Supporting Information

Cyanomethyl Ether: An Orthogonal Protecting Group for Saccharides

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General Information

All reactions (if not specifically including water as a reactant, solvent, or co-solvent) were performed under N_2 atmosphere, in oven-dried glasswares. Purification was performed on Avra silica gel 100-200 mesh. Reactions were monitored by TLC on Merck silica gel 60 F254 plates, and the compounds were detected by examination under UV light, iodine vapour and by charring with 10% sulfuric acid in water. Solvents were removed under reduced pressure below 50 °C. Acetonitrile was distilled from CaH_2 under N_2 atmosphere prior to use. Freshly prepared dried THF from Na-benzophenone under nitrogen atmosphere was used for deprotection reaction. Unless noted otherwise, ^{1}H NMR spectra were recorded in $CDCl_3$ at 400 MHz and 500 MHz, ^{13}C NMR spectra at 100 MHz and 125 MHz with chloroform (7.26 ppm for ^{1}H, 77.00 ppm for ^{13}C) as an internal reference. Chemical shifts (δ) are given in parts per million (ppm); multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants (J) are reported in hertz (Hz). HRMS analyses were performed with ESI-TOF instruments by +ve mode electrospray ionization.

General Procedures:

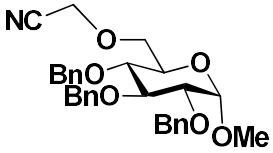
A. Synthesis of CNMe ether protected sugars: Mono-hydroxy containing partially protected sugar substrate (0.2 mmol, 1 equiv.) was dissolved in dry CH_3CN (2 mL) and the solution was cooled to 0 ^{o}C. NaH (1.2 mmol, 6 equiv., 60% oil dispersion) was added slowly to the solution and allowed to stir at 0 ^{o}C for 10 min. Subsequently, $BrCH_2CN$ (0.2 mmol, 1 equiv.) was added to the reaction mixture. After 30 min. at 0 ^{o}C, another 1 equiv. of $BrCH_2CN$ was added followed by additional 0.5 equiv. after another 30 min, to allow the complete consumption of starting material. The reaction was monitored by TLC analysis and on completion was quenched with ice water and diluted with ethyl acetate (2 mL). The aqueous layer was extracted with ethyl acetate (2 x 5 mL). The combined organic extracts were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography.

B. Deprotection of CNMe ether group: Solid naphthalene (128 mg, 1.0 mmol) was taken in an oven dried two-necked 10 ml r.b. flask and dissolved in 3.0 mL freshly dried THF. To this solution Na metal (23 mg, 1.0 mmol) was added and the solution stirred at room temperature for 2 h under N_2 atmosphere to give deep green

color of 0.33 M sodium-naphthalenide solution. To a solution of CNMe ether containing sugar in 0.50 mL dry THF was added in three portion of the freshly prepared reagent at –78 °C with time gap of 1 min. After stirring at –78 °C for 10 - 30 min, the solution was quenched with saturated NH_4Cl solution and the organic layer was washed with brine, and dried with Na_2SO_4. The solvent was removed under reduced pressure and the residue was subjected to purification through column chromatography led to pure alcohol.

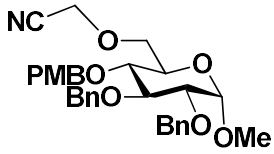
Spectral Characterization of All Newly Synthesized Compounds:

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(cyanomethyl)-α-D-glucopyranoside (3):



Following general procedure **A**, methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[1] (93 mg, 0.2 mmol was alkylated to obtain the product **3** (75 mg, 74%) as a colorless syrupy oil; R_f = 0.35 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.25 (m, 15H), 5.00 (d, J = 10.9 Hz, 1H), 4.89 (d, J = 11.0 Hz, 1H), 4.82 (dd, J = 14.8, 11.5 Hz, 2H), 4.68 – 4.57 (m, 3H), 4.17 (d, J = 6.3 Hz, 2H), 3.99 (t, J = 9.3 Hz, 1H), 3.81 – 3.66 (m, 3H), 3.58 – 3.50 (m, 2H), 3.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 138.0, 138.0, 128.5, 128.5, 128.4, 128.2, 128.1, 128.0, 127.9, 127.7, 115.7, 98.2, 82.0, 79.8, 77.2, 76.9, 75.8, 75.1, 73.5, 69.9, 69.7, 56.7, 55.4; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{30}H_{33}NNaO_6^+$ 526.2200; found 526.2194.

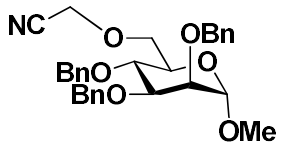
Methyl 2,3-di-*O*-benzyl-6-*O*-(cyanomethyl)-4-*O*-(p-methoxybenzyl)-α-D-glucopyranoside (4):



Following general procedure **A**, methyl 2,3-di-*O*-benzyl-4-*O*-(*p*-methoxybenzyl)-α-D-glucopyranoside[2] (99 mg, 0.2 mmol) was alkylated to obtain the product **4** (77 mg, 72%) as a colorless syrupy oil; R_f = 0.30 (20% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 10H), 7.22 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.6 Hz, 2H), 5.00 (d, J = 10.9 Hz, 1H), 4.89 – 4.74 (m, 3H), 4.65 (d, J = 12.1 Hz, 1H), 4.56 (dd, J = 12.3, 7.1 Hz, 2H), 4.20 (s, 2H), 3.98 (t, J = 9.3 Hz, 1H), 3.80 (s, 3H), 3.79 – 3.64 (m, 3H), 3.57 – 3.46 (m, 2H), 3.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

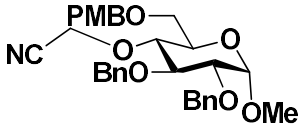
159.4, 138.7, 138.0, 130.2, 129.8, 128.5, 128.4, 128.1, 127.9, 127.9, 127.6, 115.7, 113.9, 98.2, 82.0, 79.8, 76.6, 75.73, 74.7, 73.4, 69.9, 69.7, 56.8, 55.3; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{31}H_{36}NO_7^+$ 534.2486; found 534.2484.

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(cyanomethyl)-α-D-mannopyranoside (5):



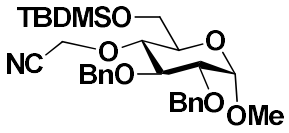
Following general procedure **A**, methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside[3] (93 mg, 0.2 mmol) was alkylated to obtain the product **5** (77 mg, 76%) as a colorless syrupy oil; R_f = 0.50 (30% ethyl acetate in hexane);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.25 (m, 15H), 4.95 (d, *J* = 10.9 Hz, 1H), 4.80 – 4.68 (m, 3H), 4.67-4.59 (m, 3H), 4.32 (d, *J* = 5.0 Hz, 2H), 4.00 – 3.84 (m, 3H), 3.83 – 3.77 (m, 2H), 3.75 – 3.69 (m, 1H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 138.2, 138.1, 128.4, 128.4, 128.1, 127.8, 127.7, 127.7, 127.6, 127.6, 116.0, 99.2, 80.1, 75.2, 74.2, 74.1, 72.7, 72.1, 71.3, 70.1, 56.7, 54.9; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{30}H_{34}NO_6^+$ 504.2381; found 504.2385.

Methyl 2,3-di-*O*-benzyl-4-*O*-(cyanomethyl)-6-*O*-(p-methoxybenzyl)-α-D-glucopyranoside (7):



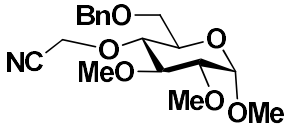
Following general procedure **A**, methyl 2,3-di-*O*-benzyl-6-*O*-(p-methoxybenzyl)-α-D-glucopyranoside[4] (99 mg, 0.2 mmol) was alkylated to obtain the product **7** (82 mg, 77%) as a colorless syrupy oil; R_f = 0.57 (20% ethyl acetate in hexane);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 12H), 6.86 (d, *J* = 8.8 Hz, 2H), 4.97 (d, *J* = 11.1 Hz, 1H), 4.74 (d, *J* = 12.1 Hz, 1H), 4.70 (d, *J* = 11.1 Hz, 1H), 4.61 (d, *J* = 12.1 Hz, 1H), 4.58 (d, *J* = 3.5 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 11.6 Hz, 1H), 4.26 (d, *J* = 15.7 Hz, 1H), 4.17 (d, *J* = 15.8 Hz, 1H), 3.95 – 3.86 (m, 1H), 3.79 (s, 3H), 3.69 – 3.58 (m, 3H), 3.54 – 3.46 (m, 2H), 3.35 (s, 3H); ^{13}C NMR (125 MHz,) δ 159.3, 138.3, 137.8, 129.7, 129.7, 128.5, 128.1, 128.0, 128.0, 127.8, 116.2, 113.8, 97.9, 81.5, 79.8, 78.1, 75.6, 73.3, 73.1, 69.1, 67.6, 57.3, 55.4, 55.2; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{31}H_{36}NO_7^+$ 534.2486; found 534.2478.

Methyl 2,3-di-*O*-benzyl-4-*O*-(cyanomethyl)-6-*O*-(tert-butyldimethylsilyl)-α-D-glucopyranoside (8):



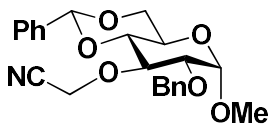
Following general procedure **A**, methyl 2,3-di-*O*-benzyl-6-*O*-(tert-butyldimethylsilyl)-α-D-glucopyranoside[5] (98 mg, 0.2 mmol) was alkylated to obtain the product **8** (97 mg, 92%) as a colorless syrupy oil: R_f = 0.60 (20% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.28 (m, 10 H), 4.99 (d, *J* = 10.9 Hz, 1H), 4.75 (dd, *J* = 11.4, 8.0 Hz, 2H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.59 (d, *J* = 3.5 Hz, 1H), 4.40 (s, 2H), 3.94 (t, *J* = 9.2 Hz, 1H), 3.83-3.78 (m, 2H), 3.58-3.53 (m, 1H), 3.47 (dd, *J* = 9.6, 3.5 Hz, 1H), 3.42 (t, *J* = 9.4 Hz, 1H), 3.37 (s, 3H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.9, 128.5, 128.5, 128.1, 128.0, 128.0, 127.9, 116.1, 97.7, 81.4, 80.3, 78.3, 75.7, 73.2, 70.5, 62.0, 57.4, 55.1, 25.9, 18.3, -5.3, -5.4; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{29}H_{42}NO_6Si^+$ 528.2776; found 528.2773.

Methyl 6-*O*-benzyl-4-*O*-(cyanomethyl)-2,3-di-*O*-methyl-α-D-glucopyranoside (9):



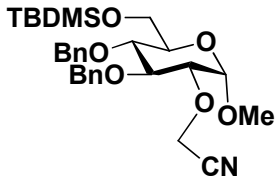
Following general procedure **A**, methyl 6-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside[6] (63 mg, 0.2 mmol) was alkylated to obtain the product **9** (57 mg, 81%) as a colorless syrupy oil; R_f = 0.32 (30% ethyl acetate in hexane double run); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.25 (m, 5H), 4.84 (d, *J* = 3.4 Hz, 1H), 4.64 (d, *J* = 12.0 H, 1H), 4.55 (d, *J* = 12.0 Hz, 1H), 4.38 (d, *J* = 15.9 H, 1H), 4.31 (d, *J* = 15.9 Hz, 1H), 3.73-3.59 (m, 6H), 3.59-3.45 (m, 5H), 3.41 (s, 3H), 3.24 (dd, *J* = 9.3, 3.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 128.4, 128.0, 127.8, 116.2, 97.3, 83.0, 82.0, 78.6, 73.5, 69.2, 68.0, 60.9, 58.8, 57.4, 55.3; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{18}H_{25}NNaO_6^+$ 374.1574; found 374.1594;

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-3-*O*-(cyanomethyl)-α-D-glucopyranoside (10):



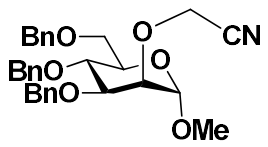
Following general procedure **A**, methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside[7] (75 mg, 0.2 mmol) was alkylated to obtain the product **10** (66 mg, 80%) as a colorless syrupy oil; R_f = 0.47 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.46 (m, 2H), 7.42-7.29 (m, 8H), 5.53 (s, 1H), 4.82 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 12.2 Hz, 1H), 4.59 (d, *J* = 3.7 Hz, 1H), 4.54 (d, *J* = 15.8 Hz, 1H), 4.48 (d, *J* = 15.8 Hz, 1H), 4.26 (dd, *J* = 10.1, 4.7 Hz, 1H), 3.95 (t, *J* = 9.2 Hz, 1H), 3.82 (td, *J* = 9.9, 4.6 Hz, 1H), 3.70 (t, *J* = 10.2 Hz, 1H), 3.57 (t, *J* = 9.3 Hz, 1H), 3.51 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 136.9, 129.2, 128.5, 128.3, 128.2, 128.1, 126.1, 116.3, 101.5, 98.8, 81.2, 79.7, 78.4, 73.7, 68.9, 61.9, 57.8, 55.4; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{23}H_{26}NO_6^+$ 412.1755; found 412.1744;

Methyl 3,4-di-*O*-benzyl-2-*O*-(cyanomethyl)-6-*O*-(tert-butyldimethylsilyl)-α-D-glucopyranoside (11):



Following general procedure **A**, methyl 3,4-di-*O*-benzyl-6-*O*-(tert-butyldimethylsilyl)-α-D-glucopyranoside[8] (98 mg, 0.2 mmol) was alkylated to obtain the product **11** (93 mg, 88%) as a colorless syrupy oil; R_f = 0.80 (15% ethyl acetate in hexane double run); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.27 (m, 10H), 4.91-4.82 (m, 3H), 4.76 (d, *J* = 11.0 Hz, 1H), 4.70 (d, *J* = 10.9 Hz, 1H), 4.41 (s, 2H), 4.02-3.96 (m, 1H), 3.88-3.79 (m, 2H), 3.63 (d, *J* = 5.4 Hz, 2H), 3.55 (dd, *J* = 9.6, 3.7 Hz, 1H), 3.43 (s, 3H), 0.92 (s, 9H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 138.1, 128.5, 128.5, 127.8, 127.8, 116.3, 97.3, 81.9, 80.8, 77.9, 75.8, 75.0, 71.5, 61.9, 56.9, 54.9, 25.9, 18.3, -5.2, -5.4; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{29}H_{42}NO_6Si^+$ 528.2776; found 528.2778.

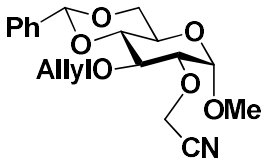
Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(cyanomethyl)-α-D-mannopyranoside (12):



Following general procedure **A**, methyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside[9] (93 mg, 0.2 mmol) was alkylated to obtain the product **12** (89 mg, 88%) as a colorless

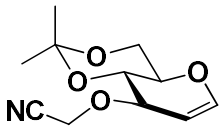
syrupy oil; R_f = 0.55 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.24 (m, 13H), 7.21-7.13 (m, 2H), 4.83 (d, *J* = 10.8 Hz, 1H), 4.80 (d, *J* = 1.6 Hz, 1H), 4.74 (d, *J* = 2.3 Hz, 2H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.61-4.41 (m, 4H), 3.98-3.87 (m, 3H), 3.79-3.66 (m, 3H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 138.1, 137.8, 128.6, 128.3, 128.3, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 116.2, 98.8, 80.2, 76.4, 75.1, 74.8, 73.5, 73.3, 71.6, 68.7, 56.6, 54.9; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{30}H_{34}NO_6^+$ 504.2381; found 504.2389.

Methyl 3-*O*-allyl-4,6-*O*-benzylidene-2-*O*-(cyanomethyl)-α-D-glucopyranoside (13):



Following general procedure **A**, methyl 3-*O*-allyl-4,6-*O*-benzylidene-α-D-glucopyranoside[10] (64 mg, 0.2 mmol) was alkylated to obtain the product **13** (64 mg, 89%) as a white amorphous solid; R_f = 0.50 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.45 (m, 2H), 7.42-7.35 (m, 3H), 6.00-5.87 (m, 1H), 5.54 (s, 1H), 5.32 (dd, *J* = 17.2, 1.5 Hz, 1H), 5.24 (dd, *J* = 10.3, 1.2 Hz, 1H), 4.81 (d, *J* = 3.7 Hz, 1H), 4.51 (d, *J* = 8.5 Hz, 2H), 4.33-4.23 (m, 2H), 4.16 (dd, *J* = 12.7, 6.5 Hz, 1H), 3.91 (t, *J* = 9.2 Hz, 1H), 3.87-3.79 (m, 1H), 3.74 (t, *J* = 10.2 Hz, 1H), 3.58 (t, *J* = 9.3 Hz, 1H), 3.49 (dd, *J* = 9.2, 3.7 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.9, 134.3, 129.2, 128.3, 126.1, 118.3, 116.3, 101.5, 98.7, 81.2, 79.7, 78.4, 72.8, 68.9, 62.0, 57.8, 55.4; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{19}H_{24}NO_6^+$ 362.1598; found 362.1599.

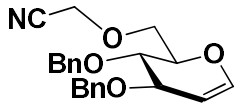
1,5-Anhydro-3-*O*-(cyanomethyl)-2-deoxy-4,6-*O*-isopropylidene-D-arabino-hex-1-enitol (14):



Following general procedure **A**, 1,5-Anhydro-2-deoxy-4,6-*O*-isopropylidene-D-arabino-hex-1-enitol[11] (37 mg, 0.2 mmol) was alkylated to obtain the product **14** (24 mg, 54%) as a colorless syrupy oil; R_f = 0.50 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (dd, *J* = 6.1, 1.5 Hz, 1H), 4.71 (dd, *J* = 6.2, 2.0 Hz, 1H), 4.42 (q, *J* = 16.1 Hz, 2H), 4.26 (dt, *J* = 7.3, 1.8 Hz, 1H), 4.05 – 3.92 (m, 2H), 3.85 (t, *J*

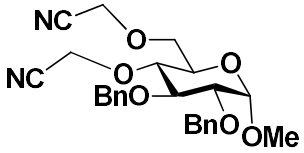
= 10.6 Hz, 1H), 3.74 (td, *J* = 10.3, 5.7 Hz, 1H), 1.56 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.4, 116.6, 100.8, 99.8, 75.6, 72.3, 69.2, 61.4, 55.5, 29.0, 18.9; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{11}H_{16}NO_4^+$ 226.1074 ; found 226.1065.

1,5-Anhydro-2-deoxy-3,4-di-*O*-benzyl-6-*O*-(cyanomethyl)-D-arabino-hex-1-enitol (15):



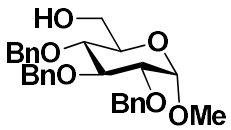
Following general procedure **A**, 1,5-Anhydro-2-deoxy-3,4-di-*O*-benzyl-D-arabino-hex-1-enitol[12] (65 mg, 0.2 mmol) was alkylated to obtain the product **15** (52 mg, 71%) as a white semi solid; R_f = 0.47 (20% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 10H), 6.40 (d, *J* = 6.0 Hz, 1H), 4.92 (dd, *J* = 6.1, 2.7 Hz, 1H), 4.86 (d, *J* = 11.4 Hz, 1H), 4.68 (dd, *J* = 13.6, 11.6 Hz, 2H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.26 (s, 2H), 4.24-4.19 (m, 1H), 4.10 – 4.03 (m, 1H), 3.93 (dd, *J* = 10.7, 5.1 Hz, 1H), 3.85 – 3.76 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.2, 138.1, 137.8, 128.5, 128.5, 128.1, 127.9, 127.8, 115.7, 100.3, 76.1, 75.3, 73.7, 73.7, 70.5, 69.7, 56.8; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{22}H_{24}NO_4^+$ 366.1700; found 366.1698.

Methyl 2,3-di-*O*-benzyl-4,6-di-*O*-(cyanomethyl)-α-D-glucopyranoside (16):



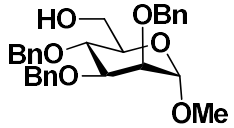
Following general procedure **A**, methyl 2,3-di-*O*-benzyl-α-D-glucopyranoside[13] (75 mg, 0.2 mmol) was alkylated to obtain the product **16** (65 mg, 72%) as a colorless syrupy oil; R_f = 0.70 (50% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.28 (m, 10H), 5.02 (d, *J* = 11.2 Hz, 1H), 4.79-4.57 (m, 4H), 4.47 (d, *J* = 16.2 Hz, 1H), 4.39 (d, *J* = 16.2 Hz, 1H), 4.31 (dd, *J* = 16.2, 5.7 Hz, 2H), 3.95 (t, *J* = 9.2 Hz, 1H), 3.86-3.76 (m, 2H), 3.69 (d, *J* = 9.9 Hz, 1H), 3.58-3.48 (m, 2H), 3.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.6, 128.6, 128.1, 128.0, 116.3, 115.6, 98.0, 81.5, 79.8, 77.1, 75.6, 73.3, 69.3, 68.6, 57.5, 56.8, 55.6; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{25}H_{29}N_2O_6^+$ 453.2020 ; found 453.2031.

Methyl 2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (19):



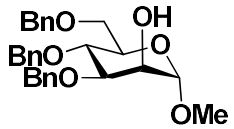
Following the general procedure **B** the compound **3** (50 mg, 0.1 mmol) was deprotected to obtain the the alcohol **19** (26 mg, 56%) as a colorless syrup: R_f = 0.19 (30% ethyl acetate in hexane); Spectral data for the column purified compound was in complete accordance with previously reported data.[1]

Methyl 2,3,4-tri-*O*-benzyl-α-D-mannopyranoside (20):



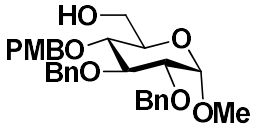
Following the general procedure **B** the compound **5** (50 mg, 0.1 mmol) was deprotected to obtain the alcohol **20** (34 mg, 74%) as a colorless syrup: R_f = 0.47 (30% ethyl acetate in hexane double run); Spectral data for the column purified compound was in complete accordance with previously reported data.[3]

Methyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (21):



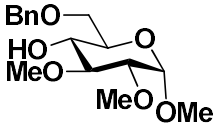
Following the general procedure **B** the compound **12** (50 mg, 0.1 mmol) was deprotected to obtain the alcohol **21** (25 mg, 54%) as a light yellow syrup; R_f = 0.22 (30% ethyl acetate in hexane); Spectral data for the column purified compound was in complete accordance with previously reported data.[9]

Methyl 2,3-di-*O*-benzyl-4-*O*-(p-methoxybenzyl)-α-D-glucopyranoside (22):



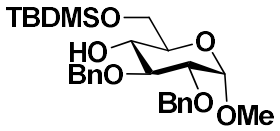
Following the general procedure **B** the compound **4** (53 mg, 0.1 mmol) was deprotected to obtain the alcohol **22** (30 mg, 61%) as a colorless syrup; R_f = 0.32 (30% ethyl acetate in hexane); Spectral data for the column purified compound was in complete accordance with previously reported data.[2]

Methyl 6-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside (23):



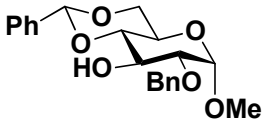
Following the general procedure **B** the compound **9** (35 mg, 0.1 mmol) was deprotected to obtain the alcohol **23** (27 mg, 88%) as a colorless syrup; R_f = 0.25 (50% ethyl acetate in hexane); Spectral data for the column purified compound was in complete accordance with previously reported data.[6]

Methyl 2,3-di-*O*-benzyl-6-*O*-(tert-butyldimethylsilyl)-α-D-glucopyranoside (24):



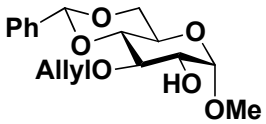
Following the general procedure **B** the compound **8** (53 mg, 0.1 mmol) was deprotected to obtain the alcohol **24** (44 mg, 92%) as a colorless syrup; R_f = 0.72 (30% ethyl acetate in hexane); Spectral data for the column purified compound was in complete accordance with previously reported data.[5]

Methyl 2-*O*-benzyl-4,6-*O*-benzylidene-α-D-glucopyranoside (25):



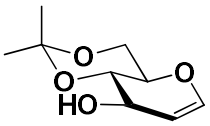
Following the general procedure **B** the compound **10** (41 mg, 0.1 mmol) was deprotected to obtain the alcohol **25** (28 mg, 75%) as a white amorphous solid: R_f = 0.25 (20% ethyl acetate in hexane); Spectral data for the column purified compound was in complete accordance with previously reported data.[7]

Methyl 3-*O*-allyl-4,6-*O*-benzylidene-α-D-glucopyranoside (26):



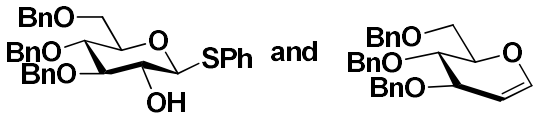
Following the general procedure **B** the compound **13** (36 mg, 0.1 mmol) was deprotected to obtain the alcohol **26** (18 mg, 56%) as a white amorphous solid: R_f = 0.30 (30% ethyl acetate in hexane); Spectral data for the column purified compound was in complete accordance with previously reported data.[10]

1,5-Anhydro-2-deoxy-4,6-*O*-isopropylidene-D-arabino-hex-1-enitol (27):



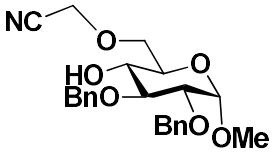
Following the general procedure **B** the compound **14** (23 mg, 0.1 mmol) was deprotected to obtain the alcohol **27** (12 mg, 67%) as a colorless syrup: R_f = 0.25 (30% ethyl acetate in hexane); Spectral data for the column purified compound was in complete accordance with previously reported data.[11]

Phenyl 3,4,6-tri-O-benzyl-1-thio-β-D-glucopyranoside (28) and 3,4,6-Tri-O-benzyl glucal (29):



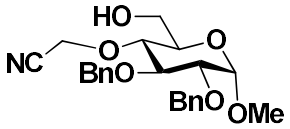
Following the general procedure **B** the compound **17** (58 mg, 0.1 mmol) was deprotected to obtain the products **28** (20 mg, 37%) and **29** (15 mg, 37%): R_f = 0.15 (15% ethyl acetate in hexane) for **28** and R_f = 0.50 (15% ethyl acetate in hexane) for **29**; Spectral data for the column purified compound was in complete accordance with previously reported data.[14, 15]

Methyl 2,3-di-*O*-benzyl-6-*O*-(cyanomethyl)-α-D-glucopyranoside (30):



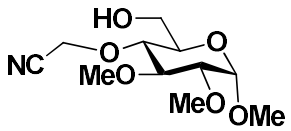
To a stirred solution of compound **7** (107 mg, 0.2 mmol) in 2 mL CH_3CN-H_2O (1:1) was added CAN (219 mg, 0.4 mmol) at 0 ^oC. After stirring for 1 h at room temperature, EtOAc and saturated $NaHCO_3$ solution were added to the reaction mixture followed by separation of the organic layer. The aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were successively washed with H_2O and brine solution before drying over anhydrous Na_2SO_4. The organic layer was filtered and concentrated *in vacuo* and the crude residue was purified by silica gel column chromatography to give the product **30** (77 mg, 93%) as colorless syrupy oil; R_f = 0.40 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.27 (m, 10H), 5.03 (d, *J* = 11.5 Hz, 1H), 4.77 (d, *J* = 12.1 Hz, 1H), 4.72 – 4.60 (m, 3H), 4.30 (s, 2H), 3.84 – 3.67 (m, 4H), 3.55 – 3.46 (m, 2H), 3.38 (s, 3H), 2.25 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 137.9, 128.7, 128.5, 128.1, 128.0, 128.0, 115.8, 98.2, 81.2, 79.6, 75.4, 73.2, 70.3, 70.0, 69.4, 57.0, 55.4; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{23}H_{27}NNaO_6^+$ 436.1731; found 436.1735.

Methyl 2,3-di-*O*-benzyl-4-*O*-(cyanomethyl)-α-D-glucopyranoside (31):



To a solution of compound **8** (106 mg, 0.2 mmol) in THF (2 mL), TBAF (2 equiv.) was added and stirred for 6 h. The reaction mixture was diluted with CH_2Cl_2 and washed with water followed by separation of the organic phase. The aqueous phase was extracted with CH_2Cl_2 (2 x 5 mL) and the combined organic layers were dried over anhydrous Na_2SO_4 and the solvent evaporated *in vacuo*. Purification by column chromatography gave light yellow semi solid alcohol **31** (59 mg, 71%); R_f = 0.15 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.27 (m, 10H), 5.01 (d, *J* = 11.1 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.72 (d, *J* = 11.1 Hz, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.57 (d, *J* = 3.5 Hz, 1H), 4.45 (d, *J* = 16.0 Hz, 1H), 4.35 (d, *J* = 16.0 Hz, 1H), 3.96 (t, *J* = 9.2 Hz, 1H), 3.87 – 3.74 (m, 2H), 3.59 (dt, *J* = 9.9, 3.0 Hz, 1H), 3.53 – 3.46 (m, 2H), 3.37 (s, 3H), 1.83 (br.s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.3, 137.8, 128.6, 128.2, 128.1, 128.0, 127.9, 116.4, 98.0, 81.4, 80.0, 77.7, 75.7, 73.3, 69.9, 61.2, 57.6, 55.4; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{23}H_{27}NNaO_6^+$ 436.1731; found 436.1728.

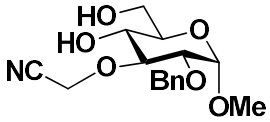
Methyl 4-*O*-(cyanomethyl)-2,3-di-*O*-methyl-α-D-glucopyranoside (32):



To a stirred solution of compound **9** (70 mg, 0.2 mmol) in DCE/H_2O (10 mL, 10:1) was added DDQ (114 mg, 0.5 mmol) at room temperature. After continuous stirring for 24 h complete consumption of starting material was observed by TLC analysis. The reaction mixture was diluted with $CHCl_3$ and the organic phase was washed with saturated $NaHCO_3$. The aqueous layer was extracted with $CHCl_3$ (2 x 7.5 mL) and the combined organic layers were subsequently washed with brine and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to give the alcohol **32** (34 mg, 65%) as colorless syrup; R_f = 0.25 (50% ethyl acetate in hexane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.83 (d, *J* = 3.5 Hz, 1H), 4.56 (d, *J* = 16.0 Hz, 1H), 4.49 (d, *J* = 16.0 Hz, 1H), 3.85 (dd, *J* = 12.1, 2.3 Hz, 1H), 3.79 (dd, *J* = 12.1, 3.7 Hz, 1H), 3.62 (s, 3H), 3.61-3.55 (m, 2H), 3.51 (s, 3H), 3.47-3.43 (m, 1H), 3.42 (s, 3H), 3.22 (dd, *J* = 9.5, 3.5

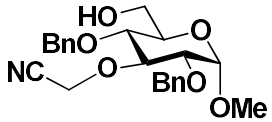
Hz, 1H); ^{13}C NMR (125 MHz,) δ 116.4, 97.4, 83.0, 82.2, 78.0, 69.8, 61.3, 60.9, 58.9, 57.6, 55.4; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{11}H_{19}NNaO_6^+$ 284.1105; found 284.1101.

Methyl 2-*O*-benzyl-3-*O*-(cyanomethyl)-α-D-glucopyranoside (33):



Compound **10** (350 mg, 0.85 mmol) was added to a stirred solution of 7 mL 80% AcOH. The solution was heated to 80 ^{o}C for 30 min and the reactant was found to be completely consumed on TLC monitoring. The reaction mixture was cooled and evaporated under reduced pressure. The residue was diluted with ethyl acetate (15 mL) and successively washed with saturated $NaHCO_3$ and brine solutions before drying over anhydrous Na_2SO_4. The solvent was removed *in vacuo* and the crude residue was purified by flash column chromatography to give the product **33** (211 mg, 77%) as a colorless syrup: R_f = 0.40 (60% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.29 (m, 5H), 4.71 (d, *J* = 12.0 Hz, 1H), 4.61 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 3.5 Hz, 1H), 4.56 (s, 2H), 3.81 (d, *J* = 3.2 Hz, 2H), 3.78 – 3.70 (m, 1H), 3.65 – 3.54 (m, 2H), 3.46 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.5, 128.6, 128.2, 128.2, 116.7, 97.6, 82.8, 79.4, 73.0, 70.5, 69.6, 62.0, 58.2, 55.3; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{16}H_{22}NO_6^+$ 324.1442 ; found 324.1444.

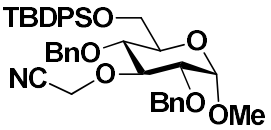
Methyl 2,4-di-*O*-benzyl-3-*O*-(cyanomethyl)-α-D-glucopyranoside (34):



Reductive cleavage of benzylidene: Compound **10** (0.24 mmol, 100 mg) was dissolved in 6 mL anhydrous CH_2Cl_2 and 100 mg 4Å MS was added to the solution. The reaction mixture was stirred at room temperature for 15 min and successively cooled to -78 ^{o}C. triethylsilane (115 μL, 0.72 mmol) and $PhBCl_2$ (111 μL, 0.84 mmol) were added sequentially at this temperature and the starting material was completely consumed after 5 min as observed on TLC analysis. The reaction was quenched with saturated $NaHCO_3$ solution and allowed to attain room temperature. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 7.5 mL). The combined organic layers were washed with water and brine solution followed by

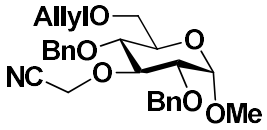
drying over anhydrous Na_2SO_4. The, organic layer was concentrated *in vacuo* and the so obtained crude residue was purified by silica gel column chromatography to give the product **34** (85 mg, 85%) as a colorless syrup: R_f = 0.25 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.21 (m, 10H), 4.86 (d, *J* = 11.1 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.63 (dd, *J* = 11.5, 7.0 Hz, 2H), 4.55 (d, *J* = 3.4 Hz, 1H), 4.51 (s, 2H), 3.85 (t, *J* = 9.1 Hz, 1H), 3.72 (ddd, *J* = 15.3, 12.0, 2.8 Hz, 2H), 3.60 (dt, *J* = 9.7, 2.9 Hz, 1H), 3.51 – 3.43 (m, 2H), 3.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.7, 137.5, 128.6, 128.6, 128.3, 128.2, 128.2, 128.1, 116.4, 97.5, 83.3, 79.8, 76.2, 75.2, 73.1, 70.4, 61.5, 58.0, 55.2; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{23}H_{28}NO_6^+$ 414.1911; found 414.1917.

