SUPPORTING INFORMATION

A. SYNTHESIS

General procedures

Melting points were recorded on an Electrothermal apparatus and are uncorrected. Optical rotations were measured with a Perkin-Elmer 241 MC and 341 polarimeters, and IR spectra (KBr disks) were obtained with FT-IR Bomem MB-120 and FT-IR JASCO-410 spectrophotometers. ^{1}H (300 and 500 MHz) and ^{13}C (75.5 and 125.8 MHz) NMR spectra were recorded on Bruker Avance-300 and Avance-500 spectrometers. The assignments of ^{1}H and ^{13}C signals were confirmed by homonuclear COSY and heteronuclear 2D correlated spectra, respectively. Mass spectra (LSIMS, EIMS, CI, FAB and LSI) were recorded on Kratos MS80-RFA and Micromass AutoSpec-Q mass spectrometers with a resolution of 1,000 or 10,000 (10% valley definition). For the FAB and LSI spectra, ions were produced by a beam of xenon atoms and Cs^{+} ions, respectively, using thioglycerol as matrix and NaI as additive. TLC was performed on aluminium pre-coated sheets (E. Merck Silica Gel 60 F_{254}); spots were visualized by UV light, by charring with 10% H_2SO_4 in EtOH and by 0.3% ninhydrine in EtOH. Column chromatography was performed using E. Merck Silica Gel 60 (40–63 μm). Microanalyses were performed at the "Servicio de Microanálisis" of University of Seville and of University Complutense of Madrid.

Method for the preparation of (*E*) and (*Z*)-2-chloroacetaldehyde *O*-alkyl oximes 1 and 2

A mixture of 2-chloroacetaldehyde diethylacetal (2.0 mL, 13.3 mmol), the corresponding *N*-alkoxyamine hydrochloride (13.3 mmol) and water (0.5 mL) was

stirred at 40º C for 24h, and then at rt for 48 h. After that, formation of two layers was observed, which were separated. The one with higher density corresponded to pure oximes **1** and **2**, which were obtained in an *E*/*Z* ratio of 7:3, as deduced from ^{1}H-NMR spectra.

(*E*)- and (*Z*)-2-Chloroacetaldehyde *O*-methyl oxime (1)

Yield: 1.16 g, 81%; IR ν_{max} 3442, 2953, 2921, 1634, 1459, 1381, 1032, 872 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *E* isomer: δ 7.33 (t, 1H, $J_{H,H}$ = 6.4 Hz, C*H*CH_2), 4.03 (d, 2H, CHC*H*$_2$), 3.79 (s, 3H, OCH_3); *Z* isomer: δ 6.73 (t, 1H, $J_{H,H}$ = 4.9 Hz, C*H*CH_2), 4.15 (d, 2H, CHC*H*$_2$), 3.83 (s, 3H, CH_3); ^{13}C-NMR (75.5 MHz, $CDCl_3$) *E* isomer: δ 145.1 (=*C*H), 61.9 (OCH_3), 39.9 (CH_2Cl); *Z* isomer: δ 146.3 (=CH), 62.2 (OMe), 35.0 (CH_2Cl). NMR data of **1** are in agreement with reported values in literature.[1]

(*E*)- and (*Z*)-2-Chloroacetaldehyde *O*-benzyl oxime (2)

Yield: 2.06 g, 84%; IR ν_{max} 3426, 3033, 2932, 2876, 1623, 1445, 1367, 1251, 920, 855, 742 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *E* isomer: δ 7.41 (t, 1H, $J_{H,H}$ = 6.4 Hz, C*H*CH_2), 7.32-7.21 (m, 5H, Ar-H), 5.02 (s, 2H, PhC*H*$_2$), 4.02 (d, 2H, CHC*H*$_2$); *Z* isomer: δ 6.78 (t, 1H, $J_{H,H}$ = 4.9 Hz, C*H*CH_2), 7.26 (m, 5H, Ar-H), 5.07 (s, 2H, PhC*H*$_2$), 4.18 (d, 2H, CHC*H*$_2$); ^{13}C-NMR (75.5 MHz, $CDCl_3$) *E* isomer: δ 145.9 (=CH), 137.1 128.7, 128.5, 128.3 (Ar-C), 76.6 (Ph*C*H_2), 40.2 (CH_2Cl); *Z* isomer: δ 147.2 (=CH), 137.3, 128.7, 128.5, 128.3 (Ar-C), 76.8 (Ph*C*H_2), 35.5 (CH_2Cl); HREI-MS *m/z* calcd for $C_9H_{10}NOCl$, (M^+): 183.0451, found: 183.0451.

1 G. B. Jones, C. J. Moody, A. Padwa, and J. M. Kassir, *J. Chem. Soc., Perkin Trans 1*, 1991, 1721-1727.

(*E*)- and (*Z*)-2-Bromoacetaldehyde-*O*-benzyloxime (3)

A mixture of benzyloxyamine hydrochloride (1.03 g, 6.44 mmol), $NaHCO_3$ (596 mg, 7.09 mmol) and water (20 mL) was stirred at room temperature until no CO_2 bubbling was observed. Then, the mixture was extracted with CH_2Cl_2 (2 x 15 mL). The organic layer was washed with water (2 x 10 mL), dried ($MgSO_4$) and concentrated to dryness. To the colourless liquid residue 2 M H_2SO_4 (1.61 mL, 3.22 mmol) and 2-bromoacetaldehyde diethylacetal (1.00 mL, 6.44 mmol) were added and the mixture was stirred at 40º C for 24 h, and at room temperature for 48 h. After that, formation of two layers was observed and separated. The one with higher density corresponded to pure oxime **3**, which was obtained in an *E*/*Z* ratio of 7:3, as deduced from its ^{1}H-NMR spectrum. Yield 1.1 g, 74%; IR ν_{max} 3445, 3031, 2927, 1611, 1496, 1455, 1367, 1208, 855, 736, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) *E* isomer: δ 7.54 (t, 1H, $J_{H,H}$ = 6.8 Hz, C*H*CH_2), 7.35 (m, 5H, Ar-H), 5.10 (s, 2H, PhC*H*$_2$), 3.96 (d, 2H, CHC*H*$_2$); *Z* isomer: δ 7.35 (m, 5H, Ar-H), 6.96 (t, 1H, $J_{H,H}$ = 6.0 Hz, C*H*CH_2), 5.17 (s, 2H, PhC*H*$_2$), 4.04 (d, 2H, CHC*H*$_2$); ^{13}C-NMR (75.5 MHz, $CDCl_3$) *E* isomer: δ 146.0 (=CH), 128.6, 128.4, 128.3, 128.2 (Ar-C), 76.6 (Ph*C*H_2), 26.6 (CH_2Br); *Z* isomer: δ 137.1 (=CH), 128.6, 128.4, 128.3, 128.2 (Ar-C), 76.7 (Ph*C*H_2), 19.8 (CH_2Br); HREI-MS *m/z* calcd for $C_9H_{10}NOBr$, (M^+): 226.9946, found: 226.9957.

General method for the reduction of the 2-haloacetaldehyde *O*-alkyl oximes 1–3

The oxime (10.0 mmol) was dissolved in glacial acetic acid (5.0 mL), $NaBH_3CN$ (1.283 mg, 22.0 mmol) was slowly added, at 0º C, and the mixture was stirred for 2 days at room temperature. After removing acetic acid, co-evaporating with ethanol, the residue

was dissolved in EtOAc and washed with water. The organic layer was dried ($MgSO_4$) and concentrated to dryness, and the colourless syrupy residues were purified by column chromatography (hexane→1:2 EtOAc–hexane).

(±)-2-Chloro-*N*-methoxyethanamine cyanoborane (6)

Reduction of **1** gave **6**. Yield: 430 mg, 29%; mp 61–64 ºC (from EtOAc–hexane); R_F 0.51 (1:1 EtOAc–hexane); IR ν_{max} 3034, 2835, 2462, 2427, 2345, 2211, 1434, 1303, 1116, 1023, 945, 668 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.48 (m, 1H, NH), 3.94 (ddd, 1H, $J_{2a,2b}$ = 11.9 Hz, $J_{1a,2a}$ = 5.1 Hz, $J_{1b,2a}$ = 9.3 Hz, H-2a), 3.87 (s, 3H, Me), 3.76 (ddd, 1H, $J_{2a,2b}$ = 11.9, $J_{1b,2b}$ = 3.9 Hz, $J_{1a,2b}$ = 5.5 Hz, H-2b), 3.60 (dddd, 1H, $J_{1a,1b}$ = 14.3 Hz, $J_{1b,2a}$ = 9.3 Hz, $J_{1b,2b}$ = 3.9 Hz, $J_{1b,NH}$ = 9.0 Hz, H-1b), 3.44 (dddd, 1H, $J_{1a,2a}$ = 5.1 Hz, $J_{1a,2b}$ = 5.5 Hz, $J_{1a,1b}$ = 14.3 Hz, $J_{1a,NH}$ = 3.2 Hz, H1a), 1.85 (m, 2H, BH_2CN); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 60.3 (OCH_3), 57.0 (NCH_2), 38.3 (CH_2Cl); ^{11}B-NMR (96 MHz, DMSO-d_6) δ –21.0 (br t, $J_{B,H}$ = 95 Hz, BH_2CN); HRLSI-MS *m/z* calcd for $C_4H_{11}{}^{11}BN_2OCl$, $[M + H]^+$: 149.0653, found: 149.0645.

***N*-Benzyloxy-2-chloroethanamine (4), (±)-*N*-benzyloxy-2-chloroethanamine-cyanoborane (7), and (*E*)-*N*-benzyloxy-(2-chloroethyl)formamidine-cyanoborane (9)**

Reduction of **2** gave a mixture of **4**, **7** and **9**, purified by column chromatography. Eluted first was **4**. Yield: 260 mg, 14%; R_F = 0.73 (1:2 EtOAc–hexane); IR ν_{max} 3446, 3269, 3031, 2958, 2919, 1634, 1495, 1364, 1006, 742, 698 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.34 (m, 5H, Ar-H), 5.39 (br s, 1H, NH), 4.73 (s, 2H, PhCH_2), 3.72 (t, 2H, $J_{H,H}$ = 5.7 Hz, CH_2Cl), 3.20 (t, 2H, NCH_2); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 137.8,

128.5, 128.0 (Ar-C), 76.3 (Ph*C*H_2), 53.4 (NCH_2), 42.1 (CH_2Cl); HRLSI-MS *m/z* calcd for $C_9H_{12}ClNNaO$, $[M + Na]^+$: 208.0505, found: 208.0511.

Eluted second was **7**. Yield: 1.057 g, 47%; mp 102–104 ºC (from EtOAc–hexane); R_F 0.31 (1:2 EtOAc–hexane); IR ν_{max} 3044, 2902, 2435, 2205, 1477, 1302, 1124, 1092, 987, 941, 746, 696 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43 (m, 5H, Ar-H), 7.01 (m, 1H, NH), 5.14 and 5.09 (2d, 1H each, $J_{Ha,Hb}$ = 11.3 Hz, PhC*H*$_2$), 3.86 (m, 1H, H2a), 3.68 (m, 2H, H2b, H1a), 3.43 (m, H1b), 1.85 (m, 2H, BH_2CN); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 132.0, 130.2, 130.0, 129.5 (Ar-C), 74.1 (Ph*C*H_2), 57.8 (NCH_2), 38.5 (CH_2Cl); HRLSI-MS *m/z* calcd for $C_{10}H_{14}{}^{11}BN_2ONaCl$, $[M + Na]^+$: 247.0785, found: 247.0777.

Eluted third was **9**. Yield: 201 mg, 8%; R_F = 0.22 (1:1 EtOAc–hexane); IR ν_{max} 3359, 3237, 2384, 1672, 1455, 1339, 1008, 746, 699 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.49 (d, 1H, $J_{H,NH}$= 16.2 Hz, C*H*NH), 7.40 (m, 5H, Ar-H), 6.66 (br d, 1H, NH), 4.92 (s, 2H, PhC*H*$_2$), 3.70 (s, 4H, NCH_2, CH_2Cl), 2.00 (m, 2H, BH_2CN); ^{1}H-NMR (300 MHz, DMSO-d_6) δ 8.38 (br d, 1H, NH), 7.81 (d, 1H, $J_{H,NH}$ = 15.7 Hz, CH=N), 7.47 (m, 5H, Ar-H), 4.94 (s, 2H, $PhCH_2$), 3.97 (t, 2H, $J_{H,H}$ = 5.1 Hz, CH_2), 3.82 (t, 2H, CH_2), 1.80 (m, 2H, BH_2CN); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 155.4 (CH=N), 133.0, 130.3, 129.7, 129.5 (Ar-C), 77.4 (Ph*C*H_2), 54.4 (NCH_2), 39.8 (CH_2Cl); ^{11}B-NMR (96 MHz, $CDCl_3$) δ –22.7 (br t, $J_{B,H}$= 112.9 Hz, BH_2CN); HRCI-MS *m/z* calcd for $C_{11}H_{16}{}^{11}BClN_3O$, $[M + H]^+$: 252.1075, found: 252.1076.

_N_-Benzyloxy-2-bromoethanamine (5), (±)-_N_-benzyloxy-2-bromoethanamine-cyanoborane (8), and (_E_)-_N_-benzyloxy-(2-bromoethyl)formamidine-cyanoborane (10)

Reduction of **3** gave a mixture of **5**, **8** and **10**, purified by column chromatography. Eluted first was **5**. Yield: 345 mg, 15%; R_F = 0.67 (1:2 EtOAc–hexane); IR ν_{max} 3452, 3033, 2953, 2921, 2859, 1668, 1641, 1451, 1366, 742, 699 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.35 (m, 5H, Ar-H), 5.63 (br s, 1H, NH), 4.77 (s, 2H, PhCH_2), 3.59 (t, 2H, $J_{H,H}$ = 5.9 Hz, CH_2Br), 3.25 (t, 2H, NCH_2); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 137.7, 128.6, 128.5 (Ar-C), 76.4 (PhCH_2), 53.3 (NCH_2), 31.1 (CH_2Br). HRLSI-MS *m/z* calcd for $C_9H_{12}BrNNaO$, $[M + Na]^+$: 252.0000, found: 251.9996.

Eluted second was **8**. Yield: 1.668 g, 62%; mp 95-98 ºC (from EtOAc–hexane); R_F = 0.38 (1:2 EtOAc–hexane); IR ν_{max} 3425, 3041, 2899, 2830, 2439, 2312, 2203, 1474, 1422, 1278, 1121, 1090, 1005, 984, 931, 746, 696 cm^{-1}; ^{1}H-NMR (500 MHz, $CDCl_3$) δ 7.44 (m, 5H, Ar-H), 6.90 (m, 1H, NH), 5.13, 5.10 (2d, 1H each, $J_{H,H}$ = 11.3 Hz, PhCH_2), 3.74 (ddt, 1H, $J_{1a,1b}$ = 14.0 Hz, $J_{1a,NH}$ = 8.9 Hz, $J_{1a,2a}$ = 4.1 Hz, $J_{1a,2b}$ = 4.2 Hz, H1a), 3.67 (ddd, 1H, $J_{2a,2b}$ = 11.0 Hz, $J_{1b,2a}$ = 9.5 Hz, $J_{1a,2a}$ = 4.1 Hz, H2a), 3.54 (dt, 1H, $J_{2a,2b}$ = 11.0 Hz, $J_{1b,2b}$ = 4.3 Hz, $J_{1a,2b}$ = 4.2 Hz, H2b), 3.49 (dddd, 1H, $J_{1a,1b}$ = 14.0 Hz, $J_{1b,2a}$ = 9.5 Hz, $J_{1b,2b}$ = 4.3 Hz, $J_{1b,NH}$ = 2.9 Hz, H1b), 1.85 (br t, 2H, $J_{B,H}$ = 129 Hz, BH_2CN); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 132.0, 130.3, 130.1, 129.6 (Ar-C), 74.2 (PhCH_2), 57.8 (NCH_2), 26.6 (CH_2Br); HRLSI-MS *m/z* calcd for $C_{10}H_{14}{}^{11}BN_2ONaBr$, $[M + Na]^+$: 291.0280, found: 291.0281; Anal. calcd for $C_{10}H_{14}BN_2OBr$: C, 44.66; H, 5.25; N: 10.42; found: C, 44.49; H: 5.09; N: 10.52.

Eluted third was **10**. Yield: 177 mg, 6%; R_F = 0.73 (40:1 EtOAc–hexane); IR ν_{max} 3444, 2953, 2384, 1671, 1455, 1339, 1266, 1115, 144, 699 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.51 (d, 1H, $J_{H,NH}$ = 15.9 Hz, CH=N), 7.39 (m, 5H, Ar-H), 6.70 (br d, 1H, NH), 4.91 (s, 2H, PhC*H*$_2$), 3.79 (t, 2H, $J_{H,H}$ = 5.6 Hz, NCH_2), 3.53 (t, 2H, CH_2Br), 2.10 (m, 2H, BH_2CN); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 155.1 (CH=N), 133.0, 130.2, 129.7, 129.3 (Ar-C), 77.2 (Ph*C*H$_2$), 54.0 (NCH_2), 27.3 (CH_2Br); HRLSI-MS *m/z* calcd for $C_{11}H_{15}{}^{11}BBrN_3NaO$, $[M + Na]^+$: 318.0389, found: 318.0382.

2-Azido-*N*-benzyloxyethanamine (11) and (±) 2-azido-*N*-benzyloxyethanamine-cyanoborane (12)

A suspension of **7** (250 mg, 1.11 mmol) and NaN_3 (87 mg, 1.34 mmol) in DMF (3.0 mL) was stirred at rt overnight. Then, the solvent was removed under reduced pressure and the residue was purified by column chromatography (hexane→ 1:2 EtOAc–hexane) to give **11** and **12**. Eluted first was **11**. Yield: 48 mg, 22%; R_F = 0.63 (1:2 EtOAc–hexane); IR ν_{max} 2918, 2859, 2103, 1451, 1286, 1014, 742, 694 cm^{-1}; ^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.37–7.27 (m, 5H, Ar-H), 5.73 (br s, 1H, NH), 4.72 (s, 2H, PhC*H*$_2$), 3.47 (t, 2H, $J_{H,H}$ = 5.6 Hz, CH_2N_3), 3.06 (br t, 2H, NCH_2); ^{13}C-RMN (75.5 MHz, $CDCl_3$) δ 137.8, 128.6, 128.1 (Ar-C), 76.5 (Ph*C*H$_2$), 51.1 (NCH_2), 48.9 (CH_2N_3); HRLSI-MS *m/z* calcd for $C_9H_{12}N_4NaO$, $[M + Na]^+$: 215.0909, found: 215.0916.

Eluted second was **12**. Yield: 137 mg, 53%; R_F = 0.34 (1:2 EtOAc–hexane); IR ν_{max} 3385, 3038, 2965, 2895, 2437, 2105, 1450, 1266, 1104, 997, 750, 703 cm^{-1}; ^{1}H-RMN (300 MHz, $CDCl_3$) δ 7.51–739 (m, 5H, Ar-H), 6.87 (br s, 1H, NH), 5.10, 5.07 (2d, 1H each, $J_{H,H}$ = 11.7 Hz, PhC*H*$_2$), 3.75 (ddd, 1H, $J_{2a,2b}$ = 13.8 Hz, $J_{2a,1b}$ = 10.1 Hz, $J_{2a,1a}$ =

4.0 Hz, H-2a), 3.57 (dt, 1H, $J_{2a,2b}$ = 13.8 Hz, $J_{2b,1a}$ = $J_{2b,1b}$ = 4.0 Hz, H-2b), 3.42 (ddt, 1H, $J_{1a,1b}$ = 14.0 Hz, $J_{2b,NH}$ = 8.0 Hz, $J_{1a,2a}$ = 4.0 Hz, $J_{1a,2b}$ = 4.0 Hz, H-1a), 3.21 (m, 1H, $J_{1b,NH}$ = 3.9 Hz, H-1b); ^{13}C-RMN (75.5 MHz, $CDCl_3$) δ 132.2, 130.3, 129.9, 129.5 (Ar-C), 73.9 (Ph*C*H_2), 55.3 (NCH_2), 45.8 (CH_2N_3); HRLSI-MS *m/z* calcd for $C_{10}H_{14}{}^{11}BN_5NaO$, $[M + Na]^+$: 254.1189, found: 254.1184.

Benzylamine-cyanoborane (18)

A solution of **7** or **8** (0.37 mmol) and benzylamine (0.37 mmol) in THF (2.0 mL) was kept at rt for 24 h. Then, the solvent was reduced under reduced pressure and the residue was purified by column chromatography (hexane → 1:3 EtOAc–hexane) to give **18**. Yield: 34 mg, 63% (from **7**); 50 mg, 93% (from **8**); IR ν_{max} 3216, 3131, 3036, 2959, 2413, 2309, 2189, 1603, 1456, 1372, 1296, 1204, 1131, 965, 742, 695 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.41–7.35 (m, 5H, Ar-H), 6.16 (s, 2H, NH_2), 3.81 (m, 2H, PhC*H*$_2$), 1.60 (m, 2H, BH_2CN); ^{13}C-NMR (75.5 MHz, D_2O) δ 137.3, 129.8, 129.7, 129.3 (Ar-C), 51.5 (Ph*C*H_2); HREI-MS *m/z* calcd for $C_8H_{12}{}^{11}BN_2$, $[M + H]^+$: 147.1094, found: 147.1102.

1,3,4,6-Tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose-cyanoborane (19)

To a 1:1 mixture of CH_2Cl_2–sat. aq. $NaHCO_3$ (40 mL) was added 1,3,4,6,-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-glucopyranose hydrochloride (150 mg, 0.39 mmol), and the corresponding mixture was vigorously stirred for 30 min. Then, the organic layer was separated, washed with water up to neutral pH, dried over $MgSO_4$, filtered and concentrated to dryness. The residue was dissolved in anhydrous THF (5.0 mL), and to the corresponding solution was added **7** (88 mg, 0.39 mmol); the corresponding mixture

was kept stirring at rt for 24 h. Then, the solvent was removed under reduced pressure, and the residue was purified by column chromatography (hexane → 1:2 EtOAc–hexane) to give **19**. Yield: 86 mg, 57%; mp: 164-166 ºC; R_F = 0.43 (1:2 EtOAc–Hexane); IR ν_{max} 3447, 3221, 3107, 2942, 2431, 1750, 1600, 1434, 1372, 1218, 1047, 903 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 5.88 (d, 1H, $J_{1,2}$ = 8.6 Hz, H-1), 5.43 (dd, 1H, $J_{2,3}$ = 10.2 Hz, $J_{3,4}$ = 9.1 Hz, H-3), 5.33, 5.18 (2m, 2H, NH_2), 5.04 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 4.31 (dd, 1H, $J_{5,6a}$ = 4.3 Hz, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.10 (dd, 1H, $J_{5,6b}$ = 2.0 Hz, H-6b), 3.90 (ddd, 1H, H-5), 3.24 (m, 1H, H-2), (2.21, 2.11, 2.07, 2.03 (4s, 3H each, 4OAc), 1.75 (m, 2H, BH_2CN); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 171.2, 170.7, 169.7, 169.2 (4 *C*OCH_3), 90.4 (C-1), 72.7 (C-5), 70.9 (C-3), 68.2 (C-4), 61.4 (C-6), 57.6 (C-2), 21.1, 21.0, 20.8, 20.7 (4 CO*C*H_3); HRLSI-MS *m/z* calcd for $C_{15}H_{23}{}^{11}BN_2NaO_9$, $[M + Na]^+$: 409.1394, found: 409.1396; Anal. calcd for $C_{15}H_{23}BN_2O_9$: C, 46.65; H: 6.00; N: 7.25; found: C, 47.06; H: 5.91; H: 7.04.

_N_-Benzyloxy-2-chloro-_N_-(β-D-glucopyranosyl)ethanamine (20)

A mixture of **7** (1.1 mmol) and D-glucose (1.1 mmol) in methanol (4.0 mL) and acetic acid (60 µL, 1.1 mmol) was refluxed for 3.5 h. Then, the solvent was removed under reduced pressure and corresponding *N*-glycosides were purified by column chromathography (EtOAc → 20:1 EtOAc:MeOH) to give **20**. Yield: 363 mg, 94%; $[\alpha]_D^{20}$ −1 (*c* 1.0, MeOH); R_F = 0.52 (10:1 EtOAc–MeOH); IR ν_{max} 3389, 2942, 2835, 1641, 1451, 1362, 1079, 1028, 748, 701 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 7.36 (m, 5H, Ar-H), 4.87, 4.82 (2d, 1H each, $J_{Ha,Hb}$ = 10.5 Hz, PhCH_2), 4.16 (d, 1H, $J_{1,2}$ = 9.0 Hz, H-1), 3.83 (dd, 1H, $J_{5,6a}$ = 2,3 Hz, $J_{6a,6b}$ = 12.1 Hz, H-6a), 3.70 (t, 2H, $J_{H,H}$ = 6.9 Hz, CH_2Cl), 3.66 (dd, 1H, $J_{5,6b}$ = 5,3 Hz, H6b), 3.51 (t, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 3.40 (t, 1H,

$J_{3,4}$ = 8.8 Hz, H-3), 3.37 (m, 1H, NCHa), 3.30 (t, 1H, $J_{4,5}$ = 8.8 Hz, H-4), 3.28 (m, 1H, NCHb), 3.24 (ddd, 1H, H-5); ^{13}C-NMR (125.7 MHz, CD_3OD) δ 136.4, 128.9, 128.0, 127.9 (Ar-C), 93.6 (C-1), 79.2 (C-5), 77.9 (C-3), 76.7 (Ph*C*H_2), 70.2 (C-2), 69.7 (C-4), 61.2 (C-6), 54.6 (NCH_2), 40.9 (CH_2Cl); HRLSI-MS *m/z* calcd for $C_{15}H_{22}NO_6NaCl$, $[M + Na]^+$: 370.1033, found: 370.1039.

_N_-benzyloxy-2-bromo-_N_-(β-D-glucopyranosyl)ethanamine (21)

A mixture of **8** (1.1 mmol) and D-glucose (1.1 mmol) in methanol (4.0 mL) and acetic acid (60 μL, 1.1 mmol) was refluxed for 3.5 h. Then, the solvent was removed under reduced pressure and the residue was purified by column chromathography (EtOAc → 20:1 EtOAc–MeOH) to give **21**: 239 mg, 55%; $[\alpha]_D^{20}$ –4 (*c* 1.1, MeOH); R_F = 0.31 (10:1 EtOAc–MeOH); IR ν_{max} 3387, 2925, 2888, 1572, 1454, 1368, 1080, 1026, 916, 748, 701, 634 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 7.38 (m, 5H, Ar-H), 4.90, 4.85 (2d, 1H each, $J_{Ha,Hb}$= 11.3 Hz, PhC*H*$_2$), 4.20 (d, 1H, $J_{1,2}$ = 9.0 Hz, H-1), 3.86 (dd, 1H, $J_{5,6a}$ = 2.0 Hz, $J_{6a,6b}$ = 12.2 Hz, H-6a), 3.69 (dd, 1H, $J_{5,6b}$ = 5.3 Hz, H-6b), 3.57 (t, 2H, $J_{H,H}$ = 6.8 Hz, CH_2Br), 3.53 (t, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 3.44 (m, 1H, NCHa), 3.43 (t, 1H, $J_{3,4}$ = 8.5 Hz, H-3), 3.36 (m, 1H, NCHb), 3.33 (t, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 3.27 (ddd, 1H, H-5); ^{13}C-NMR (125.7 MHz, CD_3OD) δ 137.9, 130.4, 129.5, 129.4 (Ar-C), 95.0 (C-1), 79.8 (C-5), 79.3 (C-3), 78.2 (Ph*C*H_2), 71.7 (C-2), 71.2 (C-4), 62.8 (C-6), 56.2 (NCH_2), 30.3 (CH_2Br); HRLSI-MS *m/z* calcd for $C_{15}H_{22}BrNNaO_6$, $[M + Na]^+$: 414.0528, found: 414.0539.

2-Azido-*N*-benzyloxy-*N*-(β-D-glucopyranosyl)ethanamine (22)

A mixture of **12** (1.1 mmol) and D-glucose (1.1 mmol) in methanol (4.0 mL) and acetic acid (60 μL, 1.1 mmol) was refluxed for 3.5 h. Then, the solvent was removed under reduced pressure and the residue was purified by column chromathography (EtOAc → 20:1 EtOAc:MeOH) to give **22**: 256 mg, 65%. $[\alpha]_D^{20}$ 0 (*c* 0.4, MeOH); R_F = 0.31 (10:1 EtOAc–MeOH); IR ν_{max} 3382, 2924, 2101, 1569, 1446, 1373, 1273, 1077, 1020, 910, 745, 698 cm^{-1}; ^{1}H-RMN (500 MHz, CD_3OD) δ 7.42–7.30 (m, 5H, Ar-H), 4.88, 4.82 (2d, 1H each, $J_{H,H}$ = 10.6 Hz, PhCH_2), 4.16 (d, 1H, $J_{1,2}$ = 9.0 Hz, H-1), 3.83 (dd, 1H, $J_{6a,6b}$ = 12.2 Hz, $J_{5,6a}$ = 2.2 Hz, H-6a), 3.66 (dd, 1H, $J_{5,6b}$ = 5.3 Hz, H-6b), 3.53 (t, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 3.48 (m, 2H, $J_{H,H}$ = 6.2 Hz, CH_2N_3), 3.40 (t, 1H, $J_{3,4}$ = 8.9, H-3), 3.32 (m, 1H, H-4), 3.27 (m, 1H, NCHa), 3.26 (m, 1H, H-5), 3.15 (m, 1H, NCHb); ^{13}C-RMN (125.7 MHz, CD_3OD) δ 137.9, 130.4, 129.5, 129.4 (Ar-C), 95.0 (C-1), 79.8 (C-5), 79.5 (C-3), 78.1 (PhCH_2) 71.7 (C-2), 71.2 (C-4), 62.7 (C-6), 53.0 (NCH_2), 50.2 (CH_2N_3); HRCI-MS *m/z* calcd for $C_{15}H_{23}N_4O_6$, $[M + H]^+$: 355.1618, found: 355.1592.

2-Chloro-*N*-benzyloxy-*N*-(β-D-xylopyranosyl)ethanamine (23)

A mixture of **7** (200 mg, 0.89 mmol) and D-xylose (134 mg, 0.89 mmol) in methanol (4.0 mL) and acetic acid (100 μL, 1.75 mmol) was refluxed for 6.0 h. Then, the solvent was removed under reduced pressure and the residue was purified by column chromathography (EtOAc) to give **23**: 198 mg, 70%; $[\alpha]_D^{23}$ +30 (*c* 1.0, MeOH); R_F 0.27 (EtOAc); ^{1}H-RMN (500 MHz, CD_3OD) δ 7.35 (m, 5H, Ar-H), 4.84, 4.79 (2d, 1H each, $J_{H,H}$= 10.7 Hz, PhCH_2), 4.09 (d, 1H, $J_{1,2}$ = 9.0 Hz, H-1), 3.86 (dd, 1H, $J_{4,5a}$ = 5.4 Hz, $J_{5a,5b}$ = 11.2 Hz, H-5a), 3.64 (m, 2H, CH_2Cl), 3.49 (t, 1H, $J_{2,3}$ = 9.0 Hz, H-2), 3.47

(m, 1H, H-4), 3.35 (t, 1H, $J_{3,4}$ = 9.1 Hz, H-3), 3.28, 3.19 (2m, 1H each, CH_2N), 3.17 (m, 1H, H-5b); ^{13}C-RMN (125 MHz, CD_3OD) δ 138.3, 130.3, 129.5, 129.4 (Ar-C), 96.1 (C-1), 79.5 (C-3), 78.1 (Ph*C*H_2), 71.8 (C-2), 71.1 (C-4), 69.0 (C-5), 56.0 (CH_2Cl), 42.5 (CH_2N); HRLSI-MS m/z calcd for $C_{14}H_{20}ClNNaO_5$, $[M + Na]^+$: 340.0928, found: 340.0937.

2-Chloro-*N*-benzyloxy-*N*-(β-D-galactopyranosyl)ethanamine (24) and 2-chloro-*N*-benzyloxy-*N*-(β-D-galactofuranosyl)ethanamine (25)

A mixture of **7** (143 mg, 0.64 mmol) and D-galactose (115 mg, 0.64 mmol) in methanol (5.0 mL) and acetic acid (50 µL, 0.88 mmol) was refluxed for 9.0 h. Then, the solvent was removed under reduced pressure and the residue was purified by column chromathography (EtOAc→20:1 EtOAc–MeOH).

Eluted first was **25**: 19 mg, 9%; R_F 0.23 (20:1 EtOAc–MeOH); $[\alpha]_D^{20}$ +60 (*c* 0.9, MeOH); ^{1}H-NMR (500 MHz, CD_3OD) δ 7.42–7.31 (m, 5H, Ar-H), 4.87, 4.83 (2d, 1H each, $J_{H,H}$= 10.5 Hz, PhC*H*$_2$), 4.57 (d, 1H, $J_{1,2}$= 5.9 Hz, H-1), 4.28 (dd, 1H, $J_{2,3}$= 7.0 Hz, H-2), 4.13 (dd, 1H, $J_{3,4}$=8.1 Hz, H-3), 3.89 (dd, 1H, $J_{4,5}$= 2.1 Hz, H-4), 3.72-3.61 (m, 5H, H-5, H-6a, H-6b, CH_2Cl), 3.22 (m, 2H, CH_2N); ^{13}C-RMN (75.5 MHz, CD_3OD) δ 138.3, 130.2, 129.6, 129.3 (Ar-C), 100.1 (C-1), 83.0 (C-4), 78.7 (C-2, Ph*C*H_2), 77.3 (C-3), 72.1 (C-5), 64.6 (C-6), 56.7 (CH_2N), 42.3 (CH_2Cl); HRCI-MS m/z calcd for $C_{15}H_{23}ClNO_6$, $[M + Na]^+$:348.1214, found: 348.1225.

Eluted second was **24:** 115 mg, 52%; R_F 0.11 (20:1 EtOAc–MeOH); $[\alpha]_D^{20}$ –2 (*c* 0.7, MeOH); IR ν_{max} 3340, 2923, 1648, 1444, 1362, 1250, 1041, 741, 702 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 7.36–7.29 (m, 5H, Ar-H), 4.85, 4.80 (2d, 1H each, $J_{H,H}$ = 10.7

Hz, PhCH_2), 4.17 (d, 1H, $J_{1,2}$= 9.1 Hz, H-1), 3.84 (dd, 1H, $J_{3,4}$= 3.3 Hz, $J_{4,5}$ = 0.6 Hz, H-4), 3.76 (dd, 1H, $J_{5,6a}$=6.9 Hz, $J_{6a,6b}$= 11.5 Hz, H-6a), 3.74 (t, 1H, $J_{2,3}$= 9.1 Hz, H-2), 3.68 (dd, 1H, $J_{5,6b}$= 5.1 Hz, H-6b), 3.67 (t, 2H, $J_{H,H}$= 6.7 Hz, CH_2-Cl), 3.51 (dd, 1H, H-3), 3.50 (m, 1H, H-5), 3.36, 3.26 (2m, 1H each, CH_2N); ^{13}C-RMN (125 MHz, CD_3OD) δ 138.3, 130.5, 129.6, 129.4 (Ar-C), 95.8 (C-1), 78.6 (Ph*C*H_2), 77.9 (C-5), 76.3 (C-3), 70.7 (C-4), 69.3 (C-2), 62.9 (C-6), 55.5 (CH_2N), 42.6 (CH_2Cl); HRCI-MS m/z calcd for $C_{15}H_{23}ClNO_6$, [M + H]: 348.1214, found: 348.1215.

