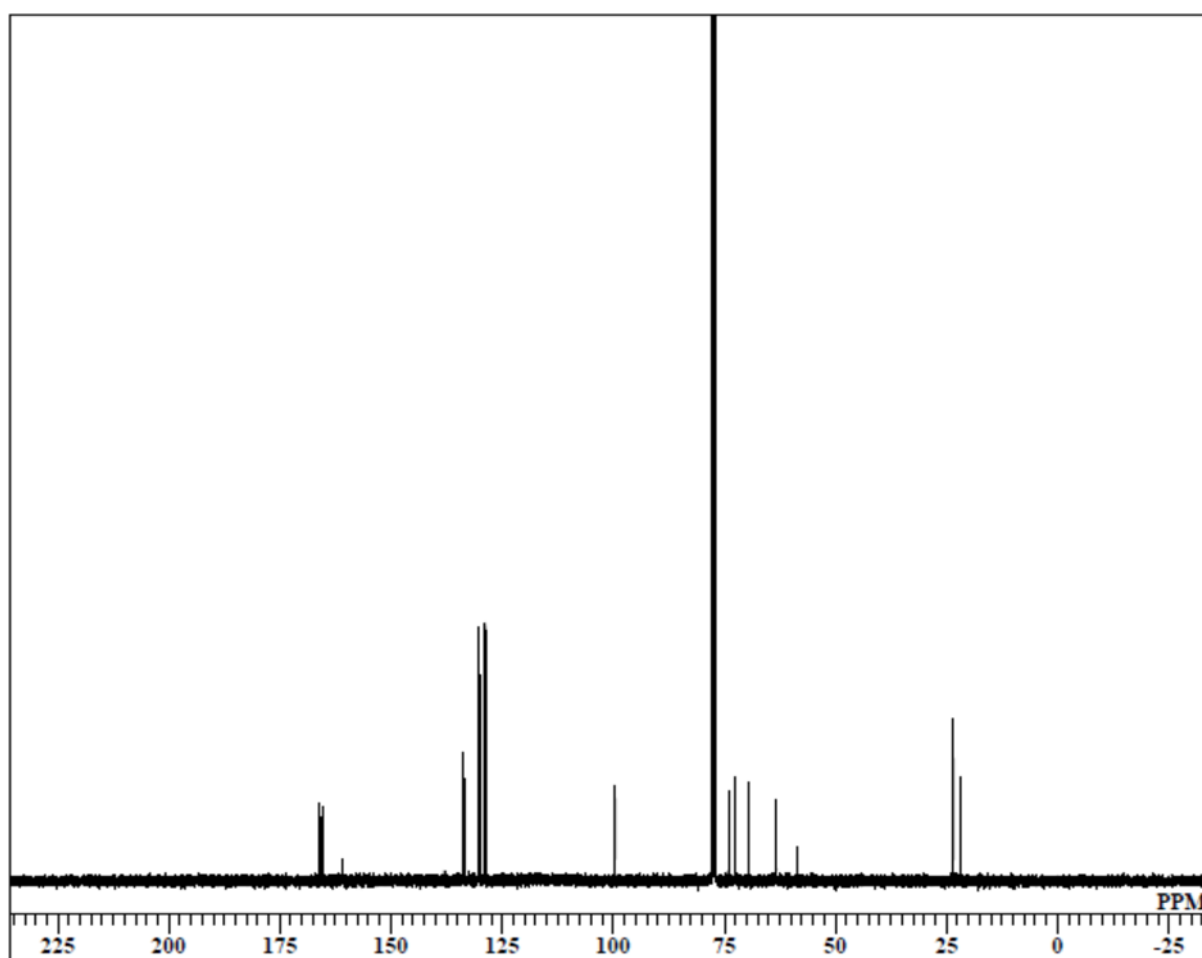


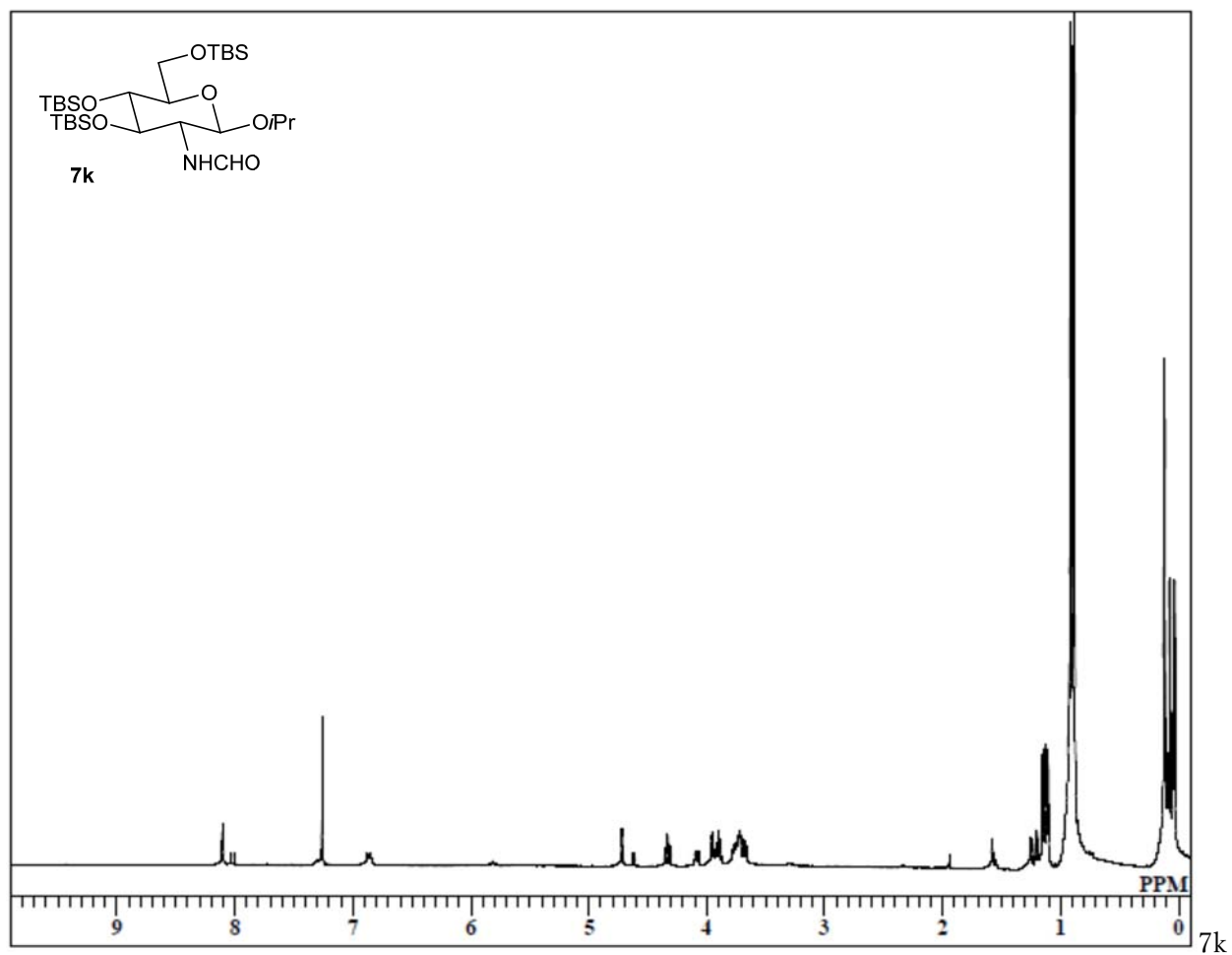
7j





6j





7k

