Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Gold-catalyzed Highly Efficient Benzylation of Alcohols with *N*-Cbz-*N*-benzyl-progargylamine

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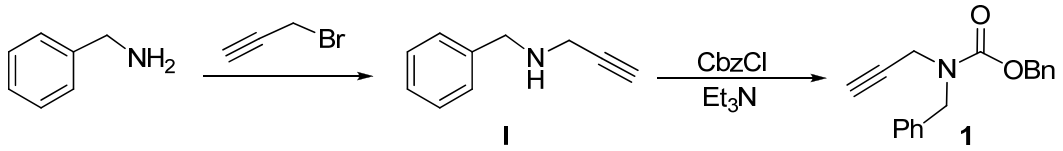
General information

Commercial grade solvents were distilled prior to use. Column chromatography was performed using either 300-400 Mesh silica gels. Thin layer chromatography (TLC) was performed on silica gel GF254 plates. Visualization of spots on TLC plate was accomplished with UV light at 254 nm or by dipping the plate into an H_2SO_4-EtOH solution followed by heating.

NMR spectra were obtained on a Bruker AVANCE DMX 400 spectrometer operating at 400 MHz for 1H-NMR, 100 MHz for ^{13}C-NMR. Unless otherwise noted, all the NMR spectra were recorded at room temperature. Chemical shifts were quoted in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet. Coupling constants *J* were reported in hertz unit (Hz). Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and chemical shifts were reported in ppm referenced to the center line of a triplet at 77.0 ppm of $CDCl_3$. Mass spectra were obtained on a HP5989A or a VG Quatro mass spectrometer.

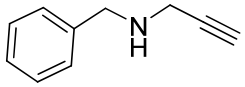
Unless otherwise noted, all the reagents and intermediates were obtained commercially and used without purification. Dichloromethane (DCM) was distilled over CaH_2. Analytical and spectral data of all the known compounds are exactly matching with the reported values.

Preparation of benzylation reagent *N*-Cbz-*N*-benzyl-progargylamine



Scheme 1. Preparation of Cbz-protected *N*-Benzyl-progargylamine

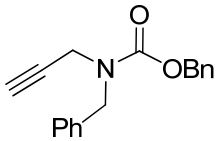
_N_-Benzyl-_N_-prop-2-ynylamine (I)



To a stirred benzylamine (10 mL, 91.6 mmol) was added dropwise propargylic bromide (1.64 mL, 15.3 mmol) over 30 min at room temperature. The solution was stirred overnight. The resulting solution was then quenched with water and extracted with Et_2O. The combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The resulting residue was purified by gel column chromatography (petroleum ether-ethyl acetate, 2:1) to provide the *N*-Benzyl-*N*-prop-2-ynylamine as colourless oil (1.34 g, 57%). (The spectral data was in agreement with the reported data. [1])

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.21 (m, 10H), 5.2 (s, 2H), 4.62 (s, 2H), 3.80 (s, *J* 2H), 3.43 (s, 2H), 2.23 (s, 1H).

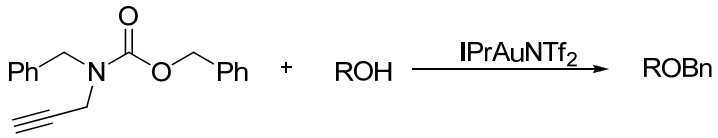
Preparation of _N_-Cbz-_N_-benzyl-progargylamine (1)



To a stirred mixture of benzyl chloroformate (15 mmol, 2.55 g) and Et_3N (15 mmol, 2 mL) in CH_2C1_2 (20 mL) at room temperature was dropwise added over 0.5 h a solution

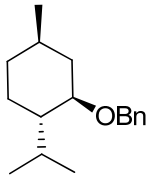
of *N*-benzyl-*N*-prop-2-ynylamine (10.0 mmol, 1.45g) in CH_2C1_2 (10 mL). The mixtures were stirred for 1 h and then diluted with CH_2C1_2 (20 mL). The mixture was washed with saturated $NaHCO_3$ (20 mL), brine (20 mL) and dried over Na_2SO_4. Removal of the solvent, followed by chromatography over silica gel (EtOAc-hexanes, 1:4), afforded the goal product (2.65 g, 95.0%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.22 (m, 8H), 5.20 (s, 2H), 4.62 (s, 2H), 4.08 (s, 1H), 3.98 (s, 1H), 2.23 (s, 1H). ^{13}C NMR (100MHz, $CDCl_3$): δ 155.7, 136.7, 136.3, 128.5, 128.4, 128.2, 128.0, 127.9, 127.5, 78.7, 72.1, 67.6, 49.5, 35.6. HRMS (ESI): m/z [M +H$^+$] calcd for $C_{11}H_{12}NO_2$ 190.0868, found 190.0869.

General procedure for the synthesis of benzyl ethers compounds



To a stirred mixture of alcohol (0.1 mmol) and *N*-Cbz- *N*-benzyl-progargylamine (61 mg, 0.11 mmol) in CH_2Cl_2 (2.0 mL) at room temperature under Ar atmosphere was added $IPrAuNTf_2$ (8 mg, 0.01 mmol). After stirring at room temperature for 2 h (as monitored by TLC), the mixture was filtered through a Celite® pad and concentrated. The residue was purified by silica gel column chromatography to provide products.

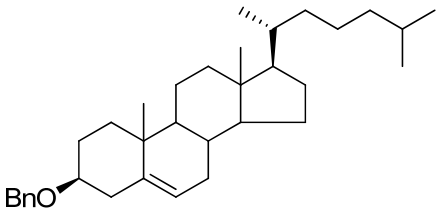
(1*R*, 2*S*, 5*R*)- (–)-*O*-benzylmenthol (3a) [2]



Yield: 24 mg (94%); colorless oil. $[\alpha]_D^{20}$-46.6 (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.23 (m, 5 H), 4.65 (d, *J* = 11.5 Hz, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 3.17

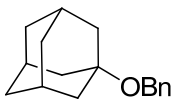
(td, J = 10.5, 4.2 Hz, 1H), 2.37-2.24 (m, 1H), 2.23-2.16 (m, 1H), 1.70-1.58 (m, 2H), 1.33 (m, 2H), 0.94 (d, J = 6.9 Hz, 3H), 0.90 (d, J = 6.9 Hz, 3H), 0.71 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100MHz, $CDCl_3$): δ 139.1, 128.2, 127.8, 127.4, 78.7, 70.4, 48.3, 40.3, 34.5, 31.5, 25.5, 23.2, 22.4, 21.0, 16.0. HRMS (ESI): m/z [M +H$^+$] calcd for $C_{17}H_{27}O$ 247.2062, found 247.2060.

_O_-Benzyl cholesterol (3b) [3]



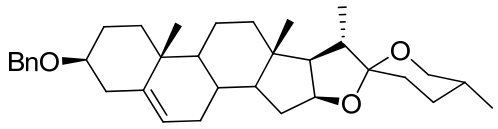
Yield: 42mg (89%); White solid; m.p 117-119 ^{o}C. $[\alpha]_D^{20}$-31.7 (c 0.1, $CHCl_3$). ^{1}HNMR (400 MHz, $CDCl_3$): δ 7.15- 7.40 (m, 5H), 5.30-5.40 (m, 1H), 4.58 (s, 2H), 3.20-3.40 (m, 1H), 0.80-2.50 (m, 43H); ^{13}C NMR (100MHz, $CDCl_3$): δ 140.9, 139.0, 128.3, 127.7, 127.5, 127.3, 121.8, 78.5, 69.8, 56.7, 56.1, 50.1, 42.3, 39.7, 39.5, 39.1, 37.2, 36.8, 36.7, 36.1, 31.8, 29.6, 28.4, 28.2, 24.2, 23.8, 22.8, 22.5, 21.0, 19.3, 18.7, 11.8. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{34}H_{53}O$ 477.4096, found 477.4097.

Benzyl adamantyl ether (3c) [4]



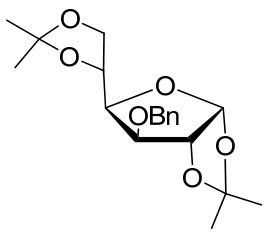
Yield: 20 mg (83%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.20 (m, 5H), 4.51 (s, 2H), 2.18 (s, 3H), 1.88-1.82 (m, 6H), 1.74-1.55 (m, 6H); ^{13}C NMR (100MHz, $CDCl_3$): δ 140.1, 128.2, 127.4, 127.0, 72.7, 62.3, 41.7, 36.4, 30.5. HRMS (ESI): m/z [M +H$^+$] calcd for $C_{17}H_{23}O$ 243.1749, found 243.1751.

_O_-Benzyl diosin (3d)



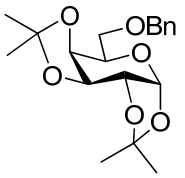
Yield: 44 mg (87%); colorless oil. $[\alpha]_D^{20}$-46.1 (*c* 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 4.56 (s, 2H), 4.40 (dd, *J* = 14.8, 7.6 Hz, 1H), 3.48 (m, 1H), 3.37 (t, *J* = 11.8 Hz, 1H), 3.30-3.24 (m, 1H), 2.45-2.41(m, 1H), 2.28 (t, *J* = 3.2 Hz, 1H), 1.99-1.95 (m, 3H), 1.88-1.84 (m, 2H), 1.79-17.1 (m, 2H), 1.68-1.41 (m, 10H), 1.32-1.20 (m, 3H), 1.20-1.11(m, 3H), 1.03 (s, 3H), 0.98 (d, *J* = 3.6 Hz, 3H), 0.96-0.93 (m, 1H), 0.79 (s, 3H), 0.78 (d, *J* = 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.0, 138.0, 128.5, 127.6, 121.2, 109.2, 80.7, 78.5, 66.7, 62.1, 56.5, 50.0, 41.5, 40.2, 39.7, 39.2, 37.1, 32.0, 31.8, 31.3, 30.2, 28.7, 28.4, 20.8, 19.3, 17.1, 16.2, 14.4. HRMS (ESI): m/z [M +H^+] calcd for $C_{34}H_{49}O_3$ 505.3682; found 505.3685.

1, 2:5, 6-Di-*O*-isopropylidene-3-*O*-benzyl-α-D-glucofranose (3e) [5]



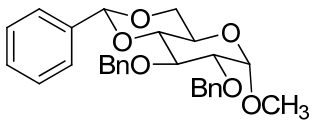
Yield: 30 mg (85%); Colorless oil. $[\alpha]_D^{20}$-23.8 (*c* 1.0, EtOH). ^1H NMR (400 MHz, $CDCl_3$): δ 7.37-7.25 (m, 5H), 5.89 (d, *J* = 3.6 Hz, 1H), 4.69 (d, *J* = 11. 6 Hz, 1H), 4.63 (d, *J* = 11.6 Hz, 1H), 4.57 (d, *J* = 2.8 Hz, 1H), 4.39 (dt, *J* = 6.8, 6.0 Hz, 1H), 4.15 (dd, *J* = 7.2, 2.4 Hz, 1H), 4.02-3.98 (m, 2H), 1.48 (s, 3H), 1.42 (s, 3H), 1.37 (s, 3H), 1.30 (s, 3H);^{13}C NMR (100Hz, $CDCl_3$): δ 137.5, 128.3, 127.7, 127.5, 111.7, 108.9, 105.2, 82.5, 81.6, 81.2, 72.4, 72.3, 67.3, 26.7, 26.2, 25.4. HRMS (ESI): m/z [M +$Na]^+$ calcd for $C_{19}H_{26}NaO_6$ 373.1627, found 373.1626.

1, 2:3, 4-Di-*O*-isopropylidene-6-*O*-benzyl-α-D-galactopyranose (3f)



Yield: 24 mg (94%); colorless oil. $[\alpha]_D^{20}$ +36.1 (*c* 0.1, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.35- 7.28 (5H, m), 5.53 (d, *J* = 4.8 Hz, 1H), 4.63 (d, *J* = 12.0 Hz, 1H), 4.58 (d, *J* = 2.0 Hz, 1H), 4.53(d, *J* = 12.0 Hz, 1H), 4.30 (dd, *J* = 2.0, 4.8 Hz, 1H), 4.28 (dd, *J* = 8.0, 6.8 Hz, 1H), 4.0 (t, *J* = 5.6 Hz, 1H), 3.67 (dd, *J* = 10.0, 5.6 Hz, 1H), 3.62 (dd, *J* = 10.0, 6.8 Hz, 1H), 1.53(s, 3H), 1.44 (s, 3H), 1.33 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100Hz, $CDCl_3$): δ 138.2, 128.2, 127.5, 127.4, 109.0, 108.4, 96.2, 73.1, 71.0, 70.5, 68.7, 66.7, 25.9, 25.8, 24.0, 24.3. HRMS (ESI): m/z [M +H^+] calcd for $C_{19}H_{27}O_6$ 351.1806, found 351.1809.

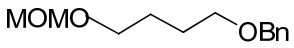
Methyl 4, 6-*O*-benzylidene-2, 3-Di-*O*-benzyl-α-D-glucopyranoside (3g) [6]



Yield: 38 mg (82%); white solid; M.p.95-97 ^oC. $[\alpha]_D^{20}$ -29.1 (*c* 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ 7.48-7.50 (m, 2H), 7.24-7.39 (m, 13H), 5.55 (s, 1H), 4.92 (d, *J* = 11.2 Hz, 1H), 4.86 (d, *J* = 12.4 Hz, 1H), 4.84 (d, *J* = 11.2 Hz, 1H), 4.70 (d, *J* = 12.4 Hz, 1H), 4.60 (1H, d, *J* = 3.2 Hz), 4.27 (dd, *J* = 10.0, 4.0 Hz, 1H), 4.05 (1H, t, *J* = 9.2 Hz, H-3), 3.83-3.79 (1H, m, H-5), 3.71 (t, *J* = 9.6 Hz, 1H), 3.60 (d, *J* = 9.6 Hz,), 3.56 (1H, dd, *J* = 9.2, 3.6 Hz) 3.41 (3H, s); ^{13}C NMR(100 MHz, $CDCl_3$): δ 138.7, 138.1, 137.3, 128.8, 128.3, 128.2, 128.1, 128.0, 127.8, 127.5, 126.0, 101.2, 99.2, 82.0 , 79.1 ,78.5 , 75.3, 73.7 , 69.0 , 62.2, 55.3. HRMS (ESI): m/z [M +H^+] calcd for $C_{28}H_{31}O_6$ 463.2042; found

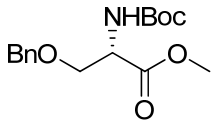
463.2041.

4-Methoxymethoxy-1-benzyoxy-propane (3h)



Yield: 21 mg (95%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 4H), 7.27 (m, H), 4.61(s, 2H), 4.50 (s, 2H), 3.54 (t, J = 5.6 Hz, 2H), 3.51(t, J = 5.6 Hz, 2H), 3.34 (s, 3H), 1.69 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.4, 55.0, 67.4, 69.9, 72.8, 96.3, 127.4, 127.5, 128.3, 138.5, 128.3, 127.5, 127.4, 96.3, 72.8, 69.9, 67.4, 55.0, 26.4. HRMS (ESI): m/z [M +H]$^{+}$ calcd for $C_{13}H_{21}O_3$ 225.1491, found 225.1493.

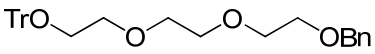
***O*-Benzyl-*N*-Boc-L-serine methyl ester (3i)** [7]



Yield: 28 mg (93%); Colorless oil. $[\alpha]_D^{20}$-28.2 (*c* 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24–7.34 (m, 5H), 5.76 (s, 1H), 5.20 (s, 1H), 4.69 (s, 2H), 3.76 (s, 3H), 1.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.2, 154.0, 137.8, 128.1, 127.3, 127.0, 81.4, 74.6, 71.4, 55.9, 55.3, 29.2.

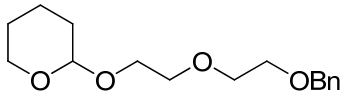
HRMS (ESI): m/z [M +H^{+}] calcd for $C_{16}H_{24}NO_5$ 310.1654, found 310.1653.

1, 1, 1, 12-Tetraphenyl-2, 5, 8, 11-tetraoxadodecane (3j)



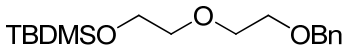
Yield: 46 mg (97%); Colorless oil. ^{1}H NMR (400 MHz; $CDCl_3$): δ 7.47-7.45 (m, 6H), 7.32-7.19 (m, 14H), 3.71-3.66 (m, 8H), 3.63-3.61 (m, 2H), 4.55 (s, 2H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 144.1, 138.2, 128.6, 128.3 127.7, 127.5, 126.8, 86.4, 73.2, 70.7 69.4 63.3. HRMS (ESI): m/z [M +H]$^{+}$ calcd for $C_{32}H_{35}O_4$ 483.2535, found 483.2537.

2-(2-(2-(Benzyloxy)ethoxy)ethoxy)tetrahydro-2H-pyran (3k)



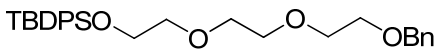
Yield: 23 mg (95%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.29 (m, 4H), 7.28-7.27 (m, 1H), 4.64 (d, J = 3.6 Hz, 1H), 4.57 (s, 2H), 3.90-3.87 (m, 2H), 3.86-3.84 (m, 4H), 3.70-3.68 (m, 2H), 3.65-3.60 (m, 3H), 3.50-3.47 (m, 1H), 1.86-1.79 (m, 1H), 1.79-1.71(m, 1H), 1.68-1.51(m, 4H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 138.2, 128.2, 127.2, 127.5, 98.8, 73.1, 70.6, 70.5, 69.4, 66.6, 62.1, 30.5, 25.3, 19.4.

9, 9, 10, 10-Tetramethyl-1-phenyl-2, 5, 8-trioxa-9-silaundecane (3l)



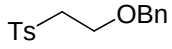
Yield: 29 mg (94%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.4-7.27 (m, 5H), 4.57(s, 2H), 3.77 (t, J = 5.6 Hz, 2H), 3.68 (t, J = 4.0 Hz, 2H), 3.62 (t, J = 4.0 Hz, 2H), 3.57 (t, J = 5.6 Hz, 2H), 0.89 (s, 9H), 0.66 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 128.3, 127.7, 127.5, 73.2, 72.6, 70.7, 69.5, 62.7, 25.9, 18.3, -5.26. HRMS (ESI): m/z [M +H]$^{+}$ calcd for $C_{17}H_{31}O_3Si$ 311.2042, found 311.2041.

14, 14-Dimethyl-1, 13, 13-triphenyl-2, 6, 9, 12-tetraoxa-13-silapentadecane (3m)



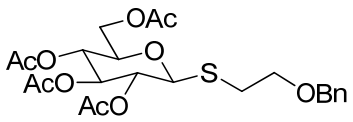
Yield: 46 mg (96%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (s, 2H), 7.67 (s, 2H), 7.43-7.27 (m, 11H), 4.55 (s, 2H), 3.80 (t, J = 5.2 Hz, 2H), 3.68-3.59 (m, 10H), 1.04 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.2, 136.6, 135.6, 135.3, 133.6, 129.5, 128.4, 127.5, 73.1, 72.3, 70.6, 69.3, 63.3, 26.7, 19.1. HRMS (ESI): m/z [M +H]$^{+}$ calcd for $C_{29}H_{39}O_4Si$ 479.2618, found 479.2617.

2-Benzyloxyethyl *p*-toluenesulfonate (3n)



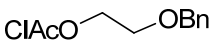
Yield: 27 mg (94%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80-7.78 (m, 2H), 7.34-7.24 (m, 5H), 4.47 (s, 2H), 4.19 (t, J = 4.4 Hz, 2H), 3.65 (t, J = 4.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 137.5, 132.9, 129.7, 129.5, 128.3, 127.9, 127.7, 73.1, 69.2, 67.2, 21.5. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{16}H_{19}O_3S$ 291.1055, found 291.1057.

2'-Benzyloxyethyl 2, 3, 4, 6-tetra-*O*-acetyl-β-D-thioglucopyranoside (3o)



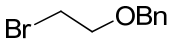
Yield: 43 mg (87%); Colorless oil. $[\alpha]_D^{20}$-12.1 (*c* 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.25 (m, 5H), 5.20 (t, J = 9.2 Hz, 1H), 5.07 (t, J = 9.6 Hz, 1H), 5.04 (t, J = 9.6 Hz, 1H), 4.59 (d, J = 10.0 Hz, 1H), 4.54 (s, 2H), 4.21(dd, J =12.4, 8.4 Hz, 1H), 4.09 (dd, J =12.4, 4.0 Hz, 1H), 3.71-3.62 (m, 3H), 2.97 (t, J = 6.8 Hz, 1H), 2.81(t, J = 6.8 Hz, 1H), 2.06 (s, 3H), 2.05 (s, 3H), 2.02 (s, 3H), 2.01 (s, 3H); ^{13}C NMR (100 MHz; $CDCl_3$): δ 170.5, 170.1, 169.3, 137.9, 128.4, 127.7, 127.6, 83.5, 75.7, 73.7, 72.9, 69.9, 68.1, 62.0, 29.5, 20.6, 20.5. HRMS (ESI): m/z $[M+H^+]$ calcd for $C_{23}H_{31}O_{10}S$ 499.1638, found 449.1639.

2'-(Benzyloxy)ethyl 2-chloroacetate (3p)



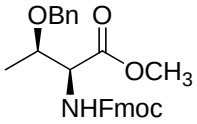
Yield: 22 mg (96%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 5H), 4.56 (s, 2H), 4.36 (t, J = 4.4 Hz, 2H), 4.09 (s, 2H), 3.69 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.2, 137.6, 128.4, 127.6, 73.1, 67.4, 65.2, 40.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_{14}ClO_3$ 229.0631, found 229.0630.

Benzyl 2-bromoethylether (3q) [8]



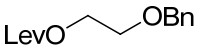
Yield: 19 mg (91%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.35 (m, 4H), 7.24-7.29 (m, 1H), 4.58 (s, 2H), 3.77 (t, J = 6.0 Hz, 2H), 3.48 (t, J = 6.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 128.4, 137.6, 128.4, 127.8, 127.6, 73.0, 69.8, 30.4. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_9H_{12}BrO$ 215.0072, found215.0071.

_O_-Benzyl-_N_-Fmoc-L-threonine methyl ester (3r)



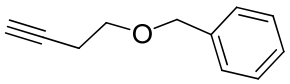
Yield: 38 mg (86%); Colorless oil. $[\alpha]_D^{20}$-16.7 (*c* 0.1, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) : δ 7.75 (d, J = 8.0 Hz, 2H), 7.62 (t, J = 7.6 Hz, 2H), 7.41-7.26 (m, 9H), 5.57 (d, J = 9.6 Hz, 1H), 4.58 (d, J = 12.0 Hz, 1H), 4.41 (m, 4H), 4.25 (t, J = 7.2 Hz, 1H), 4.17-4.05 (m, 1H), 3.68 (s, 3H), 1.26 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 156.7, 143.9, 143.7, 141.2, 137.7, 128.8, 128.3, 127.7, 127.6, 127.0, 125.1, 119.9, 74.1, 70.8, 67.2, 58.7, 52.3, 47.1, 16.1. HRMS (ESI): m/z [M +H$^+$] calcd for $C_{27}H_{28}NO_5$ 446.1967, found 446.1969.

2-(Benzyloxy)ethyl 4-oxopentanoate (3s)



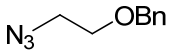
Yield: 25 mg (98%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.35 (m, 5H), 4.56 (s, 2H), 4.25 (t, J = 4.8 Hz, 3H), 3.66 (t, J = 4.8 Hz, 2H), 2.74 (t, J = 4.8 Hz, 2H), 2.61 (t, J = 4.8 Hz, 2H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.4, 172.6, 137.8, 128.3, 127.6, 73.0, 67.7, 63.7, 37.8, 29.7, 27.8. HRMS (ESI): m/z [M +H]$^+$ calcd for $C_{14}H_{19}O_4$ 251.1283, found 251.1286.

1-Benzyloxy-3- propyne (3t) [9]



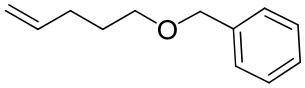
Yield: 15 mg (93%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 - 7.24 (m, 5H), 4.55 (s, 2H), 3.59 (t, 2H, J = 6.9 Hz), 2.48-2.51 (m, 2H), 1.99(s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.9, 128.3, 127.6, 81.2, 69.2, 68.0, 19.8. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_{13}O$ 161.0966, found 161.0967.

1-Azido-2-benzyloxyethane (3u)



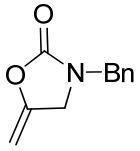
Yield: 16 mg (89%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (m, 4H), 7.24 (m, 1H), 4.57(s, 2H), 3.64 (t, J = 4.4 Hz, 2H), 3.40 (t, J = 4.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 128.4, 127.7, 127.5, 76.6, 73.2, 68.8, 50.7. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_9H_{12}N_3O$ 178.0980, found 178.0983.

1-Benzyloxy-4-pentene (3v) [10]



Yield: 17 mg (92%); Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.32 (m, 4H), 7.32-7.26 (m, 1H), 5.80 (ddt, J = 16.8, 9.6, 4.0 Hz, 1H), 5.03-4.93 (m, 2H), 4.48 (s, 2H), 3.46 (t, J = 6.4 Hz, 2H), 2.19-2.12 (m, 2H), 1.74-1.67 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 138.2, 128.3, 127.5, 127.4, 114.6, 72.8, 69.6, 30.3, 28.9. HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{12}H_{17}O$ 177.1279, found 177.1279.

***N*-Benzyl-5-methylidene-2-oxazolidinone (D)** [11]

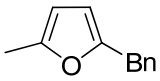


It was separated while compound **3a** was prepared. Yield: 17 mg (88%); White solid; M.p. 49-51 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.32 (m, 3H), 7.30 (dd, J = 9.2, 3.2 Hz, 2H), 4.74 (d, J = 2.4 Hz, 1H), 4.46 (s, 2H), 4.24 (d, J = 2.4 Hz, 1H), 4.02 (s, J = 2.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.59, 148.8, 134.9, 128.9, 128.1, 128.1, 86.7, 47.7, 47.1. HRMS (ESI): m/z [M +H]$^{+}$ calcd for $C_{10}H_{12}NO_2$ 190.0868, found 190.0869.

General Procedure of the IPrAuNTf$_2$ -catalyzed Friedel-Crafts reaction of 2-methyfuran

To a stirred mixture of 2-methlyfuran (0.5 mmol) and *N*-Cbz- *N*-benzyl-progargylamine (61 mg, 0.1 mmol) in CH_2Cl_2 (2.0 mL) at room temperature under Ar atmosphere was added IPrAuNTf$_2$ (8 mg, 0.01 mmol). After stirring at room temperature for 2 h (as monitored by TLC), the mixture was filtered through a Celite® pad and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether) to provide 2-benzyl-5-methylfuran.

2-benzyl-5-methylfuran (F2)



Yield: 12 mg (69%); colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (s, 3H), 3.91 (s, 2H), 5.86 (s, 2H), 7.30-7.22 (m, 5H). The spectral data fully corresponds to the reported data. [12] HRMS (ESI): m/z [M +H^{+}] calcd for $C_{12}H_{13}O$ 173.0966, found 173.0967.

