Supporting Information

Palladium-Catalyzed Intramolecular Coupling of Amino-tethered Vinyl Halides with Ketones, Esters, and Nitriles Using Potassium Phenoxide as the Base

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Table of Contents:

General Methods. ^1H- and ^{13}C NMR spectra were recorded using Me_4Si as the internal standard. Chemical shifts are reported in ppm downfield (δ) from Me_4Si. TLC was carried out on SiO_2 (silica gel 60 F_{254}) and the spots were located with UV light, iodoplatinate reagent or 1% aqueous $KMnO_4$. Flash chromatography was carried out on SiO_2 (silica gel 60, 230-400 mesh ASTM). Drying of organic extracts during workup of reactions was performed over anhydrous Na_2SO_4. Evaporation of solvents was accomplished with a rotatory evaporator.

SYNTHESIS OF THE STARTING MATERIALS

Ketones **1**,[1] **3**,[1] **6**,[2] **13**,[1] and **15**[1] have been prepared following the procedures described previously.

4-[*N*-Benzyl-*N*-(*Z*)-(3-iodo-2-methyl-2-propenyl)amino]cyclohexanone (8). To a solution of 4-(*N*-benzylamino)cyclohexanone[3] (0.74 g, 3.6 mmol) in CH_3CN (12 mL) were added K_2CO_3 (1.07 g, 7.7 mmol), and (*Z*)-3-bromo-1-iodo-2-methylpropene[4] (1.22 g, 4.7 mmol). After stirring at 55 ºC for 24 h, the solvent was removed *in vacuo* and the resulting residue was partitioned between dichloromethane and brine. The organic extracts were dried and concentrated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give ketone **8**; yield: 1.22 g (88%); ^1H NMR ($CDCl_3$, 300 MHz) δ 1.79 (m, 2H), 1.87 (d, $J = 1.5$ Hz, 3H), 2.19 (dm, $J = 12.9$ Hz, 2H), 2.35 (td, $J = 14.1$ and 5.7 Hz, 2H), 2.44 (dm, $J = 12.9$ Hz, 2H), 2.92 (tt, $J = 12$ and 3.5 Hz, 1H), 3.21 (s, 2H), 3.60 (s, 2H), 5.98 (d, $J = 1.5$ Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, DEPT) δ 22.6 (CH_3), 27.5 (CH_2), 40.2 (CH_2), 53.7 (CH_2), 55.9 (CH), 56.8 (CH_2), 76.6 (CH), 126.8 (CH), 128.1 (CH), 128.4 (CH), 139.9 (C), 145.5 (C), 210.9 (C).

2-{[*N*-Benzyl-*N*-(2-bromo-2-propenyl)amino]methyl}cyclohexanone (11). To a solution of *N*-benzyl-*N*-(2-bromo-2-propenyl)amine[5] (0.6 g, 2.7 mmol) in MeOH (4 mL) was added dropwise 10% HCl/Et_2O (16 mL). The solvent was removed *in vacuo*, the residue was dissolved in AcOH (5 mL), and paraformaldehyde (90 mg, 30 mmol) and cyclohexanone (0.57 mL, 5.4 mmol) were added. The resulting solution was stirred at 60 ºC for 2.5 h, the solvent was removed *in vacuo*, and the residue was partitioned

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[1] D. Solé, F. Diaba, J. Bonjoch, *J. Org. Chem.* **2003**, *68*, 5746-5749.
[2] J. Bonjoch, F. Diaba, G. Puigbó, E. Peidró, D. Solé, *Tetrahedron Lett.* **2003**, *44*, 8387-8390.
[3] J. Quirante, C. Escolano, M. Massot, J. Bonjoch, *Tetrahedron* **1997**, *53*, 1391-1402.
[4] R. C. Larock, X. Han, *J. Org. Chem.* **1999**, *64*, 1875-1887.
[5] D. Solé, Y. Cancho, A. Llebaria, J. M. Moretó, A. Delgado, *J. Org. Chem.* **1996**, *61*, 5895-5904.

between diethyl ether and 10% aqueous HCl. The aqueous layer was basified with Na_2CO_3 and extracted with dichloromethane. The organic extracts were dried and concentrated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give ketone **11**; yield: 0.55 g (60%);^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.20-2.60 (m, 10H), 2.85 (q, *J* = 8.8 Hz, 1H), 3.13 (d, *J* = 15 Hz, 1H), 3.32 (d, *J* = 15 Hz, 1H), 3.41 (d, *J* = 13.6 Hz, 1H), 3.75 (d, *J* = 13.6 Hz, 1H), 5.56 (s, 1H), 5.87 (d, *J* = 1.2 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 24.4 (CH_2), 27.8 (CH_2), 32.2 (CH_2), 41.9 (CH_2), 48.9 (CH), 53.0 (CH_2), 58.4 (CH_2), 62.7 (CH_2), 118.7 (CH_2), 126.9 (CH), 128.1 (CH), 128.8 (CH), 132.1 (C), 138.8 (C), 212.7 (C).

1-[*N*-Benzyl-*N*-(3-bromo-3-butenyl)amino]-2-propanone (18). A mixture of 2,4-dibromobutene[3] (1.5 g, 7 mmol), benzylamine (3.8 mL, 34.8 mmol), K_2CO_3 (1.95 g, 14 mmol), and LiI (180 mg) was stirred at 70 ºC for 24 h. The mixture was partitioned between dichloromethane and water. The organic extracts were dried, and the solvent and the excess of benzylamine were removed *in vacuo* to give *N*-benzyl-*N*-(3-bromo-3-butenyl)amine (1 g, 60%), which was used in the next step without purification.

To a solution of crude *N*-benzyl-*N*-(3-bromo-3-butenyl)amine (0.38 g, 1.6 mmol) in CH_3CN (15 mL) were added chloroacetone (95%, 0.21 mL, 2.5 mmol), *N*,*N*-diisopropylethylamine (0.85 mL, 4.9 mmol), and LiI (30 mg). After stirring at reflux for 24 h the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane and washed with saturated aqueous Na_2CO_3 and brine. The organic layer was dried and concentrated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give ketone **18**; yield: 0.22 g (46%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.09 (s, 3H), 2.61 (t, *J* = 7 Hz, 2H), 2.82 (t, *J* = 7 Hz, 2H), 3.23 (s, 2H), 3.69 (s, 2H), 5.44 (d, *J* = 1.7 Hz, 1H), 5.61 (d, *J* = 1.7 Hz, 1H), 7.20-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 27.5 (CH_3), 39.5 (CH_2), 52.9 (CH_2), 58.5 (CH_2), 63.9 (CH_2), 117.8 (CH_2), 127.2 (CH), 128.2 (CH), 128.8 (CH), 132.0 (C), 138.3 (C), 208.6 (C).

Methyl 4-[*N*-Benzyl-*N*-(2-bromo-2-propenyl)amino]butyrate (20). To a solution of *N*-benzyl-*N*-(2-bromo-2-propenyl)amine (0.5 g, 2.2 mmol) in isobutyl methyl ketone (5 mL) were added K_2CO_3 (0.3 g, 2.2 mmol) and methyl 4-iodobutyrate (0.3 mL, 2.2 mmol). After stirring at reflux for 5 h the mixture was partitioned between dichloromethane and water. The organic extracts were dried and concentrated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give ester **20**; yield:

0.46 g (65%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.80 (tt, *J* = 7.4 and 6.6 Hz, 2H), 2.38 (t, *J* = 7.4 Hz, 2H), 2.50 (t, *J* = 6.6 Hz, 2H), 3.25 (s, 2H), 3.61 (s, 2H), 3.63 (s, 3H), 5.58 (d, *J* = 1 Hz, 1H), 5.90 (d, *J* = 1 Hz, 1H), 7.18-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 22.3 (CH_2), 31.5 (CH_2), 51.5 (CH_3), 51.9 (CH_2), 57.8 (CH_2), 62.0 (CH_2), 118.3 (CH_2), 126.9 (CH), 128.1 (CH), 128.7 (CH), 132.2 (C), 138.8 (C), 174.0 (C).

Methyl 3-[*N*-Benzyl-*N*-(2-bromo-2-propenyl)amino]propionate (22). A solution of benzylamine (2 mL, 18.3 mmol) and methyl acrylate (1.9 mL, 21 mmol) in EtOH (5 mL) was stirred at room temperature for 18 h. The solvent was removed *in vacuo*, the residue was dissolved in CH_3CN (70 mL), and K_2CO_3 (5.1 g, 36.9 mmol), 2,3-dibromopropene (80%, 2.6 mL, 20.1 mmol), and LiI (100 mg) were added. After stirring at 55 ºC for 1.5 h and at room temperature for 16 h, the solvent was removed *in vacuo*, and the resulting residue was partitioned between dichloromethane and water. The organic extracts were dried and concentrated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give ester **22**; yield: 5.4 g (95%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.50 (t, *J* = 7.2 Hz, 2H), 2.88 (t, *J* = 7.2 Hz, 2H), 3.29 (s, 2H), 3.65 (s, 3H), 3.66 (s, 2H), 5.58 (s, 1H), 5.90 (s, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, DEPT) δ 32.6 (CH_2), 48.9 (CH_2), 51.5 (CH_3), 57.6 (CH_2), 61.8 (CH_2), 118.4 (CH_2), 127.1 (CH), 128.2 (CH), 128.6 (CH), 131.7 (C), 138.5 (C), 172.7 (C).

Methyl 3-[*N*-Benzyl-*N*-(2-bromo-2-propenyl)amino]-2-methylpropionate (24). A solution of benzylamine (1.1 mL, 10 mmol) and methyl methacrylate (2.4 mL, 22 mmol) in MeOH (50 mL) was stirred at reflux for 48 h. The solvent was removed *in vacuo*, the residue was dissolved in CH_3CN (100 mL), and K_2CO_3 (2.65 g, 19.2 mmol), 2,3-dibromopropene (80%, 1.5 mL, 11.6 mmol), and LiI (100 mg) were added. After stirring at 55 ºC for 1.5 h and at room temperature for 16 h, the solvent was removed *in vacuo*, and the resulting residue was partitioned between dichloromethane and water. The organic extracts were dried and concentrated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give ester **24**; yield: 2.8 g (87%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.13 (d, *J* = 6.6 Hz, 3H), 2.51 (dd, *J* = 12.3 and 6.6 Hz, 1H), 2.72 (dquint, *J* = 8.1 and 6.6 Hz, 1H), 2.83 (dd, *J* = 12.3 and 8.1 Hz, 1H), 3.23 (d, *J* = 15.3 Hz, 1H), 3.29 (d, *J* = 15.3 Hz, 1H), 3.60 (d, *J* = 13.8 Hz, 1H), 3.66 (s, 3H), 3.68 (d, *J* = 13.8 Hz, 1H), 5.57 (dt, *J* = 1.2 and 0.6 Hz, 1H), 5.85 (q, *J* = 1.2 Hz, 1H), 7.20-7.35 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, DEPT) δ 15.3 (CH_3), 38.5 (CH), 51.6 (CH_3), 57.0 (CH_2), 57.9

(CH_2), 62.1 (CH_2), 118.5 (CH_2), 126.9 (CH), 128.1 (CH), 128.7 (CH), 131.5 (C), 138.4 (C), 175.9 (C).