2-Chloro-*N*-benzyloxy-*N*-(α-D-mannopyranosyl)ethanamine (26), 2-chloro-*N*-benzyloxy-*N*-(β-D-mannopyranosyl)ethanamine (27), and 2-chloro-*N*-benzyloxy-*N*-(α-D-mannofuranosyl)ethanamine (28)

A mixture of **4** (91 mg, 0.49 mmol) and D-mannose (84 mg, 0.47 mmol) in methanol (4.0 mL) and acetic acid (40 μL, 0.70 mmol) was refluxed for 5.0 h. Then, the solvent was removed under reduced pressure and the residue was purified by column chromathography (EtOAc→EtOAc–MeOH 20:1) to afford compounds **26**–**28** as a non-separable mixture in a 2:1:2 ratio, as deduced from ^{1}H-NMR data: 130 mg, 76%; R_F 0.34 (EtOAc–MeOH 10:1); IR ν_{max} 3377, 2924, 2362, 1653, 1065, 741, 698 cm^{-1}; ^{1}H-NMR (500 MHz, D_2O) δ 7.50–7.44 (m, Ar-H), data for **26**: δ 4.94, 4.87 (2d, 1H each, $J_{H,H}$= 10.3 Hz, PhCH_2), 4.39 (d, 1H, $J_{1,2}$ = 2.3 Hz, H-1), 4.32 (d, 1H, $J_{2,3}$=3.4 Hz, H-2), 3.99 (dd, 1H, $J_{3,4}$=8.8 Hz, H-3), 3.93 (dd, 1H, H-5), 3.88 (dd, 1H, $J_{5,6a}$=2.6 Hz, $J_{6a,6b}$=12.3 Hz, H-6a), 3.87 (t, 2H, $J_{H,H}$= 6.5 Hz, CH_2Cl), 3.74 (dd, 1H, $J_{5,6b}$= 6.4 Hz, H-6b), 3.73 (t, 1H, $J_{4,5}$=9.2 Hz, H-4), 3.44 (m, 1H, CH_aN), 3.11 (m, 1H, CH_bN); data for **27**: δ 4.95, 4.90 (2d, 1H each, $J_{H,H}$= 9.9 Hz, PhCH_2), 4.38 (d, 1H, $J_{1,2}$= 0.9 Hz, H-1), 4.17 (dd, 1H, $J_{2,3}$= 2.6 Hz, H-2), 3.94 (dd, 1H, $J_{5,6a}$= 2.3 Hz, $J_{6a,6b}$= 12.2 Hz, H-6a), 3.84

(m, 2H, CH_2Cl), 3.78 (dd, 1H, $J_{5,6b}$=6.2 Hz, H-6b), 3.63 (m, 2H, H-3, H-4), 3.42 (ddd, 1H, $J_{4,5}$=8.7 Hz, H-5). 3.93 (m, 1H, H-3), 3.54 (m, 1H, CH_aN), 3.32 (m, 1H, CH_bN); data for **28**: δ 4.94, 4.90 (2d, 1H each, $J_{H,H}$= 10.2 Hz, PhCH_2), 4.73 (d, 1H, $J_{1,2}$= 7.1 Hz, H-1), 4. 48 (dd, 1H, $J_{2,3}$= 4.3 Hz, H-2), 4.32 (dd, 1H, $J_{3,4}$= 2.4 Hz, H-3), 4.00 (dd, 1H, $J_{4,5}$= 9.0 Hz, H-4), 3.93 (m, 1H, H-5), 3.81 (dd, 1H, $J_{5,6a}$= 2.7, Hz, $J_{6a,6b}$= 12.1 Hz, H-6a), 3.64 (dd, 1H, $J_{5,6a}$= 5.8 Hz, H-6b), 3.34 (m, 1H, CH_aN), 3.26 (m, 1H, CH_bN); ^{13}C-NMR (125 MHz, D_2O) δ 135.7, 135.6, 129.6, 129.4, 128.9, 129.0, 128.9, 128.8 (Ar-C), data for **26**: 92.5 (C-1), 77.3 (PhCH_2), 75.6 (C-5), 71.1 (C-3), 68.5 (C-2), 67.2 (C-4), 61.2 (C-6), 55.5 (CH_2N), 41.1 (CH_2-Cl); data for **27**: 92.0 (C-1), 78.6 (C-5), 77.0 (PhCH_2), 74.1 (C-3), 69.8 (C-2), 66.9 (C-4), 61.1 (C-6), 55.1 (CH_2N), 41.3 (CH_2Cl); data for **28**: 97.8 (C-1), 80.0 (C-4), 77.7 (PhCH_2), 72.3 (C-2), 71.5 (C-3), 69.0 (C-5), 63.1 (C-6), 55.3 (CH_2N), 41.3 (CH_2Cl); HRLSIMS *m/z* calcd for $C_{15}H_{22}NO_6NaCl$, $[M + Na]^+$: 370.1033, found: 370.1037.

(*E*) and (*Z*)-1,2-*O*-Isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose-5-*O*-benzyloxime (30)

To a solution of 1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose **29**[2] (235 mg, 1.25 mmol) in pyridine (3 mL) was added benzyloxyamine hydrochloride (240 mg, 1.5 mmol, 1.2 equiv.) and the mixture was kept stirring at rt for 12 h. Then, it was concentrated to dryness and the residue was purified by column chromatography (1:10→1:2 EtOAc–hexane) to give **30** as a 2:1 *E*/*Z* mixture as deduced from ^{1}H-NMR: 321 mg, 87%; $[\alpha]_D^{24}$ –67 (*c* 1.0, CH_2Cl_2); R_F 0.5 (1:2 EtOAc–hexane); IR ν_{max} 3400, 2388, 1783, 1295, 1260, 1162, 1092, 984, 847, 698, 644 cm^{-1}; ^{1}H-RMN (300 MHz, $CDCl_3$) *E* isomer: δ 7.57 (d, 1H, $J_{4,5}$= 4.6 Hz, H-5), 7.43–7.27 (m, 5H, Ar-H), 5.98 (d,

[2] R. N. Monrad and R. Madsen, *J. Org. Chem.* 2007, **72**, 9782–9785.

1H, $J_{1,2}$= 3.7 Hz, H-1), 5.11 (s, 2H, PhCH_2), 4.69 (dd, 1H, $J_{3,4}$= 2.6 Hz, H-4), 4.54 (d, 1H, $J_{2,3}$~ 0 Hz, H-2), 4.33 (d, 1H, H-3), 1.49, 1.32 (2s, 3H each, C(CH_3)$_2$); *Z* isomer: δ 6.86 (d, 1H, $J_{4,5}$= 3.1 Hz, H-5), 5.96 (d, 1H, $J_{1,2}$= 3.7 Hz, H-1), 5.16, 5.14 (2d, 1H each, $J_{H,H}$= 12.5 Hz, PhCH_2), 5.07 (t, 1H, $J_{3,4}$= 3.0 Hz, H-4), 4.58 (d, 1H, H-3), 4.53 (d, 1H, $J_{2,3}$~ 0 Hz, H-2); 1.49, 1.32 (2s, 3H each, C(CH_3)$_2$); ^{13}C-NMR (75,5 MHz,$CDCl_3$) δ 137.3, 136.9, 128.8, 128.7, 128.5, 128.4, 128.3 (Ar-C); *E* isomer: δ 146.9 (C-5), 112.1 (*C*(CH_3)$_2$), 105.1 (C-1), 84.9 (C-2), 77.6 (C-4), 76.6 (Ph*C*H_2), 76.1 (C-3), 26.9, 26.3 (C(*C*H_3)$_2$); *Z* isomer: δ 149.3 (C-5), 112.0 (*C*(CH_3)$_2$), 104.7 (C-1), 85.1 (C-2), 78.4 (C-4), 76.9 (Ph*C*H_2), 75.9 (C-3), 27.1, 26.3 (C(*C*H_3)$_2$); HRLSI-MS *m/z* calcd for $C_{15}H_{19}NNaO_5$, $[M + Na]^+$: 316.1161, found: 316.1160.

5-Benzyloxyamino-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (31) and *N*-benzyloxy-*N*-(5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)amino cyanoborane (32)

To a solution of (*E*) and (*Z*)-1,2-*O*-isopropylidene-α-D-*xylo*-pentodialdo-1,4-furanose-5-*O*-benzyloxime (**30**) (295 mg, 1.01 mmol) in AcOH (4 mL) was added $NaBH_3CN$ (158 mg, 2.51 mmol, 2.5 equiv.) and the corresponding mixture was kept stirring at rt for 21 h. Then, it was concentrated to dryness, and the residue was dissolved in EtOAc (30 mL), washed with water (3 x 30 mL), dried over $MgSO_4$, and filtered. The filtrate was concentrated to dryness and purified by column chromatography (hexane→1:1 hexane–EtOAc).

Eluted first was **31**. Yield: 202 mg, 68%; $[\alpha]_D^{25}$+17 (*c* 1.0, CH_2Cl_2); R_F 0.3 (1:2 EtOAc–hexane); IR ν_{max} 3384, 2925, 2862, 2355, 2157, 1457, 1379, 1270, 1221, 1078, 1004, 910, 861, 817, 748, 688, 644 cm^{-1}; ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.36–7.29 (m,

5H, Ar-H), 5.88 (d, 1H, $J_{1,2}$= 3.7 Hz, H-1), 4.72 (s, 2H, PhCH_2), 4.50 (d, 1H, $J_{2,3}$~ 0 Hz, H-2), 4.29 (m, 1H, H-4), 4.20 (d, 1H, $J_{3,4}$= 2.6 Hz, H-3), 3.52 (dd, 1H, $J_{4,5a}$= 5.9 Hz, $J_{5a,5b}$= 13.2 Hz, H-5a), 3.29 (dd, 1H, $J_{4,5b}$= 3.3 Hz, H-5b), 1.48, 1.31 (2s, 3H each, C(CH_3)$_2$); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 136.8, 128.6, 128.6, 128.3 (Ar-C), 111.6 (*C*(CH_3)$_2$), 104.7 (C-1), 85.4 (C-2), 78.0 (C-4), 76.6 (C-5), 76.4 (Ph*C*H_2), 50.1 (C-3), 26.8, 26.1 (C(CH_3)$_2$); HRLSI-MS *m/z* calcd for $C_{15}H_{21}NNaO_5$, $[M + Na]^+$: 318.1317, found: 318.1334; Anal. calcd for $C_{15}H_{21}NO_5$: C, 61.00; H, 7.17; N, 4.74, found: C, 61.06; H, 7.23; N, 4.60.

Eluted second was **32**. Yield: 74 mg, 22%; $[\alpha]_D^{24}$ –67 (*c* 1.0, CH_2Cl_2); R_F 0.2 (1:2 EtOAc–hexane); ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.43–7.35 (m, 5H, Ar-H), major diastereoisomer: 7.13 (br d, 1H, NH), 5.87 (d, 1H, $J_{1,2}$= 3.5 Hz, H-1), 5.10, 4.99 (2d, 1H each, $J_{H,H}$= 10.3 Hz, PhCH_2), 4.52 (dt, 1H, $J_{3,4}$= 2.6 Hz, $J_{4,5b}$= 8.7 Hz, H-4), 4.51 (d, 1H, $J_{2,3}$~ 0 Hz, H-2), 4.22 (d, 1H, $J_{3,4}$= 2.6 Hz, H-3), 3.59 (ddd, 1H, $J_{5a,5b}$= 14.5 Hz, $J_{5a,NH}$= 9.2 Hz, $J_{5a,4}$= 3.3 Hz, H-5a), 3.49 (ddd, 1H, $J_{5a,5b}$= 14.5 Hz, $J_{5b,NH}$= 2.0 Hz, $J_{5b,4}$= 8.7 Hz H-5b), 1.52, 1.32 (2s, 3H each, C(CH_3)$_2$); minor diastereoisomer: 7.20 (br t, 1H, NH), 5.85 (d, 1H, $J_{1,2}$= 3.5 Hz, H-1), 5.04 (s, 2H, PhCH_2), 4.49 (d, 1H, $J_{2,3}$~ 0 Hz, H-2), 4.33 (td, $J_{3,4}$= 3.0 Hz, $J_{4,5a}$=$J_{4,5b}$= 6.5 Hz, H-4), 4.20 (d, 1H, $J_{3,4}$= 3.0 Hz, H-3), 3.54 (m, 2H, H-5a, H-5b), 1.46, 1.29 (2s, 3H each, C(CH_3)$_2$); ^{13}C-NMR (75.5 MHz, $CDCl_3$) major diastereoisomer δ 132.4 129.9, 129.8, 129.2 (Ar-C), 112.3 (*C*(CH_3)$_2$), 104.9 (C-1), 86.0 (C-2), 74.7 (C-3), 74.6 (Ph*C*H_2), 74.4 (C-4), 56.4 (C-5), 27.1, 26.4 (C(*C*H_3)$_2$); minor diastereoisomer δ 132.5, 129.7, 129.4, 128.8 (Ar-C), 112.5 (*C*(CH_3)$_2$), 105.0 (C-1), 85.7 (C-2), 76.8 (C-3), 73.5 (Ph*C*H_2), 75.7 (C-4), 55.4 (C-5), 27.1, 26.5 (C(*C*H_3)$_2$); HRLSI-MS *m/z* calcd for $C_{16}H_{23}BN_2NaO_5$, $[M + Na]^+$: 357.1598, found: 357.1609.

5-Benzyloxyamino-5-deoxy-5-*N*-(β-D-glucopyranosyl)-1,2-*O*-isopropylidene-α-D-xylofuranose (33)

To a solution of 5-benzyloxyamino-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose **31** (128 mg, 0.43 mmol) in MeOH (8 mL) was added D-glucose (71 mg, 0.38 mmol) and AcOH (0.1 mL), and the corresponding mixture was refluxed for 6 h. After that, it was concentrated to dryness, and the residue was purified by column chromatography (EtOAc→5:1 EtOAc–MeOH) to give **33**: 161 mg, 90%; $[\alpha]_D^{26}$ –42 (*c* 1.0, MeOH); R_F 0.20 (5:1 EtOAc–MeOH); IR ν_{max} 3300, 1685, 1541, 1305, 1240, 1019, 793, 723 cm^{-1}; ^{1}H-NMR (300 MHz, CD_3OD) δ 7.42–7.31 (m, 5H, Ar-H), 5.92 (d, 1H, $J_{1,2}$= 3.8 Hz, H-1), 4.86 (s, 2H, PhCH_2), 4.50 (d, 1H, $J_{2,3}$~ 0 Hz, H-2), 4.46 (ddd, 1H, $J_{3,4}$= 2.7 Hz, $J_{4,5a}$= 5.6 Hz, $J_{4,5b}$= 7.5 Hz, H-4), 4.19 (d, 1H, $J_{1',2'}$= 8.9 Hz, H-1'), 4.06 (d, 1H, H-3), 3.84 (dd, 1H, $J_{5',6'a}$= 2.1 Hz, $J_{6'a,6'b}$= 12.2 Hz, H-6'a) 3.67 (dd, 1H, $J_{5',6'b}$= 5.0 Hz, H-6'b), 3.55 (t, 1H, $J_{2',3'}$= 8.9 Hz, H-2'), 3.43 (t, 1H, $J_{3',4'}$= 8.9 Hz, H-3'), 3.32 (dd, 1H, $J_{5a,5b}$= 14.0 Hz, $J_{4,5a}$= 5.6 Hz, H-5a), 3.31 (t, 1H, $J_{4',5'}$= 9.0 Hz, H-4'), 3.27 (m, 1H, H-5'), 3.19 (dd, 1H, $J_{4,5b}$= 7.5 Hz, H-5b), 1.46, 1.31 (2s, 3H each, C(CH_3)$_2$); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 137.8, 130.3, 129.5, 129.4 (Ar-C), 112.6 (*C*(CH$_3$)$_2$) 106.3 (C-1), 94.9 (C-1'), 86.7 (C-2), 79.8 (C-4'), 79.5 (C-3'), 79.3 (C-4), 77.9 (Ph*C*H$_2$), 76.3 (C-3), 71.9 (C-2'), 71.3 (C-5'), 62.7 (C-6'), 52.5 (C-5), 27.2, 26.4 (C(*C*H$_3$)$_2$); HRLSI-MS *m/z* calcd for $C_{21}H_{31}NNaO_{10}$, $[M + Na]^+$: 480.1847, found: 480.1851; Anal. calcd for $C_{21}H_{31}NO_{10}$: C, 55.13; H, 6.83; N, 3.06, found: C, 55.25; H, 6.87; N, 2.84.

5-Benzyloxyamino-5-deoxy-5-*N*-(β-D-xylopyranosyl)-1,2-*O*-isopropylidene-α-D-xylofuranose (34)

To a solution of 5-benzyloxyamino-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose **31** (200 mg, 0.68 mmol) in MeOH (20 mL) was added D-xylose (91 mg, 0.61 mmol) and AcOH (0.2 mL), and the corresponding mixture was refluxed for 6 h. After that, it was concentrated to dryness and the residue was purified by column chromatography (20:1→10:1 CH_2Cl_2–MeOH) to give **34**: 221 mg, 85%; $[\alpha]_D^{25}$ –38 (*c* 1.1, MeOH); R_F 0.44 (10:1 EtOAc–MeOH); IR ν_{max} 3384, 2914, 1444, 1371, 1216, 1061, 1012, 857, 741, 707 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 7.39–7.29 (m, 5H, Ar-H), 5.90 (d, 1H, $J_{1,2}$= 3.8 Hz, H-1), 4.83 (s, 2H, PhCH_2), 4.48 (d, 1H, $J_{2,3}$~ 0 Hz, H-2), 4.40 (ddd, 1H, $J_{3,4}$= 2.8 Hz, $J_{4,5a}$= 5.6 Hz, $J_{4,5b}$= 7.5 Hz, H-4), 4.10 (d, 1H, $J_{1',2'}$= 9.0 Hz, H-1'), 4.02 (d, 1H, H-3), 3.89 (dd, 1H, $J_{4',5a'}$= 5.5 Hz, $J_{5a',5b'}$= 11.2 Hz, H-5a'), 3.51 (t, 1H, $J_{1',2'}$=$J_{2',3'}$= 9.0 Hz, H-2'), 3.47 (ddd, 1H, $J_{3',4'}$= 9.1 Hz, $J_{4',5a'}$= 5.5 Hz, $J_{4',5b'}$= 11.0 Hz, H-4'), 3.36 (t, 1H, H-3'), 3.29 (dd, 1H, $J_{5a,5b}$= 13.9 Hz, H-5a), 3.17 (t, 1H, H-5b'), 3.12 (dd, 1H, H-5b), 1.43, 1.29 (2s, 3H each, C(CH_3)$_2$); ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 138.3, 130.1, 129.6, 129.3 (Ar-C), 112.7 (*C*(CH_3)$_2$), 106.4 (C-1), 95.9 (C-1'), 86.8 (C-2), 79.6 (C-4), 77.7 (Ph*C*H_2), 76.4 (C-3), 76.4 (C-3′), 72.0 (C-2'), 71.3 (C-4'), 69.1 (C-5'), 52.4 (C-5) 27.3, 26.5 (C(*C*H_3)$_2$); HRLSI-MS *m/z* calcd for $C_{20}H_{29}NNaO_9$, $[M + Na]^+$; 450.1740, found: 450.1757; Anal. calcd for $C_{20}H_{29}NO_9$: C, 56.20 ; H, 6.84 ; N, 3.28, found: C, 56.21; H, 7.16; N, 3.08.

5-Benzyloxyamino-5-deoxy-5-*N*-(β-D-galactopyranosyl)-1,2-*O*-isopropylidene-α-D-xylofuranose (35)

To a solution of 5-benzyloxyamino-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose **31** (200 mg, 0.68 mmol) in MeOH (20 mL) was added D-galactose (110 mg, 0.61 mmol) and AcOH (0.2 mL), and the corresponding mixture was refluxed for 6 h. After that, it was concentrated to dryness, and the residue was crystallized from ethanol to give **35**:

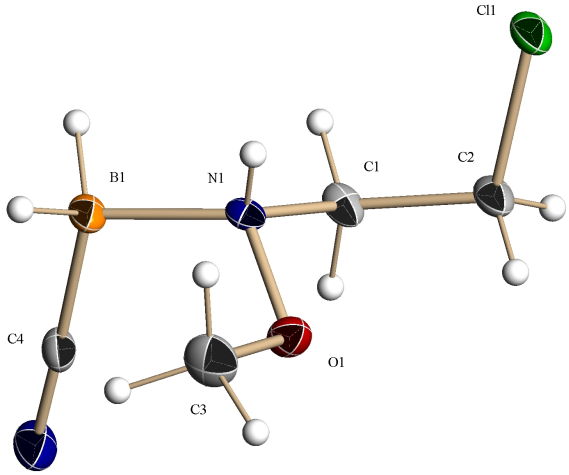
263 mg, 85%; $[\alpha]_D^{21}$ +32 (*c* 1.0, MeOH); R_F 0.26 (5:1 EtOAc–MeOH); IR ν_{max} 3452, 3273, 2924, 1653, 1371, 1206, 1075, 1008, 979, 750, 726, 697 cm^{-1}; ^{1}H-NMR (500 MHz, CD_3OD) δ 7.33–7.28 (m, 5H, Ar-H), 5.90 (d, 1H, $J_{1,2}$= 3.7 Hz, H-1), 4.84 (s, 2H, PhCH_2), 4.49 (d, 1H, $J_{2,3}$~ 0 Hz, H-2), 4.44 (td, 1H, $J_{3,4}$= 2.9 Hz, $J_{4,5a}$= 6.0 Hz, $J_{4,5b}$= 7.0 Hz, H-4), 4.17 (d, 1H, $J_{1',2'}$= 9.0 Hz, H-1'), 4.04 (d, 1H, $J_{3,4}$= 2.9 Hz, H-3), 3.85 (dd, 1H, $J_{3',4'}$= 3.4 Hz, $J_{4',5'}$= 0.9 Hz, H-4'), 3.81 (t, 1H, $J_{2',3'}$= 9.4 Hz, H-2'), 3.77 (dd, 1H, $J_{5',6'a}$= 6.8 Hz, $J_{6'a,6'b}$= 11.5 Hz, H-6'a), 3.69 (dd, 1H, $J_{5',6'b}$= 5.1 Hz, H-6'b), 3.51 (ddd, 1H, H-5'), 3.54 (dd, 1H, Hz, H-3'), 3.39 (dd, 1H, $J_{5a,5b}$= 14.1 Hz, $J_{5a,4}$= 6.0 Hz, H-5a), 3.19 (dd, 1H, $J_{5b,4}$= 7.0 Hz, H-5b), 1.44, 1.30 (2s, 3H each, C(CH_3)$_2$); ^{13}C-NMR (75.5 MHz, CD_3OD) δ 138.0, 130.1, 129.5, 129.2 (Ar-C), 112.5 (*C*(CH_3)$_2$), 106.2 (C-1), 95.4 (C-1'), 86.6 (C-2), 79.6 (C-4), 78.6 (C-5'), 77.5 (Ph*C*H_2), 76.3 (C-3), 76.1 (C-3'), 70.6 (C-4'), 69.3 (C-2'), 62.7 (C-6'), 51.7 (C-5), 27.1, 26.3 (C(*C*H_3)$_2$); HRLSI-MS *m/z* calcd for $C_{21}H_{31}NNaO_{10}$, $[M + Na]^+$: 480.1846, found: 480.1862.

B. X-Ray Structural Characterization of New Compounds 6, 7 and 8

B.1 General procedures.

A single crystals of suitable size of **6**, **7** and **8**, coated with dry perfluoropolyether was mounted on a glass fiber and fixed in a cold nitrogen stream [T = 173(2) K] to the goniometer head. Data collections were performed on Bruker-Nonius X8APEX-II CCD diffractometer, using monochromatic radiation λ(Mo $K_{\alpha 1}$) = 0.71073 Å, by means of ω and φ scans. The data were reduced (SAINT)[3] and corrected for Lorentz polarization effects and absorption by multiscan method applied by SADABS[4] . The structure were solved by direct methods (SIR-2002)[5] and refined against all F^2 data by full-matrix least-squares techniques (SHELXTL-6.12).[6] All the non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were included from calculated positions and refined riding on their respective carbon atoms with isotropic displacement parameters.

B.2. X-Ray data of 6



[3] SAINT 6.02, BRUKEI

[4] SADABS George Sheldrick, Bruker AXS, Inc., Madison,Wisconsin, USA, 1999.

[5] M.C.Burla, M. Camalli, B. Carrozzini, G.L. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna SIR2002: the program; *J. Appl. Cryst*, (2003). **36**, 1103.

[6] [7] SHELXTL 6.14, Bruker AXS, Inc., Madison, Wisconsin, USA, 2000–2003.

Figure 1. ORTEP drawing of **6** showing thermal ellipsoids. at the 50% probability level.

Table 1. Crystal data and structure refinement of **6**.

Empirical formula	$C_4H_{10}BClN_2O$	
Formula weight	148.40	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\bar{1}$	
Unit cell dimensions	a = 6.2785(6) Å	α= 83.088(3)°.
	b = 6.5034(6) Å	β= 87.368(4)°.
	c = 9.6048(9) Å	γ = 78.440(3)°.
Volume	381.34(6) $Å^3$	
Z	2	
Density (calculated)	1.292 Mg/m^3	
Absorption coefficient	0.424 mm^{-1}	
F(000)	156	
Crystal size	0.44 x 0.33 x 0.18 mm^3	
Theta range for data collection	2.14 to 30.59°.	
Index ranges	-8<=h<=8, -9<=k<=5, -13<=l<=12	
Reflections collected	6575	
Independent reflections	2301 [R(int) = 0.0335]	
Completeness to theta = 25.00°	98.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9276 and 0.8171	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2301 / 0 / 92	
Goodness-of-fit on F^2	1.095	
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.0956	
R indices (all data)	R1 = 0.0566, wR2 = 0.1140	
Largest diff. peak and hole	0.683 and -0.386 $e.Å^{-3}$	

B.3. X-ray data of 7

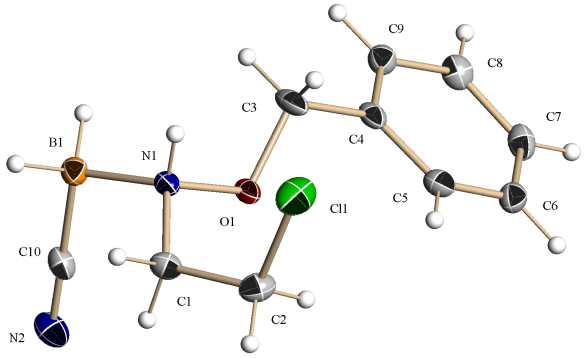


Figure 2. ORTEP drawing of **7** showing thermal ellipsoids at the 50% probability level.

Table 2. Crystal data and structure refinement of **7**.

Empirical formula	$C_{10}H_{14}BClN_2O$	
Formula weight	224.49	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.5051(4) Å	α= 90°.
	b = 12.3772(5) Å	β= 92.1500(10)°.
	c = 9.9685(4) Å	γ = 90°.
Volume	1171.93(8) $Å^3$	
Z	4	
Density (calculated)	1.272 Mg/m^3	
Absorption coefficient	0.300 mm^{-1}	
F(000)	472	
Crystal size	0.50 x 0.30 x 0.23 mm^3	
Theta range for data collection	3.44 to 30.53°.	
Index ranges	-13<=h<=13, -17<=k<=17, -14<=l<=14	
Reflections collected	33074	
Independent reflections	3579 [R(int) = 0.0320]	
Completeness to theta = 30.53°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9341 and 0.8643	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3579 / 0 / 145	
Goodness-of-fit on F^2	1.047	

Final R indices [I>2sigma(I)]	R1 = 0.0317, wR2 = 0.0851
R indices (all data)	R1 = 0.0412, wR2 = 0.0893
Largest diff. peak and hole	0.397 and -0.274 e.Å^{-3}

B.4. X-Ray data of 8

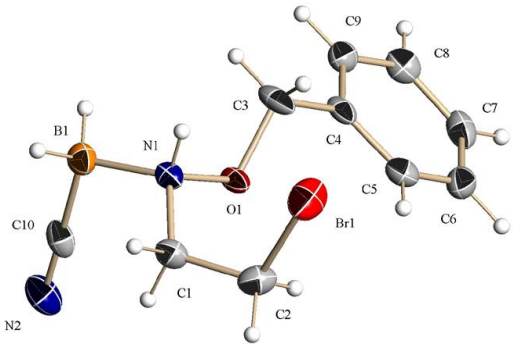


Figure 3. ORTEP drawing for **8** showing thermal ellipsoids. at the 50% probability level.

Table 3. Crystal data and structure refinement of **8**.

Empirical formula	$C_{10}H_{14}BBrN_2O$	
Formula weight	268.95	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 9.6308(3) Å	α= 90°.
	b = 12.4411(4) Å	β= 92.716(2)°.
	c = 9.9555(4) Å	γ = 90°.
Volume	1191.51(7) Å^3	
Z	4	
Density (calculated)	1.499 Mg/m^3	
Absorption coefficient	3.425 mm^{-1}	
F(000)	544	
Crystal size	0.50 x 0.40 x 0.30 mm^3	
Theta range for data collection	3.31 to 28.82°.	
Index ranges	-6<=h<=13, -15<=k<=16, -13<=l<=13	
Reflections collected	15111	
Independent reflections	3094 [R(int) = 0.0399]	
Completeness to theta = 28.82°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.3464 and 0.2091	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3094 / 1 / 139	

Goodness-of-fit on F^2	1.025
Final R indices [I>2sigma(I)]	R1 = 0.0369, wR2 = 0.0736
R indices (all data)	R1 = 0.0632, wR2 = 0.0829
Largest diff. peak and hole	0.626 and -0.615 e.$Å^{-3}$

B.5. Crystal packing

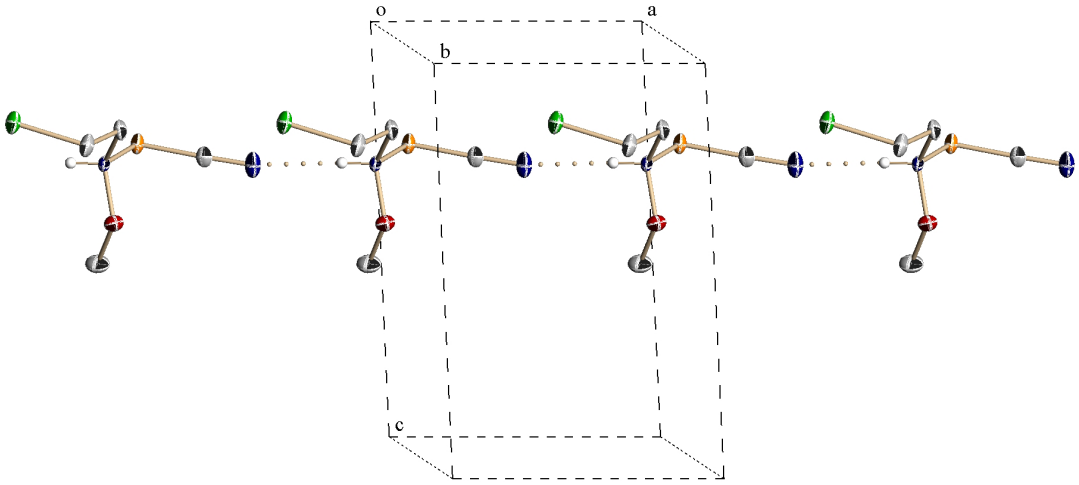


Figure 4. Crystal packing motif showing the chained hydrogen-bond structures of 6.

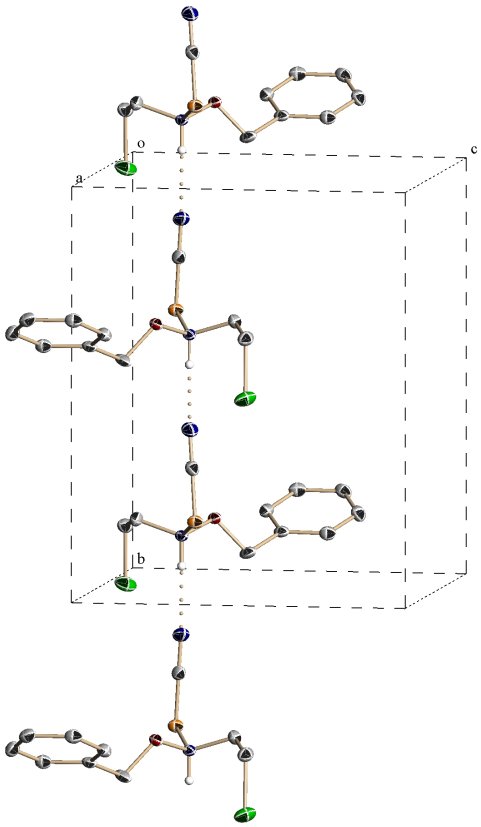


Figure 5. Crystal packing motif showing the chained hydrogen-bond structures of 7.

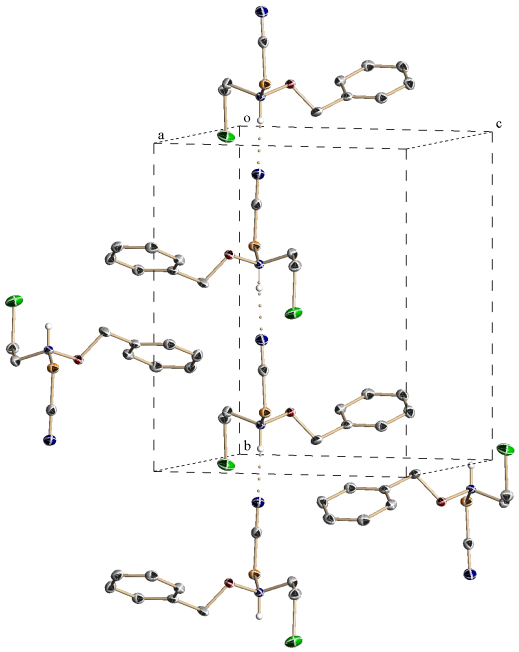


Figure 6. Crystal packing motif showing as the different chains of hydrogen-bond structures of 7 are interconnected through aromatic π–π stacking interactions.

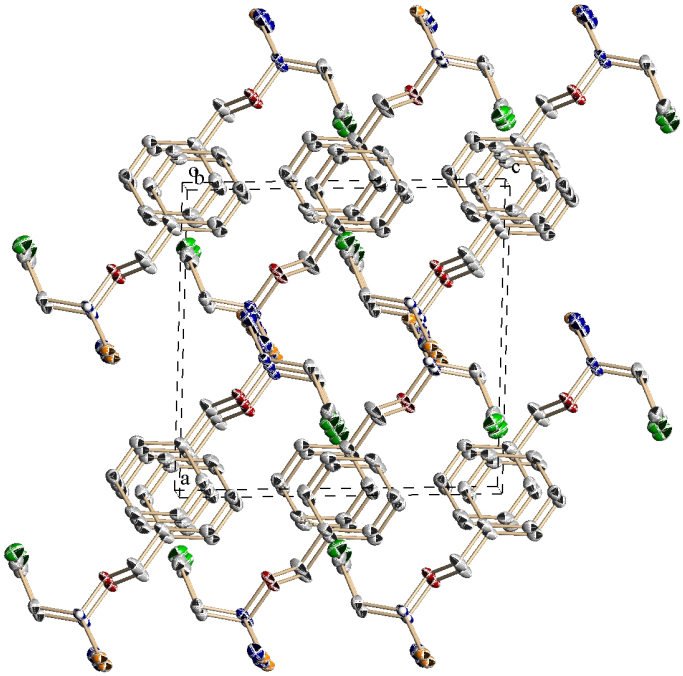


Figure 7. Crystal packing motif of 7 showing another view of the aromatic π–π stacking interactions along the b axis.