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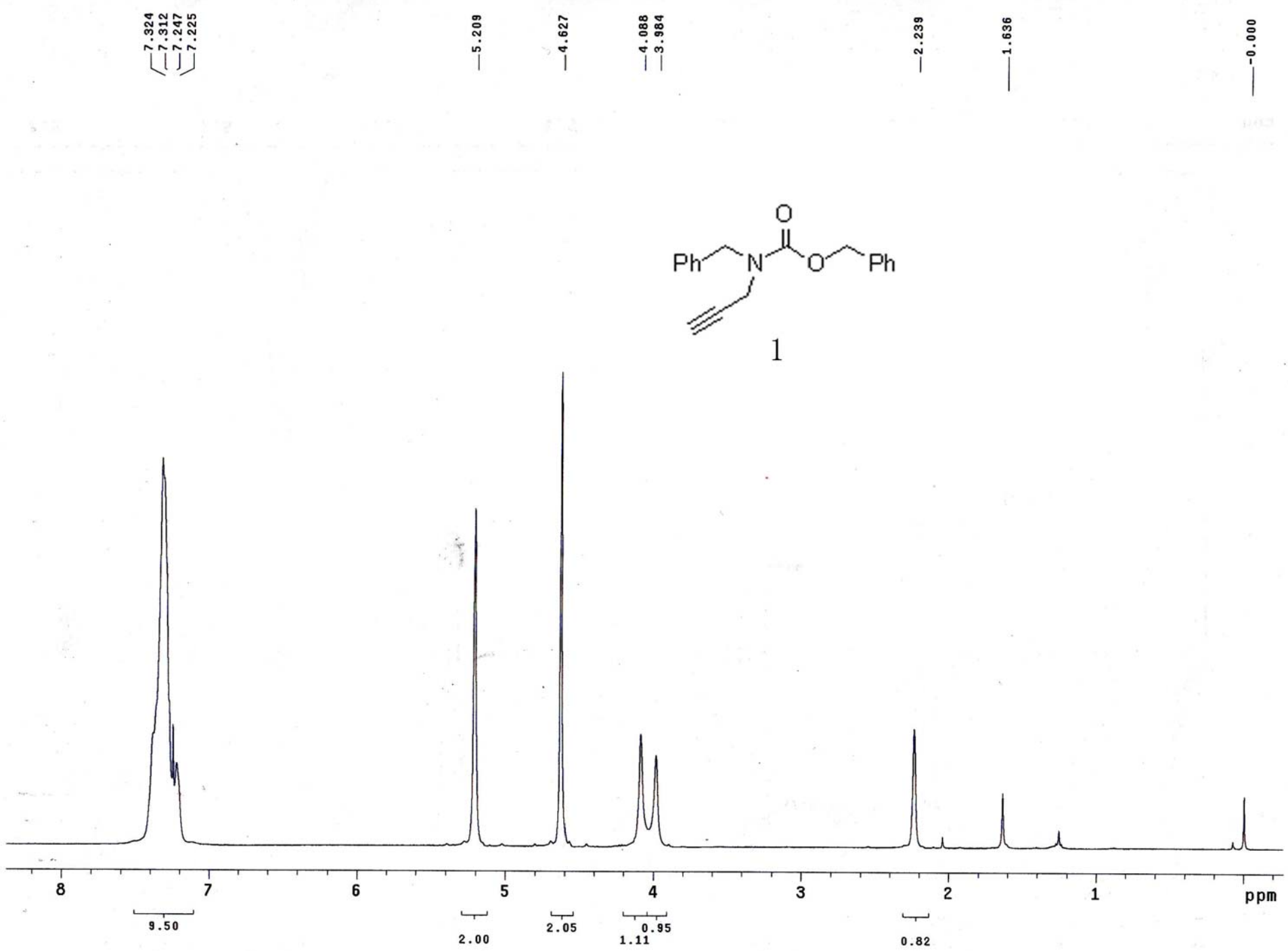
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4.088
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1.636
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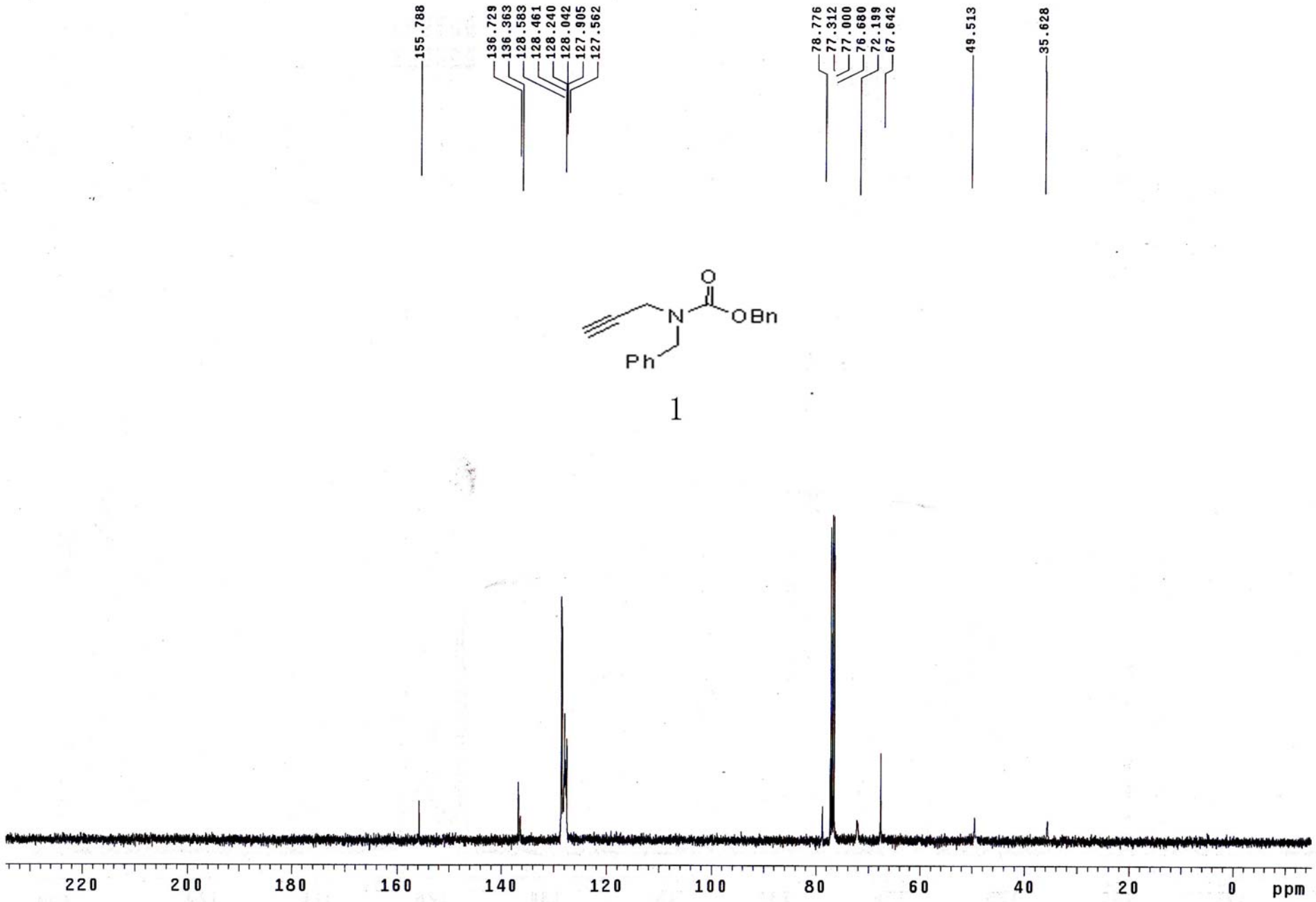
Ph
N
O
Ph
1
8
7
6
5
4
3
2
1
ppm
9.50
2.00
2.05
1.11
0.95
0.82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77.000
76.680
72.199
67.642
49.513
35.628
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OBn
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200
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140
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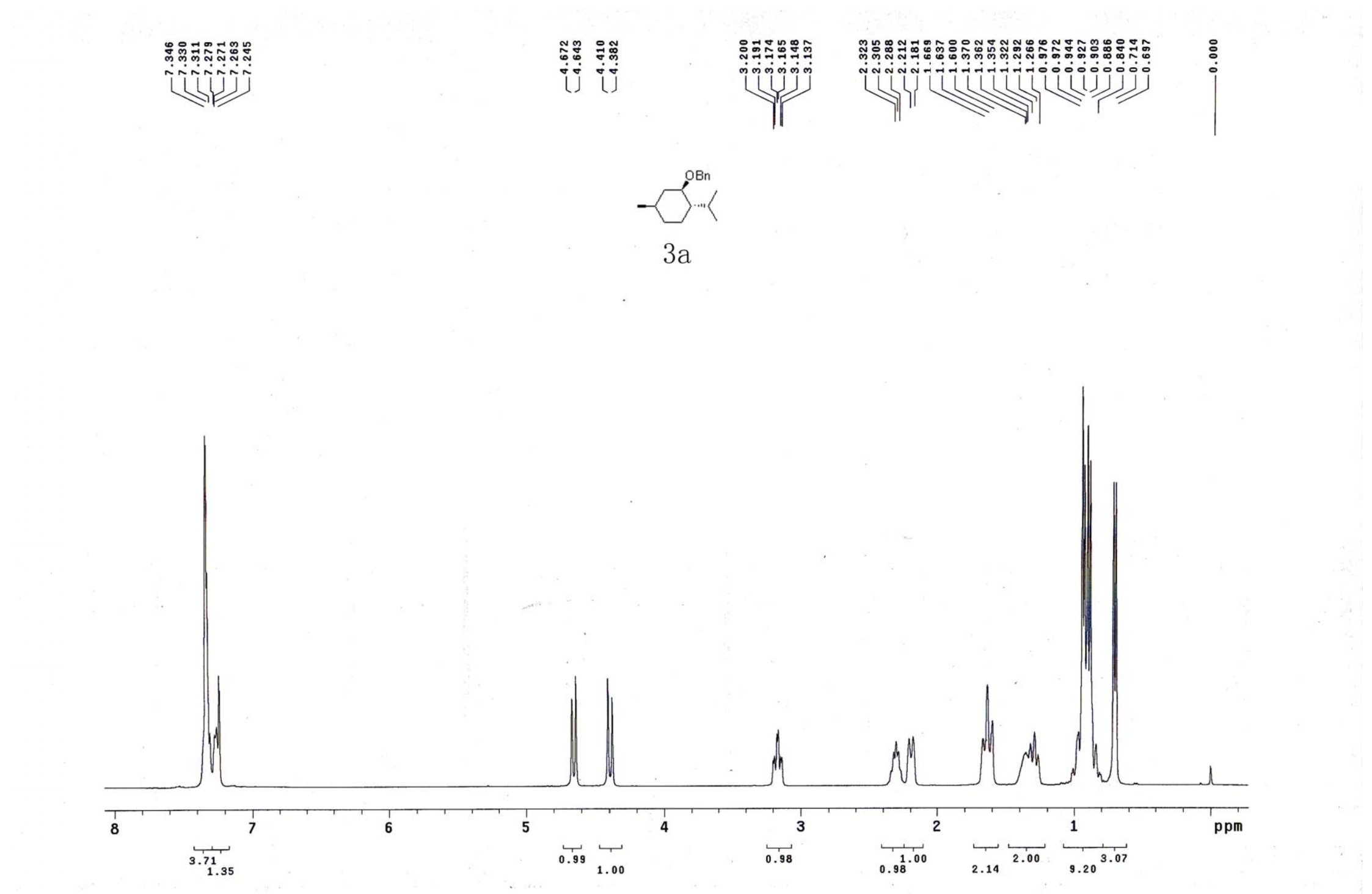
100
80
60
40
20
0
ppm

1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7.245
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4.410
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3.200
3.191
3.174
3.165
3.148
3.137
2.323
2.305
2.288
2.212
2.181
1.669
1.637
1.600
1.370
1.362
1.354
1.322
1.292
1.266
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0.972
0.944
0.927
0.903
0.886
0.840
0.714
0.697
0.000
OBn
8
7
6
5
4
3
2
1
ppm
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0.99
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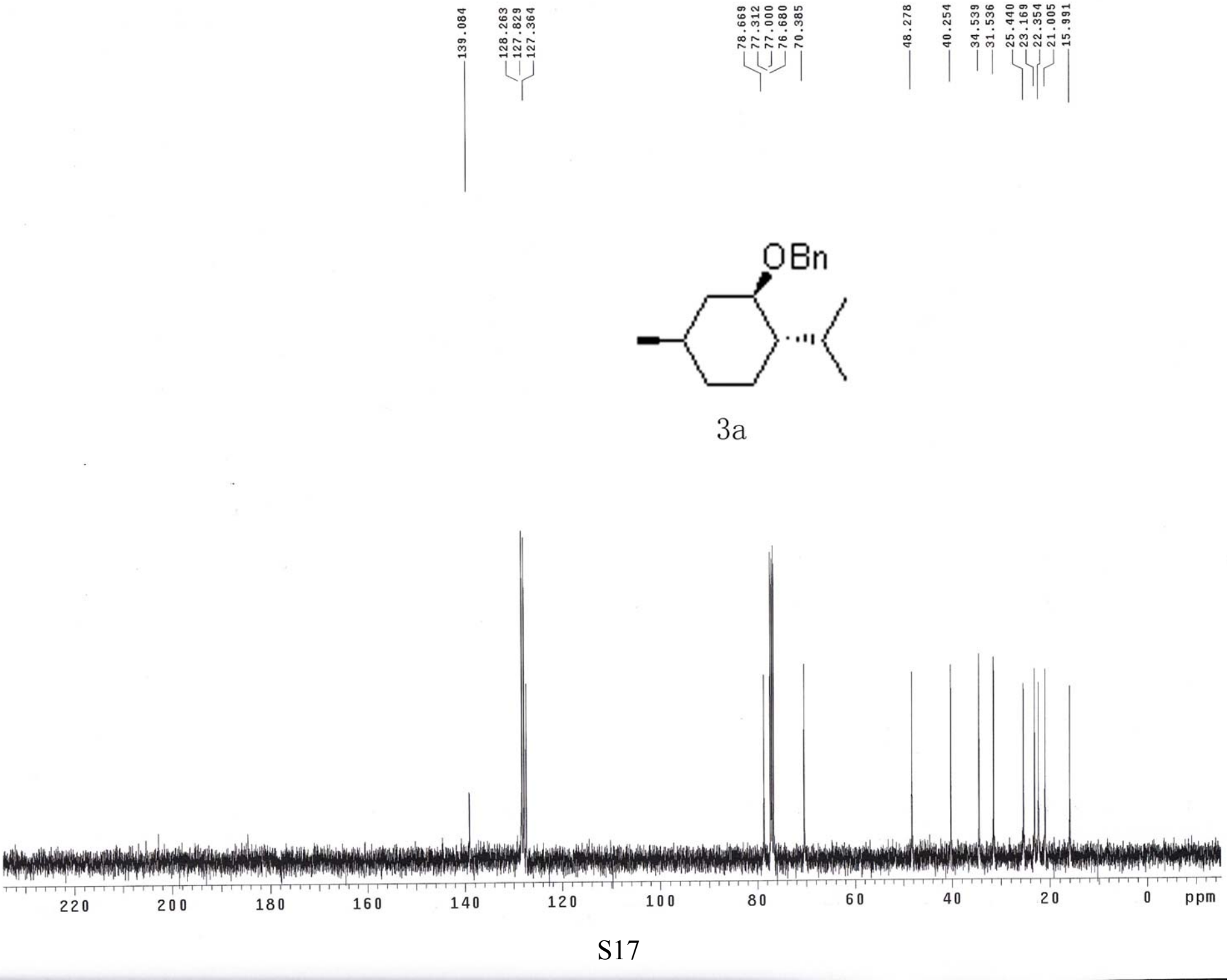
2.14
2.00
9.20
3.07

3a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40.254
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25.440
23.169
22.354
21.005
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140
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100
80
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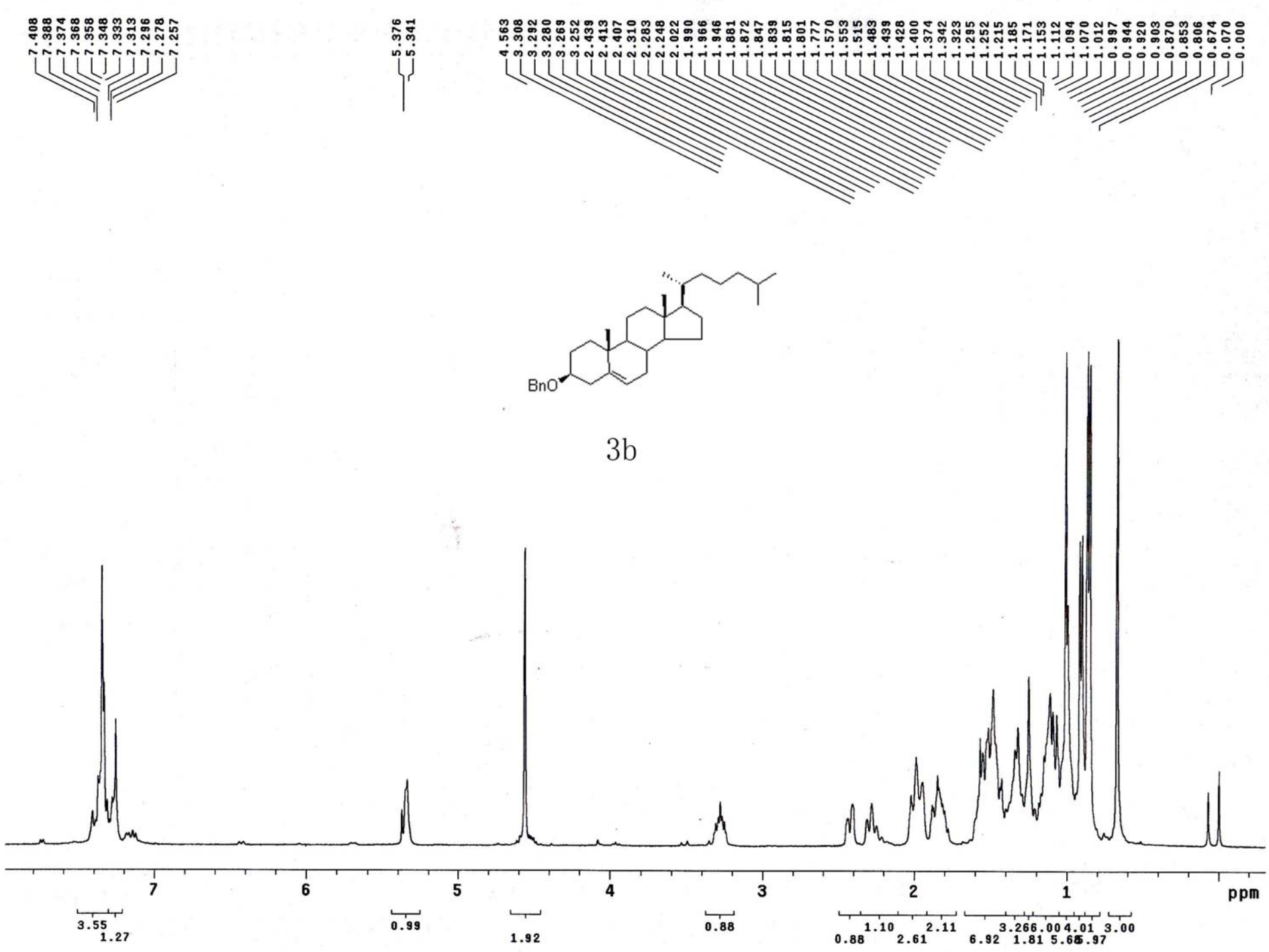
ppm

3a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3.292
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1.872
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BnO
7
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5
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3
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ppm
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0.88
1.10
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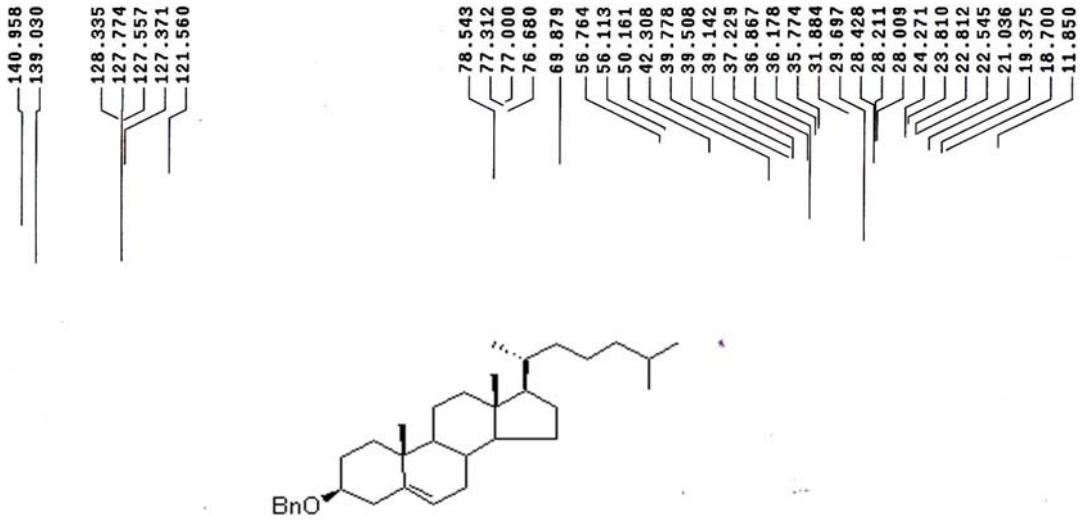
4.01
5.68
3.00
5.97

3b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56.113
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39.142
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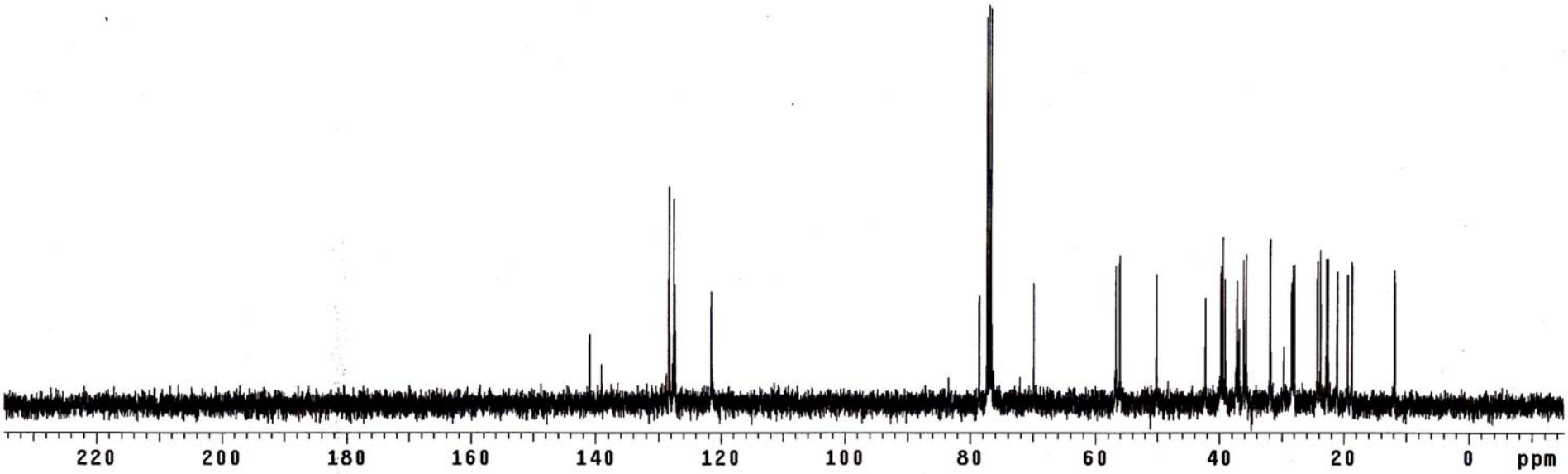
BnO