Methyl 2,4-di-*O*-benzyl-3-*O*-(cyanomethyl)-6-*O*-(tert-butyldiphenylsilyl)-α-D-glucopyranoside (35):



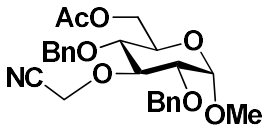
To a solution of compound **34** (41 mg, 0.1 mmol) in 0.2 ml dry CH_2Cl_2, imidazole (20 mg, 0.3 mmol) and TBDPSCl (38 μL, 0.15 mmol) were added at 0 ^{o}C. The reaction mixture was allowed to stir at room temperature for 1 h. After complete consumption of starting material, it was quenched with ice water and diluted with CH_2Cl_2. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layers were washed with brine solution and dried over anhydrous Na_2SO_4. The organic phase was concentrated *in vacuo* and the crude residue was purified by flash column chromatography to obtain the compound **35** (59 mg, 91%) as colorless syrup: R_f = 0.50 (10% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.64 (m, 4H), 7.45 – 7.32 (m, 11H), 7.29 – 7.25 (m, 3H), 7.21 (dd, *J* = 6.8, 2.8 Hz, 2H), 4.82 (d, *J* = 10.8 Hz, 1H), 4.75 (d, *J* = 11.9 Hz, 1H), 4.67 (d, *J* = 11.9 Hz, 1H), 4.63 (d, *J* = 3.5 Hz, 1H), 4.57 (d, *J* = 10.8 Hz, 1H), 4.51 (d, *J* = 3.7 Hz, 2H), 3.89 – 3.80 (m, 3H), 3.67 – 3.61 (m, 1H), 3.56 (d, *J* = 8.8 Hz, 1H), 3.50 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.32 (s, 3H), 1.05 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 137.7, 135.8, 135.6, 133.5, 133.2, 129.7, 129.6, 128.6, 128.4, 128.2, 128.1, 128.1, 127.8, 127.7, 127.6, 116.5, 97.1, 83.6, 80.0, 76.9, 75.3, 73.0, 71.2, 62.7, 58.0, 54.9, 26.8, 19.3; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{39}H_{45}NNaO_6Si^+$ 674.2908; found 674.2911.

Methyl 6-*O*-allyl-2,4-di-*O*-benzyl-3-*O*-(cyanomethyl)-α-D-glucopyranoside (36):



To a solution of compound **34** (70 mg, 0.17 mmol) in 1.5 mL DMF, NaH (14 mg, 0.34 mmol) and allyl bromide (22 µL, 0.225 mmol) were added at 0 °C. The reaction mixture was allowed to stir at room temperature for 1 h. After complete consumption of the starting material, the reaction mixture was quenched with ice water and diluted with EtOAc (5 mL). The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with brine solution followed by drying over anhydrous Na_2SO_4. The organic phase was concentrated *in vacuo* and the crude residue was purified by flash column chromatography to procure the compound **36** (65 mg, 84%) as a white amorphous solid: R_f = 0.50 (20% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.28 (m, 10H), 5.95-5.83 (m, 1H), 5.26 (dd, *J* = 17.2, 1.1 Hz, 1H), 5.19 (d, *J* = 10.4 Hz, 1H), 4.84 (d, *J* = 11.0 Hz, 1H), 4.72 (d, *J* = 12.0 Hz, 1H), 4.66-4.58 (m, 3H), 4.50 (s, 2H), 4.01 (dd, *J* = 12.7, 5.8 Hz, 1H), 3.94 (dd, *J* = 12.8, 5.8 Hz, 1H), 3.82 (t, *J* = 9.1 Hz, 1H), 3.70 – 3.54 (m, 4H), 3.51 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.0, 137.6, 134.3, 128.6, 128.5, 128.2, 128.2, 128.2, 127.9, 117.6, 116.5, 97.5, 83.4, 79.6, 76.6, 75.3, 73.1, 72.5, 69.7, 68.1, 58.0, 55.1; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{26}H_{32}NO_6^+$ 454.2224; found 454.2222.

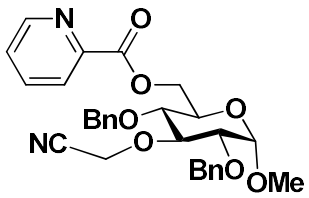
Methyl 6-*O*-acetyl-2,4-di-*O*-benzyl-3-*O*-(cyanomethyl)-α-D-glucopyranoside (37):



To a magnetically stirred solution of compound **34** (50 mg, 0.12 mmol) in 0.6 mL DCM, acetic anhydride (28 µL, 0.3 mmol) and Et_3N (42 µL, 0.3 mmol) were added at 0 °C. The reaction mixture was allowed to stir at room temperature for 5 h until the reactant was completely consumed. The reaction was concentrated under reduced pressure and the crude reside was purified by silica gel column chromatography to procure the product **37** (47 mg, 86%) as a white semi solid. R_f = 0.30 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 10H), 4.85 (d, *J* = 10.9 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.60 – 4.55 (m,

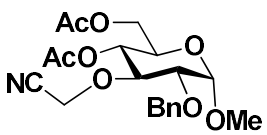
2H), 4.52 (d, *J* = 2.8 Hz, 2H), 4.23 (d, *J* = 3.2 Hz, 2H), 3.86 (t, *J* = 9.1 Hz, 1H), 3.76 (dt, *J* = 9.9, 3.3 Hz, 1H), 3.50 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.40 (t, *J* = 9.4 Hz, 1H), 3.33 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 137.5, 137.4, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 116.3, 97.3, 83.4, 79.8, 76.3, 75.3, 73.1, 68.3, 62.8, 58.0, 55.2, 20.8; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{25}H_{30}NO_7^+$ 456.2017; found 456.2020.

Methyl 2,4-di-*O*-benzyl-3-*O*-(cyanomethyl)-6-*O*-picoloyl-α-D-glucopyranoside (38):



To a magnetically stirred solution of compound **34** (0.169 mmol, 70 mg) in 2 mL dry DCM was added picolinic acid (0.186 mmol, 23 mg) and stirred at 0 °C for 30 min. A solution containing the mixture of DCC (0.253 mmol, 52 mg) and DMAP (4 mg) in dry DCM (2 mL) were added to the solution at 0 °C, and the reaction mixture was allowed to stir at room temperature overnight. The progress of reaction was monitored through TLC analysis and on complete consumption of the reactant, it was filtered through a pad of celite. The filtrate was concentrated in vacuo and the crude residue was purified by flash chromatography to obtain the product **38** (77 mg, 88%) as a colorless syrup: R_f = 0.34 (25% ethyl acetate in hexane double run); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (d, *J* = 4.3 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 7.83 (t, *J* = 7.1 Hz, 1H), 7.48 (dd, *J* = 6.8, 4.7 Hz, 1H), 7.42 – 7.20 (m, 10H), 4.88 (d, *J* = 11.0 Hz, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.68 – 4.49 (m, 7H), 3.97-3.85 (m, 2H), 3.58 – 3.50 (m, 2H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 150.0, 147.7, 137.5, 137.5, 136.9, 128.6, 128.5, 128.4, 128.2, 128.1, 128.0, 126.9, 125.1, 116.3, 97.3, 83.5, 79.8, 75.3, 73.1, 68.5, 64.0, 58.0, 55.2; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{29}H_{31}N_2O_7^+$ 519.2126; found 519.2140.

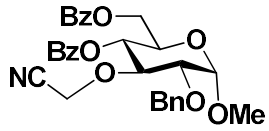
Methyl 4,6-di-*O*-acetyl-2-*O*-benzyl-3-*O*-(cyanomethyl)-α-D-glucopyranoside (39):



To a magnetically stirred solution of compound **33** (100 mg, 0.31 mmol) in 0.6 mL DCM, acetic anhydride (147 µL, 1.55 mmol) and Et_3N (216 µL, 1.55 mmol) were

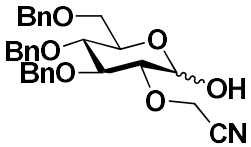
added at 0 °C. The reaction mixture was allowed to stired at rt for 24 h and then concentrated under reduced pressure. The crude residue was purified by flash column chromatography to yield the product **39** (115 mg, 91%) as a white semi solid: R_f = 0.36 (30% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.28 (m, 5H), 4.96-4.89 (m, 1H), 4.69 (d, *J* = 12.0 Hz, 1H), 4.63-4.57 (m, 2H), 4.49 (d, *J* = 16.4 Hz, 1H), 4.42 (d, *J* = 16.4 Hz, 1H), 4.23 (dd, *J* = 12.3, 4.8 Hz, 1H), 4.03 (dd, *J* = 12.3, 2.3 Hz, 1H), 3.92-3.84 (m, 2H), 3.57 (dd, *J* = 9.5, 3.5 Hz, 1H), 3.37 (s, 3H), 2.14 (s, 3H), 2.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 169.9, 137.2, 128.7, 128.4, 128.1, 116.4, 97.4, 79.9, 79.6, 73.2, 68.1, 67.3, 62.0, 58.1, 55.5, 20.9, 20.7; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{20}H_{25}NNaO_8^+$ 430.1472; found 430.1489.

Methyl 4,6-di-*O*-benzoyl-2-*O*-benzyl-3-*O*-(cyanomethyl)-α-D-glucopyranoside (40):



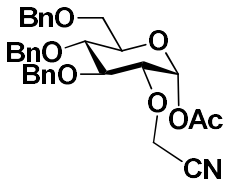
Benzoyl chloride (144 μL, 1.24 mmol) was added dropwise to a stirred solution of **33** (100 mg, 0.31 mmol) in dry pyridine (1.5 mL) at 0 ˚C. The reaction mixture was stirred at room temperature and reaction was monitored by TLC analysis. After 8 h, the reaction was quenched with water and diluted with dichloromethane. The organic layer was separated and successively washed with 5% $CuSO_4.5H_2O$ solution, saturated aqueous $NaHCO_3$ and water. The organic layer was dried over anhydrous Na_2SO_4 and then concentrated *in vacuo*. Purification of the crude residue by column chromatography gave the product **40** (153 mg, 93%) as a colorless syrup: R_f = 0.45 (20% ethyl acetate in hexane); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.8 Hz, 2H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.66-7.22 (m, 11H), 5.34 (t, *J* = 9.7 Hz, 1H), 4.77 (d, *J* = 12.0 Hz, 1H), 4.74-4.49 (m, 4H), 4.48-4.34 (m, 2H), 4.26-4.11 (m, 2H), 3.71 (dd, *J* = 9.4, 3.5 Hz, 1H), 3.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.9, 137.3, 133.5, 133.0, 130.1, 130.1, 129.7, 129.0, 128.7, 128.4, 128.3, 128.3, 128.2, 116.1, 97.4, 79.9, 79.5, 73.3, 69.6, 67.6, 63.1, 58.0, 55.5; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{30}H_{29}NNaO_8^+$ 554.1785; found 554.1783.

3,4,6-Tri-*O*-benzyl-2-*O*-(cyanomethyl)-α/β-D-glucopyranose (41):



Deprotection of -SPh group: To a solution of NIS (580 mg, 2.58 mmol) in water-acetone (1:20) mixture was added compound **17** (500 mg, 0.86 mmol) at 0 ^{o}C. The reaction mixture was stirred at room temperature for 3 h. On consumption of the reactant, the reaction was quenched with Et_3N and $Na_2S_2O_3$ solution. The compound was extracted with EtOAc (3 x 10 mL). The combined organic layers was then successively washed with brine solution and dried over anhydrous Na_2SO_4. The organic phase was concentrated under reduced pressure and the crude residue was purified by flash chromatography to obtain the anomeric mixture of product **41** (370 mg, 88%) as white amorphous solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.24 (m, 26H), 7.21 – 7.10 (m, 4H), 5.41 (d, *J* = 3.5 Hz, 1H), 4.88 (d, *J* = 11.0 Hz, 2H), 4.84-4.75 (m, 4H), 4.65 – 4.46 (m, 9H), 4.38 (d, *J* = 1.9 Hz, 2H), 4.09-3.98 (m, 2H), 3.72-3.45 (m, 9H), 3.32 (t, *J* = 8.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 138.1, 137.8, 137.7, 137.7, 137.6, 128.5, 128.4, 128.1, 128.0, 127.9, 127.8, 127.8, 116.3, 116.2, 96.6, 90.7, 83.8, 83.5, 81.4, 80.8, 78.1, 77.6, 75.8, 75.7, 75.0, 74.6, 73.5, 70.2, 68.8, 68.5, 57.0, 56.7; HRMS (ESI): calcd m/z for $[M+H]^+$ for $C_{29}H_{31}NNaO_6^+$ 512.2044; found 512.2047.

Acetyl 3,4,6-tri-*O*-benzyl-2-*O*-(cyanomethyl)-α-D-glucopyranoside (42):



To a magnetically stirred solution of compound **41** (68 mg, 0.14 mmol) in 0.7 mL DCM, acetic anhydride (33 μL, 0.35 mmol) and Et_3N (49 μL, 0.35 mmol) were added at 0 ^{o}C. The reaction mixture was allowed to stir at room temperature for 1 h. The reaction mixture was subsequently concentrated under reduced pressure and the crude reside was purified by column chromatography to obtain the product **42** (63 mg, 85%) as a colorless oil: R_f = 0.42 (20% ethyl acetate in hexane double run); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 13H), 7.21 – 7.09 (m, 2H), 5.53 (d, *J* = 8.1 Hz, 1H), 4.88 (d, *J* = 11.1 Hz, 1H), 4.78 (d, *J* = 10.9 Hz, 2H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.48 (d, *J* = 12.1 Hz, 1H), 4.35 (s, 2H), 3.80-3.71 (m, 3H), 3.66 (t, *J* = 9.1 Hz, 1H), 3.57 – 3.52 (m, 1H), 3.49 (t, *J* = 8.6 Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 137.9, 137.7, 128.5, 128.4, 128.4, 128.0, 127.9, 127.9,

127.8, 115.9, 92.8, 84.2, 82.1, 75.9, 75.5, 75.0, 73.6, 67.8, 57.7, 21.1; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{31}H_{33}NNaO_7^+$ 554.2149; found 554.2151.

Allyl deprotection: To a solution of compound **36** (91 mg, 0.2 mmol) in 2 mL dry MeOH/DCM (1:1), $PdCl_2$ (18 mg, 0.1 mmol) was added under nitrogen atmosphere. The reaction mixture was stirred for 12 h and on complete consumption of the reactant as shown by TLC analysis, it was filtered. The filtrate was washed with methanol and concentrated under reduced pressure. The crude compound was purified on silica gel column chromatography to obtain the product **34** (62 mg, 75%) as a colorless syrup.

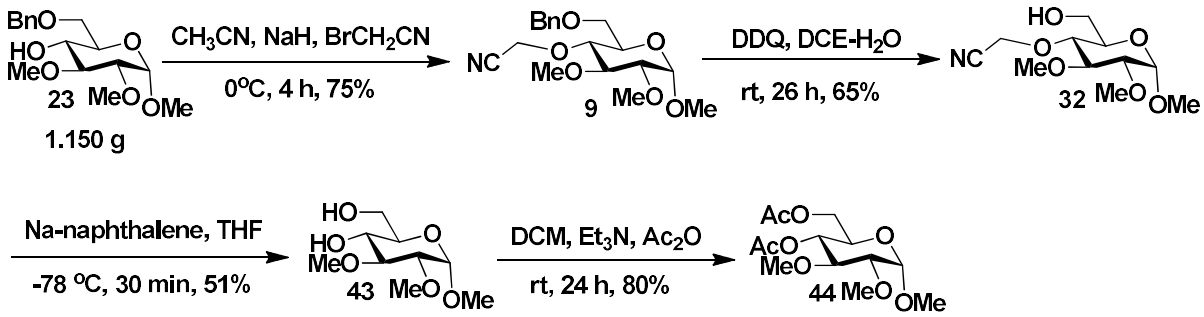
Acetate deprotection: To a magnetically stirred solution of compound **37** (91 mg, 0.2 mmol) was added 30% aq. NH_3 and methanol (15 mL, 1:3). The solution was stirred vigorously for 1 h at room temperature. After complete deacetylation, the solvent was removed under reduced pressure and the residue diluted with EtOAc followed by washing with water and brine solution. The organic layer was evaporated *in vacuo* and the crude product was purified by column chromatography to give the alcohol **34** (74 mg, 90%) as a colorless syrup.

Picolyl group deprotection: Anhydrous Iron (III) chloride (3 mg, 0.017 mmol) was added to a solution of a Pico derivative **38** (30 mg, 0.058 mmol) in 1 mL MeOH-DCM (1:1), and the resulting mixture was stirred under N_2 at room temperature for 3 h. After completion, the reaction mixture was evaporated under reduced pressure. The residue was diluted with DCM (5 mL) and washed with saturated aq. $NaHCO_3$ (5 mL) and water (2 x 5 mL) successively. The organic phase was separated, dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified on silica gel column chromatography to give the alcohol **34** (21 mg, 88%) as a colorless oil.

Deprotection of anomeric -OAc group: To a solution of compound **42** (48 mg, 0.09 mmol) in 0.5 mL CH_3CN, hydrazine hydrate (7 µL, 0.135 mmol) was added at 0 ^oC. The reaction mixture was stirred at room temperature and monitored by TLC analysis. On complete consumption of starting material after 30 min the reaction was diluted with EtOAc and quenched with saturated $NaHCO_3$ solution. The organic layer was separated and the aqueous layer was extracted with EtOAc (2 x 5 mL). The combined organic layers were washed with water and brine solution and subsequently dried over anhydrous Na_2SO_4. The organic phase was concentrated *in vacuo* and the crude

residue was purified by column chromatography to give the anomeric mixture of product **41** (38 mg, 86%) as white amorphous solid.

Gram scale synthesis:



Following general procedure **A**, methyl 6-*O*-benzyl-2,3-di-*O*-methyl-α-D-glucopyranoside[6] **23** (1.150 mg, 3.68 mmol) was alkylated to obtain the product **9** (969 mg, 75%) as a colorless syrupy oil; R_f = 0.32 (30% ethyl acetate in hexane double run);

Following above mentioned procedure, benzyl ether group from the compound **9** (900 mg, 2.56 mmol) was deprotected to give alcohol **32** (434 mg, 65%) in 26 h at rt as colorless syrup; R_f = 0.25 (50% ethyl acetate in hexane);

Following the general procedure **B** the compound **32** (424 mg, 1.62 mmol) was deprotected to obtain the diol **43** (183 mg, 51%) as a colorless syrup; R_f = 0.28 (100% ethyl acetate); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (d, *J* = 3.6 Hz, 1H), 3.88 – 3.77 (m, 2H), 3.66 – 3.59 (m, 4H), 3.54 – 3.43 (m, 5H), 3.43 (s, 3H), 3.21 (dd, *J* = 9.2, 3.5 Hz, 1H), 2.99 (br. s, 1H), 2.29 (br. s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 97.5, 82.8, 81.9, 70.7, 70.3, 62.3, 61.2, 58.5, 55.2; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_9H_{18}NaO_6^+$ 245.0996; found 245.0999; Spectral data for the column purified compound was in complete accordance with previously reported data.[16]

To a magnetically stirred solution of compound **43** (160 mg, 0.72 mmol) in 1.4 mL DCM, acetic anhydride (341 μL, 3.6 mmol) and Et_3N (502 μL, 3.6 mmol) were added at 0 ^oC. The reaction mixture was allowed to stired at rt for 24 h and then concentrated under reduced pressure. The crude residue was purified by flash column chromatography to yield the product **44** (176 mg, 80%) as a colorless syrupy oil: R_f = 0.35 (50% ethyl acetate in hexane); ^1H NMR (400 MHz, $CDCl_3$) δ 4.95 – 4.87 (m, 1H), 4.85 (d, *J* = 3.6 Hz, 1H), 4.21 (dd, *J* = 12.3, 5.0 Hz, 1H), 4.03 (dd, *J* = 12.3, 2.2 Hz, 1H), 3.83 (ddd, *J* = 10.2, 4.9, 2.2 Hz, 1H), 3.56 (t, *J* = 9.5 Hz, 1H), 3.51 (s, 3H), 3.50 (s, 3H), 3.42 (s, 3H), 3.31 (dd, *J* = 9.6, 3.6 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 169.7, 97.6, 81.3, 80.7, 69.8, 67.5, 62.3, 60.8, 59.2, 55.4, 20.8, 20.7; HRMS (ESI): calcd m/z for $[M+Na]^+$ for $C_{13}H_{22}NaO_8^+$ 329.1207; found 329.1209.

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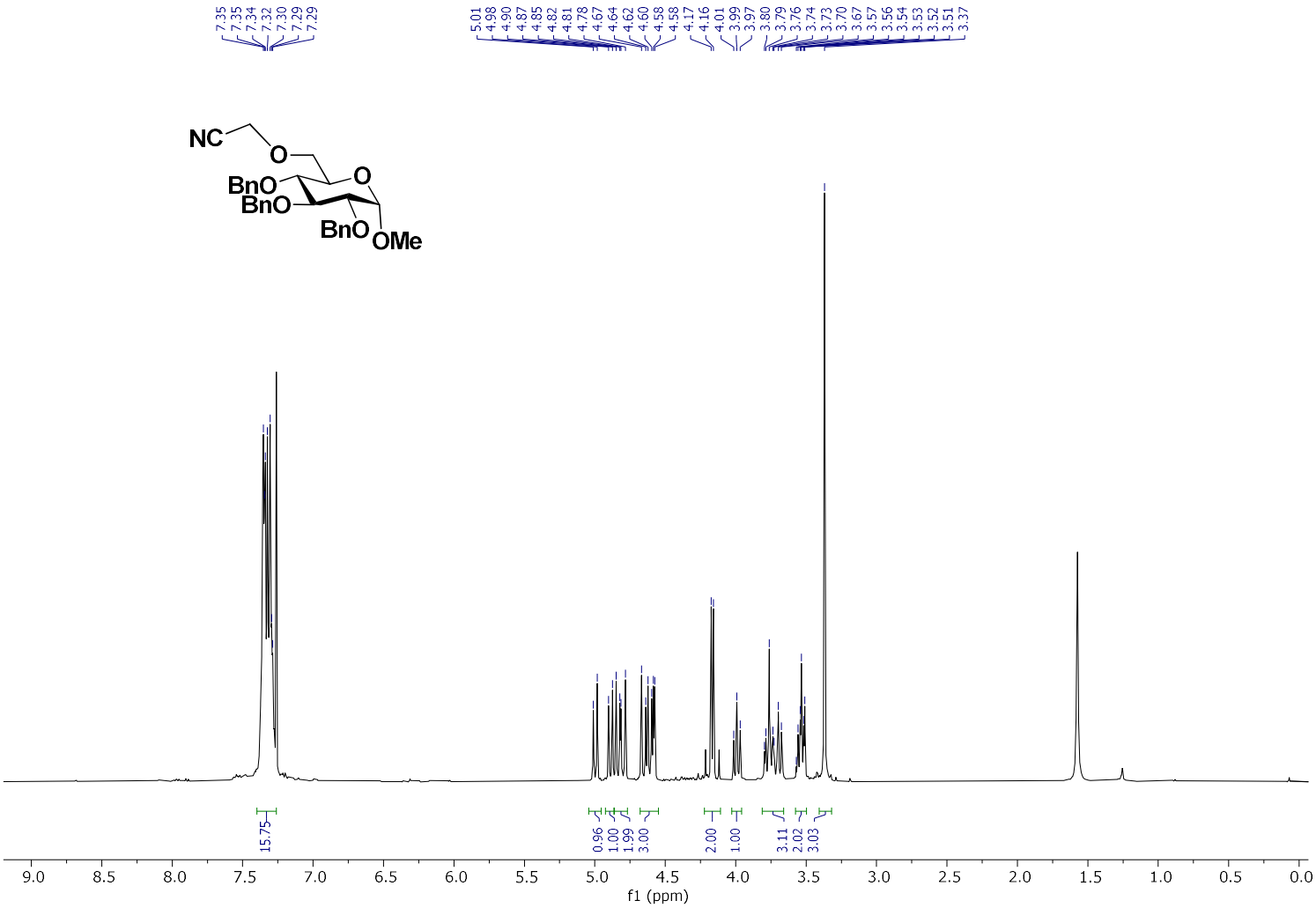
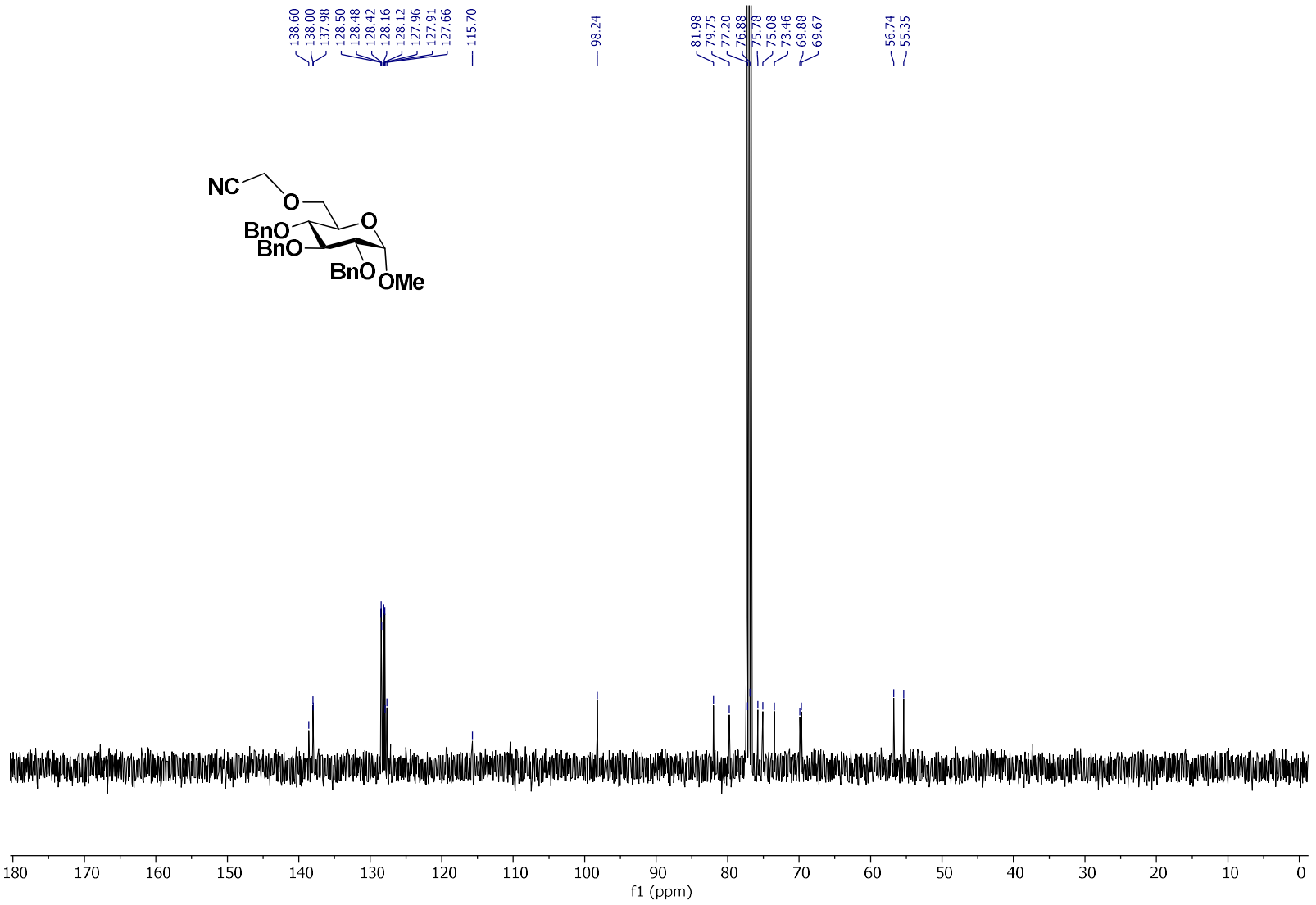
^{1}H and ^{13}C NMR Spectra of Newly Synthesized Compounds

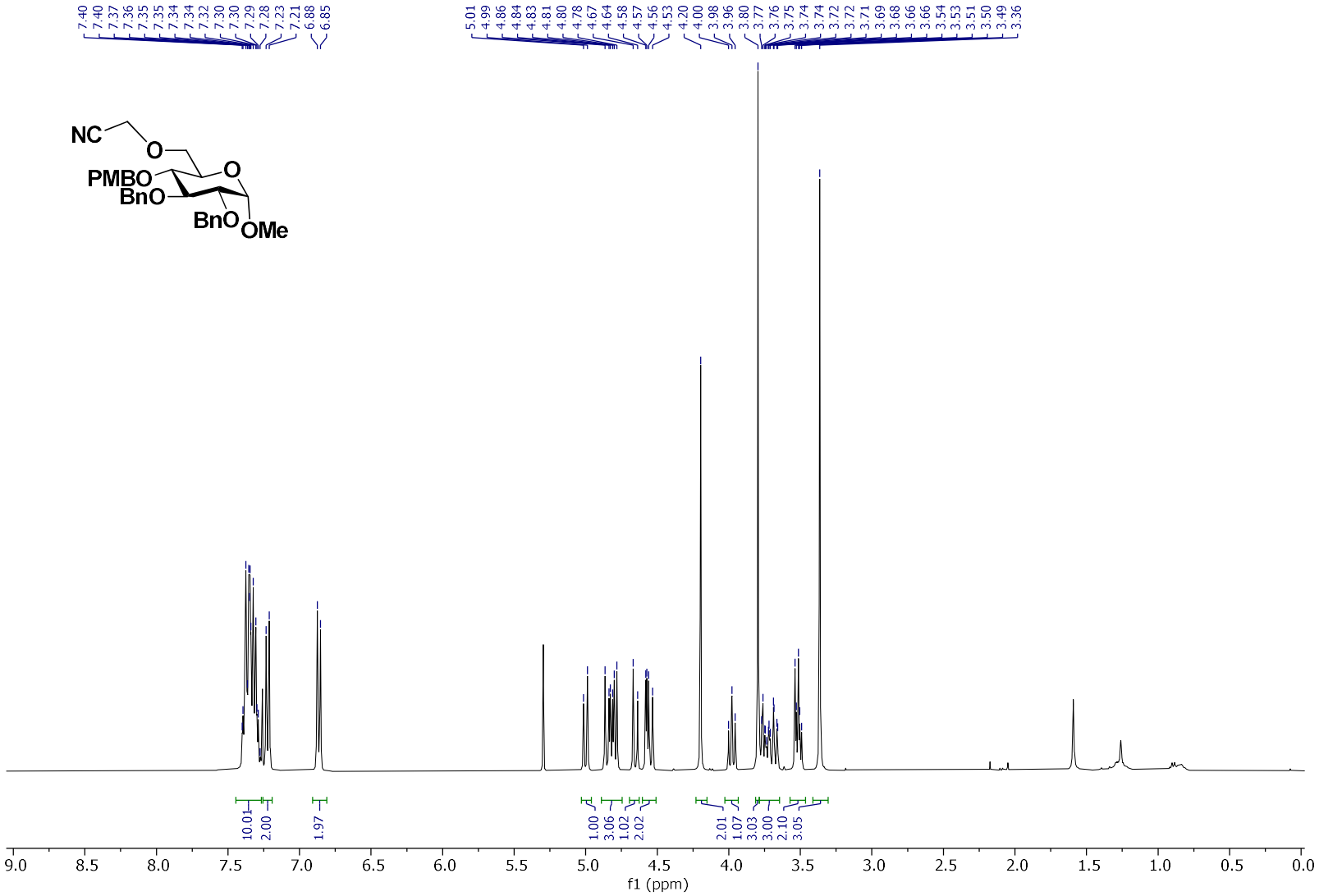
^{1}H NMR (400 MHz, $CDCl_3$) of compound 3



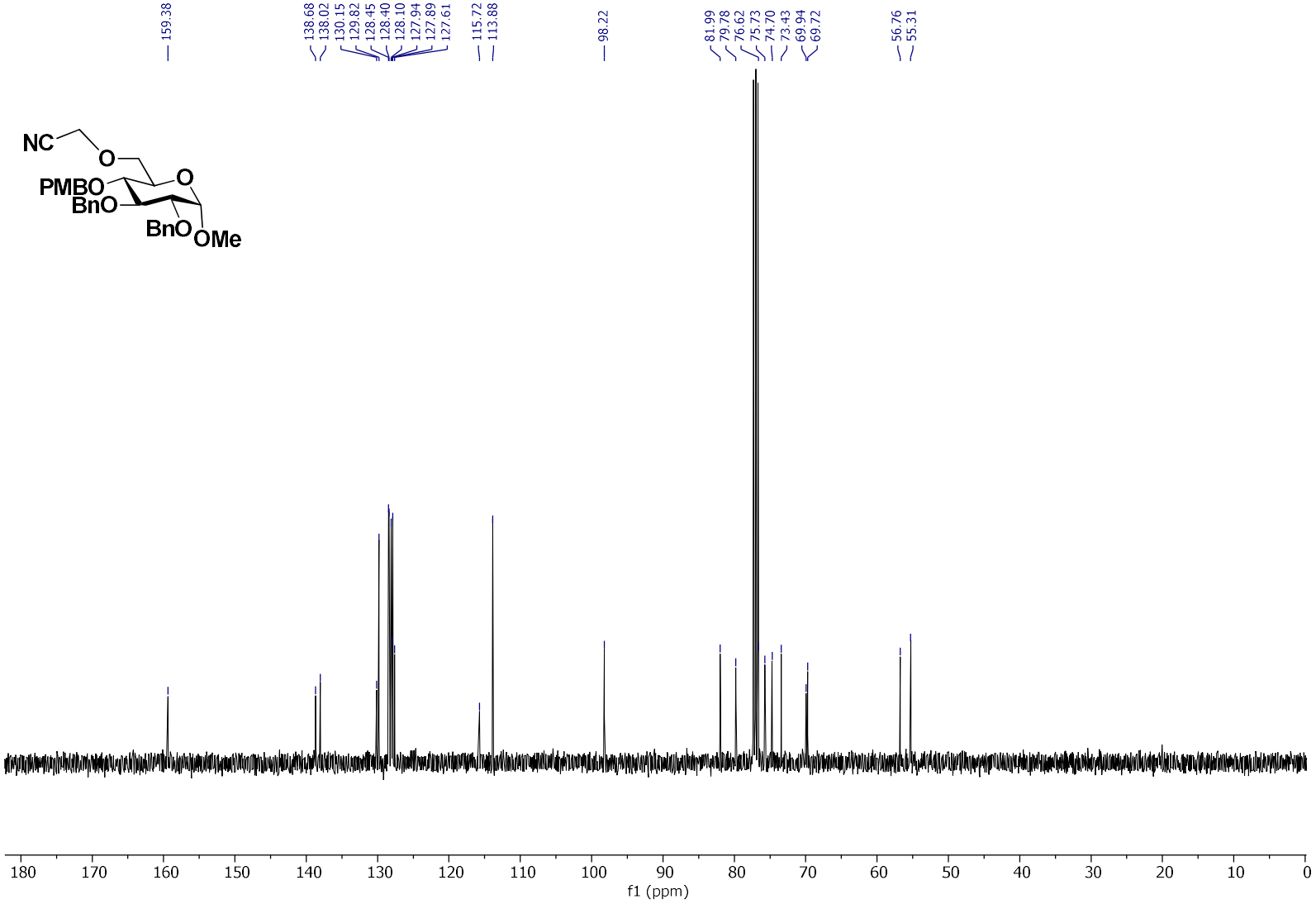
^{13}C NMR (100 MHz, $CDCl_3$) of compound 3