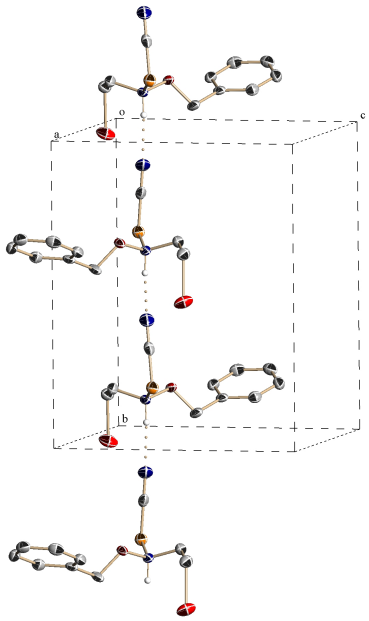


Figure 8. Crystal packing motif showing the chained hydrogen-bond structures of 8.

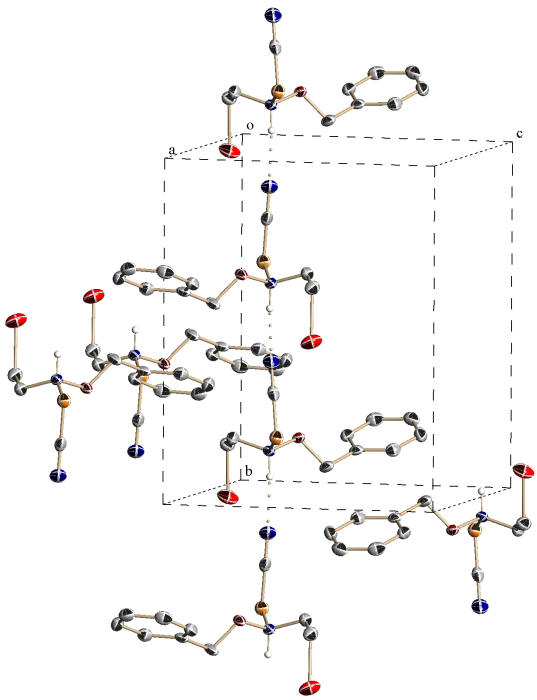
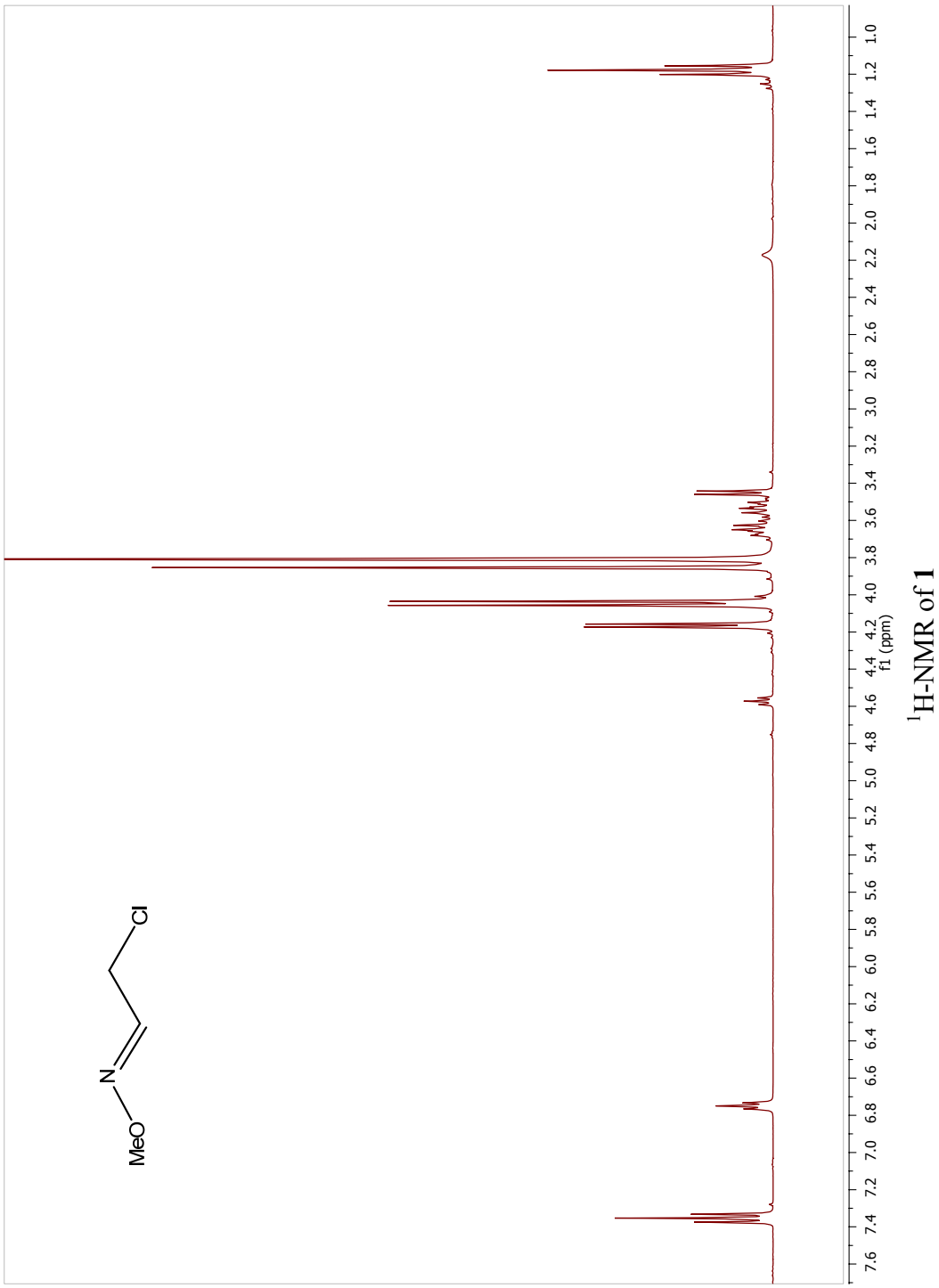
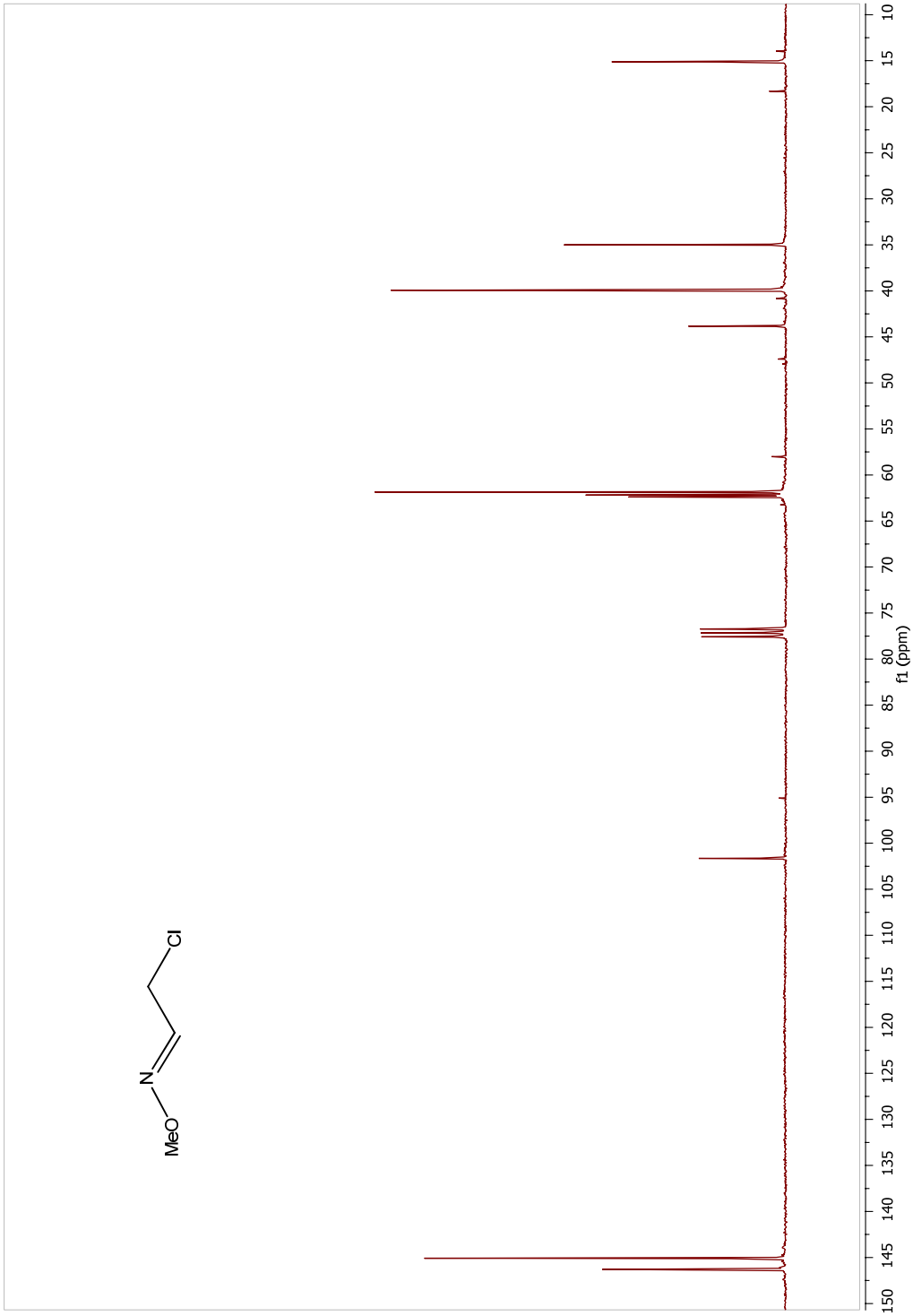


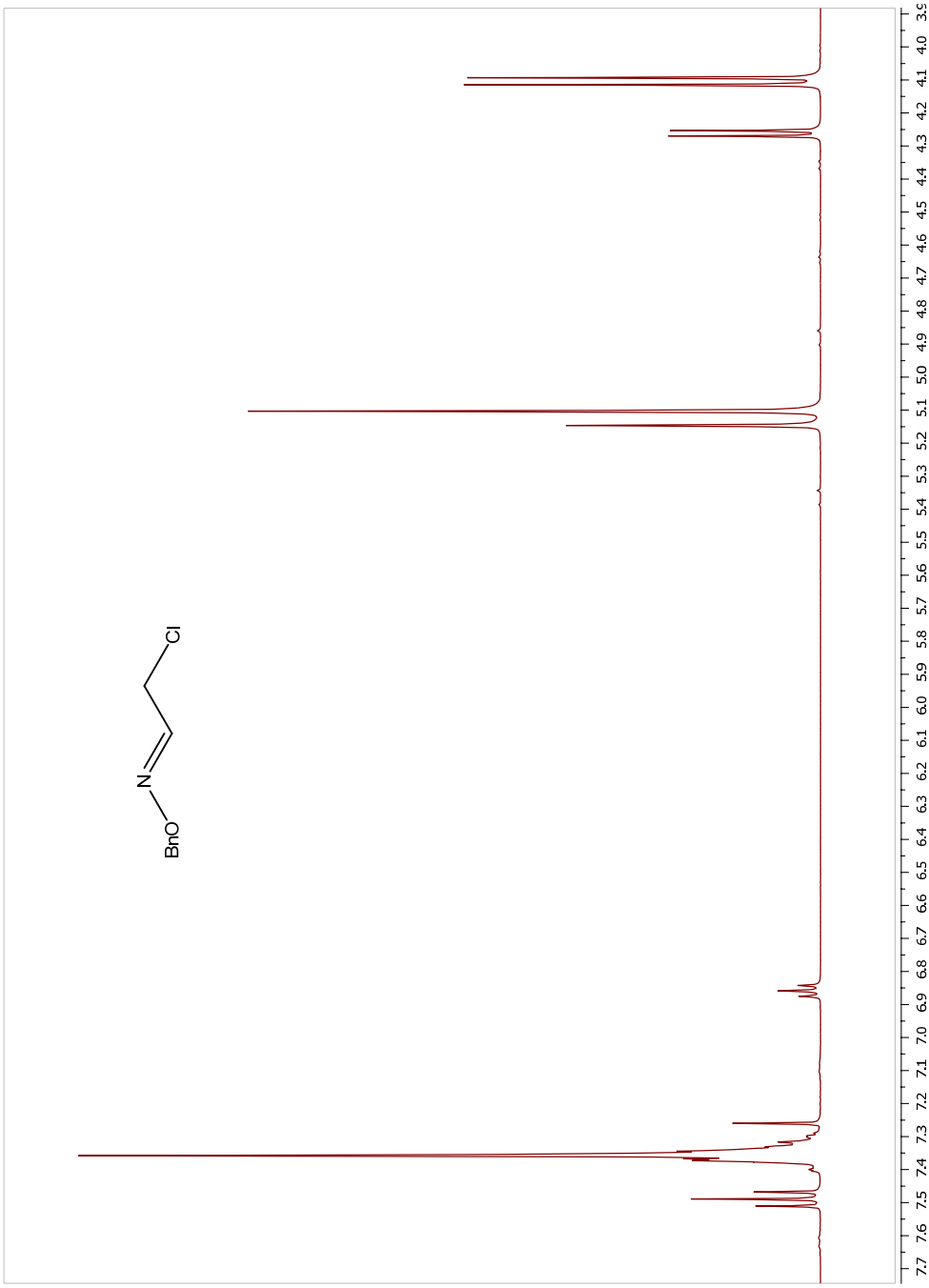
Figure 9. Crystal packing motif showing as the different chains of hydrogen-bond structures of 8 are interconnected through aromatic π–π stacking interactions.