3b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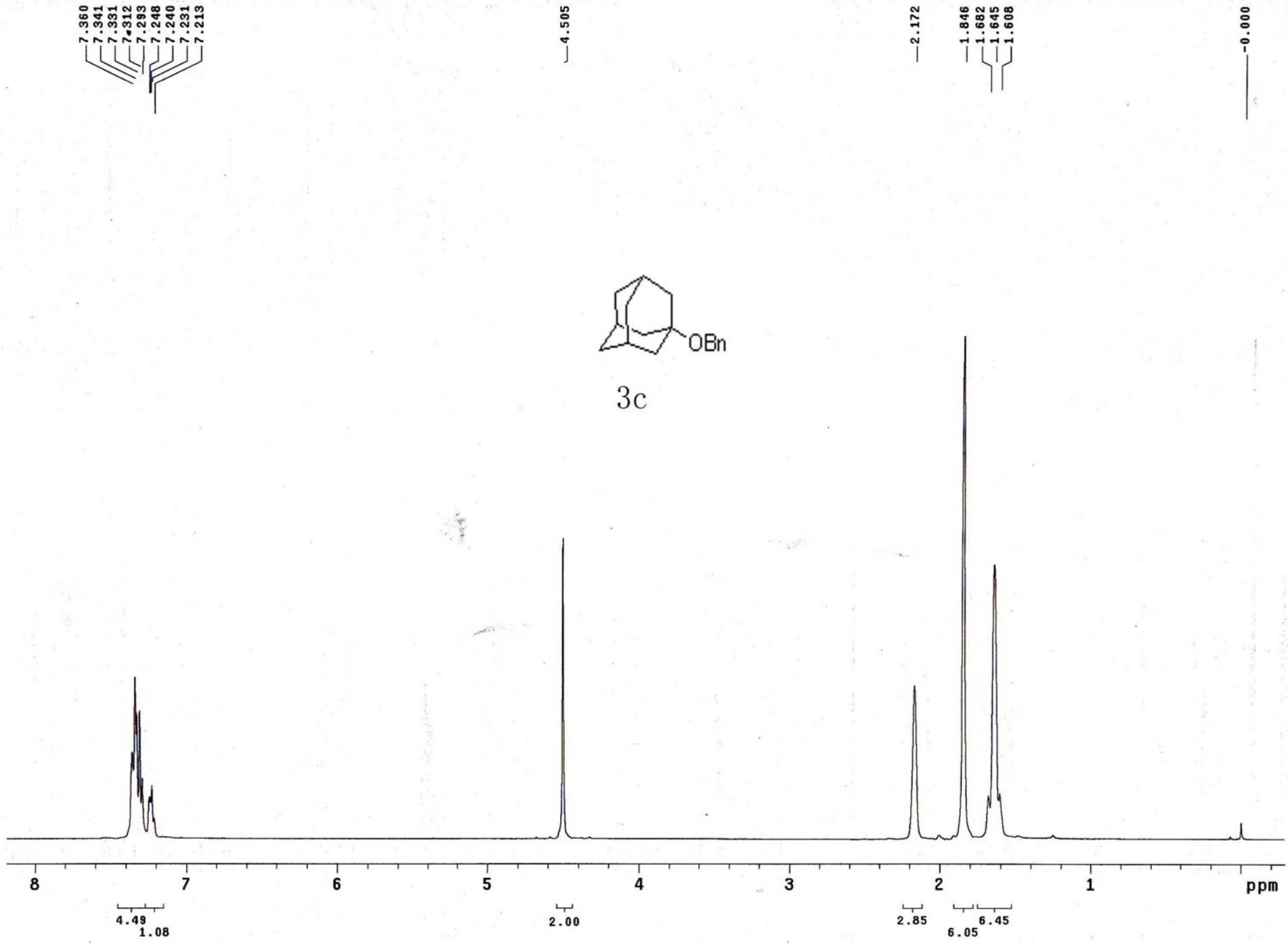
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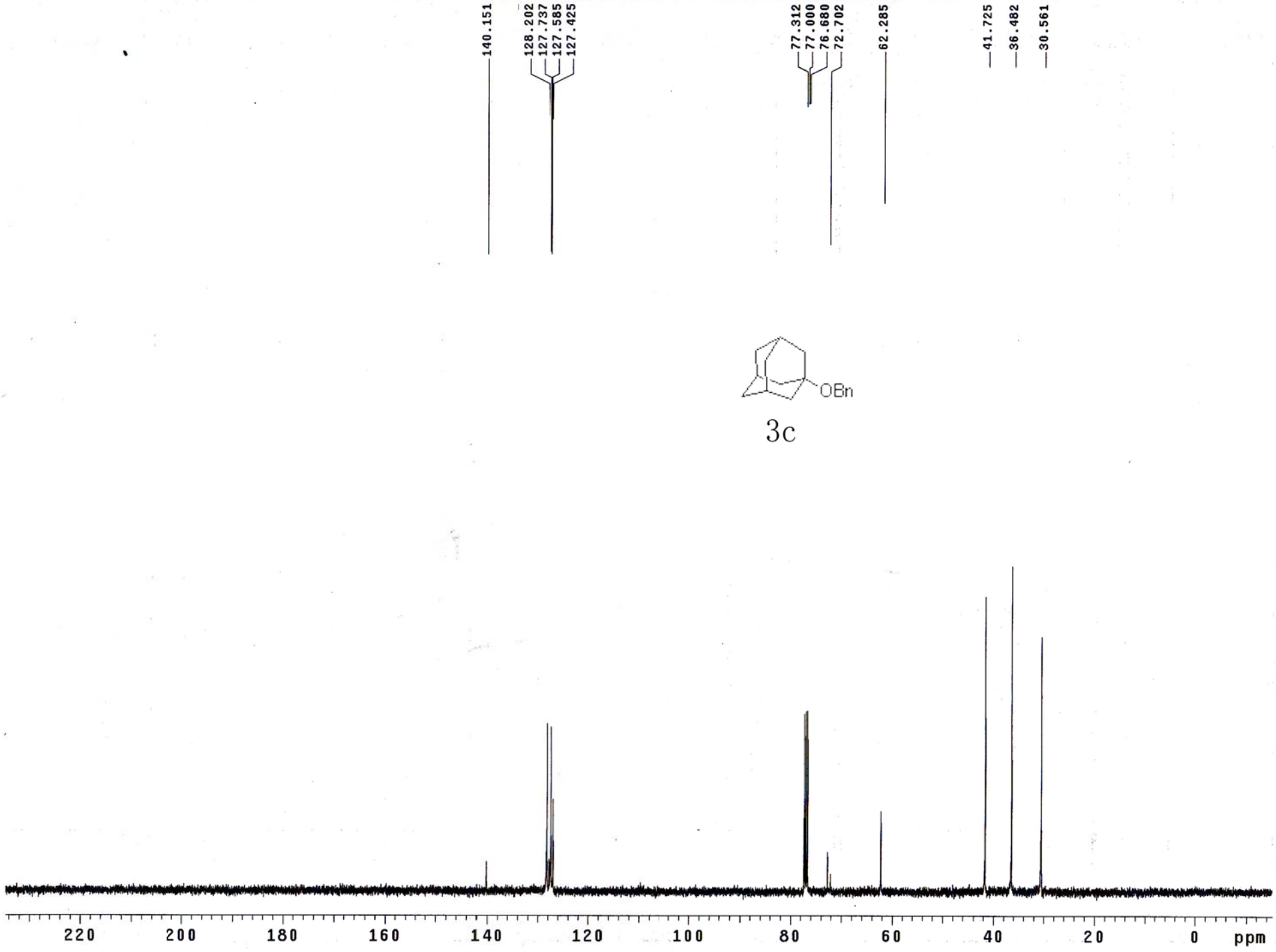
6.45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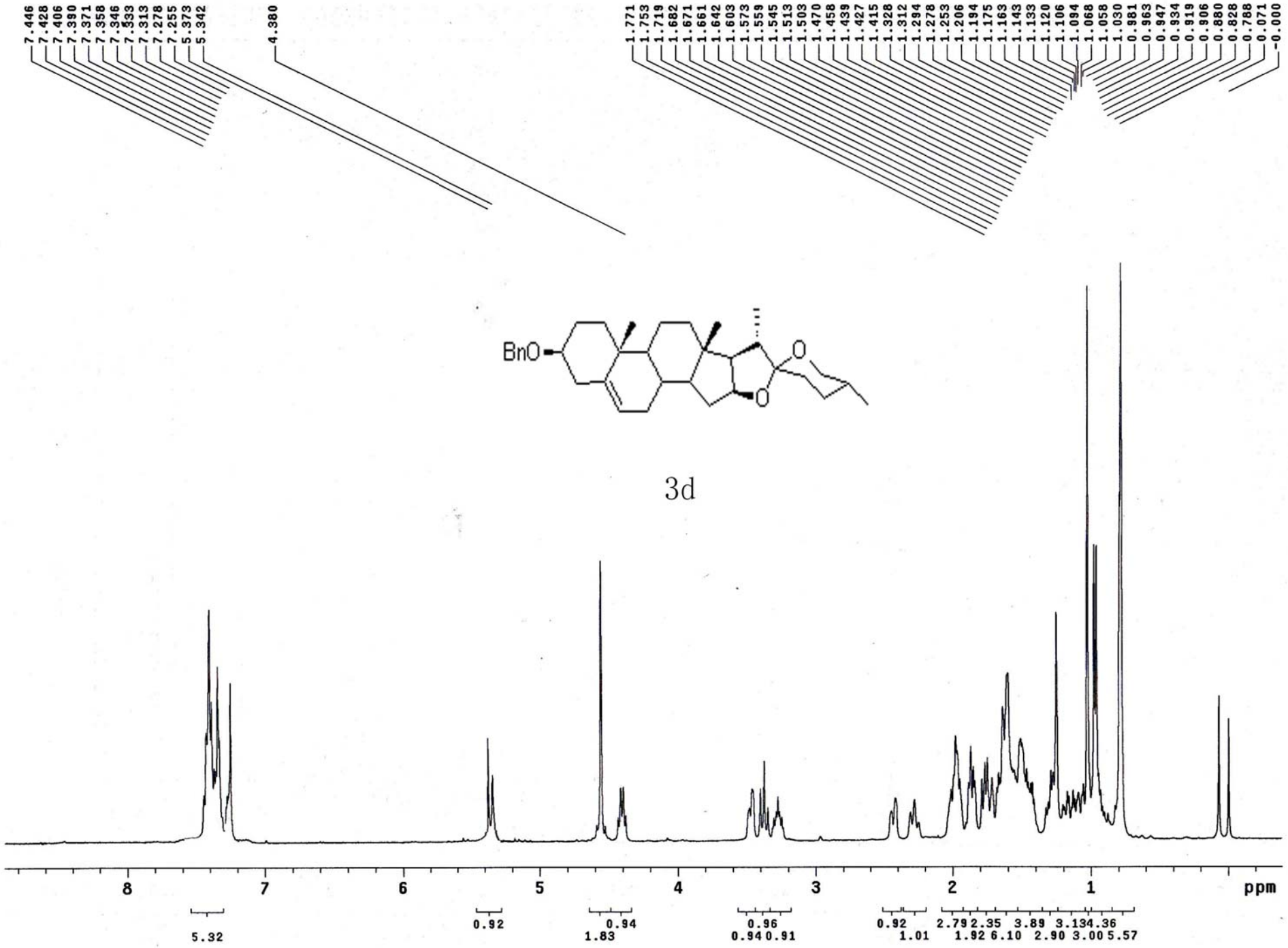
ppm

3c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7
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0.96
0.94 0.91
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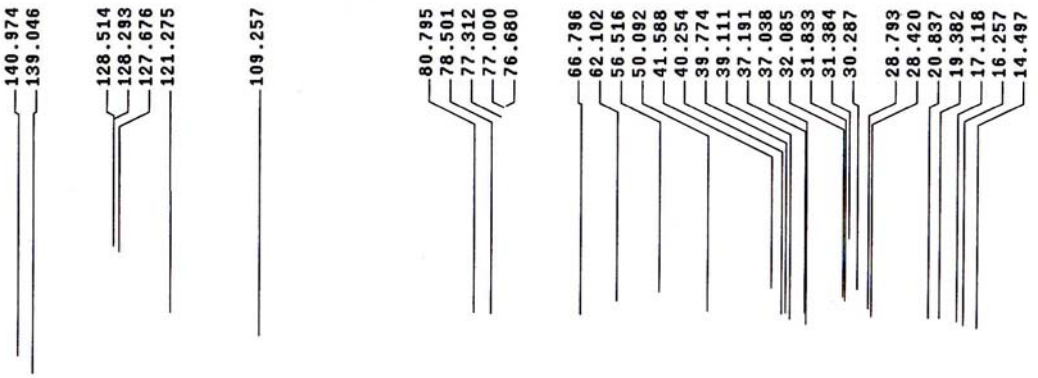
2.79 2.35
1.92 6.10
3.89
2.90
3.13 4.36
3.00 5.57

3d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77.312
77.000
76.680
66.796
62.102
56.516
50.092
41.588
40.254
39.774
39.111
37.191
37.038
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28.793
28.420
20.837
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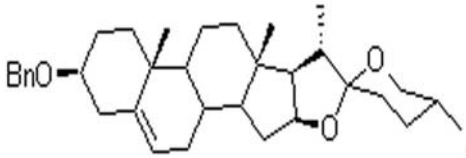
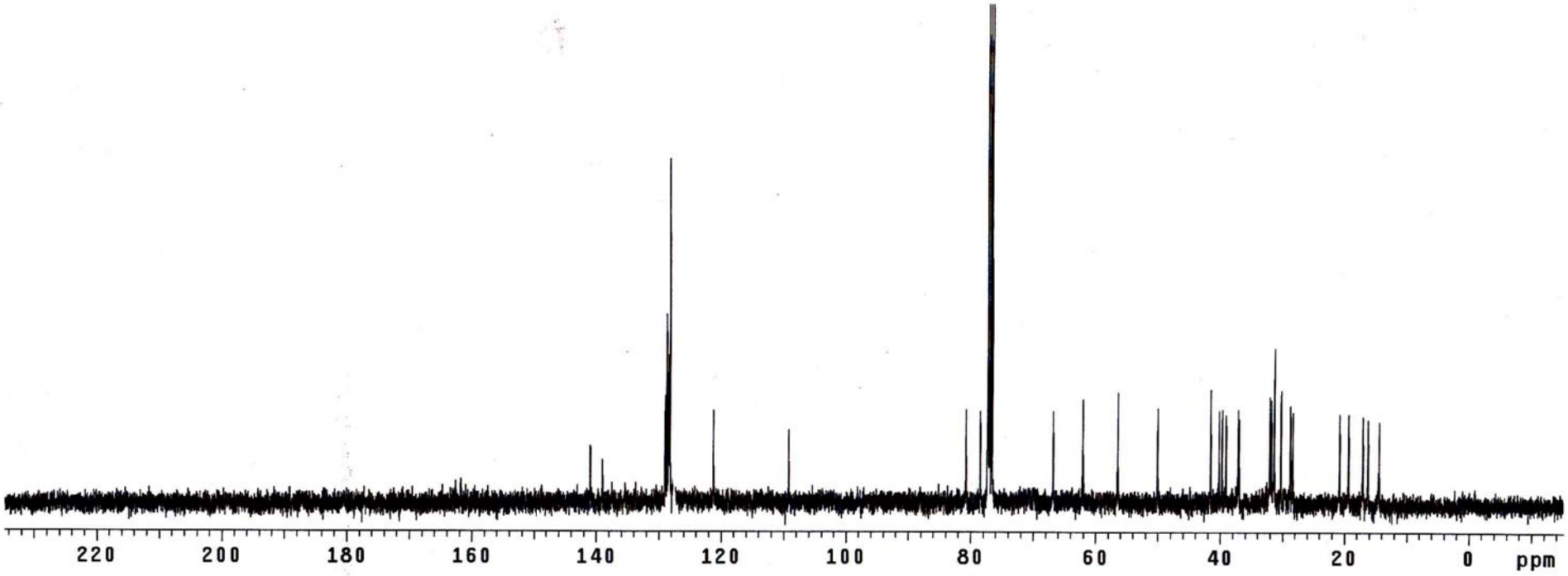
14.497


BnO
O
O

3d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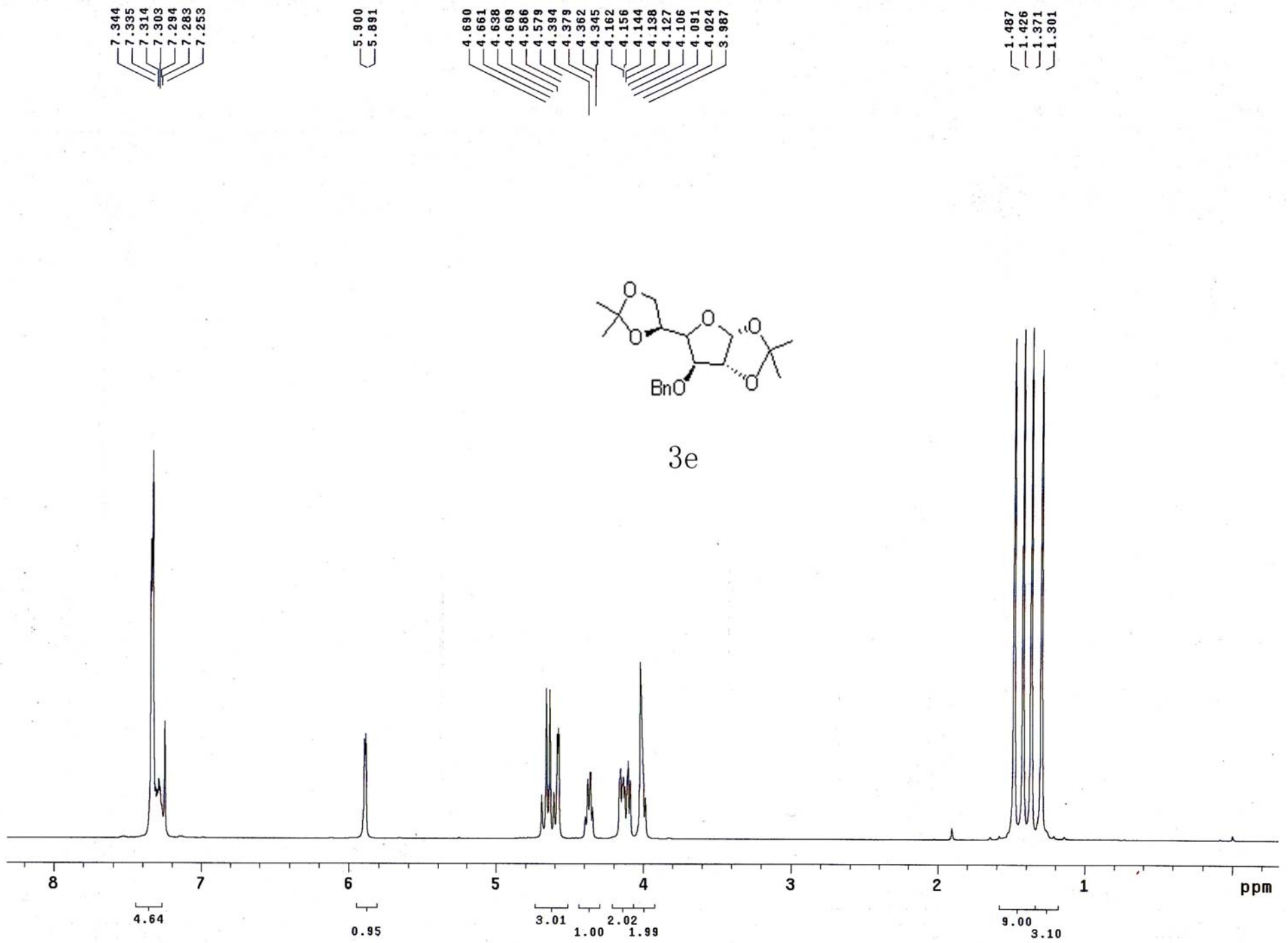
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7.303
7.294
7.283
7.253
5.900
5.891
4.690
4.661
4.638
4.609
4.586
4.579
4.394
4.379
4.362
4.345
4.162
4.156
4.144
4.138
4.127
4.106
4.091
4.024
3.987
1.487
1.426
1.371
1.301
BnO
8
7
6
5
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ppm
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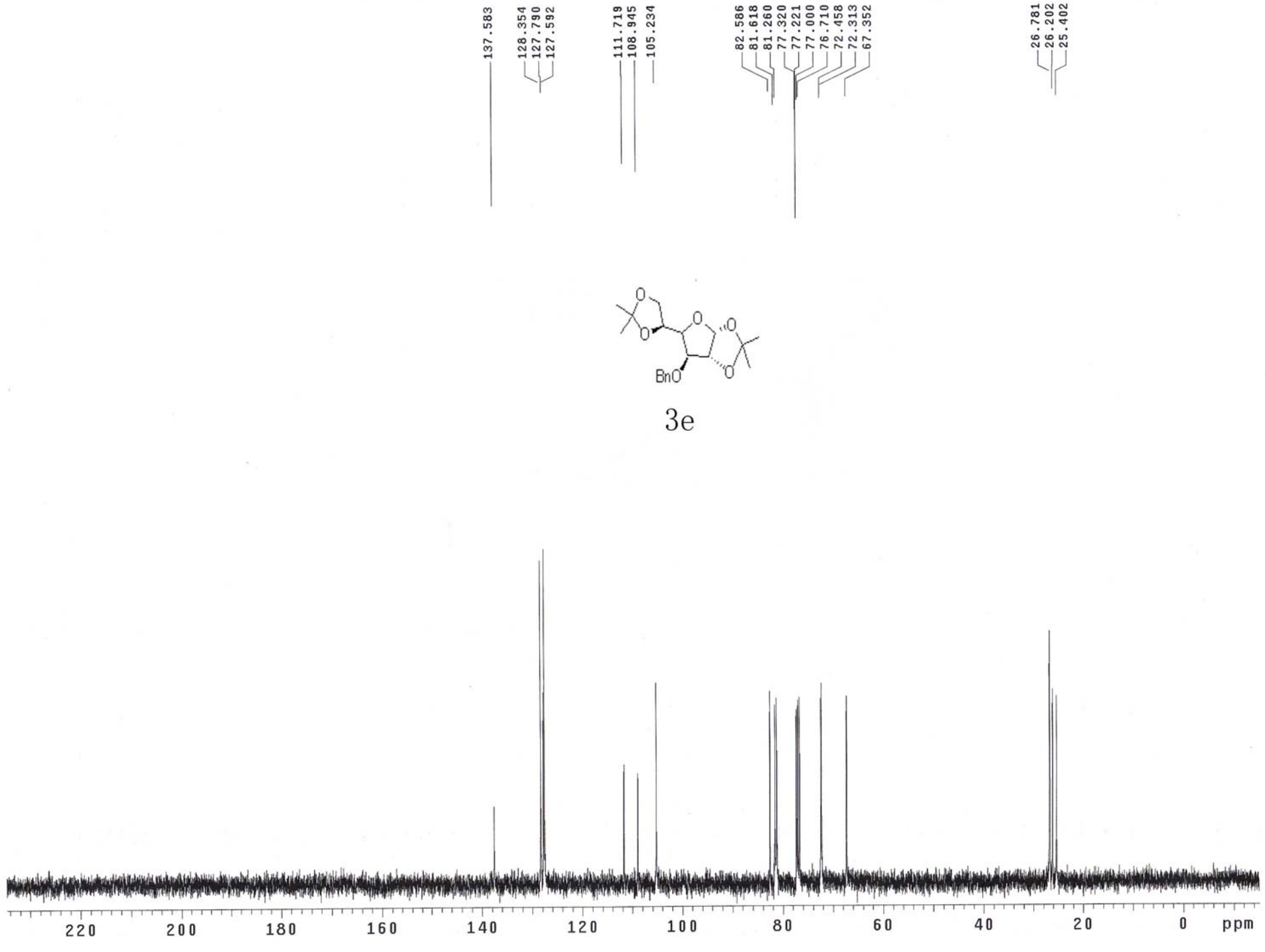
1.00
2.02
1.99
9.00
3.10

3e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82.586
81.618
81.260
77.320
77.221
77.000
76.710
72.458
72.313
67.352
26.781
26.202
25.402
BnO
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200
180
160
140
120
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60
40
20
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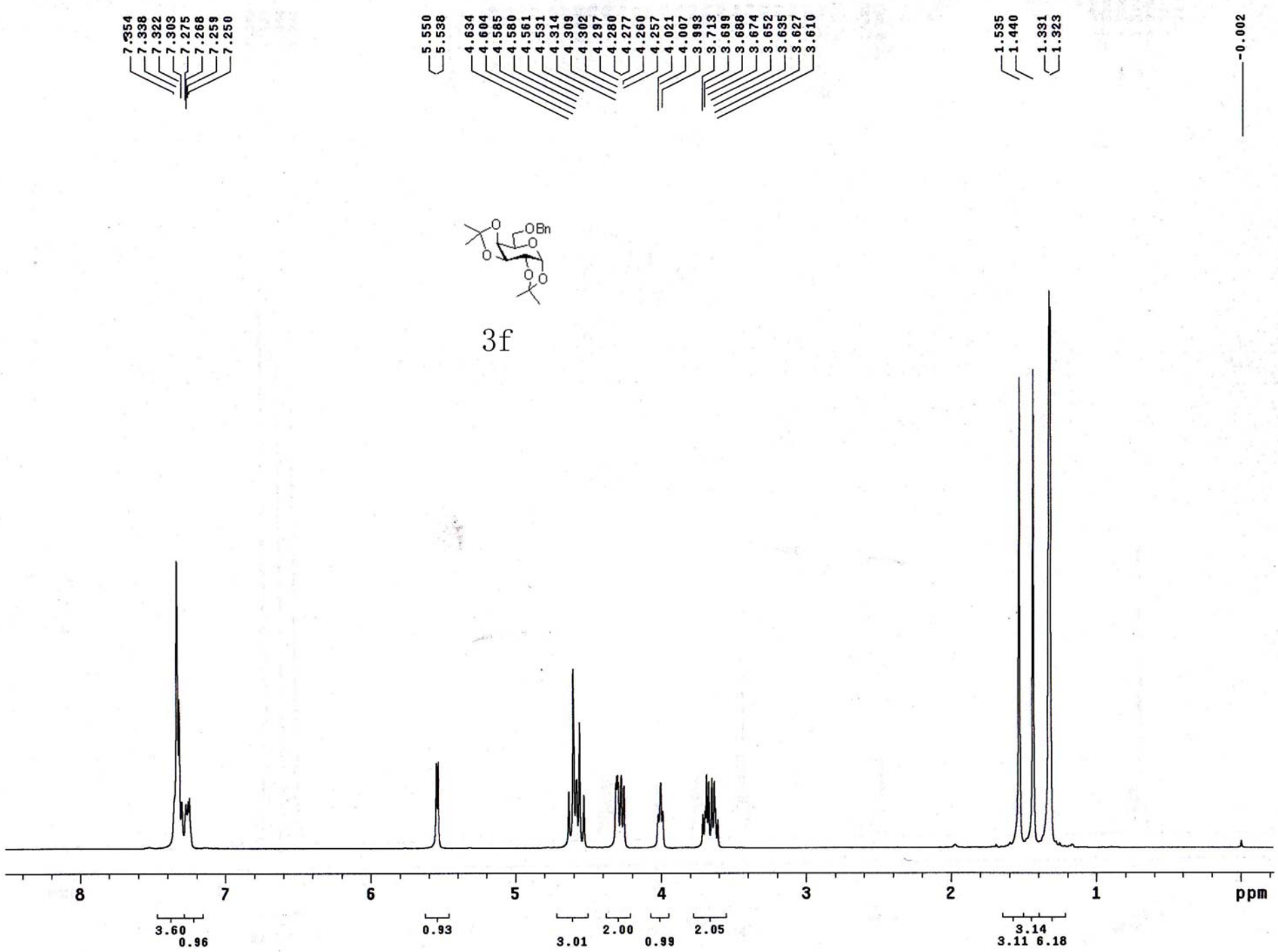
ppm