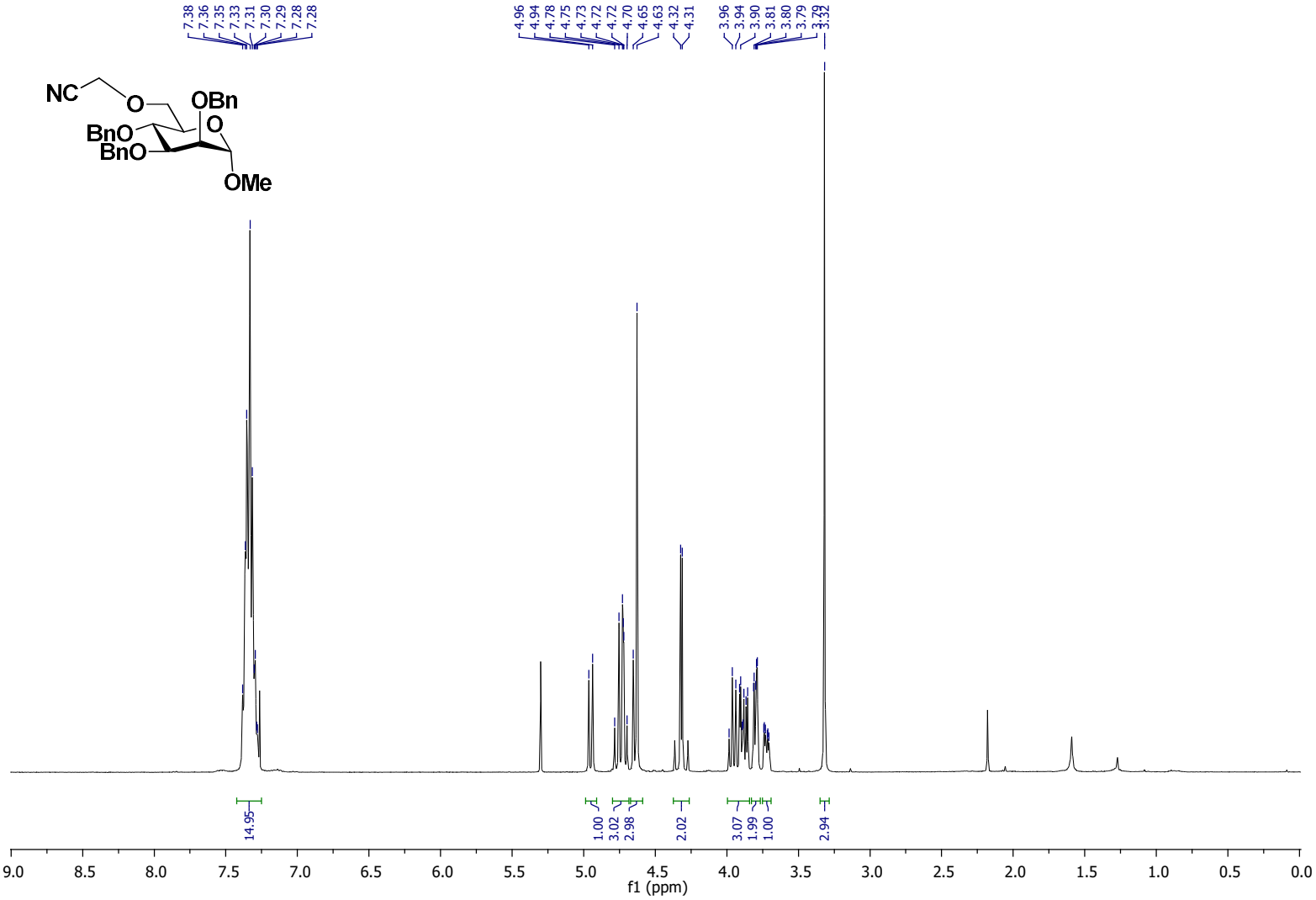
^{1}H NMR (400 MHz, $CDCl_3$) of compound 4



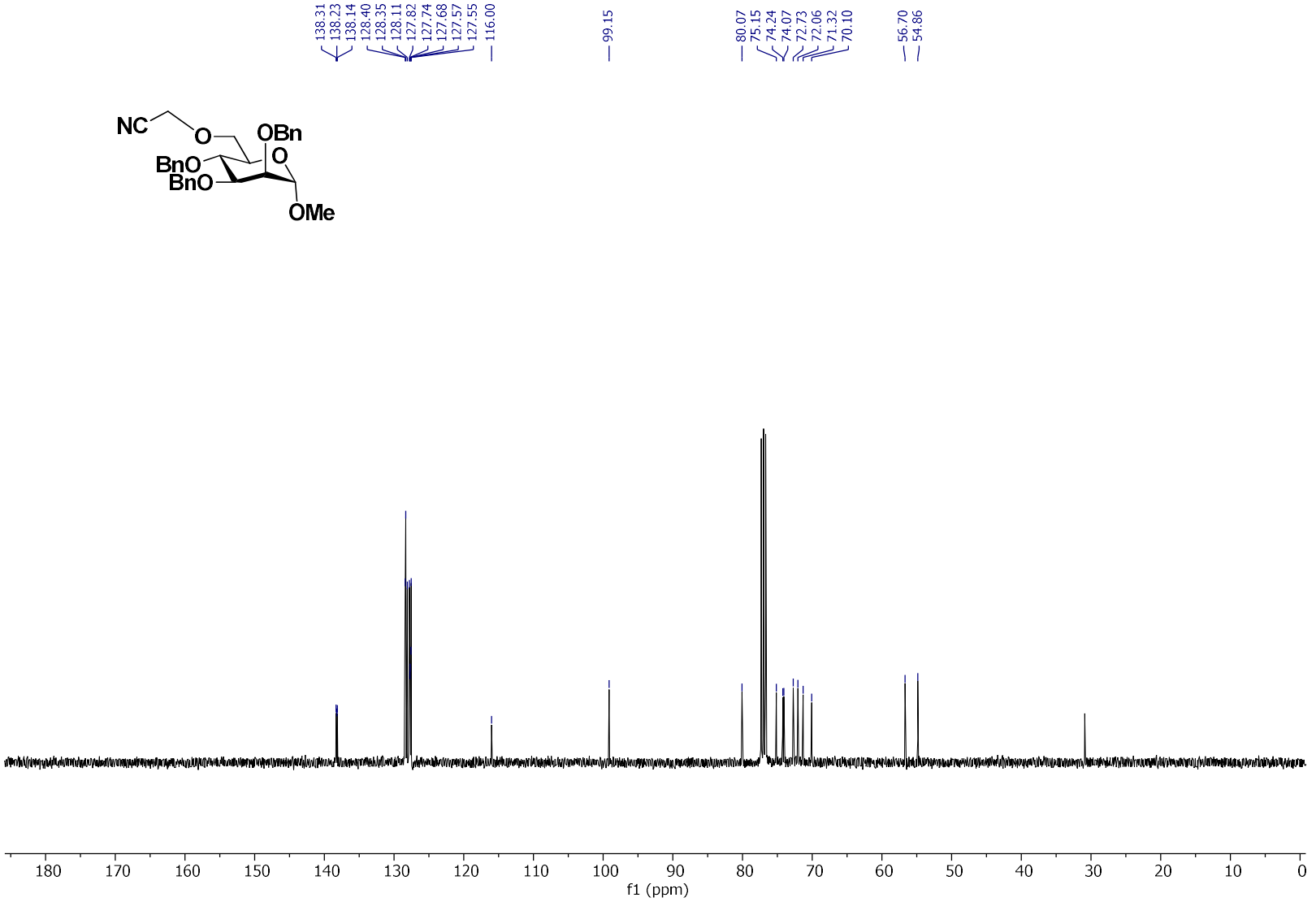
^{13}C NMR (100 MHz, $CDCl_3$) of compound 4



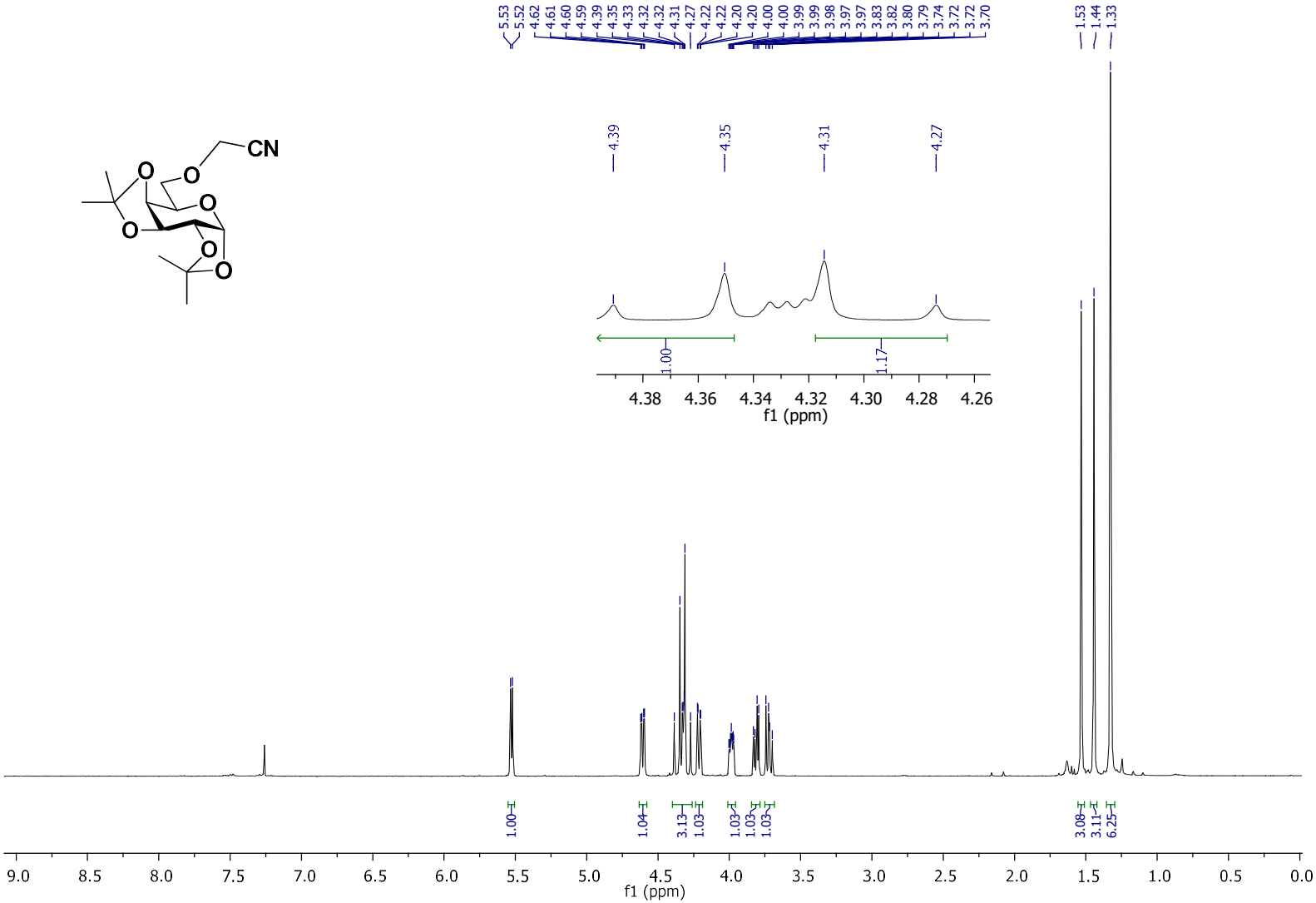
^{1}H NMR (400 MHz, $CDCl_3$) of compound 5



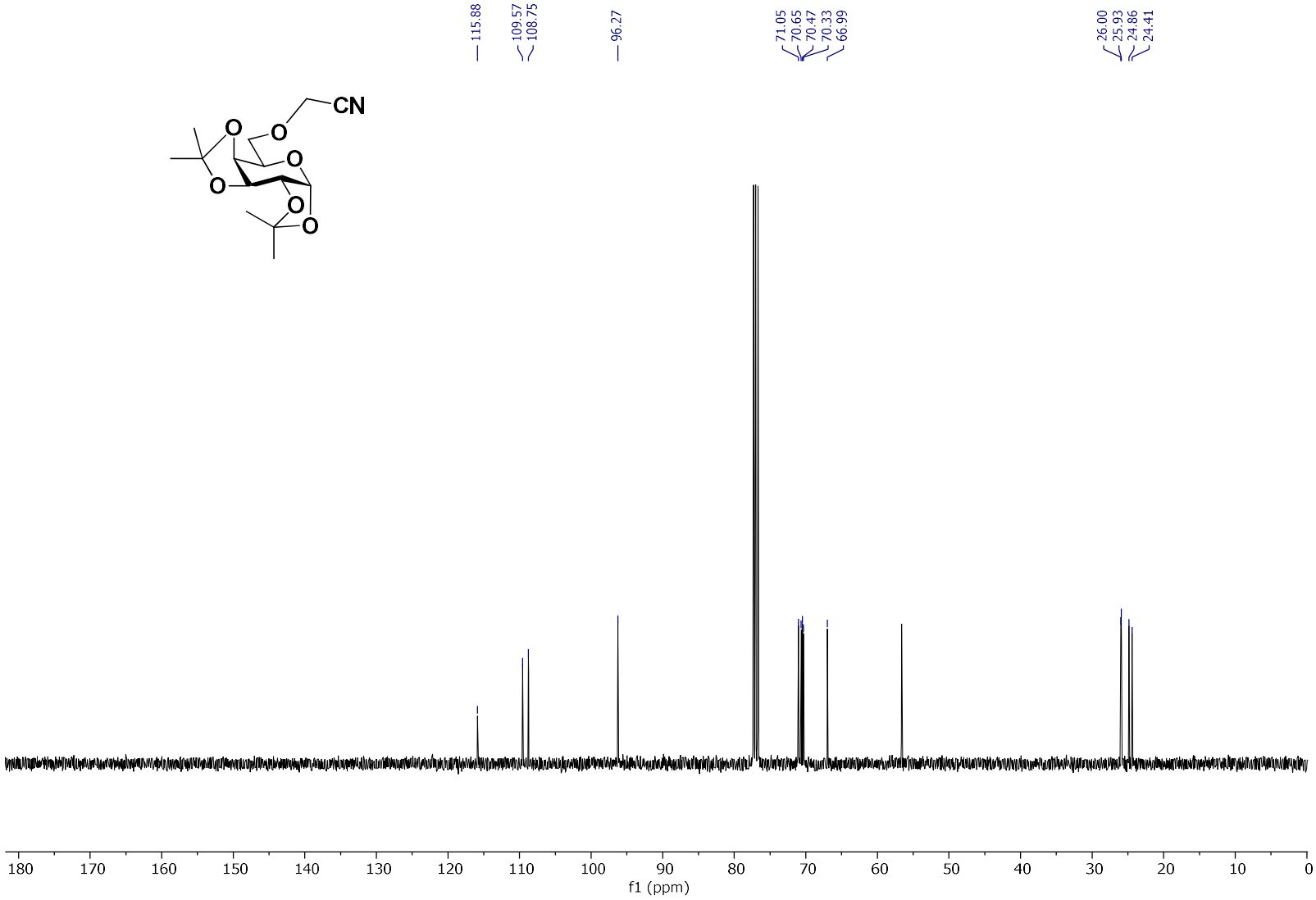
^{13}C NMR (100 MHz, $CDCl_3$) of compound 5



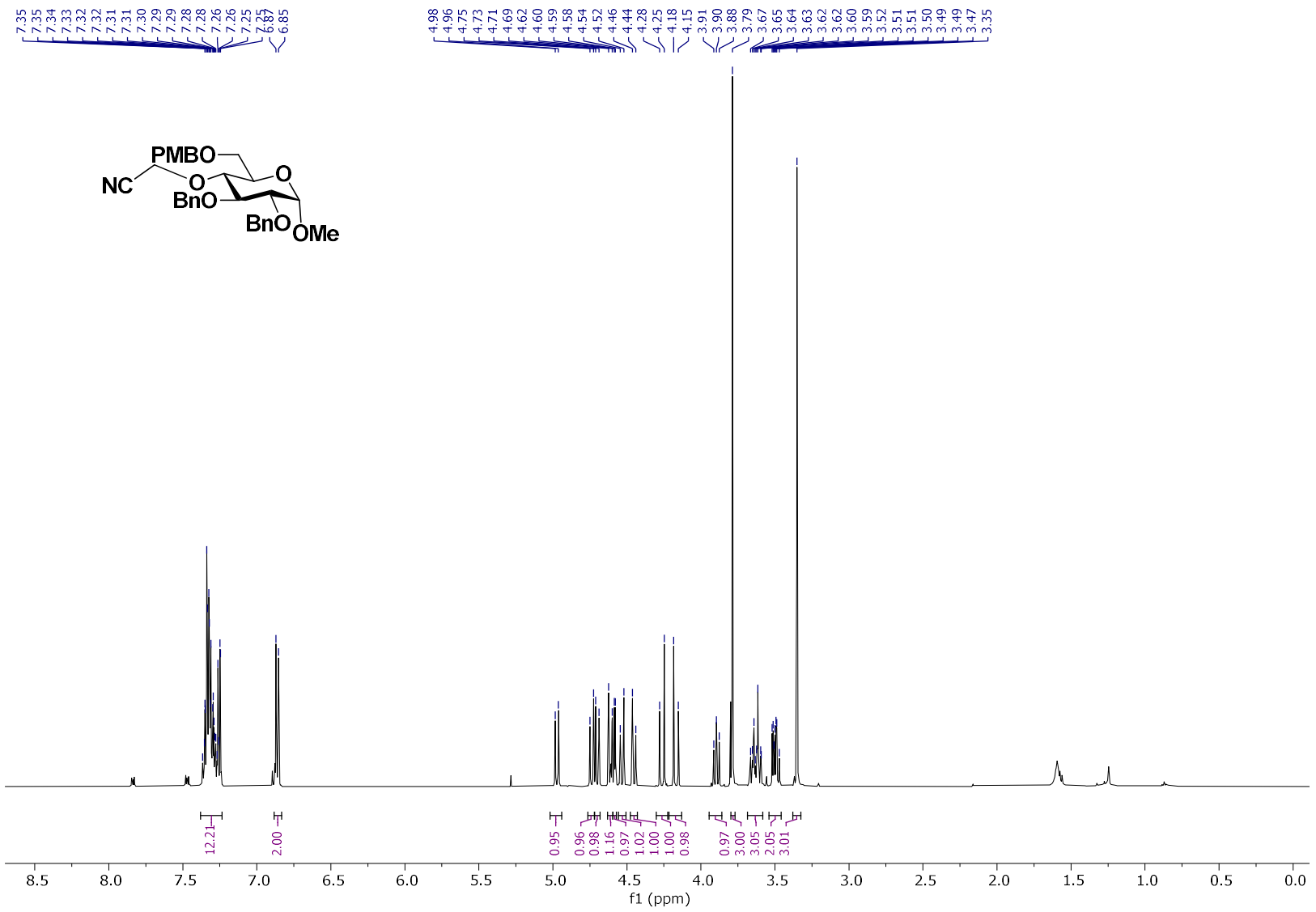
^{1}H NMR (400 MHz, $CDCl_3$) of compound 6



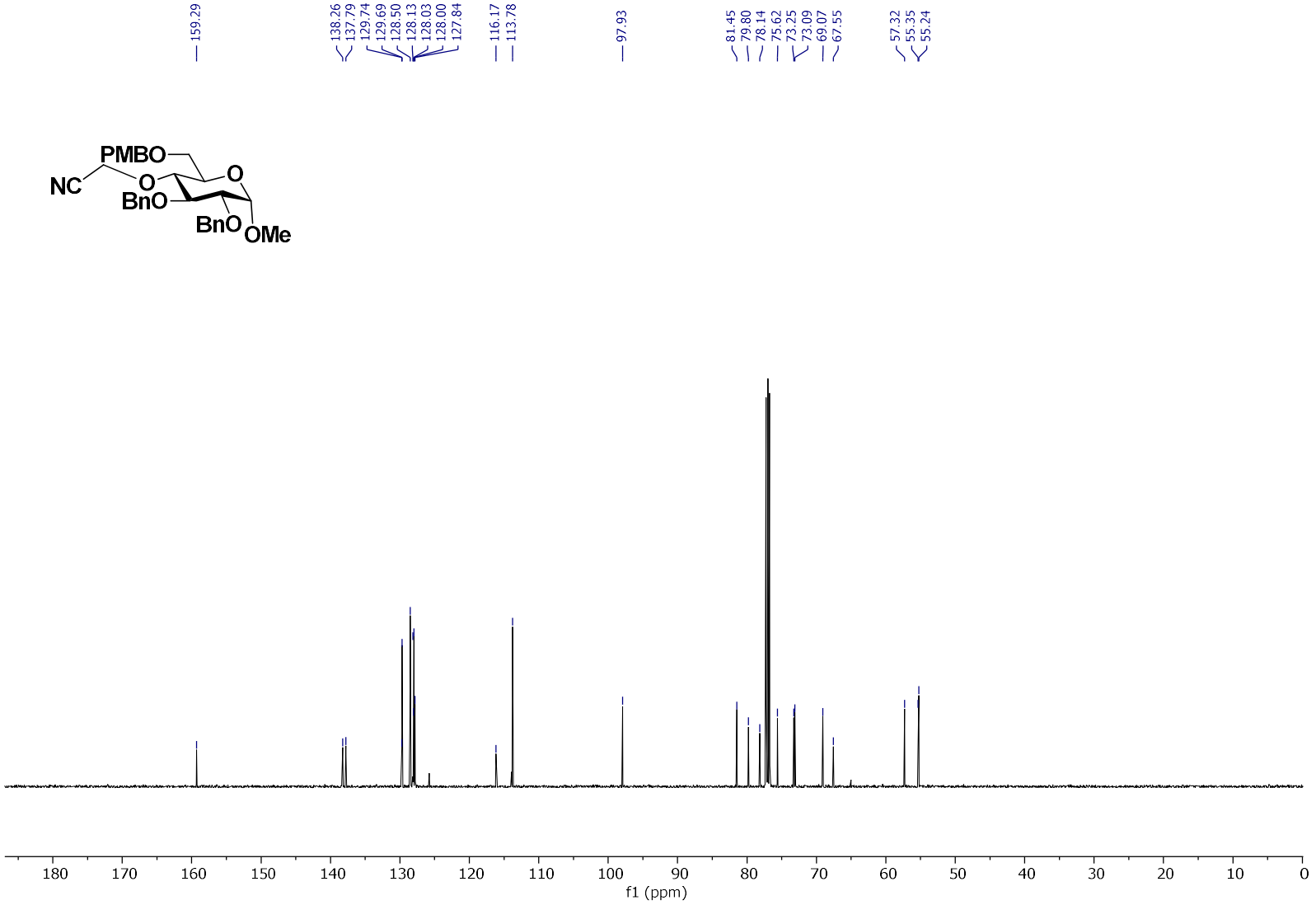
^{13}C NMR (100 MHz, $CDCl_3$) of compound 6



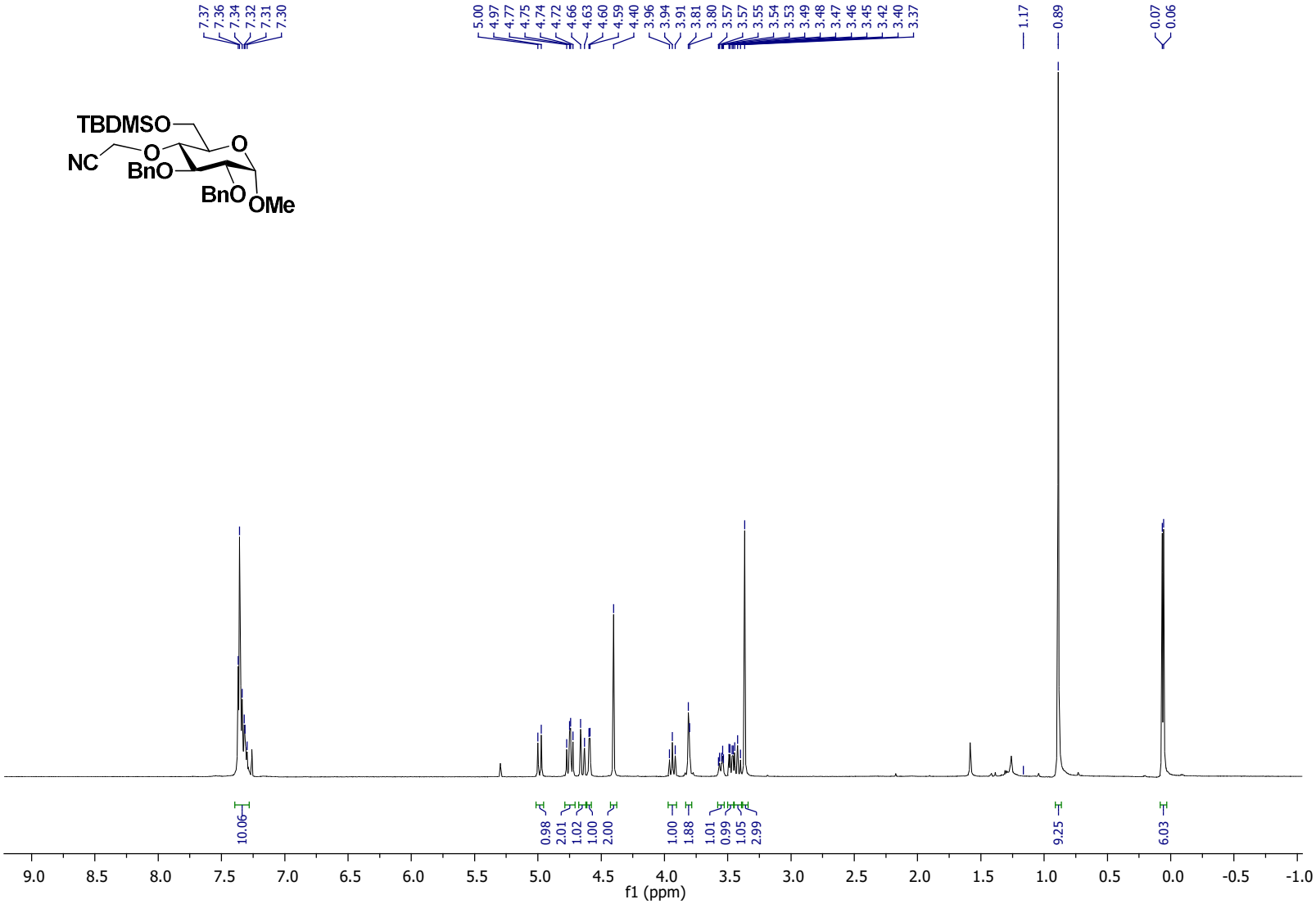
^{1}H NMR (500 MHz, $CDCl_3$) of compound 7



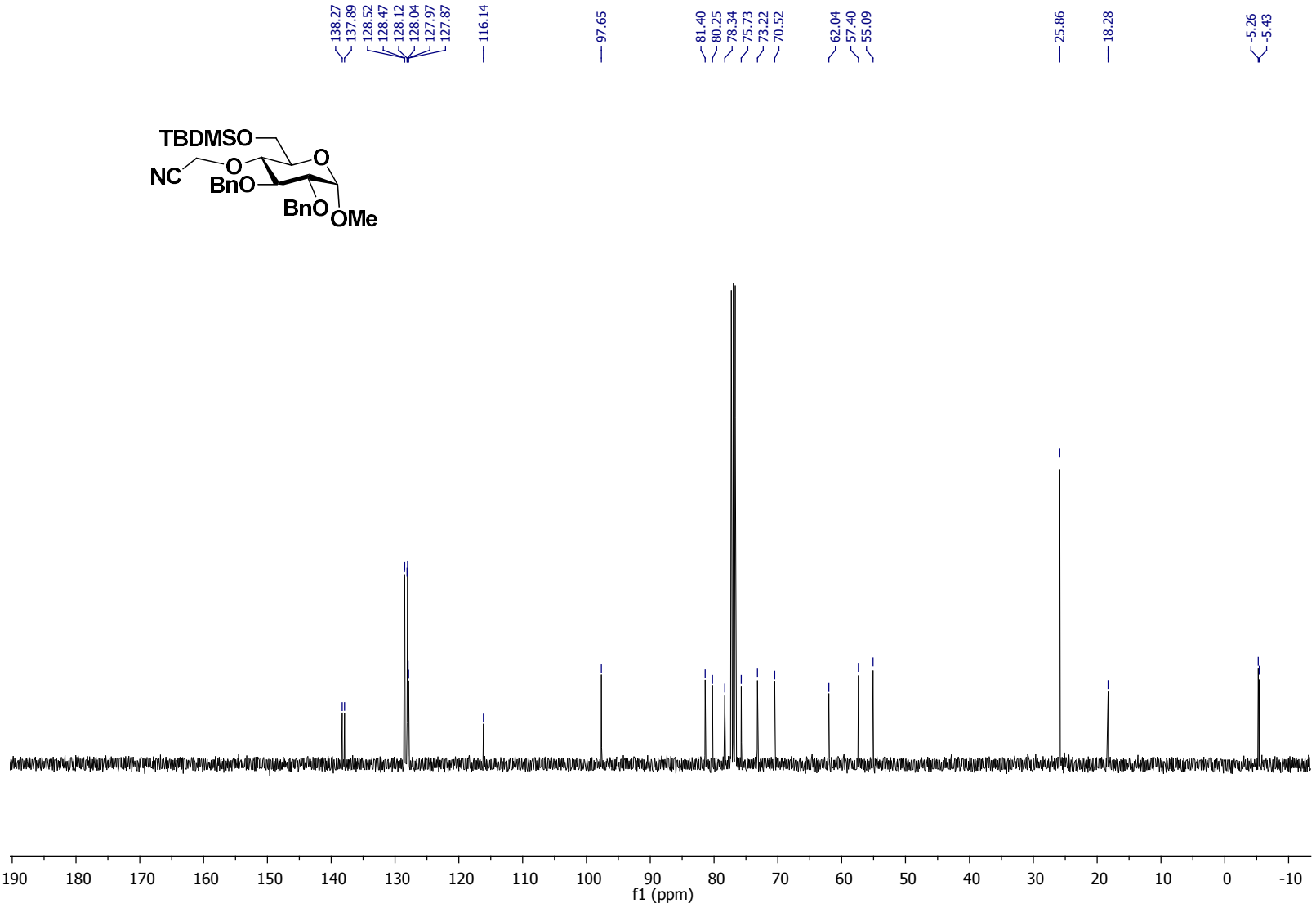
^{13}C NMR (125 MHz, $CDCl_3$) of compound 7