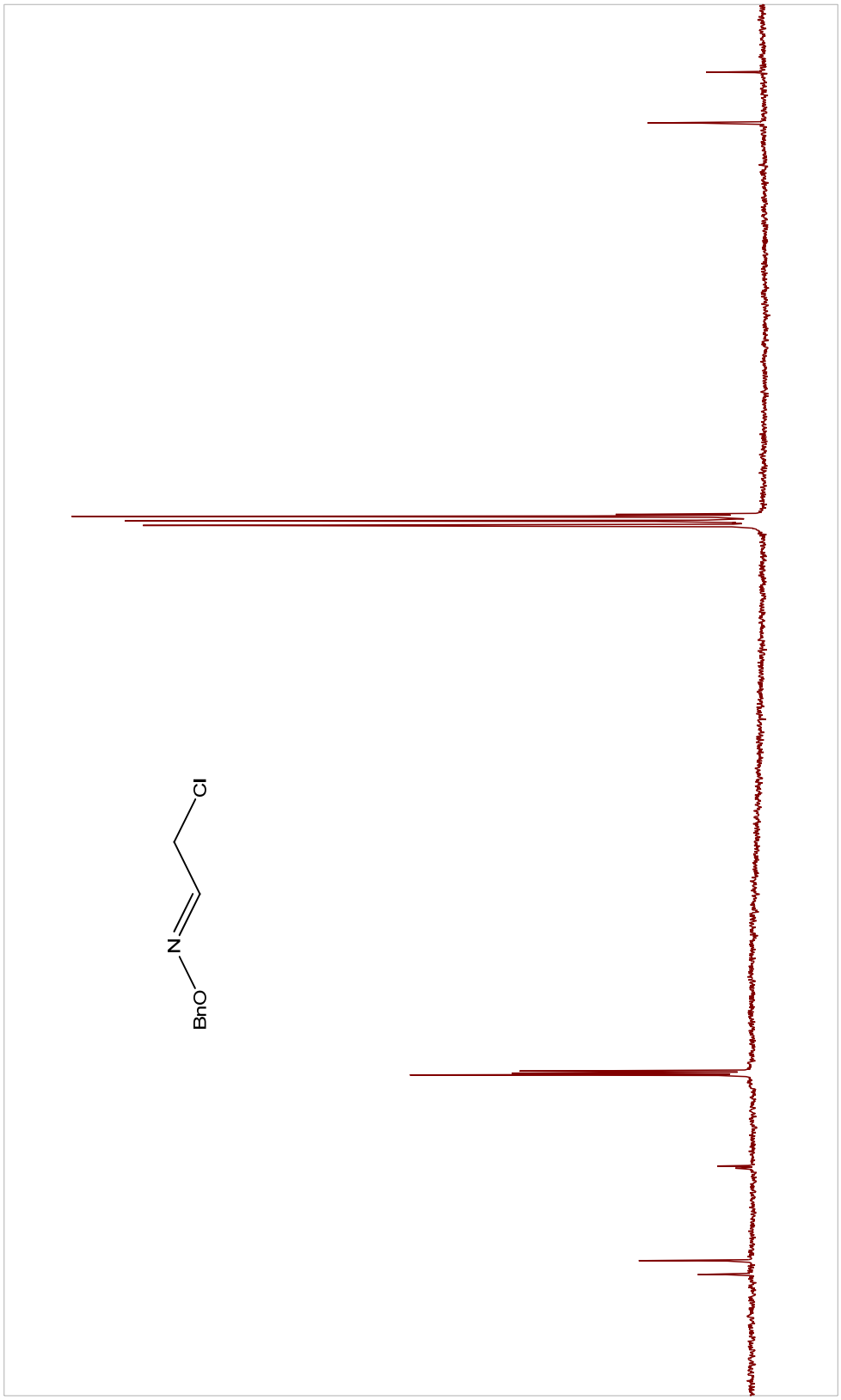
^{1}H-NMR of **1**



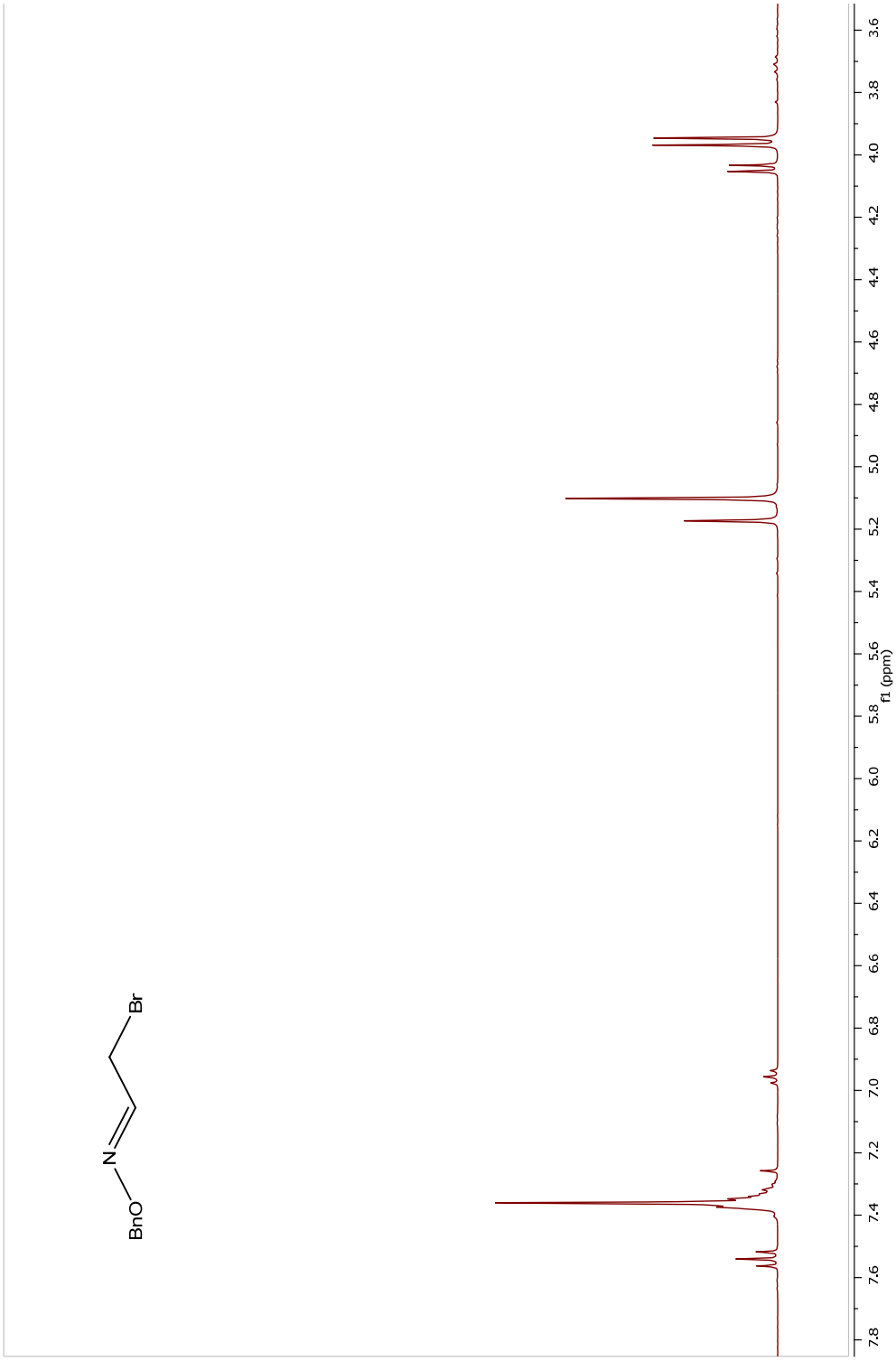
^{13}C-NMR of **1**



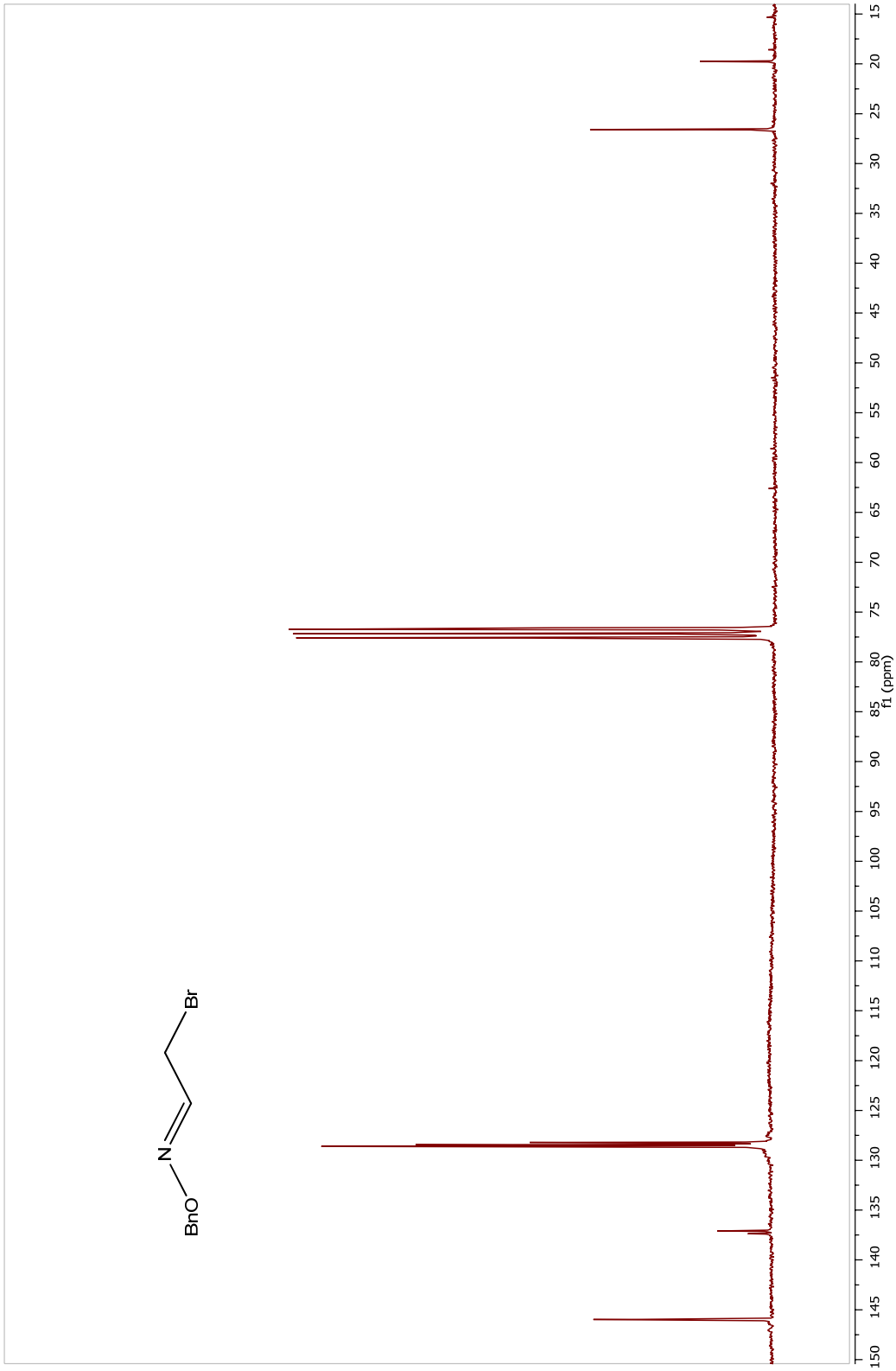
^{1}H-NMR of **2**



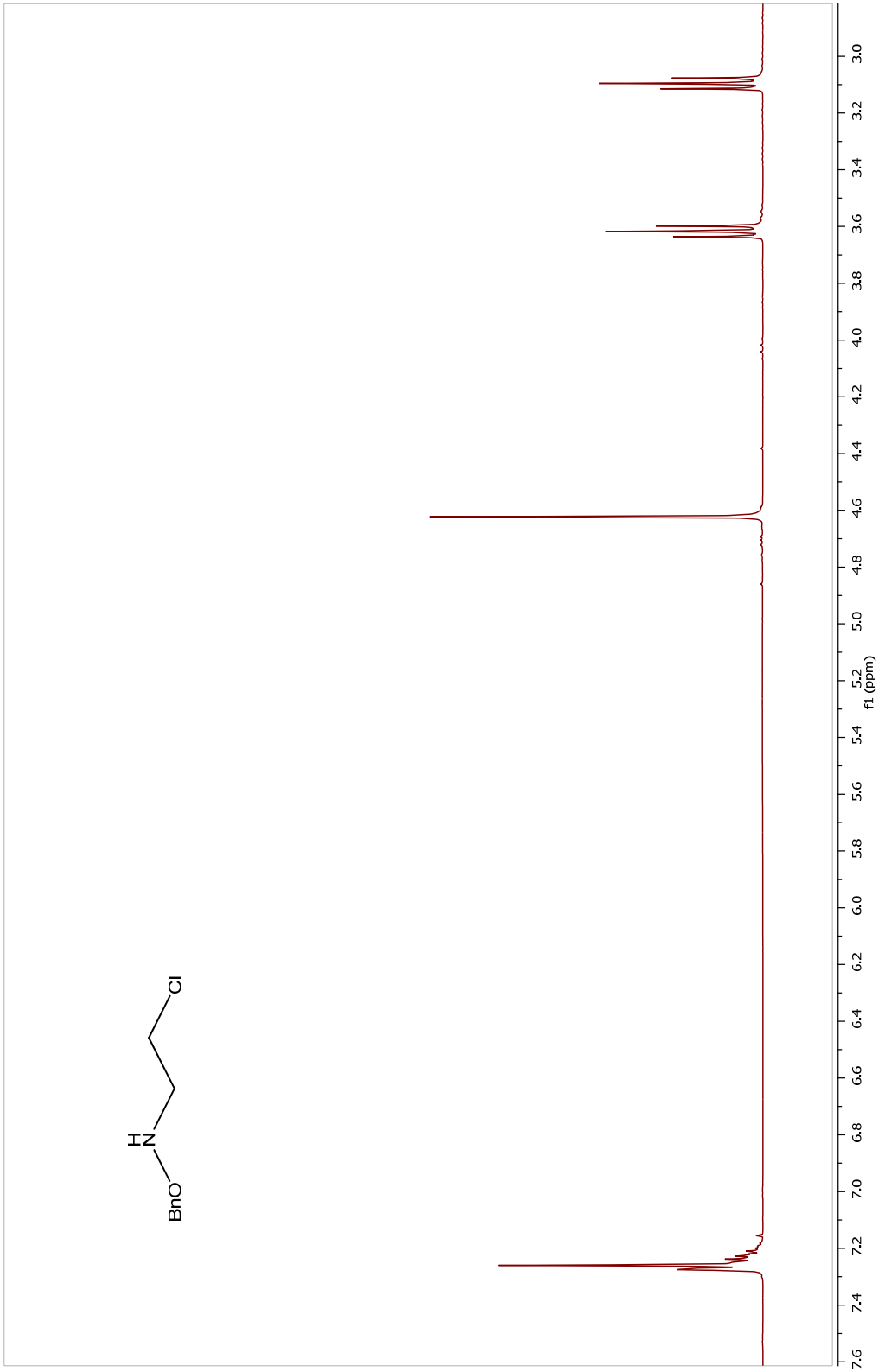
^{13}C-NMR of **2**



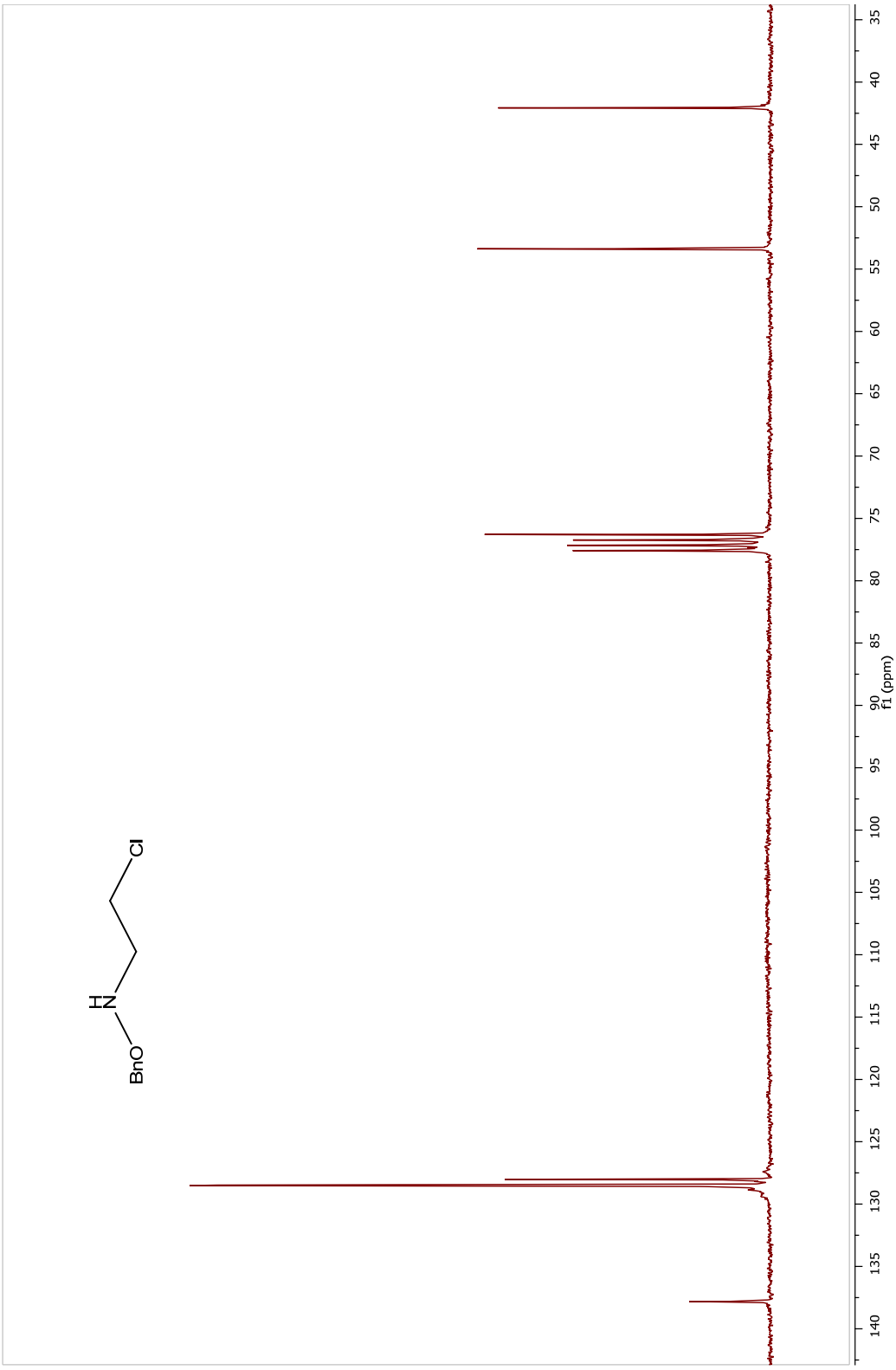
^{1}H-NMR of **3**



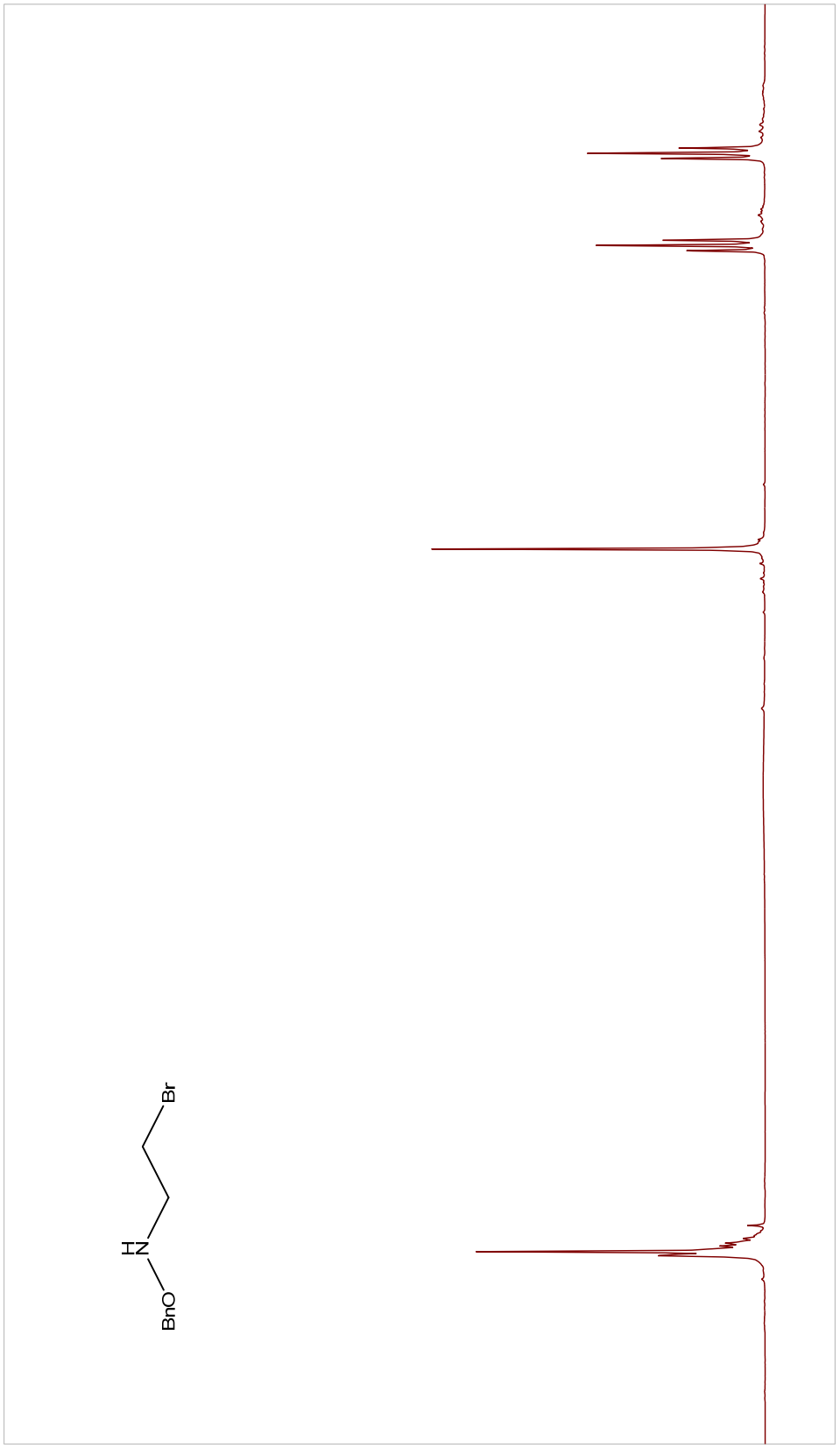
^{13}C-NMR of **3**



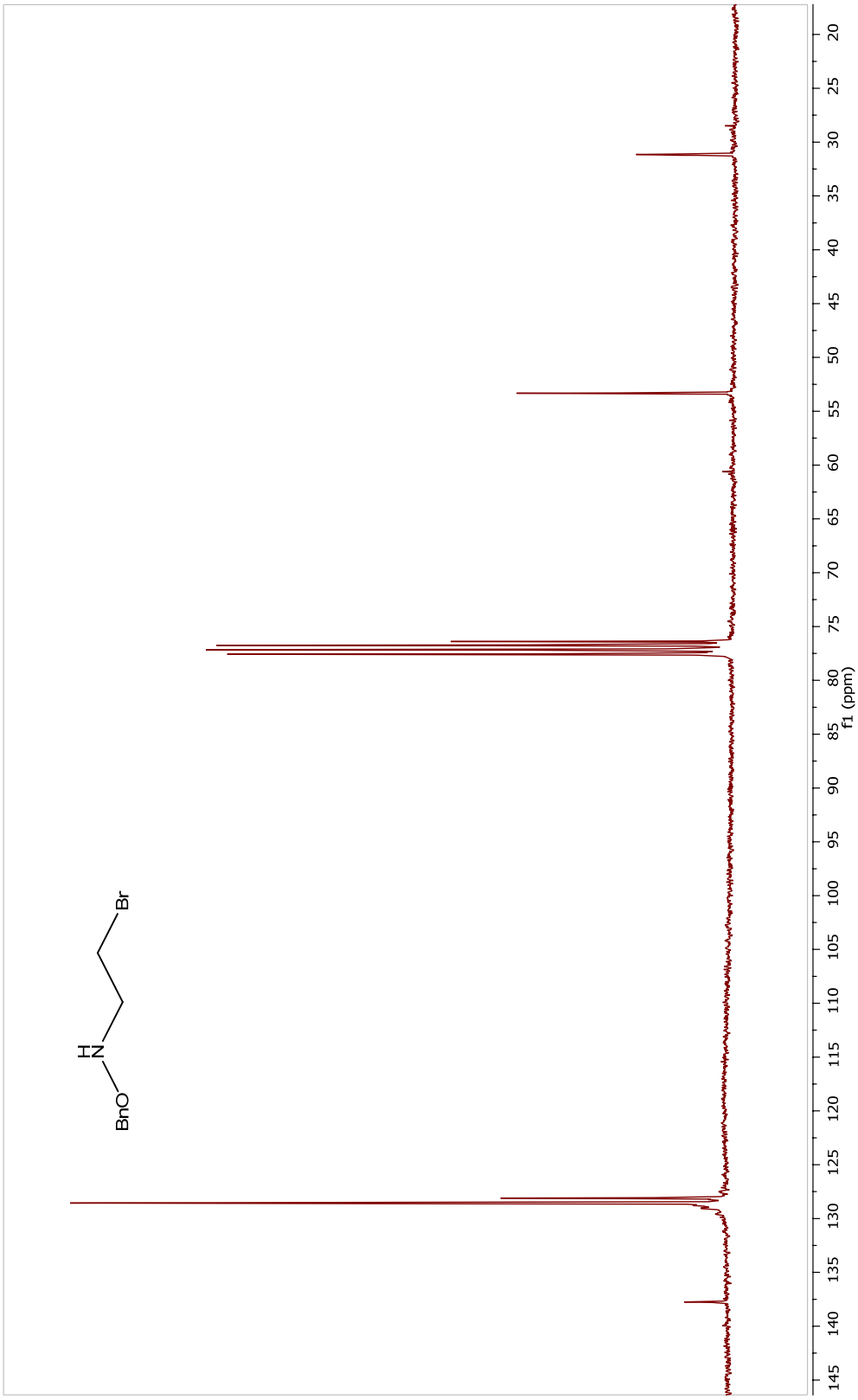
^{1}H-NMR of **4**



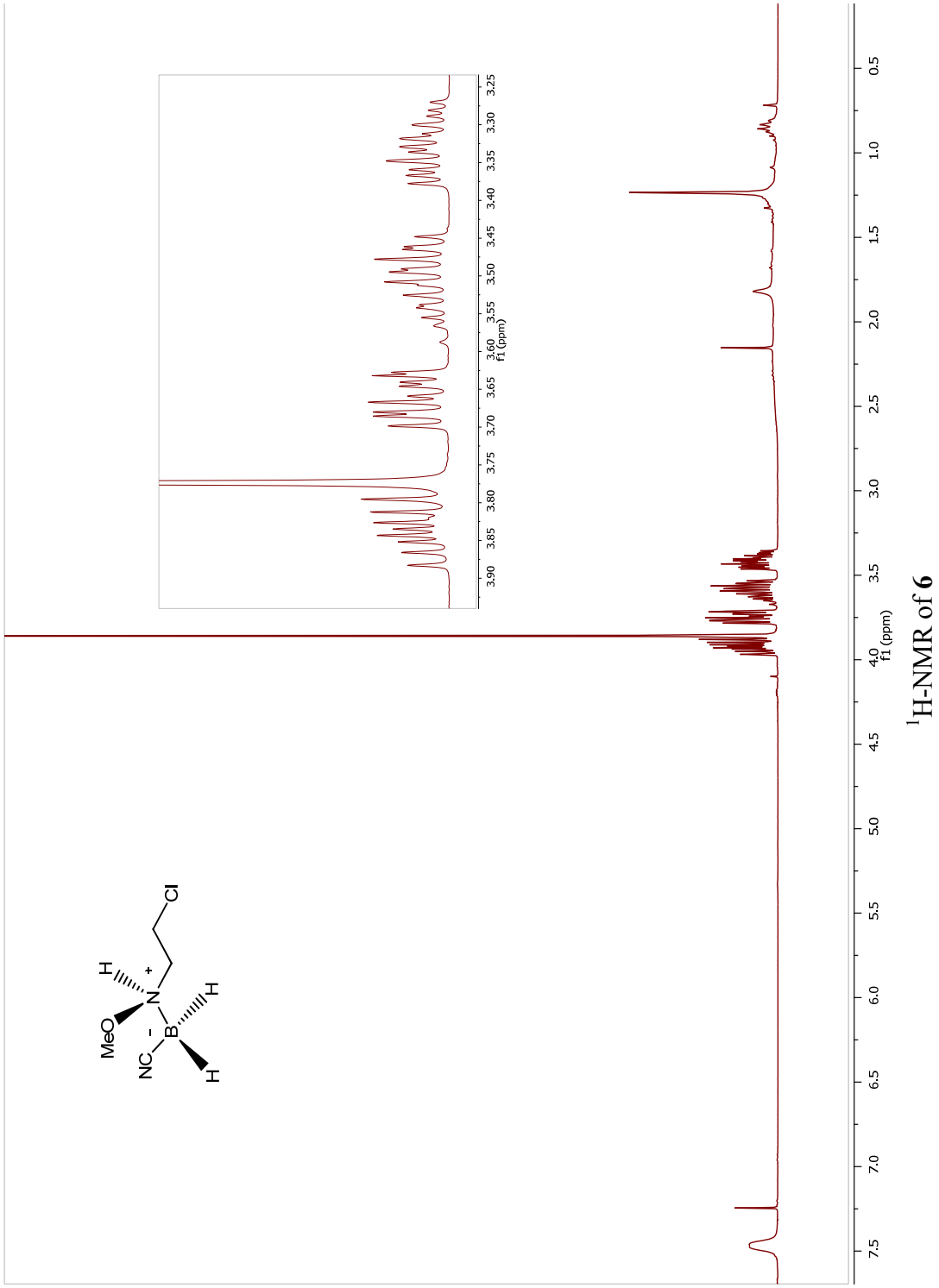
^{13}C-NMR of **4**


Br
HN
BnO
8.0
7.8
7.6
7.4
7.2
7.0
6.8
6.6
6.4
6.2
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
f1 (ppm)

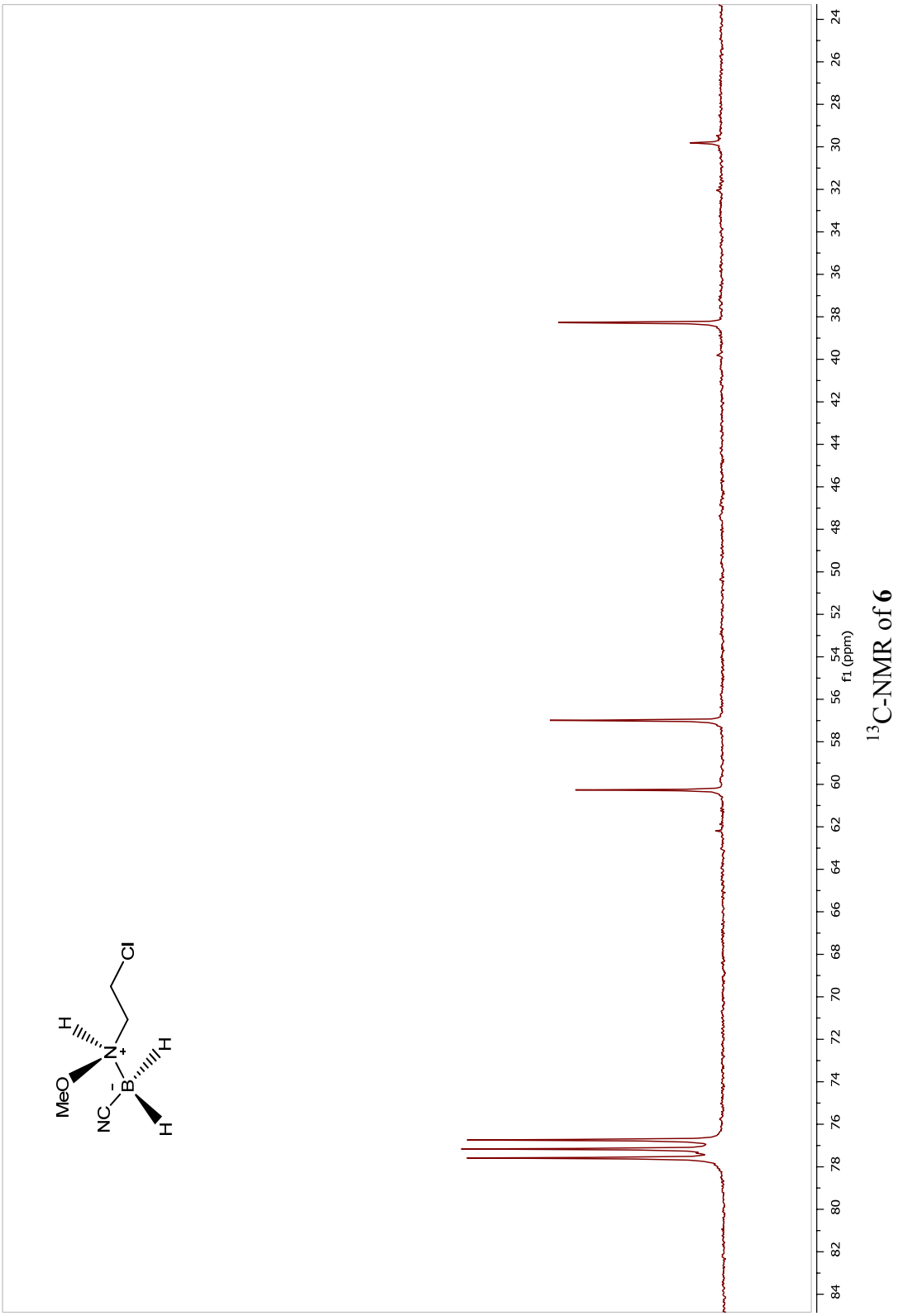
^{1}H-NMR of **5**



^{13}C-NMR of **5**

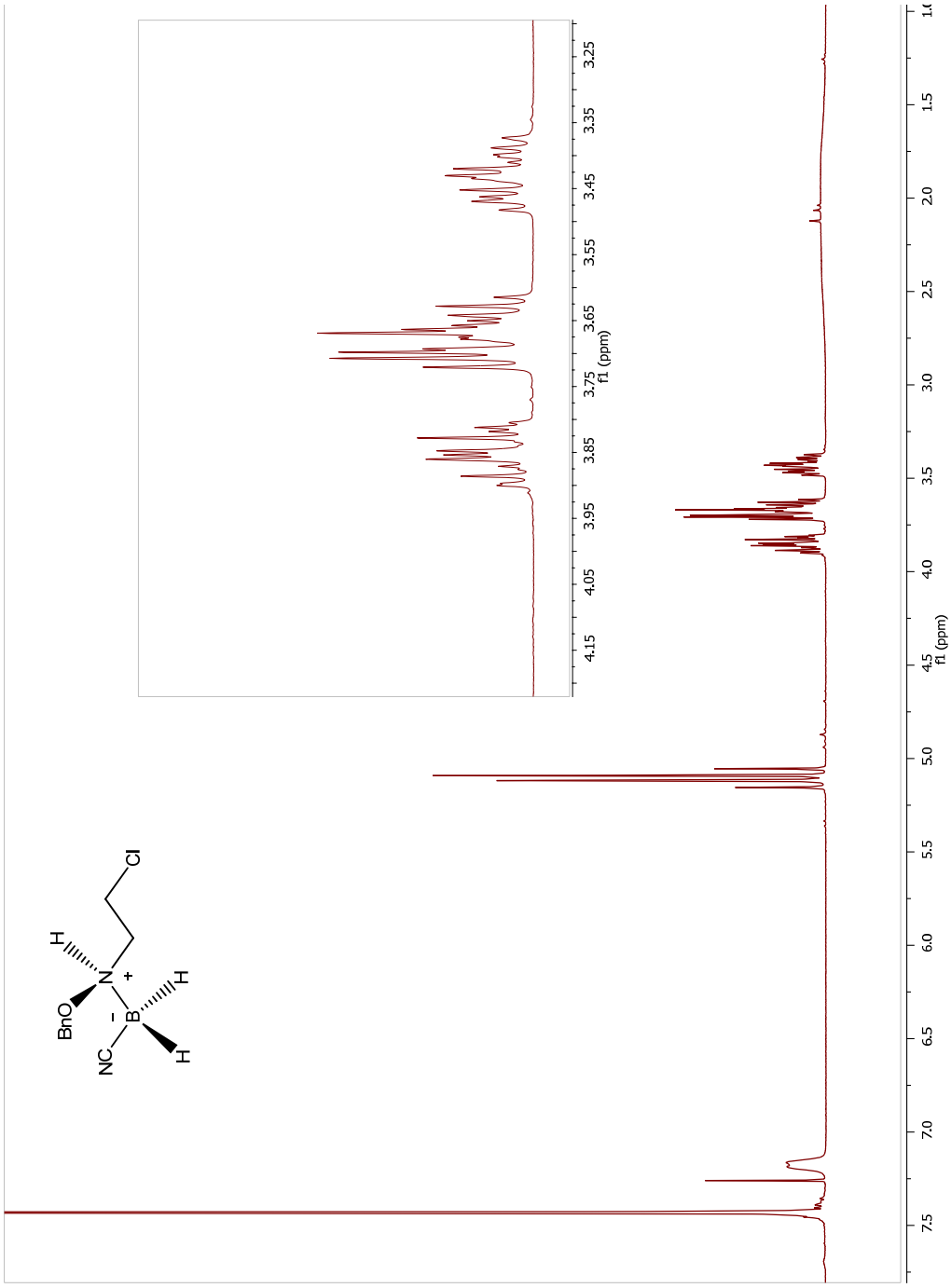


^{1}H-NMR of **6**

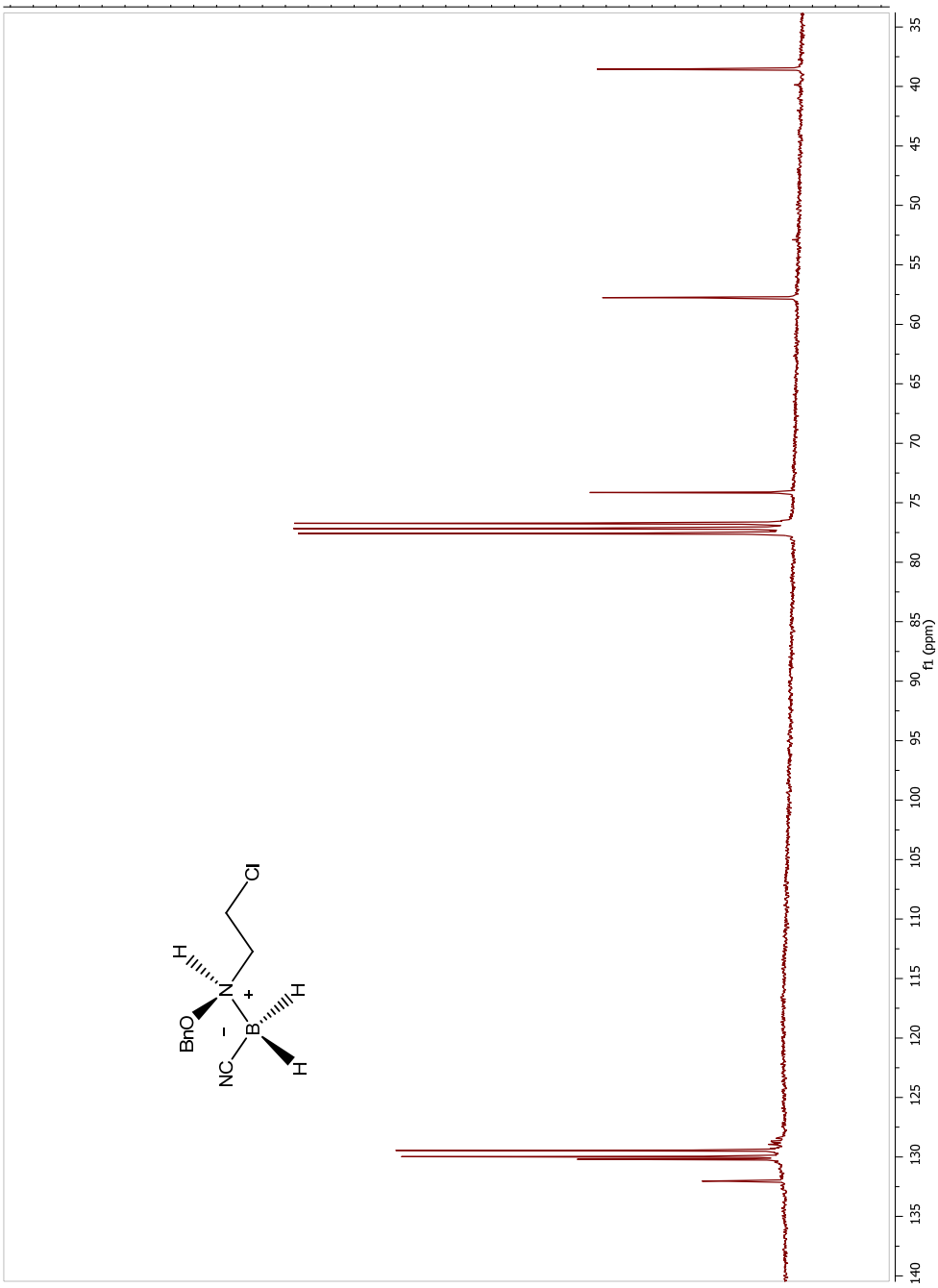


^{13}C-NMR of **6**

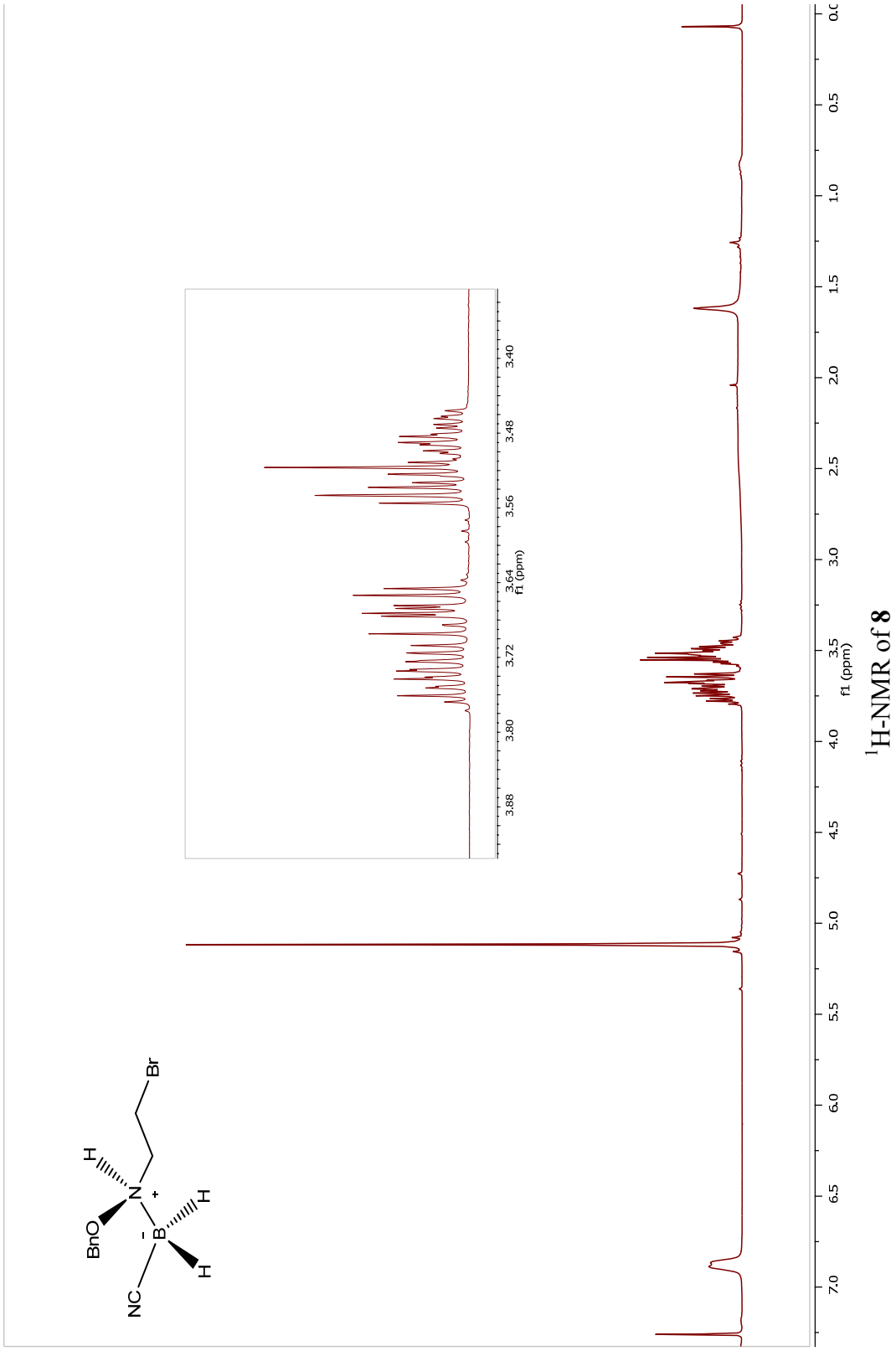
^{11}B-NMR of **6**


Cl
H
BnO
N
+
B
-
H
NC
H
3.25
3.35
3.45
3.55
3.65
3.75
3.85
3.95
4.05
4.15
f1 (ppm)
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)

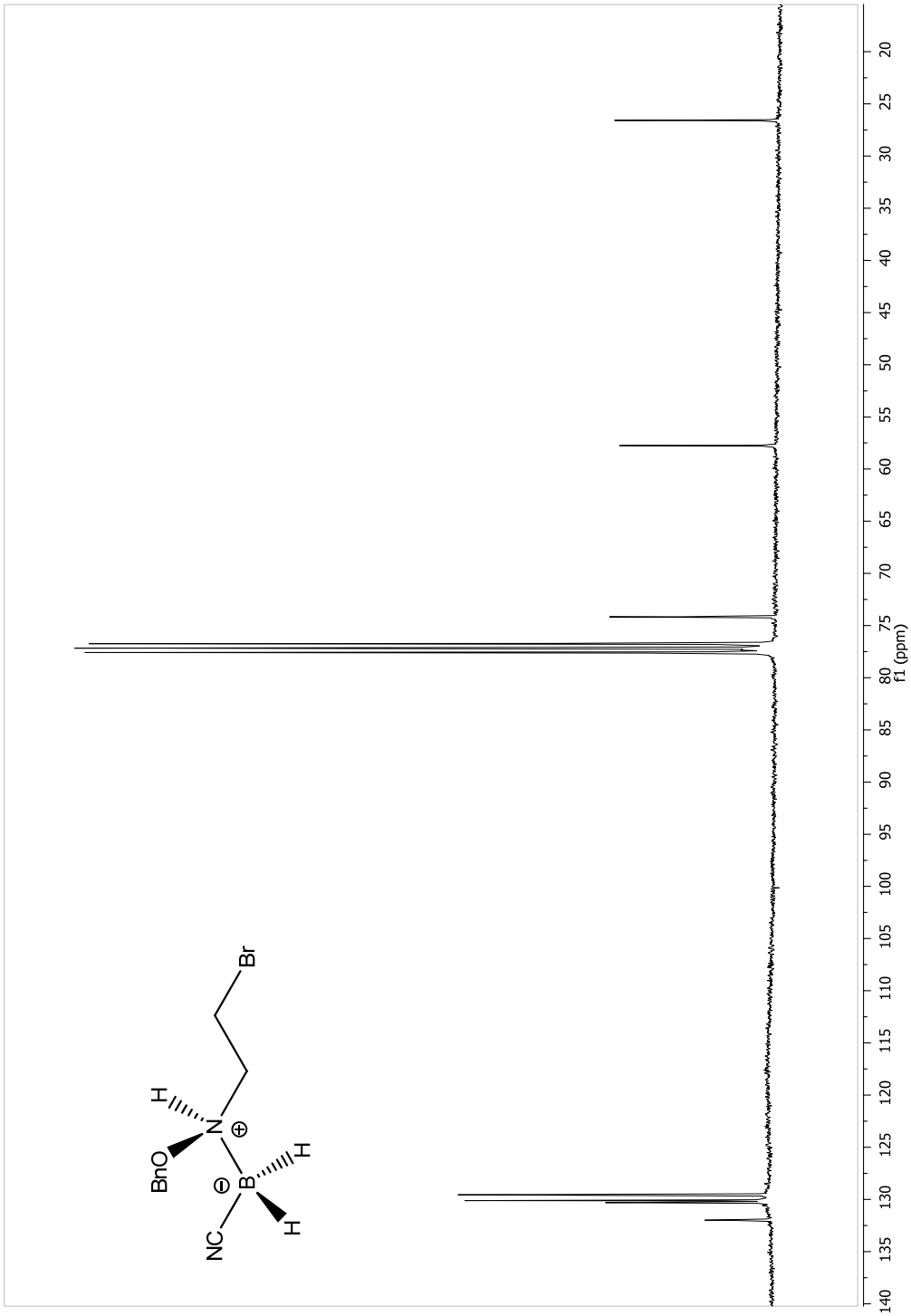
^{1}H-NMR of **7**


Cl
H
N
+
BnO
B
H
-
NC
H
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140
f1 (ppm)

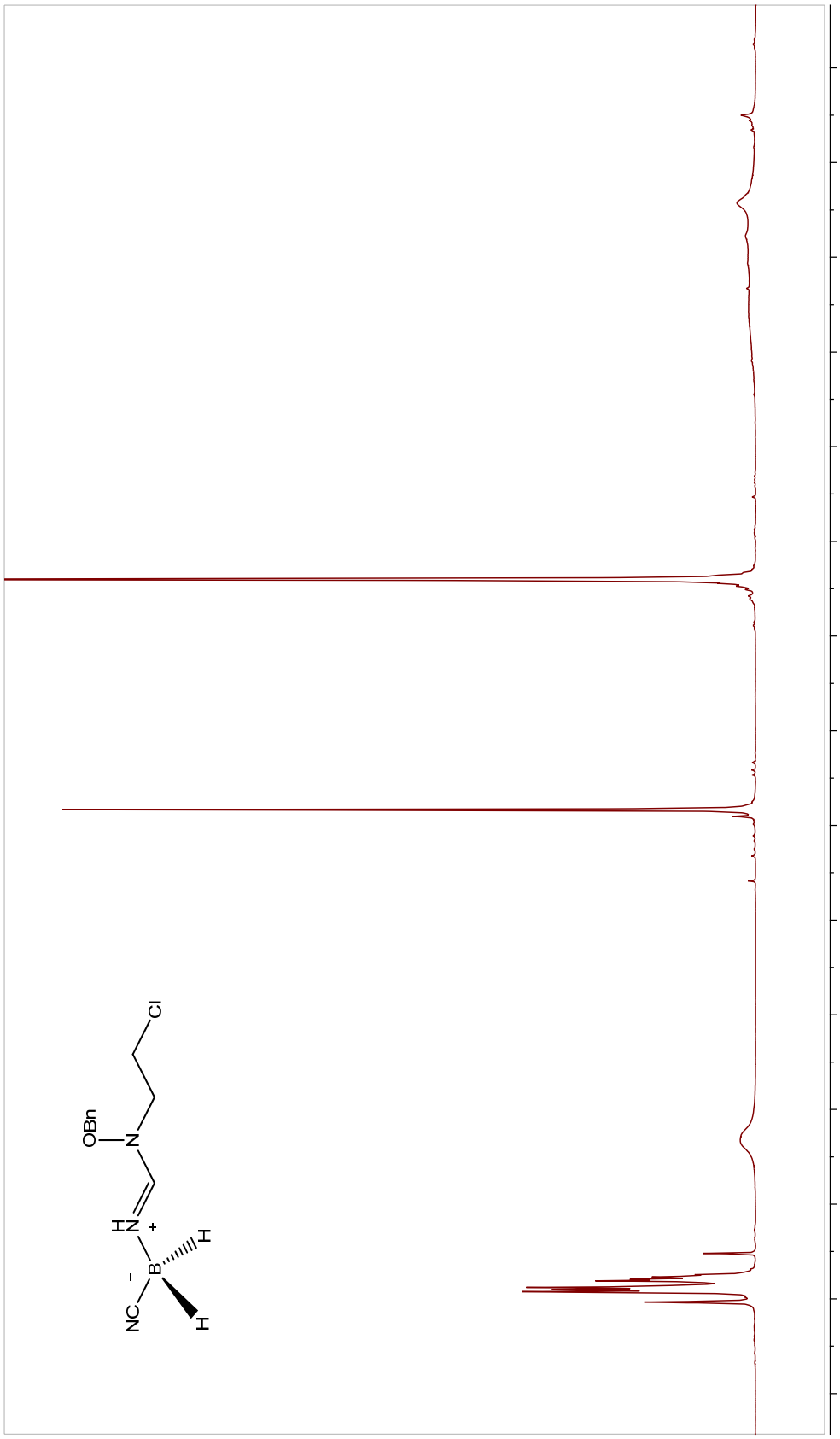
^{13}C-NMR of **7**



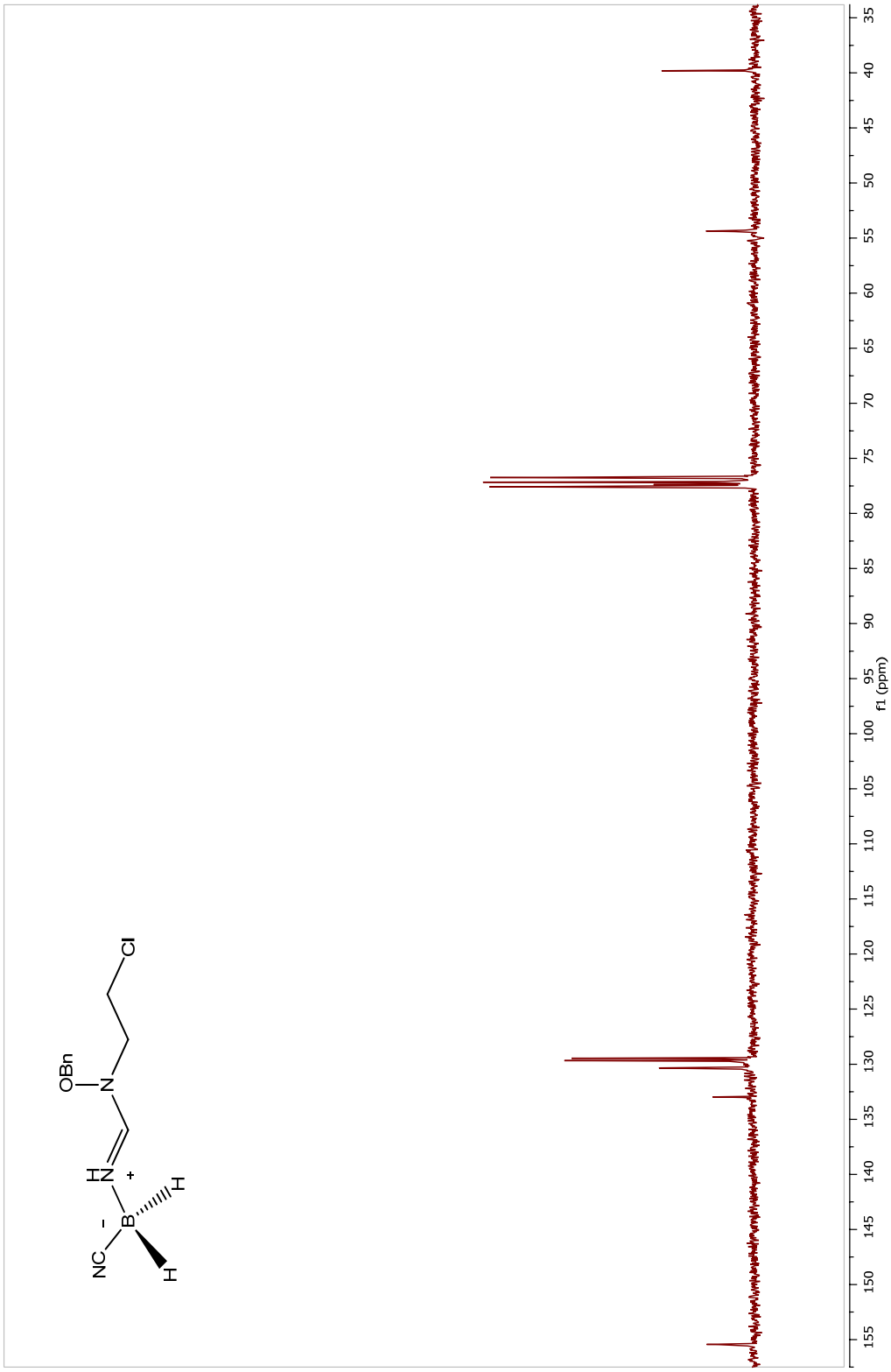
^{1}H-NMR of **8**


Br
H
N
⊕
BnO
B
⊖
H
NC
H
f1 (ppm)
20
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140