3e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7.259
7.250
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5.538
4.634
4.604
4.585
4.580
4.561
4.531
4.314
4.309
4.302
4.297
4.280
4.277
4.260
4.257
4.021
4.007
3.993
3.713
3.699
3.688
3.674
3.652
3.635
3.627
3.610
1.535
1.440
1.331
1.323
-0.002
OBn
3f
8
7
6
5
4
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0.99
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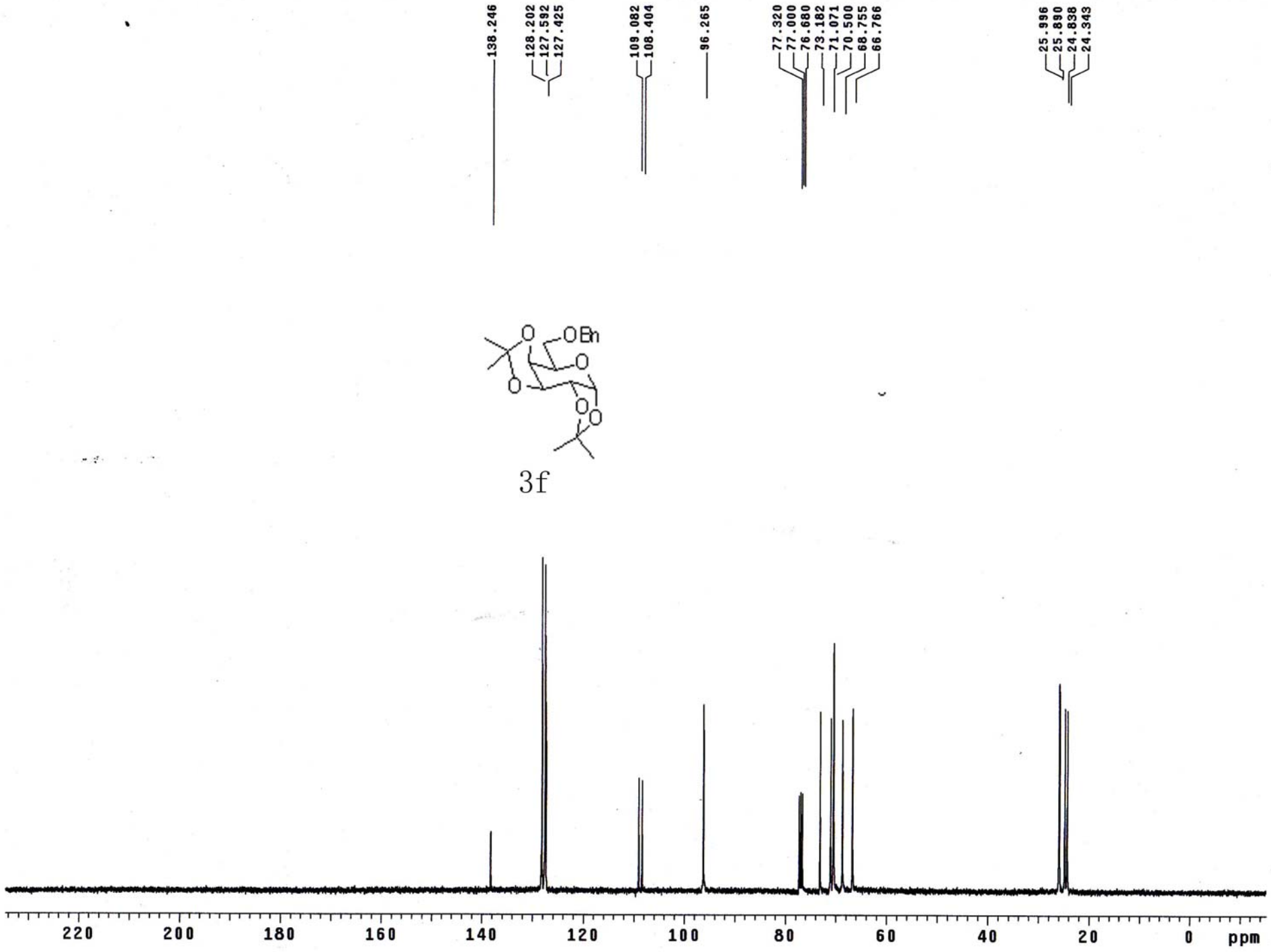
3.11
6.18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127.592
127.425
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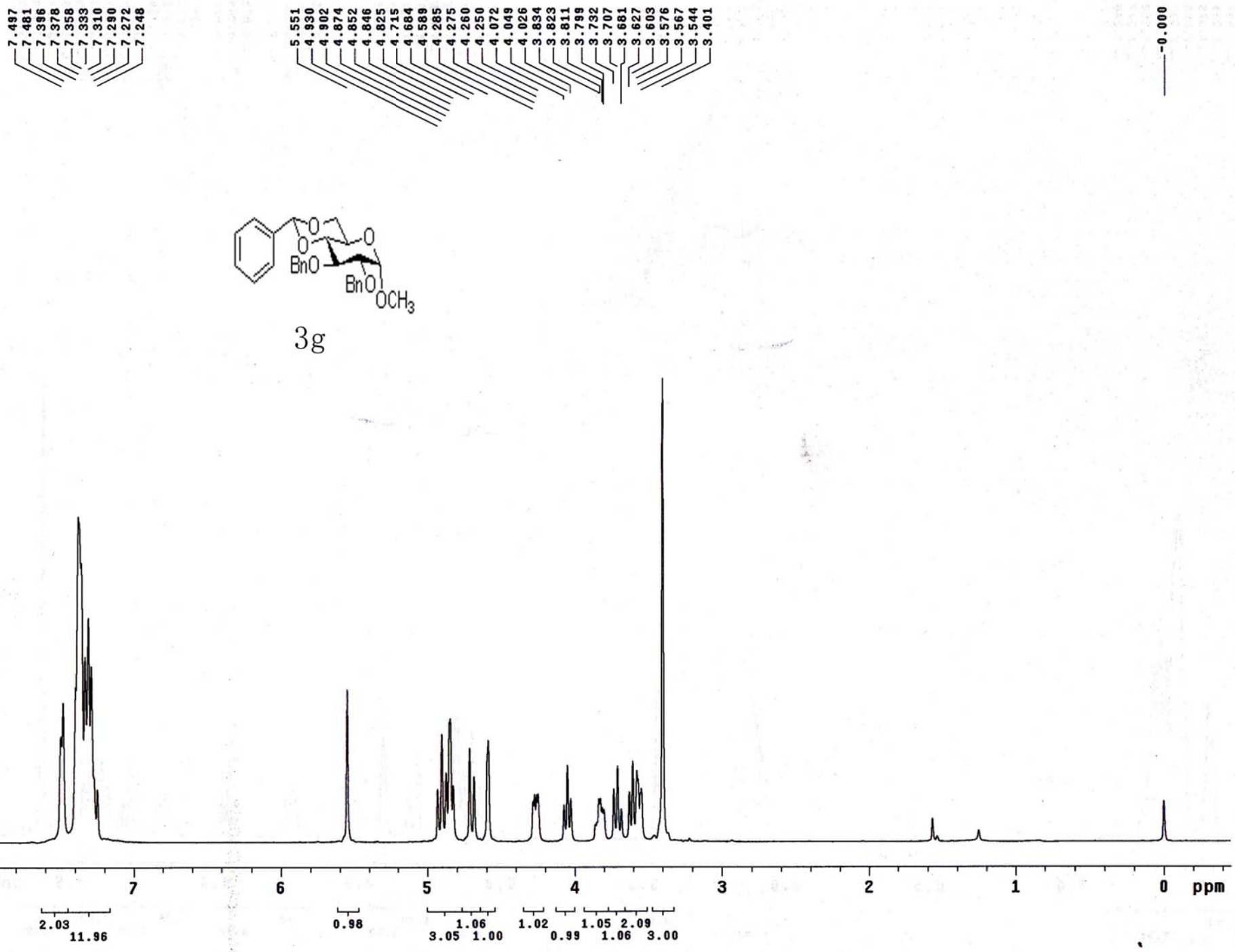
108.404
96.265
77.320
77.000
76.680
73.182
71.071
70.500
68.755
66.766
25.996
25.890
24.838
24.343
OBn
O
O
O
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3f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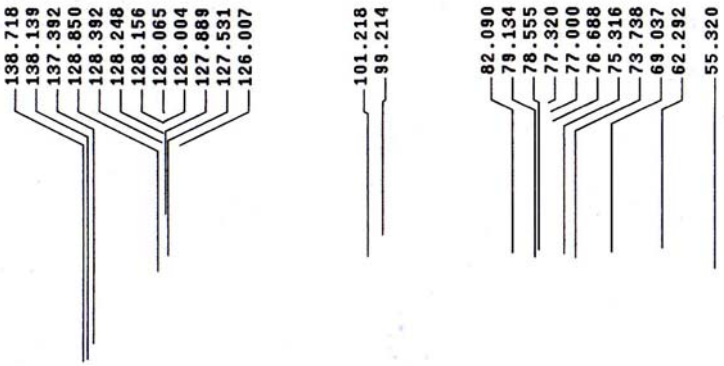
7.333
7.310
7.290
7.272
7.248
5.551
4.930
4.902
4.874
4.852
4.846
4.825
4.715
4.684
4.589
4.285
4.275
4.260
4.250
4.072
4.049
4.026
3.834
3.823
3.811
3.799
3.732
3.707
3.681
3.627
3.603
3.576
3.567
3.544
3.401
-0.000
BnO
BnO
OCH3
3g
8
7
6
5
4
3
2
1
0
ppm
2.03
11.96
0.98
1.06
3.05
1.00
1.02
0.99
1.05
1.06
2.09
3.00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138.139
137.392
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128.392
128.248
128.156
128.065
128.004
127.889
127.531
126.007
101.218
99.214
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79.134
78.555
77.320
77.000
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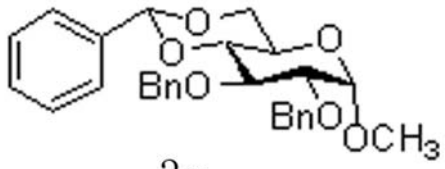
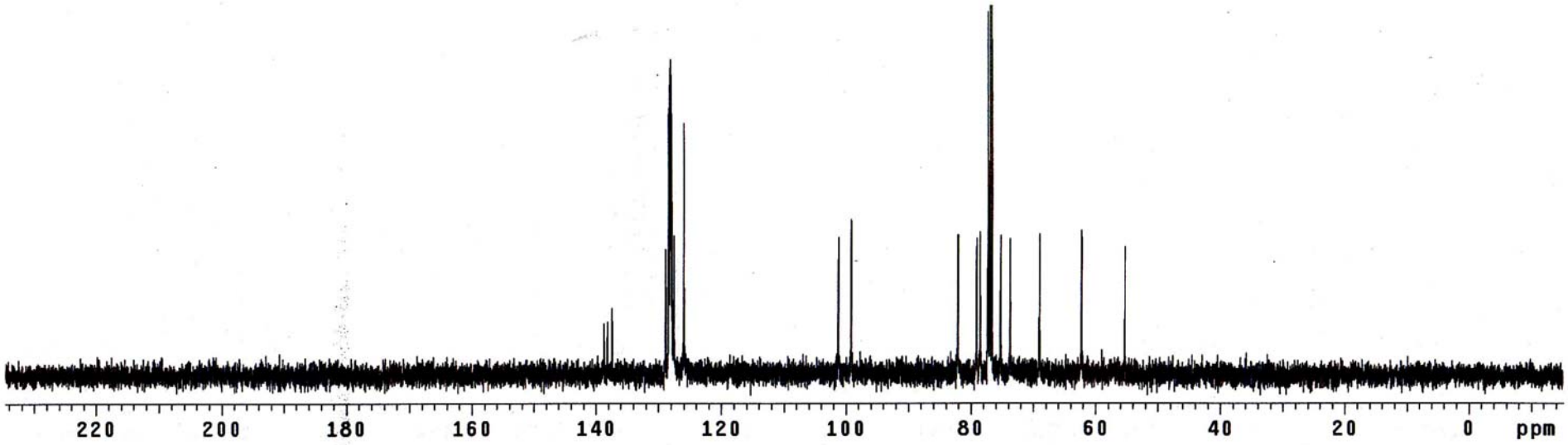
75.316
73.738
69.037
62.292
55.320


O
O
O
BnO
BnO
OCH3

3g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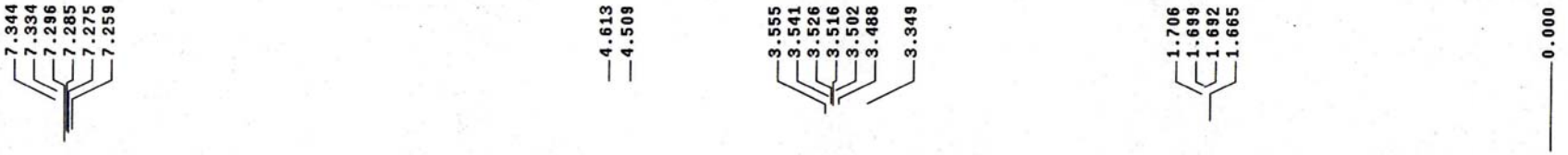
200
180
160
140
120
100
80
60
40
20
0
ppm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7.285
7.275
7.259
4.613
4.509
3.555
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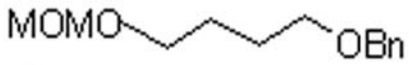
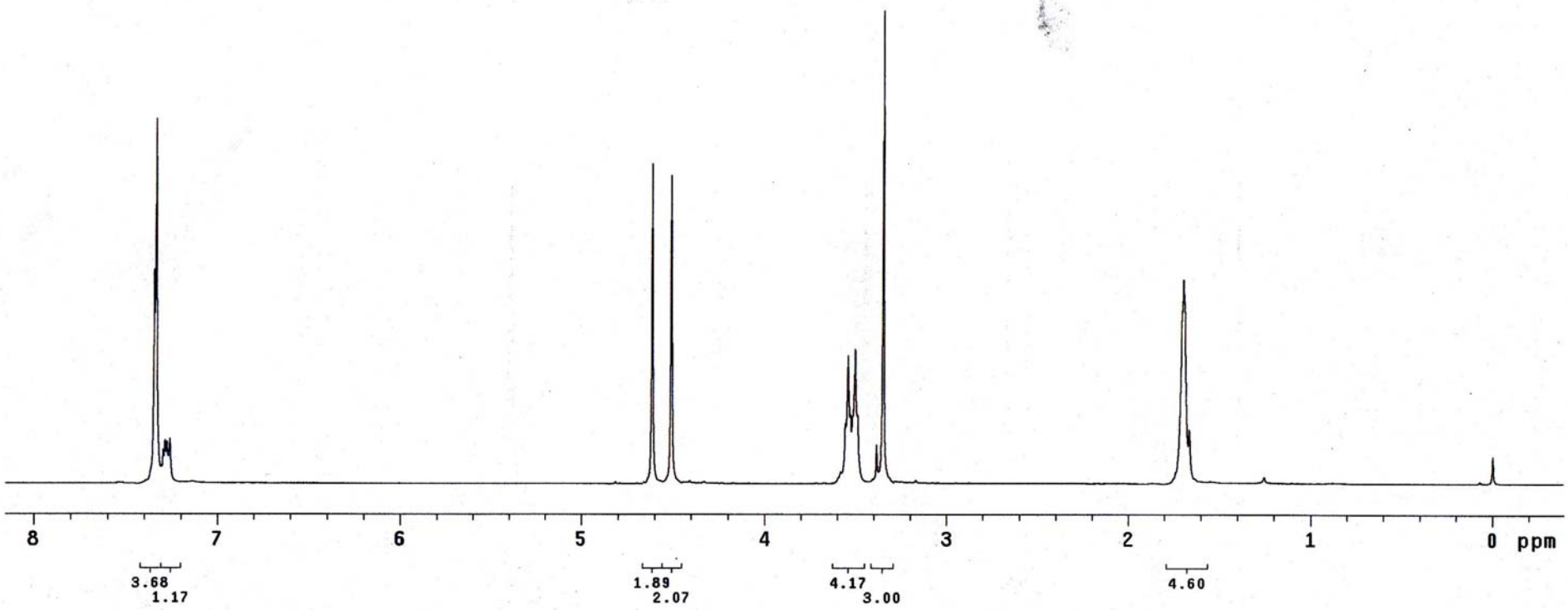
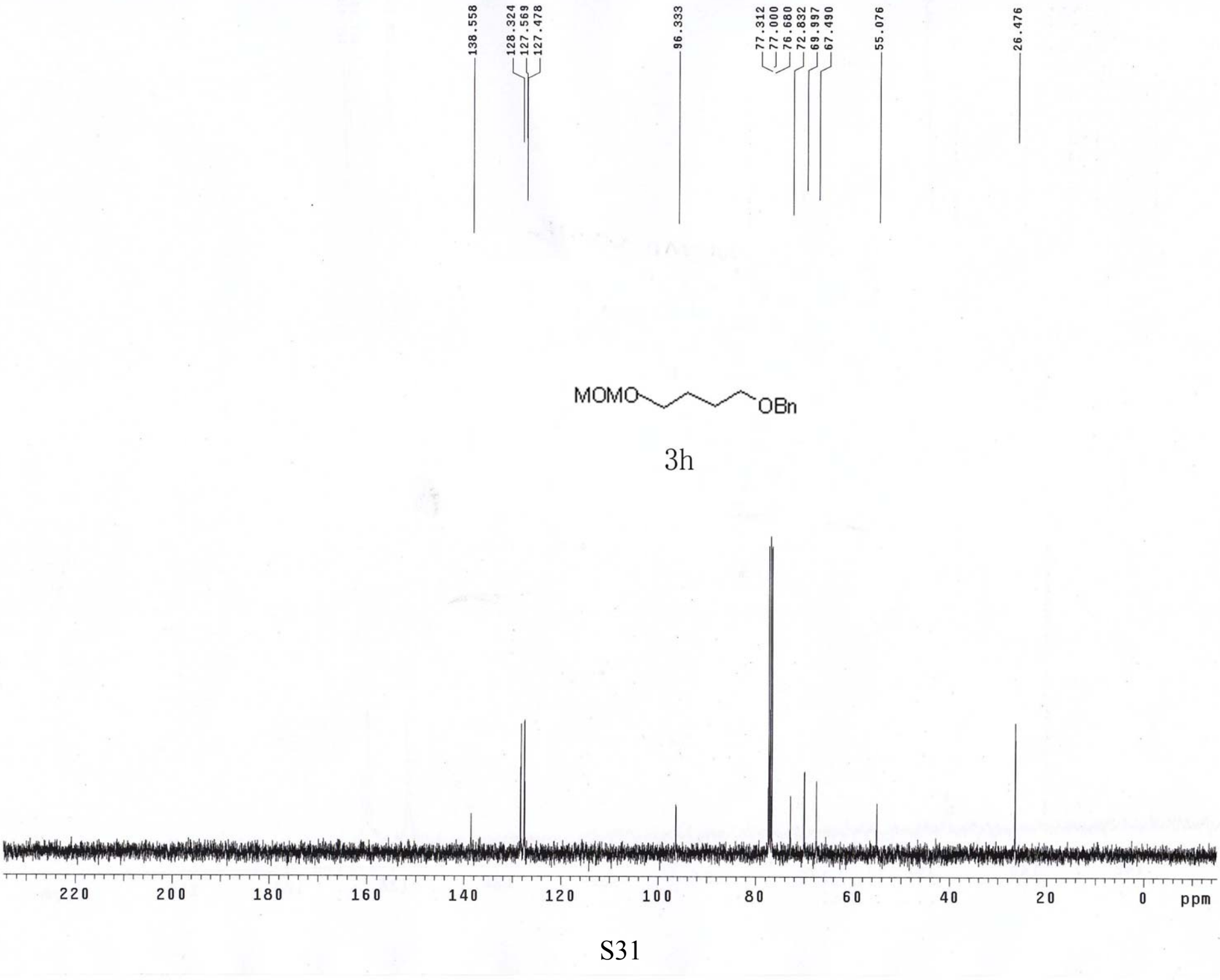
3.526
3.516
3.502
3.488
3.349
1.706
1.699
1.692
1.665
0.000


MOMO
OBn

3h


8
7
6
5
4
3
2
1
0 ppm
3.68
1.17
1.89
2.07
4.17
3.00
4.60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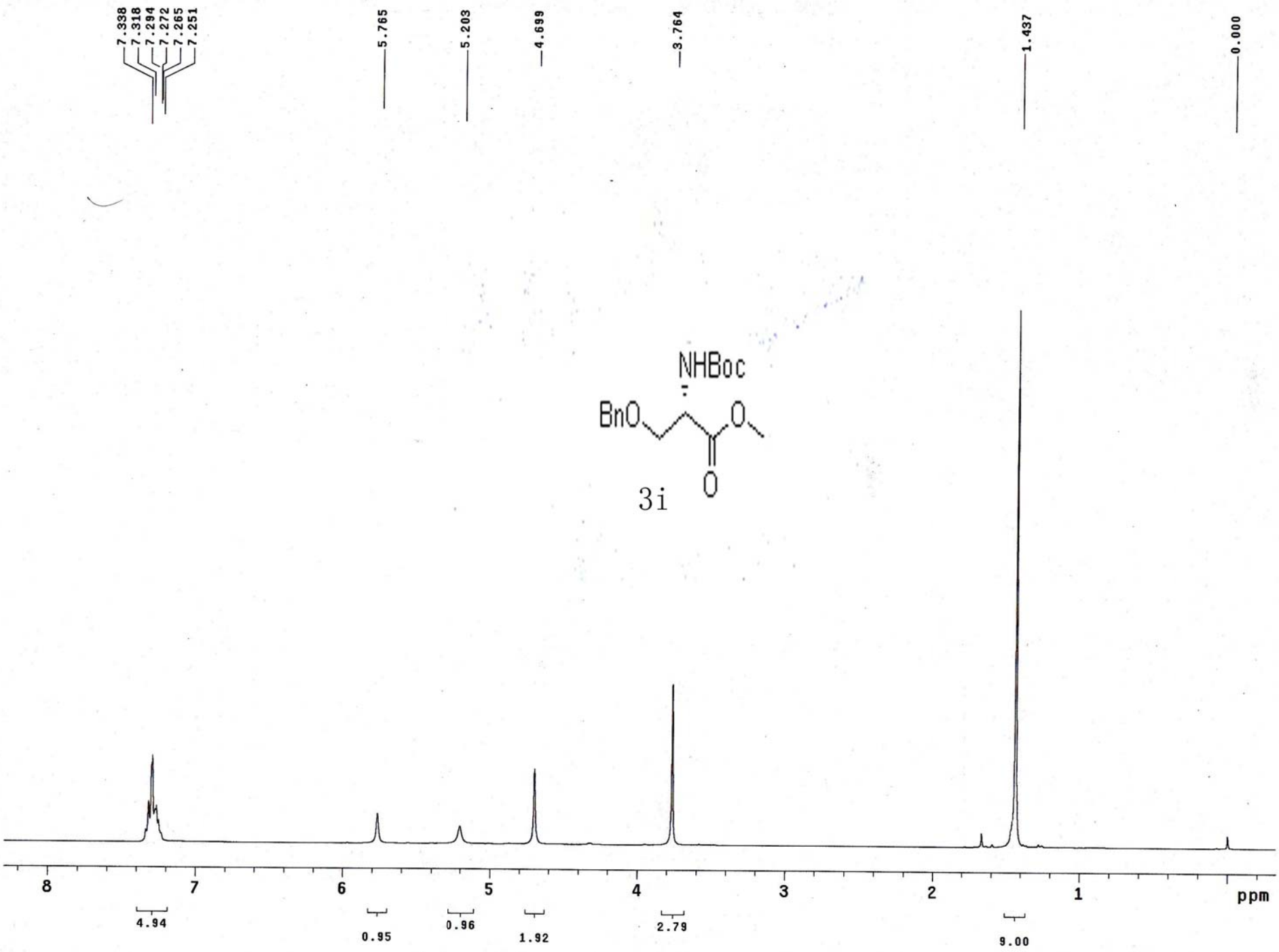
127.569
127.478
96.333
77.312
77.000
76.680
72.832
69.997
67.490
55.076
26.476
MOMO
OBn
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3h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7.318
7.294
7.272
7.265
7.251
5.765
5.203
4.699
3.764
1.437
0.000
NHBoc
BnO
O
O
3i
8
7
6
5
4
3
2
1
ppm
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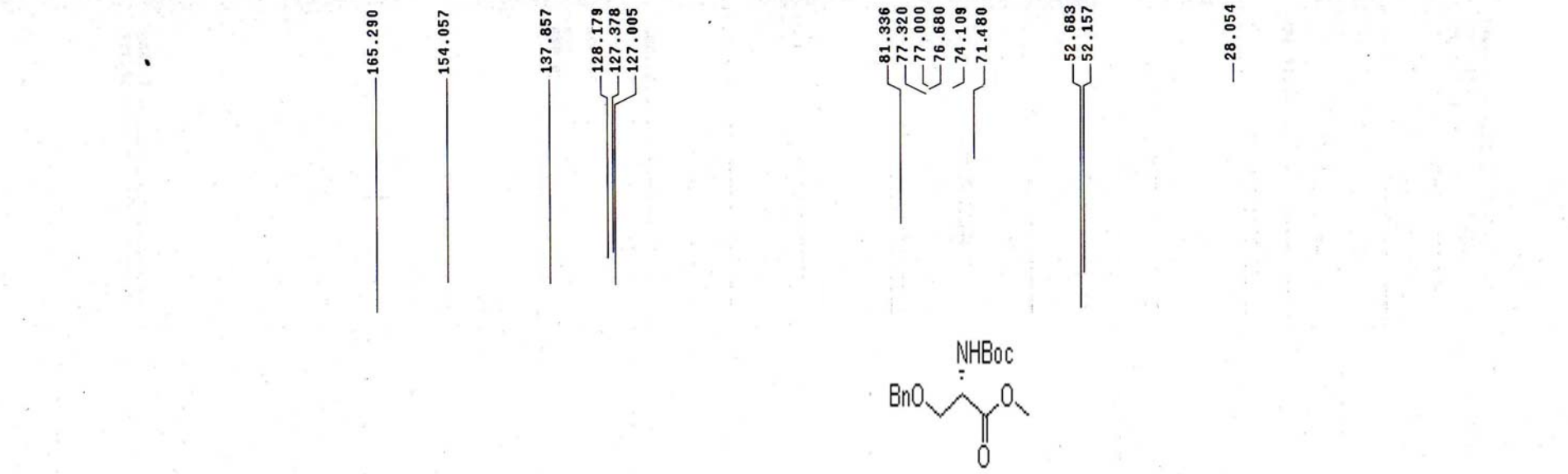
0.95
0.96
1.92
2.79
9.00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137.857
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127.378
127.005
81.336
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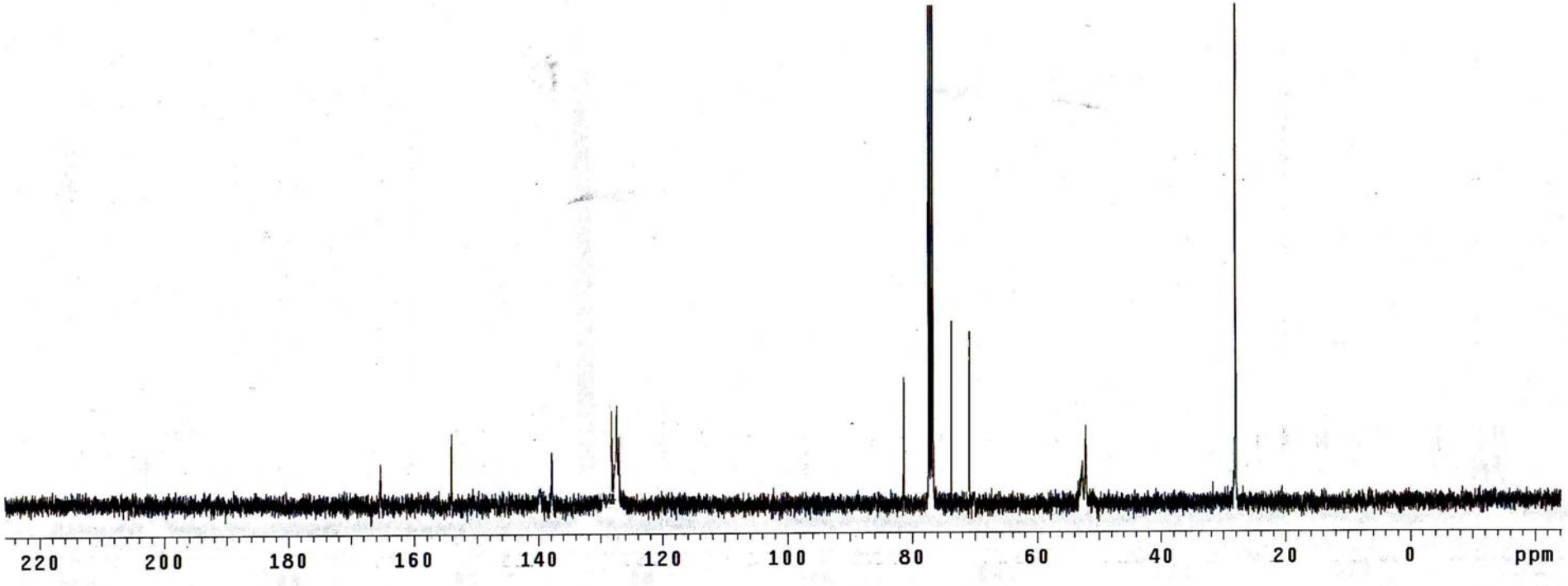
77.000
76.680
74.109
71.480
52.683
52.157
28.054
NHBoc
BnO
O
O