Methyl 2-[*N*-Benzyl-*N*-(3-bromo-3-butenyl)amino]acetate (28). To a solution of *N*-benzyl-*N*-(3-bromo-3-butenyl)amine (0.33 g, 1.4 mmol) in CH_3CN (10 mL) were added methyl bromoacetate (0.2 mL, 2.1 mmol), *N*,*N*-diisopropylethylamine (0.72 mL, 4.2 mmol), and LiI (30 mg). After stirring at reflux for 24 h the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane and washed with saturated aqueous Na_2CO_3 and brine. The organic layer was dried and concentrated. The residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give ester **28**; yield: 0.2 g (46%); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.61 (t, J = 7 Hz, 2H), 2.95 (t, J = 7 Hz, 2H), 3.35 (s, 2H), 3.69 (s, 3H), 3.83 (s, 2H), 5.44 (d, J = 1.8 Hz, 1H), 5.62 (s, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 39.9 (CH_2), 51.3 (CH_3), 52.3 (CH_2), 53.9 (CH_2), 57.9 (CH_2), 117.7 (CH_2), 127.1 (CH), 128.2 (CH), 128.8 (CH), 132.1 (C), 138.6 (C), 171.6 (C).

3-[*N*-Benzyl-*N*-(2-bromo-2-propenyl)amino]propionitrile (30). To a mixture of $LiClO_4$[6] (0.25 g, 2.3 mmol) and acrylonitrile (0.15 mL, 2.3 mmol) was added *N*-benzyl-*N*-(2-bromo-2-propenyl)amine (0.7 g, 3.1 mmol). After stirring at room temperature under an argon atmosphere for 2 h, dichloromethane (10 mL) was added, and $LiClO_4$ was removed by filtration. The solvent was evaporated and the residue was purified by flash chromatography (SiO_2, CH_2Cl_2) to give nitrile **30**; yield: 0.2 g (32%); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.43 (t, J = 7 Hz, 2H), 2.87 (t, J = 7 Hz, 2H), 3.36 (s, 2H), 3.70 (s, 2H), 5.61 (s, 1H), 5.95 (d, J = 1.2 Hz, 1H), 7.20-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 16.5 (CH_2), 48.7 (CH_2), 57.6 (CH_2), 61.9 (CH_2), 118.5 (C), 119.0 (CH_2), 127.3 (CH), 128.3 (CH), 128.5 (CH), 130.8 (C), 137.7 (C).

2-[*N*-Benzyl-*N*-(3-bromo-3-butenyl)amino]acetonitrile (32). To a solution of *N*-benzyl-*N*-(3-bromo-3-butenyl)amine (0.4 g, 1.7 mmol) in CH_3CN (20 mL) were added K_2CO_3 (0.7 g, 5 mmol) and iodoacetonitrile (0.13 mL, 1.8 mmol). After stirring at 55 ºC for 24 h, the solvent was removed *in vacuo* and the resulting residue was partitioned between dichloromethane and water. The organic extracts were dried and concentrated.

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[6] N. Azizi, M. R. Saidi, *Tetrahedron* **2004**, *60*, 383-387.

The residue was purified by flash chromatography (SiO_2, from hexane to 95:5 hexane/EtOAc) to give nitrile **32**; yield: 0.42 g (88%); ^1H NMR ($CDCl_3$, 200 MHz) δ 2.66 (t, *J* = 6.6 Hz, 2H), 2.90 (t, *J* = 6.6 Hz, 2H), 3.45 (s, 2H), 3.70 (s, 2H), 5.51 (d, *J* = 1.8 Hz, 1H), 5.67 (dt, *J* = 1.8 and 1 Hz, 1H), 7.20-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 39.4 (CH_2), 41.4 (CH_2), 52.2 (CH_2), 58.0 (CH_2), 114.7 (C), 118.3 (CH_2), 127.8 (CH), 128.6 (CH), 128.9 (CH), 131.3 (C), 136.8 (C).

^{1}H AND ^{13}C NMR DATA FOR THE NEW COMPOUNDS

2-Benzyl-4-methyl-2-azabicyclo[4.3.1]dec-4-en-7-one (9). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.58 (s, 3H), 1.79 (dddd, *J* = 14.1, 12.3, 5.4, and 2.4 Hz, 1H), 2.04 (dddd, *J* = 14.7, 6, 2.4, and 1.2 Hz, 1H), 2.16-2.32 (m, 2H), 2.59 (dtd, *J* = 14.7, 3.6, and 1.3 Hz, 1H), 2.83 (d, *J* = 16.5 Hz, 1H), 3.02-3.14 (m, 2H), 3.27 (ddd, *J* = 15.5, 12.3, and 7 Hz, 1H), 3.57 (d, *J* = 16.5 Hz, 1H), 3.58 (d, *J* = 15 Hz, 1H), 4.00 (d, *J* = 15 Hz, 1H), 5.40 (dm, *J* = 6 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, DEPT) δ 24.6 (CH_3), 30.7 (CH_2), 31.9 (CH_2), 34.8 (CH_2), 50.2 (CH), 52.9 (CH_2), 55.3 (CH), 59.6 (CH_2), 123.4 (CH), 126.8 (CH), 127.8 (CH), 128.3 (CH), 140.2 (C), 212.2 (C), one C was not observed.

2-Benzyl-4-methylene-2-azaspiro[4.5]decan-6-one (12). ^1H NMR ($CDCl_3$, 300 MHz) δ 1.60-2.08 (m, 6H), 2.38-2.56 (m, 2H), 2.75 (d, *J* = 9.3 Hz, 1H), 2.95 (d, *J* = 9.3 Hz, 1H), 3.27 (ddd, *J* = 13.2, 2.1, and 1.8 Hz, 1H), 3.33 (ddd, *J* = 13.2, 2.1 and 1.8 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H), 3.67 (d, *J* = 13.2 Hz, 1H), 4.95 (t, *J* = 2.1 Hz, 1H), 5.17 (t, *J* = 1.8 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, DEPT) δ 22.4 (CH_2), 27.0 (CH_2), 38.1 (CH_2), 39.9 (CH_2), 59.8 (2 CH_2), 60.5 (C), 63.1 (CH_2), 107.4 (CH_2), 126.9 (CH), 128.2 (CH), 128.4 (CH), 138.5 (C), 150.3 (C), 210.3 (C).

2-Acetyl-1-benzyl-3-methylpyrrole (19). ^1H NMR ($CDCl_3$, 200 MHz) δ 2.39 (s, 3H), 2.41 (s, 3H), 5.52 (s, 2H), 6.04 (d, *J* = 2.6 Hz, 1H), 6.80 (d, *J* = 2.6 Hz, 1H), 7.02-7.10 (m, 2H), 7.20-7.35 (m, 3H); ^{13}C NMR ($CDCl_3$, 100.6 MHz, DEPT) δ 16.2 (CH_3), 30.6 (CH_3), 53.3 (CH_2), 111.7 (CH), 126.8 (CH), 127.2 (CH), 128.5 (CH), 129.1 (CH), 129.6 (C), 130.1 (C), 138.7 (C), 188.7(C).

Methyl 1-benzyl-3-methyl-1,2,5,6-tetrahydropyridine-4-carboxylate (21). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.98 (s, 3H), 2.43 (m, 2H), 2.56 (m, 2H), 3.01 (broad s, 2H), 3.59 (s, 2H), 3.72 (s, 3H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 19.3 (CH_3), 26.8 (CH_2), 49.4 (CH_2), 51.2 (CH_3), 59.2 (CH_2), 62.2 (CH_2), 122.1 (C), 127.1 (CH), 128.3 (CH), 129.0 (CH), 137.7 (C), 145.2 (C), 168.0 (C).

Methyl 1-benzyl-4-methyl-3-pyrroline-3-carboxylate (23). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.11 (broad t, J = 0.9 Hz, 3H), 3.59 (td, J = 3.9 and 0.9 Hz, 2H), 3.71 (m, 2H), 3.74 (s, 3H), 3.80 (s, 2H), 7.25-7.42 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 14.1 (CH_3), 51.0 (CH_3), 60.0 (2 CH_2), 65.7 (CH_2), 124.6 (C), 127.1 (CH), 128.3 (CH), 128.5 (CH), 138.8 (C), 152.2 (C), 164.7 (C).

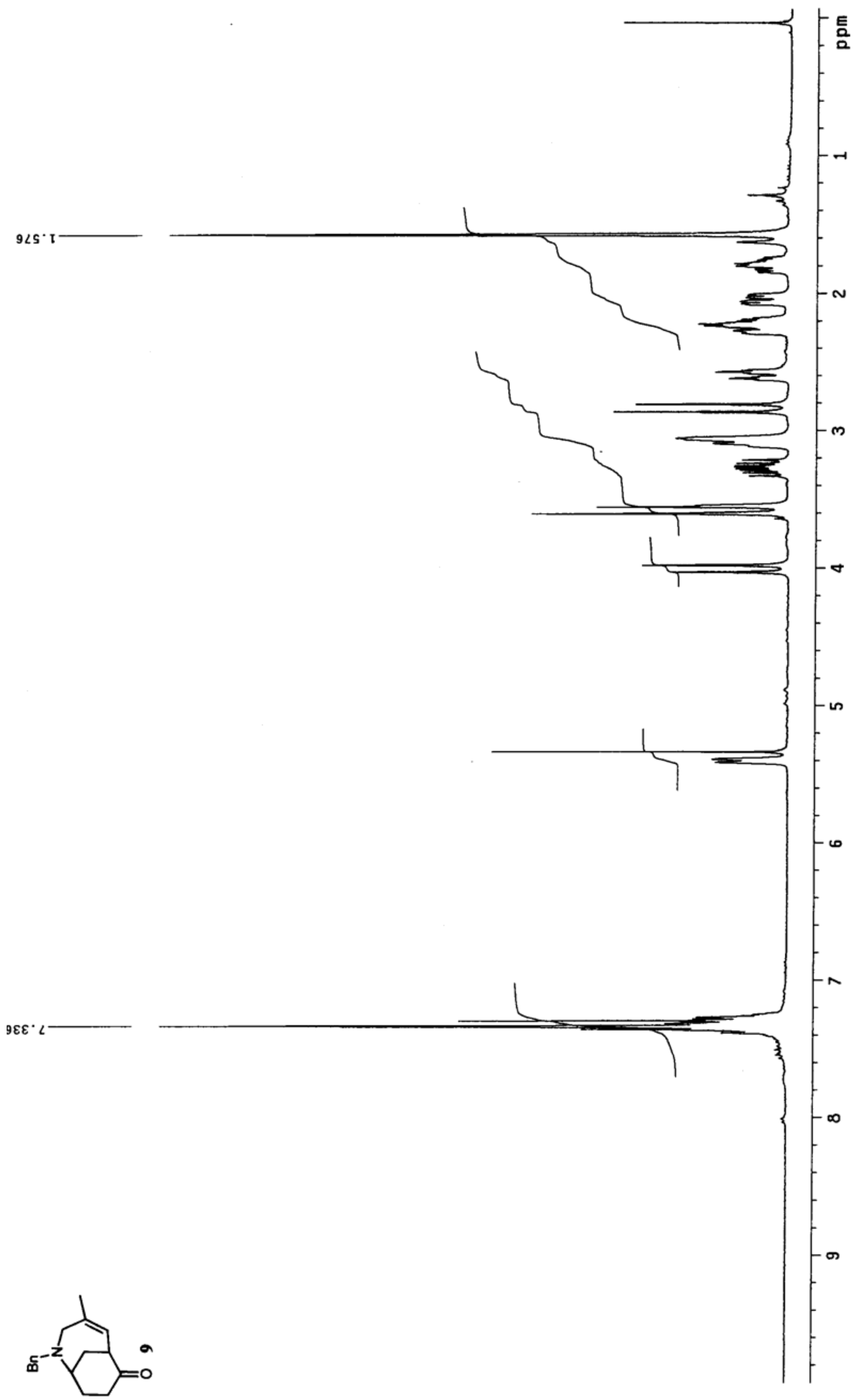
Methyl 1-benzyl-3-methyl-4-methylenepyrrolidine-3-carboxylate (25). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.43 (s, 3H), 2.54 (d, J = 9.2 Hz, 1H), 3.17 (d, J = 9.2 Hz, 1H), 3.24 (dt, J = 13.2 and 2.2 Hz, 1H), 3.34 (dt, J = 13.2 and 2.2 Hz, 1H), 3.60 (d, J = 13.2 Hz, 1H), 3.68 (d, J = 13.2 Hz, 1H), 3.70 (s, 3H), 5.01 (t, J = 2.2 Hz, 1H), 5.07 (t, J = 2.2 Hz, 1H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, DEPT) δ 24.6 (CH_3), 52.2 (C), 52.3 (CH_3), 59.3 (CH_2), 59.9 (CH_2), 64.1 (CH_2), 106.9 (CH_2), 126.9 (CH), 128.2 (CH), 128.5 (CH), 138.5 (C), 151.8 (C), 175.2 (C).