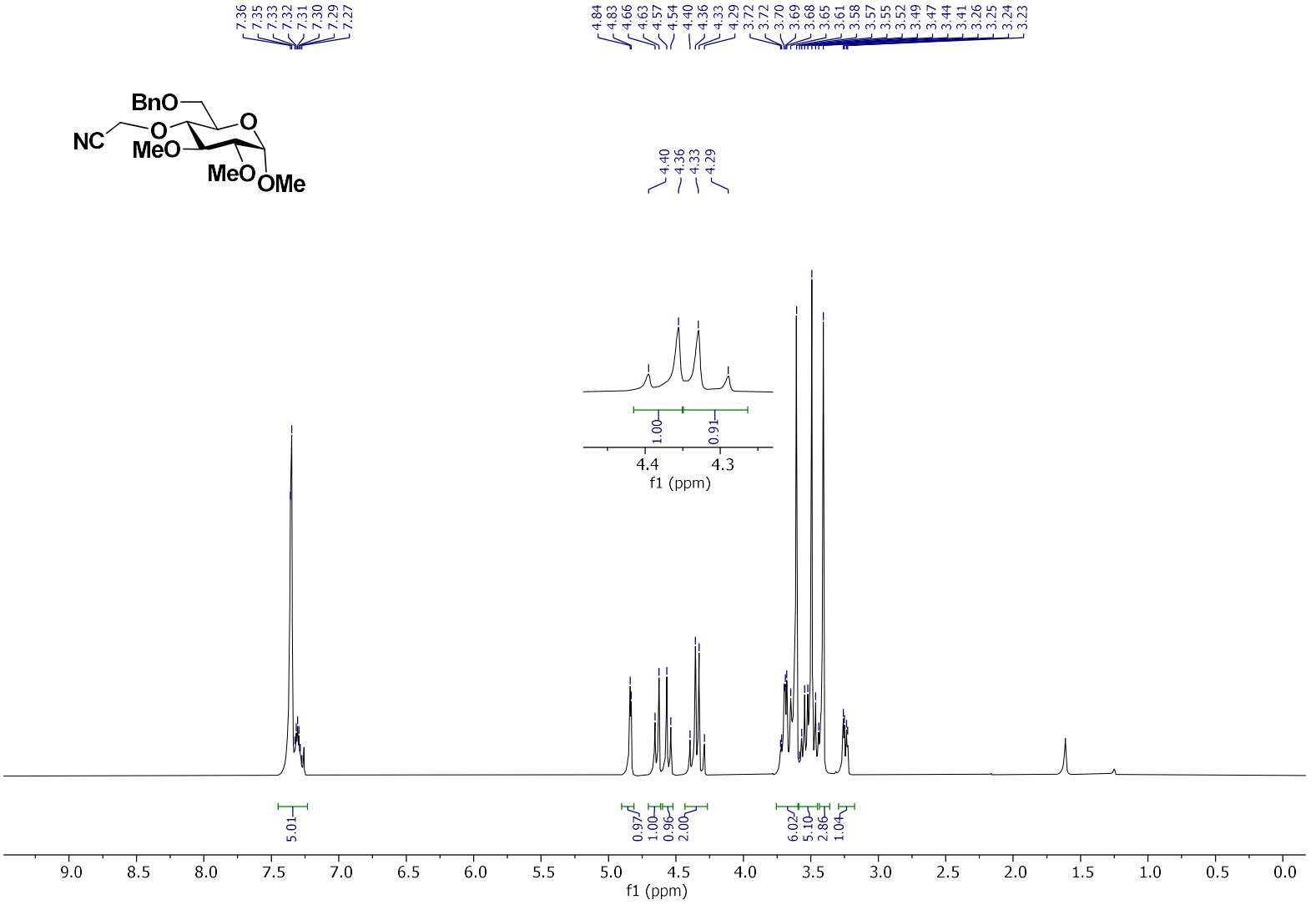
^{1}H NMR (400 MHz, $CDCl_3$) of compound 8



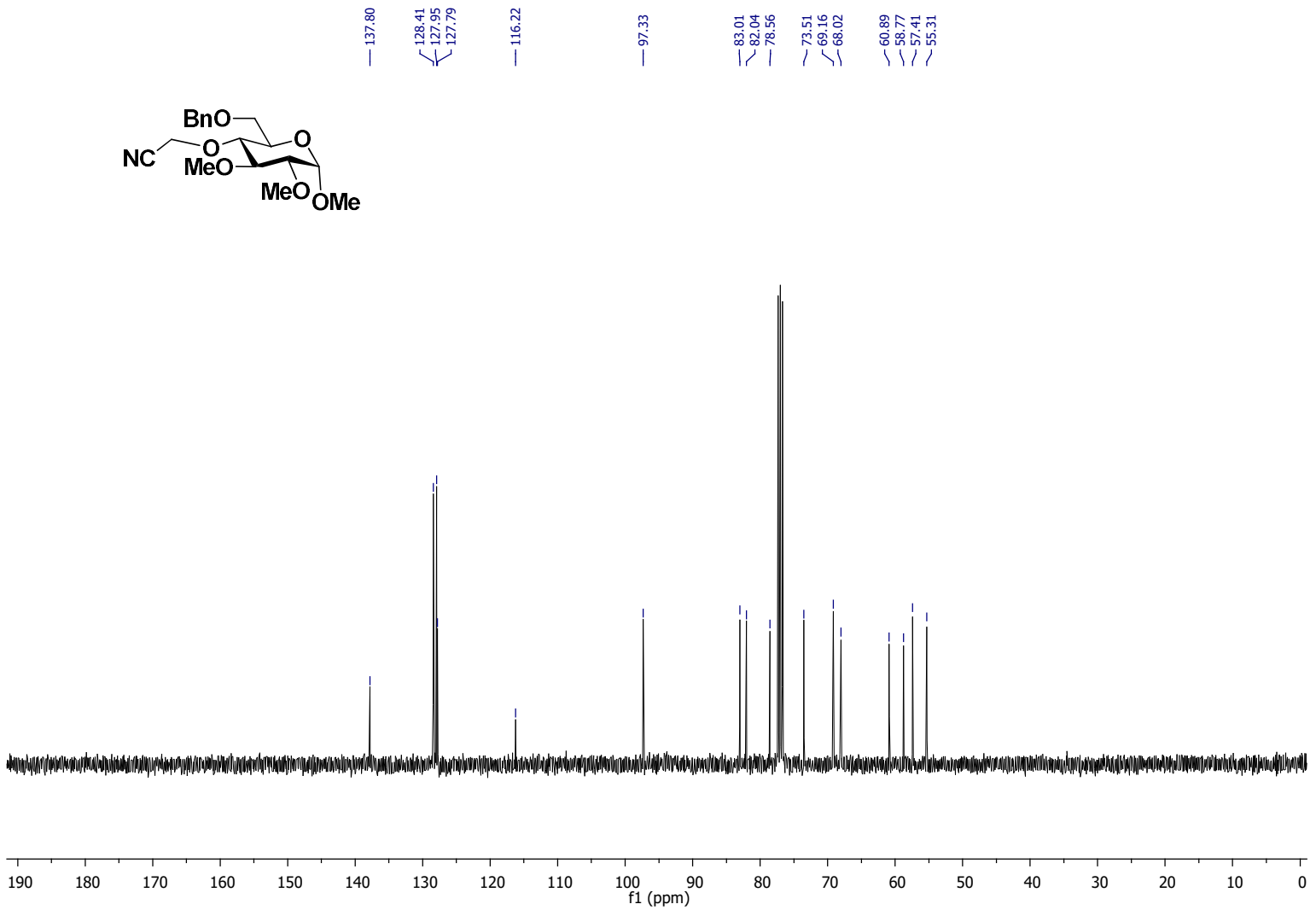
^{13}C NMR (100 MHz, $CDCl_3$) of compound 8



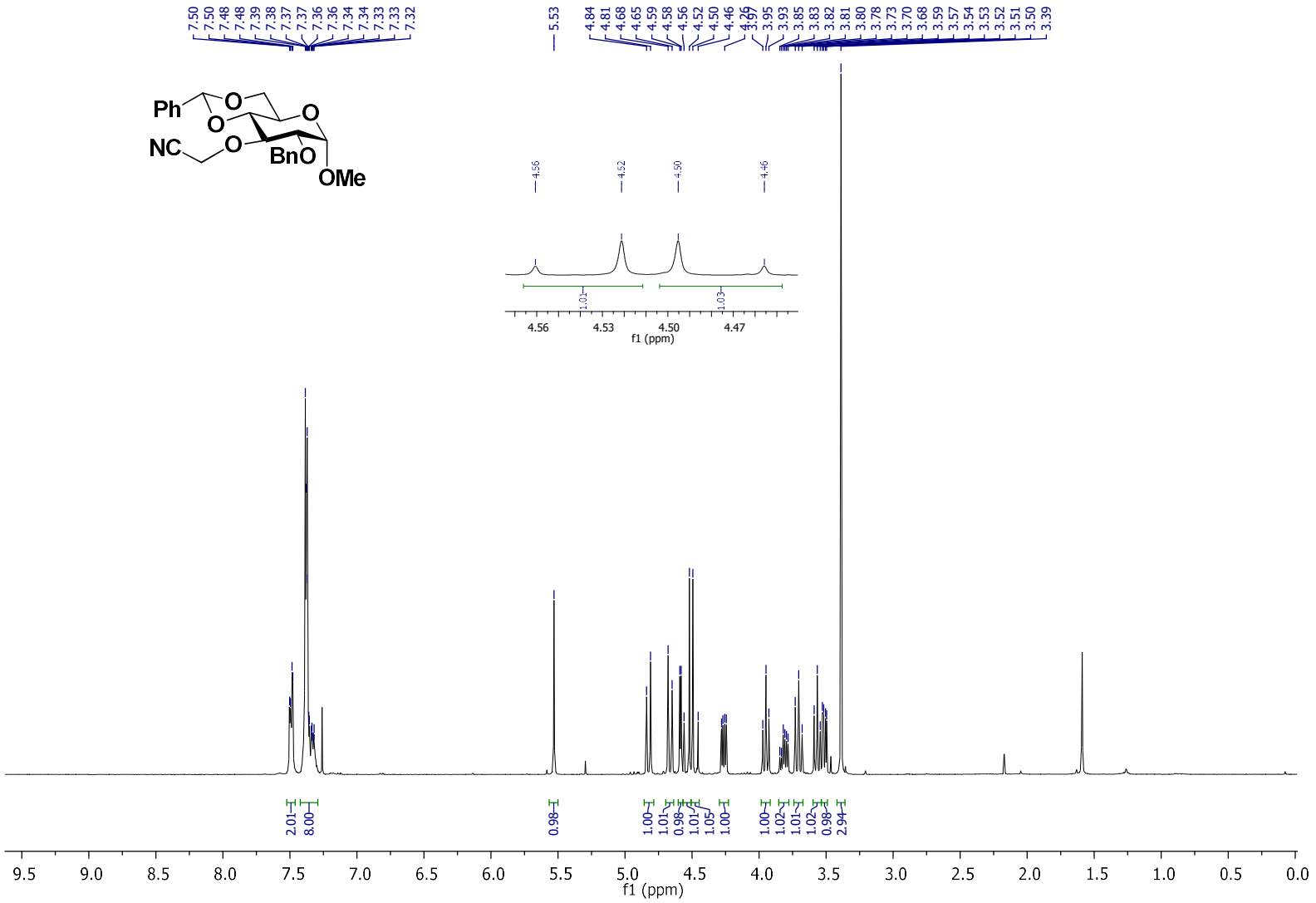
^{1}H NMR (400 MHz, $CDCl_3$) of compound 9



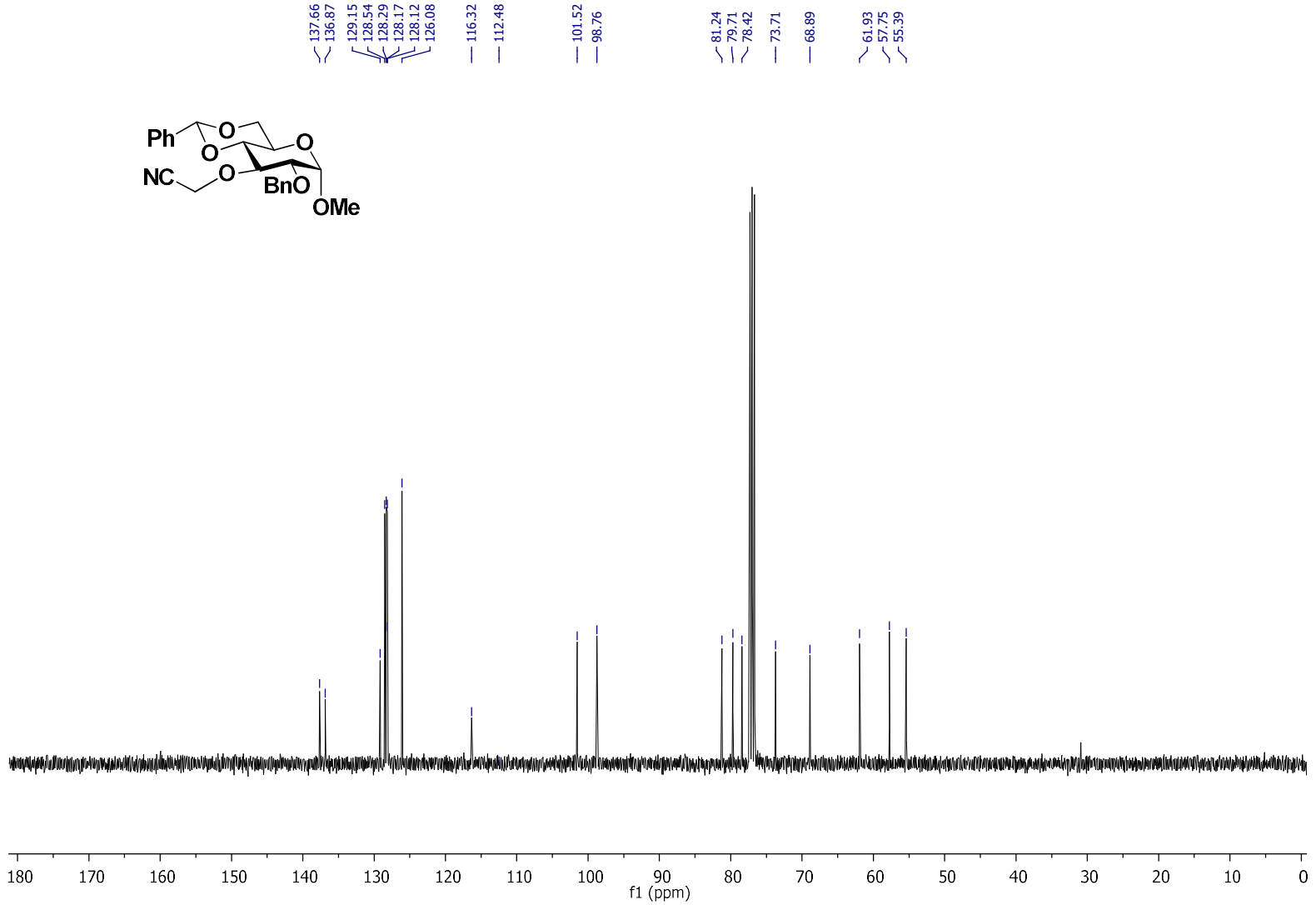
^{13}C NMR (100 MHz, $CDCl_3$) of compound 9



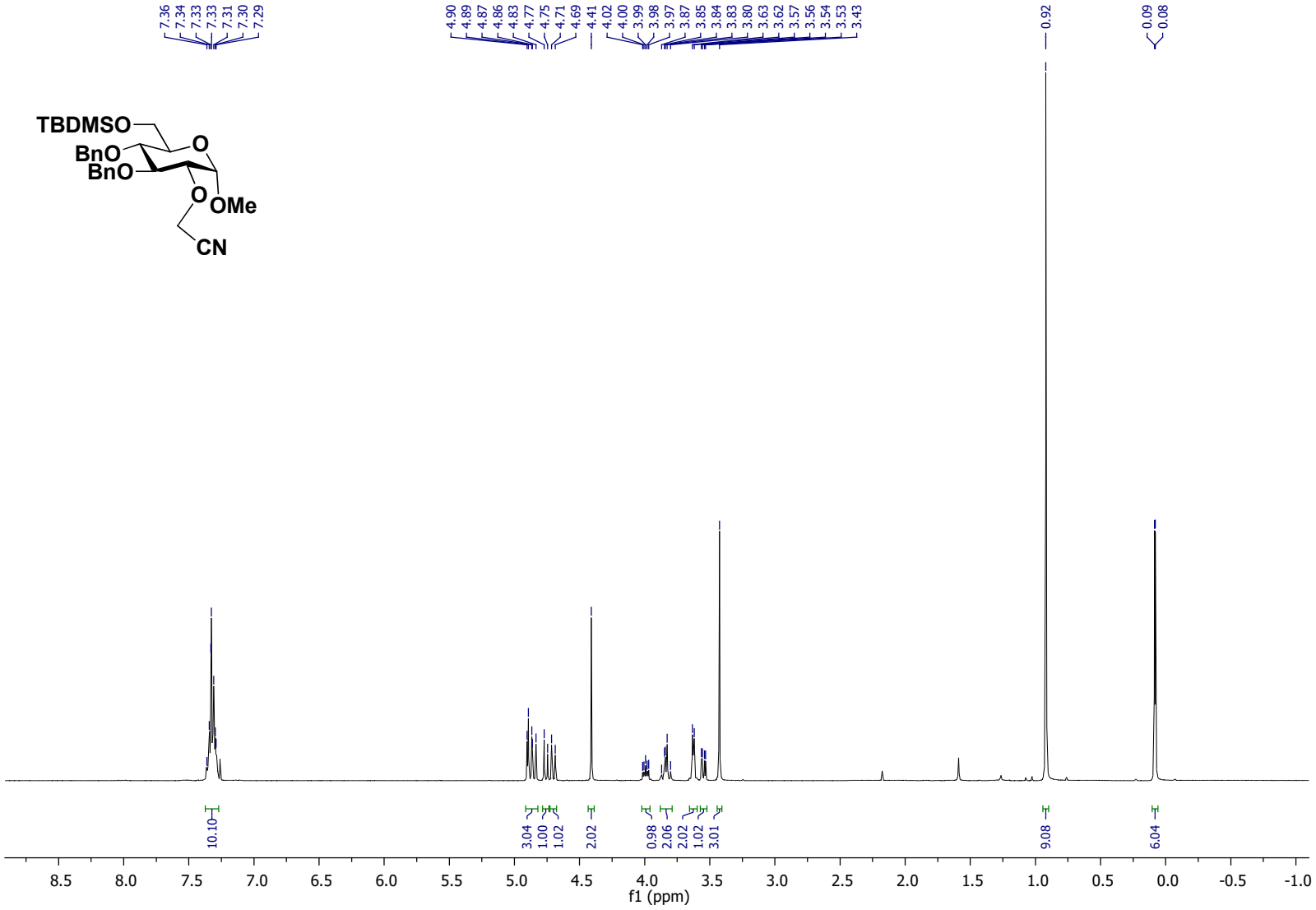
^{1}H NMR (400 MHz, $CDCl_3$) of compound 10



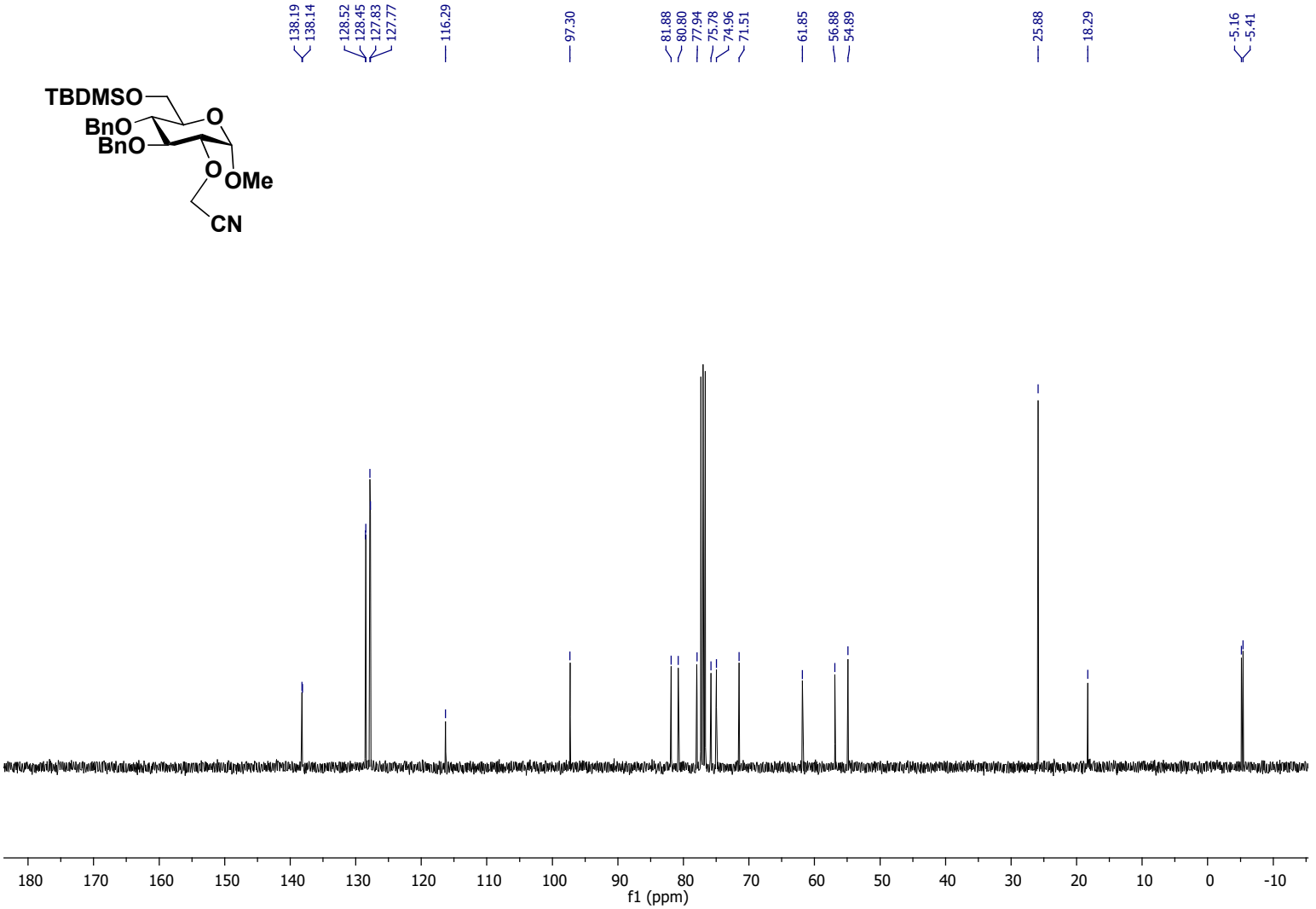
^{13}C NMR (100 MHz, $CDCl_3$) of compound 10



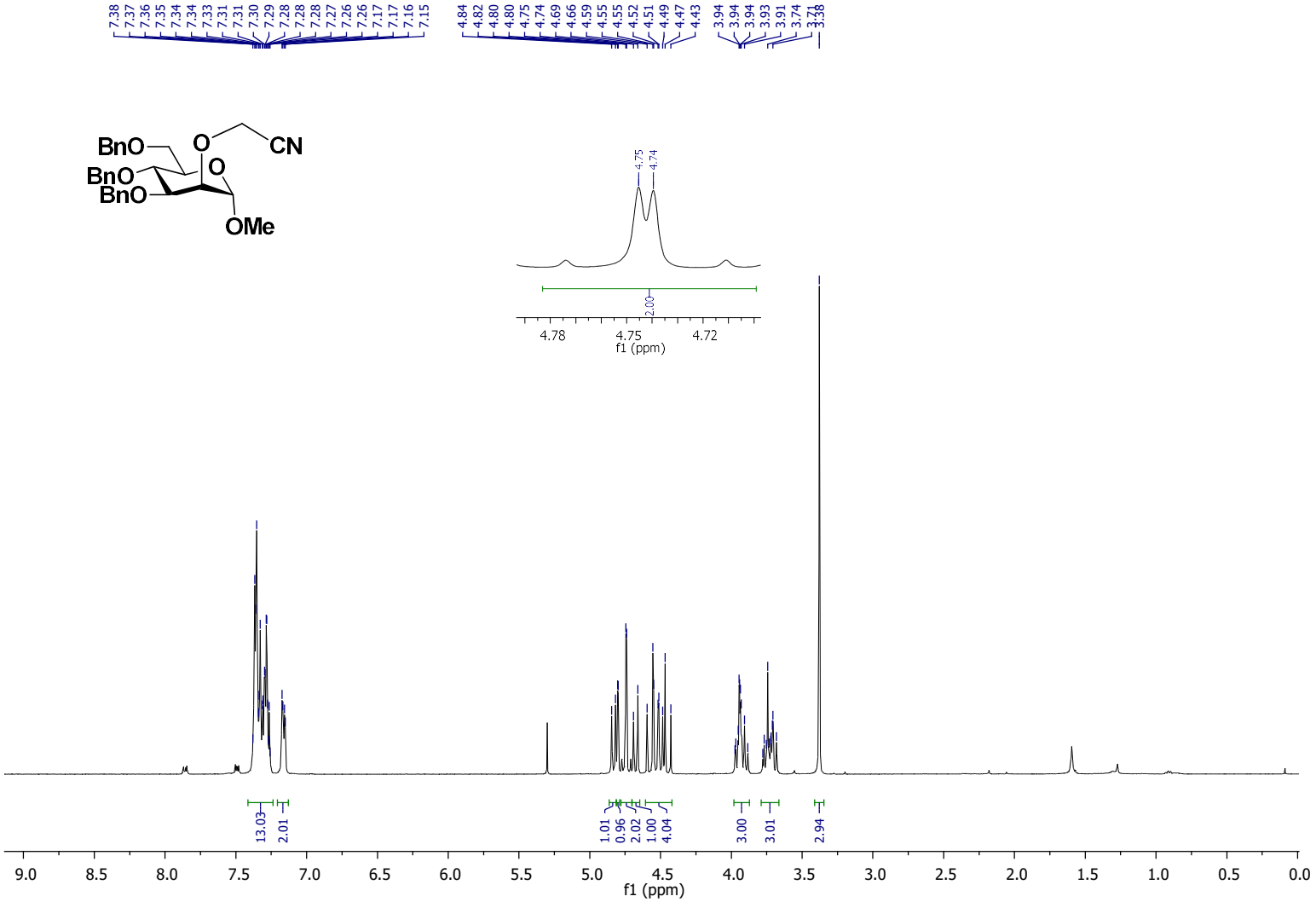
^{1}H NMR (400 MHz, $CDCl_3$) of compound 11



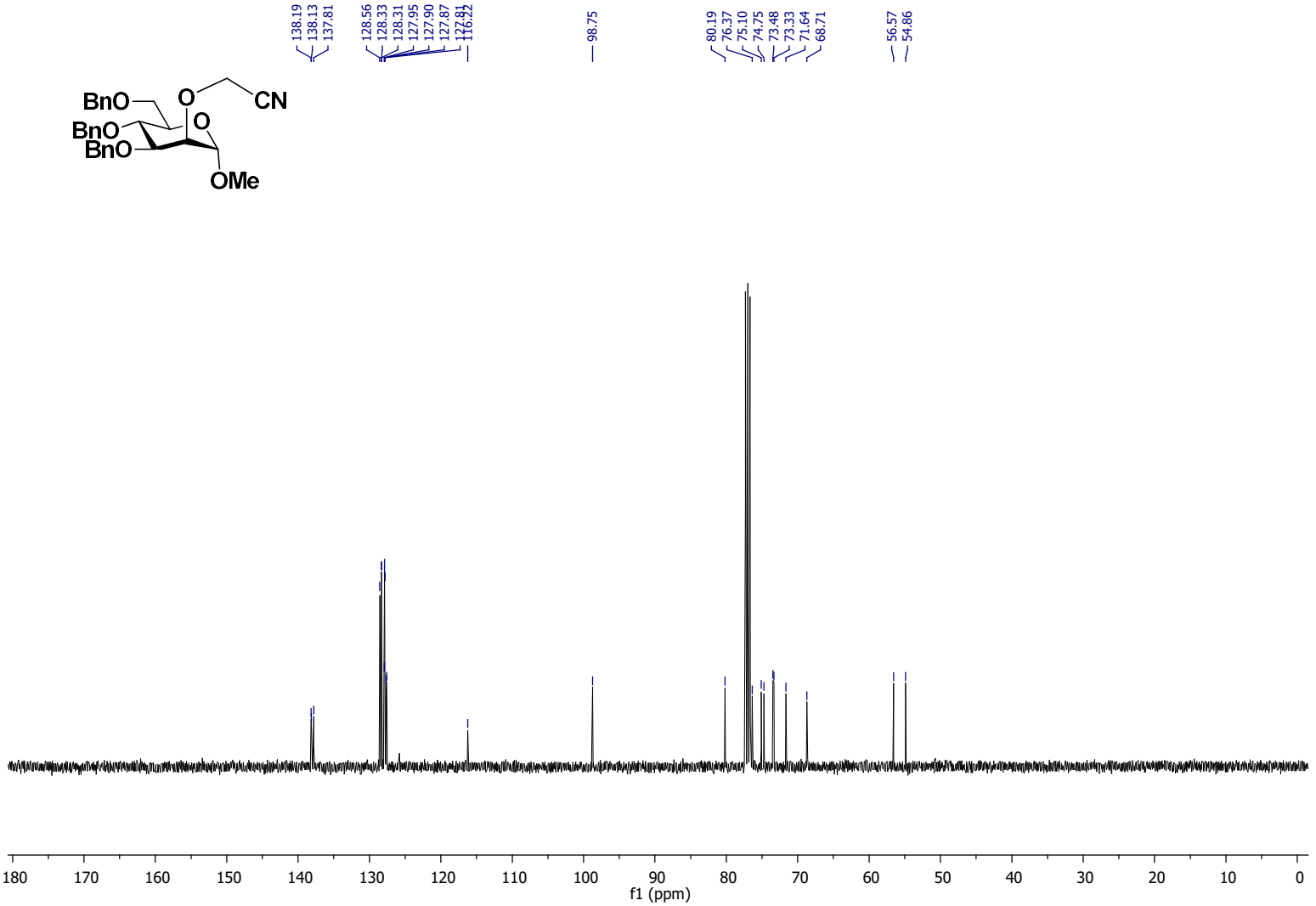
^{13}C NMR (100 MHz, $CDCl_3$) of compound 11



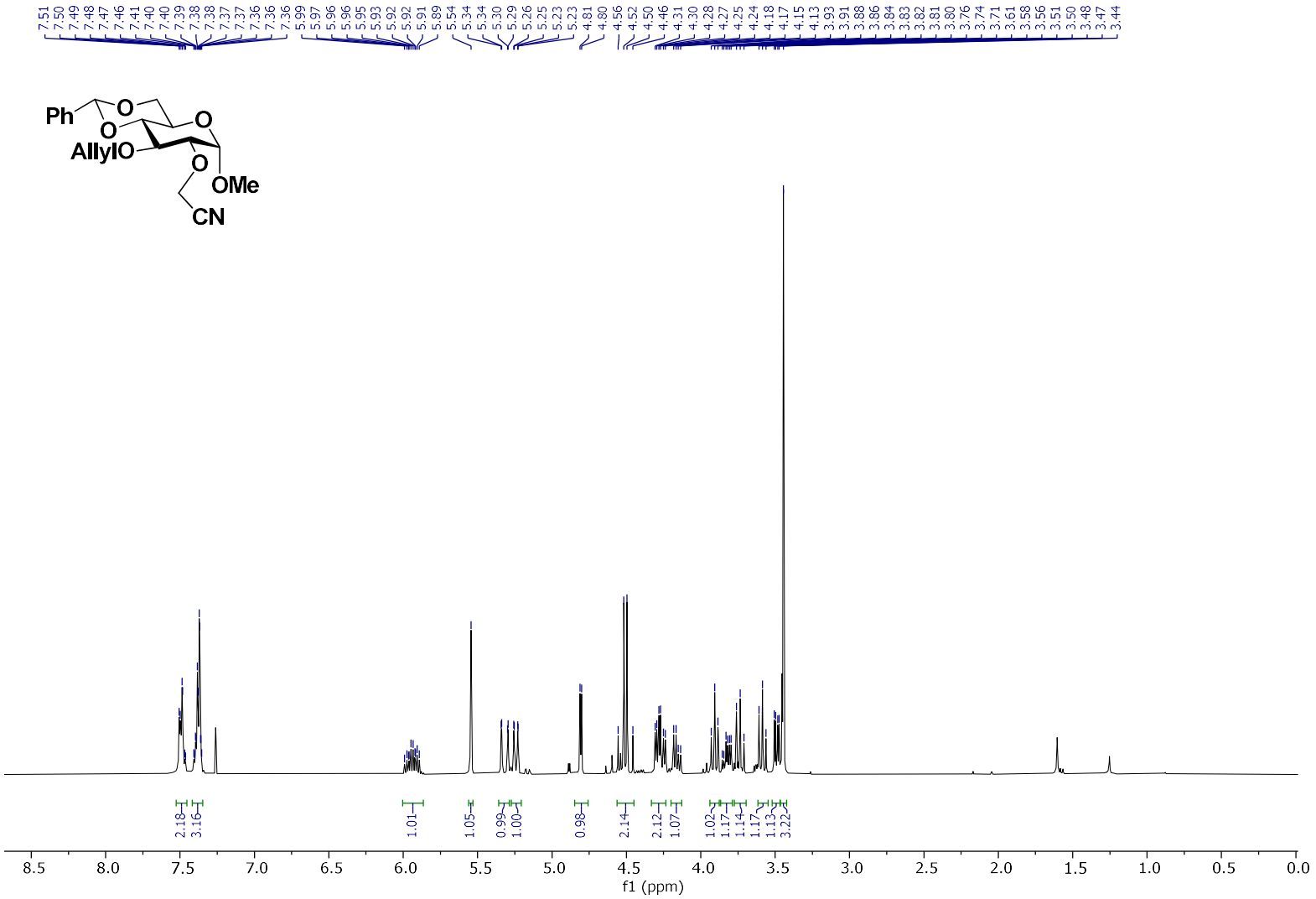
^{1}H NMR (400 MHz, $CDCl_3$) of compound 12