3i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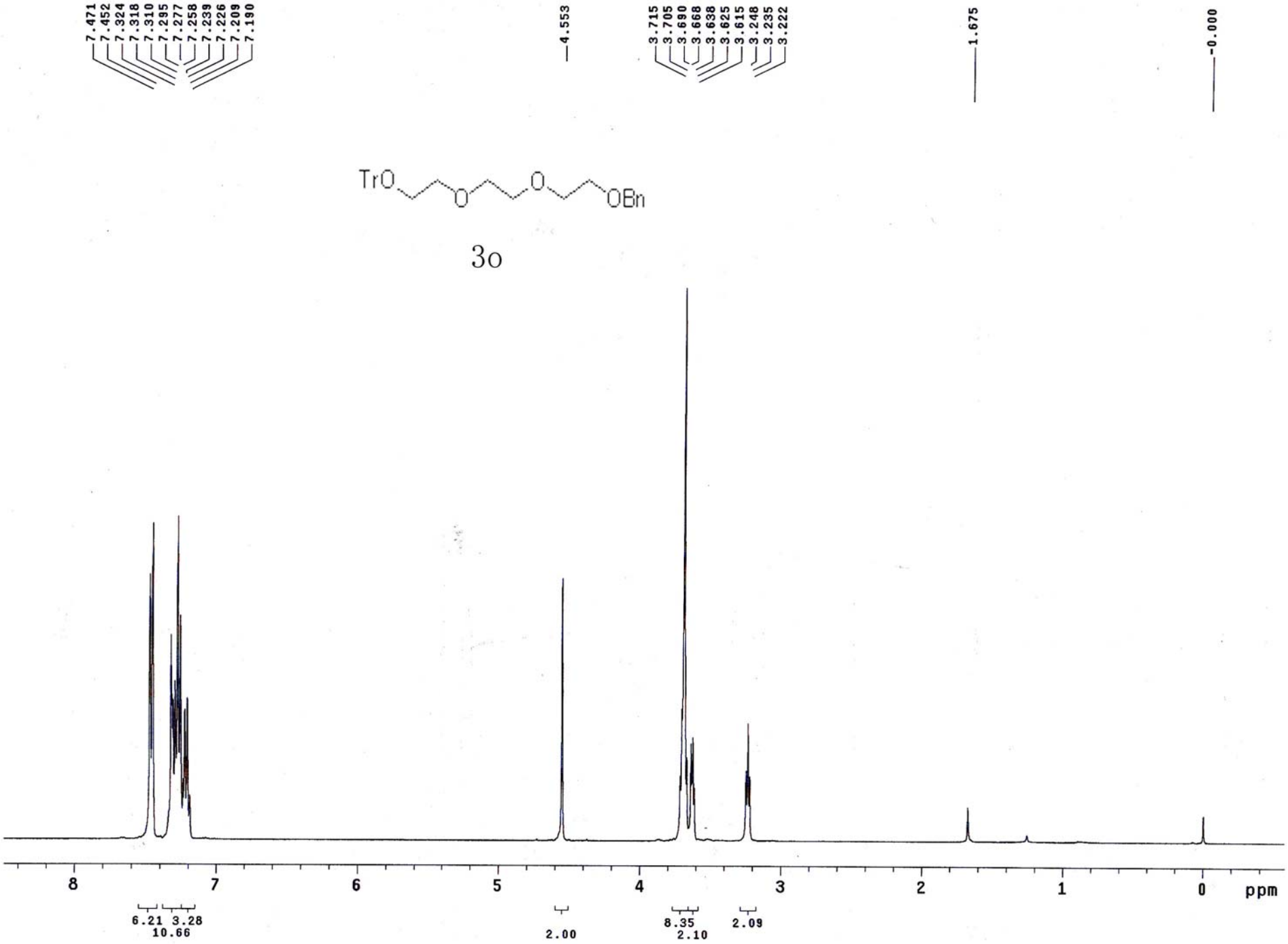
200
180
160
140
120
100
80
60
40
20
0
ppm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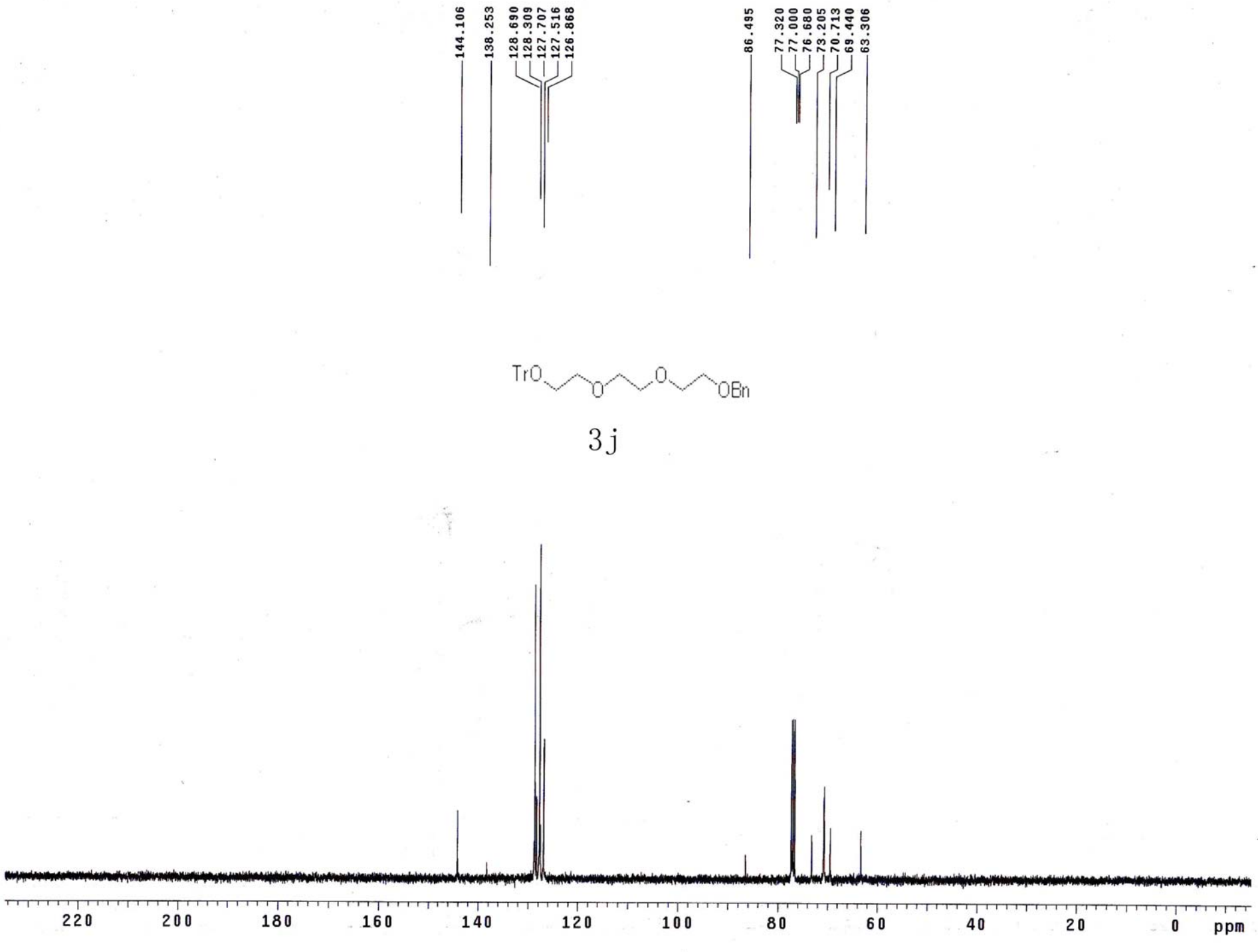
7.310
7.295
7.277
7.258
7.239
7.226
7.209
7.190
4.553
3.715
3.705
3.690
3.668
3.638
3.625
3.615
3.248
3.235
3.222
1.675
0.000
TrO
O
O
OBn
8
7
6
5
4
3
2
1
0
ppm
6.21
3.28
10.66
2.00
8.35
2.10
2.09

3o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128.309
127.707
127.516
126.868
86.495
77.320
77.000
76.680
73.205
70.713
69.440
63.306
TrO
O
O
OBn
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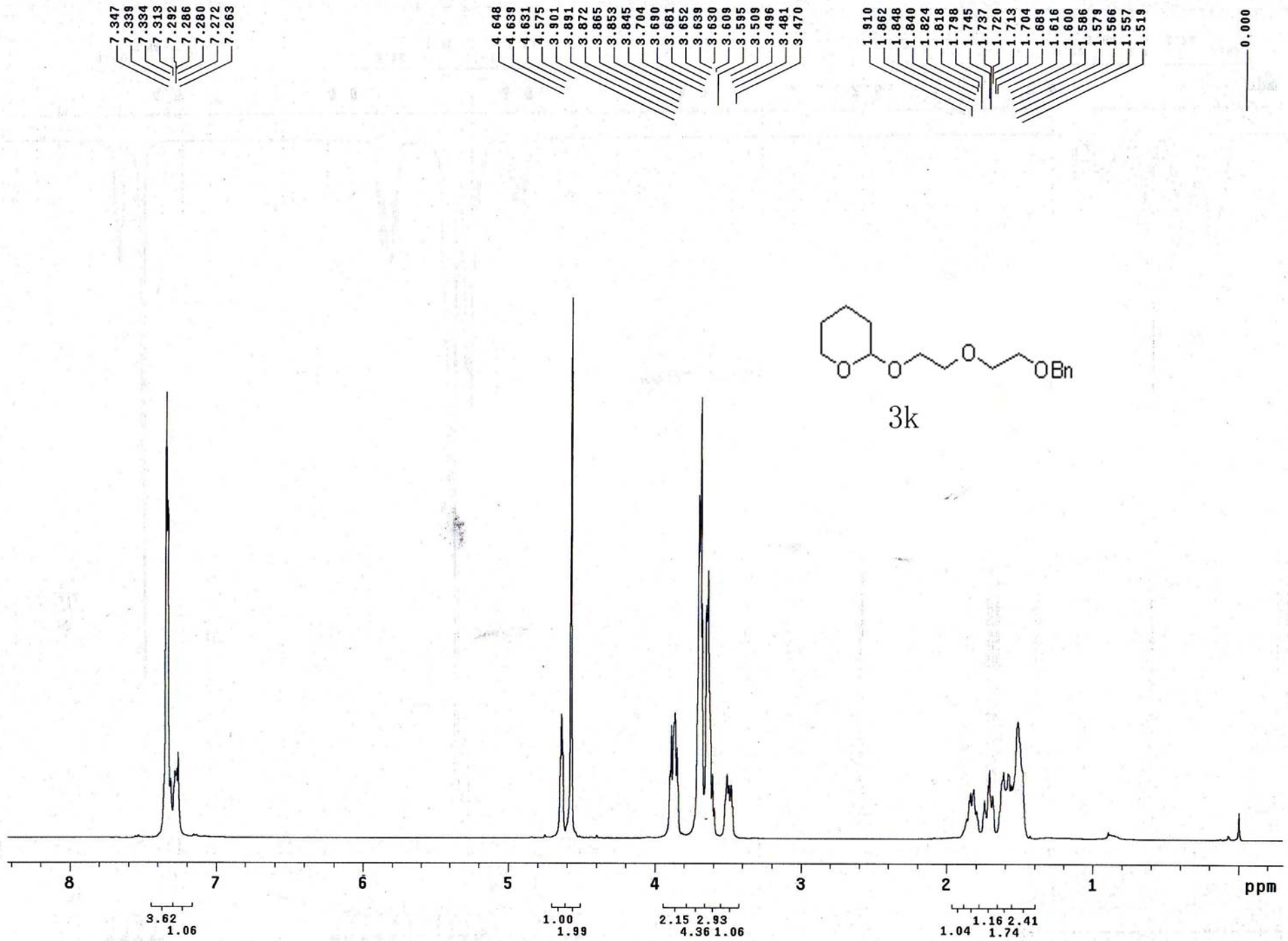
200
180
160
140
120
100
80
60
40
20
0
ppm

3j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7.313
7.292
7.286
7.280
7.272
7.263
4.648
4.639
4.631
4.575
3.901
3.891
3.872
3.865
3.853
3.845
3.704
3.690
3.681
3.652
3.639
3.630
3.609
3.595
3.509
3.496
3.481
3.470
1.910
1.862
1.848
1.840
1.824
1.818
1.798
1.745
1.737
1.720
1.713
1.704
1.689
1.616
1.600
1.586
1.579
1.566
1.557
1.519
0.000
O
O
O
OBn
3k
8
7
6
5
4
3
2
1
ppm
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1.99
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2.93
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1.06
1.04
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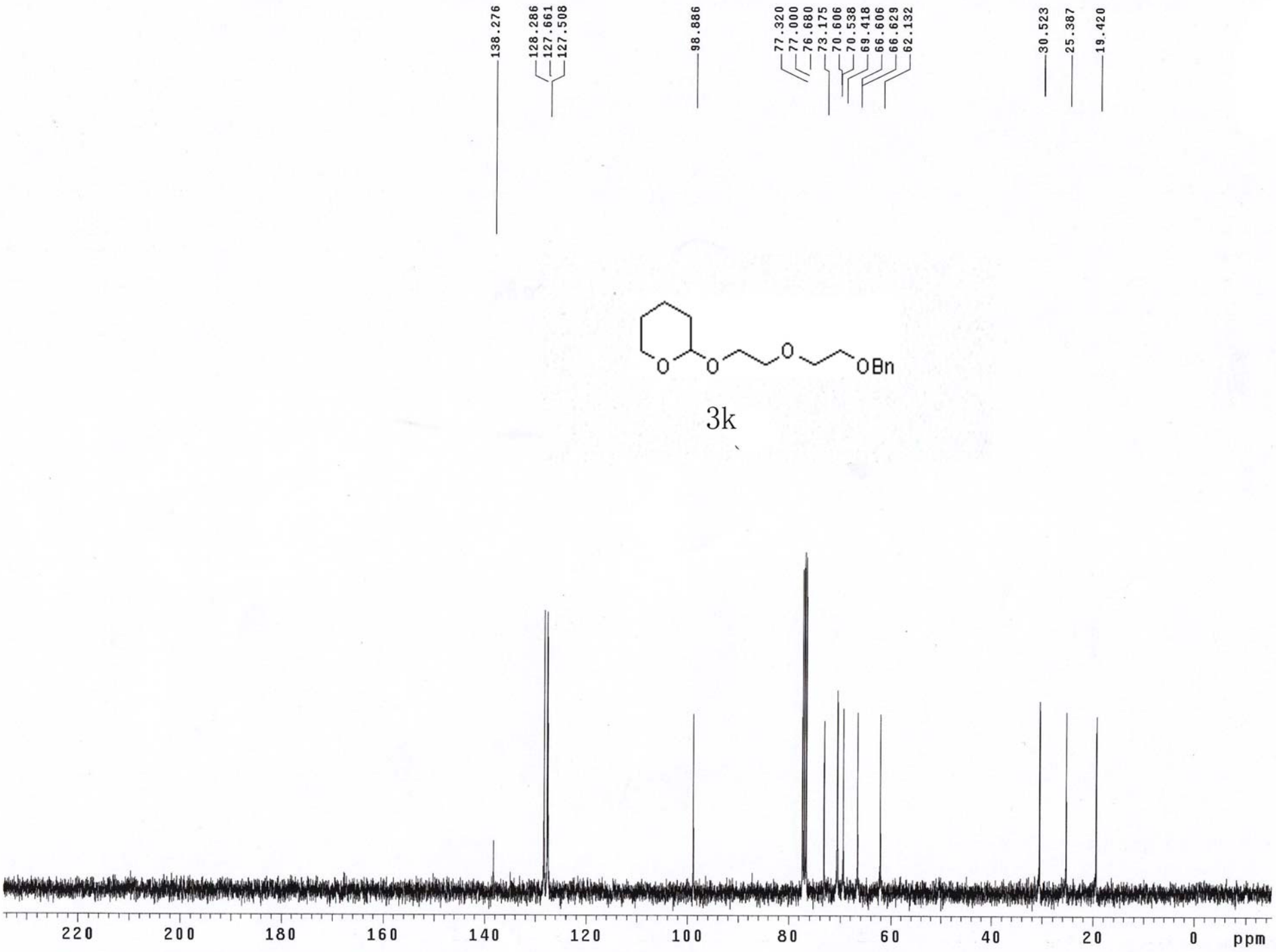
1.74
2.41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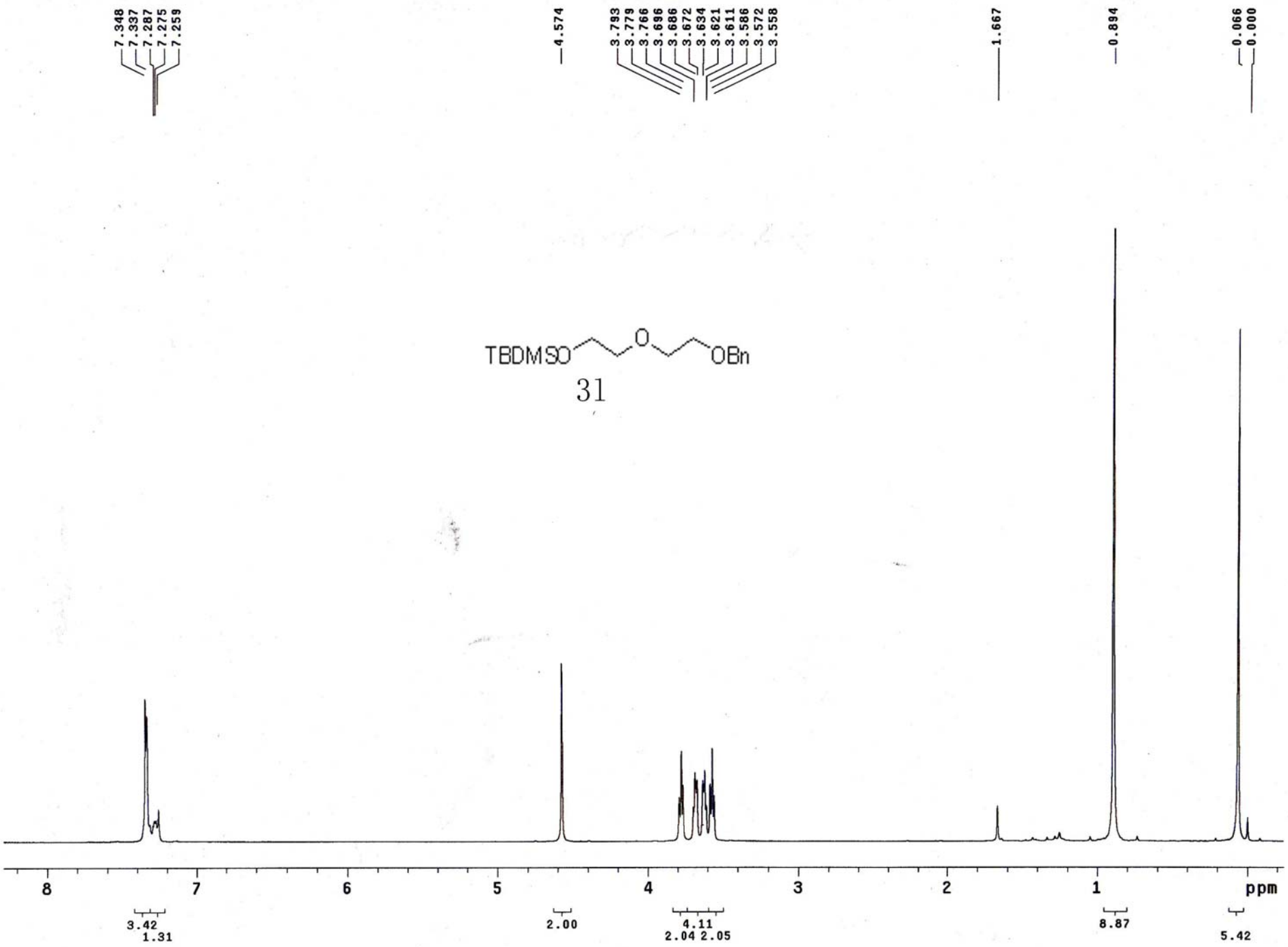
77.000
76.680
73.175
70.606
70.538
69.418
66.606
66.629
62.132
30.523
25.387
19.420
O
O
O
OBn
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3k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7.275
7.259
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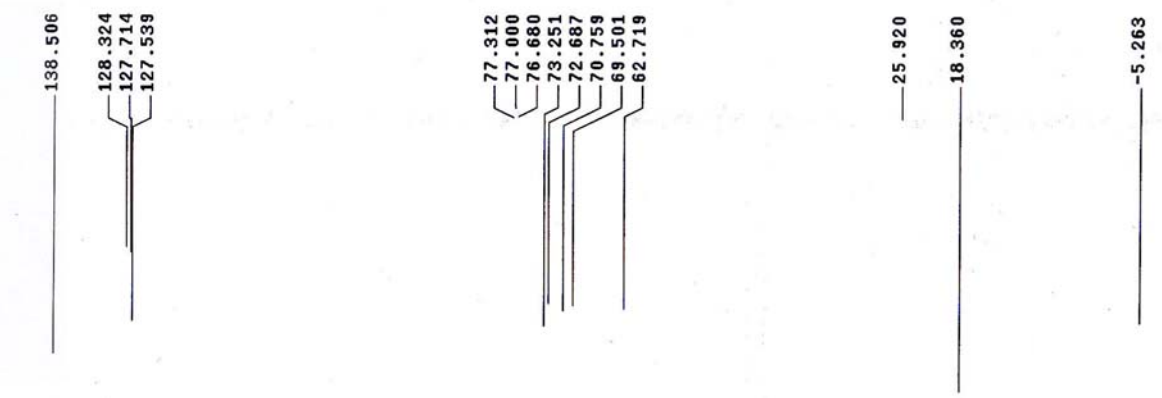
3.793
3.779
3.766
3.686
3.686
3.672
3.634
3.621
3.611
3.586
3.572
3.558
1.667
0.894
0.066
0.000
TBDMSO
O
OBn
31
8
7
6
5
4
3
2
1
ppm
3.42
1.31
2.00
4.11
2.04 2.05
8.87
5.42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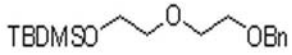
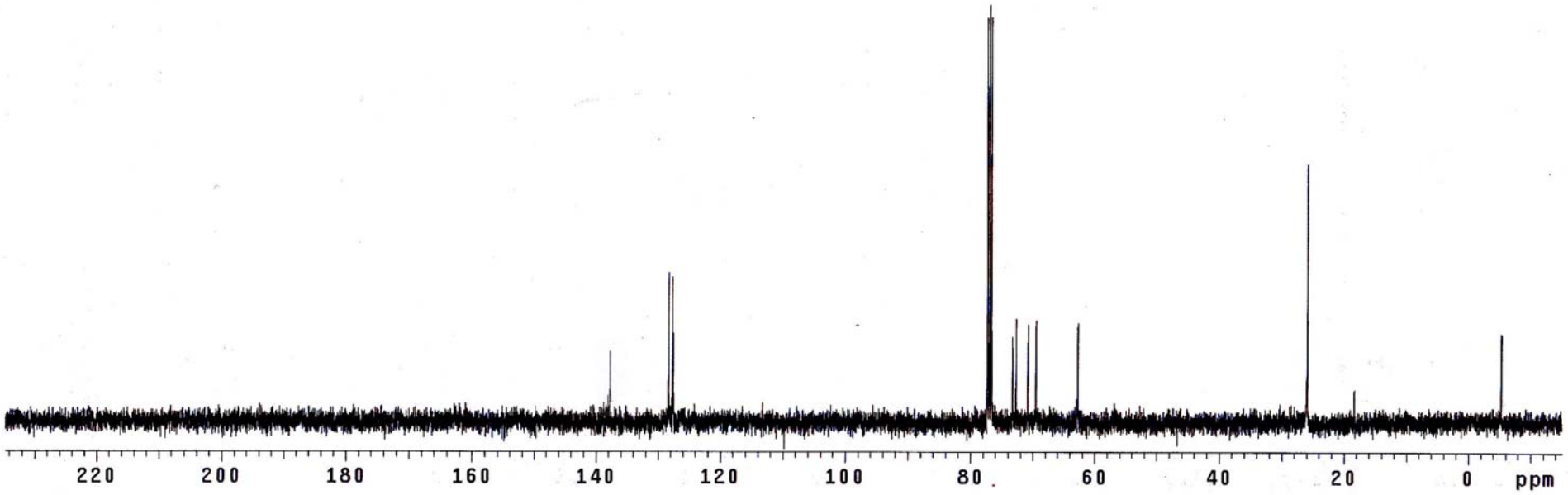
76.680
73.251
72.687
70.759
69.501
62.719
25.920
18.360
-5.263