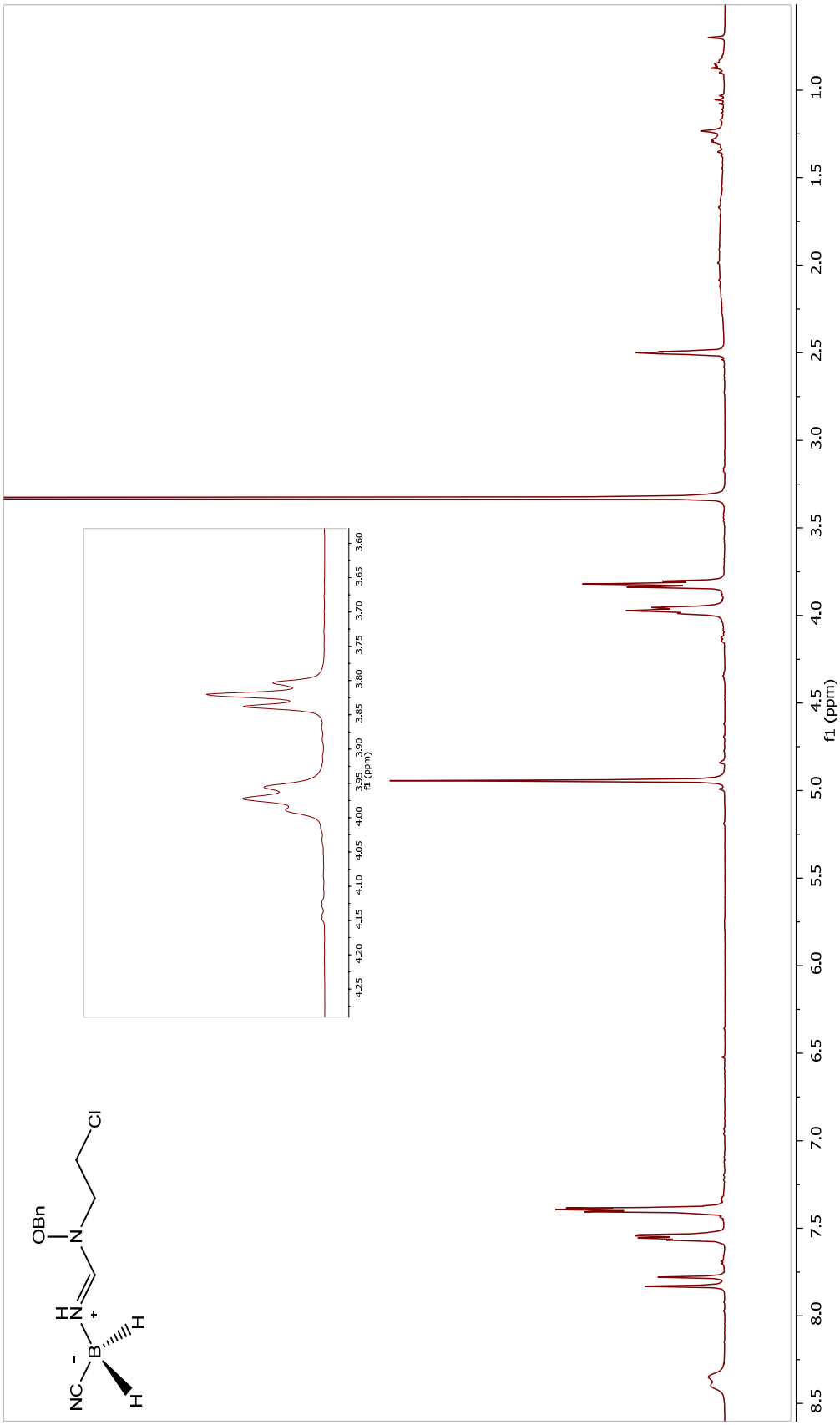
^{13}C-NMR of **8**



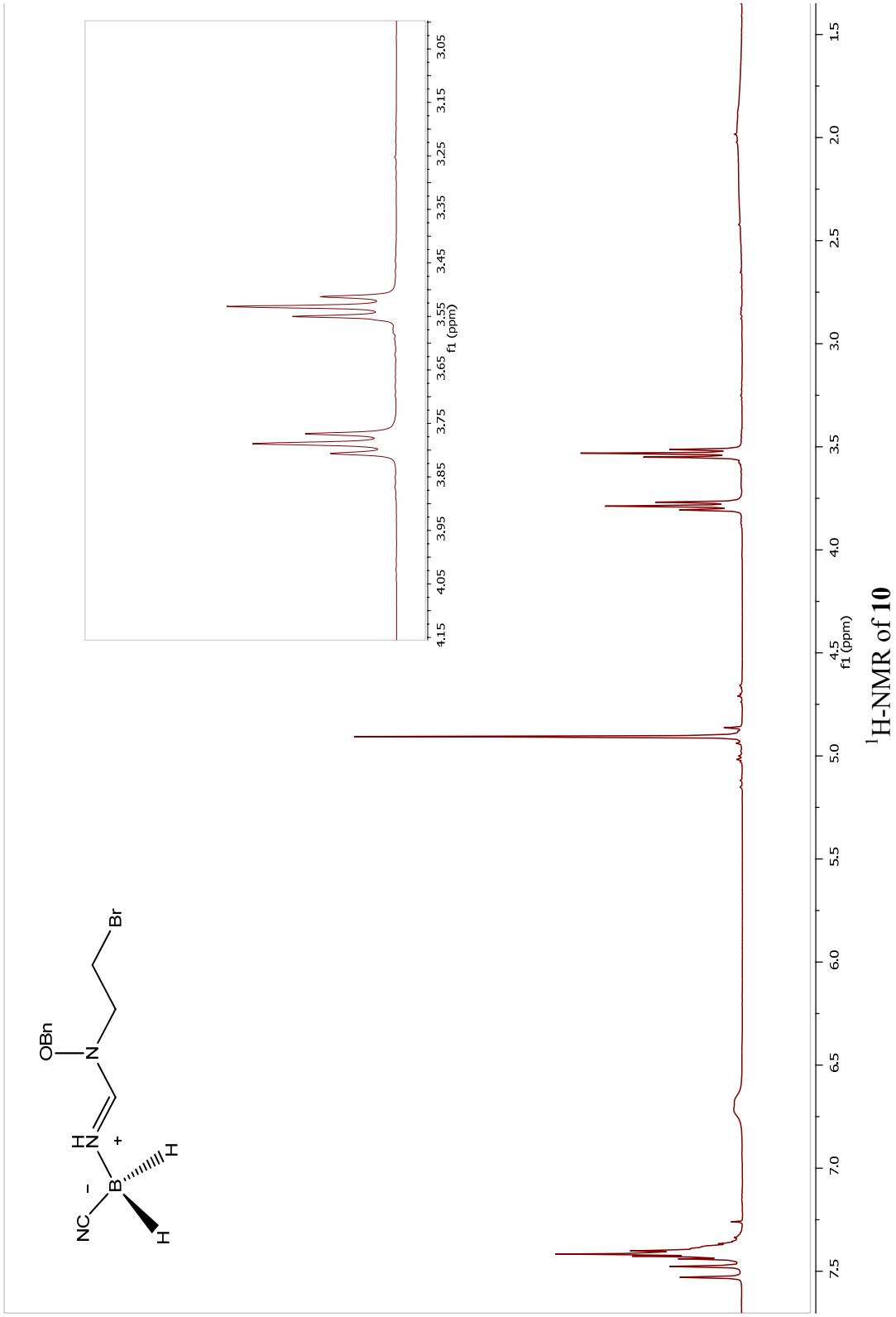
^{1}H-NMR of **9** ($CDCl_3$)



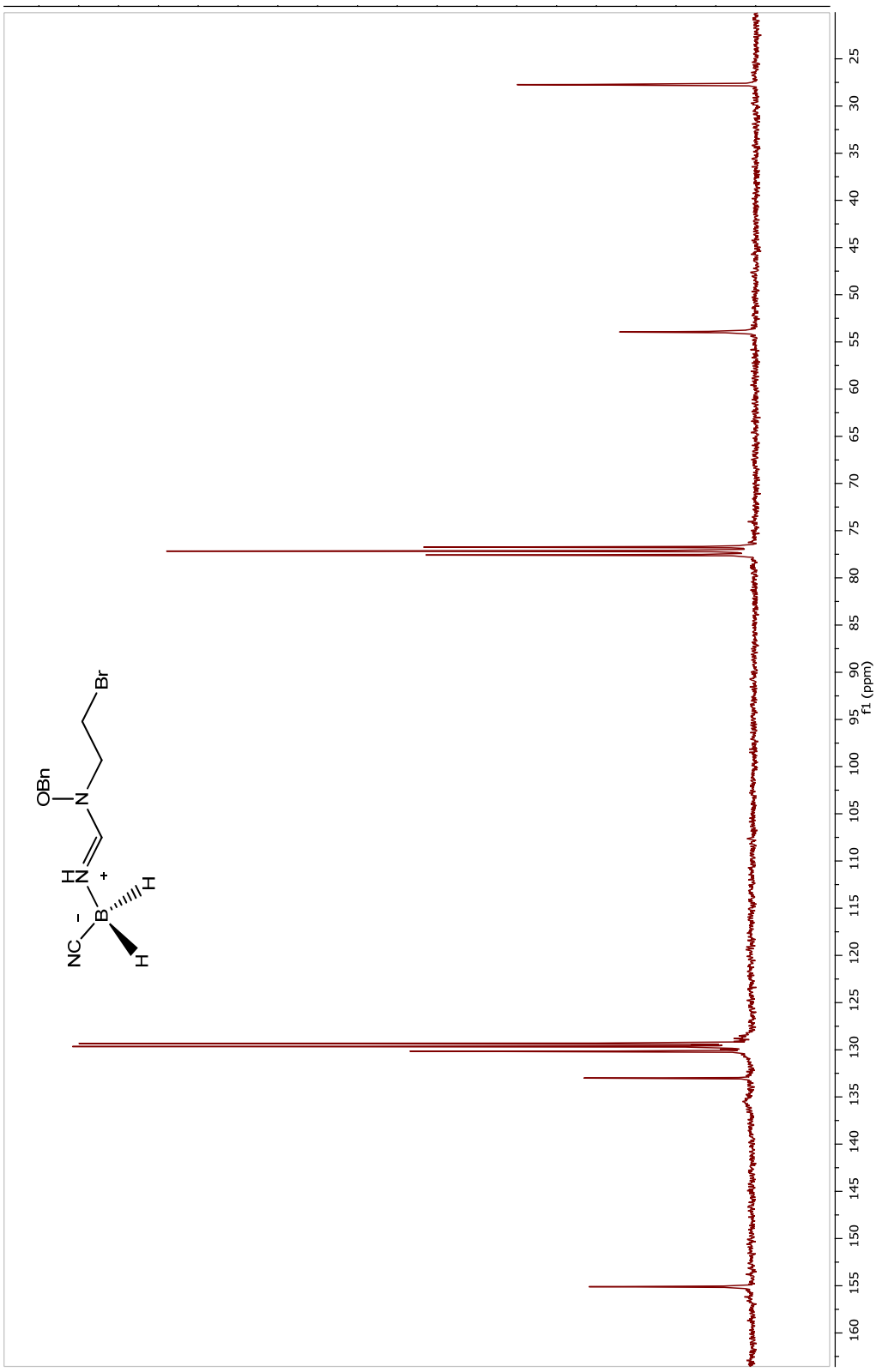
^{13}C-NMR of **9** ($CDCl_3$)



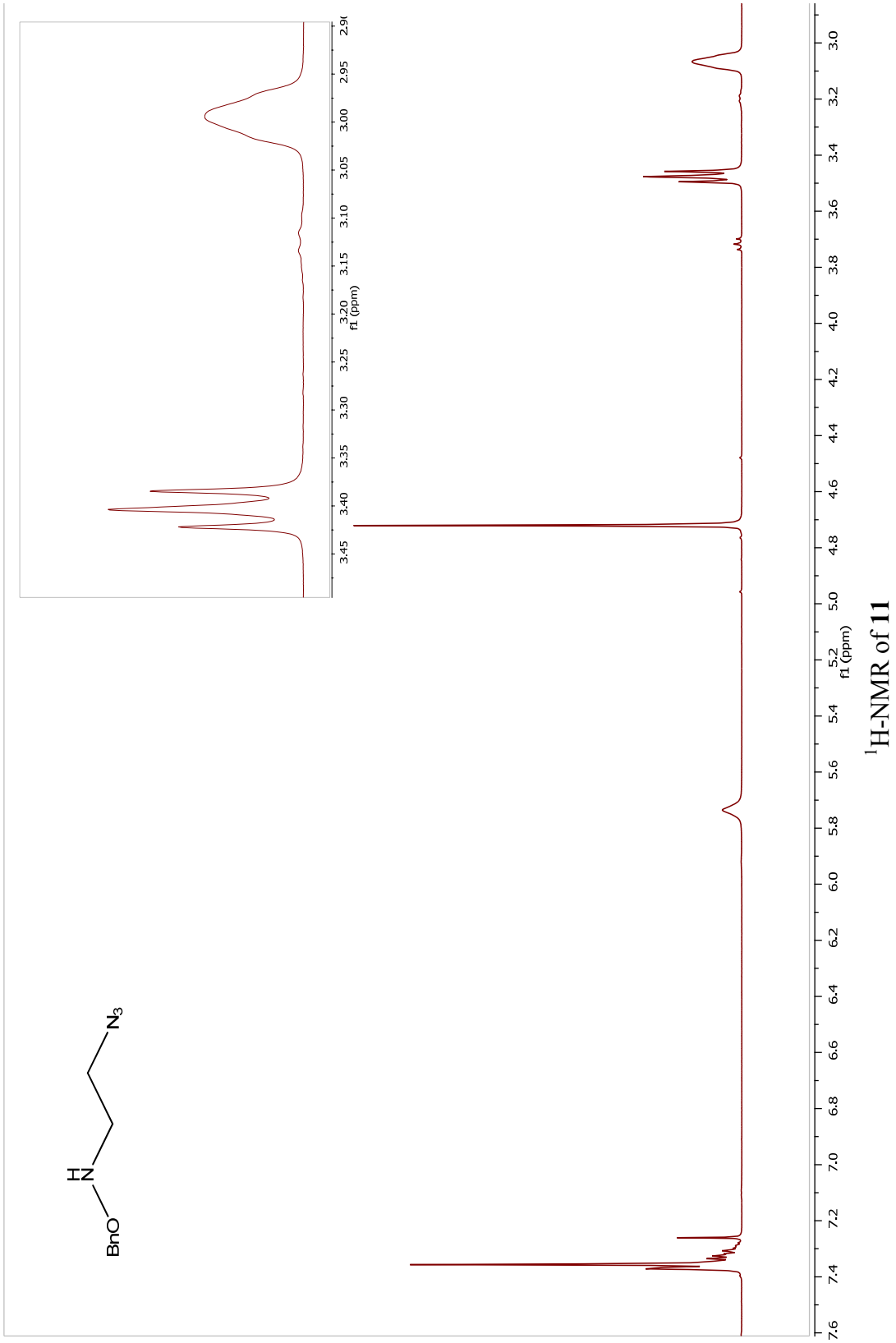
^{1}H-NMR of **9** (DMSO-*d6*)



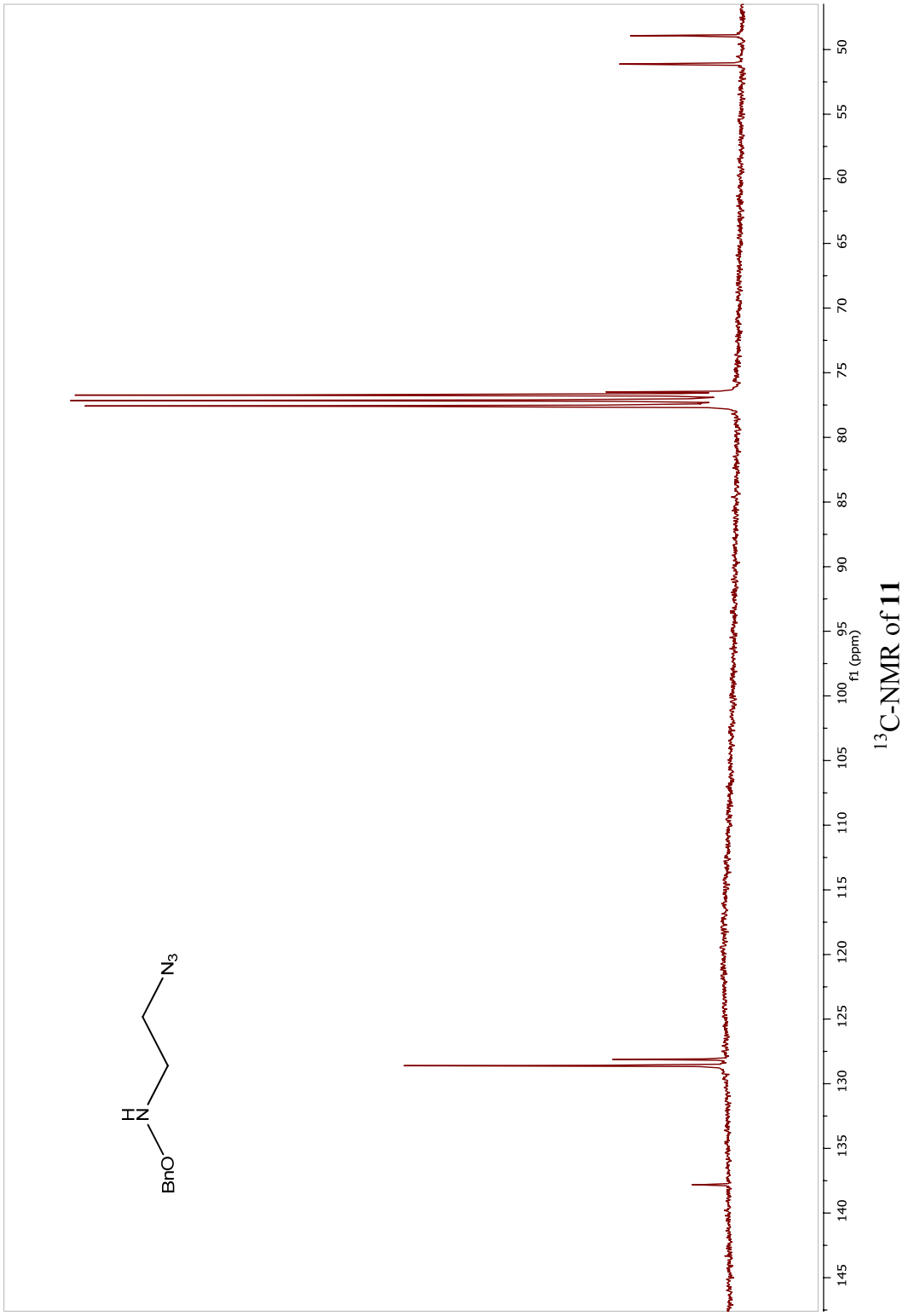
^{1}H-NMR of **10**



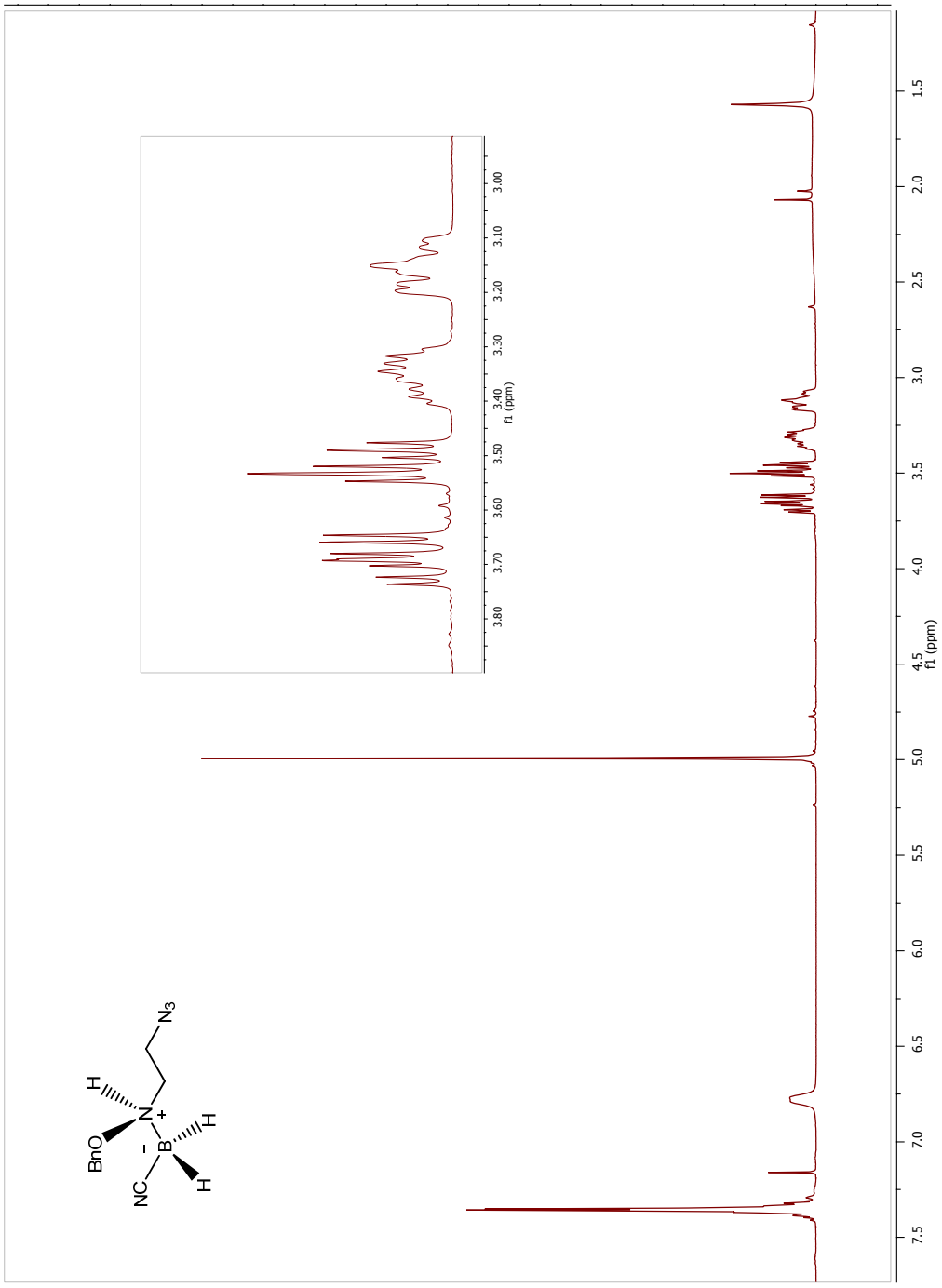
^{13}C-NMR of **10**



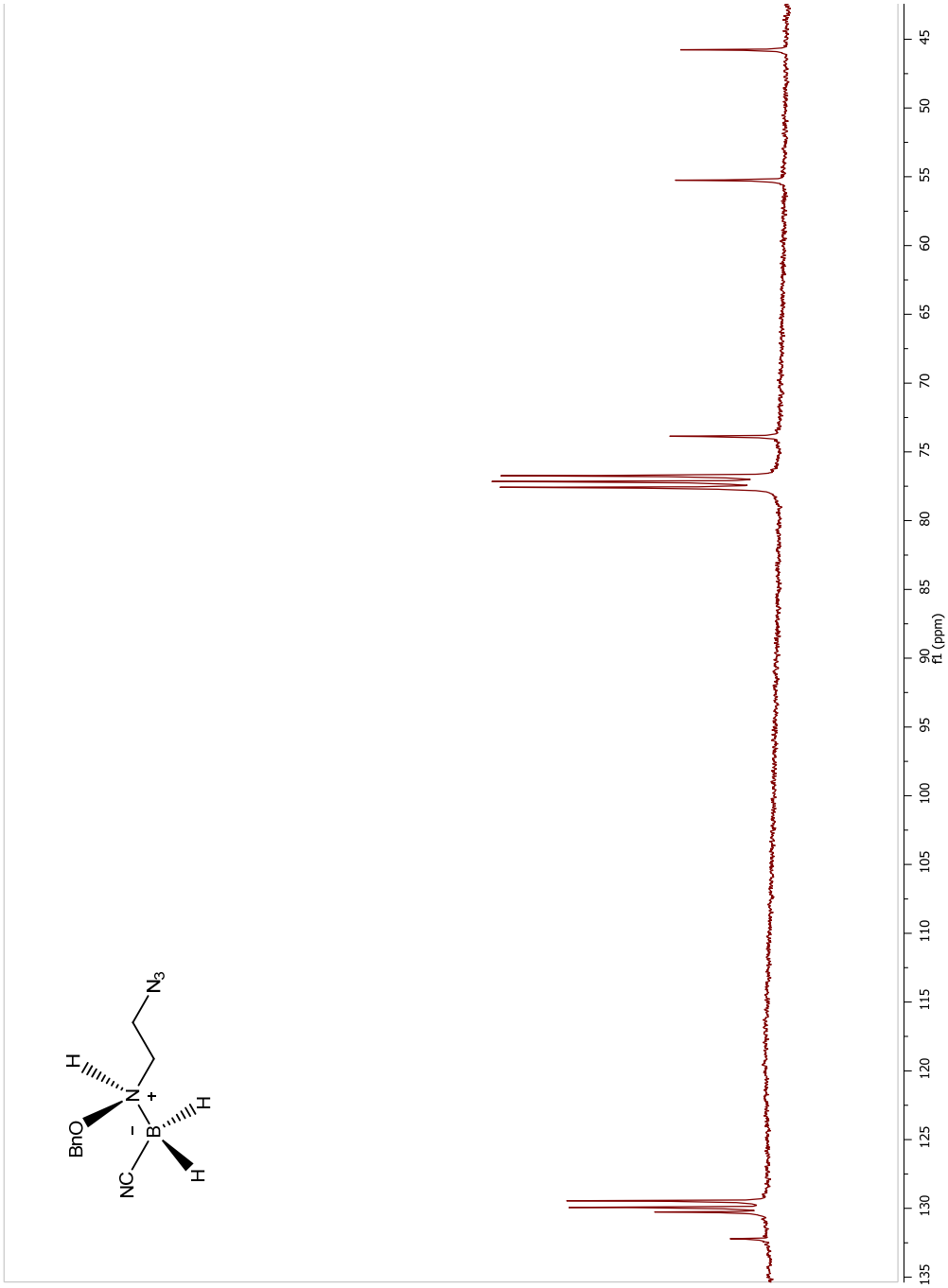
^{1}H-NMR of **11**



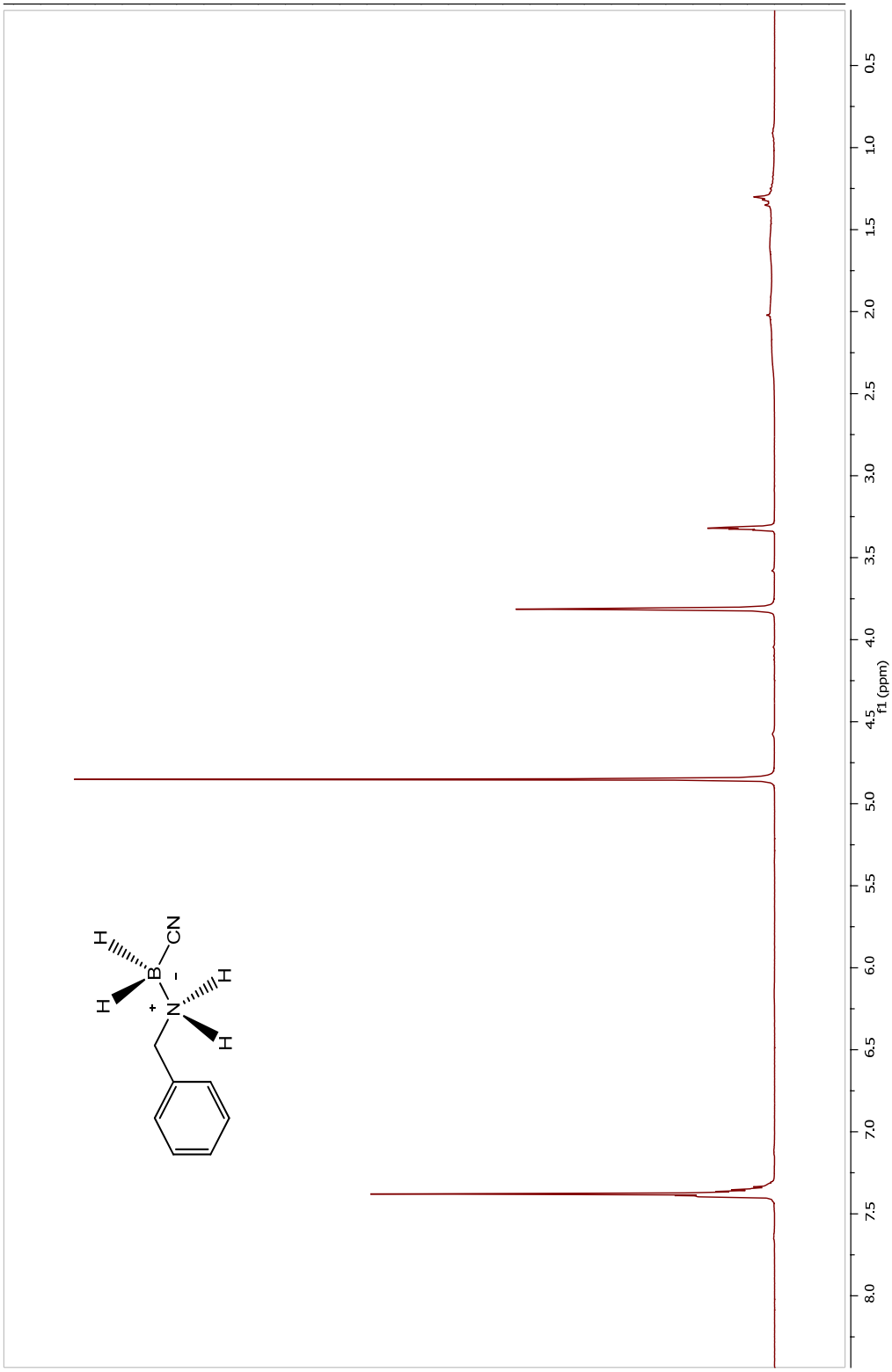
^{13}C-NMR of **11**


H
BnO
N+
B
-
NC
H
H
N3
f1 (ppm)
3.40
3.00
3.10
3.20
3.30
3.50
3.60
3.70
3.80
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5