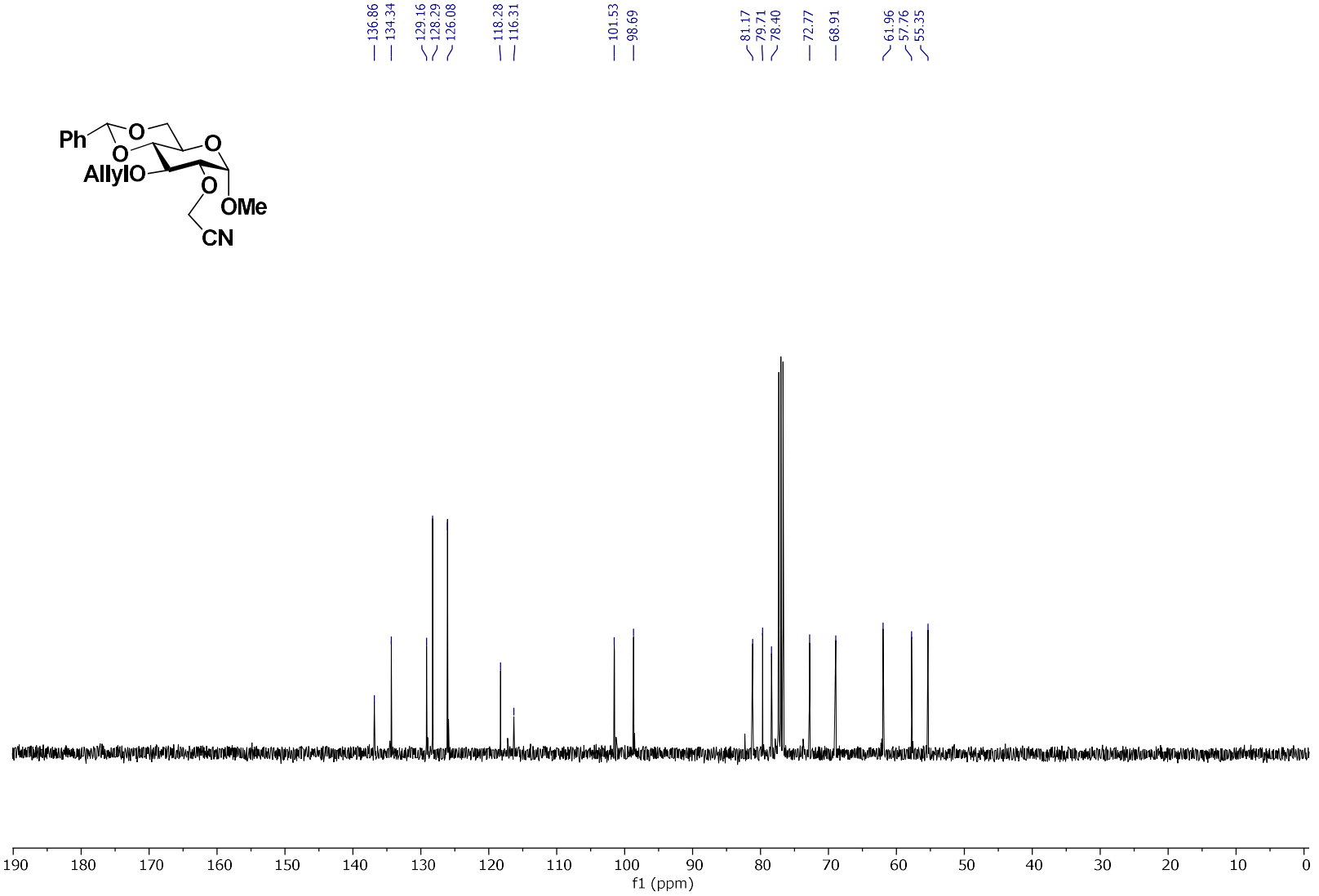
^{13}C NMR (100 MHz, $CDCl_3$) of compound 12



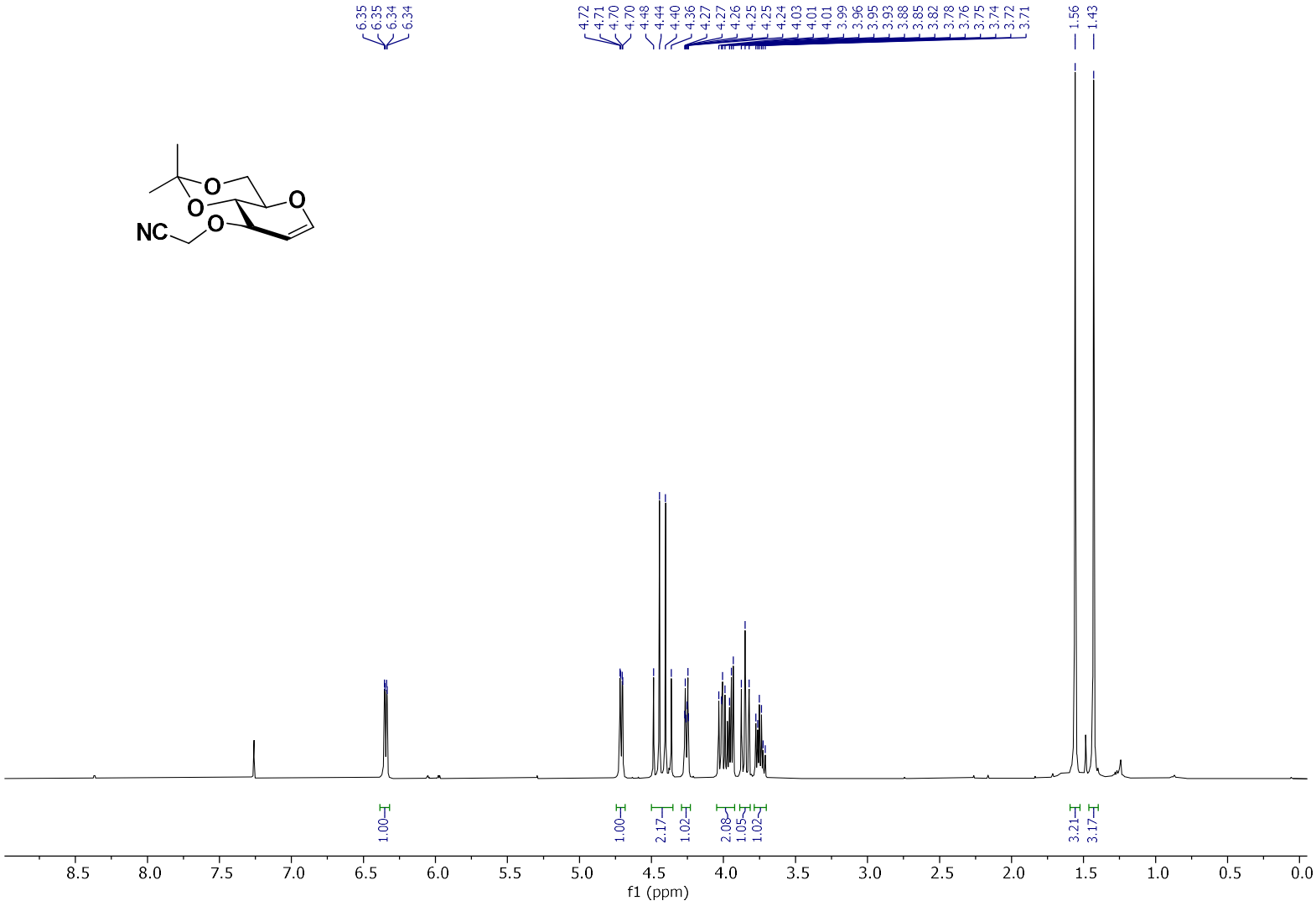
^{1}H NMR (400 MHz, $CDCl_3$) of compound 13



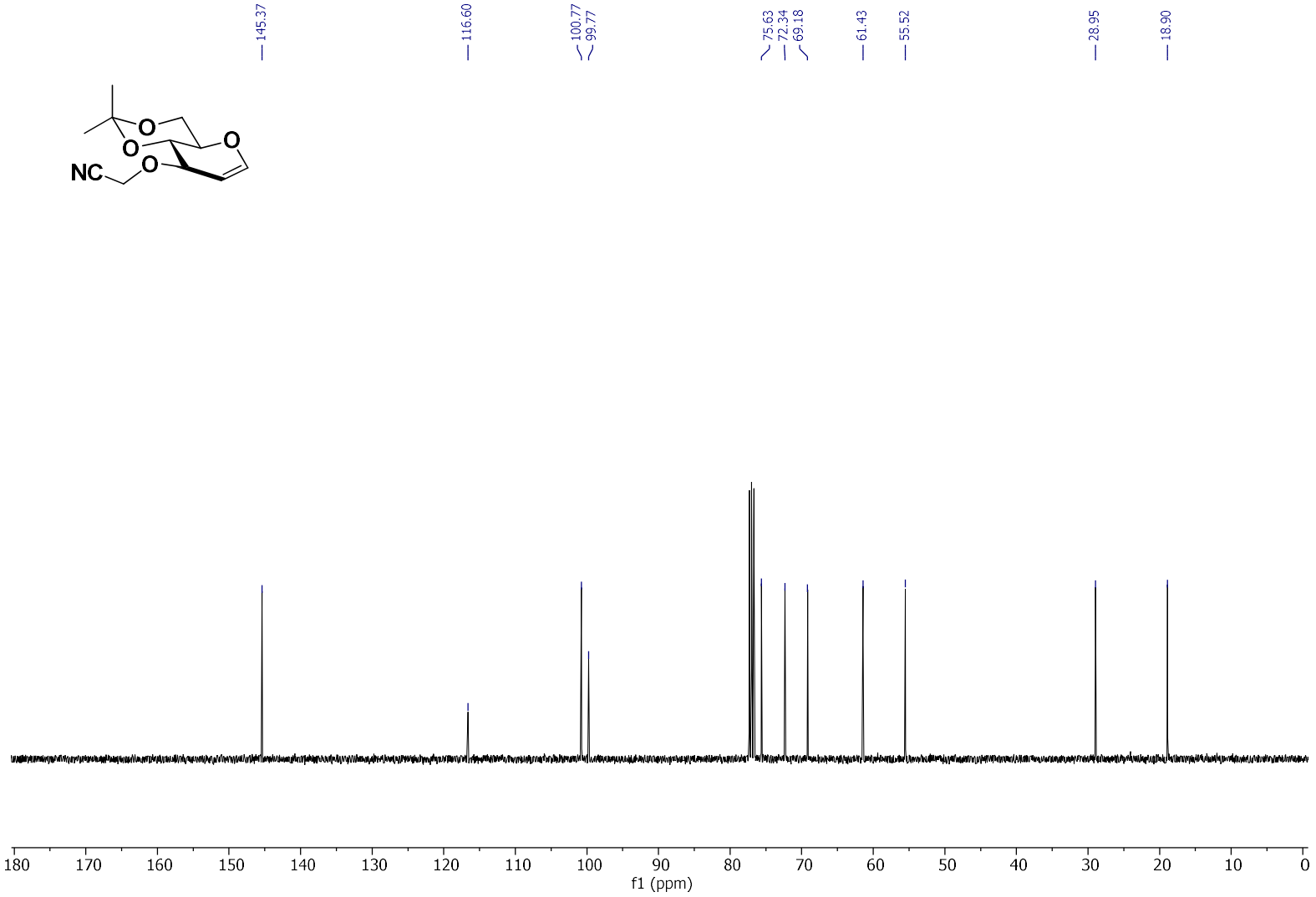
^{13}C NMR (100 MHz, $CDCl_3$) of compound 13



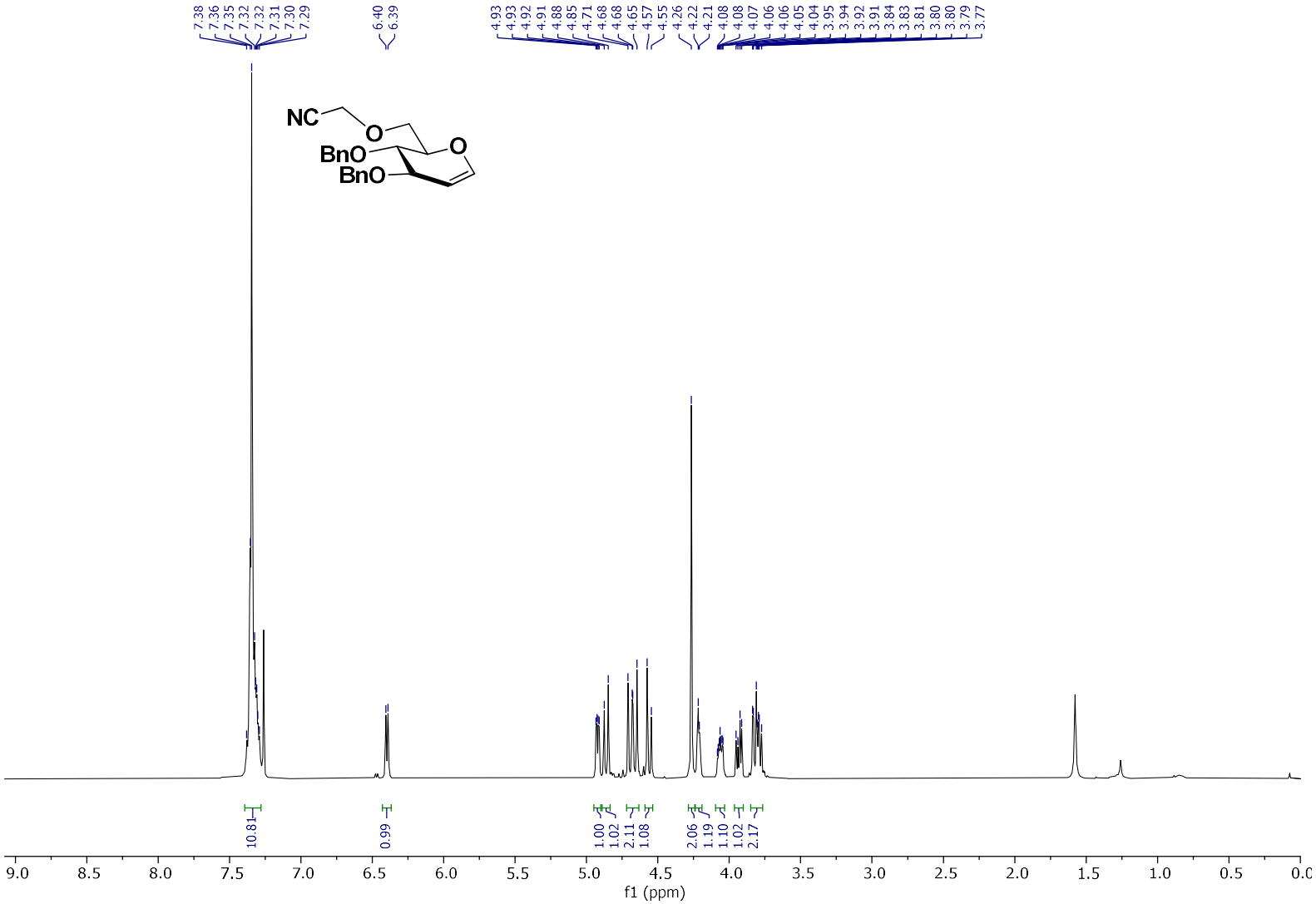
^{1}H NMR (400 MHz, $CDCl_3$) of compound 14



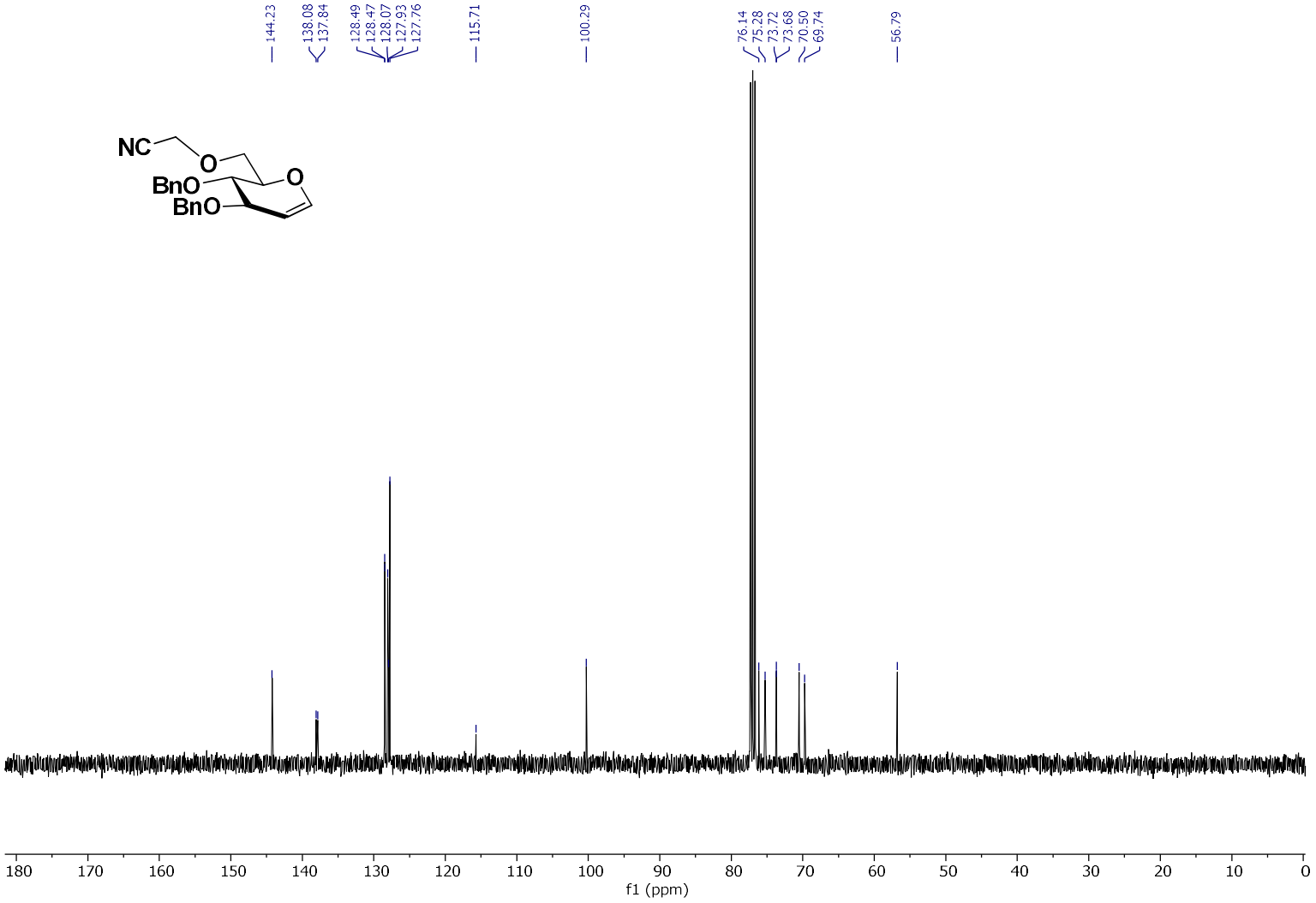
^{13}C NMR (100 MHz, $CDCl_3$) of compound 14



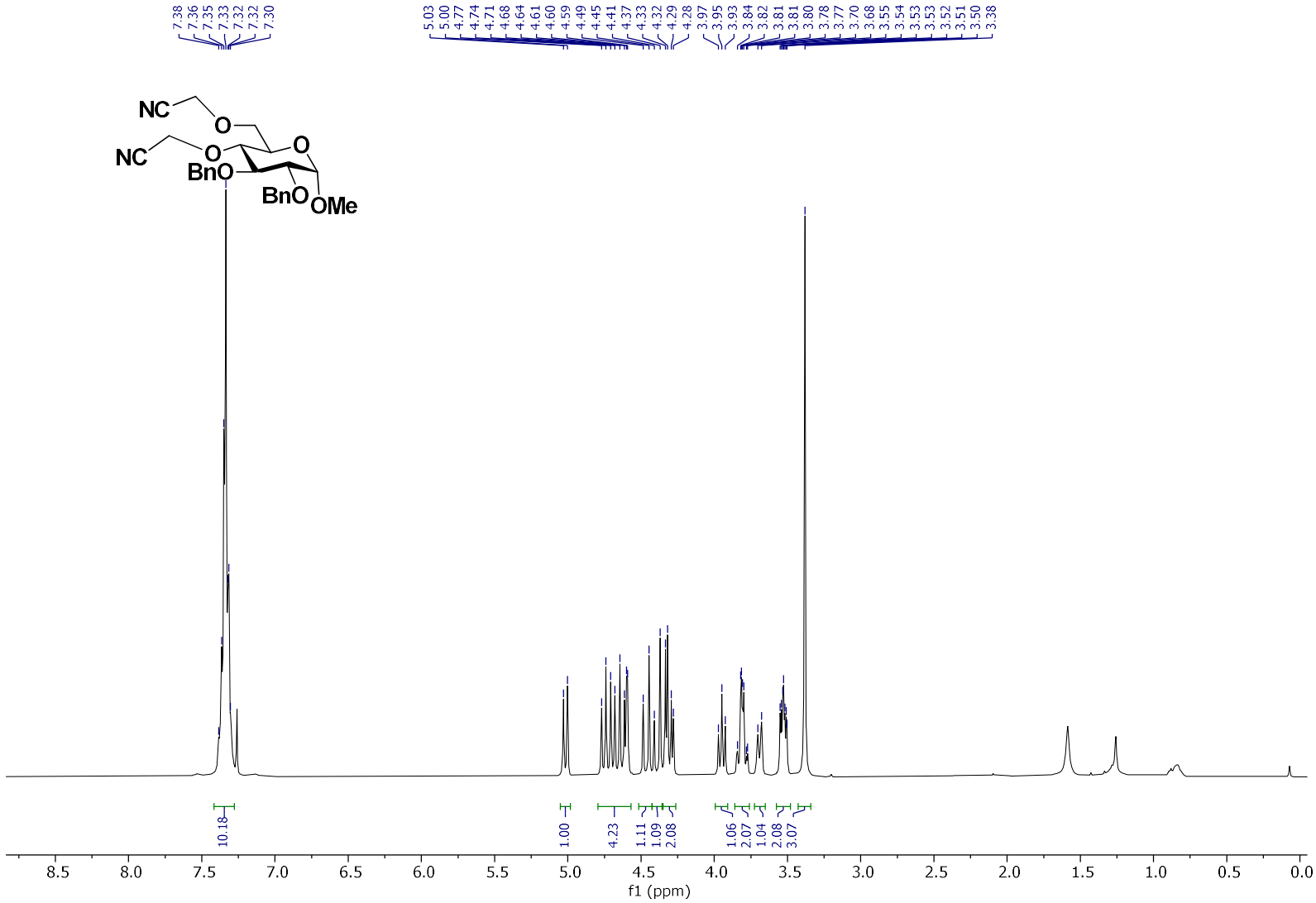
^{1}H NMR (400 MHz, $CDCl_3$) of compound 15



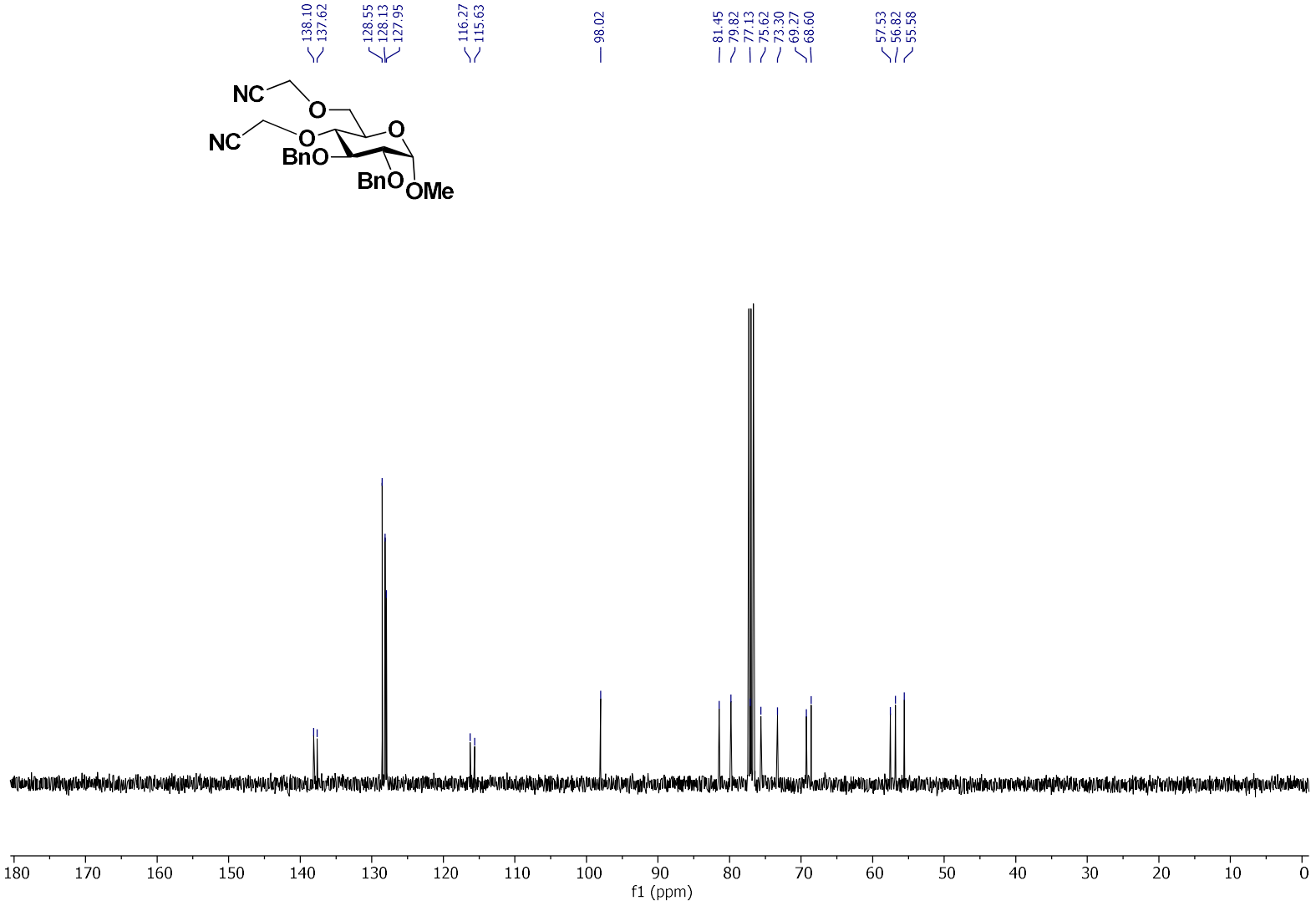
^{13}C NMR (100 MHz, $CDCl_3$) of compound 15



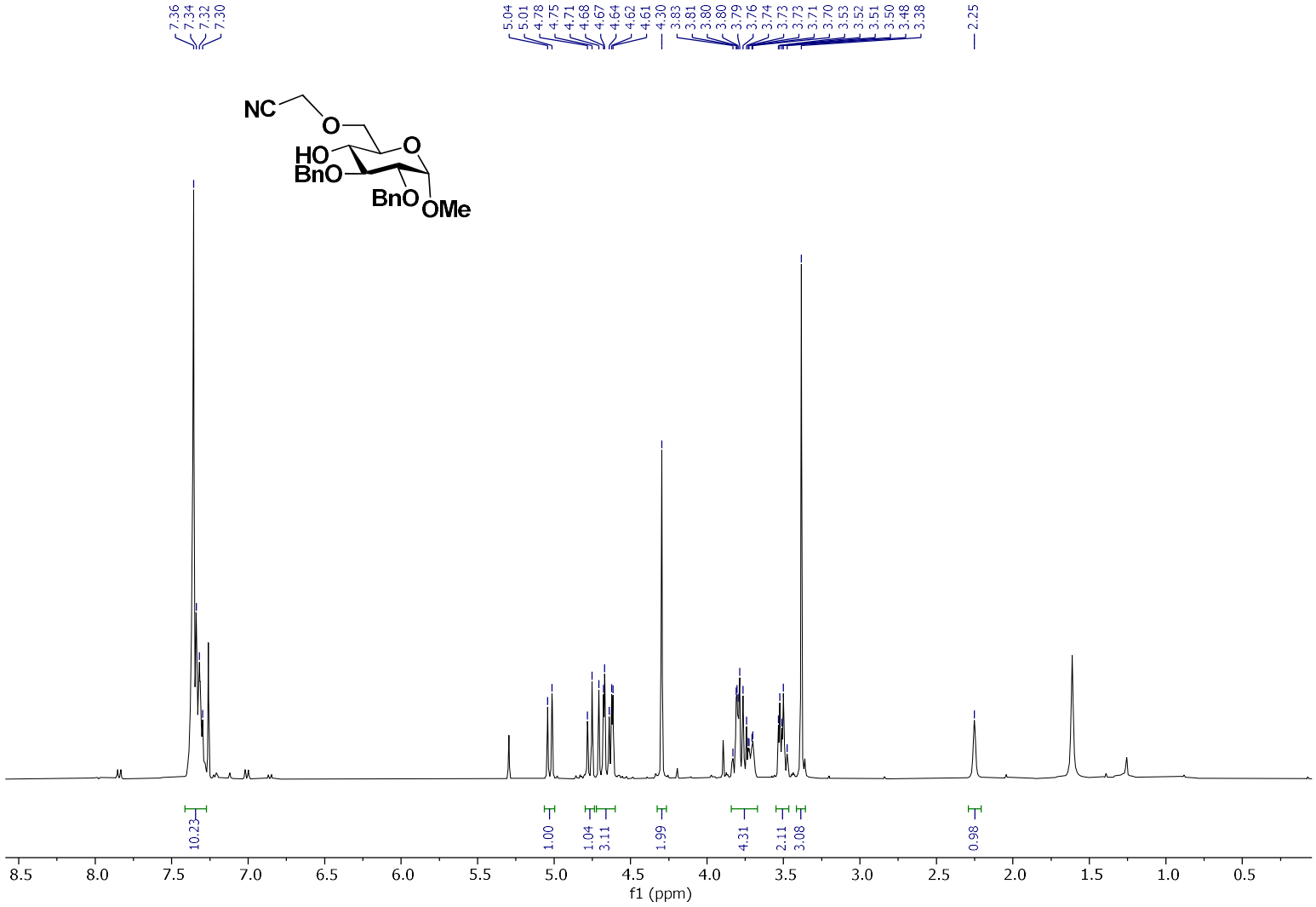
^{1}H NMR (400 MHz, $CDCl_3$) of compound 16



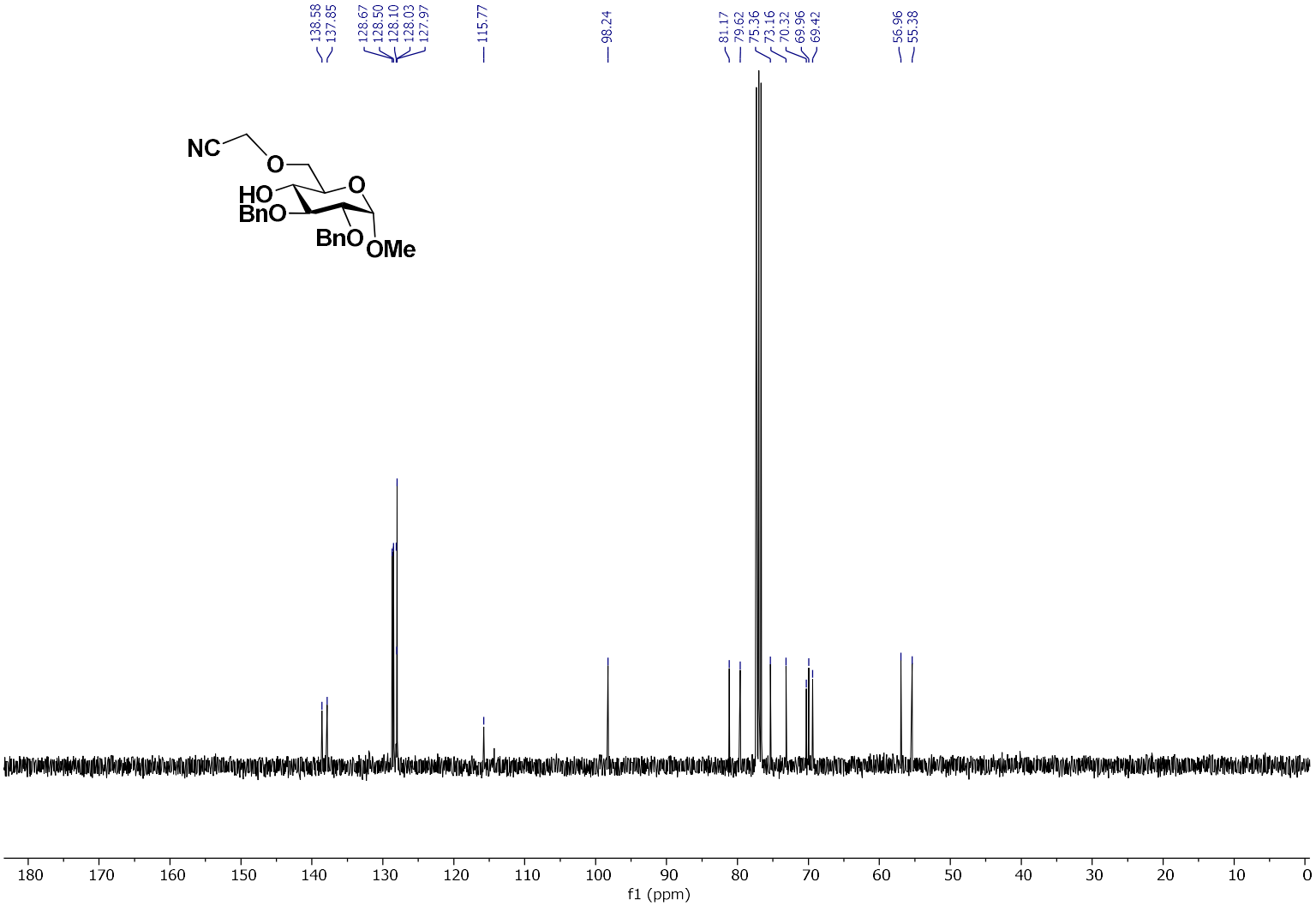
^{13}C NMR (100 MHz, $CDCl_3$) of compound 16