TBDMSO
O
OBn

31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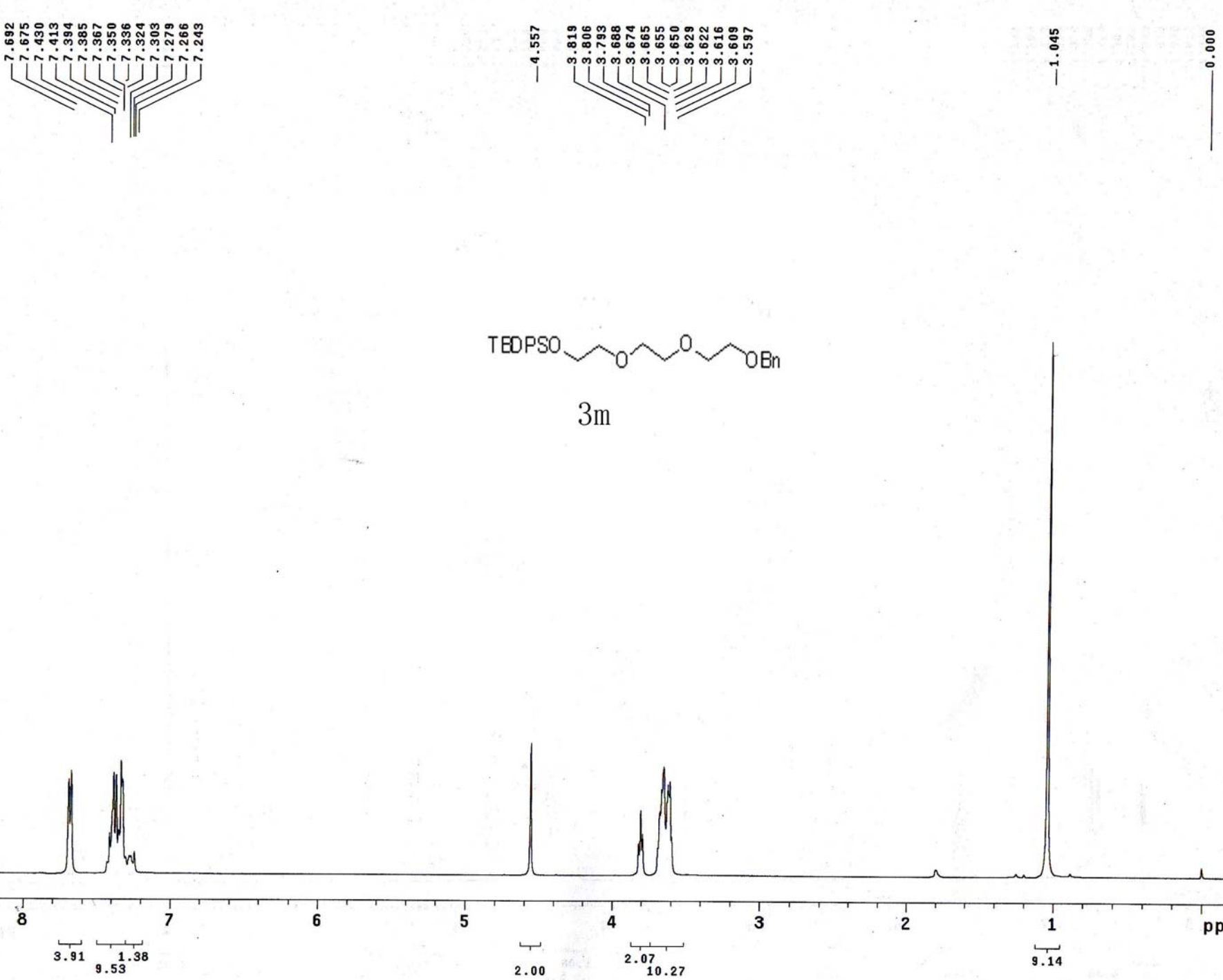
200
180
160
140
120
100
80
60
40
20
0
ppm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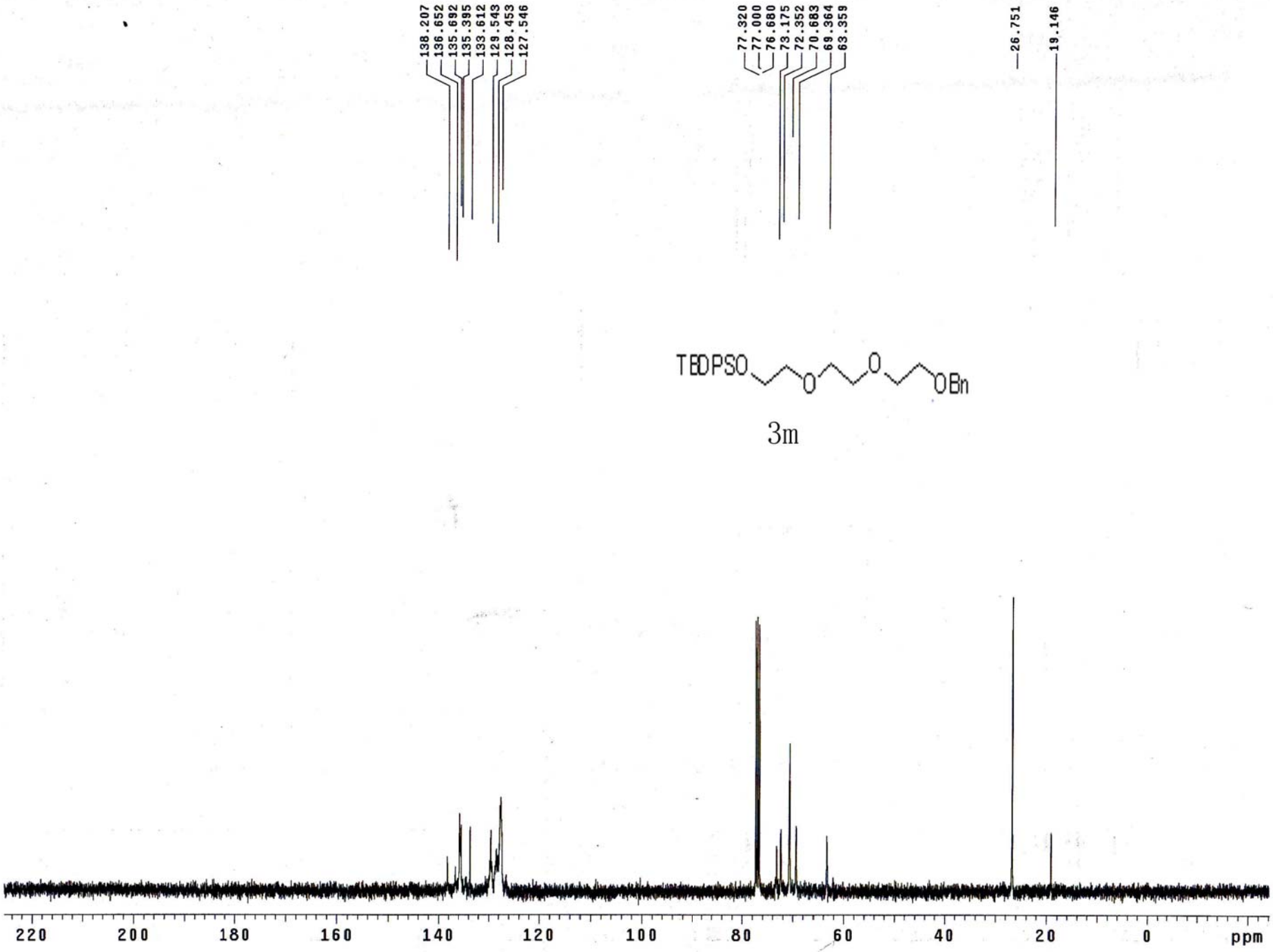
7.394
7.385
7.367
7.350
7.336
7.324
7.303
7.279
7.266
7.243
4.557
3.819
3.806
3.793
3.688
3.674
3.665
3.655
3.650
3.629
3.622
3.616
3.609
3.597
1.045
0.000
TBDPSO
O
O
OBn
3m
8
7
6
5
4
3
2
1
ppm
3.91
1.38
9.53
2.00
2.07
10.27
9.14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129.543
128.453
127.546
77.320
77.000
76.680
73.175
72.352
70.683
69.364
63.359
26.751
19.146
TBDPSO
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O
OBn
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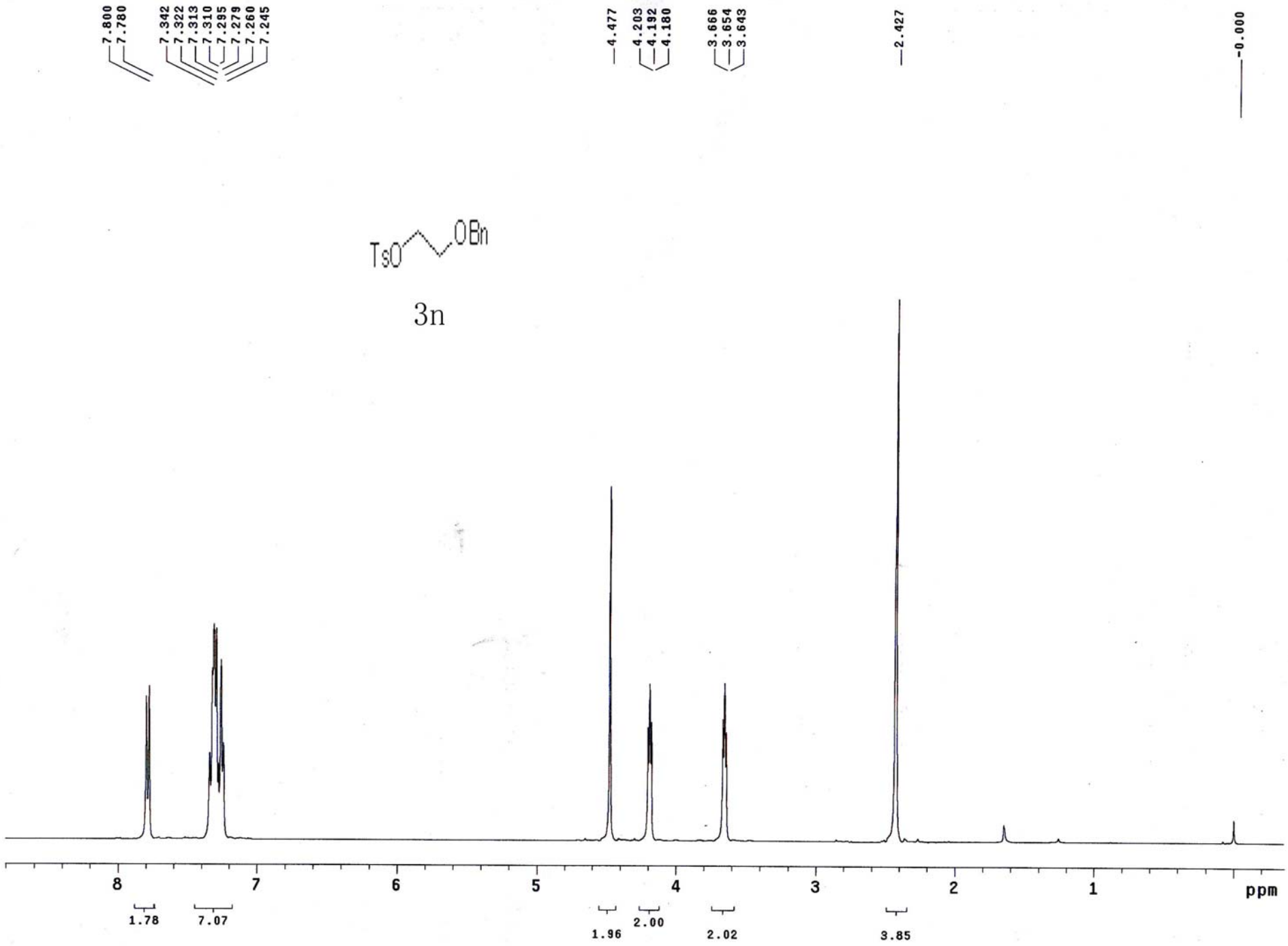
180
160
140
120
100
80
60
40
20
0
ppm

3m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7.313
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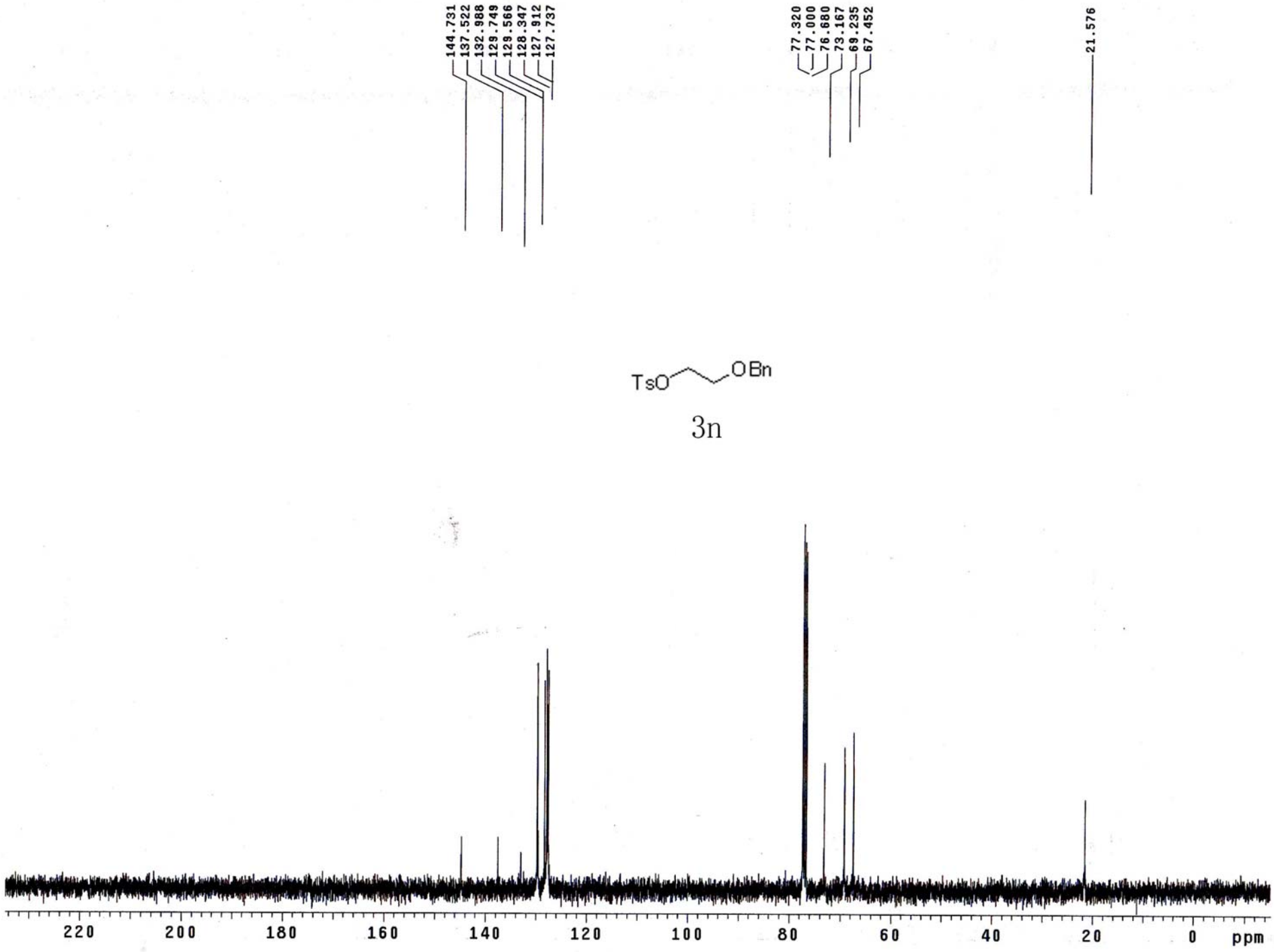
7.295
7.279
7.260
7.245
4.477
4.203
4.192
4.180
3.666
3.654
3.643
2.427
0.000
TsO
OBn
3n
8
7
6
5
4
3
2
1
ppm
1.78
7.07
1.96
2.00
2.02
3.85


144.731
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132.988
129.749
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128.347
127.912
127.737
77.320
77.000
76.680
73.167
69.235
67.452
21.576
TsO
OBn
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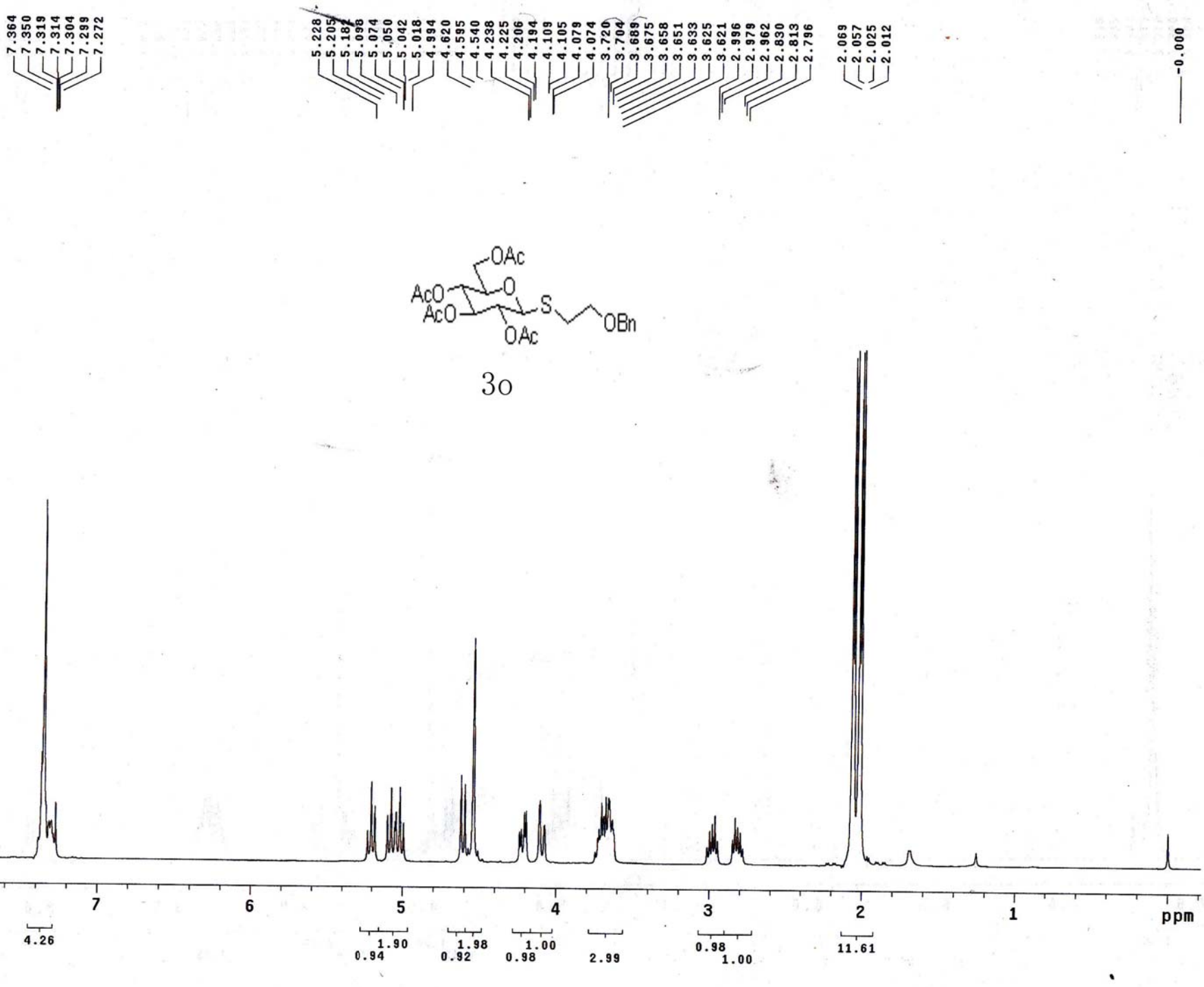
200
180
160
140
120
100
80
60
40
20
0
ppm

3n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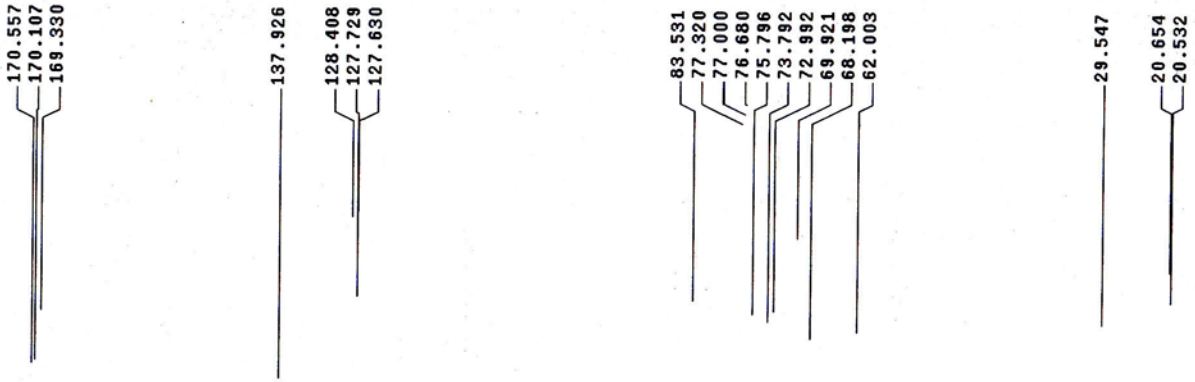
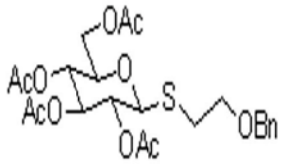
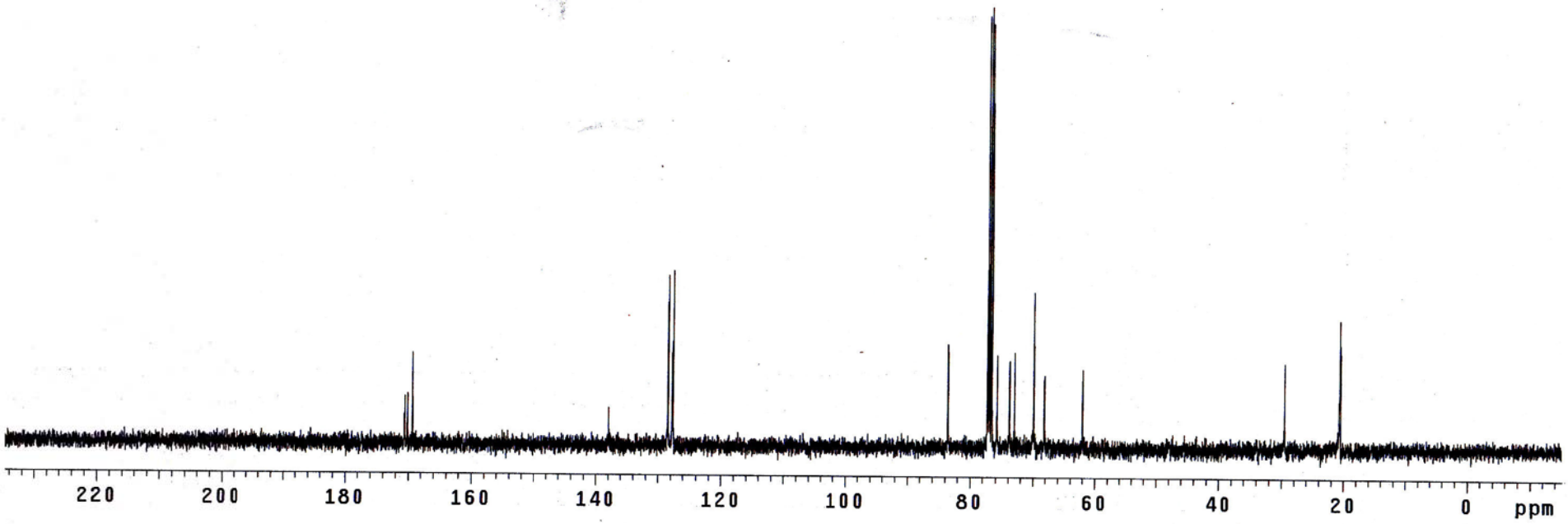
7.314
7.304
7.299
7.272
5.228
5.205
5.187
5.098
5.074
5.050
5.042
5.018
4.984
4.620
4.595
4.540
4.238
4.225
4.206
4.194
4.109
4.105
4.079
4.074
3.720
3.704
3.689
3.675
3.658
3.651
3.633
3.625
3.621
2.996
2.979
2.962
2.830
2.813
2.796
2.069
2.057
2.025
2.012
-0.000
OAc
AcO
O
S
OBn
AcO
OAc
8
7
6
5
4
3
2
1
ppm
4.26
1.90
0.94
1.98
0.92
1.00
0.98
2.99
0.98
1.00
11.61

3o


170.557
170.107
169.330
137.926
128.408
127.729
127.630
83.531
77.320
77.000
76.680
75.796
73.792
72.992
69.921
68.198
62.003
29.547
20.654
20.532


OAc
AcO
O
AcO
S
OBn
OAc

3o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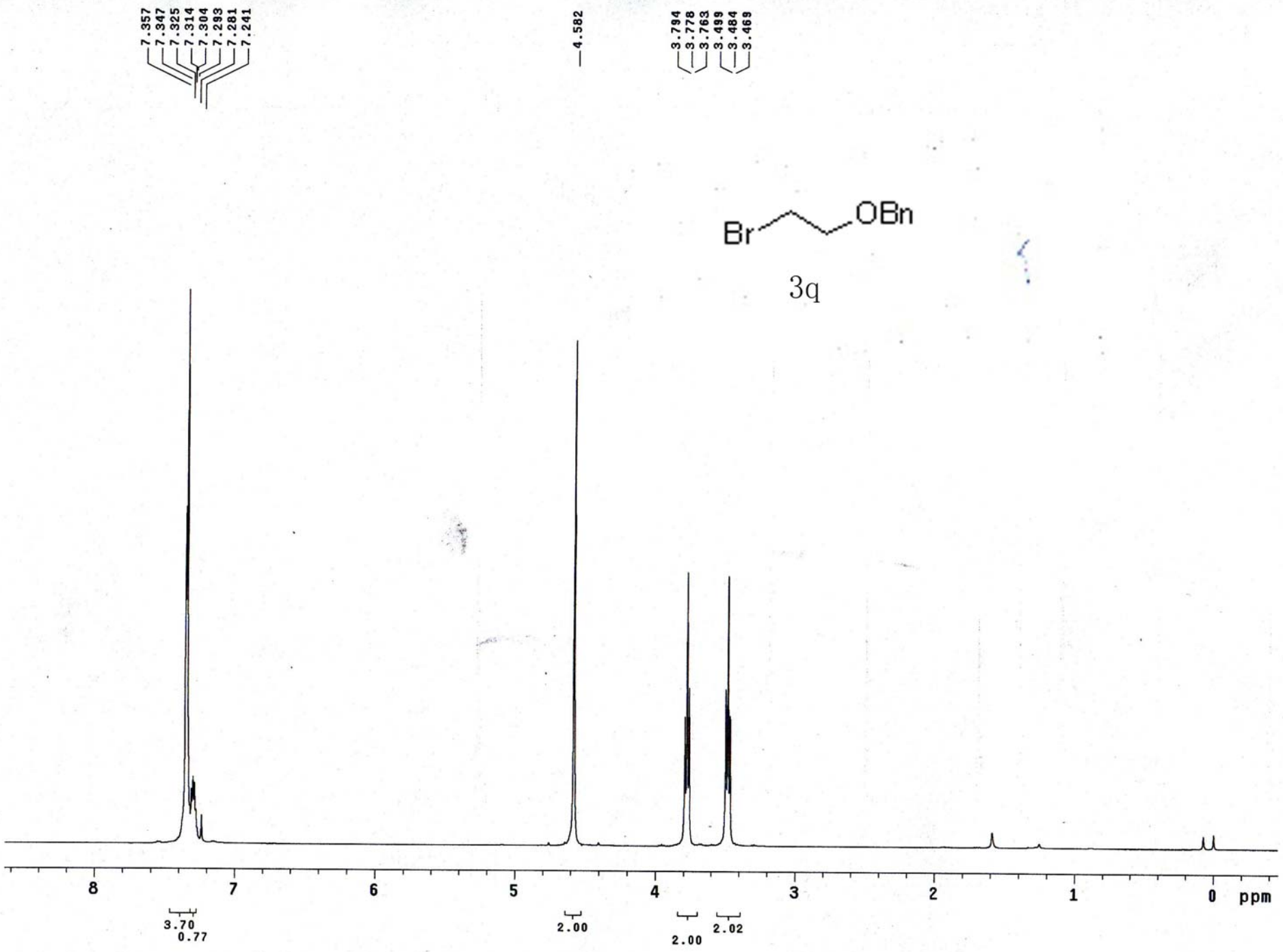
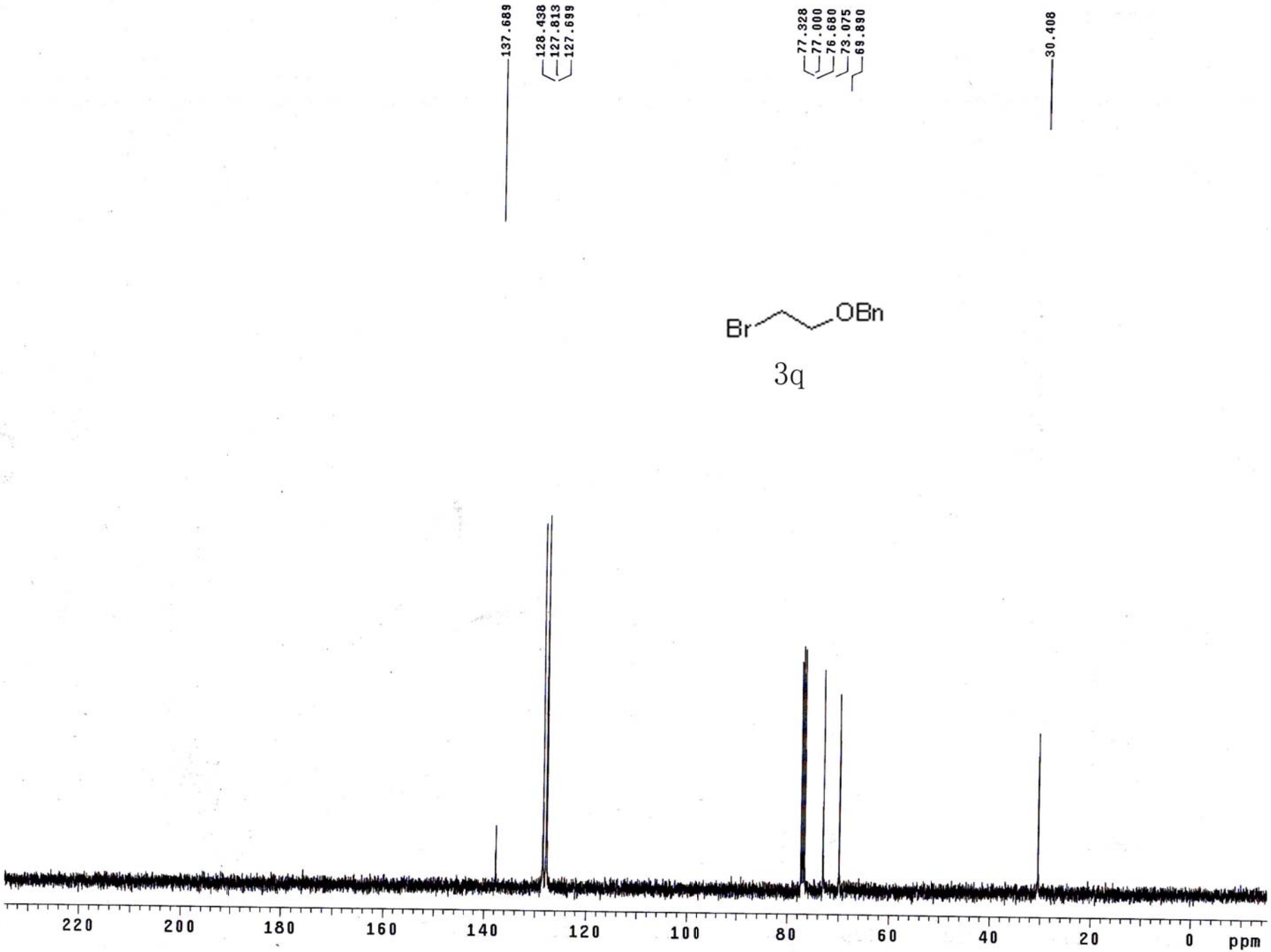
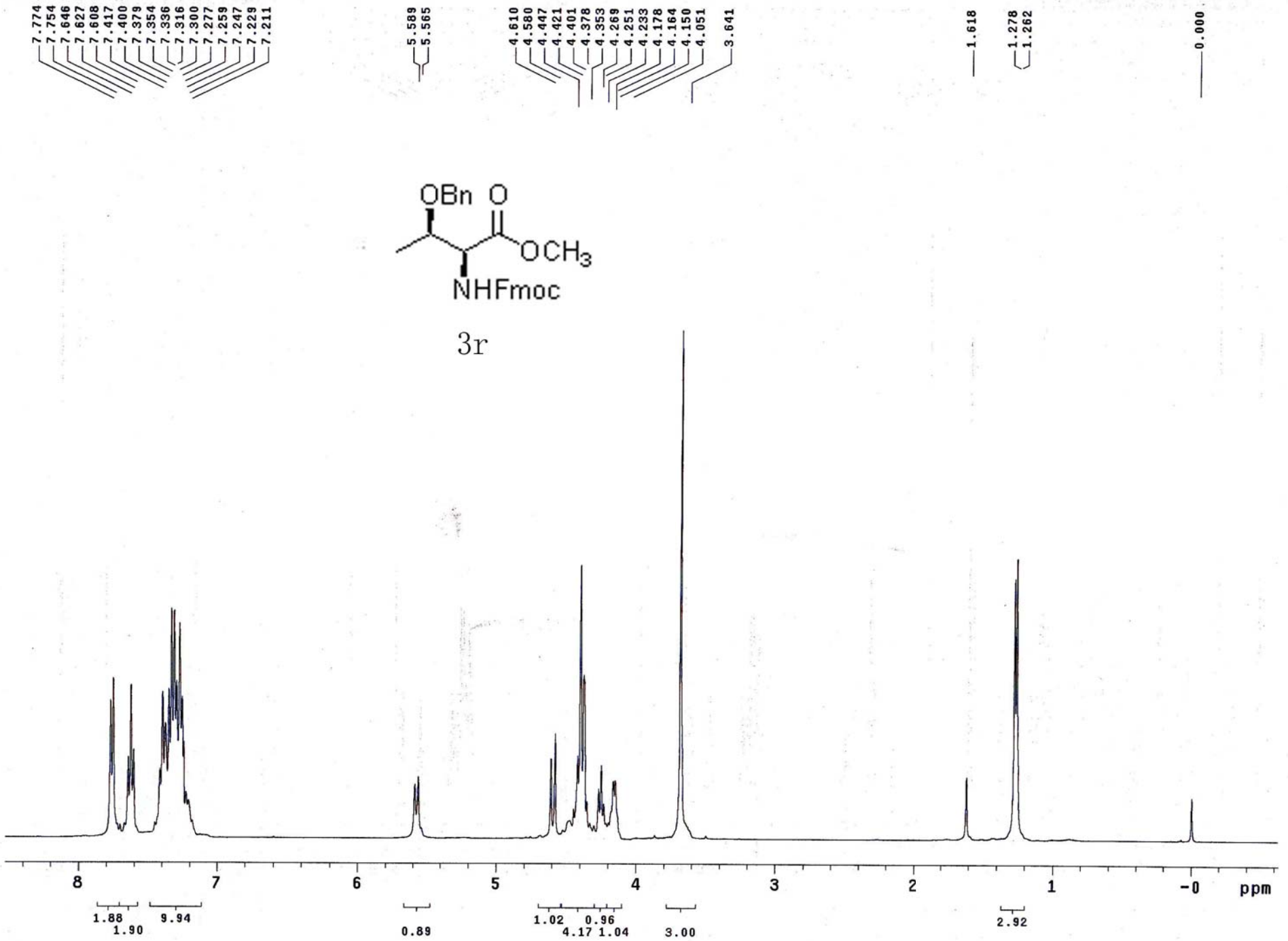
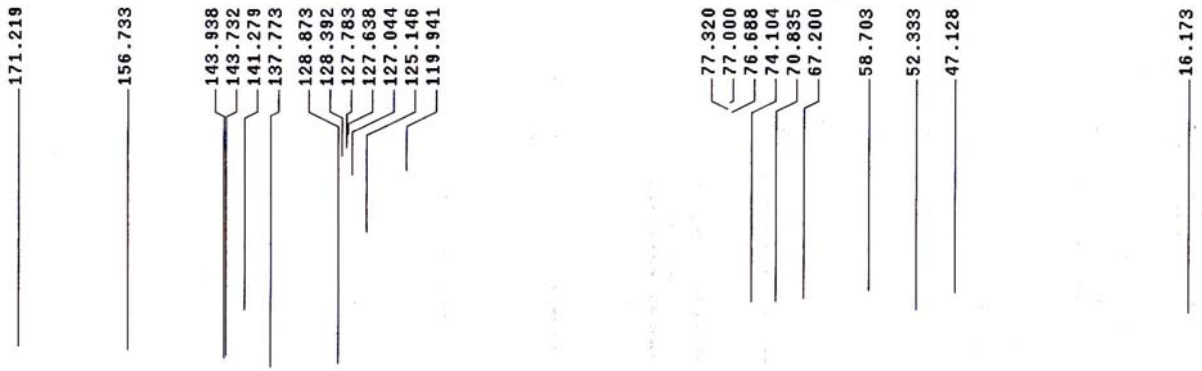
200
180
160
140
120
100
80
60
40
20
0
ppm