Methyl 1-benzyl-3-methyl-2-pyrroline-2-carboxylate (29). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.97 (t, J = 1.5 Hz, 3H), 2.43 (td, J = 9.4 and 0.8 Hz, 2H), 3.00 (t, J = 9.4 Hz, 2H), 3.84 (s, 3H), 4.04 (s, 2H), 7.20-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 14.7 (CH_3), 35.8 (CH_2), 51.4 (CH_3), 51.4 (CH_2), 57.6 (CH_2), 97.1 (C), 114.8 (C), 127.0 (CH), 128.2 (CH), 128.7 (CH), 138.5 (C), 163.7 (C).

1-Benzyl-4-methyl-3-pyrroline-3-carbonitrile (31). ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.97 (broad s, 3H), 3.53 (m, 2H), 3.64 (m, 2H), 3.78 (s, 2H), 7.24-7.38 (m, 5H); ^{13}C NMR ($CDCl_3$, 50 MHz, DEPT) δ 14.7 (CH_3), 59.7 (CH_2), 60.0 (CH_2), 63.6 (CH_2), 106.3 (C), 114.7 (C), 127.3 (CH), 128.4 (CH), 128.5 (CH), 138.2 (C), 157.2 (C).

1-Benzyl-3-methyl-2-pyrroline-2-carbonitrile (33). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.92 (t, J = 1.5 Hz, 3H), 2.47 (tq, J = 9.3 and 1.5 Hz, 2H), 2.98 (t, J = 9.3 Hz, 2H), 4.02 (s, 2H), 7.26-7.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 75.5 MHz, DEPT) δ 14.2 (CH_3), 34.8

(CH_2), 52.6 (CH_2), 57.2 (CH_2), 113.6 (C), 121.1 (C), 127.5 (CH), 128.4 (CH), 128.6 (CH), 132.9 (C), 137.1 (C).