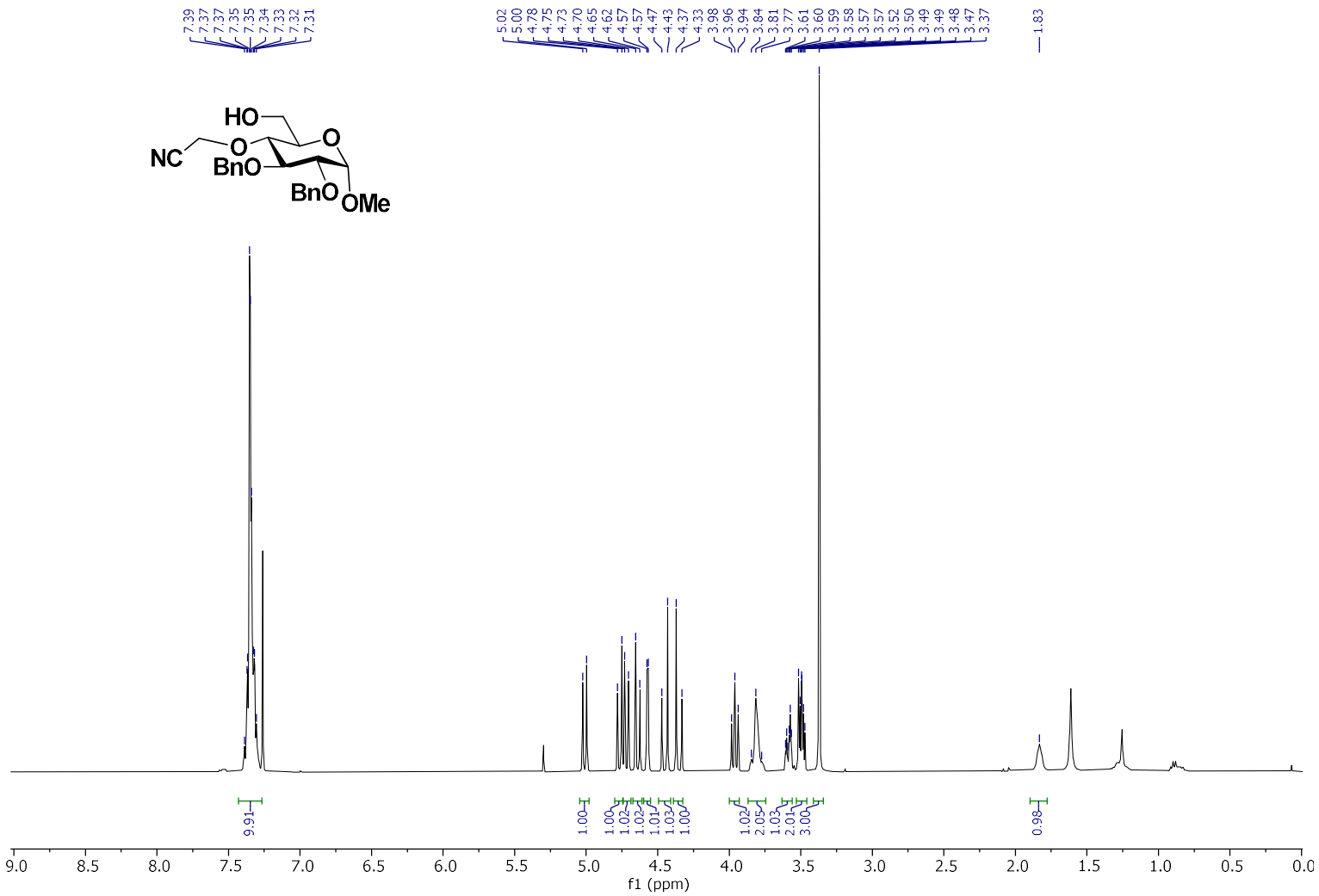
^{1}H NMR (400 MHz, $CDCl_3$) of compound 30



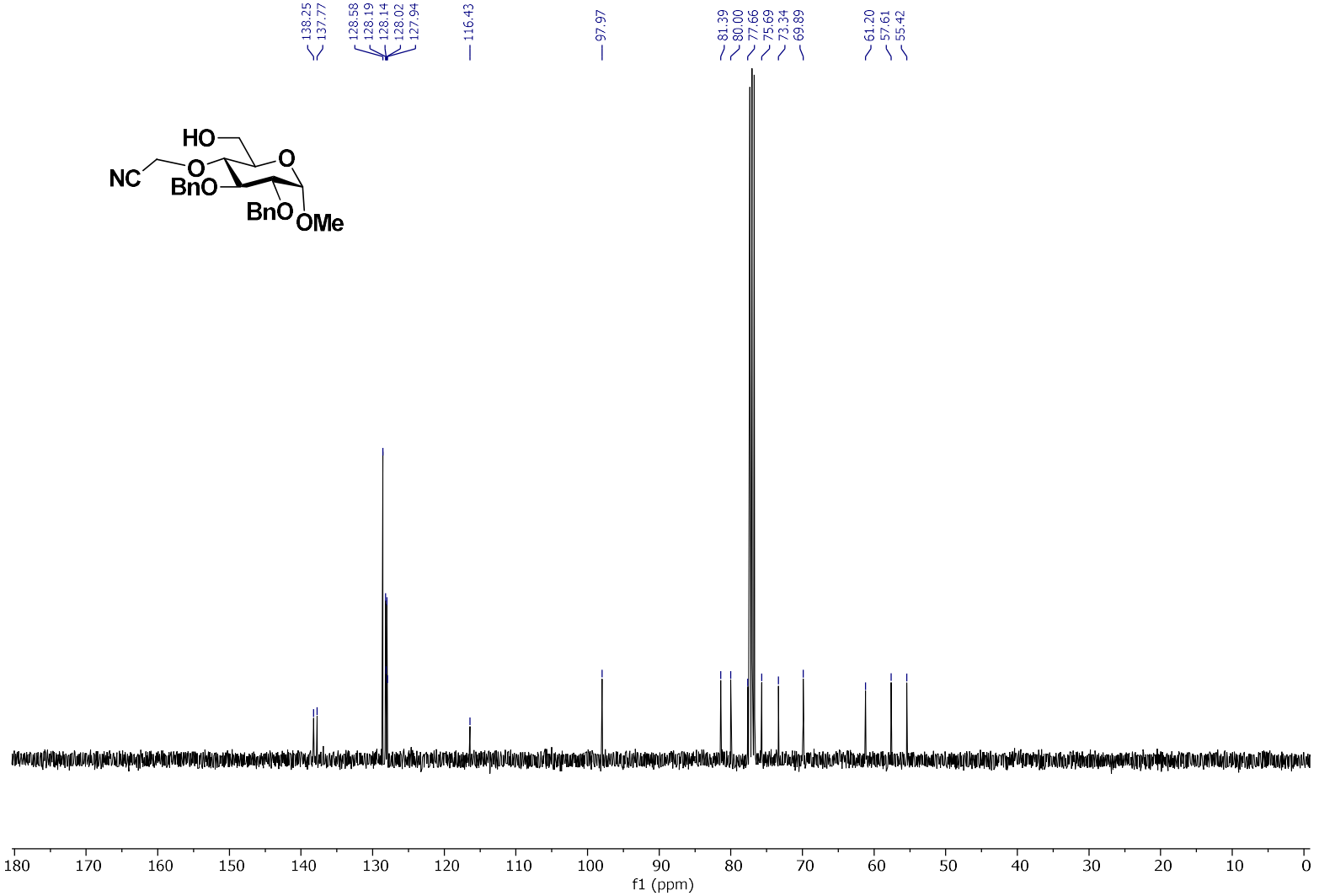
^{13}C NMR (100 MHz, $CDCl_3$) of compound 30



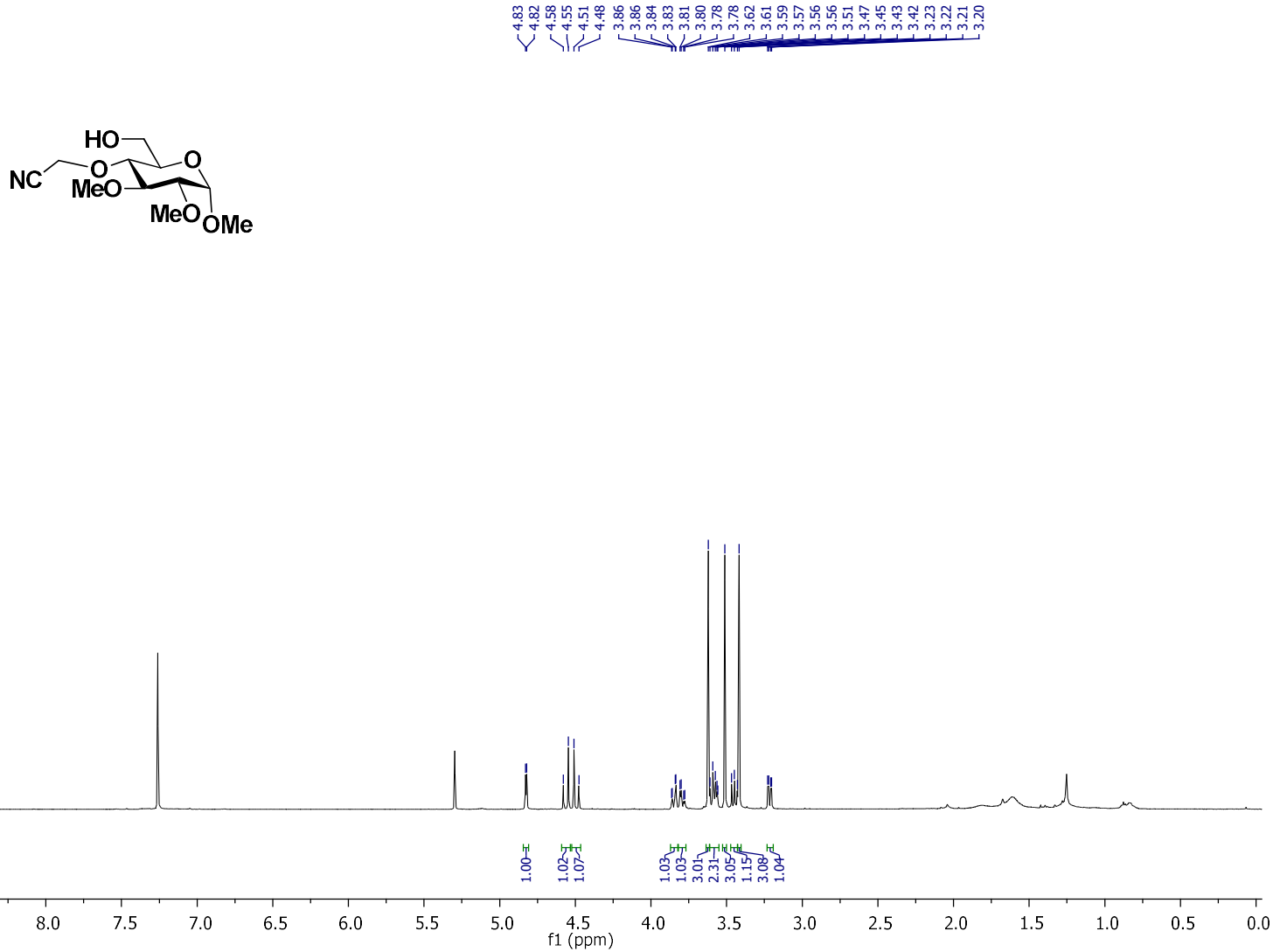
^{1}H NMR (400 MHz, $CDCl_3$) of compound 31



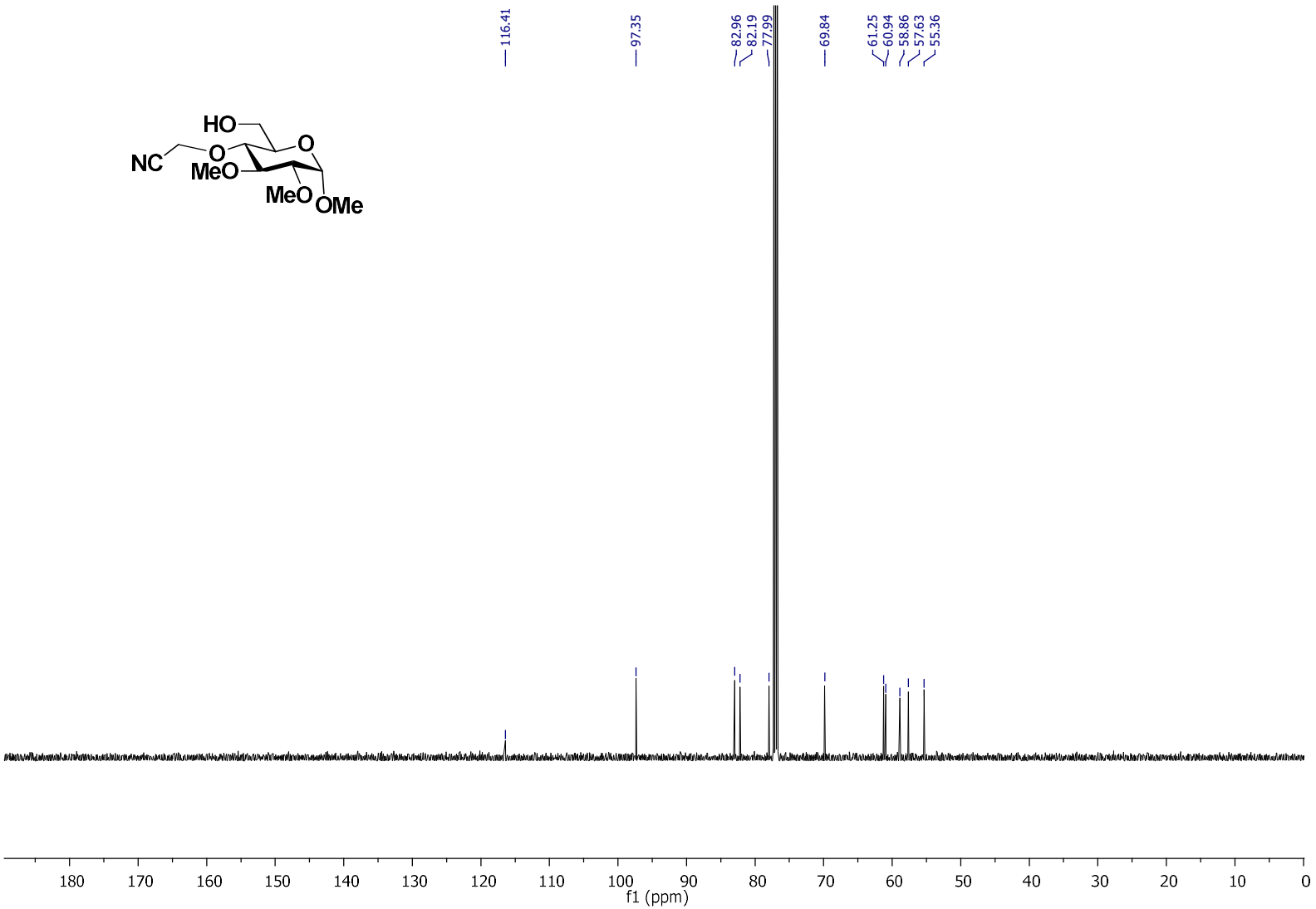
^{13}C NMR (100 MHz, $CDCl_3$) of compound 31



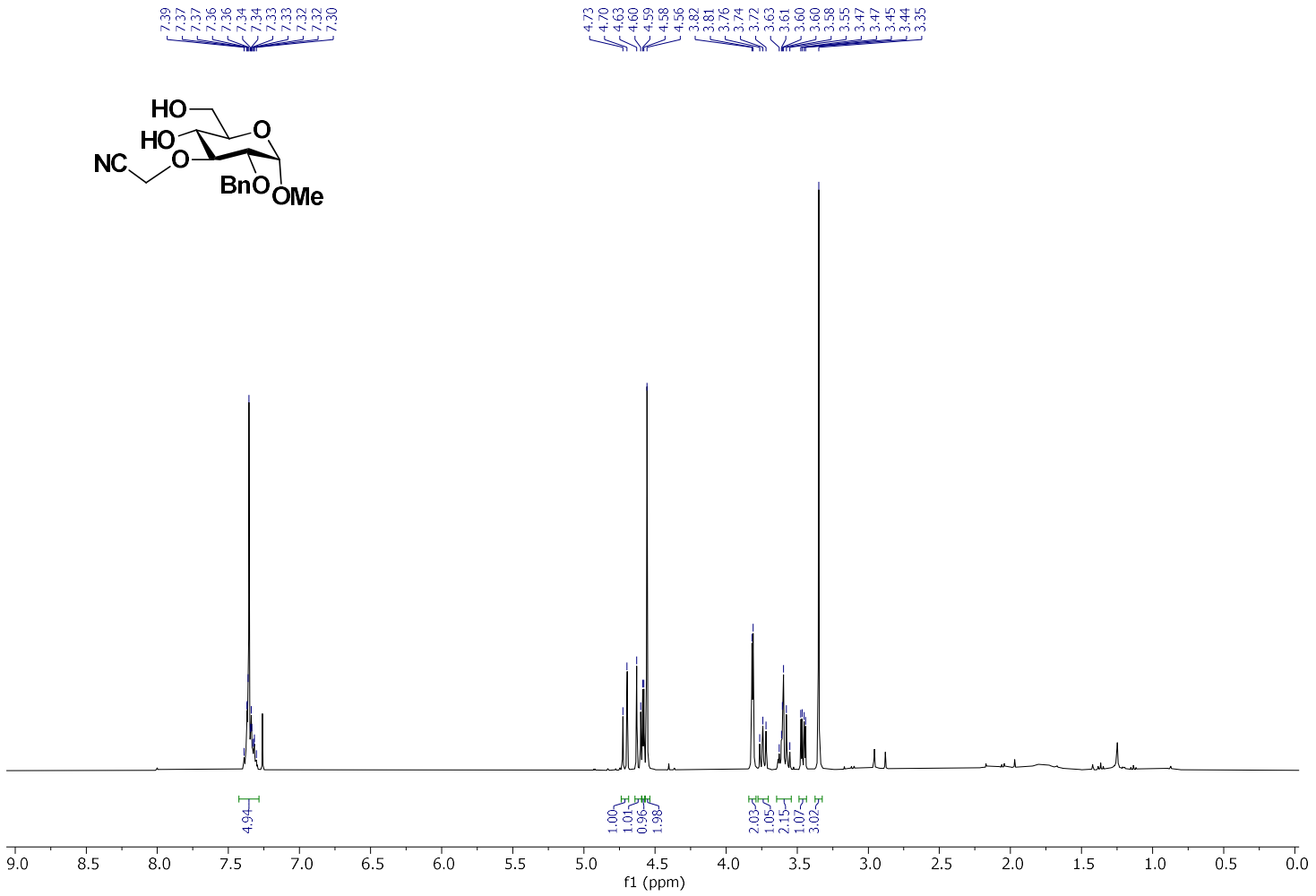
^{1}H NMR (500 MHz, $CDCl_3$) of compound 32



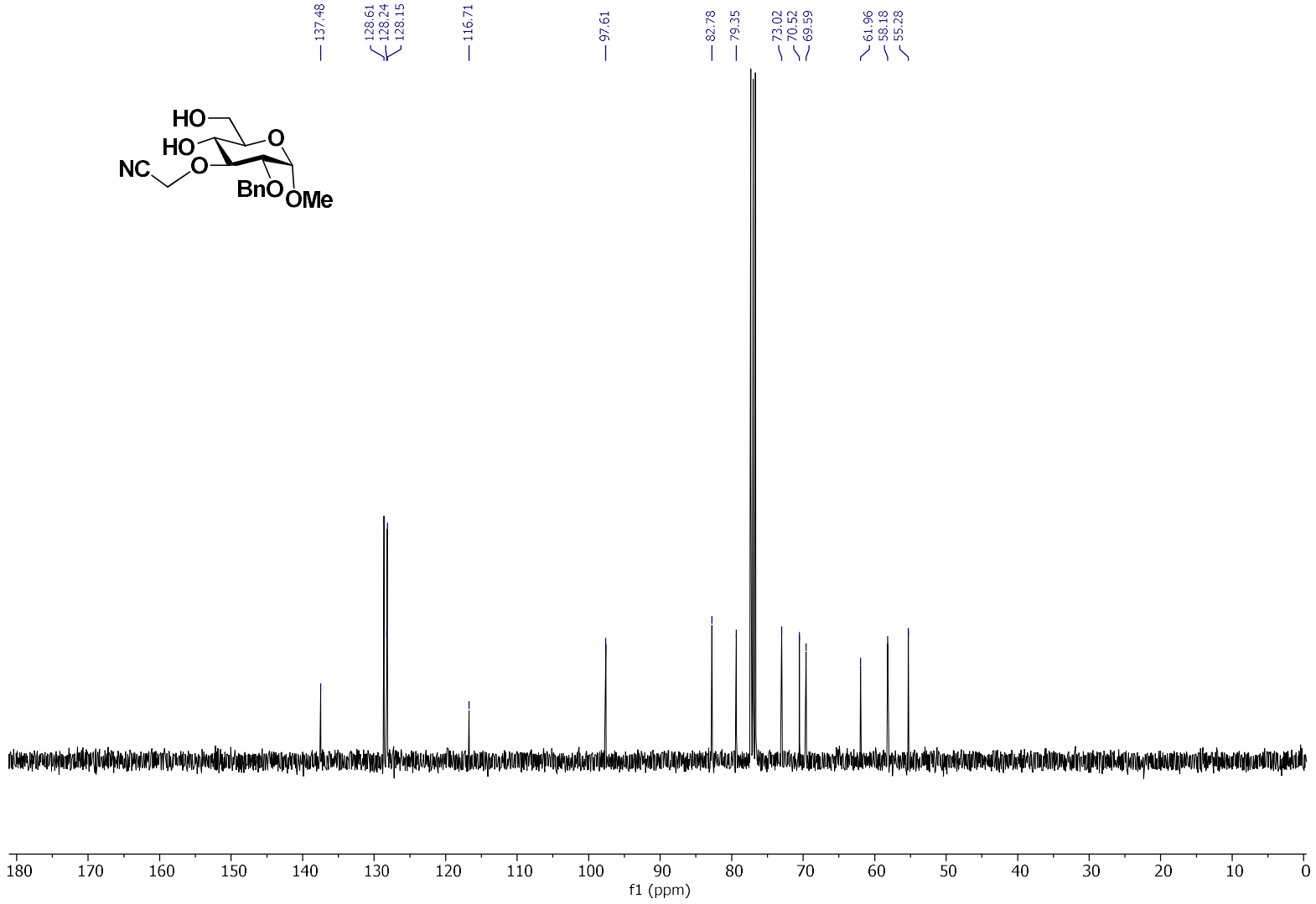
^{13}C NMR (125 MHz, $CDCl_3$) of compound 32



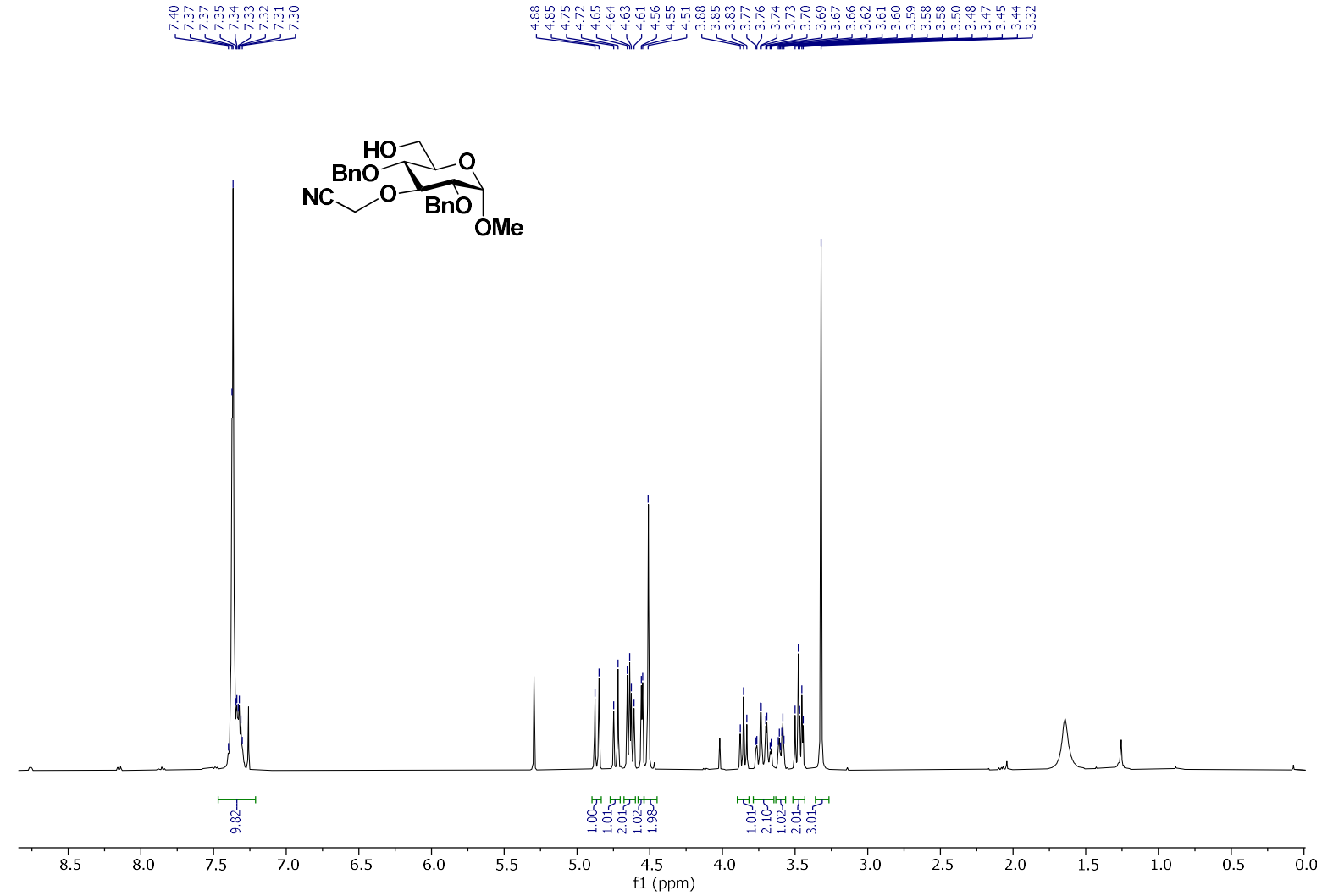
^{1}H NMR (400 MHz, $CDCl_3$) of compound 33



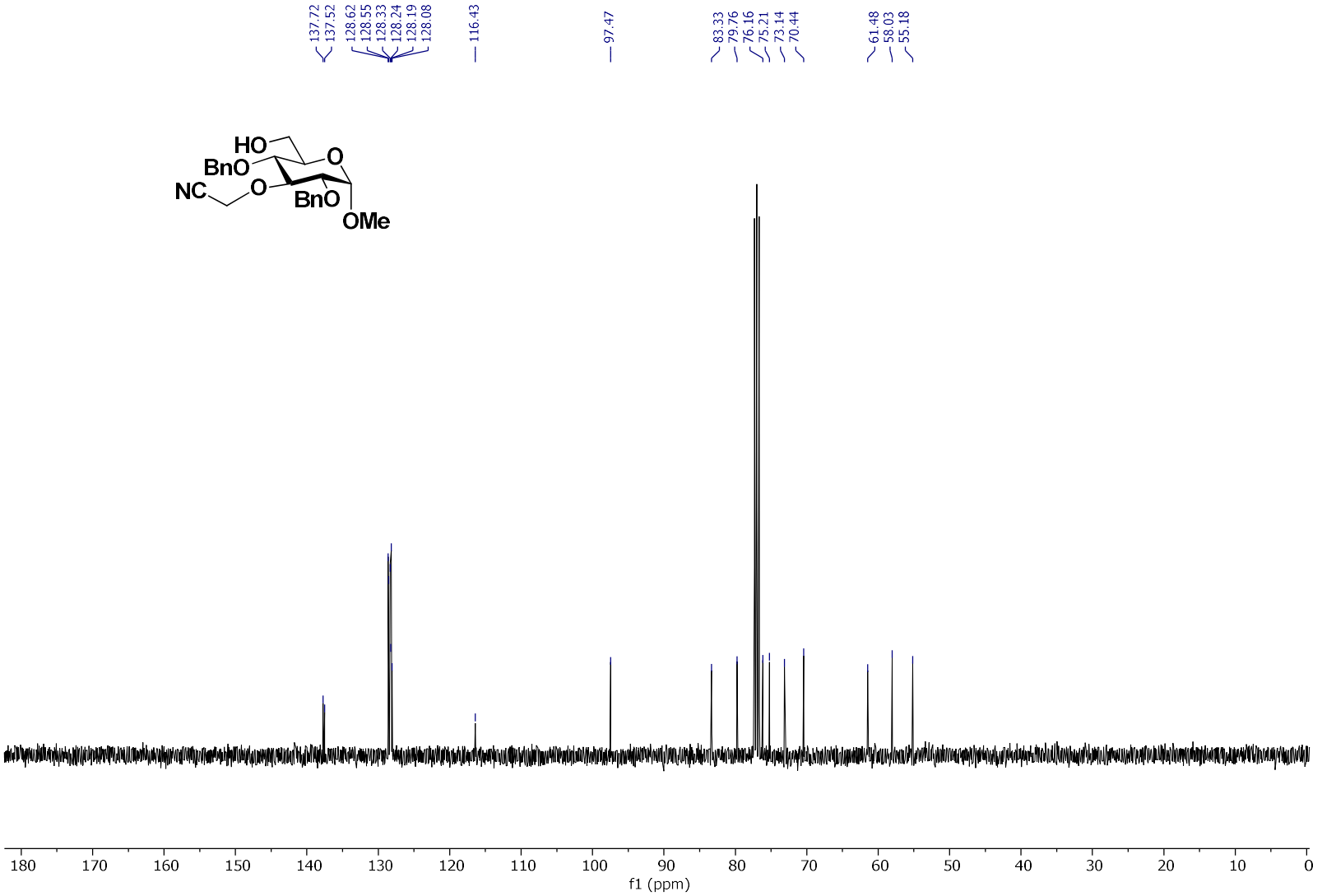
^{13}C NMR (100 MHz, $CDCl_3$) of compound 33



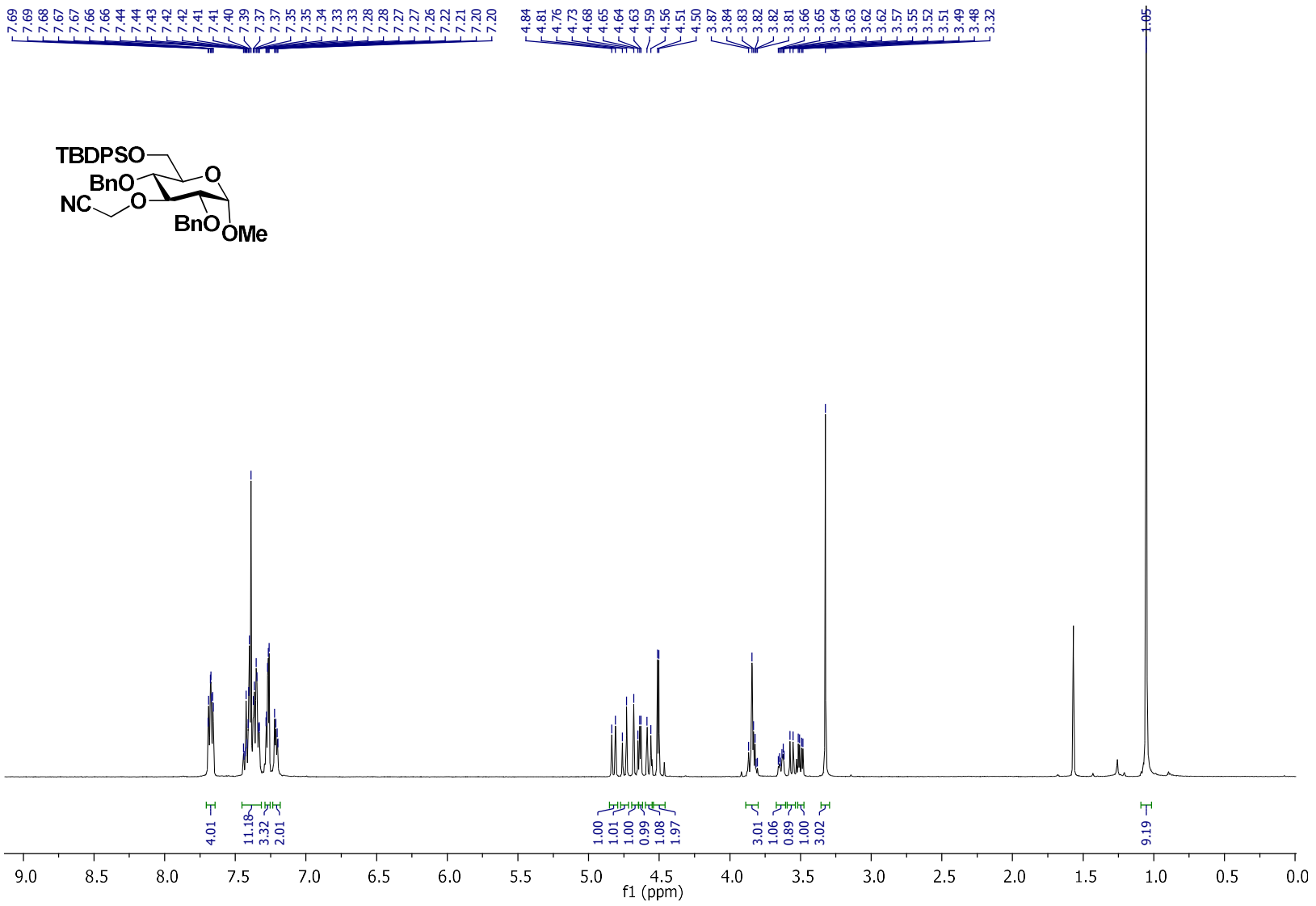
^{1}H NMR (400 MHz, $CDCl_3$) of compound 34