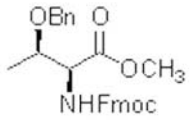

7.357
7.347
7.325
7.314
7.304
7.293
7.281
7.241
4.582
3.794
3.778
3.763
3.499
3.484
3.469
Br
OBn
3q
8
7
6
5
4
3
2
1
0
ppm
3.70
0.77
2.00
2.00
2.02


137.689
128.438
127.813
127.699
77.328
77.000
76.680
73.075
69.890
30.408
Br
OBn
220
200
180
160
140
120
100
80
60
40
20
0
ppm

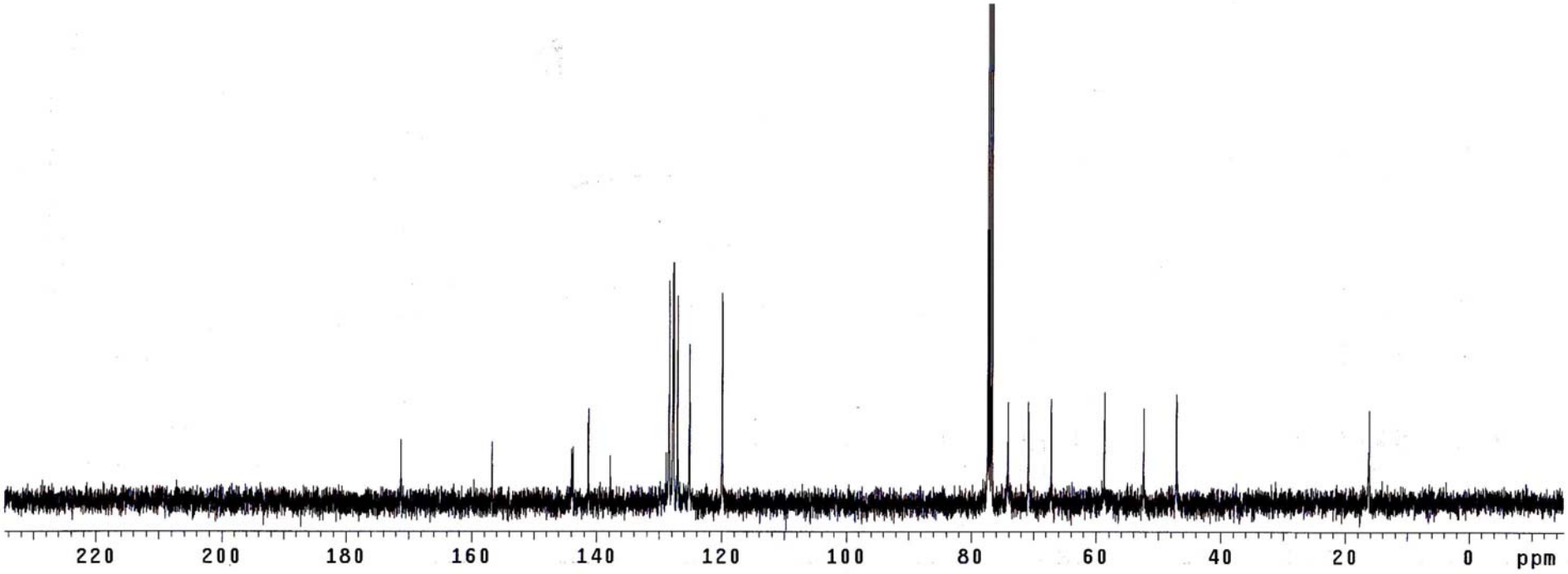
3q

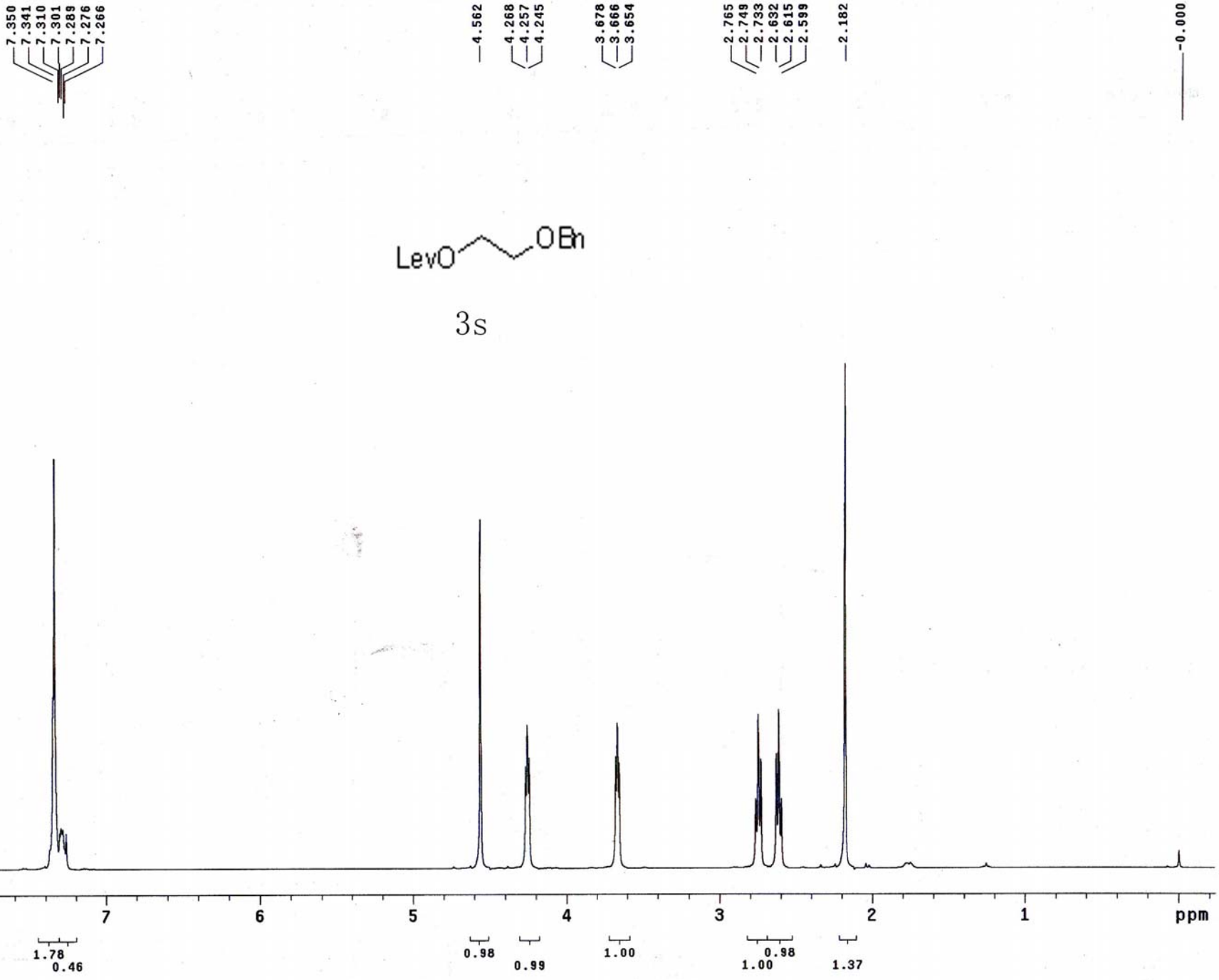

7.774
7.754
7.646
7.627
7.608
7.417
7.400
7.379
7.354
7.336
7.316
7.300
7.277
7.259
7.247
7.229
7.211
5.589
5.565
4.610
4.580
4.447
4.421
4.401
4.378
4.353
4.269
4.251
4.233
4.178
4.164
4.150
4.051
3.641
1.618
1.278
1.262
0.000
OBn
O
OCH3
NHFmoc
3r
8
7
6
5
4
3
2
1
-0
ppm
1.88
1.90
9.94
0.89
1.02
0.96
4.17
1.04
3.00
2.92


171.219
156.733
143.938
143.732
141.279
137.773
128.873
128.392
127.783
127.638
127.044
125.146
119.941
77.320
77.000
76.688
74.104
70.835
67.200
58.703
52.333
47.128
16.173

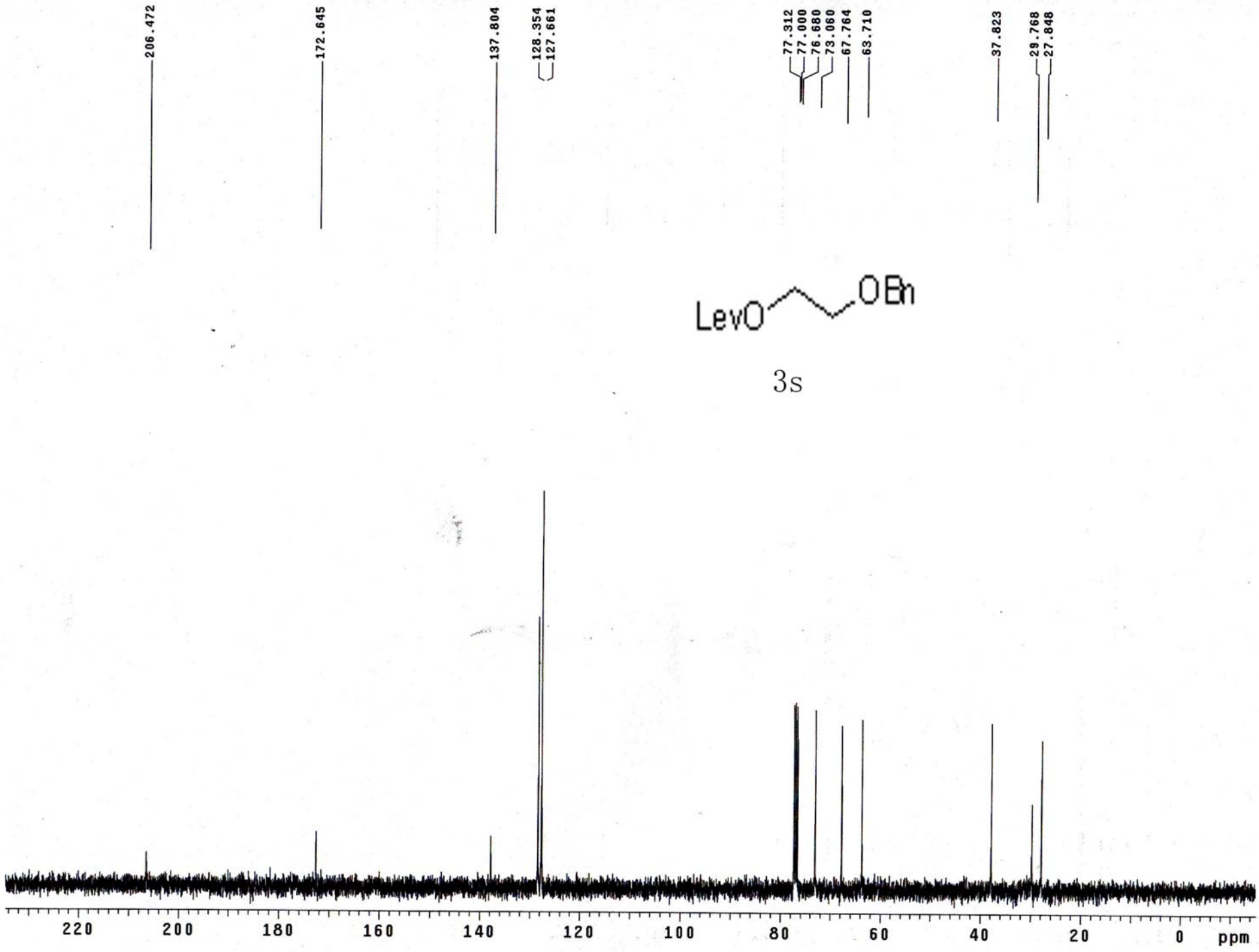

OBn
O
OCH3
NHFmoc

3r

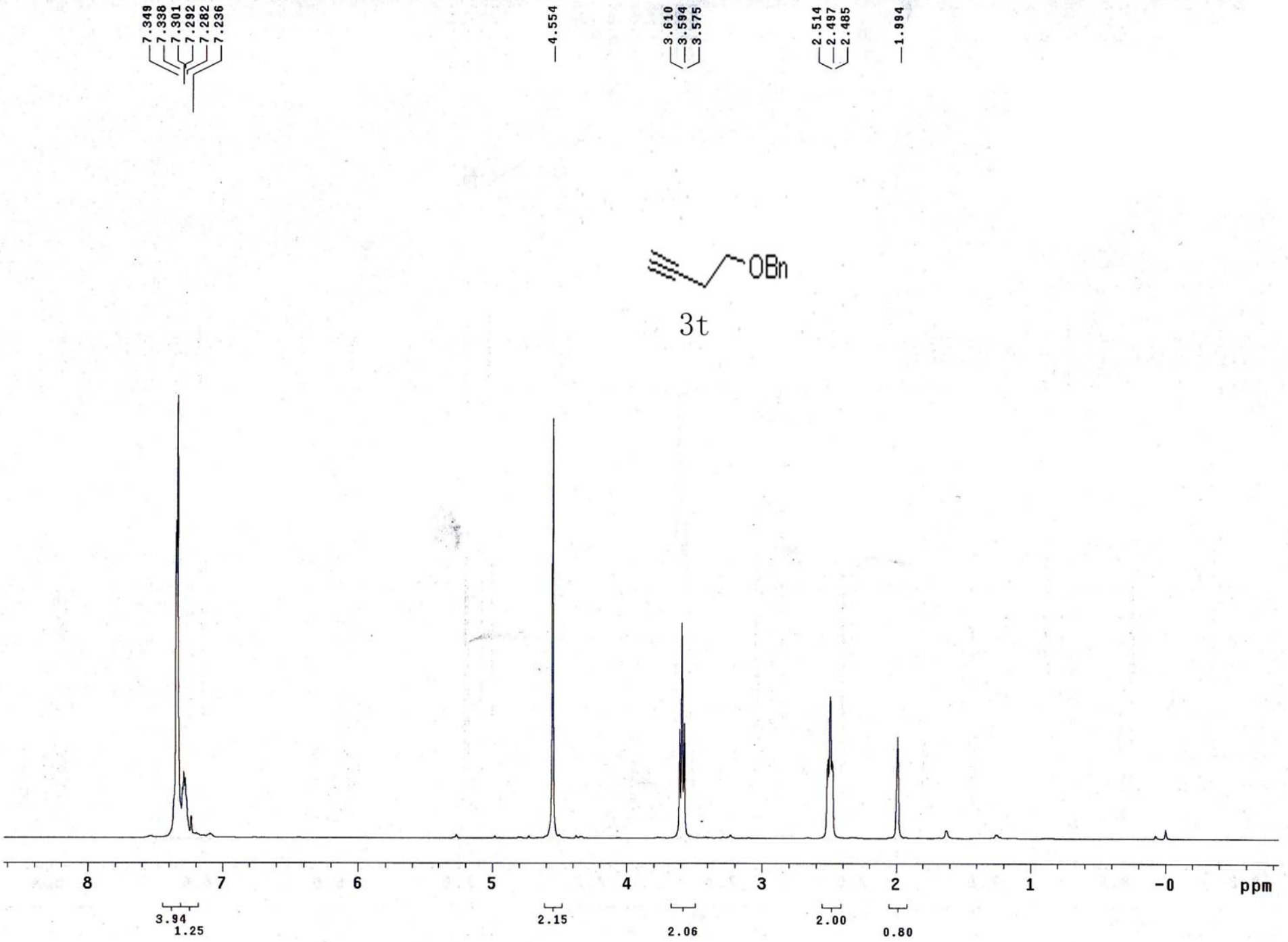

220
200
180
160
140
120
100
80
60
40
20
0
ppm

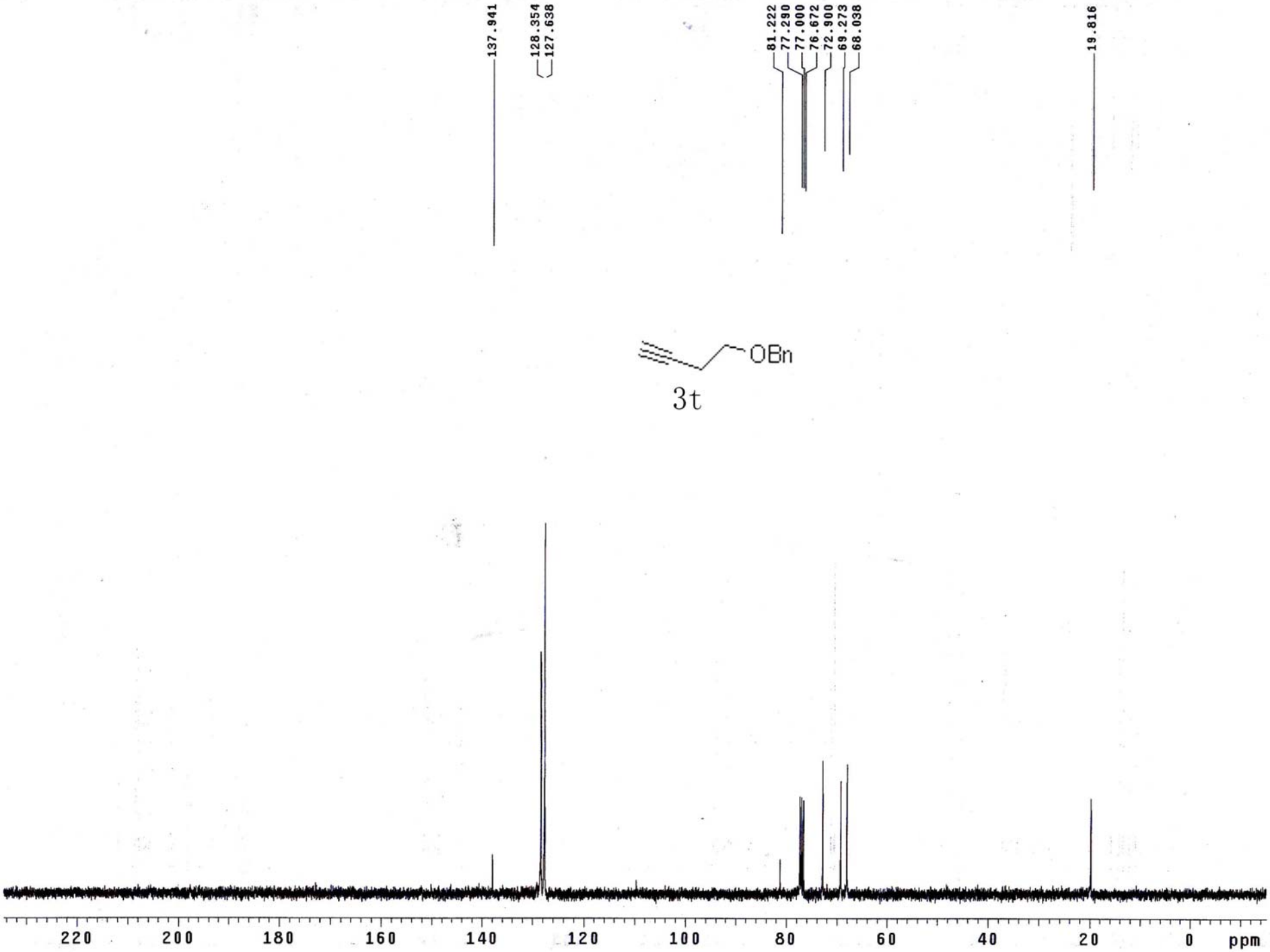

7.350
7.341
7.310
7.301
7.289
7.276
7.266
4.562
4.268
4.257
4.245
3.678
3.666
3.654
2.765
2.749
2.733
2.632
2.615
2.599
2.182
0.000
LevO
OBn
8
7
6
5
4
3
2
1
ppm
1.78
0.46
0.98
0.99
1.00
1.00
0.98
1.37