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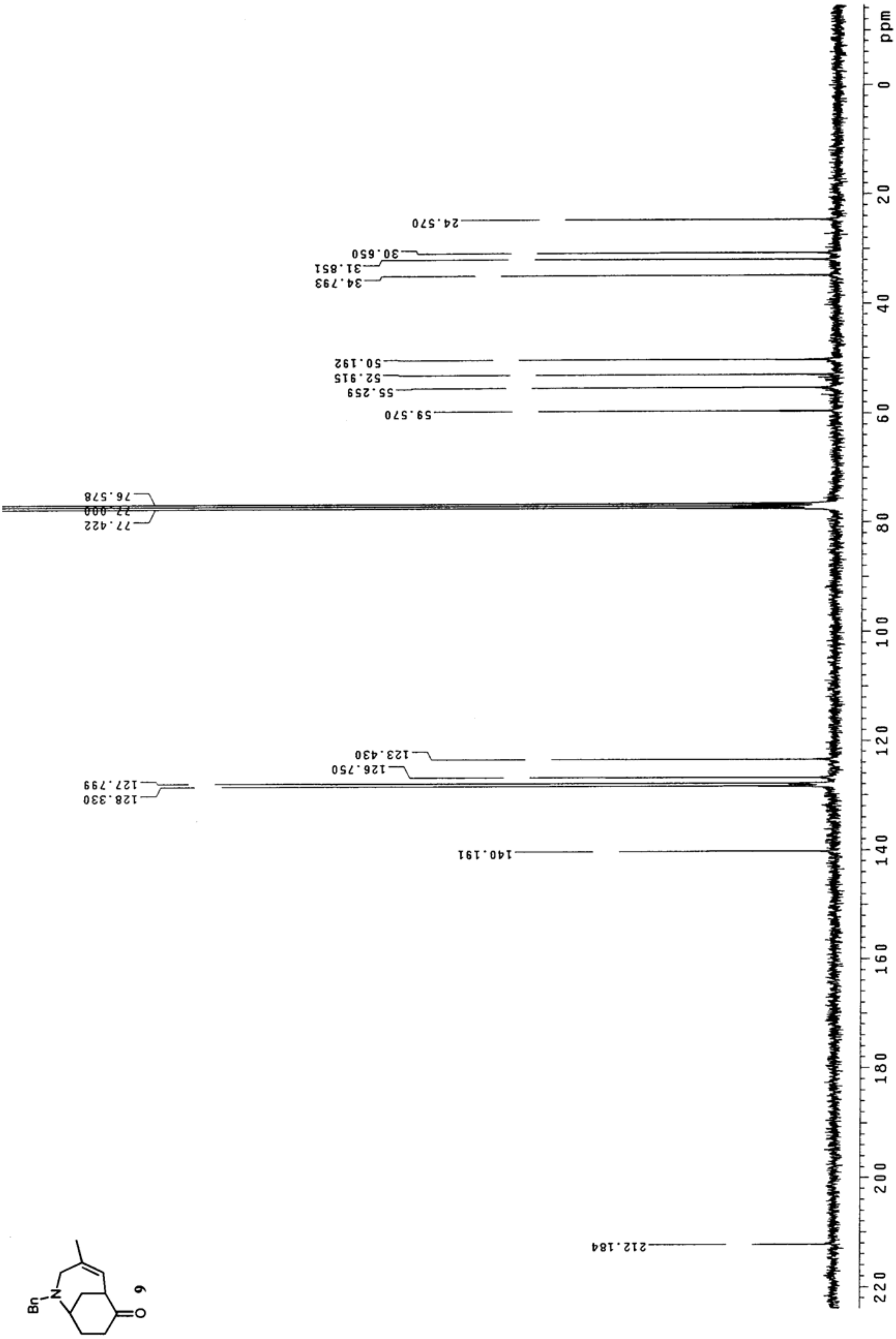
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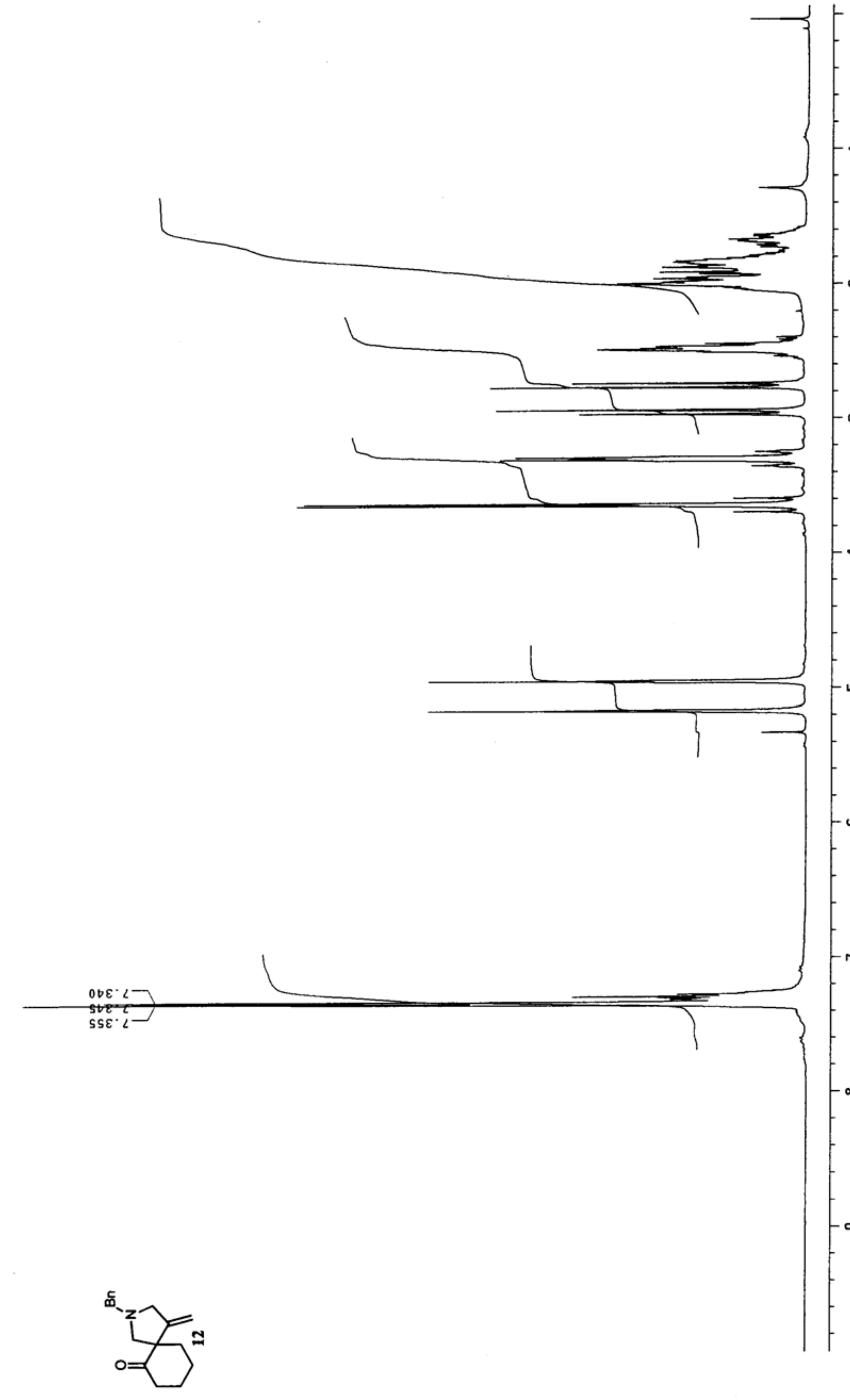
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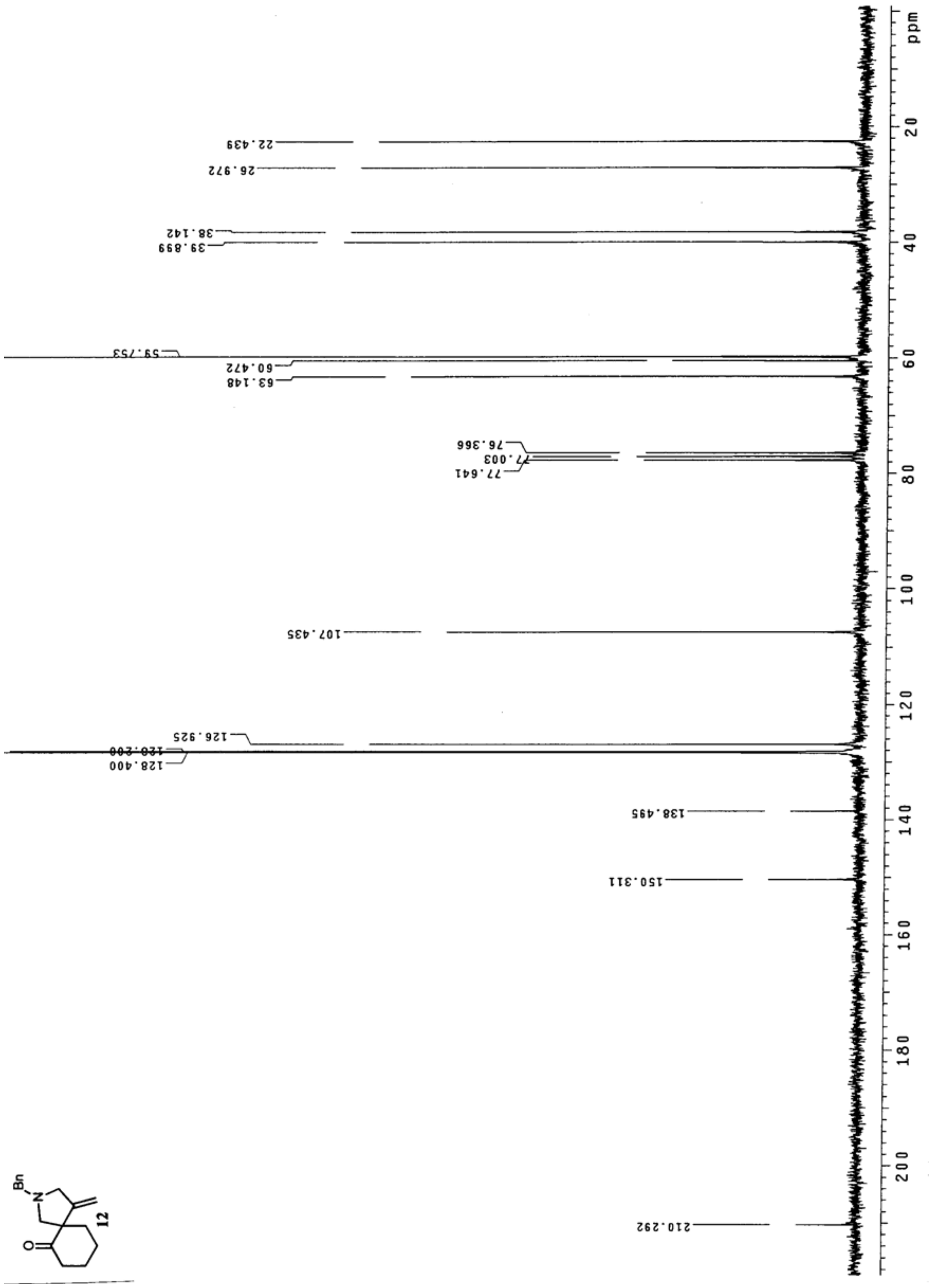