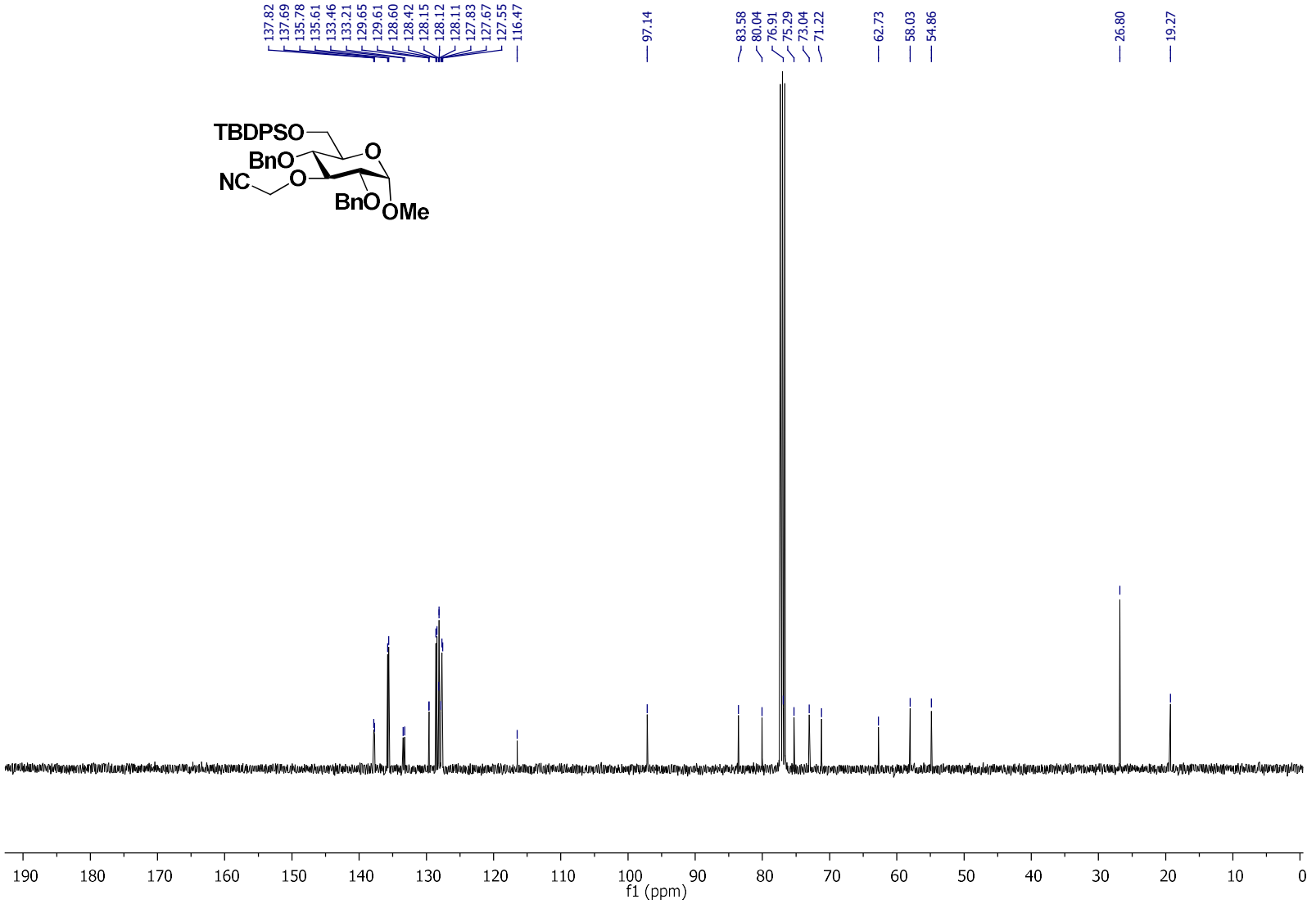
^{13}C NMR (100 MHz, $CDCl_3$) of compound 34



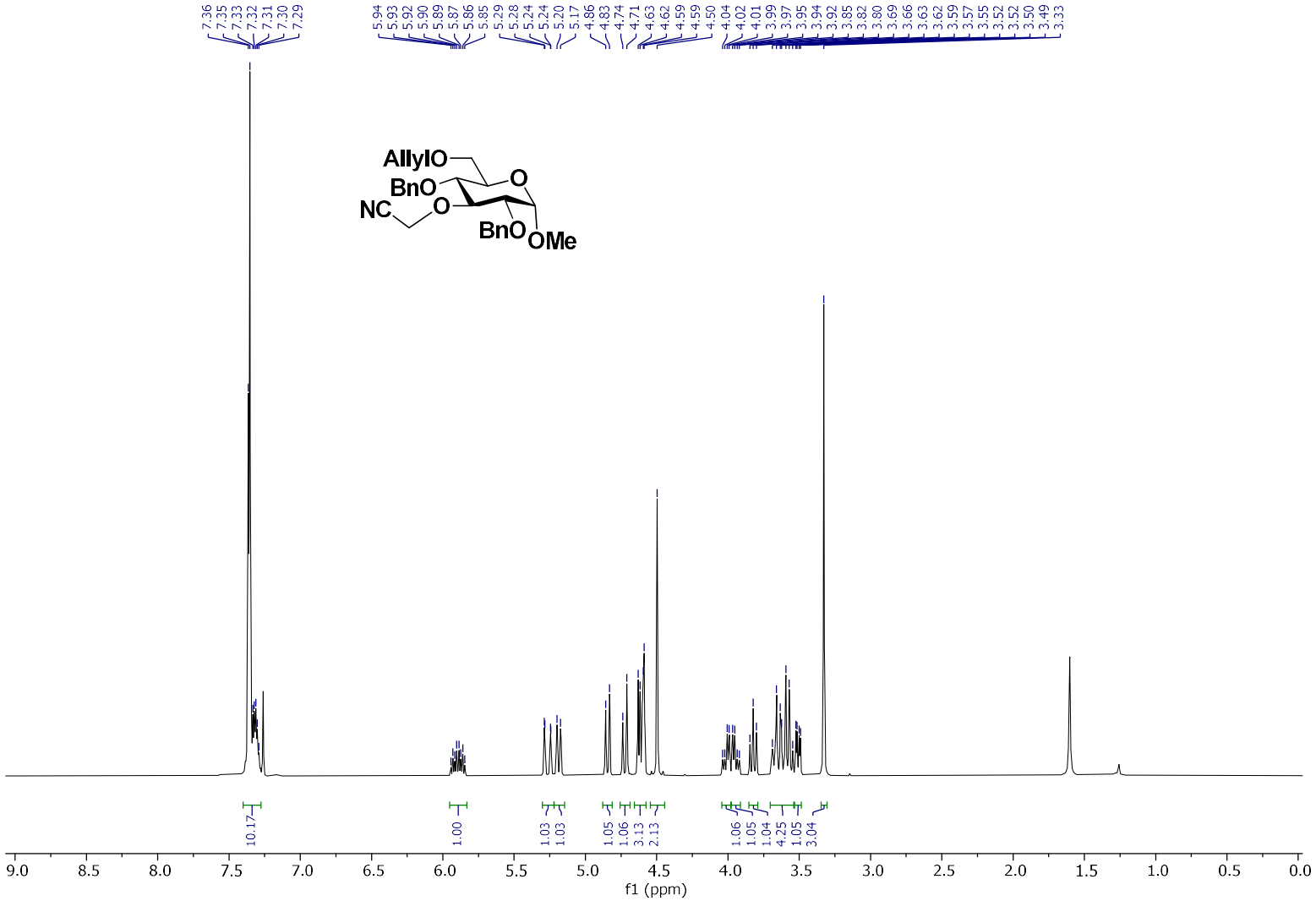
^{1}H NMR (400 MHz, $CDCl_3$) of compound 35



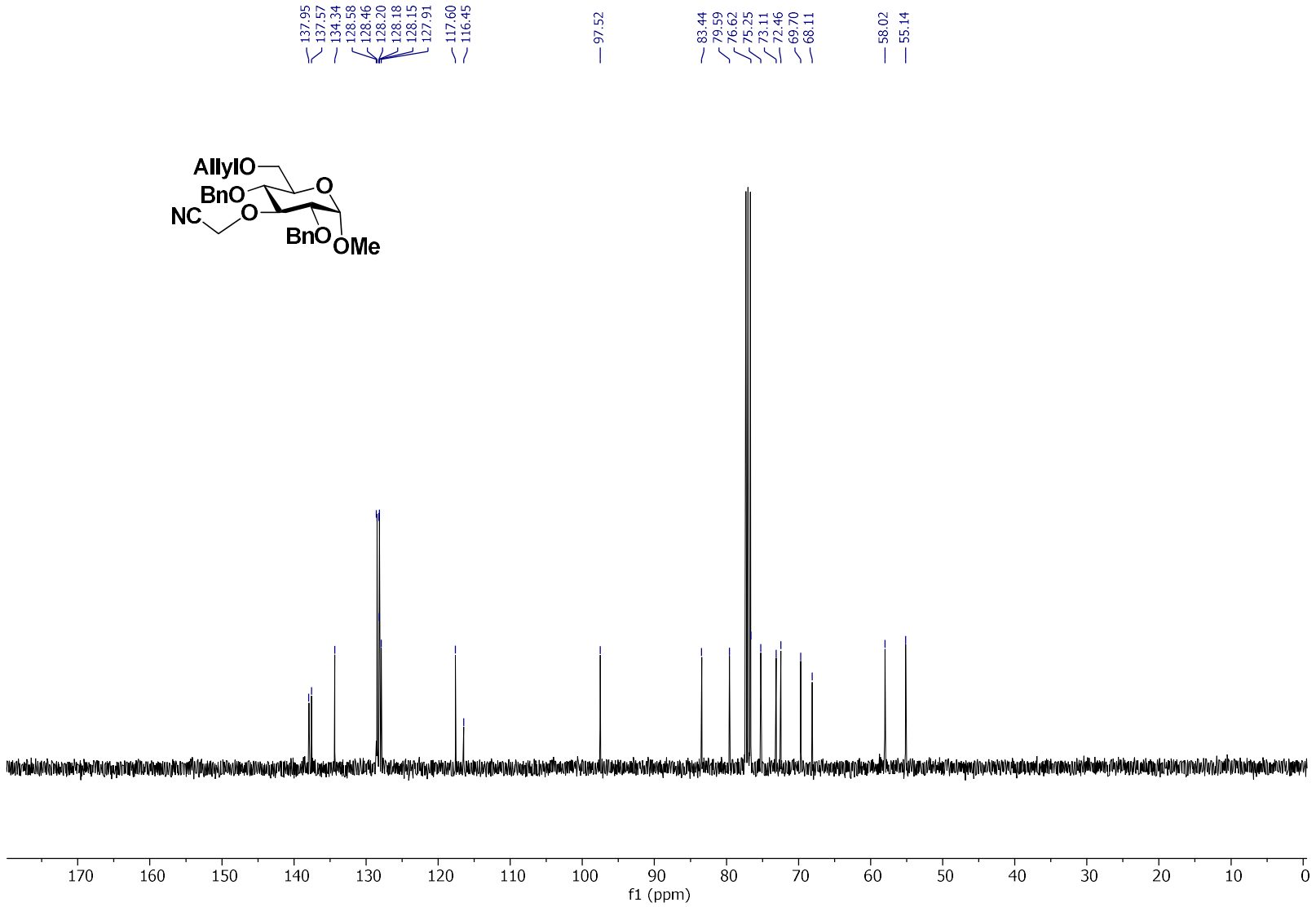
^{13}C NMR (100 MHz, $CDCl_3$) of compound 35



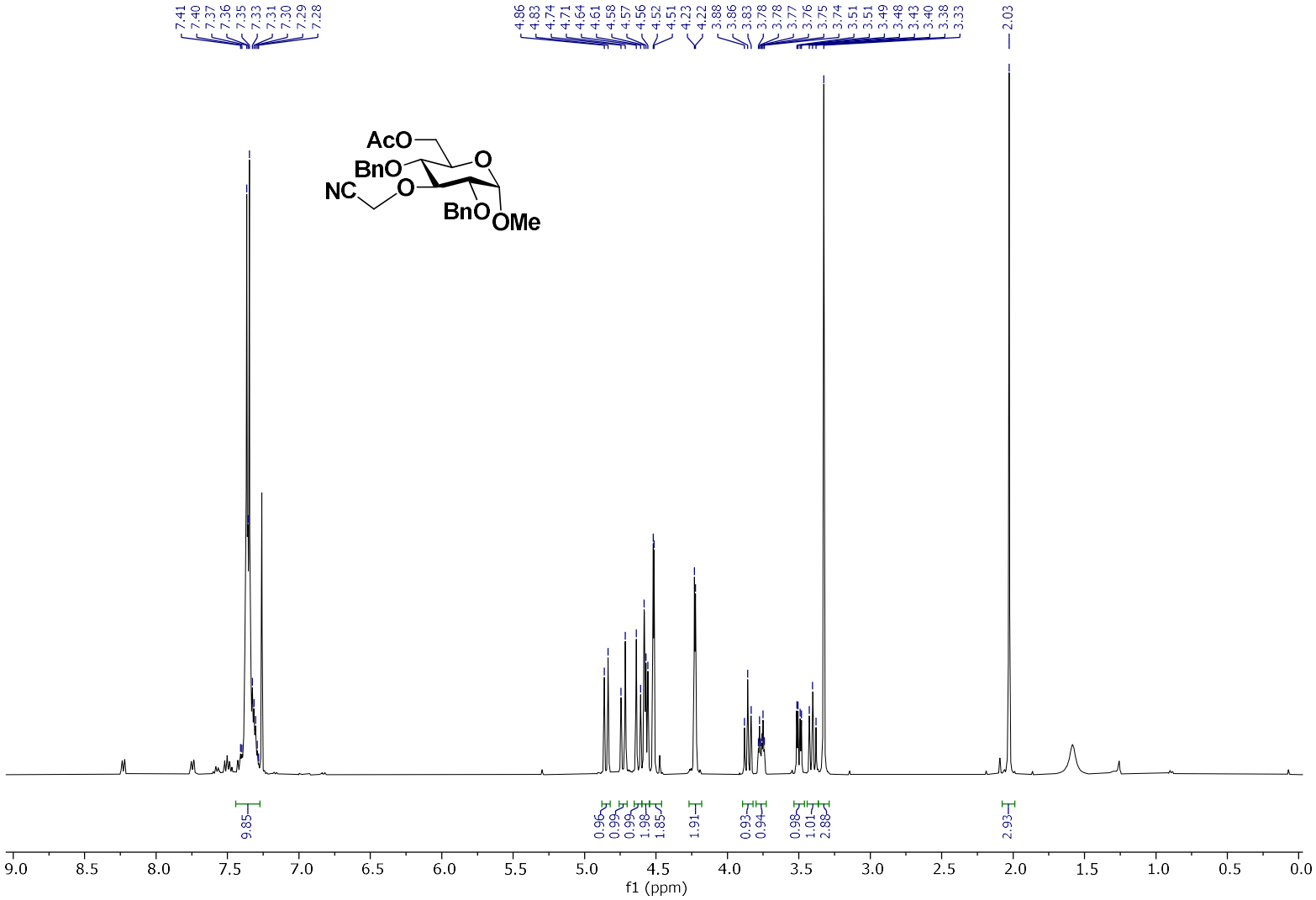
^{1}H NMR (400 MHz, $CDCl_3$) of compound 36



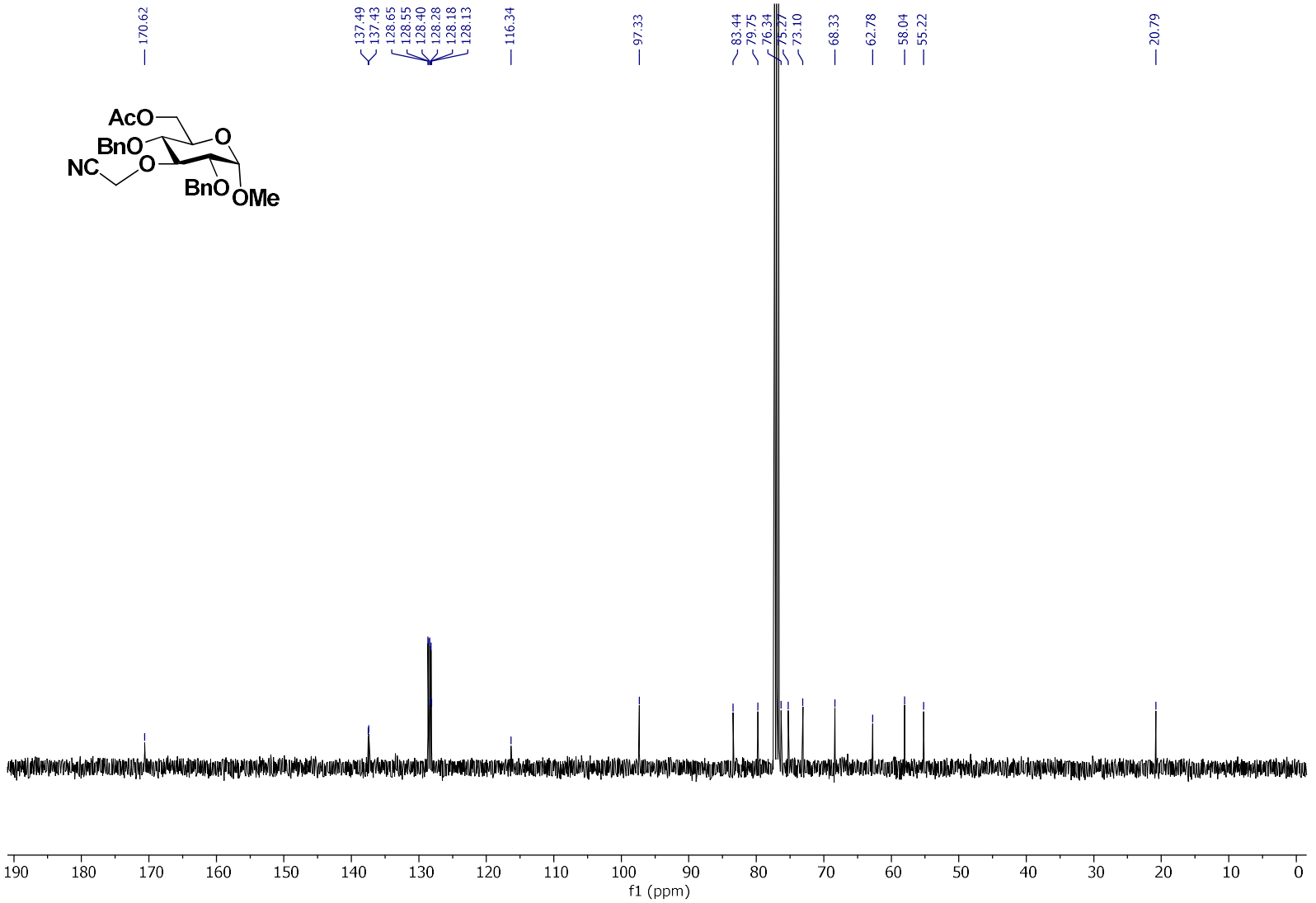
^{13}C NMR (100 MHz, $CDCl_3$) of compound 36



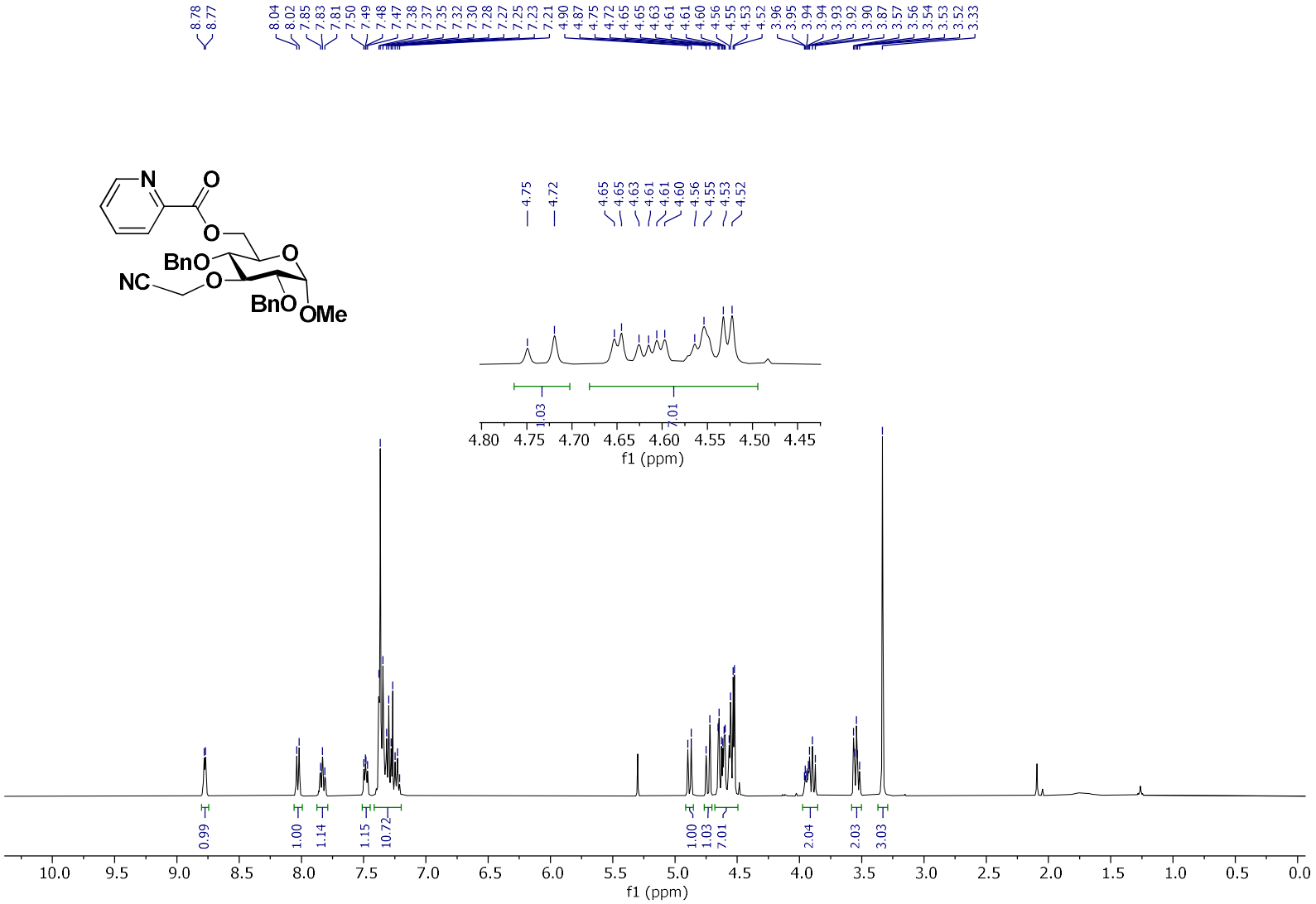
^{1}H NMR (400 MHz, $CDCl_3$) of compound 37



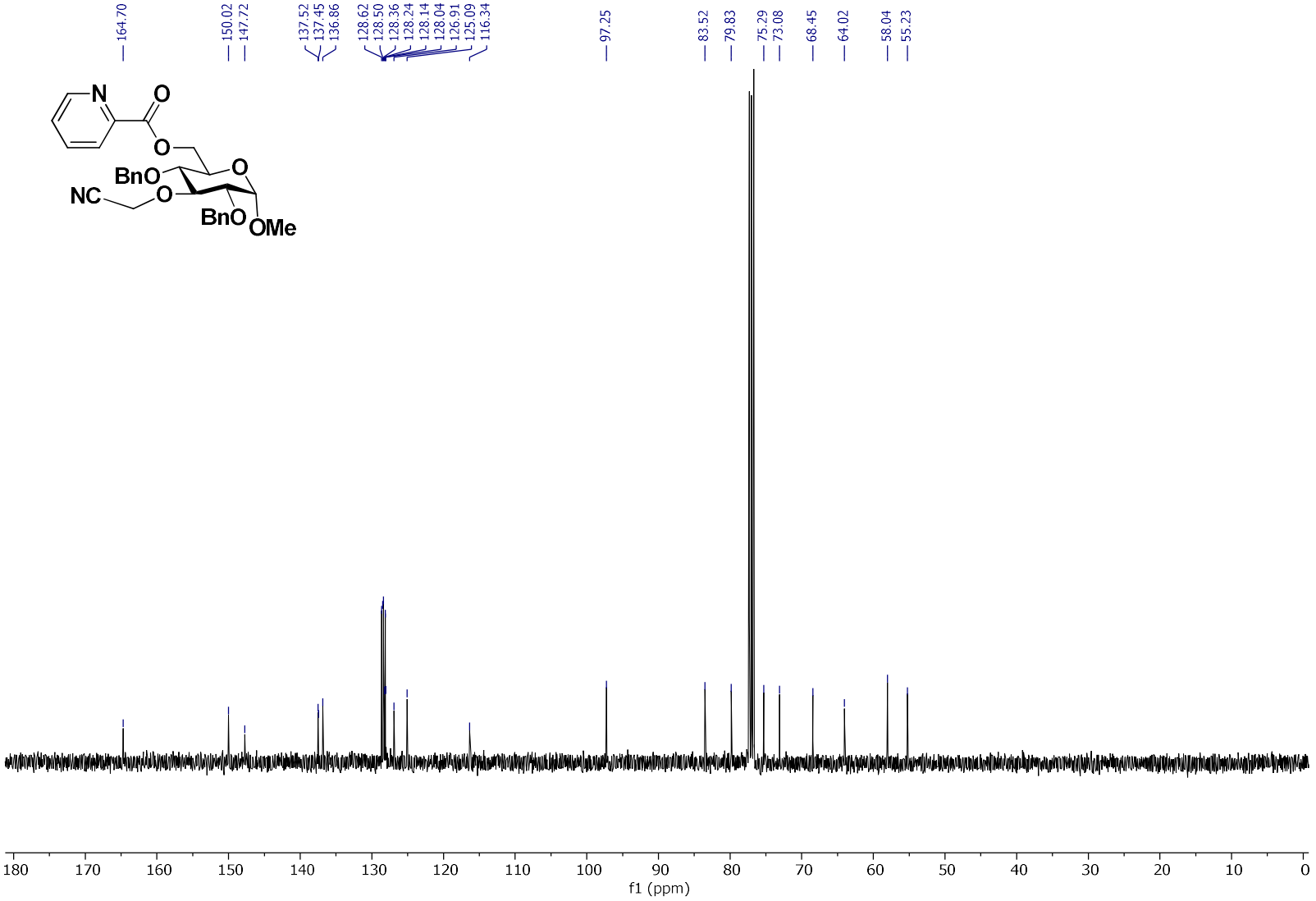
^{13}C NMR (100 MHz, $CDCl_3$) of compound 37



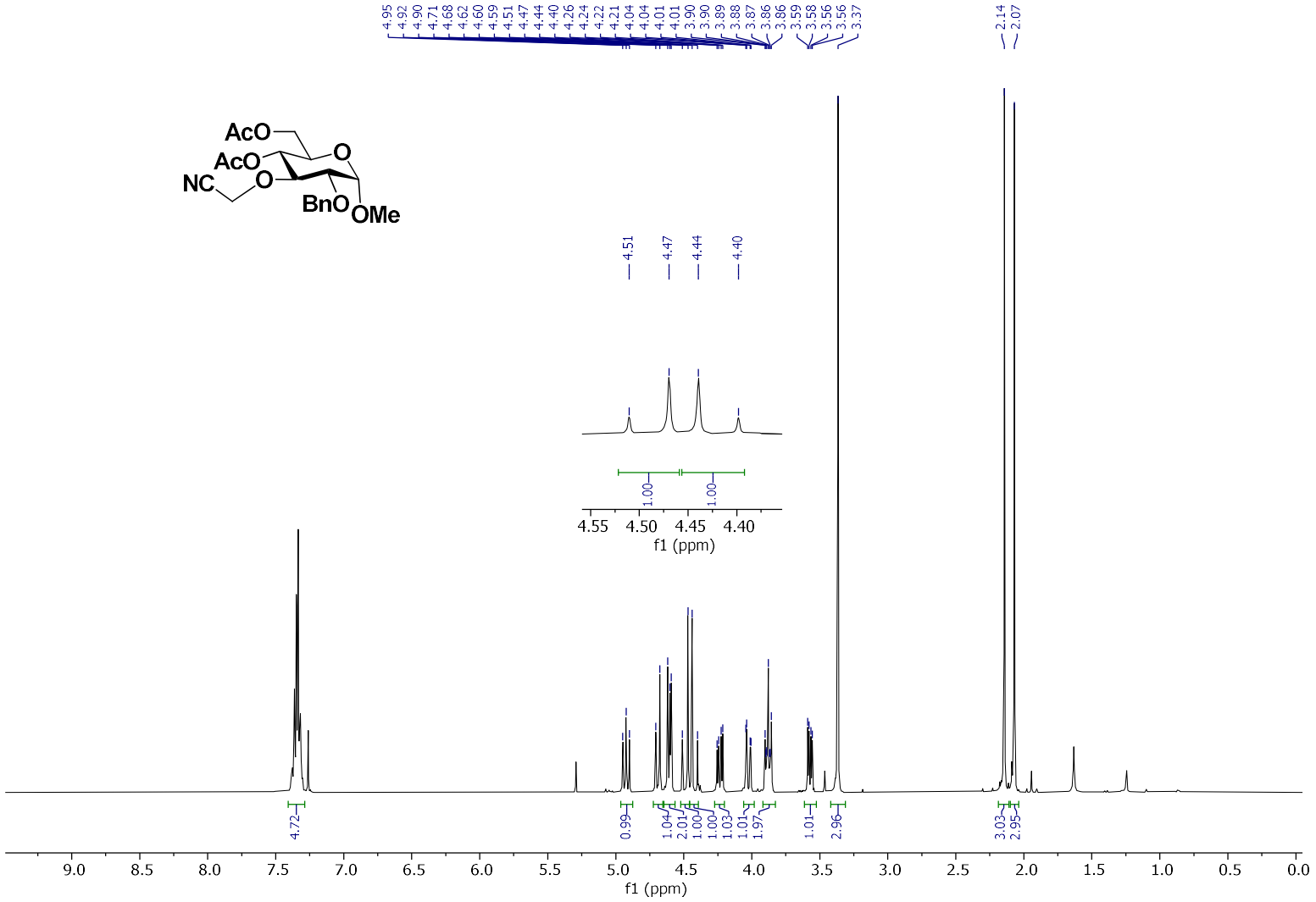
^{1}H NMR (400 MHz, $CDCl_3$) of compound 38



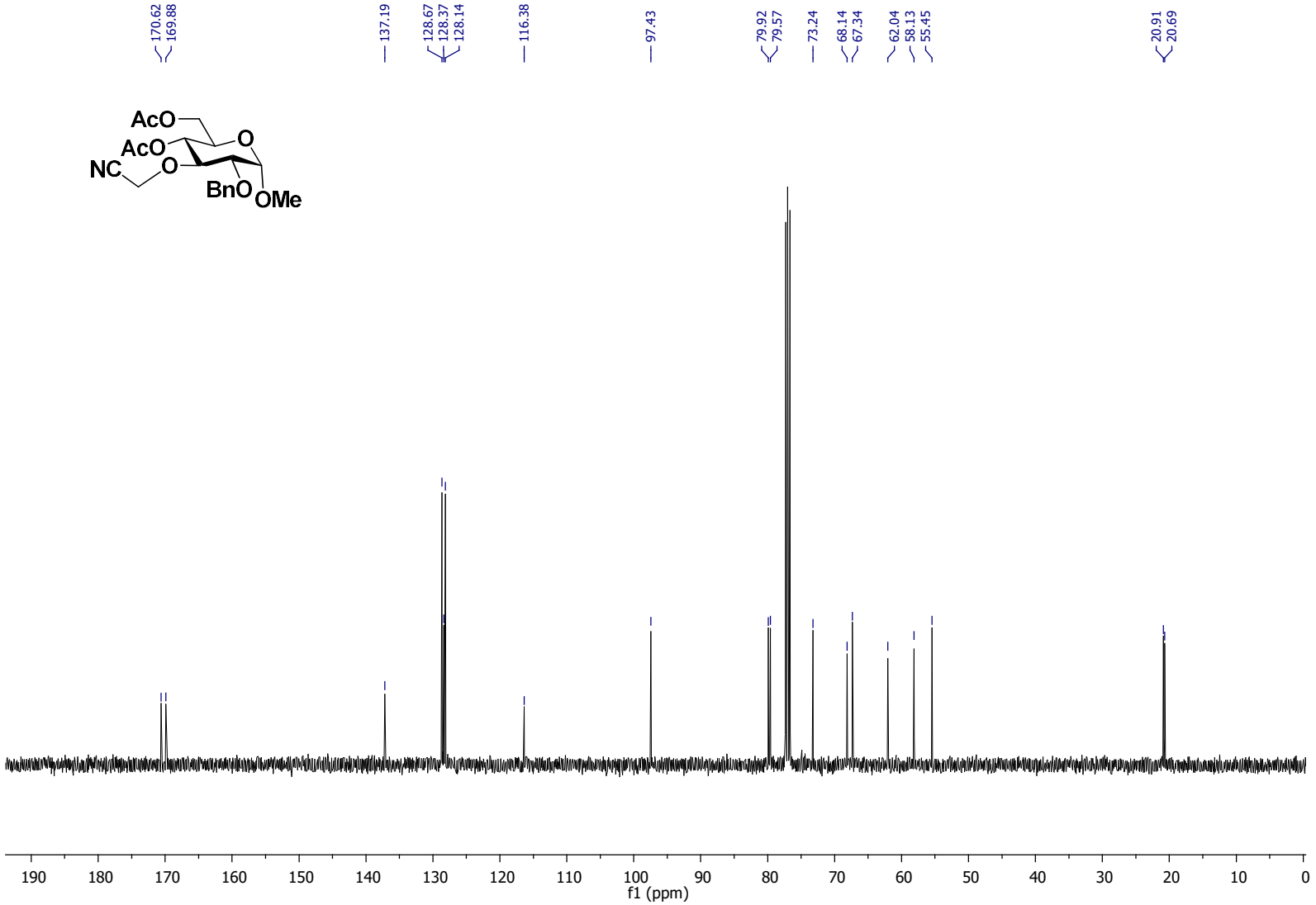
^{13}C NMR (100 MHz, $CDCl_3$) of compound 38