3s

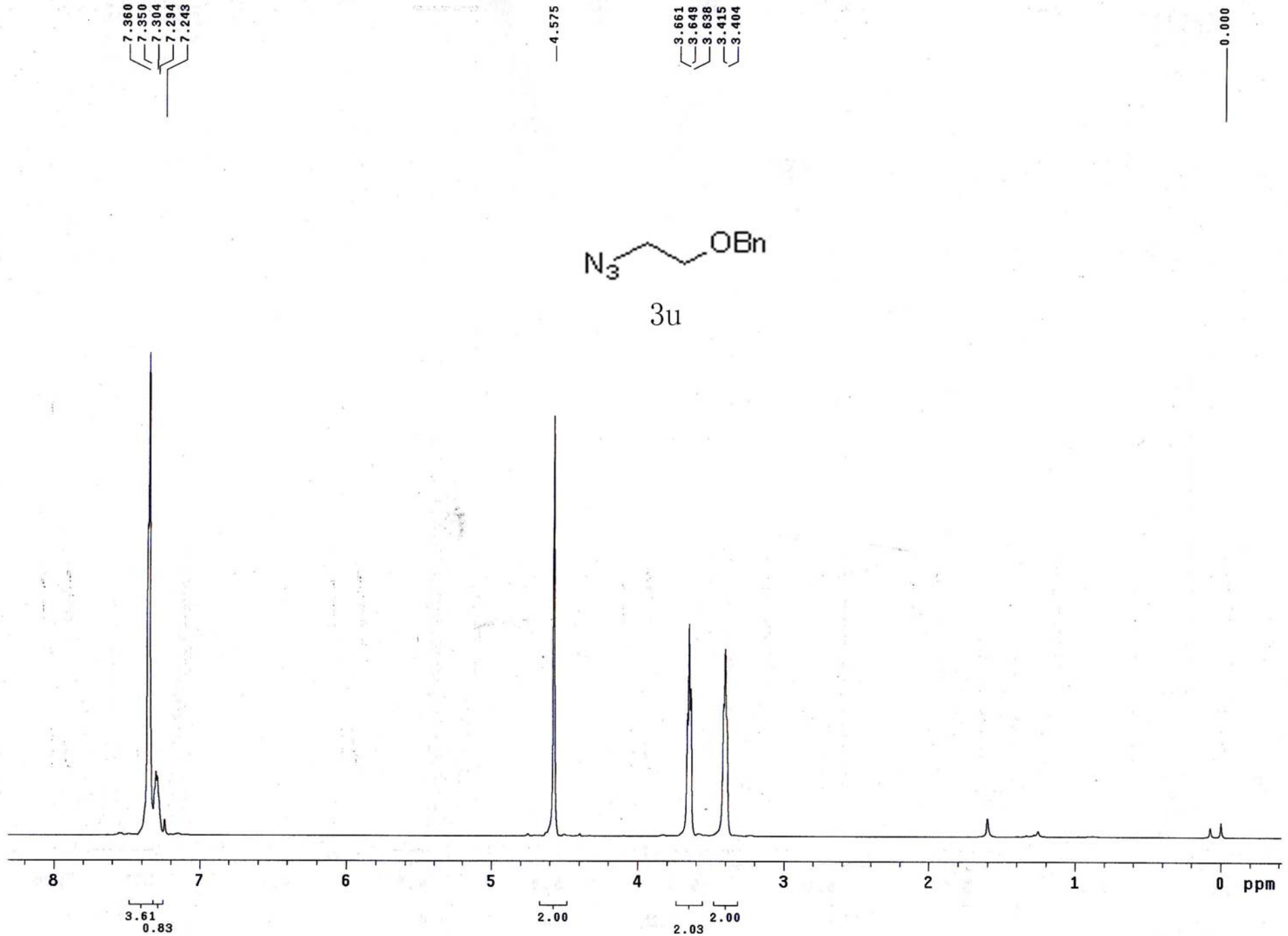

206.472
172.645
137.804
128.354
127.661
77.312
77.000
76.680
73.060
67.764
63.710
37.823
29.768
27.848
LevO
OBn
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3s

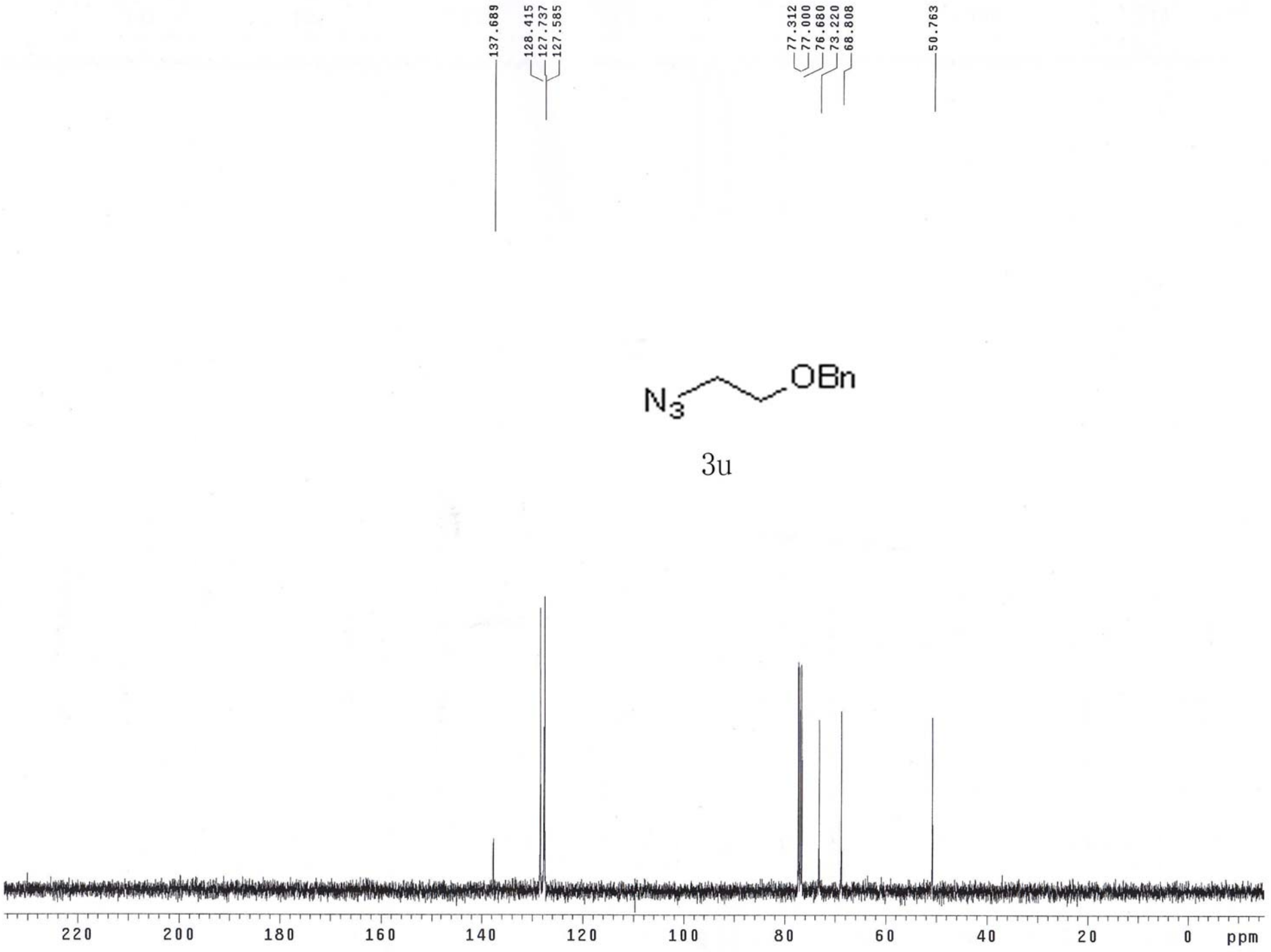

7.349
7.338
7.301
7.292
7.282
7.236
4.554
3.610
3.594
3.575
2.514
2.497
2.485
1.994
OBn
3t
8
7
6
5
4
3
2
1
-0
ppm
3.94
1.25
2.15
2.06
2.00
0.80


137.941
128.354
127.638
81.222
77.290
77.000
76.672
72.900
69.273
68.038
19.816
OBn
220
200
180
160
140
120
100
80
60
40
20
0
ppm

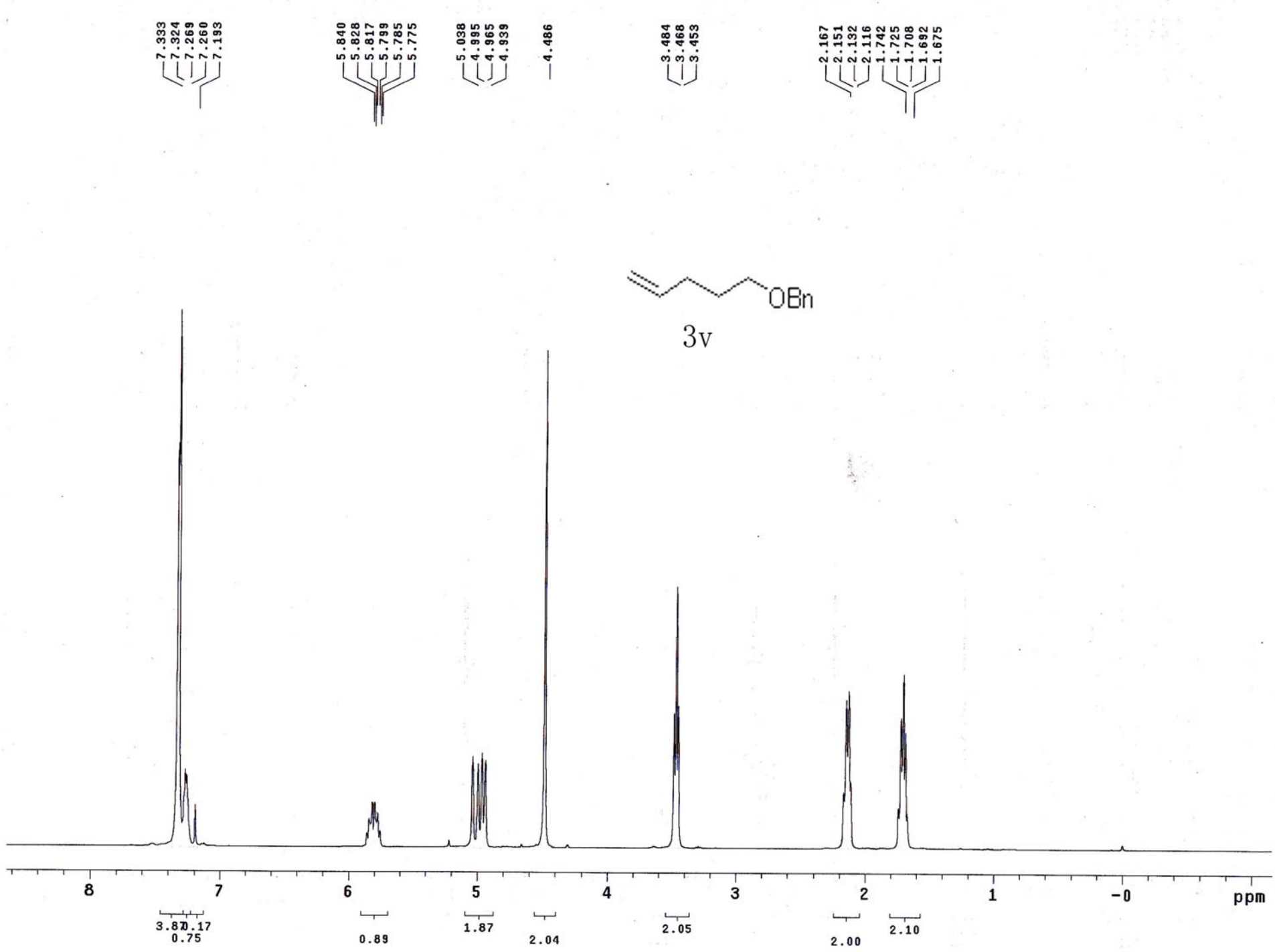
3t

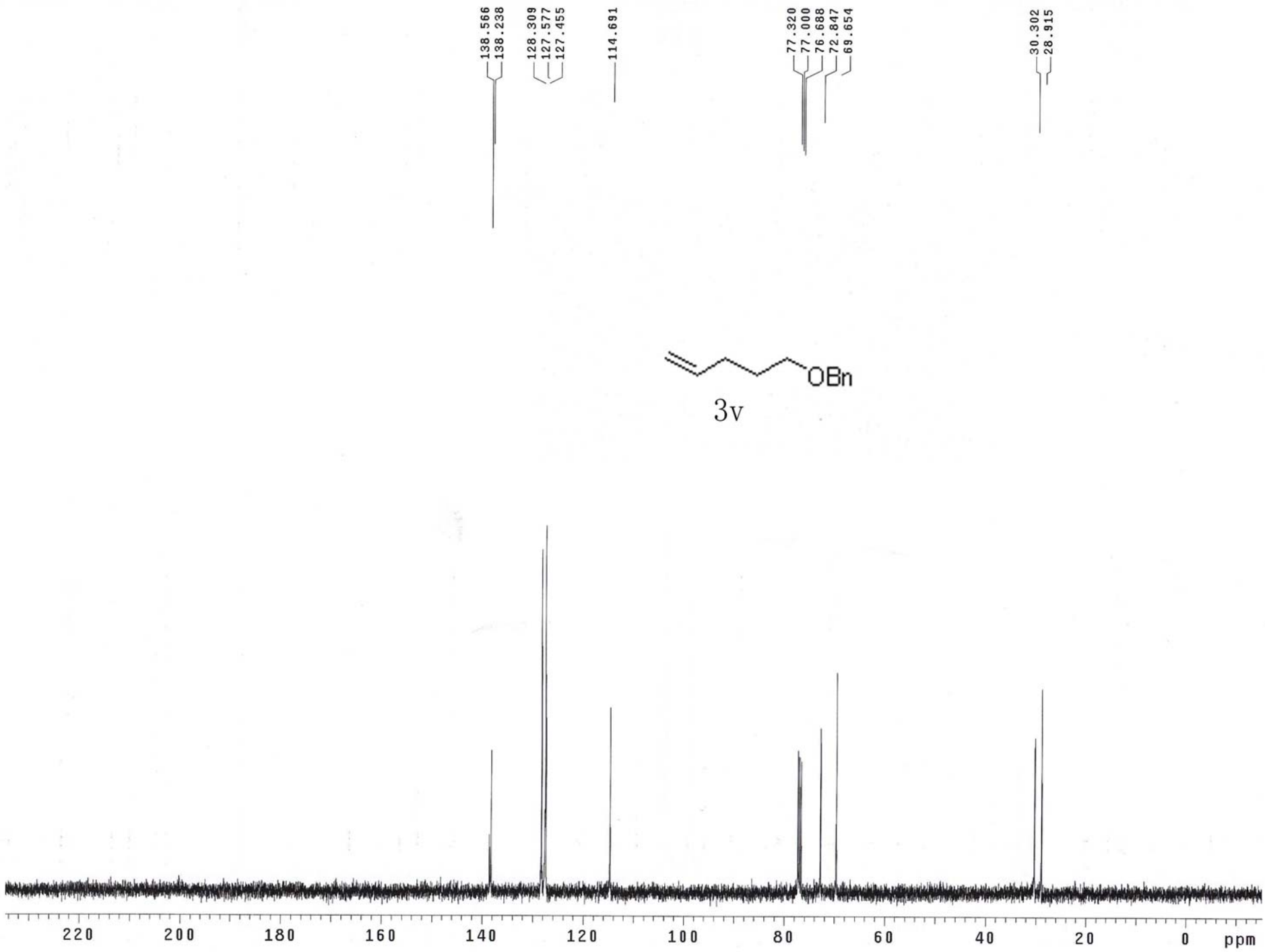

7.360
7.350
7.304
7.294
7.243
4.575
3.661
3.649
3.638
3.415
3.404
0.000
N3
OBn
8
7
6
5
4
3
2
1
0
ppm
3.61
0.83
2.00
2.03
2.00

3u

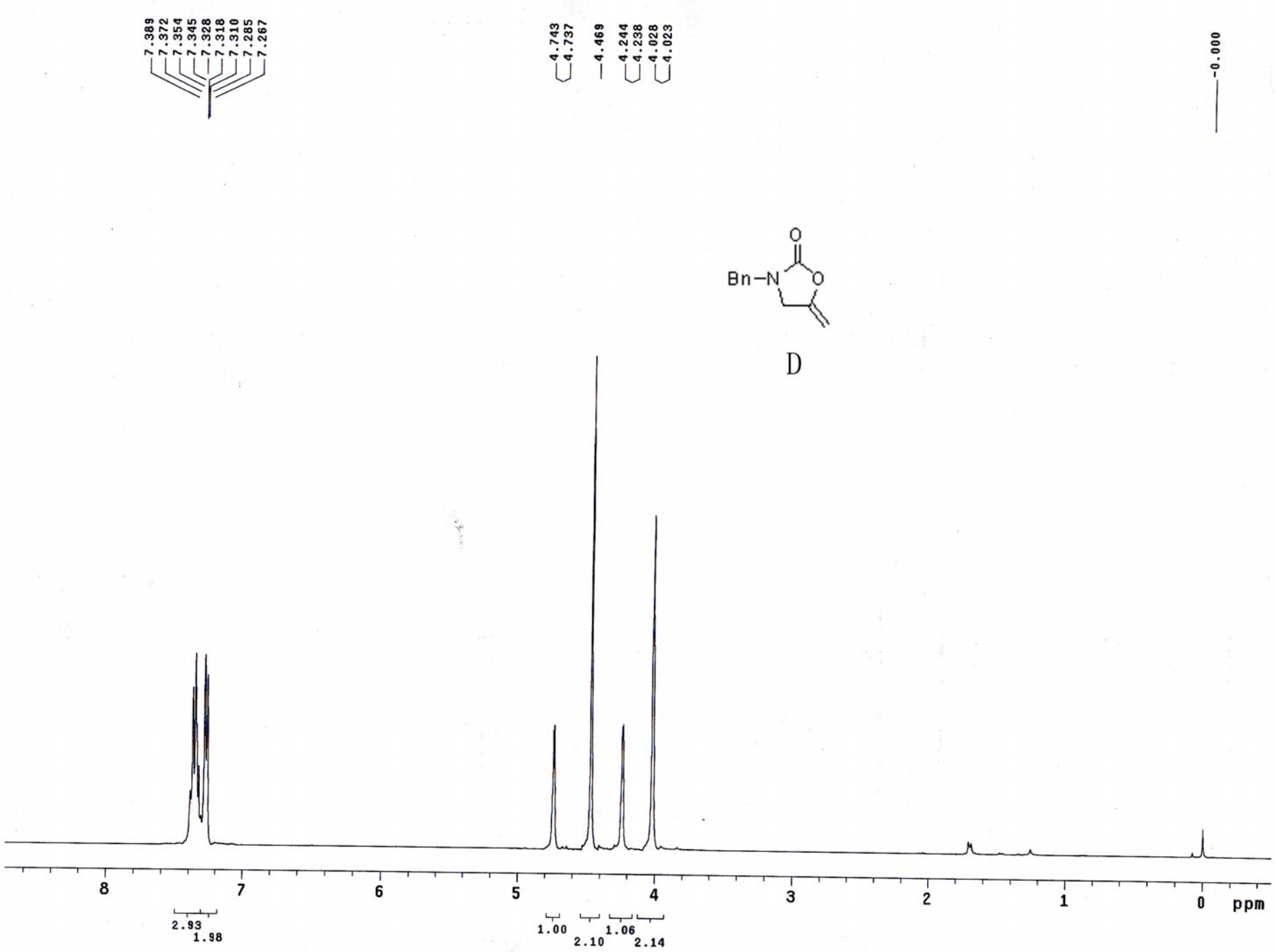

137.689
128.415
127.737
127.585
77.312
77.000
76.680
73.220
68.808
50.763
N3
OBn
220
200
180
160
140
120
100
80
60
40
20
0
ppm

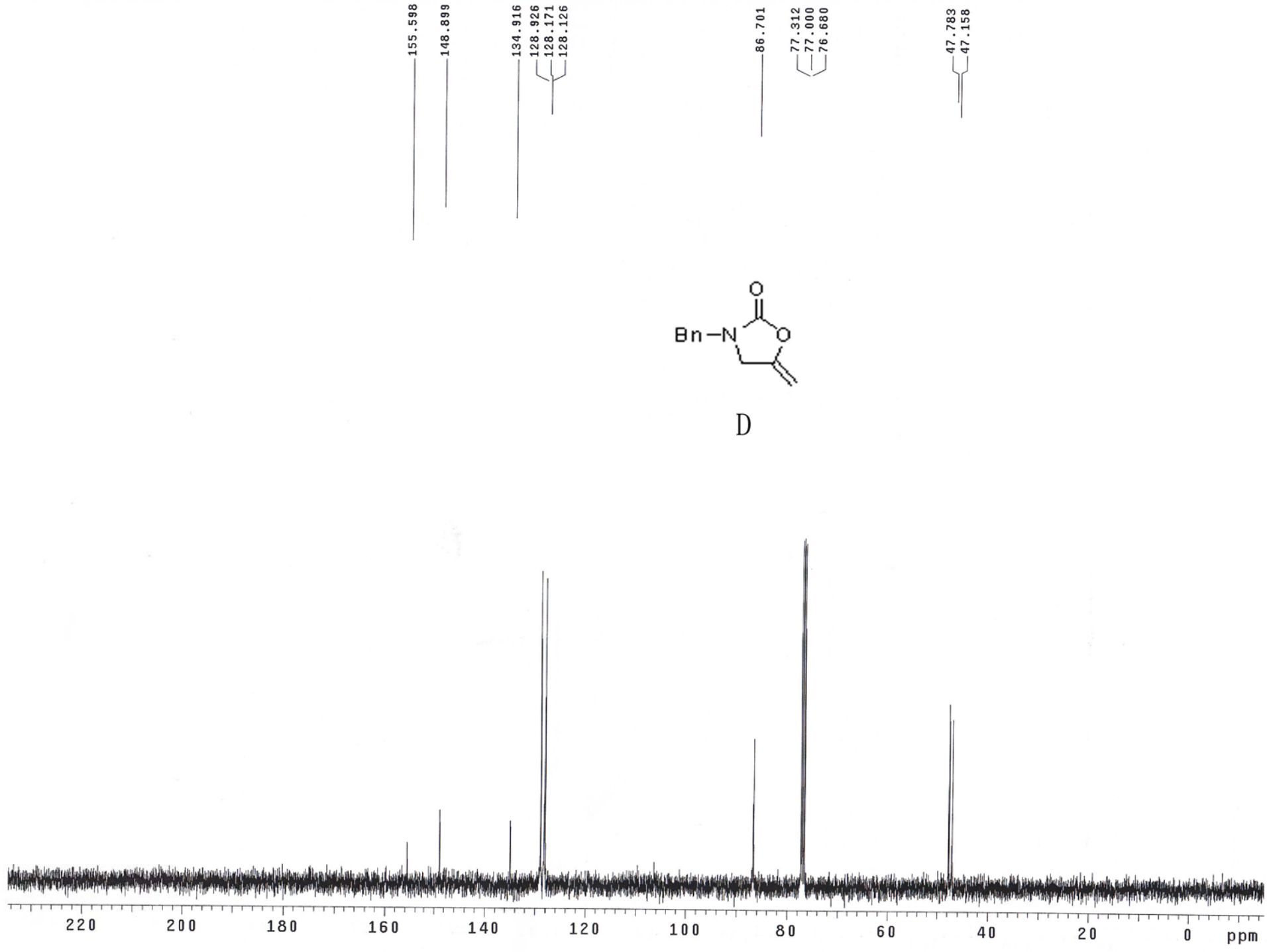
3u


7.333
7.324
7.269
7.260
7.193
5.840
5.828
5.817
5.799
5.785
5.775
5.038
4.995
4.965
4.939
4.486
3.484
3.468
3.453
2.167
2.151
2.132
2.116
1.742
1.725
1.708
1.692
1.675
OBn
3v
8
7
6
5
4
3
2
1
-0
ppm
3.87
0.17
0.75
0.89
1.87
2.04
2.05
2.00
2.10

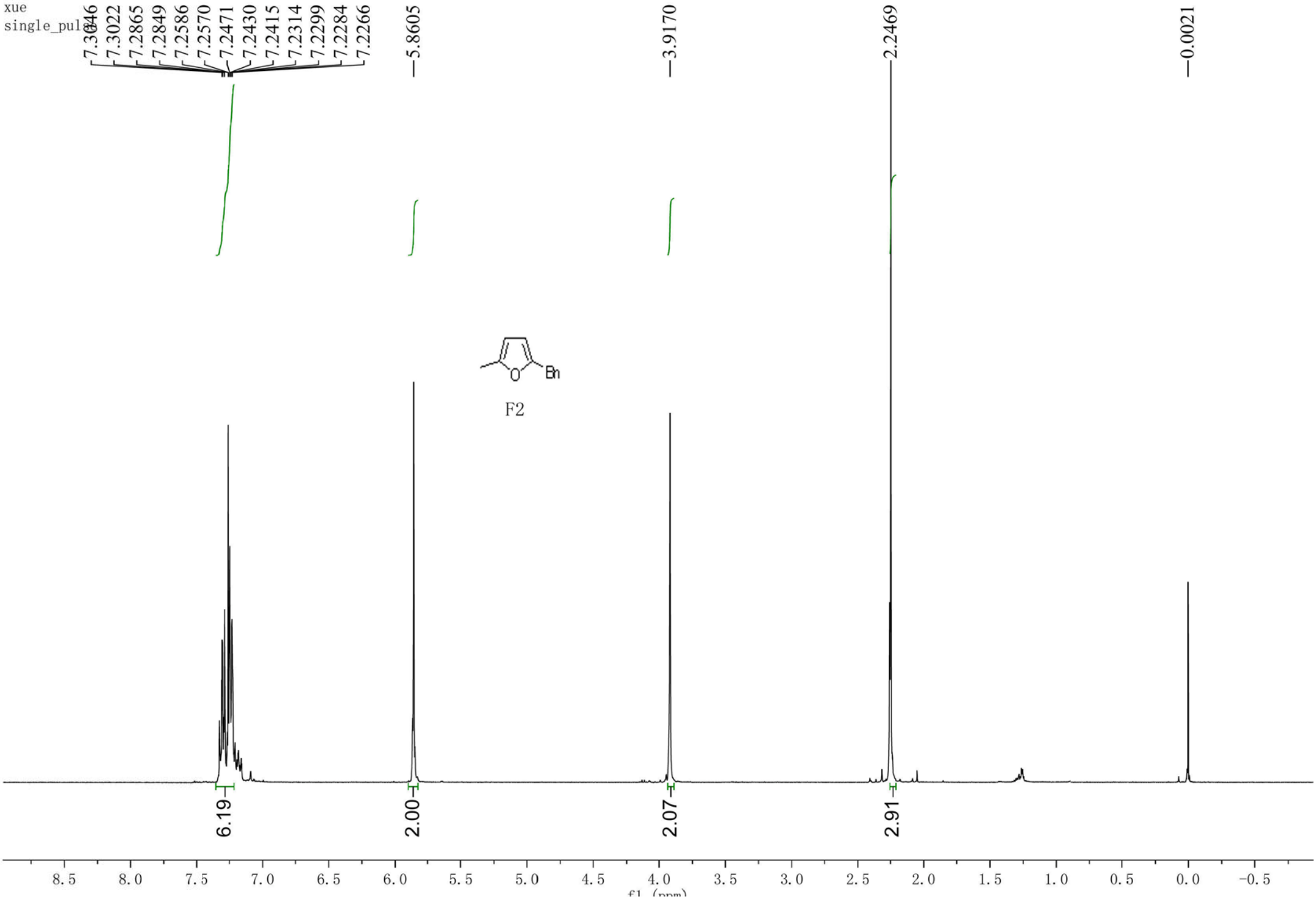

138.566
138.238
128.309
127.577
127.455
114.691
77.320
77.000
76.688
72.847
69.654
30.302
28.915
OBn
220
200
180
160
140
120
100
80
60
40
20
0
ppm

3v


7.389
7.372
7.354
7.345
7.328
7.318
7.310
7.285
7.267
4.743
4.737
4.469
4.244
4.238
4.028
4.023
-0.000
Bn–N
O
O
O
D
8
7
6
5
4
3
2
1
0
ppm
2.93
1.98
1.00
2.10
1.06
2.14


155.598
148.899
134.916
128.926
128.171
128.126
86.701
77.312
77.000
76.680
47.783
47.158
Bn–N
O
O
220
200
180
160
140
120
100
80
60
40
20
0
ppm

D


xue
single_pulse
7.3046
7.3022
7.2865
7.2849
7.2586
7.2570
7.2471
7.2430
7.2415
7.2314
7.2299
7.2284
7.2266
5.8605
3.9170
2.2469
0.0021
Bn
F2
6.19
2.00
2.07
2.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)