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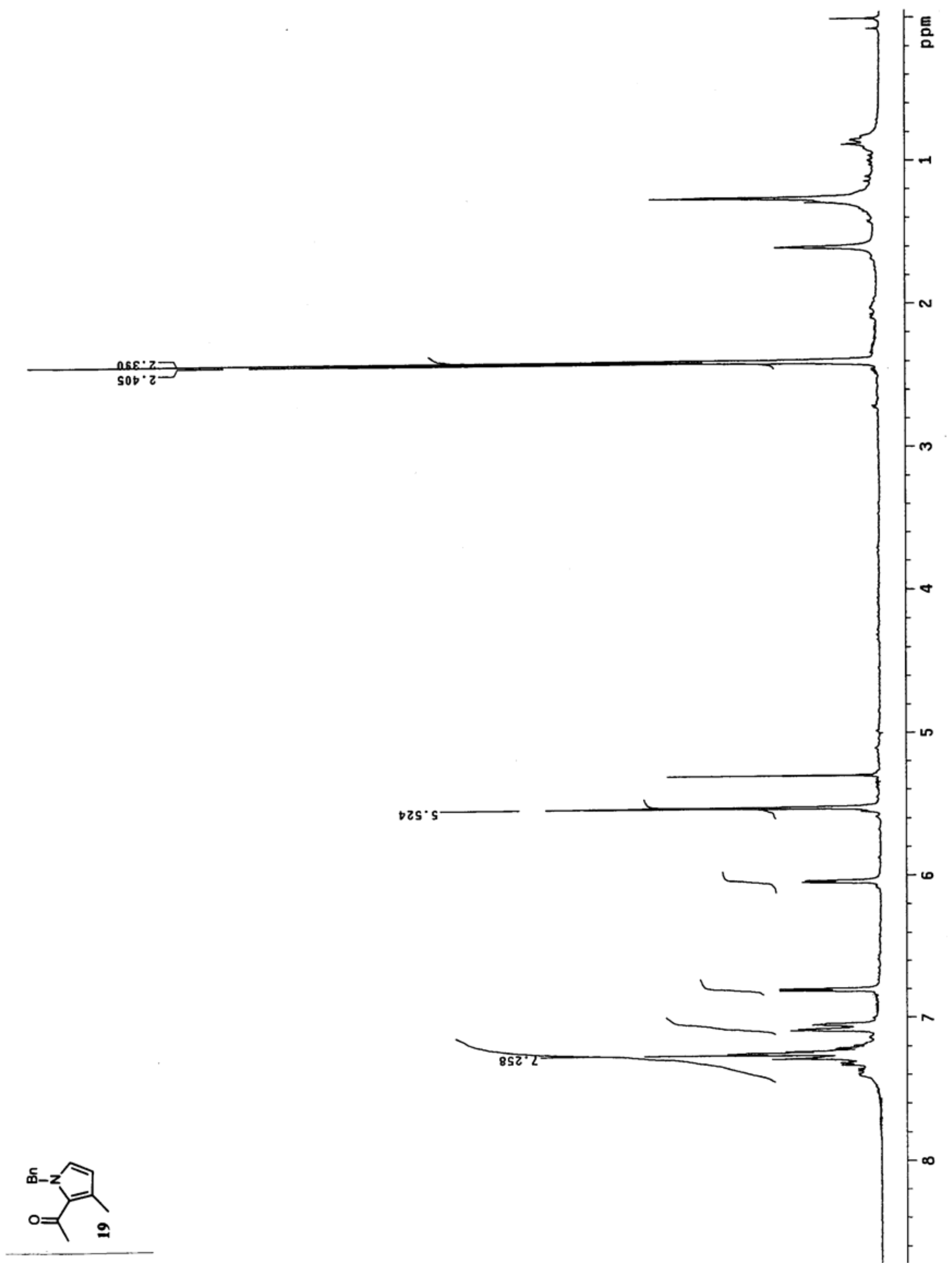
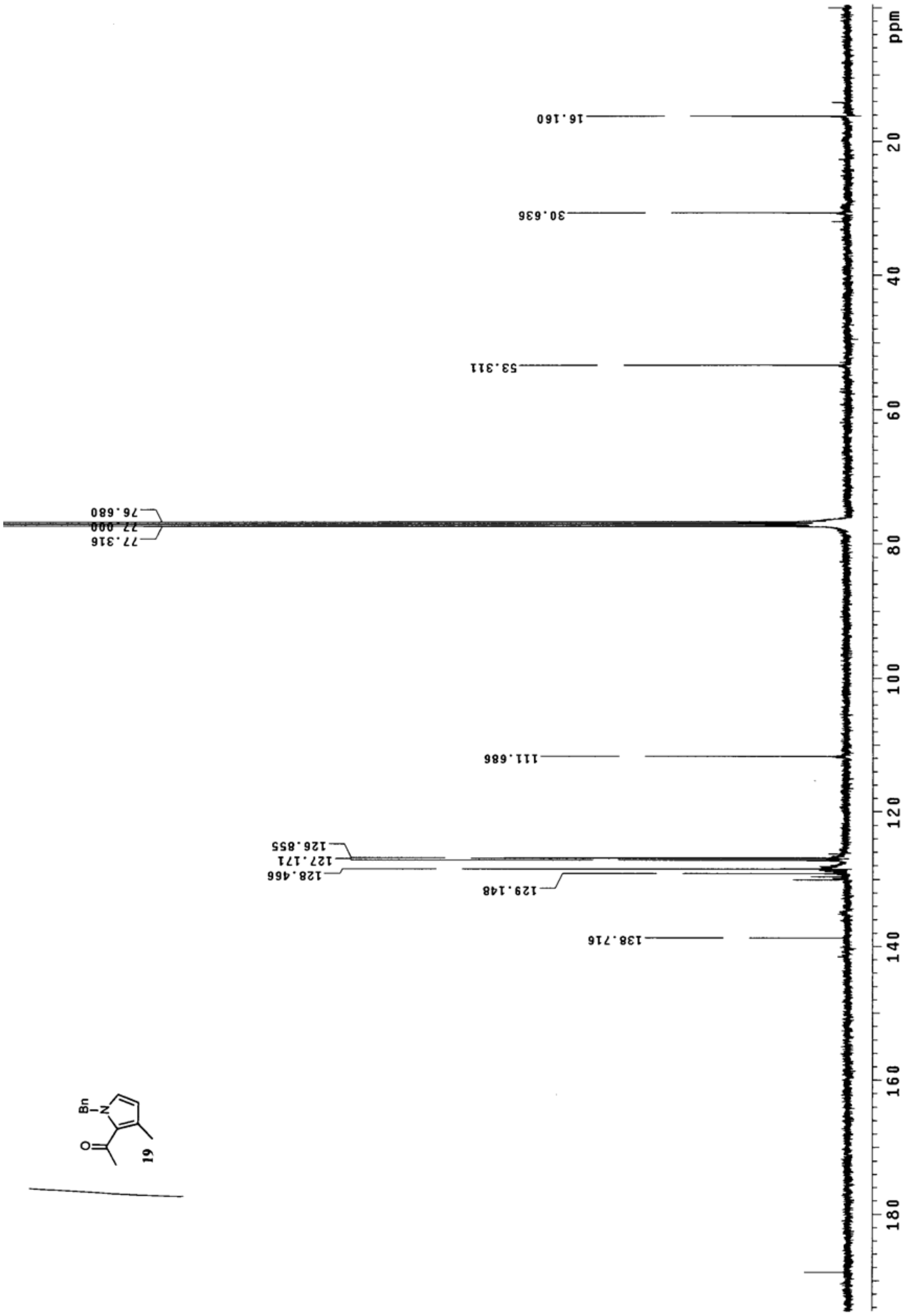
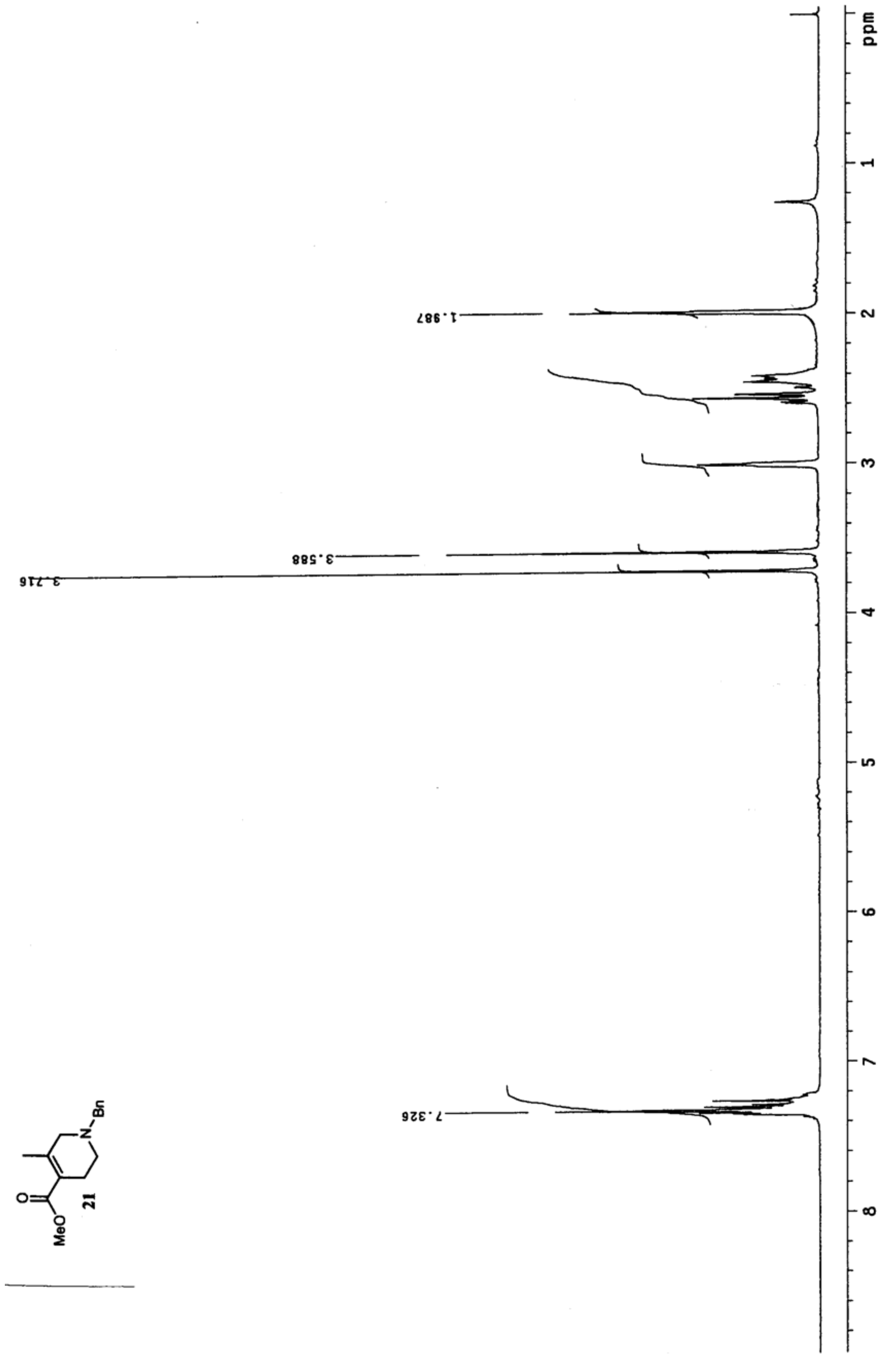
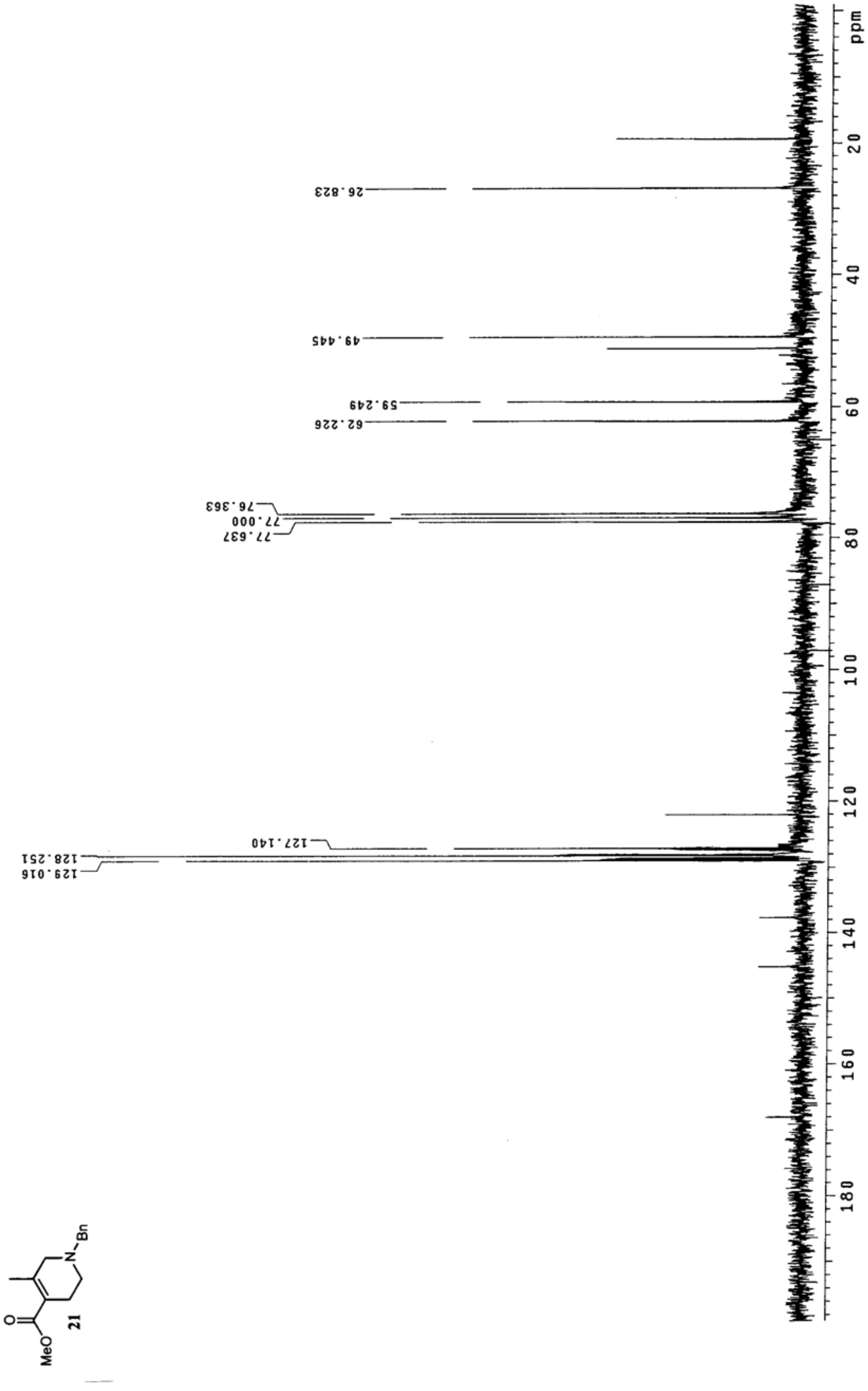
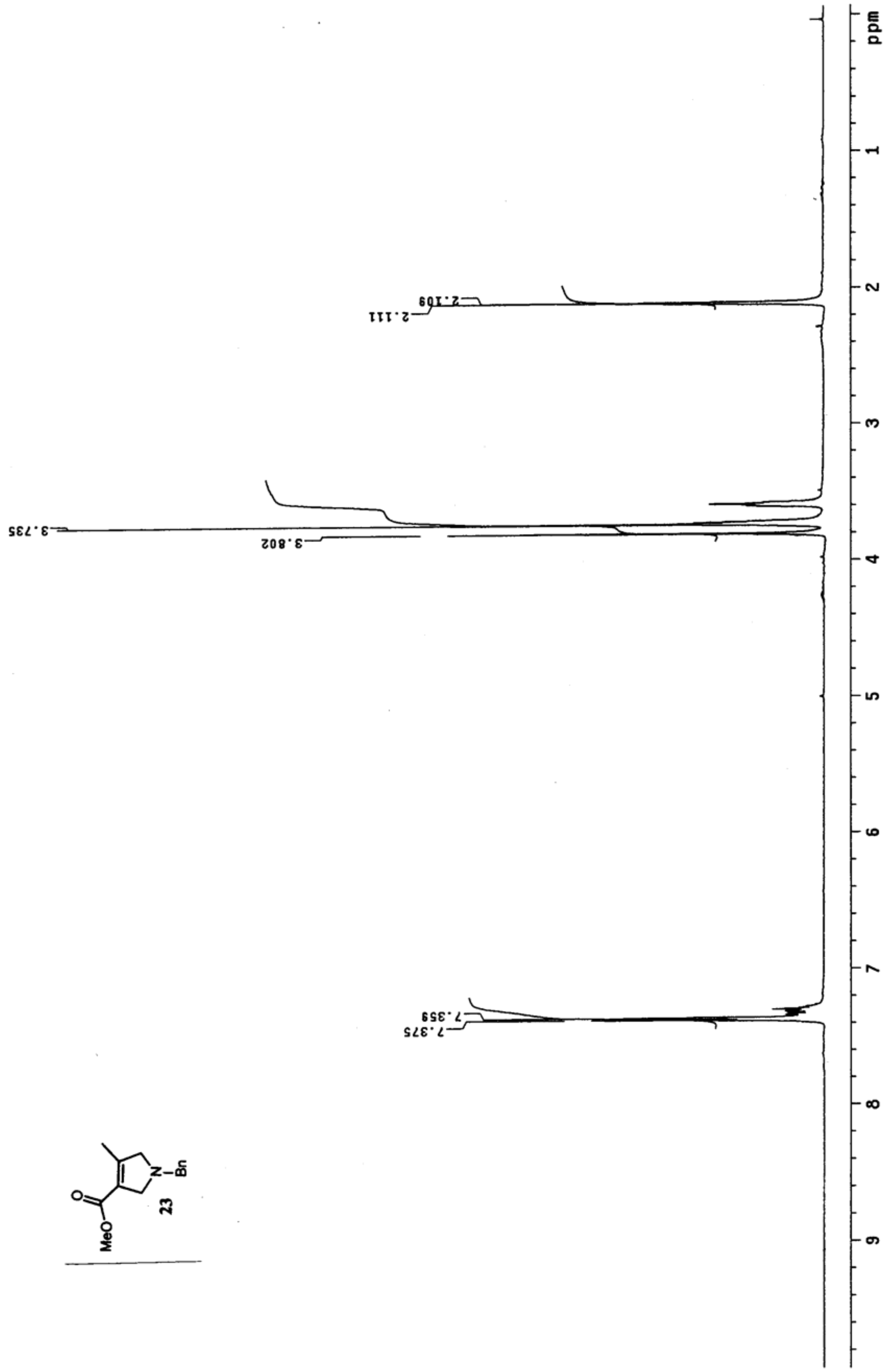