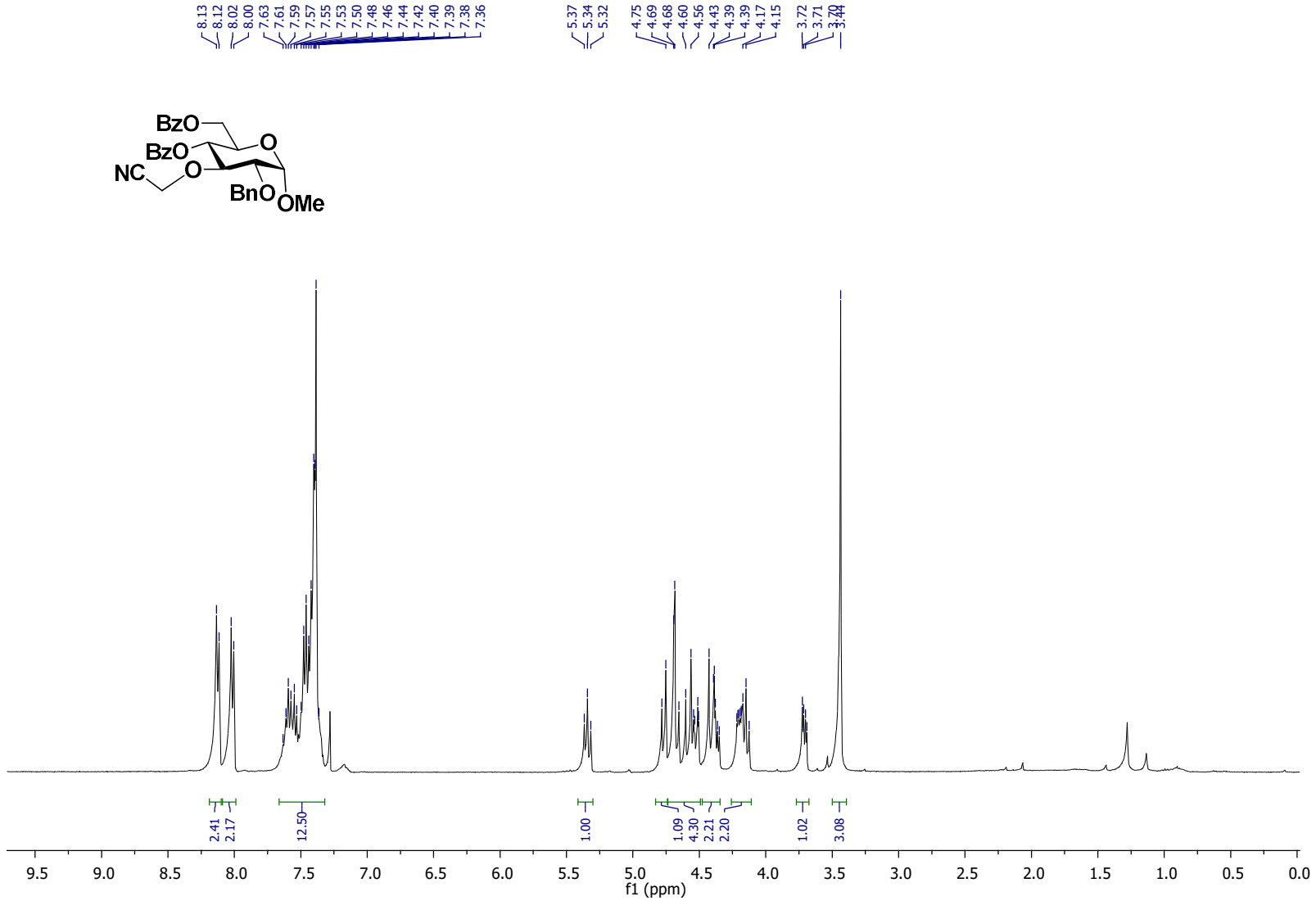
^{1}H NMR (400 MHz, $CDCl_3$) of compound 39



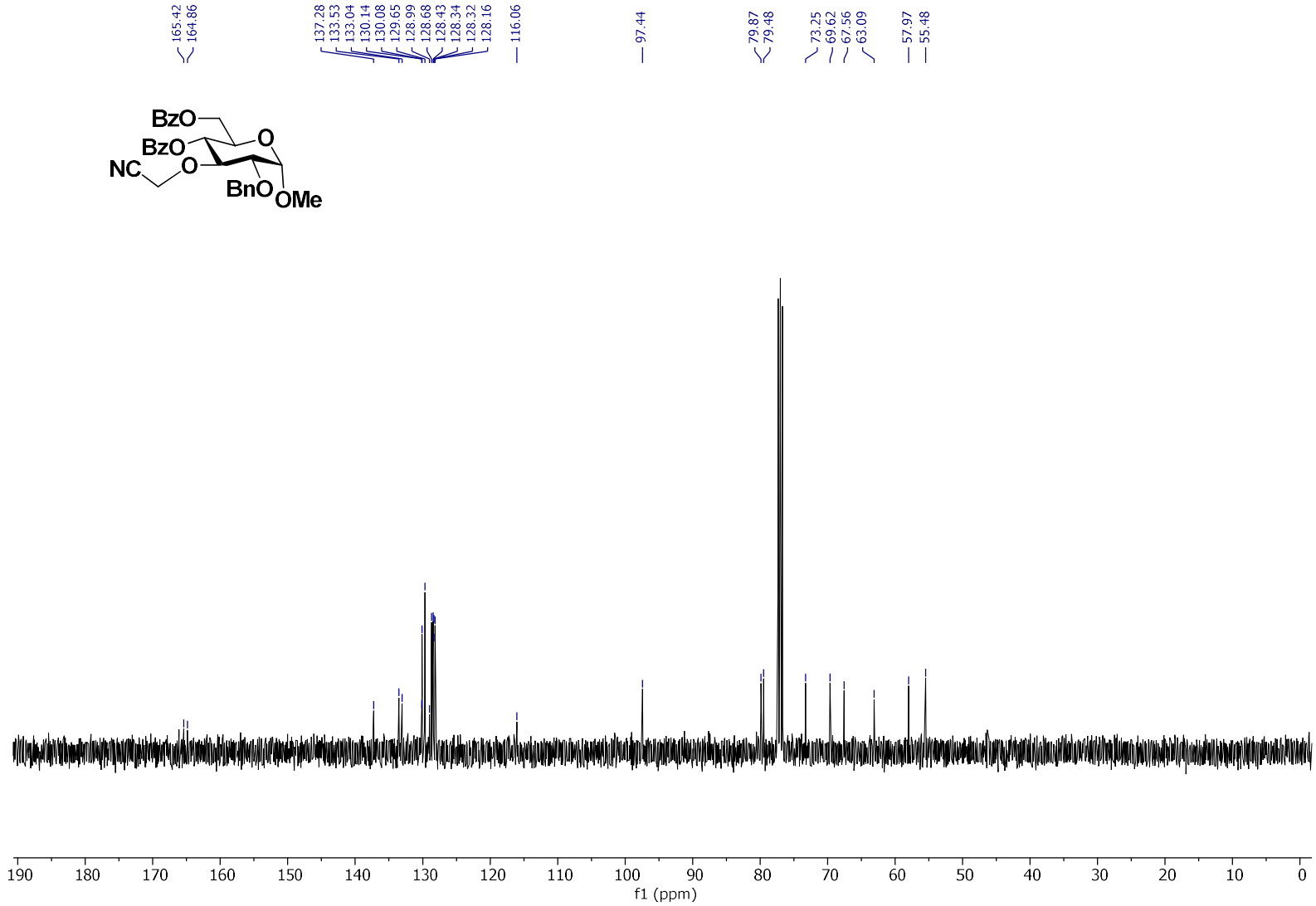
^{13}C NMR (100 MHz, $CDCl_3$) of compound 39



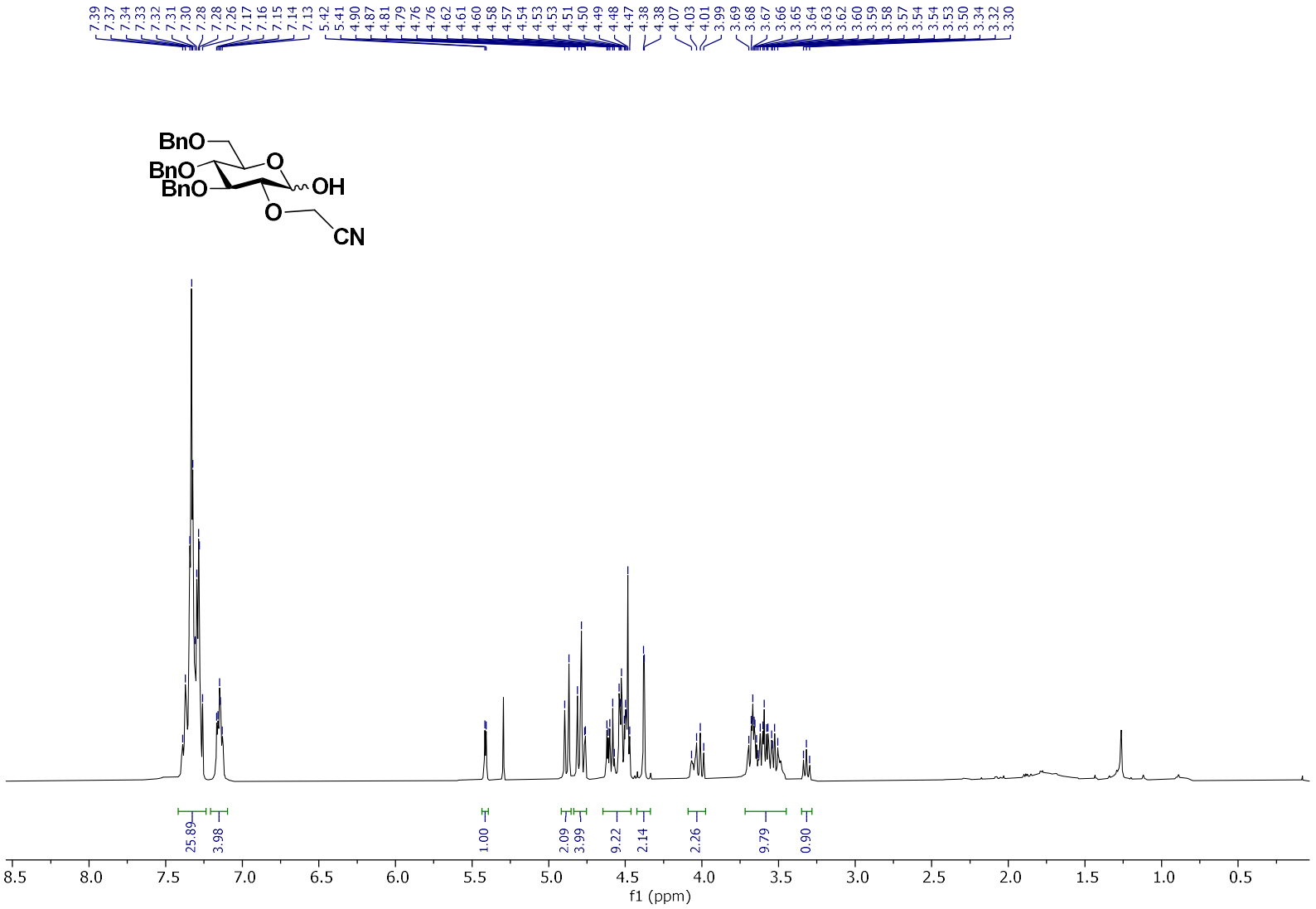
^{1}H NMR (400 MHz, $CDCl_3$) of compound 40



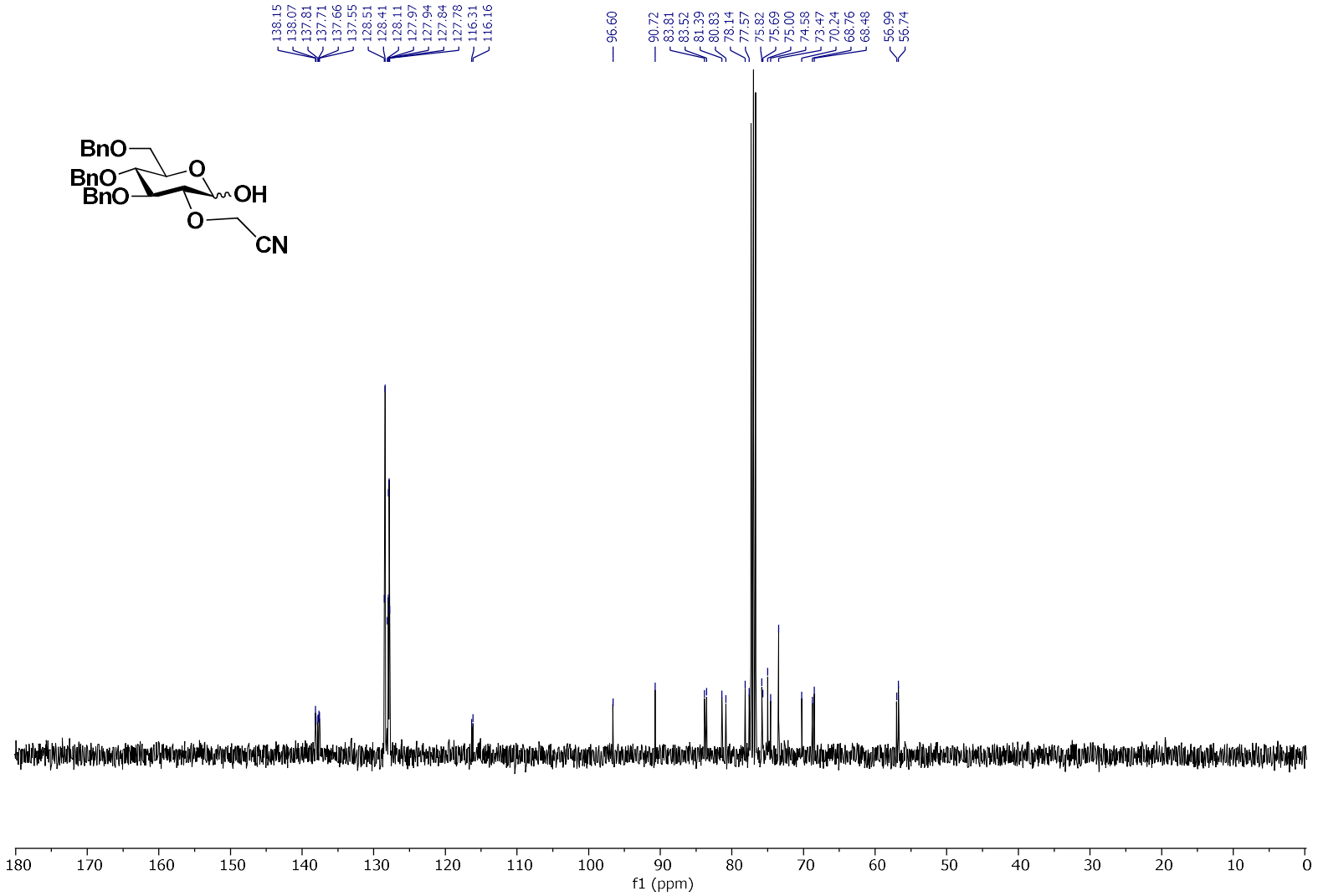
^{13}C NMR (100 MHz, $CDCl_3$) of compound 40



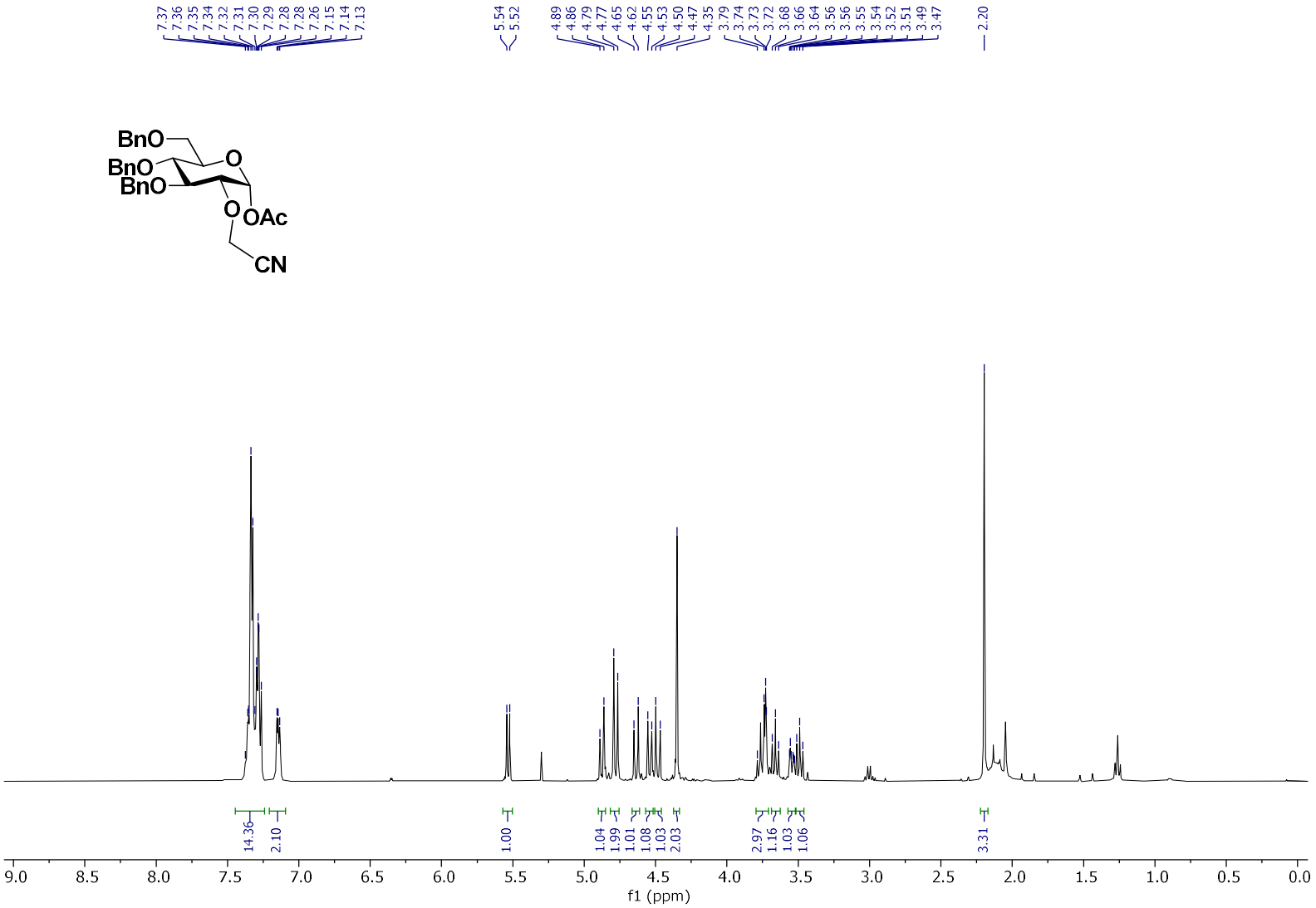
^{1}H NMR (400 MHz, $CDCl_3$) of compound 41



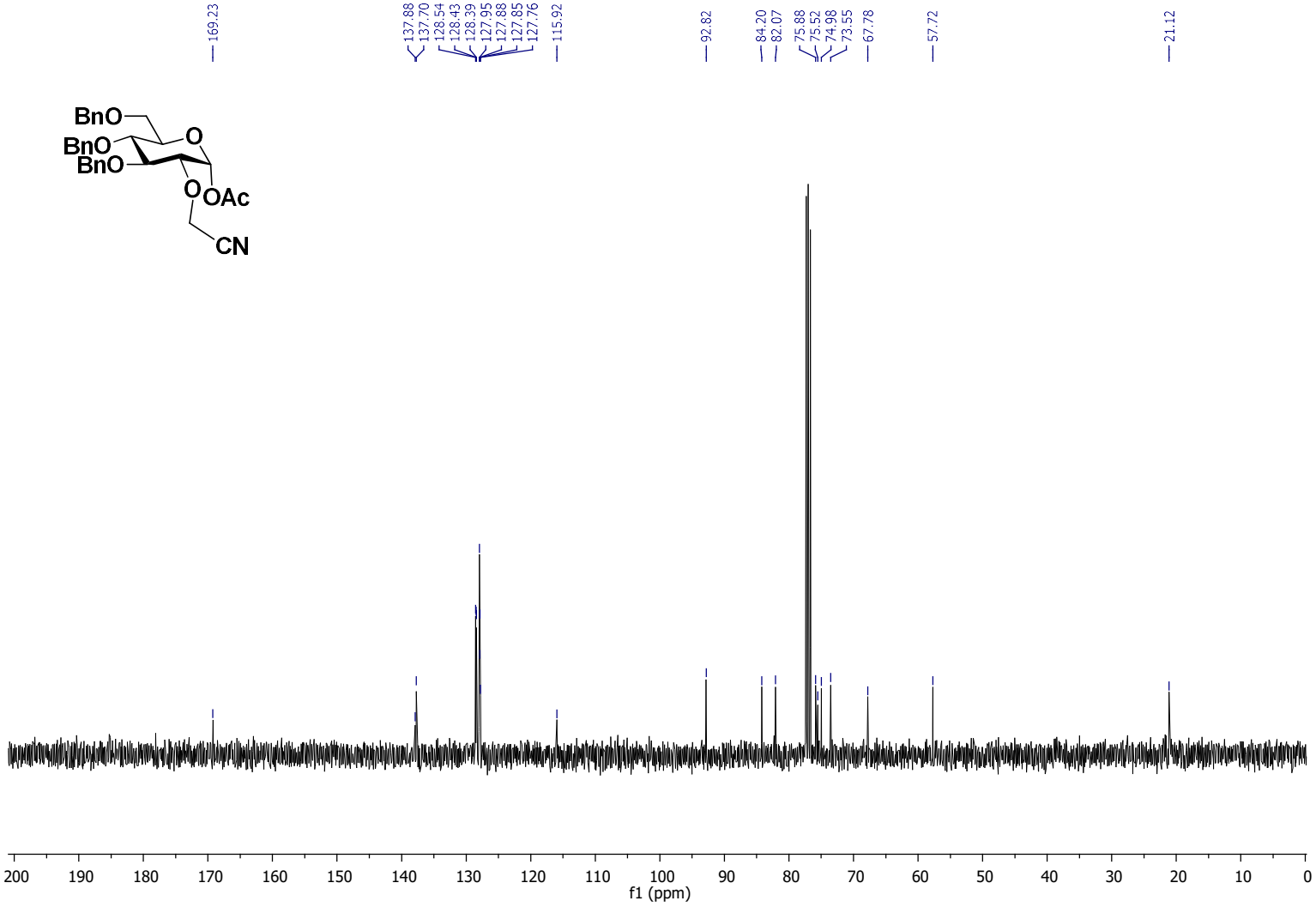
^{13}C NMR (100 MHz, $CDCl_3$) of compound 41



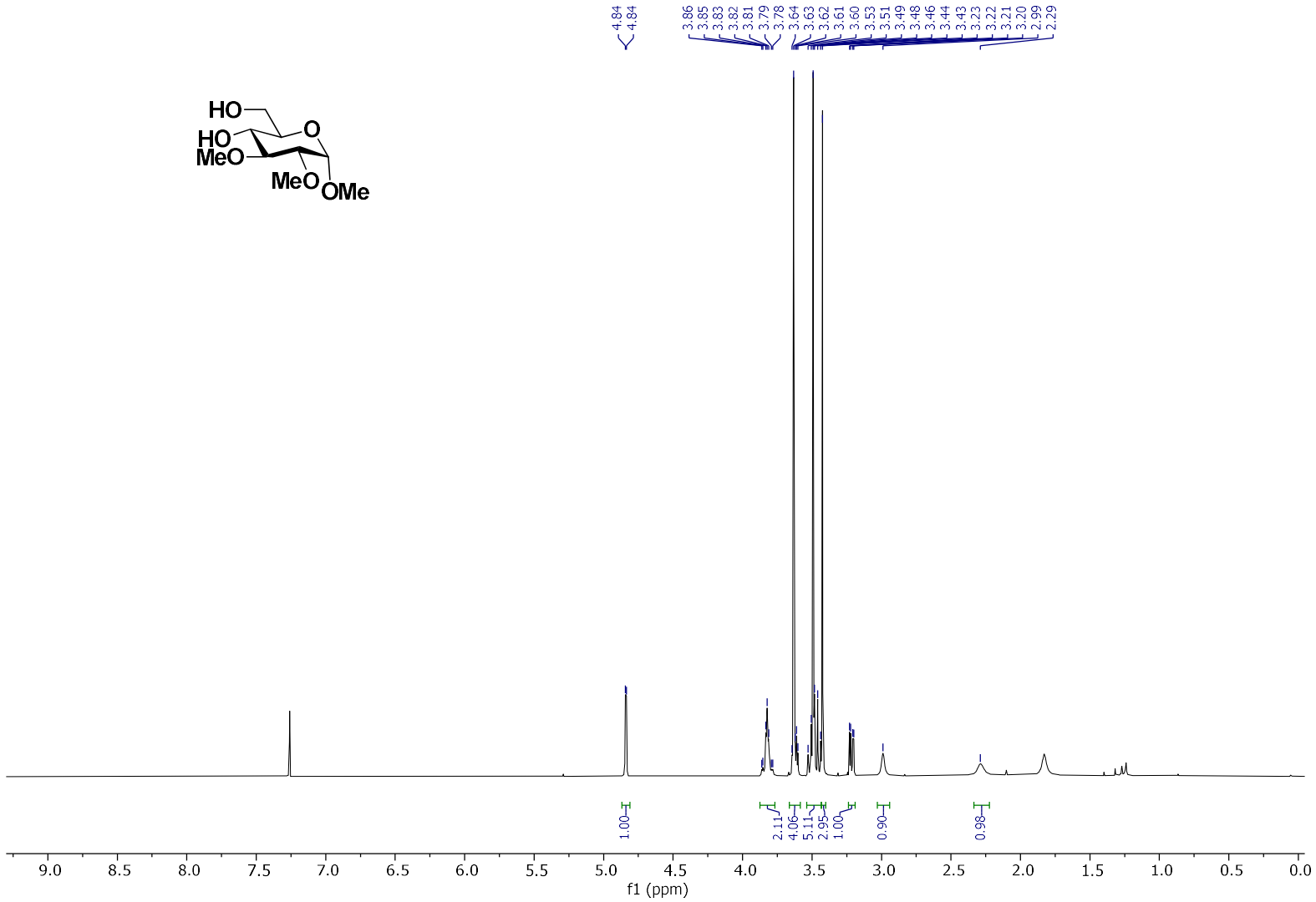
^{1}H NMR (400 MHz, $CDCl_3$) of compound 42



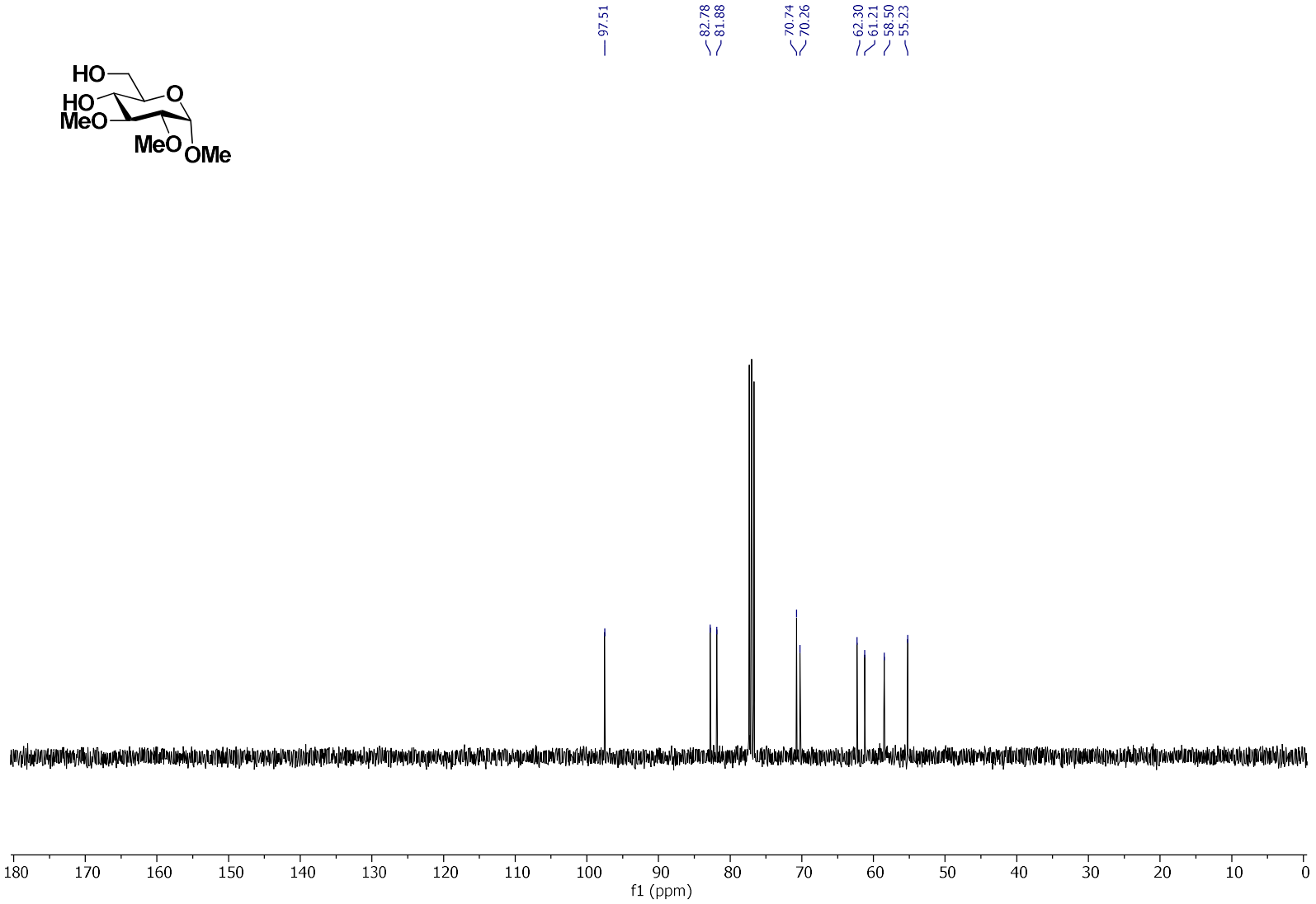
^{13}C NMR (100 MHz, $CDCl_3$) of compound 42



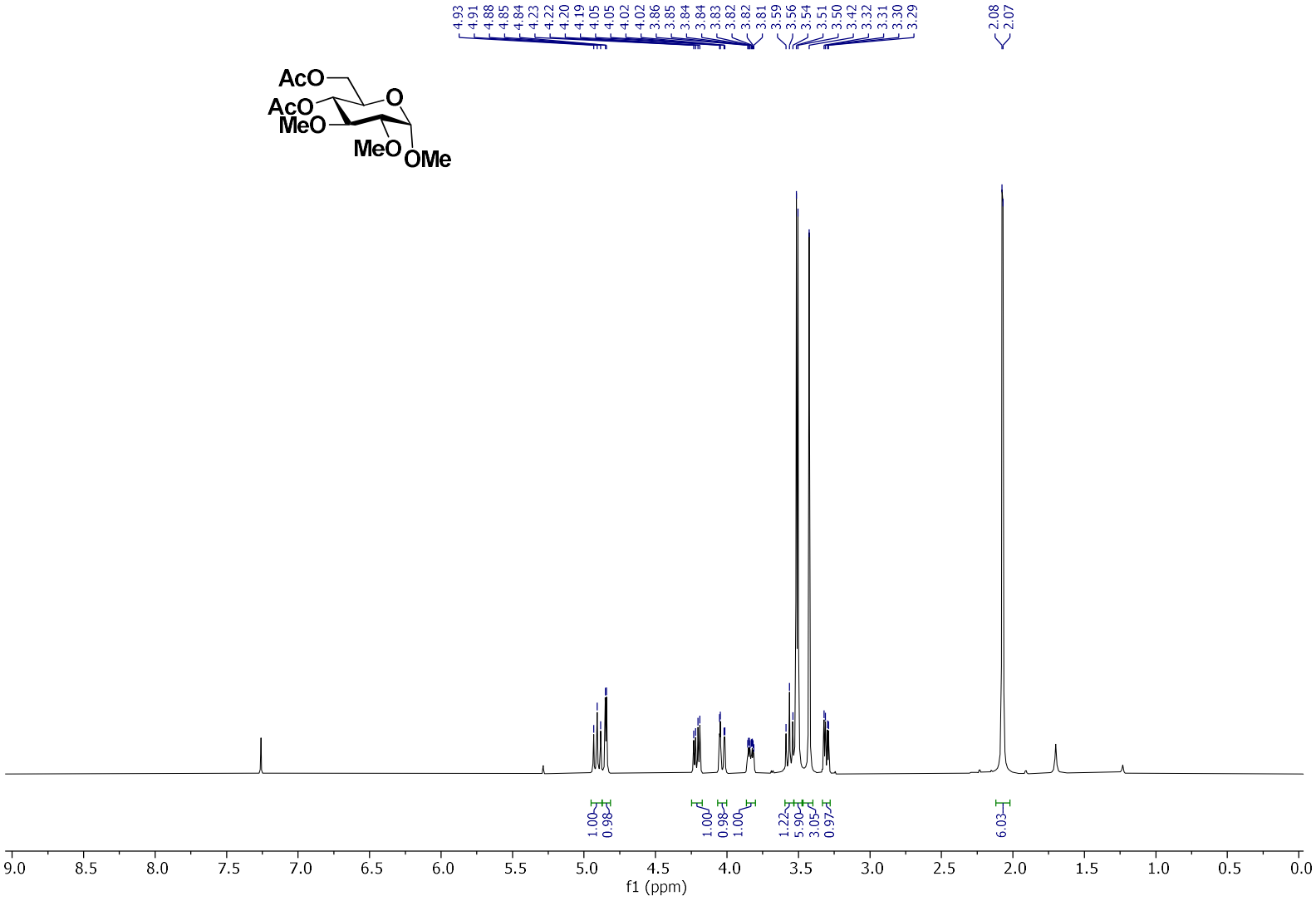
^{1}H NMR (400 MHz, $CDCl_3$) of compound 43



^{13}C NMR (100 MHz, $CDCl_3$) of compound 43



^{1}H NMR (400 MHz, $CDCl_3$) of compound 44



^{13}C NMR (100 MHz, $CDCl_3$) of compound 44