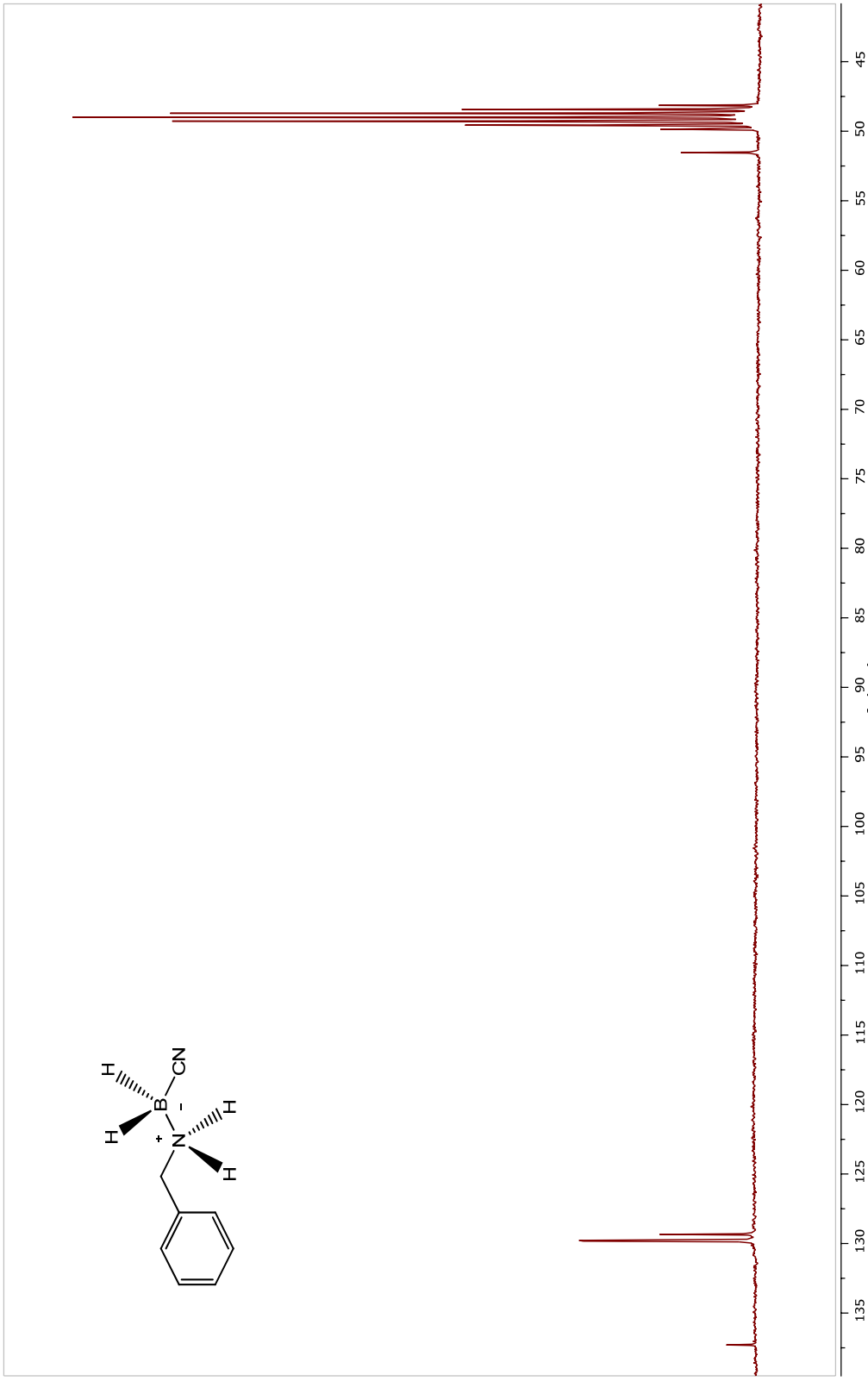
^{1}H-NMR of **12**



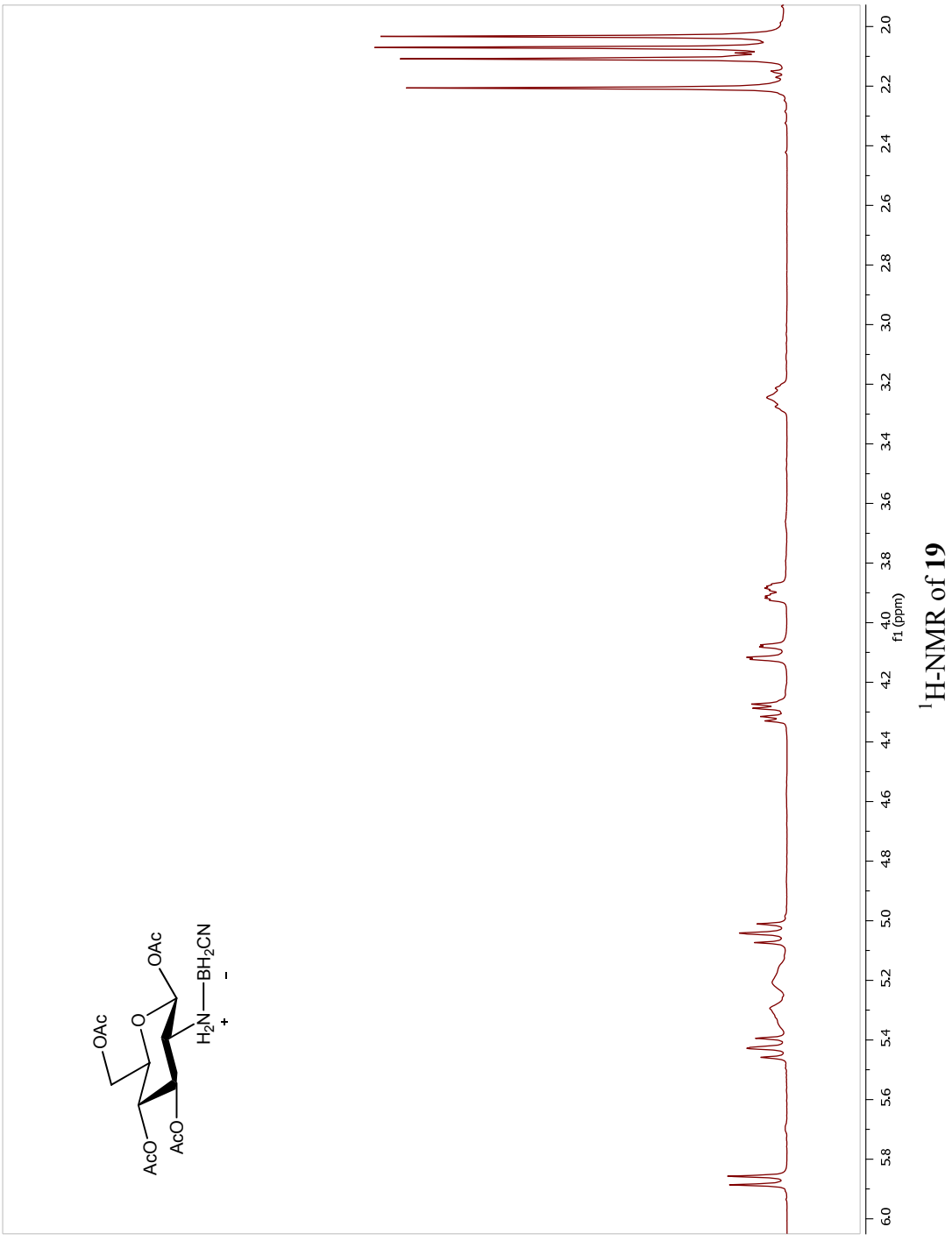
^{13}C-NMR of **12**



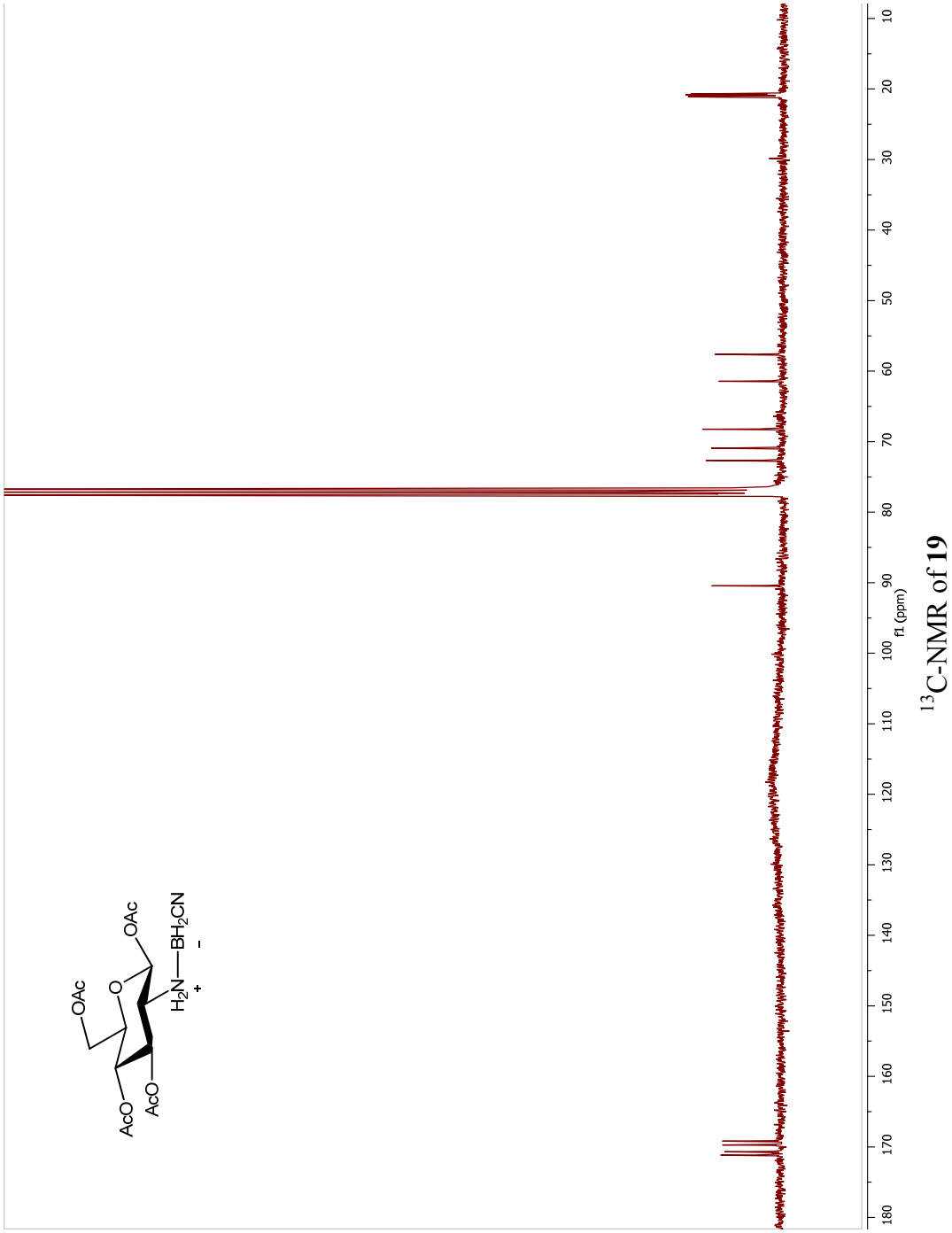
^{1}H-NMR of **18**



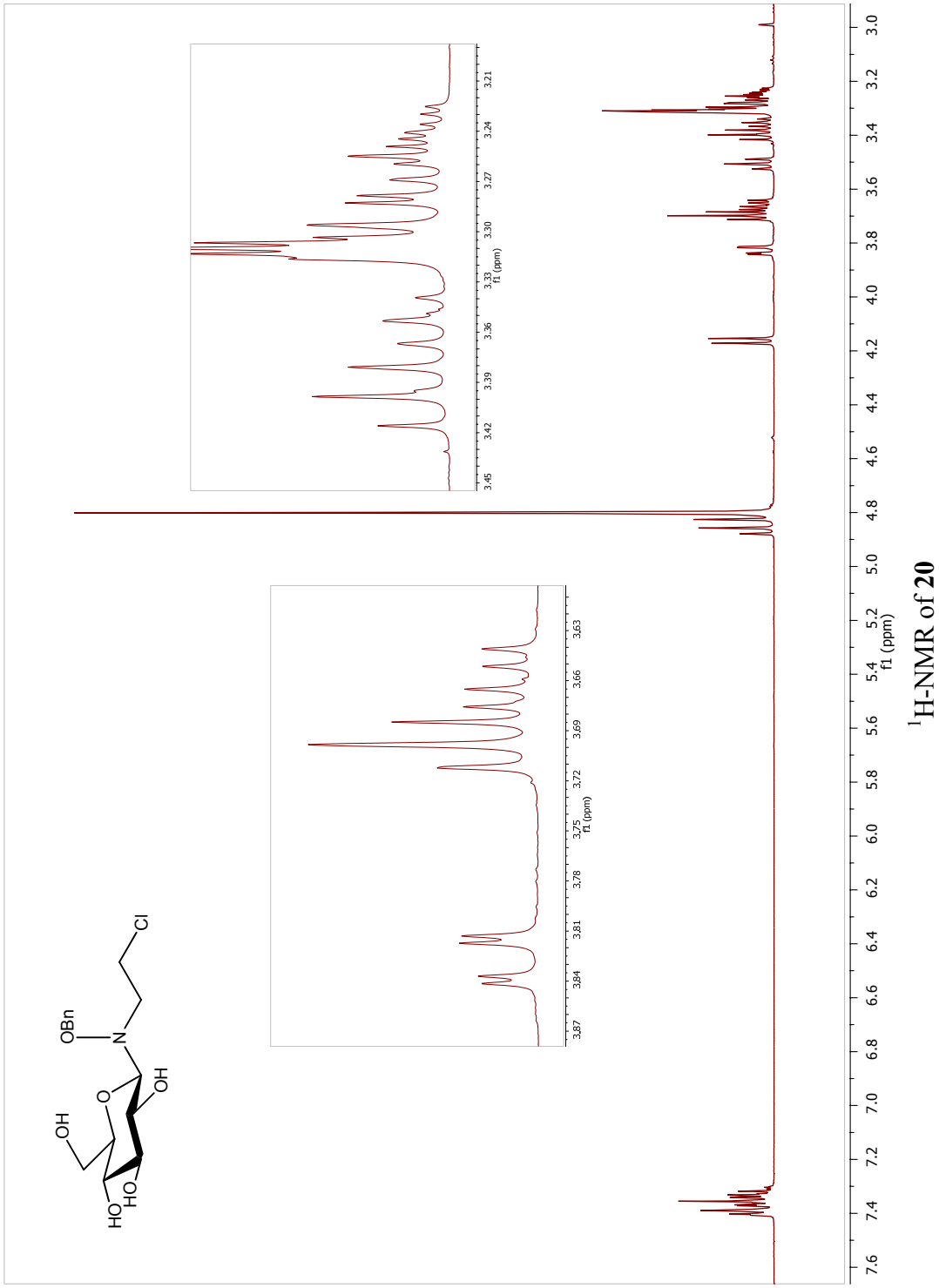
^{13}C-NMR of **18**


OAc
O
OAc
BH2CN
H2N
AcO
AcO
6.0
5.8
5.6
5.4
5.2
5.0
4.8
4.6
4.4
4.2
4.0
3.8
3.6
3.4
3.2
3.0
2.8
2.6
2.4
2.2
2.0
f1 (ppm)