2.390
2.405
5.524
7.258
ppm
1
2
3
4
5
6
7
8
Bn
N
O
19

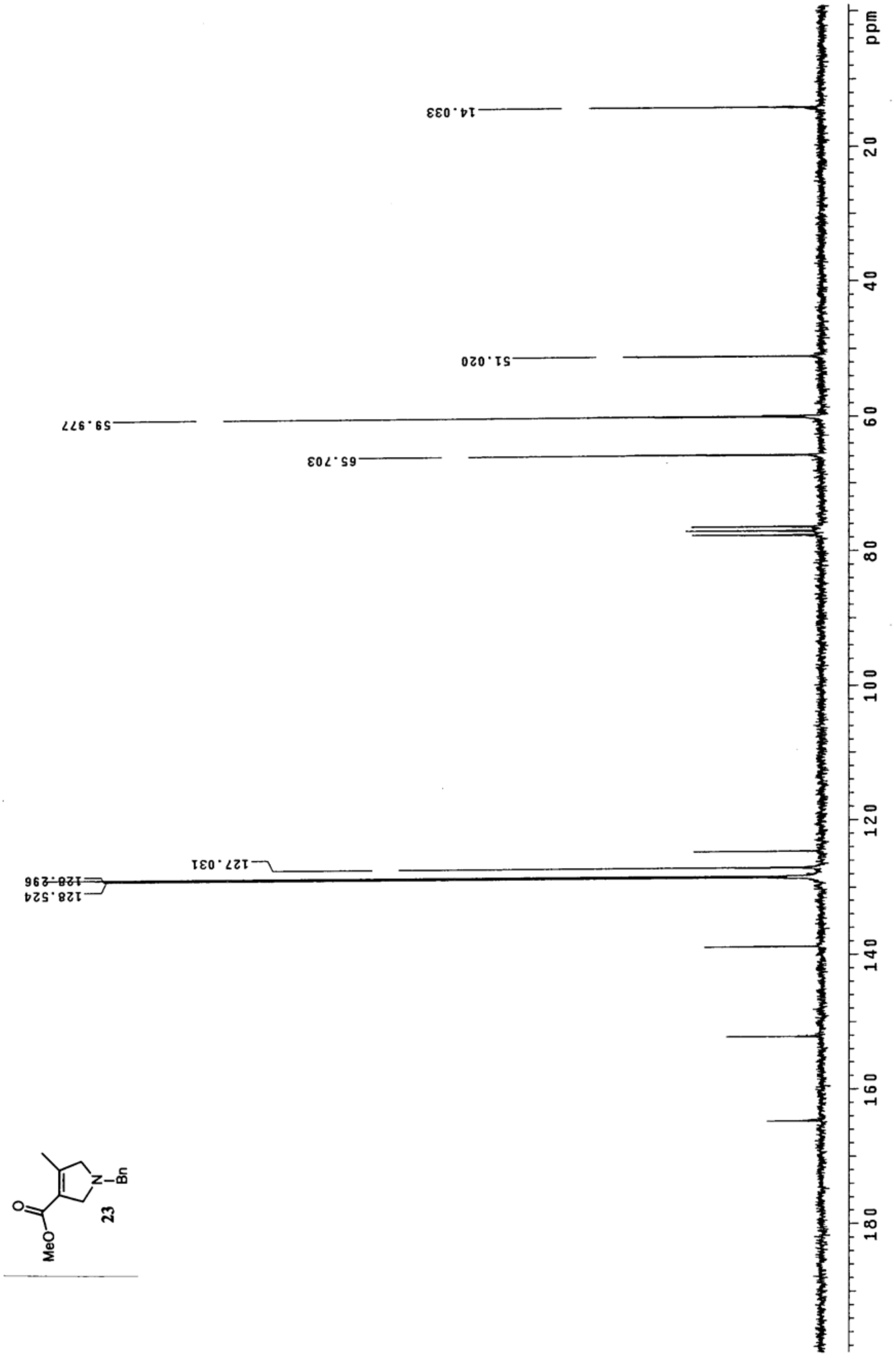

16.160
30.636
53.311
76.680
77.000
77.316
111.686
126.855
127.171
128.466
129.148
138.716
ppm
20
40
60
80
100
120
140
160
180
Bn
N
O
19

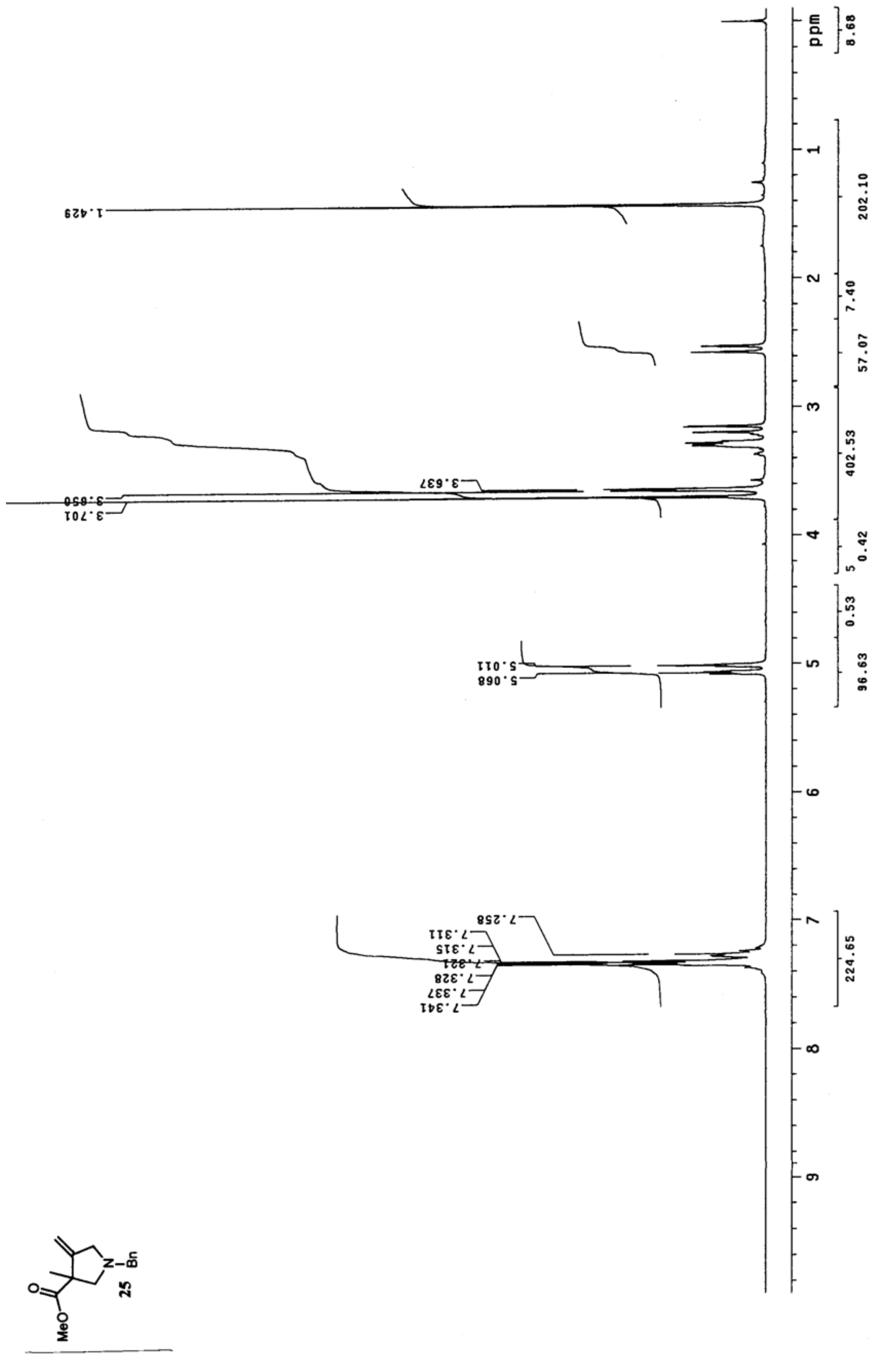

MeO
O
N
Bn
21
7.326
3.716
3.588
1.987
ppm
1
2
3
4
5
6
7
8


MeO
O
N
Bn
129.016
128.251
127.140
77.637
77.000
76.363
62.226
59.249
49.445
26.823
180
160
140
120
100
80
60
40
20
ppm

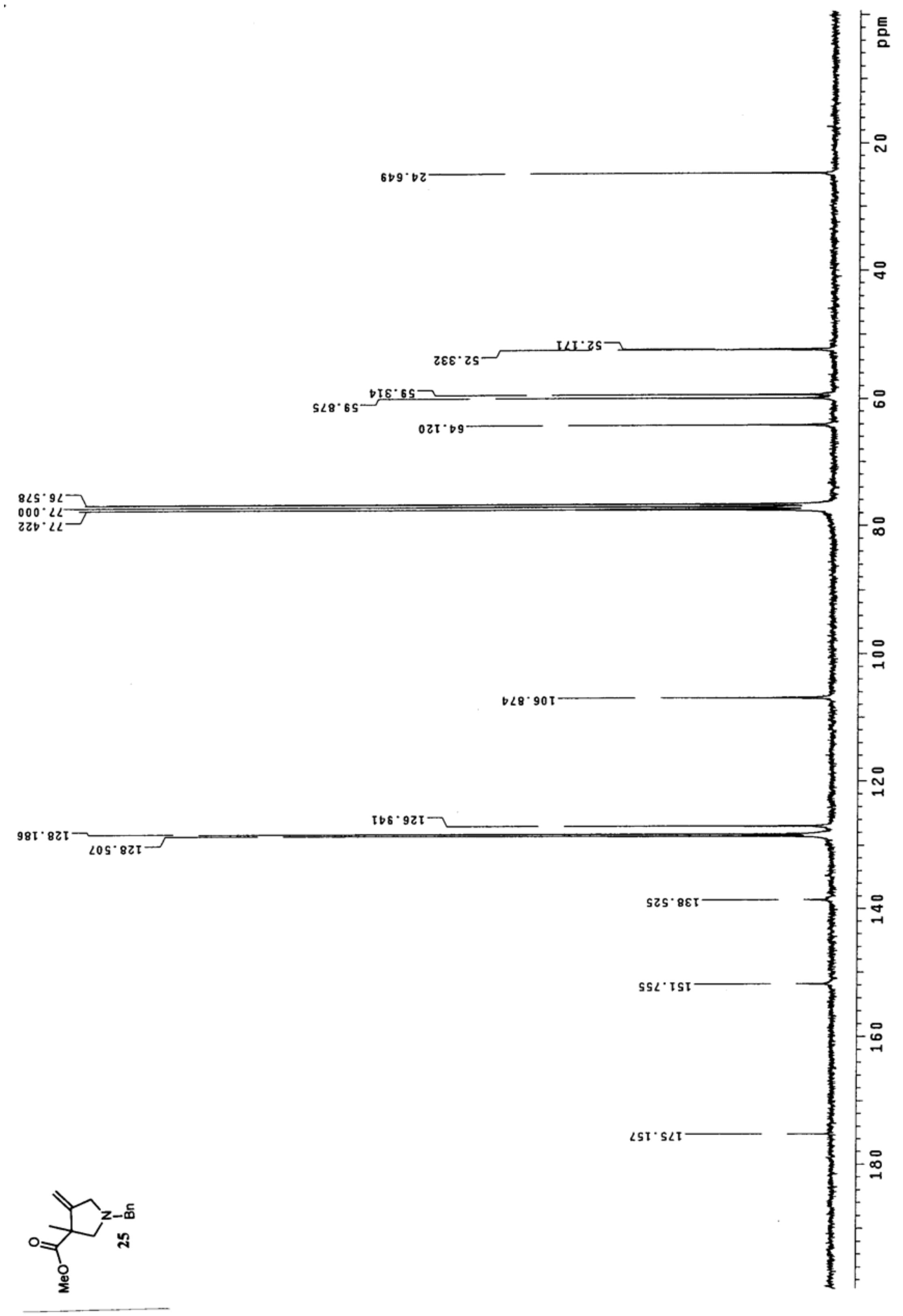
21


ppm
1
2
3
4
5
6
7
8
9
2.109
2.111
3.735
3.802
7.359
7.375
MeO
O
N
Bn
23

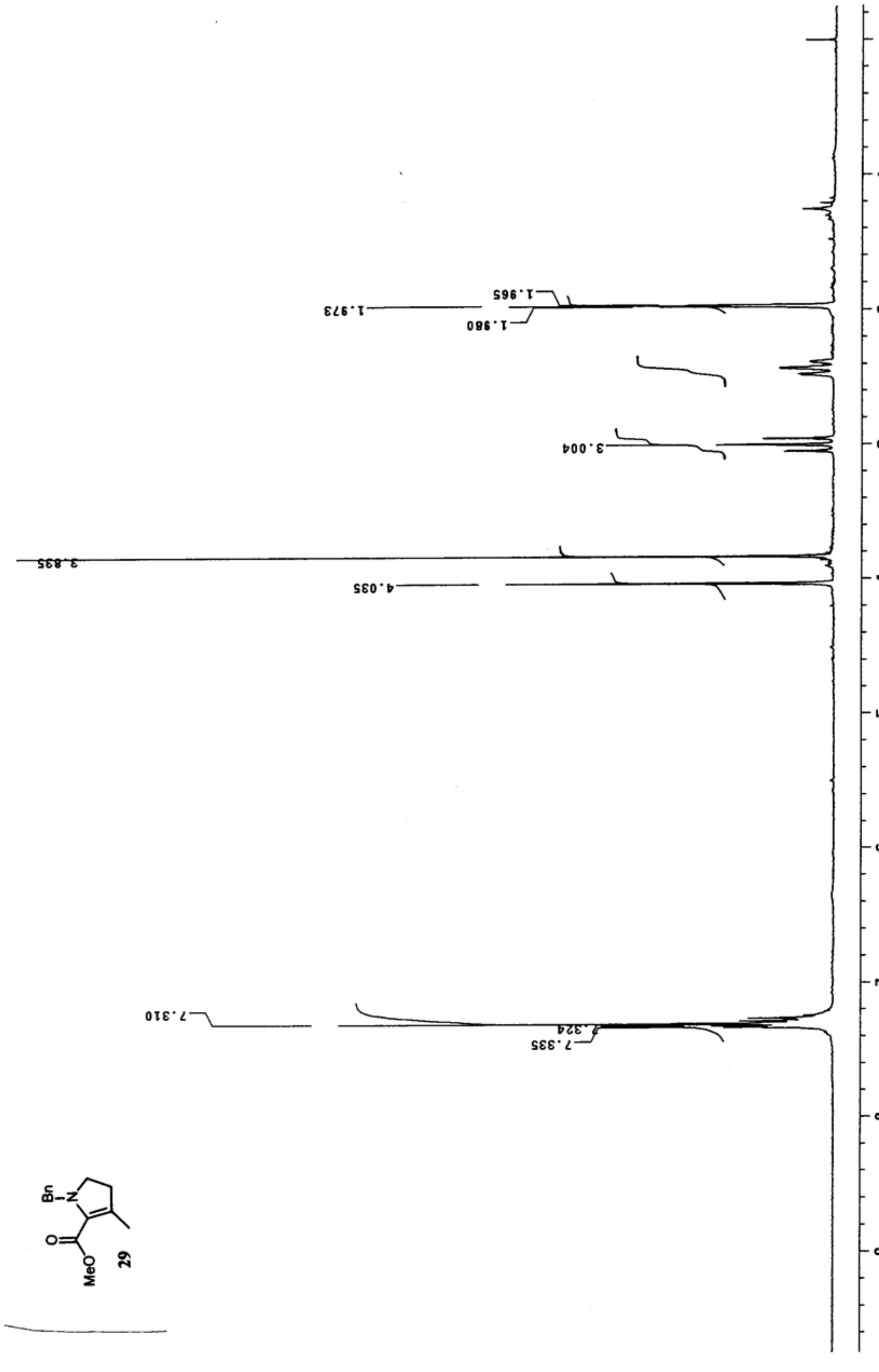

14.033
51.020
59.977
65.703
127.031
128.296
128.524
ppm
20
40
60
80
100
120
140
160
180
MeO
O
N
Bn
23

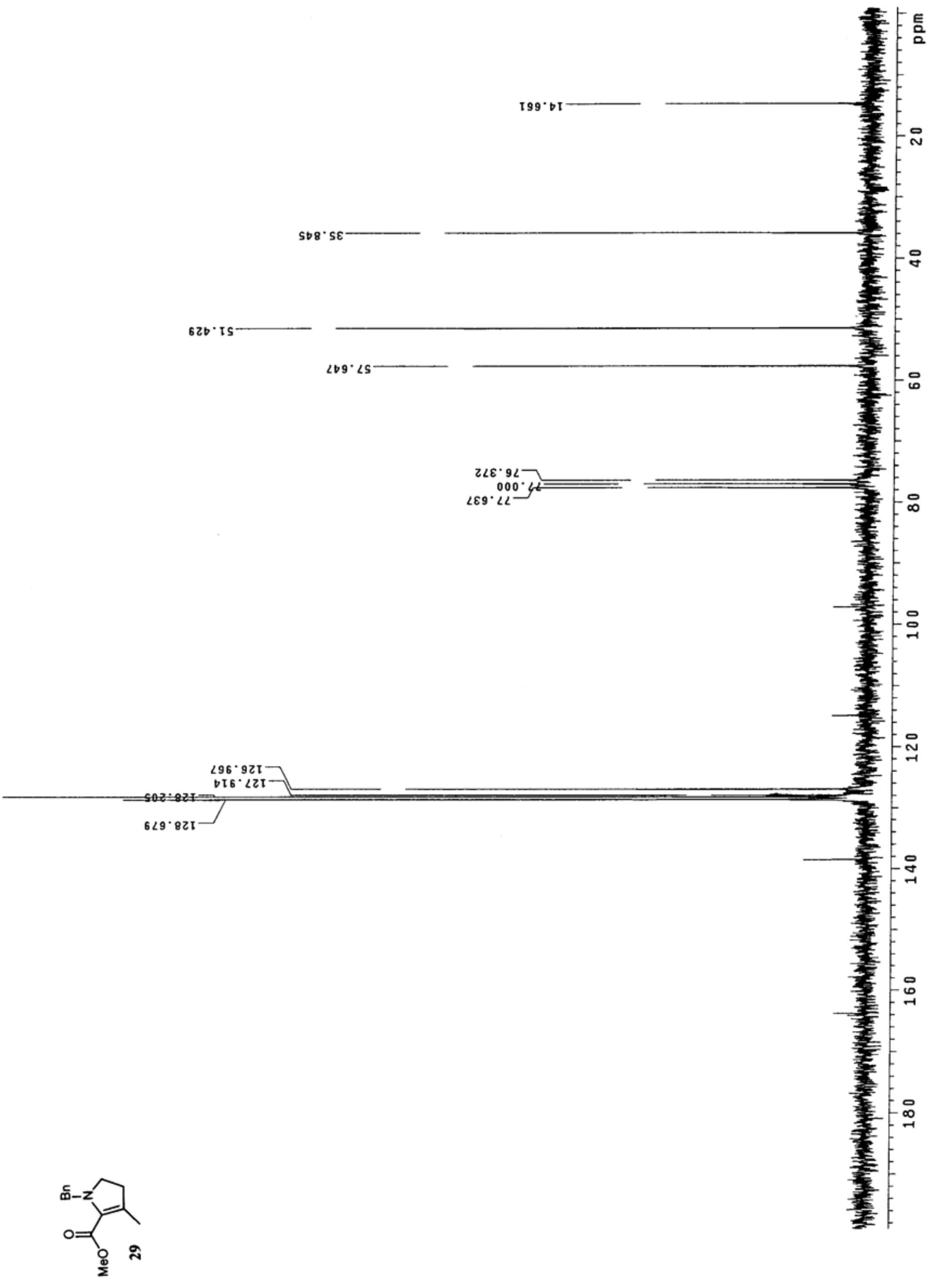

MeO
O
N
Bn
1.429
3.637
3.650
3.701
5.011
5.068
7.258
7.311
7.315
7.321
7.328
7.337
7.341
ppm
1
2
3
4
5
6
7
8
9
8.68
202.10
7.40
57.07
402.53
5
0.42
0.53
96.63
224.65

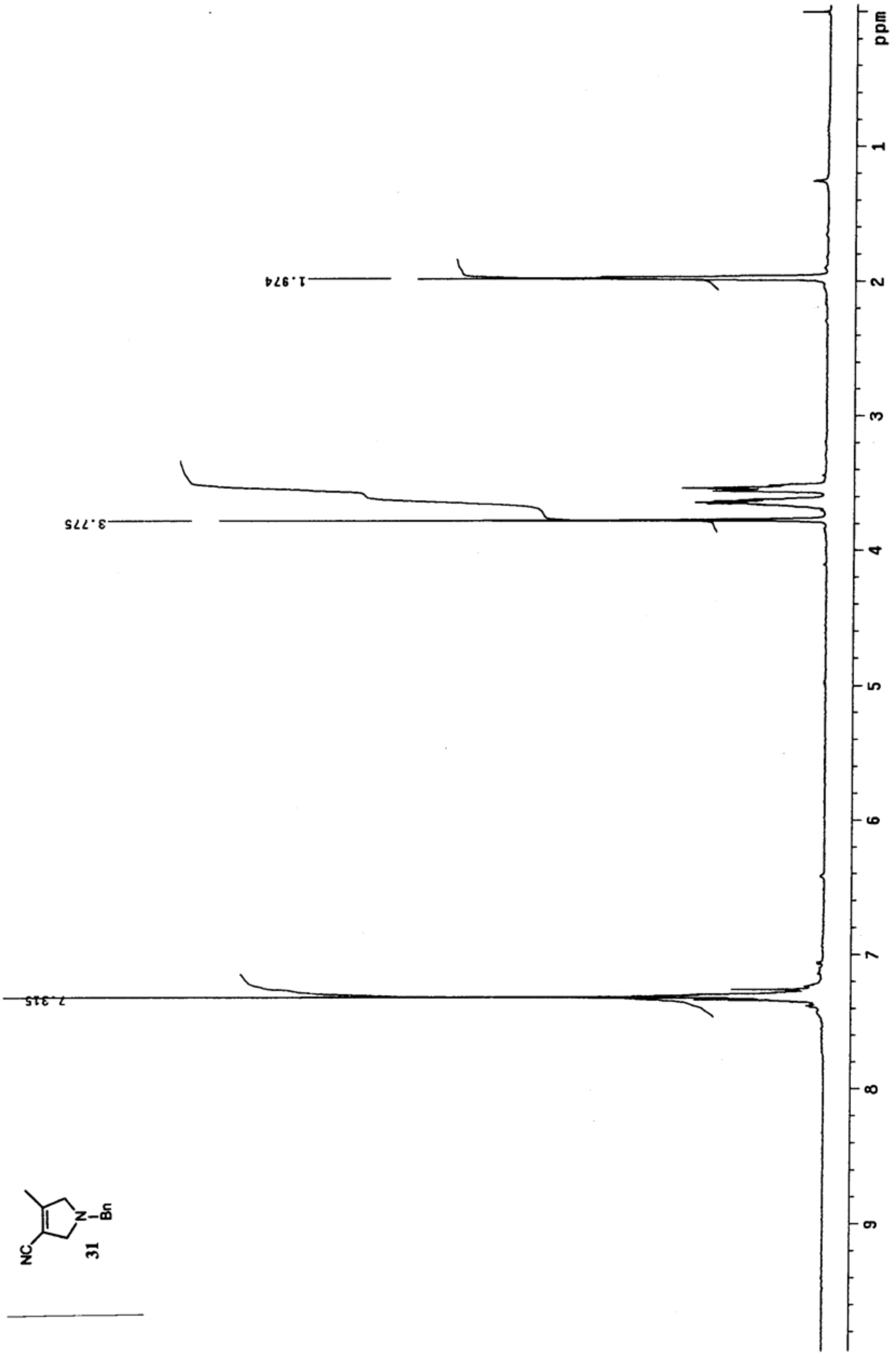
25


ppm
20
40
60
80
100
120
140
160
180
24.649
52.171
52.332
59.314
59.875
64.120
76.578
77.000
77.422
106.874
126.941
128.186
128.507
138.525
151.755
175.157
MeO
O
N
Bn