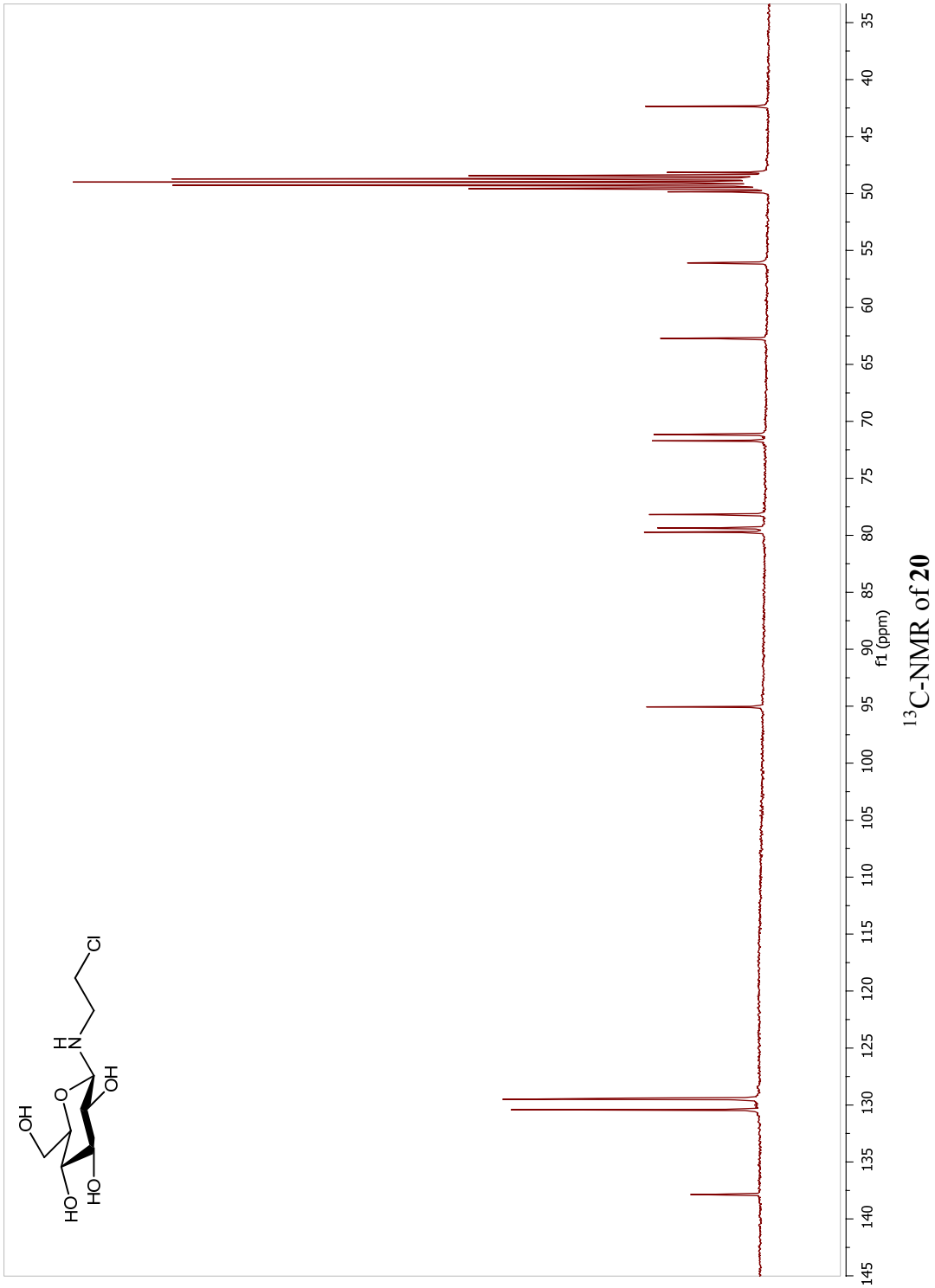
^{1}H-NMR of **19**



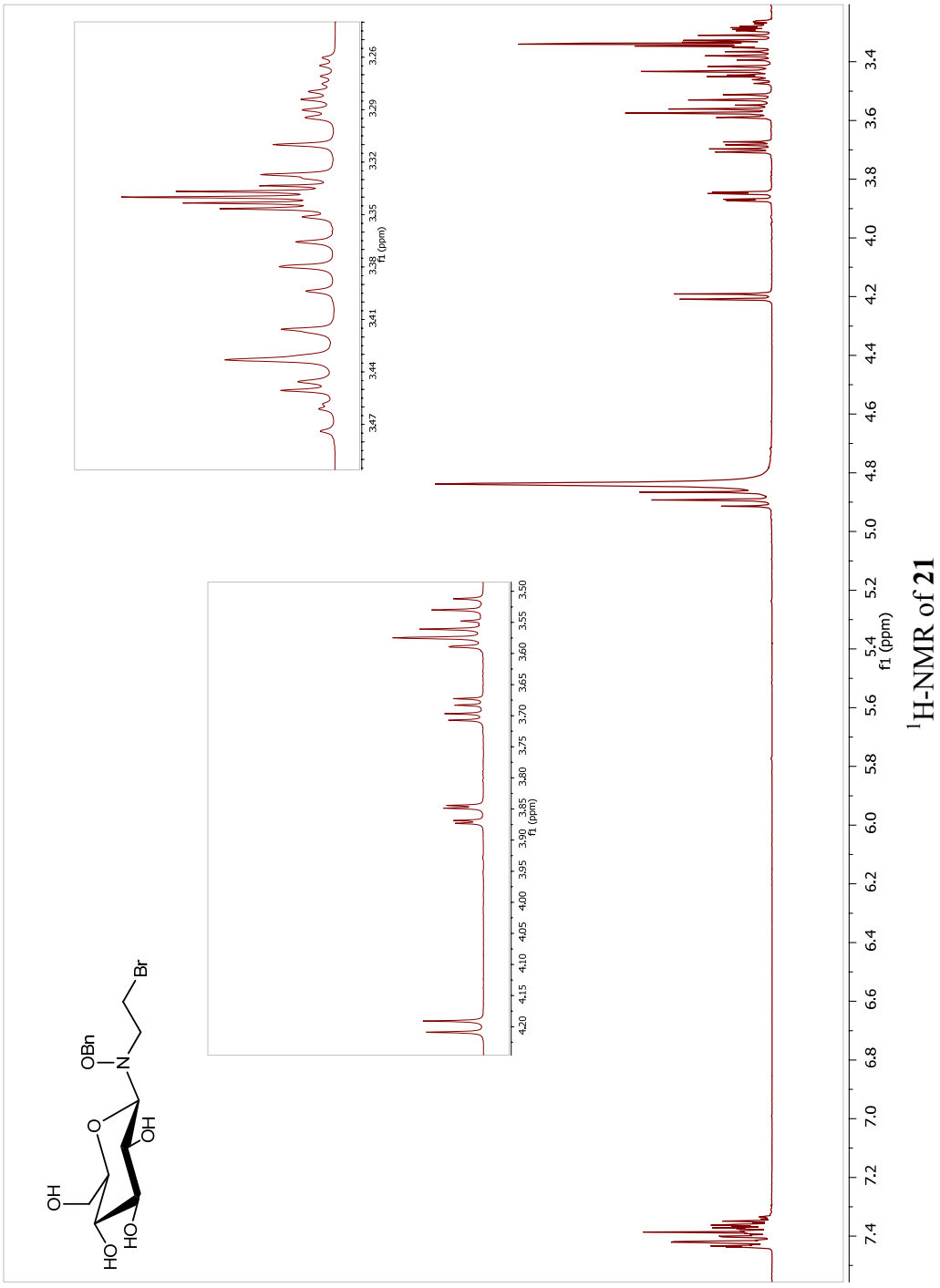
^{13}C-NMR of **19**



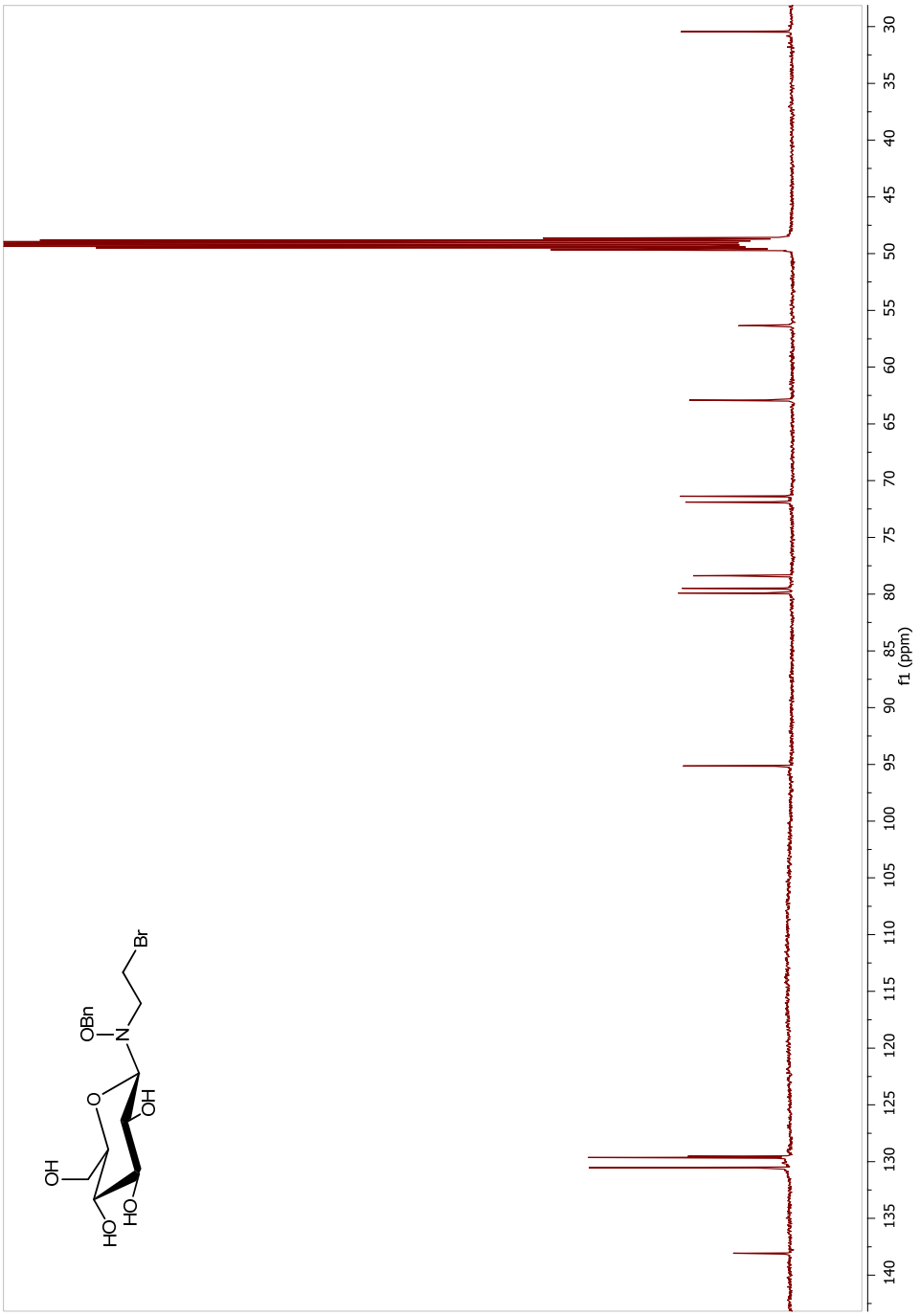
^{1}H-NMR of **20**



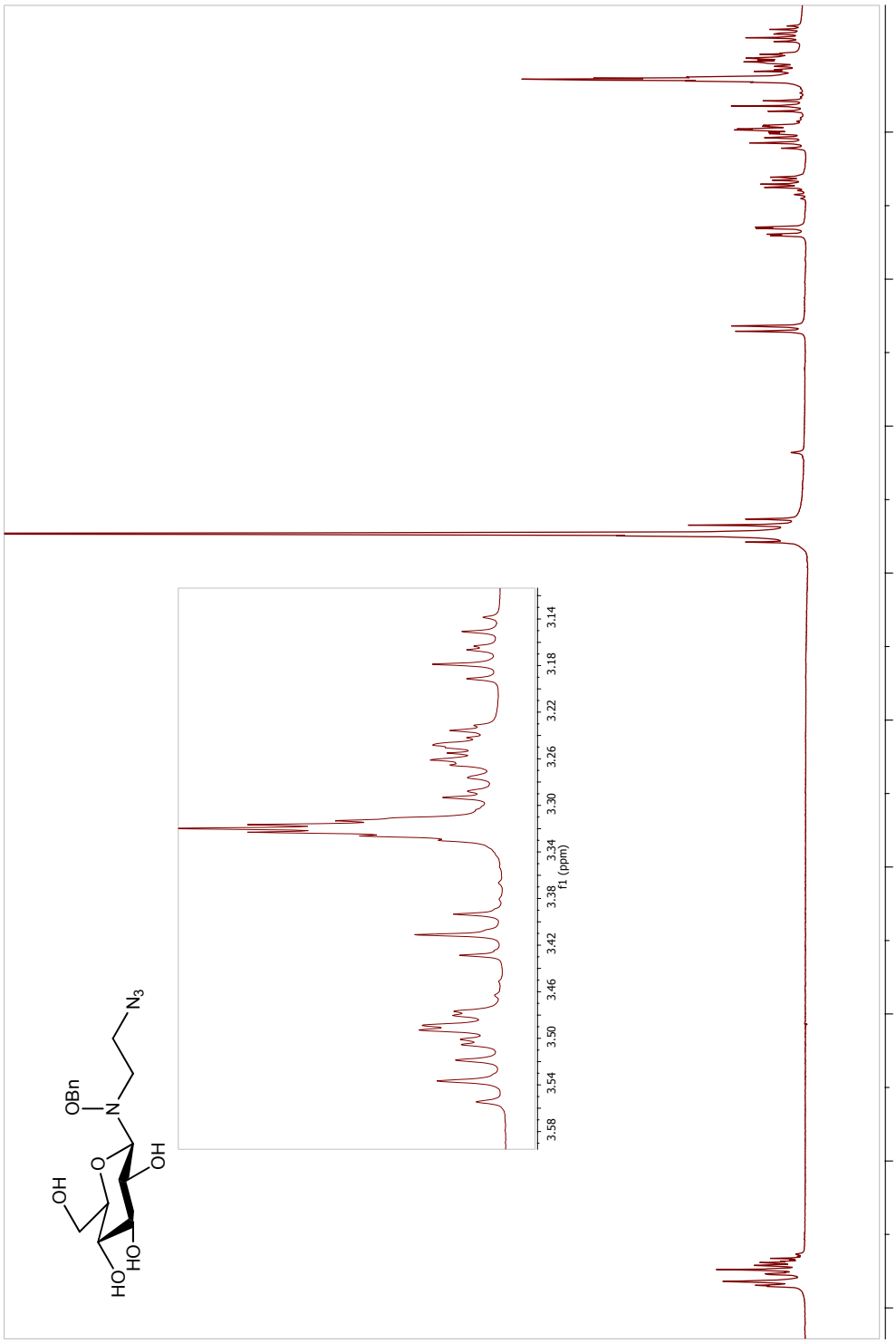
^{13}C-NMR of **20**



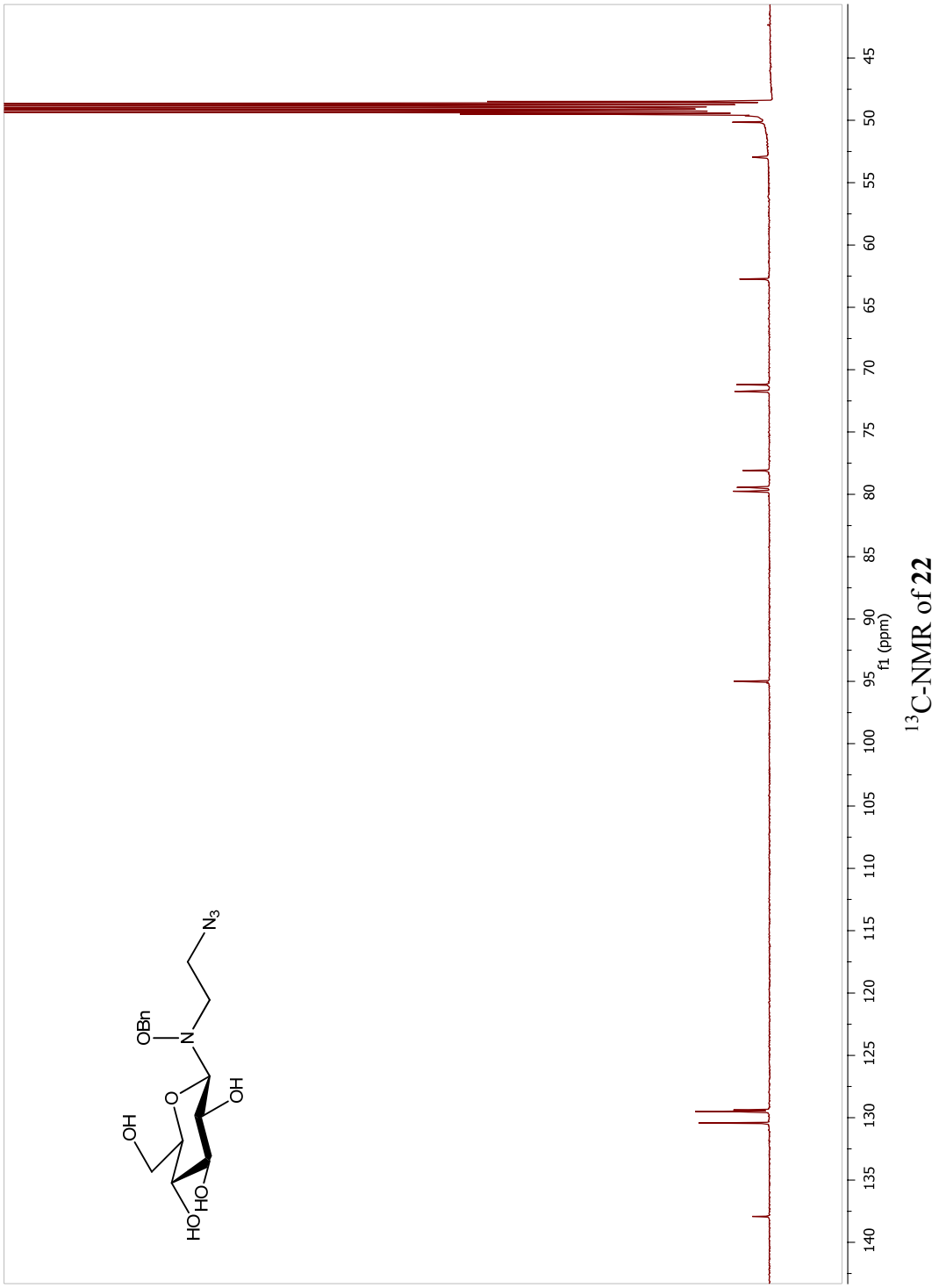
^{1}H-NMR of **21**



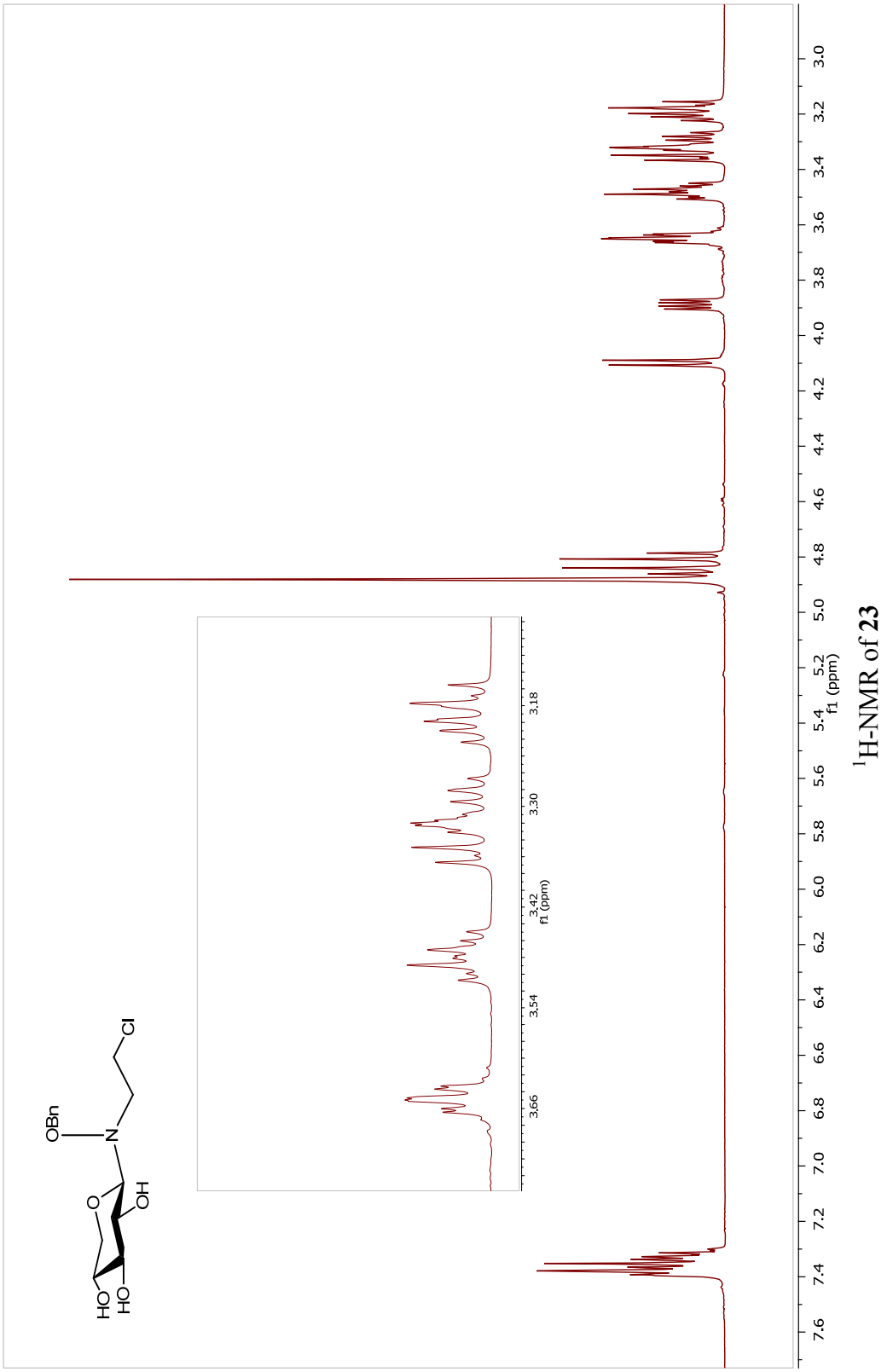
^{13}C-NMR of **21**



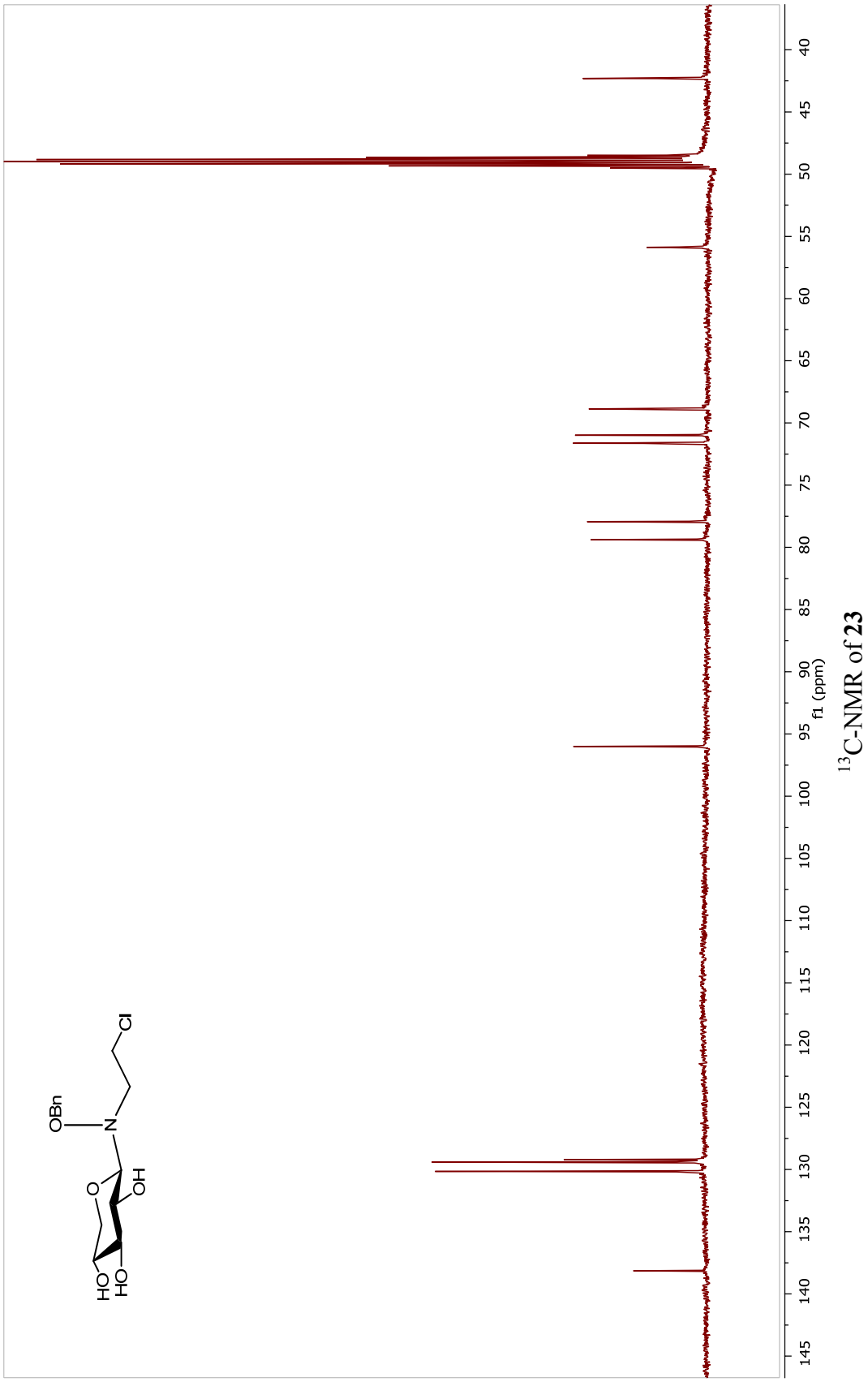
^{1}H-NMR of **22**



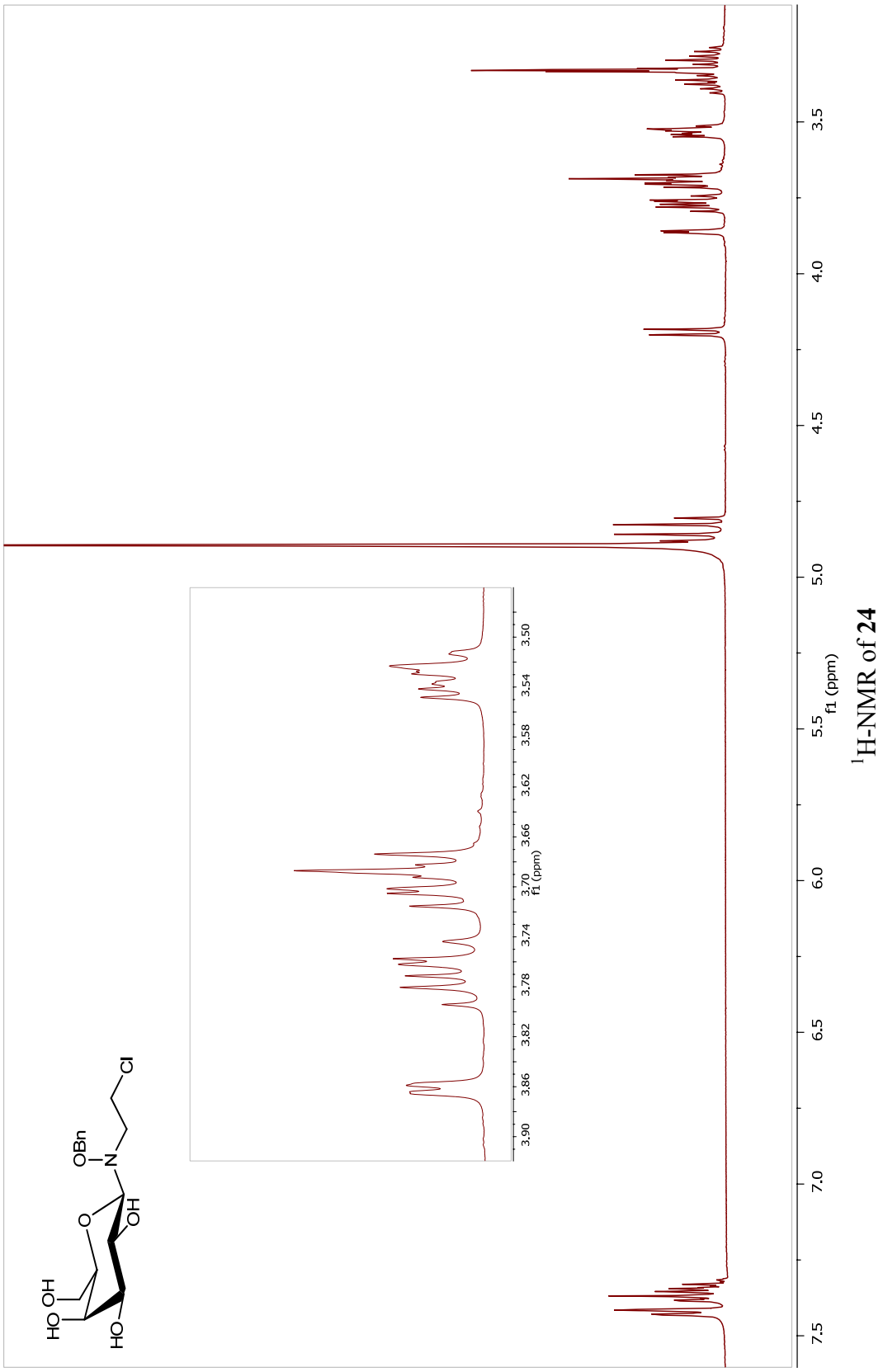
^{13}C-NMR of **22**



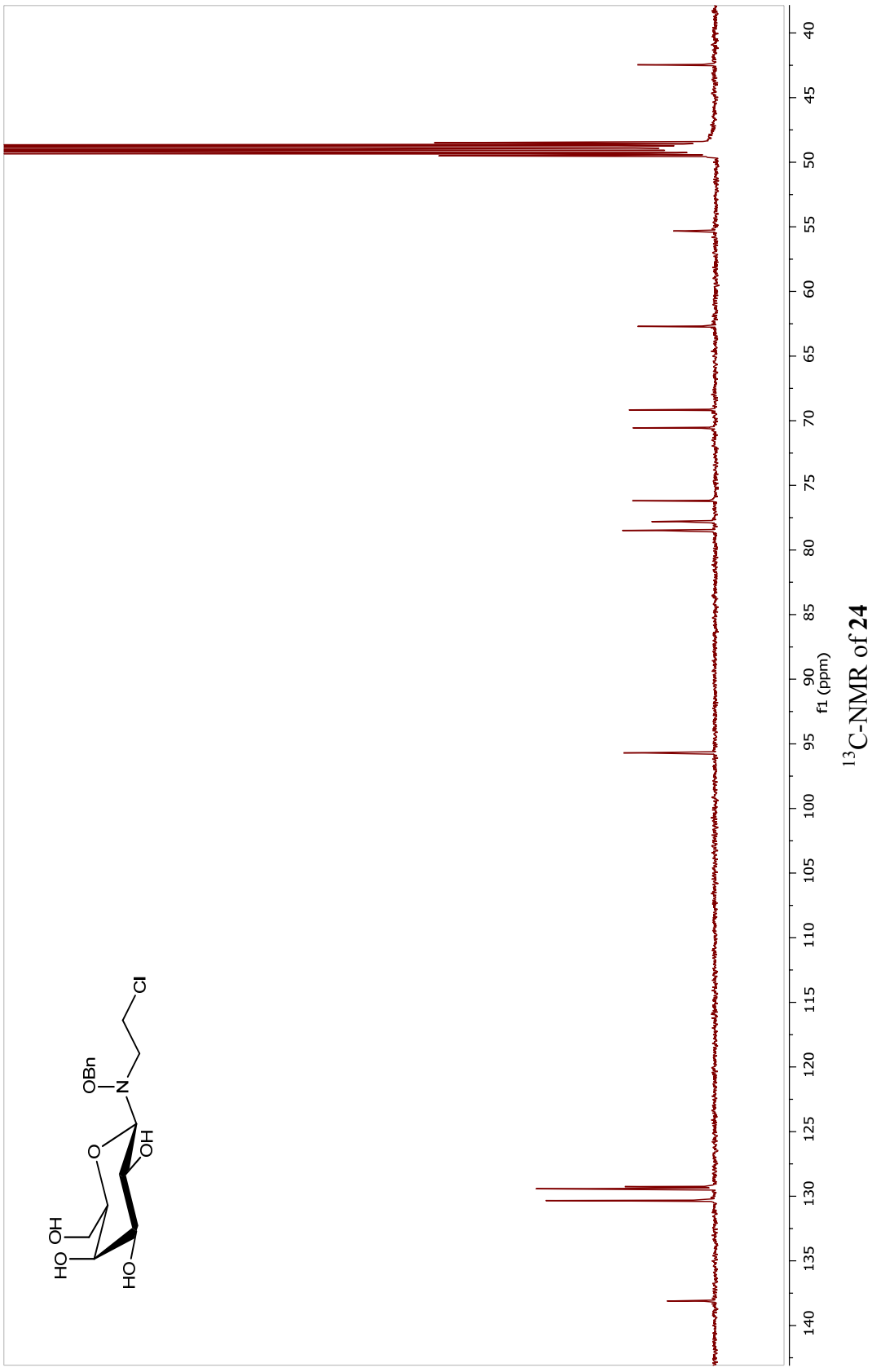
^{1}H-NMR of **23**



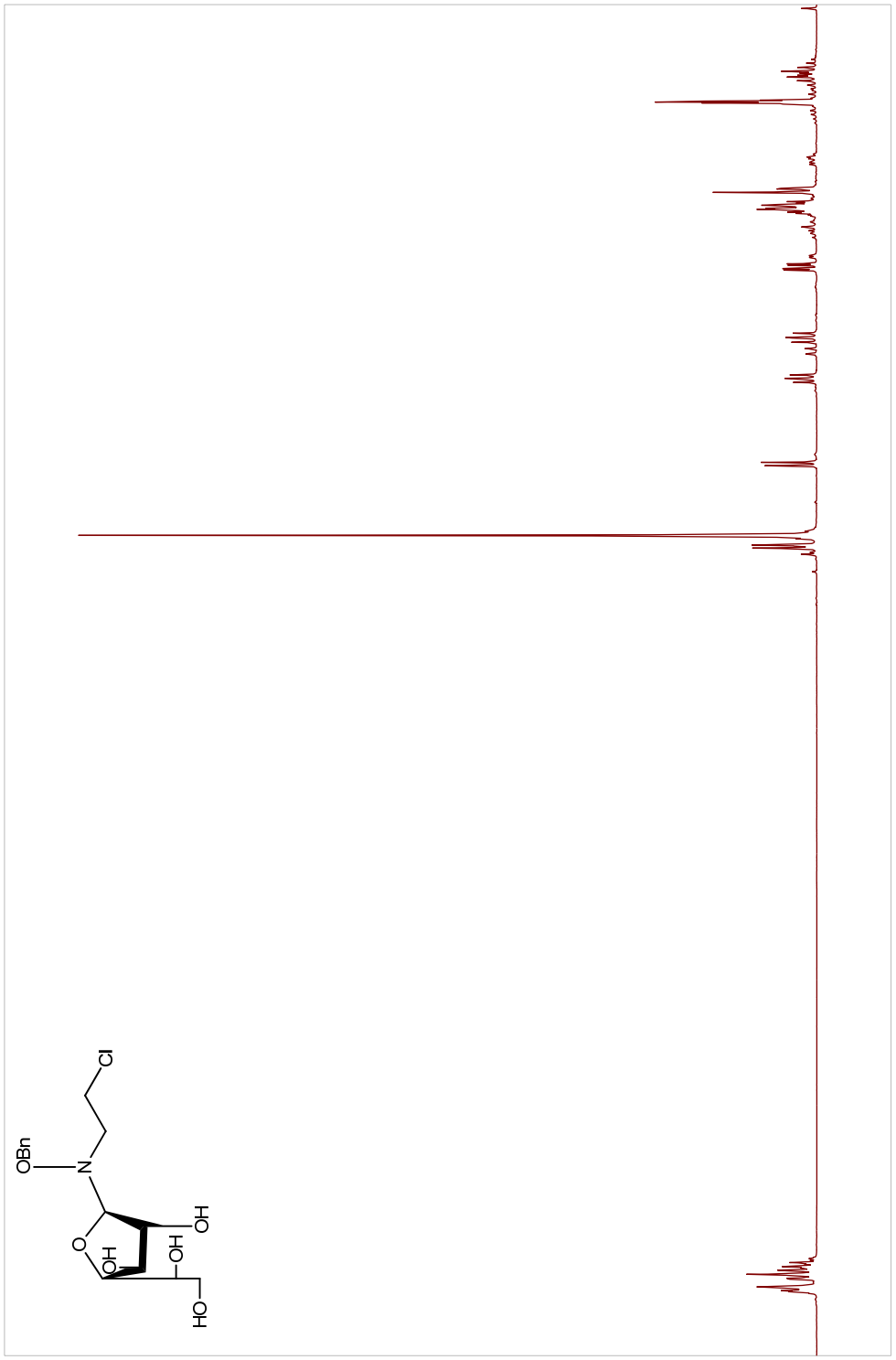
^{13}C-NMR of **23**



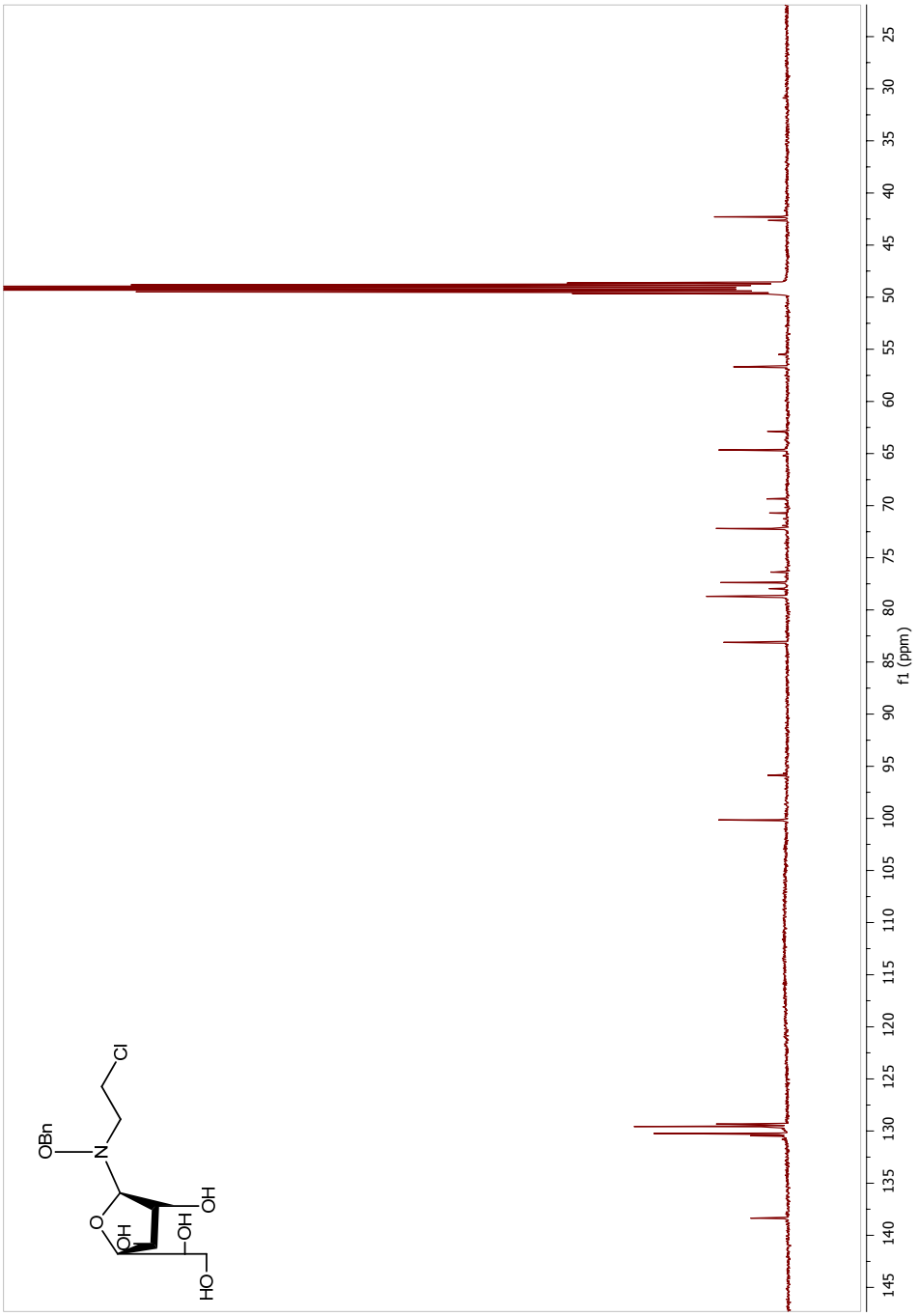
^{1}H-NMR of **24**



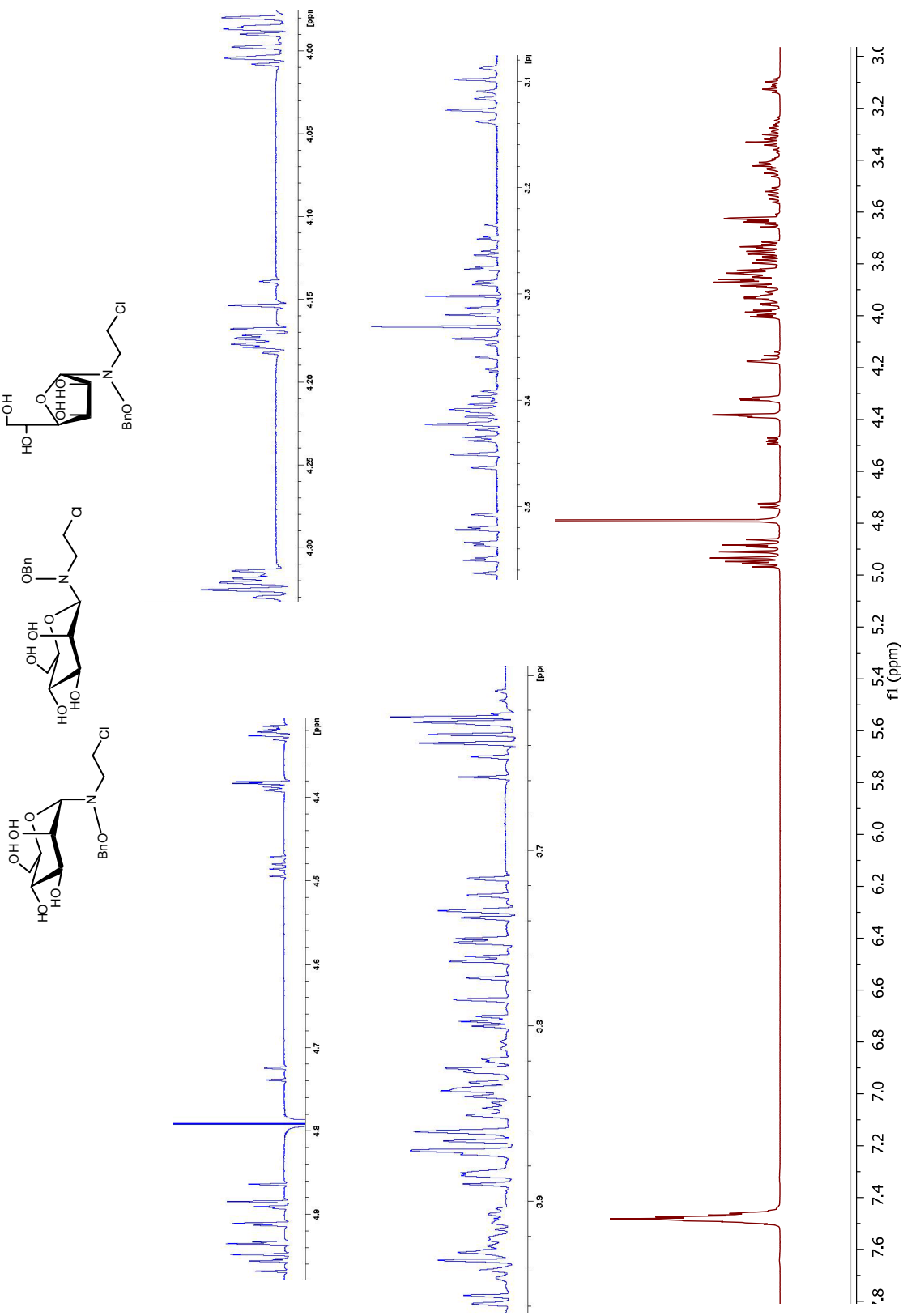
^{13}C-NMR of **24**



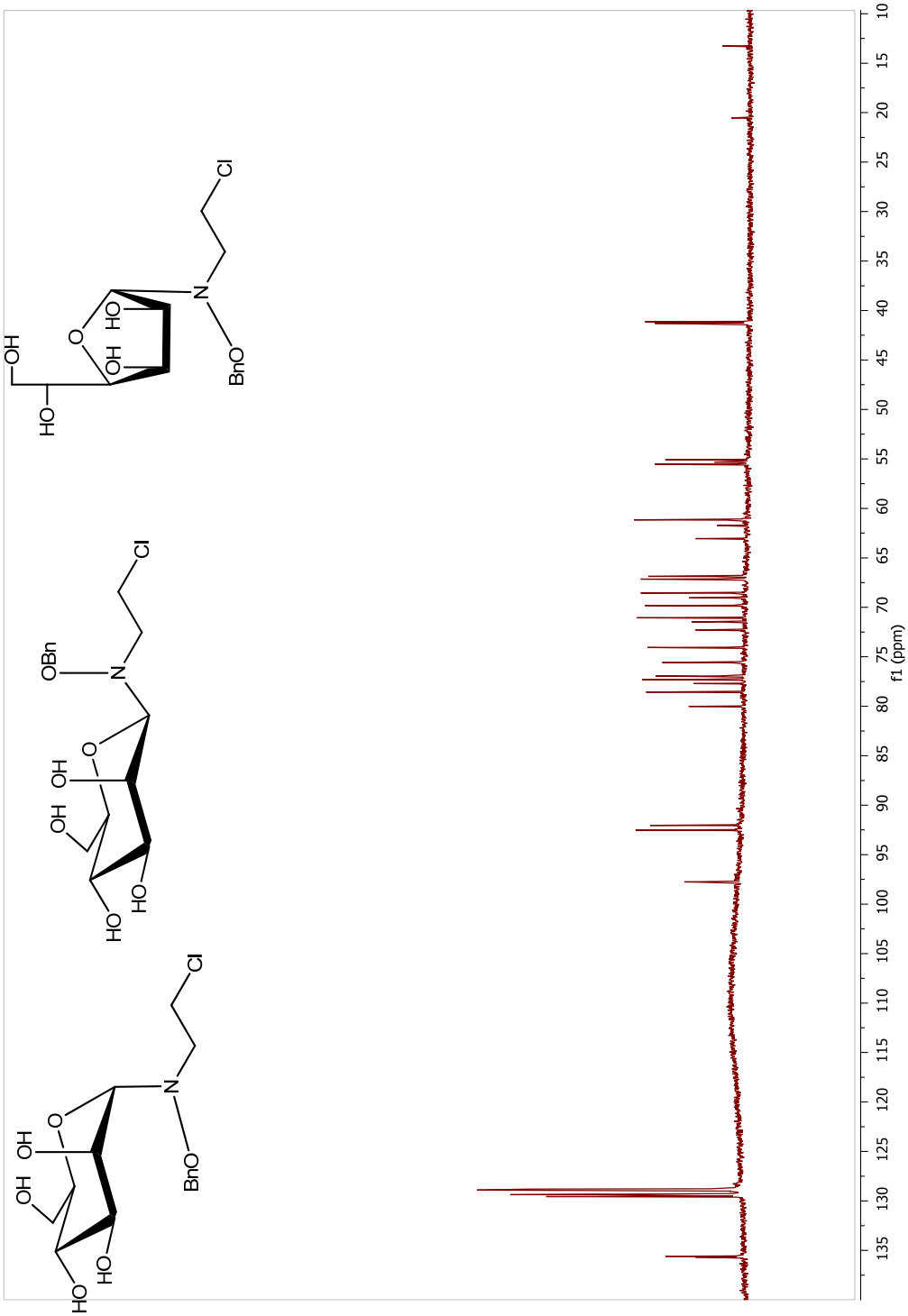
^{1}H-NMR of **25**



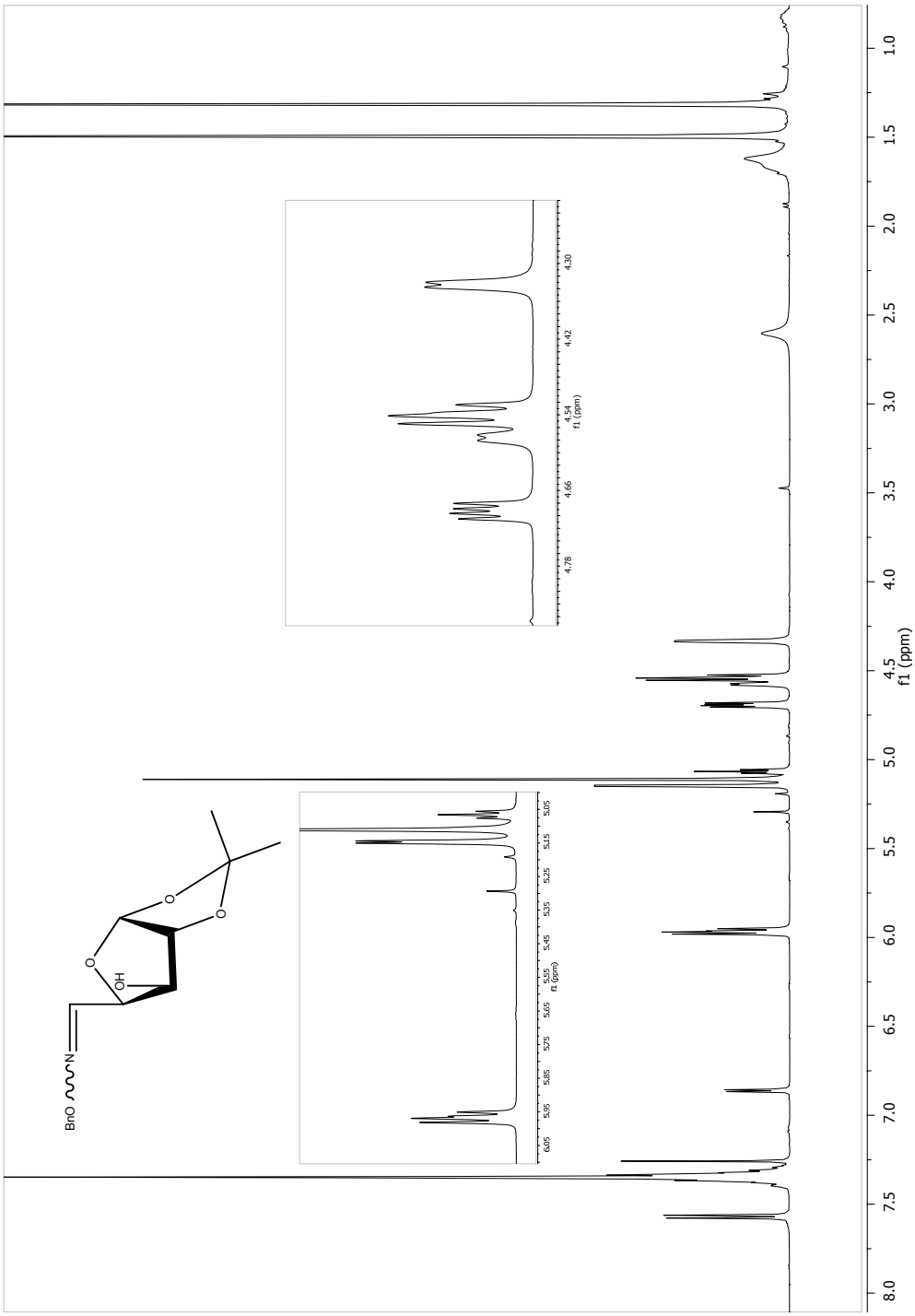
^{13}C-NMR of **25**



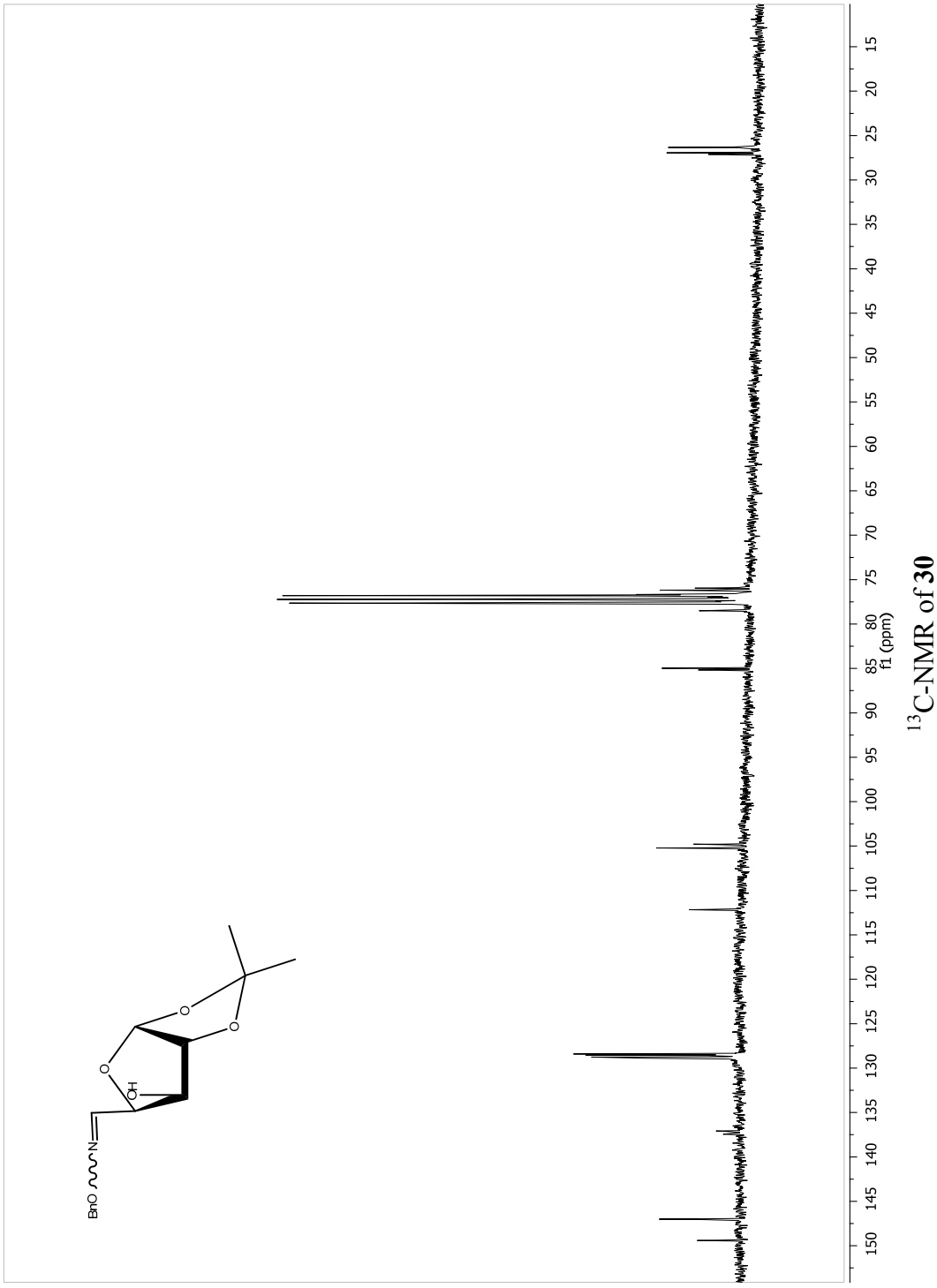
^{1}H-NMR of **26-28**



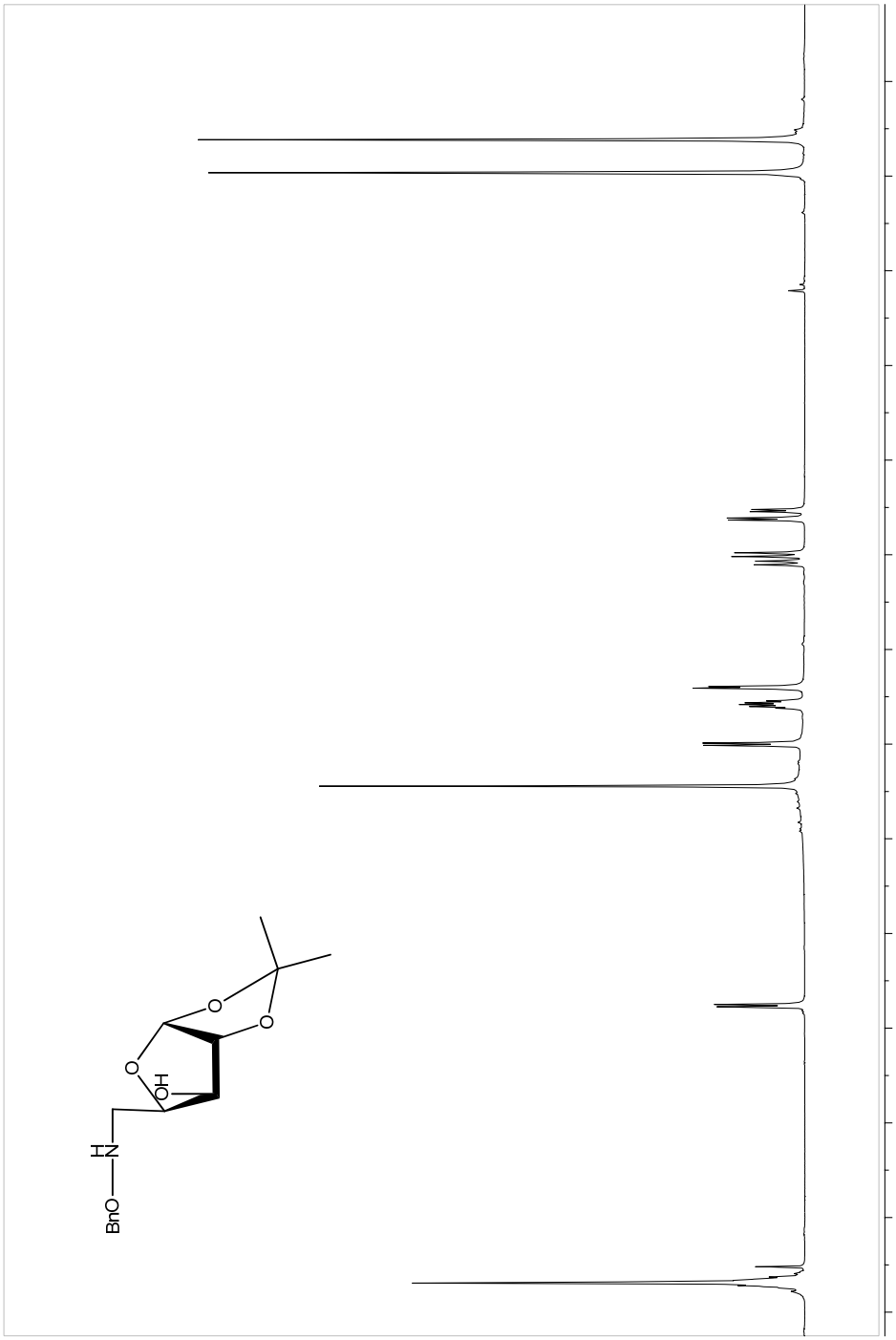
^{13}C-NMR of **26-28**


BnO
OH
O
O
O
f1 (ppm)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
7.5
8.0
4.30
4.42
4.54
4.66
4.78
5.05
5.15
5.25
5.35
5.45
5.55
5.65
5.75
5.85
5.95
6.05