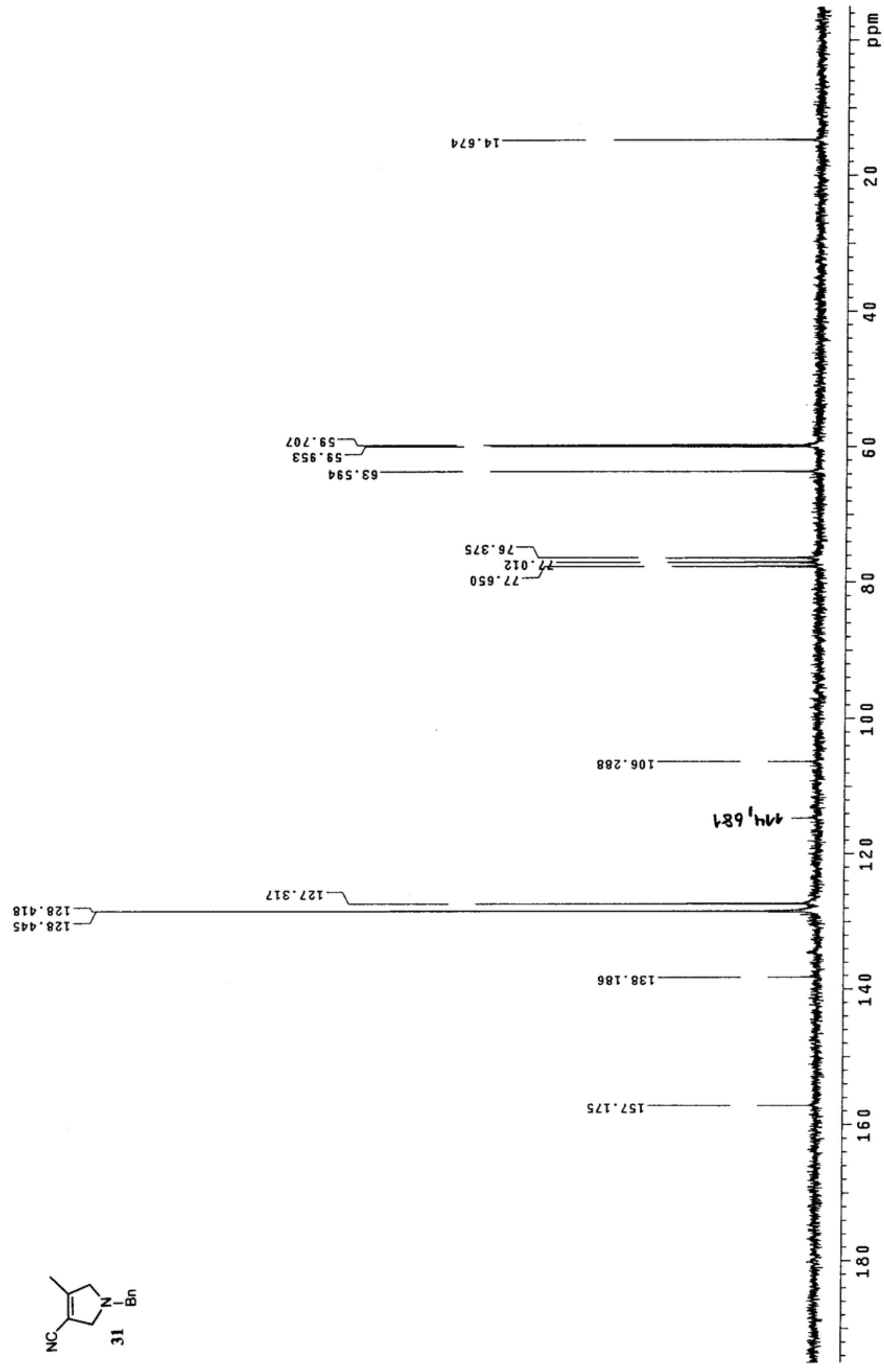
25

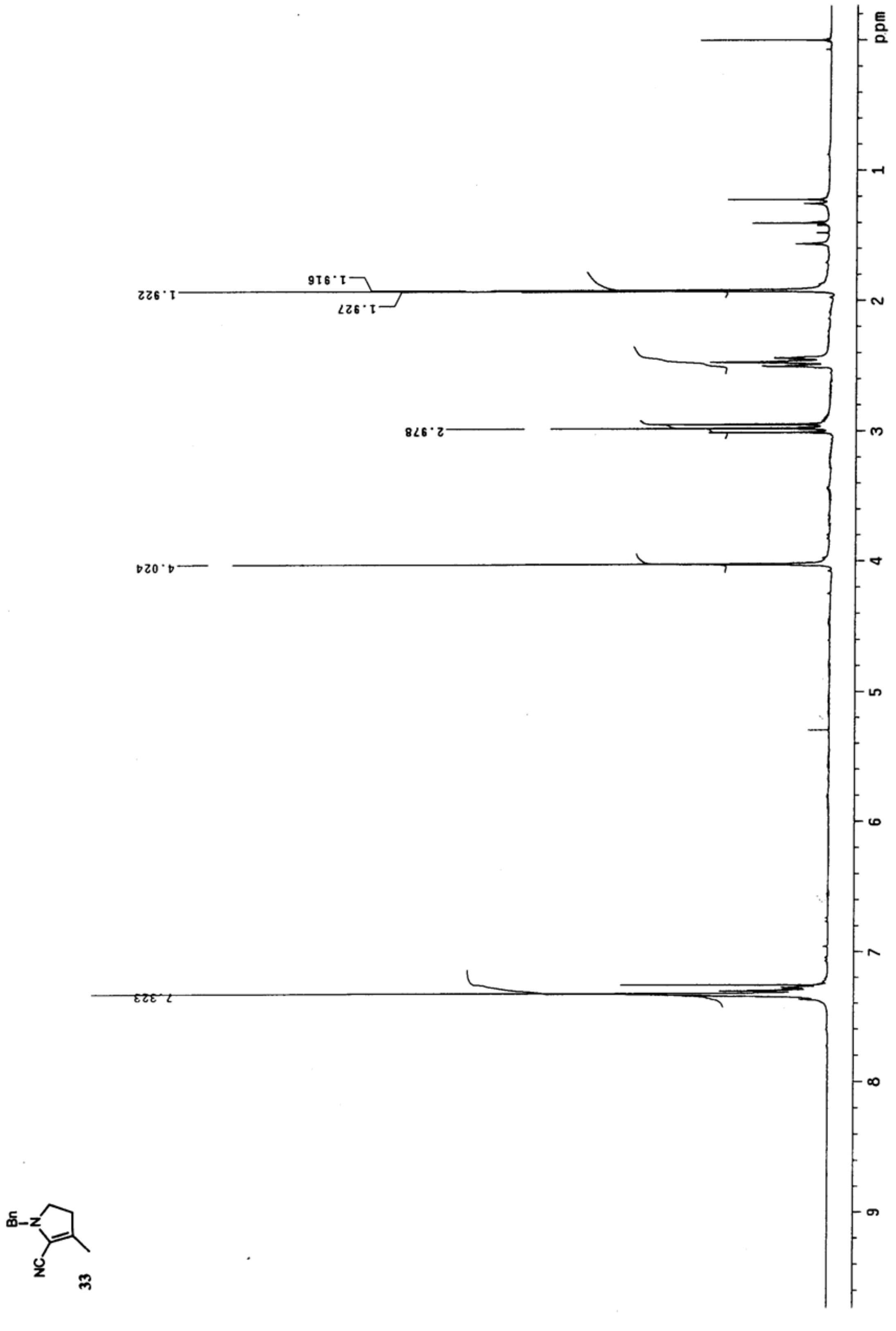

MeO
O
N
Bn
29
7.335
7.324
7.310
4.035
3.835
3.004
1.980
1.973
1.965
9
8
7
6
5
4
3
2
1
ppm


14.661
35.845
51.429
57.647
76.372
77.000
77.637
126.967
127.914
128.205
128.679
ppm
20
40
60
80
100
120
140
160
180
Bn
N
O
MeO
29

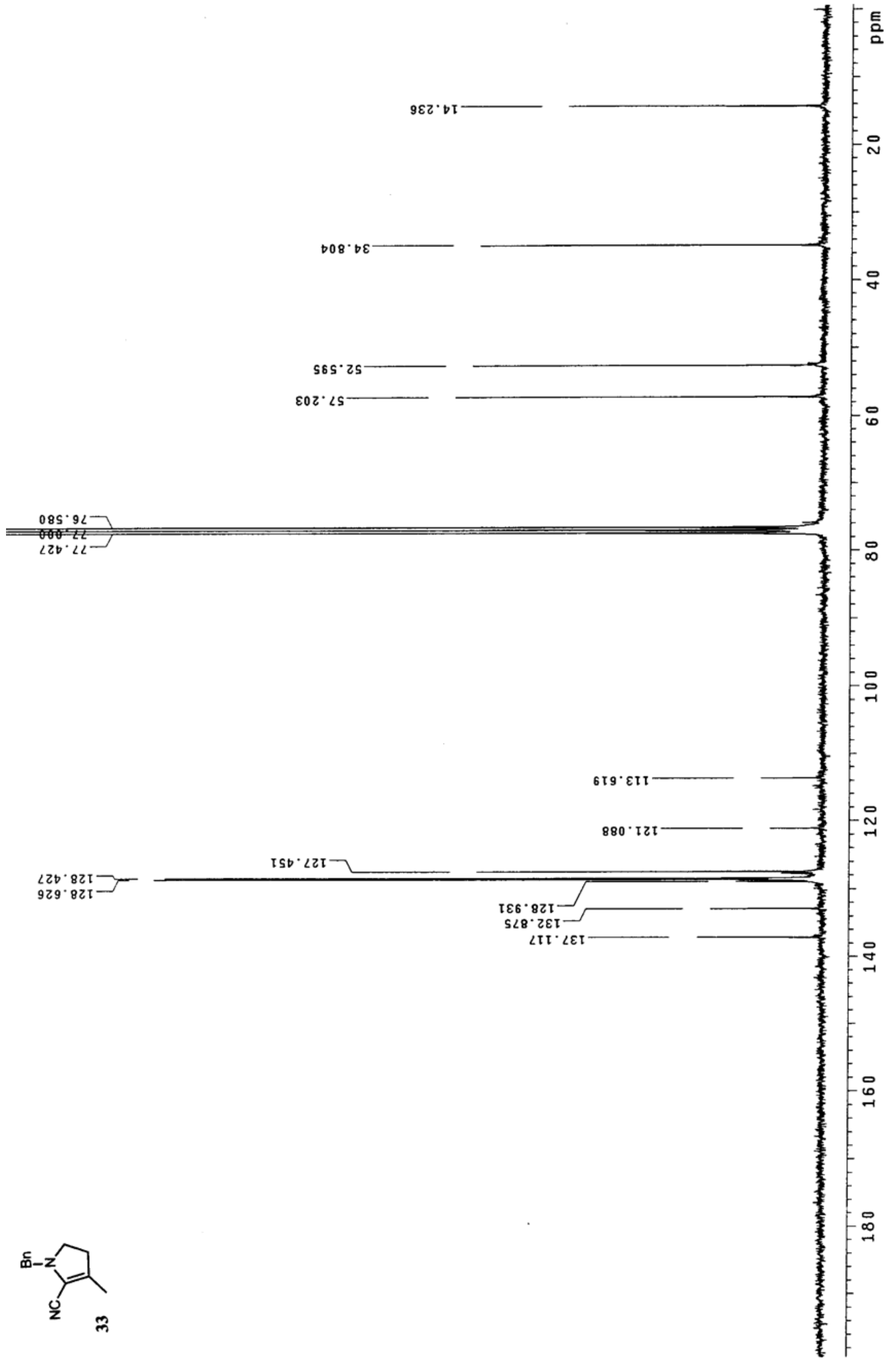


31


NC
N
Bn
31
14.674
59.707
59.953
63.594
76.375
77.012
77.650
106.288
114,681
127.317
128.418
128.445
138.186
157.175
ppm
20
40
60
80
100
120
140
160
180



33


14.236
34.804
52.595
57.203
76.580
77.000
77.427
113.619
121.088
127.451
128.427
128.626
128.931
132.875
137.117
ppm
20
40
60
80
100
120
140
160
180
Bn
N
NC
33