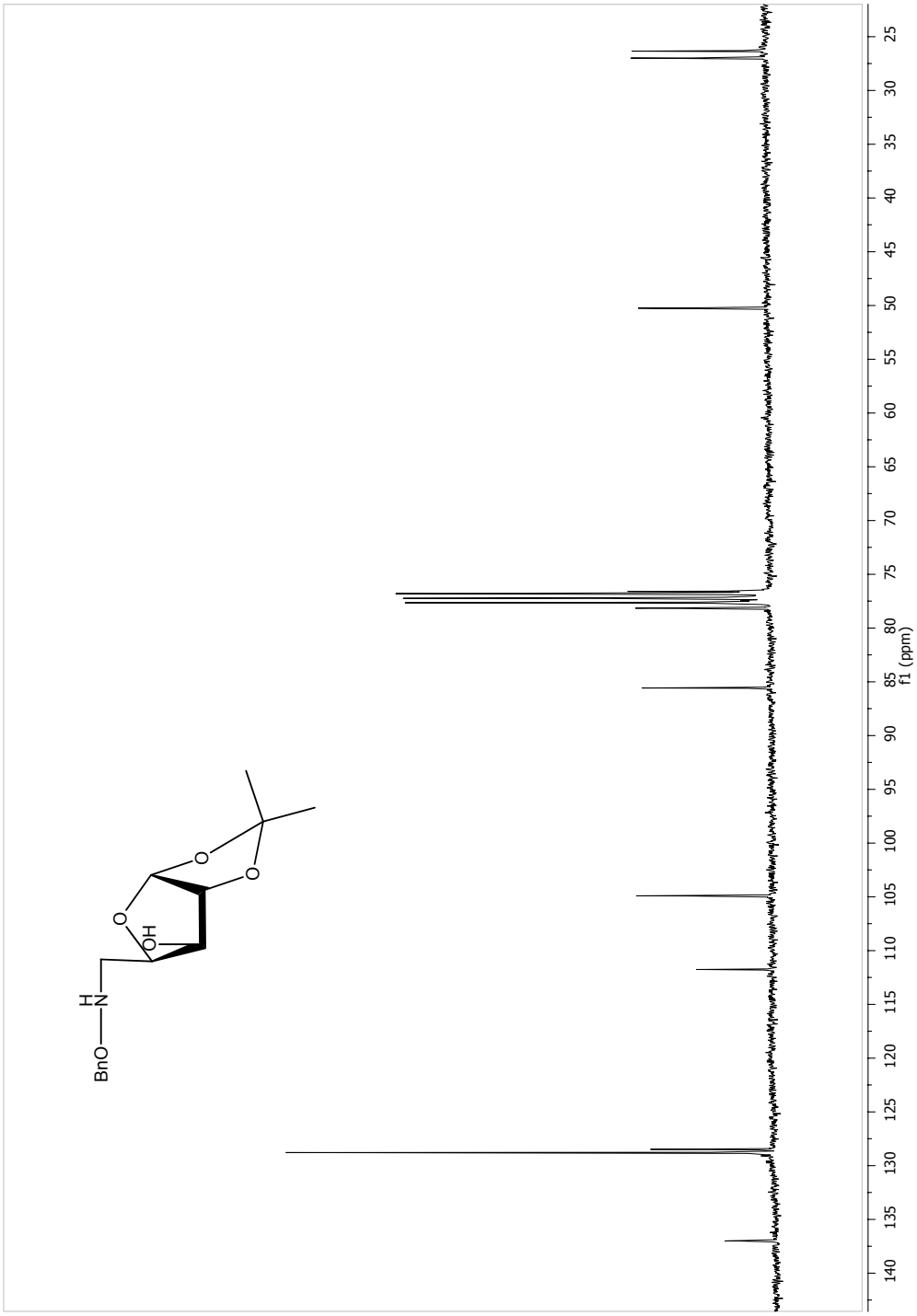
^{1}H-NMR of **30**



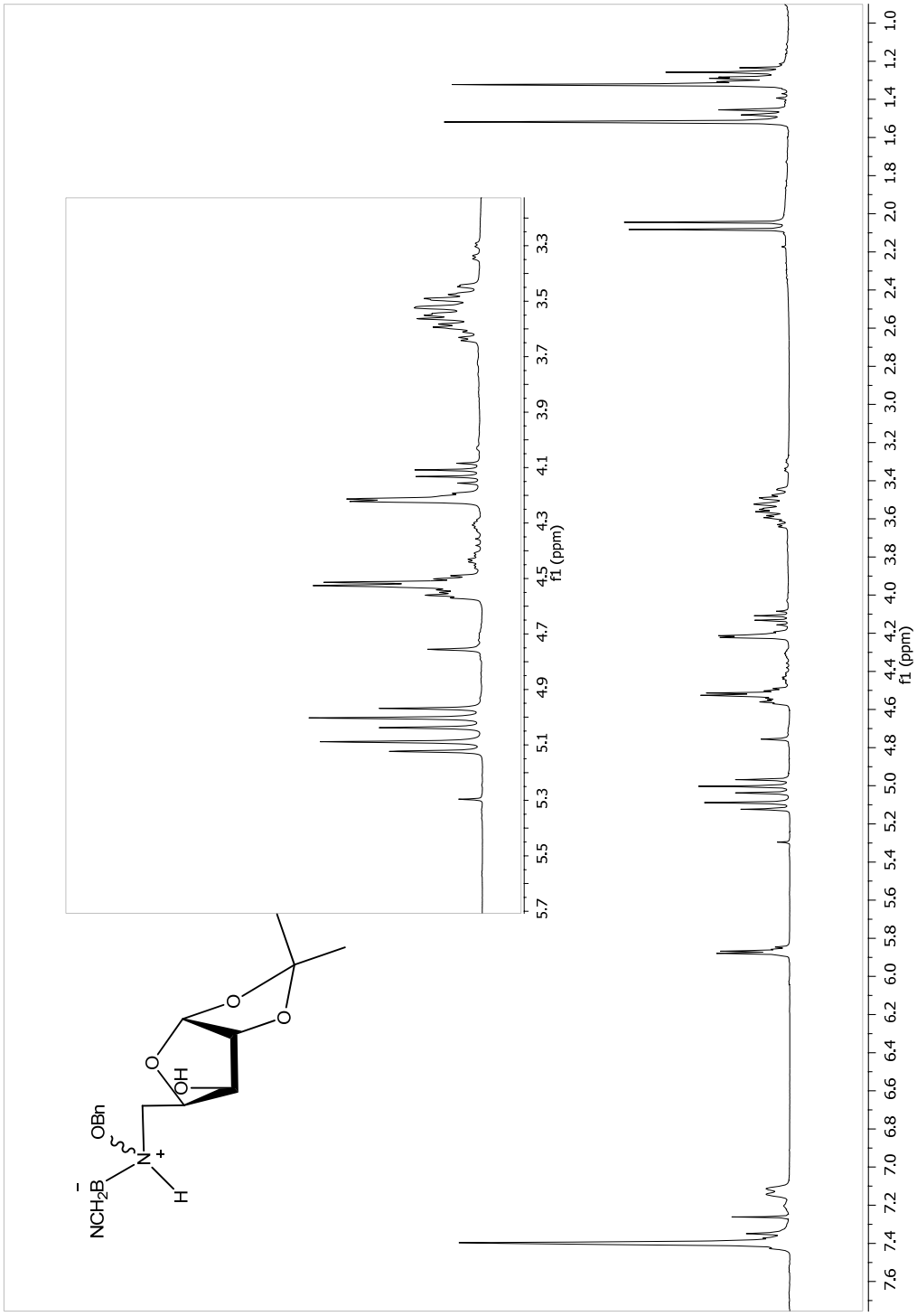
^{13}C-NMR of **30**



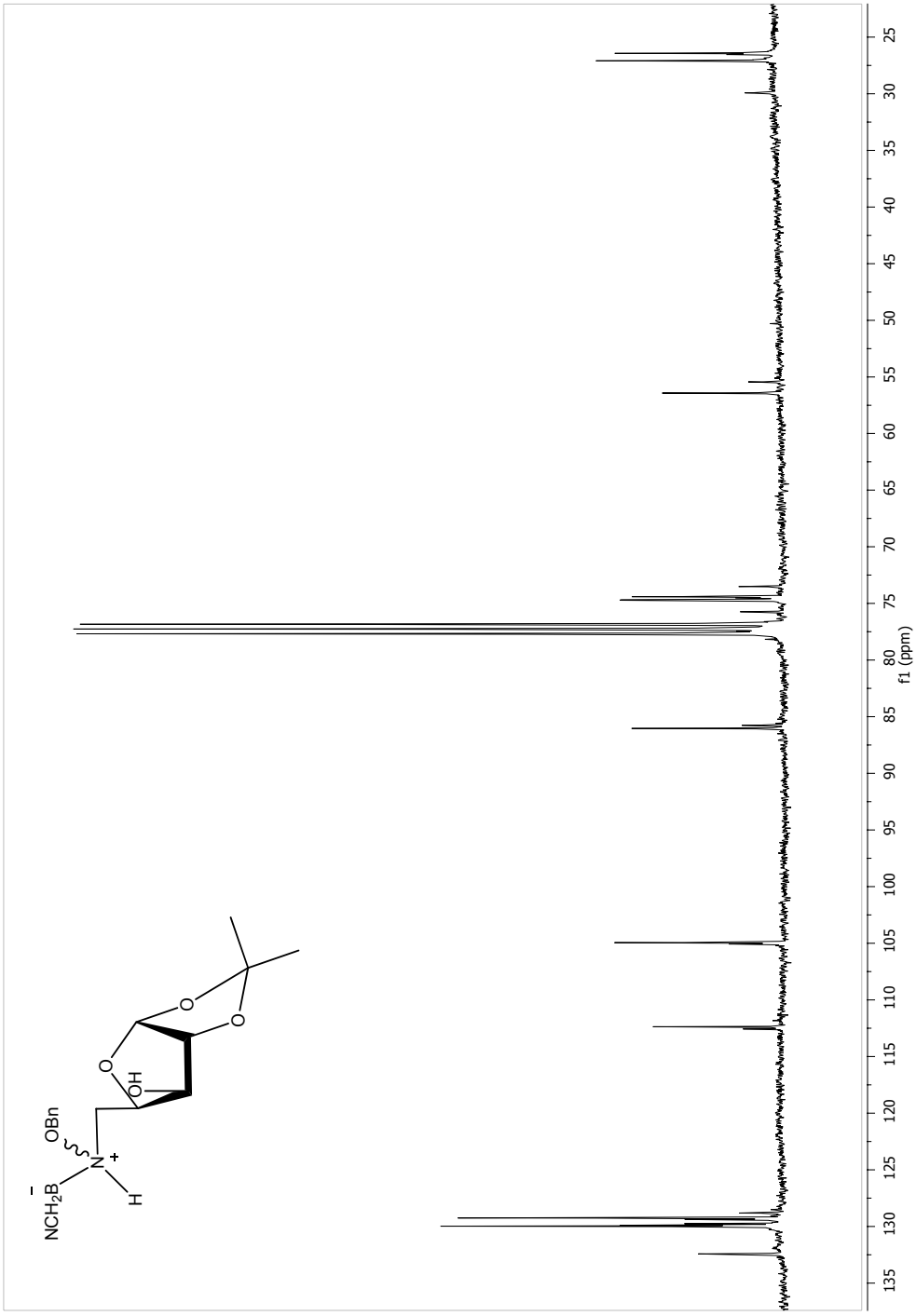
^{1}H-NMR of **31**



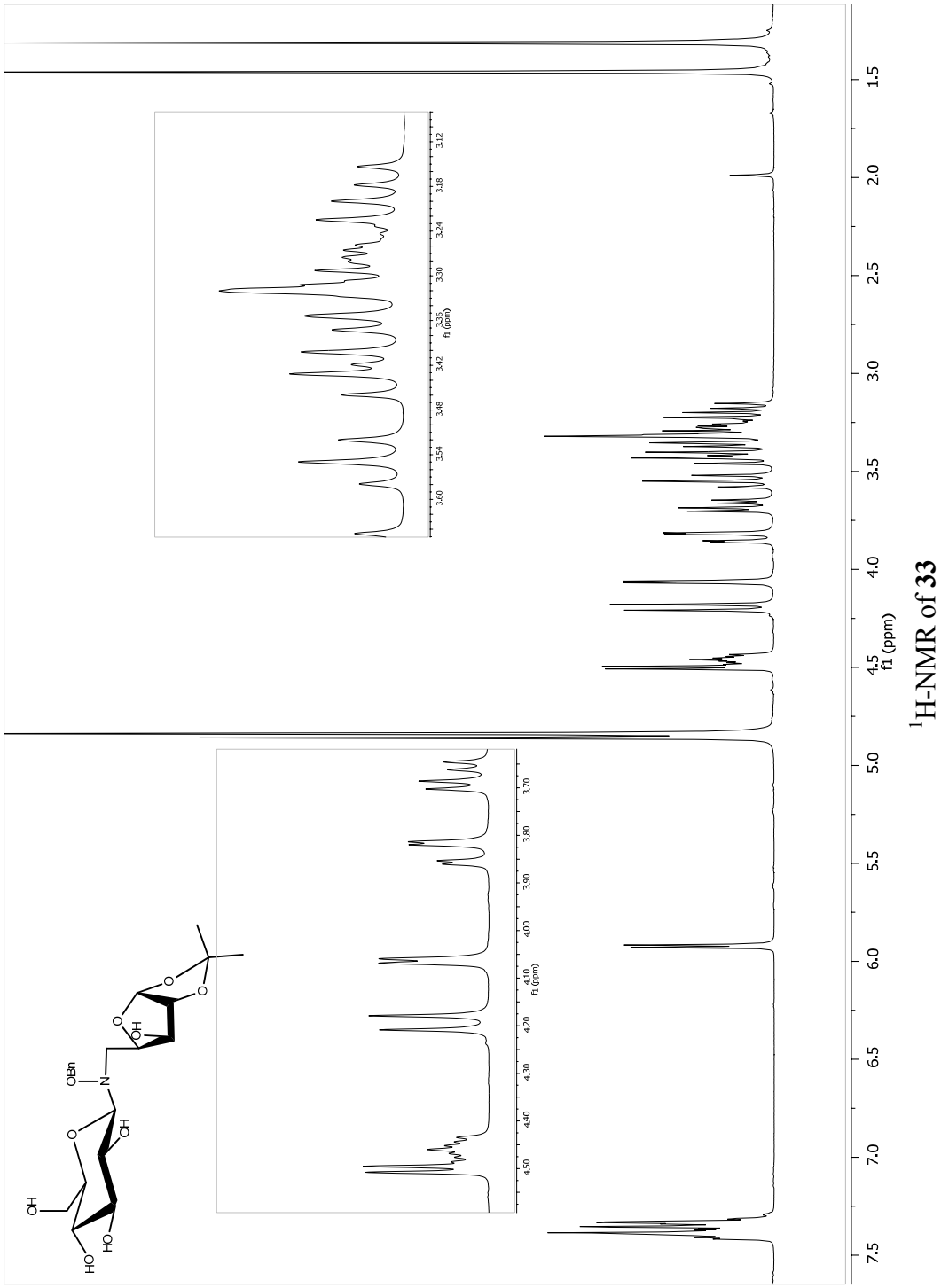
^{13}C-NMR of **31**



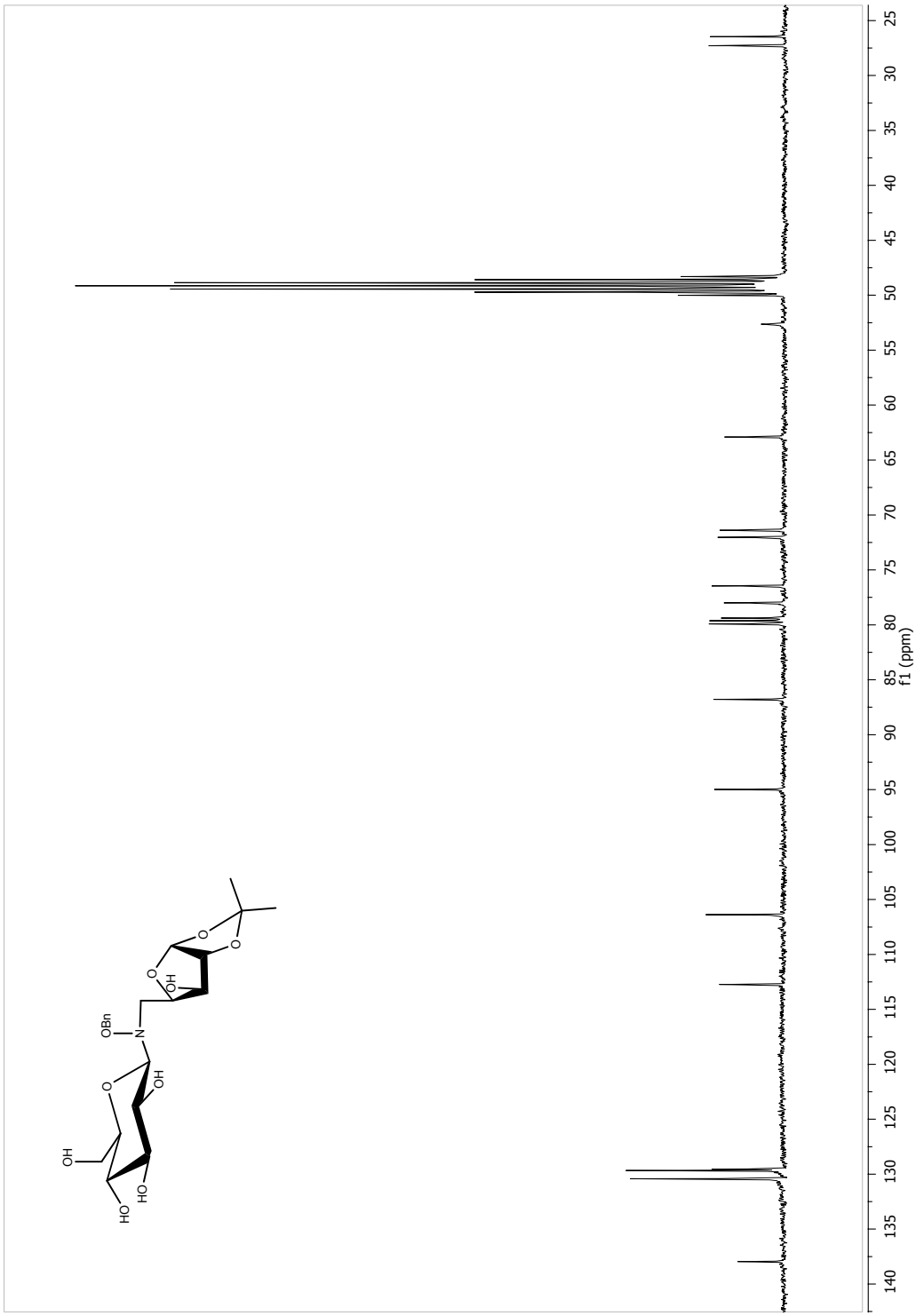
^{1}H-NMR of **32**



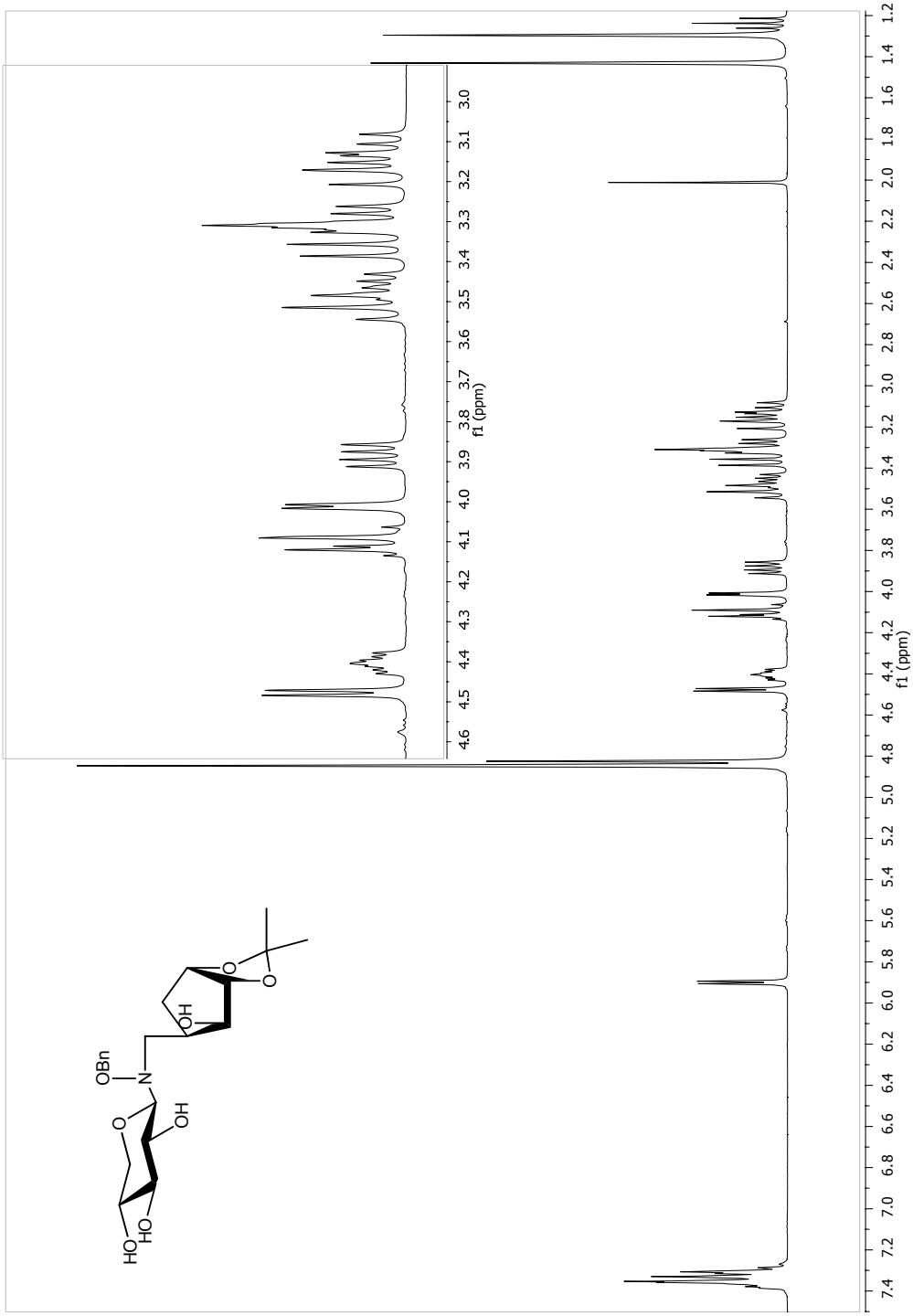
^{13}C-NMR of **32**



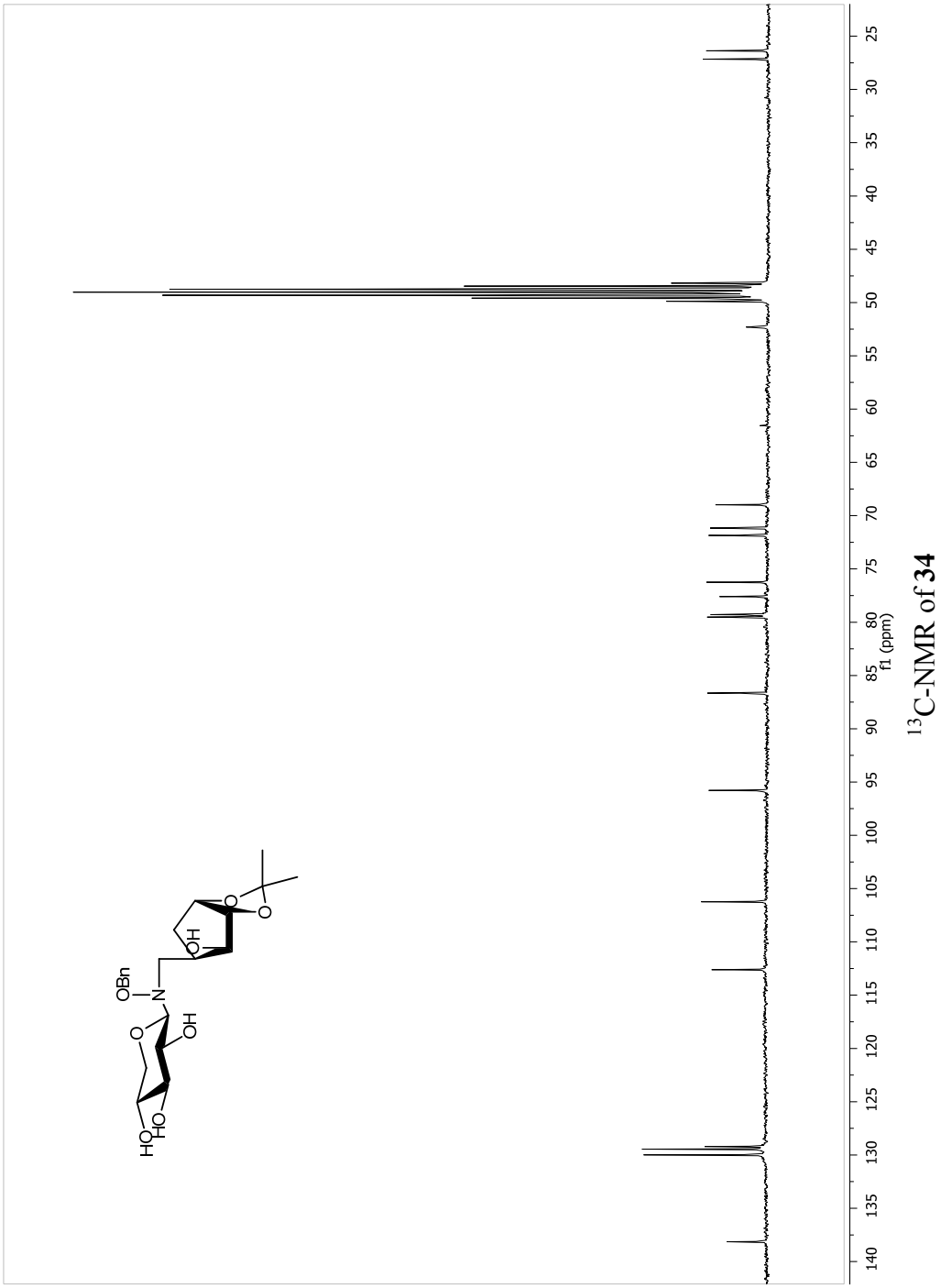
^{1}H-NMR of **33**



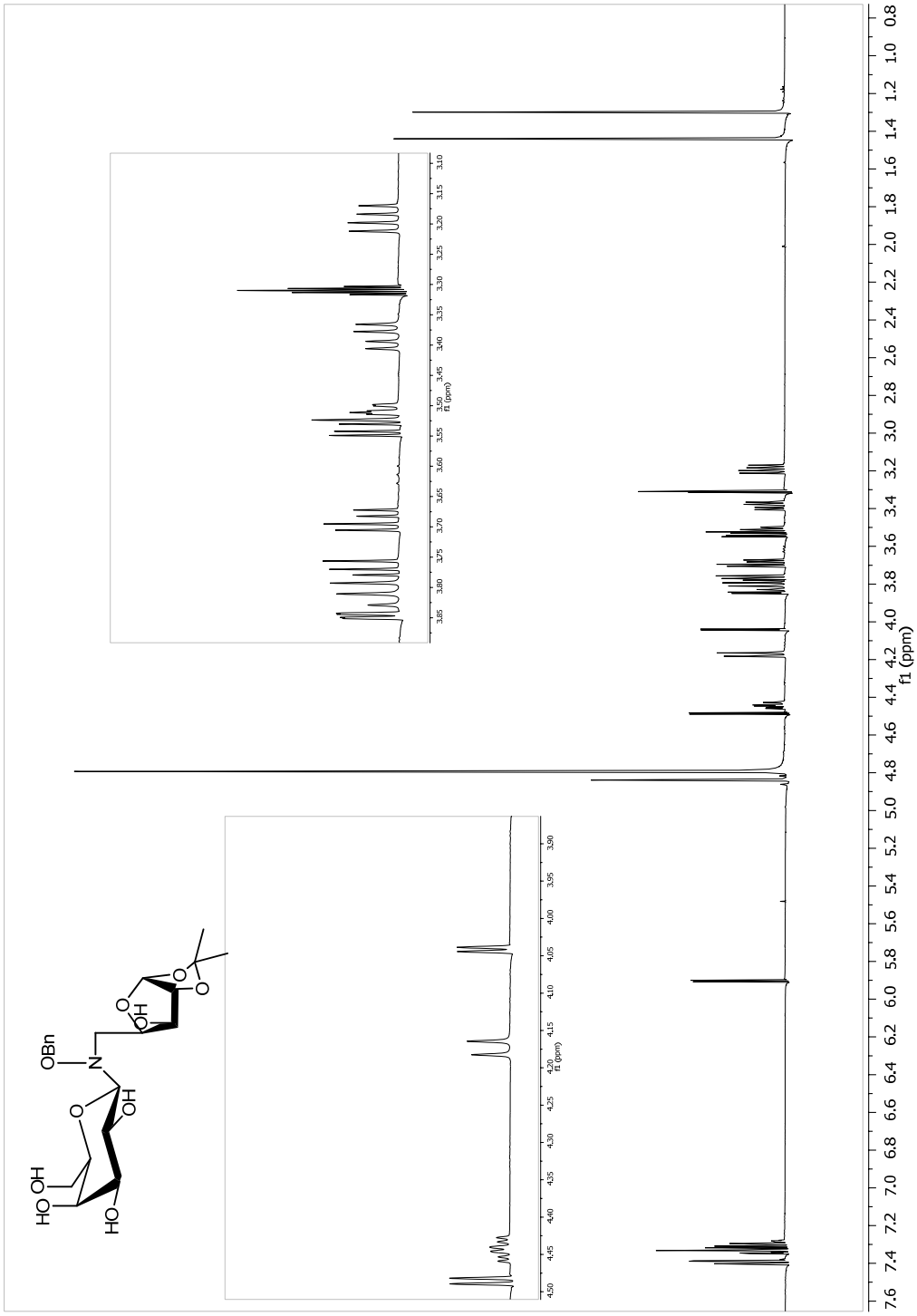
^{13}C-NMR of **33**



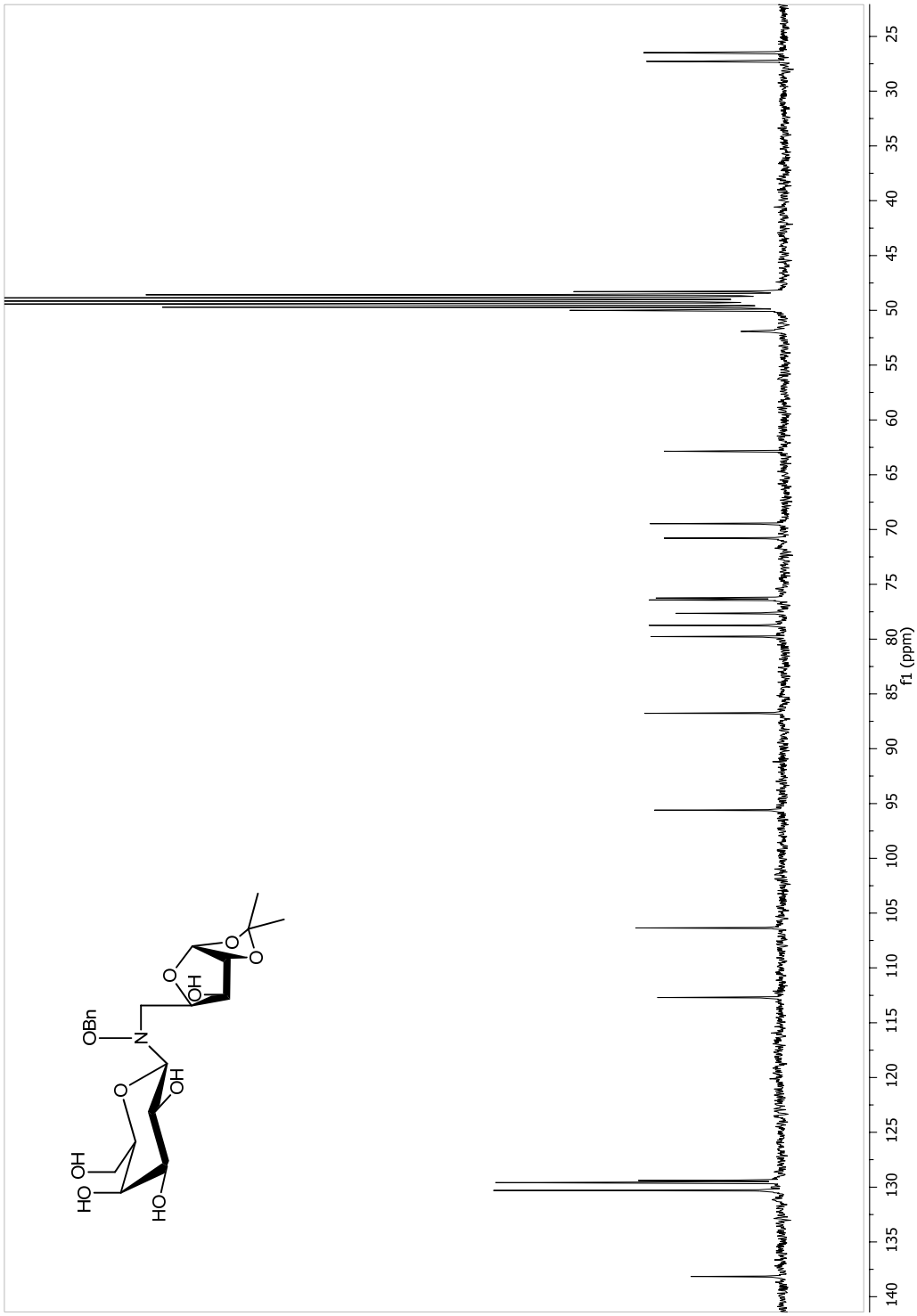
^{1}H-NMR of **34**


OBn
N
OH
HO
HO
O
OH
O
O
f1 (ppm)
25
30
35
40
45
50
55
60
65
70
75
80
85
90
95
100
105
110
115
120
125
130
135
140

^{13}C-NMR of **34**



^{1}H-NMR of **35**



^{13}C-NMR of **35**